Ligand-Regulated Regiodivergent Enantioselective Allylic Alkylations of Trifluoromethylated Ketones

Yi Zhu[1,3#], Yifan Ni[1#], Chenxi Lu[2], Xiaochen Wang[1], Yi Wang[1*], Xiao-Song Xue[2*] and Yi Pan[1]

1. State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, Collaborative Innovation Center of Advanced Microstructures, MOE Key Laboratory of High Performance Polymer Materials and Technology, School of Chemistry & Chemical Engineering, Nanjing University, Nanjing, 210023 China.

2. State Key Laboratory of Elemento-organic Chemistry, College of Chemistry, Nankai University, Tianjin, 300071 China

3. Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, 214122 Wuxi, Jiangsu, China

Supporting Information

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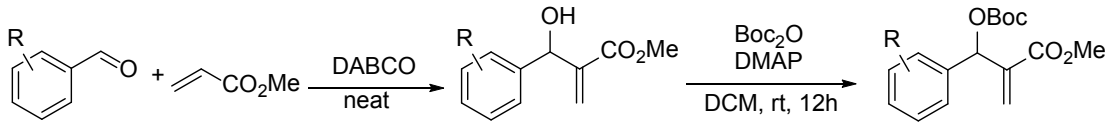
General information

All commercial reagents were used without additional purification unless otherwise specified. Solvents were purified and dried according to standard methods prior to use. All reactions were carried out in flame-dried glassware with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. All experiments were monitored by thin layer chromatography (TLC) using UV light as visualizing agent. TLC was performed on pre-coated silica gel plated. Column chromatography was performed using silica gel 60 (300-400 mesh). ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) were measured on a Bruker AVANCE III-400 spectrometer. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{19}F NMR (471 MHz) were measured on a Bruker AVANCE III-500 spectrometer. Chemical shifts are reported in ppm (δ) relative to internaltetramethylsilane (TMS, δ 0.0 ppm) or with the solvent reference relative to TMS employed as the internal standard. Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), broad (br) and multiplet (m)], coupling constants [Hz], integration). Melting points are uncorrected. Values of optical rotation were measured on Rudolph Automatic Polarimeter A21101 at the wavelength of the sodium D-line (589 nm). Infrared spectra were obtained on Bruker Vector 22 in KBr pellets. HRMS were recorded on a LTQ-Orbitrap XL (Thermofisher, USA). HPLC analysis was performed on Shimadzu SPD-20A using Daicel Chiralpak IG-3 Column.

Preparation of the MBH adducts [1]

Procedure A

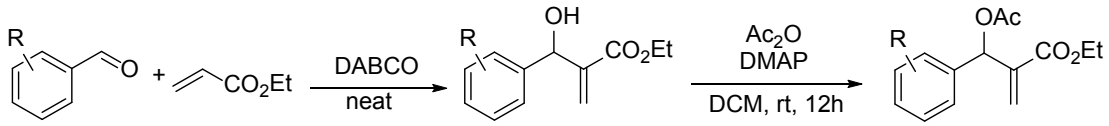


In a round bottom flask fitted with a magnetic stir-bar, aldehyde (1.0 equiv.) and methyl acrylate (4.0 equiv.) were taken. Required amount of DABCO (1.0 equiv.) was added to the neat reaction mixture and the resulting reaction mixture was stirred at 25 °C vigorously. After specified reaction time, the reaction mixture was diluted with CH_2Cl_2 (15.0 mL) and then washed with 1M aqueous HCl (15.0 mL) followed by sat. aqueous

$NaHCO_3$ solution (15.0 mL) and brine. Organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 20.0 mL). Combined organic layer was dried over anh. Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica-gel (230-400 mesh) using petroleum ether : ethyl acetate (10:1) to obtain as thick oil.

MBH alcohol (1.0 equiv.) was taken in a flame dried round bottom flask and dissolved it by dry dichloromethane (DCM) (4mL/mmol) then catalytic amount (10 mol%) of 4-DMAP was added followed by Boc_2O (1.3 equiv.) was added. The reaction mixture was diluted with additional amount of DCM then washed with water twice. The organic fractions were combined dried with anhydrous Na_2SO_4 and evaporated by rotary evaporator. The crude material was purified by 100-200 flash chromatography using petroleum ether/ethyl acetate (20:1).

Procedure B

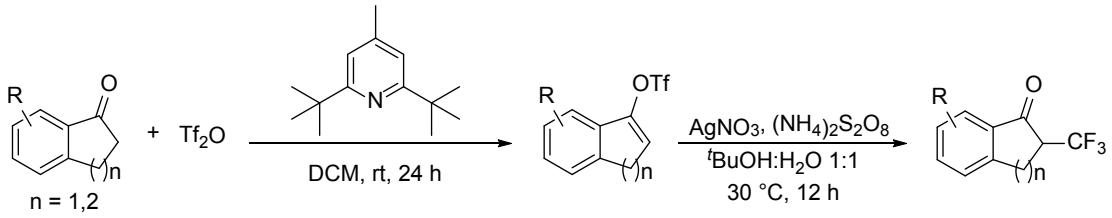


In a round bottom flask fitted with a magnetic stir-bar, aldehyde (1.0 equiv.) and ethyl acrylate (4.0 equiv.) were taken. Required amount of DABCO (1.0 equiv.) was added to the neat reaction mixture and the resulting reaction mixture was stirred at 25 °C vigorously. After specified reaction time, the reaction mixture was diluted with CH_2Cl_2 (15.0 mL) and then washed with 1M aqueous HCl (15.0 mL) followed by sat. aqueous $NaHCO_3$ solution (15.0 mL) and brine. Organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 20.0 mL). Combined organic layer was dried over anh. Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica-gel (230-400 mesh) using petroleum ether /ethyl acetate (10:1) to obtain as thick oil.

MBH alcohol (1.0 equiv.) was taken in a flame dried round bottom flask and dissolved it by dry dichloromethane (DCM) (4mL/mmol) then catalytic amount (10 mol%) of 4-DMAP was added followed by Ac_2O (1.3 equiv.) was added. The reaction mixture was diluted with additional amount of DCM then washed with water twice. The organic

fractions were combined dried with anhydrous Na_2SO_4 and evaporated by rotary evaporator. The crude material was purified by 100-200 flash chromatography using petroleum ether/ethyl acetate (20:1).

Preparation of the *a*-CF_3 ketones [2]

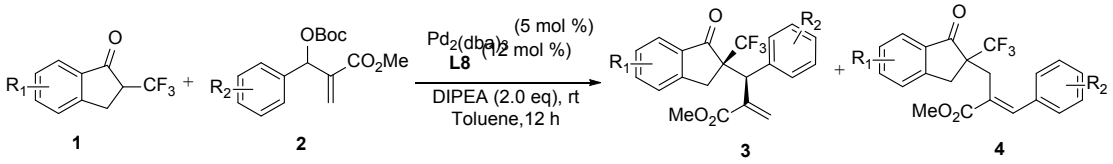


2,6-di-*tert*-butyl-4-methylpyridine (17 mmol) and trifluoromethanesulfonic anhydride (18 mmol) were added to the solution of cyclohexanone (15 mmol) in dichloromethane (45 mL). The reaction mixture was stirred overnight, and evaporated to dryness. Petroleum ether was added and the solid pyridinium triflate was filtered off (the free base can be recovered) which was washed with petroleum ether. The combined petroleum ether solution was washed subsequently with cool HCl (1 M) and saturated brine, and dried over Na_2SO_4.The mixture was purified by flash column chromatography on silica gel using petroleum ether as an eluent to get the product.

An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, $(NH_4)_2S_2O_8$ (12 mmol), AgNO3 (0.10 mmol) and corresponding enol triflate (10 mmol). Solid reagents were weighed first followed by liquid reagents. ^{t}BuOH (20 mL) and H_2O (20 mL) were added. The reaction tube was stirred vigorously at 30 °C. After 12 h, the reaction mixture was diluted with dichloromethane. The organic layer was separated and the aqueous layer was washed with dichloromethane (3×10 mL). The combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent.

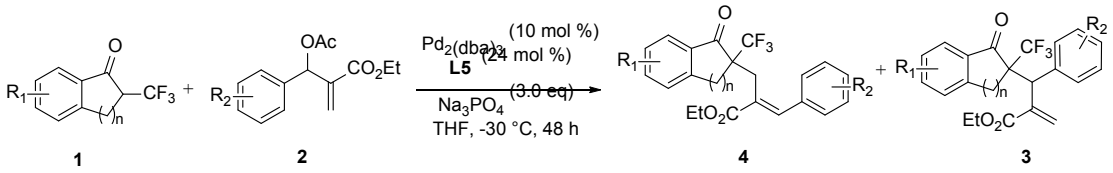
Procedures for asymmetric allylic alkylation

Procedure A (C1-selective product)



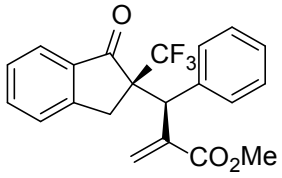
To a reaction tube with magnetic stirring bar were added the chiral ligand **L8** (0.06 mmol), $Pd_2(dba)_3$ (0.0025 mmol) and Toluene (0.4 mL) under argon. The mixture was stirred for 30 minutes at room temperature. Then the mixture was sequentially added **1** (0.05 mmol) and **2** (0.06 mmol) and DIPEA (0.1 mmol). The resulting mixture was stirred for 12 h at room temperature. Then the solvent was removed *in vacuo*. The ratio of **3**/**4** and the distereomeric ratios of **3** were determined by ^{19}F NMR analysis of the crude mixture. The crude product was purified by flash chromatography on silica gel with ethyl acetate/petroleum ether (1/10) and then dichloromethane/petroleum ether (1:1) as the eluent to afford compound **3** as a white solid. The *ee* value of **3** was determined by HPLC analysis using a Chiralcel IG-3 column.

Procedure B (C3-selective product)



To a 10-mL schlenk tube equipped with magnetic stirring bar were added the chiral ligand **L5** (0.012 mmol), $Pd_2(dba)_3$ (0.005 mmol) and THF (0.4 mL) under argon. The mixture was stirred for 20 minutes at room temperature and another 20 minutes at -30 □. Then the mixture was sequentially added **1** (0.05 mmol), Na_3PO_4 (0.15 mmol) and **2** (0.06 mmol in 0.6 mL THF). The resulting mixture was stirred for 48 h at -30 □. Then the reaction was quenched by addition of saturated ammonium chloride solution (2 mL) and water (10 mL), and the mixture was extracted with ethyl acetate (2 × 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The ratio of **4**/**3** and the E/Z value of **4** were determined by ^{19}F NMR analysis of the crude mixture. The crude product was purified by flash chromatography on silica gel with ethyl acetate/petroleum ether (1/10) as the eluent to

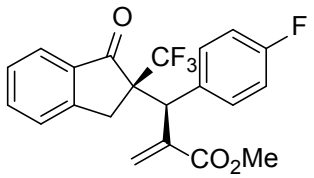
afford compound **4** as a colorless oil. The *ee* value of **4** was determined by HPLC analysis using a Chiralcel IG-3 column.



3a

Methyl-2-((*S*)-((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(phenyl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 17.4 mg (93% yield), 95:5 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_{D}$ 111.4° (c = 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.66 (td, *J* = 7.5, 1.2 Hz, 1H), 7.49 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.39 – 7.34 (m, 2H), 7.33 – 7.23 (m, 3H), 6.15 (s, 1H), 5.38 (d, *J* = 1.1 Hz, 1H), 5.14 (d, *J* = 1.1 Hz, 1H), 3.81 (d, *J* = 18.4 Hz, 1H), 3.61 (s, 3H), 3.37 (d, *J* = 18.4 Hz, 1H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.31 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.5, 166.7, 151.7, 139.4, 137.2, 137.0, 136.0, 129.9, 128.4, 128.4, 127.8, 126.4, 125.8 (q, *J* = 284.7 Hz), 125.5, 124.9, 60.3 (q, *J* = 22.4 Hz), 52.4, 46.0, 32.3. IR (cm^{-1}): 2953, 1716, 1605, 1456, 1258, 1148, 963, 775, 703, 472. HRMS (ESI^+): calcd. for [$C_{21}H_{17}F_3O_3$+H^+] 375.1203, found 375.1201. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol/hexane = 1:9), 1.0 mL/min; t_R = 8.2 min (major), 11.1 min (minor).

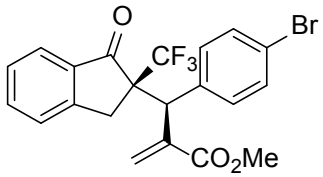


3b

Methyl-2-((*S*)-(4-fluorophenyl)((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 17.9 mg (91% yield), 94:6 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_{D}$ 65.1° (c = 0.4, $CHCl_3$); ^{1}H

NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.66 (td, *J* = 7.5, 1.2 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.29 (m, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 6.13 (s, 1H), 5.34 (d, *J* = 1.3 Hz, 1H), 5.13 (d, *J* = 1.2 Hz, 1H), 3.78 (d, *J* = 18.3 Hz, 1H), 3.59 (s, 3H), 3.36 (d, *J* = 18.3 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.31 (s, 3F) , -114.63 (s, 1F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.2, 166.5, 162.3 (d, *J* = 246.8 Hz), 151.5, 139.3, 136.7, 136.1, 132.9 (d, *J* = 3.3 Hz), 131.5 (d, *J* = 8.0 Hz), 128.5 , 126.5 , 125.8 (q, *J* = 284.6 Hz), 125.3 , 124.9 , 115.3 (d, *J* = 21.5 Hz), 60.3 (q, *J* = 22.4 Hz), 52.4, 45.2, 32.0. IR (cm^{-1}): 2956, 1720, 1605, 1441, 1256, 1141, 960, 841, 783, 602, 516. HRMS (ESI$^+$): calcd. for [$C_{21}H_{16}F_4O_3$+H$^+$] 393.1108, found 393.1109. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane = 1:9), 1.0 mL/min; t_R = 7.9 min (major), 12.7 min (minor).

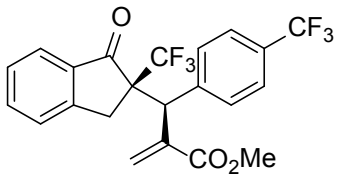


3c

Methyl-2-((*S*)-(4-bromophenyl)((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 18.3 mg (81% yield), 87:13 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_D$ 190.5^o (c = 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.68 (td, *J* = 7.4, 1.3 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.40 (m, 3H), 7.26 – 7.22 (m, 2H), 6.14 (s, 1H), 5.34 (d, *J* = 1.1 Hz, 1H), 5.10 (d, *J* = 1.1 Hz, 1H), 3.76 (d, *J* = 18.4 Hz, 1H), 3.61 (s, 3H), 3.36 (d, *J* = 18.4 Hz, 1H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.29 (s, 3F); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.1, 166.4, 151.4, 139.0, 136.7, 136.3, 136.2, 131.6, 131.6, 128.5, 126.5, 125.7 (q, *J* = 284.7 Hz), 125.6, 125.0, 122.0, 60.1 (q, *J* = 22.5 Hz), 52.4, 45.4, 32.0. IR (cm^{-1}): 2956, 1709, 1605, 1441, 1256, 1163, 1008, 953, 781, 673, 590. HRMS (ESI$^+$): calcd. for [$C_{21}H_{16}BrF_3O_3$+H$^+$] 453.0308, found 453.0304.

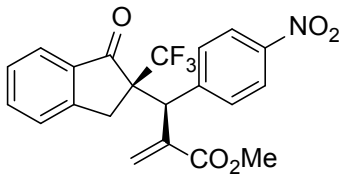
The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 8.7 min (major), 23.9 min (minor).



3d

methyl-2-((*S*)-((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(4-(trifluoromethyl)phenyl)methyl)acrylate

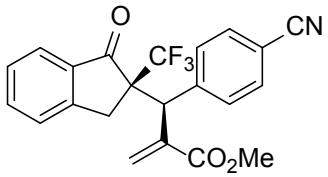
The title compound was prepared according to the General Procedure A as a white solid, 19.9 mg (90% yield), 93:7 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_D$ 111.0° (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.68 (td, *J* = 7.5, 1.2 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.48 (m, 3H), 7.48 – 7.42 (m, 1H), 6.18 (s, 1H), 5.38 (d, *J* = 1.1 Hz, 1H), 5.21 (d, *J* = 1.1 Hz,1H), 3.81 (d, *J* = 18.3 Hz, 1H), 3.60 (s, 3H), 3.38 (d, *J* = 18.3 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.62 (s, 3F), -68.29 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.9, 166.3, 151.4, 141.4, 138.8, 136.7, 136.3, 130.4, 130.0 (q, *J* = 32.6 Hz), 128.6, 126.5, 126.0, 125.7 (q, *J* = 284.6 Hz), 125.4 (q, *J* = 3.6 Hz), 125.0, 124.1 (q, *J* = 272.1 Hz), 60.1 (q, *J* = 22.6 Hz), 52.5, 45.7, 32.0. IR (cm^{-1}): 2961, 2365, 1709, 1607, 1457, 1329, 1258, 1159, 1115, 1070, 884, 785, 623. HRMS (ESI^+): calcd. for $[C_{22}H_{16}F_6O_3+Na^+]$ 465.0896, found 465.0898. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 6.1 min (major), 10.1 min (minor).



3e

methyl-2-((*S*)-(4-nitrophenyl)((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 18.9 mg (90% yield), 94:6 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_{D}$ 86.0° (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.24 – 8.10 (m, 2H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.70 (td, *J* = 7.4, 1.2 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.53 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.50 – 7.43 (m, 1H), 6.21 (s, 1H), 5.40 (d, *J* = 1.1 Hz, 1H), 5.23 (d, *J* = 1.1 Hz, 1H), 3.82 (d, *J* = 18.3 Hz, 1H), 3.60 (s, 3H), 3.39 (d, *J* = 18.3 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.25 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.5, 166.1, 151.2, 147.5, 145.0, 138.3, 136.5, 136.4, 130.8, 128.7, 126.5, 126.5, 125.6 (q, *J* = 284.7 Hz), 125.1, 123.6, 60.1 (q, *J* = 22.8 Hz), 52.6, 45.8, 31.9. IR (cm^{-1}): 2956, 1718, 1519, 1349, 1259, 1146, 960, 935, 699, 596. HRMS (ESI^+): calcd. for $[C_{21}H_{16}F_3NO_5+H^+]$ 420.1053, found 420.1055. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=3:7), 1.0 mL/min; t_R = 7.6 min (major), 18.3 min (minor).

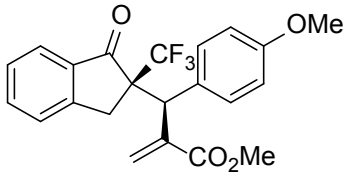


3f

Methyl-2-((*S*)-(4-cyanophenyl)((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 18.6 mg (93% yield), 95:5 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_{D}$ 143.2° (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.70 (td, *J* = 7.5, 1.3 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.51 (t, *J* = 8.0 Hz, 4H), 7.47 (t, *J* = 7.3 Hz, 1H), 6.19 (s, 1H), 5.38 (d, *J* = 1.2 Hz, 1H), 5.17 (d, 1H), 3.78 (d, *J* = 18.3 Hz, 1H), 3.38 (d, *J* = 18.3 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.28 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.6, 166.2, 151.2, 142.9, 138.4, 136.6, 136.4, 132.2, 130.7, 128.5, 126.5, 126.3, 125.5 (q, *J* = 284.8 Hz), 125.1, 118.6, 111.9, 60.1 (q, *J* = 22.8 Hz), 52.6, 46.0, 31.9. IR (cm^{-1}): 2954, 2229, 1718, 1262, 1156, 1029, 1101, 787, 742, 598. HRMS (ESI^+): calcd. for $[C_{22}H_{16}F_3NO_3+Na^+]$ 422.0974, found 422.0978. The enantiomeric

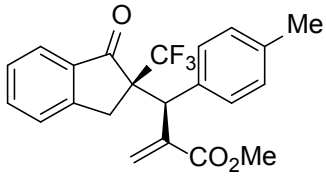
excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=4:6), 1.0 mL/min; t_R = 6.6 min (major), 15.3 min (minor).



3g

Methyl-2-((*S*)-(4-methoxyphenyl)((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 21.1 mg (90% yield), 91:9 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_D$ 110.9° (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.67 (td, *J* = 7.5, 1.2 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.36 – 7.24 (m, 2H), 6.88 – 6.79 (m, 2H), 6.12 (s, 1H), 5.34 (d, *J* = 1.2 Hz, 1H), 5.12 (d, *J* = 1.2 Hz, 1H), 3.80 (s, 3H), 3.81 (d, *J* = 18.3 Hz, 1H), 3.62 (s, 3H), 3.37 (d, *J* = 18.4 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.34 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.6, 166.8, 159.1, 151.7, 139.6, 136.9, 136.0, 131.0, 129.0, 128.4, 126.4, 125.9 (q, *J* = 284.6 Hz), 125.0, 124.9, 113.8, 60.3 (q, *J* = 22.4 Hz), 55.3, 52.3, 45.2, 32.2. IR (cm^{-1}): 2956, 2361, 1716, 1507, 1256, 1153, 1031, 951, 787, 669, 451. HRMS (ESI^+): calcd. for [$C_{22}H_{19}F_3O_4$+H^+] 405.1308, found 405.1305. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 11.6 min (major), 19.0 min (minor).

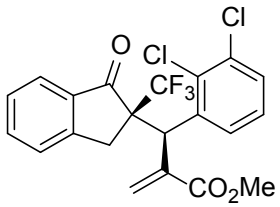


3h

Methyl-2-((*S*)-((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(p-tolyl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 17.7 mg (91% yield), 92:8 **3**/**4**, >20:1 d.r., 98% *ee*. $[\alpha]^{25}_D$ 117.6° (c = 0.2, $CHCl_3$); ^{1}H

NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.12 (s, 1H), 5.35 (s, 1H), 5.11 (s, 1H), 3.81 (d, *J* = 18.4 Hz, 1H), 3.60 (d, *J* = 0.9 Hz, 3H), 3.35 (d, *J* = 18.4 Hz, 1H), 2.32 (s, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.31 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.6, 166.8, 151.7, 139.6, 137.5, 136.9, 136.0, 134.1, 129.8, 129.2, 128.3, 126.4, 125.8 (q, *J* = 284.6 Hz), 125.3, 124.9, 60.3 (q, *J* = 22.4 Hz), 52.3, 45.5, 32.2, 21.2. IR (cm^{-1}): 2954, 1720, 1607, 1439, 1258, 1150, 965, 814, 740, 675, 598. HRMS (ESI$^+$): calcd. for [$C_{22}H_{19}F_3O_3$+H$^+$] 389.1359, found 389.1360. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 8.3 min (major), 13.7 min (minor).

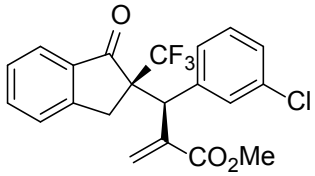


3i

Methyl-2-((*S*)-(2,3-dichlorophenyl)((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 21.3 mg (96% yield), 99:1 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_D$ 22.1° (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.65 (td, *J* = 7.4, 1.3 Hz, 1H), 7.47 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.36 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.32 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 6.26 (s, 1H), 5.77 (d, *J* = 1.1 Hz 1H), 5.59 (d, *J* = 1.1 Hz, 1H), 3.84 (d, *J* = 18.0 Hz, 1H), 3.62 (s, 3H), 3.45 (d, *J* = 18.0 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.34 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.9, 166.4, 151.6, 138.3, 137.7, 136.4, 136.2, 134.1, 129.8, 128.7, 128.6, 128.4, 126.5, 126.3, 125.6 (q, *J* = 284.8 Hz), 124.9, 60.0 (q, *J* = 23.1 Hz), 52.4, 43.4, 32.7. IR (cm^{-1}): 2948, 1726, 1598, 1422, 1202, 1133, 974, 788, 680, 472. HRMS (ESI$^+$): calcd. for [$C_{21}H_{15}Cl_2F_3O_3$+H$^+$] 443.0423, found 443.0424. The enantiomeric

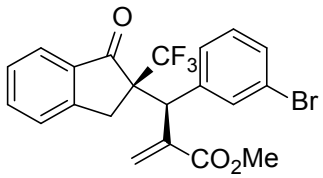
excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 8.9 min (major), 12.3 min (minor).



3j

Methyl-2-((*S*)-(3-chlorophenyl)((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

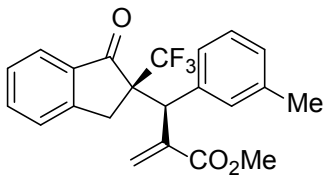
The title compound was prepared according to the General Procedure A as a white solid, 19.2 mg (94% yield), 95:5 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_D$ 100.3° (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.67 (td, *J* = 7.5, 1.2 Hz, 1H), 7.51 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.31 – 7.21 (m, 3H), 6.16 (s, 1H), 5.36 (d, *J* = 1.1 Hz, 1H), 5.12 (d, *J* = 1.1 Hz, 1H), 3.78 (d, *J* = 18.4 Hz, 1H), 3.61 (s, 3H), 3.38 (d, *J* = 18.3 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.30 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.0, 166.4, 151.4, 139.3, 138.8, 136.7, 136.2, 134.2, 129.7, 128.5, 128.4, 128.1, 126.5, 125.9, 125.7 (q, *J* = 284.6 Hz), 124.9, 60.1 (q, *J* = 22.7 Hz), 52.4, 45.5, 32.1. IR (cm^{-1}): 2950, 1715, 1598, 1440, 1258, 1146, 960, 930, 781, 738, 701, 617. HRMS (ESI^+): calcd. for [$C_{21}H_{16}ClF_3O_3$+H^+] 409.0813, found 409.0811. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 7.8 min (major), 12.6 min (minor).



3k

Methyl-2-((*S*)-(3-bromophenyl)((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 19.5 mg (86% yield), 93:7 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_{D}$ 135.4° (c = 1.6, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.68 (td, *J* = 7.4, 1.2 Hz, 1H), 7.52 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.48 (t, *J* = 1.8 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.40 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.9 Hz, 1H), 6.17 (s, 1H), 5.36 (d, *J* = 1.2 Hz, 1H), 5.10 (d, *J* = 1.1 Hz, 1H), 3.76 (d, *J* = 18.3 Hz, 1H), 3.62 (s, 3H), 3.38 (d, *J* = 18.3 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.30 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.0, 166.4, 151.4, 139.6, 138.8, 136.7, 136.2, 132.5, 131.0, 123.0, 128.9, 128.5, 126.5, 126.0, 125.7 (q, *J* = 284.8 Hz), 125.0, 122.4, 60.1 (q, *J* = 22.6 Hz), 52.5, 45.5, 32.1. IR (cm^{-1}): 2950, 1713, 1590, 1438, 1256, 1142, 960, 791, 698, 615. HRMS (ESI^+): calcd. for $[C_{21}H_{16}BrF_3O_3+H^+]$ 453.0308, found 453.0307. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 8.1 min (major), 14.5 min (minor).

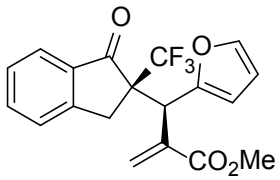


3l

Methyl-2-((*S*)-((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(m-tolyl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 17.1 mg (88% yield), 91:9 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_{D}$ 78.0° (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.65 (td, *J* = 7.5, 1.2 Hz, 1H), 7.49 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.20 – 7.13 (m, 3H), 7.09 – 7.04 (m, 1H), 6.15 (s, 1H), 5.39 (d, *J* = 1.1 Hz, 1H), 5.11 (d, *J* = 1.0 Hz, 1H), 3.79 (d, *J* = 18.4 Hz, 1H), 3.61 (s, 3H), 3.37 (d, *J* = 18.3 Hz, 1H), 2.32 (s, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.27 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.5, 166.8, 151.7, 139.4, 134.0, 137.0, 136.9, 136.0, 130.6, 128.5, 128.3, 128.2, 126.9, 126.4, 125.8 (q, *J* = 284.6 Hz), 125.6, 124.8, 60.2 (q, *J* = 22.5 Hz), 52.3, 45.8, 33.1, 21.6. IR

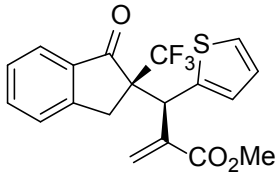
(cm^{-1}): 2954, 1720, 1604, 1439, 1258, 1150, 965, 785, 703, 676, 613. HRMS (ESI^+): calcd. for [$C_{22}H_{19}F_3O_3$+Na^+] 411.1179, found 411.1175. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 7.5 min (major), 10.5 min (minor).



3m

Methyl-2-((*S*)-furan-2-yl((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

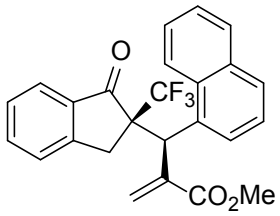
The title compound was prepared according to the General Procedure A as a white solid, 15.5 mg (85% yield), 98:2 **3**/**4**, >20:1 d.r., 98% *ee*. $[\alpha]^{25}_D$ 78.5° (c = 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.63 (td, *J* = 7.5, 1.2 Hz, 1H), 7.46 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.32 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.30 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.26 (dd, *J* = 3.2, 0.9 Hz, 1H), 6.16 (s, 1H), 5.87 – 5.82 (m, 1H), 5.20 (s, 1H), 3.90 (d, *J* = 18.4 Hz, 1H), 3.69 (s, 3H), 3.47 (d, *J* = 18.4 Hz, 1H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -69.96 (s, 3F); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.5, 166.7, 152.2, 151.0, 142.6, 136.7, 136.2, 136.0, 129.0, 128.2, 126.2, 125.6 (q, *J* = 284.6 Hz), 124.7, 110.6, 109.4, 52.5, 39.2, 32.6. HRMS (ESI^+): calcd. for [$C_{19}H_{15}F_3O_4$+H^+] 365.0995, found 365.0993. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 8.5 min (major), 22.6 min (minor).



3n

Methyl-2-((*S*)-((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(thiophen-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 15.8 mg (83% yield), 98:2 **3**/**4**, >20:1 d.r., 98% *ee*. $[\alpha]^{25}_{D}$ 87.4° (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 5.1 Hz, 1H), 7.05 (d, *J* = 3.5 Hz, 1H), 6.93 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.15 (s, 1H), 5.60 (s, 1H), 5.46 (s, 1H), 3.90 (d, *J* = 18.3 Hz, 1H), 3.67 (s, 3H), 3.48 (d, *J* = 18.2 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.93 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.9, 166.6, 152.0, 140.1, 139.2, 136.5, 136.1, 128.4, 127.2, 126.8, 126.4, 125.6 (q, *J* = 284.7 Hz), 125.5, 125.0, 60.5 (q, *J* = 22.6 Hz), 52.5, 41.5, 33.0. IR (cm^{-1}): 2958, 2853, 1709, 1605, 1442, 1258, 1142, 965, 795, 713, 617. HRMS (ESI^+): calcd. for [$C_{19}H_{15}F_3O_3S+H^+$] 381.0767, found 381.0766. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 8.1 min (major), 11.7 min (minor).

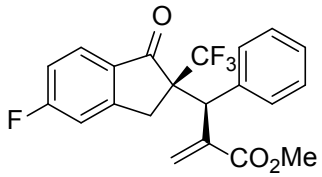


3o

Methyl-2-((*S*)-naphthalen-1-yl((*R*)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 17.4 mg (82% yield), 87:13 **3**/**4**, 15:1 d.r., >99% *ee*. $[\alpha]^{25}_{D}$ 132.4° (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 8.7 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.55 – 7.48 (m, 1H), 7.47 – 7.41 (m, 3H), 7.36 – 7.30 (m, 1H), 6.22 (s, 1H), 6.12 (s, 1H), 5.52 (d, *J* = 1.0 Hz, 1H), 3.83 (d, *J* = 18.1 Hz, 1H), 3.57 (s, 3H), 3.44 (d, *J* = 18.1 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.19 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.6, 167.1, 151.9, 139.7, 136.8, 136.0, 134.2, 132.3, 128.9, 128.6, 128.3, 127.0, 126.7, 126.4, 126.3, 125.9, 125.9 (d, *J* = 284.7 Hz), 124.8, 124.5, 124.1, 60.0 (q, *J* = 22.7 Hz), 52.4, 40.1, 33.1. IR (cm^{-1}):

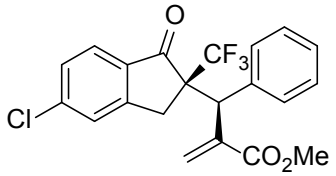
2920, 1724, 1606, 1436, 1278, 1253, 1152, 962, 786, 690. HRMS (ESI^+): calcd. for [$C_{25}H_{19}F_3O_3$+Na^+] 447.1179, found 447.1180. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 8.7 min (major), 13.1 min (minor).



3p

Methyl-2-((*S*)-((*R*)-5-fluoro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(phenyl)methyl)acrylate

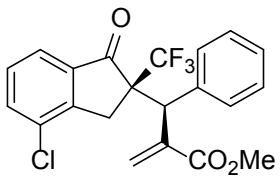
The title compound was prepared according to the General Procedure A as a white solid, 18.0 mg (92% yield), 93:7 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_D$ 101.9° (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (dd, *J* = 8.3, 5.2 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.31 – 7.23 (m, 3H), 7.17 – 7.09 (m, 2H), 6.17 (s, 1H), 5.42 (d, *J* = 1.1 Hz, 1H), 5.11 (d, *J* = 1.1 Hz, 1H), 3.79 (d, *J* = 18.5 Hz, 1H), 3.61 (s, 3H), 3.35 (d, *J* = 18.5 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.38 (s, 3F), -99.99 (s, 1F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.5, 167.8 (d, *J* = 258.9 Hz), 166.7, 154.6 (d, *J* = 10.4 Hz), 139.3, 136.9, 133.2, 129.8, 128.5, 127.9, 127.3 (d, *J* = 10.7 Hz), 125.7 (q, *J* = 284.7 Hz), 125.8, 116.8 (d, *J* = 23.8 Hz), 113.3 (d, *J* = 22.7 Hz), 60.6 (q, *J* = 22.6 Hz), 52.4, 46.0, 32.3. IR (cm^{-1}): 2954, 1724, 1595, 1484, 1438, 1258, 1150, 1085, 948, 824, 703, 606. HRMS (ESI^+): calcd. for [$C_{21}H_{16}F_4O_3$+H^+] 415.0928, found 415.0930. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=2:8), 1.0 mL/min; t_R = 5.6 min (major), 7.0 min (minor).



3q

Methyl-2-((*S*)-((*R*)-5-chloro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(phenyl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 18.0 mg (88% yield), 90:10 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_{D}$ 106.1° (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 1.5 Hz, 1H), 7.41 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.35 – 7.32 (m, 2H), 7.31 – 7.25 (m, 3H), 6.17 (s, 1H), 5.40 (d, *J* = 1.1 Hz, 1H), 5.13 (d, *J* = 1.1 Hz, 1H), 3.78 (d, *J* = 18.5 Hz, 1H), 3.61 (s, 3H), 3.33 (d, *J* = 18.5 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.35 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.0, 166.6, 153.0, 142.7, 139.3, 136.9, 135.2, 129.8, 129.3, 128.5, 127.9, 126.7, 125.6 (q, *J* = 284.7 Hz), 126.0, 125.8, 60.5 (q, *J* = 22.7 Hz), 52.4, 46.0, 32.1. IR (cm^{-1}): 2954, 1722, 1601, 1438, 1258, 1150, 1071, 957, 706, 605, 424. HRMS (ESI^+): calcd. for [$C_{21}H_{16}ClF_3O_3$+H^+] 409.0813, found 409.0814. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=2:8), 1.0 mL/min; t_R = 5.7 min (major), 6.8 min (minor).

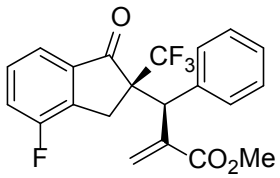


3r

Methyl-2-((*S*)-((*R*)-4-chloro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(phenyl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 17.4 mg (85% yield), 90:10 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_{D}$ 69.3° (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.75 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.36 (dd, *J* = 9.8, 7.5 Hz, 3H), 7.33 – 7.29 (m, 3H), 7.29 – 7.25 (m, 1H), 6.16 (s, 1H), 5.38 (d, *J* = 1.1 Hz, 1H), 5.14 (d, *J* = 0.9 Hz, 1H), 3.70 (d, *J* = 18.7 Hz, 1H), 3.61 (s, 3H), 3.30 (d, *J* = 18.7 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.16 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.8, 166.6, 151.4, 139.2, 138.7, 138.6, 136.8, 130.2, 129.8, 128.5, 127.9, 125.8, 125.6 (q, *J* = 284.7 Hz), 123.6, 121.8, 60.6 (q, *J* = 22.6 Hz), 52.4, 46.0, 33.5. IR (cm^{-1}): 2950, 1720, 1593, 1457, 1265,1154, 1090,

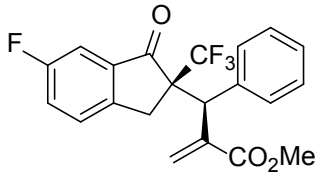
964, 798, 701, 630. HRMS (ESI$^+$): calcd. for [$C_{21}H_{16}ClF_3O_3$+H^+] 409.0813, found 409.0810. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=2:8), 1.0 mL/min; t_R = 5.2 min (major), 6.7 min (minor).



3s

Methyl-2-((*S*)-((*R*)-4-fluoro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(phenyl)methyl)acrylate

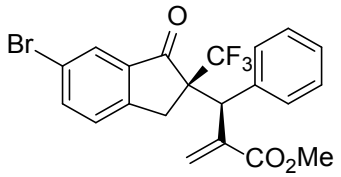
The title compound was prepared according to the General Procedure A as a white solid, 16.5 mg (83% yield), 85:15 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_D$ 120.8^o (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.46 (td, *J* = 7.8, 4.5 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.35 – 7.26 (m, 3H), 6.19 (s, 1H), 5.42 (d, *J* = 1.1 Hz, 1H), 5.17 (d, *J* = 1.1 Hz, 1H), 3.82 (d, *J* = 18.6 Hz, 1H), 3.63 (s, 3H), 3.41 (d, *J* = 18.6 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.33 (s, 3F), -117.86 (s, 1F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.3, 166.6, 159.7 (d, *J* = 251.9 Hz), 139.4 (d, *J* = 2.7 Hz), 139.3, 137.5 (d, *J* = 19.3 Hz), 136.8, 130.5 (d, *J* = 6.3 Hz), 129.8, 128.5, 127.9, 125.7, 125.5 (q, *J* = 284.7 Hz), 122.1 (d, *J* = 19.7 Hz), 120.6 (d, *J* = 3.9 Hz), 60.4 (q, *J* = 22.7 Hz), 52.4, 46.0, 28.3. IR (cm^{-1}): 2954, 1720, 1619, 1483, 1437, 1247, 1146, 995, 798, 699, 609, 544. HRMS (ESI$^+$): calcd. for [$C_{21}H_{16}F_4O_3$+H^+] 393.1108, found 393.1109. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=2:8), 1.0 mL/min; t_R = 5.0 min (major), 5.9 min (minor).



3t

Methyl-2-((*S*)-((*R*)-6-fluoro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(phenyl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 17.7 mg (90% yield), 91:9 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_{D}$ 125.7° (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 2H), 7.39 – 7.32 (m, 3H), 7.31 – 7.23 (m, 3H), 6.17 (s, 1H), 5.41 (d, *J* = 1.1 Hz, 1H), 5.09 (d, *J* = 1.1 Hz, 1H), 3.77 (d, *J* = 18.2 Hz, 1H), 3.61 (s, 3H), 3.33 (d, *J* = 18.2 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.32 (s, 3F), -112.70 (s, 1F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.6, 166.6, 162.7 (d, *J* = 249.9 Hz), 147.1, 139.3, 138.5 (d, *J* = 8.6 Hz), 136.9, 129.8, 128.5, 127.9, 127.9, 125.6 (q, *J* = 284.6 Hz), 125.7, 123.8 (d, *J* = 23.8 Hz), 110.7 (d, *J* = 22.2 Hz), 61.2 (q, *J* = 22.6 Hz), 52.4, 46.1, 31.9. IR (cm^{-1}): 2956, 1716, 1628, 1489, 1441, 1295, 1264, 1139, 963, 766, 609. HRMS (ESI^+): calcd. for [$C_{21}H_{16}F_4O_3$+H^+] 393.1108, found 393.1109. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=2:8), 1.0 mL/min; t_R = 5.8 min (major), 7.5 min (minor).

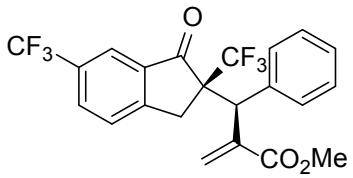


3u

Methyl-2-((*S*)-((*R*)-6-bromo-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(phenyl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 18.1 mg (80% yield), 93:7 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_{D}$ 43.0° (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 1.9 Hz, 1H), 7.75 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.32 (m, 2H), 7.31 – 7.25 (m, 3H), 6.18 (s, 1H), 5.39 (d, *J* = 1.1 Hz, 1H), 5.11 (s d, *J* = 1.1 Hz, 1H), 3.74 (d, *J* = 18.4 Hz, 1H), 3.61 (s, 3H), 3.30 (d, *J* = 18.4 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.32 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.1, 166.6, 150.2, 139.3, 138.8, 138.5, 136.9, 129.8, 128.5, 127.9, 127.9, 127.7, 125.8, 125.6 (q, *J* = 284.7 Hz), 122.6, 60.8 (q, *J* = 22.6 Hz), 52.4, 46.1, 32.1. IR (cm^{-1}): 2961, 1718, 1600, 1451, 1258, 1161, 1025, 814, 703, 605, 498. HRMS (ESI^+): calcd. for [$C_{21}H_{16}BrF_3O_3$+H^+] 453.0308, found 453.0307.

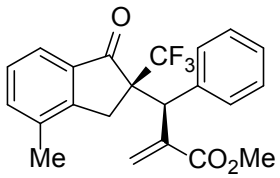
The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=2:8), 1.0 mL/min; t_R = 6.3 min (major), 7.5 min (minor).



3v

Methyl-2-((*S*)-((*R*)-1-oxo-2,6-bis(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(phenyl)methyl)acrylate

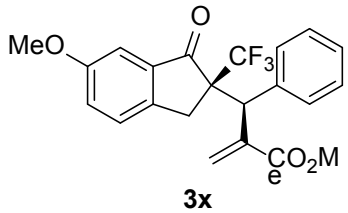
The title compound was prepared according to the General Procedure A as a white solid, 20.4 mg (92% yield), 93:7 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_D$ 110.1° (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 – 8.06 (m, 1H), 7.91 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 6.21 (s, 1H), 5.44 (d, *J* = 1.1 Hz, 1H), 5.15 (d, *J* = 1.1 Hz, 1H), 3.90 (d, *J* = 18.7 Hz, 1H), 3.64 (s, 3H), 3.45 (d, *J* = 18.9 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.61 (s, 3F) , -68.32 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.3, 166.6, 154.8, 139.3, 137.1, 136.8, 132.4 (q, *J* = 3.4 Hz), 131.3 (q, *J* = 33.3 Hz), 129.8, 128.6, 128.1, 127.2, 126.1, 125.3 (q, *J* = 284.7 Hz), 123.5 (q, *J* = 272.8 Hz), 122.0 (q, *J* = 3.9 Hz), 60.7 (q, *J* = 22.8 Hz), 52.4, 46.2, 32.6. IR (cm^{-1}): 2956, 1724, 1627, 1453, 1332, 1254, 1129, 1060, 958, 703, 680. HRMS (ESI^+): calcd. for [$C_{22}H_{16}F_6O_3$+Na^+] 465.0896, found 465.0898. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=2:8), 1.0 mL/min; t_R = 4.7 min (major), 5.4 min (minor).



3w

Methyl-2-((*S*)-((*R*)-4-methyl-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(phenyl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 17.7 mg (91% yield), 94:6 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_{D}$ 122.1° (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.27 (m, 3H), 6.15 (s, 1H), 5.38 (d, *J* = 1.1 Hz, 1H), 5.17 (d, *J* = 1.1 Hz, 1H), 3.68 (d, *J* = 18.3 Hz, 1H), 3.61 (s, 3H), 3.26 (d, *J* = 18.3 Hz, 1H), 2.39 (s, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.19 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.8, 166.7, 150.5, 139.4, 137.2, 136.7, 136.5, 135.7, 129.9, 128.6, 128.4, 127.7, 125.8 (q, *J* = 284.6 Hz), 125.5, 122.3, 60.3 (q, *J* = 22.4 Hz), 52.3, 46.1, 31.2, 18.0. IR (cm^{-1}): 2954, 1724, 1593, 1438, 1258, 1150, 956, 798, 703, 608. HRMS (ESI^+): calcd. for $[C_{22}H_{19}F_3O_3+Na^+]$ 411.1179, found 411.1181. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=2:8), 1.0 mL/min; t_R = 6.1 min (major), 7.6 min (minor).

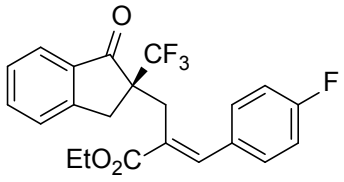


3x

Methyl-2-((*S*)-((*R*)-6-methoxy-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)(phenyl)methyl)acrylate

The title compound was prepared according to the General Procedure A as a white solid, 18.2 mg (90% yield), 91:9 **3**/**4**, >20:1 d.r., >99% *ee*. $[\alpha]^{25}_{D}$ 165.4° (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.34 (m, 3H), 7.32 – 7.20 (m, 5H), 6.14 (s, 1H), 5.37 (d, *J* = 1.2 Hz, 1H), 5.14 (d, *J* = 1.2 Hz, 1H), 3.84 (s, 3H), 3.73 (d, *J* = 18.0 Hz, 1H), 3.60 (s, 3H), 3.27 (d, *J* = 18.1 Hz, 1H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.32 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.4, 166.7, 160.0, 144.5, 139.4, 138.1, 137.1, 129.9, 128.4, 127.8, 127.1, 125.8 (q, *J* = 284.7 Hz), 125.5, 125.3, 61.1 (q, *J* = 22.5 Hz), 55.8, 52.3, 45.9, 31.5. IR (cm^{-1}): 2960, 1703, 1618, 1491, 1254, 1137, 1023, 964, 784, 701, 608, 541. HRMS (ESI^+): calcd. for $[C_{22}H_{19}F_3O_4+H^+]$ 405.1308, found 405.1309. The enantiomeric excess was determined by HPLC with an IG-3

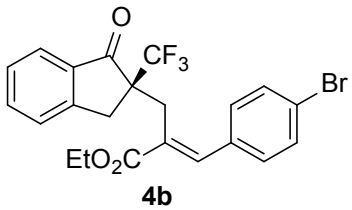
column at 254 nm (2-propanol:hexane=2:8), 1.0 mL/min; t_R = 6.9 min (major), 9.4 min (minor).



4a

Ethyl-(*R,E*)-3-(4-fluorophenyl)-2-((1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

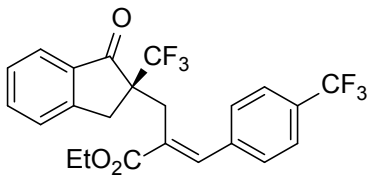
The title compound was prepared according to the General Procedure B as a colorless oil, 9.3 mg (46% yield), 95:5 **4**/**3**, 15:1 E/Z, 95% *ee*. $[\alpha]^{25}_D$ -20.0° (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 – 7.71 (m, 1H), 7.70 (s, 1H), 7.60 (td, *J* = 7.5, 1.2 Hz, 1H), 7.42 – 7.32 (m, 4H), 7.14 – 7.05 (m, 2H), 3.99 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.86 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.40 (d, *J* = 14.5 Hz, 1H), 3.34 (d, *J* = 17.7 Hz, 1H), 3.30 (d, *J* = 14.4 Hz, 1H), 3.23 (d, *J* = 17.7 Hz, 1H), 1.12 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -72.14 (s, 3F), -111.26 (s, 1F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.4, 167.6, 163.0 (d, *J* = 250.3 Hz), 151.4, 142.4, 135.7, 135.6 (d, *J* = 2.0 Hz), 131.2 (d, *J* = 8.4 Hz), 130.8 (d, *J* = 3.5 Hz), 128.1, 127.6, 126.4 (q, *J* = 282.6 Hz), 126.3, 124.6, 116.0 (d, *J* = 21.9 Hz), 61.3, 56.2 (q, *J* = 23.8 Hz), 33.2, 28.5, 14.0. IR (cm^{-1}): 2920, 1720, 1601, 1508, 1279, 1228, 1197, 1153, 1107, 833, 788, 740, 522. HRMS (ESI^+): calcd. for [$C_{22}H_{18}F_4O_3$+Na^+] 429.1084, found 429.1085. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 9.8 min (major), 18.9 min (minor).



4b

Ethyl-(*R,E*)-3-(4-bromophenyl)-2-((1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure B as a colorless oil, 11.7 mg (50% yield), 95:5 **4**/**3**, 18:1 E/Z, 93% *ee*. $[\alpha]^{25}_{D}$ -26.2° (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.7 Hz, 1H), 7.66 (s, 1H), 7.61 (td, *J* = 7.5, 1.2 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.42 – 7.36 (m, 2H), 7.24 – 7.18 (m, 2H), 4.00 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.87 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.39 (d, *J* = 14.4 Hz, 1H), 3.34 (d, *J* = 17.7 Hz, 1H), 3.28 (d, *J* = 14.4 Hz, 1H), 3.22 (d, *J* = 17.6 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -72.08 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.3, 167.5, 151.4, 142.2, 135.7, 135.5, 133.6, 132.1, 130.7, 128.5, 128.2, 126.4 (q, *J* = 282.6 Hz), 126.3, 124.7, 123.4, 61.4, 56.2 (q, *J* = 23.9 Hz), 33.3, 28.6, 14.0. IR (cm^{-1}): 2922, 1724, 1608, 1487, 1369, 1278, 1235, 1153, 1111, 1010, 788, 740, 516. HRMS (ESI^+): calcd. for [$C_{22}H_{18}F_3BrO_3$+Na^+] 489.0284, found 489.0283. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 11.7 min (major), 21.2 min (minor).

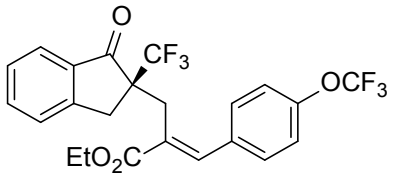


4c

Ethyl-(*R*,*E*)-2-((1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)-3-(4-(trifluoromethyl)phenyl)acrylate

The title compound was prepared according to the General Procedure B as a colorless oil, 9.8 mg (43% yield), 95:5 **4**/**3**, 13:1 E/Z, 93% *ee*. $[\alpha]^{25}_{D}$ -18.7° (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.70 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.60 (td, *J* = 7.4, 1.2 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.40 – 7.36 (m, 2H), 4.02 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.91 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.42 – z3.31 (m, 2H), 3.26 (d, *J* = 14.5 Hz, 1H), 3.22 (d, *J* = 17.7 Hz, 1H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.79 (s, 3F) , -72.07 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.2, 167.3, 151.3, 141.7, 138.4, 135.8, 135.5, 130.8 (q, *J* = 32.6 Hz), 129.9, 129.3, 128.2, 126.3 (q, *J* = 282.5 Hz), 126.3, 125.8 (q, *J* = 3.7 Hz), 124.7, 124.0 (q, *J* = 272.2 Hz), 61.5, 56.2 (q, *J* = 24.1 Hz), 33.5, 28.6, 14.0. IR (cm^{-1}): 2922, 1720, 1610, 1466, 1323, 1273, 1153, 1111, 1068, 1016, 934. 854, 788, 598, 512. HRMS

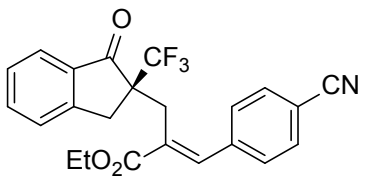
(ESI$^+$): calcd. for [$C_{23}H_{18}F_6O_3$+Na^+] 479.1052, found 479.1053. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 7.9 min (major), 14.3 min (minor).



4d

Ethyl-(*R,E*)-2-((1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)-3-(4-(trifluoromethoxy)phenyl)acrylate

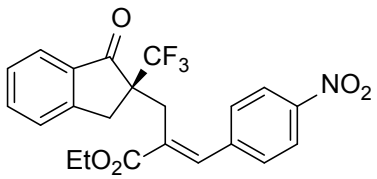
The title compound was prepared according to the General Procedure B as a colorless oil, 11.1 mg (47% yield), 94:6 **4**/**3**, 19:1 E/Z, 95% *ee*. $[\alpha]^{25}_D$ -14.1° (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 – 7.69 (m, 2H), 7.60 (td, *J* = 7.5, 1.2 Hz, 1H), 7.41 – 7.35 (m, 4H), 7.26 – 7.23 (m, 2H), 4.01 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.88 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.39 (d, *J* = 14.6 Hz, 1H), 3.35 (d, *J* = 17.7 Hz, 1H), 3.28 (d, *J* = 14.5 Hz, 1H), 3.23 (d, *J* = 17.6 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -57.75 (s, 3F), -72.10 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.3, 167.4, 151.4, 149.5, 141.8, 135.7, 135.5, 133.3, 130.7, 128.7, 128.2, 126.4 (q, *J* = 282.5 Hz), 126.3, 124.7, 121.1, 120.5 (q, *J* = 257.9 Hz), 61.4, 56.2 (q, *J* = 23.8 Hz), 33.3, 28.6, 14.0. IR (cm^{-1}): 2922, 1720, 1608, 1508, 1467, 1256, 1215, 1156, 1111, 1016, 933, 855, 788, 740, 541. HRMS (ESI$^+$): calcd. for [$C_{23}H_{18}F_3NO_3$+Na^+] 495.1001, found 495.1000. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 7.0 min (major), 11.5 min (minor).



4e

Ethyl-(*R,E*)-3-(4-cyanophenyl)-2-((1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

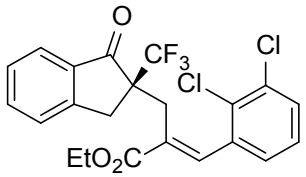
The title compound was prepared according to the General Procedure B as a colorless oil, 11.1 mg (47% yield), 94:6 **4**/**3**, 19:1 E/Z, 95% *ee*. $[\alpha]^{25}_{D}$ 130.4° (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 – 7.67 (m, 4H), 7.62 (td, *J* = 7.4, 1.2 Hz, 1H), 7.48 – 7.35 (m, 4H), 4.03 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.93 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.41 – 3.33 (m, 2H), 3.23 (m, 2H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -72.07 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.1, 167.1, 151.4, 141.1, 139.5, 135.9, 135.4, 132.5, 130.6, 129.6, 128.3, 126.3, 126.2 (q, *J* = 282.6 Hz), 124.7, 118.5, 112.5, 61.7, 56.2 (q, *J* = 23.9 Hz), 33.7, 28.6, 14.0. IR (cm^{-1}): 2922, 1720, 1605, 1467, 1370, 1273, 1235, 1194, 1153, 1098, 1013, 934, 857, 826, 788, 740, 557. HRMS (ESI^+): calcd. for [$C_{23}H_{18}F_3NO_3$+Na^+] 436.1131, found 436.1132. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=2:8), 1.0 mL/min; t_R = 12.7 min (major), 27.7 min (minor).



4f

Ethyl-(*R*,*E*)-3-(4-nitrophenyl)-2-((1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

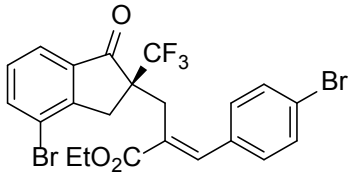
The title compound was prepared according to the General Procedure B as a colorless oil, 10.2 mg (47% yield), 95:5 **4**/**3**, 10:1 E/Z, 96% *ee*. $[\alpha]^{25}_{D}$ -30.2° (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.29 – 8.23 (m, 2H), 7.74 (s, 1H), 7.70 (m, 1H), 7.62 (td, *J* = 7.5, 1.2 Hz, 1H), 7.49 (m, 2H), 7.40 (m, 2H), 4.04 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.95 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.42 – 3.33 (m, 2H), 3.24 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -72.06 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.0, 167.1, 151.4, 147.7, 141.4, 140.7, 135.9, 135.4, 131.1, 129.8, 128.3, 126.3, 126.2 (q, *J* = 282.5 Hz), 124.8, 124.0, 61.7, 56.2 (q, *J* = 24.2 Hz), 33.8, 28.7, 14.0. IR (cm^{-1}): 2933, 1713, 1597, 1519, 1343, 1224, 1105, 1025, 928, 851, 749, 687. HRMS (ESI^+): calcd. for [$C_{22}H_{18}F_3NO_5$+Na^+] 456.1029, found 456.1030. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=2:8), 1.0 mL/min; t_R = 14.1 min (major), 30.6 min (minor).



4g

Ethyl-(*R,E*)-3-(2,3-dichlorophenyl)-2-((1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate (a mixture of isomers with 10:1 E/Z)

The title compound was prepared according to the General Procedure B as a colorless oil, 9.4 mg (41% yield), 95:5 **4**/**3**, 10:1 E/Z, 99% *ee*. $[\alpha]^{25}_{D}$ -2.8° (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-d) δ 7.72 (s, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.60 (td, J = 7.5, 1.2 Hz, 1H), 7.47 (dd, J = 8.0, 1.6 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.29 – 7.23 (m, 1H), 7.19 (d, J = 7.6, 1.2 Hz, 1H), 4.06 (dq, J = 10.8, 7.2 Hz, 1H), 3.94 (dq, J = 10.8, 7.2 Hz, 1H), 3.38 – 3.24 (m, 2H), 3.19 – 3.08 (m, 2H), 1.16 (t, J = 7.1 Hz, 3H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -72.59 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-d) δ 199.2, 167.0, 151.6, 143.5, 140.6, 135.8, 135.8, 133.7, 132.2, 130.8, 130.3, 128.2, 128.1, 127.7, 126.4, 126.2 (q, J = 282.6 Hz) 124.7, 61.6, 56.1 (q, J = 23.9 Hz), 32.9, 27.9, 14.0. IR (cm^{-1}): 2924, 1720, 1608, 1448, 1410, 1370, 1277, 1228, 1153, 1097, 1026, 787, 736, 470. HRMS (ESI^+): calcd. for $[C_{22}H_{17}Cl_2F_3O_3+Na^+]$ 479.0399, found 479.0400. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 10.5 min (major), 14.3 min (minor).

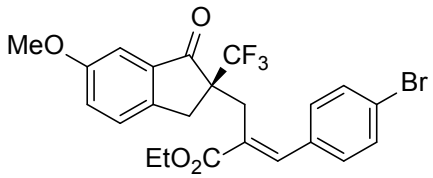


4h

Ethyl-(*R,E*)-2-((4-bromo-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)-3-(4-bromophenyl)acrylate

The title compound was prepared according to the General Procedure B as a colorless oil, 10.9 mg (40% yield), 92:8 **4**/**3**, 12:1 E/Z, 84% *ee*. $[\alpha]^{25}_{D}$ -10.6° (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.62 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.39 – 7.34 (m, 1H), 7.23 – 7.19 (m, 2H),

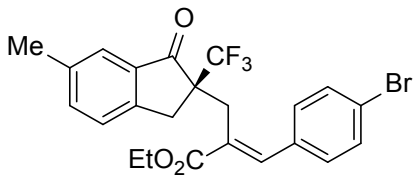
4.01 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.93 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.38 (d, *J* = 14.6 Hz, 1H), 3.29 (d, *J* = 10.0 Hz, 1H), 3.26 (d, *J* = 13.7 Hz, 1H), 3.16 (d, *J* = 18.1 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -72.10 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.4, 167.3, 148.9, 142.6, 137.4, 135.3 , 133.5, 132.6, 132.1, 130.6, 129.7, 128.0, 126.1 (q, *J* = 282.6 Hz), 123.5, 122.9, 61.5, 56.5 (q, *J* = 24.2 Hz), 32.4, 28.5, 14.0. IR (cm^{-1}): 2921, 1703, 1601, 1487, 1461, 1263, 1231, 1153, 1107, 1074, 1008, 943, 807, 744, 501. HRMS (ESI$^+$): calcd. for [$C_{22}H_{17}Br_2F_3O_3$+Na$^+$] 566.9389, not found. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:19), 1.0 mL/min; t_R = 10.3 min (major), 19.2 min (minor).



4i

Ethyl-(*R,E*)-3-(4-bromophenyl)-2-((6-methoxy-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

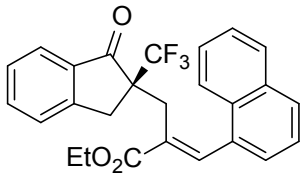
The title compound was prepared according to the General Procedure B as a colorless oil, 9.2 mg (37% yield), 92:8 **4**/**3**, 15:1 E/Z, 90% *ee*. $[\alpha]^{25}_D$ -13.5^o (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (s, 1H), 7.55 – 7.50 (m, 2H), 7.27 – 7.25 (m, 2H), 7.23 – 7.17 (m, 4H), 7.11 (d, *J* = 2.4 Hz, 1H), 4.02 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.92 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.83 (s, 3H), 3.38 (d, *J* = 14.6 Hz, 1H), 3.30 – 3.19 (m, 2H), 3.12 (d, *J* = 17.3 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -72.15 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.3, 167.5, 159.9, 144.3, 142.0, 136.8, 133.7, 132.1, 130.7, 128.5, 127.0, 126.4 (q, *J* = 282.6 Hz), 125.2, 123.4, 105.6, 61.4, 57.0 (q, *J* = 24.1 Hz), 55.8, 32.6, 28.6, 14.0. IR (cm^{-1}): 2920, 1715, 1631, 1489, 1433, 1275, 1226, 1151, 1107, 1073, 1010, 818, 766, 511. HRMS (ESI$^+$): calcd. for [$C_{23}H_{20}BrF_3O_4$+Na$^+$] 519.0389, found 519.0386. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 16.0 min (major), 25.1 min (minor).



4j

Ethyl-(*R,E*)-3-(4-bromophenyl)-2-((6-methyl-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure B as a colorless oil, 9.1 mg (38% yield), 92:8 **4**/**3**, 12:1 E/Z, 90% *ee*. $[\alpha]^{25}_{D}$ -10.0° (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 7.55 – 7.50 (m, 2H), 7.49 (d, *J* = 1.6 Hz, 1H), 7.41 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.23 – 7.18 (m, 2H), 4.01 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.89 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.37 (d, *J* = 14.5 Hz, 1H), 3.31 – 3.23 (m, 2H), 3.14 (d, *J* = 17.5 Hz, 1H), 2.39 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -72.08 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.4, 167.5, 148.8, 142.0, 138.3, 137.0, 135.7, 133.7, 132.1, 130.7, 128.6, 126.4 (q, *J* = 282.6 Hz), 125.9, 124.5, 123.4, 61.4, 56.5 (q, *J* = 23.8 Hz), 33.0, 28.6, 21.2, 14.0. IR (cm^{-1}): 2922, 1709, 1584, 1489, 1353, 1280, 1232, 1174, 1146, 1092, 1008, 956, 822, 646, 505. HRMS (ESI^+): calcd. for [$C_{23}H_{20}BrF_3O_3$+Na^+] 503.0440, found 503.0441. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 12.3 min (major), 19.1 min (minor).

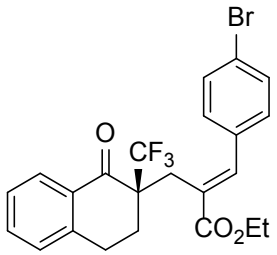


4k

Ethyl-(*R,E*)-3-(naphthalen-1-yl)-2-((1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-inden-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure B as a colorless oil, 8.8 mg (40% yield), 93:7 **4**/**3**, 9:1 E/Z, 98% *ee*. $[\alpha]^{25}_{D}$ -14.5° (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.81 – 7.74 (m, 2H), 7.65 – 7.61 (m, 1H), 7.49 – 7.36 (m, 6H), 7.25 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.21 (td, *J* = 7.5, 0.9 Hz, 1H), 7.14 (dt, *J* = 7.6, 1.0 Hz, 1H), 4.00 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.88 (dq, *J* = 10.8, 7.1

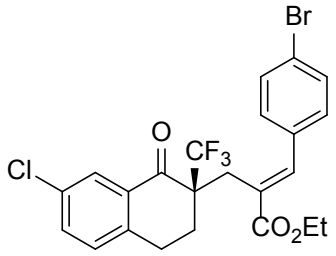
Hz, 1H), 3.28 (d, *J* = 14.3 Hz, 1H), 3.19 (d, *J* = 14.2 Hz, 1H), 3.07 (d, *J* = 17.6 Hz, 1H), 2.97 (d, *J* = 17.7 Hz, 1H), 1.11 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -72.37 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.3, 167.3, 151.3, 142.5, 135.6, 135.5, 133.6, 132.0, 131.6, 130.0, 129.3, 128.8, 128.0, 126.7, 126.4, 126.2 (q, *J* = 282.5 Hz), 126.1, 126.1, 125.4, 124.5, 124.4, 61.4, 56.3 (q, *J* = 24.1 Hz), 32.9, 28.3, 14.0. IR (cm^{-1}): 2931, 1720, 1607, 1447, 1367, 274, 1228, 1150, 1100, 1034, 936, 863, 803, 781, 736, 688, 423. HRMS (ESI$^+$): calcd. for [$C_{26}H_{21}F_3O_3$+Na^+] 461.1335, found 461.1332. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 14.7 min (major), 28.1 (minor).



4l

Ethyl-(*R,E*)-3-(4-bromophenyl)-2-((1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-2-yl)methyl)acrylate

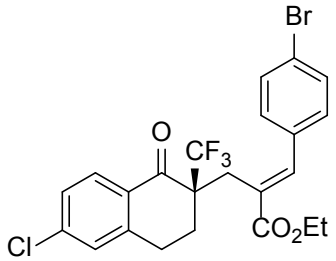
The title compound was prepared according to the General Procedure B as a white solid, 9.0 mg (37% yield), 91:9 **4**/**3**, 10:1 E/Z, 99% *ee*. $[\alpha]^{25}_D$ -13.2° (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.69 (s, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.28 (td, *J* = 7.7, 1.2 Hz, 1H), 7.17 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.16 – 7.11 (m, 2H), 4.18 – 4.02 (m, 2H), 3.05 – 2.85 (m, 2H), 2.32 (ddd, *J* = 14.1, 8.5, 5.6 Hz, 1H), 2.13 (dt, *J* = 14.0, 5.8 Hz, 1H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -69.85 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.9, 167.9, 142.3, 141.4, 134.1, 133.9, 131.8, 130.3, 129.3, 128.5, 128.3, 127.1, 126.5 (q, *J* = 285.4 Hz), 122.8, 61.4 , 53.7 (q, *J* = 22.0 Hz), 27.9, 27.1, 24.7, 14.0. IR (cm^{-1}): 2939, 1709, 1686, 1601, 1487, 1455, 1368, 1262, 1234, 1170, 1121, 1074, 930, 741. HRMS (ESI$^+$): calcd. for [$C_{23}H_{20}BrF_3O_3$+Na^+] 503.0440, found 503.0443. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 16.6 min (major), 19.3 min (minor).



4m

Ethyl-(*R,E*)-3-(4-bromophenyl)-2-((7-chloro-1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure B as a white solid, 9.0 mg (43% yield), 93:7 **4**/**3**, 12:1 E/Z, 99% *ee*. $[\alpha]^{25}_{D}$ -14.8° (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 2.3 Hz, 1H), 7.69 (s, 1H), 7.50 – 7.37 (m, 3H), 7.18 – 7.07 (m, 4H), 4.18 – 4.05 (m, 2H), 3.36 – 3.26 (m, 2H), 3.01 – 2.86 (m, 2H), 2.30 (ddd, *J* = 14.2, 8.5, 5.6 Hz, 1H), 2.12 (dt, *J* = 14.1, 5.7 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -69.98 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 190.7, 167.8, 141.6, 140.4, 134.0, 133.7, 133.3, 132.9, 131.8, 130.3, 130.1, 129.0, 128.1, 126.3 (q, *J* = 285.4 Hz), 122.8, 61.5, 53.6 (q, *J* = 22.3 Hz), 27.8, 26.9, 24.2, 14.1. IR (cm^{-1}): 2939, 1716, 1595, 1446, 1368, 1299, 1252, 1224, 1159, 1081, 1006, 963, 811, 630, 503. HRMS (ESI^+): calcd. for $[C_{23}H_{19}BrClF_3O_3+Na^+]$ 537.0050, found 537.0049. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 14.5 min (major), 23.9 min (minor).

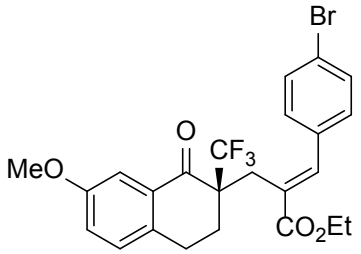


4n

Ethyl-(*R,E*)-3-(4-bromophenyl)-2-((6-chloro-1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure B as a white solid, 9.0 mg (45% yield), 93:7 **4**/**3**, 10:1 E/Z, 99% *ee*. $[\alpha]^{25}_{D}$ -14.3° (c = 0.1, $CHCl_3$); ^{1}H

NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.5 Hz, 1H), 7.70 (s, 1H), 7.48 – 7.43 (m, 2H), 7.30 – 7.25 (m, 1H), 7.19 (d, *J* = 2.0 Hz, 1H), 7.16 – 7.12 (m, 2H), 4.20 – 4.05 (m, 2H), 3.31 (s, 2H), 3.00 – 2.91 (m, 2H), 2.31 (ddd, *J* = 14.1, 8.4, 5.6 Hz, 1H), 2.12 (dt, *J* = 14.0, 5.9 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -69.91 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 190.9, 167.9, 143.8, 141.6, 140.4, 134.1, 131.9, 130.3, 130.1, 129.1, 128.5, 128.4, 127.7, 126.4 (q, *J* = 285.4 Hz), 122.9, 61.5, 53.6 (q, *J* = 22.2 Hz), 27.8, 27.1, 24.6, 14.2. IR (cm^{-1}): 2930, 1709, 1683, 1592, 1444, 1366, 1301, 1280, 1234, 1157, 1157, 1072, 930, 814, 759, 503, 430. HRMS (ESI$^+$): calcd. for [$C_{23}H_{19}BrClF_3O_3$+Na$^+$] 537.0050, found 537.0051. The enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=1:9), 1.0 mL/min; t_R = 15.7 min (minor), 17.3 min (major).



4o

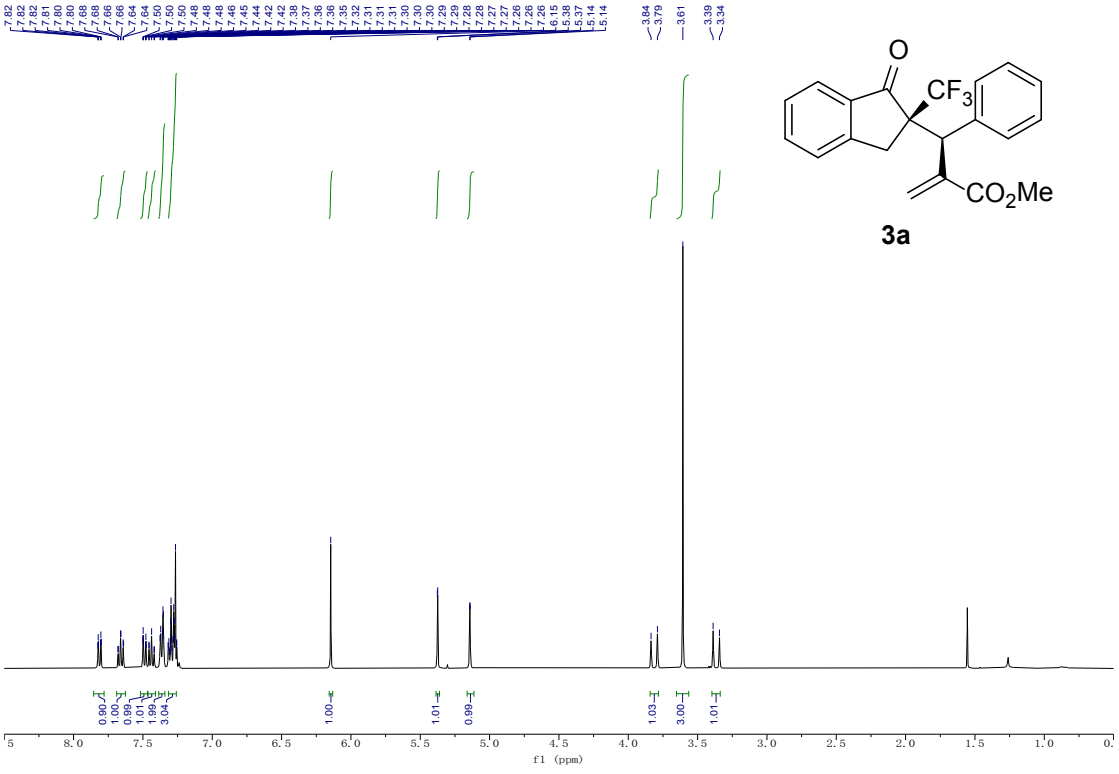
Ethyl-(*R,E*)-3-(4-bromophenyl)-2-((7-methoxy-1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-2-yl)methyl)acrylate

The title compound was prepared according to the General Procedure B as a white solid, 13.0 mg (51% yield), 94:6 **4**/**3**, 16:1 E/Z, 99% *ee*. $[\alpha]^{25}_D$ -20.9° (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (s, 1H), 7.43 – 7.38 (m, 2H), 7.32 (d, *J* = 2.6 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.09 – 7.01 (m, 2H), 4.20 – 4.03 (m, 2H), 3.80 (s, 3H), 3.39 – 3.23 (m, 2H), 2.97 – 2.80 (m, 2H), 2.30 (ddd, *J* = 14.2, 8.7, 5.6 Hz, 1H), 2.11 (dt, *J* = 14.0, 5.7 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -69.95 (s, 3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.8, 167.9, 158.5, 141.3, 134.9, 134.1, 132.5, 131.8, 130.3, 129.7, 129.3, 126.5 (q, *J* = 286.2 Hz), 122.7, 122.3, 110.2, 61.4, 55.5, 53.6 (q, *J* = 22.1 Hz), 28.1, 27.0, 23.9, 14.1. IR (cm^{-1}): 2930, 1687, 1610, 1498, 1422, 1366, 1329, 1250, 1170, 1071, 1010, 971, 814, 501. HRMS (ESI$^+$): calcd. for [$C_{24}H_{22}BrF_3O_4$+Na$^+$] 533.0546, found 533.0542. The

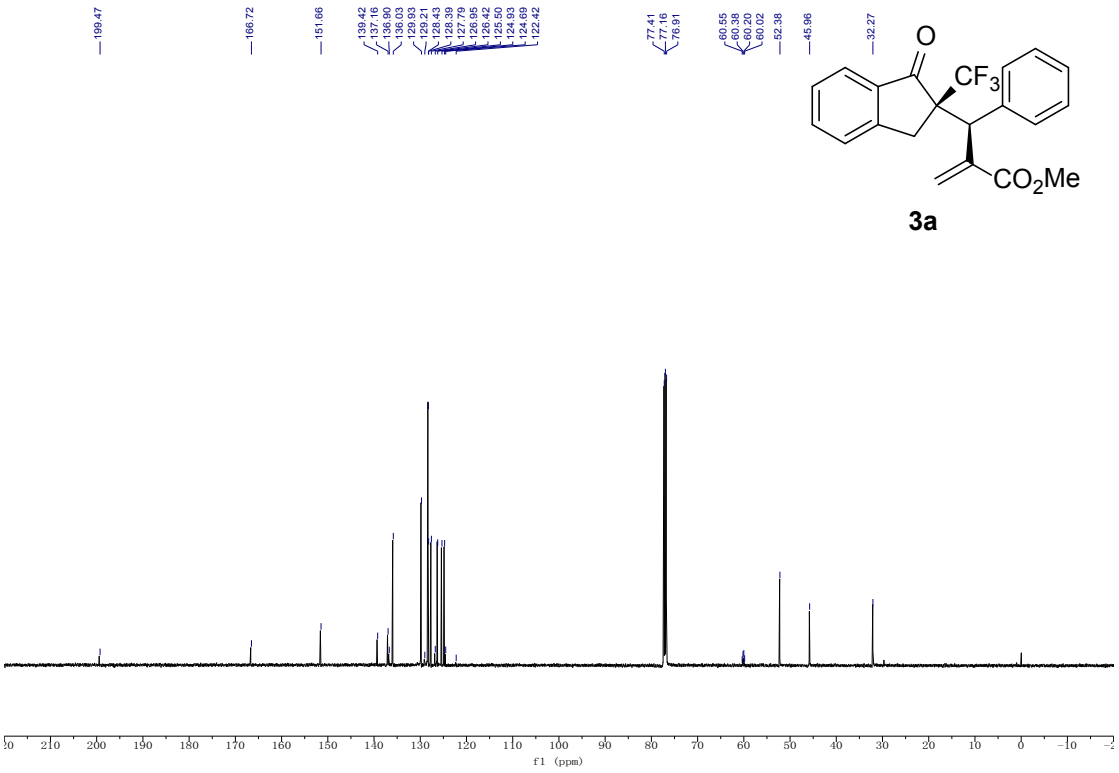
enantiomeric excess was determined by HPLC with an IG-3 column at 254 nm (2-propanol:hexane=2:8), 1.0 mL/min; t_R = 19.0 min (major), 25.1 min (minor).

NMR data

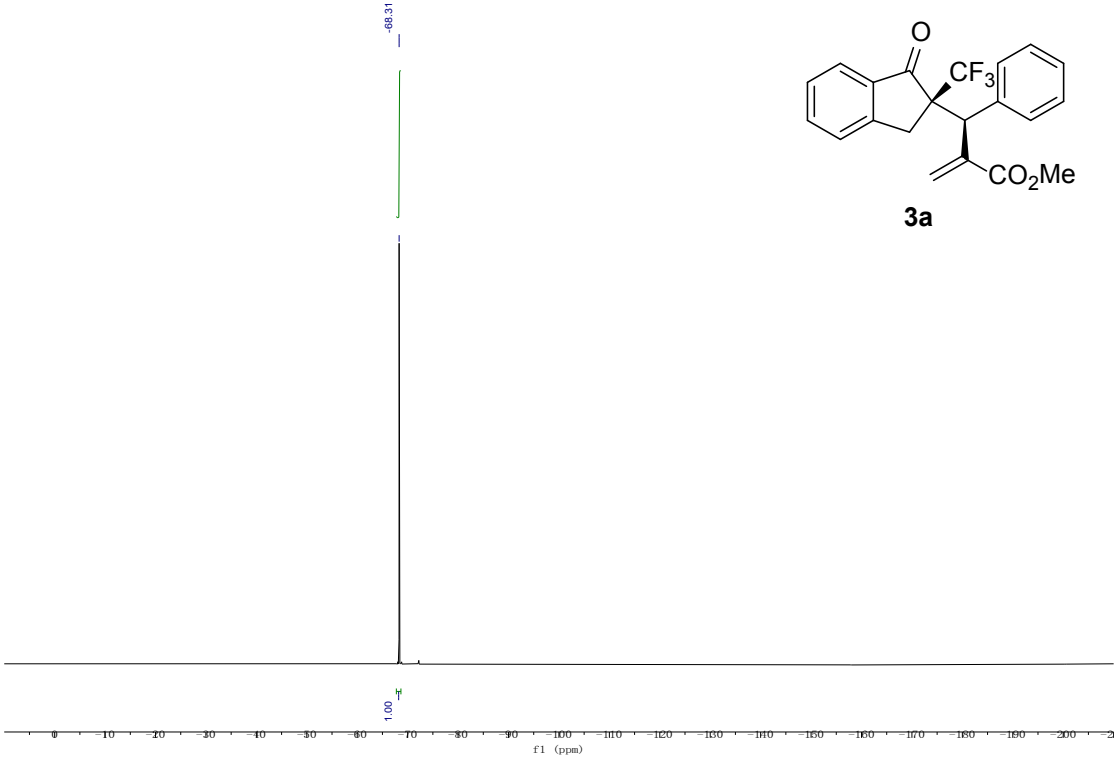
^{1}H NMR spectrum of 3a



^{13}C NMR spectrum of 3a

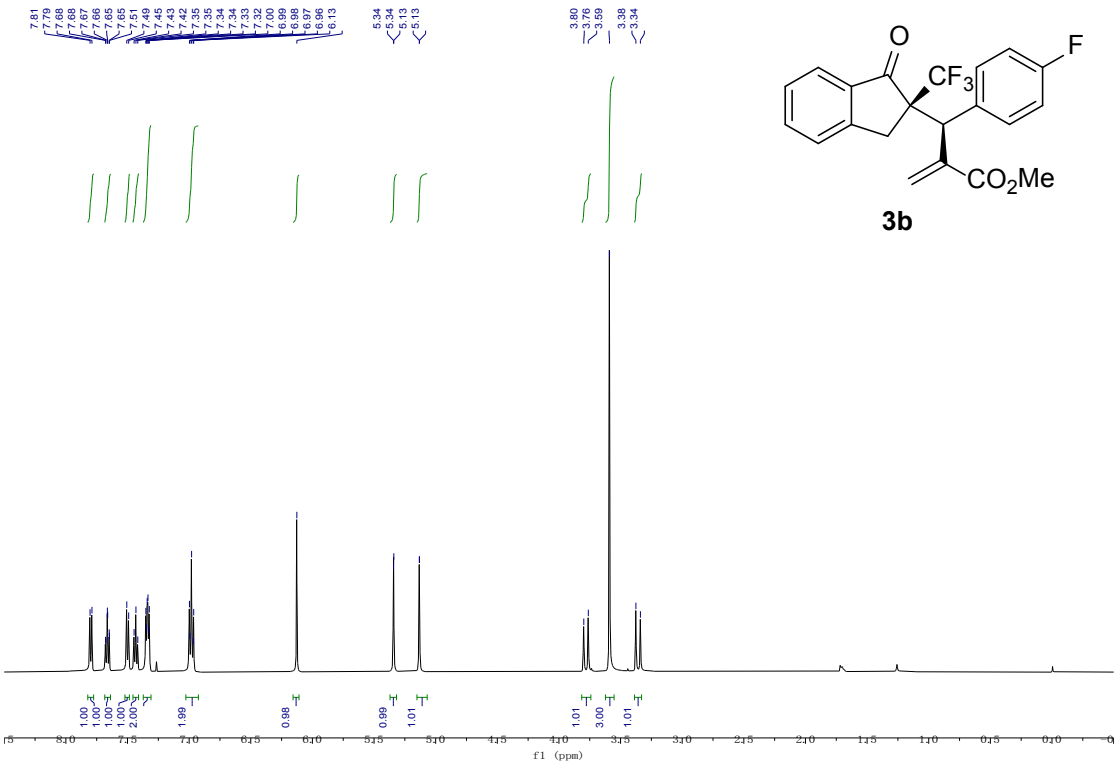


^{19}F NMR spectrum of 3a



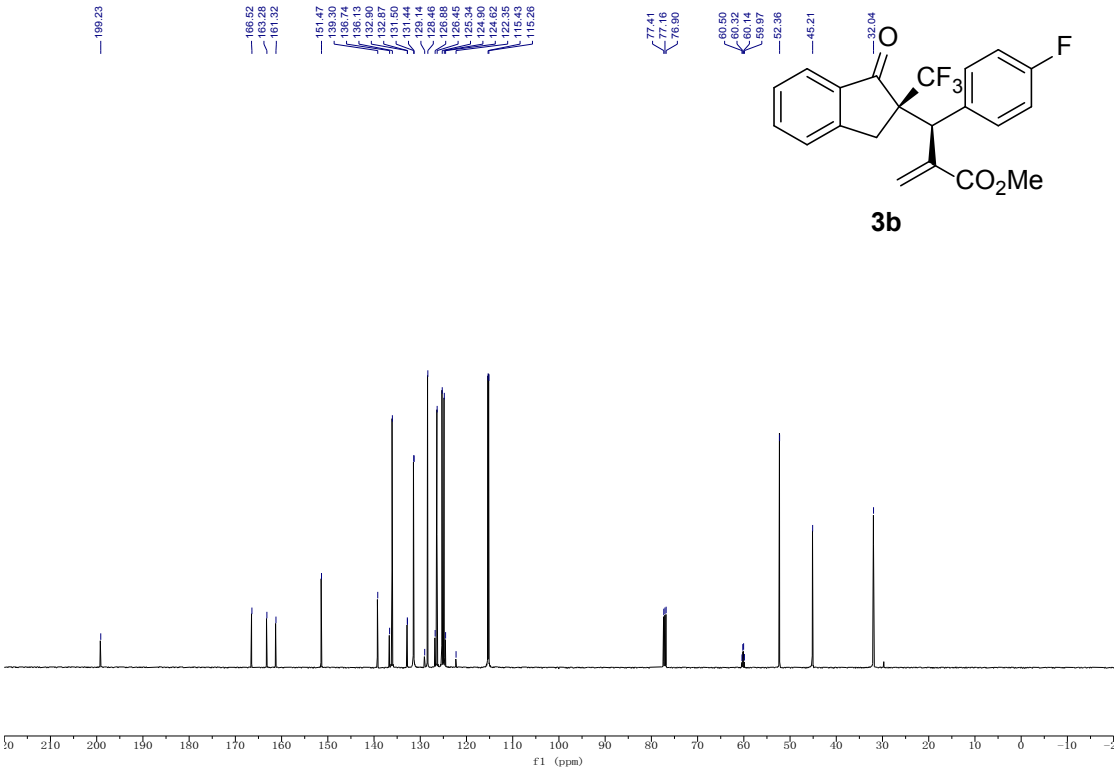
3a

^{1}H NMR spectrum of 3b

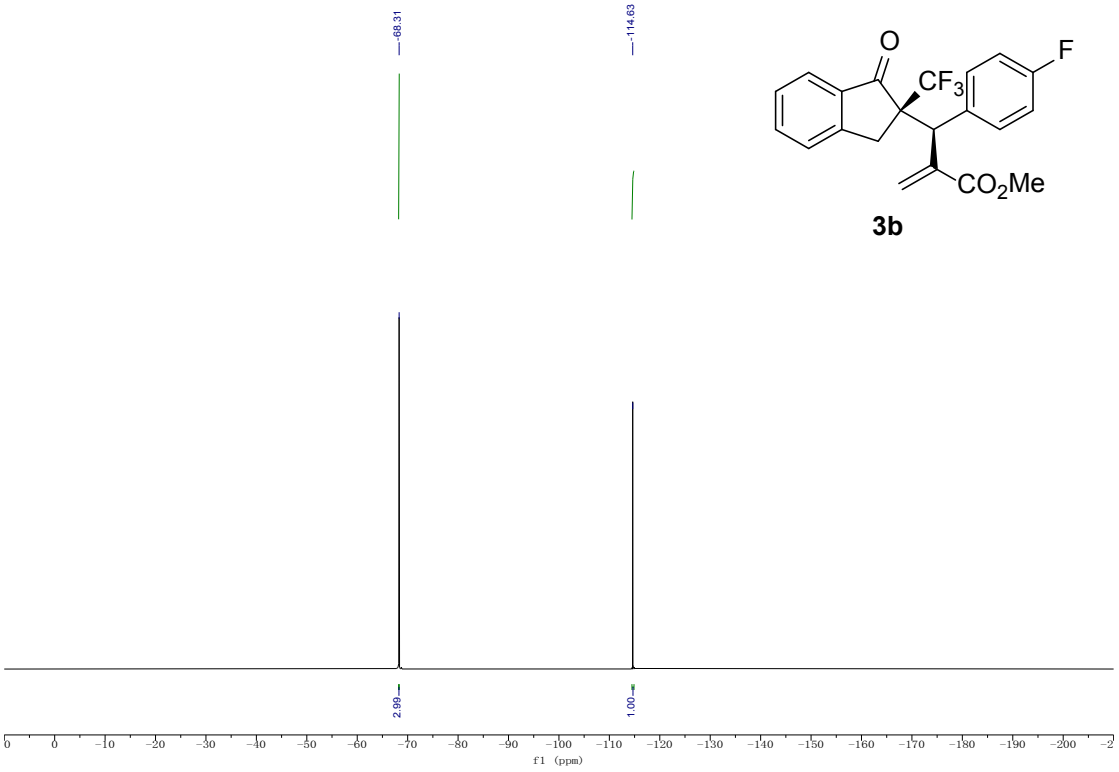


3b

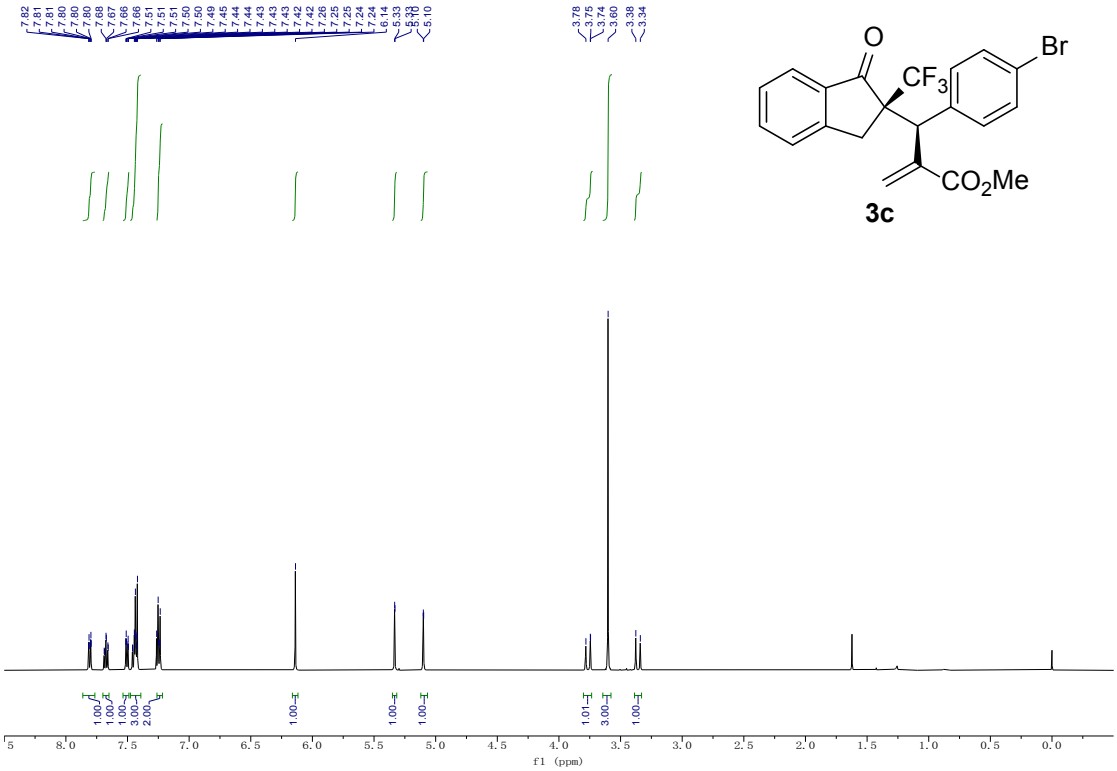
^{13}C NMR spectrum of 3b



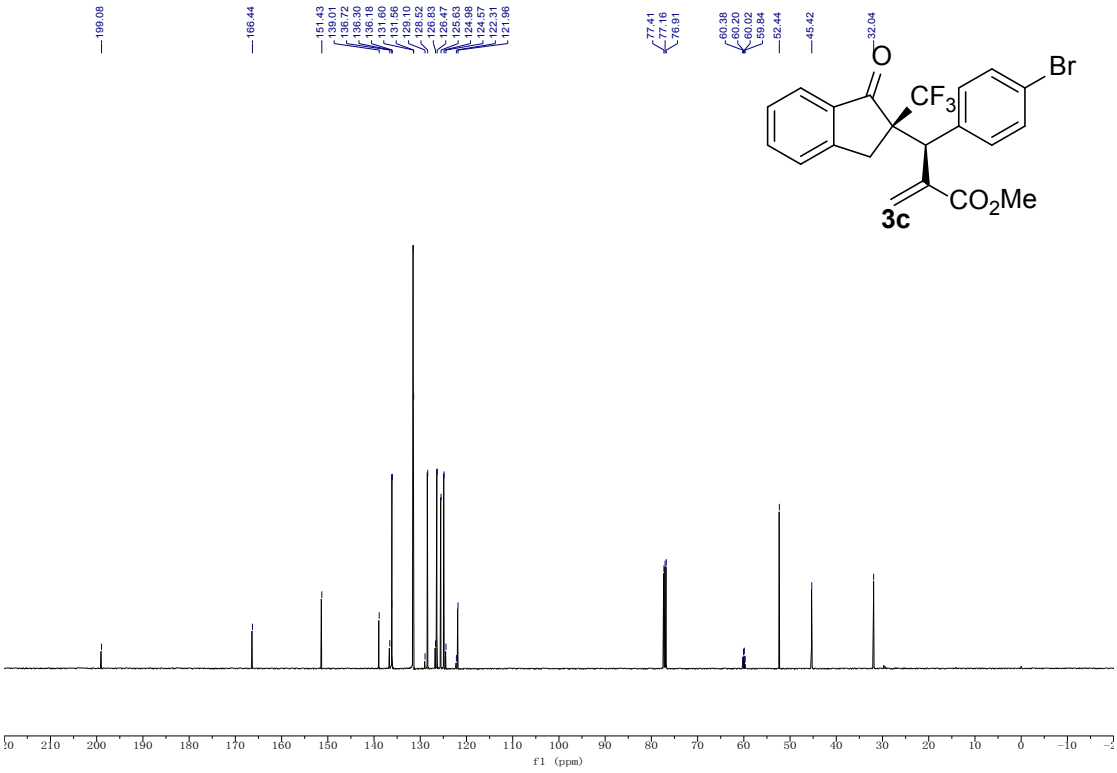
^{19}F NMR spectrum of 3b



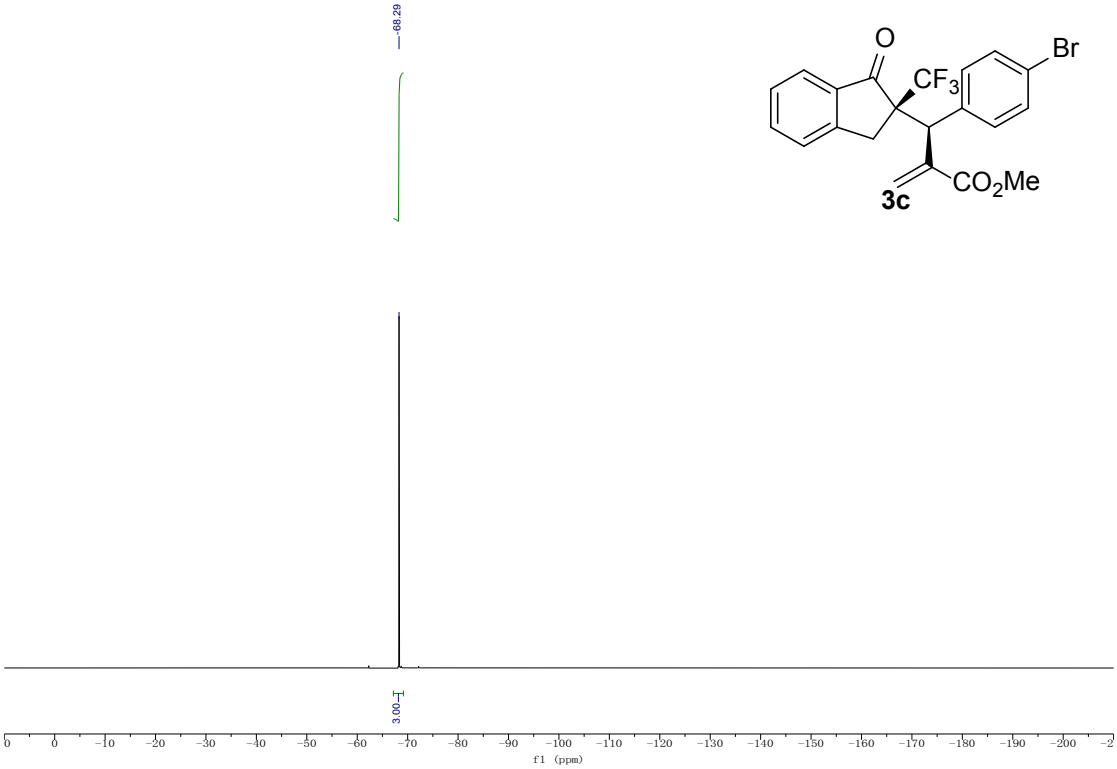
^{1}H NMR spectrum of 3c



^{13}C NMR spectrum of 3c

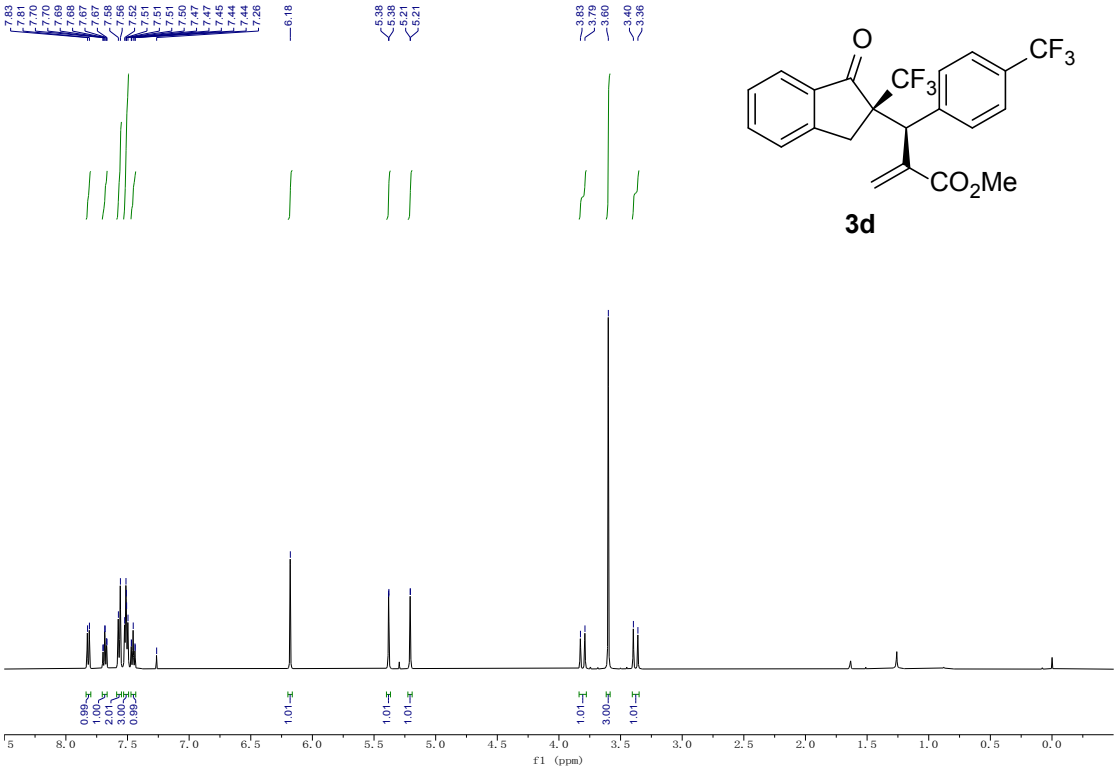


^{19}F NMR spectrum of 3c



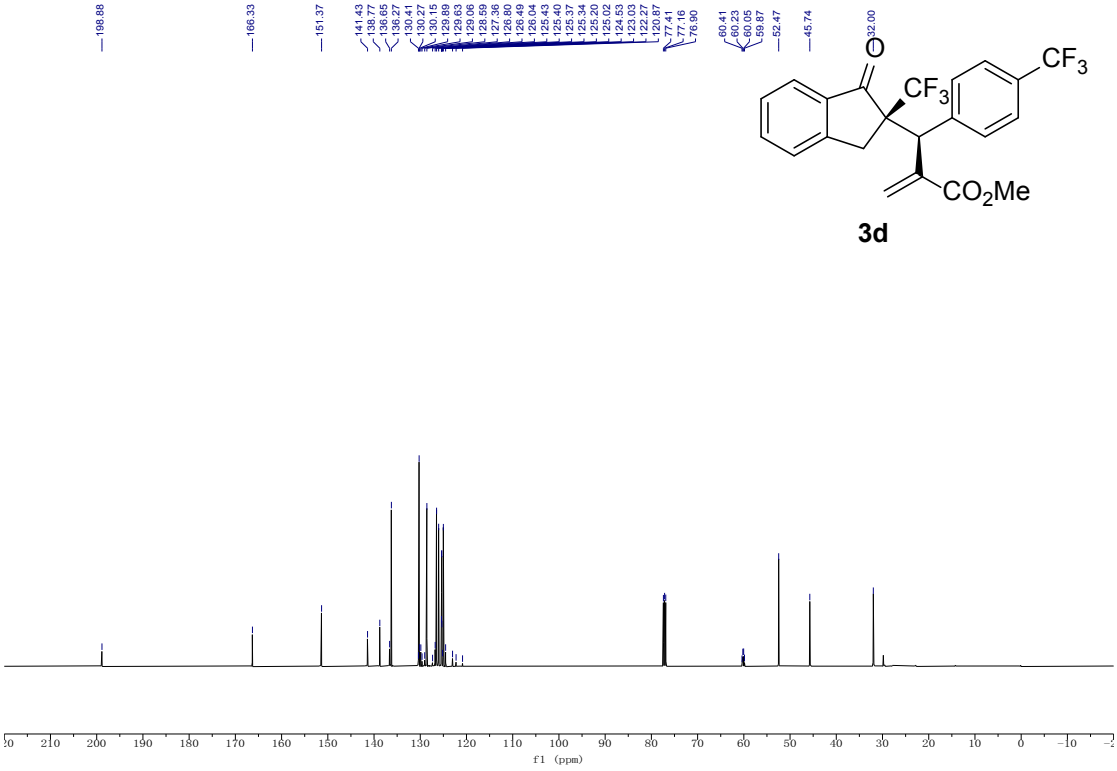
3c

^{1}H NMR spectrum of 3d

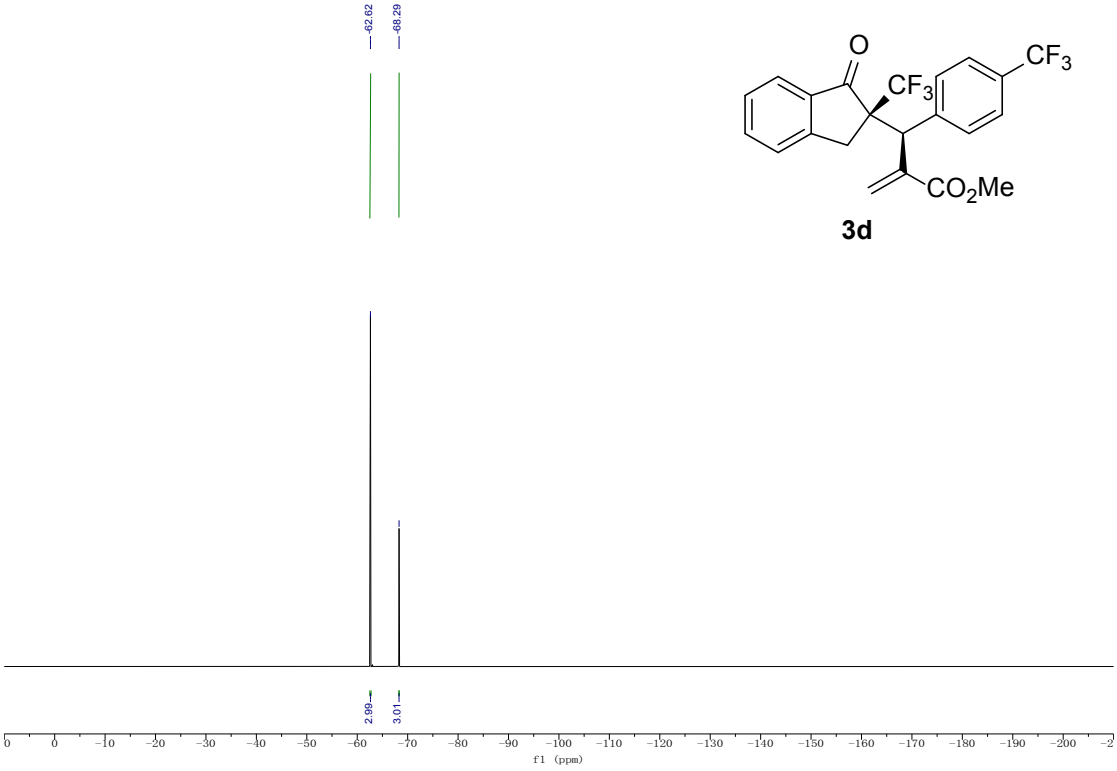


3d

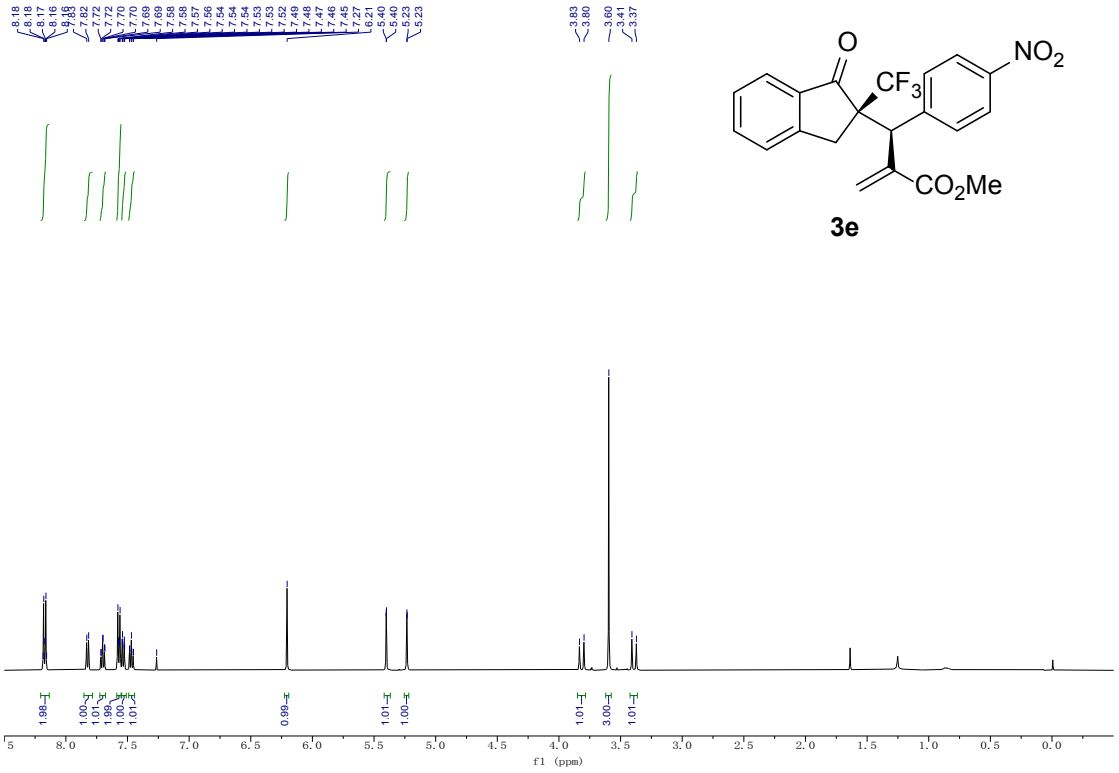
^{13}C NMR spectrum of 3d



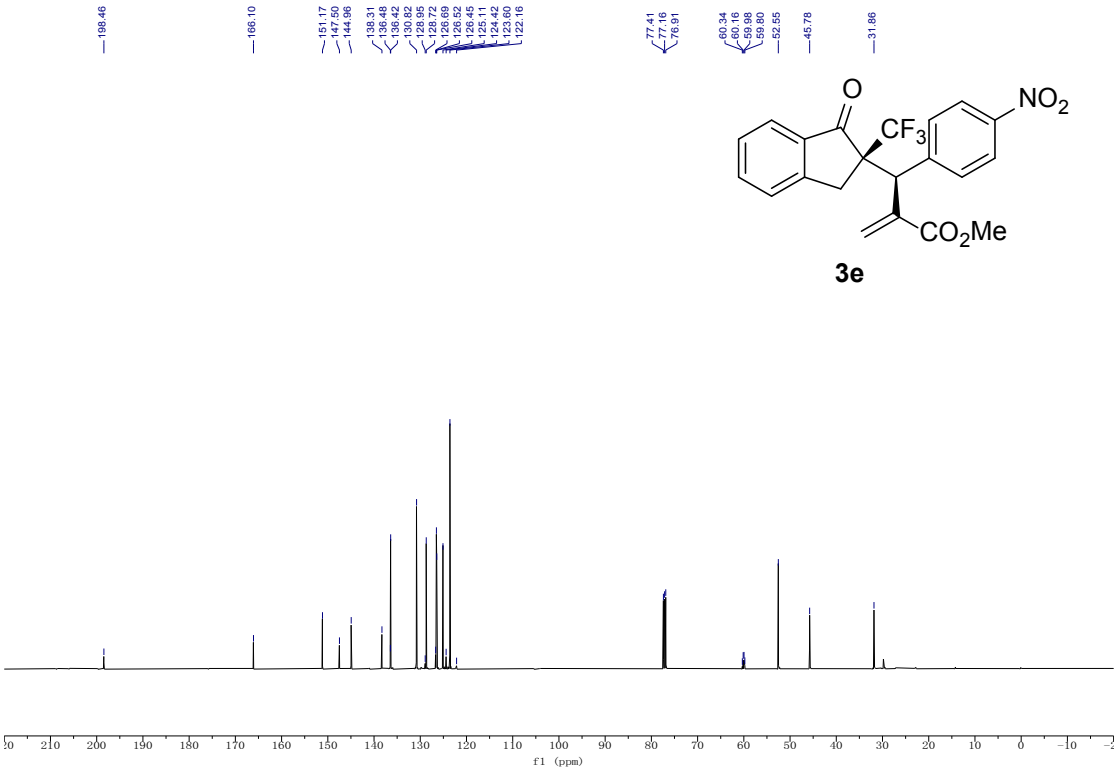
^{19}F NMR spectrum of 3d



^{1}H NMR spectrum of 3e



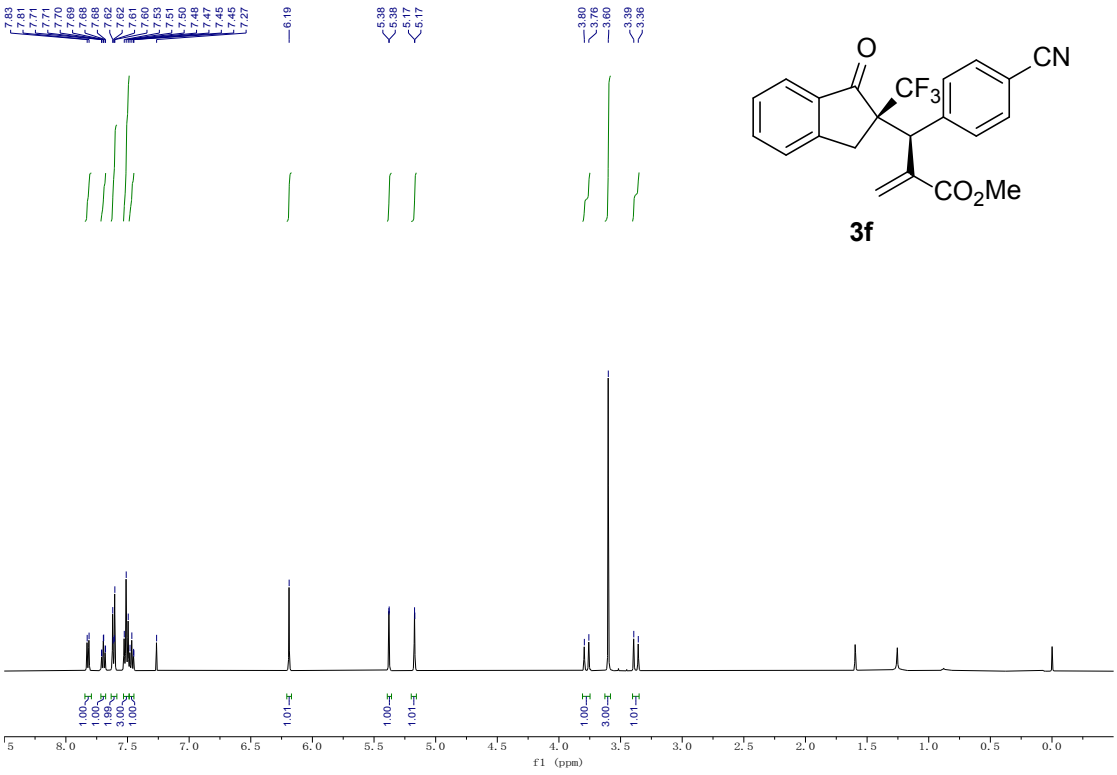
^{13}C NMR spectrum of 3e



^{19}F NMR spectrum of 3e

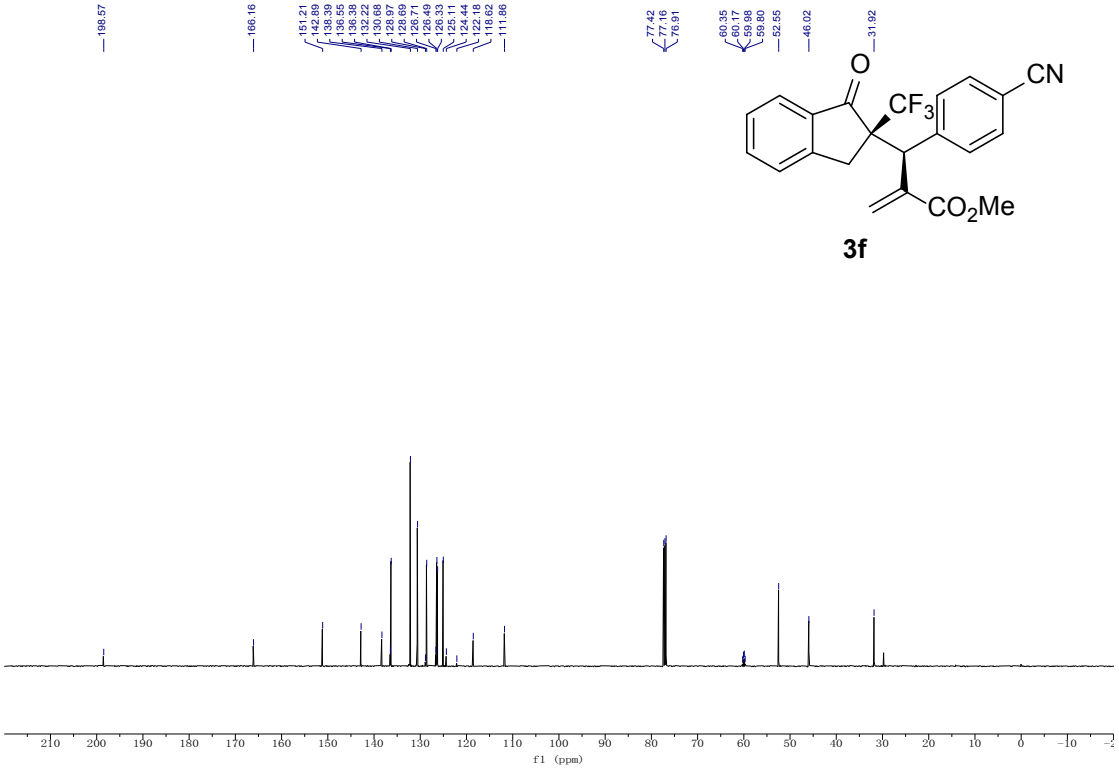
3e

^{1}H NMR spectrum of 3f

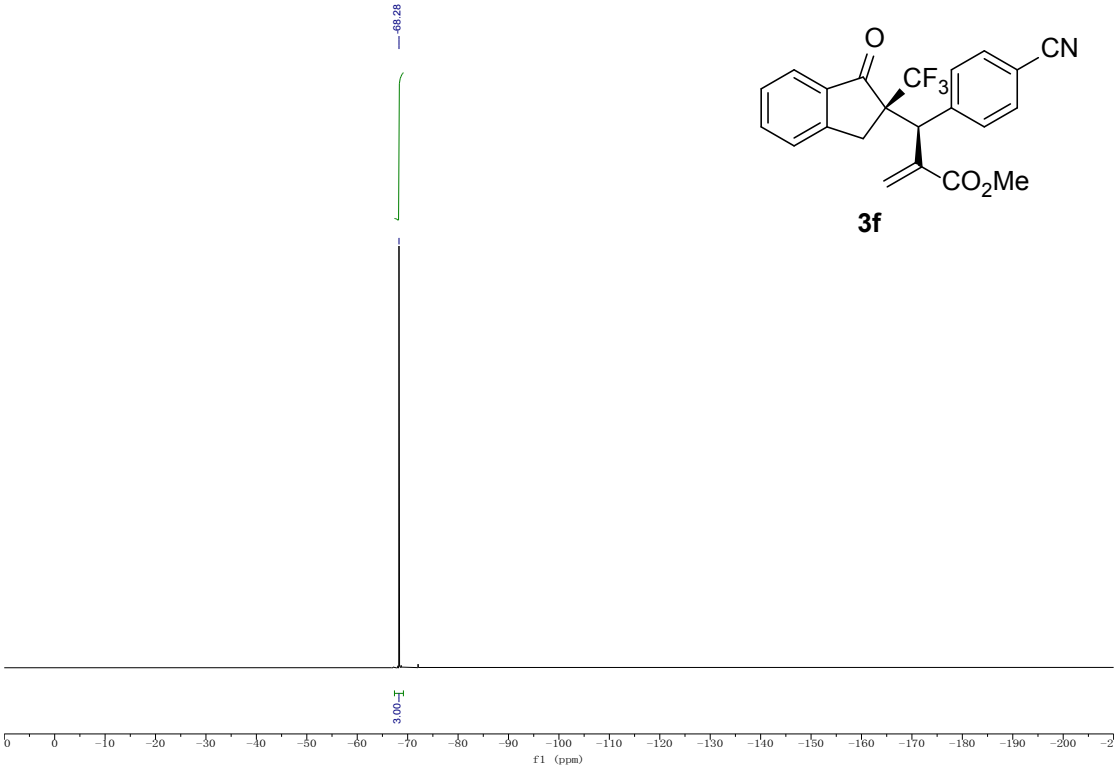


3f

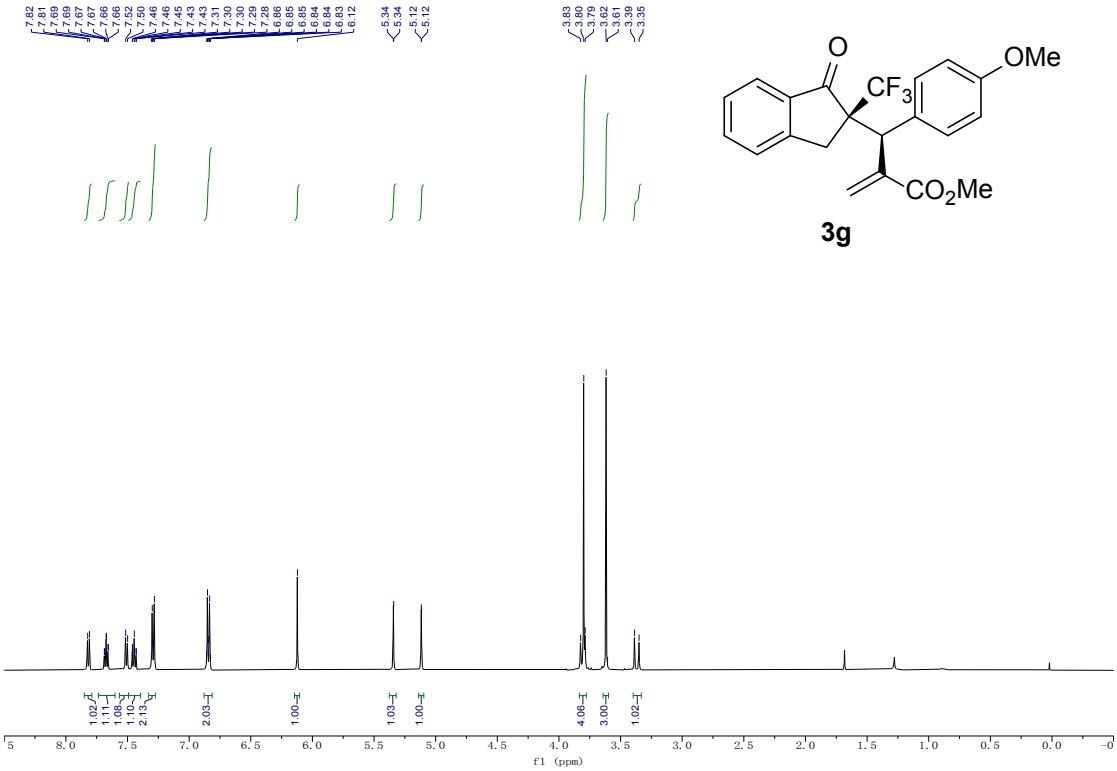
^{13}C NMR spectrum of 3f



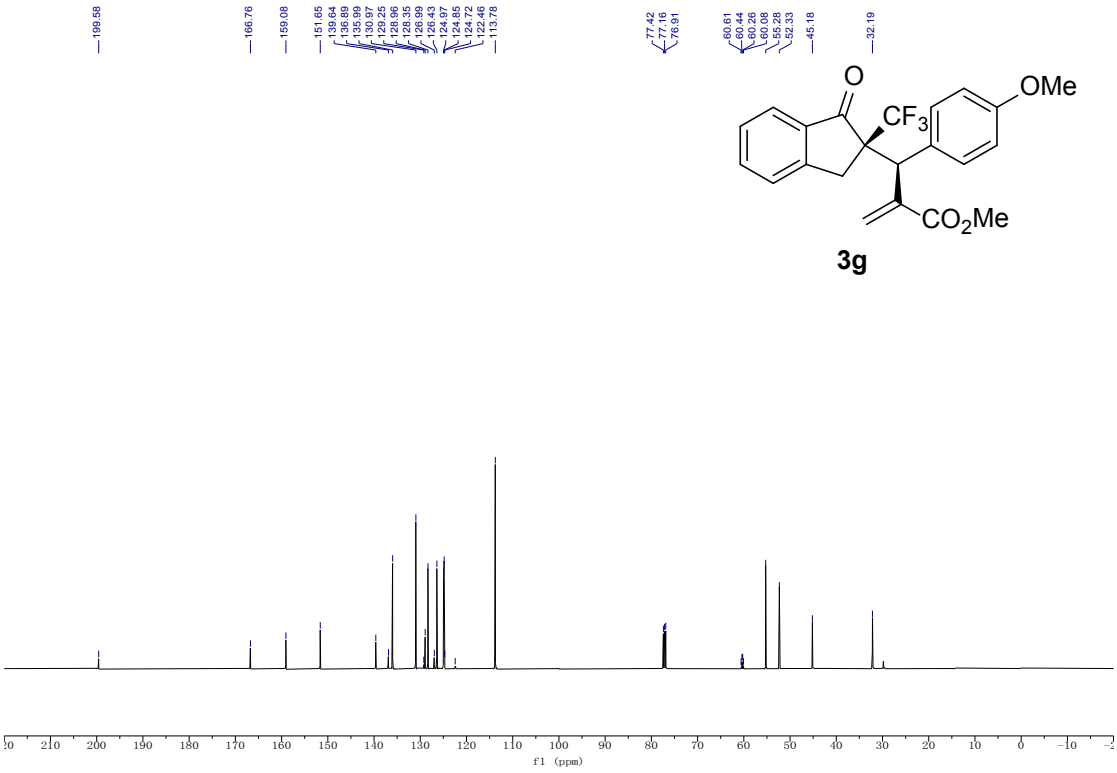
^{19}F NMR spectrum of 3f



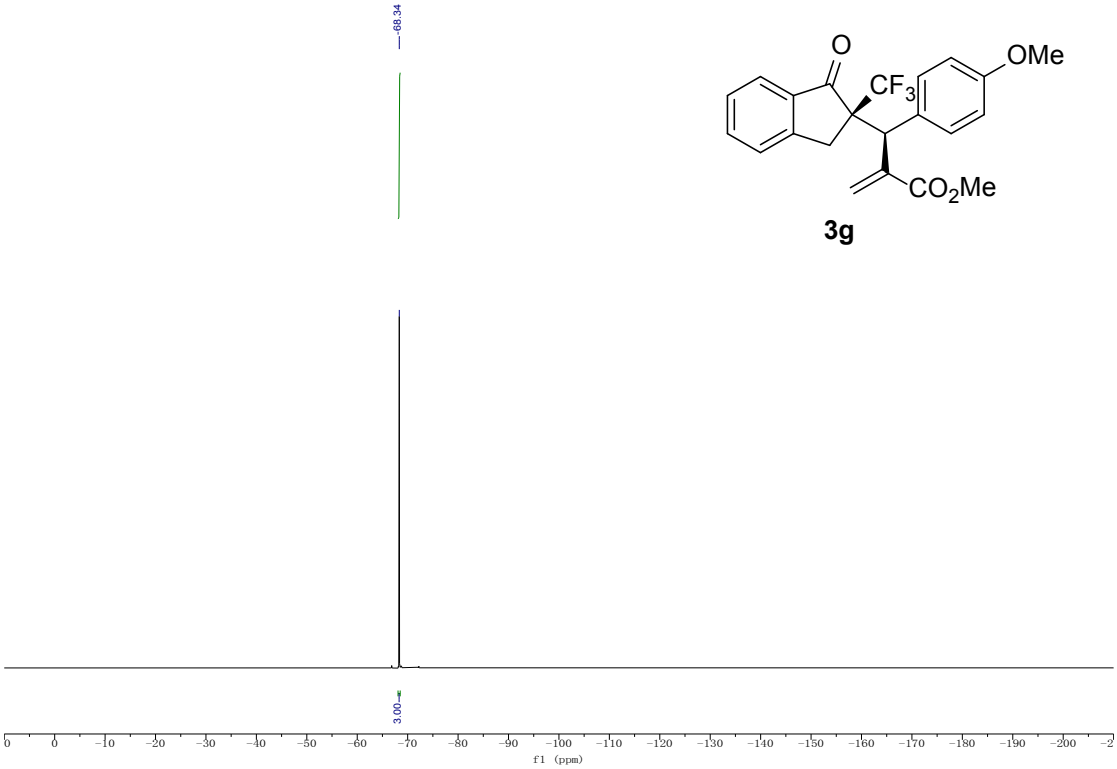
^{1}H NMR spectrum of 3g



^{13}C NMR spectrum of 3g

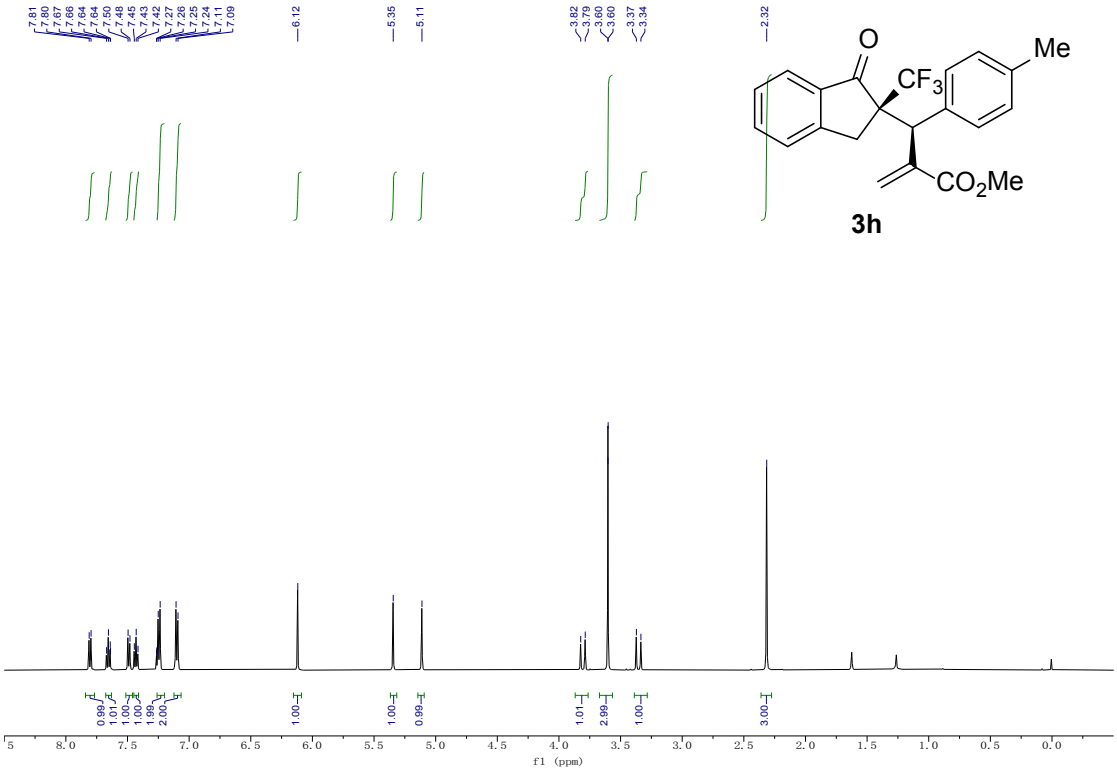


^{19}F NMR spectrum of 3g



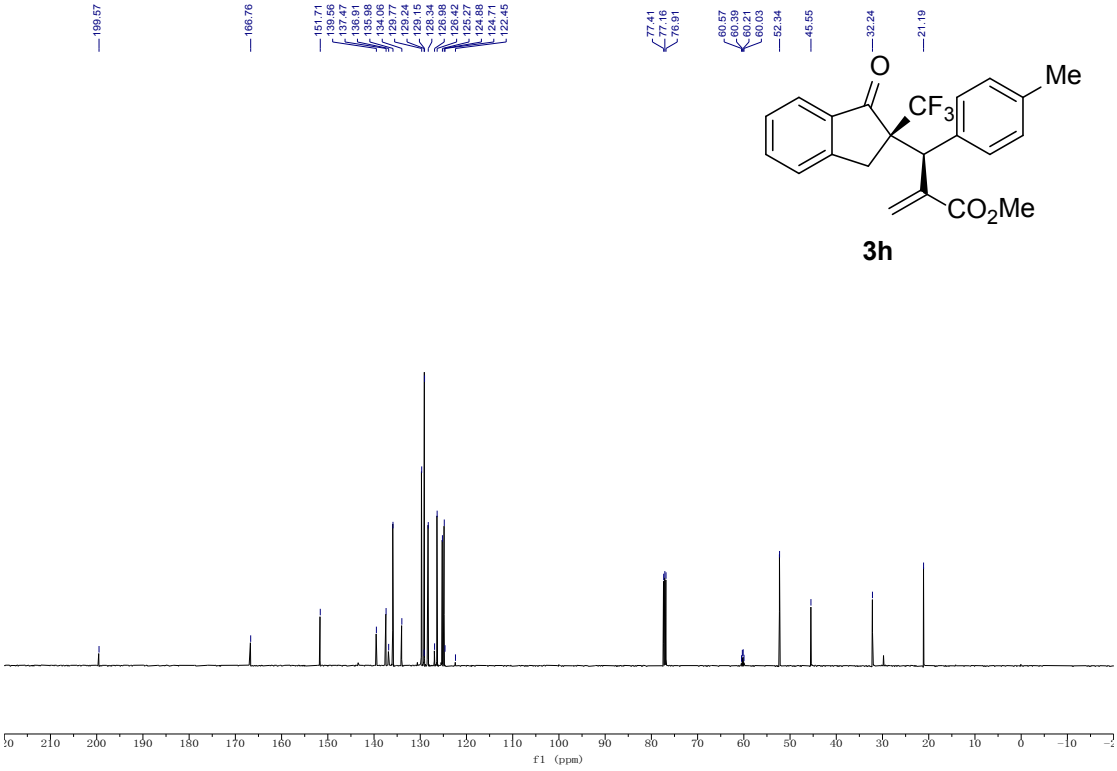
3g

^{1}H NMR spectrum of 3h

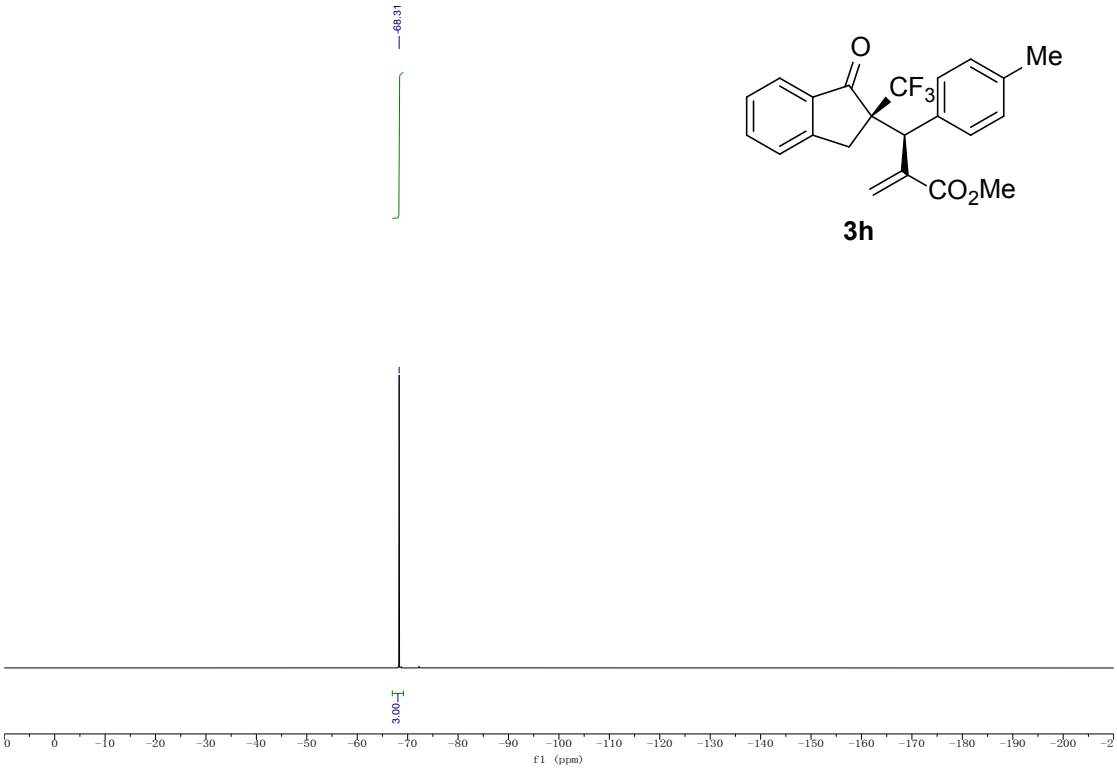


3h

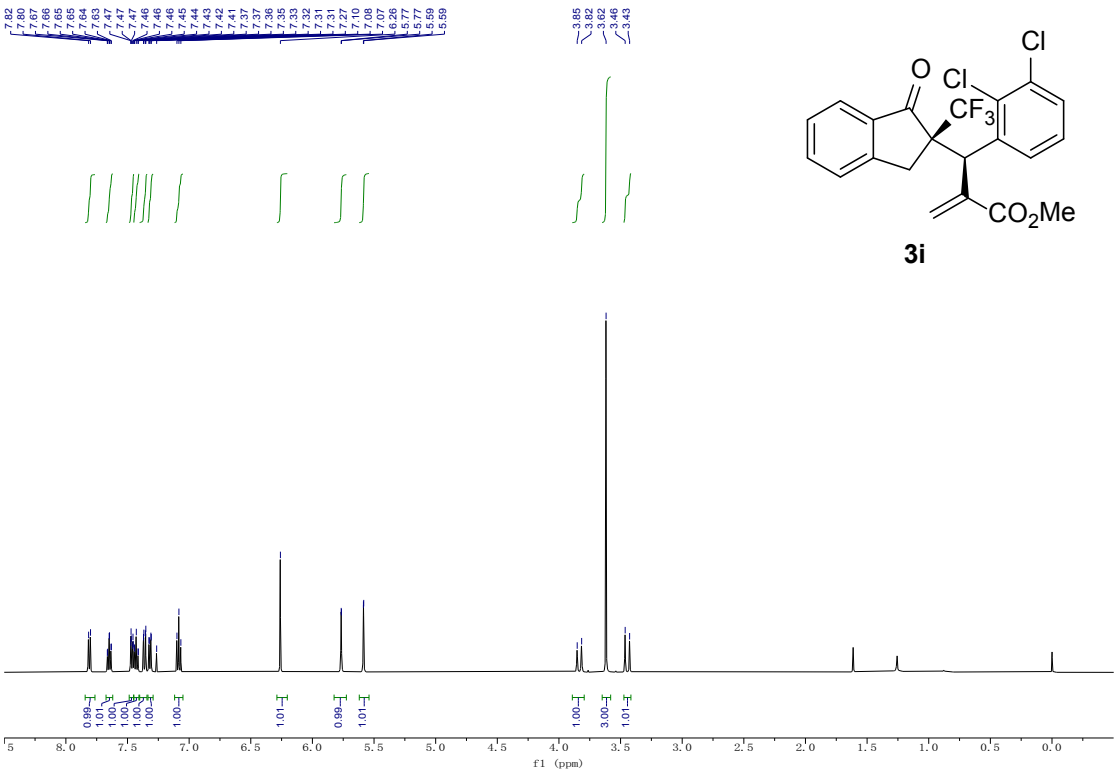
^{13}C NMR spectrum of 3h



^{19}F NMR spectrum of 3h

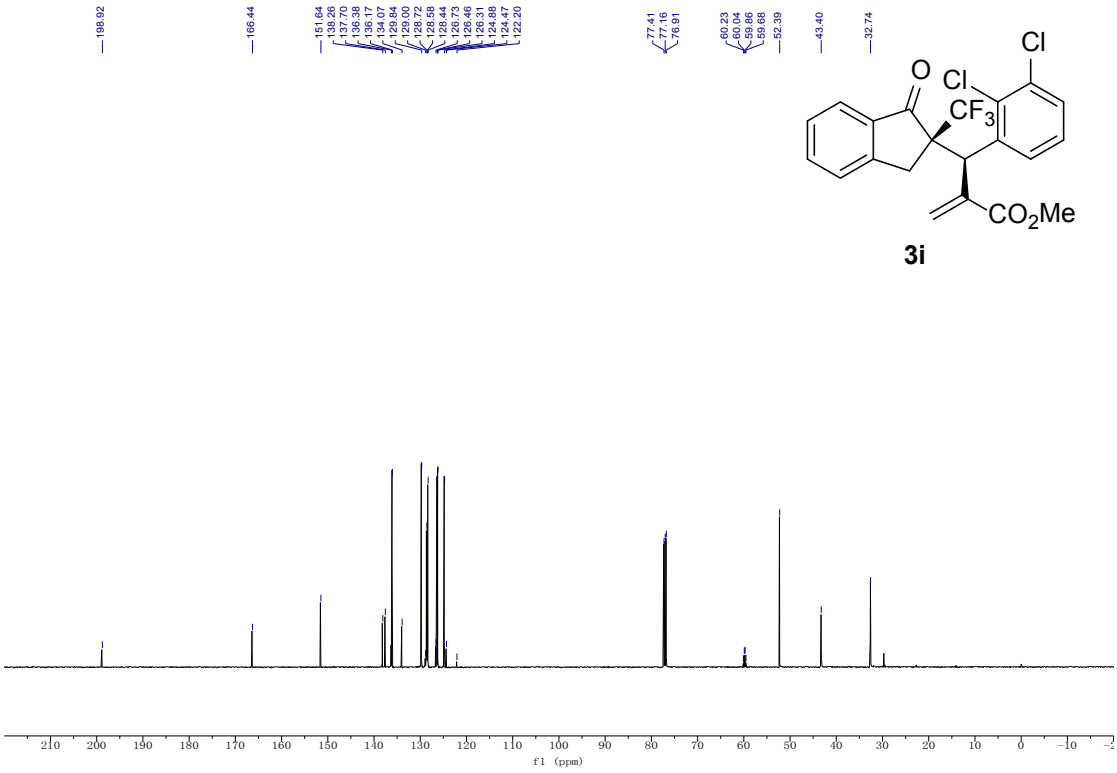


^{1}H NMR spectrum of 3i



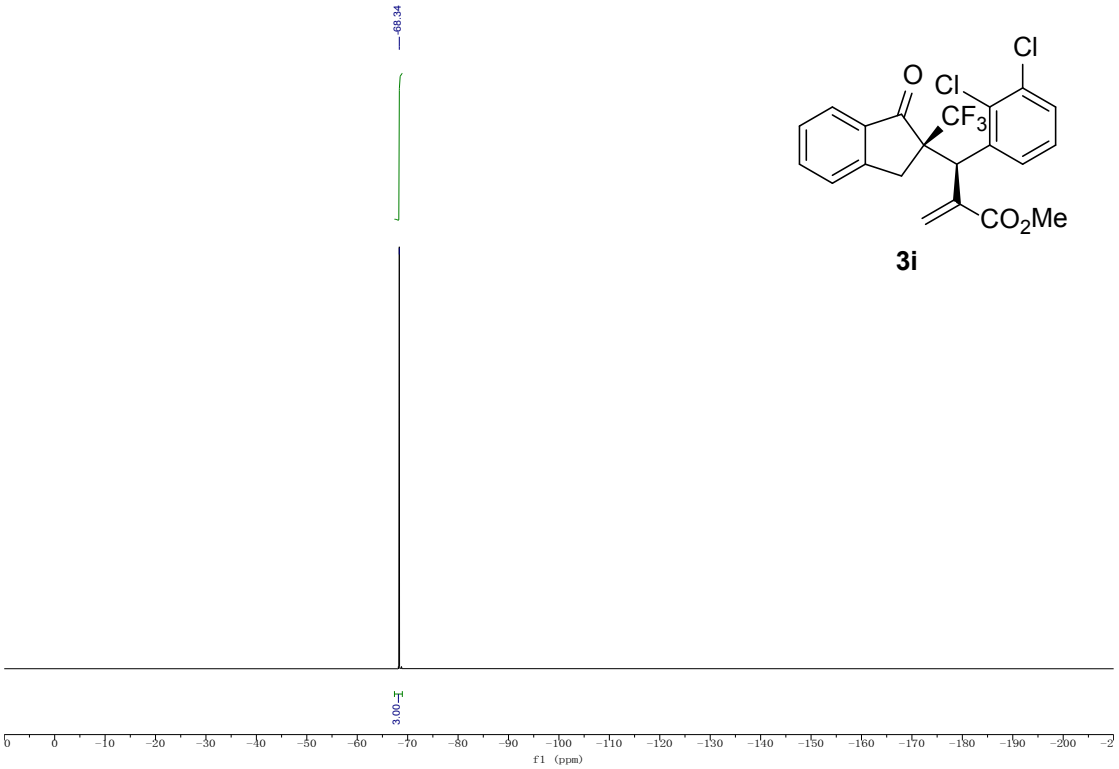
3i

^{13}C NMR spectrum of 3i



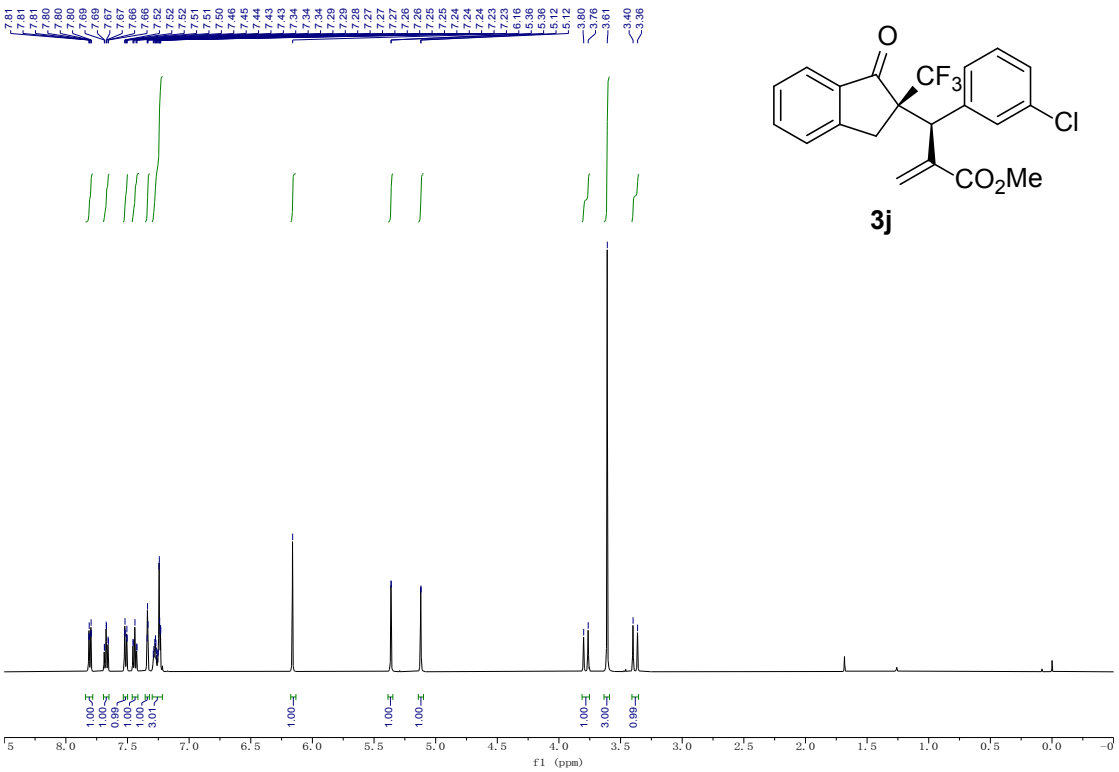
3i

^{19}F NMR spectrum of 3i



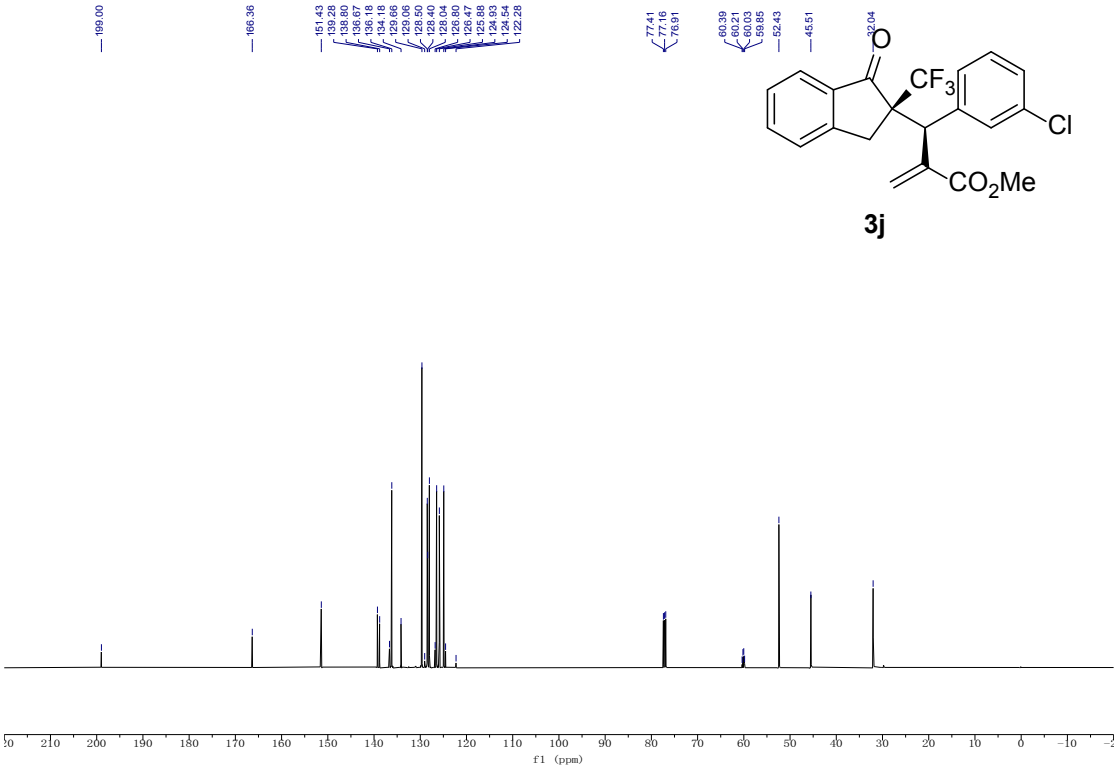
3i

^{1}H NMR spectrum of 3j

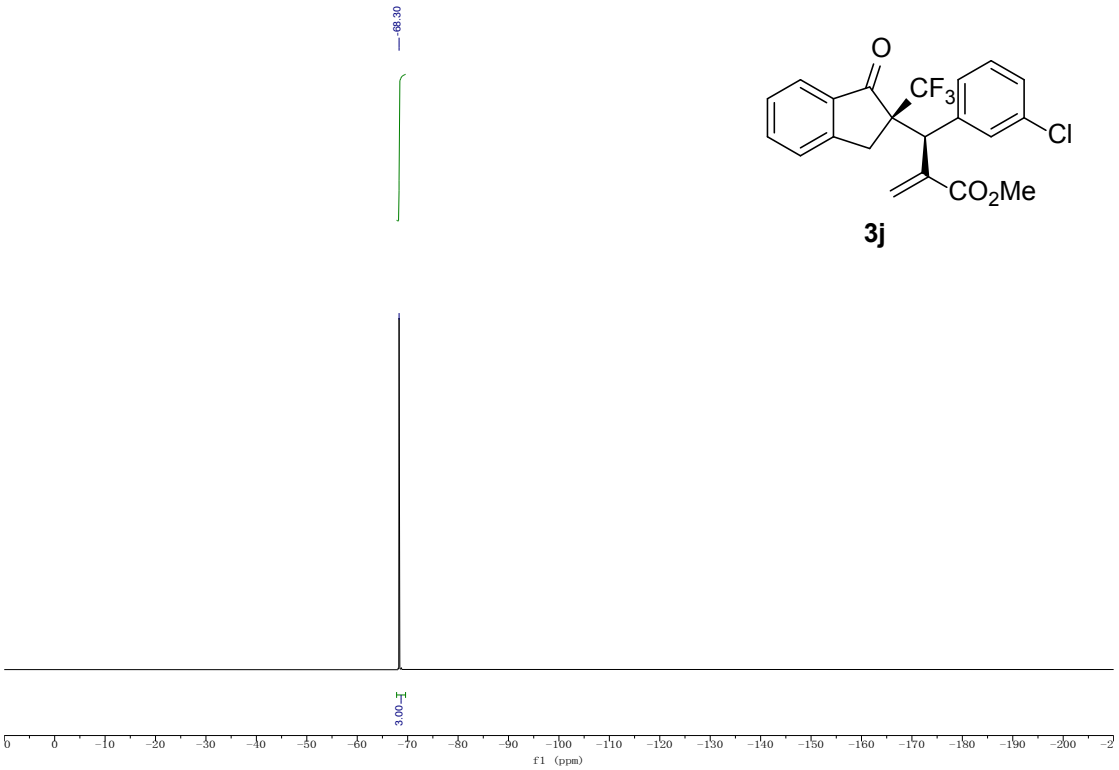


3j

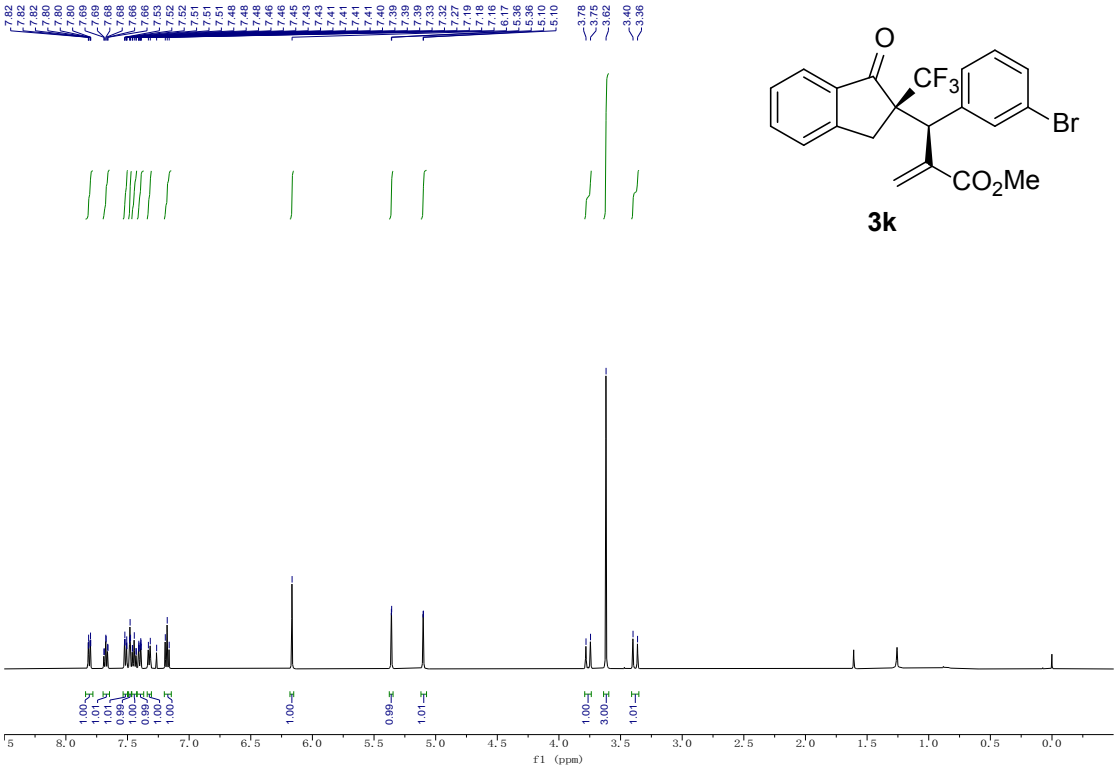
^{13}C NMR spectrum of 3j



^{19}F NMR spectrum of 3j

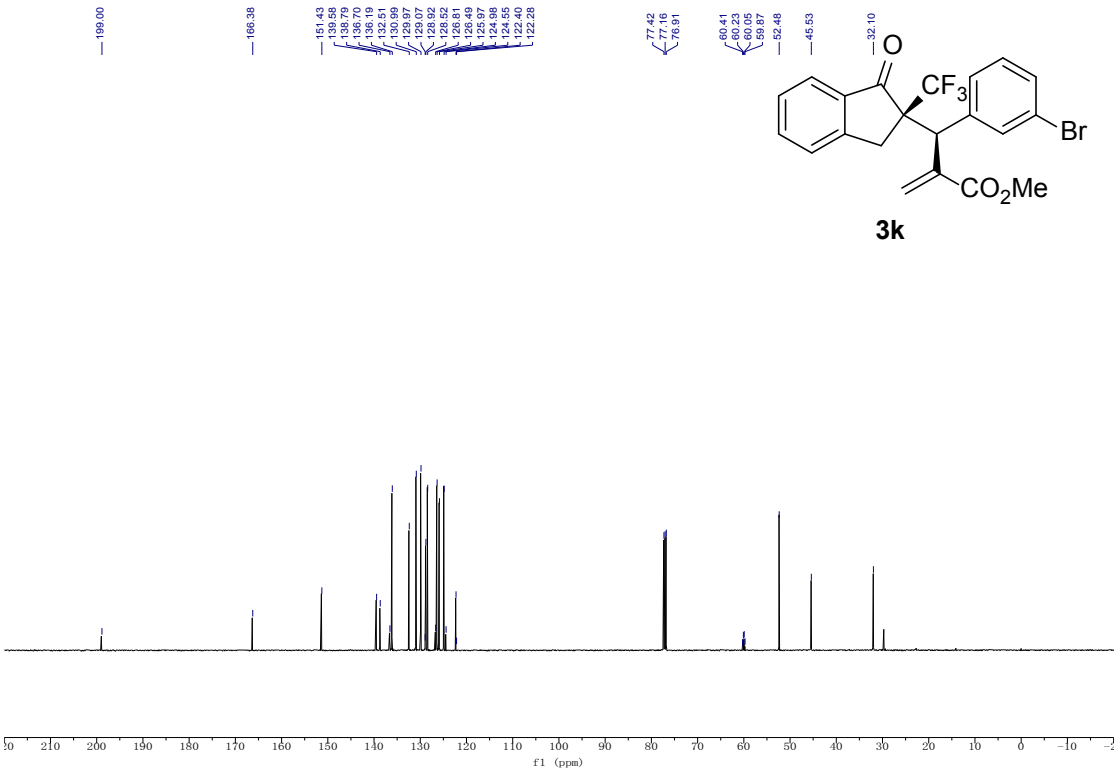


^{1}H NMR spectrum of 3k



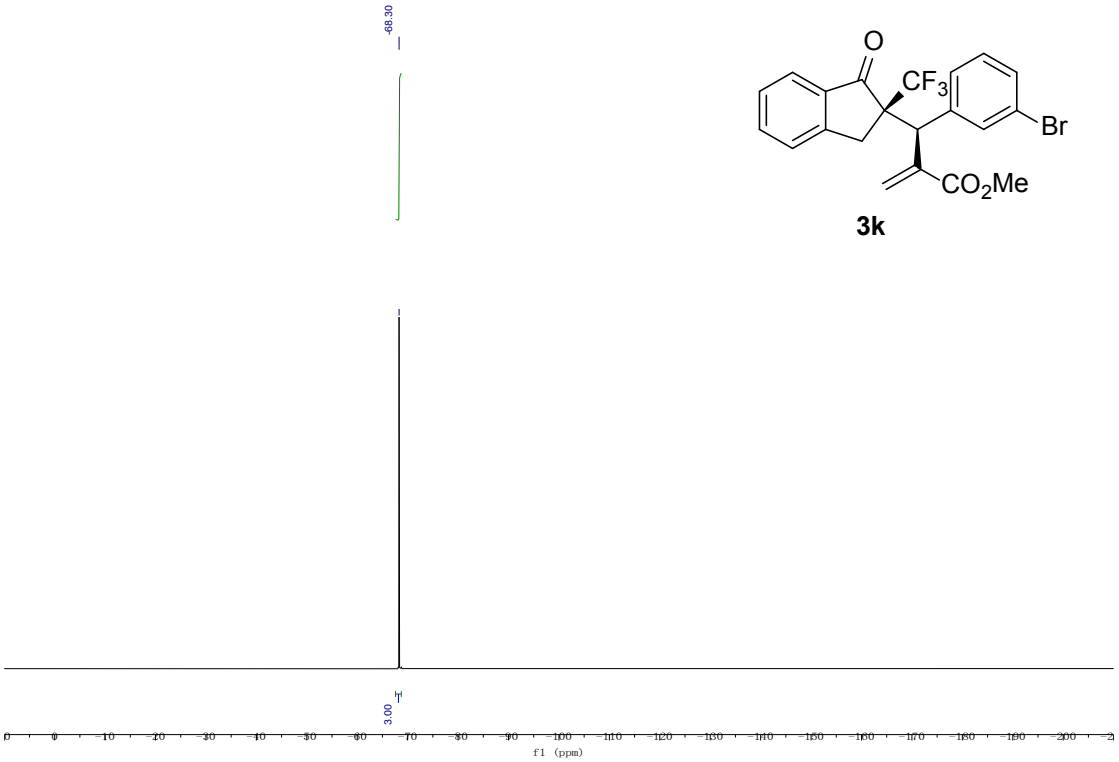
3k

^{13}C NMR spectrum of 3k



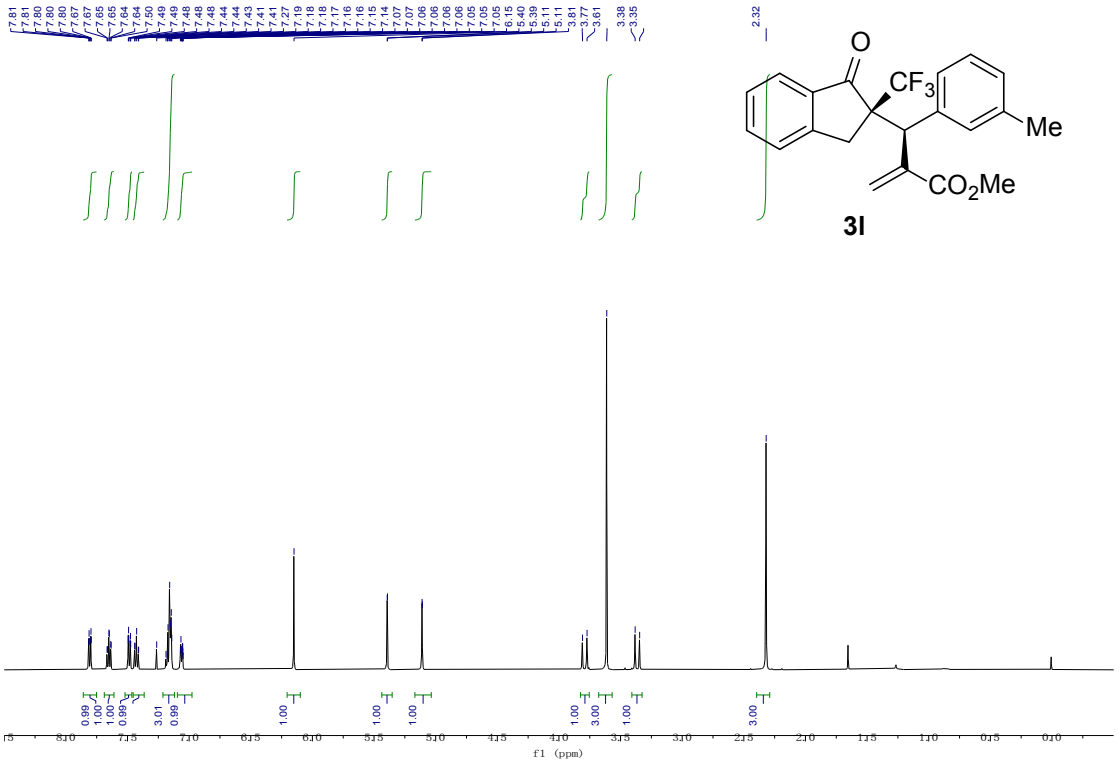
3k

^{19}F NMR spectrum of 3k



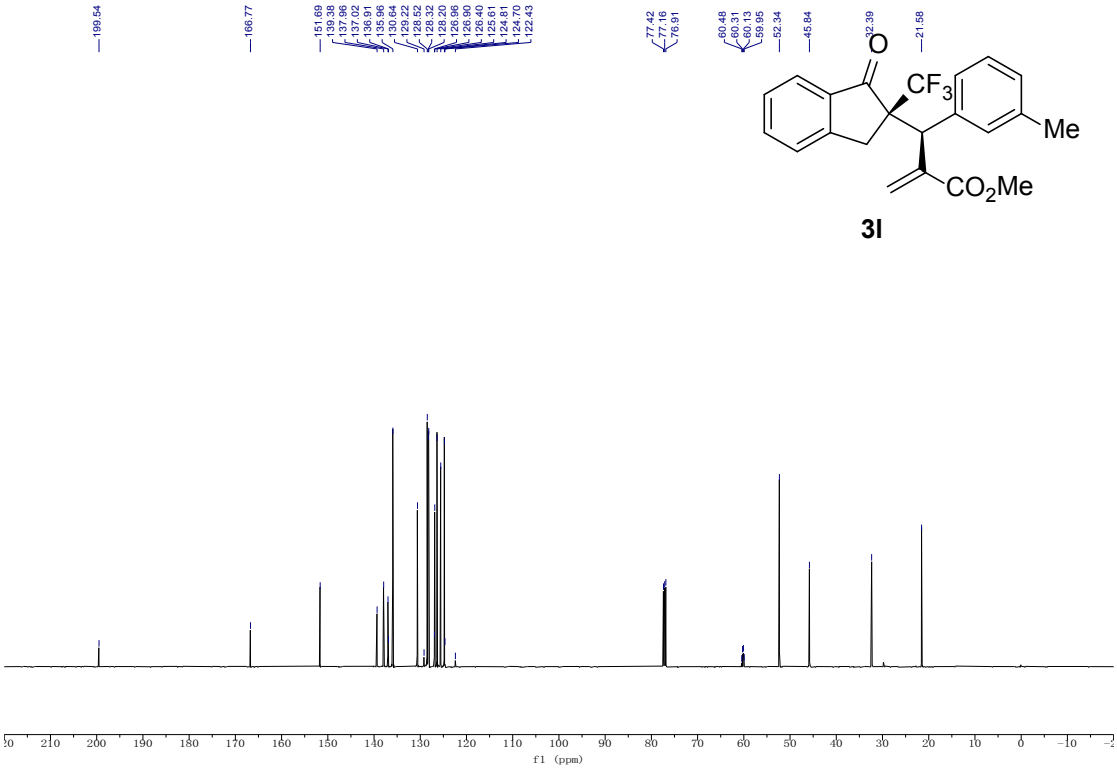
3k

^{1}H NMR spectrum of 3l



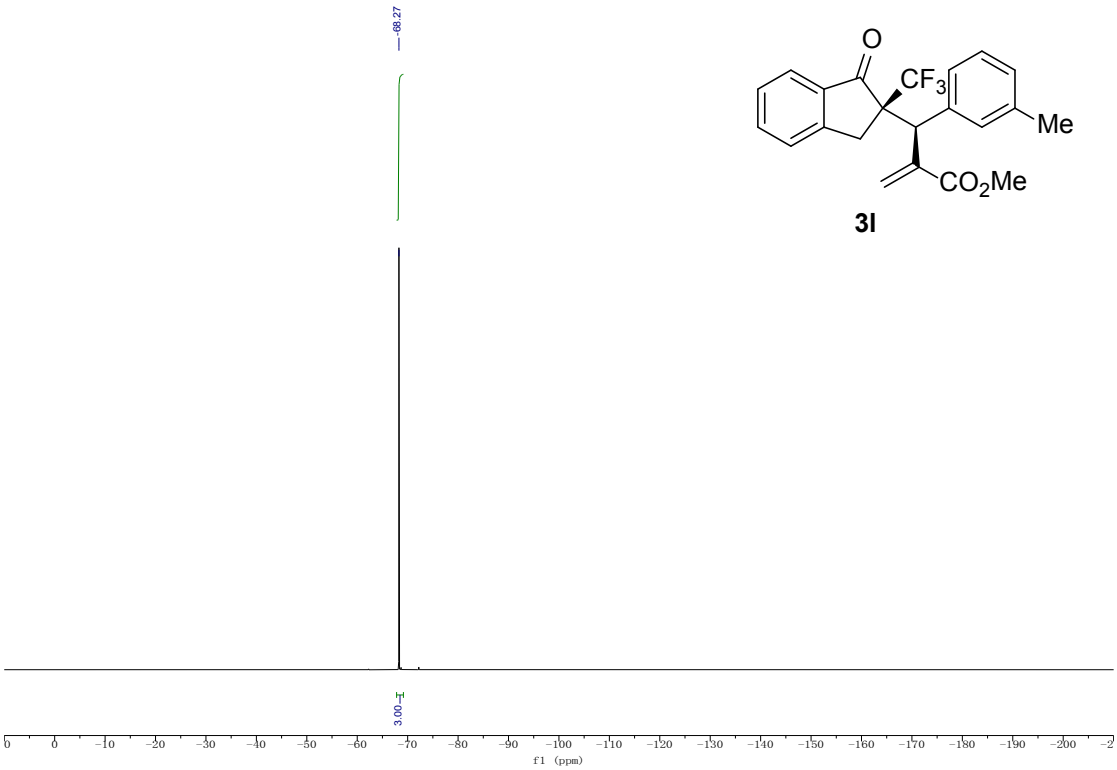
3l

^{13}C NMR spectrum of 3l



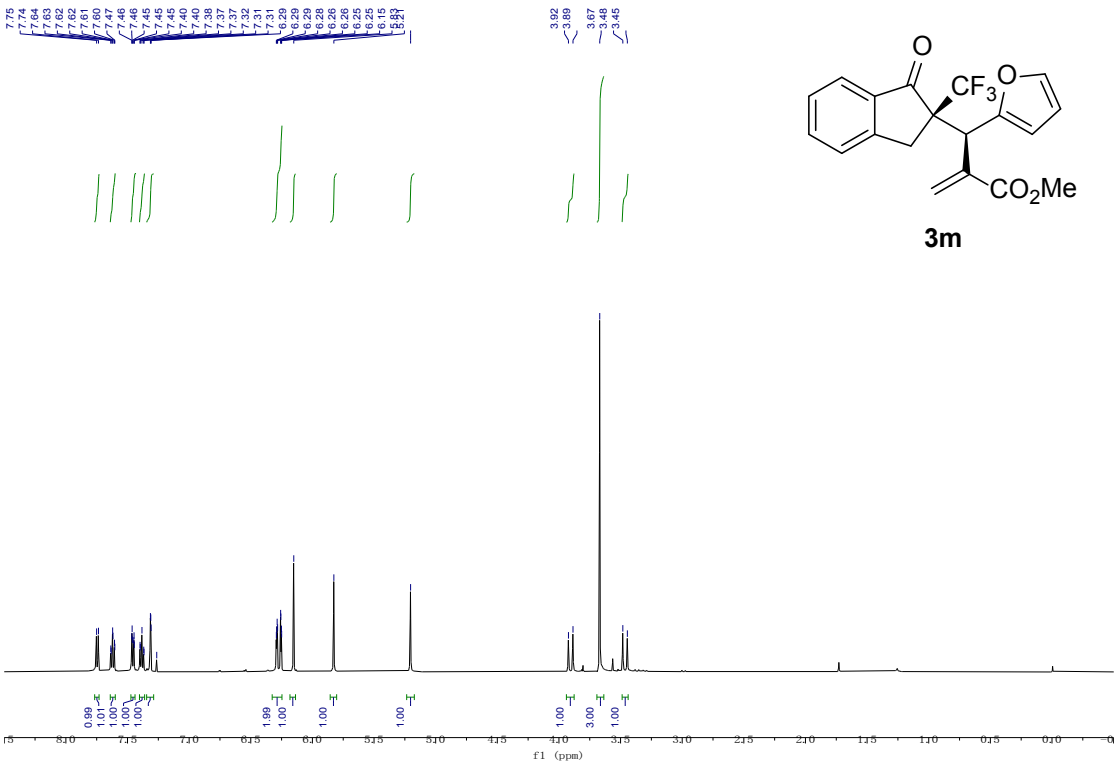
3l

^{19}F NMR spectrum of 3l



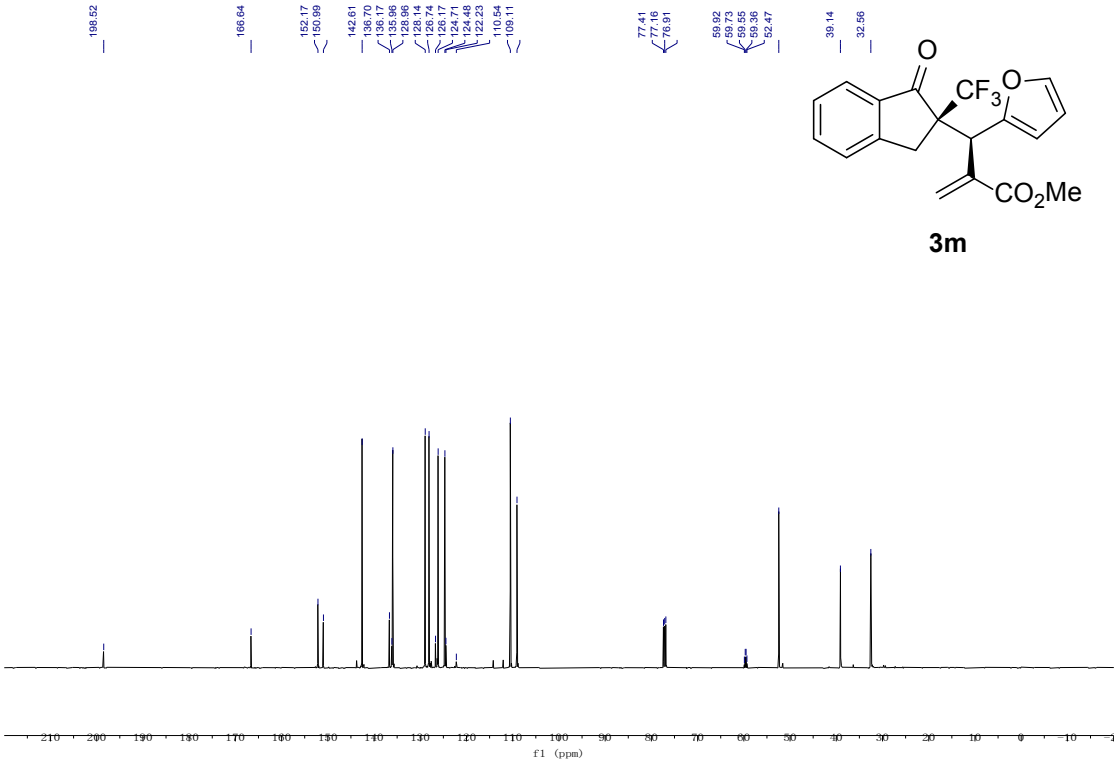
3l

^{1}H NMR spectrum of 3m



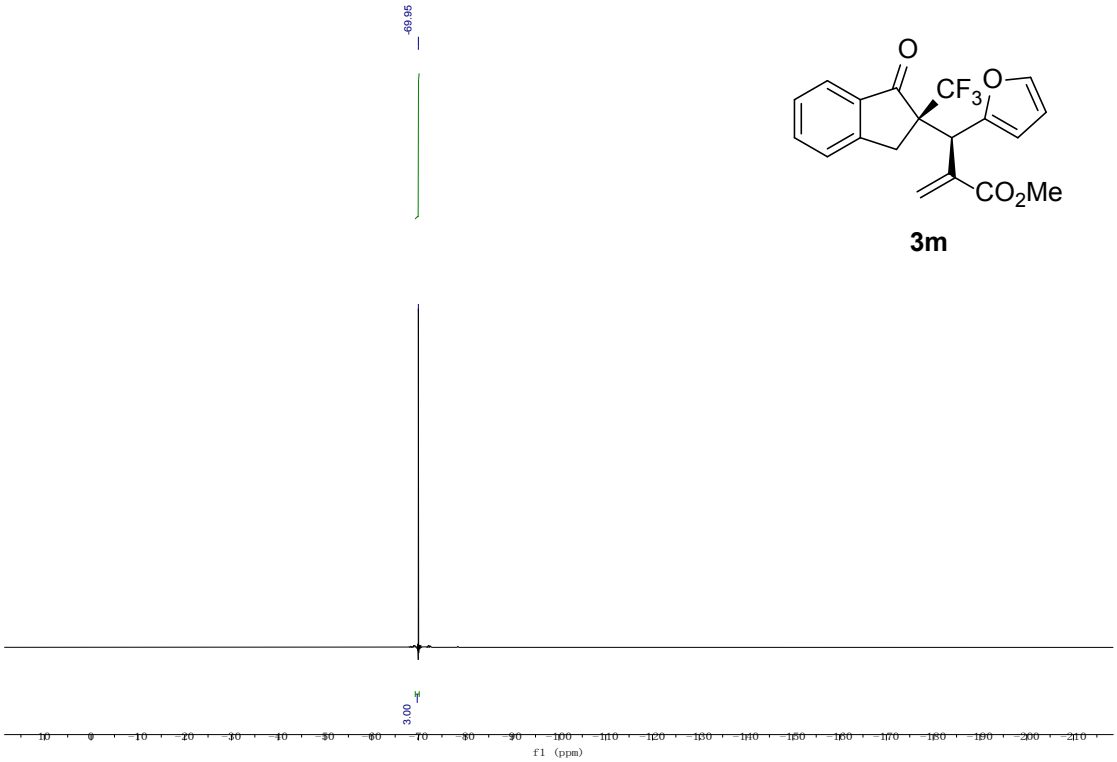
3m

^{13}C NMR spectrum of 3m



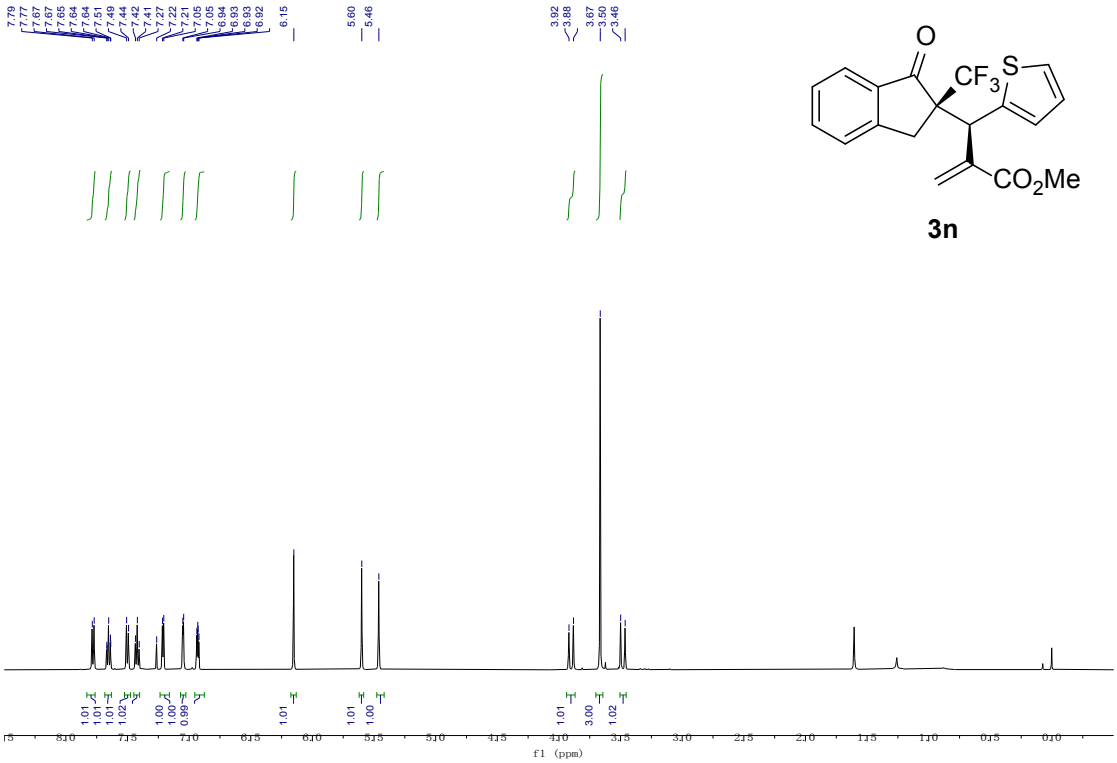
3m

^{19}F NMR spectrum of 3m



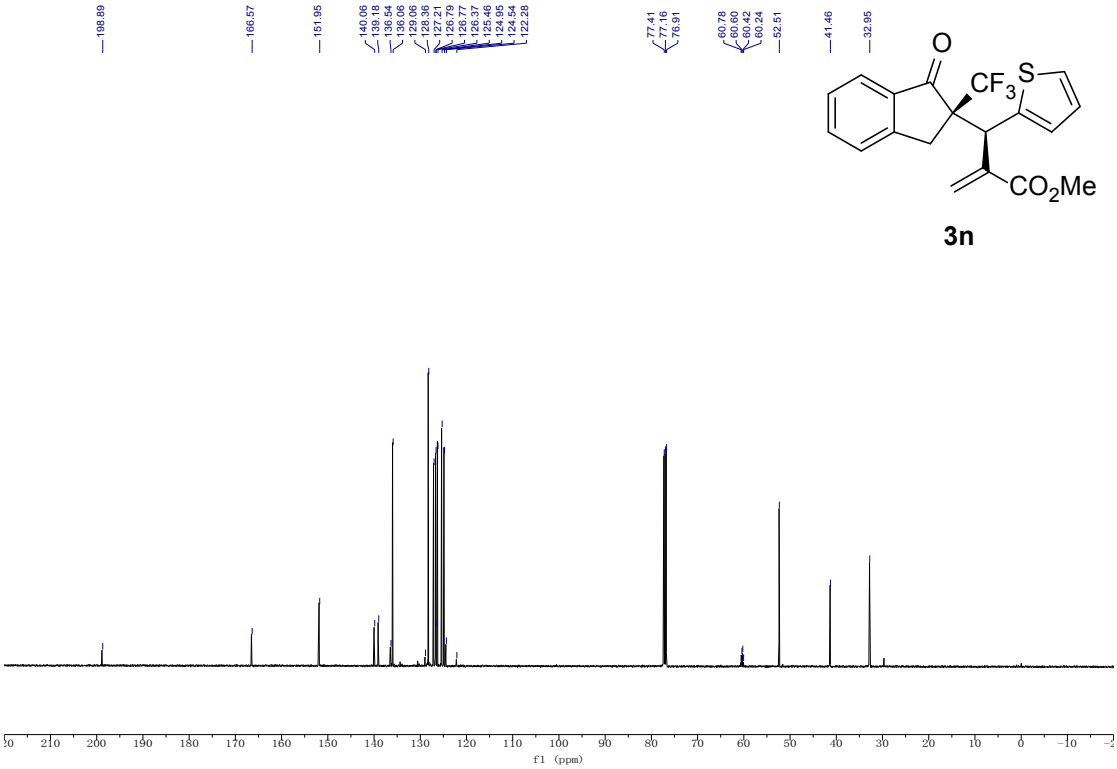
3m

^{1}H NMR spectrum of 3n

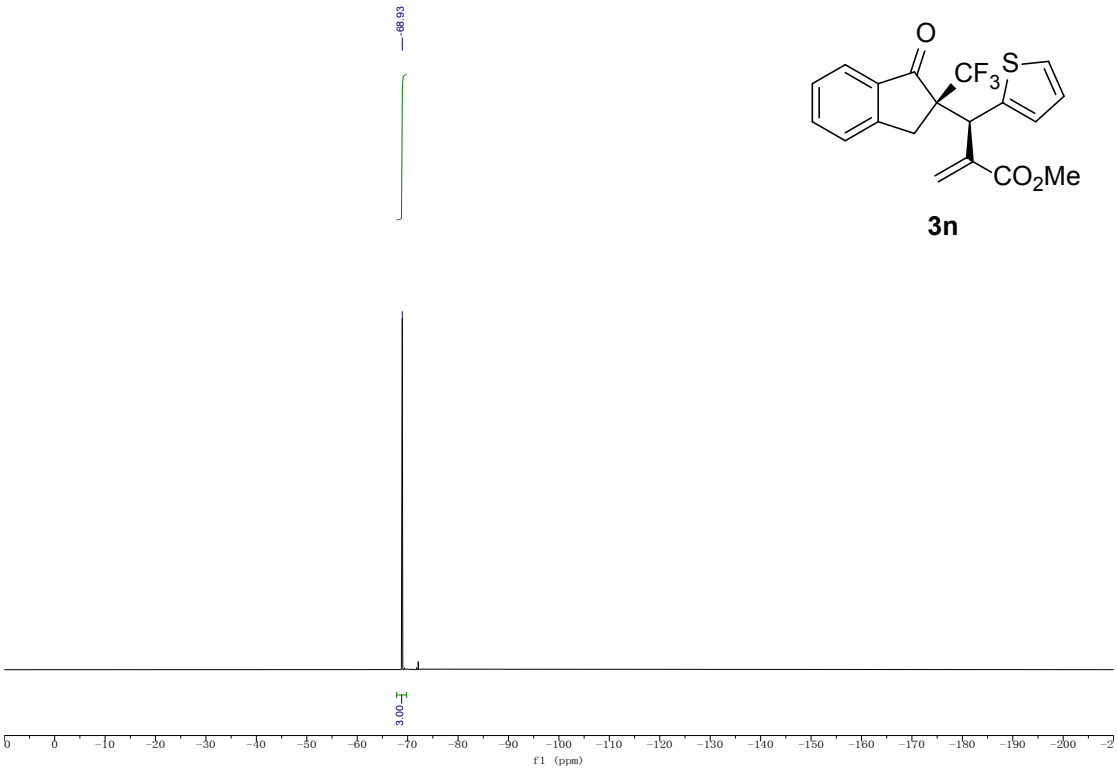


3n

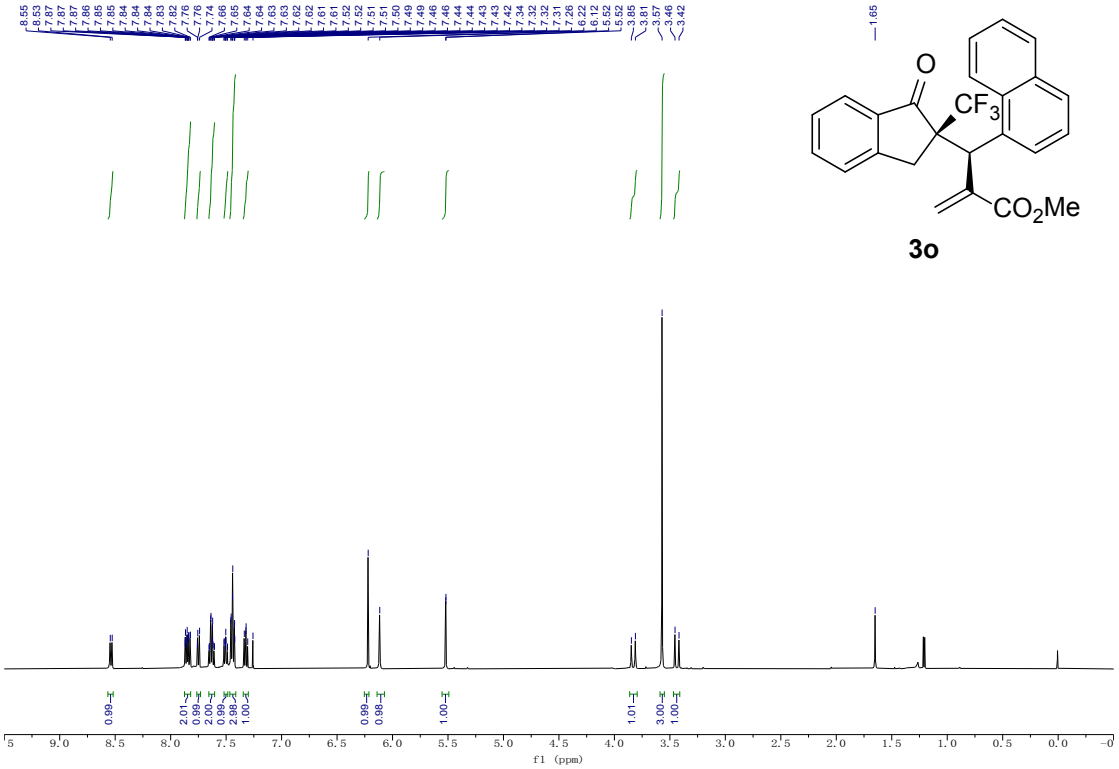
^{13}C NMR spectrum of 3n



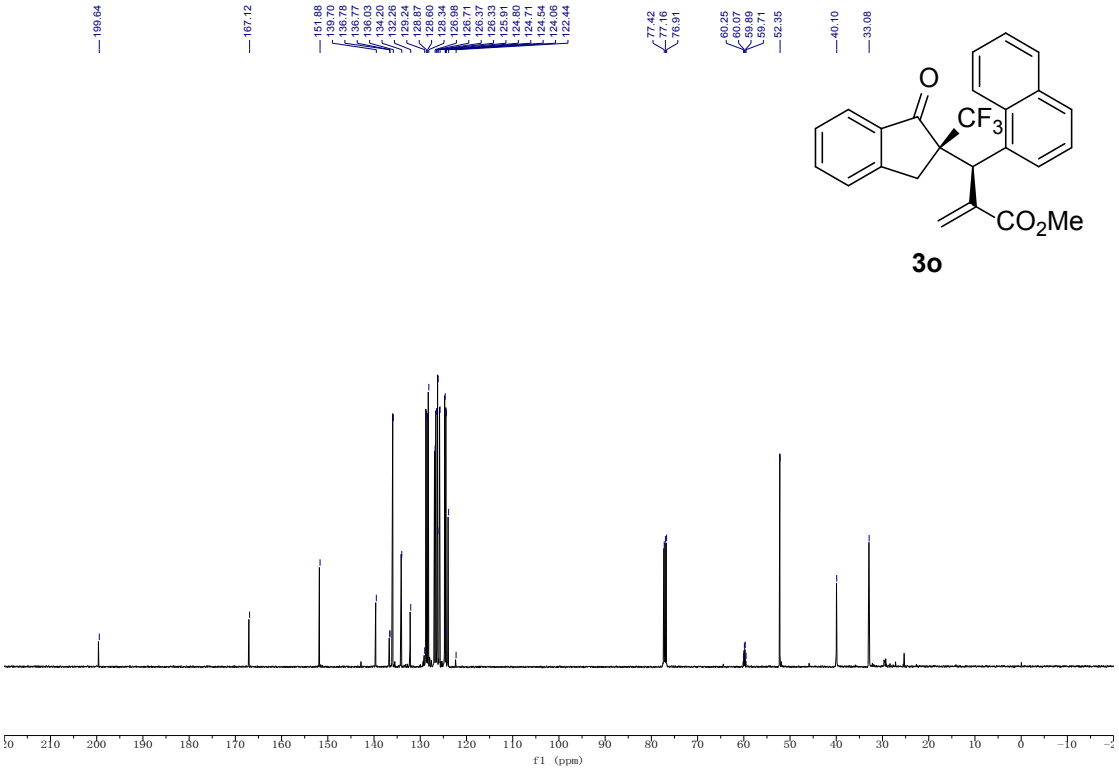
^{19}F NMR spectrum of 3n



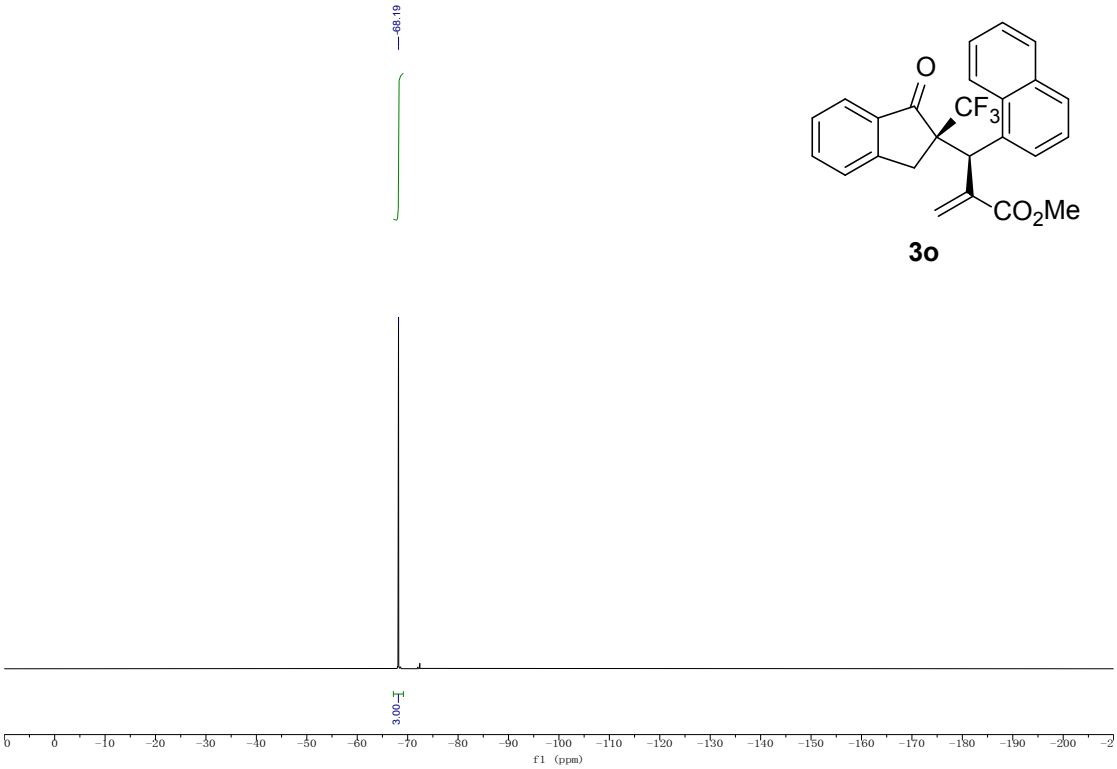
^{1}H NMR spectrum of 3o



^{13}C NMR spectrum of 3o

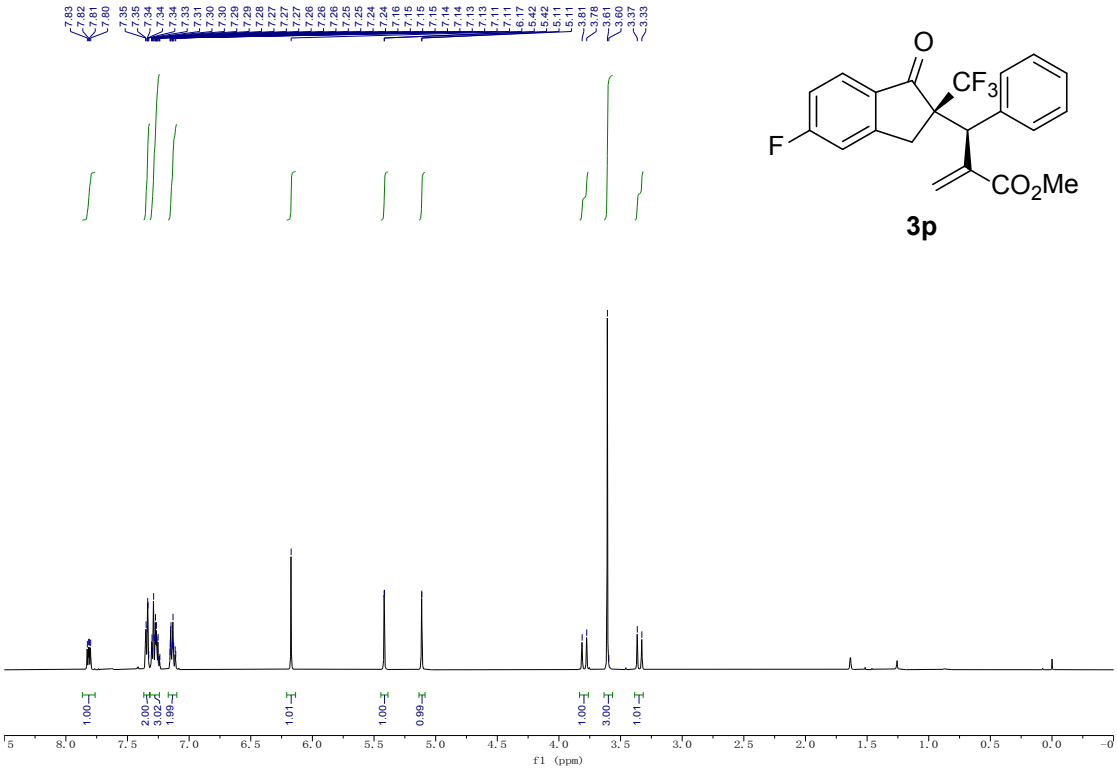


^{19}F NMR spectrum of 3o



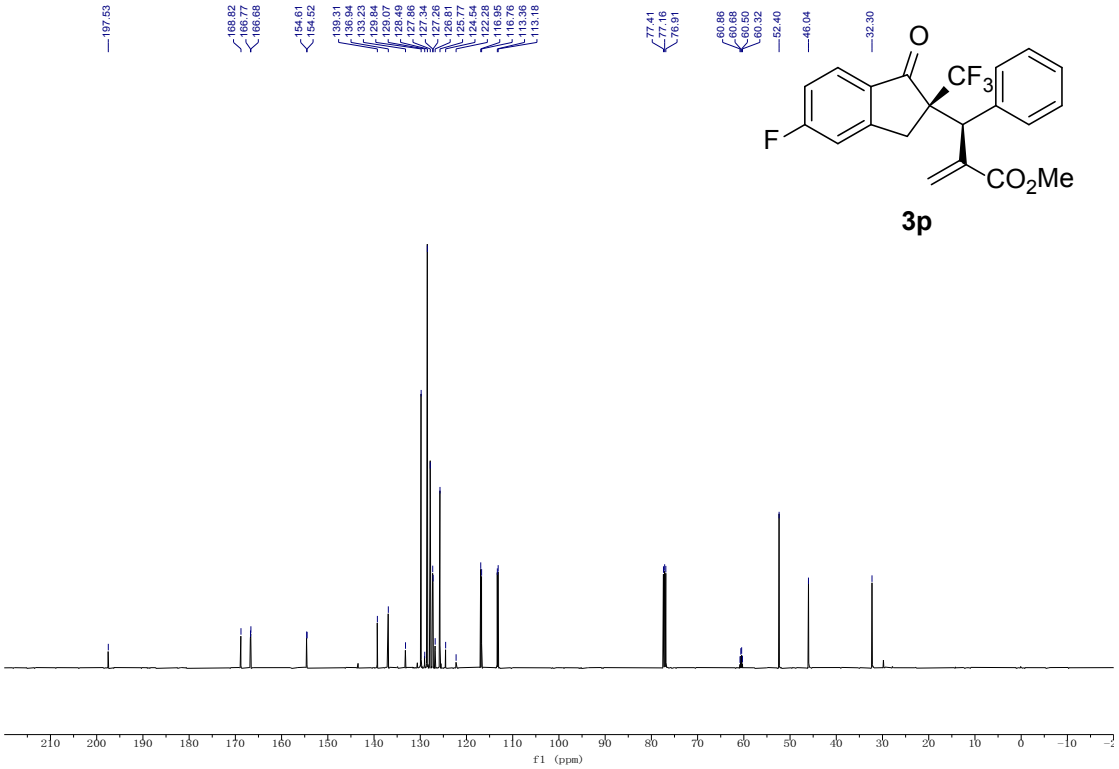
3o

^{1}H NMR spectrum of 3p



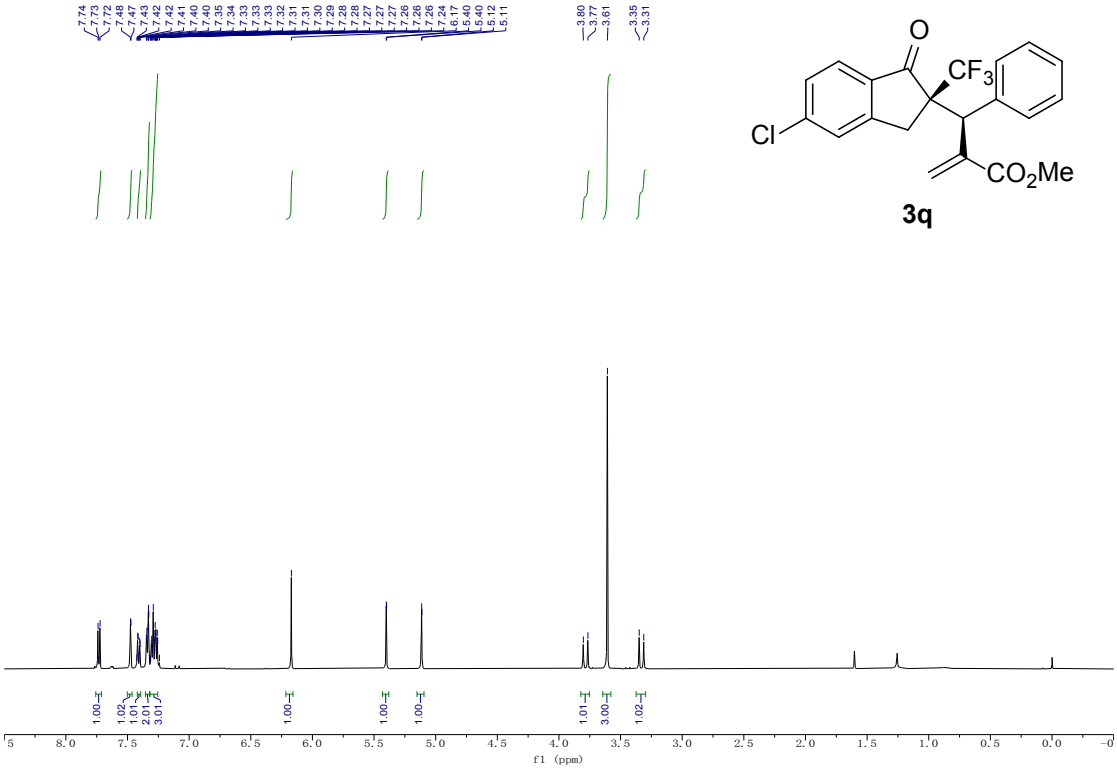
3p

^{13}C NMR spectrum of 3p



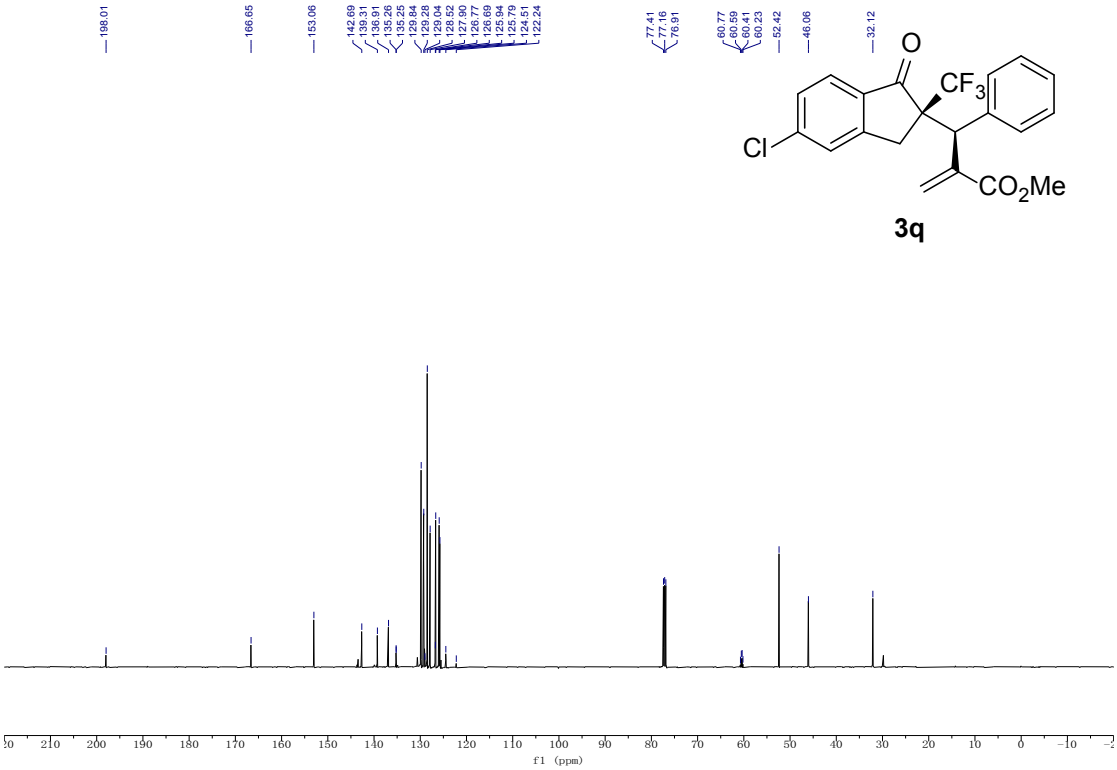
^{19}F NMR spectrum of 3p

^{1}H NMR spectrum of 3q



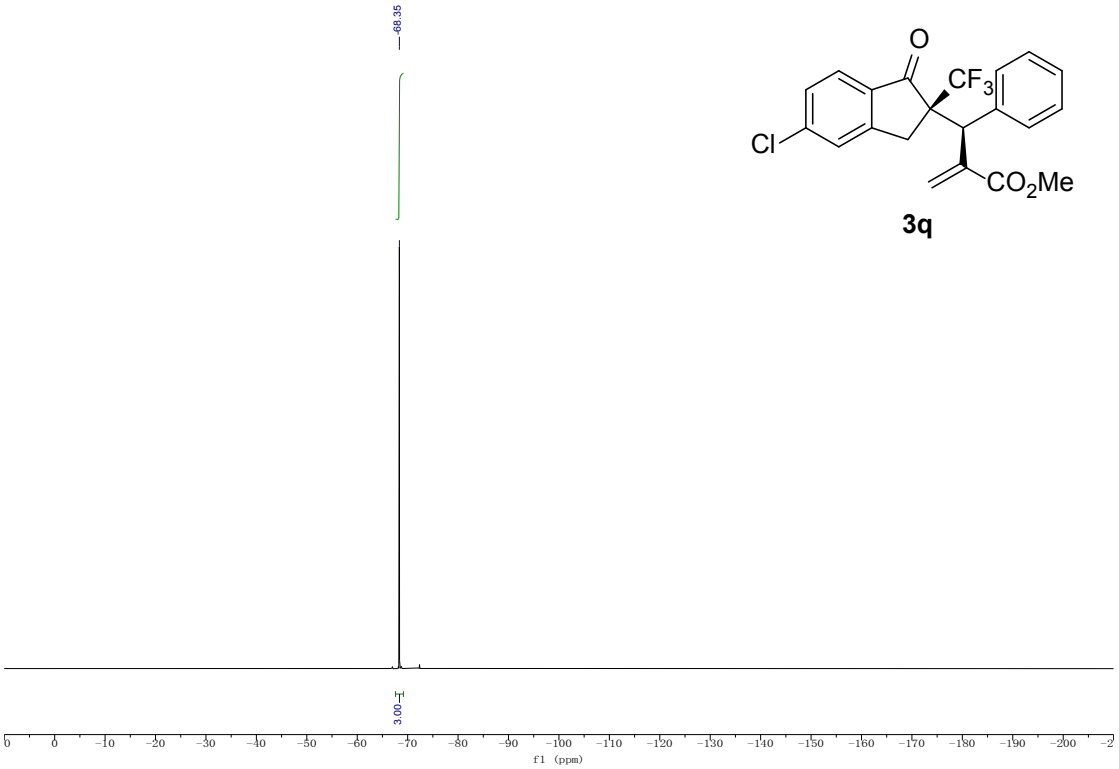
3q

^{13}C NMR spectrum of 3q



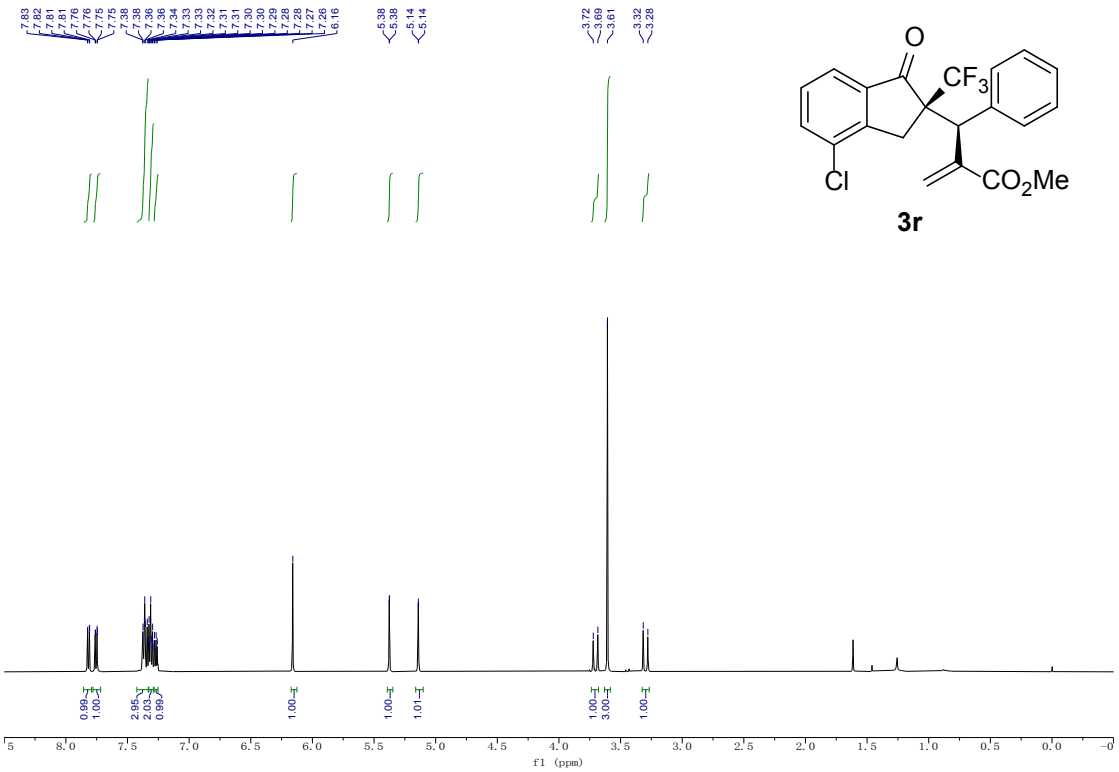
3q

^{19}F NMR spectrum of 3q



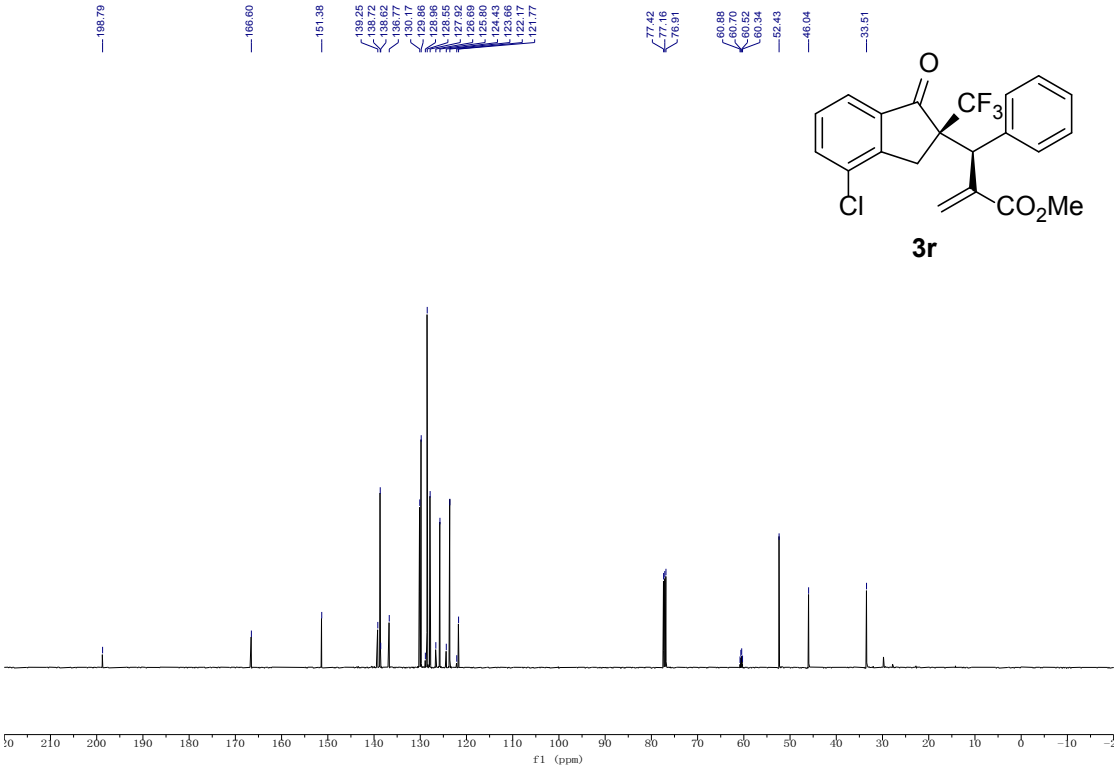
3q

^{1}H NMR spectrum of 3r

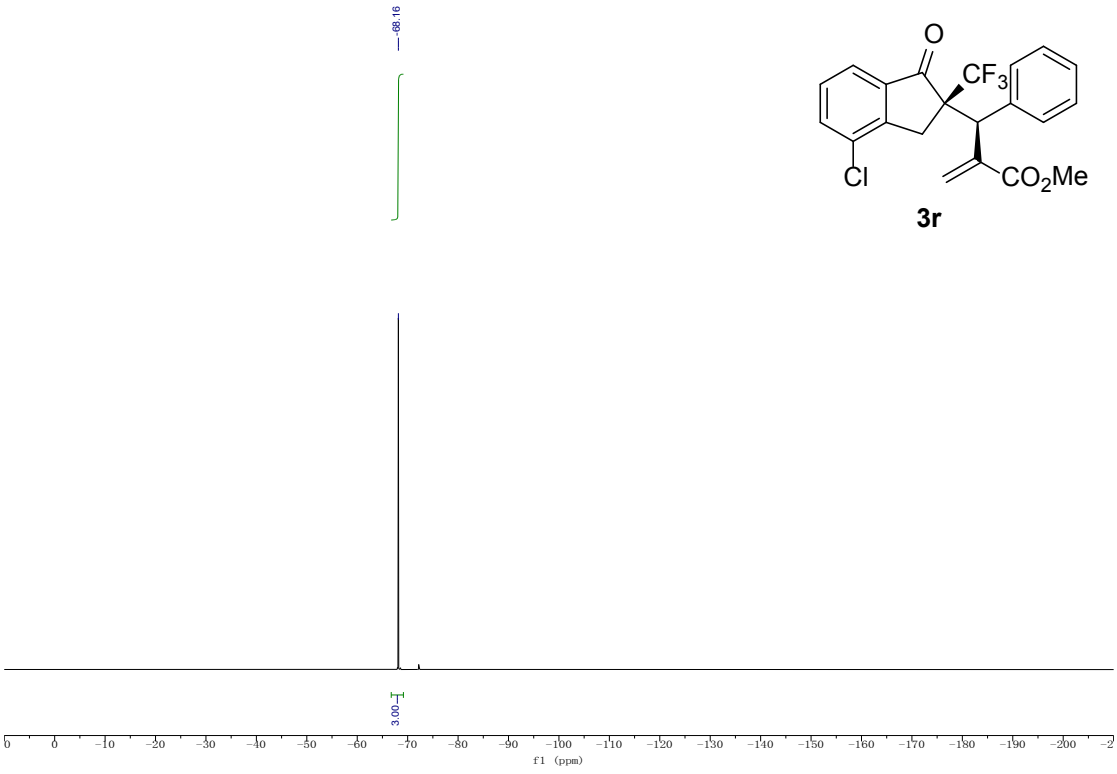


3r

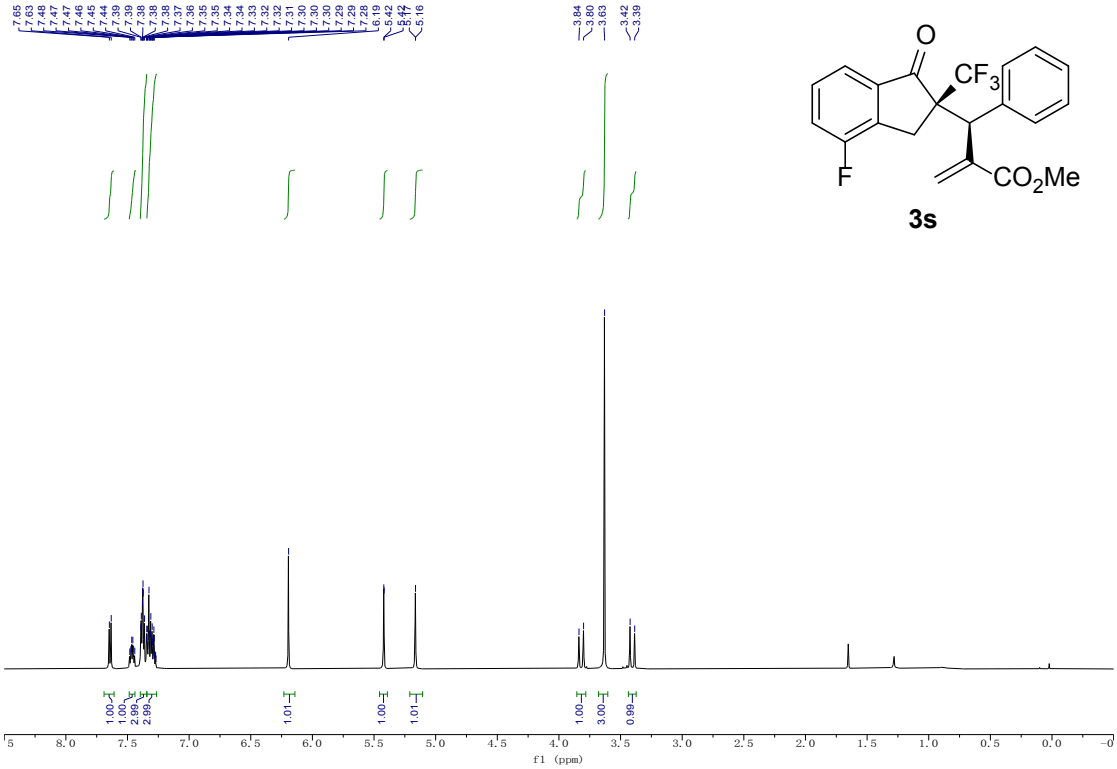
^{13}C NMR spectrum of 3r



^{19}F NMR spectrum of 3r

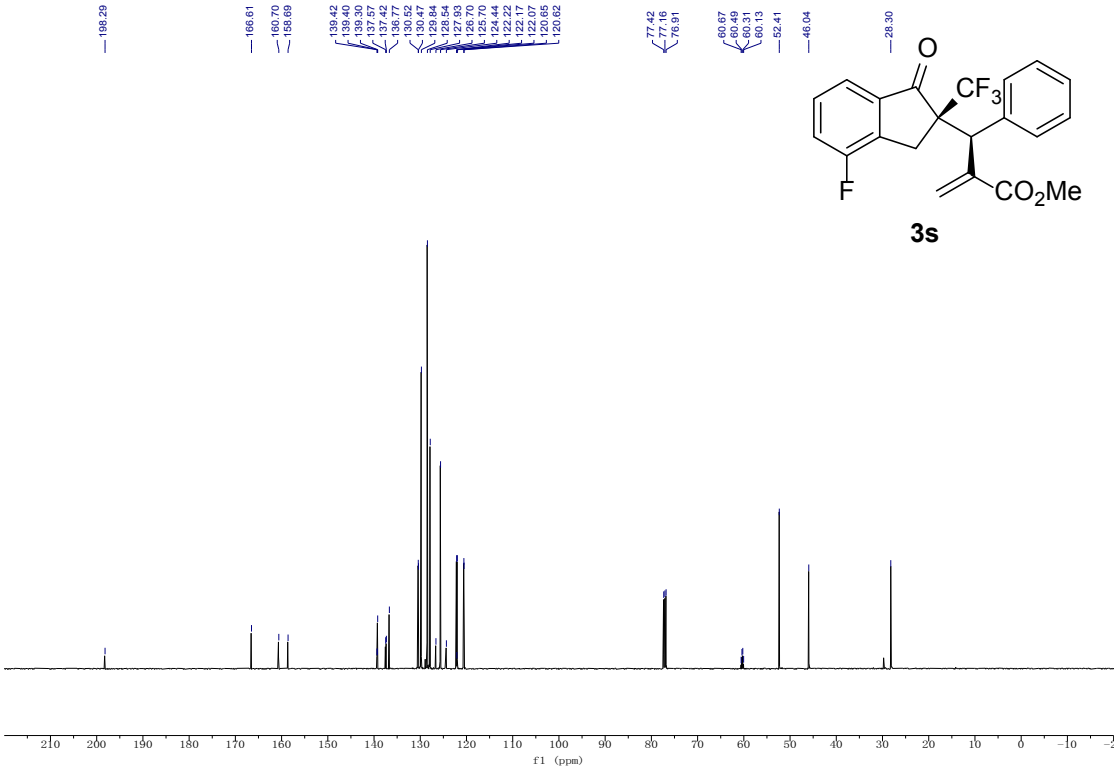


^{1}H NMR spectrum of 3s



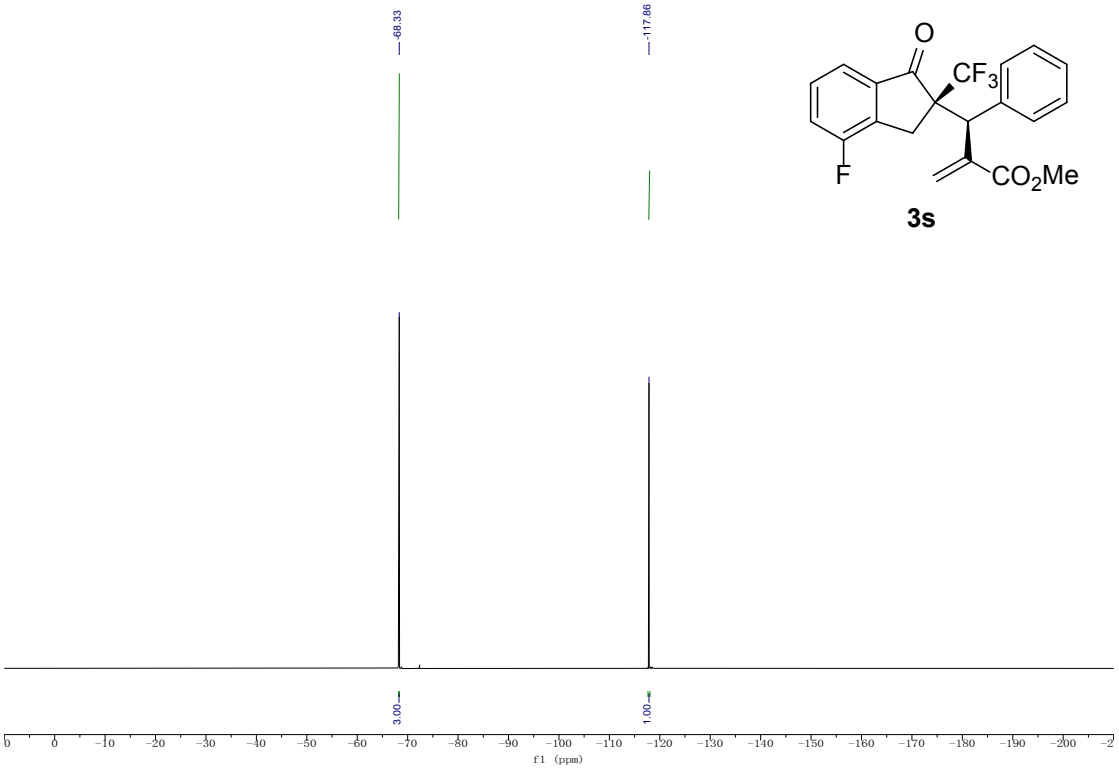
3s

^{13}C NMR spectrum of 3s



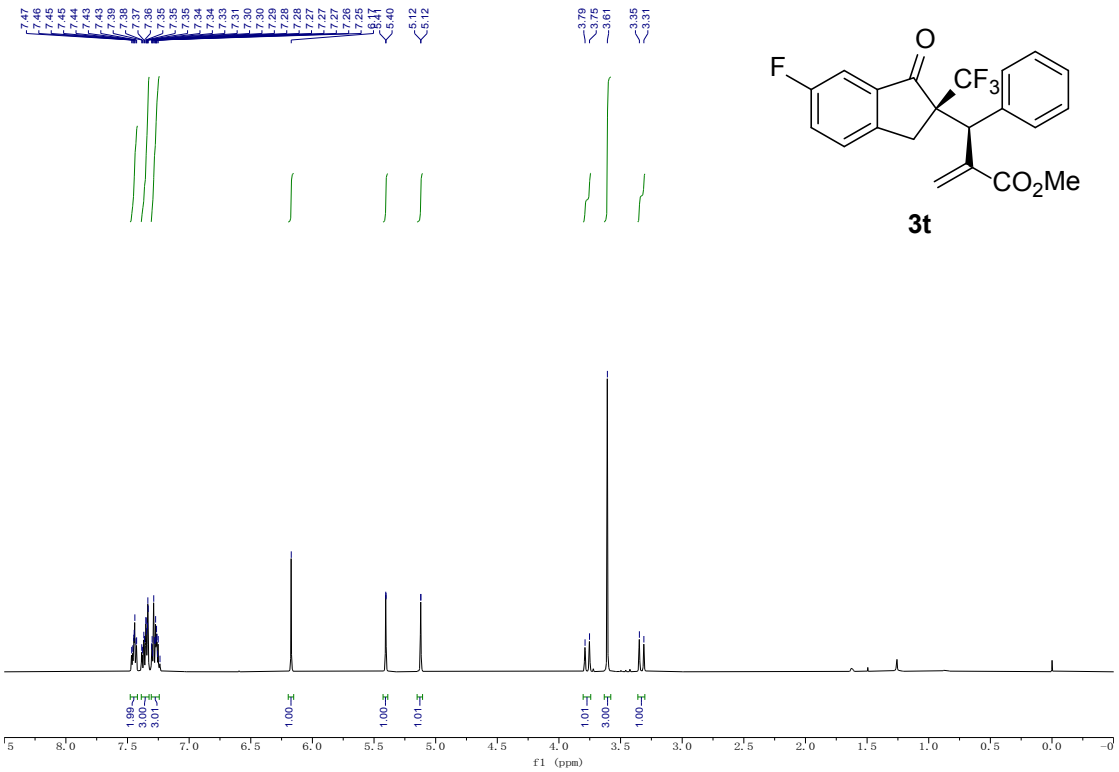
3s

^{19}F NMR spectrum of 3s



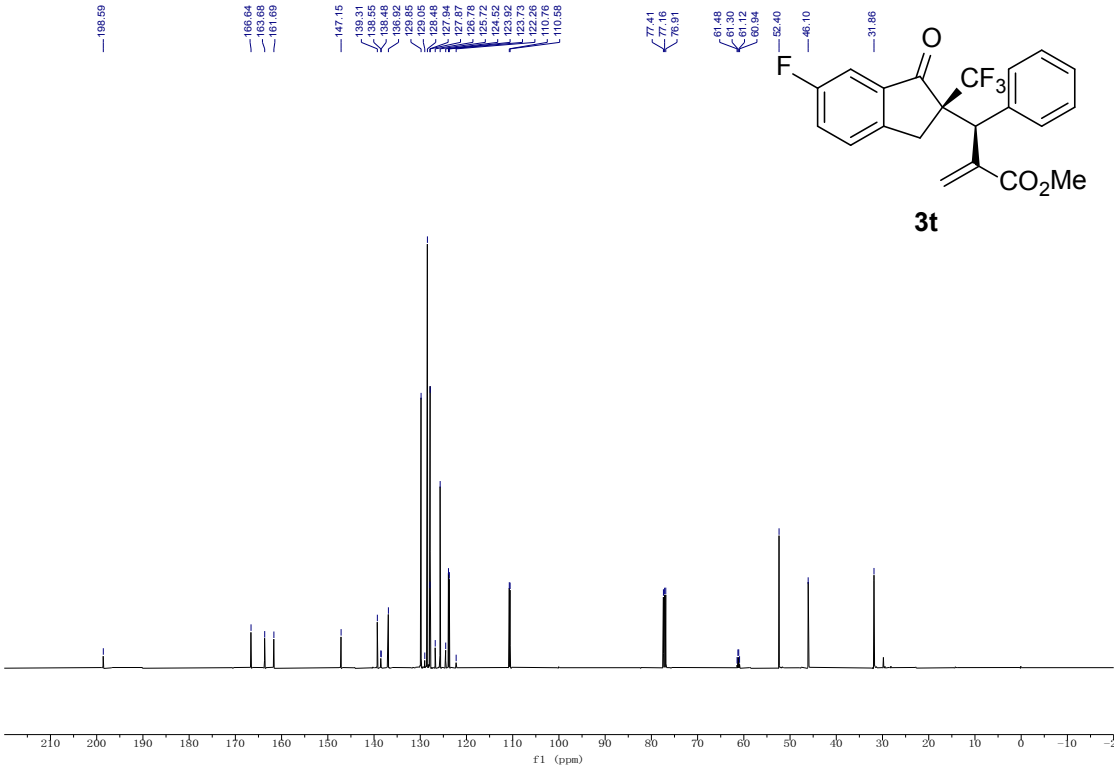
3s

^{1}H NMR spectrum of 3t

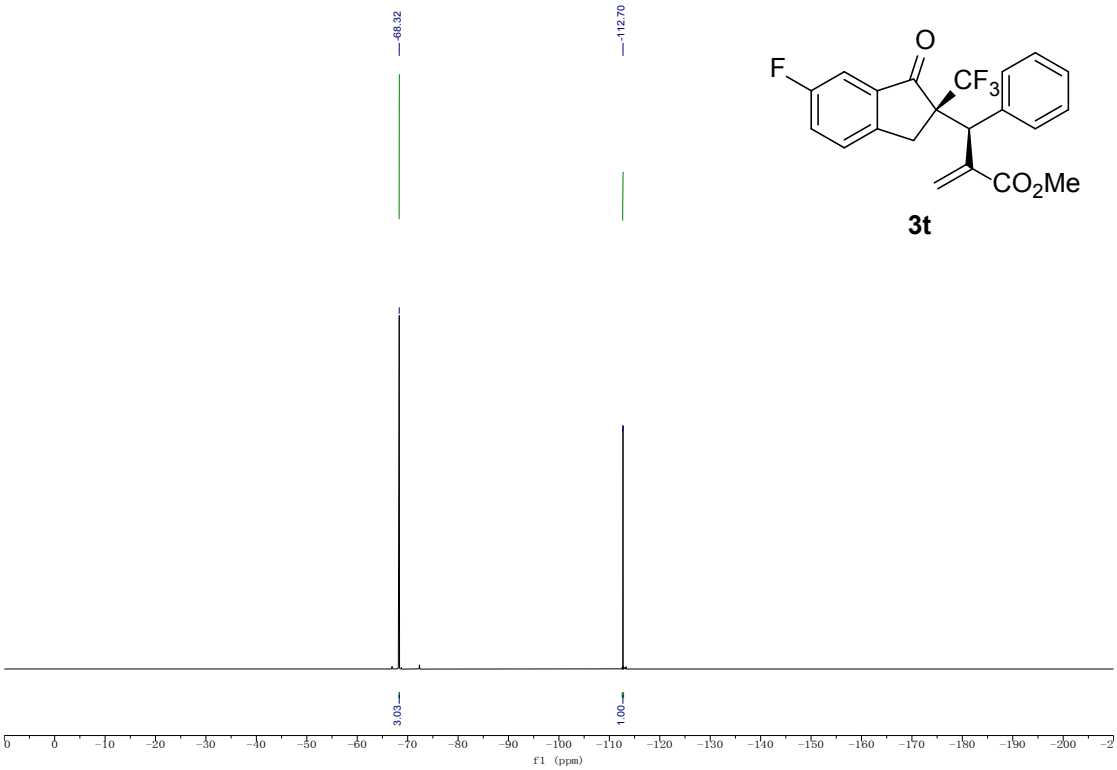


3t

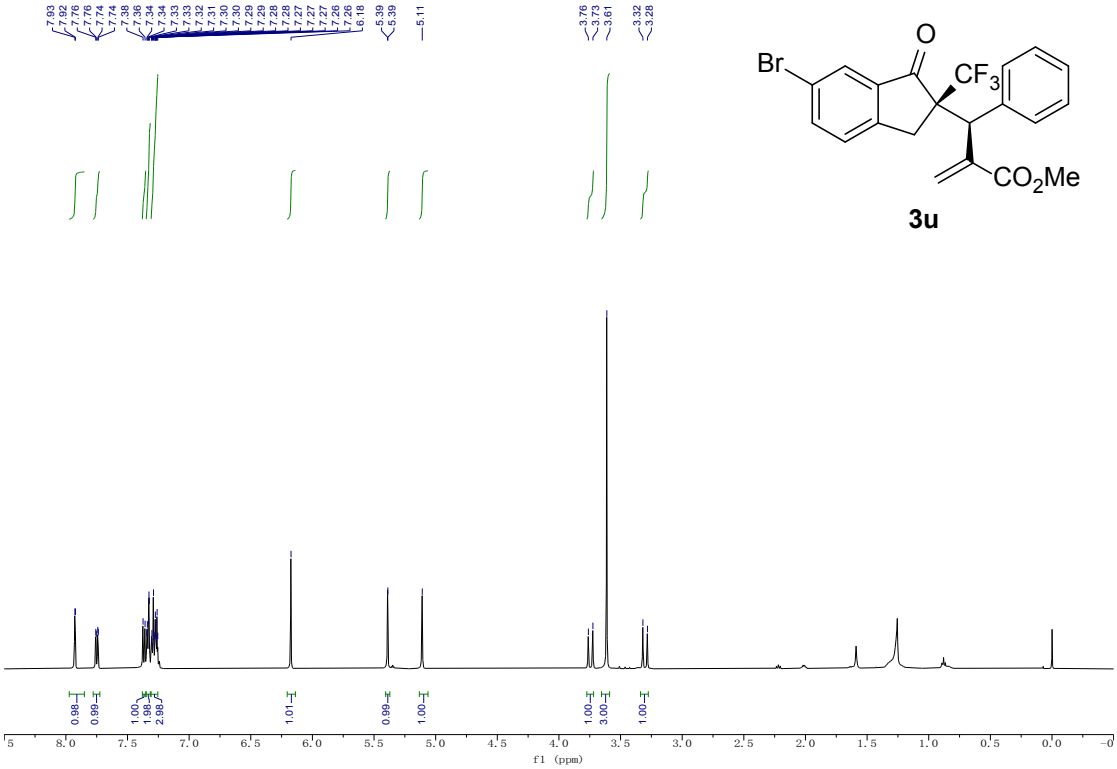
^{13}C NMR spectrum of 3t



^{19}F NMR spectrum of 3t

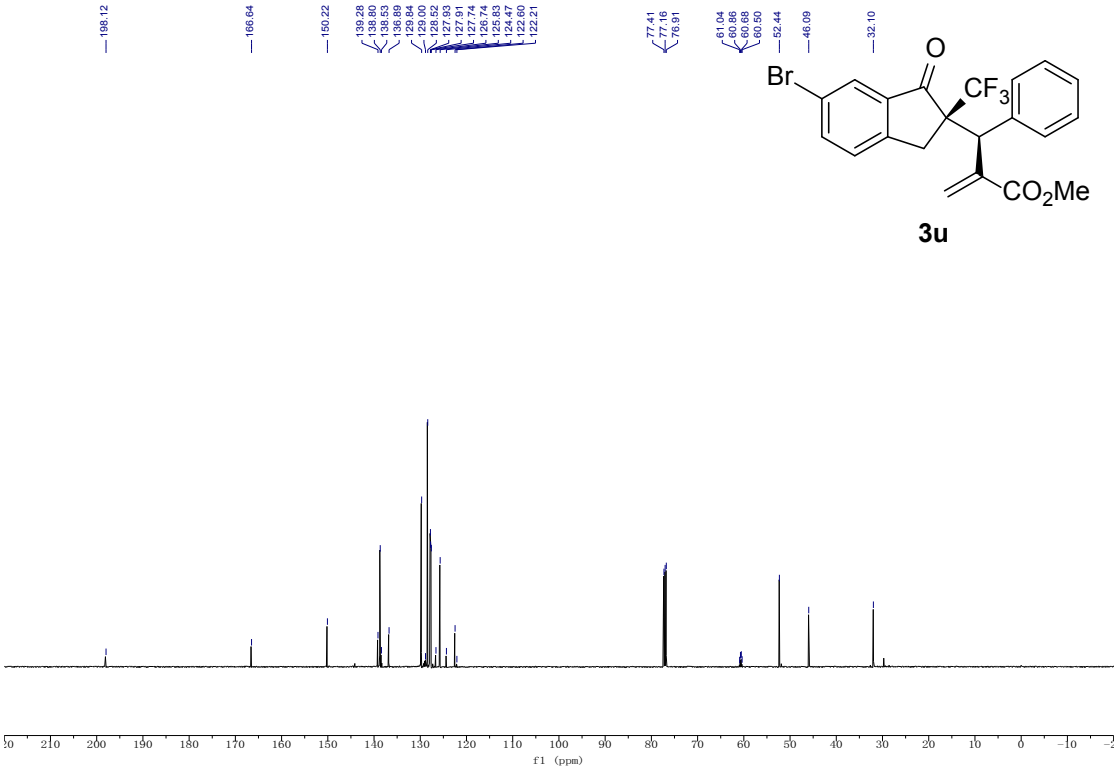


^{1}H NMR spectrum of 3u



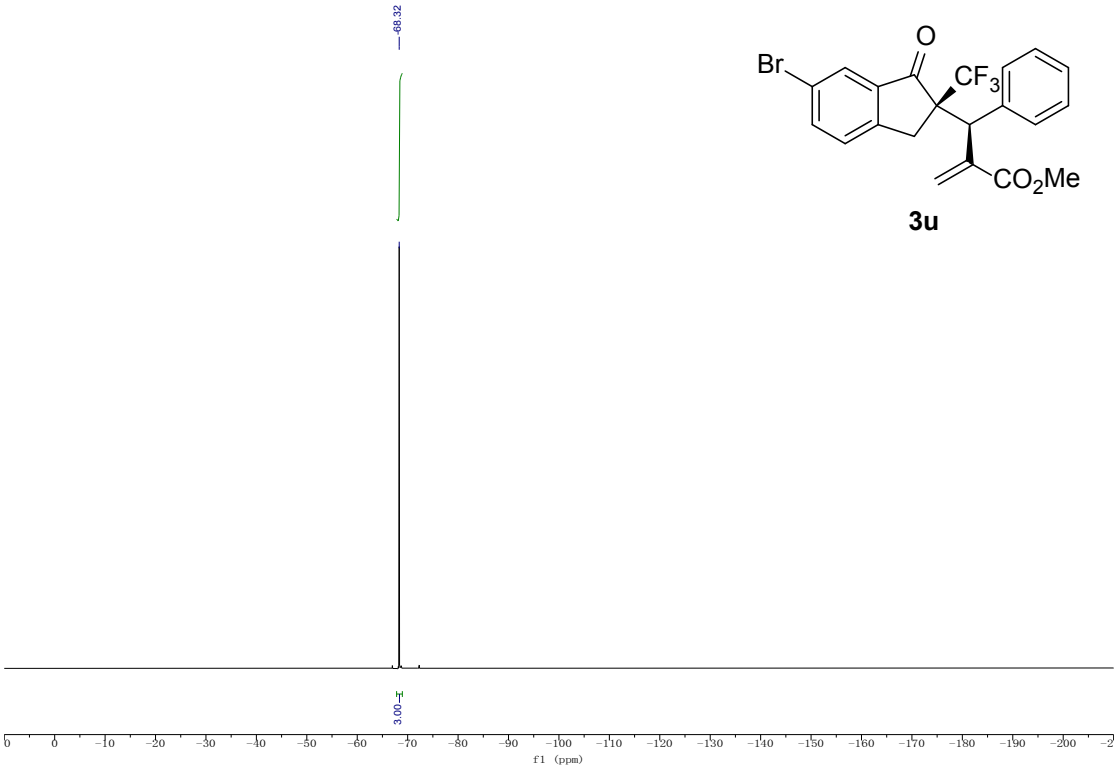
3u

^{13}C NMR spectrum of 3u



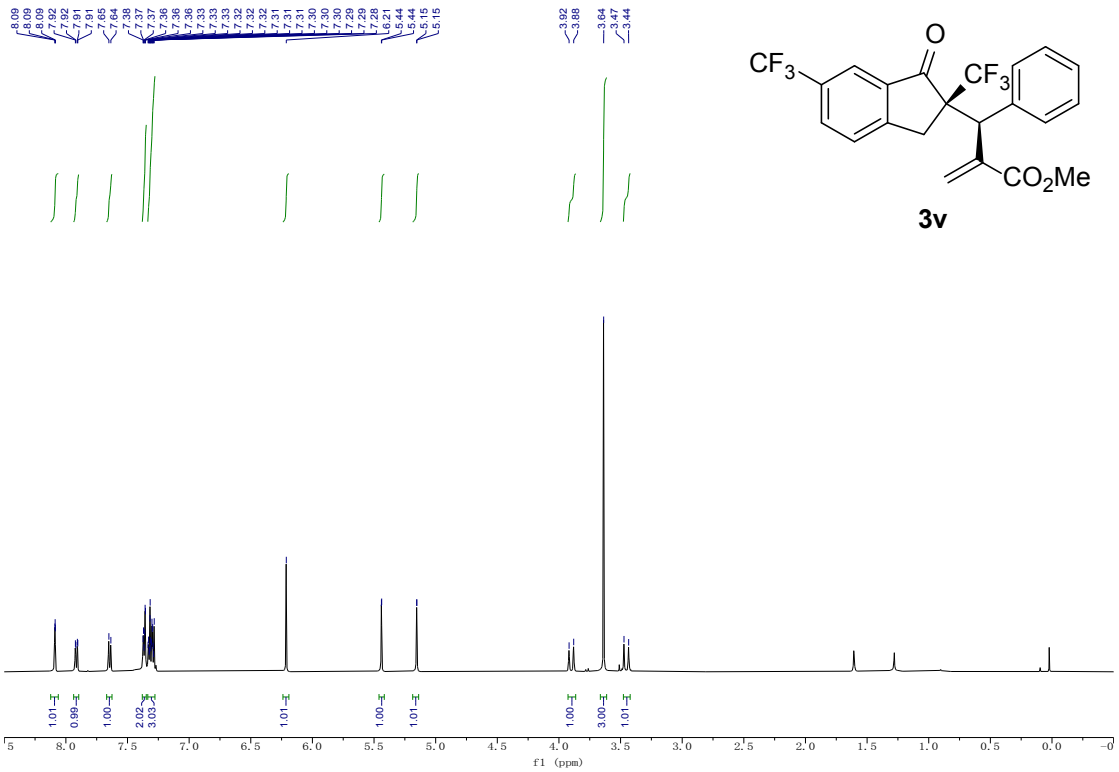
3u

^{19}F NMR spectrum of 3u



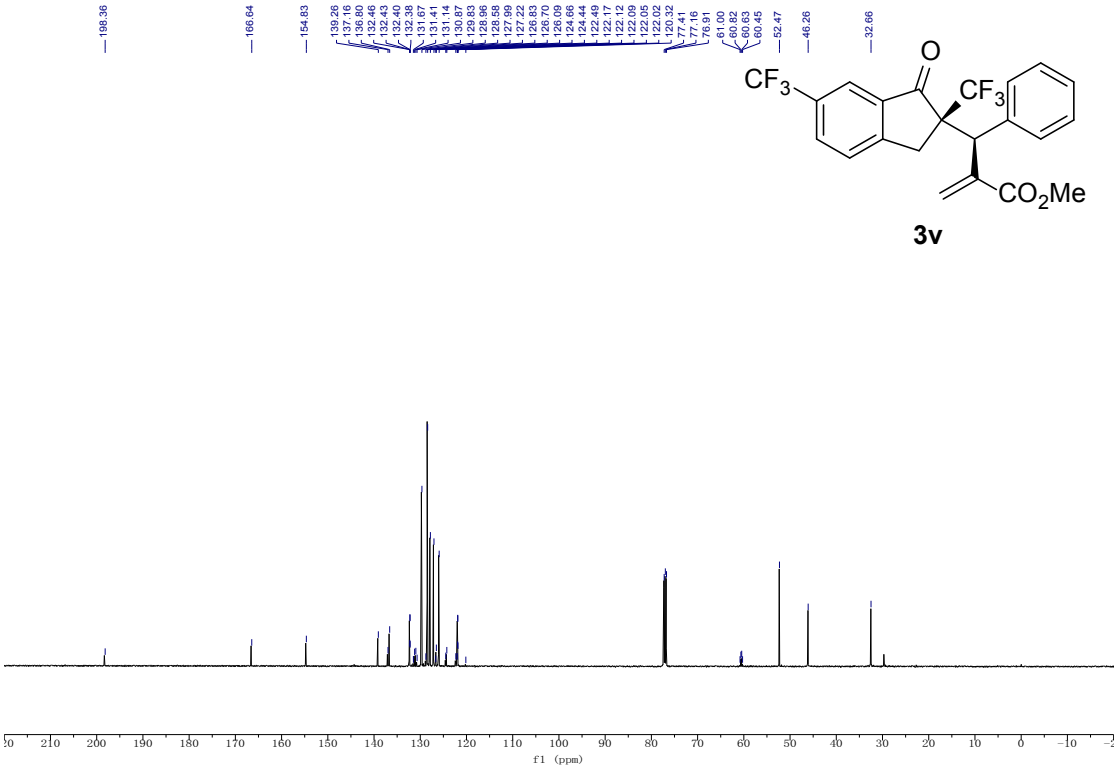
3u

^{1}H NMR spectrum of 3v

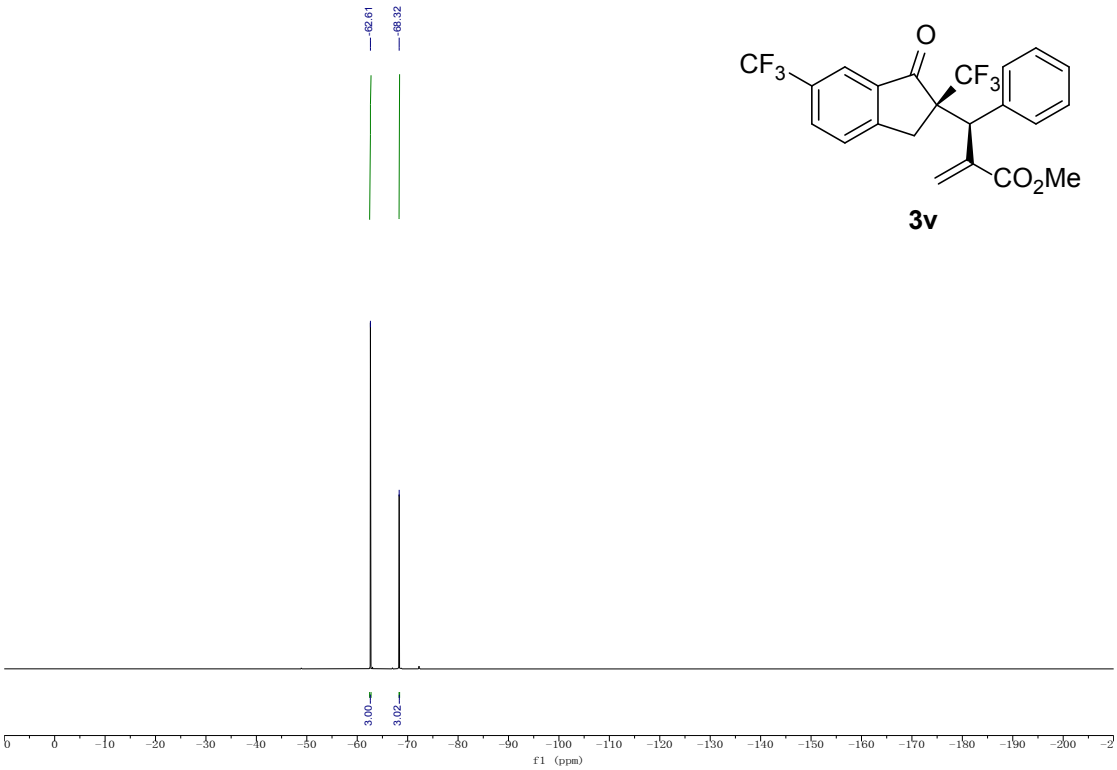


3v

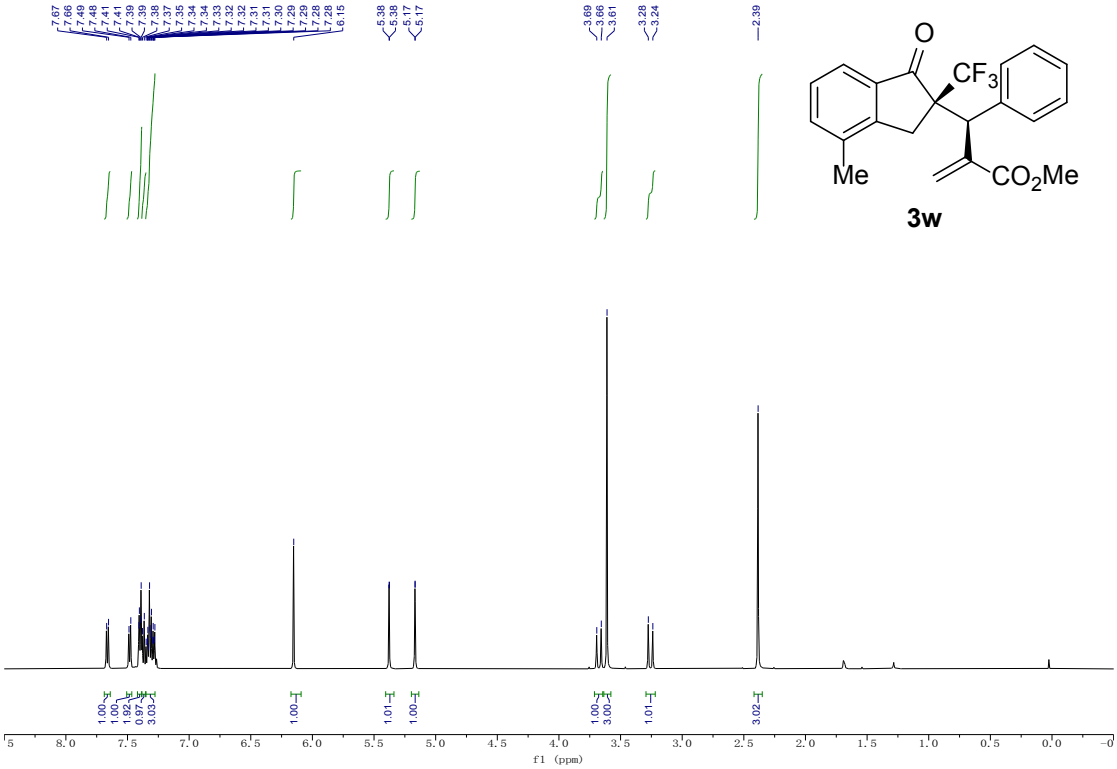
^{13}C NMR spectrum of 3v



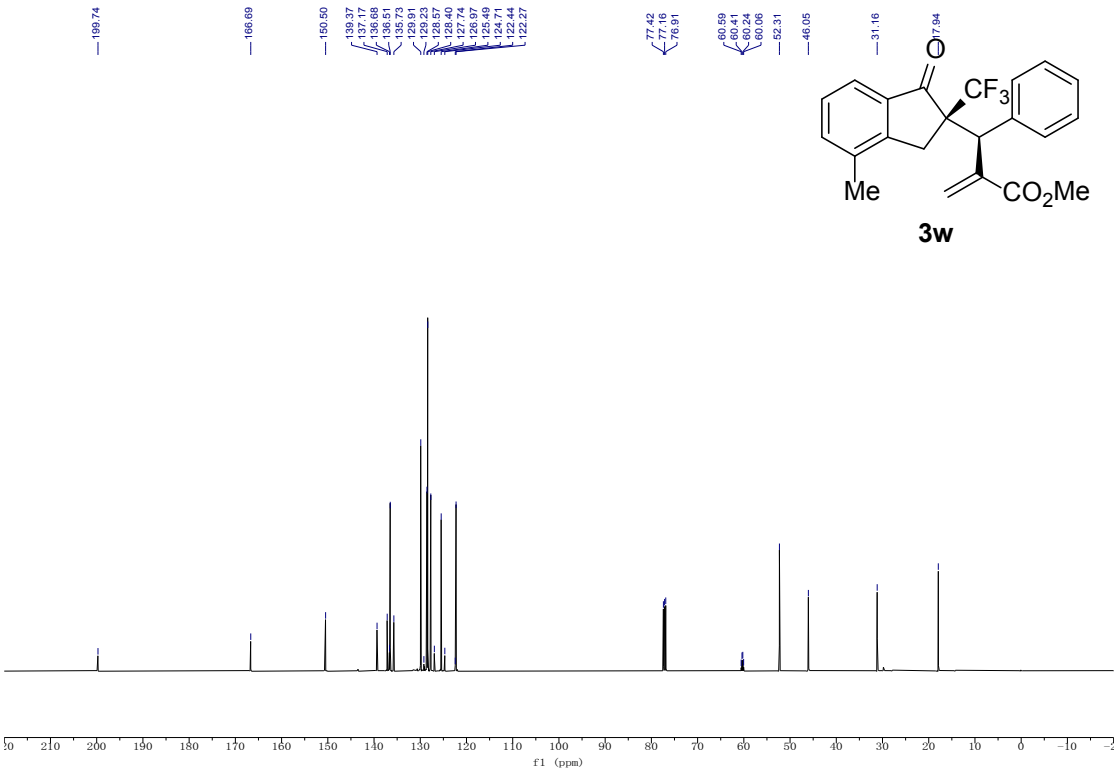
^{19}F NMR spectrum of 3v



^{1}H NMR spectrum of 3w



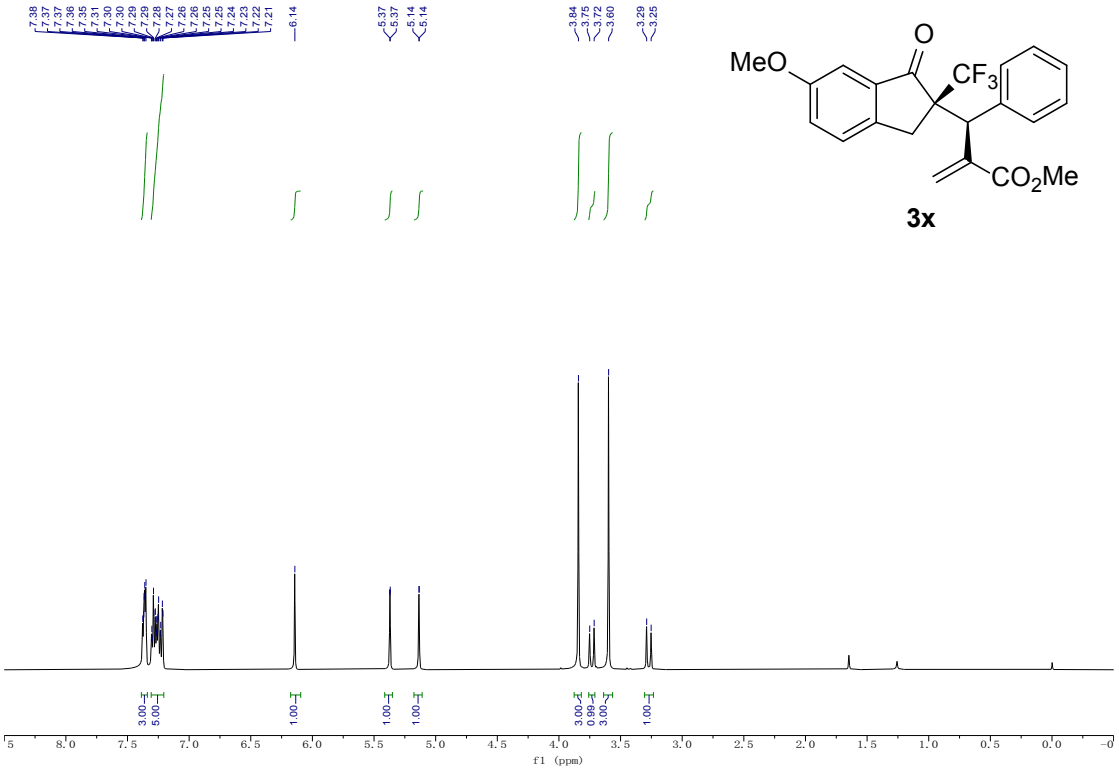
^{13}C NMR spectrum of 3w



^{19}F NMR spectrum of 3w

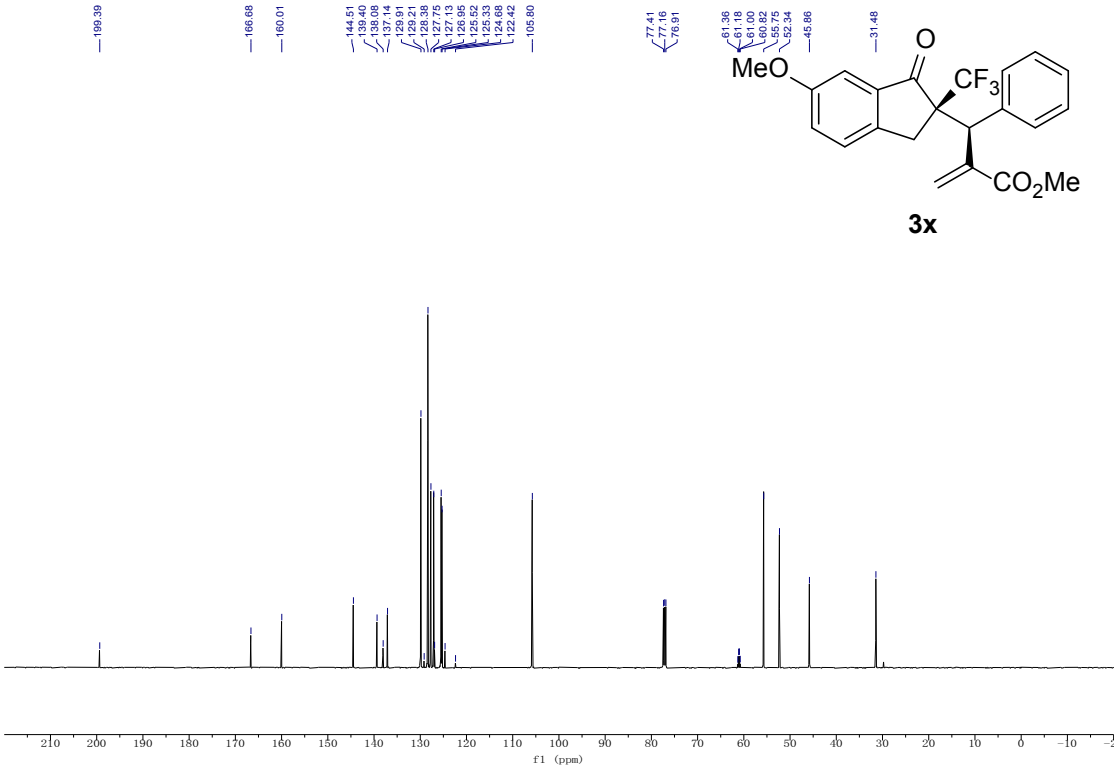
3w

^{1}H NMR spectrum of 3x

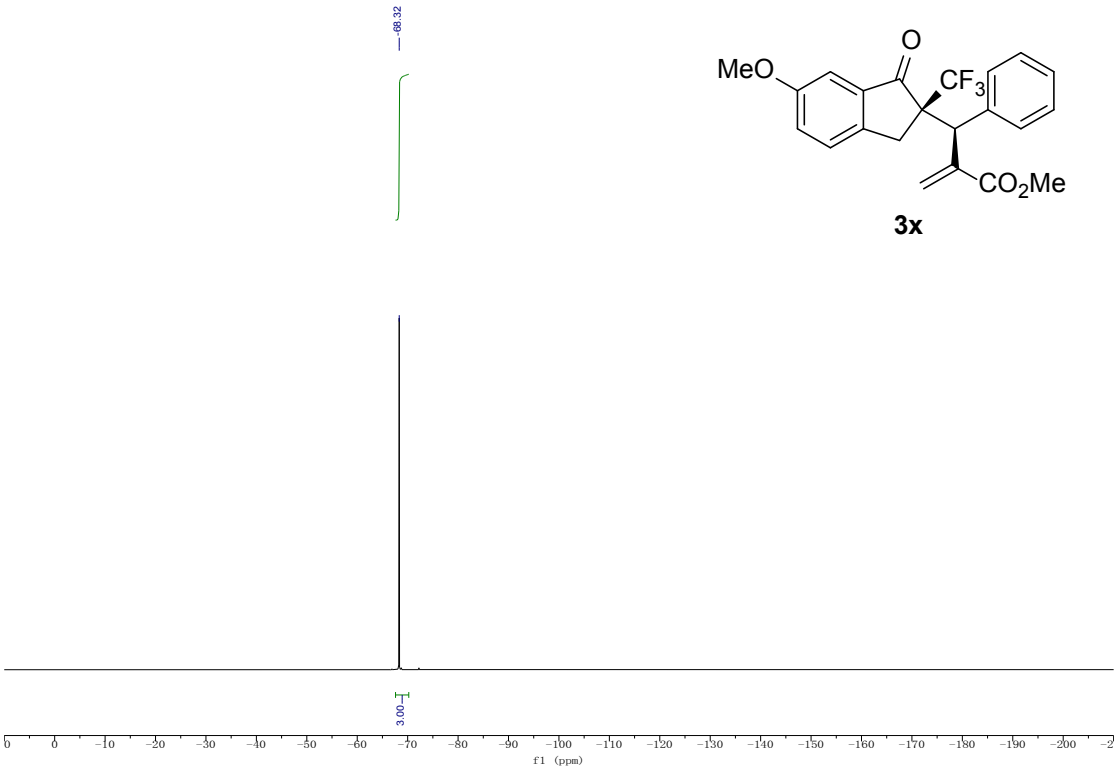


3x

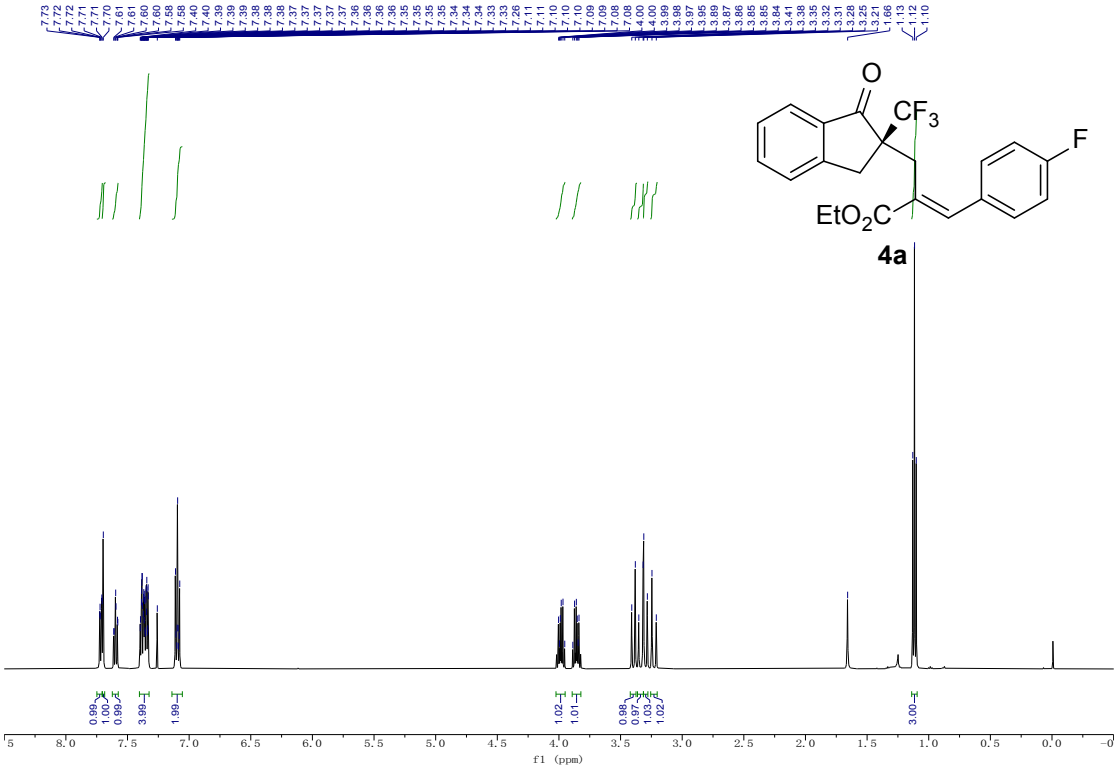
^{13}C NMR spectrum of 3x



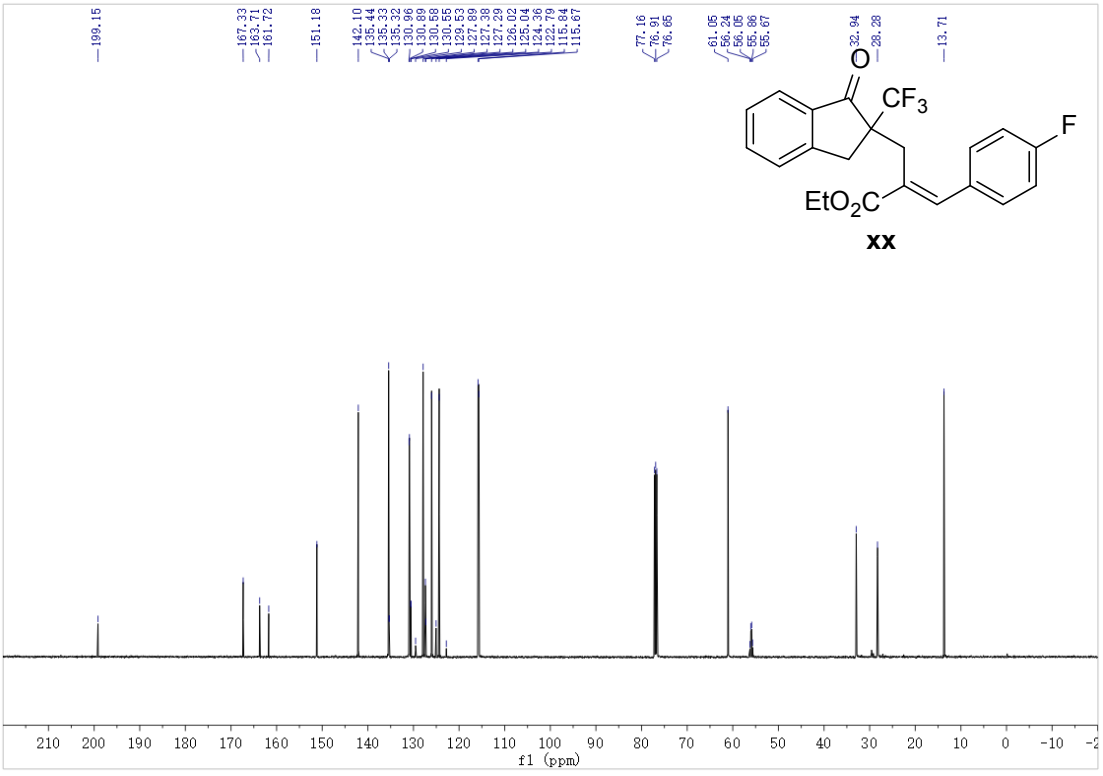
^{19}F NMR spectrum of 3x



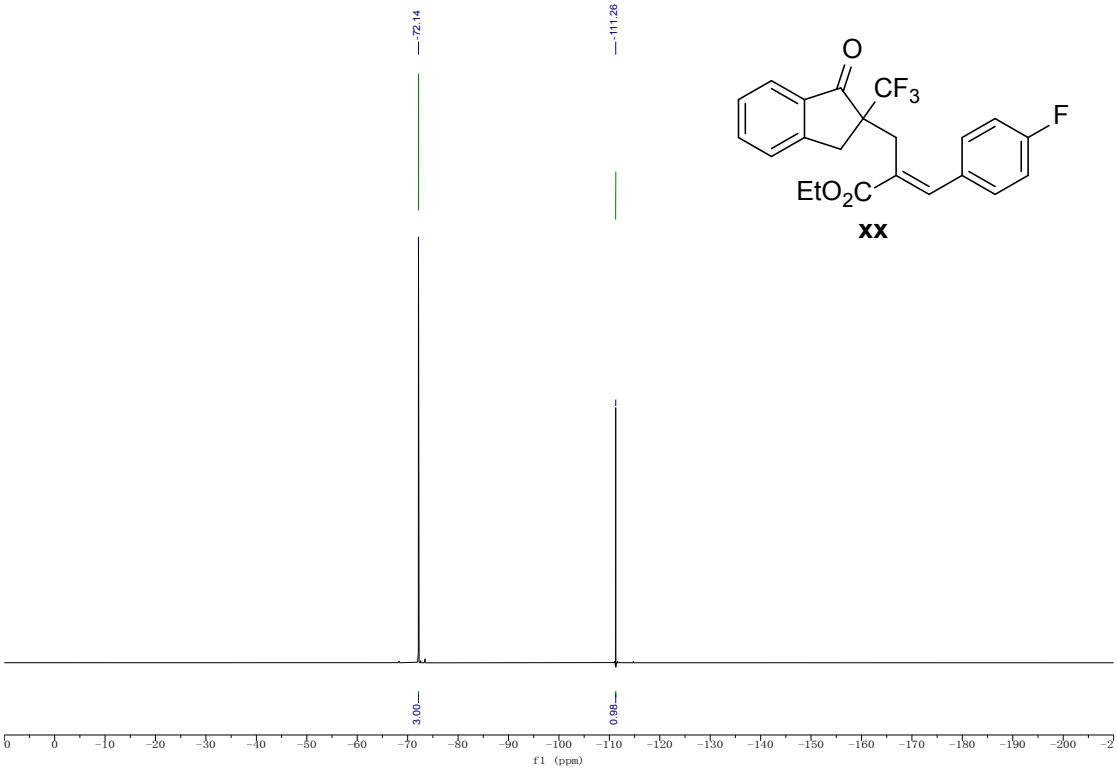
^{1}H NMR spectrum of 4a



^{13}C NMR spectrum of xx

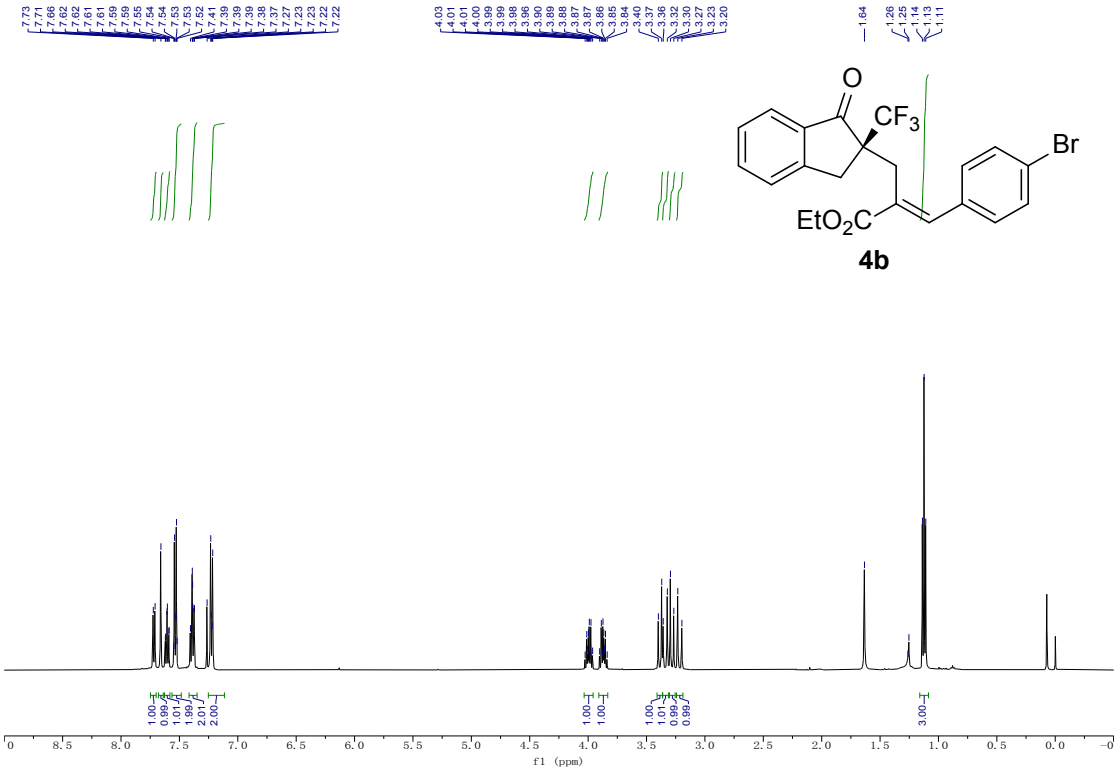


^{19}F NMR spectrum of xx



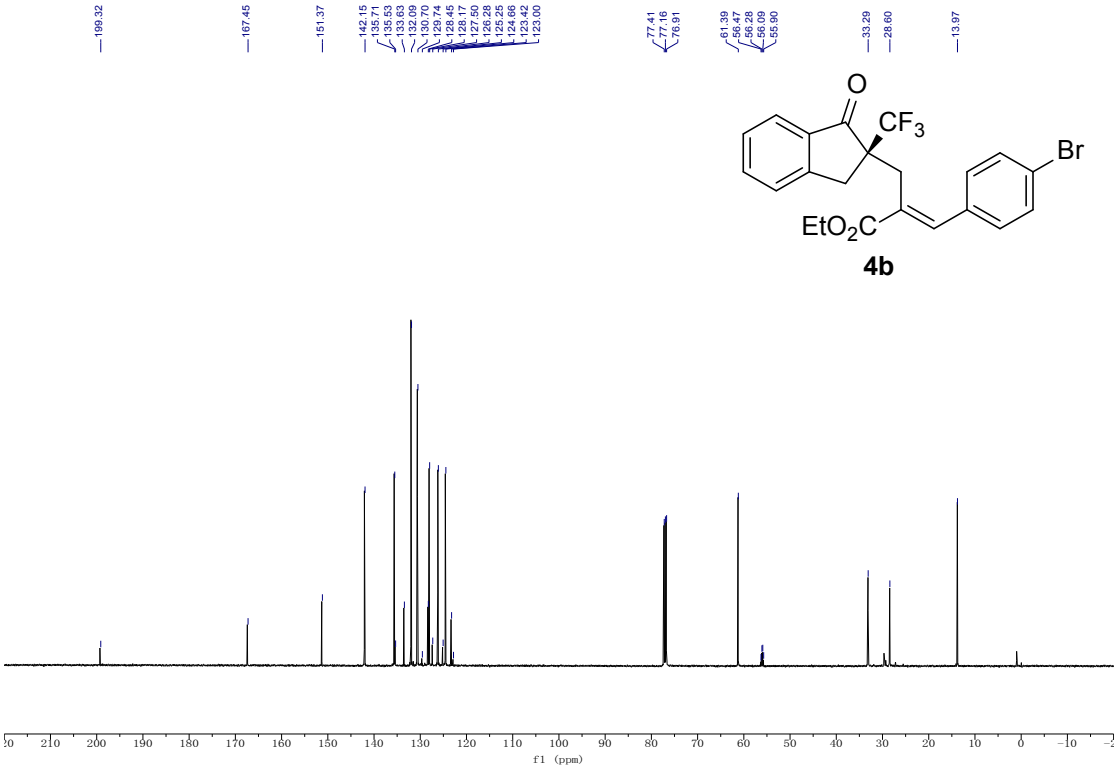
xx

^{1}H NMR spectrum of 4b

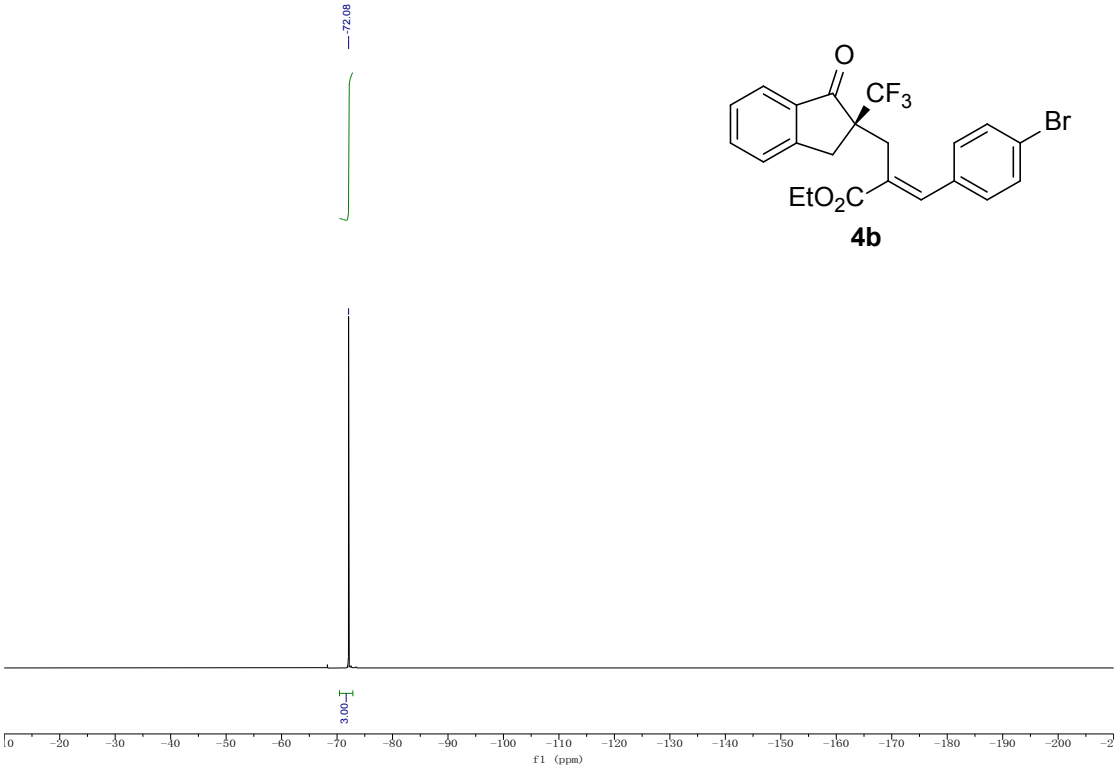


4b

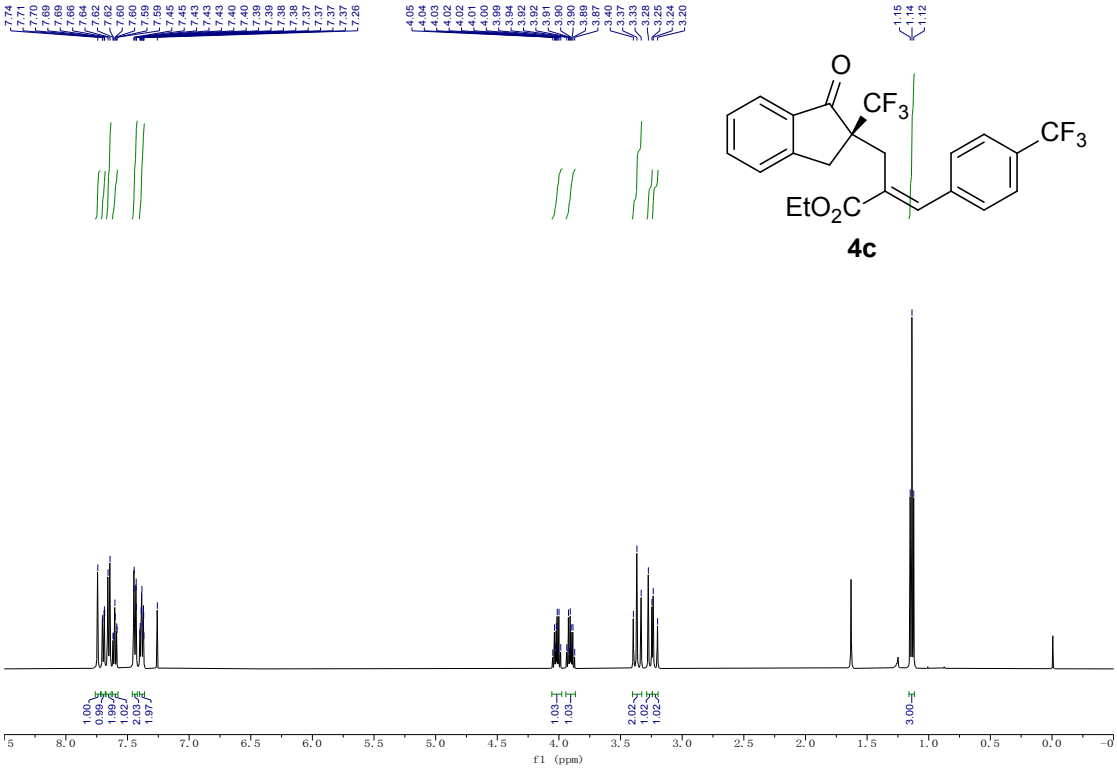
^{13}C NMR spectrum of 4b



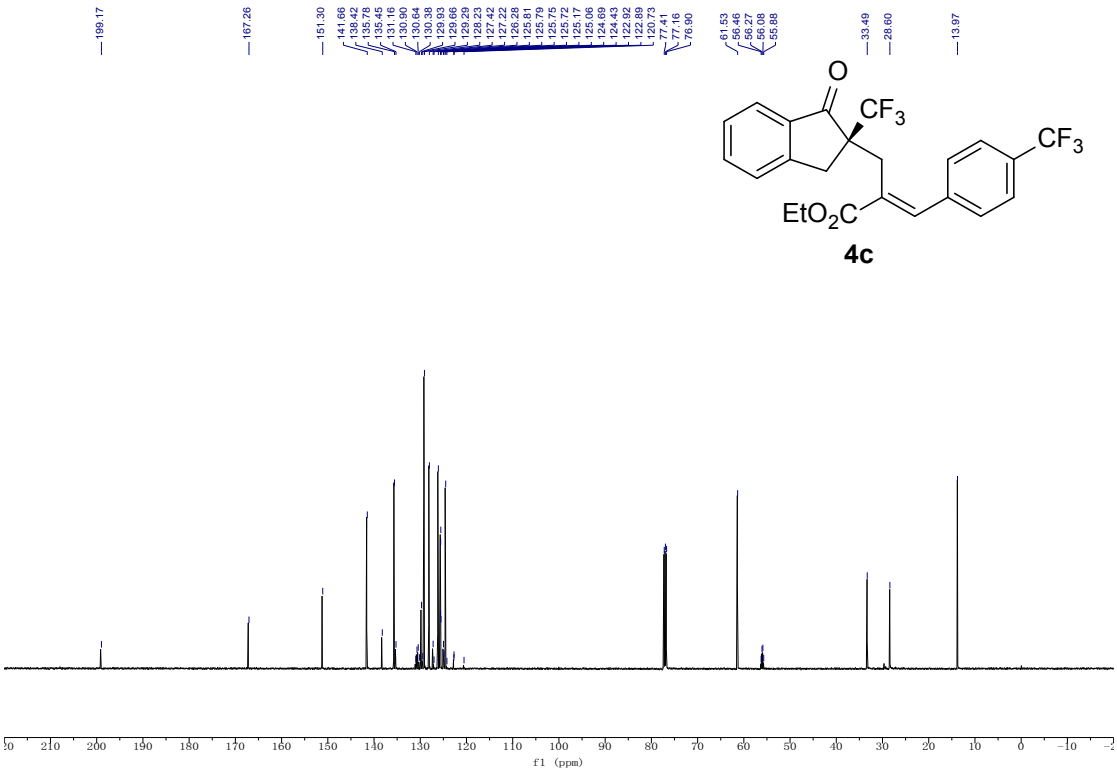
^{19}F NMR spectrum of 4b



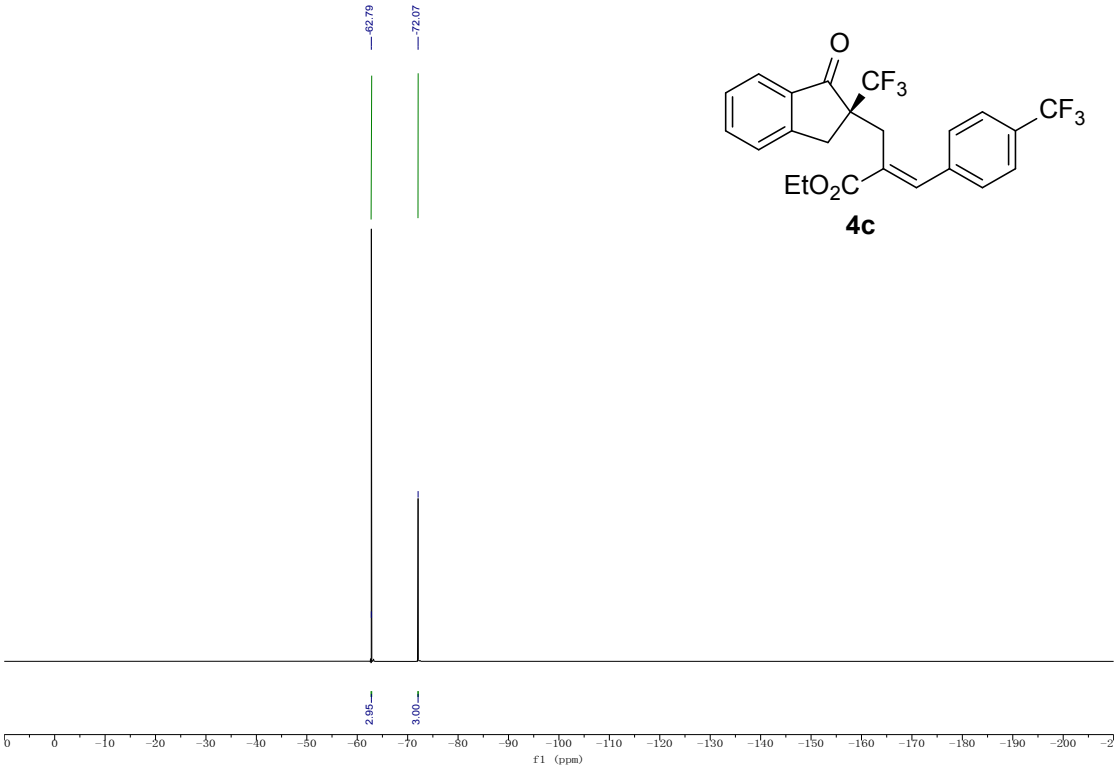
^{1}H NMR spectrum of 4c



^{13}C NMR spectrum of 4c

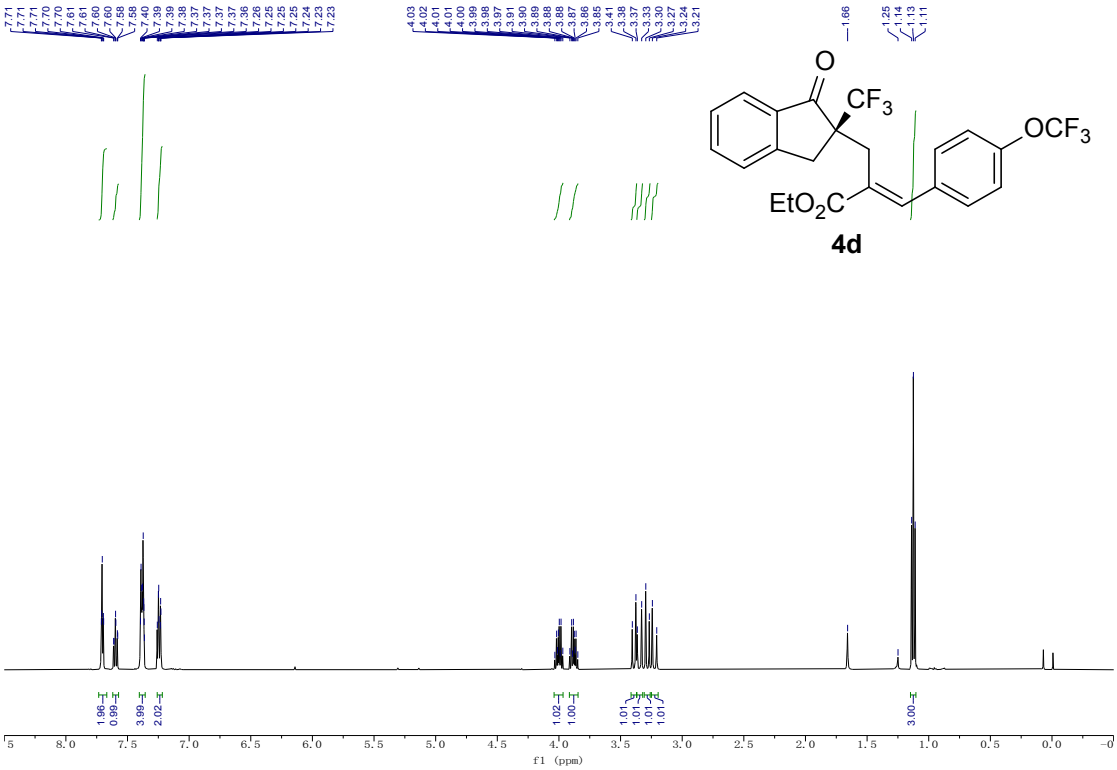


^{19}F NMR spectrum of 4c



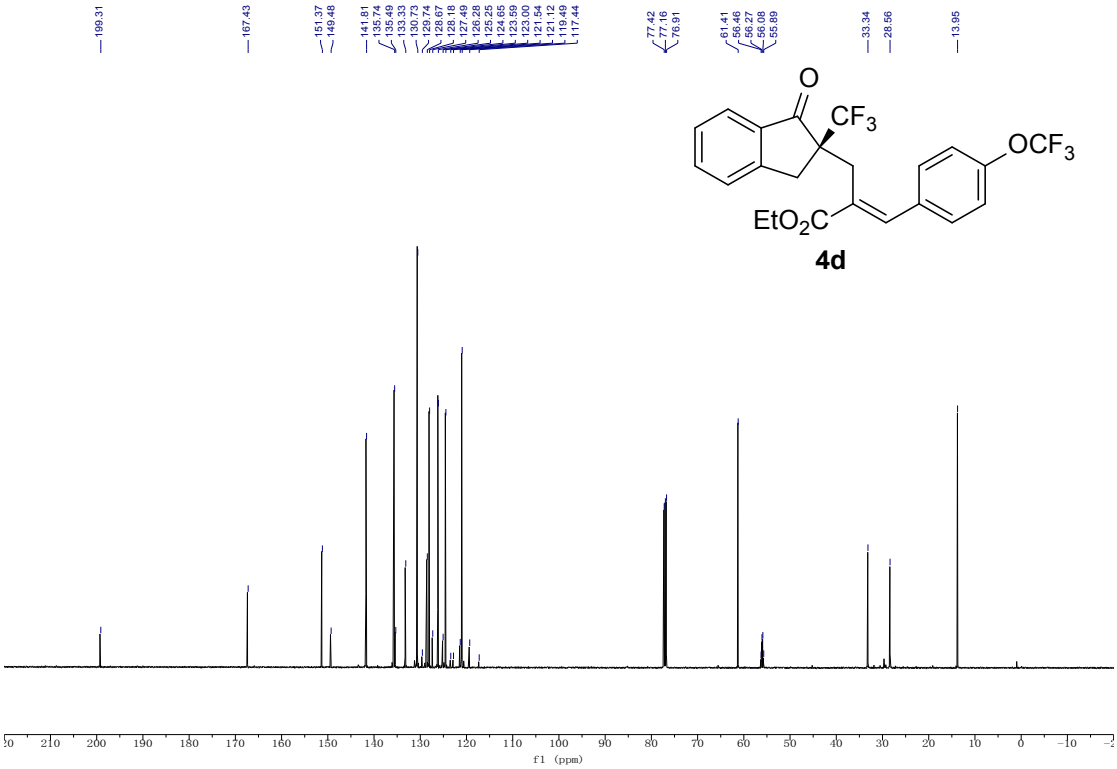
4c

^{1}H NMR spectrum of 4d

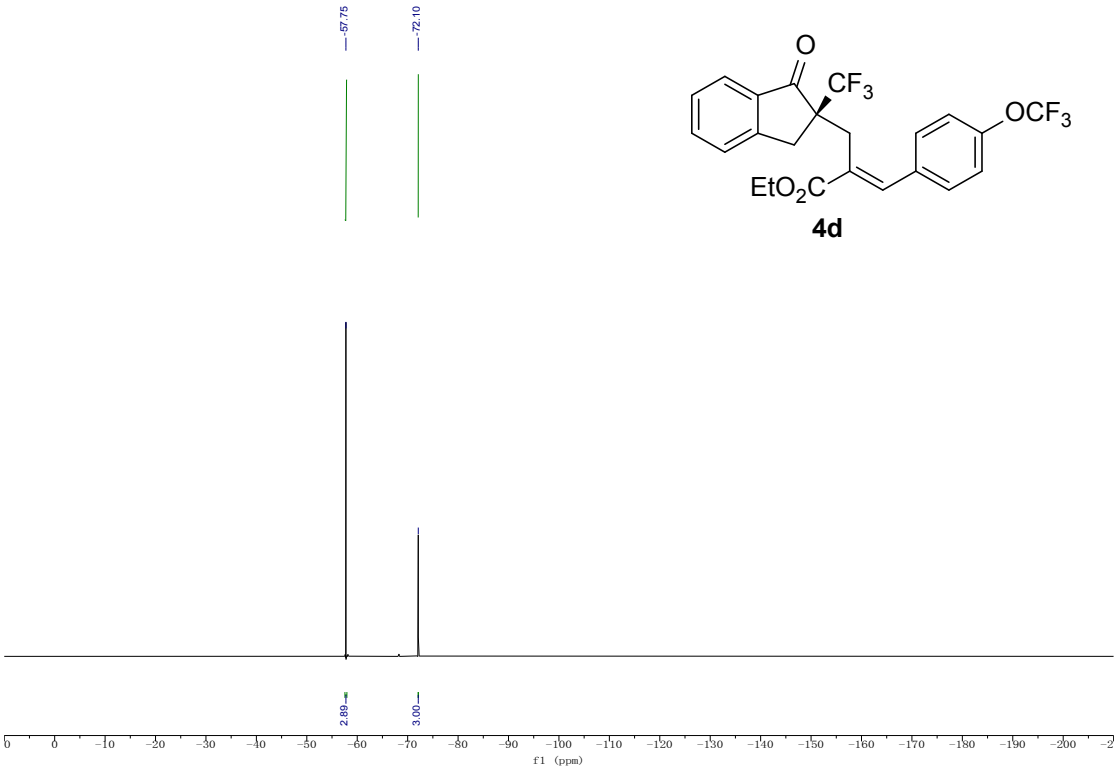


4d

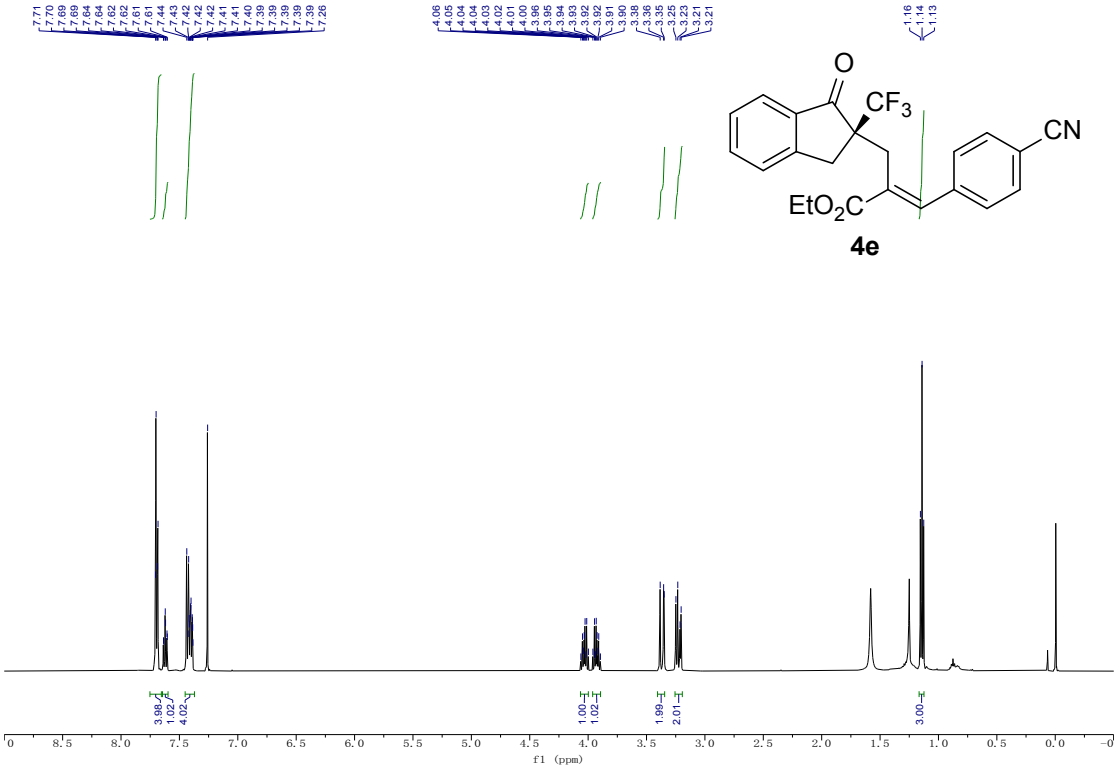
^{13}C NMR spectrum of 4d



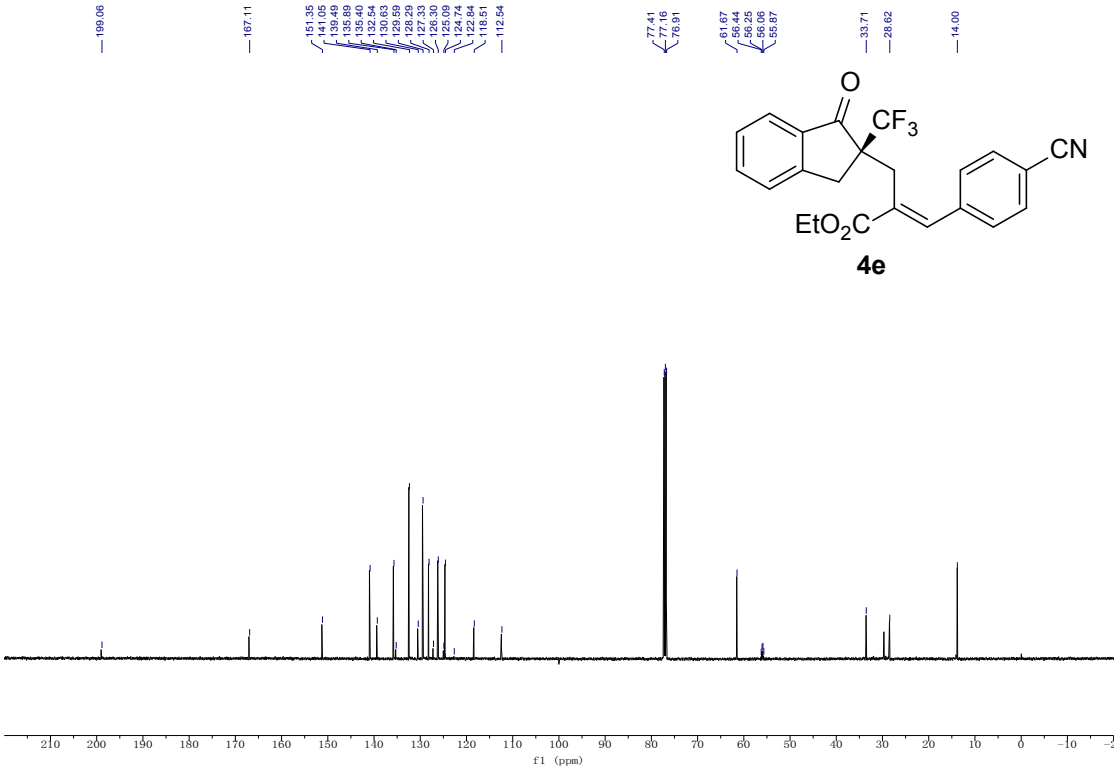
^{19}F NMR spectrum of 4d



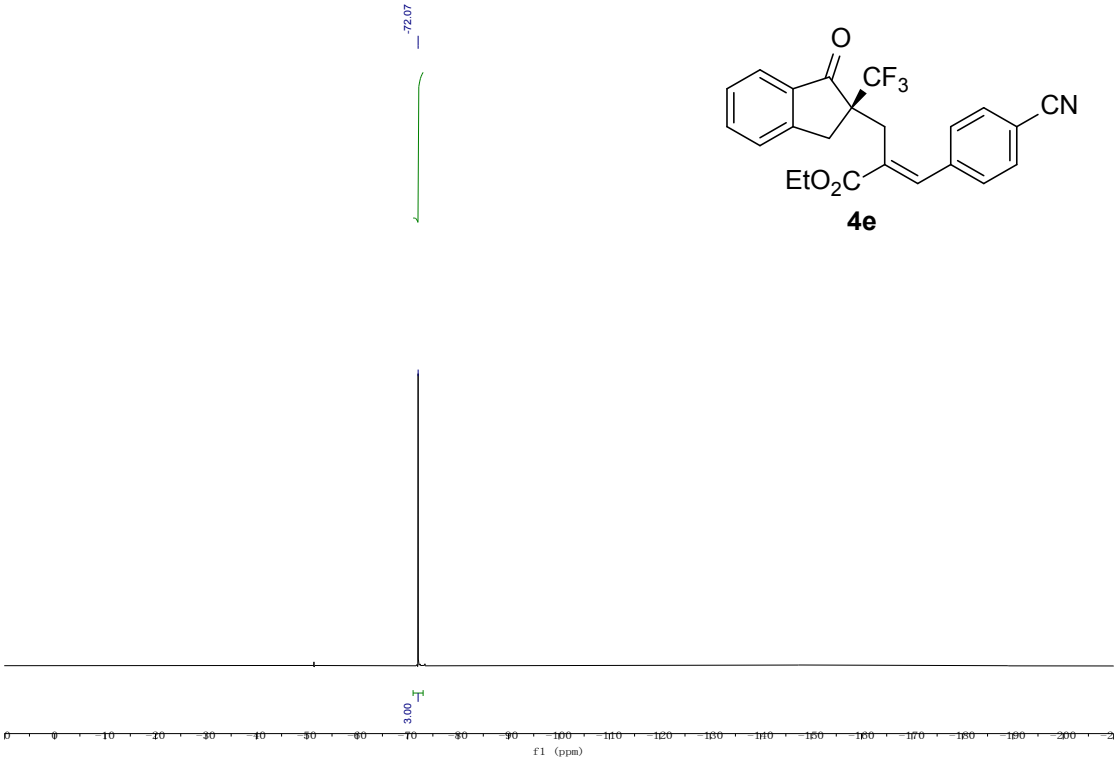
^{1}H NMR spectrum of 4e



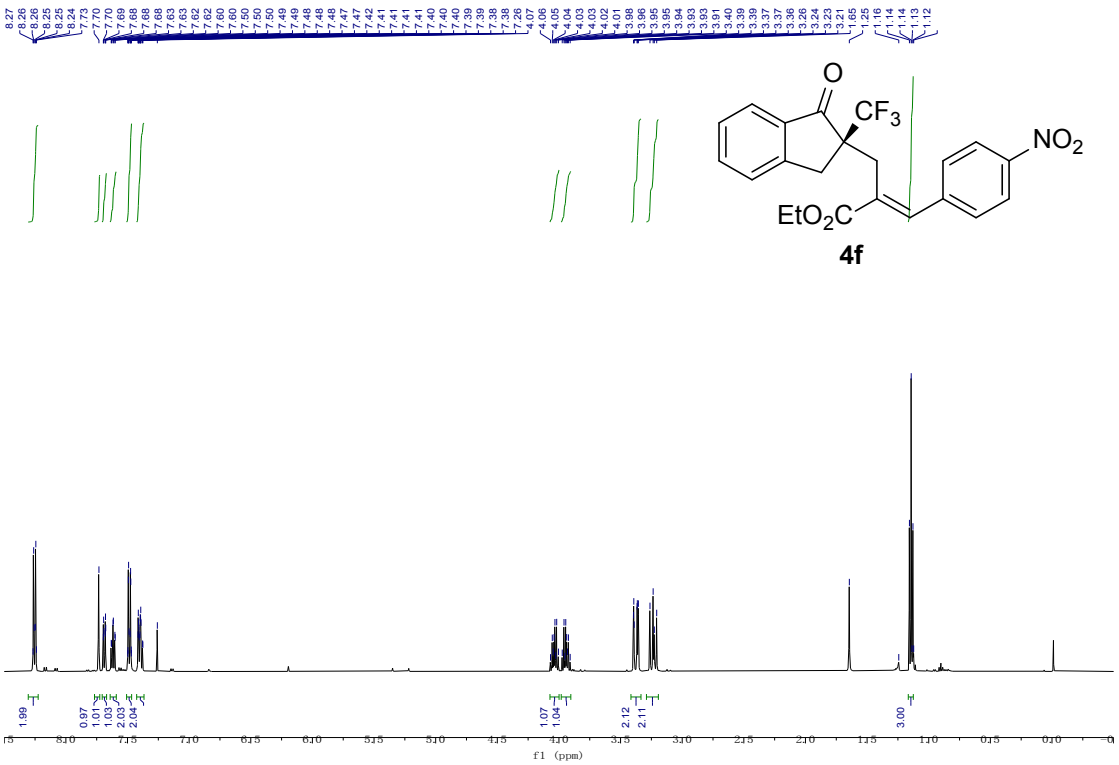
^{13}C NMR spectrum of 4e



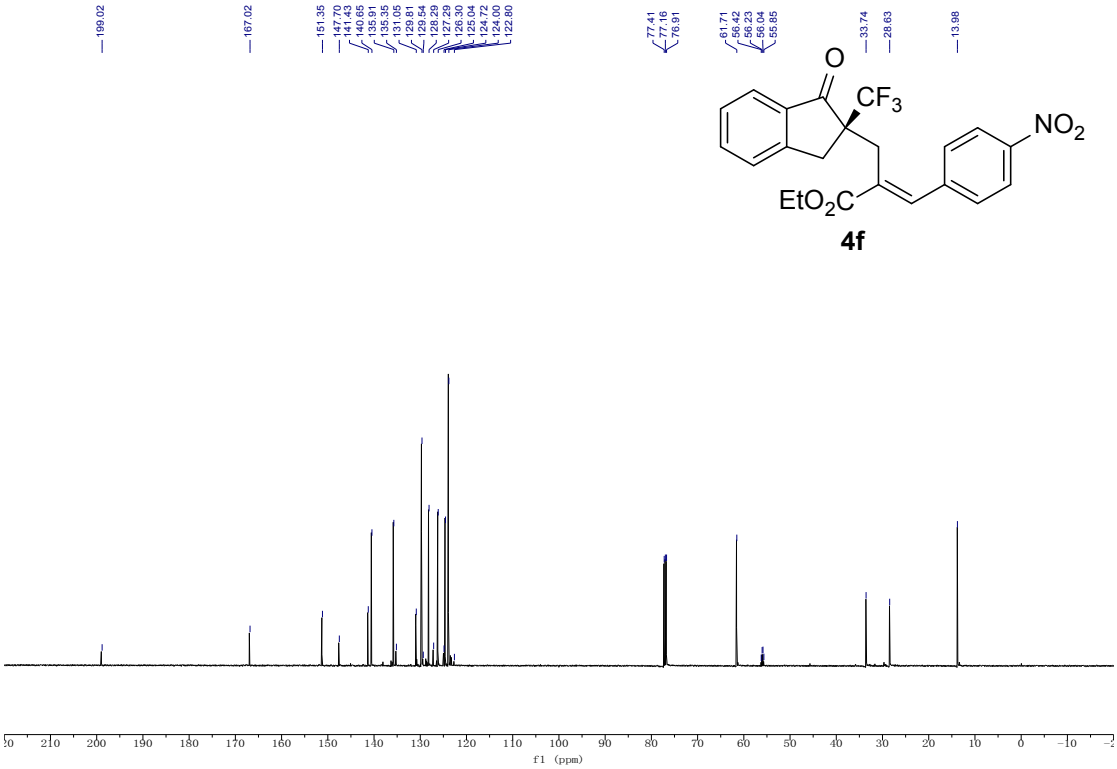
^{19}F NMR spectrum of 4e



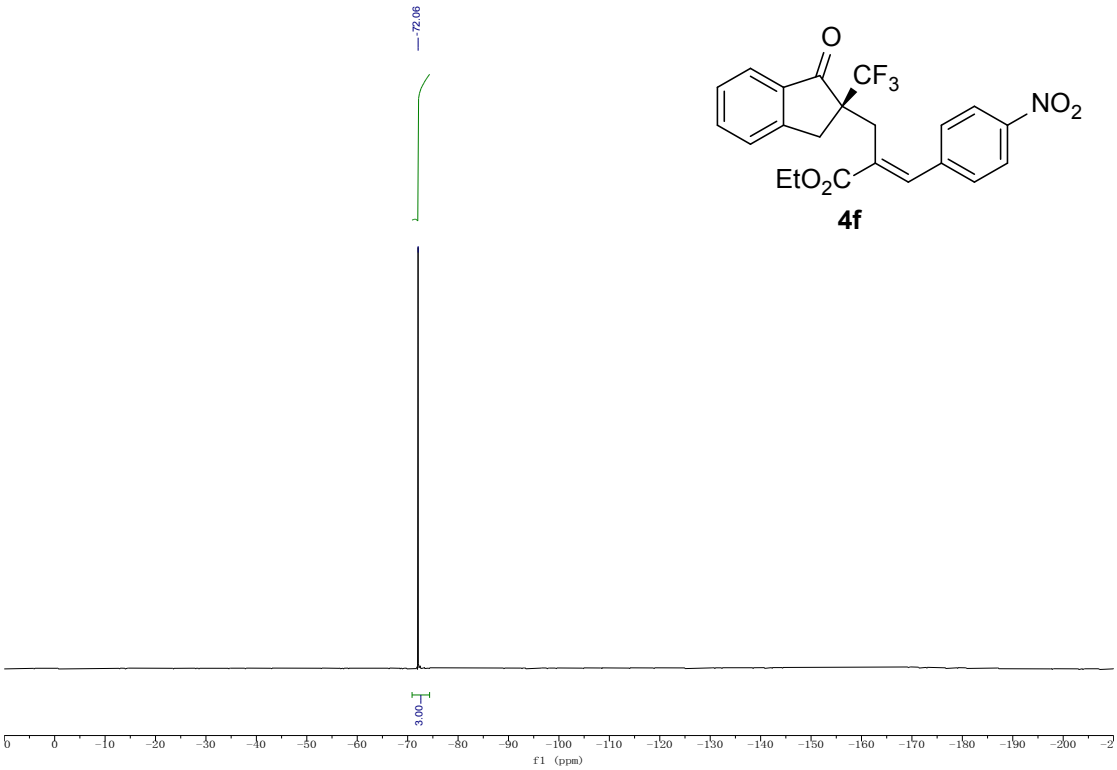
^{1}H NMR spectrum of 4f



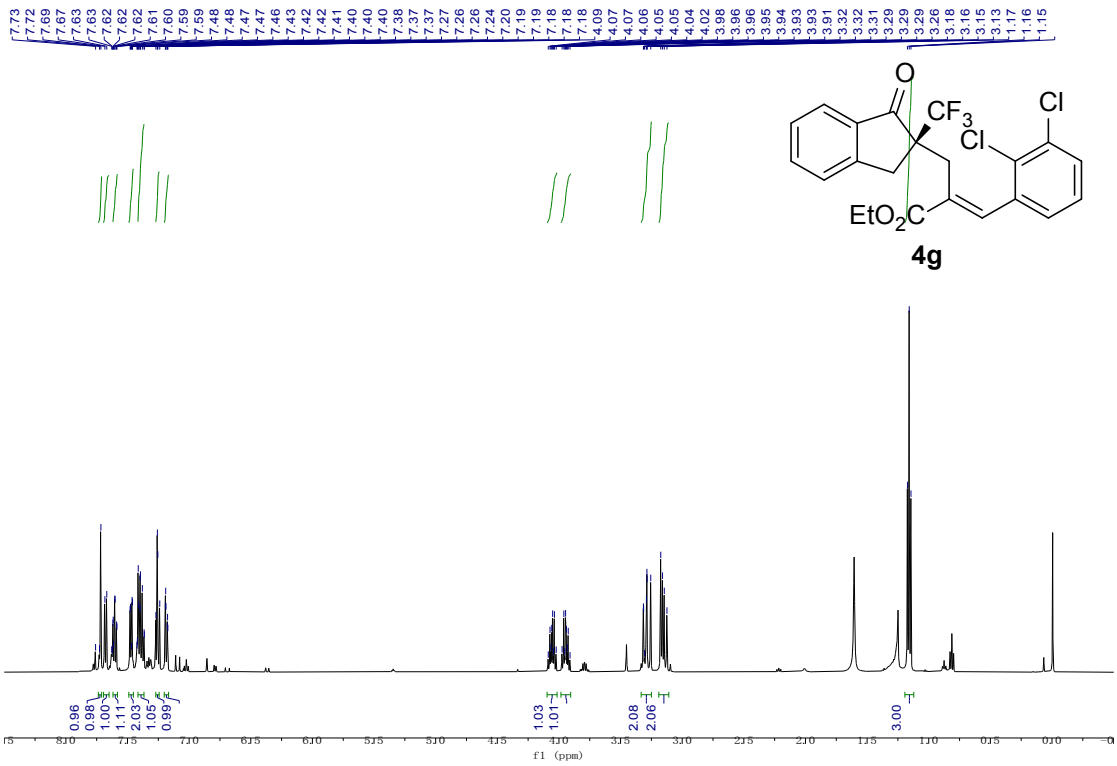
^{13}C NMR spectrum of 4f



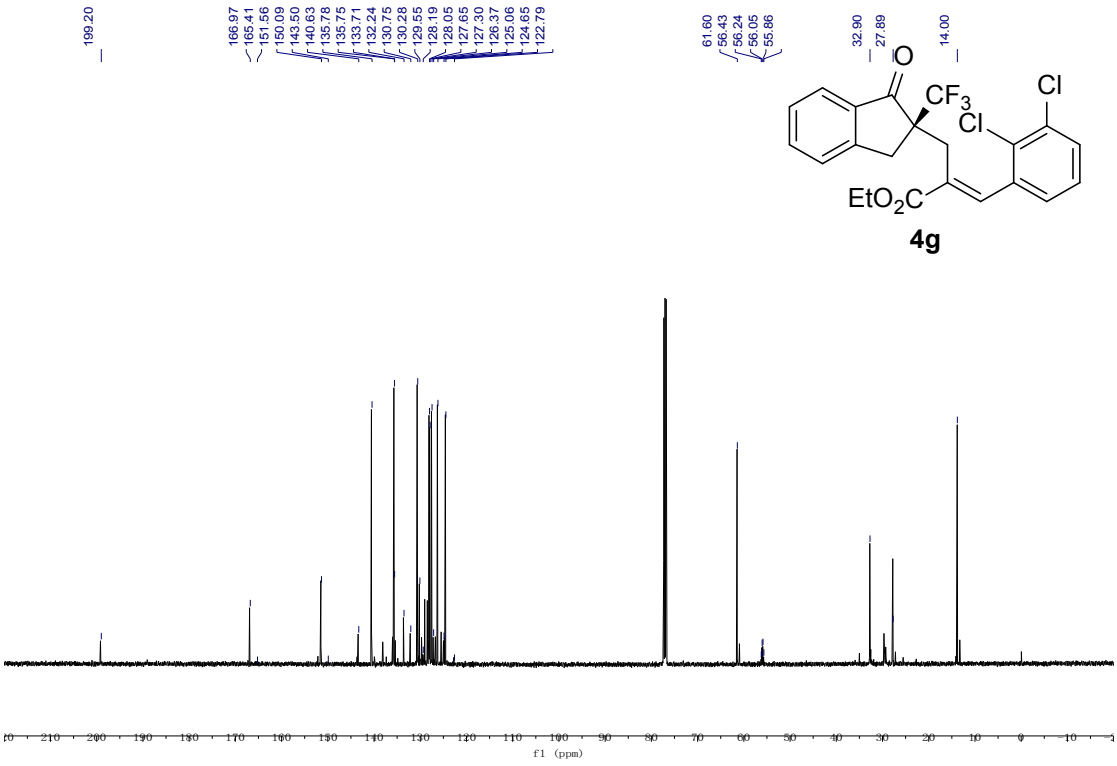
^{19}F NMR spectrum of 4f



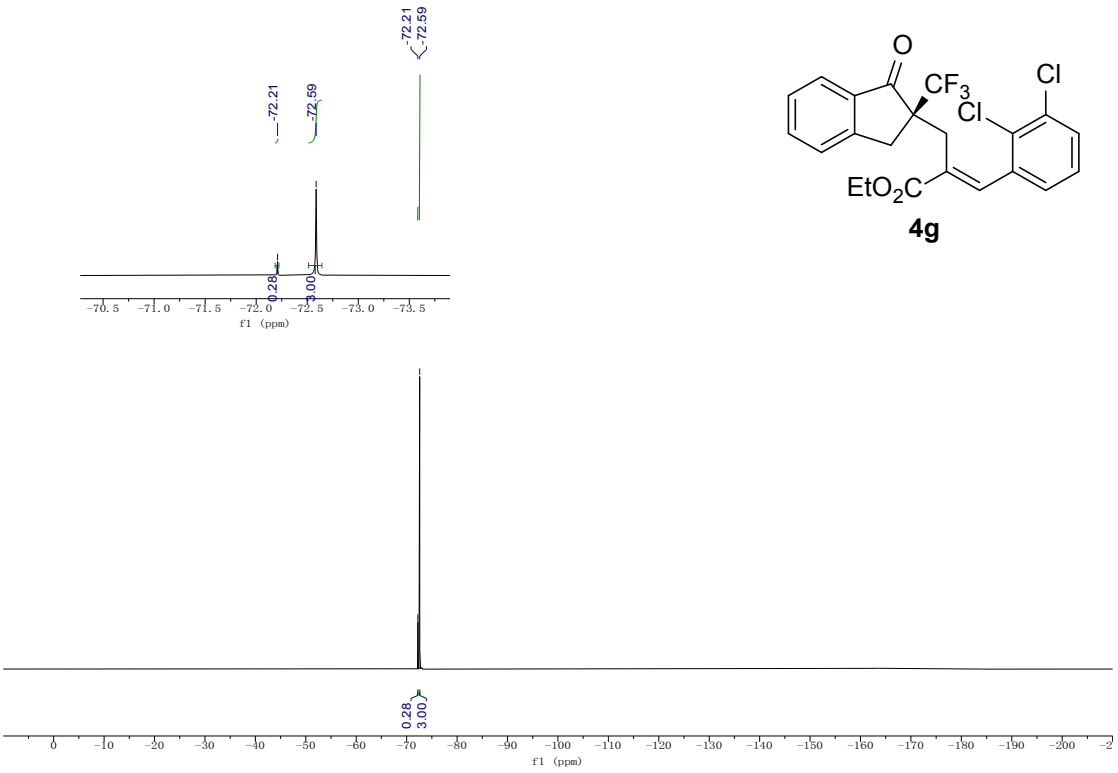
^{1}H NMR spectrum of 4g (a mixture of isomers with 10:1 E/Z)



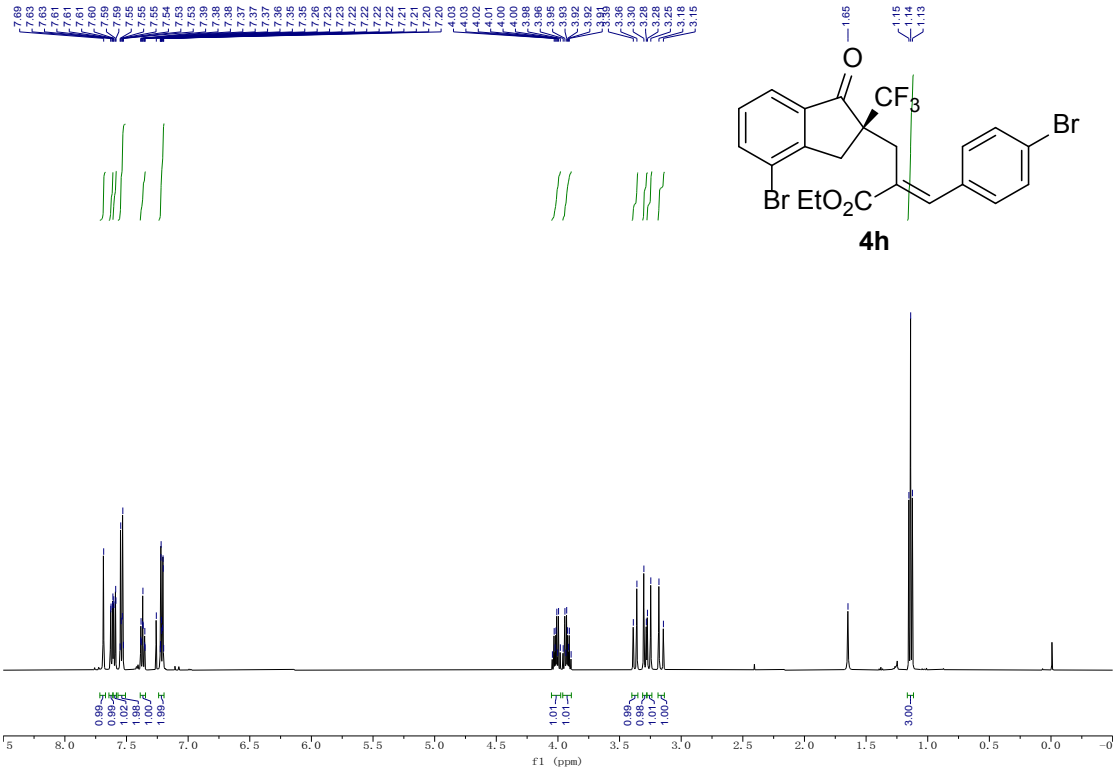
^{13}C NMR spectrum of 4g (a mixture of isomers with 10:1 E/Z)



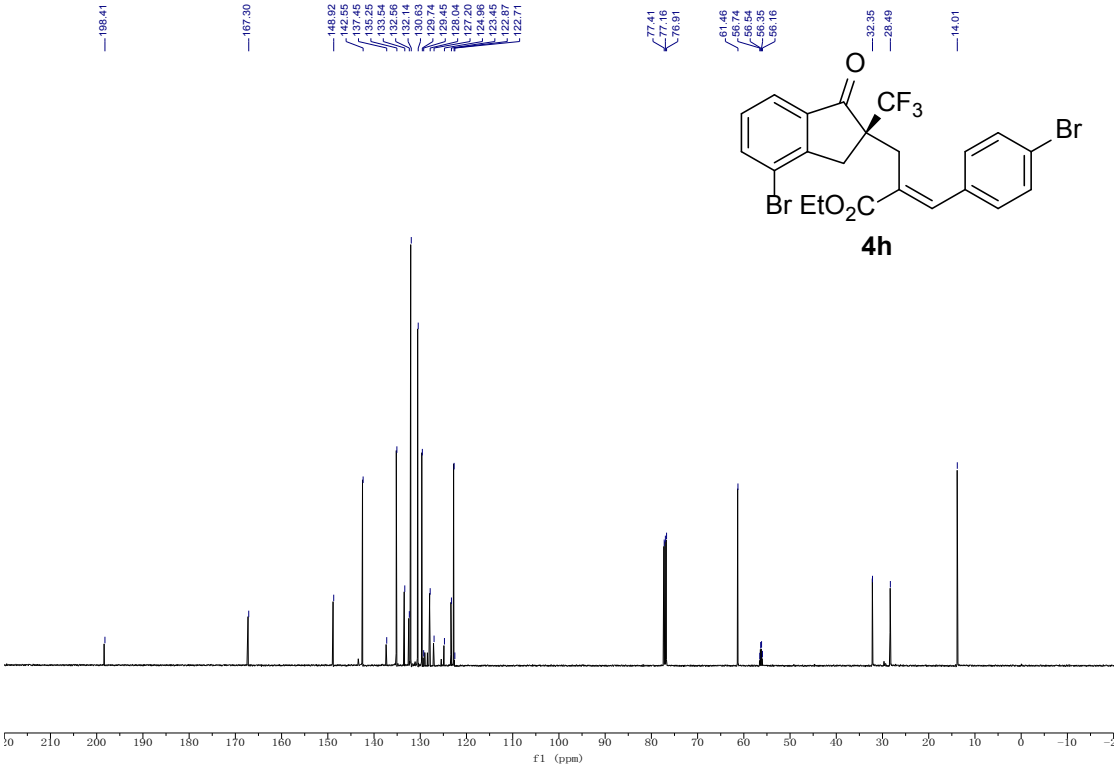
^{19}F NMR spectrum of 4g (a mixture of isomers with 10:1 E/Z)



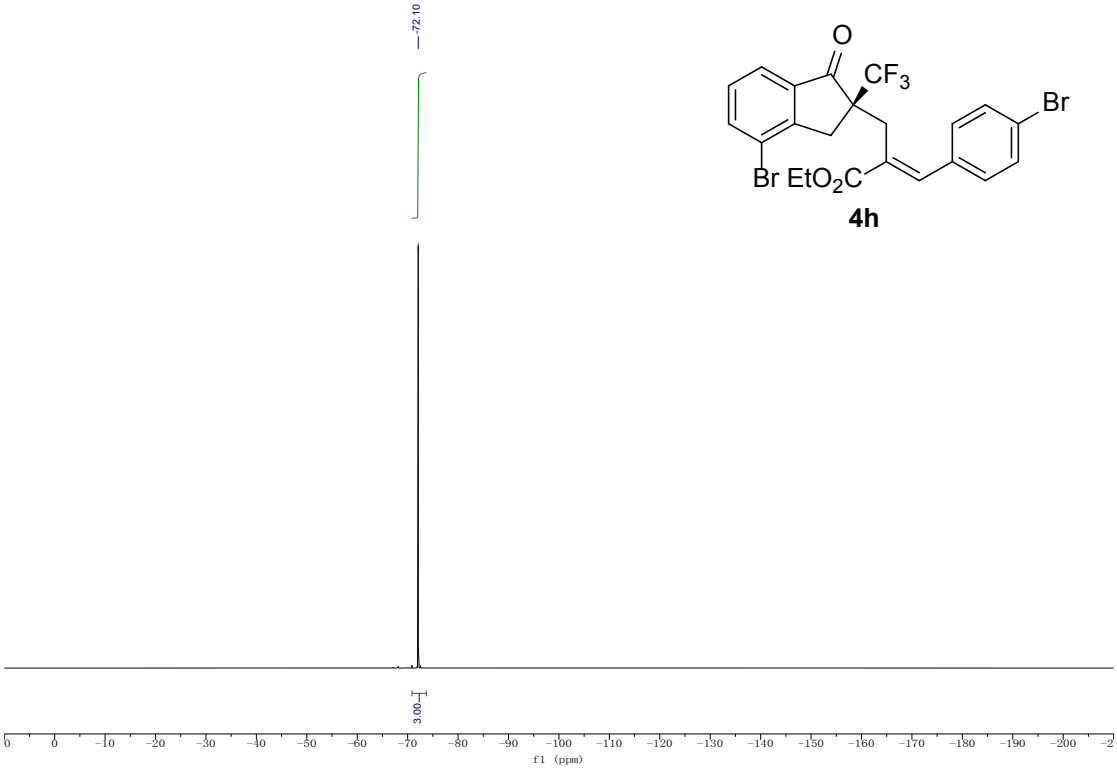
^{1}H NMR spectrum of 4h



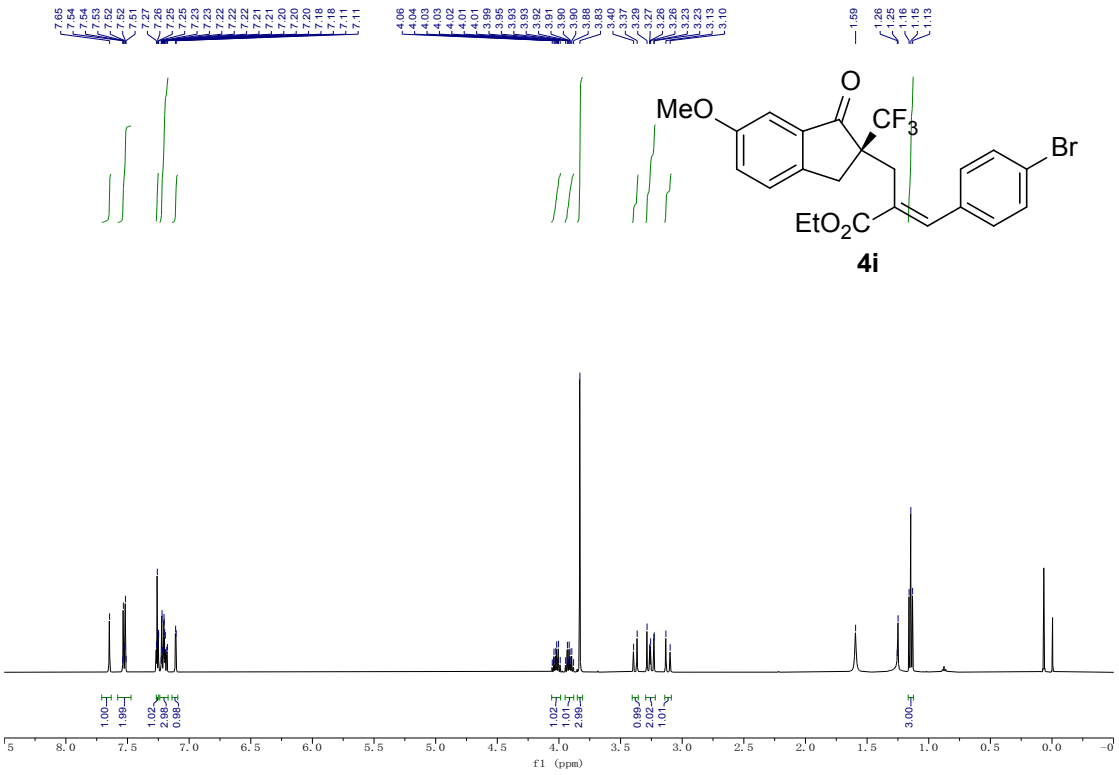
^{13}C NMR spectrum of 4h



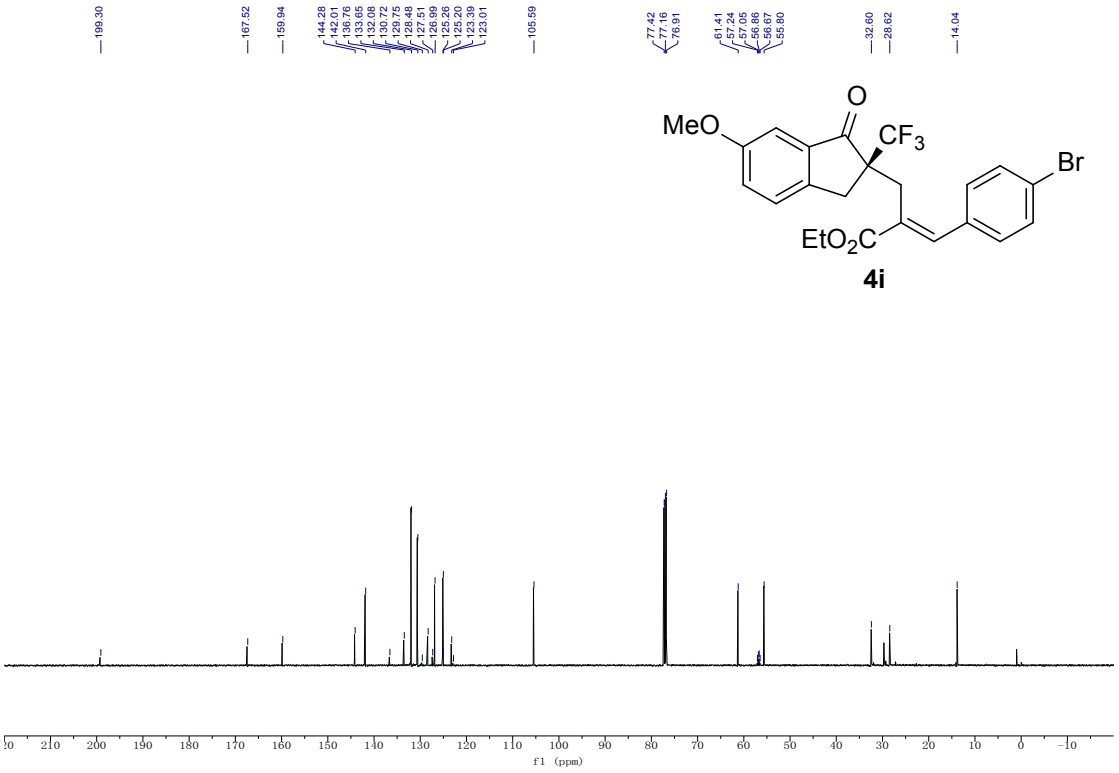
^{19}F NMR spectrum of 4h



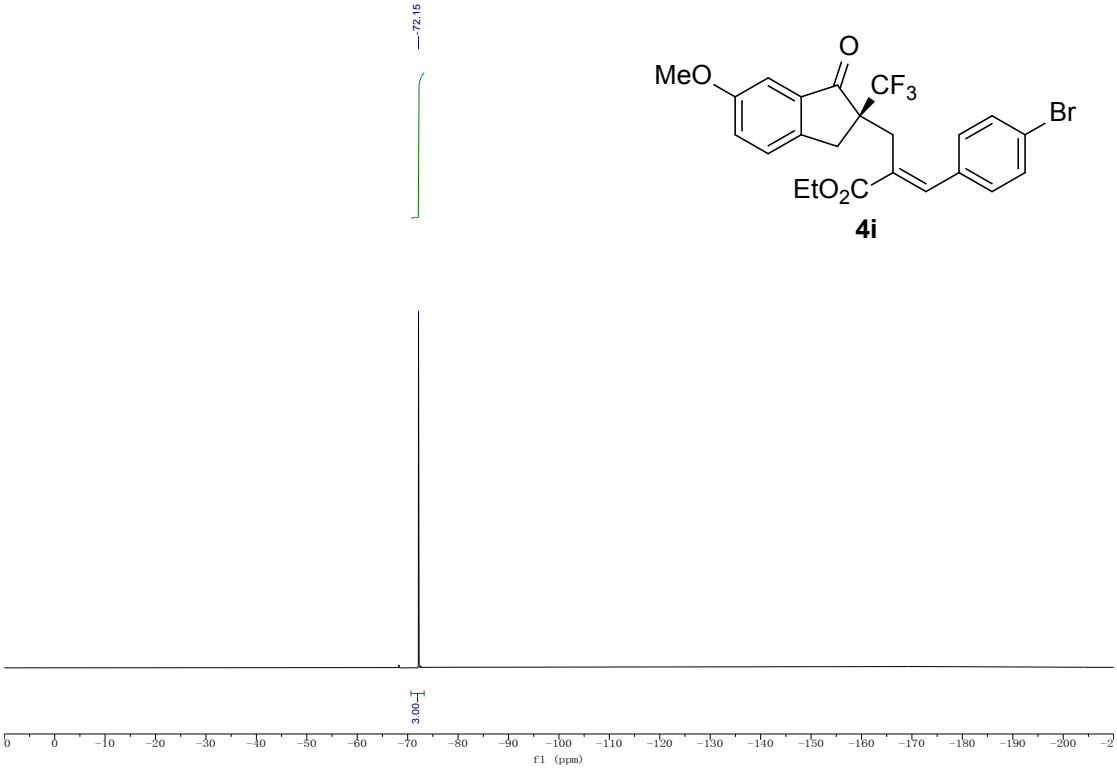
^{1}H NMR spectrum of 4i



^{13}C NMR spectrum of 4i

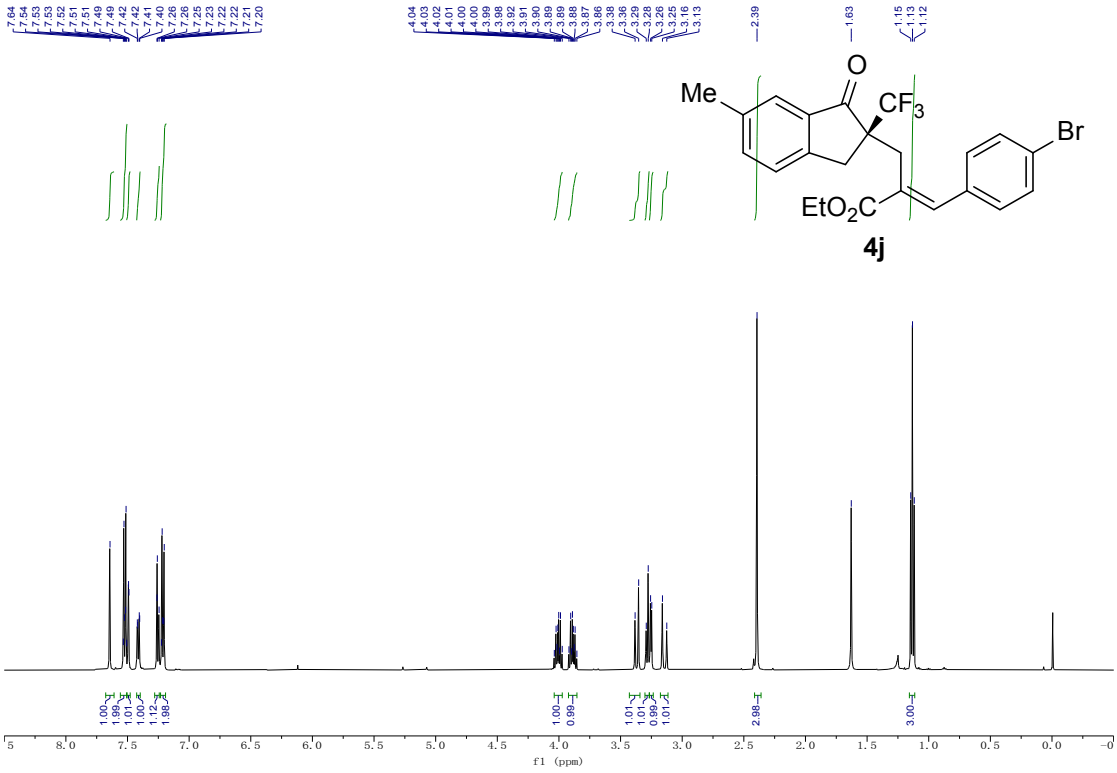


^{19}F NMR spectrum of 4i



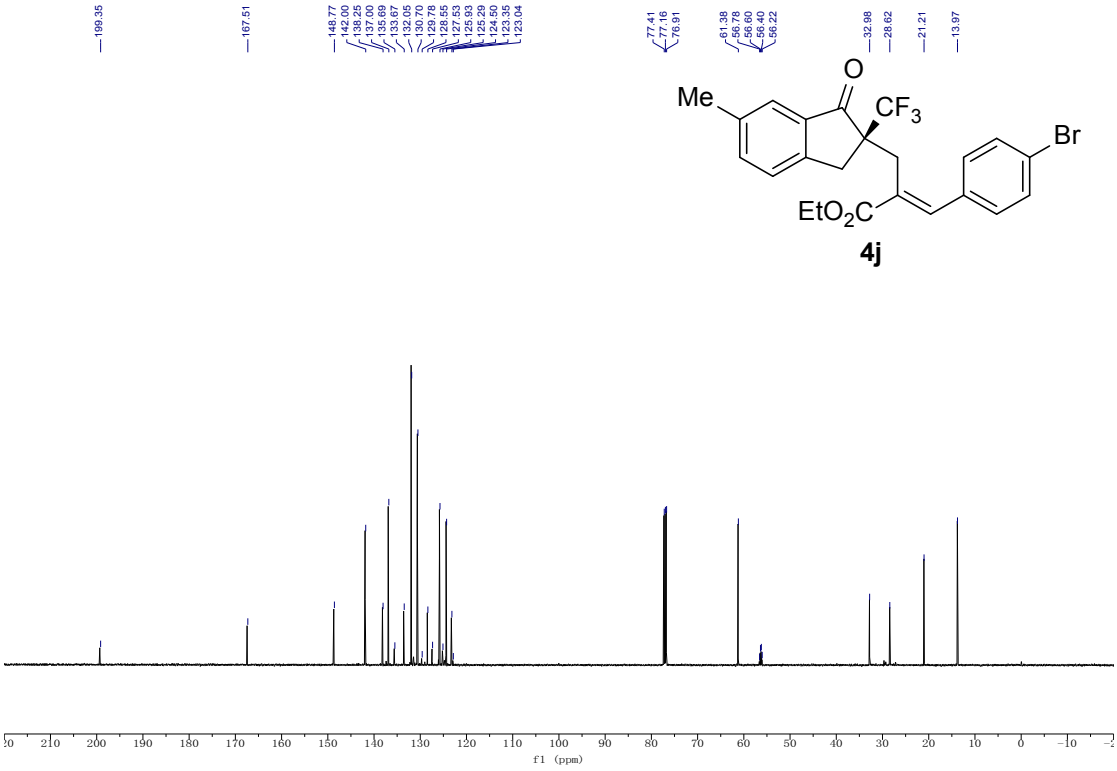
4i

^{1}H NMR spectrum of 4j

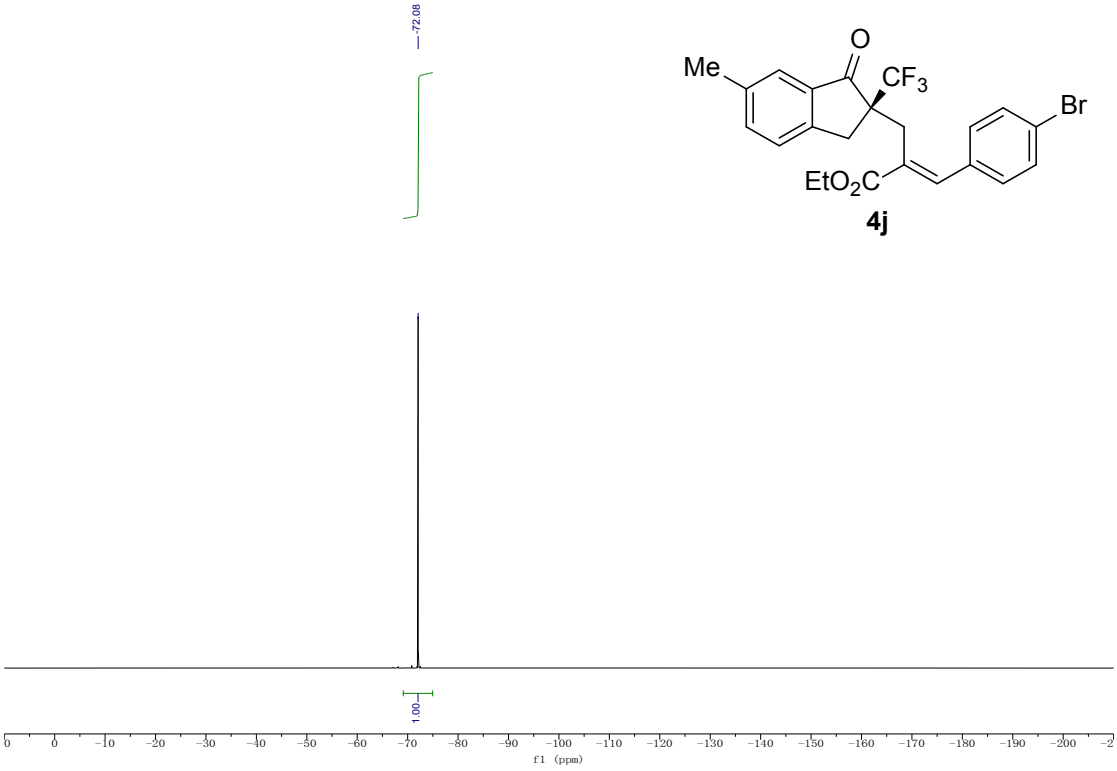


4j

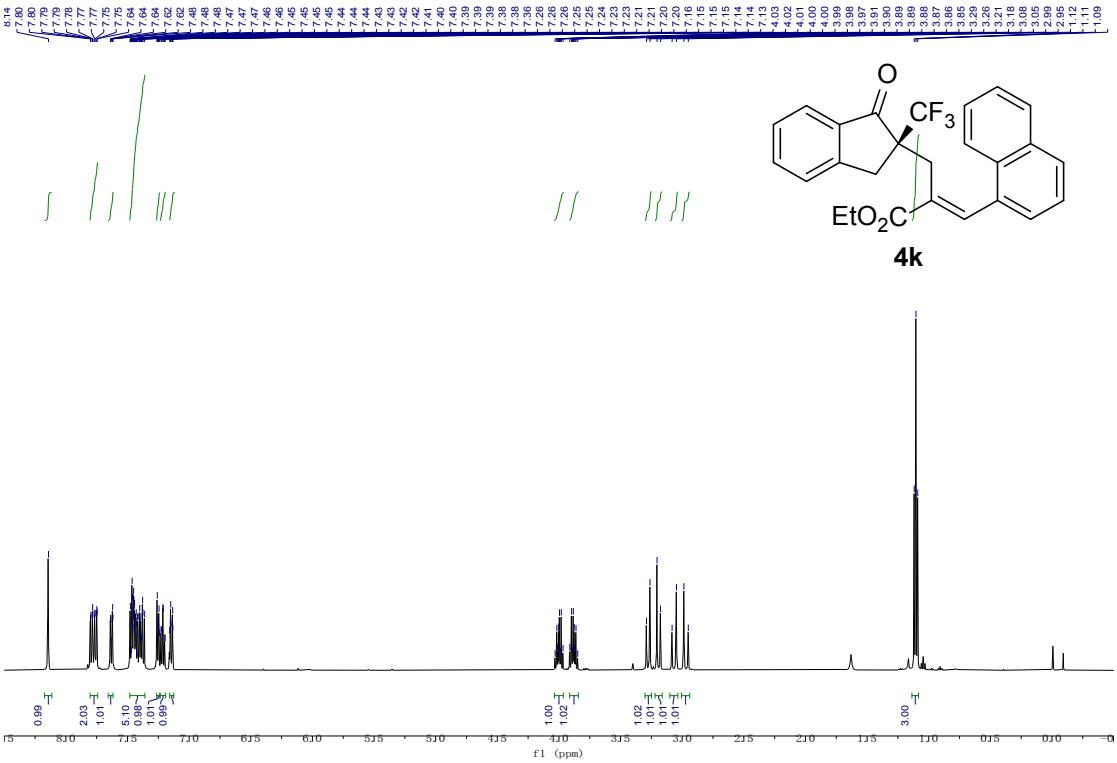
^{13}C NMR spectrum of 4j



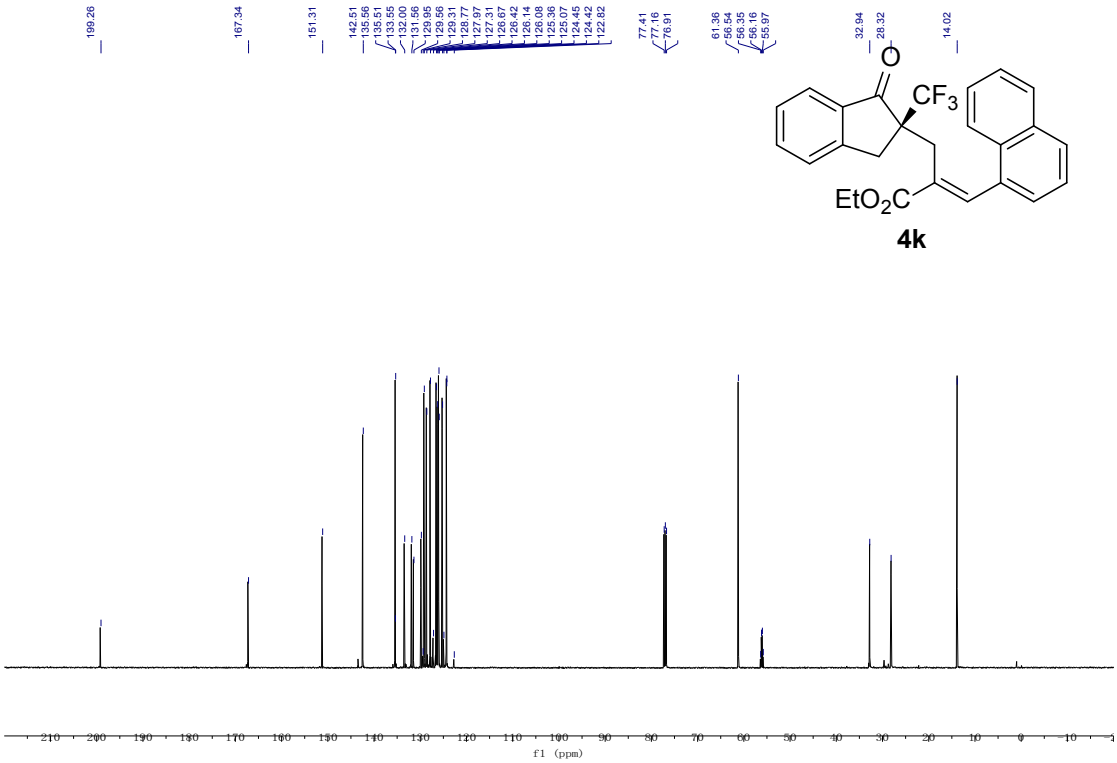
^{19}F NMR spectrum of 4j



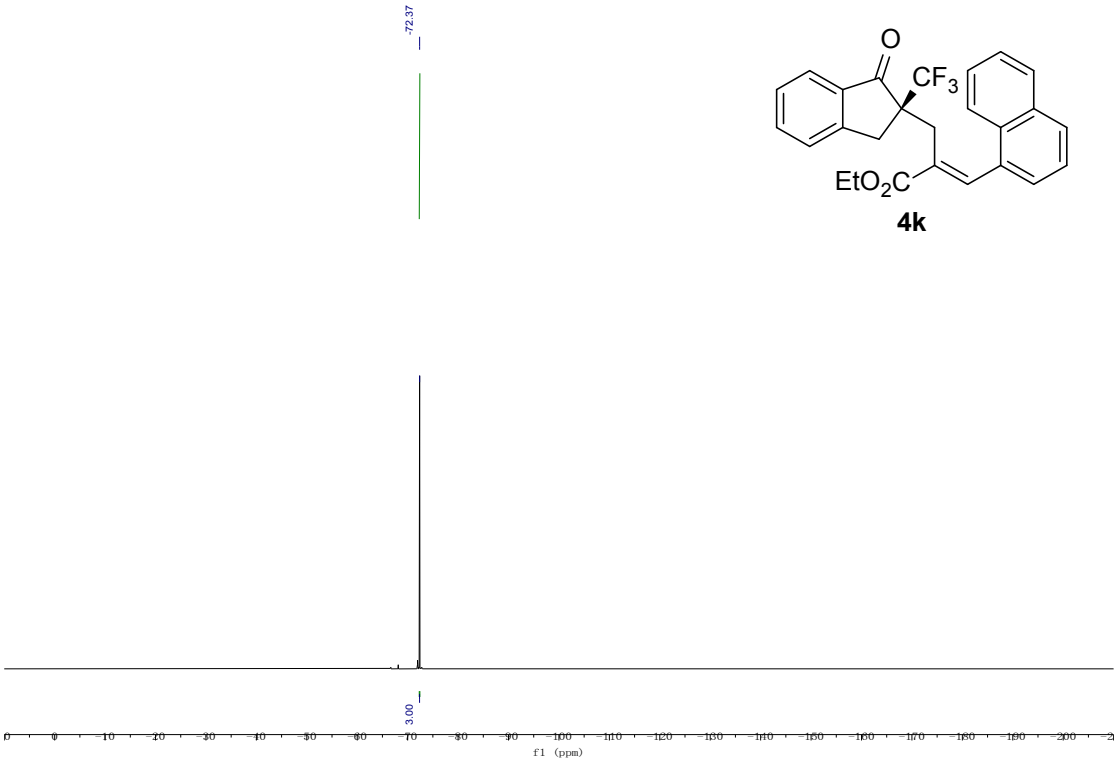
^{1}H NMR spectrum of 4k



^{13}C NMR spectrum of 4k

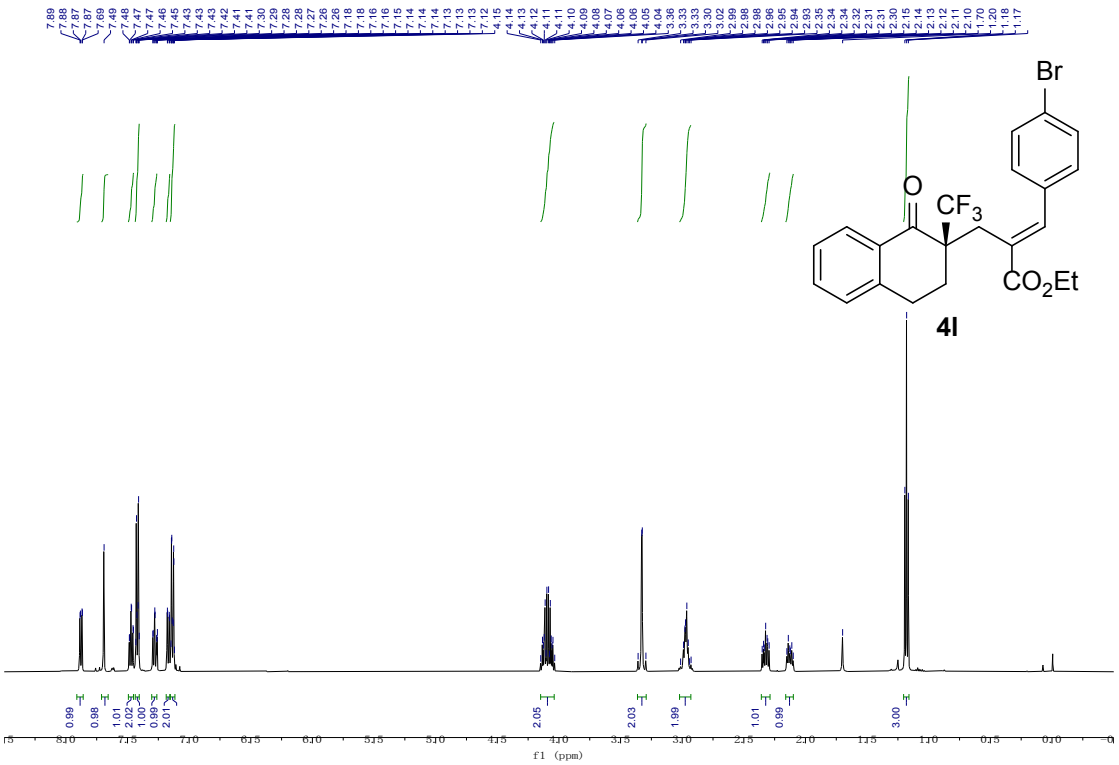


^{19}F NMR spectrum of 4k



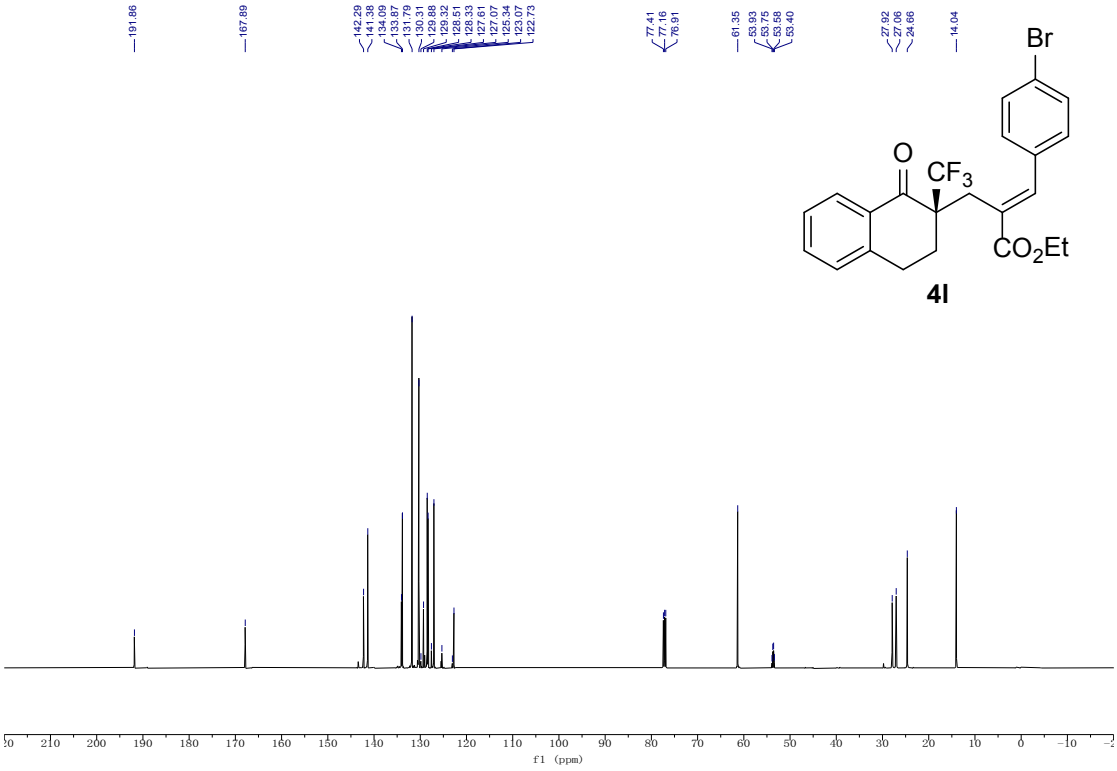
4k

^{1}H NMR spectrum of 4l

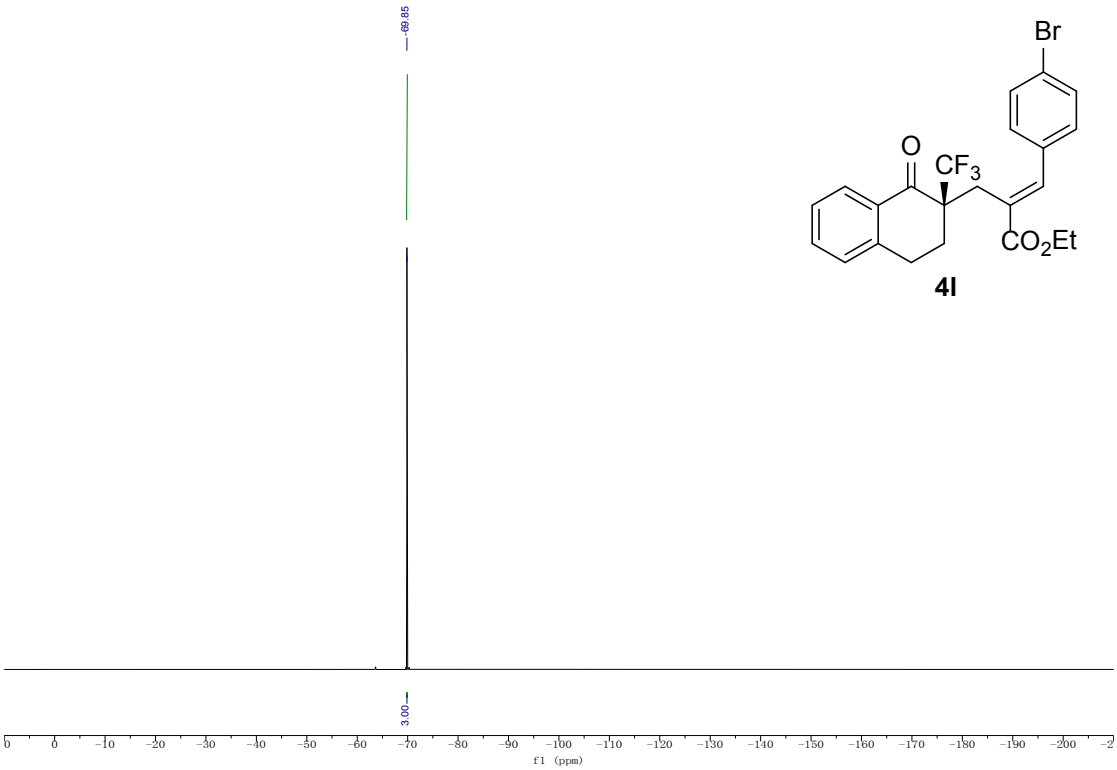


4l

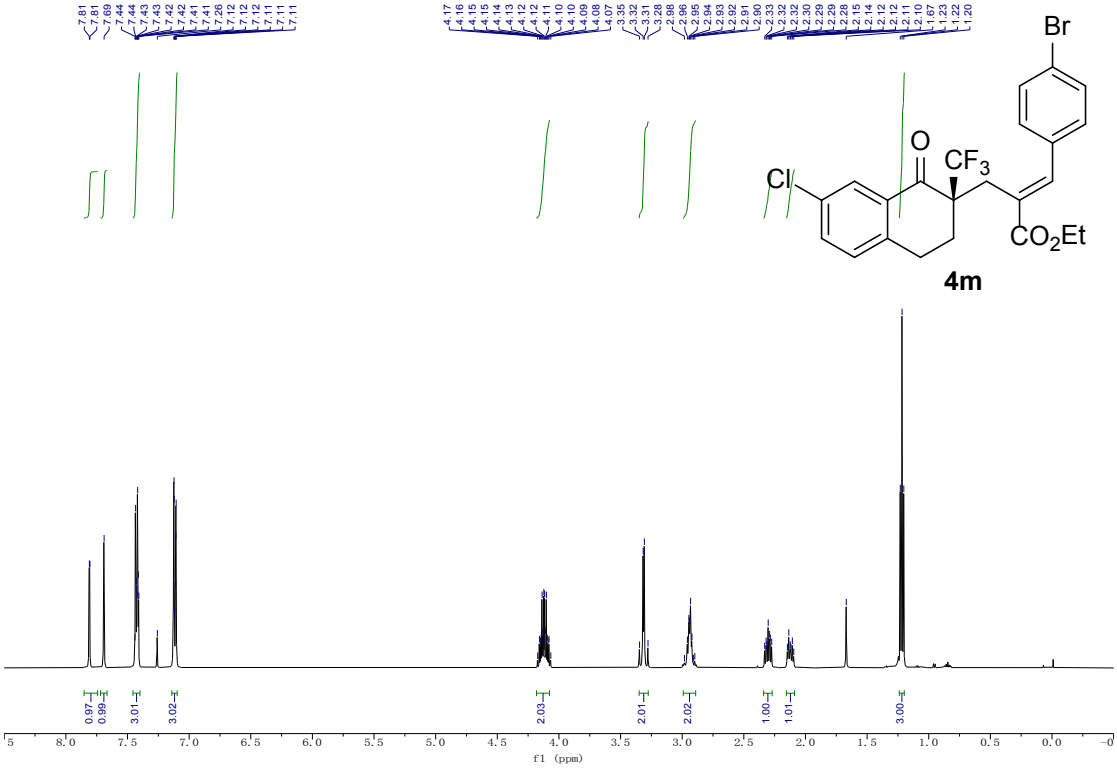
^{13}C NMR spectrum of 4l



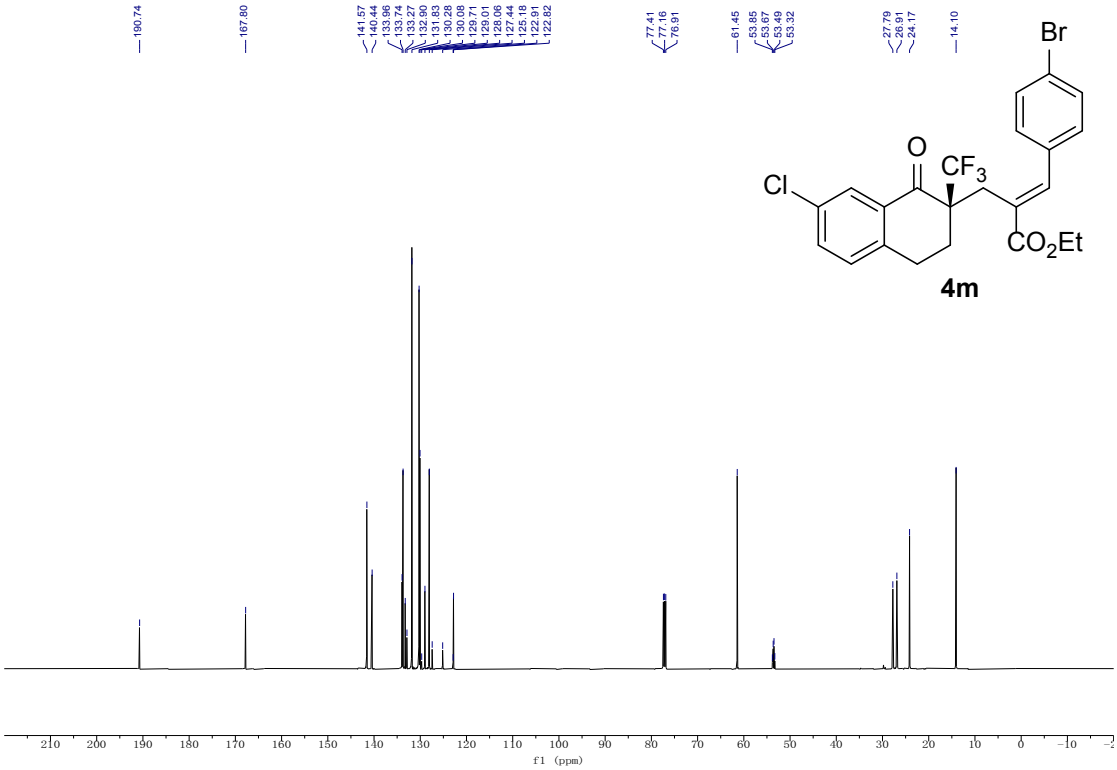
^{19}F NMR spectrum of 4l



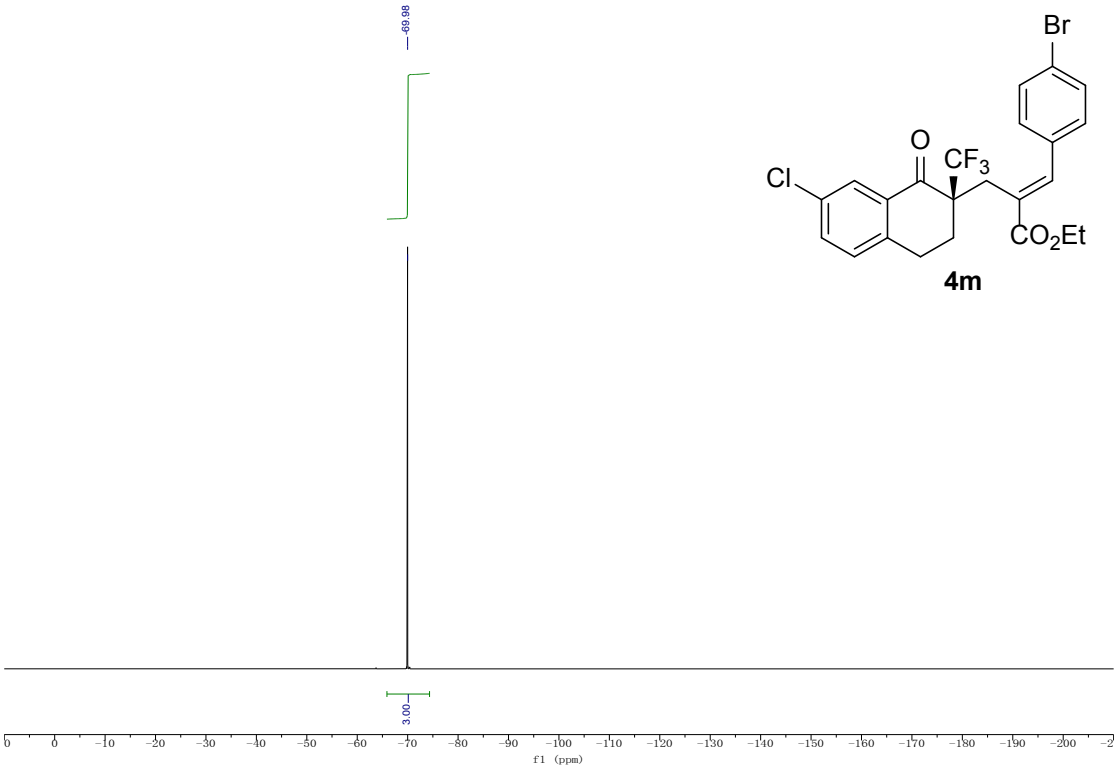
^{1}H NMR spectrum of 4m



^{13}C NMR spectrum of 4m

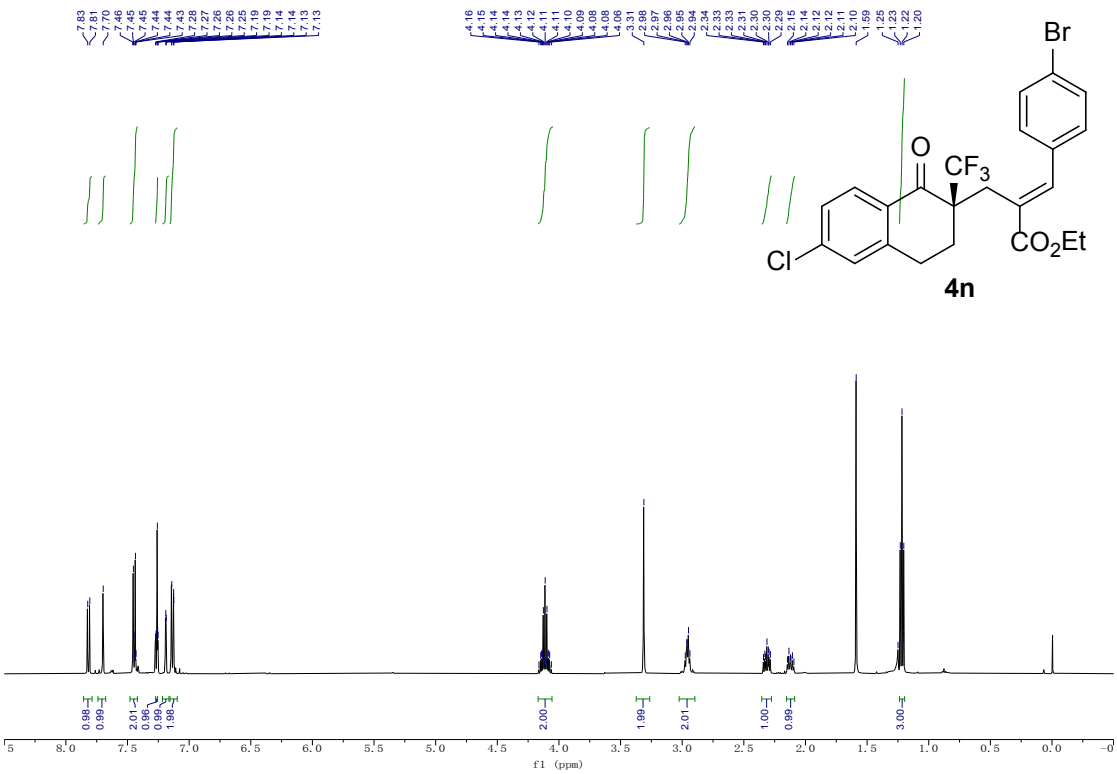


^{19}F NMR spectrum of 4m



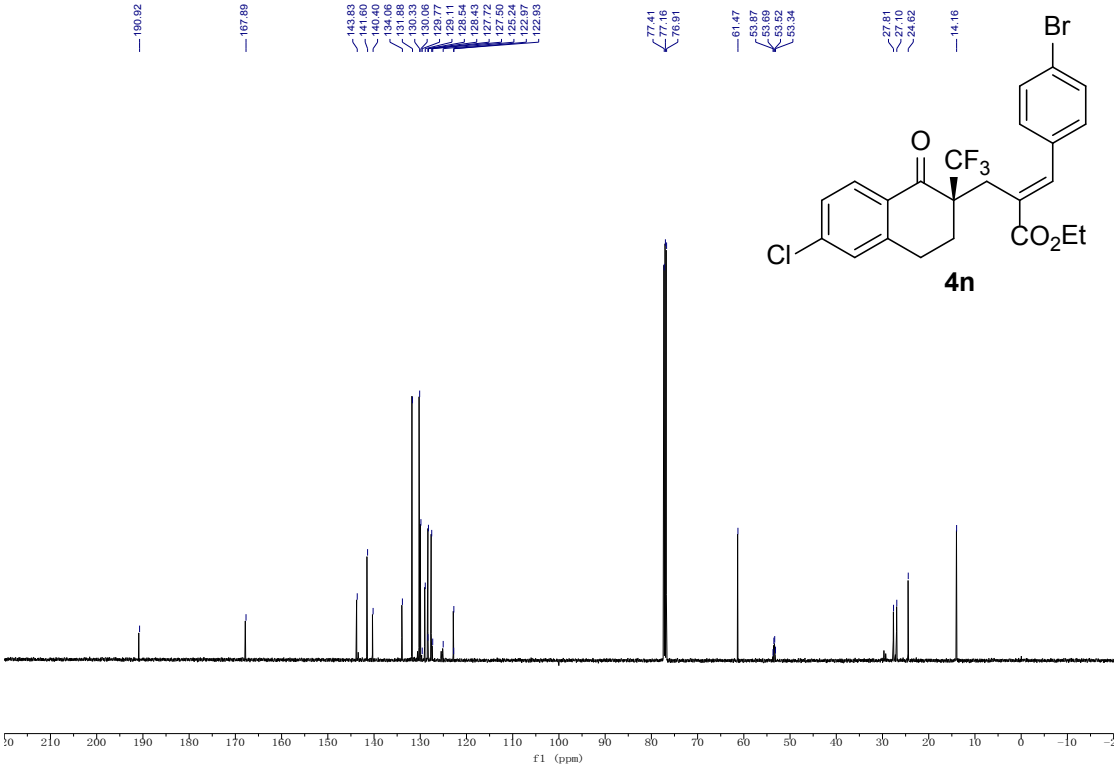
4m

^{1}H NMR spectrum of 4n

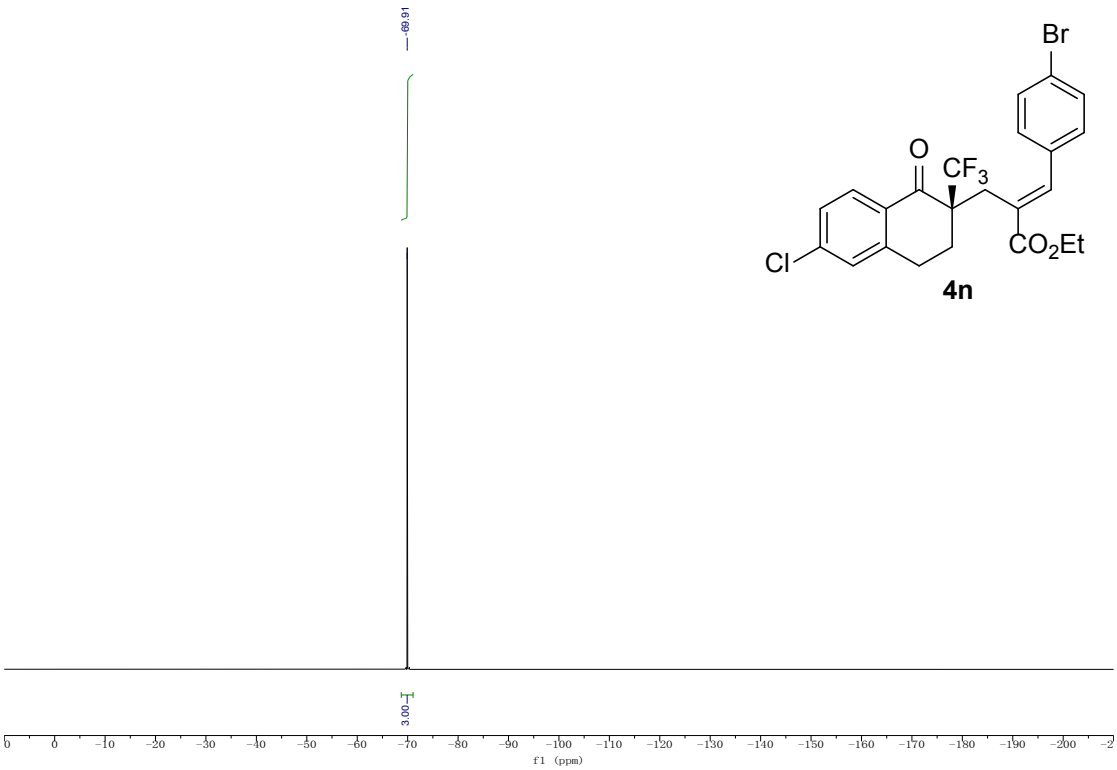


4n

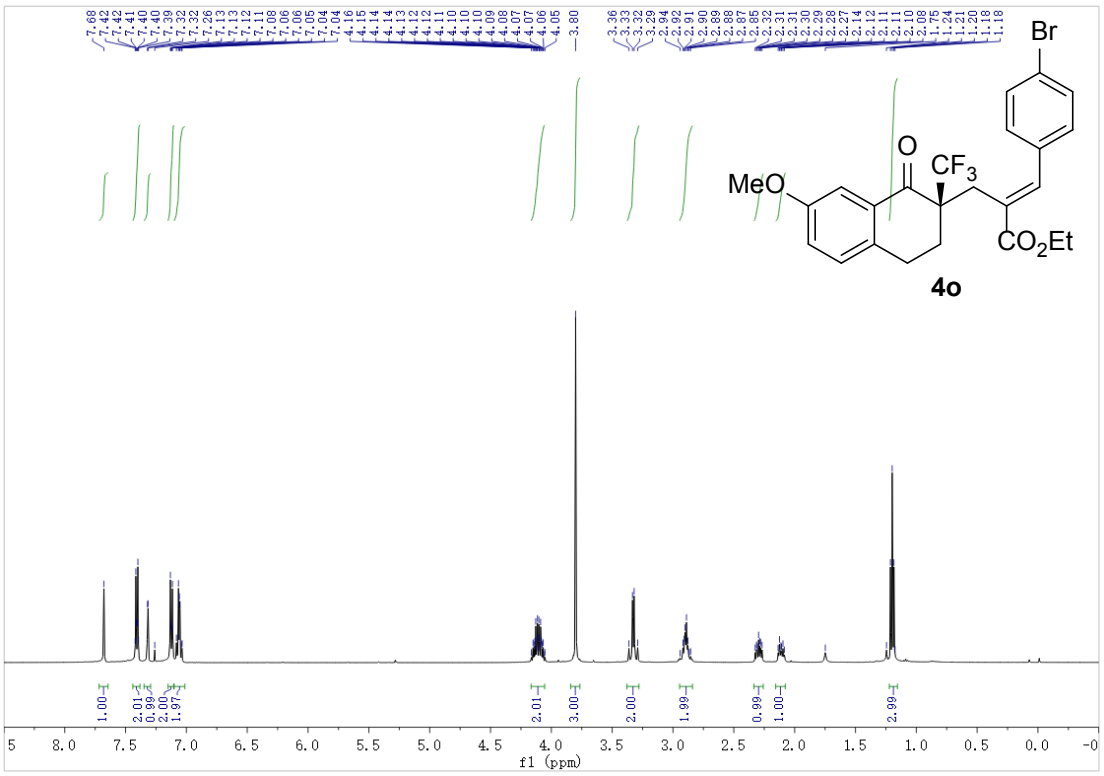
^{13}C NMR spectrum of 4n



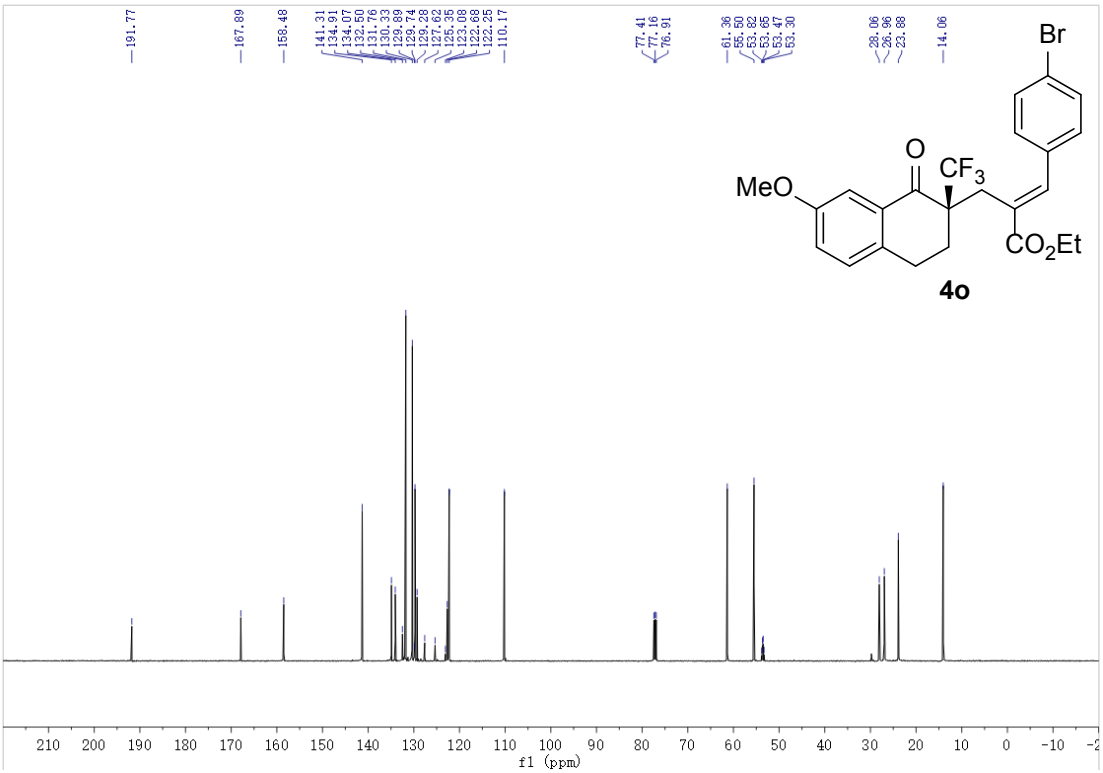
^{19}F NMR spectrum of 4n



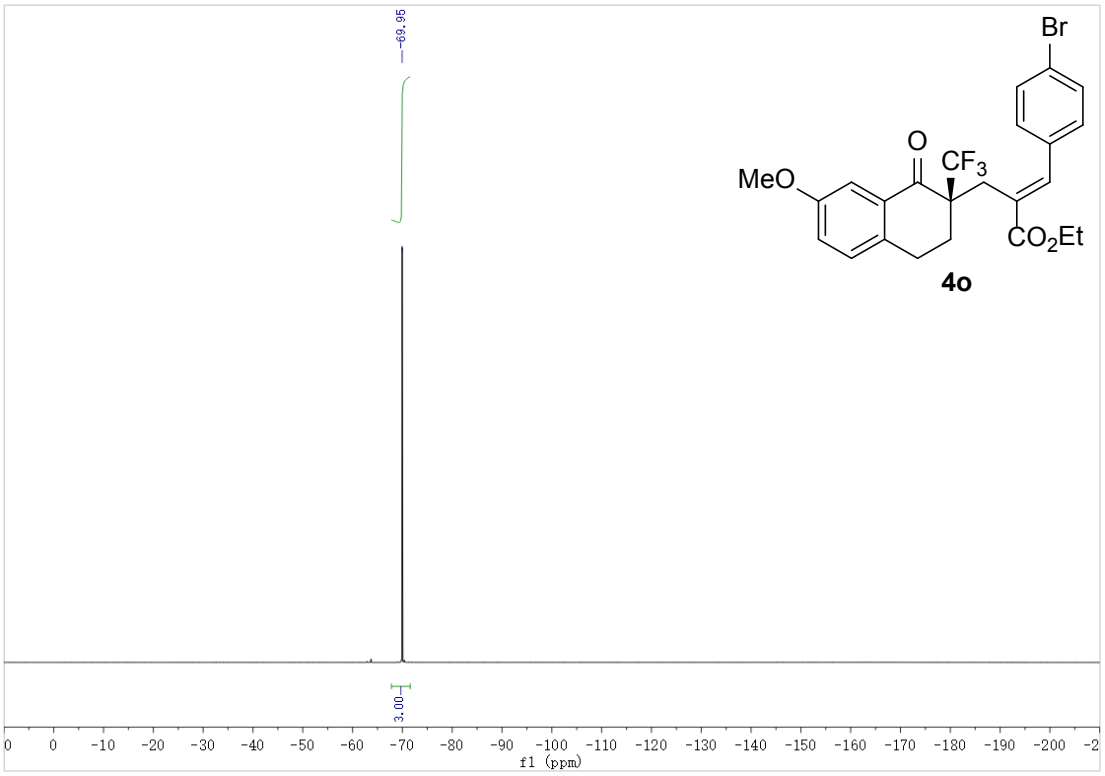
^{1}H NMR spectrum of 4o



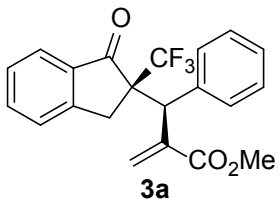
^{13}C NMR spectrum of 4o



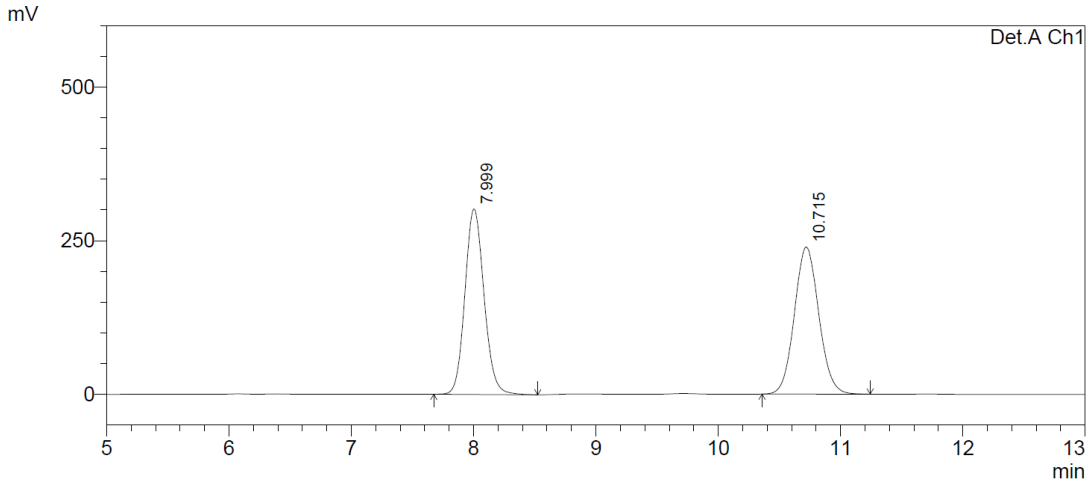
^{19}F NMR spectrum of 4o



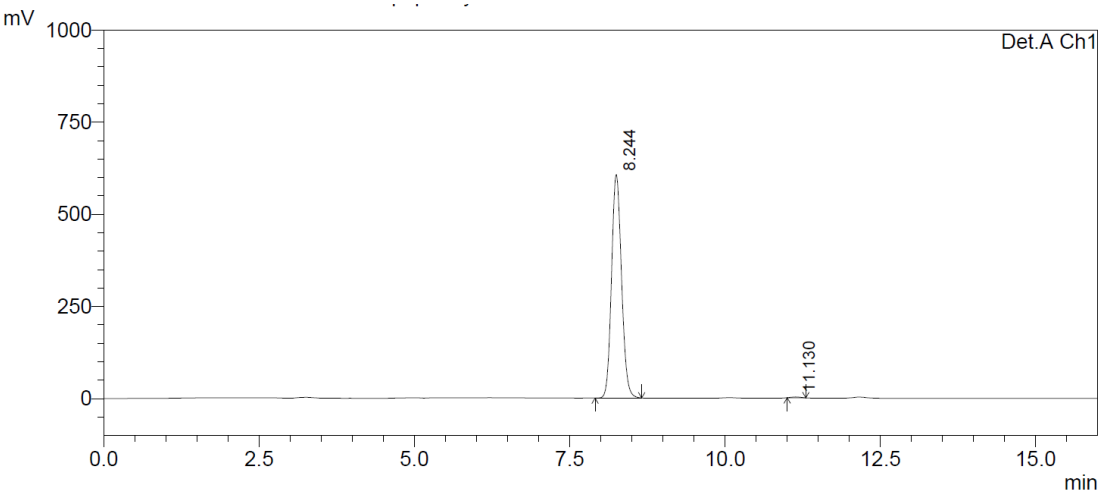
HPLC Chromatograms



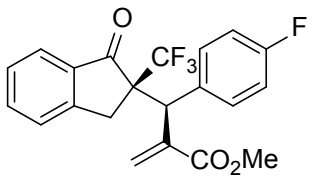
3a



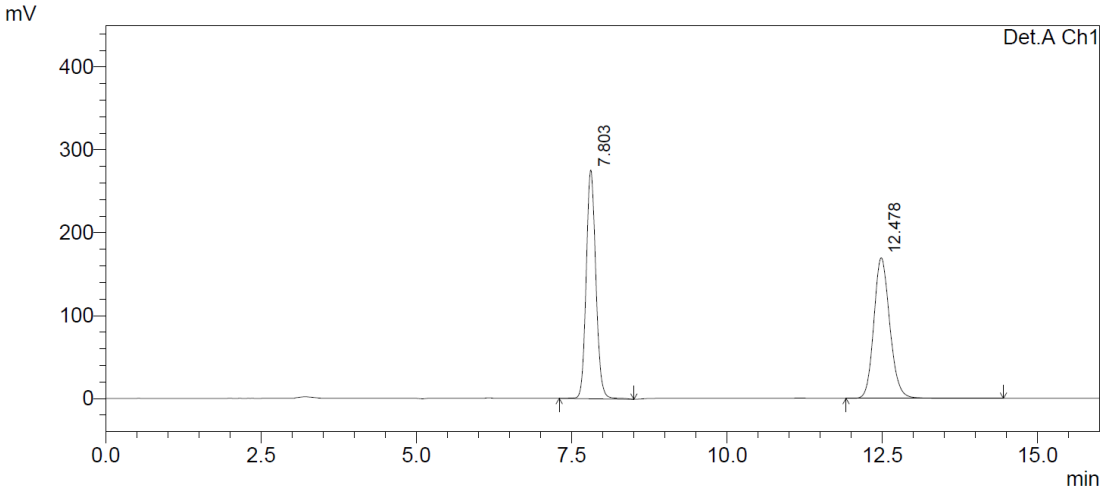
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.999	3284245	302099	49.621	55.780
2	10.715	3334462	239494	50.379	44.220
Total		6618707	541594	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.244	6788246	606644	99.651	99.630
2	11.130	23743	2256	0.349	0.370
Total		6811988	608900	100.000	100.000

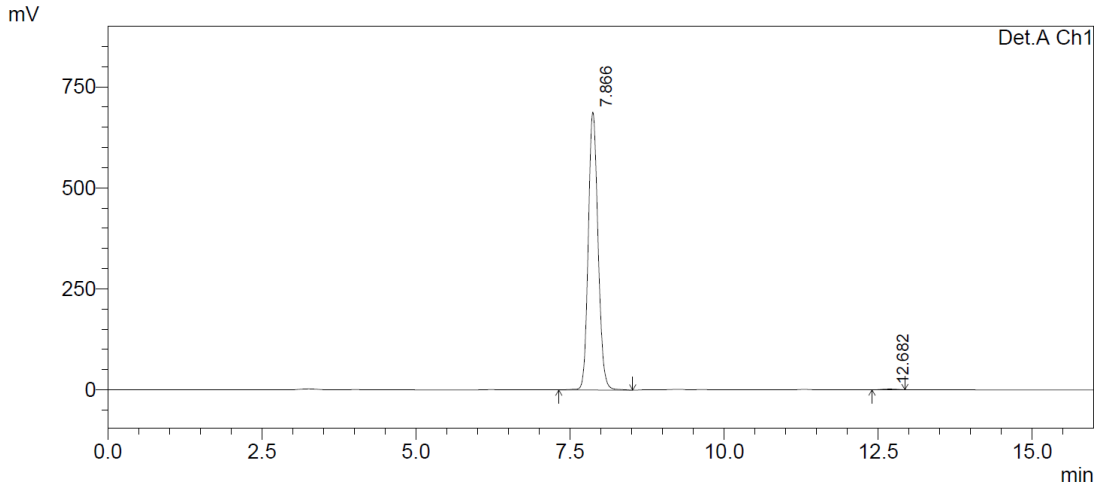


3b

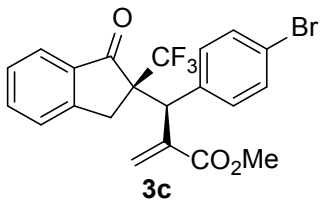


Detector A Ch1 254nm

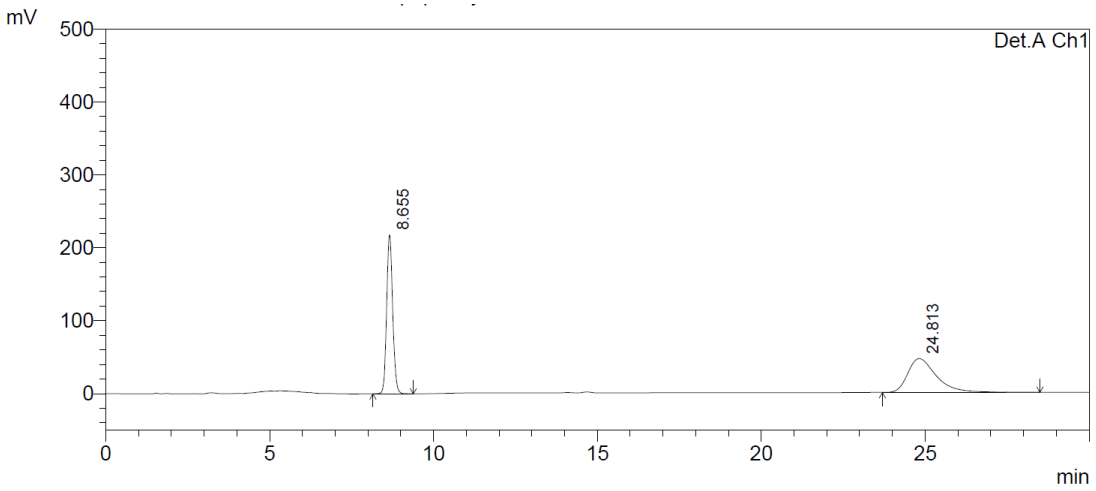
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.803	2988576	276177	49.592	61.923
2	12.478	3037764	169825	50.408	38.077
Total		6026339	446002	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.866	7576452	687931	99.633	99.744
2	12.682	27872	1763	0.367	0.256
Total		7604324	689695	100.000	100.000

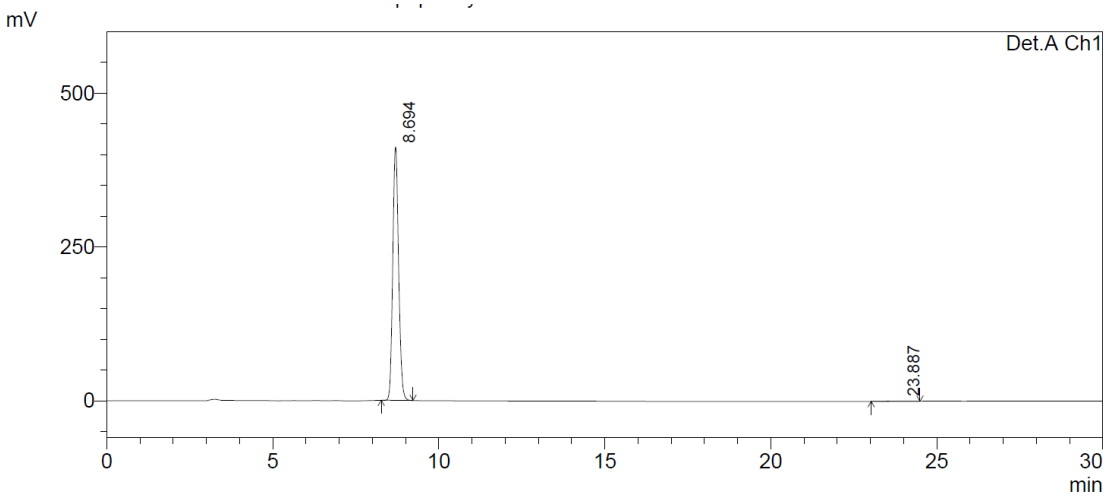


3c



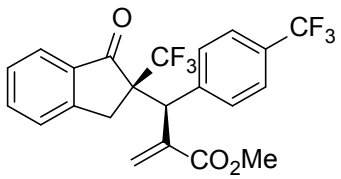
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.655	2795753	218347	49.517	82.419
2	24.813	2850261	46576	50.483	17.581
Total		5646014	264923	100.000	100.000

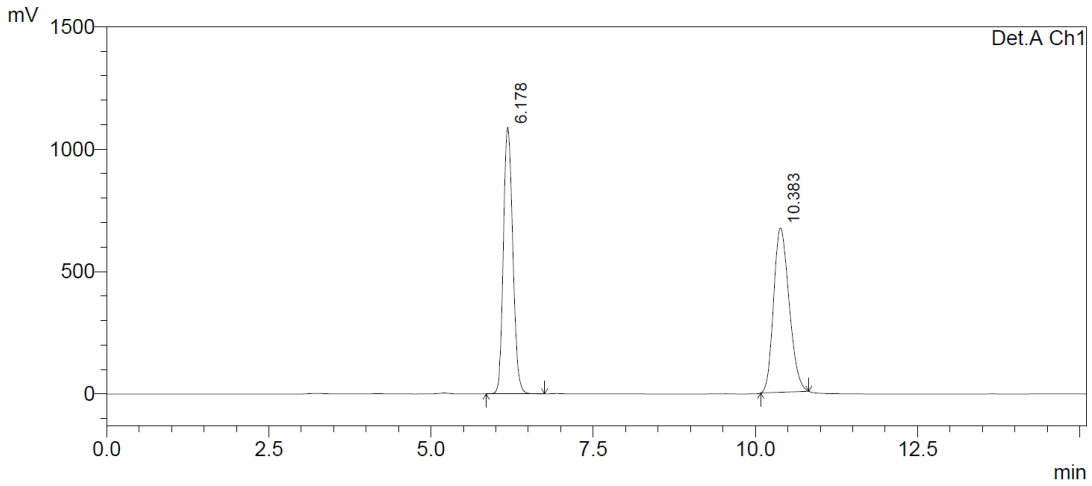


Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.694	5032603	412197	99.731	99.928
2	23.887	13598	298	0.269	0.072
Total		5046201	412495	100.000	100.000

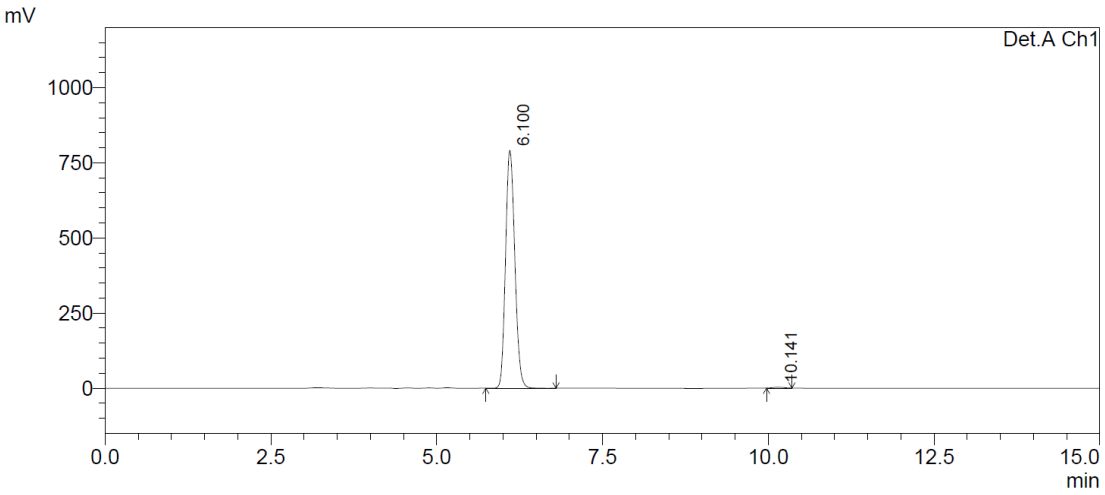


3d



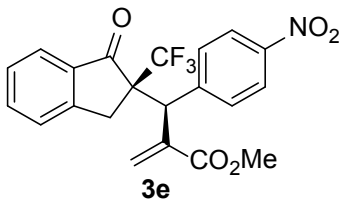
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.178	10991902	1089356	49.604	61.889
2	10.383	11167573	670824	50.396	38.111
Total		22159476	1760179	100.000	100.000

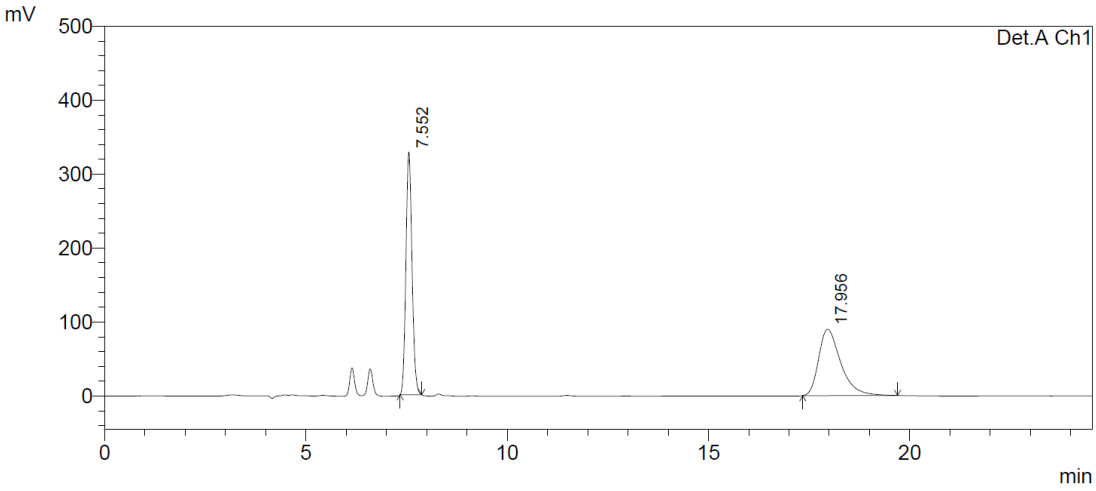


Detector A Ch1 254nm

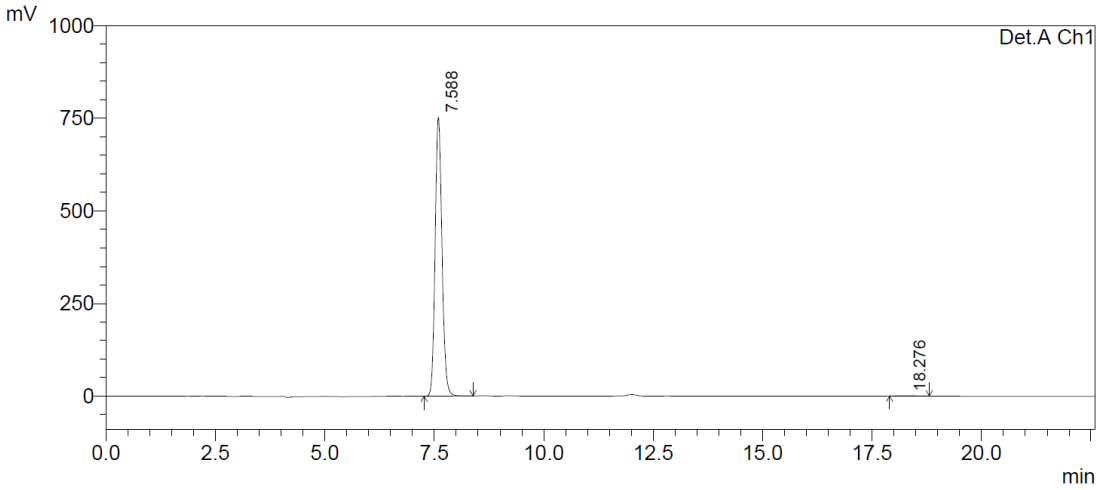
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.100	7692825	790687	99.577	99.669
2	10.141	32663	2629	0.423	0.331
Total		7725488	793316	100.000	100.000



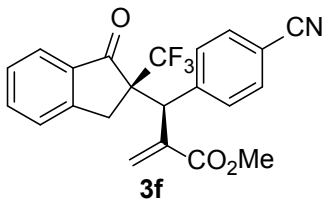
3e



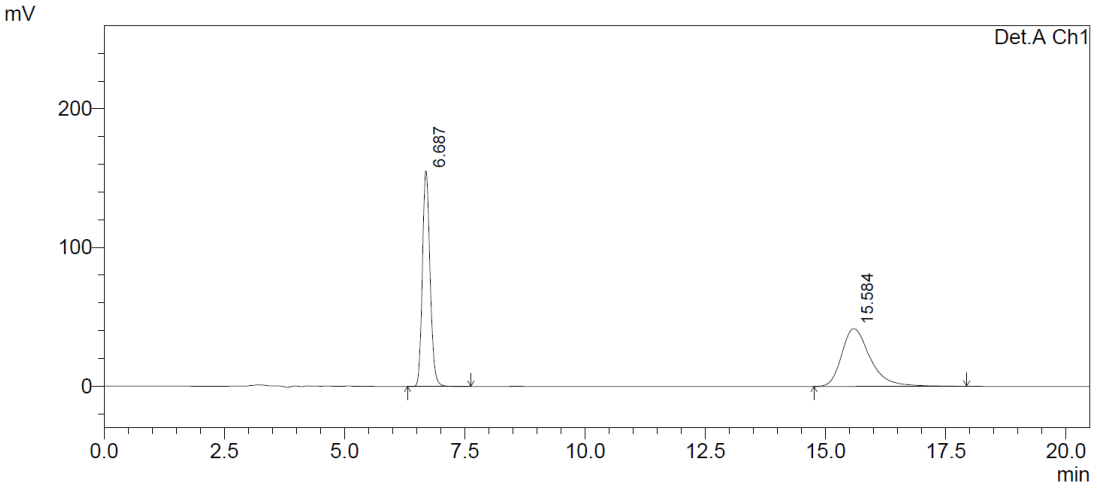
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.552	3463107	328285	50.373	78.534
2	17.956	3411888	89732	49.627	21.466
Total		6874995	418017	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.588	8177263	753138	99.709	99.896
2	18.276	23900	785	0.291	0.104
Total		8201164	753923	100.000	100.000

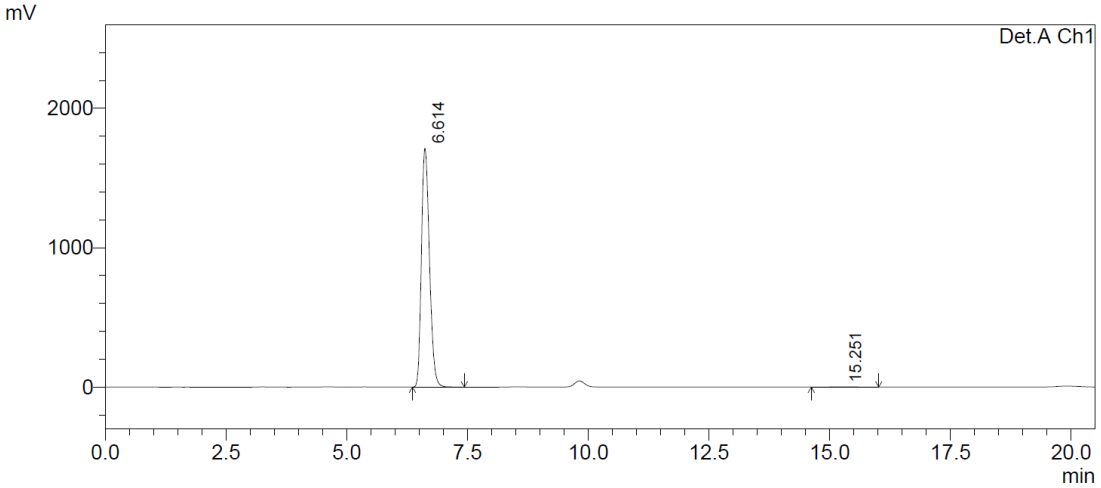


3f

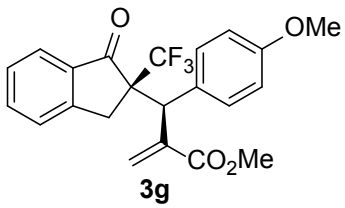


Detector A Ch1 254nm

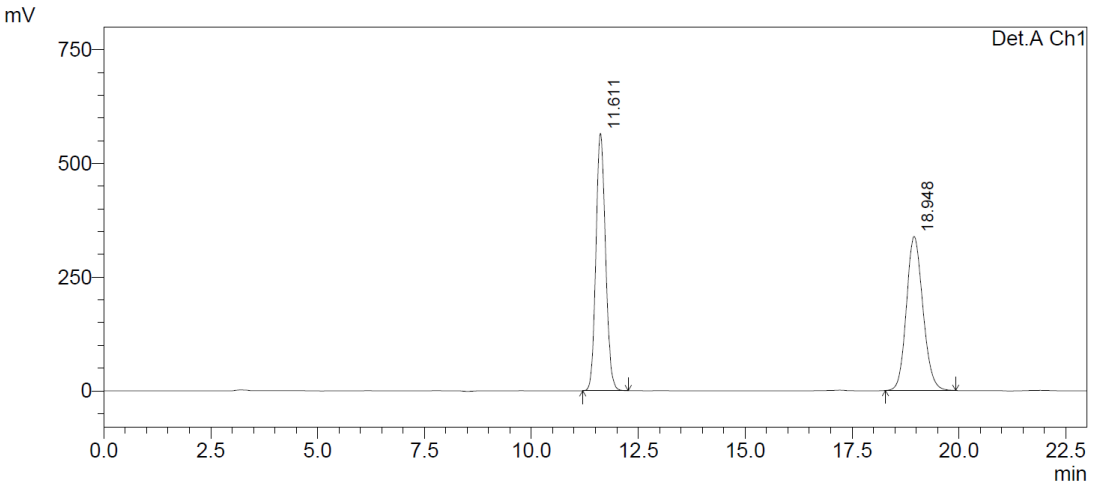
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.687	1719573	155595	50.148	78.887
2	15.584	1709457	41642	49.852	21.113
Total		3429030	197236	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.614	19822732	1714930	99.672	99.894
2	15.251	65175	1827	0.328	0.106
Total		19887908	1716757	100.000	100.000

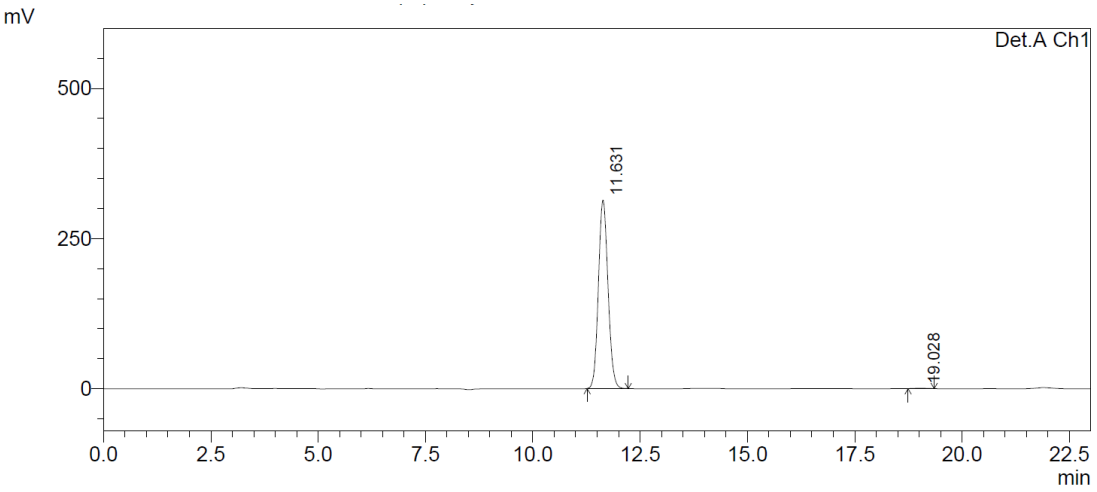


3g



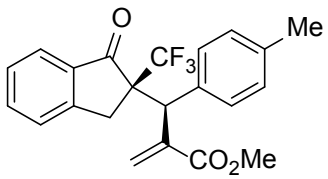
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.611	8855317	566282	49.299	62.573
2	18.948	9107092	338705	50.701	37.427
Total		17962409	904987	100.000	100.000

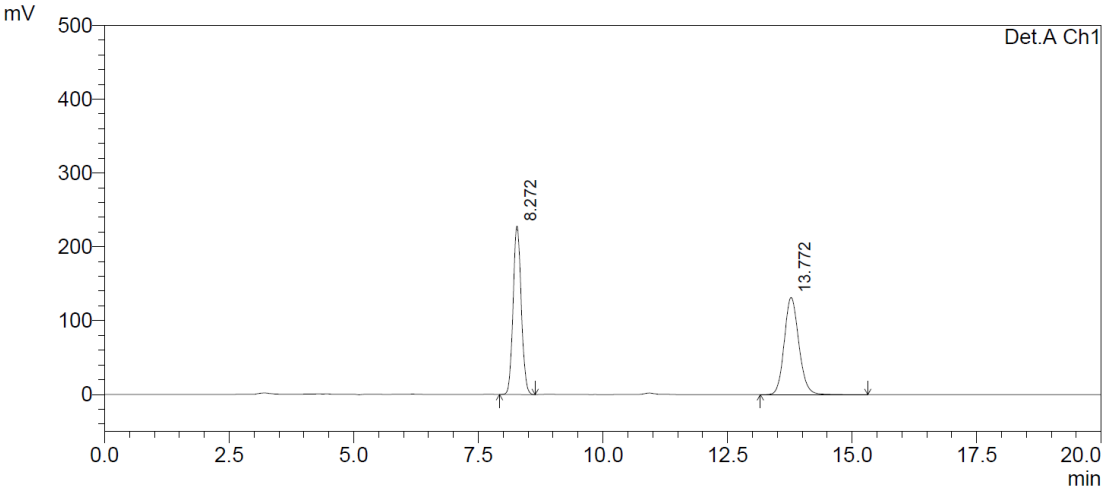


Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.631	4881322	313825	99.681	99.755
2	19.028	15646	771	0.319	0.245
Total		4896968	314596	100.000	100.000

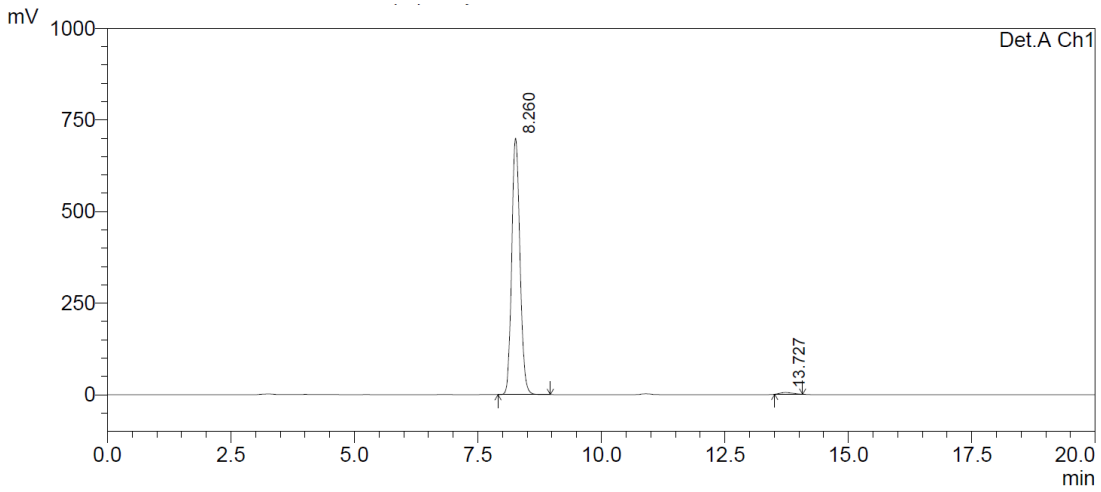


3h

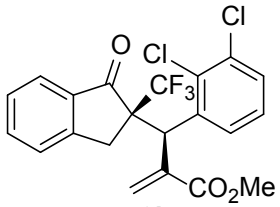


Detector A Ch1 254nm

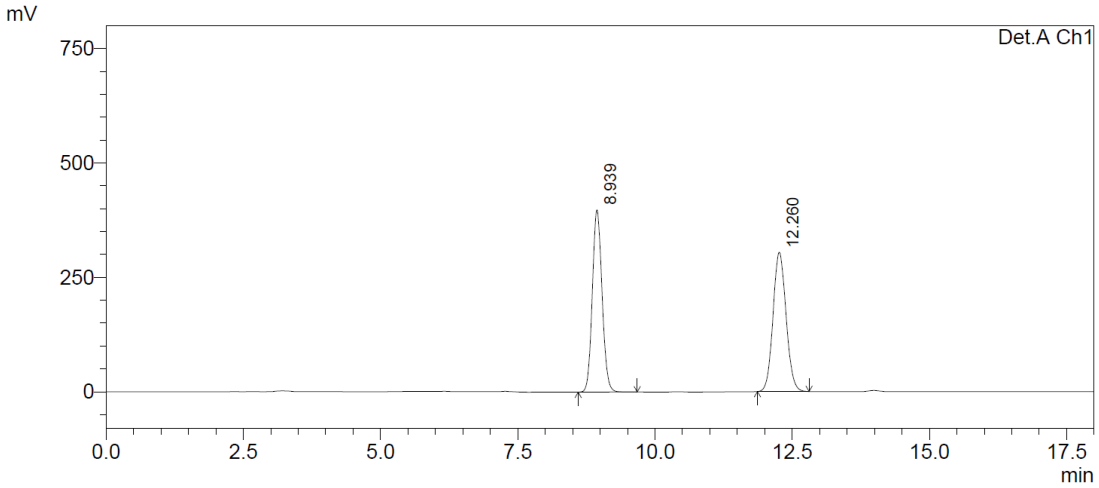
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.272	2592178	228333	49.171	63.424
2	13.772	2679587	131676	50.829	36.576
Total		5271765	360009	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.260	8137587	700042	98.994	99.343
2	13.727	82712	4633	1.006	0.657
Total		8220298	704675	100.000	100.000

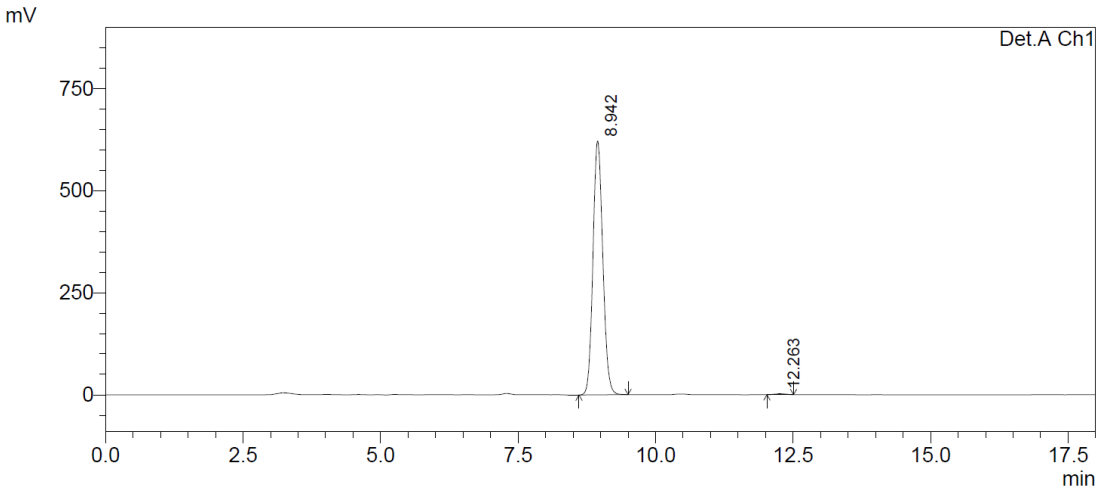


3i



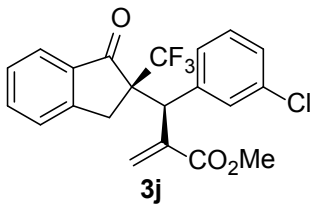
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.939	4919823	398344	49.390	56.683
2	12.260	5041281	304417	50.610	43.317
Total		9961104	702761	100.000	100.000

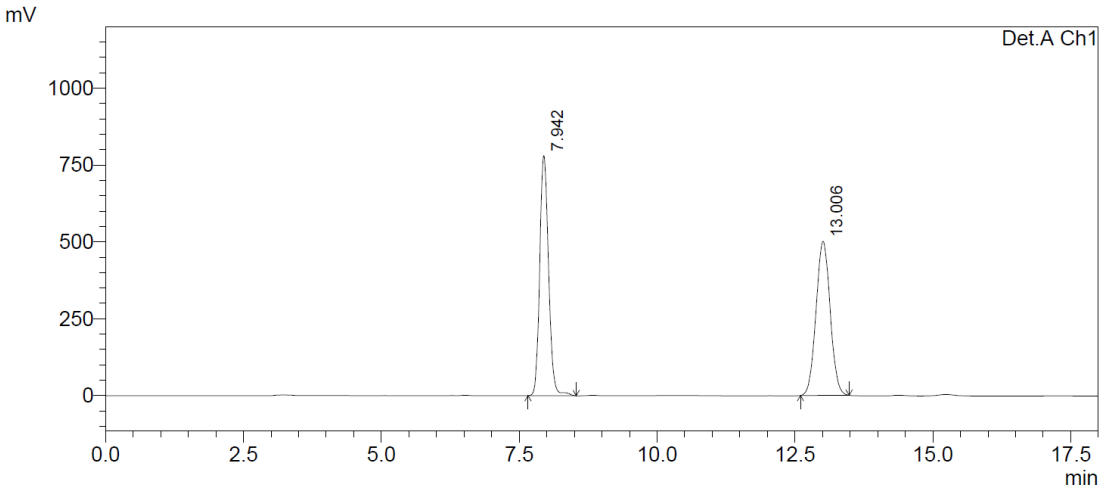


Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.942	7737619	621227	99.578	99.639
2	12.263	32765	2252	0.422	0.361
Total		7770384	623479	100.000	100.000

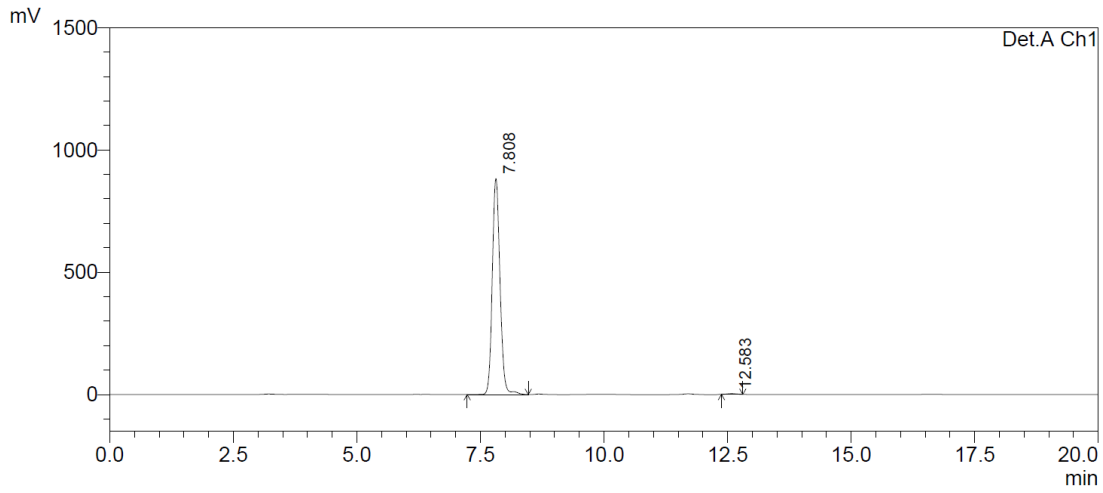


3j



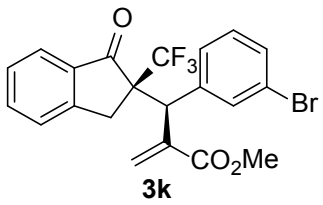
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.942	8707126	780424	49.302	60.898
2	13.006	8953518	501101	50.698	39.102
Total		17660644	1281525	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.808	9594424	882337	99.595	99.684
2	12.583	39026	2798	0.405	0.316
Total		9633450	885135	100.000	100.000



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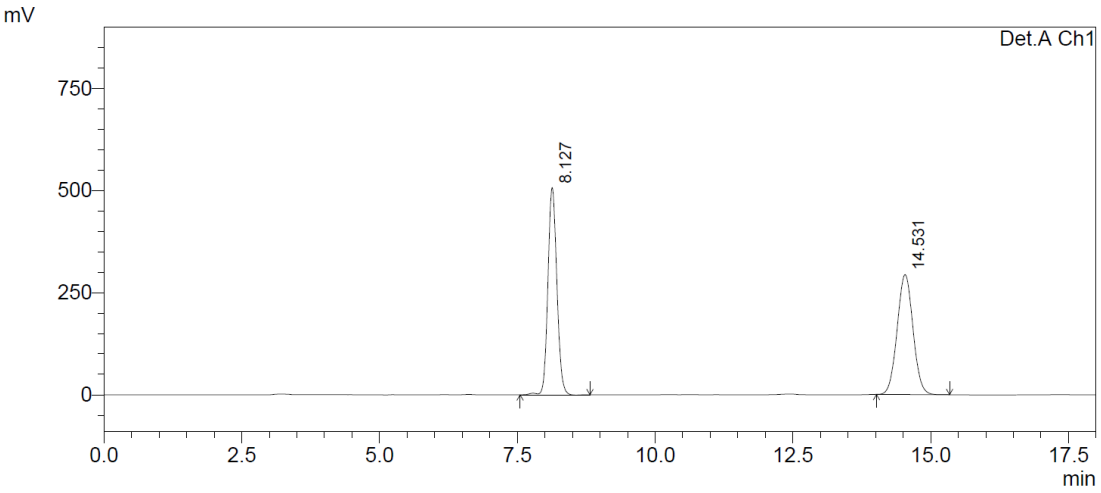
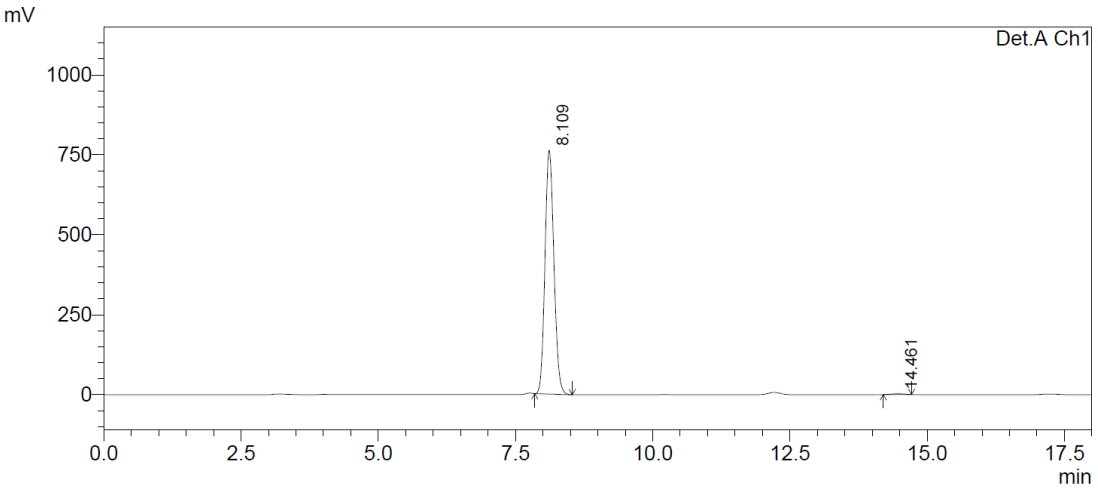


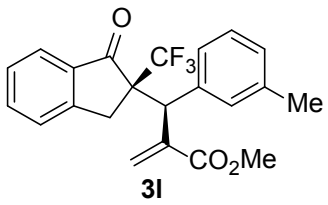
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.127	5727998	507351	49.415	63.370
2	14.531	5863570	293264	50.585	36.630
Total		11591568	800615	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.109	8634183	761872	99.534	99.678
2	14.461	40440	2459	0.466	0.322
Total		8674622	764331	100.000	100.000



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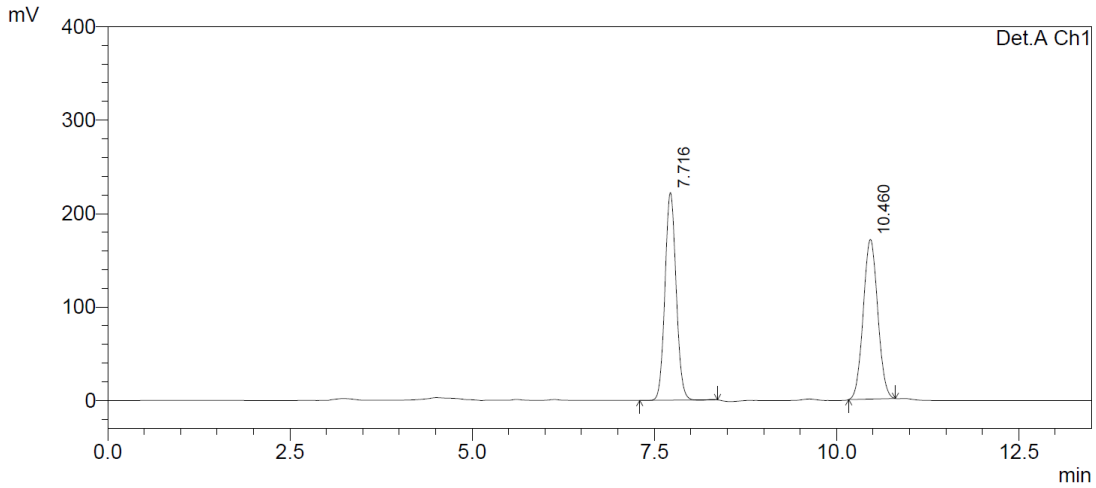
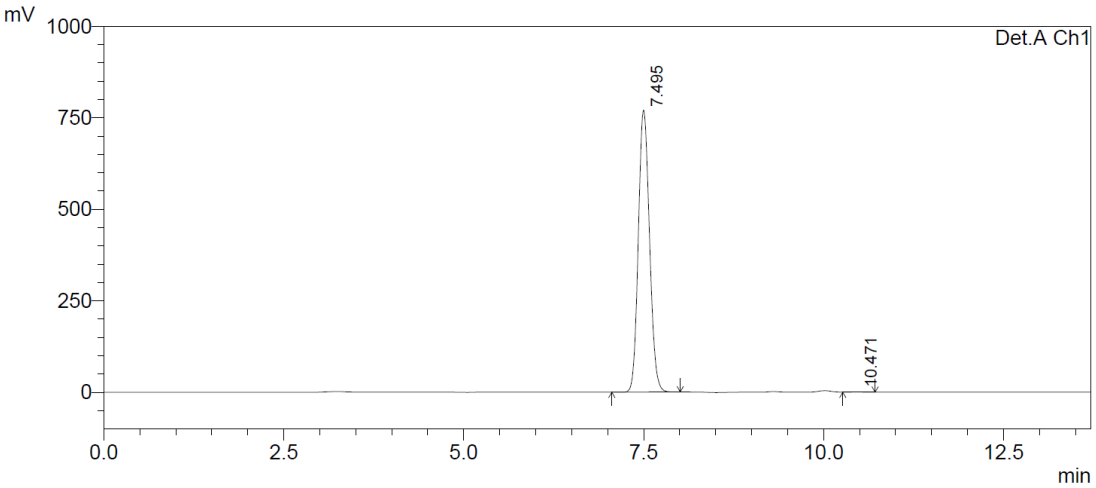
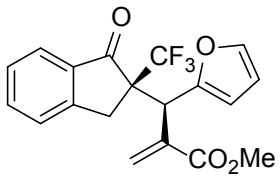


Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.716	2363430	222104	49.989	56.505
2	10.460	2364506	170968	50.011	43.495
Total		4727936	393072	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.495	8320486	771180	99.906	99.906
2	10.471	7836	727	0.094	0.094
Total		8328322	771908	100.000	100.000



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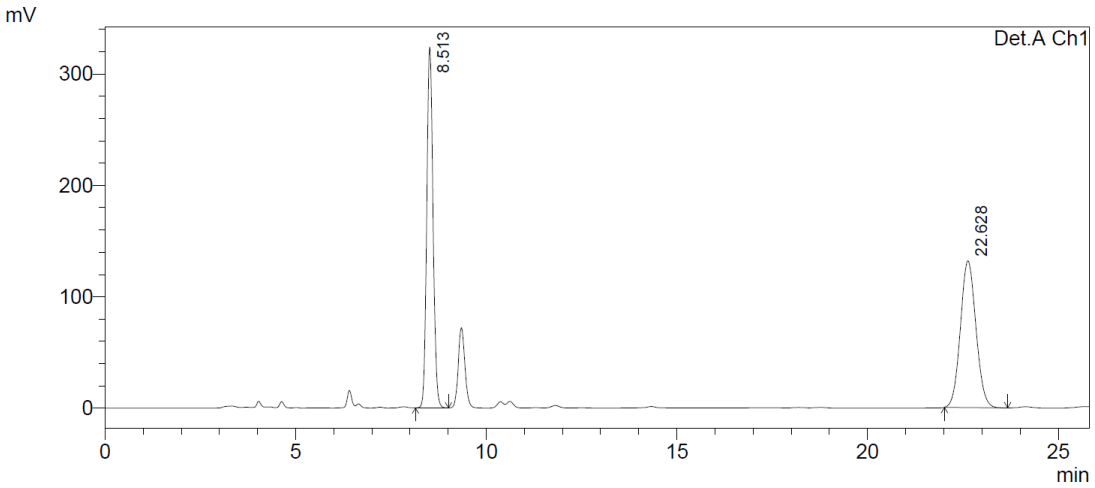
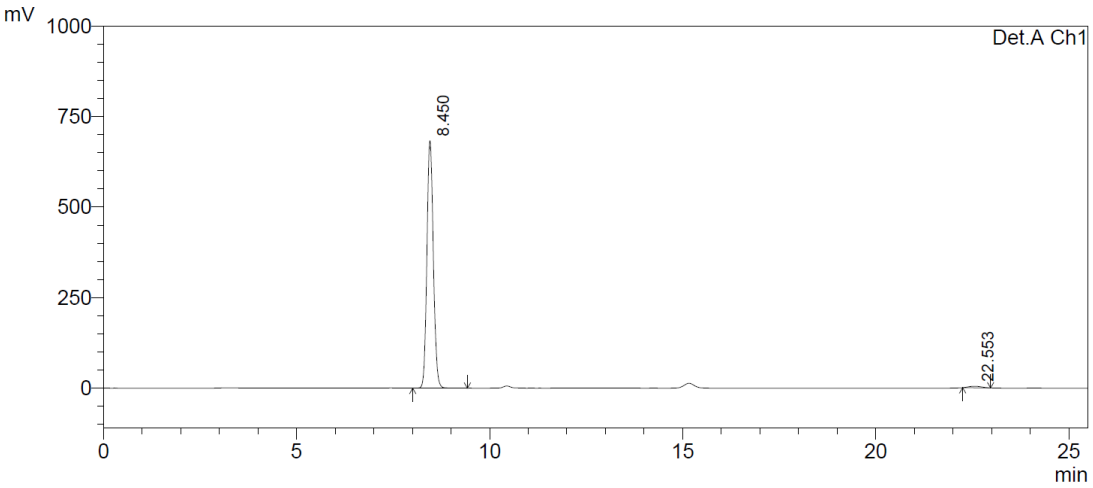
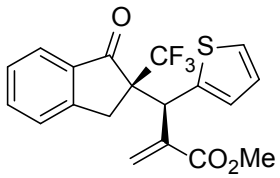


Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.513	3698312	323976	49.759	71.097
2	22.628	3734078	131708	50.241	28.903
Total		7432390	455685	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.450	7886898	683233	98.771	99.385
2	22.553	98123	4231	1.229	0.615
Total		7985020	687463	100.000	100.000



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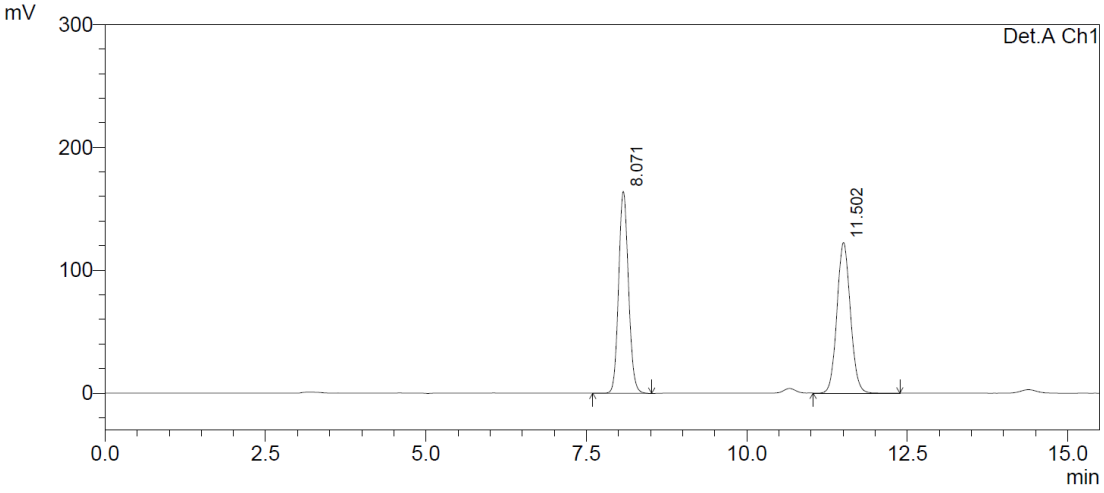
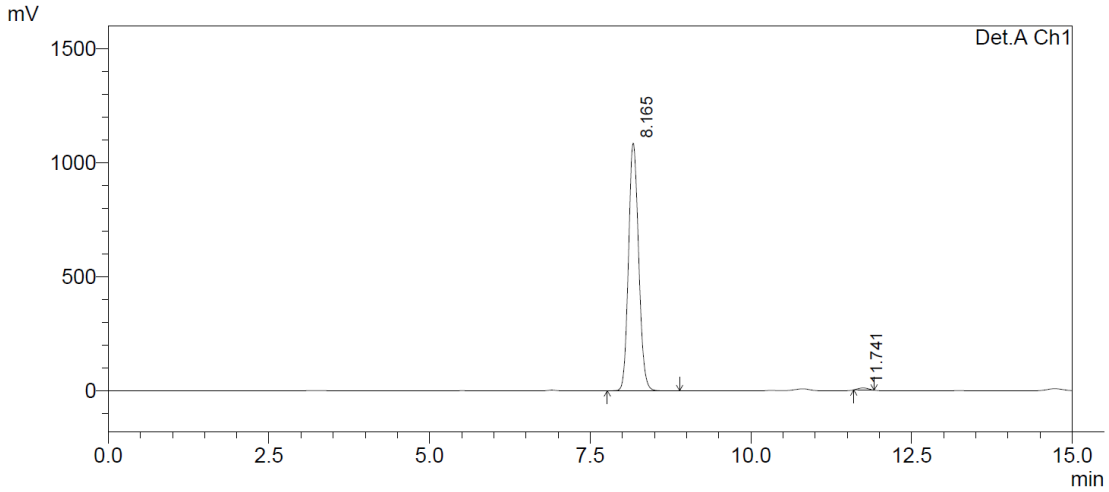


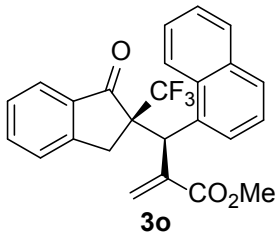
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.071	1757012	164518	49.516	57.296
2	11.502	1791365	122619	50.484	42.704
Total		3548377	287137	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.165	11930904	1086130	99.172	99.162
2	11.741	99672	9183	0.828	0.838
Total		12030576	1095314	100.000	100.000



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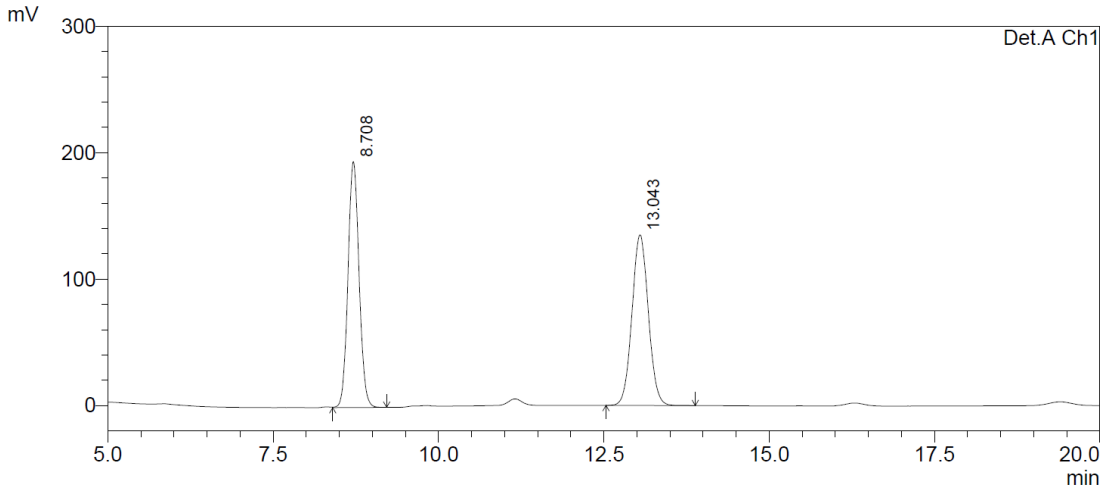
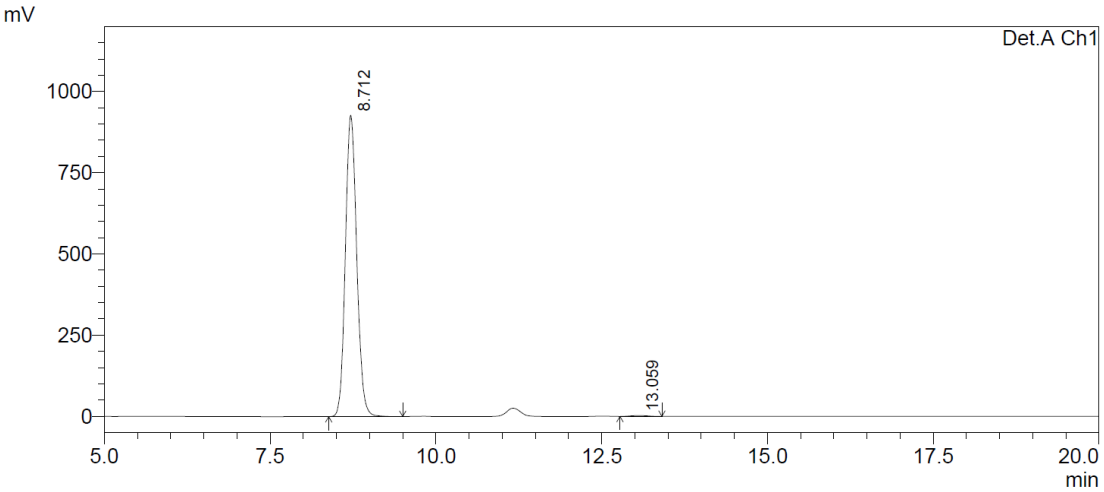
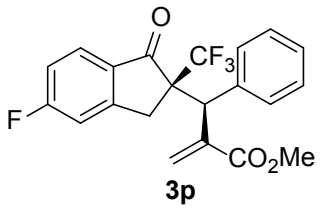


Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.708	2262598	194399	49.310	59.018
2	13.043	2325896	134988	50.690	40.982
Total		4588494	329387	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.712	11040122	927932	99.616	99.718
2	13.059	42559	2621	0.384	0.282
Total		11082681	930553	100.000	100.000



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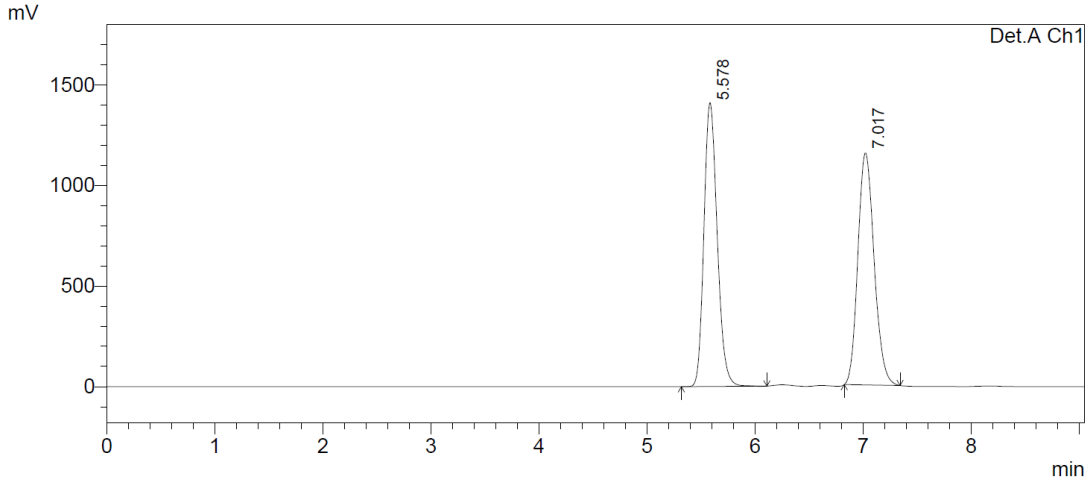
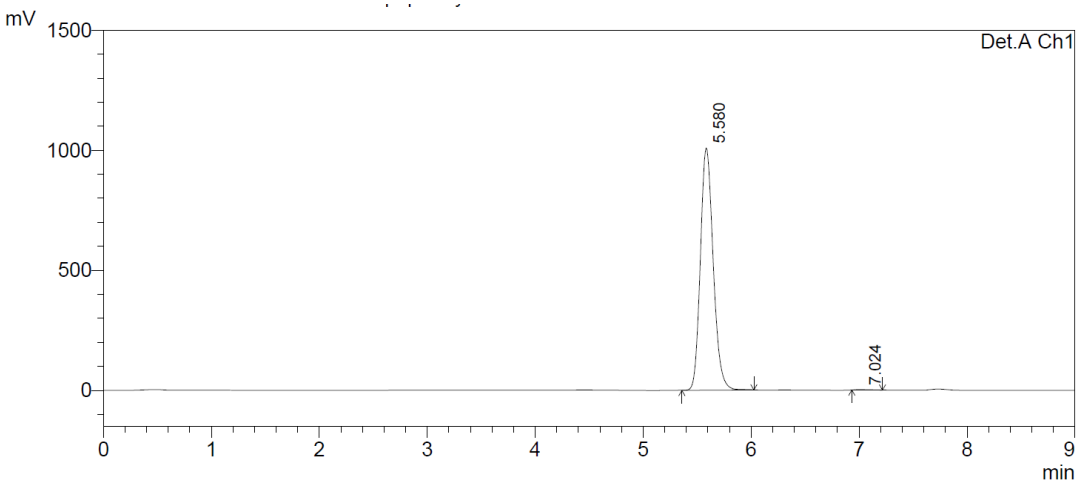
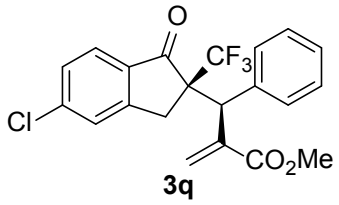


Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.578	12065843	1411784	50.039	55.063
2	7.017	12047033	1152144	49.961	44.937
Total		24112876	2563928	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.580	8339250	1009280	99.813	99.789
2	7.024	15653	2130	0.187	0.211
Total		8354903	1011410	100.000	100.000



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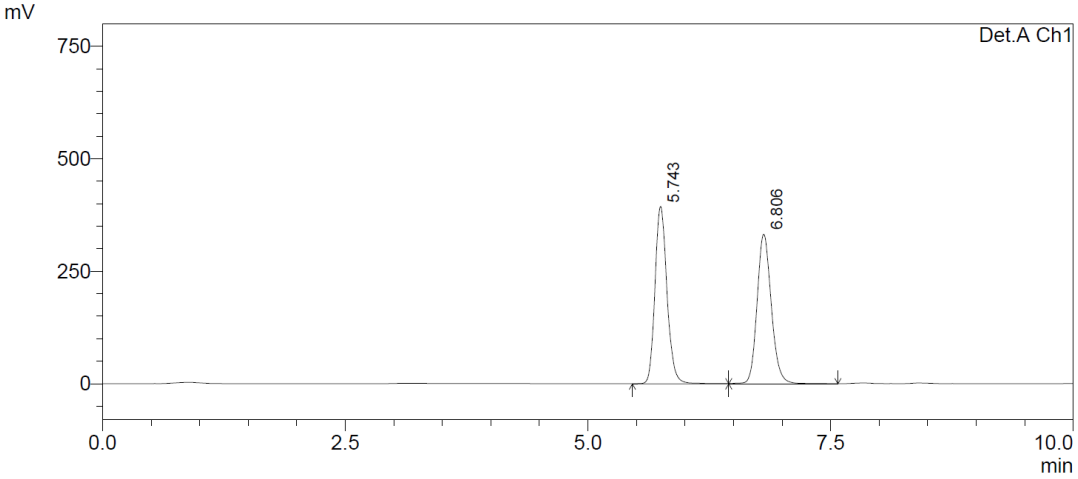
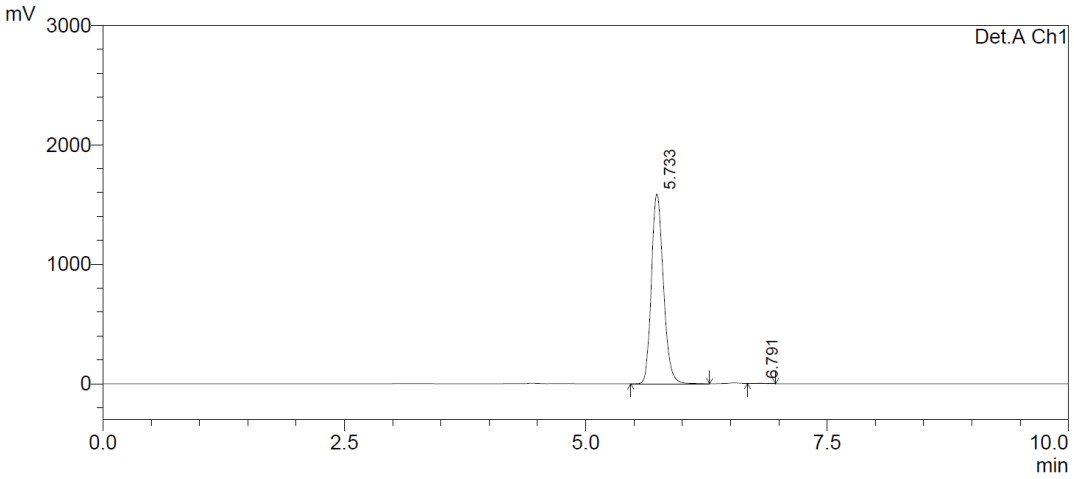


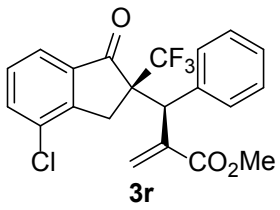
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.743	3431400	394901	50.176	54.268
2	6.806	3407368	332788	49.824	45.732
Total		6838769	727689	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.733	13755590	1589973	99.764	99.767
2	6.791	32571	3717	0.236	0.233
Total		13788161	1593689	100.000	100.000



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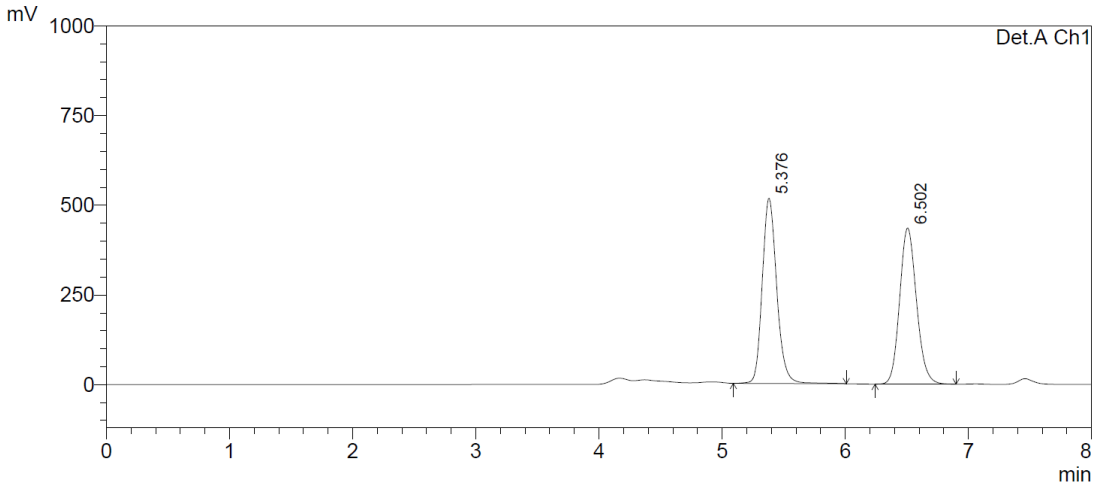
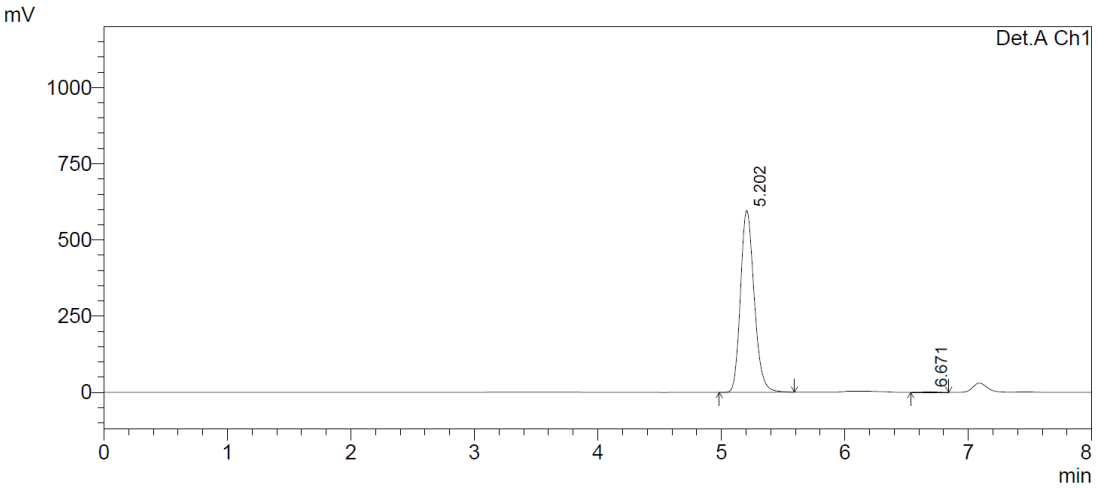
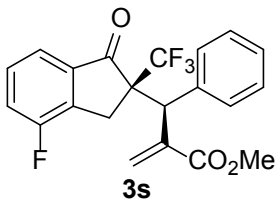


Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.376	4215297	516239	50.450	54.235
2	6.502	4140169	435622	49.550	45.765
Total		8355466	951861	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.202	4602778	596509	99.763	99.779
2	6.671	10921	1321	0.237	0.221
Total		4613700	597830	100.000	100.000



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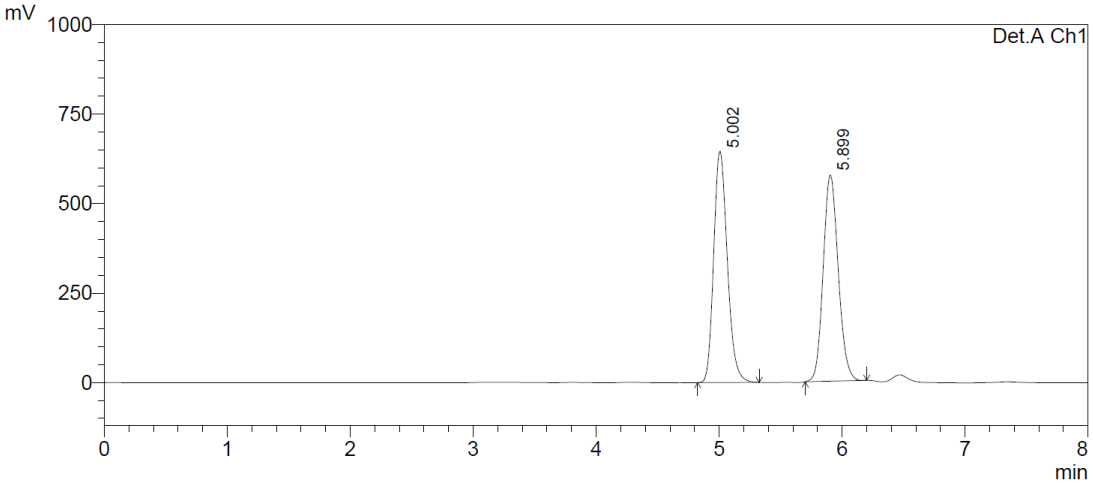
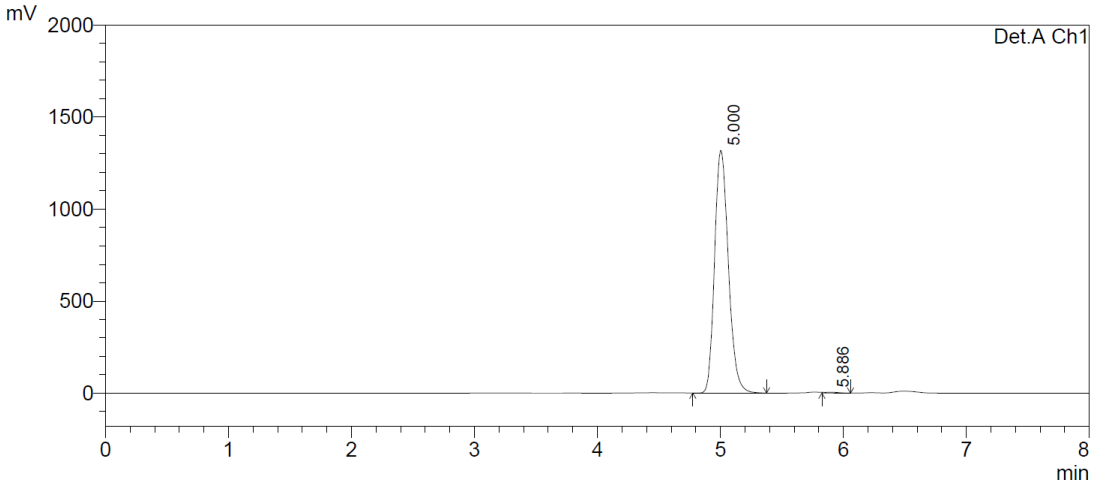


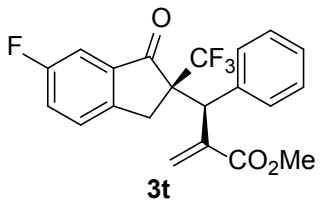
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.002	4979484	646666	50.429	52.893
2	5.899	4894804	575930	49.571	47.107
Total		9874288	1222596	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.000	10285667	1318126	99.597	99.653
2	5.886	41569	4593	0.403	0.347
Total		10327236	1322719	100.000	100.000



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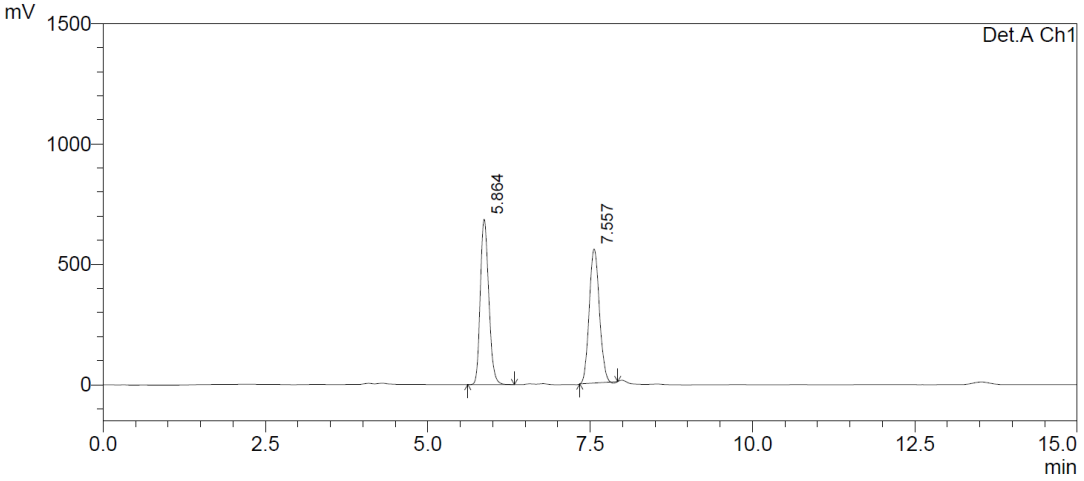
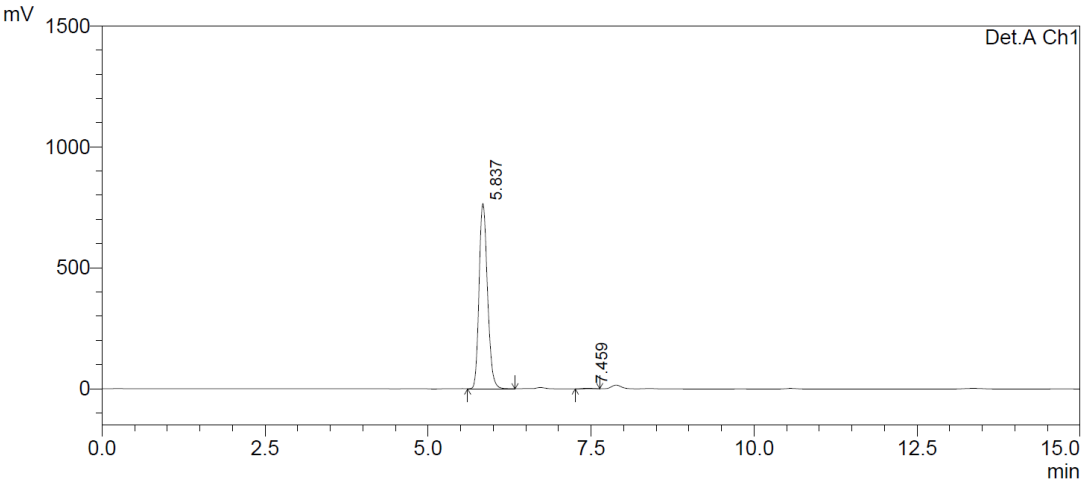


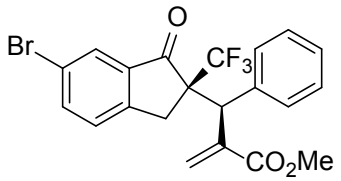
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.864	6221963	686920	50.671	55.238
2	7.557	6057286	556651	49.329	44.762
Total		12279250	1243571	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.837	6909883	767652	99.657	99.680
2	7.459	23761	2465	0.343	0.320
Total		6933644	770118	100.000	100.000



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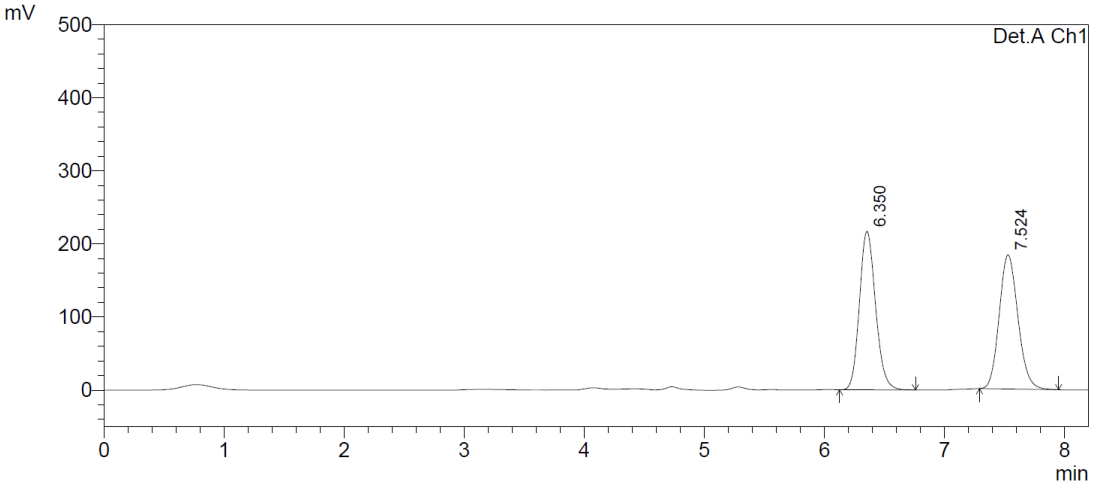
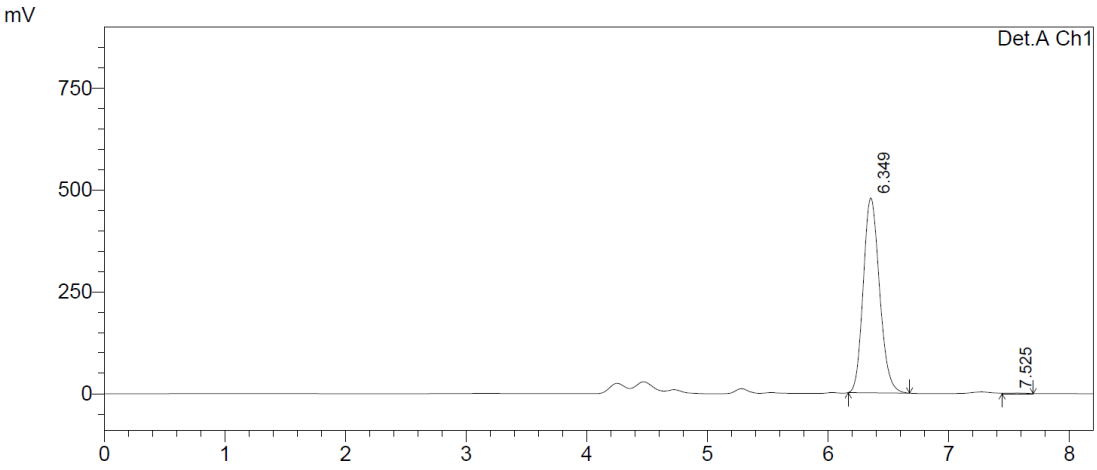
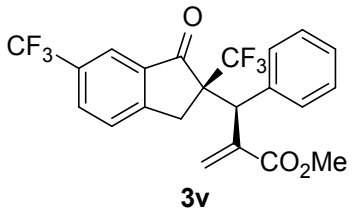


Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.350	2027794	216742	50.383	54.127
2	7.524	1996961	183688	49.617	45.873
Total		4024755	400429	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.349	4492633	478288	99.523	99.559
2	7.525	21512	2119	0.477	0.441
Total		4514144	480407	100.000	100.000



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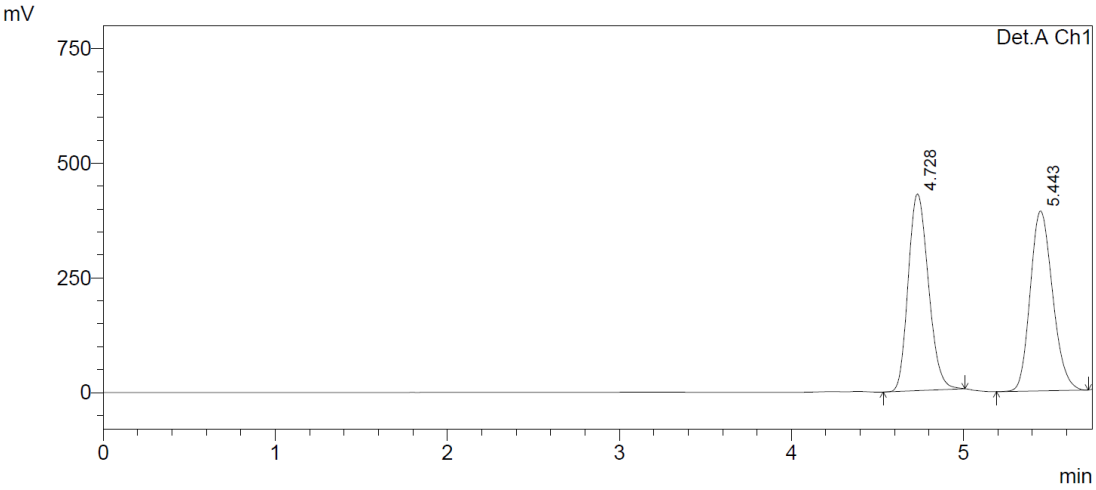
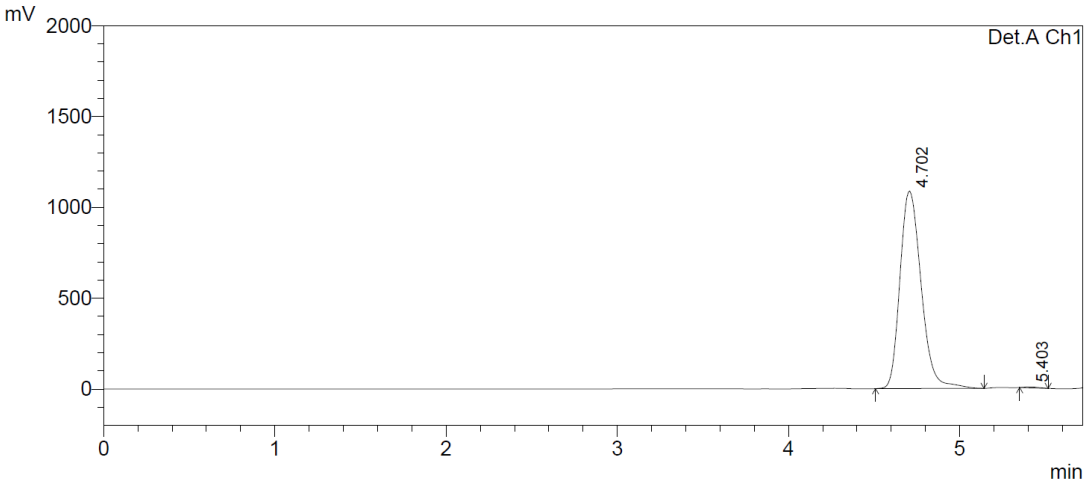
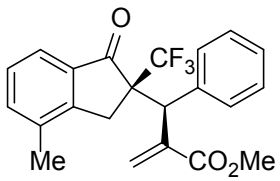


Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.728	3510462	429519	49.715	52.243
2	5.443	3550674	392637	50.285	47.757
Total		7061136	822156	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.702	9360679	1087823	99.694	99.539
2	5.403	28730	5034	0.306	0.461
Total		9389409	1092857	100.000	100.000



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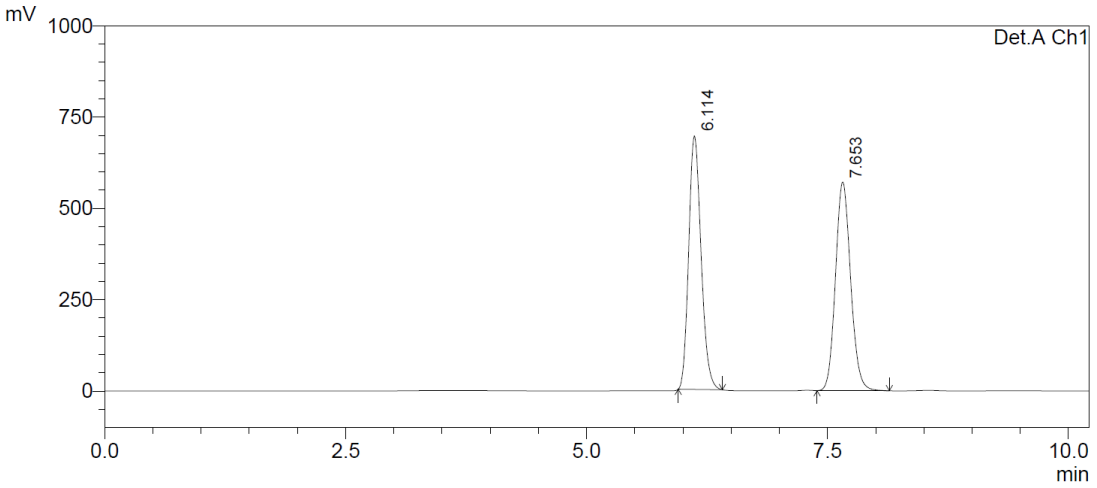
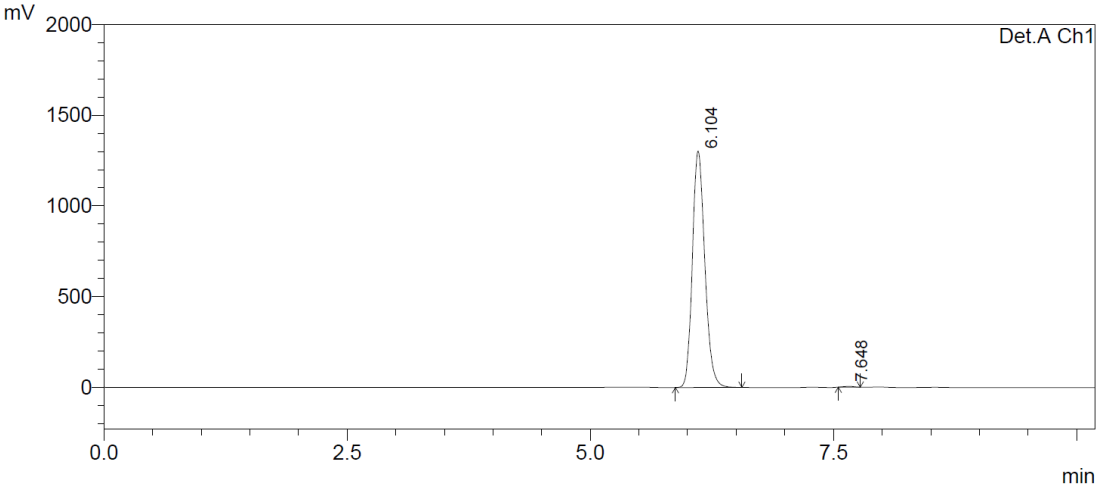
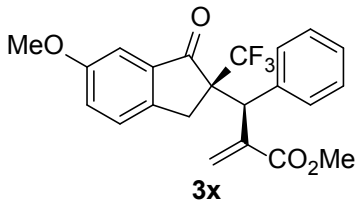


Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.114	6220657	694926	49.878	54.859
2	7.653	6251138	571831	50.122	45.141
Total		12471794	1266757	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.104	11607516	1303538	99.723	99.682
2	7.648	32213	4165	0.277	0.318
Total		11639729	1307703	100.000	100.000



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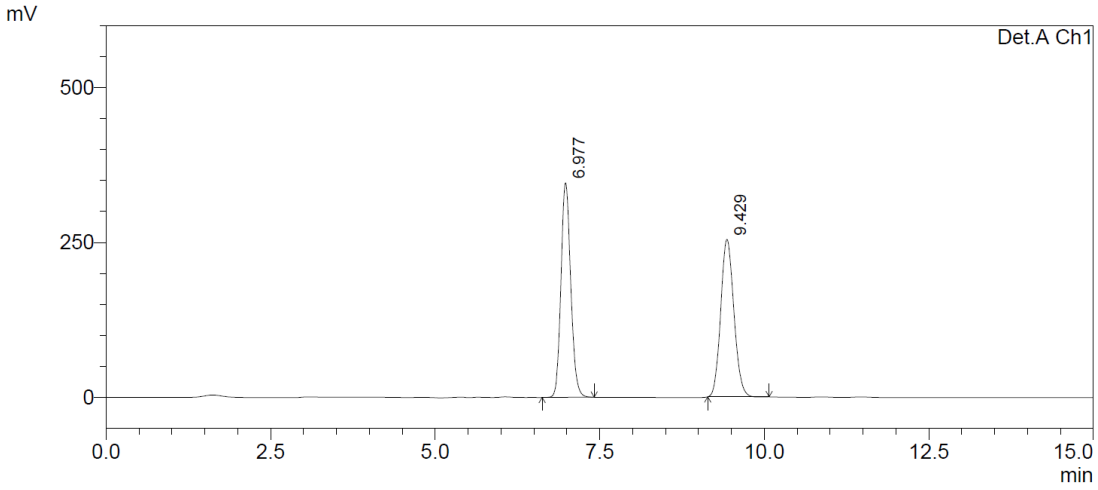
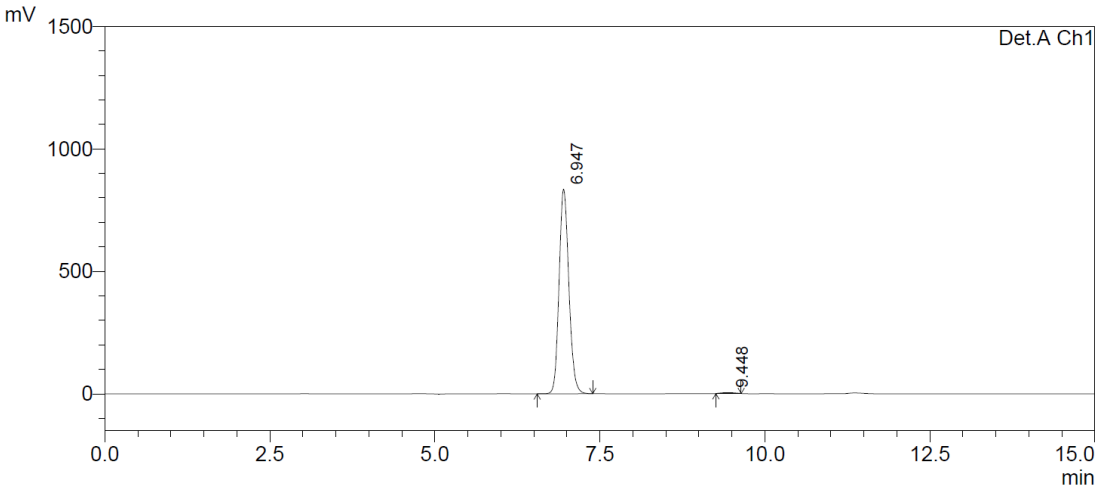


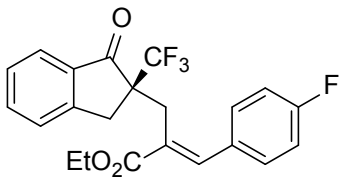
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.977	3577142	346404	50.262	57.665
2	9.429	3539779	254319	49.738	42.335
Total		7116920	600723	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.947	8615413	835371	99.362	99.514
2	9.448	55283	4082	0.638	0.486
Total		8670696	839453	100.000	100.000



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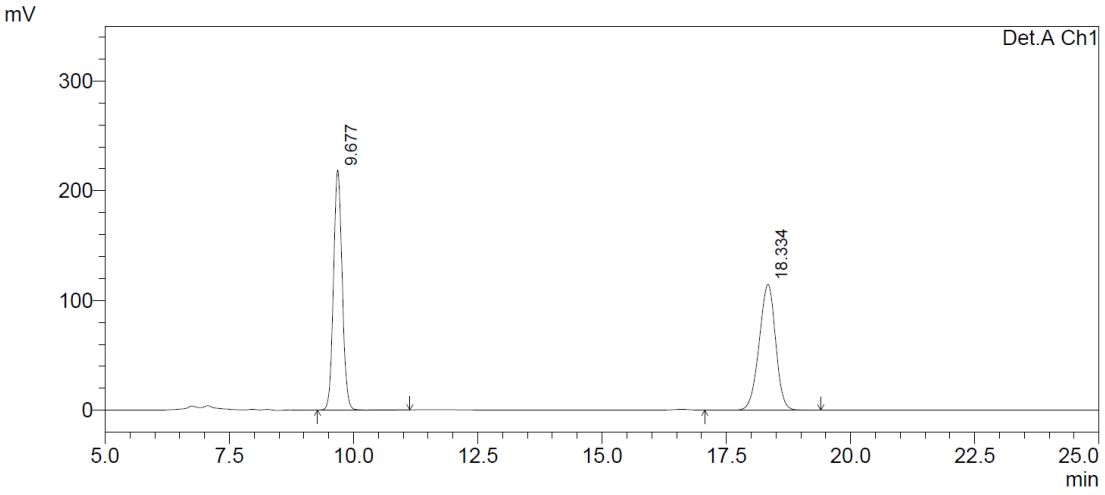
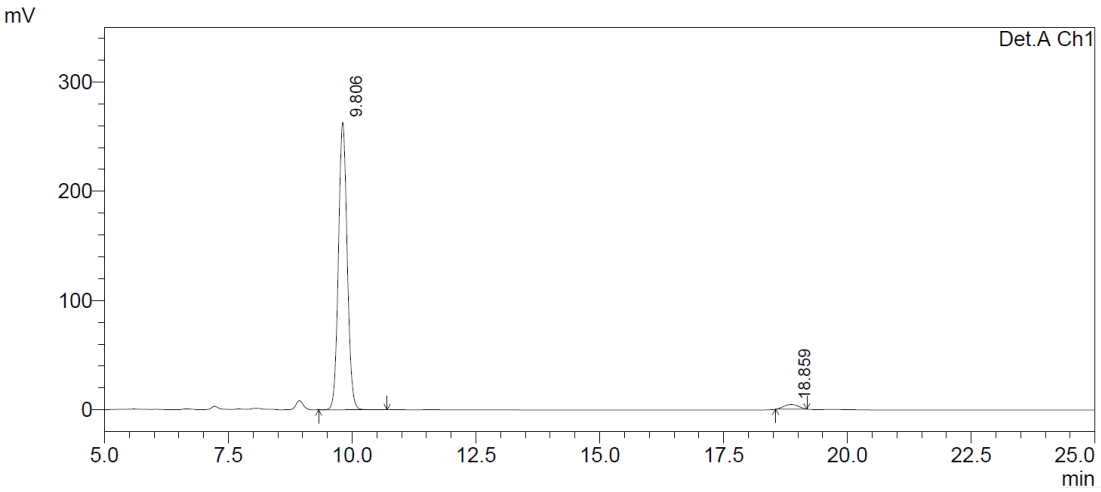


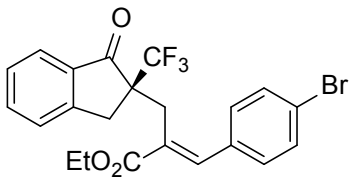
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.677	2645400	219050	50.071	65.648
2	18.334	2637927	114625	49.929	34.352
Total		5283327	333675	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.806	3224339	263386	97.360	98.363
2	18.859	87421	4383	2.640	1.637
Total		3311760	267769	100.000	100.000



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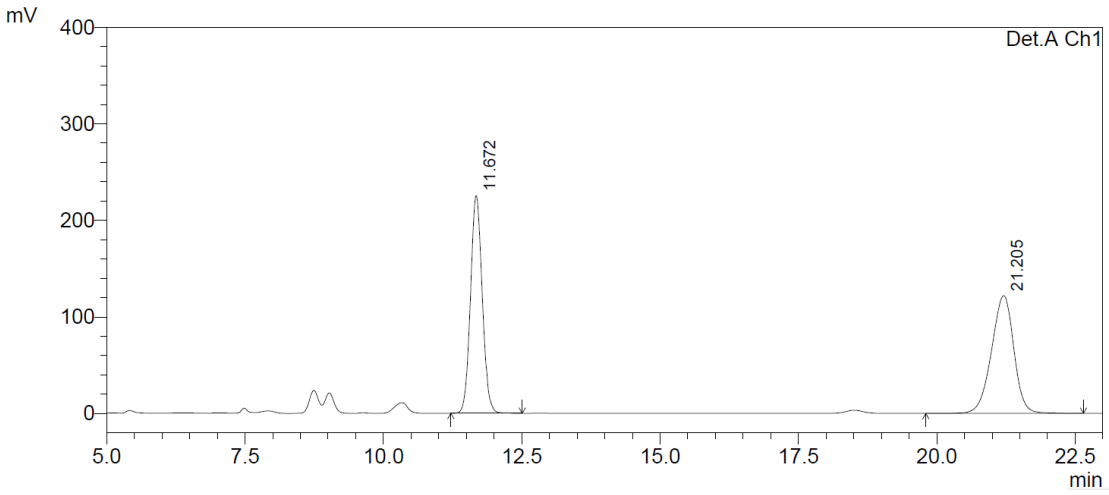
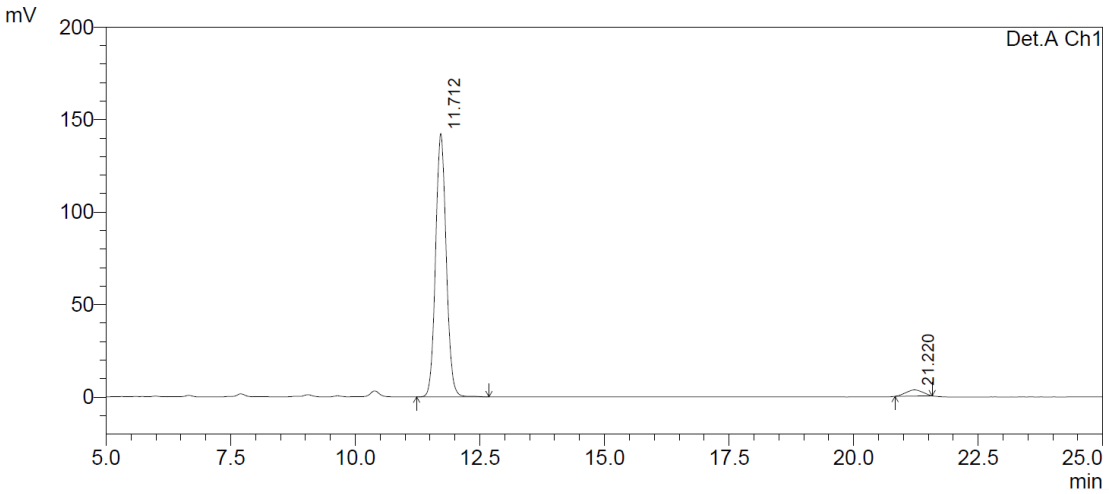


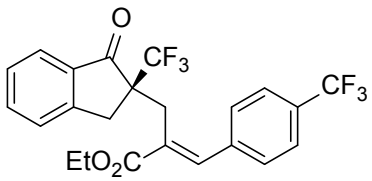
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.672	3337517	225605	49.284	64.906
2	21.205	3434464	121981	50.716	35.094
Total		6771981	347586	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.712	2116563	142484	96.525	97.752
2	21.220	76194	3277	3.475	2.248
Total		2192756	145761	100.000	100.000



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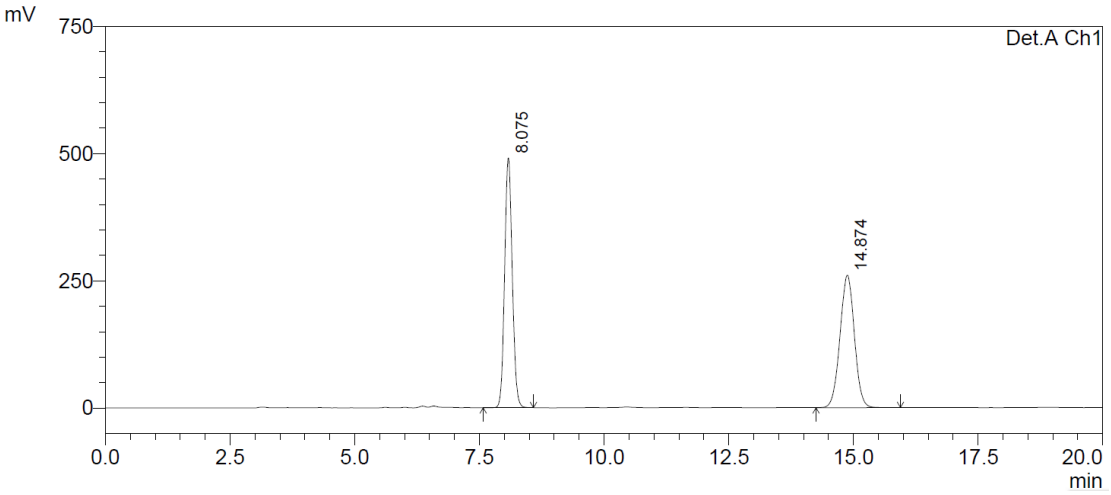
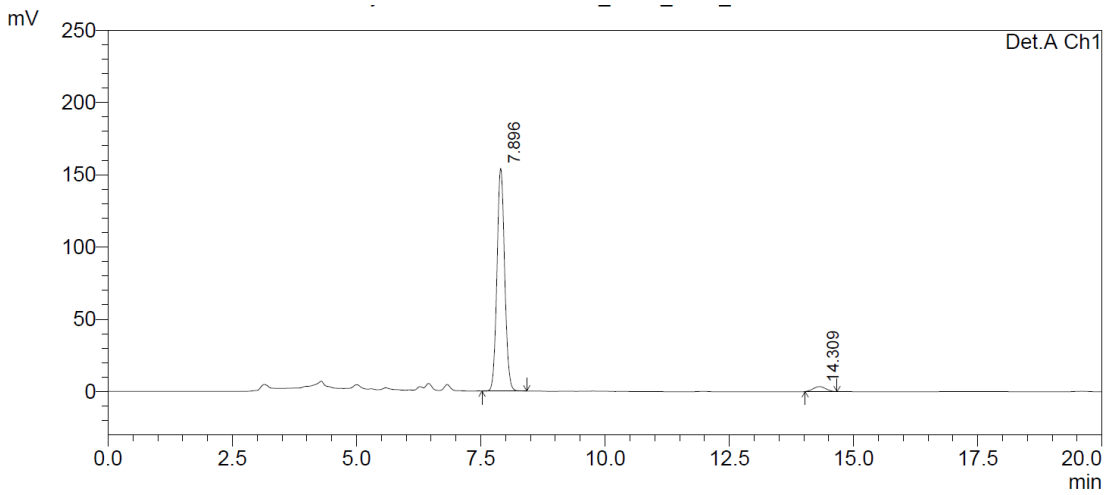
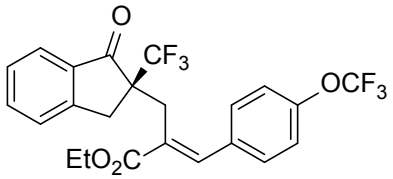


Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.075	5228790	490811	49.973	65.352
2	14.874	5234500	260214	50.027	34.648
Total		10463290	751024	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.896	1658573	154184	96.437	97.794
2	14.309	61273	3478	3.563	2.206
Total		1719846	157662	100.000	100.000



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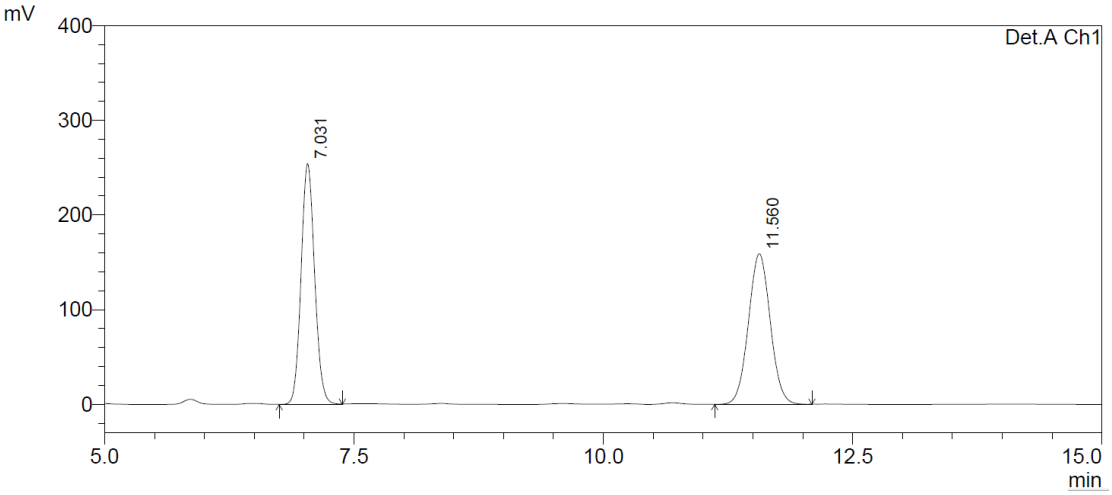
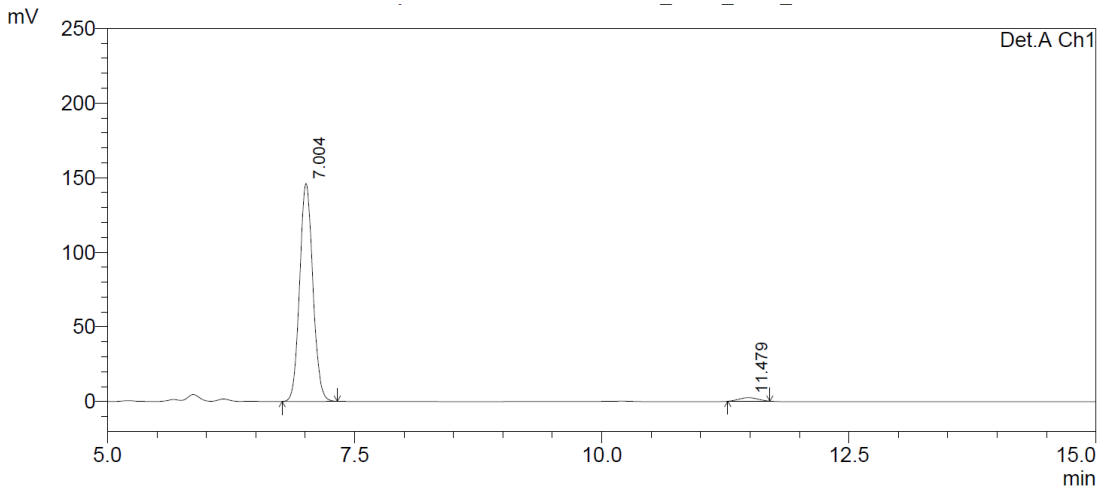


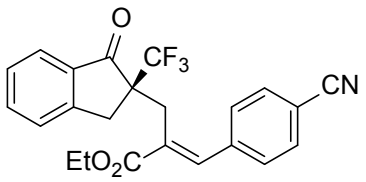
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.031	2410950	254690	49.747	61.534
2	11.560	2435511	159211	50.253	38.466
Total		4846461	413901	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.004	1358134	146045	97.765	98.411
2	11.479	31046	2358	2.235	1.589
Total		1389180	148403	100.000	100.000



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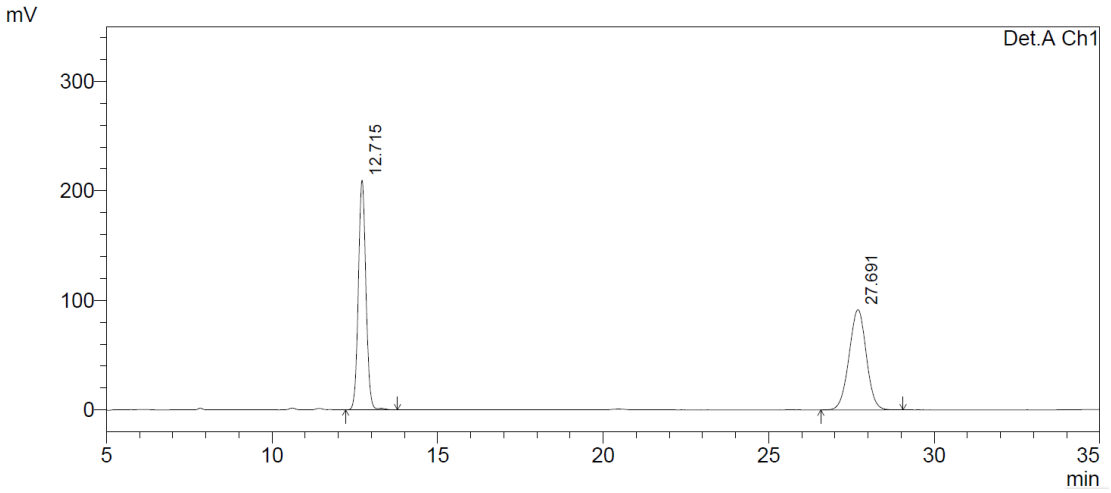
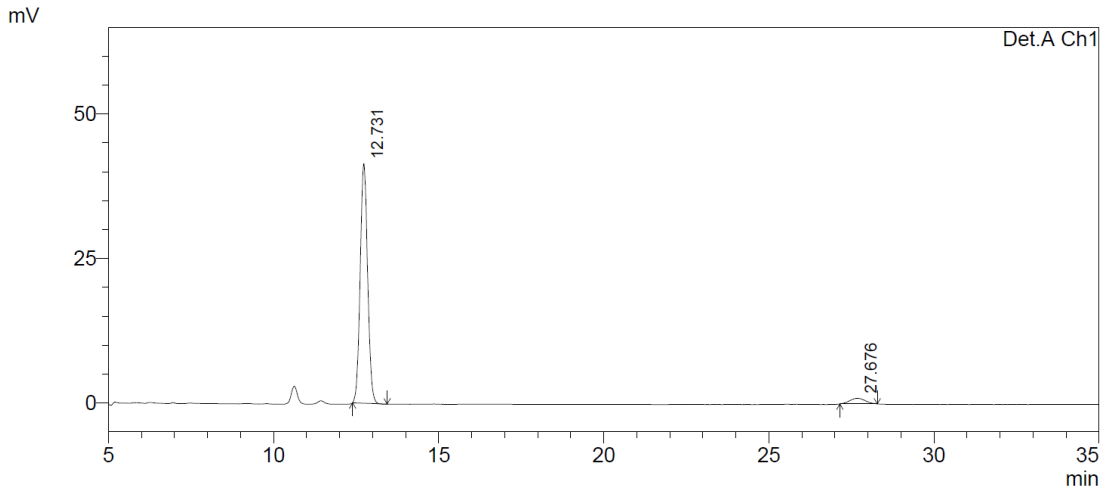


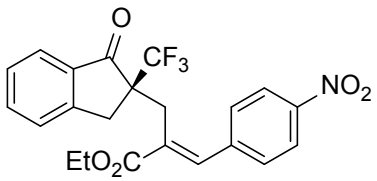
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.715	3329817	209735	50.113	69.624
2	27.691	3314795	91506	49.887	30.376
Total		6644613	301241	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.731	648995	41521	95.347	97.705
2	27.676	31673	975	4.653	2.295
Total		680669	42496	100.000	100.000



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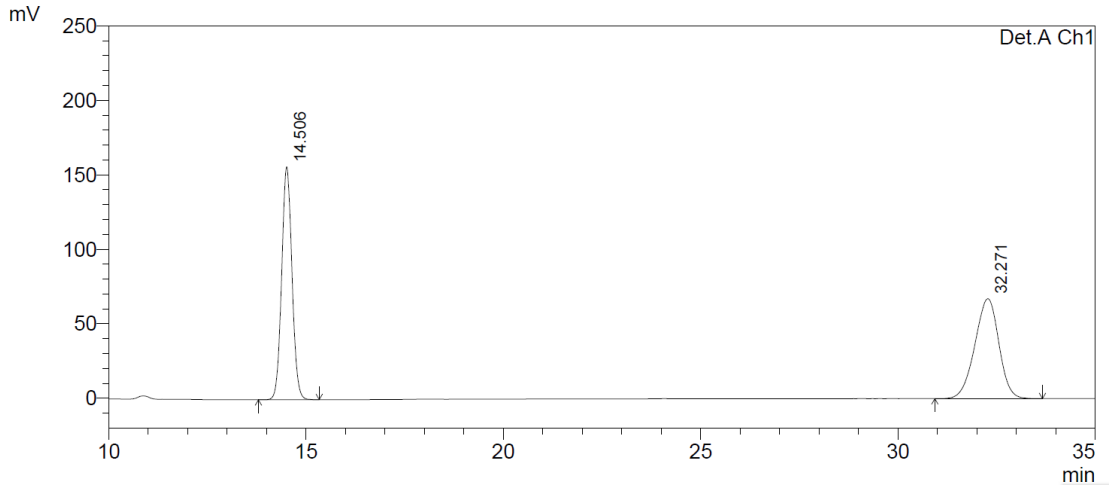
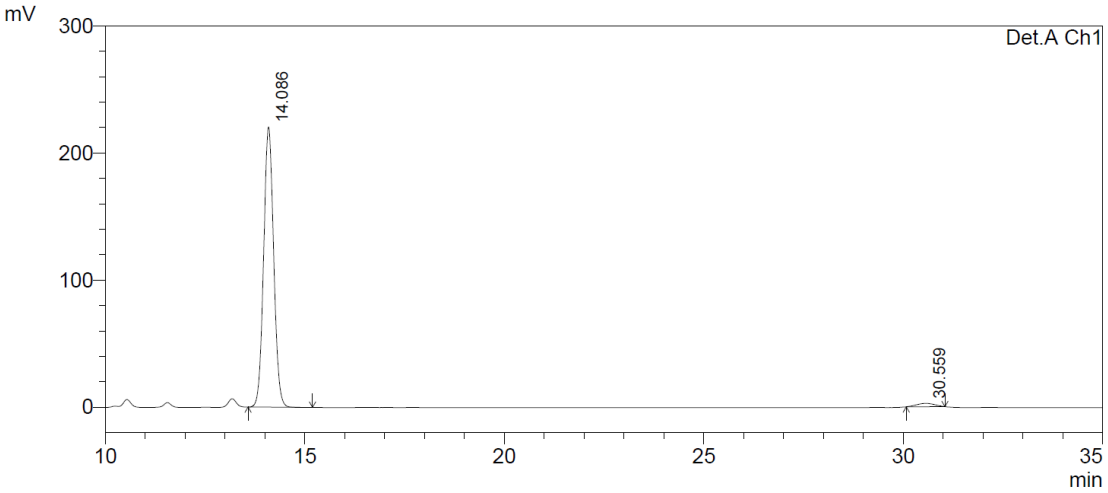


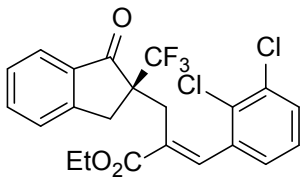
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.506	2840616	156297	50.042	69.972
2	32.271	2835899	67075	49.958	30.028
Total		5676515	223372	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.086	3852572	220504	97.883	98.826
2	30.559	83322	2620	2.117	1.174
Total		3935894	223124	100.000	100.000



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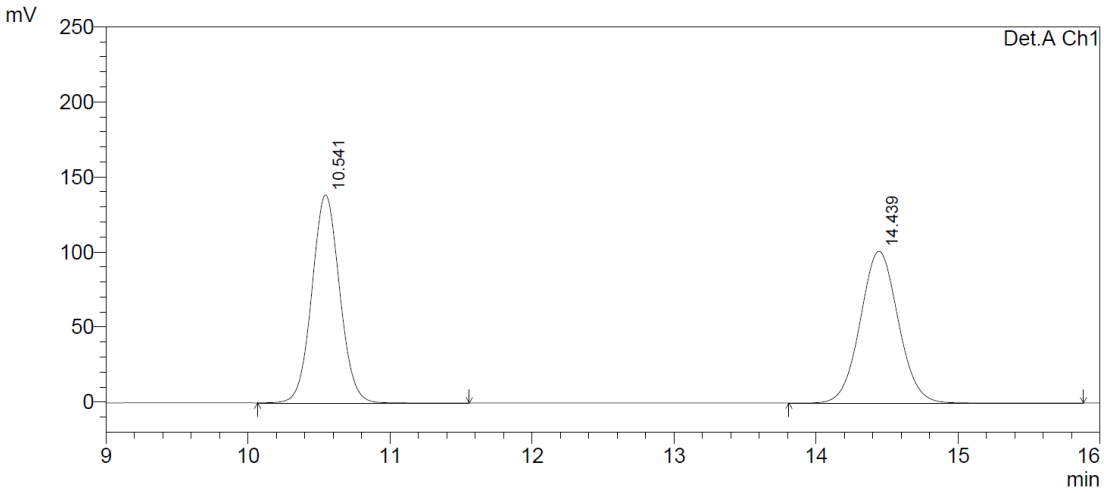
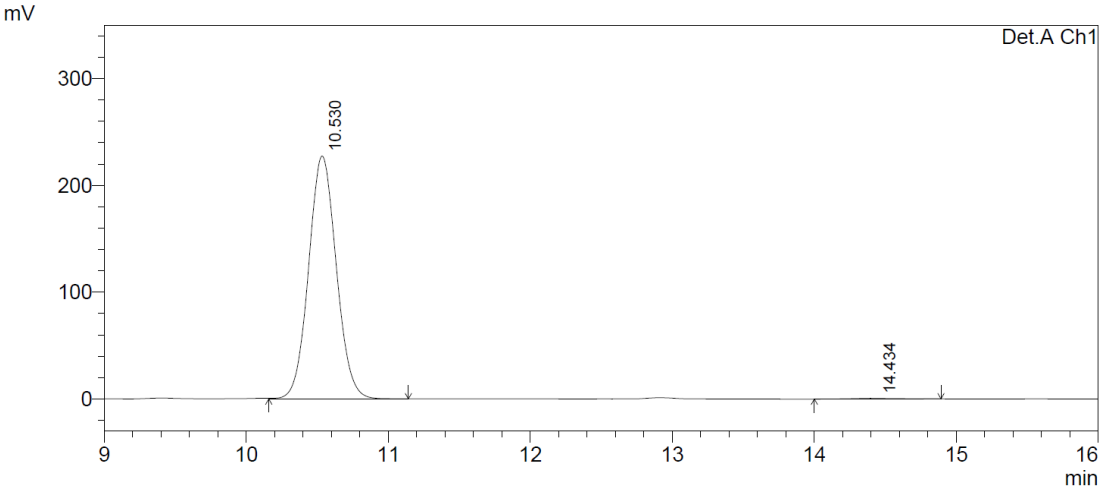


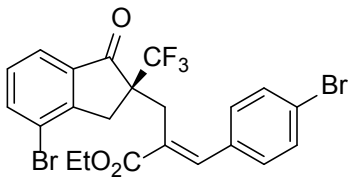
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.541	1885946	138586	50.120	57.819
2	14.439	1876924	101105	49.880	42.181
Total		3762870	239691	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.530	3088968	227645	99.666	99.744
2	14.434	10336	583	0.334	0.256
Total		3099305	228228	100.000	100.000



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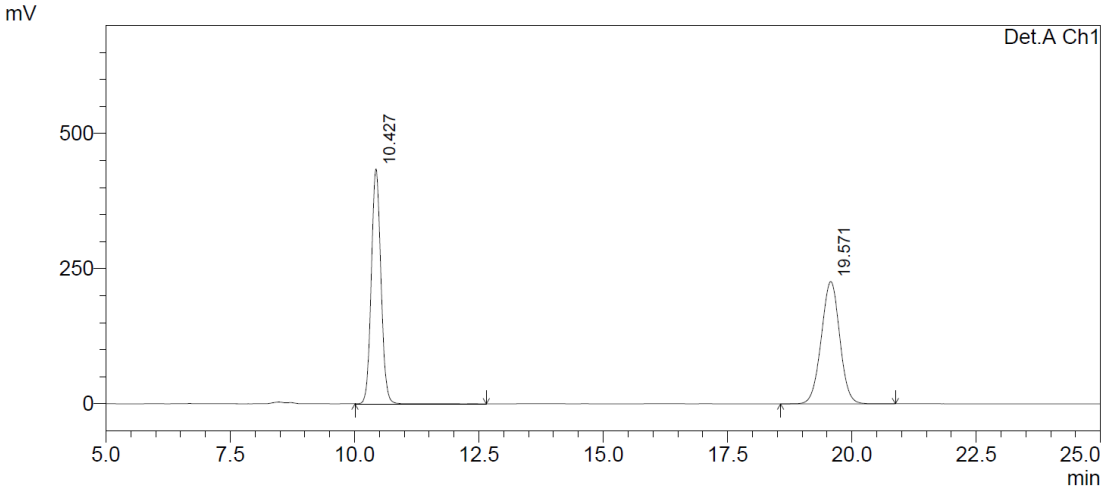
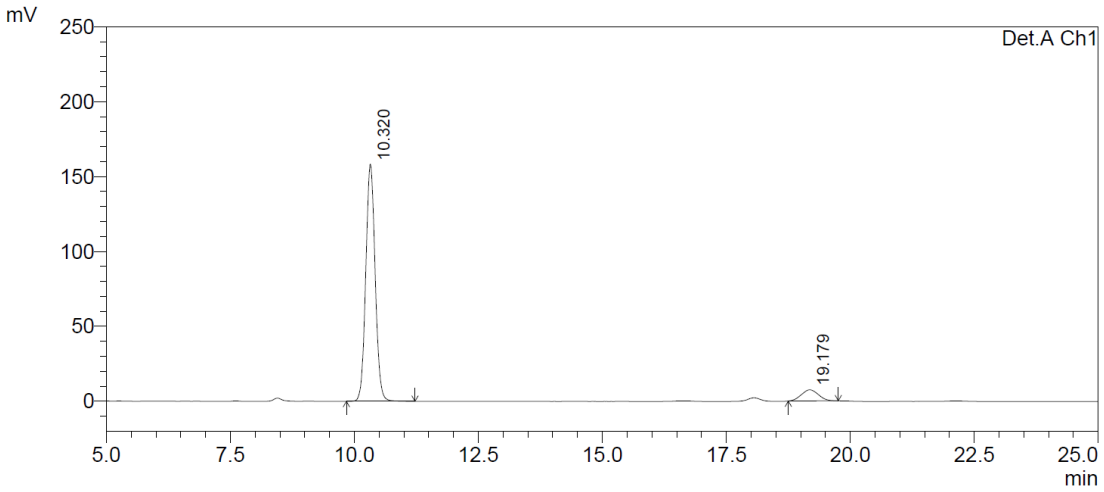
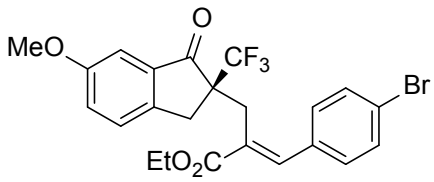


Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.427	5842440	434560	50.014	65.757
2	19.571	5839208	226302	49.986	34.243
Total		11681647	660862	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.320	2080597	158355	92.198	95.536
2	19.179	176061	7399	7.802	4.464
Total		2256659	165754	100.000	100.000



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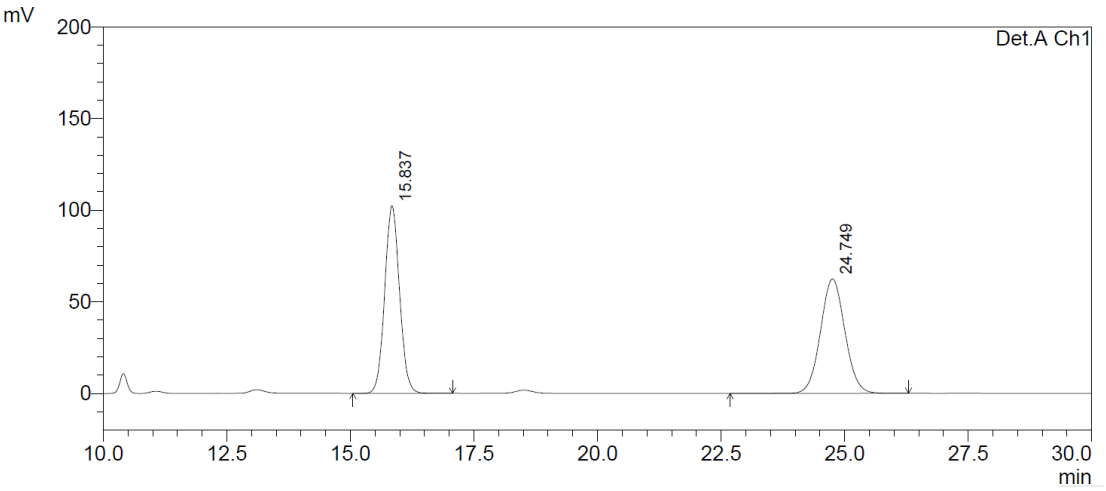
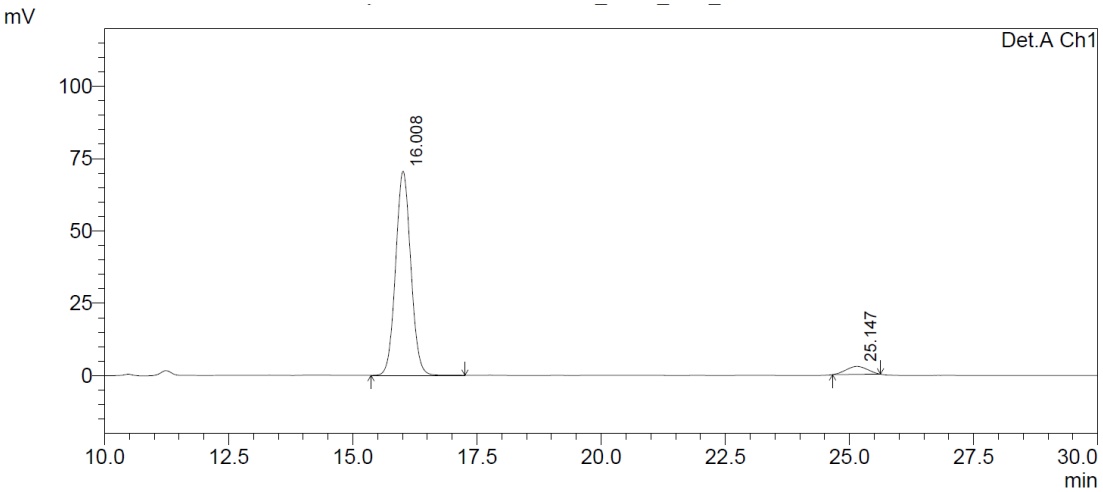


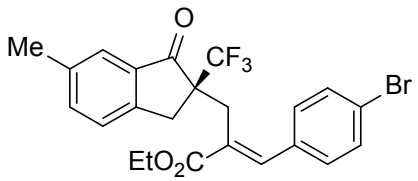
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.837	2141578	102351	50.048	62.128
2	24.749	2137434	62391	49.952	37.872
Total		4279013	164741	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.008	1502869	70602	94.814	96.262
2	25.147	82207	2741	5.186	3.738
Total		1585076	73344	100.000	100.000



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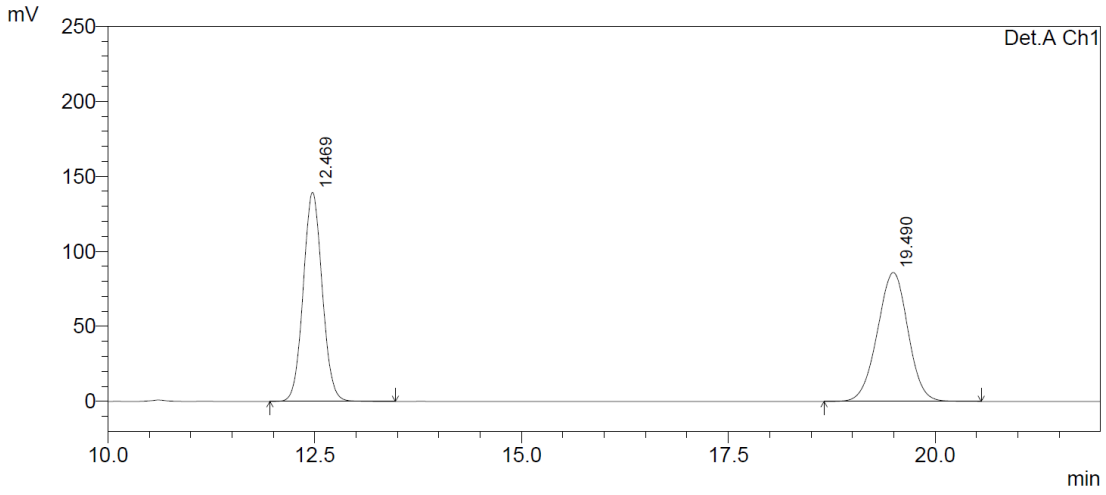
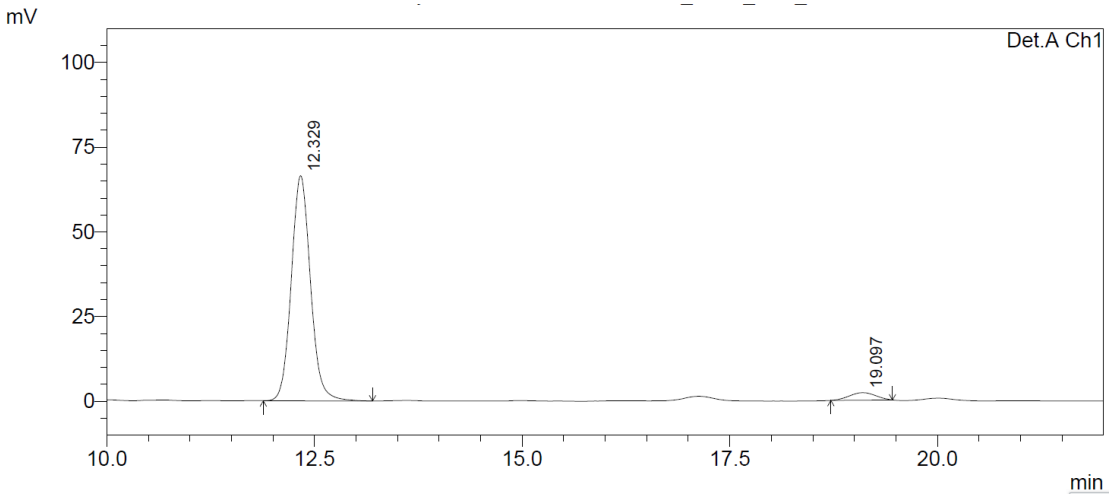


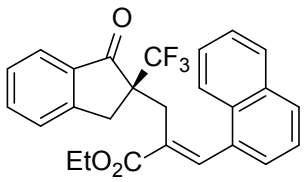
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.469	2226649	139330	50.138	61.847
2	19.490	2214428	85952	49.862	38.153
Total		4441077	225282	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.329	1070766	66503	95.622	96.763
2	19.097	49023	2225	4.378	3.237
Total		1119790	68728	100.000	100.000



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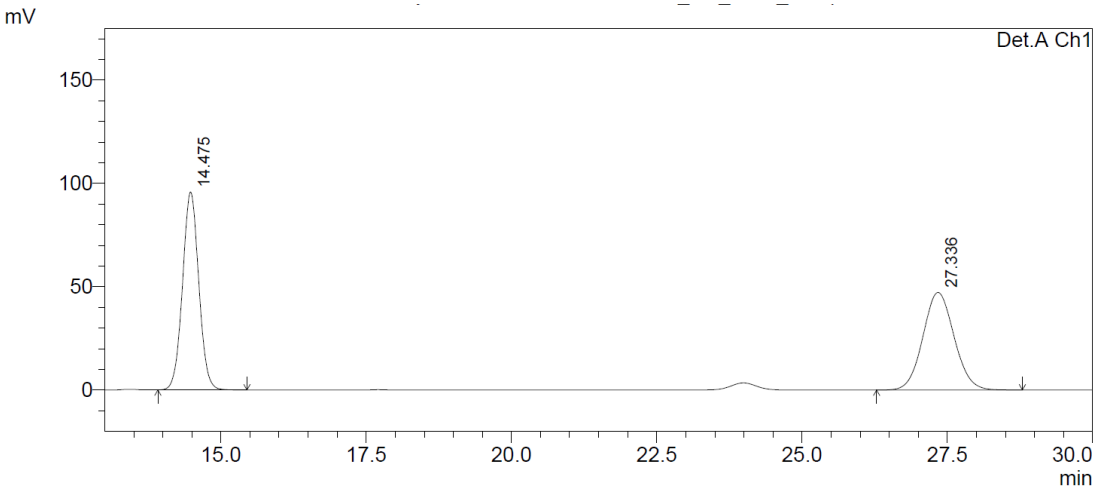
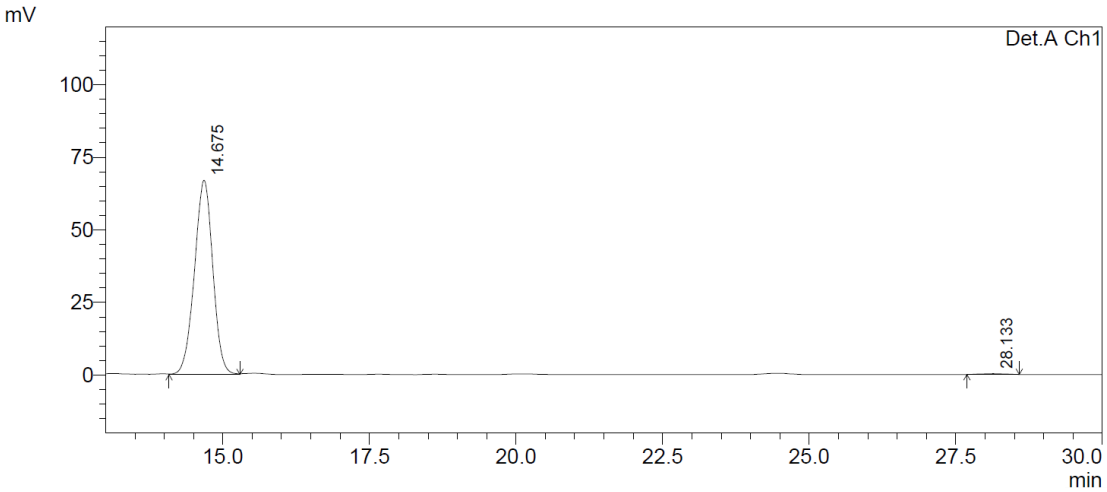


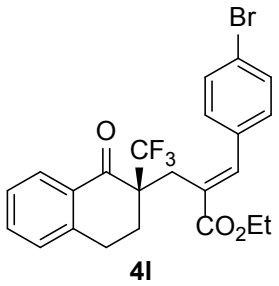
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.475	1865123	95804	51.427	66.989
2	27.336	1761637	47210	48.573	33.011
Total		3626760	143015	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.675	1464180	66959	99.487	99.623
2	28.133	7557	254	0.513	0.377
Total		1471736	67212	100.000	100.000



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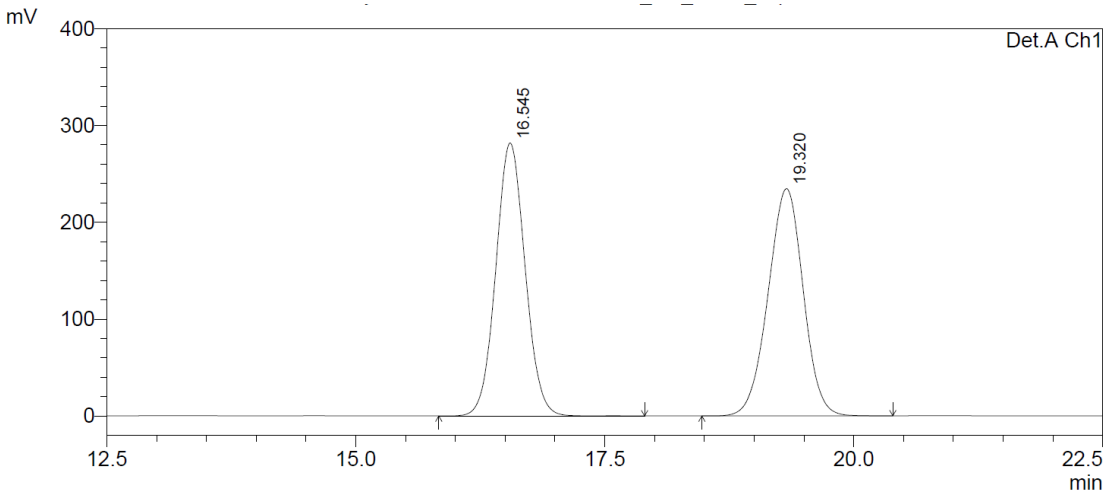
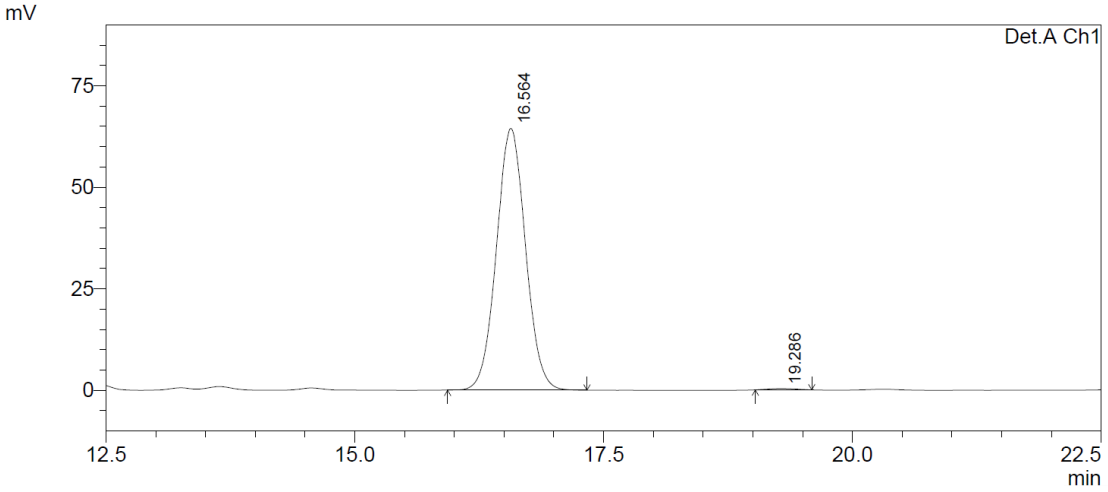
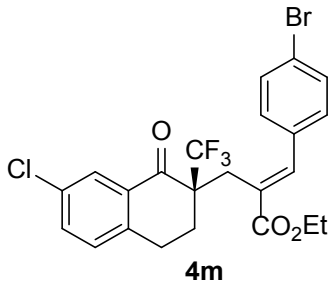


Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.545	5764414	281997	50.032	54.576
2	19.320	5757029	234703	49.968	45.424
Total		11521443	516700	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.564	1314145	64478	99.521	99.495
2	19.286	6321	327	0.479	0.505
Total		1320466	64805	100.000	100.000



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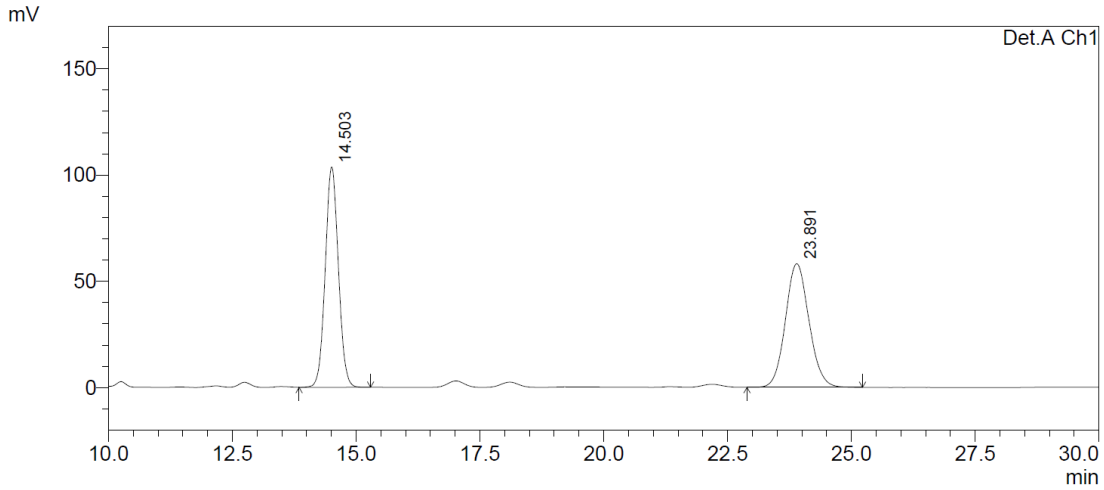
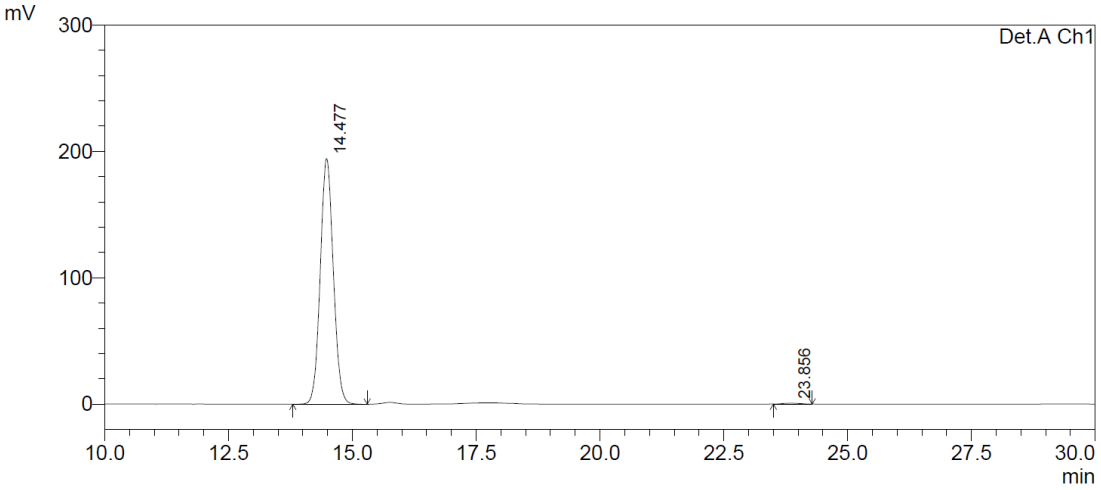
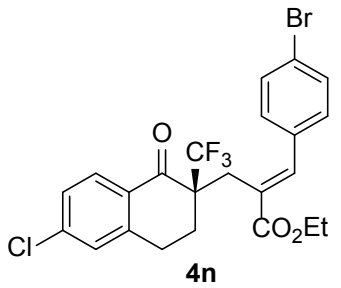


Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.503	1915679	103677	49.841	64.054
2	23.891	1927883	58183	50.159	35.946
Total		3843561	161860	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.477	3565142	194397	99.592	99.711
2	23.856	14588	564	0.408	0.289
Total		3579730	194961	100.000	100.000



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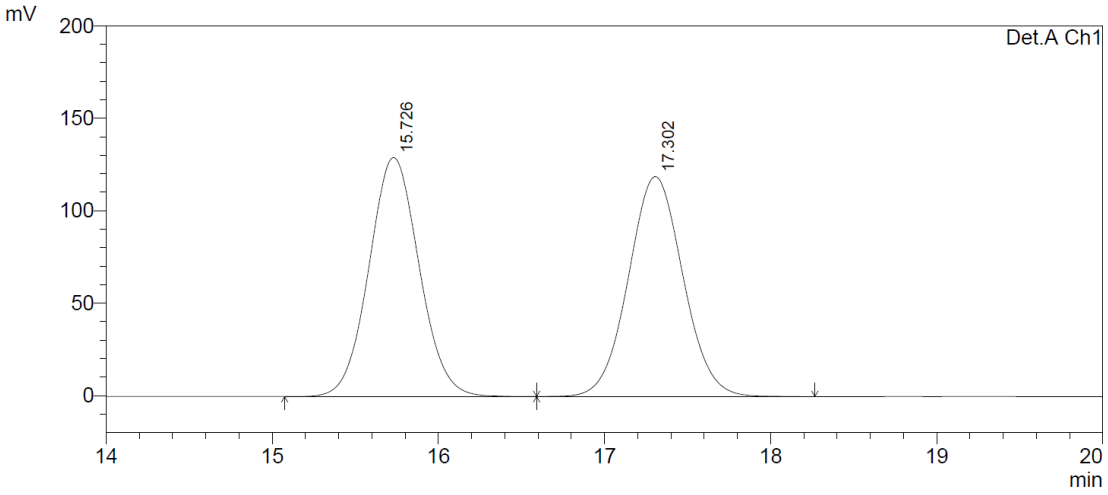
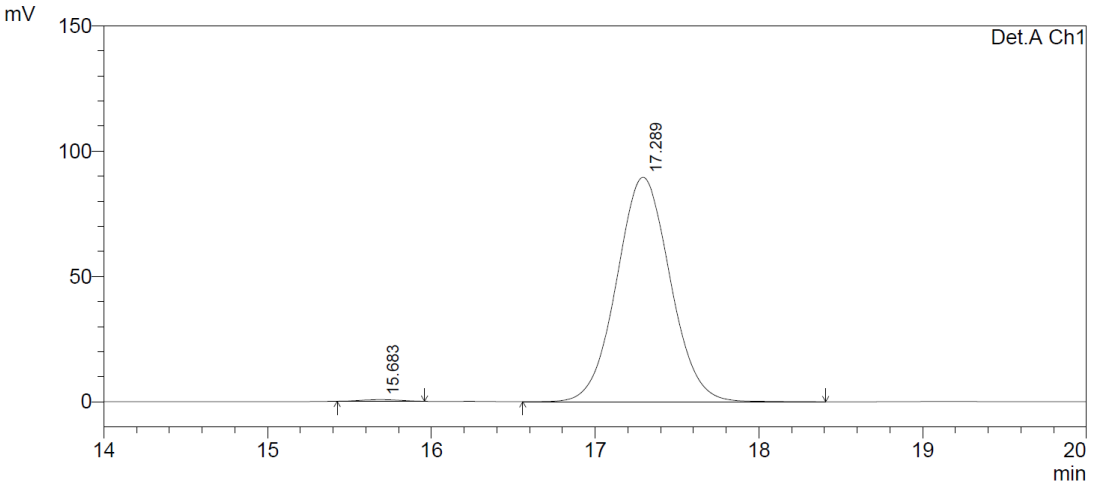


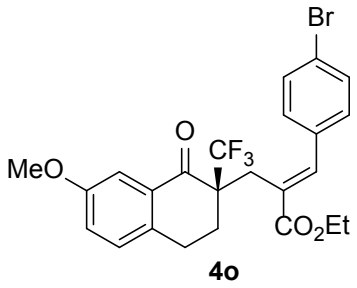
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.726	2717210	129286	49.995	52.077
2	17.302	2717767	118971	50.005	47.923
Total		5434977	248257	100.000	100.000

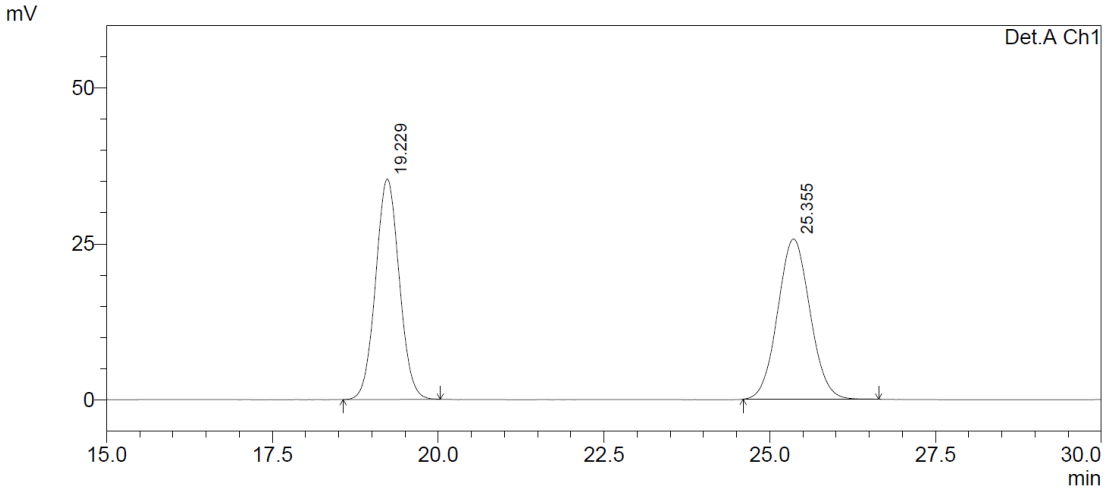


Detector A Ch1 254nm

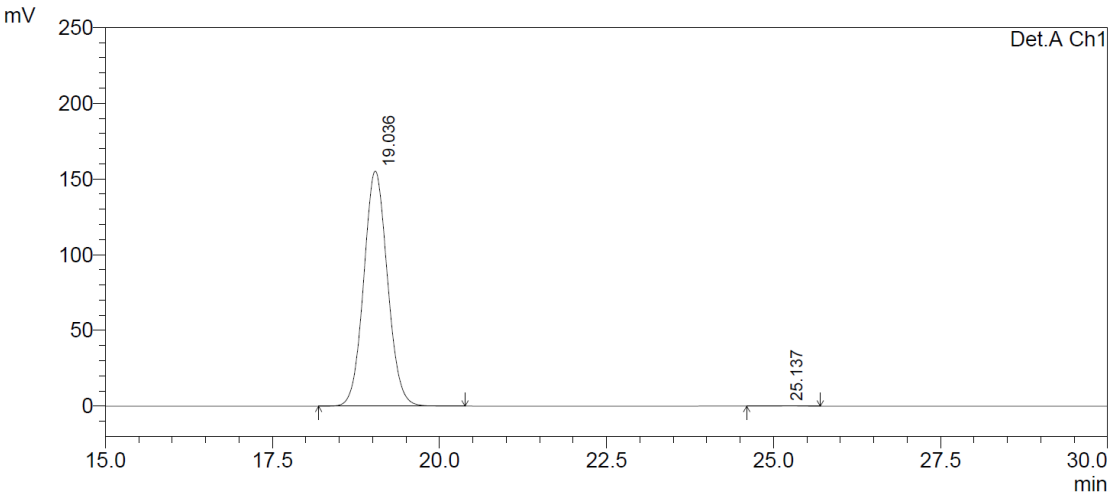
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.683	11158	667	0.546	0.739
2	17.289	2032135	89514	99.454	99.261
Total		2043292	90181	100.000	100.000



4o



Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.229	877621	35330	50.198	57.910
2	25.355	870690	25679	49.802	42.090
Total		1748311	61009	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.036	3837902	155199	99.790	99.832
2	25.137	8065	261	0.210	0.168
Total		3845967	155460	100.000	100.000

X-ray crystallography

Single crystal of the product **3i** was obtained by recrystallization from CH2Cl2/*n*-hexane. X-ray diffractional data and the refinement were shown in Table *S*1. The absolute configuration of **3i** was determined to be (*R*,*S*) by X-ray crystallographic analysis (Figure *S1*).

CIF files of **3i** can be obtained from the Cambridge Crystallographic Data Centre using deposition numbers 1911158. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (1223) 336 033; e-mail:deposit@ccdc.cam.ac.uk].

Table *S*1. Crystal data and structure refinement for 3i.

Bond precision:	C-C = 0.0049 A	Wavelength = 0.71073	
Cell:	a = 7.0725 (12)	b = 9.9051 (17)	c = 27.867 (5)
	alpha = 90	beta = 90	gamma = 90
Temperature:	296 K		
	Calculated 1952.2(6)	Reported	
Volume		1952.2(6)	
Space group Hall	P 21 21 21	P 21 21 21	
group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C21 H15 Cl2 F3 O3	C21 H15 Cl2 F3 O3	
Sum formula	C21 H15 Cl2 F3 O3	C21 H15 Cl2 F3 O3	
Mr	443.23	443.23	
Dx,g cm-3	1.508	1.508	
Z	4	4	
Mu (mm-1)	0.381	0.381	
F000	904.0	904.0	
F000’	905.72		
h,k,lmax	8,11,33	8,11,33	
Nref	3447 [2013]	3447	
Tmin,Tmax	0.917, 0.934	0.643, 0.746	
Tmin’	0.916		

Correction method= # Reported T Limits: Tmin = 0.643 Tmax = 0.746

AbsCorr = MULTI-SCAN

Data completeness = 1.71 / 1.00	Theta(max) = 25.002
R(reflections) = 0.0371 (2647)	wR2(reflections) = 0.0741 (3447)
S = 0.963	Npar = 263

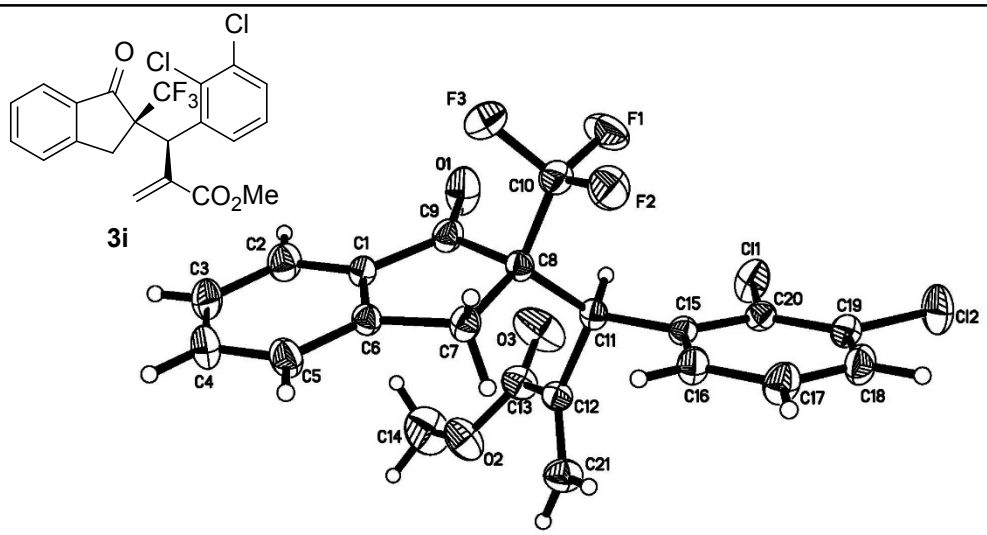


Figure *S*1. X-ray crystal structure of (*R*,*S*)-**3i**

Single crystal of the product **4n** was obtained by recrystallization from CH2Cl2/*n*-hexane. X-ray diffractional data and the refinement were shown in Table *S*2. The absolute configuration of **4n** was determined to be (*R*,*E*) by X-ray crystallographic analysis (Figure *S2*).

CIF files of **4n** can be obtained from the Cambridge Crystallographic Data Centre using deposition numbers 2009810. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (1223) 336 033; e-mail:deposit@ccdc.cam.ac.uk].

Table *S*2. Crystal data and structure refinement for 4n.

Bond precision:	C-C = 0.0074 A	Wavelength = 0.71073	
Cell:	a = 6.4217 (5)	b = 9.9437 (8)	c = 17.0193 (16)
	alpha = 90	beta = 95.419 (3)	gamma = 90
Temperature:	296 K		

	Calculated 1081.92(16)	Reported
Volume		1081.92(16)
Space group Hall	P 21	P 21
group	P 2yb	P 2yb
Moiety formula	C23 H19 Br Cl F3 O3	C23 H19 Br Cl F3 O3
Sum formula	C23 H19 Br Cl F3 O3	C23 H19 Br Cl F3 O3
Mr	515.73	515.74
Dx,g cm-3	1.583	1.583
Z	2	2
Mu (mm-1)	2.072	2.072
F000	520.0	520.0
F000’	520.00	
h,k,lmax	8, 13, 22	8, 13, 22
Nref	5382 [2843]	4436
Tmin,Tmax	0.149, 0.661	0.230, 0.682
Tmin’	0.116	

Correction method= # Reported T Limits: Tmin = 0.643 Tmax = 0.746

AbsCorr = MULTI-SCAN

Data completeness = 1.56 / 0.82 Theta(max) = 28.276

R(reflections) = 0.0424 (2968) wR2(reflections) = 0.1284 (4436)

S = 1.009 Npar = 282

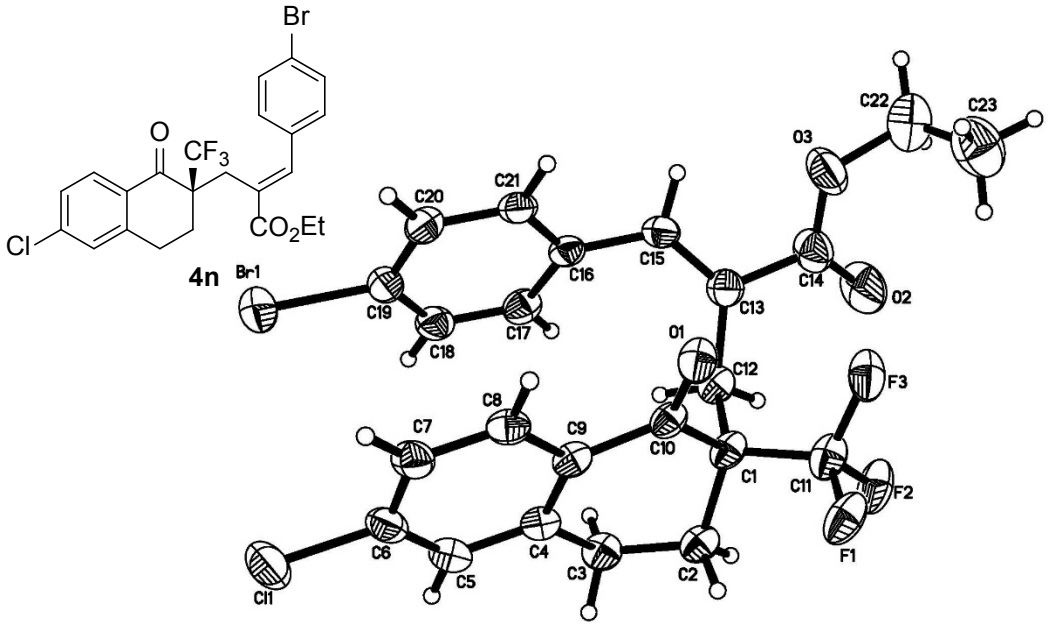


Figure *S*2. X-ray crystal structure of (*R*,*E*)-**4n**

Computational details:

All calculations were carried out at the (SMD:THF)-M06L/6-311++G(2d,p)-SDD//(SMD:THF)-B3LYP/6-31G(d)-LANL2DZ[3a-f] level of theory with *Gaussian 09* program[4] and visualized with CYLview[5].

1. Discussion on inner/outer sphere nucleophilic addition:

For C1-attack, the lowest energy transition state for outer-sphere addition is 2.7 kcal/mol lower than that for inner-sphere (Figure S1). Accordingly, the outer-sphere is preferred over the inner sphere nucleophilic addition.

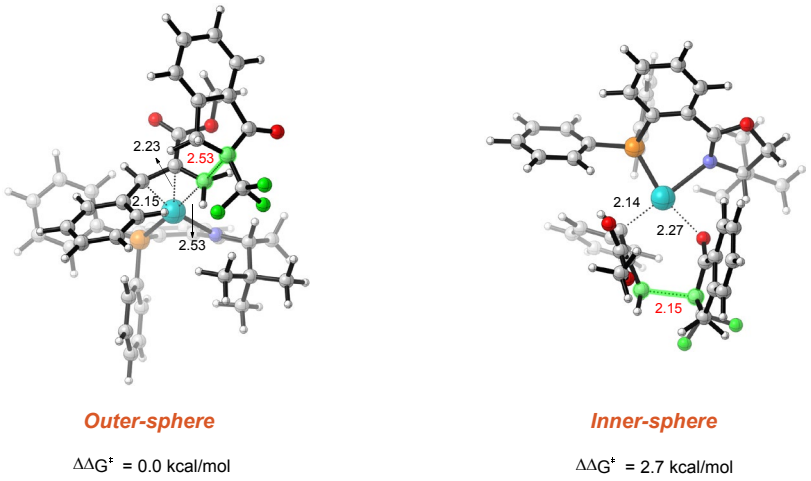
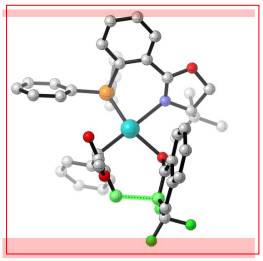
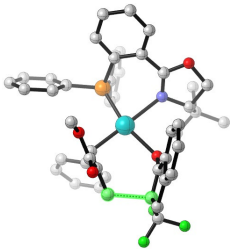


Figure S1 Optimized geometry of transition states and their relative free energy for outer-sphere and inner-sphere nucleophilic addition at (SMD:THF)-M06L/6-311++G(2d,p)-SDD//(SMD: THF)-B3LYP/6-31G(d)-LANL2DZ level of theory. Bond lengths are denoted in Å.

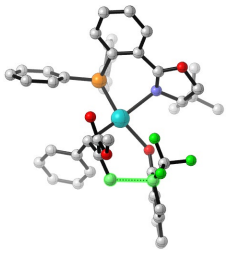
endo:



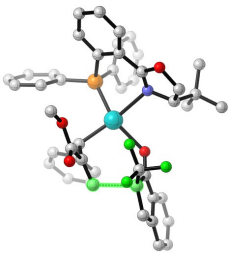
ΔΔG‡ = 2.7



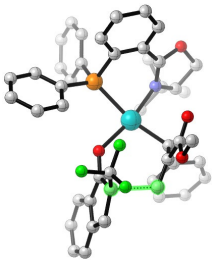
ΔΔG‡ = 3.2



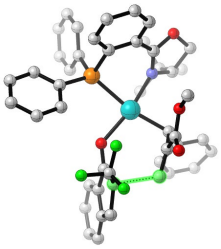
ΔΔG‡ = 3.9



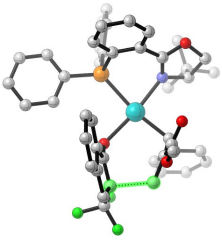
ΔΔG‡ = 4.9



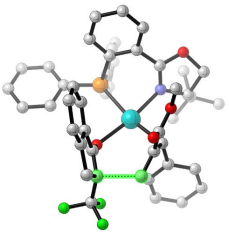
ΔΔG‡ = 12.7



ΔΔG‡ = 13.7

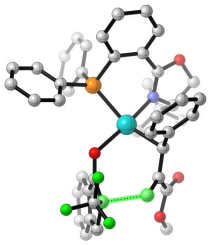


ΔΔG‡ = 15.8

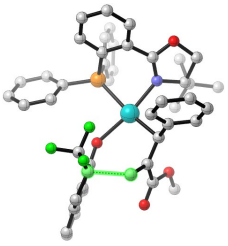


ΔΔG‡ = 16.0

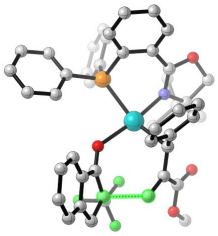
exo:



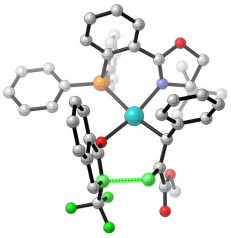
ΔΔG‡ = 5.7



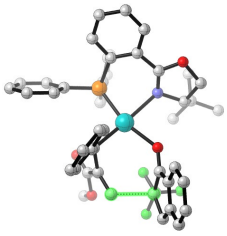
ΔΔG‡ = 4.3



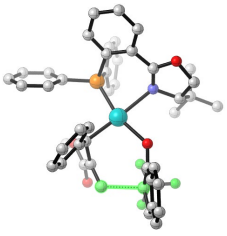
ΔΔG‡ = 9.1



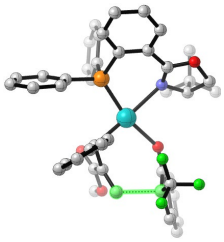
ΔΔG‡ = 10.5



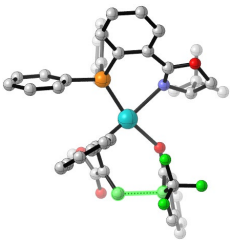
ΔΔG‡ = 12.6



ΔΔG‡ = 18.1



ΔΔG‡ = 15.5



ΔΔG‡ = 16.8

Figure S2 Conformers and their relative free energies for C1-attack inner-sphere transition states at (SMD:THF)-M06L/6-311++G(2d,p)-SDD//(SMD: THF)-B3LYP/6-31G(d)-LANL2DZ level of theory. Energies are relative to the lowest outer-sphere addition transition state and denoted in kcal/mol. The lowest energy transition state for inner-sphere addition is marked in red.

2. Discussion on conformers of outer-sphere nucleophilic addition

As shown in **Figure S3**, possible conformers could originate from the following 5 factors. (1). The direction for allyl moiety relative to the PHOX ligand could form exo-/endo- conformers; (2). The direction of methyl ester moiety could generate two conformers; (3) cis-/trans/ conformers of the allyl moiety; (4) Conformers on allyl moiety resulted in two faces and two terminal carbons that are subjected to nucleophilic attack; (5). Conformers formed by two attacking faces of nucleophiles.

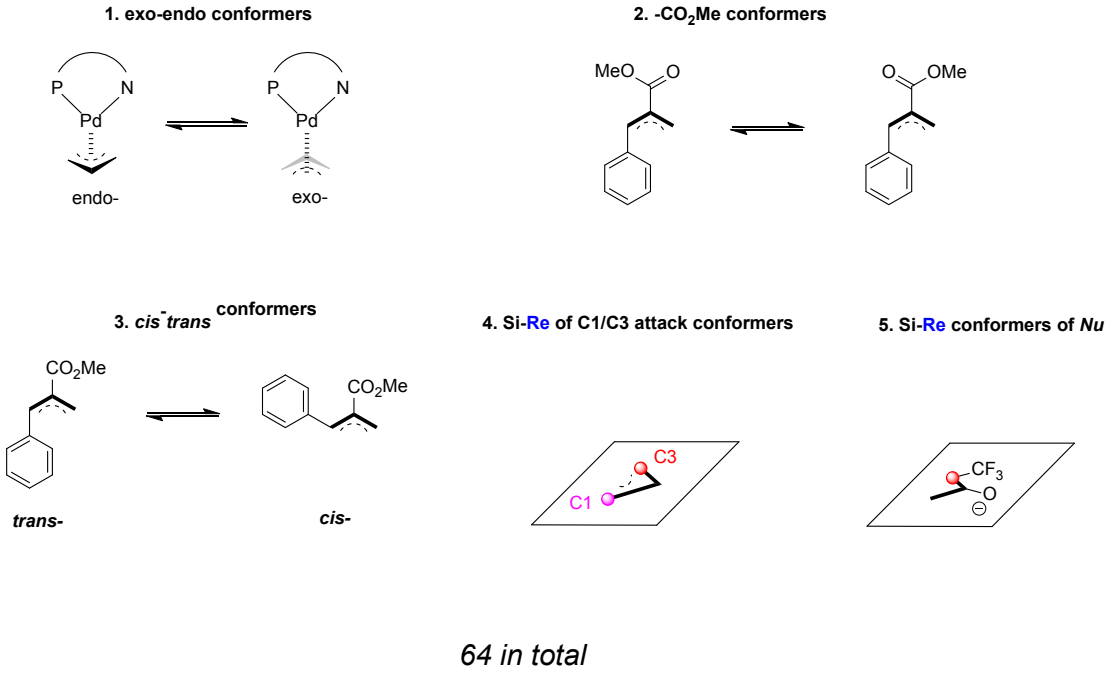


Figure S3 Types of Conformers for outer-sphere nucleophilic addition.

endo:

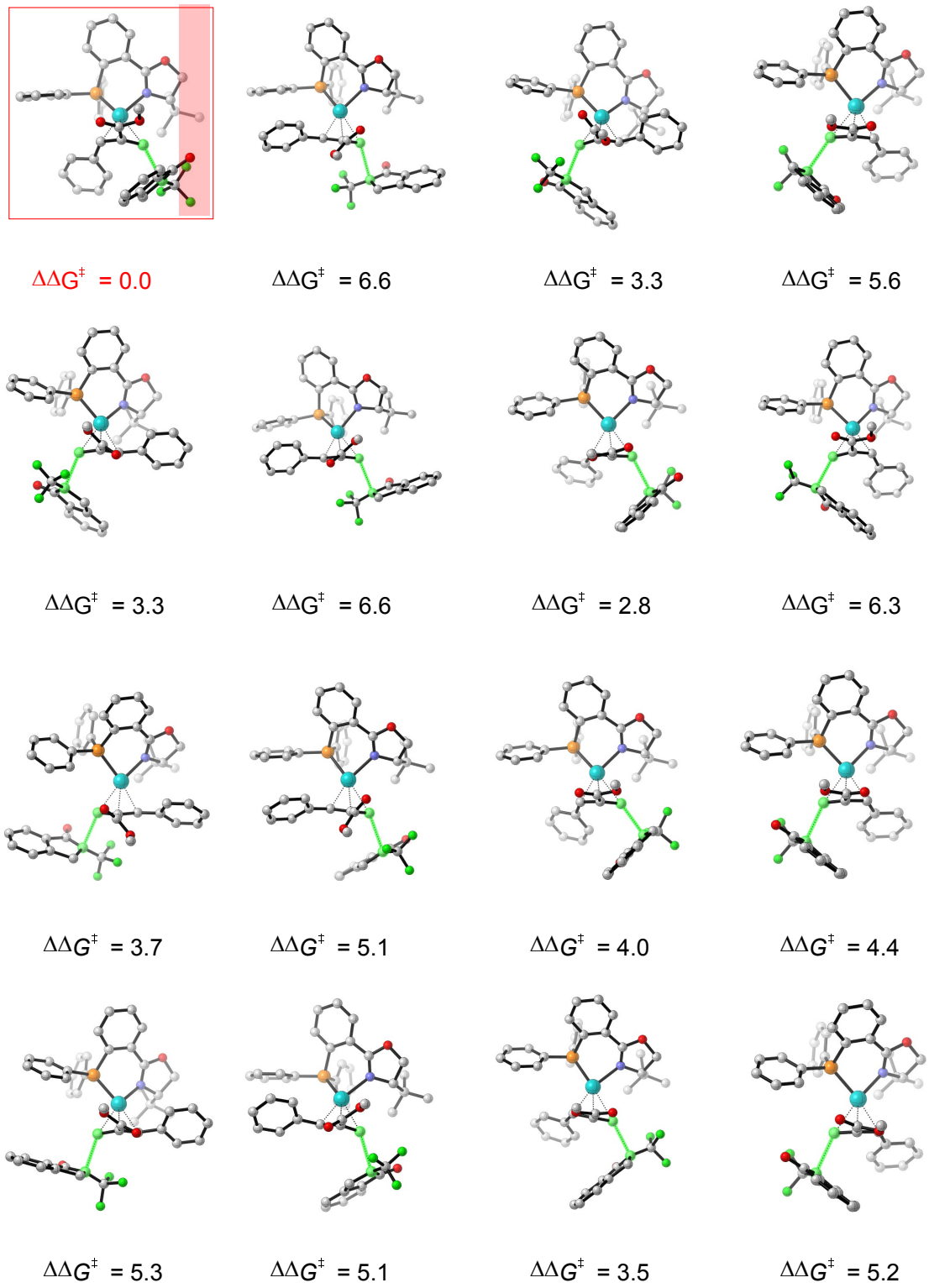


Figure S4 *Endo*- conformers and their relative free energies for C1-attack outer-sphere transition states at (SMD:THF)-M06L/6-311++G(2d,p)-SDD//(SMD: THF)-B3LYP/6-31G(d)-LANL2DZ level of theory. Energies are relative to the lowest outer-sphere addition transition state and denoted in kcal/mol. The lowest energy transition state for outer-sphere addition is marked in red.

exo:

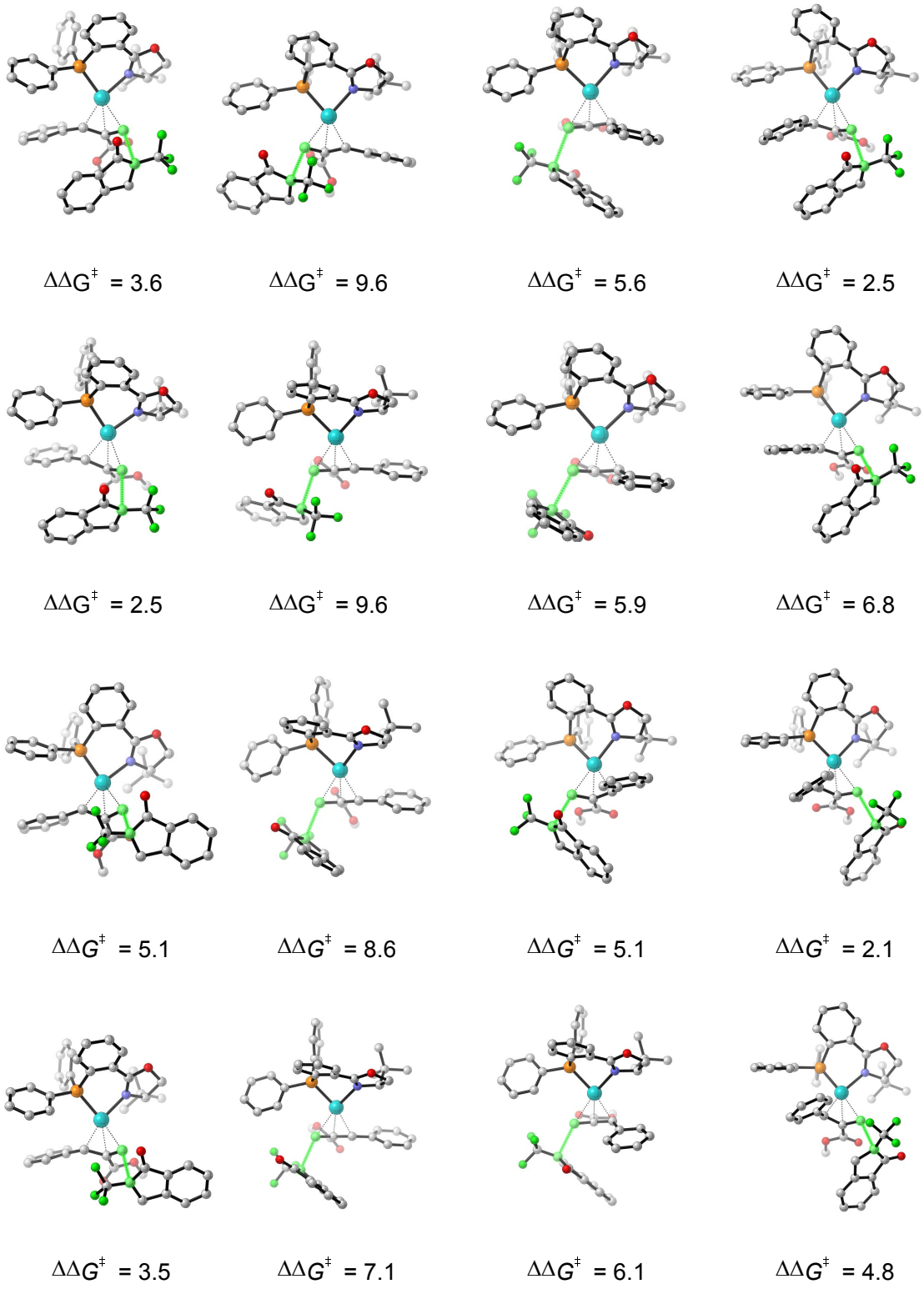


Figure S5 *Exo*- conformers and their relative free energies for C3-attack outer-sphere transition states at (SMD:THF)-M06L/6-311++G(2d,p)-SDD//(SMD: THF)-B3LYP/6-31G(d)-LANL2DZ level of theory. Energies are relative to the lowest outer-sphere addition transition state and denoted in kcal/mol.

endo:

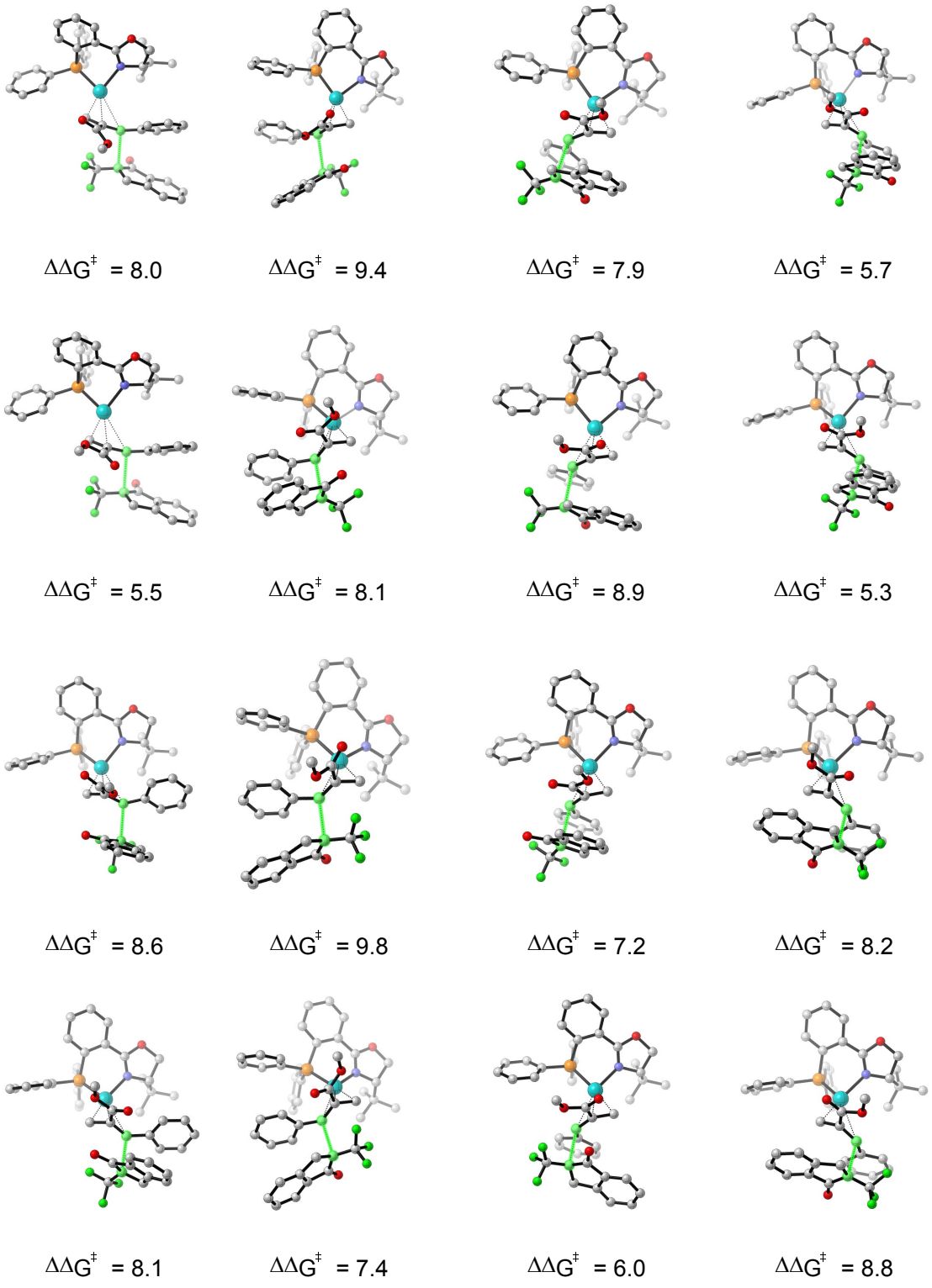
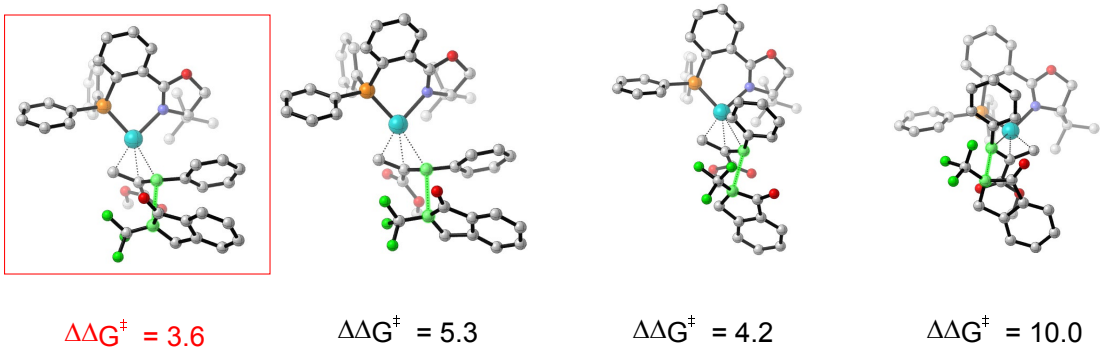
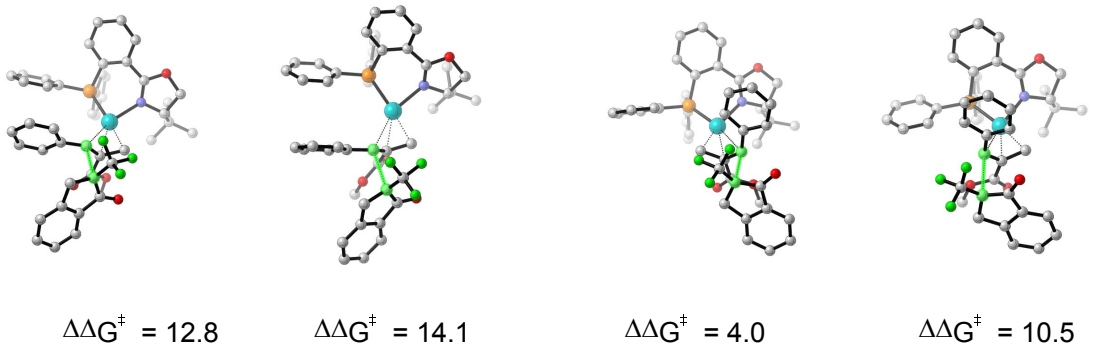


Figure S6 *Endo*- conformers and their relative free energies for C1-attack outer-sphere transition states at (SMD:THF)-M06L/6-311++G(2d,p)-SDD//(SMD: THF)-B3LYP/6-31G(d)-LANL2DZ level of theory. Energies are relative to the lowest outer-sphere addition transition state and denoted in kcal/mol.

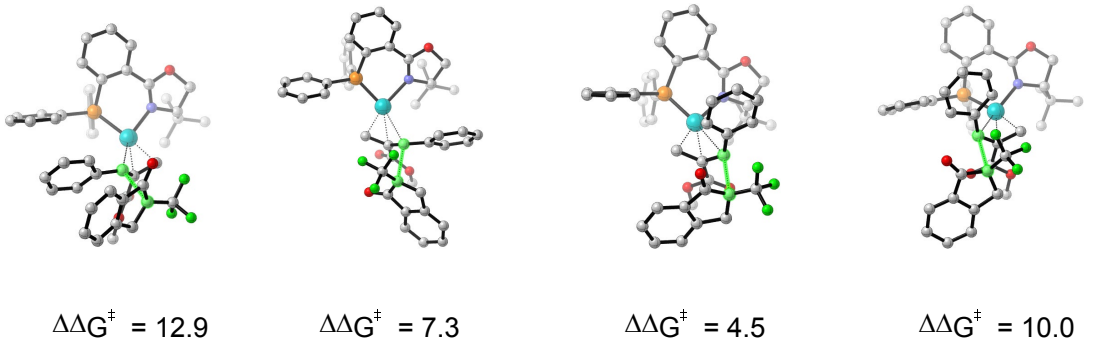
exo:



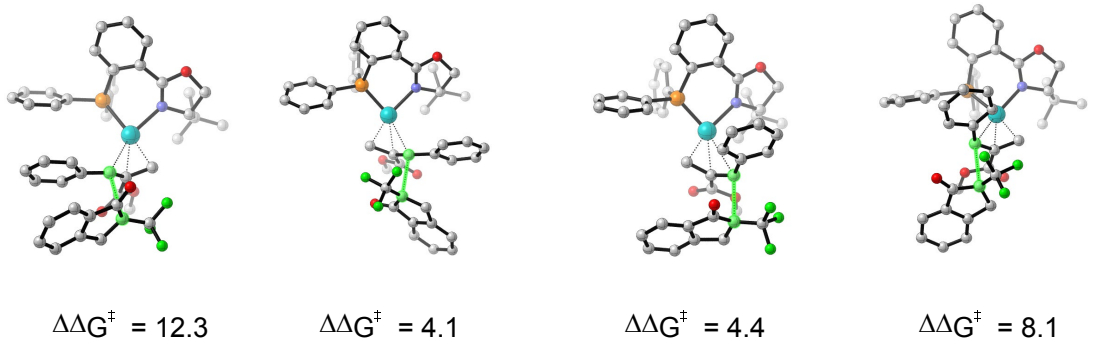
$\Delta\Delta G^{\ddagger}$ = 3.6 $\Delta\Delta G^{\ddagger}$ = 5.3 $\Delta\Delta G^{\ddagger}$ = 4.2 $\Delta\Delta G^{\ddagger}$ = 10.0



$\Delta\Delta G^{\ddagger}$ = 12.8 $\Delta\Delta G^{\ddagger}$ = 14.1 $\Delta\Delta G^{\ddagger}$ = 4.0 $\Delta\Delta G^{\ddagger}$ = 10.5



$\Delta\Delta G^{\ddagger}$ = 12.9 $\Delta\Delta G^{\ddagger}$ = 7.3 $\Delta\Delta G^{\ddagger}$ = 4.5 $\Delta\Delta G^{\ddagger}$ = 10.0



$\Delta\Delta G^{\ddagger}$ = 12.3 $\Delta\Delta G^{\ddagger}$ = 4.1 $\Delta\Delta G^{\ddagger}$ = 4.4 $\Delta\Delta G^{\ddagger}$ = 8.1

Figure S7 *Exo*- conformers and their relative free energies for C1-attack outer-sphere transition states at (SMD:THF)-M06L/6-311++G(2d,p)-SDD//(SMD: THF)-B3LYP/6-31G(d)-LANL2DZ level of theory. Energies are relative to the lowest outer-sphere addition transition state and denoted in kcal/mol. The lowest energy transition state for C1-attack outer-sphere addition is marked in red.

3. Atomic coordinates:

(Only the lowest energy transition state structures are listed)

C3-Attack (inner-sphere)

Pd	0.06854100	0.02283200	-0.10440800
C	-0.54342200	2.08133200	-0.03575600
C	-1.92469500	2.10864700	0.42992200
C	-3.07442500	2.13549900	-0.37766000
N	0.76722800	-2.23380400	-0.19176700
P	2.27322400	0.31620000	0.56069000
H	0.10617000	2.47586100	0.74059200
H	-3.98446900	2.52550800	0.06020100
H	-2.93616200	2.37262400	-1.42655000
C	0.08151900	-3.25160300	-1.02836300
C	0.25762600	-4.54791900	-0.20130400
O	1.19078500	-4.18228800	0.84957200
C	1.34947800	-2.83841500	0.78360700
C	2.17709800	-2.26302900	1.86809200
C	2.66081600	-0.92574600	1.88915300
H	0.69649900	-5.38346500	-0.74789000
H	-0.66830200	-4.88065200	0.27692000
H	-0.97076300	-2.96313700	-1.07923700
C	0.61203100	-3.32505600	-2.49409900
C	-0.18925200	-4.41607900	-3.23421200
H	-0.03484300	-5.41424200	-2.80678200
H	-1.26567200	-4.20326500	-3.21103900
H	0.11806500	-4.46142100	-4.28598700
C	2.11352800	-3.65776500	-2.54269600
H	2.33895300	-4.63387400	-2.09502300
H	2.45870100	-3.69286300	-3.58317100
H	2.70823300	-2.89933400	-2.02251900
C	0.35728500	-1.97989100	-3.19767100
H	0.67300100	-2.03581600	-4.24728100
H	-0.70595800	-1.71766400	-3.17452200
H	0.91224600	-1.16544500	-2.72277500
C	3.65658500	4.38385500	2.35417000
C	4.41418000	3.78983300	1.34274300
C	4.02658200	2.56164800	0.80087900
C	2.87058500	1.91306400	1.26436000
C	2.10647100	2.52309100	2.27701800
C	2.50369800	3.74612500	2.82054900
H	3.96027700	5.33933000	2.77376400
H	5.31162800	4.27888200	0.97297400
H	4.63104900	2.11437100	0.01895000
H	1.19291300	2.05435300	2.63228500

H	1.90398000	4.20416500	3.60269700
C	5.33276100	-0.53086300	-2.84461600
C	5.58300500	-1.02526500	-1.56249400
C	4.67374100	-0.78963000	-0.52795100
C	3.49743900	-0.06216900	-0.76847900
C	3.25157100	0.42726200	-2.06251400
C	4.16721700	0.19887300	-3.09136300
H	6.04138900	-0.71490200	-3.64778600
H	6.48779500	-1.59353300	-1.36299100
H	4.88695400	-1.17203400	0.46540400
H	2.34285100	0.98571200	-2.26669200
H	3.96369200	0.58479500	-4.08662400
C	3.45561400	-0.53051000	2.97539700
H	3.84633900	0.47919400	3.01063400
C	2.50034300	-3.12760000	2.92908500
H	2.12757300	-4.14413200	2.90729000
C	3.76505200	-1.40102300	4.02228200
H	4.38326600	-1.05222000	4.84481700
C	3.28166000	-2.70588100	4.00151900
H	3.50914500	-3.39562300	4.80899300
C	-2.08577700	2.11583500	1.89817100
O	-1.17864800	2.08533600	2.72463800
O	-3.38761500	2.19402600	2.28988300
C	-0.14988500	2.62908400	-1.37306500
C	-0.62262500	2.12135400	-2.59894300
C	0.76191100	3.70330900	-1.41885900
C	-0.21128500	2.67346700	-3.81406200
H	-1.29754000	1.27541200	-2.59800100
C	1.17306700	4.25524400	-2.63308500
H	1.14564700	4.11178000	-0.48739900
C	0.68680000	3.74394300	-3.83959900
H	-0.59377300	2.26066700	-4.74460700
H	1.87378100	5.08688700	-2.63543800
H	1.00584400	4.17169300	-4.78660200
C	-3.61592800	2.19552800	3.70325100
H	-3.15033900	3.06532000	4.17731200
H	-4.69955200	2.24053600	3.82681800
H	-3.22519200	1.28437800	4.16521900
C	-4.78819900	-0.72085800	1.30966800
C	-3.48317000	-1.16253900	1.04486100
C	-2.79713400	-1.98297300	1.94603500
C	-3.44400200	-2.36258200	3.12328500
C	-4.74872700	-1.92110200	3.39122700
C	-5.42770400	-1.09147400	2.48992500

H	-1.78365300	-2.31031900	1.73221300
H	-2.93560500	-3.00185600	3.84036900
H	-5.23865400	-2.22638000	4.31233100
H	-6.43728200	-0.75226500	2.70981300
C	-3.04359600	-0.63555000	-0.26487800
O	-1.91451000	-0.84577100	-0.78991400
C	-4.06376300	0.25749300	-0.73945000
C	-5.28336200	0.14811800	0.17685400
H	-6.13425900	-0.31964700	-0.33691400
H	-5.63378000	1.12294400	0.53666000
C	-4.37689500	0.37331400	-2.18898800
F	-3.29625600	0.39990300	-3.00250400
F	-5.14178900	-0.67333100	-2.63331700
F	-5.10584600	1.49011800	-2.46759800

Zero-point correction=	0.787634 (Hartree/Particle)
Thermal correction to Energy=	0.823654
Thermal correction to Enthalpy=	0.824424
Thermal correction to Gibbs Free Energy=	0.722561
Sum of electronic and zero-point Energies=	-2901.305243
Sum of electronic and thermal Energies=	-2901.269223
Sum of electronic and thermal Enthalpies=	-2901.268453
Sum of electronic and thermal Free Energies=	-2901.370316

C1-Attack (outer-sphere)

Pd	-0.49274300	-0.01127900	-0.21238200
C	1.57713400	0.78136200	-0.46995900
C	1.98391100	-0.44785100	0.07612000
C	0.70300700	1.73186100	0.18369200
N	-1.20023900	-2.04379300	-0.71261500
P	-2.75064500	0.61103700	-0.24280900
H	2.32509600	-1.24074700	-0.57193100
H	0.41444200	2.53920800	-0.48376400
H	1.77544500	-0.69870700	1.10266600
C	-0.47025700	-3.29159700	-0.35180400
C	-0.92088500	-4.25327700	-1.47115800
O	-2.10676200	-3.61701400	-2.02296800
C	-2.09776100	-2.33827300	-1.59253800
H	-1.21043200	-5.25052100	-1.14227000
C	-5.15568200	-0.83341700	3.46367200
C	-3.92966500	-0.17842300	3.60984000
C	-3.22044200	0.24046100	2.48378100

C	-3.73887500	0.02257700	1.19464000
C	-4.97303200	-0.63142300	1.05636800
C	-5.67391800	-1.05974600	2.18712200
H	-5.70280300	-1.16740700	4.34111500
H	-3.51927400	-0.00060400	4.60011000
H	-2.26442100	0.74126200	2.60884600
H	-5.39380100	-0.80778700	0.07150100
H	-6.62636200	-1.56886800	2.06634400
C	-3.70924300	5.12913100	-0.76057300
C	-4.42686800	4.38513700	0.17741500
C	-4.16892400	3.02106300	0.34245000
C	-3.18045200	2.39097400	-0.42783000
C	-2.45630200	3.14912200	-1.36561900
C	-2.72552200	4.50679300	-1.53597700
H	-3.91209500	6.18924800	-0.88625800
H	-5.19218100	4.86281200	0.78332100
H	-4.73968000	2.45492400	1.07139200
H	-1.68003400	2.67756800	-1.96249900
H	-2.16134800	5.07956700	-2.26695500
C	-4.76353500	-1.28633400	-4.01730700
C	-5.16087600	-0.04322600	-3.53435400
C	-4.54511200	0.48631200	-2.39820600
C	-3.52685500	-0.19841700	-1.72041900
C	-3.13032200	-1.47289100	-2.21047700
C	-3.76199600	-1.99175900	-3.35480600
H	-5.22653300	-1.71154000	-4.90278200
H	-5.94448100	0.51988700	-4.03318200
H	-4.86677800	1.45574500	-2.03469700
H	-3.45668700	-2.96144400	-3.72792800
H	-0.18512000	-4.33441000	-2.27716600
C	-0.76026200	-3.78417600	1.10317700
C	0.06534000	-5.06522500	1.34318100
H	-0.24264300	-5.89285400	0.69369500
H	1.13502200	-4.88470500	1.17858700
H	-0.05878200	-5.40158700	2.37937700
C	-2.25686900	-4.07792400	1.31283300
H	-2.63150700	-4.84539900	0.62496000
H	-2.42658600	-4.44581600	2.33165800
H	-2.86743300	-3.17751600	1.18340800
C	-0.29919900	-2.72367800	2.12028900
H	-0.52015800	-3.06241000	3.14011300
H	0.78194100	-2.55717500	2.05729600
H	-0.80829700	-1.76486100	1.97114300
H	0.60158900	-3.09160300	-0.42922800

C	0.62434300	2.14503400	1.60651800
C	1.27594000	1.51805600	2.68715100
C	-0.16297700	3.28286700	1.89166000
C	1.12880400	1.99896600	3.98955100
H	1.92359500	0.66748600	2.52750000
C	-0.31230400	3.75826000	3.19238800
H	-0.65881500	3.79799800	1.07322400
C	0.33069700	3.11422300	4.25366700
H	1.65075700	1.49790700	4.80085100
H	-0.92459800	4.63744200	3.37609900
H	0.22105600	3.48361700	5.26975500
C	1.83785900	1.07084900	-1.92355600
O	1.57345800	2.12847200	-2.47147000
O	2.40709200	0.03527300	-2.56317000
C	2.75230300	0.25429000	-3.94174300
H	3.42456300	1.11022700	-4.03892400
H	3.25271600	-0.65918700	-4.26410600
H	1.85388900	0.42622900	-4.54179900
C	5.56619300	0.22240400	-1.04060200
C	5.51698600	1.26525000	-0.10643300
C	6.04931400	2.51495300	-0.42215900
C	6.64676200	2.69732600	-1.67555100
C	6.70808400	1.64568100	-2.60250500
C	6.16445800	0.39723100	-2.28960300
H	6.01240200	3.33529500	0.29176000
H	7.07228400	3.66446300	-1.93248500
H	7.18205200	1.80766500	-3.56779700
H	6.20403700	-0.42946700	-2.99471700
C	4.40679800	-0.61477500	0.81229600
C	4.15105300	-1.59417300	1.86815500
F	3.47385800	-1.05265500	2.93788600
F	3.41440700	-2.67017600	1.46544200
F	5.28115200	-2.14369100	2.43918700
C	4.85286000	0.79124400	1.16994800
H	5.56881500	0.81087600	2.00795500
H	4.02790800	1.45726900	1.46190400
C	4.93335300	-1.01048000	-0.46884700
O	4.89041300	-2.11544800	-1.04264500

Zero-point correction= 0.786289 (Hartree/Particle)
Thermal correction to Energy= 0.822883
Thermal correction to Enthalpy= 0.823653
Thermal correction to Gibbs Free Energy= 0.718355
Sum of electronic and zero-point Energies= -2901.305321

Sum of electronic and thermal Energies= -2901.268727
Sum of electronic and thermal Enthalpies= -2901.267957
Sum of electronic and thermal Free Energies= -2901.373255

C3-Attack (outer-sphere)

Pd	-0.80339100	0.10515700	0.25131400
C	1.14642700	0.73229500	1.25923400
C	0.21053400	1.78381500	0.90863500
C	1.95627400	0.22974400	0.20072200
N	-1.40182700	-1.92078600	-0.44366200
P	-2.90597100	0.81764500	-0.41793700
H	-0.27346700	2.33279500	1.71032700
H	0.45064200	2.39366100	0.04114500
H	1.83418900	0.80494800	-0.71190600
C	-0.81956100	-3.18293200	0.08544800
C	-1.04695700	-4.15928200	-1.08790000
O	-2.02367100	-3.48257000	-1.92489000
C	-2.06659300	-2.19635100	-1.51457600
H	-1.46864800	-5.12542900	-0.81293800
C	-6.24164600	-0.33010200	2.60780000
C	-5.05820600	0.27952600	3.03458500
C	-4.06535300	0.60421100	2.11011900
C	-4.25204900	0.33819300	0.74176200
C	-5.44399800	-0.27099000	0.32084100
C	-6.43049700	-0.60649100	1.25245600
H	-7.01117000	-0.59085800	3.32929600
H	-4.90337600	0.49512300	4.08832200
H	-3.14205700	1.06504400	2.45111100
H	-5.60962100	-0.48475100	-0.73032900
H	-7.34756100	-1.08150900	0.91437200
C	-3.44602300	5.35560200	-1.26140900
C	-4.45166300	4.66673100	-0.58074400
C	-4.31894600	3.29956200	-0.32283800
C	-3.16996500	2.61040400	-0.74059300
C	-2.15848400	3.31317000	-1.41841400
C	-2.29998300	4.67506100	-1.68337400
H	-3.55131700	6.41886000	-1.45937100
H	-5.34417600	5.19066200	-0.24923900
H	-5.11240500	2.77619200	0.20109100
H	-1.25891000	2.79394100	-1.73799000
H	-1.51106400	5.20534800	-2.20966800
C	-4.00156600	-1.10143000	-4.54077700

C	-4.45358300	0.16727200	-4.19100100
C	-4.11771600	0.70084800	-2.94527000
C	-3.33165400	-0.00517400	-2.02367600
C	-2.87882800	-1.30557100	-2.37985100
C	-3.22753100	-1.82719300	-3.63877600
H	-4.24612500	-1.53040800	-5.50795100
H	-5.06253500	0.74758100	-4.87833600
H	-4.47655500	1.69125100	-2.68951700
H	-2.87913300	-2.81549500	-3.91124600
H	-0.14504600	-4.31223200	-1.68813500
C	-1.43255800	-3.62906100	1.45096900
C	-0.72160200	-4.92806200	1.88384700
H	-0.91230100	-5.76062200	1.19633100
H	0.36455400	-4.78438600	1.94504600
H	-1.07356200	-5.23820800	2.87498300
C	-2.94869100	-3.87167300	1.34236200
H	-3.19354000	-4.65732900	0.61727600
H	-3.34855100	-4.19001300	2.31247900
H	-3.48160500	-2.95988000	1.05031300
C	-1.16190300	-2.55235100	2.51794600
H	-1.54281800	-2.88331700	3.49225700
H	-0.08735300	-2.36430100	2.62742600
H	-1.65182700	-1.60476200	2.27101800
H	0.24987200	-3.02104300	0.24384700
C	2.59461800	-1.06773200	-0.05439800
C	2.78983800	-1.39579800	-1.41813400
C	2.98002000	-2.02437700	0.91016800
C	3.31588200	-2.62566700	-1.80199900
H	2.51971500	-0.66894400	-2.17904200
C	3.51674200	-3.25187800	0.51965300
H	2.86886900	-1.79213800	1.95972400
C	3.68182600	-3.56396400	-0.83214700
H	3.44866700	-2.84797000	-2.85731300
H	3.81253300	-3.96826900	1.28201800
H	4.09822500	-4.52345700	-1.12739900
C	1.26577400	0.33036500	2.69042900
O	2.17654100	-0.31380000	3.18644900
O	0.24935400	0.81194900	3.44130400
C	0.32623900	0.53149300	4.84897500
H	-0.55350000	1.00436400	5.28771500
H	0.30692100	-0.54622600	5.03314300
H	1.23696700	0.95664400	5.27978700
C	5.46063500	0.67144800	-1.43952700
C	5.99931300	0.22016300	-0.22772900

C	7.05148200	-0.69419600	-0.22800200
C	7.56304500	-1.13447000	-1.45530100
C	7.02815500	-0.67026900	-2.66673900
C	5.96645200	0.23693500	-2.66596200
H	7.47562600	-1.05996600	0.70484100
H	8.38884700	-1.84193200	-1.46992300
H	7.44368800	-1.02338000	-3.60761300
H	5.53601600	0.60688400	-3.59340500
C	4.20244800	1.69230200	0.25023500
C	3.68381100	2.86988700	0.94793000
F	3.24831600	2.59386100	2.22014500
F	4.63665600	3.85822900	1.14076400
F	2.66261200	3.49643000	0.31338600
C	4.34773300	1.64015000	-1.18136900
O	3.70042900	2.21661400	-2.07892300
C	5.27812000	0.86892300	0.93437500
H	4.87328700	0.11579100	1.62617400
H	5.96959500	1.48860300	1.52744300

Zero-point correction=	0.786308 (Hartree/Particle)
Thermal correction to Energy=	0.822680
Thermal correction to Enthalpy=	0.823450
Thermal correction to Gibbs Free Energy=	0.719346
Sum of electronic and zero-point Energies=	-2901.300030
Sum of electronic and thermal Energies=	-2901.263657
Sum of electronic and thermal Enthalpies=	-2901.262887
Sum of electronic and thermal Free Energies=	-2901.366991

C1-Attack precursor

Pd	-0.31166500	-0.84253300	0.48144100
C	-1.92616300	-1.81540000	1.60149800
C	-1.05155100	-2.84133500	1.21005600
C	-2.52127500	-0.93800400	0.63672300
N	1.82017000	-1.17588700	0.41467800
P	0.17374900	1.38436800	-0.15098700
H	-0.46837500	-3.35998200	1.96217900
H	-2.91283600	-0.01758700	1.05981200
H	-1.14271600	-3.33276000	0.24871300
C	2.44863400	-2.48332200	0.07119200
C	3.83171500	-2.35170000	0.74556500
O	3.95292600	-0.92931500	1.03244000
C	2.73023900	-0.39105600	0.89281700

H	4.68076500	-2.62772400	0.12227600
C	1.60805300	1.83249100	-4.54418600
C	0.45904300	1.09890200	-4.23615700
C	0.04823500	0.96532200	-2.90959900
C	0.77947500	1.57612500	-1.87574100
C	1.92885000	2.31688500	-2.19260000
C	2.34024900	2.43997100	-3.52216200
H	1.93105600	1.92936000	-5.57702900
H	-0.11523400	0.62463700	-5.02716000
H	-0.84544500	0.39112800	-2.68174300
H	2.50432400	2.80015800	-1.40953300
H	3.23323200	3.01304800	-3.75613700
C	-3.08954500	4.62526700	0.47998900
C	-2.32103000	4.64553300	-0.68519000
C	-1.32986700	3.68246200	-0.89195400
C	-1.10461100	2.68564600	0.06972900
C	-1.88672000	2.66674100	1.23840800
C	-2.86869100	3.63586000	1.44296400
H	-3.85998800	5.37510800	0.63684900
H	-2.48826400	5.41169800	-1.43716900
H	-0.73611400	3.71255700	-1.79955900
H	-1.73141100	1.89634300	1.98860300
H	-3.46483600	3.61327100	2.35089400
C	3.66620500	2.81252800	2.60734000
C	2.65514300	3.68514700	2.21696700
C	1.62884500	3.23162800	1.38421900
C	1.58328600	1.90825000	0.92795800
C	2.62162200	1.02157700	1.32161400
C	3.64941400	1.49489200	2.15496900
H	4.46795500	3.14894800	3.25760300
H	2.65535700	4.71749100	2.55419200
H	0.85169800	3.92696900	1.08840900
H	4.43972400	0.81692400	2.45331000
H	3.88988000	-2.88449100	1.69912600
C	2.48060300	-2.78951300	-1.45993500
C	3.13335000	-4.17427300	-1.64968500
H	4.17915500	-4.19549600	-1.32288000
H	2.59042900	-4.95102700	-1.09612700
H	3.11871700	-4.45002200	-2.71041600
C	3.27754000	-1.72700300	-2.23769400
H	4.32546600	-1.67725800	-1.91863200
H	3.27697900	-1.96969900	-3.30665200
H	2.83905900	-0.72933000	-2.12773600
C	1.04438600	-2.85849300	-2.01039400

H	1.06363500	-3.11190400	-3.07720100
H	0.45656400	-3.62968600	-1.49747600
H	0.52001000	-1.90183200	-1.90756200
H	1.86438600	-3.27178400	0.55358600
C	-3.12649100	-1.30234500	-0.66371300
C	-3.40359400	-2.62514100	-1.05852300
C	-3.52921800	-0.25496100	-1.51865700
C	-4.03024200	-2.88781100	-2.27703200
H	-3.16955700	-3.45343300	-0.39872700
C	-4.14915400	-0.52016400	-2.73729600
H	-3.35510300	0.77359300	-1.21385800
C	-4.39705800	-1.84060700	-3.12564800
H	-4.24442100	-3.91590900	-2.55624500
H	-4.44916000	0.30370900	-3.37914100
H	-4.88744600	-2.04971900	-4.07234600
C	-1.97514700	-1.35121200	3.04230500
O	-2.58717600	-0.36738300	3.41326200
O	-1.29927800	-2.16520700	3.86102200
C	-1.31169300	-1.80721300	5.26046000
H	-2.33758100	-1.77272300	5.63471900
H	-0.74836500	-2.59250500	5.76446800
H	-0.83118700	-0.83662100	5.40890600

Zero-point correction=	0.649264 (Hartree/Particle)
Thermal correction to Energy=	0.677050
Thermal correction to Enthalpy=	0.677820
Thermal correction to Gibbs Free Energy=	0.594496
Sum of electronic and zero-point Energies=	-2141.901775
Sum of electronic and thermal Energies=	-2141.873989
Sum of electronic and thermal Enthalpies=	-2141.873219
Sum of electronic and thermal Free Energies=	-2141.956544

C1-Attack precursor

Pd	-0.31269600	-0.53179300	-0.52320800
C	-1.68139300	-2.35662100	-0.76846800
C	-0.29159200	-2.54718800	-1.09545800
C	-2.38942600	-1.39858300	-1.50208800
N	-0.60799700	1.60403200	-0.23625300
P	1.94463400	-0.15351400	-0.13078200
H	0.28659500	-3.24761500	-0.50073500
H	-0.00499500	-2.50141200	-2.14598900
H	-1.94173600	-1.14478000	-2.46377500

C	-1.86001200	2.23343600	0.27249100
C	-1.81358900	3.60958500	-0.41765300
O	-0.41431600	3.76054000	-0.79266000
C	0.13418800	2.53315400	-0.74588100
H	-2.07429300	4.45878300	0.21203900
C	2.95736900	0.51375100	4.34409300
C	2.13356500	-0.54232500	3.94455400
C	1.82561500	-0.71706600	2.59527200
C	2.35343100	0.15809800	1.62996400
C	3.18389700	1.21390900	2.03604400
C	3.47890400	1.39024700	3.39025500
H	3.19038100	0.65366800	5.39607200
H	1.72476100	-1.22628200	4.68309100
H	1.17769600	-1.53420500	2.29037700
H	3.60369200	1.89691500	1.30439000
H	4.11938900	2.21266000	3.69661600
C	4.90124600	-3.39580800	-1.64906800
C	5.03540800	-2.90003900	-0.35155600
C	4.16177300	-1.91667700	0.12117600
C	3.13894200	-1.42731400	-0.70457700
C	3.00560200	-1.93567700	-2.00913400
C	3.88652800	-2.90858800	-2.47906500
H	5.58260500	-4.15943400	-2.01382600
H	5.82243500	-3.27360200	0.29773400
H	4.28245300	-1.53537500	1.12962100
H	2.21792600	-1.56625900	-2.66045400
H	3.77764600	-3.29030400	-3.49044300
C	3.23629100	3.61898100	-2.55950200
C	4.12471000	2.57488100	-2.32143400
C	3.70948400	1.46837000	-1.57659900
C	2.41229800	1.37796700	-1.05460300
C	1.51274700	2.45428900	-1.28211200
C	1.94613400	3.55776800	-2.03727400
H	3.53927400	4.48168000	-3.14503900
H	5.13722500	2.60945900	-2.71266700
H	4.41203600	0.66053200	-1.40514800
H	1.25889100	4.37539700	-2.21573300
H	-2.40403700	3.64112100	-1.33850100
C	-1.94606300	2.27388600	1.83214100
C	-3.31550200	2.87810000	2.20577100
H	-3.42493700	3.91287900	1.86063000
H	-4.13887100	2.29219200	1.77866300
H	-3.43964900	2.88353300	3.29496600
C	-0.81636600	3.11590800	2.45325200

H	-0.84793500	4.16312100	2.13093100
H	-0.90862700	3.11216400	3.54575800
H	0.17225500	2.71126400	2.20872500
C	-1.87509800	0.84273200	2.39294800
H	-2.02423600	0.85637500	3.47948600
H	-2.65551200	0.20631800	1.95905400
H	-0.90361300	0.37716000	2.19734000
H	-2.70848900	1.64984100	-0.09278900
C	-3.73185100	-0.83575500	-1.31955000
C	-4.30678200	-0.18782200	-2.43336800
C	-4.47337300	-0.87486500	-0.12009000
C	-5.57916000	0.37616100	-2.36383100
H	-3.74684000	-0.13942900	-3.36431800
C	-5.74328500	-0.30674600	-0.05196600
H	-4.06295600	-1.34262800	0.76659300
C	-6.30431900	0.31705100	-1.17169200
H	-6.00281000	0.86069300	-3.23910500
H	-6.29825500	-0.35050000	0.88111500
H	-7.29622600	0.75620600	-1.11186000
C	-2.25971500	-3.14971900	0.37472000
O	-3.31253000	-3.74856200	0.29348700
O	-1.44411300	-3.19510800	1.43755000
C	-1.86902300	-4.05428500	2.52073800
H	-1.08845800	-3.97387000	3.27705500
H	-2.82709300	-3.71706100	2.92317700
H	-1.95705000	-5.08636400	2.17232700

Zero-point correction=	0.649046 (Hartree/Particle)
Thermal correction to Energy=	0.676858
Thermal correction to Enthalpy=	0.677628
Thermal correction to Gibbs Free Energy=	0.594053
Sum of electronic and zero-point Energies=	-2141.900516
Sum of electronic and thermal Energies=	-2141.872704
Sum of electronic and thermal Enthalpies=	-2141.871934
Sum of electronic and thermal Free Energies=	-2141.955509

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