Supplementary Information

Enantioselective Transition-Metal Catalysis via an Anion-Binding Approach

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General information

Procedures

All reactions were performed in screw-cap glass vials or round-bottom flasks fitted with rubber septa under a positive pressure of nitrogen, unless noted otherwise. Reactions were monitored by thin-layer chromatography (TLC) using Silica Gel 60 F254 glass plates (EMD) impregnated with a fluorescent indicator. TLC plates were visualized by exposure to ultraviolet light ($\lambda = 254$ nm) and/or by submersion in aqueous ceric ammonium molybdate, aqueous potassium permanganate, or ethanolic *p*-anisaldehyde solutions followed by brief heating. All solutions were concentrated by rotary evaporation, unless noted otherwise. Flash column chromatography (FCC) was performed using silica gel SiliaFlash P60 (230–400 mesh, SiliCycle).

Materials

All reagents purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar, TCI, Strem, Matrix Scientific, Oakwood, Beantown Chemical) were used without further purification. Extraction and chromatography solvents (EMD or BDH) were used without purification. Reaction solvents (*N*,*N*-dimethylformamide (DMF), dichloromethane (DCM), tetrahydrofuran (THF), diethyl ether, *tert*-butyl methyl ether (TBME), benzene, toluene, 1,4-dioxane) were dried by passing through columns of activated alumina.

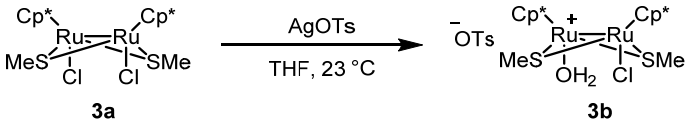
Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using Bruker AVANCE NEO 400 (400 MHz), Varian Unity/Inova500 (500 MHz), or Agilent DD2 600 (600 MHz) NMR spectrometers. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.26 ppm, CHD_2COCD_3: δ 2.05 ppm, C_6HD_5: δ 7.16 ppm, $CHDCl_2$: δ 5.32 ppm, CHD_2CN: δ 1.94 ppm, CHD_2OD: δ 3.31 ppm). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet and/or multiple resonances, app = apparent, br = broad), coupling constants (*J*) in Hertz, integration. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded using Bruker AVANCE NEO 400 (101 MHz) or Varian Unity/Inova500 (126 MHz) NMR spectrometers. Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to the carbon resonance of the NMR solvent ($CDCl_3$: δ 77.2 ppm, $(CD_3)_2CO$: δ 29.8 ppm, CD_3CN: δ 1.3 ppm, CD_3OD: 49.0 ppm, CD_2Cl_2: δ 53.8 ppm). Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded using Bruker AVANCE NEO 400 (376 MHz) or Varian Unity/Inova500 (470 MHz) instruments. Fluorine chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to internal standards (Ph*F*: δ −113.15 ppm, PhCF_3: δ −63.72 ppm) or are reported without reference. Boron nuclear magnetic resonance (^{11}B NMR) spectra were recorded using Bruker AVANCE NEO 400 (128 MHz) instrument. Boron chemical shifts are expressed in parts per million (ppm, δ scale) without reference. Phosphorus nuclear magnetic resonance (^{31}P NMR) spectra were recorded using Bruker AVANCE NEO 400 (162 MHz) instrument. Phosphorus chemical shifts are expressed in parts per million (ppm, δ scale) without reference. Fourier transform infrared (FTIR) spectra were obtained using Bruker ALPHA FTIR spectrometer. Data are represented as follows: frequency of absorption (cm^{-1}), intensity of absorption (vs = very strong, s = strong, m = medium, w = weak, br = broad). Mass spectra were recorded on a Thermo Q Exactive Plus Quadrupole-Orbitrap spectrometer. High-performance liquid chromatography (HPLC) analysis was performed using an Ag-

ilent Technologies 1200 series instrument with commercial CHIRALPAK and CHIRACEL columns. Gas chromatography (GC) analysis was performed using an Agilent 7890A series GC system equipped with commercially available columns. Supercritical-fluid chromatography (SFC) analysis was performed using a JASCO SFC-4000 SFC system with commercially available columns. X-ray data were collected on a Bruker APEX DUO CCD or a Bruker APEX II CCD diffractometers using $Cu_{K\alpha}$ or $Mo_{K\alpha}$ radiation, respectively.

References corresponding to the main text of the manuscript are included in this document[1–57].

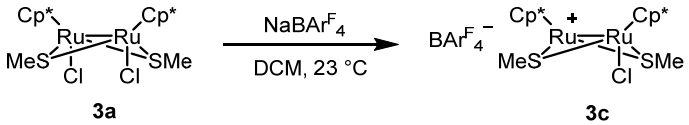
Synthesis and characterization of ruthenium complexes



3a **3b**

Ruthenium tosylate complex (3b)

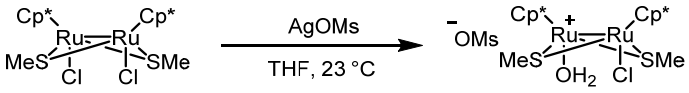
Ruthenium tosylate complex **3b** was prepared according to a modified literature procedure[58]. Silver tosylate (44 mg, 0.15 mmol, 1.0 equiv) was added to a stirred solution of ruthenium chloride complex **3a** (100 mg, 0.15 mmol, 1 equiv) in tetrahydrofuran (2 mL) at 23 °C. The flask was wrapped into aluminum foil to keep the reaction mixture in darkness. The suspension was stirred at 23 °C for 20 hours. The mixture was then filtered through a syringe filter, and the filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane (0.8 mL), and the resulting solution was transferred into a glass vial. A layer of diethyl ether (3 mL) was added on top of the solution of crude ruthenium tosylate complex **3b** in dichloromethane, and the vial was kept at 23 °C for 2 days. The formed black crystals of **3b** were collected, washed with diethyl ether, and dried in vacuo (95 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 7.8 Hz, 2H), 2.66 (br s, 2H), 2.52 (s, 6H), 2.30 (s, 3H), 1.68 (s, 30H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.1, 128.6, 126.2, 96.1, 21.5, 15.4, 10.6. Crystals of **3b** suitable for analysis by X-ray crystallography were prepared by slow diffusion of benzene into a solution of **3b** in dichloromethane at 23 °C (see page S115 for details).



3a **3c**

Ruthenium tetrakis(3,5-(trifluoromethyl)phenyl)borate (BAr^F_4) complex (3c)

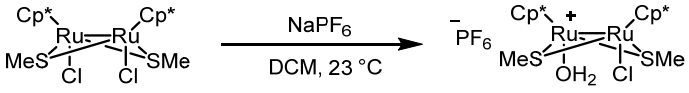
Sodium tetrakis(3,5-(trifluoromethyl)phenyl)borate (83 mg, 0.094 mmol, 1.0 equiv) was added to a stirred solution of ruthenium chloride complex **3a** (60 mg, 0.094 mmol, 1 equiv) in dichloromethane (1 mL) at 23 °C. The suspension was stirred at 23 °C for 20 hours. The mixture was then filtered through a syringe filter, and the filtrate was concentrated in vacuo. The residue was dissolved in dichloromethane (0.4 mL), and the resulting solution was transferred into a glass vial. A layer of pentane (1 mL) was added on top of the solution of crude ruthenium BAr^F_4 complex **3c** in dichloromethane, and the vial was kept at 23 °C for 2 days. The formed black crystals of **3c** were collected, washed with pentane, and dried in vacuo. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 8H), 7.53 (s, 4H), 2.68 (s, 6H), 1.63 (s, 30H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (q, J = 49.9 Hz), 135.0, 129.4–128.8 (m), 124.7 (q, J = 272.5 Hz), 117.9–117.4 (m), 97.1, 23.8, 10.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ −6.63. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.36. Crystals of **3c** suitable for analysis by X-ray crystallography were prepared by slow diffusion of pentane into a solution of **3c** in diethyl ether at 23 °C (see page S123 for details).



3a 3d

Ruthenium mesylate complex (3d)

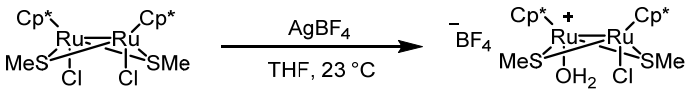
Ruthenium mesylate complex **3d** was prepared according to a modified literature procedure[58]. Silver mesylate (64 mg, 0.31 mmol, 1.0 equiv) was added to a stirred solution of ruthenium chloride complex **3a** (200 mg, 0.31 mmol, 1 equiv) in tetrahydrofuran (5 mL) at 23 °C. The flask was wrapped into aluminum foil to keep the reaction mixture in darkness. The suspension was stirred at 23 °C for 20 hours. The mixture was then filtered through a syringe filter, and the filtrate was concentrated in vacuo. The residue was dissolved in dichloromethane (0.8 mL), and the resulting solution was transferred into a glass vial. A layer of diethyl ether (3 mL) was added on top of the solution of crude ruthenium mesylate complex **3d** in dichloromethane, and the vial was kept at 23 °C for 2 days. The formed black crystals of **3d** were collected, washed with diethyl ether, and dried in vacuo. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (s, 2H), 2.64 (s, 3H), 2.56 (s, 6H), 1.69 (s, 30H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 96.1, 39.5, 15.4, 10.6. Crystals of **3d** suitable for analysis by X-ray crystallography were prepared by slow diffusion of diethyl ether into a solution of **3d** in dichloromethane at 23 °C (see page S146 for details).



3a 3e

Ruthenium hexafluorophosphate complex (3e)

Sodium hexafluorophosphate (13 mg, 0.078 mmol, 1.0 equiv) was added to a stirred solution of ruthenium chloride complex **3a** (50 mg, 0.078 mmol, 1 equiv) in dichloromethane (1.5 mL) at 23 °C. The suspension was stirred at 23 °C for 20 hours. The mixture was then filtered through a syringe filter, and the filtrate was concentrated in vacuo. The residue was dissolved in dichloromethane (0.4 mL), and the resulting solution was transferred into a glass vial. A layer of pentane (1 mL) was added on top of the solution of crude ruthenium hexafluorophosphate complex **3e** in dichloromethane, and the vial was kept at 23 °C for 2 days. The formed black crystals of **3e** were collected, washed with pentane, and dried in vacuo. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (s, 6H), 1.77 (s, 2H), 1.71 (s, 30H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 97.1, 21.8, 10.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.33 (d, J = 712.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ −144.49 (hept, J = 712.3 Hz).



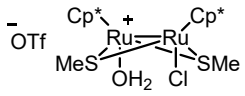
3a 3f

Ruthenium tetrafluoroborate complex (3f)

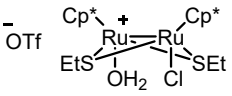
Silver tetrafluoroborate (21 mg, 0.11 mmol, 1.0 equiv) was added to a stirred solution of ruthenium chloride complex **3a** (70 mg, 0.11 mmol, 1 equiv) in tetrahydrofuran (2 mL) at 23 °C. The suspension was stirred at 23 °C for 20 hours. The mixture was then filtered through a syringe filter, and the filtrate was concentrated in vacuo. The residue was dissolved in dichloromethane (0.4 mL), and the resulting solution was transferred into a glass vial. A layer of pentane (1 mL) was added on top of the solution of crude ruthenium tetrafluoroborate complex **3f** in dichloromethane, and

the vial was kept at 23 °C for 2 days. The formed black crystals of **3f** were collected, washed with pentane, and dried in vacuo. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55 (s, 6H), 2.47 (s, 2H), 1.67 (s, 30H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 96.5, 17.1, 10.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ −1.16. ^{19}F NMR (376 MHz, $CDCl_3$) δ −151.52 to −152.17 (m).

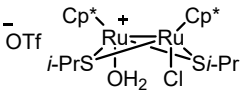
Complexes **3g**, **3h**, and **3i** were prepared according to literature procedures, and their spectroscopic data were in accordance with those reported[59].



3g



3h



3i

Synthesis and characterization of hydrogen-bond donors

Synthesis of hydrogen-bond donor 4d

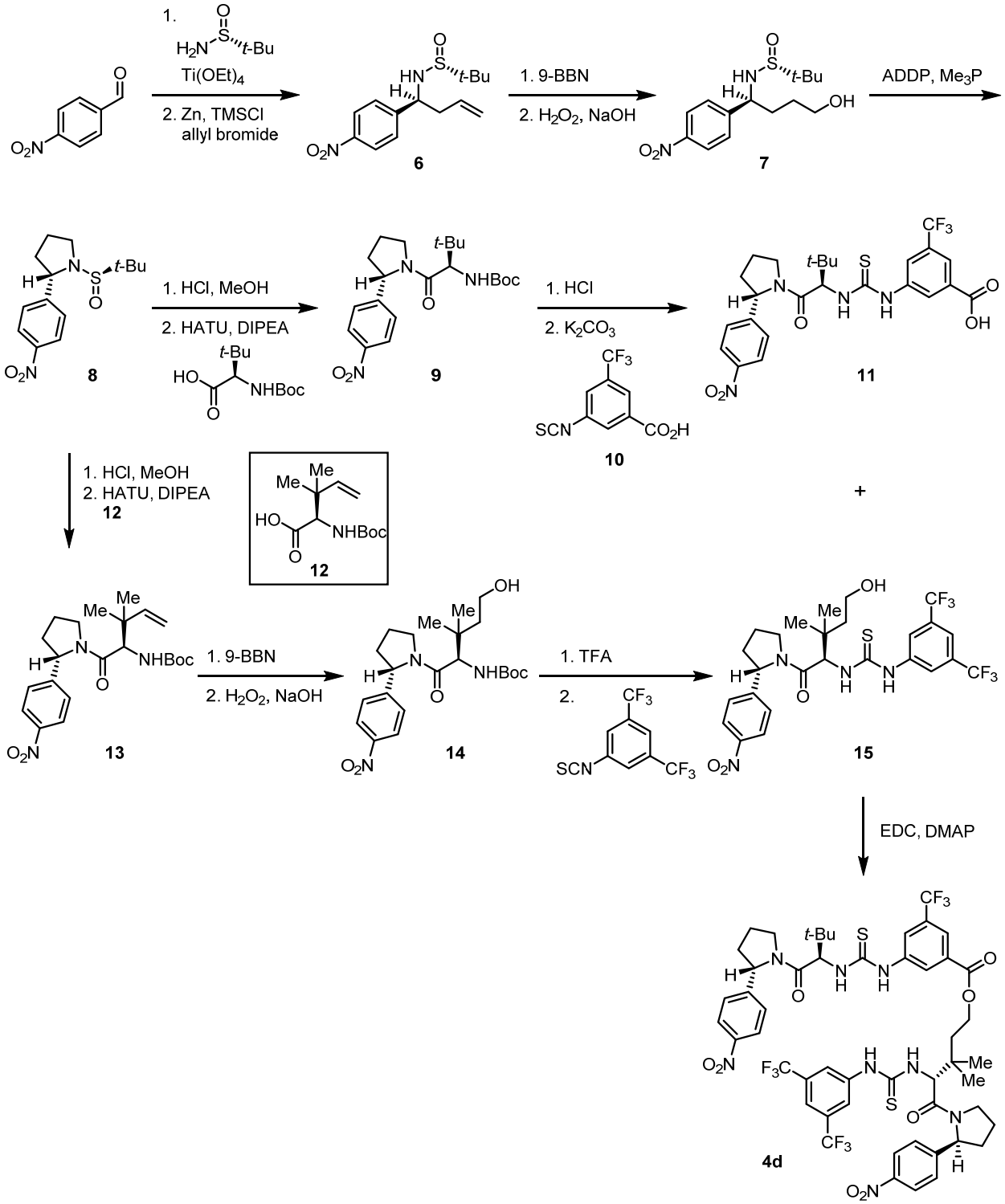
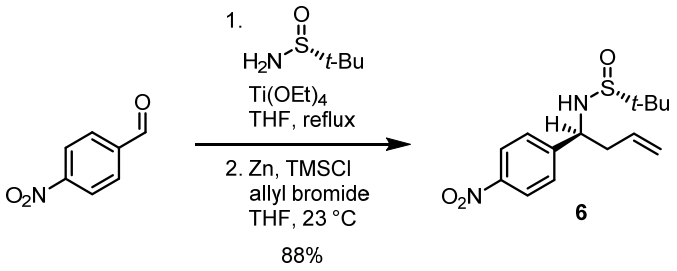


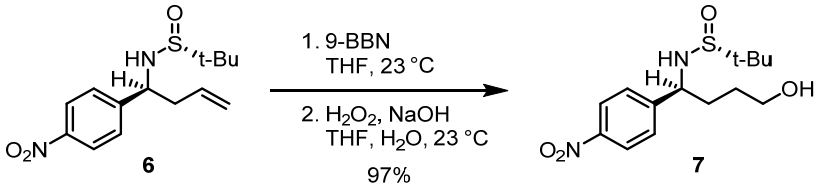
Figure S1 Synthetic route for preparation of **4d**.



Sulfinamide 6

(*R*)-2-Methyl-2-propanesulfinamide (3.55 g, 29.3 mmol, 1.1 equiv) was added to a stirred solution of 4-nitrobenzaldehyde (4.00 g, 26.6 mmol, 1 equiv) in tetrahydrofuran (43 mL) at 23 °C. Titanium tetraethoxide (11.2 mL, 53.2 mmol, 2.2 equiv) was added, and the resulting mixture was heated to reflux. The solution was stirred at reflux for 15 hours, and then was allowed to cool down to ambient temperature. A saturated aqueous solution of sodium bicarbonate (5 mL) was added, and the mixture was filtered through a plug of silica gel eluting with ethyl acetate (100 mL). The filtrate was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to yield a sulfinimine intermediate that was used in the next step without further purification.

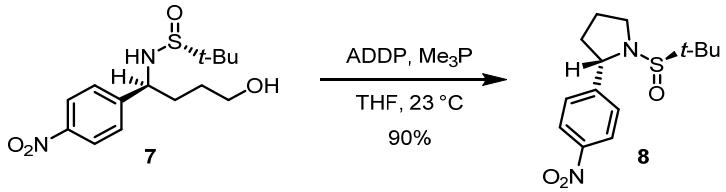
Trimethylsilyl chloride (0.17 mL, 1.33 mmol, 0.05 equiv) was added to a stirred suspension of zinc powder (1.91 g, 29.3 mmol, 1.1 equiv) in tetrahydrofuran (135 mL) at 23 °C. The mixture was allowed to stir for 5 minutes at 23 °C, and then allyl bromide (2.53 mL, 29.3 mmol, 1.1 equiv) was added dropwise. The mixture was allowed to stir at 23 °C until the zinc was completely consumed (about 1 hour). The preformed solution of allylzinc bromide in tetrahydrofuran was transferred by cannula to a solution of the sulfinimine intermediate in tetrahydrofuran (135 mL) at 23 °C. The reaction mixture was stirred at 23 °C for 24 hours. Water (50 mL) and ethyl acetate (75 mL) were added at 23 °C, and the phases were separated. The aqueous layer was extracted with ethyl acetate (2 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product mixture was purified by flash column chromatography (10–40% acetone in hexanes) to yield **6** as a yellow solid (6.97 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25–8.17 (m, 2H), 7.54–7.46 (m, 2H), 5.71 (dddd, J = 16.5, 10.4, 8.3, 5.9 Hz, 1H), 5.28–5.07 (m, 2H), 4.60 (ddd, J = 7.7, 5.4, 1.7 Hz, 1H), 3.73 (s, 1H), 2.66–2.55 (m, 1H), 2.53–2.42 (m, 1H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 147.6, 133.1, 128.5, 123.9, 120.4, 56.5, 56.1, 43.2, 22.7. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{14}H_{20}N_2O_3S+H]^+$: 297.1267; found: 297.1267.



Alcohol 7

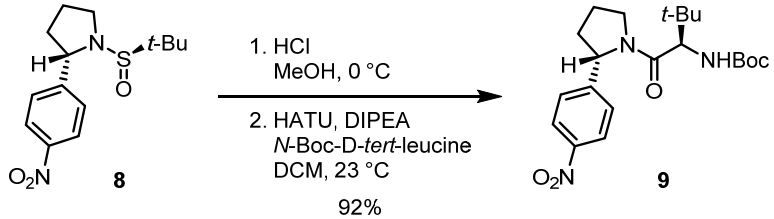
A 9-borabicylo(3.3.1)nonane solution in tetrahydrofuran (9-BBN, 0.5 M in THF; 20.8 mL, 10.4 mmol, 3.0 equiv) was added dropwise to a stirred solution of sulfinamide **6** (1.03 g, 3.48 mmol, 1 equiv) in tetrahydrofuran (35 mL) at 0 °C, and the solution was allowed to warm to 23 °C. The mixture was allowed to stir for 3 hours at 23 °C. After this time, an aqueous solution of sodium hydroxide (2 M; 15.8 mL, 12.6 mmol, 9.1 equiv) and an aqueous solution of hydrogen

peroxide (50 wt %; 7.7 mL, 136 mmol, 39.1 equiv) were added dropwise at 23 °C. The mixture was allowed to stir at 23 °C for 2 hours. After this time, the reaction mixture was diluted with ethyl acetate (50 mL), and brine (25 mL) was added. The phases were separated, and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (diethyl ether then 0–10% methanol in dichloromethane) to yield **7** as a white solid (1.06 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.17 (m, 2H), 7.53–7.45 (m, 2H), 4.56 (app t, J = 6.9 Hz, 1H), 4.00 (s, 1H), 3.79–3.50 (m, 2H), 1.99–1.90 (m, 3H), 1.70–1.47 (m, 2H), 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 147.4, 128.4, 123.9, 61.9, 58.9, 56.0, 35.5, 29.0, 22.7. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{14}H_{22}N_2O_4S+H]^+$: 315.1373; found: 315.1373.



Pyrrolidine 8

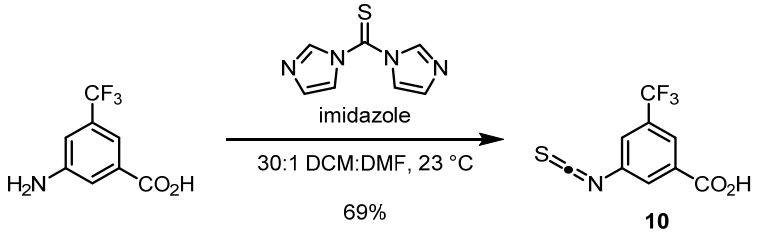
A solution of trimethyl phosphine in tetrahydrofuran (1 M in THF; 18.3 mL, 18.3 mmol, 1.5 equiv) was added to a stirred solution of alcohol **7** (3.83 g, 12.2 mmol, 1 equiv) in tetrahydrofuran (120 mL) in a flame-dried round-bottom flask at 0 °C. 1,1′-(Azodicarbonyl)dipiperidine (ADDP; 4.61 g, 18.3 mmol, 1.5 equiv) was added at 0 °C. The mixture was allowed to warm to 23 °C and was stirred at this temperature for 1 hour. Ethyl acetate (50 mL) and water (25 mL) were added, and the phases were separated. The aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product mixture was purified by flash column chromatography (0–20% diethyl ether in dichloromethane) to yield **8** as a yellow oil (3.27 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 4.75 (app t, J = 7.4 Hz, 1H), 3.94 (app td, J = 9.4, 3.9 Hz, 1H), 3.01 (app dt, J = 10.1, 7.6 Hz, 1H), 2.37–2.28 (m, 1H), 2.06–1.83 (m, 2H), 1.83–1.70 (m, 1H), 1.12 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 147.1, 128.0, 123.7, 68.7, 57.4, 42.3, 36.1, 26.4, 23.8. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{14}H_{20}N_2O_3S+H]^+$: 297.1267; found: 297.1266.



Amide 9

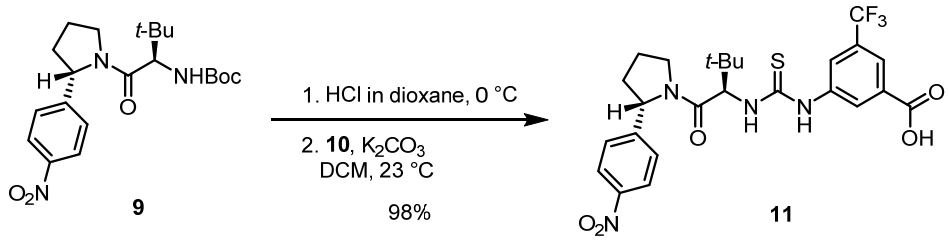
A 4.0 M HCl solution in dioxane (2.1 mL, 8.4 mmol, 5.0 equiv) was added to a stirred solution of pyrrolidine **8** (500 mg, 1.7 mmol, 1 equiv) in methanol (3 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 45 minutes, and then was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (30 mL), and the solution was washed with a saturated aqueous solution

of sodium bicarbonate (20 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic fractions were dried over anhydrous magnesium sulfate, the dried solution was filtered, and the filtrate was concentrated in vacuo. The crude pyrrolidine was dissolved in dichloromethane (4 mL), and the solution was cooled to 0 °C. *N*,*N*-Diisopropylethylamine (DIPEA; 0.88 mL, 5.1 mmol, 3.0 equiv), *N*-Boc-D-*tert*-leucine (390 mg, 1.7 mmol, 1.0 equiv), and *N*-[(dimethylamino)-1H-1,2,3-triazolo-[4,5-b]pyridin-1-ylmethylene]-*N*-methylmethanaminium hexafluorophosphate *N*-oxide (HATU; 770 mg, 2.0 mmol, 1.2 equiv) were added sequentially at 0 °C. The resulting mixture was allowed to warm up to 23 °C and was stirred at this temperature for 15 hours. After this time, the mixture was diluted with ethyl acetate (30 mL) and was washed with a saturated aqueous solution of sodium bicarbonate (20 mL). The aqueous layer was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with a saturated aqueous solution of ammonium chloride (15 mL) and brine (5 mL). The organic layer was dried over anhydrous magnesium sulfate, the solution was filtered, and the filtrate was concentrated under reduced pressure. The crude product mixture was purified by flash column chromatography (10–30% ethyl acetate in hexanes) to provide amide **9** as a white solid (630 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$; 10:1 mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ 8.08 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 5.19 (dd, *J* = 8.3, 2.8 Hz, 1H), 5.06 (d, *J* = 9.8 Hz, 1H), 4.33–4.20 (m, 2H), 3.79–3.70 (m, 1H), 2.40–2.26 (m, 1H), 2.06–1.91 (m, 2H), 1.88–1.76 (m, 1H), 1.46 (s, 9H), 1.02 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$; 10:1 mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ 171.1, 156.5, 150.9, 146.8, 126.3, 123.9, 80.0, 60.7, 59.0, 48.4, 34.3, 34.2, 28.4, 26.5, 23.7. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{21}H_{31}N_3O_5+H]^+$: 406.2336; found: 406.2333.



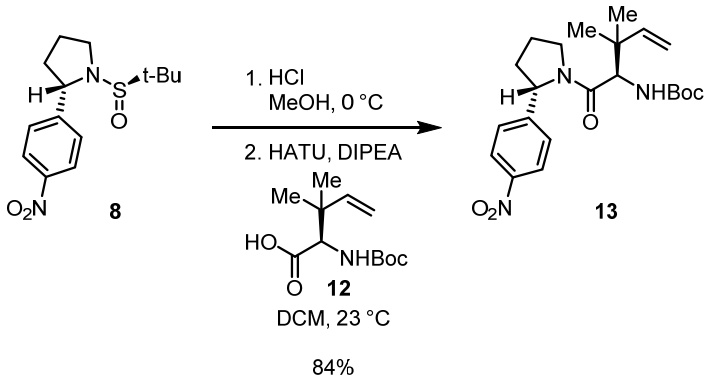
Isothiocyanate 10

3-Amino-5-(trifluoromethyl)benzoic acid (1.50 g, 7.3 mmol, 1 equiv) was dissolved in *N*,*N*-dimethylformamide (2 mL), and dichloromethane (60 mL) was added. Imidazole (50 mg, 0.7 mmol, 0.1 equiv) and 1,1′-thiocarbonyldiimidazole (1.69 g, 9.5 mmol, 1.3 equiv) were added at 23 °C, and the resulting mixture was allowed to stir at 23 °C for 15 hours. After this time, the mixture was concentrated under reduced pressure. The residue was dissolved in diethyl ether (50 mL), and 0.5 M hydrochloric acid (40 mL) was added. The phases were separated, and the aqueous phase was extracted with diethyl ether (3 × 80 mL). The combined organic layers were washed with water (5 mL) and were dried over anhydrous magnesium sulfate. The dried solution was filtered, and the filtrate was concentrated under reduced pressure. The crude product mixture was purified by flash column chromatography (20% ethyl acetate in dichloromethane) to provide isothiocyanate **10** as a light-yellow solid (1.24 g, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.53 (br s, 1H), 8.25 (s, 1H), 8.12 (s, 1H), 7.70 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 140.4, 133.8, 133.2 (q, *J* = 34.1 Hz), 132.0, 130.5, 127.5 (q, *J* = 3.8 Hz), 125.4 (q, *J* = 3.8 Hz), 122.8 (q, *J* = 272.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.06. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_9H_4F_3NO_2S+H]^+$: 245.9842; found: 245.9841.



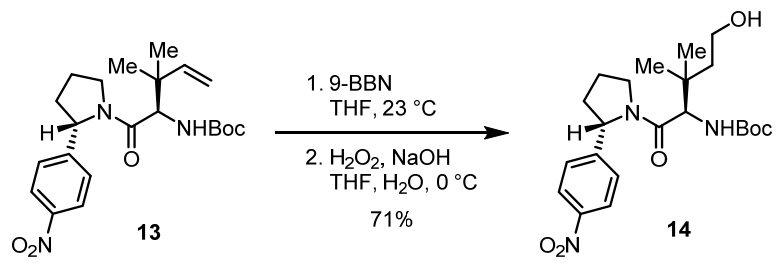
Carboxylic acid 11

A 4.0 M HCl solution in dioxane (7.8 mL, 31 mmol, 20 equiv) was added to amide **9** (630 mg, 1.6 mmol, 1 equiv) in a round-bottom flask at 0 °C. The resulting solution was allowed to warm up to 23 °C and was stirred at this temperature for 1.5 hours. A saturated aqueous solution of sodium bicarbonate (20 mL) was added carefully, and the mixture was extracted with ethyl acetate (3 × 40 mL). The combined organic fractions were dried over anhydrous magnesium sulfate, the solution was filtered, and the filtrate was concentrated under reduced pressure. The crude pyrrolidine was dissolved in dichloromethane (15 mL). Potassium carbonate (322 mg, 2.3 mmol, 1.5 equiv) and isothiocyanate **10** (384 mg, 1.6 mmol, 1.0 equiv) were added sequentially at 23 °C. The resulting mixture was stirred at 23 °C for 15 hours and then was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (60 mL), and 0.3 M hydrochloric acid (40 mL) was added carefully. The phases were separated, and the aqueous phase was extracted with ethyl acetate (3 × 40 mL). The combined organic fractions were dried over anhydrous magnesium sulfate, the solution was filtered, and the filtrate was concentrated under reduced pressure. The crude product mixture was purified by flash column chromatography (10–40% acetone in hexanes followed by 2% acetic acid in 50% acetone in hexanes) to provide carboxylic acid **11** as a white solid (859 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$; 7:1 mixture of rotamers—resonances corresponding to the major rotamer are labeled maj, resonances corresponding to the minor rotamer are labeled min) δ 12.59–10.44 (m, 1H; maj + min), 9.86–9.62 (m, 1H; maj + min), 9.08 (s, 0.9H; maj), 9.00 (s, 0.1H; min), 8.64 (d, J = 9.8 Hz, 0.1H; min), 8.29 (d, J = 8.7 Hz, 0.2H; min), 8.10 (d, J = 9.7 Hz, 0.9H; maj), 7.94 (d, J = 8.7 Hz, 1.8H; maj), 7.79–7.68 (m, 2H; maj + min), 7.57 (d, J = 8.7 Hz, 0.2H; min), 7.22 (d, J = 8.7 Hz, 1.8H; maj), 6.07 (dd, J = 9.0, 1.8 Hz, 0.1H; min), 5.63 (d, J = 9.7 Hz, 0.9H; maj), 5.22 (dd, J = 8.2, 3.6 Hz, 0.9H; maj), 5.17 (d, J = 9.9 Hz, 0.1H; min), 4.65–4.52 (m, 0.9H; maj), 3.99–3.86 (m, 0.9H; maj), 3.85–3.77 (m, 0.2H; min), 2.53–2.35 (m, 1H; maj + min), 2.14–1.99 (m, 2H; maj + min), 1.93–1.82 (m, 1H; maj + min), 1.14 (s, 8H; maj), 0.73 (s, 1H; min). ^{13}C NMR (101 MHz, $CDCl_3$; 7:1 mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ 180.8, 171.8, 168.9, 149.4, 147.0, 141.2, 131.9 (q, J = 33.1 Hz), 130.4, 126.4, 124.7–124.4 (m), 124.1, 123.7 (q, J = 272.8 Hz), 121.3–120.9 (m), 120.9–120.6 (m), 61.6, 61.5, 49.7, 35.8, 34.2, 26.7, 23.8. ^{19}F NMR (376 MHz, $CDCl_3$; 7:1 mixture of rotamers—resonances corresponding to the major rotamer are labeled maj, resonances corresponding to the minor rotamer are labeled min) δ −62.85 (maj), −62.89 (min). HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{25}H_{27}F_3N_4O_5S+H]^+$: 553.1727; found: 553.1725.



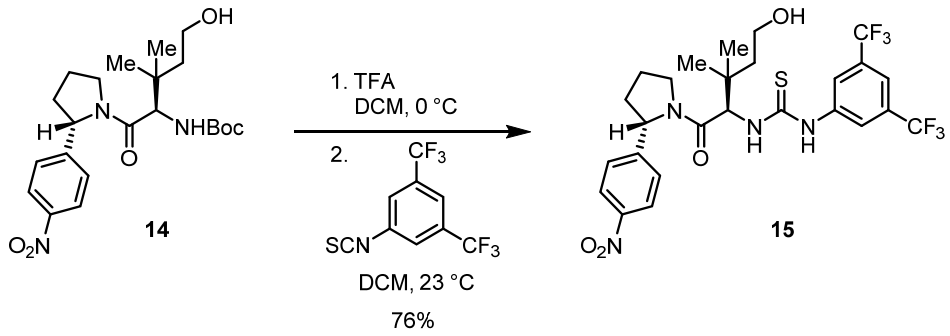
Amide 13

A 4.0 M HCl solution in dioxane (4.2 mL, 16.9 mmol, 5.0 equiv) was added to a stirred solution of pyrrolidine **8** (1.00 g, 3.4 mmol, 1 equiv) in methanol (5 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 45 minutes, and then was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (50 mL), and the solution was washed with a saturated aqueous solution of sodium bicarbonate (20 mL). The aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic fractions were dried over anhydrous magnesium sulfate, the dried solution was filtered, and the filtrate was concentrated in vacuo. The crude pyrrolidine was dissolved in dichloromethane (8 mL), and the solution was cooled to 0 °C. *N*,*N*-Diisopropylethylamine (1.76 mL, 10.1 mmol, 3.0 equiv), carboxylic acid **12** (prepared according to a literature procedure[60]; 780 mg, 3.4 mmol, 1.0 equiv), and HATU (1.54 g, 4.1 mmol, 1.2 equiv) were added sequentially at 0 °C. The resulting mixture was allowed to warm up to 23 °C and was stirred at this temperature for 15 hours. The mixture was diluted with ethyl acetate (50 mL) and was washed with a saturated aqueous solution of sodium bicarbonate (20 mL). The aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with a saturated aqueous solution of ammonium chloride (15 mL) and brine (5 mL). The organic layer was dried over anhydrous magnesium sulfate, the solution was filtered, and the filtrate was concentrated under reduced pressure. The crude product mixture was purified by flash column chromatography (10–30% ethyl acetate in hexanes) to provide amide **13** as a white solid (1.18 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$; 10:1 mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ 8.10 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 6.02 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.20 (dd, *J* = 8.2, 3.0 Hz, 1H), 5.13–5.10 (m, 1H), 5.08 (dd, *J* = 11.4, 1.0 Hz, 1H), 5.02 (d, *J* = 9.4 Hz, 1H), 4.32 (d, *J* = 9.5 Hz, 1H), 4.29–4.21 (m, 1H), 3.81–3.71 (m, 1H), 2.40–2.27 (m, 1H), 2.04–1.94 (m, 2H), 1.89–1.78 (m, 1H), 1.47 (s, 9H), 1.15 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$; 10:1 mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ 170.4, 156.3, 150.8, 146.8, 143.2, 126.3, 123.8, 114.1, 80.0, 60.8, 58.5, 48.4, 39.7, 34.2, 28.4, 24.5, 23.7, 23.2. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{22}H_{31}N_3O_5+H]^+$: 418.2336; found: 418.2333.



Alcohol 14

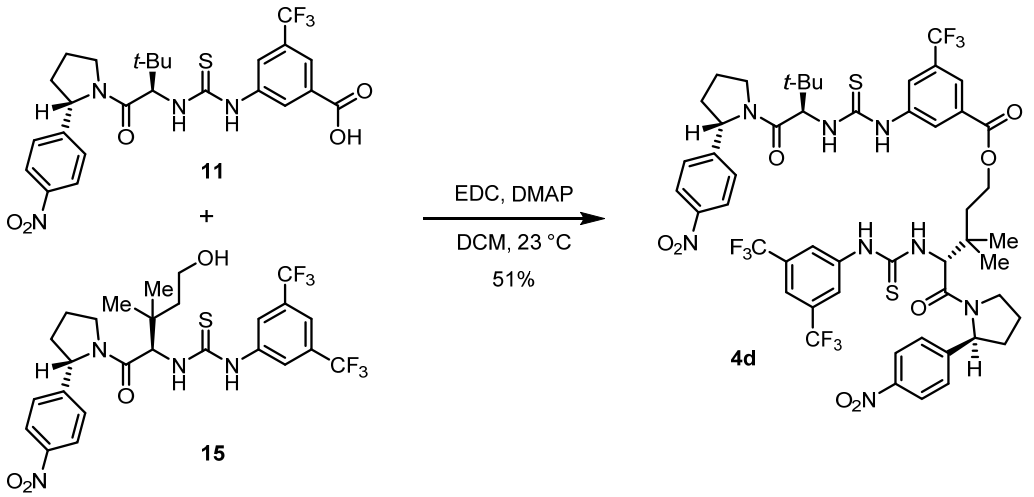
A solution of 9-borabicylo(3.3.1)nonane (9-BBN, 0.5 M in THF; 16.9 mL, 8.43 mmol, 3.0 equiv) was added to a solution of amide **13** (1.17 g, 2.81 mmol, 1 equiv) in tetrahydrofuran (28 mL) at 0 °C. The mixture was allowed to warm to 23 °C and was stirred at this temperature for 3 hours. An aqueous solution of sodium hydroxide (2 M; 12.8 mL, 25.6 mmol, 9.1 equiv) and an aqueous solution of hydrogen peroxide (50 wt %; 6.2 mL, 109 mmol, 39.1 equiv) were added dropwise at 23 °C. The mixture was allowed to stir at 23 °C for 2 hours. Ethyl acetate (50 mL) and brine (25 mL) were added, and the phases were separated. The aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (75 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product mixture was purified by flash column chromatography (10–80% ethyl acetate in hexanes) to yield **14** as a white solid (870 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$; 7:1 mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ 8.12 (d, J = 8.7 Hz, 2H), 7.31–7.25 (overlapping with a solvent signal; m, 2H), 6.39 (d, J = 9.9 Hz, 1H), 5.24 (dd, J = 8.2, 2.4 Hz, 1H), 4.53 (d, J = 10.0 Hz, 1H), 4.38–4.29 (m, 1H), 3.86–3.60 (m, 3H), 2.41–2.28 (m, 1H), 2.06–1.94 (m, 2H), 1.93–1.80 (m, 2H), 1.49 (s, 9H), 1.45–1.39 (m, 1H), 1.10 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$; 7:1 mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ 171.9, 156.9, 150.3, 147.0, 126.3, 124.0, 79.9, 60.8, 58.8, 58.4, 48.6, 41.6, 36.3, 34.2, 28.5, 27.2, 24.7, 23.5. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{22}H_{33}N_3O_6+H]^+$: 436.2442; found: 436.2440.



Thiourea 15

Trifluoroacetic acid (3 mL) was added to a solution of alcohol **14** (411 mg, 0.94 mmol, 1 equiv) in dichloromethane (2 mL) in a round-bottom flask at 0 °C. The resulting solution was stirred at this temperature for 30 minutes. A saturated aqueous solution of sodium bicarbonate (10 mL) was added carefully, and the mixture was extracted with dichloromethane (3 × 10 mL). The combined organic fractions were dried over anhydrous sodium sulfate, the solution was filtered, and the filtrate was concentrated under reduced pressure. The crude amine was dissolved in dichloromethane (6.3 mL), and 3,5-bis(trifluoromethyl)phenyl isothiocyanate (190 µL, 1.08 mmol, 1.15 equiv) was

added at 23 °C. The resulting mixture was stirred at 23 °C for 16 hours. After this time, the mixture was concentrated, and the crude product mixture was purified by flash column chromatography (20–60% ethyl acetate in dichloromethane) to yield **15** as a white solid (430 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$; 8:1 mixture of rotamers—resonances corresponding to the major rotamer are labeled maj, resonances corresponding to the minor rotamer are labeled min) δ 9.36 (s, 0.9H; maj), 9.25 (s, 0.1H; min), 8.91 (d, J = 9.0 Hz, 0.9H; maj), 8.69 (d, J = 9.7 Hz, 0.1H; min), 8.24 (d, J = 8.7 Hz, 0.2H; min), 8.06 (d, J = 8.7 Hz, 1.8H; maj), 7.99 (s, 0.2H; min), 7.84 (s, 1.8H; maj), 7.66 (s, 0.1H; min), 7.62 (s, 0.9H; maj), 7.50 (d, J = 8.6 Hz, 0.2H; min), 7.36 (d, J = 8.7 Hz, 1.8H; maj), 6.36 (d, J = 8.0 Hz, 0.1H; min), 5.39 (d, J = 9.1 Hz, 0.9H; maj), 5.28–5.16 (m, 1H; maj + min), 4.86–4.72 (m, 0.9H; maj), 4.63–4.27 (m, 1H; maj + min), 3.92–3.79 (m, 0.9H; maj), 3.74–3.59 (m, 1.2H; maj + min), 3.58–3.43 (m, 1H; maj + min), 2.46–2.28 (m, 1H; maj + min), 2.10–1.77 (m, 4H; maj + min), 1.53–1.40 (m, 0.9H; maj), 1.38–1.29 (m, 0.1H; min), 1.23 (s, 2.7H; maj), 1.18 (s, 2.7H; maj), 0.77 (s, 0.3H; min), 0.49 (s, 0.3H; min). ^{13}C NMR (101 MHz, $CDCl_3$; 8:1 mixture of rotamers—resonances corresponding to the major rotamer are labeled maj, resonances corresponding to the minor rotamer are labeled min) δ 181.1 (maj), 181.0 (min), 172.6 (min), 171.2 (maj), 150.7 (min), 149.8 (maj), 147.5 (min), 147.0 (maj), 138.9 (min), 139.6 (maj), 132.4 (q, J = 33.4 Hz; maj), 132.2 (q, J = 33.4 Hz; min), 127.6 (min), 126.5 (maj), 124.2 (min), 124.1–124.0 (m; min), 123.9–123.7 (m; maj), 123.9 (maj), 123.2 (q, J = 272.8 Hz; min), 123.1 (q, J = 272.8 Hz; maj), 119.2–118.8 (m; maj + min), 63.2 (maj), 62.0 (min), 61.7 (min), 61.5 (maj), 58.5 (min), 58.3 (maj), 49.0 (maj), 48.1 (min), 41.6 (maj), 41.5 (min), 37.3(4) (min), 37.3(1) (maj), 35.5 (min), 34.2 (maj), 28.7 (maj), 27.7 (min), 25.5 (maj), 25.0 (maj), 23.3 (maj), 21.4 (min). ^{19}F NMR (376 MHz, $CDCl_3$; 8:1 mixture of rotamers—resonances corresponding to the major rotamer are labeled maj, resonances corresponding to the minor rotamer are labeled min) δ −62.97 (min), −63.04 (maj). HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{26}H_{28}F_6N_4O_4S+H]^+$: 607.1808; found: 607.1804.



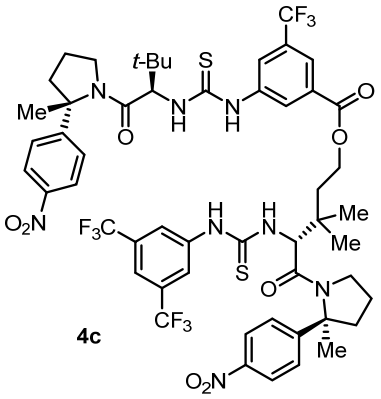
Hydrogen-bond donor 4d

A round-bottom flask was charged with **11** (330 mg, 0.60 mmol, 1.02 equiv) and **15** (355 mg, 0.59 mmol, 1 equiv). Anhydrous dichloromethane (2.5 mL) was added at 23 °C, and the resulting solution was stirred at 23 °C to homogeneity. *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC; 134 mg, 0.7 mmol, 1.2 equiv) and 4-(dimethylamino)pyridine (DMAP; 7.1 mg, 0.06 mmol, 0.1 equiv) were then added at 23 °C. The reaction mixture was stirred at 23 °C for 20 hours. Dichloromethane (10 mL) was added, and the mixture was washed with a saturated aqueous

solution of sodium bicarbonate (5 mL), a saturated aqueous solution of ammonium chloride (5 mL), and brine (5 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude material was purified by flash column chromatography (10–70% ethyl acetate in hexanes) to afford **4d** as a white solid (340 mg, 51% yield). ^{1}H NMR (400 MHz, CD_3CN; mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ 8.77 (s, 1H), 8.74 (s, 1H), 8.36 (s, 1H), 8.08 (s, 2H), 8.04 (s, 1H), 8.02–7.95 (m, 5H), 7.70 (s, 1H), 7.43–7.36 (m, 4H), 7.15 (d, *J* = 9.2 Hz, 1H), 7.05 (d, *J* = 9.0 Hz, 1H), 5.43 (d, *J* = 9.2 Hz, 1H), 5.28 (d, *J* = 9.0 Hz, 1H), 5.20–5.12 (m, 2H), 4.52–4.46 (m, 2H), 4.46–4.37 (m, 2H), 3.93–3.80 (m, 2H), 2.43–2.26 (m, 2H), 2.02–1.83 (m, 6H), 1.80–1.68 (m, 2H), 1.19 (s, 3H), 1.17 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN; mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ 182.6(4), 182.6(2), 170.7, 170.3, 165.5, 152.4, 152.3, 147.5(1), 147.4(6), 141.9, 141.5, 132.7, 132.0 (q, *J* = 33.4 Hz), 131.4 (q, *J* = 32.7 Hz), 128.2, 127.7, 127.6, 124.6 (q, *J* = 272.1 Hz), 124.6–124.5 (m), 124.3 (q, *J* = 272.1 Hz), 124.2(2), 124.1(9), 124.2–124.1 (m), 122.5 (q, *J* = 3.9 Hz), 118.9–118.6 (m), 63.4(3), 63.3(9), 62.5, 61.9, 61.8, 49.5, 49.3, 38.3, 38.1, 35.9, 34.7 (two overlapping signals), 27.0, 24.2, 24.1(2), 24.0(9), 24.0(6). ^{19}F NMR (376 MHz, CD_3CN; mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ −63.38, −63.49. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{51}H_{53}F_9N_8O_8S_2+H]^+$: 1141.3357; found: 1141.3355.

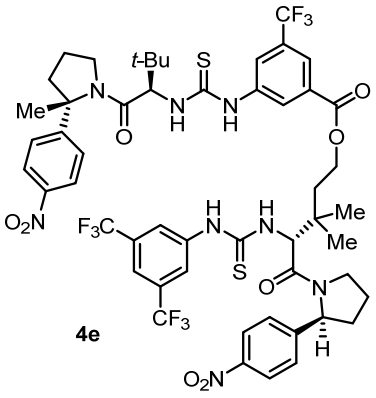
Hydrogen-bond donors **4a**, **4b**, **4av**, and **4aw** were prepared according to literature procedures, and their spectroscopic data were in accordance with those reported[46,47,61].

Note: Hydrogen-bond donors **4f**, **4k**, **4o**, **4p**, **4s**, **4t**, **4u**, **4v**, **4w**, **4aa**, **4ah**, **4aj**, and **4am** contain an inseparable residual impurity coming from a commercial solution of hydrogen chloride in dioxane (Sigma-Aldrich) used in the last synthetic step. A control experiment showed that this impurity does not affect either enantioselectivity or the rate of the asymmetric propargylic substitution.

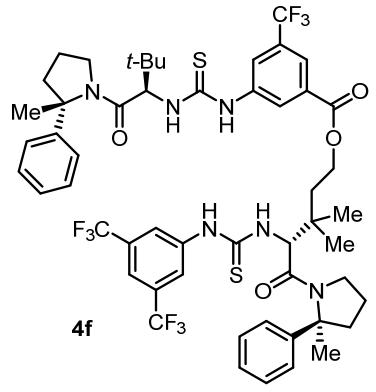


4c

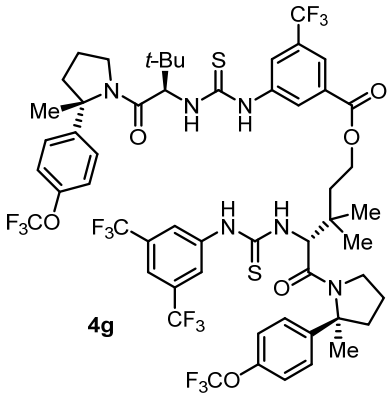
4c: Hydrogen-bond donor **4c** was prepared according to an analogous procedure as reported on page S8 for the preparation of catalyst **4d**. ^{1}H NMR (400 MHz, CD_3CN) δ 8.76 (s, 1H), 8.75 (s, 1H), 8.40 (s, 1H), 8.11 (s, 2H), 8.08 (s, 1H), 8.03–7.94 (m, 5H), 7.73 (s, 1H), 7.53–7.43 (m, 4H), 7.06 (d, *J* = 9.1 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 1H), 5.37 (d, *J* = 9.1 Hz, 1H), 5.21 (d, *J* = 9.0 Hz, 1H), 4.58–4.44 (m, 4H), 3.99–3.80 (m, 2H), 2.15–2.04 (m, 2H), 1.93–1.83 (m, 12H), 1.83–1.72 (m, 2H), 1.22 (s, 3H), 1.15 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.7(2), 182.7(0), 170.3, 169.8, 165.5, 155.5(0), 155.4(6), 147.1(0), 147.0(5), 141.9, 141.4, 132.9, 132.1 (q, *J* = 33.4 Hz), 131.6 (q, *J* = 32.9 Hz), 128.3, 127.4, 127.3, 124.7 (q, *J* = 3.8 Hz), 124.6 (q, *J* = 271.8 Hz), 124.4–124.2 (m), 124.3 (q, *J* = 272.1 Hz), 123.9, 123.8, 122.7 (q, *J* = 3.9 Hz), 119.0–118.7 (m), 68.4, 68.3, 63.8, 63.4, 62.7, 51.0, 50.9, 44.7(3), 44.6(9), 38.4, 38.1, 36.0, 27.0, 25.0(2), 24.9(5), 24.4, 24.1, 23.4, 23.3. ^{19}F NMR (376 MHz, CD_3CN) δ −63.35, −63.46. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{53}H_{57}F_9N_8O_8S_2+H]^+$: 1169.3670, found: 1169.3670.



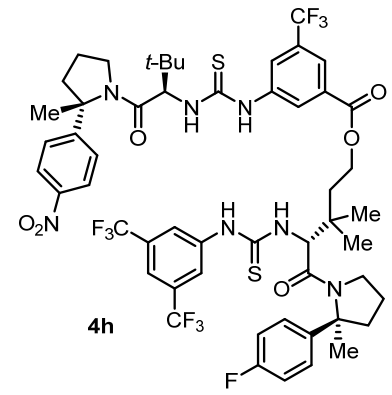
4e: Hydrogen-bond donor **4e** was prepared according to an analogous procedure as reported on page S8 for the preparation of catalyst **4d**. ^{1}H NMR (400 MHz, CD_3CN; 6:1 mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ 8.76 (s, 1H), 8.73 (s, 1H), 8.40 (s, 1H), 8.11–8.05 (m, 3H), 8.05–7.94 (m, 5H), 7.71 (s, 1H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 9.1 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 5.42 (d, *J* = 9.1 Hz, 1H), 5.21 (d, *J* = 9.0 Hz, 1H), 5.16 (dd, *J* = 8.2, 2.5 Hz, 1H), 4.59–4.47 (m, 3H), 4.47–4.38 (m, 1H), 3.96–3.80 (m, 2H), 2.42–2.27 (m, 1H), 2.15–2.04 (m, 1H), 1.93–1.48 (m, 11H), 1.19 (s, 3H), 1.17 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN; 6:1 mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ 182.7, 182.6, 170.3, 170.2, 165.5, 155.5, 152.4, 147.5, 147.1, 141.9, 141.5, 132.9, 132.0 (q, *J* = 33.3 Hz), 131.5 (q, *J* = 33.0 Hz), 128.2, 127.7, 127.4, 124.8–124.5 (m), 124.6 (q, *J* = 271.8 Hz), 124.4–124.1 (m, two overlapping signals), 124.3 (q, *J* = 272.1 Hz), 123.8, 122.7–122.5 (m), 119.0–118.7 (m), 68.3, 63.8, 63.4, 62.4, 61.9, 50.9, 49.5, 44.7, 38.3, 38.0, 36.0, 34.7, 27.0, 25.0, 24.2(2), 24.1(5), 26.1, 23.3. ^{19}F NMR (376 MHz, CD_3CN; 6:1 mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ −63.35, −63.47. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{52}H_{55}F_9N_8O_8S_2+H]^+$: 1155.3513, found: 1155.3504.



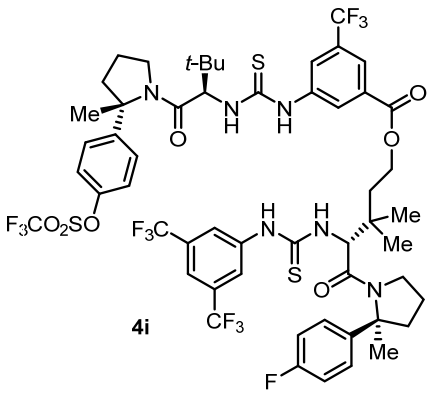
4f: Hydrogen-bond donor **4f** was prepared according to an analogous procedure as reported on page S8 for the preparation of catalyst **4d**. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4f** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4f** are reported.) δ 9.75 (s, 1H), 9.63 (s, 1H), 8.54 (s, 1H), 8.46 (s, 1H), 8.41 (s, 2H), 8.00 (s, 1H), 7.76 (s, 1H), 7.58 (d, *J* = 9.4 Hz, 1H), 7.40 (d, *J* = 9.3 Hz, 1H), 7.32–7.23 (m, 4H), 7.22–7.14 (m, 4H), 7.14–7.05 (m, 2H), 5.58 (d, *J* = 9.4 Hz, 1H), 5.43 (d, *J* = 9.3 Hz, 1H), 4.65–4.48 (m, 4H), 4.03–3.85 (m, 2H), 2.17–2.01 (m, 2H), 2.01–1.84 (m, 12H), 1.84–1.67 (m, 2H), 1.29 (s, 3H), 1.22 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4f** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4f** are reported.) δ 182.6(4), 182.6(1), 169.9, 169.5, 165.2, 147.3(4), 147.3(0), 142.8, 142.3, 132.7, 132.0 (q, *J* = 33.1 Hz), 131.2 (q, *J* = 33.1 Hz), 128.5, 128.5, 127.6, 126.4(9), 126.4(6), 126.1(0), 126.0(5), 124.6 (q, overlapping with other signals), 124.3 (q, *J* = 272.1 Hz), 124.1–123.8 (m), 123.5–123.2 (m), 121.8–121.5 (m), 118.0–117.6 (m), 68.4, 68.3, 63.3, 63.2, 62.3, 50.9, 50.8, 45.2(0), 45.1(7), 38.3, 38.2, 36.0, 27.0, 25.7, 25.6, 24.3, 23.9, 22.8(4), 22.8(0). ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4f** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4f** are reported.) δ −63.39, −63.50. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{53}H_{59}F_9N_6O_4S_2+H]^+$: 1079.3968, found: 1079.3975.



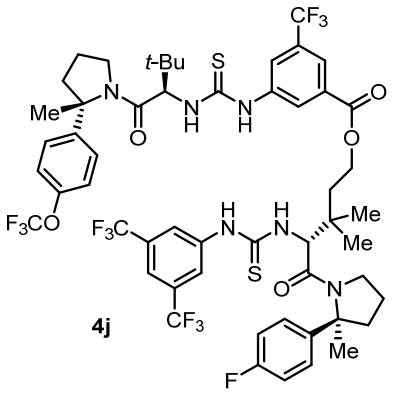
4g: Hydrogen-bond donor **4g** was prepared according to an analogous procedure as reported on page S8 for the preparation of catalyst **4d**. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4g** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4g** are reported.) δ 9.75 (s, 1H), 9.64 (s, 1H), 8.54 (s, 1H), 8.44 (s, 1H), 8.39 (s, 2H), 8.00 (s, 1H), 7.76 (s, 1H), 7.57 (d, *J* = 9.4 Hz, 1H), 7.47–7.35 (m, 5H), 7.17–7.08 (m, 4H), 5.52 (d, *J* = 9.4 Hz, 1H), 5.36 (d, *J* = 9.2 Hz, 1H), 4.69–4.59 (m, 2H), 4.57 (app t, *J* = 7.1 Hz, 2H), 4.04–3.86 (m, 2H), 2.20–2.09 (m, 2H), 2.07–1.87 (m, 12H), 1.87–1.72 (m, 2H), 1.28 (s, 3H), 1.22 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4g** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4g** are reported.) δ 182.7(1), 182.6(8), 170.0, 169.6, 165.2, 147.9–147.8 (m), 147.9–147.8 (m), 146.8(6), 146.8(2), 142.7, 142.3, 132.7, 132.0 (q, *J* = 33.4 Hz), 131.3 (q, *J* = 32.9 Hz), 128.0(2), 127.9(6), 127.5, 124.7 (q, *J* = 271.8 Hz), 124.3 (q, *J* = 272.1 Hz), 124.0–123.8 (m), 123.5–123.3 (m), 121.8–121.5 (m), 121.4 (q, *J* = 255.0 Hz), 121.4 (q, *J* = 255.0 Hz), 121.0, 121.0, 118.0–117.6 (m), 68.0, 67.9, 63.3(0), 63.2(5), 62.4, 50.8, 50.7, 45.1, 45.0, 38.3, 38.0, 35.9, 27.0, 25.6, 25.5, 24.3, 23.9, 22.9(9), 22.9(5). ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4g** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4g** are reported.) δ −58.58, −58.68, −63.44, −63.56. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{55}H_{57}F_{15}N_6O_6S_2+H]^+$: 1247.3614, found: 1247.3617.



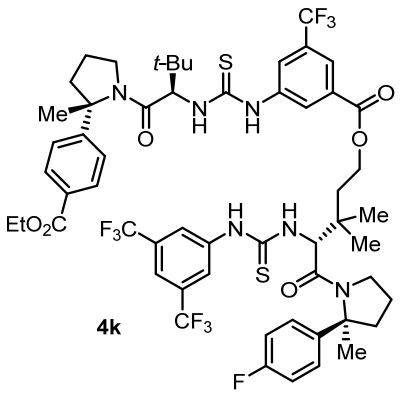
4h: Hydrogen-bond donor **4h** was prepared according to an analogous procedure as reported previously, starting from 4′-nitroacetophenone[47,62]. ^{1}H NMR (400 MHz, CD_3CN) δ 8.77 (s, 1H), 8.72 (s, 1H), 8.39 (s, 1H), 8.10 (s, 2H), 8.07 (s, 1H), 8.01 (s, 1H), 8.00–7.95 (m, 2H), 7.72 (s, 1H), 7.51–7.45 (m, 2H), 7.26–7.19 (m, 2H), 7.14 (d, *J* = 9.2 Hz, 1H), 7.00 (d, *J* = 9.0 Hz, 1H), 6.91–6.82 (m, 2H), 5.40 (d, *J* = 9.2 Hz, 1H), 5.21 (d, *J* = 9.0 Hz, 1H), 4.59–4.42 (m, 4H), 3.96–3.80 (m, 2H), 2.13–1.99 (m, 2H), 1.91–1.81 (m, 12H), 1.81–1.68 (m, 2H), 1.21 (s, 3H), 1.16 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.7, 182.7, 170.3, 169.9, 165.5, 161.9 (d, *J* = 242.3 Hz), 155.5, 147.1, 143.5 (d, *J* = 2.9 Hz), 142.0, 141.4, 132.9, 132.1 (q, *J* = 33.2 Hz), 131.6 (q, *J* = 33.1 Hz), 128.3, 128.0 (d, *J* = 7.6 Hz), 127.4, 124.7 (q, *J* = 3.6 Hz), 124.6 (q, *J* = 271.9 Hz), 124.4 (q, *J* = 3.2 Hz), 124.3 (q, *J* = 272.1 Hz), 123.8, 122.7 (q, *J* = 3.4 Hz), 118.8 (q, *J* = 3.4 Hz), 115.2 (d, *J* = 21.1 Hz), 68.3, 68.2, 63.8, 63.5, 62.8, 51.0, 50.9, 45.1, 44.8, 38.4, 38.3, 36.0, 27.0, 25.6, 25.0, 24.4, 24.1, 23.3, 23.0. ^{19}F NMR (376 MHz, CD_3CN) δ −63.34, −63.45, −119.57. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{53}H_{57}F_{10}N_7O_6S_2+H]^+$: 1142.3725; found: 1142.3705.



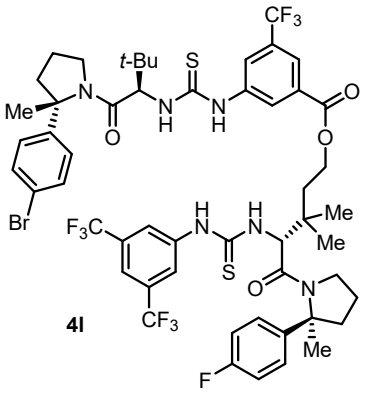
4i: Hydrogen-bond donor **4i** was prepared according to an analogous procedure as reported previously, starting from 4-acetylphenyl triflate[47,62]. ^{1}H NMR (400 MHz, CD_3CN) δ 8.75 (s, 1H), 8.72 (s, 1H), 8.39 (s, 1H), 8.15–8.05 (m, 3H), 8.01 (s, 1H), 7.73 (s, 1H), 7.44–7.35 (m, 2H), 7.28–7.20 (m, 2H), 7.19–7.10 (m, 3H), 7.01 (d, J = 9.0 Hz, 1H), 6.93–6.80 (m, 2H), 5.41 (d, J = 9.2 Hz, 1H), 5.22 (d, J = 9.1 Hz, 1H), 4.57–4.40 (m, 4H), 3.94–3.81 (m, 2H), 2.14–1.98 (m, 2H), 1.92–1.78 (m, 12H), 1.79–1.64 (m, 2H), 1.21 (s, 3H), 1.16 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.7(8), 182.7(6), 170.3, 169.9, 165.5, 162.0 (d, J = 242.2 Hz), 148.6(3), 148.6(1), 143.5 (d, J = 2.9 Hz), 142.0, 141.5, 132.9, 132.1 (q, J = 33.3 Hz), 131.5 (q, J = 32.8 Hz), 128.5, 128.3, 128.0 (d, J = 7.9 Hz), 124.8–124.6 (m), 124.6–124.3 (m), 124.6 (q, J = 272.1 Hz), 124.3 (q, J = 272.1 Hz), 122.8–122.5 (m), 121.5, 119.0–118.7 (m), 115.2 (d, J = 21.2 Hz), 68.2, 68.1, 63.8, 63.5, 62.7, 51.0, 50.9, 45.1, 45.0, 38.4, 38.3, 36.0, 27.0, 25.6, 25.4, 24.4, 24.1, 23.1, 23.0; the signal corresponding to the carbon atom of the ((trifluoromethyl)sulfonyl)oxy group could not be unambiguously identified. ^{19}F NMR (376 MHz, CD_3CN) δ −63.37, −63.47, −74.08, −119.58. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{54}H_{57}F_{13}N_6O_7S_3+H]^+$: 1245.3316; found: 1245.3280.



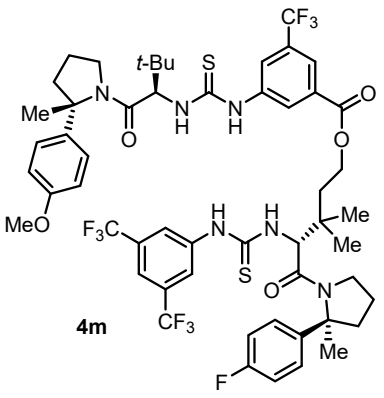
4j: Hydrogen-bond donor **4j** was prepared according to an analogous procedure as reported previously, starting from 4′-(trifluoromethoxy)acetophenone[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4j** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4j** are reported.) δ 9.76 (s, 1H), 9.64 (s, 1H), 8.54 (s, 1H), 8.44 (s, 1H), 8.41 (s, 2H), 8.00 (s, 1H), 7.76 (s, 1H), 7.59 (d, J = 9.4 Hz, 1H), 7.43 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 6.5 Hz, 1H), 7.34–7.27 (m, 2H), 7.13 (d, J = 8.3 Hz, 2H), 6.96–6.86 (m, 2H), 5.53 (d, J = 9.4 Hz, 1H), 5.35 (d, J = 9.2 Hz, 1H), 4.67–4.50 (m, 4H), 4.04–3.85 (m, 2H), 2.20–2.07 (m, 2H), 2.07–1.87 (m, 12H), 1.86–1.71 (m, 2H), 1.28 (s, 3H), 1.22 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4j** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4j** are reported.) δ 182.7, 182.6, 170.0, 169.6, 165.2, 161.9 (d, J = 242.0 Hz), 147.9–147.8 (m), 146.9, 143.4 (d, J = 2.9 Hz), 142.8, 142.3, 132.7, 132.0 (q, J = 33.4 Hz), 131.3 (q, J = 32.7 Hz), 128.0(3), 127.9(9) (d, J = 6.9 Hz), 127.3, 124.7 (q, J = 272.1 Hz), 124.3 (q, J = 271.8 Hz), 123.9–123.7 (m), 123.5–123.2 (m), 121.8–121.5 (m), 121.4 (q, J = 255.0 Hz), 121.0, 117.9–117.6 (m), 114.9 (d, J = 21.2 Hz), 68.0, 67.9, 63.3(0), 63.2(7), 62.4, 50.8, 50.7, 45.1(1), 45.0(5), 38.3, 28.1, 35.9, 27.0, 25.6(4), 25.5(6), 24.3, 23.9, 23.0, 22.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4j** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4j** are reported.) δ −58.58, −63.44, −63.51, −119.85. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{54}H_{57}F_{13}N_6O_5S_2+H]^+$: 1181.3697, found: 1181.3699.



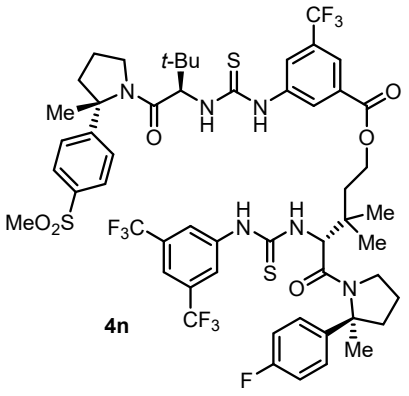
4k: Hydrogen-bond donor **4k** was prepared according to an analogous procedure as reported previously, starting from methyl 4-acetylbenzoate[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4k** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4k** are reported.) δ 9.78 (s, 1H), 9.68 (s, 1H), 8.56 (s, 1H), 8.46 (s, 1H), 8.40 (s, 2H), 8.00 (s, 1H), 7.87–7.79 (m, 2H), 7.75 (s, 1H), 7.61 (d, *J* = 9.3 Hz, 1H), 7.49–7.37 (m, 3H), 7.35–7.25 (m, 2H), 6.96–6.84 (m, 2H), 5.53 (d, *J* = 9.4 Hz, 1H), 5.38 (d, *J* = 9.2 Hz, 1H), 4.70–4.48 (m, 4H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.02–3.88 (m, 2H), 2.19–2.07 (m, 2H), 2.04–1.86 (m, 12H), 1.86–1.72 (m, 2H), 1.32–1.25 (m, 6H), 1.22 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4k** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4k** are reported.) δ 182.6(2), 182.6(1), 170.0, 169.6, 166.5, 165.2, 161.9 (d, *J* = 242.3 Hz), 152.9, 143.4 (d, *J* = 2.9 Hz), 142.8, 142.2, 132.7, 132.0 (q, *J* = 33.1 Hz), 131.3 (q, *J* = 32.9 Hz), 129.7, 129.0, 128.0 (d, *J* = 7.6 Hz), 127.4, 126.4, 124.7 (q, *J* = 271.7 Hz), 124.3 (q, *J* = 272.1 Hz), 123.9–123.6 (m), 123.5–123.2 (m), 121.8–121.5 (m), 117.9–117.6 (m), 114.9 (d, *J* = 21.1 Hz), 68.2, 68.0, 63.3(0), 63.2(5), 62.4, 61.1, 50.8, 50.7, 45.1, 45.0, 38.3, 38.2, 35.9, 27.0, 25.7, 25.4, 24.3, 23.9, 23.1, 22.9, 14.5. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4k** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4k** are reported.) δ −63.36, −63.49, −119.82. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{56}H_{62}F_{10}N_6O_6S_2+H]^+$: 1169.4085, found: 1169.4092.



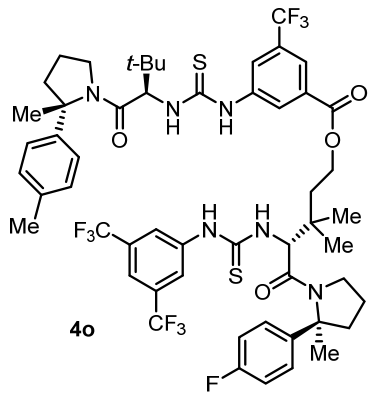
4l: Hydrogen-bond donor **4l** was prepared according to an analogous procedure as reported previously, starting from 4′-bromoacetophenone[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4l** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4l** are reported.) δ 9.78 (s, 1H), 9.66 (s, 1H), 8.54 (s, 1H), 8.46 (s, 1H), 8.41 (s, 2H), 8.00 (s, 1H), 7.75 (s, 1H), 7.59 (d, *J* = 9.4 Hz, 1H), 7.41 (d, *J* = 9.2 Hz, 1H), 7.36–7.22 (m, 6H), 6.95–6.87 (m, 2H), 5.53 (d, *J* = 9.4 Hz, 1H), 5.35 (d, *J* = 9.2 Hz, 1H), 4.66–4.50 (m, 4H), 4.02–3.85 (m, 2H), 2.17–1.85 (m, 14H), 1.85–1.71 (m, 2H), 1.28 (s, 3H), 1.22 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4l** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4l** are reported.) δ 182.7, 182.6, 170.0, 169.6, 165.2, 161.9 (d, *J* = 242.3 Hz), 147.0, 143.4 (d, *J* = 2.9 Hz), 142.8, 142.2, 132.7, 132.0 (q, *J* = 33.4 Hz), 131.4, 131.3 (q, *J* = 32.7 Hz), 128.5, 128.0 (d, *J* = 8.0 Hz), 127.6, 124.7 (q, *J* = 271.8 Hz), 124.3 (q, *J* = 272.1 Hz), 123.9 (q, *J* = 4.0 Hz), 123.5–123.3 (m), 121.7 (q, *J* = 4.1 Hz), 119.9, 117.9–117.6 (m), 114.9 (d, *J* = 21.1 Hz), 68.0, 67.9, 63.3(0), 63.2(6), 62.4, 50.8, 50.7, 45.1, 45.0, 38.3, 38.2, 35.9, 27.0, 25.7, 25.4, 24.4, 23.9, 23.0, 22.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4l** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4l** are reported.) δ −63.36, −63.48, −119.81. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{53}H_{57}BrF_{10}N_6O_4S_2+H]^+$: 1177.2959, found: 1177.2967.



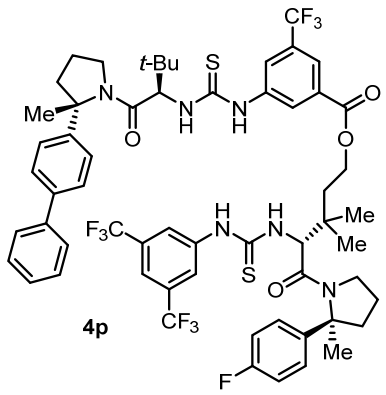
4m: Hydrogen-bond donor **4m** was prepared according to an analogous procedure as reported previously, starting from 4′-(methoxy)acetophenone[47,62]. ^{1}H NMR (400 MHz, CD_3CN + 5 drops of DMSO-d_6) δ 10.09 (s, 1H), 9.97 (s, 1H), 8.51 (s, 1H), 8.33 (s, 1H), 8.29 (s, 2H), 8.02–7.88 (m, 2H), 7.75 (d, J = 9.2 Hz, 1H), 7.70 (s, 1H), 7.29–7.20 (m, 2H), 7.19–7.09 (m, 2H), 6.96–6.85 (m, 2H), 6.76–6.66 (m, 2H), 5.41 (d, J = 9.3 Hz, 1H), 5.30 (d, J = 9.3 Hz, 1H), 4.58–4.41 (m, 4H), 3.94–3.78 (m, 2H), 3.68 (s, 3H), 2.10–1.97 (m, 2H), 1.94–1.79 (m, 12H), 1.80–1.64 (m, 2H), 1.21 (s, 3H), 1.17 (s, 3H), 1.07 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN + 5 drops of DMSO-d_6) δ 182.5(8), 182.5(5), 170.1, 169.8, 165.7, 161.9 (d, J = 242.3 Hz), 158.7, 143.7 (d, J = 3.0 Hz), 142.8, 142.4, 139.7, 132.7, 131.8 (q, J = 33.2 Hz), 131.2 (q, J = 32.7 Hz), 128.0 (d, J = 7.9 Hz), 127.5, 127.4, 124.7 (q, J = 272.0 Hz), 124.5 (q, J = 272.1 Hz), 124.0–123.7 (m), 123.6–123.2 (m), 121.9–121.5 (m), 118.1–117.8 (m), 115.1 (d, J = 21.2 Hz), 113.9, 68.0, 67.9, 63.5, 63.1, 62.3, 55.7, 51.0, 50.9, 45.3, 45.2, 38.3, 38.2, 36.1, 27.1, 25.6, 25.5, 24.5, 24.1, 23.1, 23.0. ^{19}F NMR (376 MHz, CD_3CN + 5 drops of DMSO-d_6) δ −63.22, −63.36, −119.72. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{54}H_{60}F_{10}N_6O_5S_2+H]^+$: 1127.3980; found: 1127.3959



4n: Hydrogen-bond donor **4n** was prepared according to an analogous procedure as reported previously, starting from 4′-(methylsulfonyl)acetophenone[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4n** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4n** are reported.) δ 9.76 (s, 1H), 9.68 (s, 1H), 8.58 (s, 1H), 8.42 (s, 1H), 8.41 (s, 2H), 8.00 (s, 1H), 7.81–7.76 (m, 2H), 7.75 (s, 1H), 7.62 (d, J = 9.5 Hz, 1H), 7.60–7.55 (m, 2H), 7.44 (d, J = 9.1 Hz, 1H), 7.34–7.27 (m, 2H), 6.95–6.86 (m, 2H), 5.52 (d, J = 9.4 Hz, 1H), 5.35 (d, J = 9.1 Hz, 1H), 4.71–4.50 (m, 4H), 4.02–3.88 (m, 2H), 3.05 (s, 3H), 2.23–1.87 (m, 14H), 1.87–1.71 (m, 2H), 1.29 (s, 3H), 1.23 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4n** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4n** are reported.) δ 182.6(2), 182.6(0), 170.0, 169.6, 165.3, 161.9 (d, J = 242.2 Hz), 153.7, 143.4 (d, J = 3.2 Hz), 142.8, 142.2, 139.7, 132.7, 132.0 (q, J = 33.1 Hz), 131.3 (q, J = 33.1 Hz), 128.0 (d, J = 7.8 Hz), 127.6, 127.5, 127.2, 124.6 (q, J = 272.1 Hz), 124.3 (q, J = 272.1 Hz), 123.9–123.7 (m), 123.5–123.2 (m), 121.9–121.5 (m), 117.9–117.5 (m), 114.9 (d, J = 21.1 Hz), 68.2, 68.0, 63.3(3), 63.2(9), 62.5, 50.8, 50.7, 45.1, 44.9, 44.2, 38.2, 38.1, 35.9, 27.0, 25.7, 25.3, 24.3, 23.9, 23.1, 22.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4n** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4n** are reported.) δ −63.36, −63.49, −119.84. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{54}H_{60}F_{10}N_6O_6S_3+H]^+$: 1175.3650, found: 1175.3647.

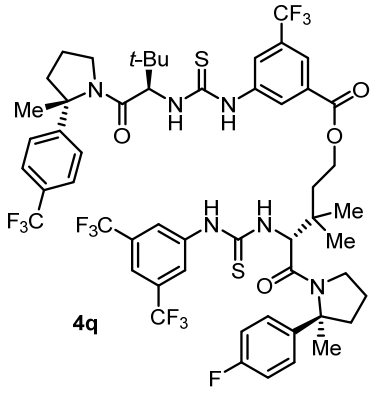


4o: Hydrogen-bond donor **4o** was prepared according to an analogous procedure as reported previously, starting from 4′-methylacetophenone[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4o** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4o** are reported.) δ 9.76 (s, 1H), 9.64 (s, 1H), 8.53 (s, 1H), 8.47 (s, 1H), 8.40 (s, 2H), 8.00 (s, 1H), 7.76 (s, 1H), 7.60 (d, J = 9.3 Hz, 1H), 7.41 (d, J = 9.4 Hz, 1H), 7.34–7.26 (m, 2H), 7.15 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 8.1 Hz, 2H), 6.95–6.86 (m, 2H), 5.53 (d, J = 9.4 Hz, 1H), 5.42 (d, J = 9.4 Hz, 1H), 4.65–4.50 (m, 4H), 4.02–3.93 (m, 1H), 3.90 (app td, J = 9.3, 6.8 Hz, 1H), 2.21 (s, 3H), 2.16–1.84 (m, 14H), 1.84–1.68 (m, 2H), 1.28 (s, 3H), 1.22 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4o** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4o** are reported.) δ 182.6(4), 182.6(0), 169.9, 169.6, 165.2, 161.9 (d, J = 242.0 Hz), 144.4, 143.4 (d, J = 3.3 Hz), 142.8, 142.3, 135.6, 132.7, 132.0 (q, J = 33.1 Hz), 131.2 (q, J = 32.7 Hz), 129.2, 128.0 (d, J = 7.6 Hz), 127.5, 126.1, 124.7 (q, J = 271.9 Hz), 124.3 (q, J = 272.0 Hz), 124.1–123.8 (m), 123.5–123.2 (m), 121.8–121.5 (m), 117.9–117.6 (m), 114.9 (d, J = 21.1 Hz), 68.1, 68.0, 63.3, 63.2, 62.4, 50.8, 50.7, 45.2, 45.1, 38.3, 38.1, 36.0, 27.0, 25.8, 25.7, 24.3, 23.9, 22.9, 22.8, 20.8. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4o** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4o** are reported.) δ −63.37, −63.50, −119.84. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{54}H_{60}F_{10}N_6O_4S_2+H]^+$: 1111.4031, found: 1111.4032.



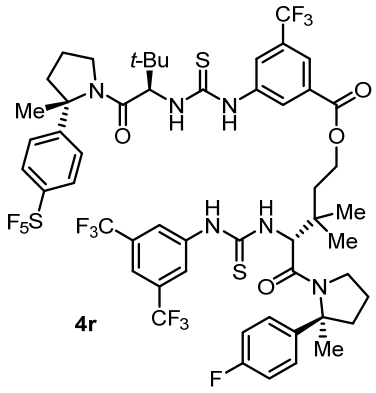
4p: Hydrogen-bond donor **4p** was prepared according to an analogous procedure as reported previously, starting from 4′-phenylacetophenone[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4p** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4p** are reported.) δ 9.75 (s, 1H), 9.66 (s, 1H), 8.58 (s, 1H), 8.48 (s, 1H), 8.40 (s, 2H), 7.99 (s, 1H), 7.75 (s, 1H), 7.60–7.52 (m, 3H), 7.52–7.46 (m, 2H), 7.45–7.35 (m, 5H), 7.33–7.24 (m, 3H), 6.95–6.86 (m, 2H), 5.52 (d, J = 9.4 Hz, 1H), 5.44 (d, J = 9.3 Hz, 1H), 4.67–4.58 (m, 2H), 4.54 (app t, J = 7.1 Hz, 2H), 4.00–3.89 (m, 2H), 2.20–1.71 (m, 16H), 1.26 (s, 3H), 1.20 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4p** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4p** are reported.) δ 182.7, 182.6, 170.0, 169.6, 165.2, 161.9 (d, J = 242.0 Hz), 146.7, 143.4 (d, J = 3.0 Hz), 142.7, 142.3, 141.4, 139.1, 132.6, 132.0 (q, J = 33.3 Hz), 131.2 (q, J = 32.9 Hz), 129.6, 128.0 (d, J = 8.1 Hz), 127.9, 127.6, 127.4, 127.0, 126.8, 124.6 (q, J = 271.9 Hz), 124.3 (q, J = 272.1 Hz), 124.0–123.8 (m), 123.5–123.3 (m), 121.8–121.5 (m), 117.9–117.6 (m), 114.9 (d, J = 21.2 Hz), 68.2, 68.0, 63.3(0), 63.2(5), 62.4, 50.8(2), 50.7(9), 45.2, 45.1, 38.2, 38.1, 36.0, 27.0, 25.7, 25.6, 24.3, 23.9, 23.0, 22.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4p** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4p** are reported.) δ −63.34, −63.49,

−119.82. HRMS (ESI): *m/z* $[M+H]^+$ calculated for $[C_{59}H_{62}F_{10}N_6O_4S_2+H]^+$: 1173.4187, found: 1173.4194.



4q

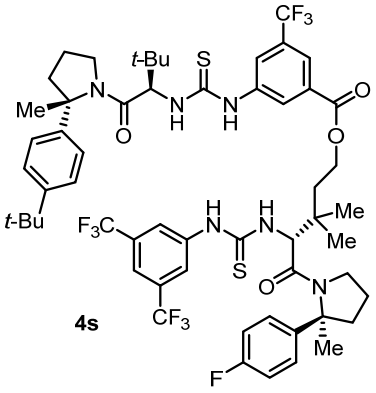
4q: Hydrogen-bond donor **4q** was prepared according to an analogous procedure as reported previously, starting from 4′-(trifluoromethyl)acetophenone[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4q** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4q** are reported.) δ 9.78 (s, 1H), 9.65 (s, 1H), 8.54 (s, 1H), 8.47 (s, 1H), 8.41 (s, 2H), 8.00 (s, 1H), 7.75 (s, 1H), 7.58 (d, *J* = 9.3 Hz, 1H), 7.56–7.49 (m, 4H), 7.40 (d, *J* = 9.3 Hz, 1H), 7.34–7.27 (m, 2H), 6.96–6.88 (m, 2H), 5.53 (d, *J* = 9.4 Hz, 1H), 5.36 (d, *J* = 9.2 Hz, 1H), 4.68–4.59 (m, 2H), 4.56 (app t, *J* = 7.1 Hz, 2H), 4.02–3.91 (m, 2H), 2.23–2.07 (m, 2H), 2.04–1.88 (m, 12H), 1.88–1.70 (m, 2H), 1.28 (s, 3H), 1.22 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4q** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4q** are reported.) δ 182.7, 182.6, 170.0, 169.6, 165.2, 161.9 (d, *J* = 242.3 Hz), 152.3, 143.4 (d, *J* = 3.3 Hz), 142.8, 142.3, 132.7, 132.0 (q, *J* = 33.2 Hz), 131.3 (q, *J* = 32.9 Hz), 128.2 (q, *J* = 31.6 Hz), 128.0 (d, *J* = 8.0 Hz), 127.5, 127.0, 125.5–125.2 (m), 125.4 (q, *J* = 271.0 Hz), 124.7 (q, *J* = 272.5 Hz), 124.3 (q, *J* = 272.1 Hz), 123.9–123.7 (m), 123.5–123.3 (m), 121.8–121.5 (m), 117.9–117.5 (m), 114.9 (d, *J* = 21.1 Hz), 68.1, 68.0, 63.3(2), 63.2(6), 62.4, 50.8, 50.7, 45.1, 44.9, 38.3, 38.2, 35.9, 27.0, 25.7, 25.3, 24.3, 23.9, 23.1, 22.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4q** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4q** are reported.) δ −62.77, −63.44, −63.51, −119.84. HRMS (ESI): *m/z* $[M+H]^+$ calculated for $[C_{54}H_{57}F_{13}N_6O_4S_2+H]^+$: 1165.3748, found: 1165.3750.



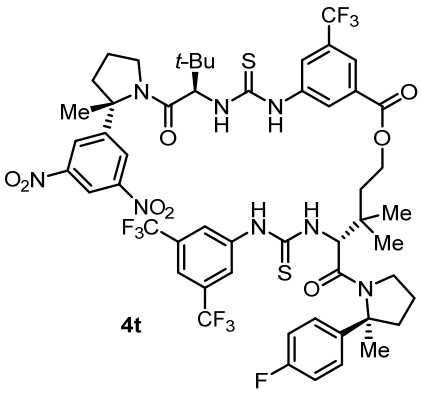
4r

4r: Hydrogen-bond donor **4r** was prepared according to an analogous procedure as reported previously, starting from 4′-(pentafluorosulfanyl)acetophenone[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4r** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4r** are reported.) δ 9.81 (s, 1H), 9.69 (s, 1H), 8.53 (s, 1H), 8.45 (s, 1H), 8.41 (s, 2H), 8.00 (s, 1H), 7.75 (s, 1H), 7.70–7.64 (m, 2H), 7.62 (d, *J* = 9.4 Hz, 1H), 7.58–7.52 (m, 2H), 7.42 (d, *J* = 9.1 Hz, 1H), 7.35–7.25 (m, 2H), 6.95–6.85 (m, 2H), 5.54 (d, *J* = 9.4 Hz, 1H), 5.33 (d, *J* = 9.1 Hz, 1H), 4.70–4.59 (m, 2H), 4.57 (app t, *J* = 7.1 Hz, 2H), 4.03–3.88 (m, 2H), 2.25–2.05 (m, 2H), 2.03–1.68 (m, 14H), 1.28 (s, 3H), 1.23 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4r** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4r** are reported.) δ 182.7, 182.6, 170.0, 169.6, 165.2, 161.9 (d, *J* = 242.2 Hz), 152.2, 152.1 (app p, *J* = 16.6 Hz), 143.4 (d, *J* = 3.1 Hz), 142.8, 142.2, 132.7, 132.0 (q, *J* = 33.3 Hz), 131.3 (q, *J* = 32.9 Hz), 128.0 (d, *J* = 7.8 Hz), 127.4, 127.0, 126.2–125.8 (m), 124.6 (q, *J* = 271.8 Hz), 124.3 (q, *J* = 271.9 Hz), 123.9–123.6 (m), 123.5–123.2 (m), 121.8–121.5 (m), 117.9–

117.5 (m), 114.9 (d, J = 21.2 Hz), 68.0, 67.9, 63.3, 63.2, 62.4, 50.8, 50.6, 45.1, 44.8, 38.3, 38.1, 35.8, 27.0, 25.6, 25.1, 24.3, 23.8, 23.2, 22.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4r** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4r** are reported.) δ 85.29 (p, J = 148.3 Hz), 62.70 (d, J = 148.1 Hz), −63.45, −63.51, −119.84. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{53}H_{57}F_{15}N_6O_4S_3+H]^+$: 1223.3437, found: 1223.3432.

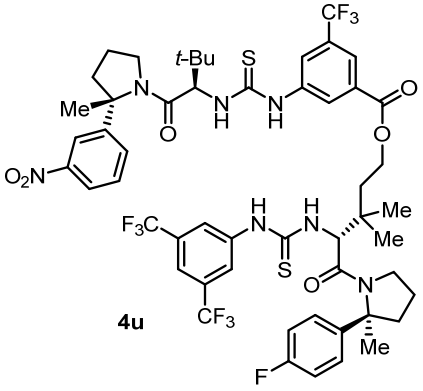


4s: Hydrogen-bond donor **4s** was prepared according to an analogous procedure as reported previously, starting from 4′-*tert*-butylacetophenone[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4s** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4s** are reported.) δ 9.77 (s, 1H), 9.66 (s, 1H), 8.55 (s, 1H), 8.48 (s, 1H), 8.41 (s, 2H), 8.00 (s, 1H), 7.76 (s, 1H), 7.61 (d, J = 9.4 Hz, 1H), 7.38 (d, J = 9.4 Hz, 1H), 7.34–7.26 (m, 2H), 7.25–7.17 (m, 4H), 6.95–6.87 (m, 2H), 5.53 (d, J = 9.4 Hz, 1H), 5.43 (d, J = 9.4 Hz, 1H), 4.66–4.49 (m, 4H), 4.02–3.93 (m, 1H), 3.90 (app td, J = 9.4, 7.0 Hz, 1H), 2.18–1.84 (m, 14H), 1.84–1.69 (m, 2H), 1.28 (s, 3H), 1.25–1.18 (m, 12H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4s** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4s** are reported.) δ 182.7, 182.6, 169.9, 169.6, 165.2, 161.9 (d, J = 242.3 Hz), 148.9, 144.3, 143.4 (d, J = 2.9 Hz), 142.8, 142.3, 132.7, 132.0 (q, J = 33.1 Hz), 131.2 (q, J = 32.5 Hz), 128.0 (d, J = 8.0 Hz), 127.4, 125.9, 125.4, 124.7 (q, J = 272.1 Hz), 124.3 (q, J = 271.9 Hz), 123.9–123.7 (m), 123.5–123.2 (m), 121.7–121.4 (m), 117.9–117.6 (m), 114.9 (d, J = 21.1 Hz), 68.1, 68.0, 63.3, 63.2, 62.4, 50.8(2), 50.7(5), 45.2, 45.1, 38.3, 38.1, 36.0, 34.7, 31.6, 27.0, 25.9, 25.7, 24.3, 23.9, 22.9, 22.8. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4s** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4s** are reported.) δ −63.36, −63.50, −119.84. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{57}H_{66}F_{10}N_6O_4S_2+H]^+$: 1153.4500, found: 1153.4504.

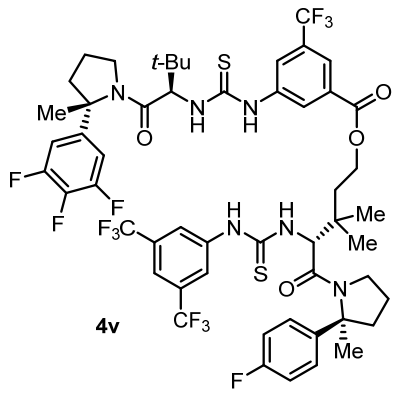


4t: Hydrogen-bond donor **4t** was prepared according to an analogous procedure as reported previously, starting from 3′,5′-dinitroacetophenone[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4t** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4t** are reported.) δ 9.74 (s, 1H), 9.57 (s, 1H), 8.75 (t, J = 2.0 Hz, 1H), 8.54 (s, 1H), 8.48 (s, 1H), 8.45 (d, J = 2.0 Hz, 2H), 8.40 (s, 2H), 8.00 (s, 1H), 7.75 (s, 1H), 7.57 (d, J = 9.4 Hz, 1H), 7.45 (d, J = 9.2 Hz, 1H), 7.34–7.25 (m, 2H), 6.97–6.86 (m, 2H), 5.52 (d, J = 9.4 Hz, 1H), 5.48 (d, J = 9.2 Hz, 1H), 4.73 (ddd, J = 10.0, 7.5, 5.2 Hz, 1H), 4.66–4.58 (m, 1H), 4.56 (app t, J = 7.3 Hz, 2H), 4.10–3.90 (m, 2H), 2.38–2.13 (m, 2H), 2.13–1.86 (m, 13H), 1.86–1.72 (m, 1H), 1.27 (s, 3H), 1.22 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4t** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4t** are reported.) δ 182.7, 182.6, 170.5, 169.6, 165.3, 161.9 (d, J = 241.8 Hz), 152.3, 149.3, 143.4 (d,

J = 3.1 Hz), 142.7, 142.2, 132.6, 132.0 (q, J = 33.3 Hz), 131.2 (q, J = 32.9 Hz), 128.0 (d, J = 7.8 Hz), 127.8, 126.6, 124.7 (q, J = 272.1 Hz), 124.3 (q, J = 272.1 Hz), 124.5 (q, J = 3.7 Hz), 123.5–123.3 (m), 121.8 (q, J = 3.9 Hz), 117.9–117.6 (m), 116.9, 114.9 (d, J = 21.2 Hz), 68.0, 67.8, 63.2, 63.0, 62.5, 50.8, 50.7, 45.1, 44.5, 38.3, 38.1, 36.0, 26.9, 25.7, 24.8, 24.3, 23.9, 23.4, 22.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4t** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4t** are reported.) δ −63.30, −63.51, −119.83. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{53}H_{56}F_{10}N_8O_8S_2+H]^+$: 1187.3576, found: 1187.3579.

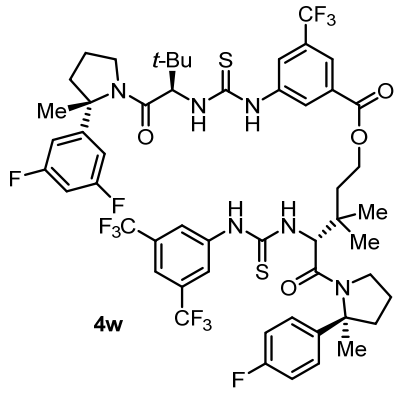


4u: Hydrogen-bond donor **4u** was prepared according to an analogous procedure as reported previously, starting from 3′-nitroacetophenone[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4u** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4u** are reported.) δ 9.76 (s, 1H), 9.61 (s, 1H), 8.53 (s, 1H), 8.48 (s, 1H), 8.40 (s, 2H), 8.06 (t, J = 2.0 Hz, 1H), 8.03–7.96 (m, 2H), 7.79 (ddd, J = 7.9, 1.9, 1.0 Hz, 1H), 7.75 (s, 1H), 7.57 (d, J = 9.4 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.42 (d, J = 9.2 Hz, 1H), 7.35–7.25 (m, 2H), 6.96–6.86 (m, 2H), 5.53 (d, J = 9.4 Hz, 1H), 5.44 (d, J = 9.3 Hz, 1H), 4.72–4.50 (m, 4H), 4.04–3.90 (m, 2H), 2.27–2.16 (m, 1H), 2.16–1.87 (m, 13H), 1.87–1.72 (m, 2H), 1.28 (s, 3H), 1.22 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4u** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4u** are reported.) δ 182.7, 182.6, 170.2, 169.6, 165.3, 161.9 (d, J = 242.2 Hz), 149.9, 149.1, 143.4 (d, J = 3.2 Hz), 142.7, 142.2, 132.8, 132.6, 132.0 (q, J = 33.2 Hz), 131.2 (q, J = 32.8 Hz), 129.8, 128.0 (d, J = 7.8 Hz), 127.8, 124.7 (q, J = 271.6 Hz), 124.3 (q, J = 271.9 Hz), 124.3 (q, J = 3.7 Hz), 123.5–123.2 (m), 121.8 (q, J = 3.9 Hz), 121.6, 120.9, 118.0–117.5 (m), 114.9 (d, J = 21.1 Hz), 68.0, 67.9, 63.2, 63.1, 62.4, 50.8, 50.7, 45.1, 44.8, 38.3, 38.1, 36.0, 26.9, 25.7, 25.2, 24.3, 23.9, 23.1, 22.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4u** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4u** are reported.) δ −63.34, −63.50, −119.84. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{53}H_{57}F_{10}N_7O_6S_2+H]^+$: 1142.3725, found: 1142.3730.



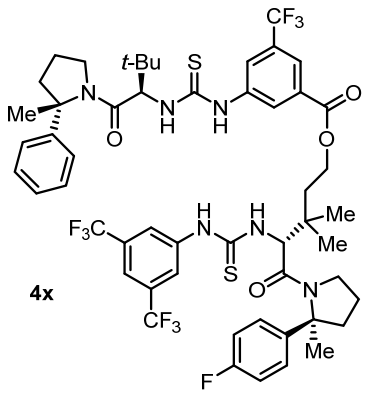
4v: Hydrogen-bond donor **4v** was prepared according to an analogous procedure as reported previously, starting from 3′,4′,5′-trifluoroacetophenone[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4v** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4v** are reported.) δ 9.76 (s, 1H), 9.69 (s, 1H), 8.49 (s, 1H), 8.46 (s, 1H), 8.40 (s, 2H), 8.00 (s, 1H), 7.75 (s, 1H), 7.60 (d, J = 9.4 Hz, 1H), 7.46 (d, J = 9.0 Hz, 1H), 7.34–7.26 (m, 2H), 7.19–7.08 (m, 2H), 6.95–6.86 (m, 2H), 5.53 (d, J = 9.4 Hz, 1H), 5.27 (d, J = 9.0 Hz, 1H), 4.74–4.47 (m, 4H), 4.03–3.85 (m, 2H), 2.20–2.07 (m, 2H), 2.05–1.86 (m, 12H), 1.86–1.72 (m, 2H), 1.28 (s, 3H), 1.22 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4v** undergoes a slow H→D exchange in $(CD_3)_2CO$

of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4v** are reported.) δ 182.7, 182.6, 170.2, 169.6, 165.2, 161.9 (d, J = 242.3 Hz), 151.3 (ddd, J = 246.1, 9.7, 3.8 Hz), 145.1 (td, J = 6.4, 4.0 Hz), 143.4 (d, J = 3.1 Hz), 142.8, 142.2, 138.2 (dt, J = 247.1, 15.7 Hz), 132.7, 132.0 (q, J = 33.2 Hz), 131.3 (q, J = 32.8 Hz), 128.0 (d, J = 7.8 Hz), 127.6, 124.7 (q, J = 271.8 Hz), 124.3 (q, J = 271.9 Hz), 124.2 (q, J = 3.8 Hz), 123.5–123.2 (m), 121.8 (d, J = 3.9 Hz), 118.0–117.6 (m), 114.9 (d, J = 21.2 Hz), 111.0–110.6 (m), 68.0, 67.8, 63.5, 63.2, 62.4, 50.8, 50.6, 45.1, 44.7, 38.3, 38.1, 35.7, 27.0, 25.6, 25.1, 24.3, 23.9, 23.1, 22.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4v** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4v** are reported.) δ −63.43, −63.51, −119.83, −137.60 (d, J = 20.4 Hz), −167.34 (t, J = 20.4 Hz). HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{53}H_{55}F_{13}N_6O_4S_2+H]^+$: 1151.3591, found: 1151.3584.



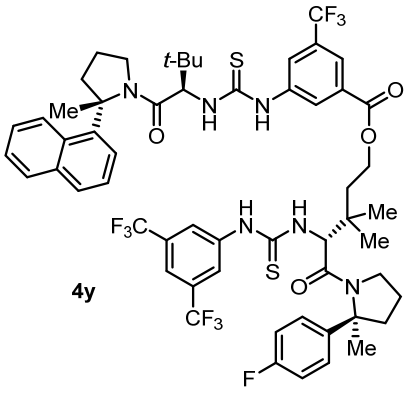
4w

4w: Hydrogen-bond donor **4w** was prepared according to an analogous procedure as reported previously, starting from 3′,5′-difluoroacetophenone[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4w** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4w** are reported.) δ 9.79 (s, 1H), 9.67 (s, 1H), 8.50 (s, 1H), 8.47 (s, 1H), 8.41 (s, 2H), 8.00 (s, 1H), 7.75 (s, 1H), 7.60 (d, J = 9.4 Hz, 1H), 7.43 (d, J = 9.2 Hz, 1H), 7.35–7.26 (m, 2H), 7.00–6.85 (m, 4H), 6.77–6.68 (m, 1H), 5.53 (d, J = 9.4 Hz, 1H), 5.34 (d, J = 9.2 Hz, 1H), 4.70–4.58 (m, 2H), 4.56 (app t, J = 7.1 Hz, 2H), 4.03–3.85 (m, 2H), 2.20–2.07 (m, 2H), 2.04–1.88 (m, 12H), 1.88–1.72 (m, 2H), 1.28 (s, 3H), 1.22 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4w** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4w** are reported.) δ 182.8, 182.6, 170.1, 169.6, 165.2, 163.7 (dd, J = 245.2, 13.1 Hz), 161.9 (d, J = 242.3 Hz), 152.7 (t, J = 8.3 Hz), 143.4 (d, J = 3.0 Hz), 142.8, 142.2, 132.7, 132.0 (q, J = 33.2 Hz), 131.2 (q, J = 32.8 Hz), 128.0 (d, J = 7.8 Hz), 127.6, 124.7 (q, J = 272.1 Hz), 124.3 (q, J = 272.1 Hz), 124.3 (q, J = 3.7 Hz), 123.6–123.2 (m), 121.8 (q, J = 3.9 Hz), 118.0–117.5 (m), 114.9 (d, J = 21.2 Hz), 109.8–109.1 (m), 101.6 (t, J = 25.8 Hz), 68.0(3), 68.0(1), 63.3, 63.2, 62.4, 50.8, 50.7, 45.1, 44.8, 38.3, 38.1, 35.8, 27.0, 25.7, 25.2, 24.3, 23.9, 23.1, 22.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4w** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4w** are reported.) δ −63.40, −63.50, −112.09, −119.84. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{53}H_{56}F_{12}N_6O_4S_2+H:]^+$: 1133.3686, found: 1133.3691.



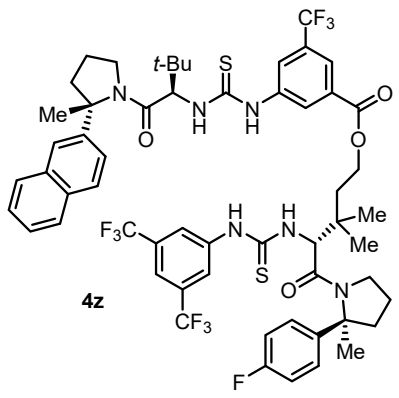
4x

4x: Hydrogen-bond donor **4x** was prepared according to an analogous procedure as reported previously, starting from acetophenone[47,62]. ^{1}H NMR (400 MHz, CD_3CN) δ 8.76–8.63 (m, 2H), 8.37 (s, 1H), 8.15–8.04 (m, 3H), 8.00 (s, 1H), 7.73 (s, 1H), 7.28–6.99 (m, 9H), 6.92–6.78 (m, 2H), 5.41 (d, *J* = 9.2 Hz, 1H), 5.32 (d, *J* = 9.2 Hz, 1H), 4.58–4.40 (m, 4H), 3.94–3.78 (m, 2H), 2.11–1.99 (m, 2H), 1.93–1.78 (m, 12H), 1.77–1.63 (m, 2H), 1.22 (s, 3H), 1.16 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.8, 182.7, 170.2, 169.9, 165.5, 161.9 (d, *J* = 242.1 Hz), 147.5, 143.5 (d, *J* = 3.0 Hz), 142.0, 141.5, 132.9, 132.1 (q, *J* = 33.3 Hz), 131.5 (q, *J* = 33.0 Hz), 128.8, 128.5, 128.0 (d, *J* = 7.8 Hz), 126.7, 126.1, 125.1–124.8 (m), 124.7–124.4 (m), 122.8–122.5 (m), 124.7 (q, *J* = 272.1 Hz), 124.3 (q, *J* = 272.1 Hz), 119.0–118.8 (m), 115.2 (d, *J* = 21.2 Hz), 68.5, 68.2, 63.7, 63.4, 62.8, 51.1, 51.0, 45.2, 45.1, 38.5, 38.3, 36.2, 27.1, 25.5(9), 25.5(7), 24.5, 24.2, 23.0(2), 22.9(8). ^{19}F NMR (376 MHz, CD_3CN) δ −63.33, −63.44, −119.52. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{53}H_{58}F_{10}N_6O_4S_2+H]^+$: 1097.3874; found: 1097.3848.

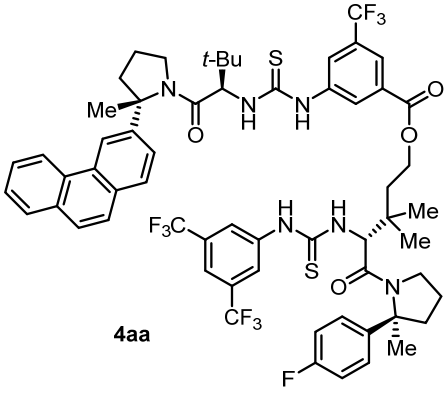


4y

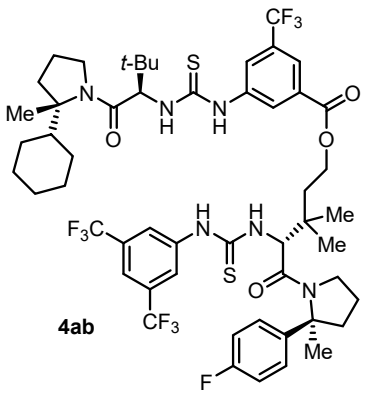
4y: Hydrogen-bond donor **4y** was prepared according to an analogous procedure as reported previously, starting from 1-acetylnapthalene[47,62]. ^{1}H NMR (400 MHz, CD_3CN) δ 8.78 (s, 1H), 8.59 (br s, 1H), 8.19 (s, 1H), 8.12 (s, 2H), 8.05–7.93 (m, 2H), 7.89 (s, 1H), 7.83–7.76 (m, 1H), 7.71 (s, 1H), 7.68–7.61 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.40–7.26 (m, 3H), 7.26–7.16 (m, 3H), 6.89–6.80 (m, 2H), 6.63 (br s, 1H), 5.53–5.38 (m, 2H), 4.64–4.41 (m, 4H), 4.18–4.03 (m, 1H), 3.94–3.81 (m, 1H), 2.55–2.38 (m, 1H), 2.35–1.63 (m, 15H), 1.24 (s, 3H), 1.19 (s, 3H), 1.02 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.8, 182.4, 169.9, 169.6, 165.4, 161.9 (d, *J* = 242.0 Hz), 143.4 (d, *J* = 3.1 Hz), 142.0, 141.6, 141.0, 135.5, 132.9, 132.0 (q, *J* = 33.3 Hz), 131.4 (q, *J* = 33.0 Hz), 130.5, 130.2, 128.6, 128.4, 128.0 (d, *J* = 7.9 Hz), 126.4, 125.8, 125.7, 125.4, 125.1, 125.0–124.7 (m), 124.6 (q, *J* = 271.8 Hz), 124.5–124.2 (m), 124.3 (q, *J* = 272.1 Hz), 122.9–122.6 (m), 119.0–118.6 (m), 115.1 (d, *J* = 21.2 Hz), 68.6, 68.2, 63.5, 62.8 (two overlapping signals), 51.1, 49.7, 45.1, 41.7, 38.5, 38.2, 36.3, 26.8, 25.6 (two overlapping signals), 24.4, 24.1, 23.9, 23.0. ^{19}F NMR (376 MHz, CD_3CN) δ −63.31, −63.45, −119.54. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{57}H_{60}F_{10}N_6O_4S_2+H]^+$: 1147.4031, found: 1147.4019.



4z: Hydrogen-bond donor **4z** was prepared according to an analogous procedure as reported previously, starting from 2-acetylnapthalene[47,62]. ^{1}H NMR (400 MHz, CD_3CN) δ 8.98 (s, 1H), 8.78 (s, 1H), 8.33 (s, 1H), 8.14 (s, 1H), 8.03 (s, 2H), 7.99 (s, 1H), 7.74–7.56 (m, 5H), 7.41–7.29 (m, 2H), 7.29–7.08 (m, 5H), 6.91–6.78 (m, 2H), 5.37 (d, J = 9.2 Hz, 1H), 5.34 (d, J = 9.3 Hz, 1H), 4.66–4.55 (m, 1H), 4.54–4.38 (m, 3H), 3.95–3.78 (m, 2H), 2.14–2.04 (m, 1H), 2.04–1.98 (m, 2H), 1.95 (s, 3H), 1.91–1.77 (m, 8H), 1.78–1.64 (m, 2H), 1.20 (s, 3H), 1.13 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.8, 182.7, 170.5, 169.9, 165.5, 161.91 (d, J = 242.3 Hz), 144.2, 143.5 (d, J = 2.9 Hz), 141.8, 141.4, 133.9, 132.9, 132.6, 132.1 (q, J = 33.4 Hz), 131.5 (q, J = 33.1 Hz), 128.7, 128.4, 128.2, 128.1, 128.0 (d, J = 8.0 Hz), 126.7, 126.4, 124.9, 124.8, 124.8–124.6 (m), 124.6–124.3 (m), 122.8–122.5 (m), 124.6 (q, J = 271.8 Hz), 124.3 (q, J = 272.1 Hz), 119.1–118.7 (m), 115.1 (d, J = 21.3 Hz), 68.9, 68.2, 64.0, 63.4, 62.8, 51.1, 51.0, 45.1, 44.8, 38.5, 38.3, 35.9, 27.1, 25.7, 25.6, 24.4, 24.2, 23.0(3), 22.9(9). ^{19}F NMR (376 MHz, CD_3CN) δ −63.24, −63.40, −119.54. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{57}H_{60}F_{10}N_6O_4S_2+H]^+$: 1147.4031; found: 1147.4005.

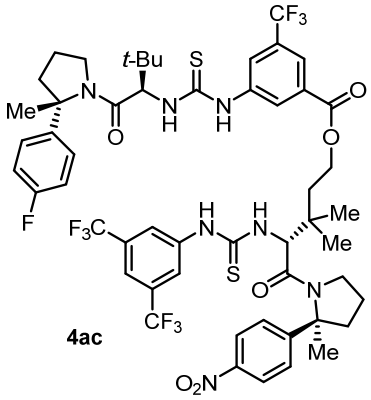


4aa: Hydrogen-bond donor **4aa** was prepared according to an analogous procedure as reported previously, starting from 3-acetylphenanthrene[47,62]. ^{1}H NMR (400 MHz, CD_3CN) δ 8.94 (s, 1H), 8.82 (s, 1H), 8.65 (d, J = 8.3 Hz, 1H), 8.30 (s, 1H), 8.23 (s, 1H), 8.09 (s, 2H), 8.05 (s, 1H), 7.97 (s, 1H), 7.82–7.75 (m, 2H), 7.69 (s, 1H), 7.67–7.62 (m, 2H), 7.57–7.52 (m, 1H), 7.39–7.32 (m, 1H), 7.25–7.18 (m, 3H), 7.18–7.06 (m, 2H), 6.93–6.84 (m, 2H), 5.56 (d, J = 9.4 Hz, 1H), 5.35 (d, J = 9.2 Hz, 1H), 4.75–4.60 (m, 1H), 4.53–4.39 (m, 3H), 4.04–3.91 (m, 1H), 3.87–3.74 (m, 1H), 2.22–1.96 (m, 5H), 1.91–1.65 (m, 11H), 1.17 (s, 3H), 1.12 (s, 9H), 1.09 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.7, 182.2, 170.4, 169.7, 165.4, 161.9 (d, J = 242.0 Hz), 145.3, 143.5 (d, J = 2.8 Hz), 141.9, 141.3, 133.0, 132.8, 132.0 (q, J = 33.3 Hz), 131.4 (q, J = 33.1 Hz), 131.1, 130.9, 130.3, 129.4, 129.3, 128.0 (d, J = 7.8 Hz), 127.8, 127.4, 127.3 (two overlapping signals), 127.2, 125.3, 124.6 (q, J = 271.8 Hz), 124.5–124.4 (m), 124.4–124.1 (m), 124.3 (q, J = 272.1 Hz), 123.9, 122.6–122.3 (m), 119.7, 118.9–119.7 (m), 115.1 (d, J = 21.2 Hz), 68.9, 68.2, 63.6, 63.4, 62.7, 51.2, 51.0, 45.1, 45.0, 38.3, 38.2, 36.4, 27.0, 26.0, 25.5, 24.4, 24.0, 23.0, 22.9. ^{19}F NMR (376 MHz, CD_3CN) δ −63.27, −63.44, −119.57. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{61}H_{62}F_{10}N_6O_4S_2+H]^+$: 1197.4187, found: 1197.4172.



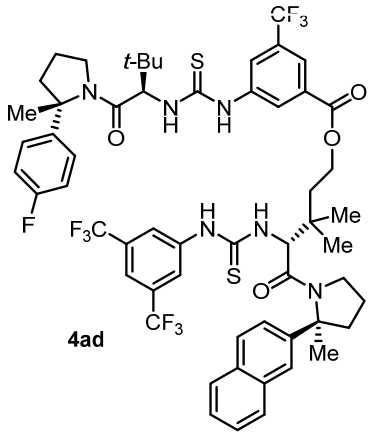
4ab

4ab: Hydrogen-bond donor **4ab** was prepared according to an analogous procedure as reported previously, starting from cyclohexyl methyl ketone[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4ab** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4ab** are reported.) δ 9.77 (s, 1H), 9.64 (s, 1H), 8.48 (s, 1H), 8.45–8.36 (m, 3H), 7.98 (s, 1H), 7.75 (s, 1H), 7.61 (d, *J* = 9.3 Hz, 1H), 7.45 (d, *J* = 9.4 Hz, 1H), 7.36–7.24 (m, 2H), 6.95–6.85 (m, 2H), 5.54 (d, *J* = 9.4 Hz, 1H), 5.41 (d, *J* = 9.5 Hz, 1H), 4.67–4.48 (m, 3H), 4.03–3.86 (m, 2H), 3.80–3.70 (m, 1H), 2.59–2.47 (m, 1H), 2.17–2.07 (m, 1H), 2.04–1.88 (m, 8H), 1.88–1.76 (m, 3H), 1.76–1.65 (m, 2H), 1.65–1.54 (m, 2H), 1.54–1.46 (m, 2H), 1.44 (s, 3H), 1.28 (s, 3H), 1.23 (s, 3H), 1.96–0.99 (m, 12H), 0.99–0.84 (m, 2H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4ab** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4ab** are reported.) δ 182.6, 182.4, 169.9, 169.6, 165.2, 161.8 (d, *J* = 242.2 Hz), 143.3 (d, *J* = 2.9 Hz), 142.7, 142.2, 132.6, 132.0 (q, *J* = 33.2 Hz), 131.2 (q, *J* = 32.8 Hz), 127.9 (d, *J* = 7.8 Hz), 127.5, 124.6 (q, *J* = 272.1 Hz), 124.3 (q, *J* = 272.1 Hz), 123.9 (q, *J* = 3.6 Hz), 123.5–123.2 (m), 121.6 (q, *J* = 3.8 Hz), 117.9–117.6 (m), 114.9 (d, *J* = 21.2 Hz), 69.3, 68.0, 63.2, 62.9, 62.4, 51.1, 50.8, 45.1, 43.5, 38.3, 38.1, 36.1, 34.8, 29.0, 27.6, 27.3, 27.2, 27.1, 26.9, 25.6, 24.3, 23.9, 23.6, 23.2, 22.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4ab** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4ab** are reported.) δ −63.41, −63.51, −119.83. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{53}H_{64}F_{10}N_6O_4S_2+H]^+$: 1103.4344, found: 1103.4346.

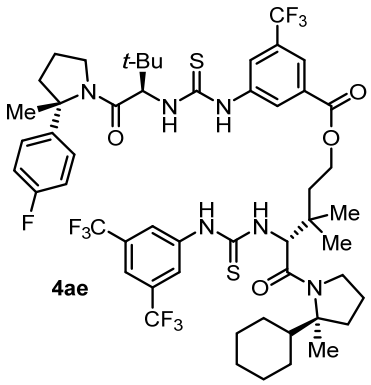


4ac

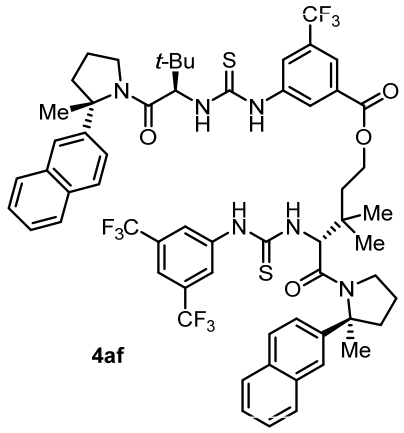
4ac: Hydrogen-bond donor **4ac** was prepared according to an analogous procedure as reported previously[47,62] and as reported on page S8 for the preparation of catalyst **4d**. ^{1}H NMR (400 MHz, CD_3CN) δ 8.81–8.70 (m, 2H), 8.36 (s, 1H), 8.09 (s, 2H), 8.08 (s, 1H), 8.02–7.96 (m, 3H), 7.73 (s, 1H), 7.51–7.44 (m, 2H), 7.27–7.18 (m, 2H), 7.08 (dd, *J* = 11.7, 9.4 Hz, 2H), 6.89–6.80 (m, 2H), 5.37 (d, *J* = 9.1 Hz, 1H), 5.25 (d, *J* = 9.2 Hz, 1H), 4.59–4.41 (m, 4H), 4.00–3.89 (m, 1H), 3.89–3.79 (m, 1H), 2.16–1.99 (m, 2H), 1.94–1.75 (m, 13H), 1.74–1.62 (m, 1H), 1.22 (s, 3H), 1.14 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.7, 182.7, 170.3, 169.9, 165.5, 161.9 (d, *J* = 242.0 Hz), 155.5, 147.1, 143.4 (d, *J* = 3.1 Hz), 141.8, 141.5, 132.8, 132.1 (q, *J* = 33.3 Hz), 131.5 (q, *J* = 33.0 Hz), 128.5, 128.0 (d, *J* = 7.8 Hz), 127.3, 125.0–124.7 (m), 124.6–124.3 (m), 124.6 (q, *J* = 271.8 Hz), 124.3 (q, *J* = 272.1 Hz), 123.9, 122.8–122.5 (m), 119.1–118.8 (m), 115.1 (d, *J* = 21.2 Hz), 68.4, 68.2, 63.8, 63.4, 62.7, 51.0, 50.9, 45.1, 44.7, 38.4, 38.2, 36.1, 27.0, 25.6, 25.0, 24.4, 24.1, 23.3, 23.0. ^{19}F NMR (376 MHz, CD_3CN) δ −63.34, −63.45, −119.46. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{53}H_{57}F_{10}N_7O_6S_2+H]^+$: 1142.3725, found: 1142.3735.



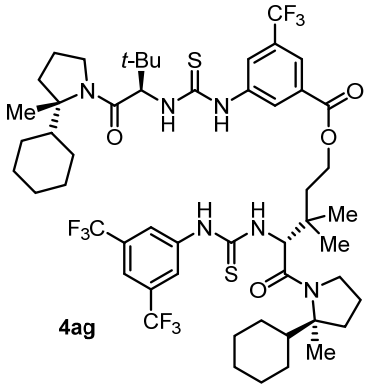
4ad: Hydrogen-bond donor **4ad** was prepared according to an analogous procedure as reported previously[47,62]. ^{1}H NMR (400 MHz, CD_3CN) δ 8.88 (s, 1H), 8.84 (s, 1H), 8.31 (s, 1H), 8.13 (s, 2H), 8.08 (s, 1H), 7.98 (s, 1H), 7.76–7.61 (m, 5H), 7.42–7.32 (m, 2H), 7.31–7.18 (m, 4H), 7.07 (d, *J* = 9.3 Hz, 1H), 6.89–6.81 (m, 2H), 5.47 (d, *J* = 9.2 Hz, 1H), 5.24 (d, *J* = 9.1 Hz, 1H), 4.69–4.58 (m, 1H), 4.57–4.37 (m, 3H), 3.99–3.88 (m, 1H), 3.89–3.79 (m, 1H), 2.13–2.00 (m, 2H), 1.92–1.65 (m, 14H), 1.24 (s, 3H), 1.17 (s, 3H), 1.07 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.8, 182.7, 170.3, 170.1, 165.5, 161.9 (d, *J* = 242.3 Hz), 144.4, 143.4 (d, *J* = 3.3 Hz), 142.0, 141.4, 134.0, 132.8, 132.7, 132.1 (q, *J* = 33.3 Hz), 131.5 (q, *J* = 32.7 Hz), 128.7, 128.5, 128.4, 128.1, 128.0 (d, *J* = 8.0 Hz), 126.7, 126.4, 124.9, 124.9–124.6 (m), 124.7, 124.6 (q, *J* = 272.1 Hz), 124.4 (q, *J* = 272.1 Hz), 124.4–124.1 (m), 122.8–122.5 (m), 119.1–118.7 (m), 115.1 (d, *J* = 21.2 Hz), 68.9, 68.2, 63.8, 63.4, 62.9, 51.2, 50.9, 45.2, 44.8, 38.5, 38.1, 36.1, 27.1, 25.7, 25.6, 24.5, 24.2, 23.1, 23.0. ^{19}F NMR (376 MHz, CD_3CN) δ −63.29, −63.38, −119.41. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{57}H_{60}F_{10}N_6O_4S_2+H]^+$: 1147.4031; found: 1147.3994.



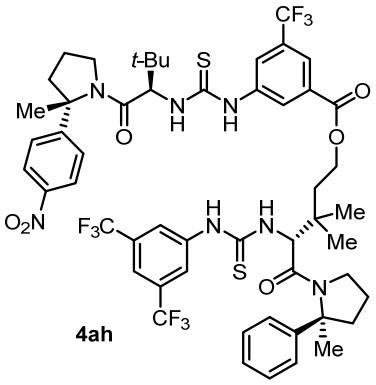
4ae: Hydrogen-bond donor **4ae** was prepared according to an analogous procedure as reported previously[47,62]. ^{1}H NMR (400 MHz, CD_3CN) δ 8.83 (s, 1H), 8.79 (s, 1H), 8.37 (s, 1H), 8.12–8.05 (m, 3H), 7.98 (s, 1H), 7.71 (s, 1H), 7.28–7.21 (m, 2H), 7.19 (d, *J* = 9.5 Hz, 1H), 7.06 (d, *J* = 9.1 Hz, 1H), 6.91–6.82 (m, 2H), 5.41 (d, *J* = 9.4 Hz, 1H), 5.25 (d, *J* = 9.1 Hz, 1H), 4.55–4.42 (m, 3H), 3.94–3.77 (m, 2H), 3.74–3.63 (m, 1H), 2.48–2.36 (m, 1H), 2.10–1.97 (m, 1H), 1.93–1.80 (m, 8H), 1.81–1.73 (m, 2H), 1.73–1.61 (m, 3H), 1.61–1.51 (m, 2H), 1.51–1.40 (m, 2H), 1.39 (s, 3H), 1.19–1.14 (m, 6H), 1.19–0.98 (m, 12H), 0.94–0.81 (m, 2H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.7, 182.5, 170.2, 169.6, 165.5, 161.9 (d, *J* = 242.0 Hz), 143.5 (d, *J* = 3.0 Hz), 142.0, 141.5, 132.9, 132.1 (q, *J* = 33.4 Hz), 131.5 (q, *J* = 32.9 Hz), 128.4, 128.0 (d, *J* = 7.8 Hz), 124.8 (q, *J* = 3.6 Hz), 124.6 (q, *J* = 271.8 Hz), 124.4–124.0 (m), 124.3 (q, *J* = 271.8 Hz), 122.6 (q, *J* = 3.8 Hz), 118.9–118.6 (m), 115.1 (d, *J* = 21.2 Hz), 69.8, 68.1, 63.8, 63.6, 62.5, 51.4, 50.9, 45.1, 43.7, 38.4, 38.3, 36.1, 34.8, 29.0, 27.6, 27.3, 27.2 (two overlapping signals), 27.0, 25.6, 24.1(1), 24.0(9), 23.7, 23.3, 23.0. ^{19}F NMR (376 MHz, CD_3CN) δ −63.35, −63.48, −119.47. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{53}H_{64}F_{10}N_6O_4S_2+H]^+$: 1103.4344, found: 1103.4347.



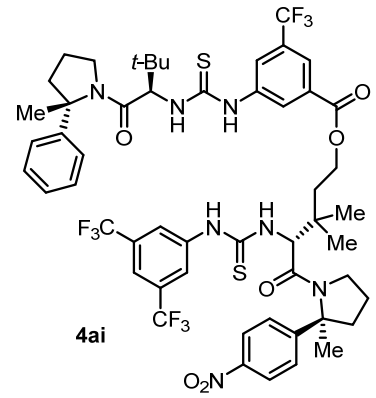
4af: Hydrogen-bond donor **4af** was prepared according to an analogous procedure as reported on page S8 for the preparation of catalyst **4d**. ^{1}H NMR (400 MHz, CD_3CN) δ 9.00 (s, 1H), 8.87 (s, 1H), 8.29 (s, 1H), 8.12–8.01 (m, 3H), 7.97 (s, 1H), 7.75–7.55 (m, 9H), 7.50–7.08 (m, 8H), 5.45 (d, *J* = 9.2 Hz, 1H), 5.33 (d, *J* = 9.2 Hz, 1H), 4.67–4.55 (m, 2H), 4.55–4.43 (m, 2H), 4.01–3.80 (m, 2H), 2.13–1.64 (m, 16H), 1.23 (s, 3H), 1.16 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.7 (two overlapping signals), 170.5, 170.0, 165.4, 144.4, 144.2, 141.8, 141.2, 133.9(4), 133.9(0), 132.8, 132.7, 132.6, 132.0 (q, *J* = 33.3 Hz), 131.4 (d, *J* = 32.9 Hz), 128.7, 128.6, 128.5, 128.4, 128.2–128.1 (m), 128.1, 128.0, 126.7, 126.4, 126.3, 124.9, 124.8, 124.7, 124.6 (q, *J* = 272.1 Hz), 124.4–124.0 (m), 124.3 (q, *J* = 272.1 Hz), 122.9–122.5 (m), 119.1–118.7 (m), 68.9, 68.8, 63.9, 63.4, 62.8, 51.1, 51.0, 44.8, 44.7, 38.6, 38.0, 35.9, 27.1, 25.7, 25.6, 24.5, 24.2, 23.0(3), 23.0(0) (three signals in the aromatic region were not identified because they presumably overlap with other signals). ^{19}F NMR (376 MHz, CD_3CN) δ −63.21, −63.33. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{61}H_{63}F_9N_6O_4S_2+H]^+$: 1179.4281, found: 1179.4277.



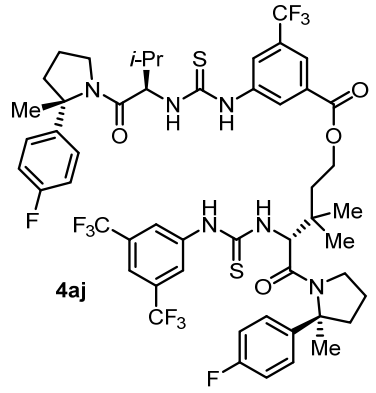
4ag: Hydrogen-bond donor **4ag** was prepared according to an analogous procedure as reported on page S8 for the preparation of catalyst **4d**. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4ag** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4ag** are reported.) δ 9.77 (s, 1H), 9.63 (s, 1H), 8.47 (s, 1H), 8.41 (s, 1H), 8.36 (s, 2H), 7.97 (s, 1H), 7.73 (s, 1H), 7.63 (d, *J* = 9.6 Hz, 1H), 7.44 (d, *J* = 9.4 Hz, 1H), 5.54 (d, *J* = 9.6 Hz, 1H), 5.41 (d, *J* = 9.5 Hz, 1H), 4.54 (app t, *J* = 7.1 Hz, 2H), 3.98 (app dt, *J* = 10.5, 5.6 Hz, 1H), 3.92 (app dt, *J* = 10.4, 5.4 Hz, 1H), 3.83–3.68 (m, 2H), 2.61–2.47 (m, 2H), 2.03–1.92 (m, 4H), 1.91–1.77 (m, 4H), 1.77–1.66 (m, 4H), 1.66–1.54 (m, 4H), 1.54–1.47 (m, 4H), 1.46 (s, 3H), 1.44 (s, 3H), 1.26–1.02 (m, 21H), 1.00–0.88 (m, 4H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4ag** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4ag** are reported.) δ 182.4(9), 182.4(7), 169.9, 169.5, 165.2, 142.8, 142.3, 132.7, 132.0 (q, *J* = 33.4 Hz), 131.2 (q, *J* = 32.5 Hz), 127.5, 124.6 (q, *J* = 271.8 Hz), 124.3 (q, *J* = 272.0 Hz), 124.0–123.7 (m), 123.4–123.2 (m), 121.7–121.5 (m), 117.8–117.5 (m), 69.5, 69.3, 63.4, 62.9, 62.1, 51.3, 51.1, 43.5(0), 43.4(6), 38.3, 38.2, 36.2, 34.8, 34.8, 29.0(0), 28.9(7), 27.6(0), 25.5(8), 27.2(9), 27.2(9), 27.2(7), 27.2(2), 27.1(8), 27.1(5), 26.9, 24.1, 23.9, 23.7, 23.6, 23.3, 23.2. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4ag** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4ag** are reported.) δ −63.41, −63.53. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{53}H_{71}F_9N_6O_4S_2+H]^+$: 1091.4907, found: 1091.4912.



4ah: Hydrogen-bond donor **4ah** was prepared according to an analogous procedure as reported on page S8 for the preparation of catalyst **4d**. ^{1}H NMR (400 MHz, CD_3CN) δ 8.74 (s, 1H), 8.68 (s, 1H), 8.39 (s, 1H), 8.11 (s, 2H), 8.06 (s, 1H), 8.00 (s, 1H), 7.99–7.94 (m, 2H), 7.72 (s, 1H), 7.51–7.45 (m, 2H), 7.24–7.19 (m, 2H), 7.18–7.11 (m, 3H), 7.10–7.04 (m, 1H), 7.01 (d, J = 9.0 Hz, 1H), 5.45 (d, J = 9.3 Hz, 1H), 5.21 (d, J = 9.0 Hz, 1H), 4.58–4.42 (m, 4H), 3.95–3.85 (m, 2H), 2.15–2.00 (m, 2H), 1.92–1.65 (m, 14H), 1.22 (s, 3H), 1.16 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.7 (two overlapping signals), 170.3, 169.8, 165.5, 155.5, 147.4, 147.1, 142.0, 141.4, 132.9, 132.0 (q, J = 33.1 Hz), 131.5 (q, J = 33.1 Hz), 128.8, 128.3, 127.4, 126.8, 126.1, 124.8 (q, J = 4.0 Hz), 124.6 (q, J = 271.8 Hz), 124.5 (q, J = 3.1 Hz), 124.3 (q, J = 271.8 Hz), 123.8, 122.7 (q, J = 3.9 Hz), 119.0–118.7 (m), 68.5, 68.3, 63.8, 63.5, 62.7, 51.1, 50.9, 45.1, 44.7, 38.4, 38.3, 36.0, 27.0, 25.5, 25.0, 24.4, 24.1, 23.3, 23.0. ^{19}F NMR (376 MHz, CD_3CN) δ −63.33, −63.45. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{53}H_{58}F_9N_7O_6S_2+H]^+$: 1124.3819, found: 1124.3809.

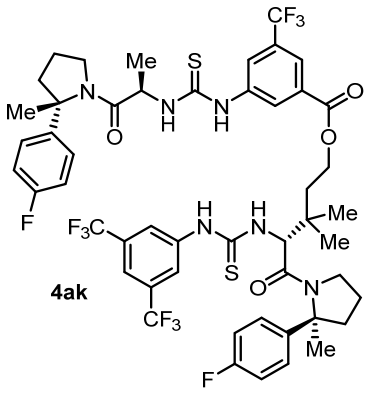


4ai: Hydrogen-bond donor **4ai** was prepared according to an analogous procedure as reported on page S8 for the preparation of catalyst **4d**. ^{1}H NMR (400 MHz, CD_3CN) δ 8.74 (s, 1H), 8.72 (s, 1H), 8.38 (s, 1H), 8.14–8.06 (m, 3H), 8.04–7.94 (m, 3H), 7.74 (s, 1H), 7.48 (d, J = 8.9 Hz, 2H), 7.26–7.18 (m, 2H), 7.18–7.00 (m, 5H), 5.37 (d, J = 9.1 Hz, 1H), 5.31 (d, J = 9.2 Hz, 1H), 4.59–4.43 (m, 4H), 4.01–3.78 (m, 2H), 2.14–1.99 (m, 2H), 1.91–1.64 (m, 14H), 1.22 (s, 3H), 1.15 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.7(3), 182.6(9), 170.2, 169.9, 165.5, 155.5, 147.4, 147.1, 141.9, 141.5, 132.8, 132.1, (q, J = 33.4 Hz), 131.5 (q, J = 32.7 Hz), 128.7, 128.4, 127.3, 126.7, 126.1, 125.0–124.7 (m), 124.6–124.3 (m), 123.9, 122.7–122.4 (m), 119.1–118.7 (m), 124.6 (q, J = 272.1 Hz), 124.3 (q, J = 272.1 Hz), 68.5, 68.4, 63.7, 63.4, 62.7, 51.0 (two overlapping signals), 45.2, 44.7, 38.4, 38.2, 36.2, 27.0, 25.6, 25.0, 24.4, 24.1, 23.4, 23.0. ^{19}F NMR (376 MHz, CD_3CN) δ −63.34, −63.45. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{53}H_{58}F_9N_7O_6S_2+H]^+$: 1124.3819, found: 1124.3820.

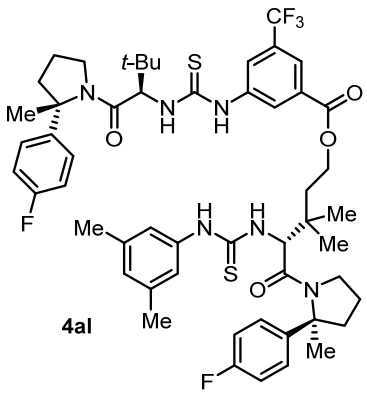


4aj: Hydrogen-bond donor **4aj** was prepared according to an analogous procedure as reported previously, using *N*-Boc-D-valine instead of *N*-Boc-D-*tert*-leucine[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4aj** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4aj** are reported.) δ 9.70 (s, 1H), 9.00 (s, 1H), 8.43–8.36 (m, 3H), 8.25 (s, 1H), 8.03–7.91 (m, 2H), 7.75 (s, 1H), 7.60 (d, J = 9.3 Hz, 1H), 7.39–7.26 (m, 4H), 6.95–6.86 (m, 2H), 6.86–6.77 (m, 2H), 5.53 (d, J = 9.4 Hz, 1H), 5.26–5.14 (m, 1H), 4.66–4.40 (m, 4H), 4.05–3.84 (m, 2H), 2.23–2.05 (m, 3H), 2.02–1.88 (m,

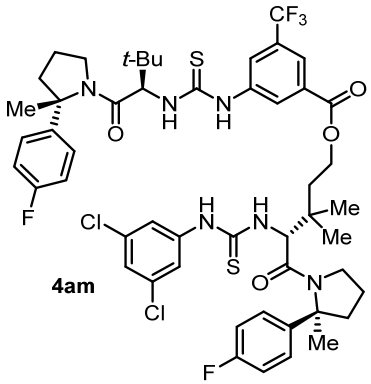
12H), 1.88–1.73 (m, 2H), 1.27 (s, 3H), 1.22 (s, 3H), 1.12 (d, J = 6.8 Hz, 3H), 1.06 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4aj** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4aj** are reported.) δ 183.1, 182.7, 173.3, 170.1, 165.2, 161.8 (d, J = 242.6 Hz), 161.5 (d, J = 243.4 Hz), 143.3 (d, J = 3.0 Hz), 142.8 (d, J = 3.0 Hz), 142.5, 140.9, 131.8 (q, J = 33.1 Hz), 131.8, 131.1, 130.5 (q, J = 32.6 Hz), 127.8 (d, J = 7.8 Hz), 127.6 (d, J = 7.8 Hz), 127.4–127.2 (m), 124.5 (q, J = 272.3 Hz), 124.3 (q, J = 272.3 Hz), 124.3–124.0 (m), 122.9–122.5 (m), 118.2–117.8 (m), 115.1 (d, J = 21.2 Hz), 115.0 (d, J = 21.2 Hz), 68.9, 68.2, 63.7, 63.0, 62.8, 50.9, 50.3, 45.1, 45.0, 38.4, 38.2, 31.9, 25.7, 25.2, 24.4, 24.2, 22.9, 19.8, 19.3, 19.3. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4aj** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4aj** are reported.) δ −63.02, −63.35, −119.65, −119.33. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{52}H_{55}F_{11}N_6O_4S_2+H]^+$: 1101.3623, found: 1101.3628.



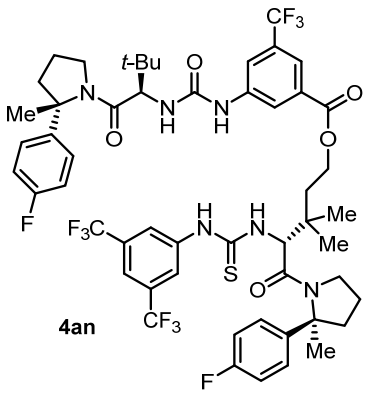
4ak: Hydrogen-bond donor **4ak** was prepared according to an analogous procedure as reported previously, using *N*-Boc-D-alanine instead of *N*-Boc-D-*tert*-leucine[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4ak** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4ak** are reported.) δ 9.46 (s, 1H), 8.99–8.86 (m, 1H), 8.31 (s, 2H), 8.28–8.20 (m, 2H), 7.98–7.84 (m, 3H), 7.72 (s, 1H), 7.40–7.33 (m, 2H), 7.33–7.25 (m, 2H), 6.84–6.75 (m, 2H), 6.69–6.58 (m, 2H), 5.52 (d, J = 9.2 Hz, 1H), 5.24–5.13 (m, 1H), 4.69–4.58 (s, 1H), 4.58–4.38 (m, 2H), 4.32–4.20 (m, 1H), 4.10–3.95 (m, 1H), 3.95–3.81 (m, 1H), 2.20–2.08 (m, 2H), 2.05–1.71 (m, 14H), 1.50 (d, J = 7.1 Hz, 3H), 1.28 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4ak** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4ak** are reported.) δ 182.6, 182.5, 173.7, 170.0, 165.2, 161.8 (d, J = 242.3 Hz), 161.7 (d, J = 242.7 Hz), 143.4 (d, J = 3.2 Hz), 142.8 (d, J = 2.8 Hz), 142.6, 141.1, 131.8 (q, J = 33.4 Hz), 131.8, 130.5 (q, J = 32.7 Hz), 130.0, 128.0–127.7 (m, two overlapping signals), 126.3–126.1 (m), 124.6 (q, J = 272.5 Hz), 124.3 (q, J = 272.1 Hz), 124.0–123.7 (m), 122.4–122.1 (m), 118.0–117.6 (m), 115.3–114.7 (m, two overlapping signals), 68.6, 68.2, 63.0, 62.7, 53.6, 50.9, 49.4, 45.1, 44.9, 38.3, 38.2, 25.7, 25.0, 24.4, 24.1, 23.1, 22.9, 16.7. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4ak** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4ak** are reported.) δ −63.10, −63.43, −119.20, −119.61. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{50}H_{51}F_{11}N_6O_4S_2+H]^+$: 1073.3310, found: 1073.3317.



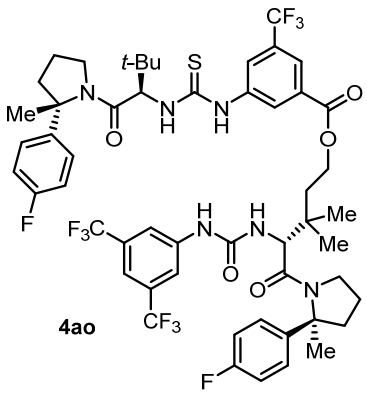
4al: Hydrogen-bond donor **4al** was prepared according to an analogous procedure as reported previously, using 3,5-dimethylphenyl isothiocyanate instead of 3,5-(trifluoromethyl)phenyl isothiocyanate[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4al** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4al** are reported.) δ 9.76 (s, 1H), 9.22 (s, 1H), 8.53 (s, 1H), 8.49 (s, 1H), 8.00 (s, 1H), 7.55 (d, *J* = 9.2 Hz, 1H), 7.39–7.23 (m, 4H), 7.03–6.84 (m, 7H), 6.82 (s, 1H), 5.52 (d, *J* = 9.4 Hz, 1H), 5.37 (d, *J* = 9.3 Hz, 1H), 4.69–4.45 (m, 4H), 4.00–3.84 (m, 2H), 2.22 (s, 6H), 2.16–2.06 (m, 2H), 2.02–1.82 (m, 12H), 1.83–1.68 (m, 2H), 1.22 (s, 3H), 1.14 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4al** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4al** are reported.) δ 182.8, 182.2, 170.2, 169.9, 165.2, 161.9 (d, *J* = 242.0 Hz), 161.9 (d, *J* = 242.2 Hz), 143.4 (d, *J* = 3.1 Hz), 143.3 (d, *J* = 2.9 Hz), 142.3, 139.8, 138.6, 132.7, 131.3 (q, *J* = 32.7 Hz), 128.3, 128.0(6) (d, *J* = 7.8 Hz), 128.0(4) (d, *J* = 8.0 Hz), 127.6, 124.7 (q, *J* = 271.9 Hz), 123.8 (q, *J* = 3.6 Hz), 122.7, 121.7 (q, *J* = 3.9 Hz), 115.0 (d, *J* = 21.2 Hz), 114.9 (d, *J* = 21.1 Hz), 68.1, 68.0, 63.4, 63.3, 62.5, 50.8(4), 50.7(8), 45.2(3), 45.1(9), 38.6, 38.1, 36.0, 27.1, 25.9, 25.7, 24.3, 24.0, 23.0, 22.9, 21.3. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4al** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4al** are reported.) δ −63.36, −119.68, −119.87. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{53}H_{63}F_5N_6O_4S_2+H]^+$: 1007.4345, found: 1007.4345.



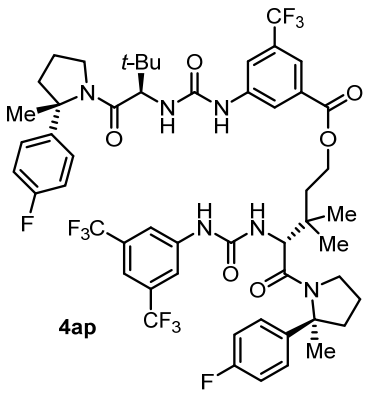
4am: Hydrogen-bond donor **4am** was prepared according to an analogous procedure as reported previously, using 3,5-dichlorophenyl isothiocyanate instead of 3,5-(trifluoromethyl)phenyl isothiocyanate[47,62]. ^{1}H NMR (400 MHz, CD_3CN) δ 8.83 (s, 1H), 8.67 (s, 1H), 8.35 (s, 1H), 8.11 (s, 1H), 7.99 (s, 1H), 7.42 (d, *J* = 1.8 Hz, 2H), 7.27–7.20 (m, 4H), 7.19 (t, *J* = 1.8 Hz, 1H), 7.11 (d, *J* = 9.1 Hz, 1H), 6.97 (d, *J* = 9.1 Hz, 1H), 6.93–6.80 (m, 4H), 5.35 (d, *J* = 9.1 Hz, 1H), 5.25 (d, *J* = 9.2 Hz, 1H), 4.55–4.41 (m, 4H), 3.92–3.79 (m, 2H), 2.10–1.98 (m, 2H), 1.92–1.79 (m, 12H), 1.79–1.63 (m, 2H), 1.19 (s, 3H), 1.11 (s, 3H), 1.09 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.7, 182.3, 170.3, 169.8, 165.5, 161.9 (d, *J* = 242.0 Hz), 161.9 (d, *J* = 242.0 Hz), 143.4 (d, *J* = 3.1 Hz), 143.3 (d, *J* = 3.0 Hz), 141.9, 141.5, 135.4, 132.8, 131.5 (q, *J* = 33.0 Hz), 128.4, 128.2–127.8 (m, two overlapping signals), 125.5, 124.9–124.6 (m), 124.6 (q, *J* = 271.8 Hz), 122.7, 122.7–122.5 (m), 115.2 (d, *J* = 21.2 Hz), 115.1 (d, *J* = 21.2 Hz), 68.2(2), 68.1(9), 63.8, 63.4, 62.7, 51.0, 50.9, 45.2, 45.1, 38.5, 38.2, 36.1, 27.1, 25.7, 25.6, 24.4, 24.1, 23.0(0), 22.9(5). ^{19}F NMR (376 MHz, CD_3CN) δ −63.28, −119.36, −119.48. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{51}H_{57}Cl_2F_5N_6O_4S_2+H]^+$: 1047.3253, found: 1047.3258.



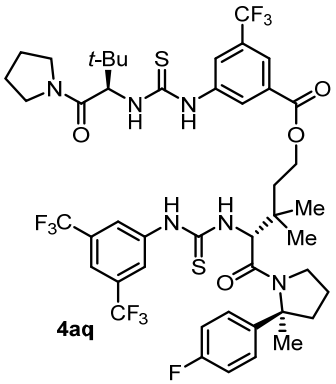
4an: Hydrogen-bond donor **4an** was prepared according to an analogous procedure as reported previously[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4an** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4an** are reported.) δ 9.81 (s, 1H), 8.73 (s, 1H), 8.41 (s, 2H), 8.34 (s, 1H), 8.29 (s, 1H), 7.85 (s, 1H), 7.75 (s, 1H), 7.60 (d, *J* = 9.3 Hz, 1H), 7.36–7.22 (m, 4H), 6.97–6.80 (m, 4H), 6.06 (d, *J* = 9.2 Hz, 1H), 5.52 (d, *J* = 9.4 Hz, 1H), 4.66–4.48 (m, 4H), 4.32–4.23 (m, 1H), 4.01–3.85 (m, 2H), 2.16–1.86 (m, 14H), 1.85–1.70 (m, 2H), 1.27 (s, 3H), 1.22 (s, 3H), 1.07 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4an** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4an** are reported.) δ 182.6, 170.8, 169.6, 165.5, 161.9(0) (d, *J* = 242.0 Hz), 161.8(6) (d, *J* = 241.8 Hz), 156.2, 143.6 (d, *J* = 3.2 Hz), 143.4 (d, *J* = 3.2 Hz), 142.9, 142.8, 133.0, 132.0 (q, *J* = 33.3 Hz), 131.8 (q, *J* = 32.2 Hz), 128.0 (d, *J* = 7.6 Hz), 127.9 (d, *J* = 7.6 Hz), 124.9 (q, *J* = 271.6 Hz), 124.3 (q, *J* = 272.1 Hz), 123.4–123.2 (m), 123.0, 119.2–118.9 (m), 118.9–118.7 (m), 117.9–117.6 (m), 114.9(4) (d, *J* = 21.2 Hz), 114.8(6) (d, *J* = 21.1 Hz), 68.0, 67.7, 63.2, 62.4, 59.2, 50.8, 50.6, 45.1, 38.3, 38.1, 35.2, 26.8, 25.8, 25.7, 24.3, 23.8, 22.9, 22.8, one signal overlaps with the solvent signal at δ = 29.8 ppm. ^{19}F NMR (376 MHz, $(CD_3)_2CO$; **4an** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4an** are reported.) δ −63.42, −63.51, −119.84, −119.90. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{53}H_{57}F_{11}N_6O_5S+H]^+$: 1099.4008, found: 1099.4010.



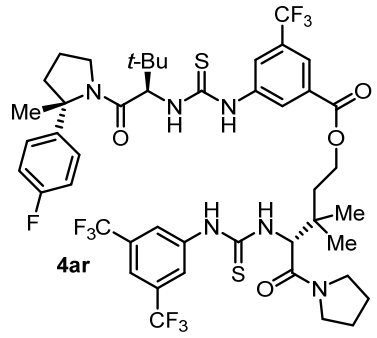
4ao: Hydrogen-bond donor **4ao** was prepared according to an analogous procedure as reported previously[47,62]. ^{1}H NMR (400 MHz, $(CD_3)_2CO$; **4ao** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4ao** are reported.) δ 9.63 (s, 1H), 8.82 (s, 1H), 8.53 (s, 1H), 8.45 (s, 1H), 8.18 (s, 2H), 8.02 (s, 1H), 7.59 (s, 1H), 7.39 (d, *J* = 9.1 Hz, 1H), 7.35–7.28 (m, 2H), 7.28–7.22 (m, 2H), 6.97–6.89 (m, 2H), 6.89–6.82 (m, 2H), 6.23 (d, *J* = 9.3 Hz, 1H), 5.37 (d, *J* = 9.3 Hz, 1H), 4.75 (d, *J* = 9.4 Hz, 1H), 4.63–4.47 (m, 3H), 4.33–4.22 (m, 1H), 4.01–3.84 (m, 2H), 2.16–2.06 (m, 2H), 2.04–1.84 (m, 12H), 1.84–1.70 (m, 2H), 1.22 (s, 3H), 1.17 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$; **4ao** undergoes a slow H→D exchange in $(CD_3)_2CO$ of the acidic thiourea NH groups. Only resonances corresponding to the all-protium **4ao** are reported.) δ 182.7, 170.4, 170.0, 165.3, 161.9(0) (d, *J* = 242.1 Hz), 161.8(6) (d, *J* = 242.0 Hz), 156.1, 143.5(0) (d, *J* = 2.5 Hz), 143.4(7) (d, *J* = 3.0 Hz), 143.3, 142.3, 132.7, 132.5 (q, *J* = 32.9 Hz), 131.3 (q, *J* = 32.9 Hz), 128.1 (d, *J* = 7.8 Hz), 127.8 (d, *J* = 7.9 Hz), 127.6, 124.7 (q, *J* = 272.1 Hz), 124.5 (q, *J* = 271.7 Hz), 123.9 (q, *J* = 3.8 Hz), 121.7 (q, *J* = 3.6 Hz), 118.6–118.2 (m), 115.3–115.0 (m), 114.9(4) (d, *J* = 21.2 Hz), 114.8(8) (d, *J* = 21.2 Hz), 67.9, 67.8, 63.3(1), 63.2(6), 58.3, 50.7, 45.2, 45.1, 38.1, 37.5, 36.0, 27.0, 25.7(4), 25.6(7), 24.1, 23.7, 22.9, 22.8, one signal overlaps with the solvent signal at δ = 29.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.72, −62.99, −117.48, −117.80. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{53}H_{57}F_{11}N_6O_5S+H]^+$: 1099.4008, found: 1099.4002.



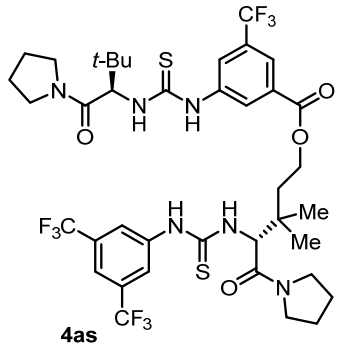
4ap: Hydrogen-bond donor **4ap** was prepared according to an analogous procedure as reported previously[47,62]. ^{1}H NMR (400 MHz, CD_3CN) δ 8.25 (s, 1H), 7.95 (s, 2H), 7.93 (s, 1H), 7.90 (s, 1H), 7.84 (s, 1H), 7.80 (s, 1H), 7.55 (s, 1H), 7.24–7.13 (m, 4H), 6.91–6.80 (m, 4H), 5.83 (d, J = 9.3 Hz, 1H), 5.70 (d, J = 9.1 Hz, 1H), 4.66 (d, J = 9.3 Hz, 1H), 4.51 (d, J = 9.1 Hz, 1H), 4.48–4.38 (m, 2H), 4.21–4.09 (m, 2H), 3.89–3.72 (m, 2H), 2.09–1.97 (m, 2H), 1.92–1.78 (m, 12H), 1.78–1.62 (m, 2H), 1.13 (s, 3H), 1.11 (s, 3H), 1.03 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 170.9, 170.5, 165.9, 161.9(3) (d, J = 242.0 Hz), 161.9(0) (d, J = 242.0 Hz), 156.3, 156.1, 143.7 (d, J = 3.3 Hz), 143.6 (d, J = 3.1 Hz), 142.7, 142.2, 133.1, 132.4 (q, J = 33.0 Hz), 131.7 (q, J = 32.5 Hz), 127.9 (d, J = 7.9 Hz), 127.8 (d, J = 7.8 Hz), 124.8 (q, J = 272.1 Hz), 124.5 (q, J = 272.1 Hz), 123.0, 119.8 (q, J = 3.9 Hz), 119.3 (q, J = 3.8 Hz), 118.8 (q, J = 4.1 Hz), 116.0–115.6 (m), 115.1 (d, J = 21.2 Hz), 115.1 (d, J = 21.2 Hz), 67.9, 67.8, 63.4, 59.3, 58.4, 50.9, 50.8, 45.0(9), 45.0(5), 38.0, 37.5, 35.4, 26.8, 25.6(2), 25.5(6), 24.1, 23.6, 22.9 (two overlapping signals). ^{19}F NMR (376 MHz, CD_3CN) δ −63.41, −63.55, −119.72, −119.76. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{53}H_{57}F_{11}N_6O_6+H]^+$: 1083.4237, found: 1083.4246.



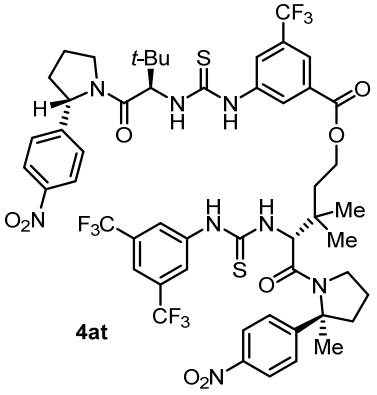
4aq: Hydrogen-bond donor **4aq** was prepared according to an analogous procedure as reported previously[47]. ^{1}H NMR (400 MHz, CD_3CN) δ 8.93 (s, 1H), 8.86 (s, 1H), 8.25 (s, 1H), 8.12 (s, 2H), 8.09 (s, 1H), 7.94 (s, 1H), 7.71 (s, 1H), 7.60 (d, J = 8.1 Hz, 1H), 7.29 (d, J = 7.3 Hz, 1H), 7.26–7.18 (m, 2H), 6.90–6.78 (m, 2H), 5.38 (d, J = 9.1 Hz, 1H), 5.27 (d, J = 9.1 Hz, 1H), 4.56–4.36 (m, 3H), 4.12–4.00 (m, 1H), 3.93–3.81 (m, 1H), 3.64–3.51 (m, 1H), 3.41–3.27 (m, 2H), 2.11–1.98 (s, 1H), 1.93–1.62 (m, 12H), 1.17 (s, 3H), 1.13 (s, 3H), 1.06 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.7(1), 182.6(8), 171.5, 170.0, 165.5, 161.9 (d, J = 242.3 Hz), 143.4 (d, J = 2.5 Hz), 142.1, 141.5, 132.6, 132.0 (q, J = 33.5 Hz), 131.2 (q, J = 32.8 Hz), 128.6, 128.0 (d, J = 7.9 Hz), 125.5–125.2 (m), 124.6–124.2 (m), 124.6 (q, J = 272.1 Hz), 124.3 (d, J = 272.1 Hz), 122.7–122.4 (m), 118.9–118.6 (m), 115.2 (d, J = 21.3 Hz), 68.3, 63.6, 63.3, 62.8, 51.0, 48.8, 47.0, 45.1, 38.4, 38.2, 36.3, 27.1, 26.6, 25.6, 24.8, 24.4, 24.2, 23.0. ^{19}F NMR (376 MHz, CD_3CN) δ −63.30, −63.45, −119.50. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{46}H_{52}F_{10}N_6O_4S_2+H]^+$: 1007.3405, found: 1007.3362.



4ar: Hydrogen-bond donor **4ar** was prepared according to an analogous procedure as reported previously[47,62]. ^{1}H NMR (400 MHz, CD_3CN) δ 8.88 (s, 1H), 8.78 (s, 1H), 8.34 (s, 1H), 8.07 (s, 1H), 7.99 (s, 2H), 7.97 (s, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.66 (s, 1H), 7.27–7.19 (m, 2H), 7.17 (d, *J* = 9.2 Hz, 1H), 6.86–6.77 (m, 2H), 5.39 (d, *J* = 9.2 Hz, 1H), 5.26 (d, *J* = 9.1 Hz, 1H), 4.53–4.35 (m, 3H), 4.12–4.00 (m, 1H), 3.90–3.80 (m, 1H), 3.66–3.54 (m, 1H), 3.43–3.28 (m, 2H), 2.10–1.97 (m, 1H), 1.93–1.61 (m, 12H), 1.17 (s, 3H), 1.15 (s, 3H), 1.07 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.8, 182.7, 171.4, 170.5, 165.5, 161.9 (d, *J* = 242.2 Hz), 143.4 (d, *J* = 3.1 Hz), 141.8, 141.5, 132.8, 131.8 (q, *J* = 33.3 Hz), 131.4 (q, *J* = 32.8 Hz), 128.5, 128.0 (d, *J* = 7.8 Hz), 125.1–124.6 (m, two overlapping signals), 124.6 (q, *J* = 271.8 Hz), 124.3 (q, *J* = 272.1 Hz), 122.7–122.4 (m), 119.0–118.7 (m), 115.1 (d, *J* = 21.2 Hz), 68.2, 63.8, 63.3, 63.1, 50.9, 49.0, 47.3, 45.1, 38.3, 38.2, 36.2, 27.1, 26.6, 25.6, 24.7, 24.5(0), 24.4(8), 23.0. ^{19}F NMR (376 MHz, CD_3CN) δ −63.30, −63.44, −119.32. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{46}H_{52}F_{10}N_6O_4S_2+H]^+$: 1007.3405, found: 1007.3400.

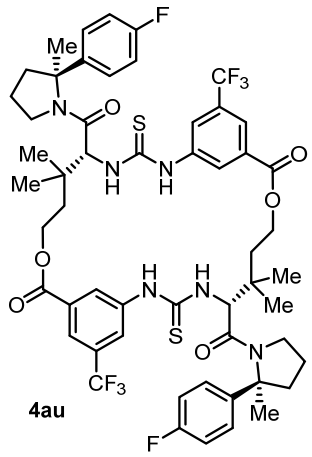


4as: Hydrogen-bond donor **4as** was prepared according to an analogous procedure as reported previously[47]. ^{1}H NMR (400 MHz, CD_3CN) δ 9.09 (s, 1H), 9.02 (s, 1H), 8.20 (s, 1H), 8.09–7.96 (m, 4H), 7.92 (s, 1H), 7.89 (d, *J* = 9.2 Hz, 1H), 7.65 (s, 1H), 5.41 (d, *J* = 9.1 Hz, 1H), 5.30 (d, *J* = 9.0 Hz, 1H), 4.52–4.32 (m, 2H), 4.18–4.02 (m, 2H), 3.71–3.53 (m, 2H), 3.47–3.19 (m, 4H), 2.00–1.87 (m, 4H), 1.86–1.63 (m, 6H), 1.16 (s, 3H), 1.10 (s, 3H), 1.07 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 182.9, 182.8, 172.3, 171.8, 165.4, 141.9, 141.4, 132.5, 131.7 (q, *J* = 33.6 Hz), 131.4 (q, *J* = 33.8 Hz), 128.9, 125.8 (q, *J* = 3.3 Hz), 124.8 (q, *J* = 3.5 Hz), 124.6 (q, *J* = 271.8 Hz), 124.3 (q, *J* = 272.1 Hz), 122.6 (q, *J* = 3.8 Hz), 118.9–118.5 (m), 63.9, 63.2, 63.1, 49.1, 49.0, 47.4, 47.3, 38.3, 38.1, 36.2, 27.3, 26.6 (two overlapping signals), 24.6(8), 24.6(7), 24.6, 24.4. ^{19}F NMR (376 MHz, CD_3CN) δ −63.27, −63.44. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{39}H_{47}F_9N_6O_4S_2+H]^+$: 899.3029, found: 899.3037.



4at: Hydrogen-bond donor **4at** was prepared according to an analogous procedure as reported on page S8 for the preparation of catalyst **4d**. ^{1}H NMR (400 MHz, CD_3CN; 11:1 mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ 8.76 (s, 1H), 8.73 (s 1H), 8.35 (s, 1H), 8.11 (s, 2H), 8.05 (s, 1H), 8.03–7.94 (m, 5H), 7.72 (s, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 9.1 Hz, 1H), 7.01 (d, *J* = 9.0 Hz, 1H), 5.37 (d, *J* = 9.1 Hz, 1H), 5.27 (d, *J* = 9.0 Hz, 1H), 5.19–5.12 (m, 1H), 4.60–4.36 (m, 4H), 3.99–3.88 (m, 1H), 3.88–3.79 (m, 1H), 2.40–2.26 (m, 1H), 2.15–2.04 (m, 1H), 1.93–1.83 (m, 9H), 1.83–1.68 (m, 2H), 1.21 (s, 3H), 1.15 (s, 3H), 1.08 (s, 9H). ^{13}C NMR

(101 MHz, CD_3CN; 11:1 mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ 182.7, 182.6, 170.7, 169.9, 165.5, 155.4, 152.5, 147.5, 147.1, 141.9, 141.4, 132.8, 132.1 (q, J = 33.4 Hz), 131.5 (q, J = 32.9 Hz), 128.2, 127.7, 127.3, 124.8–124.6 (m), 124.6 (q, J = 272.1 Hz), 124.4–124.0 (m, two overlapping signals), 124.3 (q, J = 271.8 Hz), 123.9, 122.8–122.5 (m), 119.0–118.6 (m), 68.4, 63.4(3), 63.4(1), 62.7, 61.8, 51.0, 49.3, 44.7, 38.3, 38.1, 35.9, 34.7, 26.9, 25.0, 24.4, 24.1(1), 24.0(6), 23.3. ^{19}F NMR (376 MHz, CD_3CN; 11:1 mixture of rotamers—only resonances corresponding to the major rotamer are reported) δ −63.35, −63.46. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{52}H_{55}F_9N_8O_8S_2+H]^+$: 1155.3513, found: 1155.3511.

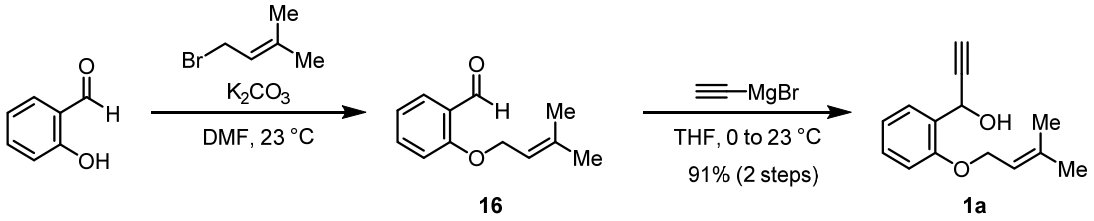


4au

4au: Macrocyclic hydrogen-bond donor **4au** was prepared according to an analogous procedure as reported previously[48]. ^1H NMR (400 MHz, CD_3OD; hydrogen atoms corresponding to thiourea moieties were not detected due to complete H→D exchange in CD_3OD) δ 8.84 (s, 2H), 8.08 (s, 2H), 8.03 (s, 2H), 7.40–7.29 (m, 4H), 6.95–6.84 (m, 4H), 5.46 (s, 2H), 4.68–4.59 (m, 2H), 4.59–4.49 (m, 4H), 3.86–3.74 (m, 2H), 2.25–2.13 (m, 2H), 2.13–2.00 (m, 2H), 2.00–1.89 (m, 2H), 1.88 (s, 6H), 1.86–1.71 (m, 6H), 1.29 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (101 MHz, CD_3OD, contaminated by n-hexane residues ($\delta_{n\text{-hexane}}$ 32.7, 23.7, 14.4 ppm)) δ 183.4, 171.2, 166.5, 162.6 (d, J = 243.1 Hz), 143.2 (d, J = 3.1 Hz), 142.4, 133.0, 132.1 (q, J = 32.9 Hz), 128.3 (d, J = 7.8 Hz), 128.2, 125.1 (q, J = 4.0 Hz), 125.0 (q, J = 271.8 Hz), 122.9 (q, J = 3.8 Hz), 115.3 (d, J = 21.3 Hz), 69.1, 63.8, 62.9, 51.8, 45.7, 38.4, 38.1, 25.5, 24.6, 24.4, 23.7. ^{19}F NMR (376 MHz, CD_3OD) δ −64.42, −120.09. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{54}H_{58}F_8N_6O_6S_2+H]^+$: 1103.3804, found: 1103.3812.

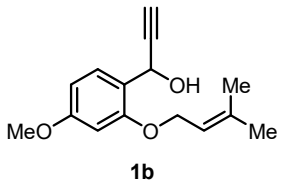
Synthesis and characterization of substrates

Synthesis of propargylic alcohol 1a



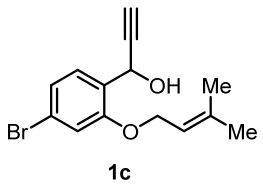
Propargylic alcohol **1a** was prepared according to a modified literature procedure[63]. Salicylaldehyde (435 µL, 4.09 mmol, 1 equiv) was added to a stirred suspension of potassium carbonate (849 mg, 6.14 mmol, 1.5 equiv) in *N*,*N*-dimethylformamide (13 mL) at 23 °C. 3,3-Dimethylallyl bromide (710 µL, 6.14 mmol, 1.5 equiv) was added at 23 °C, and the resulting yellow suspension was stirred at 23 °C for 17 hours. Water (20 mL) was added, and the mixture was extracted with diethyl ether (2 × 75 mL). The combined organic layers were washed with water (10 mL) and brine (2 × 10 mL). The organic phase was dried over anhydrous magnesium sulfate, the dried solution was filtered, and the filtrate was concentrated in vacuo to provide crude aldehyde **16**. The aldehyde product was used in the next step without further purification.

Crude aldehyde **16** (see the paragraph above) was dissolved in tetrahydrofuran (10 mL), and the solution was cooled to 0 °C. Ethynylmagnesium bromide (0.5 M solution in tetrahydrofuran; 12.3 mL, 6.14 mmol, 1.5 equiv) was added slowly at 0 °C, and the resulting mixture was stirred at 0 °C for 10 minutes. The mixture was allowed to warm to 23 °C and was stirred at this temperature for additional 2 hours (TLC: 20% ethyl acetate in hexanes; $KMnO_4$). The mixture was cooled to 0 °C, and a saturated aqueous solution of ammonium chloride (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 25 mL), and the combined organic fractions were washed with brine (10 mL). The organic layer was dried over anhydrous magnesium sulfate, the dried solution was filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (20% ethyl acetate in hexanes) to provide propargylic alcohol **1a** as a yellow oil (805 mg, 91% yield over two steps). Spectroscopic data of **1a** were in accordance with those reported in the literature[63]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.30 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.98 (app t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 5.69 (dd, *J* = 6.2, 2.3 Hz, 1H), 5.57–5.41 (m, 1H), 4.67–4.52 (m, 2H), 3.20 (d, *J* = 6.2 Hz, 1H), 2.61 (d, *J* = 2.1 Hz, 1H), 1.80 (s, 3H), 1.75 (s, 3H).



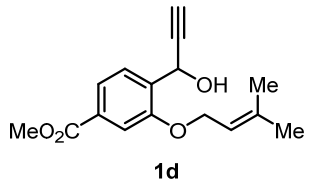
1b

1b: Propargylic alcohol **1b** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 4-methoxysalicylaldehyde. Spectroscopic data for **1b** were in accordance with those reported in the literature[63]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 9.0 Hz, 1H), 6.52–6.44 (m, 2H), 5.64 (dd, *J* = 6.2, 2.3 Hz, 1H), 5.53–5.44 (m, 1H), 4.62–4.51 (m, 2H), 3.81 (s, 3H), 3.00 (d, *J* = 6.3 Hz, 1H), 2.60 (d, *J* = 2.3 Hz, 1H), 1.79 (s, 3H), 1.74 (s, 3H).



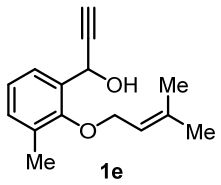
1c

1c: Propargylic alcohol **1c** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 4-bromosalicylaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 8.1 Hz, 1H), 7.11 (dd, J = 8.1, 1.8 Hz, 1H), 7.05 (d, J = 1.8 Hz, 1H), 5.68–5.59 (m, 1H), 5.51–5.42 (m, 1H), 4.63–4.52 (m, 2H), 2.99 (d, J = 4.2 Hz, 1H), 2.61 (d, J = 2.3 Hz, 1H), 1.84–1.78 (m, 3H), 1.78–1.72 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 139.3, 129.2, 127.9, 123.9, 123.1, 118.8, 115.8, 82.8, 74.5, 65.8, 60.7, 25.9, 18.4. FTIR (neat), cm^{-1}: 3398 (br), 3295 (w), 2931 (w), 1590 (vs), 1577 (m), 1483 (s), 1404 (m), 1382 (m), 1232 (vs), 990 (vs), 938 (s), 883 (s), 632 (m). HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{14}H_{15}BrO_2+H]^+$: 293.0183, found: 293.0188.



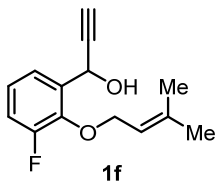
1d

1d: Propargylic alcohol **1d** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 4-(methoxycarbonyl)salicylaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, J = 7.8, 1.5 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 1.5 Hz, 1H), 5.74–5.66 (m, 1H), 5.53–5.44 (m, 1H), 4.72–4.59 (m, 2H), 3.92 (s, 3H), 3.20 (d, J = 5.8 Hz, 1H), 2.63 (d, J = 2.3 Hz, 1H), 1.83–1.78 (m, 3H), 1.79–1.74 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 156.1, 139.3, 133.5, 131.5, 127.9, 122.4, 119.0, 113.0, 82.7, 74.7, 65.7, 61.1, 52.4, 25.9, 18.5. FTIR (neat), cm^{-1}: 3290 (w), 2918 (w), 1707 (s), 1433 (s), 1416 (m), 1293 (vs), 1273 (s), 1238 (m), 1099 (s), 1028 (vs), 989 (m), 758 (vs), 645 (m). HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{16}H_{18}O_4+H]^+$: 273.1132, found: 273.1137.



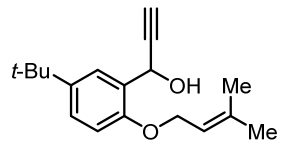
1e

1e: Propargylic alcohol **1e** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 3-methoxysalicylaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.6, 1.7 Hz, 1H), 7.18 (ddd, J = 7.6, 1.7, 0.9 Hz, 1H), 7.06 (app t, J = 7.6 Hz, 1H), 5.76–5.67 (m, 1H), 5.66–5.57 (m, 1H), 4.55 (dd, J = 11.1, 7.2 Hz, 1H), 4.41 (dd, J = 11.1, 7.2 Hz, 1H), 3.02 (br s, 1H), 2.63 (d, J = 2.3 Hz, 1H), 2.33 (s, 3H), 1.87–1.77 (m, 3H), 1.77–1.70 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 139.0, 133.9, 132.1, 131.8, 125.8, 124.5, 120.2, 84.2, 74.5, 70.6, 61.1, 26.0, 18.3, 16.6. FTIR (neat), cm^{-1}: 3416 (br), 3289 (w), 2974 (w), 2917 (w), 1467 (m), 1380 (m), 1253 (s), 1186 (vs), 1006 (s), 969 (vs), 784 (s), 758 (s), 637 (vs). HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{15}H_{18}O_2+H]^+$: 229.1234, found: 229.1234.



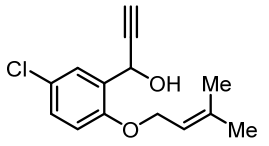
1f

1f: Propargylic alcohol **1f** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 3-fluorosalicylaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.29 (m, 1H), 7.12–7.00 (m, 2H), 5.66 (dd, J = 6.6, 2.3 Hz, 1H), 5.60–5.52 (m, 1H), 4.71 (d, J = 7.4 Hz, 1H), 2.98 (d, J = 6.6 Hz, 1H), 2.63 (d, J = 2.3 Hz, 1H), 1.81–1.76 (m, 3H), 1.74–1.69 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7, 144.2, 140.2, 135.2, 123.9 (d, J = 5.4 Hz), 123.1 (d, J = 2.5 Hz), 119.8, 117.4 (d, J = 11.3 Hz), 83.4, 74.6, 70.7 (d, J = 4.4 Hz), 61.0, 26.0, 18.2. ^{19}F NMR (471 MHz, $CDCl_3$–$PhCF_3$) δ −129.92. FTIR (neat), cm^{-1}: 3408 (br), 3296 (w), 2931 (w), 1474 (vs), 1267 (s), 1205 (m), 948 (s), 887 (m), 787 (m), 754 (s), 638 (s). HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{14}H_{15}FO_2+H]^+$: 233.0983, found: 233.0983.



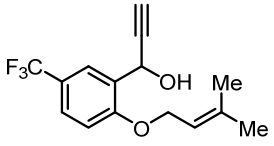
1g

1g: Propargylic alcohol **1g** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 5-*tert*-butylsalicylaldehyde. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.5 Hz, 1H), 7.30 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 5.65 (dd, *J* = 6.6, 2.3 Hz, 1H), 5.54–5.46 (m, 1H), 4.65–4.52 (m, 2H), 3.28 (d, *J* = 6.6 Hz, 1H), 2.62 (d, *J* = 2.3 Hz, 1H), 1.79 (s, 3H), 1.74 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 143.7, 138.5, 127.9, 126.4, 125.3, 119.7, 111.9, 83.4, 74.3, 65.5, 62.3, 34.4, 31.7, 26.0, 18.4. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{18}H_{24}O_2+H]^+$: 271.1704, found: 271.1707.



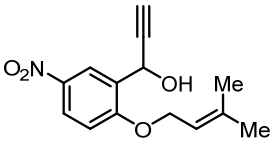
1h

1h: Propargylic alcohol **1h** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 5-chlorosalicylaldehyde. Spectroscopic data for **1h** were in accordance with those reported in the literature[63]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 2.6 Hz, 1H), 7.25 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 5.65 (s, 1H), 5.50–5.42 (m, 1H), 4.62–4.52 (m, 2H), 3.06 (br s, 1H), 2.64 (d, *J* = 2.3 Hz, 1H), 1.82–1.78 (m, 3H), 1.77–1.71 (m, 3H).



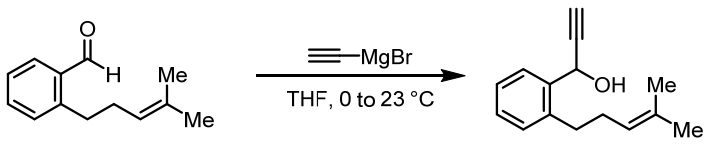
1i

1i: Propargylic alcohol **1i** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 5-(trifluoromethyl)salicylaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.3 Hz, 1H), 7.56 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 1H), 5.76–5.68 (m, 1H), 5.51–5.43 (m, 1H), 4.71–4.60 (m, 2H), 2.99 (br s, 1H), 2.65 (d, *J* = 2.3 Hz, 1H), 1.83–1.78 (m, 3H), 1.78–1.74 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 139.3, 129.4, 127.0 (q, *J* = 3.9 Hz), 125.1 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.3 Hz), 122.9 (q, *J* = 33.0 Hz), 118.8, 111.9, 82.6, 74.6, 65.8, 60.3, 25.8, 18.3. ^{19}F NMR (471 MHz, $CDCl_3$–PhF) δ −61.61. FTIR (neat), cm^{-1}: 3403 (br), 3309 (w), 2935 (w), 1618 (w), 1505 (w), 1328 (s), 1259 (m), 1158 (m), 1112 (vs), 1080 (m), 989 (m), 818 (w), 640 (m). HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{15}H_{15}F_3O_2+H]^+$: 283.0951, found: 283.0955.



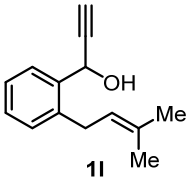
1j

1j: Propargylic alcohol **1j** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 5-nitrosalicylaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.77–7.71 (m, 2H), 5.73 (s, 1H), 5.51–5.43 (m, 1H), 4.74–4.66 (m, 2H), 3.01 (br s, 1H), 2.65 (d, *J* = 2.3 Hz, 1H), 1.83–1.80 (m, 3H), 1.80–1.78 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 148.9, 140.1, 135.5, 128.3, 118.3, 116.0, 107.2, 82.1, 75.0, 66.2, 60.3, 25.9, 18.5. FTIR (neat), cm^{-1}: 3422 (br), 3250 (w), 2916 (w), 1589 (m), 1508 (m), 1491 (m), 1335 (s), 1271 (vs), 1009 (s), 659 (m). HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{15}NO_4+H]^+$: 260.0928, found: 260.0930.



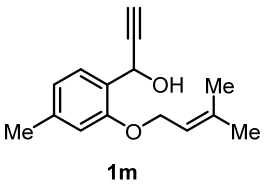
17 **1k**

Propargylic alcohol **1k** was prepared from aldehyde **17** that was synthesized according to a literature procedure[64]. Ethynylmagnesium bromide (0.5 M solution in tetrahydrofuran; 9.4 mL, 4.70 mmol, 1.5 equiv) was added slowly to a solution of aldehyde **17** (590 mg, 3.13 mmol, 1 eq) in THF (10 mL) at 0 °C, and the resulting mixture was stirred at 0 °C for 2 hours (TLC: 20% ethyl acetate in hexanes; $KMnO_4$). A saturated aqueous solution of ammonium chloride (20 mL) was added, and the resulting mixture was extracted with ethyl acetate (3 × 25 mL). The combined organic fractions were washed with brine (10 mL). The organic layer was dried over anhydrous magnesium sulfate, the dried solution was filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (20% ethyl acetate in hexanes) to provide propargylic alcohol **1k** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.68 (m, 1H), 7.33–7.17 (m, 3H), 5.74–5.66 (m, 1H), 5.24–5.15 (m, 1H), 2.86–2.70 (m, 2H), 2.65 (d, J = 2.3 Hz, 1H), 2.39–2.26 (m, 2H), 2.14–2.04 (m, 1H), 1.70 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 137.9, 133.0, 130.1, 128.9, 127.0, 126.6, 123.6, 84.0, 74.9, 61.8, 32.5, 30.2, 25.9, 17.8. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{15}H_{18}O+H]^+$: 215.1430, found: 215.1431.



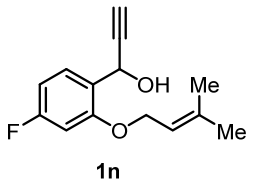
1l

1l: Propargylic alcohol **1l** was prepared according to a literature procedure, and its spectroscopic data were in accordance with those reported in the literature[65]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.66 (m, 1H), 7.33–7.16 (m, 3H), 5.67 (d, J = 2.2 Hz, 1H), 5.34–5.20 (m, 1H), 3.63–3.40 (m, 2H), 2.66 (d, J = 2.3 Hz, 1H), 2.25 (br s, 1H), 1.78–1.74 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 137.9, 133.3, 129.9, 129.0, 127.0, 126.7, 123.0, 83.7, 74.9, 62.0, 31.4, 25.9, 18.1.



1m

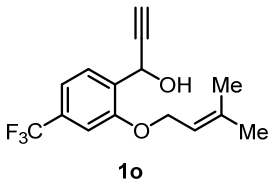
1m: Propargylic alcohol **1m** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 4-methylsalicylaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 7.6 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 6.74 (s, 1H), 5.68–5.60 (m, 1H), 5.53–5.46 (m, 1H), 4.64–4.51 (m, 2H), 3.17 (d, J = 6.0 Hz, 1H), 2.59 (d, J = 2.2 Hz, 1H), 2.35 (s, 3H), 1.83–1.78 (m, 3H), 1.77–1.72 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 139.9, 138.4, 127.8, 125.9, 121.5, 119.5, 113.1, 83.5, 73.9, 65.3, 61.2, 25.8, 21.7, 18.3. FTIR (neat), cm^{-1}: 3288 (w), 2917 (w), 1611 (m), 1504 (m), 1284 (s), 1258 (s), 1194 (m), 1115 (s), 1012 (vs), 947 (s), 817 (m), 795 (s), 636 (s). HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{15}H_{18}O_2+H]^+$: 229.1234, found: 229.1233.



1n

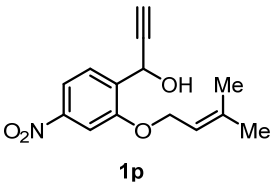
1n: Propargylic alcohol **1n** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 4-fluorosalicylaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, J = 8.4, 6.6 Hz, 1H), 6.72–6.56 (m, 2H), 5.66 (d, J = 2.3 Hz, 1H), 5.51–5.43 (m, 1H), 4.63–4.50 (m, 2H), 2.99 (br s, 1H), 2.61 (d, J = 2.3 Hz, 1H), 1.85–1.78 (m, 3H), 1.77–1.71 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6 (d, J = 269.5 Hz), 157.4 (d, J = 8.1 Hz), 139.3, 129.1 (d, J = 8.3 Hz), 124.7, 118.9, 107.1 (d, J = 16.1 Hz), 100.6 (d, J = 19.6 Hz), 83.0, 74.4, 65.8, 60.8, 26.0, 18.5. ^{19}F

NMR (471 MHz, $CDCl_3$–$PhCF_3$) δ −111.55 to −111.64 (m). FTIR (neat), cm^{-1}: 3405 (br), 3301 (w), 2917 (w), 1599 (s), 1498 (s), 1276 (s), 1157 (s), 1098 (m), 1003 (vs), 961 (s), 832 (s), 637 (m). HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{15}FO_2+H]^+$: 233.0983, found: 233.0984.



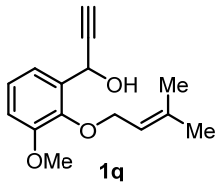
1o

1o: Propargylic alcohol **1o** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 4-(trifluoromethyl)salicylaldehyde. ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.24 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.14–7.10 (m, 1H), 5.76–5.66 (m, 1H), 5.52–5.43 (m, 1H), 4.70–4.60 (m, 2H), 3.15 (br s, 1H), 2.63 (d, *J* = 2.3 Hz, 1H), 1.83–1.78 (m, 3H), 1.78–1.73 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 139.6, 132.4, 131.9 (q, *J* = 32.5 Hz), 128.3, 124.0 (q, *J* = 272.3 Hz), 118.7, 117.8 (q, *J* = 3.8 Hz), 109.1 (q, *J* = 3.8 Hz), 82.6, 74.7, 65.9, 60.7, 25.9, 18.4. ^{19}F NMR (471 MHz, $CDCl_3$–PhF) δ −62.70. FTIR (neat), cm^{-1}: 3296 (w), 1424 (m), 1319 (m), 1241 (s), 1156 (s), 1110 (vs), 1078 (m), 1030 (s), 1014 (vs), 911 (m), 864 (m), 662 (m), 632 (m). HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{15}H_{15}F_3O_2+H]^+$: 283.0951, found: 283.0955.



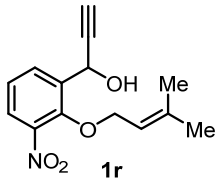
1p

1p: Propargylic alcohol **1p** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 4-nitrosalicylaldehyde. ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.78–7.70 (m, 2H), 5.77–5.69 (m, 1H), 5.52–5.42 (m, 1H), 4.77–4.65 (m, 2H), 2.98 (d, *J* = 5.6 Hz, 1H), 2.65 (d, *J* = 2.3 Hz, 1H), 1.83–1.81 (m, 3H), 1.81–1.78 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 148.9, 140.1, 135.5, 128.3, 118.3, 116.0, 107.2, 82.1, 75.1, 66.2, 60.3, 25.9, 18.5. FTIR (neat), cm^{-1}: 3298 (m), 2916 (w), 2861 (w), 1520 (vs), 1345 (vs), 1252 (vs), 1034 (s), 1013 (vs), 806 (m), 739 (s), 661 (m), 631 (s). HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{15}NO_4+H]^+$: 260.0928, found: 260.0930.



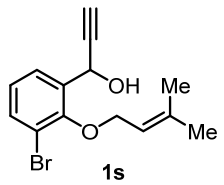
1q

1q: Propargylic alcohol **1q** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 3-methoxysalicylaldehyde. Spectroscopic data for **1q** were in accordance with those reported in the literature[63]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.07 (app t, *J* = 7.9 Hz, 1H), 6.91 (dd, *J* = 8.2, 1.6 Hz, 1H), 5.69–5.62 (m, 1H), 5.61–5.55 (m, 1H), 4.70–4.61 (m, 2H), 3.88 (s, 3H), 3.17 (d, *J* = 6.2 Hz, 1H), 2.62 (d, *J* = 2.3 Hz, 1H), 1.82–1.76 (m, 3H), 1.75–1.69 (m, 3H).



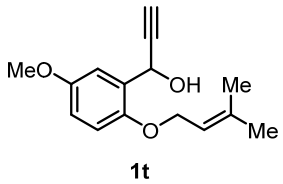
1r

1r: Propargylic alcohol **1r** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 3-nitrosalicylaldehyde. ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 2.8 Hz, 1H), 8.23 (dd, *J* = 9.1, 2.8 Hz, 1H), 6.97 (d, *J* = 9.1 Hz, 1H), 5.73 (d, *J* = 2.1 Hz, 1H), 5.51–5.43 (m, 1H), 4.77–4.66 (m, 2H), 2.87 (br s, 1H), 2.68 (d, *J* = 2.3 Hz, 1H), 1.81 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 141.4, 140.3, 129.7, 126.1, 124.0, 118.2, 111.8, 82.0, 75.3, 66.4, 60.2, 26.0, 18.6. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{15}NO_4+H]^+$: 260.0928, found: 260.0931.



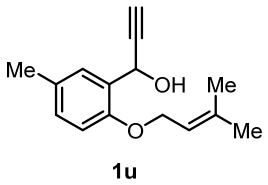
1s

1s: Propargylic alcohol **1s** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 3-bromosalicylaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60–7.51 (m, 2H), 7.04 (app t, J = 7.8 Hz, 1H), 5.74 (d, J = 2.3 Hz, 1H), 5.67–5.59 (m, 1H), 4.72–4.59 (m, 2H), 2.87 (br s, 1H), 2.66 (d, J = 2.4 Hz, 1H), 1.86–1.79 (m, 3H), 1.79–1.73 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 140.2, 136.2, 134.2, 127.5, 125.8, 119.6, 117.8, 83.5, 75.0, 71.1, 60.9, 26.1, 18.4. FTIR (neat), cm^{-1}: 3410 (br), 3295 (w), 2973 (w), 2916 (w), 1442 (vs), 1380 (m), 1221 (s), 1119 (m), 1019 (s), 962 (s), 938 (s), 780 (s), 732 (m), 691 (s), 633 (s). HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{15}BrO_2+H]^+$: 293.0183, found: 293.0186.



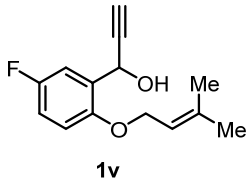
1t

1t: Propargylic alcohol **1t** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 5-methoxysalicylaldehyde. Spectroscopic data for **1t** were in accordance with those reported in the literature[63]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, J = 3.0 Hz, 1H), 6.86 (d, J = 8.9 Hz, 1H), 6.81 (dd, J = 8.9, 3.0 Hz, 1H), 5.68–5.62 (m, 1H), 5.51–5.44 (m, 1H), 4.62–4.50 (m, 2H), 3.79 (s, 3H), 3.25 (d, J = 5.4 Hz, 1H), 2.62 (d, J = 2.3 Hz, 1H), 1.80–1.77 (m, 3H), 1.75–1.71 (m, 3H).



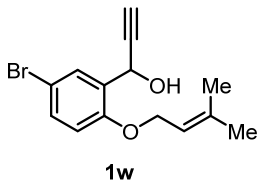
1u

1u: Propargylic alcohol **1u** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 5-methylsalicylaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 2.3 Hz, 1H), 7.08 (ddd, J = 8.3, 2.3, 0.9 Hz, 1H), 6.82 (d, J = 8.3 Hz, 1H), 5.68–5.60 (m, 1H), 5.52–5.45 (m, 1H), 4.63–4.52 (m, 2H), 3.24 (d, J = 4.8 Hz, 1H), 2.61 (d, J = 2.3 Hz, 1H), 2.30 (s, 3H), 1.82–1.77 (m, 3H), 1.76–1.71 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 138.5, 130.4, 130.1, 128.7, 128.5, 119.7, 112.4, 83.4, 74.2, 65.7, 61.7, 25.9, 20.7, 18.4. FTIR (neat), cm^{-1}: 3436 (br), 3288 (w), 2918 (w), 1497 (vs), 1233 (vs), 1006 (vs), 962 (s), 806 (m), 649 (s). HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{15}H_{18}O_2+H]^+$: 229.1234, found: 229.1234.



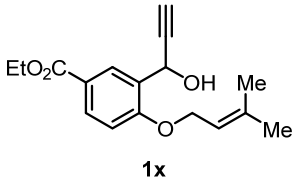
1v

1v: Propargylic alcohol **1v** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 5-fluorosalicylaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, J = 8.8, 3.1 Hz, 1H), 6.97 (ddd, J = 9.1, 7.9, 3.2 Hz, 1H), 6.85 (dd, J = 9.0, 4.3 Hz, 1H), 5.72–5.61 (m, 1H), 5.51–5.41 (m, 1H), 4.63–4.50 (m, 2H), 3.14 (br s, 1H), 2.63 (d, J = 2.3 Hz, 1H), 1.83–1.78 (m, 3H), 1.76–1.70 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 156.2, 152.4, 139.0, 130.3 (d, J = 5.4 Hz), 119.3, 115.4 (m), 113.4 (d, J = 6.9 Hz), 82.6, 74.8, 66.2, 61.0, 26.0, 18.5. ^{19}F NMR (471 MHz, $CDCl_3$–$PhCF_3$) δ −123.76 (m). FTIR (neat), cm^{-1}: 3415 (br), 3301 (w), 2917 (w), 1491 (vs), 1245 (m), 1188 (vs), 1000 (m), 973 (s), 879 (m), 809 (m), 648 (m). HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{15}FO_2+H]^+$: 233.0983, found: 233.0983.



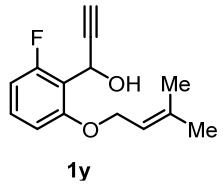
1w

1w: Propargylic alcohol **1w** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 5-bromosalicylaldehyde. Spectroscopic data for **1w** were in accordance with those reported in the literature[63]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 2.5 Hz, 1H), 7.39 (dd, J = 8.7, 2.5 Hz, 1H), 6.79 (d, J = 8.7 Hz, 1H), 5.65 (d, J = 4.8 Hz, 1H), 5.49–5.42 (m, 1H), 4.62–4.53 (m, 2H), 3.16–2.93 (m, 1H), 2.64 (d, J = 2.3 Hz, 1H), 1.81–1.77 (m, 3H), 1.76–1.71 (m, 1H).



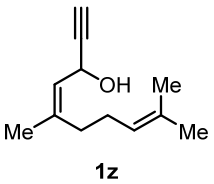
1x

1x: Propargylic alcohol **1x** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 5-(ethoxycarbonyl)salicylaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, J = 2.2 Hz, 1H), 8.02 (dd, J = 8.6, 2.2 Hz, 1H), 6.93 (d, J = 8.7 Hz, 1H), 5.72–5.65 (m, 1H), 5.52–5.43 (m, 1H), 4.71–4.60 (m, 2H), 4.36 (qd, J = 7.1, 1.1 Hz, 2H), 3.04 (br s, 1H), 2.63 (d, J = 2.3 Hz, 1H), 1.82–1.78 (m, 3H), 1.78–1.74 (m, 3H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 159.9, 139.4, 132.0, 129.6, 128.7, 123.2, 118.9, 111.7, 82.9, 74.5, 65.8, 61.1, 61.0, 25.9, 18.5, 14.6. FTIR (neat), cm^{-1}: 3438 (br), 3296 (w), 2980 (w), 2916 (w), 1695 (m), 1607 (m), 1239 (vs), 1122 (s), 1018 (s), 983 (s), 769 (s), 732 (m), 657 (m). HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{17}H_{20}O_4+H]^+$: 287.1289, found: 287.1294.



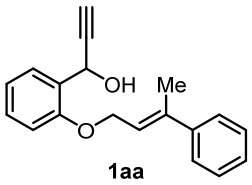
1y

1y: Propargylic alcohol **1y** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 6-fluorosalicylaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.18 (m, 1H), 6.77–6.66 (m, 2H), 5.81–5.72 (m, 1H), 5.55–5.45 (m, 1H), 4.70–4.57 (m, 2H), 3.81 (d, J = 11.2 Hz, 1H), 2.49 (d, J = 2.4 Hz, 1H), 1.83–1.78 (m, 3H), 1.77–1.73 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 157.8 (d, J = 5.9 Hz), 139.4, 130.0 (d, J = 9.8 Hz), 118.9, 117.1, 108.5(6), 108.6(3) (d, J = 22.5 Hz), 83.7, 72.4, 66.2, 56.2 (d, J = 6.9 Hz), 26.0, 18.5. ^{19}F NMR (471 MHz, $CDCl_3$–$PhCF_3$) δ −118.74 (t, J = 2.8 Hz). FTIR (neat), cm^{-1}: 3537 (br), 3295 (w), 2916 (w), 1614 (s), 1467 (s), 1226 (s), 1023 (vs), 778 (s). HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{14}H_{15}FO_2+H]^+$: 233.0983, found: 233.0984.



1z

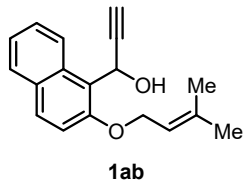
1z: Propargylic alcohol **1z** was prepared according to a literature procedure, and its spectroscopic data were in accordance with those reported in the literature[66]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44–5.38 (m, 1H), 5.16–5.03 (m, 2H), 2.48 (d, J = 2.2 Hz, 1H), 2.19–2.05 (m, 4H), 1.78 (d, J = 4.5 Hz, 1H), 1.77 (d, J = 1.3 Hz, 3H), 1.69 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 133.0, 125.2, 123.7, 84.6, 72.6, 58.8, 32.4, 26.5, 25.9, 23.5, 17.9.



1aa

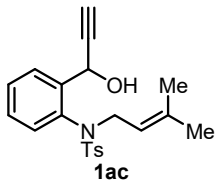
1aa: Propargylic alcohol **1aa** was prepared according to a literature procedure, and its spectroscopic data were in accordance with those reported in the literature[44]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 7.5, 1.6 Hz, 1H), 7.46–7.40 (m, 2H), 7.39–7.27 (m, 4H), 7.04–6.95 (m, 2H), 6.10–6.03 (m, 1H), 5.73 (dd, J = 6.4, 2.2 Hz, 1H), 4.90–4.81

(m, 2H), 3.11 (d, J = 6.5 Hz, 1H), 2.62 (d, J = 2.3 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 142.5, 139.8, 130.0, 128.8, 128.5, 128.2, 127.8, 126.0, 122.5, 121.3, 112.3, 83.3, 74.3, 66.0, 61.5, 16.7.



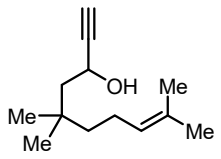
1ab

1ab: Propargylic alcohol **1ab** was prepared according to a literature procedure, and its spectroscopic data were in accordance with those reported in the literature[63]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.7 Hz, 1H), 7.86–7.76 (m, 2H), 7.54 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.42–7.36 (m, 1H), 7.29 (d, J = 9.1 Hz, 1H), 6.41 (dd, J = 8.1, 2.4 Hz, 1H), 5.61–5.52 (m, 1H), 4.81–4.68 (m, 2H), 3.81 (d, J = 8.1 Hz, 1H), 2.55 (d, J = 2.4 Hz, 1H), 1.81 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 139.1, 131.3, 130.6, 129.7, 128.8, 127.1, 124.1, 123.4, 121.9, 119.5, 115.4, 84.6, 73.1, 67.1, 58.2, 26.0, 18.5.



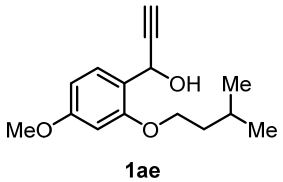
1ac

1ac: Propargylic alcohol **1ac** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from *N*-(2-formylphenyl)-4-methyl-*N*-(3-methylbut-2-en-1-yl)benzenesulfonamide that was prepared according to a literature procedure[67]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.8, 1.5 Hz, 1H), 7.54 (d, J = 8.3 Hz, 2H), 7.43–7.36 (m, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.18–7.12 (m, 1H), 6.42 (dd, J = 8.0, 1.0 Hz, 1H), 6.00 (d, J = 2.3 Hz, 1H), 5.09–5.00 (m, 1H), 4.50 (dd, J = 13.5, 6.8 Hz, 1H), 3.79–3.63 (m, 2H), 2.55 (d, J = 2.3 Hz, 1H), 2.46 (s, 3H), 1.60 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 143.0, 139.8, 136.3, 134.9, 129.8(3), 129.8(0), 129.6, 129.3, 128.1, 127.4, 117.1, 83.4, 73.8, 59.6, 49.9, 25.9, 21.8, 17.7. HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{21}H_{23}NO_3S+H]^+$: 370.1471, found: 370.1468.



1ad

1ad: Propargylic alcohol **1ad** was prepared according to a literature procedure, and its spectroscopic data were in accordance with those reported in the literature[68]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15–5.03 (m, 1H), 4.53–4.39 (m, 1H), 2.48 (d, J = 2.1 Hz, 1H), 1.99–1.88 (m, 2H), 1.75–1.70 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.33–1.24 (m, 2H), 1.00–0.92 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.3, 125.1, 86.5, 73.0, 59.9, 49.5, 42.8, 32.8, 27.6(4), 27.5(9), 25.9, 22.9, 17.8.

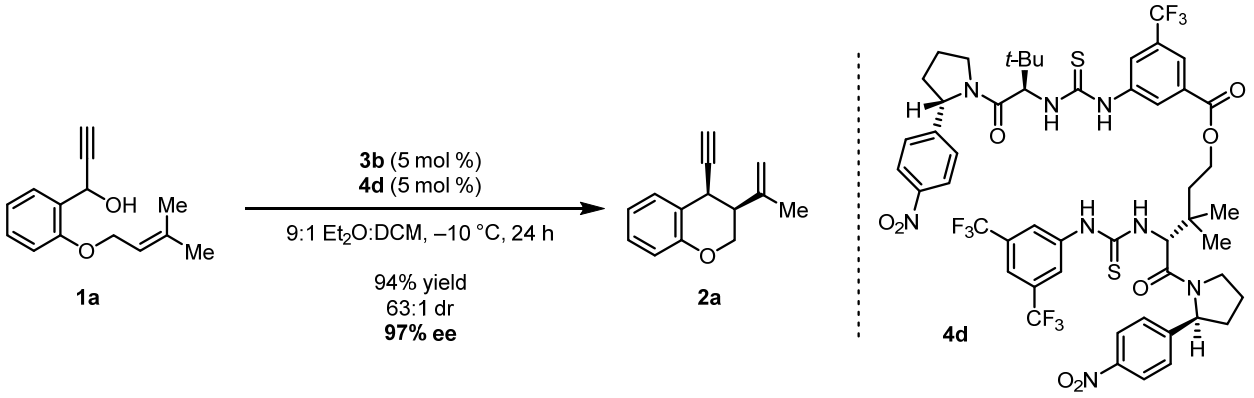


1ae

1ae: Propargylic alcohol **1ae** was prepared according to the procedure described on page S39 for the preparation of propargylic alcohol **1a**, starting from 4-methoxysalicylaldehyde and using 1-bromo-3-methylbutane instead of 3,3-dimethylallyl bromide in the first synthetic step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.42 (m, 1H), 6.51–6.54 (m, 2H), 5.62 (dd, J = 6.3, 2.3 Hz, 1H), 4.12–3.97 (m, 2H), 3.81 (s, 3H), 2.94 (d, J = 6.3 Hz, 1H), 2.59 (d, J = 2.3 Hz, 1H), 1.94–1.78 (m, 1H), 1.77–1.67 (m, 2H), 0.97 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 157.5, 128.8, 121.4, 104.3, 99.8, 83.6, 73.9, 66.9, 61.1, 55.6, 38.0, 25.3, 22.7(4), 22.6(9). HRMS (ESI): m/z $[M+H]^+$ calculated for $[C_{15}H_{20}O_3+H]^+$: 249.1485, found: 249.1486.

Catalytic enantioselective propargylic substitution

General reaction procedure



Ruthenium tosylate complex **3b** (7.9 mg, 0.01 mmol, 0.05 equiv) and hydrogen-bond donor **4d** (11.4 mg, 0.01 mmol, 0.05 equiv) were added to a 20 mL septum-capped vial equipped with a stir bar. The vial was then placed under a nitrogen atmosphere, and the catalysts were dissolved in dichloromethane (1 mL). Diethyl ether (8.7 mL) was then added, and the solution was cooled to −10 °C (cryocool). A solution of substrate **1a** (43.3 mg, 0.2 mmol, 1 equiv) in diethyl ether (0.3 mL) was added at −10 °C, and the reaction mixture was allowed to stir at −10 °C for 24 hours. After this time, the vial was removed from the cooling bath, and the mixture was concentrated in vacuo. The residue was purified by flash column chromatography (0–15% diethyl ether in hexanes) to afford (3*S*,4*R*)-4-ethynyl-3-(prop-1-en-2-yl)chromane (**2a**) as a colorless oil (37.4 mg, 94% yield, 63:1 dr, 97% ee). Reported yield corresponds to an isolated purified product as a mixture of diastereomers. The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.73 ppm and δ_{minor} = 4.89 ppm, respectively. The enantiomeric excess was determined by HPLC analysis (CHIRALCEL OD-H, 0.3% isopropanol in hexanes, 1 mL/min) of a purified mixture of products by integration of signals at t_r(major) = 16.649 min and t_r(minor) = 12.574 min. Spectroscopic data for **2a** were in accordance with those reported in the literature[9]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 6.9 Hz, 1H), 7.16 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 6.90 (app td, *J* = 7.4, 1.2 Hz, 1H), 6.84 (dd, *J* = 8.3, 1.2 Hz, 1H), 5.01 (s, 1H), 4.73 (s, 1H), 4.35 (ddd, *J* = 10.7, 3.5, 1.7 Hz, 1H), 4.28 (app t, *J* = 10.4 Hz, 1H), 3.97 (app dt, *J* = 4.5, 2.0 Hz, 1H), 2.67 (app dt, *J* = 9.4, 4.2 Hz, 1H), 2.25 (d, *J* = 2.5 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 142.2, 123.0, 128.8, 121.8, 120.7, 117.2, 112.1, 83.3, 72.9, 65.8, 41.5, 31.8, 22.6. HRMS (ESI): *m/z* $[M+H]^+$ calculated for $[C_{14}H_{14}O+H]^+$: 199.1117, found: 199.1117.

Synthesis of racemic standards

Racemic standards were prepared using the following procedure. Ruthenium tosylate complex **3b** (4.0 mg, 5 μmol, 0.1 equiv) was added to a stirred solution of a propargylic alcohol (0.05 mmol, 1 equiv) in dichloromethane (1.5 mL) at 23 °C. The resulting mixture was stirred at 23 °C for 15 hours. The mixture was concentrated, and the residue was purified by flash column chromatography to provide a racemic sample of a cyclized product.

Product scope

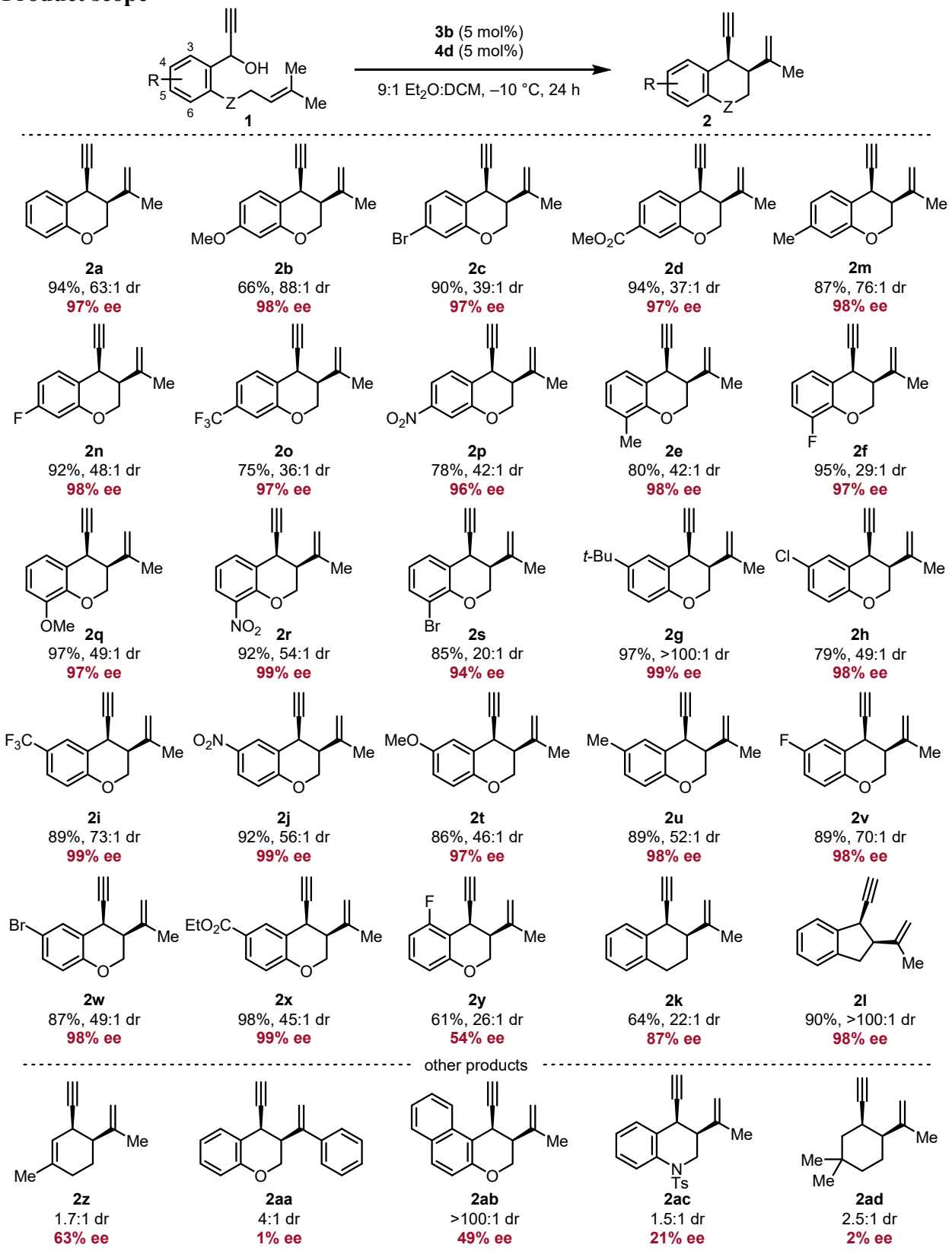
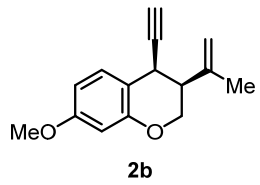
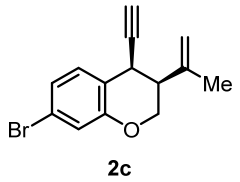


Figure S2 Products of the stereoselective propargylic substitution reaction.



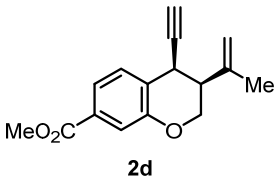
2b

2b: (3*S*,4*R*)-4-ethynyl-7-methoxy-3-(prop-1-en-2-yl)chromane (**2b**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1b** (49.3 mg, 0.2 mmol) and isolated as a colorless oil (30.0 mg, 66% yield, 88:1 dr, 98% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.72 ppm and δ_{minor} = 4.88 ppm, respectively. The enantiomeric excess was determined by SFC analysis (CHIRALPAK IH, 0.2% methanol) of a purified mixture of products by integration of signals at t_r(major) = 2.800 min and t_r(minor) = 3.547 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.5 Hz, 1H), 6.51 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.39 (d, *J* = 2.6 Hz, 1H), 5.00 (s, 1H), 4.72 (s, 1H), 4.33 (ddd, *J* = 10.7, 3.4, 1.6 Hz, 1H), 4.26 (app t, *J* = 10.4 Hz, 1H), 3.93–3.89 (m, 1H), 3.76 (s, 3H), 2.65 (app dt, *J* = 9.1, 4.0 Hz, 1H), 2.23 (d, *J* = 2.5 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 154.4, 142.4, 130.5, 114.2, 112.1, 108.0, 101.7, 83.6, 72.7, 66.0, 55.5, 41.7, 31.3, 22.7. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{15}H_{16}O_2+H]^+$: 229.1223, found: 229.1223.



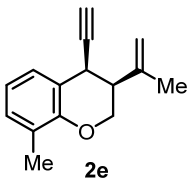
2c

2c: (3*S*,4*R*)-7-bromo-4-ethynyl-3-(prop-1-en-2-yl)chromane (**2c**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1c** (59.0 mg, 0.2 mmol) and isolated as a pale-yellow oil (50.1 mg, 90% yield, 39:1 dr, 97% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.97 ppm and δ_{minor} = 5.13 ppm, respectively. The enantiomeric excess was determined by SFC analysis (CHIRALPAK ID, 1% methanol) of a purified mixture of products by integration of signals at t_r(major) = 4.143 min and t_r(minor) = 2.810 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.32 (m, 1H), 7.31–7.23 (m, 2H), 5.25 (s, 1H), 4.97 (s, 1H), 4.58 (ddd, *J* = 10.8, 3.4, 1.7 Hz, 1H), 4.51 (app t, *J* = 10.5 Hz, 1H), 4.16 (app dt, *J* = 4.6, 2.1 Hz, 1H), 2.88 (app dt, *J* = 9.4, 4.2 Hz, 1H), 2.50 (d, *J* = 2.5 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 141.7, 131.1, 123.8, 121.6, 120.9, 120.2, 112.4, 82.7, 73.3, 66.0, 41.2, 31.5, 22.6. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{13}BrO+H]^+$: 277.0223, found: 277.0223.



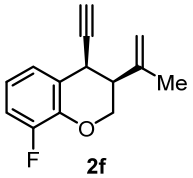
2d

2d: Methyl (3*S*,4*R*)-4-ethynyl-3-(prop-1-en-2-yl)chromane-7-carboxylate (**2d**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1d** (54.9 mg, 0.2 mmol) and isolated as a pale-yellow solid (48.1 mg, 94% yield, 37:1 dr, 97% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.74 ppm and δ_{minor} = 4.89 ppm, respectively. The enantiomeric excess was determined by HPLC analysis (CHIRALPAK AS-H, 3% isopropanol in hexanes, 1 mL/min) of a purified mixture of products by integration of signals at t_r(major) = 9.032 min and t_r(minor) = 11.360 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.51 (d, *J* = 1.7 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 5.05–4.97 (m, 1H), 4.74 (d, *J* = 1.2 Hz, 1H), 4.38 (ddd, *J* = 10.8, 3.4, 1.7 Hz, 1H), 4.30 (app t, *J* = 10.5 Hz, 1H), 4.00 (app dt, *J* = 4.6, 2.1 Hz, 1H), 3.89 (s, 3H), 2.67 (app dt, *J* = 9.3, 4.1 Hz, 1H), 2.27 (d, *J* = 2.5 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 153.4, 141.7, 130.7, 130.0, 126.7, 121.6, 118.5, 112.4, 82.5, 73.5, 66.0, 52.2, 41.2, 31.9, 22.5. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{16}H_{16}O_3+H]^+$: 257.1172, found: 257.1173.



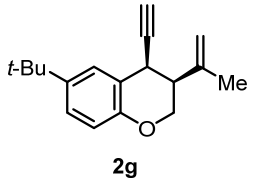
2e

2e: (3*S*,4*R*)-4-ethynyl-8-methyl-3-(prop-1-en-2-yl)chromane (**2e**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1e** (46.1 mg, 0.2 mmol) and isolated as a colorless oil (34.1 mg, 80% yield, 42:1 dr, 98% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.73 ppm and δ_{minor} = 4.89 ppm, respectively. The enantiomeric excess was determined by HPLC analysis (CHIRALCEL OJ-H, 0.1% isopropanol in hexanes, 1 mL/min) of a purified mixture of products by integration of signals at t_r(major) = 9.858 min and t_r(minor) = 16.678 min. Spectroscopic data for **2e** were in accordance with those reported in the literature[9]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.1 Hz, 1H), 6.81 (app t, *J* = 7.5 Hz, 1H), 5.06–4.92 (m, 1H), 4.73 (s, 1H), 4.41 (ddd, *J* = 10.7, 3.1, 1.8 Hz, 1H), 4.29 (app t, *J* = 10.7 Hz, 1H), 3.96 (app dt, *J* = 4.4, 2.0 Hz, 1H), 2.65 (app dt, *J* = 9.2, 3.7 Hz, 1H), 2.24 (d, *J* = 2.5 Hz, 1H), 2.19 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 142.4, 129.8, 127.6, 126.4, 121.2, 120.1, 111.9, 83.6, 72.9, 65.8, 41.5, 32.0, 22.6, 16.2. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{15}H_{16}O+H]^+$: 213.1274, found: 213.1273.



2f

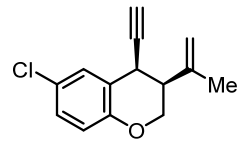
2f: (3*S*,4*R*)-4-ethynyl-8-fluoro-3-(prop-1-en-2-yl)chromane (**2f**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1f** (46.9 mg, 0.2 mmol) and isolated as a colorless oil (41.2 mg, 95% yield, 29:1 dr, 97% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.75 ppm and δ_{minor} = 4.90 ppm, respectively, and by ^{19}F NMR analysis of a crude product mixture by integration of signals at δ_{major} = −136.52 ppm and δ_{minor} = −137.18 ppm, respectively. The enantiomeric excess was determined by HPLC analysis (CHIRALCEL OJ-H, 0.1% isopropanol in hexanes, 1 mL/min) of a purified mixture of products by integration of signals at t_r(major) = 35.327 min and t_r(minor) = 28.931 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 7.8 Hz, 1H), 6.97 (ddd, *J* = 10.9, 8.1, 1.6 Hz, 1H), 6.83 (app td, *J* = 8.0, 4.9 Hz, 1H), 5.02 (s, 1H), 4.75 (s, 1H), 4.46 (ddd, *J* = 10.7, 3.2, 1.7 Hz, 1H), 4.33 (app t, *J* = 10.6 Hz, 1H), 3.99 (app dt, *J* = 4.5, 2.0 Hz, 1H), 2.69 (app dt, *J* = 10.9, 4.0 Hz, 1H), 2.27 (d, *J* = 2.5 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8 (d, *J* = 245.5 Hz), 142.0 (d, *J* = 11.5 Hz), 141.7, 124.9 (d, *J* = 3.6 Hz), 124.3 (d, *J* = 1.7 Hz), 120.1 (d, *J* = 7.2 Hz), 115.0 (d, *J* = 18.0 Hz), 112.4, 82.7, 73.4, 66.1, 41.3, 31.5 (d, *J* = 2.8 Hz), 22.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −136.52. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{13}FO+H]^+$: 217.1023, found: 217.1023.



2g

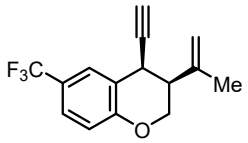
2g: (3*S*,4*R*)-6-(*tert*-butyl)-4-ethynyl-3-(prop-1-en-2-yl)chromane (**2g**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1g** (54.5 mg, 0.2 mmol) and isolated as a pale-yellow oil (49.4 mg, 97% yield, >100:1 dr, 99% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.72 ppm and δ_{minor} = 4.89 ppm. The enantiomeric excess was determined by GC analysis (Cyclosil-β, 130 °C to 200 °C, 1 °C/min) of a purified mixture of products by integration of signals at t_r(major) = 32.364 min and t_r(minor) = 33.838 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 2.5 Hz, 1H), 7.20 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 5.00 (d, *J* = 1.3 Hz, 1H), 4.72 (s, 1H), 4.32 (ddd, *J* = 10.6, 3.3, 1.7 Hz, 1H), 4.26 (app t, *J* = 10.5 Hz, 1H), 3.96 (app dt, *J* = 4.6, 2.1 Hz, 1H), 2.66 (app dt, *J* = 9.4, 4.1

Hz, 1H), 2.24 (d, *J* = 2.5 Hz, 1H), 1.88 (s, 3H), 1.30 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 143.5, 142.4, 126.6, 126.0, 120.9, 116.6, 111.9, 83.5, 72.8, 65.7, 41.7, 34.2, 32.1, 31.7, 22.6. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{18}H_{22}O+H]^+$: 255.1743, found: 255.1744.



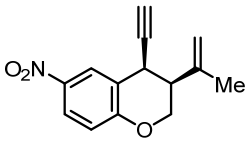
2h

2h: (3*S*,4*R*)-6-chloro-4-ethynyl-3-(prop-1-en-2-yl)chromane (**2h**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1h** (50.1 mg, 0.2 mmol) and isolated as a yellow oil (36.7 mg, 79% yield, 49:1 dr, 98% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.73 ppm and δ_{minor} = 4.88 ppm, respectively. The enantiomeric excess was determined by SFC analysis (CHIRALPAK IF, 1% methanol) of a purified mixture of products by integration of signals at t_r(major) = 4.763 min and t_r(minor) = 4.167 min. Spectroscopic data for **2h** were in accordance with those reported in the literature[9]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 2.6 Hz, 1H), 7.11 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 5.01 (s, 1H), 4.73 (s, 1H), 4.33 (ddd, *J* = 10.8, 3.3, 1.6 Hz, 1H), 4.26 (app t, *J* = 10.4 Hz, 1H), 3.93 (app dt, *J* = 4.6, 2.1 Hz, 1H), 2.64 (app dt, *J* = 9.2, 4.2 Hz, 1H), 2.27 (d, *J* = 2.5 Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 141.8, 129.5, 128.8, 125.3, 123.2, 118.5, 112.44, 82.6, 73.5, 66.0, 41.3, 31.7, 22.6. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{13}ClO+H]^+$: 233.0728, found: 233.0728.



2i

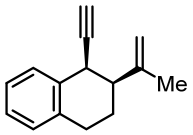
2i: (3*S*,4*R*)-4-ethynyl-3-(prop-1-en-2-yl)-6-(trifluoromethyl)chromane (**2i**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1i** (53.3 mg, 0.2 mmol) and isolated as a colorless oil (47.5 mg, 89% yield, 73:1 dr, 99% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.74 ppm and δ_{minor} = 4.90 ppm, respectively. The enantiomeric excess was determined by GC analysis (Cyclosil-β, 130 °C to 145 °C, 1 °C/min) of a purified mixture of products by integration of signals at t_r(major) = 14.817 min and t_r(minor) = 16.458 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.2 Hz, 1H), 7.41 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 5.03 (s, 1H), 4.74 (s, 1H), 4.40 (ddd, *J* = 10.8, 3.5, 1.7 Hz, 1H), 4.33 (app t, *J* = 10.5 Hz, 1H), 4.00 (app dt, *J* = 4.6, 2.1 Hz, 1H), 2.66 (app dt, *J* = 9.3, 4.2 Hz, 1H), 2.29 (d, *J* = 2.5 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2 (q, *J* = 1.5 Hz), 141.5, 127.5 (q, *J* = 3.9 Hz), 125.9 (q, *J* = 3.6 Hz), 124.4 (q, *J* = 271.8 Hz), 122.9 (q, *J* = 32.7 Hz), 122.1, 117.6, 112.6, 82.3, 73.8, 66.2, 41.2, 31.8, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −61.49. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{15}H_{13}F_3O+H]^+$: 267.0991, found: 267.0992.



2j

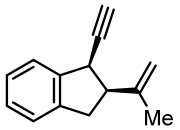
2j: (3*S*,4*R*)-4-ethynyl-6-nitro-3-(prop-1-en-2-yl)chromane (**2j**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1j** (52.2 mg, 0.2 mmol) and isolated as a white solid (44.5 mg, 92% yield, 56:1 dr, 99% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.76 ppm and δ_{minor} = 4.91 ppm, respectively. The enantiomeric excess was determined by SFC analysis (CHIRALPAK IH, 4% methanol) of a purified mixture of products by integration of signals at t_r(major) = 3.047 min and t_r(minor) = 3.323 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.8 Hz, 1H), 8.06 (dd, *J* = 9.1, 2.8 Hz, 1H), 6.92 (d, *J* = 9.1 Hz, 1H), 5.07–5.02 (m, 1H), 4.76 (s, 1H), 4.46 (ddd, *J* = 10.9, 3.5, 1.7 Hz, 1H),

4.39 (dd, J = 10.9, 10.1 Hz, 1H), 4.04 (app dt, J = 4.4, 2.0 Hz, 1H), 2.68 (app dt, J = 9.5, 4.2 Hz, 1H), 2.33 (d, J = 2.6 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 141.4, 141.0, 126.3, 124.8, 122.5, 117.8, 113.0, 81.7, 74.4, 66.8, 41.0, 31.8, 22.5. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{13}NO_3+H]^+$: 244.0968, found: 244.0969.



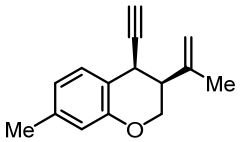
2k

2k: (1*R*,2*S*)-1-ethynyl-2-(prop-1-en-2-yl)-1,2,3,4-tetrahydronaphthalene (**2k**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1k** (42.9 mg, 0.2 mmol) and isolated as a pale-yellow oil (25.2 mg, 64% yield, 22:1 dr, 87% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 2.17 ppm and δ_{minor} = 2.20 ppm, respectively. The enantiomeric excess was determined by GC analysis (Cyclosil-β, 130 °C to 145 °C, 1 °C/min) of a purified mixture of products by integration of signals at t_r(major) = 13.907 min and t_r(minor) = 15.126 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.27 (m, 1H), 7.20–7.10 (m, 3H), 5.00–4.97 (m, 1H), 4.88 (s, 1H), 4.02–3.93 (m, 1H), 2.97 (ddd, J = 17.1, 5.9, 2.4 Hz, 1H), 2.84 (ddd, J = 17.3, 11.5, 6.4 Hz, 1H), 2.42 (d, J = 11.7 Hz, 1H), 2.17 (d, J = 2.6 Hz, 1H), 2.13–2.00 (m, 1H), 2.00–1.91 (m, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 136.5, 135.8, 129.6, 129.5, 127.1, 126.1, 111.3, 84.7, 72.1, 44.1, 35.5, 29.3, 23.2, 22.3. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{15}H_{16}+H]^+$: 197.1325, found: 197.1324.



2l

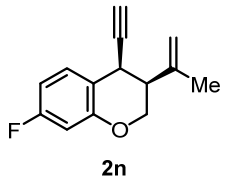
2l: (1*R*,2*S*)-1-ethynyl-2-(prop-1-en-2-yl)-2,3-dihydro-1H-indene (**2l**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1l** (40.1 mg, 0.2 mmol) and isolated as a pale-yellow oil (32.9 mg, 90% yield, >100:1 dr, 98% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 2.20 ppm and δ_{minor} = 2.25 ppm, respectively. The enantiomeric excess was determined by HPLC analysis (CHIRALCEL OD-H, 0.2% isopropanol in hexanes, 1 mL/min) of a purified mixture of products by integration of signals at t_r(major) = 11.328 min and t_r(minor) = 8.616 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.32 (m, 1H), 7.25–7.17 (m, 3H), 4.91 (s, 1H), 4.86 (s, 1H), 4.18 (dd, J = 7.5, 2.4 Hz, 1H), 3.31–3.21 (m, 1H), 3.18–3.00 (m, 2H), 2.20 (d, J = 2.6 Hz, 1H), 1.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 142.6, 142.5, 127.6, 126.9, 124.6, 124.2, 111.9, 83.0, 71.8, 51.5, 39.9, 35.5, 21.8. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{14}+H]^+$: 183.1168, found: 183.1167.



2m

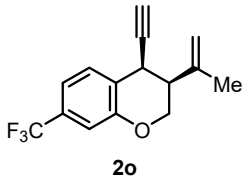
2m: (3*S*,4*R*)-4-ethynyl-7-methyl-3-(prop-1-en-2-yl)chromane (**2m**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1m** (46.1 mg, 0.2 mmol) and isolated as a colorless oil (37.0 mg, 87% yield, 76:1 dr, 98% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.72 ppm and δ_{minor} = 4.88 ppm, respectively. The enantiomeric excess was determined by SFC analysis (CHIRALPAK IB, 1% methanol) of a purified mixture of products by integration of signals at t_r(major) = 3.150 min and t_r(minor) = 2.767 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 7.8 Hz, 1H), 6.73 (dd, J = 7.8, 1.7 Hz, 1H), 6.66 (s, 1H), 5.00 (s, 1H), 4.72 (s, 1H), 4.32 (ddd, J = 10.7, 3.4, 1.6 Hz, 1H), 4.26 (app t, J = 10.4 Hz, 1H), 3.93 (app dt, J = 4.6, 2.0 Hz, 1H), 2.65 (app dt, J = 9.3, 4.2 Hz, 1H), 2.29 (s, 3H), 2.23 (d, J = 2.5 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 142.3, 138.9, 129.7, 121.8,

118.8, 117.4, 112.0, 83.5, 72.7, 65.8, 41.6, 31.5, 22.6, 21.3. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{15}H_{16}O+H]^+$: 213.1274, found: 213.1273.



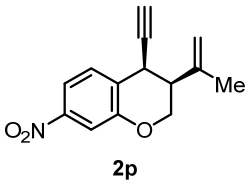
2n

2n: (3*S*,4*R*)-4-ethynyl-7-fluoro-3-(prop-1-en-2-yl)chromane (**2n**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1n** (46.9 mg, 0.2 mmol) and isolated as a pale-yellow oil (40.0 mg, 92% yield, 48:1 dr, 98% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.73 ppm and δ_{minor} = 4.89 ppm, respectively, and by ^{19}F NMR analysis of a crude product mixture by integration of signals at δ_{major} = −113.42 ppm and δ_{minor} = −113.92 ppm, respectively. The enantiomeric excess was determined by HPLC analysis (CHIRALCEL OJ-H, 0.5% isopropanol in hexanes, 1 mL/min) of a purified mixture of products by integration of signals at t_r(major) = 9.850 min and t_r(minor) = 15.553 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.5, 6.4 Hz, 1H), 6.63 (app td, *J* = 8.4, 2.6 Hz, 1H), 6.55 (dd, *J* = 10.2, 2.6 Hz, 1H), 5.01 (d, *J* = 0.8 Hz, 1H), 4.73 (s, 1H), 4.34 (ddd, *J* = 10.7, 3.4, 1.6 Hz, 1H), 4.27 (app t, *J* = 10.5 Hz, 1H), 3.97–3.90 (m, 1H), 2.72–2.59 (m, 1H), 2.25 (d, *J* = 2.5 Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, *J* = 244.8 Hz), 154.5 (d, *J* = 12.2 Hz), 141.9, 130.9 (d, *J* = 10.0 Hz), 117.7 (d, *J* = 3.0 Hz), 112.3, 108.1 (d, *J* = 22.0 Hz), 104.1 (d, *J* = 24.5 Hz), 83.1 (d, *J* = 1.4 Hz), 73.1, 65.9, 41.4, 31.4, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ −113.42. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{13}FO+H]^+$: 217.1023, found: 217.1024.



2o

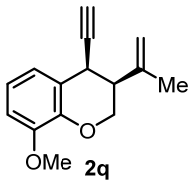
2o: (3*S*,4*R*)-4-ethynyl-3-(prop-1-en-2-yl)-7-(trifluoromethyl)chromane (**2o**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1o** (56.9 mg, 0.2 mmol) and isolated as a pale-yellow oil (40.0 mg, 75% yield, 36:1 dr, 97% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.75 ppm and δ_{minor} = 4.90 ppm, respectively. The enantiomeric excess was determined by GC analysis (Cyclosil-β, 130 °C to 145 °C, 1 °C/min) of a purified mixture of products by integration of signals at t_r(major) = 15.673 min and t_r(minor) = 16.679 min. ^{1}H NMR (400 MHz, $CDCl_3$) 7.36 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.10 (s, 1H), 5.03 (s, 1H), 4.75 (s, 1H), 4.39 (ddd, *J* = 10.8, 3.4, 1.7 Hz, 1H), 4.31 (app t, *J* = 10.5 Hz, 1H), 4.10–3.91 (m, 1H), 2.67 (app dt, *J* = 9.3, 4.1 Hz, 1H), 2.28 (d, *J* = 2.5 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 141.6, 131.2 (q, *J* = 32.6 Hz), 130.6, 125.5 (q, *J* = 1.5 Hz), 123.9 (q, *J* = 272.1 Hz), 117.2 (q, *J* = 3.8 Hz), 114.5 (q, *J* = 4.0 Hz), 112.6, 82.4, 73.7, 66.1, 41.2, 31.8, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.79. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{15}H_{13}F_3O+H]^+$: 267.0991, found: 267.0993.



2p

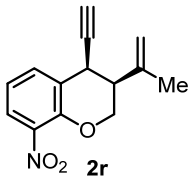
2p: (3*S*,4*R*)-4-ethynyl-7-nitro-3-(prop-1-en-2-yl)chromane (**2p**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1p** (52.2 mg, 0.2 mmol) and isolated as a white solid (37.8 mg, 78% yield, 42:1 dr, 96% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.75 ppm and δ_{minor} = 4.90 ppm, respectively. The enantiomeric excess was determined by HPLC analysis (CHIRALPAK AD-H, 0.7% isopropanol in hexanes, 1 mL/min) of a purified mixture of products by integration of signals at t_r(major) = 15.787 min and t_r(minor) = 12.520 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* =

8.4, 2.3 Hz, 1H), 7.70 (d, *J* = 2.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 5.06–5.03 (m, 1H), 4.75 (s, 1H), 4.42 (ddd, *J* = 10.9, 3.3, 1.7 Hz, 1H), 4.34 (app t, *J* = 10.9 Hz, 1H), 4.04 (app dt, *J* = 4.6, 2.1 Hz, 1H), 2.68 (app dt, *J* = 9.3, 4.2 Hz, 1H), 2.30 (d, *J* = 2.5 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 148.2, 141.0, 130.6, 128.7, 115.2, 112.8, 112.6, 81.6, 74.1, 66.3, 40.8, 31.8, 22.4. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{13}NO_3+H]^+$: 244.0968, found: 244.0968.



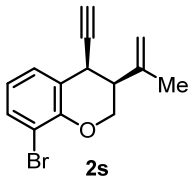
2q

2q: (3*S*,4*R*)-4-ethynyl-8-methoxy-3-(prop-1-en-2-yl)chromane (**2q**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1q** (49.3 mg, 0.2 mmol) and isolated as a colorless oil (44.5 mg, 97% yield, 49:1 dr, 97% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.74 ppm and δ_{minor} = 4.89 ppm, respectively. The enantiomeric excess was determined by HPLC analysis (CHIRALPAK AD-H, 2% isopropanol in hexanes, 1 mL/min) of a purified mixture of products by integration of signals at t_r(major) = 9.556 min and t_r(minor) = 8.755 min. Spectroscopic data for **2q** were in accordance with those reported in the literature[9]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92–6.82 (m, 2H), 6.78 (dd, *J* = 6.5, 3.0 Hz, 1H), 5.01 (s, 1H), 4.74 (s, 1H), 4.48 (ddd, *J* = 10.7, 3.1, 1.8 Hz, 1H), 4.32 (app t, *J* = 10.7 Hz, 1H), 3.96 (app dt, *J* = 4.6, 2.1 Hz, 1H), 3.87 (s, 3H), 2.68 (app dt, *J* = 8.7, 3.6 Hz, 1H), 2.25 (d, *J* = 2.5 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 142.9, 142.0, 122.5, 121.7, 120.3, 112.1, 110.2, 83.1, 73.0, 66.1, 56.0, 41.3, 31.7, 22.6. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{15}H_{16}O_2+H]^+$: 229.1223, found: 229.1223.



2r

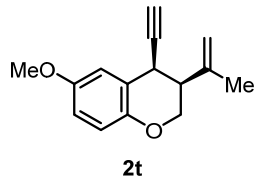
2r: (3*S*,4*R*)-4-ethynyl-8-nitro-3-(prop-1-en-2-yl)chromane (**2r**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1r** (52.2 mg, 0.2 mmol) and isolated as a pale-yellow solid (44.7 mg, 92% yield, 54:1 dr, 99% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.75 ppm and δ_{minor} = 4.91 ppm, respectively. The enantiomeric excess was determined by HPLC analysis (CHIRALPAK AS-H, 4% isopropanol in hexanes, 1 mL/min) of a purified mixture of products by integration of signals at t_r(major) = 15.026 min and t_r(minor) = 16.350 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.7 Hz, 1H), 8.06 (dd, *J* = 9.1, 2.7 Hz, 1H), 6.92 (d, *J* = 9.1 Hz, 1H), 5.04 (s, 1H), 4.75 (s, 1H), 4.46 (ddd, *J* = 10.9, 3.4, 1.7 Hz, 1H), 4.39 (app t, *J* = 10.5 Hz, 1H), 4.07–4.00 (m, 1H), 2.68 (app dt, *J* = 8.9, 3.9 Hz, 1H), 2.33 (d, *J* = 2.5 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 141.3, 141.0, 126.3, 124.8, 122.5, 117.8, 112.9, 81.7, 74.4, 66.8, 40.9, 31.8, 22.5. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{13}NO_3+H]^+$: 244.0968, found: 244.0968.



2s

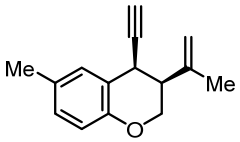
2s: (3*S*,4*R*)-8-bromo-4-ethynyl-3-(prop-1-en-2-yl)chromane (**2s**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1s** (59.0 mg, 0.2 mmol) and isolated as a colorless oil (47.2 mg, 85% yield, 20:1 dr, 94% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.74 ppm and δ_{minor} = 4.90 ppm, respectively. The enantiomeric excess was determined by GC analysis (Cyclosil-β, 130 °C to 200 °C, 1 °C/min) of a purified mixture of products by integration of signals at t_r(major) = 39.875 min and t_r(minor) = 40.550 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.23–7.17

(m, 1H), 6.79 (app t, J = 7.8 Hz, 1H), 5.04–4.99 (m, 1H), 4.74 (s, 1H), 4.50 (ddd, J = 10.7, 3.1, 1.8 Hz, 1H), 4.36 (app t, J = 10.7 Hz, 1H), 3.99–3.95 (m, 1H), 2.67 (app dt, J = 8.8, 3.7 Hz, 1H), 2.27 (d, J = 2.5 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 141.6, 132.5, 129.2, 123.5, 121.5, 112.4, 111.1, 82.7, 73.6, 66.7, 41.3, 32.0, 22.6. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{13}BrO+H]^+$: 277.0223, found: 277.0224.



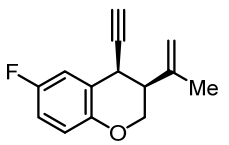
2t

2t: (3*S*,4*R*)-4-ethynyl-6-methoxy-3-(prop-1-en-2-yl)chromane (**2t**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1t** (49.3 mg, 0.2 mmol) and isolated as a yellow oil (39.4 mg, 86% yield, 46:1 dr, 97% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.73 ppm and δ_{minor} = 4.89 ppm, respectively. The enantiomeric excess was determined by SFC analysis (CHIRALPAK IE, 2% methanol) of a purified mixture of products by integration of signals at t_r(major) = 4.000 min and t_r(minor) = 3.680 min. Spectroscopic data for **2t** were in accordance with those reported in the literature[9]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91–6.60 (m, 3H), 5.00 (s, 1H), 4.73 (s, 1H), 4.30 (ddd, J = 10.7, 3.3, 1.6 Hz, 1H), 4.23 (app t, J = 10.4 Hz, 1H), 3.94 (app dt, J = 4.6, 2.0 Hz, 1H), 3.77 (s, 3H), 2.66 (app dt, J = 9.2, 4.1 Hz, 1H), 2.25 (d, J = 2.5 Hz, 1H), 1.88 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 147.5, 142.3, 122.0, 117.8, 115.3, 114.0, 112.1, 83.2, 72.9, 65.8, 55.8, 41.7, 32.1, 22.6. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{15}H_{16}O_2+H]^+$: 229.1223, found: 229.1223.



2u

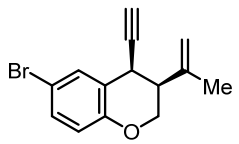
2u: (3*S*,4*R*)-4-ethynyl-6-methyl-3-(prop-1-en-2-yl)chromane (**2u**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1u** (46.1 mg, 0.2 mmol) and isolated as a colorless oil (37.9 mg, 89% yield, 52:1 dr, 98% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.73 ppm and δ_{minor} = 4.88 ppm, respectively. The enantiomeric excess was determined by SFC analysis (CHIRALPAK IB N-5, 1% methanol) of a purified mixture of products by integration of signals at t_r(major) = 3.427 min and t_r(minor) = 3.143 min. Spectroscopic data for **2u** were in accordance with those reported in the literature[9]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 2.2 Hz, 1H), 6.97 (dd, J = 8.3, 2.2 Hz, 1H), 6.74 (d, J = 8.3 Hz, 1H), 5.00 (s, 1H), 4.72 (s, 1H), 4.32 (ddd, J = 10.7, 3.4, 1.7 Hz, 1H), 4.25 (app t, J = 10.4 Hz, 1H), 3.92 (app dt, J = 4.6, 2.0 Hz, 1H), 2.65 (app dt, J = 9.3, 4.2 Hz, 1H), 2.28 (s, 3H), 2.25 (d, J = 2.5 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 142.3, 130.2, 129.9, 129.5, 121.3, 116.9, 112.0, 83.5, 72.8, 65.8, 41.6, 31.8, 22.6, 20.6. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{15}H_{16}O+H]^+$: 213.1274, found: 213.1273.



2v

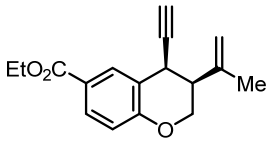
2v: (3*S*,4*R*)-4-ethynyl-6-fluoro-3-(prop-1-en-2-yl)chromane (**2v**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1v** (46.9 mg, 0.2 mmol) and isolated as a pale-yellow oil (38.4 mg, 89% yield, 70:1 dr, 98% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.73 ppm and δ_{minor} = 4.89 ppm, respectively. The enantiomeric excess was determined by HPLC analysis (CHIRALCEL OJ-H, 0.5% isopropanol in hexanes, 1 mL/min) of a purified mixture of products by integration of signals at t_r(major) = 10.512 min and t_r(minor) = 12.007 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (dd, J =

8.7, 3.0 Hz, 1H), 6.87 (ddd, *J* = 9.1, 7.9, 3.0 Hz, 1H), 6.78 (dd, *J* = 9.0, 4.8 Hz, 1H), 5.01 (s, 1H), 4.73 (s, 1H), 4.32 (ddd, *J* = 10.8, 3.3, 1.6 Hz, 1H), 4.24 (app t, *J* = 10.4 Hz, 1H), 3.94 (app dt, *J* = 4.5, 2.0 Hz, 1H), 2.65 (app dt, *J* = 9.2, 4.2 Hz, 1H), 2.27 (d, *J* = 2.5 Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (d, *J* = 238.8 Hz), 149.5 (d, *J* = 2.1 Hz), 141.9, 122.6 (d, *J* = 7.3 Hz), 118.0 (d, *J* = 8.0 Hz), 115.9 (d, *J* = 4.4 Hz), 115.6 (d, *J* = 4.5 Hz), 112.4, 82.7, 73.3, 66.0, 41.4, 31.9, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −123.83. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{13}FO+H]^+$: 217.1023, found: 217.1021.



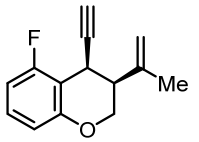
2w

2w: (3*S*,4*R*)-6-bromo-4-ethynyl-3-(prop-1-en-2-yl)chromane (**2w**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1w** (59.0 mg, 0.2 mmol) and isolated as a yellow oil (48.4 mg, 87% yield, 49:1 dr, 98% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.72 ppm and δ_{minor} = 4.88 ppm, respectively. The enantiomeric excess was determined by SFC analysis (CHIRALPAK IF, 4% methanol) of a purified mixture of products by integration of signals at t_r(major) = 2.800 min and t_r(minor) = 2.400 min. Spectroscopic data for **2w** were in accordance with those reported in the literature[9]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 2.4, 0.7 Hz, 1H), 7.24 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 1H), 5.01 (s, 1H), 4.72 (s, 1H), 4.33 (ddd, *J* = 10.8, 3.3, 1.7 Hz, 1H), 4.26 (app t, *J* = 10.4 Hz, 1H), 3.93 (app dt, *J* = 4.6, 2.1 Hz, 1H), 2.63 (app dt, *J* = 9.3, 4.2 Hz, 1H), 2.27 (d, *J* = 2.5 Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 141.7, 132.5, 131.7, 123.8, 119.0, 112.6, 112.5, 82.5, 73.5, 66.0, 41.2, 31.7, 22.6. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{13}BrO+H]^+$: 277.0223, found: 277.0224.



2x

2x: Ethyl (3*S*,4*R*)-4-ethynyl-3-(prop-1-en-2-yl)chromane-6-carboxylate (**2x**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1x** (57.7 mg, 0.2 mmol) and isolated as a colorless oil (52.8 mg, 98% yield, 45:1 dr, 99% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 4.74 ppm and δ_{minor} = 4.89 ppm, respectively. The enantiomeric excess was determined by SFC analysis (CHIRALPAK IG, 4% methanol) of a purified mixture of products by integration of signals at t_r(major) = 3.160 min and t_r(minor) = 5.207 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 2.1 Hz, 1H), 7.85 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 5.02 (s, 1H), 4.74 (s, 1H), 4.45–4.25 (m, 4H), 4.00 (app dt, *J* = 4.5, 2.1 Hz, 1H), 2.66 (app dt, *J* = 9.4, 4.3 Hz, 1H), 2.28 (d, *J* = 2.5 Hz, 1H), 1.88 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 157.4, 141.6, 132.1, 130.5, 123.0, 121.7, 117.1, 112.4, 82.6, 73.6, 66.2, 60.8, 41.2, 31.7, 22.6, 14.5. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{17}H_{18}O_3+H]^+$: 271.1329, found: 271.1330.



2y

2y: (3*S*,4*R*)-4-ethynyl-5-fluoro-3-(prop-1-en-2-yl)chromane (**2y**) was prepared according to the general procedure described on page S47, starting from propargylic alcohol **1y** (46.9 mg, 0.2 mmol) and isolated as a colorless oil (26.3 mg, 61% yield, 26:1 dr, 54% ee). The diastereomeric ratio was determined by ^{1}H NMR analysis of a crude product mixture by integration of signals at δ_{major} = 5.03 ppm and δ_{minor} = 4.91 ppm, respectively, and by ^{19}F NMR analysis of a crude product mixture by integration of signals at δ_{major} =

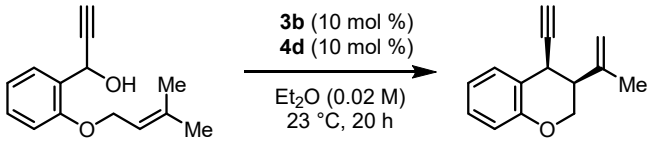
−118.37 ppm and δ_{minor} = −116.45 ppm, respectively. The enantiomeric excess was determined by HPLC analysis (CHIRALCEL OJ-H, 0.5% isopropanol in hexanes, 1 mL/min) of a purified mixture of products by integration of signals at t_r(major) = 7.641 min and t_r(minor) = 9.915 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (app td, *J* = 8.3, 6.6 Hz, 1H), 6.68–6.61 (m, 2H), 5.03 (d, *J* = 1.3 Hz, 1H), 4.73 (s, 1H), 4.37 (ddd, *J* = 10.7, 3.3, 1.9 Hz, 1H), 4.29 (app t, *J* = 10.9 Hz, 1H), 4.11 (app dt, *J* = 4.7, 2.2 Hz, 1H), 2.59 (app dt, *J* = 11.0, 4.0 Hz, 1H), 2.20 (d, *J* = 2.4 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9 (d, *J* = 246.3 Hz), 154.5 (d, *J* = 6.8 Hz), 141.5, 128.8 (d, *J* = 10.4 Hz), 112.6 (d, *J* = 3.1 Hz), 112.1, 110.6 (d, *J* = 20.6 Hz), 106.8 (d, *J* = 21.4 Hz), 81.6, 72.3, 65.5, 40.6, 25.8 (d, *J* = 3.5 Hz), 22.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ −118.37. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $[C_{14}H_{13}FO+H]^+$: 217.1023, found: 217.1022.

Examination of reaction parameters of the enantioselective propargylic substitution

General reaction procedure for screening study

Unless described otherwise, a hydrogen-bond donor (3 μmol, 0.1 equiv) and a ruthenium complex (3 μmol, 0.1 equiv) were suspended in the indicated solvent (1.0 mL), and the resulting suspension was stirred at 23 °C for 20 minutes. Temperature of the mixture was adjusted to the indicated temperature. A solution of propargylic alcohol **1a** (6.5 mg, 0.03 mmol, 1 equiv) in the indicated solvent (0.5 mL) was added, and the mixture was stirred at the indicated temperature for 20 hours. Then, the reaction mixture was diluted with hexanes (1.5 mL) and was filtered through a plug of silica gel (4 × 0.5 cm) in a glass Pasteur pipette eluting with 50% diethyl ether in hexanes (20 mL). The filtrate was concentrated in vacuo. Diastereomeric ratio of the product was determined by ^{1}H NMR analysis of the crude product mixture. The residue was purified by flash column chromatography (3% diethyl ether in hexanes). Enantiomeric excess of the major diastereomer of the product was determined by HPLC analysis (CHIRALPAK OD-H, 0.3% isopropanol in hexanes, 1 mL/min). Conversion of **1a** and yield of **2a** were determined by ^{1}H NMR analysis of the crude product mixture using 1,3,5-trimethoxybenzene as an internal standard that was added to the reaction mixture prior filtration of the mixture through a plug of silica gel.

Table S1 Examination of the effect of exclusion of either ruthenium tosylate complex **3b** or hydrogen-bond donor **4d** from the reaction mixture. Conversion of **1a** and yield of **2a** were determined by ^{1}H NMR analysis of the crude product mixture using 1,3,5-trimethoxybenzene as an internal standard that was added to the reaction mixture prior filtration of the mixture through a plug of silica gel.

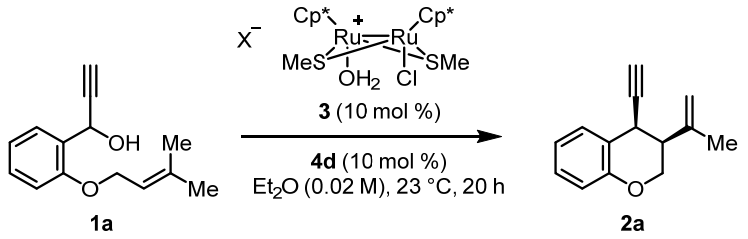


1a **2a**

modification to standard screening conditions	conversion of 1a (%)	yield of 2a (%)	dr	ee (%)
none	≥99	≥99	36:1	95
ruthenium complex **3b** excluded	0	0	–	–
HBD **4d** excluded	12	8	5:1	–

Structure of ruthenium catalyst

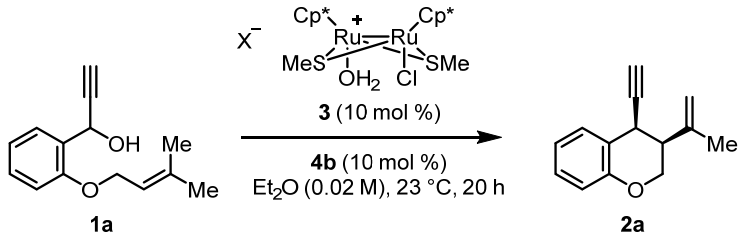
Table S2 Evaluation of the effect of the identity of the anion of ruthenium complex on the stereoselectivity of the propargylic substitution co-catalyzed by **4d**.



1a 2a

3	anion (X)	dr	ee (%)
3a	Cl	8:1	66
3d	OMs	44:1	95
3b	OTs	36:1	95
3g	OTf	28:1	87
3e	PF_6	24:1	85
3f	BF_4	12:1	75
3c	$BAr^F{}_4$	5:1	0

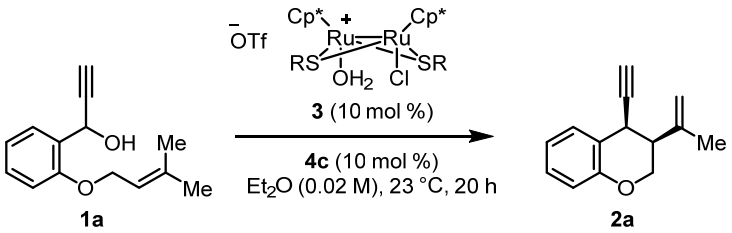
Table S3 Evaluation of the effect of the identity of the anion of ruthenium complex on the stereoselectivity of the propargylic substitution co-catalyzed by **4b**.



1a 2a

3	anion (X)	dr	ee (%)
3a	Cl	11:1	30
3d	OMs	13:1	74
3b	OTs	13:1	76
3g	OTf	9:1	59
3e	PF_6	9:1	49
3f	BF_4	7:1	34

Table S4 Evaluation of different alkyl groups of thiolate ligands of ruthenium complex.



3	R	dr	ee (%)
3g	Me	14:1	79
3h	Et	18:1	75
3i	*i*-Pr	21:1	39

Structure of hydrogen-bond donor

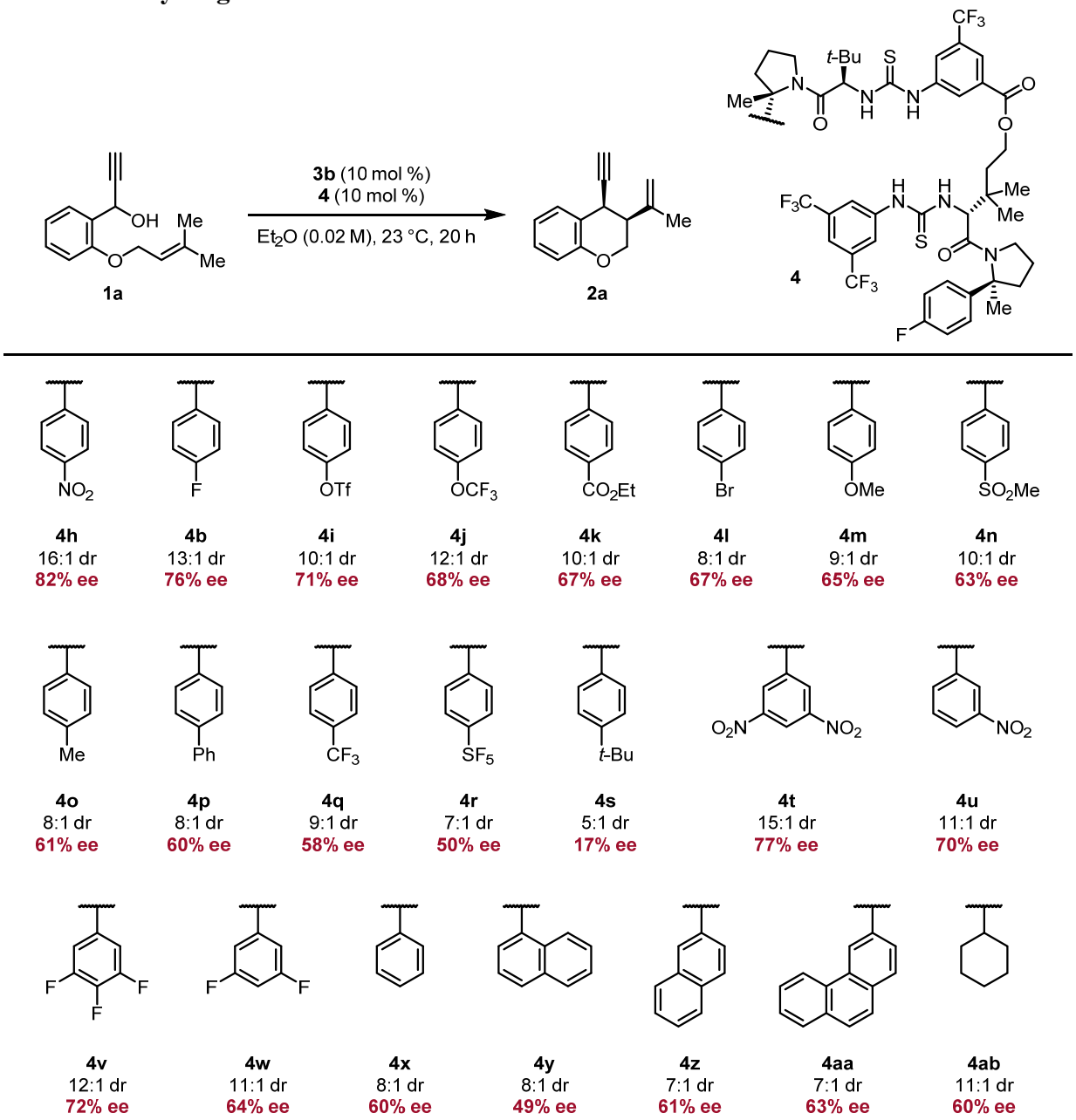


Figure S3 Evaluation of hydrogen-bond donors with different aryl substituents at the northern pyrrolidine ring.

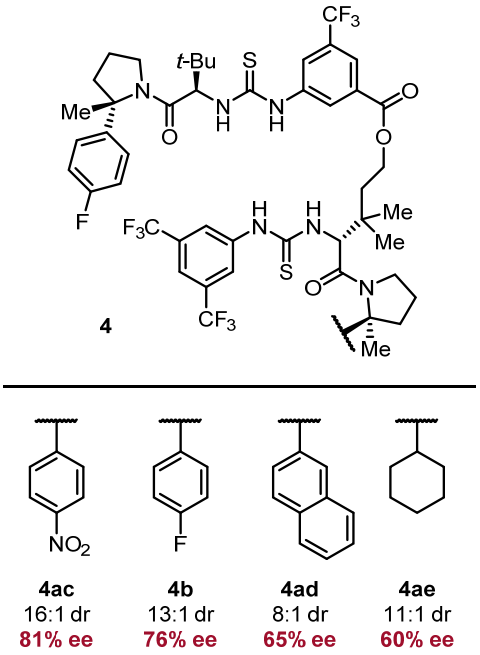


Figure S4 Evaluation of hydrogen-bond donors with different aryl substituents at the southern pyrrolidine ring.

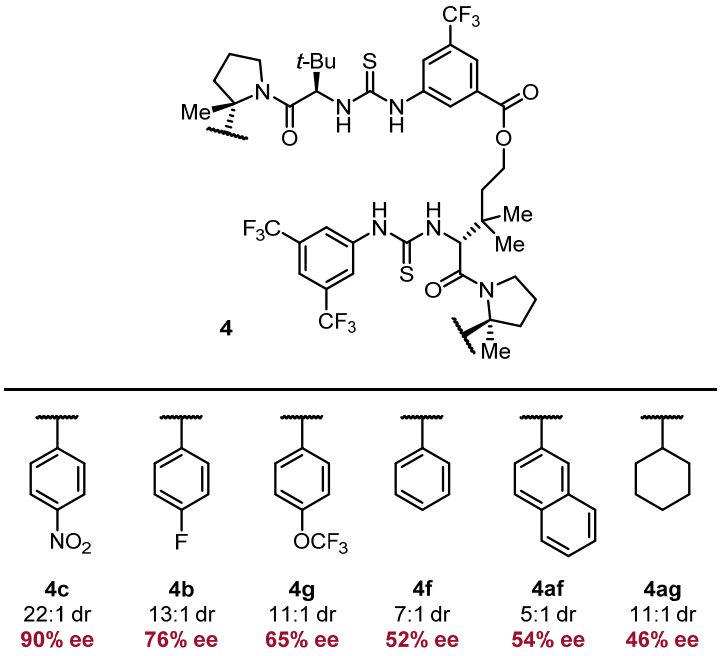
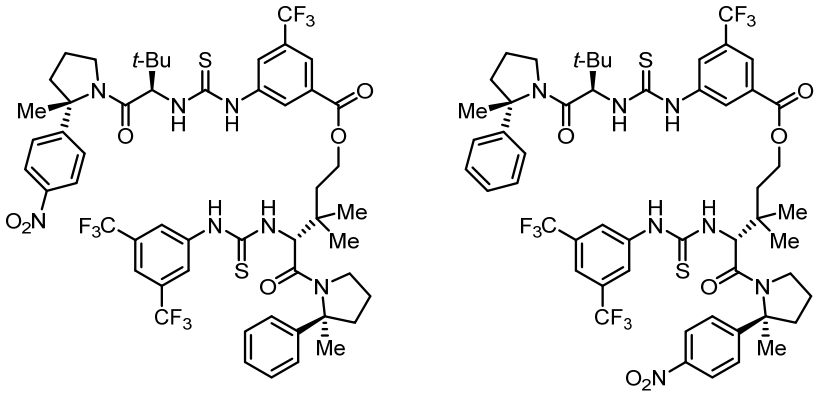


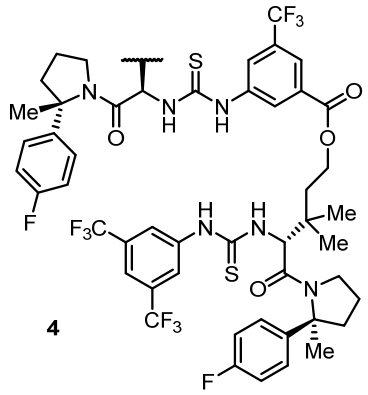
Figure S5 Evaluation of hydrogen-bond donors with different aryl substituents at the southern and the northern pyrrolidine rings.



4ah
14:1 dr
78% ee

4ai
11:1 dr
73% ee

Figure S6 Evaluation of hydrogen-bond donors with different aryl substituents at the southern and the northern pyrrolidine rings.



4

4b
13:1 dr
76% ee

4aj
16:1 dr
76% ee

4ak
11:1 dr
67% ee

Figure S7 Evaluation of hydrogen-bond donors with different α-substituent at the northern amino-acid substructure.

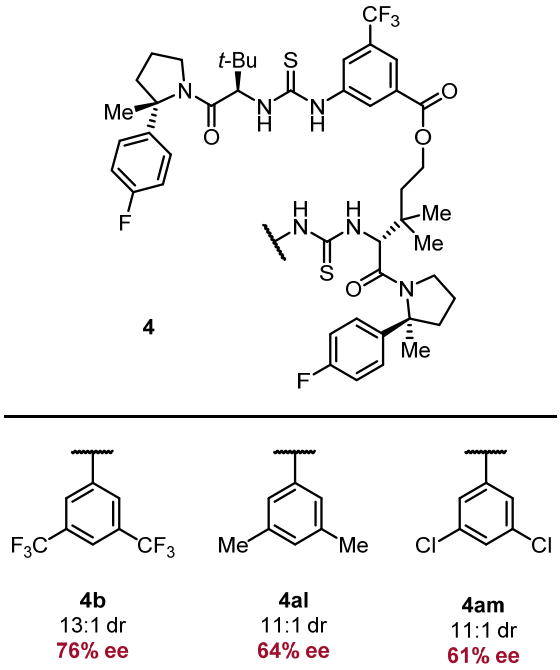


Figure S8 Evaluation of hydrogen-bond donors with different aryl substituents at the southern thiourea.

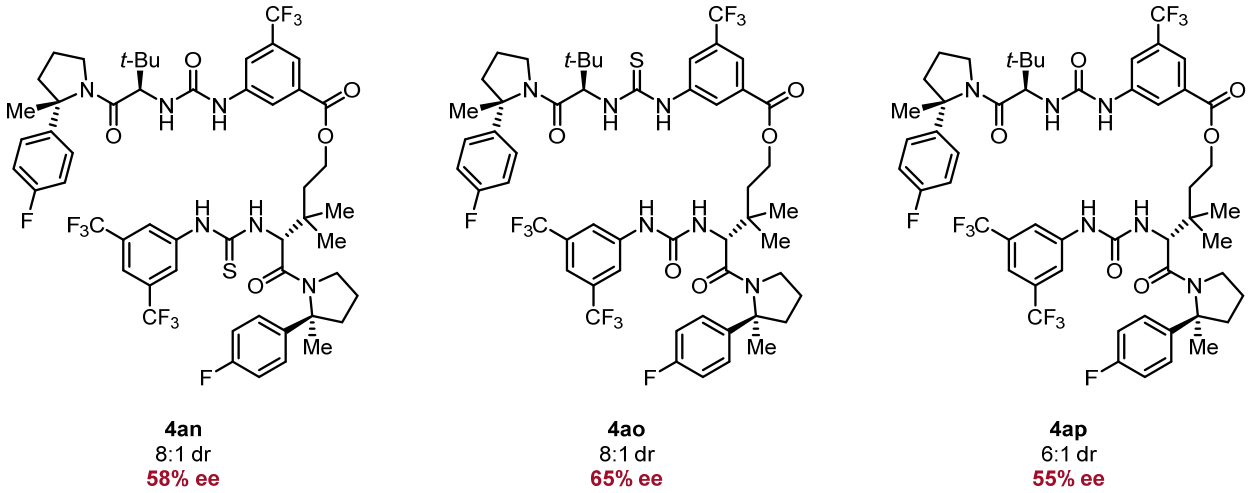


Figure S9 Evaluation of hydrogen-bond donors with modified (thio)urea substructures.

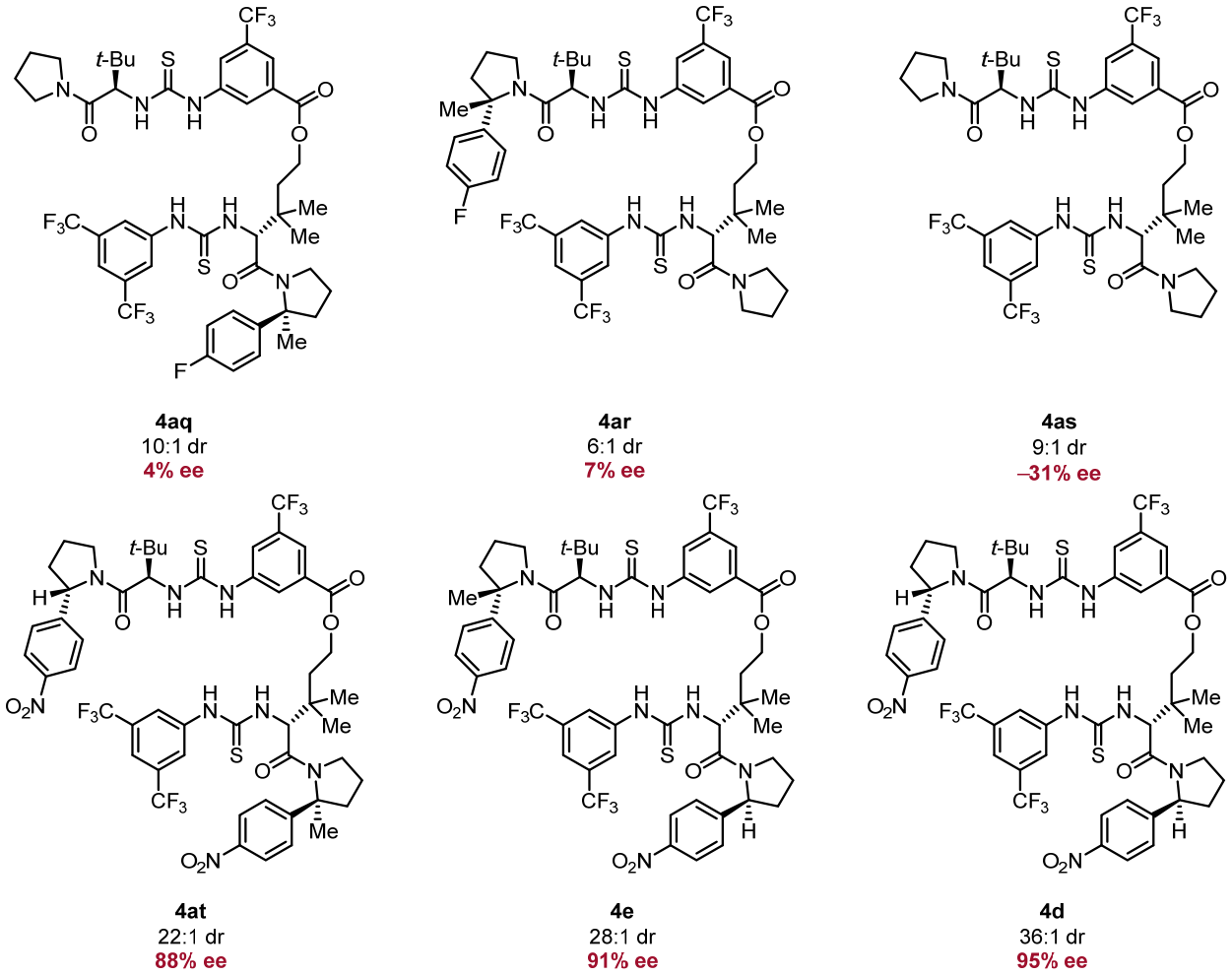


Figure S10 Evaluation of hydrogen-bond donors with modified aryl-pyrrolidine substructures.

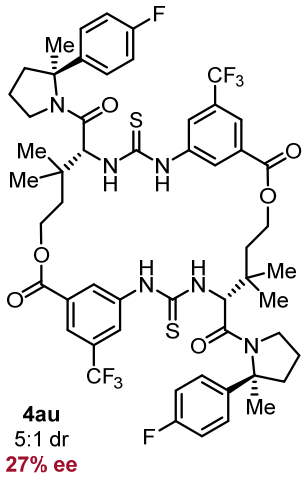


Figure S11 Evaluation of a macrocyclic hydrogen-bond donor.

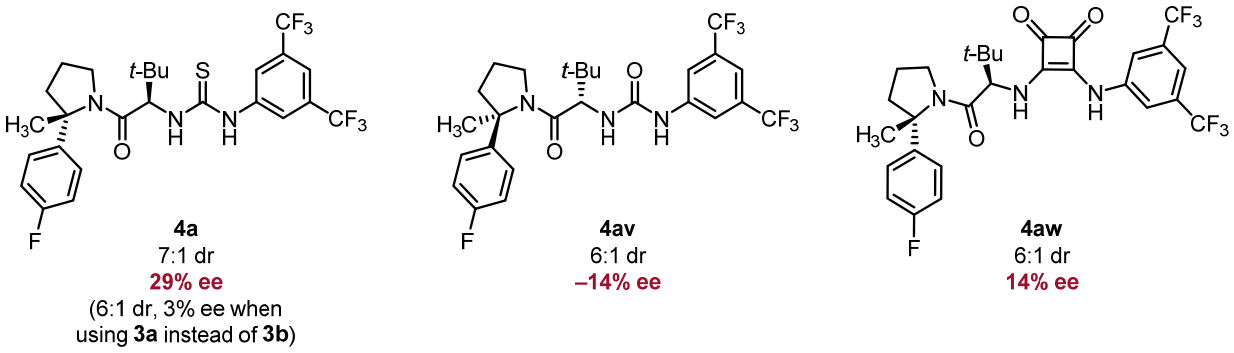
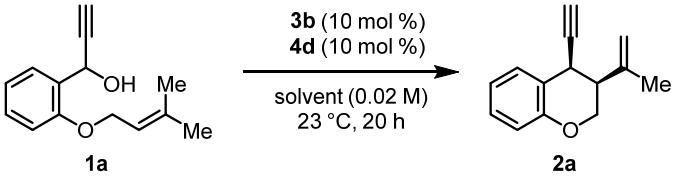


Figure S12 Evaluation of monomeric hydrogen-bond donors.

Reaction solvent and temperature

Table S5 Examination of the effect of solvent on stereoselectivity of the propargylic substitution.



solvent	ε	dr	ee (%)	$-\Delta\Delta G^{\ddagger}$ (kcal mol^{-1})
CCl_4	2.24	35:1	95	2.16
9:1 CCl_4:DCM	–	30:1	93	–
benzene	2.28	12:1	86	1.52
19:1 benzene:DCM	–	11:1	85	–
Et_2O	4.27	36:1	95	2.16
9:1 Et_2O:DCM	–	33:1	94	–
TBME	4.50	31:1	91	1.80
EtOAc	6	12:1	81	1.33
THF	7.52	6:1	63	0.87
DCM	9.08	5:1	10	0.12
1,2-DCE	10.42	4:1	8	0.09

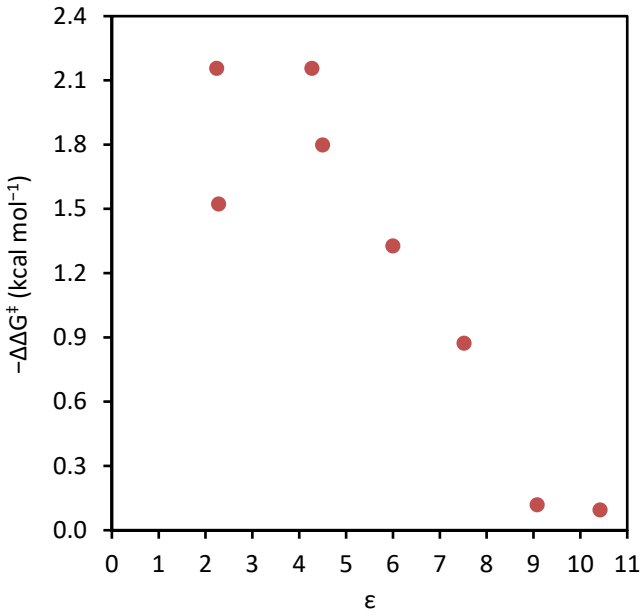
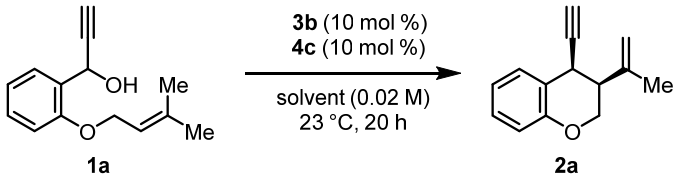


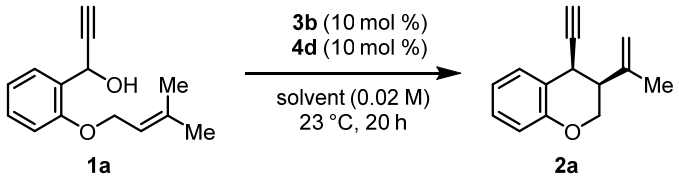
Figure S13 Correlation between solvent polarity (dielectric constant) and enantioselectivity of the propargylic substitution.

Table S6 Examination of the effect of solvent on stereoselectivity of the propargylic substitution with hydrogen-bond donor **4c**.



solvent	ε	dr	ee (%)
CCl_4	2.24	18:1	88
9:1 CCl_4:DCM	–	15:1	84
benzene	2.28	8:1	77
19:1 benzene:DCM	–	8:1	76
toluene	2.38	10:1	81
Et_2O	4.27	22:1	90
9:1 Et_2O:DCM	–	18:1	87
TBME	4.50	19:1	87
CPME	4.76	17:1	86
chlorobenzene	5.69	7:1	67
EtOAc	6	8:1	74
2-MeTHF	6.97	8:1	72
DME	7.3	5:1	51
THF	7.52	5:1	55
DCM	9.08	5:1	14
1,2-DCE	10.42	4:1	12

Table S7 Examination of the effect of solvent polarity on the stereoselectivity of the propargylic substitution by variation of volume ratio of diethyl ether and dichloromethane in a solvent blend.



φ(Et₂O)	φ(DCM)	ee (%)	−ΔΔG‡ (kcal mol⁻¹)
1.0	0	90	1.73
0.9	0.1	87	1.57
0.8	0.2	82	1.36
0.7	0.3	78	1.23
0.6	0.4	72	1.07
0.5	0.5	63	0.87
0.4	0.6	49	0.63
0.3	0.7	41	0.51
0.2	0.8	29	0.35
0.1	0.9	22	0.25
0	1.0	14	0.17

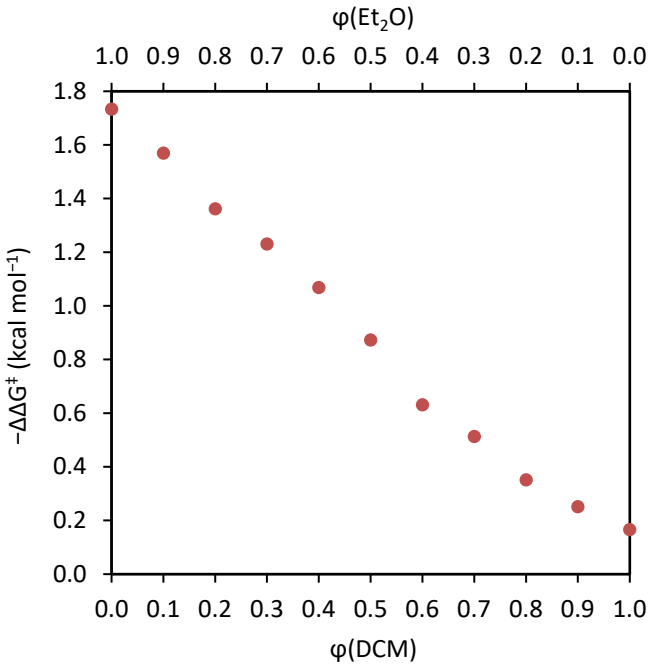
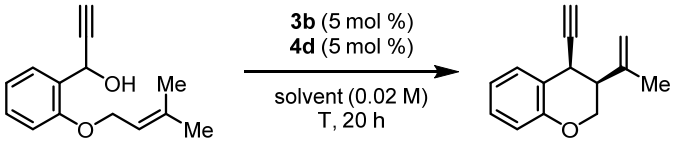


Figure S14 Correlation between volume ratio of diethyl ether [φ(Et2O)] (top horizontal axis) and volume ratio of dichloromethane [φ(DCM)] (bottom horizontal axis) and enantioselectivity.

Reaction temperature

Table S8 Evaluation of reaction conditions with lower catalysts loading (5 mol %). Optimization of temperature and solvent. Conversion of **1a** and yield of **2a** were determined by ^{1}H NMR analysis of the crude product mixture using 1,3,5-trimethoxybenzene as an internal standard that was added to the reaction mixture prior filtration of the mixture through a plug of silica gel.



1a **2a**

solvent	T (°C)	conversion of 1a (%)	yield of 2a (%)	dr	ee (%)
9:1 Et_2O:DCM	23	≥99	98	39:1	94
9:1 Et_2O:DCM	0	≥99	≥99	58:1	97
9:1 Et_2O:DCM	−10	96	97	63:1	98
9:1 Et_2O:DCM	−20	83	82	55:1	98
Et_2O	23	≥99	≥99	44:1	96
Et_2O	−10	56	58	73:1	98

Optimization of loading of hydrogen-bond donor and ruthenium complex

Table S9 Examination of the effect of catalyst loading and temperature on yield and enantioselectivity. Conversion of **1a** and yield of **2a** were determined by ^{1}H NMR analysis of the crude product mixture using 1,3,5-trimethoxybenzene as an internal standard that was added to the reaction mixture prior filtration of the mixture through a plug of silica gel.

1a **2a**

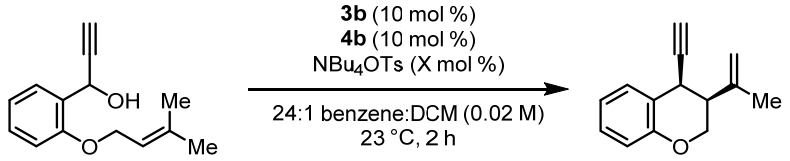
X (mol %)	T (°C)	conversion of 1a (%)	yield of 2a (%)	dr	ee (%)
10	23	≥99	≥99	33:1	94
10	4	≥99	≥99	48:1	97
10	−10	≥99	≥99	69:1	98
7	23	≥99	≥99	31:1	93
7	4	≥99	≥99	45:1	97
7	−10	≥99	≥99	55:1	97
5	23	≥99	98	39:1	94
5	0	≥99	≥99	58:1	97
5	−10	96	97	63:1	98

Experiments probing the role of the HBD in the enantioselective propargylic substitution

Inhibition of hydrogen-bond donor by addition of exogenous tosylate anion

Addition of tetrabutylammonium tosylate as a source of exogenous tosylate anion led to inhibition of the propargylic substitution reaction as concluded by determination of product yield and enantioselectivity of reactions containing various amounts of tetrabutylammonium tosylate. This observation is consistent with the hypothesis that hydrogen-bond donors interact with the catalytically relevant ruthenium complexes through binding their anions.

Table S10 Examination of the effect of added tetrabutylammonium tosylate (0–80 mol %) on yield and enantioselectivity of the propargylic substitution. General reaction procedure described on page S58 was followed. A 24:1 mixture of benzene:DCM was used to ensure full solubility of all reaction components. Yield of **2a** was determined by ^{1}H NMR analysis of the crude product mixture using 1,3,5-trimethoxybenzene as an internal standard that was added to the reaction mixture prior filtration of the mixture through a plug of silica gel.



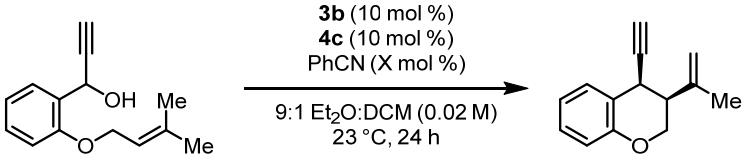
1a **2a**

X (mol %)	NMR yield (%)	ee (%)
0	84	84
5	77	78
10	59	57
20	40	51
40	25	44
80	14	36

Inhibition of ruthenium catalyst by addition of competitive ligand

Addition of benzonitrile led to inhibition of the propargylic substitution reaction as concluded by the determination of product yield of reactions containing various amounts of benzonitrile. Benzonitrile was presumed to be capable of coordinating to the ruthenium tosylate complex **3b**. This observation is consistent with the hypothesis that hydrogen-bond donor does not interact with ruthenium complexes present in the propargylic substitution reaction as a ligand, since an acceleration rather than an inhibition of the reaction in the presence of a hydrogen-bond donor was observed (see page S108 for details).

Table S11 Examination of the effect of added benzonitrile (0–100 mol %) on yield and enantioselectivity of the propargylic substitution. General reaction procedure described on page S58 was followed. Yield of **2a** was determined by ^{1}H NMR analysis of the crude product mixture using 1,3,5-trimethoxybenzene as an internal standard that was added to the reaction mixture prior filtration of the mixture through a plug of silica gel.

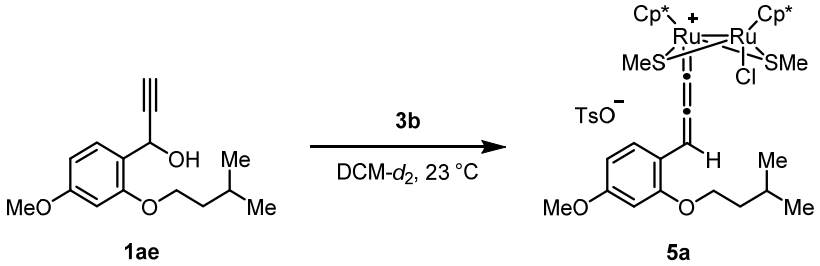


1a **2a**

X (mol %)	NMR yield (%)	ee (%)
0	93	93
10	56	92
100	0	–

NMR titration study

Stock solutions of model ruthenium-allenylidene complexes **5a** and **5b**, lacking the nucleophilic alkene moiety, were prepared from the corresponding propargylic alcohol **1ae**.



1ae **5a**

Preparation of a stock solution of ruthenium-allenylidene tosylate complex **5a**

A solution of propargylic alcohol **1ae** (3.6 mg, 14.4 µmol, 1 equiv) in dichloromethane-d_2 (360 µL) was added to a glass half-dram vial charged with ruthenium tosylate complex **3b** (11.4 mg, 14.4 µmol, 1.0 equiv) at 23 °C. The resulting dark violet mixture was stirred at 23 °C for 20 minutes, and then was directly used for the NMR binding study. **5a**: ^{1}H NMR (400 MHz, DCM-d_2) δ 8.67 (s, 1H), 7.73–7.63 (m, 3H), 7.12 (d, J = 7.9 Hz, 2H), 6.57 (dd, J = 9.1, 2.1 Hz, 1H), 6.35 (d, J = 2.2 Hz, 1H), 4.10 (t, J = 6.6 Hz, 2H), 3.92 (s, 3H), 2.66 (s, 6H), 2.33 (s, 3H), 1.89–1.78 (m, 16H), 1.79–1.71 (m, 2H), 1.66 (s, 15H), 0.97 (d, J = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, DCM-d_2) δ 287.7, 170.9, 170.7, 166.0, 149.0, 143.9, 138.7, 134.3, 129.3, 128.6, 126.3, 110.5, 104.4, 98.9, 98.5, 68.4, 57.0, 37.7, 25.4, 22.6, 21.3, 20.3, 10.9, 10.6.

1ae **5b**

Preparation of a stock solution of ruthenium-allenylidene BAr$^F_4$ complex **5b**

A solution of propargylic alcohol **1ae** (1.5 mg, 6.0 µmol, 1 equiv) in dichloromethane-d_2 (150 µL) was added to a glass half-dram vial charged with ruthenium BAr$^F_4$ complex **3c** (8.9 mg, 6.0 µmol, 1.0 equiv) at 23 °C. Benzene-d_6 (150 µL) was added at 23 °C. The resulting dark violet mixture was stirred at 23 °C for 20 minutes, and then was directly used for the NMR binding study. **5b**: ^{1}H NMR (400 MHz, DCM-d_2) δ 8.68 (s, 1H), 7.75–7.71 (m, 8H), 7.69 (d, J = 9.1 Hz, 1H), 7.56 (s, 4H), 6.55 (dd, J = 9.0, 2.1 Hz, 1H), 6.34 (d, J = 2.3 Hz, 1H), 4.10 (t, J = 6.5 Hz, 2H), 3.90 (s, 3H), 2.66 (s, 6H), 1.83–1.78 (m, 16H), 1.77–1.72 (m, 2H), 1.65 (s, 15H), 0.96 (d, J = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, DCM-d_2) δ 287.9, 170.9, 170.7, 166.0, 162.1 (q, J = 49.8 Hz), 149.1, 135.1, 134.3, 129.9–128.6 (m), 129.0, 124.9 (q, J = 272.3 Hz), 118.0–117.5 (m), 110.4, 104.3, 98.9, 98.4, 68.4, 56.8, 37.7, 25.4, 22.5, 20.3, 10.8, 10.5. ^{11}B NMR (128 MHz, DCM-d_2) δ −6.48 to −6.72 (m). ^{19}F NMR (376 MHz, DCM-d_2) δ −62.84.

A stock solution of hydrogen-bond donor **4d** in benzene-d_6 (6 mM) was prepared by mixing hydrogen-bond donor **4d** (9.6 mg, 8.4 µmol) and benzene-d_6 (1400 µL). A stock solution of hydrogen-bond donor **4d** in dichloromethane-d_2 (6 mM) was prepared by mixing hydrogen-bond donor **4d** (5.5 mg, 4.8 µmol) and dichloromethane-d_2 (800 µL).

Experiment I: Addition of hydrogen-bond donor **4d** to ruthenium-allenylidene tosylate complex **5a** in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2

Four oven-dried NMR tubes were filled with nitrogen gas, capped with rubber septa, and sealed with parafilm. Each NMR tube was charged with the stock solution of ruthenium-allenylidene tosylate complex **5a** in dichloromethane-d_2 (30 µL, 1.2 µmol) and a respective volume of the stock solution of hydrogen-bond donor **4d** in benzene-d_6 (IA: 0 µL, IB: 100 µL, IC: 200 µL, ID: 300 µL). Benzene-d_6 was added to bring the total volume of each sample to 600 µL. ^{1}H NMR spectra of the prepared mixtures were collected at 25 °C and were referenced to the residual solvent signal of benzene-d_6 (7.160 ppm) (Figure S15). ^{1}H NMR Chemical shifts of the ruthenium-allenylidene tosylate complex **5a** (except the 3-methylbutyl substituent) in the presence of varied amounts of hydrogen-bond donor **4d** are reported in Table S12.

Experiment II: Addition of hydrogen-bond donor **4d** to ruthenium-allenylidene $BAr^F{}_4$ complex **5b** in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2

Four oven-dried NMR tubes were filled with nitrogen gas, capped with rubber septa, and sealed with parafilm. Each NMR tube was charged with the stock solution of ruthenium-allenylidene $BAr^F{}_4$ complex **5b** in a 1:1 mixture of benzene-d_6 and dichloromethane-d_2 (60 µL, 1.2 µmol) and a respective volume of the stock solution of hydrogen-bond donor **4d** in benzene-d_6 (IIA: 0 µL, IIB: 100 µL, IIC: 200 µL, IID: 300 µL). Benzene-d_6 was added to bring the total volume of each sample to 600 µL. ^{1}H NMR spectra of the prepared mixtures were collected at 25 °C and were referenced to the residual solvent signal of benzene-d_6 (7.160 ppm) (Figure S16). ^{1}H NMR Chemical shifts of the ruthenium-allenylidene $BAr^F{}_4$ complex **5b** (except the 3-methylbutyl substituent) in the presence of varied amounts of hydrogen-bond donor **4d** are reported in Table S13.

Experiment III: Addition of hydrogen-bond donor **4d** to ruthenium-allenylidene tosylate complex **5a** in dichloromethane-d_2

Four oven-dried NMR tubes were filled with nitrogen gas, capped with rubber septa, and sealed with parafilm. Each NMR tube was charged with the stock solution of ruthenium-allenylidene tosylate complex **5a** in dichloromethane-d_2 (30 µL, 1.2 µmol) and a respective volume of the stock solution of hydrogen-bond donor **4d** in dichloromethane-d_2 (IIIA: 0 µL, IIIB: 100 µL, IIIC: 200 µL, IIID: 300 µL). Dichloromethane-d_2 was added to bring the total volume of each sample to 600 µL. ^{1}H NMR spectra of the prepared mixtures were collected at 25 °C and were referenced to the residual solvent signal of dichloromethane-d_2 (5.320 ppm) (Figure S17). ^{1}H NMR Chemical shifts of the ruthenium-allenylidene tosylate complex **5a** (except the 3-methylbutyl substituent) in the presence of varied amounts of hydrogen-bond donor **4d** are reported in Table S14.

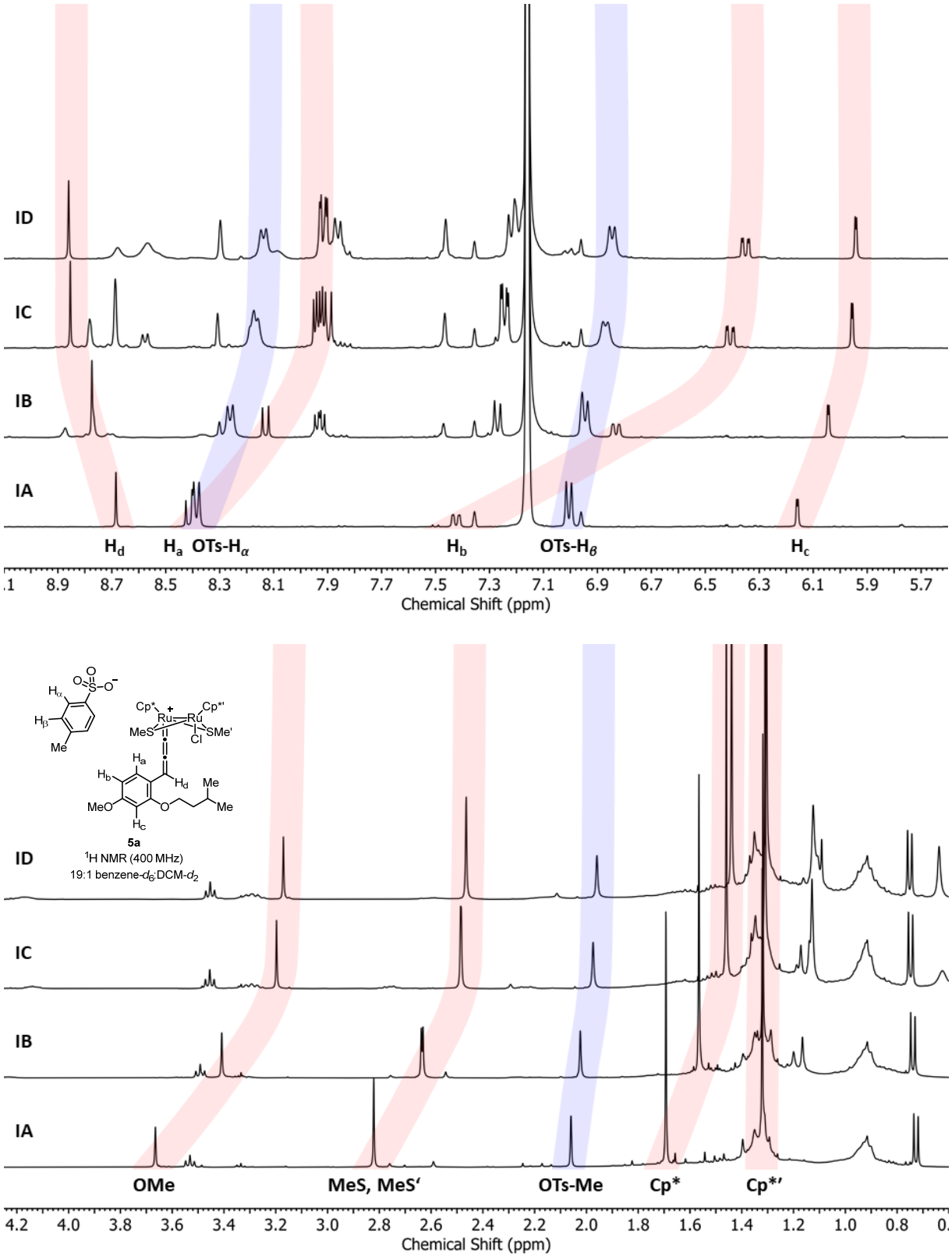


Figure S15 ^{1}H NMR spectra of ruthenium-allenylidene tosylate complex **5a** and varied amount of hydrogen-bond donor **4d** (A: 0 equiv, B: 0.5 equiv, C: 1.0 equiv, D: 2.0 equiv) in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 at 25 °C.

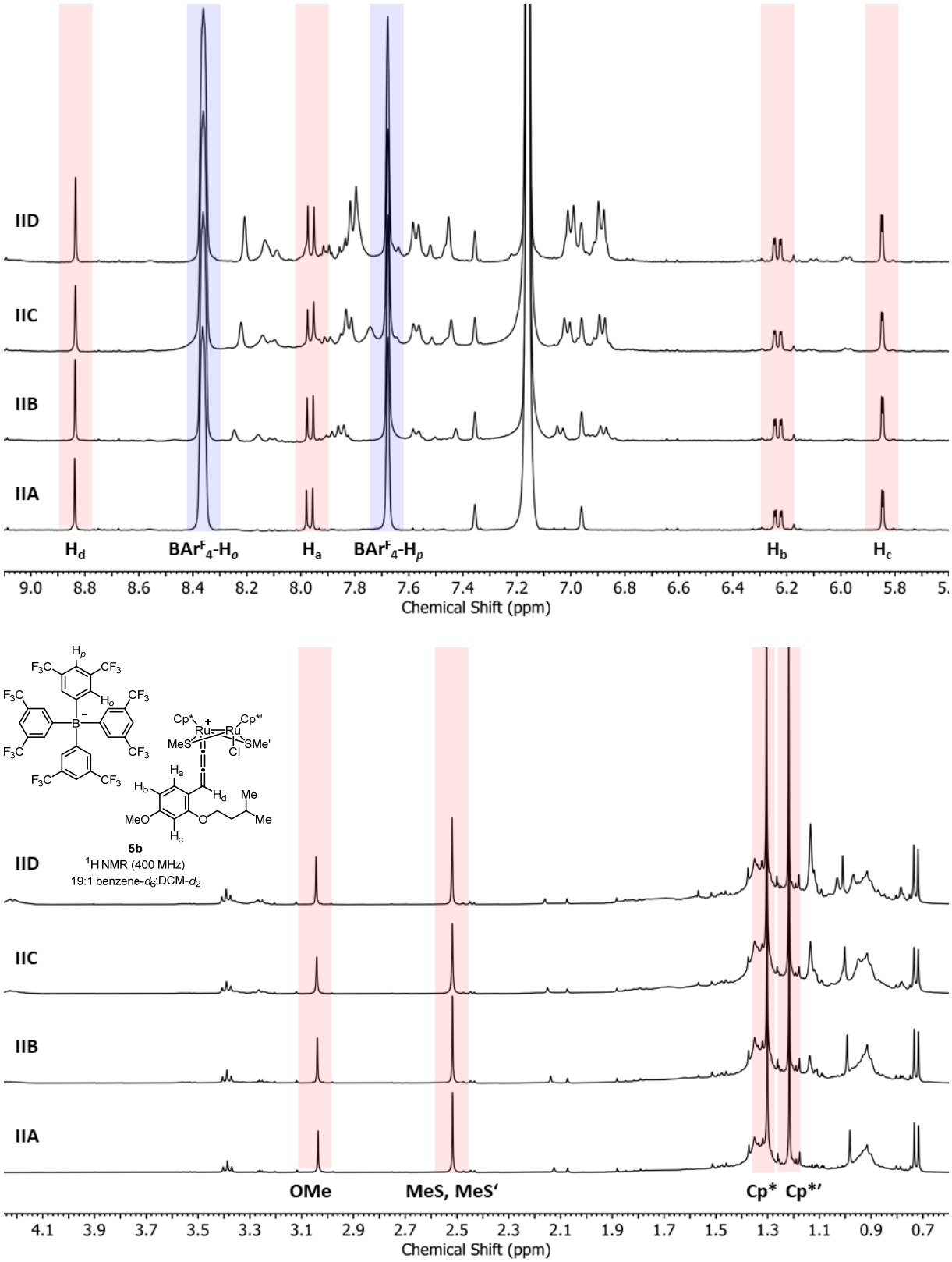


Figure S16 ^{1}H NMR spectra of ruthenium-allenylidene BAr^{F}_{4} complex **5b** and varied amount of hydrogen-bond donor **4d** (A: 0 equiv, B: 0.5 equiv, C: 1.0 equiv, D: 2.0 equiv) in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 at 25 °C.

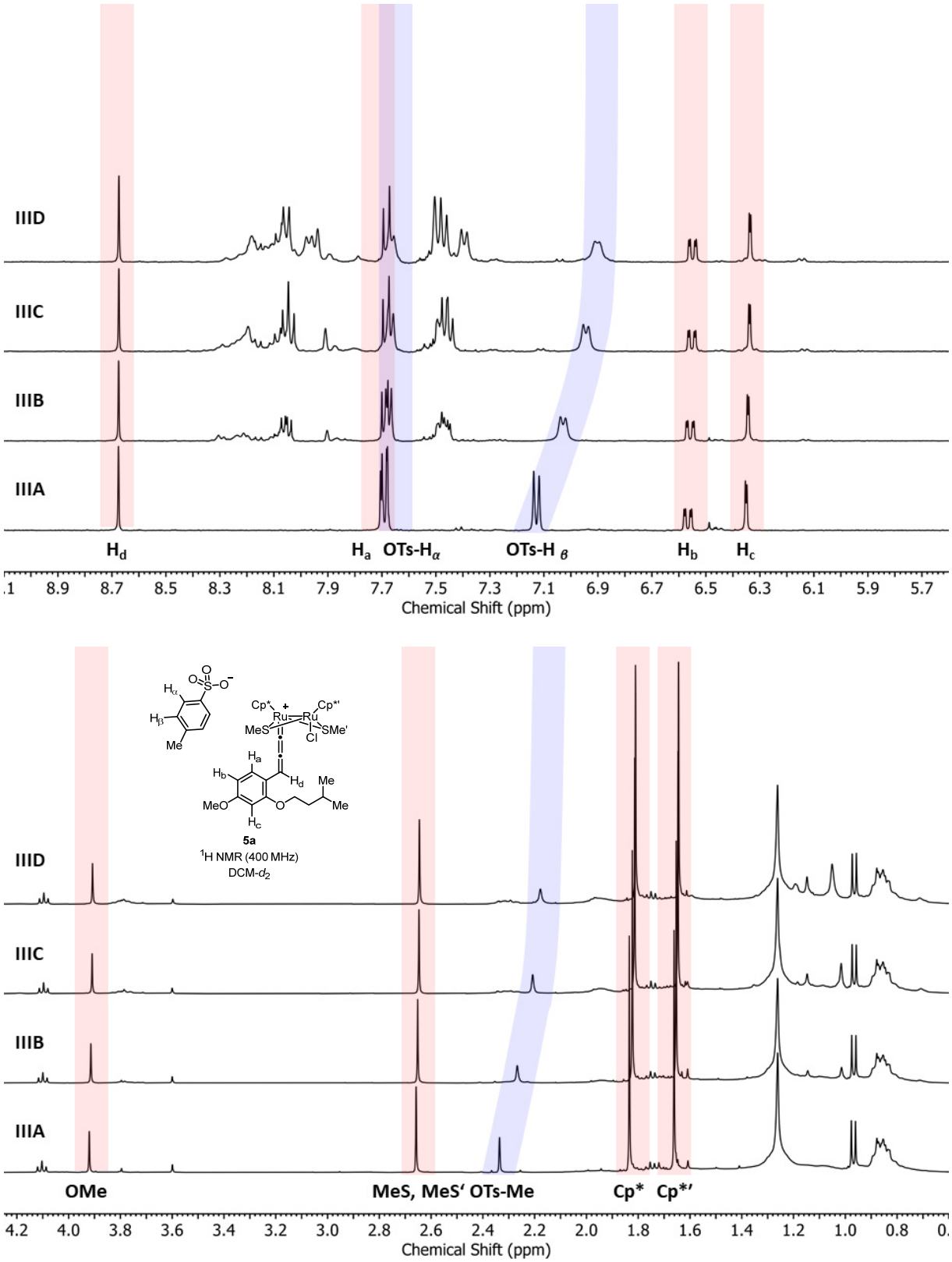


Figure S17 ^{1}H NMR spectra of ruthenium-allenylidene tosylate complex **5a** and varied amount of hydrogen-bond donor **4d** (A: 0 equiv, B: 0.5 equiv, C: 1.0 equiv, D: 2.0 equiv) in dichloromethane-d_2 at 25 °C.

Table S12 ^{1}H NMR chemical shift values of selected hydrogen atoms or groups of hydrogen atoms of ruthenium-allenylidene tosylate complex **5a** in the presence of 0–1.5 equivalents of hydrogen-bond donor **4d** in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 ([**5a**] = 2 mM) at 25 °C.

spec-trum	**4d** (equiv)	δ_{Cp*} (ppm)	$\delta_{Cp*'}$ (ppm)	δ_{MeS} (ppm)	$\delta_{MeS'}$ (ppm)	δ_{Ha} (ppm)	δ_{Hb} (ppm)	δ_{Hc} (ppm)	δ_{Hd} (ppm)	δ_{OMe} (ppm)	$\delta_{OTs\text{-}H\alpha}$ (ppm)	$\delta_{OTs\text{-}H\beta}$ (ppm)	$\delta_{OTs\text{-}Me}$ (ppm)
IA	0	1.693	1.321	2.821	2.821	8.414	7.425	6.159	8.685	3.665	8.386	7.006	2.060
IB	0.5	1.565	1.319	2.631	2.638	8.130	6.831	6.044	8.774	3.408	8.261	6.946	2.024
IC	1.0	1.460	1.310	2.484	2.486	7.939	6.408	5.956	8.854	3.197	8.166	6.870	1.974
ID	1.5	1.439	1.304	2.464	2.464	7.913	6.351	5.942	8.860	3.170	8.138	6.845	1.959
$\Delta\delta_{A-D}$ (ppm)		0.254	0.017	0.357	0.357	0.501	1.074	0.217	−0.175	0.495	0.248	0.161	0.101

Table S13 ^{1}H NMR chemical shift values of selected hydrogen atoms or groups of hydrogen atoms of ruthenium-allenylidene BAr^F_4 complex **5b** in the presence of 0–1.5 equivalents of hydrogen-bond donor **4d** in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 ([**5b**] = 2 mM) at 25 °C.

spec-trum	**4d** (equiv)	δ_{Cp*} (ppm)	$\delta_{Cp*'}$ (ppm)	δ_{MeS} (ppm)	$\delta_{MeS'}$ (ppm)	δ_{Ha} (ppm)	δ_{Hb} (ppm)	δ_{Hc} (ppm)	δ_{Hd} (ppm)	δ_{OMe} (ppm)	$\delta_{BArF4\text{-}Ho}$ (ppm)	$\delta_{BArF4\text{-}Hp}$ (ppm)
IIA	0	1.302	1.216	2.517	2.517	7.968	6.233	5.845	8.838	3.037	8.363	7.678
IIB	0.5	1.302	1.217	2.517	2.517	7.966	6.233	5.846	8.836	3.039	8.362	7.678
IIC	1.0	1.303	1.218	2.518	2.518	7.964	6.232	5.847	8.835	3.042	8.361	7.678
IID	1.5	1.304	1.218	2.519	2.519	7.963	6.235	5.848	8.835	3.044	8.361	7.678
$\Delta\delta_{A-D}$ (ppm)		−0.002	−0.002	−0.002	−0.002	0.005	−0.002	−0.003	0.003	−0.007	0.002	0.000

Table S14 ^{1}H NMR chemical shift values of selected hydrogen atoms or groups of hydrogen atoms of ruthenium-allenylidene tosylate complex **5a** in the presence of 0–1.5 equivalents of hydrogen-bond donor **4d** in dichloromethane-d_2 ([**5a**] = 2 mM) at 25 °C.

spec-trum	**4d** (equiv)	δ_{Cp*} (ppm)	$\delta_{Cp*'}$ (ppm)	δ_{MeS} (ppm)	$\delta_{MeS'}$ (ppm)	δ_{Ha} (ppm)	δ_{Hb} (ppm)	δ_{Hc} (ppm)	δ_{Hd} (ppm)	δ_{OMe} (ppm)	$\delta_{OTs\text{-}H\alpha}$ (ppm)	$\delta_{OTs\text{-}H\beta}$ (ppm)	$\delta_{OTs\text{-}Me}$ (ppm)
IIIA	0	1.834	1.661	2.658	2.658	7.692	6.567	6.351	8.676	3.920	7.692	7.128	2.336
IIIB	0.5	1.823	1.653	2.652	2.652	7.689	6.558	6.344	8.675	3.914	7.675	7.029	2.267
IIIC	1.0	1.814	1.647	2.647	2.647	7.685	6.552	6.338	8.674	3.909	7.665	6.945	2.208
IIID	1.5	1.810	1.644	2.645	2.645	7.683	6.549	6.336	8.674	3.908	7.664	6.910	2.178
$\Delta\delta_{A-D}$ (ppm)		0.024	0.017	0.013	0.013	0.009	0.018	0.015	0.002	0.012	0.028	0.218	0.158

Comparison of ^{1}H NMR spectra of ruthenium-allenylidene complexes containing anions with different coordinating ability

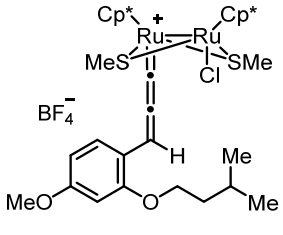
Addition of hydrogen-bond donor **4d** to a solution of ruthenium-allenylidene tosylate complex **5a** in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 led to change of chemical shift values of signals corresponding to **5a** (see page S73 for details). We noted that the signals of **5a** underwent a shift in the direction toward signals of the ruthenium-allenylidene BAr^F_4 complex **5b**, and that the ^{1}H NMR spectrum of the **5a**–**4d** complex resembled the ^{1}H NMR spectrum of **5b** more that the ^{1}H NMR spectrum of **5a** in the absence of **4d**. To examine the possibility that hydrogen-bond donor **4d** decreases the coordinating ability of the tosylate anion of the ruthenium-allenylidene complex **5a** resulting in the shift of signals toward signals of the ruthenium-allenylidene complex **5b** containing a non-coordinating anion BAr^F_4, we compared ^{1}H NMR spectra of four ruthenium-allenylidene complexes containing anions with different coordinating ability (Table S15). We observed that the chemical shift values of signals corresponding to the ruthenium-allenylidene cation were affected by the identity of the counterion, and that the chemical shift of signals correlated with the coordinating ability of the anion (Table S16, Figure S18)[21]. This study suggested that the interaction between the hydrogen-bond donor **4d** and tosylate of **5a** in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 decreases the coordinating ability of tosylate.

Table S15 Anions examined in this study.

Anion (X)	complex	spectrum	coordinating ability index[a]
OTs	**5a**	IVA	−0.2
BF_4	**5d**	IVB	−1.1
PF_6	**5e**	IVC	−1.6
BAr^F_4	**5b**	IVD	−3.4

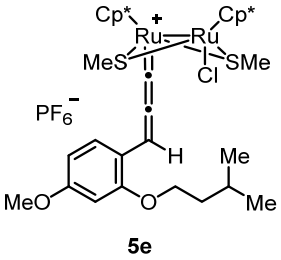
[a]Coordinating ability index values were adopted from the literature[21].

Ruthenium-allenylidene tosylate complex **5a** and ruthenium-allenylidene BAr^F_4 complex **5b** were prepared according to procedures described on page S73.



5d

5d: A solution of ruthenium-allenylidene tetrafluoroborate complex **5d** in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 was prepared according to the procedure described on page S73 for the preparation of a solution of ruthenium-allenylidene tosylate complex **5a** using ruthenium tetrafluoroborate complex **3f** instead of ruthenium tosylate complex **3b**. ^{1}H NMR (400 MHz, DCM-d_2) δ 8.67 (s, 1H), 7.70 (d, J = 9.0 Hz, 1H), 6.61–6.54 (m, 1H), 6.36 (d, J = 2.3 Hz, 1H), 4.11 (t, J = 6.6 Hz, 2H), 3.92 (s, 3H), 2.66 (s, 6H), 1.84 (s, 15H), 1.80–1.70 (m, 3H), 1.66 (s, 15H), 0.97 (d, J = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, DCM-d_2) δ 287.9, 170.9, 170.8, 166.0, 148.9, 134.3, 129.3, 110.5, 104.4, 98.9, 98.5, 68.4, 56.9, 37.7, 25.4, 22.6, 20.3, 10.8, 10.5. ^{11}B NMR (128 MHz, DCM-d_2) δ −1.17. ^{19}F NMR (376 MHz, DCM-d_2) δ −153.17 ($^{10}BF_4^-$), −153.22 ($^{11}BF_4^-$).



5e

5e: A solution of ruthenium-allenylidene hexafluorophosphate complex **5e** in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 was prepared according to the procedure described on page S73 for the preparation of a solution of ruthenium-allenylidene tosylate complex **5a** using ruthenium hexafluorophosphate complex **3e** instead of ruthenium tosylate complex **3b**. ^{1}H NMR (400 MHz, DCM-d_2) δ 8.67 (s, 1H), 7.70 (d, J = 9.0 Hz, 1H), 6.61–6.55 (m, 1H), 6.35 (d, J = 2.3 Hz, 1H), 4.11 (t, J = 6.6 Hz, 2H), 3.92 (s, 3H), 2.66 (s, 6H), 1.84 (s, 15H), 1.82–1.69 (m, 3H), 1.66 (s, 15H), 0.97 (d, J = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, DCM-d_2) δ 288.1, 171.0, 170.9, 165.9, 148.9, 134.2, 129.3, 110.4, 104.4, 98.9, 98.5, 68.4, 56.9, 37.7, 25.4, 22.6, 20.3, 10.8, 10.5. ^{19}F NMR (376 MHz, DCM-d_2) δ −73.50 (d, J = 710.3 Hz).^{31}P NMR (162 MHz, DCM-d_2) δ −144.53 (hept, J = 710.2 Hz).

Table S16 Comparison of ^{1}H NMR chemical shift values of selected hydrogen atoms or groups of hydrogen atoms of ruthenium-allenylidene complexes containing different anions (**5a**, **5b**, **5d**, **5e**; 2 mM) with chemical shift values of signals corresponding to the **5a**–**4d** complex (spectrum IC, Figure S15) in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 at 25 °C.

spec-trum	com-plex	δ_{Cp^*} (ppm)	$\delta_{Cp^{*\prime}}$ (ppm)	δ_{MeS} (ppm)	$\delta_{MeS\prime}$ (ppm)	δ_{Ha} (ppm)	δ_{Hb} (ppm)	δ_{Hc} (ppm)	δ_{Hd} (ppm)	δ_{OMe} (ppm)
IVA	**5a**	1.693	1.321	2.819	2.819	8.409	7.414	6.144	8.685	3.653
IVB	**5d**	1.624	1.319	2.768	2.768	8.295	7.184	6.091	8.688	3.580
IVC	**5e**	1.602	1.311	2.730	2.730	8.206	7.060	6.022	8.711	3.513
IVD	**5b**	1.307	1.220	2.518	2.518	7.963	6.235	5.849	8.835	3.045
IC	**5a**–**4d**	1.460	1.310	2.484	2.486	7.939	6.408	5.956	8.854	3.197

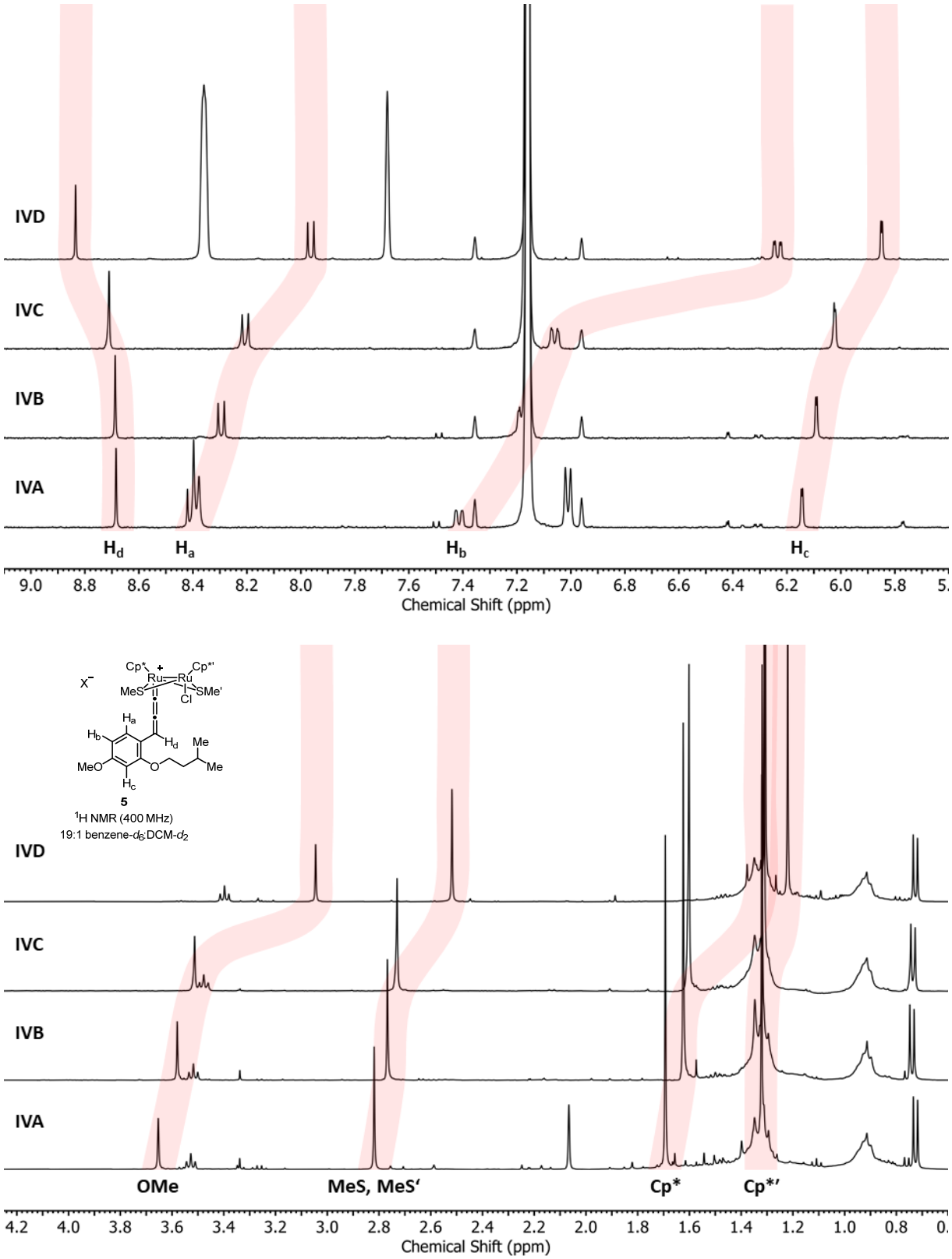


Figure S18 ^{1}H NMR spectra of ruthenium-allenylidene complexes containing anions with different coordinating ability (A: X = OTs (**5a**), B: X = BF_4 (**5d**), C: X = PF_6 (**5e**), D: X = $BAr^F{}_4$ (**5b**)) in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 at 25 °C.

Study of binding interaction between ruthenium complexes and hydrogen-bond donors

Job plot analysis

The binding stoichiometry between hydrogen-bond donor **4d** and ruthenium tosylate complex **3b** in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 at 25 °C was determined by the method of continuous variation (Job plot analysis)[69] using ^{1}H NMR spectroscopy. A stock solution of hydrogen-bond donor **4d** (8.0 mg, 7.0 μmol, 2.0 mM) in a mixture of benzene-d_6 (3325 μL) and dichloromethane-d_2 (175 μL) was prepared. A stock solution of ruthenium tosylate complex **3b** (5.5 mg, 7.0 μmol, 2 mM) in a mixture of benzene-d_6 (3325 μL) and dichloromethane-d_2 (175 μL) was prepared. Eleven oven-dried NMR tubes were charged with varied volumes of prepared stock solutions of **3b** and **4d** (600 μL total). The total concentration of **3b** and **4d** was kept constant ([**3b**] + [**4d**] = 2 mM), and the relative concentrations of **3b** and **4d** were varied as reported in Table S17. ^{1}H NMR spectra of the prepared mixtures were collected at 25 °C and were referenced to the residual solvent peak for benzene-d_6 (7.160 ppm). Changes of chemical shifts of two signals corresponding to ruthenium tosylate complex **3b** were utilized for determination of the binding stoichiometry between **3b** and **4d** (Figure S19). The Job plot was constructed using absolute values of change of a chemical shift multiplied by mole fraction of the corresponding component ($|\Delta\delta \times \chi|$) as a function of the mole fraction (χ). The maximum response at $\chi = 0.5$ for both resonances is indicative of a 1:1 binding between hydrogen-bond donor **4d** and ruthenium tosylate complex **3b** in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 at 25 °C.

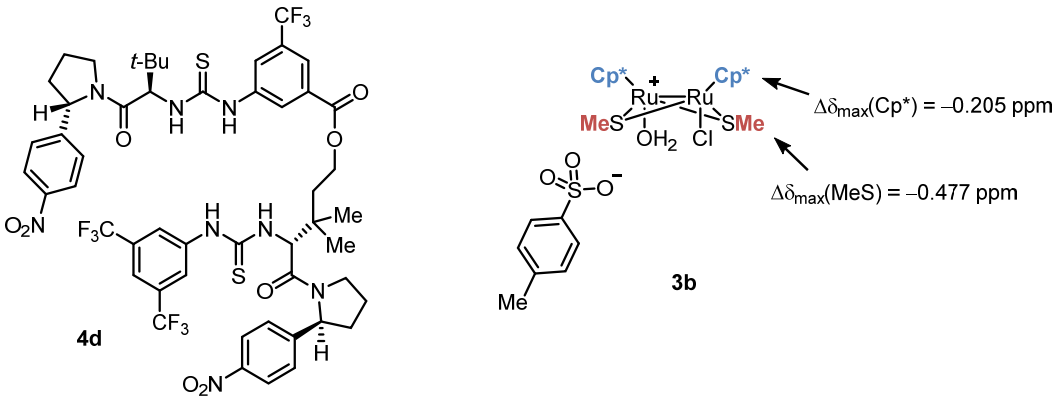


Figure S19 Depiction of groups of hydrogen atoms selected for the Job analysis and the maximum change of chemical shift of the corresponding ^{1}H NMR signal upon binding. A positive value indicates a downfield shift of the ^{1}H NMR chemical shift upon binding, whereas a negative value represents an upfield shift of the ^{1}H NMR chemical shift.

Table S17 Data describing the binding between hydrogen-bond donor **4d** and ruthenium tosylate complex **3b** in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 at 25 °C.

$V_{\mathbf{3b}}$ (μL)	$V_{\mathbf{4d}}$ (μL)	$X_{\mathbf{3b}}$	δ_{Cp^*} (ppm)	$\Delta\delta_{Cp^*}$ (ppm)	$\lvert\chi_{\mathbf{3b}} \times \Delta\delta_{Cp^*}\rvert$ (ppm)	δ_{MeS} (ppm)	$\Delta\delta_{MeS}$ (ppm)	$\lvert\chi_{\mathbf{3b}} \times \Delta\delta_{MeS}\rvert$ (ppm)
600	0	1.00	1.296	0	0	2.590	0	0
450	150	0.75	1.239	–0.057	0.043	2.449	–0.141	0.106
400	200	0.67	1.206	–0.090	0.060	2.371	–0.219	0.146

360	240	0.60	1.170	–0.126	0.076	2.289	–0.301	0.181
330	270	0.55	1.138	–0.158	0.087	2.219	–0.371	0.204
300	300	0.50	1.103	–0.193	0.097	2.142	–0.448	0.224
270	330	0.45	1.091	–0.205	0.092	2.113	–0.477	0.215
240	360	0.40	1.091	–0.205	0.082	2.114	–0.476	0.190
200	400	0.33	1.092	–0.204	0.068	2.115	–0.475	0.158
150	450	0.25	1.092	–0.204	0.051	2.116	–0.474	0.119
0	600	0.00	–	–	–	–	–	–

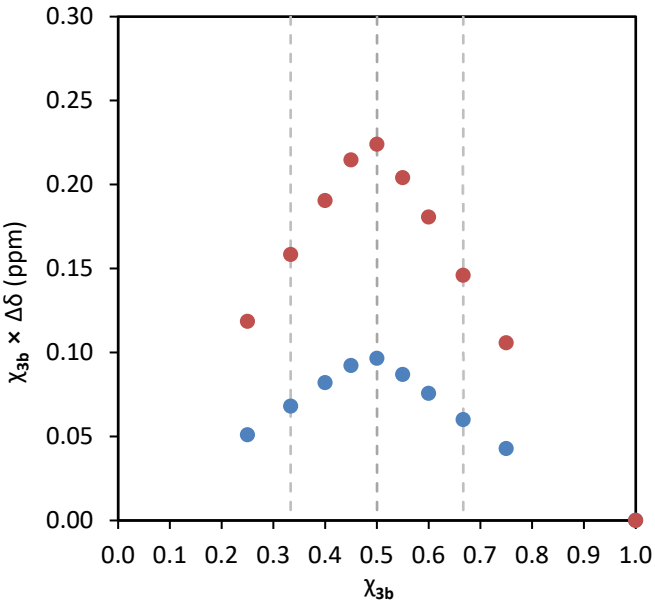
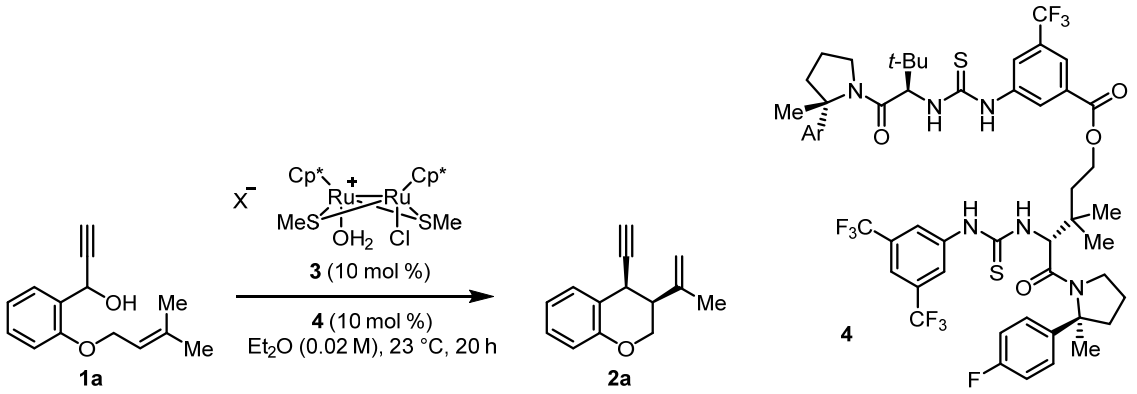


Figure S20 Graphical representation of the response of the ^{1}H NMR signals of the ruthenium tosylate complex **3b** to binding to hydrogen-bond donor **4d** in a 19:1 mixture of benzene-d_6 and dichloromethane-d_2 at 25 °C.

Examination of interaction between arenes of the HBD and the arene of the tosylate anion

Table S18 Enantioselectivity of the propargylic substitution reaction catalyzed by hydrogen-bond donors containing various aryl-pyrrolidine substituents in the presence of either ruthenium tosylate complex **3b** or ruthenium mesylate complex **3d**. General reaction procedure for screening study described on page S58 was followed.



4	Ar	X = OTs (3b)		X = OMs (3d)	
		ee (%)	−ΔΔG‡ (kcal mol^{-1})	ee (%)	−ΔΔG‡ (kcal mol^{-1})
4h	4-(NO_2)Ph	82	1.36	81	1.33
4b	4-FPh	76	1.17	74	1.12
4l	4-BrPh	67	0.95	68	0.98
4q	4-(CF_3)Ph	58	0.78	61	0.83
4r	4-(SF_5)Ph	50	0.65	51	0.66
4v	3,4,5-F_3Ph	72	1.07	70	1.02
4z	2-Nap	61	0.83	60	0.82

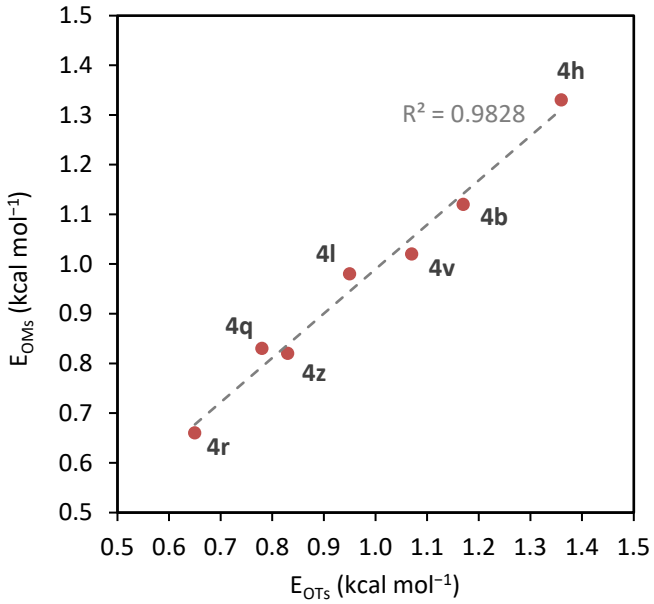


Figure S21 Correlation between enantioselectivity of the propargylic substitution catalyzed by ruthenium tosylate complex **3b** and ruthenium mesylate complex **3d**.

It was observed that the enantioselectivity of the propargylic substitution promoted by ruthenium tosylate complex **3b** correlates with the enantioselectivity of the reaction catalyzed by ruthenium mesylate complex **3d** across a range of hydrogen-bond donors containing various substituents at the northern pyrrolidine ring. This correlation is inconsistent with the possibility that the aryl substituent at the northern pyrrolidine ring is engaged in a specific interaction with the arene of the tosylate anion during the enantiodetermining event. Such interaction would be absent in the reaction system containing a mesylate anion that lacks the arene functionality. Therefore, if an arene interaction between the aryl at the pyrrolidine ring and the arene of tosylate exists and affects the enantioselectivity, no correlation between the enantioselectivities of reactions catalyzed by ruthenium tosylate complex **3b** and ruthenium mesylate complex **3d** is expected.

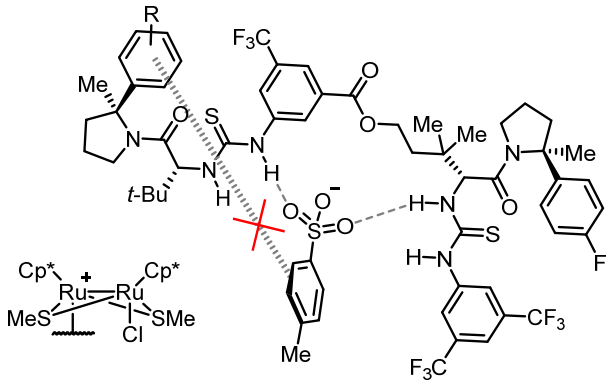
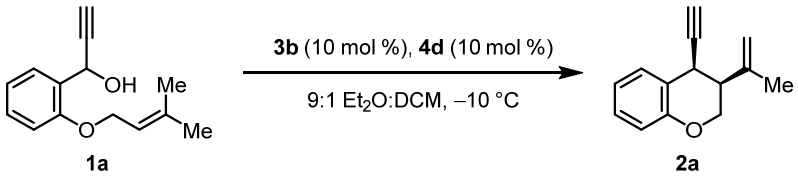


Figure S22 Depiction of a potential interaction between the aryl substituent at the pyrrolidine ring and the arene of tosylate anion, which was examined in this experiment.

ROESY NMR analysis of a ruthenium-allenylidene mesylate–HBD complex

A solution structure of a 1:1 complex of ruthenium-allenylidene mesylate **5c** and hydrogen-bond donor **4e** was studied in order to elucidate their specific mode of interaction. Conditions for the ROESY NMR experiment were optimized to facilitate analysis of spectroscopic data while mimicking the developed co-catalytic reaction system as closely as possible.

Table S19 Effect of modifications to the optimal system using 10 mol % of catalysts that are relevant to conditions used in the ROESY NMR experiment.



1a **2a**

modification to the optimal system	dr	ee (%)
none	69:1	98
23 °C instead of −10 °C	33:1	94
Et_2O instead of 9:1 Et_2O:DCM, 23 °C instead of −10 °C	36:1	95
9:1 CCl_4:DCM instead of 9:1 Et_2O:DCM, 23 °C instead of −10 °C	30:1	93
3d instead of **3b**, Et_2O instead of 9:1 Et_2O:DCM, 23 °C instead of −10 °C	44:1	95
4e instead of **4d**, Et_2O instead of 9:1 Et_2O:DCM, 23 °C instead of −10 °C	28:1	91

A 1:1 complex of ruthenium-allenylidene mesylate **5c** and hydrogen-bond donor **4e** was prepared from the corresponding propargylic alcohol **1ae**. Ruthenium mesylate complex **3d** (2.0 mg, 2.8 μmol, 1 equiv) and hydrogen-bond donor **4e** (3.2 mg, 2.8 μmol, 1.0 equiv) were dissolved in dichloromethane-d_2 (70 μL) at 23 °C. Tetrachloromethane (230 μL, deoxygenated by the freeze-pump-thaw method) was added, and the resulting mixture was stirred at 23 °C for 5 minutes. A solution of propargylic alcohol **1ae** (0.7 mg, 2.9 μmol, 1.05 equiv) in tetrachloromethane (200 μL, deoxygenated by the freeze-pump-thaw method) was added at 23 °C, and the resulting dark purple mixture was stirred at 23 °C for 10 minutes. Additional portion of tetrachloromethane (200 μL, deoxygenated by the freeze-pump-thaw method) was added, and the solution was transferred to an NMR tube filled with nitrogen gas, capped with a rubber septum, and sealed with parafilm. Due to limited stability of ruthenium-allenylidene mesylate complex **5c**, the sample was analyzed within 9 hours of its preparation. ROESY spectrum was collected at 25 °C using the EASY ROESY pulse sequence[70] (roesyadjsphpr, basic frequency for channel F1 (BF1) = 400.49 MHz, number of scans (NS) = 24, relaxation delay (D1) = 4 s, acquisition time = 0.15 s (F1) and 0.019 s (F2), pulse for ROESY spinlock (P15) = 150 ms, transmitter frequency offset (O1) = 6.00 ppm, spectral width (SW) = 17.10 ppm). The spectrum was analyzed using MestReNova software. Integrated volumes of ROE crosspeaks were converted to interatomic distances using the following equation:

$$r_{ab} = r_{ref} \sqrt[6]{\frac{I_{ref}}{I_{ab}}}$$

where r_{ab} is the interatomic distance between hydrogens *a* and *b*, r_{ref} is the distance between reference hydrogens (1.78 Å for geminal hydrogens or 2.42 Å for *ortho* aromatic hydrogens), I_{ref} is the volume of the ROE crosspeak corresponding to the reference pair of hydrogens, and I_{ab} is the volume of the ROE crosspeak corresponding to hydrogens *a* and *b*. The interatomic distances reported in Table S20 and Figure S26 are average values of distances calculated using three different reference pairs of hydrogens: H18–H18′ (1.78 Å), H19–H19′ (1.78 Å), and Ha–Hb (2.42 Å). A tolerance of ±10% of the calculated distance value is applied to account for experimental errors. To calculate an average interatomic distance for hydrogens of groups of equivalent hydrogens, the integrated volumes of ROE crosspeaks were divided by the number of possible interatomic interactions between the group of equivalent hydrogens and a proximal hydrogen/a group of equivalent hydrogens (n) (n = 3 for Me–H crosspeaks, n = 9 for Me–Me crosspeaks, n = 27 for *t*-Bu–Me crosspeaks, etc.).

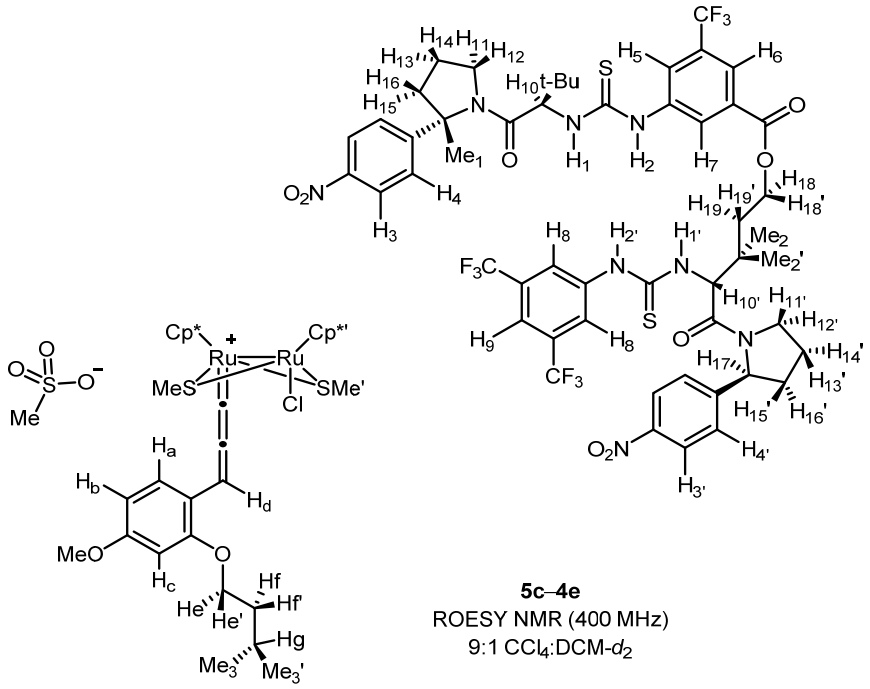


Figure S23 Labeling of atoms and groups of the ruthenium-allenylidene mesylate–hydrogen-bond donor complex.

Ruthenium-allenylidene mesylate complex **5c**: ^{1}H NMR (400 MHz, DCM-d_2) δ 8.67 (s, 1H), 7.69 (d, J = 9.0 Hz, 1H), 6.57 (dd, J = 9.0, 1.9 Hz, 1H), 6.36 (d, J = 2.3 Hz, 1H), 4.11 (t, J = 6.6 Hz, 2H), 3.93 (s, 3H), 2.66 (s, 6H), 2.58 (s, 3H), 1.89–1.69 (m, 18H), 1.66 (s, 15H), 0.97 (d, J = 6.5 Hz, 6H). ^{13}C NMR (126 MHz, DCM-d_2) δ 287.7, 170.9, 170.7, 165.9, 148.9, 134.2, 129.3, 110.4, 104.4, 98.9, 98.5, 68.4, 57.0, 39.6, 37.7, 25.4, 22.5, 20.3, 10.9, 10.5.

^{1}H NMR [400 MHz, 9:1 CCl_4:DCM-d_2. Two rotamers of **4e** are observed under the specified conditions in a 10:1 ratio as determined by integration of signals at δ_{major} = 5.18 ppm and δ_{minor} = 5.47 ppm, respectively. Only resonances corresponding to the major rotamer are reported. The spectrum contains signals corresponding to unreacted **1ae**: δ 7.38 (d, J = 8.0 Hz, 1H), 6.46–6.39 (m, 2H), 5.48 (dd, J = 6.7, 2.2 Hz, 1H), 4.12–4.01 (m, 2H), 3.82 (s, 3H), 2.50 (d, J = 6.8 Hz, 1H), 2.46 (d, J = 2.3 Hz, 1H), 1.92 (app dh, J = 13.1, 6.6 Hz, 1H), 1.83–1.72 (m, 1H), 1.05 (app d, J = 6.6 Hz,

6H)]. δ 10.65–10.40 (m, 2H; H_2 + H_2'), 9.71 (s, 1H; H_5), 8.59 (s, 1H; H_d), 8.55 (s, 2H; H_8), 8.27–8.21 (m, 1H; H_1'), 8.19 (s, 1H; H_7), 8.04 (d, J = 8.7 Hz, 2H; H_3'), 8.00 (d, J = 8.8 Hz, 2H; H_3), 7.91 (s, 1H; H_6), 7.83 (d, J = 7.1 Hz, 1H; H_1), 7.63 (d, J = 9.0 Hz, 1H; H_a), 7.58 (d, J = 8.8 Hz, 2H; H_4), 7.55 (s, 1H; H_9), 7.48 (d, J = 8.6 Hz, 2H; H_4'), 6.63 (dd, J = 9.1, 1.9 Hz, 1H; H_b), 6.24 (d, J = 1.9 Hz, 1H; H_c), 5.18 (d, J = 8.1 Hz, 1H; H_{17}), 5.03 (d, J = 7.2 Hz, 1H; H_{10}'), 4.98–4.90 (m, 1H; H_{11}), 4.87 (d, J = 7.4 Hz, 1H; H_{10}), 4.86–4.79 (m, 1H; H_{11}'), 4.60–4.47 (m, 1H; H_{18} or H_{18}'), 4.28–4.15 (m, 1H; H_{18} or H_{18}'), 4.12–4.03 (m, 2H; H_e + H_e'), 3.86 (s, 3H; OMe), 3.84–3.82 (m, 1H; H_{12}), 3.82–3.79 (m, 1H; H_{12}'), 2.71 (s, 3H; OMs), 2.46 (s, 3H; SMe or SMe′), 2.44 (s, 3H; SMe or SMe′), 2.43–2.36 (m, 1H; H_{19}), 2.36–2.24 (m, 1H; H_{16}'), 2.13–2.05 (m, 1H; H_{15} or H_{16}), 2.06–1.98 (m, 1H; H_{19}'), 2.05–1.97 (m, 2H; H_{13}' + H_{14}'), 2.00–1.91 (m, 1H; H_{15} or H_{16}), 1.95–1.85 (m, 2H; H_{13} + H_{14}), 1.93 (s, 3H; Me_1), 1.89–1.84 (m, 1H; H_g); 1.87–1.78 (m, 1H; H_{15}'), 1.84–1.75 (m, 2H; H_f + H_f'), 1.54 (s, 15H; Cp*), 1.46 (s, 15H; Cp*′), 1.25 (s, 3H; Me_2'), 1.21 (s, 3H; Me_2), 1.16 (s, 9H; *t*-Bu), 1.02 (d, J = 6.4 Hz, 6H; Me_3 + Me_3').

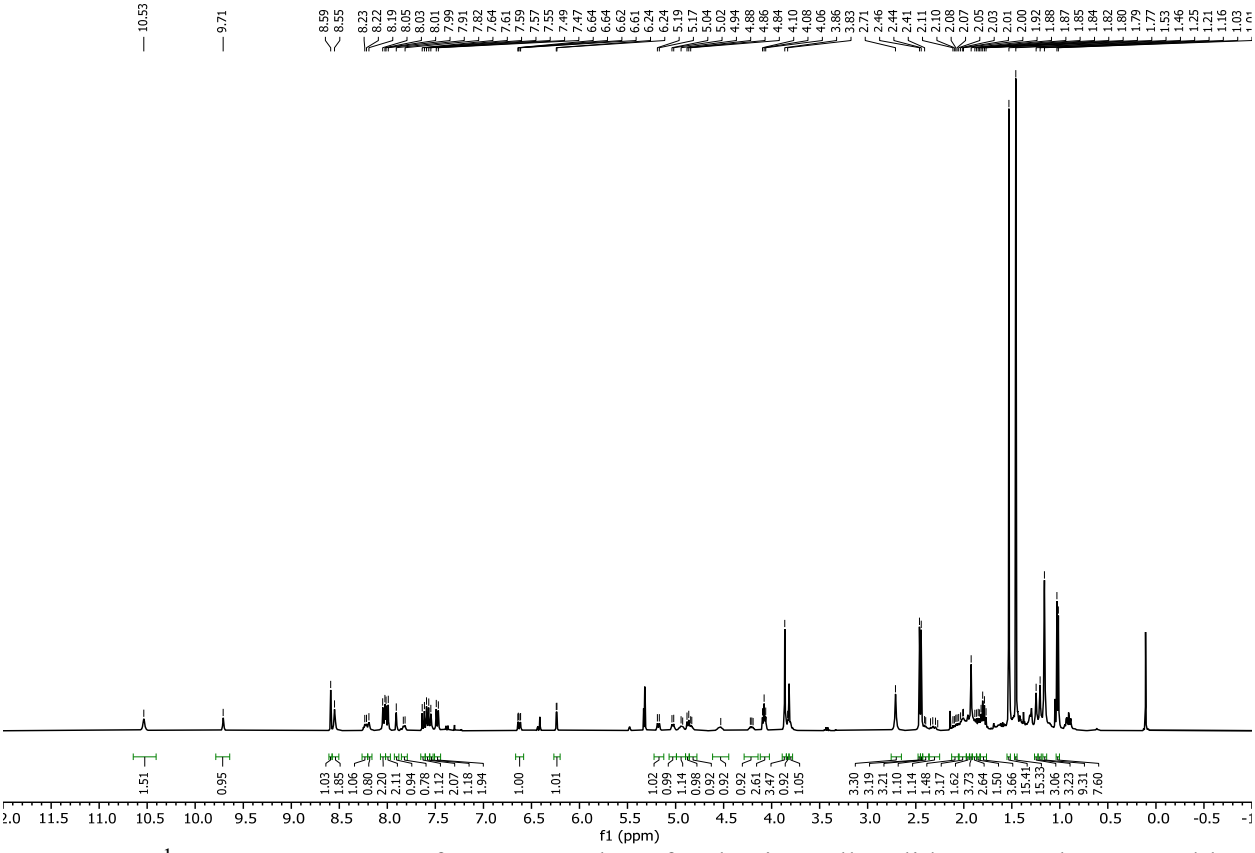


Figure S24 ^{1}H NMR spectrum of a 1:1 complex of ruthenium-allenylidene mesylate **5c** and hydrogen-bond donor **4e** in a 9:1 mixture of tetrachloromethane and dichloromethane-d_2 at 25 °C.

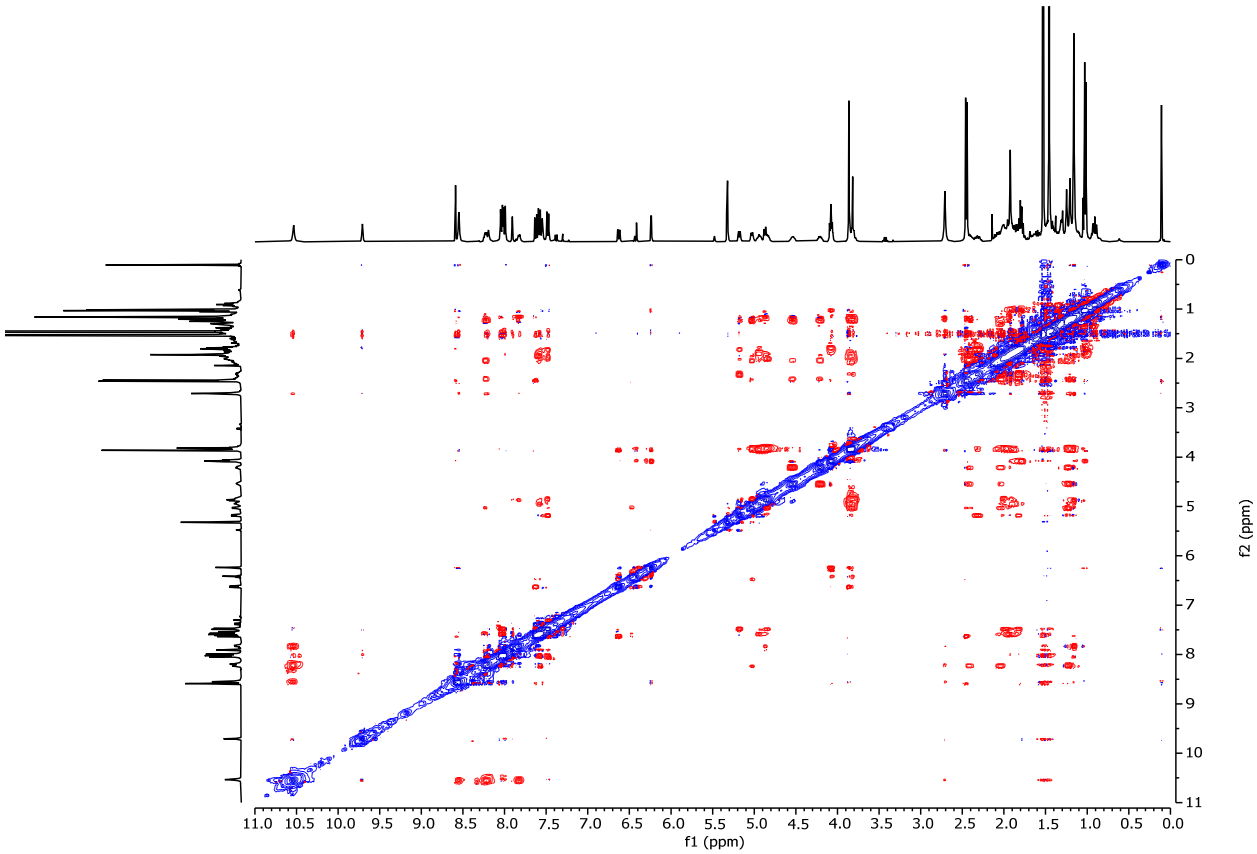
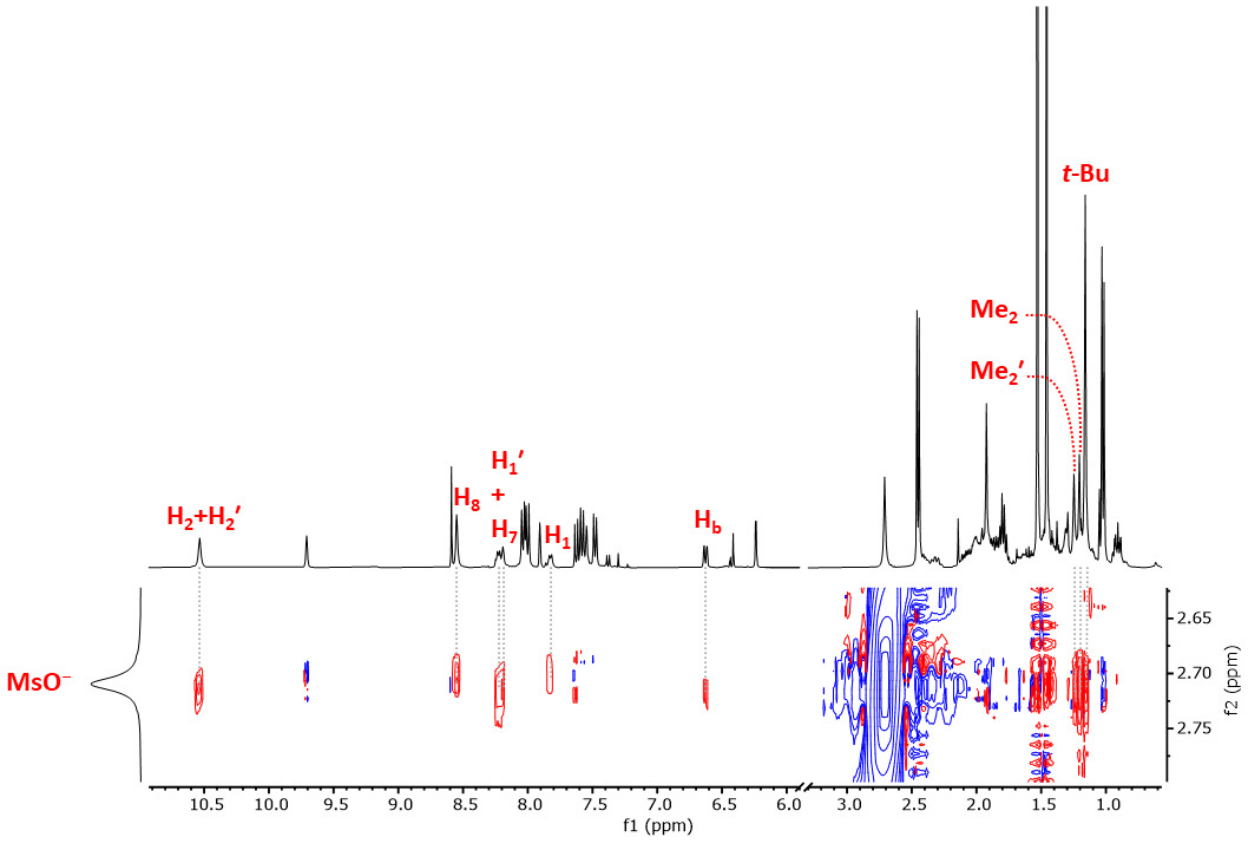
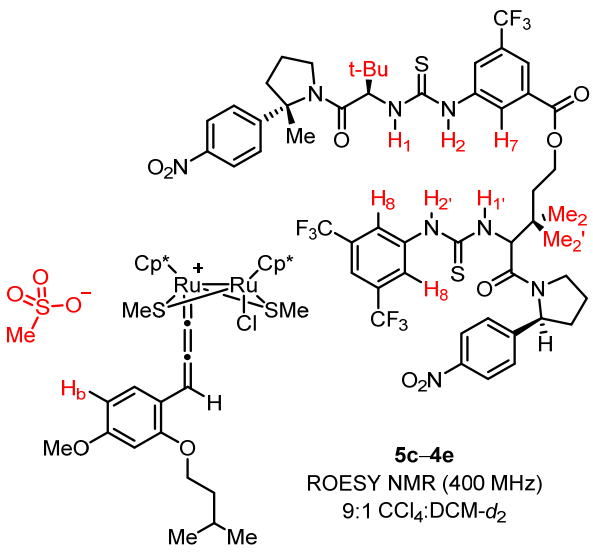


Figure S25 ROESY spectrum of a 1:1 complex of ruthenium-allenylidene mesylate **5c** and hydrogen-bond donor **4e** in a 9:1 mixture of tetrachloromethane and dichloromethane-d_2 at 25 °C.

Table S20 ROESY-derived intramolecular interatomic hydrogen distances for the **5c**–**4e** complex.

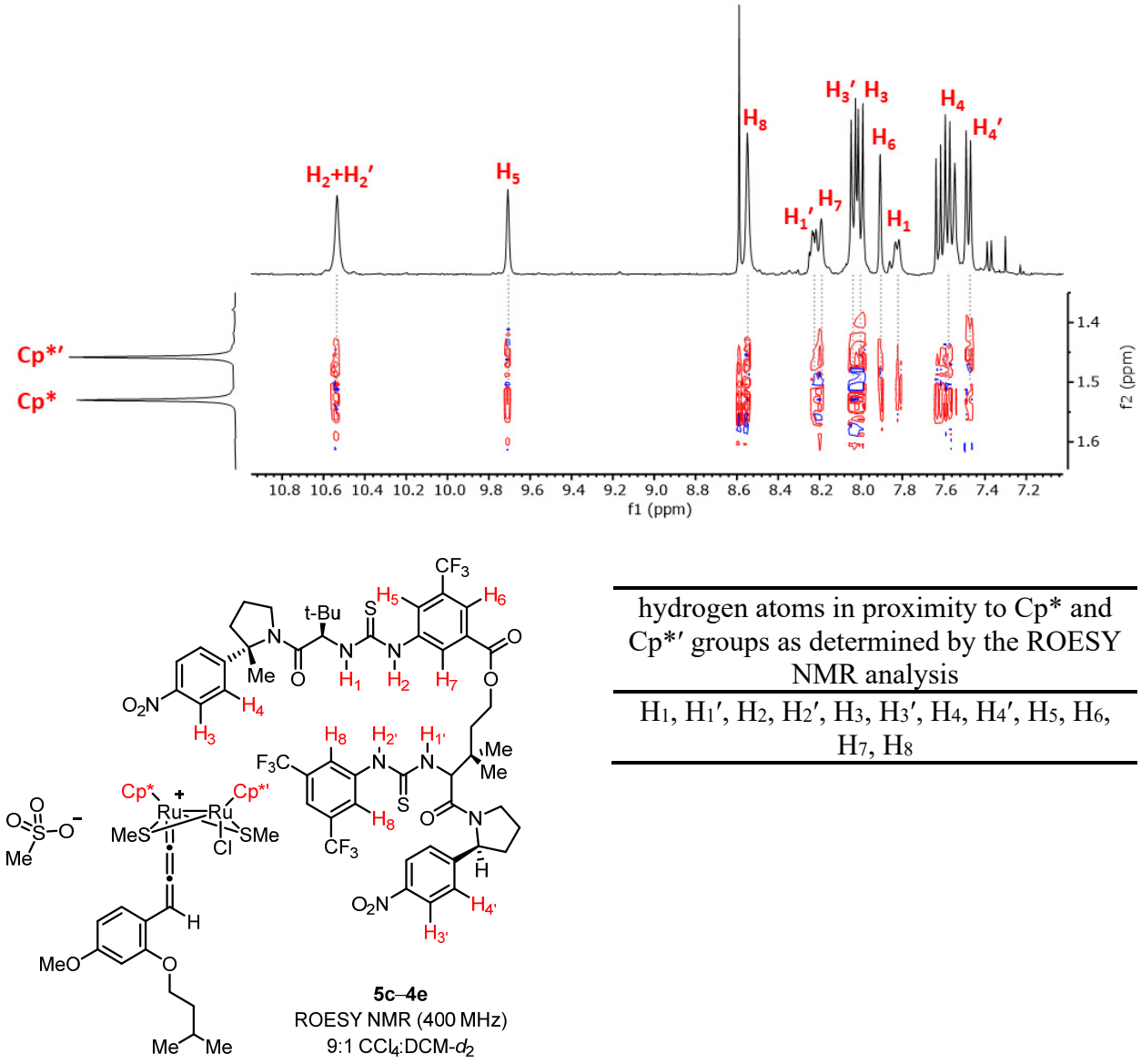
hydrogen pair	ROESY-derived distance (Å)	hydrogen pair	ROESY-derived distance (Å)
H_{18}–H_{18}'	1.79 ± 0.18	H_{17}–H_{15}'	2.70 ± 0.27
H_{19}–H_{19}'	1.79 ± 0.18	H_{17}–H_{16}'	2.22 ± 0.22
H_a–H_b	2.39 ± 0.24	H_{12}'–Me_2	2.64 ± 0.26
H_1–H_{10}	2.99 ± 0.30	H_{12}'–Me_2'	2.85 ± 0.28
H_1'–H_{10}'	3.04 ± 0.30	H_b–OMe	2.95 ± 0.29
H_{10}'–H_{11}'	2.17 ± 0.22	H_c–OMe	3.54 ± 0.35
H_{10}'–H_{12}'	2.15 ± 0.21	H_c–(H_e + H_e')	2.49 ± 0.25





hydrogen pair	ROESY-derived distance (Å)
OMs–Hb	4.69 ± 0.47
OMs–*t*-Bu	4.94 ± 0.49
OMs–Me_2	4.53 ± 0.45
OMs–Me_2'	5.34 ± 0.53
OMs–H_1	4.21 ± 0.42
OMs–H_1'	–
OMs–H_2	–
OMs–H_2'	–
OMs–H_7	–
OMs–H_8	4.61 ± 0.46
OMs–H_{19}	–

Figure S26 Hydrogen atoms in proximity of the mesylate anion. Interatomic distances were not calculated for overlapping signals.



5c–4e
ROESY NMR (400 MHz)
9:1 CCl_4:DCM-d_2

hydrogen atoms in proximity to Cp* and Cp*′ groups as determined by the ROESY NMR analysis
H_1, H_1', H_2, H_2', H_3, H_3', H_4, H_4', H_5, H_6, H_7, H_8

Figure S27 Hydrogen atoms in proximity of the cyclopentadienyl groups.

Computational details

Density functional theory (DFT) calculations were conducted using the Gaussian 09 program package[71] on the Cannon cluster supported by Harvard University's Faculty of Arts and Sciences Research Computing group. Structural images were generated using CYLview[72].

Initial geometries of a complex comprised of ruthenium-allenylidene mesylate **5c** and bis-thiourea **4e** were generated by placing the structure of **5c** in different orientations within the structure of **4e** informed by the interatomic distances derived from the ROESY NMR experiment (see p S86). The resulting structures of the complex were optimized using Grimme's semi-empirical method GFN2-xTB[73]. A constrained conformational search was performed using Grimme's *crest*[74,75]. Conformation III and the lowest-energy conformations obtained from the conformational search were submitted to gas-phase geometric optimization using B3LYP/LANL2DZ(Ru),6-31G(d)[76–82]. Final electronic energies of the optimized structures were calculated using ωB97X-D/SDD(Ru),6-311++G(d,p),PCM(CCl_4)[83,84]. ωB97X-D/SDD(Ru),6-311++G(d,p) level of theory was selected because it has been previously applied by Nishibayashi in a similar system[85–87]. The lowest-energy structures corresponding to different possible orientations of **5c** within the structure of **4e** are provided.

The ROESY-derived average interatomic distances of hydrogens of methyl groups were compared to average distances derived from the computational model using the following equation:

$$r_{average} = \left(\frac{1}{3}\sum_{i}^{3} r_i^{-3}\right)^{-\frac{1}{3}}$$

where r_i is the measured distance between a hydrogen of the methyl group and the proximal hydrogen.

The ROESY-derived average interatomic distances of hydrogens of groups of equivalent protons other than methyl groups were compared to average distances derived from the computational model using the following equation:

$$r_{average} = \left(\frac{1}{N}\sum_{i}^{N} r_i^{-6}\right)^{-\frac{1}{6}}$$

where N is the number of equivalent hydrogen atoms in the group and r_i is the measured distance between a hydrogen of the group of equivalent hydrogens and the proximal hydrogen[88].

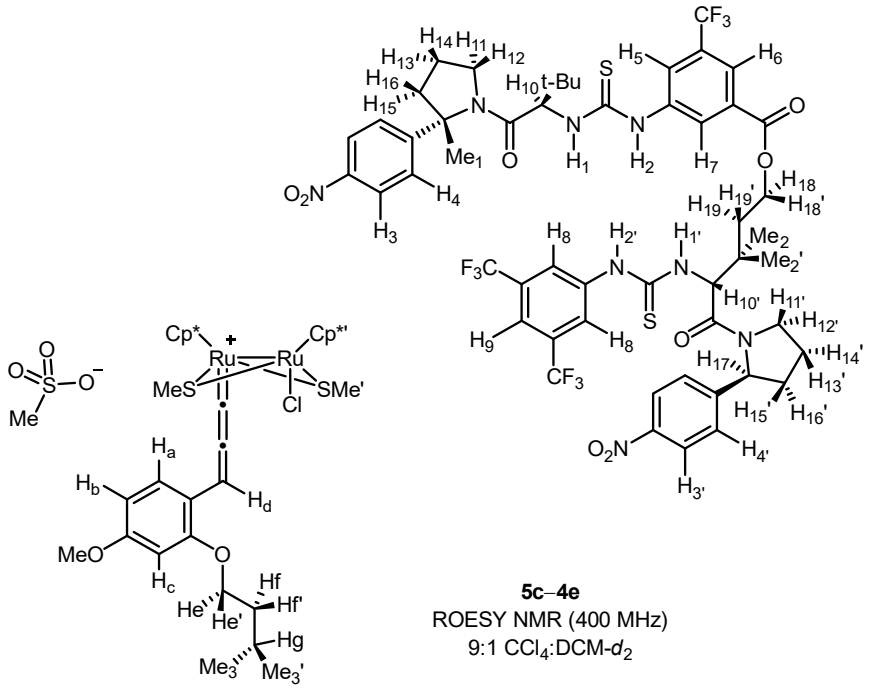


Figure S28 Labeling of atoms and groups of the ruthenium-allenylidene mesylate–hydrogen-bond donor complex.

Conformation I

ΔE: 0.00 kcal/mol (defined)

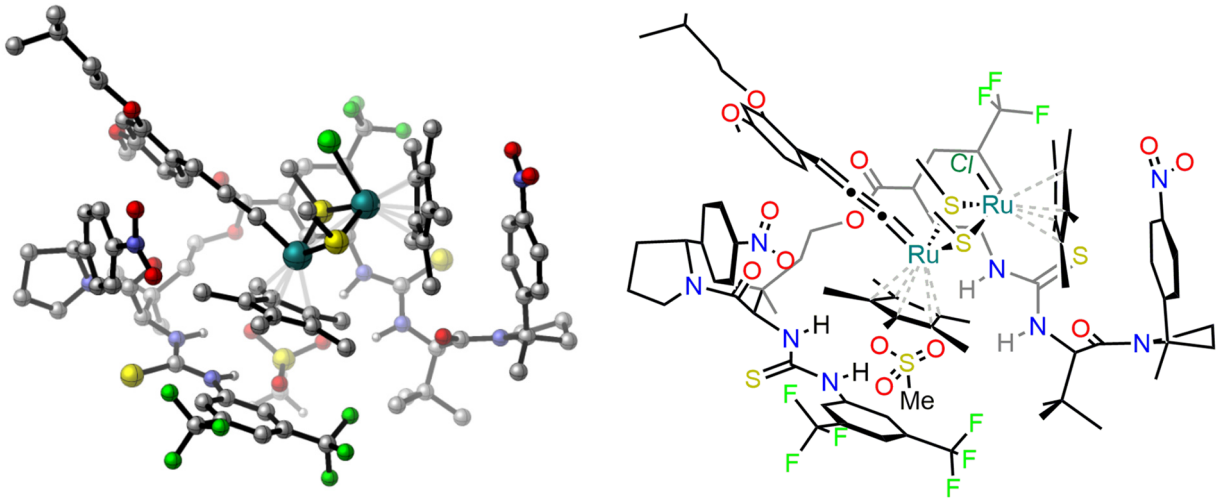


Table S21 Comparison of ROESY-derived interatomic hydrogen distances to computed distances corresponding to conformation I of the **5c**–**4e** complex.

hydrogen pair	ROESY-derived distance (Å)	computed distance (Å)	violation (Å)
H_1–H_{10}	2.99 ± 0.30	2.87	0.00
H_{17}–H_{16}'	2.22 ± 0.22	2.38	0.00
H_{17}–H_{15}'	2.70 ± 0.27	2.75	0.00
H_1'–H_{10}'	3.04 ± 0.30	2.88	0.00

H_{10}'–H_{11}'	2.17 ± 0.22	2.16	0.00
H_{10}'–H_{12}'	2.15 ± 0.21	2.54	0.17
Me_2–H_{12}'	2.64 ± 0.26	2.71	0.00
Me_2'–H_{12}'	2.85 ± 0.28	4.62	1.49
H_8–OMs	4.61 ± 0.46	5.29	0.22
H_1–OMs	4.21 ± 0.42	4.64	0.01
t-Bu–OMs	4.94 ± 0.49	4.34	–0.11

Charge: 0
Multiplicity: 1

Ru	0.08912200	1.02638600	-1.52795600
N	-3.10819000	-1.12664300	3.22804100
N	-4.66589000	-2.14979400	1.97504000
N	1.57117600	-4.44780400	-0.59905700
N	2.83965100	-4.16757800	1.27429800
N	-7.71144800	-1.15555600	0.34493200
N	6.18551900	-2.83738600	1.36181800
C	-0.36014400	1.58952300	4.89134100
C	-0.04568300	0.24674900	4.67753800
C	-1.00116800	-0.63036800	4.16523400
C	-2.29272000	-0.17861800	3.84767500
C	-2.63328600	1.15657600	4.11534600
C	-1.66130400	2.01697300	4.63049400
C	1.32956200	-0.24573900	4.96248700
C	-4.42477400	-1.14051800	2.84269500
C	-5.96597900	-2.52695400	1.46537800
C	-5.91421900	-4.00499600	0.94090800
C	-7.29315500	-4.39477800	0.38189400
C	-5.59113900	-4.92476000	2.13491900
C	-4.85652600	-4.20085100	-0.16265700
C	-2.24939000	-4.44934600	-3.59581100
C	-0.75937800	-4.33803500	-3.43406200
C	1.98805200	-4.16718700	-3.03668800
C	1.44069800	-4.03299700	-4.31049000
C	0.06801900	-4.12126100	-4.53520400
C	2.82785600	-4.44260800	-0.05265600
C	4.07298500	-3.97931900	2.02442200
C	3.77990200	-3.82839100	3.55823100
C	5.11286400	-3.63619400	4.30435800
C	3.12472500	-5.13655300	4.04606900
C	2.85211200	-2.61669800	3.80341200
C	2.55762300	-2.27675000	5.26218900
C	4.83516300	-2.74483400	1.49372400
C	-6.40512700	-1.53976900	0.36271900
C	-8.66979400	-1.31743600	1.45688000
C	-9.81699000	-0.37261900	1.08581600
C	-9.79117200	-0.39173500	-0.44266000
C	-8.27900100	-0.39258900	-0.79784000
C	6.99863900	-4.06468900	1.33511800
C	8.32594400	-3.58713800	0.73571000
C	8.42971600	-2.14239300	1.24019800
C	6.97966300	-1.62364000	1.11419000
C	2.38191700	-3.81147400	-5.46275100
C	-1.99245200	3.45491200	4.92047400
C	-7.77081300	1.05209500	-0.81762600
C	-7.90969300	1.83805200	-1.97375700
C	-7.23770000	1.64593400	0.33371400
C	-6.84585000	2.98042600	0.33633700
C	-6.96247800	3.71979000	-0.83657300
C	6.70755700	-0.96021400	-0.22319000
C	7.02669400	0.39546300	-0.36213900
C	6.15013000	-1.64730300	-1.30634600
C	6.71321100	1.08734100	-1.52436600
C	5.82957300	-0.97262500	-2.47964100
C	6.07790100	0.39711000	-2.55491800
C	-7.49594000	3.16511800	-1.99812500
O	2.33753300	0.43758900	4.89216800
O	1.31189900	-1.54597300	5.29979200
O	-5.60628900	-1.17821300	-0.50552200
O	4.24855400	-1.67585200	1.30581400
F	1.76941300	-3.18092800	-6.49310700
F	2.87506000	-4.97117000	-5.94671200
F	3.44266000	-3.05143900	-5.10190300
F	-1.71761600	3.78007900	6.20237500
F	-3.28988800	3.74776200	4.69734500
F	-1.25326000	4.29480600	4.14735700
F	-2.67996000	-5.72345600	-3.47586900
F	-2.90607800	-3.73017300	-2.64979600
F	-2.66691300	-3.99827000	-4.80085400
S	4.25521600	-4.80139200	-0.89050900
S	-5.63557800	-0.09878400	3.39724100
H	0.39259700	2.26988600	5.27228400
H	-0.73285800	-1.66664800	3.98663900
H	-3.63701200	1.50684300	3.92598900
H	-2.60721600	-1.99208300	3.00607100
H	-3.87686500	-2.72900200	1.70654500
H	-6.67318600	-2.49484100	2.29617700
H	-7.27824900	-5.44398300	0.06869400
H	-8.07874700	-4.28776400	1.13835200
H	-7.56755300	-3.79238500	-0.48914300
H	-6.34279400	-4.82216700	2.92692000
H	-5.59041000	-5.97024700	1.80470400
H	-4.60942000	-4.70536400	2.56330700
H	-3.83360400	-4.09195800	0.21036000
H	-4.99336100	-3.49714900	-0.98542300

H	-0.34351600	-4.00224900	-5.52894600
H	1.95712000	-3.95923100	1.73933500
H	4.68689000	-4.87355100	1.89637900
H	4.93747400	-3.59728000	5.38441500
H	5.79670500	-4.47147800	4.11830500
H	5.61853900	-2.70973500	4.01304000
H	3.02827000	-5.13876200	5.13697100
H	2.12583400	-5.26809700	3.62444600
H	3.74096000	-6.00019000	3.77040800
H	1.87957200	-2.81153400	3.35173700
H	3.26520700	-1.73546400	3.31169100
H	3.34124900	-1.67700300	5.73109900
H	2.36137000	-3.15962300	5.87169600
H	-9.02464300	-2.35295800	1.51194600
H	-8.19377300	-1.05353600	2.40444500
H	-9.61334700	0.63619600	1.45872800
H	-10.77234300	-0.70090200	1.50361700
H	7.14898900	-4.45391100	2.34970900
H	6.50436200	-4.82612600	0.72790900
H	8.26725500	-3.60050500	-0.35802700
H	9.16891000	-4.21365600	1.03906400
H	-4.93429300	-5.21838600	-0.56214000
H	-10.31184000	0.45082900	-0.90456800
H	-10.24154200	-1.31871600	-0.81804800
H	-8.33103500	1.41063000	-2.87642300
H	-7.08357300	1.05446900	1.22889900
H	-6.42625500	3.44038300	1.22148300
H	8.73353900	-2.12919700	2.29362600
H	9.13405700	-1.52932200	0.67295400
H	7.46182700	0.93151400	0.47530900
H	5.88280700	-2.69282700	-1.20575700
H	6.89424600	2.14978200	-1.61923700
H	5.33934700	-1.47810600	-3.30229300
H	-7.57575700	3.76847100	-2.89344900
Ru	-1.67581900	3.13928800	-1.10343500
C	1.70950300	2.01829300	-1.40399000
S	-0.63262200	1.86990200	0.56363200
S	-0.73529200	2.49015800	-3.16931600
Cl	0.00471600	4.88764000	-0.81670500
C	1.31991800	-0.87126700	-1.73338300
C	0.55426100	-0.64720400	-2.92884400
C	-0.84937000	-0.85897900	-2.60662500
C	-0.94772600	-1.09986100	-1.21898900
C	0.39666800	-1.06859000	-0.66393900
C	2.80679100	-0.93227000	-1.65156400
H	3.14115600	-1.95276500	-1.86602900
H	3.18858100	-0.67557500	-0.66382000
H	3.26500400	-0.27113700	-2.38668600
C	1.09988100	-0.42658100	-4.30659200
H	0.44688200	0.23530600	-4.88224100
H	1.17582900	-1.37053700	-4.85356000
H	2.09605500	0.02161300	-4.27540400
C	-1.93443500	-0.87220400	-3.63220700
H	-2.91046000	-1.05262800	-3.18277700
H	-1.74925600	-1.66486300	-4.36387600
H	-1.96654700	0.07583900	-4.17969600
C	-2.14829900	-1.45059200	-0.40417000
H	-2.18462300	-0.85239800	0.51036000
H	-2.07886600	-2.50163800	-0.10136500
H	-3.08928100	-1.31157000	-0.93564200
C	0.72999400	-1.37430000	0.76211500
C	-3.29504800	4.73044600	-1.04413300
C	-3.31498700	3.92864700	0.14760400
C	-3.67072800	2.57406900	-0.22801000
C	-3.80626400	2.53589700	-1.64827800
C	-3.57343200	3.87349300	-2.14901900
C	-3.08469600	6.20638800	-1.09764300
H	-2.63265200	6.51105300	-2.04412200
H	-4.05478900	6.70724000	-0.99279600
H	-2.42530400	6.53562300	-0.29298300
C	-3.15614100	4.43114200	1.54391600
H	-2.99244300	3.60173000	2.23019900
H	-4.05839400	4.96834400	1.86179200
H	-2.30525300	5.11216400	1.62615500
C	-3.93095500	1.46757700	0.73679100
H	-4.35439400	0.59087700	0.24855400
H	-4.63932900	1.79077000	1.50116800
H	-3.02022500	1.16931200	1.26209000
C	-4.27997400	1.39165800	-2.48168200
H	-3.67615600	1.28754800	-3.38567400
H	-4.25762300	0.45332300	-1.92812600
H	-5.31732500	1.56322500	-2.79026300
C	-3.72683600	4.30271100	-3.57298600
H	-3.06577000	5.14059000	-3.80866800
H	-4.75931800	4.63315800	-3.74360800
H	-3.50414200	3.48491500	-4.26255300
C	0.65005300	2.72721900	1.54128000
H	0.12703500	3.37756200	2.24542300
H	1.30714400	3.31365600	0.90544200
H	1.19831800	1.96440700	2.09983400
C	0.55638300	3.59944700	-3.83383500
H	1.02858300	4.15526500	-3.02698100
H	0.06951500	4.28129200	-4.53632300
H	1.28642600	2.98160200	-4.36319000
S	-1.07378200	-4.52240800	2.21212300
O	0.18079300	-4.00784000	2.83436700
O	-0.91714700	-4.76155600	0.74781800
O	-2.28008300	-3.69813300	2.53437600
C	-1.39371900	-6.12880500	2.95347400
C	2.85374600	2.51161500	-1.26048900
C	4.04816700	2.98666600	-0.83838300
C	4.60828700	2.64135500	0.43247600
H	4.62068300	3.66304500	-1.46936400
C	5.81463600	3.24964500	0.89382900
C	4.00805800	1.66573100	1.25586100
C	4.52954800	1.30455200	2.48027500
C	5.70673200	1.93438700	2.92194500
C	6.34816800	2.90475500	2.12957400
H	1.80035900	-1.28406100	0.95888200
H	0.43131900	-2.39739700	0.99800800
H	0.18310900	-0.72658000	1.45304800
H	7.25289100	3.35661100	2.51410000

H	3.11521300	1.17542900	0.88935100
H	3.05503100	-4.09685900	-2.89833800
H	-2.31056200	-6.53053000	2.51828000
H	-1.50866900	-5.99437700	4.03049400
H	-0.54774000	-6.78349400	2.73591900
O	6.38538700	4.13598100	0.04668300
O	6.31209400	1.65455200	4.09474100
C	5.72029400	0.66244800	4.93834600
H	6.34236000	0.63478500	5.83369500
H	5.73522400	-0.31932100	4.44863500
H	4.68874800	0.91566400	5.19732200
C	7.63442100	4.74104200	0.39793300
H	8.36882800	3.95286900	0.60372400
H	7.50710500	5.33861100	1.31085700
H	0.78113400	-4.48432600	0.05549400
N	5.56545300	1.15471200	-3.69598300
N	-6.48475700	5.10048900	-0.85928600
O	-6.44511100	5.68014400	-1.94754100
O	5.85255200	2.35078300	-3.77229200
O	-6.13436900	5.60789200	0.20734200
O	4.84511000	0.56001200	-4.50190700
H	4.02714600	0.55999800	3.07965900
C	1.14916200	-4.38602400	-1.93526000
C	-0.23627800	-4.47459400	-2.15350300
H	-0.90034900	-4.62491900	-1.31247300
C	8.05390300	5.61267200	-0.77462400
H	7.22631000	6.29576000	-1.00083200
H	8.18825100	4.97631900	-1.65965100
C	9.33617800	6.42265800	-0.51744800
H	9.17193000	7.03974000	0.37905000
C	10.55318900	5.52217800	-0.26029400
H	10.43529200	4.90838400	0.63966500
H	10.72043900	4.84601600	-1.10866600
H	11.46007500	6.12309800	-0.13015700
C	9.60325500	7.36562900	-1.69737500
H	8.75450800	8.03634300	-1.87229900
H	10.49081400	7.98195300	-1.51555100
H	9.77479900	6.79539900	-2.61902700
C	-8.03733200	-1.11804200	-2.13053200
H	-8.30196100	-2.17343900	-2.01619600
H	-8.67771400	-0.70272800	-2.91452600
H	-6.99429900	-1.04856600	-2.43748000
H	6.74844700	-0.88817400	1.89201600

Conformation II

ΔE: 0.35 kcal/mol

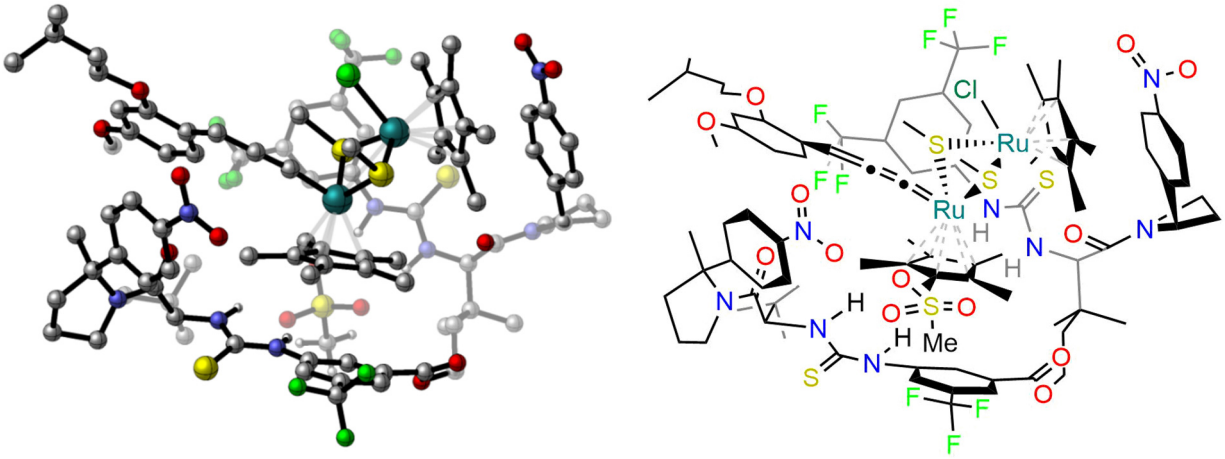


Table S22 Comparison of ROESY-derived interatomic hydrogen distances to computed distances corresponding to conformation II of the **5c**–**4e** complex.

hydrogen pair	ROESY-derived distance (Å)	computed distance (Å)	violation (Å)
H_1–H_{10}	2.99 ± 0.30	2.86	0.00
H_{17}–$H_{16'}$	2.22 ± 0.22	2.38	0.00
H_{17}–$H_{15'}$	2.70 ± 0.27	2.76	0.00
$H_{1'}$–$H_{10'}$	3.04 ± 0.30	2.89	0.00
$H_{10'}$–$H_{11'}$	2.17 ± 0.22	2.23	0.00
$H_{10'}$–$H_{12'}$	2.15 ± 0.21	2.46	0.09
Me_2–$H_{12'}$	2.64 ± 0.26	2.67	0.00

Me_2'–H_{12}'	2.85 ± 0.28	4.52	1.38
H_8–OMs	4.61 ± 0.46	5.68	0.61
H_1–OMs	4.21 ± 0.42	4.83	0.20
t-Bu–OMs	4.94 ± 0.49	5.05	0.00

Charge: 0
Multiplicity: 1

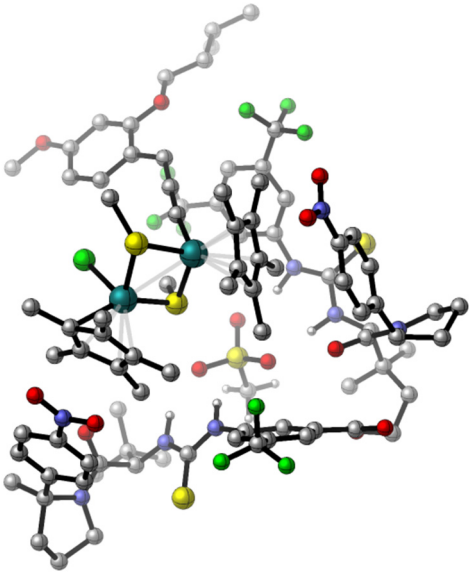
Ru	-0.11247100	-1.13370000	-1.51559900
N	-1.20960100	4.42561800	-0.94473000
N	-2.74643100	4.26155300	0.69386800
N	3.06318500	1.33770400	3.12692300
N	4.64632500	2.32781000	1.84122500
N	-6.20007700	3.33011700	0.84442900
N	7.71909000	1.01554400	0.47863200
C	1.13611300	3.92748600	-4.40510300
C	1.69403700	4.26511100	-3.17104800
C	0.87990400	4.45929900	-2.05603100
C	-0.51216600	4.30156200	-2.15030200
C	-1.08098900	3.99038400	-3.39369300
C	-0.24928000	3.81333500	-4.50031600
C	3.17611600	4.33404200	-3.03185800
C	-2.54340700	4.42283600	-0.63355200
C	-4.02183500	4.41428500	1.36572900
C	-3.78431500	4.72288300	2.88296000
C	-5.14809300	4.80782400	3.59011800
C	-3.07995100	6.08886200	2.99142900
C	-2.92792900	3.64546200	3.57538300
C	-1.40088900	0.19080600	4.60965400
C	0.03378300	-0.22310700	4.47647300
C	2.69095300	-0.94782600	4.05560400
C	1.77213700	-1.85567400	4.57599700
C	0.43532000	-1.51751200	4.78812600
C	4.38176700	1.34603300	2.73591000
C	5.97128200	2.58236500	1.29851800
C	5.99449400	3.93973800	0.50422000
C	7.40823200	4.18555200	-0.05115000
C	5.65066000	5.06542300	1.49986500
C	4.97045700	3.88779700	-0.65143100
C	4.88757300	5.11460300	-1.56055200
C	6.42423700	1.42087500	0.39226600
C	-4.88950000	3.15229900	1.17531100
C	-6.81693100	4.58148900	0.36747100
C	-8.07935800	4.10258000	-0.35267900
C	-8.48711500	2.87448900	0.46144700
C	-7.14281100	2.17934300	0.81564300
C	8.68410900	1.30652700	1.55128600
C	9.84492100	0.35200400	1.24333100
C	9.79307900	0.22381400	-0.28502200
C	8.27635300	0.16840600	-0.58329900
C	2.19878400	-3.25220800	4.93096500
C	-0.84752600	3.51622800	-5.84679700
C	-6.77188800	1.18490200	-0.28812500
C	-7.22158500	-0.14306500	-0.23348200
C	-6.03359000	1.59613400	-1.40629200
C	-5.71108600	0.70277400	-2.42117600
C	-6.13378400	-0.61967900	-2.31311500
C	7.75102700	-1.25439400	-0.59784700
C	7.76922600	-1.96042400	-1.80892600
C	7.30978400	-1.90004100	0.56230600
C	7.34373300	-3.28048000	-1.87529800
C	6.89532800	-3.22800900	0.51842200
C	6.90896600	-3.89715800	-0.70304600
C	-6.90696900	-1.05008900	-1.23790400
O	3.95792800	3.67455300	-3.69058300
O	3.53470100	5.20368700	-2.06629500
O	-4.41828100	2.03286200	1.38926700
O	5.67400800	0.95939400	-0.47093800
F	1.45744100	-4.17302400	4.26010400
F	2.02550500	-3.50907000	6.24570500
F	3.49394200	-3.49204000	4.63918300
F	-0.71000500	4.55538100	-6.69786600
F	-2.16591600	3.22681100	-5.77831900
F	-0.23799900	2.45410900	-6.43688800
F	-1.54449800	1.36373500	5.25674000
F	-1.97604200	0.35991000	3.38123400
F	-2.15446500	-0.72779300	5.25830200
S	5.59094800	0.31907700	3.32104800
S	-3.81400600	4.63590100	-1.73124800
H	1.77903000	3.75694400	-5.26062200
H	1.33664600	4.68760900	-1.09900300
H	-2.15110900	3.88960300	-3.48951200
H	-0.59581800	4.53858000	-0.13230800
H	-1.92618500	4.13570800	1.27898400
H	-4.52360500	5.28024600	0.93123400
H	-5.00536400	5.12200900	4.62954400
H	-5.80726000	5.54013000	3.10945200
H	-5.66022800	3.84064600	3.60185500
H	-3.67934900	6.88154500	2.52734600
H	-2.93554600	6.34811700	4.04663100
H	-2.09605700	6.07486100	2.51402600
H	-1.88722600	3.65372000	3.23480300
H	-3.33133700	2.64626300	3.40806400
H	-0.26703500	-2.24245300	5.17990800
H	3.85857300	2.86267100	1.47496700
H	6.66363100	2.67967700	2.13841100
H	7.44647000	5.15690400	-0.55532100
H	8.15513600	4.20820800	0.75002800
H	7.70280600	3.42276700	-0.77848100
H	5.76909300	6.04896800	1.03369600
H	4.61974700	4.98363600	1.84993700

H	6.31779300	5.03087100	2.36883400
H	3.97336000	3.78831900	-0.22769900
H	5.15104400	3.00530700	-1.26508700
H	5.58355900	5.06864800	-2.40111000
H	5.02510600	6.05468000	-1.02433400
H	-7.07336700	5.23332000	1.21291200
H	-6.13292800	5.10889000	-0.29929200
H	-7.83749400	3.81835900	-1.38191300
H	-8.85486300	4.87258100	-0.38687700
H	9.01890700	2.34935000	1.50290100
H	8.22284200	1.12681300	2.52569100
H	9.66612100	-0.62233900	1.71009900
H	10.80198900	0.73138000	1.61088800
H	-2.90278600	3.83897700	4.65354800
H	-9.16018400	2.19578700	-0.06827200
H	-8.98095900	3.18577900	1.39005800
H	-7.79305100	-0.49429200	0.61677100
H	-5.64897400	2.60763900	-1.46234700
H	-5.11032200	1.01032400	-3.26732600
H	10.22174900	1.11632000	-0.75545500
H	10.32095200	-0.65261100	-0.66846300
H	8.10334400	-1.46071000	-2.71414600
H	7.23606100	-1.34640200	1.49202400
H	7.33300600	-3.83163300	-2.80674200
H	6.53765100	-3.73805400	1.40358500
H	-7.21507400	-2.08511700	-1.18582400
Ru	1.65425100	-3.24233000	-1.03735500
C	-1.74485100	-2.08447500	-1.28134200
S	0.67337100	-1.88213900	0.58980900
S	0.60872000	-2.70875100	-3.09201100
Cl	-0.00156400	-4.97566200	-0.57765500
C	-1.26504900	0.80456500	-1.56558200
C	-0.77919600	0.47703200	-2.88155300
C	0.66643000	0.64881800	-2.87720200
C	1.06437600	0.96657800	-1.55826700
C	-0.12765900	1.03508900	-0.73819700
C	-2.69682400	0.96634300	-1.18515500
H	-3.09614300	1.87357300	-1.65089700
H	-2.83927800	1.07554800	-0.10955700
H	-3.30167200	0.12564800	-1.52703800
C	-1.63923200	0.23085800	-4.08244800
H	-1.09774300	-0.33509800	-4.84520300
H	-1.96211500	1.17560800	-4.53242200
H	-2.53721700	-0.33335100	-3.81757700
C	1.53382700	0.54679300	-4.09204600
H	2.50887100	1.00924700	-3.92158500
H	1.06094400	1.06081500	-4.93207700
H	1.68479600	-0.49742300	-4.39032300
C	2.42821100	1.29958900	-1.04767700
H	2.78152600	0.57282600	-0.31361300
H	2.39847600	2.27095000	-0.54699100
H	3.16671400	1.34770600	-1.84762700
C	-0.14069400	1.42797500	0.70126400
C	3.26632400	-4.82416100	-1.08185700
C	3.32636800	-4.05675400	0.13571100
C	3.69019500	-2.69741500	-0.21100500
C	3.78236000	-2.61664500	-1.63517400
C	3.52875200	-3.93654700	-2.16549500
C	3.05110500	-6.29864800	-1.16582900
H	2.64583600	-6.58806200	-2.13822100
H	4.01046400	-6.80991800	-1.02211200
H	2.34952100	-6.63247600	-0.39940100
C	3.20102600	-4.61197100	1.51653500
H	3.11534800	-3.81012400	2.24797700
H	4.08348100	-5.21400100	1.76566900
H	2.31584000	-5.24785900	1.60403600
C	3.99248200	-1.61761400	0.77647700
H	4.55410800	-0.80259300	0.32175500
H	4.59257300	-2.01278000	1.59837100
H	3.08293700	-1.20502400	1.22234800
C	4.23088400	-1.45160100	-2.46076500
H	3.47260300	-1.16674500	-3.19369500
H	4.46902700	-0.58549400	-1.84443700
H	5.13860800	-1.71856700	-3.01412300
C	3.64669700	-4.31658800	-3.60636800
H	2.98956900	-5.15393400	-3.85399500
H	4.67798200	-4.62911100	-3.81517800
H	3.39712700	-3.47860600	-4.26160300
C	-0.61343700	-2.66235400	1.62496900
H	-0.09395800	-3.24842100	2.38582300
H	-1.26015800	-3.30422600	1.03397000
H	-1.17079900	-1.85480300	2.10407400
C	-0.71698900	-3.84962400	-3.62317800
H	-1.13866800	-4.36525100	-2.76335700
H	-0.26929600	-4.56499800	-4.31828100
H	-1.47927700	-3.25908300	-4.13763400
S	1.35094200	4.54571700	2.13486000
O	2.30186000	4.07083800	1.08216300
O	1.38893000	3.69684000	3.35626700
O	-0.03214600	4.75895100	1.59502700
C	1.90361400	6.18400100	2.62892600
C	-2.89090000	-2.55575800	-1.08638900
C	-4.08996900	-3.00081800	-0.64365200
C	-4.66868000	-2.56895300	0.59130100
H	-4.65865500	-3.71560500	-1.23400600
C	-5.89567800	-3.13062000	1.05906900
C	-4.07190300	-1.55442600	1.36840700
C	-4.61553400	-1.12225100	2.55958800
C	-5.80618100	-1.71465000	3.01527000
C	-6.45193000	-2.70962600	2.26086700
H	-1.04181100	1.08288000	1.21003800
H	-0.09822200	2.51538300	0.79385400
H	0.72518600	1.01903900	1.22462100
H	-7.36695000	-3.13482600	2.65194300
H	-3.16762600	-1.09276100	0.99219300
H	3.71954000	-1.23616400	3.90698700
H	1.21063200	6.56526300	3.38091700
H	1.90461000	6.82751600	1.74722000
H	2.90950900	6.10225500	3.04444300
O	-6.45518100	-4.06033100	0.25536200
O	-6.41414000	-1.37473200	4.17191900
C	-5.75287300	-0.44741500	5.03557300

H	-6.36490900	-0.40130700	5.93680900
H	-5.69622400	0.54624800	4.57834600
H	-4.74352800	-0.78965500	5.28543900
C	-7.78342900	-4.52246200	0.52247700
H	-8.43996600	-3.65545700	0.66550600
H	-7.78953900	-5.11372600	1.44835900
H	2.54845600	2.21126900	2.97817000
N	6.42285500	-5.27390400	-0.76927000
N	-5.70872100	-1.59446700	-3.31571400
O	-6.12708800	-2.75058400	-3.21179000
O	6.32970800	-5.79949400	-1.88123900
O	-4.94106000	-1.21335100	-4.20155500
O	6.12297700	-5.83337700	0.28665600
H	-4.13611300	-0.32414300	3.10347800
C	2.27162100	0.35394300	3.73249700
C	0.93332500	0.71021800	3.97007400
H	0.60603700	1.72005100	3.75002100
C	-8.20518700	-5.36116400	-0.67339400
H	-7.46150600	-6.15596200	-0.80785400
H	-8.15972900	-4.73485700	-1.57440100
C	-9.60603100	-5.98118100	-0.53605900
H	-9.62349000	-6.58072400	0.38696100
C	-10.70702100	-4.91545300	-0.43405000
H	-10.59951700	-4.28799800	0.45779000
H	-10.68984200	-4.25706600	-1.31215300
H	-11.69694200	-5.38282300	-0.38779100
C	-9.87677200	-6.92293400	-1.71623200
H	-9.11676300	-7.70968900	-1.78129100
H	-10.85631900	-7.40445800	-1.61934600
H	-9.86745200	-6.36973300	-2.66375000
C	-7.22772200	1.51621500	2.19736800
H	-7.37750700	2.29132200	2.95534600
H	-8.07641500	0.82858600	2.25495700
H	-6.31134300	0.97139900	2.41371900
H	8.03942200	0.62113800	-1.55132200

Conformation III

ΔE: 7.07 kcal/mol



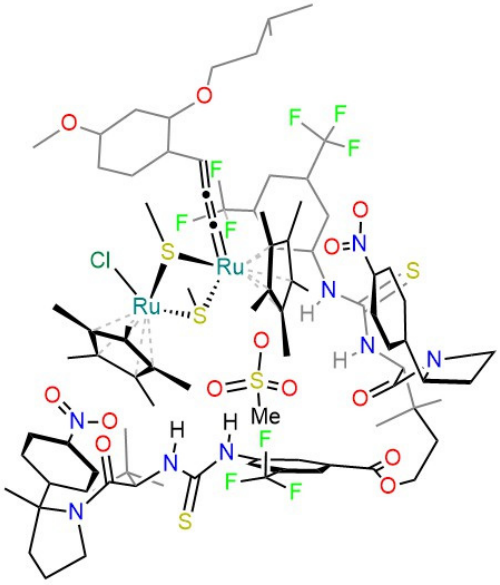


Table S23 Comparison of ROESY-derived interatomic hydrogen distances to computed distances corresponding to conformation III of the **5c**–**4e** complex.

hydrogen pair	ROESY-derived distance (Å)	computed distance (Å)	violation (Å)
H_1–H_{10}	2.99 ± 0.30	2.90	0.00
H_{17}–H_{16}'	2.22 ± 0.22	2.36	0.00
H_{17}–H_{15}'	2.70 ± 0.27	2.73	0.00
H_1'–H_{10}'	3.04 ± 0.30	2.94	0.00
H_{10}'–H_{11}'	2.17 ± 0.22	2.12	0.00
H_{10}'–H_{12}'	2.15 ± 0.21	2.51	0.14

Me_2–H_{12}'	2.64 ± 0.26	3.51	0.59
Me_2'–H_{12}'	2.85 ± 0.28	5.29	2.15
H_8–OMs	4.61 ± 0.46	5.49	0.42
H_1–OMs	4.21 ± 0.42	3.72	–0.07
t-Bu–OMs	4.94 ± 0.49	3.62	–0.83

Charge: 0
Multiplicity: 1

C	3.48601900	4.75963600	0.56073500
C	2.90810500	4.75581500	-0.70900600
C	2.93319200	3.59591200	-1.48731900
C	3.56847000	2.45000700	-1.02139100
C	4.17186600	2.45107500	0.23907200
C	4.11191900	3.60110200	1.02703700
N	3.52925100	1.29380400	-1.83376200
C	2.32171800	6.00950000	-1.25194800
O	2.14792400	7.03761500	-0.61994700
O	2.05481700	5.88161400	-2.56553100
C	4.60013700	0.59013800	-2.29824300
N	4.24697800	-0.45147600	-3.08637900
C	5.19019600	-1.33097800	-3.74901900
C	4.52408100	-2.01143400	-4.98937000
C	5.52527300	-2.99511000	-5.62103400
C	4.19372100	-0.91129100	-6.01298200
C	3.23884200	-2.77939700	-4.62267200
C	-4.24577600	-2.73895100	-3.09350400
C	-4.57132800	-1.38905200	-2.51861000
C	-3.75612200	-0.31349000	-2.85588000
C	-3.98508500	0.95615600	-2.29681900
C	-5.04545200	1.11372000	-1.38884400
C	-5.84361700	0.01876600	-1.06480700
C	-5.62924700	-1.24029800	-1.62561200
N	-3.07223800	1.95557600	-2.65756100
C	-3.05106800	3.30484900	-2.42319400
N	-1.86762900	3.86686200	-2.79653900
C	-1.57223500	5.26958600	-2.56519000
C	-0.80212000	5.92564700	-3.78254300
C	-1.90418200	6.43264800	-4.73593500
C	0.03829800	4.89277500	-4.55211400
C	0.05535100	7.15421500	-3.32817300
C	1.57739100	7.02177000	-3.29716300
C	-0.90589000	5.39171400	-1.18991700
C	5.73122300	-2.37143200	-2.74940100
O	4.95261200	-3.04195500	-2.06676800
N	7.07654700	-2.54751800	-2.66893800
C	8.11069200	-1.81212900	-3.41647900
C	9.36593500	-2.66558600	-3.22176400
C	9.16892100	-3.24901900	-1.82014000
C	7.64752200	-3.55959000	-1.73778500
O	-0.09265200	4.55816800	-0.78843600
N	-1.27370500	6.45458700	-0.42462700
C	-2.32390200	7.45123400	-0.71031300
C	-2.35539200	8.31786400	0.56034600
C	-0.94933100	8.14636000	1.15272900
C	-0.63612700	6.66072800	0.87846500
C	-6.99054000	0.19901900	-0.11004800
F	-8.18447700	0.21037600	-0.75393600
F	-6.90482500	1.34363000	0.59460100
F	-7.06123500	-0.81739600	0.79203500
C	4.66421000	3.56852500	2.42226200
F	3.69448900	3.27007900	3.33768300
F	5.18002000	4.75733000	2.79634600
F	5.62761300	2.63460900	2.57411400
H	3.46219600	5.66431900	1.15710700
H	2.45385200	3.57712400	-2.45371600
H	4.68052400	1.56595200	0.59237100
H	2.60508000	1.00673800	-2.16185400
H	3.25168900	-0.63664000	-3.18985500
H	6.00800700	-0.70326000	-4.10476500
H	5.08627900	-3.44296200	-6.51902700
H	6.45085400	-2.49229400	-5.92487000
H	5.78265000	-3.80962700	-4.93628200
H	5.09905700	-0.38309200	-6.33546100
H	3.72098200	-1.34824700	-6.90005600
H	3.50555300	-0.17435800	-5.59156700
H	2.43738400	-2.11744800	-4.27918300
H	3.42901800	-3.51685700	-3.84025000
H	-2.92537400	-0.45371700	-3.53693800
H	-5.23403800	2.07881000	-0.94580000
H	-6.25254600	-2.08208000	-1.35858400
H	-2.25101100	1.56891600	-3.13957500
H	-1.04335500	3.25183700	-2.80943700
H	-2.53853700	5.76515700	-2.50384400
H	-1.46870400	6.80257900	-5.67171900
H	-2.60347600	5.62496900	-4.97807800
H	-2.47841500	7.24928400	-4.28204500
H	0.57729600	5.38377400	-5.37029600
H	0.75798200	4.38167600	-3.91394200
H	-0.61897300	4.14108500	-4.99754900
H	-0.26266100	7.50217300	-2.34545700
H	-0.13891000	7.98588900	-4.01820200
H	2.01024700	7.92630600	-2.86211900
H	1.98311800	6.87801900	-4.30042500
H	7.84446900	-1.71848700	-4.46987900
H	8.22096600	-0.80397500	-3.00078900
H	10.28261200	-2.07644000	-3.31202900
H	9.40296700	-3.46294700	-3.97222800
H	-2.05851400	8.05251400	-1.58752000
H	-3.27987800	6.95794800	-0.91132400

H	-3.10609800	7.93337300	1.25854100
H	-2.60588600	9.35882600	0.33977900
S	-4.33869300	4.20929900	-1.78834600
S	6.20693300	0.99433600	-1.94240000
F	-5.30020100	-3.58907700	-3.02000500
F	-3.88435300	-2.66120400	-4.39096000
F	-3.21850000	-3.32690200	-2.43704000
H	2.86536600	-3.29918000	-5.51285700
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H	9.76624400	-4.14375400	-1.62491100
C	7.15917200	-3.33624800	-0.30776300
C	6.86583800	-4.40133900	0.55190300
C	7.08665100	-2.02627900	0.19466700
C	6.49272700	-4.17588500	1.87307400
H	6.90473100	-5.42220200	0.19318100
C	6.71953000	-1.78155000	1.51044800
H	7.27069300	-1.18373300	-0.46444800
C	6.41931200	-2.86565900	2.33653100
H	6.64890900	-0.77199800	1.89556300
C	7.34553500	-4.96690200	-2.27641900
H	7.69580600	-5.04344600	-3.30994100
H	7.86065000	-5.73643400	-1.69344200
H	6.27095500	-5.15789600	-2.25696200
H	-0.21912800	8.75761600	0.61124800
H	-0.89310700	8.39716900	2.21496400
C	-1.19955500	5.75732200	1.95594900
C	-0.46307200	5.56809900	3.13422800
C	-2.46335600	5.16560600	1.83636700
C	-0.98506500	4.83668400	4.19263700
H	0.52950100	6.00171500	3.21892100
C	-3.00706900	4.43975200	2.88994200
H	-3.02157200	5.25534100	0.91019000
C	-2.26361200	4.29517700	4.05863600
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H	-3.98827000	3.99020200	2.81571800
H	6.25113600	-4.99344000	2.53983000
N	5.99866800	-2.62520200	3.71250200
N	-2.83421900	3.54529600	5.17018500
O	5.70087500	-3.60089900	4.40724300
O	5.95007900	-1.45860900	4.10975900
O	-3.98435800	3.11649700	5.05176500
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O	-0.97579500	0.41792300	-3.88904800
O	1.34300400	-0.17303900	-3.14117600
C	1.06156800	1.35631900	-5.26483300
H	1.06325500	0.47356700	-5.90651600
H	2.07712300	1.73696600	-5.13652900
H	0.42010300	2.13219300	-5.68537100
Ru	-1.05570300	-0.59574700	2.35356100
Ru	1.10451600	-2.41412000	2.12965100
C	-2.43521200	-1.73145300	1.69742400
S	-0.37159800	-2.21291400	3.93054700
S	0.25648700	-0.99173500	0.44830100
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C	-0.55435700	1.28822300	3.77666800
C	-1.90577000	0.76847100	3.94185100
C	-4.08292200	0.79137000	2.49206900
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H	-4.46441300	-0.07930700	3.02999800
H	-4.30590100	0.65664400	1.43310900
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H	-1.05453300	1.89899000	-0.25764500
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H	-2.65171700	1.14803700	-0.10374500
C	0.75203500	2.38843000	1.78003400
H	1.54364700	2.63051000	2.48823100
H	0.43766100	3.30897600	1.27827200
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C	0.43397100	1.39250600	4.89445600
H	0.66856000	0.40804100	5.31474500
H	0.01248300	2.00058900	5.70332500
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C	-2.48829700	0.24895900	5.22215600
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C	2.77380500	-3.61272500	2.91978800
C	2.81647200	-2.35395900	3.62016200
C	3.05405500	-1.31789300	2.66319900
C	3.21586200	-1.93992200	1.37485200
C	3.23534700	-4.39914700	0.47091100
H	3.64145200	-3.97286000	-0.44694200
H	3.94139800	-5.15796900	0.82703700
H	2.28474900	-4.89662800	0.25566400
C	2.63971100	-4.97315500	3.52373300
H	2.09660100	-4.93428200	4.47172800
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H	2.09509000	-5.63806100	2.84898300
C	2.74877800	-2.16913600	5.10015600
H	2.28388200	-1.21684800	5.36552400
H	3.76917900	-2.17915300	5.50002700
H	2.18025200	-2.96850000	5.58043600
C	3.30418600	0.12320300	2.95451300
H	2.90826100	0.76152600	2.16524600
H	2.84926100	0.42523000	3.89755300
H	4.38077500	0.31109600	3.03797100
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H	-1.83847500	-3.97473800	3.11761200
H	-2.49964000	-3.12236600	4.55914200
C	-0.68918800	-1.78295500	-0.90044600
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H	-5.50827200	-2.50671200	0.95996600
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C	-3.38653700	-5.06002800	0.11480800
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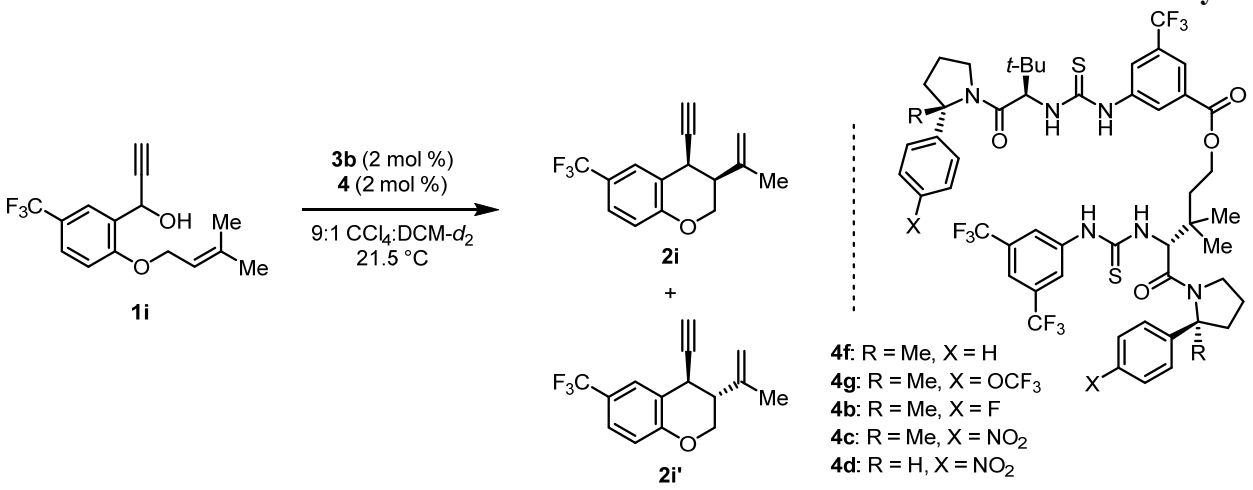
C	-5.78703600	-6.04918400	-0.93014200
H	-2.90913700	1.06087100	5.82362800
H	-1.72521100	-0.25672700	5.81925000
H	-3.28991300	-0.46638900	5.01783400
H	-6.68554100	-6.46826100	-1.36299300
H	-2.45949700	-4.66158500	0.51616900
H	-2.46196700	-6.84579100	-0.59529800
O	-6.86352700	-4.02143100	-0.17947400
O	-4.71456700	-7.96981200	-1.67472300
C	-3.54773100	-8.76827200	-1.85321000
H	-3.87911000	-9.65641100	-2.39217300
H	-3.11777200	-9.06189700	-0.88869200
H	-2.79307700	-8.23777900	-2.44487800
C	-8.06368600	-4.34262700	-0.89729900
H	-8.48976500	-5.27448000	-0.50139400
H	-7.81001300	-4.49565800	-1.95220200
C	-9.01554500	-3.17349400	-0.69942300
H	-9.09934600	-2.98291200	0.37715900
H	-8.57503500	-2.27184600	-1.13891000
C	-10.41318800	-3.39088200	-1.30054400
H	-10.84258200	-4.30110000	-0.85457100
C	-11.31647700	-2.20680600	-0.93206000
H	-10.90375100	-1.26939000	-1.32520400
H	-12.32326400	-2.33303500	-1.34587400
H	-11.40678100	-2.09898300	0.15484200
C	-10.36301100	-3.58138600	-2.82325400
H	-9.89333600	-2.71444400	-3.30533400
H	-9.79574000	-4.47298600	-3.11288500
H	-11.37265400	-3.68594300	-3.23590700
H	0.43645300	6.49326200	0.78245900

Kinetic experiments

General considerations

Kinetic experiments were performed using ^{1}H NMR spectroscopy on an INOVA-600 NMR spectrometer (600 MHz). Reactions were conducted at 21.5 ± 0.1 °C and were monitored over a period of 13–25 minutes. Spectra containing of one scan were collected at fixed 15 s intervals with 1.2 s acquisition time and 13.8 s relaxation delay. The NMR spectra were analyzed using MestReNova software after applying phase and baseline corrections. Chemical shifts were referenced to the residual protium in dichloromethane-d_2. Extracted data were analyzed and plotted using Microsoft Excel software. A least-squares algorithm was used to fit concentration versus time data to linear functions in order to obtain initial rate values.

Examination of the arene interaction and its effect on reaction rate and enantioselectivity



Procedure for kinetic experiments

Stock solutions of hydrogen-bond donors **4f**, **4g**, **4b**, **4c**, and **4d** in a mixture of dichloromethane-d_2 and tetrachloromethane were prepared by weighing the respective amount of a hydrogen-bond donor and dissolving in dichloromethane-d_2, followed by addition of tetrachloromethane:

4f: m_{4f} = 14.3 mg, n_{4f} = 13.3 μmol, V(DCM-d_2) = 946 μL, V(CCl_4) = 3.79 mL
4g: m_{4g} = 14.9 mg, n_{4g} = 11.9 μmol, V(DCM-d_2) = 853 μL, V(CCl_4) = 3.41 mL
4b: m_{4b} = 15.0 mg, n_{4b} = 13.5 μmol, V(DCM-d_2) = 961 μL, V(CCl_4) = 3.84 mL
4c: m_{4c} = 14.1 mg, n_{4c} = 12.1 μmol, V(DCM-d_2) = 861 μL, V(CCl_4) = 3.45 mL
4d: m_{4d} = 14.6 mg, n_{4d} = 12.8 μmol, V(DCM-d_2) = 914 μL, V(CCl_4) = 3.66 mL.

A stock solution of propargylic alcohol **1i** was prepared by weighing **1i** (93.2 mg, 0.33 mmol) and dissolving in a mixture of dichloromethane-d_2 (468 μL) and tetrachloromethane (8.90 mL). A stock solution of mesitylene standard was prepared by addition of mesitylene (15 μL, 0.107 mmol) to tetrachloromethane (2.76 mL). A stock solution of methyl *tert*-butyl ether (MTBE) standard was prepared by addition of MTBE (15 μL, 0.126 mmol) to tetrachloromethane (1.60 mL). A stock solution of the ruthenium tosylate complex **3b** was prepared by weighing **3b** (9.2 mg, 11.6 μmol) and dissolving in dichloromethane-d_2 (4.15 mL).

An oven-dried 5mm NMR tube filled with nitrogen gas, capped with a rubber septum, and sealed with parafilm was charged with the stock solution of substrate **1i** (200 µL, 7.00 µmol), the stock solution of mesitylene (30 µL, 1.17 µmol), the stock solution of MTBE (30 µL, 2.33 µmol), a stock solution of a hydrogen-bond donor (50 µL, 0.14 µmol), and tetrachloromethane (340 µL). The NMR tube was inverted several times. The solution of the ruthenium complex **3b** (50 µL, 0.14 µmol) was added to initiate the reaction. The NMR tube was inverted several times before inserting into the NMR probe. The time delay between addition of the stock solution of **3b** and the beginning of data acquisition was factored into kinetic models. Experiments were conducted in duplicate or triplicate.

It is assumed that reactions promoted by hydrogen-bond donors **4f**, **4g**, **4b**, **4c**, and **4d** obey the same rate law. The initial rate constants were calculated using the concentration values of product **2i** corresponding to up to 5% combined yield of product **2i** and the minor product diastereomer **2i′**. The ratio of concentrations of diastereomeric products **2i** and **2i′** was found to be constant over the monitored time in reactions promoted by the five hydrogen-bond donors examined.

Concentration of the major product **2i** was determined by integration of the two signals corresponding to the terminal alkene protons of product **2i** at δ = 4.76 ppm (1H) and δ = 5.03 ppm (1H) and the signal corresponding to the mesitylene standard at δ = 6.72 ppm (3H). The average value of the areas corresponding to the product signals was divided by one third of the area of the signal corresponding to the mesitylene standard, which represented three hydrogen atoms of mesitylene, and was multiplied by concentration of mesitylene (1.67 mM). Concentration of the minor product diastereomer **2i′** was determined by integration of the two signals corresponding to the terminal alkene protons of product **2i′** at δ = 4.92 ppm (1H) and δ = 5.07 ppm (1H) and the signal corresponding to the mesitylene standard at δ = 6.72 ppm (3H). The average value of the areas corresponding to the product signals was divided by one third of the area of the signal corresponding to the mesitylene standard, which represented three hydrogen atoms of mesitylene, and was multiplied by concentration of mesitylene (1.67 mM).

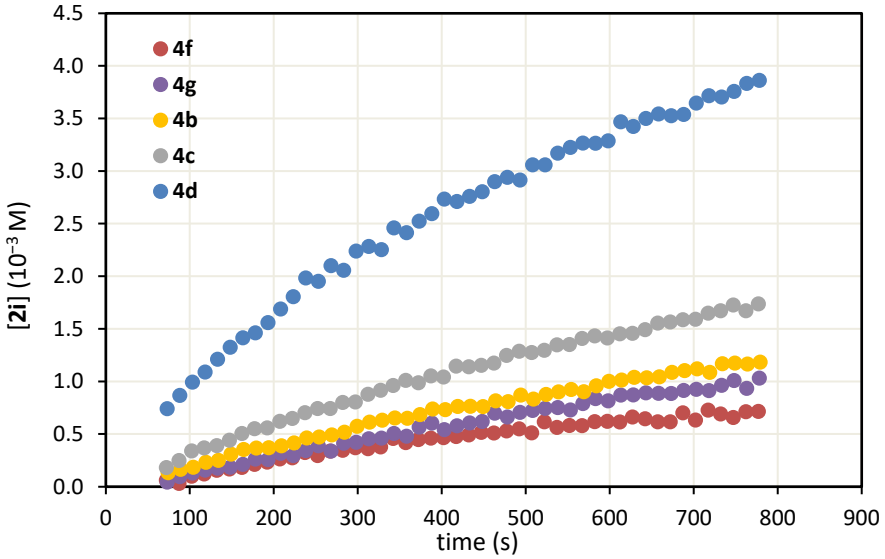


Figure S29 Representative kinetic traces of reactions catalyzed by hydrogen-bond donors **4f**, **4g**, **4b**, **4c**, and **4d**.

Rate of formation of product **2i** was found to be correlated with enantioselectivity in reactions catalyzed by the five hydrogen-bond donors selected (**4f**, **4g**, **4b**, **4c**, **4d**) (Table S24, Figure S30).

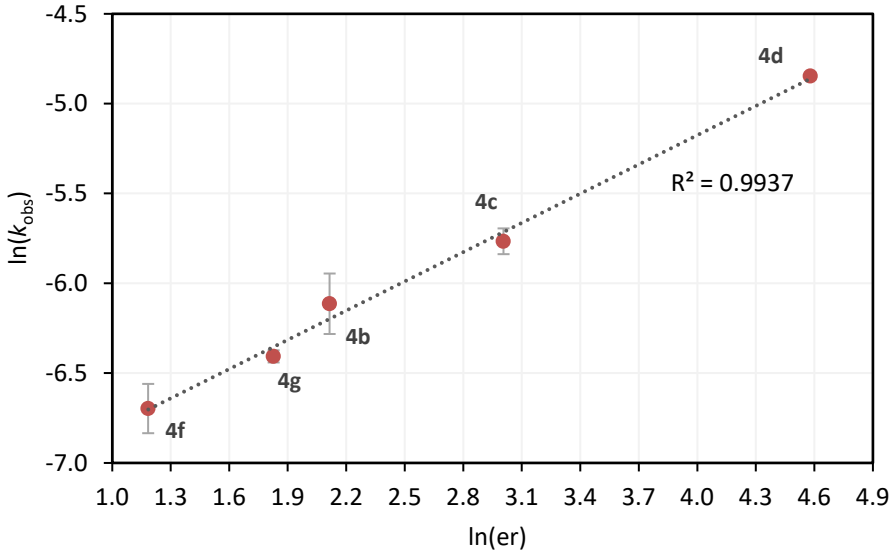


Figure S30 Correlation between rate and enantioselectivity of reactions catalyzed by hydrogen-bond donors **4f**, **4g**, **4b**, **4c**, and **4d**.

Table S24 Initial-rate constants determined in individual kinetic experiments.

4	ln(er)	run	k_{obs} (10^{-3} M s^{-1})	ln(k_{obs})	k_{maj} (10^{-3} M s^{-1})	ln(k_{maj})	k_{min} (10^{-3} M s^{-1})	ln(k_{min})
4f	1.18	1	1.120	−6.794	0.858	−7.061	0.262	−8.246
		2	1.360	−6.600	1.041	−6.867	0.319	−8.052
4g	1.83	1	1.678	−6.390	1.446	−6.539	0.232	−8.367
		2	1.588	−6.445	1.368	−6.594	0.220	−8.422
		3	1.689	−6.384	1.455	−6.533	0.234	−8.360
4b	2.11	1	2.492	−5.995	2.224	−6.109	0.268	−8.223
		2	1.964	−6.233	1.753	−6.347	0.211	−8.461
4c	3.01	1	3.336	−5.703	3.179	−5.751	0.157	−8.757
		2	3.177	−5.752	3.027	−5.800	0.150	−8.806
		3	2.898	−5.844	2.761	−5.892	0.137	−8.898
4d	4.58	1	7.756	−4.859	7.677	−4.870	0.079	−9.449
		2	7.956	−4.834	7.875	−4.844	0.081	−9.424

Table S25 Reaction characteristics and average initial-rate constants of reactions catalyzed by hydrogen-bond donors **4f**, **4g**, **4b**, **4c**, and **4d** (std. dev. = standard deviation).

HBD	ee (%)	dr	k_{obs} (10^{-3} M s^{-1})	std. dev. (10^{-3} M s^{-1})	$(k_{obs})_{rel}$	$\ln(k_{obs})$	std. dev.	$\ln(k_{maj})$	$\ln(k_{min})$
4f	53	3:1	1.240	0.170	1	−6.697	0.137	−6.964	−8.149
4g	72	5:1	1.652	0.055	1.3±0.2	−6.406	0.034	−6.555	−8.383
4b	78	7:1	2.228	0.373	1.8±0.4	−6.114	0.168	−6.228	−8.342
4c	91	12:1	3.137	0.222	2.5±0.4	−5.766	0.071	−5.814	−8.821
4d	98	30:1	7.856	0.141	6.3±0.9	−4.847	0.018	−4.857	−9.436

Initial-rate constants corresponding to the formation of the major and the minor enantiomers of product **2i** were derived from initial-rate constants of formation of product **2i** using the following equation:

$$k_{obs} = k_{major_asymm} + k_{major_rac} + k_{minor_asymm} + k_{minor_rac}$$

where k_{obs} is the initial-rate constant corresponding to formation of product **2i**, k_{major_asymm} is the initial-rate constant of formation of the major enantiomer via a pathway promoted by a hydrogen-bond donor, k_{major_rac} is the initial-rate constant of formation of the major enantiomer via pathway not involving the hydrogen-bond donor, k_{minor_asymm} is the initial-rate constant of formation of the minor enantiomer via a pathway promoted by a hydrogen-bond donor, and k_{minor_rac} is the initial-rate constant of formation of the minor enantiomer via a pathway not involving the hydrogen-bond donor.

The contribution of the racemic pathway to the overall reaction was assessed in the following experiment. The reaction rate and enantioselectivity of reactions catalyzed by a 1:1 mixture of ruthenium complex **3b** and hydrogen-bond donor **4f** or **4c** were compared to outcomes of reactions catalyzed by a 1:2 mixture of the ruthenium complex **3b** and hydrogen-bond donor **4f** or **4c**, respectively (Table S26). The initial-rate constants were determined following a similar procedure as described on page S103.

Table S26 Reaction characteristics and average initial-rate constants for reactions catalyzed by ruthenium complex **3b** and hydrogen-bond donor **4f** or **4c** in a 1:1 or a 1:2 ratios.

4	**3b**:**4**	ee (%)	dr	average k_{obs} (10^{-3} M s^{-1})	std. dev. (10^{-3} M s^{-1})	$(k_{obs})_{rel_1:2/1:1}$
4f	1:1	54	3:1	1.597	0.010	1
4f	1:2	55	3:1	1.555	0.215	1.0 ± 0.1
4c	1:1	90	12:1	3.124	0.168	1
4c	1:2	90	12:1	3.393	0.327	1.1 ± 0.1

The rate and enantioselectivity were found to be the same within the range of an experimental error for the reactions containing a 1:1 mixture of **3b** and a hydrogen-bond donor and a 1:2 mixture of

3b and the hydrogen-bond donor for both hydrogen-bond donors examined. Based on these data, initial-rate constants k_{major_rac} and k_{minor_rac} were considered equal zero. Rate of formation of product **2i** can be then expressed by equation:

$$k_{obs} = k_{major_asymm} + k_{minor_asymm}$$

Initial rate constants of formation of the individual enantiomers of product **2i** can be then calculated using the following equations:

$$k_{major_ent_asymm} = \left(\frac{er}{1+er}\right) k_{obs}$$

$$k_{minor_ent_asymm} = \left(\frac{1}{1+er}\right) k_{obs}$$

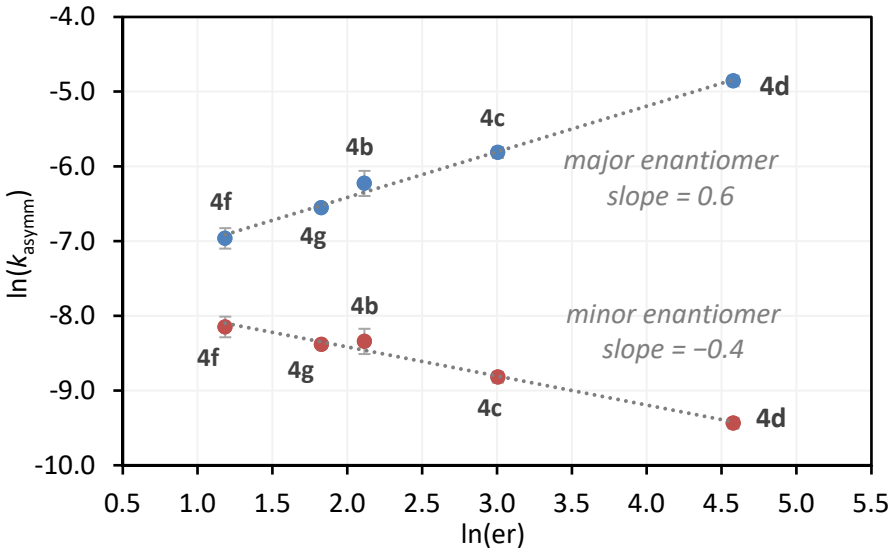
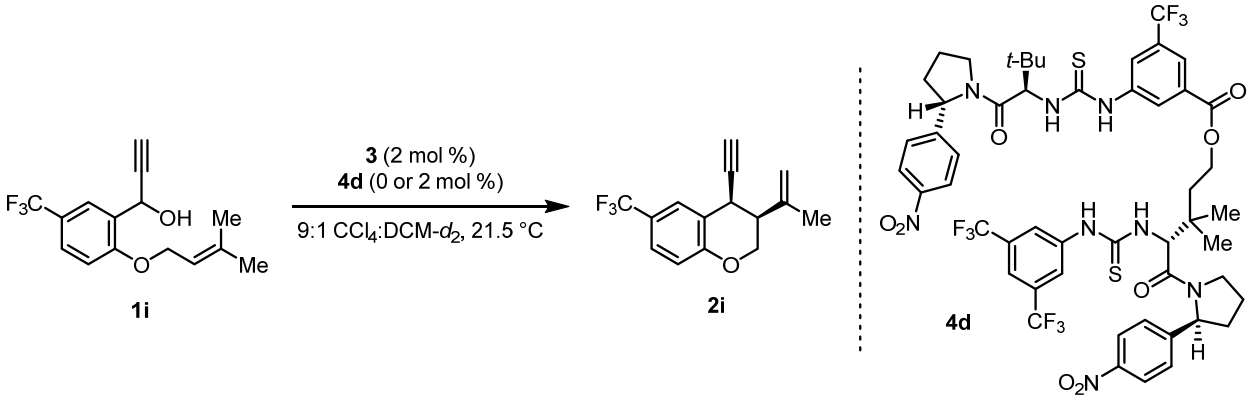


Figure S31 Correlation between rates corresponding to the two enantiomeric pathways and enantioselectivity.

Effect of the anion of the ruthenium complex on reaction rate in the presence of 4d



Procedure for kinetic experiments

Stock solutions of hydrogen-bond donors **4d** in a mixture of dichloromethane-d_2 and tetrachloromethane were prepared by weighing **4d** (14.6 mg, 12.8 μmol) and dissolving in dichloromethane-d_2 (914 μL), followed by addition of tetrachloromethane (3.66 mL). A stock solution of propargylic alcohol **1i** was prepared by weighing **1i** (93.2 mg, 0.33 mmol) and dissolving in a mixture of dichloromethane-d_2 (468 μL) and tetrachloromethane (8.90 mL). A stock solution of mesitylene standard was prepared by addition of mesitylene (15 μL, 0.107 mmol) to tetrachloromethane (2.76 mL). A stock solution of methyl *tert*-butyl ether (MTBE) standard was prepared by addition of MTBE (15 μL, 0.126 mmol) to tetrachloromethane (1.60 mL). A stock solution of the ruthenium tosylate complex **3b** was prepared by weighing **3b** (9.2 mg, 11.6 μmol) and dissolving in dichloromethane-d_2 (4.15 mL). A stock solution of the ruthenium BAr^F_4 complex **3c** was prepared by weighing **3c** (6.2 mg, 4.18 μmol) and dissolving in dichloromethane-d_2 (1.49 mL).

An oven-dried 5mm NMR tube filled with nitrogen gas, capped with a rubber septum, and sealed with parafilm was charged with the stock solution of substrate **2i** (200 μL, 7.00 μmol), the stock solution of mesitylene (30 μL, 1.17 μmol), the stock solution of MTBE (30 μL, 2.33 μmol), and the stock solution of a hydrogen-bond donor (50 μL, 0.14 μmol), and tetrachloromethane (340 μL). To determine the reaction rate in the absence of a hydrogen-bond donor, the above procedure was followed with the exception of adding a 4:1 mixture of tetrachloromethane and dichloromethane-d_2 (50 μL) instead of the stock solution of **4d**. The NMR tube was inverted several times. The solution of the ruthenium complex **3b** or **3c** (50 μL, 0.14 μmol) was added to initiate the reaction. The NMR tube was inverted several times before inserting into the NMR probe. The time delay between addition of the stock solution of **3** (**3b** or **3c**) and the beginning of data acquisition was factored into kinetic models. Experiments were conducted in duplicate.

The initial rate constants [Table S27, rows 1 (**3b** + 0 mol % of **4d**), 3 (**3c** + 0 mol % of **4d**), and 4 (**3c** + 2 mol % of **4d**)] were calculated using the concentration values of product **2i** corresponding to up to 5% combined yield of product **2i** and the minor product diastereomer **2i′**. The initial-rate constant for the reaction catalyzed by a 1:1 mixture of **3b** and **4d** [Table S27, row 2 (**3b** + 2 mol % of **4d**)] was calculated using the first five data points collected that corresponded to 7–13% combined yield of diastereomeric products **2i** and **2i′**. Concentration of the major product **2i** was determined by integration of the two signals corresponding to the terminal alkene protons of product **2i** at δ = 4.76 ppm (1H) and δ = 5.03 ppm (1H) and the signal corresponding to the mesitylene standard at δ = 6.72 ppm (3H). The average value of the areas corresponding to the product signals was divided by one third of the area of the signal corresponding to the mesitylene standard, which

represented three hydrogen atoms of mesitylene, and was multiplied by concentration of mesitylene (1.67 mM). Concentration of the minor product diastereomer **2i′** was determined by integration of the two signals corresponding to the terminal alkene protons of product **2i′** at δ = 4.92 ppm (1H) and δ = 5.07 ppm (1H) and the signal corresponding to the mesitylene standard at δ = 6.72 ppm (3H). The average value of the areas corresponding to the product signals was divided by one third of the area of the signal corresponding to the mesitylene standard, which represented three hydrogen atoms of mesitylene, and was multiplied by concentration of mesitylene (1.67 mM).

Table S27 Reaction characteristics and initial-rate constants.

3	**4d** (mol %)	ee (%)	dr	run	k_{obs} (10^{-3} M s^{-1})	average k_{obs} (10^{-3} M s^{-1})	std. dev. (10^{-3} M s^{-1})	$(k_{obs})_{HBD}/(k_{obs})_{no_HBD}$
3b	0	0	6:1	1	0.381	0.393	0.017	1
				2	0.405			
3b	2	98	30:1	1	7.756	7.856	0.141	20.0 ± 0.9
				2	7.956			
3c	0	0	2:1	1	0.204	0.212	0.011	1
				2	0.220			
3c	2	0	2:1	1	0.238	0.235	0.005	1.1 ± 0.1
				2	0.231			

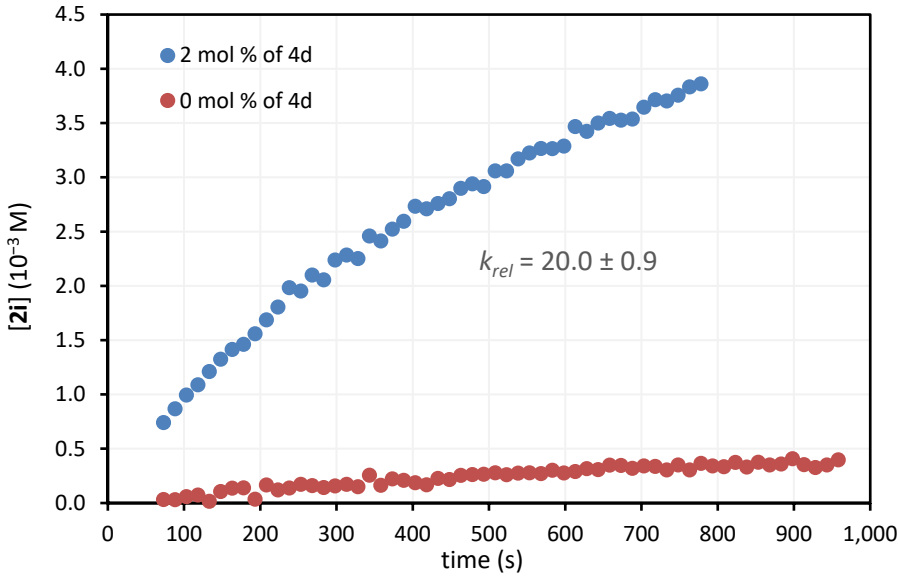


Figure S32 Representative kinetic traces of reactions catalyzed by ruthenium tosylate complex **3b** in the presence or in the absence of the hydrogen-bond donor **4d**.

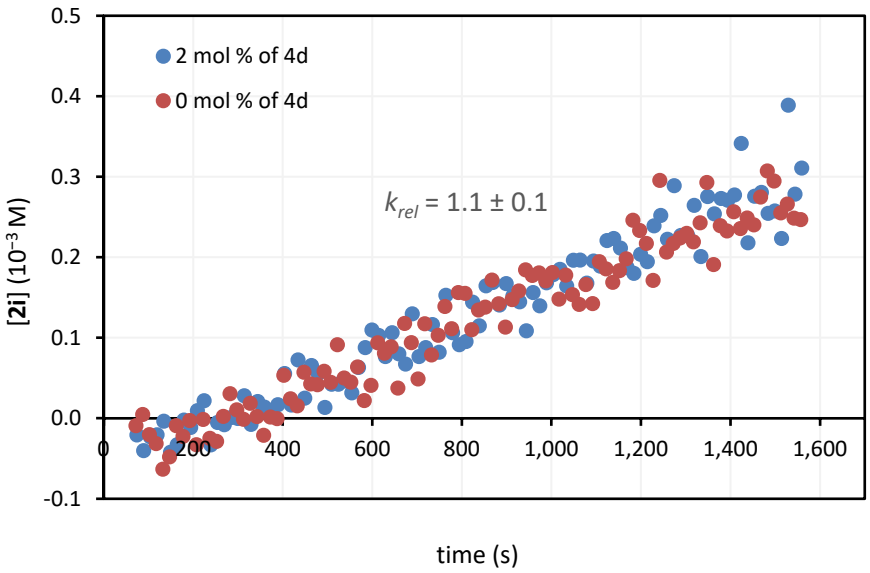


Figure S33 Representative kinetic traces of reactions catalyzed by ruthenium $BAr^F{}_4$ complex **3c** in the presence or in the absence of the hydrogen-bond donor **4d**.

X-Ray crystallography

(3*S*,4*R*)-4-ethynyl-6-nitro-3-(prop-1-en-2-yl)chromane (2j)

(3*S*,4*R*)-4-ethynyl-6-nitro-3-(prop-1-en-2-yl)chromane (**2j**) was prepared as described on page S47 using catalyst **4c**. Single crystals of **2j** were grown by cooling a saturated solution of **2j** in pentane to −20 °C in a glass vial.

A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX DUO CCD diffractometer ($Cu_{K\alpha}$ radiation, λ = 1.54178 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 1.0° scans in ω at −30°, −55°, −80°, 30°, 55°, 80° and 115° in 2θ. Data integration down to 0.84 Å resolution was carried out using SAINT V8.37 A[89] with reflection spot size optimization. Absorption corrections were made with the program SADABS[89]. The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F^2 using SHELXT-2014[90] and SHELXL-2014[91] with OLEX 2 interface[92]. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S28, and geometric parameters are shown in Table S29. The Ortep plots produced with SHELXL-2014 program, and the three-dimensional supramolecular architecture drawing was produced with Accelrys DS Visualizer 2.06[93].

Table S28 Experimental details.

Crystal data	
CCDC number	2157761
Chemical formula	$C_{14}H_{13}NO_3$
M_r	243.25
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, b, c (Å)	6.5450 (2), 7.6650 (2), 12.3450 (3)
β (°)	90.3180 (11)
V (Å3)	619.31 (3)
Z	2
Radiation type	Cu *K*α
μ (mm^{-1})	0.76
Crystal size (mm)	0.20 × 0.16 × 0.10
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector
Absorption correction	Multi-scan
	SADABS
T_{min}, T_{max}	0.807, 0.864
No. of measured, independent and observed [I > 2σ(*I*)] reflections	17248, 2079, 2049
R_{int}	0.027

$(\sin\theta/\lambda)_{max}$ (Å^{-1})	
Refinement	
R[$F^2 > 2\sigma(F^2)$], $wR(F^2)$, S	0.024, 0.066, 1.06
No. of reflections	2079
No. of parameters	175
No. of restraints	4
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.14, −0.17
H-atom treatment	H-atom parameters constrained
Absolute structure	Flack x determined using 891 quotients [(I+)−(I−)]/[(I+)+(I−)][94].
Absolute structure parameter	−0.05 (6)

Table S29 Geometric parameters (Å, º).

O1—C9	1.3620 (19)	C7—C8	1.372 (2)
O1—C1	1.441 (2)	C7—H7	0.9500
O2—N1	1.2316 (18)	C8—C9	1.392 (2)
O3—N1	1.2289 (18)	C8—H8	0.9500
N1—C6	1.460 (2)	C10—C11	1.310 (6)
C1—C2	1.513 (3)	C10—C12	1.506 (6)
C1—H1A	0.9900	C11—H11A	0.9500
C1—H1B	0.9900	C11—H11B	0.9500
C2—C10	1.518 (3)	C12—H12A	0.9800
C2—C3	1.551 (2)	C12—H12B	0.9800
C2—C10A	1.572 (10)	C12—H12C	0.9800
C2—H2A	1.0000	C13—C14	1.190 (3)
C2—H2B	1.0000	C14—H14	0.9500
C3—C13	1.468 (2)	C10A—C11A	1.330 (16)
C3—C4	1.523 (2)	C10A—C12A	1.535 (17)
C3—H3	1.0000	C11A—H11C	0.9500
C4—C5	1.388 (2)	C11A—H11D	0.9500
C4—C9	1.398 (2)	C12A—H12D	0.9800
C5—C6	1.385 (2)	C12A—H12E	0.9800
C5—H5	0.9500	C12A—H12F	0.9800
C6—C7	1.393 (2)		
C9—O1—C1	116.84 (13)	C8—C7—C6	118.17 (15)
O3—N1—O2	122.96 (14)	C8—C7—H7	120.9
O3—N1—C6	118.52 (13)	C6—C7—H7	120.9
O2—N1—C6	118.51 (13)	C7—C8—C9	120.56 (15)
O1—C1—C2	111.37 (14)	C7—C8—H8	119.7
O1—C1—H1A	109.4	C9—C8—H8	119.7
C2—C1—H1A	109.4	O1—C9—C8	115.85 (14)
O1—C1—H1B	109.4	O1—C9—C4	123.07 (14)

C2—C1—H1B	109.4	C8—C9—C4	121.07 (14)
H1A—C1—H1B	108.0	C11—C10—C12	122.0 (3)
C1—C2—C10	110.8 (3)	C11—C10—C2	124.8 (3)
C1—C2—C3	108.61 (15)	C12—C10—C2	113.3 (3)
C10—C2—C3	113.13 (19)	C10—C11—H11A	120.0
C1—C2—C10A	127.5 (6)	C10—C11—H11B	120.0
C3—C2—C10A	106.7 (6)	H11A—C11—H11B	120.0
C1—C2—H2A	108.1	C10—C12—H12A	109.5
C10—C2—H2A	108.1	C10—C12—H12B	109.5
C3—C2—H2A	108.1	H12A—C12—H12B	109.5
C1—C2—H2B	103.9	C10—C12—H12C	109.5
C3—C2—H2B	103.9	H12A—C12—H12C	109.5
C10A—C2—H2B	103.9	H12B—C12—H12C	109.5
C13—C3—C4	110.76 (13)	C14—C13—C3	179.48 (19)
C13—C3—C2	111.50 (13)	C13—C14—H14	180.0
C4—C3—C2	109.31 (13)	C11A—C10A—C12A	121.7 (11)
C13—C3—H3	108.4	C11A—C10A—C2	128.0 (11)
C4—C3—H3	108.4	C12A—C10A—C2	110.3 (9)
C2—C3—H3	108.4	C10A—C11A—H11C	120.0
C5—C4—C9	118.36 (14)	C10A—C11A—H11D	120.0
C5—C4—C3	120.60 (14)	H11C—C11A—H11D	120.0
C9—C4—C3	121.04 (14)	C10A—C12A—H12D	109.5
C6—C5—C4	119.67 (15)	C10A—C12A—H12E	109.5
C6—C5—H5	120.2	H12D—C12A—H12E	109.5
C4—C5—H5	120.2	C10A—C12A—H12F	109.5
C5—C6—C7	122.07 (14)	H12D—C12A—H12F	109.5
C5—C6—N1	119.20 (14)	H12E—C12A—H12F	109.5
C7—C6—N1	118.71 (14)		
C9—O1—C1—C2	−44.6 (2)	O2—N1—C6—C7	−4.2 (2)
O1—C1—C2—C10	−172.0 (2)	C5—C6—C7—C8	2.3 (2)
O1—C1—C2—C3	63.17 (18)	N1—C6—C7—C8	−175.98 (15)
O1—C1—C2—C10A	−167.1 (7)	C6—C7—C8—C9	−0.2 (2)
C1—C2—C3—C13	75.36 (17)	C1—O1—C9—C8	−169.82 (15)
C10—C2—C3—C13	−48.1 (3)	C1—O1—C9—C4	11.1 (2)
C10A—C2—C3—C13	−65.1 (6)	C7—C8—C9—O1	178.21 (15)
C1—C2—C3—C4	−47.45 (18)	C7—C8—C9—C4	−2.7 (2)
C10—C2—C3—C4	−170.9 (3)	C5—C4—C9—O1	−177.60 (15)
C10A—C2—C3—C4	172.1 (6)	C3—C4—C9—O1	2.8 (2)
C13—C3—C4—C5	74.00 (19)	C5—C4—C9—C8	3.3 (2)
C2—C3—C4—C5	−162.76 (15)	C3—C4—C9—C8	−176.30 (15)
C13—C3—C4—C9	−106.38 (17)	C1—C2—C10—C11	−1.2 (5)
C2—C3—C4—C9	16.9 (2)	C3—C2—C10—C11	121.1 (4)
C9—C4—C5—C6	−1.2 (2)	C1—C2—C10—C12	178.9 (3)

C3—C4—C5—C6	178.38 (14)	C3—C2—C10—C12	−58.9 (3)
C4—C5—C6—C7	−1.5 (2)	C1—C2—C10A—C11A	166.2 (12)
C4—C5—C6—N1	176.68 (14)	C3—C2—C10A—C11A	−63.3 (15)
O3—N1—C6—C5	−3.1 (2)	C1—C2—C10A—C12A	−13.6 (15)
O2—N1—C6—C5	177.47 (14)	C3—C2—C10A—C12A	116.9 (11)
O3—N1—C6—C7	175.20 (15)		

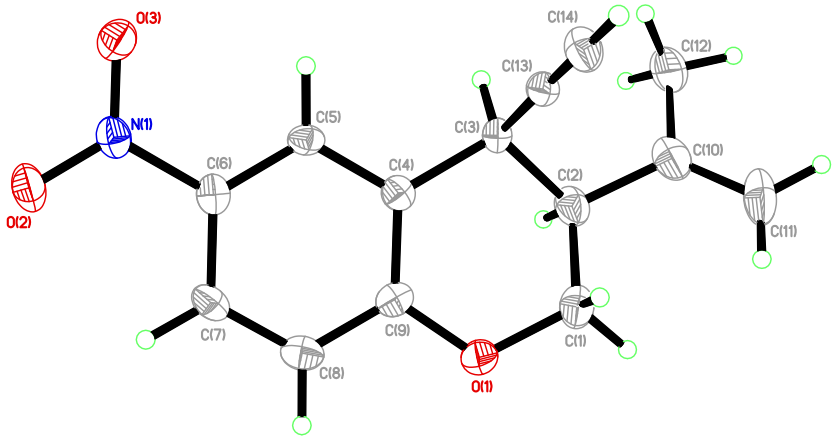


Figure S34 Perspective views showing 50% probability displacement.

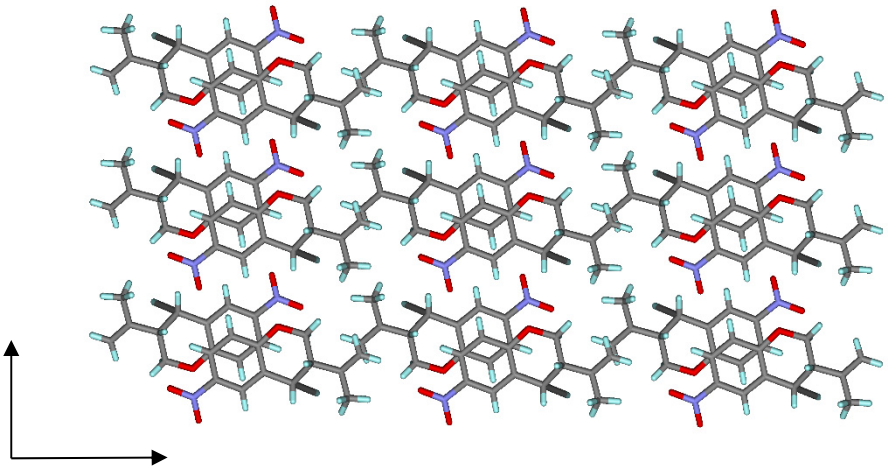


Figure S35 Three-dimensional supramolecular architecture viewed along the *b*-axis direction.

Ruthenium tosylate complex 3b

Ruthenium tosylate complex was prepared as described on page S5. Single crystals of **3b** were grown by slow diffusion of benzene into a solution of **3b** in dichloromethane in a glass vial at 23 °C.

A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer (MoK_α radiation, λ = 0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.77 Å resolution was carried out using SAINT V8.37A[89] with reflection spot size optimization. Absorption corrections were made with the program TWINABS[89,95]. The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F^2 using SHELXT-2014[90] and SHELXL-2014[91] with OLEX 2 interface[92]. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S30, geometric parameters are shown in Table S31, and hydrogen-bond parameters are listed in Table S32. The Ortep plots produced with SHELXL-2014 program, and the three-dimensional supramolecular architecture drawing was produced with Accelrys DS Visualizer 2.06[93].

Table S30 Experimental details.

Crystal data	
CCDC number	2157760
Chemical formula	$C_{29}H_{45}ClO_4Ru_2S_3$
M_r	791.42
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	100
a, *b*, *c* (Å)	8.8670 (7), 12.4541 (10), 14.4998 (11)
α, β, γ (°)	93.9944 (12), 93.5344 (11), 97.4787 (12)
V (Å^3)	1579.7 (2)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	1.27
Crystal size (mm)	0.18 × 0.15 × 0.09
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector
Absorption correction	Multi-scan TWINABS
T_{min}, T_{max}	0.637, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7279, 7279, 6173
R_{int}	0.061
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.651
Refinement	

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.070, 1.01
No. of reflections	7279
No. of parameters	372
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.67, −0.64

Table S31 Geometric parameters (Å, º).

Ru1—C2	2.195 (2)	C11—C16	1.488 (4)
Ru1—C3	2.203 (2)	C12—C13	1.441 (4)
Ru1—C4	2.207 (2)	C12—C17	1.504 (4)
Ru1—C5	2.226 (2)	C13—C14	1.424 (3)
Ru1—C1	2.241 (2)	C13—C18	1.494 (3)
Ru1—S2	2.3049 (6)	C14—C15	1.442 (4)
Ru1—S1	2.3178 (6)	C14—C19	1.502 (4)
Ru1—Cl1	2.4441 (6)	C15—C20	1.496 (4)
Ru1—Ru2	2.7836 (3)	C16—H16A	0.9800
Ru2—O1W	2.1700 (18)	C16—H16B	0.9800
Ru2—C12	2.188 (2)	C16—H16C	0.9800
Ru2—C14	2.189 (2)	C17—H17A	0.9800
Ru2—C13	2.198 (2)	C17—H17B	0.9800
Ru2—C15	2.218 (2)	C17—H17C	0.9800
Ru2—C11	2.220 (3)	C18—H18A	0.9800
Ru2—S1	2.3052 (6)	C18—H18B	0.9800
Ru2—S2	2.3140 (6)	C18—H18C	0.9800
S1—C21	1.825 (3)	C19—H19A	0.9800
S2—C22	1.818 (2)	C19—H19B	0.9800
O1W—H1WA	0.87 (4)	C19—H19C	0.9800
O1W—H1WB	0.73 (3)	C20—H20A	0.9800
C1—C5	1.428 (3)	C20—H20B	0.9800
C1—C2	1.432 (3)	C20—H20C	0.9800
C1—C6	1.491 (3)	C21—H21A	0.9800
C2—C3	1.445 (3)	C21—H21B	0.9800
C2—C7	1.494 (3)	C21—H21C	0.9800
C3—C4	1.424 (3)	C22—H22A	0.9800
C3—C8	1.501 (3)	C22—H22B	0.9800
C4—C5	1.442 (3)	C22—H22C	0.9800
C4—C9	1.494 (3)	S3—O1	1.443 (2)
C5—C10	1.500 (3)	S3—O3	1.444 (2)
C6—H6A	0.9800	S3—O2	1.468 (2)
C6—H6B	0.9800	S3—C31	1.771 (2)
C6—H6C	0.9800	C31—C32	1.376 (4)
C7—H7A	0.9800	C31—C36	1.386 (4)
C7—H7B	0.9800	C32—C33	1.398 (4)

C7—H7C	0.9800	C32—H32	0.9500
C8—H8A	0.9800	C33—C34	1.379 (4)
C8—H8B	0.9800	C33—H33	0.9500
C8—H8C	0.9800	C34—C35	1.384 (4)
C9—H9A	0.9800	C34—C37	1.511 (4)
C9—H9B	0.9800	C35—C36	1.386 (4)
C9—H9C	0.9800	C35—H35	0.9500
C10—H10A	0.9800	C36—H36	0.9500
C10—H10B	0.9800	C37—H37A	0.9800
C10—H10C	0.9800	C37—H37B	0.9800
C11—C15	1.423 (4)	C37—H37C	0.9800
C11—C12	1.424 (4)		
C2—Ru1—C3	38.36 (9)	H7B—C7—H7C	109.5
C2—Ru1—C4	63.69 (9)	C3—C8—H8A	109.5
C3—Ru1—C4	37.68 (9)	C3—C8—H8B	109.5
C2—Ru1—C5	63.02 (9)	H8A—C8—H8B	109.5
C3—Ru1—C5	62.99 (9)	C3—C8—H8C	109.5
C4—Ru1—C5	37.96 (9)	H8A—C8—H8C	109.5
C2—Ru1—C1	37.66 (9)	H8B—C8—H8C	109.5
C3—Ru1—C1	63.14 (9)	C4—C9—H9A	109.5
C4—Ru1—C1	63.14 (9)	C4—C9—H9B	109.5
C5—Ru1—C1	37.28 (8)	H9A—C9—H9B	109.5
C2—Ru1—S2	96.50 (7)	C4—C9—H9C	109.5
C3—Ru1—S2	89.53 (6)	H9A—C9—H9C	109.5
C4—Ru1—S2	117.95 (7)	H9B—C9—H9C	109.5
C5—Ru1—S2	152.50 (7)	C5—C10—H10A	109.5
C1—Ru1—S2	131.97 (6)	C5—C10—H10B	109.5
C2—Ru1—S1	152.49 (6)	H10A—C10—H10B	109.5
C3—Ru1—S1	124.59 (6)	C5—C10—H10C	109.5
C4—Ru1—S1	91.28 (6)	H10A—C10—H10C	109.5
C5—Ru1—S1	90.41 (6)	H10B—C10—H10C	109.5
C1—Ru1—S1	122.14 (6)	C15—C11—C12	108.1 (2)
S2—Ru1—S1	105.86 (2)	C15—C11—C16	125.8 (3)
C2—Ru1—Cl1	101.70 (7)	C12—C11—C16	126.1 (3)
C3—Ru1—Cl1	139.76 (7)	C15—C11—Ru2	71.22 (14)
C4—Ru1—Cl1	147.37 (6)	C12—C11—Ru2	69.94 (14)
C5—Ru1—Cl1	109.70 (6)	C16—C11—Ru2	124.05 (18)
C1—Ru1—Cl1	87.26 (7)	C11—C12—C13	108.0 (2)
S2—Ru1—Cl1	91.58 (2)	C11—C12—C17	127.2 (3)
S1—Ru1—Cl1	93.63 (2)	C13—C12—C17	124.5 (2)
C2—Ru1—Ru2	146.00 (7)	C11—C12—Ru2	72.37 (14)
C3—Ru1—Ru2	117.38 (6)	C13—C12—Ru2	71.22 (13)
C4—Ru1—Ru2	113.64 (6)	C17—C12—Ru2	127.21 (18)

C5—Ru1—Ru2	137.53 (6)	C14—C13—C12	108.0 (2)
C1—Ru1—Ru2	174.61 (6)	C14—C13—C18	127.1 (2)
S2—Ru1—Ru2	53.089 (15)	C12—C13—C18	124.6 (2)
S1—Ru1—Ru2	52.770 (16)	C14—C13—Ru2	70.72 (13)
Cl1—Ru1—Ru2	94.700 (17)	C12—C13—Ru2	70.44 (13)
O1W—Ru2—C12	105.77 (9)	C18—C13—Ru2	129.56 (17)
O1W—Ru2—C14	148.95 (9)	C13—C14—C15	107.6 (2)
C12—Ru2—C14	63.93 (9)	C13—C14—C19	126.5 (3)
O1W—Ru2—C13	143.84 (9)	C15—C14—C19	125.6 (3)
C12—Ru2—C13	38.35 (9)	C13—C14—Ru2	71.41 (13)
C14—Ru2—C13	37.87 (9)	C15—C14—Ru2	71.98 (14)
O1W—Ru2—C15	110.78 (9)	C19—C14—Ru2	127.33 (18)
C12—Ru2—C15	63.09 (9)	C11—C15—C14	108.3 (2)
C14—Ru2—C15	38.18 (10)	C11—C15—C20	125.3 (3)
C13—Ru2—C15	63.14 (9)	C14—C15—C20	126.4 (3)
O1W—Ru2—C11	90.14 (9)	C11—C15—Ru2	71.38 (15)
C12—Ru2—C11	37.70 (10)	C14—C15—Ru2	69.84 (13)
C14—Ru2—C11	63.53 (10)	C20—C15—Ru2	127.22 (18)
C13—Ru2—C11	63.28 (9)	C11—C16—H16A	109.5
C15—Ru2—C11	37.40 (11)	C11—C16—H16B	109.5
O1W—Ru2—S1	90.26 (5)	H16A—C16—H16B	109.5
C12—Ru2—S1	96.91 (7)	C11—C16—H16C	109.5
C14—Ru2—S1	119.24 (7)	H16A—C16—H16C	109.5
C13—Ru2—S1	90.61 (7)	H16B—C16—H16C	109.5
C15—Ru2—S1	153.74 (7)	C12—C17—H17A	109.5
C11—Ru2—S1	132.01 (8)	C12—C17—H17B	109.5
O1W—Ru2—S2	88.74 (6)	H17A—C17—H17B	109.5
C12—Ru2—S2	152.89 (7)	C12—C17—H17C	109.5
C14—Ru2—S2	91.78 (6)	H17A—C17—H17C	109.5
C13—Ru2—S2	125.50 (7)	H17B—C17—H17C	109.5
C15—Ru2—S2	90.53 (7)	C13—C18—H18A	109.5
C11—Ru2—S2	122.01 (8)	C13—C18—H18B	109.5
S1—Ru2—S2	105.97 (2)	H18A—C18—H18B	109.5
O1W—Ru2—Ru1	89.54 (5)	C13—C18—H18C	109.5
C12—Ru2—Ru1	147.06 (7)	H18A—C18—H18C	109.5
C14—Ru2—Ru1	115.15 (7)	H18B—C18—H18C	109.5
C13—Ru2—Ru1	119.16 (7)	C14—C19—H19A	109.5
C15—Ru2—Ru1	138.44 (8)	C14—C19—H19B	109.5
C11—Ru2—Ru1	174.79 (7)	H19A—C19—H19B	109.5
S1—Ru2—Ru1	53.186 (15)	C14—C19—H19C	109.5
S2—Ru2—Ru1	52.790 (16)	H19A—C19—H19C	109.5
C21—S1—Ru2	115.06 (9)	H19B—C19—H19C	109.5
C21—S1—Ru1	115.49 (9)	C15—C20—H20A	109.5
Ru2—S1—Ru1	74.043 (17)	C15—C20—H20B	109.5

C22—S2—Ru1	116.68 (9)	H20A—C20—H20B	109.5
C22—S2—Ru2	113.30 (9)	C15—C20—H20C	109.5
Ru1—S2—Ru2	74.121 (18)	H20A—C20—H20C	109.5
Ru2—O1W—H1WA	108 (2)	H20B—C20—H20C	109.5
Ru2—O1W—H1WB	116 (2)	S1—C21—H21A	109.5
H1WA—O1W—H1WB	108 (3)	S1—C21—H21B	109.5
C5—C1—C2	107.8 (2)	H21A—C21—H21B	109.5
C5—C1—C6	126.3 (2)	S1—C21—H21C	109.5
C2—C1—C6	125.8 (2)	H21A—C21—H21C	109.5
C5—C1—Ru1	70.79 (13)	H21B—C21—H21C	109.5
C2—C1—Ru1	69.40 (13)	S2—C22—H22A	109.5
C6—C1—Ru1	127.55 (19)	S2—C22—H22B	109.5
C1—C2—C3	107.9 (2)	H22A—C22—H22B	109.5
C1—C2—C7	125.0 (2)	S2—C22—H22C	109.5
C3—C2—C7	126.7 (2)	H22A—C22—H22C	109.5
C1—C2—Ru1	72.94 (14)	H22B—C22—H22C	109.5
C3—C2—Ru1	71.13 (13)	O1—S3—O3	114.54 (15)
C7—C2—Ru1	126.56 (19)	O1—S3—O2	112.63 (13)
C4—C3—C2	108.1 (2)	O3—S3—O2	112.42 (14)
C4—C3—C8	126.3 (2)	O1—S3—C31	106.56 (13)
C2—C3—C8	125.2 (2)	O3—S3—C31	105.48 (12)
C4—C3—Ru1	71.31 (14)	O2—S3—C31	104.20 (12)
C2—C3—Ru1	70.51 (14)	C32—C31—C36	119.6 (2)
C8—C3—Ru1	129.09 (17)	C32—C31—S3	120.9 (2)
C3—C4—C5	107.7 (2)	C36—C31—S3	119.4 (2)
C3—C4—C9	126.8 (2)	C31—C32—C33	119.7 (3)
C5—C4—C9	124.9 (2)	C31—C32—H32	120.1
C3—C4—Ru1	71.01 (14)	C33—C32—H32	120.1
C5—C4—Ru1	71.76 (13)	C34—C33—C32	121.3 (3)
C9—C4—Ru1	129.70 (17)	C34—C33—H33	119.4
C1—C5—C4	108.5 (2)	C32—C33—H33	119.4
C1—C5—C10	125.7 (2)	C33—C34—C35	118.1 (3)
C4—C5—C10	125.6 (2)	C33—C34—C37	120.5 (3)
C1—C5—Ru1	71.92 (13)	C35—C34—C37	121.4 (3)
C4—C5—Ru1	70.28 (13)	C34—C35—C36	121.3 (3)
C10—C5—Ru1	127.70 (18)	C34—C35—H35	119.3
C1—C6—H6A	109.5	C36—C35—H35	119.3
C1—C6—H6B	109.5	C31—C36—C35	119.9 (3)
H6A—C6—H6B	109.5	C31—C36—H36	120.1
C1—C6—H6C	109.5	C35—C36—H36	120.1
H6A—C6—H6C	109.5	C34—C37—H37A	109.5
H6B—C6—H6C	109.5	C34—C37—H37B	109.5
C2—C7—H7A	109.5	H37A—C37—H37B	109.5
C2—C7—H7B	109.5	C34—C37—H37C	109.5

H7A—C7—H7B	109.5	H37A—C37—H37C	109.5
C2—C7—H7C	109.5	H37B—C37—H37C	109.5
H7A—C7—H7C	109.5		
C5—C1—C2—C3	−2.2 (3)	C11—C12—C13—C14	2.4 (3)
C6—C1—C2—C3	174.9 (2)	C17—C12—C13—C14	176.2 (2)
Ru1—C1—C2—C3	−62.93 (17)	Ru2—C12—C13—C14	−61.06 (16)
C5—C1—C2—C7	−176.2 (2)	C11—C12—C13—C18	−171.4 (2)
C6—C1—C2—C7	1.0 (4)	C17—C12—C13—C18	2.4 (4)
Ru1—C1—C2—C7	123.1 (3)	Ru2—C12—C13—C18	125.2 (2)
C5—C1—C2—Ru1	60.69 (17)	C11—C12—C13—Ru2	63.46 (16)
C6—C1—C2—Ru1	−122.1 (3)	C17—C12—C13—Ru2	−122.8 (2)
C1—C2—C3—C4	2.4 (3)	C12—C13—C14—C15	−2.4 (3)
C7—C2—C3—C4	176.2 (2)	C18—C13—C14—C15	171.1 (2)
Ru1—C2—C3—C4	−61.76 (17)	Ru2—C13—C14—C15	−63.32 (16)
C1—C2—C3—C8	−171.2 (2)	C12—C13—C14—C19	−176.0 (2)
C7—C2—C3—C8	2.6 (4)	C18—C13—C14—C19	−2.4 (4)
Ru1—C2—C3—C8	124.7 (2)	Ru2—C13—C14—C19	123.2 (3)
C1—C2—C3—Ru1	64.12 (17)	C12—C13—C14—Ru2	60.88 (16)
C7—C2—C3—Ru1	−122.0 (3)	C18—C13—C14—Ru2	−125.5 (2)
C2—C3—C4—C5	−1.6 (3)	C12—C11—C15—C14	−0.1 (3)
C8—C3—C4—C5	171.9 (2)	C16—C11—C15—C14	179.3 (2)
Ru1—C3—C4—C5	−62.80 (16)	Ru2—C11—C15—C14	60.39 (16)
C2—C3—C4—C9	−172.9 (2)	C12—C11—C15—C20	176.6 (2)
C8—C3—C4—C9	0.6 (4)	C16—C11—C15—C20	−4.0 (4)
Ru1—C3—C4—C9	125.9 (2)	Ru2—C11—C15—C20	−122.9 (2)
C2—C3—C4—Ru1	61.25 (17)	C12—C11—C15—Ru2	−60.50 (17)
C8—C3—C4—Ru1	−125.3 (2)	C16—C11—C15—Ru2	118.9 (3)
C2—C1—C5—C4	1.3 (3)	C13—C14—C15—C11	1.6 (3)
C6—C1—C5—C4	−175.9 (2)	C19—C14—C15—C11	175.2 (2)
Ru1—C1—C5—C4	61.10 (16)	Ru2—C14—C15—C11	−61.36 (17)
C2—C1—C5—C10	176.3 (2)	C13—C14—C15—C20	−175.0 (2)
C6—C1—C5—C10	−0.9 (4)	C19—C14—C15—C20	−1.4 (4)
Ru1—C1—C5—C10	−123.9 (3)	Ru2—C14—C15—C20	122.0 (2)
C2—C1—C5—Ru1	−59.81 (17)	C13—C14—C15—Ru2	62.95 (16)
C6—C1—C5—Ru1	123.0 (3)	C19—C14—C15—Ru2	−123.5 (2)
C3—C4—C5—C1	0.2 (3)	O1—S3—C31—C32	−0.5 (2)
C9—C4—C5—C1	171.7 (2)	O3—S3—C31—C32	121.6 (2)
Ru1—C4—C5—C1	−62.14 (17)	O2—S3—C31—C32	−119.8 (2)
C3—C4—C5—C10	−174.8 (2)	O1—S3—C31—C36	−178.82 (19)
C9—C4—C5—C10	−3.3 (4)	O3—S3—C31—C36	−56.7 (2)
Ru1—C4—C5—C10	122.8 (2)	O2—S3—C31—C36	61.9 (2)
C3—C4—C5—Ru1	62.31 (16)	C36—C31—C32—C33	−1.5 (4)
C9—C4—C5—Ru1	−126.2 (2)	S3—C31—C32—C33	−179.78 (19)

C15—C11—C12—C13	−1.4 (3)	C31—C32—C33—C34	0.2 (4)
C16—C11—C12—C13	179.2 (2)	C32—C33—C34—C35	1.4 (4)
Ru2—C11—C12—C13	−62.71 (16)	C32—C33—C34—C37	−177.1 (3)
C15—C11—C12—C17	−175.0 (2)	C33—C34—C35—C36	−1.7 (4)
C16—C11—C12—C17	5.6 (4)	C37—C34—C35—C36	176.8 (3)
Ru2—C11—C12—C17	123.7 (3)	C32—C31—C36—C35	1.1 (4)
C15—C11—C12—Ru2	61.31 (17)	S3—C31—C36—C35	179.50 (19)
C16—C11—C12—Ru2	−118.1 (3)	C34—C35—C36—C31	0.5 (4)

Table S32 Hydrogen-bond parameters.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
O1W—H1WA···Cl1	0.87 (4)	2.14 (4)	2.978 (2)	162 (3)
O1W—H1WB···O2^{i}	0.73 (3)	1.91 (3)	2.632 (3)	171 (3)

Symmetry code(s): (i) −*x*+1, −*y*+1, −*z*+1.

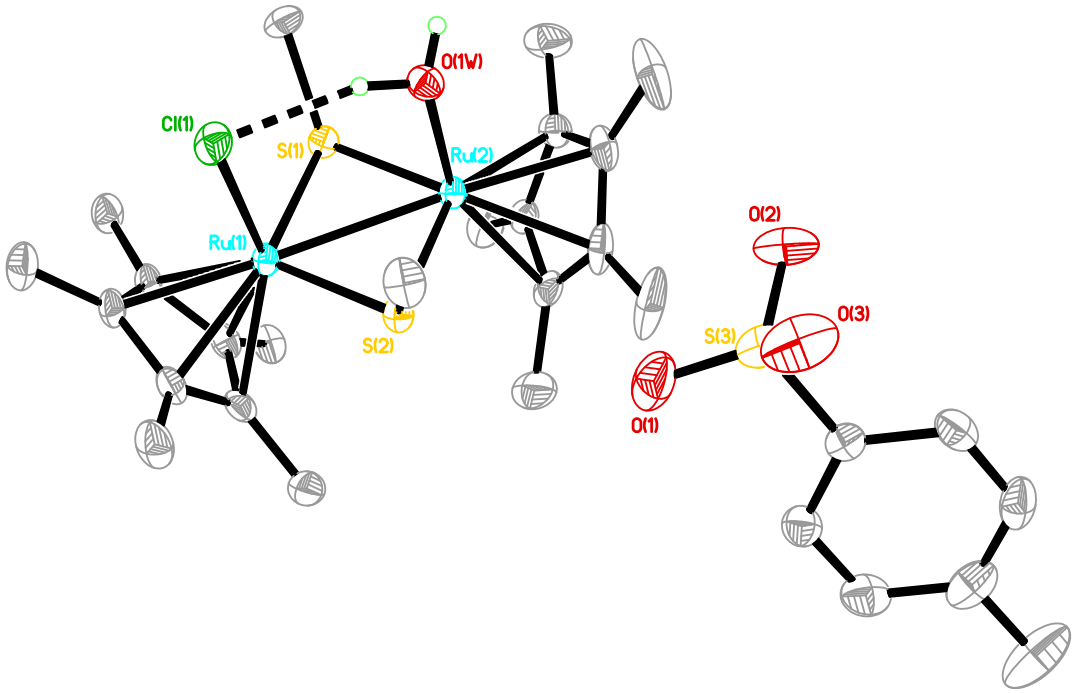


Figure S36 Perspective view showing 50% probability displacement.

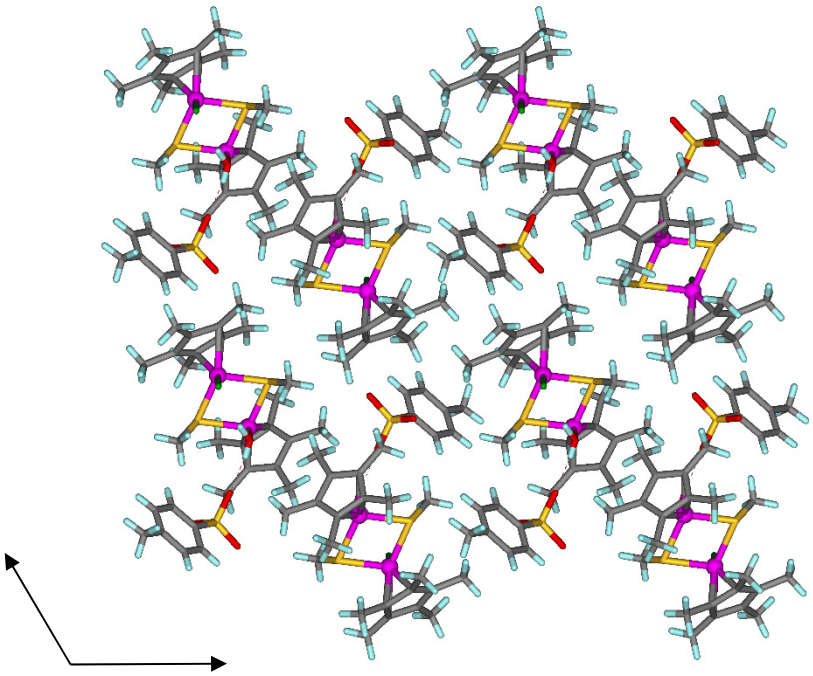


Figure S37 Three-dimensional supramolecular architecture viewed along the *a*-axis direction.

Ruthenium BAr^F_4 complex 3c

Ruthenium BAr^F_4 complex was prepared as described on page S5. Single crystals of **3c** were grown by slow diffusion of pentane into a solution of **3c** in diethyl ether in a glass vial at 23 °C.

A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.84 Å resolution was carried out using SAINT V8.37A[96] with reflection spot size optimization. Absorption corrections were made with the program TWINABS[96]. The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F^2 using SHELXT-2014[90] and SHELXL-2014[91] with OLEX 2 interface[92]. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S33, and geometric parameters are shown in Table S34. The Ortep plots produced with SHELXL-2014 program, and the other drawings were produced with Accelrys DS Visualizer 2.0[93].

Table S33 Experimental details.

Crystal data	
CCDC number	2157758
Chemical formula	$C_{54}H_{48}BClF_{24}Ru_2S_2$
M_r	1465.44
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	100
a, *b*, *c* (Å)	18.1640 (3), 18.2074 (3), 18.4198 (3)
α, β, γ (°)	83.7361 (14), 72.6067 (16), 86.1244 (14)
V (Å^3)	5774.62 (18)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.76
Crystal size (mm)	0.18 × 0.14 × 0.10
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector
Absorption correction	Multi-scan TWINABS
T_{min}, T_{max}	0.714, 0.895
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	164263, 20467, 10787
R_{int}	0.087
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.596
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.047, 0.094, 1.00
No. of reflections	20467

No. of parameters	1766
No. of restraints	1455
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.61, −1.79

Table S34 Geometric parameters (Å, º).

Ru1—C4	2.188 (5)	C38A—H38E	0.9800
Ru1—C5	2.196 (5)	C38A—H38F	0.9800
Ru1—C3	2.230 (5)	C39A—H39D	0.9800
Ru1—C1	2.249 (5)	C39A—H39E	0.9800
Ru1—C2	2.284 (5)	C39A—H39F	0.9800
Ru1—S2	2.2905 (13)	C40A—H40D	0.9800
Ru1—S1	2.3011 (13)	C40A—H40E	0.9800
Ru1—Cl1	2.4023 (13)	C40A—H40F	0.9800
Ru1—Ru2	2.5994 (6)	C41A—C45A	1.390 (16)
Ru2—C14	2.162 (5)	C41A—C42A	1.422 (15)
Ru2—C15	2.163 (5)	C41A—C46A	1.541 (15)
Ru2—C12	2.202 (5)	C42A—C43A	1.418 (15)
Ru2—C13	2.205 (5)	C42A—C47A	1.521 (16)
Ru2—C11	2.208 (4)	C43A—C44A	1.438 (15)
Ru2—S1	2.2941 (13)	C43A—C48A	1.508 (15)
Ru2—S2	2.2944 (13)	C44A—C45A	1.470 (16)
S1—C21	1.825 (5)	C44A—C49A	1.503 (16)
S2—C22	1.817 (4)	C45A—C50A	1.488 (16)
C1—C2	1.408 (6)	C46A—H46D	0.9800
C1—C5	1.442 (7)	C46A—H46E	0.9800
C1—C6	1.499 (7)	C46A—H46F	0.9800
C2—C3	1.414 (7)	C47A—H47D	0.9800
C2—C7	1.486 (6)	C47A—H47E	0.9800
C3—C4	1.447 (7)	C47A—H47F	0.9800
C3—C8	1.507 (6)	C48A—H48D	0.9800
C4—C5	1.439 (7)	C48A—H48E	0.9800
C4—C9	1.479 (7)	C48A—H48F	0.9800
C5—C10	1.490 (6)	C49A—H49D	0.9800
C6—H6A	0.9800	C49A—H49E	0.9800
C6—H6B	0.9800	C49A—H49F	0.9800
C6—H6C	0.9800	C50A—H50D	0.9800
C7—H7A	0.9800	C50A—H50E	0.9800
C7—H7B	0.9800	C50A—H50F	0.9800
C7—H7C	0.9800	F1—C67	1.324 (6)
C8—H8A	0.9800	F2—C67	1.331 (6)
C8—H8B	0.9800	F3—C67	1.348 (6)
C8—H8C	0.9800	F4—C68	1.334 (5)
C9—H9A	0.9800	F5—C68	1.326 (5)

C9—H9B	0.9800	F6—C68	1.358 (5)
C9—H9C	0.9800	F7—C75	1.326 (6)
C10—H10A	0.9800	F8—C75	1.339 (5)
C10—H10B	0.9800	F9—C75	1.324 (5)
C10—H10C	0.9800	F10—C76	1.333 (6)
C11—C15	1.423 (6)	F11—C76	1.314 (6)
C11—C12	1.456 (6)	F12—C76	1.333 (6)
C11—C16	1.505 (6)	F16—C84	1.342 (5)
C12—C13	1.411 (7)	F17—C84	1.335 (5)
C12—C17	1.484 (6)	F18—C84	1.339 (5)
C13—C14	1.408 (7)	F19—C91	1.340 (6)
C13—C18	1.492 (7)	F20—C91	1.316 (6)
C14—C15	1.448 (7)	F21—C91	1.326 (6)
C14—C19	1.505 (7)	F22—C92	1.333 (5)
C15—C20	1.482 (6)	F23—C92	1.326 (5)
C16—H16A	0.9800	F24—C92	1.327 (5)
C16—H16B	0.9800	C61—C62	1.384 (6)
C16—H16C	0.9800	C61—C66	1.406 (6)
C17—H17A	0.9800	C61—B1	1.621 (7)
C17—H17B	0.9800	C62—C63	1.374 (6)
C17—H17C	0.9800	C62—H62	0.9500
C18—H18A	0.9800	C63—C64	1.386 (6)
C18—H18B	0.9800	C63—C67	1.500 (7)
C18—H18C	0.9800	C64—C65	1.389 (6)
C19—H19A	0.9800	C64—H64	0.9500
C19—H19B	0.9800	C65—C66	1.386 (6)
C19—H19C	0.9800	C65—C68	1.500 (6)
C20—H20A	0.9800	C66—H66	0.9500
C20—H20B	0.9800	C69—C70	1.392 (6)
C20—H20C	0.9800	C69—C74	1.399 (6)
C21—H21A	0.9800	C69—B1	1.631 (7)
C21—H21B	0.9800	C70—C71	1.393 (6)
C21—H21C	0.9800	C70—H70	0.9500
C22—H22A	0.9800	C71—C72	1.377 (6)
C22—H22B	0.9800	C71—C75	1.488 (7)
C22—H22C	0.9800	C72—C73	1.390 (6)
Ru3—C35	2.183 (6)	C72—H72	0.9500
Ru3—C34	2.195 (5)	C73—C74	1.390 (6)
Ru3—C31	2.219 (5)	C73—C76	1.499 (7)
Ru3—S4	2.251 (3)	C74—H74	0.9500
Ru3—C33	2.255 (5)	C77—C78	1.389 (6)
Ru3—C32	2.272 (6)	C77—C82	1.394 (6)
Ru3—S3	2.2780 (14)	C77—B1	1.653 (7)
Ru3—Cl2	2.4155 (15)	C78—C79	1.391 (6)

Ru3—Ru4	2.6067 (19)	C78—H78	0.9500
Ru4—C44	2.159 (6)	C79—C80	1.385 (6)
Ru4—C45	2.173 (6)	C79—C83	1.497 (10)
Ru4—C42	2.179 (6)	C79—C83A	1.501 (13)
Ru4—C41	2.196 (6)	C80—C81	1.377 (6)
Ru4—C43	2.219 (6)	C80—H80	0.9500
Ru4—S4	2.244 (3)	C81—C82	1.378 (6)
Ru4—S3	2.308 (2)	C81—C84	1.494 (6)
S3—C51	1.773 (6)	C82—H82	0.9500
C51—H51A	0.9800	C83—F14	1.342 (9)
C51—H51B	0.9800	C83—F15	1.343 (9)
C51—H51C	0.9800	C83—F13	1.345 (9)
S4—C52	1.811 (5)	C83A—F15A	1.347 (12)
C52—H52A	0.9800	C83A—F14A	1.347 (12)
C52—H52B	0.9800	C83A—F13A	1.353 (12)
C52—H52C	0.9800	C85—C86	1.389 (6)
C31—C35	1.421 (7)	C85—C90	1.395 (6)
C31—C32	1.432 (7)	C85—B1	1.645 (7)
C31—C36	1.512 (7)	C86—C87	1.375 (6)
C32—C33	1.419 (7)	C86—H86	0.9500
C32—C37	1.485 (7)	C87—C88	1.381 (6)
C33—C34	1.444 (7)	C87—C91	1.502 (7)
C33—C38	1.493 (6)	C88—C89	1.390 (6)
C34—C35	1.447 (7)	C88—H88	0.9500
C34—C39	1.506 (7)	C89—C90	1.381 (6)
C35—C40	1.502 (7)	C89—C92	1.495 (6)
C36—H36A	0.9800	C90—H90	0.9500
C36—H36B	0.9800	F31—C107	1.352 (6)
C36—H36C	0.9800	F32—C107	1.326 (6)
C37—H37A	0.9800	F33—C107	1.335 (5)
C37—H37B	0.9800	F37—C115	1.378 (6)
C37—H37C	0.9800	F38—C115	1.320 (6)
C38—H38A	0.9800	F39—C115	1.278 (6)
C38—H38B	0.9800	F40—C116	1.337 (6)
C38—H38C	0.9800	F41—C116	1.330 (6)
C39—H39A	0.9800	F42—C116	1.355 (6)
C39—H39B	0.9800	F43—C123	1.346 (5)
C39—H39C	0.9800	F44—C123	1.321 (5)
C40—H40A	0.9800	F45—C123	1.329 (5)
C40—H40B	0.9800	F46—C124	1.347 (5)
C40—H40C	0.9800	F47—C124	1.324 (5)
C41—C42	1.418 (8)	F48—C124	1.344 (5)
C41—C45	1.415 (8)	F49—C131	1.326 (6)
C41—C46	1.502 (7)	F50—C131	1.334 (5)

C42—C43	1.386 (7)	F51—C131	1.339 (6)
C42—C47	1.509 (8)	C101—C106	1.394 (6)
C43—C44	1.423 (8)	C101—C102	1.398 (6)
C43—C48	1.512 (7)	C101—B2	1.647 (7)
C44—C45	1.464 (8)	C102—C103	1.406 (6)
C44—C49	1.511 (8)	C102—H102	0.9500
C45—C50	1.481 (8)	C103—C104	1.366 (6)
C46—H46A	0.9800	C103—C107	1.496 (7)
C46—H46B	0.9800	C104—C105	1.382 (6)
C46—H46C	0.9800	C104—H104	0.9500
C47—H47A	0.9800	C105—C106	1.394 (6)
C47—H47B	0.9800	C105—C108	1.488 (8)
C47—H47C	0.9800	C105—C208	1.513 (14)
C48—H48A	0.9800	C106—H106	0.9500
C48—H48B	0.9800	C108—F34	1.315 (8)
C48—H48C	0.9800	C108—F36	1.324 (7)
C49—H49A	0.9800	C108—F35	1.329 (8)
C49—H49B	0.9800	C208—F36A	1.319 (13)
C49—H49C	0.9800	C208—F34A	1.334 (13)
C50—H50A	0.9800	C208—F35A	1.335 (13)
C50—H50B	0.9800	C109—C110	1.390 (6)
C50—H50C	0.9800	C109—C114	1.402 (6)
Ru3A—C34A	2.175 (18)	C109—B2	1.636 (7)
Ru3A—C35A	2.191 (18)	C110—C111	1.386 (6)
Ru3A—C31A	2.231 (15)	C110—H110	0.9500
Ru3A—C32A	2.241 (15)	C111—C112	1.370 (6)
Ru3A—C33A	2.252 (15)	C111—C115	1.502 (7)
Ru3A—S3A	2.352 (11)	C112—C113	1.384 (6)
Ru3A—Cl2A	2.471 (7)	C112—H112	0.9500
Ru3A—S4A	2.54 (2)	C113—C114	1.393 (6)
Ru3A—Ru4A	2.587 (15)	C113—C116	1.505 (7)
Ru4A—S3A	2.123 (19)	C114—H114	0.9500
Ru4A—C44A	2.145 (15)	C117—C122	1.385 (6)
Ru4A—C45A	2.171 (15)	C117—C118	1.396 (6)
Ru4A—C43A	2.193 (14)	C117—B2	1.641 (7)
Ru4A—C41A	2.194 (15)	C118—C119	1.379 (6)
Ru4A—C42A	2.214 (14)	C118—H118	0.9500
Ru4A—S4A	2.64 (3)	C119—C120	1.388 (6)
S4A—C52A	1.791 (18)	C119—C123	1.488 (6)
C52A—H52D	0.9800	C120—C121	1.389 (6)
C52A—H52E	0.9800	C120—H120	0.9500
C52A—H52F	0.9800	C121—C122	1.379 (6)
S3A—C51A	1.796 (17)	C121—C124	1.489 (6)
C51A—H51D	0.9800	C122—H122	0.9500

C51A—H51E	0.9800	C125—C130	1.395 (6)
C51A—H51F	0.9800	C125—C126	1.402 (6)
C31A—C35A	1.399 (16)	C125—B2	1.621 (7)
C31A—C32A	1.425 (15)	C126—C127	1.375 (6)
C31A—C36A	1.511 (15)	C126—H126	0.9500
C32A—C33A	1.410 (15)	C127—C128	1.398 (6)
C32A—C37A	1.492 (16)	C127—C131	1.494 (6)
C33A—C34A	1.439 (15)	C128—C129	1.382 (6)
C33A—C38A	1.497 (15)	C128—H128	0.9500
C34A—C35A	1.453 (15)	C129—C130	1.379 (6)
C34A—C39A	1.501 (15)	C129—C232	1.483 (15)
C35A—C40A	1.501 (15)	C129—C132	1.495 (7)
C36A—H36D	0.9800	C130—H130	0.9500
C36A—H36E	0.9800	C132—F52	1.316 (7)
C36A—H36F	0.9800	C132—F54	1.330 (7)
C37A—H37D	0.9800	C132—F53	1.340 (7)
C37A—H37E	0.9800	C232—F54A	1.315 (14)
C37A—H37F	0.9800	C232—F52A	1.317 (14)
C38A—H38D	0.9800	C232—F53A	1.322 (14)
C4—Ru1—C5	38.31 (18)	S3A—Ru4A—C45A	94.3 (8)
C4—Ru1—C3	38.22 (17)	C44A—Ru4A—C45A	39.8 (5)
C5—Ru1—C3	63.01 (19)	S3A—Ru4A—C43A	115.1 (10)
C4—Ru1—C1	63.40 (19)	C44A—Ru4A—C43A	38.7 (5)
C5—Ru1—C1	37.82 (17)	C45A—Ru4A—C43A	65.4 (6)
C3—Ru1—C1	61.81 (18)	S3A—Ru4A—C41A	130.1 (8)
C4—Ru1—C2	62.42 (18)	C44A—Ru4A—C41A	63.6 (6)
C5—Ru1—C2	61.79 (18)	C45A—Ru4A—C41A	37.1 (5)
C3—Ru1—C2	36.48 (17)	C43A—Ru4A—C41A	63.4 (6)
C1—Ru1—C2	36.19 (16)	S3A—Ru4A—C42A	149.0 (9)
C4—Ru1—S2	87.61 (15)	C44A—Ru4A—C42A	63.4 (6)
C5—Ru1—S2	119.22 (16)	C45A—Ru4A—C42A	63.5 (6)
C3—Ru1—S2	92.85 (14)	C43A—Ru4A—C42A	37.5 (4)
C1—Ru1—S2	150.62 (14)	C41A—Ru4A—C42A	37.6 (5)
C2—Ru1—S2	126.77 (14)	S3A—Ru4A—Ru3A	59.0 (5)
C4—Ru1—S1	122.21 (15)	C44A—Ru4A—Ru3A	134.7 (10)
C5—Ru1—S1	89.64 (14)	C45A—Ru4A—Ru3A	151.8 (8)
C3—Ru1—S1	151.25 (14)	C43A—Ru4A—Ru3A	131.2 (9)
C1—Ru1—S1	91.45 (14)	C41A—Ru4A—Ru3A	161.5 (9)
C2—Ru1—S1	123.86 (14)	C42A—Ru4A—Ru3A	144.5 (7)
S2—Ru1—S1	109.24 (5)	S3A—Ru4A—S4A	103.5 (9)
C4—Ru1—Cl1	142.33 (15)	C44A—Ru4A—S4A	111.7 (10)
C5—Ru1—Cl1	145.10 (15)	C45A—Ru4A—S4A	145.5 (9)
C3—Ru1—Cl1	104.26 (14)	C43A—Ru4A—S4A	80.3 (8)

C1—Ru1—Cl1	107.30 (14)	C41A—Ru4A—S4A	123.5 (8)
C2—Ru1—Cl1	88.37 (13)	C42A—Ru4A—S4A	87.6 (8)
S2—Ru1—Cl1	92.54 (5)	Ru3A—Ru4A—S4A	58.2 (6)
S1—Ru1—Cl1	93.21 (5)	C52A—S4A—Ru3A	113.1 (13)
C4—Ru1—Ru2	104.17 (14)	C52A—S4A—Ru4A	105.4 (14)
C5—Ru1—Ru2	103.37 (14)	Ru3A—S4A—Ru4A	59.9 (6)
C3—Ru1—Ru2	135.88 (15)	S4A—C52A—H52D	109.5
C1—Ru1—Ru2	133.10 (13)	S4A—C52A—H52E	109.5
C2—Ru1—Ru2	164.78 (13)	H52D—C52A—H52E	109.5
S2—Ru1—Ru2	55.53 (3)	S4A—C52A—H52F	109.5
S1—Ru1—Ru2	55.42 (3)	H52D—C52A—H52F	109.5
Cl1—Ru1—Ru2	106.79 (3)	H52E—C52A—H52F	109.5
C14—Ru2—C15	39.10 (18)	C51A—S3A—Ru4A	125.1 (12)
C14—Ru2—C12	63.5 (2)	C51A—S3A—Ru3A	112.8 (10)
C15—Ru2—C12	64.20 (18)	Ru4A—S3A—Ru3A	70.4 (5)
C14—Ru2—C13	37.60 (18)	S3A—C51A—H51D	109.5
C15—Ru2—C13	63.92 (19)	S3A—C51A—H51E	109.5
C12—Ru2—C13	37.33 (18)	H51D—C51A—H51E	109.5
C14—Ru2—C11	63.99 (18)	S3A—C51A—H51F	109.5
C15—Ru2—C11	37.97 (16)	H51D—C51A—H51F	109.5
C12—Ru2—C11	38.56 (16)	H51E—C51A—H51F	109.5
C13—Ru2—C11	63.31 (18)	C35A—C31A—C32A	109.5 (13)
C14—Ru2—S1	140.54 (16)	C35A—C31A—C36A	125.6 (14)
C15—Ru2—S1	103.02 (14)	C32A—C31A—C36A	124.0 (14)
C12—Ru2—S1	117.71 (15)	C35A—C31A—Ru3A	70.0 (9)
C13—Ru2—S1	154.31 (15)	C32A—C31A—Ru3A	71.8 (7)
C11—Ru2—S1	92.53 (13)	C36A—C31A—Ru3A	116.2 (17)
C14—Ru2—S2	102.38 (14)	C33A—C32A—C31A	108.2 (13)
C15—Ru2—S2	139.43 (14)	C33A—C32A—C37A	123.8 (14)
C12—Ru2—S2	117.40 (13)	C31A—C32A—C37A	128.0 (14)
C13—Ru2—S2	92.96 (13)	C33A—C32A—Ru3A	72.2 (7)
C11—Ru2—S2	155.11 (13)	C31A—C32A—Ru3A	71.0 (7)
S1—Ru2—S2	109.35 (5)	C37A—C32A—Ru3A	122.5 (16)
C14—Ru2—Ru1	138.85 (15)	C32A—C33A—C34A	107.6 (13)
C15—Ru2—Ru1	138.63 (14)	C32A—C33A—C38A	129.2 (14)
C12—Ru2—Ru1	154.99 (14)	C34A—C33A—C38A	122.9 (14)
C13—Ru2—Ru1	148.32 (13)	C32A—C33A—Ru3A	71.3 (7)
C11—Ru2—Ru1	148.13 (13)	C34A—C33A—Ru3A	68.1 (9)
S1—Ru2—Ru1	55.68 (3)	C38A—C33A—Ru3A	120.7 (18)
S2—Ru2—Ru1	55.39 (3)	C33A—C34A—C35A	107.6 (13)
C21—S1—Ru2	104.77 (17)	C33A—C34A—C39A	128.2 (14)
C21—S1—Ru1	113.17 (17)	C35A—C34A—C39A	123.5 (14)
Ru2—S1—Ru1	68.90 (4)	C33A—C34A—Ru3A	74.0 (9)
C22—S2—Ru1	114.01 (16)	C35A—C34A—Ru3A	71.2 (10)

C22—S2—Ru2	108.41 (15)	C39A—C34A—Ru3A	128.1 (19)
Ru1—S2—Ru2	69.08 (4)	C31A—C35A—C34A	106.9 (13)
C2—C1—C5	107.7 (5)	C31A—C35A—C40A	125.9 (14)
C2—C1—C6	125.7 (5)	C34A—C35A—C40A	126.4 (14)
C5—C1—C6	126.3 (5)	C31A—C35A—Ru3A	73.1 (9)
C2—C1—Ru1	73.2 (3)	C34A—C35A—Ru3A	70.0 (10)
C5—C1—Ru1	69.1 (3)	C40A—C35A—Ru3A	130.1 (19)
C6—C1—Ru1	127.8 (4)	C31A—C36A—H36D	109.5
C1—C2—C3	109.2 (5)	C31A—C36A—H36E	109.5
C1—C2—C7	126.9 (5)	H36D—C36A—H36E	109.5
C3—C2—C7	123.9 (5)	C31A—C36A—H36F	109.5
C1—C2—Ru1	70.6 (3)	H36D—C36A—H36F	109.5
C3—C2—Ru1	69.7 (3)	H36E—C36A—H36F	109.5
C7—C2—Ru1	128.2 (3)	C32A—C37A—H37D	109.5
C2—C3—C4	108.3 (5)	C32A—C37A—H37E	109.5
C2—C3—C8	126.4 (5)	H37D—C37A—H37E	109.5
C4—C3—C8	125.1 (5)	C32A—C37A—H37F	109.5
C2—C3—Ru1	73.8 (3)	H37D—C37A—H37F	109.5
C4—C3—Ru1	69.3 (3)	H37E—C37A—H37F	109.5
C8—C3—Ru1	126.2 (3)	C33A—C38A—H38D	109.5
C5—C4—C3	106.6 (5)	C33A—C38A—H38E	109.5
C5—C4—C9	127.4 (5)	H38D—C38A—H38E	109.5
C3—C4—C9	125.6 (5)	C33A—C38A—H38F	109.5
C5—C4—Ru1	71.2 (3)	H38D—C38A—H38F	109.5
C3—C4—Ru1	72.5 (3)	H38E—C38A—H38F	109.5
C9—C4—Ru1	127.8 (4)	C34A—C39A—H39D	109.5
C4—C5—C1	108.2 (4)	C34A—C39A—H39E	109.5
C4—C5—C10	126.7 (5)	H39D—C39A—H39E	109.5
C1—C5—C10	124.7 (5)	C34A—C39A—H39F	109.5
C4—C5—Ru1	70.5 (3)	H39D—C39A—H39F	109.5
C1—C5—Ru1	73.1 (3)	H39E—C39A—H39F	109.5
C10—C5—Ru1	128.0 (4)	C35A—C40A—H40D	109.5
C1—C6—H6A	109.5	C35A—C40A—H40E	109.5
C1—C6—H6B	109.5	H40D—C40A—H40E	109.5
H6A—C6—H6B	109.5	C35A—C40A—H40F	109.5
C1—C6—H6C	109.5	H40D—C40A—H40F	109.5
H6A—C6—H6C	109.5	H40E—C40A—H40F	109.5
H6B—C6—H6C	109.5	C45A—C41A—C42A	110.3 (13)
C2—C7—H7A	109.5	C45A—C41A—C46A	128.2 (14)
C2—C7—H7B	109.5	C42A—C41A—C46A	121.5 (14)
H7A—C7—H7B	109.5	C45A—C41A—Ru4A	70.5 (7)
C2—C7—H7C	109.5	C42A—C41A—Ru4A	71.9 (7)
H7A—C7—H7C	109.5	C46A—C41A—Ru4A	124.4 (5)
H7B—C7—H7C	109.5	C43A—C42A—C41A	108.6 (13)

C3—C8—H8A	109.5	C43A—C42A—C47A	122.1 (13)
C3—C8—H8B	109.5	C41A—C42A—C47A	129.3 (14)
H8A—C8—H8B	109.5	C43A—C42A—Ru4A	70.4 (7)
C3—C8—H8C	109.5	C41A—C42A—Ru4A	70.4 (7)
H8A—C8—H8C	109.5	C47A—C42A—Ru4A	125.0 (5)
H8B—C8—H8C	109.5	C42A—C43A—C44A	106.8 (13)
C4—C9—H9A	109.5	C42A—C43A—C48A	130.4 (14)
C4—C9—H9B	109.5	C44A—C43A—C48A	122.8 (14)
H9A—C9—H9B	109.5	C42A—C43A—Ru4A	72.1 (7)
C4—C9—H9C	109.5	C44A—C43A—Ru4A	68.9 (7)
H9A—C9—H9C	109.5	C48A—C43A—Ru4A	123.9 (6)
H9B—C9—H9C	109.5	C43A—C44A—C45A	108.2 (13)
C5—C10—H10A	109.5	C43A—C44A—C49A	128.7 (14)
C5—C10—H10B	109.5	C45A—C44A—C49A	123.0 (14)
H10A—C10—H10B	109.5	C43A—C44A—Ru4A	72.4 (7)
C5—C10—H10C	109.5	C45A—C44A—Ru4A	71.0 (7)
H10A—C10—H10C	109.5	C49A—C44A—Ru4A	122.1 (7)
H10B—C10—H10C	109.5	C41A—C45A—C44A	106.1 (13)
C15—C11—C12	107.4 (4)	C41A—C45A—C50A	125.9 (15)
C15—C11—C16	127.6 (4)	C44A—C45A—C50A	128.1 (15)
C12—C11—C16	124.9 (5)	C41A—C45A—Ru4A	72.4 (7)
C15—C11—Ru2	69.3 (3)	C44A—C45A—Ru4A	69.2 (7)
C12—C11—Ru2	70.5 (3)	C50A—C45A—Ru4A	123.4 (6)
C16—C11—Ru2	128.9 (3)	C41A—C46A—H46D	109.5
C13—C12—C11	107.8 (5)	C41A—C46A—H46E	109.5
C13—C12—C17	126.5 (5)	H46D—C46A—H46E	109.5
C11—C12—C17	125.6 (5)	C41A—C46A—H46F	109.5
C13—C12—Ru2	71.5 (3)	H46D—C46A—H46F	109.5
C11—C12—Ru2	70.9 (3)	H46E—C46A—H46F	109.5
C17—C12—Ru2	126.6 (3)	C42A—C47A—H47D	109.5
C14—C13—C12	109.0 (5)	C42A—C47A—H47E	109.5
C14—C13—C18	125.2 (6)	H47D—C47A—H47E	109.5
C12—C13—C18	125.6 (6)	C42A—C47A—H47F	109.5
C14—C13—Ru2	69.5 (3)	H47D—C47A—H47F	109.5
C12—C13—Ru2	71.2 (3)	H47E—C47A—H47F	109.5
C18—C13—Ru2	129.0 (3)	C43A—C48A—H48D	109.5
C13—C14—C15	108.2 (5)	C43A—C48A—H48E	109.5
C13—C14—C19	127.4 (5)	H48D—C48A—H48E	109.5
C15—C14—C19	124.3 (6)	C43A—C48A—H48F	109.5
C13—C14—Ru2	72.9 (3)	H48D—C48A—H48F	109.5
C15—C14—Ru2	70.5 (3)	H48E—C48A—H48F	109.5
C19—C14—Ru2	125.3 (4)	C44A—C49A—H49D	109.5
C11—C15—C14	107.6 (5)	C44A—C49A—H49E	109.5
C11—C15—C20	124.6 (5)	H49D—C49A—H49E	109.5

C14—C15—C20	127.5 (5)	C44A—C49A—H49F	109.5
C11—C15—Ru2	72.7 (3)	H49D—C49A—H49F	109.5
C14—C15—Ru2	70.4 (3)	H49E—C49A—H49F	109.5
C20—C15—Ru2	127.1 (3)	C45A—C50A—H50D	109.5
C11—C16—H16A	109.5	C45A—C50A—H50E	109.5
C11—C16—H16B	109.5	H50D—C50A—H50E	109.5
H16A—C16—H16B	109.5	C45A—C50A—H50F	109.5
C11—C16—H16C	109.5	H50D—C50A—H50F	109.5
H16A—C16—H16C	109.5	H50E—C50A—H50F	109.5
H16B—C16—H16C	109.5	C62—C61—C66	115.0 (4)
C12—C17—H17A	109.5	C62—C61—B1	125.3 (4)
C12—C17—H17B	109.5	C66—C61—B1	119.4 (4)
H17A—C17—H17B	109.5	C63—C62—C61	123.4 (5)
C12—C17—H17C	109.5	C63—C62—H62	118.3
H17A—C17—H17C	109.5	C61—C62—H62	118.3
H17B—C17—H17C	109.5	C62—C63—C64	120.7 (5)
C13—C18—H18A	109.5	C62—C63—C67	118.9 (5)
C13—C18—H18B	109.5	C64—C63—C67	120.3 (5)
H18A—C18—H18B	109.5	C63—C64—C65	117.9 (5)
C13—C18—H18C	109.5	C63—C64—H64	121.1
H18A—C18—H18C	109.5	C65—C64—H64	121.1
H18B—C18—H18C	109.5	C66—C65—C64	120.4 (4)
C14—C19—H19A	109.5	C66—C65—C68	118.0 (4)
C14—C19—H19B	109.5	C64—C65—C68	121.7 (5)
H19A—C19—H19B	109.5	C65—C66—C61	122.6 (4)
C14—C19—H19C	109.5	C65—C66—H66	118.7
H19A—C19—H19C	109.5	C61—C66—H66	118.7
H19B—C19—H19C	109.5	F1—C67—F2	106.7 (5)
C15—C20—H20A	109.5	F1—C67—F3	106.3 (5)
C15—C20—H20B	109.5	F2—C67—F3	105.9 (5)
H20A—C20—H20B	109.5	F1—C67—C63	112.9 (5)
C15—C20—H20C	109.5	F2—C67—C63	111.8 (5)
H20A—C20—H20C	109.5	F3—C67—C63	112.8 (5)
H20B—C20—H20C	109.5	F5—C68—F4	108.0 (4)
S1—C21—H21A	109.5	F5—C68—F6	106.7 (4)
S1—C21—H21B	109.5	F4—C68—F6	105.4 (4)
H21A—C21—H21B	109.5	F5—C68—C65	113.8 (4)
S1—C21—H21C	109.5	F4—C68—C65	111.4 (4)
H21A—C21—H21C	109.5	F6—C68—C65	111.1 (4)
H21B—C21—H21C	109.5	C70—C69—C74	115.7 (4)
S2—C22—H22A	109.5	C70—C69—B1	123.9 (4)
S2—C22—H22B	109.5	C74—C69—B1	120.2 (4)
H22A—C22—H22B	109.5	C69—C70—C71	122.7 (5)
S2—C22—H22C	109.5	C69—C70—H70	118.6

H22A—C22—H22C	109.5	C71—C70—H70	118.6
H22B—C22—H22C	109.5	C72—C71—C70	120.0 (5)
C35—Ru3—C34	38.60 (18)	C72—C71—C75	120.7 (5)
C35—Ru3—C31	37.66 (18)	C70—C71—C75	119.3 (5)
C34—Ru3—C31	63.3 (2)	C71—C72—C73	119.1 (5)
C35—Ru3—S4	124.04 (16)	C71—C72—H72	120.4
C34—Ru3—S4	90.14 (15)	C73—C72—H72	120.4
C31—Ru3—S4	151.29 (15)	C72—C73—C74	120.0 (5)
C35—Ru3—C33	63.13 (19)	C72—C73—C76	118.5 (5)
C34—Ru3—C33	37.84 (17)	C74—C73—C76	121.4 (5)
C31—Ru3—C33	61.87 (19)	C73—C74—C69	122.4 (5)
S4—Ru3—C33	90.73 (15)	C73—C74—H74	118.8
C35—Ru3—C32	62.8 (2)	C69—C74—H74	118.8
C34—Ru3—C32	62.8 (2)	F9—C75—F7	106.1 (5)
C31—Ru3—C32	37.17 (18)	F9—C75—F8	105.0 (4)
S4—Ru3—C32	122.30 (16)	F7—C75—F8	105.9 (4)
C33—Ru3—C32	36.52 (17)	F9—C75—C71	112.6 (4)
C35—Ru3—S3	89.39 (15)	F7—C75—C71	113.4 (4)
C34—Ru3—S3	120.33 (16)	F8—C75—C71	113.1 (5)
C31—Ru3—S3	94.60 (15)	F11—C76—F10	106.4 (5)
S4—Ru3—S3	108.98 (7)	F11—C76—F12	106.5 (5)
C33—Ru3—S3	152.29 (15)	F10—C76—F12	105.2 (5)
C32—Ru3—S3	128.72 (16)	F11—C76—C73	114.0 (5)
C35—Ru3—Cl2	141.56 (16)	F10—C76—C73	112.7 (5)
C34—Ru3—Cl2	144.97 (16)	F12—C76—C73	111.4 (4)
C31—Ru3—Cl2	104.02 (16)	C78—C77—C82	115.6 (4)
S4—Ru3—Cl2	91.61 (7)	C78—C77—B1	121.9 (4)
C33—Ru3—Cl2	107.15 (14)	C82—C77—B1	122.1 (4)
C32—Ru3—Cl2	87.19 (16)	C77—C78—C79	122.6 (4)
S3—Ru3—Cl2	91.99 (6)	C77—C78—H78	118.7
C35—Ru3—Ru4	108.82 (16)	C79—C78—H78	118.7
C34—Ru3—Ru4	105.80 (16)	C80—C79—C78	120.3 (4)
C31—Ru3—Ru4	139.90 (16)	C80—C79—C83	120.0 (6)
S4—Ru3—Ru4	54.43 (8)	C78—C79—C83	119.7 (6)
C33—Ru3—Ru4	133.77 (16)	C80—C79—C83A	120.8 (8)
C32—Ru3—Ru4	168.56 (16)	C78—C79—C83A	118.7 (8)
S3—Ru3—Ru4	55.89 (6)	C81—C80—C79	117.9 (5)
Cl2—Ru3—Ru4	103.54 (7)	C81—C80—H80	121.1
C44—Ru4—C45	39.5 (2)	C79—C80—H80	121.1
C44—Ru4—C42	63.4 (3)	C80—C81—C82	121.4 (4)
C45—Ru4—C42	64.2 (3)	C80—C81—C84	118.0 (5)
C44—Ru4—C41	63.5 (2)	C82—C81—C84	120.6 (5)
C45—Ru4—C41	37.8 (2)	C81—C82—C77	122.2 (4)
C42—Ru4—C41	37.8 (2)	C81—C82—H82	118.9

C44—Ru4—C43	37.9 (2)	C77—C82—H82	118.9
C45—Ru4—C43	64.1 (2)	F14—C83—F15	107.6 (8)
C42—Ru4—C43	36.7 (2)	F14—C83—F13	105.0 (8)
C41—Ru4—C43	62.1 (2)	F15—C83—F13	106.6 (8)
C44—Ru4—S4	111.6 (2)	F14—C83—C79	113.5 (11)
C45—Ru4—S4	151.1 (2)	F15—C83—C79	113.2 (10)
C42—Ru4—S4	106.9 (2)	F13—C83—C79	110.3 (11)
C41—Ru4—S4	144.4 (2)	F15A—C83A—F14A	105.3 (11)
C43—Ru4—S4	92.07 (19)	F15A—C83A—F13A	105.8 (11)
C44—Ru4—S3	128.9 (2)	F14A—C83A—F13A	104.7 (12)
C45—Ru4—S3	96.61 (19)	F15A—C83A—C79	114.8 (14)
C42—Ru4—S3	130.9 (2)	F14A—C83A—C79	109.5 (17)
C41—Ru4—S3	99.17 (18)	F13A—C83A—C79	115.8 (17)
C43—Ru4—S3	159.74 (19)	F17—C84—F18	106.8 (4)
S4—Ru4—S3	108.18 (11)	F17—C84—F16	106.1 (4)
C44—Ru4—Ru3	138.3 (2)	F18—C84—F16	105.6 (4)
C45—Ru4—Ru3	141.8 (2)	F17—C84—C81	113.6 (4)
C42—Ru4—Ru3	153.0 (2)	F18—C84—C81	111.8 (4)
C41—Ru4—Ru3	152.29 (19)	F16—C84—C81	112.5 (4)
C43—Ru4—Ru3	144.95 (19)	C86—C85—C90	114.5 (4)
S4—Ru4—Ru3	54.69 (9)	C86—C85—B1	119.0 (4)
S3—Ru4—Ru3	54.83 (5)	C90—C85—B1	126.3 (4)
C51—S3—Ru3	114.3 (2)	C87—C86—C85	123.9 (4)
C51—S3—Ru4	106.6 (2)	C87—C86—H86	118.1
Ru3—S3—Ru4	69.28 (6)	C85—C86—H86	118.1
S3—C51—H51A	109.5	C86—C87—C88	120.1 (5)
S3—C51—H51B	109.5	C86—C87—C91	120.8 (5)
H51A—C51—H51B	109.5	C88—C87—C91	119.2 (5)
S3—C51—H51C	109.5	C87—C88—C89	118.3 (5)
H51A—C51—H51C	109.5	C87—C88—H88	120.9
H51B—C51—H51C	109.5	C89—C88—H88	120.9
C52—S4—Ru4	110.6 (2)	C90—C89—C88	120.0 (5)
C52—S4—Ru3	116.9 (2)	C90—C89—C92	120.0 (5)
Ru4—S4—Ru3	70.88 (10)	C88—C89—C92	119.9 (5)
S4—C52—H52A	109.5	C89—C90—C85	123.2 (5)
S4—C52—H52B	109.5	C89—C90—H90	118.4
H52A—C52—H52B	109.5	C85—C90—H90	118.4
S4—C52—H52C	109.5	F20—C91—F21	106.6 (5)
H52A—C52—H52C	109.5	F20—C91—F19	105.7 (5)
H52B—C52—H52C	109.5	F21—C91—F19	105.8 (5)
C35—C31—C32	109.0 (5)	F20—C91—C87	112.6 (5)
C35—C31—C36	126.9 (5)	F21—C91—C87	112.9 (5)
C32—C31—C36	123.7 (5)	F19—C91—C87	112.6 (4)
C35—C31—Ru3	69.8 (3)	F23—C92—F24	106.2 (4)

C32—C31—Ru3	73.4 (3)	F23—C92—F22	105.8 (4)
C36—C31—Ru3	127.8 (5)	F24—C92—F22	106.0 (4)
C33—C32—C31	107.6 (5)	F23—C92—C89	113.1 (4)
C33—C32—C37	124.4 (5)	F24—C92—C89	111.9 (4)
C31—C32—C37	127.9 (5)	F22—C92—C89	113.2 (4)
C33—C32—Ru3	71.1 (3)	C61—B1—C69	112.8 (4)
C31—C32—Ru3	69.4 (3)	C61—B1—C85	103.6 (4)
C37—C32—Ru3	128.3 (4)	C69—B1—C85	111.1 (4)
C32—C33—C34	108.8 (5)	C61—B1—C77	111.2 (4)
C32—C33—C38	124.9 (5)	C69—B1—C77	105.5 (4)
C34—C33—C38	126.3 (5)	C85—B1—C77	112.9 (4)
C32—C33—Ru3	72.4 (3)	C106—C101—C102	115.7 (4)
C34—C33—Ru3	68.8 (3)	C106—C101—B2	120.0 (4)
C38—C33—Ru3	125.5 (4)	C102—C101—B2	124.0 (4)
C33—C34—C35	107.0 (5)	C101—C102—C103	122.0 (4)
C33—C34—C39	127.1 (5)	C101—C102—H102	119.0
C35—C34—C39	125.5 (5)	C103—C102—H102	119.0
C33—C34—Ru3	73.3 (3)	C104—C103—C102	120.6 (5)
C35—C34—Ru3	70.3 (3)	C104—C103—C107	121.9 (5)
C39—C34—Ru3	126.6 (4)	C102—C103—C107	117.5 (5)
C31—C35—C34	107.6 (5)	C103—C104—C105	118.6 (5)
C31—C35—C40	126.1 (5)	C103—C104—H104	120.7
C34—C35—C40	125.7 (5)	C105—C104—H104	120.7
C31—C35—Ru3	72.5 (3)	C104—C105—C106	120.8 (5)
C34—C35—Ru3	71.1 (3)	C104—C105—C108	118.9 (5)
C40—C35—Ru3	128.7 (4)	C106—C105—C108	120.3 (5)
C31—C36—H36A	109.5	C104—C105—C208	124.9 (8)
C31—C36—H36B	109.5	C106—C105—C208	113.6 (7)
H36A—C36—H36B	109.5	C101—C106—C105	122.2 (5)
C31—C36—H36C	109.5	C101—C106—H106	118.9
H36A—C36—H36C	109.5	C105—C106—H106	118.9
H36B—C36—H36C	109.5	F32—C107—F33	107.2 (4)
C32—C37—H37A	109.5	F32—C107—F31	105.6 (4)
C32—C37—H37B	109.5	F33—C107—F31	105.9 (5)
H37A—C37—H37B	109.5	F32—C107—C103	112.8 (5)
C32—C37—H37C	109.5	F33—C107—C103	112.7 (4)
H37A—C37—H37C	109.5	F31—C107—C103	112.1 (5)
H37B—C37—H37C	109.5	F34—C108—F36	107.5 (7)
C33—C38—H38A	109.5	F34—C108—F35	105.8 (6)
C33—C38—H38B	109.5	F36—C108—F35	103.0 (6)
H38A—C38—H38B	109.5	F34—C108—C105	114.2 (6)
C33—C38—H38C	109.5	F36—C108—C105	111.8 (6)
H38A—C38—H38C	109.5	F35—C108—C105	113.8 (6)
H38B—C38—H38C	109.5	F36A—C208—F34A	104.8 (12)

C34—C39—H39A	109.5	F36A—C208—F35A	103.0 (12)
C34—C39—H39B	109.5	F34A—C208—F35A	103.3 (12)
H39A—C39—H39B	109.5	F36A—C208—C105	120.3 (12)
C34—C39—H39C	109.5	F34A—C208—C105	110.9 (14)
H39A—C39—H39C	109.5	F35A—C208—C105	112.7 (13)
H39B—C39—H39C	109.5	C110—C109—C114	114.9 (4)
C35—C40—H40A	109.5	C110—C109—B2	123.9 (4)
C35—C40—H40B	109.5	C114—C109—B2	120.9 (4)
H40A—C40—H40B	109.5	C111—C110—C109	122.8 (5)
C35—C40—H40C	109.5	C111—C110—H110	118.6
H40A—C40—H40C	109.5	C109—C110—H110	118.6
H40B—C40—H40C	109.5	C112—C111—C110	121.0 (5)
C42—C41—C45	109.4 (6)	C112—C111—C115	119.5 (5)
C42—C41—C46	124.0 (7)	C110—C111—C115	119.5 (5)
C45—C41—C46	126.6 (6)	C111—C112—C113	118.6 (5)
C42—C41—Ru4	70.4 (3)	C111—C112—H112	120.7
C45—C41—Ru4	70.2 (4)	C113—C112—H112	120.7
C46—C41—Ru4	127.0 (4)	C112—C113—C114	119.8 (5)
C43—C42—C41	108.5 (6)	C112—C113—C116	121.5 (5)
C43—C42—C47	126.4 (6)	C114—C113—C116	118.5 (5)
C41—C42—C47	125.0 (6)	C113—C114—C109	122.9 (5)
C43—C42—Ru4	73.2 (4)	C113—C114—H114	118.5
C41—C42—Ru4	71.7 (3)	C109—C114—H114	118.5
C47—C42—Ru4	124.5 (5)	F39—C115—F38	110.8 (5)
C42—C43—C44	108.6 (6)	F39—C115—F37	104.4 (5)
C42—C43—C48	125.5 (6)	F38—C115—F37	100.8 (4)
C44—C43—C48	125.9 (6)	F39—C115—C111	115.7 (5)
C42—C43—Ru4	70.1 (3)	F38—C115—C111	113.4 (5)
C44—C43—Ru4	68.8 (3)	F37—C115—C111	110.3 (4)
C48—C43—Ru4	127.4 (4)	F41—C116—F40	106.7 (5)
C43—C44—C45	107.6 (6)	F41—C116—F42	106.5 (4)
C43—C44—C49	125.4 (6)	F40—C116—F42	107.3 (4)
C45—C44—C49	126.7 (7)	F41—C116—C113	113.3 (5)
C43—C44—Ru4	73.3 (4)	F40—C116—C113	112.3 (5)
C45—C44—Ru4	70.8 (3)	F42—C116—C113	110.3 (4)
C49—C44—Ru4	125.6 (5)	C122—C117—C118	115.2 (4)
C41—C45—C44	105.6 (6)	C122—C117—B2	124.0 (4)
C41—C45—C50	127.4 (7)	C118—C117—B2	120.6 (4)
C44—C45—C50	126.9 (7)	C119—C118—C117	123.2 (4)
C41—C45—Ru4	72.0 (4)	C119—C118—H118	118.4
C44—C45—Ru4	69.7 (3)	C117—C118—H118	118.4
C50—C45—Ru4	125.6 (5)	C118—C119—C120	119.8 (4)
C41—C46—H46A	109.5	C118—C119—C123	119.8 (4)
C41—C46—H46B	109.5	C120—C119—C123	120.3 (5)

H46A—C46—H46B	109.5	C119—C120—C121	118.4 (4)
C41—C46—H46C	109.5	C119—C120—H120	120.8
H46A—C46—H46C	109.5	C121—C120—H120	120.8
H46B—C46—H46C	109.5	C122—C121—C120	120.2 (4)
C42—C47—H47A	109.5	C122—C121—C124	119.4 (4)
C42—C47—H47B	109.5	C120—C121—C124	120.3 (4)
H47A—C47—H47B	109.5	C121—C122—C117	123.1 (4)
C42—C47—H47C	109.5	C121—C122—H122	118.5
H47A—C47—H47C	109.5	C117—C122—H122	118.5
H47B—C47—H47C	109.5	F44—C123—F45	107.8 (5)
C43—C48—H48A	109.5	F44—C123—F43	105.7 (4)
C43—C48—H48B	109.5	F45—C123—F43	105.7 (4)
H48A—C48—H48B	109.5	F44—C123—C119	112.1 (4)
C43—C48—H48C	109.5	F45—C123—C119	112.7 (4)
H48A—C48—H48C	109.5	F43—C123—C119	112.4 (4)
H48B—C48—H48C	109.5	F47—C124—F48	105.8 (4)
C44—C49—H49A	109.5	F47—C124—F46	106.6 (4)
C44—C49—H49B	109.5	F48—C124—F46	105.1 (4)
H49A—C49—H49B	109.5	F47—C124—C121	113.4 (4)
C44—C49—H49C	109.5	F48—C124—C121	112.0 (4)
H49A—C49—H49C	109.5	F46—C124—C121	113.3 (4)
H49B—C49—H49C	109.5	C130—C125—C126	114.2 (4)
C45—C50—H50A	109.5	C130—C125—B2	126.2 (4)
C45—C50—H50B	109.5	C126—C125—B2	119.3 (4)
H50A—C50—H50B	109.5	C127—C126—C125	123.7 (4)
C45—C50—H50C	109.5	C127—C126—H126	118.1
H50A—C50—H50C	109.5	C125—C126—H126	118.1
H50B—C50—H50C	109.5	C126—C127—C128	120.1 (4)
C34A—Ru3A—C35A	38.9 (5)	C126—C127—C131	120.4 (5)
C34A—Ru3A—C31A	62.7 (7)	C128—C127—C131	119.5 (5)
C35A—Ru3A—C31A	36.9 (5)	C129—C128—C127	117.7 (4)
C34A—Ru3A—C32A	62.7 (6)	C129—C128—H128	121.1
C35A—Ru3A—C32A	62.7 (6)	C127—C128—H128	121.1
C31A—Ru3A—C32A	37.2 (4)	C130—C129—C128	120.9 (4)
C34A—Ru3A—C33A	37.9 (5)	C130—C129—C232	119.8 (9)
C35A—Ru3A—C33A	63.4 (7)	C128—C129—C232	119.0 (9)
C31A—Ru3A—C33A	61.6 (6)	C130—C129—C132	120.8 (5)
C32A—Ru3A—C33A	36.6 (4)	C128—C129—C132	118.3 (5)
C34A—Ru3A—S3A	100.8 (7)	C129—C130—C125	123.4 (4)
C35A—Ru3A—S3A	89.4 (7)	C129—C130—H130	118.3
C31A—Ru3A—S3A	115.1 (7)	C125—C130—H130	118.3
C32A—Ru3A—S3A	151.2 (7)	F49—C131—F50	107.6 (4)
C33A—Ru3A—S3A	137.7 (7)	F49—C131—F51	106.5 (5)
C34A—Ru3A—Cl2A	133.8 (7)	F50—C131—F51	104.9 (4)

C35A—Ru3A—Cl2A	136.4 (7)	F49—C131—C127	113.3 (5)
C31A—Ru3A—Cl2A	99.8 (6)	F50—C131—C127	112.5 (4)
C32A—Ru3A—Cl2A	77.9 (6)	F51—C131—C127	111.6 (5)
C33A—Ru3A—Cl2A	95.9 (7)	F52—C132—F54	107.3 (6)
S3A—Ru3A—Cl2A	124.7 (4)	F52—C132—F53	106.0 (6)
C34A—Ru3A—S4A	94.6 (7)	F54—C132—F53	104.9 (6)
C35A—Ru3A—S4A	133.4 (7)	F52—C132—C129	111.2 (6)
C31A—Ru3A—S4A	140.5 (8)	F54—C132—C129	113.8 (6)
C32A—Ru3A—S4A	104.6 (8)	F53—C132—C129	113.2 (6)
C33A—Ru3A—S4A	80.5 (8)	F54A—C232—F52A	105.0 (13)
S3A—Ru3A—S4A	100.0 (6)	F54A—C232—F53A	105.3 (13)
Cl2A—Ru3A—S4A	72.1 (5)	F52A—C232—F53A	105.0 (13)
C34A—Ru3A—Ru4A	132.3 (8)	F54A—C232—C129	114.6 (15)
C35A—Ru3A—Ru4A	139.7 (7)	F52A—C232—C129	115.4 (17)
C31A—Ru3A—Ru4A	156.9 (7)	F53A—C232—C129	110.7 (15)
C32A—Ru3A—Ru4A	157.6 (7)	C125—B2—C109	114.6 (4)
C33A—Ru3A—Ru4A	141.5 (7)	C125—B2—C117	103.2 (4)
S3A—Ru3A—Ru4A	50.6 (4)	C109—B2—C117	110.2 (4)
Cl2A—Ru3A—Ru4A	80.7 (4)	C125—B2—C101	113.4 (4)
S4A—Ru3A—Ru4A	61.9 (5)	C109—B2—C101	103.9 (4)
S3A—Ru4A—C44A	85.6 (9)	C117—B2—C101	111.9 (4)
C5—C1—C2—C3	−1.7 (5)	C62—C63—C67—F1	77.8 (6)
C6—C1—C2—C3	−176.0 (5)	C64—C63—C67—F1	−99.7 (6)
Ru1—C1—C2—C3	59.1 (3)	C62—C63—C67—F2	−42.4 (7)
C5—C1—C2—C7	175.4 (5)	C64—C63—C67—F2	140.0 (5)
C6—C1—C2—C7	1.1 (8)	C62—C63—C67—F3	−161.7 (5)
Ru1—C1—C2—C7	−123.8 (5)	C64—C63—C67—F3	20.7 (7)
C5—C1—C2—Ru1	−60.8 (3)	C66—C65—C68—F5	−171.9 (4)
C6—C1—C2—Ru1	124.9 (5)	C64—C65—C68—F5	8.6 (7)
C1—C2—C3—C4	1.4 (5)	C66—C65—C68—F4	−49.6 (6)
C7—C2—C3—C4	−175.8 (4)	C64—C65—C68—F4	130.9 (5)
Ru1—C2—C3—C4	61.1 (3)	C66—C65—C68—F6	67.6 (6)
C1—C2—C3—C8	176.9 (4)	C64—C65—C68—F6	−111.9 (5)
C7—C2—C3—C8	−0.3 (8)	C74—C69—C70—C71	2.3 (7)
Ru1—C2—C3—C8	−123.4 (5)	B1—C69—C70—C71	177.6 (4)
C1—C2—C3—Ru1	−59.7 (3)	C69—C70—C71—C72	−1.2 (7)
C7—C2—C3—Ru1	123.1 (5)	C69—C70—C71—C75	−180.0 (4)
C2—C3—C4—C5	−0.6 (6)	C70—C71—C72—C73	−0.6 (7)
C8—C3—C4—C5	−176.2 (4)	C75—C71—C72—C73	178.1 (5)
Ru1—C3—C4—C5	63.4 (3)	C71—C72—C73—C74	1.2 (7)
C2—C3—C4—C9	171.7 (5)	C71—C72—C73—C76	−176.4 (4)
C8—C3—C4—C9	−3.8 (8)	C72—C73—C74—C69	−0.1 (7)
Ru1—C3—C4—C9	−124.3 (5)	C76—C73—C74—C69	177.5 (4)

C2—C3—C4—Ru1	−64.0 (3)	C70—C69—C74—C73	−1.6 (7)
C8—C3—C4—Ru1	120.4 (5)	B1—C69—C74—C73	−177.1 (4)
C3—C4—C5—C1	−0.4 (6)	C72—C71—C75—F9	−97.9 (6)
C9—C4—C5—C1	−172.6 (5)	C70—C71—C75—F9	80.9 (6)
Ru1—C4—C5—C1	63.8 (3)	C72—C71—C75—F7	141.5 (5)
C3—C4—C5—C10	172.3 (5)	C70—C71—C75—F7	−39.7 (7)
C9—C4—C5—C10	0.2 (9)	C72—C71—C75—F8	20.9 (7)
Ru1—C4—C5—C10	−123.4 (5)	C70—C71—C75—F8	−160.3 (4)
C3—C4—C5—Ru1	−64.3 (3)	C72—C73—C76—F11	−172.7 (5)
C9—C4—C5—Ru1	123.6 (5)	C74—C73—C76—F11	9.7 (7)
C2—C1—C5—C4	1.3 (6)	C72—C73—C76—F10	−51.3 (7)
C6—C1—C5—C4	175.5 (5)	C74—C73—C76—F10	131.1 (5)
Ru1—C1—C5—C4	−62.2 (3)	C72—C73—C76—F12	66.7 (6)
C2—C1—C5—C10	−171.6 (5)	C74—C73—C76—F12	−110.9 (6)
C6—C1—C5—C10	2.6 (8)	C82—C77—C78—C79	2.1 (7)
Ru1—C1—C5—C10	124.9 (5)	B1—C77—C78—C79	175.5 (4)
C2—C1—C5—Ru1	63.5 (3)	C77—C78—C79—C80	−0.7 (7)
C6—C1—C5—Ru1	−122.2 (5)	C77—C78—C79—C83	176.8 (6)
C15—C11—C12—C13	−2.6 (5)	C77—C78—C79—C83A	−176.0 (9)
C16—C11—C12—C13	173.2 (4)	C78—C79—C80—C81	−0.4 (7)
Ru2—C11—C12—C13	−62.3 (3)	C83—C79—C80—C81	−177.9 (6)
C15—C11—C12—C17	−178.3 (4)	C83A—C79—C80—C81	174.7 (9)
C16—C11—C12—C17	−2.6 (7)	C79—C80—C81—C82	0.1 (7)
Ru2—C11—C12—C17	121.9 (5)	C79—C80—C81—C84	176.7 (4)
C15—C11—C12—Ru2	59.8 (3)	C80—C81—C82—C77	1.4 (7)
C16—C11—C12—Ru2	−124.5 (5)	C84—C81—C82—C77	−175.2 (4)
C11—C12—C13—C14	2.5 (6)	C78—C77—C82—C81	−2.4 (7)
C17—C12—C13—C14	178.3 (4)	B1—C77—C82—C81	−175.9 (4)
Ru2—C12—C13—C14	−59.5 (4)	C80—C79—C83—F14	130.8 (9)
C11—C12—C13—C18	−173.0 (4)	C78—C79—C83—F14	−46.7 (12)
C17—C12—C13—C18	2.7 (8)	C80—C79—C83—F15	7.7 (12)
Ru2—C12—C13—C18	125.0 (5)	C78—C79—C83—F15	−169.8 (8)
C11—C12—C13—Ru2	62.0 (3)	C80—C79—C83—F13	−111.7 (9)
C17—C12—C13—Ru2	−122.3 (5)	C78—C79—C83—F13	70.8 (11)
C12—C13—C14—C15	−1.5 (6)	C80—C79—C83A—F15A	−8.9 (16)
C18—C13—C14—C15	174.1 (4)	C78—C79—C83A—F15A	166.4 (10)
Ru2—C13—C14—C15	−62.0 (3)	C80—C79—C83A—F14A	109.3 (12)
C12—C13—C14—C19	−177.8 (5)	C78—C79—C83A—F14A	−75.4 (13)
C18—C13—C14—C19	−2.2 (8)	C80—C79—C83A—F13A	−132.7 (12)
Ru2—C13—C14—C19	121.7 (5)	C78—C79—C83A—F13A	42.6 (16)
C12—C13—C14—Ru2	60.5 (4)	C80—C81—C84—F17	25.3 (6)
C18—C13—C14—Ru2	−123.9 (5)	C82—C81—C84—F17	−158.1 (4)
C12—C11—C15—C14	1.6 (5)	C80—C81—C84—F18	−95.6 (5)
C16—C11—C15—C14	−174.0 (4)	C82—C81—C84—F18	81.1 (6)

Ru2—C11—C15—C14	62.2 (3)	C80—C81—C84—F16	145.8 (4)
C12—C11—C15—C20	175.9 (4)	C82—C81—C84—F16	−37.6 (6)
C16—C11—C15—C20	0.3 (8)	C90—C85—C86—C87	1.5 (7)
Ru2—C11—C15—C20	−123.6 (5)	B1—C85—C86—C87	176.1 (4)
C12—C11—C15—Ru2	−60.5 (3)	C85—C86—C87—C88	0.0 (7)
C16—C11—C15—Ru2	123.8 (5)	C85—C86—C87—C91	179.8 (5)
C13—C14—C15—C11	−0.1 (5)	C86—C87—C88—C89	−1.5 (7)
C19—C14—C15—C11	176.3 (4)	C91—C87—C88—C89	178.6 (5)
Ru2—C14—C15—C11	−63.7 (3)	C87—C88—C89—C90	1.5 (7)
C13—C14—C15—C20	−174.1 (5)	C87—C88—C89—C92	−176.1 (4)
C19—C14—C15—C20	2.3 (8)	C88—C89—C90—C85	0.1 (7)
Ru2—C14—C15—C20	122.3 (5)	C92—C89—C90—C85	177.7 (4)
C13—C14—C15—Ru2	63.6 (4)	C86—C85—C90—C89	−1.6 (7)
C19—C14—C15—Ru2	−120.1 (5)	B1—C85—C90—C89	−175.7 (4)
C35—C31—C32—C33	0.1 (7)	C86—C87—C91—F20	−93.4 (6)
C36—C31—C32—C33	−174.0 (6)	C88—C87—C91—F20	86.4 (6)
Ru3—C31—C32—C33	61.2 (4)	C86—C87—C91—F21	145.7 (5)
C35—C31—C32—C37	175.9 (6)	C88—C87—C91—F21	−34.4 (7)
C36—C31—C32—C37	1.7 (10)	C86—C87—C91—F19	26.0 (7)
Ru3—C31—C32—C37	−123.1 (6)	C88—C87—C91—F19	−154.2 (5)
C35—C31—C32—Ru3	−61.1 (4)	C90—C89—C92—F23	38.6 (6)
C36—C31—C32—Ru3	124.8 (6)	C88—C89—C92—F23	−143.9 (5)
C31—C32—C33—C34	−0.6 (6)	C90—C89—C92—F24	−81.3 (6)
C37—C32—C33—C34	−176.6 (5)	C88—C89—C92—F24	96.2 (5)
Ru3—C32—C33—C34	59.5 (4)	C90—C89—C92—F22	158.9 (4)
C31—C32—C33—C38	178.5 (5)	C88—C89—C92—F22	−23.5 (7)
C37—C32—C33—C38	2.5 (9)	C62—C61—B1—C69	−21.7 (6)
Ru3—C32—C33—C38	−121.4 (6)	C66—C61—B1—C69	165.4 (4)
C31—C32—C33—Ru3	−60.1 (4)	C62—C61—B1—C85	98.5 (5)
C37—C32—C33—Ru3	124.0 (6)	C66—C61—B1—C85	−74.4 (5)
C32—C33—C34—C35	0.9 (6)	C62—C61—B1—C77	−140.0 (4)
C38—C33—C34—C35	−178.2 (6)	C66—C61—B1—C77	47.1 (6)
Ru3—C33—C34—C35	62.6 (4)	C70—C69—B1—C61	135.8 (5)
C32—C33—C34—C39	174.6 (5)	C74—C69—B1—C61	−49.1 (6)
C38—C33—C34—C39	−4.5 (9)	C70—C69—B1—C85	20.0 (6)
Ru3—C33—C34—C39	−123.7 (6)	C74—C69—B1—C85	−164.9 (4)
C32—C33—C34—Ru3	−61.7 (4)	C70—C69—B1—C77	−102.6 (5)
C38—C33—C34—Ru3	119.2 (6)	C74—C69—B1—C77	72.5 (5)
C32—C31—C35—C34	0.5 (7)	C86—C85—B1—C61	−70.0 (5)
C36—C31—C35—C34	174.4 (6)	C90—C85—B1—C61	103.9 (5)
Ru3—C31—C35—C34	−62.9 (4)	C86—C85—B1—C69	51.4 (6)
C32—C31—C35—C40	−171.1 (5)	C90—C85—B1—C69	−134.7 (5)
C36—C31—C35—C40	2.8 (10)	C86—C85—B1—C77	169.7 (4)
Ru3—C31—C35—C40	125.6 (6)	C90—C85—B1—C77	−16.5 (7)

C32—C31—C35—Ru3	63.3 (4)	C78—C77—B1—C61	26.9 (6)
C36—C31—C35—Ru3	−122.7 (6)	C82—C77—B1—C61	−160.0 (4)
C33—C34—C35—C31	−0.8 (6)	C78—C77—B1—C69	−95.7 (5)
C39—C34—C35—C31	−174.7 (5)	C82—C77—B1—C69	77.3 (5)
Ru3—C34—C35—C31	63.8 (4)	C78—C77—B1—C85	142.8 (4)
C33—C34—C35—C40	170.8 (5)	C82—C77—B1—C85	−44.1 (6)
C39—C34—C35—C40	−3.1 (9)	C106—C101—C102—C103	−1.3 (7)
Ru3—C34—C35—C40	−124.6 (6)	B2—C101—C102—C103	−174.9 (4)
C33—C34—C35—Ru3	−64.7 (4)	C101—C102—C103—C104	1.5 (7)
C39—C34—C35—Ru3	121.5 (5)	C101—C102—C103—C107	−178.2 (4)
C45—C41—C42—C43	−4.8 (7)	C102—C103—C104—C105	−0.3 (7)
C46—C41—C42—C43	173.6 (6)	C107—C103—C104—C105	179.3 (5)
Ru4—C41—C42—C43	−64.4 (4)	C103—C104—C105—C106	−1.0 (7)
C45—C41—C42—C47	179.5 (6)	C103—C104—C105—C108	176.0 (5)
C46—C41—C42—C47	−2.1 (10)	C103—C104—C105—C208	−171.3 (9)
Ru4—C41—C42—C47	119.8 (6)	C102—C101—C106—C105	0.0 (7)
C45—C41—C42—Ru4	59.6 (4)	B2—C101—C106—C105	173.9 (4)
C46—C41—C42—Ru4	−122.0 (6)	C104—C105—C106—C101	1.2 (7)
C41—C42—C43—C44	5.4 (7)	C108—C105—C106—C101	−175.8 (5)
C47—C42—C43—C44	−179.0 (6)	C208—C105—C106—C101	172.5 (8)
Ru4—C42—C43—C44	−58.1 (5)	C104—C103—C107—F32	4.1 (7)
C41—C42—C43—C48	−174.2 (6)	C102—C103—C107—F32	−176.3 (4)
C47—C42—C43—C48	1.5 (11)	C104—C103—C107—F33	125.7 (5)
Ru4—C42—C43—C48	122.3 (6)	C102—C103—C107—F33	−54.7 (7)
C41—C42—C43—Ru4	63.5 (4)	C104—C103—C107—F31	−114.9 (5)
C47—C42—C43—Ru4	−120.9 (7)	C102—C103—C107—F31	64.7 (6)
C42—C43—C44—C45	−4.0 (7)	C104—C105—C108—F34	−164.6 (6)
C48—C43—C44—C45	175.6 (6)	C106—C105—C108—F34	12.4 (9)
Ru4—C43—C44—C45	−62.9 (4)	C104—C105—C108—F36	73.1 (8)
C42—C43—C44—C49	−179.0 (6)	C106—C105—C108—F36	−109.8 (7)
C48—C43—C44—C49	0.6 (11)	C104—C105—C108—F35	−43.0 (8)
Ru4—C43—C44—C49	122.1 (7)	C106—C105—C108—F35	134.0 (6)
C42—C43—C44—Ru4	58.9 (5)	C104—C105—C208—F36A	124.6 (12)
C48—C43—C44—Ru4	−121.6 (6)	C106—C105—C208—F36A	−46.2 (16)
C42—C41—C45—C44	2.3 (7)	C104—C105—C208—F34A	−112.6 (12)
C46—C41—C45—C44	−176.1 (6)	C106—C105—C208—F34A	76.6 (13)
Ru4—C41—C45—C44	62.0 (4)	C104—C105—C208—F35A	2.8 (16)
C42—C41—C45—C50	178.8 (6)	C106—C105—C208—F35A	−168.1 (10)
C46—C41—C45—C50	0.5 (11)	C114—C109—C110—C111	1.3 (7)
Ru4—C41—C45—C50	−121.5 (7)	B2—C109—C110—C111	174.9 (4)
C42—C41—C45—Ru4	−59.7 (4)	C109—C110—C111—C112	−1.8 (7)
C46—C41—C45—Ru4	121.9 (6)	C109—C110—C111—C115	175.3 (4)
C43—C44—C45—C41	1.0 (7)	C110—C111—C112—C113	−0.2 (7)
C49—C44—C45—C41	175.9 (6)	C115—C111—C112—C113	−177.4 (5)

Ru4—C44—C45—C41	−63.6 (4)	C111—C112—C113—C114	2.6 (7)
C43—C44—C45—C50	−175.6 (6)	C111—C112—C113—C116	177.2 (5)
C49—C44—C45—C50	−0.6 (11)	C112—C113—C114—C109	−3.1 (7)
Ru4—C44—C45—C50	119.9 (7)	C116—C113—C114—C109	−177.9 (4)
C43—C44—C45—Ru4	64.6 (4)	C110—C109—C114—C113	1.1 (7)
C49—C44—C45—Ru4	−120.5 (7)	B2—C109—C114—C113	−172.7 (4)
C35A—C31A—C32A—C33A	2.9 (13)	C112—C111—C115—F39	−7.6 (8)
C36A—C31A—C32A—C33A	173 (2)	C110—C111—C115—F39	175.2 (5)
Ru3A—C31A—C32A—C33A	63.0 (7)	C112—C111—C115—F38	−137.3 (5)
C35A—C31A—C32A—C37A	−177 (2)	C110—C111—C115—F38	45.6 (7)
C36A—C31A—C32A—C37A	−7 (3)	C112—C111—C115—F37	110.6 (5)
Ru3A—C31A—C32A—C37A	−117 (2)	C110—C111—C115—F37	−66.6 (6)
C35A—C31A—C32A—Ru3A	−60.1 (12)	C112—C113—C116—F41	148.0 (5)
C36A—C31A—C32A—Ru3A	110 (2)	C114—C113—C116—F41	−37.3 (7)
C31A—C32A—C33A—C34A	−3.6 (12)	C112—C113—C116—F40	27.0 (7)
C37A—C32A—C33A—C34A	176 (2)	C114—C113—C116—F40	−158.4 (4)
Ru3A—C32A—C33A—C34A	58.6 (11)	C112—C113—C116—F42	−92.8 (6)
C31A—C32A—C33A—C38A	−177 (2)	C114—C113—C116—F42	81.9 (6)
C37A—C32A—C33A—C38A	3 (3)	C122—C117—C118—C119	−1.5 (7)
Ru3A—C32A—C33A—C38A	−115 (2)	B2—C117—C118—C119	−176.3 (4)
C31A—C32A—C33A—Ru3A	−62.3 (7)	C117—C118—C119—C120	1.0 (7)
C37A—C32A—C33A—Ru3A	117.7 (19)	C117—C118—C119—C123	−175.5 (4)
C32A—C33A—C34A—C35A	3 (2)	C118—C119—C120—C121	0.8 (7)
C38A—C33A—C34A—C35A	177 (2)	C123—C119—C120—C121	177.3 (4)
Ru3A—C33A—C34A—C35A	63.7 (14)	C119—C120—C121—C122	−2.0 (7)
C32A—C33A—C34A—C39A	173 (2)	C119—C120—C121—C124	178.2 (4)
C38A—C33A—C34A—C39A	−13 (4)	C120—C121—C122—C117	1.5 (7)
Ru3A—C33A—C34A—C39A	−126 (3)	C124—C121—C122—C117	−178.7 (4)
C32A—C33A—C34A—Ru3A	−60.6 (9)	C118—C117—C122—C121	0.2 (7)
C38A—C33A—C34A—Ru3A	113 (2)	B2—C117—C122—C121	174.8 (4)
C32A—C31A—C35A—C34A	−1 (2)	C118—C119—C123—F44	71.8 (6)
C36A—C31A—C35A—C34A	−171 (2)	C120—C119—C123—F44	−104.7 (5)
Ru3A—C31A—C35A—C34A	−62.2 (14)	C118—C119—C123—F45	−166.4 (4)
C32A—C31A—C35A—C40A	−171 (2)	C120—C119—C123—F45	17.1 (7)
C36A—C31A—C35A—C40A	19 (4)	C118—C119—C123—F43	−47.1 (6)
Ru3A—C31A—C35A—C40A	128 (3)	C120—C119—C123—F43	136.4 (5)
C32A—C31A—C35A—Ru3A	61.2 (10)	C122—C121—C124—F47	−48.3 (6)
C36A—C31A—C35A—Ru3A	−108 (2)	C120—C121—C124—F47	131.5 (5)
C33A—C34A—C35A—C31A	−1 (2)	C122—C121—C124—F48	71.4 (6)
C39A—C34A—C35A—C31A	−172 (2)	C120—C121—C124—F48	−108.7 (5)
Ru3A—C34A—C35A—C31A	64.3 (13)	C122—C121—C124—F46	−169.9 (4)
C33A—C34A—C35A—C40A	169 (2)	C120—C121—C124—F46	9.9 (7)
C39A—C34A—C35A—C40A	−2 (4)	C130—C125—C126—C127	−0.5 (7)
Ru3A—C34A—C35A—C40A	−126 (3)	B2—C125—C126—C127	−174.3 (4)

C33A—C34A—C35A—Ru3A	−65.5 (13)	C125—C126—C127—C128	0.2 (7)
C39A—C34A—C35A—Ru3A	124 (3)	C125—C126—C127—C131	−179.8 (5)
C45A—C41A—C42A—C43A	0.0 (2)	C126—C127—C128—C129	0.0 (7)
C46A—C41A—C42A—C43A	179.8 (2)	C131—C127—C128—C129	180.0 (5)
Ru4A—C41A—C42A—C43A	−60.3 (5)	C127—C128—C129—C130	0.3 (7)
C45A—C41A—C42A—C47A	−179.9 (4)	C127—C128—C129—C232	174.4 (9)
C46A—C41A—C42A—C47A	−0.1 (4)	C127—C128—C129—C132	179.8 (5)
Ru4A—C41A—C42A—C47A	119.7 (6)	C128—C129—C130—C125	−0.6 (7)
C45A—C41A—C42A—Ru4A	60.3 (6)	C232—C129—C130—C125	−174.8 (10)
C46A—C41A—C42A—Ru4A	−119.8 (6)	C132—C129—C130—C125	179.9 (5)
C41A—C42A—C43A—C44A	−0.1 (2)	C126—C125—C130—C129	0.7 (7)
C47A—C42A—C43A—C44A	179.9 (3)	B2—C125—C130—C129	174.0 (4)
Ru4A—C42A—C43A—C44A	−60.4 (5)	C126—C127—C131—F49	−154.2 (5)
C41A—C42A—C43A—C48A	180.0 (3)	C128—C127—C131—F49	25.8 (7)
C47A—C42A—C43A—C48A	−0.1 (4)	C126—C127—C131—F50	−31.9 (7)
Ru4A—C42A—C43A—C48A	119.6 (6)	C128—C127—C131—F50	148.1 (5)
C41A—C42A—C43A—Ru4A	60.4 (5)	C126—C127—C131—F51	85.6 (6)
C47A—C42A—C43A—Ru4A	−119.7 (6)	C128—C127—C131—F51	−94.4 (6)
C42A—C43A—C44A—C45A	0.1 (4)	C130—C129—C132—F52	88.8 (7)
C48A—C43A—C44A—C45A	−179.9 (4)	C128—C129—C132—F52	−90.7 (7)
Ru4A—C43A—C44A—C45A	−62.4 (6)	C130—C129—C132—F54	−32.5 (9)
C42A—C43A—C44A—C49A	179.9 (5)	C128—C129—C132—F54	148.0 (6)
C48A—C43A—C44A—C49A	−0.1 (7)	C130—C129—C132—F53	−152.1 (6)
Ru4A—C43A—C44A—C49A	117.4 (8)	C128—C129—C132—F53	28.4 (9)
C42A—C43A—C44A—Ru4A	62.5 (6)	C130—C129—C232—F54A	6.9 (18)
C48A—C43A—C44A—Ru4A	−117.5 (6)	C128—C129—C232—F54A	−167.3 (13)
C42A—C41A—C45A—C44A	0.1 (4)	C130—C129—C232—F52A	129.1 (14)
C46A—C41A—C45A—C44A	−179.8 (4)	C128—C129—C232—F52A	−45.1 (18)
Ru4A—C41A—C45A—C44A	61.3 (6)	C130—C129—C232—F53A	−111.9 (13)
C42A—C41A—C45A—C50A	179.9 (4)	C128—C129—C232—F53A	73.9 (16)
C46A—C41A—C45A—C50A	0.1 (7)	C130—C125—B2—C109	17.9 (7)
Ru4A—C41A—C45A—C50A	−118.9 (8)	C126—C125—B2—C109	−169.1 (4)
C42A—C41A—C45A—Ru4A	−61.2 (5)	C130—C125—B2—C117	−101.9 (5)
C46A—C41A—C45A—Ru4A	119.0 (6)	C126—C125—B2—C117	71.1 (5)
C43A—C44A—C45A—C41A	−0.1 (5)	C130—C125—B2—C101	136.9 (5)
C49A—C44A—C45A—C41A	−180.0 (4)	C126—C125—B2—C101	−50.1 (6)
Ru4A—C44A—C45A—C41A	−63.4 (6)	C110—C109—B2—C125	40.7 (6)
C43A—C44A—C45A—C50A	−180.0 (5)	C114—C109—B2—C125	−146.0 (4)
C49A—C44A—C45A—C50A	0.2 (9)	C110—C109—B2—C117	156.5 (4)
Ru4A—C44A—C45A—C50A	116.7 (8)	C114—C109—B2—C117	−30.2 (6)
C43A—C44A—C45A—Ru4A	63.3 (6)	C110—C109—B2—C101	−83.5 (5)
C49A—C44A—C45A—Ru4A	−116.5 (7)	C114—C109—B2—C101	89.8 (5)
C66—C61—C62—C63	1.3 (7)	C122—C117—B2—C125	−100.7 (5)
B1—C61—C62—C63	−171.9 (4)	C118—C117—B2—C125	73.6 (5)

C61—C62—C63—C64	−2.2 (7)	C122—C117—B2—C109	136.6 (4)
C61—C62—C63—C67	−179.8 (5)	C118—C117—B2—C109	−49.1 (6)
C62—C63—C64—C65	1.6 (7)	C122—C117—B2—C101	21.6 (6)
C67—C63—C64—C65	179.1 (5)	C118—C117—B2—C101	−164.1 (4)
C63—C64—C65—C66	−0.1 (7)	C106—C101—B2—C125	169.1 (4)
C63—C64—C65—C68	179.3 (5)	C102—C101—B2—C125	−17.5 (6)
C64—C65—C66—C61	−0.7 (7)	C106—C101—B2—C109	−65.9 (5)
C68—C65—C66—C61	179.8 (4)	C102—C101—B2—C109	107.5 (5)
C62—C61—C66—C65	0.2 (7)	C106—C101—B2—C117	53.0 (6)
B1—C61—C66—C65	173.8 (4)	C102—C101—B2—C117	−133.6 (5)

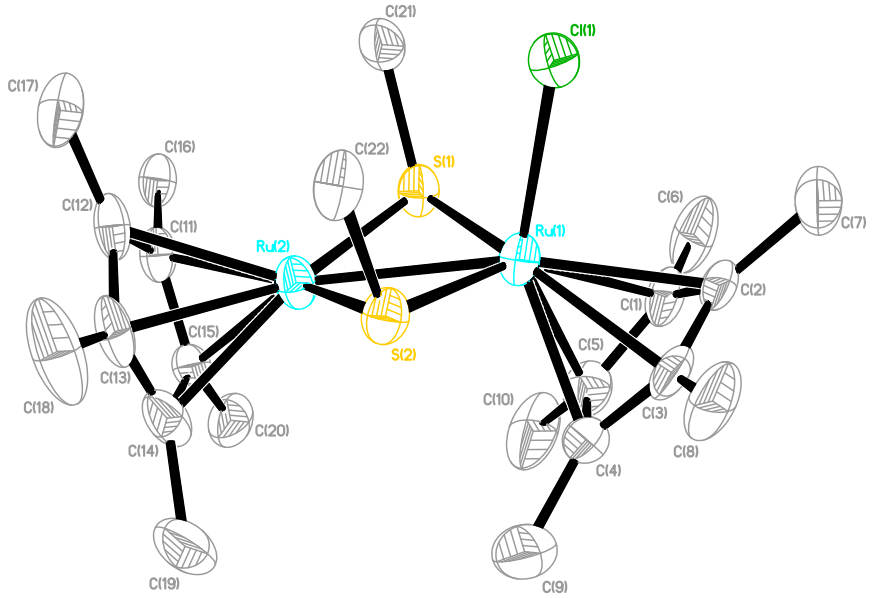


Figure S38a Perspective views of the Ru_2 cation showing 50% probability displacement.

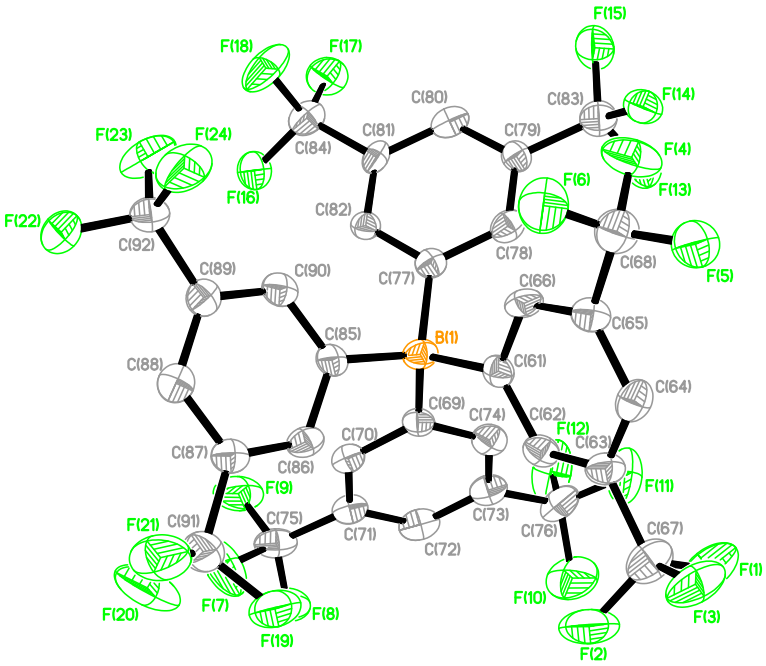


Figure S38b Perspective views of the BAr^{F}_{4} ion showing 50% probability displacement.

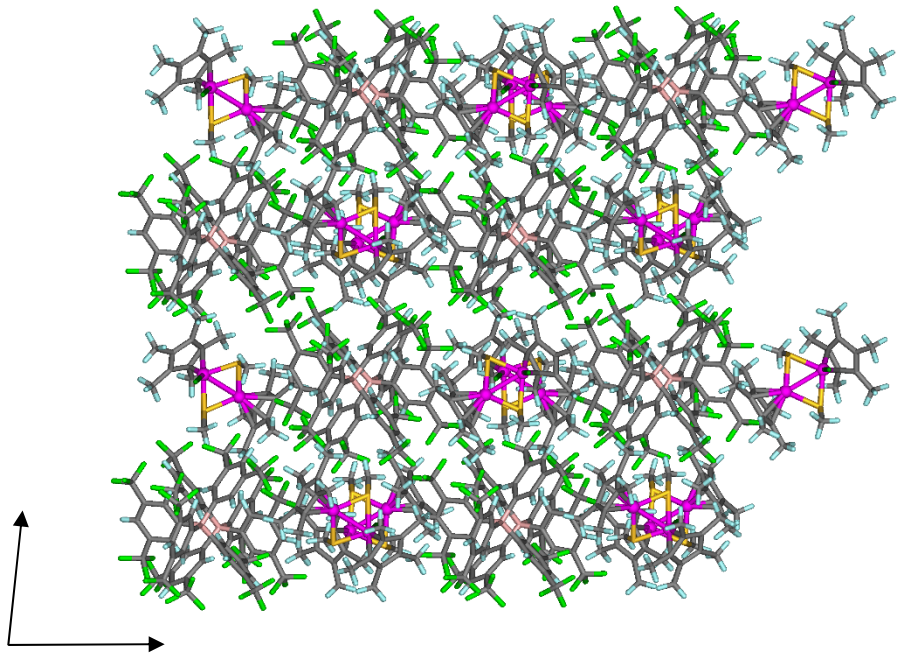


Figure S39 Three-dimensional supramolecular architecture viewed along the *c*-axis direction.

Ruthenium mesylate complex 3d

Ruthenium mesylate complex was prepared as described on page S6. Single crystals of **3d** were grown by slow diffusion of diethyl ether into a solution of **3d** in dichloromethane in a glass vial at 23 °C.

A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer (Mo$K\alpha$ radiation, λ = 0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.84 Å resolution was carried out using SAINT V8.37A[96] with reflection spot size optimization. Absorption corrections were made with the program SADABS[96]. The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F2 using SHELXT-2014[90] and SHELXL-2014[91] with OLEX 2 interface[92]. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S35, geometric parameters are shown in Table S36, and hydrogen-bond parameters are list in Table S37. The Ortep plots produced with SHELXL-2014 program, and the other drawings were produced with Accelrys DS Visualizer 2.0[93].

Table S35 Experimental details.

Crystal data	
CCDC number	2157759
Chemical formula	$C_{23}H_{41}ClO_4Ru_2S_3$
M_r	715.33
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	100
a, *b*, *c* (Å)	8.6749 (5), 11.9046 (6), 14.1587 (7)
α, β, γ (°)	76.4676 (17), 78.0500 (16), 79.7618 (17)
V (Å^3)	1377.88 (13)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	1.45
Crystal size (mm)	0.14 × 0.12 × 0.10
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.621, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	59686, 4905, 3839
R_{int}	0.112
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.597
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.038, 0.083, 1.10

No. of reflections	4905
No. of parameters	311
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.27, −0.85

Table S36 Geometric parameters (Å, º).

Ru1—O1W	2.190 (3)	C9—H9C	0.9800
Ru1—C4	2.191 (5)	C10—H10A	0.9800
Ru1—C5	2.196 (5)	C10—H10B	0.9800
Ru1—C1	2.203 (5)	C10—H10C	0.9800
Ru1—C3	2.226 (5)	C11—C15	1.433 (7)
Ru1—C2	2.248 (5)	C11—C12	1.441 (7)
Ru1—S1	2.3060 (12)	C11—C16	1.493 (7)
Ru1—S2	2.3145 (12)	C12—C13	1.429 (7)
Ru1—Ru2	2.7817 (5)	C12—C17	1.492 (7)
Ru2—C14	2.201 (5)	C13—C14	1.434 (7)
Ru2—C12	2.210 (5)	C13—C18	1.493 (7)
Ru2—C11	2.217 (5)	C14—C15	1.430 (7)
Ru2—C13	2.225 (5)	C14—C19	1.495 (7)
Ru2—C15	2.254 (5)	C15—C20	1.489 (7)
Ru2—S2	2.2995 (12)	C16—H16A	0.9800
Ru2—S1	2.3170 (12)	C16—H16B	0.9800
Ru2—Cl1	2.4440 (13)	C16—H16C	0.9800
S1—C21	1.820 (5)	C17—H17A	0.9800
S2—C22	1.813 (5)	C17—H17B	0.9800
O1W—H1WA	0.8988	C17—H17C	0.9800
O1W—H1WB	0.8337	C18—H18A	0.9800
C1—C2	1.433 (6)	C18—H18B	0.9800
C1—C5	1.440 (7)	C18—H18C	0.9800
C1—C6	1.488 (7)	C19—H19A	0.9800
C2—C3	1.448 (7)	C19—H19B	0.9800
C2—C7	1.474 (6)	C19—H19C	0.9800
C3—C4	1.443 (7)	C20—H20A	0.9800
C3—C8	1.483 (7)	C20—H20B	0.9800
C4—C5	1.424 (7)	C20—H20C	0.9800
C4—C9	1.492 (7)	C21—H21A	0.9800
C5—C10	1.496 (7)	C21—H21B	0.9800
C6—H6A	0.9800	C21—H21C	0.9800
C6—H6B	0.9800	C22—H22A	0.9800
C6—H6C	0.9800	C22—H22B	0.9800
C7—H7A	0.9800	C22—H22C	0.9800
C7—H7B	0.9800	S6—O2	1.440 (4)
C7—H7C	0.9800	S6—O3	1.449 (4)
C8—H8A	0.9800	S6—O1	1.464 (4)

C8—H8B	0.9800	S6—C23	1.757 (5)
C8—H8C	0.9800	C23—H23A	0.9800
C9—H9A	0.9800	C23—H23B	0.9800
C9—H9B	0.9800	C23—H23C	0.9800
O1W—Ru1—C4	148.70 (15)	H6A—C6—H6B	109.5
O1W—Ru1—C5	144.93 (16)	C1—C6—H6C	109.5
C4—Ru1—C5	37.88 (18)	H6A—C6—H6C	109.5
O1W—Ru1—C1	106.92 (15)	H6B—C6—H6C	109.5
C4—Ru1—C1	63.77 (18)	C2—C7—H7A	109.5
C5—Ru1—C1	38.23 (18)	C2—C7—H7B	109.5
O1W—Ru1—C3	110.55 (15)	H7A—C7—H7B	109.5
C4—Ru1—C3	38.15 (18)	C2—C7—H7C	109.5
C5—Ru1—C3	63.32 (18)	H7A—C7—H7C	109.5
C1—Ru1—C3	63.28 (18)	H7B—C7—H7C	109.5
O1W—Ru1—C2	90.59 (14)	C3—C8—H8A	109.5
C4—Ru1—C2	63.53 (17)	C3—C8—H8B	109.5
C5—Ru1—C2	63.22 (17)	H8A—C8—H8B	109.5
C1—Ru1—C2	37.55 (17)	C3—C8—H8C	109.5
C3—Ru1—C2	37.77 (17)	H8A—C8—H8C	109.5
O1W—Ru1—S1	90.74 (9)	H8B—C8—H8C	109.5
C4—Ru1—S1	119.20 (14)	C4—C9—H9A	109.5
C5—Ru1—S1	90.17 (13)	C4—C9—H9B	109.5
C1—Ru1—S1	96.17 (13)	H9A—C9—H9B	109.5
C3—Ru1—S1	153.48 (13)	C4—C9—H9C	109.5
C2—Ru1—S1	131.01 (12)	H9A—C9—H9C	109.5
O1W—Ru1—S2	89.19 (9)	H9B—C9—H9C	109.5
C4—Ru1—S2	90.88 (13)	C5—C10—H10A	109.5
C5—Ru1—S2	124.09 (14)	C5—C10—H10B	109.5
C1—Ru1—S2	152.59 (13)	H10A—C10—H10B	109.5
C3—Ru1—S2	90.56 (13)	C5—C10—H10C	109.5
C2—Ru1—S2	123.12 (12)	H10A—C10—H10C	109.5
S1—Ru1—S2	105.86 (4)	H10B—C10—H10C	109.5
O1W—Ru1—Ru2	90.47 (8)	C15—C11—C12	108.7 (4)
C4—Ru1—Ru2	114.08 (13)	C15—C11—C16	125.7 (4)
C5—Ru1—Ru2	117.47 (13)	C12—C11—C16	125.5 (4)
C1—Ru1—Ru2	145.59 (12)	C15—C11—Ru2	72.7 (3)
C3—Ru1—Ru2	138.11 (13)	C12—C11—Ru2	70.7 (3)
C2—Ru1—Ru2	175.65 (12)	C16—C11—Ru2	126.4 (3)
S1—Ru1—Ru2	53.19 (3)	C13—C12—C11	107.5 (4)
S2—Ru1—Ru2	52.68 (3)	C13—C12—C17	126.9 (5)
C14—Ru2—C12	63.25 (18)	C11—C12—C17	124.8 (5)
C14—Ru2—C11	62.79 (18)	C13—C12—Ru2	71.8 (3)
C12—Ru2—C11	37.99 (17)	C11—C12—Ru2	71.3 (3)

C14—Ru2—C13	37.80 (19)	C17—C12—Ru2	129.8 (3)
C12—Ru2—C13	37.58 (18)	C12—C13—C14	107.8 (4)
C11—Ru2—C13	62.80 (18)	C12—C13—C18	126.4 (5)
C14—Ru2—C15	37.42 (18)	C14—C13—C18	125.5 (5)
C12—Ru2—C15	63.05 (18)	C12—C13—Ru2	70.6 (3)
C11—Ru2—C15	37.37 (17)	C14—C13—Ru2	70.2 (3)
C13—Ru2—C15	62.67 (18)	C18—C13—Ru2	129.6 (3)
C14—Ru2—S2	96.29 (13)	C15—C14—C13	108.9 (4)
C12—Ru2—S2	117.85 (13)	C15—C14—C19	125.1 (5)
C11—Ru2—S2	152.32 (13)	C13—C14—C19	125.6 (5)
C13—Ru2—S2	89.52 (13)	C15—C14—Ru2	73.3 (3)
C15—Ru2—S2	131.43 (13)	C13—C14—Ru2	72.0 (3)
C14—Ru2—S1	152.85 (13)	C19—C14—Ru2	126.6 (3)
C12—Ru2—S1	92.19 (13)	C14—C15—C11	107.0 (4)
C11—Ru2—S1	90.91 (13)	C14—C15—C20	127.2 (5)
C13—Ru2—S1	125.58 (14)	C11—C15—C20	125.8 (4)
C15—Ru2—S1	122.56 (13)	C14—C15—Ru2	69.3 (3)
S2—Ru2—S1	105.99 (4)	C11—C15—Ru2	69.9 (3)
C14—Ru2—Cl1	102.13 (14)	C20—C15—Ru2	125.3 (3)
C12—Ru2—Cl1	147.08 (13)	C11—C16—H16A	109.5
C11—Ru2—Cl1	109.37 (13)	C11—C16—H16B	109.5
C13—Ru2—Cl1	139.67 (14)	H16A—C16—H16B	109.5
C15—Ru2—Cl1	87.21 (13)	C11—C16—H16C	109.5
S2—Ru2—Cl1	91.95 (4)	H16A—C16—H16C	109.5
S1—Ru2—Cl1	92.57 (4)	H16B—C16—H16C	109.5
C14—Ru2—Ru1	146.01 (13)	C12—C17—H17A	109.5
C12—Ru2—Ru1	114.26 (13)	C12—C17—H17B	109.5
C11—Ru2—Ru1	138.05 (12)	H17A—C17—H17B	109.5
C13—Ru2—Ru1	118.04 (13)	C12—C17—H17C	109.5
C15—Ru2—Ru1	175.17 (12)	H17A—C17—H17C	109.5
S2—Ru2—Ru1	53.17 (3)	H17B—C17—H17C	109.5
S1—Ru2—Ru1	52.83 (3)	C13—C18—H18A	109.5
Cl1—Ru2—Ru1	94.29 (3)	C13—C18—H18B	109.5
C21—S1—Ru1	115.52 (17)	H18A—C18—H18B	109.5
C21—S1—Ru2	114.80 (18)	C13—C18—H18C	109.5
Ru1—S1—Ru2	73.98 (4)	H18A—C18—H18C	109.5
C22—S2—Ru2	116.09 (17)	H18B—C18—H18C	109.5
C22—S2—Ru1	114.08 (17)	C14—C19—H19A	109.5
Ru2—S2—Ru1	74.15 (4)	C14—C19—H19B	109.5
Ru1—O1W—H1WA	110.7	H19A—C19—H19B	109.5
Ru1—O1W—H1WB	102.4	C14—C19—H19C	109.5
H1WA—O1W—H1WB	114.2	H19A—C19—H19C	109.5
C2—C1—C5	108.3 (4)	H19B—C19—H19C	109.5
C2—C1—C6	124.6 (4)	C15—C20—H20A	109.5

C5—C1—C6	126.6 (4)	C15—C20—H20B	109.5
C2—C1—Ru1	72.9 (3)	H20A—C20—H20B	109.5
C5—C1—Ru1	70.6 (3)	C15—C20—H20C	109.5
C6—C1—Ru1	128.4 (3)	H20A—C20—H20C	109.5
C1—C2—C3	107.5 (4)	H20B—C20—H20C	109.5
C1—C2—C7	126.5 (4)	S1—C21—H21A	109.5
C3—C2—C7	126.0 (4)	S1—C21—H21B	109.5
C1—C2—Ru1	69.5 (3)	H21A—C21—H21B	109.5
C3—C2—Ru1	70.3 (3)	S1—C21—H21C	109.5
C7—C2—Ru1	125.1 (3)	H21A—C21—H21C	109.5
C4—C3—C2	107.8 (4)	H21B—C21—H21C	109.5
C4—C3—C8	126.3 (4)	S2—C22—H22A	109.5
C2—C3—C8	125.7 (4)	S2—C22—H22B	109.5
C4—C3—Ru1	69.6 (3)	H22A—C22—H22B	109.5
C2—C3—Ru1	71.9 (3)	S2—C22—H22C	109.5
C8—C3—Ru1	127.5 (3)	H22A—C22—H22C	109.5
C5—C4—C3	108.1 (4)	H22B—C22—H22C	109.5
C5—C4—C9	127.3 (5)	O2—S6—O3	114.1 (2)
C3—C4—C9	124.1 (5)	O2—S6—O1	112.8 (2)
C5—C4—Ru1	71.3 (3)	O3—S6—O1	112.2 (2)
C3—C4—Ru1	72.2 (3)	O2—S6—C23	106.6 (3)
C9—C4—Ru1	128.6 (3)	O3—S6—C23	106.4 (3)
C4—C5—C1	108.3 (4)	O1—S6—C23	103.8 (3)
C4—C5—C10	127.1 (5)	S6—C23—H23A	109.5
C1—C5—C10	124.1 (5)	S6—C23—H23B	109.5
C4—C5—Ru1	70.9 (3)	H23A—C23—H23B	109.5
C1—C5—Ru1	71.2 (3)	S6—C23—H23C	109.5
C10—C5—Ru1	129.9 (3)	H23A—C23—H23C	109.5
C1—C6—H6A	109.5	H23B—C23—H23C	109.5
C1—C6—H6B	109.5		
C5—C1—C2—C3	−1.8 (5)	C15—C11—C12—C13	−0.2 (5)
C6—C1—C2—C3	−174.4 (4)	C16—C11—C12—C13	−175.4 (4)
Ru1—C1—C2—C3	60.3 (3)	Ru2—C11—C12—C13	63.0 (3)
C5—C1—C2—C7	178.7 (4)	C15—C11—C12—C17	170.7 (5)
C6—C1—C2—C7	6.1 (8)	C16—C11—C12—C17	−4.5 (8)
Ru1—C1—C2—C7	−119.2 (5)	Ru2—C11—C12—C17	−126.0 (5)
C5—C1—C2—Ru1	−62.1 (3)	C15—C11—C12—Ru2	−63.3 (3)
C6—C1—C2—Ru1	125.2 (5)	C16—C11—C12—Ru2	121.5 (5)
C1—C2—C3—C4	0.8 (5)	C11—C12—C13—C14	−2.1 (5)
C7—C2—C3—C4	−179.7 (4)	C17—C12—C13—C14	−172.7 (5)
Ru1—C2—C3—C4	60.7 (3)	Ru2—C12—C13—C14	60.6 (3)
C1—C2—C3—C8	176.5 (4)	C11—C12—C13—C18	171.8 (5)
C7—C2—C3—C8	−4.0 (8)	C17—C12—C13—C18	1.1 (8)

Ru1—C2—C3—C8	−123.6 (5)	Ru2—C12—C13—C18	−125.5 (5)
C1—C2—C3—Ru1	−59.8 (3)	C11—C12—C13—Ru2	−62.7 (3)
C7—C2—C3—Ru1	119.7 (5)	C17—C12—C13—Ru2	126.6 (5)
C2—C3—C4—C5	0.5 (5)	C12—C13—C14—C15	3.6 (5)
C8—C3—C4—C5	−175.2 (5)	C18—C13—C14—C15	−170.3 (5)
Ru1—C3—C4—C5	62.7 (3)	Ru2—C13—C14—C15	64.5 (3)
C2—C3—C4—C9	172.8 (4)	C12—C13—C14—C19	176.5 (5)
C8—C3—C4—C9	−2.9 (8)	C18—C13—C14—C19	2.6 (8)
Ru1—C3—C4—C9	−125.1 (5)	Ru2—C13—C14—C19	−122.6 (5)
C2—C3—C4—Ru1	−62.2 (3)	C12—C13—C14—Ru2	−60.9 (3)
C8—C3—C4—Ru1	122.2 (5)	C18—C13—C14—Ru2	125.2 (5)
C3—C4—C5—C1	−1.6 (5)	C13—C14—C15—C11	−3.7 (5)
C9—C4—C5—C1	−173.6 (5)	C19—C14—C15—C11	−176.7 (5)
Ru1—C4—C5—C1	61.7 (3)	Ru2—C14—C15—C11	60.0 (3)
C3—C4—C5—C10	170.6 (5)	C13—C14—C15—C20	177.1 (5)
C9—C4—C5—C10	−1.3 (8)	C19—C14—C15—C20	4.1 (8)
Ru1—C4—C5—C10	−126.1 (5)	Ru2—C14—C15—C20	−119.2 (5)
C3—C4—C5—Ru1	−63.3 (3)	C13—C14—C15—Ru2	−63.7 (3)
C9—C4—C5—Ru1	124.8 (5)	C19—C14—C15—Ru2	123.4 (5)
C2—C1—C5—C4	2.1 (5)	C12—C11—C15—C14	2.4 (5)
C6—C1—C5—C4	174.6 (5)	C16—C11—C15—C14	177.6 (4)
Ru1—C1—C5—C4	−61.5 (3)	Ru2—C11—C15—C14	−59.6 (3)
C2—C1—C5—C10	−170.4 (4)	C12—C11—C15—C20	−178.3 (5)
C6—C1—C5—C10	2.0 (8)	C16—C11—C15—C20	−3.2 (8)
Ru1—C1—C5—C10	126.0 (5)	Ru2—C11—C15—C20	119.7 (5)
C2—C1—C5—Ru1	63.6 (3)	C12—C11—C15—Ru2	62.0 (3)
C6—C1—C5—Ru1	−124.0 (5)	C16—C11—C15—Ru2	−122.8 (5)

Table S37 Hydrogen-bond parameters.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
O1W—H1WA···O1	0.90	1.74	2.635 (5)	171.1
O1W—H1WB···Cl1	0.83	2.17	2.993 (3)	168.2

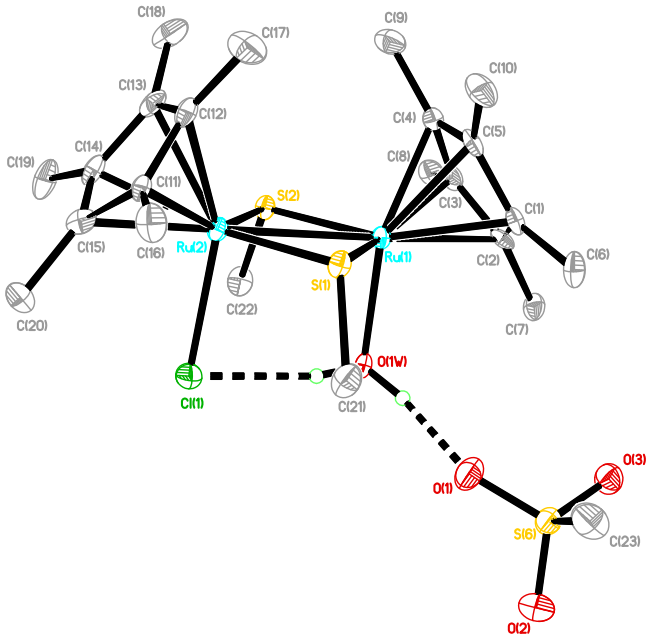


Figure S40 Perspective views showing 50% probability displacement.

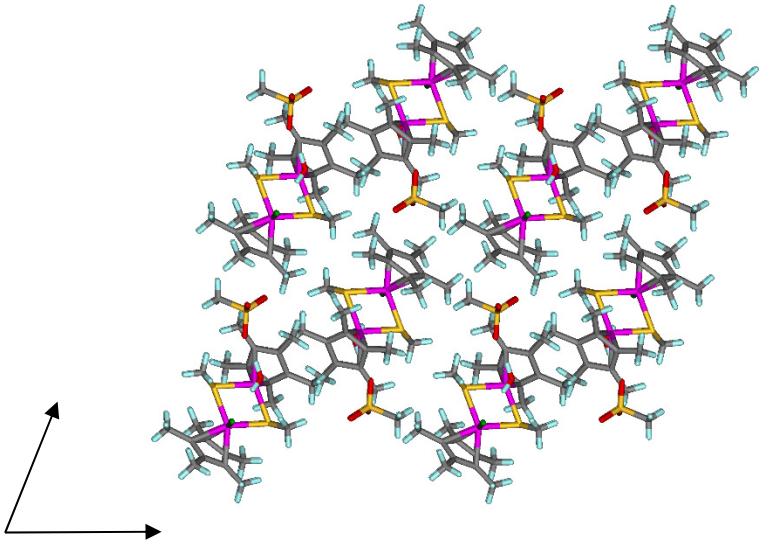
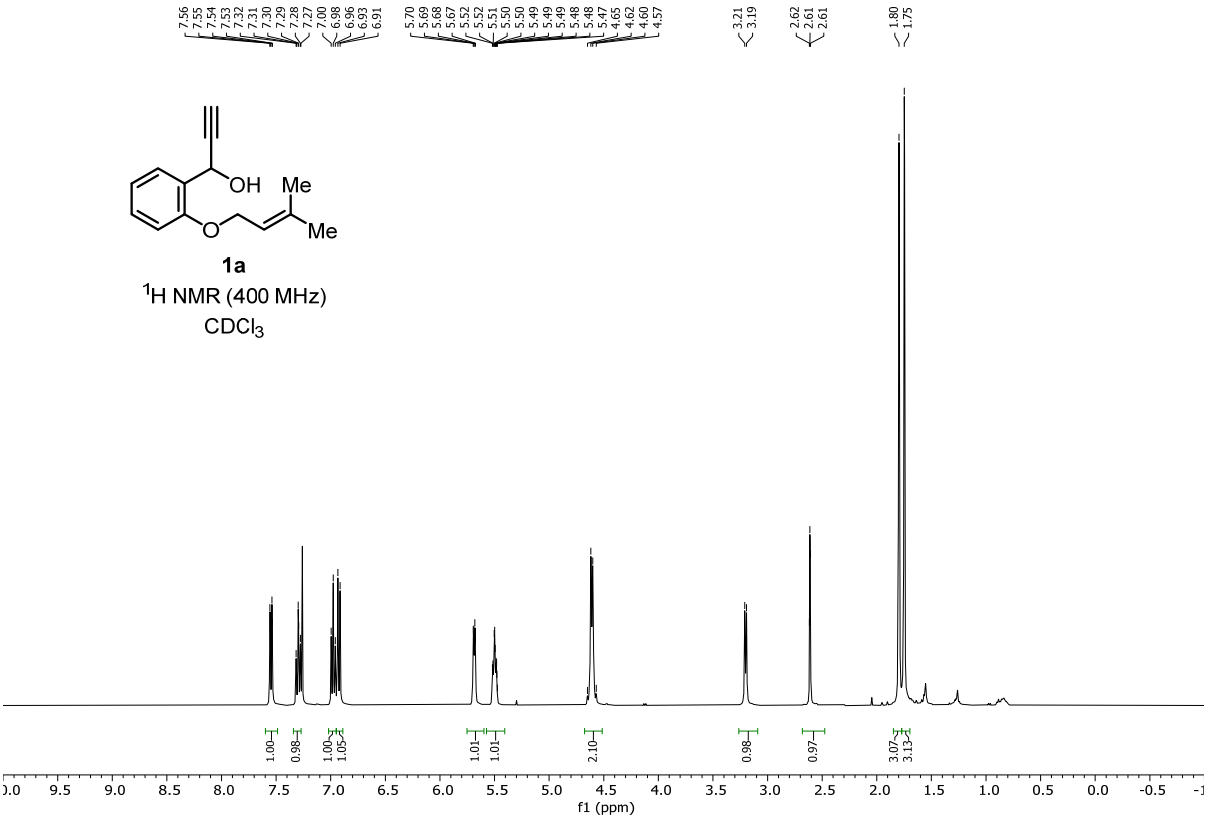
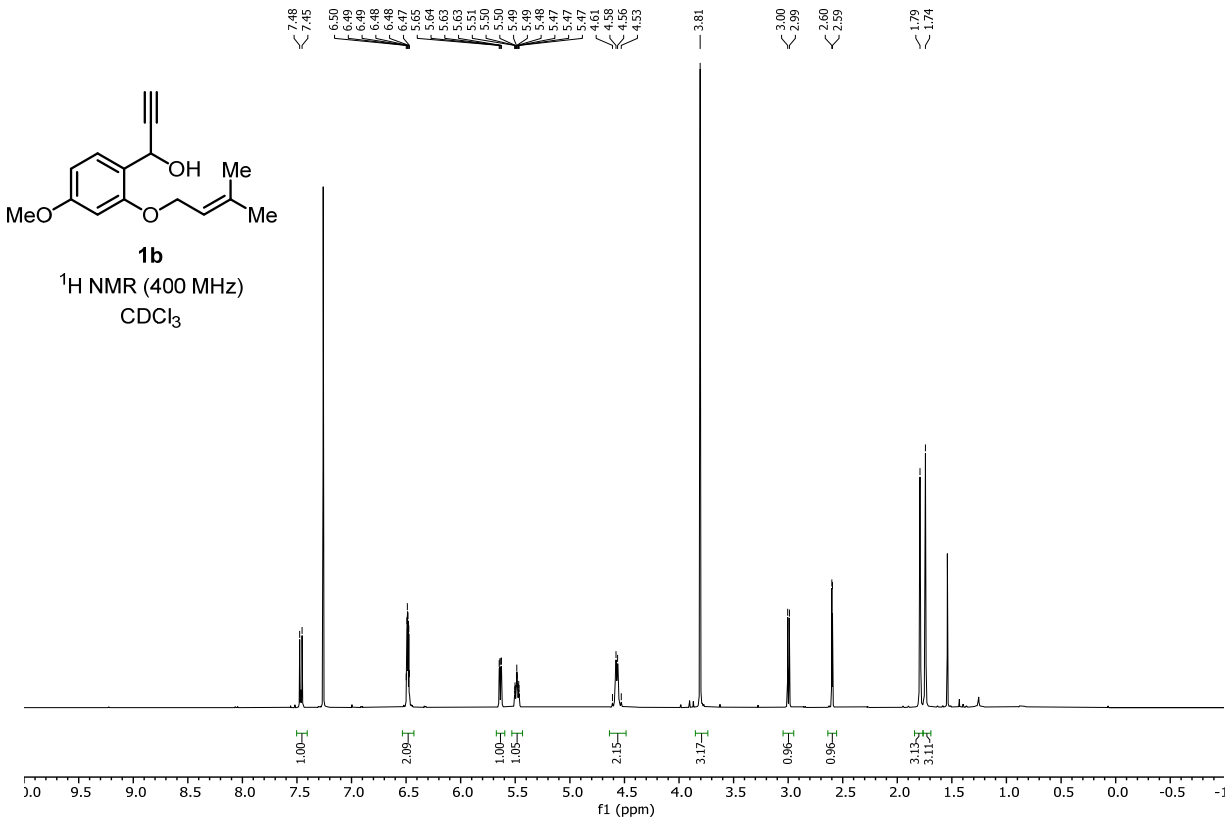
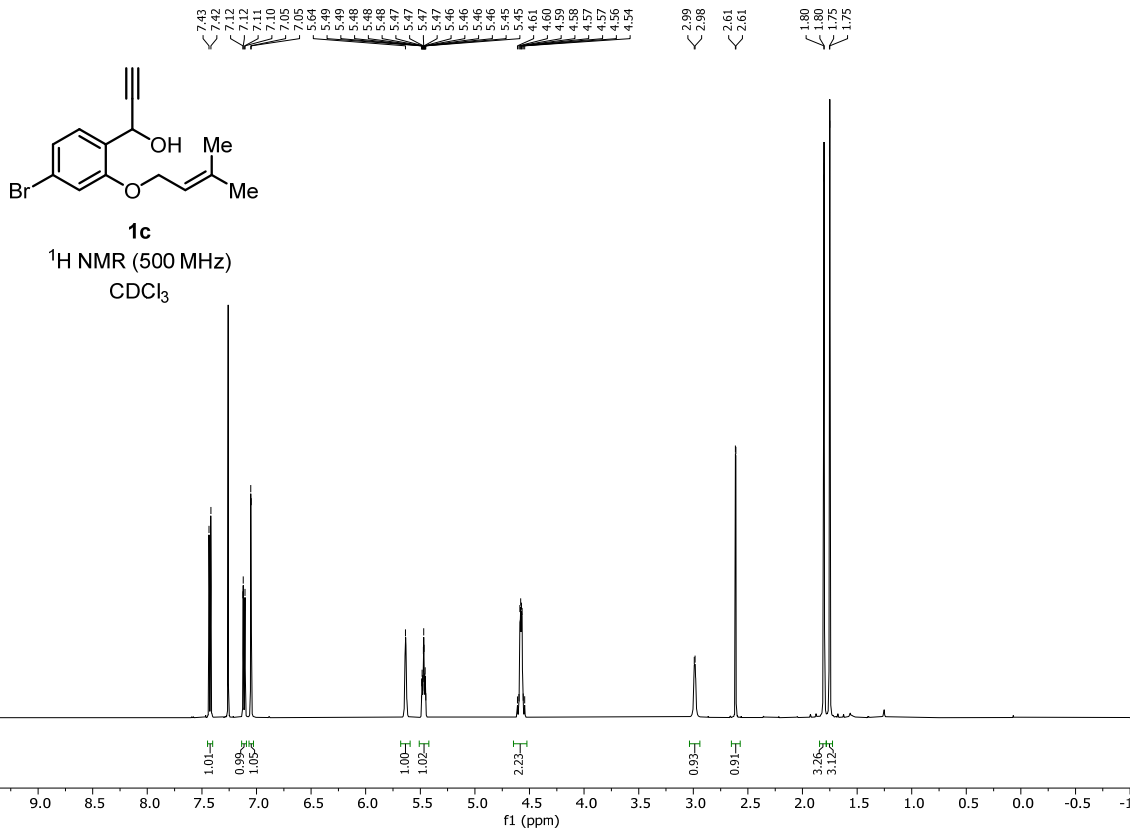


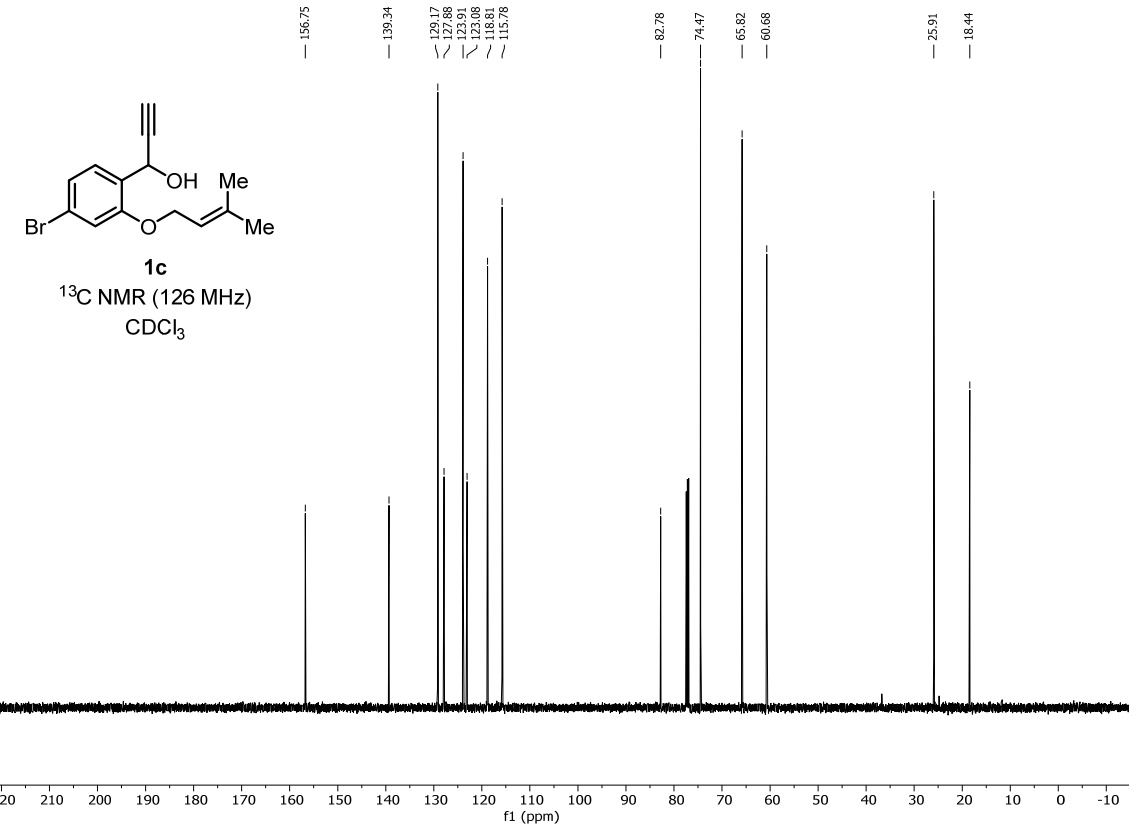
Figure S41 Three-dimensional supramolecular architecture viewed along the *a*-axis direction.

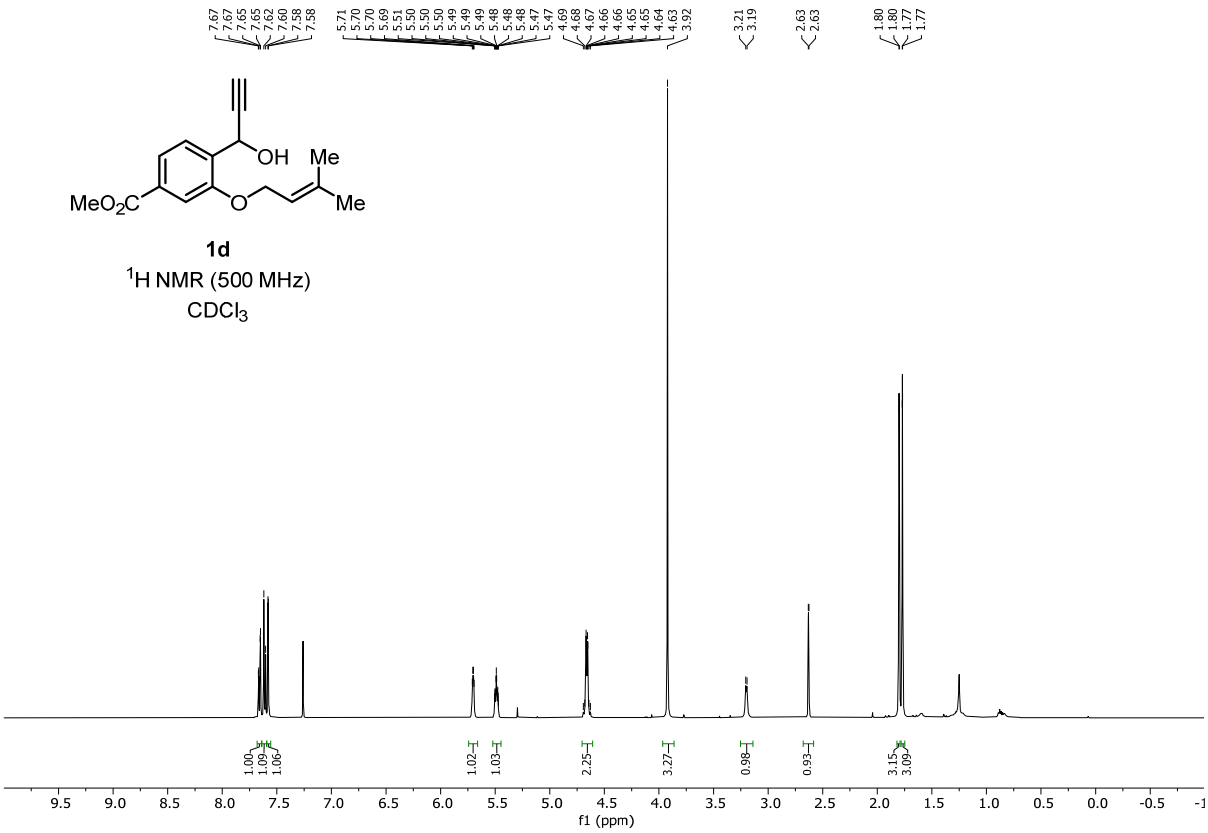
^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{31}P NMR Spectra

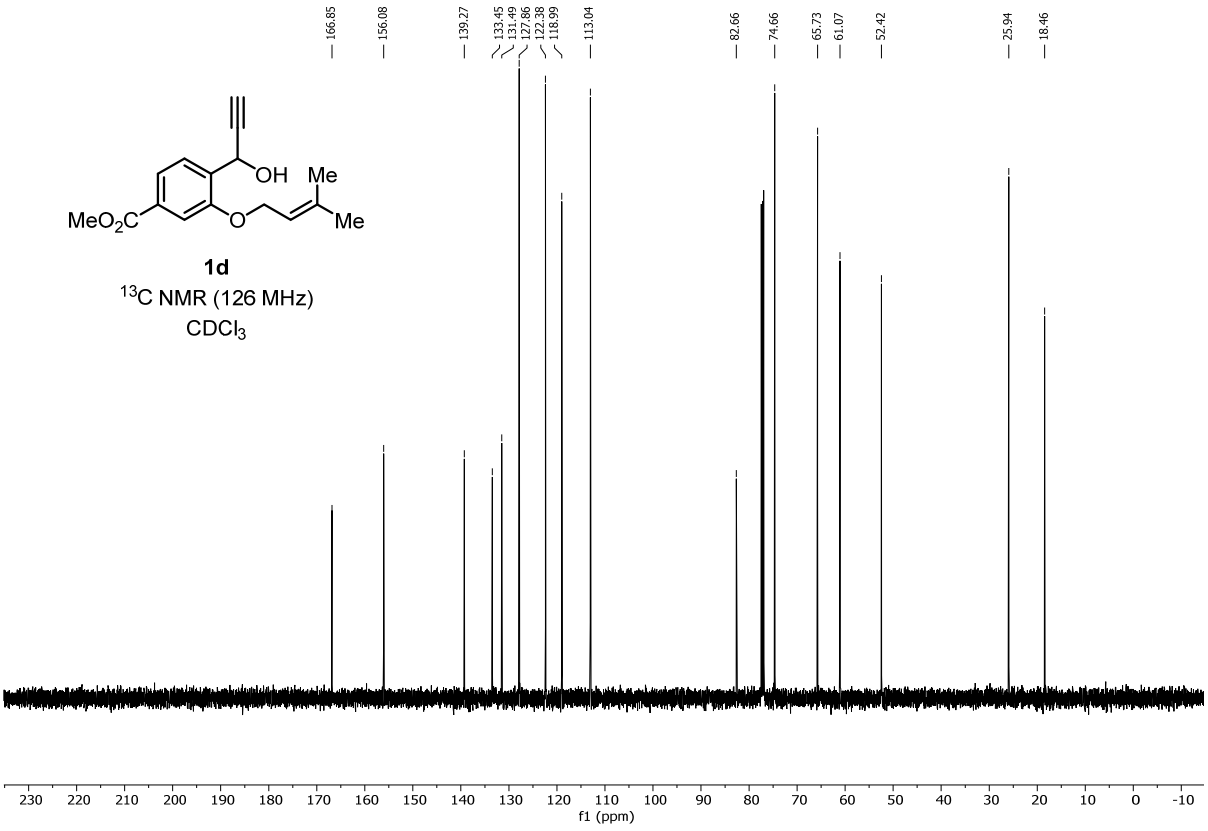


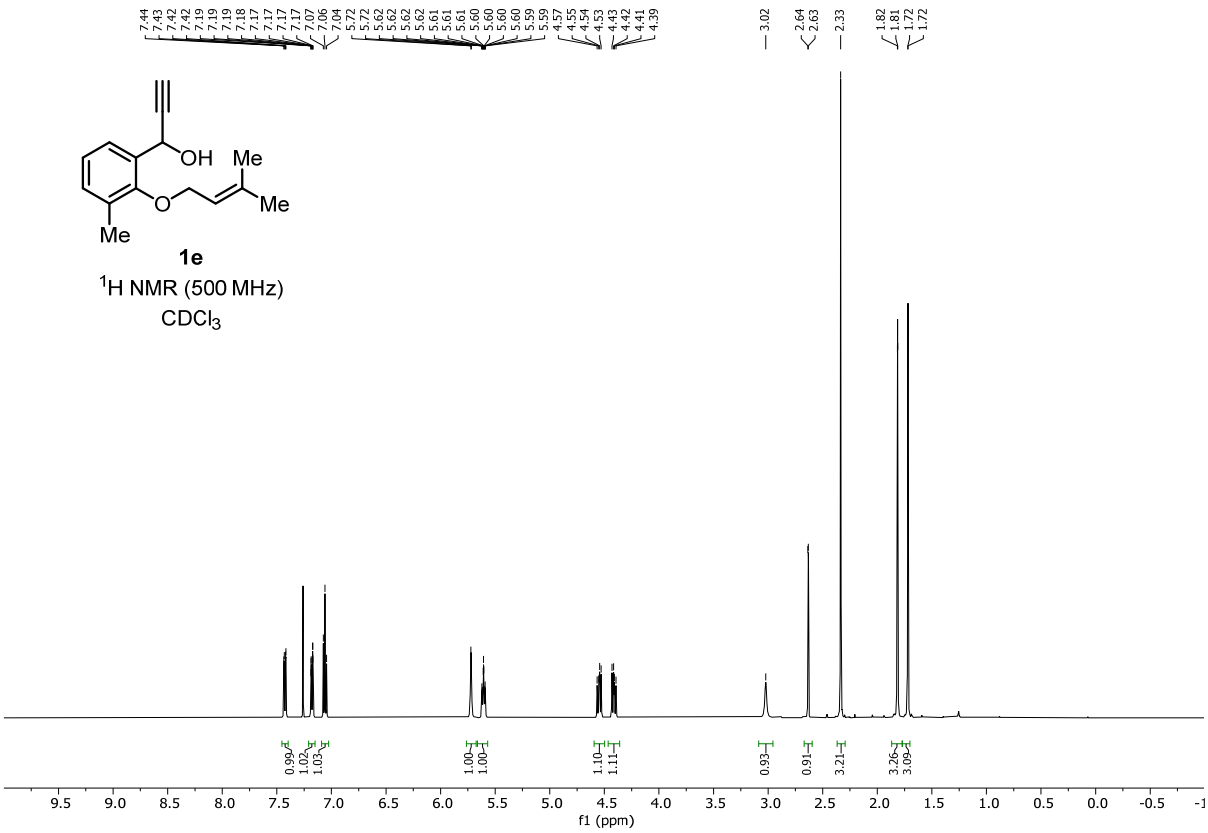


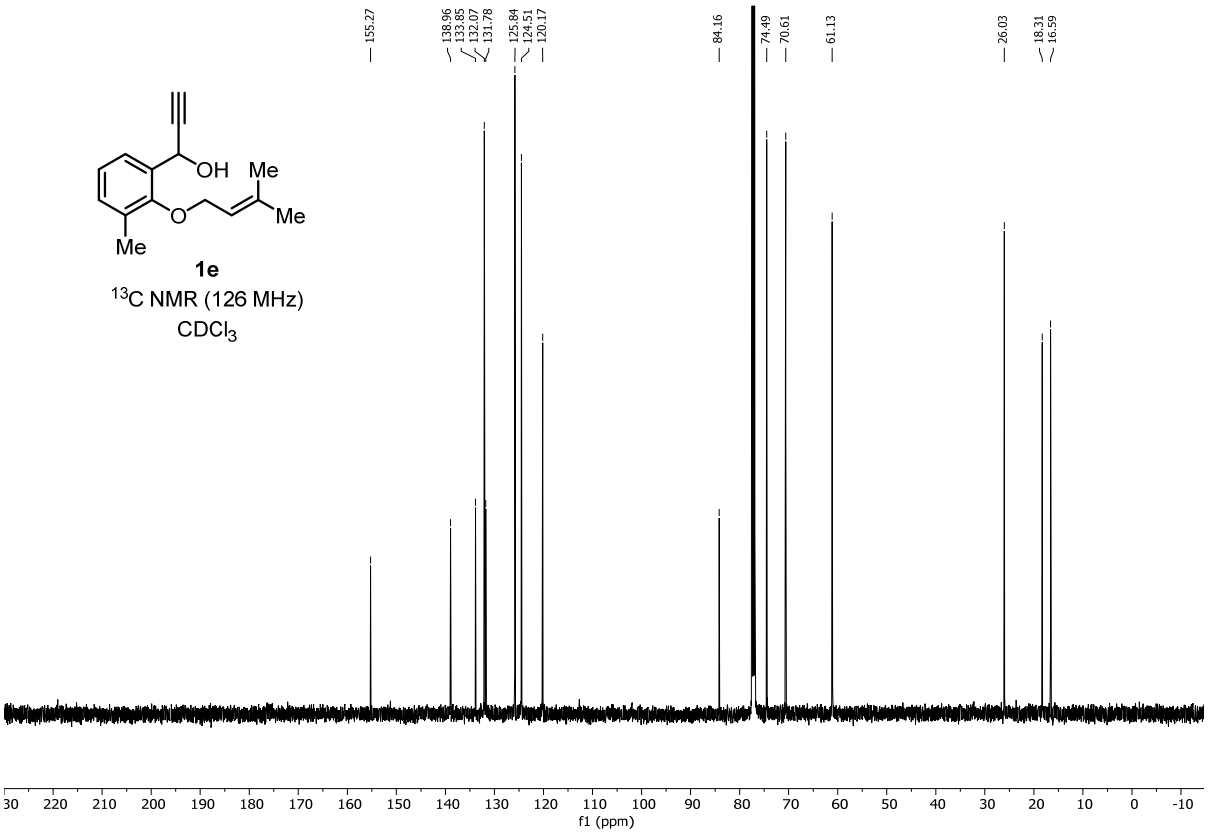

OH
Me
Br
O
Me
1c
1H NMR (500 MHz)
CDCl3
f1 (ppm)

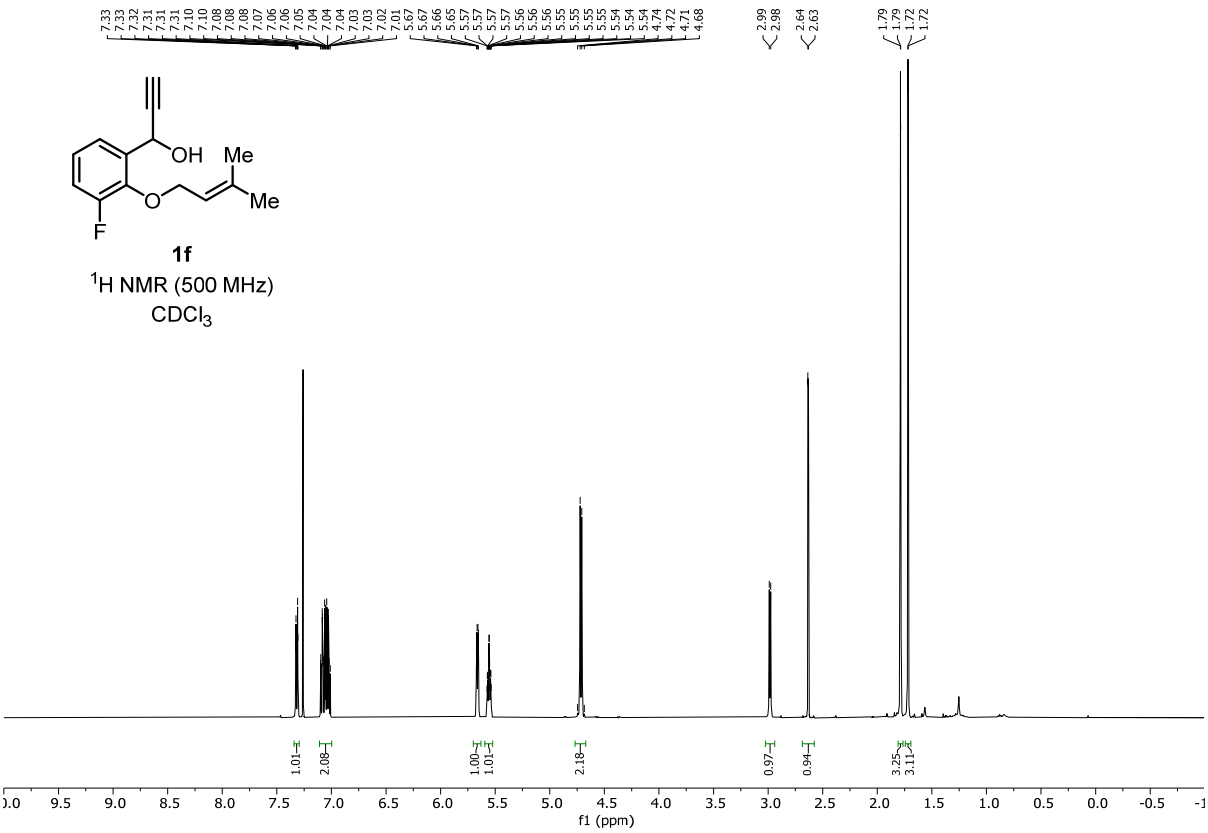

OH
Me
Br
O
Me
1c
13C NMR (126 MHz)
CDCl3
f1 (ppm)

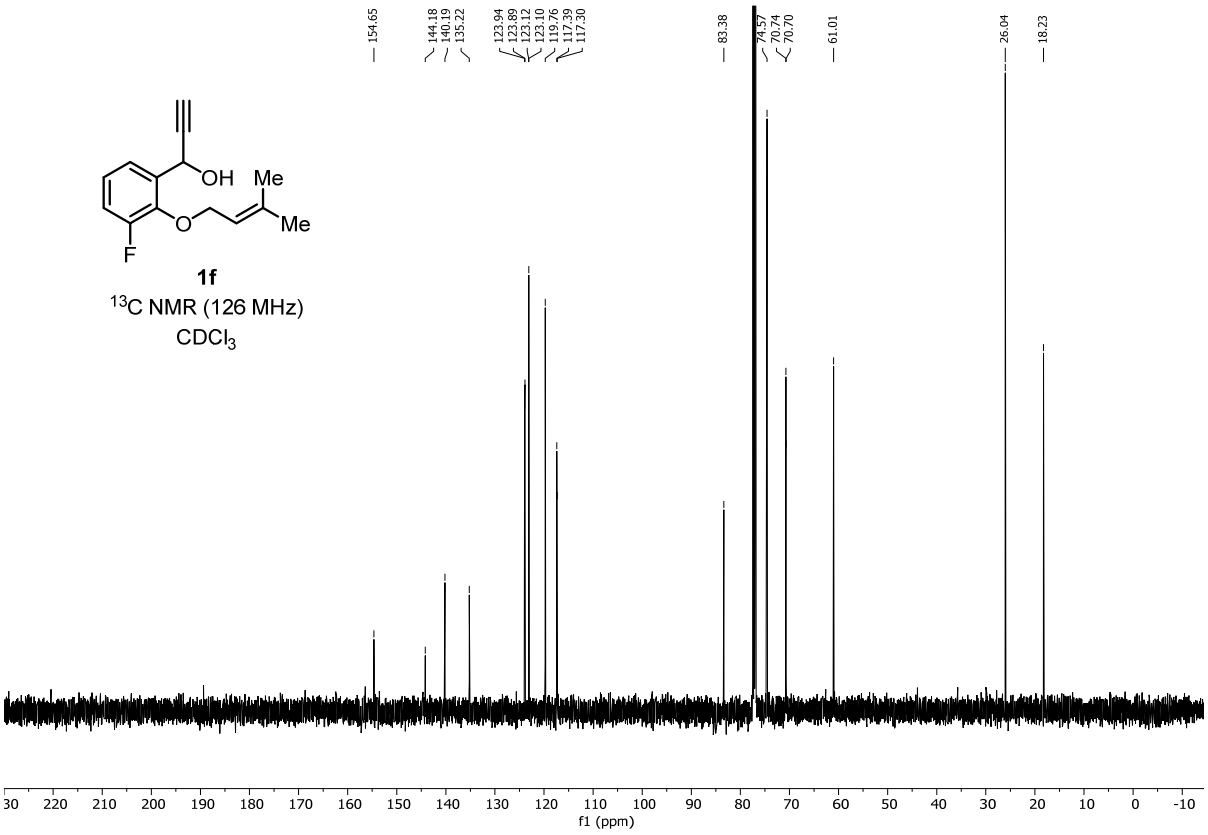

OH
Me
MeO2C
O
Me
1d
1H NMR (500 MHz)
CDCl3
f1 (ppm)

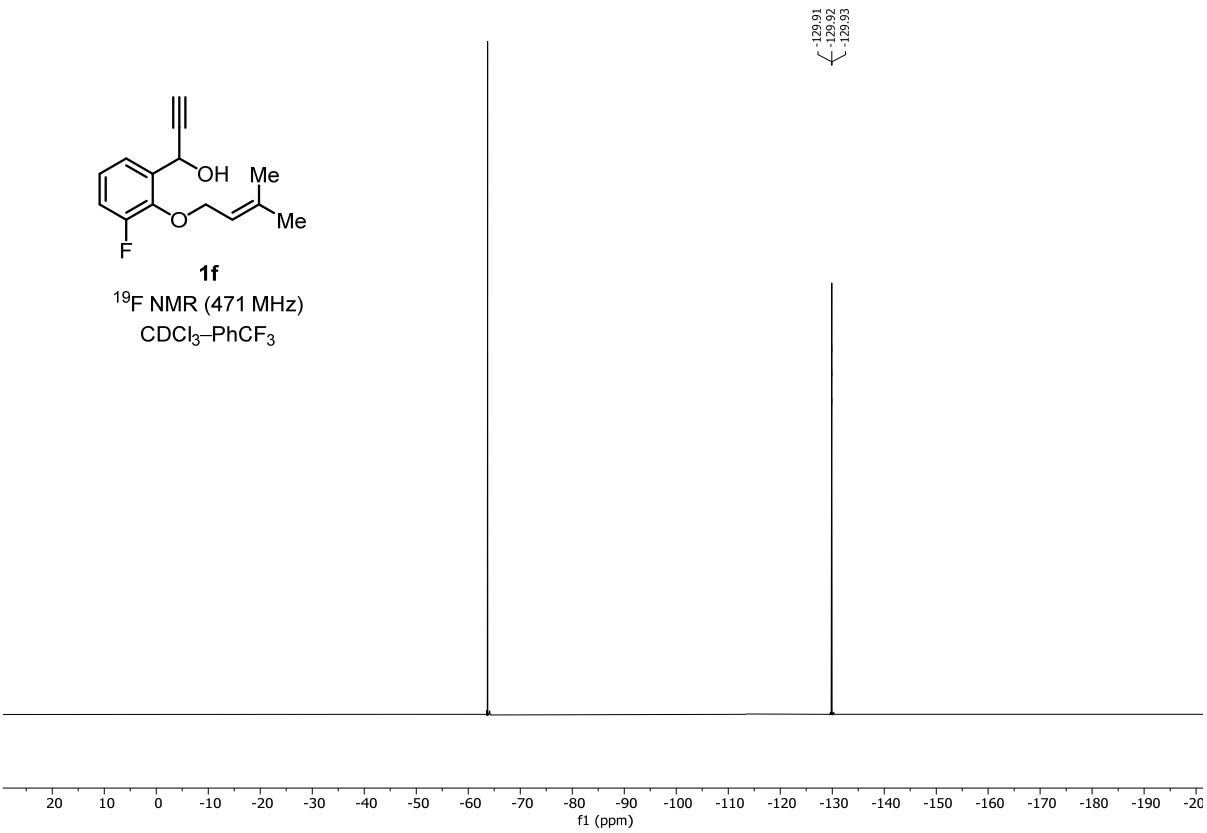

OH
Me
MeO2C
O
Me
1d
13C NMR (126 MHz)
CDCl3
f1 (ppm)

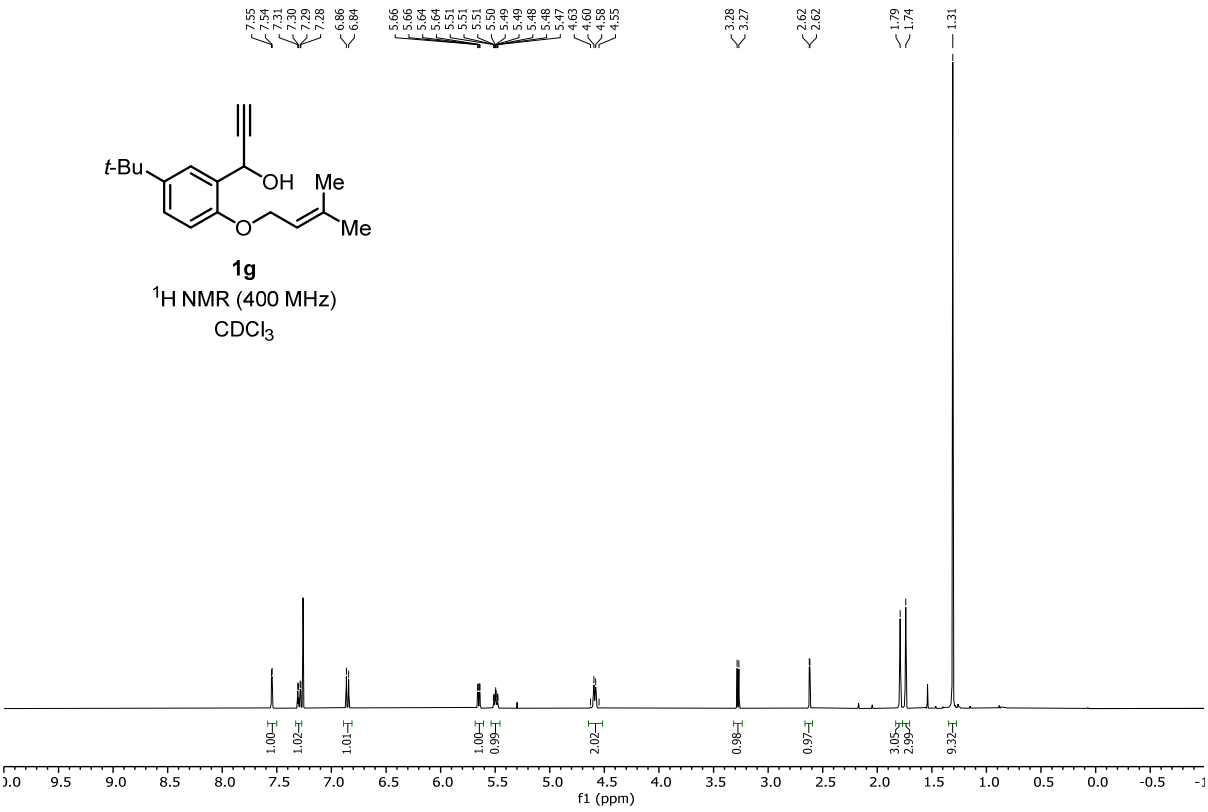

OH
Me
Me
O
Me
1e
1H NMR (500 MHz)
CDCl3
f1 (ppm)


OH
Me
Me
O
Me
1e
13C NMR (126 MHz)
CDCl3
f1 (ppm)


OH
Me
Me
O
F
1f
1H NMR (500 MHz)
CDCl3
f1 (ppm)


OH
Me
Me
O
F
1f
13C NMR (126 MHz)
CDCl3
f1 (ppm)

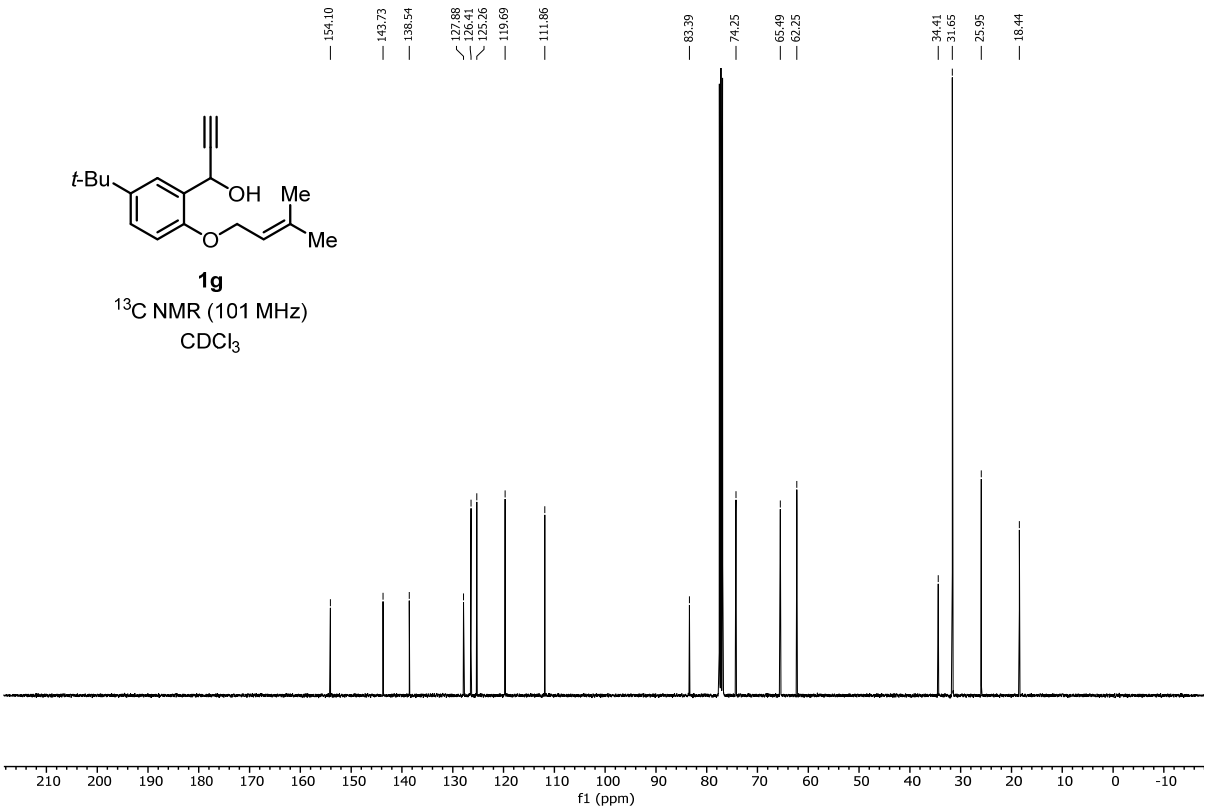

OH
Me
Me
O
F
1f
19F NMR (471 MHz)
CDCl3–PhCF3
-129.91
-129.92
-129.93
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)



1g

^{1}H NMR (400 MHz)

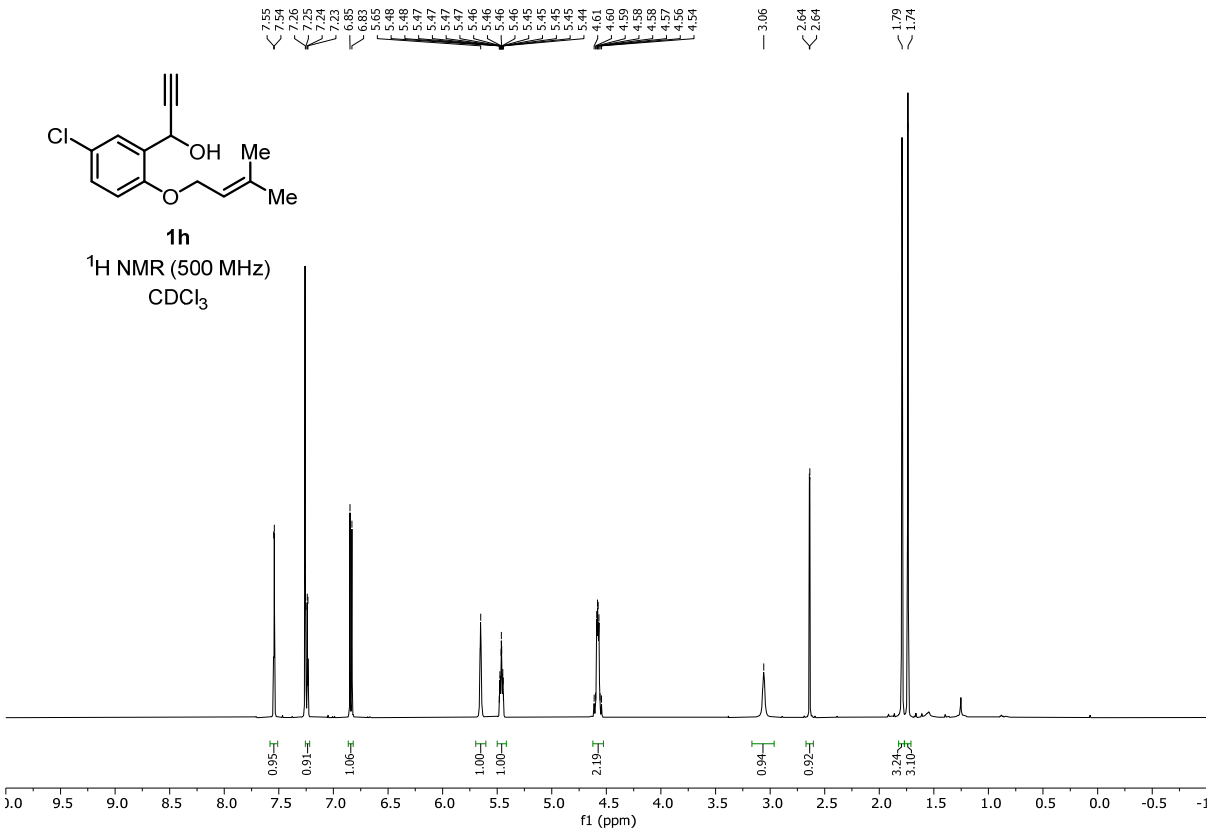
$CDCl_3$

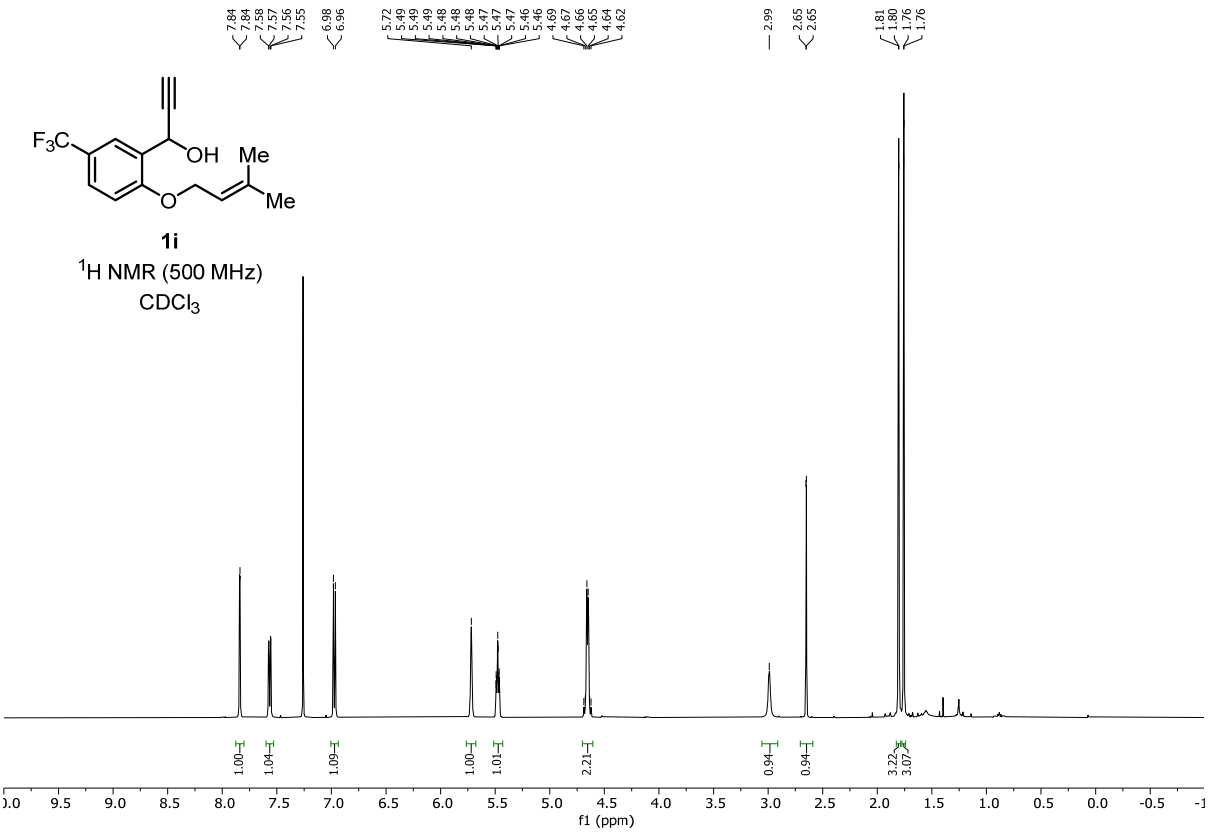


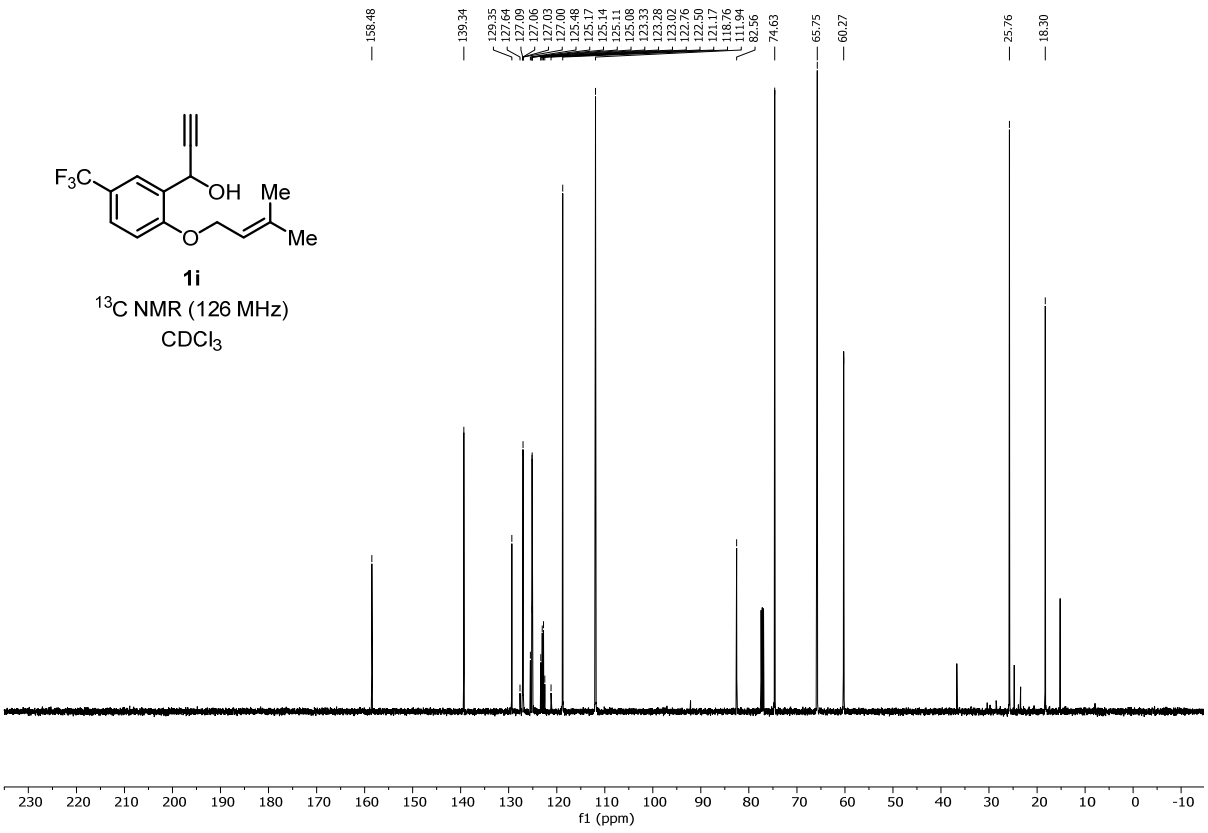
1g

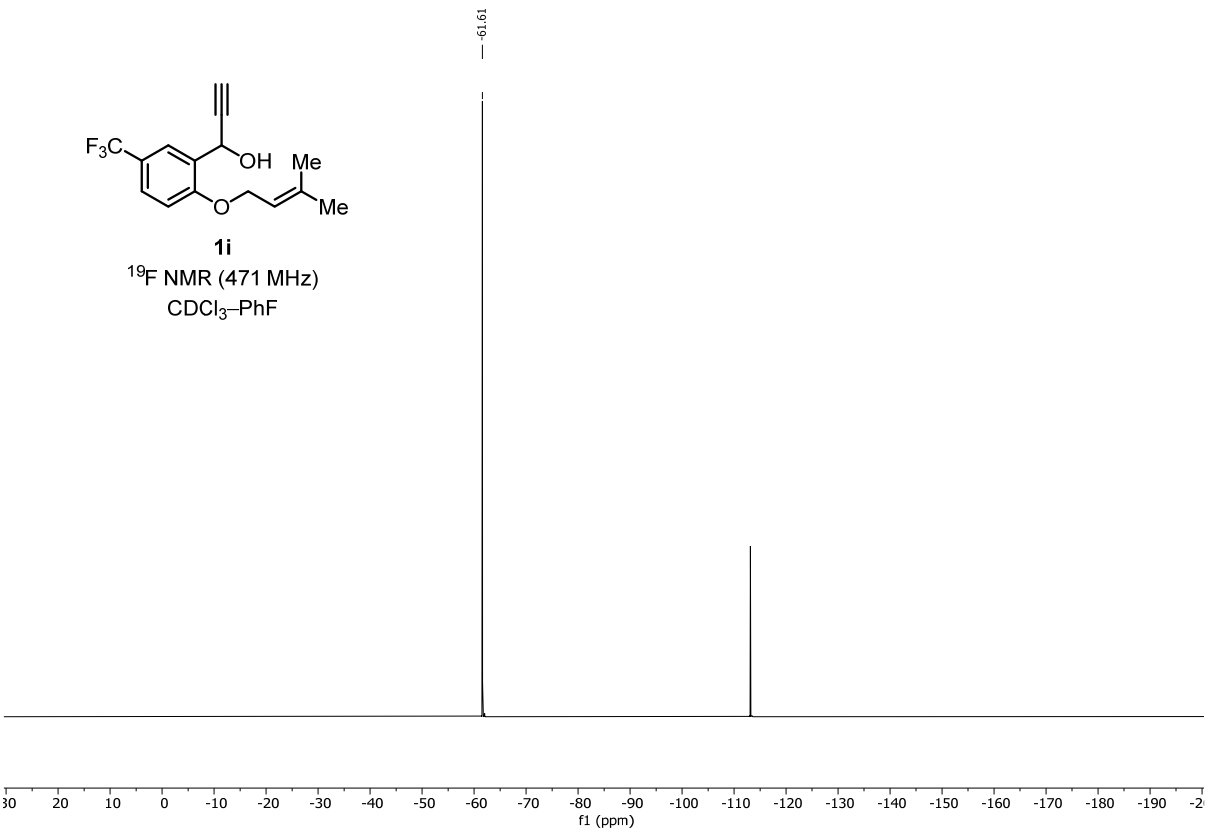
^{13}C NMR (101 MHz)

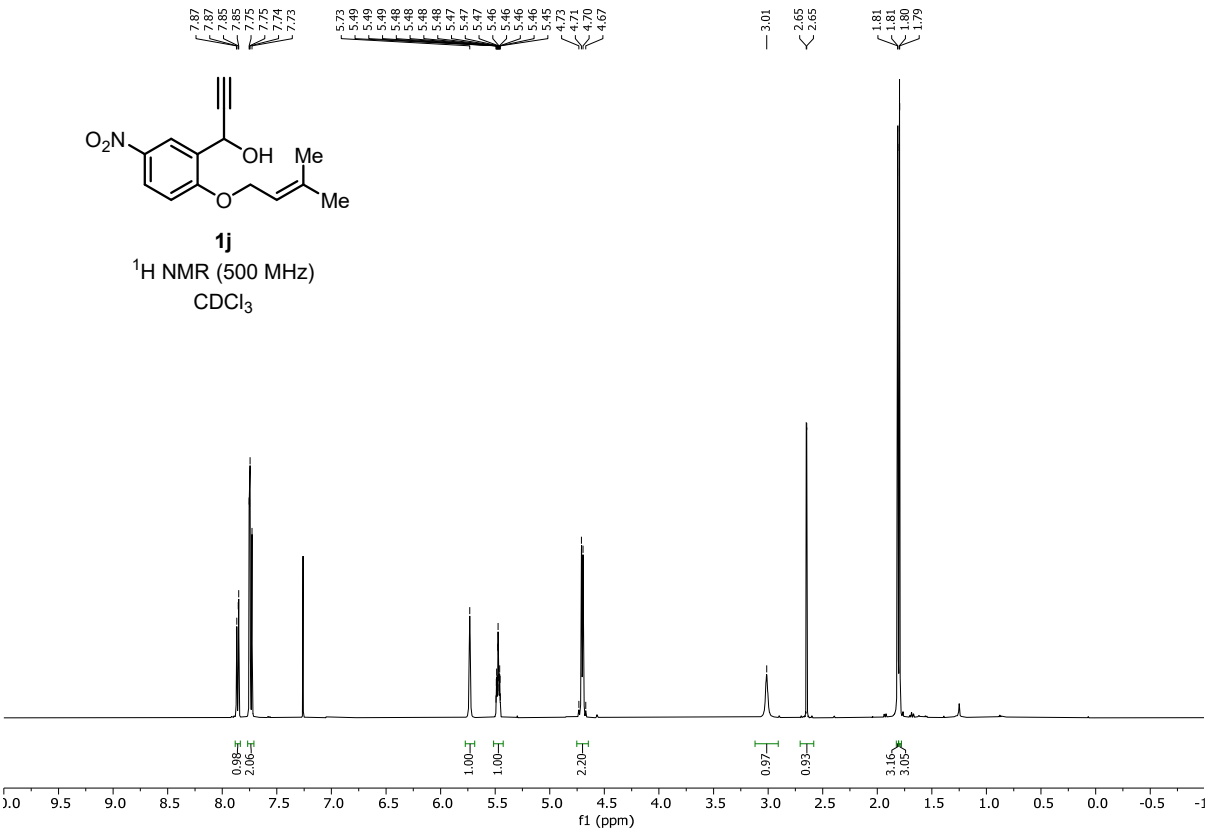
$CDCl_3$


Cl
OH
Me
Me
O
1h
1H NMR (500 MHz)
CDCl3
f1 (ppm)


F3C
OH
Me
O
Me
1i
1H NMR (500 MHz)
CDCl3
f1 (ppm)


F3C
OH
Me
O
Me
1i
13C NMR (126 MHz)
CDCl3
f1 (ppm)

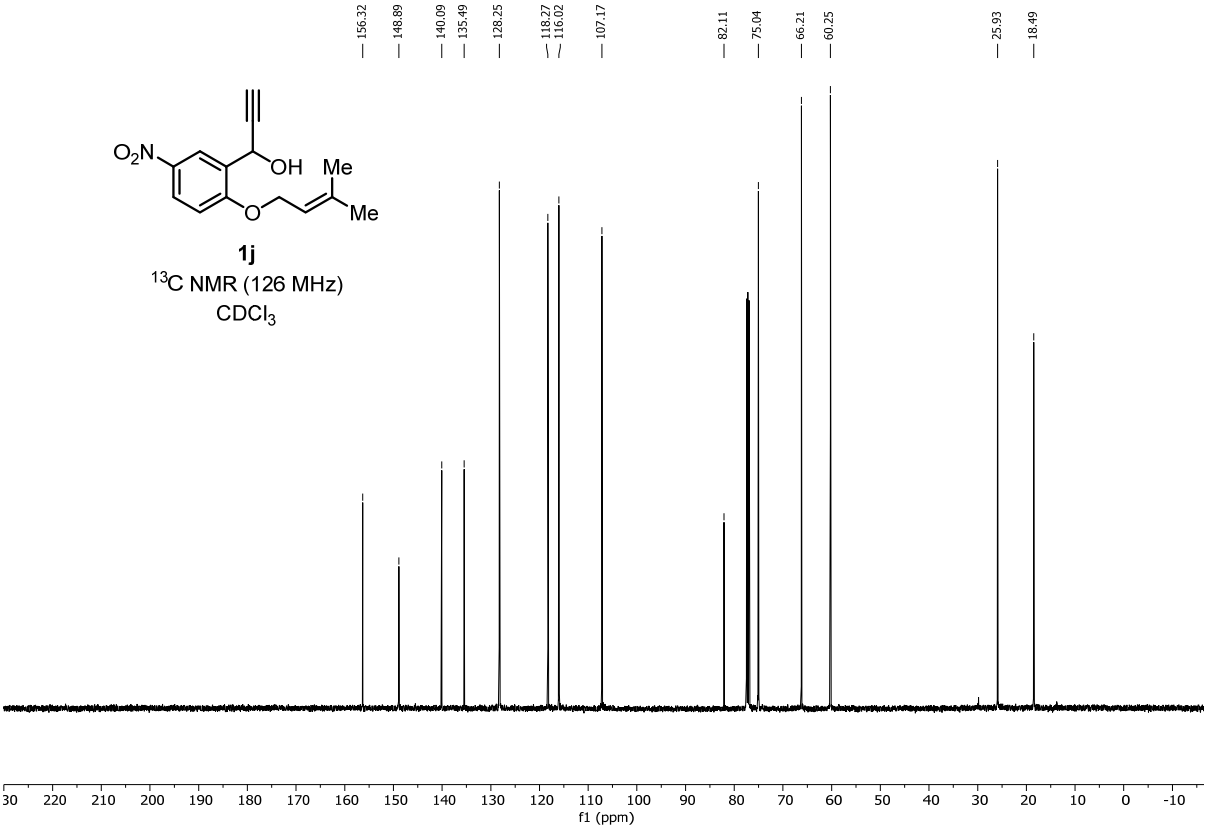

-61.61
F3C
OH
Me
Me
O
1i
19F NMR (471 MHz)
CDCl3–PhF
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)



1j

^{1}H NMR (500 MHz)

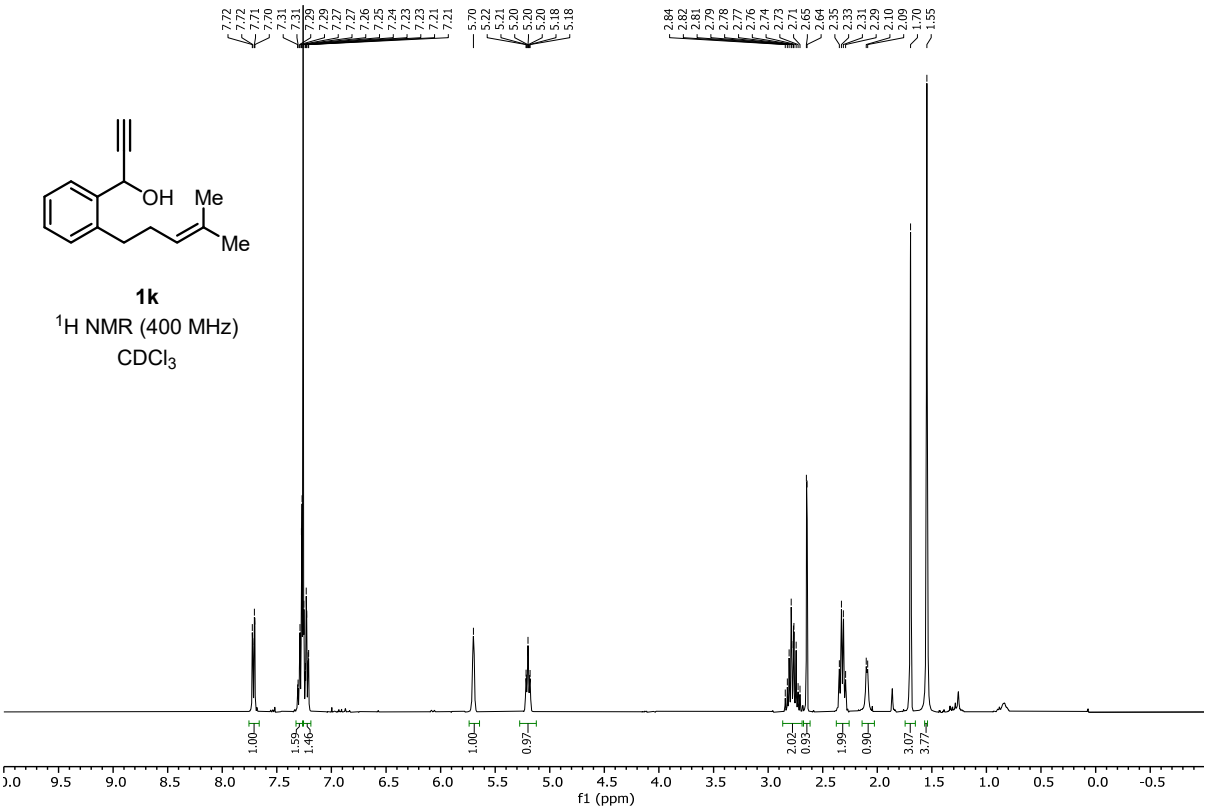
$CDCl_3$

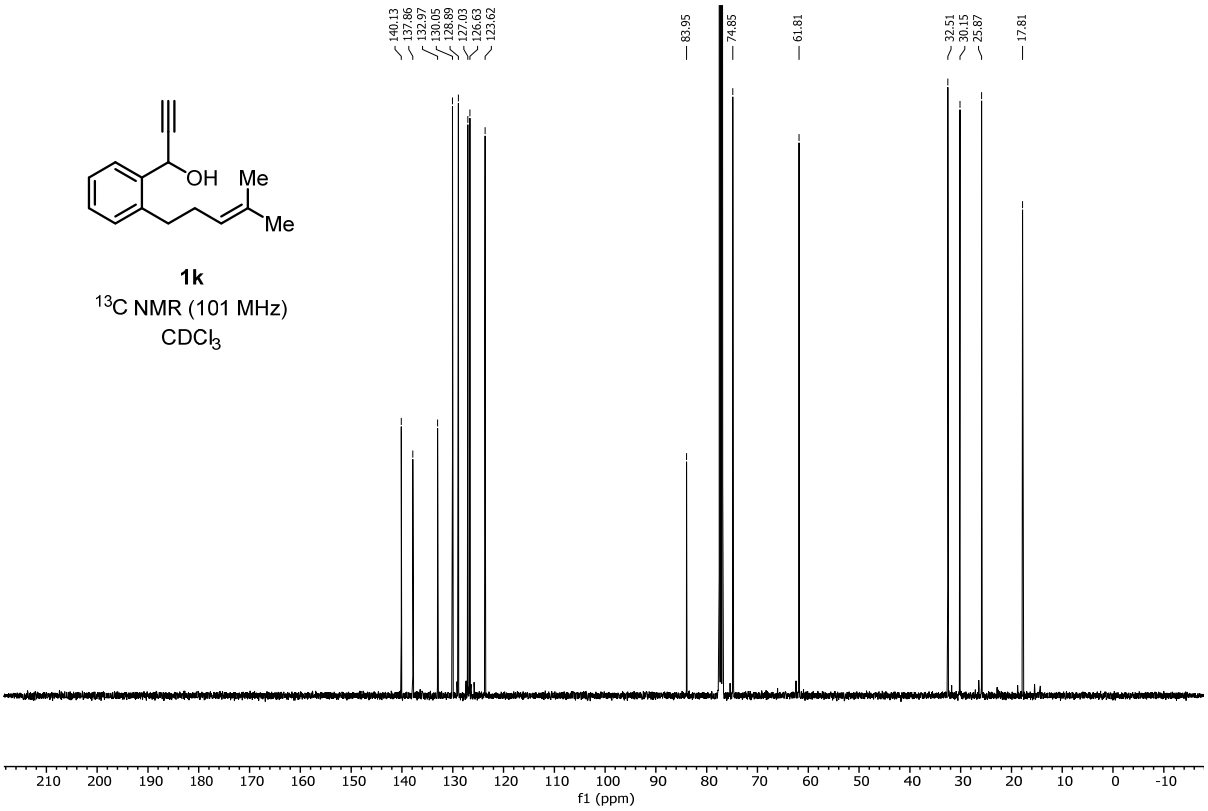


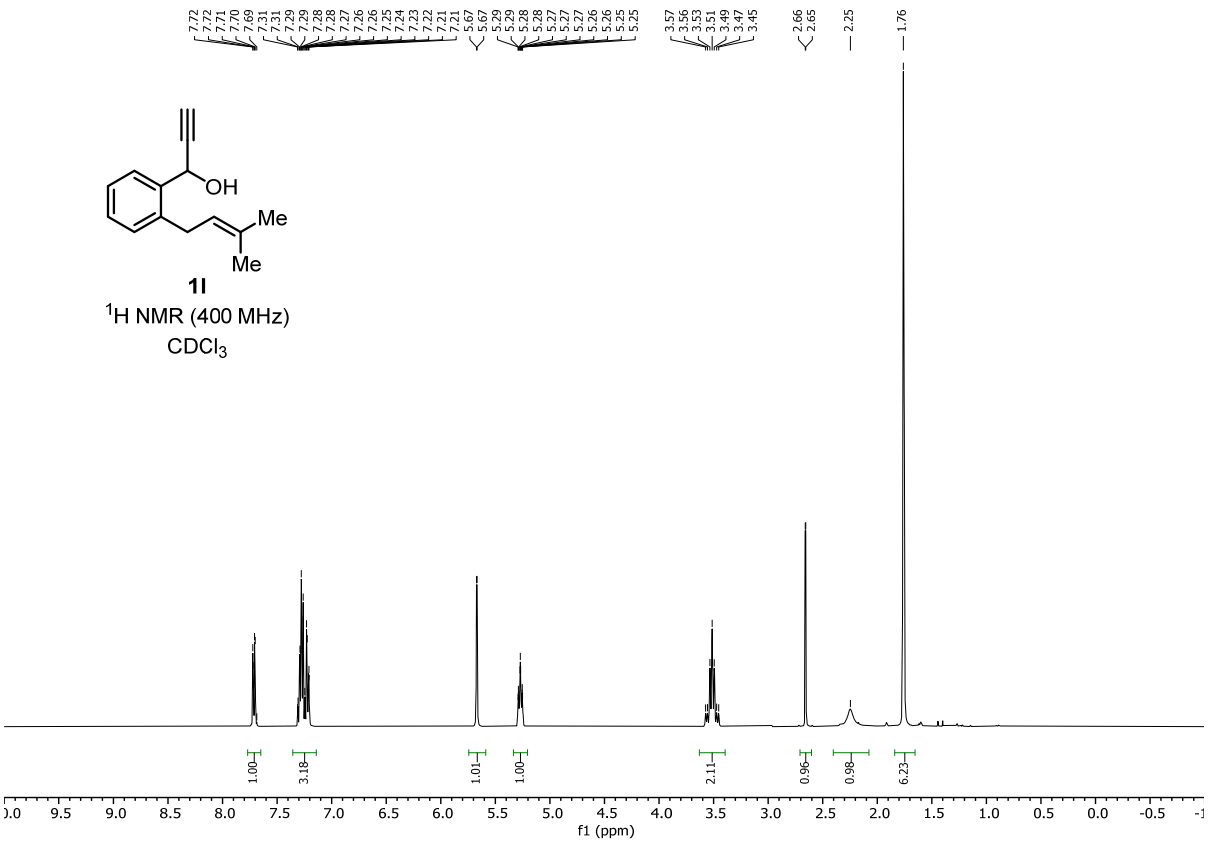
1j

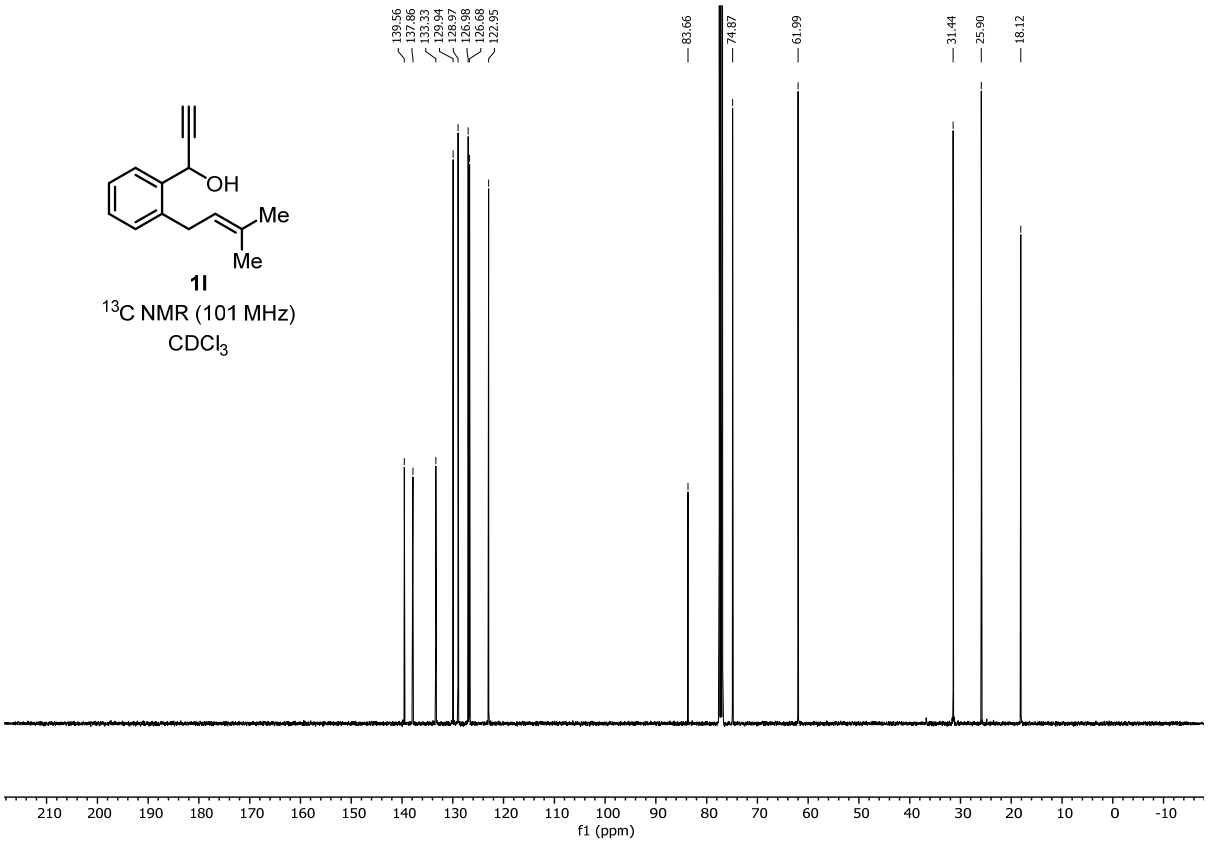
^{13}C NMR (126 MHz)

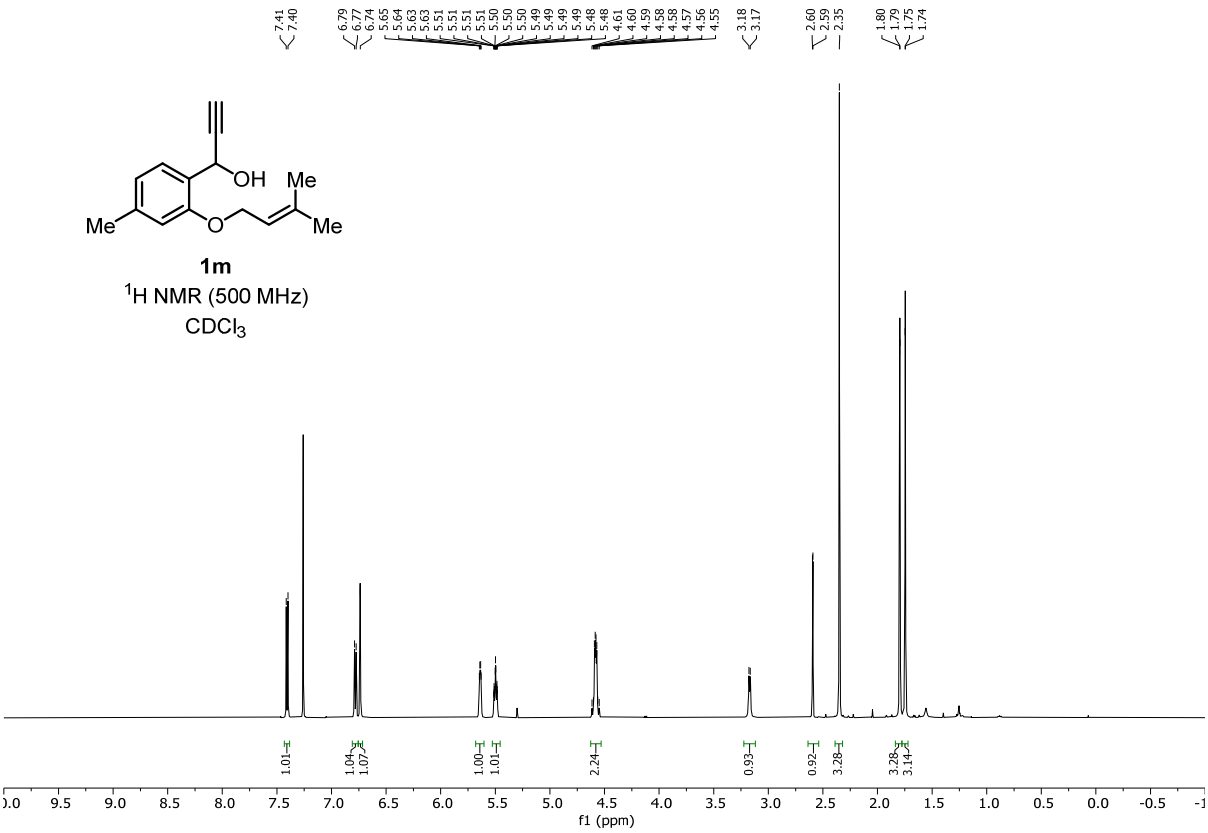
$CDCl_3$

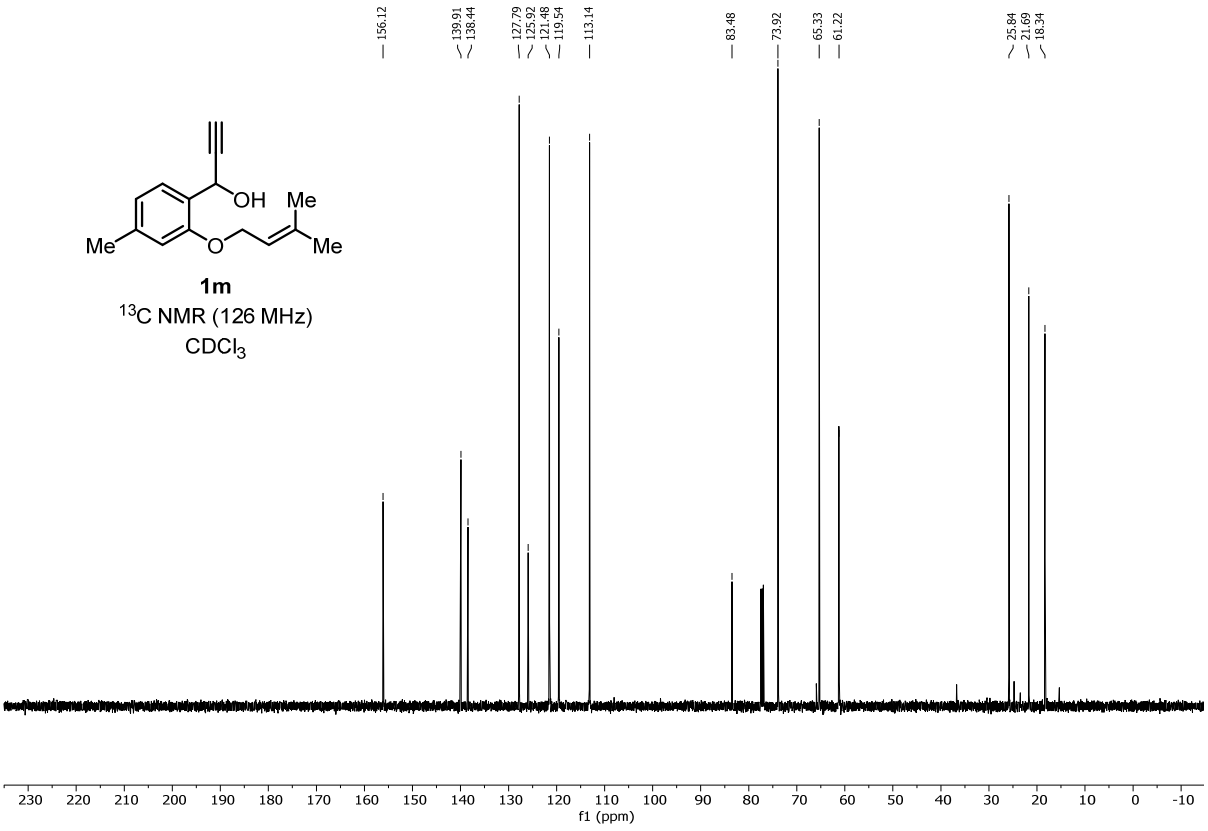

OH
Me
Me
1k
1H NMR (400 MHz)
CDCl3
f1 (ppm)

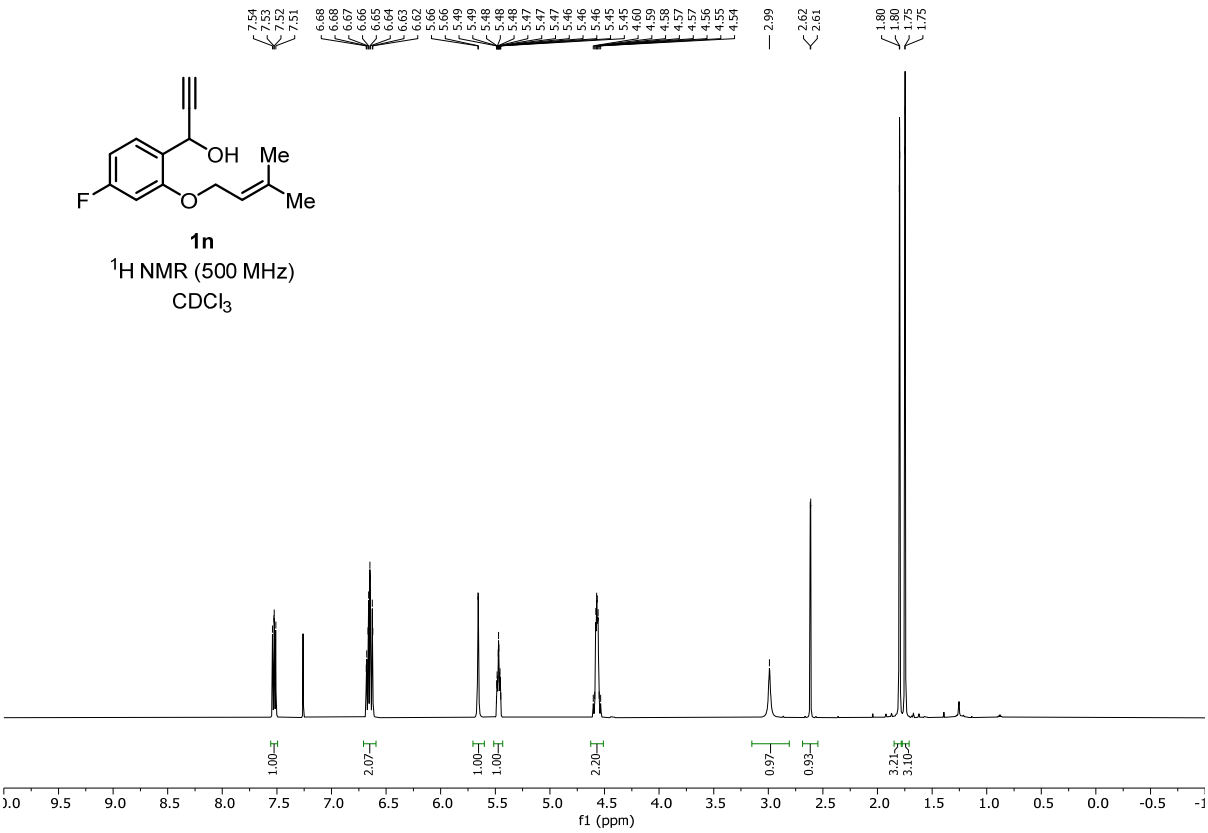

OH
Me
Me
1k
13C NMR (101 MHz)
CDCl3
f1 (ppm)

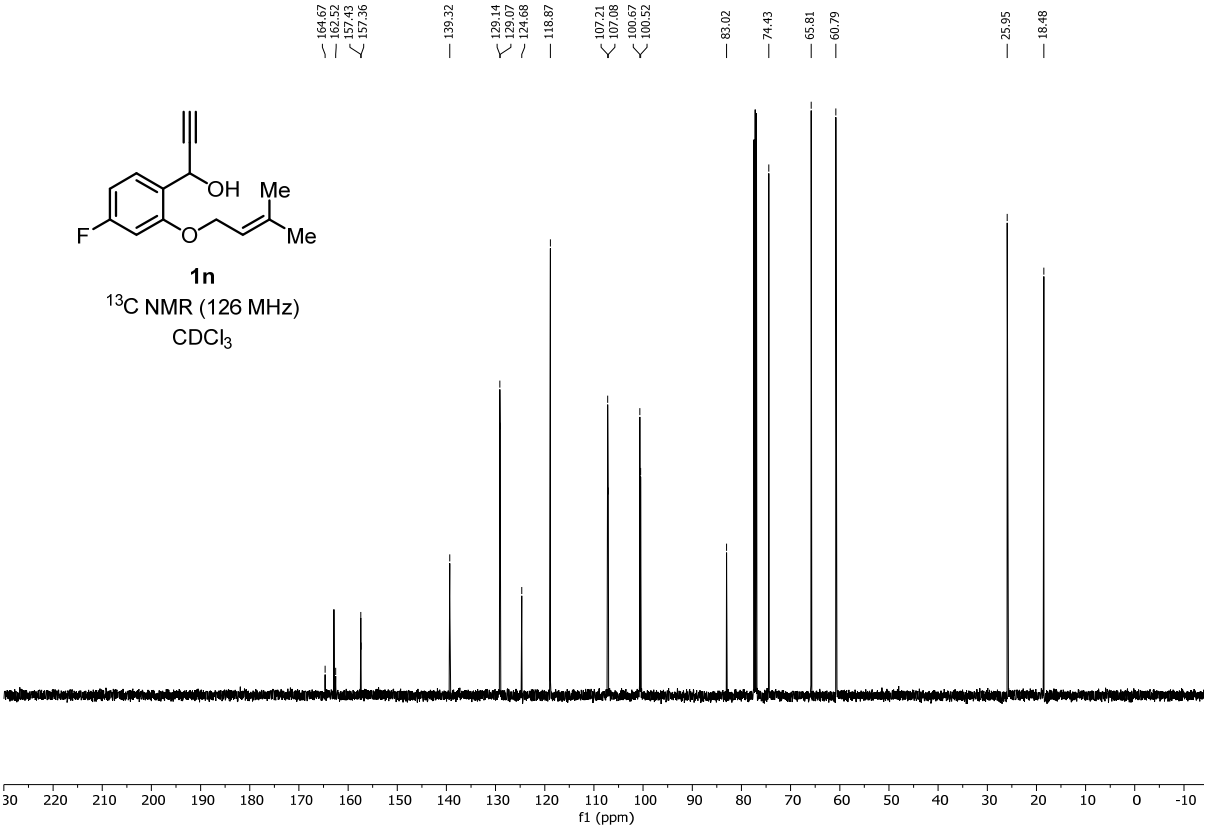

OH
Me
Me
1l
1H NMR (400 MHz)
CDCl3
f1 (ppm)


OH
Me
Me
1l
13C NMR (101 MHz)
CDCl3
f1 (ppm)


OH
Me
Me
O
Me
1m
1H NMR (500 MHz)
CDCl3
f1 (ppm)


OH
Me
Me
O
Me
1m
13C NMR (126 MHz)
CDCl3
f1 (ppm)

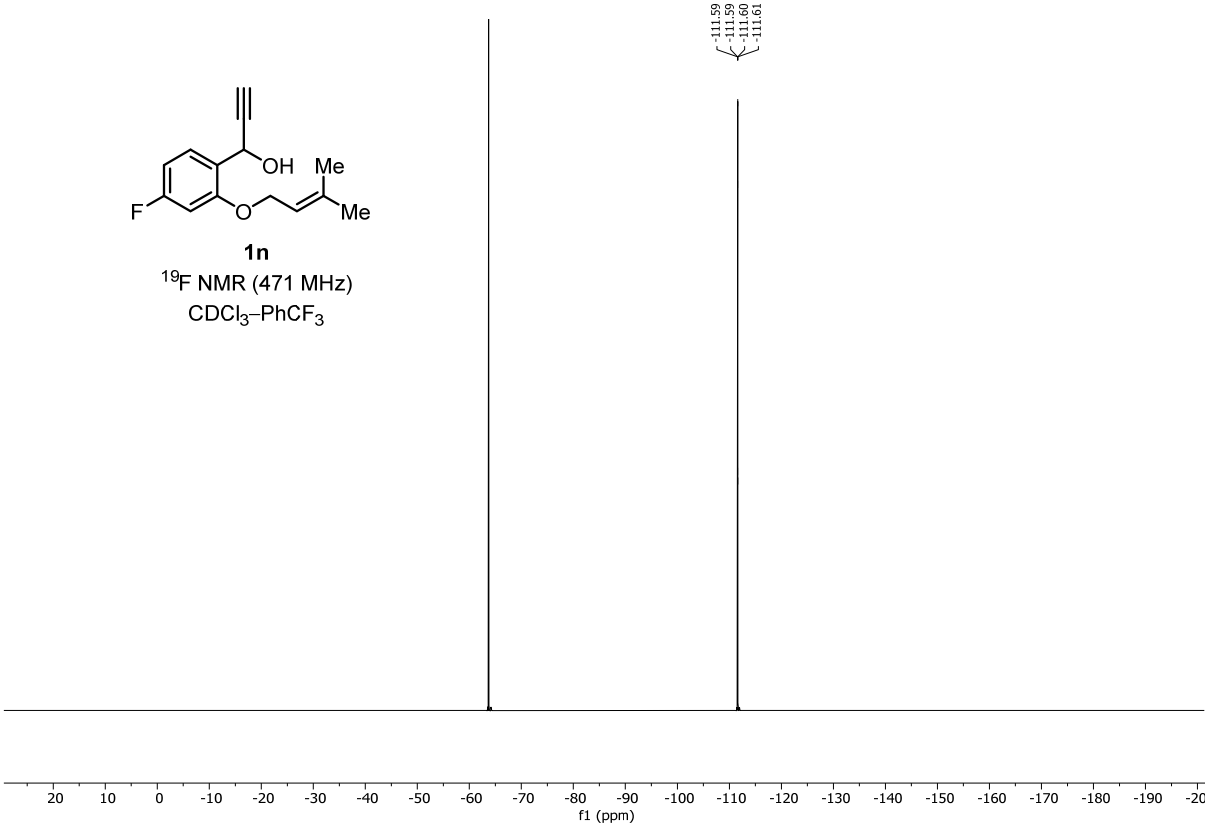

OH
Me
F
O
Me
1n
1H NMR (500 MHz)
CDCl3
f1 (ppm)

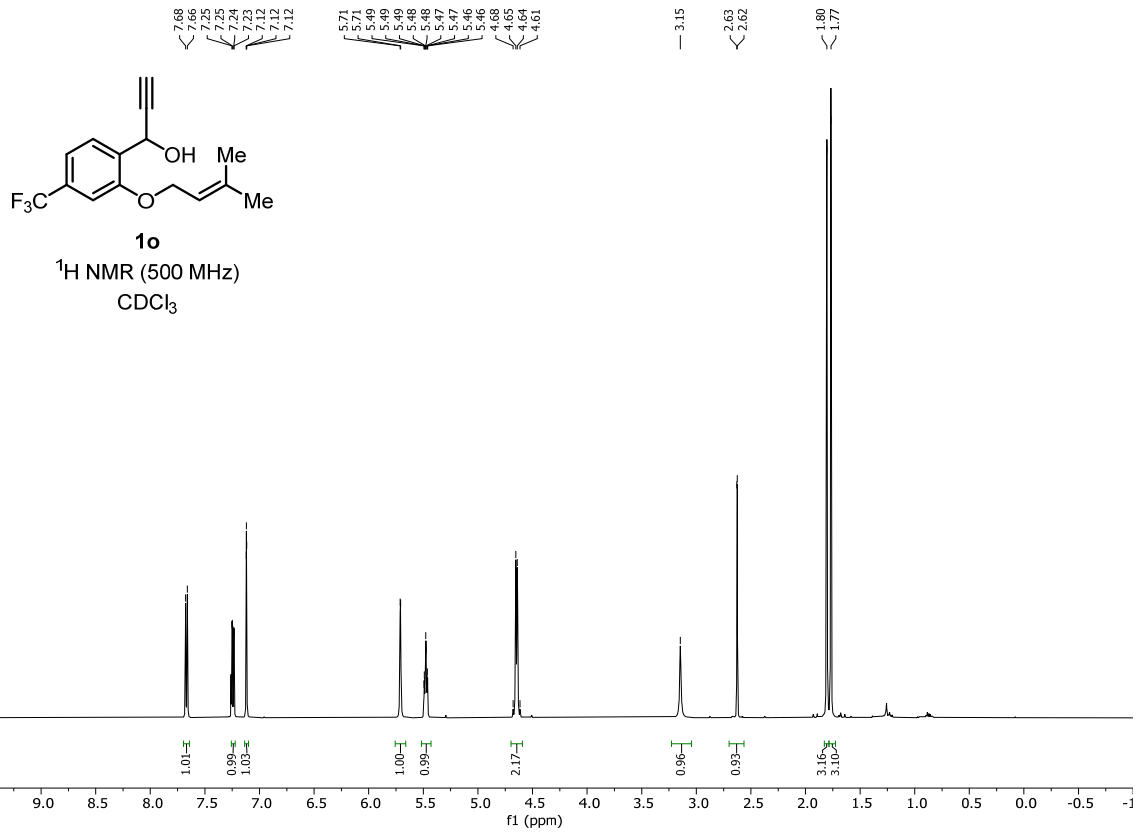

OH
Me
F
O
Me
1n
13C NMR (126 MHz)
CDCl3
f1 (ppm)

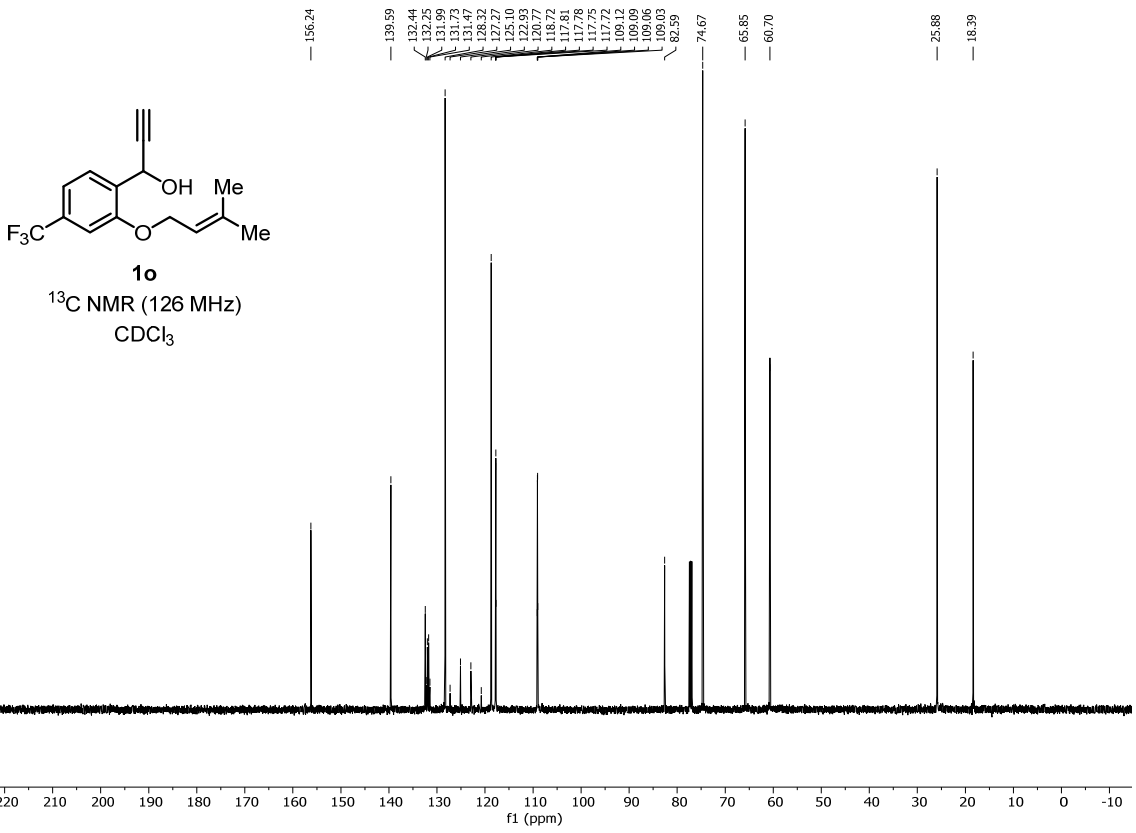
1n

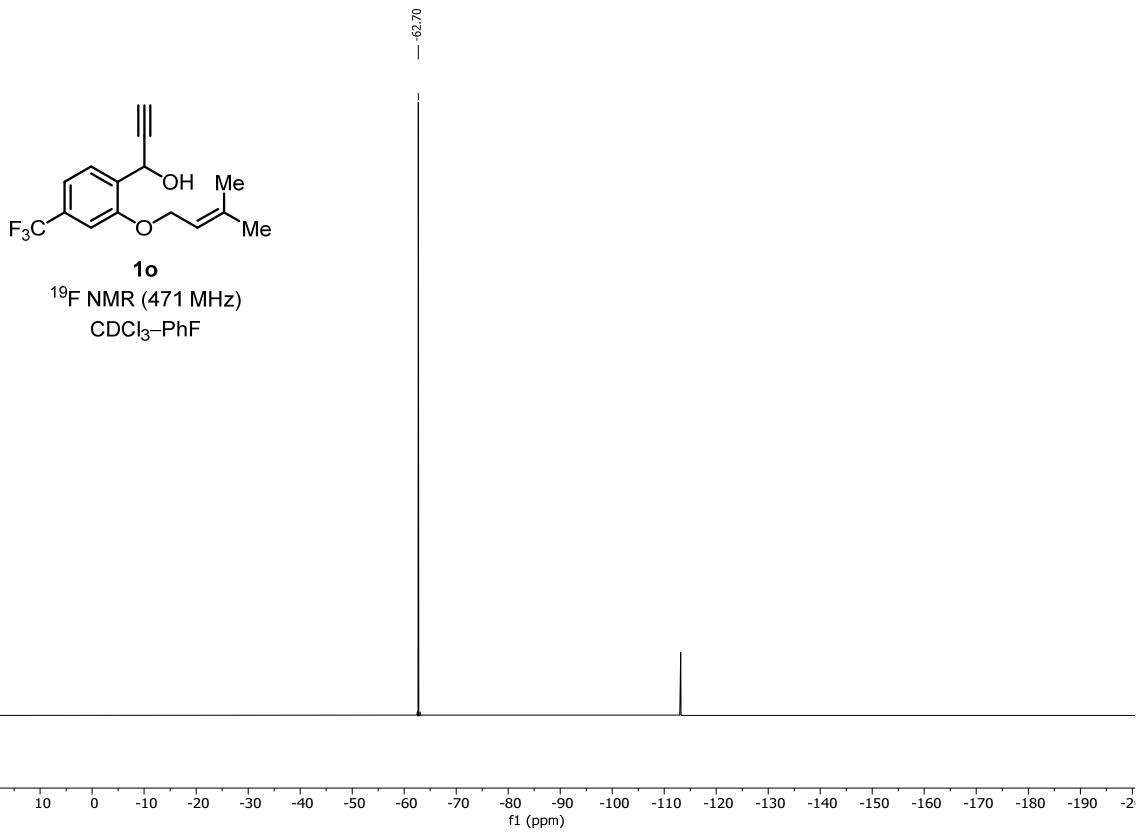
^{19}F NMR (471 MHz)

$CDCl_3$–$PhCF_3$




OH
Me
F3C
O
Me
1o
1H NMR (500 MHz)
CDCl3
f1 (ppm)

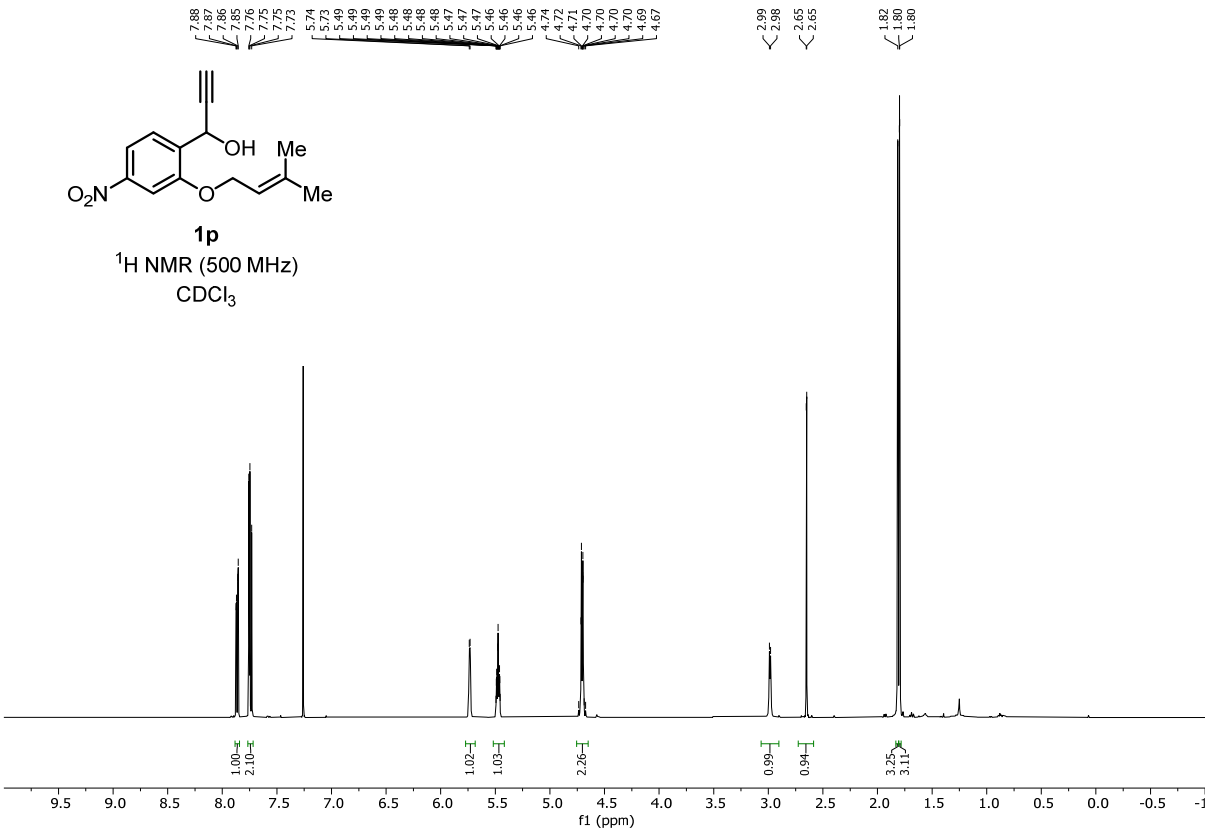

OH
Me
F3C
O
Me
1o
13C NMR (126 MHz)
CDCl3
f1 (ppm)

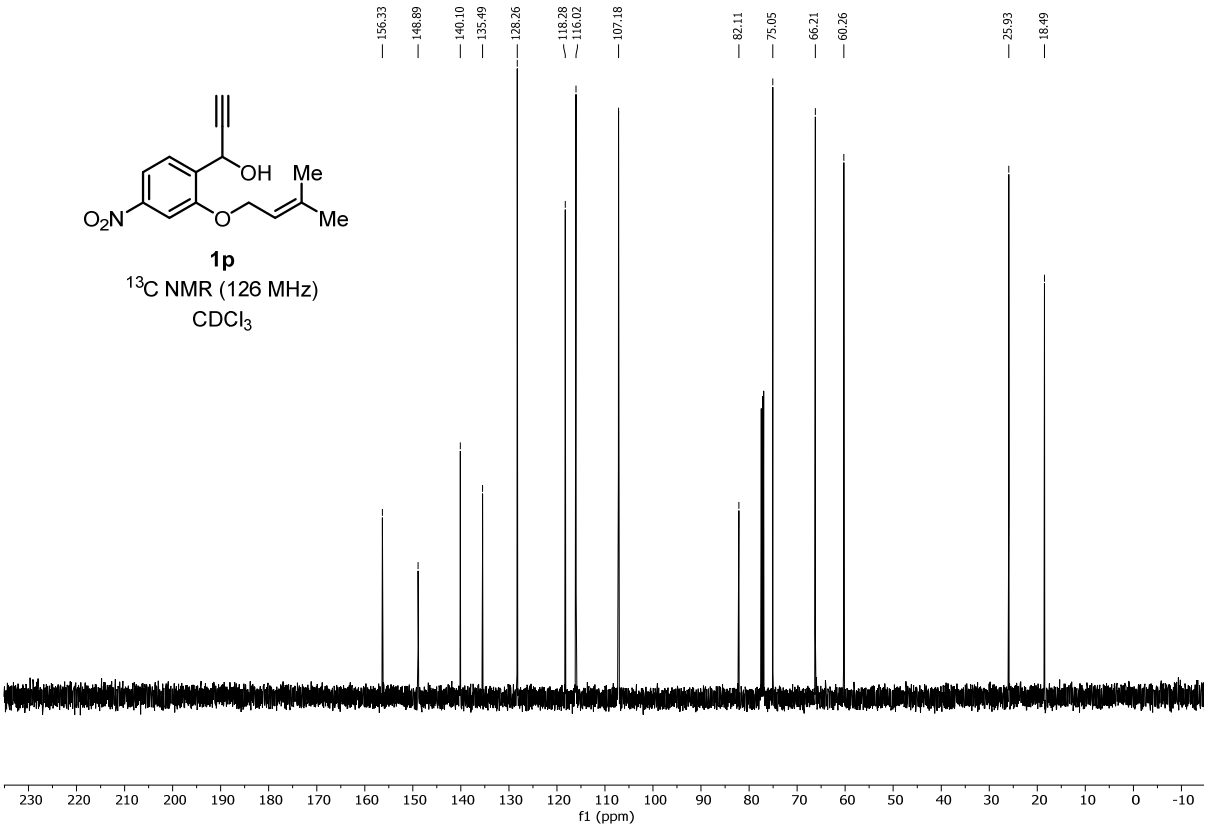


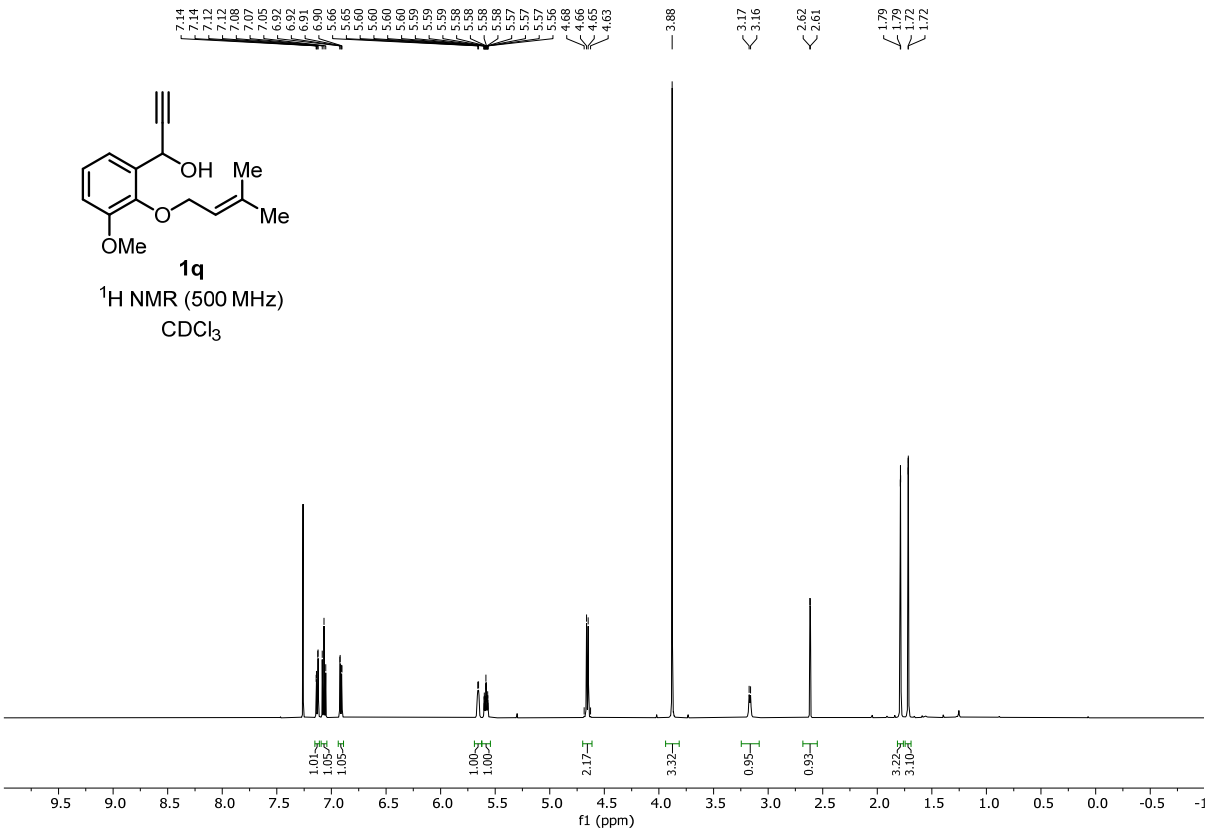
1o

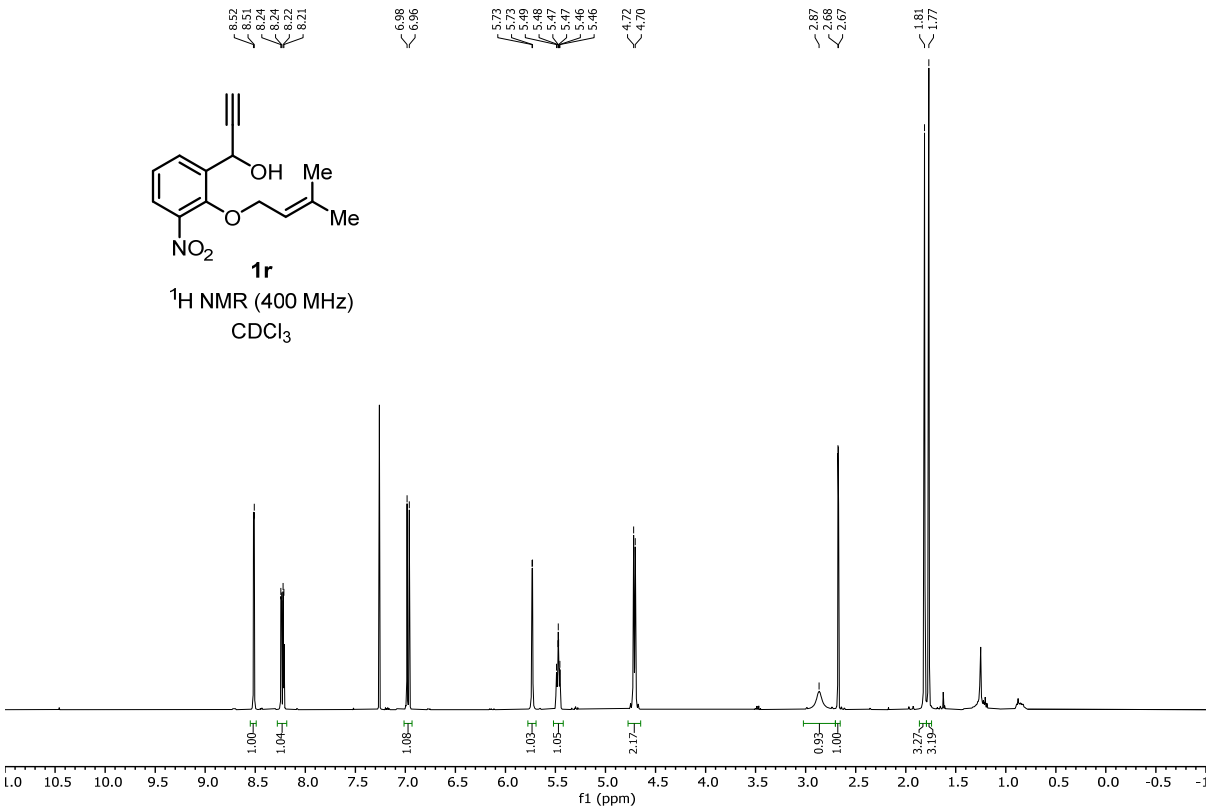
^{19}F NMR (471 MHz)

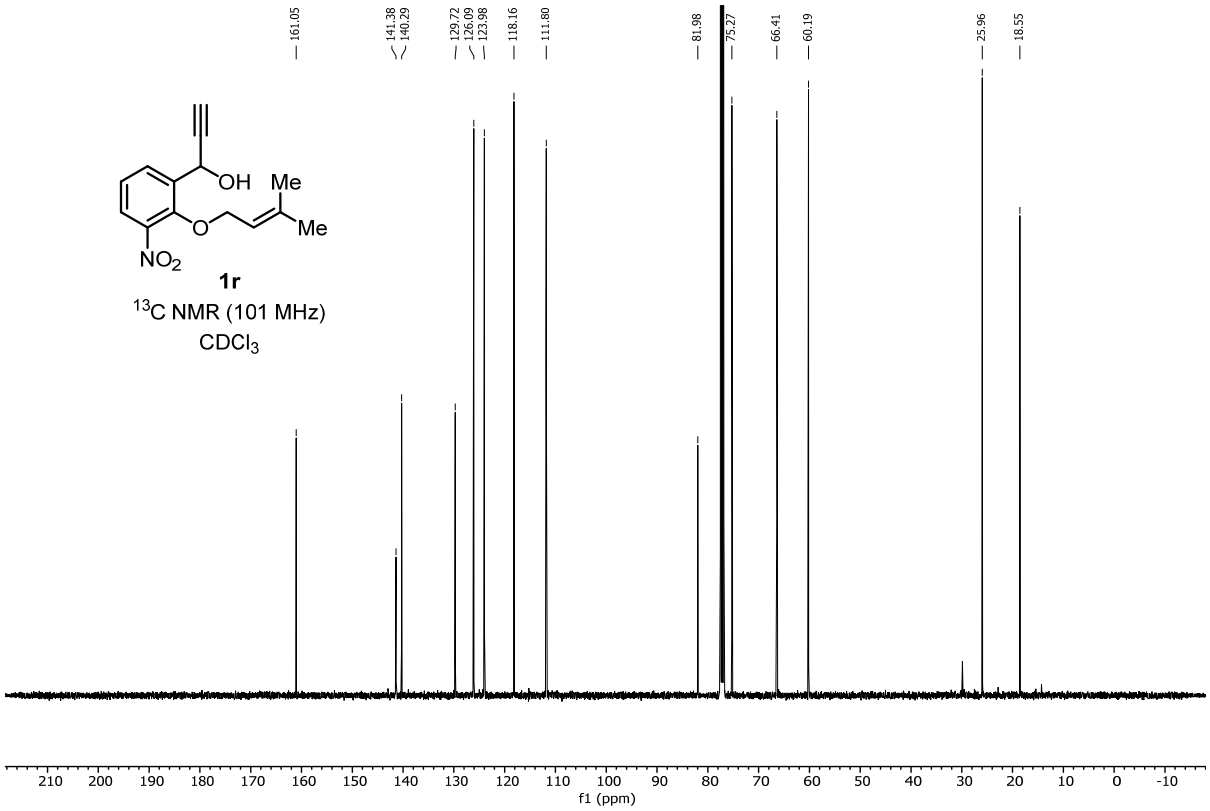
$CDCl_3$–PhF

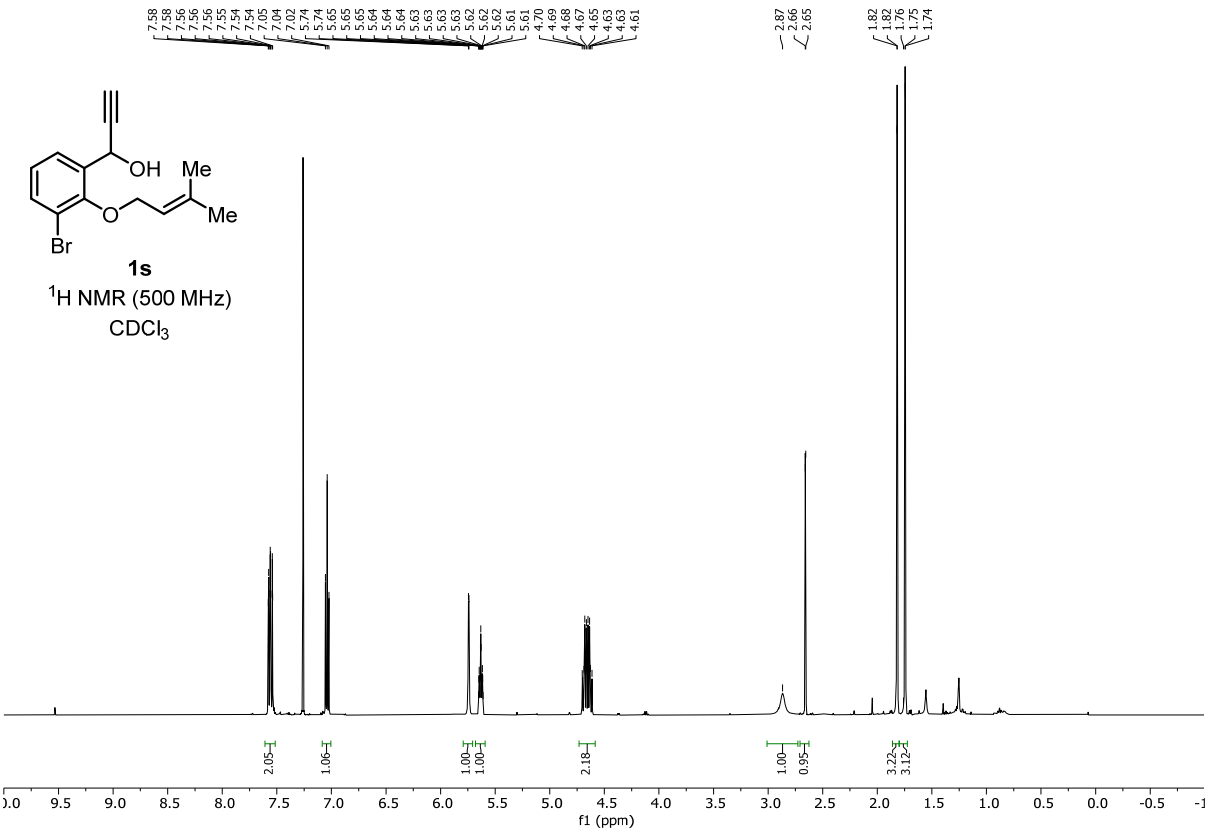

OH
Me
O_2N
O
Me
1p
^{1}H NMR (500 MHz)
$CDCl_3$
f1 (ppm)

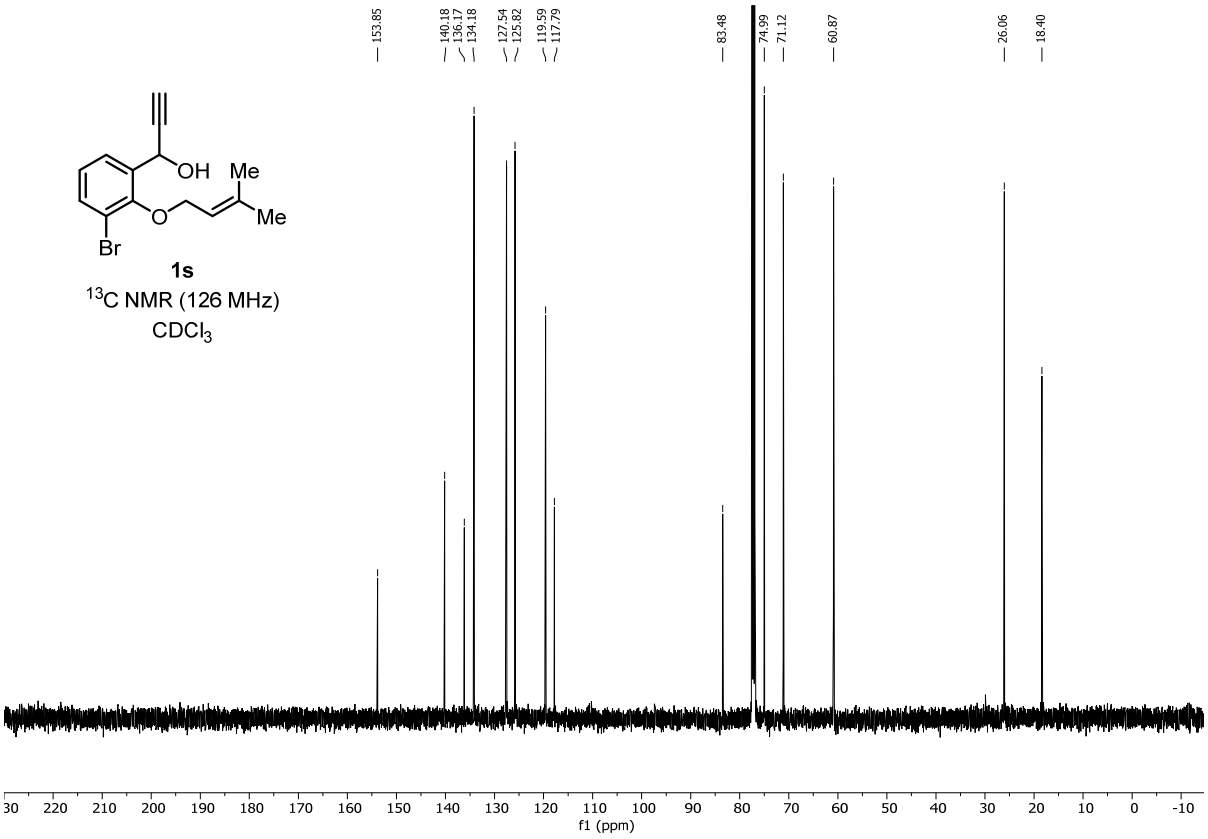

OH
Me
O_2N
O
Me
1p
^{13}C NMR (126 MHz)
$CDCl_3$
f1 (ppm)

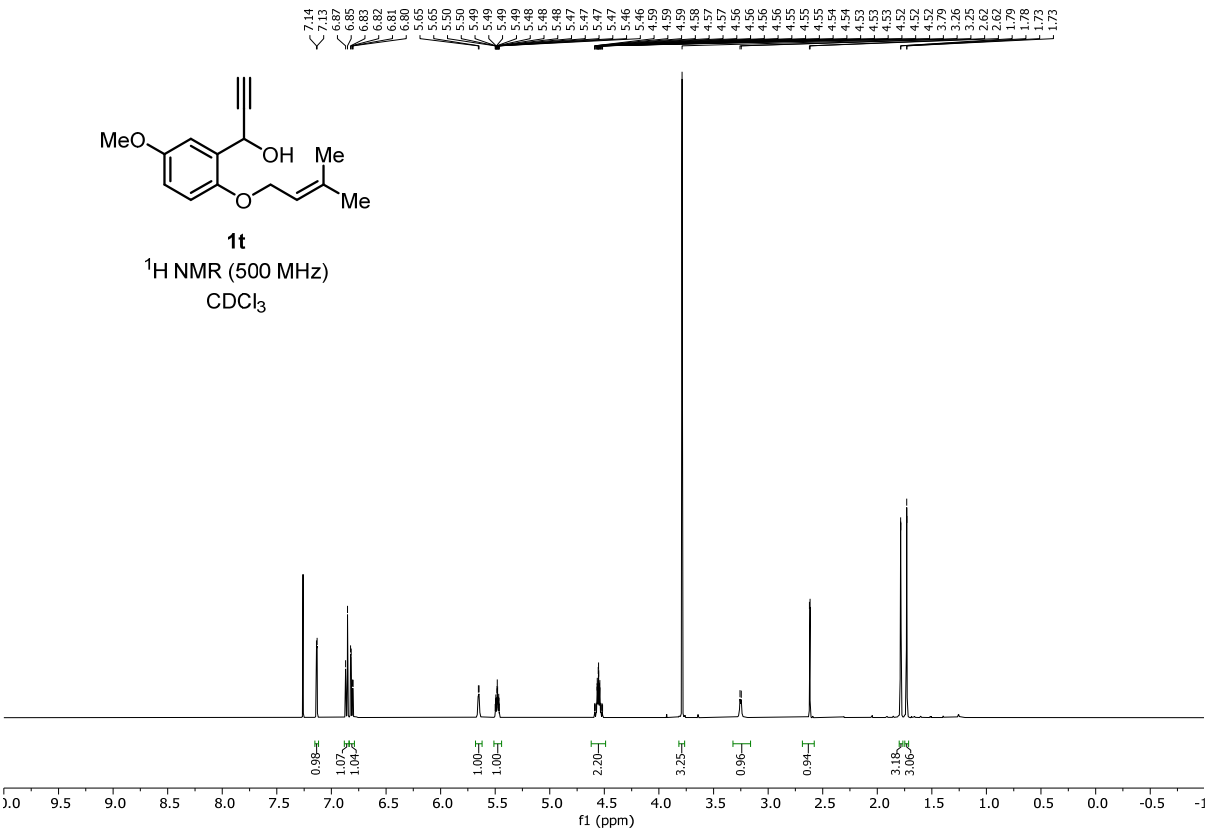

OH
Me
O
Me
OMe
1q
1H NMR (500 MHz)
CDCl3
f1 (ppm)

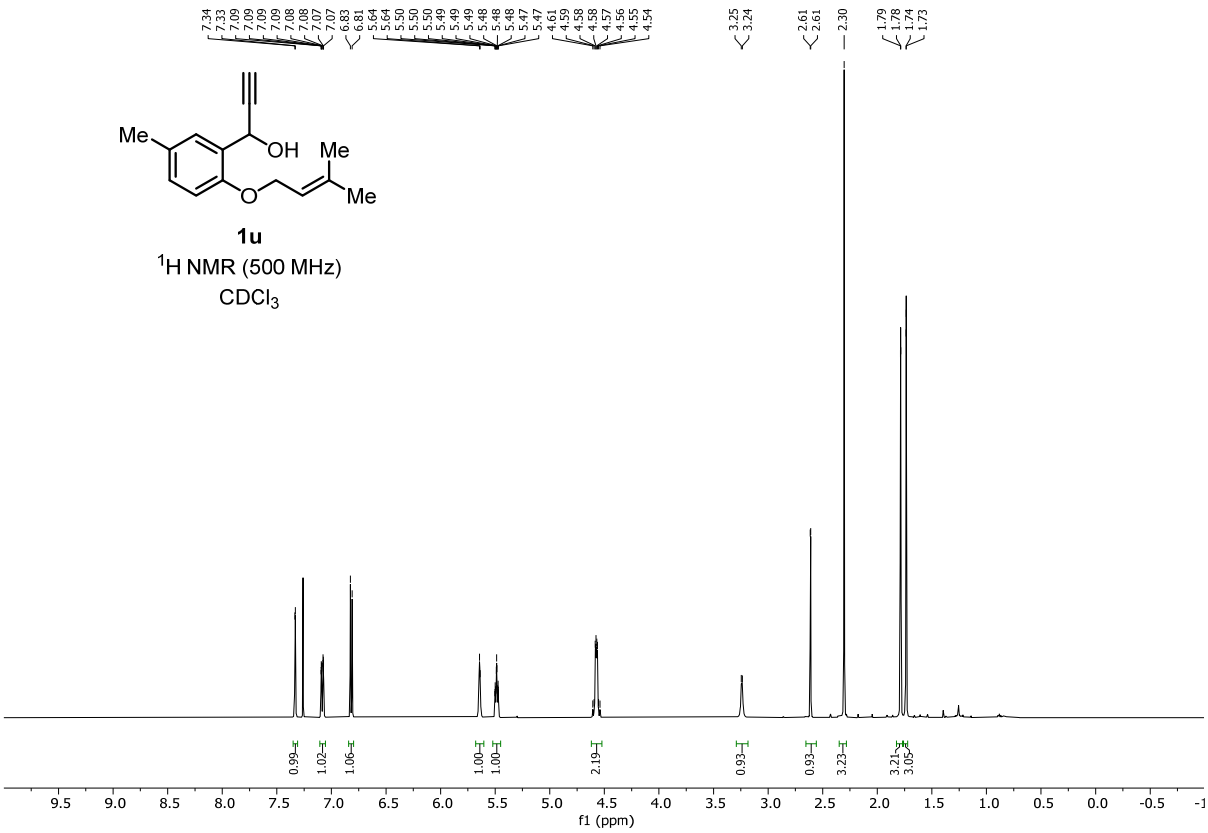

8.52
8.51
8.24
8.24
8.22
8.21
6.98
6.96
5.73
5.73
5.49
5.48
5.47
5.47
5.46
5.46
4.72
4.70
2.87
2.68
2.67
1.81
1.77
OH
Me
Me
O
NO2
1r
1H NMR (400 MHz)
CDCl3
1.00
1.04
1.08
1.03
1.05
2.17
0.93
1.00
3.27
3.19
f1 (ppm)

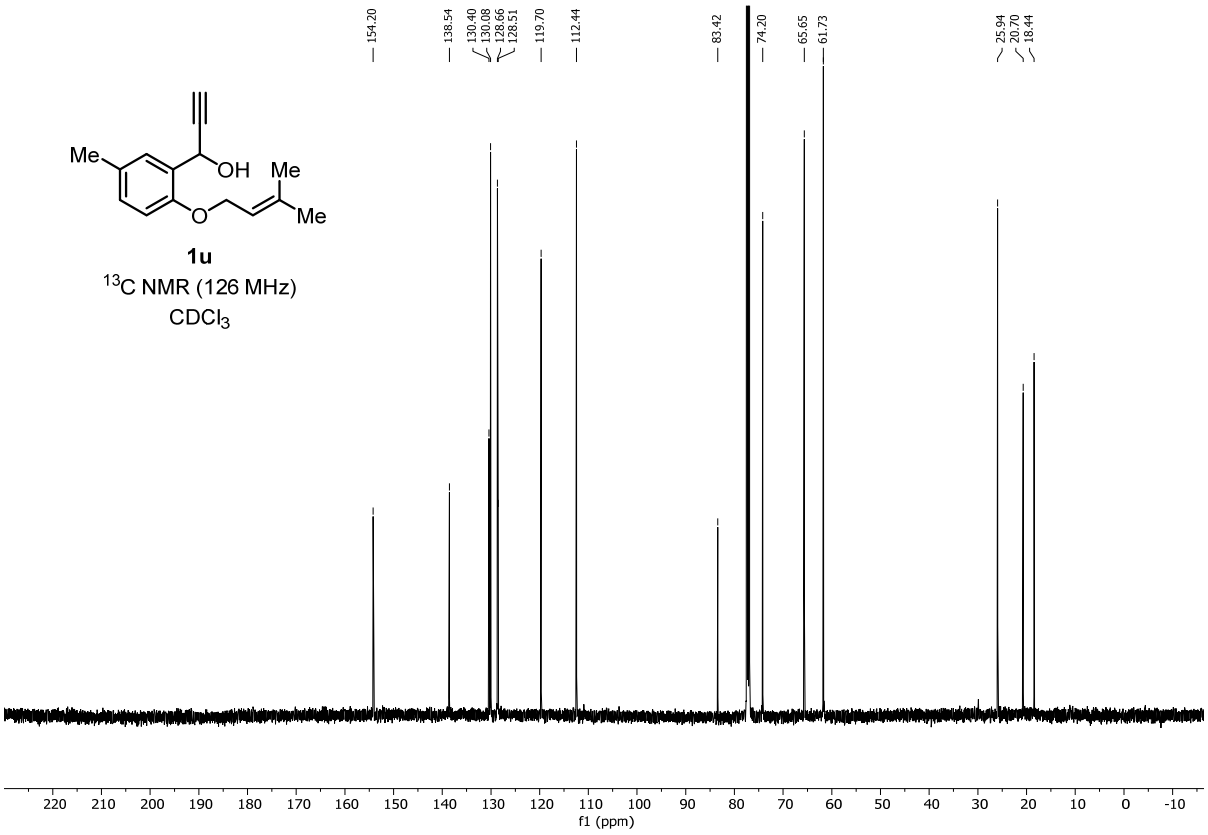

161.05
141.38
140.29
129.72
126.09
123.98
118.16
111.80
81.98
75.27
66.41
60.19
25.96
18.55
OH
Me
Me
O
NO2
1r
13C NMR (101 MHz)
CDCl3
f1 (ppm)

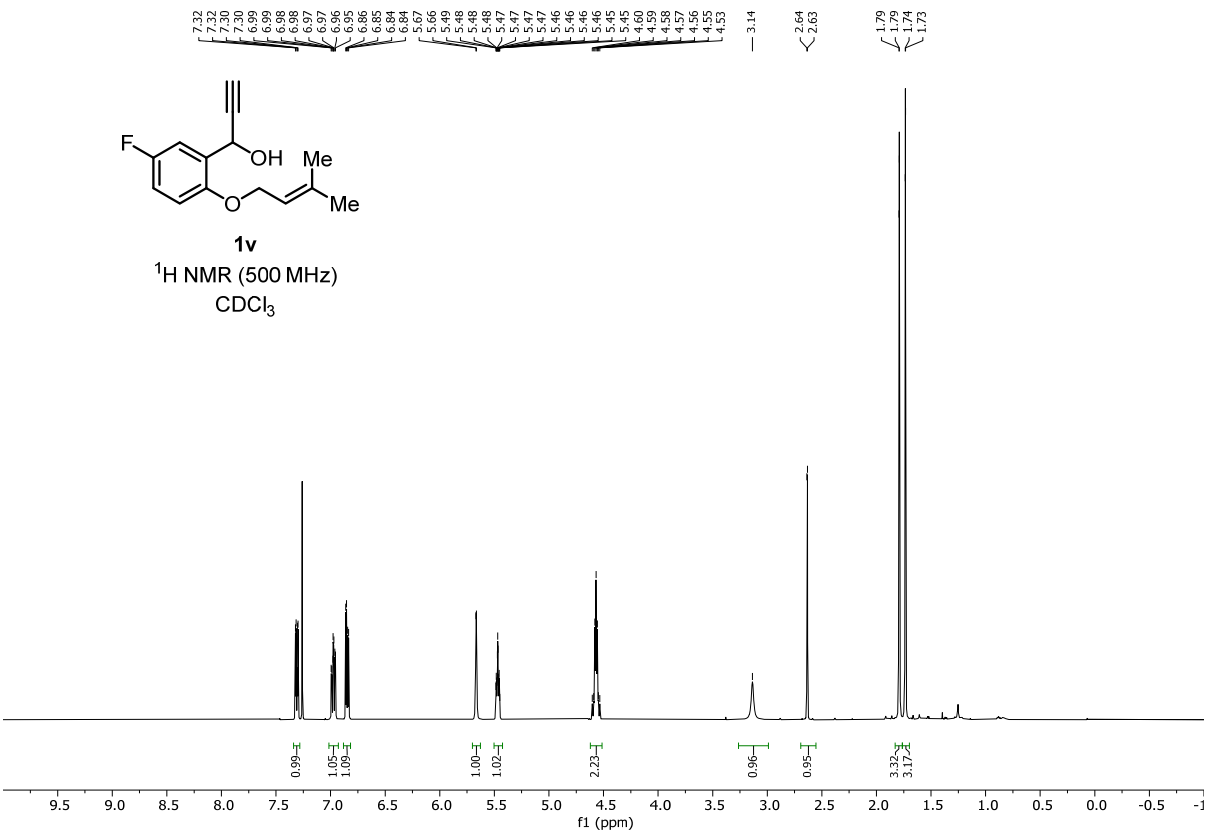

OH
Me
Me
O
Br
1s
1H NMR (500 MHz)
CDCl3
f1 (ppm)

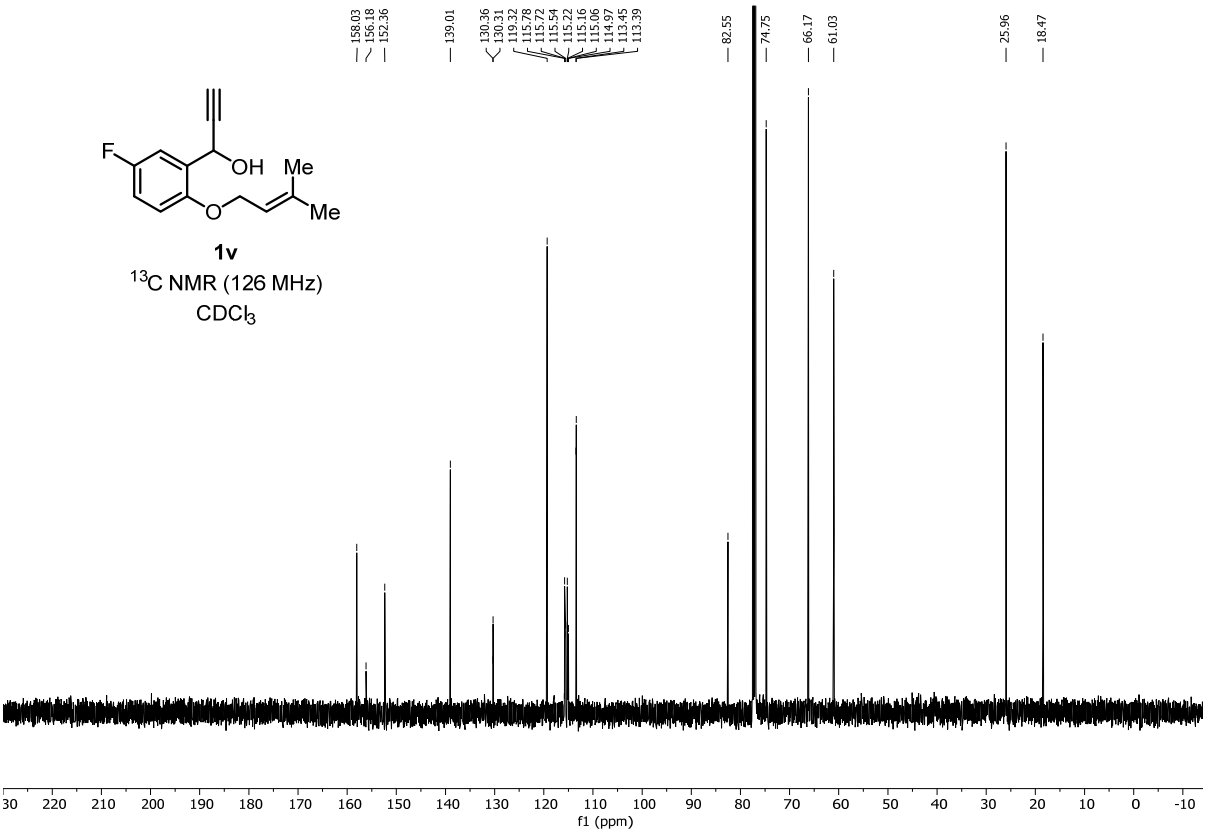

OH
Me
Me
O
Br
1s
13C NMR (126 MHz)
CDCl3
f1 (ppm)

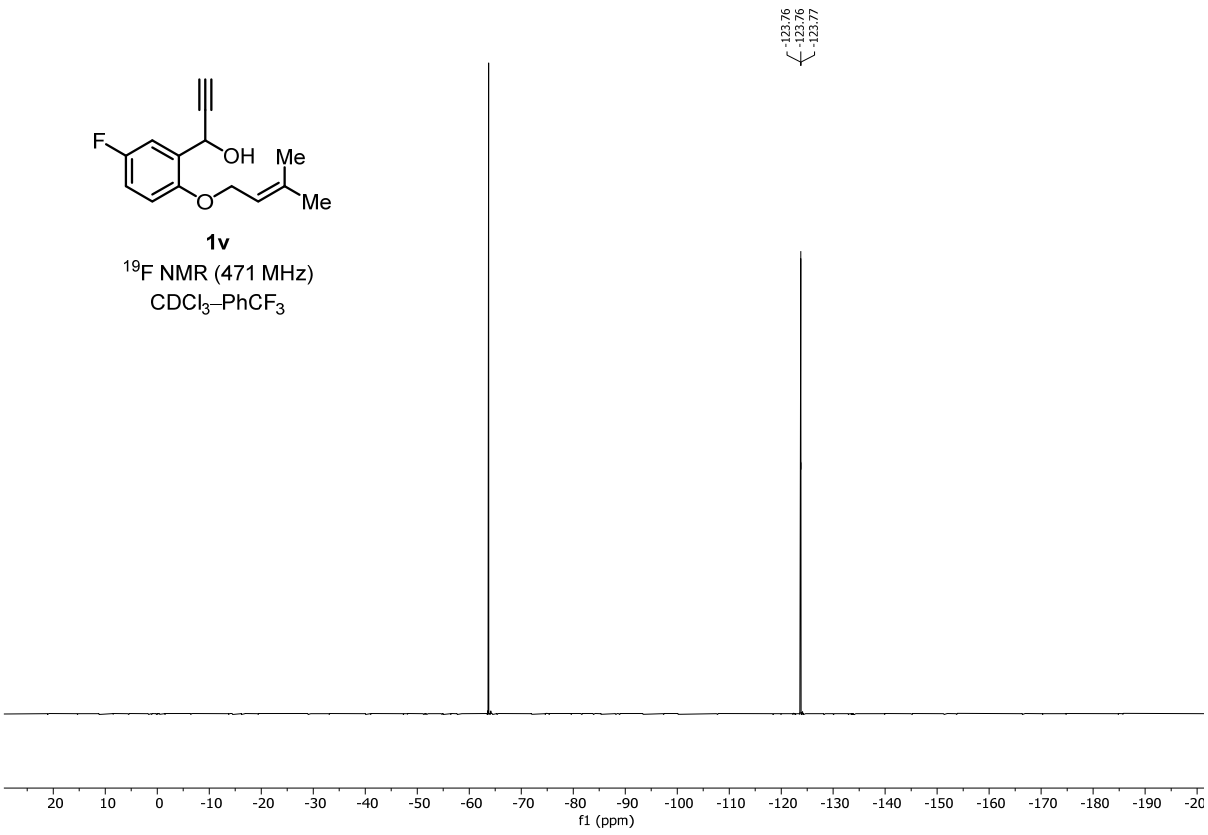

MeO
OH
Me
Me
O
1t
1H NMR (500 MHz)
CDCl3
f1 (ppm)


Me
OH
Me
Me
O
1u
1H NMR (500 MHz)
CDCl3
f1 (ppm)


Me
OH
Me
Me
O
1u
13C NMR (126 MHz)
CDCl3
f1 (ppm)


F
OH
Me
O
Me
1v
1H NMR (500 MHz)
CDCl3
f1 (ppm)

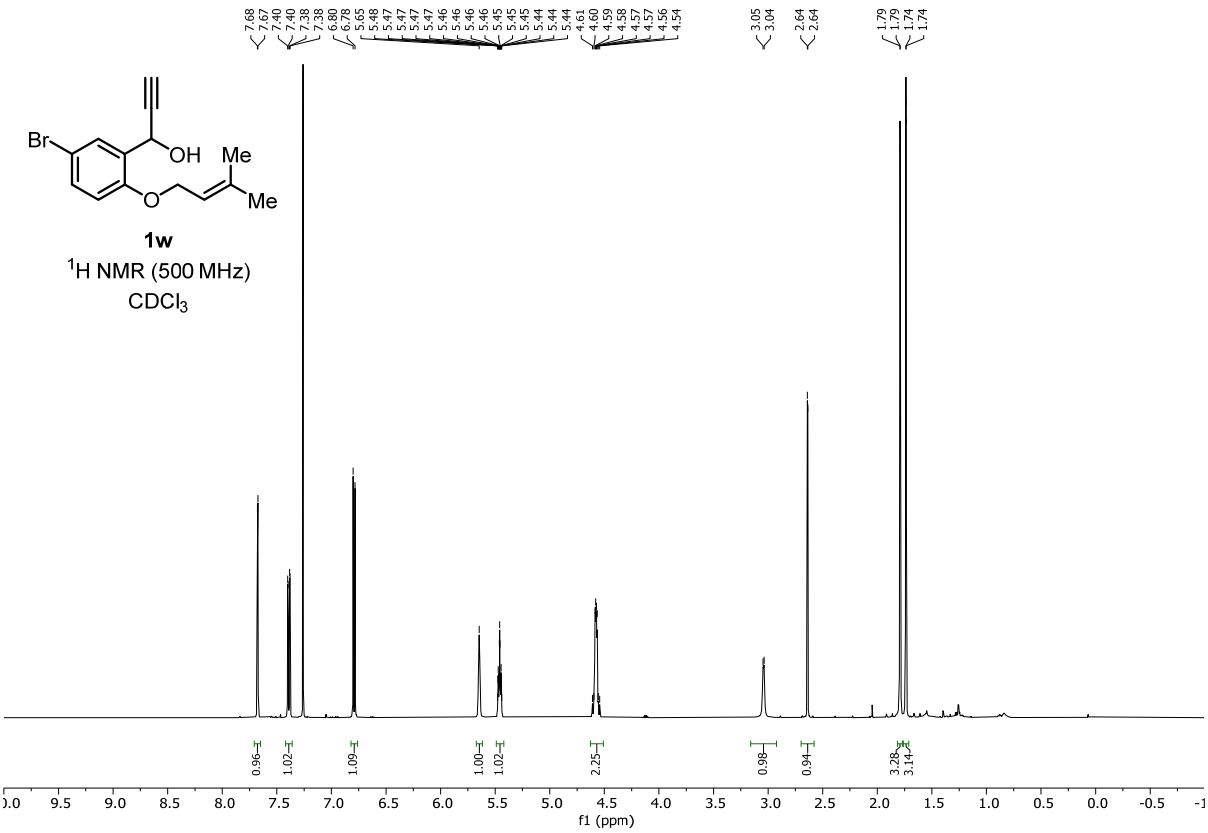

F
OH
Me
O
Me
1v
13C NMR (126 MHz)
CDCl3
f1 (ppm)

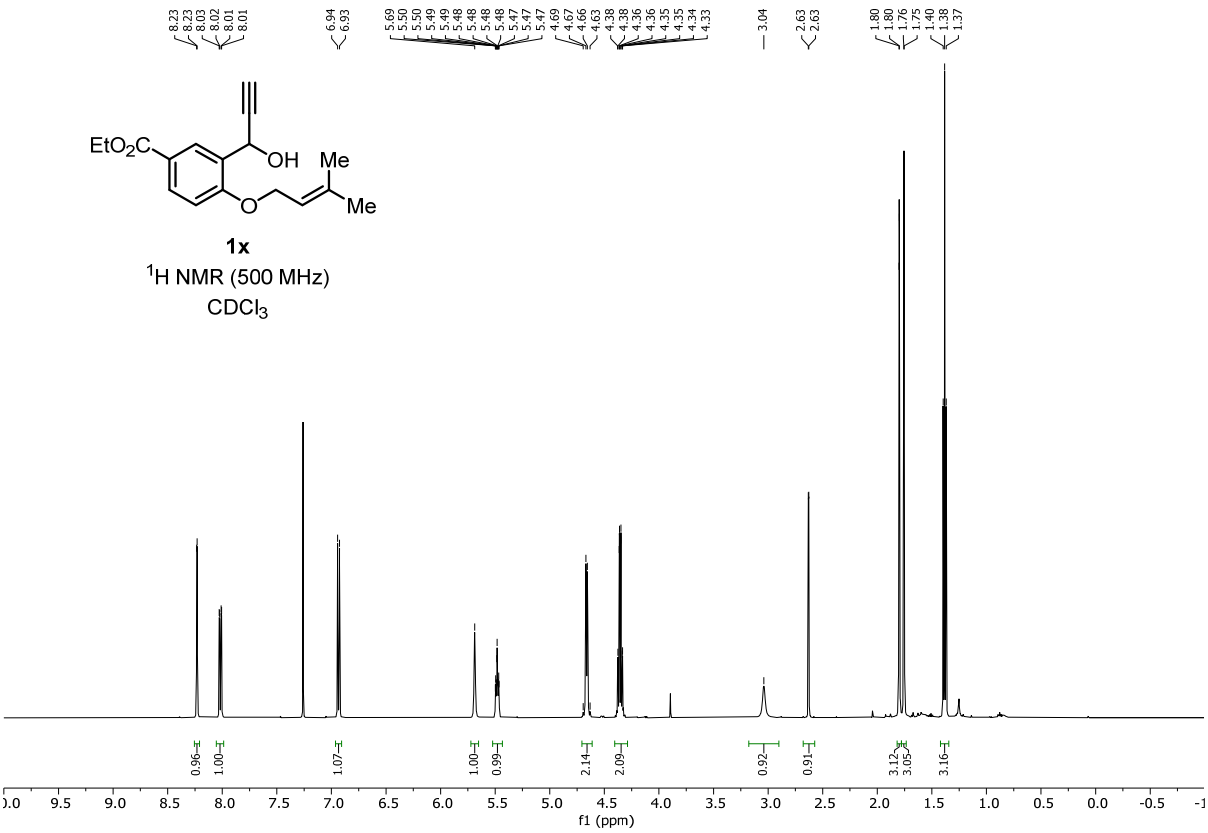


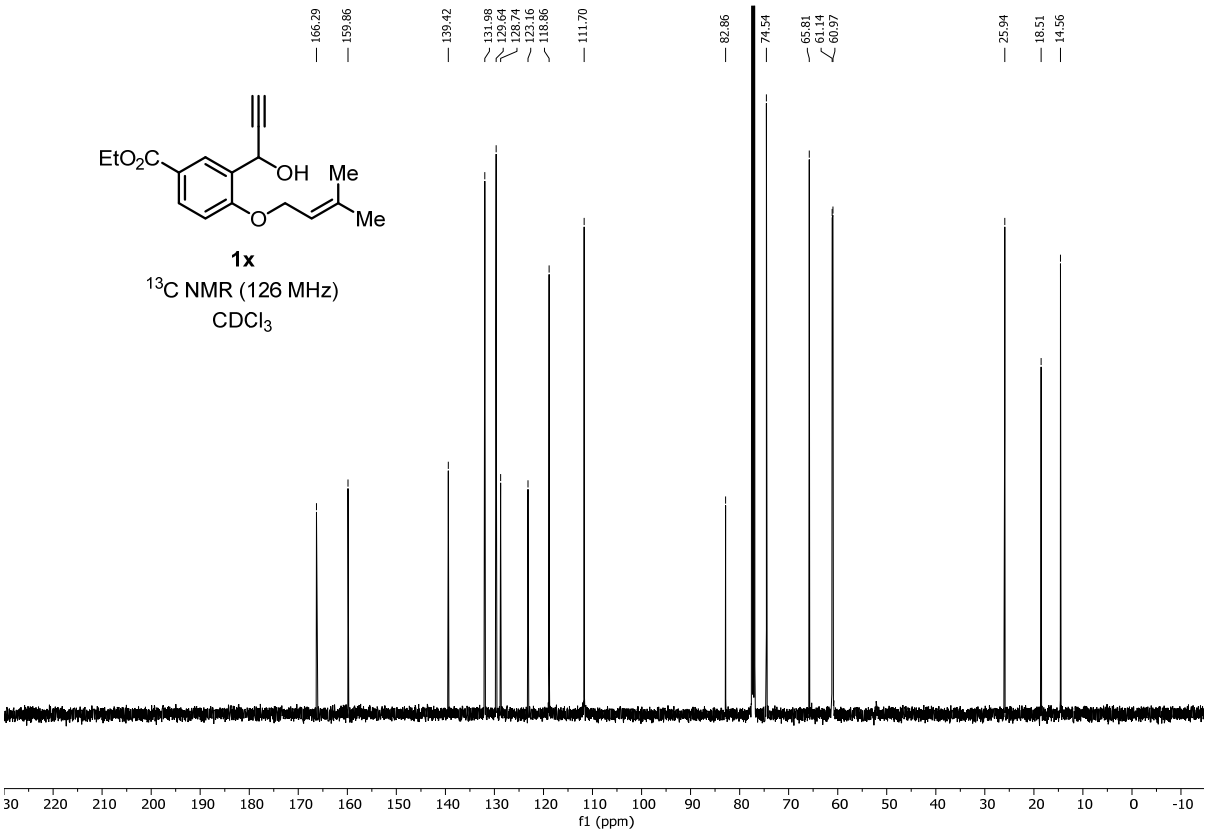
1v

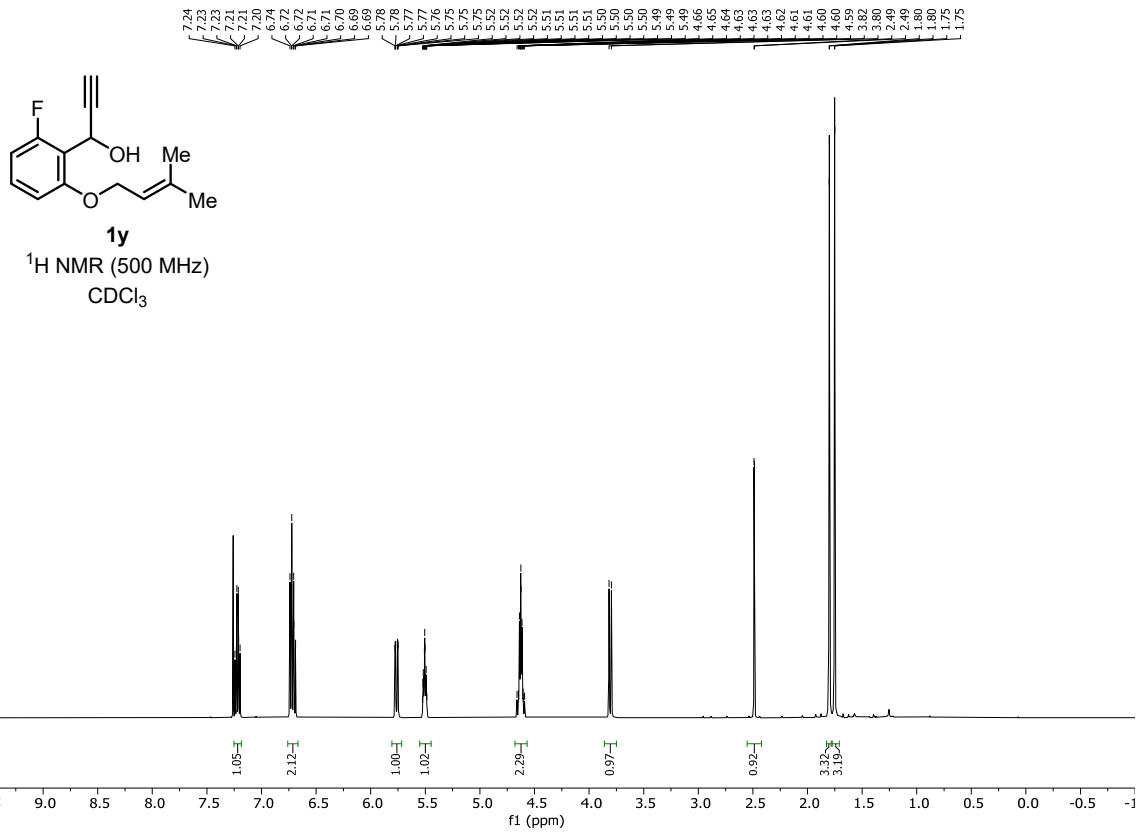
^{19}F NMR (471 MHz)

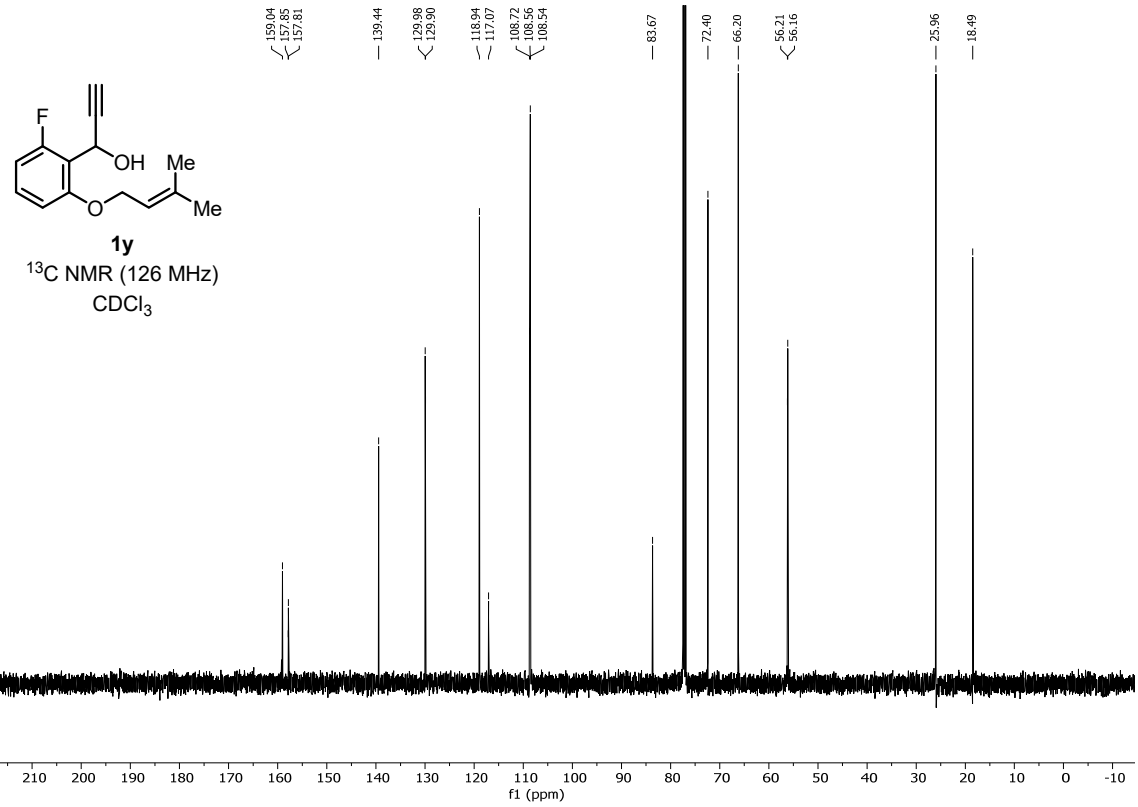
$CDCl_3$–$PhCF_3$

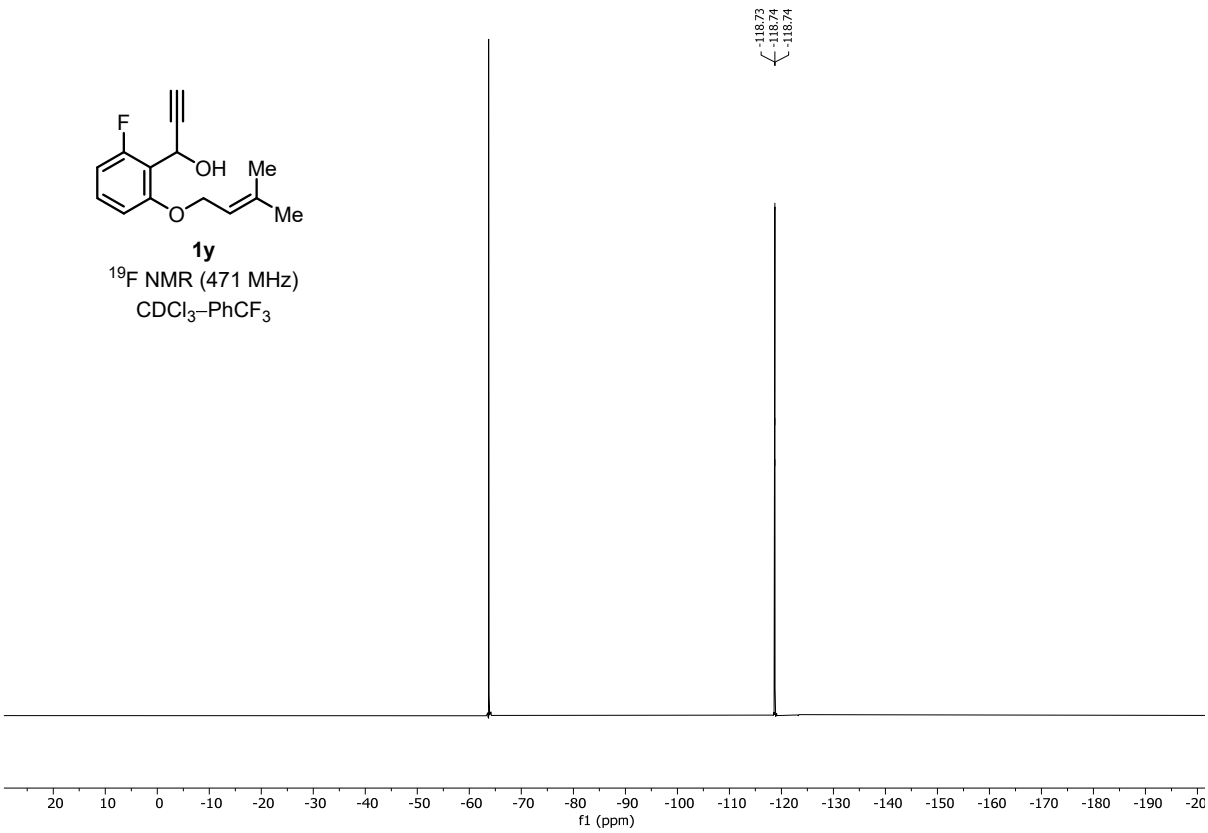

Br
OH
Me
O
Me
1w
1H NMR (500 MHz)
CDCl3
f1 (ppm)


EtO2C
OH
Me
Me
O
1x
1H NMR (500 MHz)
CDCl3
f1 (ppm)


EtO2C
OH
Me
Me
O
1x
13C NMR (126 MHz)
CDCl3
f1 (ppm)


F
OH
Me
O
Me
1y
1H NMR (500 MHz)
CDCl3
f1 (ppm)

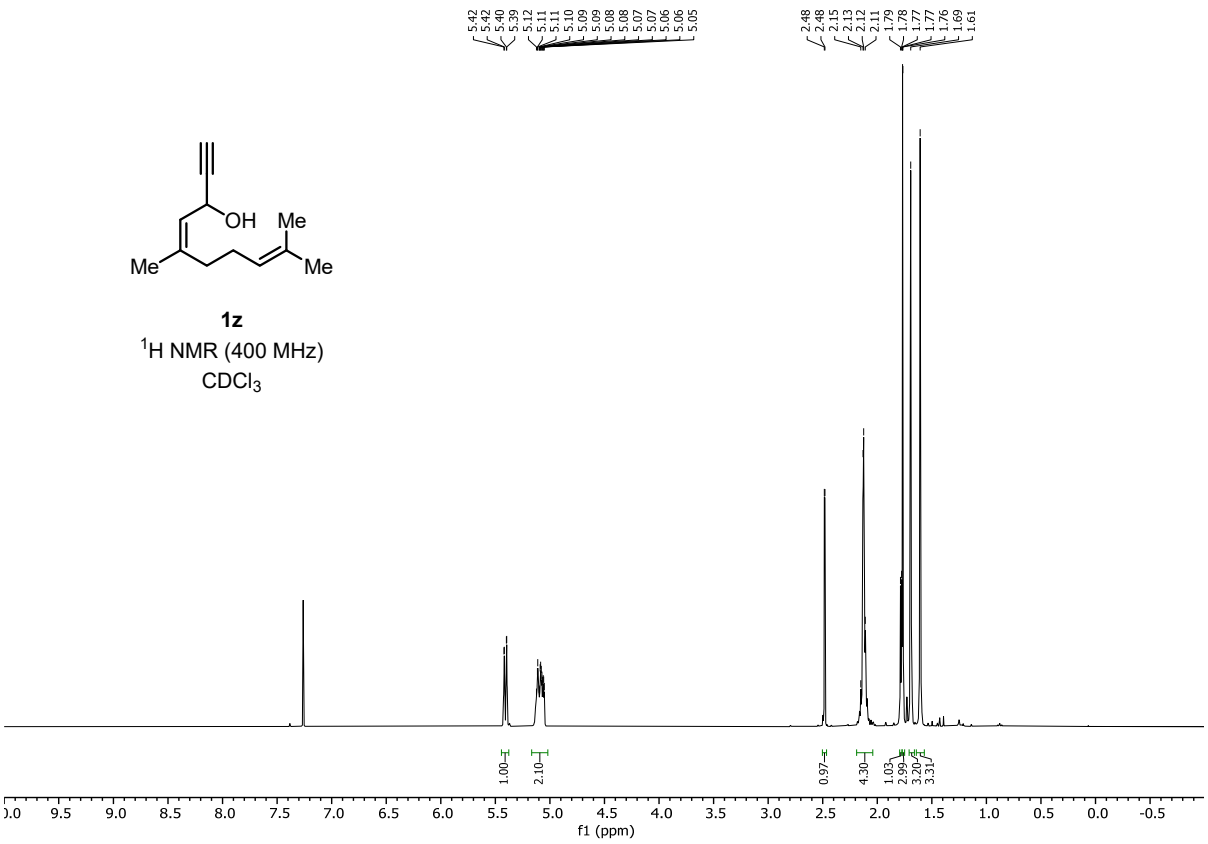

F
OH
Me
O
Me
1y
13C NMR (126 MHz)
CDCl3
f1 (ppm)



1y

^{19}F NMR (471 MHz)

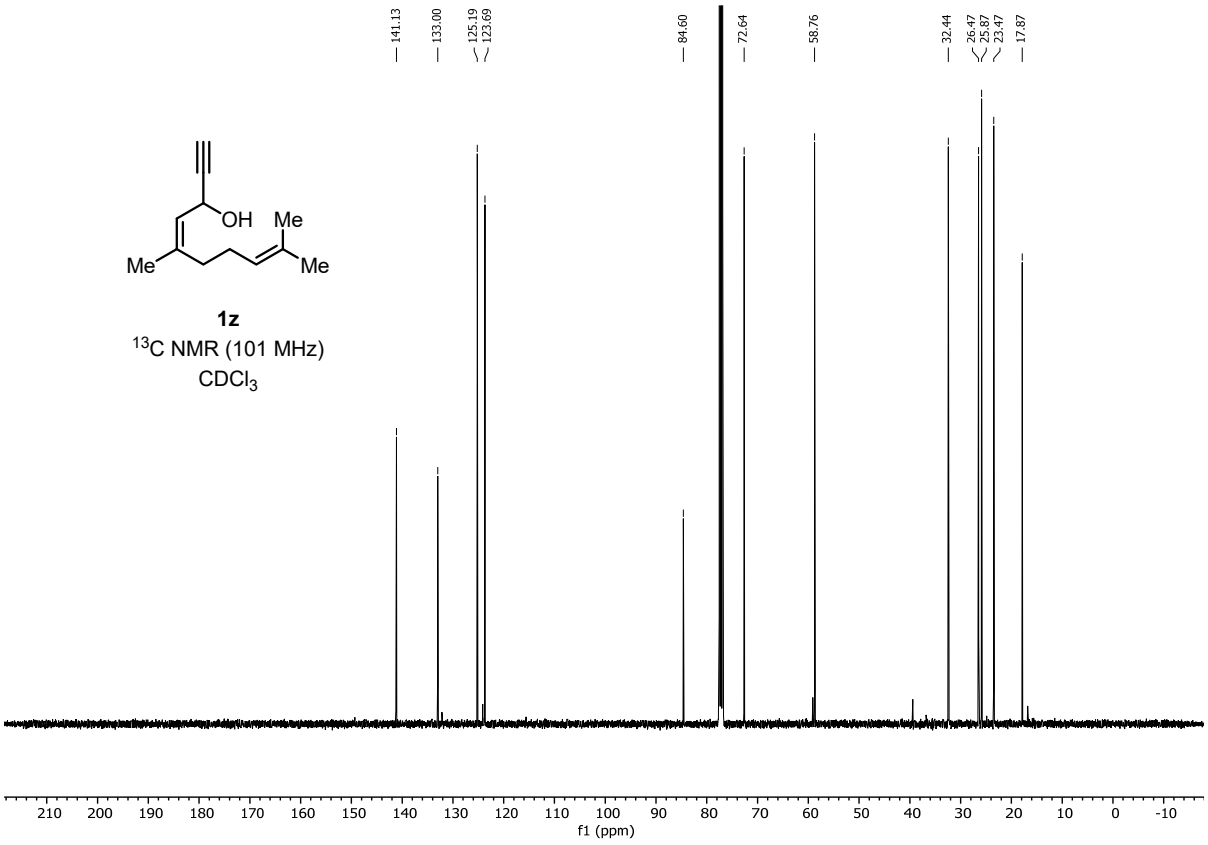
$CDCl_3$–$PhCF_3$



1z

^{1}H NMR (400 MHz)

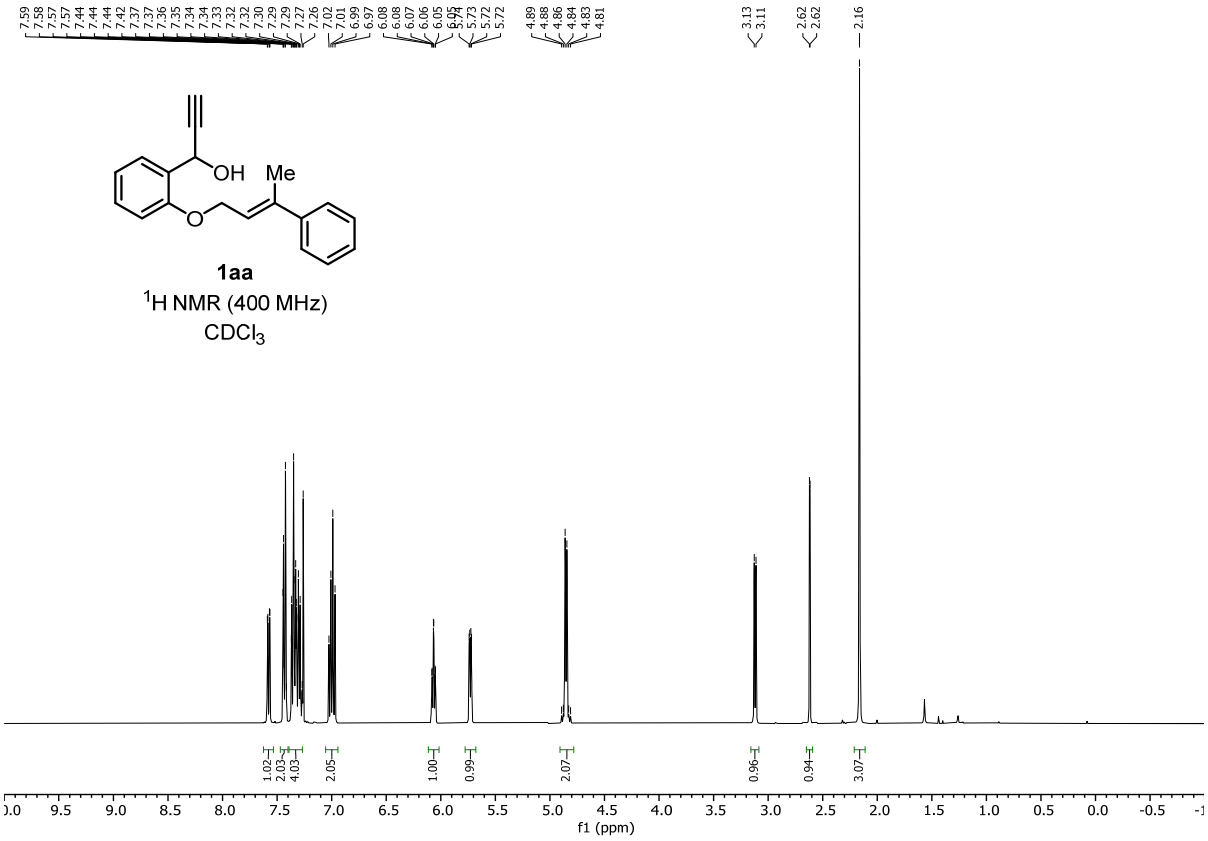
$CDCl_3$

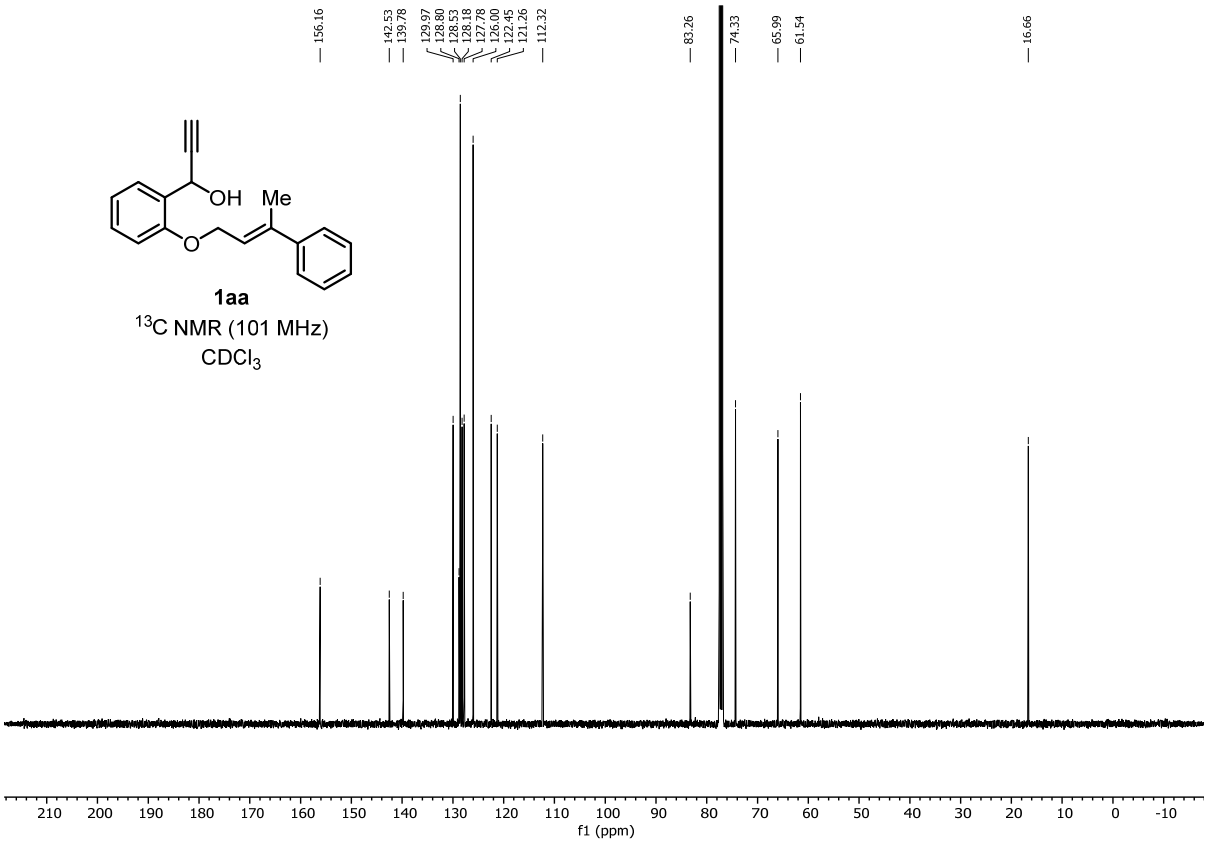


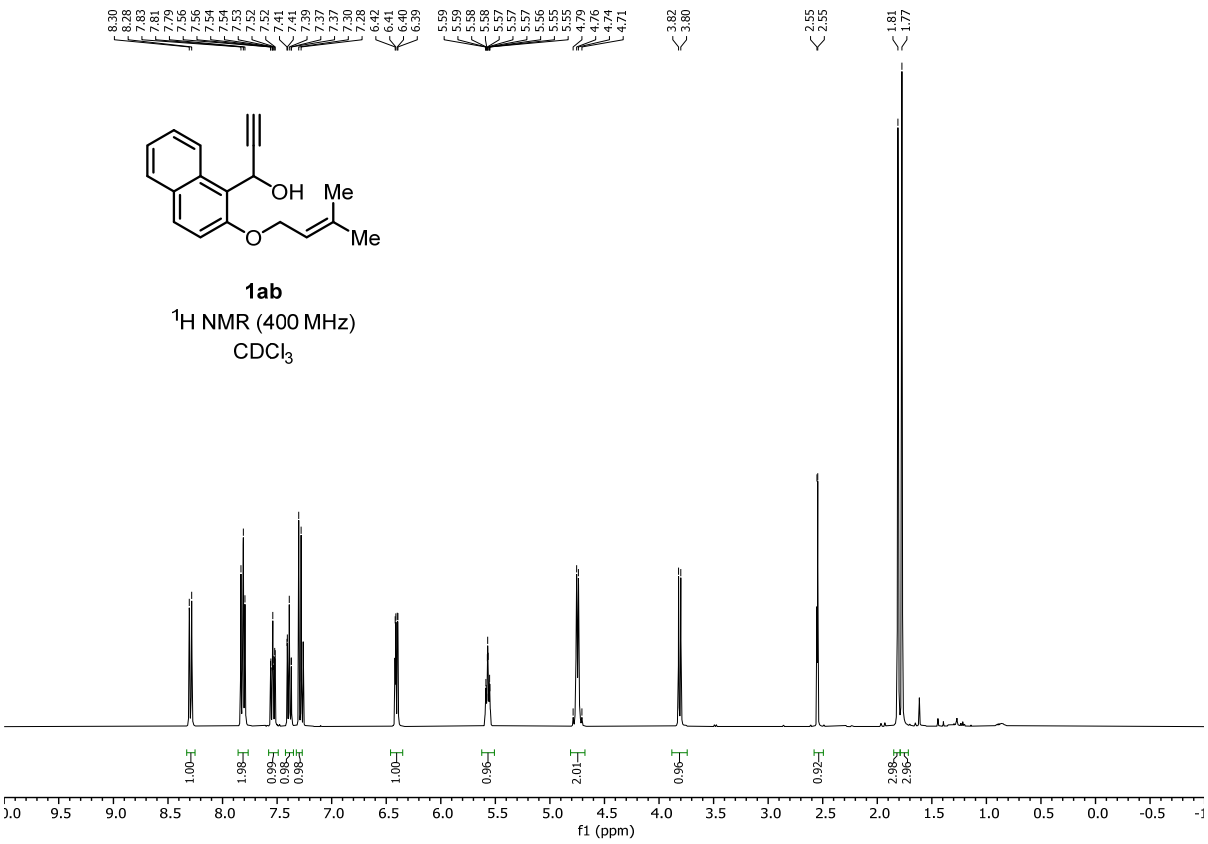
1z

^{13}C NMR (101 MHz)

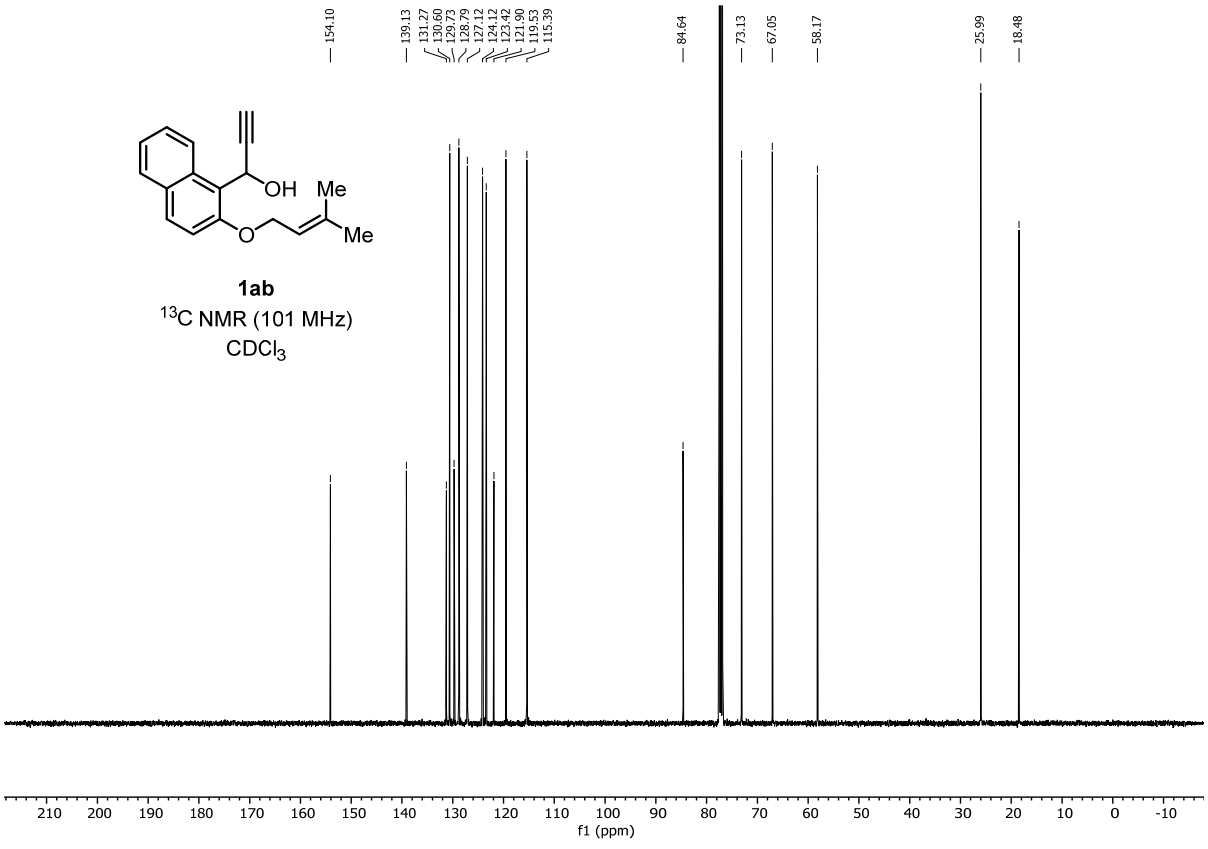
$CDCl_3$


OH
Me
O
1aa
1H NMR (400 MHz)
CDCl3
f1 (ppm)

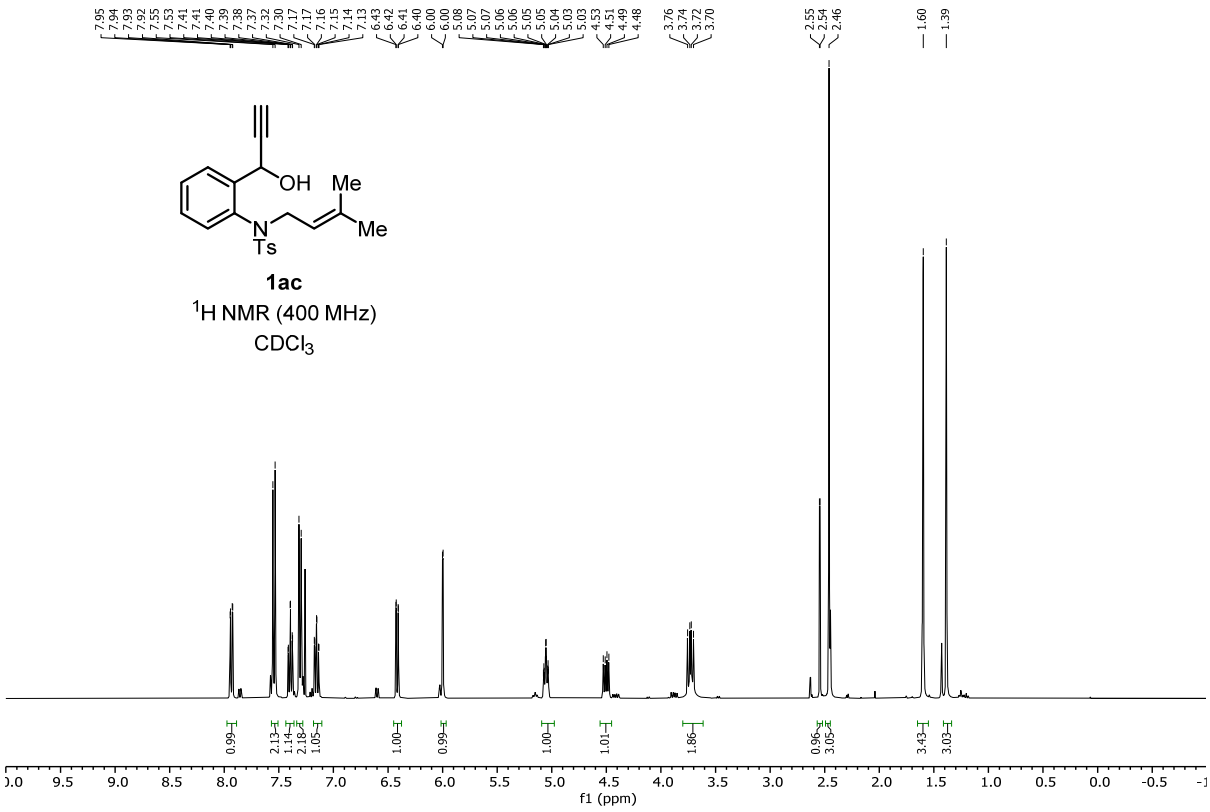

OH
Me
O
1aa
13C NMR (101 MHz)
CDCl3
f1 (ppm)

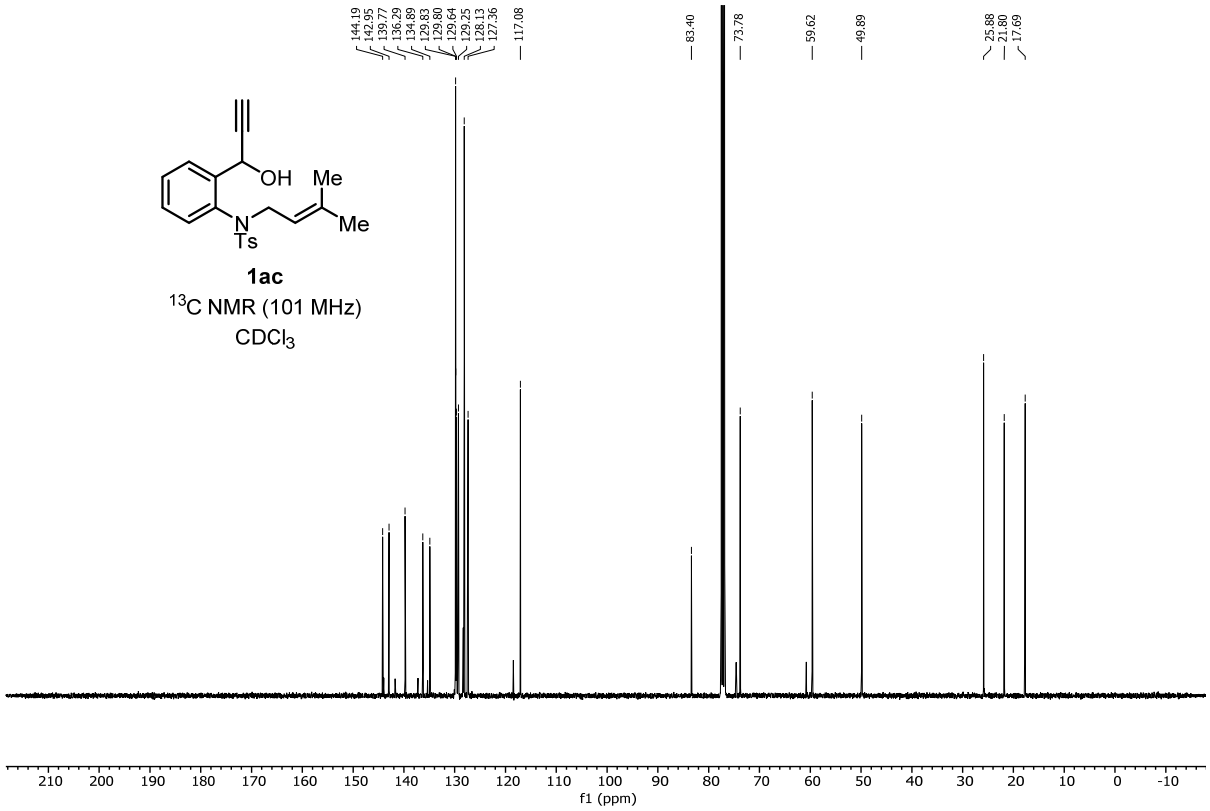


1ab
^{1}H NMR (400 MHz)
$CDCl_3$



1ab
^{13}C NMR (101 MHz)
$CDCl_3$

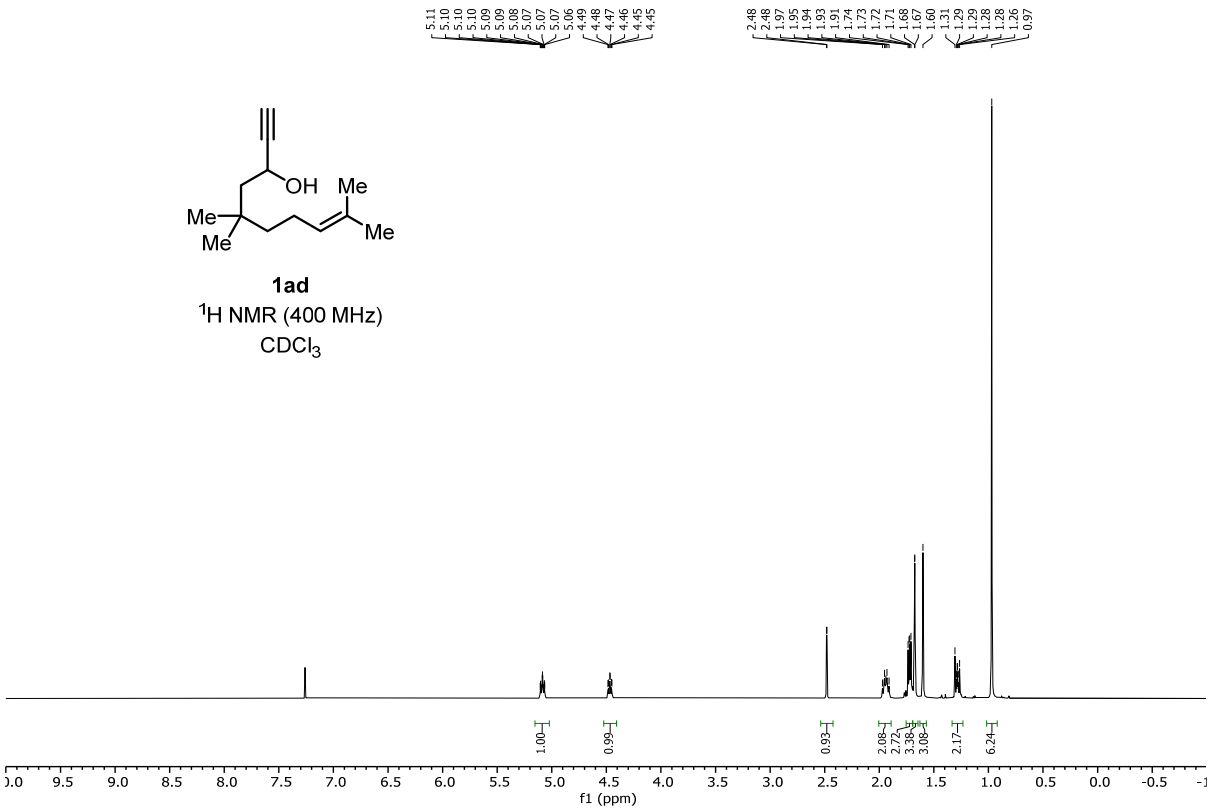

OH
Me
N
Ts
Me
1ac
1H NMR (400 MHz)
CDCl3
f1 (ppm)


OH
Me
N
Ts
Me
1ac
13C NMR (101 MHz)
CDCl3
f1 (ppm)

1ad

^{1}H NMR (400 MHz)

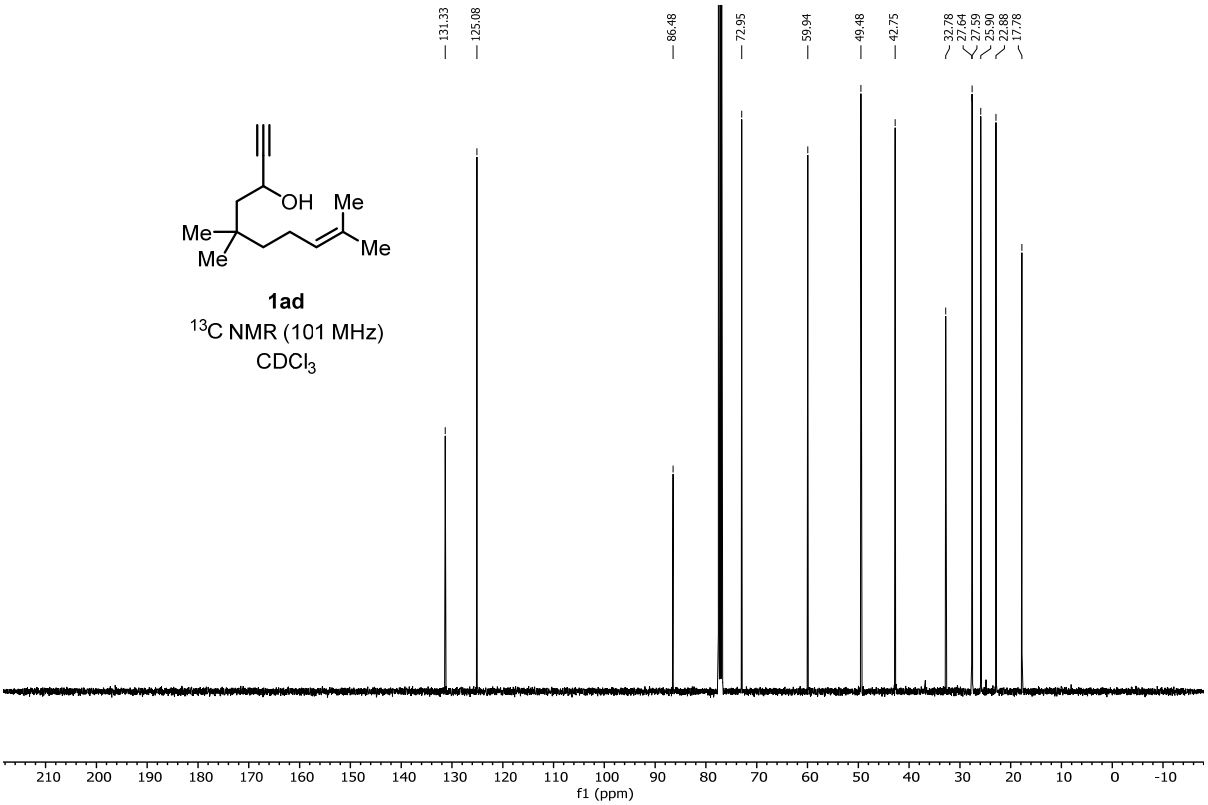
$CDCl_3$

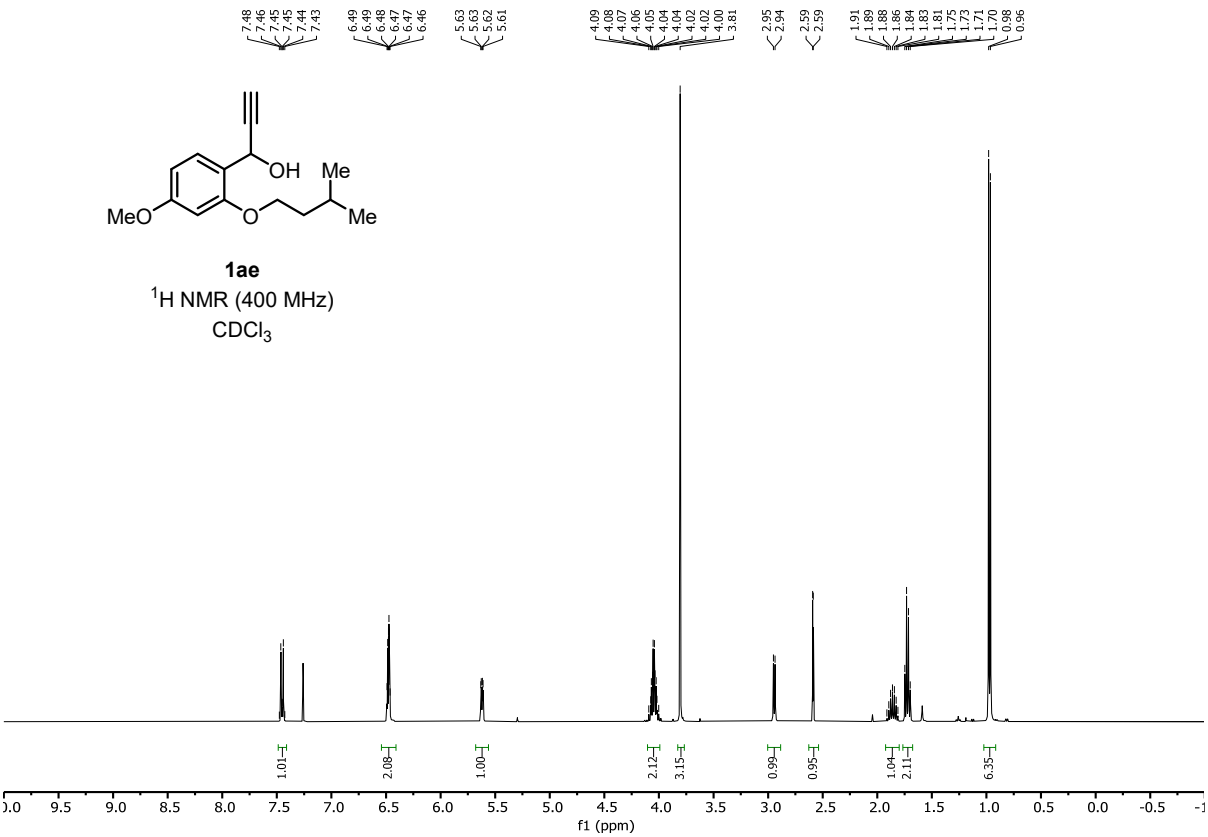


1ad

^{13}C NMR (101 MHz)

$CDCl_3$

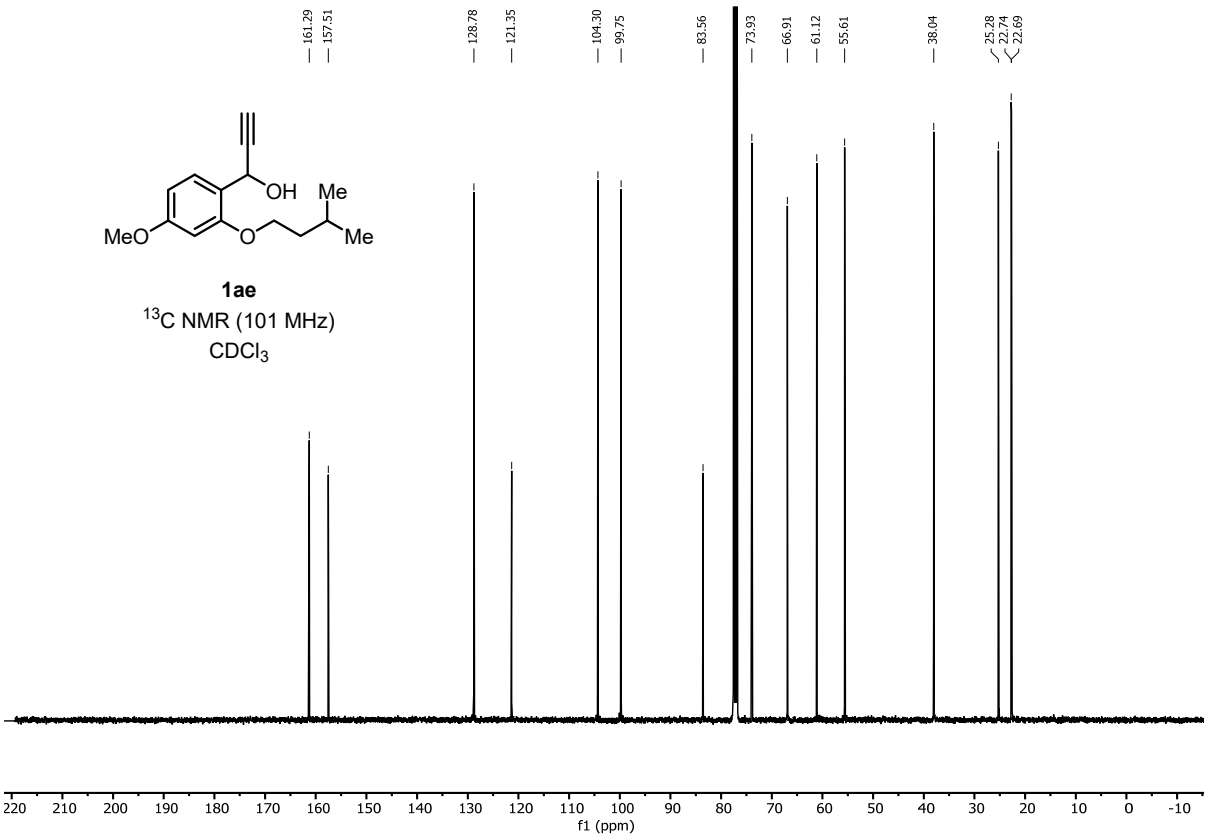




1ae

^{1}H NMR (400 MHz)

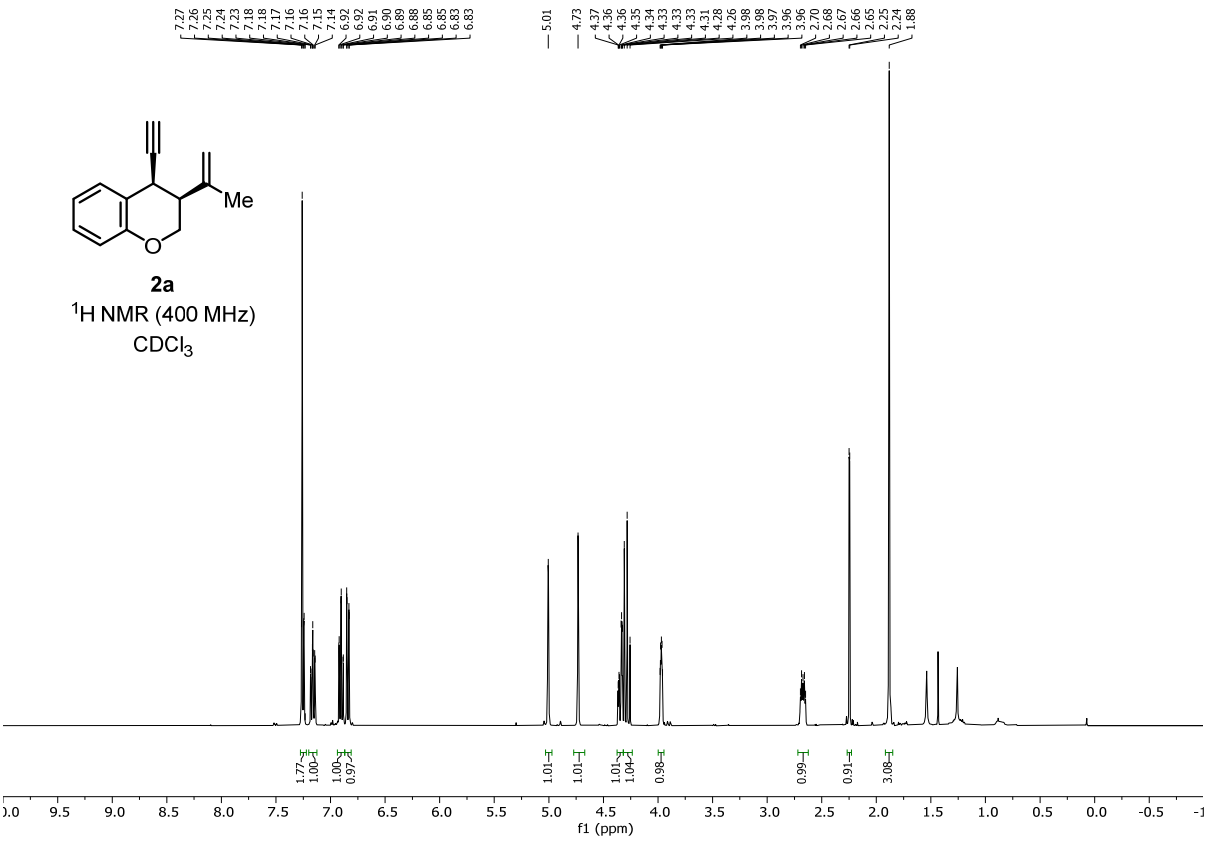
$CDCl_3$

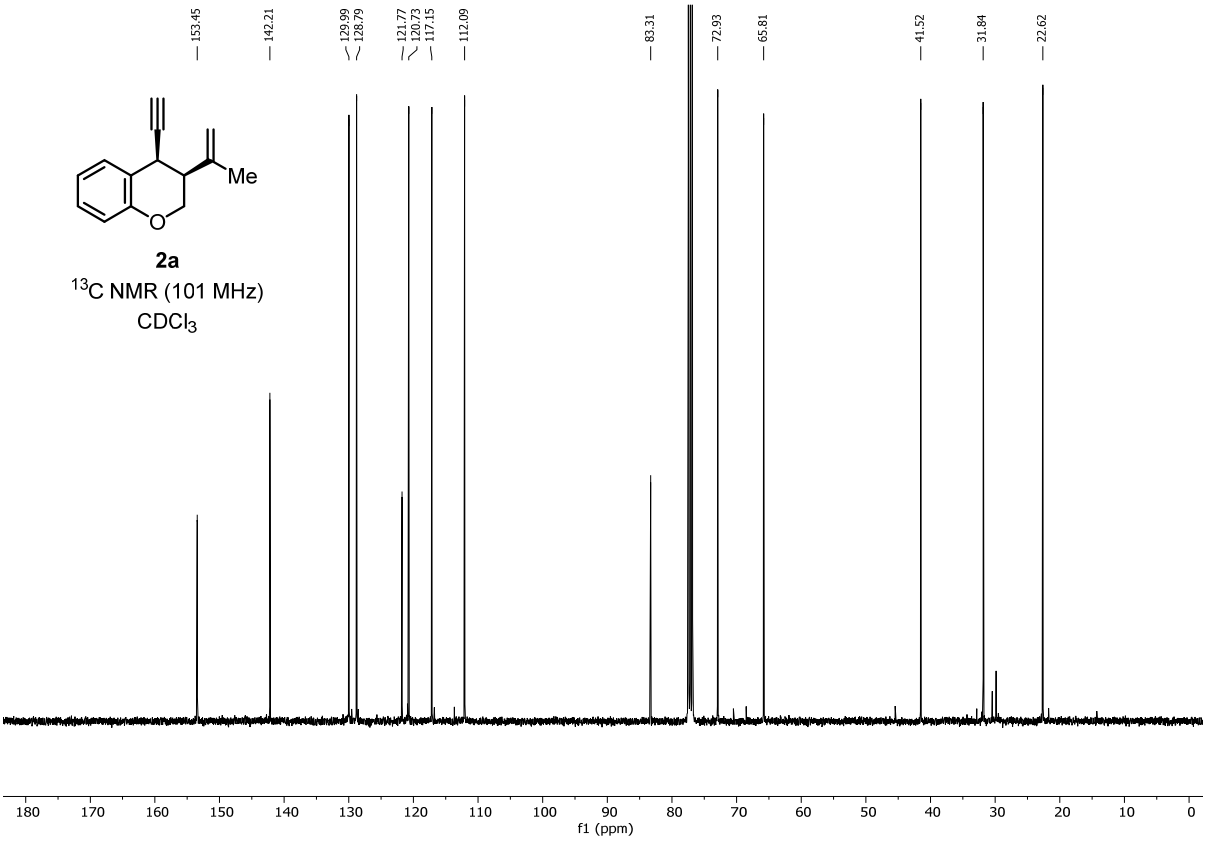


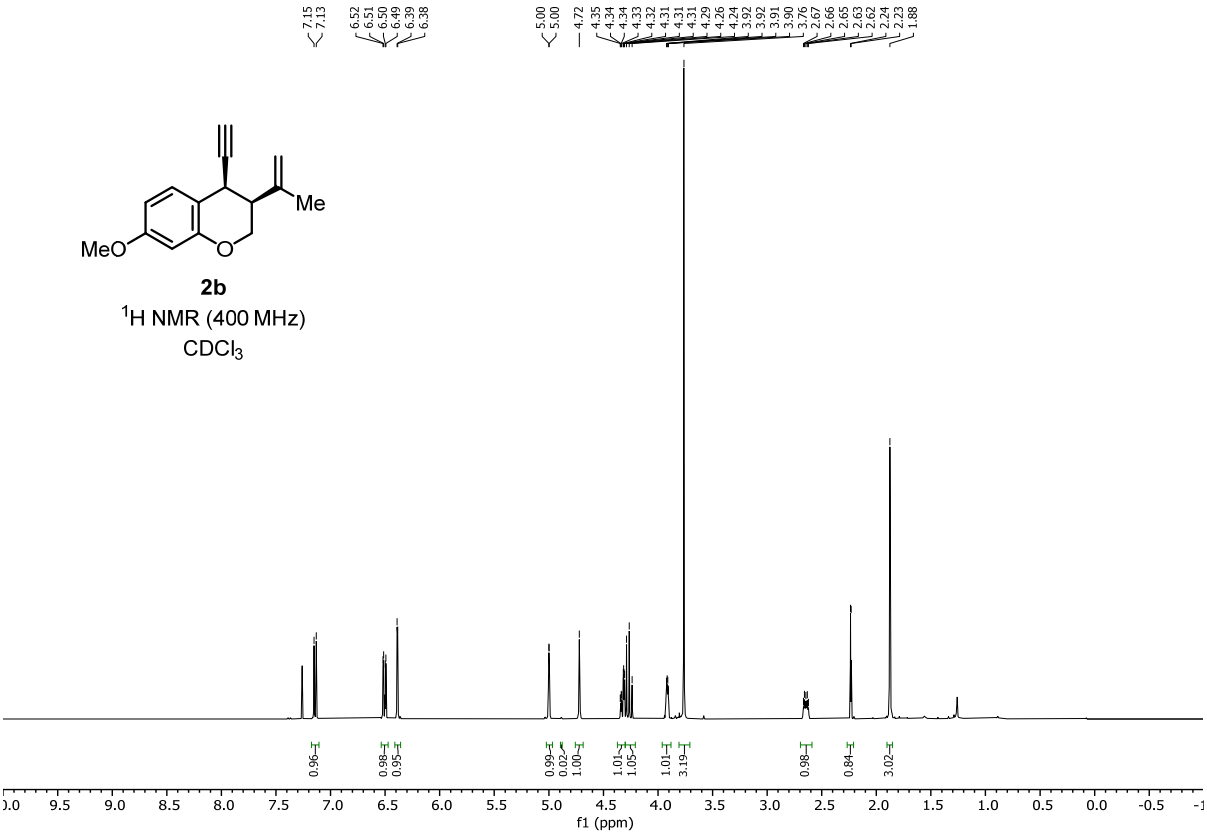
1ae

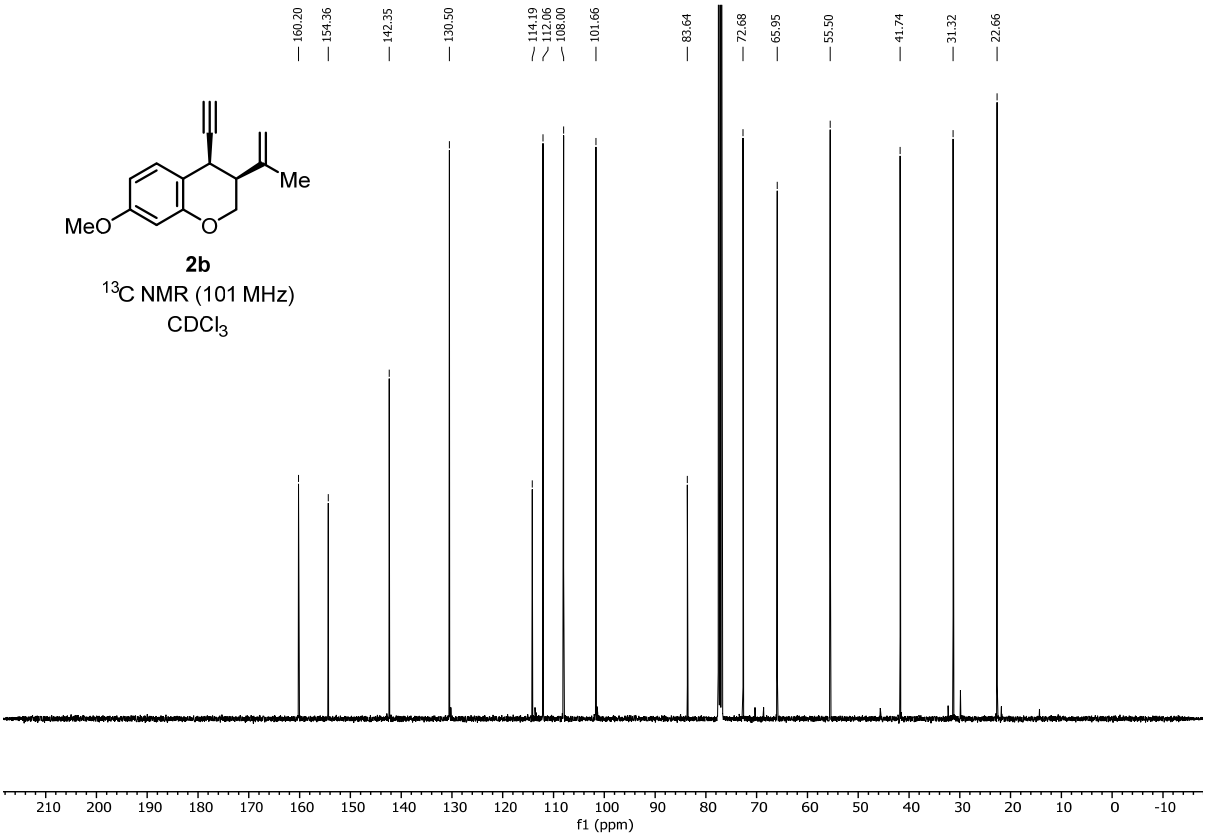
^{13}C NMR (101 MHz)

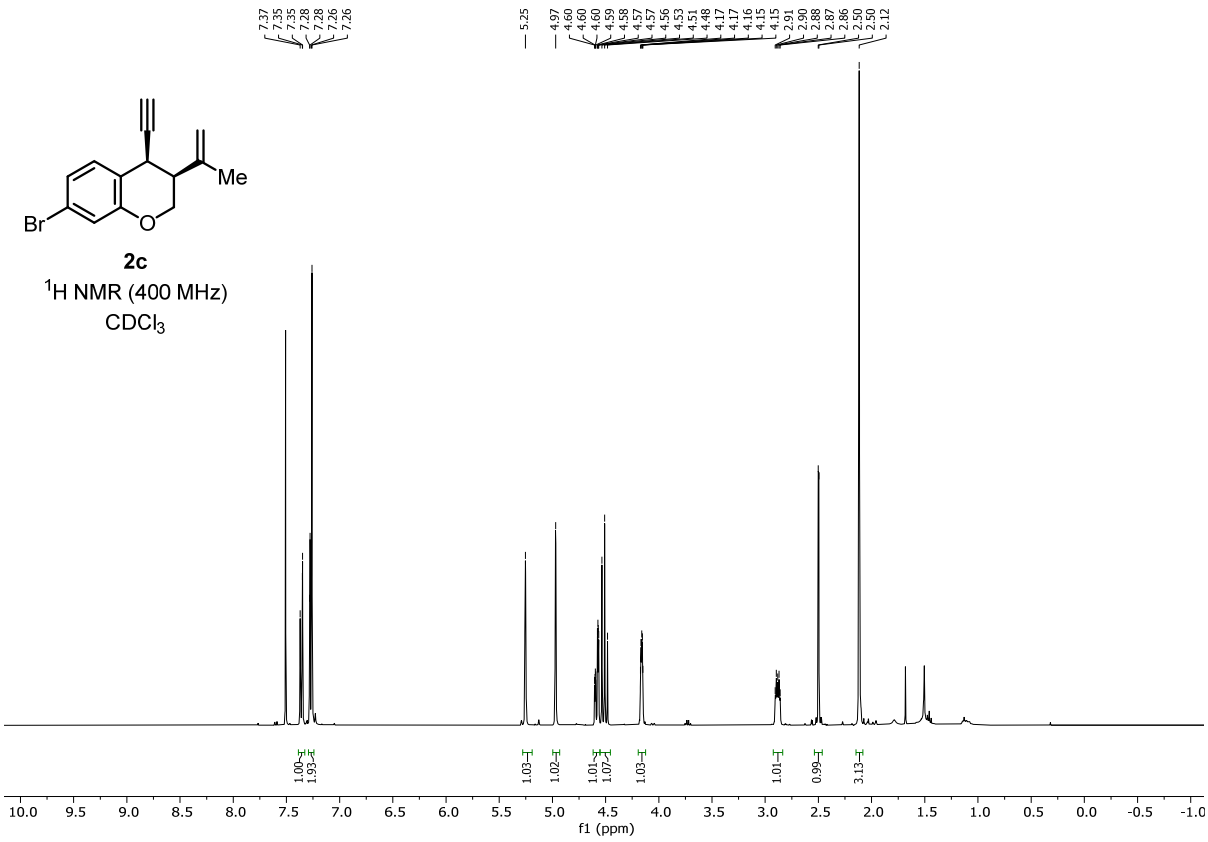
$CDCl_3$

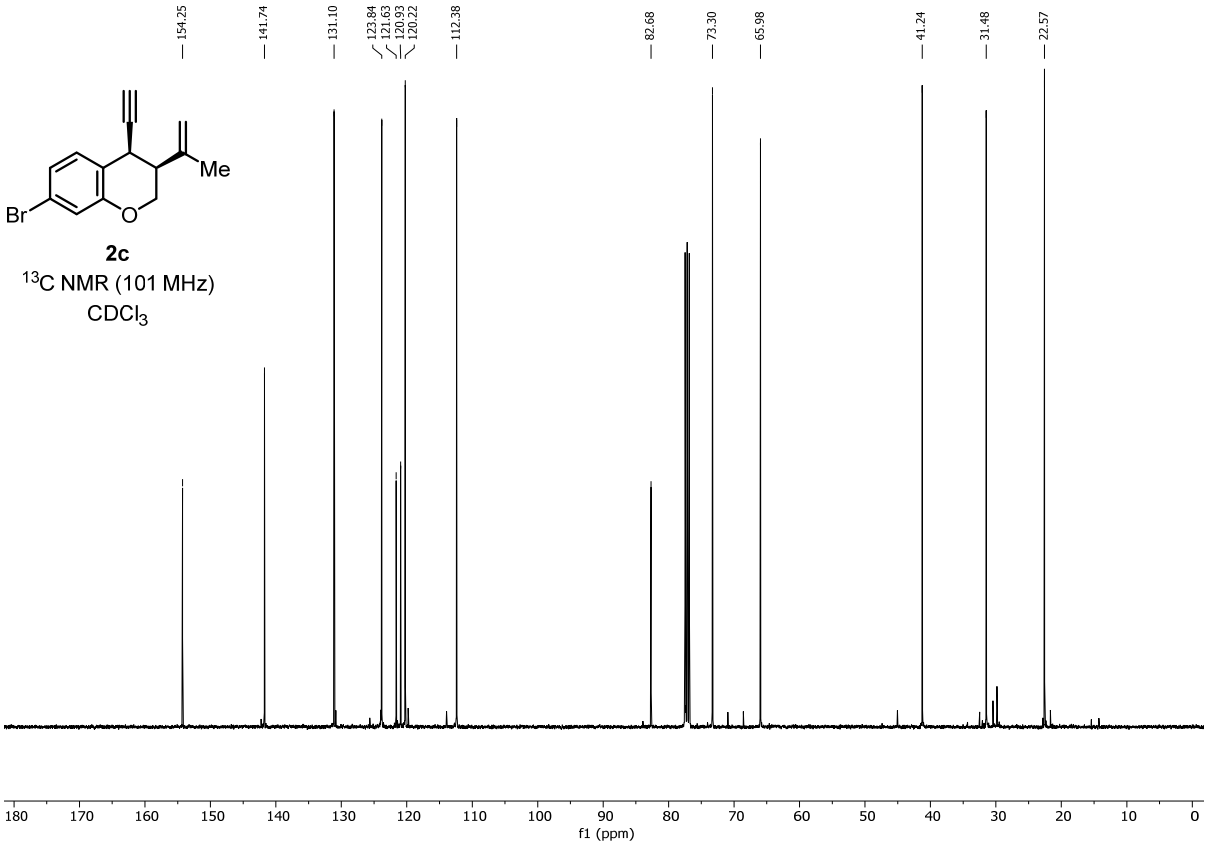

Me
O
2a
1H NMR (400 MHz)
CDCl3
f1 (ppm)

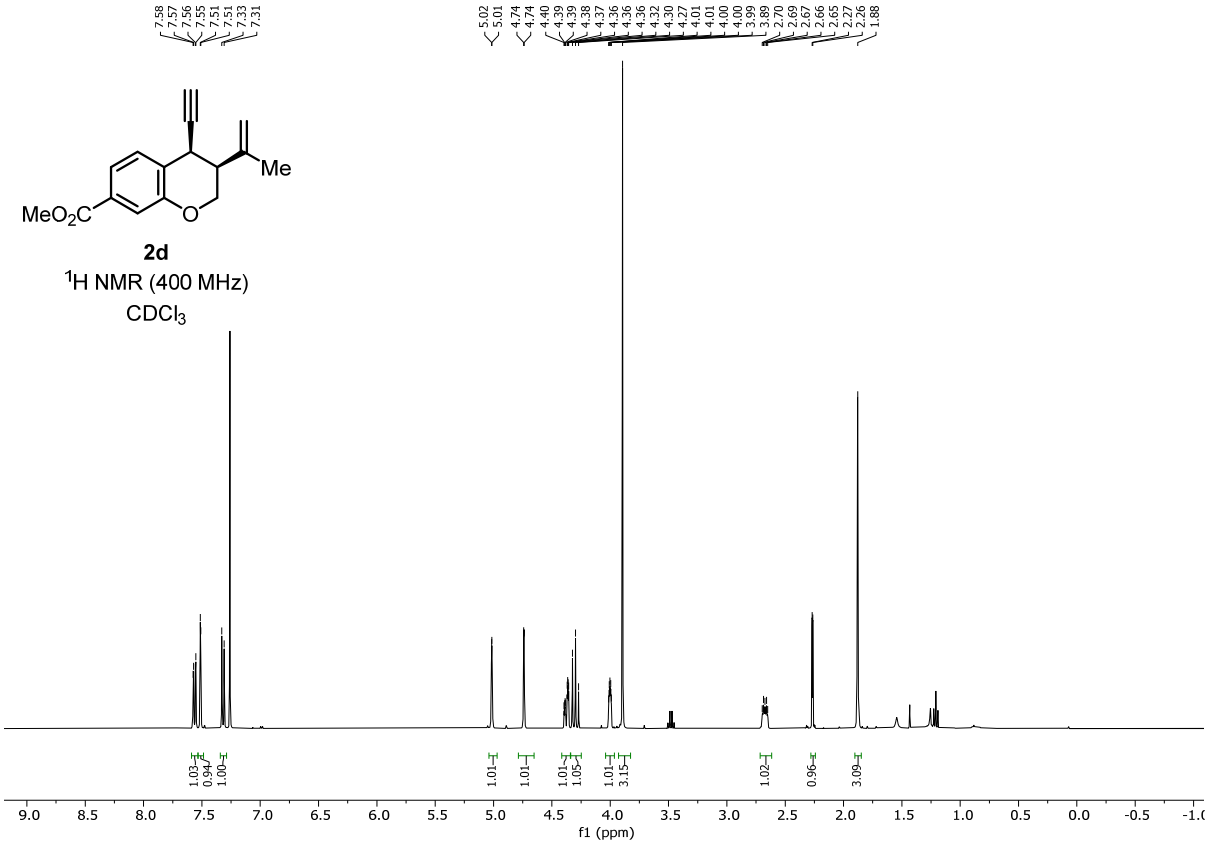

Me
O
2a
13C NMR (101 MHz)
CDCl3
f1 (ppm)

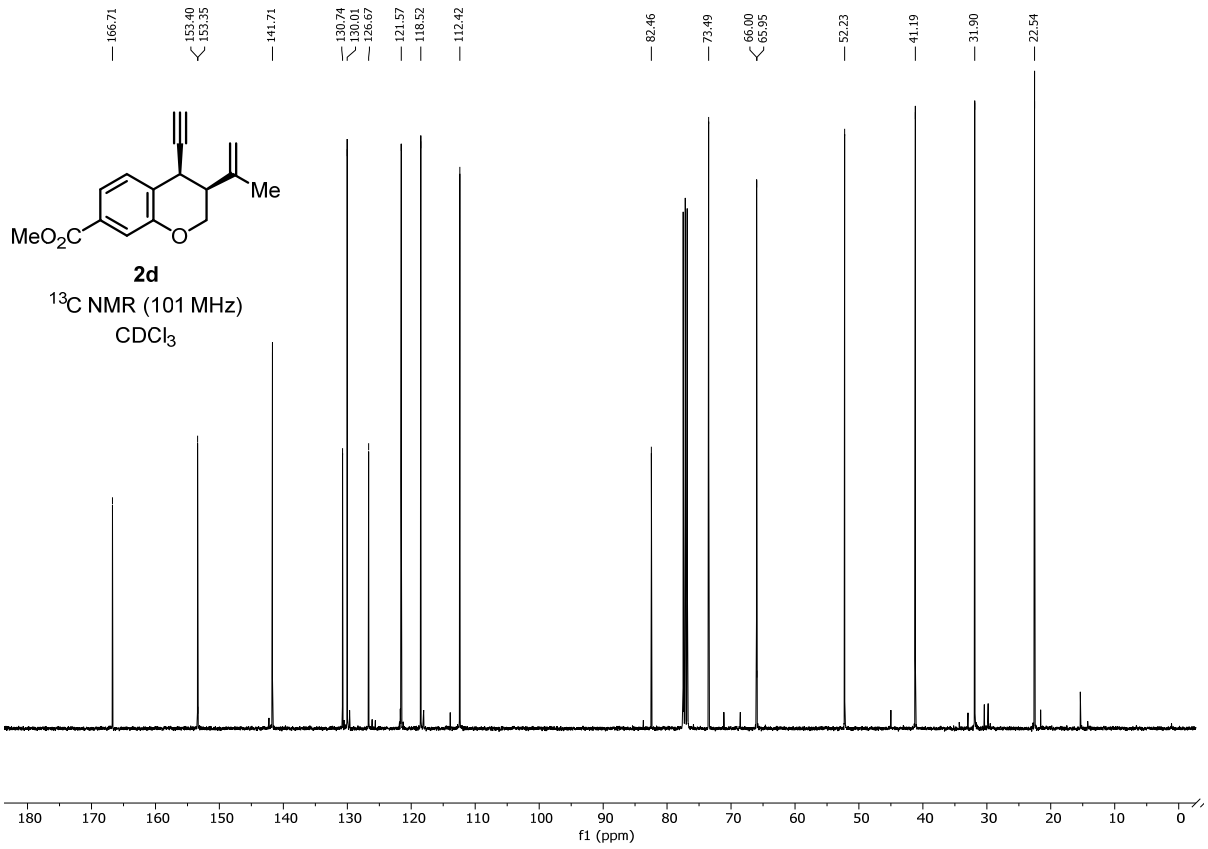

MeO
Me
O
2b
1H NMR (400 MHz)
CDCl3
f1 (ppm)

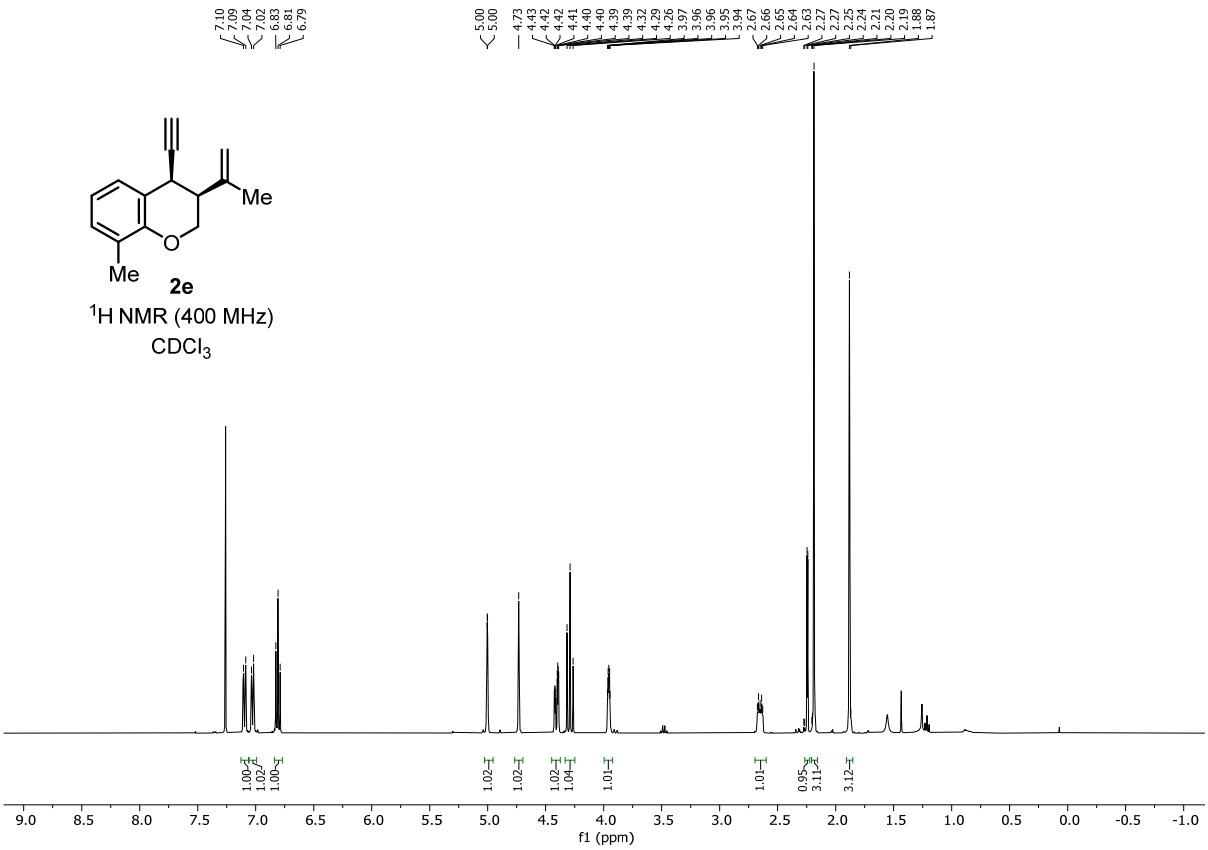

MeO
Me
O
2b
13C NMR (101 MHz)
CDCl3
f1 (ppm)

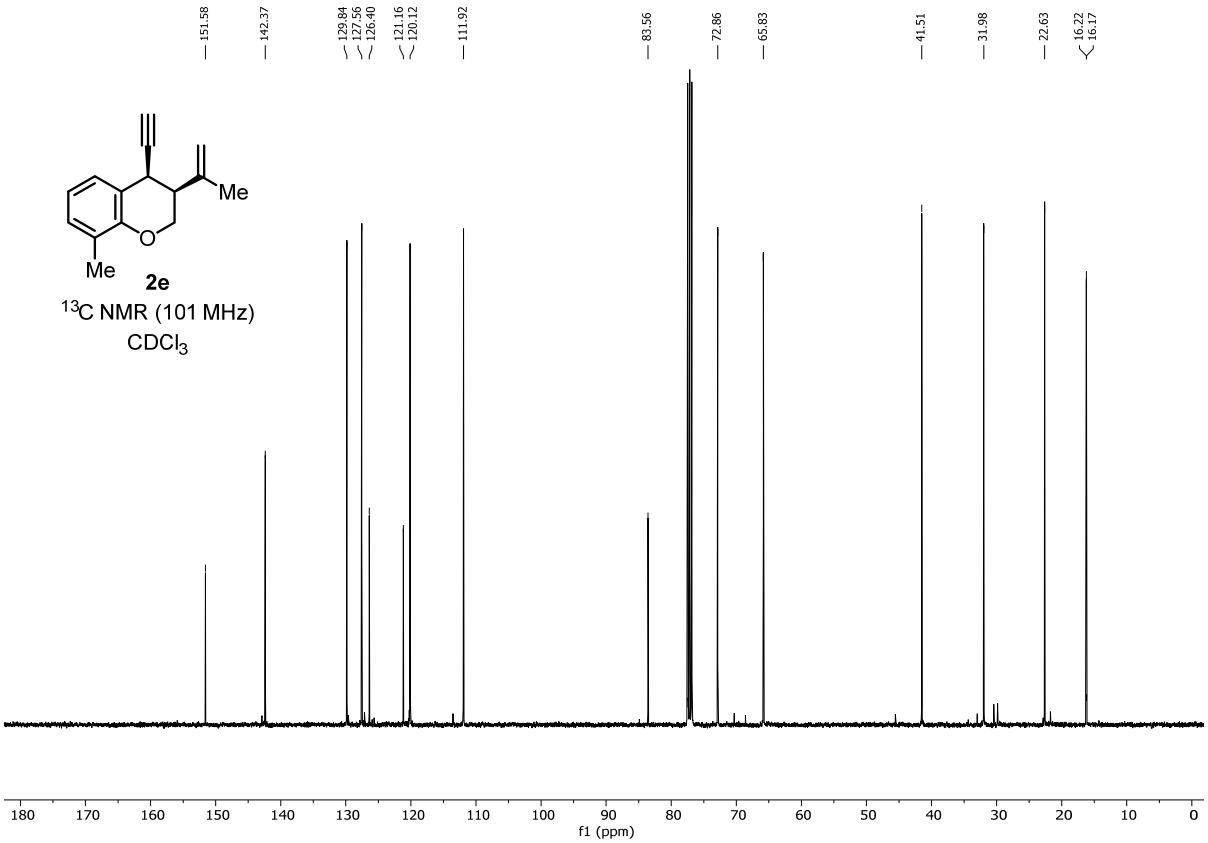

Me
Br
O
2c
1H NMR (400 MHz)
CDCl3
f1 (ppm)

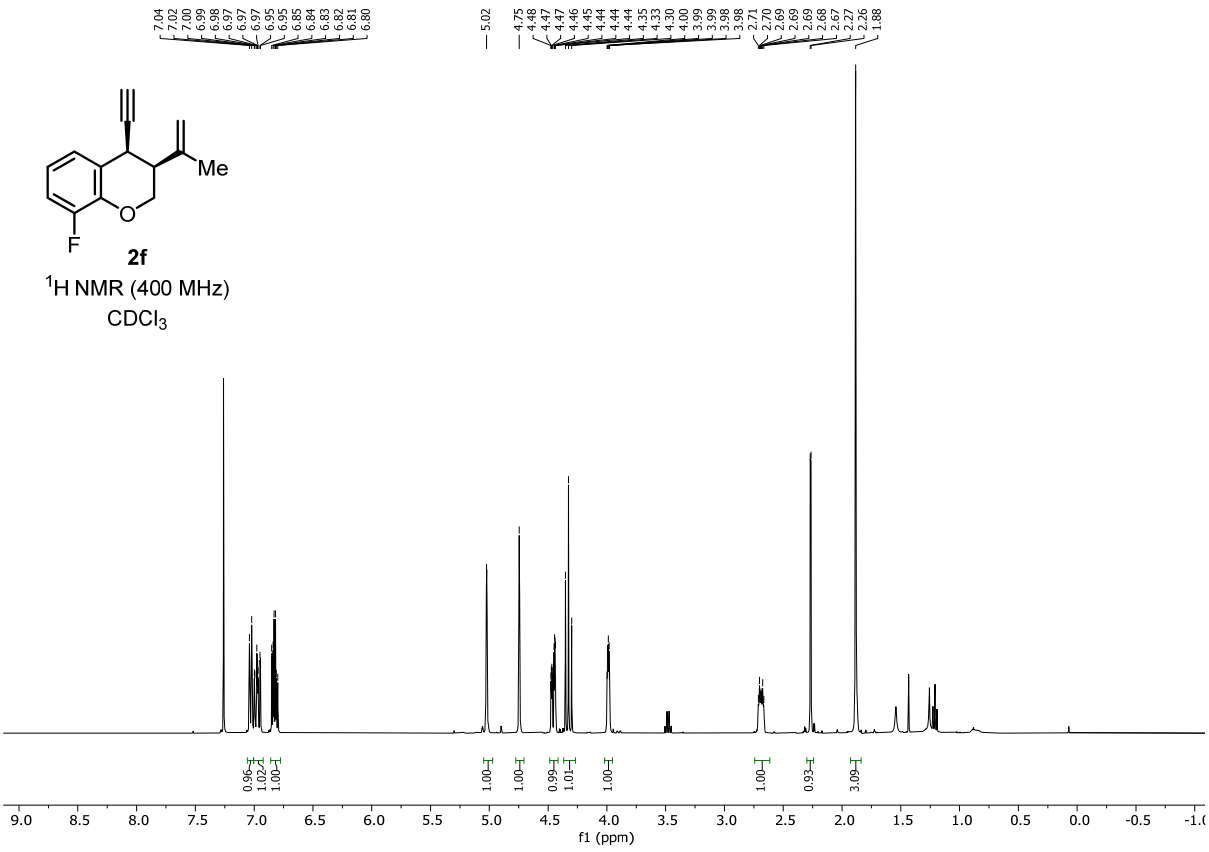

Me
Br
O
2c
13C NMR (101 MHz)
CDCl3
f1 (ppm)

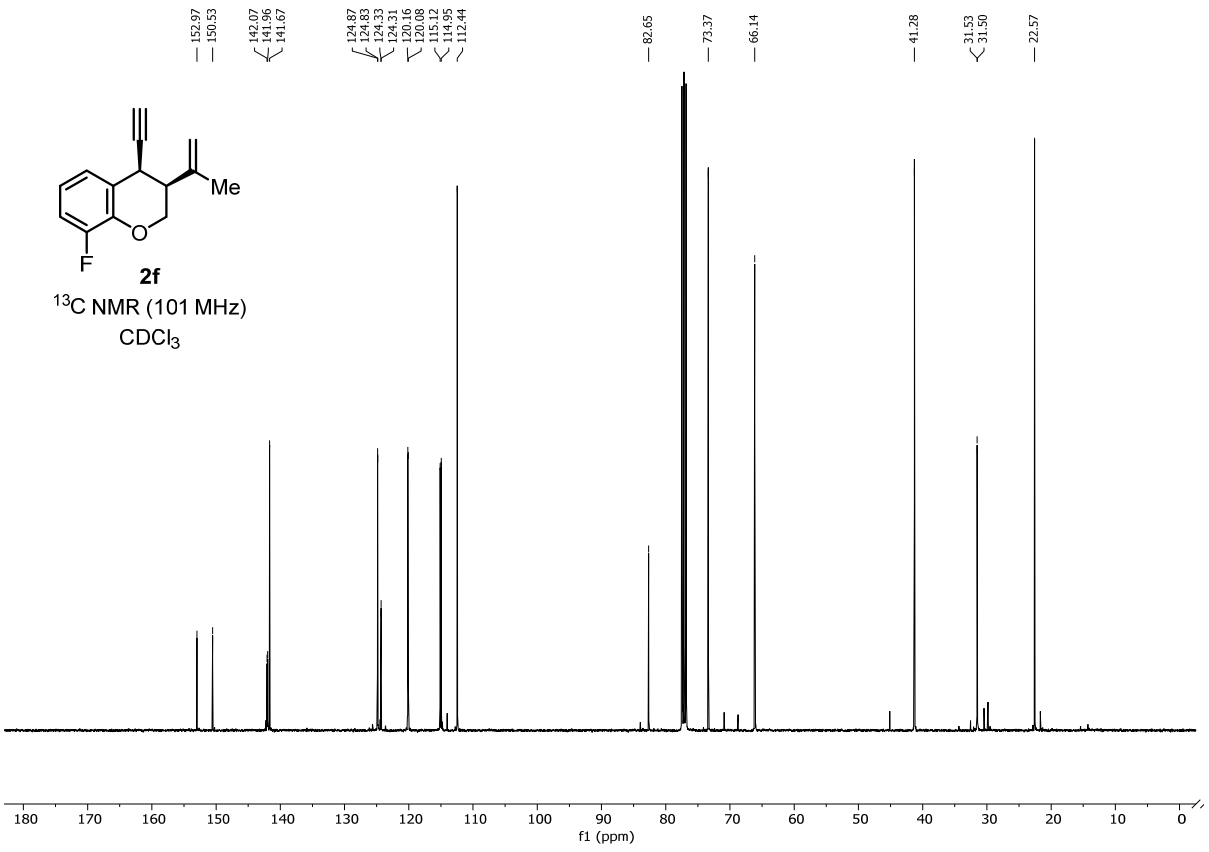

7.58
7.57
7.56
7.55
7.51
7.51
7.33
7.31
5.02
5.01
4.74
4.74
4.40
4.39
4.39
4.38
4.37
4.36
4.36
4.32
4.30
4.27
4.01
4.01
4.00
4.00
3.99
3.89
2.70
2.69
2.67
2.66
2.65
2.27
2.26
1.88
Me
MeO2C
O
2d
1H NMR (400 MHz)
CDCl3
1.03
0.94
1.00
1.01
1.01
1.01
1.05
1.01
3.15
1.02
0.96
3.09
f1 (ppm)


166.71
153.40
153.35
141.71
130.74
130.01
126.67
121.57
118.52
112.42
82.46
73.49
66.00
65.95
52.23
41.19
31.90
22.54
Me
MeO2C
O
2d
13C NMR (101 MHz)
CDCl3
f1 (ppm)


Me
O
Me
2e
1H NMR (400 MHz)
CDCl3
f1 (ppm)


Me
O
Me
2e
13C NMR (101 MHz)
CDCl3
f1 (ppm)

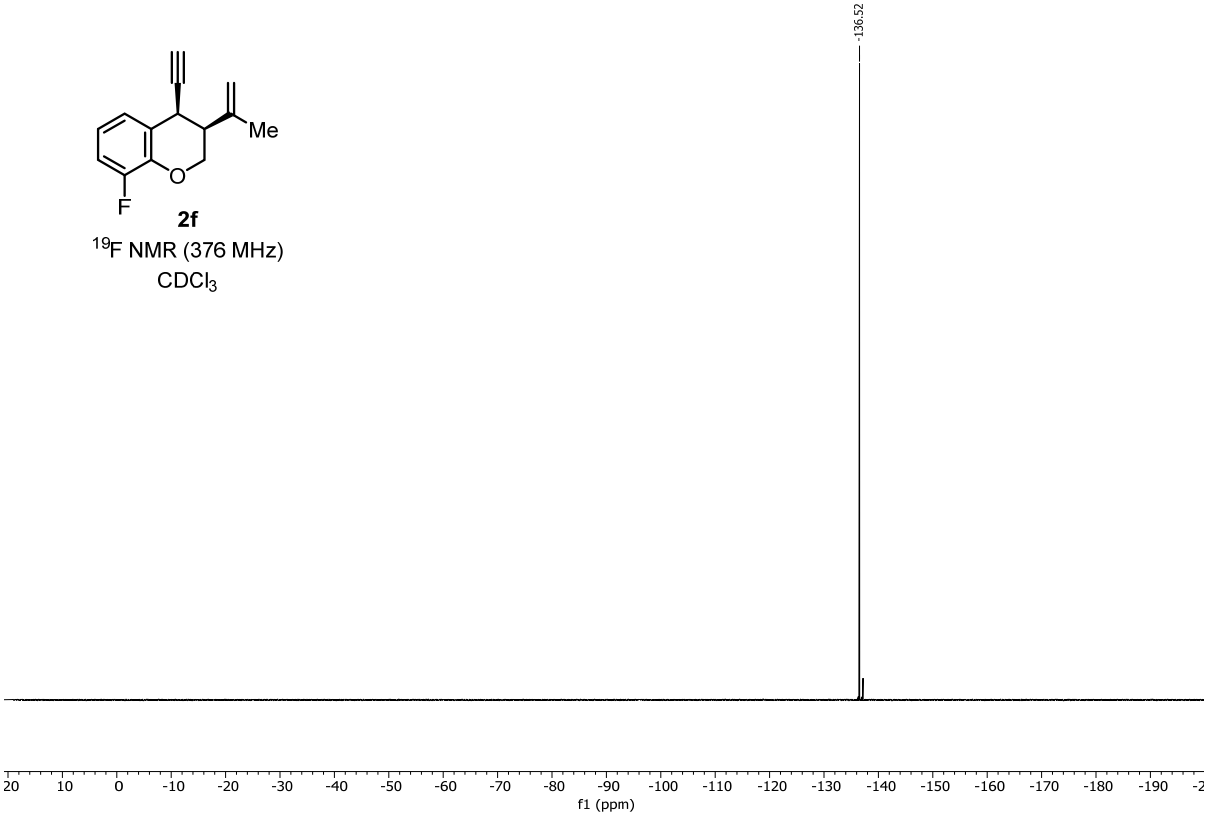

Me
O
F
2f
1H NMR (400 MHz)
CDCl3
f1 (ppm)

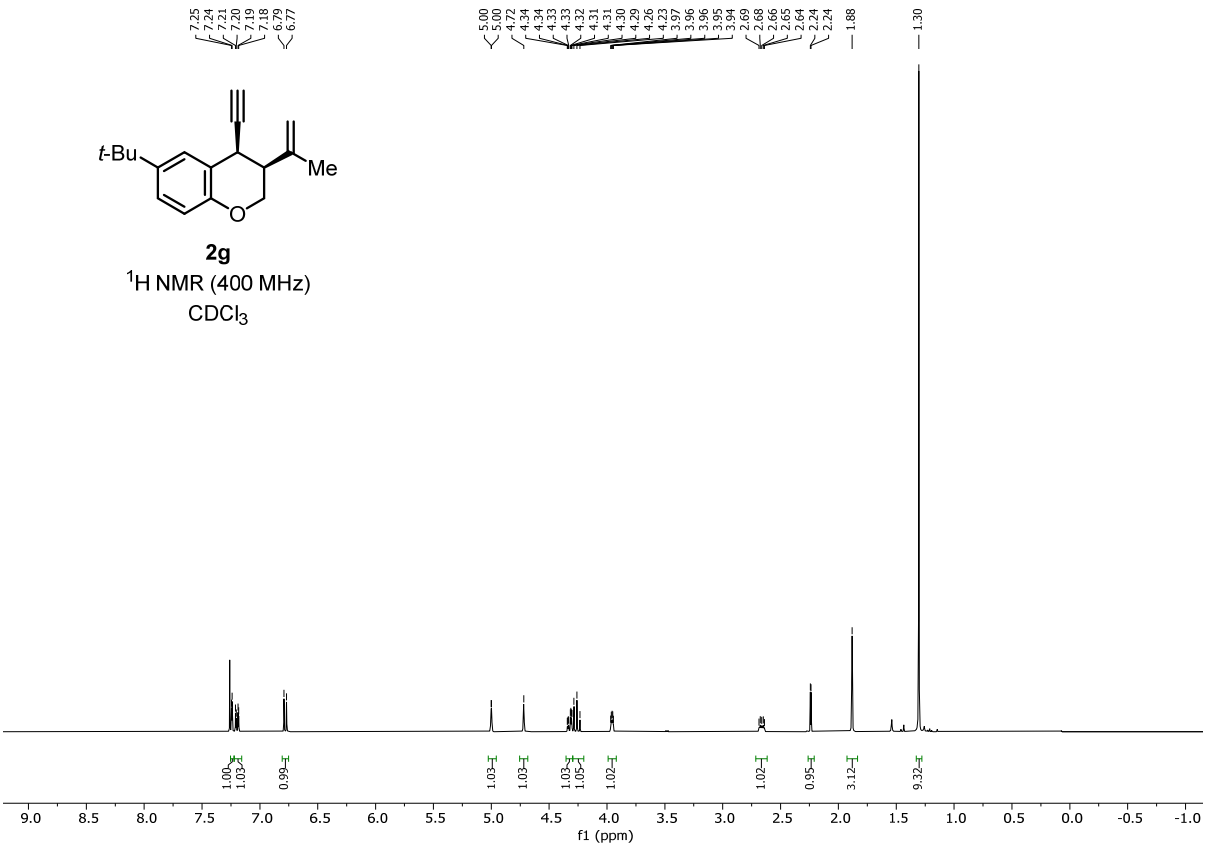

Me
O
F
2f
13C NMR (101 MHz)
CDCl3
f1 (ppm)

2f

^{19}F NMR (376 MHz)

$CDCl_3$

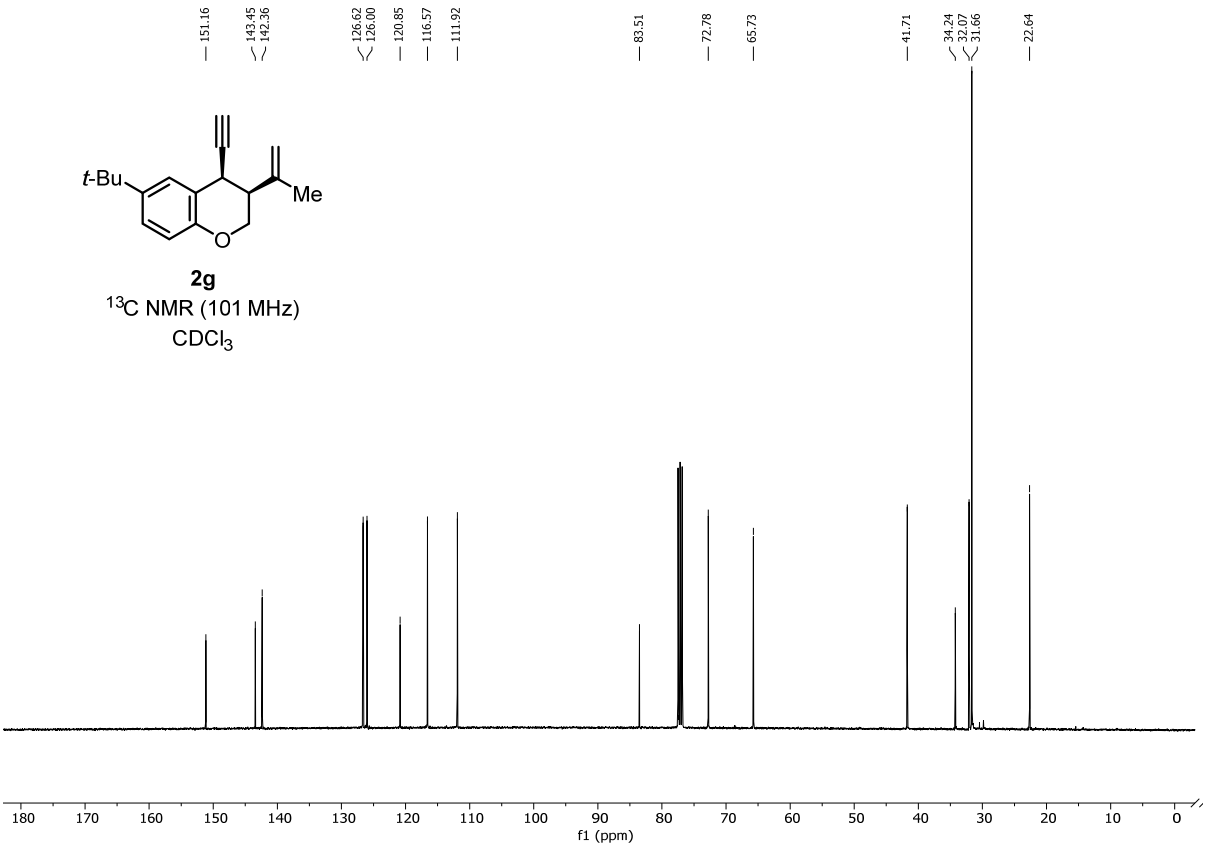




2g

^{1}H NMR (400 MHz)

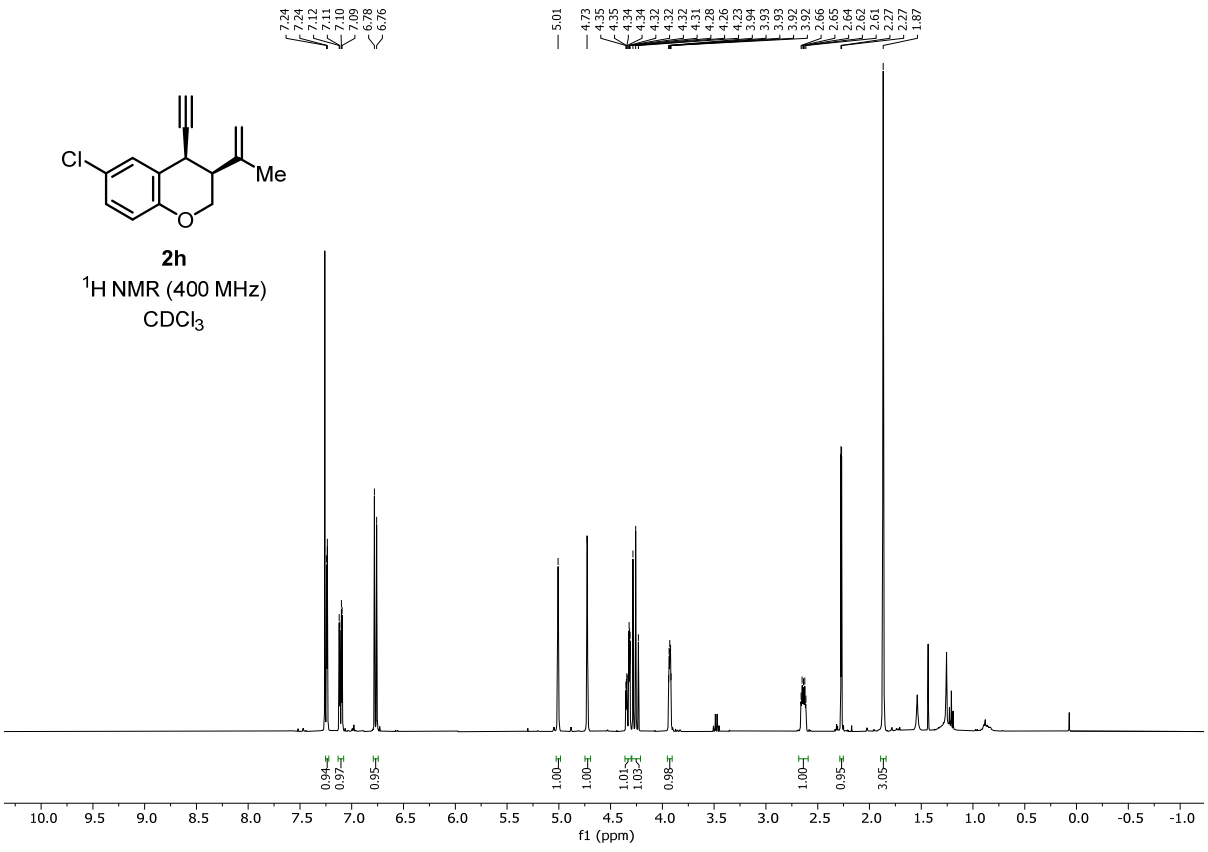
$CDCl_3$

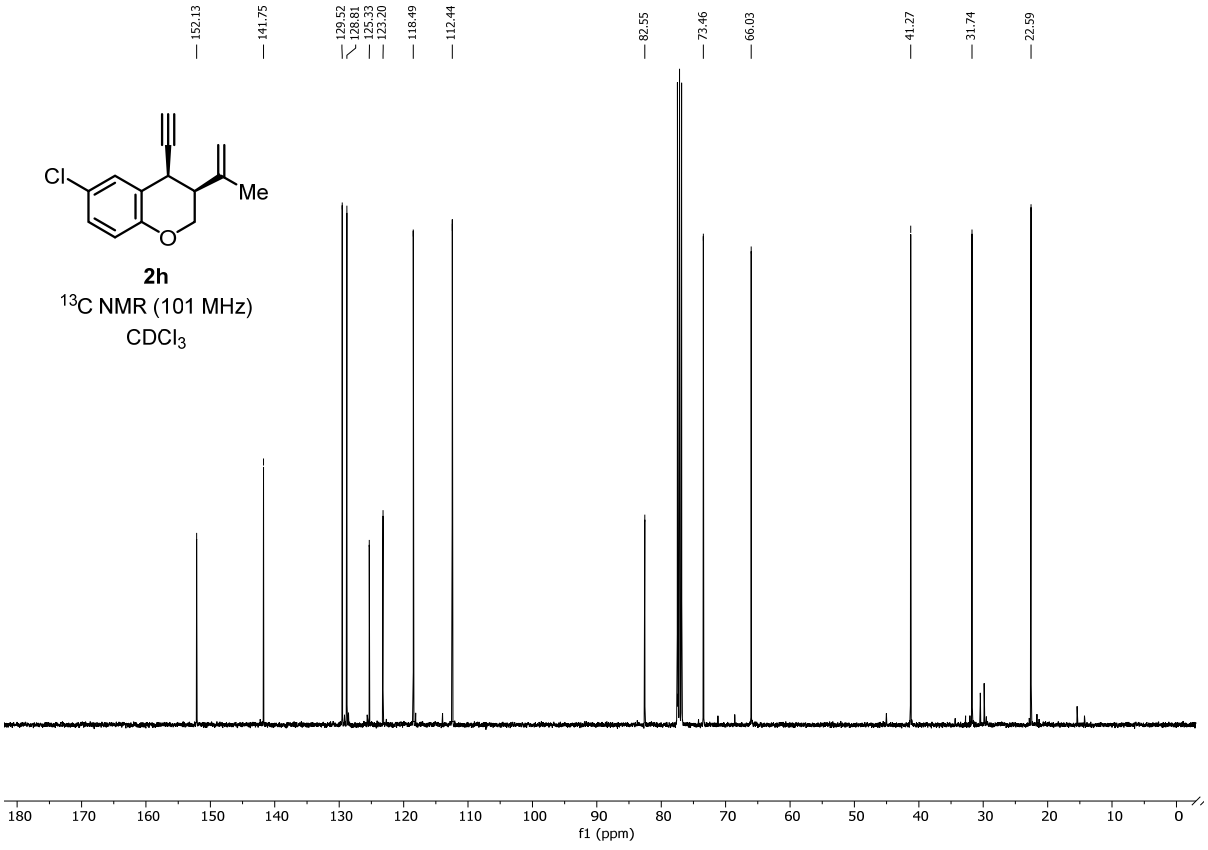


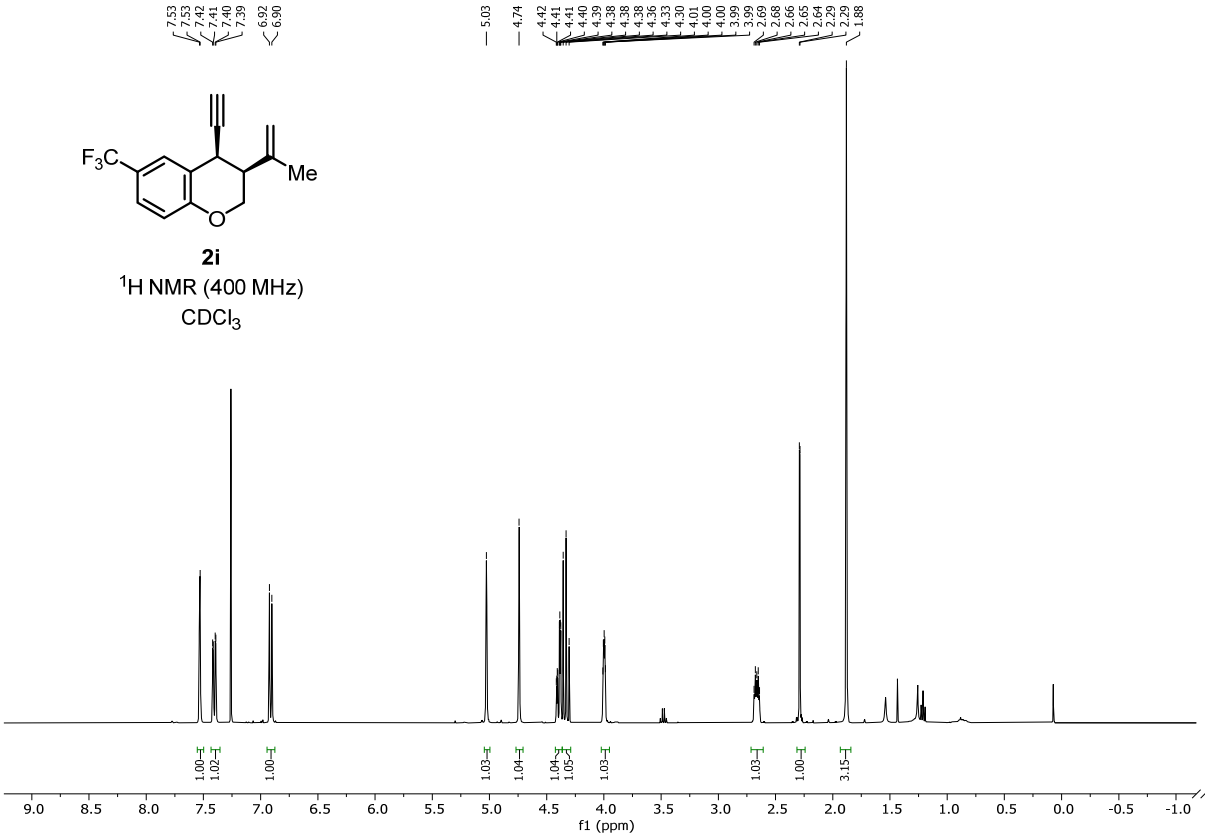
2g

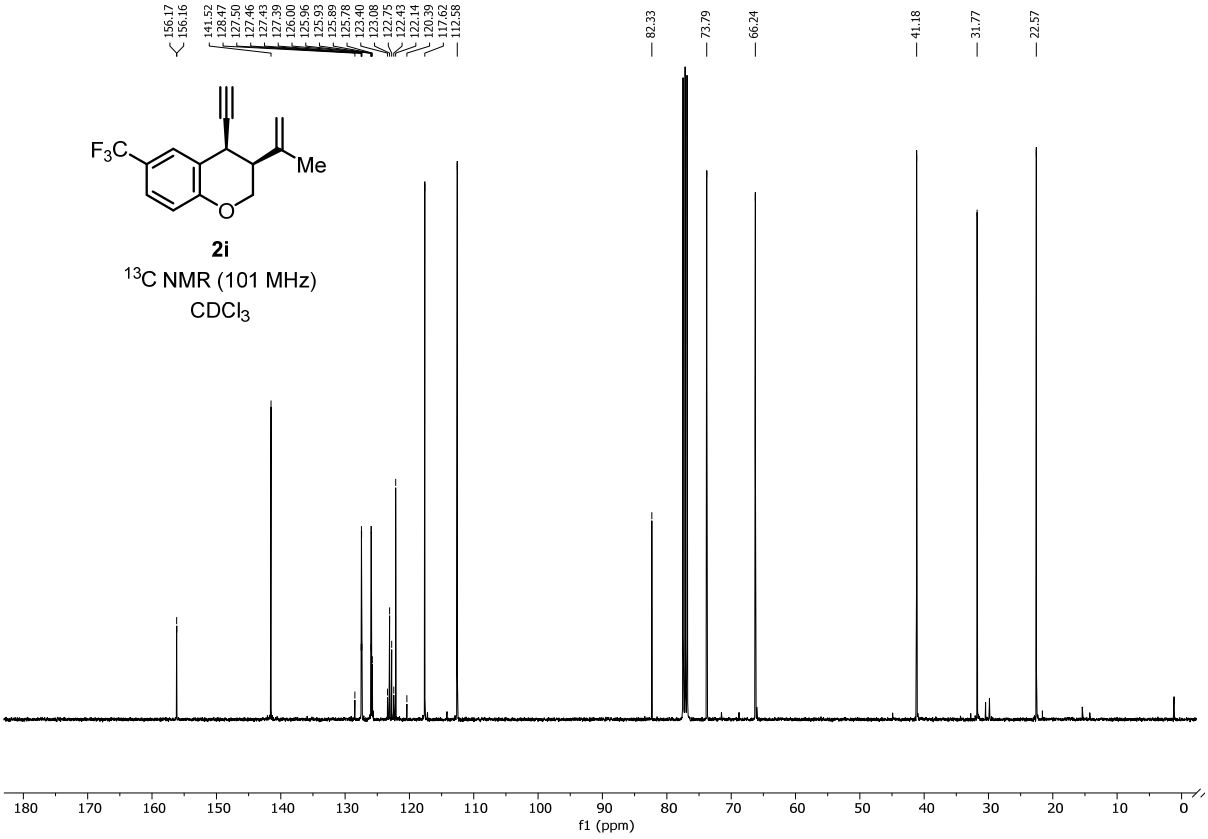
^{13}C NMR (101 MHz)

$CDCl_3$


Cl
Me
O
2h
1H NMR (400 MHz)
CDCl3
f1 (ppm)


Cl
Me
O
2h
13C NMR (101 MHz)
CDCl3
f1 (ppm)

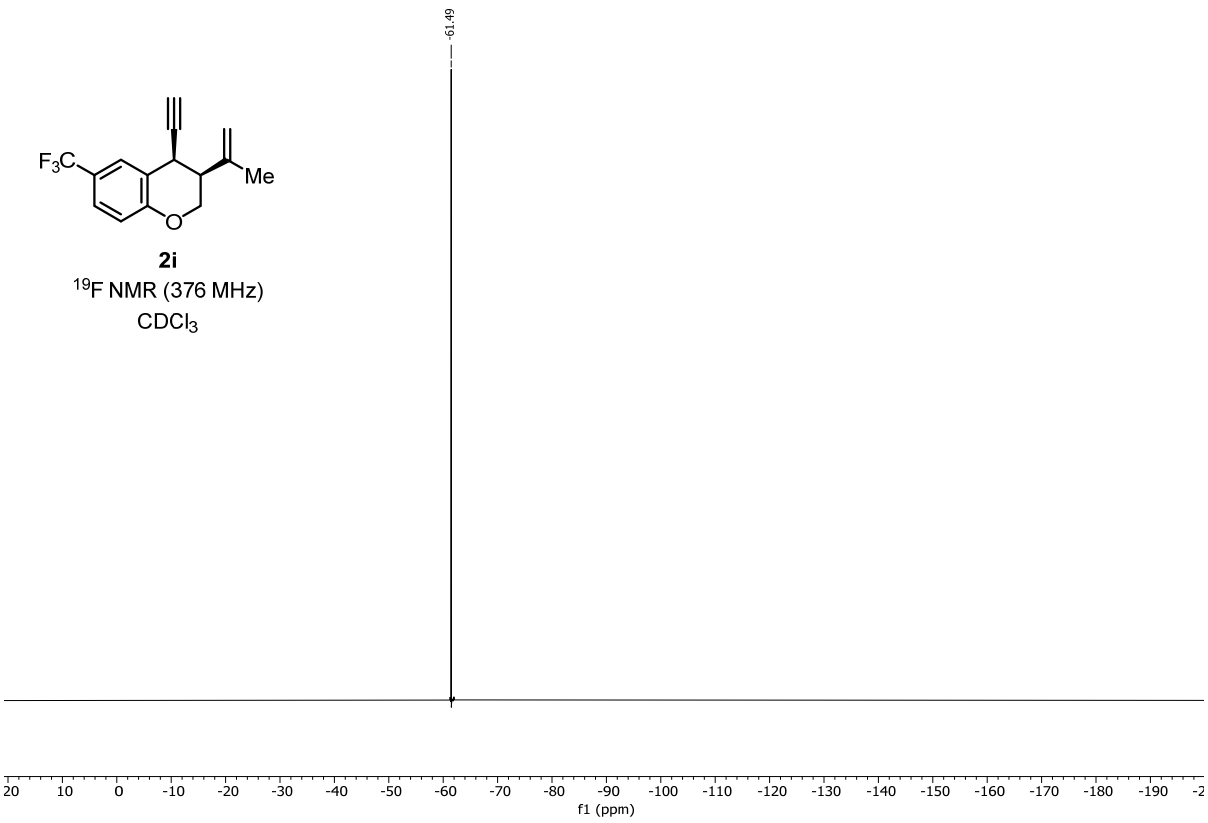

7.53
7.53
7.42
7.41
7.40
7.39
6.92
6.90
5.03
4.74
4.42
4.41
4.41
4.40
4.39
4.38
4.38
4.38
4.36
4.33
4.30
4.01
4.00
4.00
3.99
3.99
2.69
2.68
2.66
2.65
2.64
2.29
2.29
1.88
F3C
Me
O
2i
1H NMR (400 MHz)
CDCl3
1.00
1.02
1.00
1.03
1.04
1.04
1.05
1.03
1.03
1.00
3.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

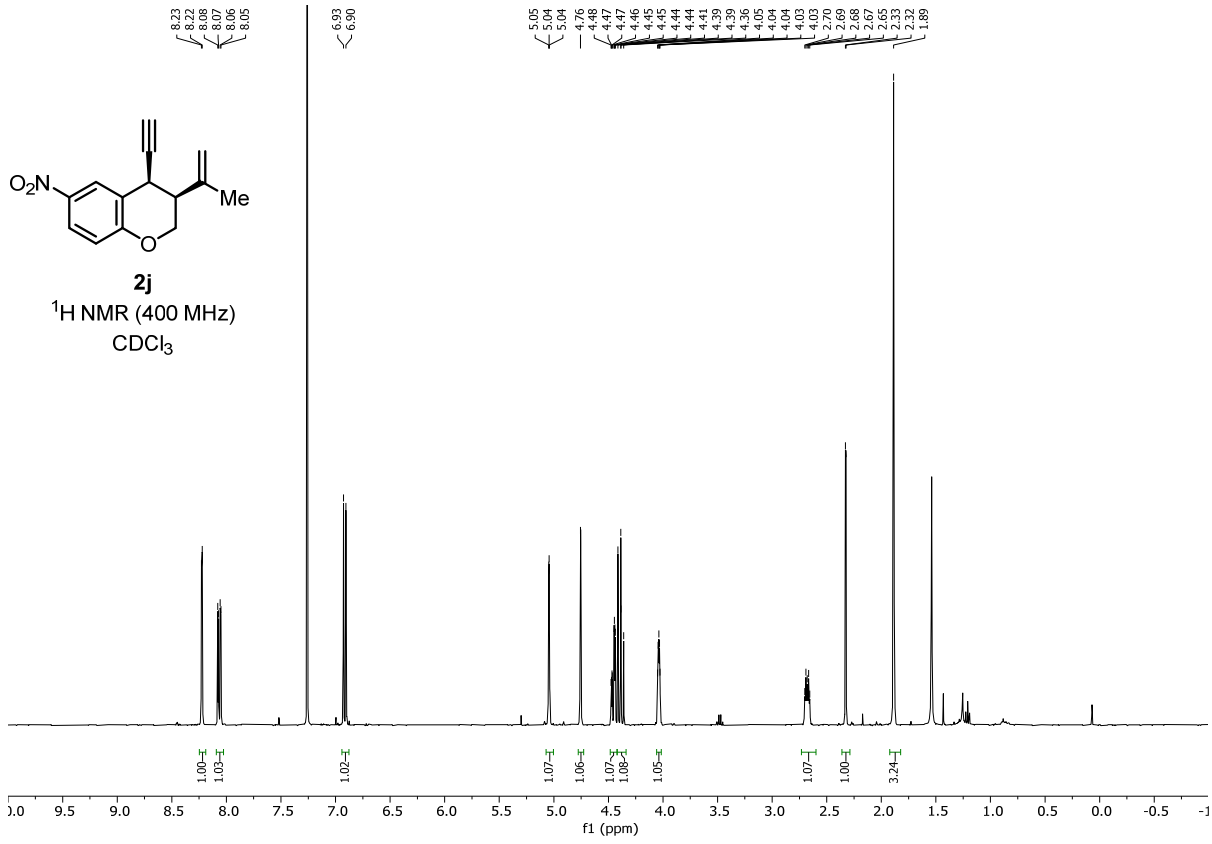

156.17
156.16
141.52
128.47
127.50
127.46
127.43
127.39
126.00
125.96
125.93
125.89
125.78
123.40
123.08
122.75
122.43
122.14
120.39
117.62
112.58
82.33
73.79
66.24
41.18
31.77
22.57
F3C
Me
O
2i
13C NMR (101 MHz)
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

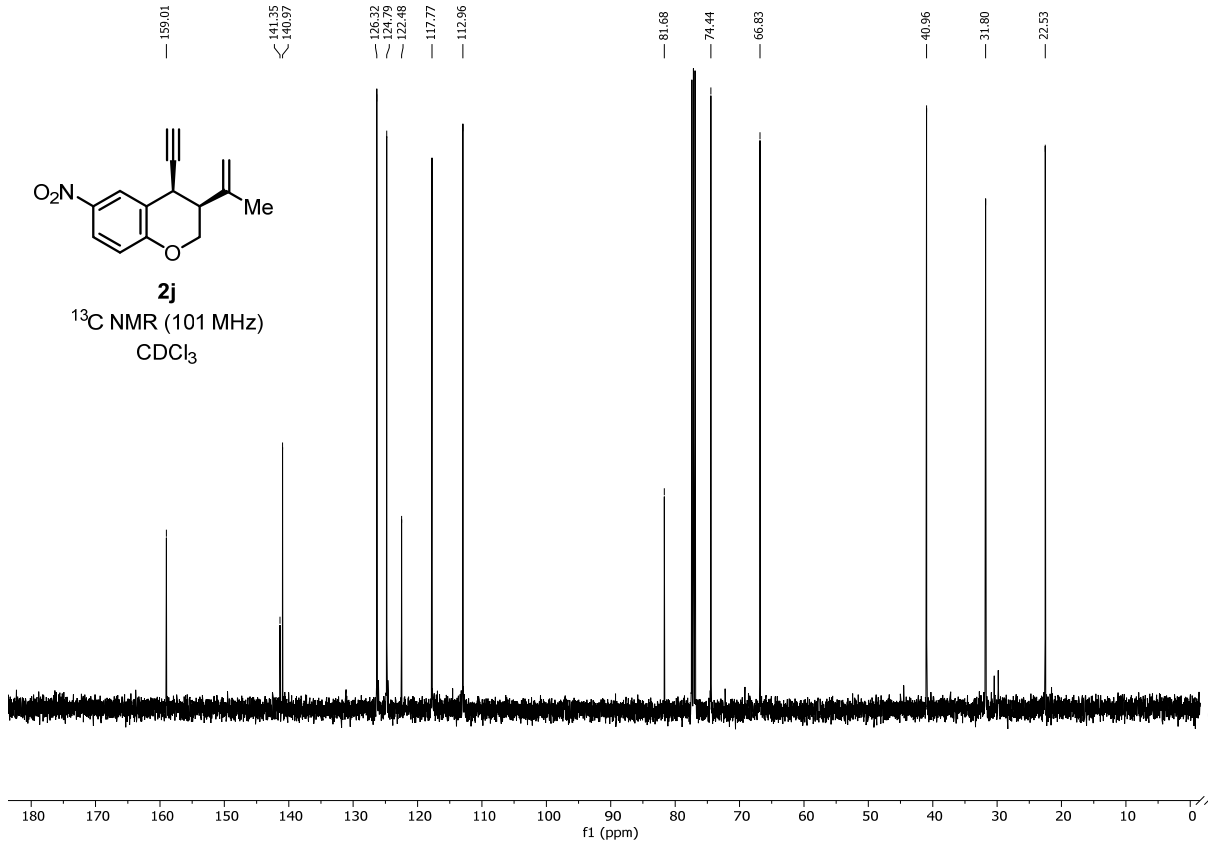
2i

^{19}F NMR (376 MHz)

$CDCl_3$




8.23
8.22
8.08
8.07
8.06
8.05
6.93
6.90
5.05
5.04
5.04
4.76
4.48
4.47
4.47
4.46
4.45
4.45
4.44
4.44
4.41
4.39
4.39
4.36
4.05
4.04
4.04
4.03
4.03
2.70
2.69
2.68
2.67
2.65
2.33
2.32
1.89
O2N
Me
O
2j
1H NMR (400 MHz)
CDCl3
1.00
1.03
1.02
1.07
1.06
1.07
1.08
1.05
1.07
1.00
3.24
f1 (ppm)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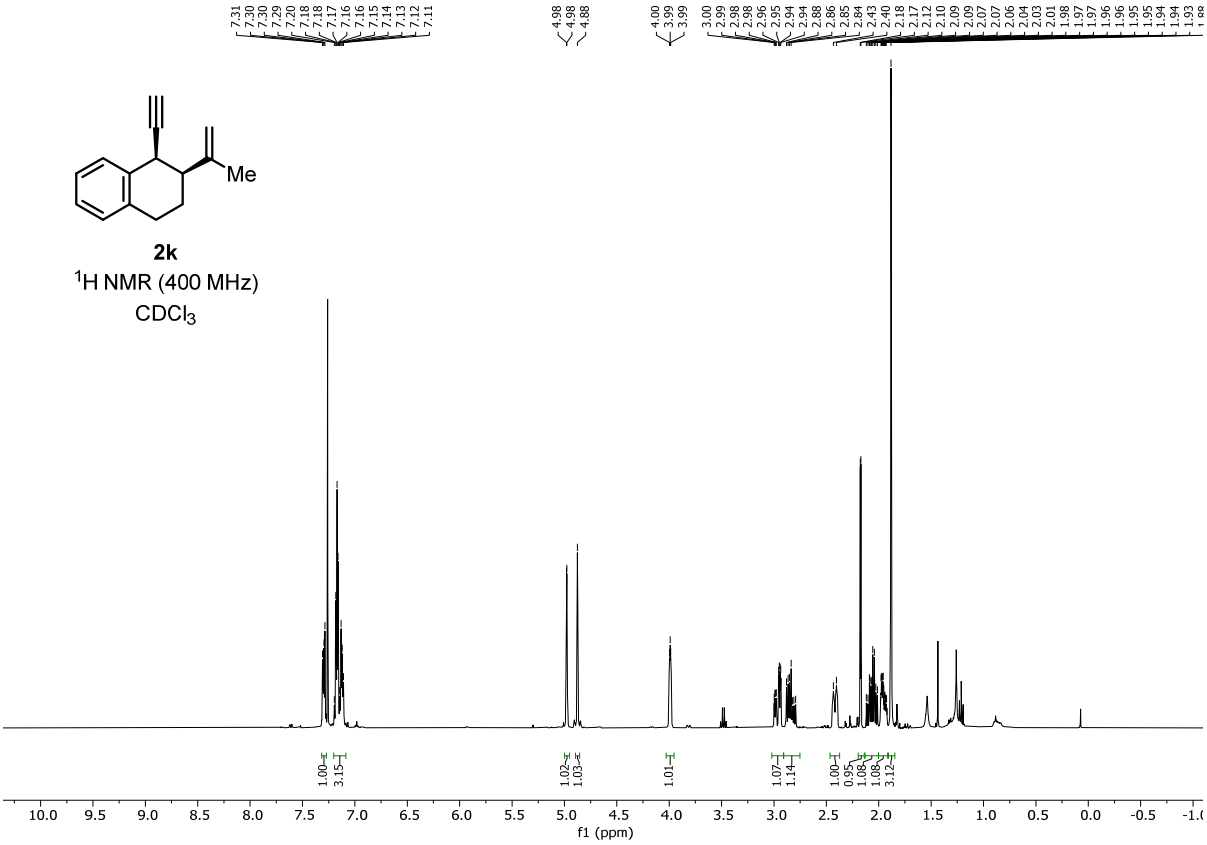
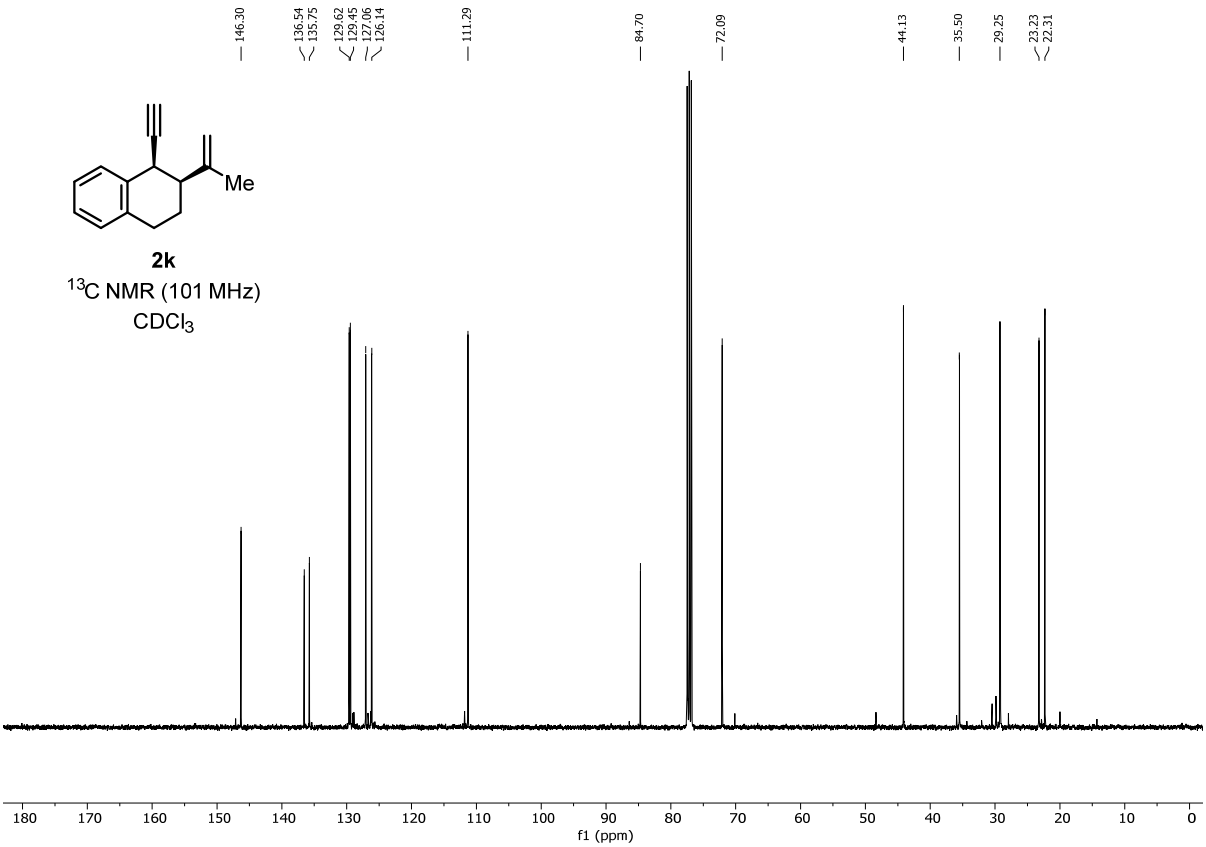
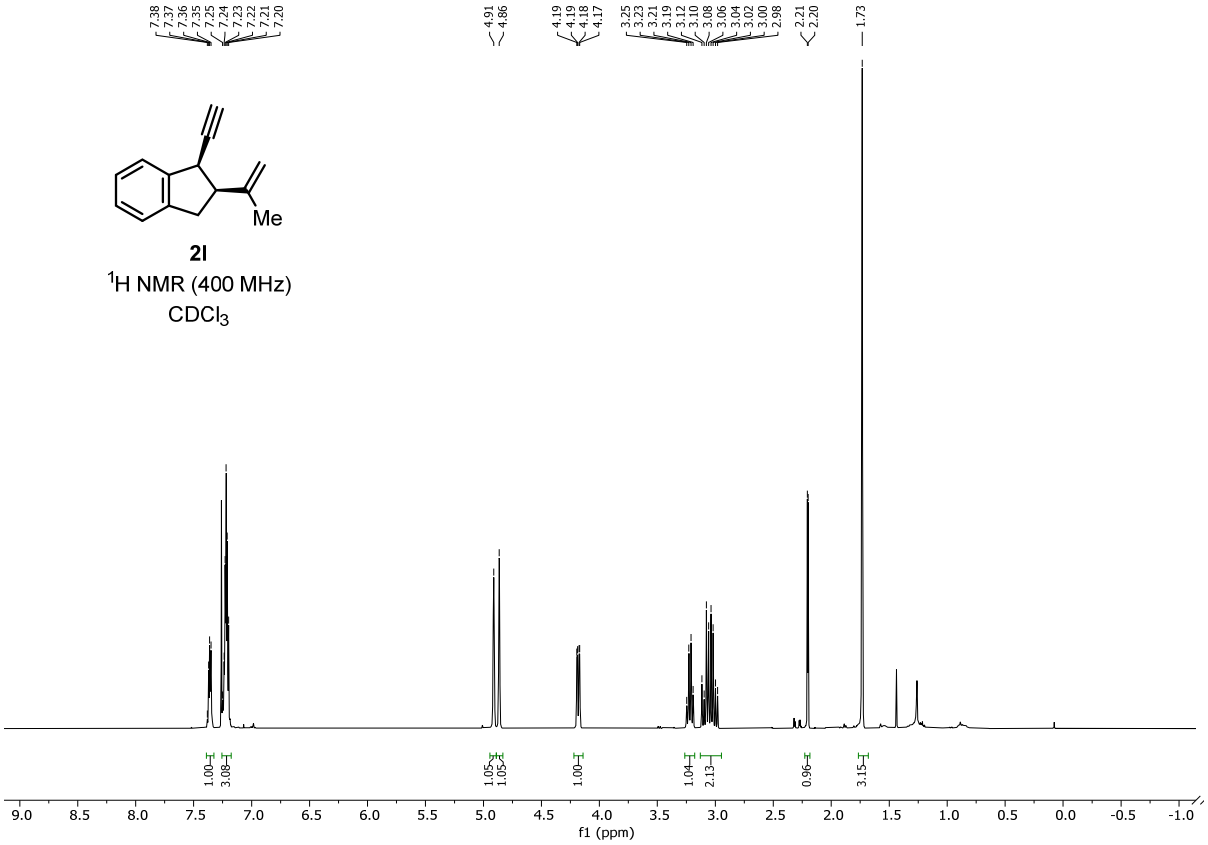
141.35
140.97
126.32
124.79
122.48
117.77
112.96
81.68
74.44
66.83
40.96
31.80
22.53
O2N
Me
O
2j
13C NMR (101 MHz)
CDCl3
f1 (ppm)


Me
2k
1H NMR (400 MHz)
CDCl3
f1 (ppm)


Me
2k
13C NMR (101 MHz)
CDCl3
f1 (ppm)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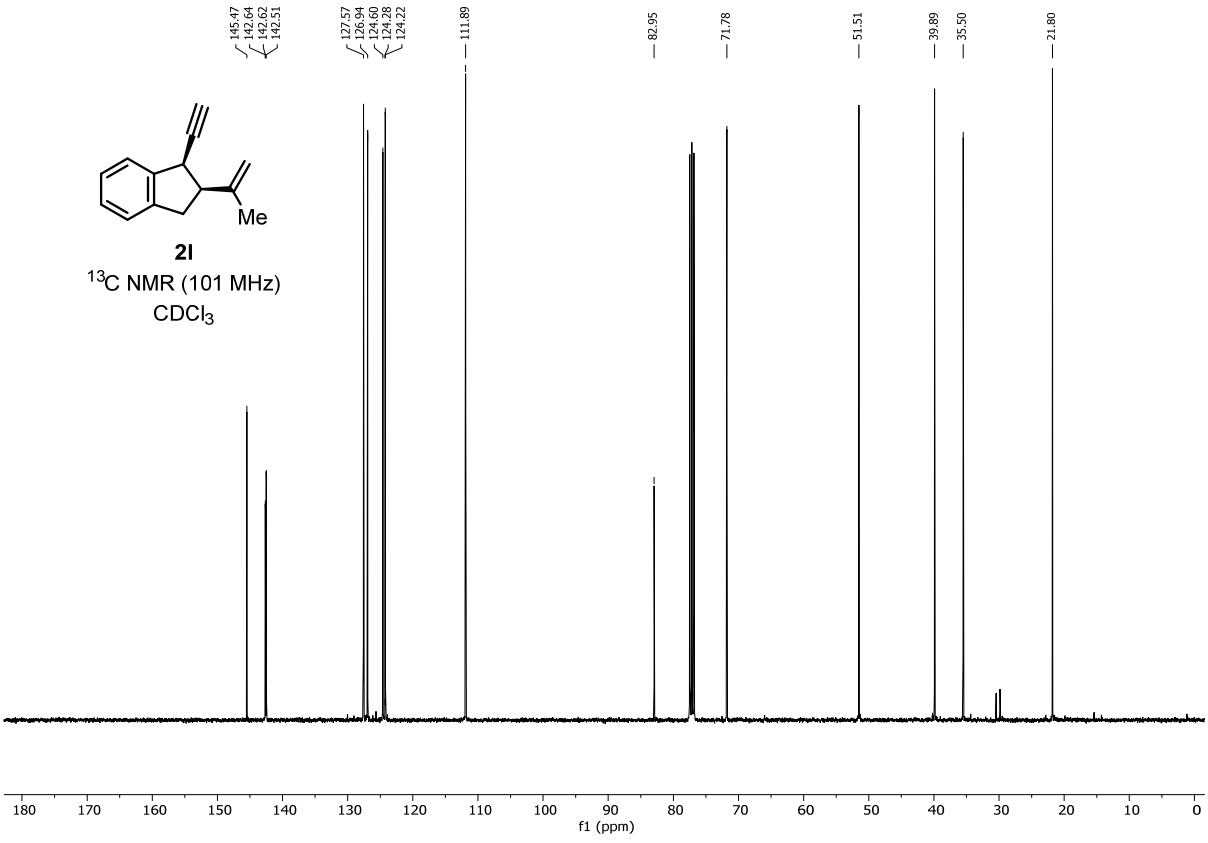
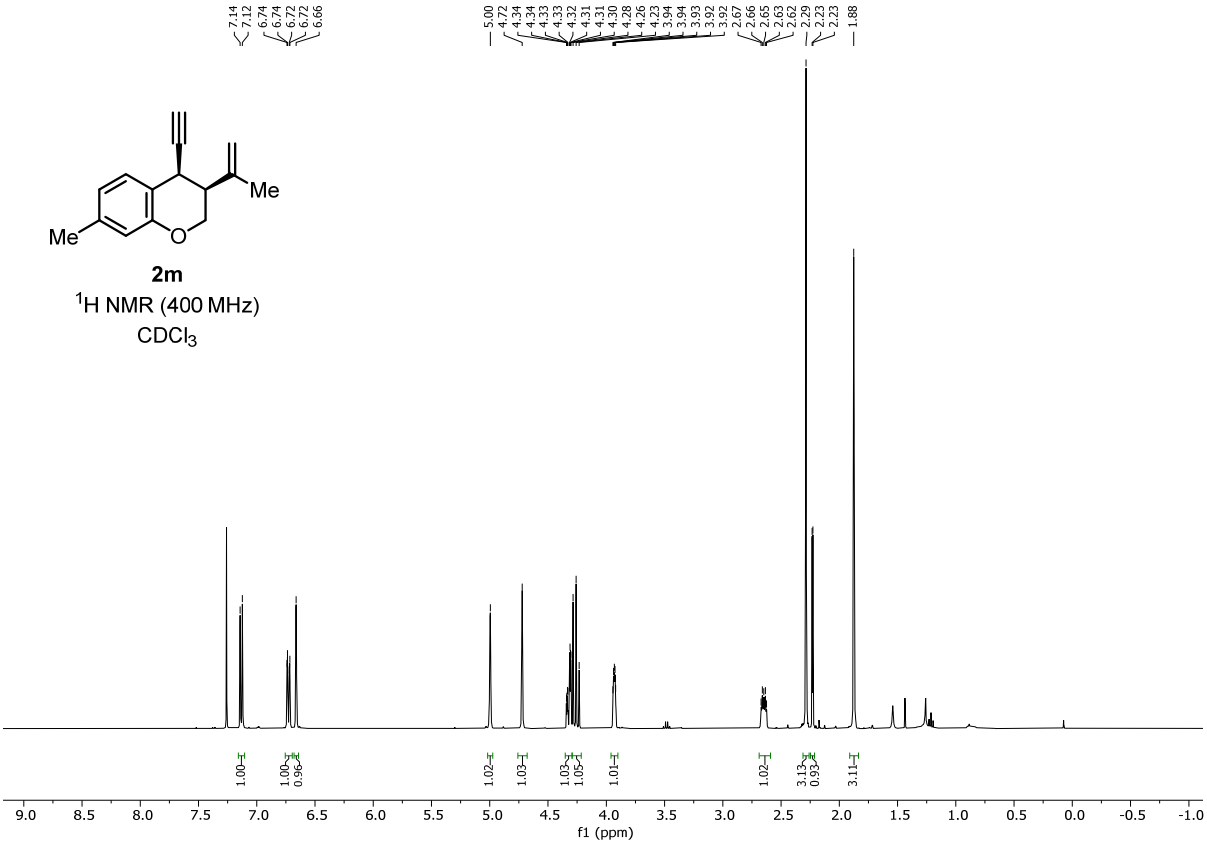
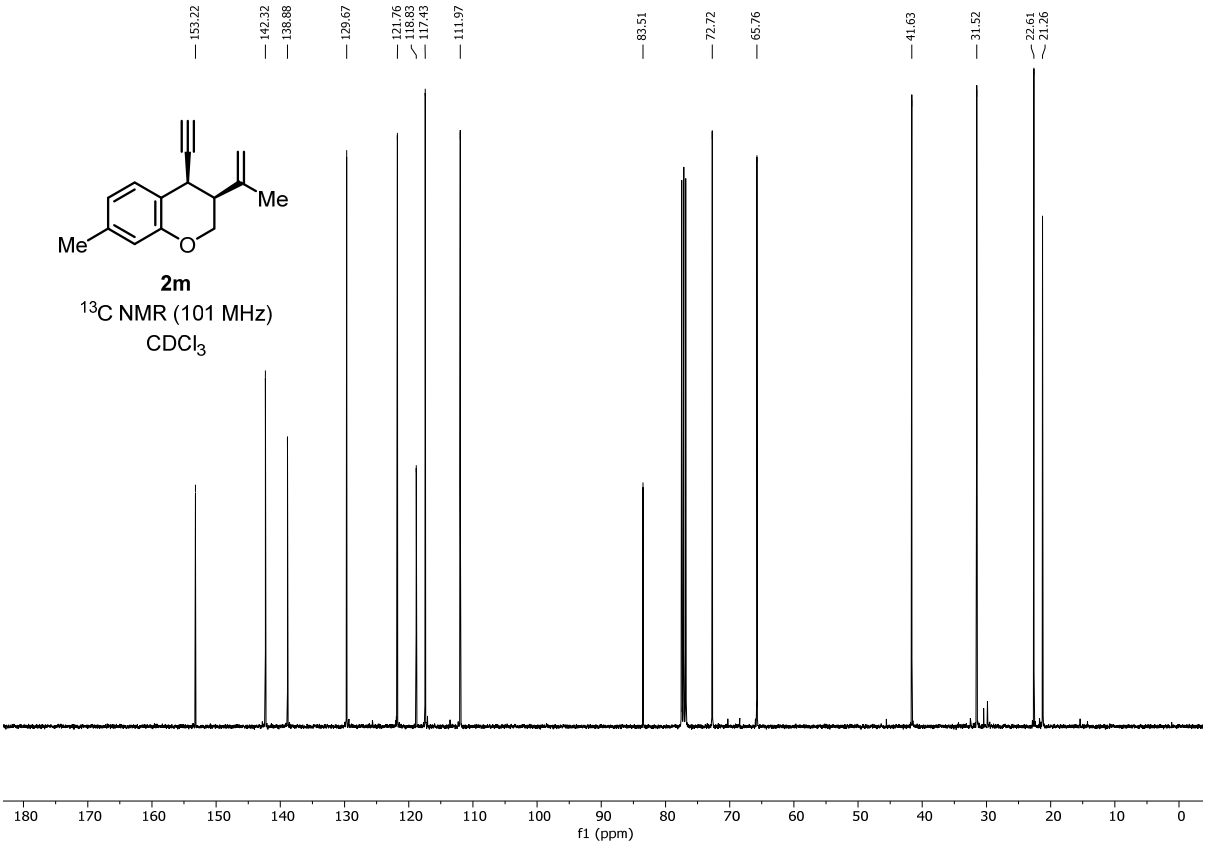
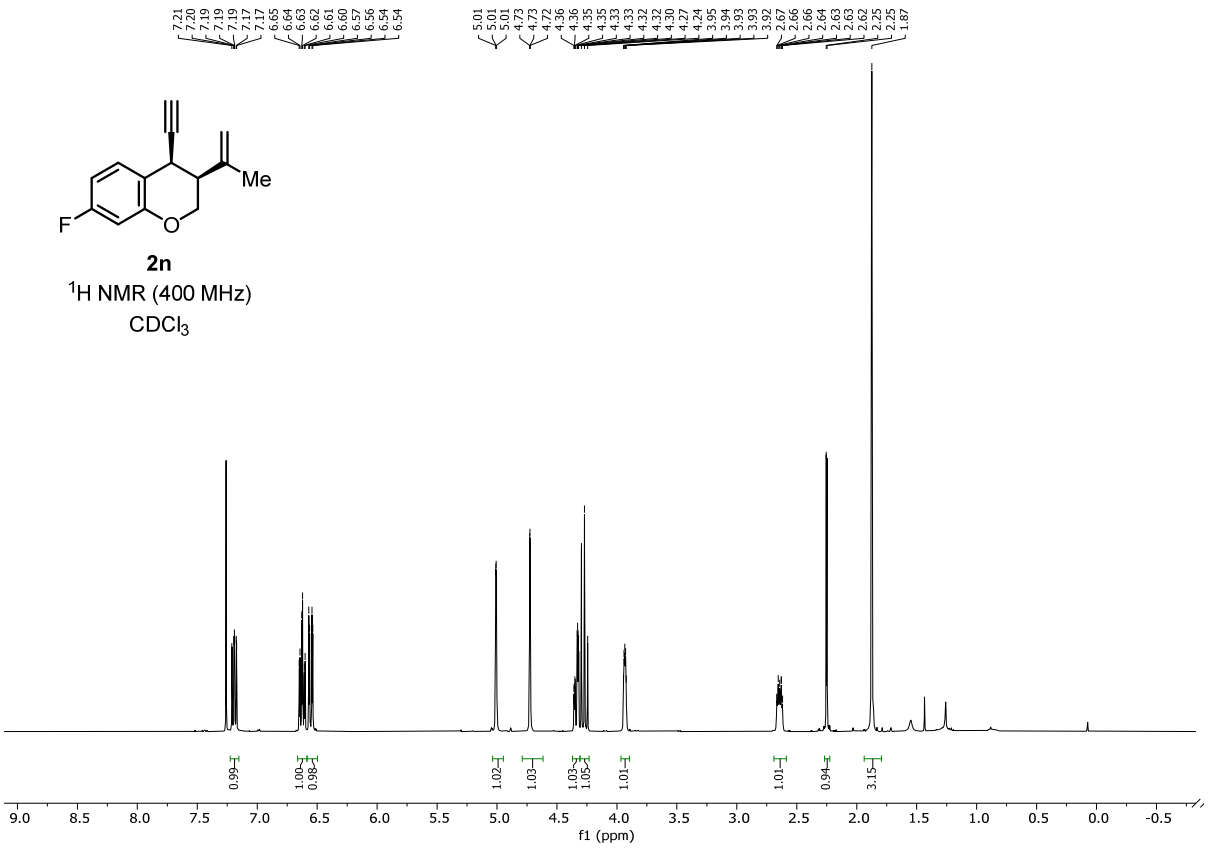
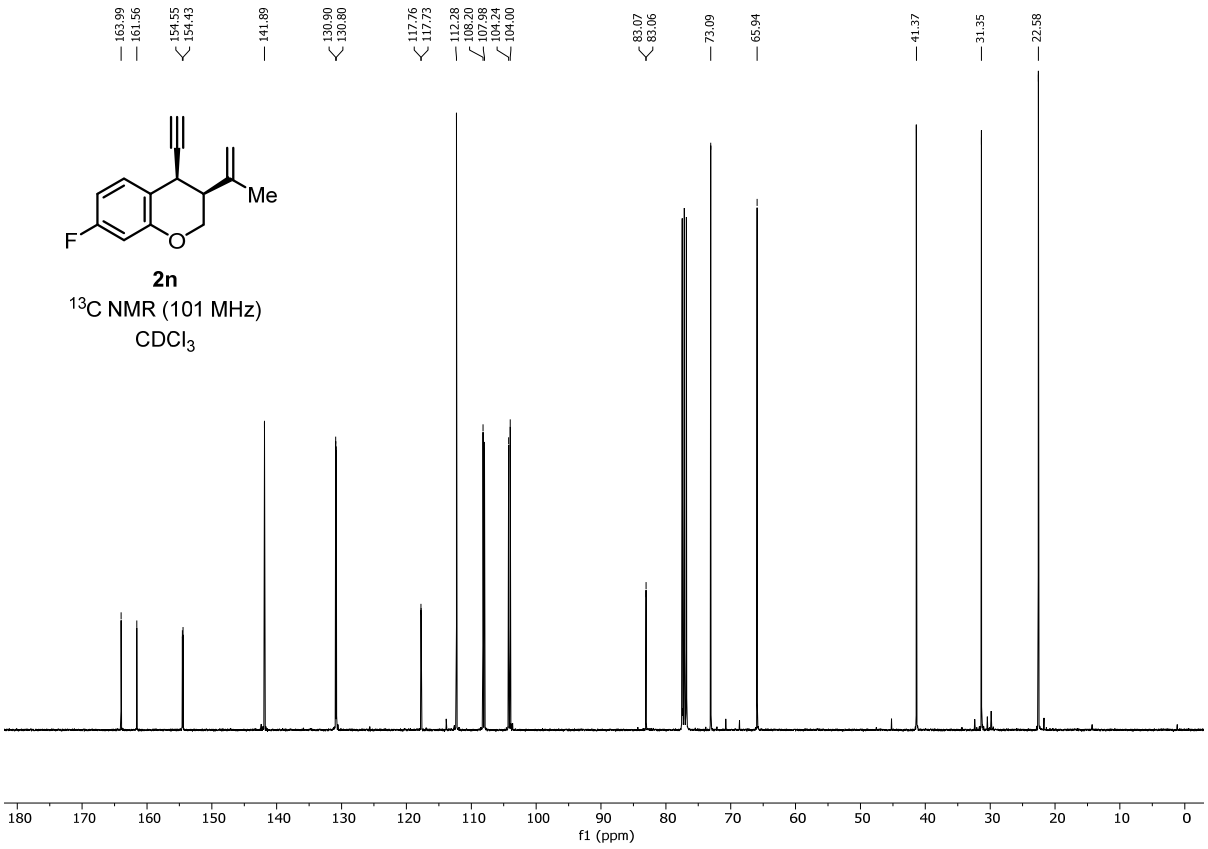
7.37
7.36
7.35
7.25
7.24
7.23
7.22
7.21
7.20
4.91
4.86
4.19
4.19
4.18
4.17
3.25
3.23
3.21
3.19
3.12
3.10
3.08
3.06
3.04
3.02
3.00
2.98
2.21
2.20
1.73
Me
2l
^{1}H NMR (400 MHz)
$CDCl_3$
1.00
3.08
1.05
1.05
1.00
1.04
2.13
0.96
3.15
f1 (ppm)


145.47
142.64
142.62
142.51
127.57
126.94
124.60
124.28
124.22
111.89
82.95
71.78
51.51
39.89
35.50
21.80
Me
2l
^{13}C NMR (101 MHz)
$CDCl_3$
f1 (ppm)


Me
Me
O
2m
1H NMR (400 MHz)
CDCl3
f1 (ppm)


Me
Me
O
2m
13C NMR (101 MHz)
CDCl3
f1 (ppm)

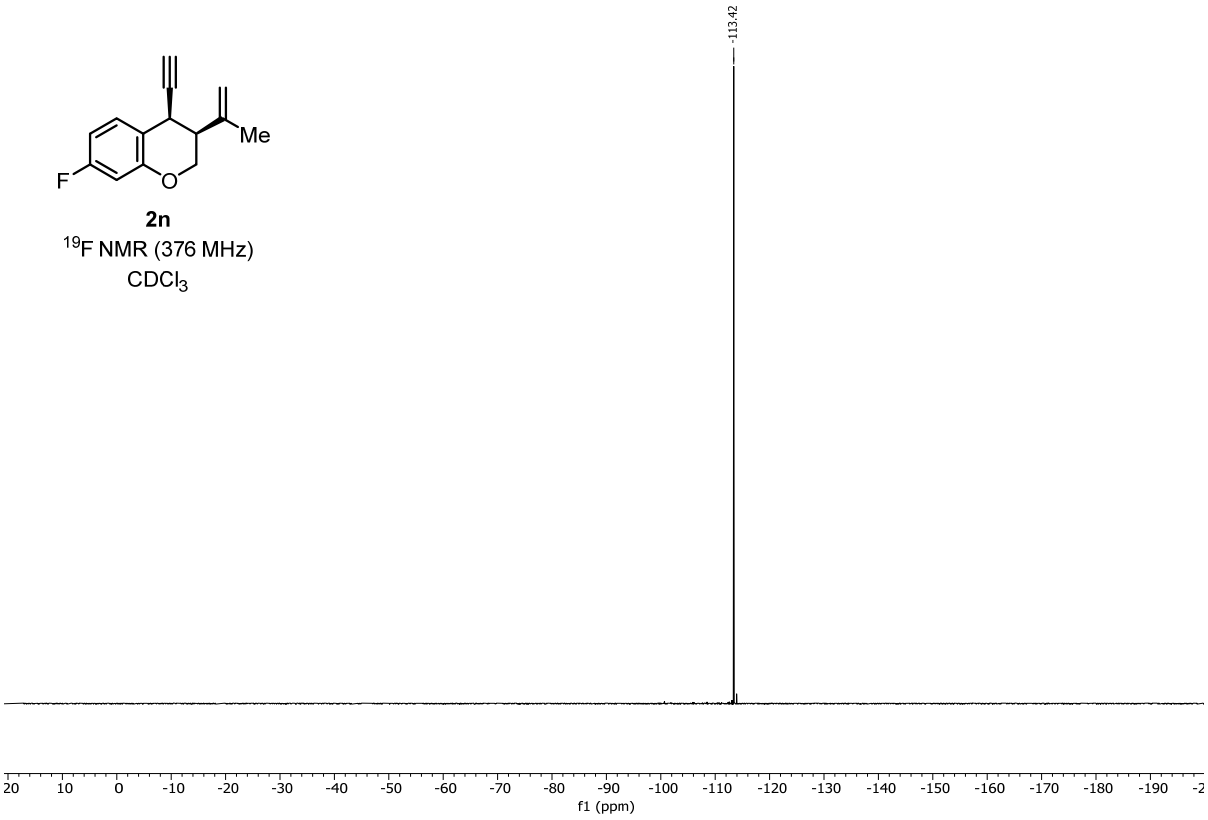

Me
F
O
2n
1H NMR (400 MHz)
CDCl3
f1 (ppm)

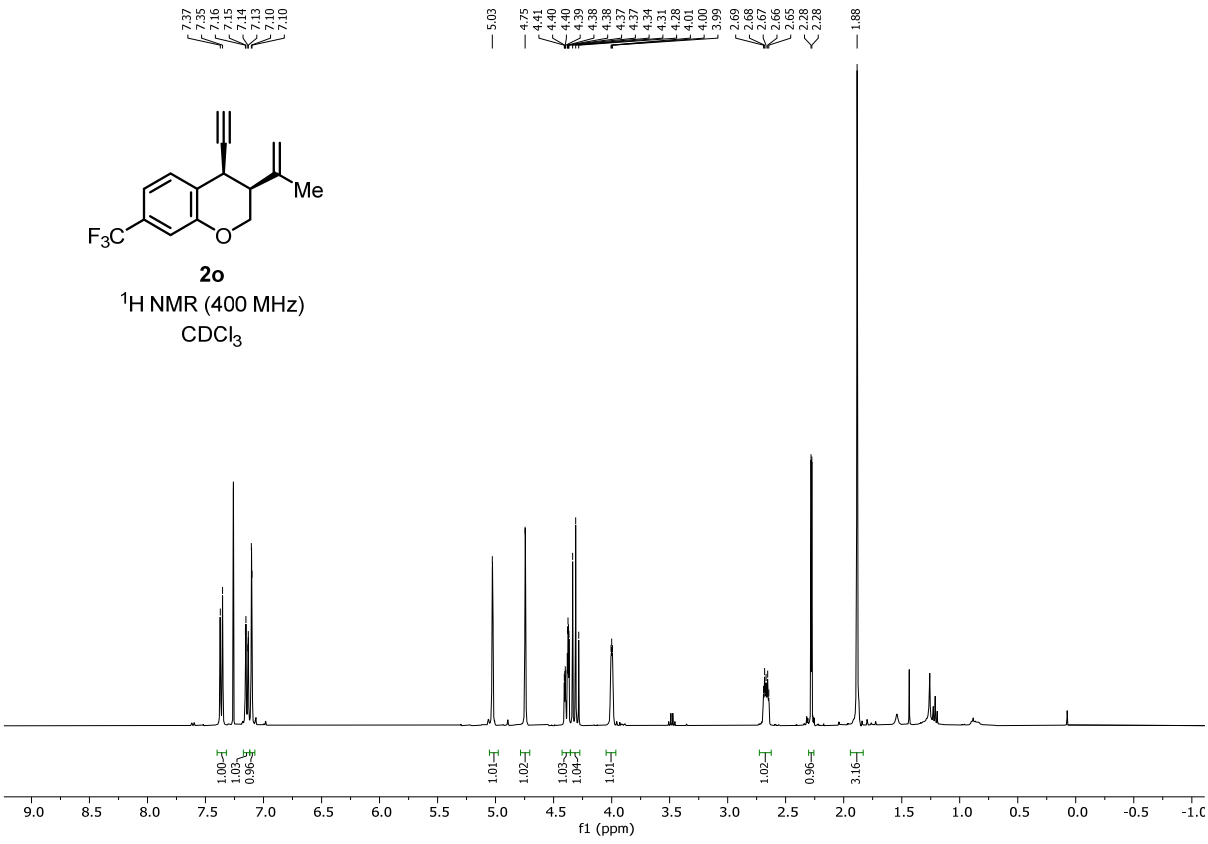

Me
F
O
2n
13C NMR (101 MHz)
CDCl3
f1 (ppm)

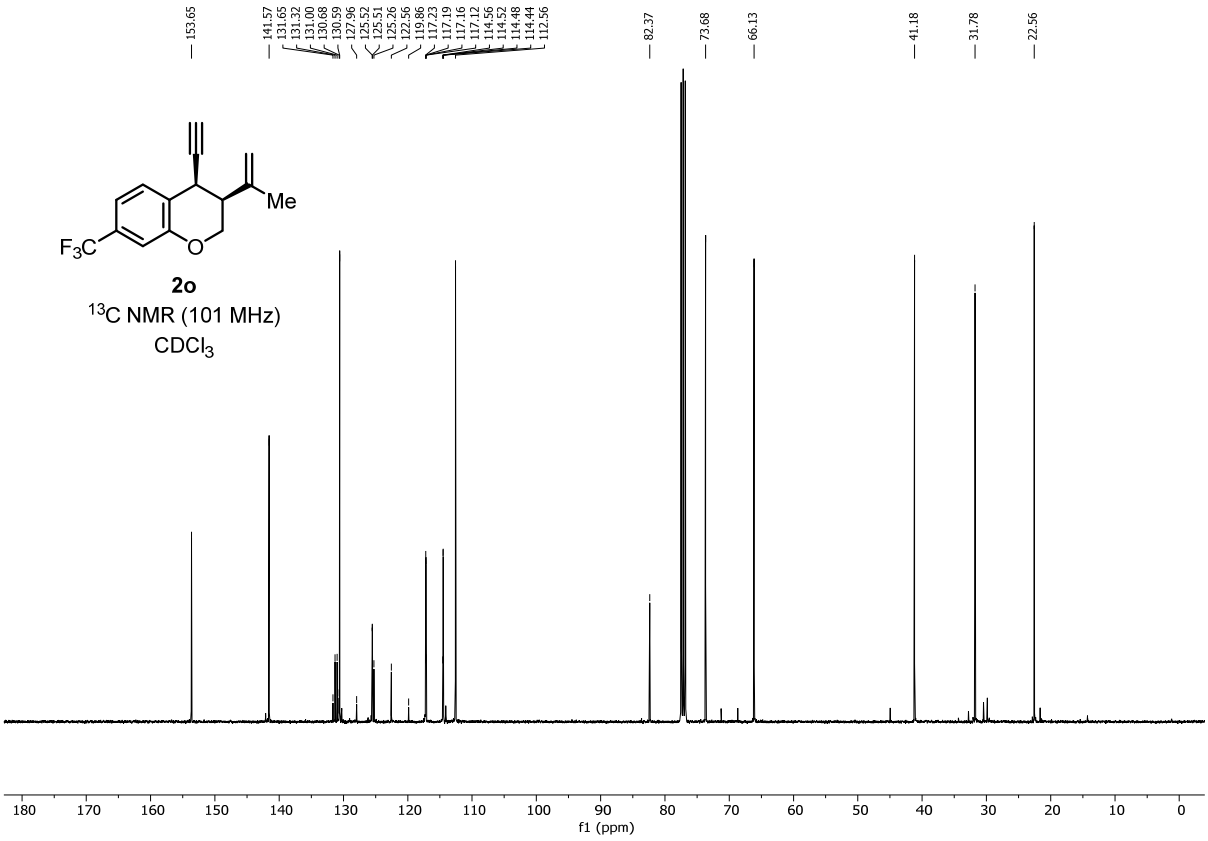
2n

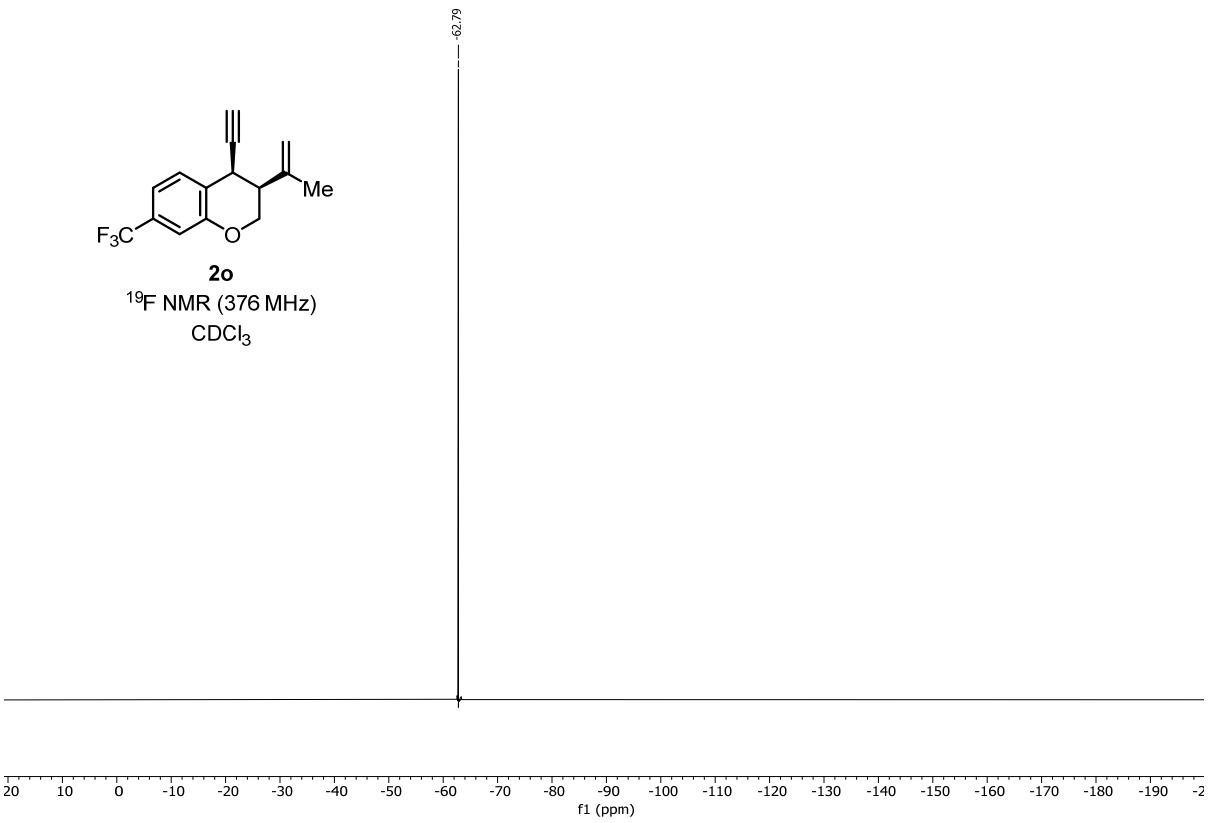
^{19}F NMR (376 MHz)

$CDCl_3$




Me
F3C
O
2o
1H NMR (400 MHz)
CDCl3
f1 (ppm)

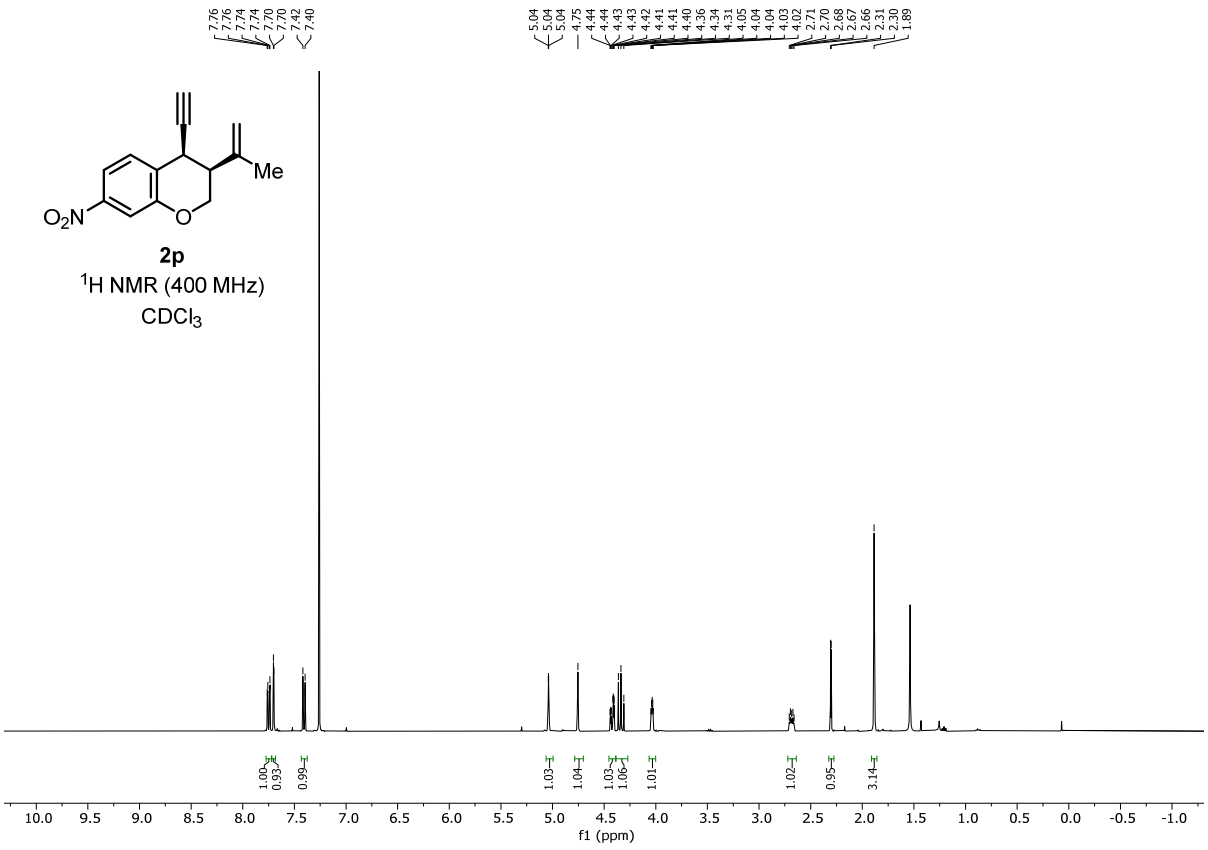

Me
F3C
O
2o
13C NMR (101 MHz)
CDCl3
f1 (ppm)

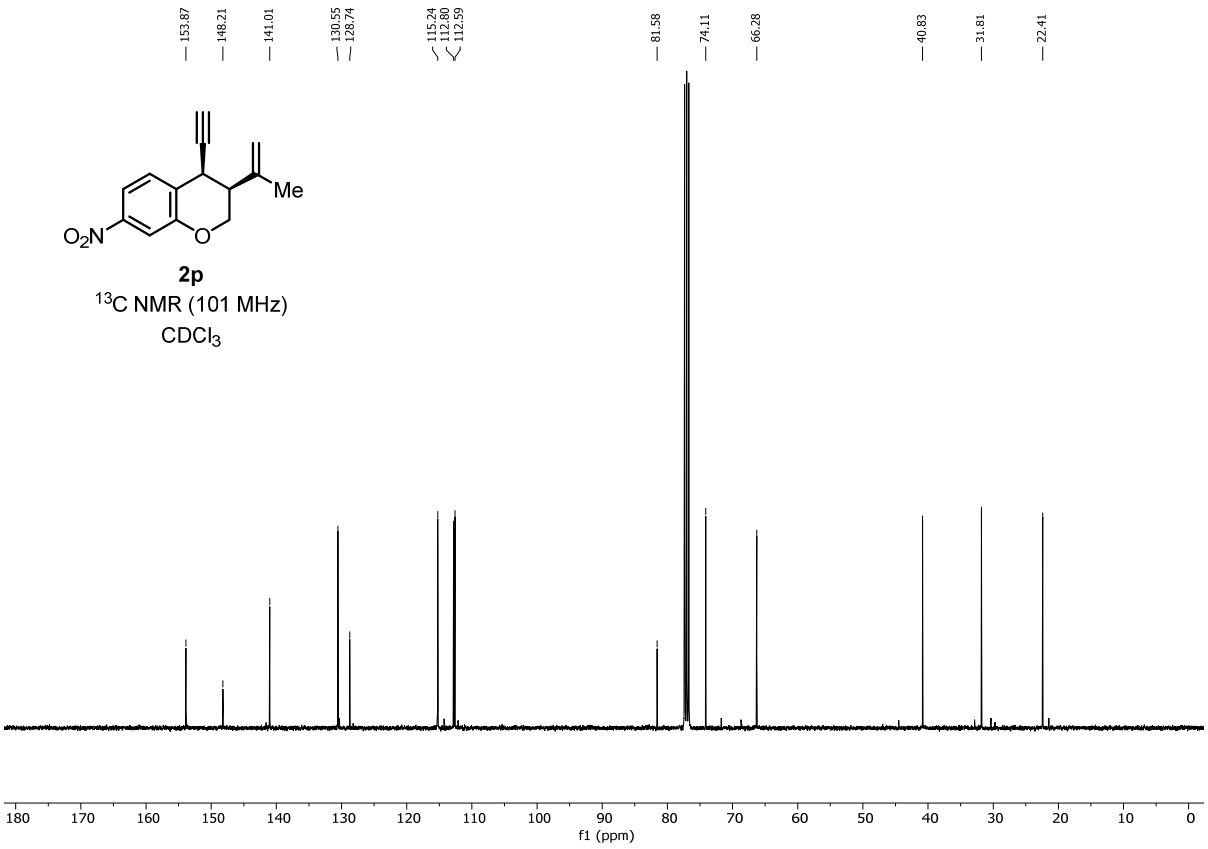


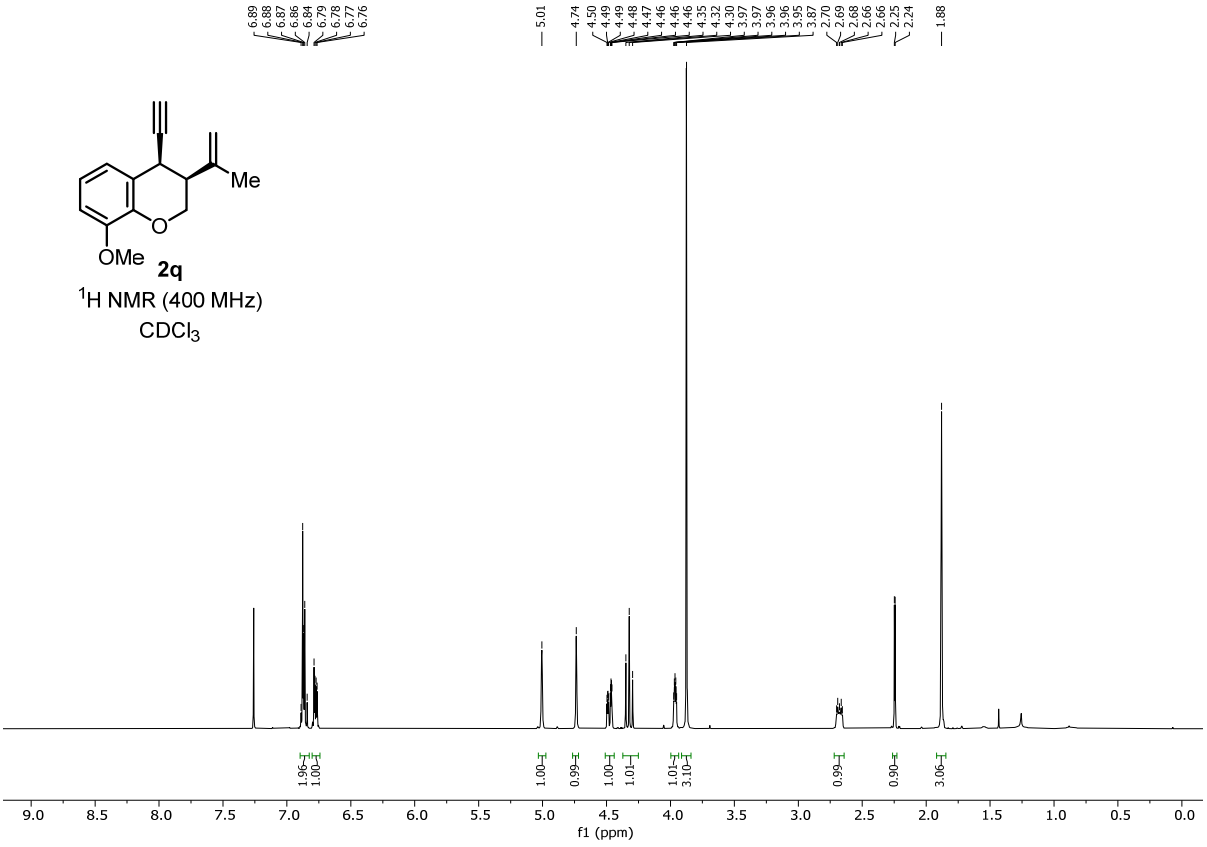
2o

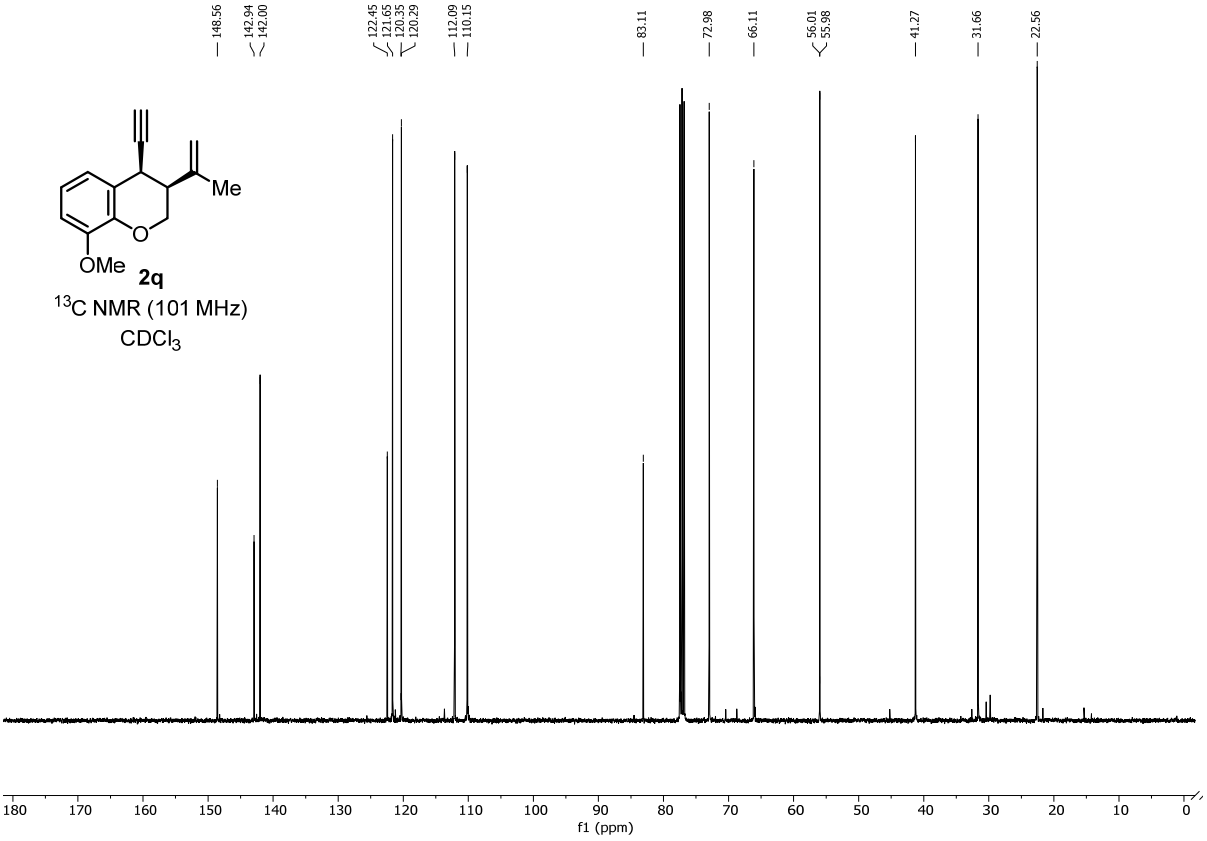
^{19}F NMR (376 MHz)

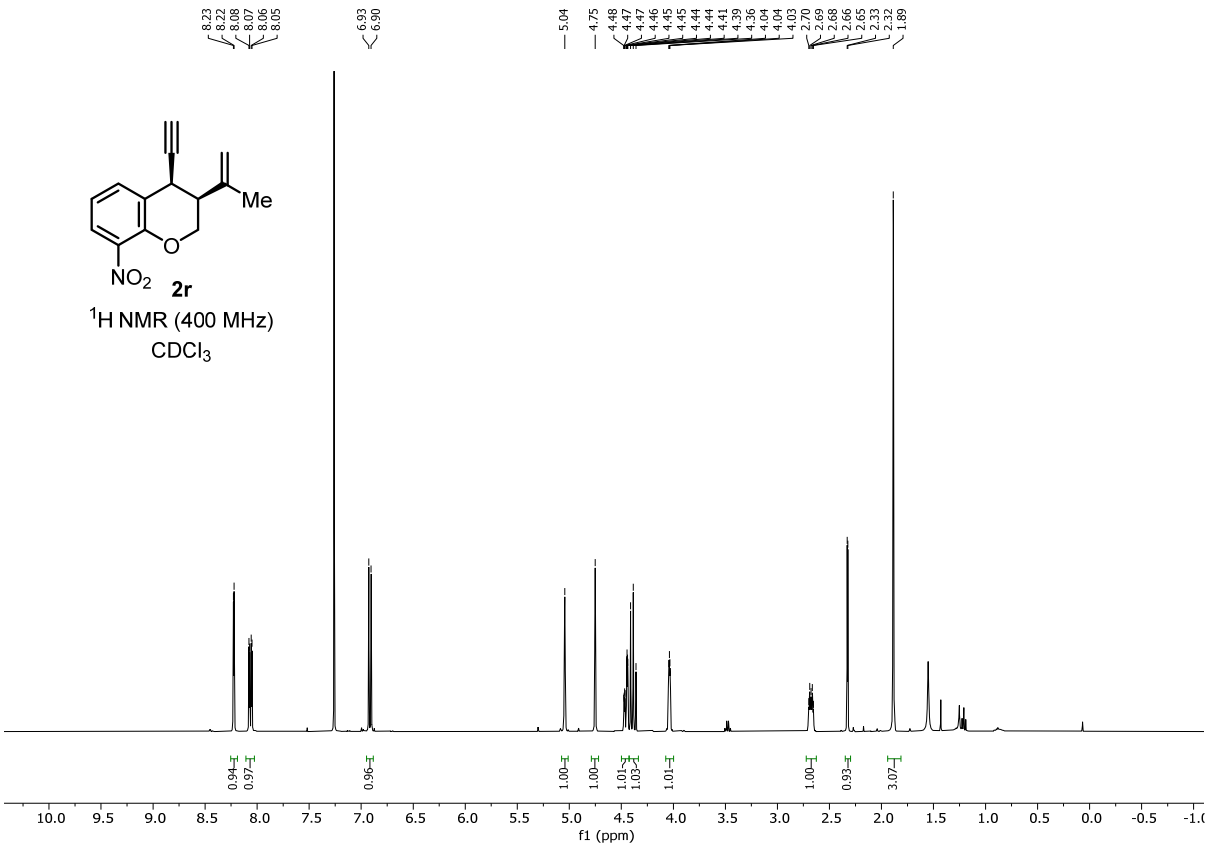
$CDCl_3$

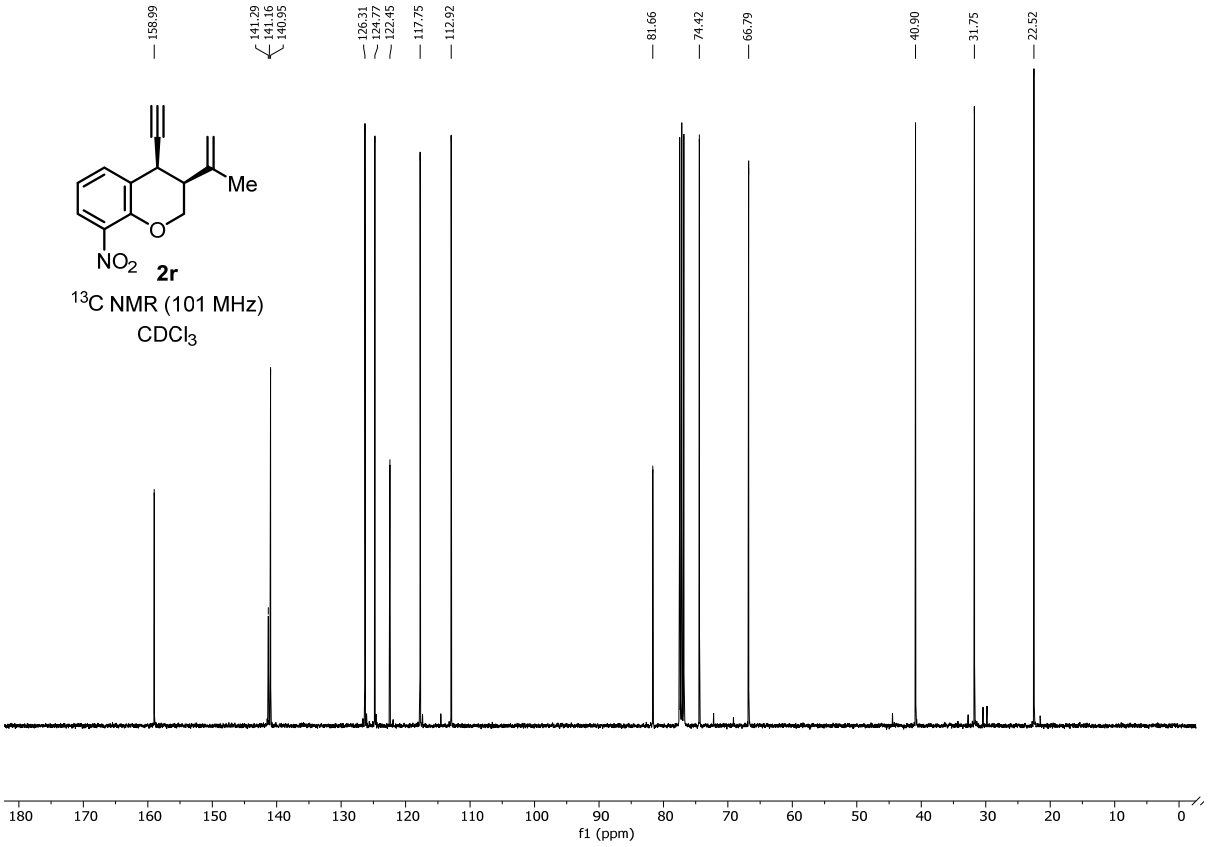

Me
O2N
O
2p
1H NMR (400 MHz)
CDCl3
f1 (ppm)

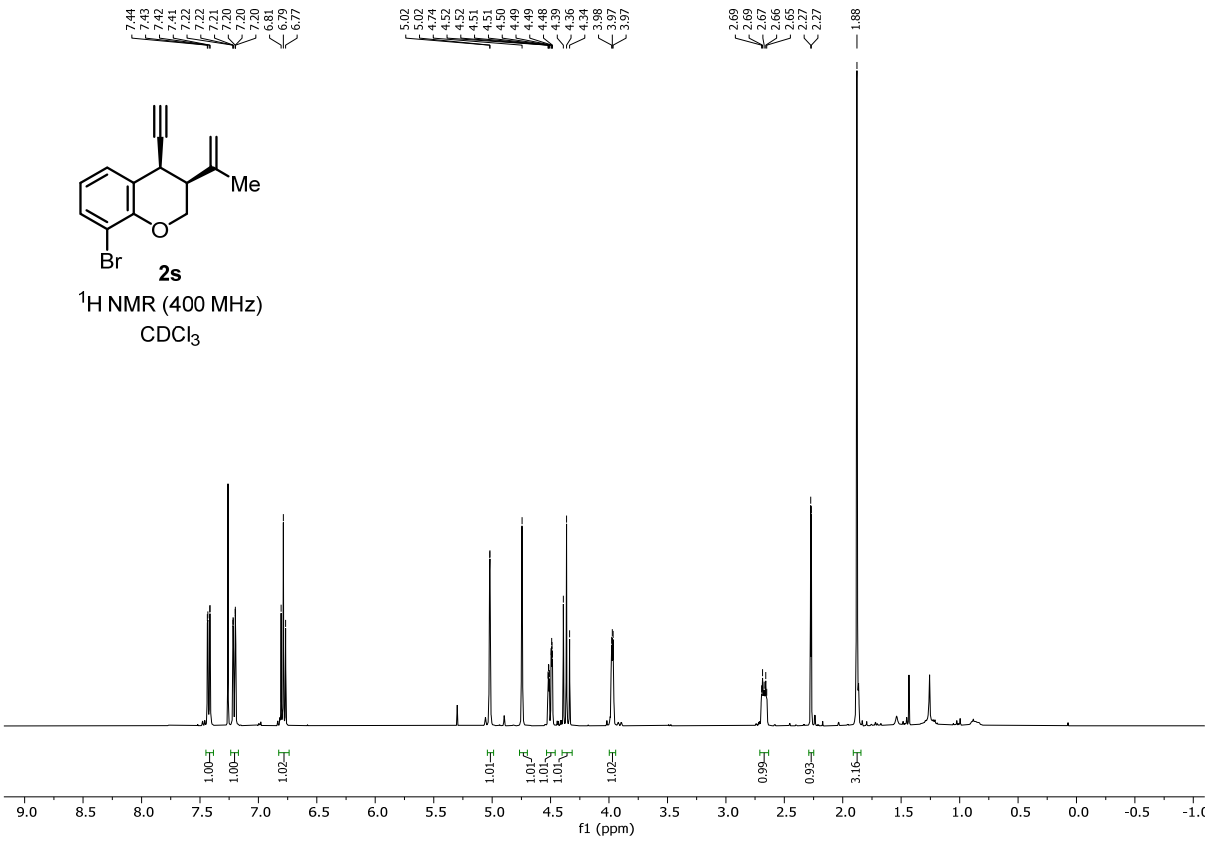

Me
O2N
O
2p
13C NMR (101 MHz)
CDCl3
f1 (ppm)

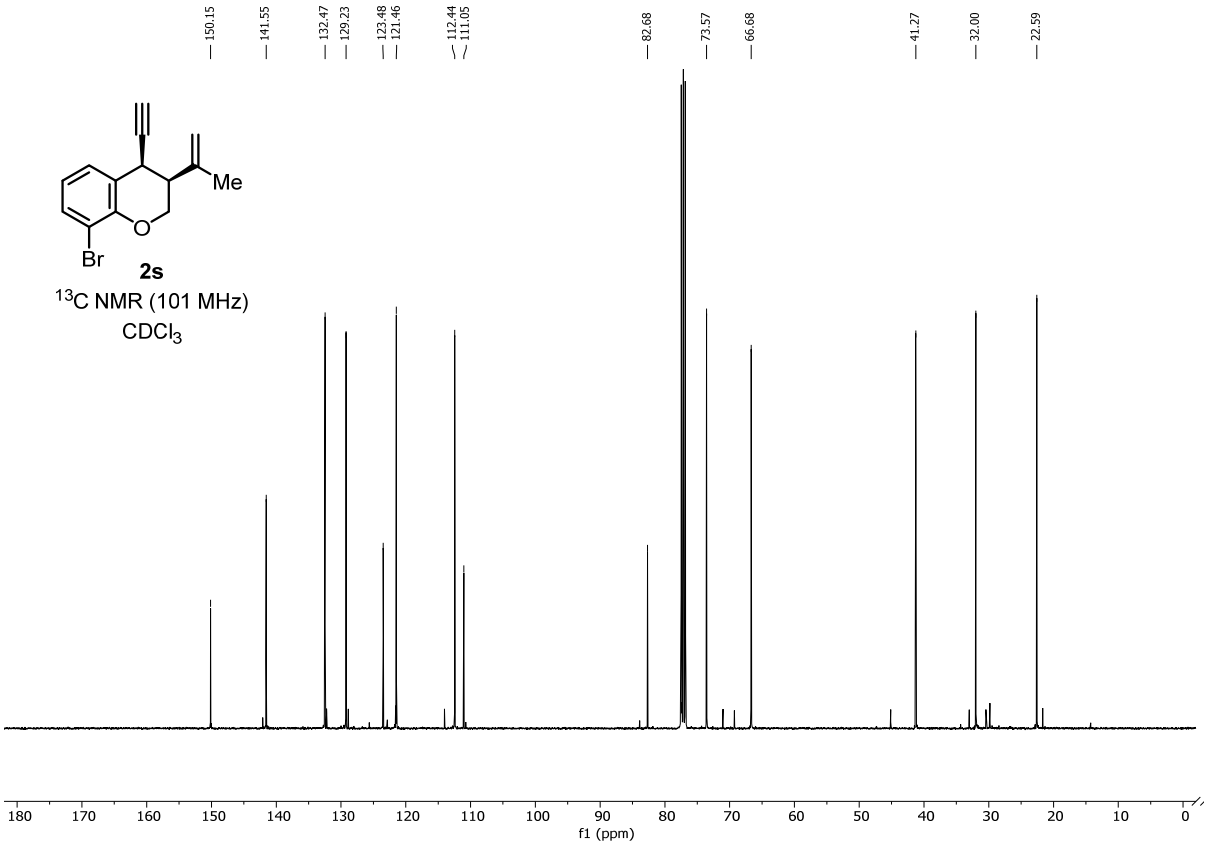

Me
O
OMe
2q
1H NMR (400 MHz)
CDCl3
f1 (ppm)

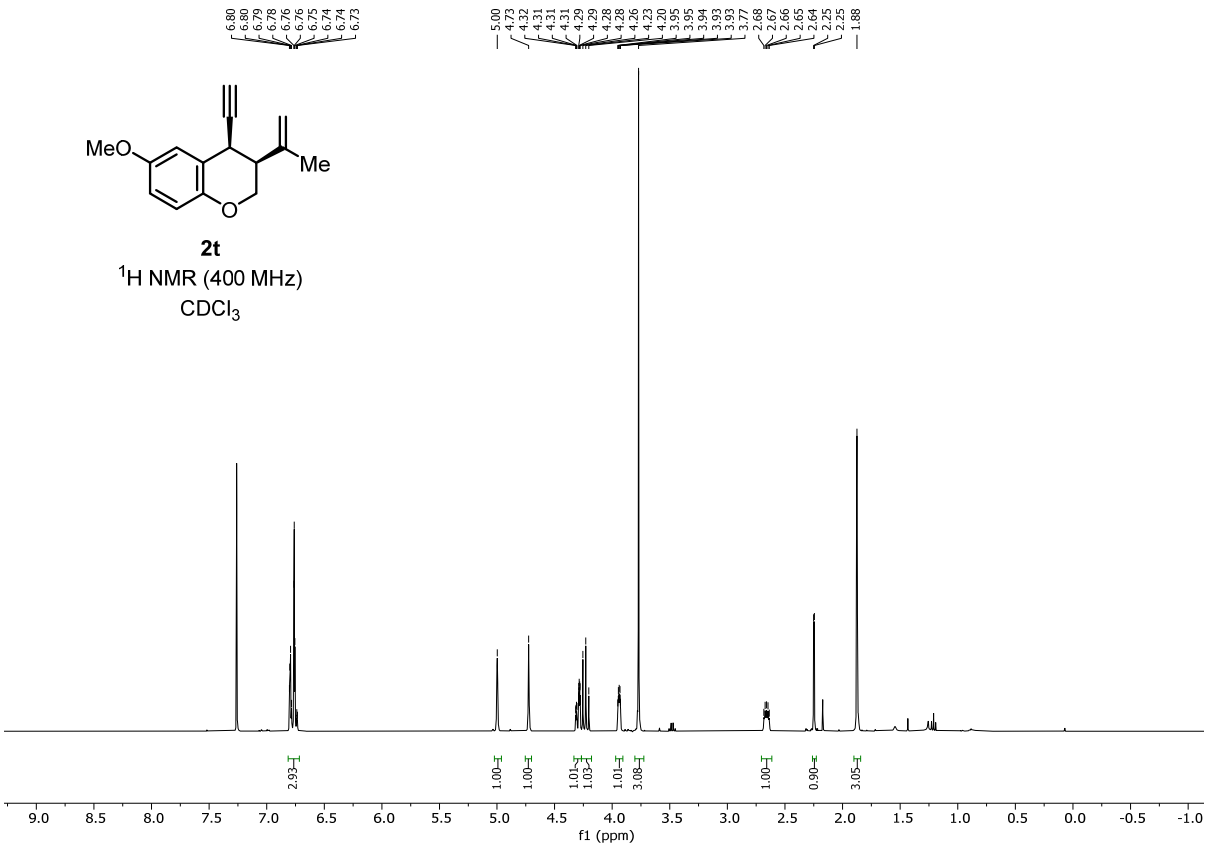

Me
O
OMe
2q
13C NMR (101 MHz)
CDCl3
f1 (ppm)

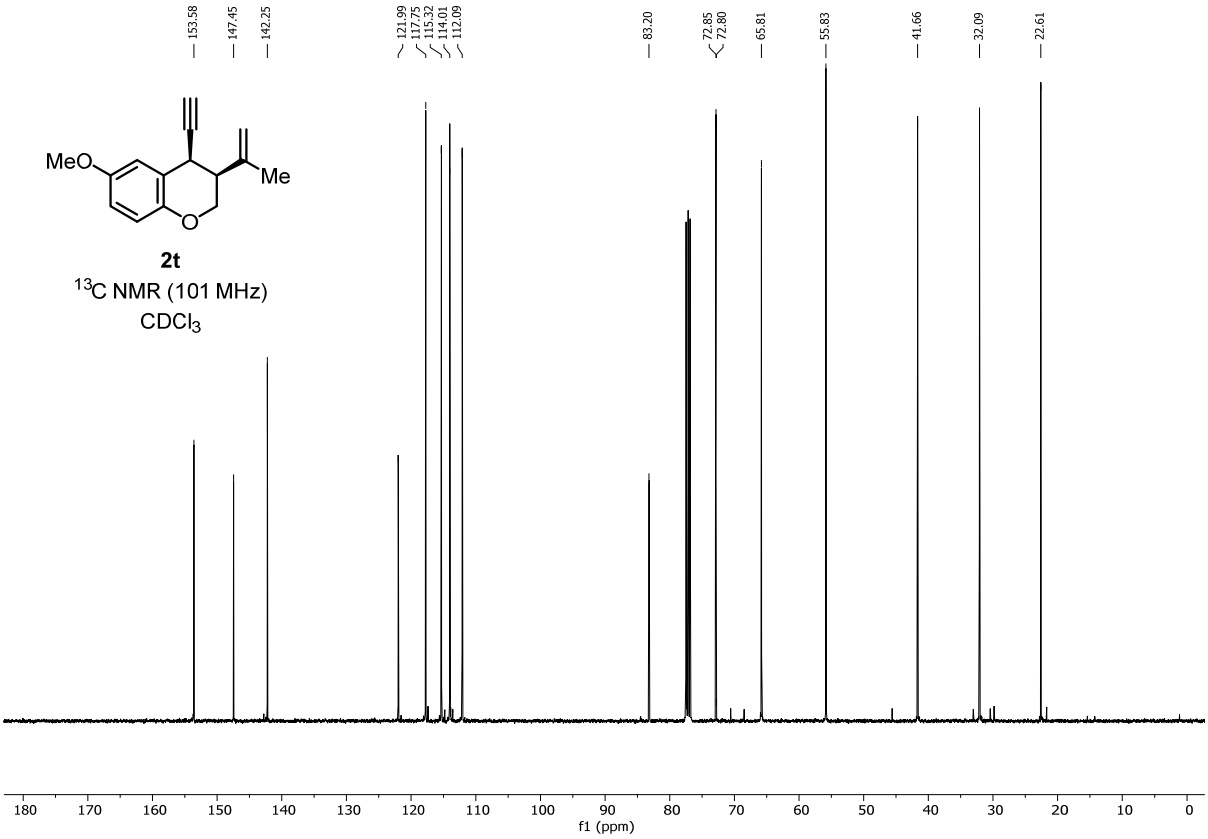

Me
O
NO2
2r
1H NMR (400 MHz)
CDCl3
f1 (ppm)

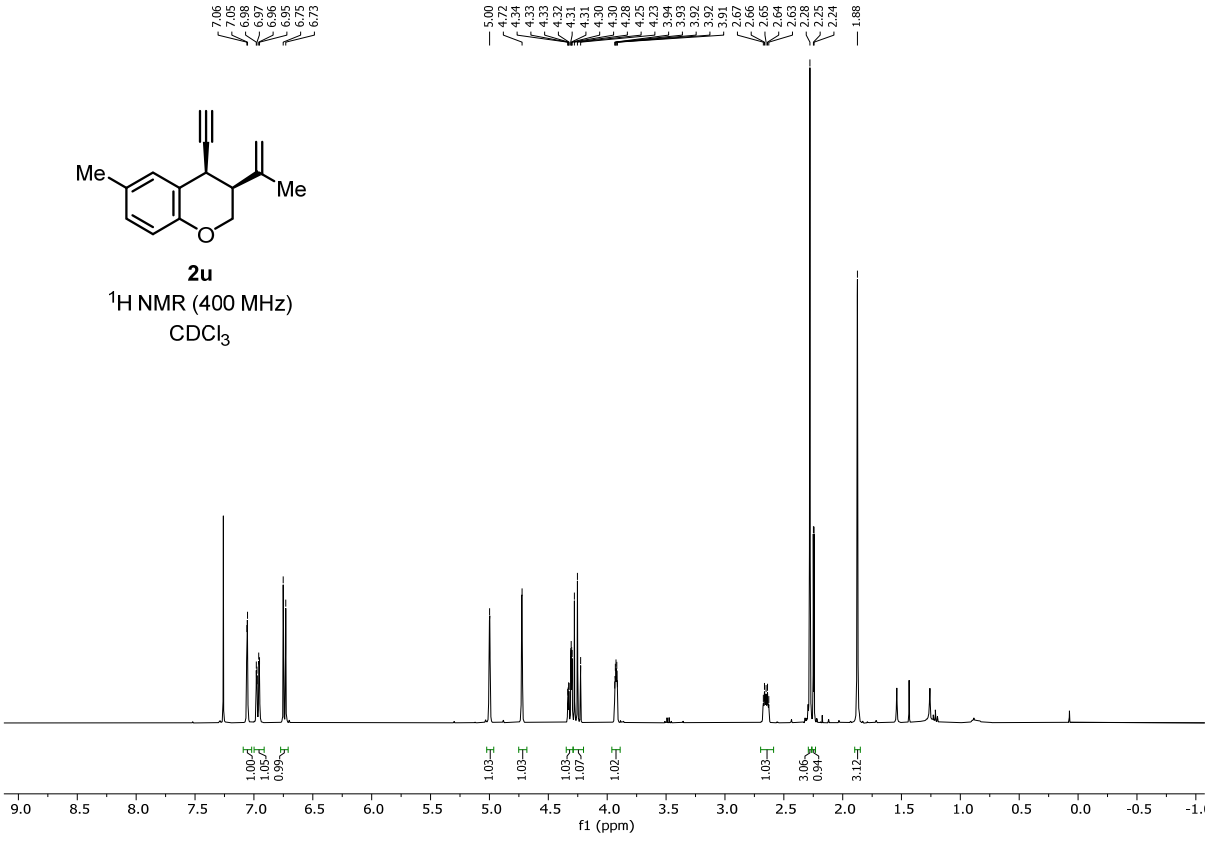

Me
O
NO2
2r
13C NMR (101 MHz)
CDCl3
f1 (ppm)

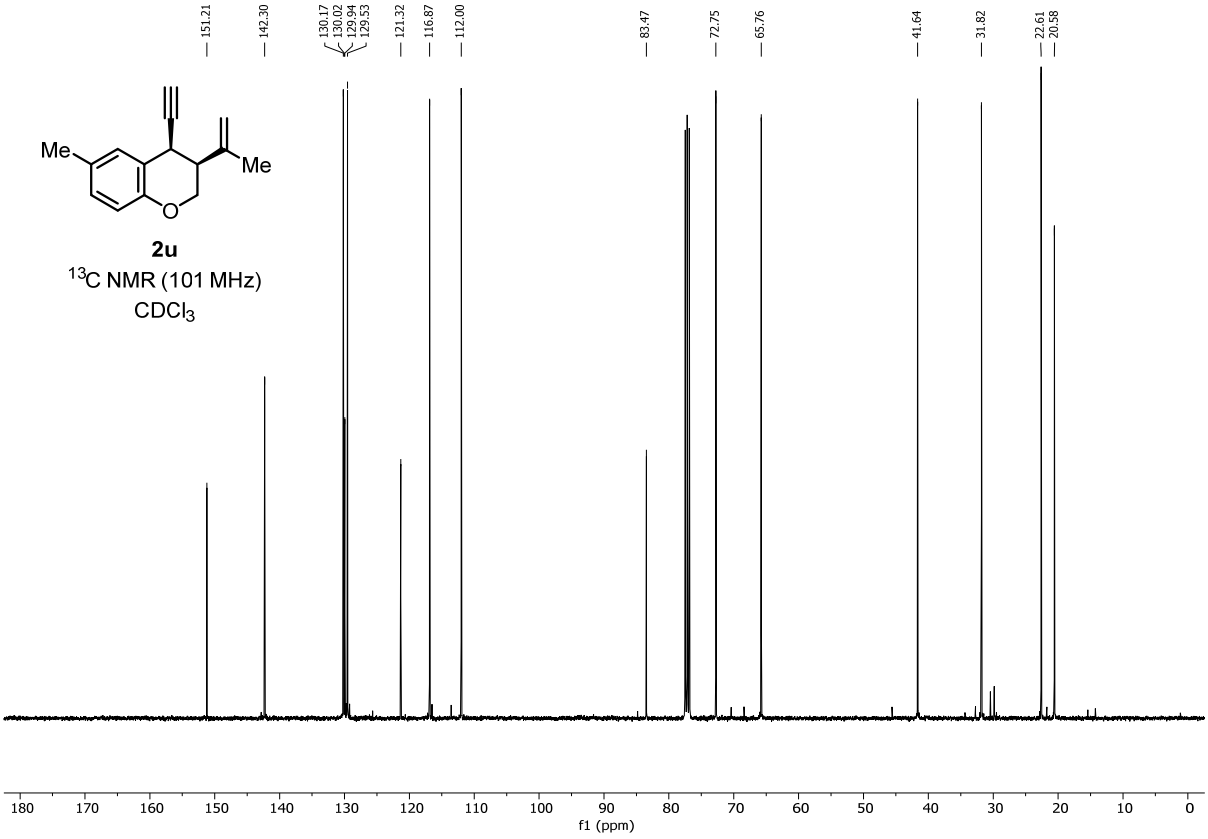

Me
Br
2s
1H NMR (400 MHz)
CDCl3
f1 (ppm)

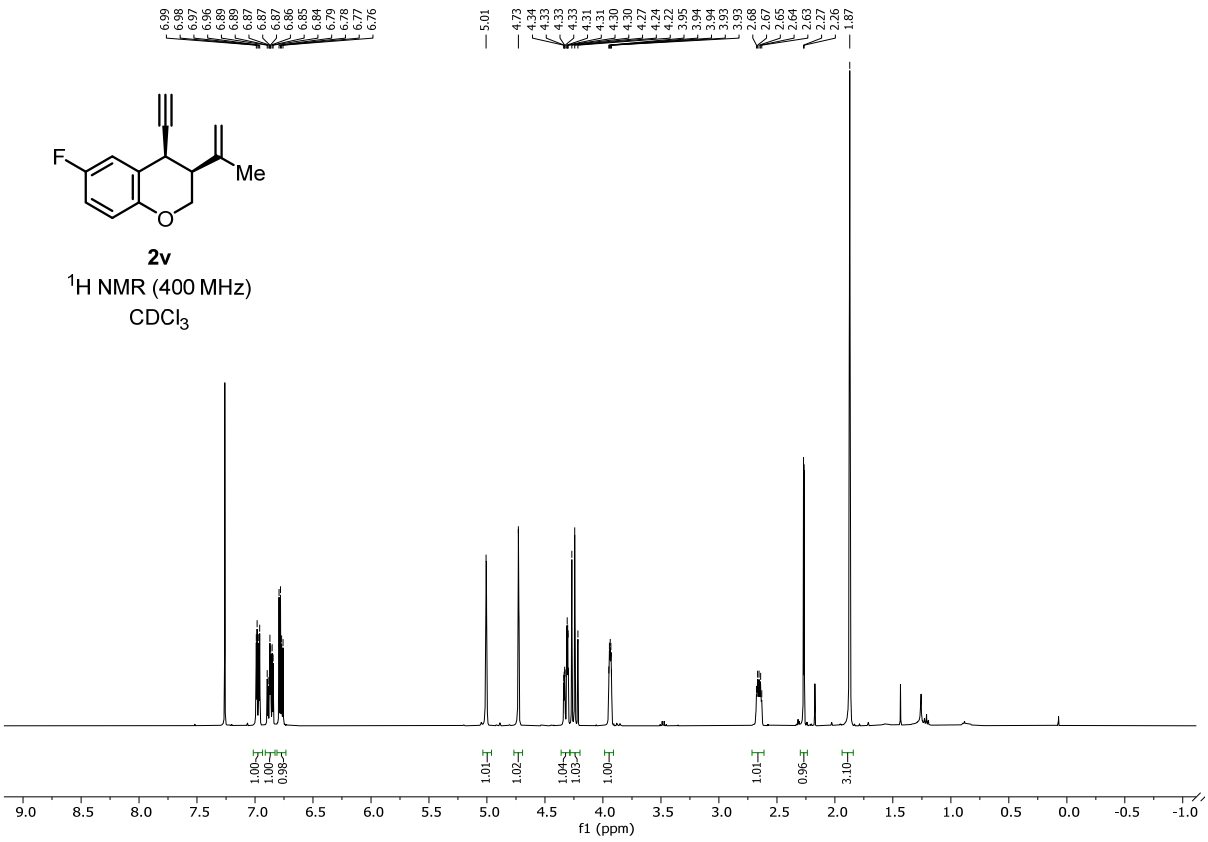

Me
Br
2s
13C NMR (101 MHz)
CDCl3
f1 (ppm)

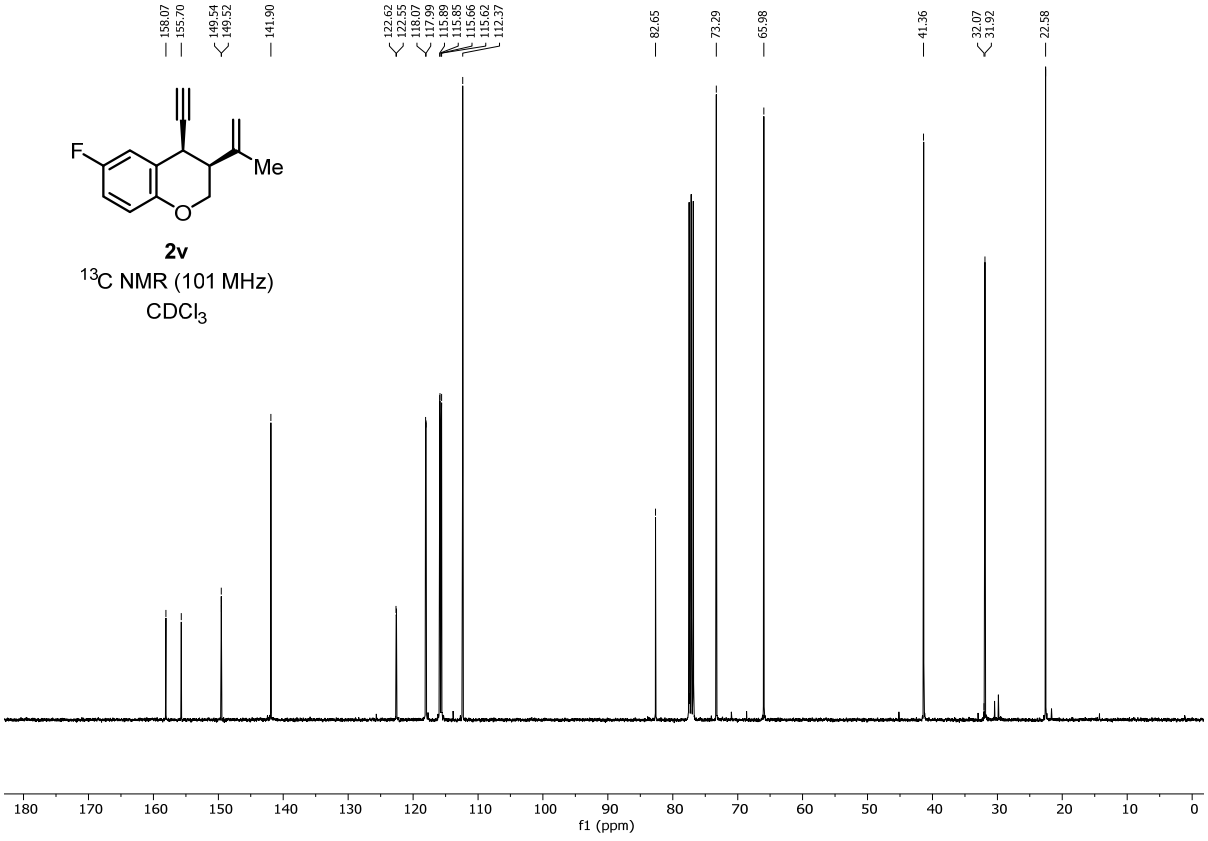

MeO
Me
O
2t
1H NMR (400 MHz)
CDCl3
f1 (ppm)


MeO
Me
O
2t
13C NMR (101 MHz)
CDCl3
f1 (ppm)


Me
Me
O
2u
1H NMR (400 MHz)
CDCl3
f1 (ppm)


Me
Me
O
2u
13C NMR (101 MHz)
CDCl3
f1 (ppm)

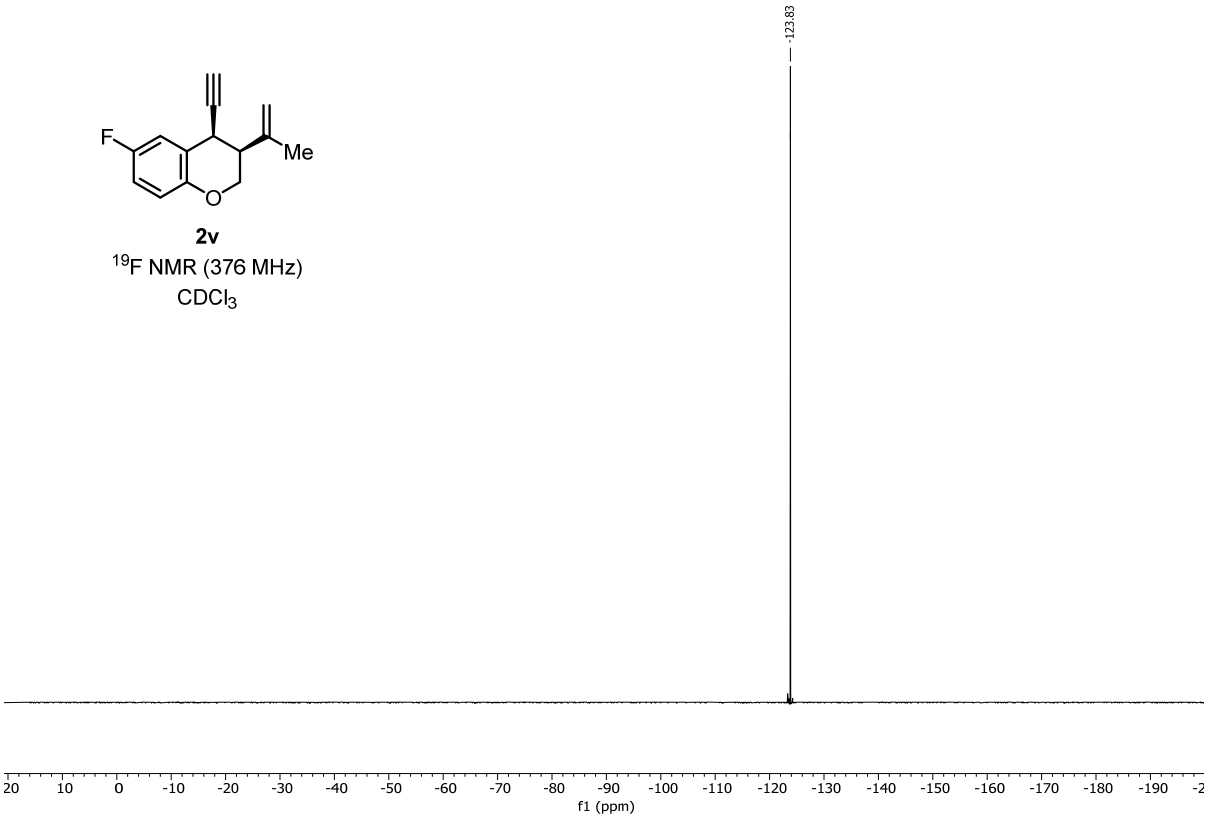

F
Me
O
2v
1H NMR (400 MHz)
CDCl3
f1 (ppm)

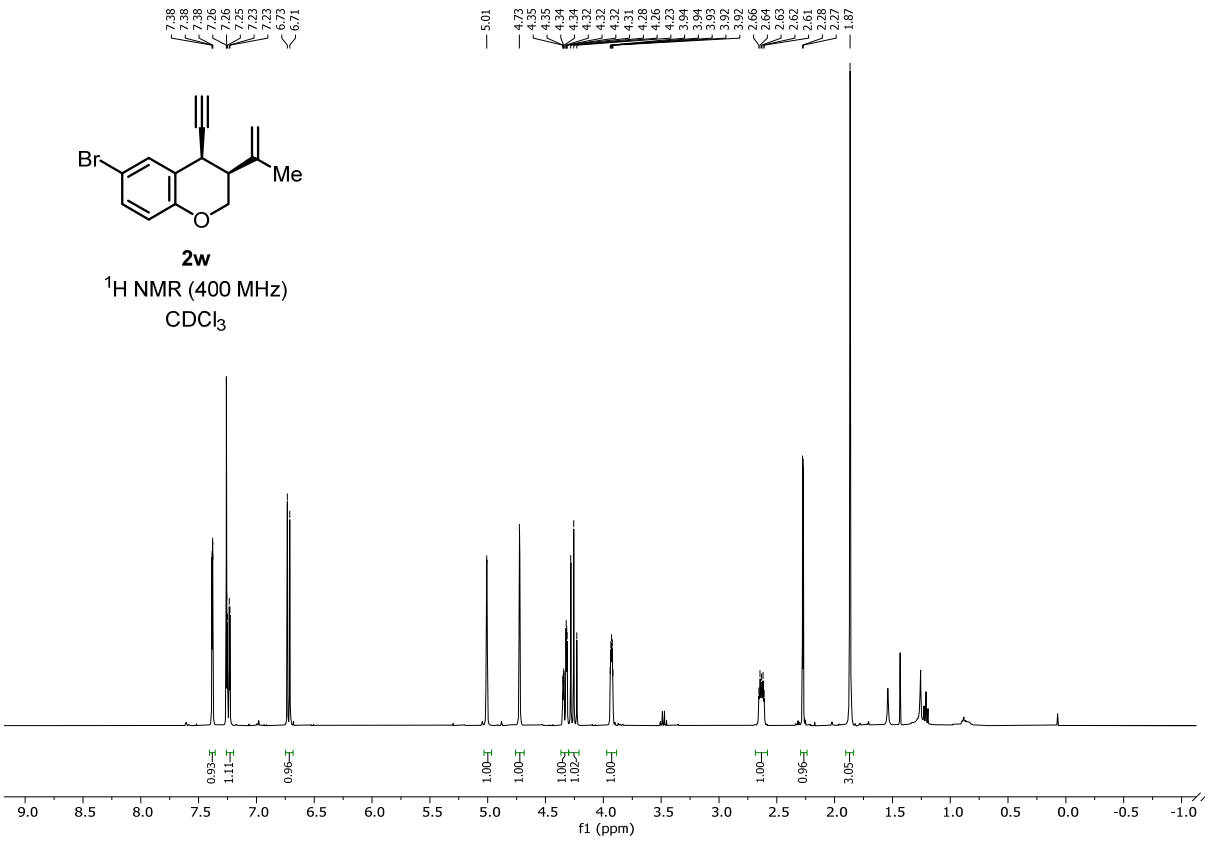

F
Me
O
2v
13C NMR (101 MHz)
CDCl3
f1 (ppm)

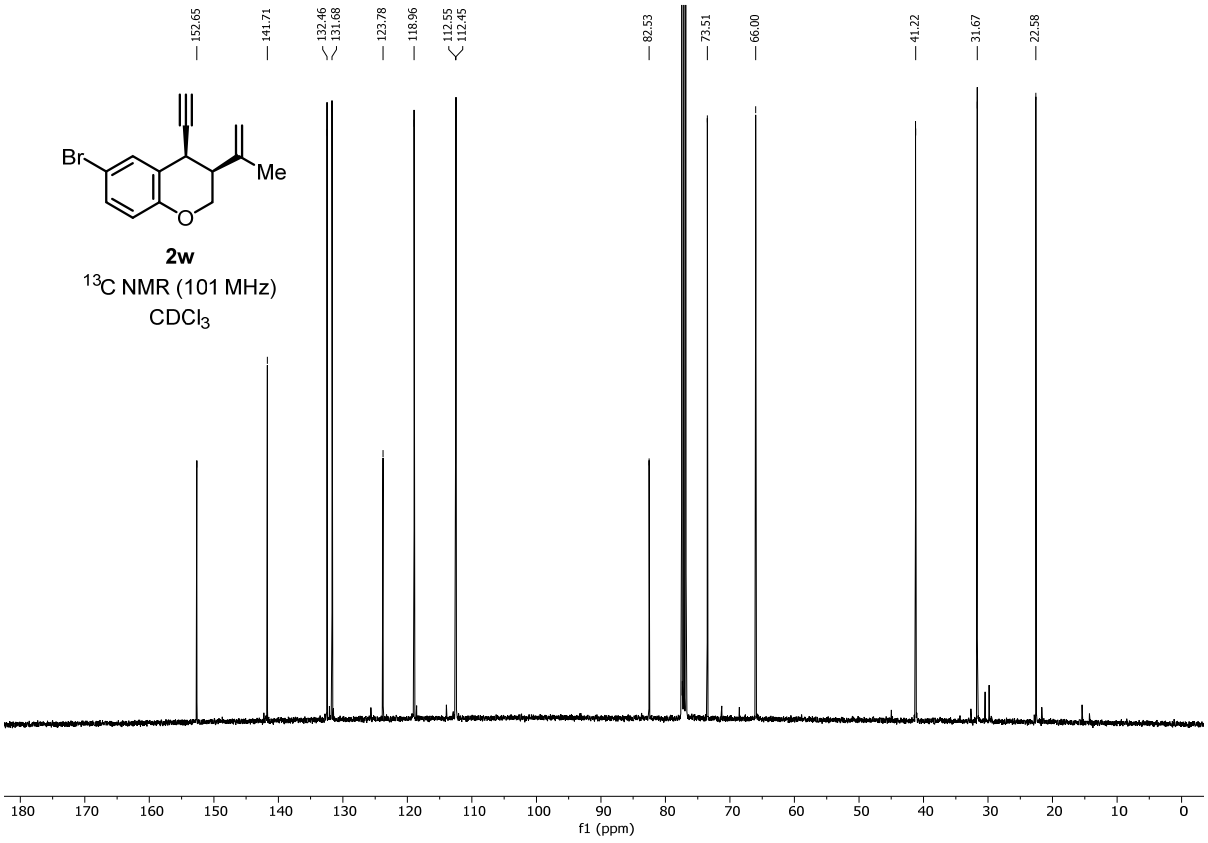
2v

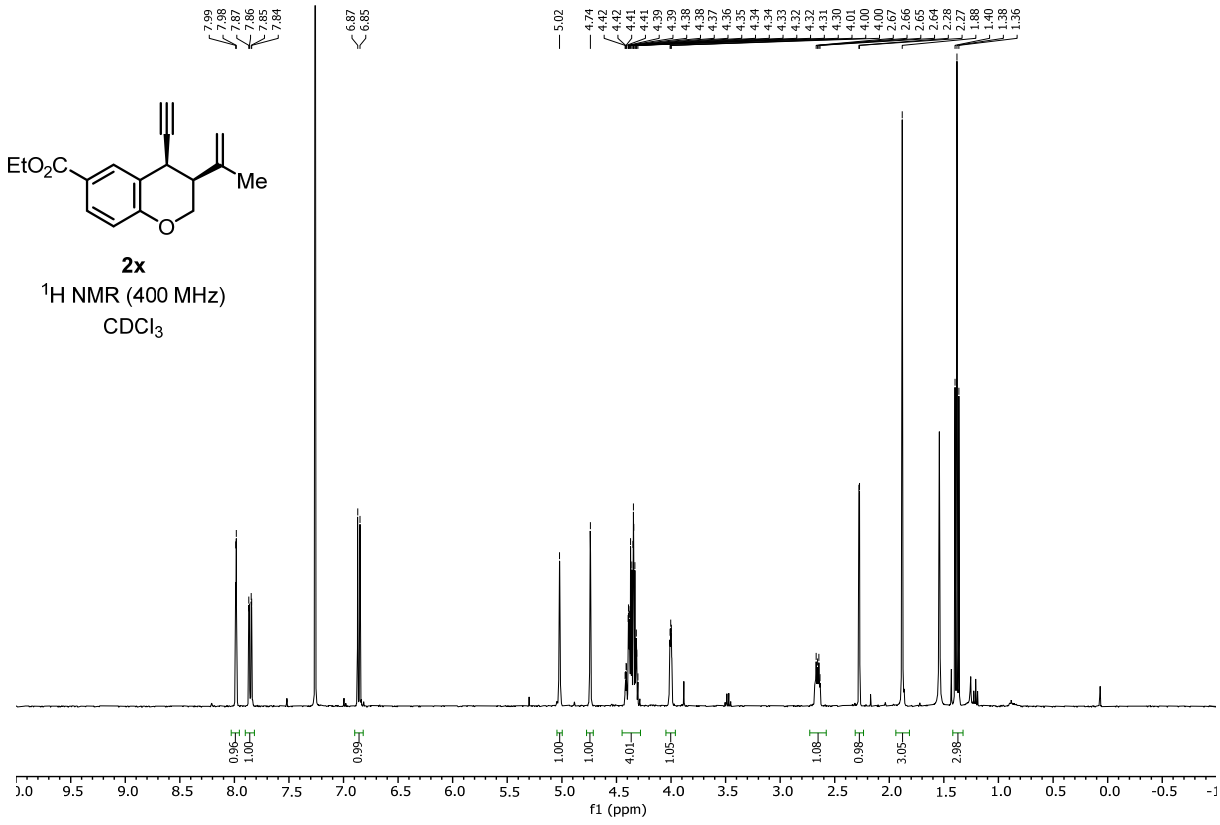
^{19}F NMR (376 MHz)

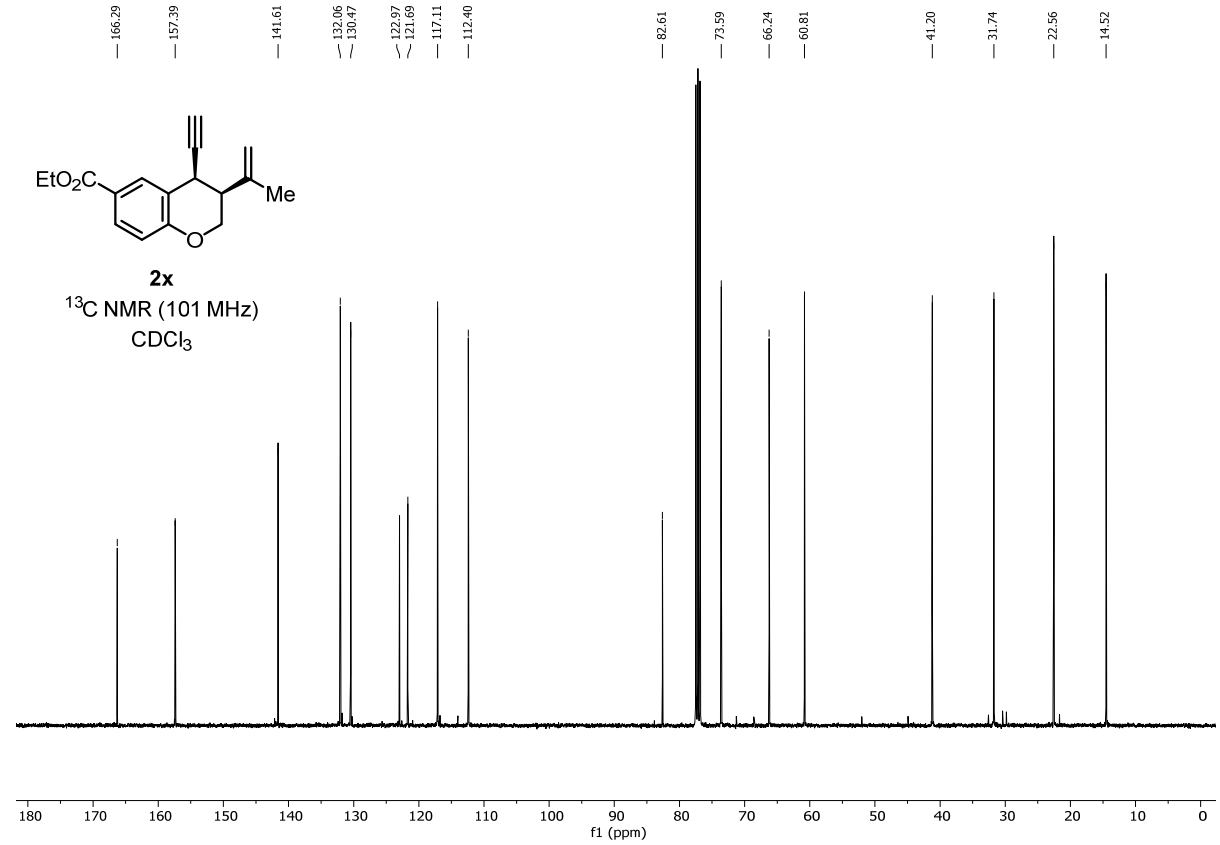
$CDCl_3$

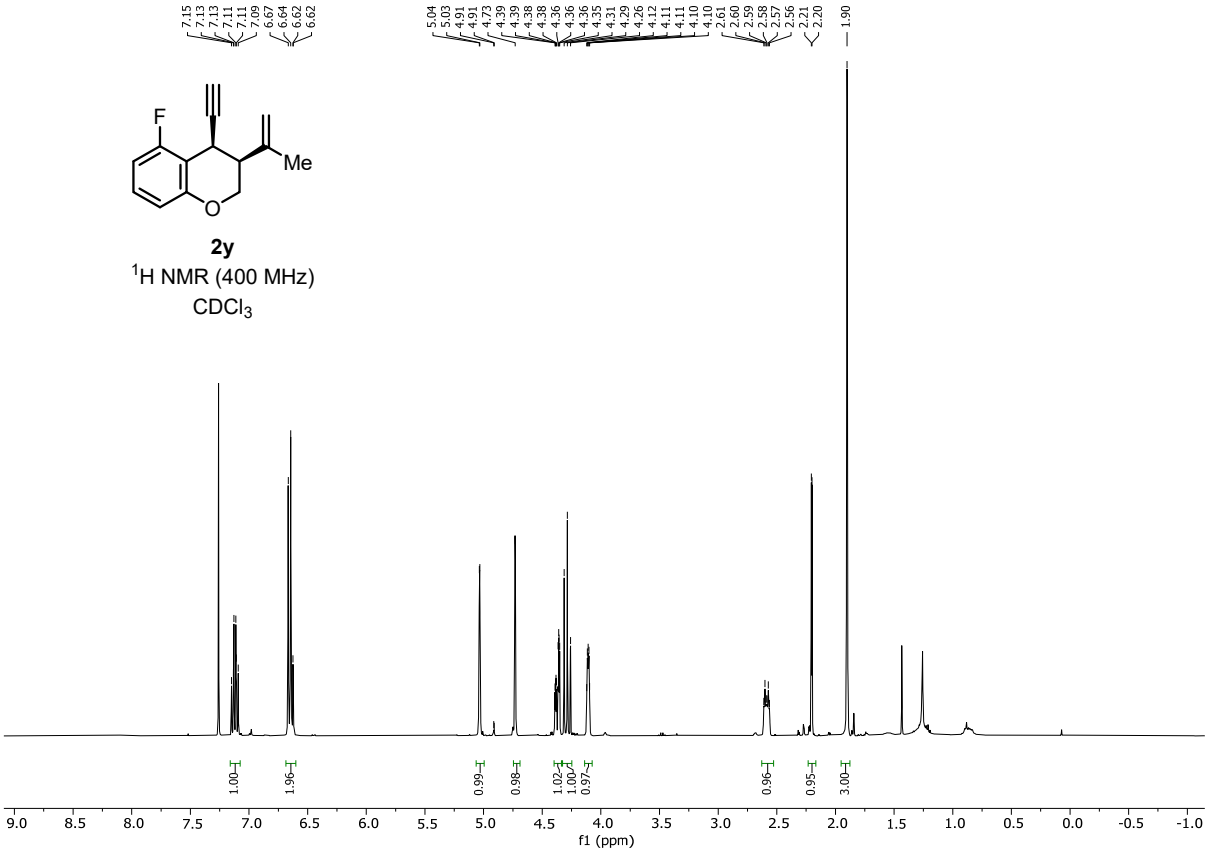


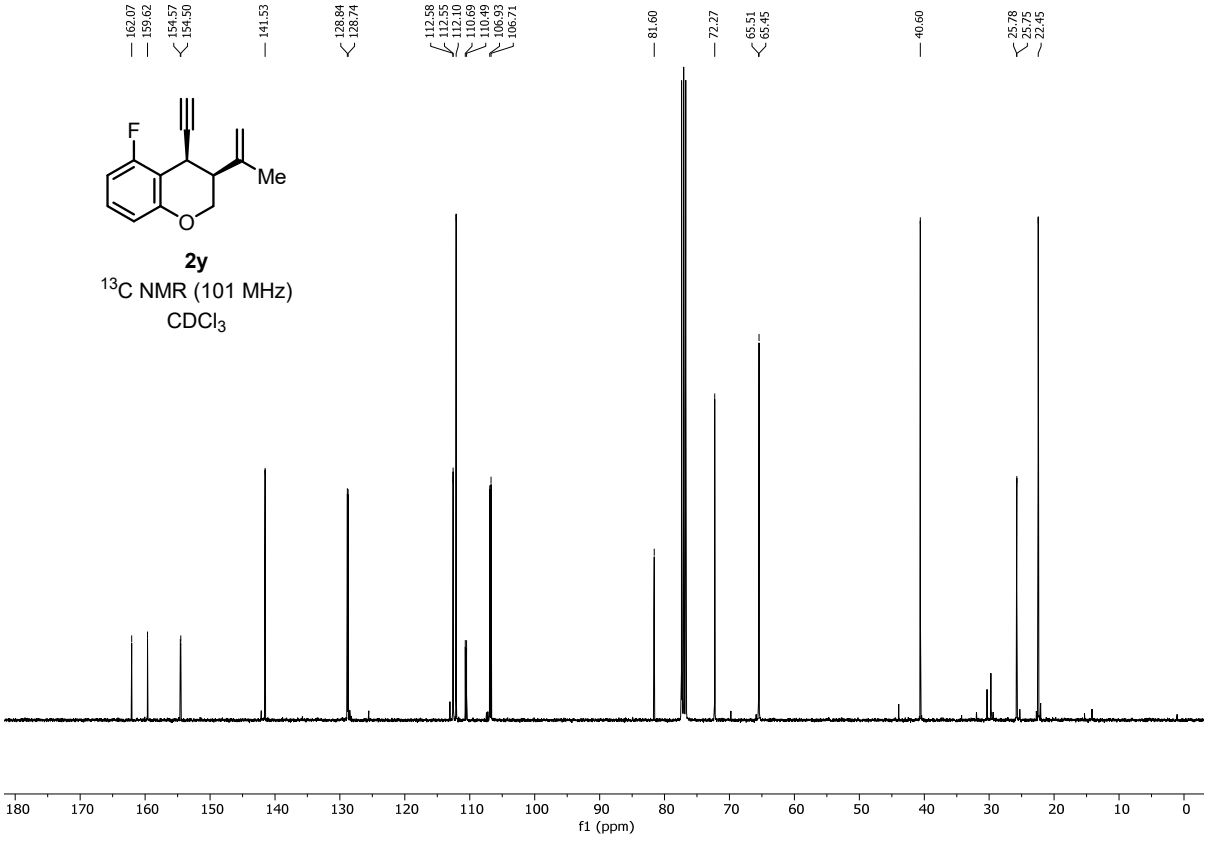

Br
Me
O
2w
1H NMR (400 MHz)
CDCl3
f1 (ppm)


Br
Me
O
2w
13C NMR (101 MHz)
CDCl3
f1 (ppm)


EtO2C
Me
O
2x
1H NMR (400 MHz)
CDCl3
f1 (ppm)


EtO2C
Me
O
2x
13C NMR (101 MHz)
CDCl3
f1 (ppm)

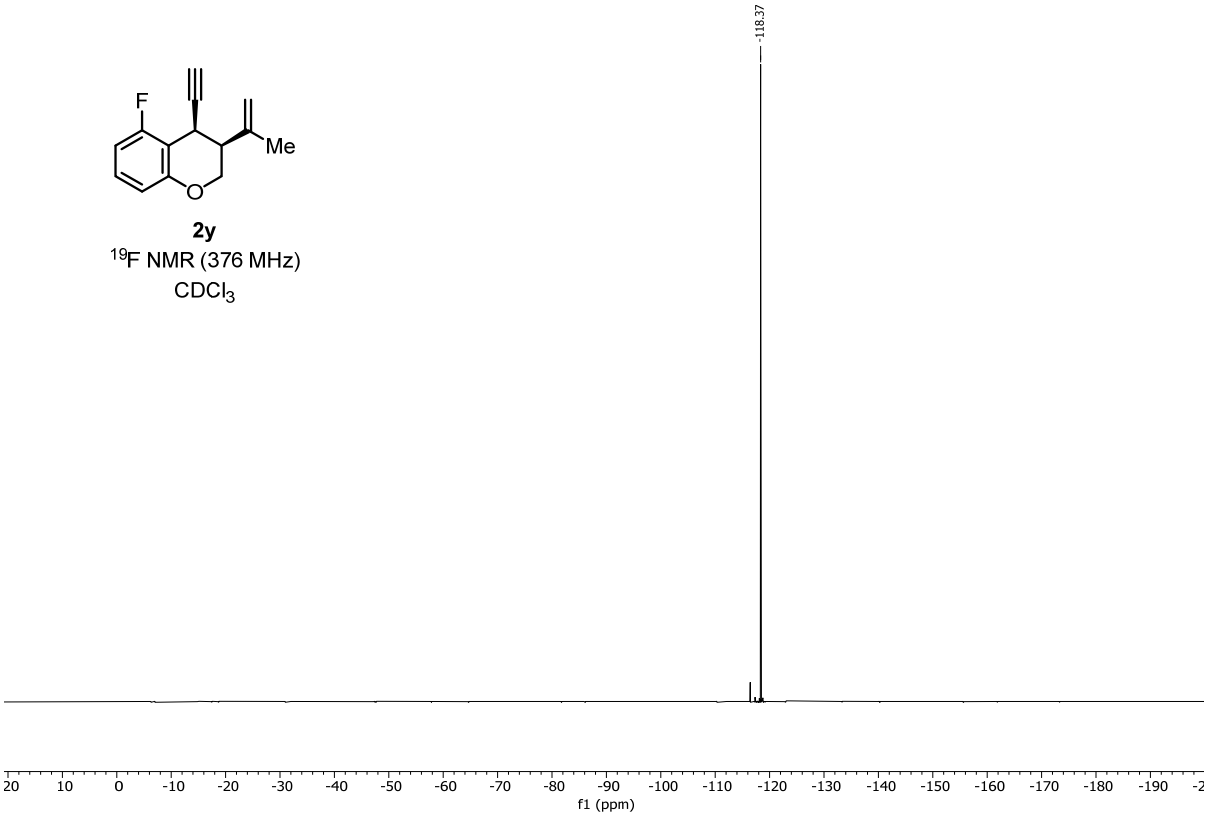

F
Me
O
2y
1H NMR (400 MHz)
CDCl3
f1 (ppm)

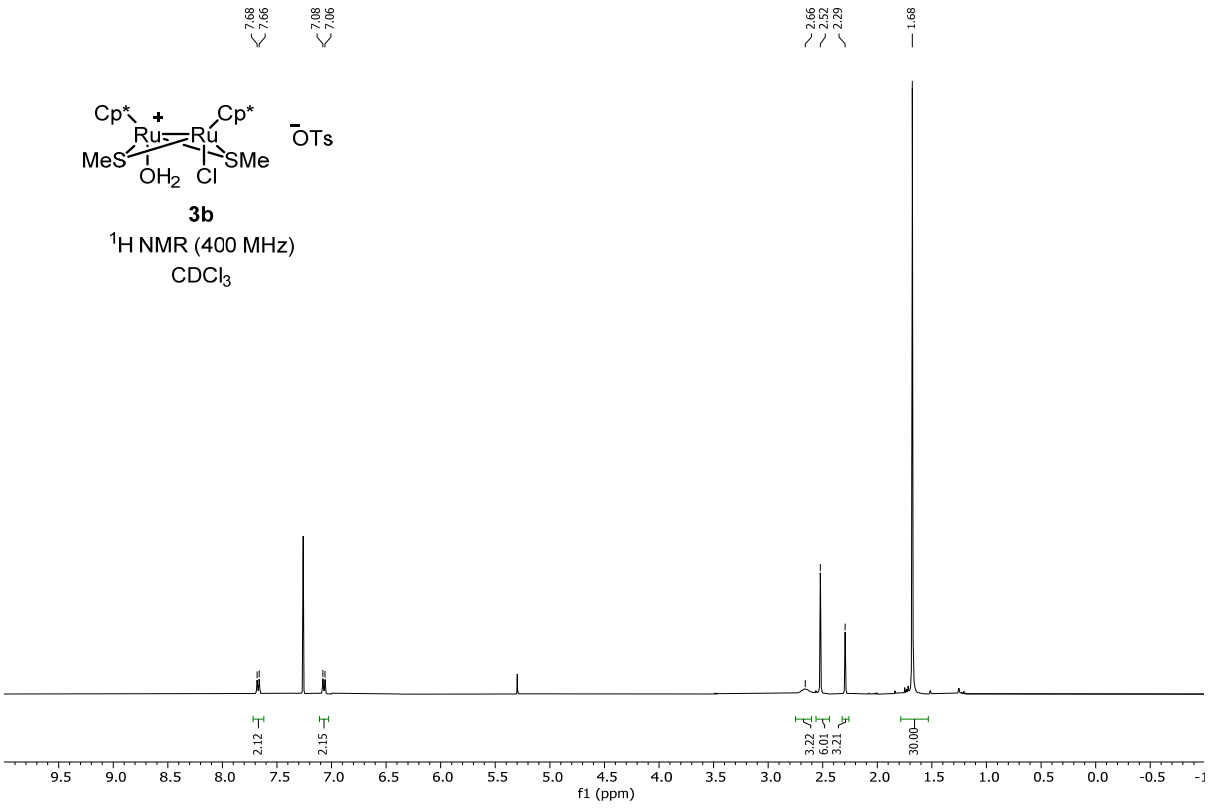

F
Me
O
2y
13C NMR (101 MHz)
CDCl3
f1 (ppm)

2y

^{19}F NMR (376 MHz)

$CDCl_3$

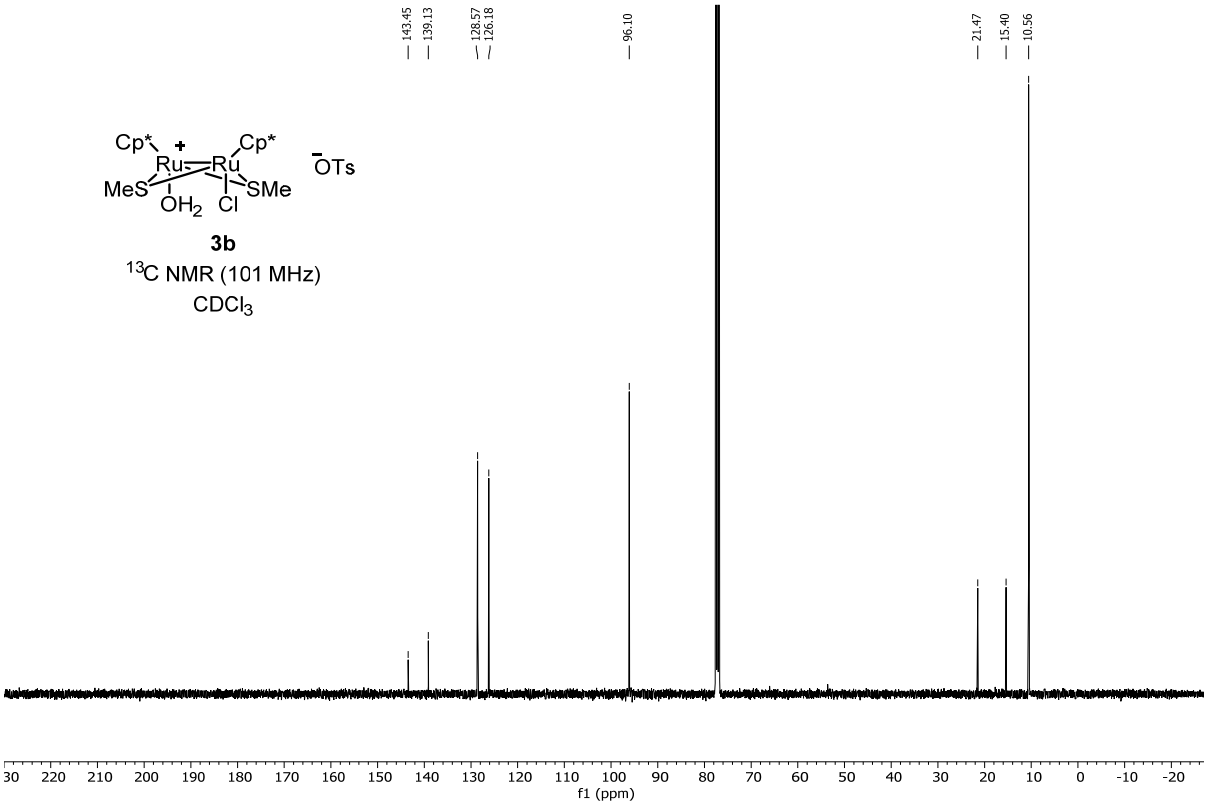




3b

^{1}H NMR (400 MHz)

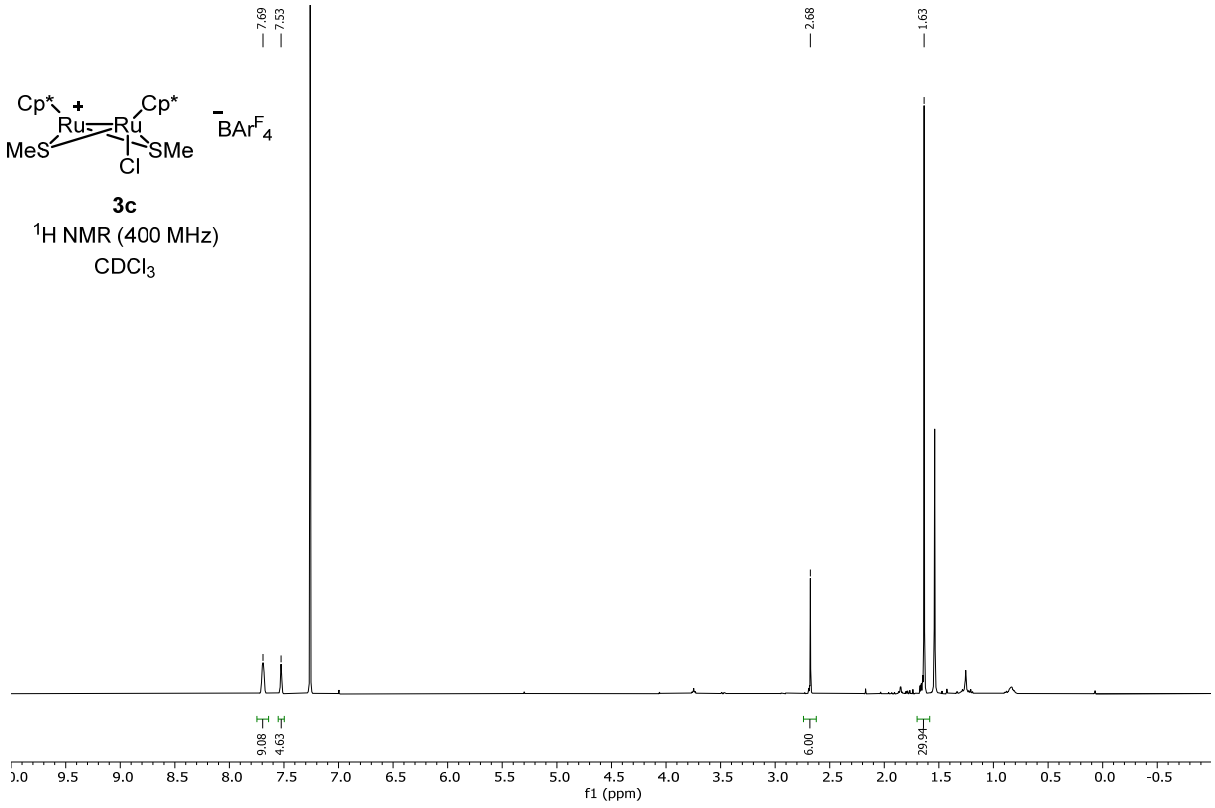
$CDCl_3$



3b

^{13}C NMR (101 MHz)

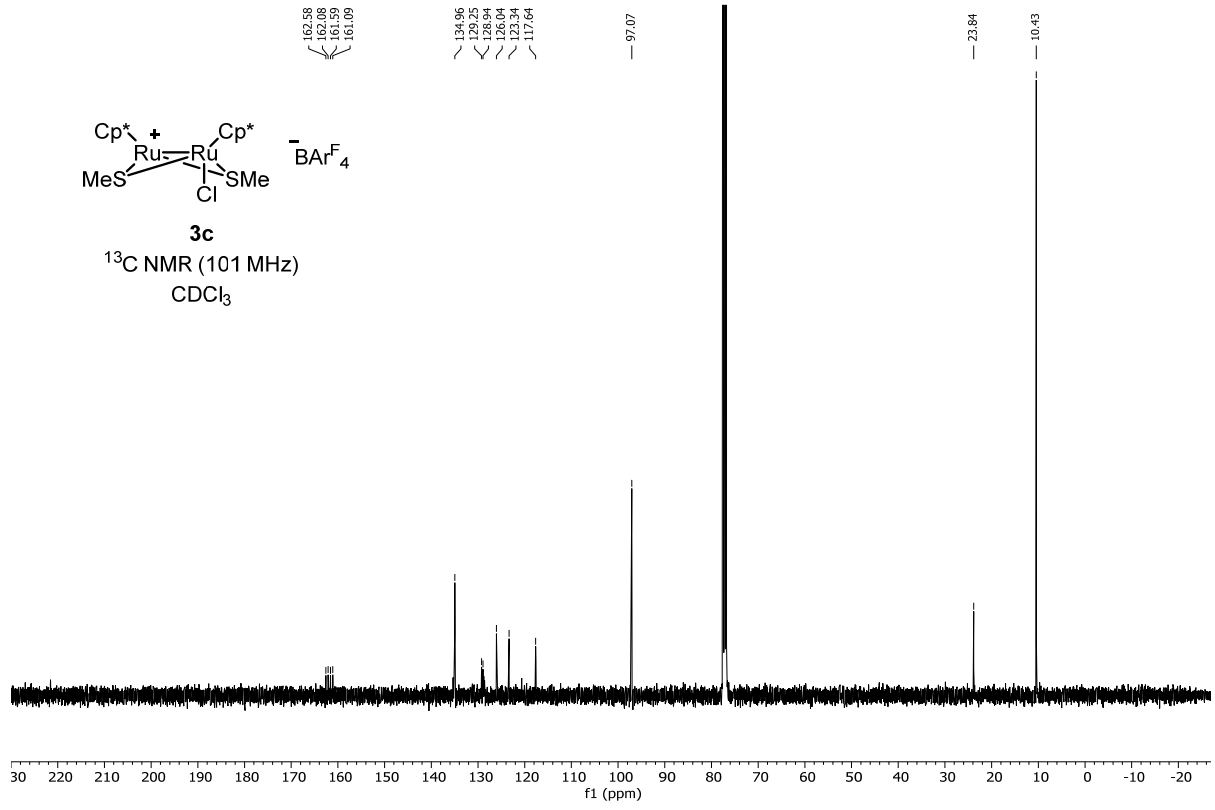
$CDCl_3$



3c

^{1}H NMR (400 MHz)

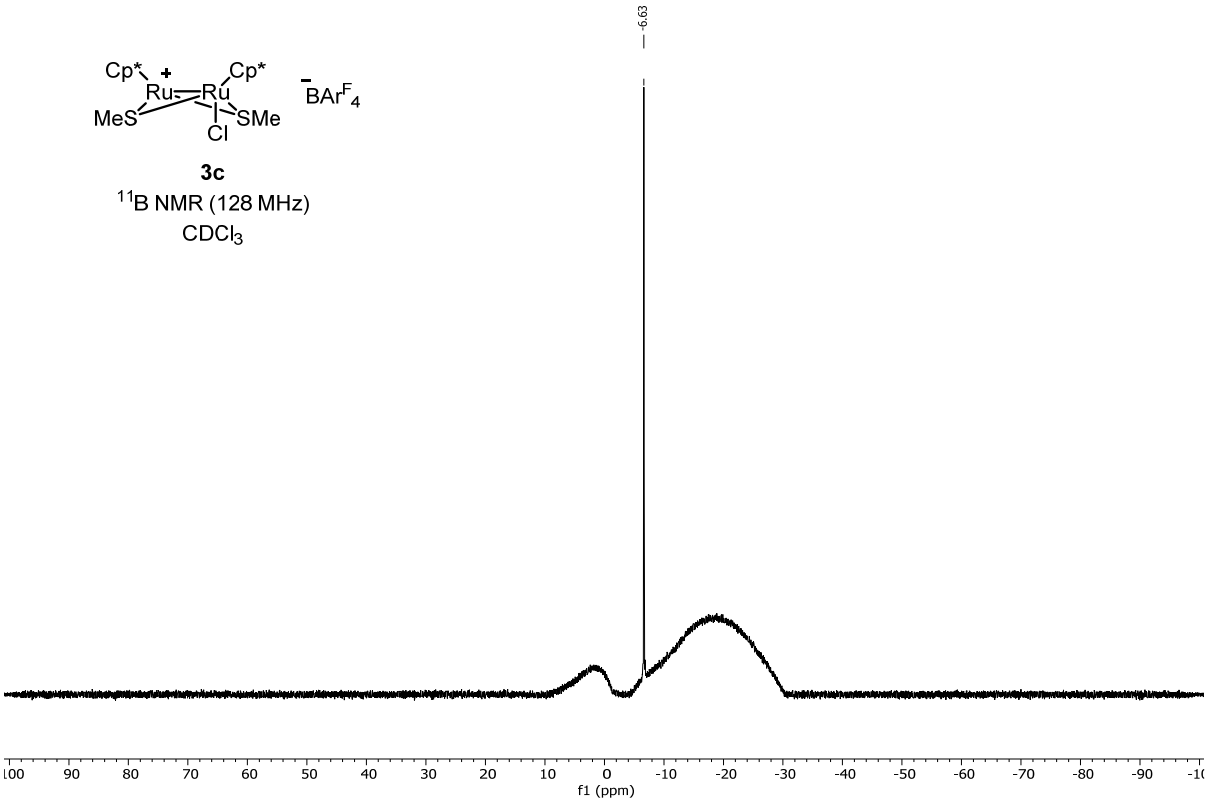
$CDCl_3$



3c

^{13}C NMR (101 MHz)

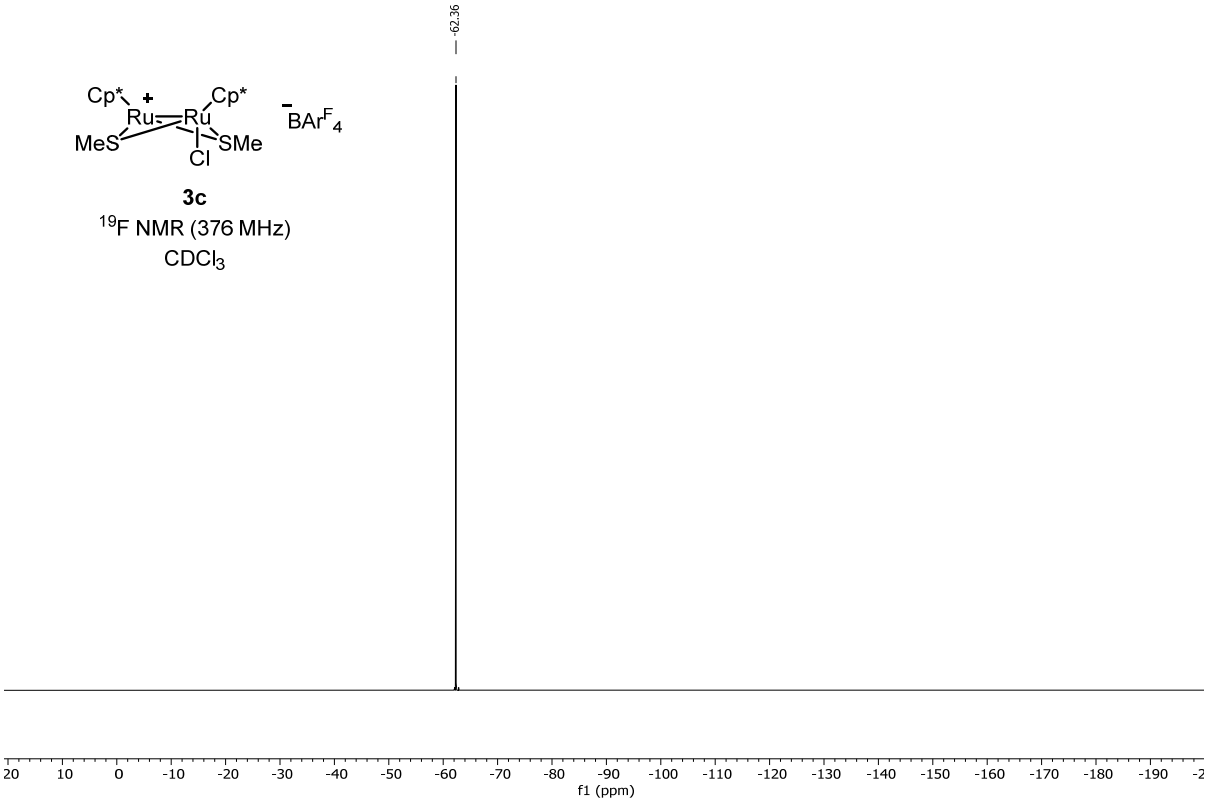
$CDCl_3$



3c

^{11}B NMR (128 MHz)

$CDCl_3$



3c

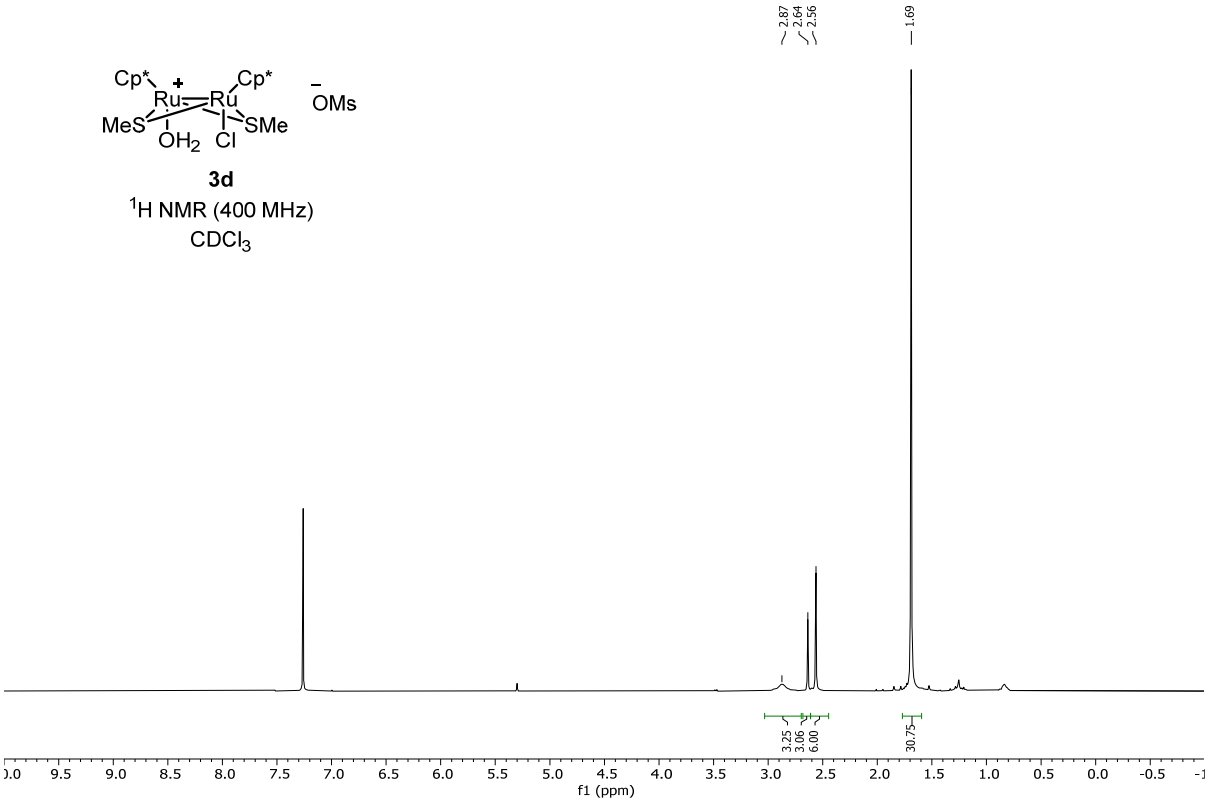
^{19}F NMR (376 MHz)

$CDCl_3$

3d

^{1}H NMR (400 MHz)

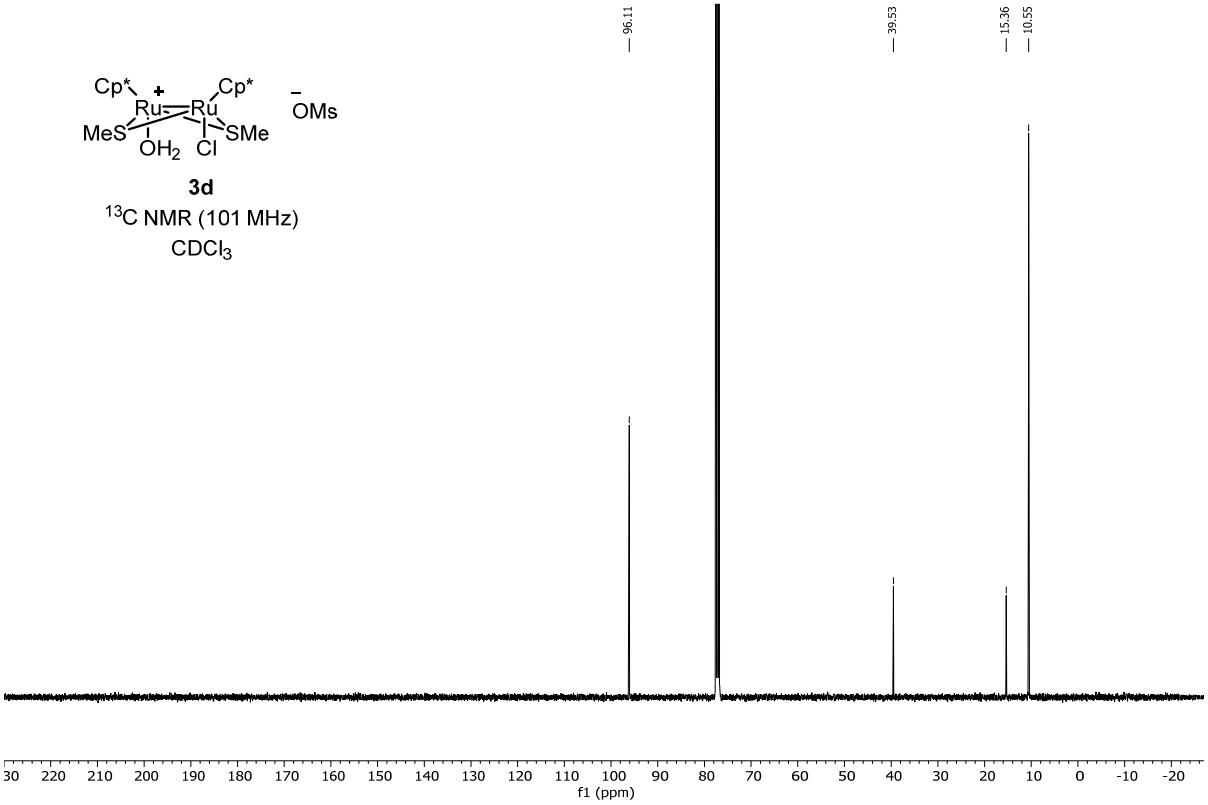
$CDCl_3$



3d

^{13}C NMR (101 MHz)

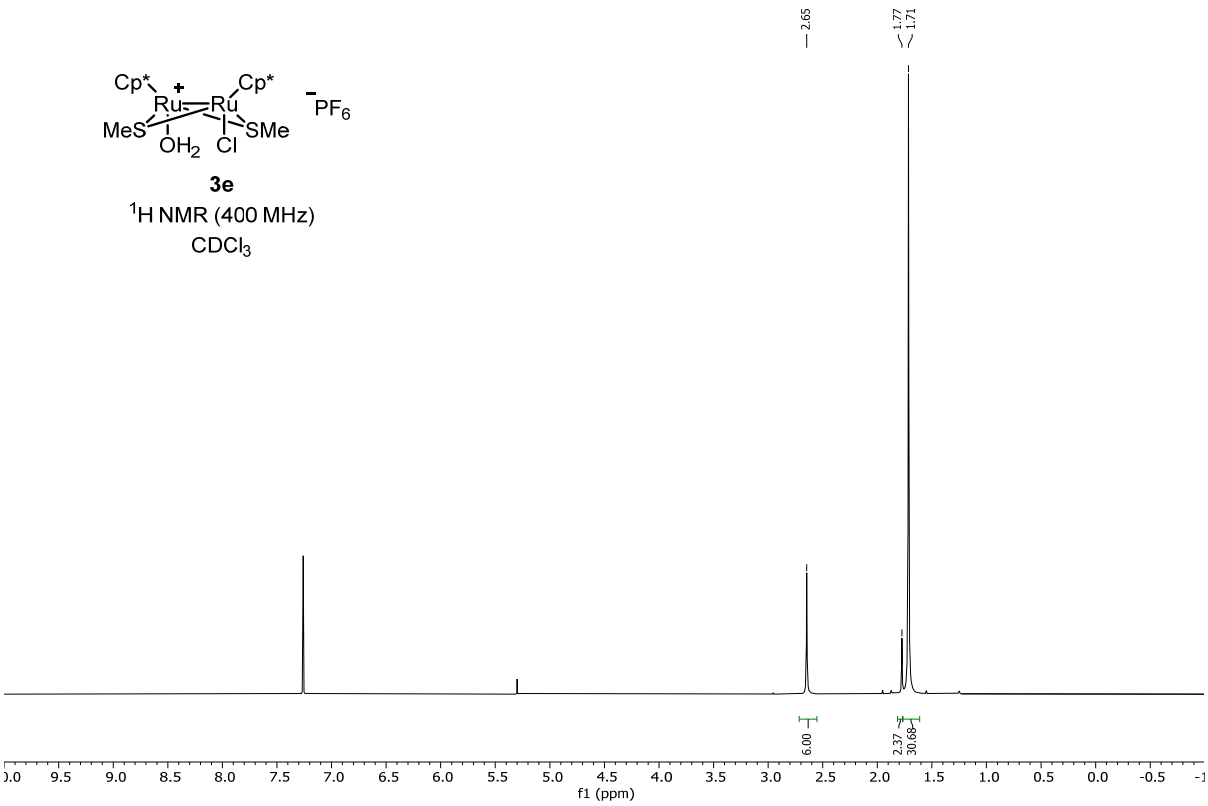
$CDCl_3$



3e

^{1}H NMR (400 MHz)

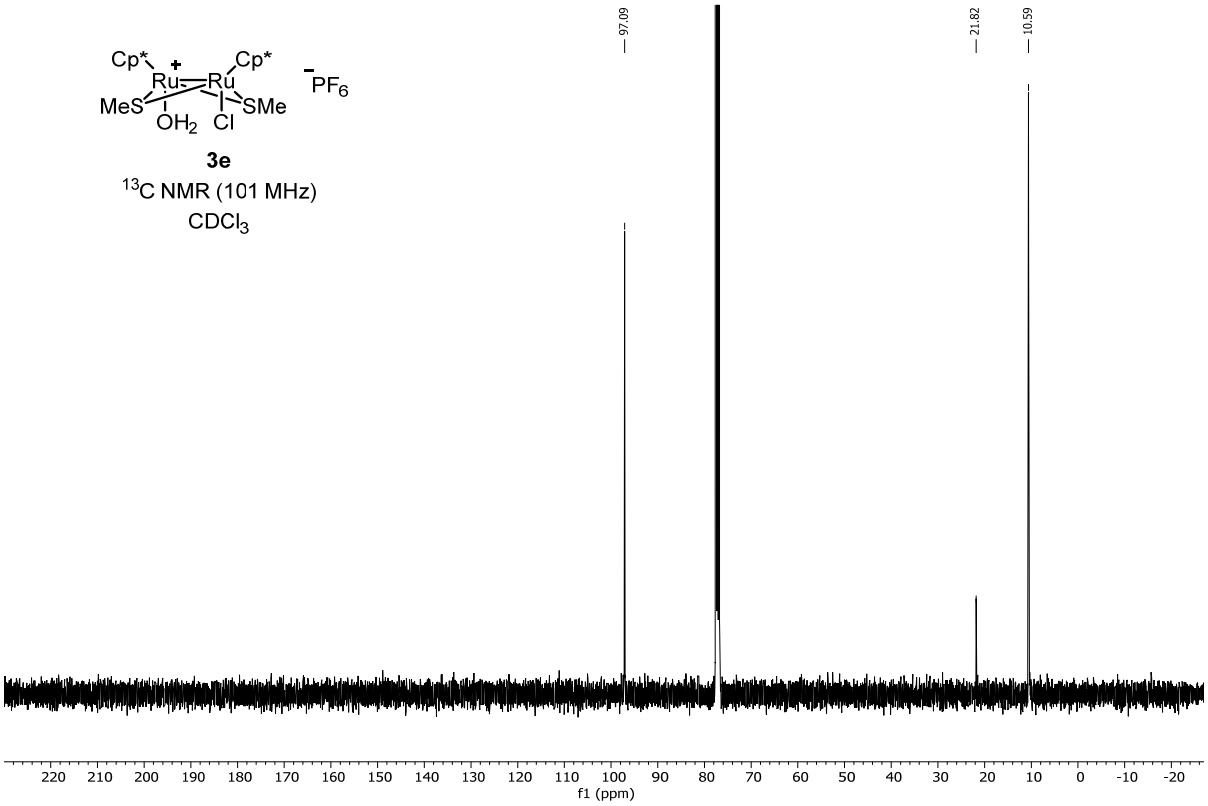
$CDCl_3$



3e

^{13}C NMR (101 MHz)

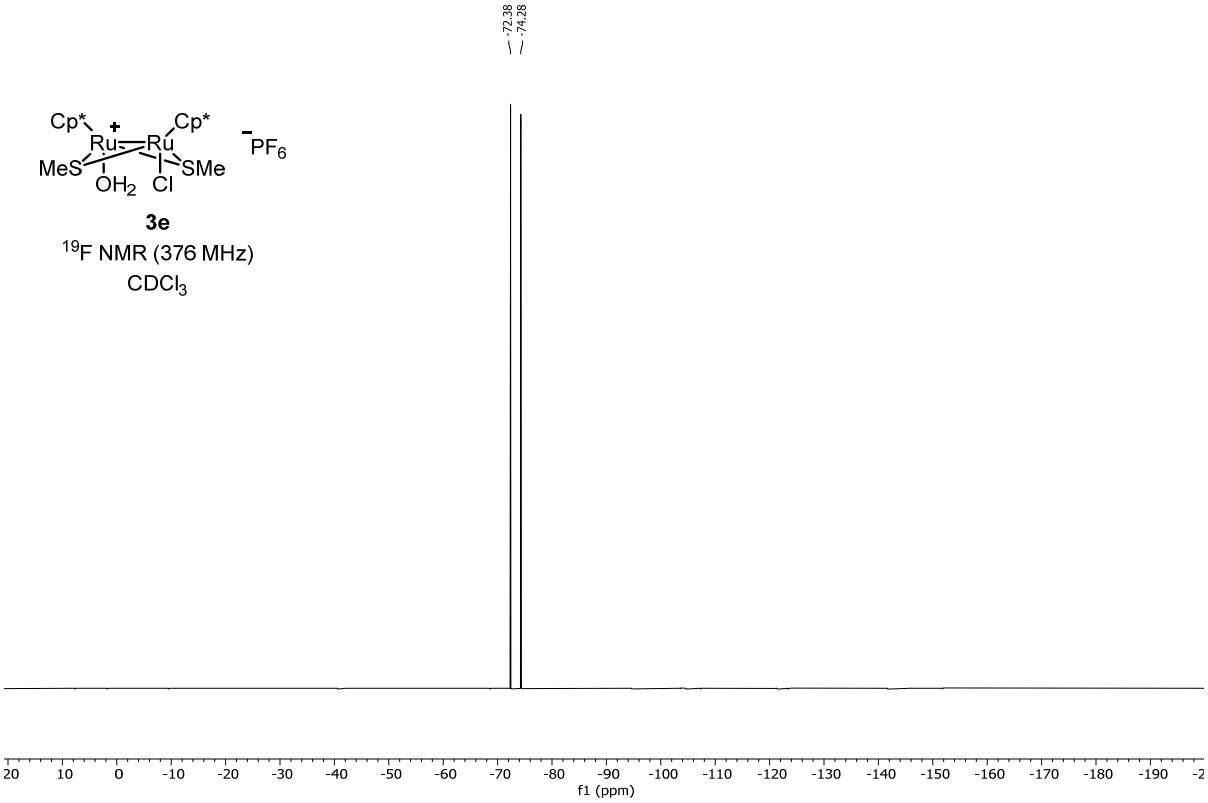
$CDCl_3$



3e

^{19}F NMR (376 MHz)

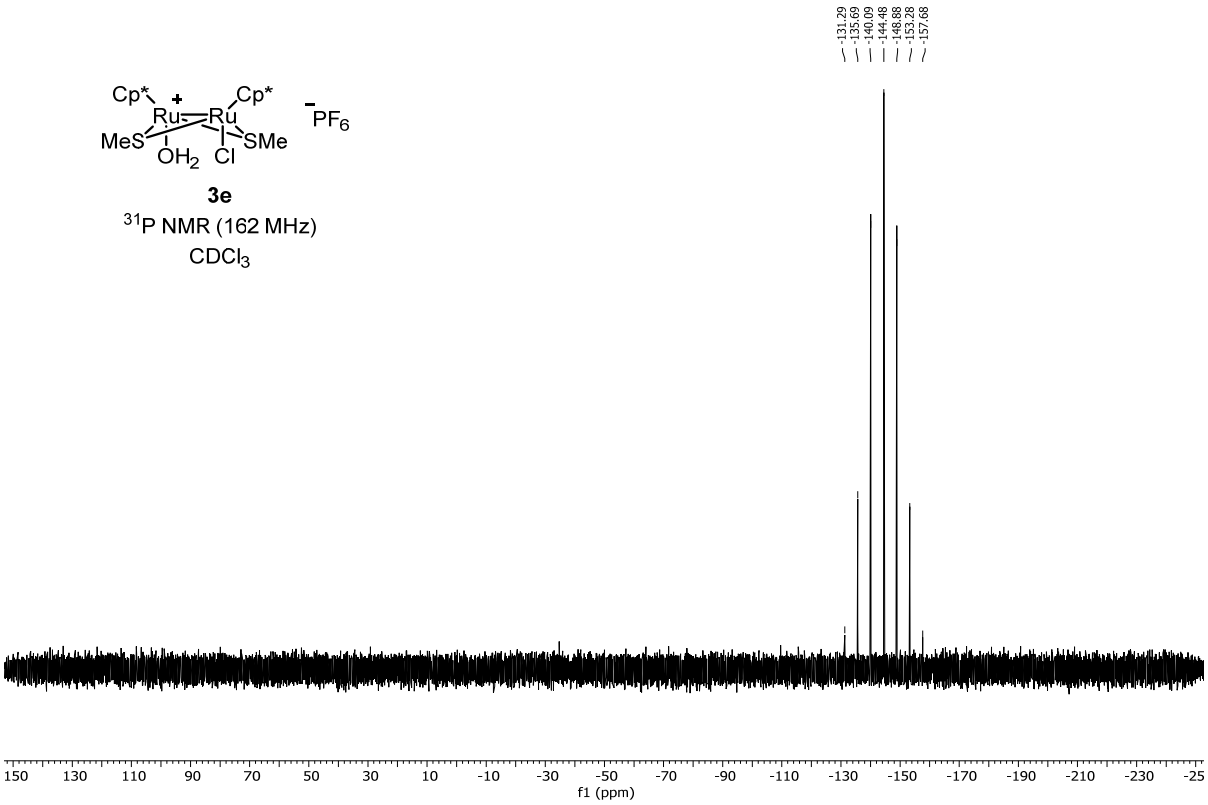
$CDCl_3$

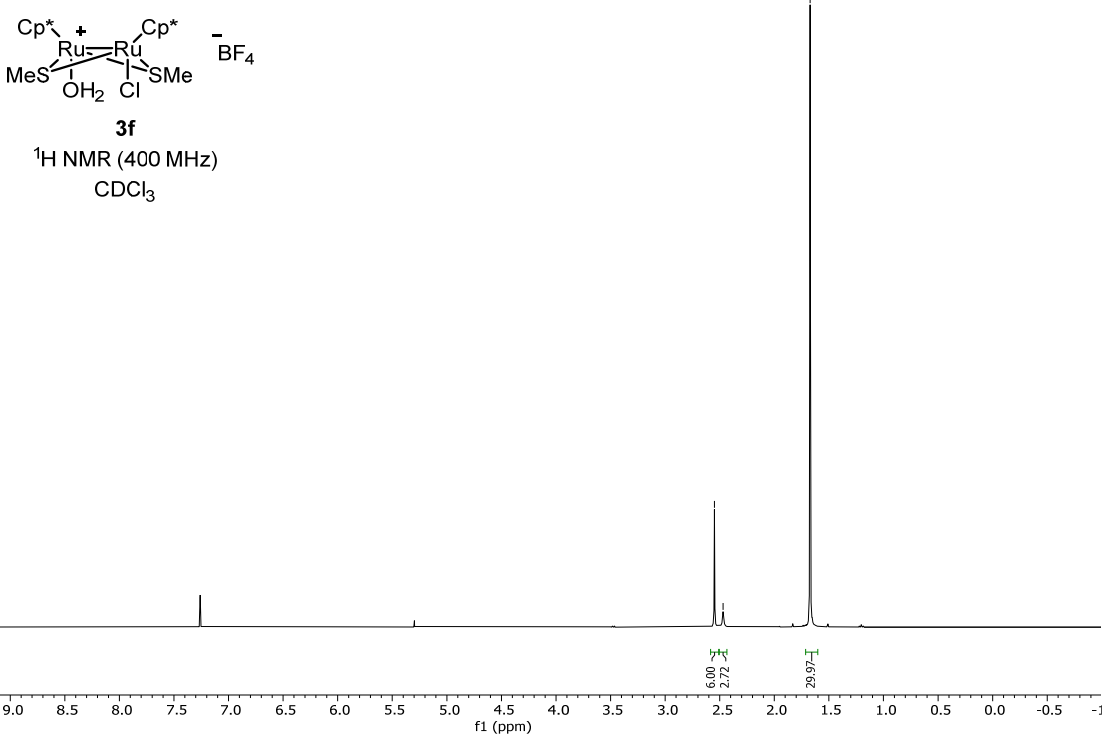


3e

^{31}P NMR (162 MHz)

$CDCl_3$

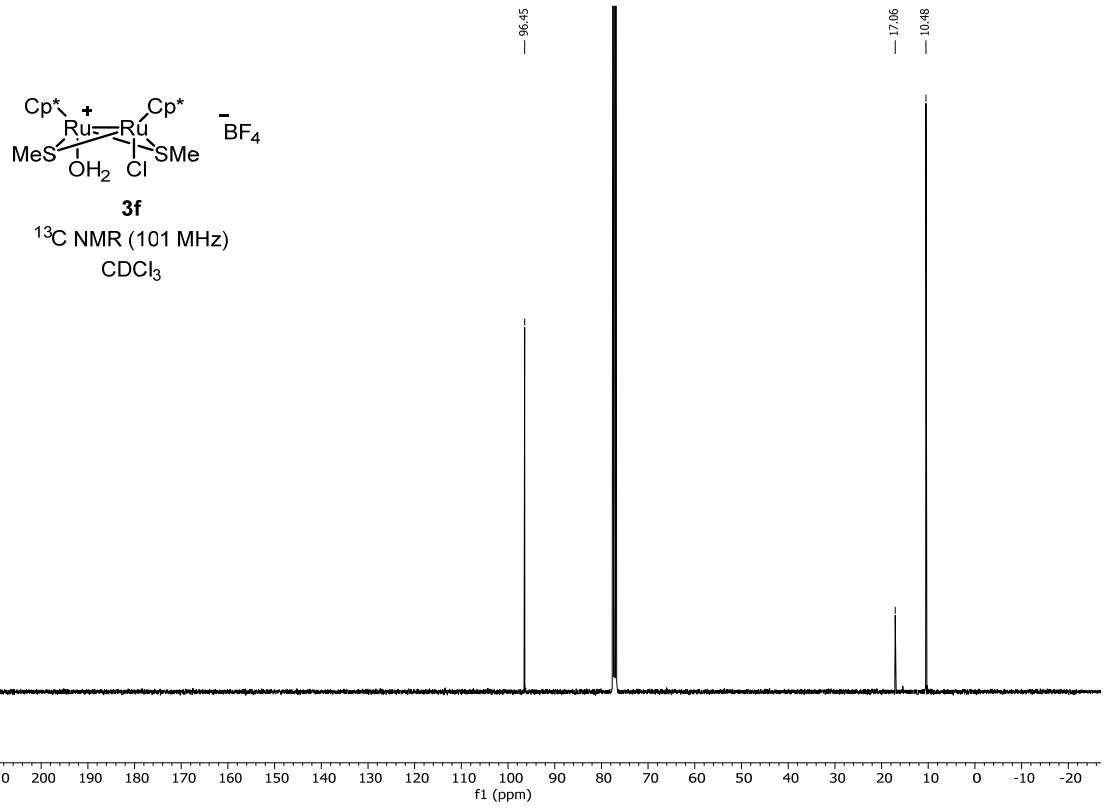




3f

^{1}H NMR (400 MHz)

$CDCl_3$



3f

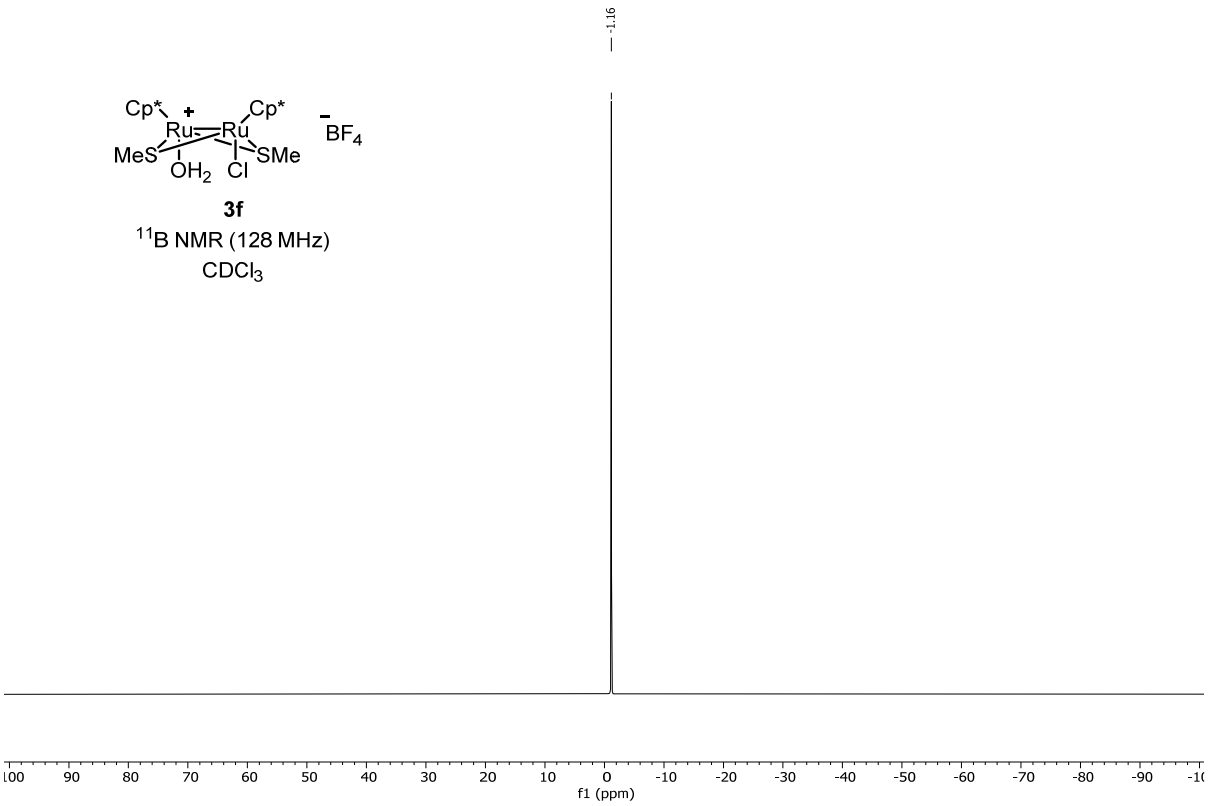
^{13}C NMR (101 MHz)

$CDCl_3$

3f

^{11}B NMR (128 MHz)

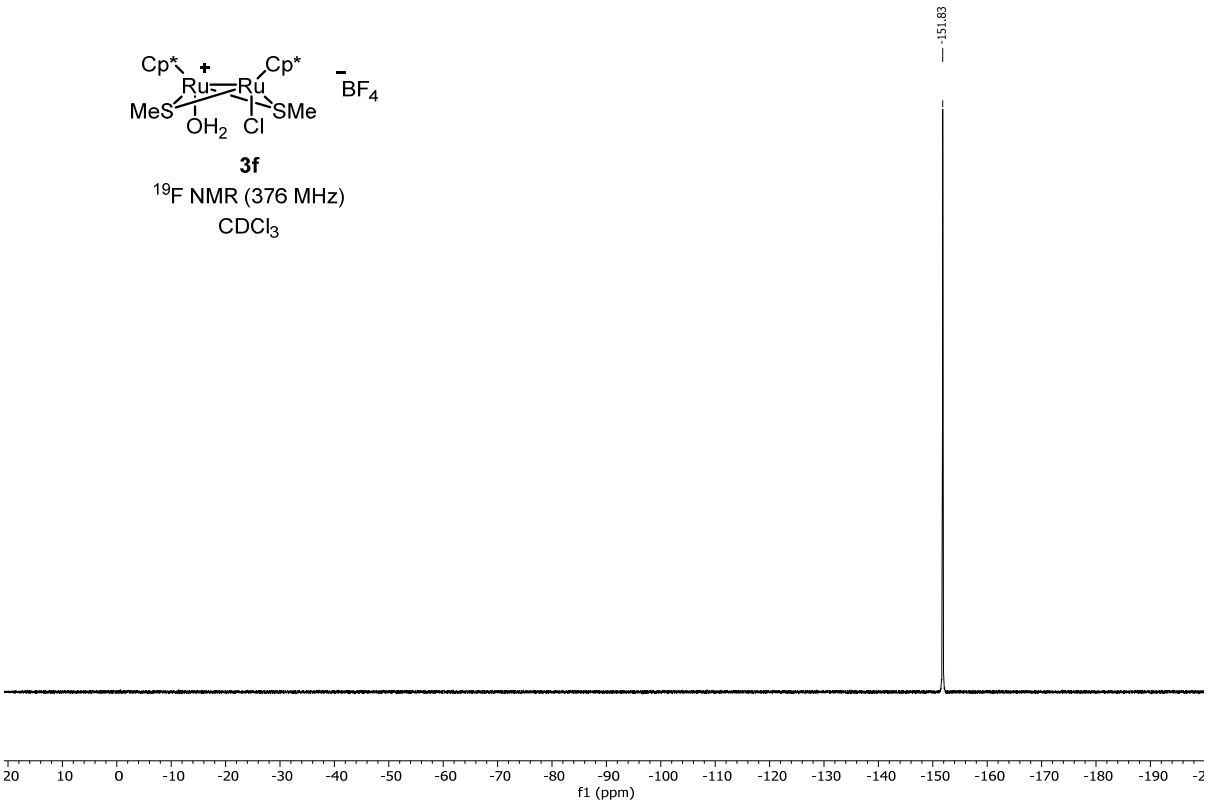
$CDCl_3$

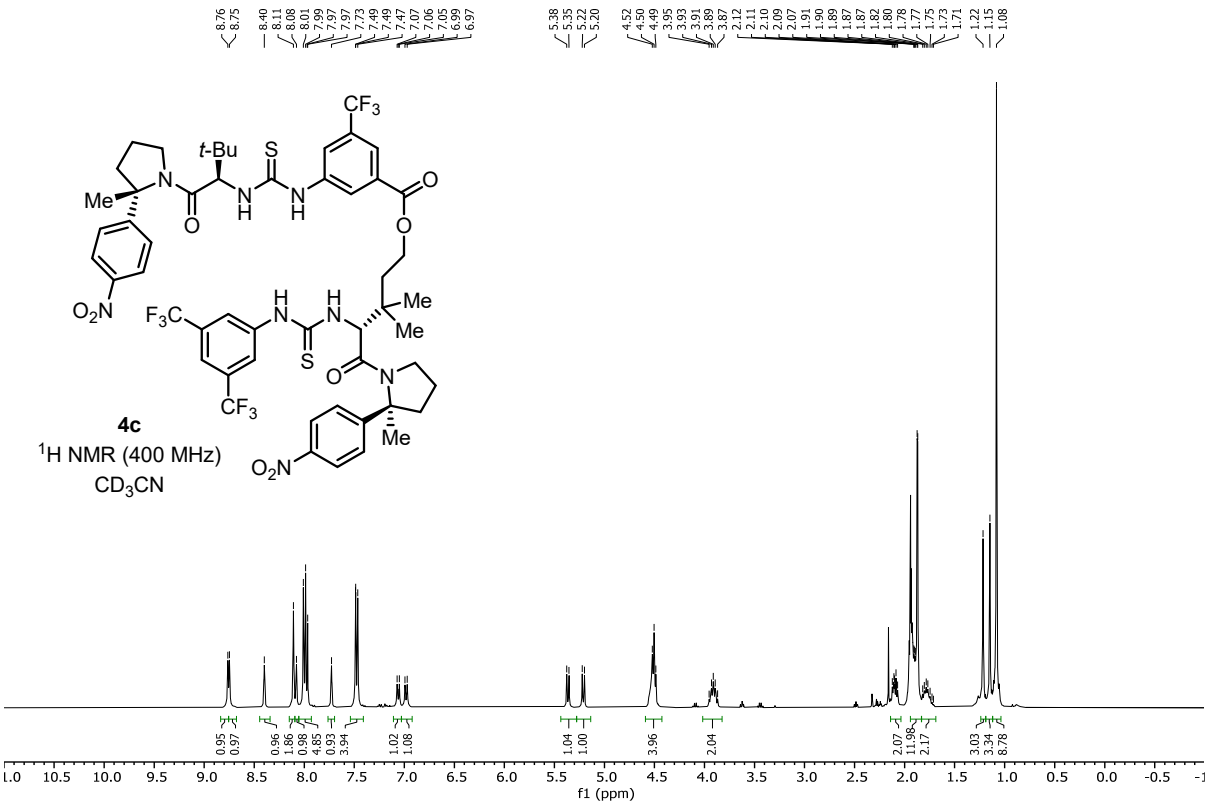


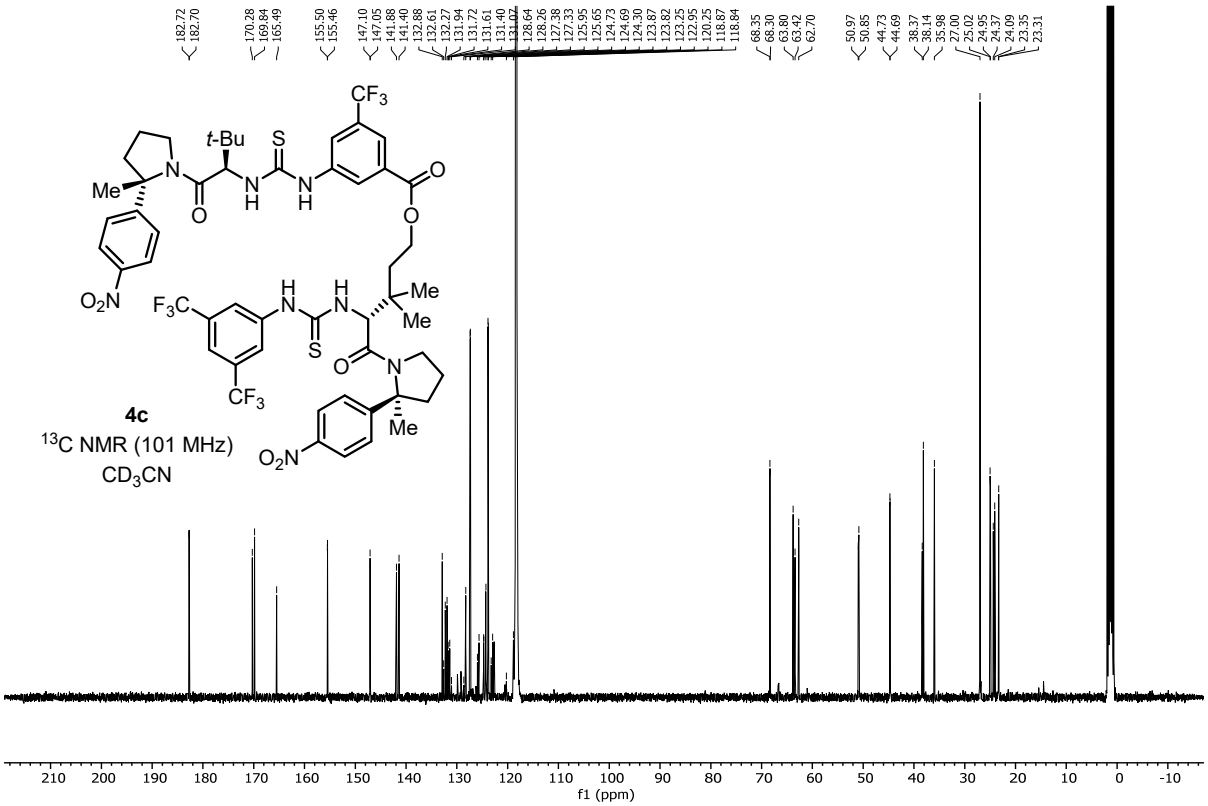
3f

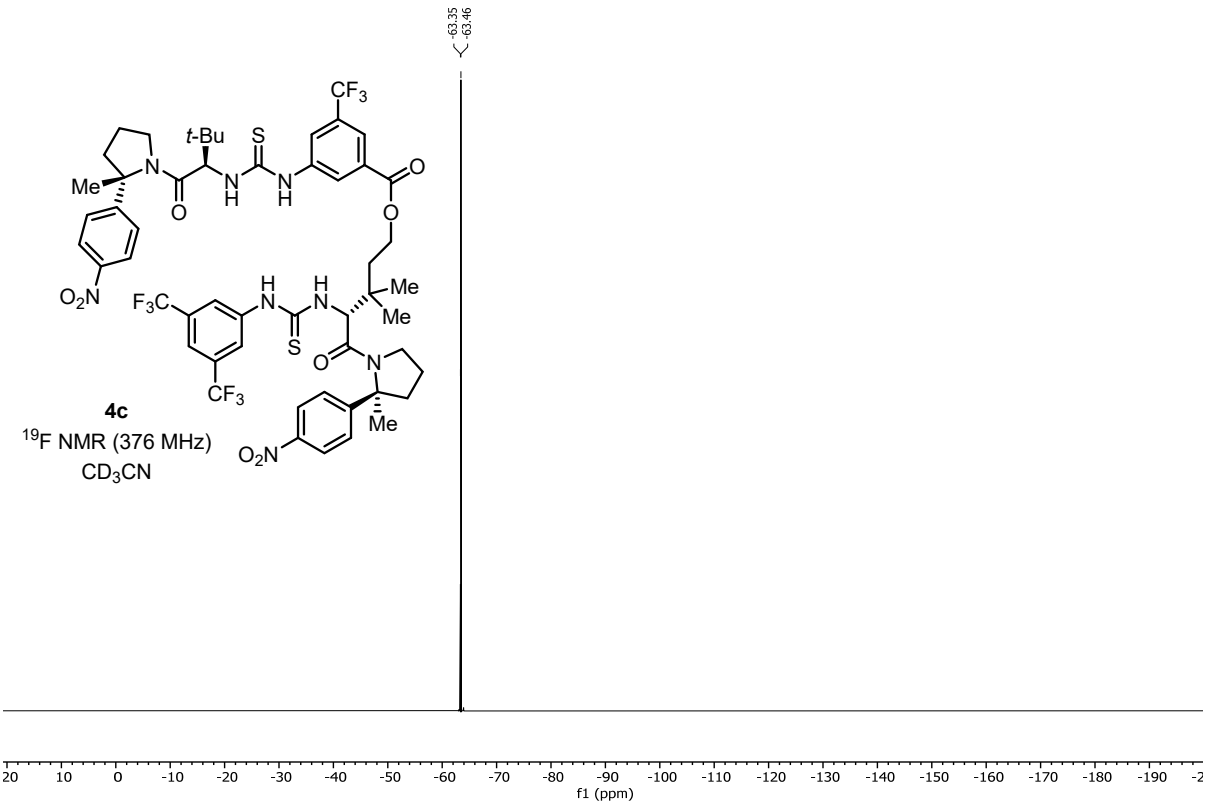
^{19}F NMR (376 MHz)

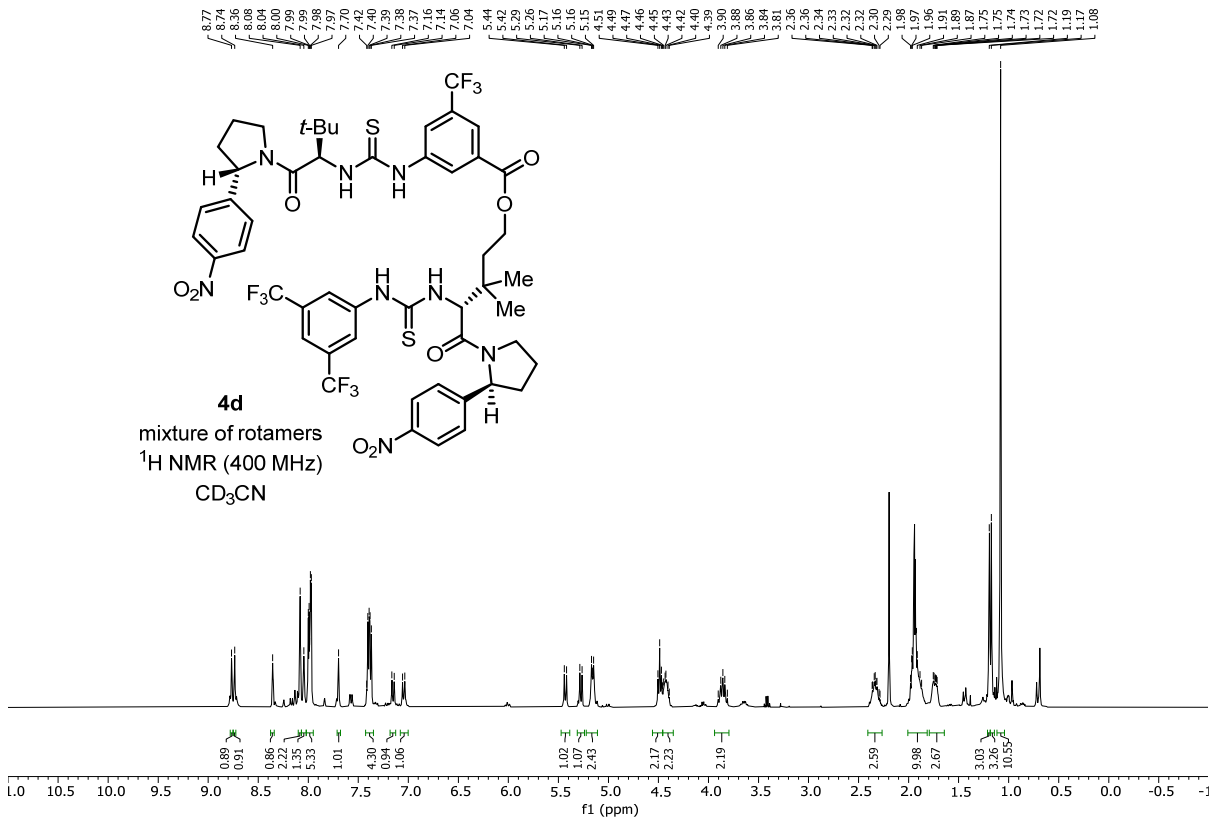
$CDCl_3$

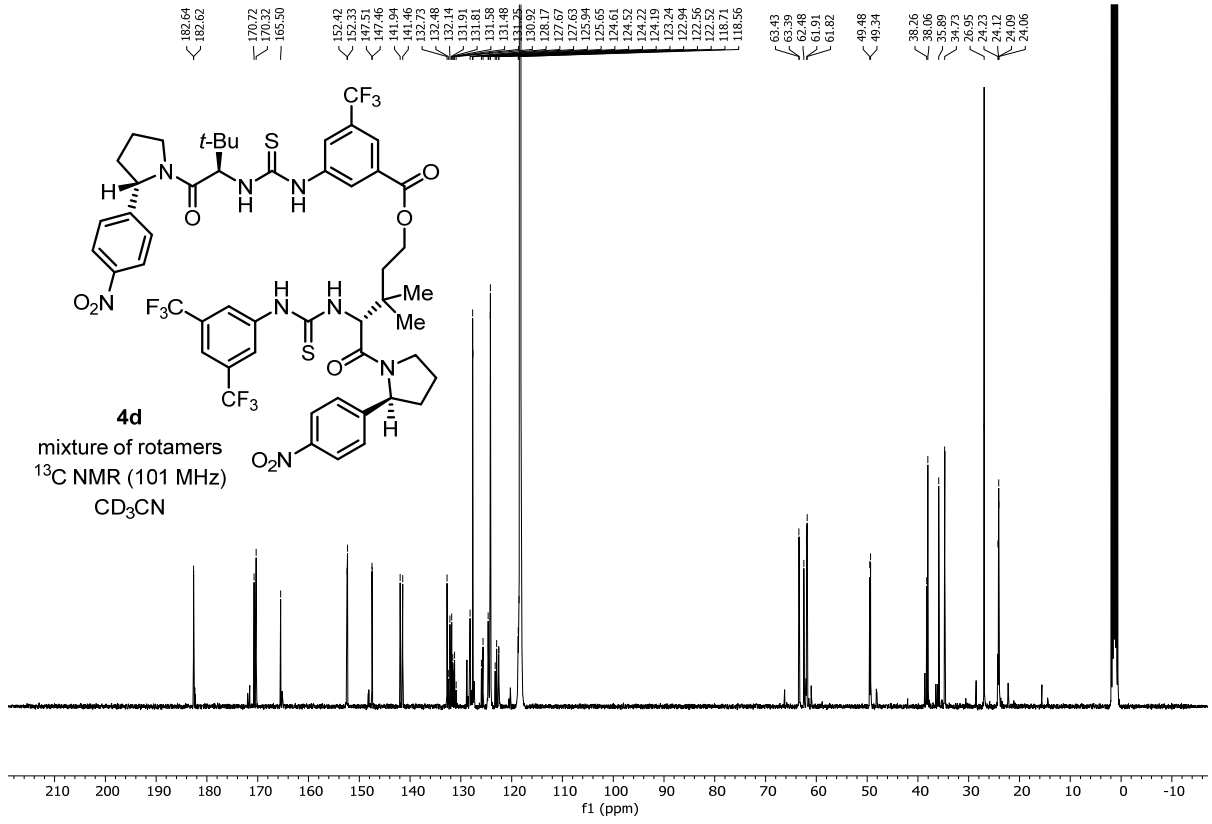


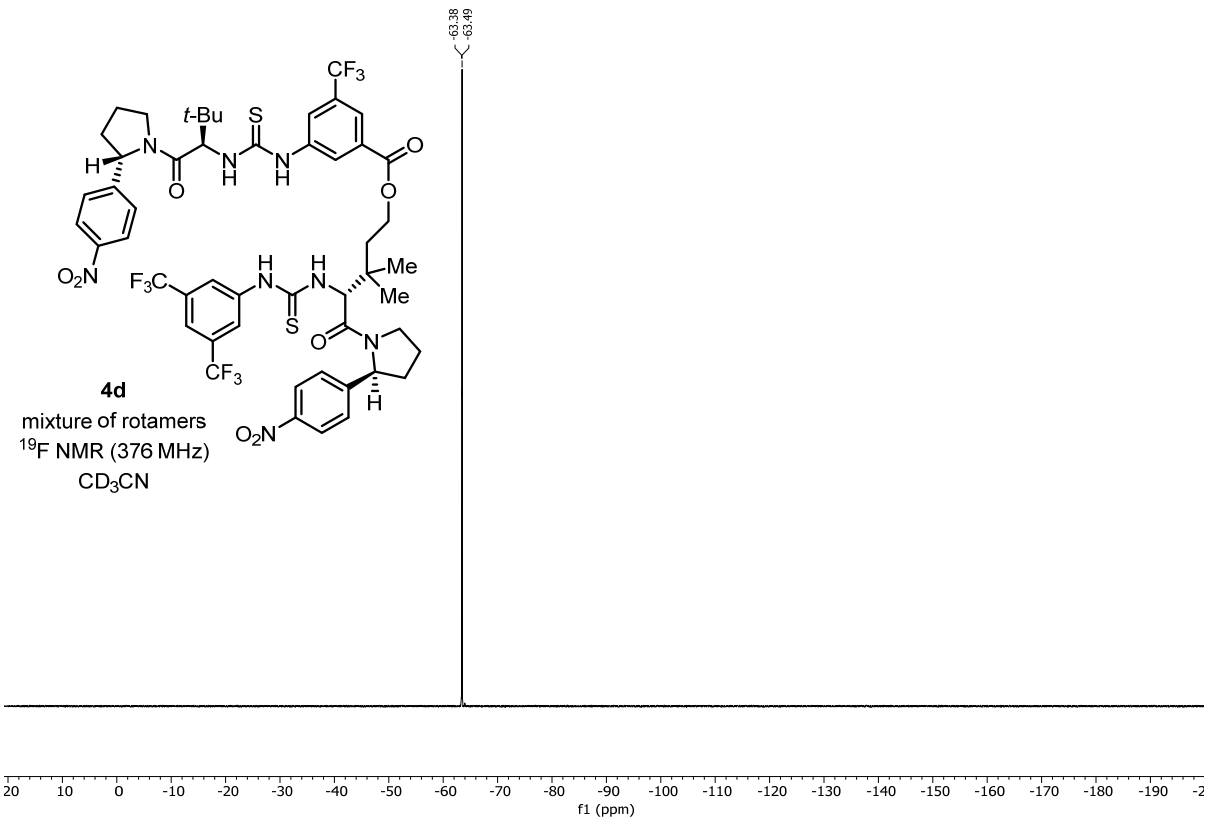

4c
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)

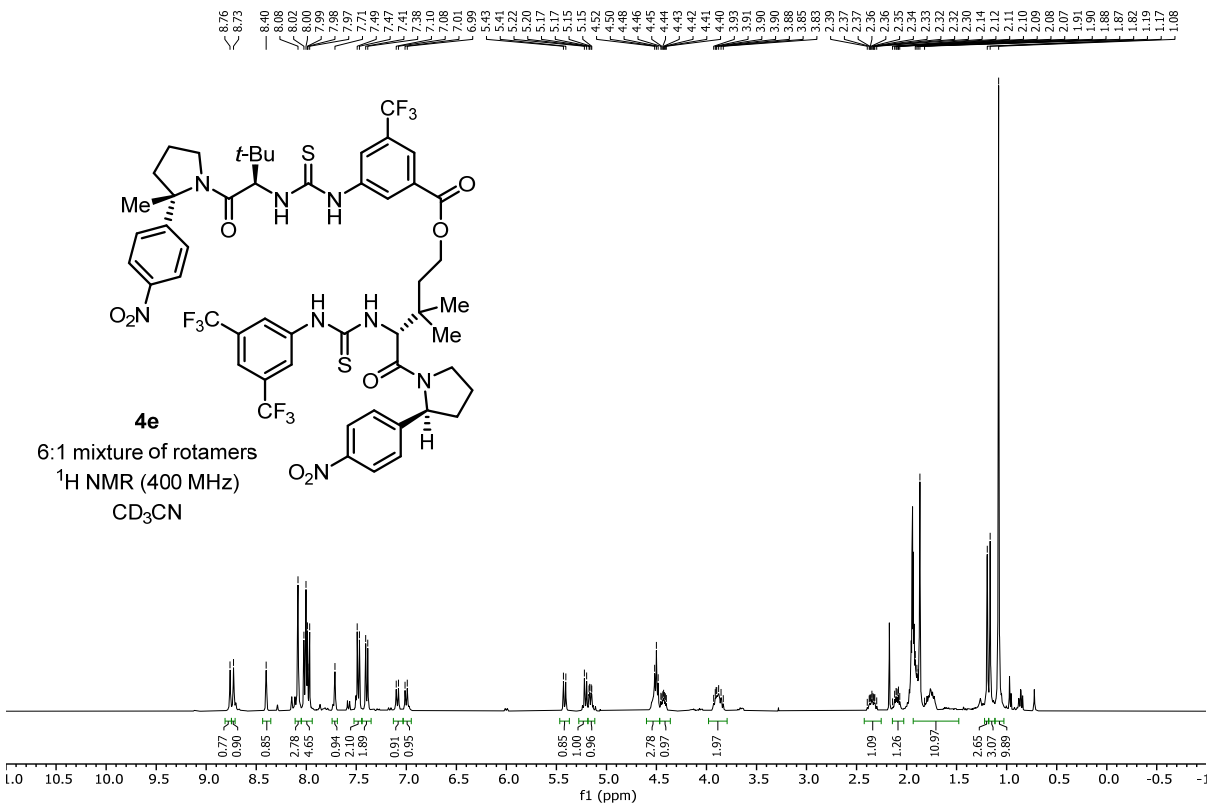

4c
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)

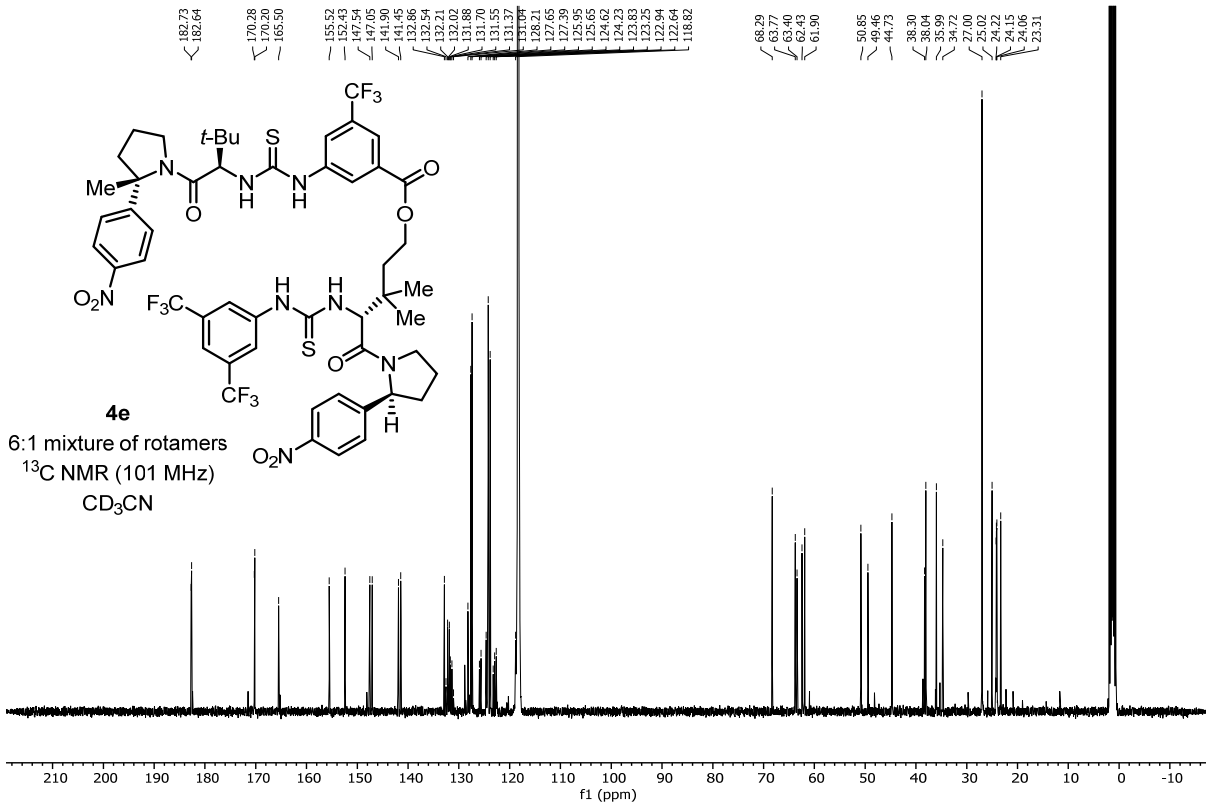

-63.35
-63.46
CF3
t-Bu
S
Me
N
N
H
N
H
O
O
O
O2N
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
O2N
4c
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

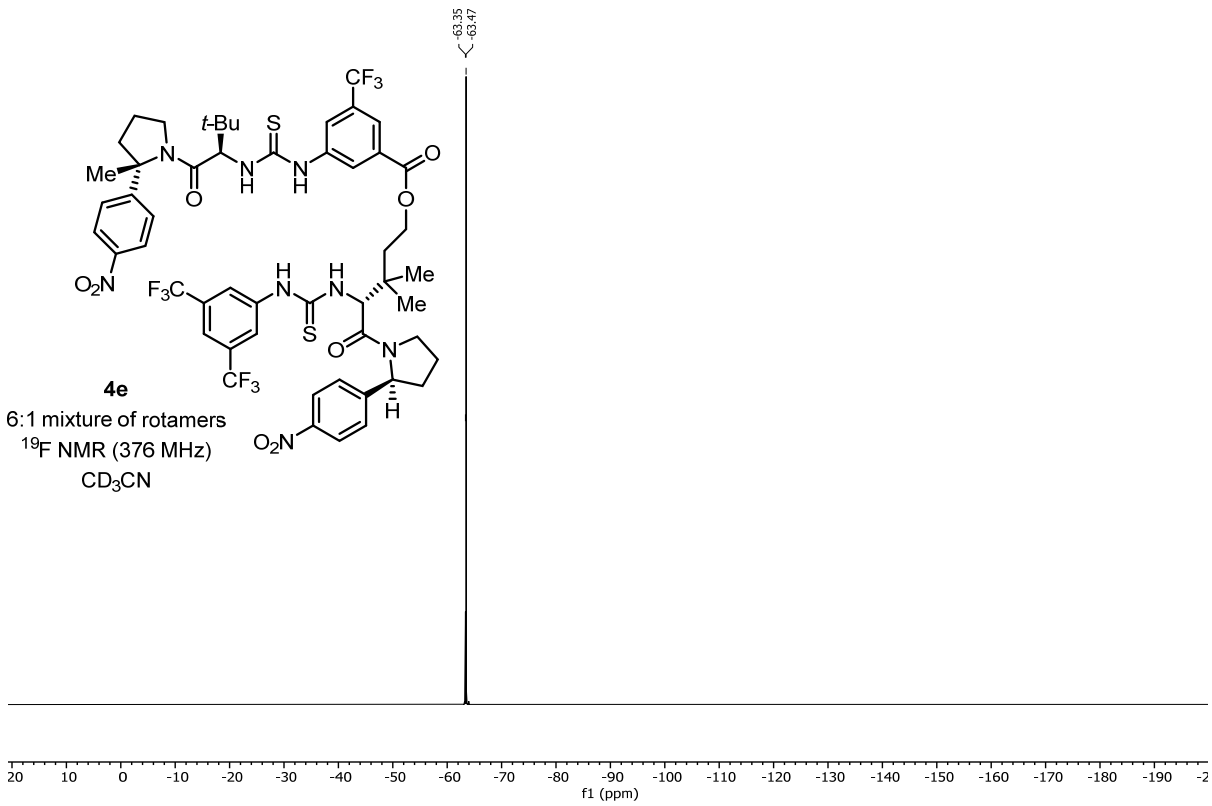

4d
mixture of rotamers
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)

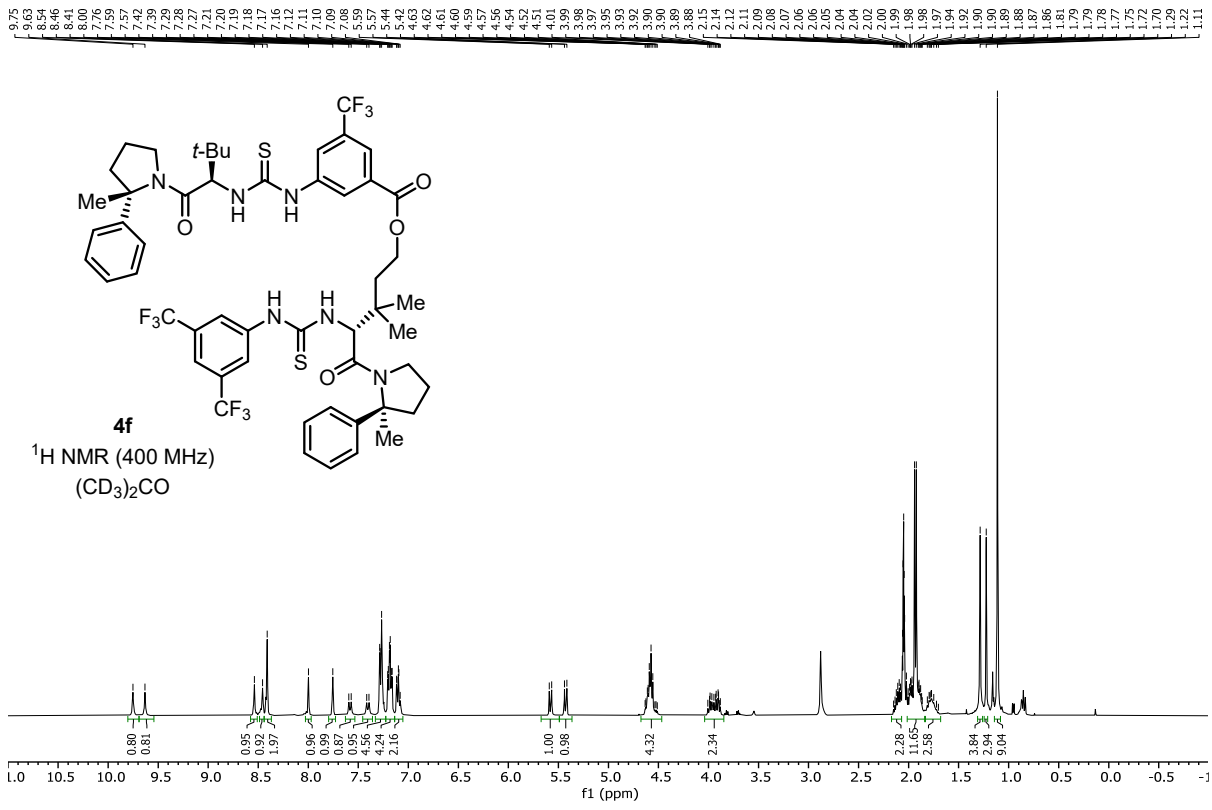

4d
mixture of rotamers
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)

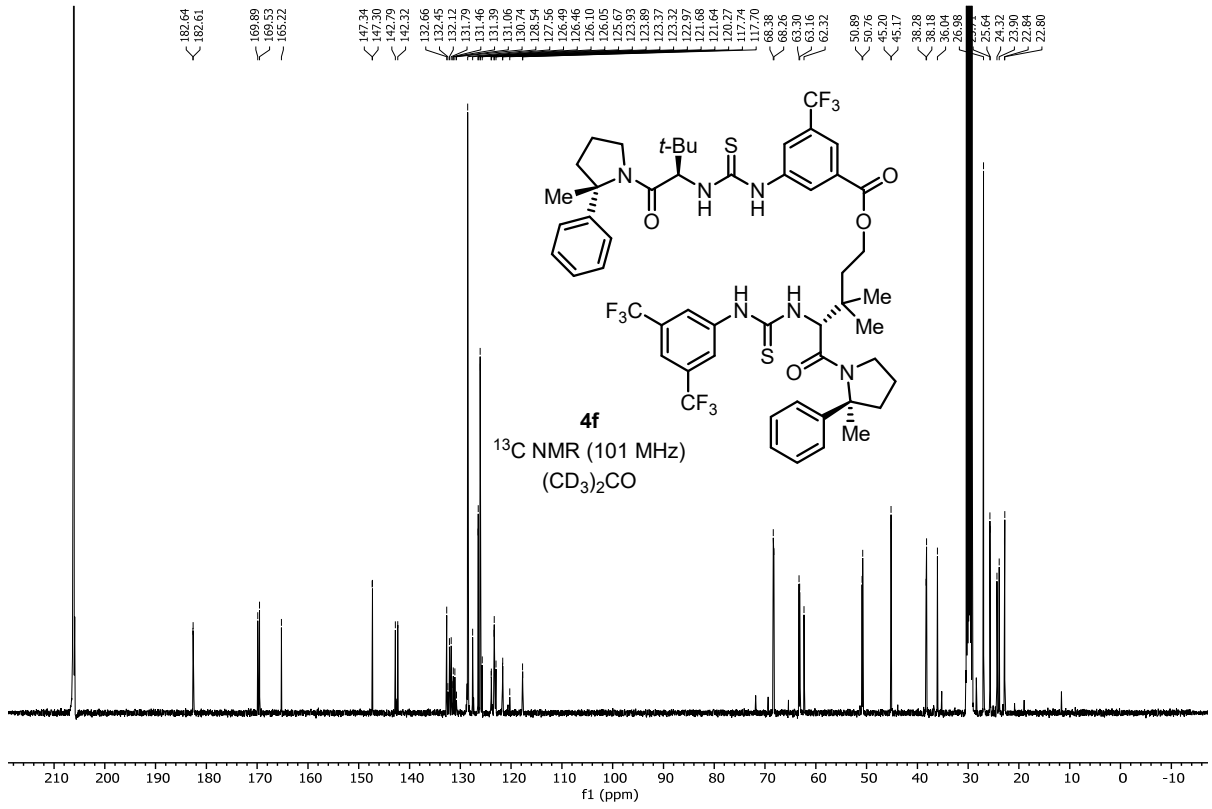

-63.38
-63.49
CF3
t-Bu
S
N
H
O
O2N
F3C
Me
Me
CF3
4d
mixture of rotamers
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

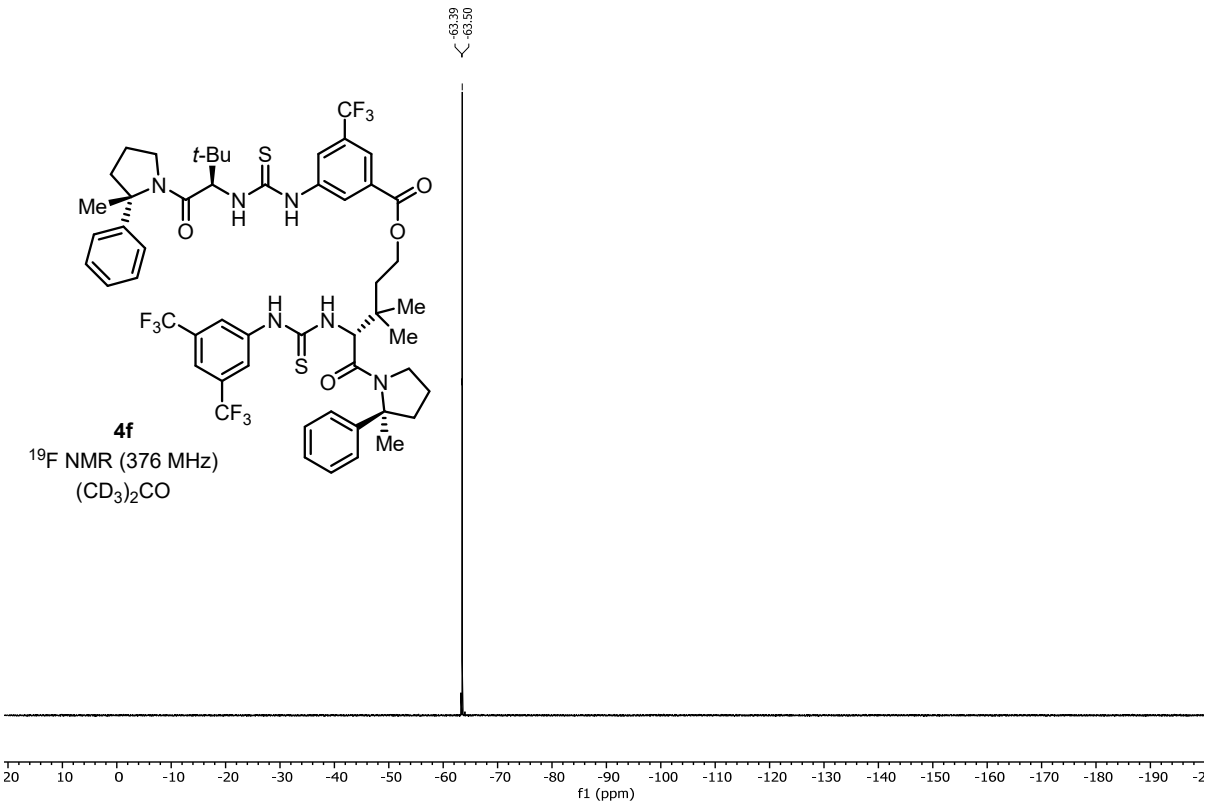

4e
6:1 mixture of rotamers
1H NMR (400 MHz)
CD3CN
f1 (ppm)

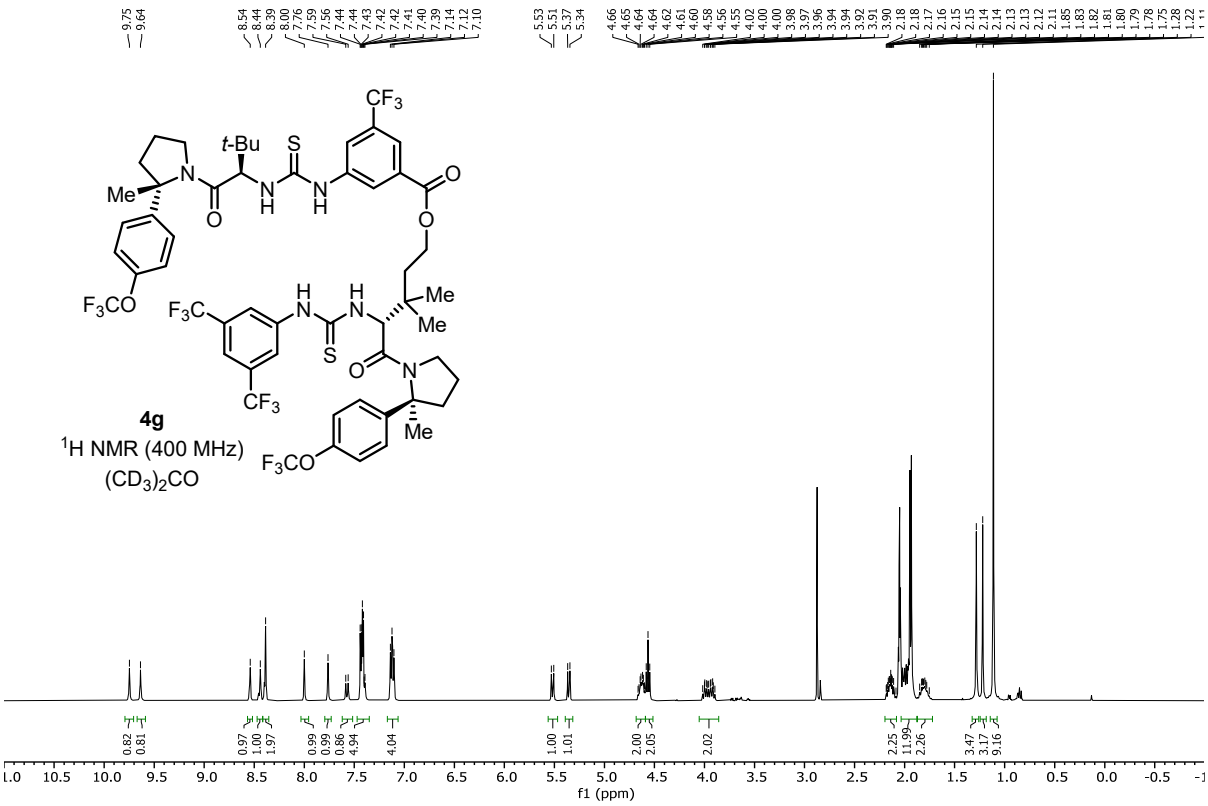

4e
6:1 mixture of rotamers
13C NMR (101 MHz)
CD3CN
f1 (ppm)

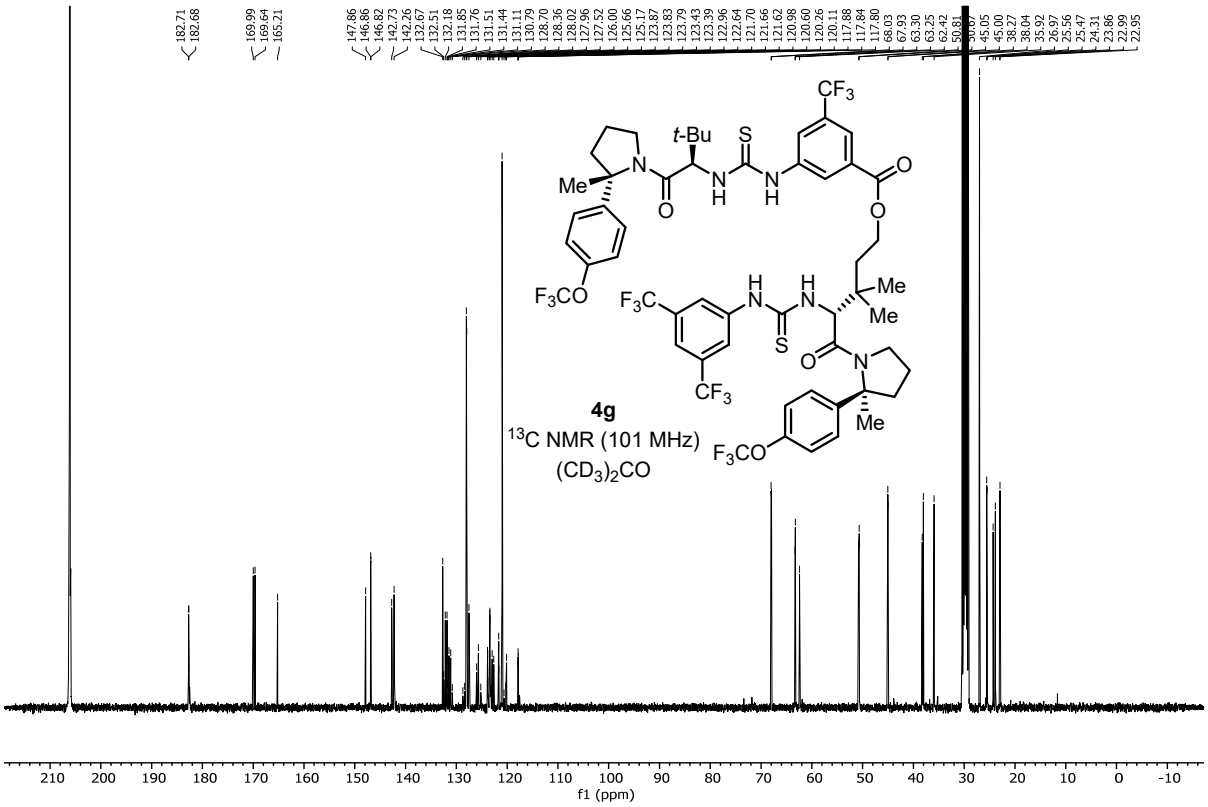

-63.35
-63.47
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
O2N
F3C
H
N
H
N
Me
Me
S
O
N
CF3
H
O2N
4e
6:1 mixture of rotamers
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

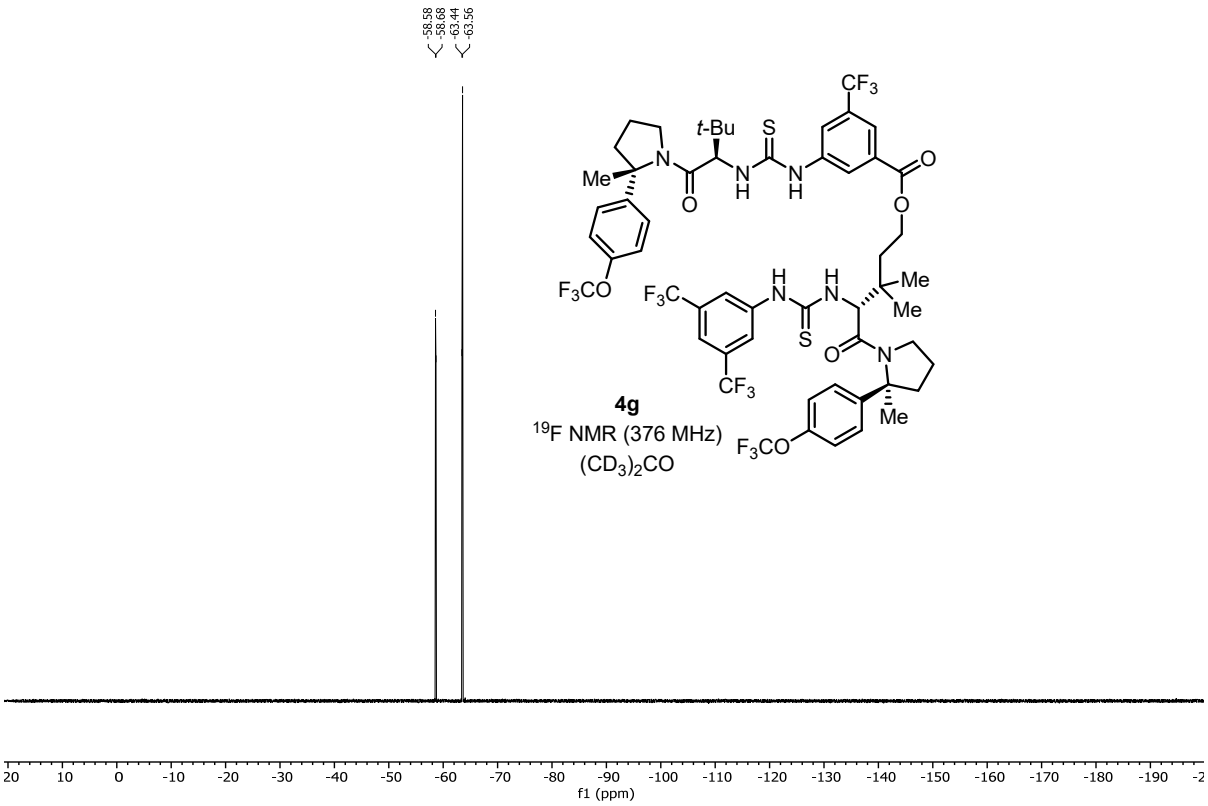

4f
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

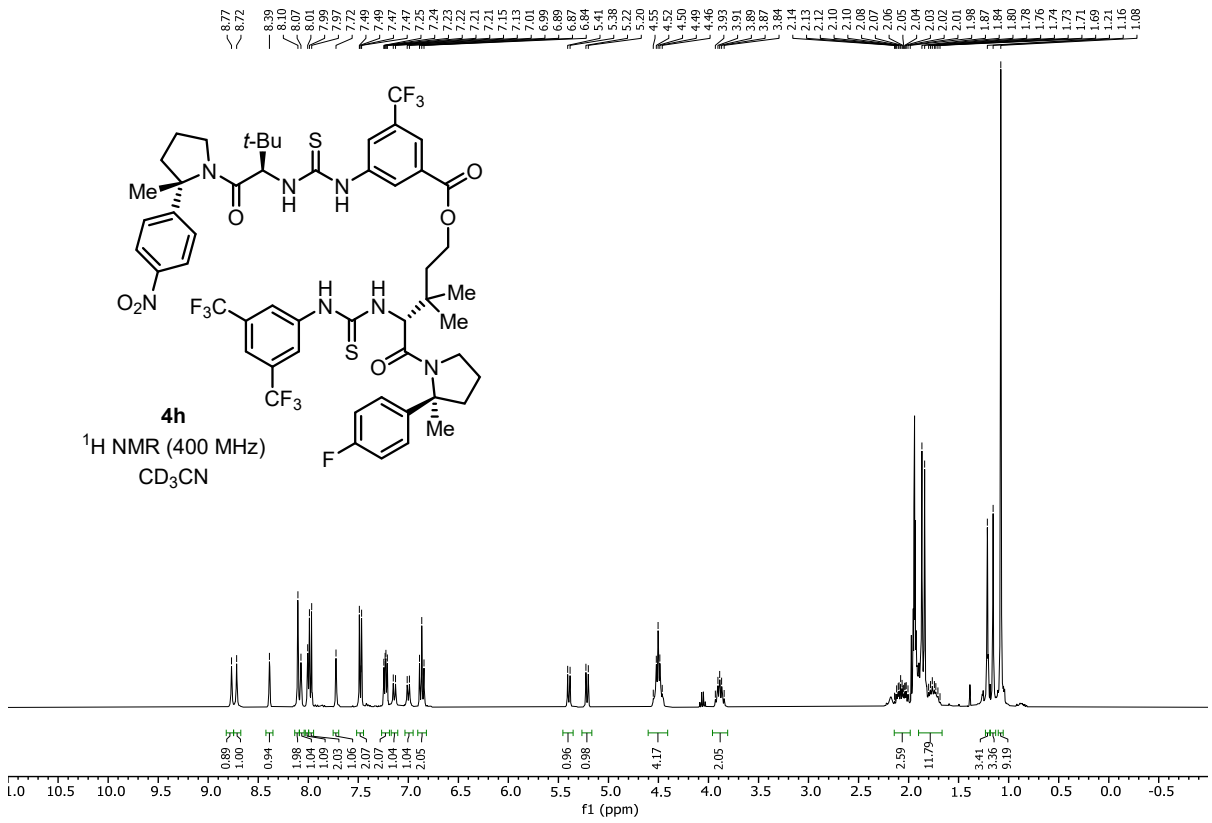

4f
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

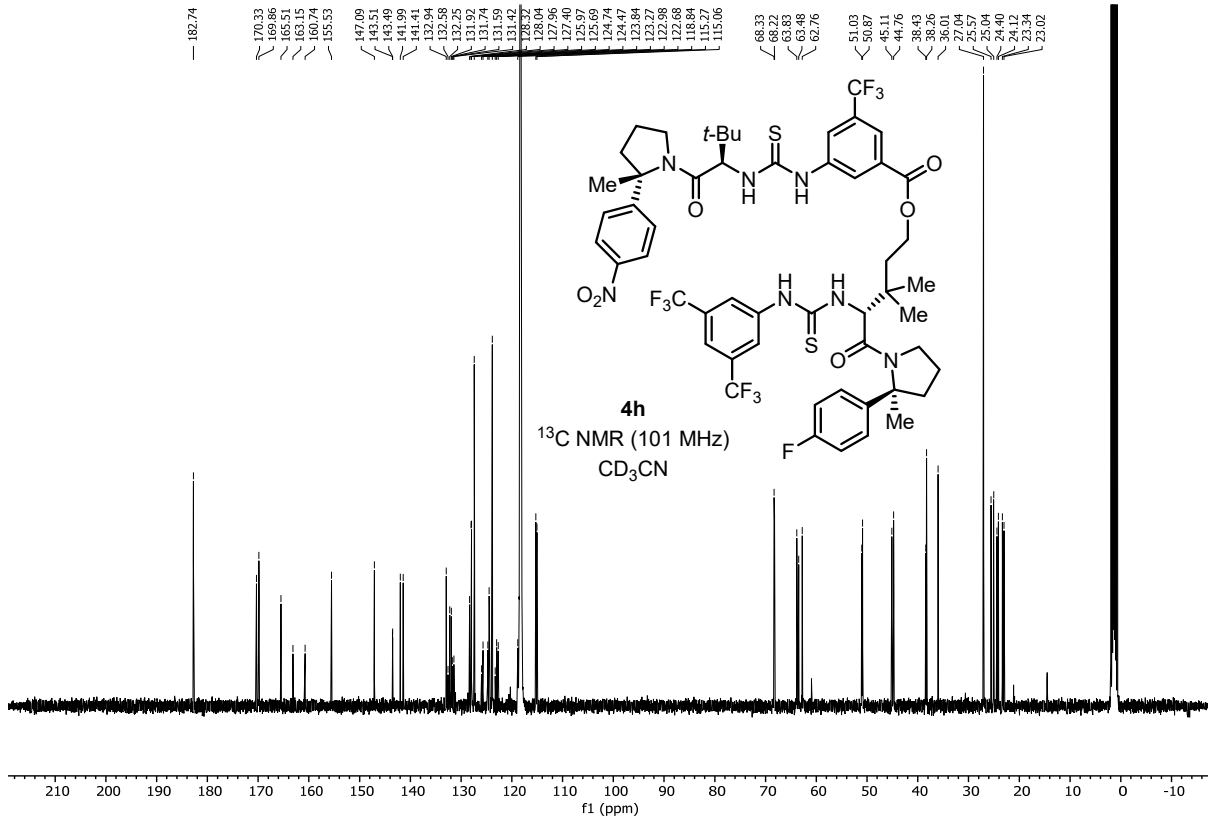

-63.39
-63.50
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
4f
19F NMR (376 MHz)
(CD3)2CO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

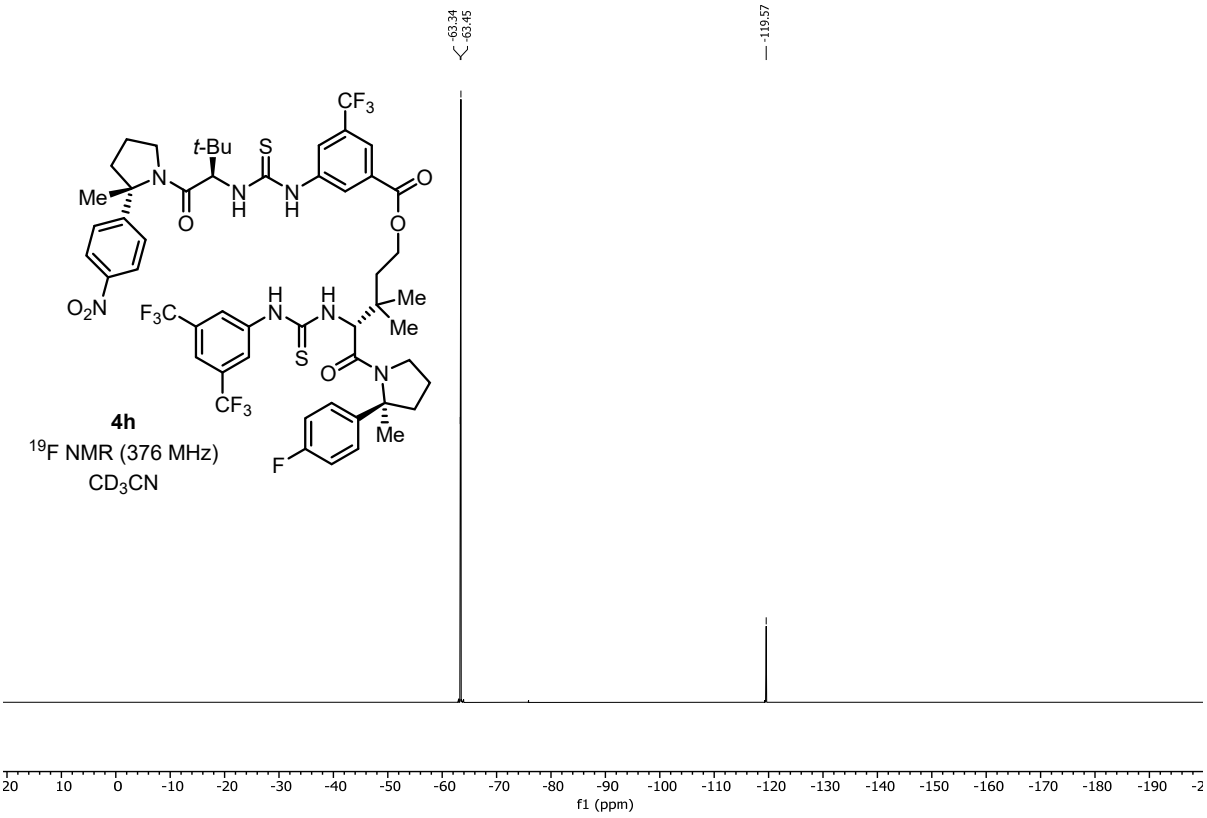

4g
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

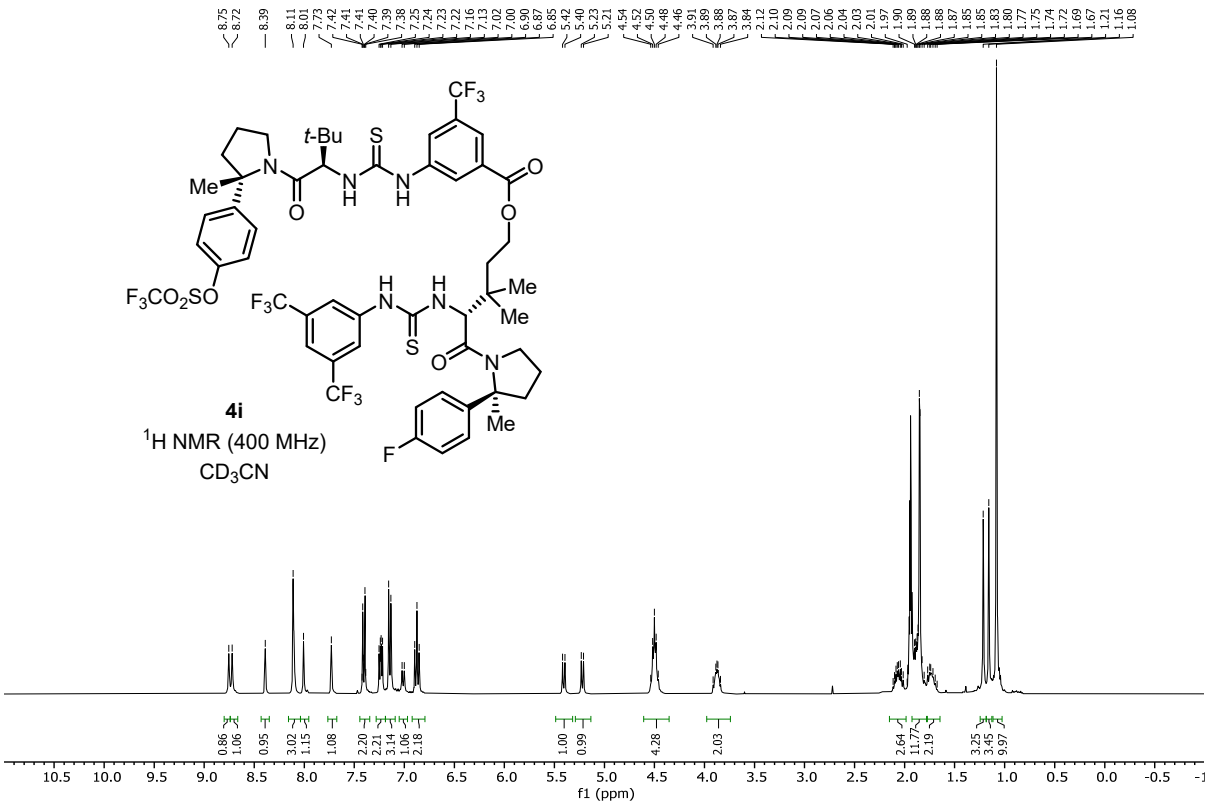

4g
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

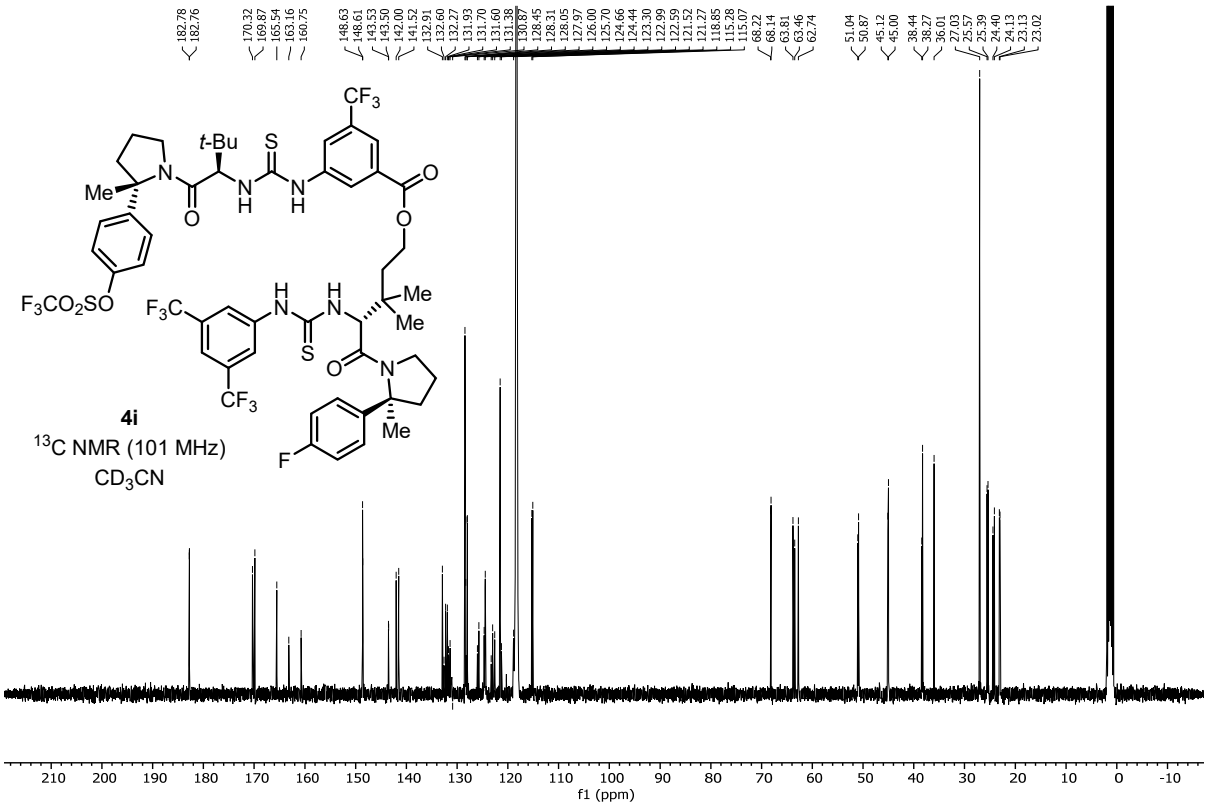

-58.58
-58.68
-63.44
-63.56
CF3
t-Bu
S
N
Me
O
N
H
N
H
O
O
F3CO
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F3CO
4g
19F NMR (376 MHz)
(CD3)2CO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

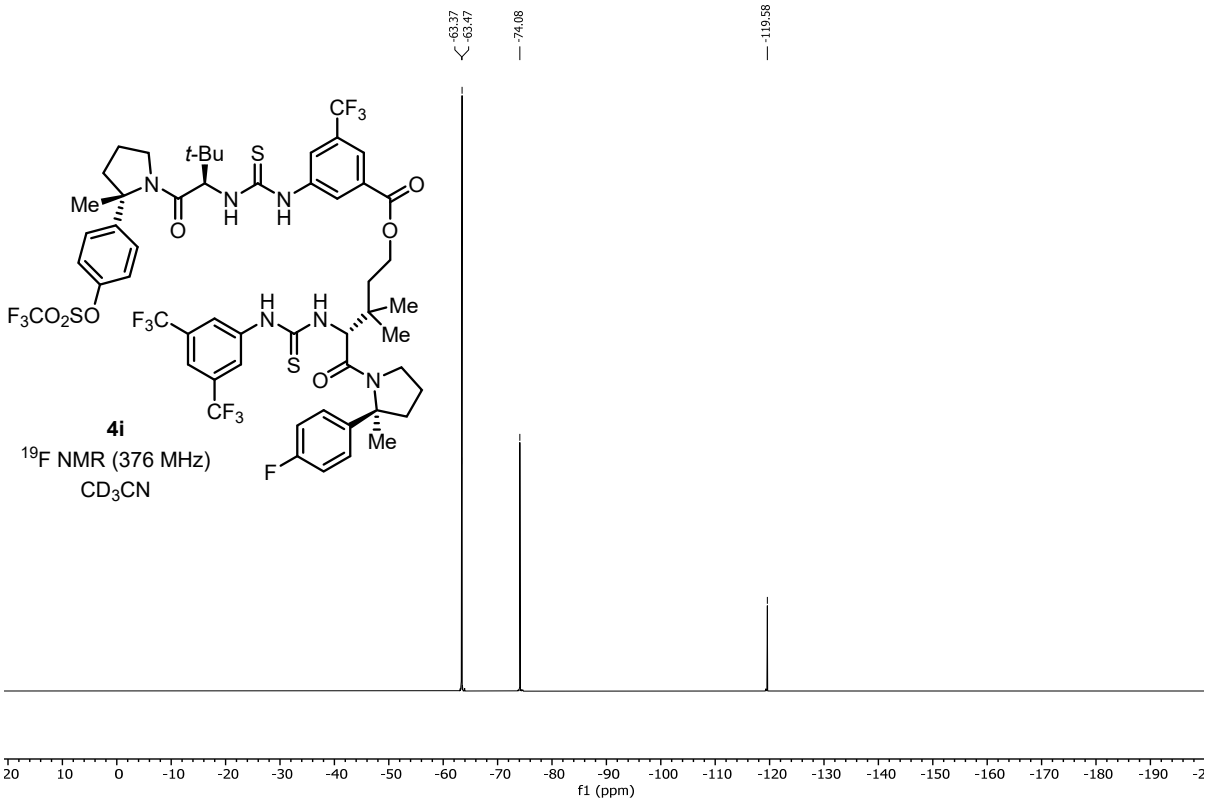

4h
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)

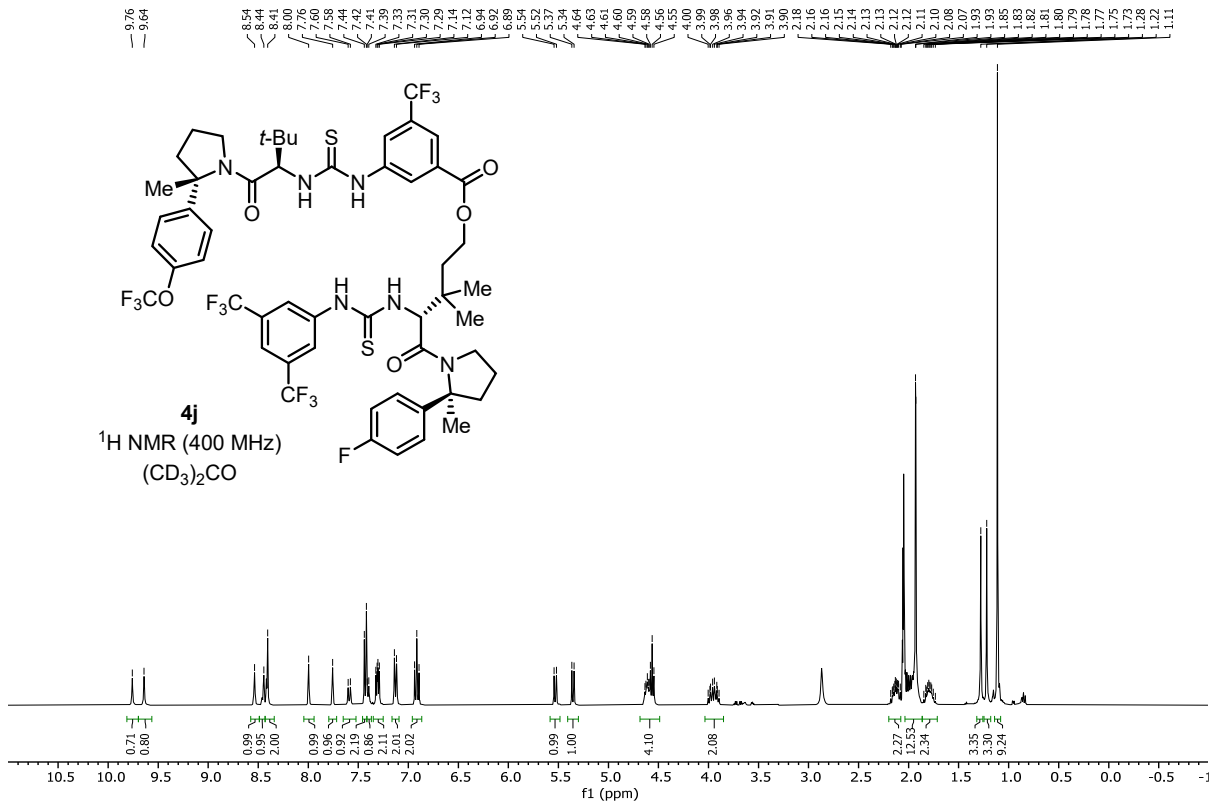

4h
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)

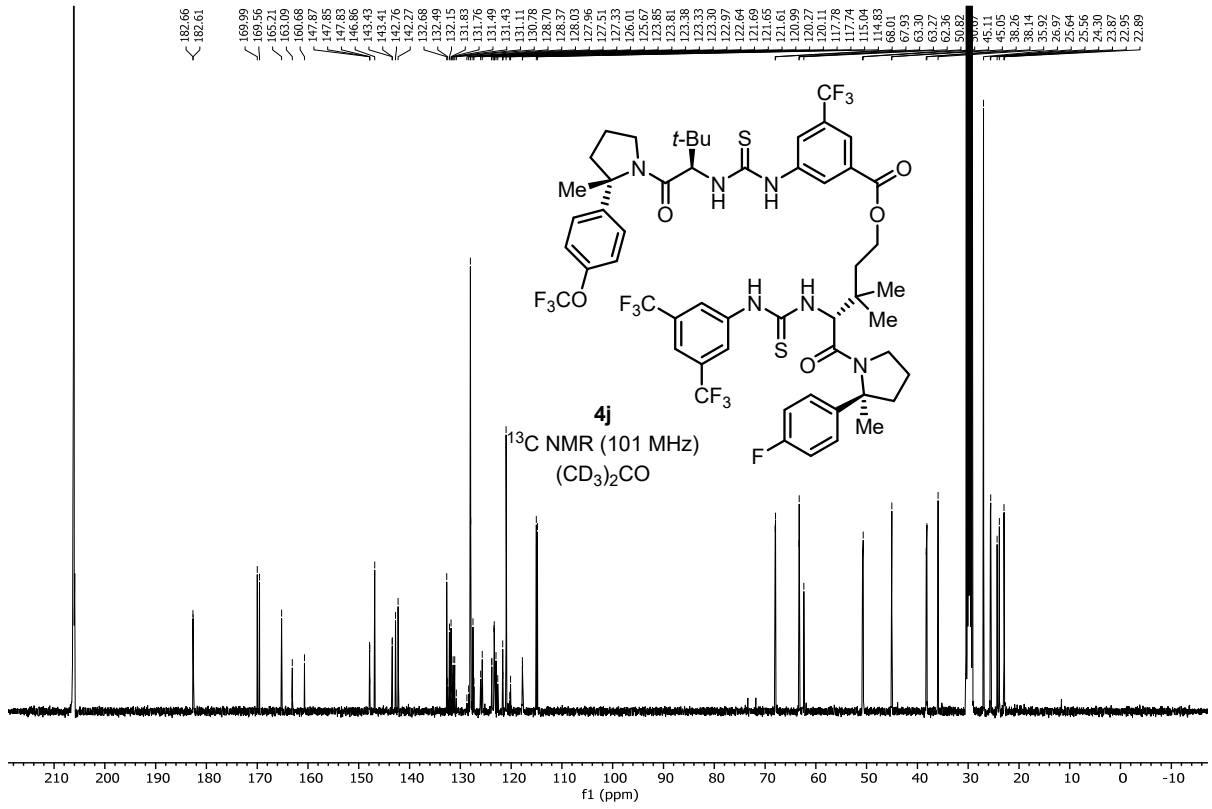

-63.34
-63.45
-119.57
CF3
t-Bu
S
Me
N
N
H
N
H
O
O
O
O2N
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4h
19F NMR (376 MHz)
CD3CN
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

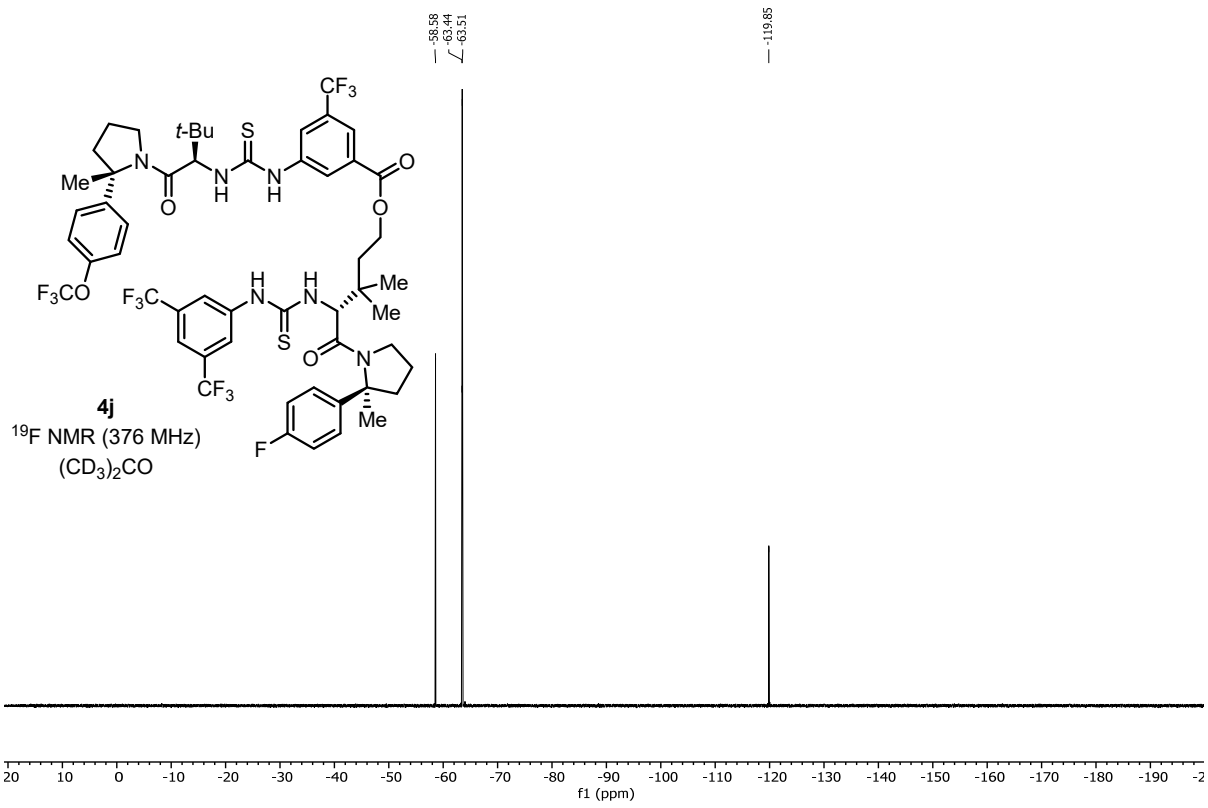

4i
1H NMR (400 MHz)
CD3CN
f1 (ppm)

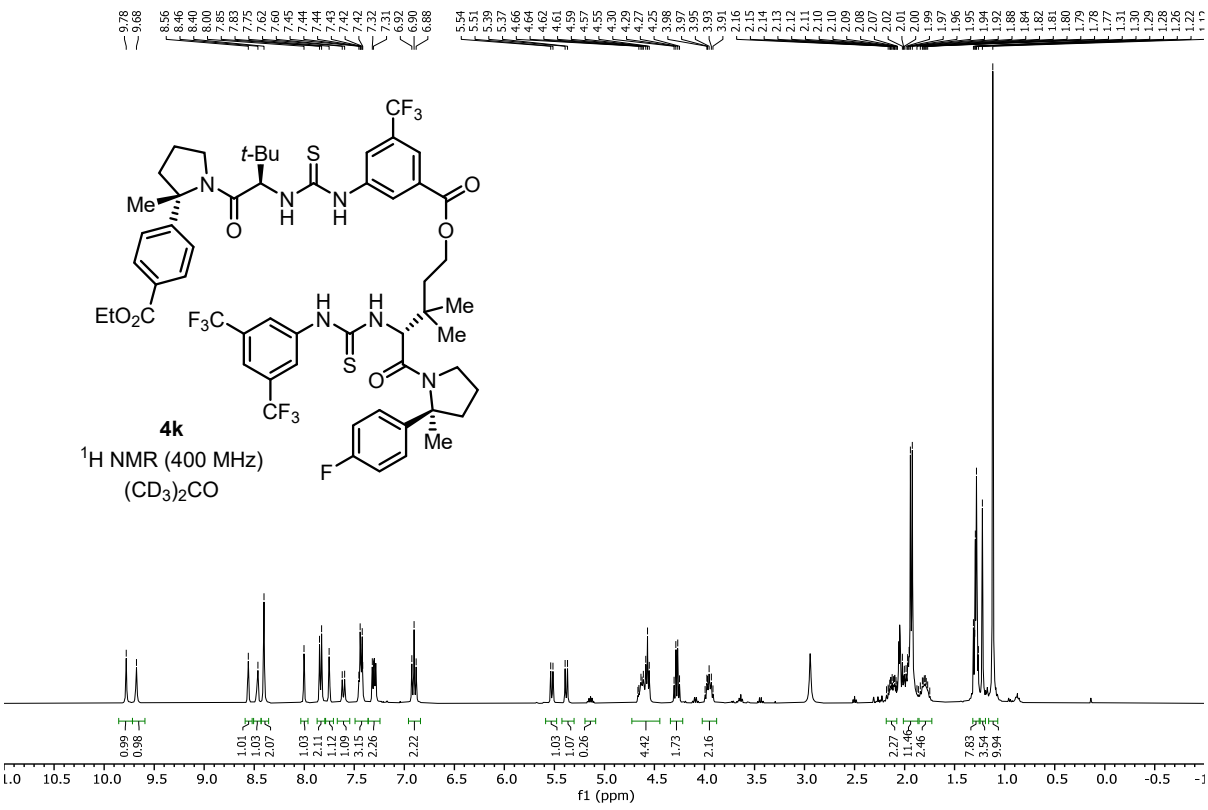

4i
13C NMR (101 MHz)
CD3CN
f1 (ppm)

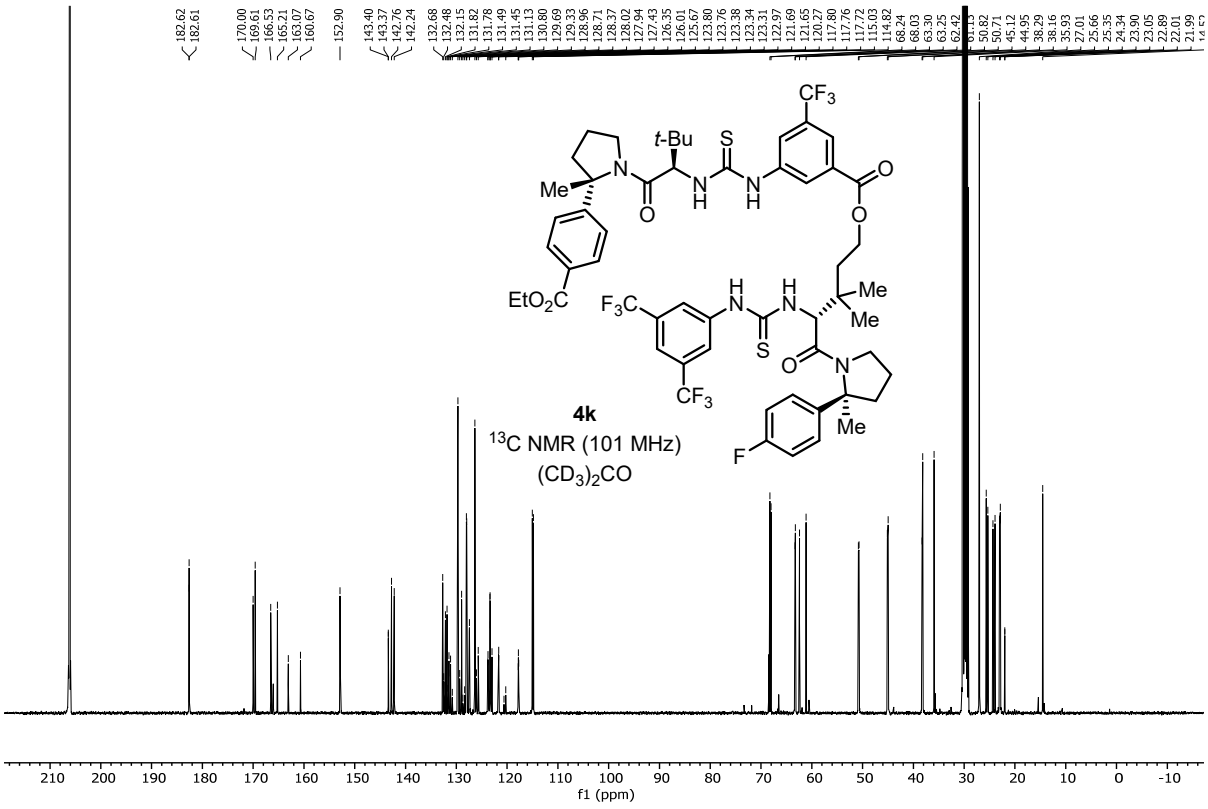

-63.37
-63.47
-74.08
-119.58
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F3CO2SO
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4i
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

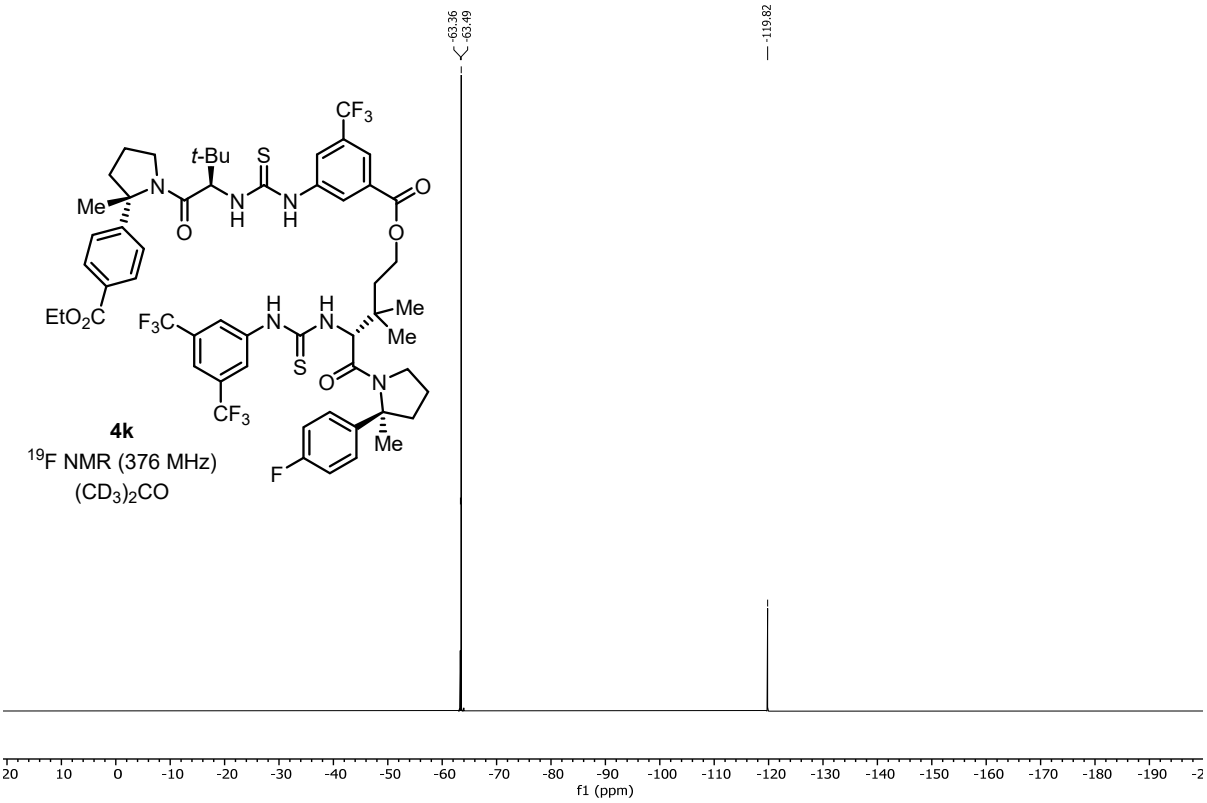

4j
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

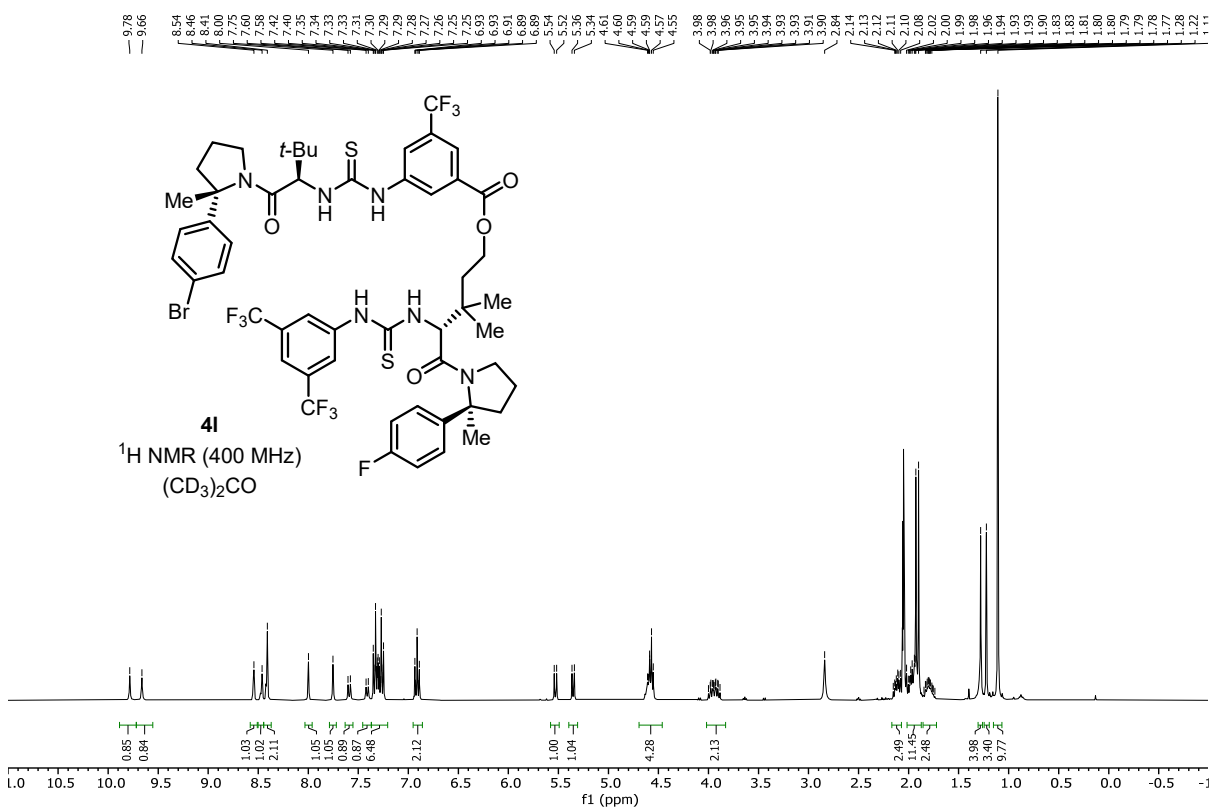

4j
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

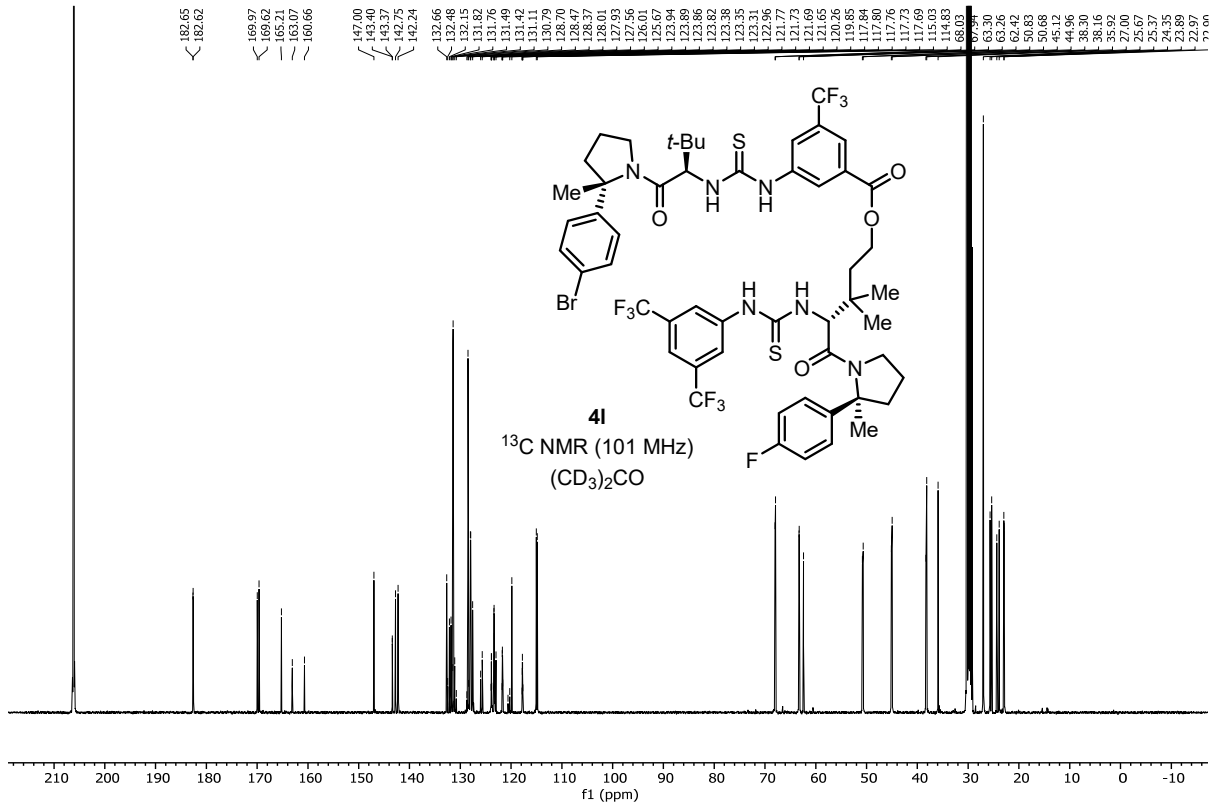

-58.58
-63.44
-63.51
-119.85
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F3CO
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4j
19F NMR (376 MHz)
(CD3)2CO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

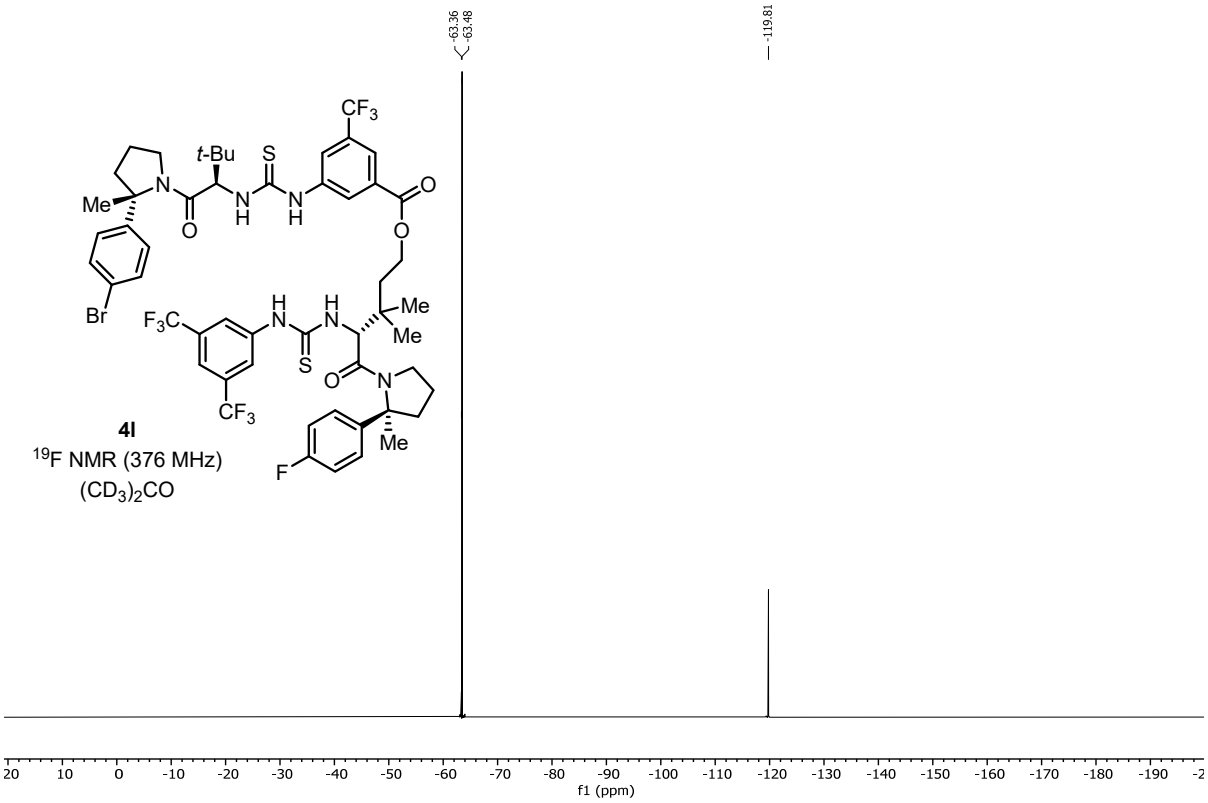

4k
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)


4k
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)


-63.36
-63.49
-119.82
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
EtO2C
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4k
19F NMR (376 MHz)
(CD3)2CO
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


4l
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

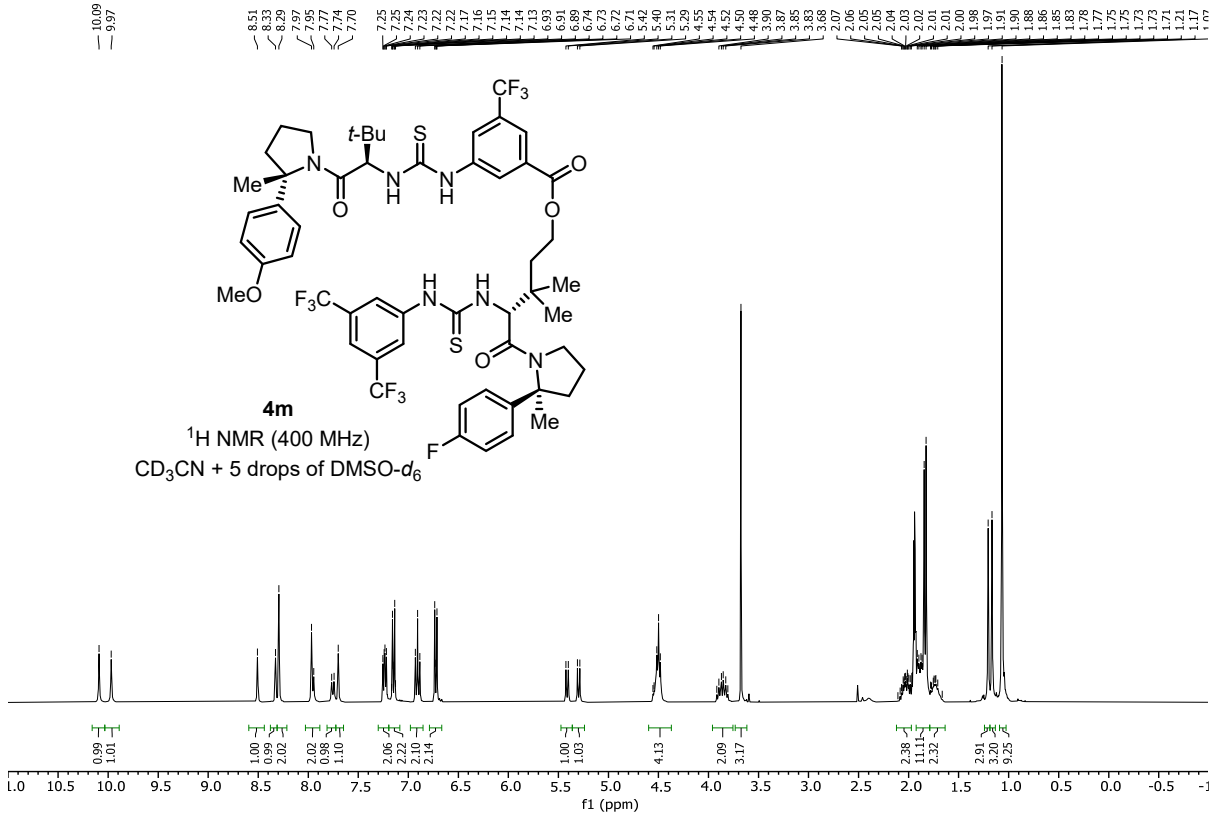

4l
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

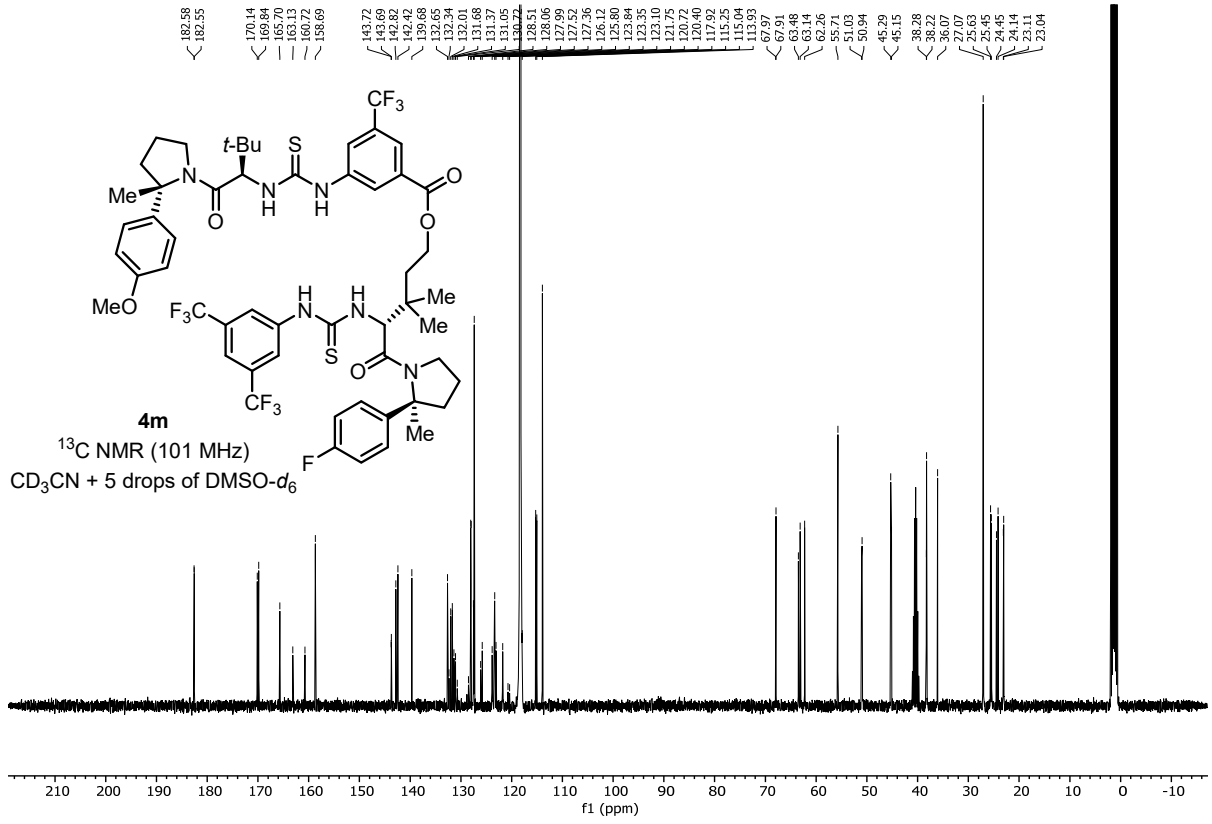


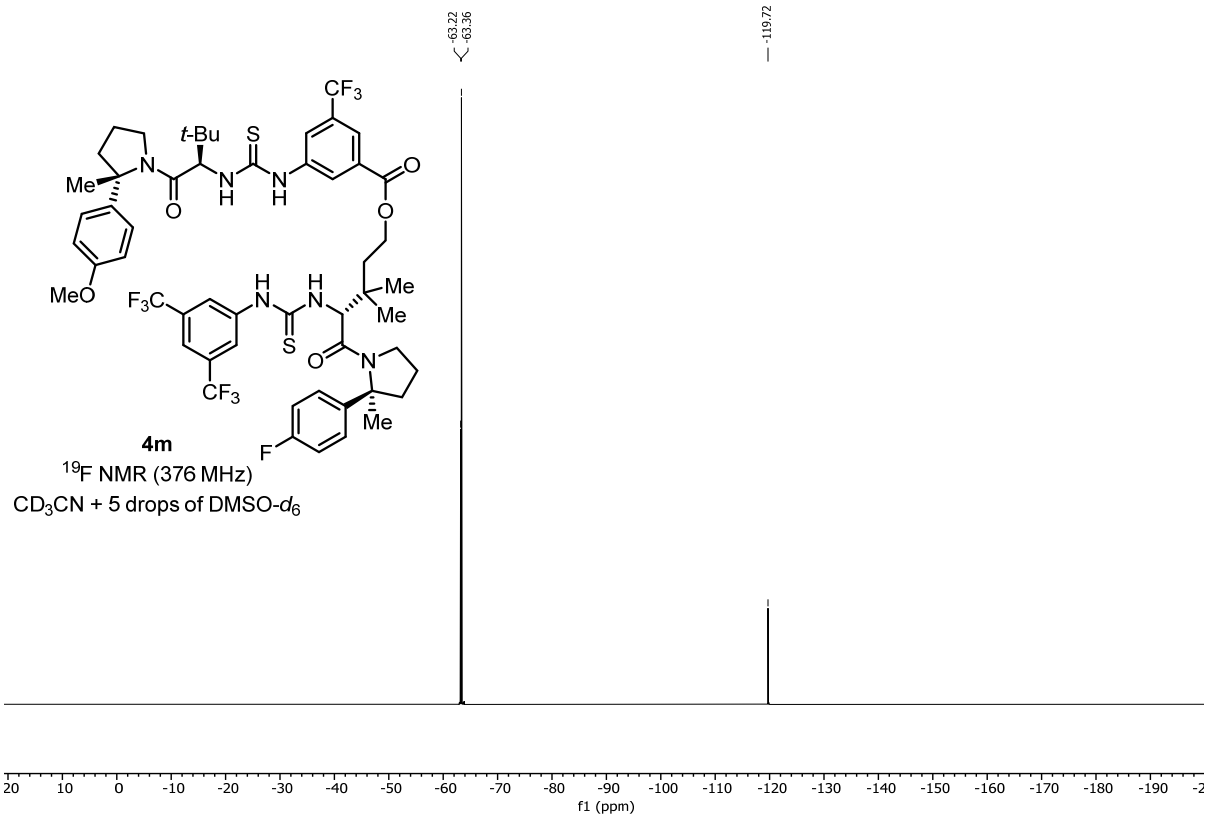
4l

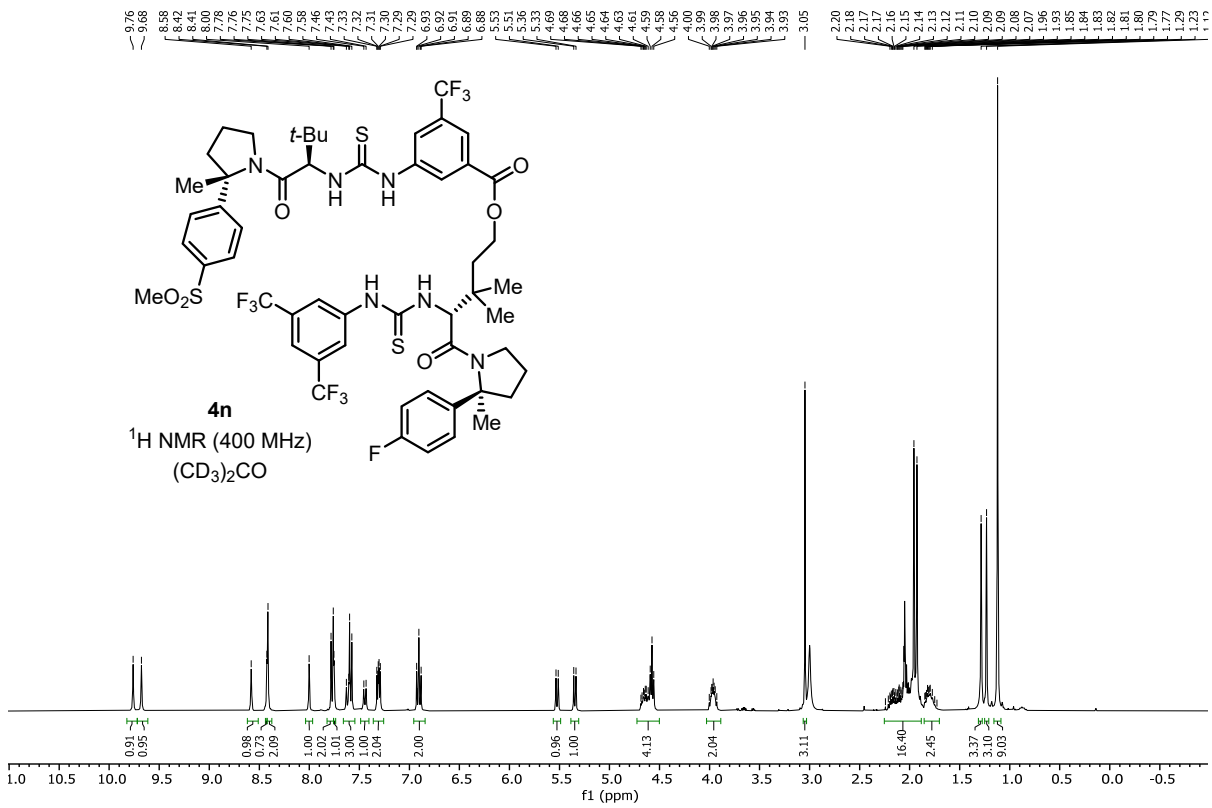
^{19}F NMR (376 MHz)

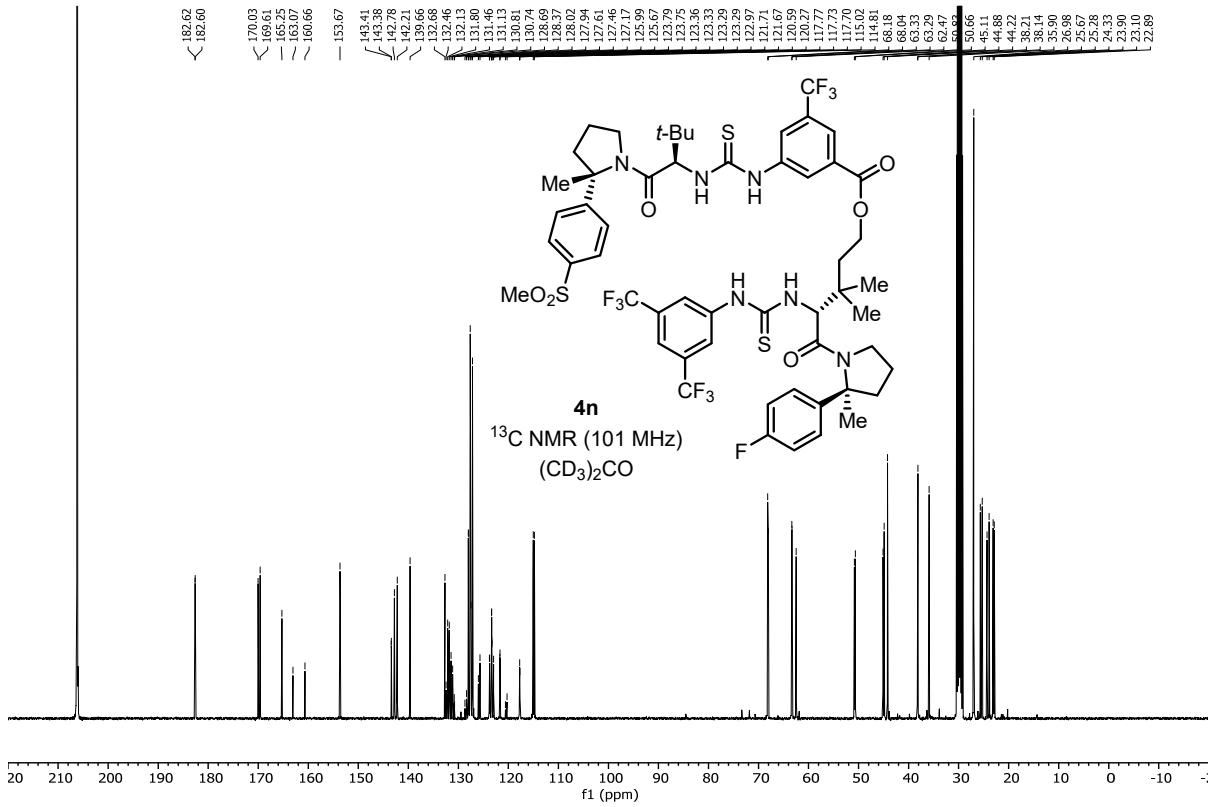
$(CD_3)_2CO$

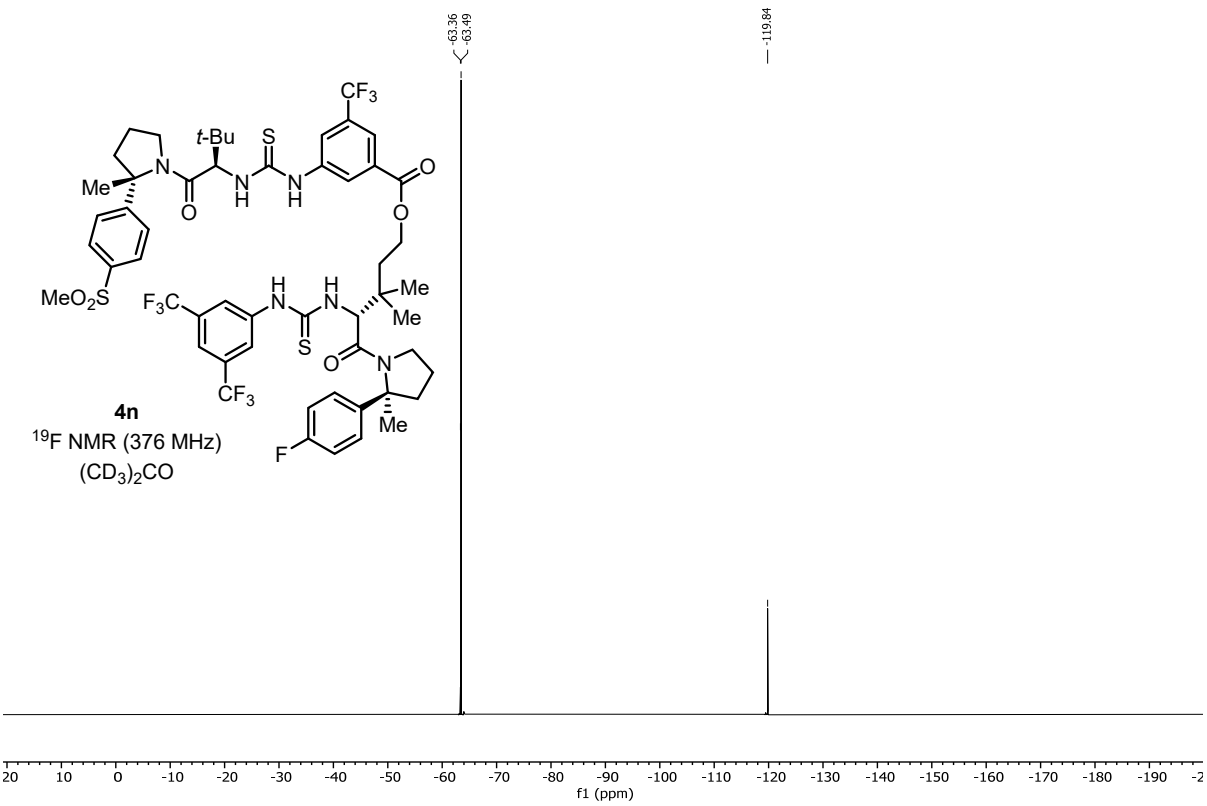

4m
1H NMR (400 MHz)
CD3CN + 5 drops of DMSO-d6
f1 (ppm)

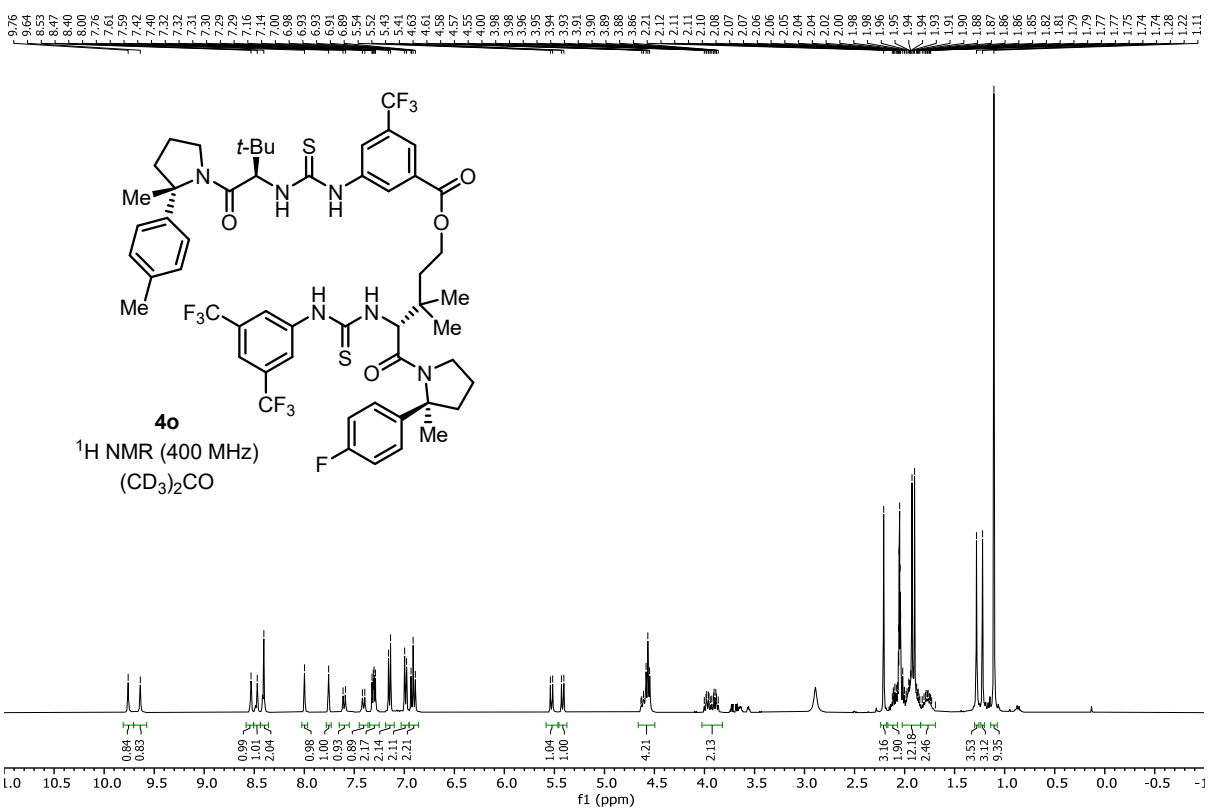

4m
13C NMR (101 MHz)
CD3CN + 5 drops of DMSO-d6
f1 (ppm)

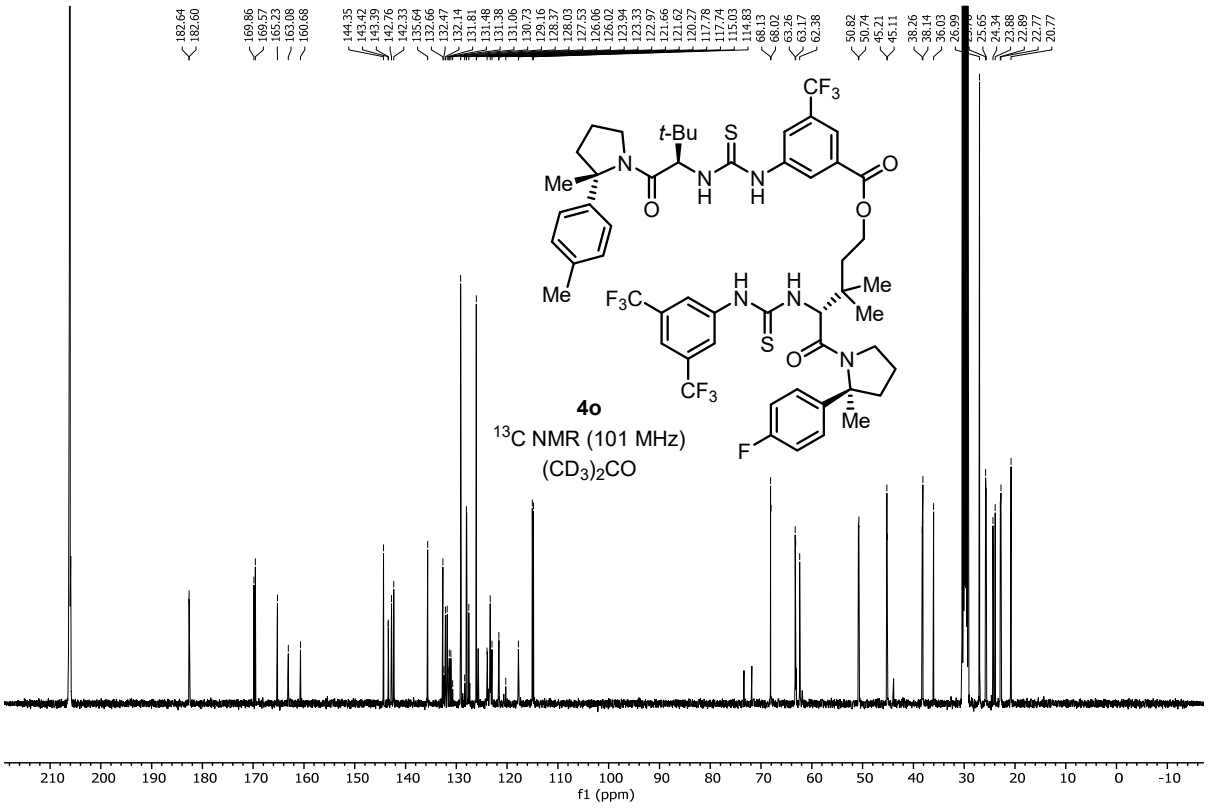

-63.22
-63.36
-119.72
CF3
t-Bu
S
N
H
Me
O
MeO
F3C
Me
CF3
F
4m
19F NMR (376 MHz)
CD3CN + 5 drops of DMSO-d6
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

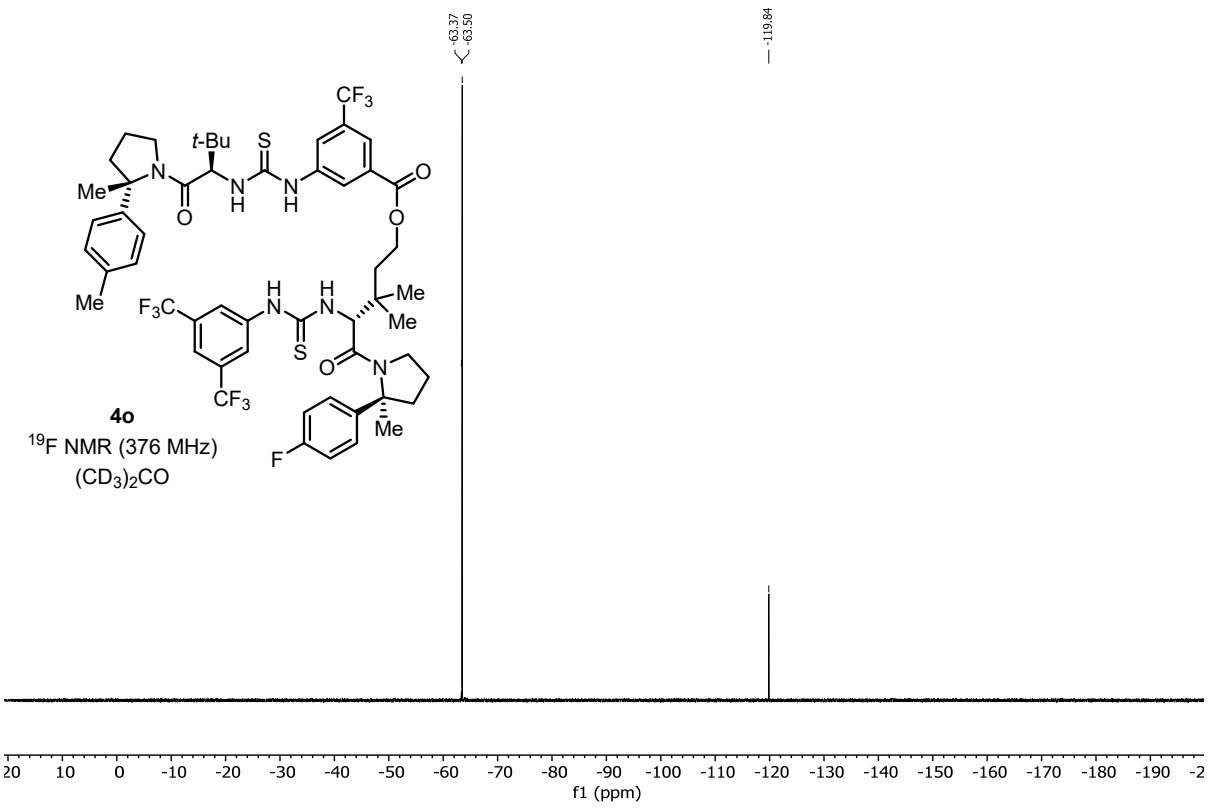

4n
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

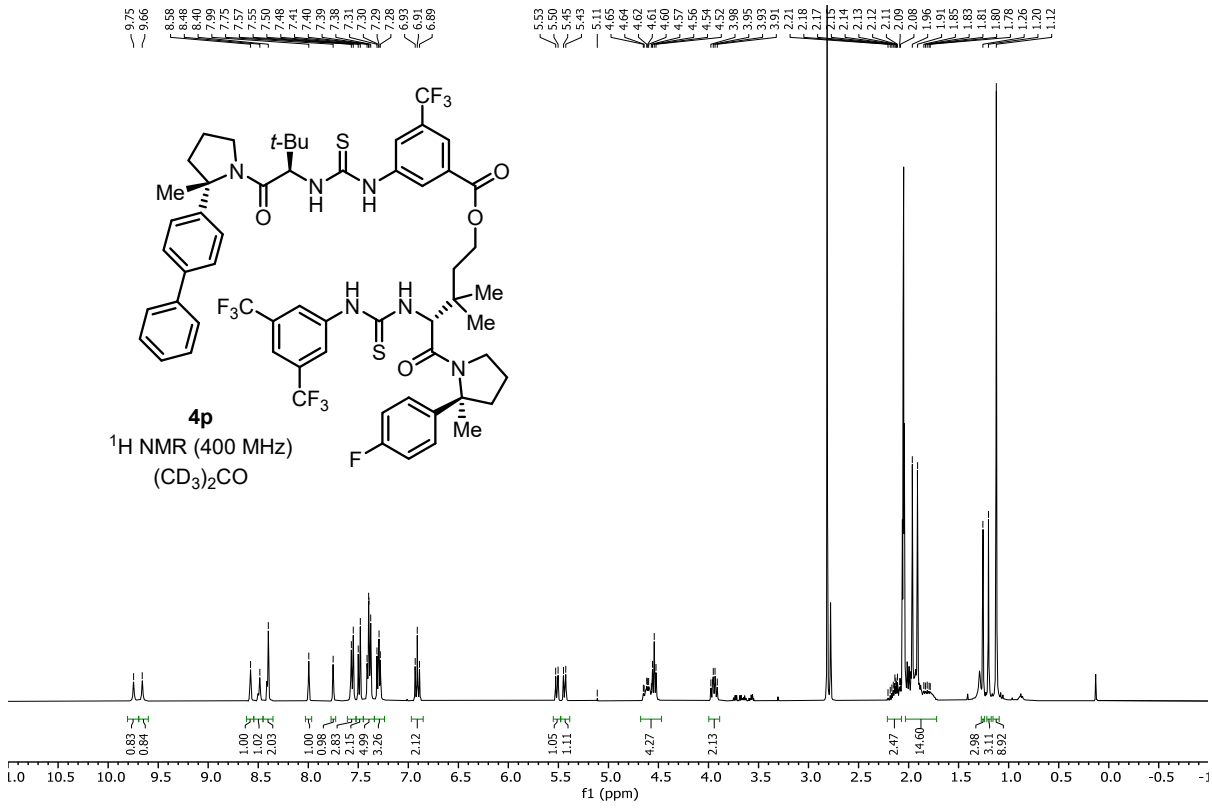

4n
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

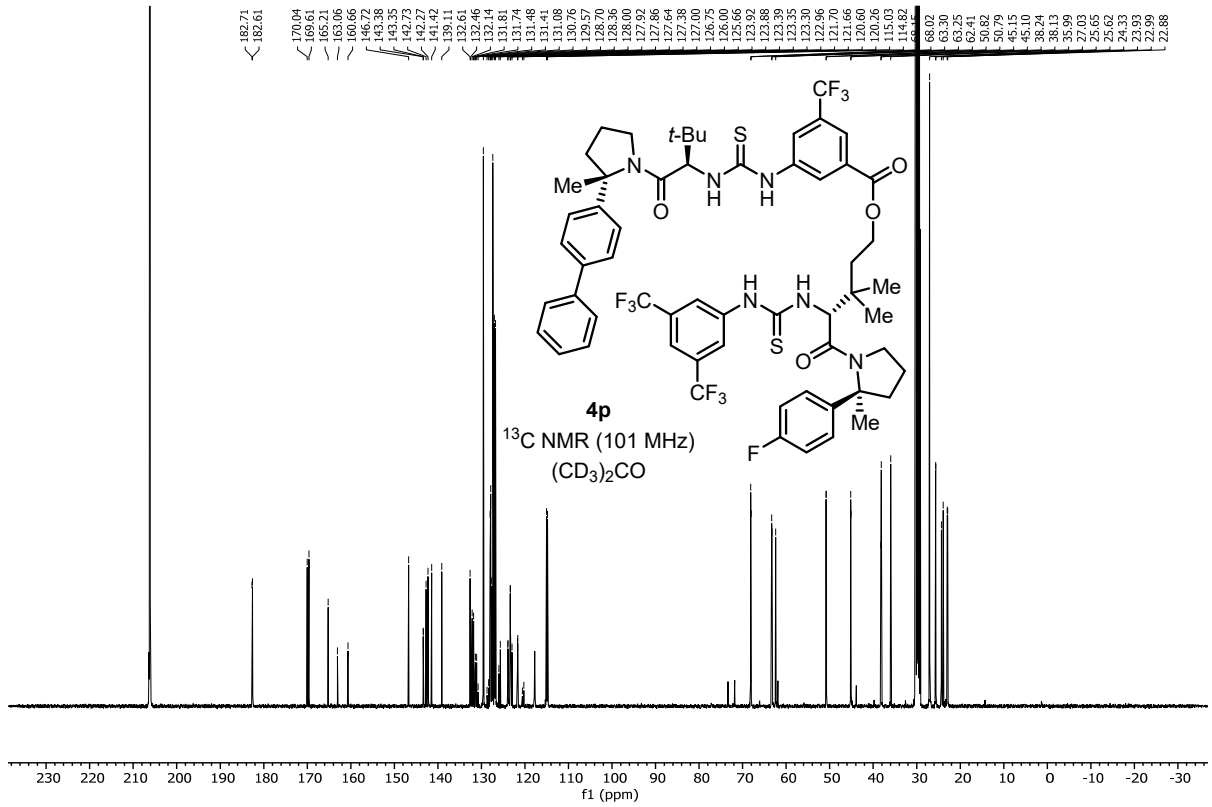

-63.36
-63.49
-119.84
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
MeO2S
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4n
19F NMR (376 MHz)
(CD3)2CO
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


4o
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

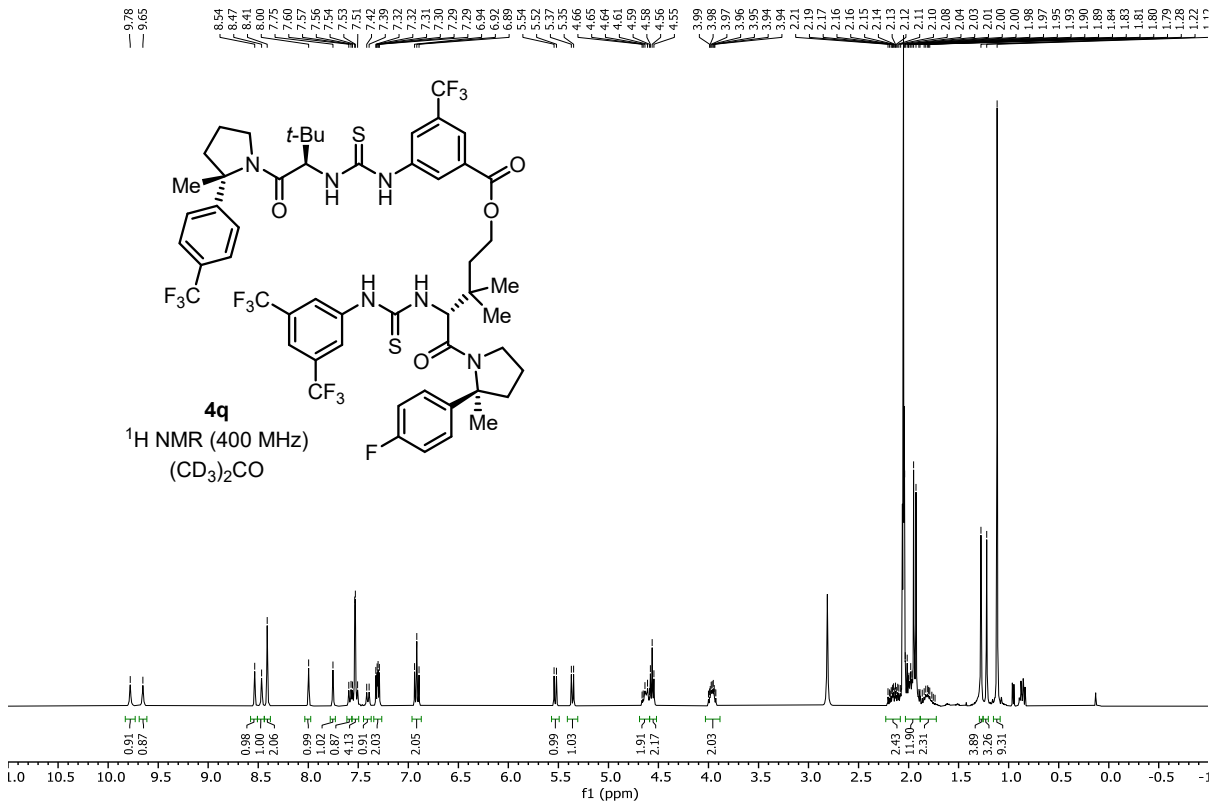

4o
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

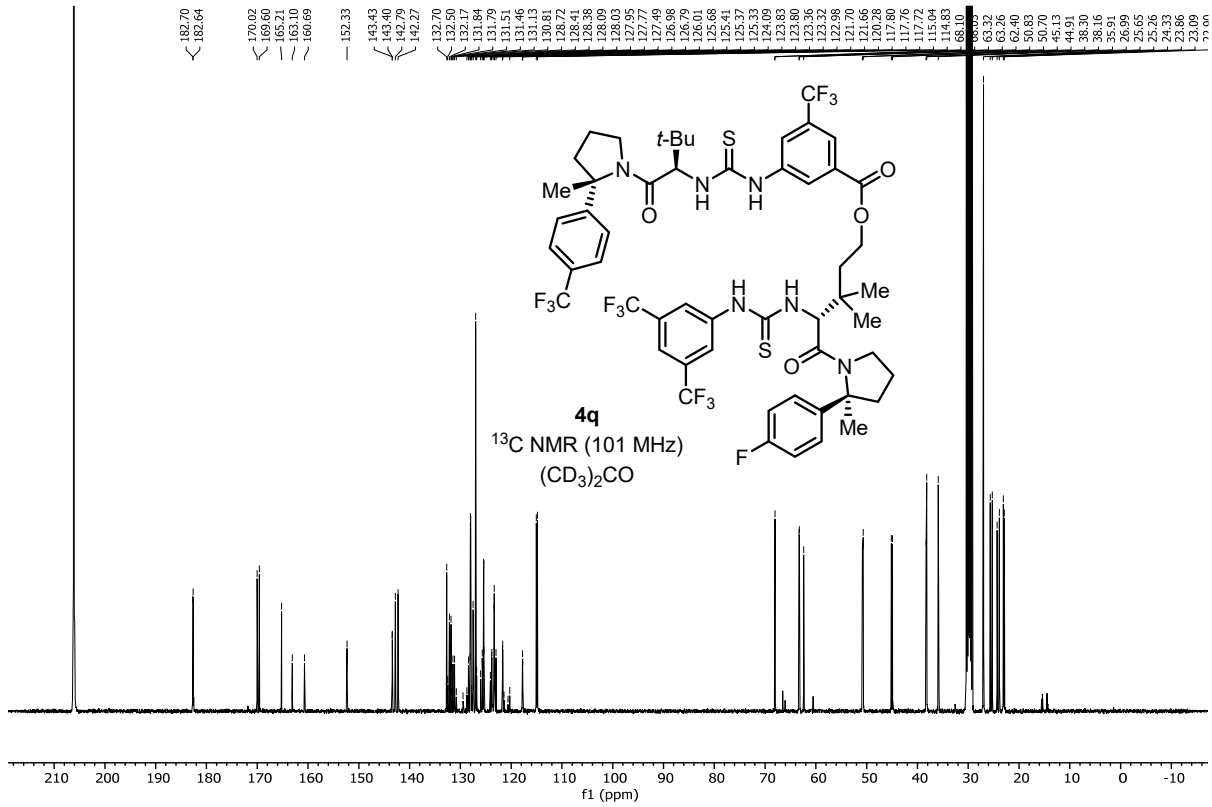

-63.37
-63.50
-119.84
CF3
t-Bu
S
N
H
N
H
Me
O
O
O
Me
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4o
19F NMR (376 MHz)
(CD3)2CO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

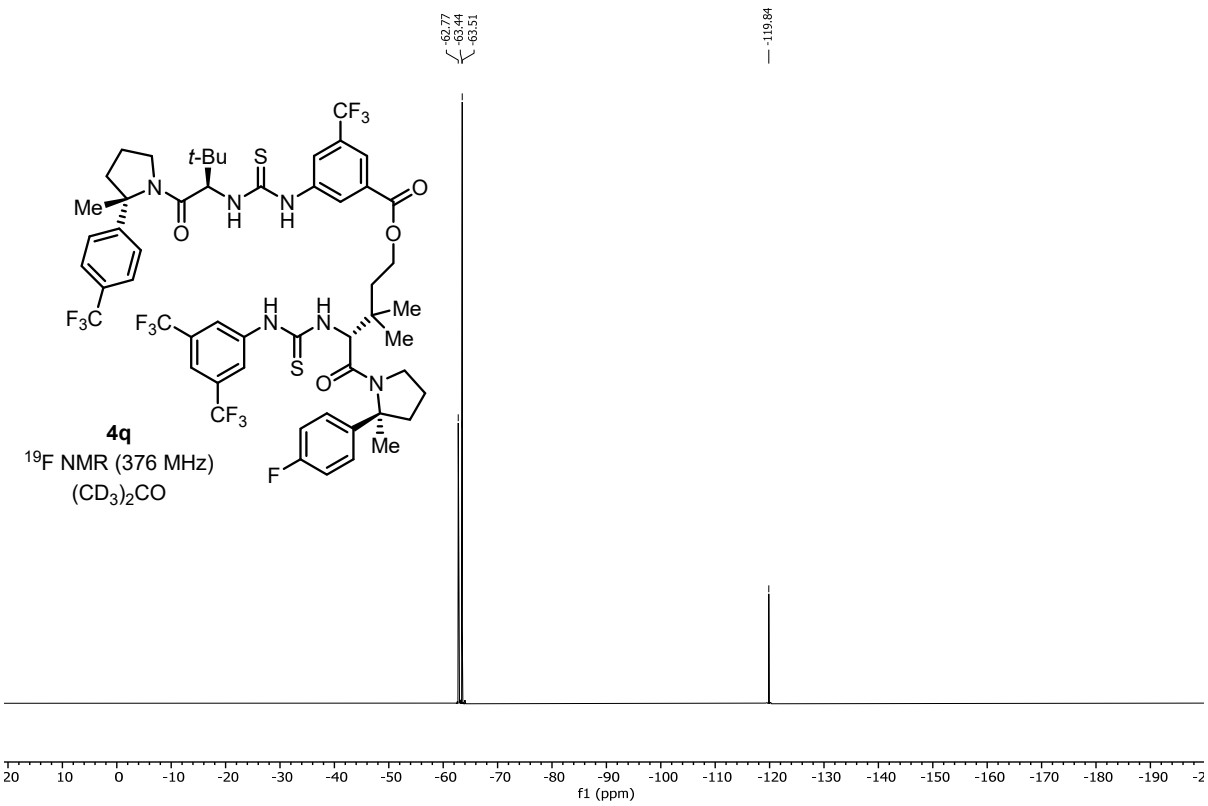

4p
1H NMR (400 MHz)
(CD3)2CO
f1 (ppm)

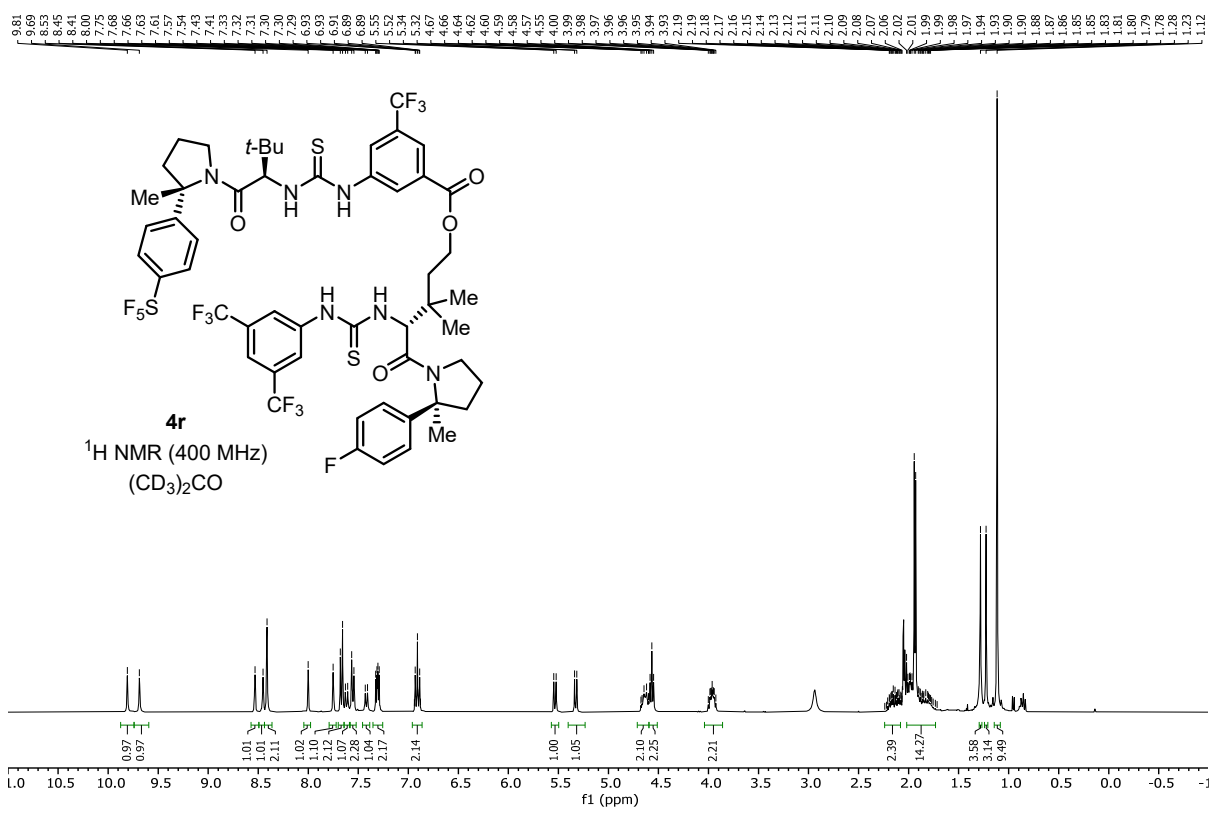

4p
13C NMR (101 MHz)
(CD3)2CO
f1 (ppm)

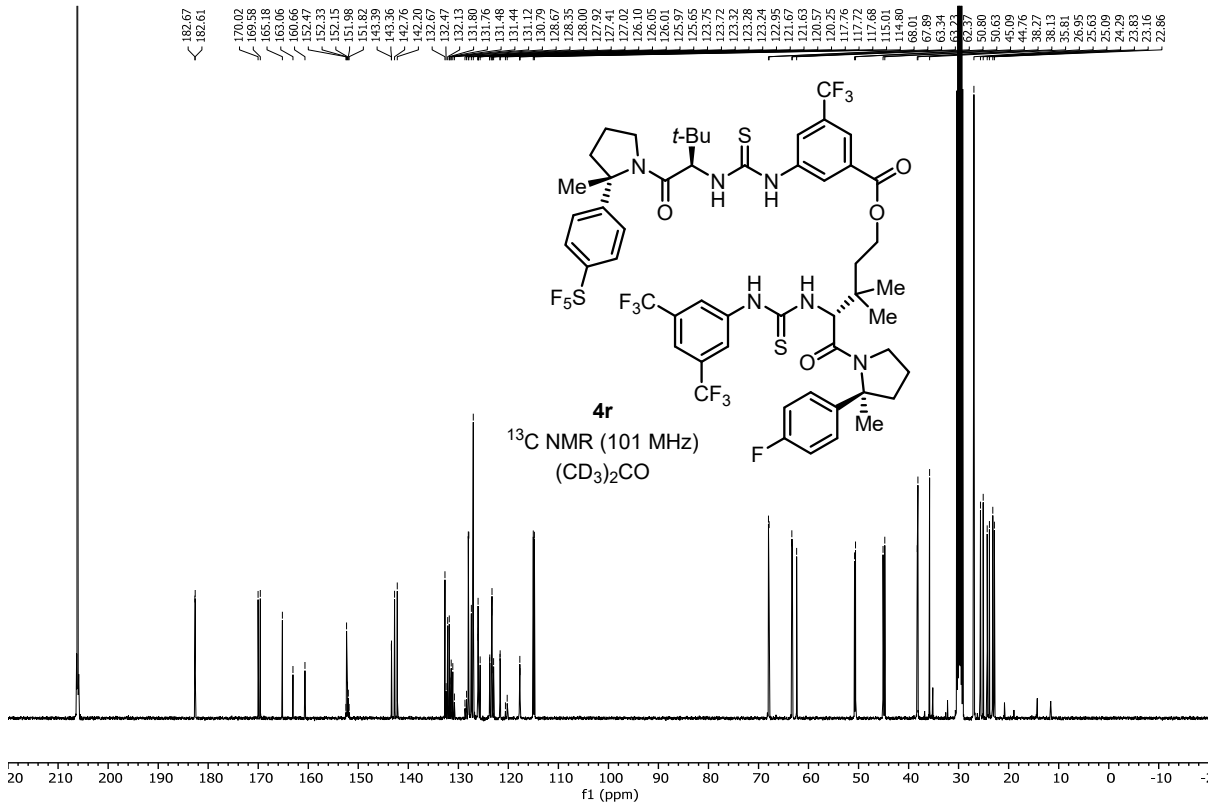
-63.34
-63.49
-119.82
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4p
19F NMR (376 MHz)
(CD3)2CO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

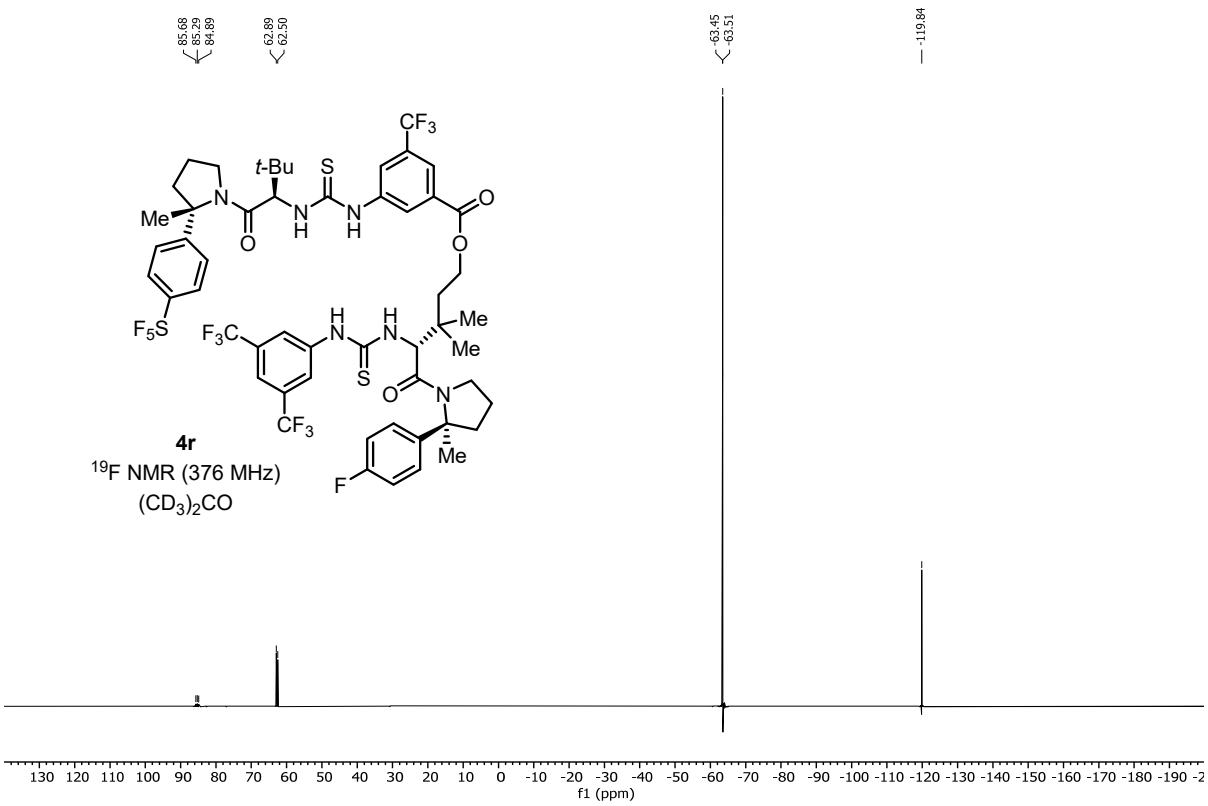

4q
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

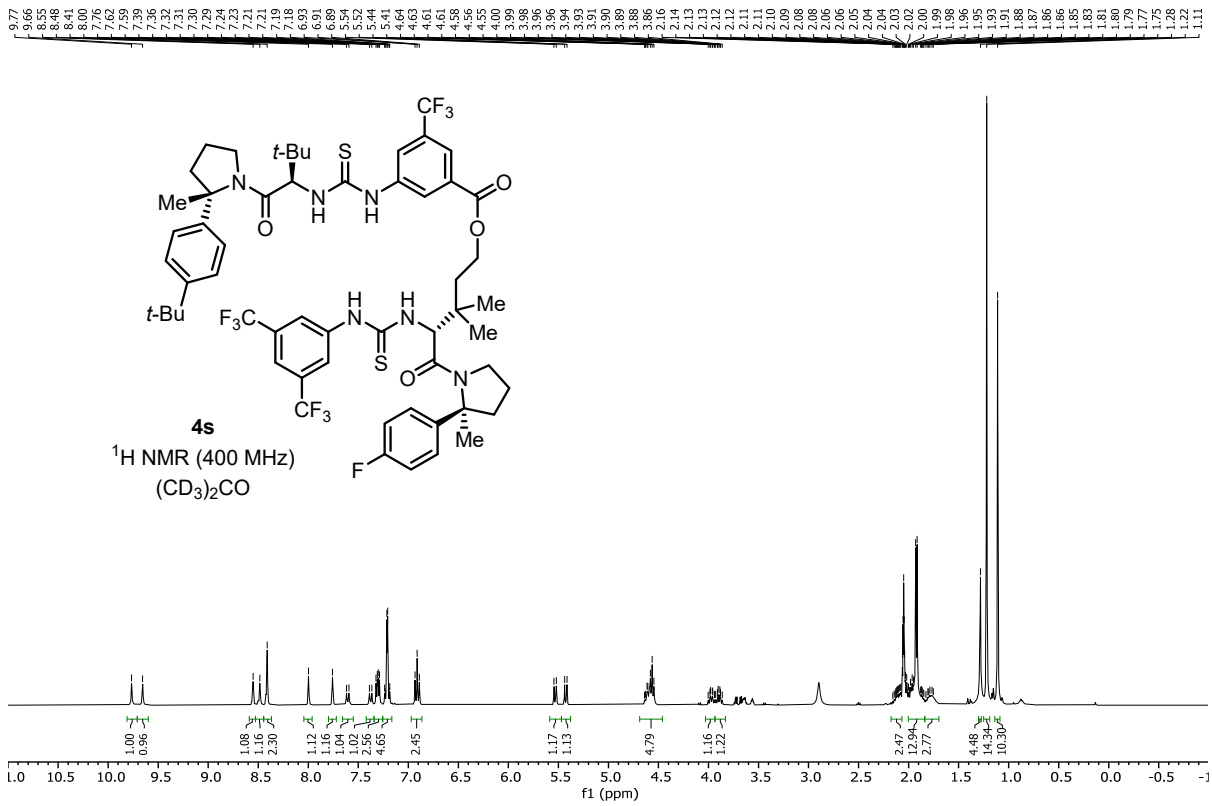

4q
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

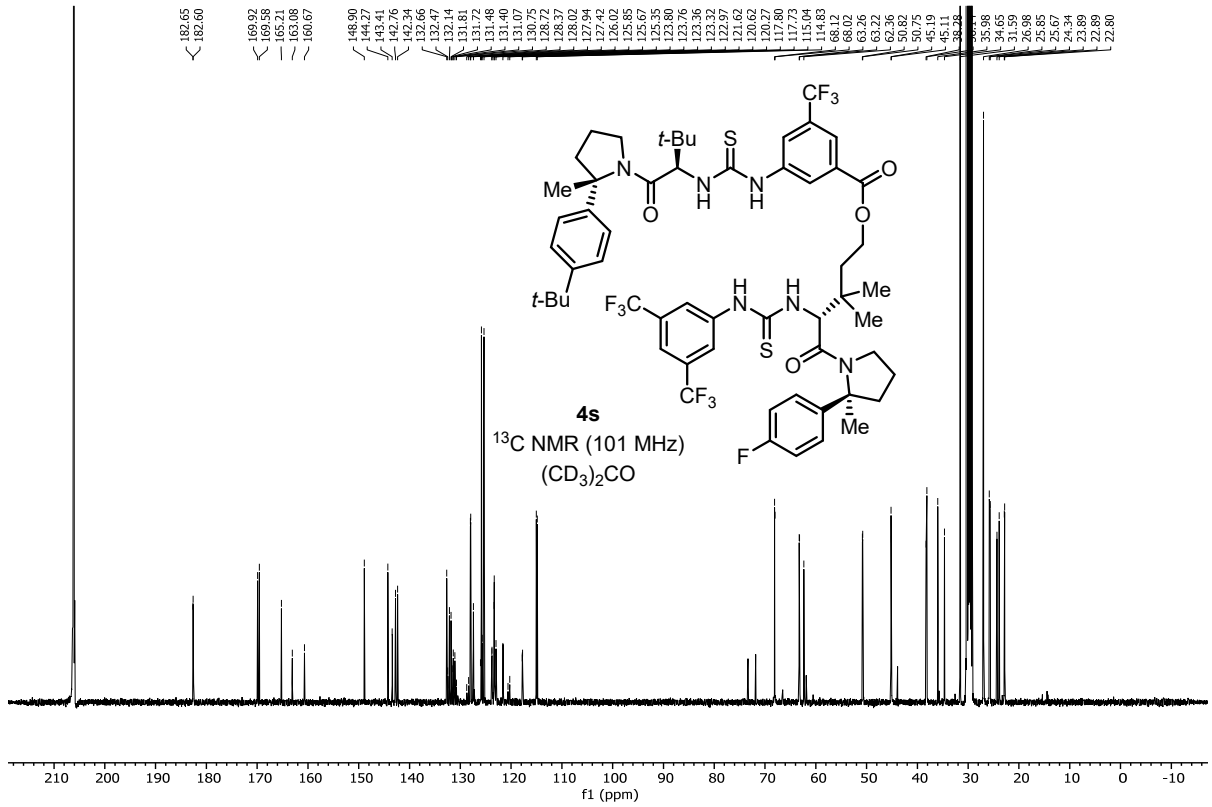

-62.77
-63.44
-63.51
-119.84
4q
19F NMR (376 MHz)
(CD3)2CO
f1 (ppm)

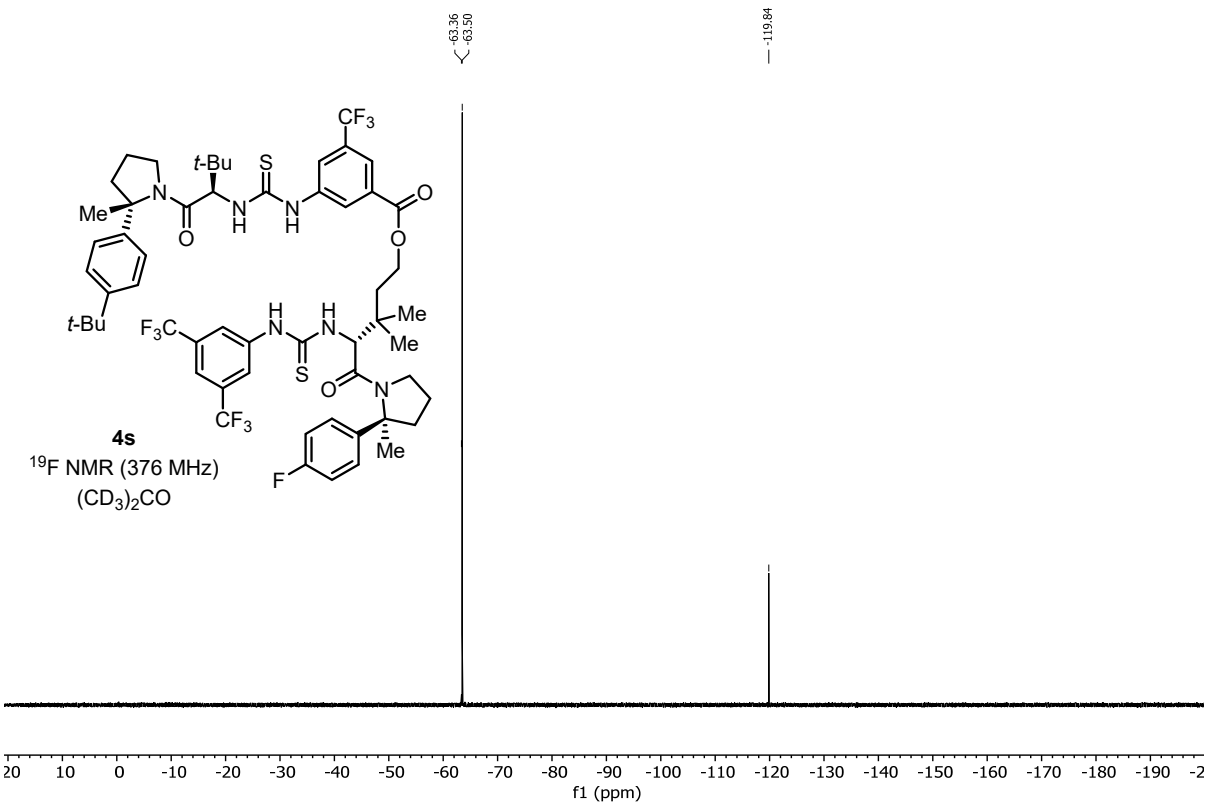

4r
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

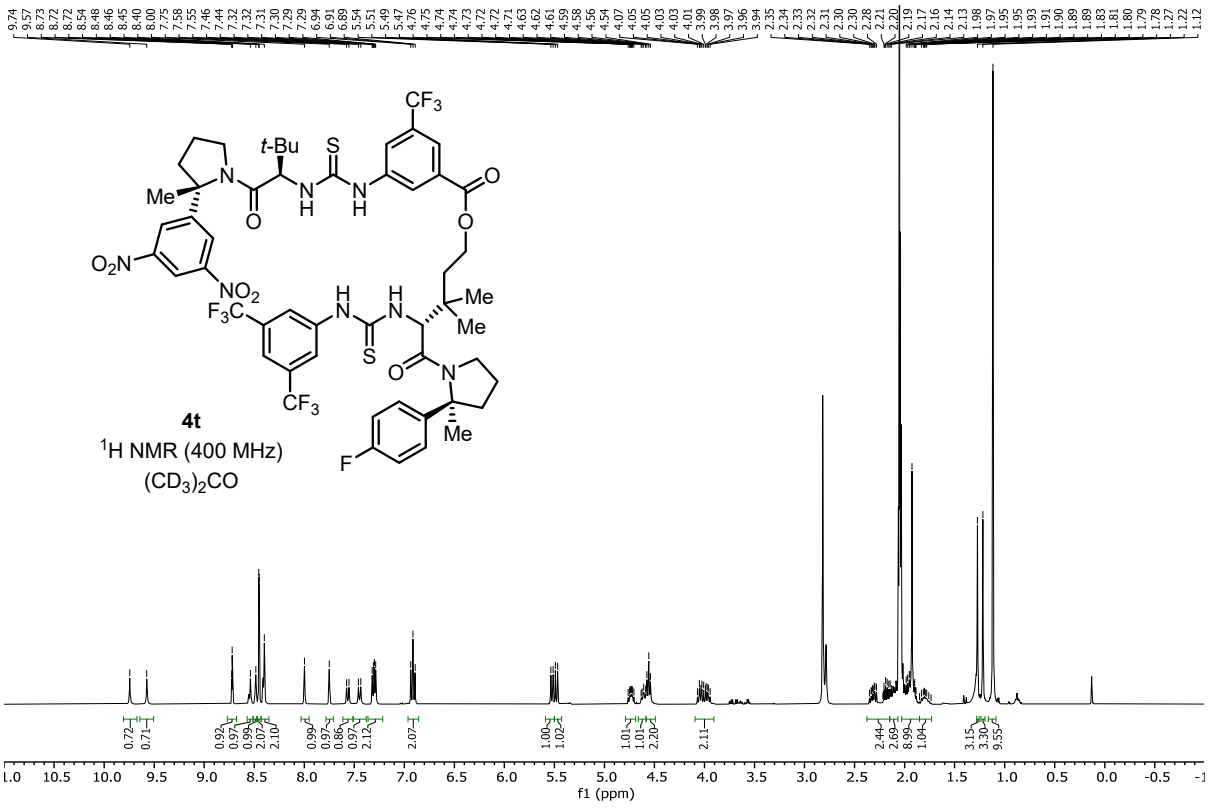

4r
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

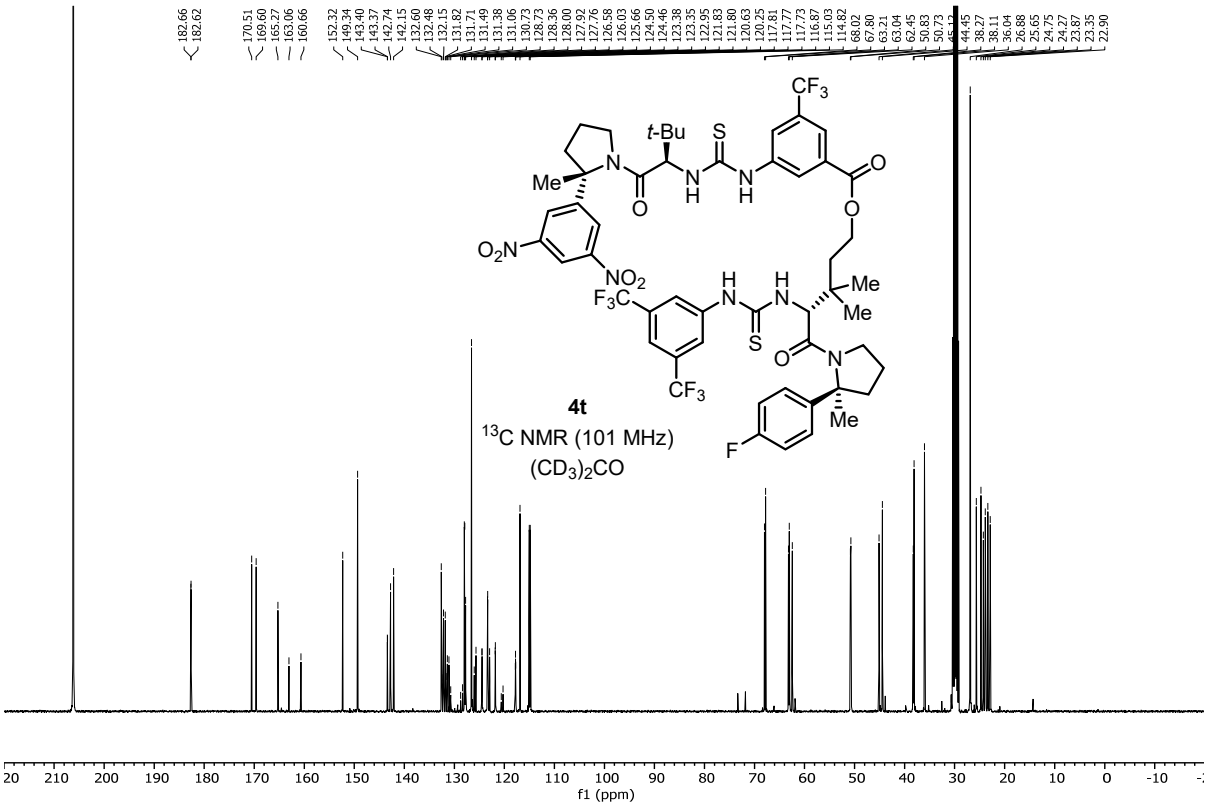

-85.68
-85.29
-84.89
-62.89
-62.50
-63.45
-63.51
-119.84
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F5S
F3C
N
H
N
H
Me
Me
S
O
N
CF3
Me
F
4r
19F NMR (376 MHz)
(CD3)2CO
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)


4s
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

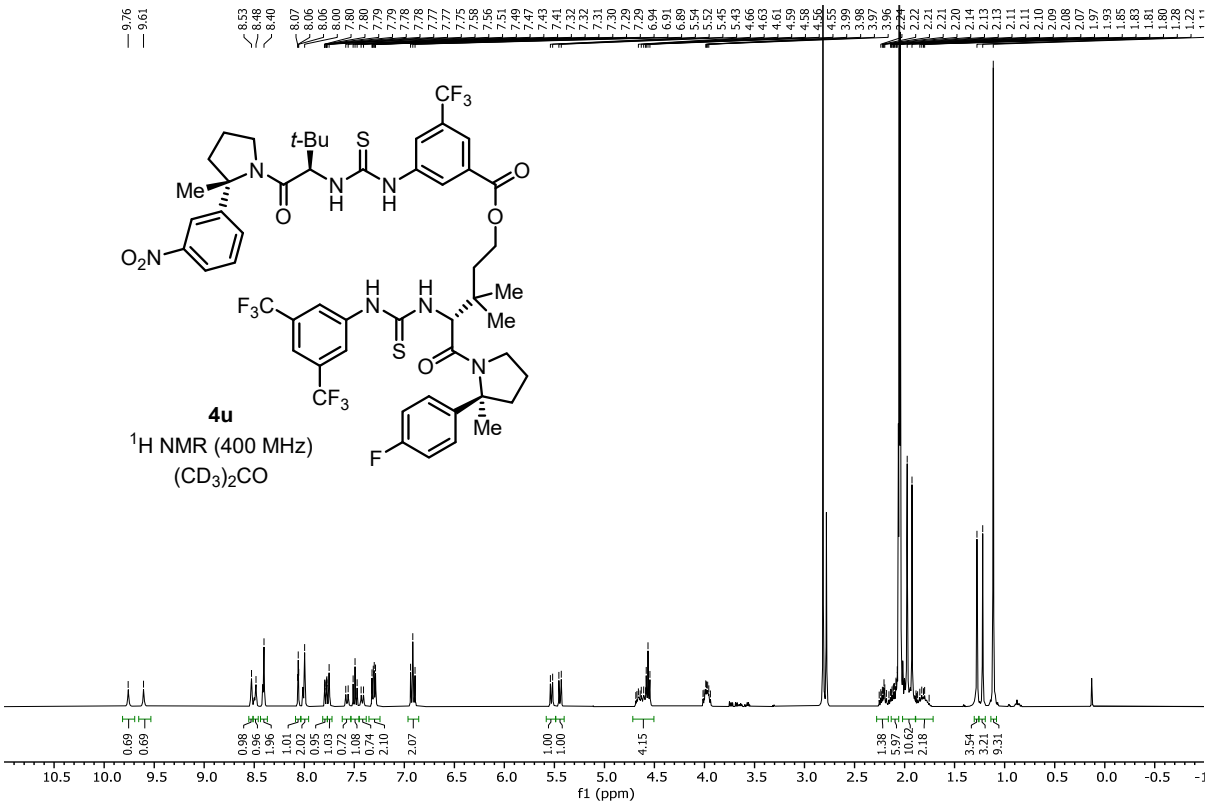

4s
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

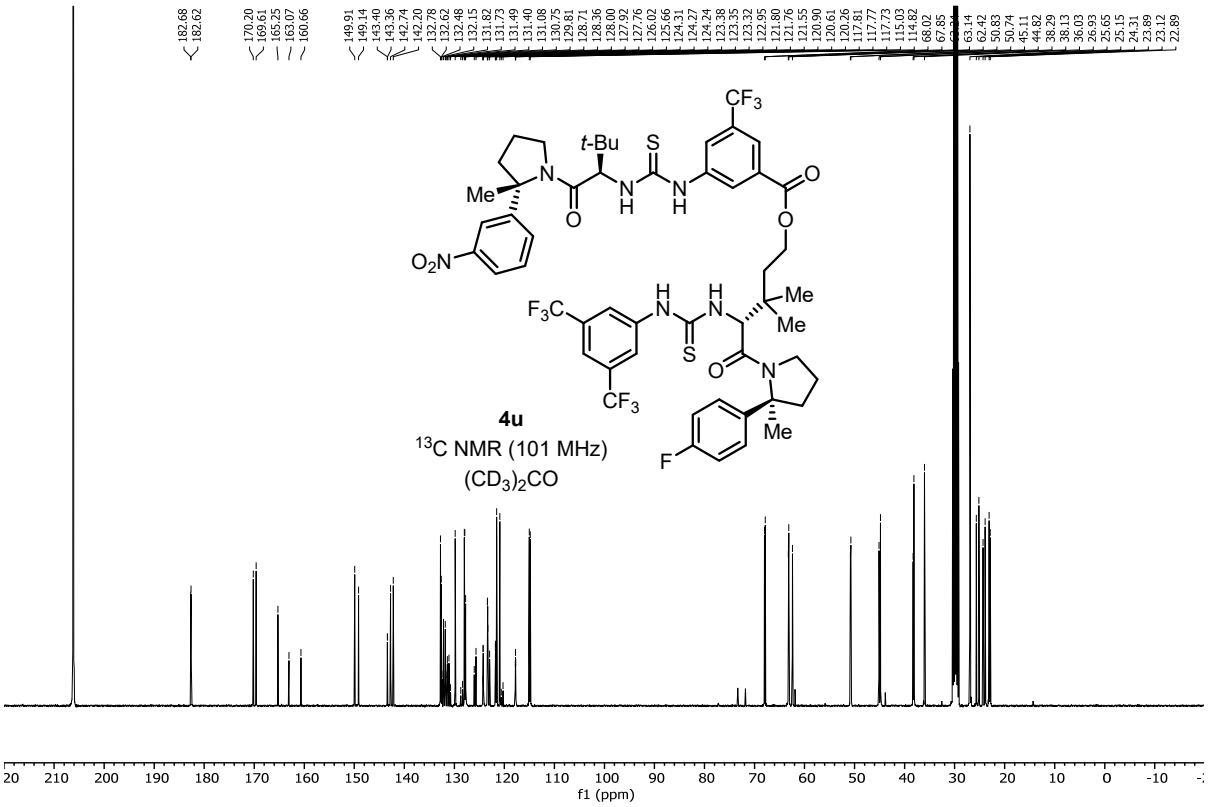

-63.36
-63.50
-119.84
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
t-Bu
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4s
19F NMR (376 MHz)
(CD3)2CO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

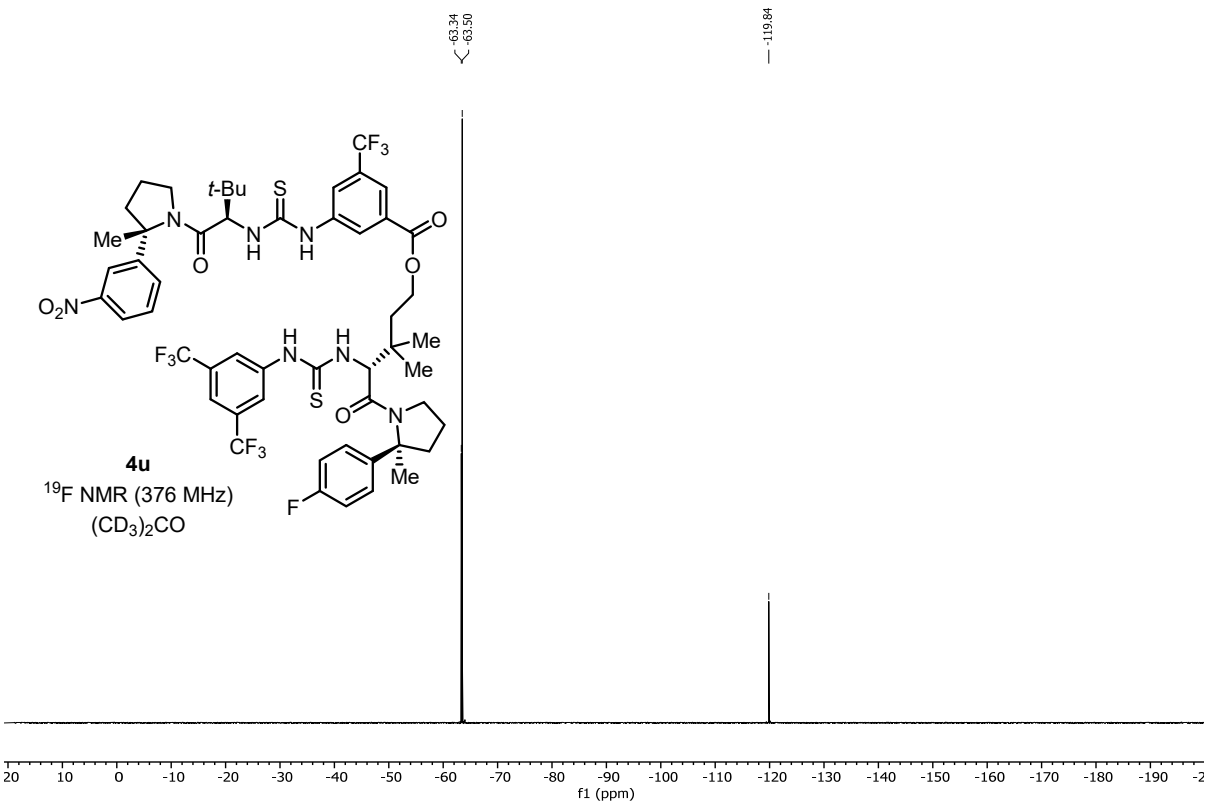

4t
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

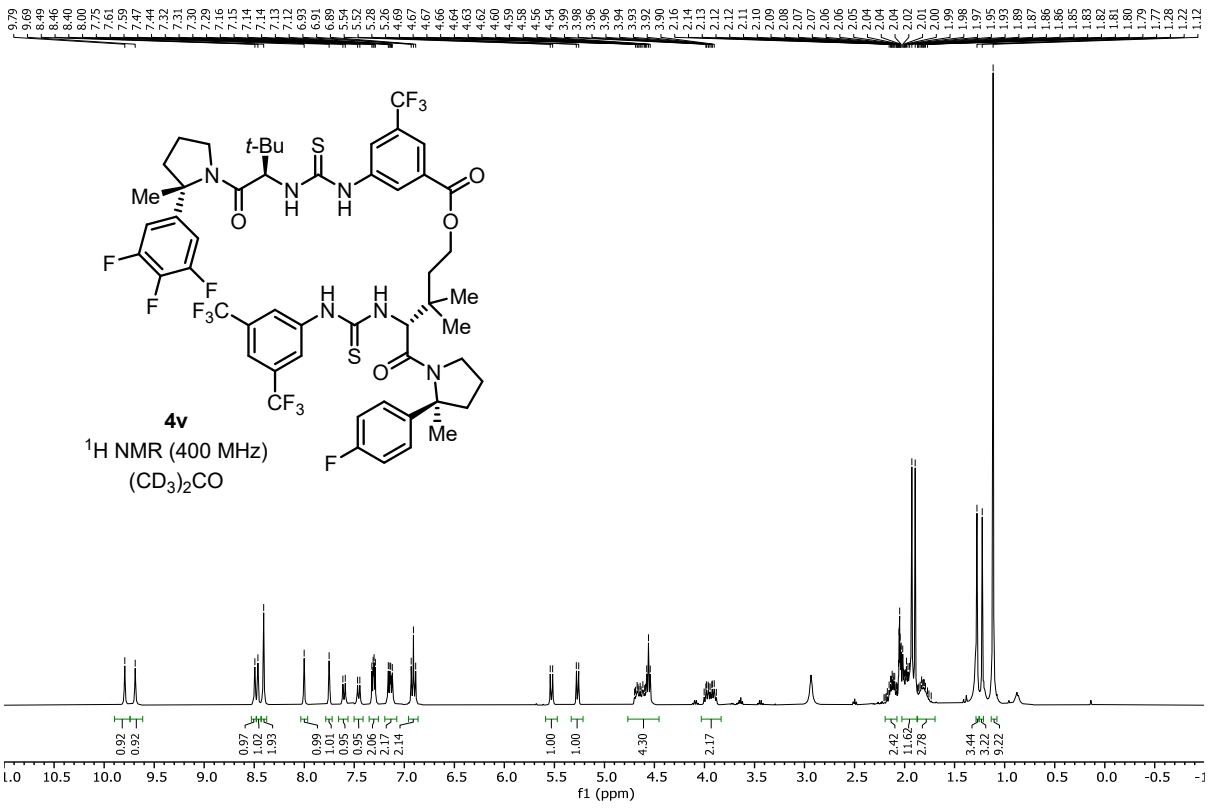

4t
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

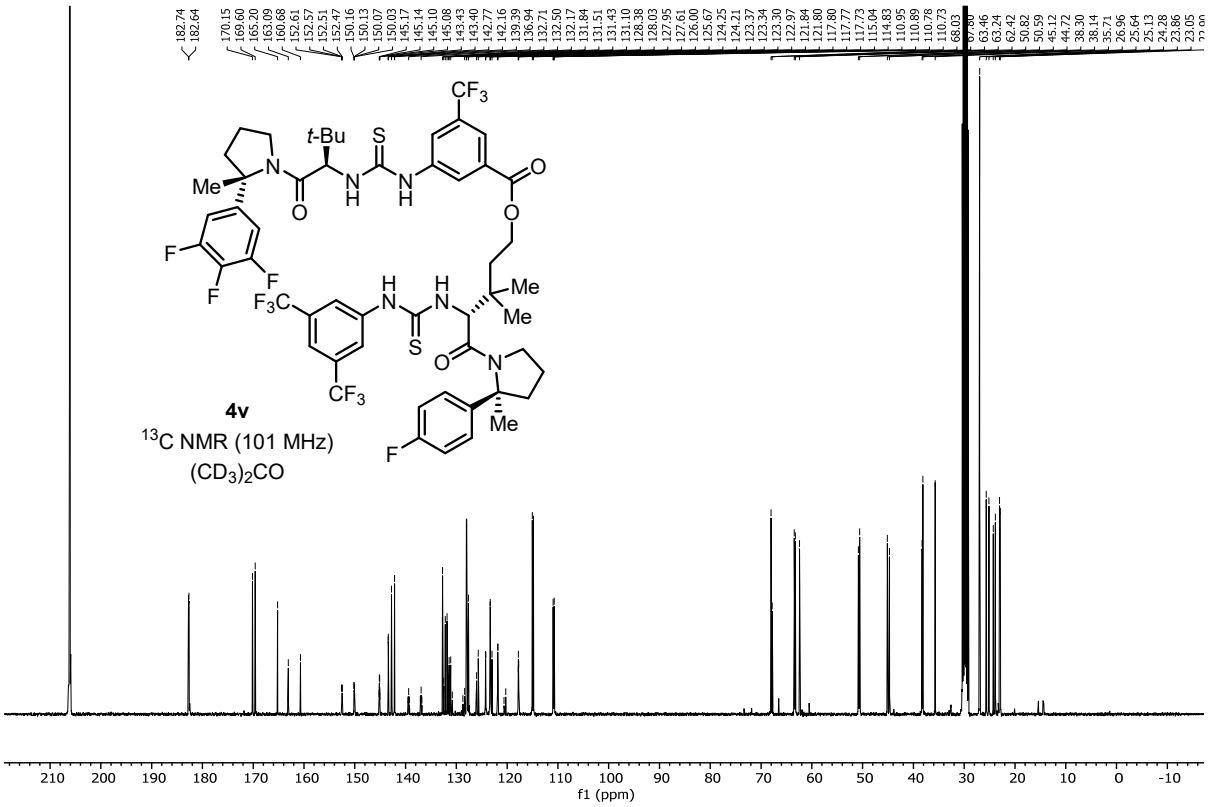
-63.30
-63.51
-119.83
CF3
t-Bu
S
N
Me
O
N
H
N
H
O
O2N
NO2
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4t
19F NMR (376 MHz)
(CD3)2CO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)


4u
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

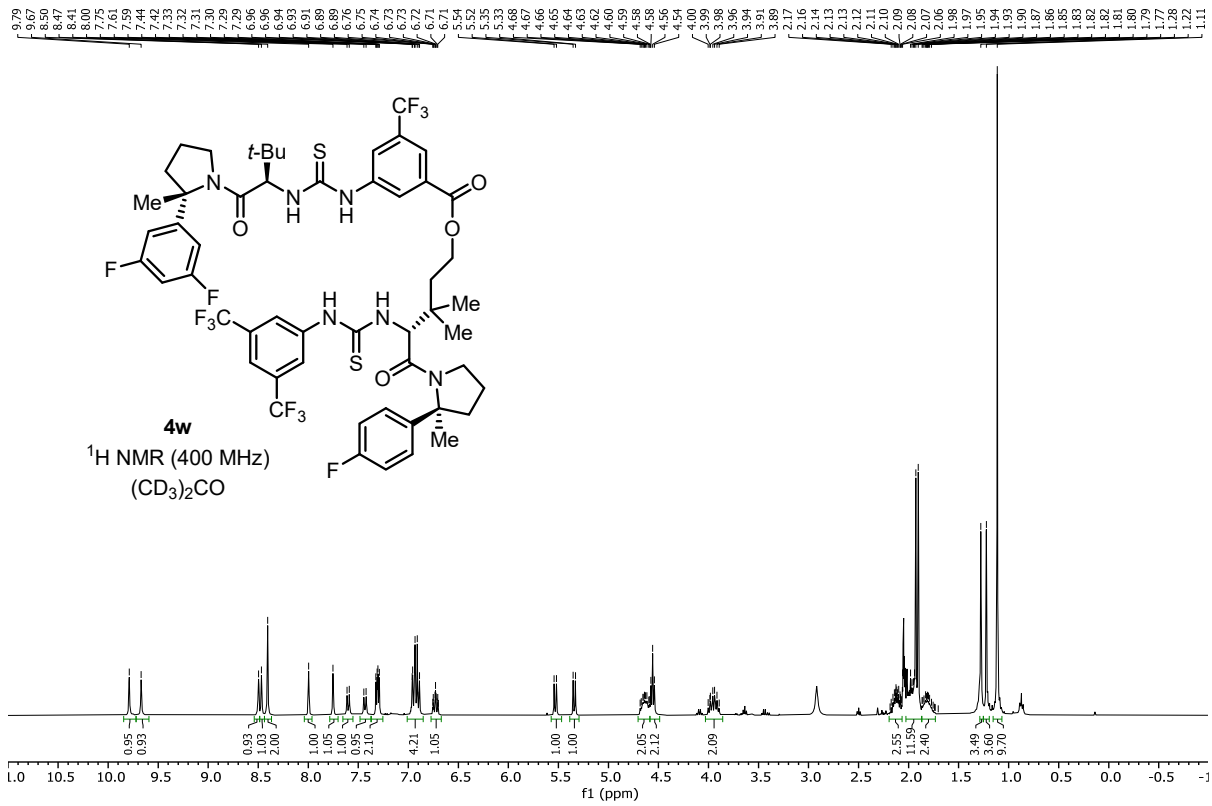

4u
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

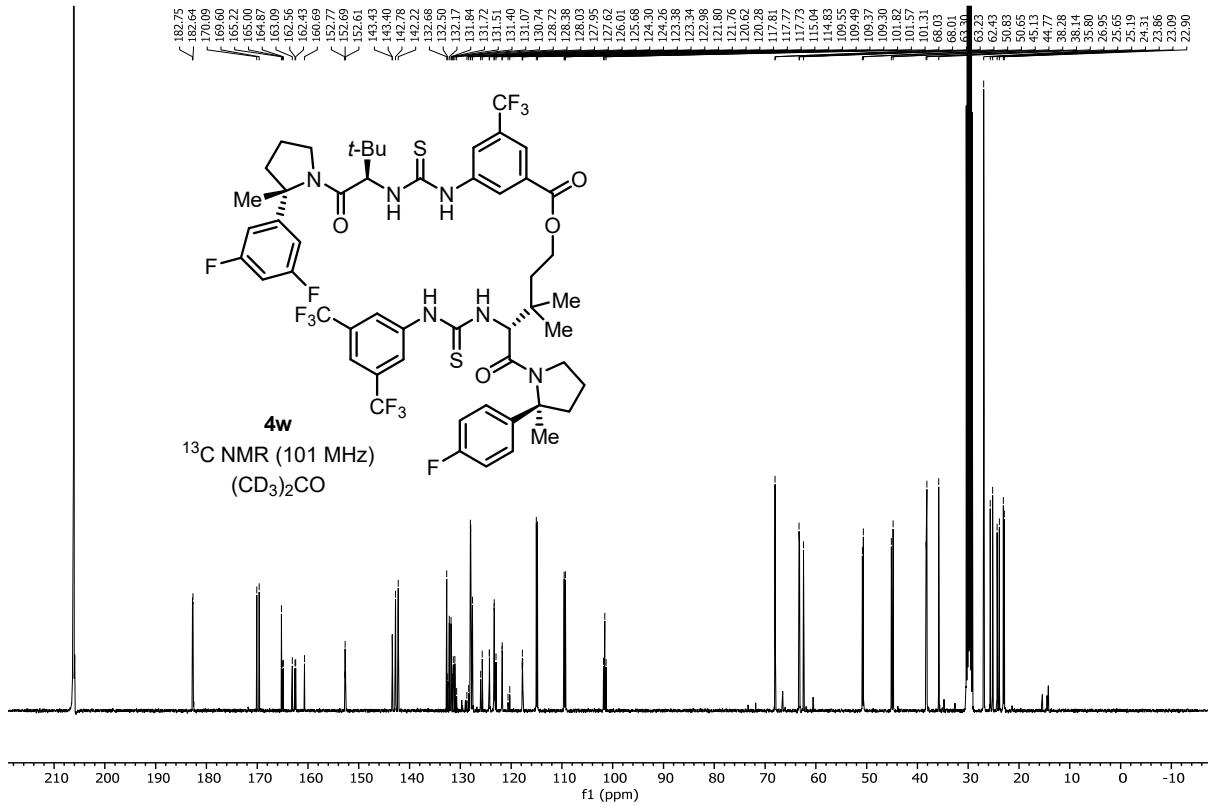

-63.34
-63.50
-119.84
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
O2N
F3C
H
N
S
H
N
Me
Me
O
N
CF3
Me
F
4u
19F NMR (376 MHz)
(CD3)2CO
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

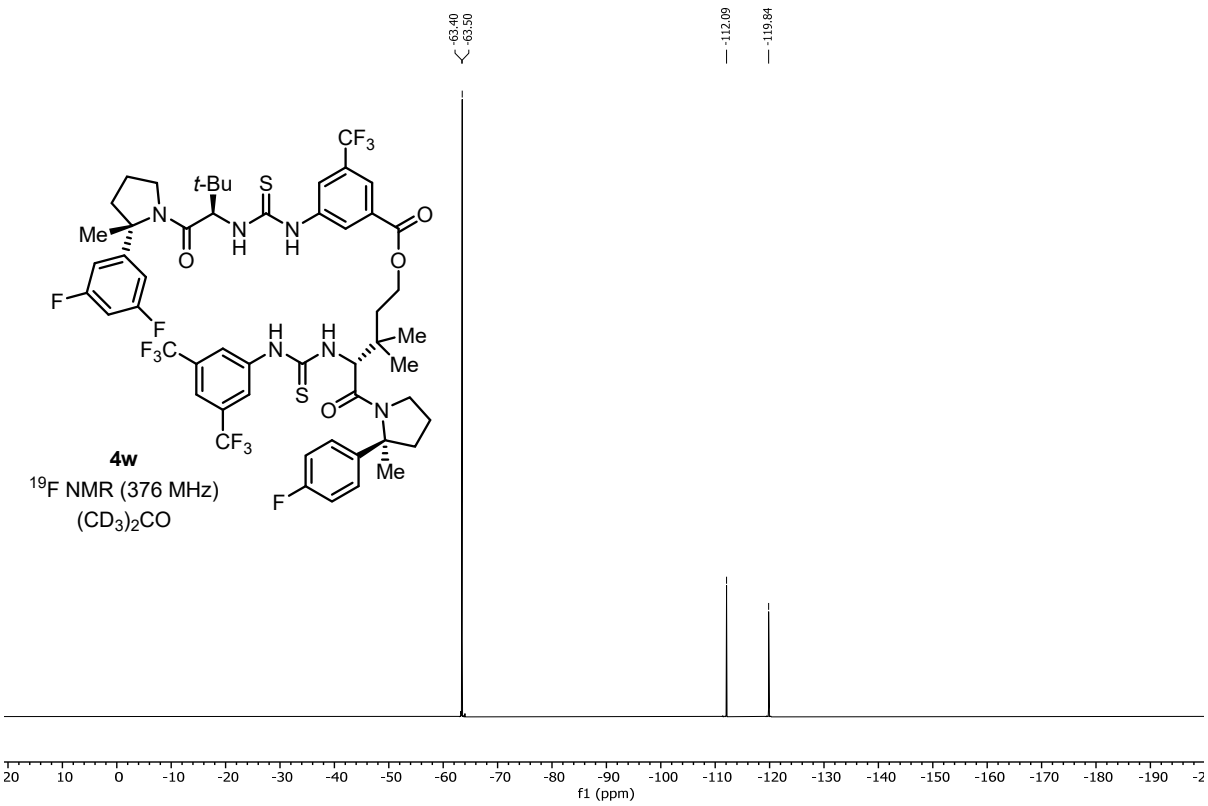

4v
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

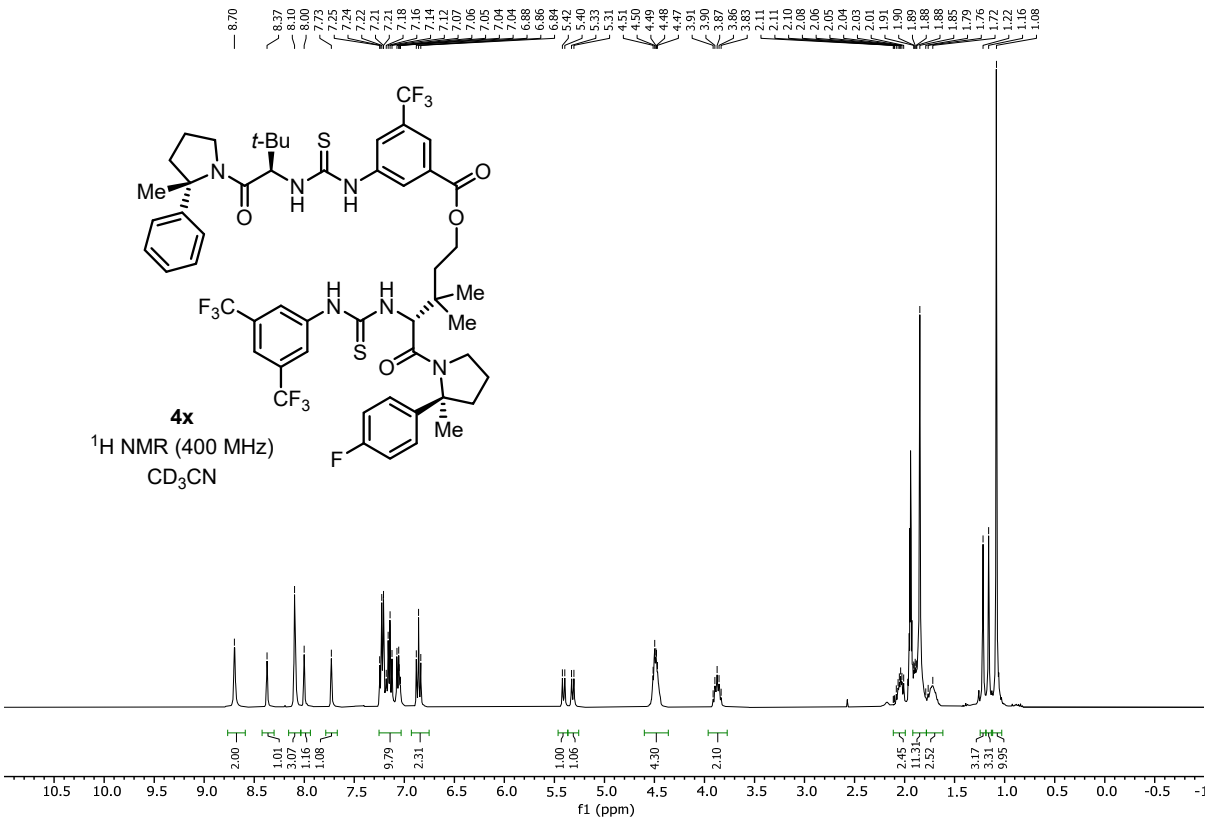

4v
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

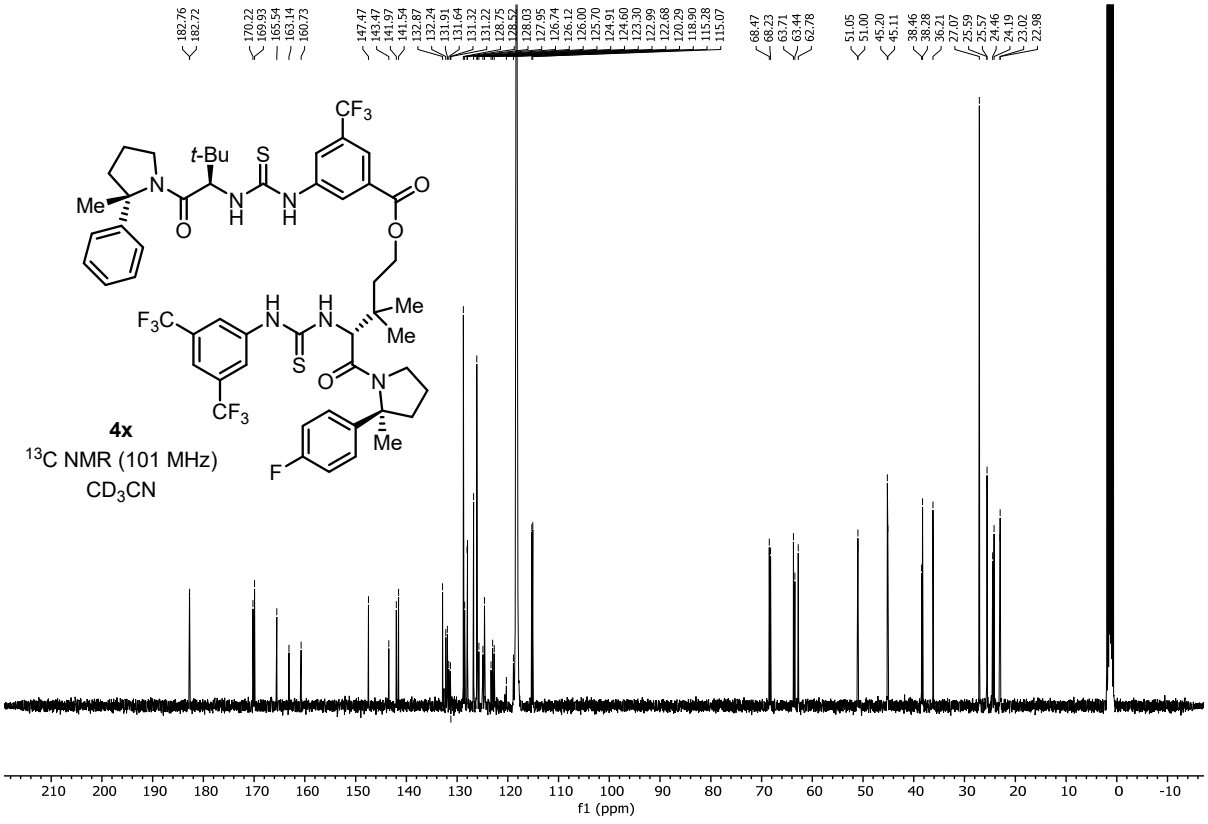
-63.43
-63.51
-119.83
-137.58
-137.63
-167.29
-167.34
-167.40
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F
F
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4v
19F NMR (376 MHz)
(CD3)2CO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

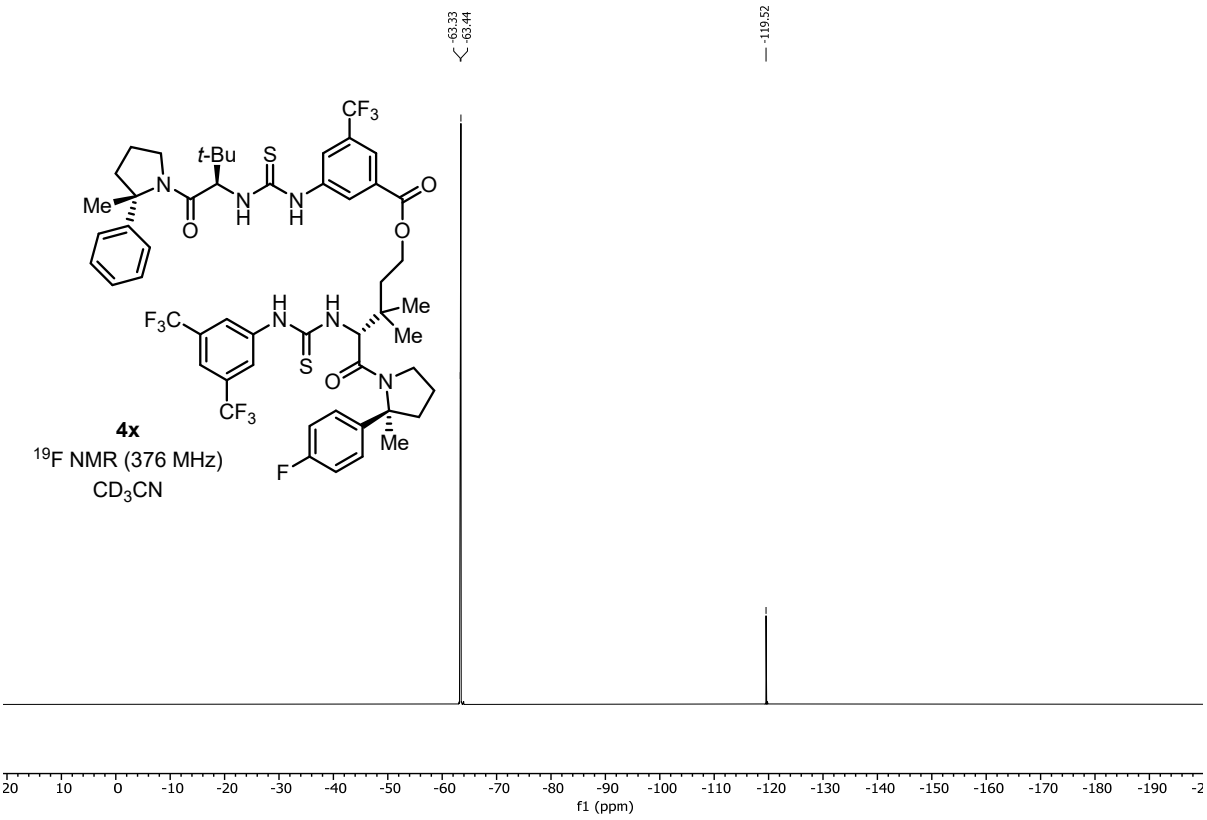

4w
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

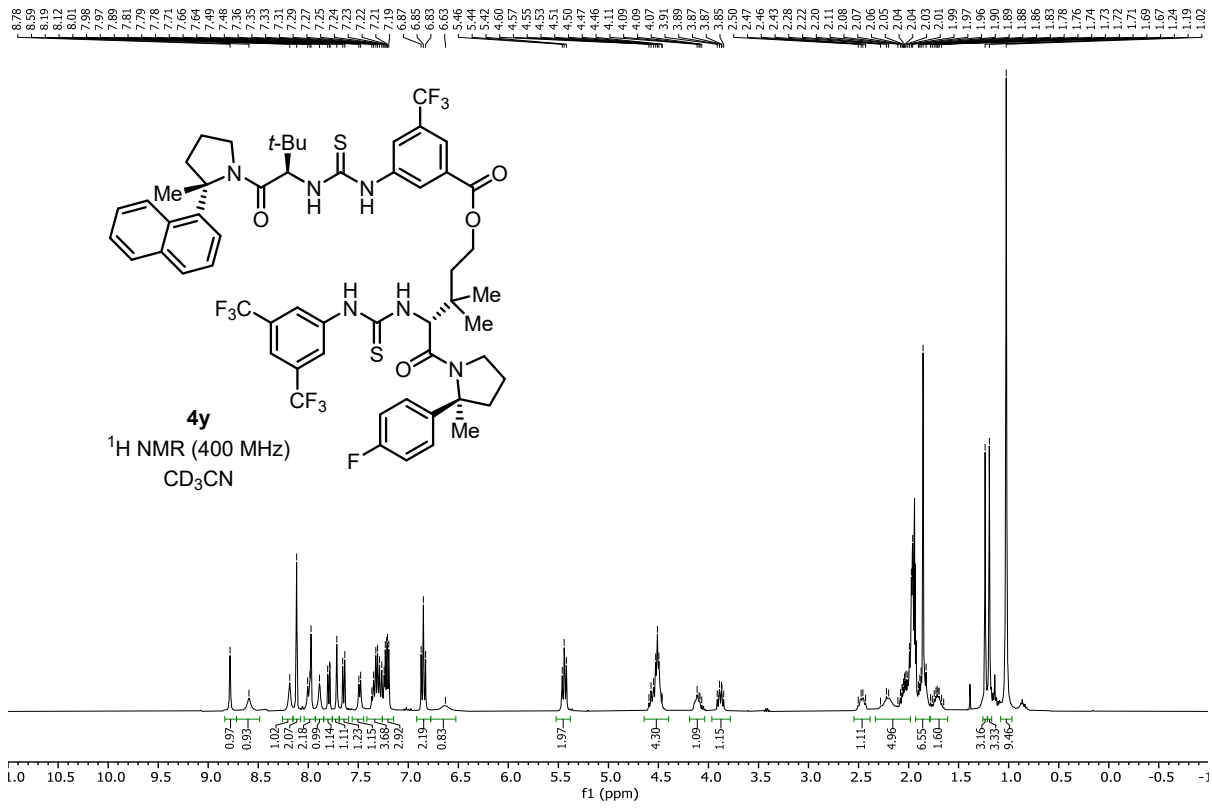

4w
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

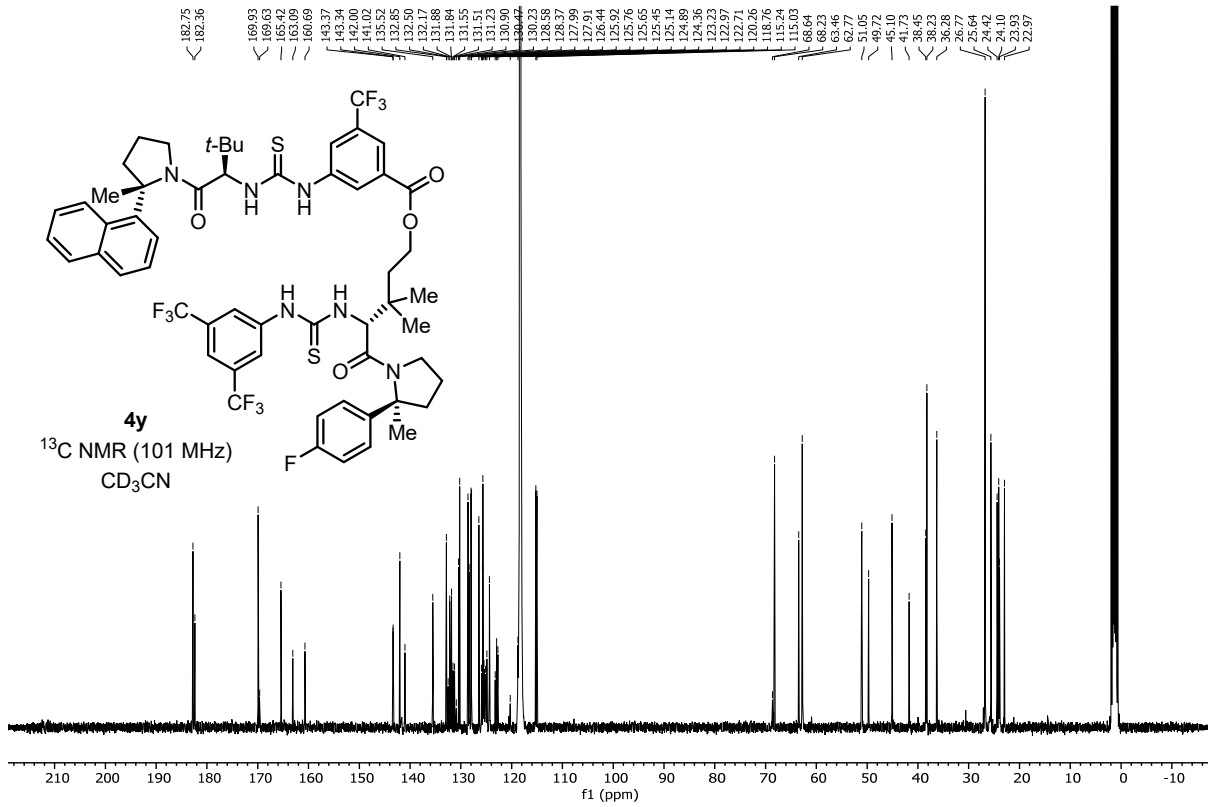

-63.40
-63.50
-112.09
-119.84
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F
F
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4w
19F NMR (376 MHz)
(CD3)2CO
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

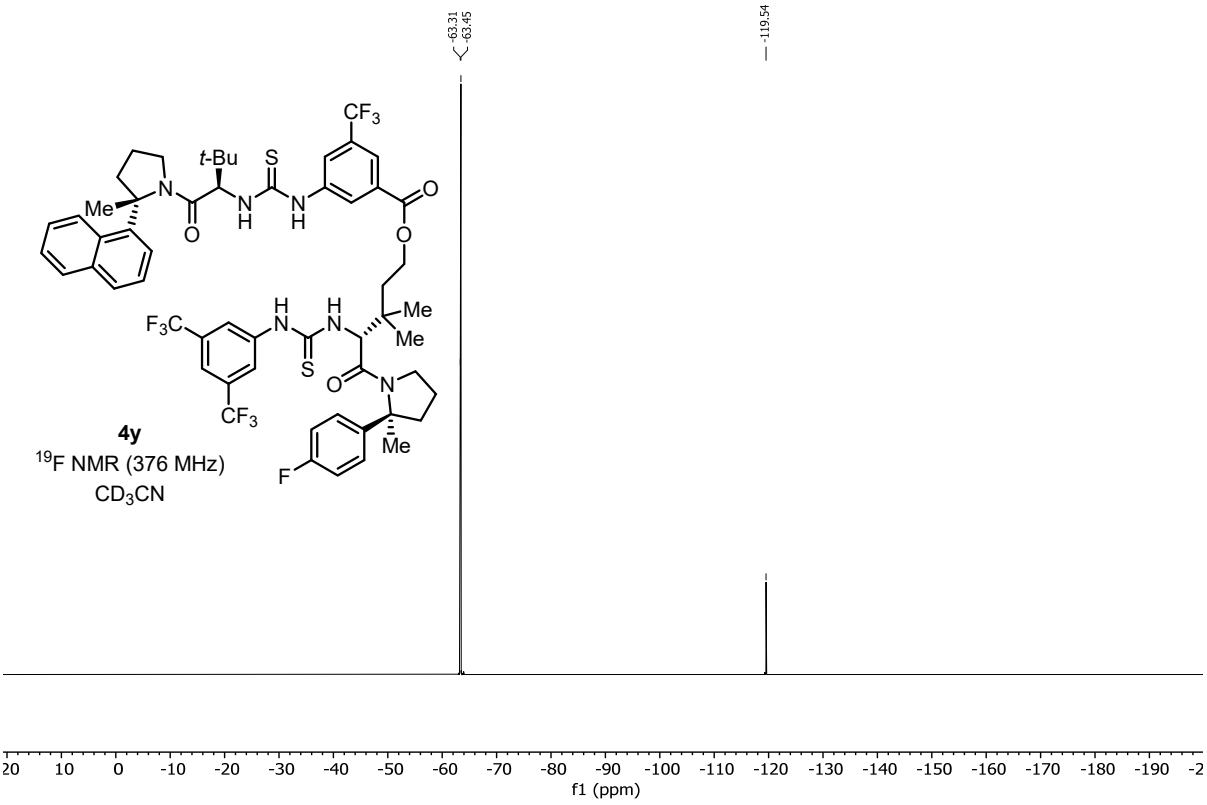

4x
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)

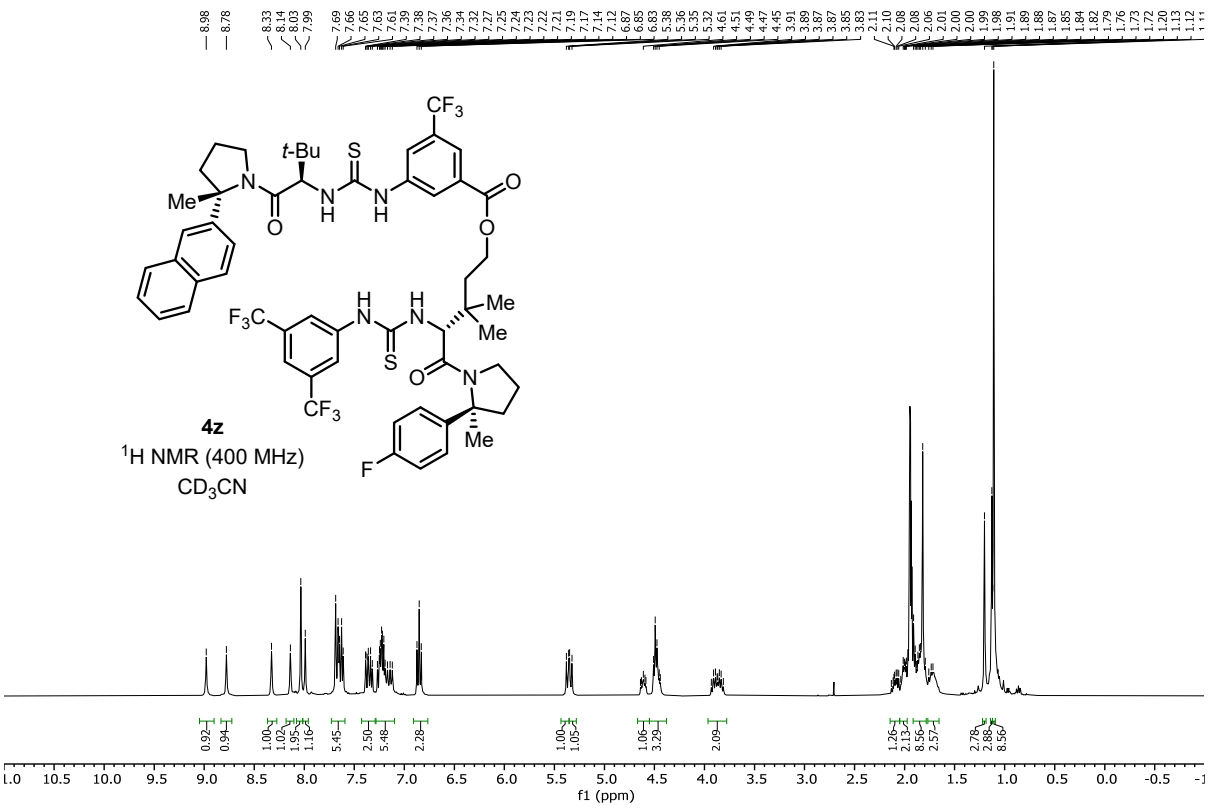

4x
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)

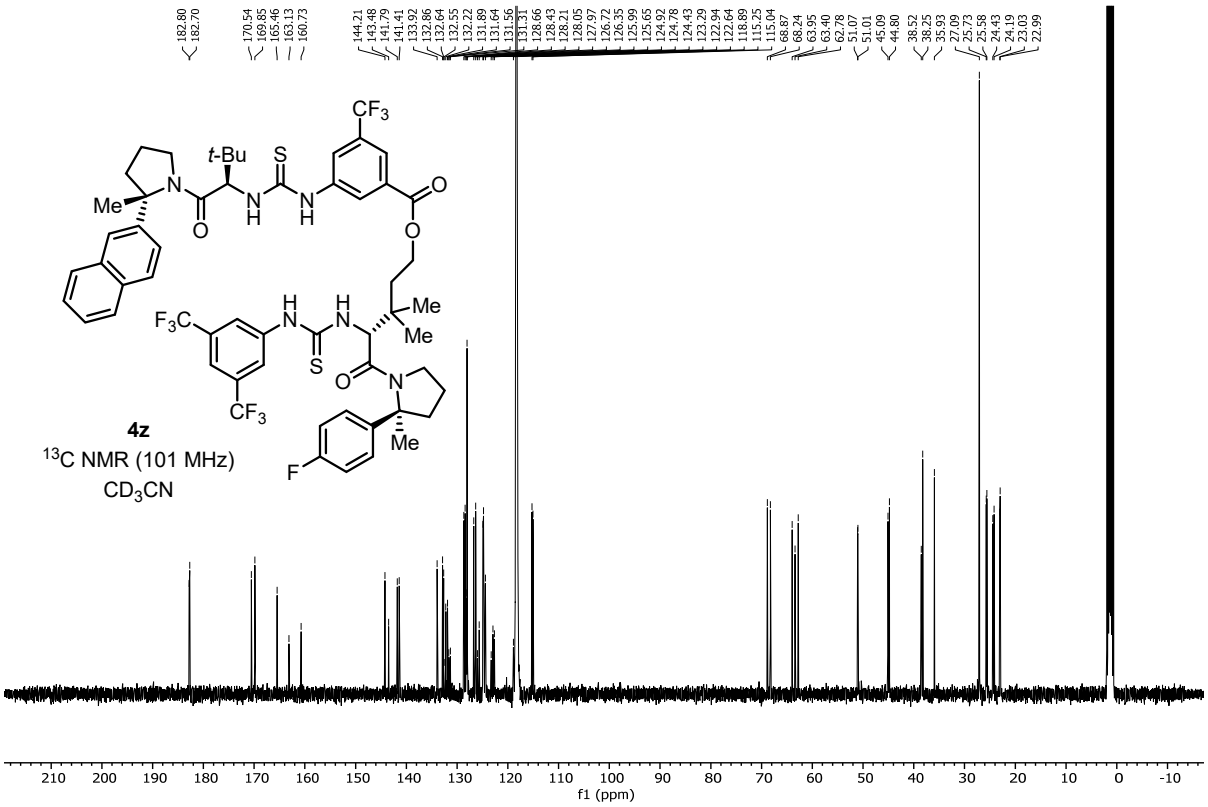

-63.33
-63.44
-119.52
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4x
19F NMR (376 MHz)
CD3CN
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

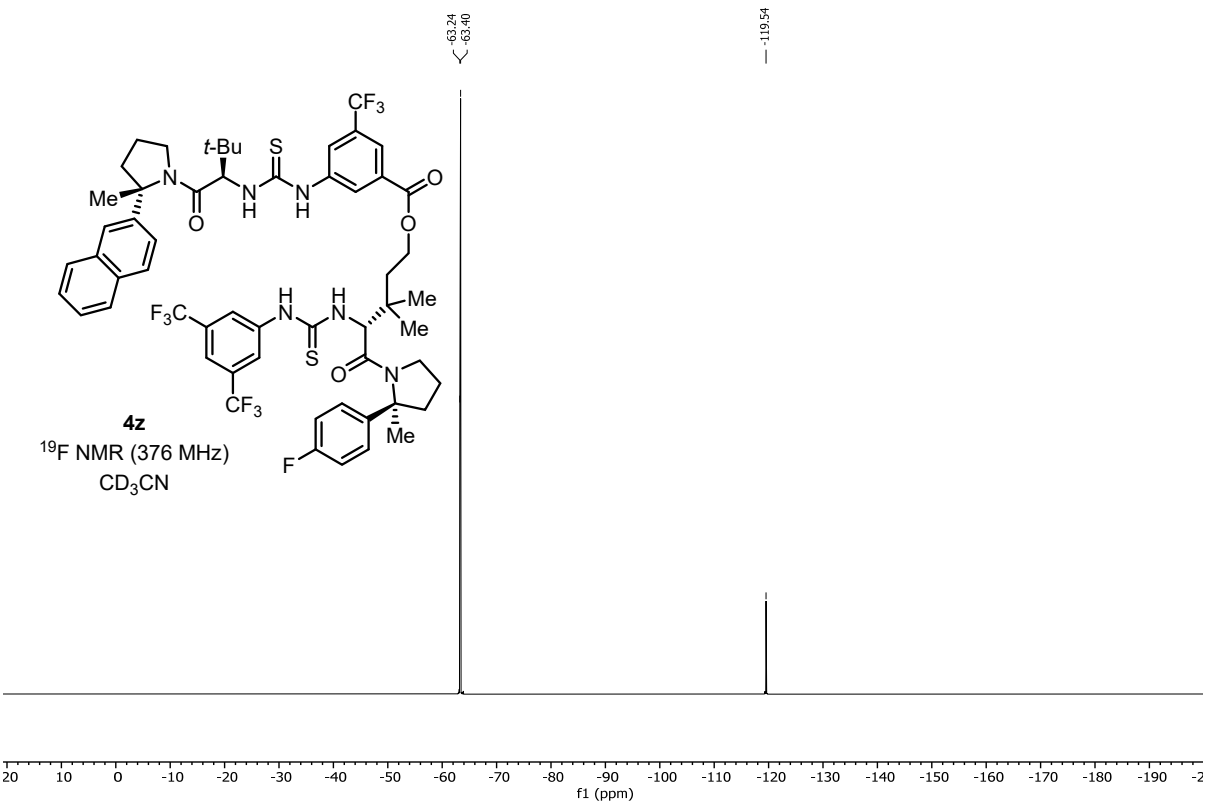

4y
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)

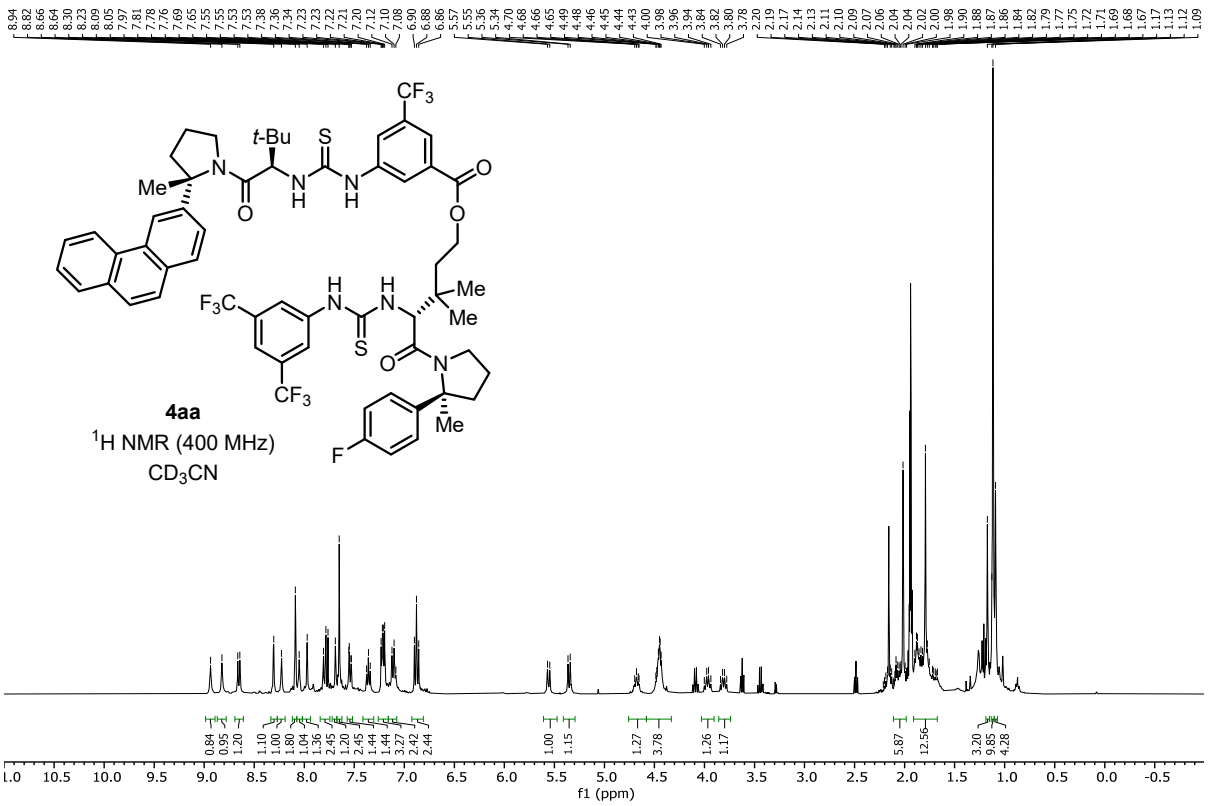

4y
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)

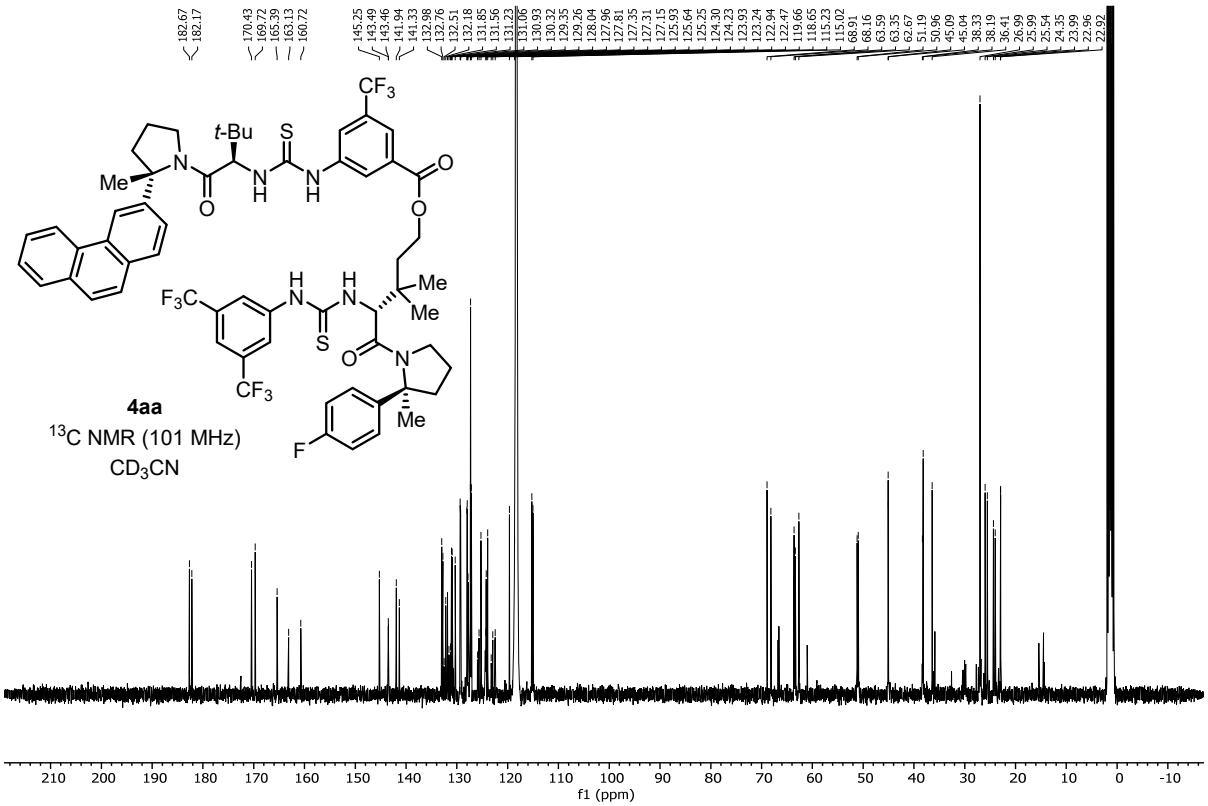

-63.31
-63.45
-119.54
CF3
t-Bu
S
Me
N
O
H
N
N
H
O
F3C
Me
Me
S
CF3
Me
F
4y
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

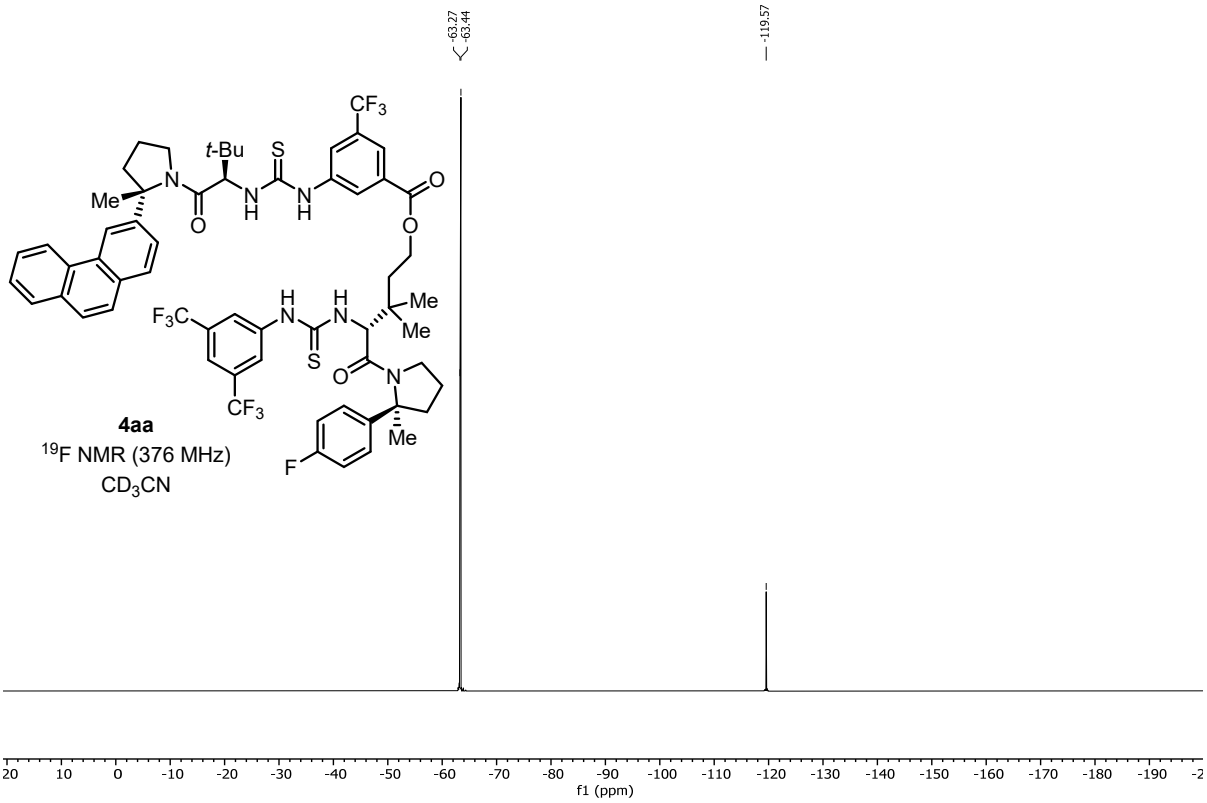

4z
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)

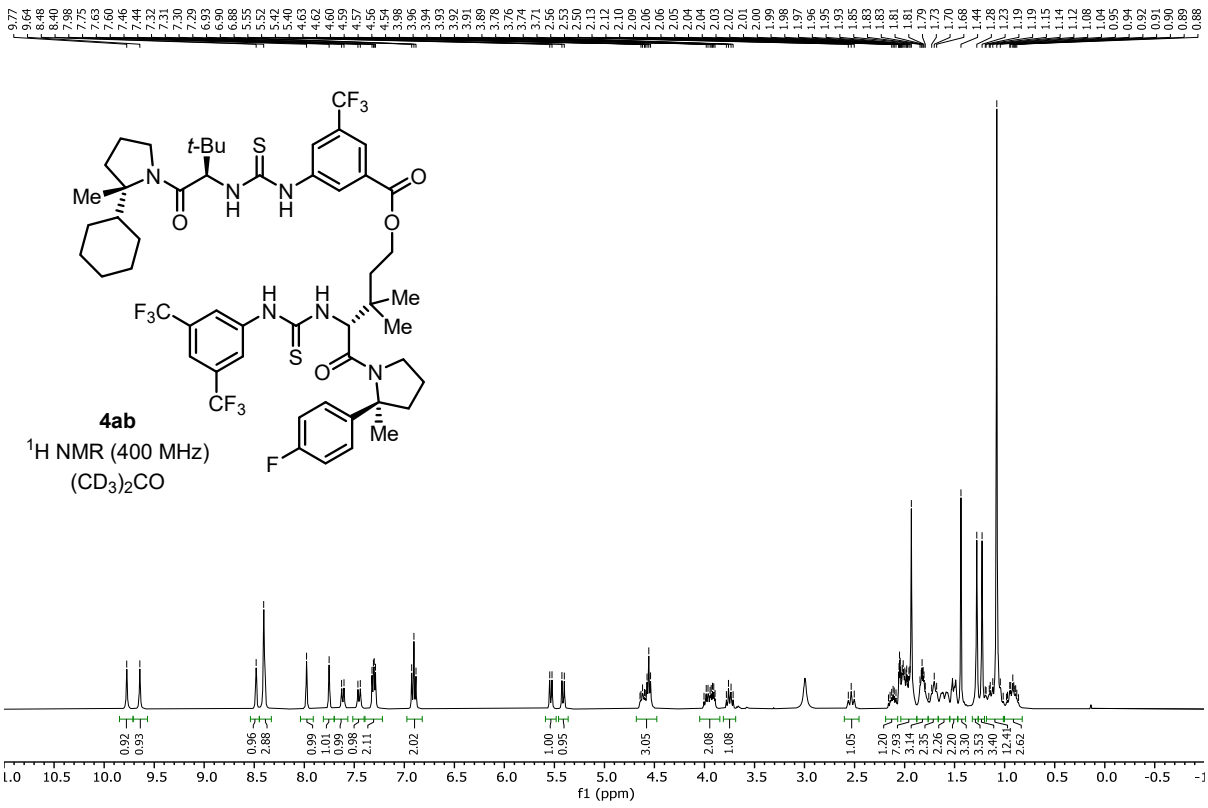

4z
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)

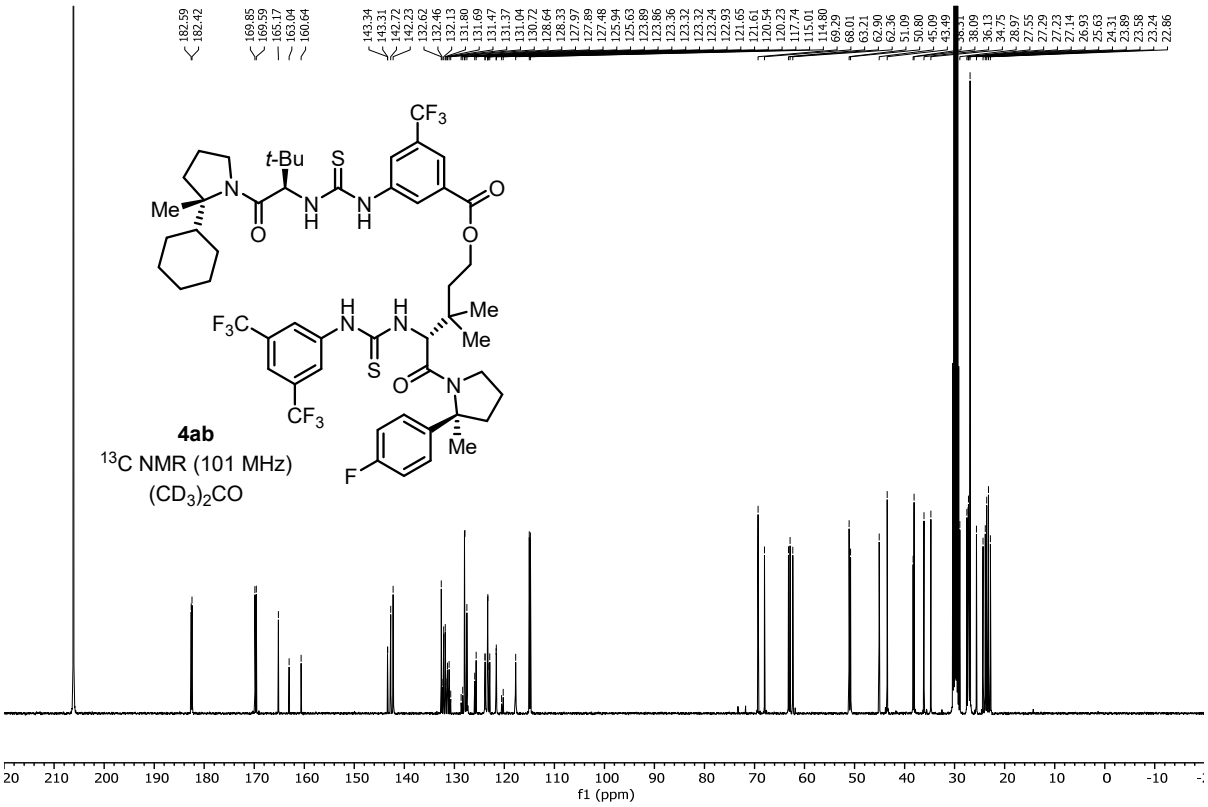

-63.24
-63.40
-119.54
CF3
t-Bu
S
Me
N
O
H
N
H
N
O
O
F3C
Me
Me
S
O
N
CF3
Me
F
4z
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

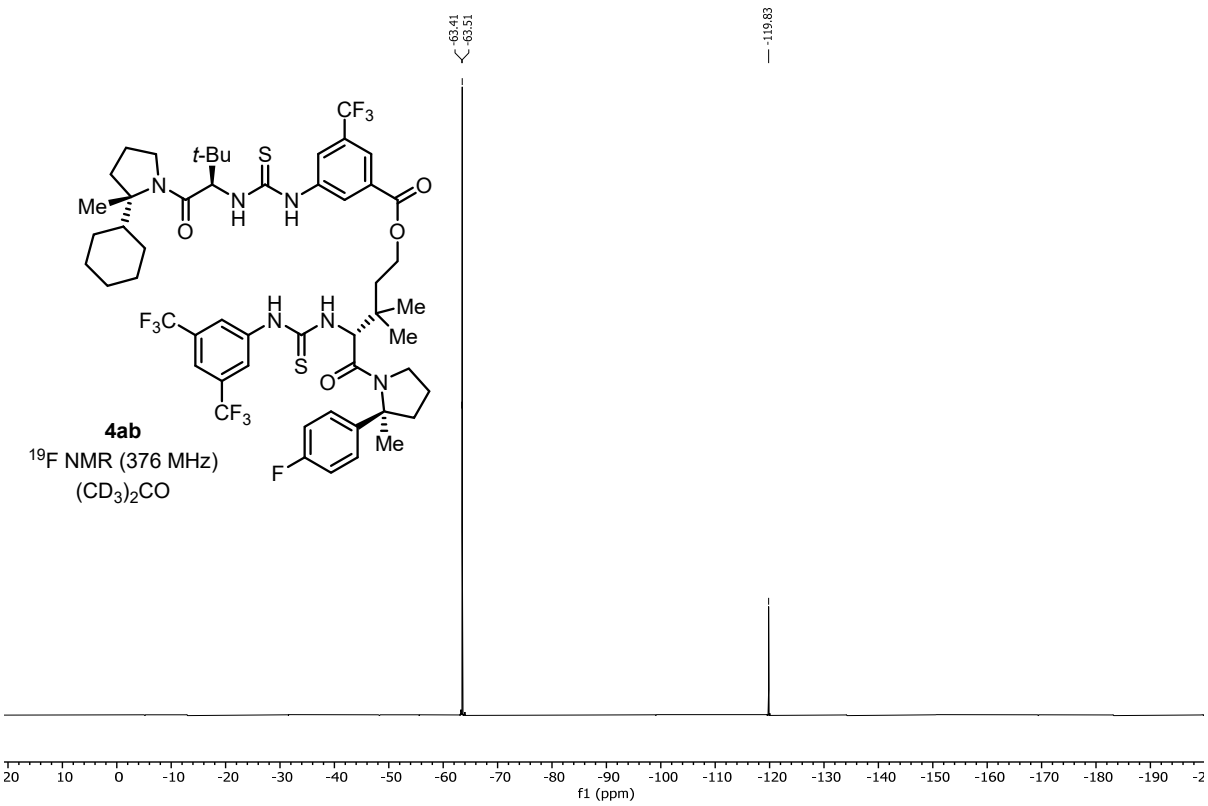

4aa
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)


4aa
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)


-63.27
-63.44
-119.57
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4aa
19F NMR (376 MHz)
CD3CN
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


4ab
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)


4ab
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)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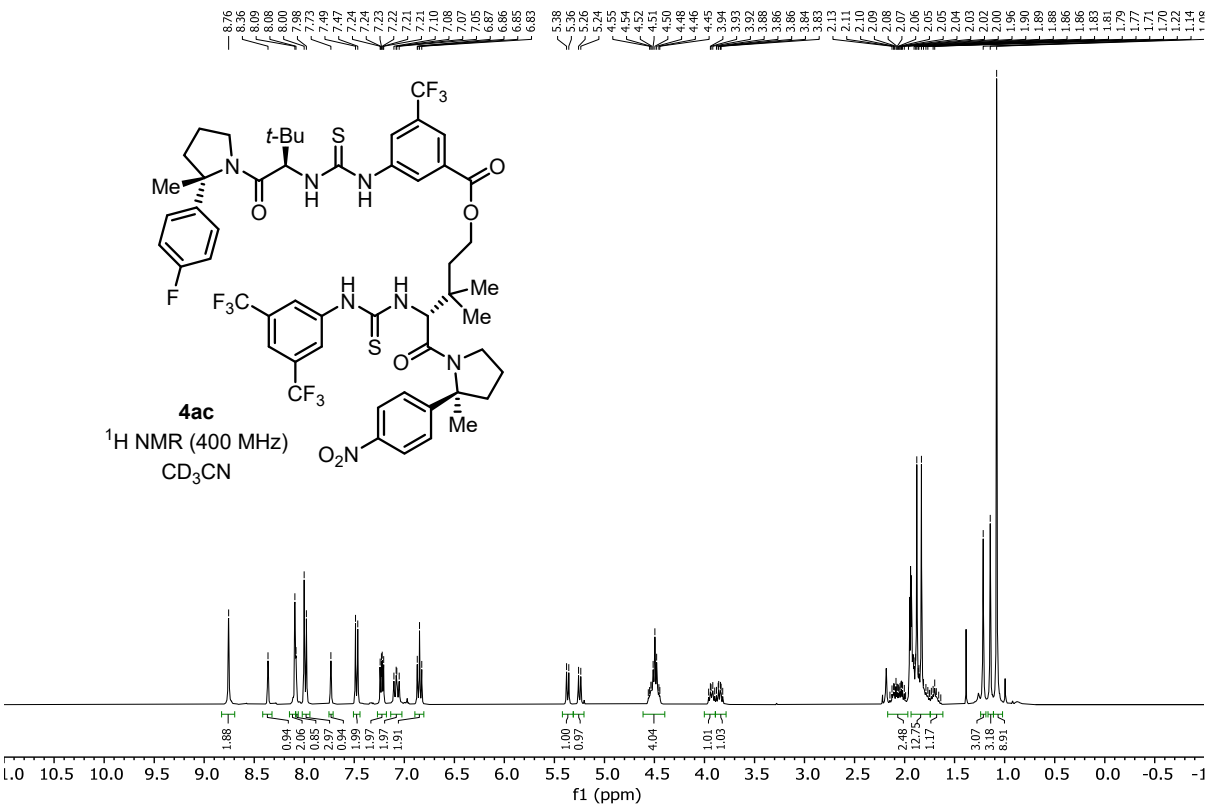
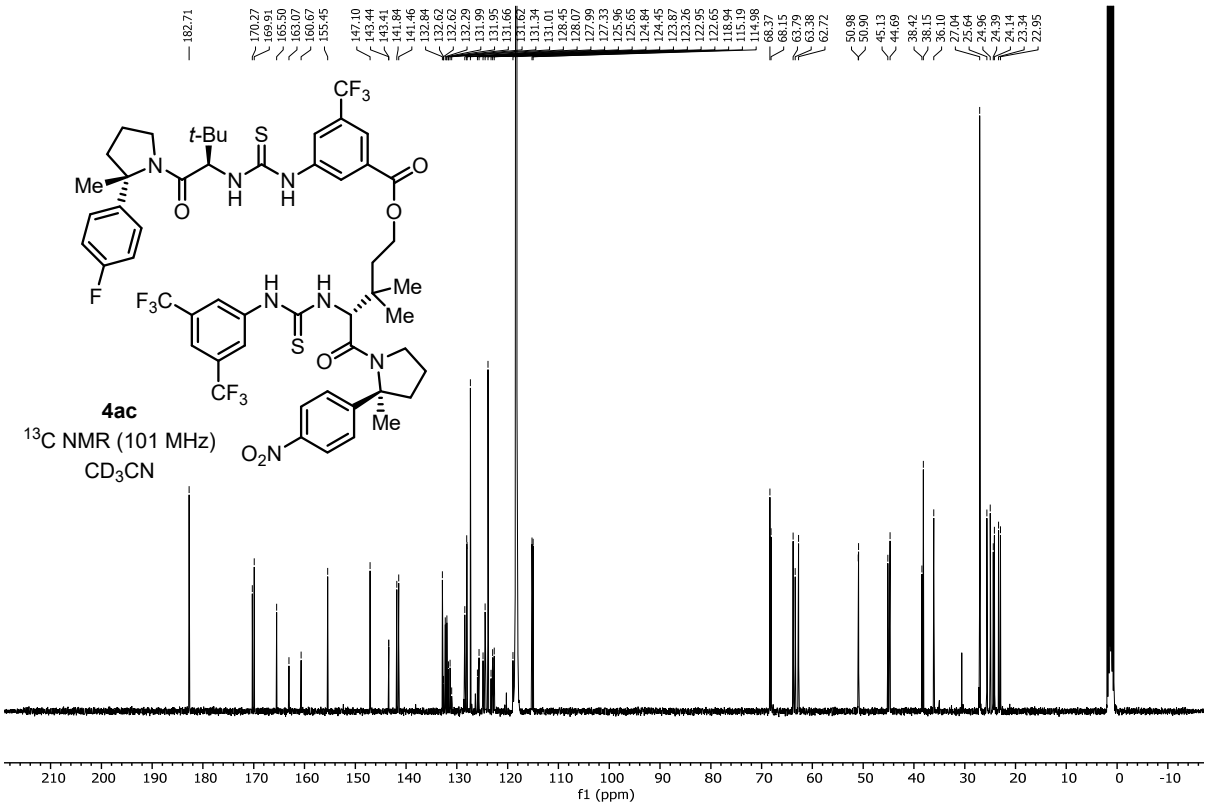
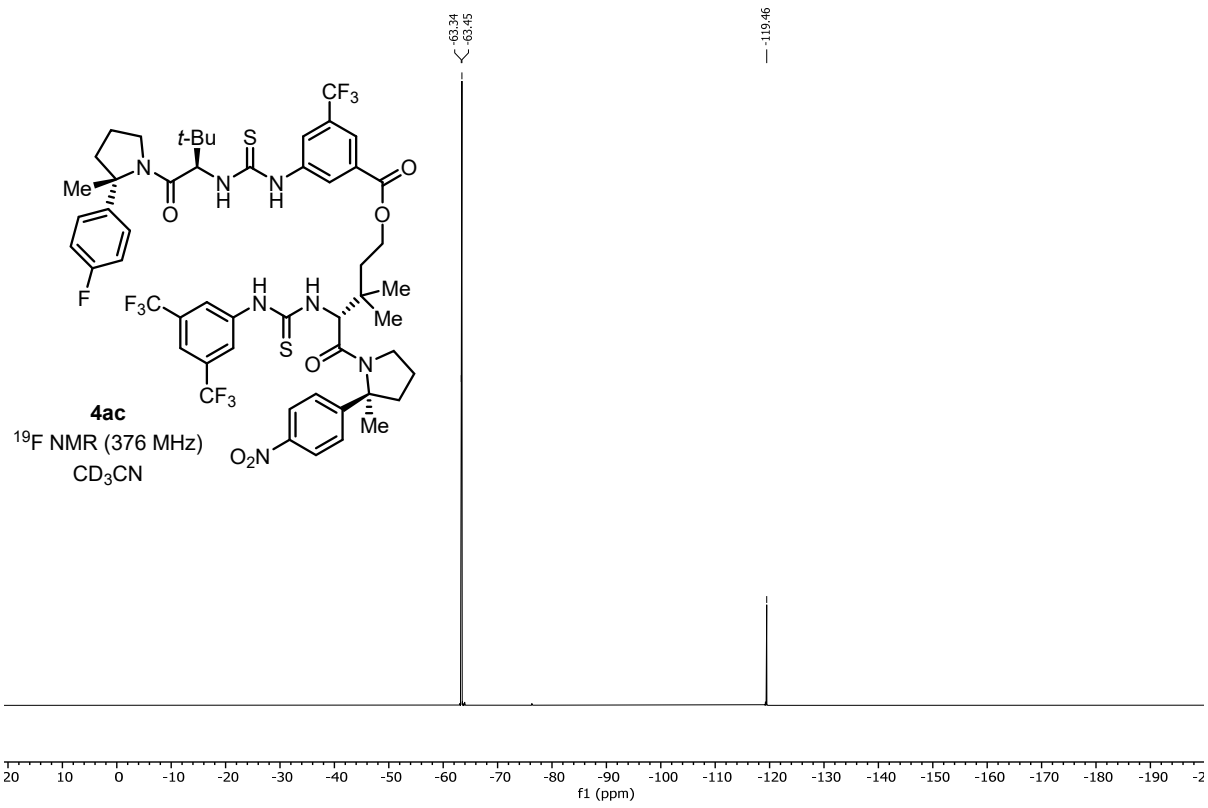
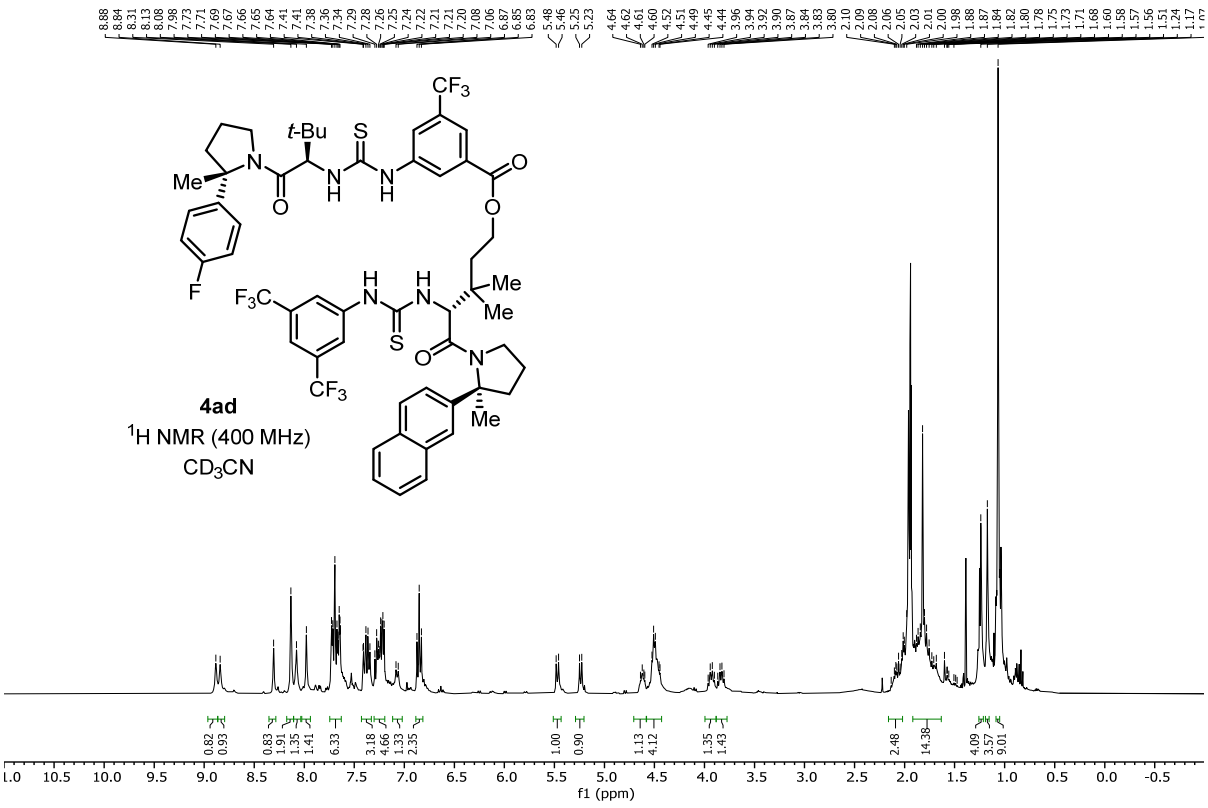
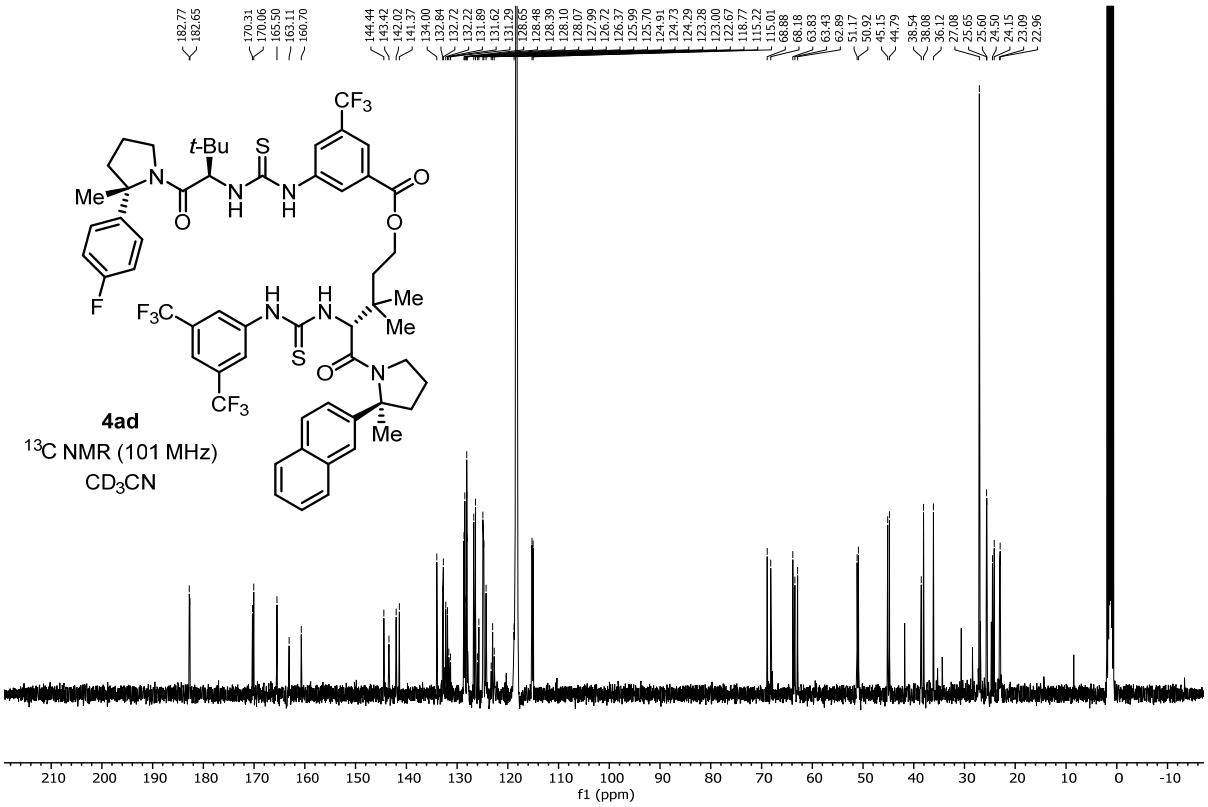
-63.51
-119.83
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4ab
19F NMR (376 MHz)
(CD3)2CO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

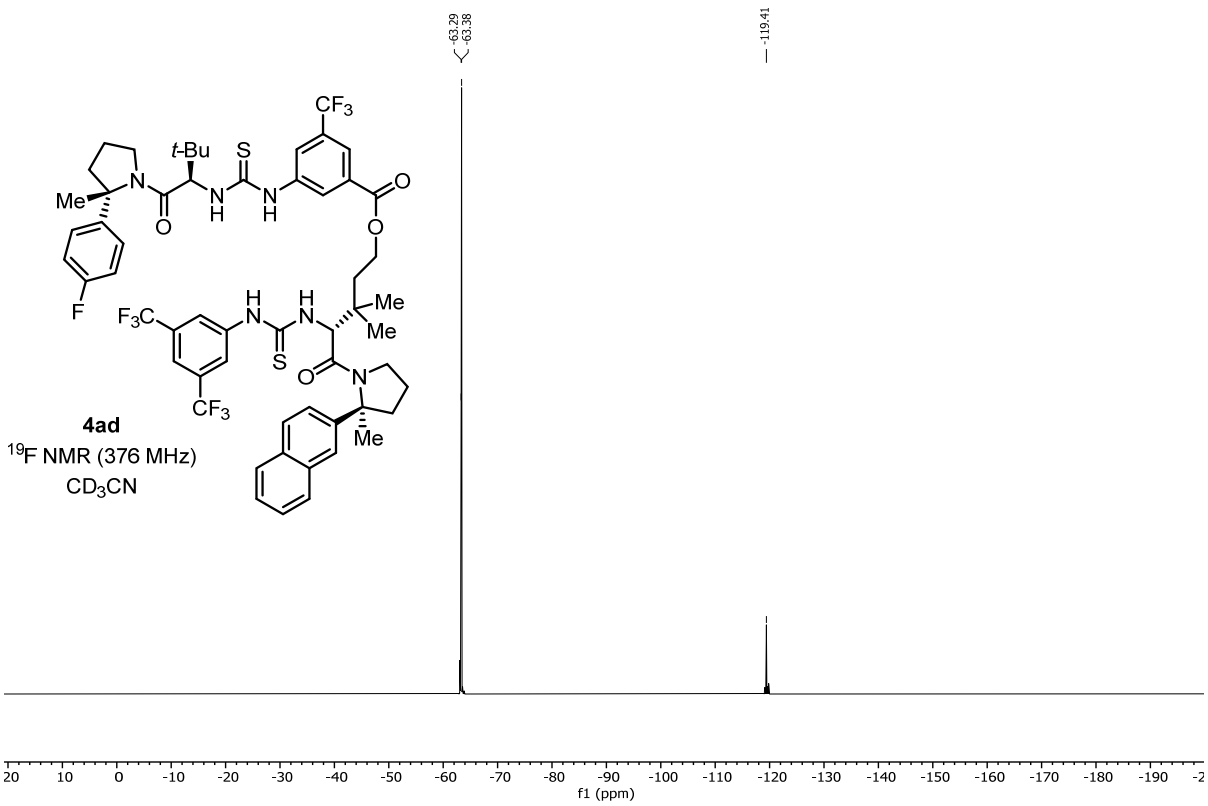

4ac
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)

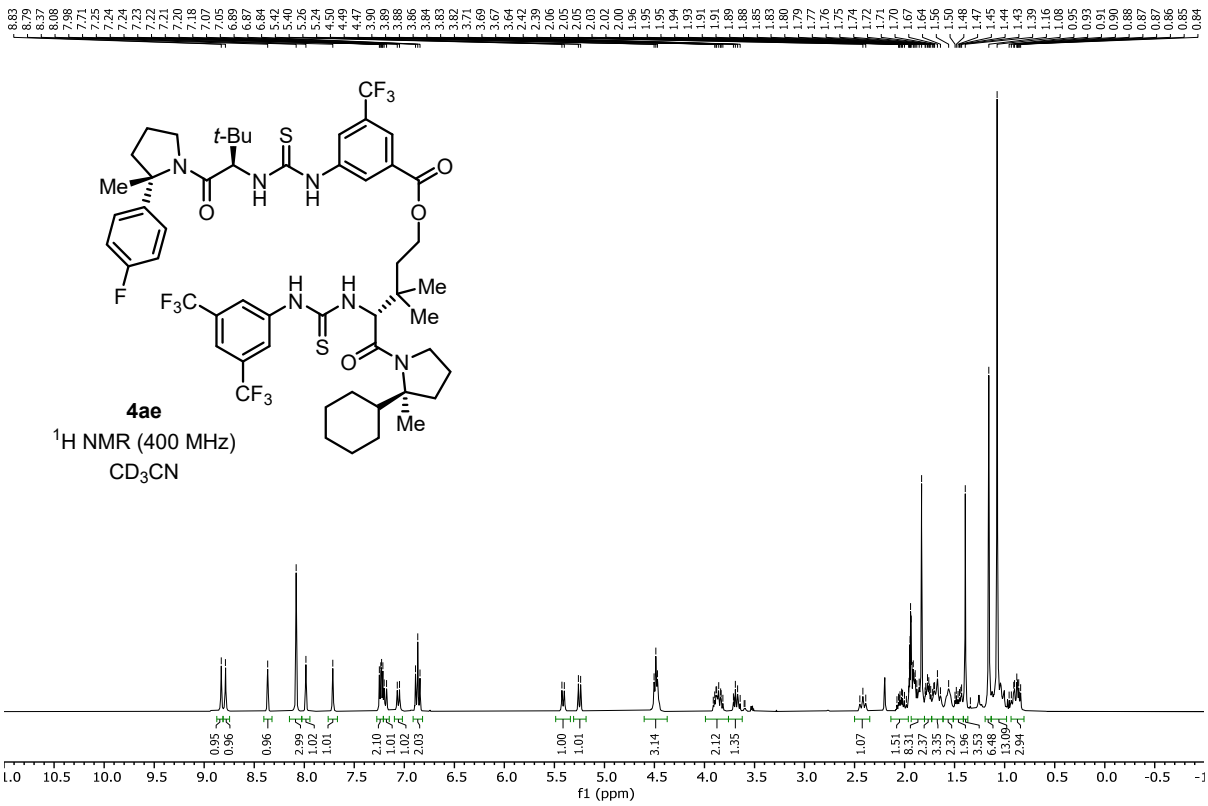

4ac
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)

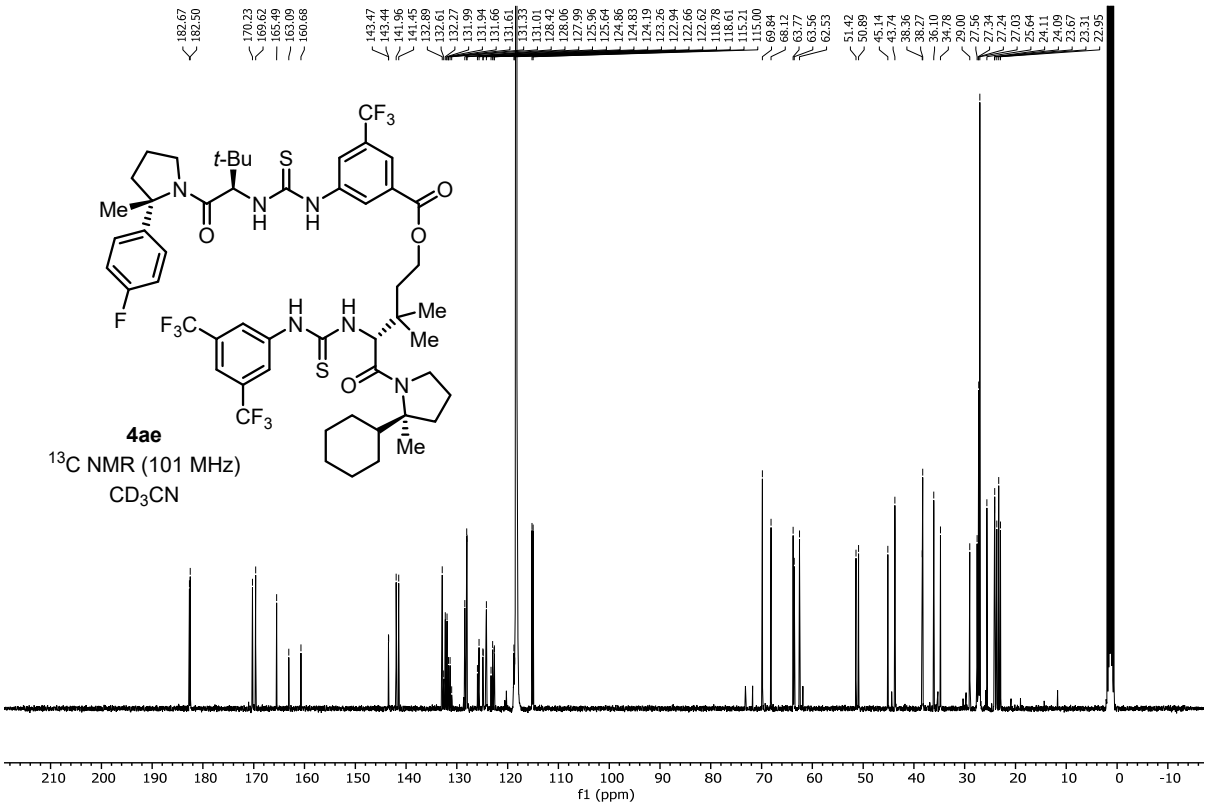

-63.34
-63.45
-119.46
CF3
t-Bu
S
N
Me
O
H
F3C
Me
CF3
O2N
4ac
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

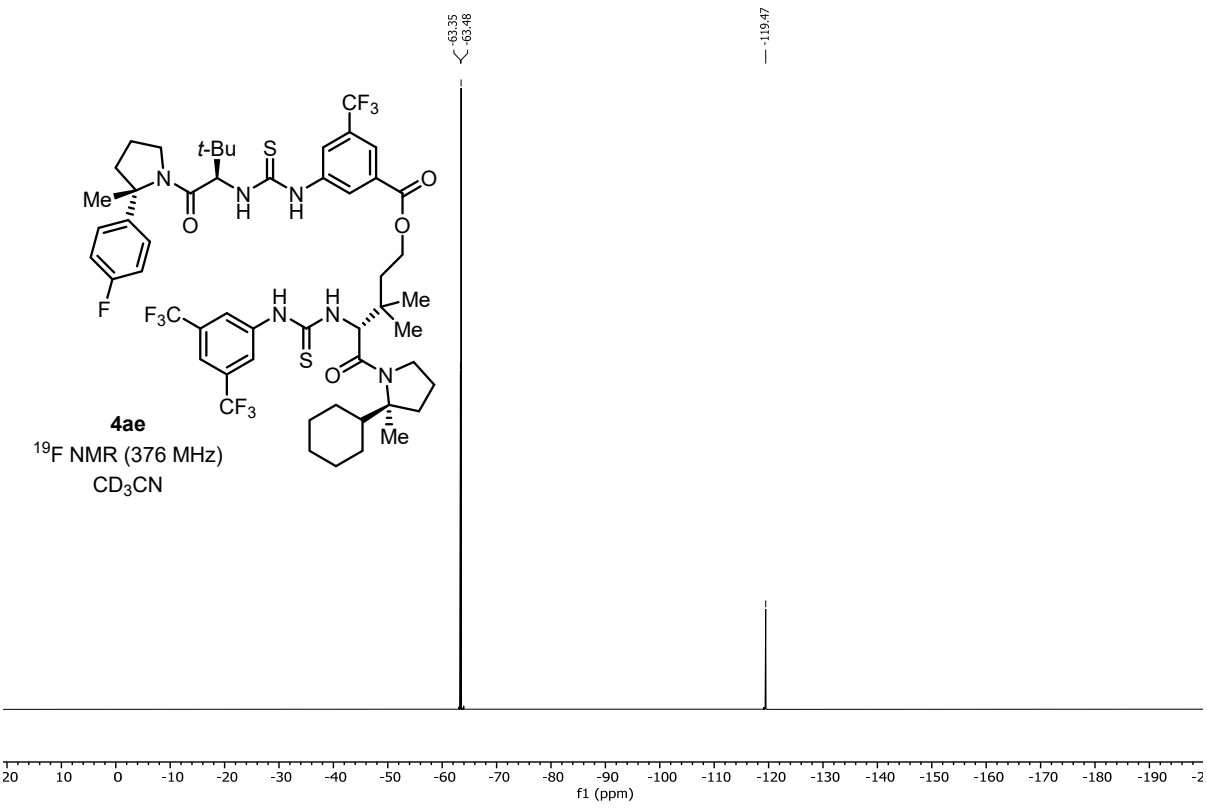

4ad
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)

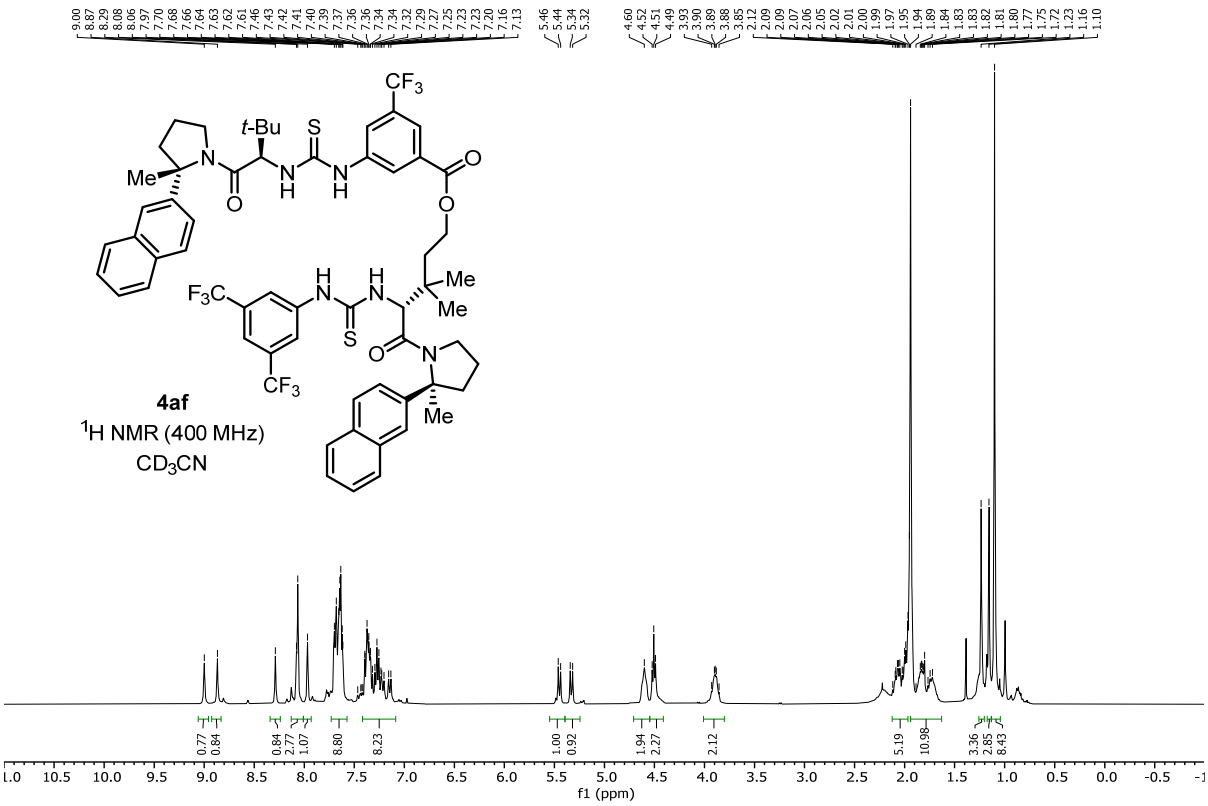

4ad
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)

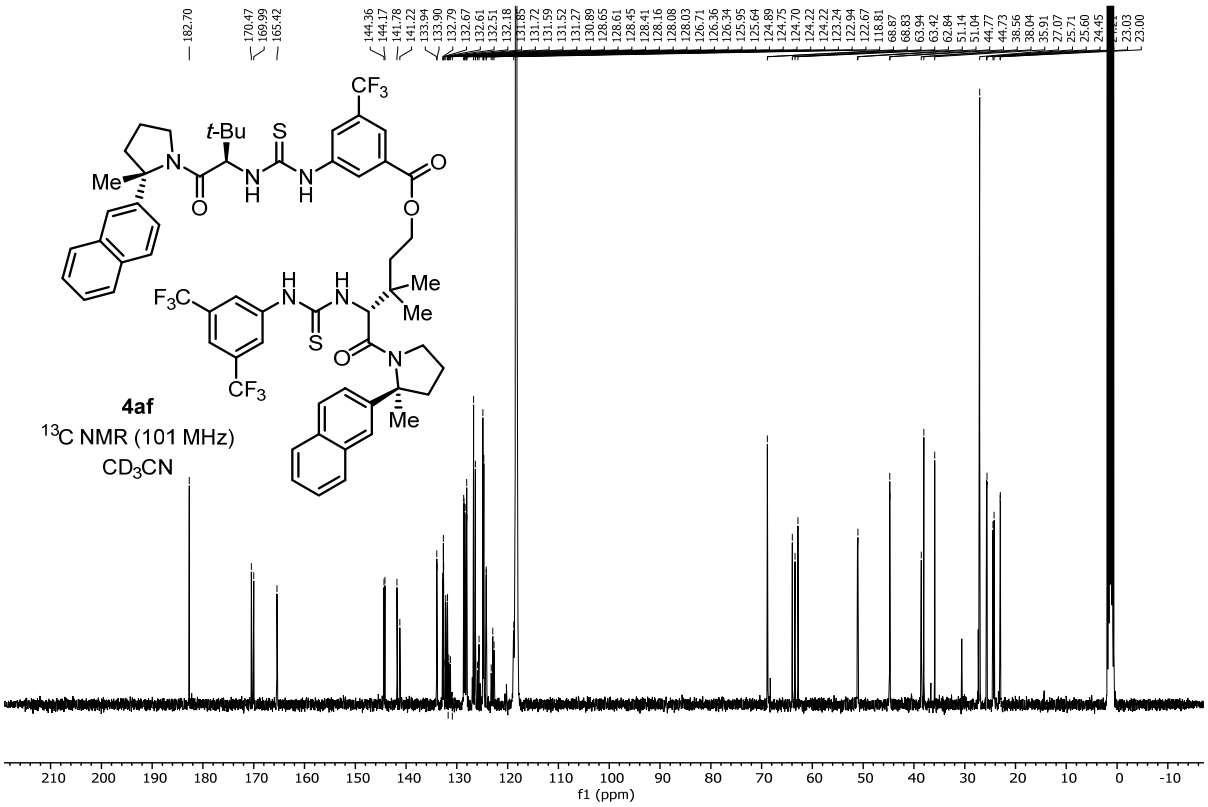

-63.29
-63.38
-119.41
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
4ad
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

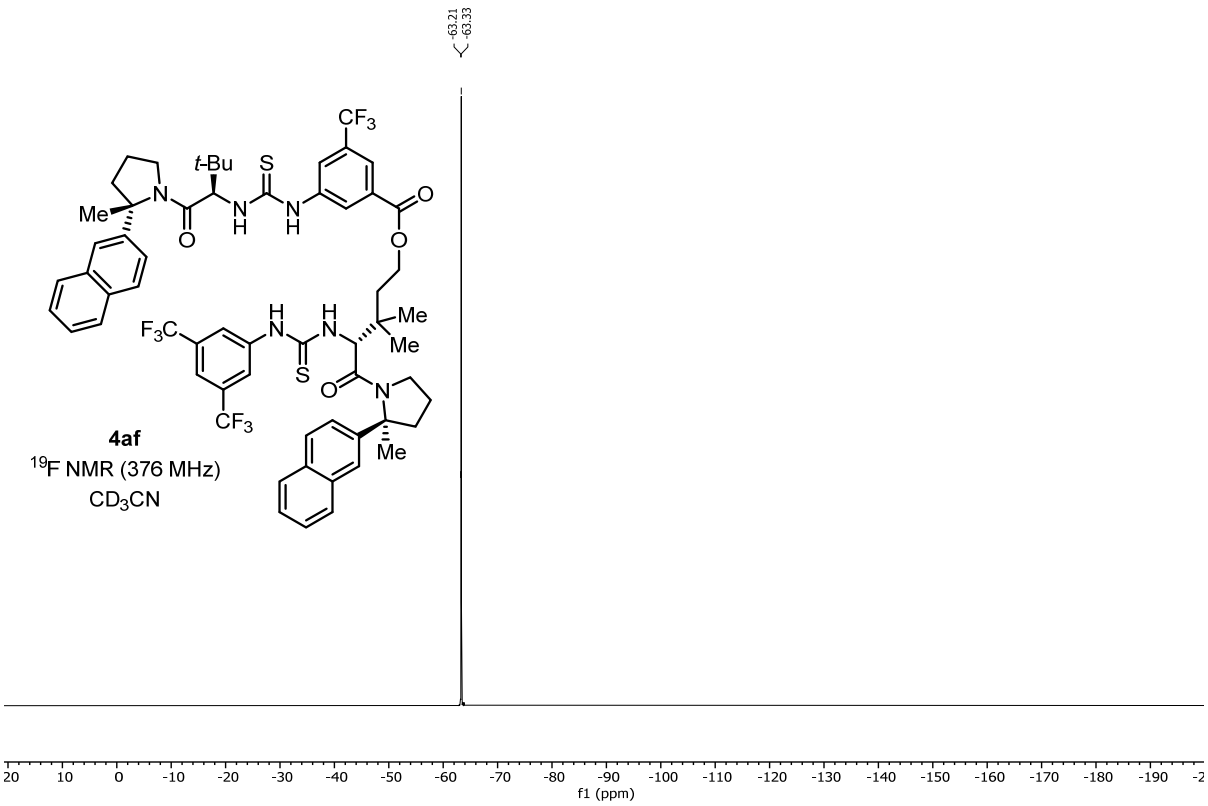

4ae
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)


4ae
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)


-63.35
-63.48
-119.47
CF3
t-Bu
S
Me
N
H
O
F
F3C
Me
Me
CF3
4ae
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


4af
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)


4af
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)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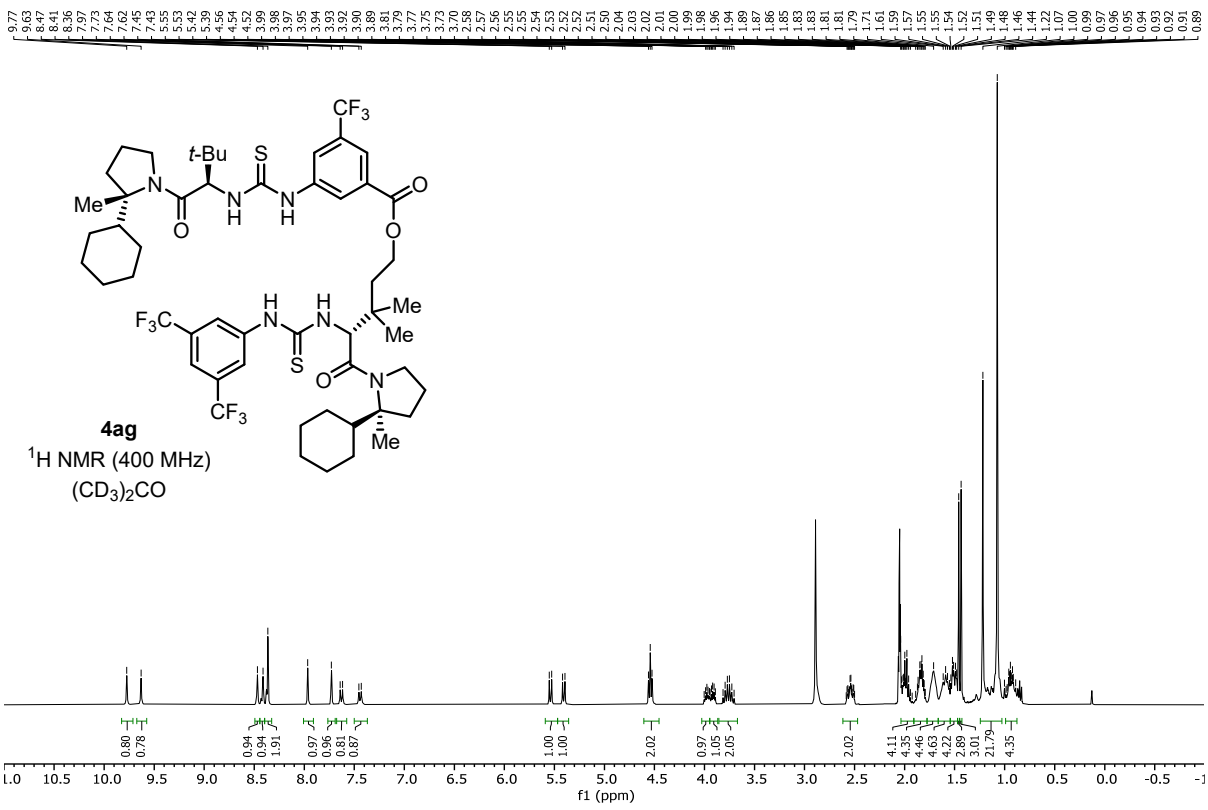
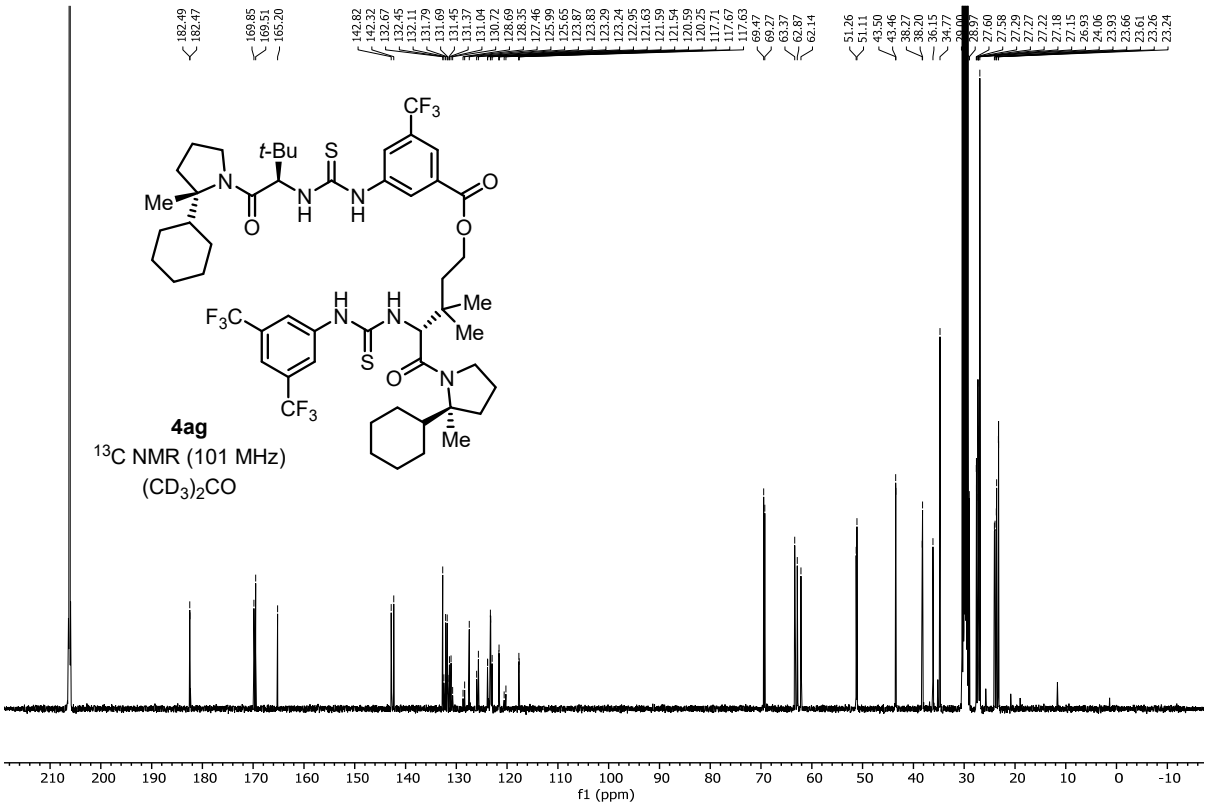
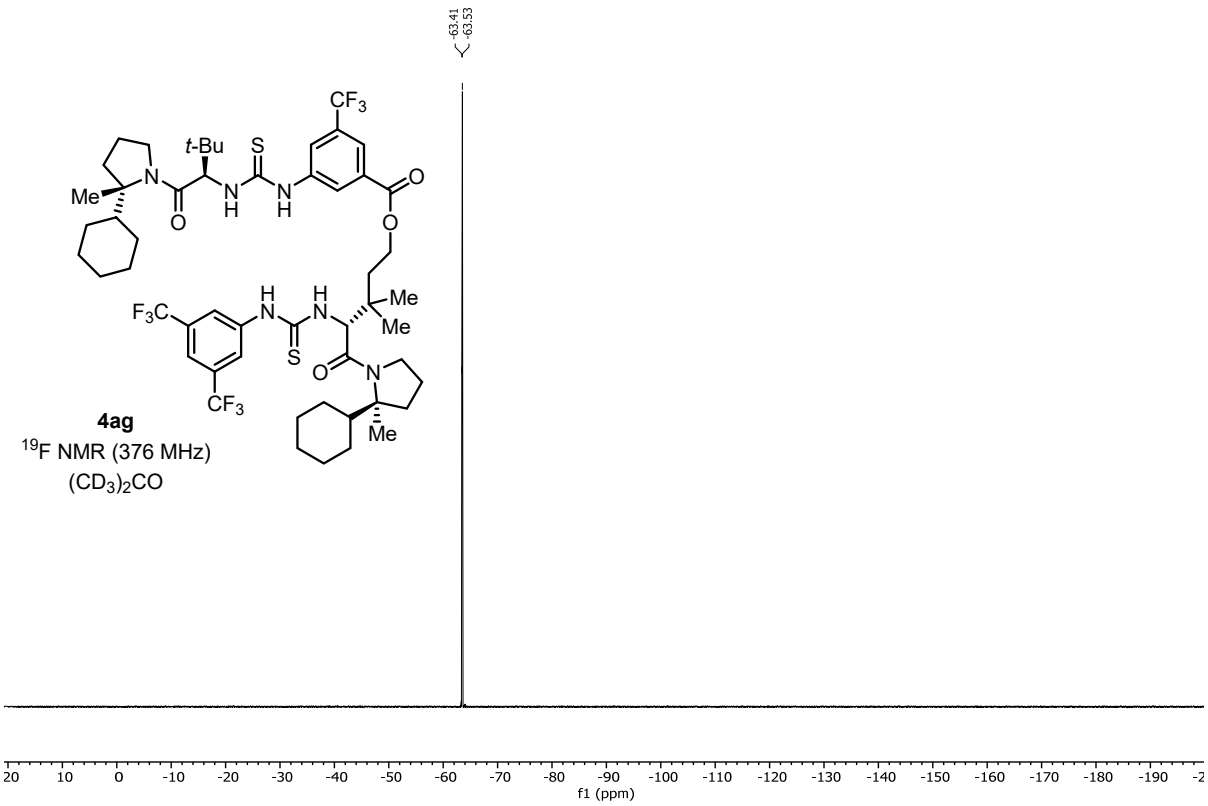
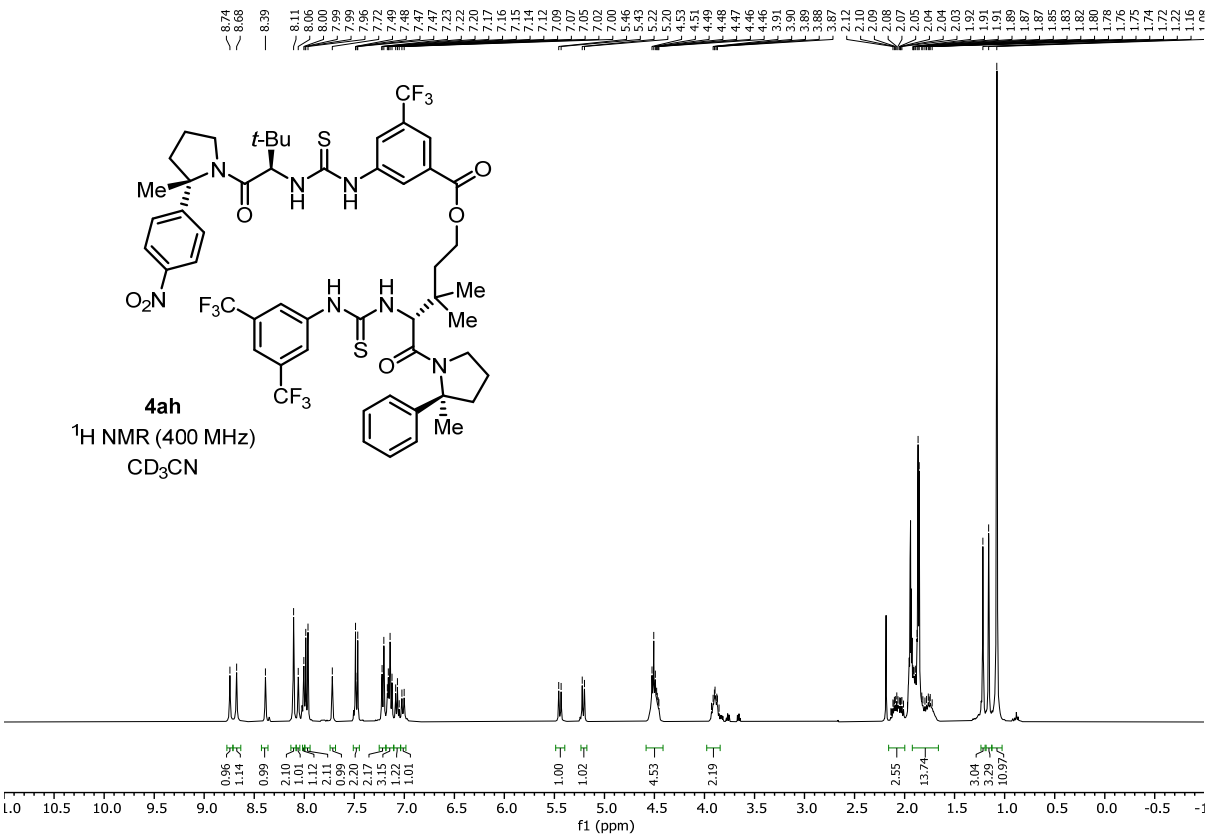
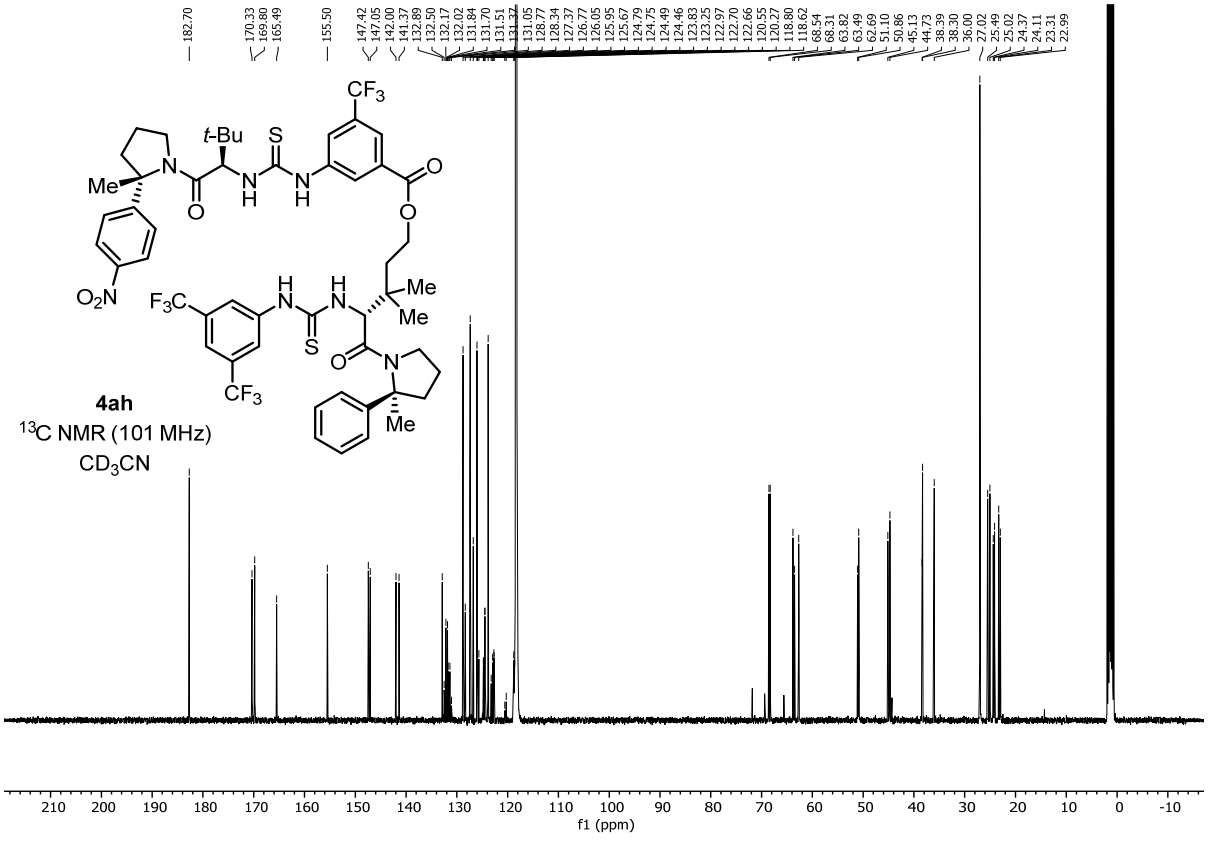
-63.33
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F3C
H
N
S
H
N
Me
Me
O
N
CF3
Me
4af
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

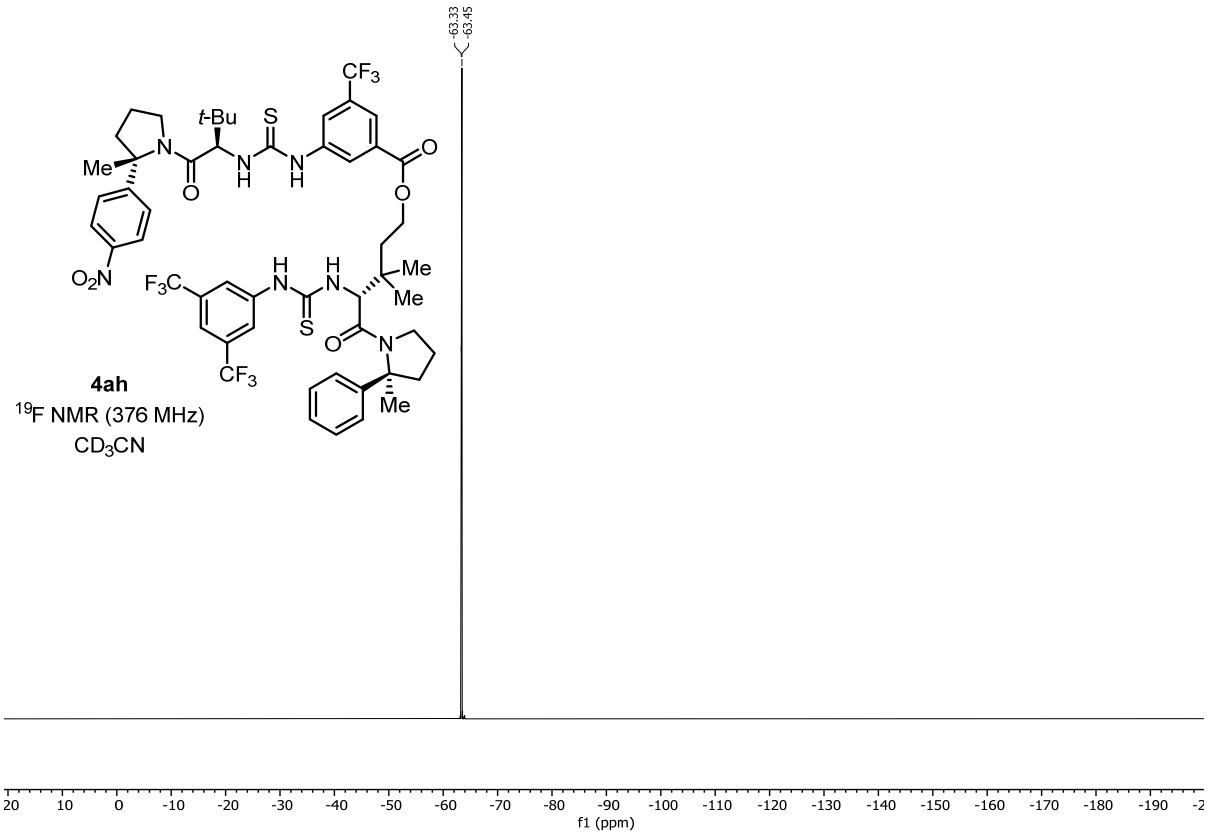

4ag
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)

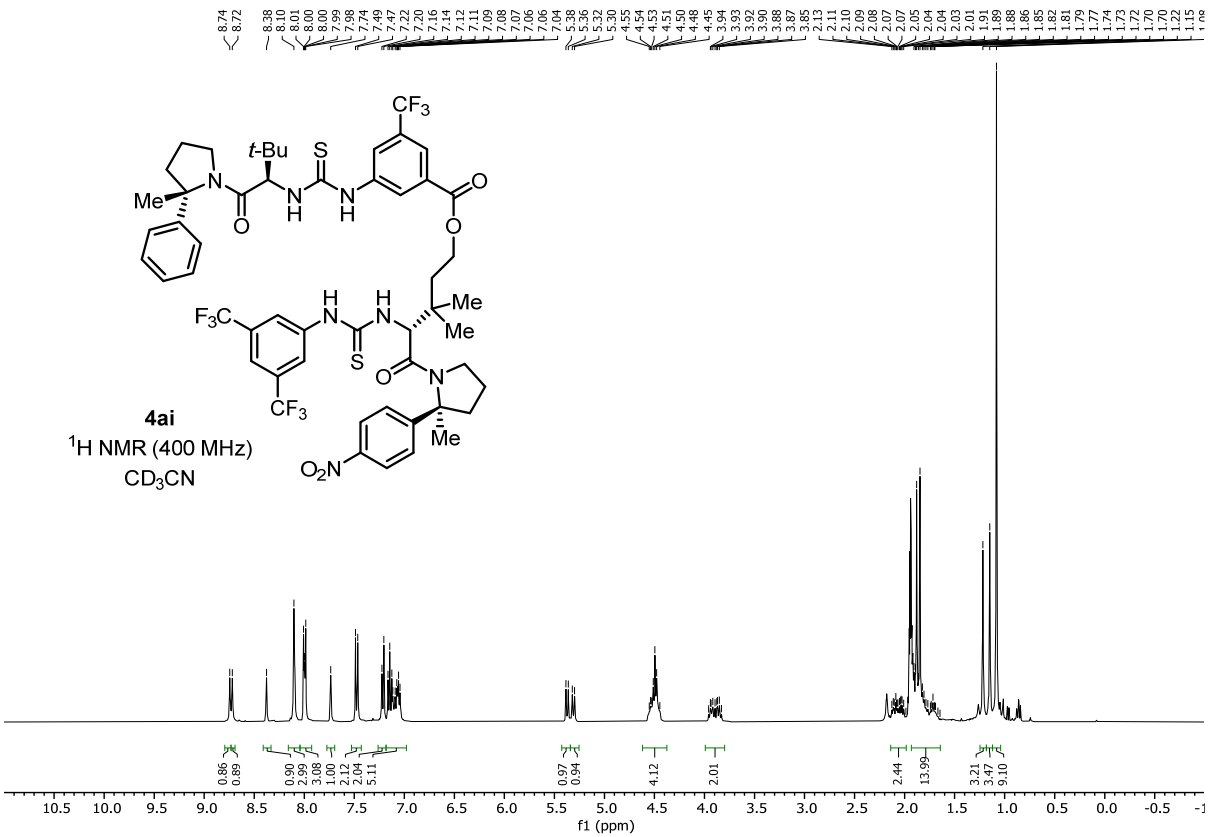

4ag
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

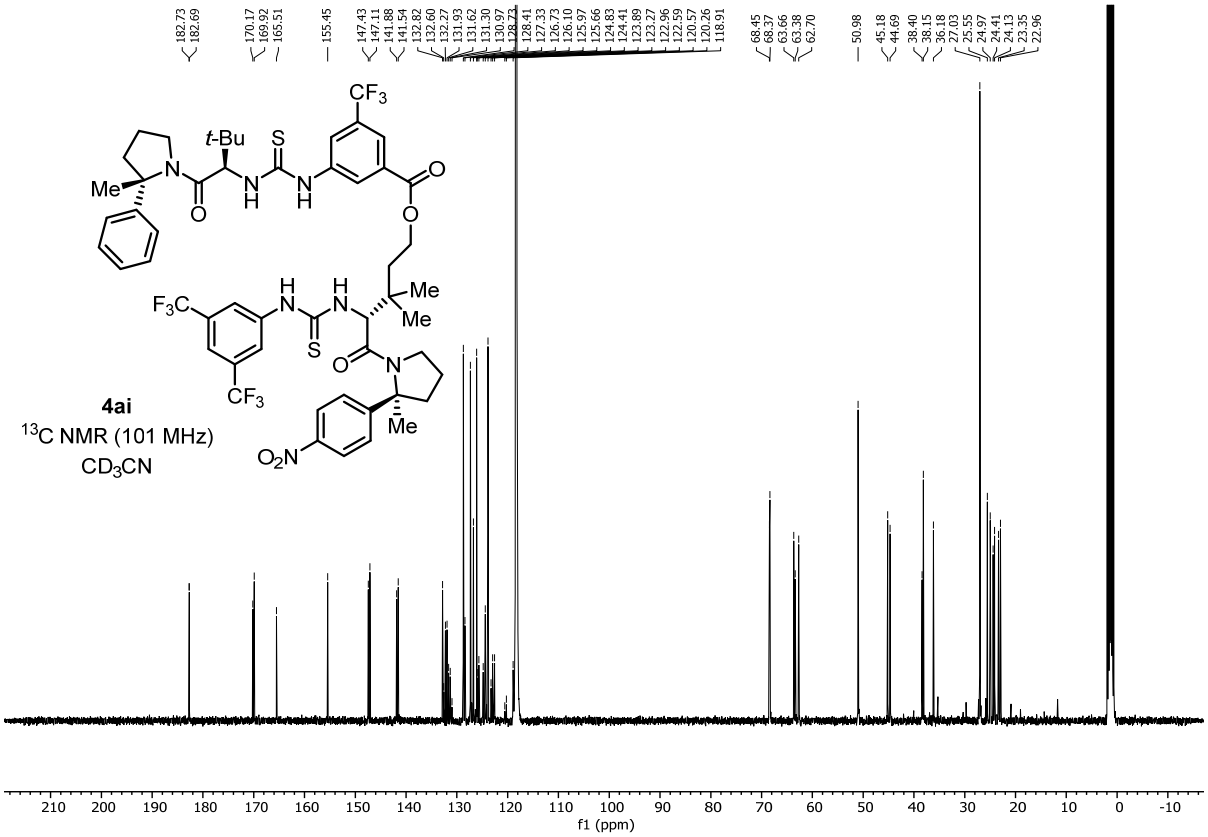

-63.41
-63.53
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
H
N
H
N
Me
Me
F3C
S
O
N
CF3
Me
4ag
19F NMR (376 MHz)
(CD3)2CO
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

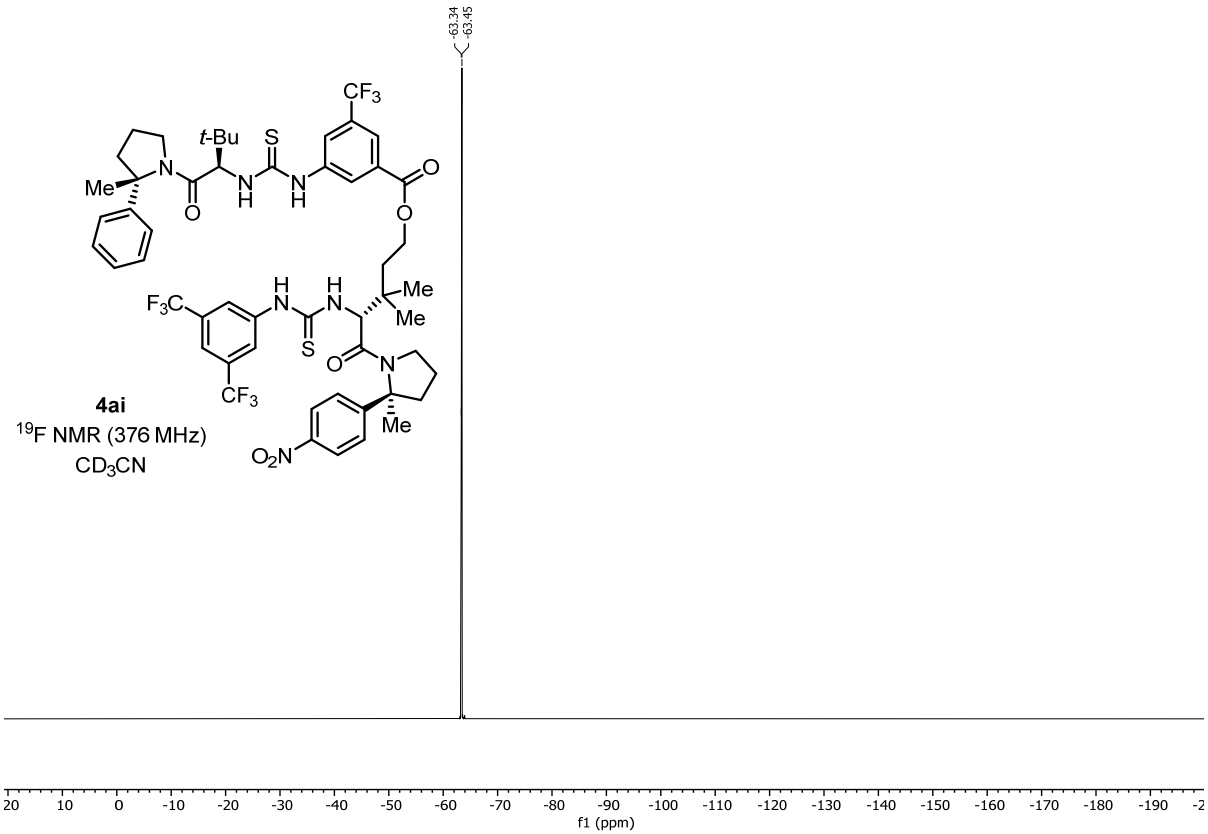

4ah
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)


4ah
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)


-63.33
-63.45
4ah
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)


4ai
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)


4ai
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)


-63.34
-63.45
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
O2N
4ai
19F NMR (376 MHz)
CD3CN
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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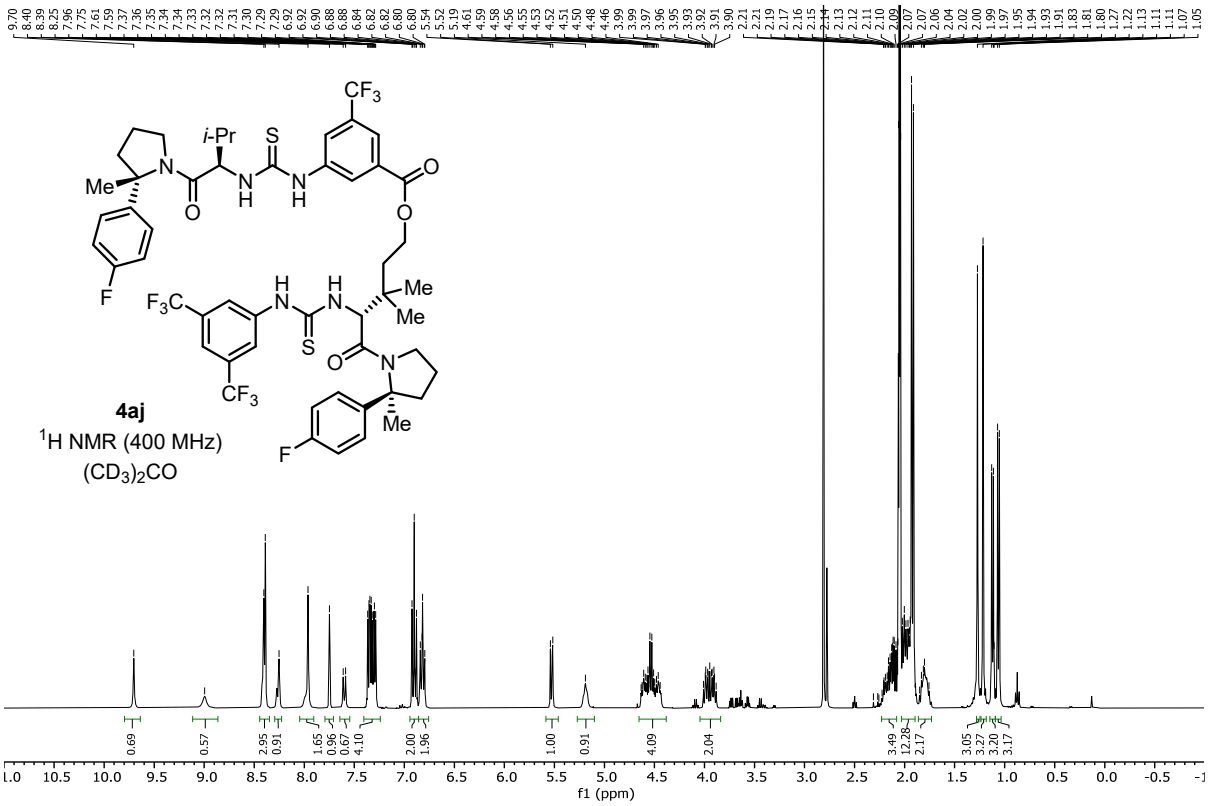
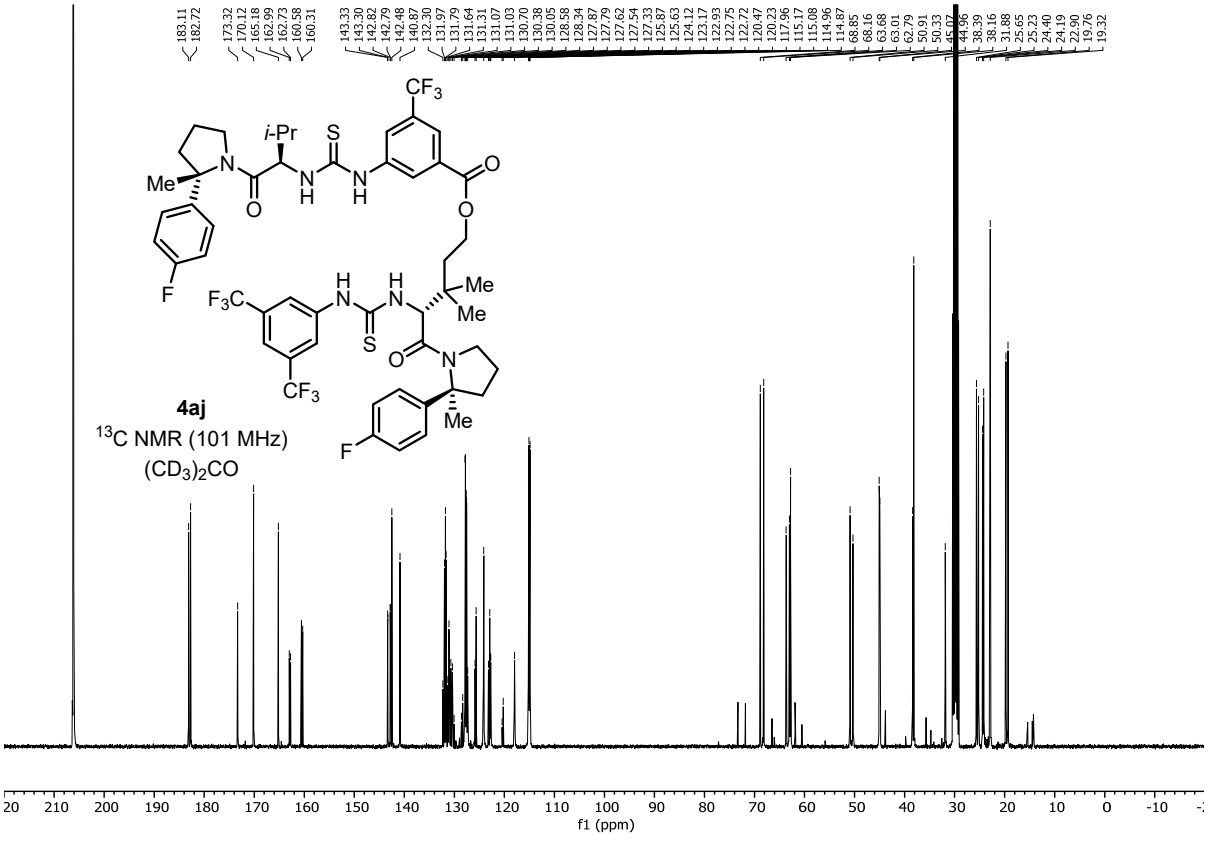
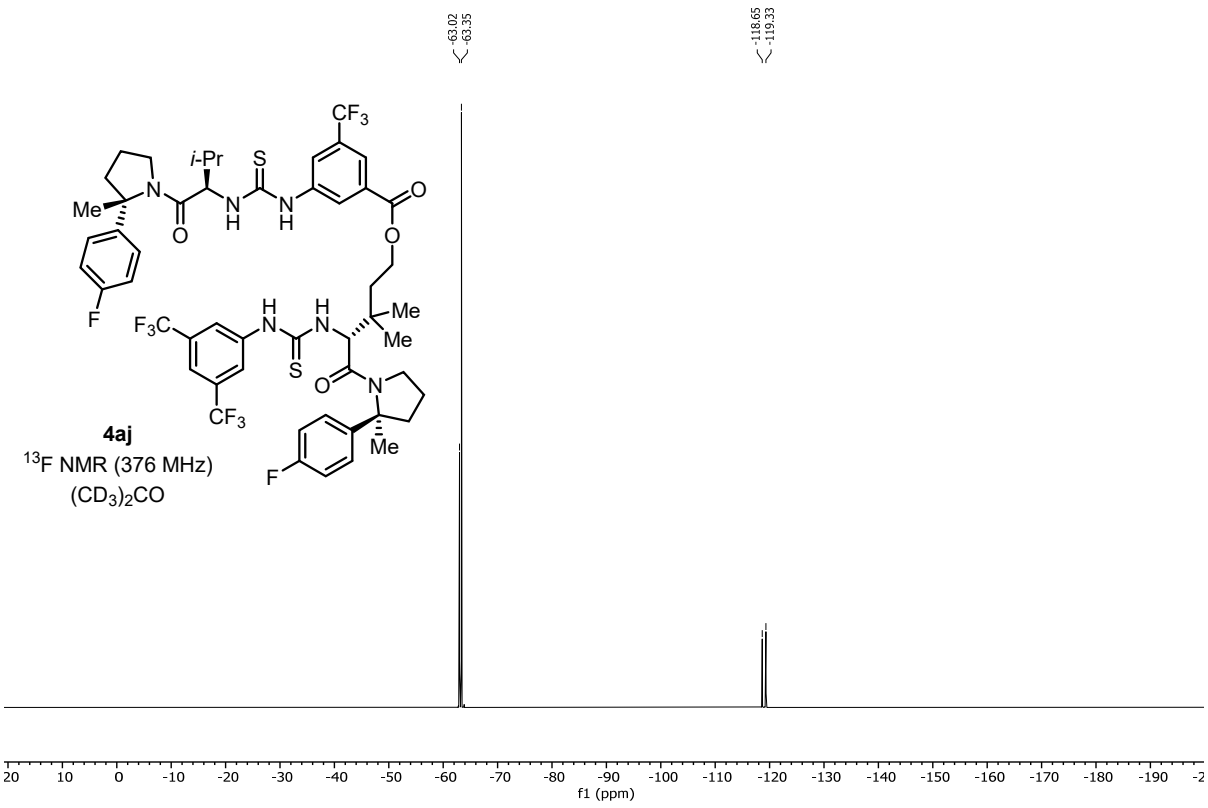
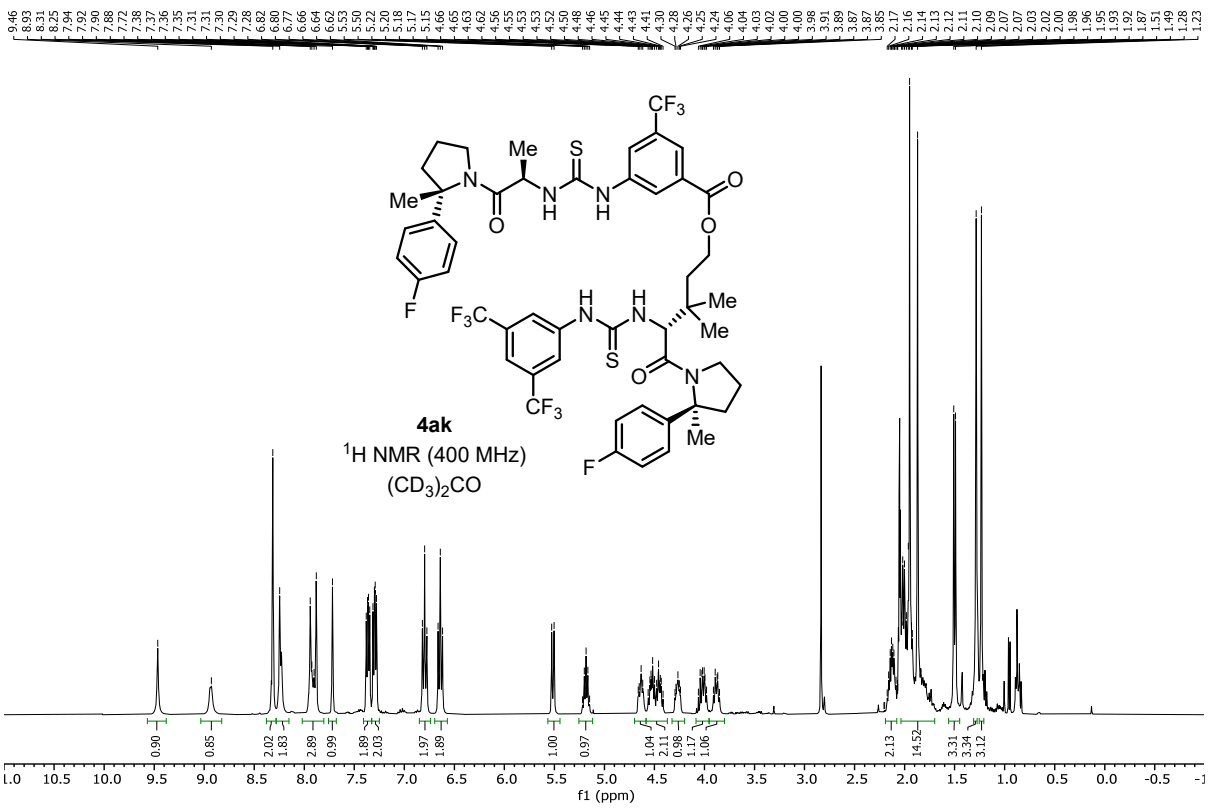
-180
-190
f1 (ppm)


4aj
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)


4aj
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)


-63.02
-63.35
-118.65
-119.33
CF3
i-Pr
S
Me
N
O
N
H
N
H
O
O
F
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
F
4aj
13F NMR (376 MHz)
(CD3)2CO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)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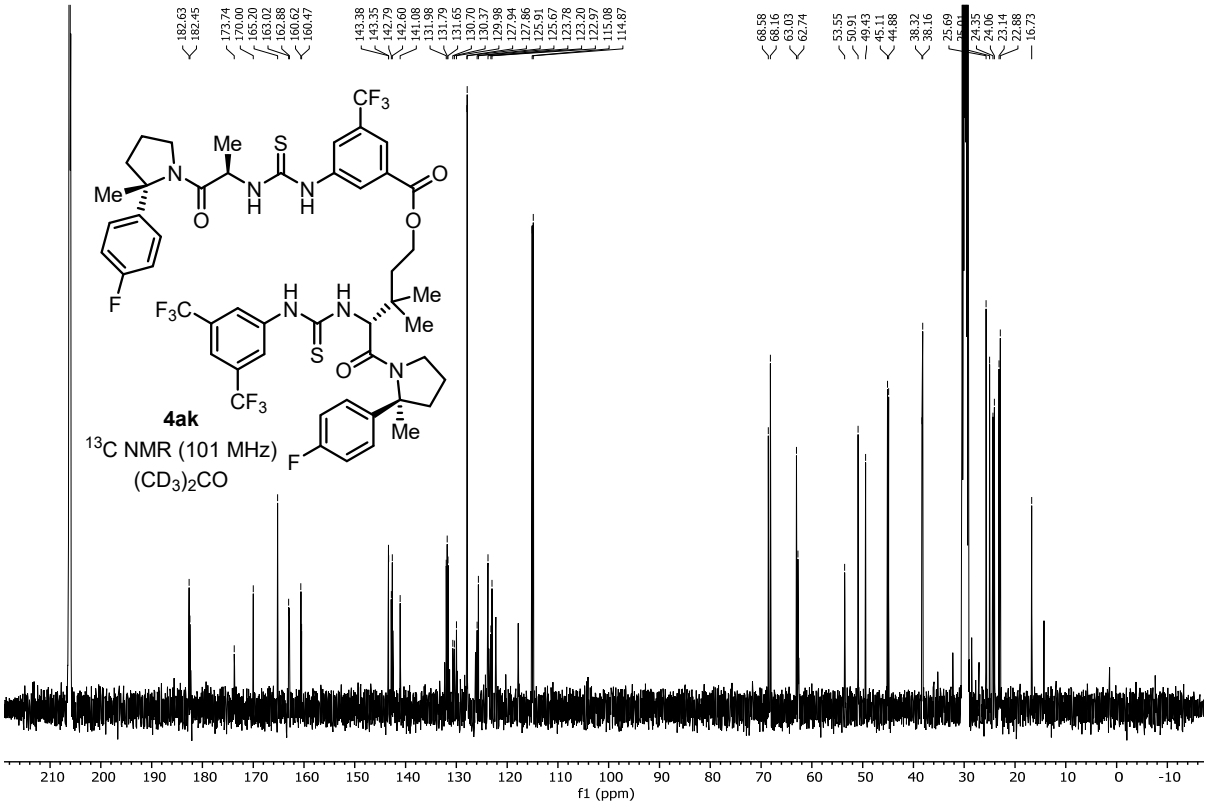
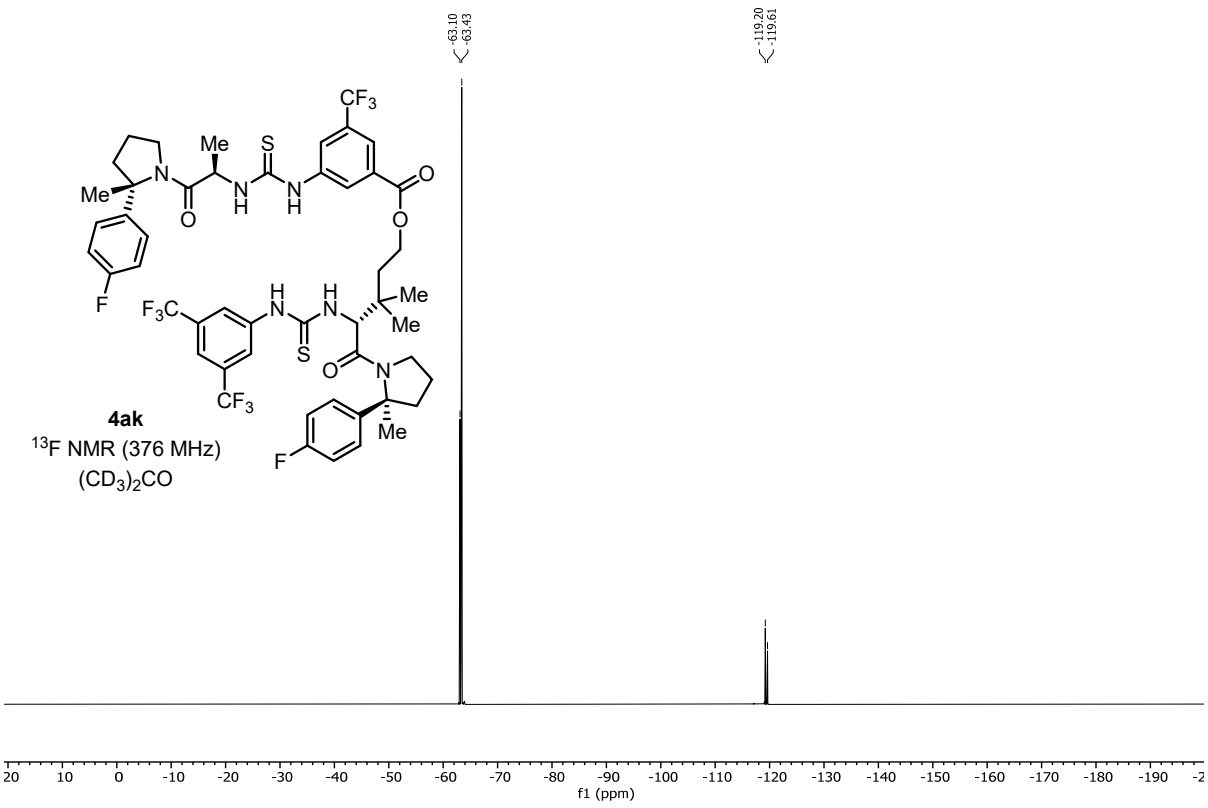
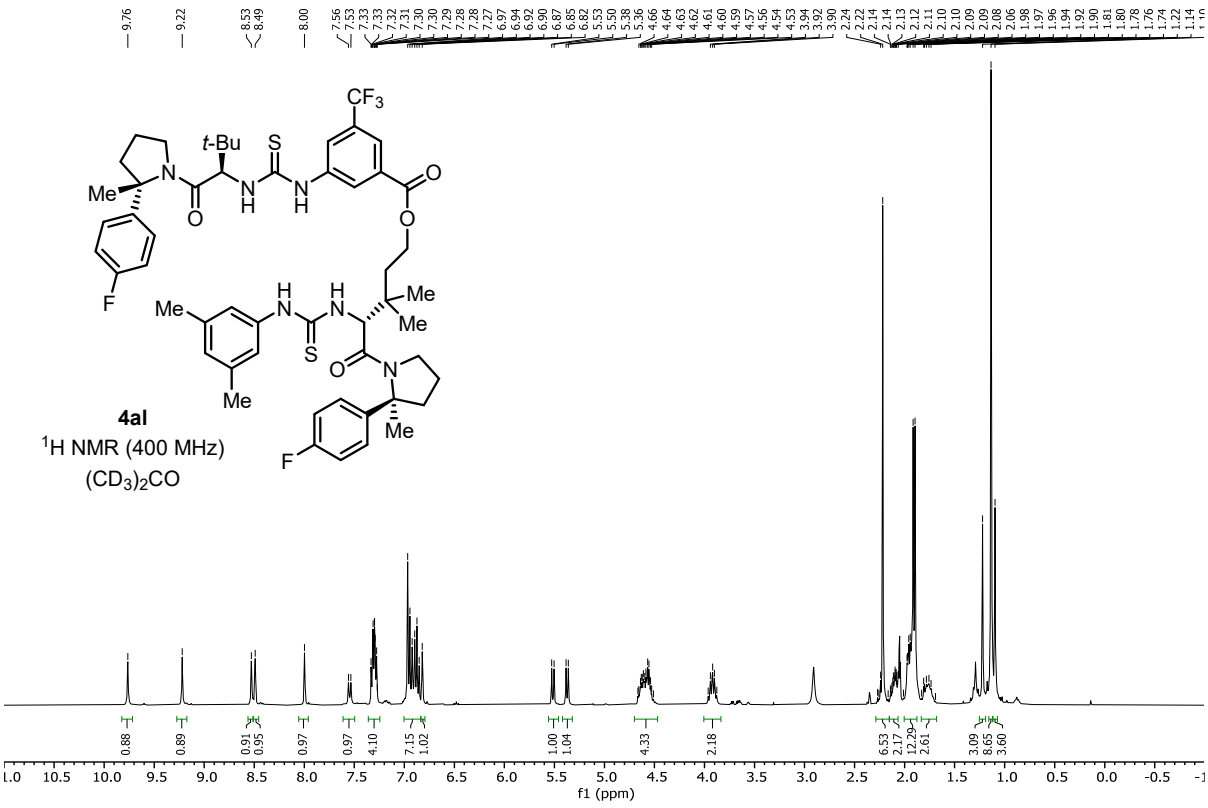
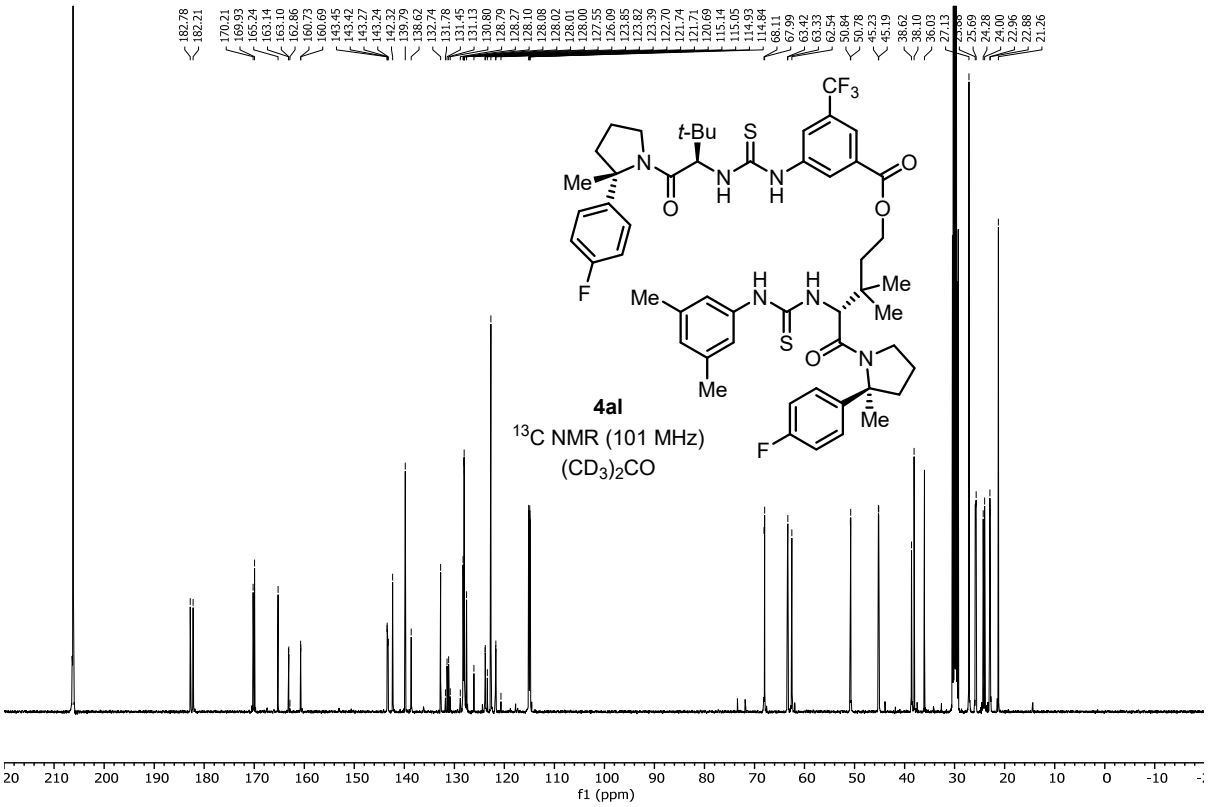
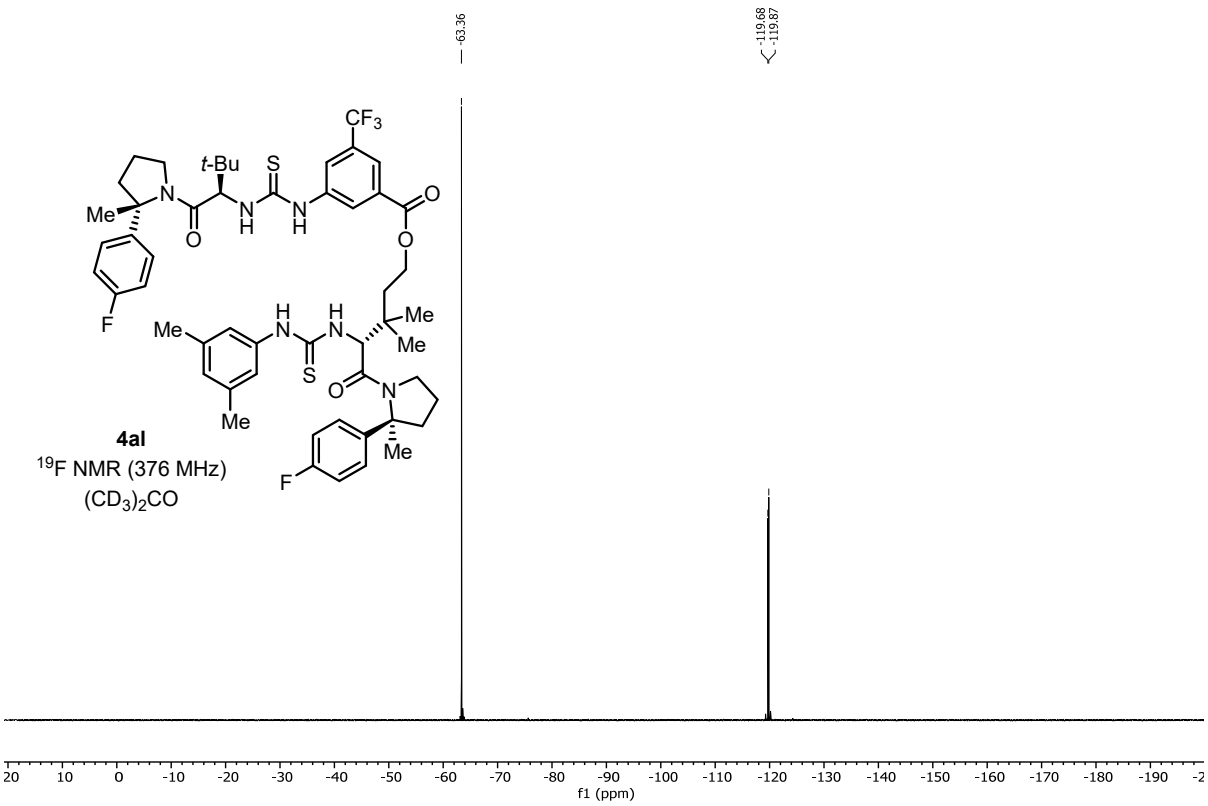
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)


4ak
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)


-63.10
-63.43
-119.20
-119.61
4ak
^{13}F NMR (376 MHz)
$(CD_3)_2CO$
f1 (ppm)


4al
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)


4al
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)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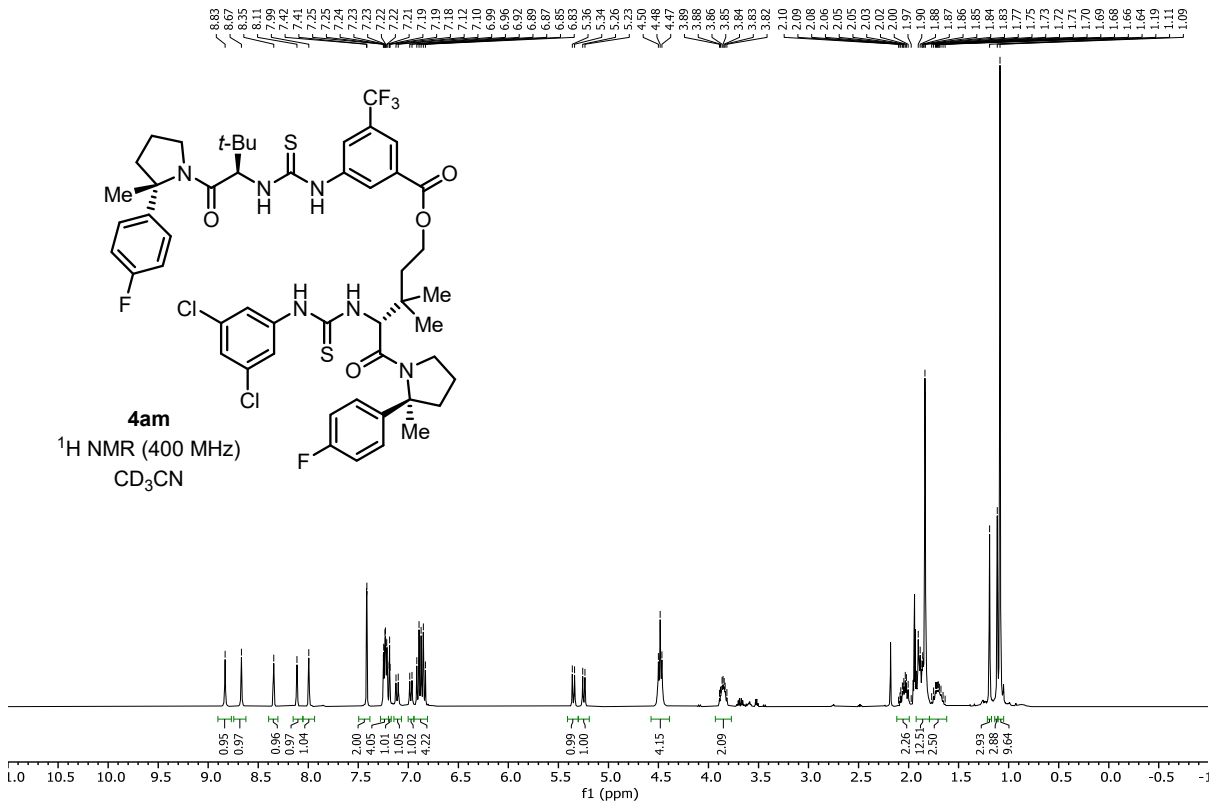
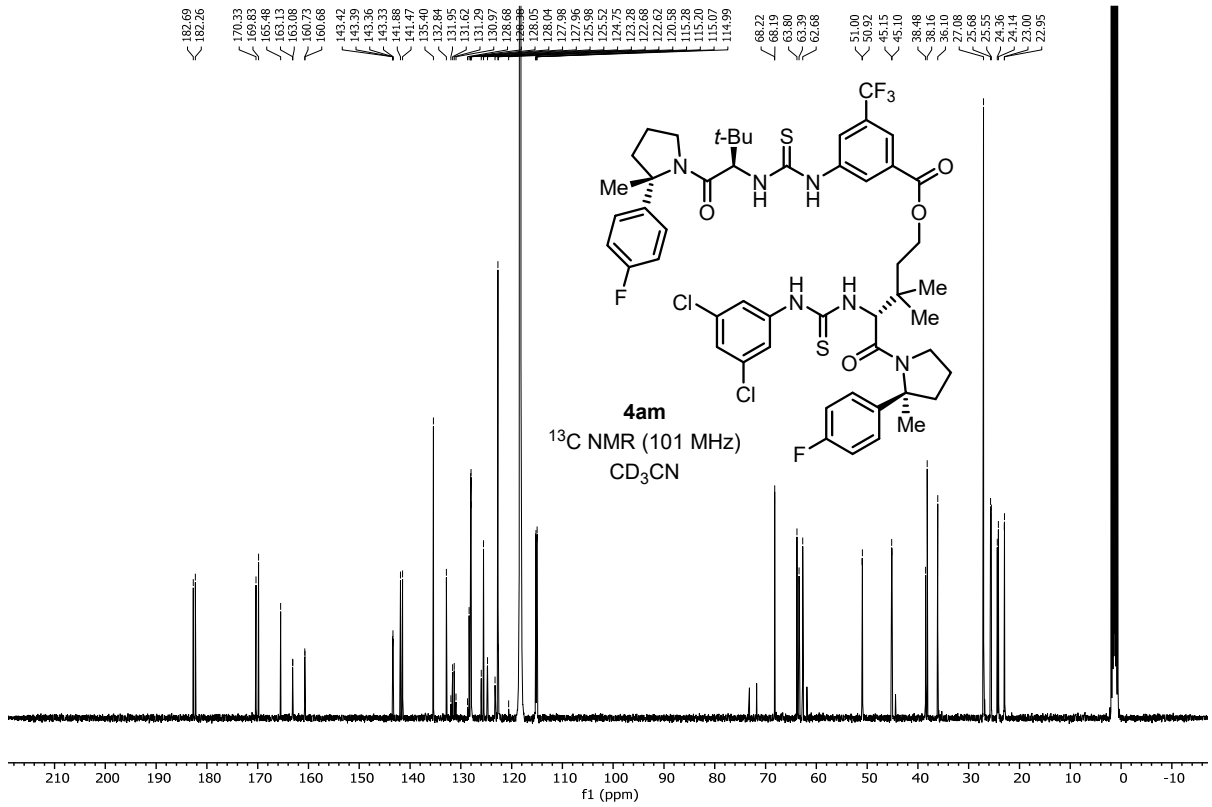
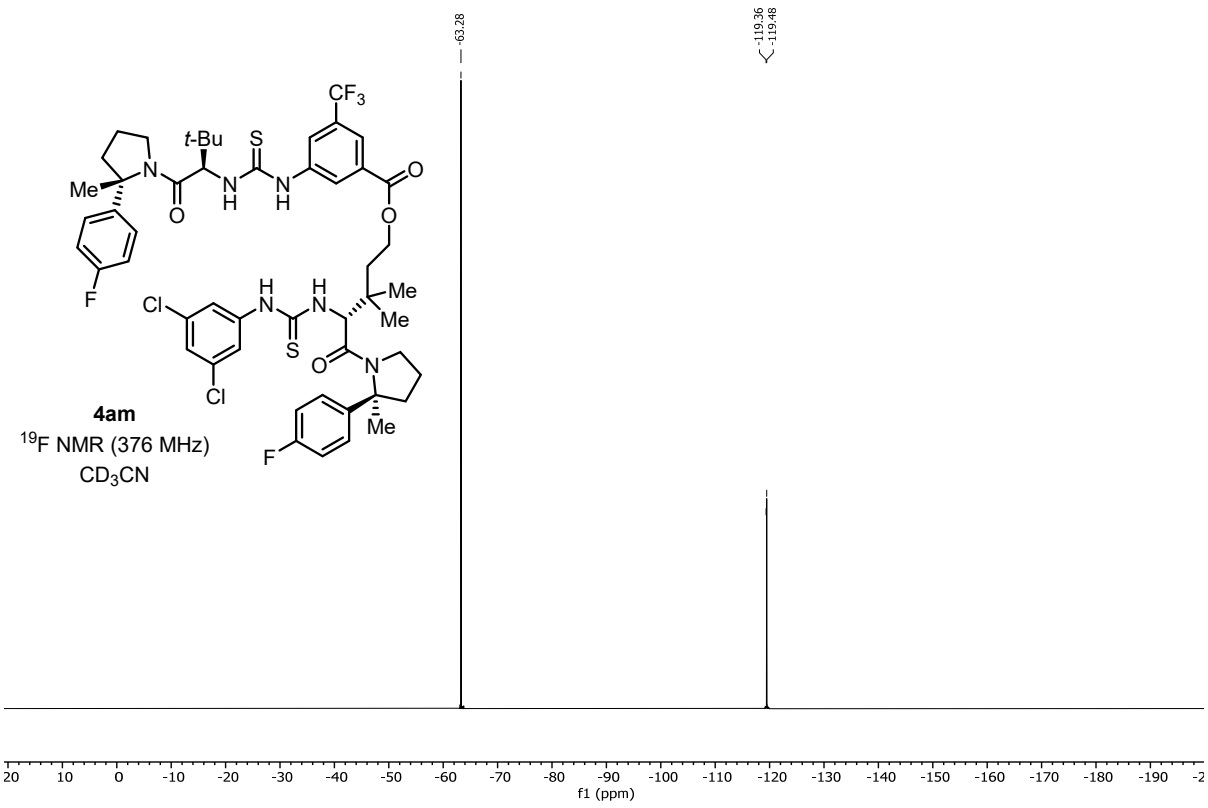
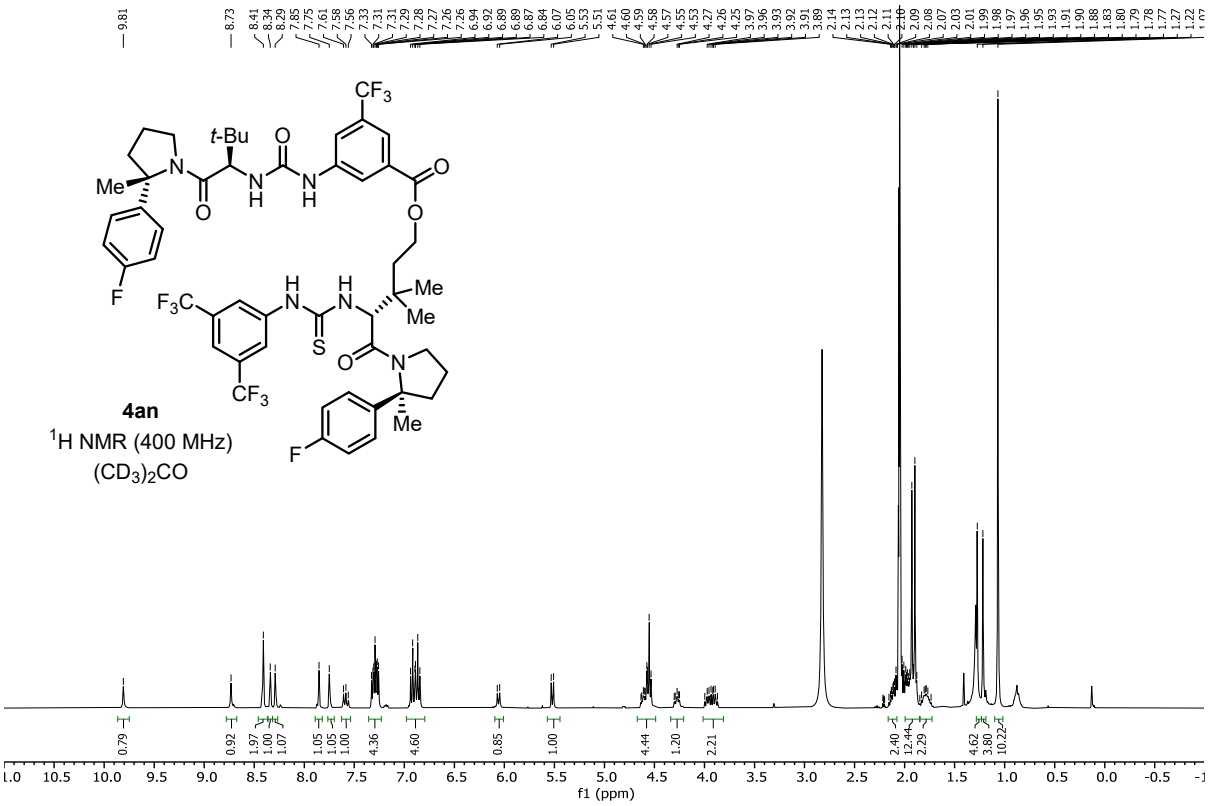
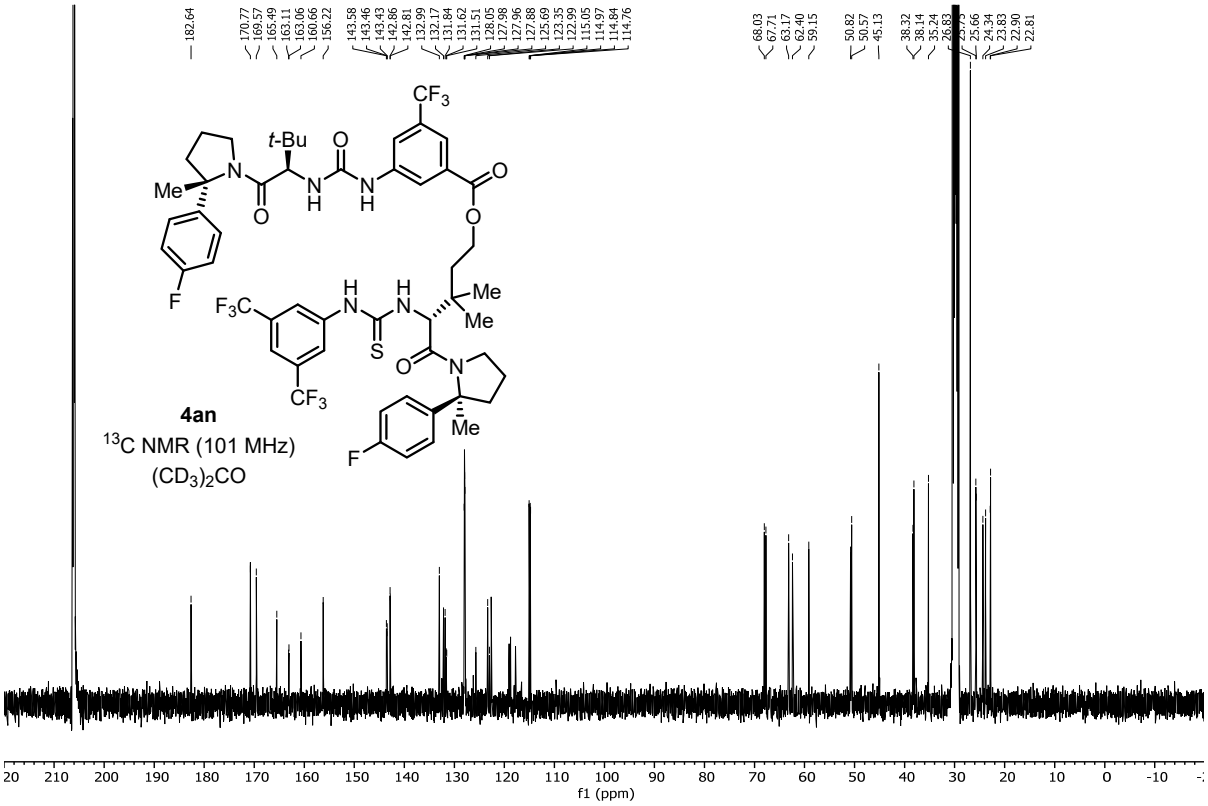
-119.68
-119.87
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F
Me
H
N
N
H
Me
Me
S
O
N
Me
Me
F
4al
19F NMR (376 MHz)
(CD3)2CO
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


4am
1H NMR (400 MHz)
CD3CN
f1 (ppm)

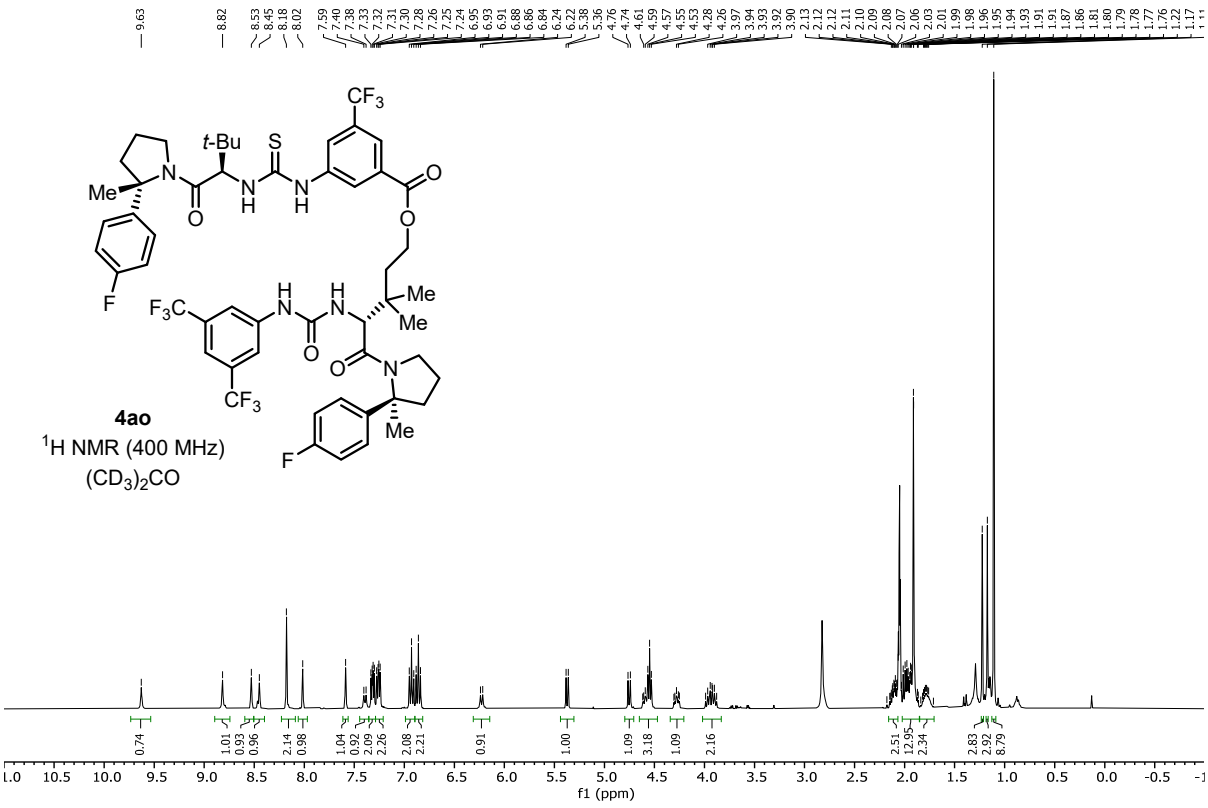

4am
13C NMR (101 MHz)
CD3CN
f1 (ppm)

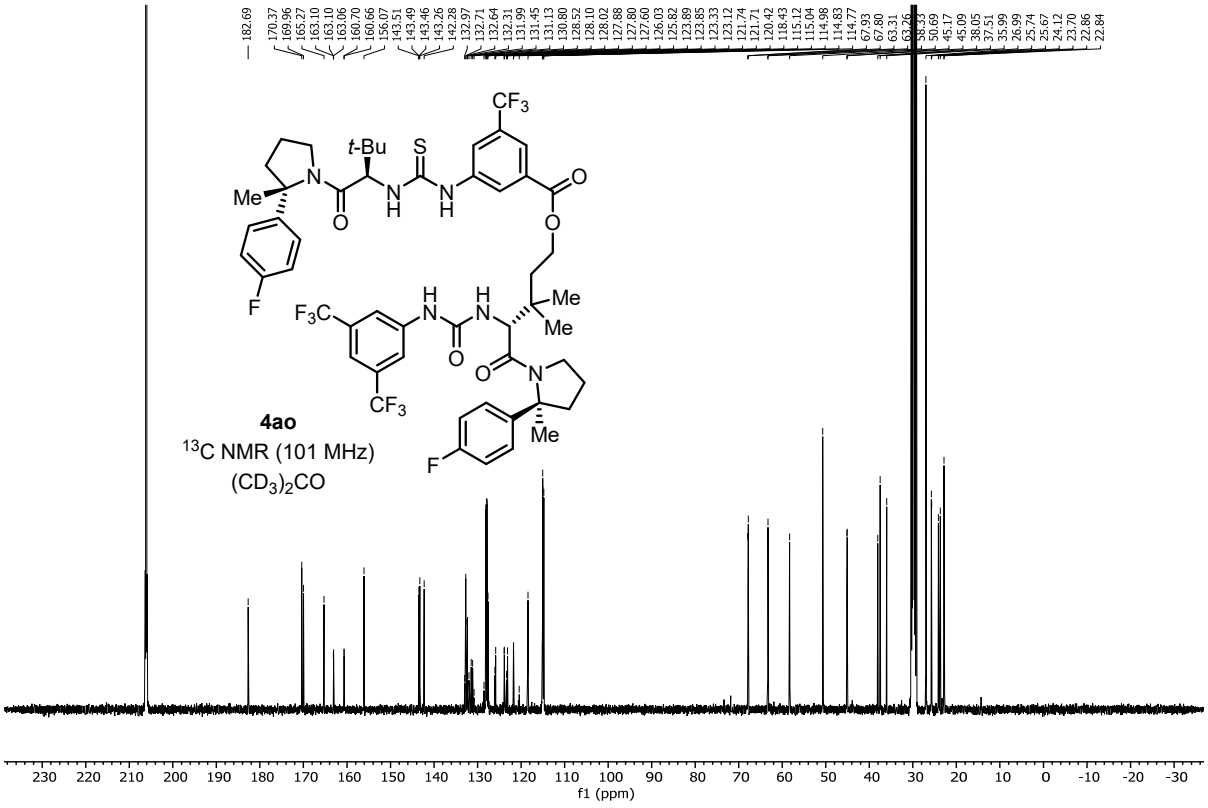

-63.28
-119.36
-119.48
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F
Cl
H
N
S
H
N
Me
Me
O
N
Cl
Me
F
4am
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

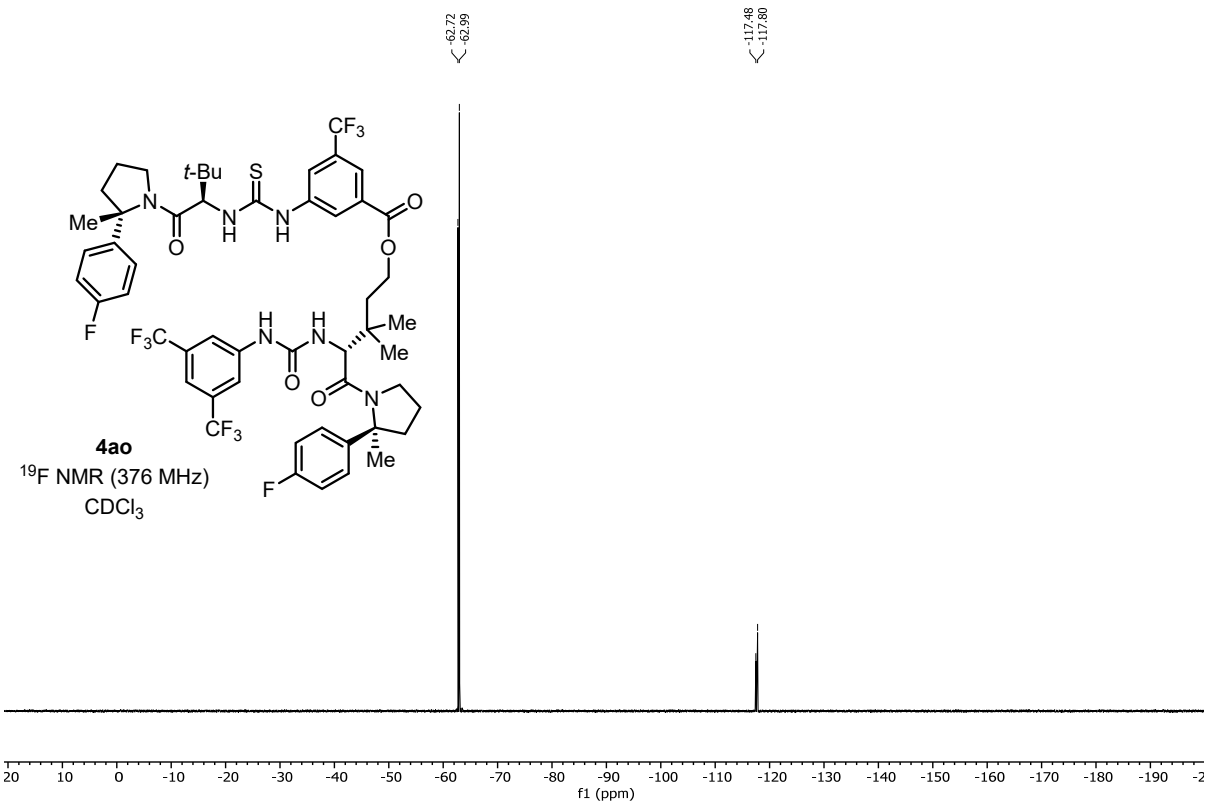

4an
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)


4an
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)

-63.42
-63.51
-119.84
-119.90
CF3
t-Bu
O
N
H
Me
F
F3C
S
Me
Me
CF3
4an
19F NMR (376 MHz)
(CD3)2CO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


4ao
^{1}H NMR (400 MHz)
$(CD_3)_2CO$
f1 (ppm)


4ao
^{13}C NMR (101 MHz)
$(CD_3)_2CO$
f1 (ppm)


-62.72
-62.99
-117.48
-117.80
CF3
t-Bu
S
Me
N
O
N
H
N
H
O
O
F
F3C
H
N
H
N
Me
Me
O
O
N
CF3
Me
F
4ao
19F NMR (376 MHz)
CDCl3
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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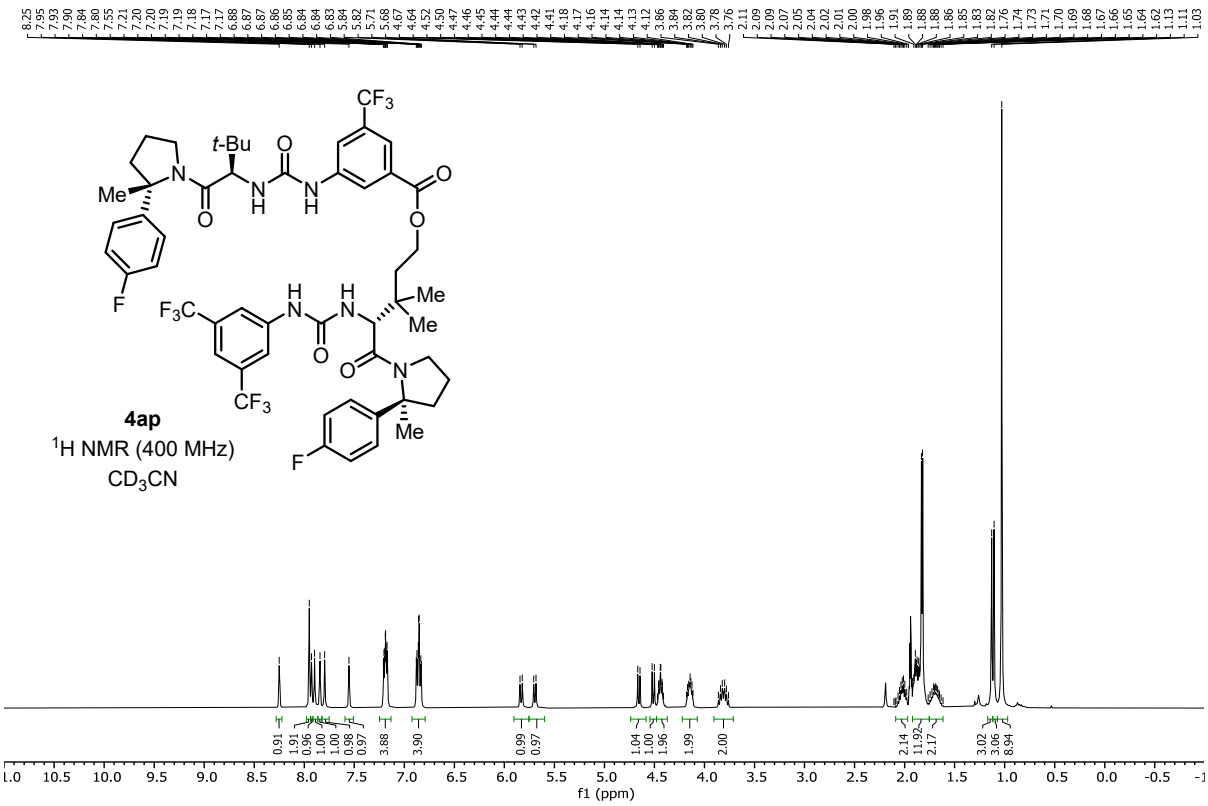
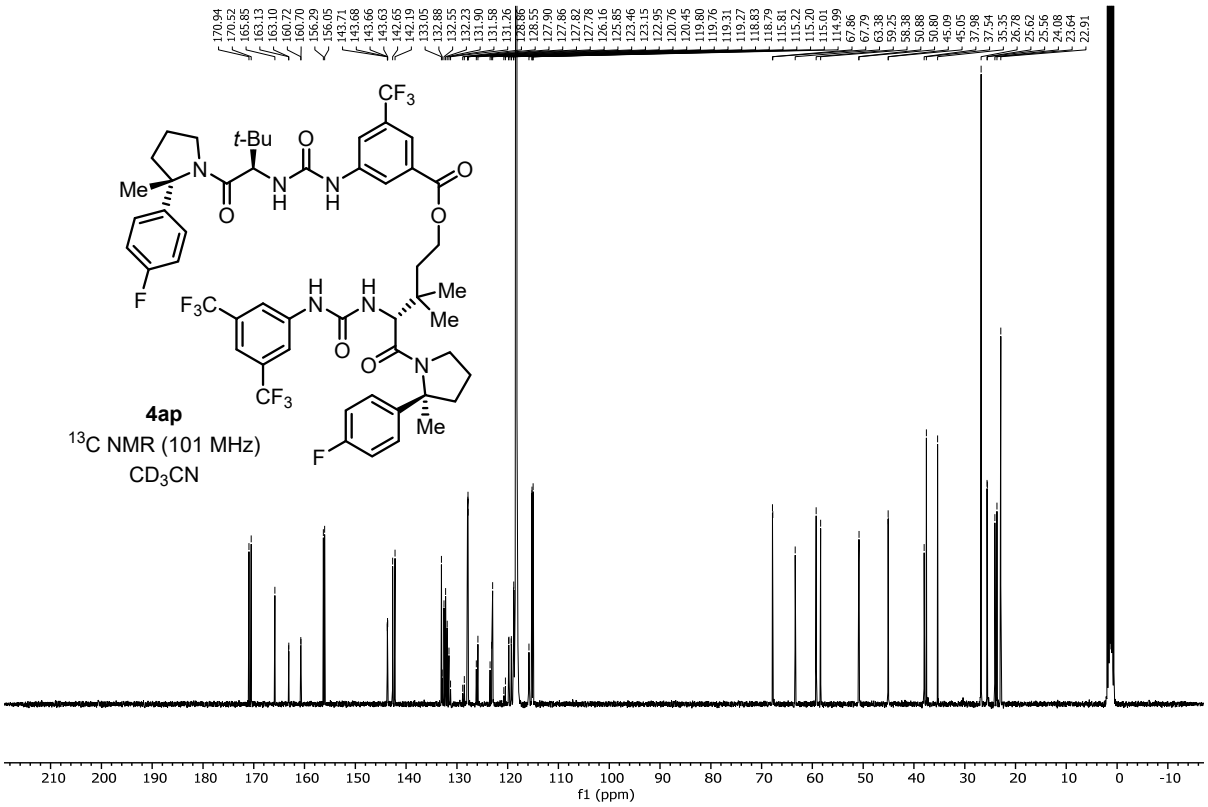
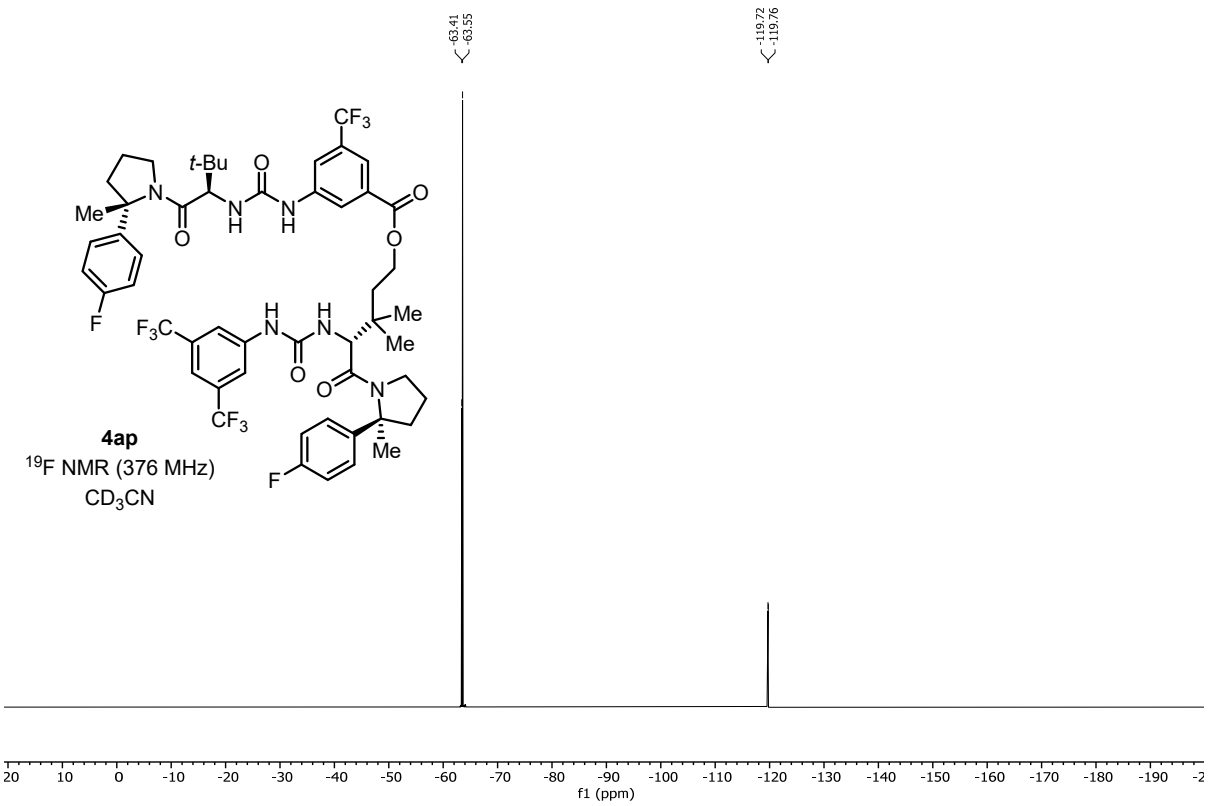
-180
-190
f1 (ppm)


4ap
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)


4ap
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)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-63.55
-119.72
-119.76
CF3
t-Bu
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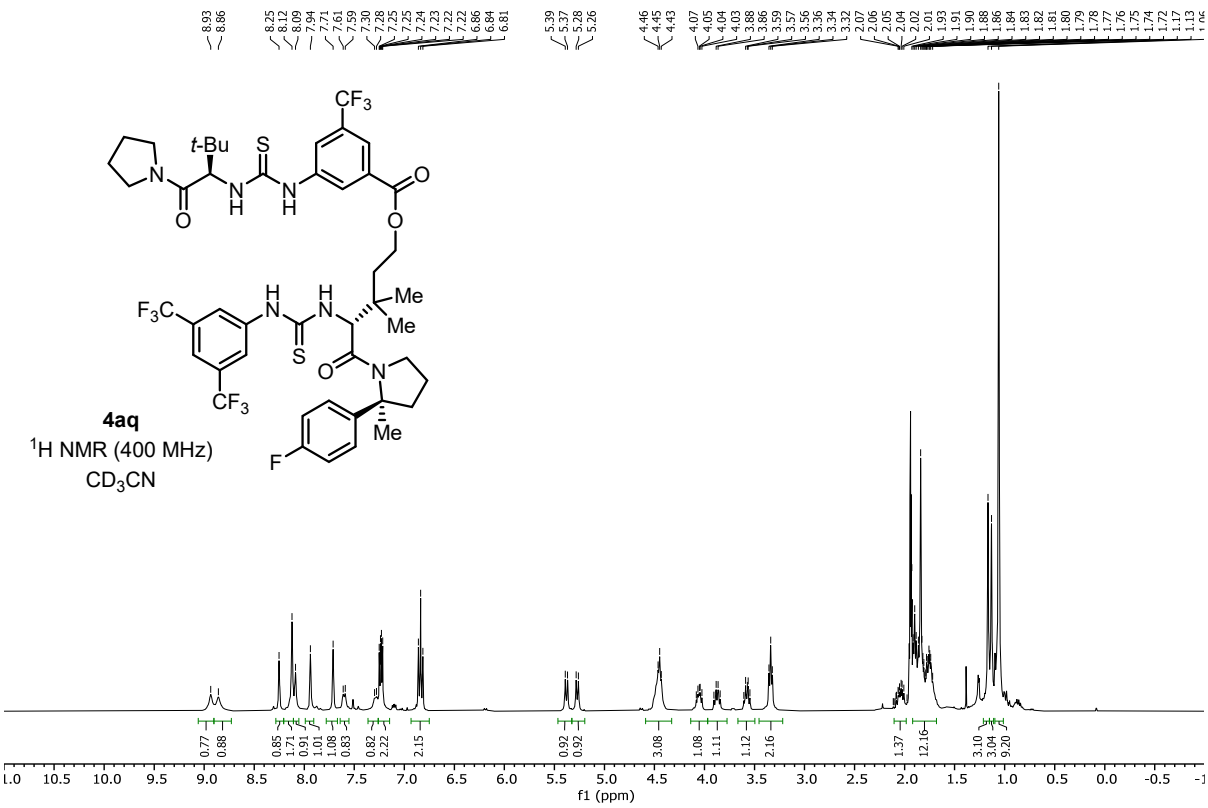
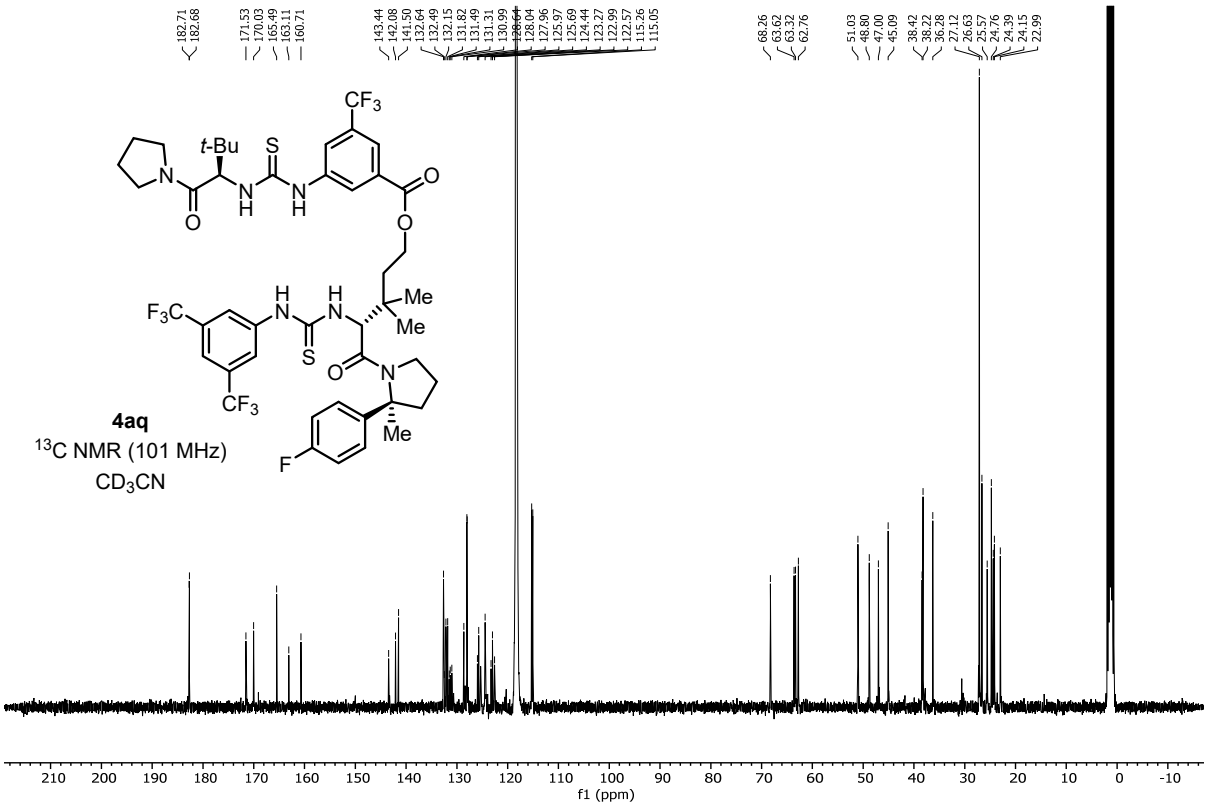
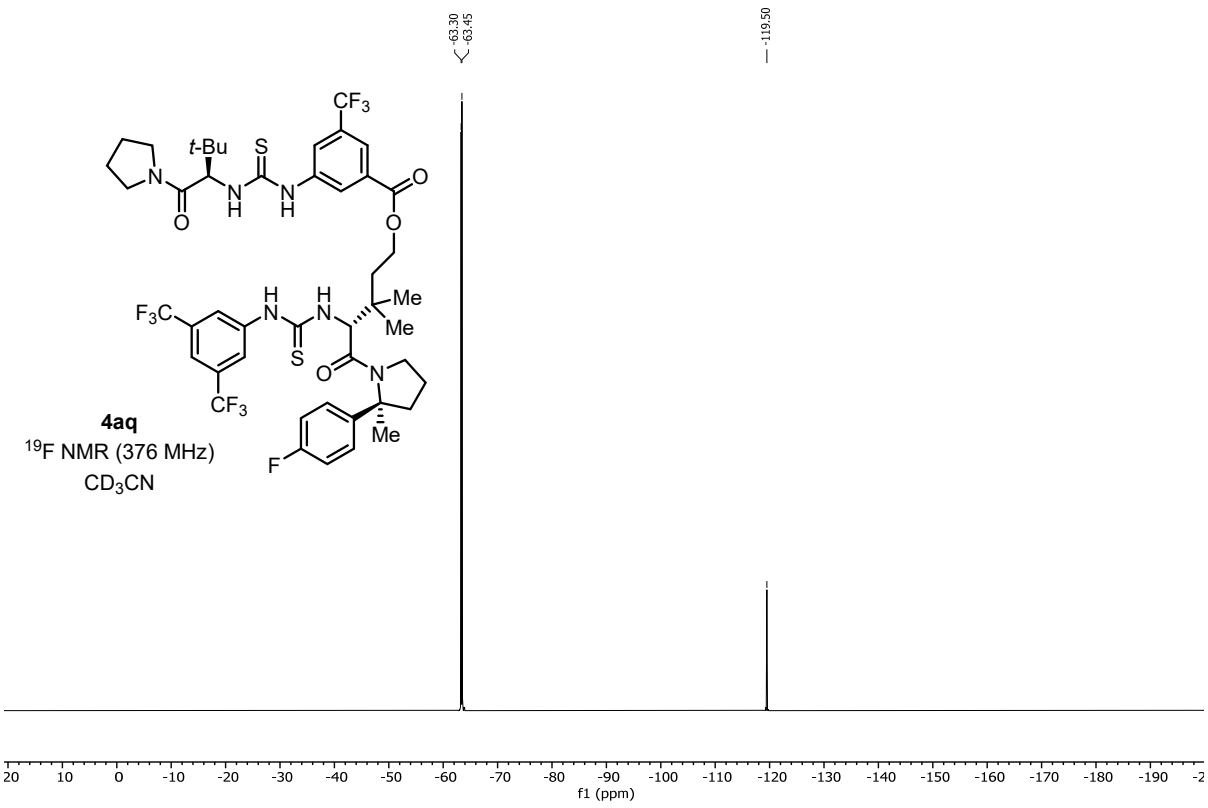
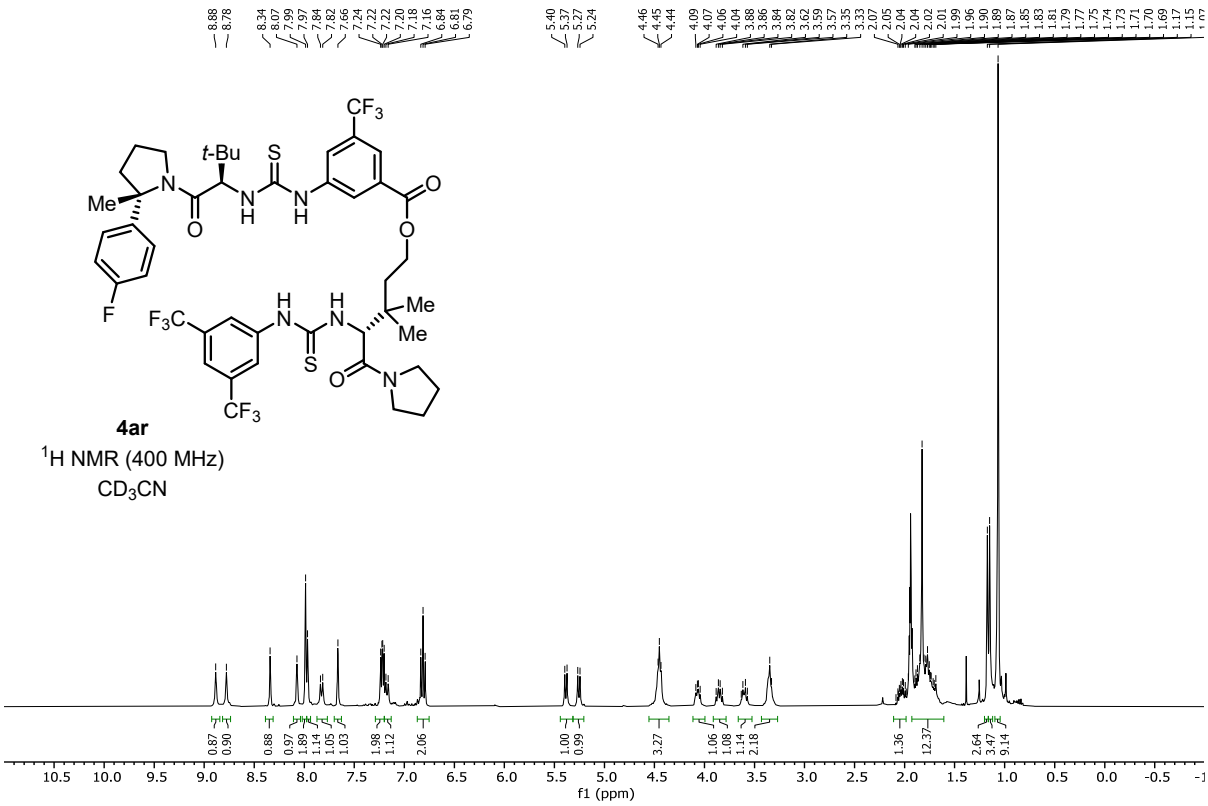
N
Me
O
N
H
N
H
O
O
F
F3C
H
N
H
N
Me
Me
O
O
N
CF3
Me
F
4ap
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)


4aq
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)


4aq
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)


-63.30
-63.45
-119.50
4aq
^{19}F NMR (376 MHz)
CD_3CN
f1 (ppm)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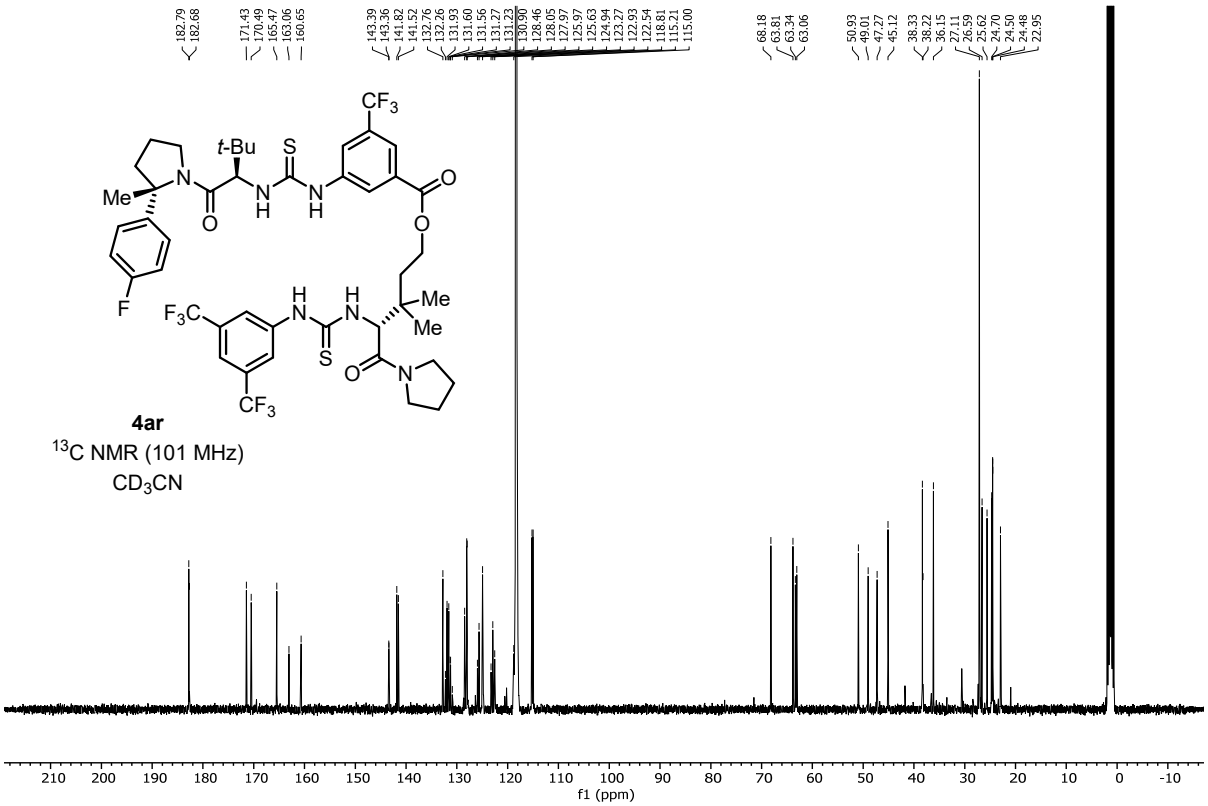
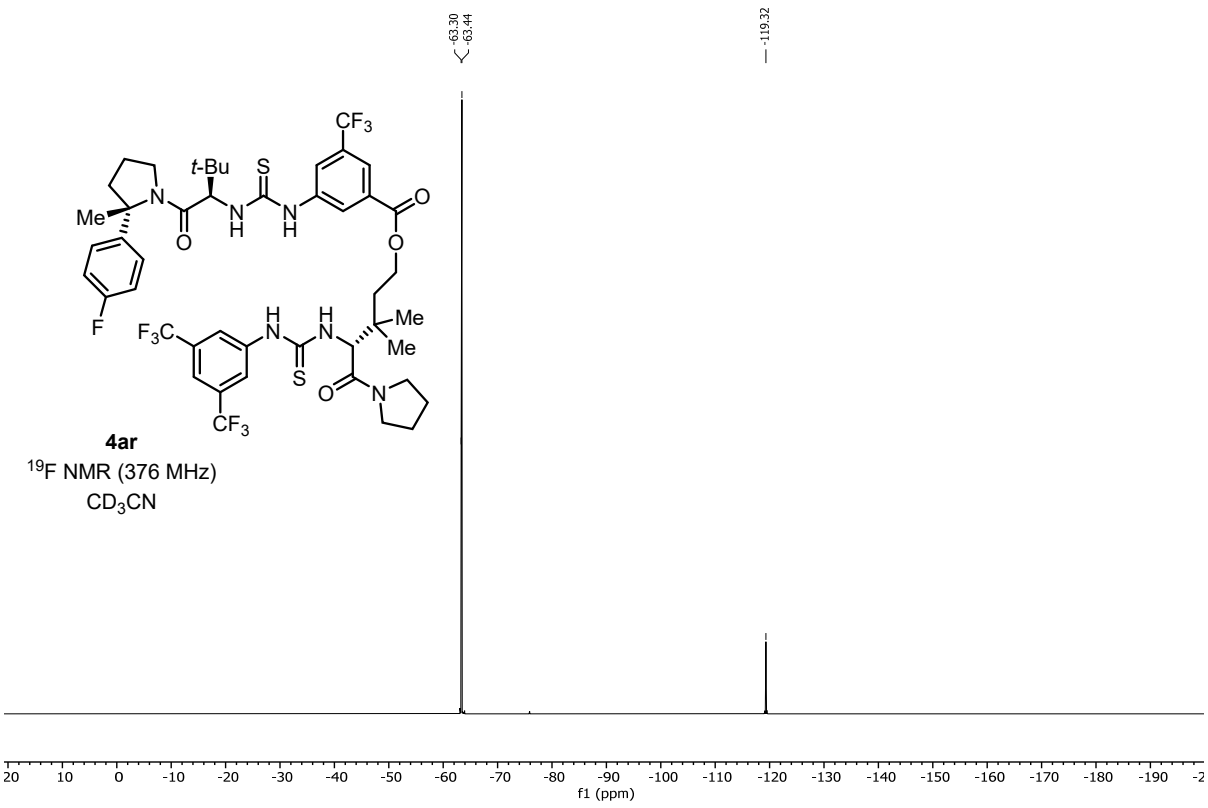
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)

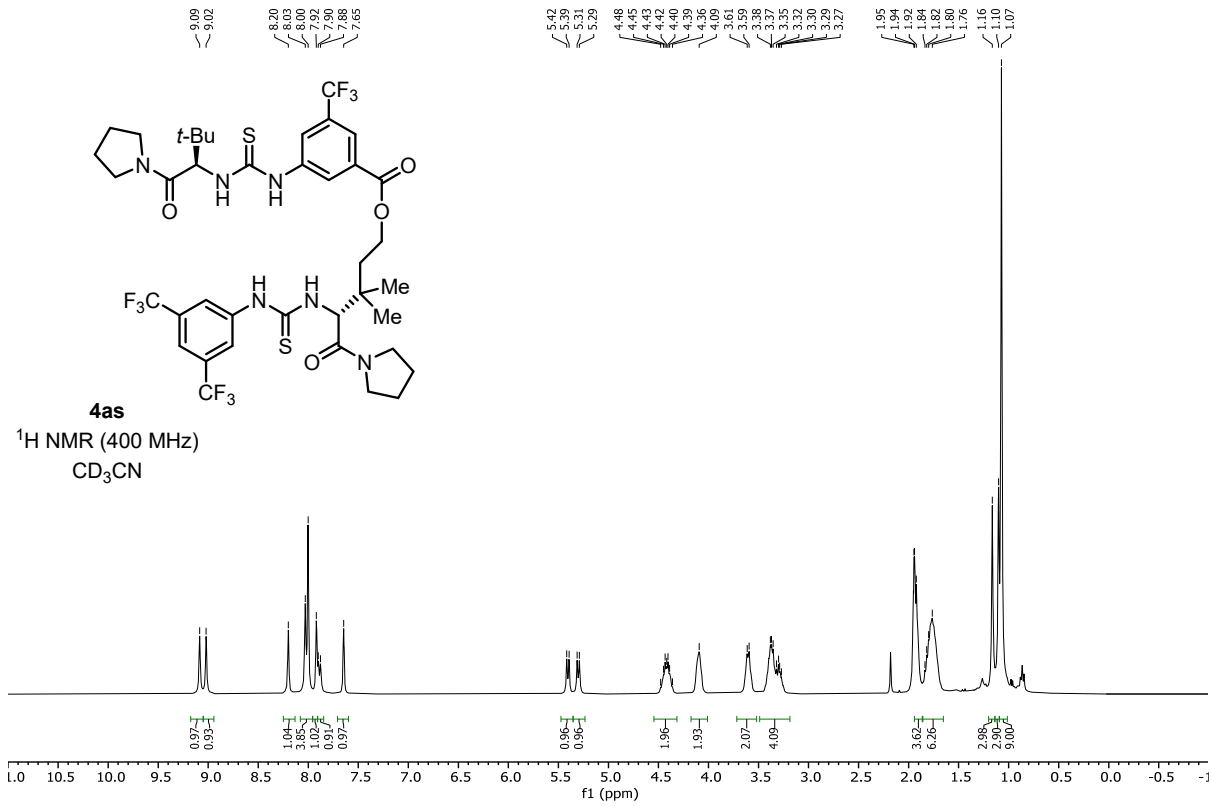

4ar
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)



4ar

^{19}F NMR (376 MHz)

CD_3CN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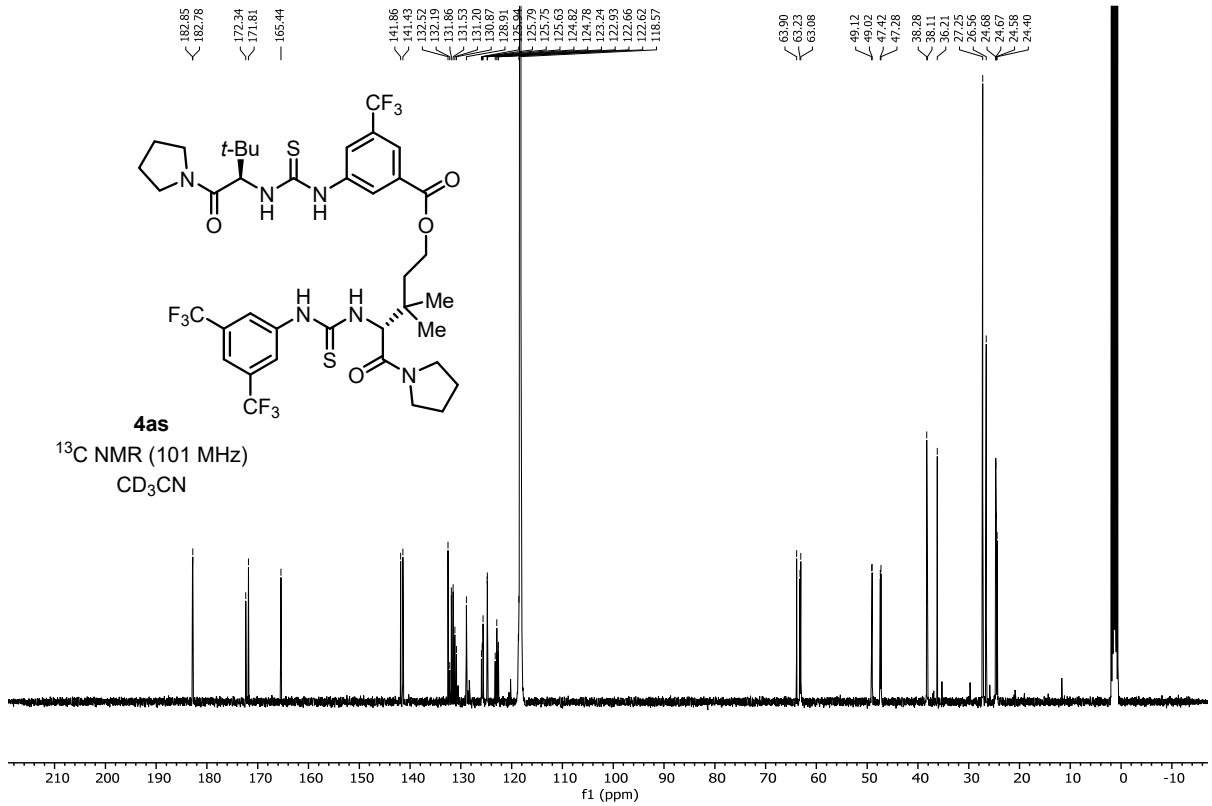
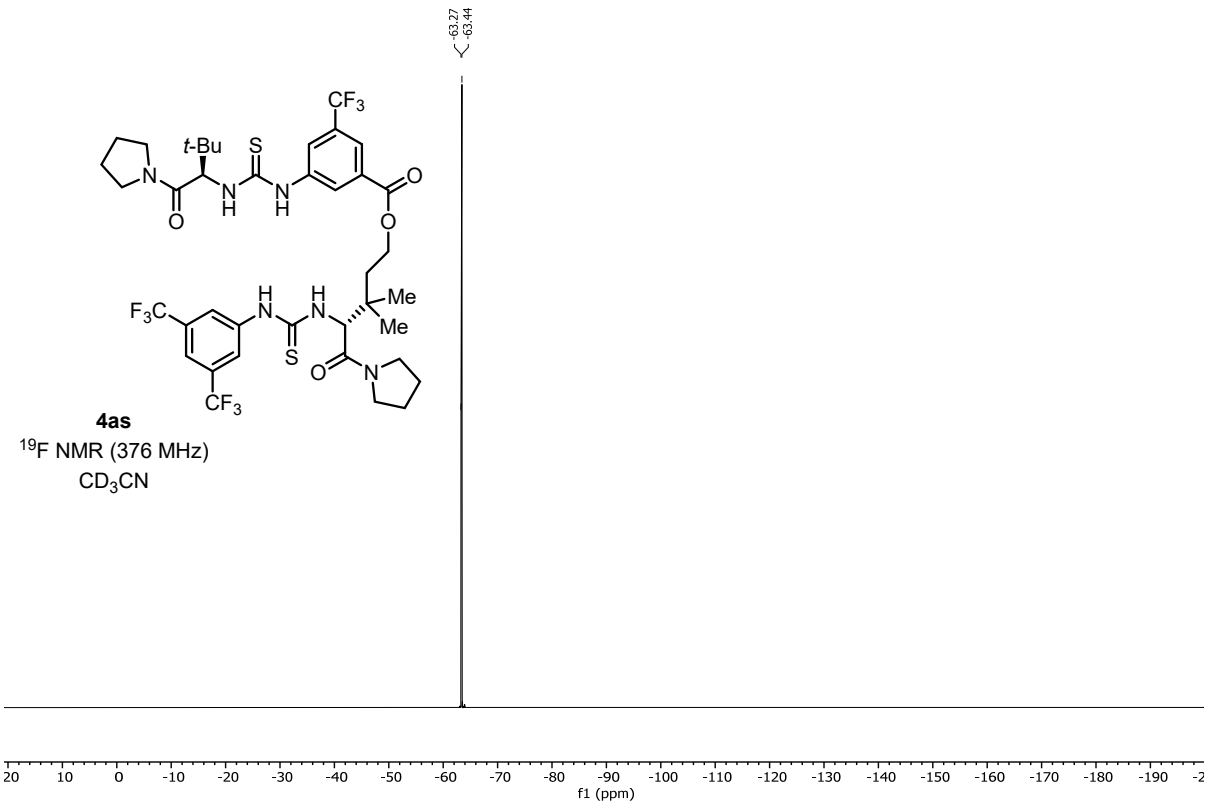
1H NMR (400 MHz)
CD3CN
f1 (ppm)


4as
13C NMR (101 MHz)
CD3CN
f1 (ppm)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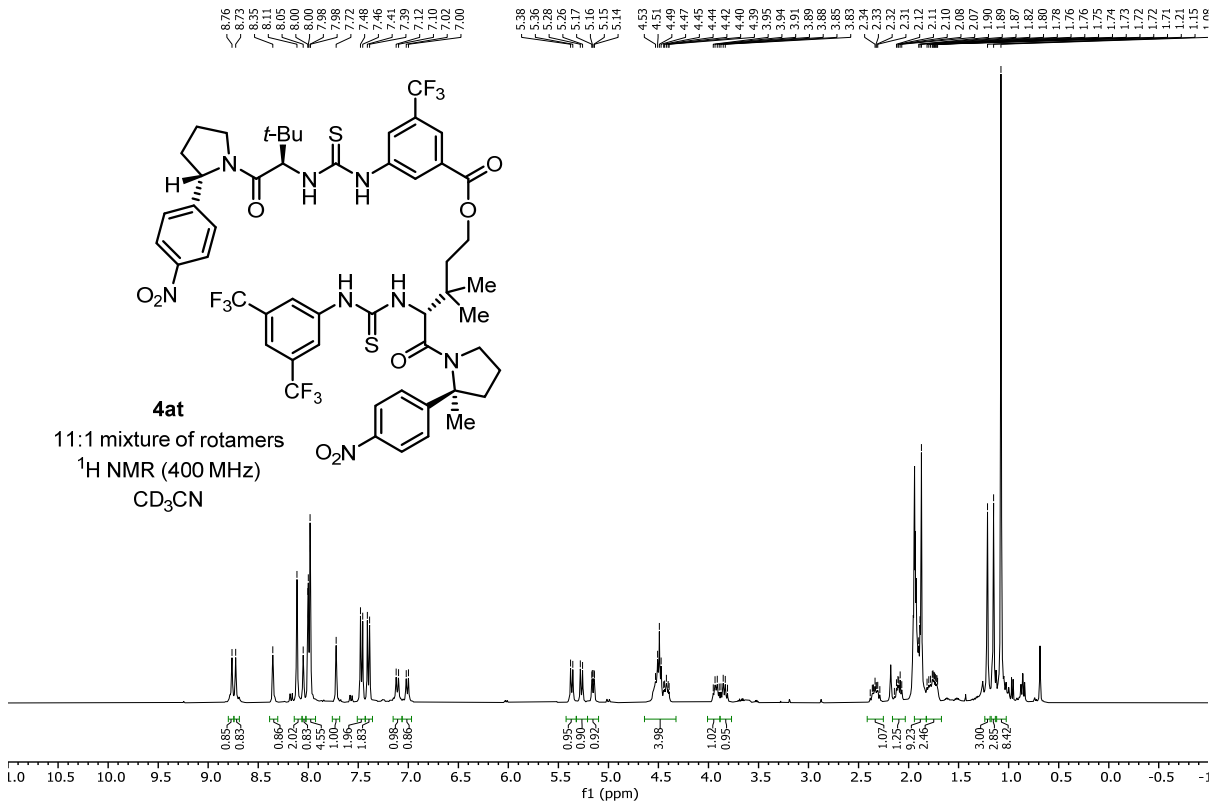
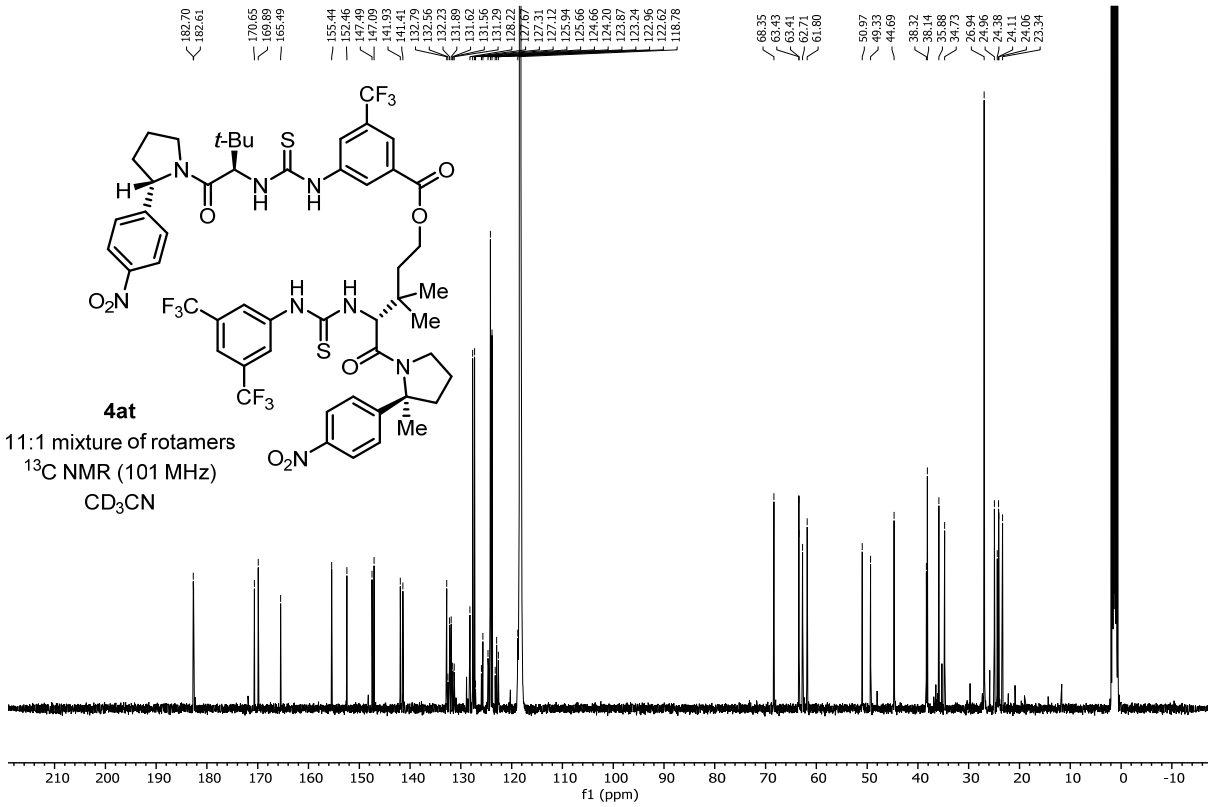
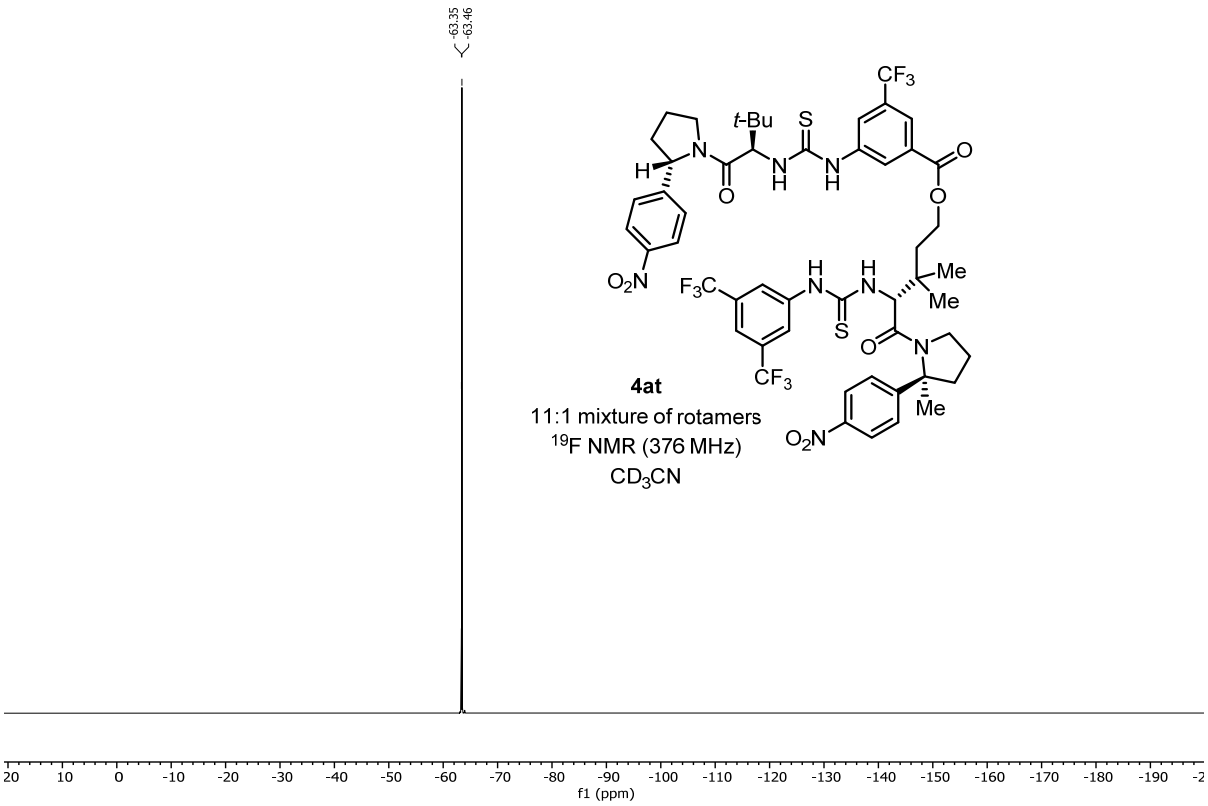
-63.44
CF3
t-Bu
S
N
H
O
F3C
Me
Me
4as
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


4at
11:1 mixture of rotamers
^{1}H NMR (400 MHz)
CD_3CN
f1 (ppm)


4at
11:1 mixture of rotamers
^{13}C NMR (101 MHz)
CD_3CN
f1 (ppm)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-63.46
CF3
t-Bu
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O
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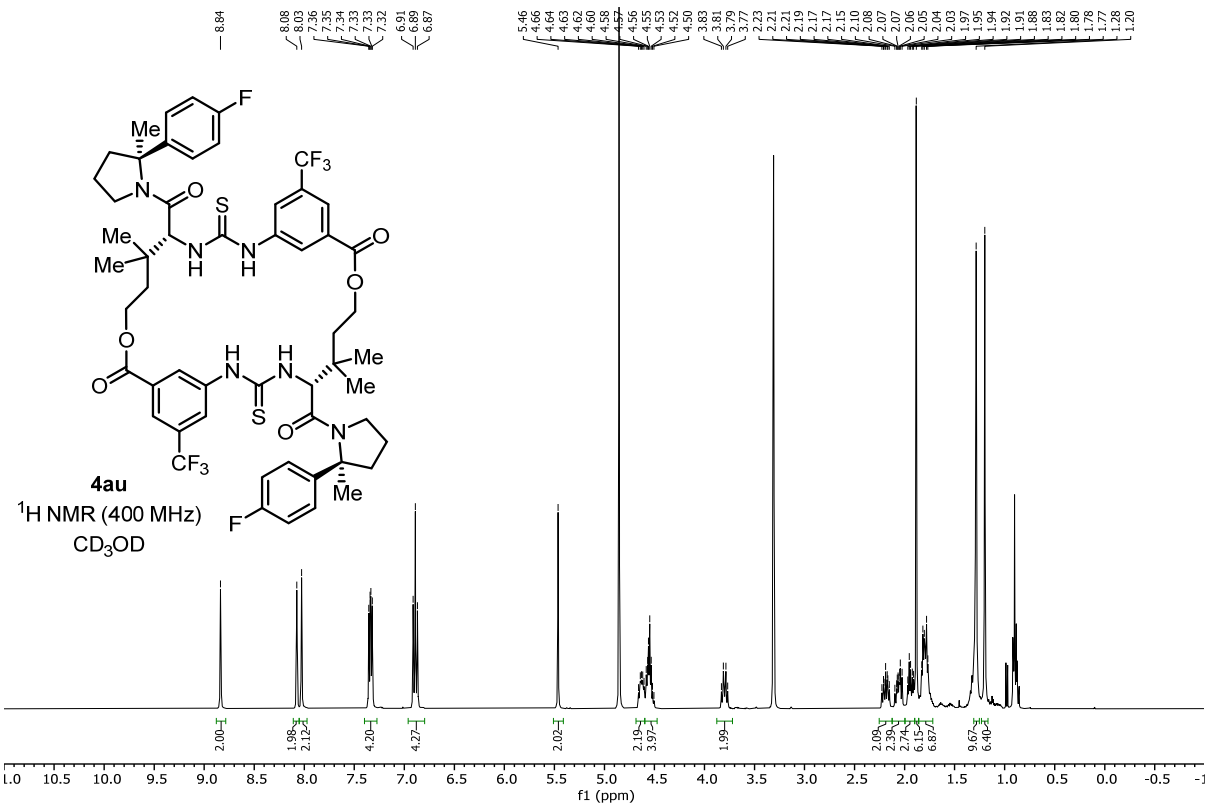
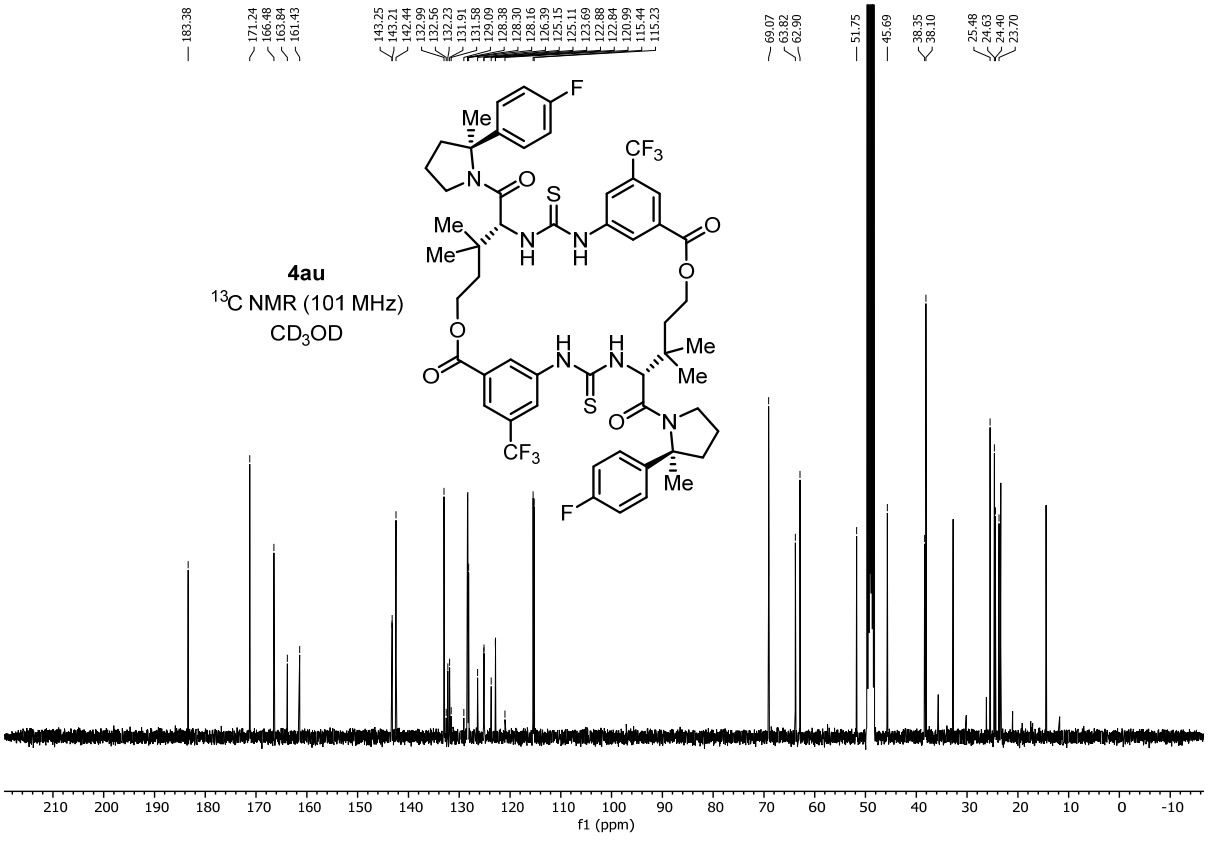
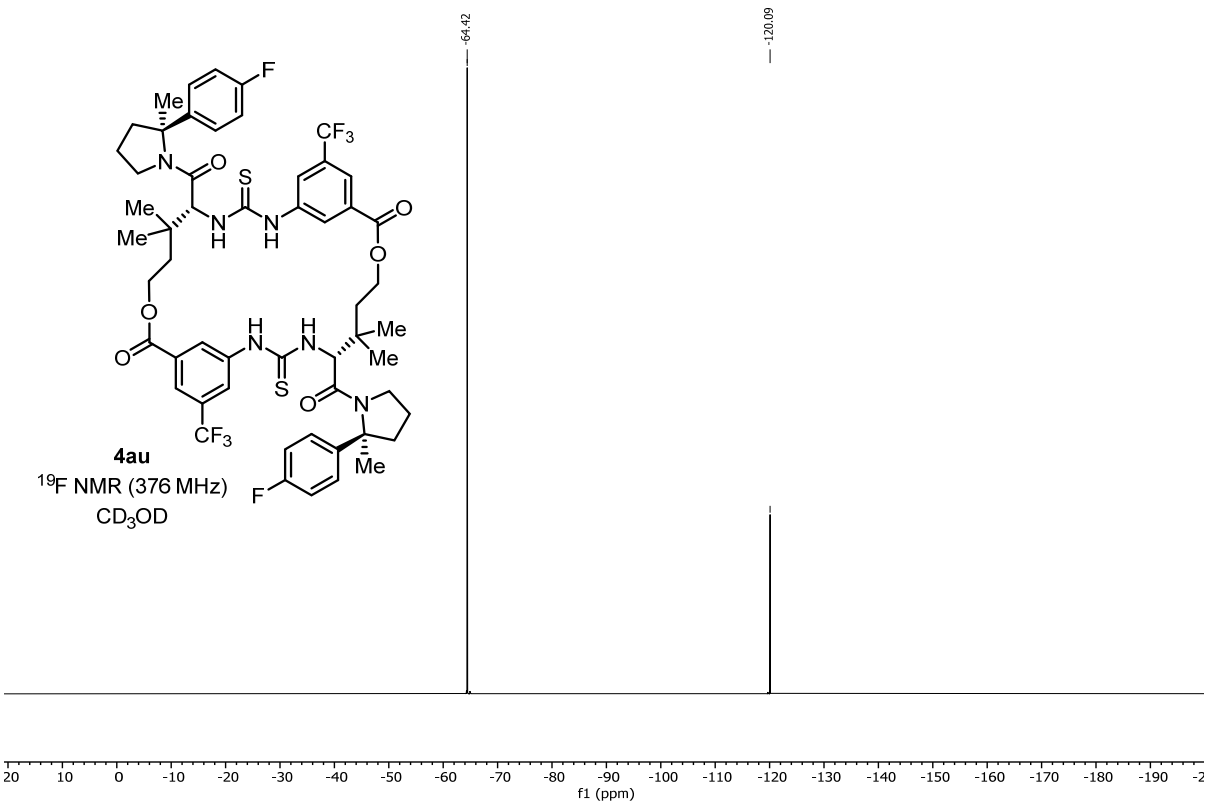
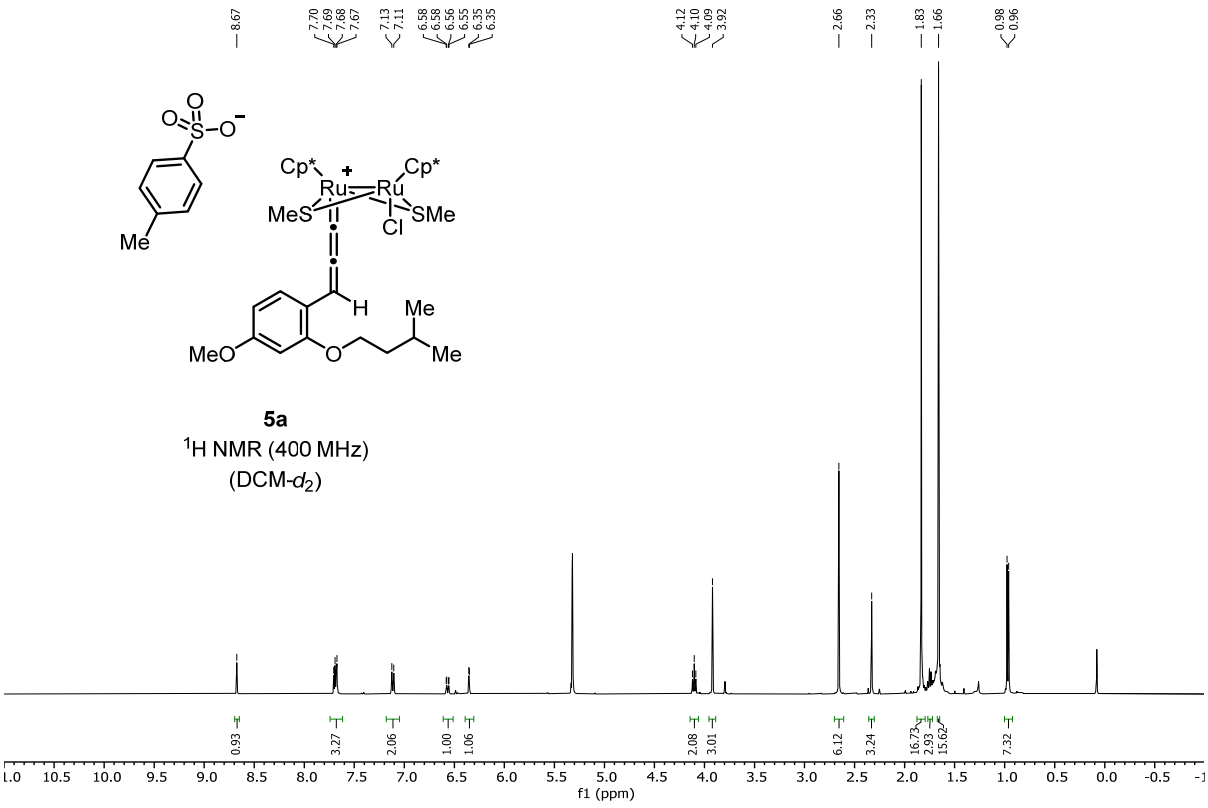
H
N
H
O
O
O2N
F3C
H
N
H
N
Me
Me
S
O
N
CF3
Me
O2N
4at
11:1 mixture of rotamers
19F NMR (376 MHz)
CD3CN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)


4au
1H NMR (400 MHz)
CD3OD
f1 (ppm)


4au
13C NMR (101 MHz)
CD3OD
f1 (ppm)

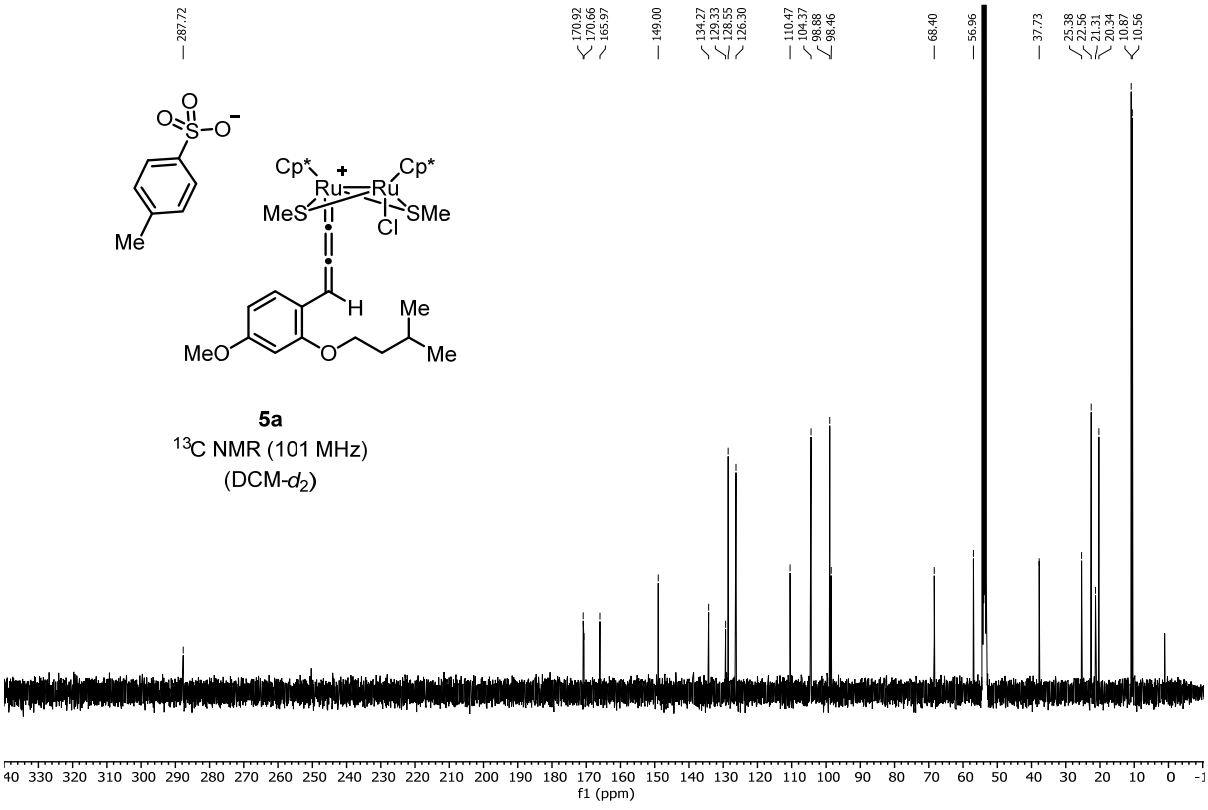

-64.42
-120.09
F
Me
CF3
N
O
S
Me
Me
N
H
N
H
O
O
O
H
N
H
N
Me
Me
O
S
N
CF3
Me
F
4au
19F NMR (376 MHz)
CD3OD
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)



5a

^{1}H NMR (400 MHz)

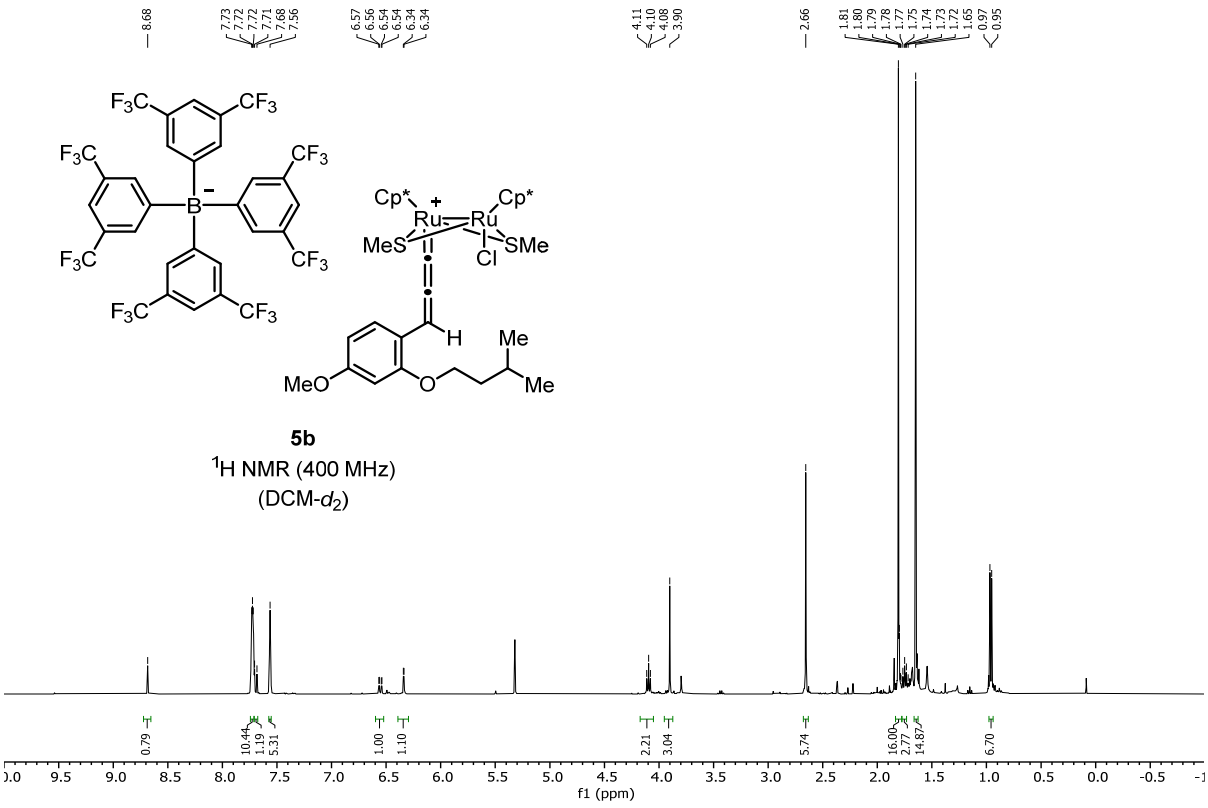
(DCM-d_2)



5a

^{13}C NMR (101 MHz)

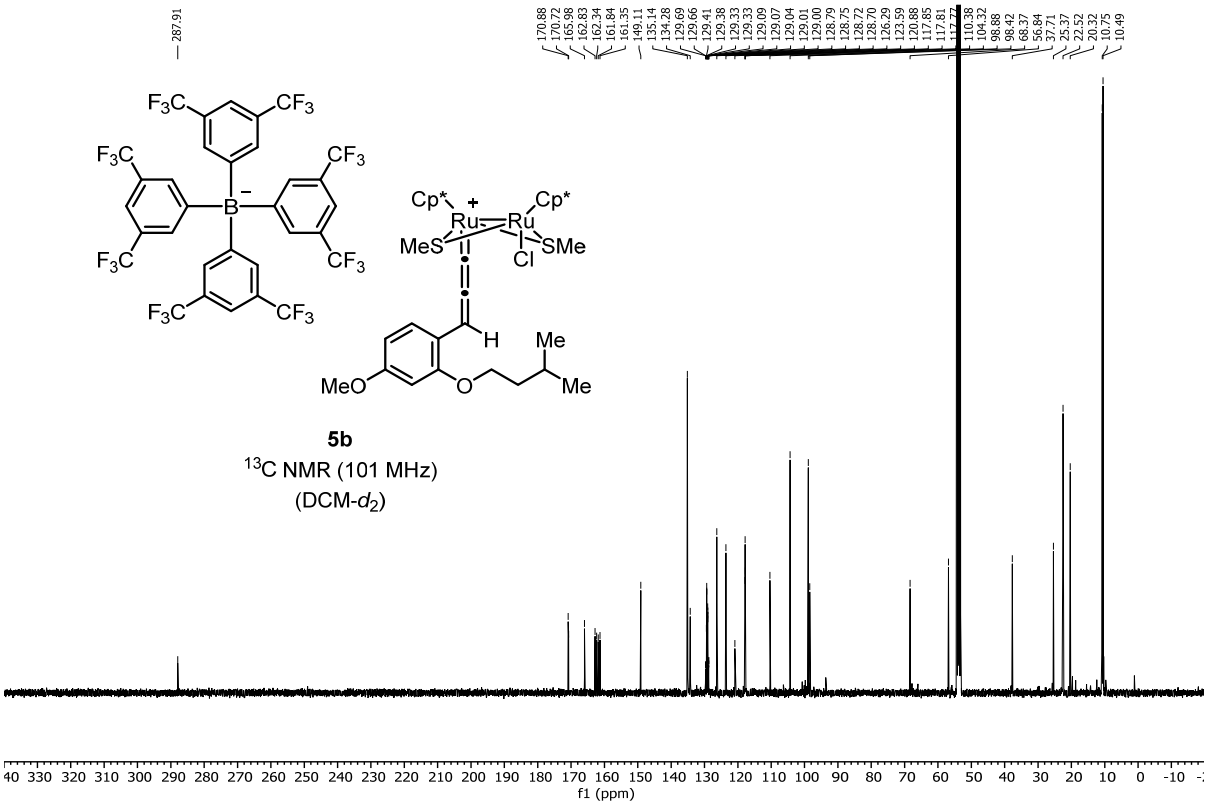
(DCM-d_2)



5b

^{1}H NMR (400 MHz)

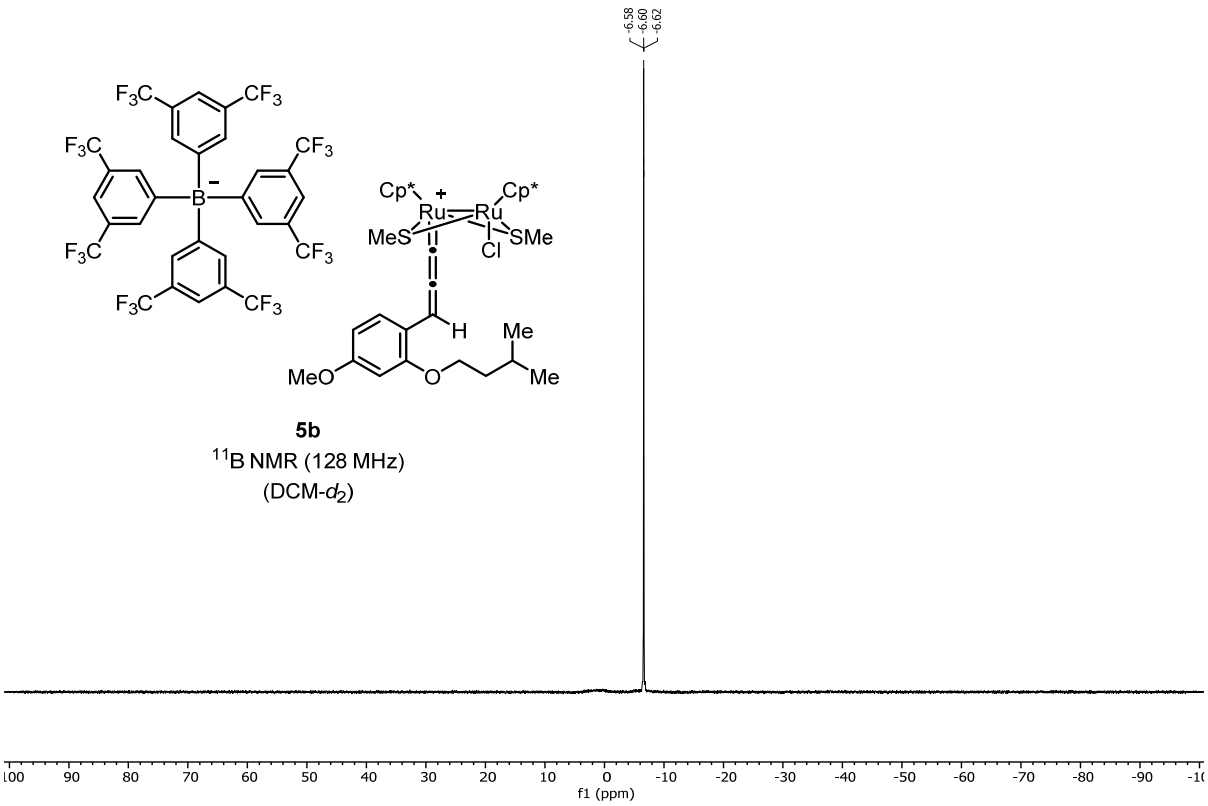
(DCM-d_2)



5b

^{13}C NMR (101 MHz)

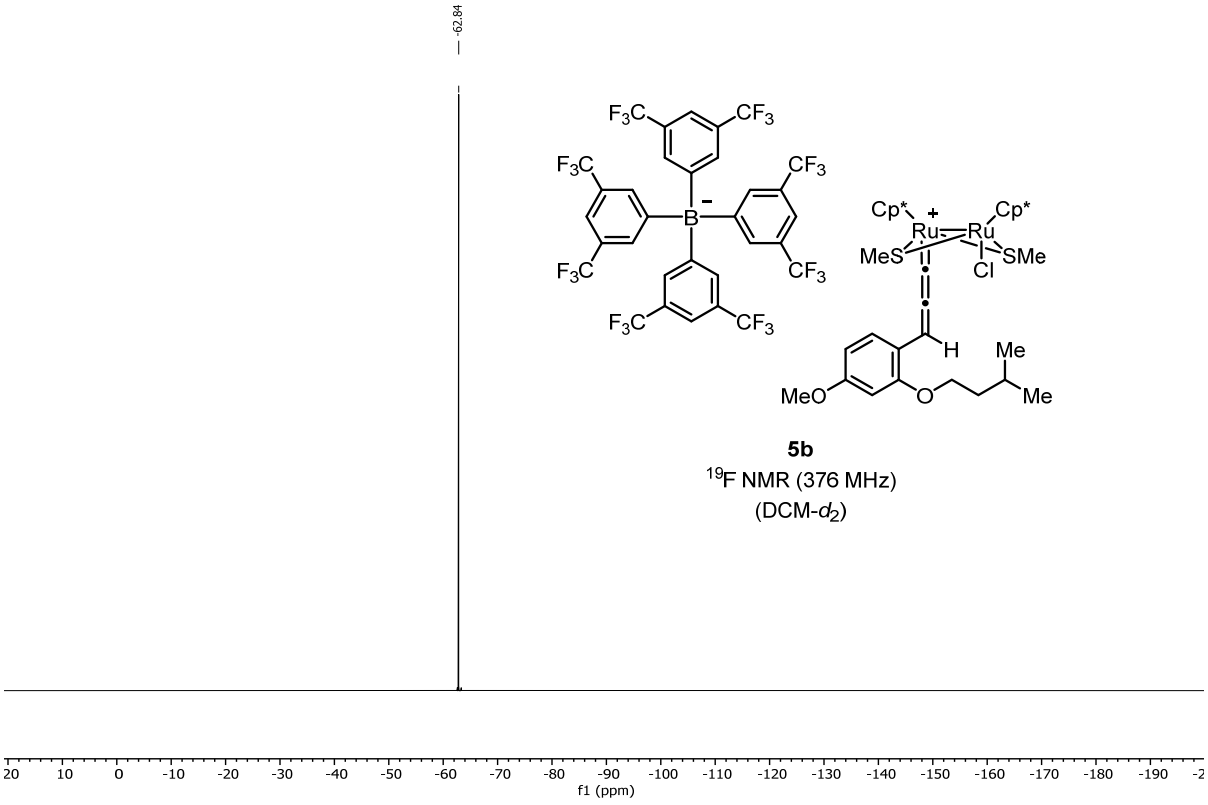
(DCM-d_2)



5b

^{11}B NMR (128 MHz)

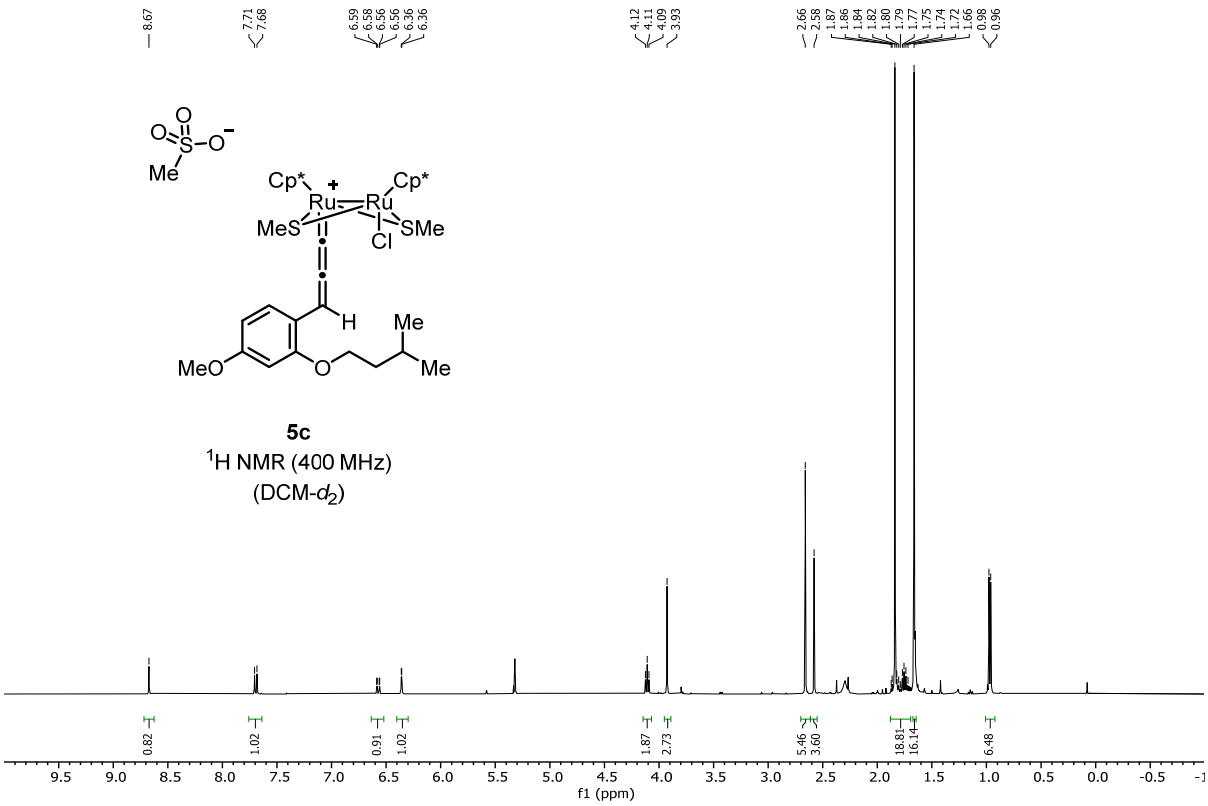
(DCM-d_2)



5b

^{19}F NMR (376 MHz)

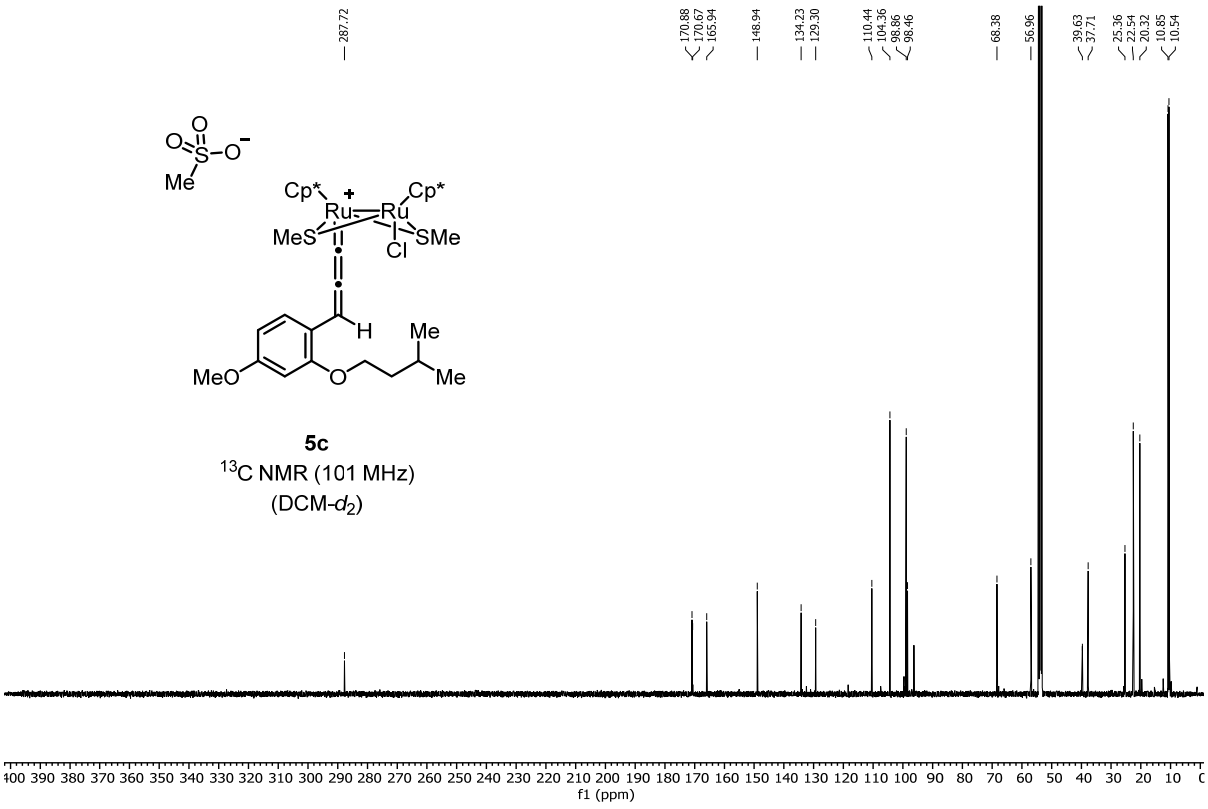
(DCM-d_2)



5c

^{1}H NMR (400 MHz)

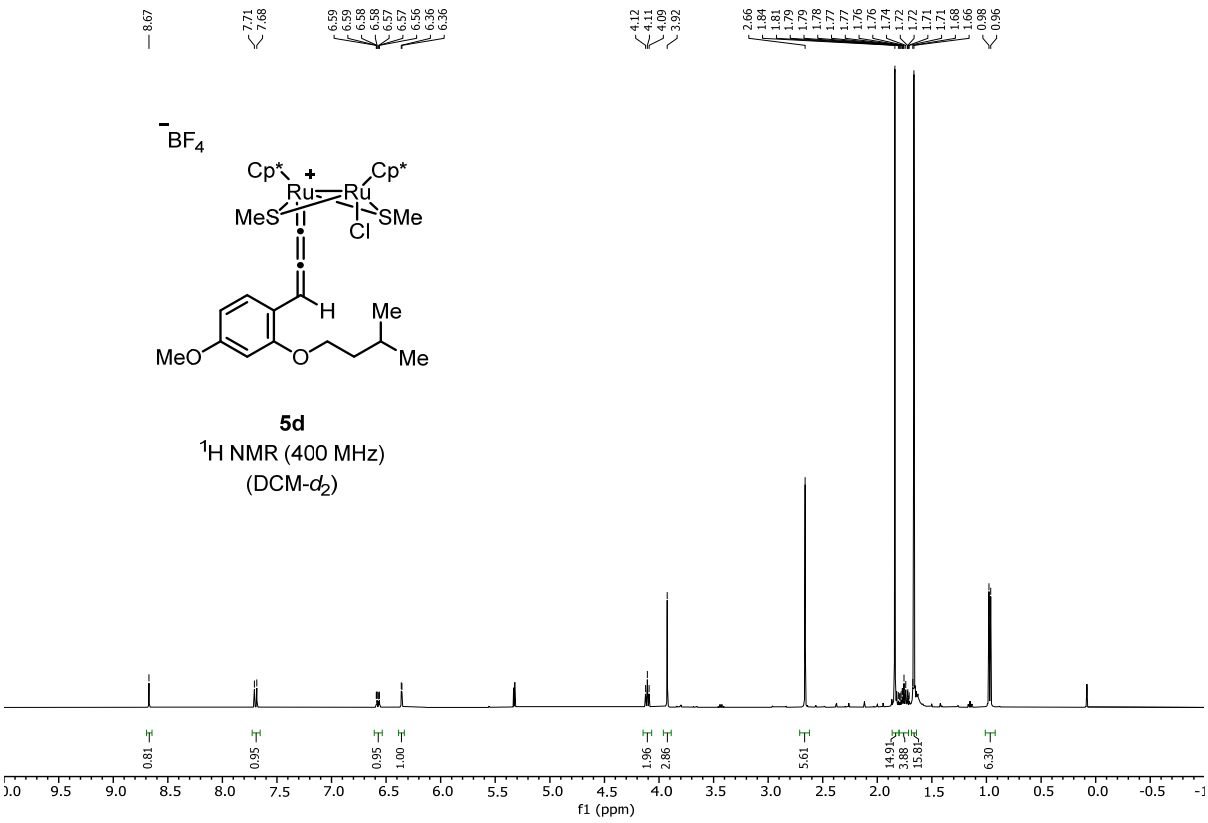
(DCM-d_2)



5c

^{13}C NMR (101 MHz)

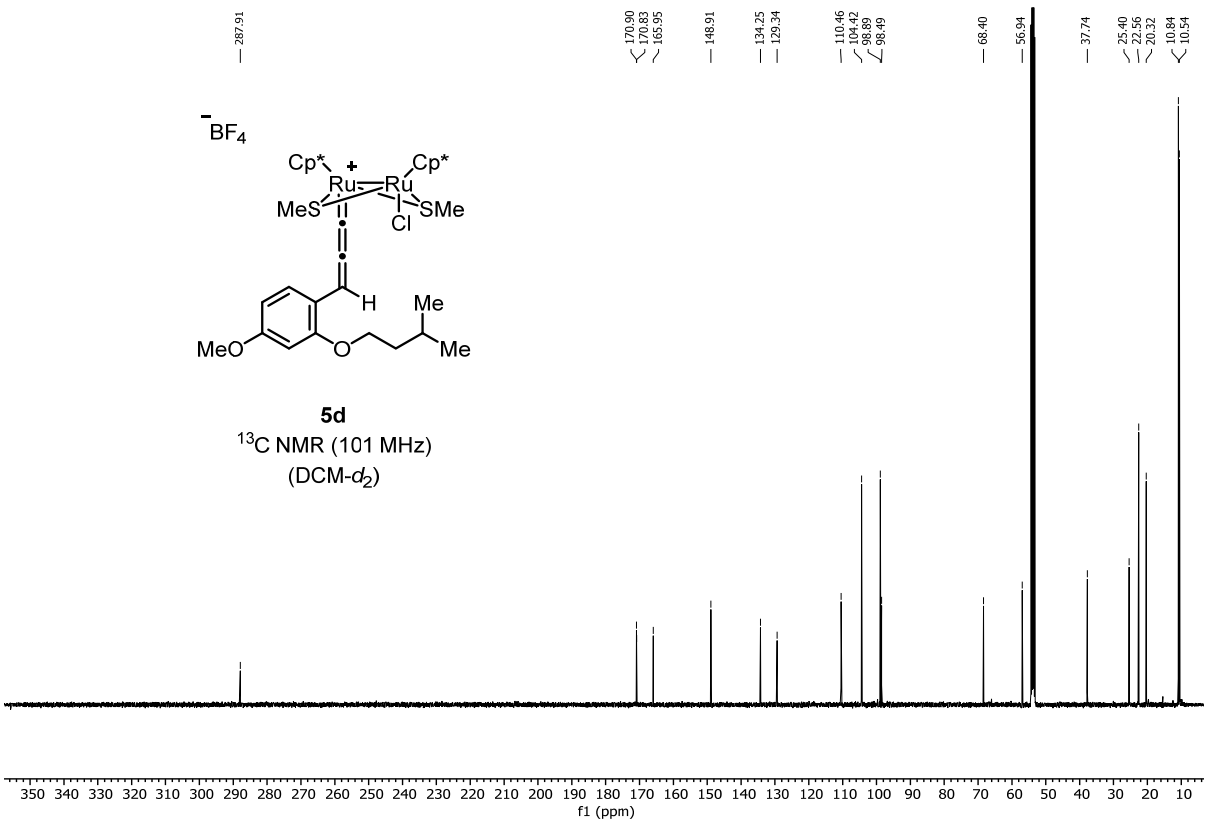
(DCM-d_2)



5d

^{1}H NMR (400 MHz)

(DCM-d_2)

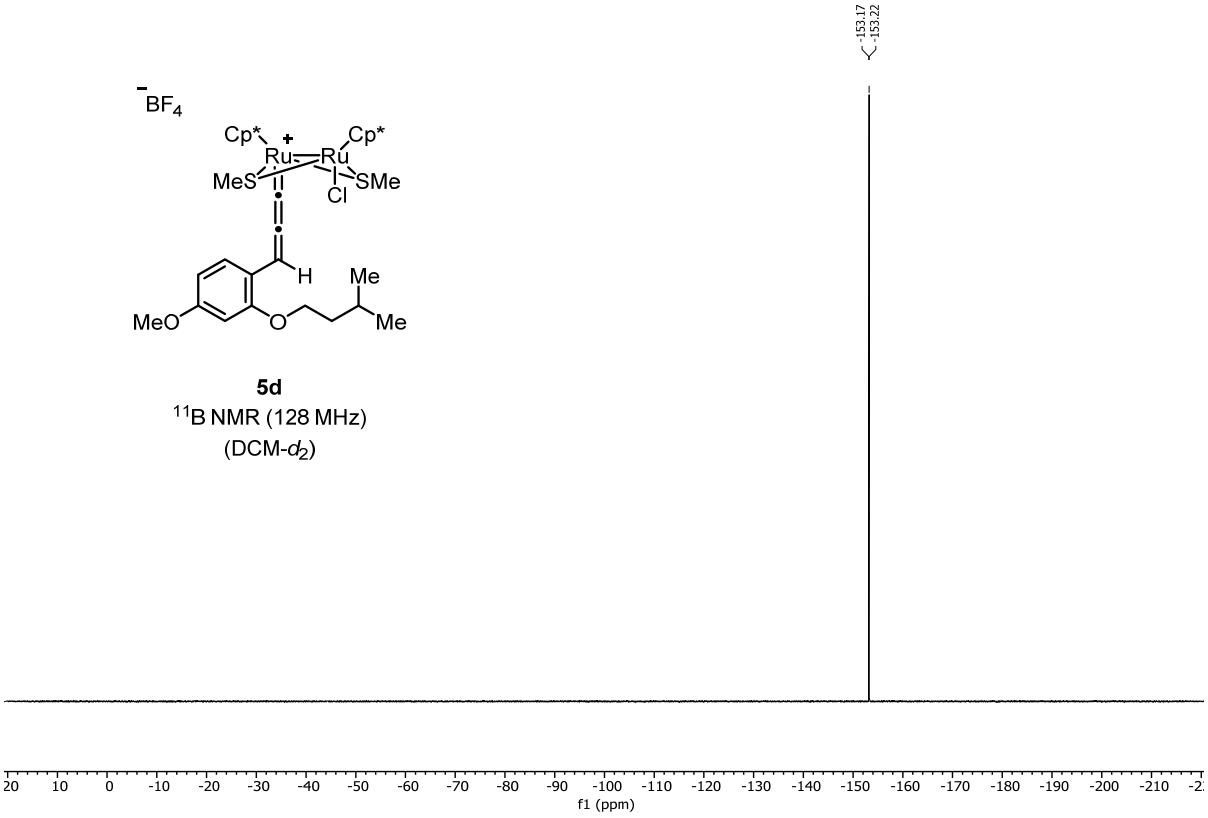


5d

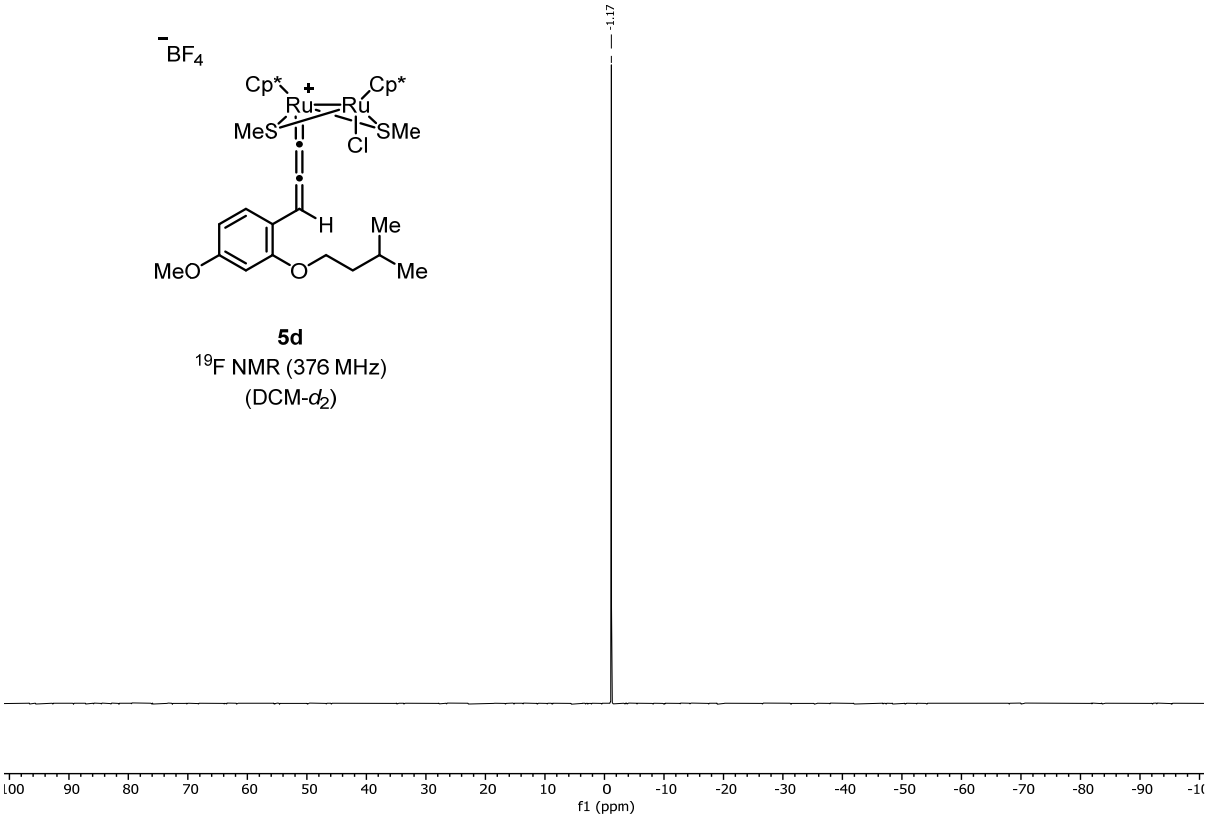
^{13}C NMR (101 MHz)

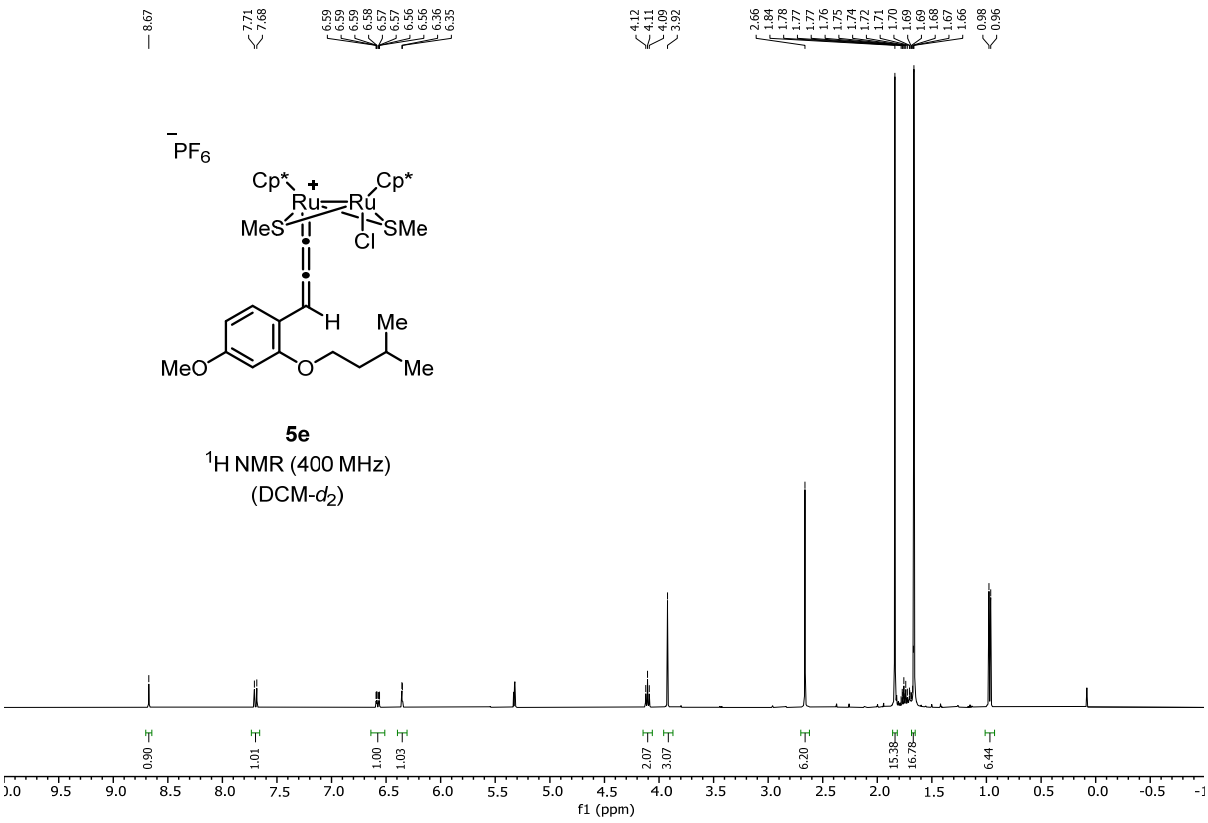
(DCM-d_2)

5d
^{11}B NMR (128 MHz)
(DCM-d_2)



5d
^{19}F NMR (376 MHz)
(DCM-d_2)

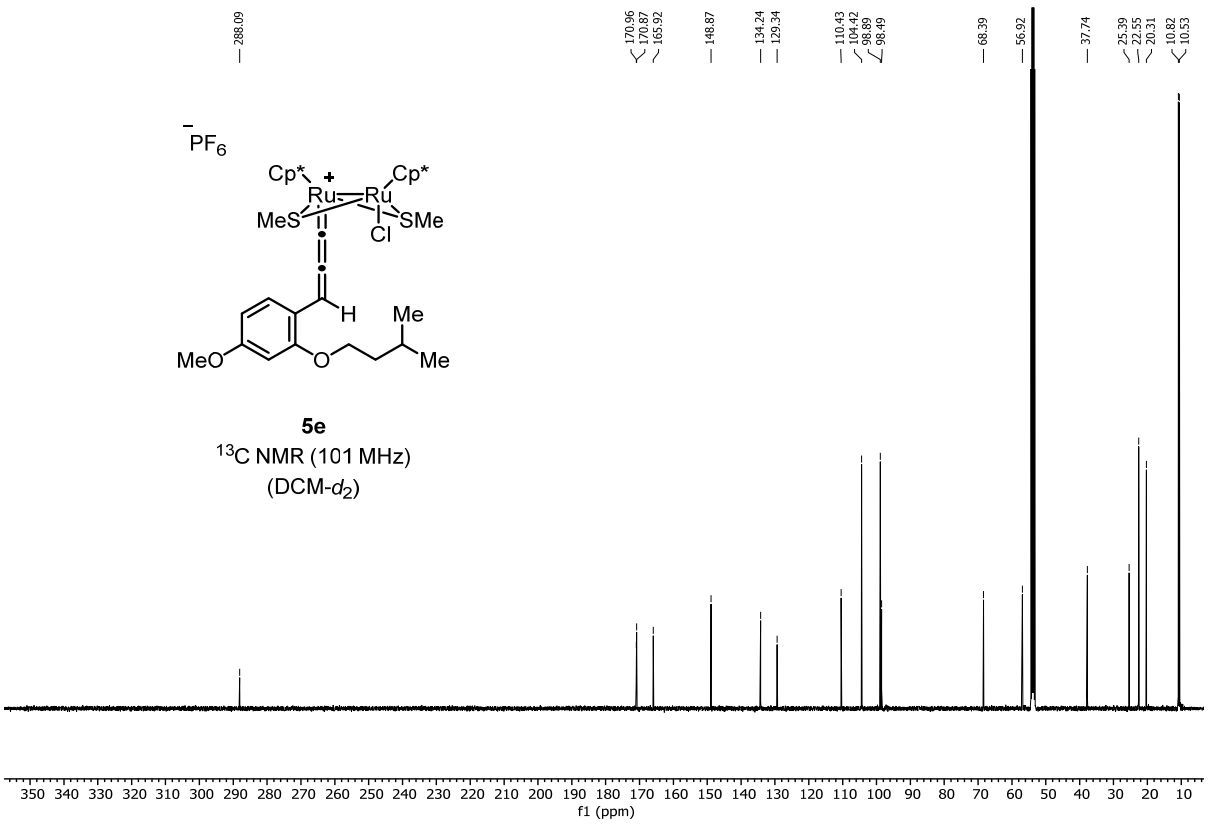




5e

^{1}H NMR (400 MHz)

(DCM-d_2)



5e

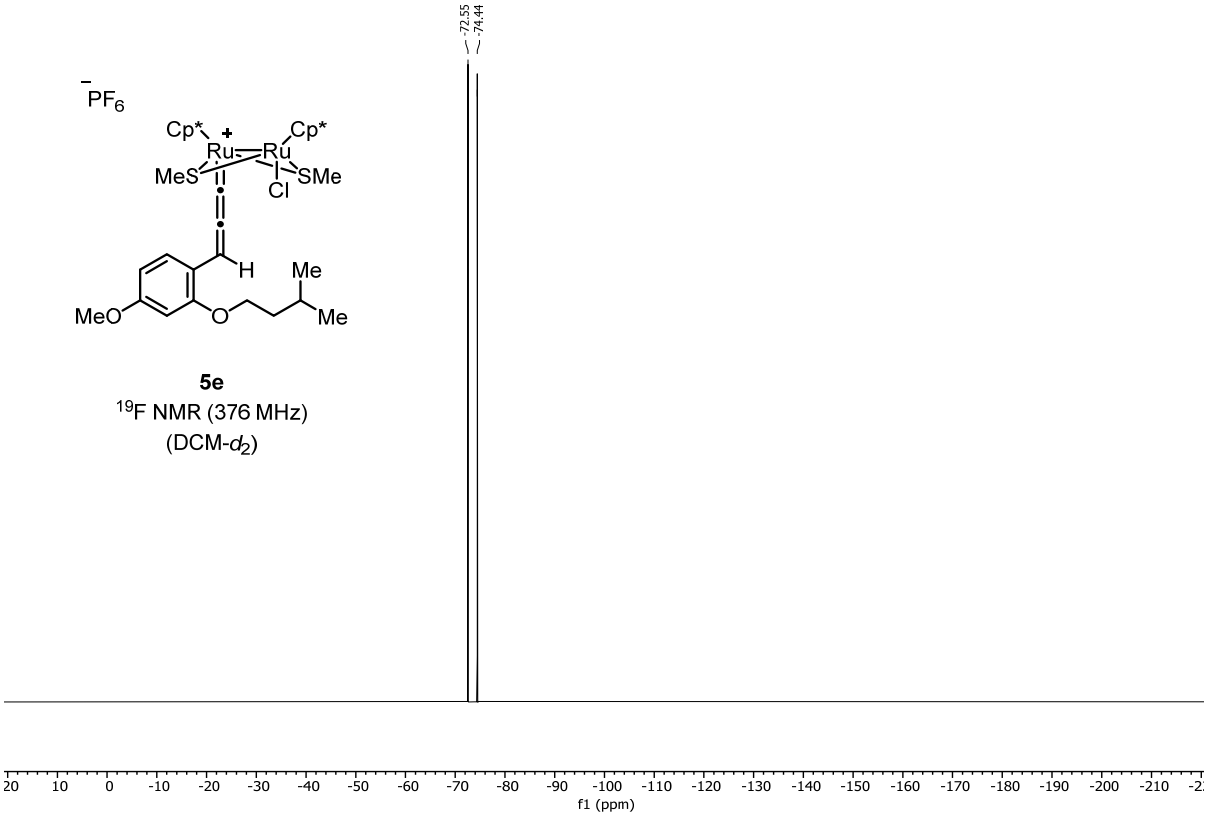
^{13}C NMR (101 MHz)

(DCM-d_2)

5e

^{19}F NMR (376 MHz)

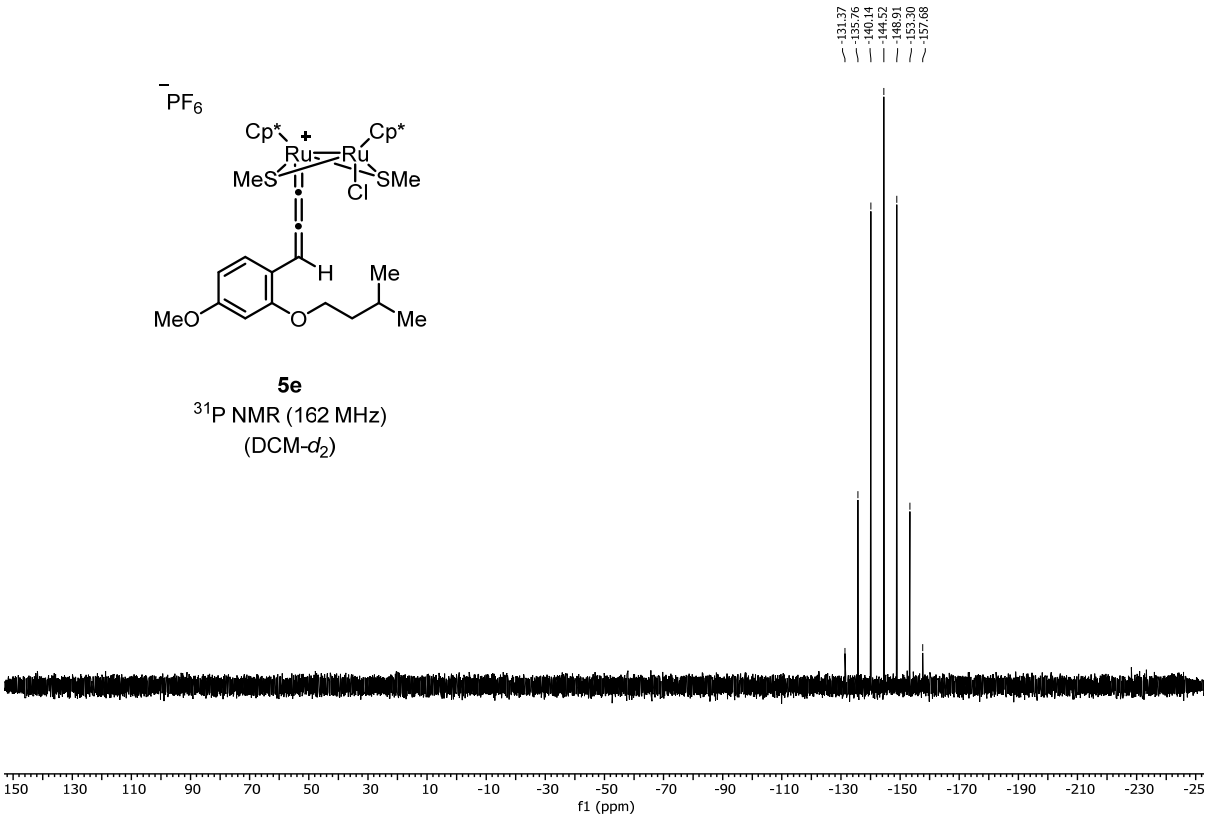
(DCM-d_2)

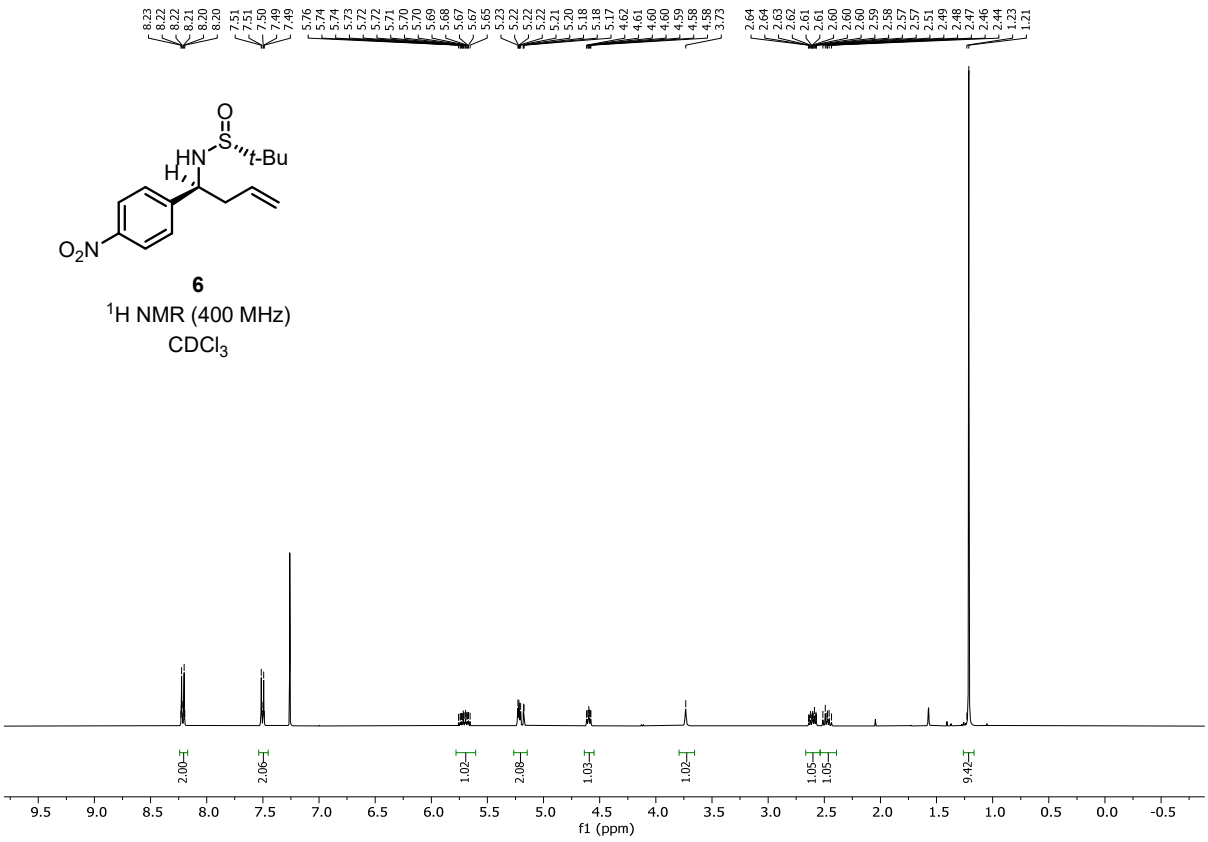


5e

^{31}P NMR (162 MHz)

(DCM-d_2)

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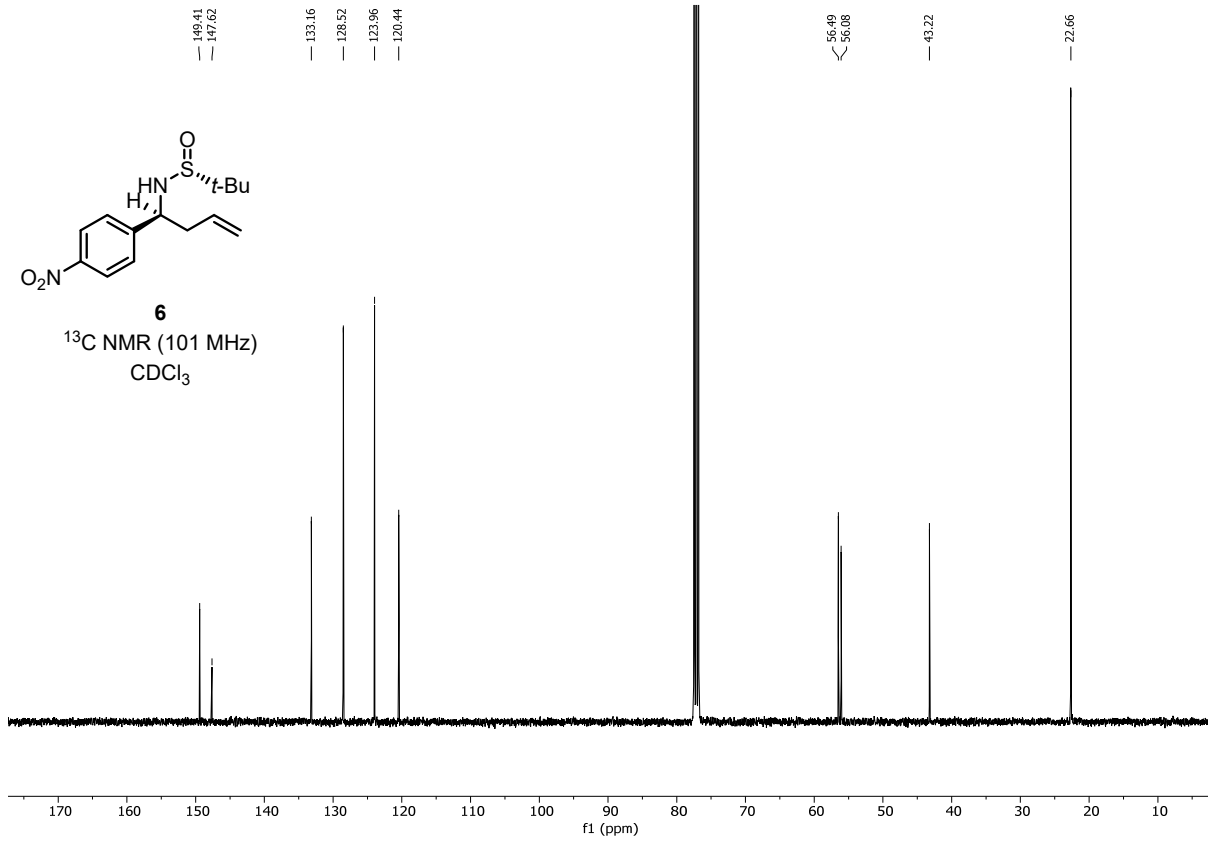
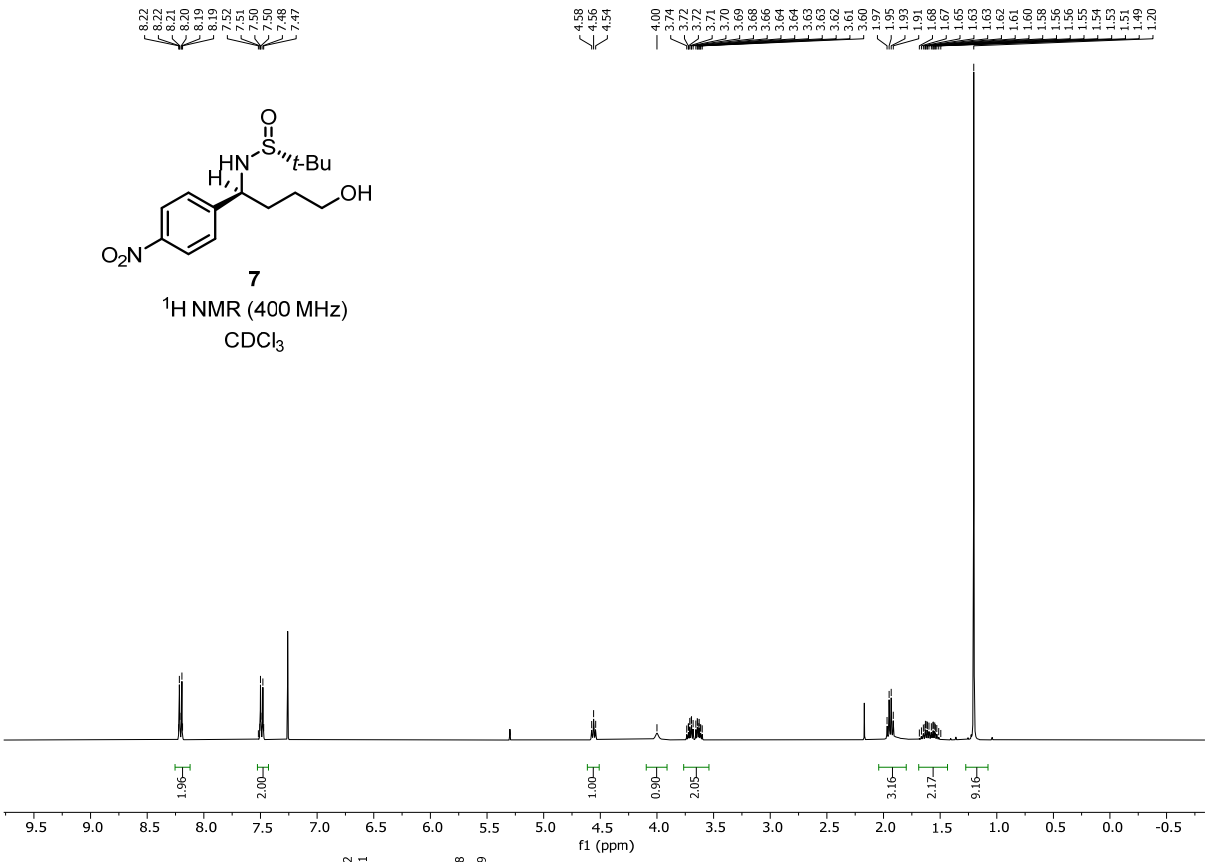
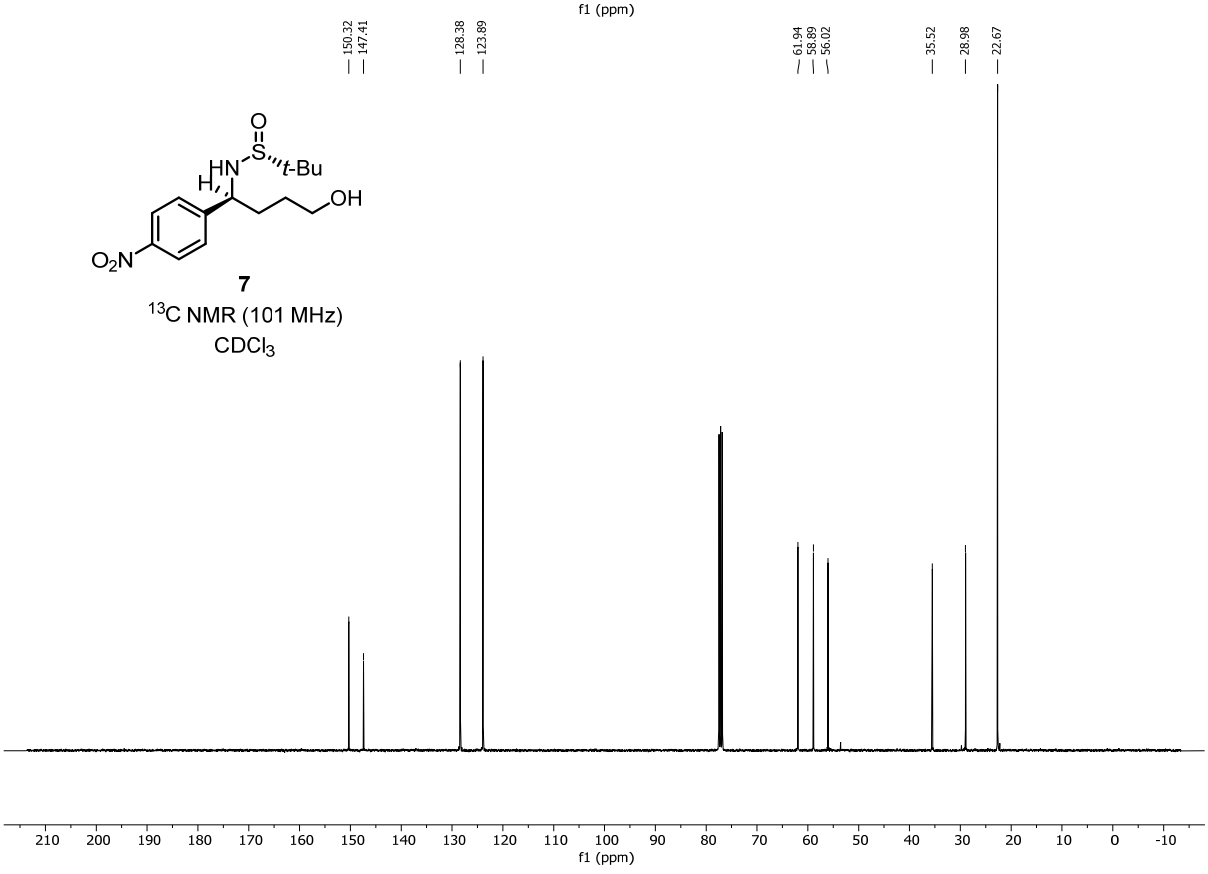
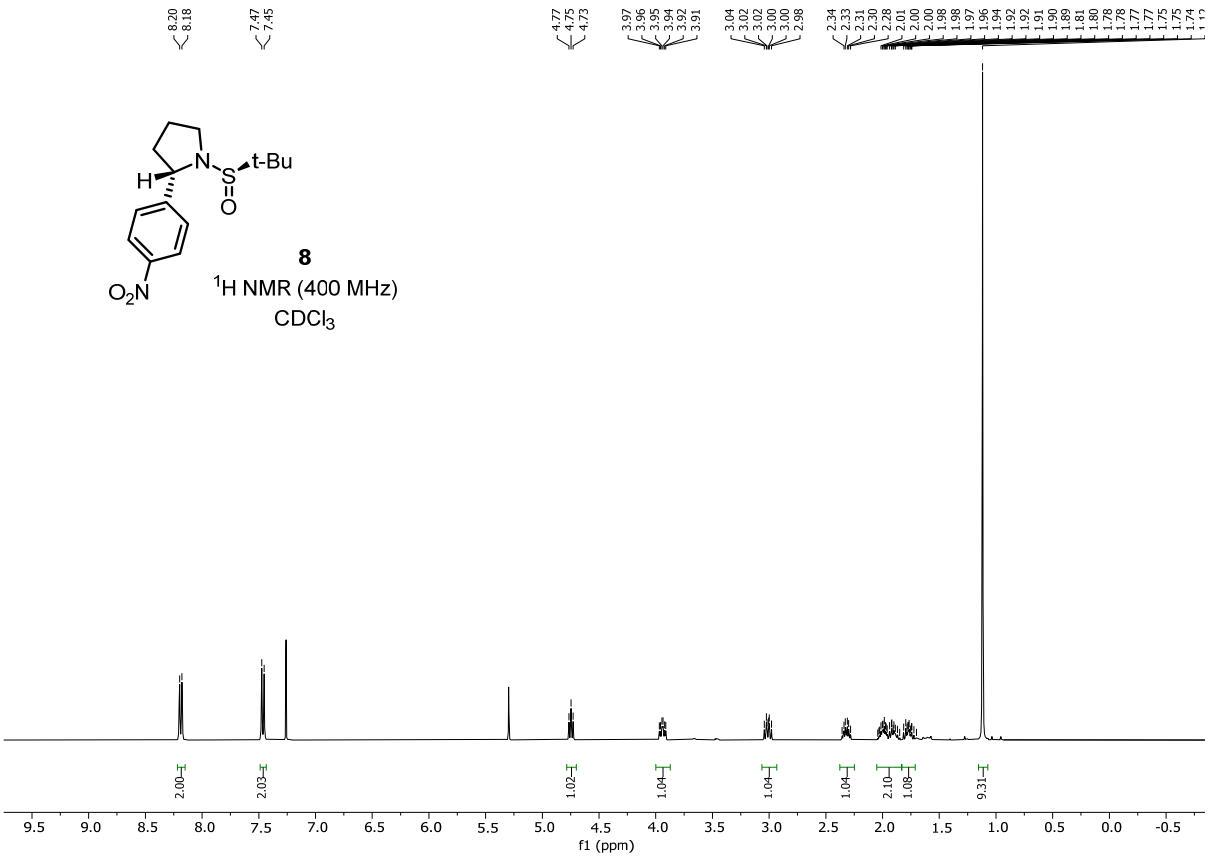
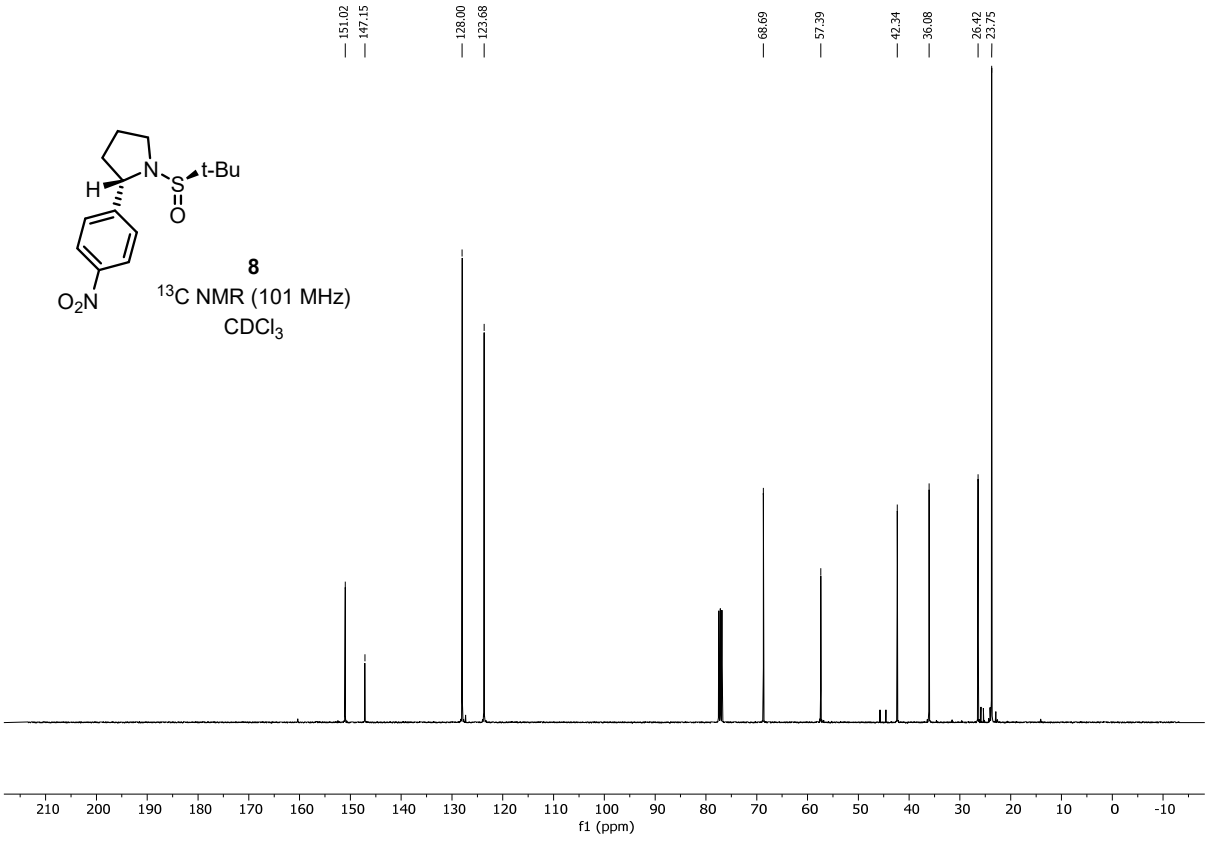
O
S
t-Bu
HN
H
O2N
6
1H NMR (400 MHz)
CDCl3
2.00 2.06 1.02 2.08 1.03 1.02 1.05 1.05 9.42
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

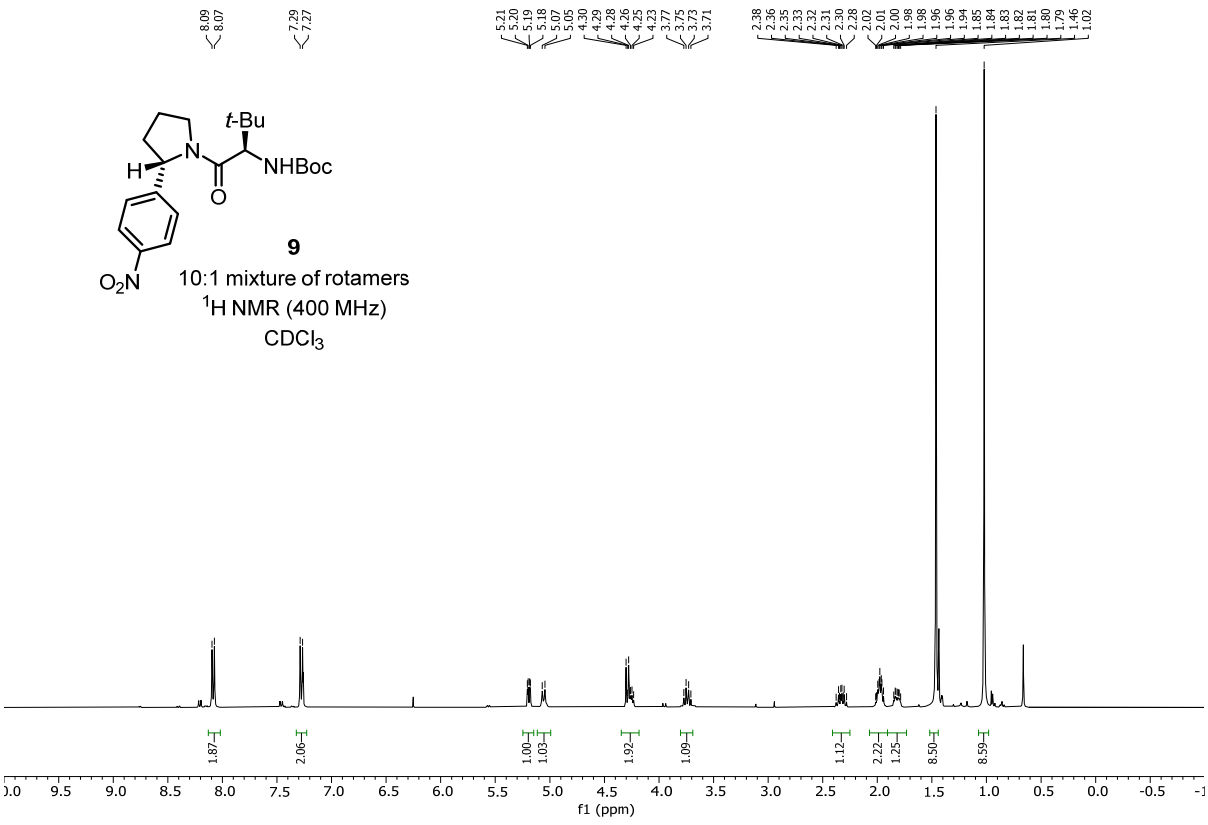

149.41 147.62 133.16 128.52 123.96 120.44 56.49 56.08 43.22 22.66
O
S
t-Bu
HN
H
O2N
6
13C NMR (101 MHz)
CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

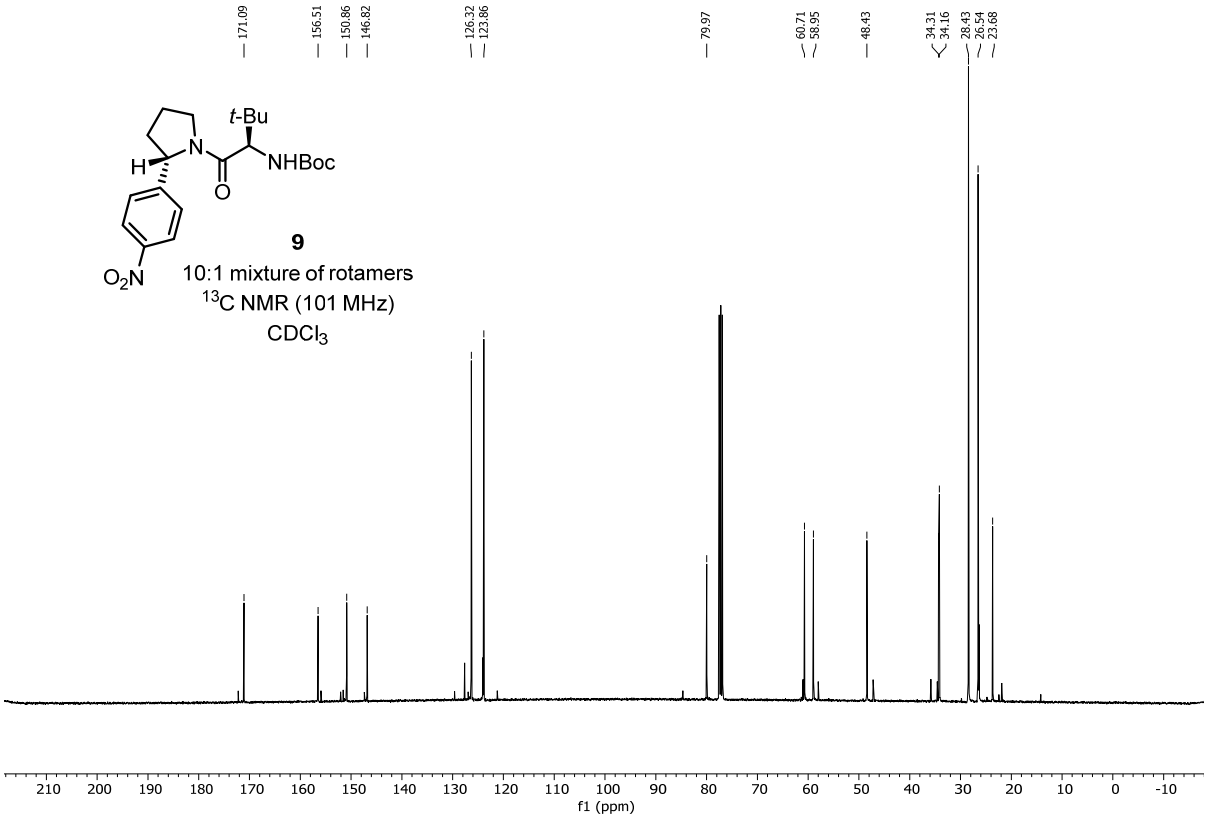

8.22
8.22
8.21
8.20
8.19
8.19
7.52
7.51
7.50
7.50
7.48
7.47
4.58
4.56
4.54
4.00
3.74
3.72
3.72
3.71
3.70
3.69
3.68
3.66
3.64
3.64
3.63
3.63
3.62
3.61
3.60
1.97
1.95
1.93
1.91
1.68
1.67
1.65
1.63
1.63
1.62
1.61
1.60
1.58
1.56
1.56
1.55
1.54
1.53
1.51
1.49
1.20
O
S
t-Bu
HN
H
OH
O2N
7
1H NMR (400 MHz)
CDCl3
1.96
2.00
1.00
0.90
2.05
3.16
2.17
9.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

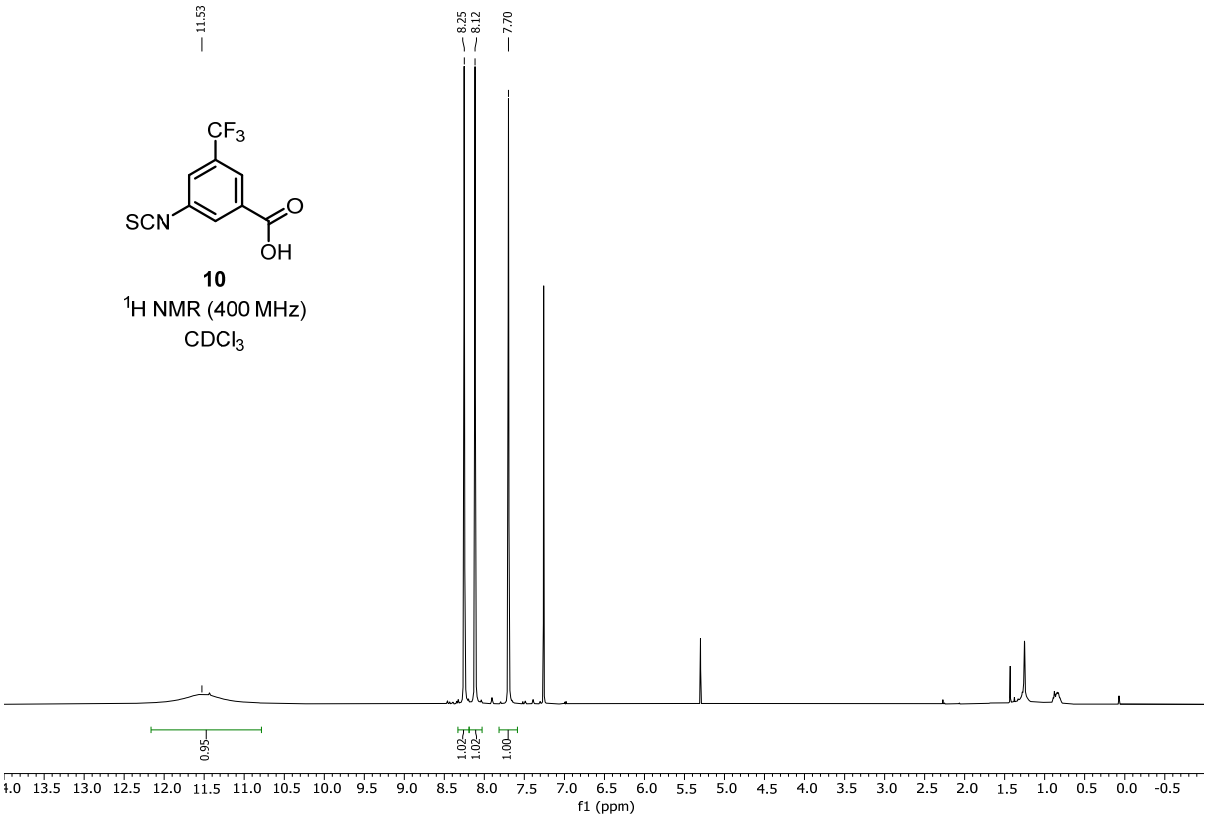

150.32
147.41
128.38
123.89
61.94
58.89
56.02
35.52
28.98
22.67
O
S
t-Bu
HN
H
OH
O2N
7
13C NMR (101 MHz)
CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

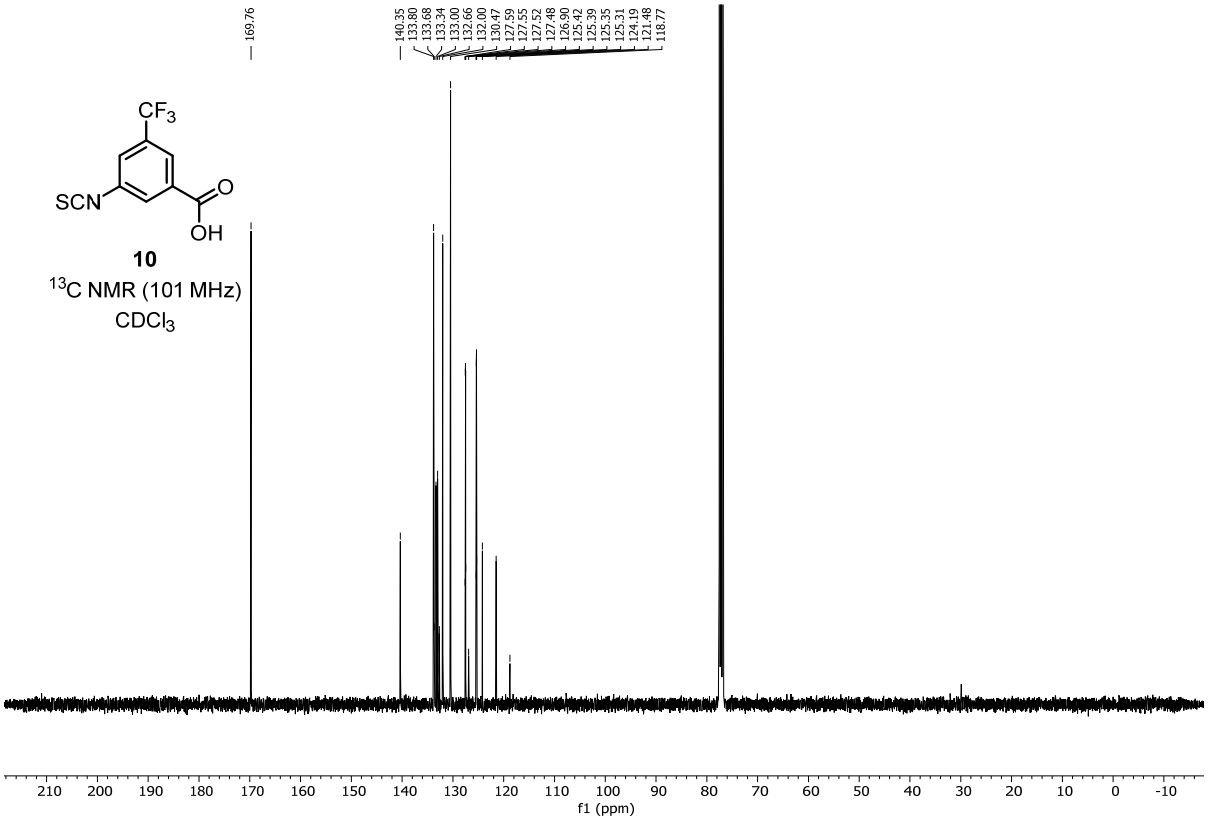

8.20
8.18
7.47
7.45
4.77
4.75
4.73
3.97
3.96
3.95
3.94
3.92
3.91
3.04
3.02
3.02
3.00
3.00
2.98
2.34
2.33
2.31
2.30
2.28
2.01
2.00
2.00
1.98
1.98
1.97
1.96
1.94
1.92
1.92
1.91
1.90
1.89
1.81
1.80
1.78
1.78
1.77
1.77
1.75
1.75
1.74
t-Bu
H
N
S
O
O2N
8
1H NMR (400 MHz)
CDCl3
2.00
2.03
1.02
1.04
1.04
1.04
2.10
1.08
9.31
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

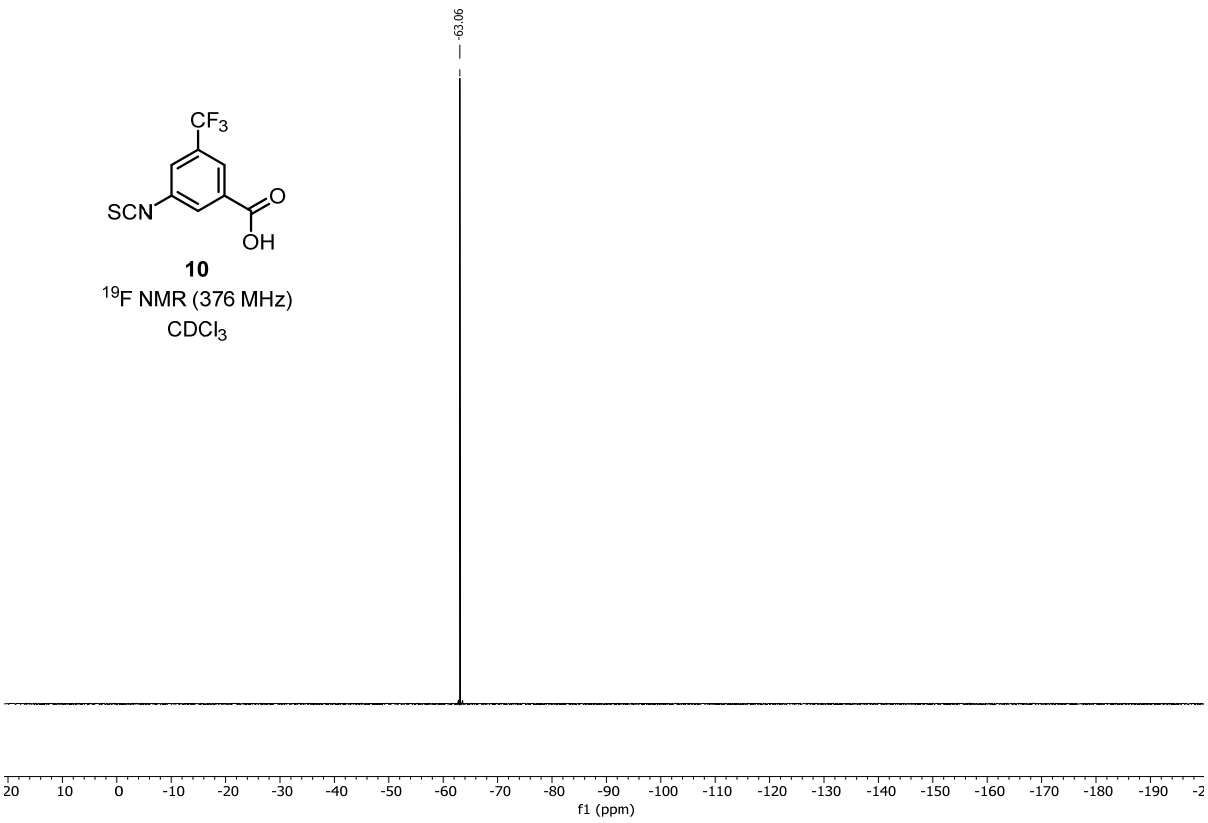

151.02
147.15
128.00
123.68
68.69
57.39
42.34
36.08
26.42
23.75
t-Bu
H
N
S
O
O2N
8
13C NMR (101 MHz)
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

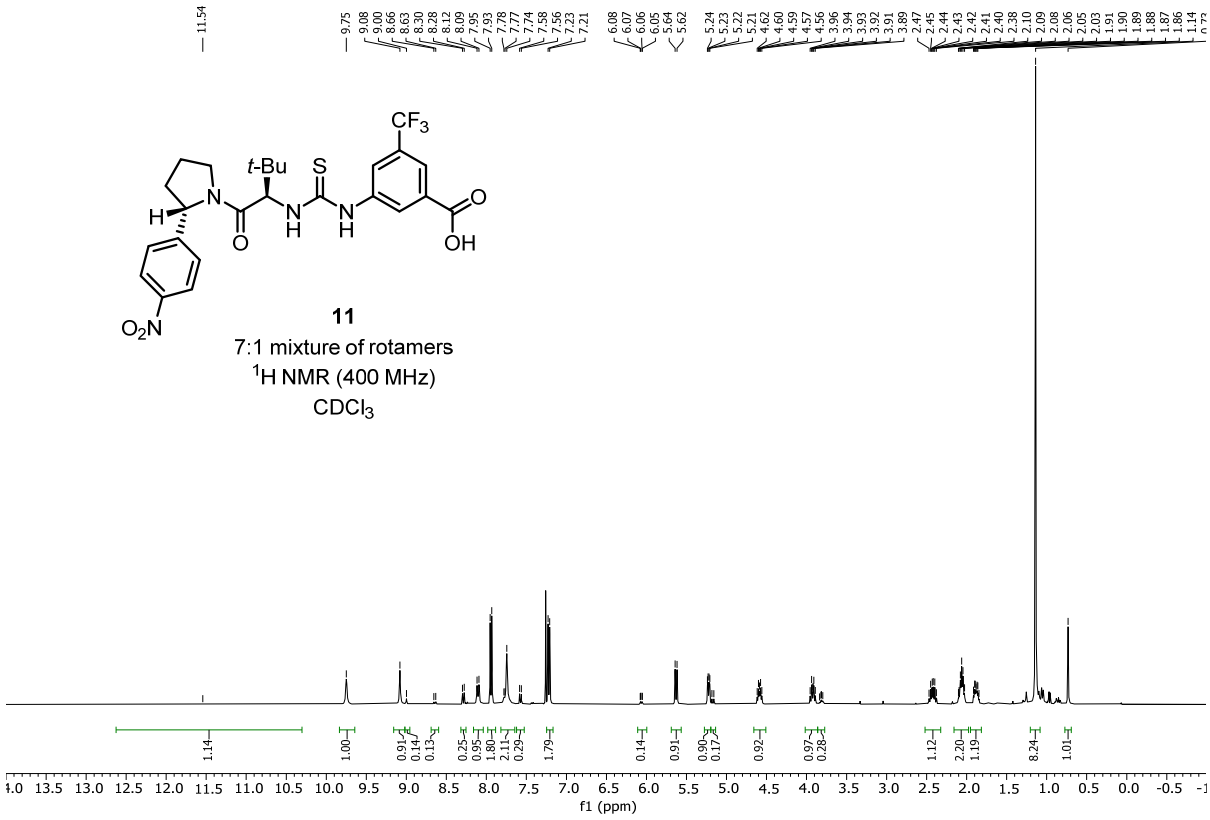

8.09
8.07
7.29
7.27
5.21
5.20
5.19
5.18
5.07
5.05
4.30
4.29
4.28
4.26
4.25
4.23
3.77
3.75
3.73
3.71
2.38
2.36
2.35
2.33
2.32
2.31
2.30
2.28
2.02
2.01
2.00
1.98
1.98
1.96
1.96
1.94
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.46
1.02
t-Bu
NHBoc
H
N
O
O2N
9
10:1 mixture of rotamers
1H NMR (400 MHz)
CDCl3
1.87
2.06
1.00
1.03
1.92
1.09
1.12
2.22
1.25
8.50
8.59
f1 (ppm)

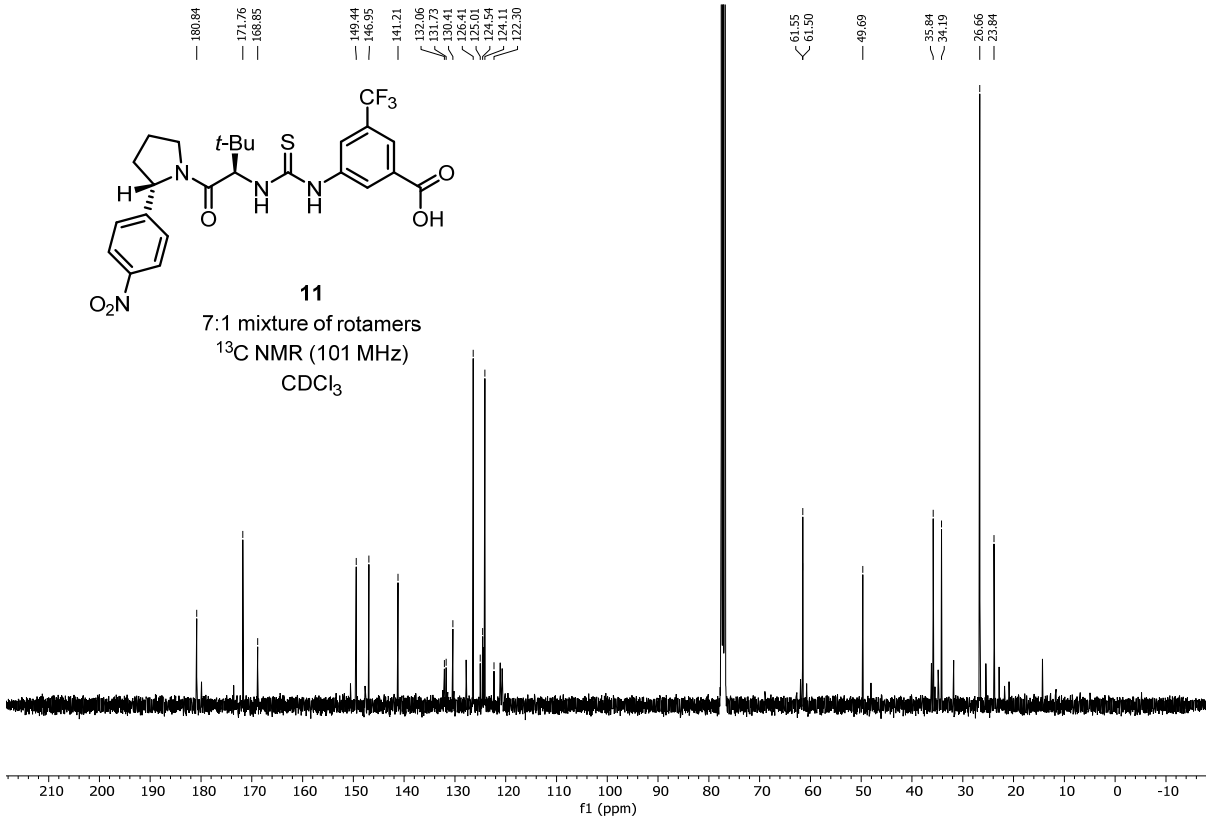

171.09
156.51
150.86
146.82
126.32
123.86
79.97
60.71
58.95
48.43
34.31
34.16
28.43
26.54
23.68
t-Bu
NHBoc
H
N
O
O2N
9
10:1 mixture of rotamers
13C NMR (101 MHz)
CDCl3
f1 (ppm)

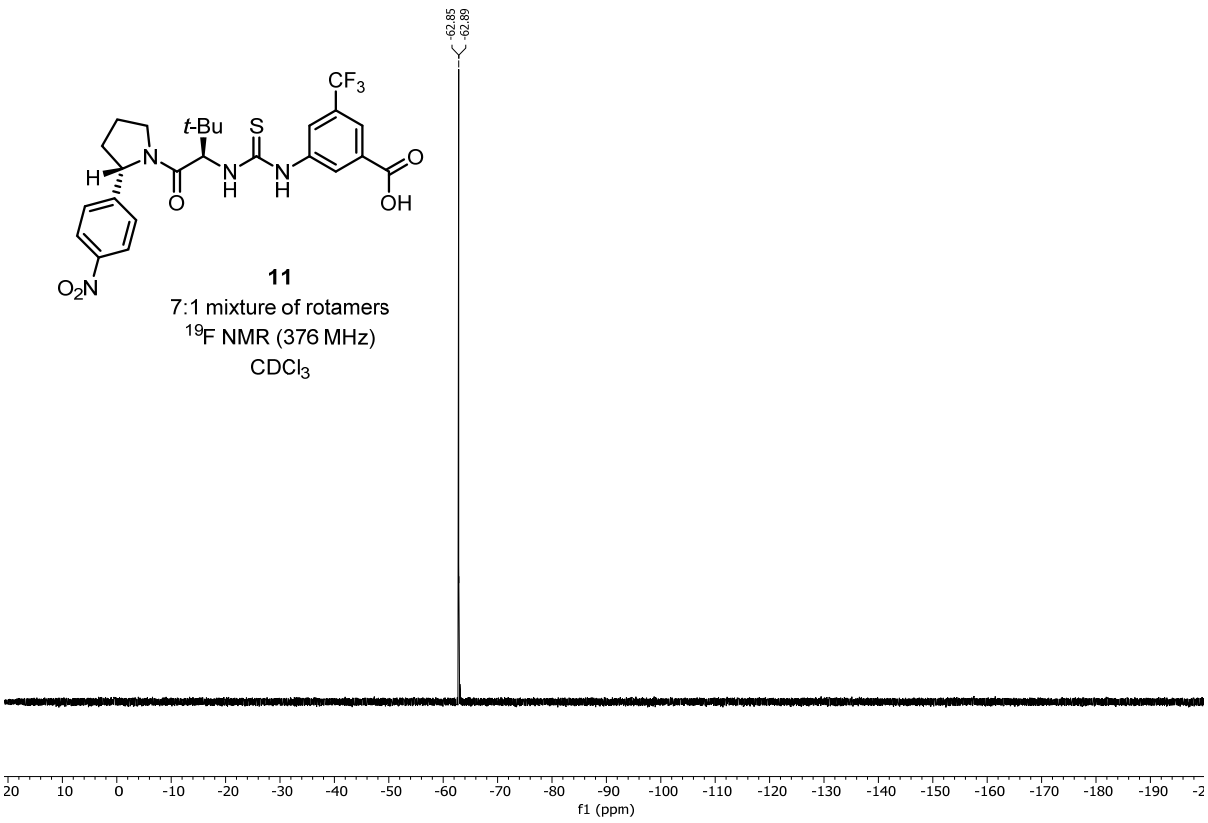

11.53
8.25
8.12
7.70
CF3
SCN
O
OH
10
1H NMR (400 MHz)
CDCl3
0.95
1.02
1.02
1.00
f1 (ppm)

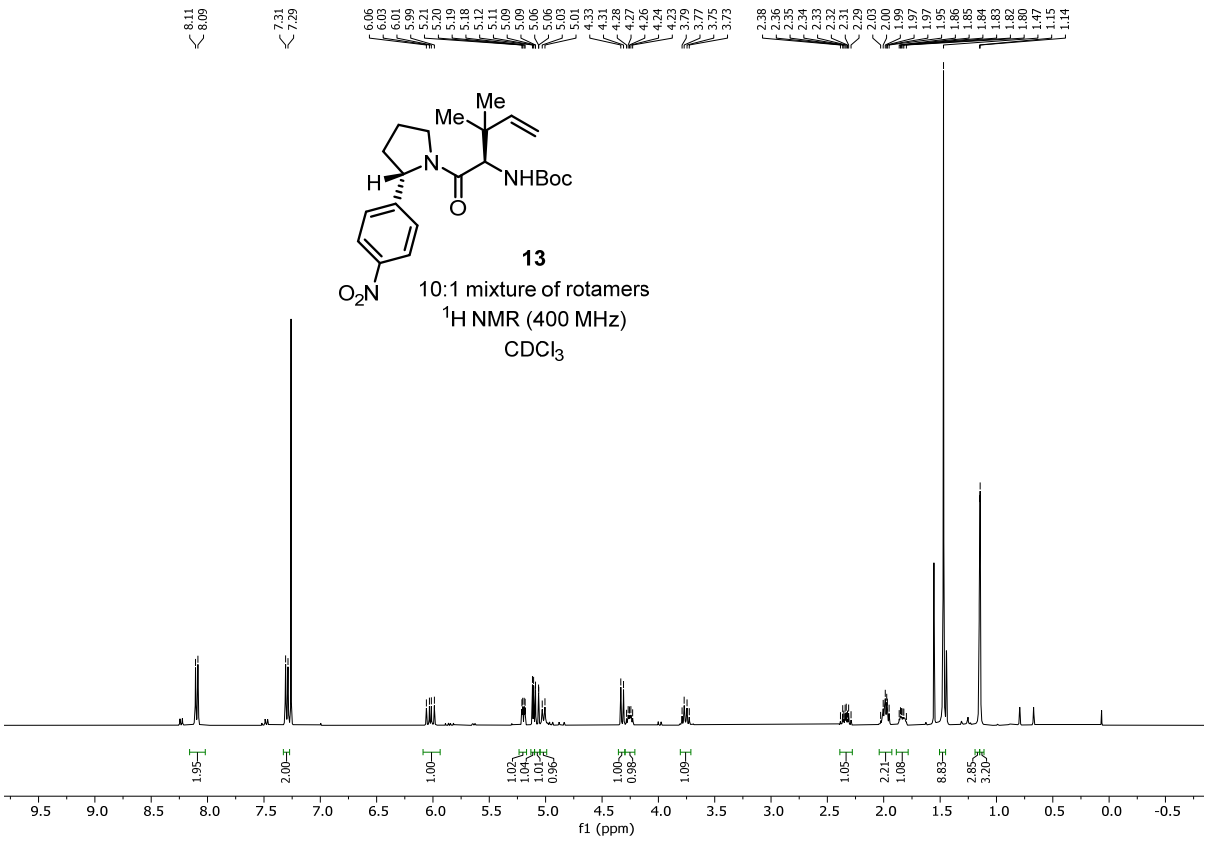

169.76
140.35
133.80
133.68
133.34
133.00
132.66
132.00
130.47
127.59
127.55
127.52
127.48
126.90
125.42
125.39
125.35
125.31
124.19
121.48
118.77
CF3
SCN
O
OH
10
13C NMR (101 MHz)
CDCl3
f1 (ppm)

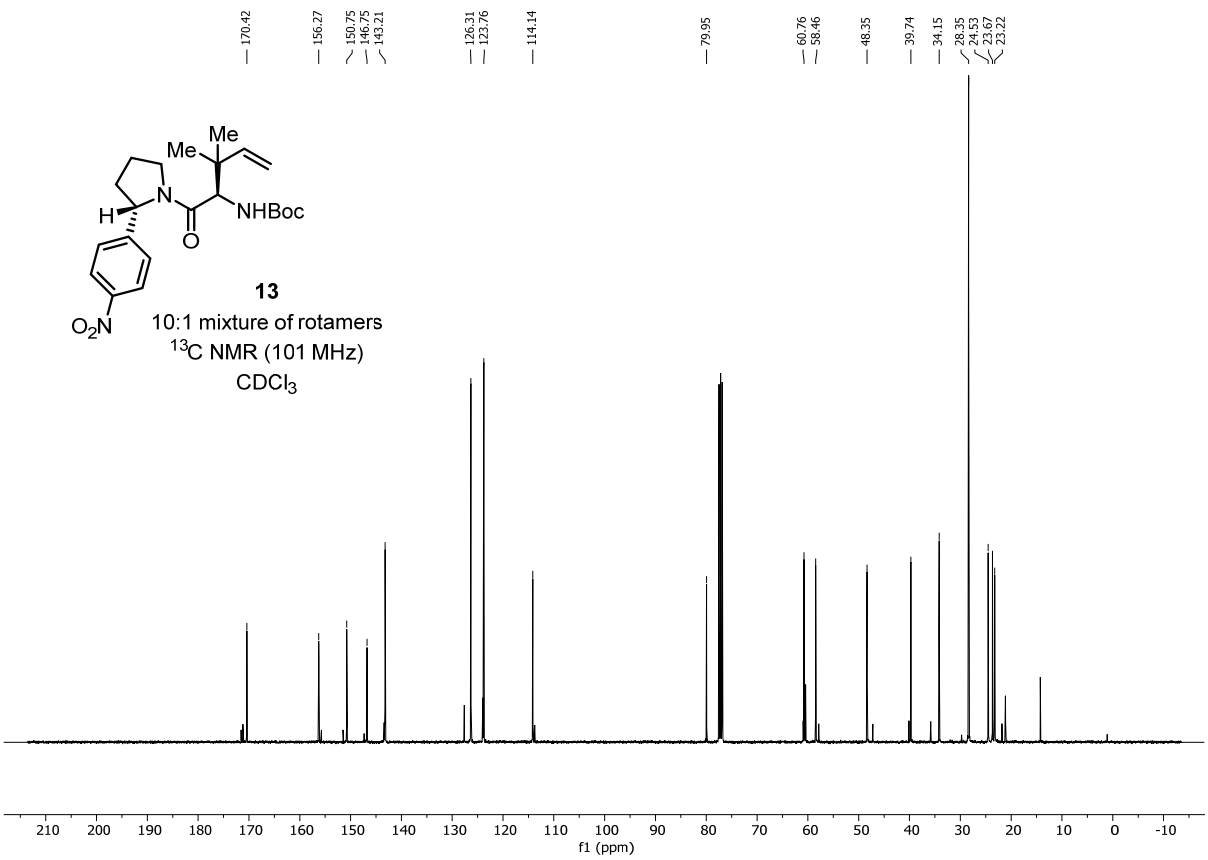

-63.06
CF3
SCN
O
OH
10
19F NMR (376 MHz)
CDCl3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

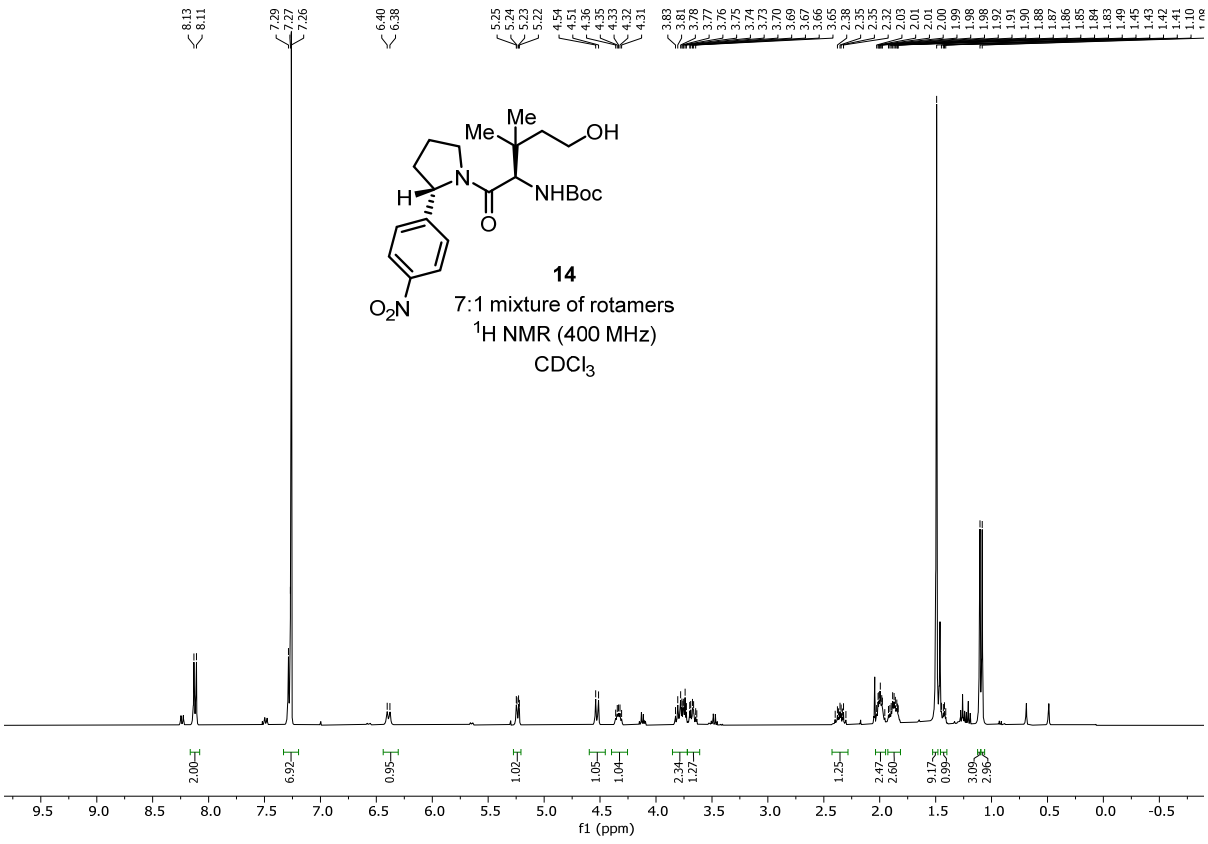

11
7:1 mixture of rotamers
1H NMR (400 MHz)
CDCl3
f1 (ppm)

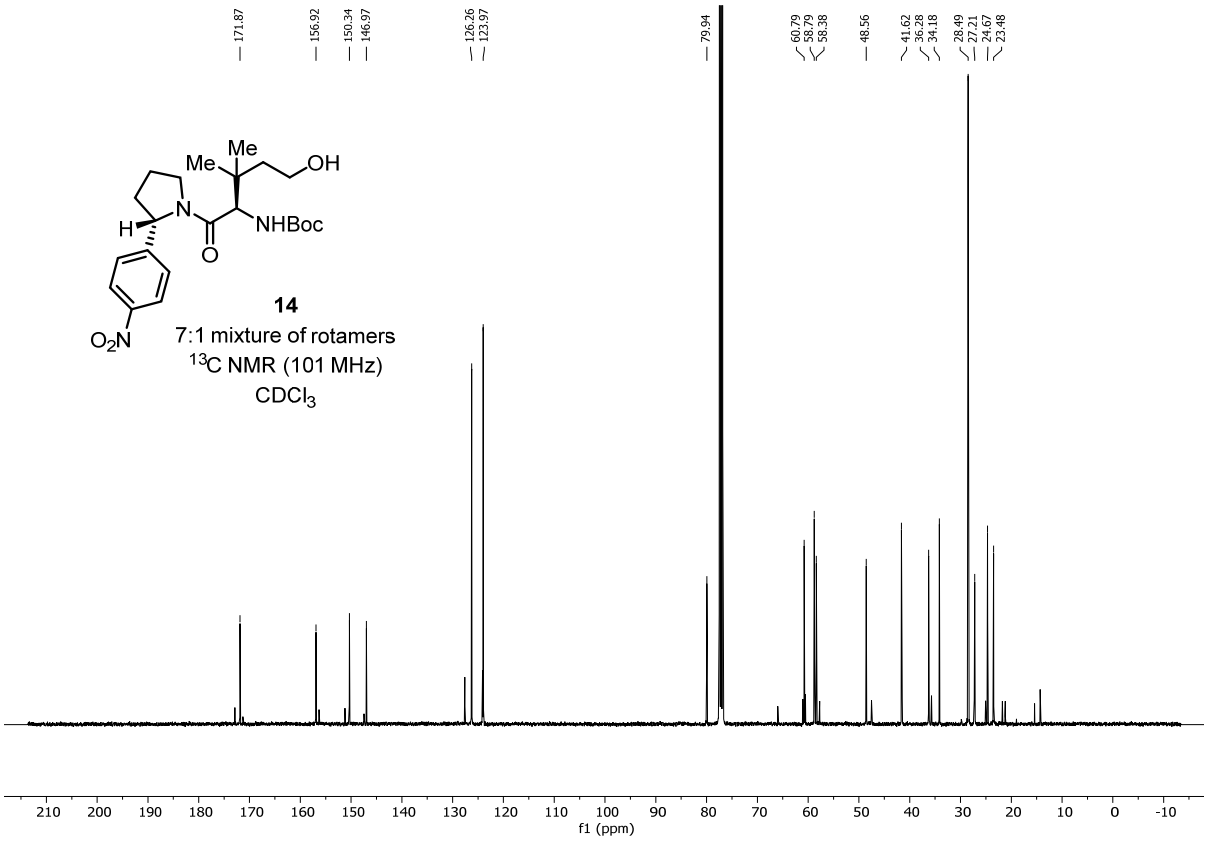

11
7:1 mixture of rotamers
13C NMR (101 MHz)
CDCl3
f1 (ppm)

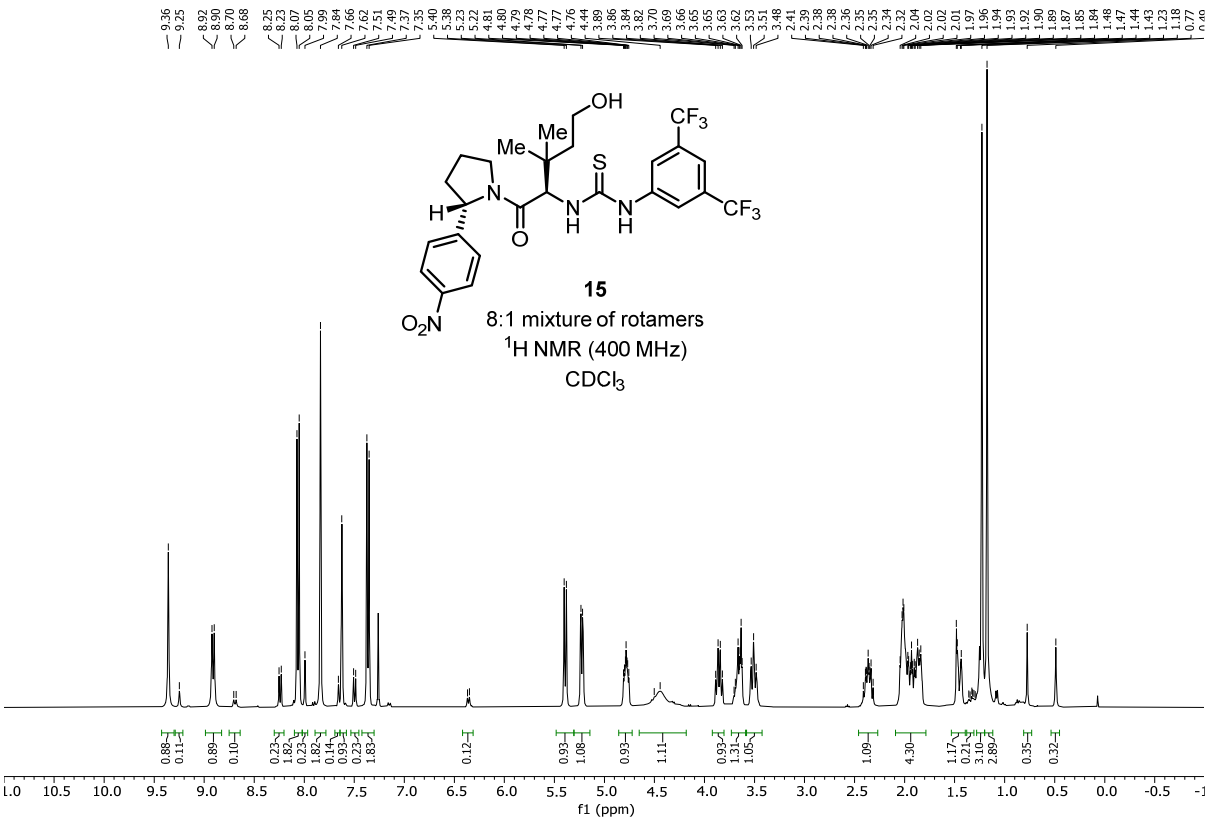

-62.85
-62.89
CF3
t-Bu
S
N
H
N
H
N
O
O
OH
O2N
11
7:1 mixture of rotamers
19F NMR (376 MHz)
CDCl3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

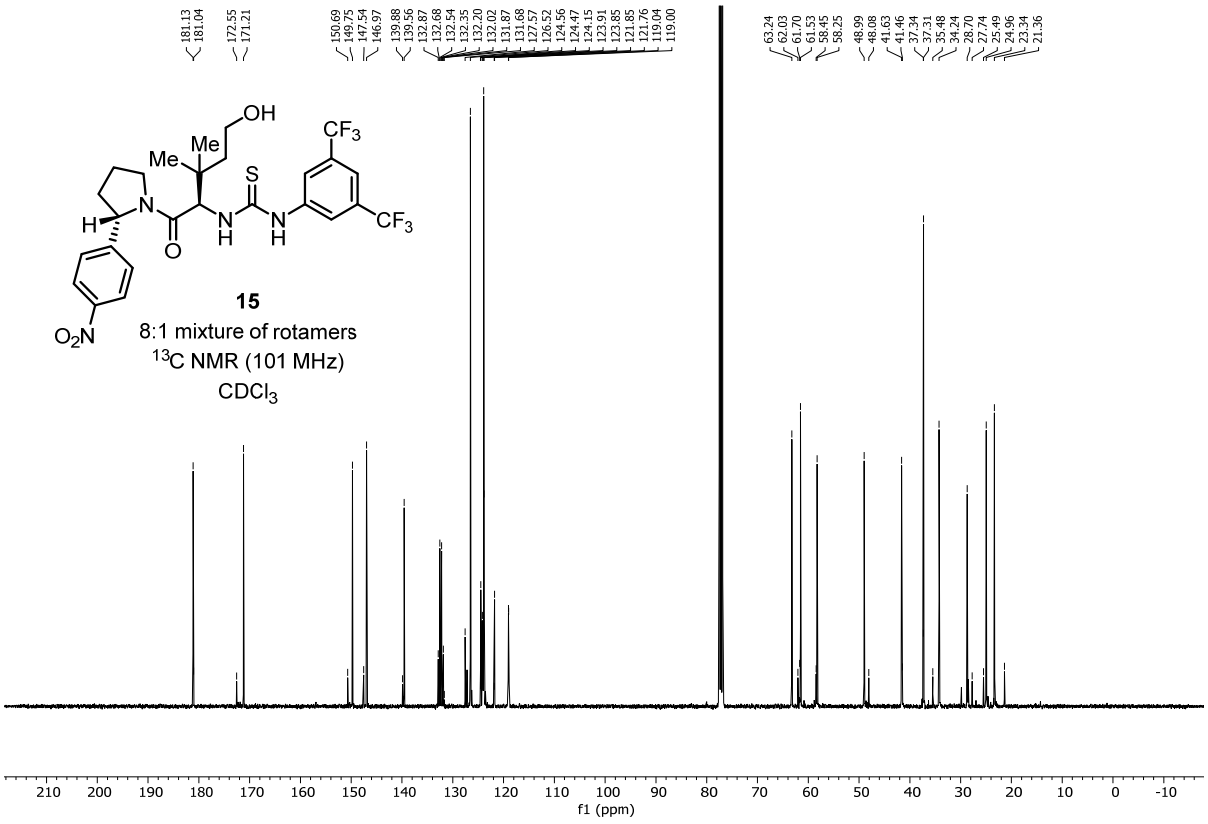

13
10:1 mixture of rotamers
1H NMR (400 MHz)
CDCl3
f1 (ppm)

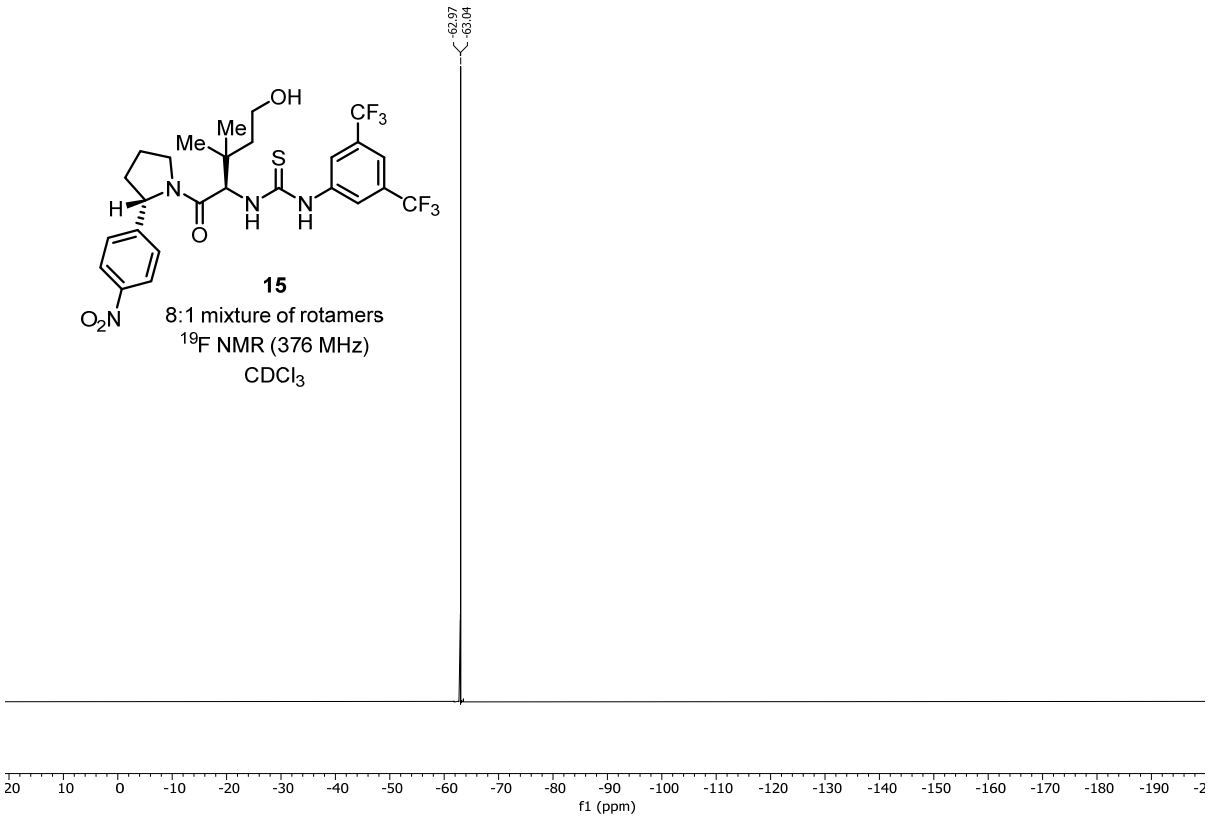

13
10:1 mixture of rotamers
13C NMR (101 MHz)
CDCl3
f1 (ppm)


14
7:1 mixture of rotamers
1H NMR (400 MHz)
CDCl3
f1 (ppm)


14
7:1 mixture of rotamers
13C NMR (101 MHz)
CDCl3
f1 (ppm)

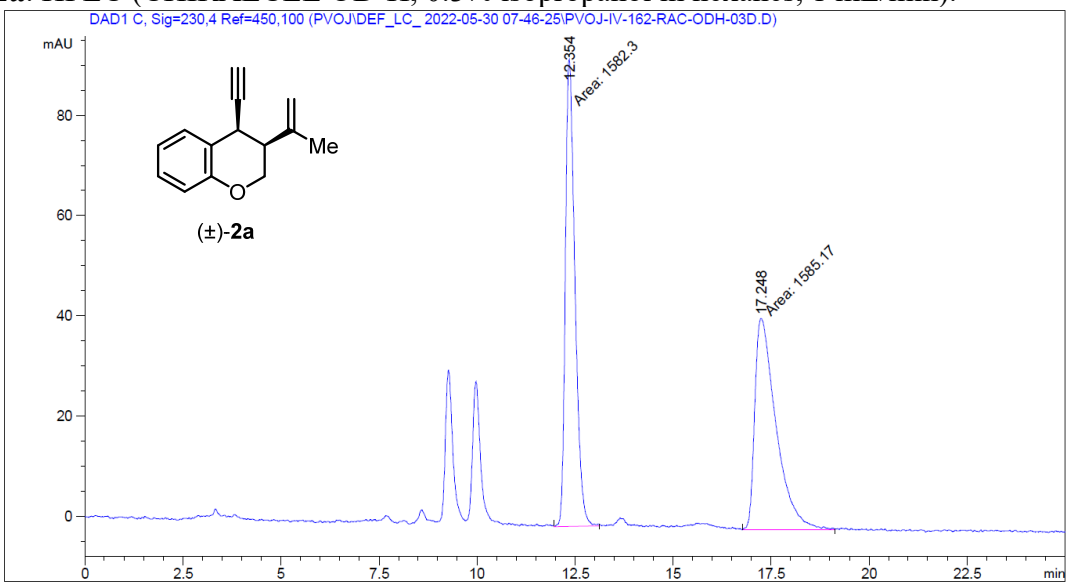

15
8:1 mixture of rotamers
1H NMR (400 MHz)
CDCl3
f1 (ppm)


15
8:1 mixture of rotamers
13C NMR (101 MHz)
CDCl3
f1 (ppm)


-62.97
-63.04
OH
Me
Me
S
CF3
N
H
N
H
N
H
CF3
O
O2N
15
8:1 mixture of rotamers
19F NMR (376 MHz)
CDCl3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

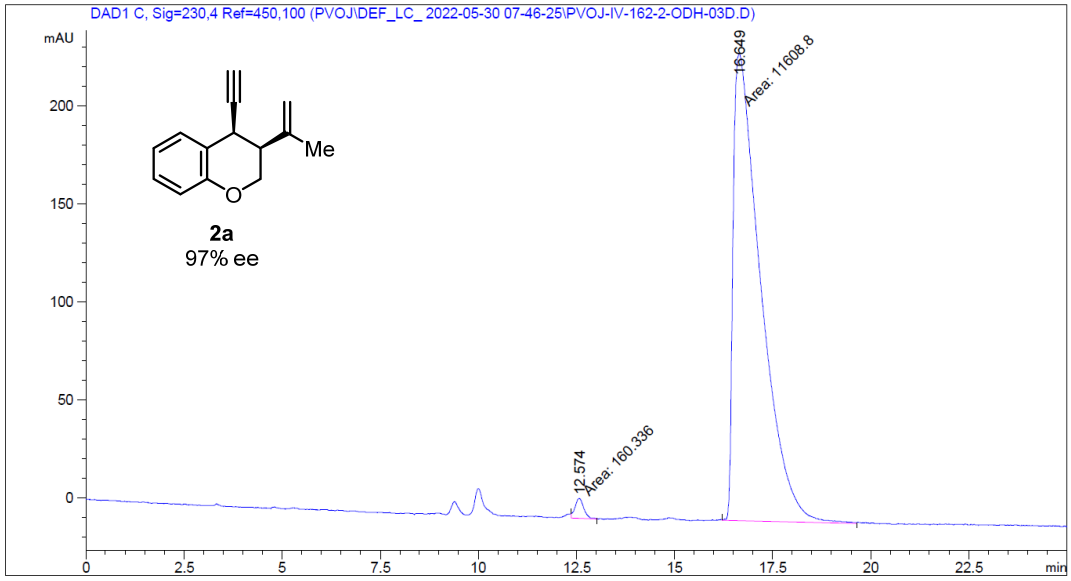
HPLC, GC, and SFC traces

2a: HPLC (CHIRALCEL OD-H, 0.3% isopropanol in hexanes, 1 mL/min).



Signal 1: DAD1 C, Sig=230,4 Ref=450,100

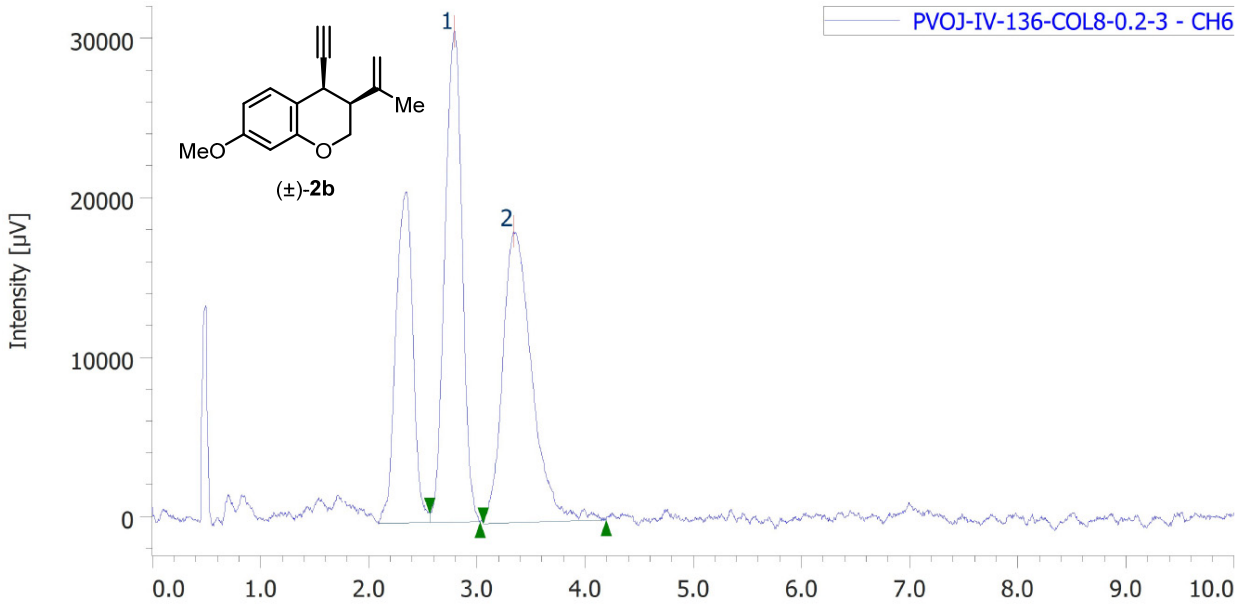
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.354	MM	0.2830	1582.30017	93.18201	49.9546
2	17.248	MM	0.6270	1585.17371	42.13841	50.0454



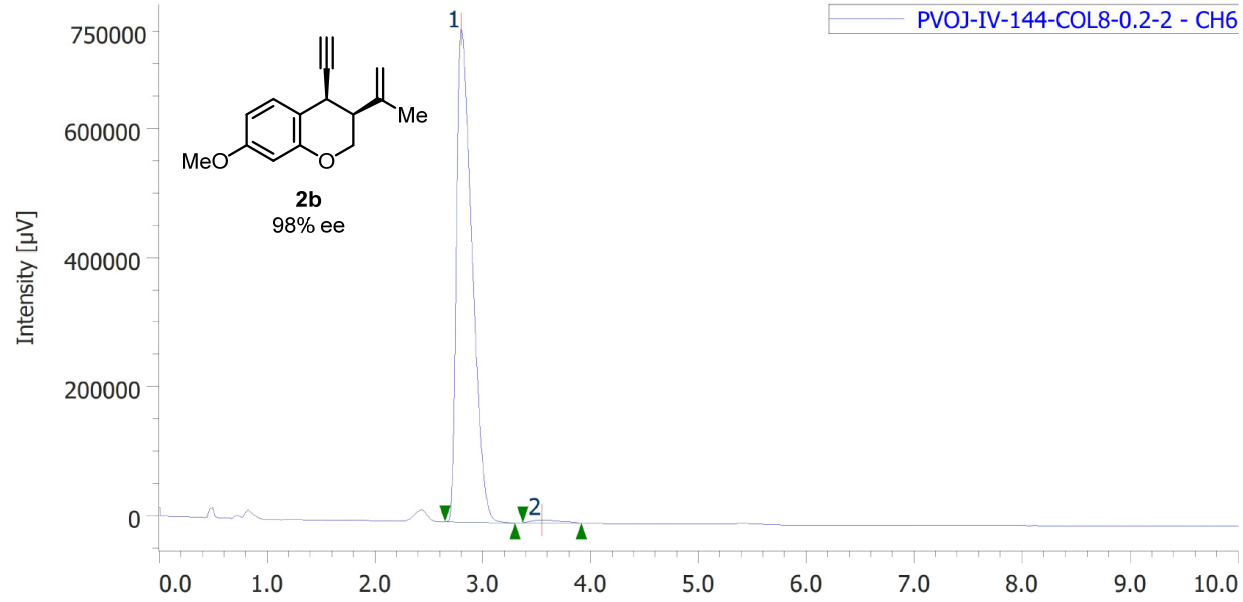
Signal 1: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.574	FM	0.2623	160.33594	10.18952	1.3623
2	16.649	MM	0.8120	1.16088e4	238.28505	98.6377

2b: SFC (CHIRALPAK IH, 0.2% methanol).

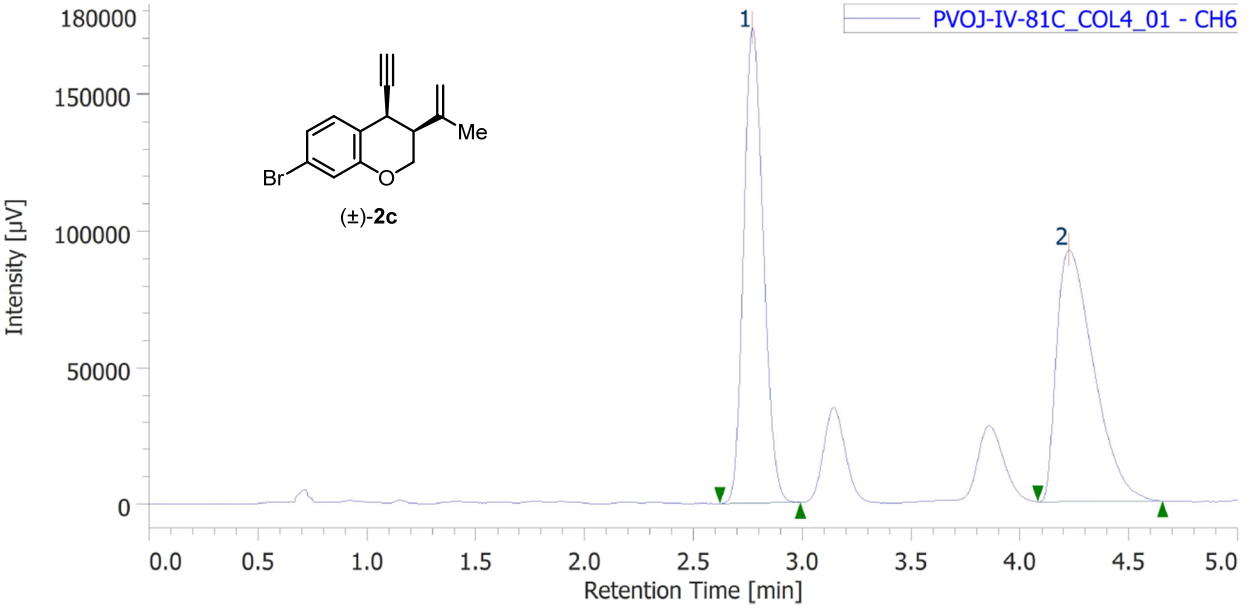


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	6	2.790	342255	49.8	1.416	0.177	30750
2	Unknown	6	3.340	345141	50.2	N/A	0.281	18260
Total				687396				49010

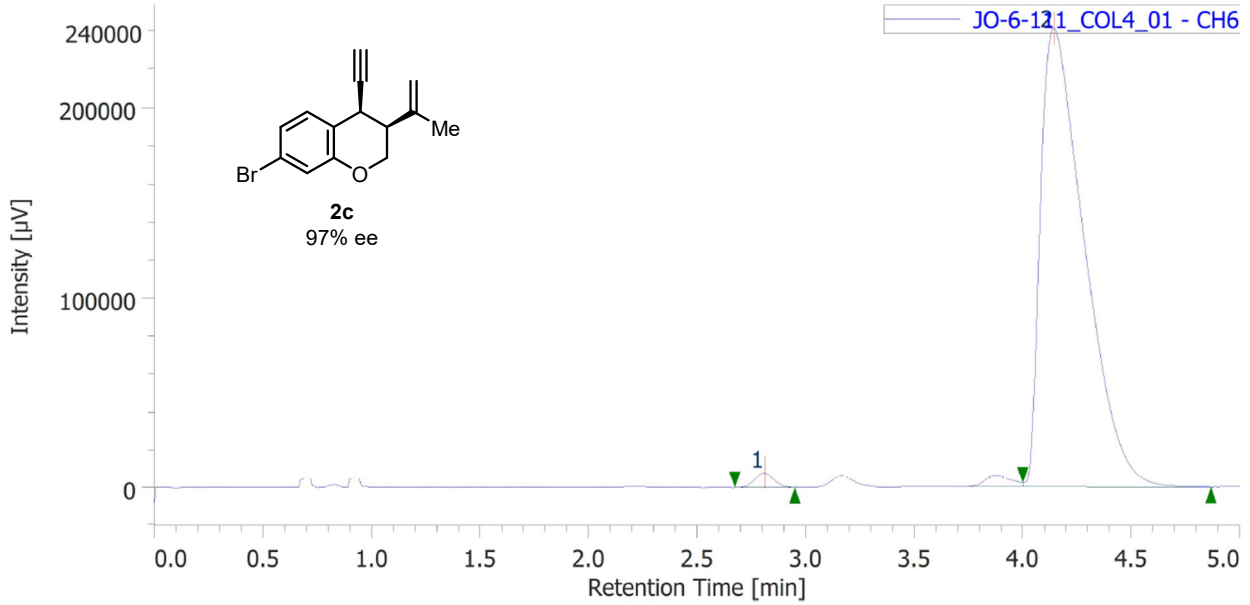


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	6	2.800	7683955	99.0	1.773	0.158	762684
2	Unknown	6	3.547	79602	1.03	N/A	0.339	4207
Total				7763557				766891

2c: SFC (CHIRALPAK ID, 1% methanol).

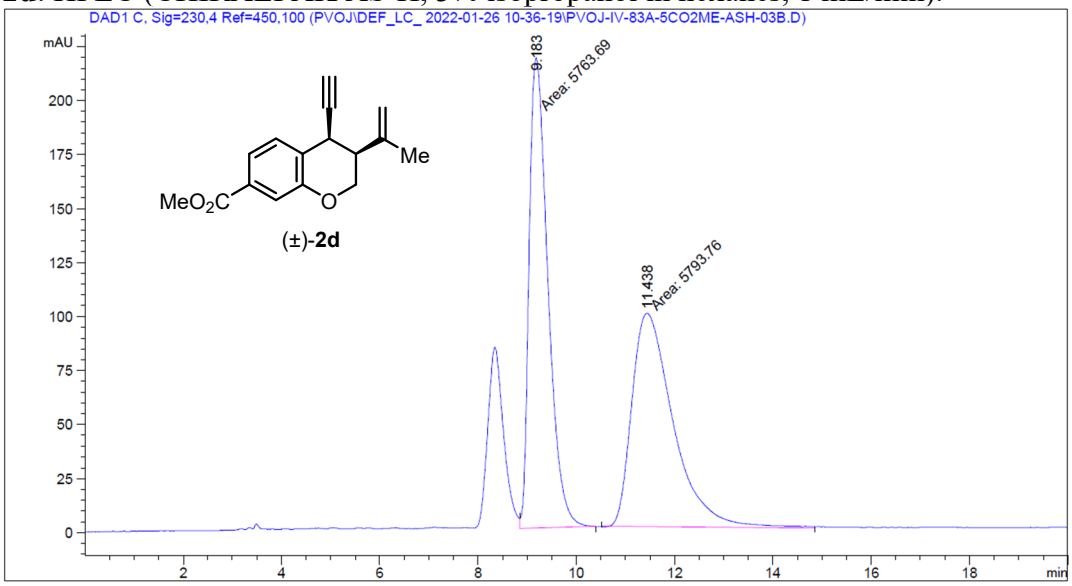


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	6	2.770	1092717	49.9	6.030	0.098	173641
2	Unknown	6	4.223	1097113	50.1	N/A	0.186	92327
Total				2189830				265968



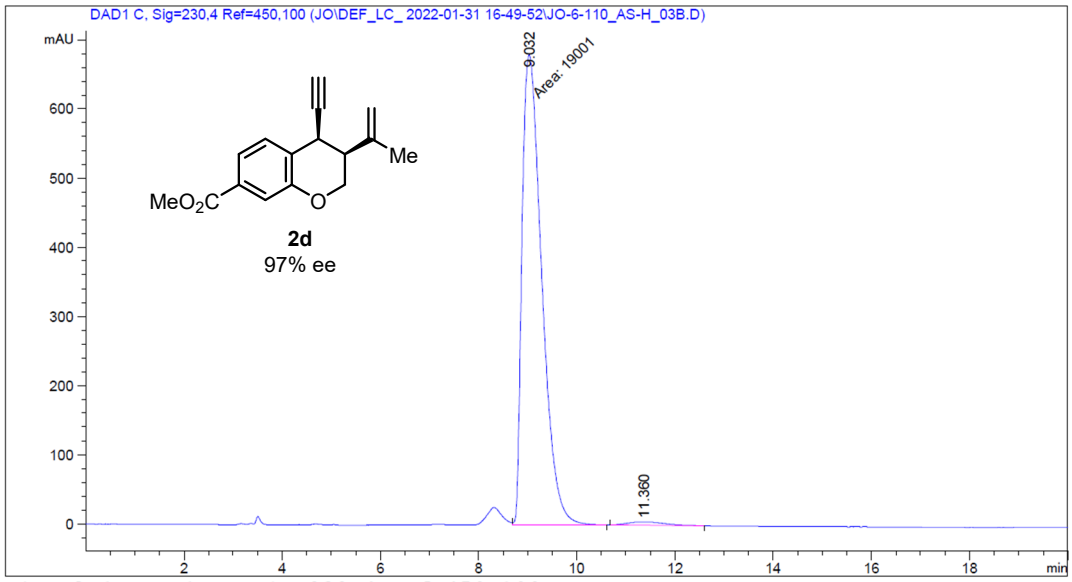
#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	6	2.810	47861	1.39	5.014	0.093	7967
2	Unknown	6	4.143	3389232	98.6	N/A	0.220	240925
Total				3437093				248892

2d: HPLC (CHIRALPAK AS-H, 3% isopropanol in hexanes, 1 mL/min).



Signal 1: DAD1 C, Sig=230,4 Ref=450,100

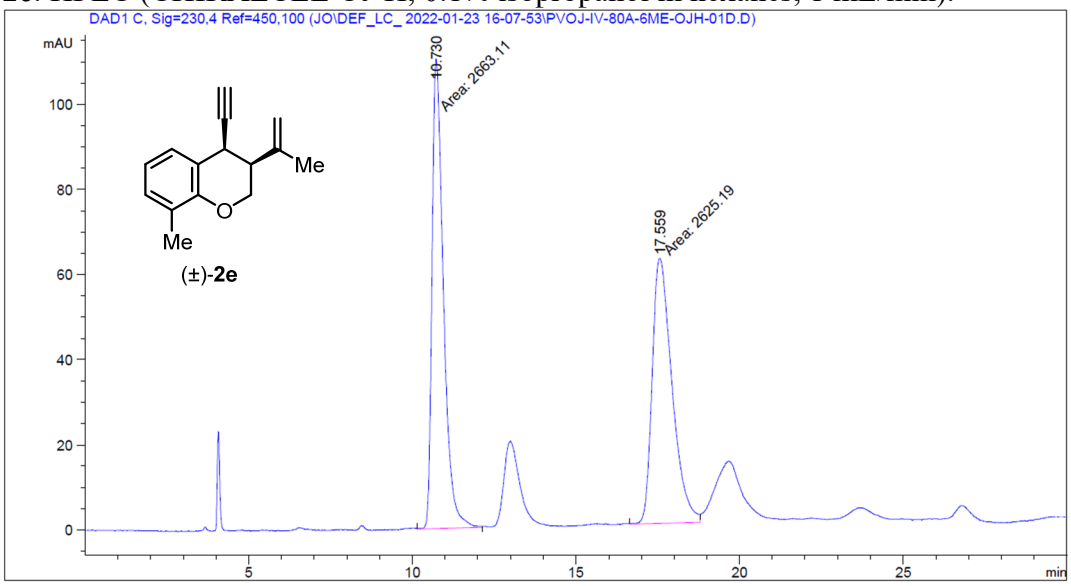
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.183	FM	0.4414	5763.69482	217.60677	49.8699
2	11.438	MM	0.9778	5793.76318	98.75874	50.1301



Signal 1: DAD1 C, Sig=230,4 Ref=450,100

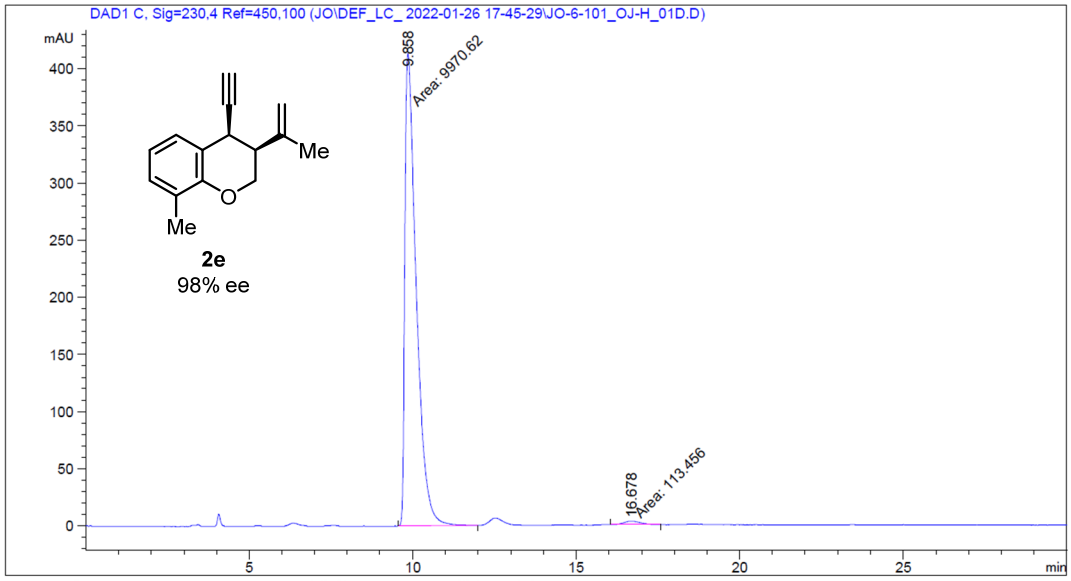
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.032	MM	0.4653	1.90010e4	680.54120	98.6434
2	11.360	BB	0.6429	261.30533	4.81669	1.3566

2e: HPLC (CHIRALCEL OJ-H, 0.1% isopropanol in hexanes, 1 mL/min).



Signal 1: DAD1 C, Sig=230,4 Ref=450,100

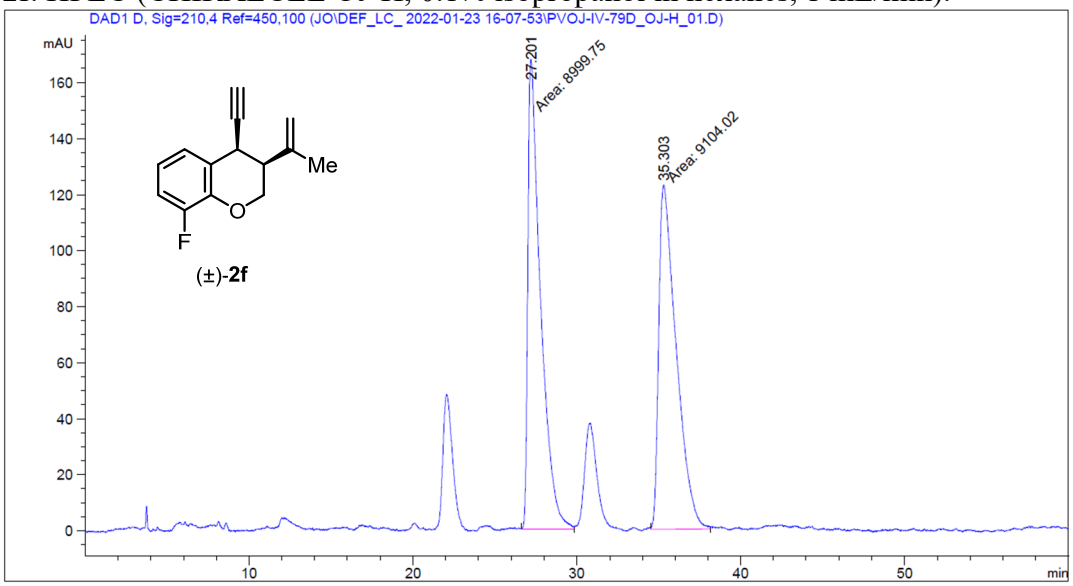
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.730	MM	0.4022	2663.11157	110.35673	50.3586
2	17.559	MF	0.7019	2625.18896	62.33172	49.6414



Signal 1: DAD1 C, Sig=230,4 Ref=450,100

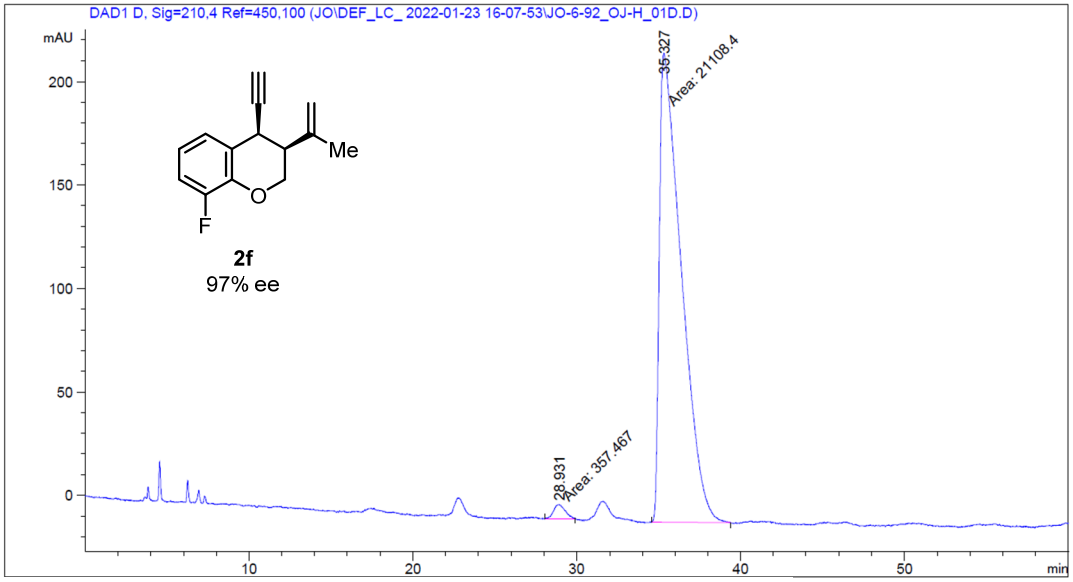
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.858	MM	0.4024	9970.62402	412.92850	98.8749
2	16.678	MM	0.6069	113.45557	3.11558	1.1251

2f: HPLC (CHIRALCEL OJ-H, 0.1% isopropanol in hexanes, 1 mL/min).



Signal 1: DAD1 D, Sig=210,4 Ref=450,100

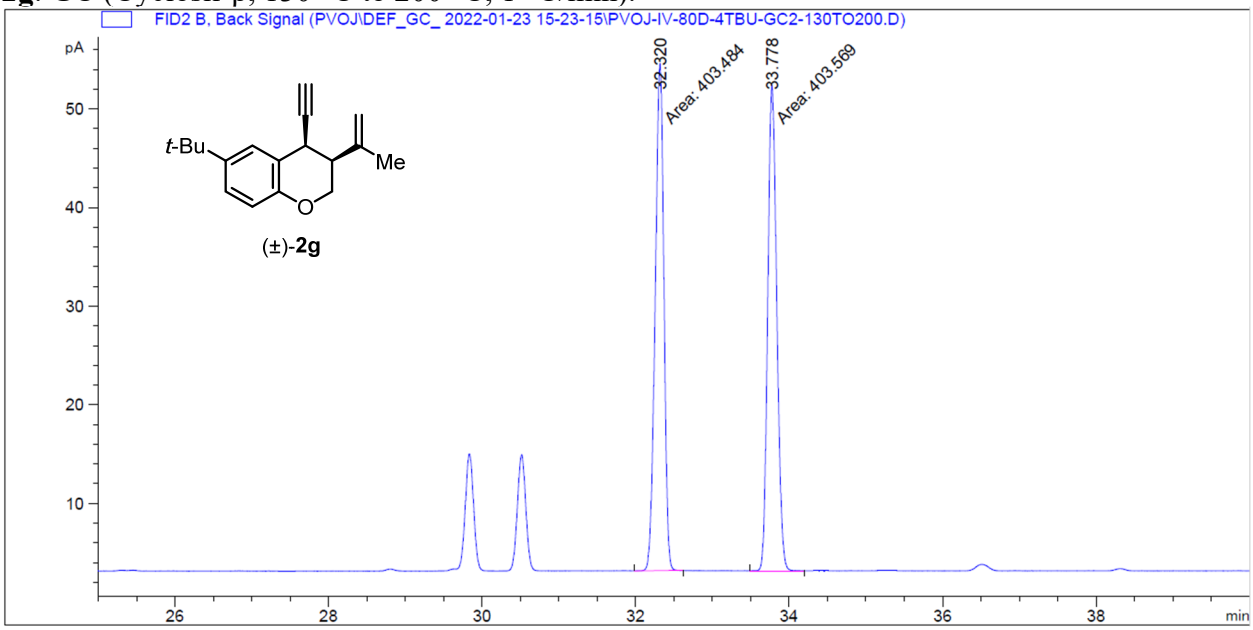
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.201	MM	0.8946	8999.74902	167.66922	49.7120
2	35.303	MM	1.2330	9104.02148	123.06190	50.2880



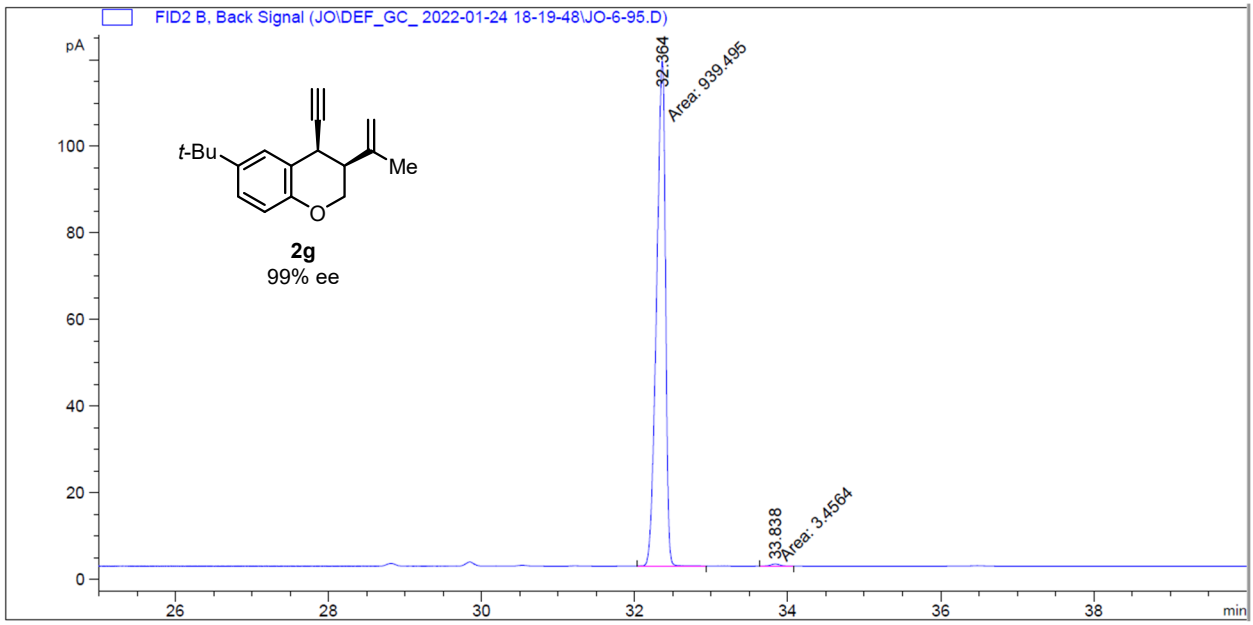
Signal 1: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.931	MM	0.8396	357.46738	7.09623	1.6653
2	35.327	MM	1.5528	2.11084e4	226.56268	98.3347

2g: GC (Cyclosil-β, 130 °C to 200 °C, 1 °C/min).

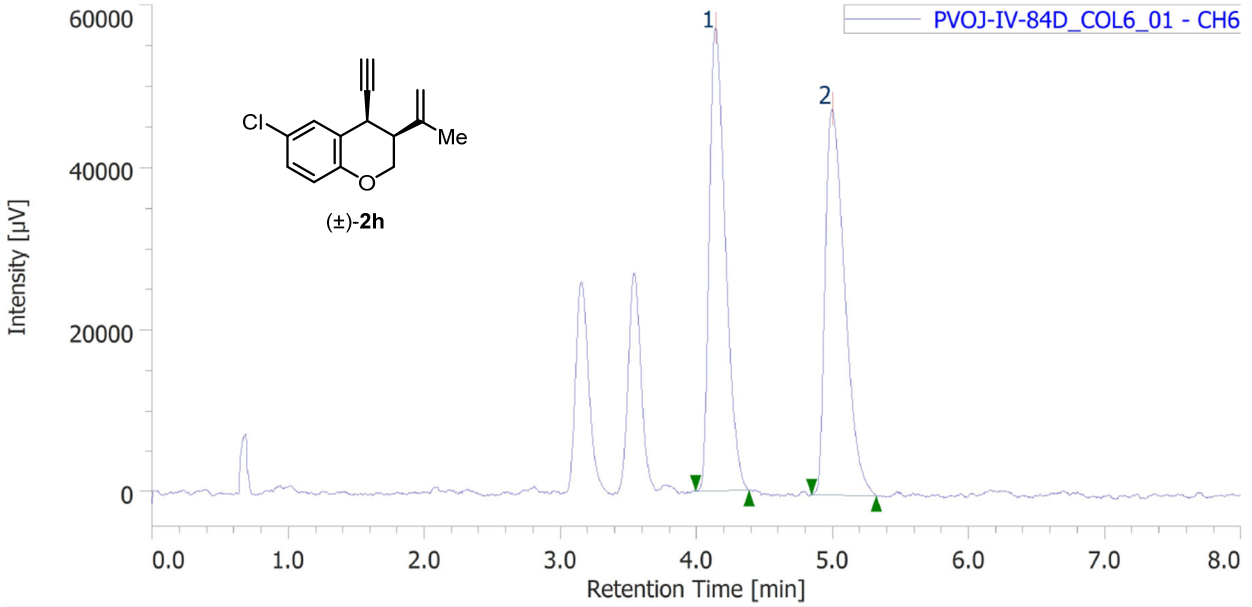


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	32.320	MM	0.1310	403.48373	51.34768	49.99471
2	33.778	MM	0.1367	403.56918	49.19307	50.00529

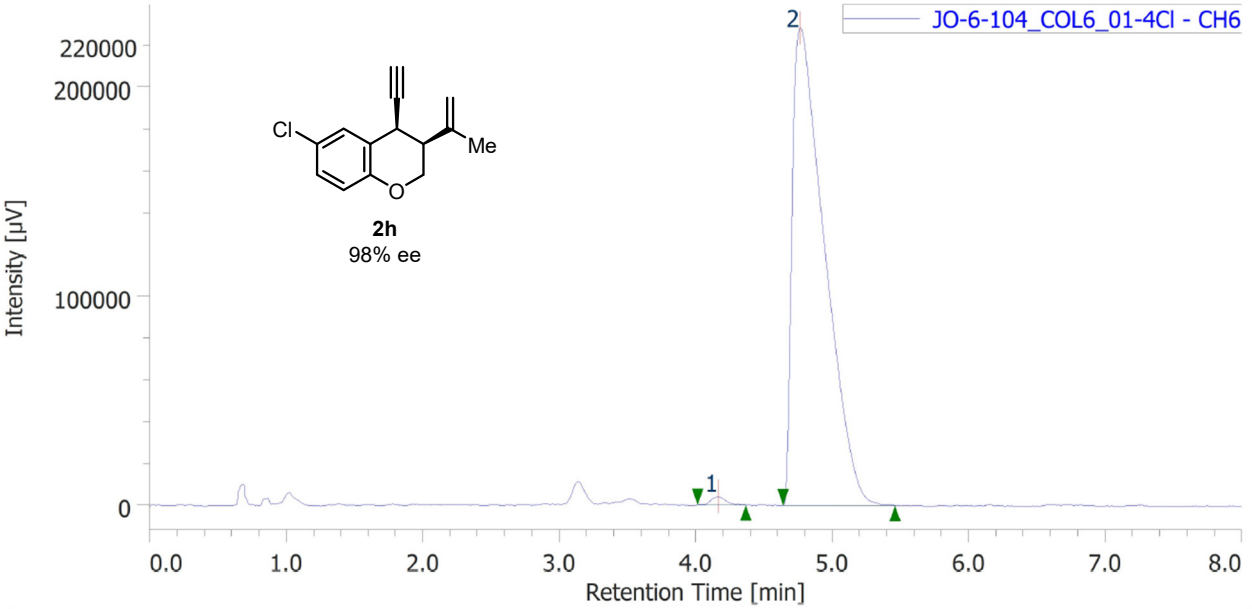


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	32.364	MM	0.1342	939.49548	116.65710	99.63345
2	33.838	MM	0.1303	3.45640	4.42007e-1	0.36655

2h: SFC (CHIRALPAK IF, 1% methanol).

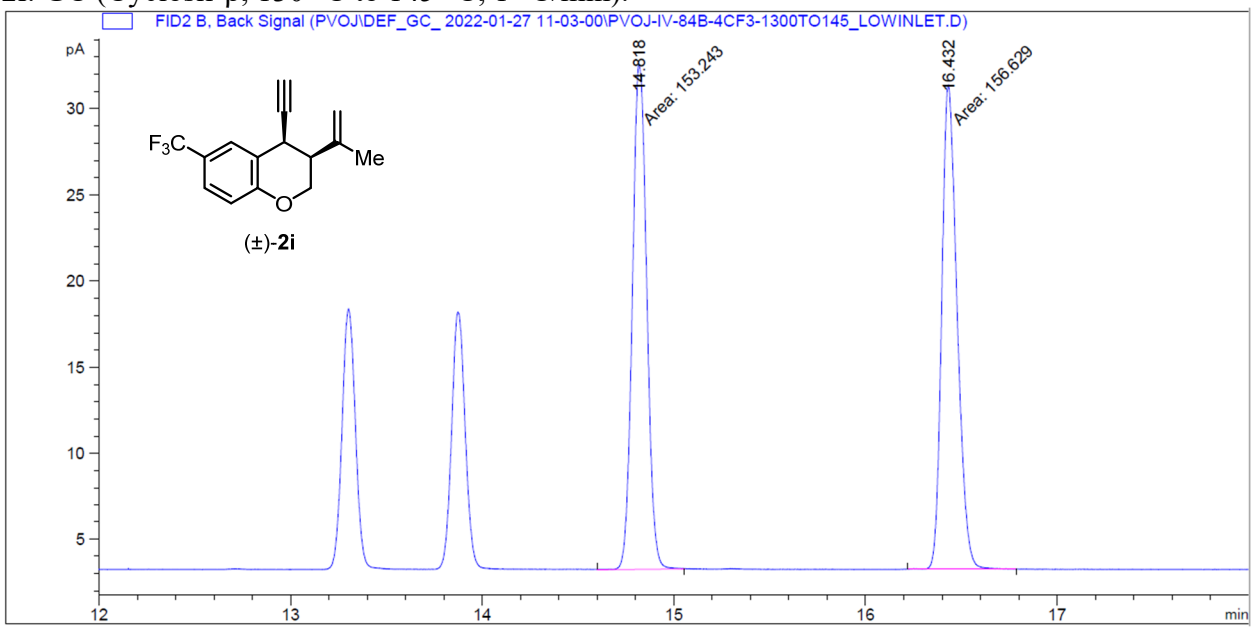


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	6	4.140	471248	49.7	3.535	0.129	57015
2	Unknown	6	4.997	477142	50.3	N/A	0.157	47679
Total				948390				104694

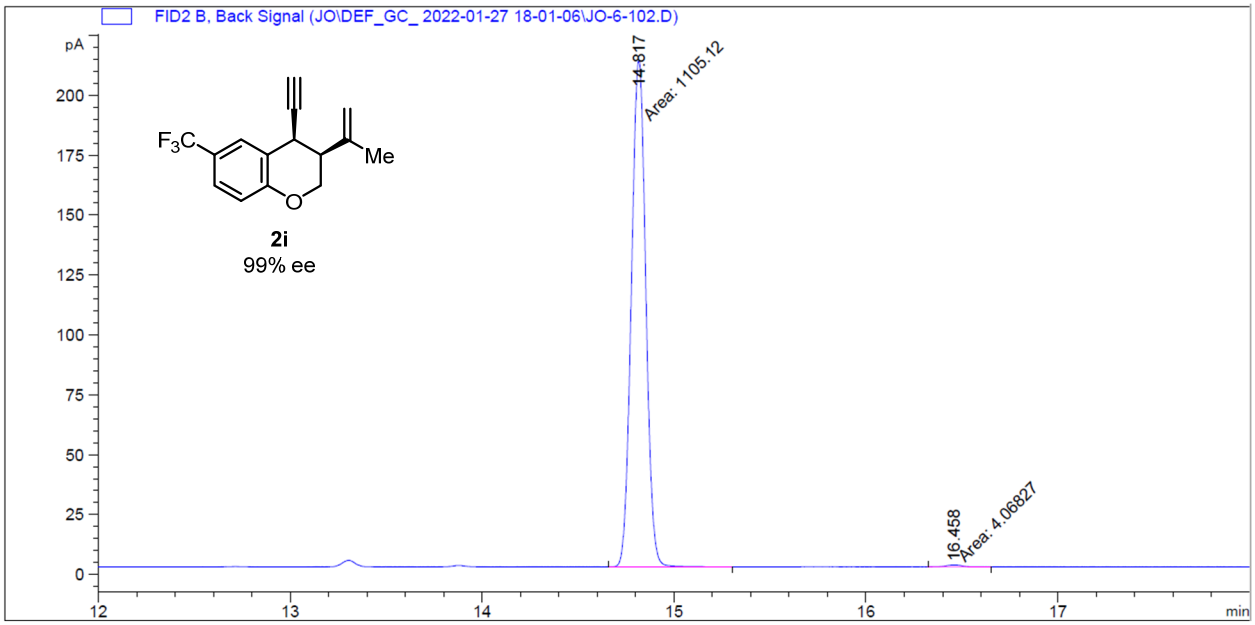


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	6	4.167	29924	0.791	1.858	0.118	3903
2	Unknown	6	4.763	3754819	99.2	N/A	0.261	228215
Total				3784743				232118

2i: GC (Cyclosil-β, 130 °C to 145 °C, 1 °C/min).

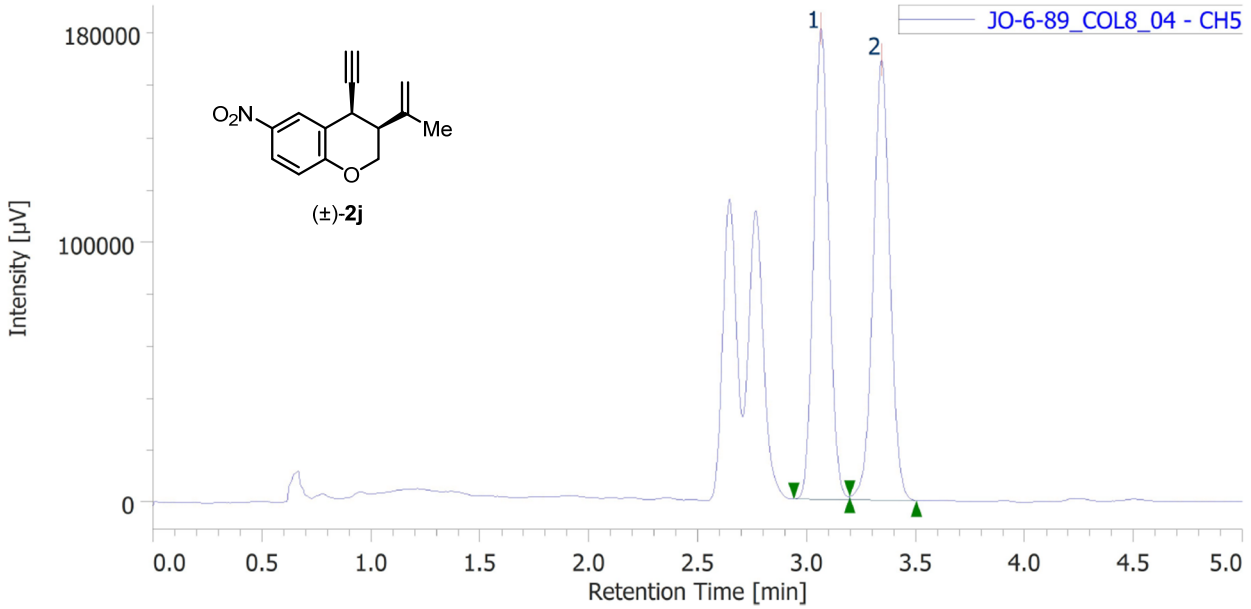


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.818	MM	0.0872	153.24303	29.30266	49.45362
2	16.432	MM	0.0928	156.62918	28.13045	50.54638

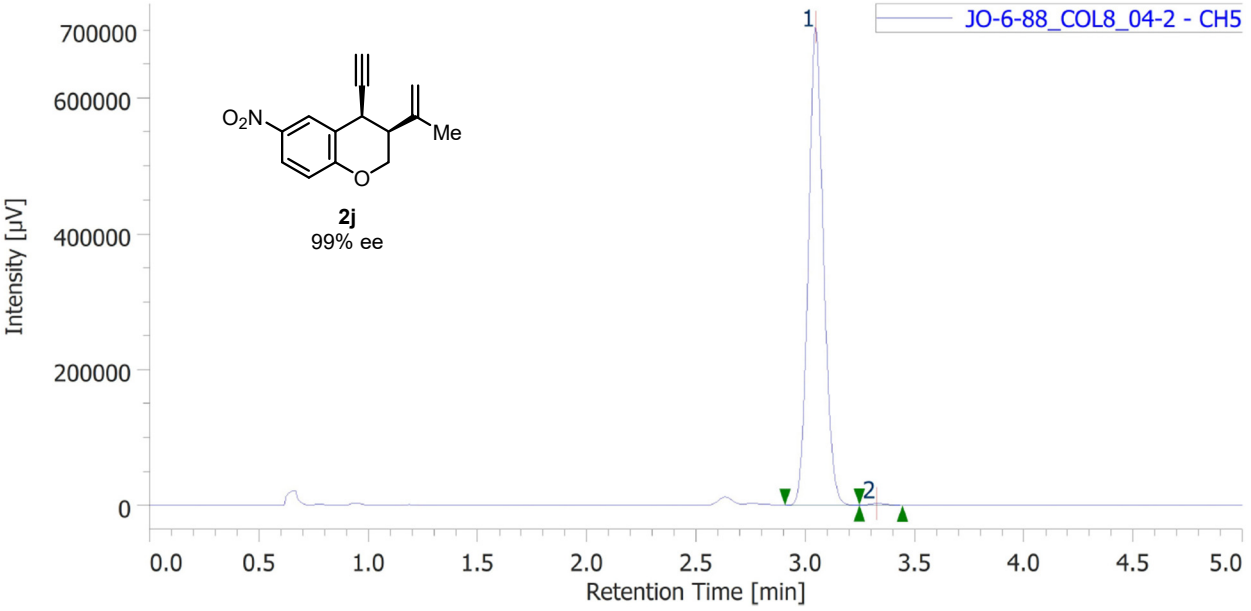


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.817	MM	0.0870	1105.12183	211.58975	99.63322
2	16.458	MM	0.0942	4.06827	7.20105e-1	0.36678

2j: SFC (CHIRALPAK IH, 4% methanol).

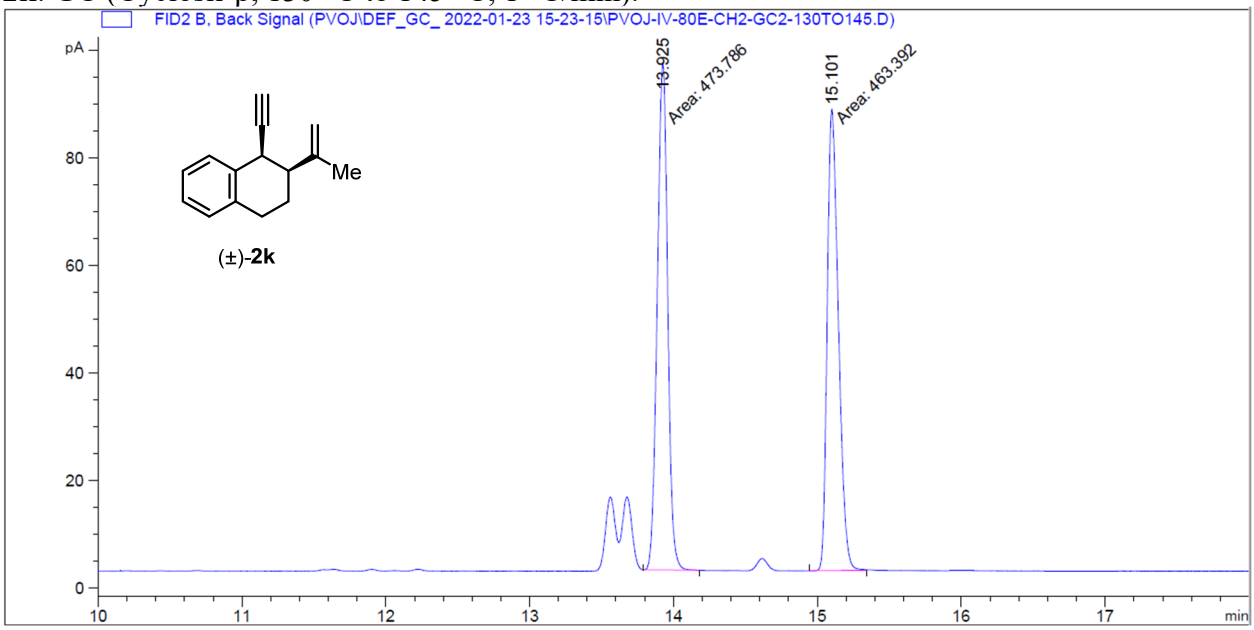


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	5	3.063	882375	49.2	2.091	0.076	180495
2	Unknown	5	3.343	910819	50.8	N/A	0.082	168727
Total				1793194				349222

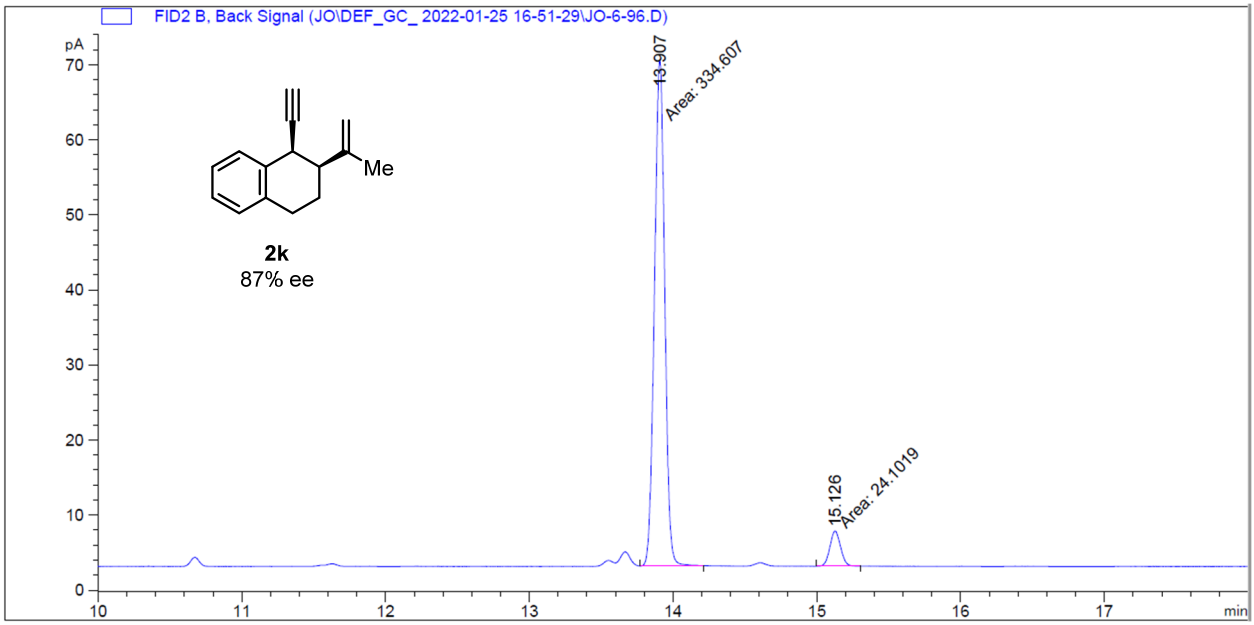


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	5	3.047	3400563	99.6	1.945	0.073	703726
2	Unknown	5	3.323	13841	0.405	N/A	0.095	2309
Total				3414404				706035

2k: GC (Cyclosil-β, 130 °C to 145 °C, 1 °C/min).

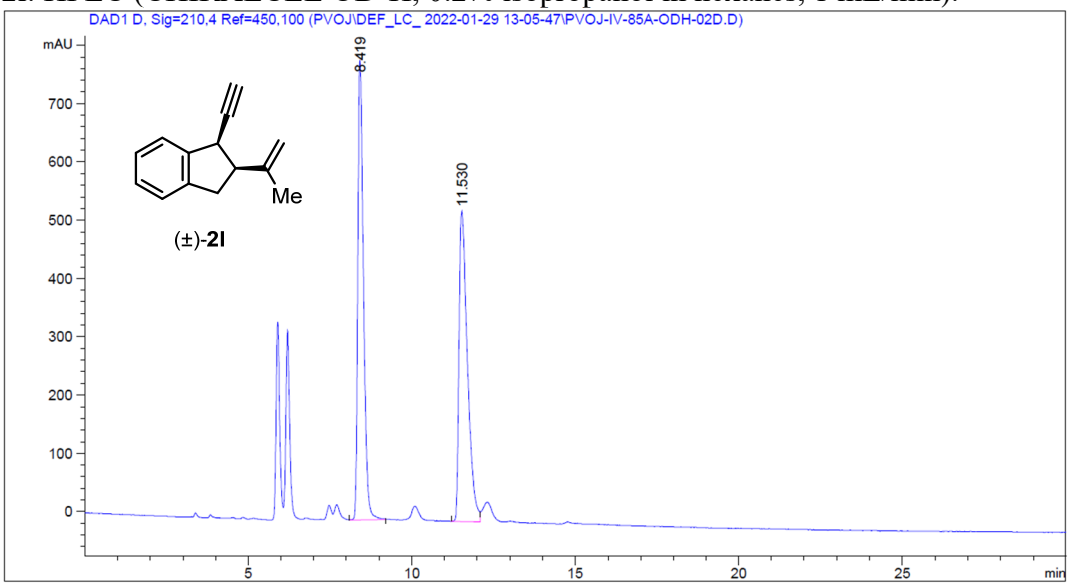


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.925	MM	0.0837	473.78592	94.31210	50.55454
2	15.101	MM	0.0899	463.39182	85.86899	49.44546



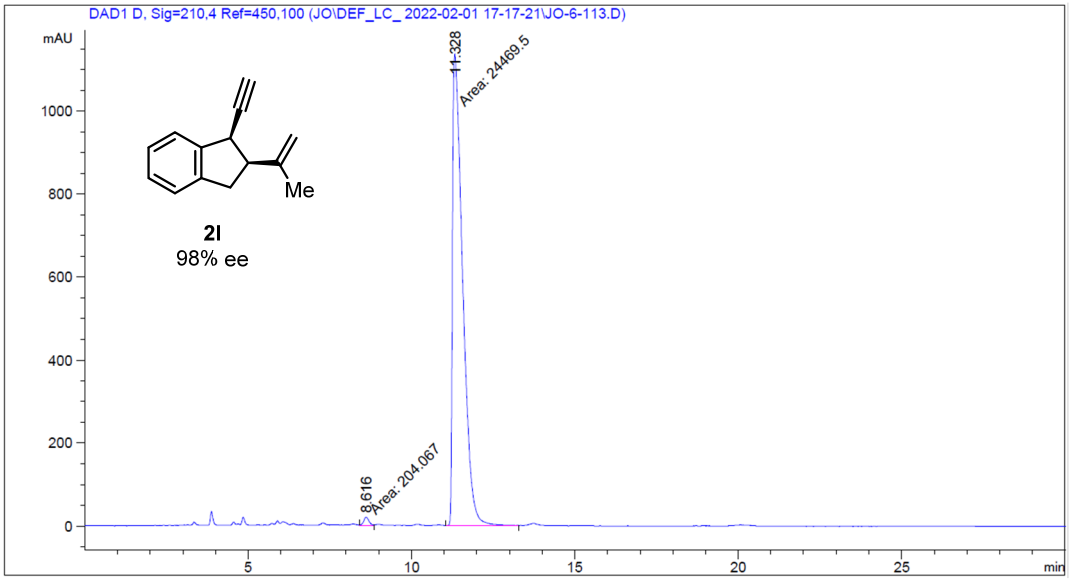
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.907	MF	0.0827	334.60672	67.43390	93.28094
2	15.126	MM	0.0859	24.10186	4.67783	6.71906

2l: HPLC (CHIRALCEL OD-H, 0.2% isopropanol in hexanes, 1 mL/min).



Signal 1: DAD1 D, Sig=210,4 Ref=450,100

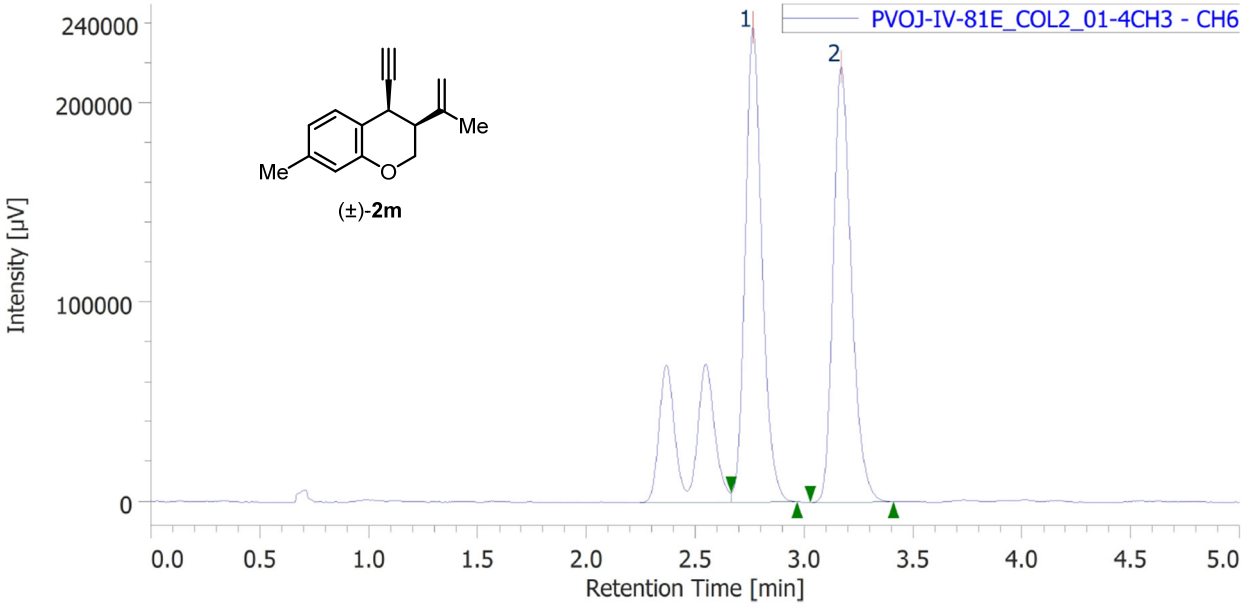
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.419	VB	0.1869	9528.38770	789.22961	50.0409
2	11.530	BV	0.2704	9512.80371	532.65656	49.9591



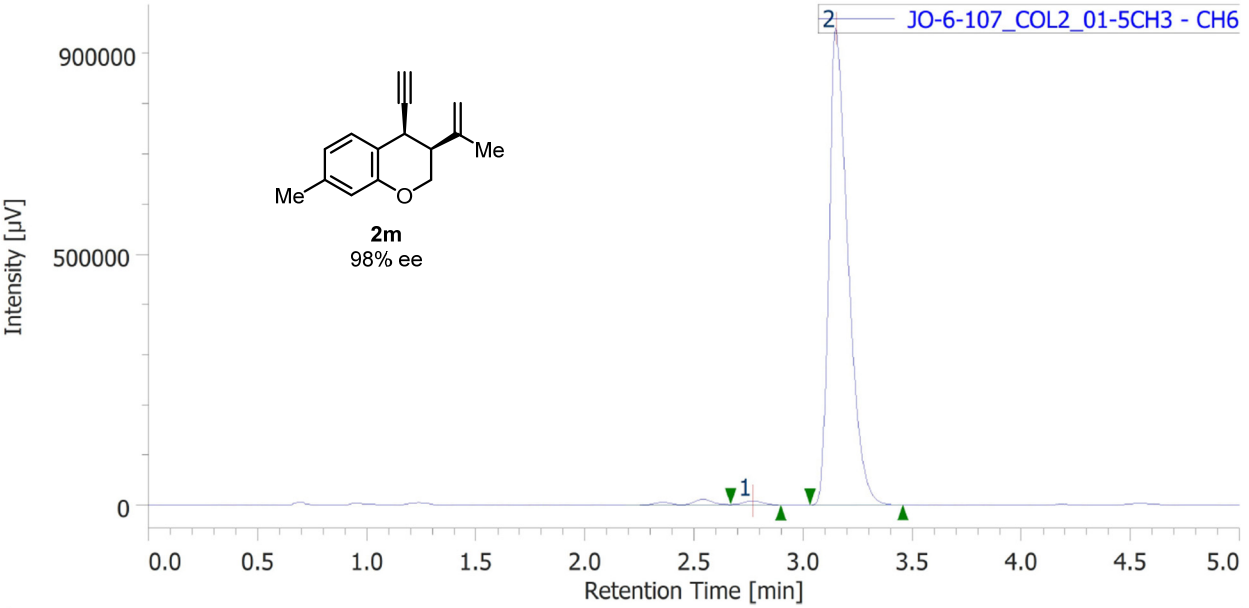
Signal 1: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.616	MM	0.1771	204.06656	19.20554	0.8271
2	11.328	MM	0.3588	2.44695e4	1136.48364	99.1729

2m: SFC (CHIRALPAK IB, 1% methanol).

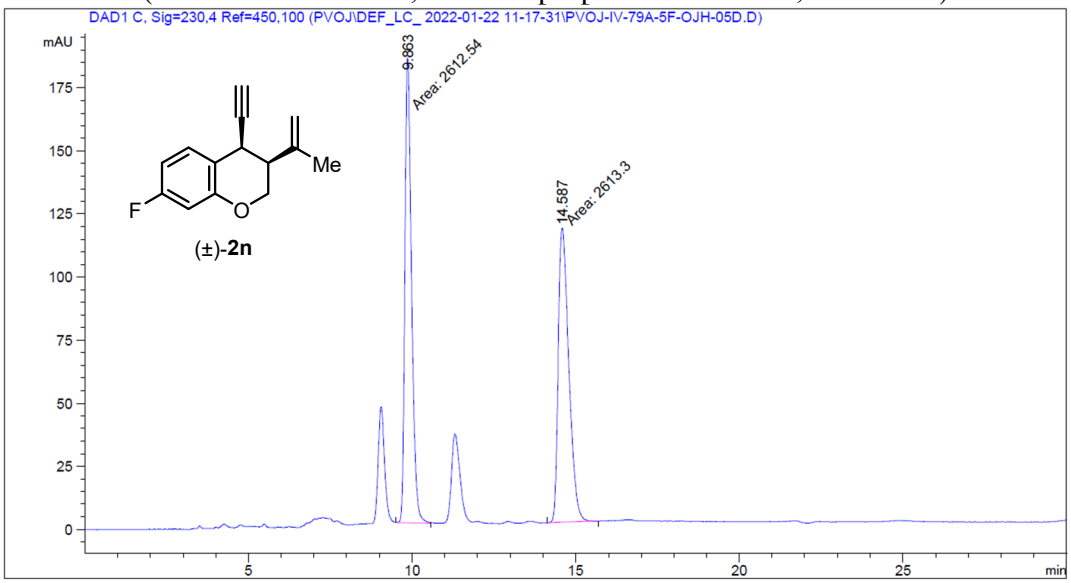


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	6	2.763	1274144	50.2	2.854	0.081	237918
2	Unknown	6	3.170	1263121	49.8	N/A	0.087	218279
Total				2537265				456197



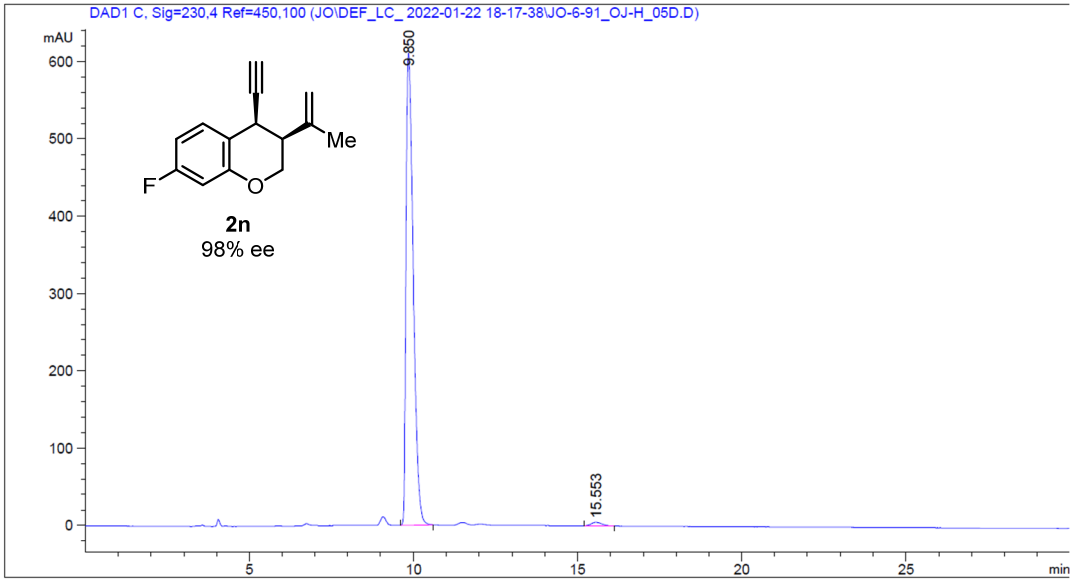
#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	6	2.767	49538	0.855	2.480	0.091	8275
2	Unknown	6	3.150	5744549	99.1	N/A	0.091	949001
Total				5794087				957276

2n: HPLC (CHIRALCEL OJ-H, 0.5% isopropanol in hexanes, 1 mL/min).



Signal 1: DAD1 C, Sig=230,4 Ref=450,100

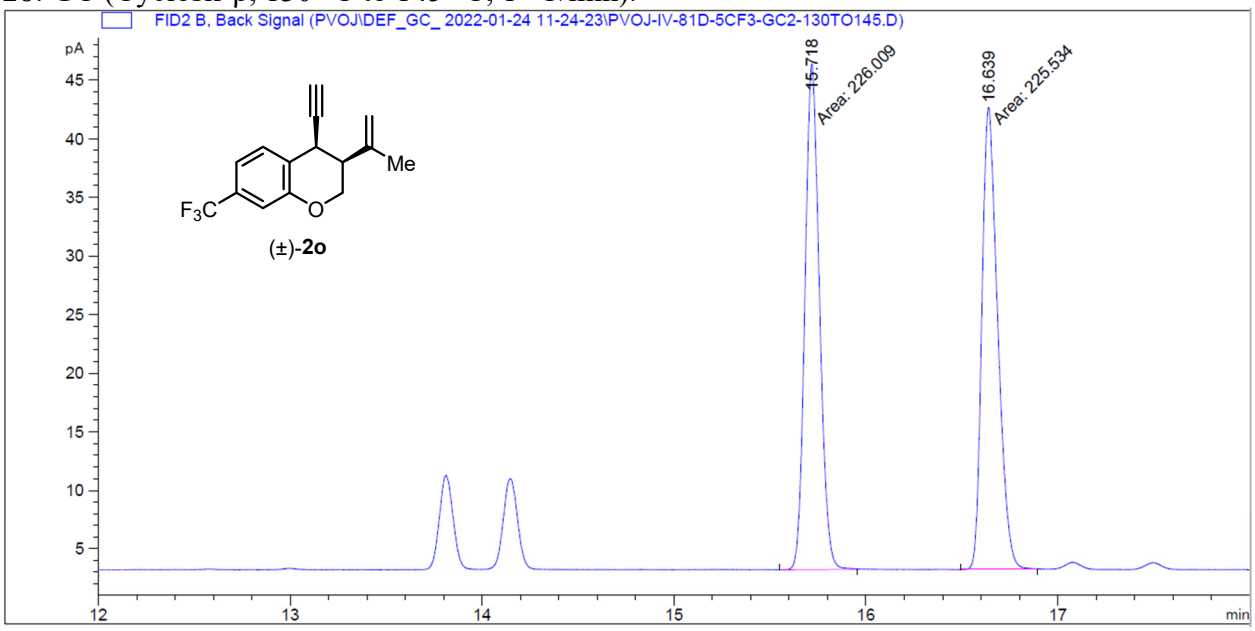
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.863	MM	0.2360	2612.54443	184.52913	49.9928
2	14.587	MM	0.3734	2613.30005	116.65353	50.0072



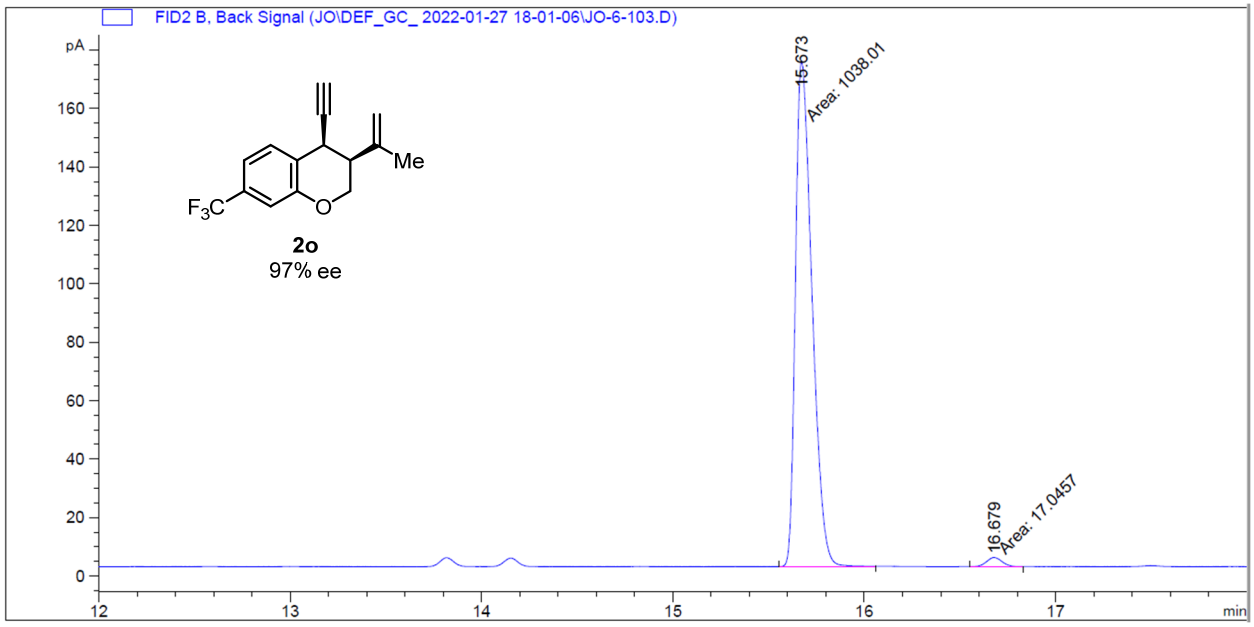
Signal 1: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.850	BB	0.2353	9276.92090	610.48285	98.9103
2	15.553	BB	0.2896	102.20033	4.55807	1.0897

2o: GC (Cyclosil-β, 130 °C to 145 °C, 1 °C/min).

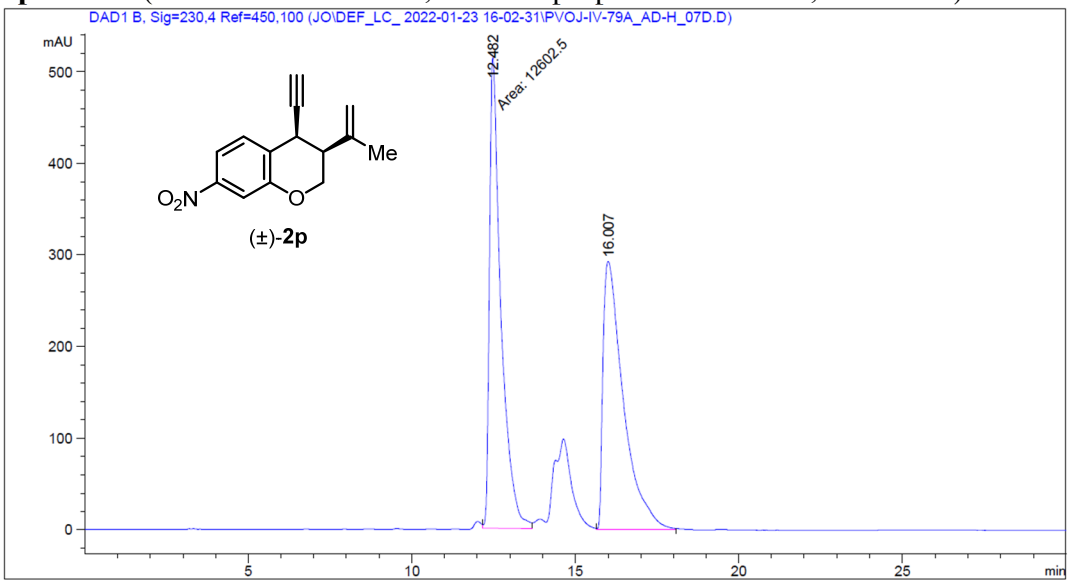


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	15.718	MM	0.0873	226.00865	43.16895	50.05257
2	16.639	MM	0.0952	225.53389	39.46764	49.94743



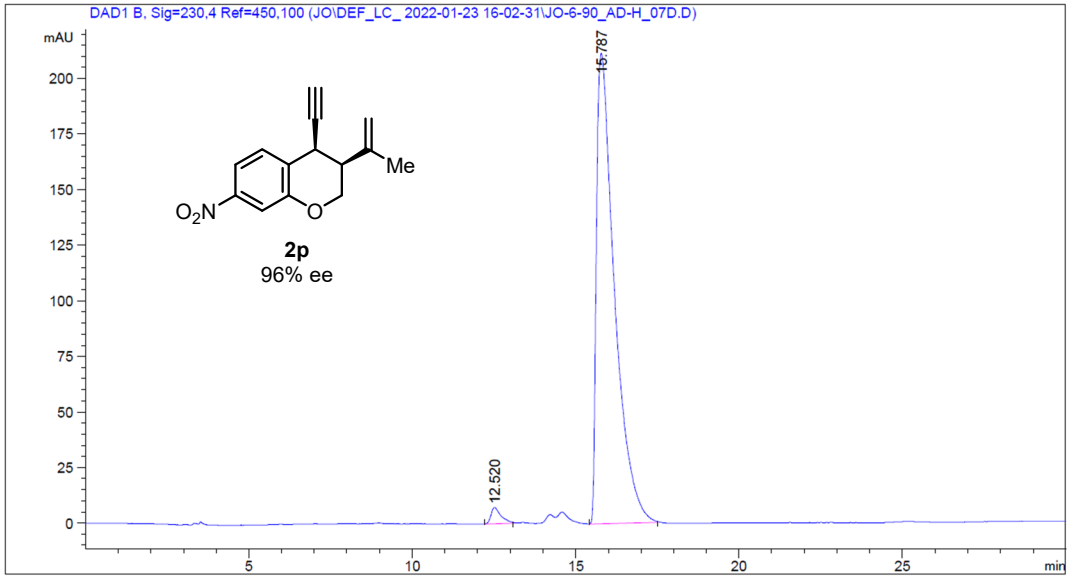
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	15.673	MM	0.0999	1038.01050	173.18431	98.38438
2	16.679	MM	0.0925	17.04574	3.07228	1.61562

2p: HPLC (CHIRALPAK AD-H, 0.7% isopropanol in hexanes, 1 mL/min).



Signal 1: DAD1 B, Sig=230,4 Ref=450,100

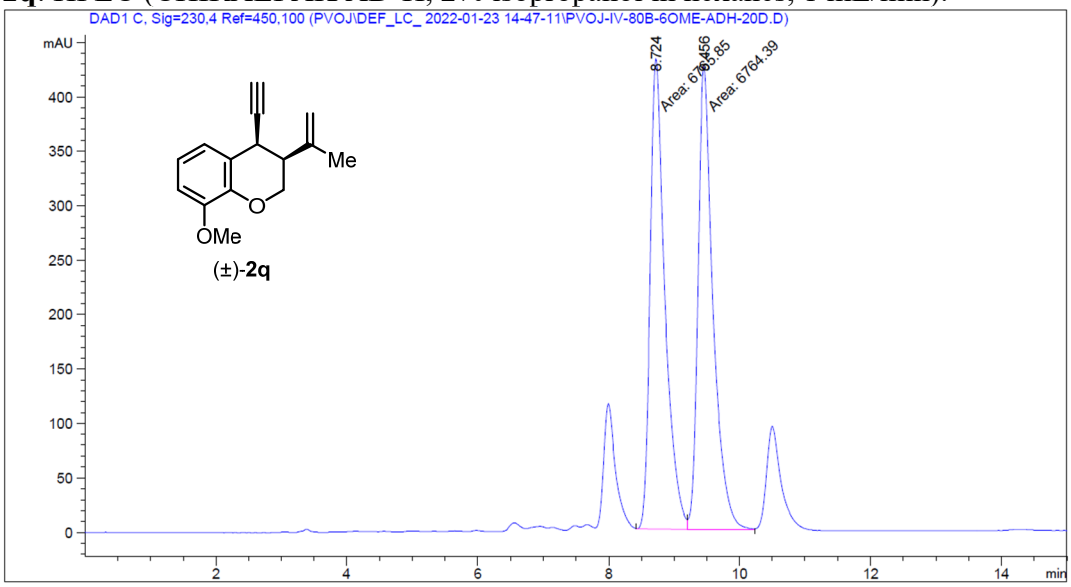
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.482	MM	0.4086	1.26025e4	514.02924	50.0132
2	16.007	VB	0.6407	1.25959e4	292.35123	49.9868



Signal 1: DAD1 B, Sig=230,4 Ref=450,100

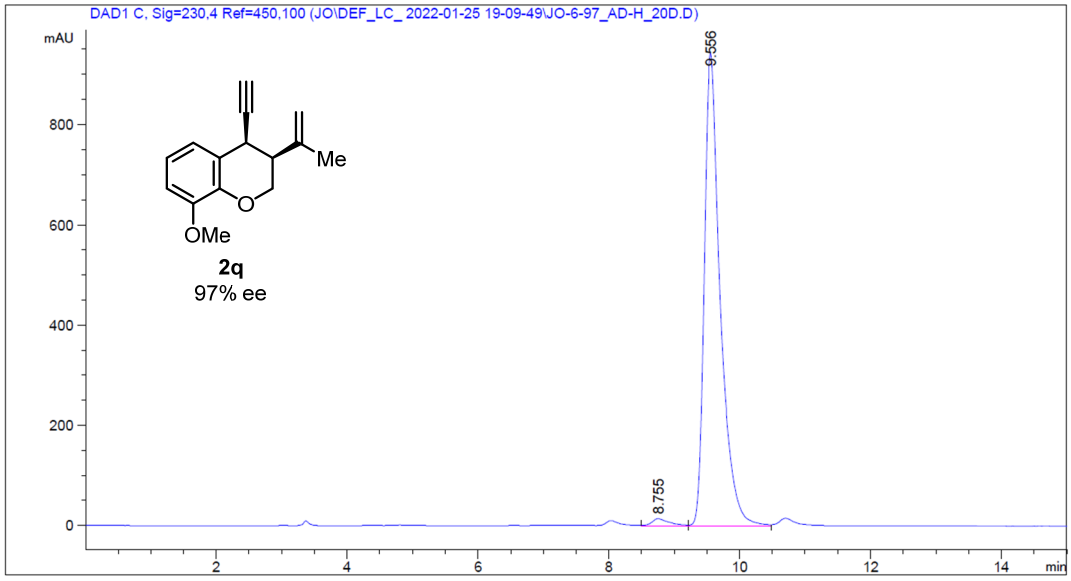
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.520	BB	0.3040	152.44286	7.28981	1.8421
2	15.787	BB	0.5656	8123.04346	211.73297	98.1579

2q: HPLC (CHIRALPAK AD-H, 2% isopropanol in hexanes, 1 mL/min).



Signal 1: DAD1 C, Sig=230,4 Ref=450,100

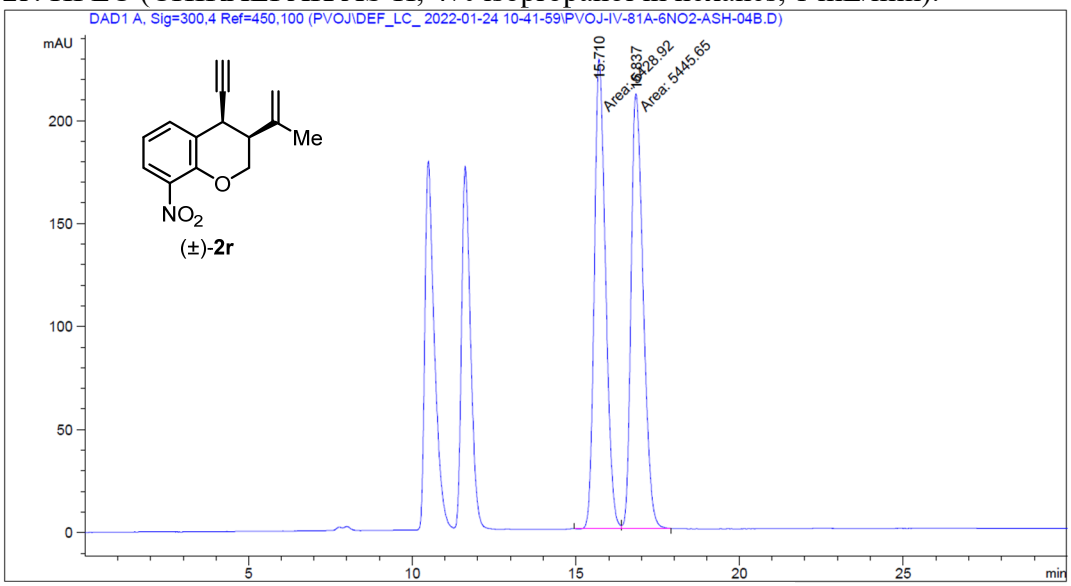
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.724	MF	0.2611	6765.85010	431.86838	50.0054
2	9.456	FM	0.2654	6764.39258	424.75623	49.9946



Signal 1: DAD1 C, Sig=230,4 Ref=450,100

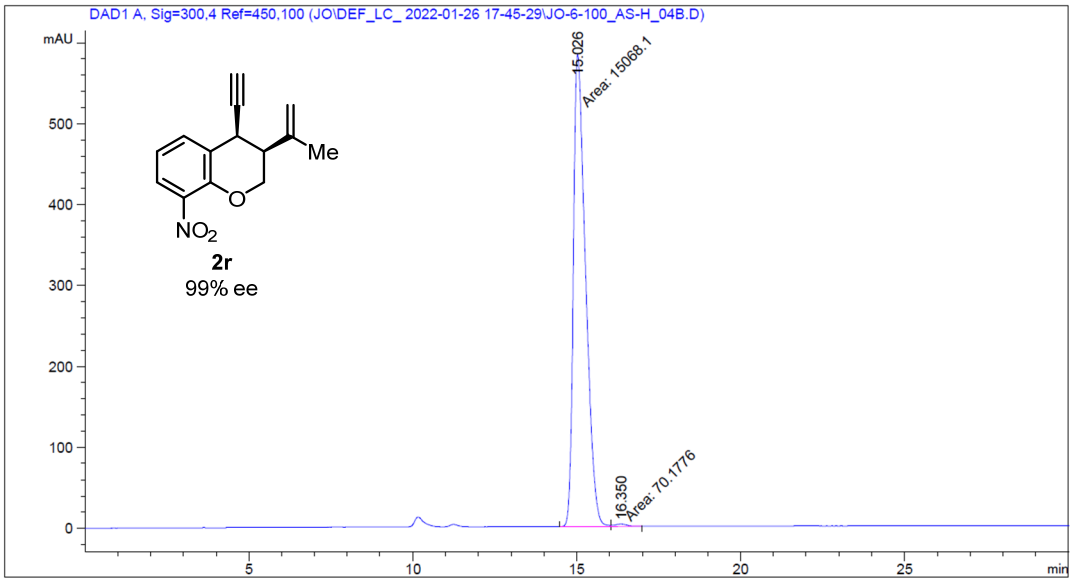
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.755	BV	0.2510	241.43642	13.73849	1.4949
2	9.556	VV	0.2490	1.59095e4	942.37299	98.5051

2r: HPLC (CHIRALPAK AS-H, 4% isopropanol in hexanes, 1 mL/min).



Signal 1: DAD1 A, Sig=300,4 Ref=450,100

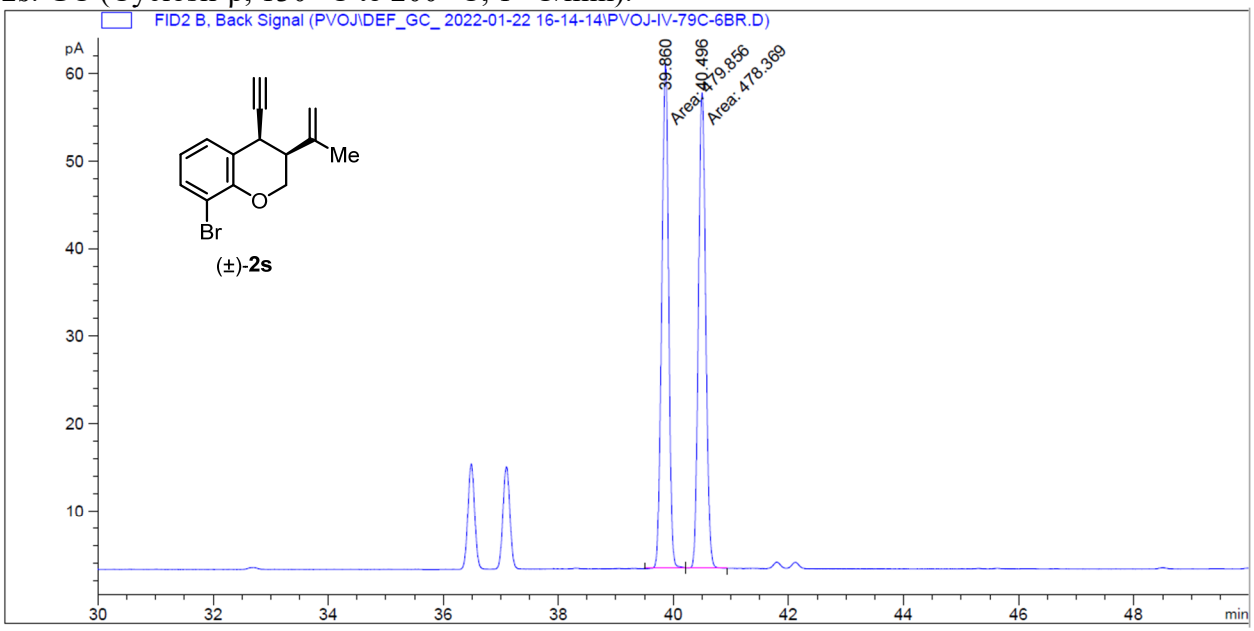
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.710	MF	0.3970	5428.92139	227.91634	49.9231
2	16.837	FM	0.4302	5445.65332	210.97432	50.0769



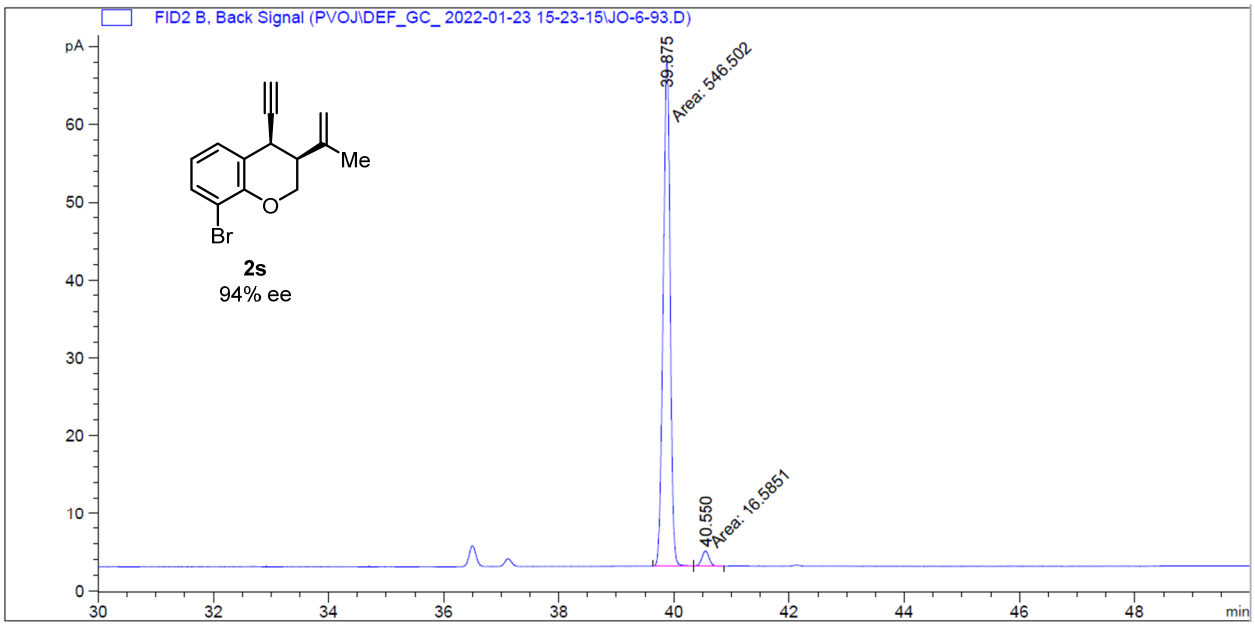
Signal 1: DAD1 A, Sig=300,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.026	MF	0.4306	1.50681e4	583.23260	99.5364
2	16.350	FM	0.4127	70.17757	2.83395	0.4636

2s: GC (Cyclosil-β, 130 °C to 200 °C, 1 °C/min).

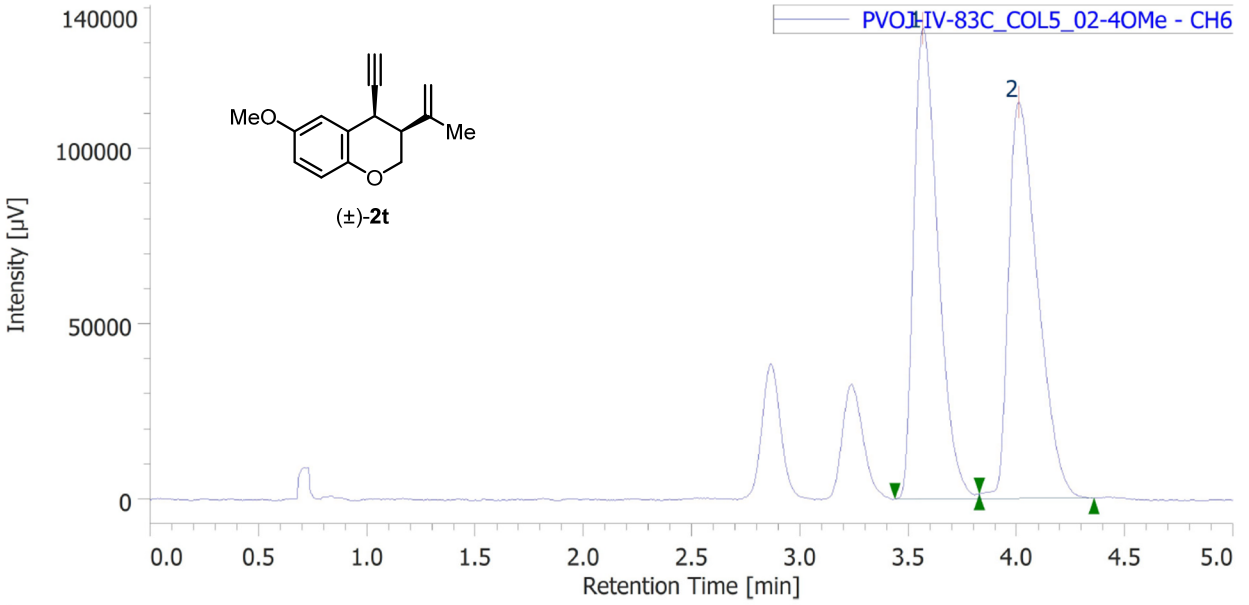


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	39.860	MM	0.1387	479.85583	57.68175	50.07759
2	40.496	MM	0.1467	478.36890	54.35320	49.92241

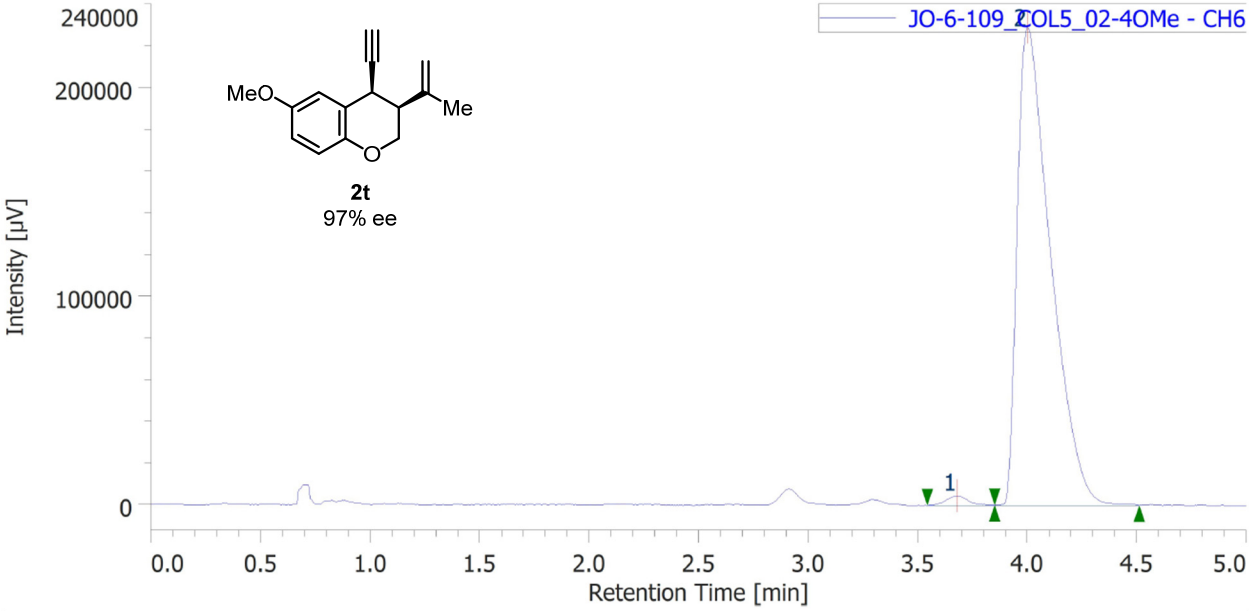


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	39.875	MF	0.1403	546.50232	64.91120	97.05461
2	40.550	FM	0.1445	16.58513	1.91278	2.94539

2t: SFC (CHIRALPAK IE, 2% methanol).

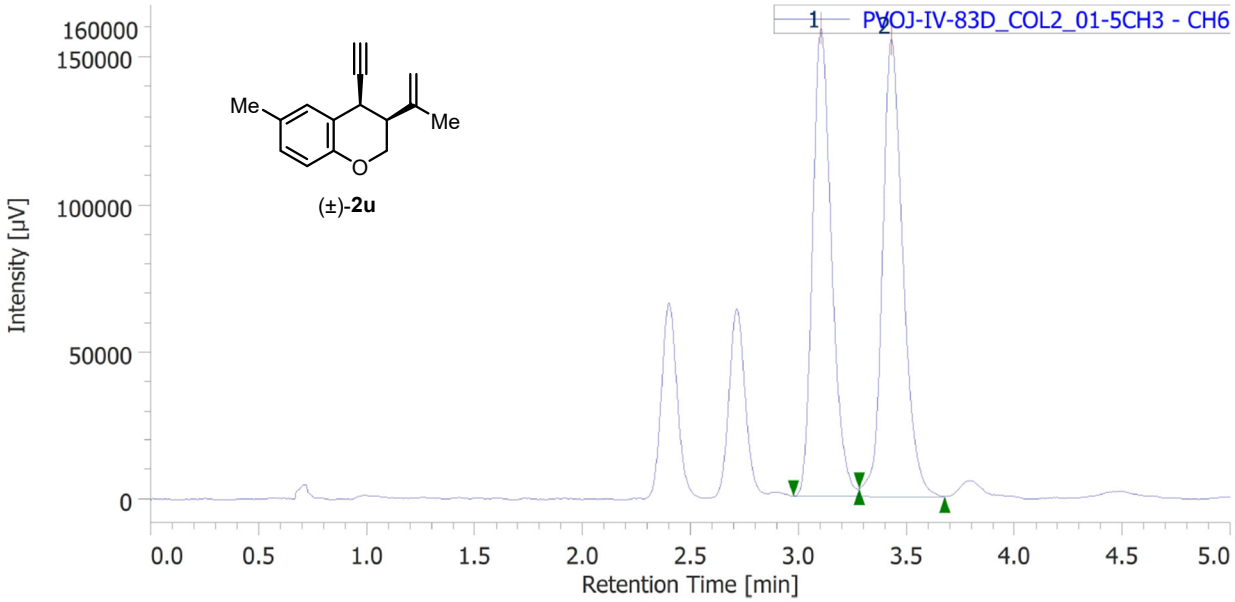


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	6	3.567	1047308	49.7	1.965	0.121	134192
2	Unknown	6	4.010	1059716	50.3	N/A	0.146	112963
Total				2107024				247155

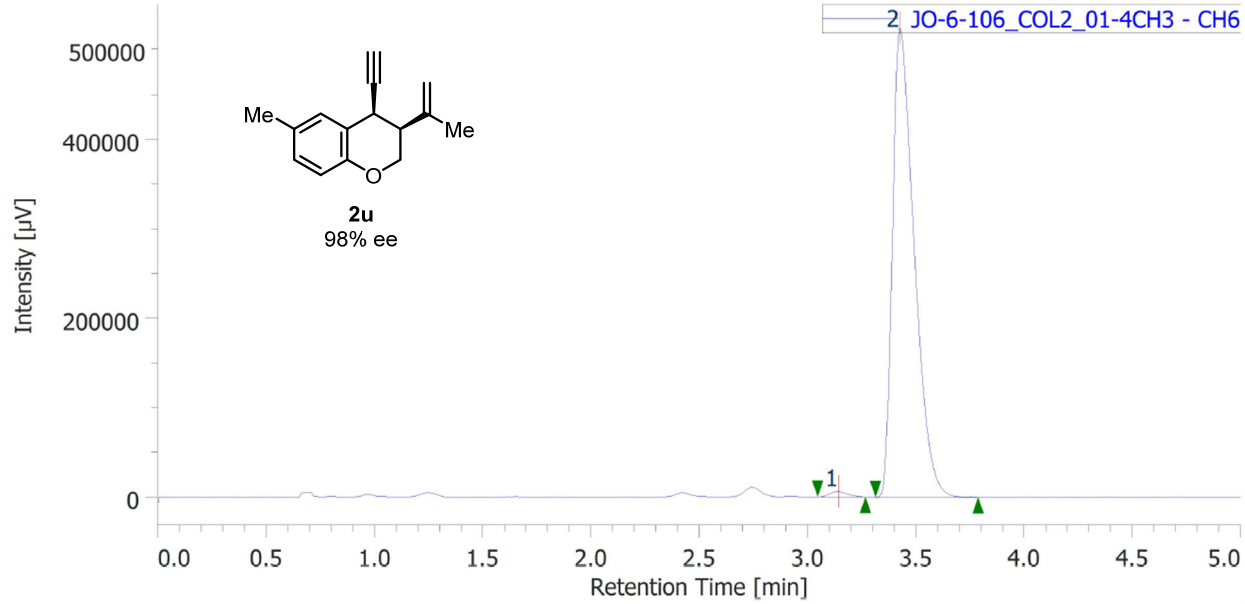


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	6	3.680	31245	1.27	1.406	0.106	4529
2	Unknown	6	4.000	2420157	98.7	N/A	0.163	229226
Total				2451402				233755

2u: SFC (CHIRALPAK IB N-5, 1% methanol).

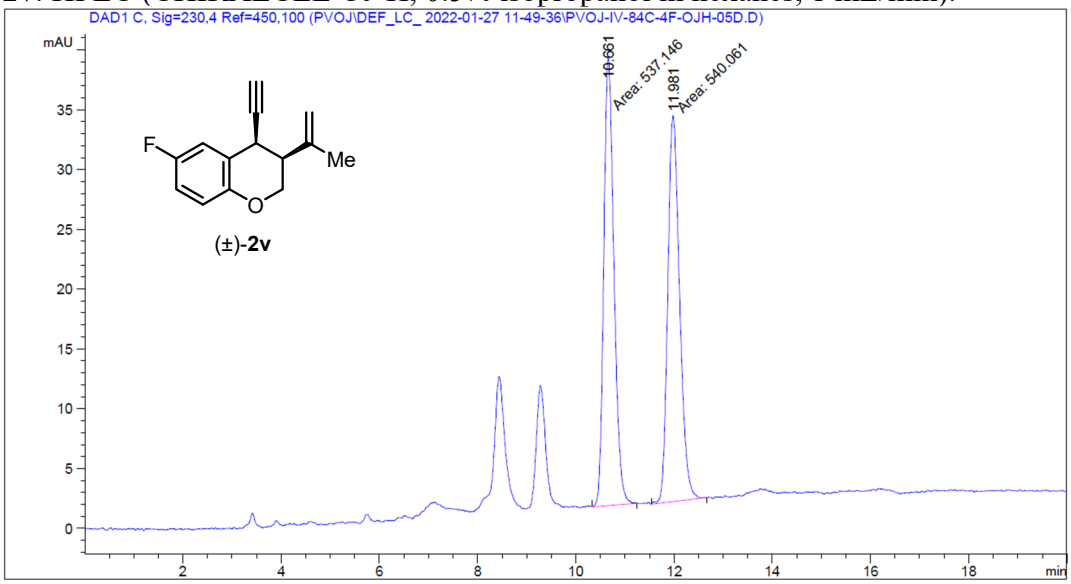


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	6	3.103	972057	48.7	2.011	0.093	158768
2	Unknown	6	3.430	1022341	51.3	N/A	0.098	155171
Total				1994398				313939



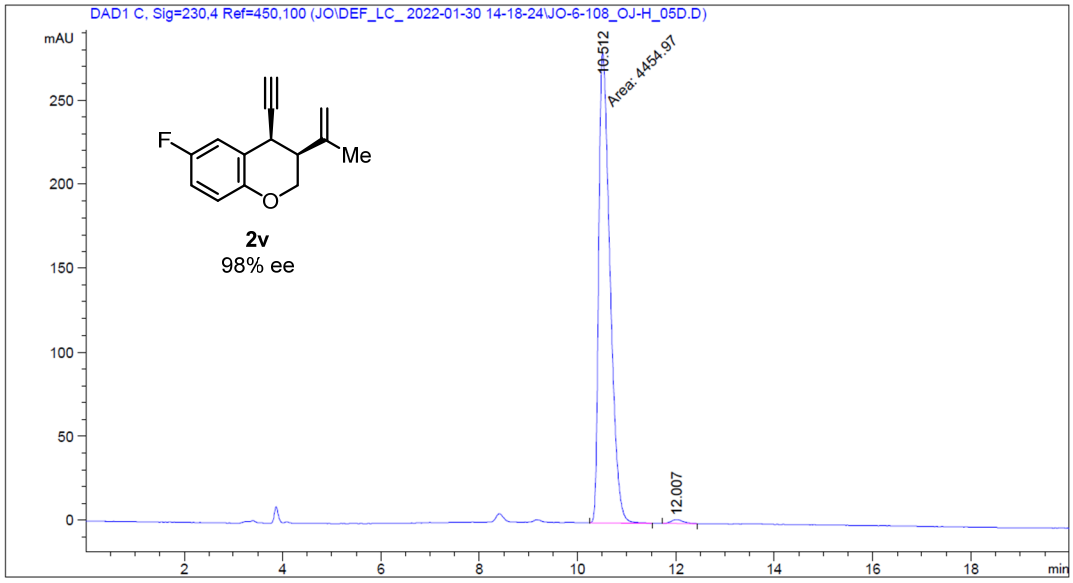
#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	6	3.143	33696	0.919	1.721	0.087	6013
2	Unknown	6	3.427	3633532	99.1	N/A	0.107	523686
Total				3667228				529699

2v: HPLC (CHIRALCEL OJ-H, 0.5% isopropanol in hexanes, 1 mL/min).



Signal 1: DAD1 C, Sig=230,4 Ref=450,100

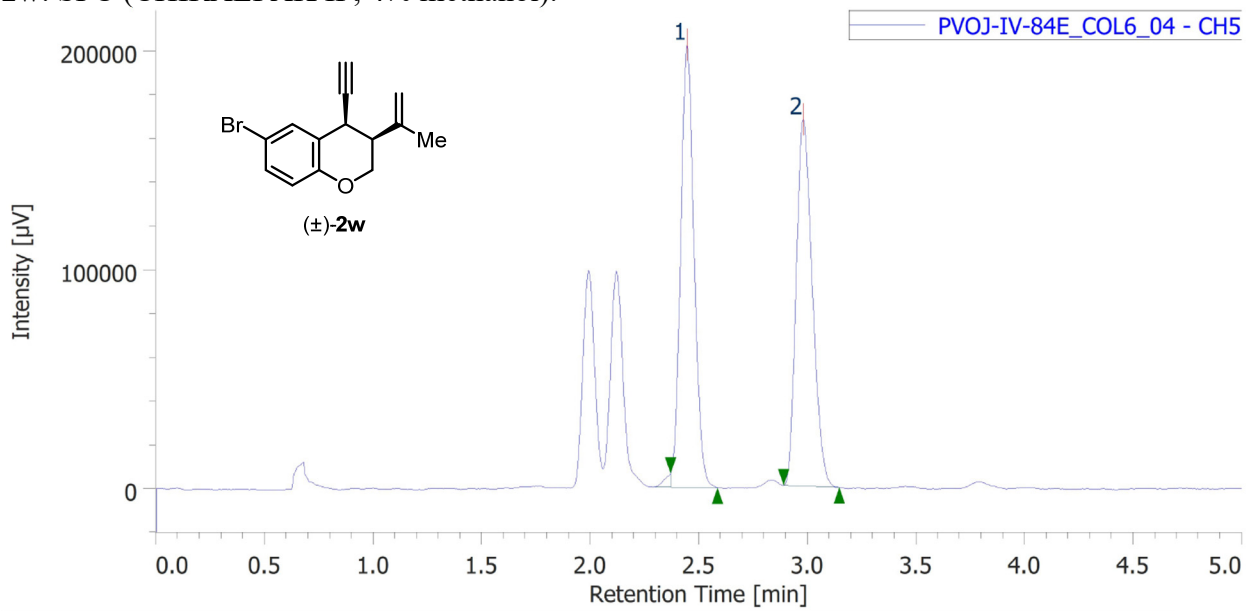
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.661	MM	0.2392	537.14551	37.42655	49.8647
2	11.981	MM	0.2789	540.06079	32.26988	50.1353



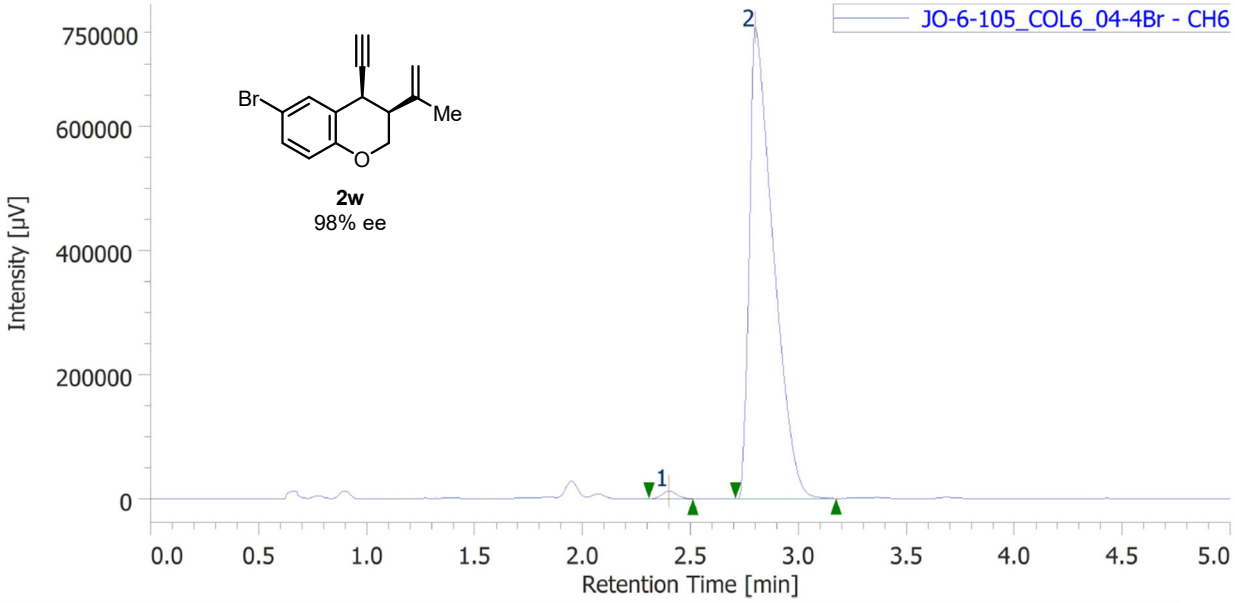
Signal 1: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.512	MM	0.2659	4454.97461	279.24466	99.1594
2	12.007	BB	0.2325	37.76383	2.19791	0.8406

2w: SFC (CHIRALPAK IF, 4% methanol).

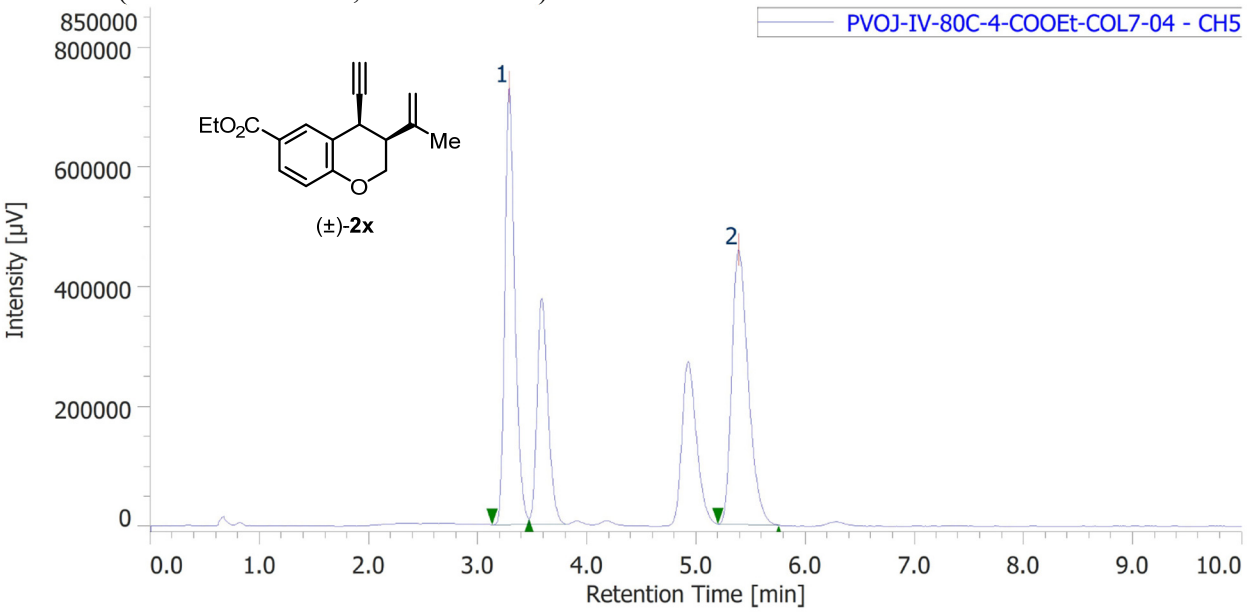


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	5	2.447	867032	50.1	4.286	0.066	201983
2	Unknown	5	2.980	862629	49.9	N/A	0.081	167302
Total				1729661				369285

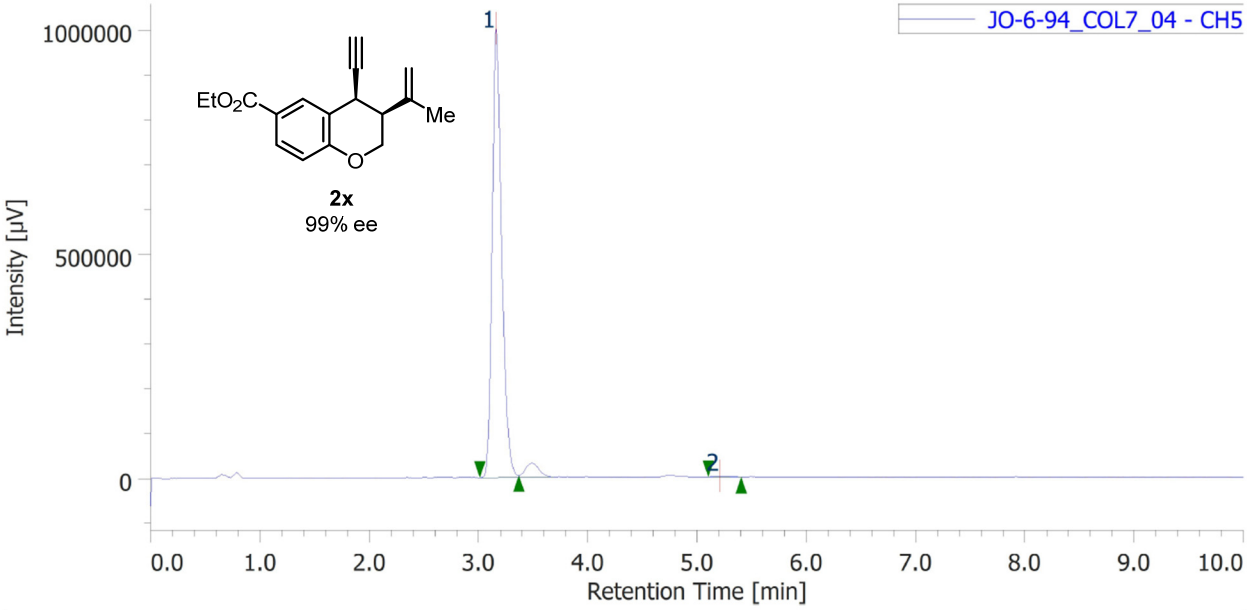


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	6	2.400	55257	0.942	2.471	0.074	11918
2	Unknown	6	2.800	5813679	99.1	N/A	0.118	758705
Total				5868936				770623

2x: SFC (CHIRALPAK IG, 4% methanol).

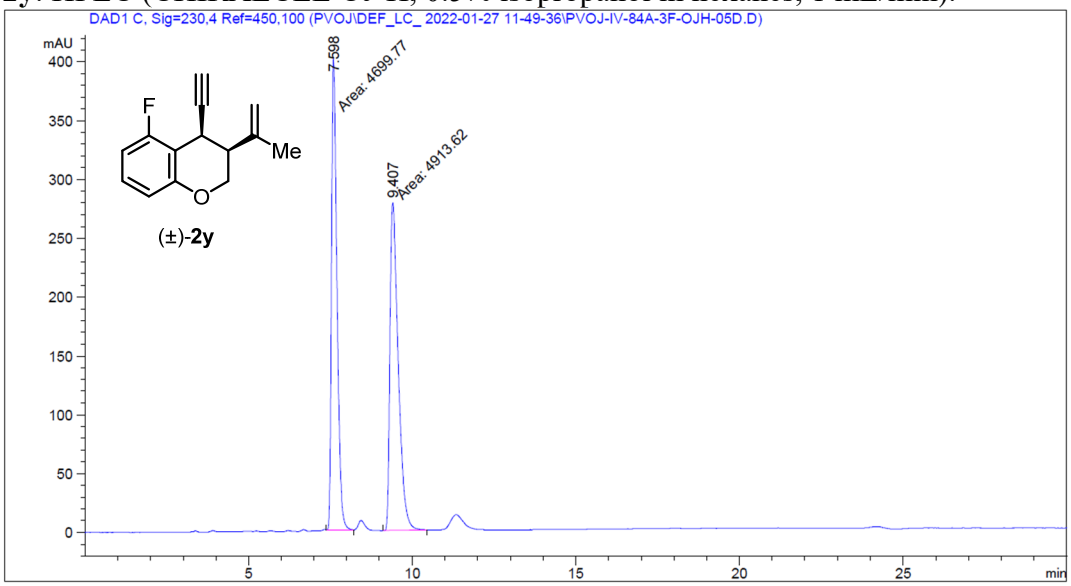


#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	5	3.287	4649710	49.1	9.675	0.096	730079
2	Unknown	5	5.390	4827445	50.9	N/A	0.161	458684
Total				9477155				1188763



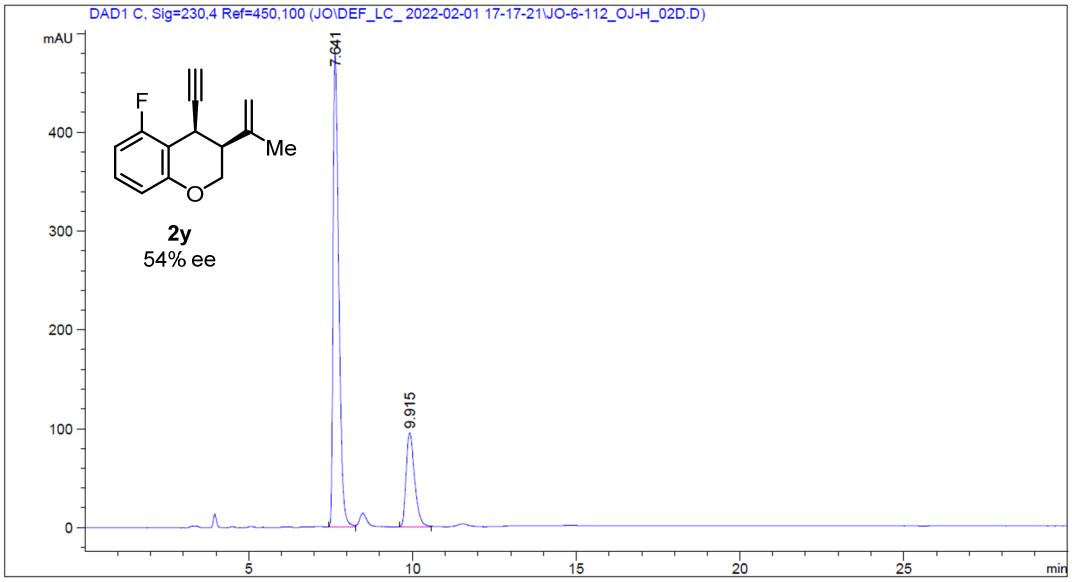
#	Peak Name	CH	tR [min]	Area [μV·sec]	Area%	Resolution	Peak Width	Height [μV]
1	Unknown	5	3.160	6052228	99.6	10.431	0.090	1000965
2	Unknown	5	5.207	22127	0.364	N/A	0.141	2543
Total				6074355				1003508

2y: HPLC (CHIRALCEL OJ-H, 0.5% isopropanol in hexanes, 1 mL/min).



Signal 1: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.598	MM	0.1956	4699.77344	400.48105	48.8877
2	9.407	MM	0.2939	4913.62354	278.67761	51.1123



Signal 1: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.641	BB	0.1841	5743.97949	478.37210	77.1499
2	9.915	BB	0.2749	1701.24133	95.02814	22.8501

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