Supporting Information

A General Radical Fluorination Platform for Organofluorine Synthesis

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General Methods

Unless specified, all reagents and starting materials were purchased from commercial sources and used as received without purification. Dry acetonitrile was used for all reactions. Flash chromatography was performed using silica gel (230−400 mesh) with hexanes, ethyl acetate, and diethyl ether as eluents. All reactions were monitored by Thin-layer chromatography (TLC) and gas chromatography (GCMS-QP2020). ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer and were described as chemical shifts in ppm, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; doublet−doublet (dd), pentet (p), multiplet (m), coupling constant in hertz (Hz), and number of protons.

General Fluorination Procedure for Alkenes (A):

In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with alkene substrate (0.50 mmol, 1.0 equiv) and anhydrous acetonitrile (3.0 mL, 0.17M). To this solution, AgF_2 (160.0 mg, 1.1 mmol, 2.2 equiv) was added at once, and the resulting mixture stirred at room temperature for 3-7 h until the complete consumption of the alkene was observed by TLC and GCMS analysis. After completion of the reaction the mixture was filtered through a celite plug and concentrated in vacuo. The resulting crude product was purified by flash chromatography on silica gel to afford the pure products.

General Fluorination Procedure for Alkynes (B):

In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with alkyne substrate (0.50 mmol, 1.0 equiv) and anhydrous acetonitrile (3.0 mL, 0.17M). To this solution, AgF_2 (364.0 mg, 2.5 mmol, 5.0 equiv) was added at once, and the resulting mixture stirred at room temperature for 3-7 h until the complete consumption of the alkyne was observed by TLC and GCMS analysis. After completion of the reaction the mixture was filtered through a celite plug and concentrated in vacuo. The resulting crude product was purified by flash chromatography on silica gel to afford the pure products.

General Fluorination Procedure for Heterocyclic Substrates (C):

In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with heterocyclic substrate (0.50 mmol, 1.0 equiv) and anhydrous acetonitrile (3.0 mL, 0.17M). To this solution, AgF_2 (217.5 mg, 1.5 mmol, 3.0 equiv) was added at once, and the resulting mixture stirred at room temperature for 3-7 h until the complete consumption of the indole was observed by TLC and GCMS analysis. After completion of the reaction the mixture was filtered through a celite plug and concentrated in vacuo. The resulting crude product was purified by flash chromatography on silica gel to afford the pure products.

General Fluorination Procedure for Hydrocarbons (D):

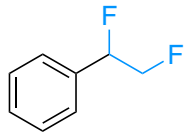
In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with alkane substrate (0.50 mmol, 1.0 equiv) and anhydrous acetonitrile (3.0 mL, 0.17M). To this solution, AgF_2 (3.0 – 6.0 equiv depending on substrate) was added at once, and the resulting mixture stirred at room temperature to 70° C (depending on substrate) for 3-7 h until the complete consumption of the alkyne was observed by TLC and GCMS analysis. After completion of the reaction the mixture was filtered through a celite plug and concentrated in vacuo. The resulting crude product was purified by flash chromatography on silica gel to afford the pure products.

General Fluorination Procedure for Carboxylic Acids (E):

In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with carboxylic acid substrate (0.50 mmol, 1.0 equiv) and anhydrous acetonitrile (3.0 mL, 0.17M). To this solution, AgF_2 (217.5 mg, 1.5 mmol, 3.0 equiv) was added at once, and the resulting mixture stirred at room temperature for 3-12 h until the complete consumption of the acid was observed by TLC and GCMS analysis. After completion of the reaction the mixture was filtered through a celite plug and concentrated in vacuo. The resulting crude product was purified by flash chromatography on silica gel to afford the pure products.

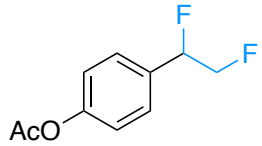
Characterization Data of products:

1,2-difluoroethyl benzene (2a): Following the **general procedure A**, the product **2a** was



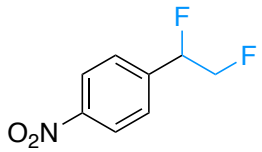
obtained in 77% yield (109 mg) as a clear viscous oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 5H), 5.72 (dddd, *J* = 48.7, 23.3, 7.4, 2.6 Hz, 1H), 4.78 – 4.47 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 129.2 (d, *J* = 1.6 Hz), 128.7, 128.4 (dd, *J* = 9.1,3.0 Hz), 125.9 (d, *J* = 6.4 Hz), 92.2 (dd, *J* = 176.6, 20.0 Hz), 84.8 (dd, *J* =178.8, 25.0 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -186.2 (d, *J* = 16.5 Hz), -222.8 (d, *J* = 14.6 Hz).

Methyl 4-(1,2-difluoroethyl)benzoate (2b): Following the **general procedure A**, the product



2b was obtained in 67% yield (135 mg) as a color less oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$). δ 7.37 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 5.68 (dddd, *J* = 48.3, 16.0, 7.2, 2.98 Hz, 1H), 4.73 – 4.44 (m, 2H), 2.3 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 151.2 (d, *J* = 2.2 Hz), 132.2 (dd, *J* = 20.2, 8.0), 127.2 (d, *J* = 6.9 Hz), 122.0, 91.7 (dd, *J* = 179.1, 20.5 Hz), 84.57 (dd, *J* = 179.1, 24.9 Hz), 21.1. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -185.48 (d, *J* =15.7 Hz), -223.3 (d, *J* =15.6 Hz).

1-Nitro-4-(1,2-difluoroethyl) benzene (2c): Following the **general procedure A**, the product



2c was obtained in 72% yield (68 mg) as a yellow viscous oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 5.81 (dddd, *J* = 47.5, 18.2, 5.4, 3.2 Hz, 1H), 4.77 – 4.58 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.3, 141.7 (dd, *J* = 20.5, 6.7 Hz), 126.7 (d, *J* = 7.9 Hz), 123.9, 91.0 (dd, *J* = 179.6, 20.5 Hz), 84.0 (dd, *J* = 180.1, 24.5 Hz), **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -189.9 (d, *J* = 14.8 Hz), -226.39 (d, *J* =14.1 Hz).

1-(1,1-Dimethylethyl)-4-(1,2-difluoroethyl) benzene (2d): Following the **general procedure A**, the product **2d** was obtained in 83% yield (76 mg) as a pale-yellow viscous oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.2 (d, *J* = 8.34 Hz, 2H), 5.58 (dddd, *J* = 48.7, 15.6, 7.5, 2.6 Hz, 1H), 4.66 – 4.34 (m, 2H), 1.23 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.4 (d, *J* = 2.1 Hz), 131.6 (dd, *J* = 20.2, 8.2 Hz), 125.8 (d, *J* = 6.7 Hz), 125.7, 92.2 (dd, *J* = 175.8, 19.8 Hz), 84.8 (dd, *J* =178.8, 25.1 Hz), 34.7, 31.2. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -184.96 (d, *J* = 14.1 Hz), -225.17 (d, *J* = 15.4 Hz).

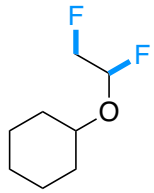
1-Methoxy-4-(1,2-difluoroethyl) benzene (2e): Following the **general procedure A**, the product **2e** was obtained in 51% yield, as a colorless viscous oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), δ 5.66 (dddd, *J* = 48.7, 16.8, 7.3, 2.45 Hz, 1H), δ 4.78 – 4.4 (m, 2H), 3.85 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.3 (d, *J* = 2.1 Hz), 127.8 (d, *J* = 6.2 Hz), 126.6 (dd, *J* = 20.5, 8.5 Hz), 114.1, 92.0 (dd, *J* = 175.4, 20.0 Hz), 84.6 (dd, *J* =179.0, 27.1 Hz), 55.3. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -63.20 (trifluorotoluene). -181.7 (d, *J* = 16.0 Hz), -222.5 (d, *J* = 16.0 Hz).

1-Methyl-4-(1,2-difluoroethyl) benzene (2f): Following the **general procedure A**, the product **2f** was obtained in 55% yield, as a colorless viscous oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$: δ 7.3 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 5.7 (dddd, *J* = 48.8, 17.3, 7.7, 2.7 Hz, 1H), 4.79 – 4.47 (m, 2H), 2.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.2 (d, *J* = 1.5 Hz), 131.6 (dd, *J* = 20.2, 8.2 Hz), 129.4, 126.0 (d, *J* = 6.2 Hz), 92.2 (dd, *J* = 175.8, 20.0 Hz), 84.8 (dd, *J* =179.8, 27.1 Hz), 21.2. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -184.6 (d, *J* = 16.1 Hz), -222.6 (d, *J* = 16.2 Hz).

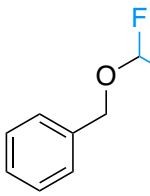
2-(1,2-Difluoroethyl)naphthalene (2g): Following the **general procedure A**, the product **2g** was obtained in 58% yield (112 mg) as a white solid after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$). δ 7.9 – 7.86 (m, 4H), 7.54 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.45 (dd, *J* = 8.4, 1.5 Hz, 1H), 5.88 (dddd, *J* = 48.4, 16.0, 7.4, 2.7 Hz, 1H), 4.86 – 4.55 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.6 (d, *J* = 1.5 Hz), 133.0, 132.0 (dd, *J* = 19.6, 7.7 Hz), 128.7, 128.2, 127.8, 126.8, 126.7, 125.6 (d, *J* = 8.0 Hz), 123.1 (d, *J* = 5.9 Hz), 92.5 (dd, *J* = 176.8, 20.1 Hz), 84.8 (dd, *J* = 179.3, 25.1 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -185.9 (d, *J* =16.1 Hz), -222.86 (d, *J* = 15.8 Hz).

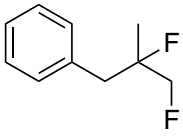
(1,2-difluoroethoxy) cyclohexanes (2h): Following the **general procedure A**, the product **2h** was obtained in 93% yield. The yield of (1,2-difluoroethoxy) cyclohexanes (**2h**) was determined by ^{1}H NMR integration relative to internal standard trifluorotoluene (0.5 eq. w.r. t. starting material). ^{1}H NMR: δ 7.56 (t, *J* = 7.7 Hz, 2H; $PhCF_3$, internal std.) with respect to **2h:** δ 5.62 (tdd, *J* = 65.1, 7.6, 4.4 Hz, 1H). **^{1}H NMR** (400 MHz, CD_3CN): δ 5.62 (tdd, *J* = 65.1, 7.6, 4.4 Hz, 1H), 4.36 (ddd, *J* = 46.4, 3.8, 1.5 Hz, 1H), 4.32 (dd, *J* = 46.5 Hz, *J* = 4.4 Hz, 1H), 3.77 – 3.71 (m, 1H), 1.73 – 1.69 (m, 3H), 1.54 – 1.48 (m, 1H), 1.44 – 1.16 (m, 6H). **^{19}F {^{1}H} NMR** (376 MHz, CD_3CN) δ -63.20 (trifluorotoluene), -131.3 (d, *J* = 19.2 Hz), -235.36 (d, *J* = 19.1 Hz).



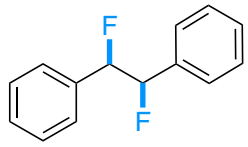
1,2-difluoroethyl benzyl ether (2i): Following the **general procedure A**, the product **2i** was obtained in 82% yield (142 mg) as a colorless liquid after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$). δ 7.32 – 7.23 (m, 5H), 5.54 – 5.34 (m, 1H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.62 (dd, *J* = 11.8, 1.6 Hz, 1H), 4.43 – 4.26 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.9, 128.6, 128.4, 128.1, 107.5 (dd, *J* = 218.4, 26.6 Hz), 81.6 (dd, *J* = 172.8, 31.5 Hz), 71.4. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -137.4 (d, *J* = 19.8 Hz), δ -234.7 (d, *J* = 19.8 Hz).



(2,3-Difluoro-2-methylpropyl)benzene (2j): Following the **general procedure A**, the product **2j** was obtained in 65% yield. The yield of (2,3-difluoro-2-methylpropyl)benzene (**2j**) was determined by ^{1}H NMR integration relative to internal standard trifluorotoluene (0.5 eq. w.r.t. starting material). ^{1}H NMR: δ 7.36 (t, *J* = 7.7 Hz, 2H; $PhCF_3$, internal std.) with respect to **2j :** δ 1.03 (dd, *J* = 21.7, 2.2 Hz, 3H). **^{1}H NMR** (400 MHz, CD_3CN): δ 7.12 – 7.0 (m, 5H), 4.29 – 4.03 (m, 2H), 2.87 – 2.68 (m, 2H), 1.03 (dd, *J* = 21.7, 2.2 Hz, 3H). **^{19}F {^{1}H} NMR** (376 MHz, CD_3CN) δ -63.20 (trifluorotoluene). -154.24 (d, *J*= 13.7 Hz), -230.06 (d, *J* = 12.4 Hz)

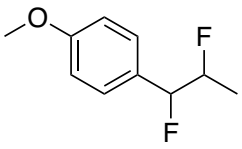


1,2-Difluoro-1,2-diphenylethane (2k): Following the **general procedure A**, the product **2k**



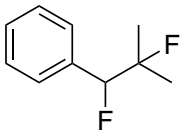
was obtained as a mixture of 1:1 diastereomers, 83% yield (182 mg) as a colorless oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$). δ 7.38 -7.27 (m, 6H), 7.18 (ddd, *J* = 25.4, 9.5, 2.0 Hz, 4H), 5.78 – 5.56 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.7 (m), 129.0 (d, *J* = 7.7 Hz), 128.2 (d, *J* = 9.8 Hz), 126.8 (m), 94.7 (ddd, *J* = 184.0, 72.2, 25.8 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -183.39, -186.67.

1-(1,2-Difluoro-propyl)-4-methoxybenzene (2l): Following the **general procedure A**, the



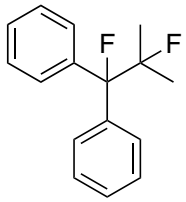
product **2l** was obtained in 92% yield as a mixture of 1:1 diastereomers. The yield of (1-(1,2-difluoro-propyl)-4-methoxybenzene (**2l**) was determined by ^{1}H NMR integration relative to internal standard trifluorotoluene (0.5 eq. w.r.t. starting material). ^{1}H NMR (used to determine conversion): δ 7.36 (t, *J* = 7.7 Hz, 2H; $PhCF_3$, internal std.) with respect to **2l :** δ 7.12 (d, *J* = 8.9 Hz, 2H). **^{1}H NMR** (400 MHz, CD_3CN): δ 7.12 (d, *J* = 8.9 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 5.36 – 5.05 (m, 1H), 4.85 – 4.6 (m, 1H), 3.59 (s, 3H), 1.09 - 0.935 (m, 3H). **^{19}F {^{1}H} NMR** (376 MHz, CD_3CN) δ -63.2 (trifluorotoluene). -180.62 (d, *J* = 14.3 Hz), -183.94 (d, *J* = 15.5 Hz), -184.93 (d, *J* = 15.8 Hz), -186.25 (d, *J* = 16.6 Hz).

(1,2-Difluoro-2-methylpropyl)benzene (2m): Following the **general procedure A**, the



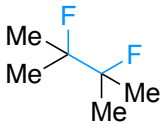
product **2m** was obtained in 61% yield. The yield of (1,2-difluoro-2-methylpropyl)benzene (2m) was determined by ^{1}H NMR integration relative to internal standard trifluorotoluene (0.5eq. w.r.t. starting material). ^{1}H NMR: δ 7.36 (t, *J* = 7.7 Hz, 2H; $PhCF_3$, internal std.) with respect to **2m :** δ 1.12 (ddd, *J* = 25.9, 21.7, 1.5 Hz, 6H). **^{1}H NMR** (400 MHz, CD_3CN): δ 7.2 – 7.17 (m, 5H), 5.2 (dd, *J* = 45.1, 16.5 Hz, 1H), 1.12 (ddd, *J* = 25.9, 21.7, 1.5 Hz, 6H). **^{19}F {^{1}H} NMR** (376 MHz, CD_3CN) δ -63.20 (trifluorotoluene). -151.61 (d, *J* = 11.2 Hz)., δ -187.42 (d, *J* = 10.4 Hz).

1,2-difluoro-2-Methyl-1-phenyl-propyl benzene (2n): Following the **general procedure A**,



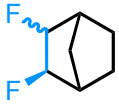
the product **2n** was obtained in 60% yield (148 mg) as a colorless oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$). δ 7.79 (d, *J* = 8.0 Hz, 4H), 7.45 (t, *J* = 15.0, 7.5 Hz, 4H), 7.4 – 7.36 (m, 2H), 1.56 (dt, *J* = 22.2, 2.5 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9 (d, *J* = 22.6 Hz), 128.1 (d, *J* = 1.6 Hz), 127.6, 126.2 (dd, *J* = 11.3, 4.4 Hz), 98.5 (dd, *J* = 180.1, 25.8 Hz), 97.8 (dd, *J* = 177.1, 32.8 Hz), 23.8 (d, *J* = 23.5 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -148.85 (d, *J* = 9.6 Hz), -156.7 (d, *J* = 9.5 Hz).

2,3-Difluoro-2,3-dimethylbutane (2o): Following the **general procedure A**, the product **2o**



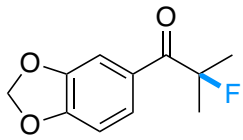
was obtained in 65% yield. The yield of 2,3-Difluoro-2,3-dimethylbutane (**2o**) was determined by ^{1}H NMR integration relative to internal standard trifluorotoluene (0.5 eq. w.r.t. starting material). ^{1}H NMR: δ 7.36 (t, *J* = 7.7 Hz, 2H; $PhCF_3$, internal std.) with respect to **2o :** δ 1.24 (d, *J* = 21.9 Hz, 12H). **^{1}H NMR** (400 MHz, CD_3CN): δ 1.24 (d, *J* = 21.9 Hz, 12H). **^{19}F {^{1}H} NMR** (376 MHz, CD_3CN) δ -63.20 (trifluorotoluene). δ -138.0.

2,3-Difluorobicyclo[2.2.1]heptane (2p): Following the **general procedure A**, the product **2p** was obtained as a mixture of 1:1 diastereomers, 60% yield (100 mg) as a white solid after



column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$). δ 4.84 (ddd, *J* = 81.1, 29.0, 4.6 Hz, 1H), 4.70 (dt, *J* = 59.6, 1.8 Hz, 1H), 4.4 (ddd, *J* = 52.5, 16.5, 2.8 Hz, 1H), 2.53 (s, 1H), 2.39 (dd, *J* = 9.3, 5.1 Hz, 1H), 1.93 (d, *J* = 10.3 Hz, 1H), 1.72 – 1.63 (m, 3H), 1.44 – 1.22 (m, 10H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -172.2, δ -197.0, -198.28.

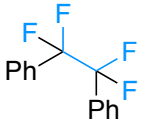
1-(1,3-benzodioxol-5-yl)-2-fluoro-2-methyl-1-propanone (2q): Following the **general**



procedure A, the product **2q** was obtained in 57% yield (110 mg) as an off white solid after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$). δ 7.73 (dd, *J* = 8.4,1.7 Hz, 1H), 7.5 (d, *J* = 1.5 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.97 (s, 2H), 1.61 (d, *J* = 21.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.4 (d, *J* = 25.5 Hz), 151.8, 147.8, 128.4 (d, *J* = 4.4),

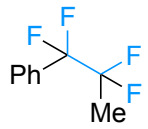
126.7 (d, J = 10.4), 109.9 (d, J = 7.8 Hz), 107.8 (d, J = 2.0 Hz), 101.8, 100.0 (d, J = 180.7), 25.8 (d, J = 23.8 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -142.4.

1,2-Diphenyltetrafluoroethane (4a): Following the **general procedure B**, the product **4a** was



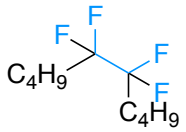
obtained in 86% yield (110.0 mg) as a white crystalline solid after column chromatography (eluent = hexanes/ ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.4 (m, 10H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.7, 131.0, 128.4 (d, J = 9.2 Hz), 128.1, 127.0 (m). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -111.72.

(1,1,2,2-Tetrafluoropropyl) benzene (4b): Following the **general procedure B**, the product



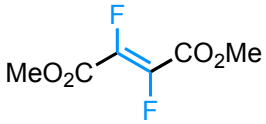
4b was obtained in 67% yield (130.0 mg) as a white crystalline solid after column chromatography (eluent = hexanes/ ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.38 (m, 5H), 1.76 (tt, J = 18.6, 1.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.9 (d, J = 3.5 Hz), 131.5, 130.9 (t, J = 12.3 Hz), 130.9, 128.3, 126.7 (t, J = 6.6 Hz), 17.7 (t, J = 25.2 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -107.0 (m), -112.3, (m).

5,5,6,6-Tetrafluorodecane (4c): Following the **general procedure B**, the product **4c** was

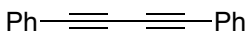


obtained as a mixture of product and starting material, in 61 % yield (150.0 mg) as a colorless oil after column chromatography (eluent = hexanes/ ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.24 (dq, J = 20.8, 6.9, 1.9 Hz, 4H), 1.52 – 1.49 (m, 8H), 0.95 – 0.93 (m, 8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 82.9 (d, J = 164.7 Hz), 38.3 (d, J = 22.3 Hz), 30.4 (d, J = 2.3 Hz), 18.1 (dd, J = 46.0, 3.2 Hz), 13.5. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -115.6, -170.4.

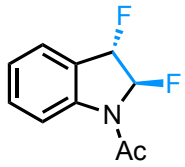
Dimethyl 2,3-difluorofumarate (4d′): Following the **general procedure B**, the product **4d′**



was obtained in 83 % yield (182.0 mg) as an opaque crystalline solid after column chromatography (eluent = hexanes/ ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.93 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1 – 158.9 (m), 144.8 (dd, J = 321.4, 88.8 Hz), 53.2. **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -145.0.

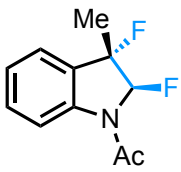
1,4-Diphenyl-1,3-butadiyne (4e″) Following the **general procedure B**, the product **4e″** was  obtained in 79 % yield (80.0 mg) as a white solid after column chromatography (eluent = hexanes/ ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 -7.32 (m, 10H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.5, 129.2, 128.5, 121.8, 81.6, 73.9.

1-(2,3-Difluoroindolin-1-yl) ethan-1-one (6a): Following the **general procedure C**, the



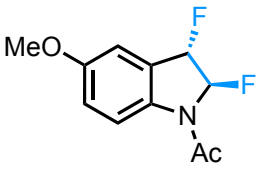
product **6a** was obtained in 56% yield (55.3 mg) as a colorless viscous oil after column chromatography (eluent = hexanes / ethyl acetate 90:10 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.28 (dd, *J* = 59.5, 13.2 Hz, 1H), 5.81 (dd, *J* = 52.1, 14.1 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 168.9 (d, *J* = 3.0 Hz), 143.8, 132.4 (d, *J* = 4.6 Hz), 126.6, 124.8 (d, *J* = 3.5 Hz), 124.0 (d, *J* = 17.6 Hz), 117.2, 101.1 (dd, *J* = 210.0, 38.9 Hz), 92.5 (dd, *J* = 182.3, 37.4 Hz), 23.0. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -170.95 (d, *J* = 10.9 Hz), -144.59 (d, *J* = 10.7 Hz).

1-(2,3-Difluoro-3-methylindolin-1-yl) ethan-1-one (6b): Following the **general procedure**



C, the product **6b** was obtained in 49% yield (52.0 mg) as a colorless oil after column chromatography (eluent = hexanes / ethyl acetate 90:10 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.5 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.09 (dd, *J* = 61.7, 13.0 Hz, 1H), 2.41 (s, 3H), 1.86 (dd, *J* = 4.9, 21.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.0 (d, *J* = 3.0 Hz), 142.9, 132.0 (d, *J* = 3.8 Hz), 127.9 (d, *J* = 19.8 Hz), 124.7 (d, *J* = 3.1 Hz), 123.7, 117.2, 102.1 (dd, *J* = 216.7, 46.0 Hz), 97.9 (dd, *J* = 176.2, 28.5 Hz), 23.1, 17.2 (dd, *J* = 26.9, 6.8 Hz). **^{19}F NMR** (376 MHz, CDCl3) δ -145.34 (d, *J* = 14.4 Hz), -129.75 (d, *J* = 14.4 Hz).

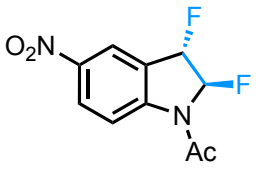
1-(2,3-Difluoro-5-methoxyindolin-1-yl) ethan-1-one (6c): Following the **general procedure C**, the product **6c** was obtained in 67% yield (76.0 mg) as a colorless viscous oil after column



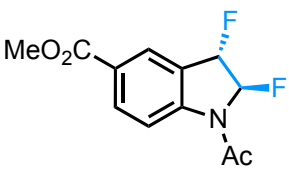
chromatography (eluent = hexanes/ ethyl acetate 85:15 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.9 Hz, 1H), 7.04 (t, *J* = 2.1 Hz, 1H), 7.00 (dt, *J* = 2.8, 5.6 Hz, 1H), 6.26 (dd, *J* = 59.6, 13.1 Hz, 1H), 5.77 (dd, *J* = 52.7, 13.9 Hz, 1H), 3.81 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 168.5 (d, *J* = 2.8 Hz), 156.9 (d, *J* = 3.9 Hz), 137.5, 125.1 (d, *J* = 17.6 Hz), 118.1 (d, *J* = 2.4 Hz), 117.8 (d,

J = 4.7 Hz), 111.6, 101.4 (dd, *J* = 210.8, 39.4 Hz), 92.6 (dd, *J* = 183.1, 37.4 Hz), 55.7, 22.8. **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -171.54 (d, *J* = 11.1 Hz), -144.32 (d, *J* = 11.2 Hz).

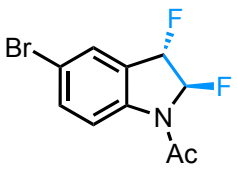
1-(2,3-Difluoro-5-nitroindolin-1-yl) ethan-1-one (6d): Following the **general procedure C**, the product **6d** was obtained in 75% yield (90.7mg) as a colorless viscous oil after column chromatography (eluent = hexanes/ ethyl acetate 70:30 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 – 8.39 (m, 3H), 6.39 (dd, *J* = 58.8, 13.4 Hz, 1H), 5.89 (dd, *J* = 51.9, 13.7 Hz, 1H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 169.1 (d, *J* = 3.0 Hz), 148.41 (t, *J* = 3.7 Hz), 144.5 (d, *J* = 3.7 Hz), 128.6 (d, *J* = 3.6 Hz), 125.1(d, *J* = 17.9 Hz), 122.8 (d, *J* = 1.3 Hz), 117.2, 101.3 (dd, *J* = 213.1, 38.7 Hz), 91.1 (dd, *J* = 185.7, 37.7 Hz), 23.1. **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -173.33, -144.56.



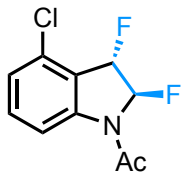
1-(2,3-Difluoro-5-methyl ester indolin-1-yl) ethan-1-one (6e): Following the **general procedure C**, the product **6e** was obtained in 66% yield (84.2 mg) as a colorless oil after column chromatography (eluent = hexanes/ ethyl acetate 65:35 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.57 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.32 (dd, *J* = 59.5, 13.2 Hz, 1H), 5.81 (dd, *J* = 52.1, 14.2 Hz, 1H), 3.91 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 168.9 (d, *J* = 3.0 Hz), 166.1, 143.9, 134.0 (d, *J* = 4.4 Hz), 128.2 (d, *J* = 17.4 Hz), 126.5, 126.3 (d, *J* = 3.0 Hz), 117.9, 101.1 (dd, *J* = 211.2, 38.5 Hz), 91.8 (dd, *J* = 182.4, 38.0 Hz), 52.4, 23.0. **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -173.39 (d, *J* = 7.5 Hz), -144.16 (d, *J* = 6.3 Hz).



1-(5-Bromo-2,3-difluoroindolin-1-yl) ethan-1-one (6f): Following the **general procedure C**, the product **6f** was obtained in 61% yield (84.0 mg) as a colorless viscous oil after column chromatography (eluent = hexanes/ ethyl acetate 88:12 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.0 Hz, 1H), 7.64 – 7.57 (m, 2H), 6.26 (dd, *J* = 59.3, 13.1 Hz, 1H), 5.78 (dd, *J* = 52.9, 14.2 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 168.9 (d, *J* = 2.9 Hz), 142.9, 135.3 (d, *J* = 4.3 Hz), 129.7, 126.0 (d, *J* = 18.8 Hz), 118.7, 117.2, 101.0 (dd, *J* = 211.4, 39.1 Hz), 91.7 (dd, *J* = 183.7, 37.0 Hz), 23.0. **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -144.34 (d, *J* = 10.0 Hz), -172.13 (d, *J* = 9.5 Hz).

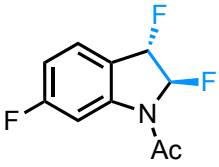


1-(4-Chloro-2,3-difluoroindolin-1-yl) ethan-1-one (6g): Following the **general procedure C**, the product **6g** was obtained in 74% yield (85.5 mg) as a colorless viscous oil after column



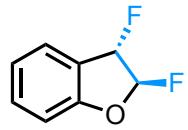
chromatography (eluent = hexanes/ ethyl acetate 88:12 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.3 Hz, 1H), 7.41 (td, *J* = 8.1, 2.6 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 6.29 (dd, *J* = 59.3, 12.9 Hz, 1H), 5.92 (dd, *J* = 51.9, 13.7 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 168.9 (d, *J* = 2.7 Hz), 145.0, 133.9 (d, *J* = 3.9 Hz), 132.8, 125.0 (d, *J* = 2.9 Hz), 122.6 (d, *J* = 16.5 Hz), 115.6, 100.7 (dd, *J* = 211.9, 39.9 Hz), 91.0 (dd, *J* = 185.2, 37.9 Hz), 23.0. **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -177.44 (d, *J* = 9.4 Hz), -144.45 (d, *J* = 9.3 Hz).

1-(2,3,6-Trifluoroindolin-1-yl) ethan-1-one (6h): Following the **general procedure C**, the product **6h** was obtained in 60% yield (64.5 mg) as a colorless viscous oil after column



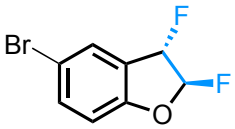
chromatography (eluent = hexanes/ ethyl acetate 90:10 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 9.6 Hz, 1H), 7.49 – 7.45 (m, 1H), 6.88 (td, *J* = 8.6, 2.4 Hz, 1H), 6.29 (dd, *J* = 59.6, 13.1 Hz, 1H), 5.77 (dd, *J* = 53.6, 14.1 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.9 (d, *J* = 3.0 Hz), 166.2 (dd, *J* = 249.4, 4.5 Hz), 145.4 (d, *J* = 12.8 Hz), 127.9 (d, *J* = 10.9 Hz), 119.8 (d, *J* = 18.1 Hz), 111.8 (dd, *J* = 23.6, 3.6 Hz), 105.5 (dd, *J* = 29.7 Hz), 101.7 (dd, *J* = 210., 39.9 Hz), 91.8 (dd, *J* = 182.7, 37.0 Hz), 22.9. **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -169.62 (t, *J* = 9.7 Hz), -144.45 (d, *J* = 10.1 Hz), -105.79 (d, *J* = 9.4 Hz).

2,3-Difluoro-2,3-dihydrobenzofuran (6i): Following the **general procedure C**, the product

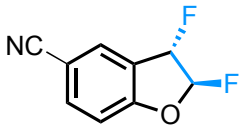


6i was obtained in 52% yield. The yield of 2,3-difluoro-2,3-dihydrobenzofuran (**6i**) was determined by ^{1}H NMR integration relative to internal standard trifluorotoluene (1.0 eq. w.r.t. starting material) ^{1}H NMR: δ 7.72 (d, *J* = 7.4 Hz, 2H; $PhCF_3$, internal std.) with respect to **6i :** δ 6.38 (dd, *J* = 57.3, 11.3 Hz, 1H). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.42 (m, 2H), 7.22 – 7.11 (m, 2H), 6.38 (dd, *J* = 57.3, 11.3 Hz, 1H). 5.99 (dd, *J* = 54.2, 11.1 Hz, 1H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -176.41(d, *J* = 12.3 Hz), -134.95 (d, *J* = 12.3 Hz).

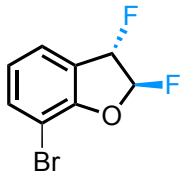
5-Bromo-2,3-difluoro-2,3-dihydrobenzofuran (6j): Following the general procedure C, the product **6j** was obtained in 55% yield. (64.3 mg) as a colorless viscous oil after column chromatography (eluent = hexanes/ ethyl acetate 95:05 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (t, *J* = 2.3 Hz, 1H), 7.56 (dt, *J* = 8.6, 2.4 Hz, 1H), 6.95 (d, *J* = 8.6 Hz 1H), 6.27 (dd, *J* = 58.0, 11.5 Hz, 1H), 5.85 (dd, *J* = 54.4, 11.6 Hz, 1H). **^{13}C NMR** (101 MHz, CDCl3) δ 159.5 (dd, *J* = 4.6, 2.9 Hz), 135.8 (d, *J* = 4.7 Hz), 129.9 (d, *J* = 1.6 Hz), 123.4 (d, *J* = 17.7 Hz), 115.1, 113.9 (dd, *J* = 232.3, 40.9 Hz), 113.1 (d, *J* = 2.2 Hz), 93.2 (dd, *J* = 184.4, 39.5 Hz). **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -176.37(d, *J* = 9.7 Hz), -132.78 (d, *J* = 9.7 Hz).



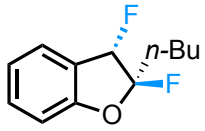
5-Cyano-2,3-difluoro-2,3-dihydrobenzofuran (6k): Following the general procedure C, the product **6k** was obtained in 61% yield. (55.0 mg) as a colorless viscous oil after column chromatography (eluent = hexanes/ ethyl acetate 90:10 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 1H), 6.36 (dd, *J* = 57.2, 11.6 Hz, 1H), 5.91 (dd, *J* = 54.4, 11.6 Hz, 1H). **^{13}C NMR** (101 MHz, CDCl3) δ 163.3, 137.5 (d, *J* = 3.9 Hz), 131.5 (d, *J* = 1.5 Hz), 122.9 (d, *J* = 19.1 Hz),118.0, 114.1 (dd, *J* = 234.7, 40.9 Hz), 112.7 (d, *J* = 2.2 Hz), 107.1 (d, *J* = 3.1 Hz), 92.4 (dd, *J* = 186.2, 37.9 Hz). **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -177.38 (d, *J* = 8.2 Hz), -133.21 (d, *J* = 8.2 Hz).



7-Bromo-2,3-difluoro-2,3-dihydrobenzofuran (6l): Following the general procedure C, the product **6l** was obtained in 51% yield. (59.0 mg) as a colorless viscous oil after column chromatography (eluent = hexanes/ ethyl acetate 95:05 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.47 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.31 (dd, *J* = 57.4, 11.6 Hz, 1H). 5.92 (dd, *J* = 54.4, 11.6 Hz, 1H). **^{13}C NMR** (101 MHz, CDCl3) δ 157.9 (dd, *J* = 4.4, 3.2 Hz), 135.9 (d, *J* = 4.5 Hz), 125.9 (d, *J* = 1.6 Hz), 124.5 (d, *J* = 3.0 Hz), 122.7 (d, *J* = 18.3 Hz), 113.6 (dd, *J* = 234.3, 40.9 Hz), 104.1 (d, *J* = 3.3 Hz), 94.1 (dd, *J* = 185.2, 37.9 Hz). **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -175.63(d, *J* = 9.7 Hz), -132.88 (d, *J* = 9.7 Hz).

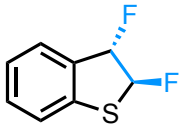


2-Butyl-2,3-Difluoro-2,3-dihydrobenzofuran (6m): Following the **general procedure C**, the product **6m** was obtained in 47% (49.8 mg) yield as a colorless oil after column chromatography (eluent = Hexane/ ethyl acetate 97:03 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.8 Hz, 1H), 7.35 (d, *J* = 7.6 Hz,

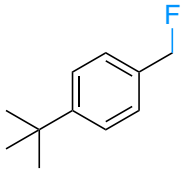


1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 6.8 Hz, 1H), 5.85 (dd, *J* = 56.0, 13.1 Hz, 1H), 2.14 – 2.05 (m, 2H), 1.64 – 1.57 (m, 2H), 1.49 – 1.40 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.3 (d, *J* = 7.6 Hz), 131.8 (d, *J* = 3.1 Hz), 125.9, 123.2 (d, *J* = 2.9 Hz), 122.6 (d, *J* = 2.3 Hz), 118.4 (dd, *J* = 244.6, 14.3 Hz), 110.9, 91.8 (dd, *J* = 199.1, 18.5 Hz), 35.3 (d, *J* = 27.5 Hz), 24.3 (d, *J* = 3.8 Hz), 22.5, 13.8. **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -123.21(d, *J* = 12.3 Hz), -194.38 (d, *J* = 12.3 Hz).

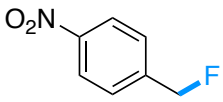
2,3-Difluoro-2,3-dihydrobenzothiophene (6n): Following the **general procedure C**, the product **6n** was obtained in 53% yield. The yield of 2,3-difluoro-2,3-dihydrobenzothiophene (**6n**) was determined by ^{1}H NMR integration. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 1H), 7.53 – 7.42 (m, 1H), 7.30 – 7.17 (m, 2H), 6.33 (dd, *J* = 54.2, 10.5 Hz, 1H). 5.96 (dd, *J* = 54.2, 11.1 Hz, 1H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -176.14(d, *J* = 12.3 Hz), -159.47 (d, *J* = 12.3 Hz).



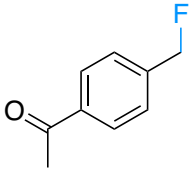
1-(1,1-Dimethylethyl)-4-(fluoromethyl)benzene (8a): Following the **general procedure D** (3.0 equivalents of AgF_2 at room temperature), the product **8a** was obtained in 83% yield (74 mg) as a colorless viscous oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.24 (dd, *J* = 8.5, 2.1 Hz, 2H), 5.26 (d, *J* = 48.2 Hz, 2H), 1.25 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 128.7, 127.6 (d, *J* = 5.5 Hz), 125.6 (d, *J* = 1.6 Hz), 125.2, 84.6 (d, *J* = 165.1 Hz) 31.5, 31.3. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -204.38.



1-(Fluoromethyl)-4-nitrobenzene (8b): Following the **general procedure D** (6.0 equivalents of AgF_2 at 60 °C), the product **8b** was obtained in 26% yield (40 mg) as a white solid after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 5.52 (d, *J* = 46.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.9, 143.4 (d, *J* = 17.7), 127.04 (d, *J* = 7.0 Hz), 123.8, 82.9 (d, *J* = 171.0 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -215.66.

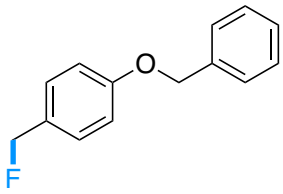


1-[4-(Fluoromethyl)phenyl]ethenone (8c): Following the **general procedure D** (6.0 equivalents of AgF_2 at 60 °C), the product **8c** was obtained in 35% yield (54 mg) as a colorless viscous oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.12 Hz, 2H), 5.46 (d, *J* = 47.2 Hz, 2H), 2.62 (s,

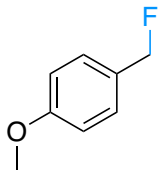


3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.6, 141.4 (d, *J* = 17.2), 137.2 (d, *J* = 2.2 Hz), 128.6, 126.8 (d, *J* = 6.8 Hz)), 83.6 (d, *J* = 168.2 Hz), 26.6. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -213.1.

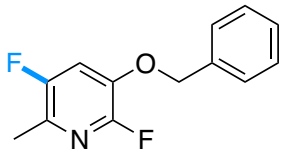
1-(Fluoromethyl)-4-phenoxybenzene (8d): Following the **general procedure D** (3.0 equivalents of AgF_2 at room temperature), the product **8d** was obtained in 61% yield (132 mg) as a colorless viscous oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 5H), 7.36 – 7.33 (m, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 5.32 (d, *J* = 48.4 Hz, 2H), 5.11 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4 (d, *J* = 3.5 Hz), 136.6 (d, *J* = 30.5 Hz), 129.9 (d, *J* = 4.6 Hz), 128.7 (d, *J* = 4.6 Hz), 128.1, 128.1, 127.5, 127.1, 114.9, 84.5 (d, *J* = 164.8 Hz), 70.05. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -199.58.



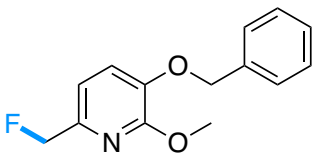
1-(Fluoromethyl)-4-methoxybenzene (8e): Following the **general procedure D** (3.0 equivalents of AgF_2 at room temperature), the product **8e** was obtained in 63% yield (100 mg) and 19% di, as a colorless viscous oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.7, 2.2 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 5.32 (d, *J* = 48.7 Hz, 2H), 3.84 (s, 3H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -199.23.



3-(benzyloxy)-2,5-difluoro-6-methylpyridine (8f): Following the **general procedure D** (6.0 equivalents of AgF_2 at 60 °C), the product **8f** was obtained in 40% as an off white solid after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 -7.35 (m, 5H), 7.04 (t, *J* = 8.5 Hz, 1H), 5.11 (s, 2H), 2.34 (d, *J* = 3.0 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -86.9 (d, *J* = 30.4 Hz), -127.1 (d, *J* = 30.4 Hz).

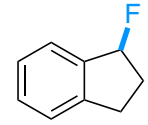


3-(benzyloxy)-6-(fluoromethyl)-2-methoxypyridine (8g): Following the **general procedure D** (3.0 equivalents of AgF_2 at 60 °C), the product **8g** was obtained in 37%, 25% inseparable mixture of mono and difluoro compound, as an off white solid after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). Mono fluoro product: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7-16 (m, 5H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 5.17 (d, *J* = 47.5 Hz, 2H), 5.03 (s, 2H), 3.91 (s, 3H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -212.9.

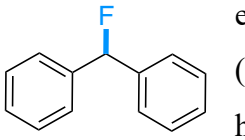


Di fluoro product: **^{1}H NMR** (400 MHz, CD_3CN) δ 7.27 – 7-16 (m, 5H), 6.97 (dd, *J* = 8.3, 2.4 Hz, 2H), 6.39 (t, *J* = 56.0 Hz, 1H), 5.04 (s, 2H), 3.93 (s, 3H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -114.4.

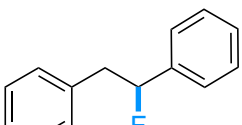
1-Fluoro-2,3-dihydro-1H-indene (8h): Following the **general procedure D** (6.0 equivalents of AgF_2 at 60 °C), the product **8h** was obtained in 40% yield. The yield of 1-fluoro-2,3-dihydro-1H-indene **(8h)** was determined by ^{1}H NMR integration relative to internal standard trifluorotoluene (0.5 eq. w.r.t. starting material). ^{1}H NMR: δ 7.56 (t, *J* = 7.7 Hz, 2H; $PhCF_3$, internal std.) with respect to **8h :** δ 5.99 (ddd, *J* = 58.2, 6.3, 2.5 Hz, 1H). **^{1}H NMR** (400 MHz, CD_3CN): δ 7.48 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.28 – 7.24 (m, 1H), 5.99 (ddd, *J* = 58.2, 6.3, 2.5 Hz, 1H), 2.48 – 2.31 (m, 2H), 2.25 – 2.21(m, 2H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -159.96.



1,1′-(Fluoromethylene)bis[benzene] (8i): Following the **general procedure D** (6.0 equivalents of AgF_2 at 60 °C), the product **8i** was obtained in 74% yield (138 mg) as a colorless viscous oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). ^{1}H NMR integration relative to internal standard trifluorotoluene (0.5 eq. w.r. t. starting material). ^{1}H NMR (used to determine conversion): δ 7.36 (t, *J* = 7.7 Hz, 2H; $PhCF_3$, internal std.) with respect to **8i :** δ 6.53 (d, *J* = 46.8 Hz, 1H). **^{1}H NMR** (400 MHz, CD_3CN): δ 7.39 – 7.32 (m, 10H), 6.53 (d, *J* = 46.8 Hz, 1H). **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -168.45.



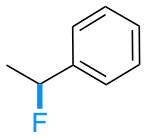
1,1′-(1-Fluoro-1,2-ethanediyl)bis[benzene] (8j): Following the **general procedure D** (6.0 equivalents of AgF_2 at 60 °C), the product **8j** was obtained in 30% yield (60 mg) as a colorless viscous oil after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 3H), 7.48 – 7.46 (m, 3H), 7.34 – 7.17 (m, 4H), 5.86 (ddd, *J* = 47.3, 8.1, 4.9 Hz, 1H), 3.44 (m, 2H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -172.9.



4-(1-Fluoroethyl)-1,1′-biphenyl (8k): Following the **general procedure D** (6.0 equivalents of AgF_2 at 60 °C), the product **8k** was obtained in 55% yield (110 mg) as an off white solid after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.37 (m, 9H), 5.69 (dq, *J* = 47.8, 6.5 Hz, 1H), 1.7 (dd, *J* = 23.8, 6.4 Hz, 3H). **^{13}C NMR**

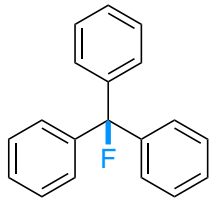
(151 MHz, $CDCl_3$) δ 141.2 (d, *J* = 1.8 Hz), 140.7, 140.4 (d, *J* = 19.8 Hz) 128.8, 127.4, 127.3, 127.2, 125.7 (d, *J* = 6.7 Hz), 90.8 (d, *J* = 167.3), 22.9 (d, *J* = 25.2 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -166.56.

1-Fluoroethyl)benzene (8l): Following the **general procedure D** (6.0 equivalents of AgF_2 at



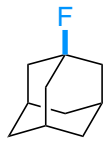
room temperature, anhydrous acetonitrile-*d*$_3$), the product **8l** was obtained in 60% yield. The yield of (1-Fluoroethyl)benzene **(8l)** was determined by ^{1}H NMR integration relative to internal standard trifluorotoluene (0.5 eq. w.r.t. starting material). ^{1}H NMR: δ 7.56 (t, *J* = 7.7 Hz, 2H; $PhCF_3$, internal std.) with respect to **8l :** ^{1}H NMR: δ 7.56 (t, *J* = 7.7 Hz, 2H; $PhCF_3$, internal std.) with respect to δ 1.54 (dq, *J* = 24.1, 6.5 Hz, 3H). **^{1}H NMR** (400 MHz, CD_3Cl) δ 7.44 – 7.34 (m, 5H), 5.62 (dq, *J* = 47.9, 6.5 Hz, 1H), 1.54 (dd, *J* = 24.1, 6.5 Hz, 2H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -167.0

1,1′,1′′-(Fluoromethylidyne)tris[benzene] (8m): Following the **general procedure D** (6.0



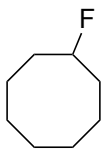
equivalents of AgF_2 at 60 °C), the product **8m** was obtained in 76% yield (198 mg) as a white solid after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.4 (m, 6H), 7.35 (t, *J* =15.0, 7.2 Hz, 2H), 7.3 – 7.25 (m, 5H), 7.19 (d, *J* = 7.9 Hz, 2H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -127.0.

1-Fluoroadamantane (8n): Following the **general procedure D** (6.0 equivalents of AgF_2 at



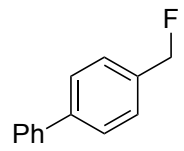
70 °C), the product **8n** was obtained in 58% yield (90 mg) as a white solid after column chromatography (eluent = hexanes / ethyl acetate 80:20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 1.88 (dd, *J* = 8.9, 3.23 Hz, 6H), 1.62 (t, *J* = 17.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 77.2, 42.7 (d, *J* = 17.5 Hz), 35.9 (d, *J* = 2.2 Hz), 31.5 (d, *J* = 9.2 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -128.4.

1-Fluorocyclooctane (8o): Following the general procedure E at room temperature using



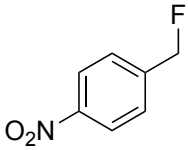
CD_3CN, the yield of 1-Fluorocyclooctane **8o** (59%) was determined by ^{1}H NMR integration relative to internal standard trifluorotoluene (0.5 eq. w.r.t. starting material). ^{1}H NMR: δ 7.56 (t, *J* = 7.7 Hz, 2H; $PhCF_3$, internal std.) with respect to δ 4.73-4.55 (m, 1H). **^{1}H NMR** (400 MHz, CD_3Cl) δ 4.73-4.55 (m, 1H), 1.87-1.79 (m, 3H), 1.67-1.61 (m, 3H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -159.0.

4-(Fluoromethyl)-1,1'-biphenyl (10a) (from Flebinac): Following the **general procedure E**,



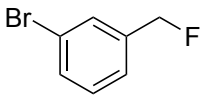
the product **10a** was obtained in 83% yield (77.2 mg) as a white solid after column chromatography (eluent = hexanes/ ethyl acetate 95:05 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (t, *J* = 8.9 Hz, 4H), 7.49 (t, *J* = 7.0 Hz, 4H), 7.40 (t, *J* = 7.0 Hz, 1H), 5.46 (d, *J* = 47.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7 (d, *J* = 3.4 Hz), 140.6, 135.1 (d, *J* = 17.6 Hz), 128.8, 128.1 (d, *J* = 5.7 Hz), 127.5, 127.4, 127.2, 84.3 (d, *J* = 166.2 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -206.16.

1-(Fluoromethyl)-4-nitrobenzene (10b): Following the **general procedure E**, the product



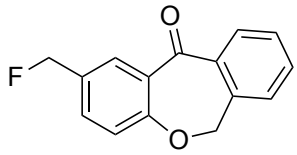
10b was obtained in 62% yield (48.0 mg) as a colorless viscous oil after column chromatography (eluent = hexanes/ ethyl acetate 85:15 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 5.52 (d, *J* = 46.5 Hz, 2H). **^{13}C NMR** (101 MHz, CDCl3) δ 147.9, 143.4 (d, *J* = 17.1 Hz), 127.0 (d, *J* = 7.0 Hz), 126.6, 82.9 (d, *J* = 170.2 Hz). **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -215.64.

1-Bromo-3-(fluoromethyl) benzene (10c): Following the **general procedure E**, the product



10c was obtained in 31% yield. The yield of 1-bromo-3-(fluoromethyl) benzene **(10c)** was determined by ^{1}H NMR integration relative to internal standard dimethyl maleate (1.0 eq. w.r.t. starting material) ^{1}H NMR: δ 6.16 (s, 2H; dimethyl maleate internal std.) with respect to **10c**: δ 5.24 (d, *J* =47.6 Hz, 2H). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 2H), 7.20 – 7.11 (m, 2H), 5.24 (d, *J* =47.6 Hz, 2H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -209.61.

2-(Fluoromethyl) dibenzo [b,e]oxepin-11(6H)-one (10d): (from Isoxepac): Following the



general procedure E, the product **10d** was obtained in 81% yield (98.0 mg) as a white solid after column chromatography (eluent = hexanes/ ethyl acetate 90:10 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (t, *J* = 2.3 Hz, 1H), 7.88 (t, *J* = 7.5 Hz, 1H), 7.58 – 7.42 (m, 3H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 5.35 (d, *J* = 48.4 Hz, 2H), 5.18 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.6, 161.6 (d, *J* = 2.4 Hz), 140.3, 135.4, 134.9 (d, *J* = 4.5 Hz), 132.9, 131.7 (d, *J* = 6.0 Hz), 129.9 (d, *J* = 18.0 Hz), 129.4, 129.3, 127.9, 125.0 (d, *J* = 1.5 Hz), 121.3 (d, *J* = 1.5 Hz), 83.9 (d, *J* = 165.9 Hz), 73.6. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -203.60.

Fluorodiphenylmethane (10e): Following the **general procedure E**, the product **10e** was obtained in 68% yield (63.0 mg) as a colorless oil after column chromatography (eluent = hexanes). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.10 (m, 10H), 6.37 (d, *J* = 47.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.9 (d, 2C, *J* = 21.2 Hz), 128.5(4C), 128.4 (d, 4C, *J* = 1.8 Hz), 126.6 (d, 2C, *J* = 6.6 Hz), 94.5 (d, *J* = 172.1 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -166.62.

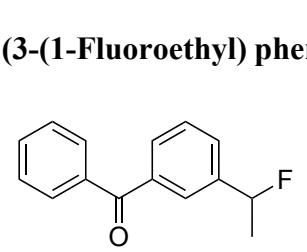
1-(1-Fluoroethyl)-3-phenoxybenzene (10f): Following the **general procedure E**, the product **10f** was obtained in 46% yield (49.7 mg) as a colorless oil after column chromatography (eluent = hexane/ ethyl acetate 95:05 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 3H), 7.16 – 7.08 (m, 3H), 7.03 (dd, *J* = 7.5, 1.4 Hz, 3H), 5.60 (dq, *J* = 47.2, 6.4 Hz, 1H), 1.63 (dd, *J* = 24.0, 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.5, 156.9 148.3 (d, *J* = 15.2 Hz), 143.6 (d, *J* = 19.6 Hz), 129.8 (2C), 123.4, 119.0 (2C), 115.6 (d, *J* = 7.3 Hz), 90.5 (d, *J* = 168.5 Hz), 22.9 (d, *J* = 25.4 Hz). **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -167.84.

1-(1-Fluoroethyl)-4-isobutylbenzene (10g) (from Ibuprofen): (Org. Lett. 2022, 24, 5376−5380): Following the **general procedure E**, the product **10g** was obtained in 61% yield. The yield of 1-(1-fluoroethyl)-4-isobutylbenzene (**10g)** was determined by 1H NMR integration relative to internal standard dimethyl maleate (1.0 eq. w.r.t. starting material) ^{1}H NMR (used to determine conversion): δ 6.15 (s, 2H; dimethyl maleate internal std.) relative to **10g**: δ 5.46 (dq, *J* = 48.1, 5.9 Hz, 1H). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 – 7.12 (m, 2H), 7.07 – 7.01 (m, 2H), 5.46 (dq, *J* = 48.1, 5.9 Hz, 1H), 2.34 (d, *J* = 7.3 Hz, 2H), 1.49 (dd, *J* = 23.7, 6.5 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 6H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -164.31.

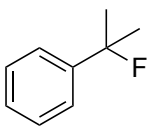
2-Fluoro-4-(1-fluoroethyl)-1,1'-biphenyl (10h): Following the **general procedure E**, the product **10h** was obtained in 67% yield (73.0 mg) as a colorless viscous oil after column chromatography (eluent = hexanes/ ethyl acetate 95:05 v/v). R_f = 0.5 (hexanes: ethyl acetate = 95:05). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 2H), 7.48 (d, *J* = 7.4 Hz, 3H), 7.42 – 7.39 (m, 1H), 7.21 (t, *J* = 6.6 Hz, 2H), 5.68 (dq, *J* = 47.9, 6.5 Hz, 1H), 1.7 (dd, *J* = 24.1, 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 159.8 (d, *J* = 249.1 Hz), 142.9 (dd, *J* = 20.2, 7.6 Hz), 135.4, 130.8 (d, *J* = 3.1 Hz), 129.0 (d, *J* = 2.8 Hz), 128.5 (2C), 127.8 (2C), 121.0 (dd, *J* = 6.5, 3.4 Hz), 113.1 (d, *J* = 7.9 Hz), 112.9 (d, *J* =

7.2 Hz), 90.0 (dd, *J* = 168.9, 1.6 Hz), 22.8 (d, *J* = 24.8 Hz). **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -168.32, -117.42.

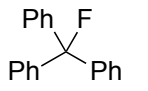
(3-(1-Fluoroethyl) phenyl) (phenyl) methanone (10i): Following the **general procedure E**, the product **10i** was obtained in 72% yield (82.0 mg) as a colorless viscous oil after column chromatography (eluent = hexanes/ ethyl acetate 90:10 v/v). R_f = 0.5 (hexanes: ethyl acetate = 90:10). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.8, 1.4 Hz, 3H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 6.9 Hz, 2H), 7.80 (td, *J* = 7.7, 2.6 Hz, 3H), 5.69 (dq, *J* = 47.5, 6.4 Hz, 1H), 1.67 (dd, *J* = 23.8, 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 196.4, 141.9 (d, *J* = 20.1 Hz), 137.8, 137.4, 132.6, 130.0, 129.9 (d, *J* = 1.9 Hz), 129.1 (d, *J* = 6.6 Hz), 128.5, 128.3, 126.7 (d, *J* = 6.9 Hz), 90.4 (d, *J* = 169.4 Hz), 22.9 (d, *J* = 25.0 Hz). **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -168.56.

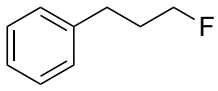


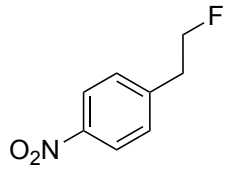
2-(4-(1-Fluoroethyl) cyclopentane-1-one (10j): Following the **general procedure E**, the product **10j** was obtained in 68% yield (74.0 mg) as a colorless oil after column chromatography (eluent = hexane/ ethyl acetate 95:05 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 5.61 (dq, *J* = 48.6, 6.5 Hz, 1H) 3.16 (dd, *J* = 14.2, 4.2 Hz, 1H), 2.57 (dd, *J* = 13.8, 9.0 Hz, 1H), 2.39 – 2.32 (m, 2H), 2.17 – 2.07 (m, 2H), 2.02 – 1.93 (m, 1H), 1.80 – 1.71 (m, 1H), 1.65 (dd, *J* = 23.9, 6.6 Hz, 3H), 1.60 – 1.51 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.0, 140.1 (d, *J* = 2.1 Hz), 139.3 (d, *J* = 19.6 Hz), 129.0 (2C), 125.4 (d, *J* = 6.4 Hz, 2C), 90.8 (d, *J* = 166.2 Hz), 50.9, 38.1, 35.2, 29.1, 22.7(d, *J* = 26.1 Hz), 20.5. **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -165.42.

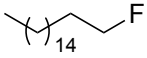


(2-Fluoropropan-2-yl) benzene (10k): Following the **general procedure E**, the product **10k** was obtained in 61% yield. The yield of (2-fluoropropan-2-yl) benzene (**10k**) was determined by ^{1}H NMR integration relative to internal standard dimethyl maleate (0.5 eq. w.r.t. starting material) ^{1}H NMR (used to determine conversion): δ 3.67 (s, 6H; dimethyl maleate, internal std.) relative to **10k**: δ 1.57 (d, *J* = 21.9 Hz, 6H). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.15 (m, 5H), 1.57 (d, *J* = 21.9 Hz, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -137.00.

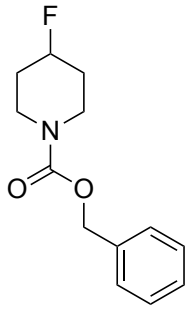
(Fluoromethanetriyl)tribenzene (10l): Following the **general procedure E**, the product **10l**  was obtained in 89% yield. The yield of (fluoromethanetriyl)tribenzene **(10l)** was determined by ^{1}H NMR integration relative to the internal standard trifluoro toluene (0.5 eq. w.r.t. starting material) ^{1}H NMR (used to determine conversion): δ 7.58 - 7.42 (m, 5H; $PhCF_3$ int. std.) relative to **10l :** δ 7.30-7.11 (m, 15H). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.11 (m, 15H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -126.43.

(3-Fluoropropyl) benzene (10m): Following the **general procedure E**, the product **10m** was  obtained in 51% yield (35.0 mg) as a colorless oil after column chromatography (eluent = Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H), 7.23-7.20 (m, 3H), 4.47 (dt, *J* = 47.5, 6.0 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.09-1.96 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 128.5 (2C), 128.4 (2C), 126.0, 83.0 (d, *J* = 165.3 Hz), 32.0 (d, *J* = 19.8 Hz), 31.3 (d, *J* = 5.4 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -219.99.

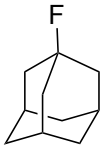
1-(2-Fluoroethyl)-4-nitrobenzene (10n): Following the **general procedure E**, the product **10n** was obtained in 52% yield (43.9 mg) as a yellowish oil after column chromatography  (eluent = hexanes / ethyl acetate 85:15 v/v). R_f = 0.4 (hexanes: ethyl acetate = 85:15). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.9 Hz, 2H), 7.43 (d, *J* = 8.9 Hz, 2H), 4.70 (dt, *J* = 47.0, 6.2 Hz, 2H), 3.13 (dt, *J* = 25.5, 6.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0, 145.1 (d, *J* = 4.0 Hz), 129.8, 123.7, 82.9 (d, *J* = 170.3 Hz), 36.7 (d, *J* = 20.8 Hz). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -217.02.

1-Fluoroheptadecane (10o): Following the **general procedure E**, the product **10o** was obtained in 53% yield (68.4 mg) as a colorless oil after column chromatography (eluent =  hexanes). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.45 (dt, *J* = 47.2, 6.0 Hz, 2H), 1.77 – 1.63 (m, 2H), 1.28 (m, 28H), 0.90 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 84.2 (d, *J* = 164 Hz), 31.9, 30.4 (d, *J* = 19.4 Hz), 29.7(4C), 29.6(4C), 29.5 (d, *J* = 3.7 Hz), 29.3, 29.2, 25.1 (d, *J* = 5.8 Hz), 22.7, 14.1. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -217.96.

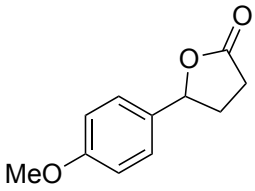
Benzyl-4-fluoropiperidine-1-carboxylate (10p): Following the **general procedure E**, the product **10p** was obtained in 58% yield (68.7 mg) as a colorless oil after column chromatography (eluent = hexanes/ ethyl acetate 90:10 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 5H), 5.16 (s, 2H), 4.84 (dquint, *J* = 47.9, 5.0 Hz, 1H), 3.64 – 3.54 (m, 4H), 1.85 (dd, *J* = 16.5, 4.7 Hz, 4H). **^{13}C NMR** (101 MHz, CDCl3) δ 155.2, 136.7, 128.5, 128.0, 127.9, 87.8 (d, *J* = 170.4 Hz), 67.2, 39.9 (d, *J* = 5.8 Hz), 31.1 (d, *J* = 18.8 Hz). **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -182.91.



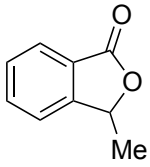
1-Fluoroadamantane (10q): Following the **general procedure E**, the product **10q** was obtained in 55% yield (42.3 mg) as a colorless viscous oil after column chromatography (eluent = hexanes). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 1.90 (dd, *J* = 5.4, 3.0 Hz, 6H), 1.68 – 1.61 (m, 6H). **^{13}C NMR** (101 MHz, CDCl3) δ 92.5 (d, *J* =182.0 Hz), 42.7 (d, *J* = 17.4 Hz), 35.8 (d, *J* = 2.0 Hz), 31.5 (d, *J* = 10.0 Hz). **^{19}F {^{1}H} NMR** (376 MHz, CDCl3) δ -128.50.



5-(4-methoxyphenyl)dihydrofuran-2(3*H*)-one (10r′): Following the **general procedure E**, the product **10r′** was obtained in 72% yield (69.0 mg) as a white solid after column chromatography (eluent = Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.39-5.35 (m, 1H), 3.73 (s, 3H), 2.59-2.50 (m, 3H), 2.15-2.06 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.9, 159.7, 131.1, 126.9 (2C), 114.1 (2C), 81.3, 55.3, 30.9, 29.2.



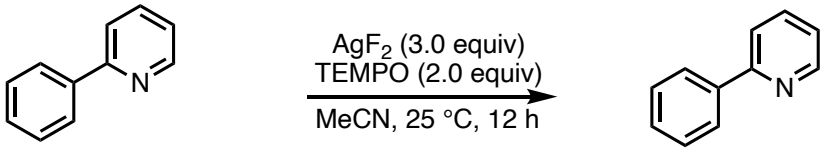
3-methyl-2,3-dihydro-1*H*-inden-1-one (10s′): Following the **general procedure E**, the product **10s′** was obtained in 67% yield (49.5 mg) as a white solid after column chromatography (eluent = Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 5.57 (q, *J* = 6.9 Hz, 1H), 1.64 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.4, 151.1, 134.0, 129.0, 125.7, 125.6, 121.5, 76.7, 20.4.



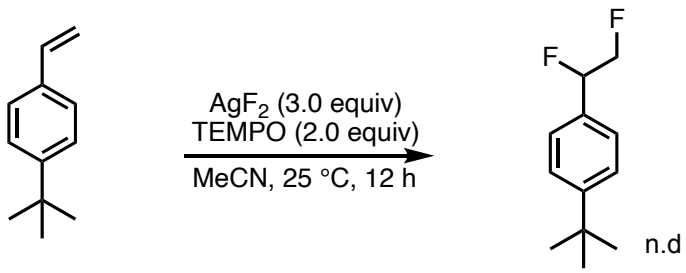
3-phenyl-2,3-dihydro-1*H*-inden-1-one (10t′): Following the **general procedure E**, the product **10t′** was obtained in 63% yield (66.0 mg) as a white solid after column chromatography (eluent = Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.28-7.22 (m, 4H), 7.18-7.17 (m, 2H), 6.30 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5, 149.7, 136.4, 134.3, 129.4, 129.3, 128.9 (2C), 126.9 (2C), 125.6, 125.5, 122.9, 82.7.

Mechanistic experiments:

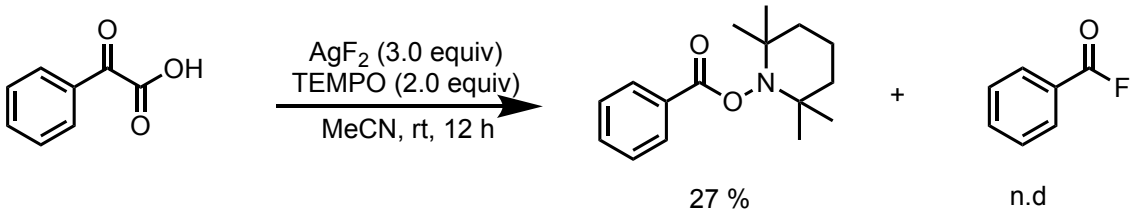
Radical Trap Experiment with TEMPO



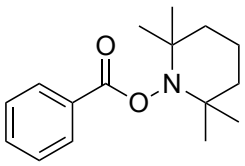
In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with 2-phenyl pyridine (1.0 mmol, 1.0 equiv), TEMPO (312.5 mg, 2.0 mmol, 2.0 equiv) and anhydrous acetonitrile (6.0 mL, 0.34M). To this solution, AgF_2 (437.5 mg, 3.0 mmol, 3.0 equiv) was added at once, and the resulting mixture stirred at room temperature for 12 h. **GCMS:** m/z – 155.0 (rt - 7.0), 156.0 (rt – 4.55). Shows neither formation of fluorinated product nor any TEMPO adduct, but unreacted starting material in the reaction mass along with unreacted TEMPO was detected.



In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with 4-^{t}Bu-styrene(1.0 mmol, 1.0 equiv), TEMPO (312.5 mg, 2.0 mmol, 2.0 equiv) and anhydrous acetonitrile (6.0 mL, 0.34M). To this solution, AgF_2 (437.5 mg, 3.0 mmol, 3.0 equiv) was added at once, and the resulting mixture stirred at room temperature for 12 h.
GCMS analysis shows neither formation of fluorinated product nor any TEMPO adduct, but unreacted starting material in the reaction mass along with unreacted TEMPO was detected.

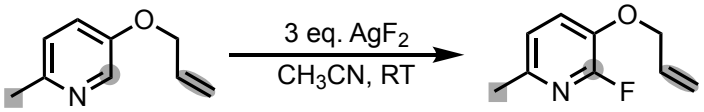


In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with



phenylglyoxylic acid (0.50 mmol, 1.0 equiv), TEMPO (156.0 mg, 1.0 mmol, 2.0 equiv) and anhydrous acetonitrile (3.0 mL, 0.17M). To this solution, AgF_2 (217.5 mg, 1.5 mmol, 3.0 equiv) was added at once, and the resulting mixture stirred at room temperature for 12 h. After completion of the reaction the mixture was filtered through a celite plug and concentrated in vacuo. The resulting crude product was purified by flash chromatography on silica gel to afford the pure TEMPO adduct product. The product was obtained in 27% yield (35.7 mg) as a white solid after column chromatography (eluent = hexanes / ethyl acetate 85:15 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 1.85 – 1.70 (m, 3H), 1.63 – 1.60 (m, 2H), 1.51 – 1.47 (m, 1H), 1.31 (s, 6H), 1.15 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 132.9, 129.7, 129.6, 128.5, 60.4, 39.1, 32.0, 20.9, 17.0.

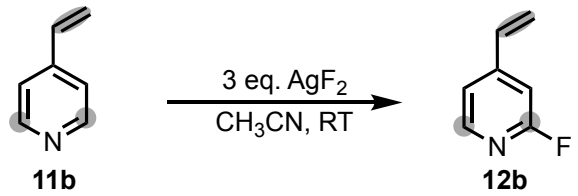
Intramolecular competition experiments



11a **12a**

exclusive product

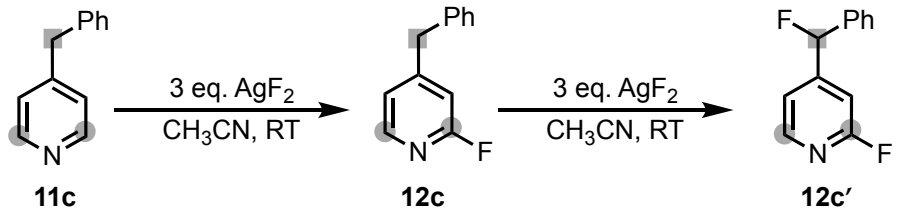
2-Fluoro-6-methyl-3-(2-propen-1-yloxy) pyridine (12a): In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with 2-Methyl-5-(2-propen-1-yloxy) pyridine (1.0 mmol, 1.0 equiv) and anhydrous acetonitrile (6.0 mL, 0.34M). To this solution, AgF_2 (437 mg, 3.0 mmol, 3.0 equiv) was added at once, and the resulting mixture stirred at room temperature for 6 h until the complete consumption of the alkene was observed by TLC and GCMS analysis. After completion of the reaction the mixture was filtered through a celite plug and concentrated in vacuo. The resulting crude product was purified by flash chromatography on silica gel (eluent = hexanes / ethyl acetate 80:20 v/v). to afford the pure product **12a**, 73% yield (122 mg) as a yellow viscous oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.12 (dd, *J* = 10.3, 8.0 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 5.99 – 5.89 (m, 1H), 5.28 (ddd, *J* = 44.5, 17.2, 1.3 Hz, 2H), 4.50 (d, *J* = 5.4 Hz, 2H), 2.33 (s, 3H).



11b **12b**

exclusive product

3-Ethenyl-2-fluoropyridine (12b): In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with 4-vinylpyridine (1.0 mmol, 1.0 equiv) and anhydrous acetonitrile (6.0 mL, 0.34M). To this solution, AgF_2 (321 mg, 2.2 mmol, 2.2 equiv) was added at once, and the resulting mixture stirred at room temperature for 6 h until the complete consumption of the alkene was observed by TLC and GCMS analysis. After completion of the reaction the mixture was filtered through a celite plug and concentrated in vacuo. The resulting crude product was purified by flash chromatography on silica gel (eluent = hexanes / ethyl acetate 80:20 v/v). to afford the pure product **12b**, 62% yield (89 mg) as a yellow viscous oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 5.4 Hz, 1H), 7.17 (dt, *J* = 5.2, 1.6 Hz, 1H), 6.88 (s, 1H), 6.67 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.99 (d, *J* = 17.6 Hz, 1H), 5.55 (d, *J* = 10.9 Hz, 1H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -68.71.



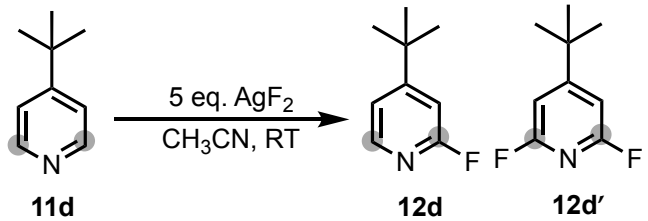
11c **12c** **12c′**

major product isolated

~40% conversion

2-fluoro-4-(phenylmethyl)pyridine (12c): In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with 4-benzylpyridine (1.0 mmol, 1.0 equiv) and anhydrous acetonitrile (6.0 mL, 0.34M). To this solution, AgF_2 (437.6 mg, 3.0 mmol, 3.0 equiv) was added at once, and the resulting mixture stirred at room temperature for 12 h until the complete consumption of the alkene was observed by TLC and GCMS analysis. After completion of the reaction the mixture was filtered through a celite plug and concentrated in vacuo. The resulting crude product was purified by flash chromatography on silica gel (eluent = hexanes / ethyl acetate 80:20 v/v). to afford the pure product **12c**, 80% yield (150 mg) as a yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 5.2 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.19 – 7.16 (m, 1H), 7.09 – 7.07 (m, 2H), 6.9 (d, 5.1 Hz, 1H), 6.62 (s, 1H), 3.90 (s, 2H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -68.63.

2-fluoro-4-(fluorophenylmethyl)pyridine (12c′): In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with 2-fluoro-4-(phenylmethyl)pyridine (1.0 mmol, 1.0 equiv) and anhydrous acetonitrile (6.0 mL, 0.34M). To this solution, AgF_2 (437.6 mg, 3.0 mmol, 3.0 equiv) was added at once, and the resulting mixture stirred at room temperature for 12 h. The resulting crude product was purified by flash chromatography on silica gel (eluent = hexanes / ethyl acetate 80:20 v/v) to afford 1:1 mixture of product and starting material, as a yellow solid. ^{1}H NMR integration relative to starting material 2-fluoro-4-(phenylmethyl)pyridine (12c). ^{1}HNMR: δ 8.00 (d, *J* = 5.1 Hz, 1H) 2-fluoro-4-(phenylmethyl)pyridine (12c) with respect to **12c′ :** δ 8.11 (d, *J* = 5.2 Hz, 1H), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 5.2 Hz, 1H), 7.32 – 7.30 (m, 3H), 7.26 – 7.24 (m, 2H), 7.03 (d, 5.6 Hz, 1H), 6.85 (s, 1H), 6.33 (d, *J* = 47.0 Hz, 1H). **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -68.63, -171.18.



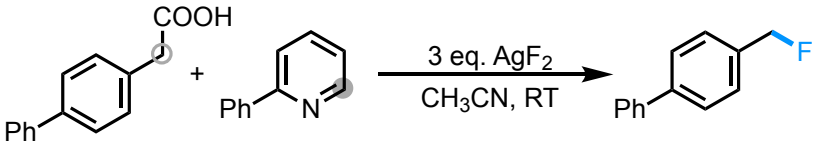
11d **12d** **12d′**

mixture of products observed

2-fluoro-4-(tert-butyl)pyridine (12d): In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with t-butyl pyridine (1.0 mmol, 1.0 equiv) and anhydrous acetonitrile (6.0 mL, 0.34M). To this solution, AgF_2 (730.0 mg, 5.0 mmol, 5.0 equiv) was added at once, and the resulting mixture stirred at room temperature for 12 h. The resulting crude product was purified by flash chromatography on silica gel (eluent = hexanes / ethyl acetate 80:20 v/v) to afford **12d**, as a pale yellow liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 5.3 Hz, 1H), 7.15 (dt, *J* = 5.4, 1.8 Hz, 1H), 6.88 (s, 1H), 1.31 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3 (d, *J* = 7.6 Hz), 164.4 (d, *J* = 237.6 Hz), 147.2 (d, *J* = 15.4 Hz), 118.6 (d, *J* = 3.8 Hz), 106.2 (d, *J* = 37.2 Hz), 35.1(d, *J* = 2.4 Hz), 30.4.

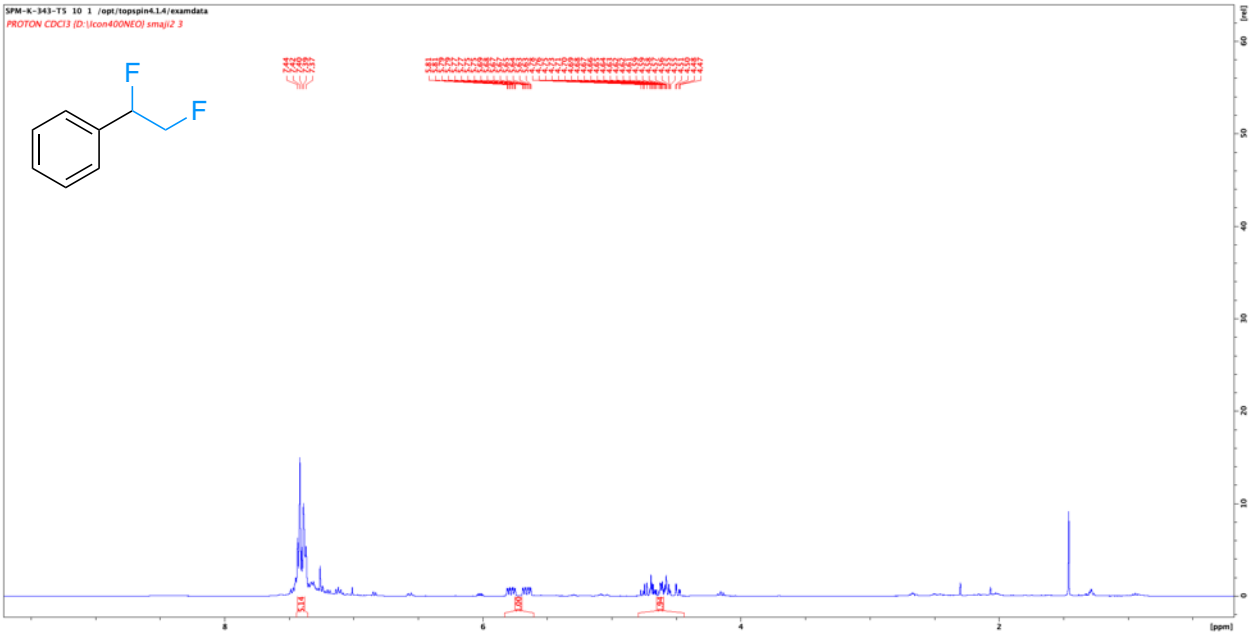
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ -69.0.

Note: GCMS shows 10% difluoro compound **(12d′)** in the reaction mass.

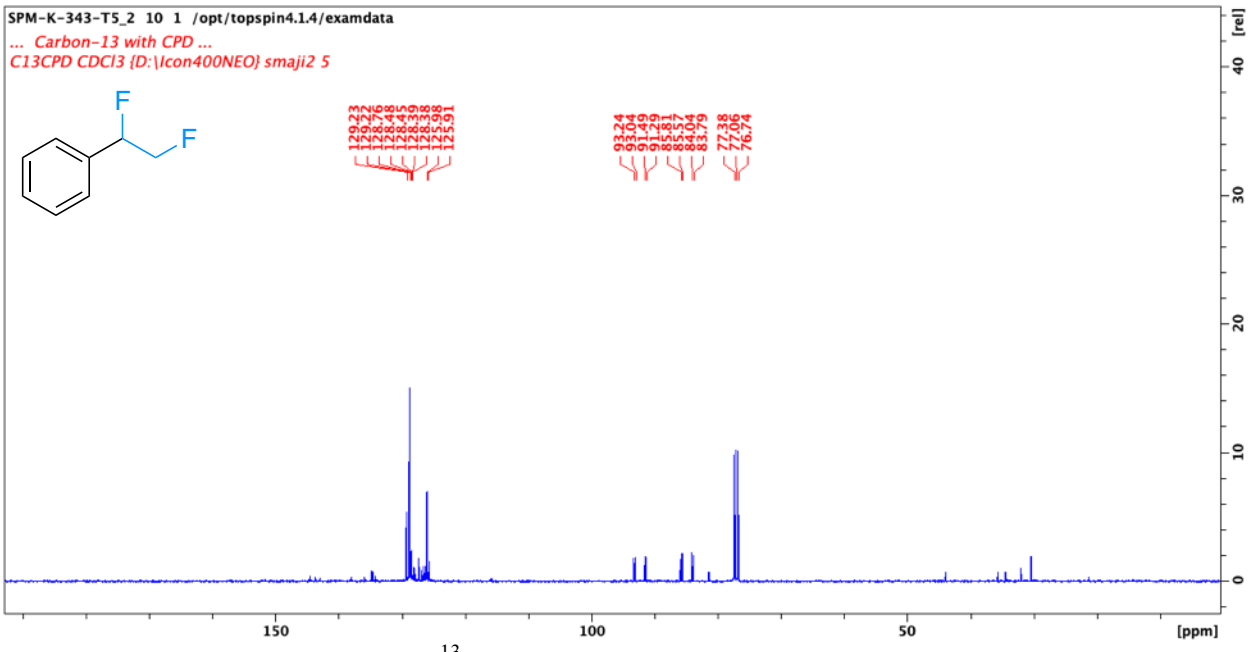


Intermolecular competition reaction: In the glovebox, an oven-dried 10 mL vial equipped with a stir bar was charged with 2-phenyl pyridine (1.0 mmol, 1.0 equiv), 4-phenyl phenyl acetic acid **9a** (1.0 mmol, 1.0 equiv), and anhydrous acetonitrile (6.0 mL, 0.34M). To this solution, AgF_2 (437.5 mg, 3.0 mmol, 3.0 equiv) was added at once, and the resulting mixture stirred at room temperature for 12 h. GCMS analysis shows exclusive formation of 4-(Fluoromethyl)-1,1'-biphenyl compound **10a**.

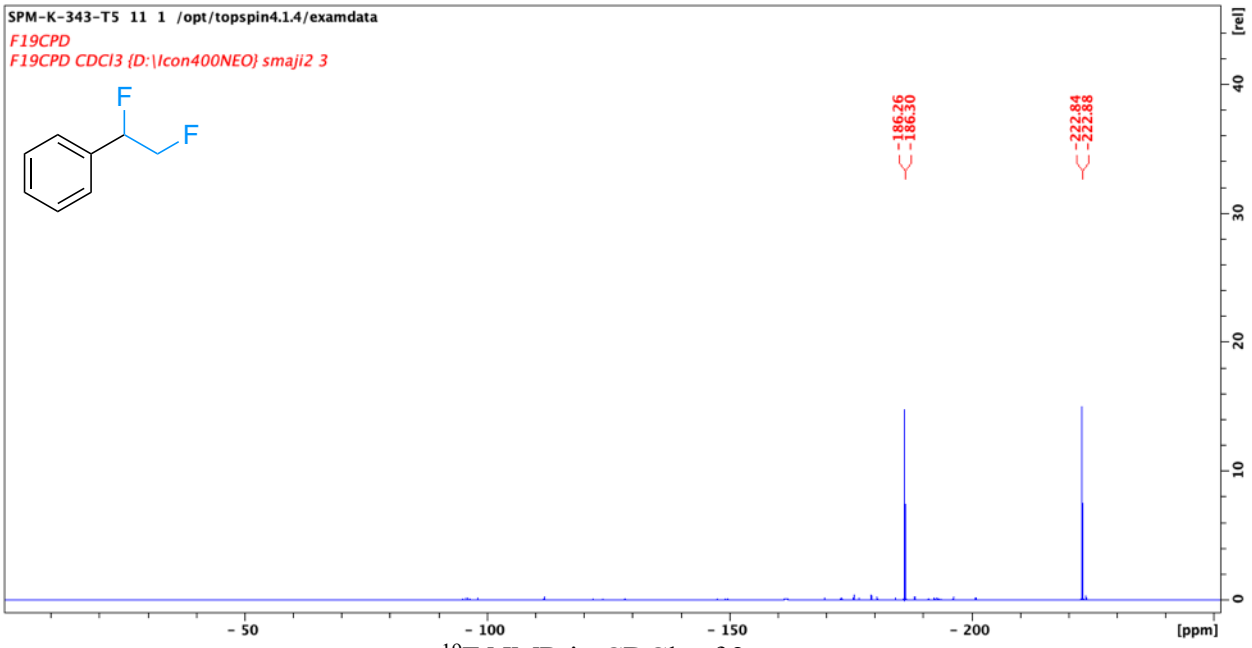
^{1}H, ^{13}C and ^{19}F NMR Spectra of Fluorinated products



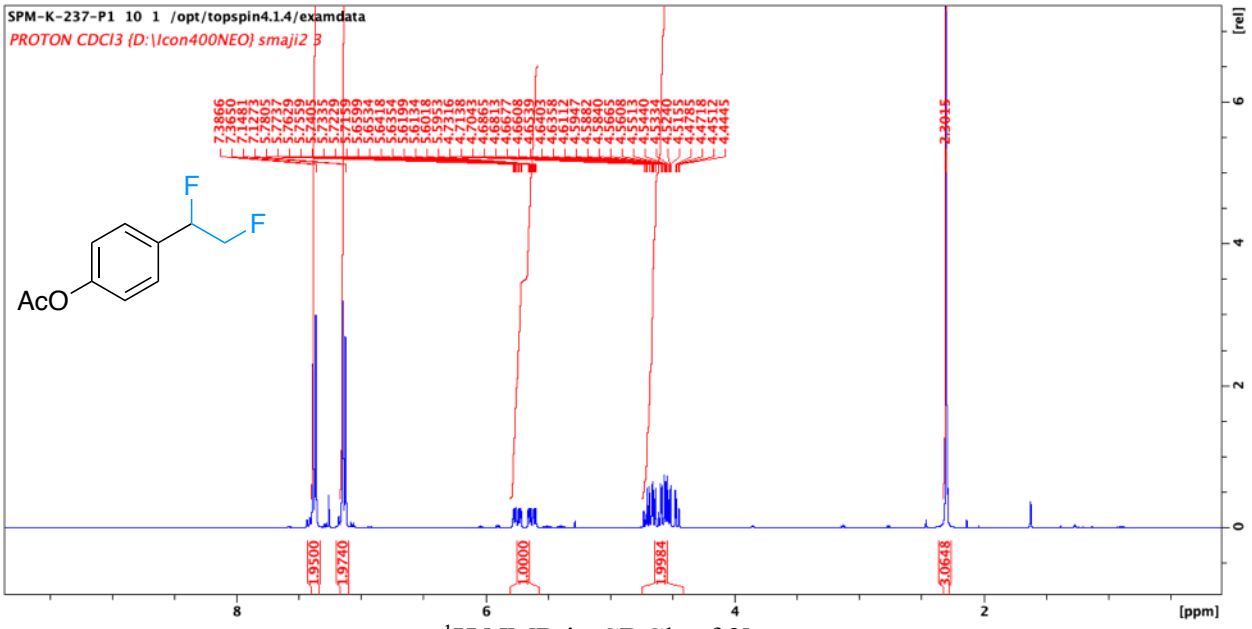
^{1}H NMR in $CDCl_3$ of **2a**



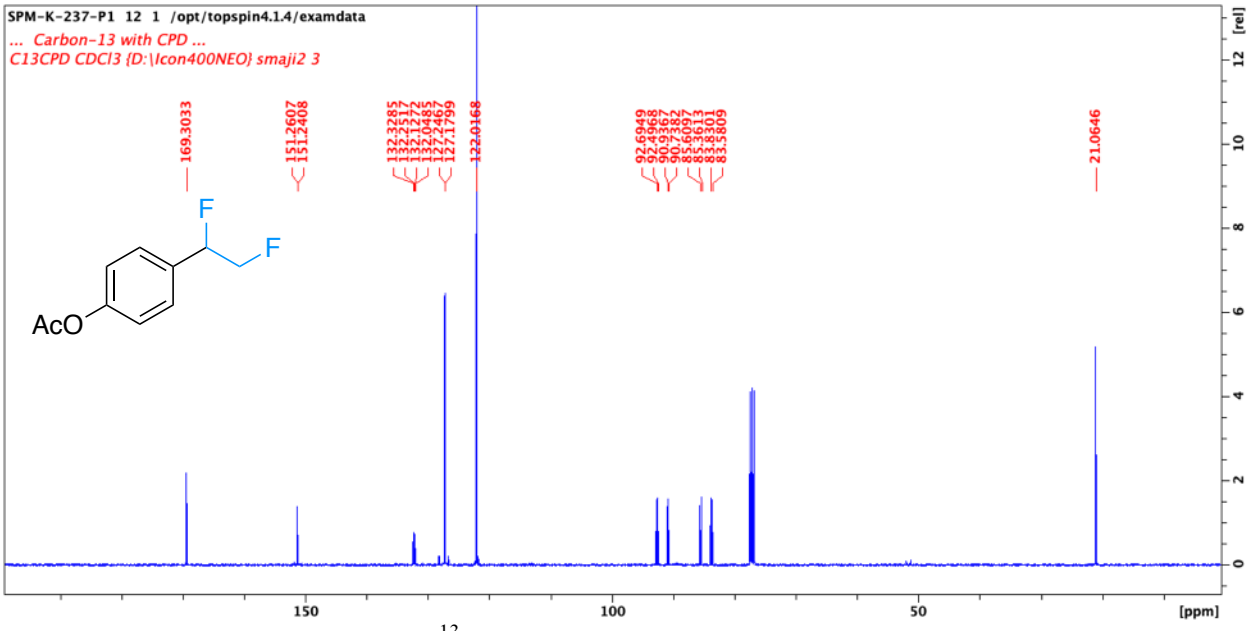
^{13}C NMR spectrum of **2a**



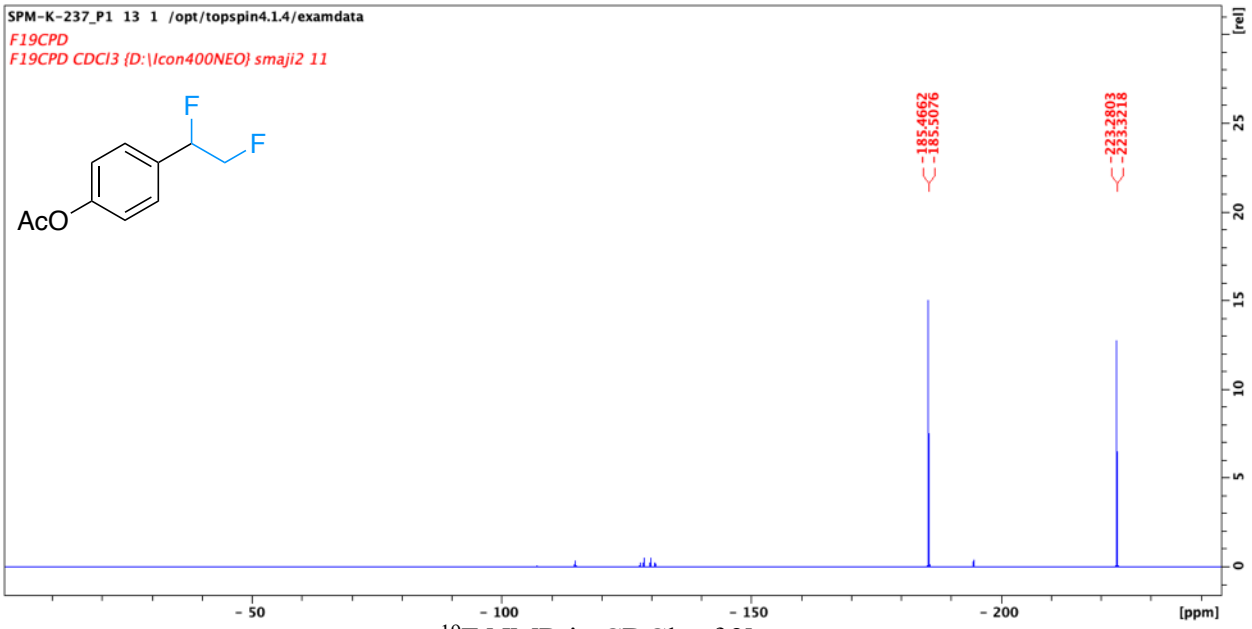
^{19}F NMR in $CDCl_3$ of **2a**



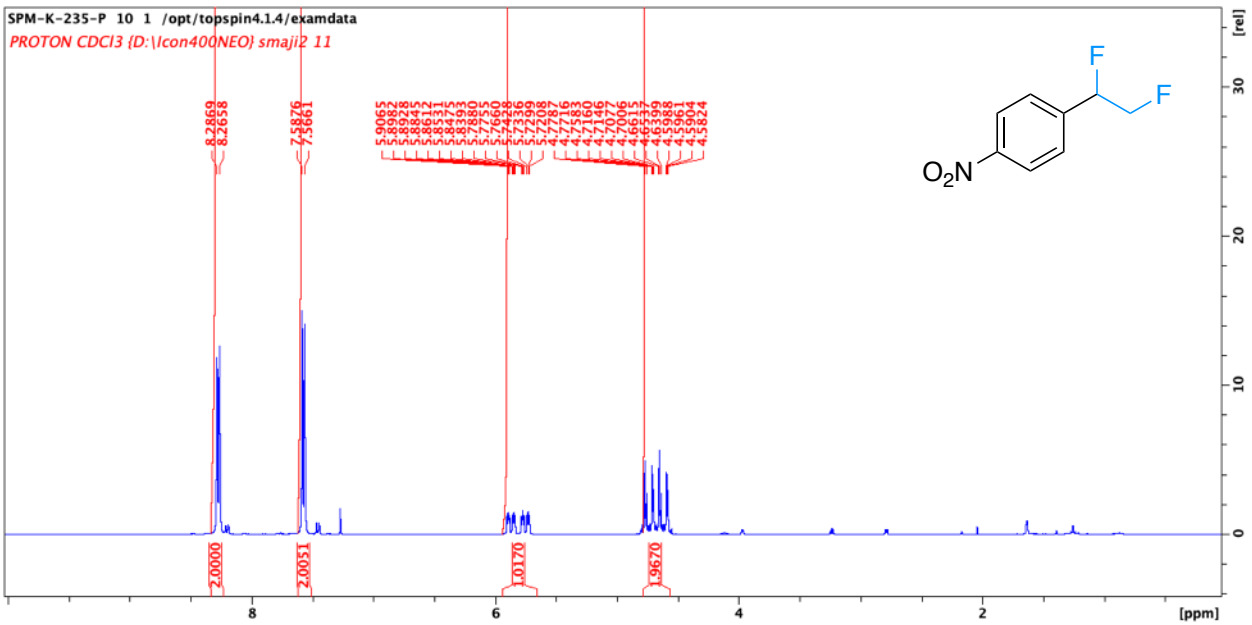
^{1}H NMR in $CDCl_3$ of **2b**



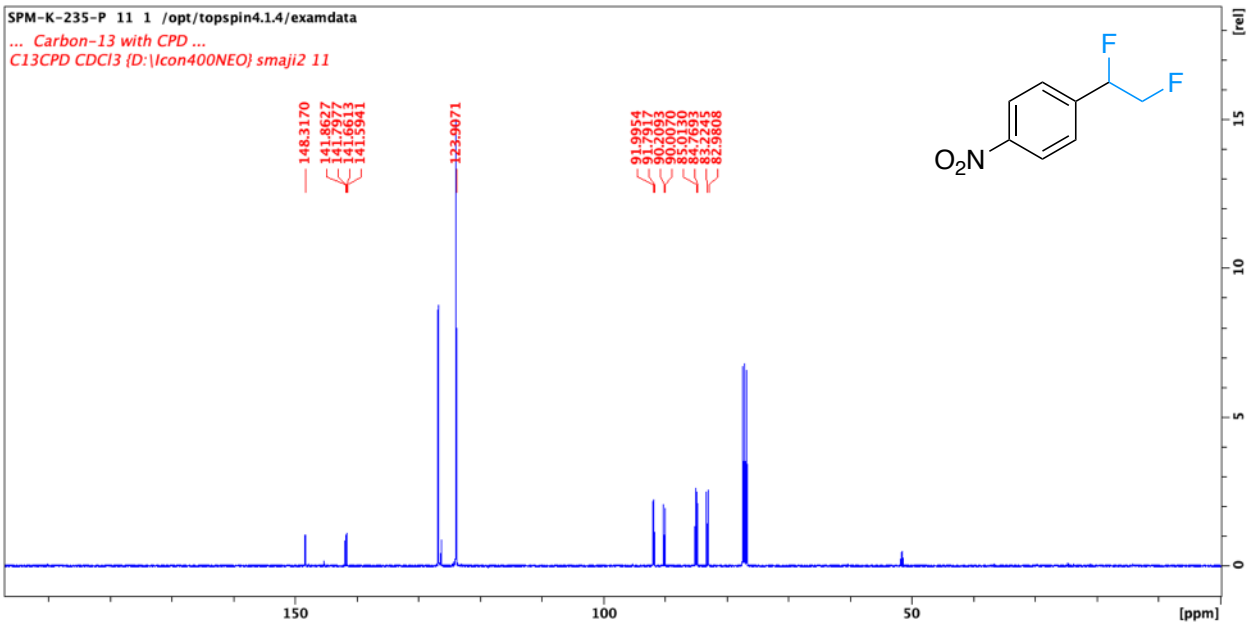
^{13}C NMR spectrum of **2b**



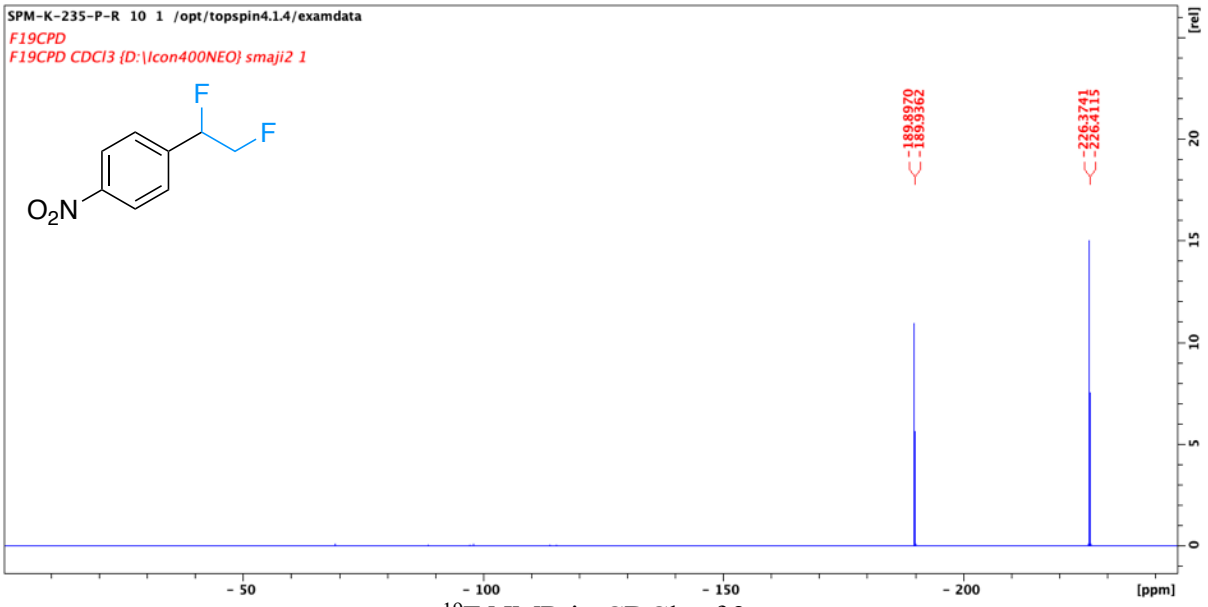
^{19}F NMR in $CDCl_3$ of **2b**



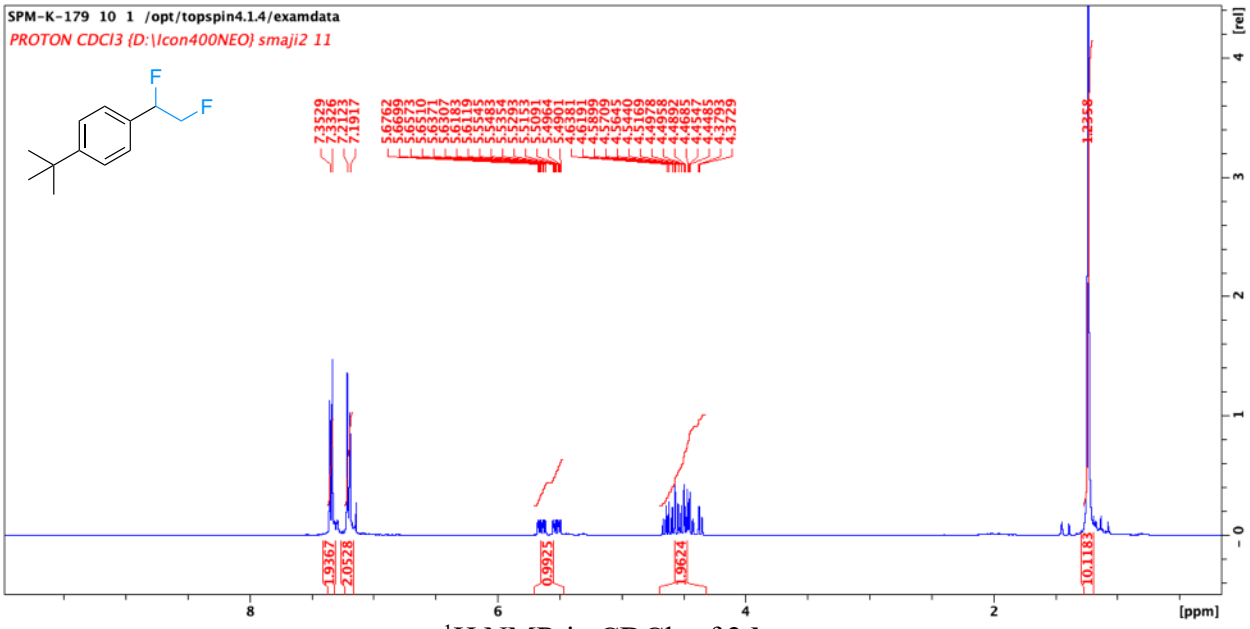
^{1}H NMR in $CDCl_3$ of **2c**



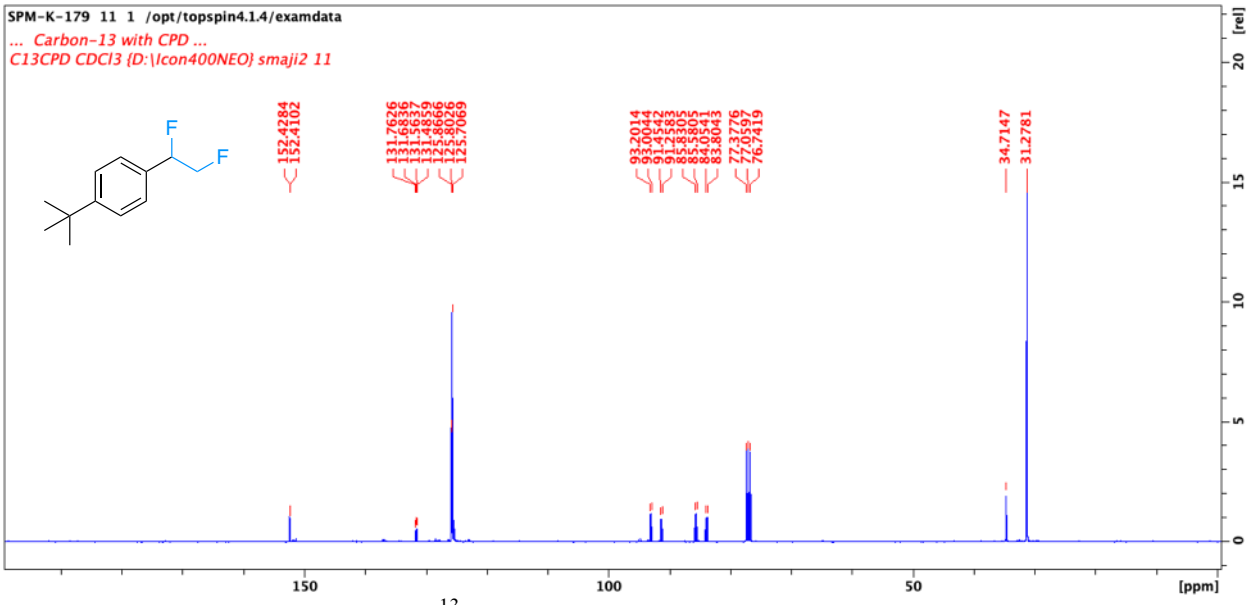
^{13}C NMR spectrum of **2c**



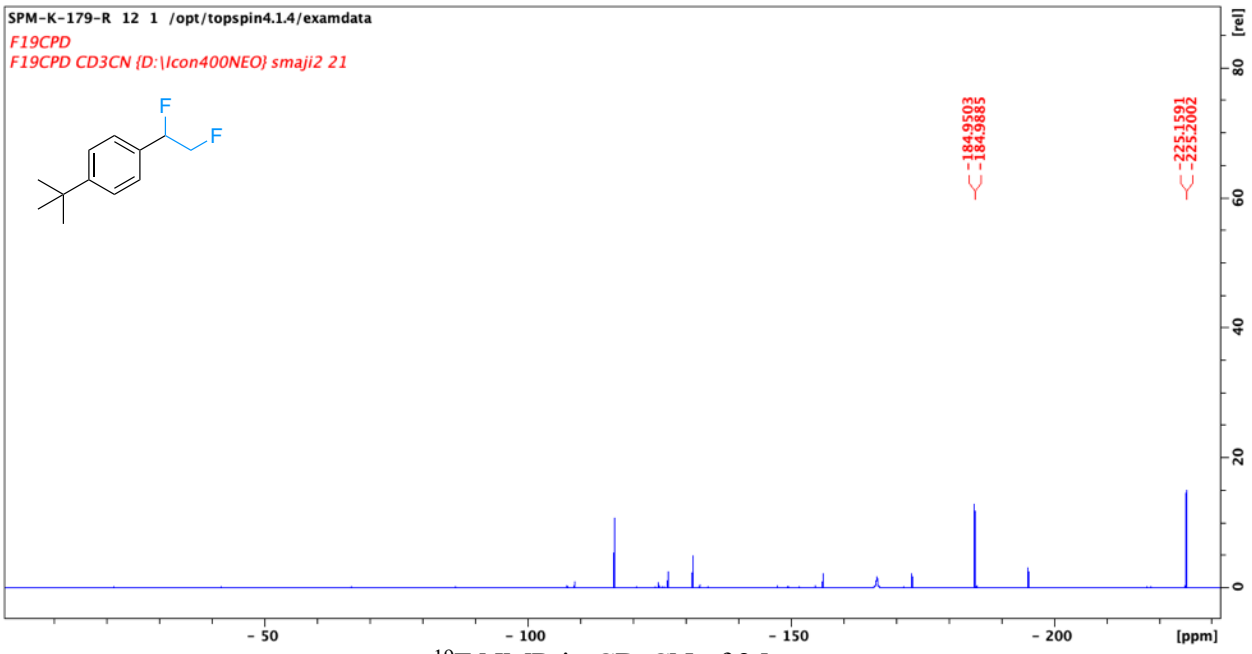
^{19}F NMR in $CDCl_3$ of **2c**



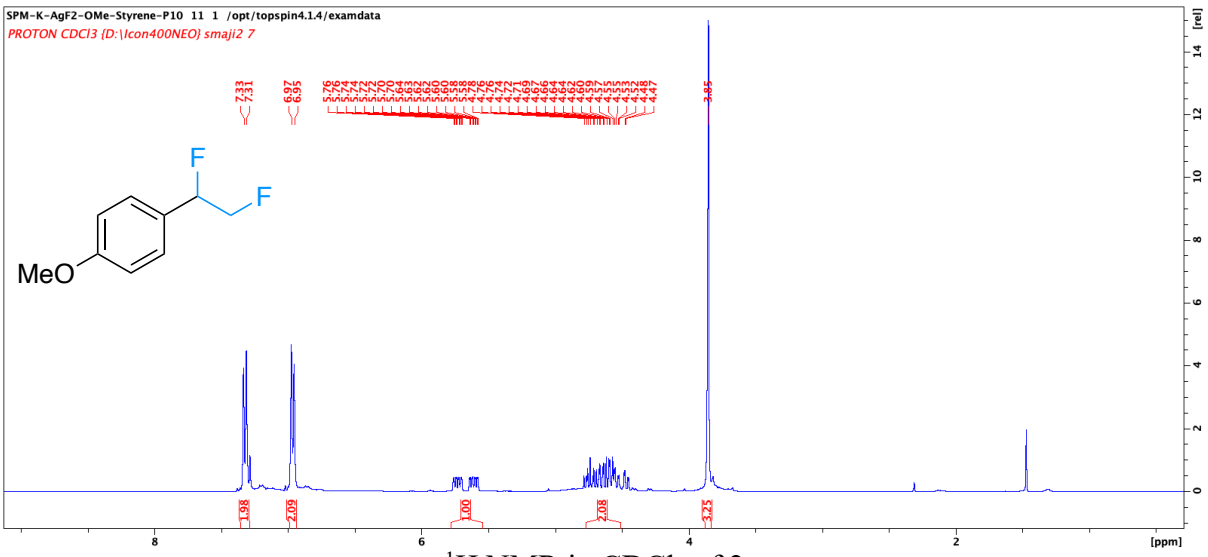
^{1}H NMR in $CDCl_3$ of **2d**



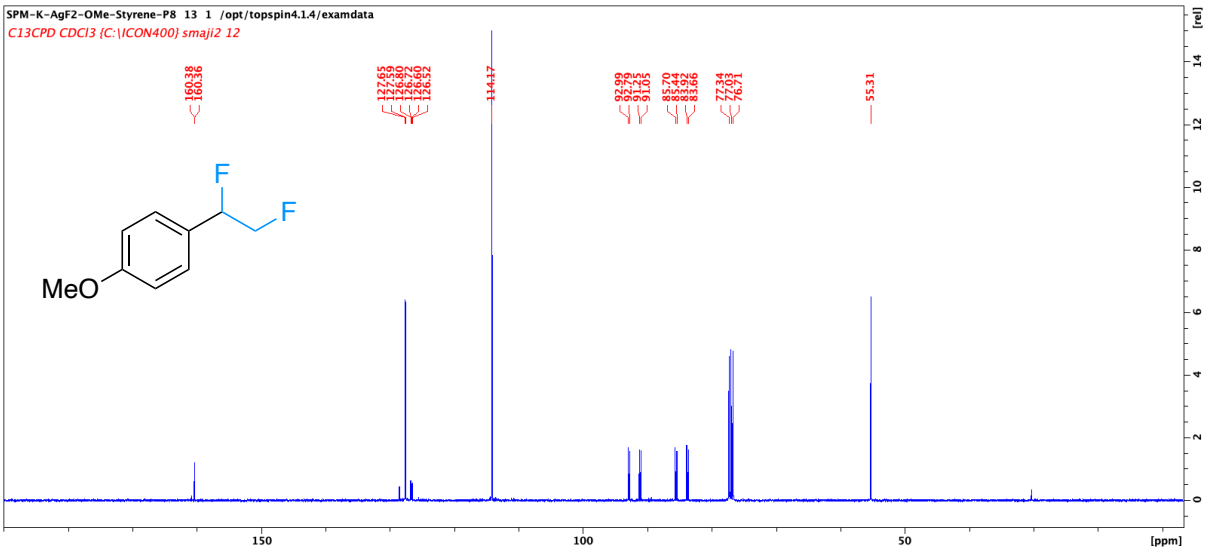
^{13}C NMR spectrum of **2d**



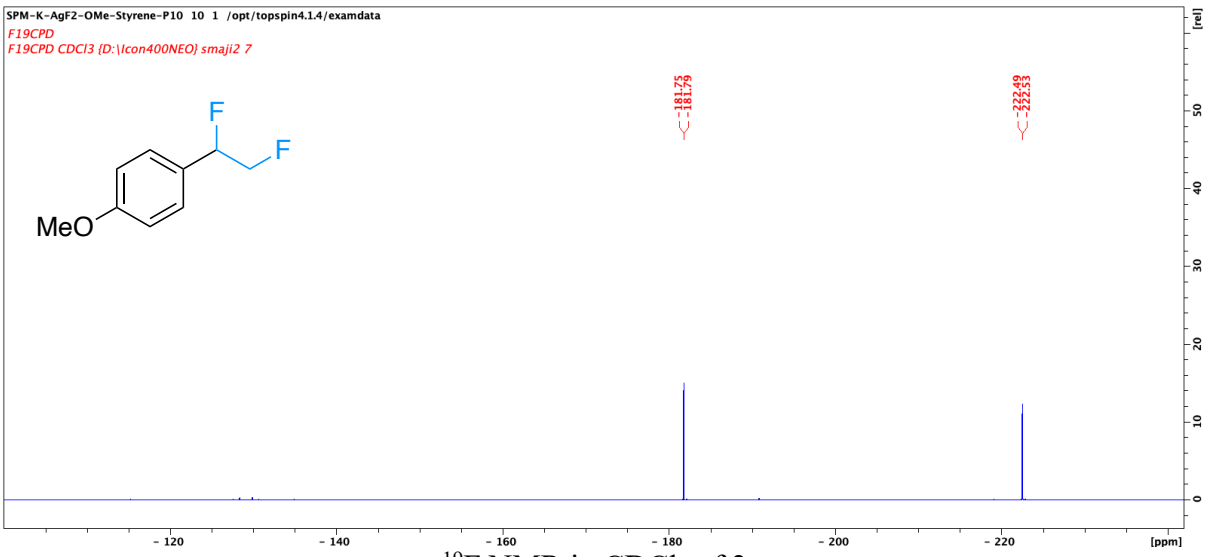
^{19}F NMR in CD_3CN of **2d**



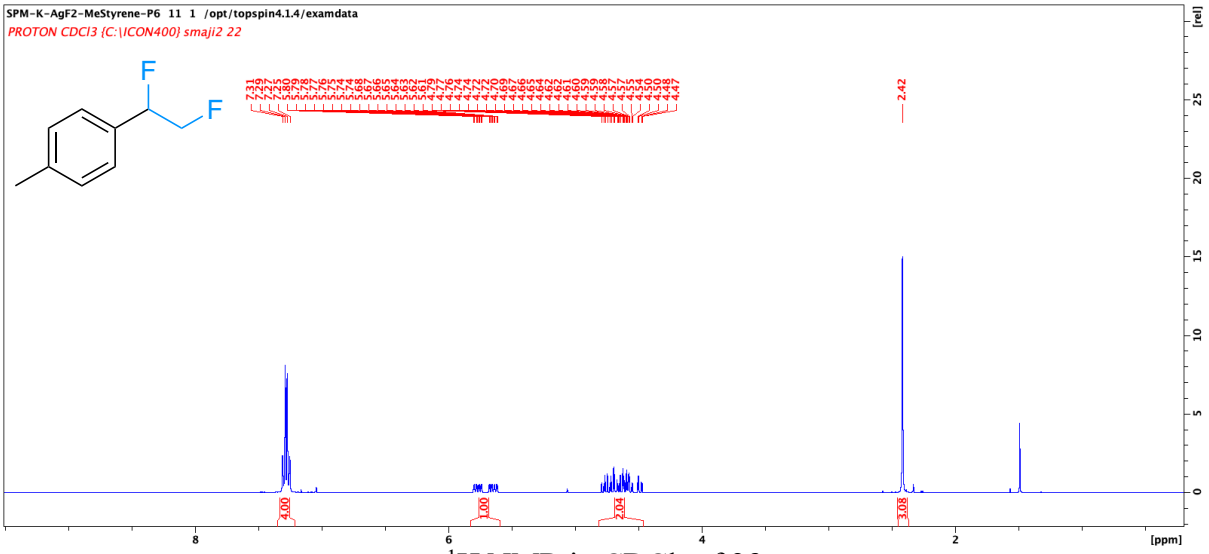
^{1}H NMR in $CDCl_3$ of **2e**



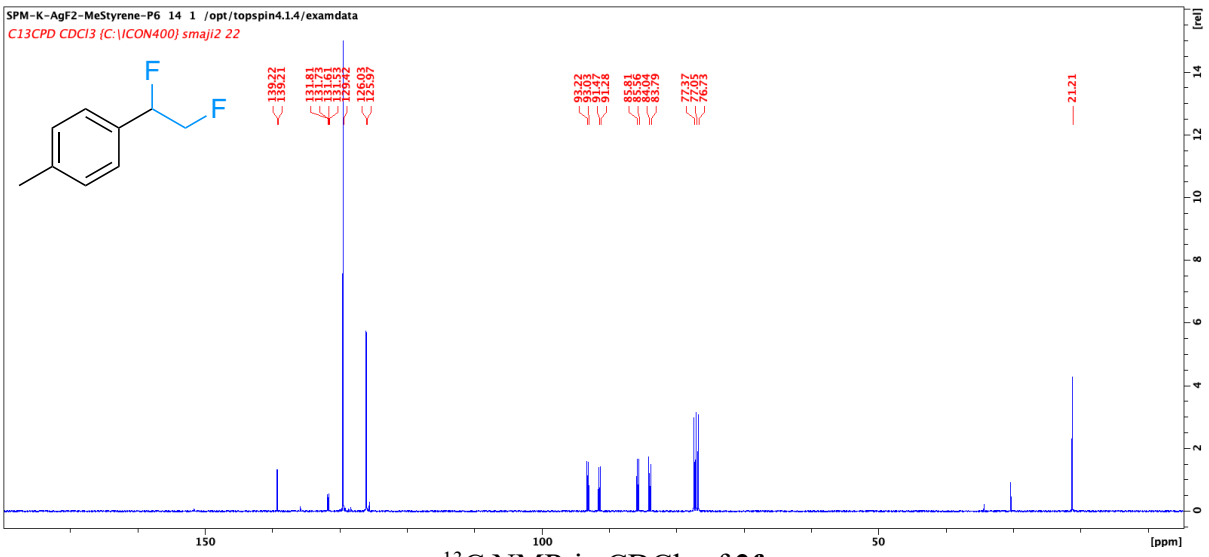
^{13}C NMR in $CDCl_3$ of **2e**



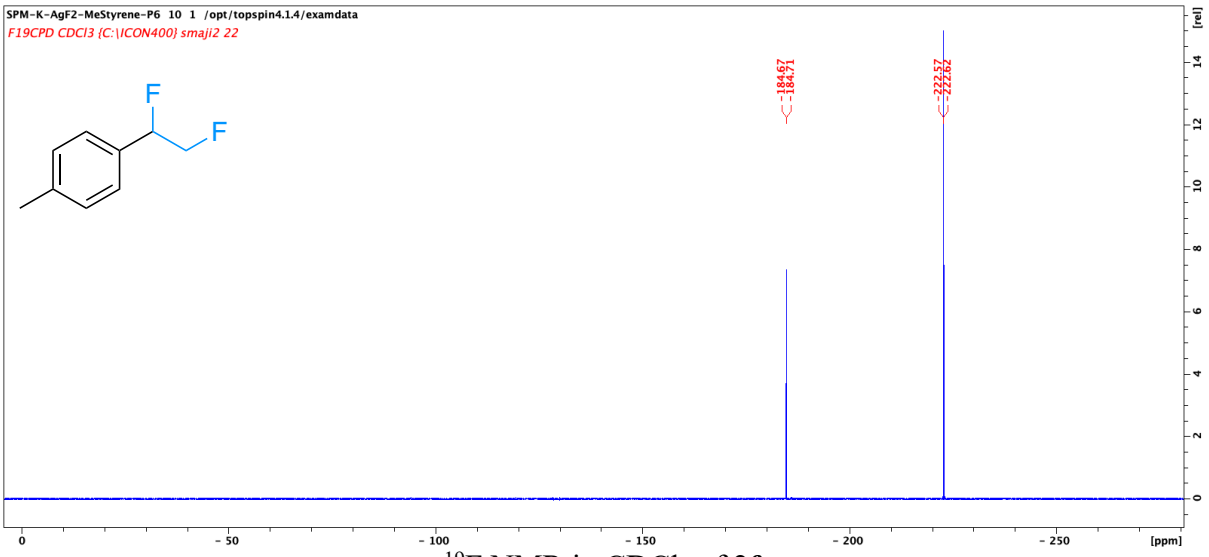
^{19}F NMR in $CDCl_3$ of **2e**



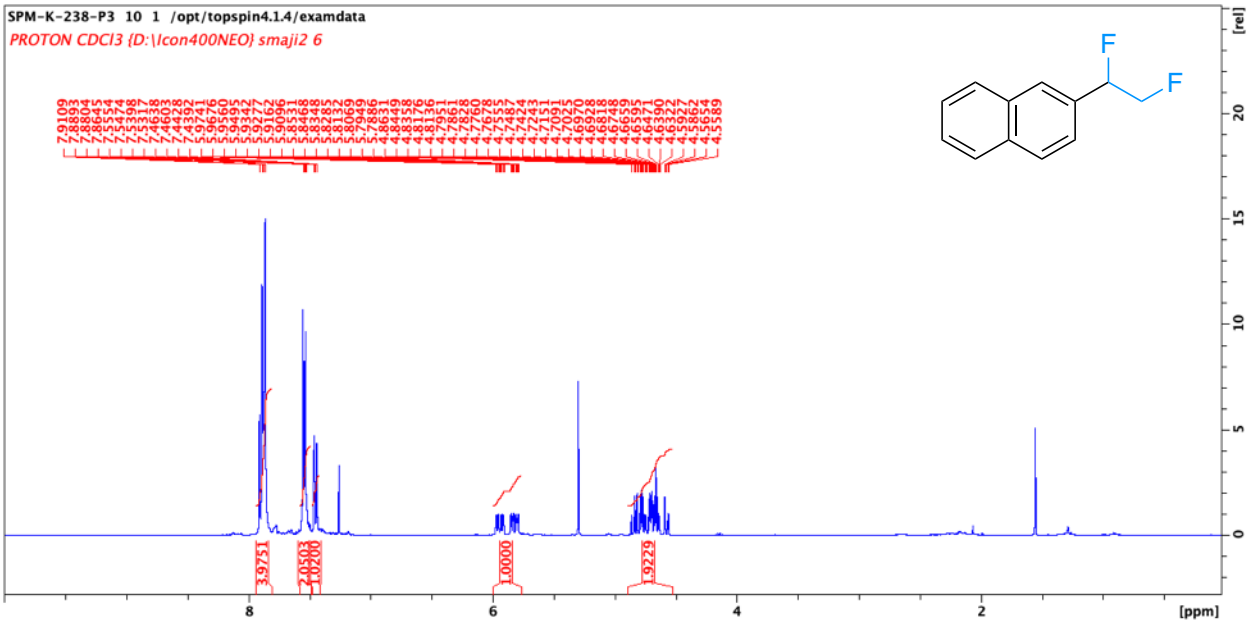
^{1}H NMR in $CDCl_3$ of **2f**



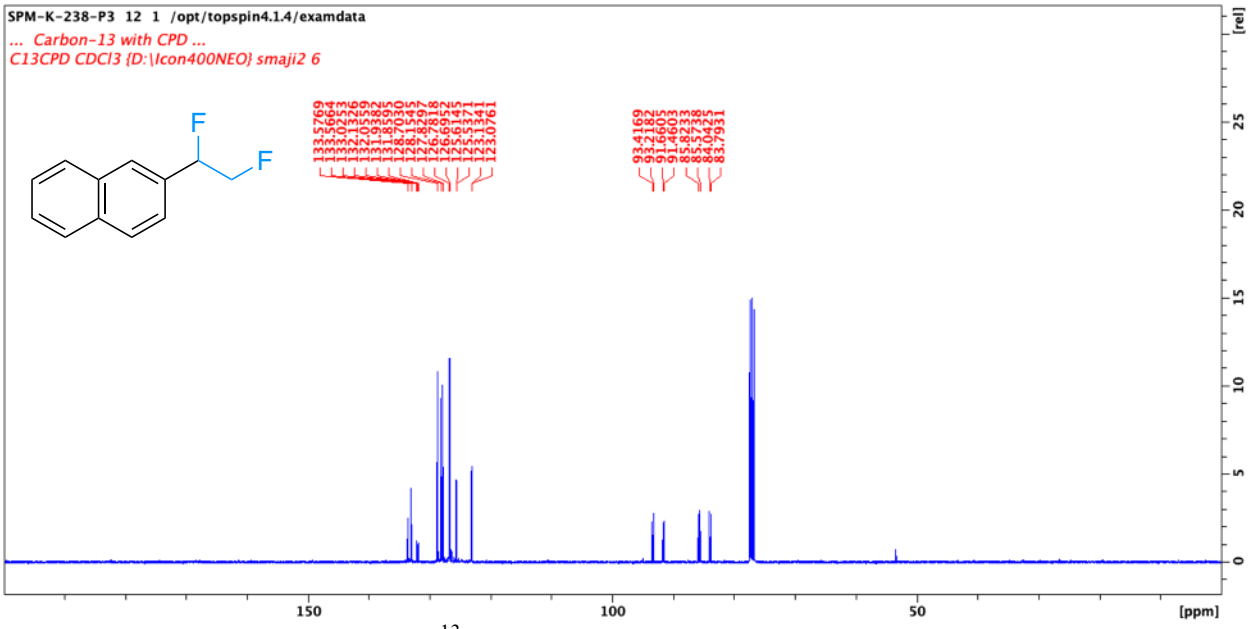
^{13}C NMR in $CDCl_3$ of **2f**



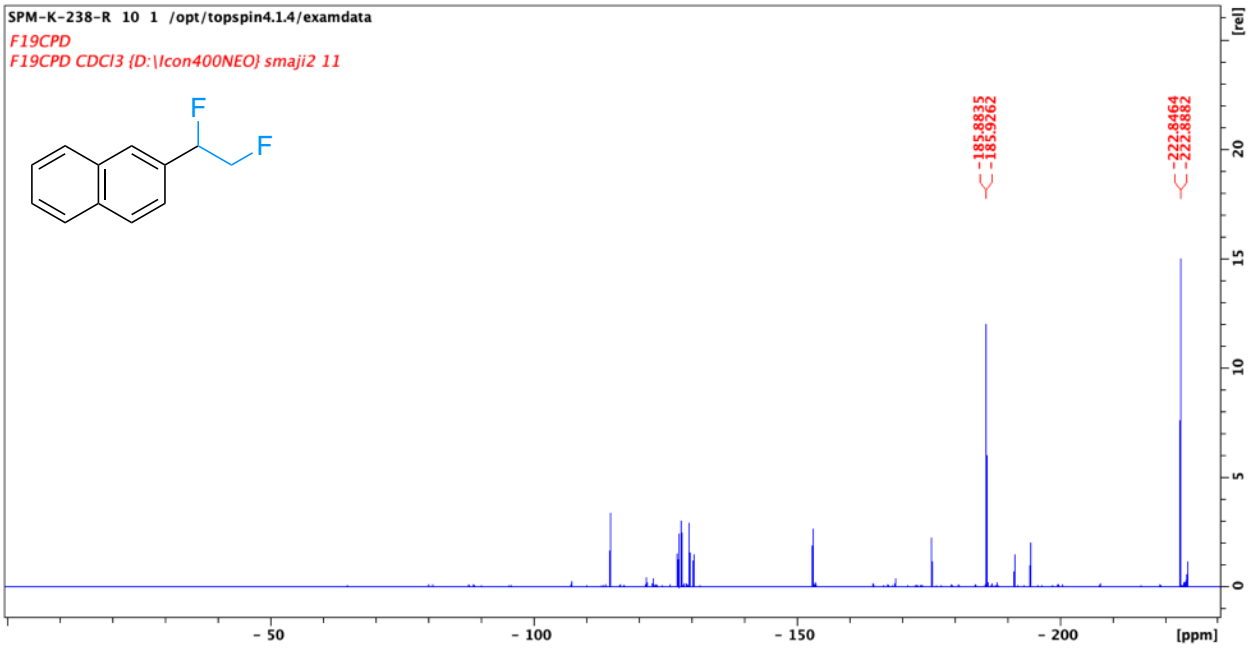
^{19}F NMR in $CDCl_3$ of **2f**



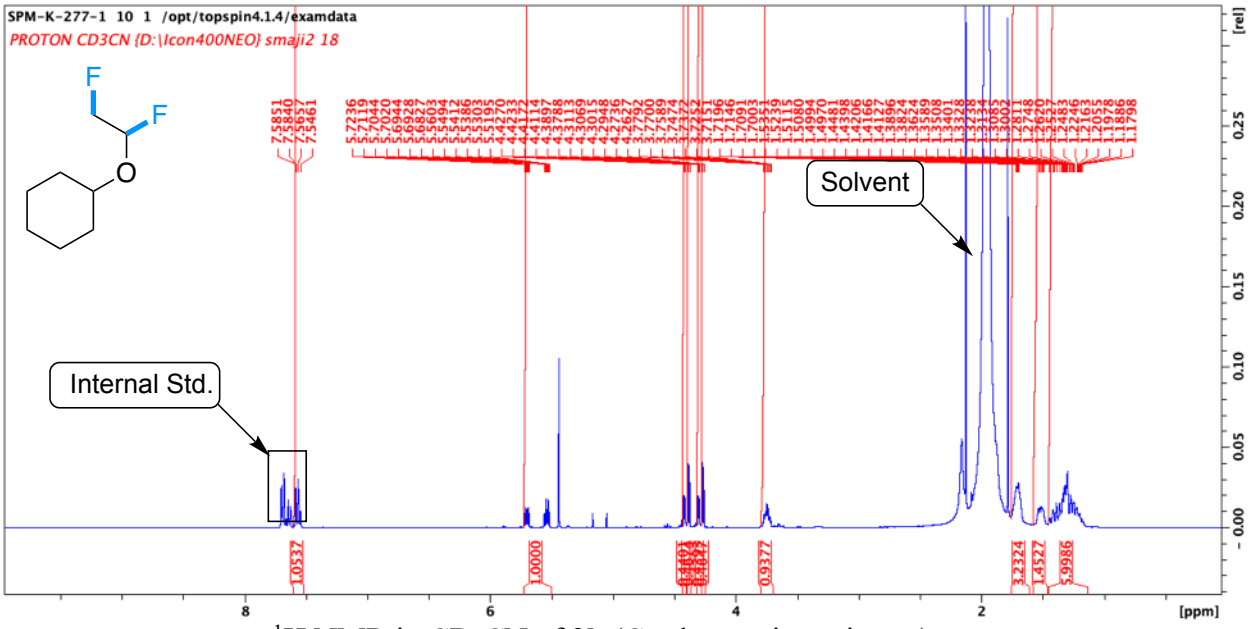
^{1}H NMR in $CDCl_3$ of **2g**



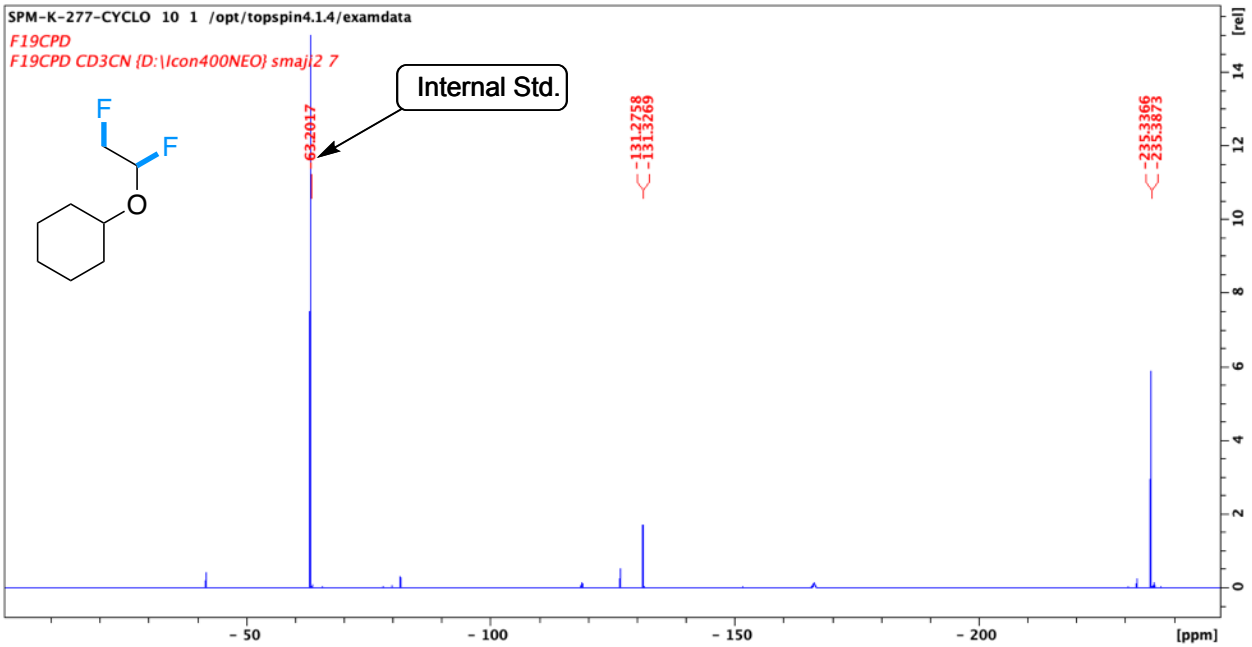
^{13}C NMR spectrum of **2g**



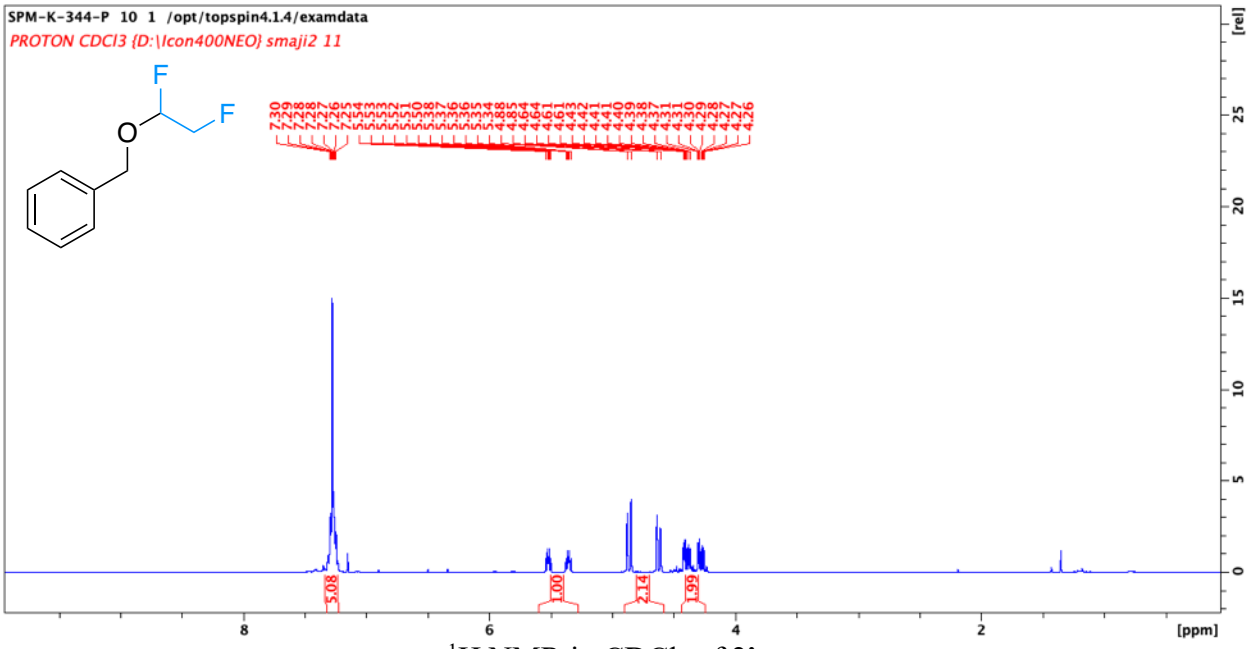
^{19}F NMR in $CDCl_3$ of **2g**



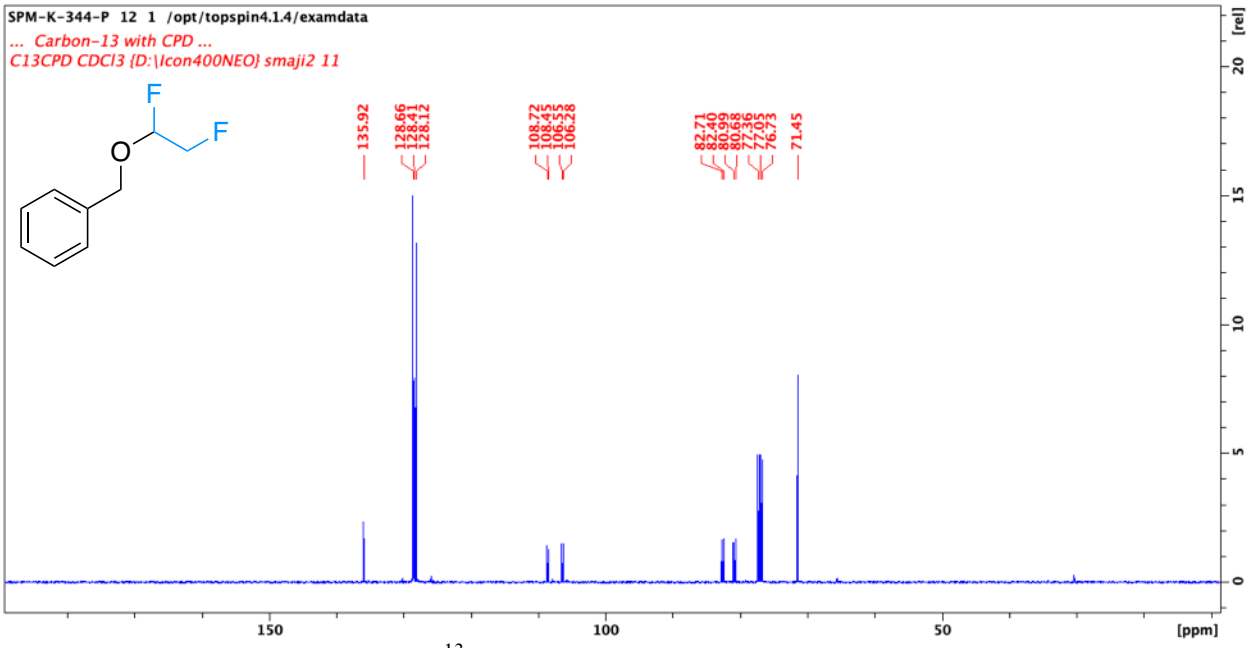
^{1}H NMR in CD_3CN of **2h** (Crude reaction mixture)



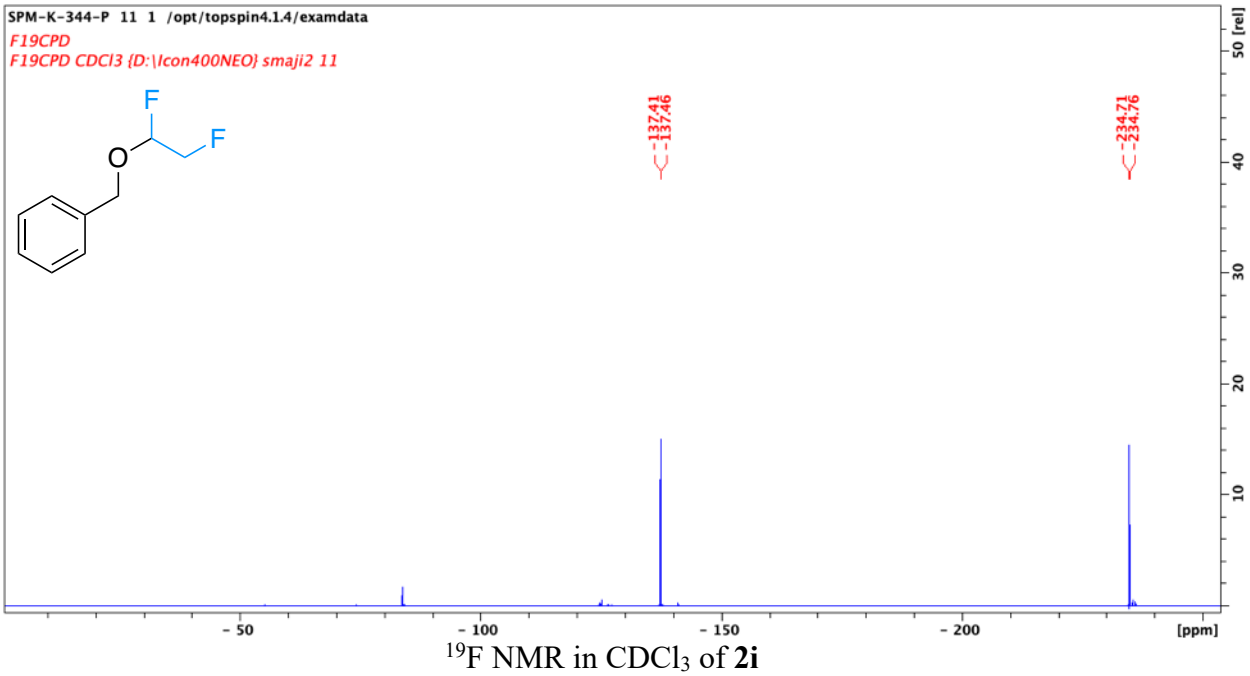
^{19}F NMR in CD_3CN of **2h** (Crude reaction mixture)



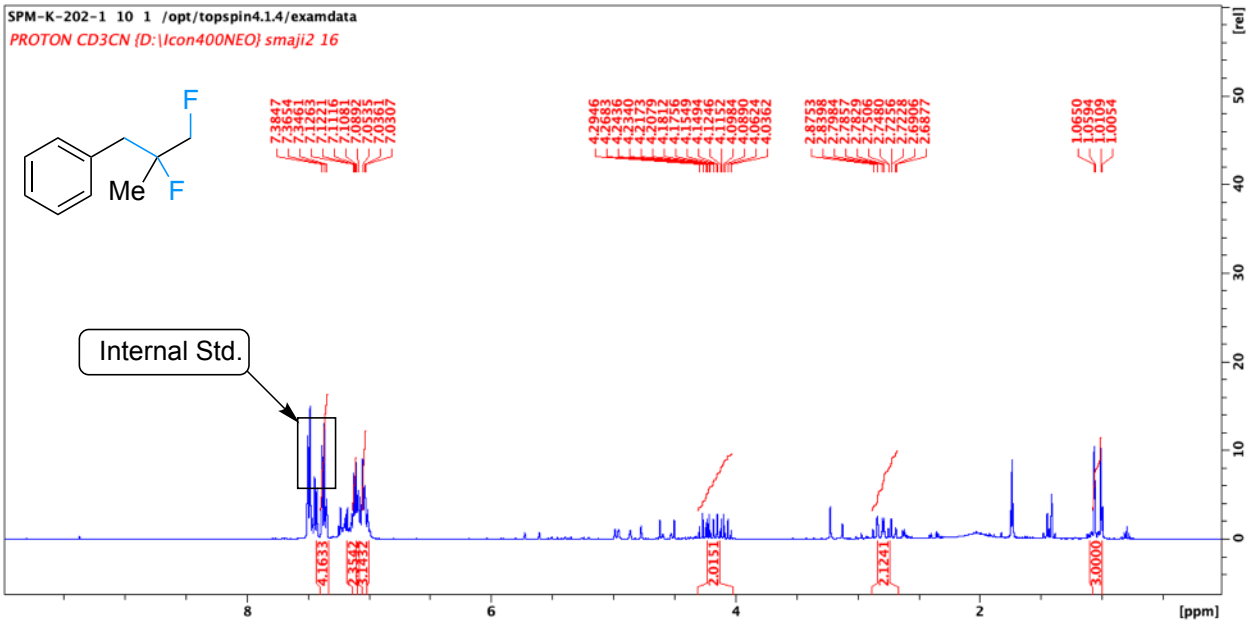
^{1}H NMR in $CDCl_3$ of **2i**



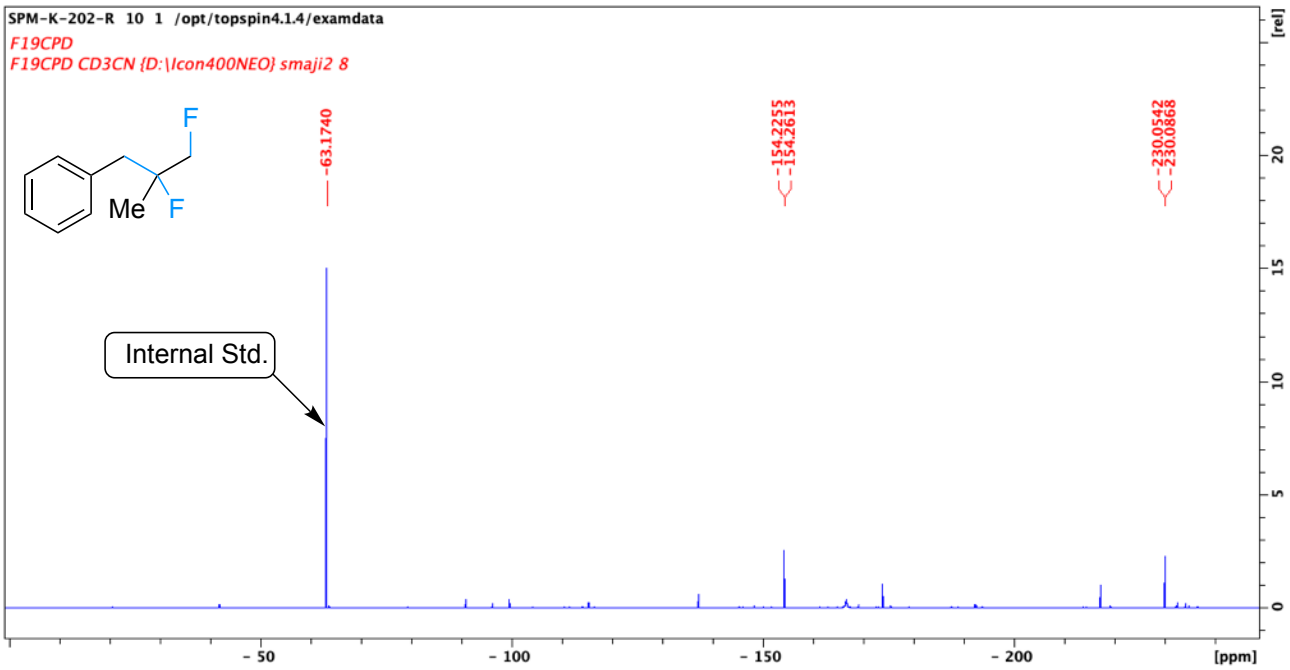
^{13}C NMR spectrum of **2i**



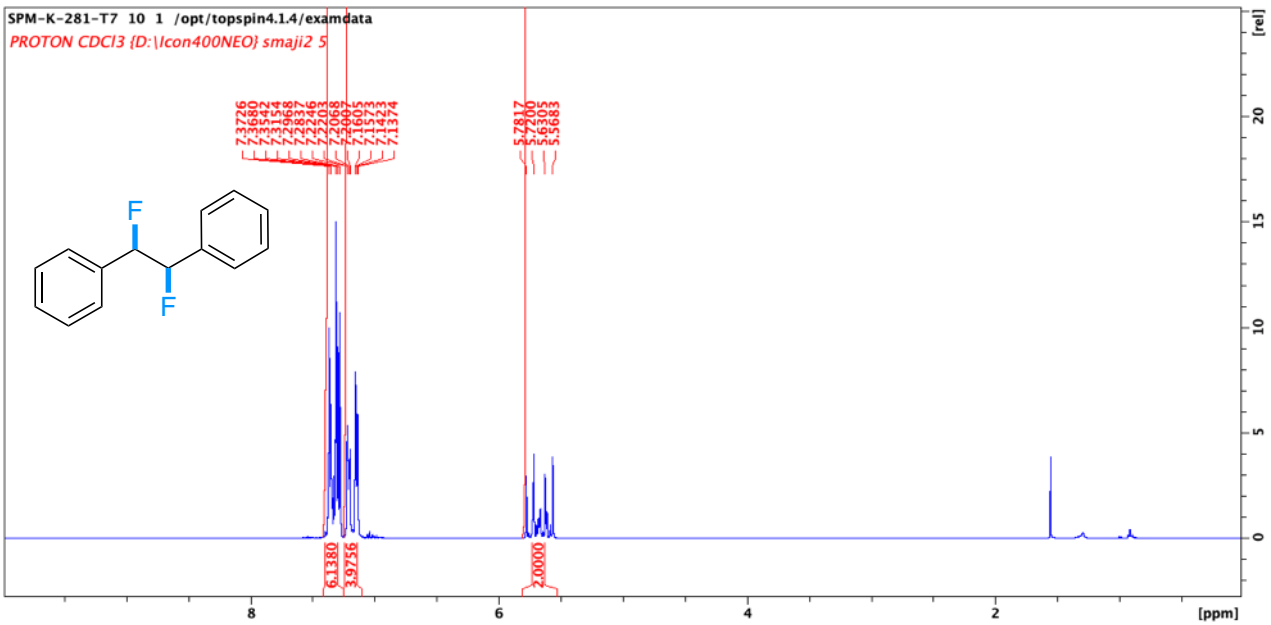
^{19}F NMR in $CDCl_3$ of **2i**



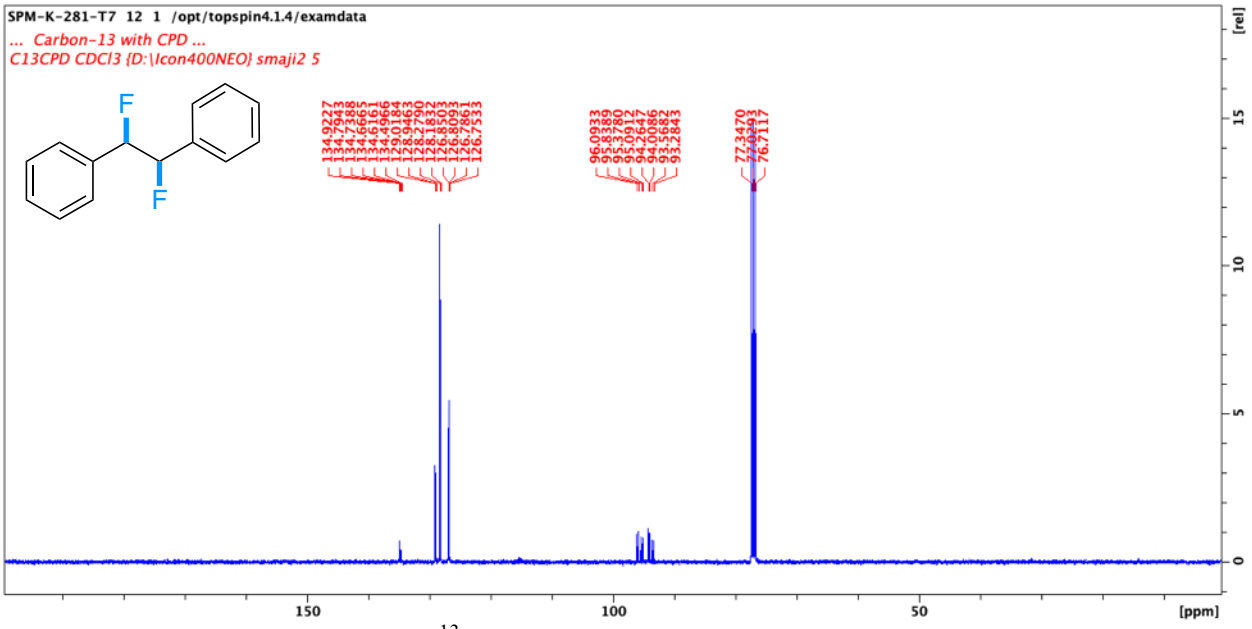
^{1}H NMR in CD_3CN of **2j** (Crude reaction mixture)



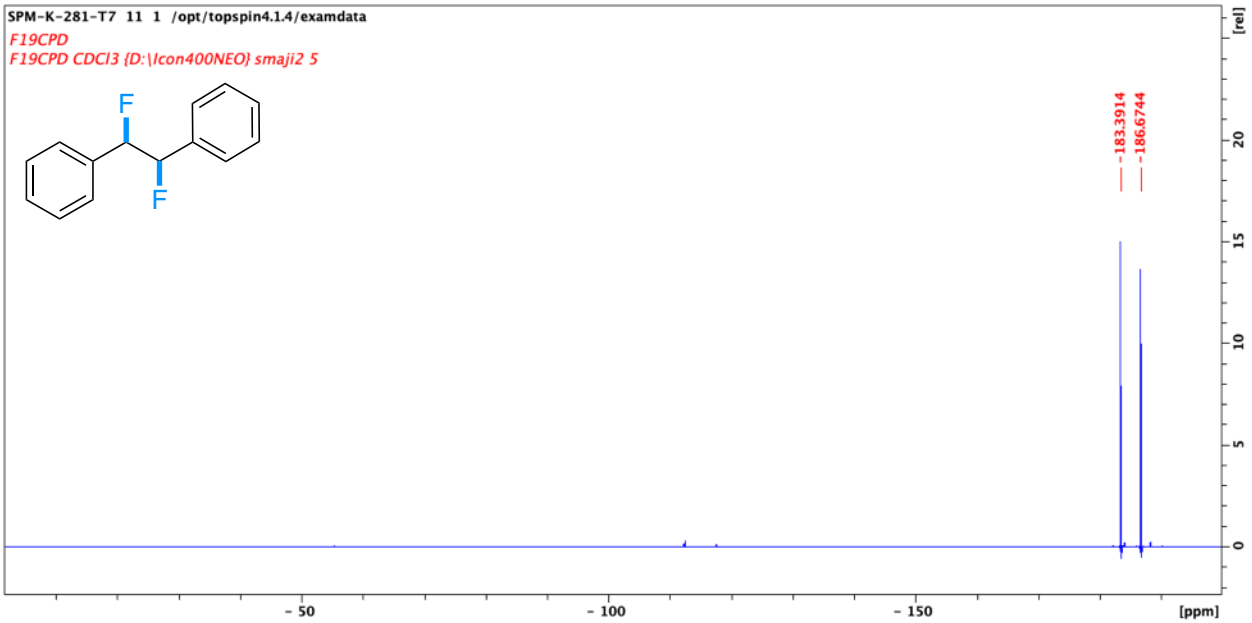
^{19}F NMR in CD_3CN of **2j** (Crude reaction mixture)



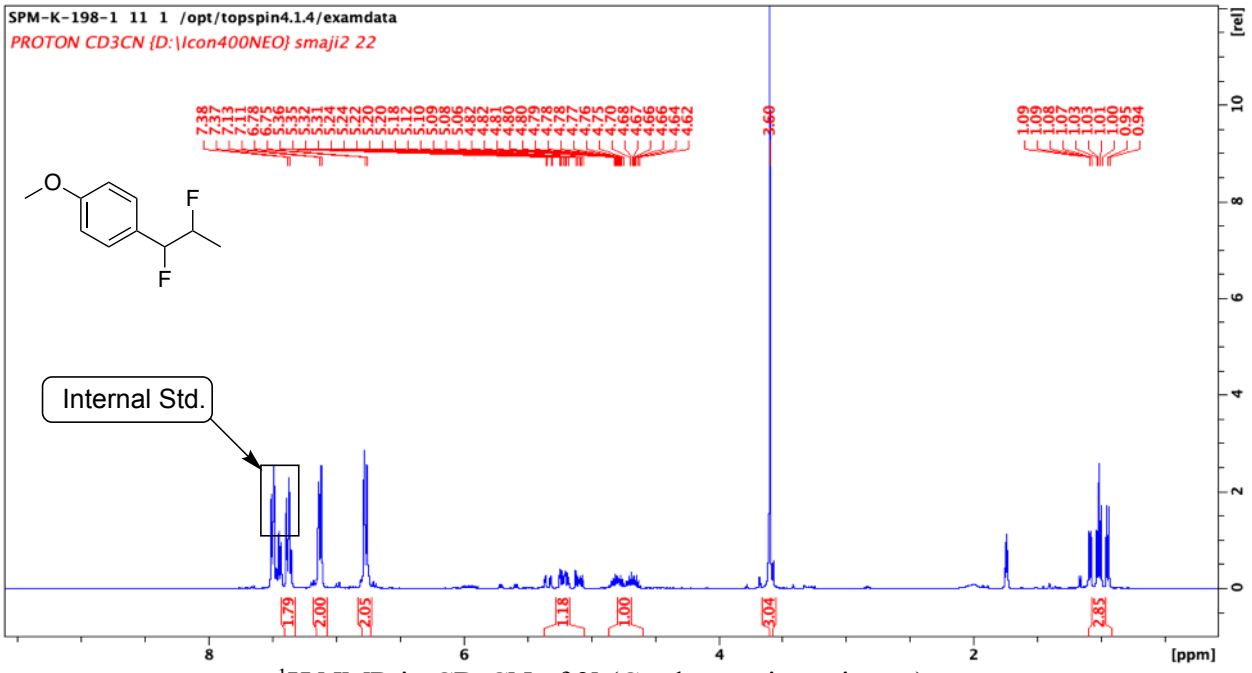
^{1}H NMR in $CDCl_3$ of **2k**



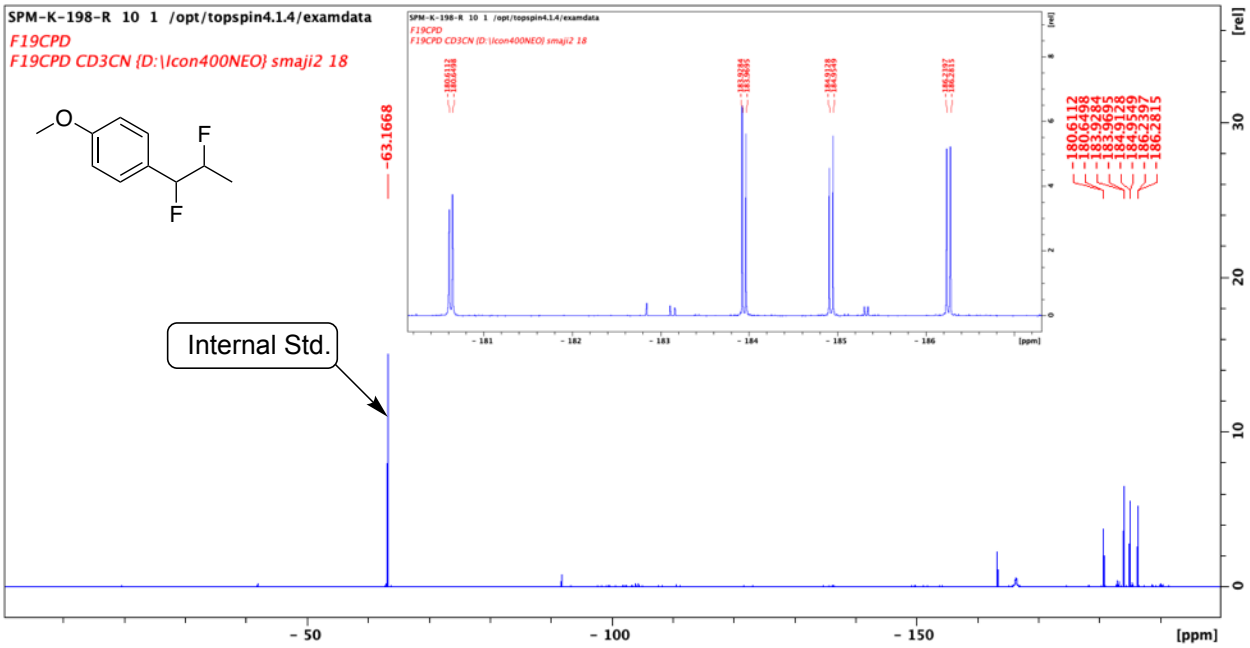
^{13}C NMR spectrum of **2k**



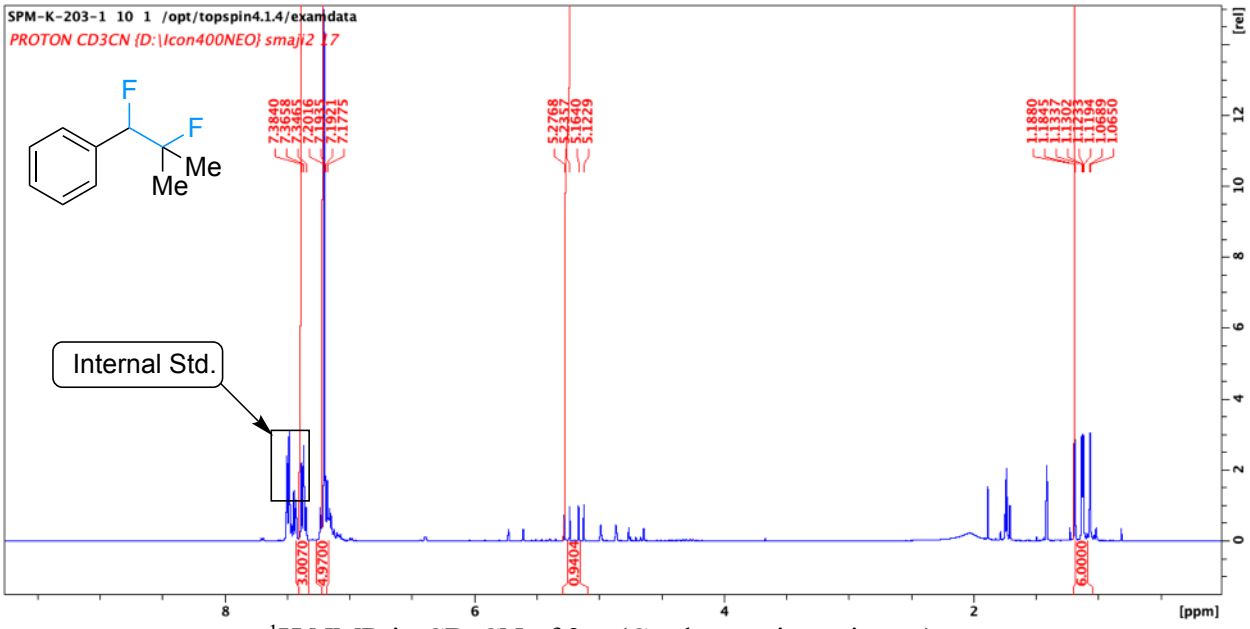
^{19}F NMR in $CDCl_3$ of **2k**



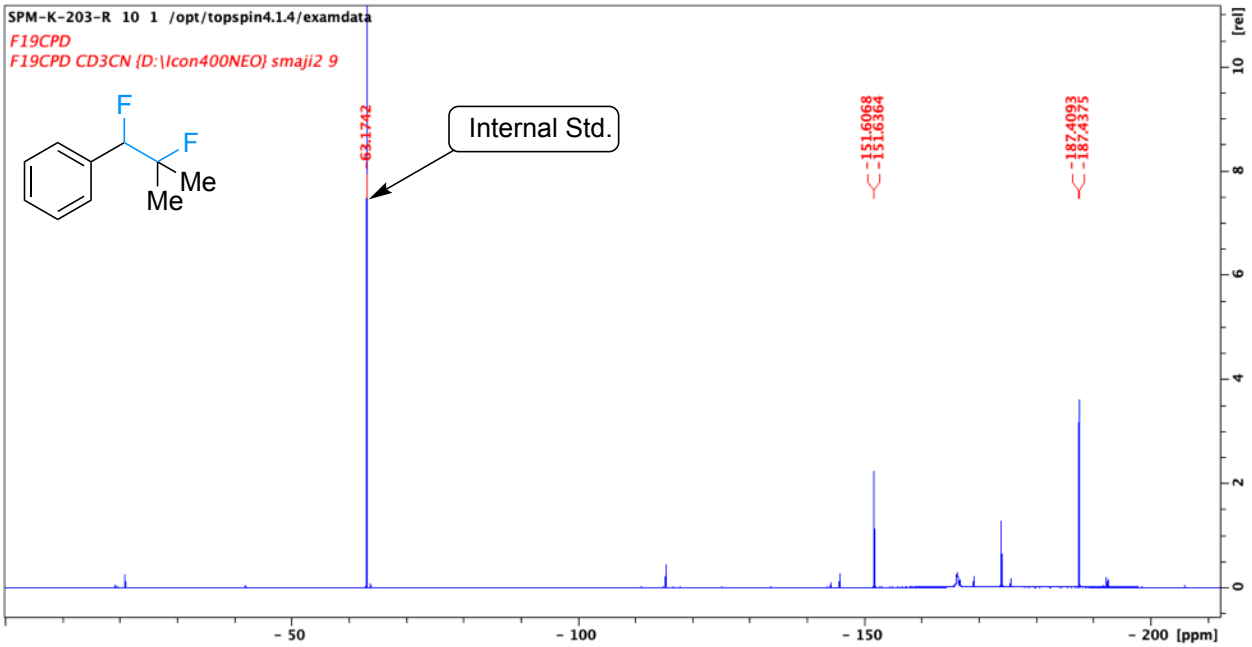
^{1}H NMR in CD_3CN of **2l** (Crude reaction mixture)



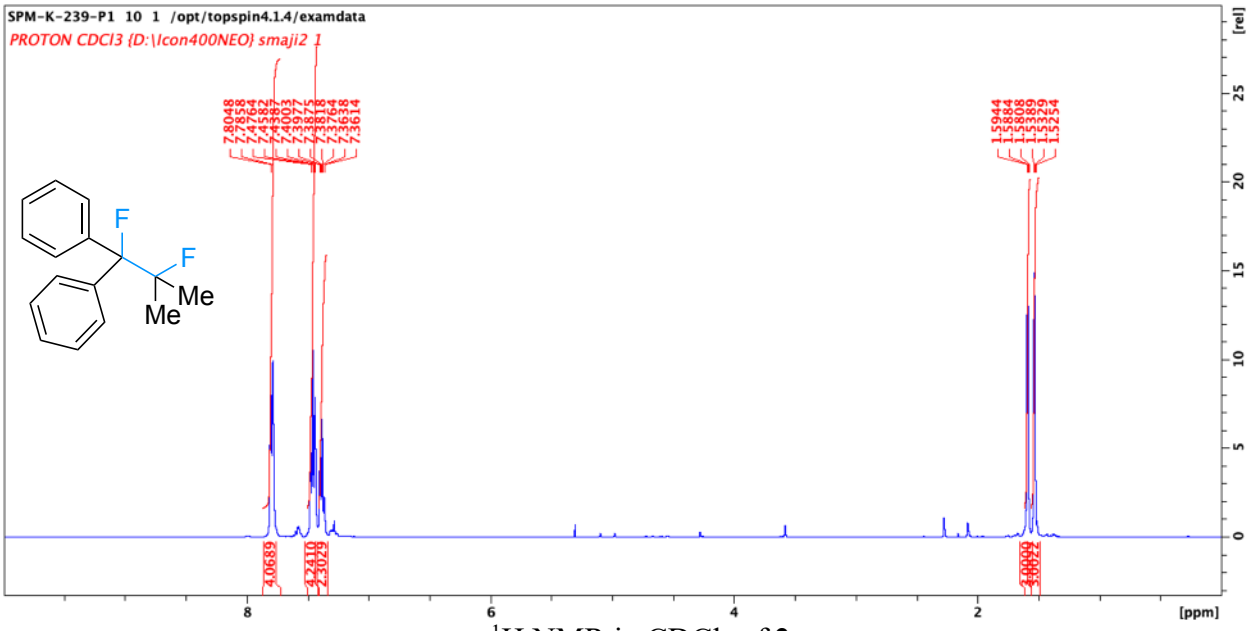
^{19}F NMR in CD_3CN of **2l** (Crude reaction mixture)



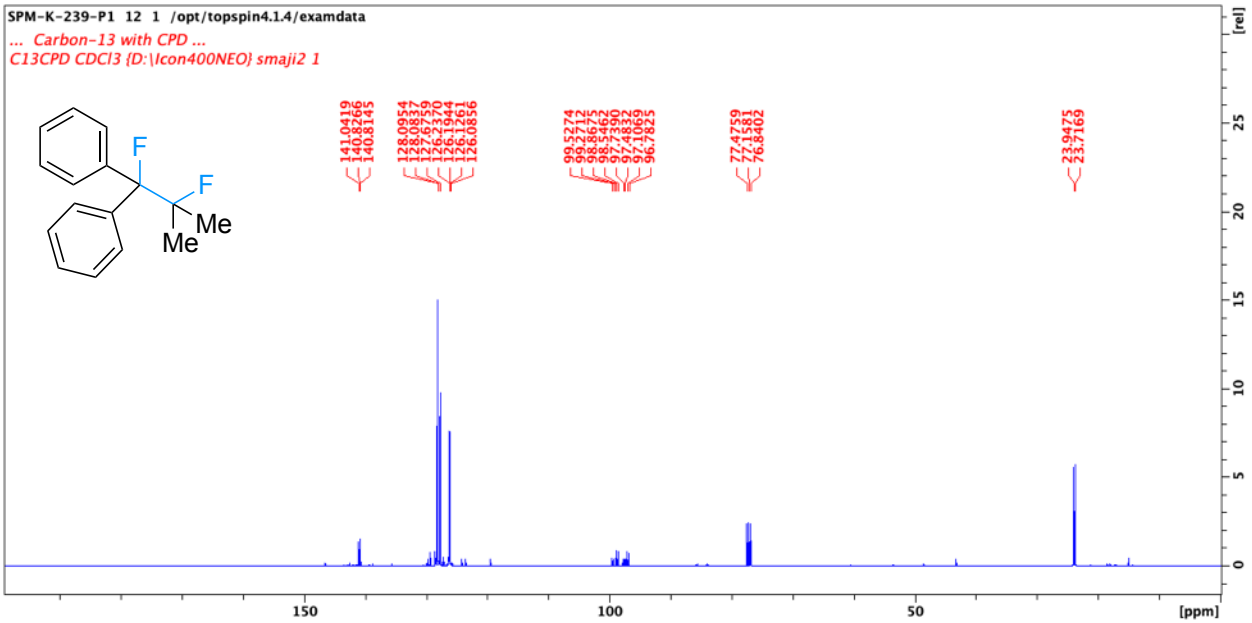
^{1}H NMR in CD_3CN of **2m** (Crude reaction mixture)



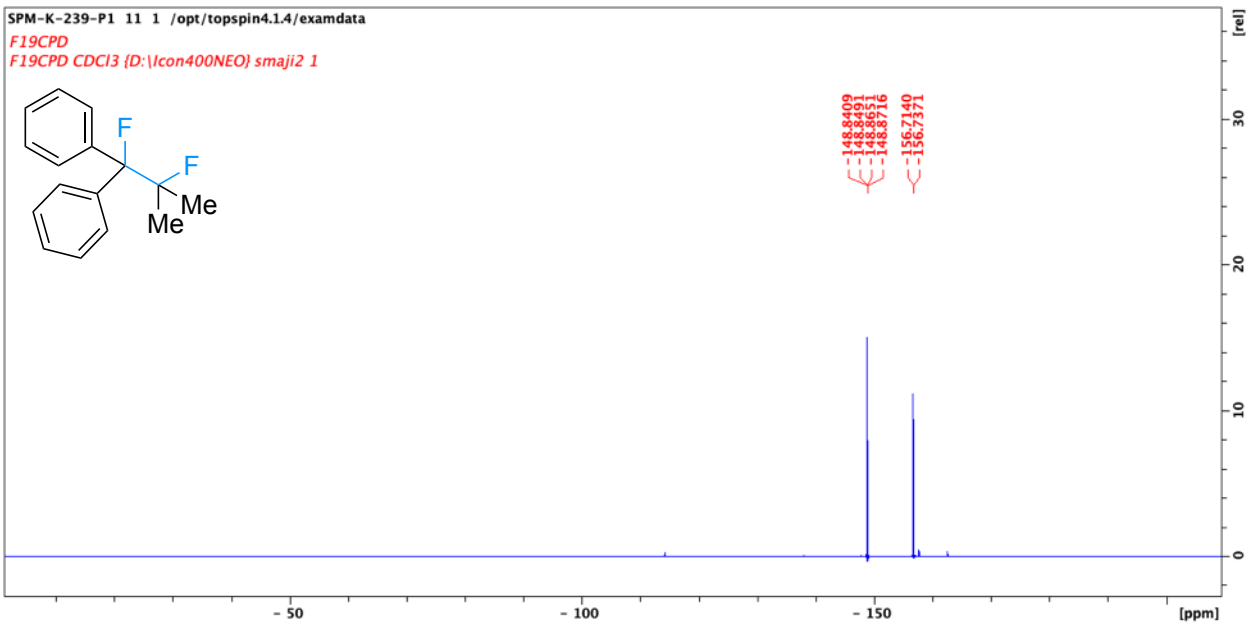
^{1}H NMR in CD_3CN of **2m** (Crude reaction mixture)



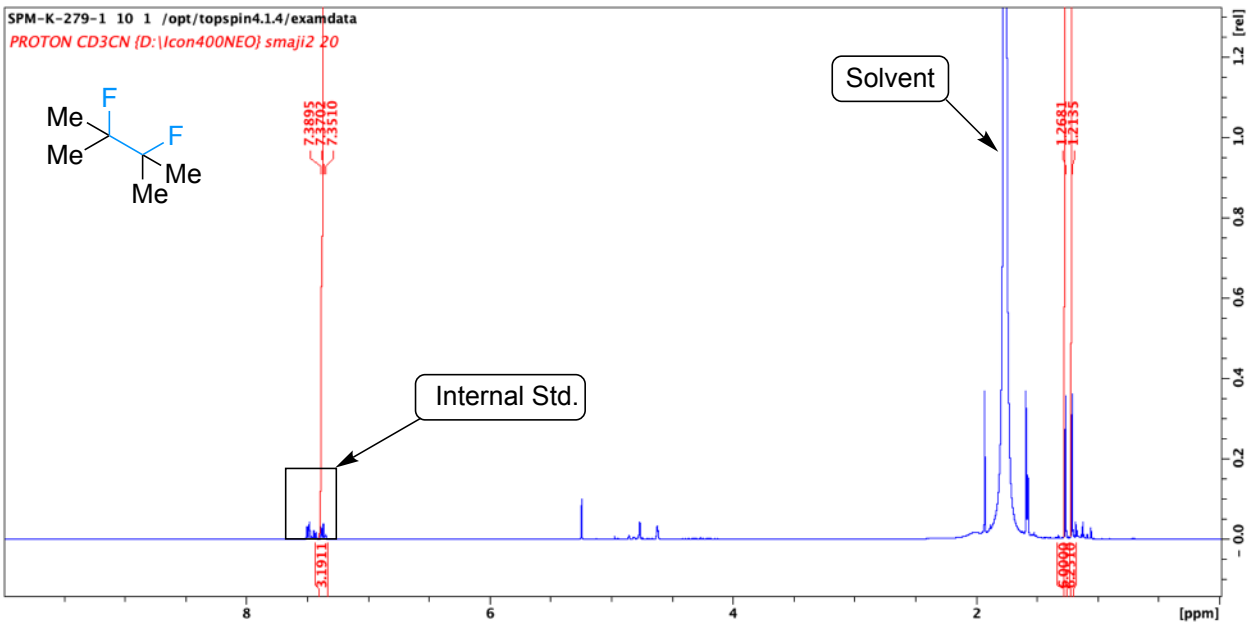
^{1}H NMR in $CDCl_3$ of **2n**



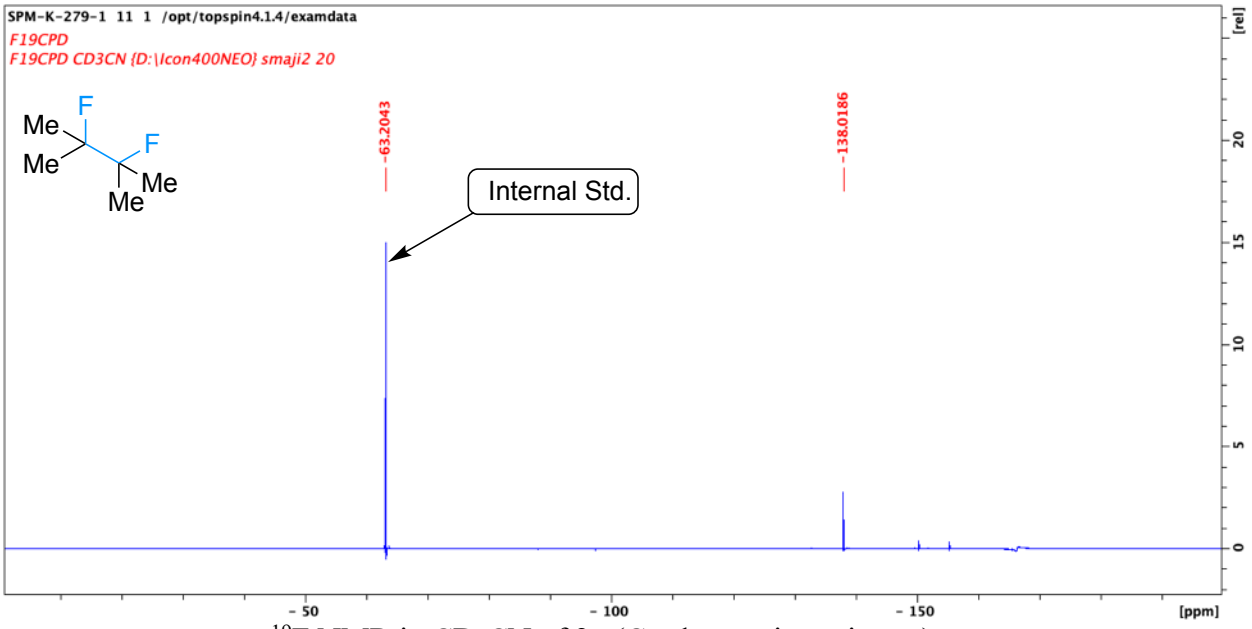
^{13}C NMR spectrum of **2n**



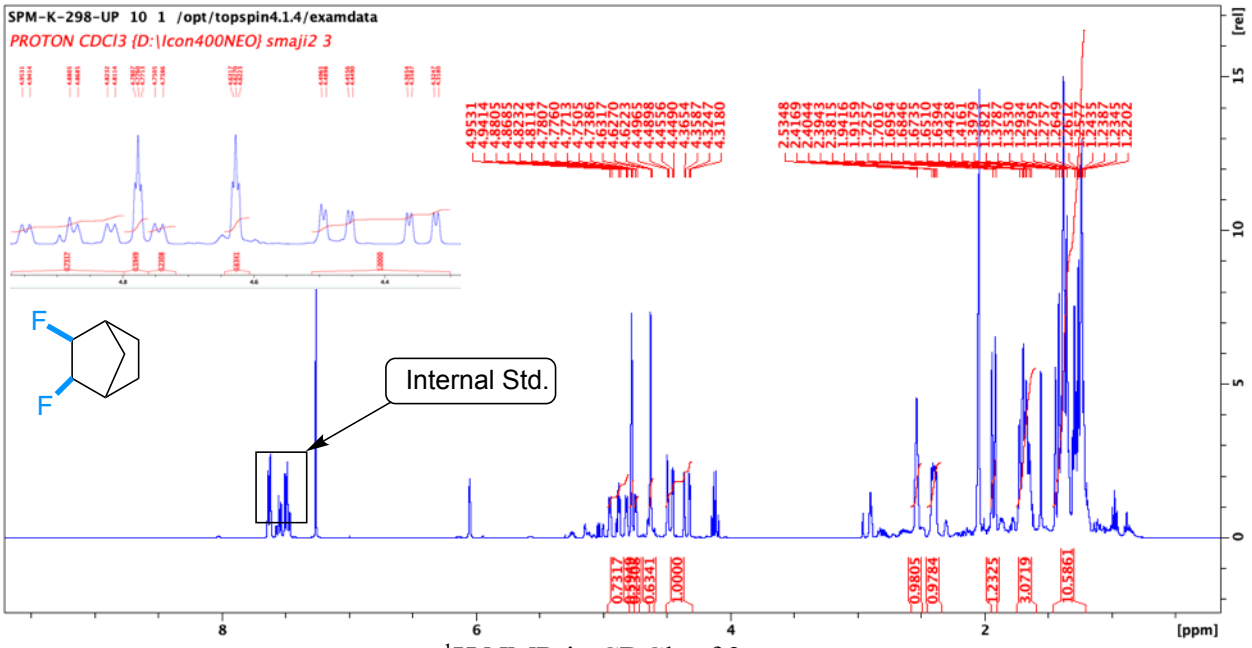
^{19}F NMR in $CDCl_3$ of **2n**



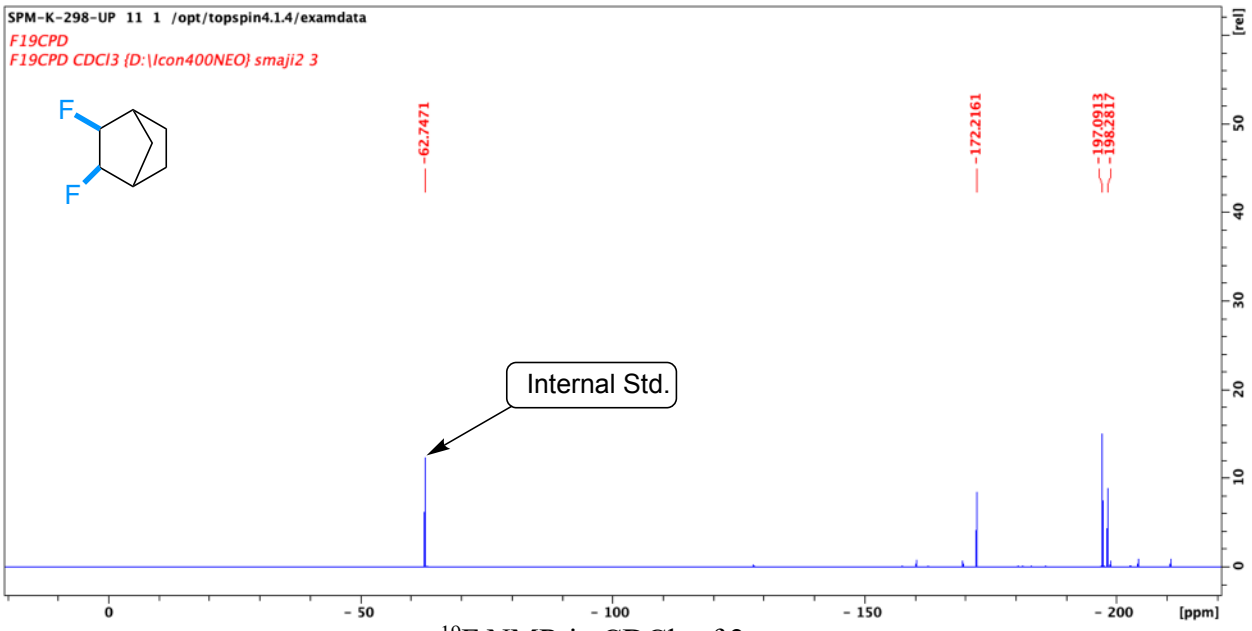
^{1}H NMR in CD_3CN of **2o** (Crude reaction mixture)



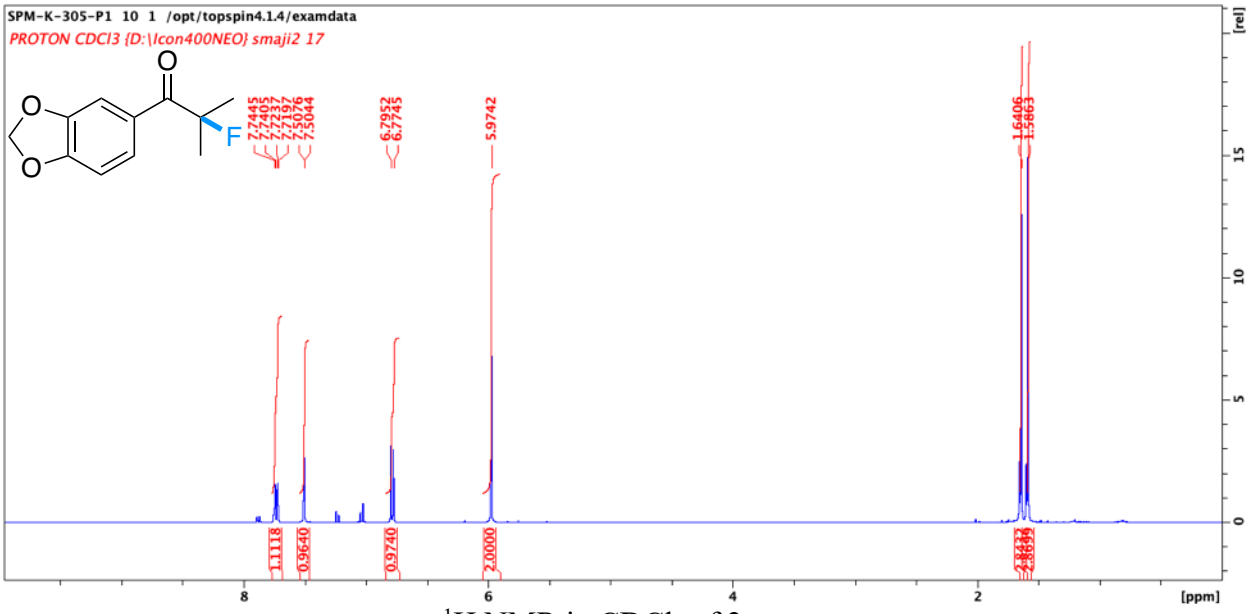
^{19}F NMR in CD_3CN of **2o** (Crude reaction mixture)



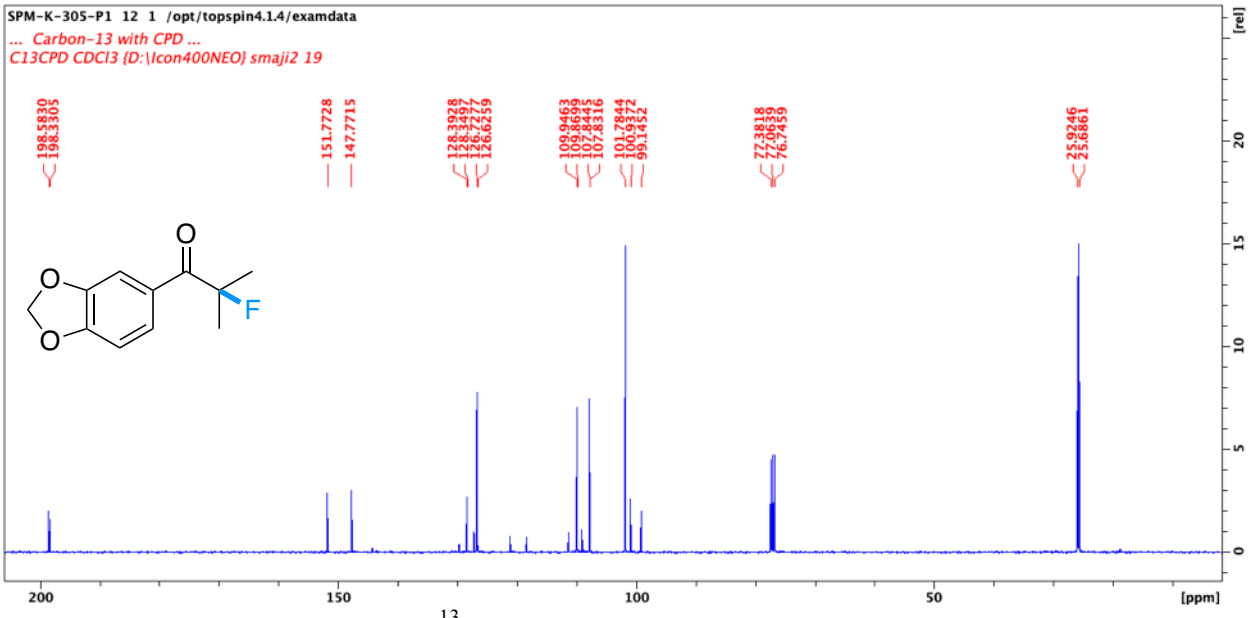
^{1}H NMR in $CDCl_3$ of **2p**



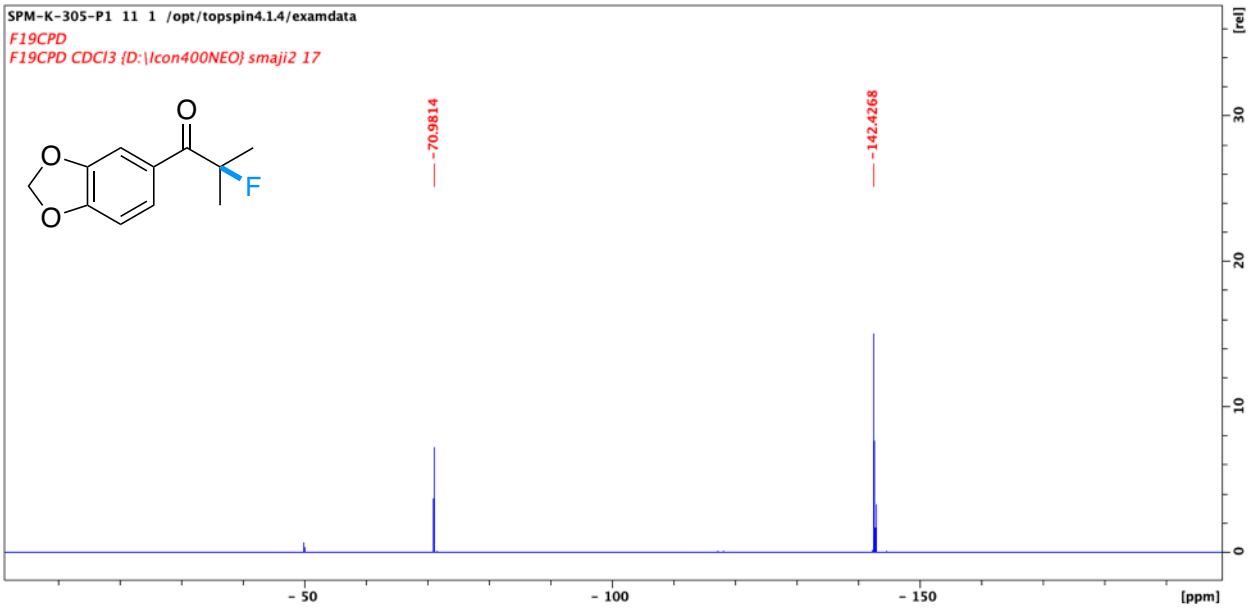
^{19}F NMR in $CDCl_3$ of **2p**



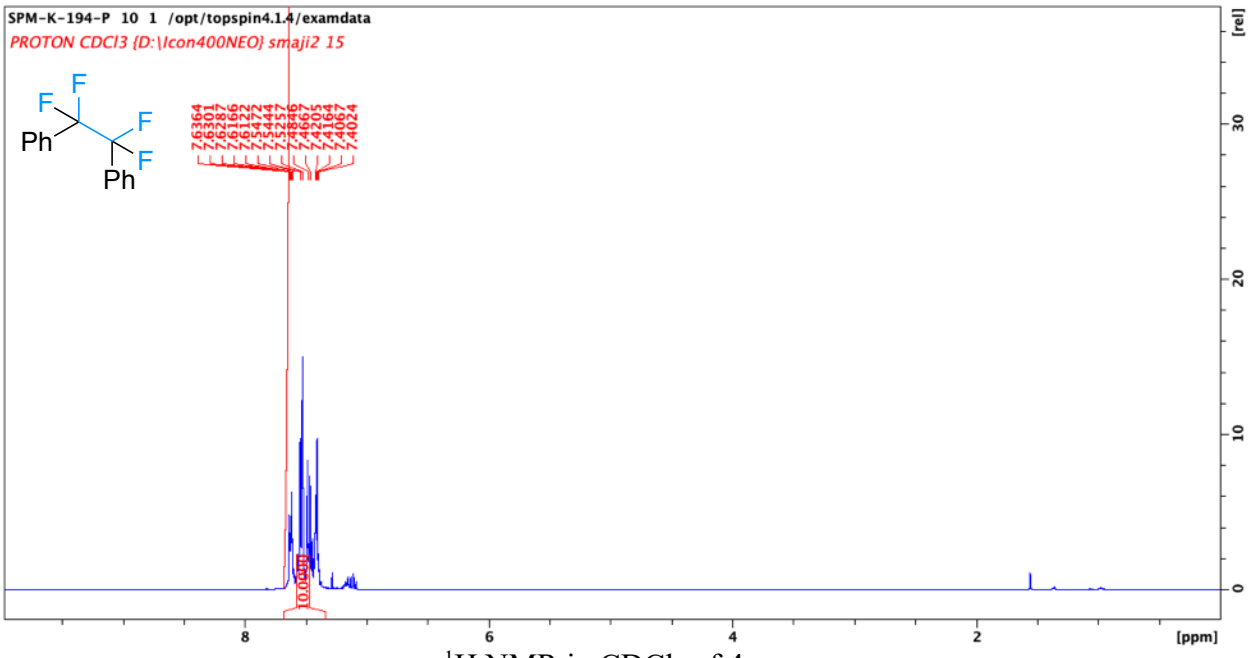
^{1}H NMR in $CDCl_3$ of **2q**



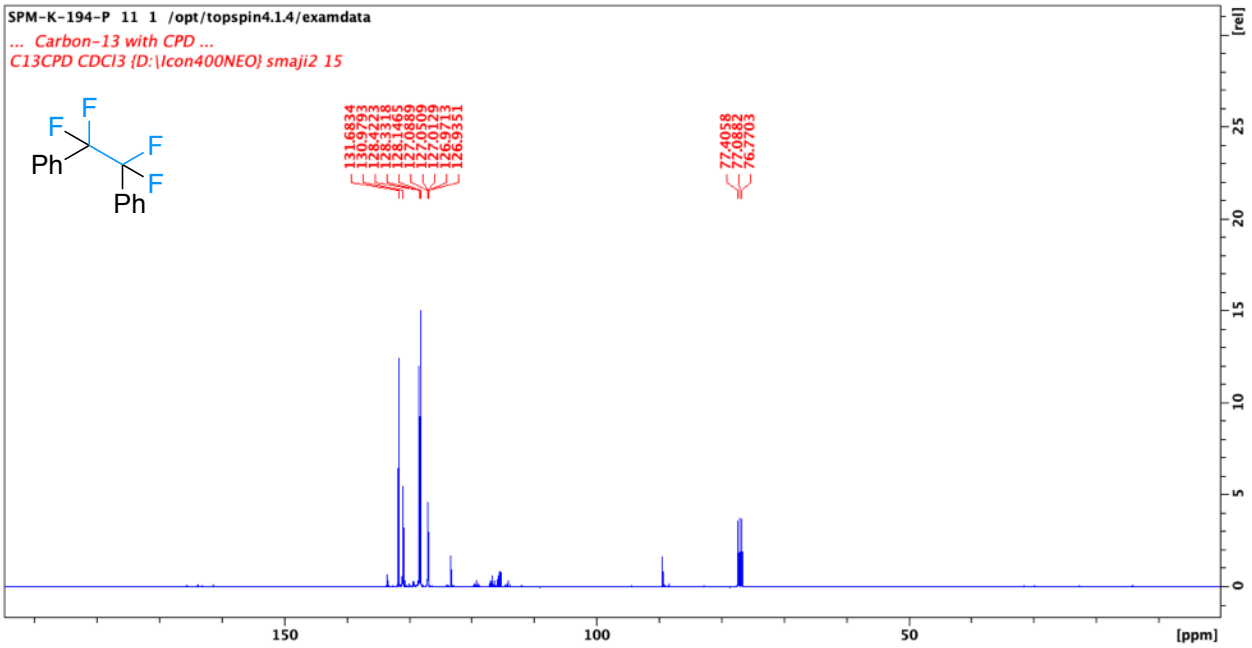
^{13}C NMR spectrum of **2q**



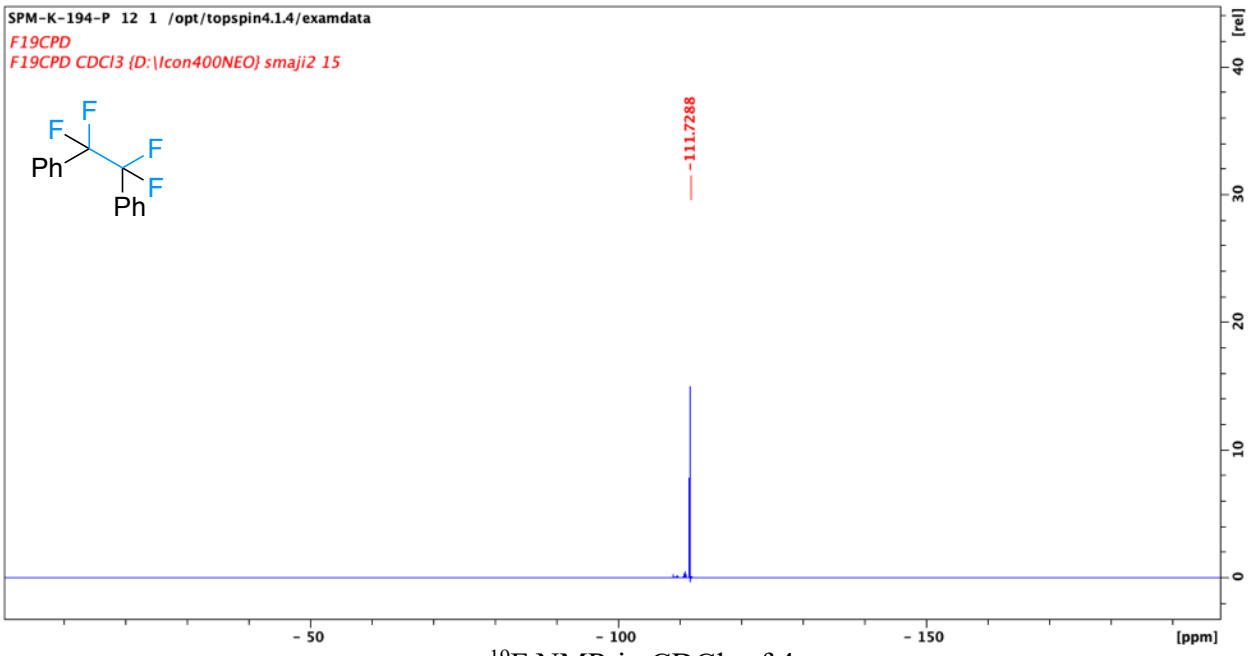
^{19}F NMR in $CDCl_3$ of **2q**



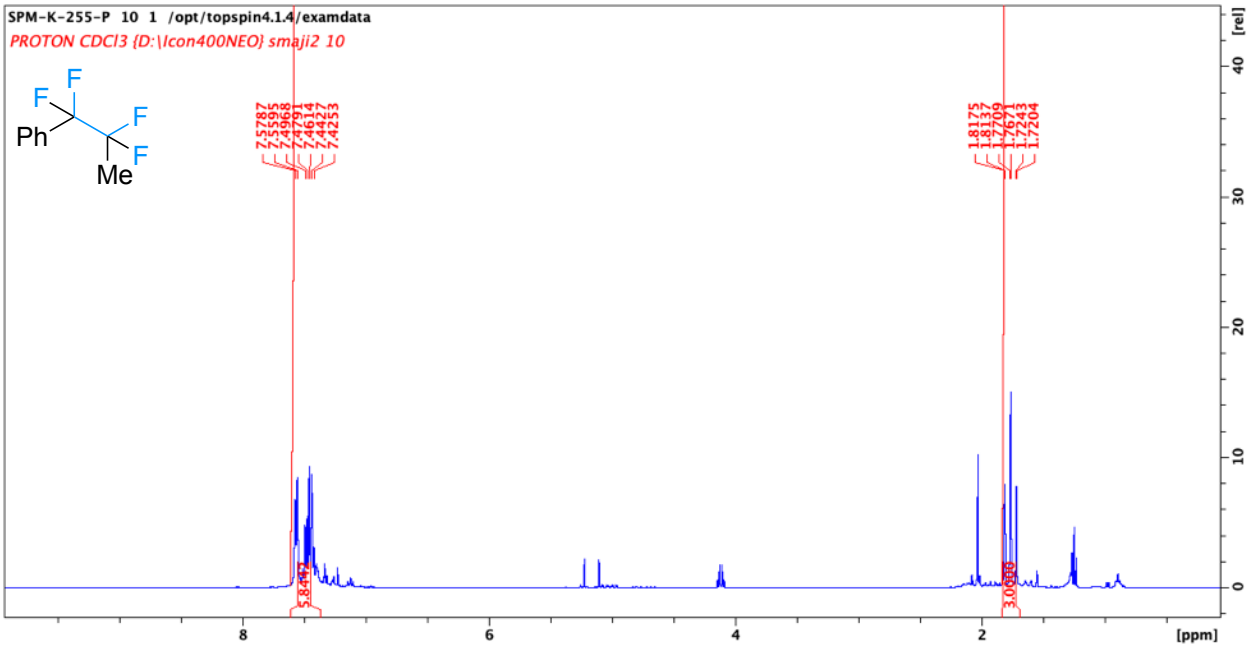
^{1}H NMR in $CDCl_3$ of **4a**



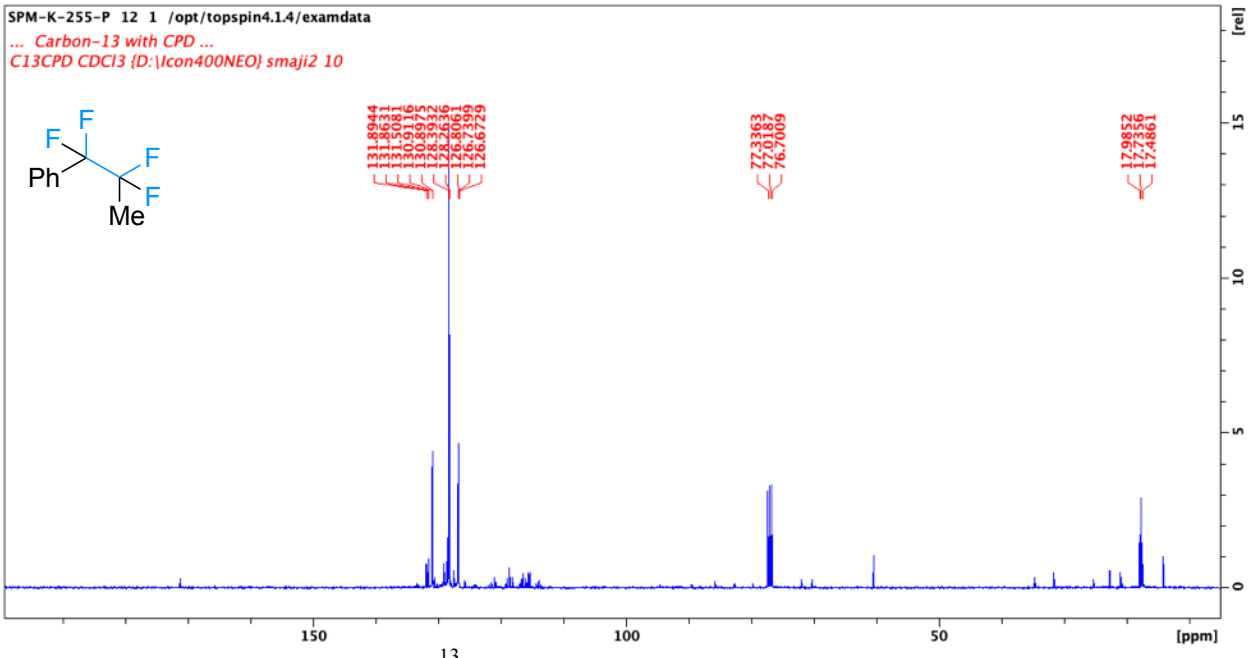
^{13}C NMR spectrum of **4a**



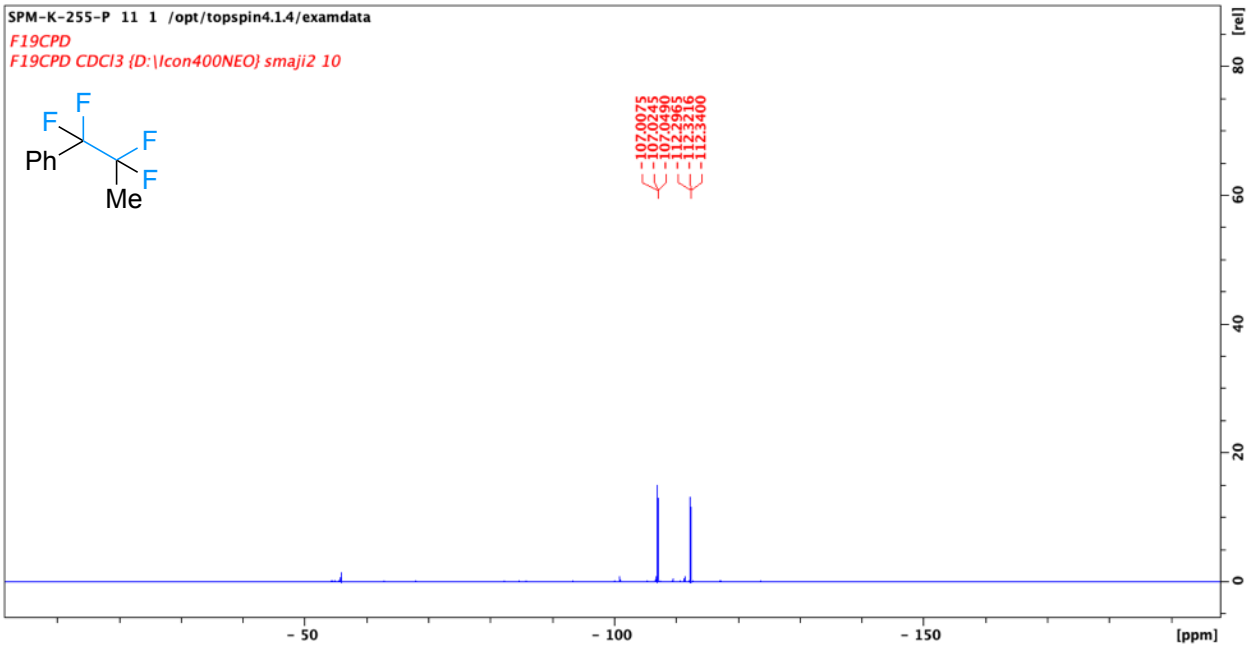
^{19}F NMR in $CDCl_3$ of **4a**



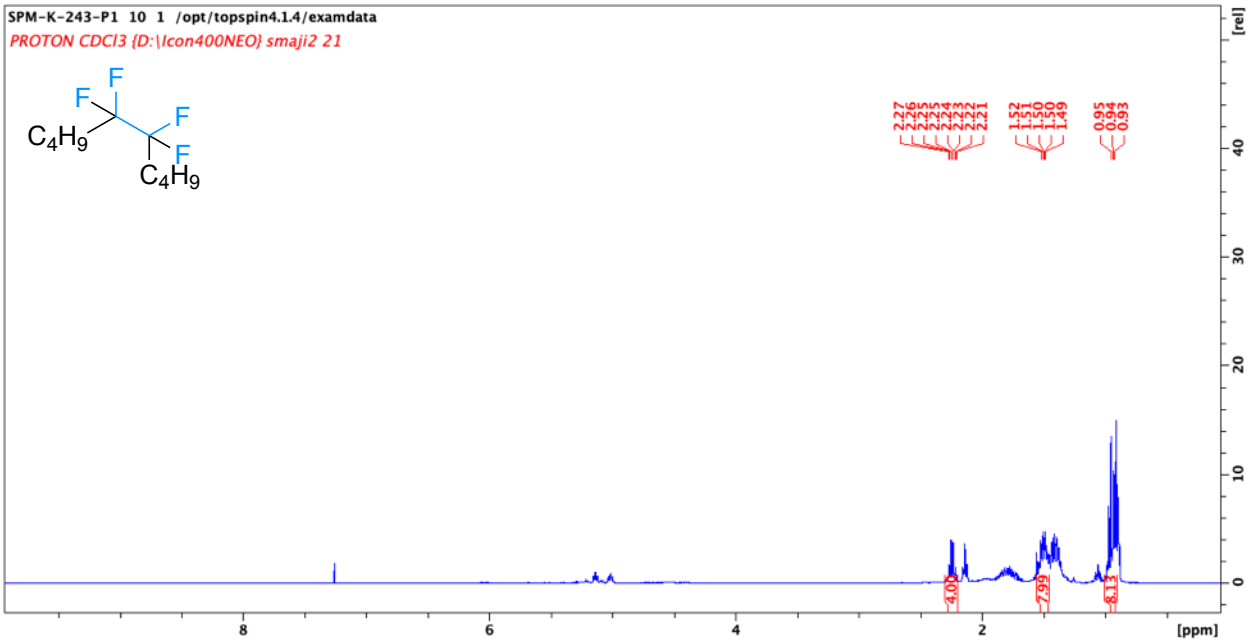
^{1}H NMR in $CDCl_3$ of **4b**



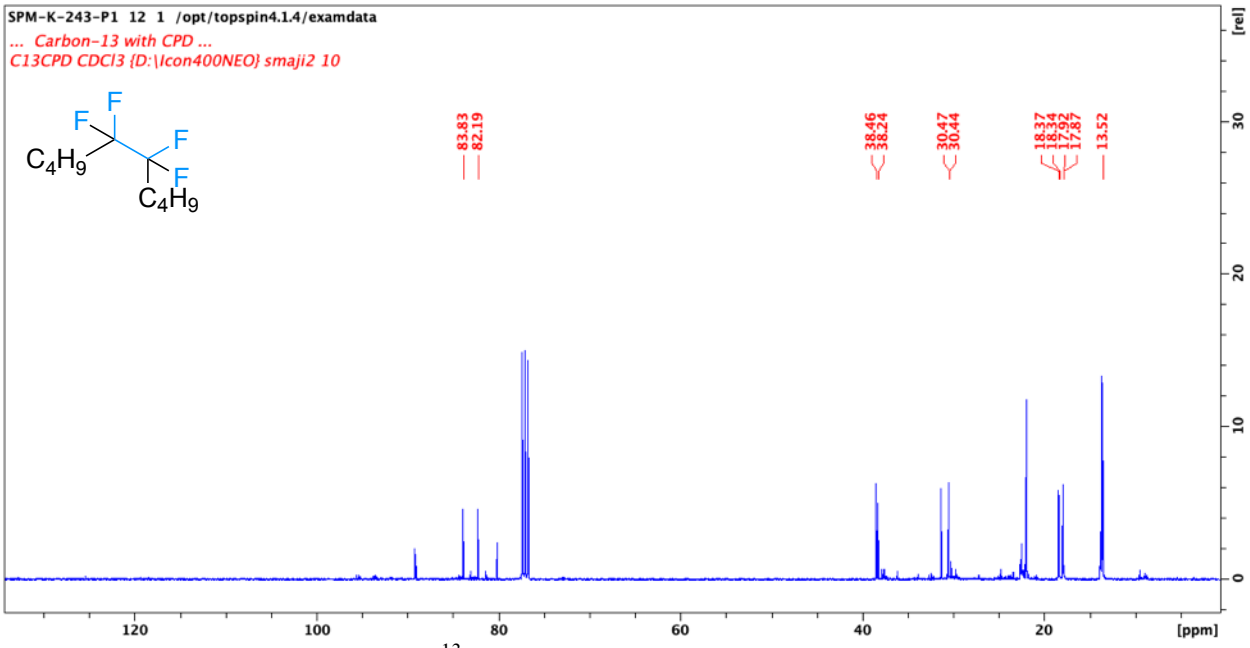
^{13}C NMR spectrum of **4b**



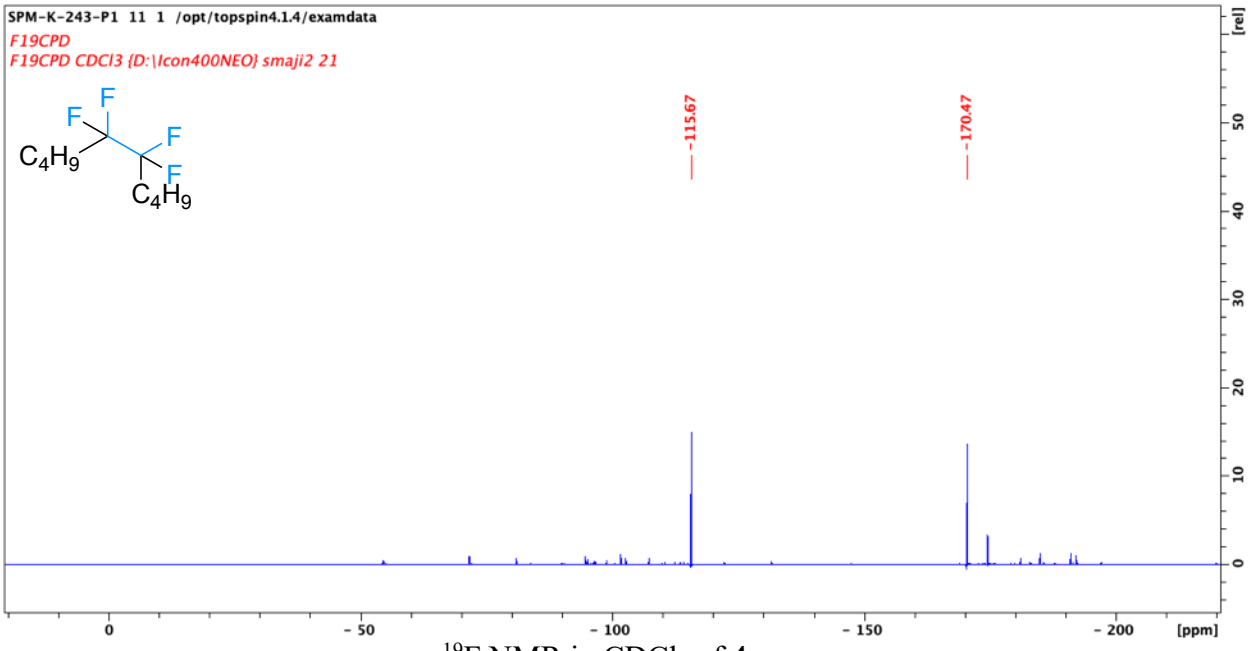
^{19}F NMR in $CDCl_3$ of **4b**



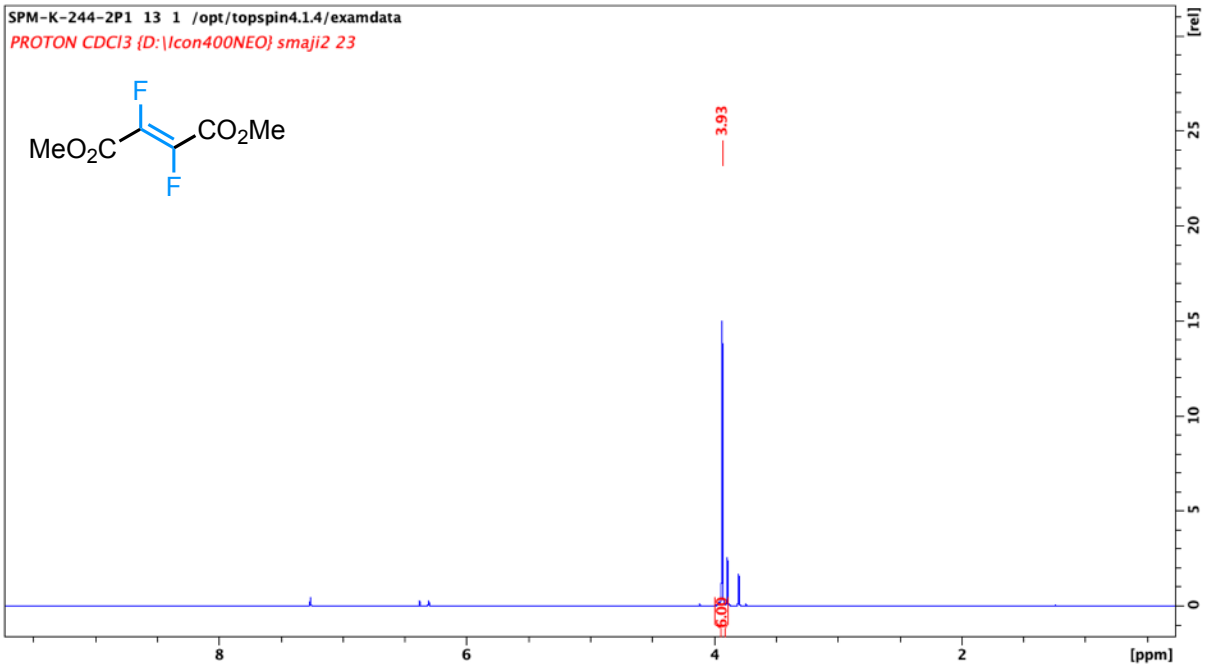
^{1}H NMR in $CDCl_3$ of **4c**



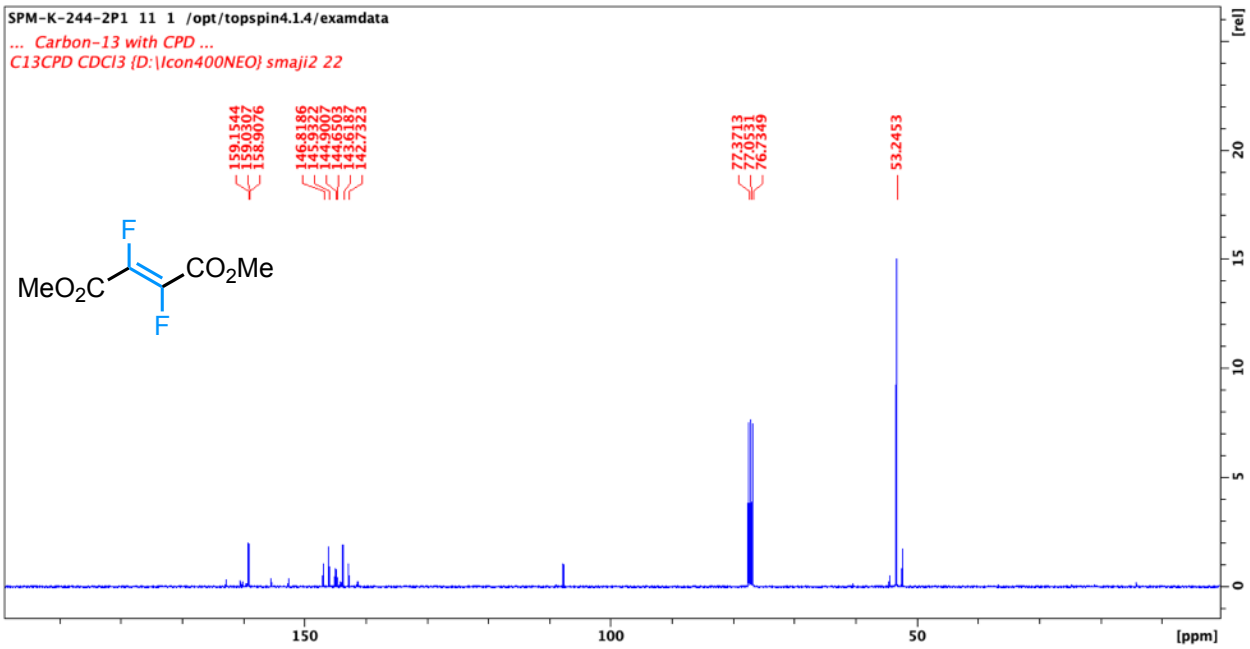
^{13}C NMR spectrum of **4c**



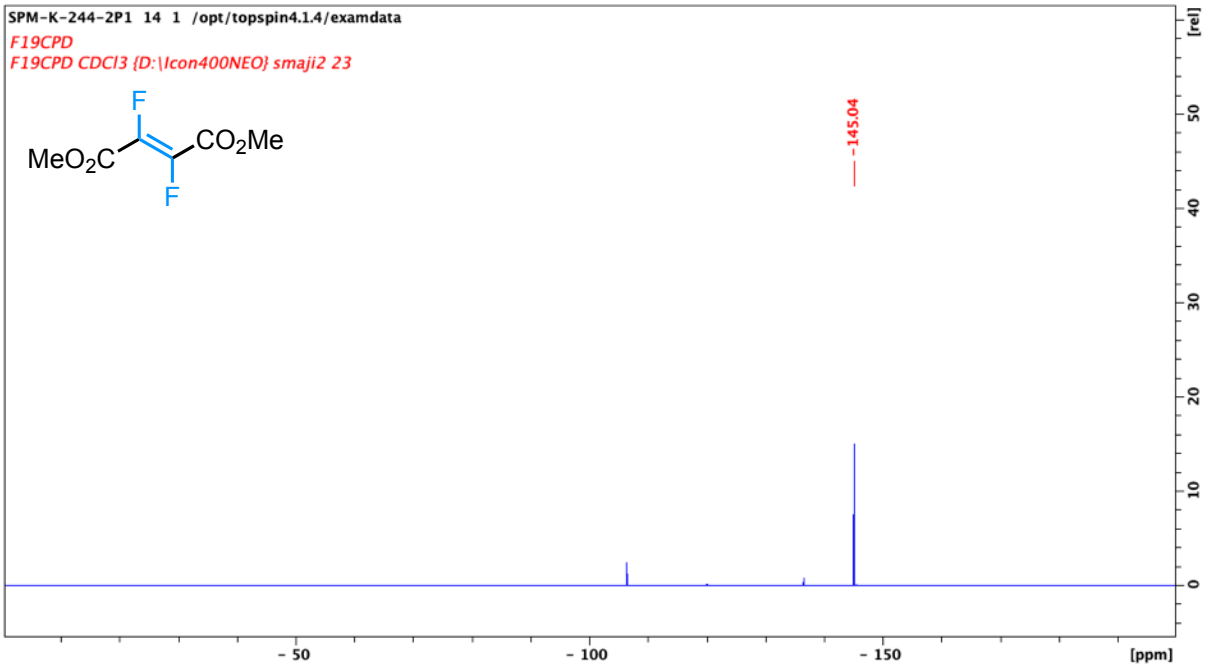
^{19}F NMR in $CDCl_3$ of **4c**



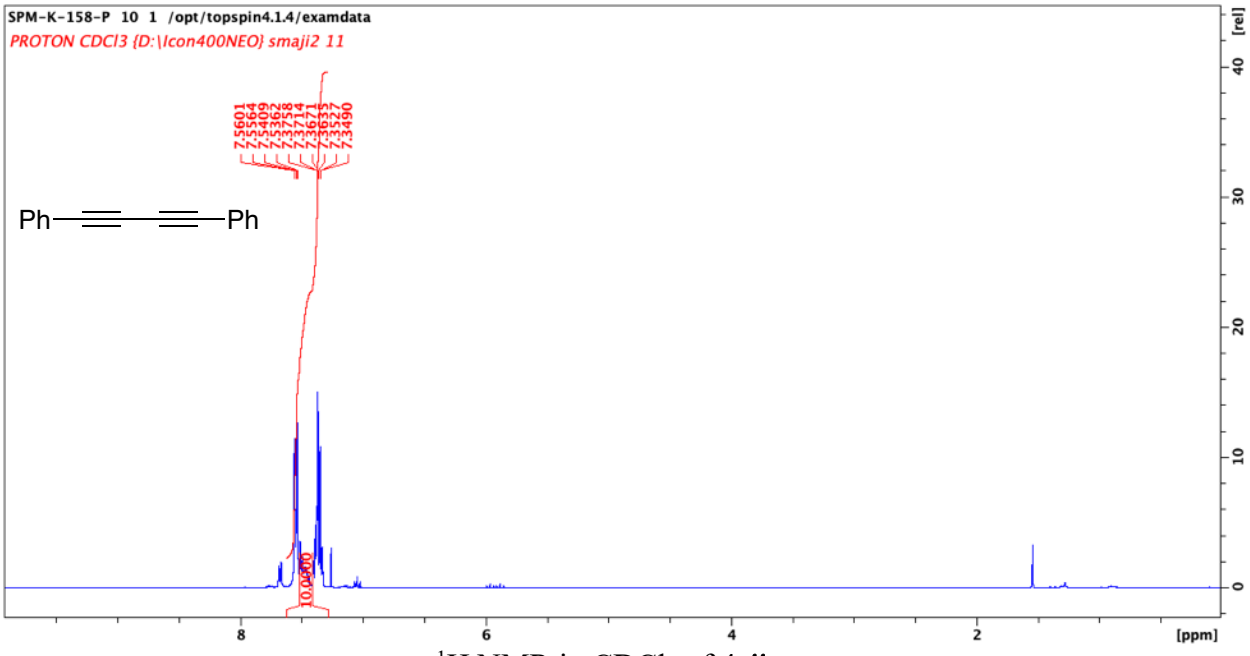
^{1}H NMR in $CDCl_3$ of **4d′**



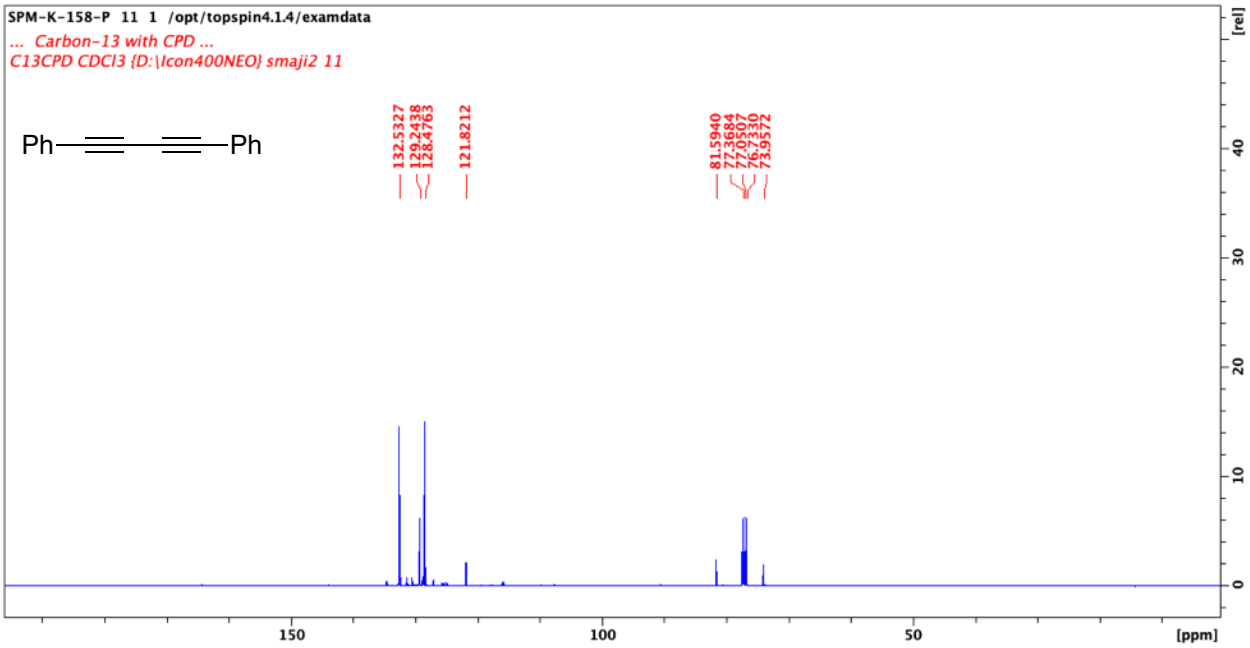
^{13}C NMR spectrum of **4d′**



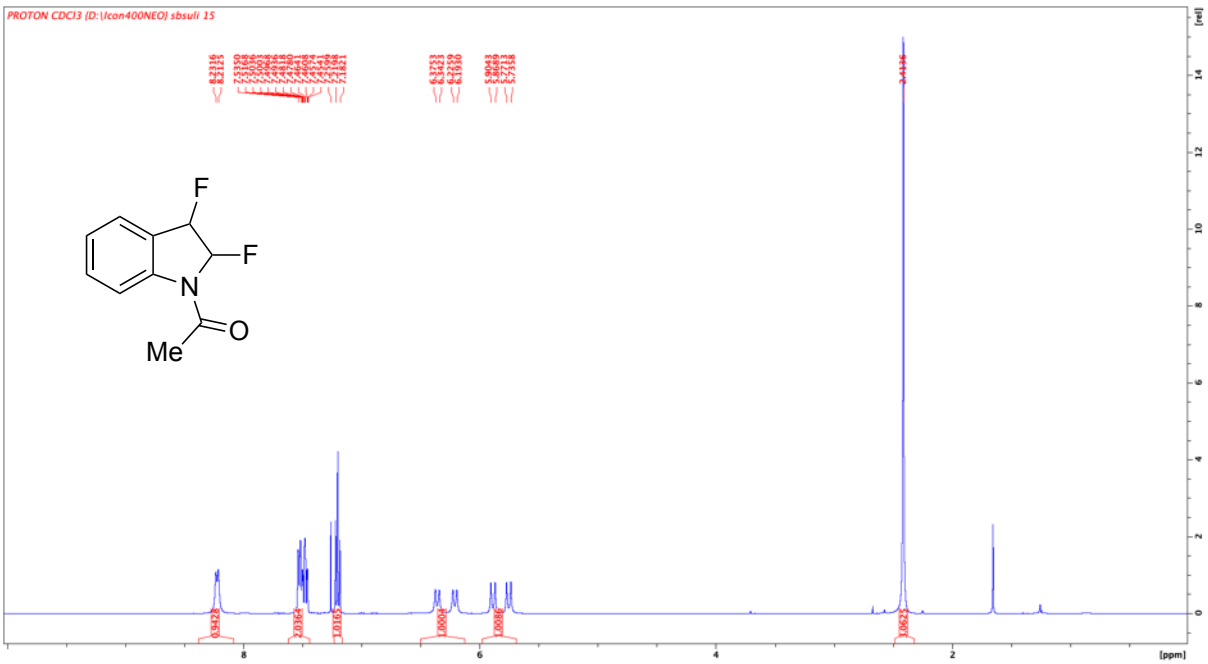
^{19}F NMR in $CDCl_3$ of **4d′**



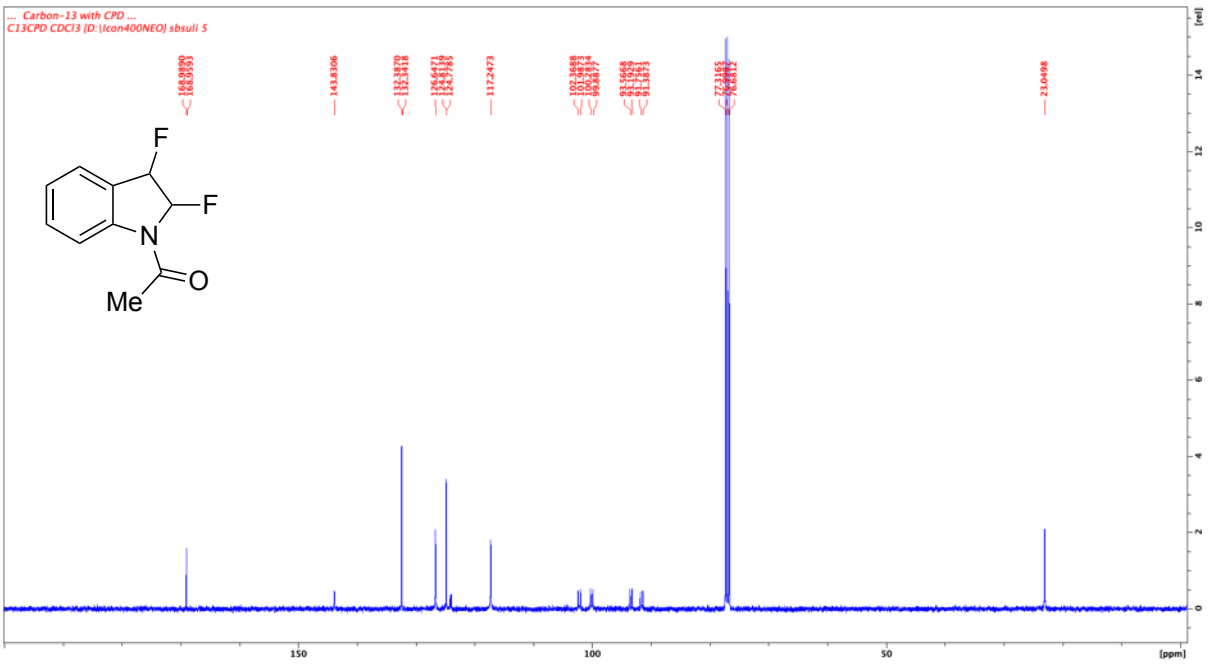
^{1}H NMR in $CDCl_3$ of **4e″**



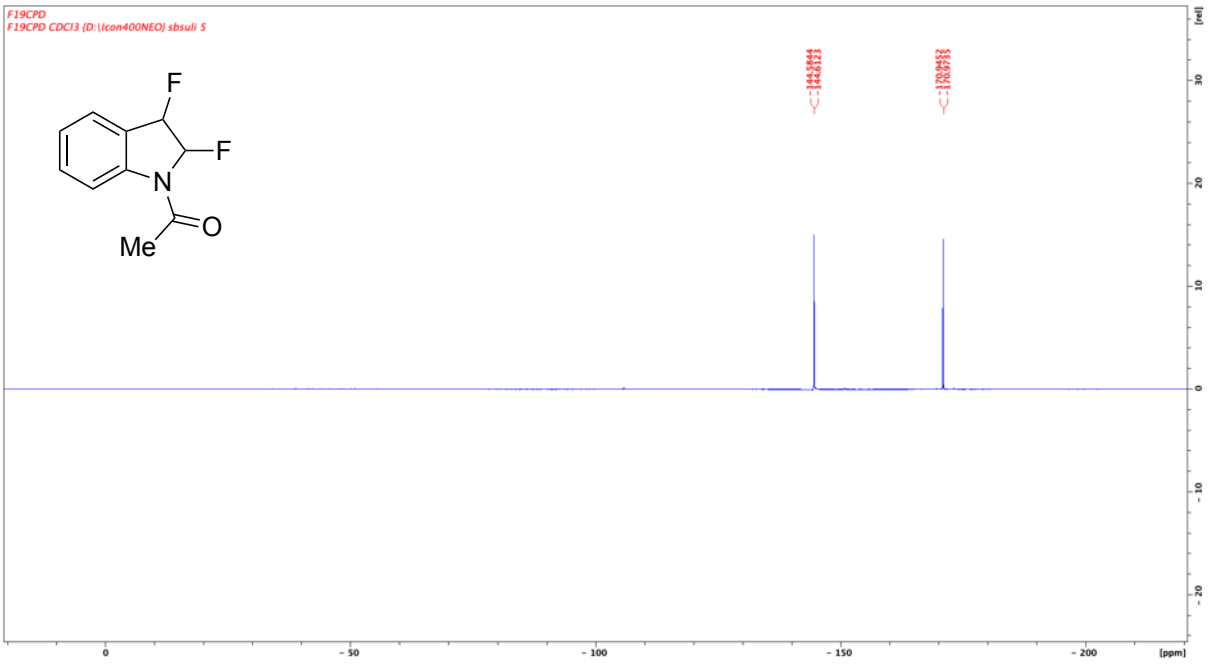
^{13}C NMR spectrum of **4e″**



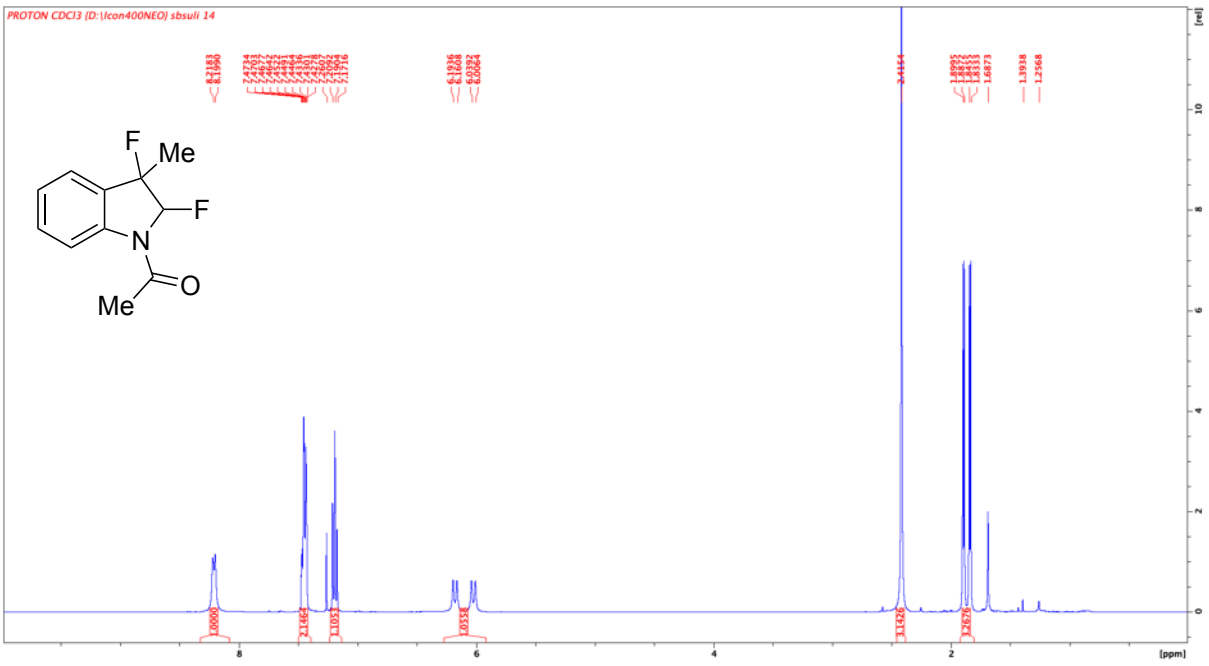
^{1}H NMR spectrum of **6a**



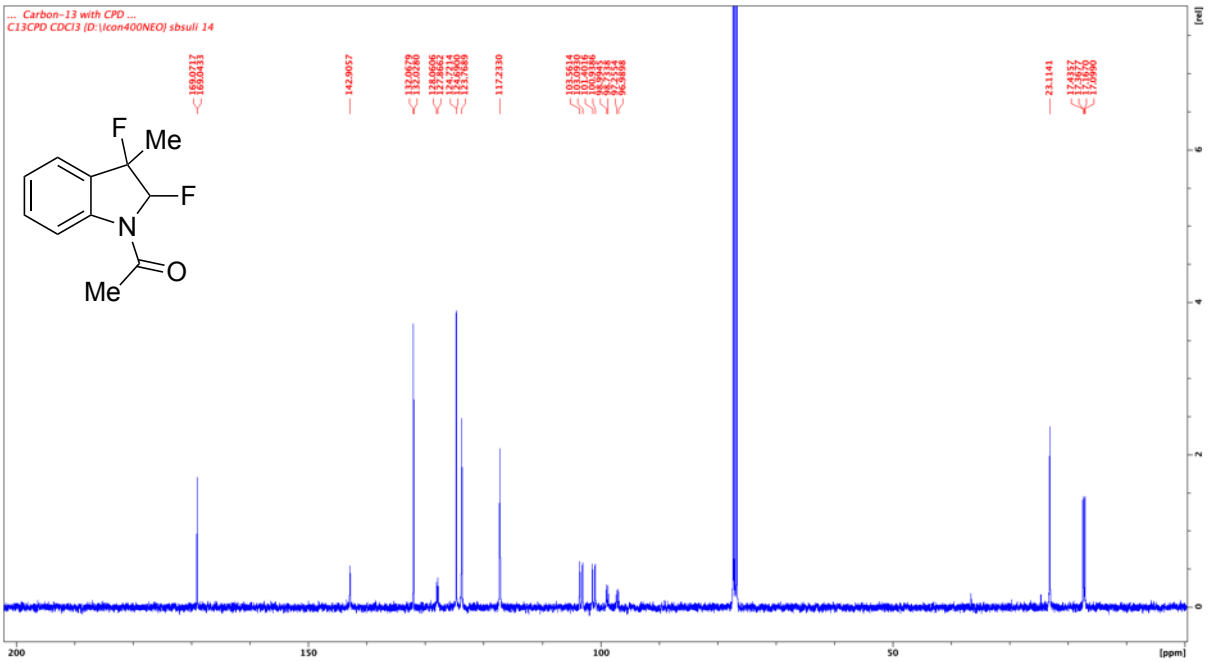
^{13}C NMR spectrum of **6a**



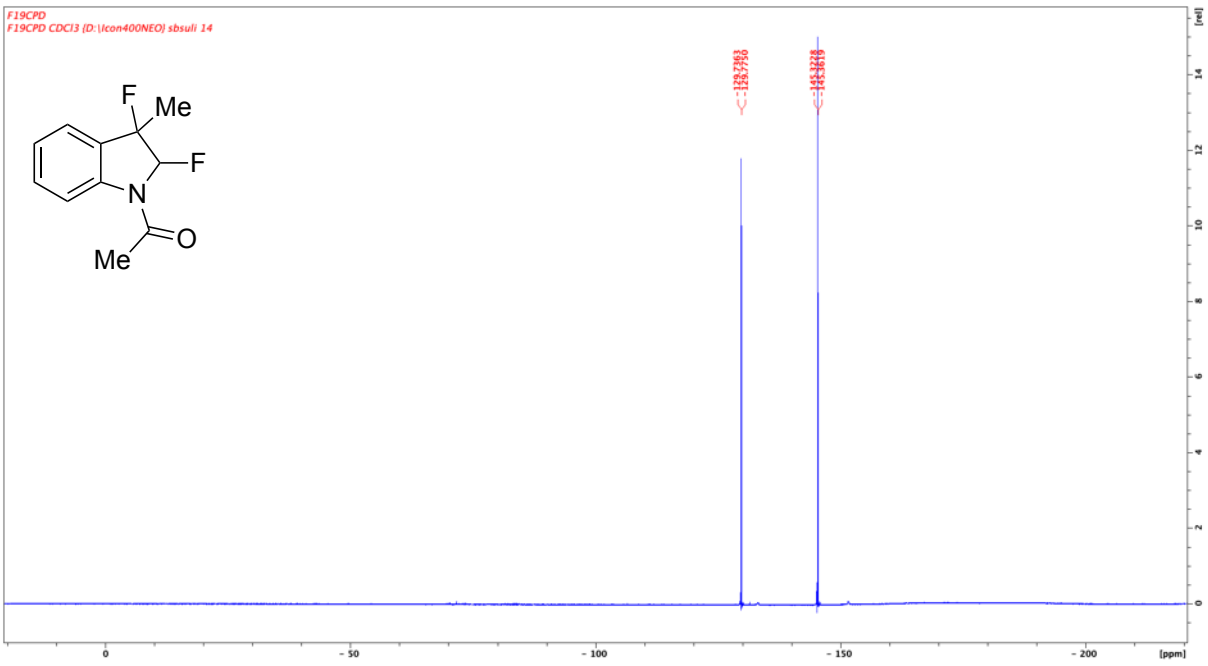
^{19}F NMR spectrum of **6a**



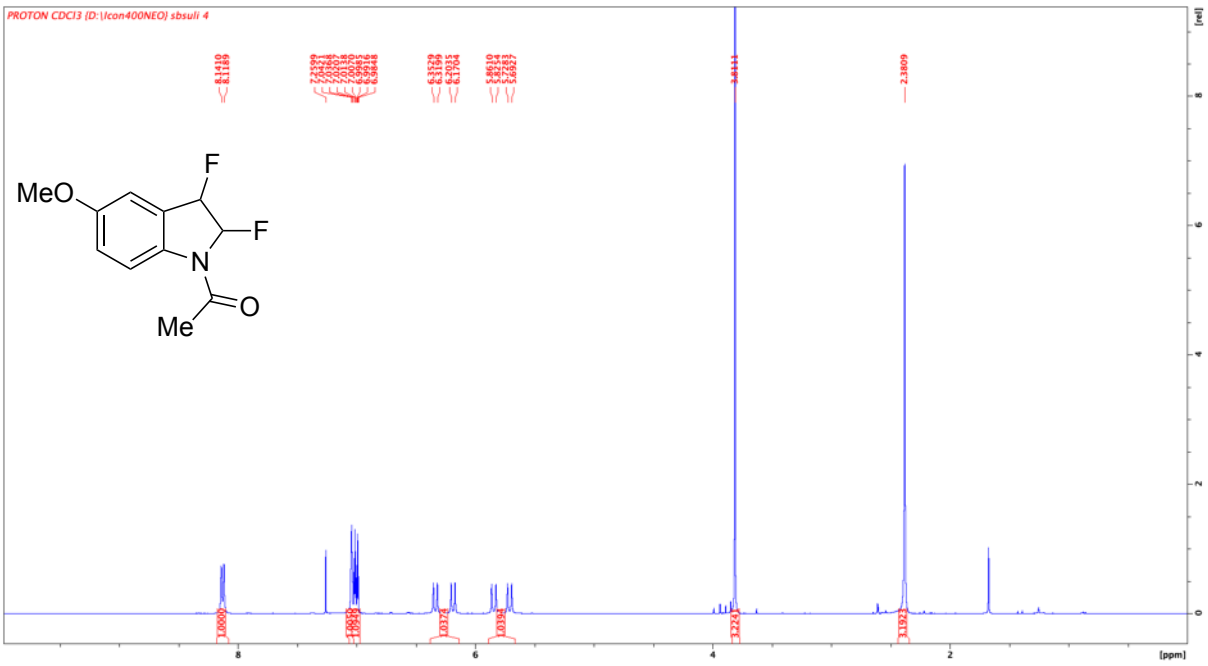
^{1}H NMR spectrum of **6b**



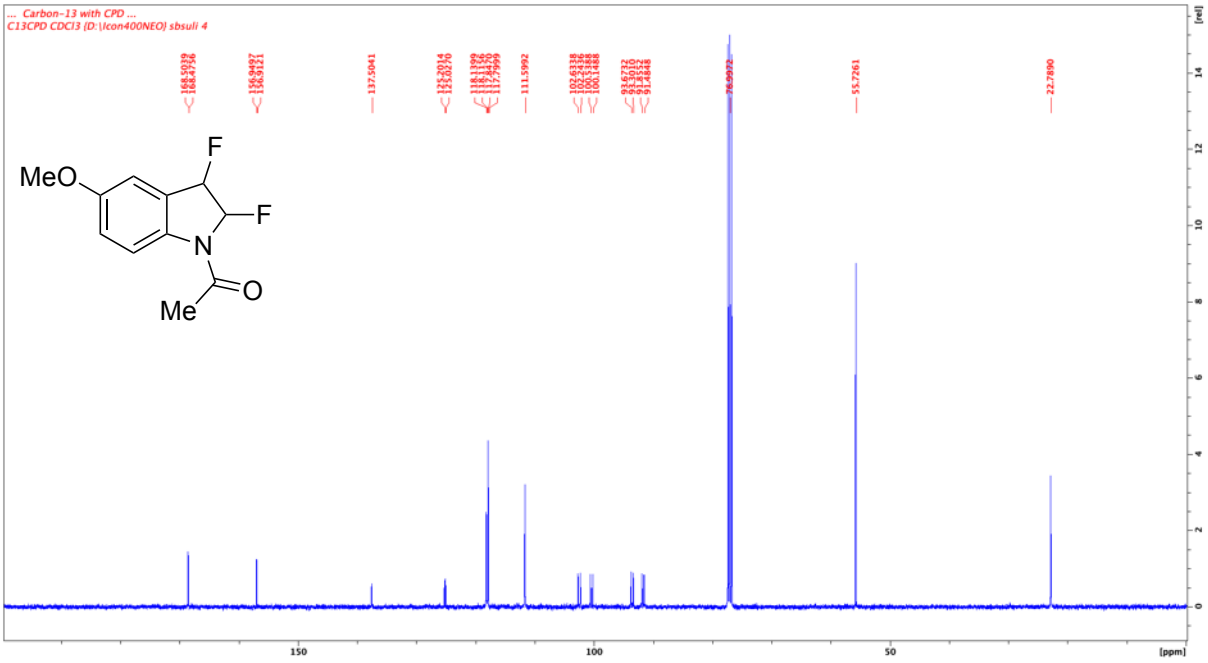
^{13}C NMR spectrum of **6b**



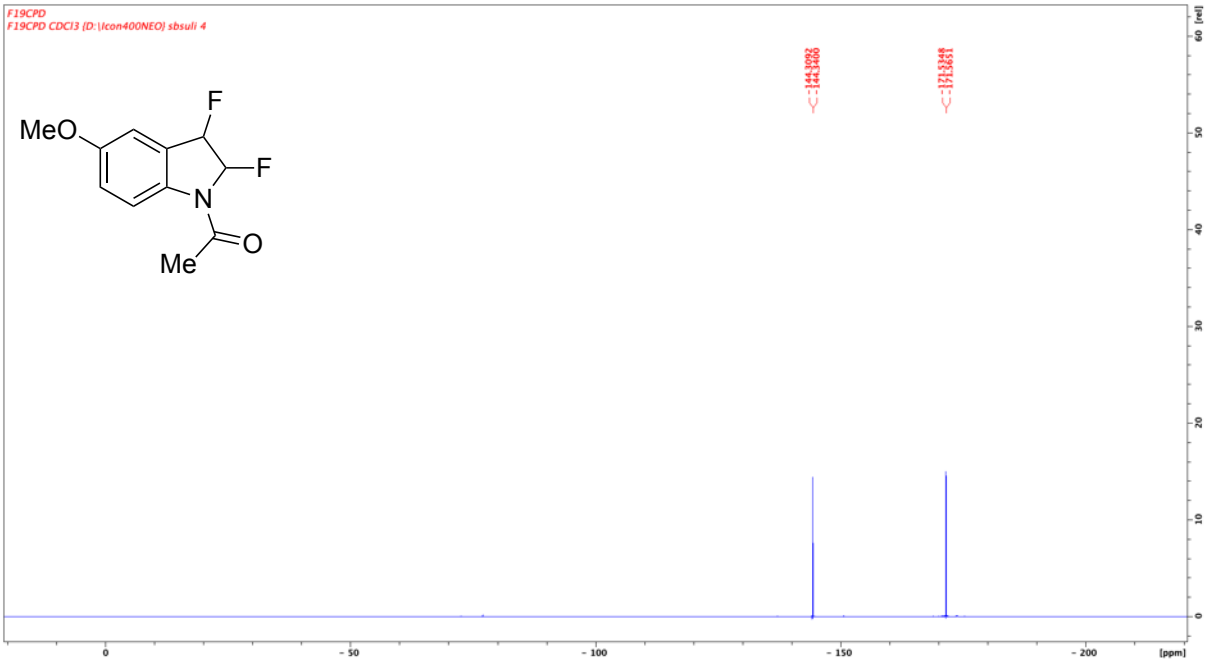
^{19}F NMR spectrum of **6b**



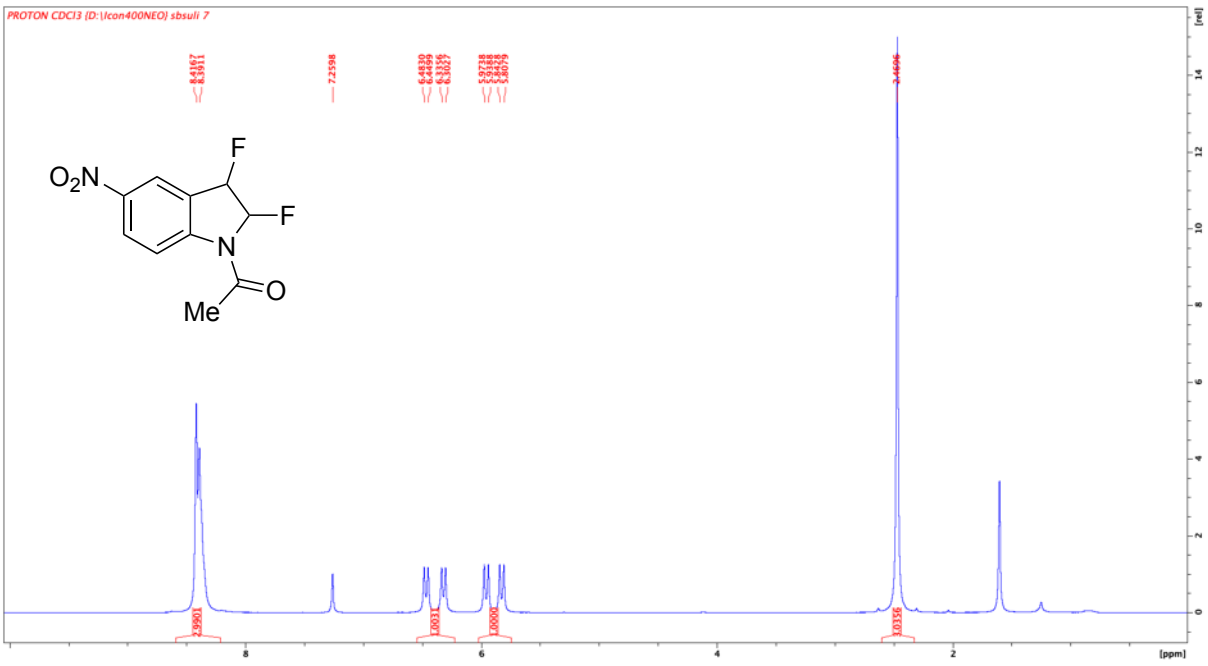
^{1}H NMR spectrum of **6c**



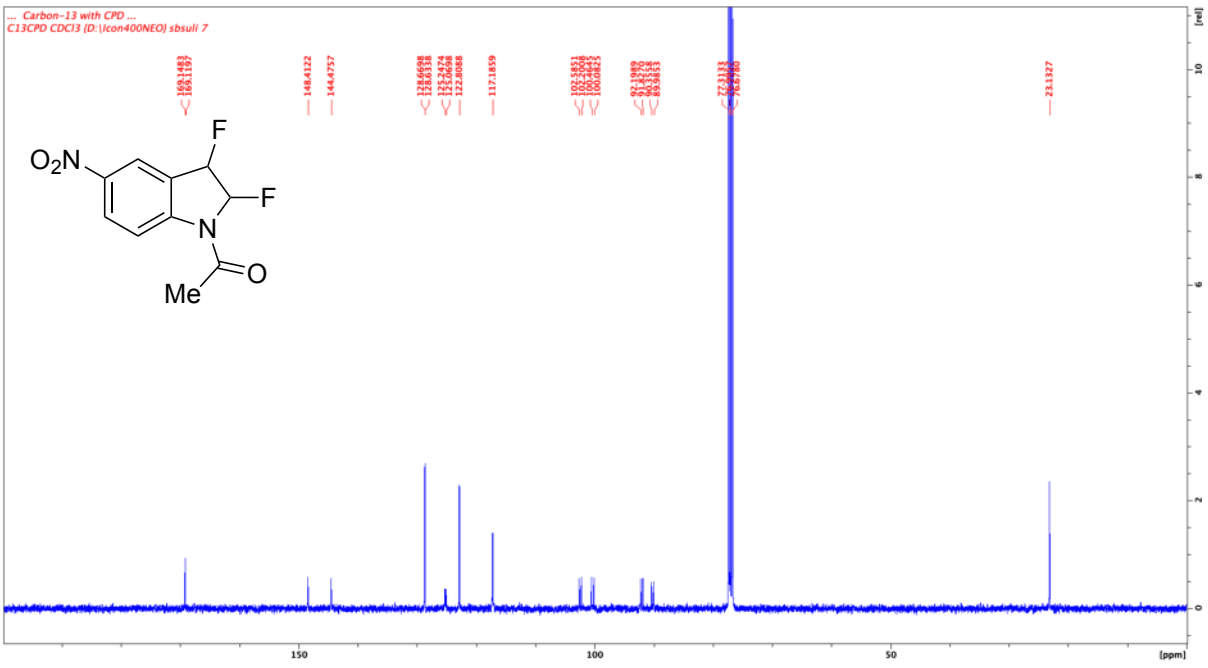
^{13}C NMR spectrum of **6c**



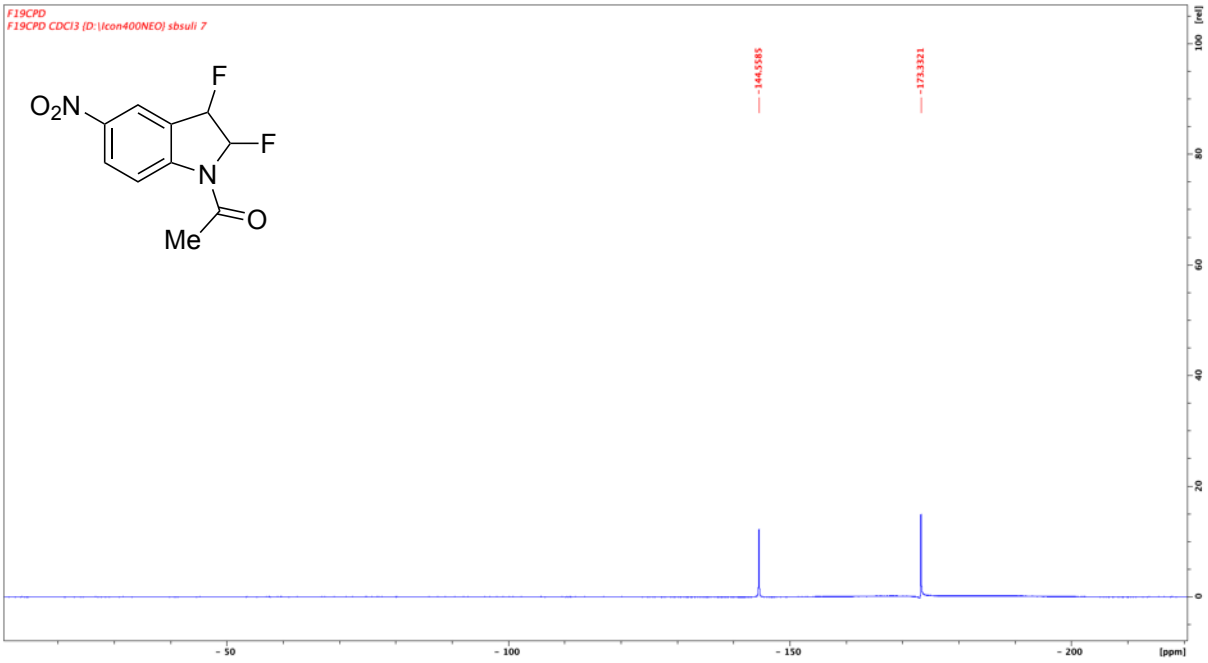
^{19}F NMR spectrum of **6c**



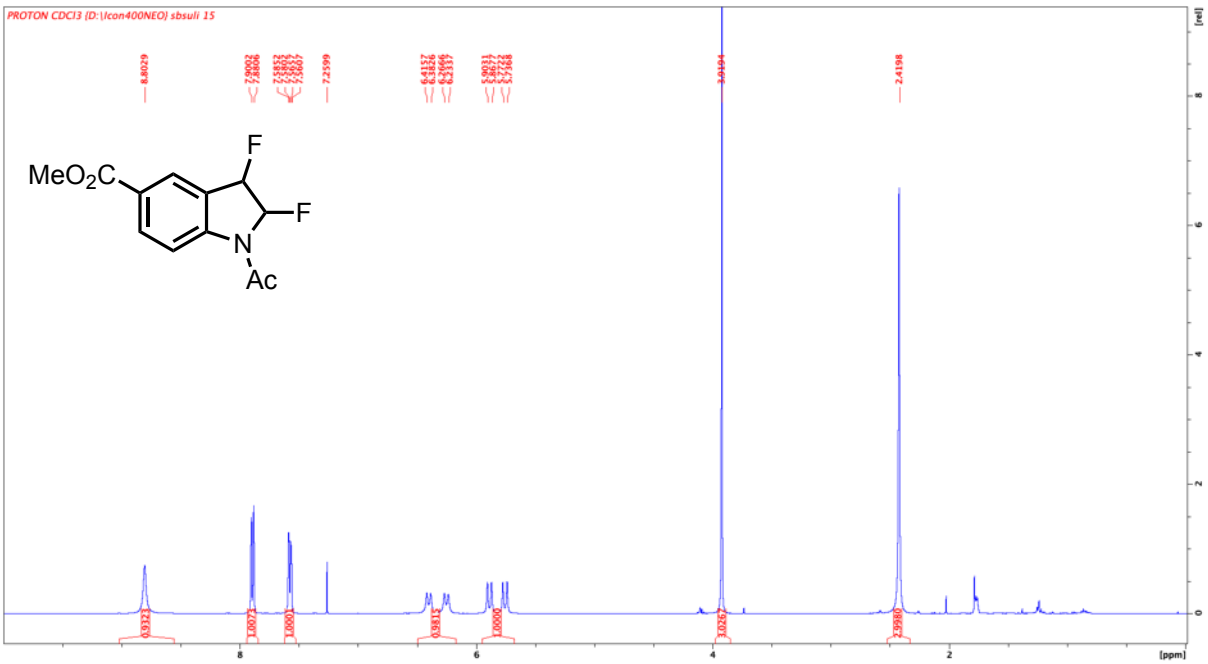
^{1}H NMR spectrum of **6d**



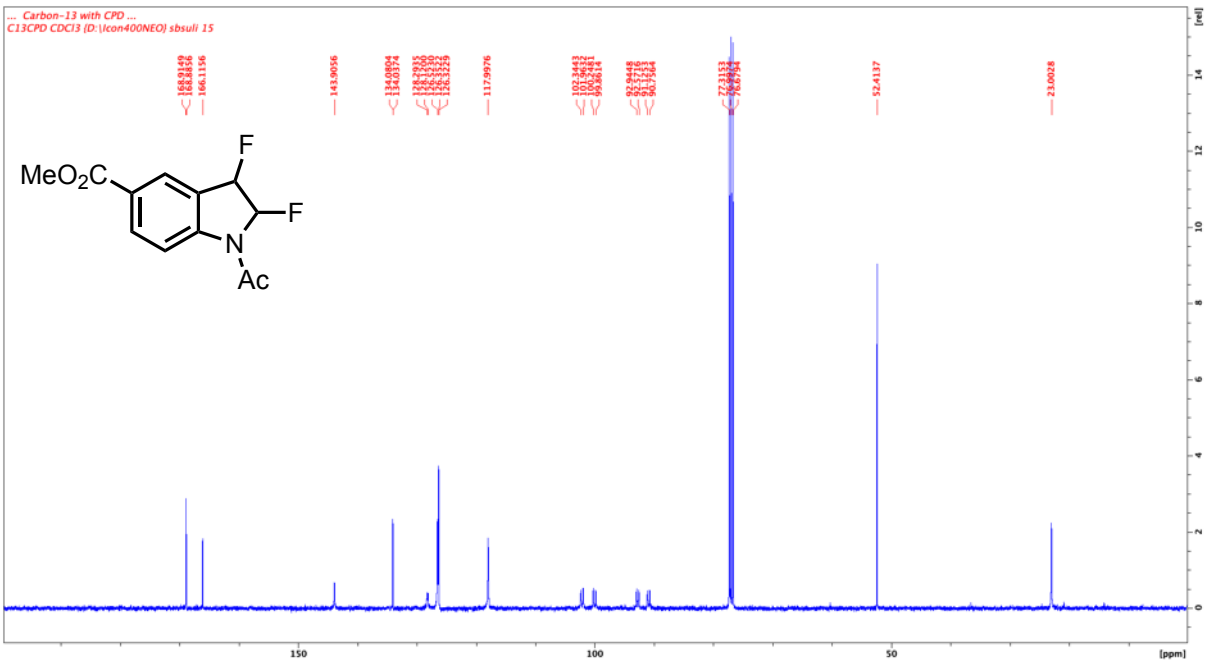
^{13}C NMR spectrum of **6d**



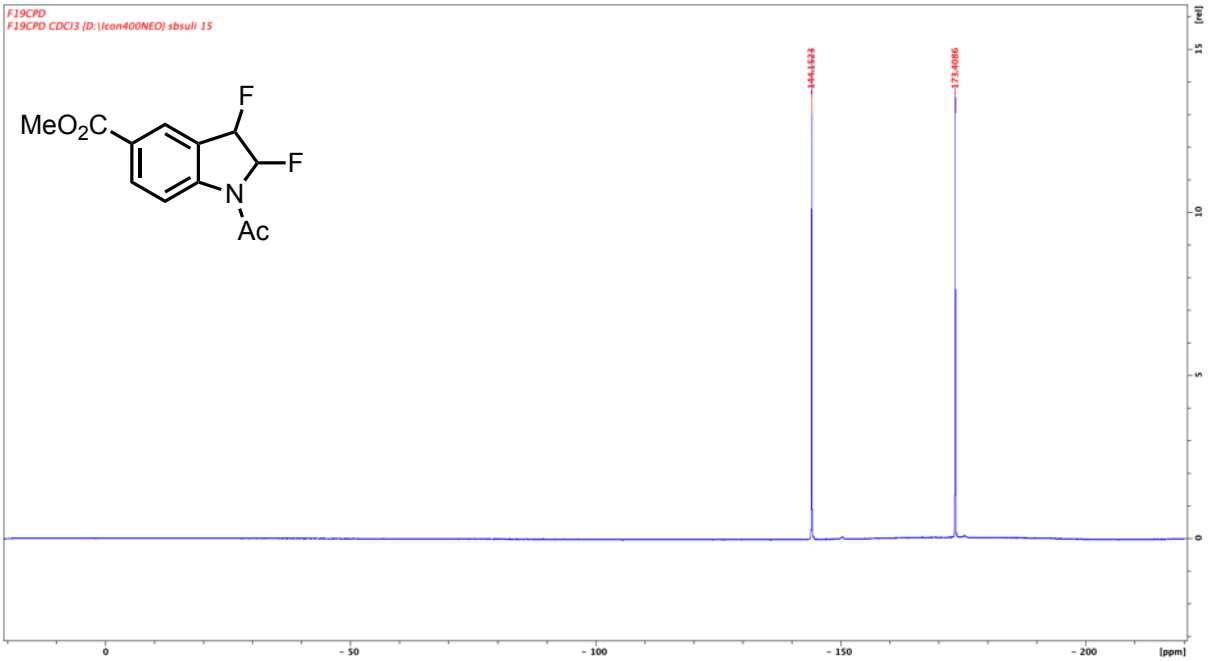
^{19}F NMR spectrum of **6d**



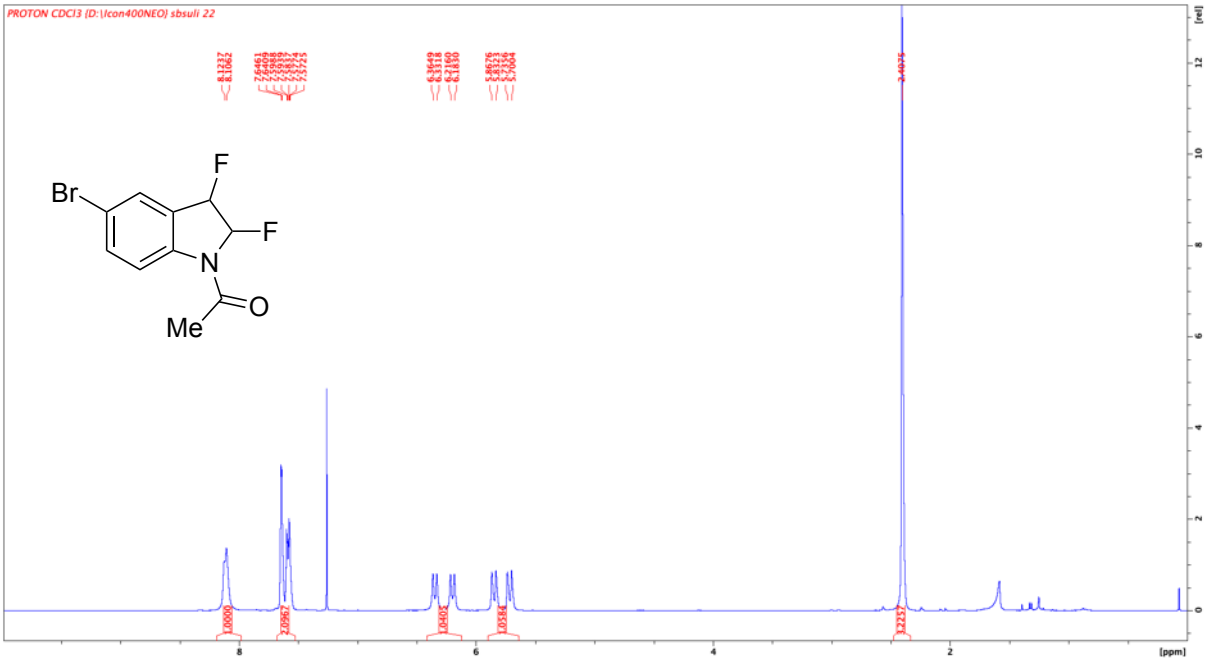
^{1}H NMR spectrum of **6e**



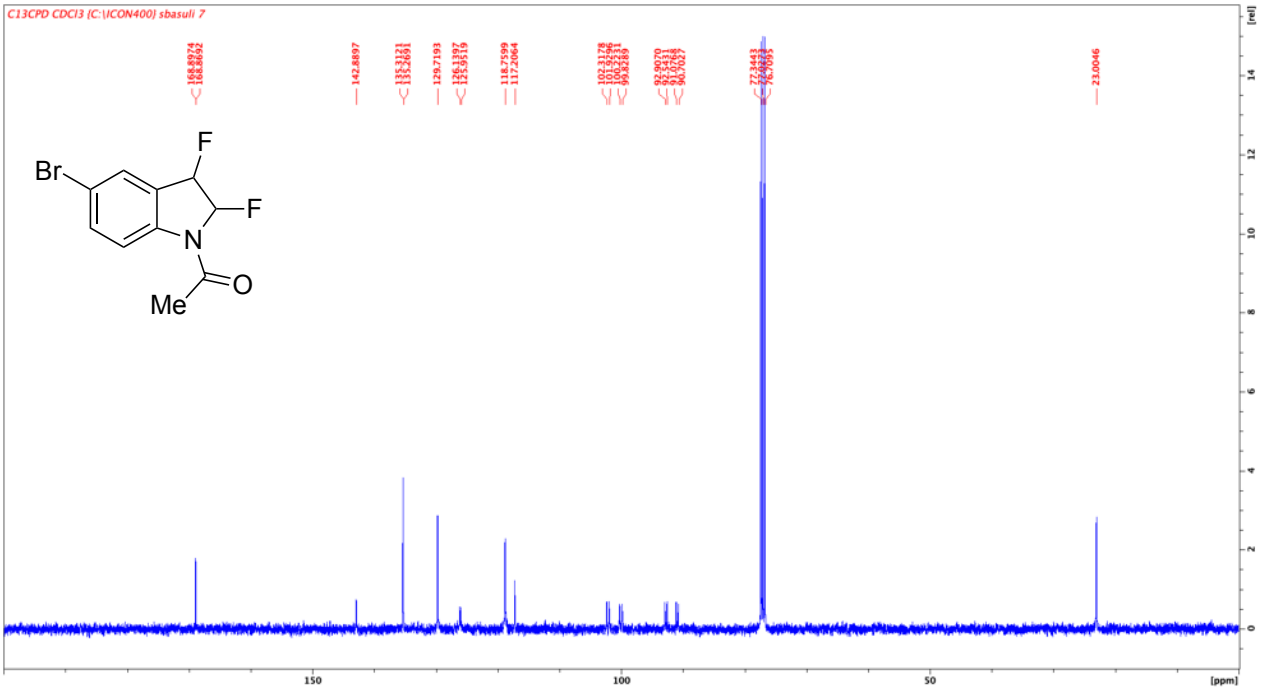
^{13}C NMR spectrum of **6e**



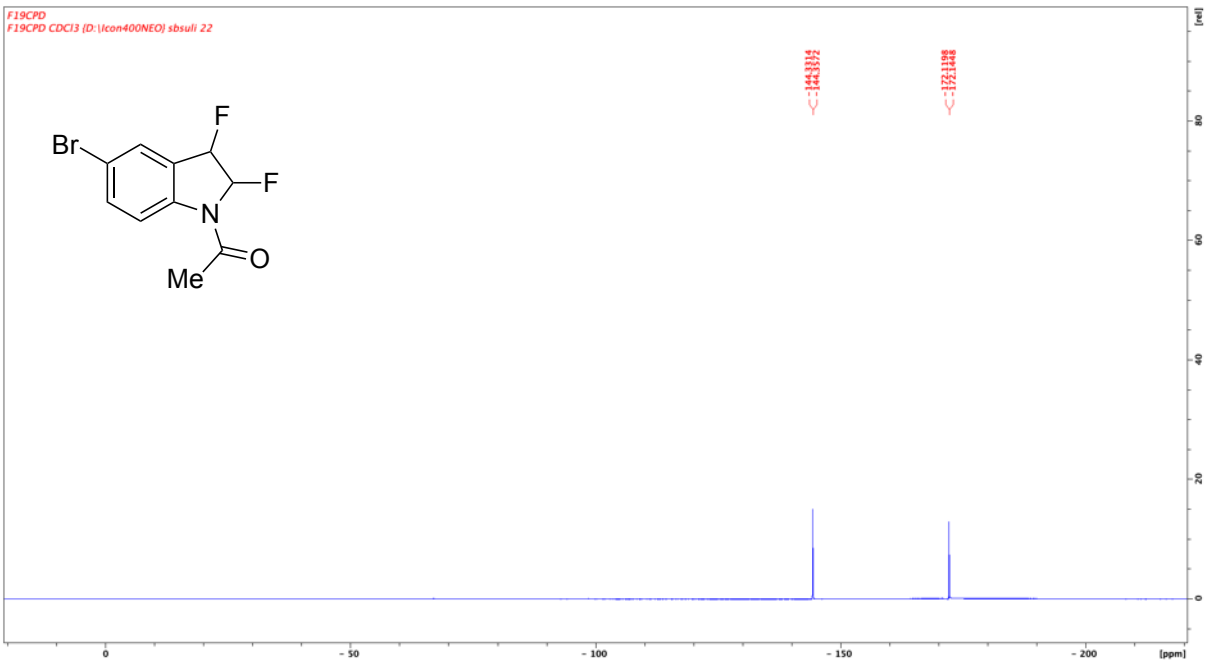
^{19}F NMR spectrum of **6e**



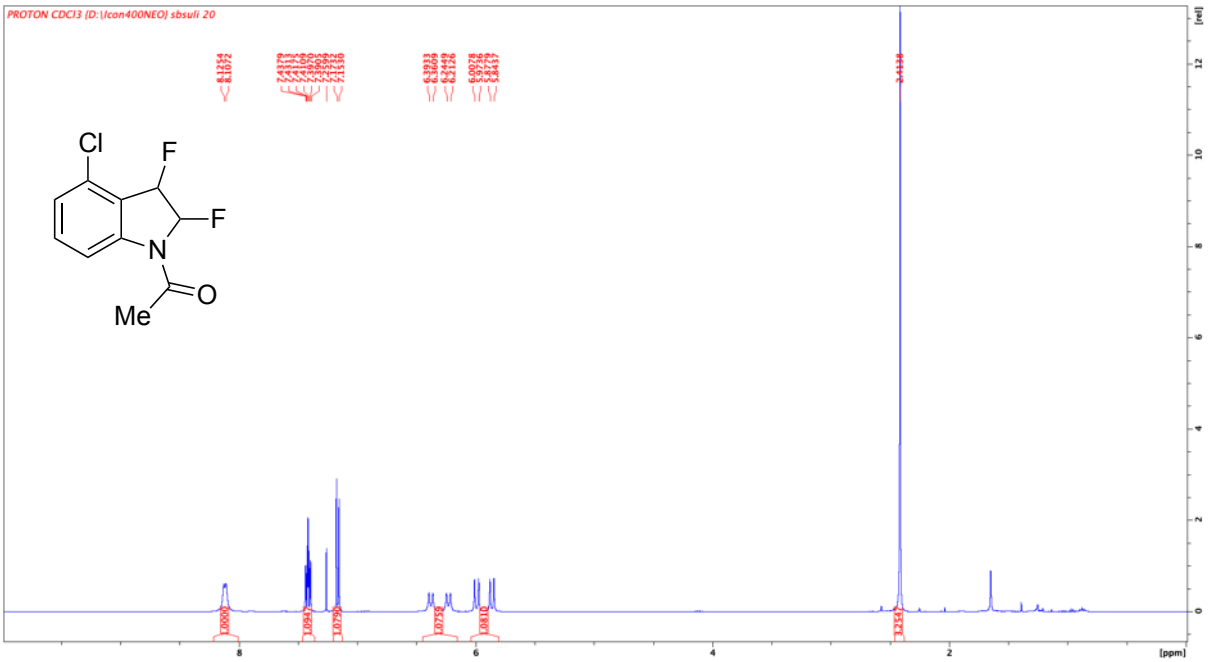
^{1}H NMR spectrum of **6f**



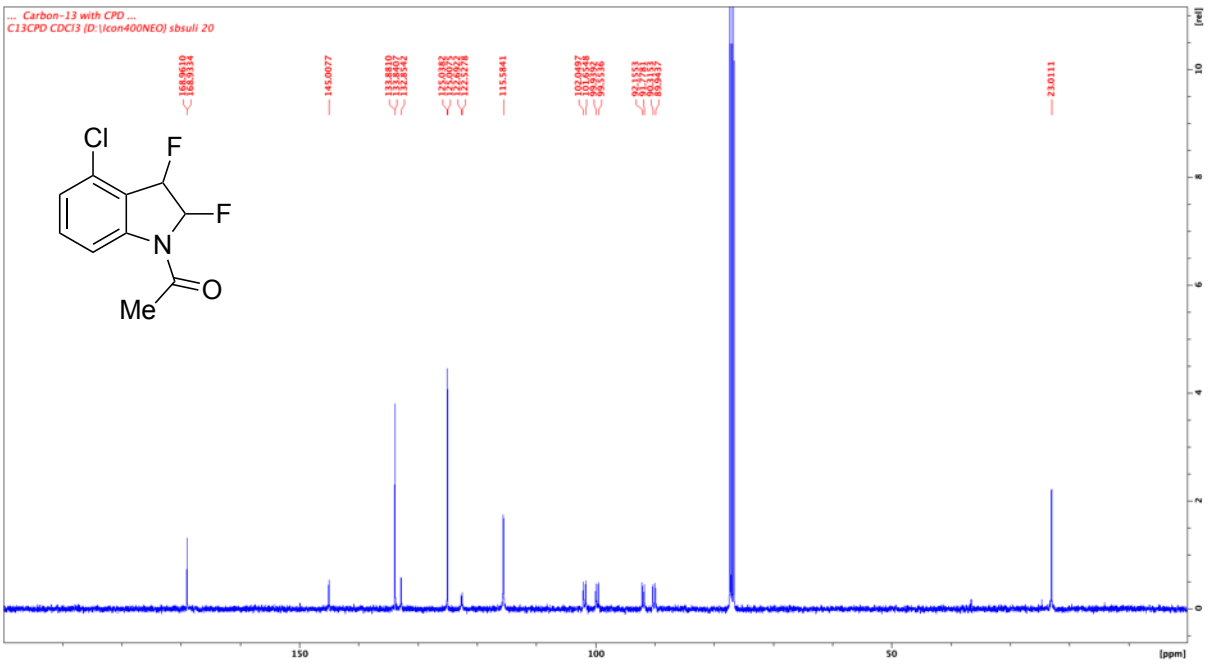
^{13}C NMR spectrum of **6f**



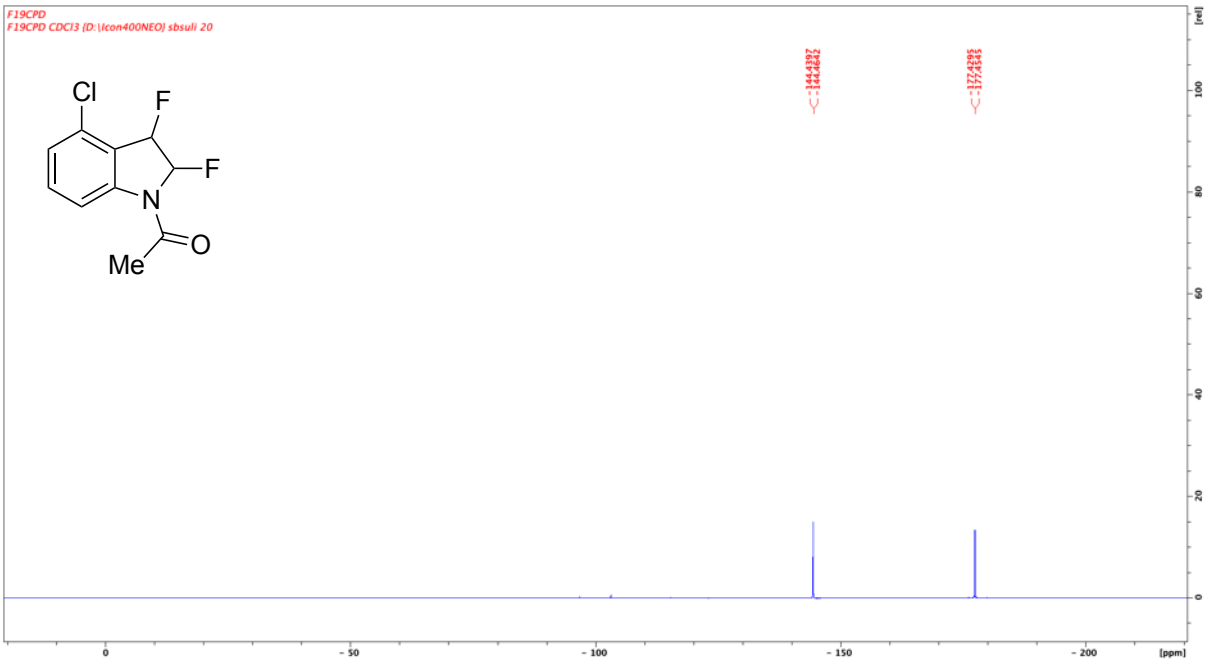
^{19}F NMR spectrum of **6f**



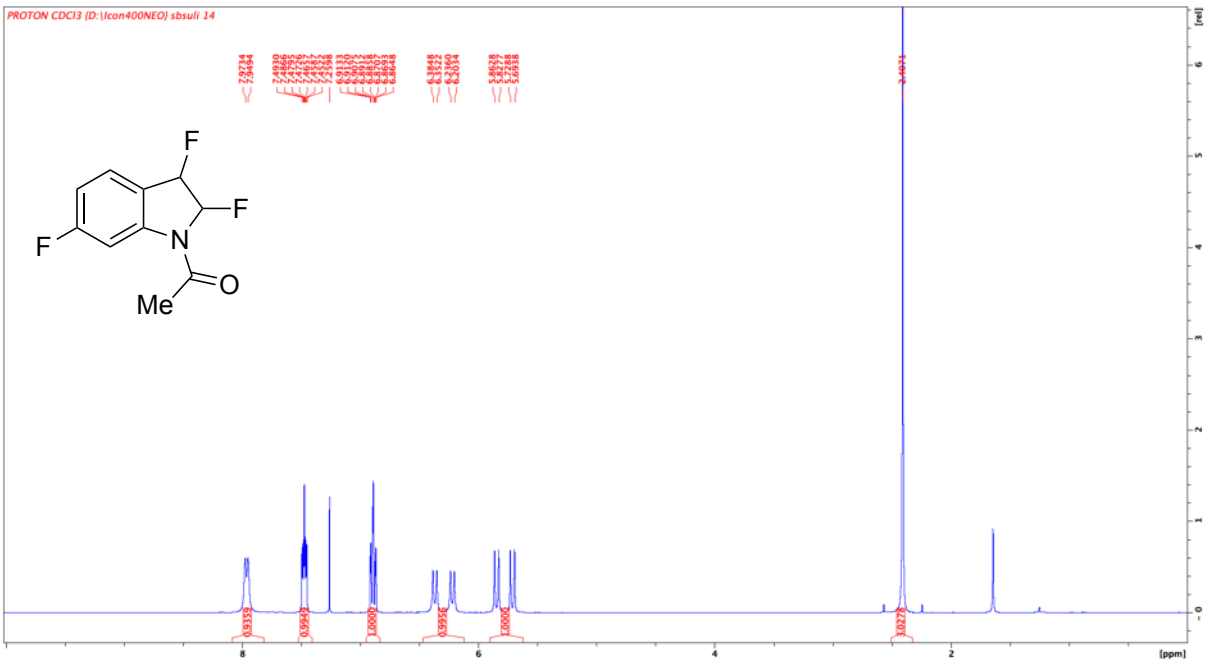
^{1}H NMR spectrum of **6g**



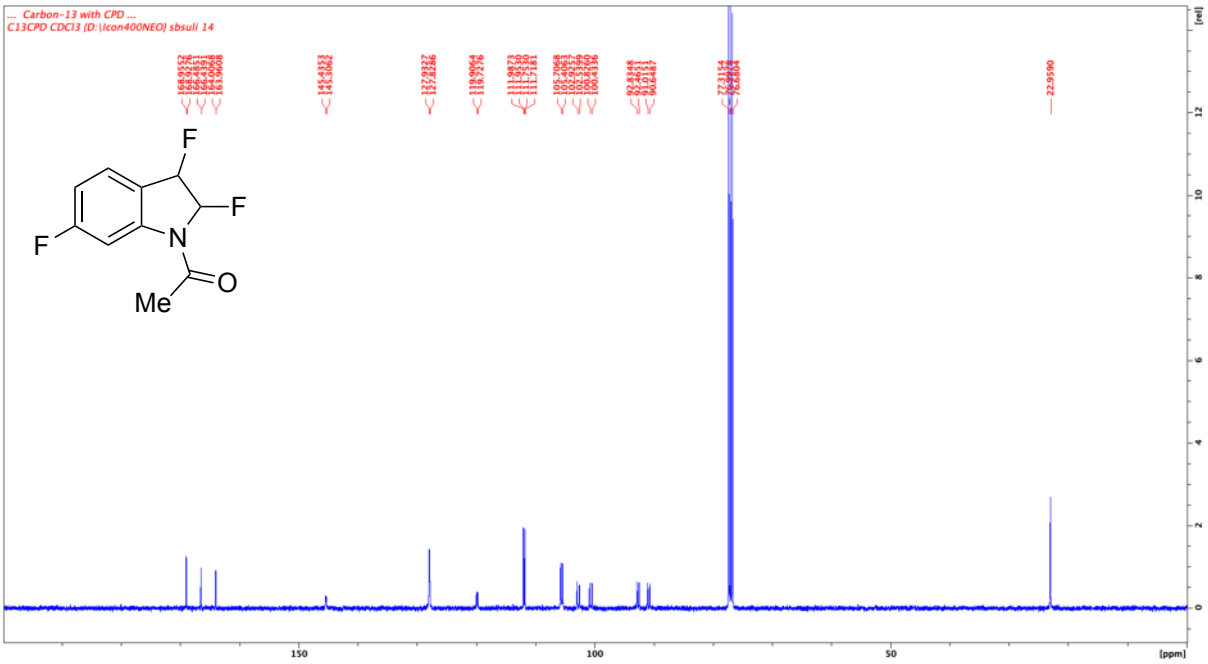
^{13}C NMR spectrum of **6g**



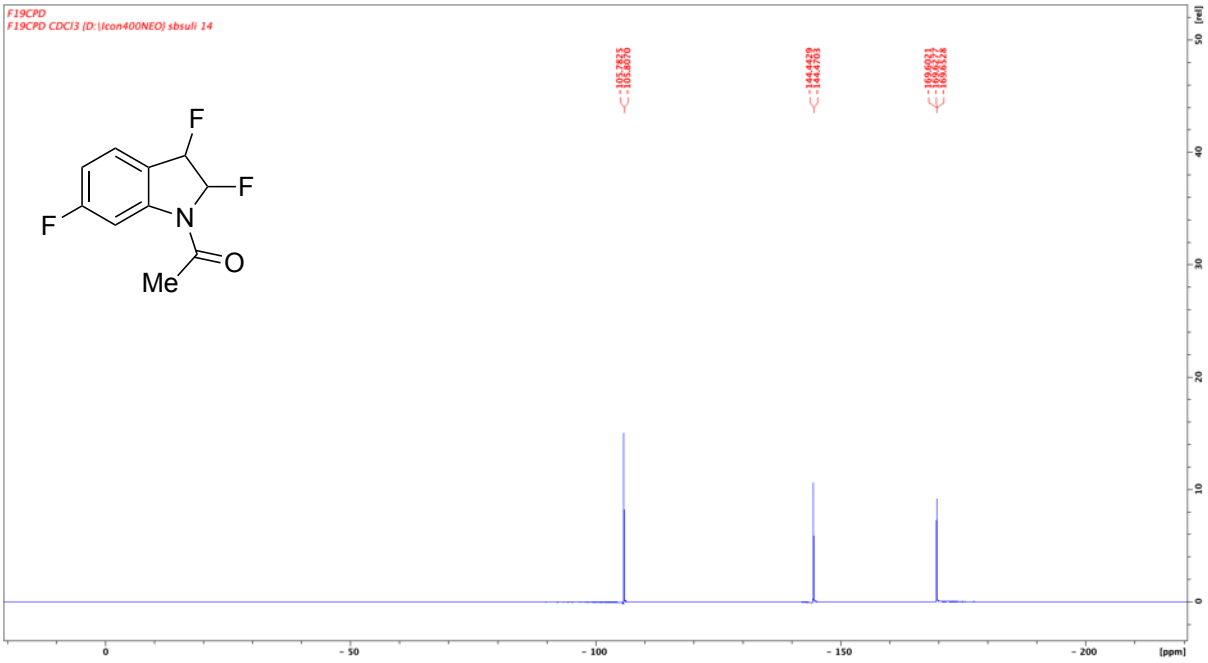
^{19}F NMR spectrum of **6g**



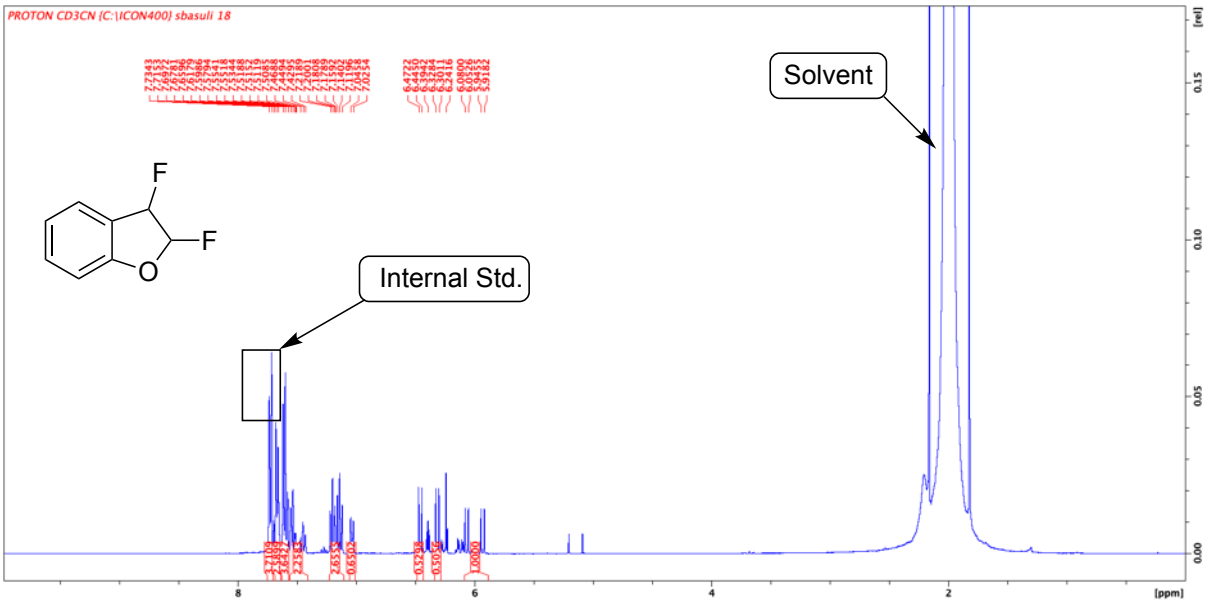
^{1}H NMR spectrum of **6h**



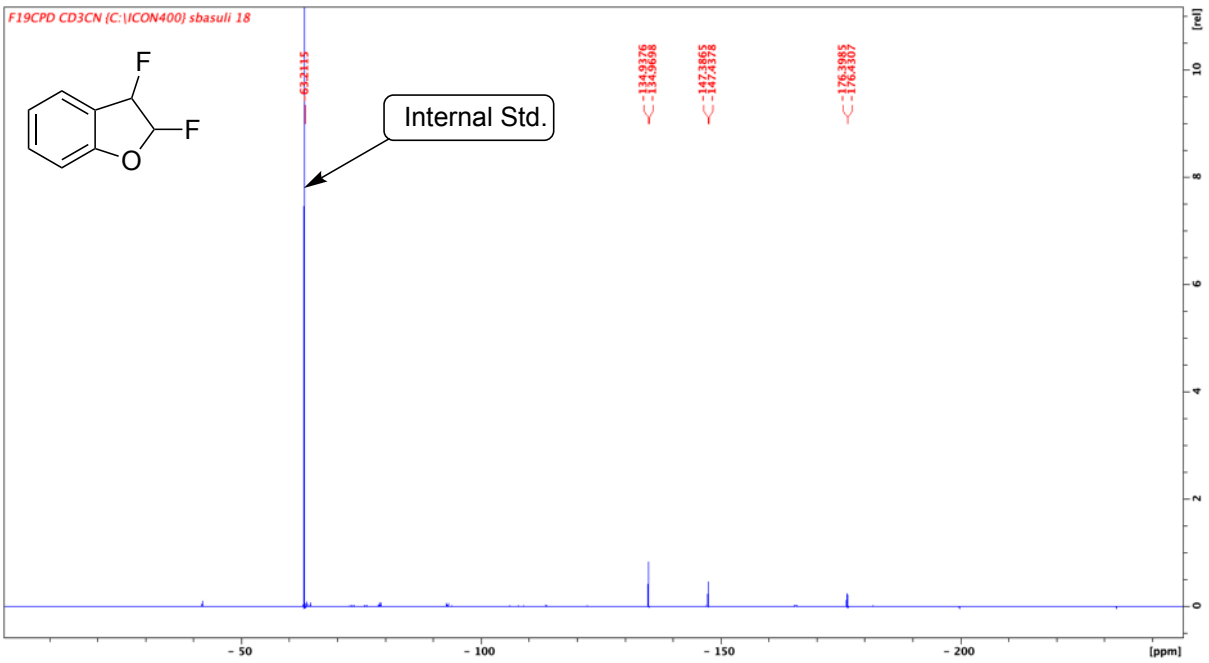
^{13}C NMR spectrum of **6h**



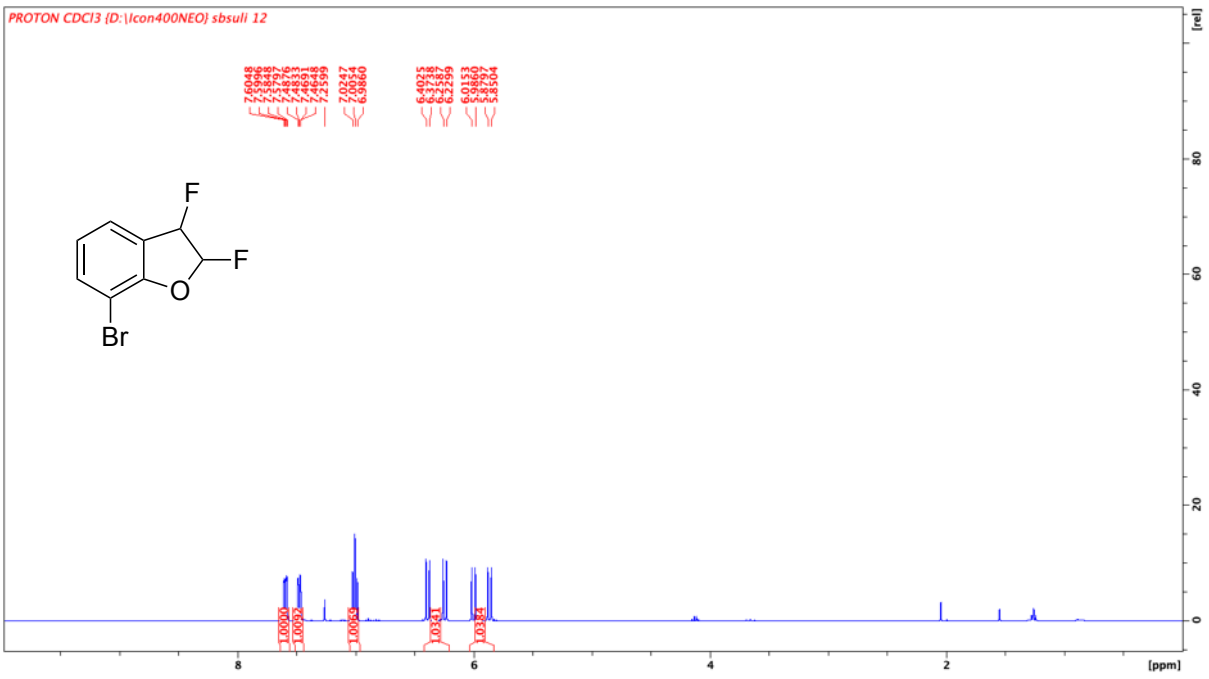
^{19}F NMR spectrum of **6h**



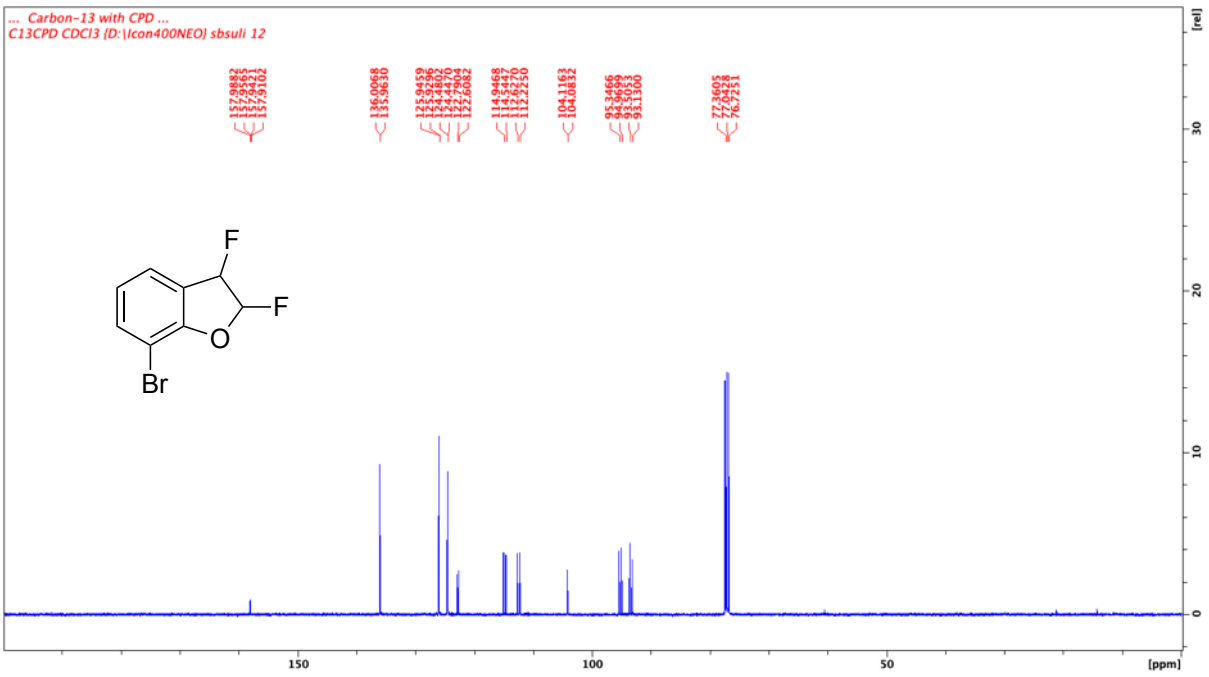
^{1}H NMR spectrum of **6i** (Crude reaction mixture)



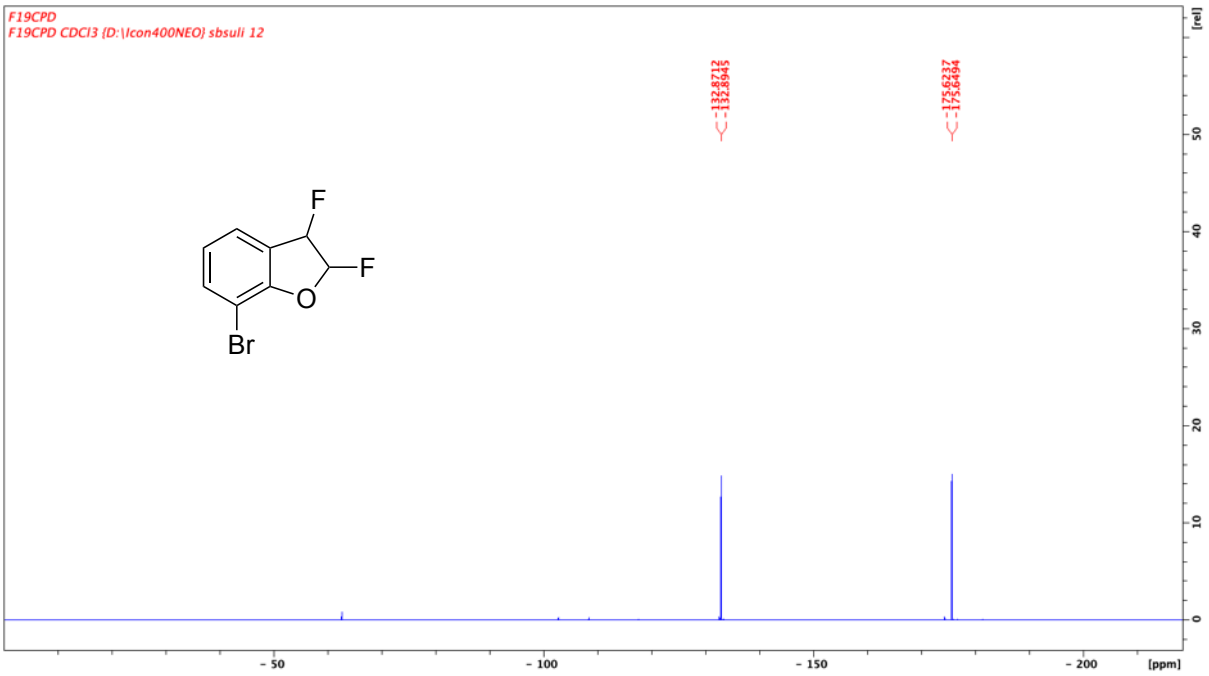
^{19}F NMR spectrum of **6i** (Crude reaction mixture)



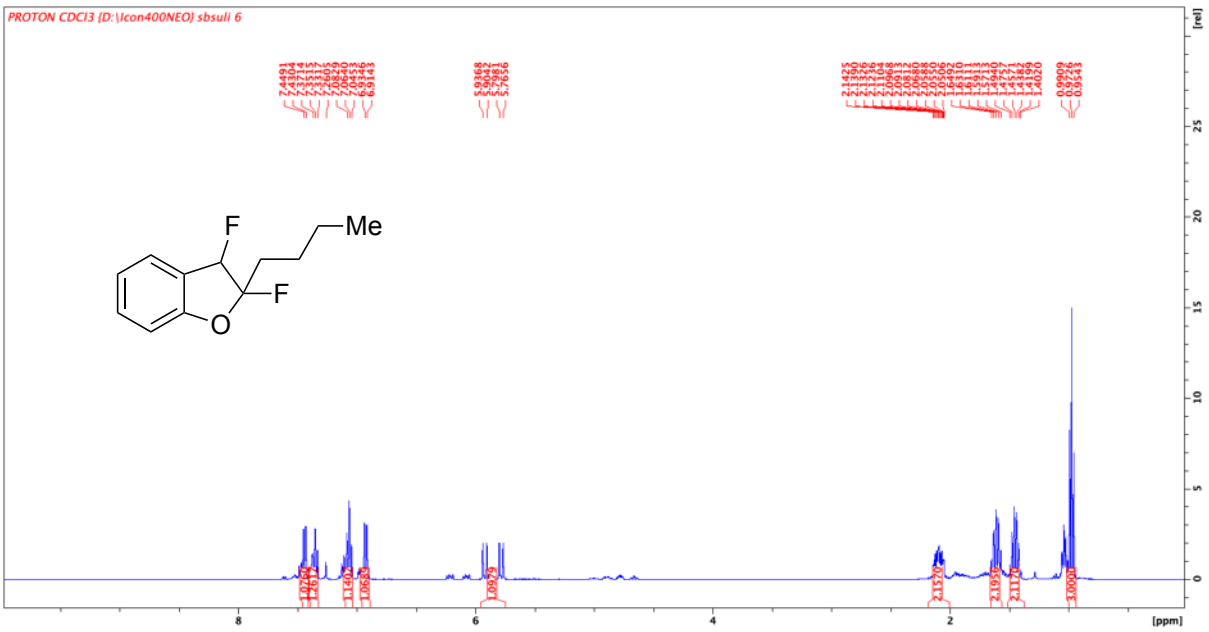
^{1}H NMR spectrum of **6l**



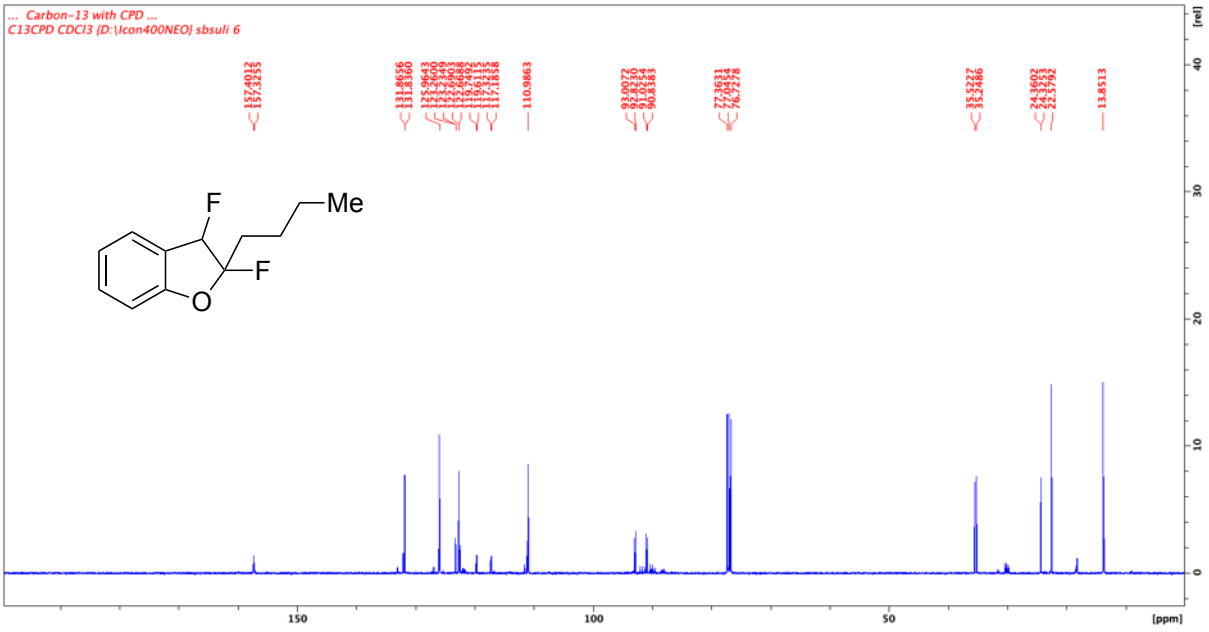
^{13}C NMR spectrum of **6l**



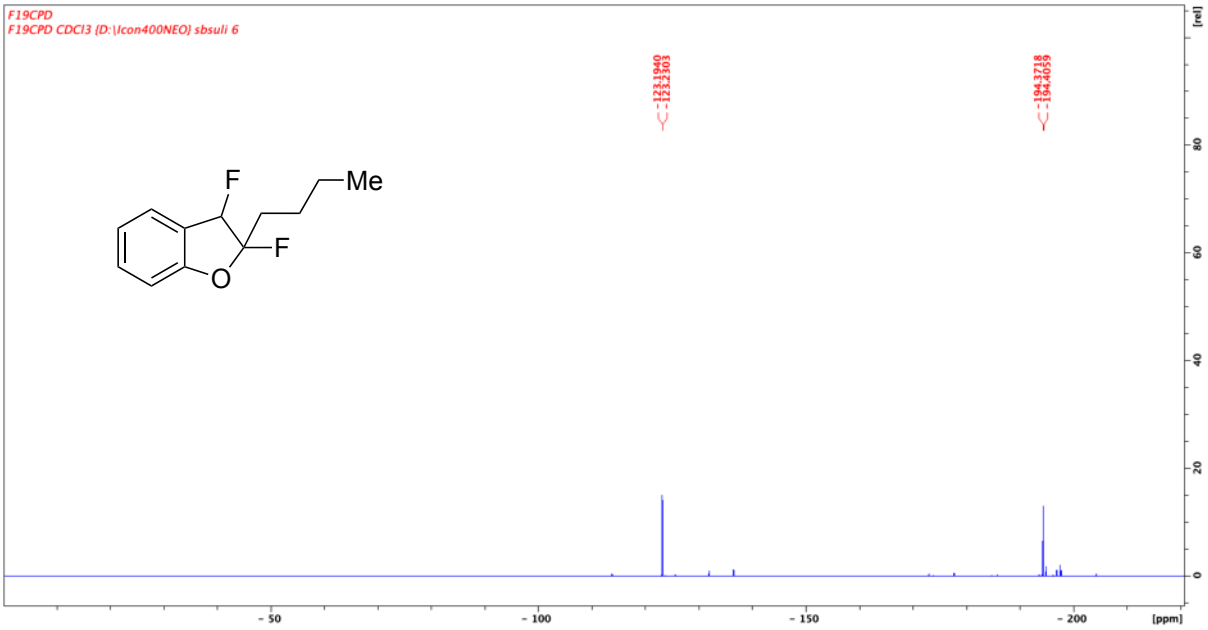
^{19}F NMR spectrum of **6l**



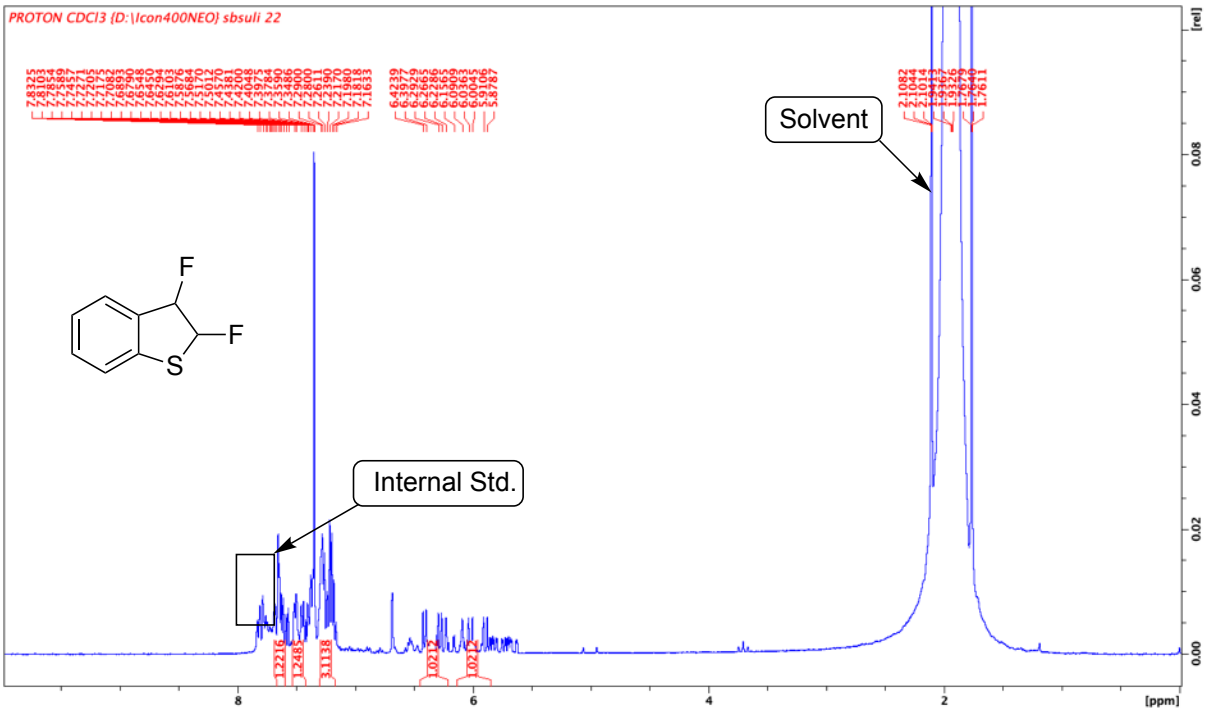
^{1}H NMR spectrum of **6m**



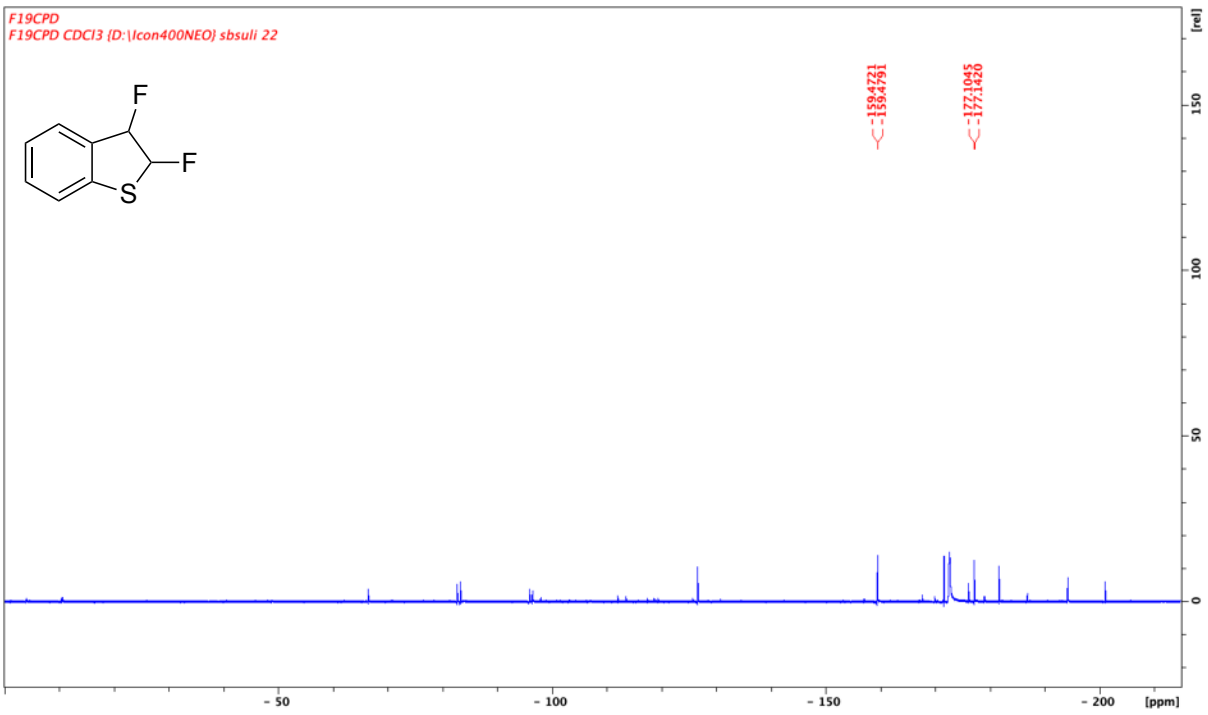
^{13}C NMR spectrum of **6m**



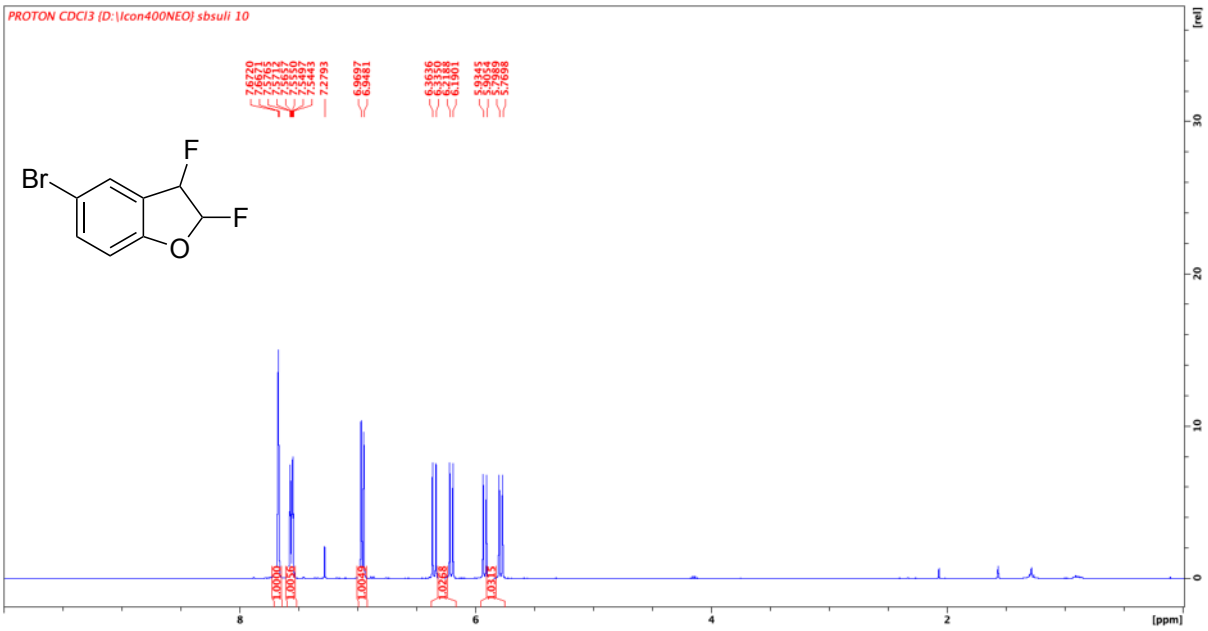
^{19}F NMR spectrum of **6m**



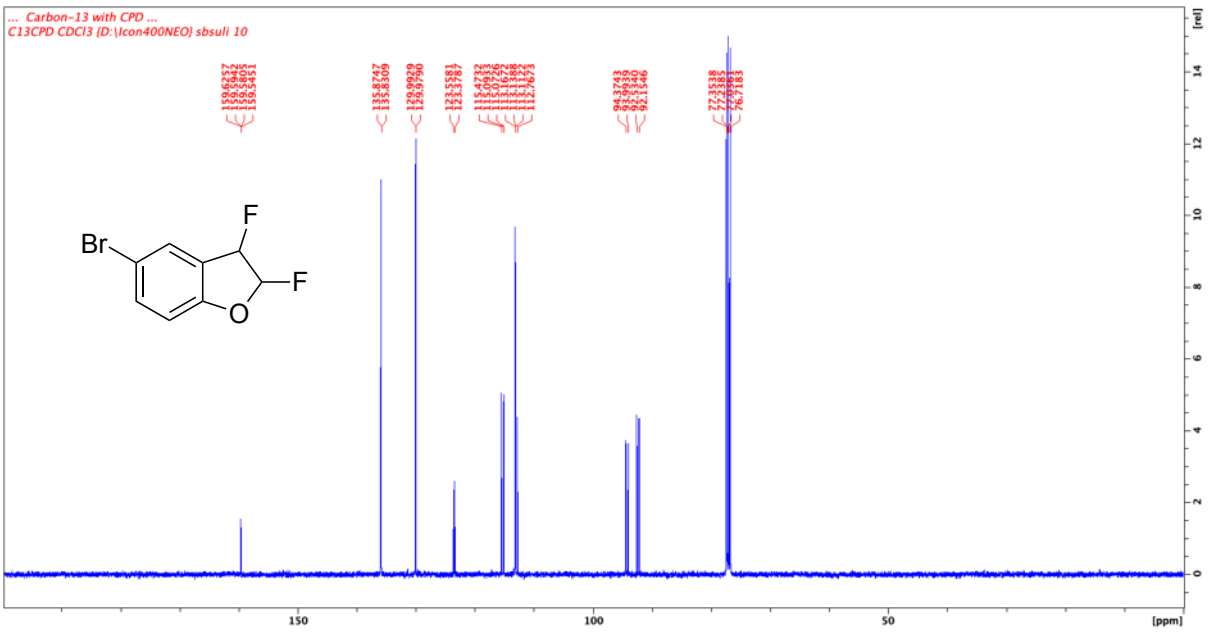
^{1}H NMR spectrum of **6n** (Crude reaction mixture)



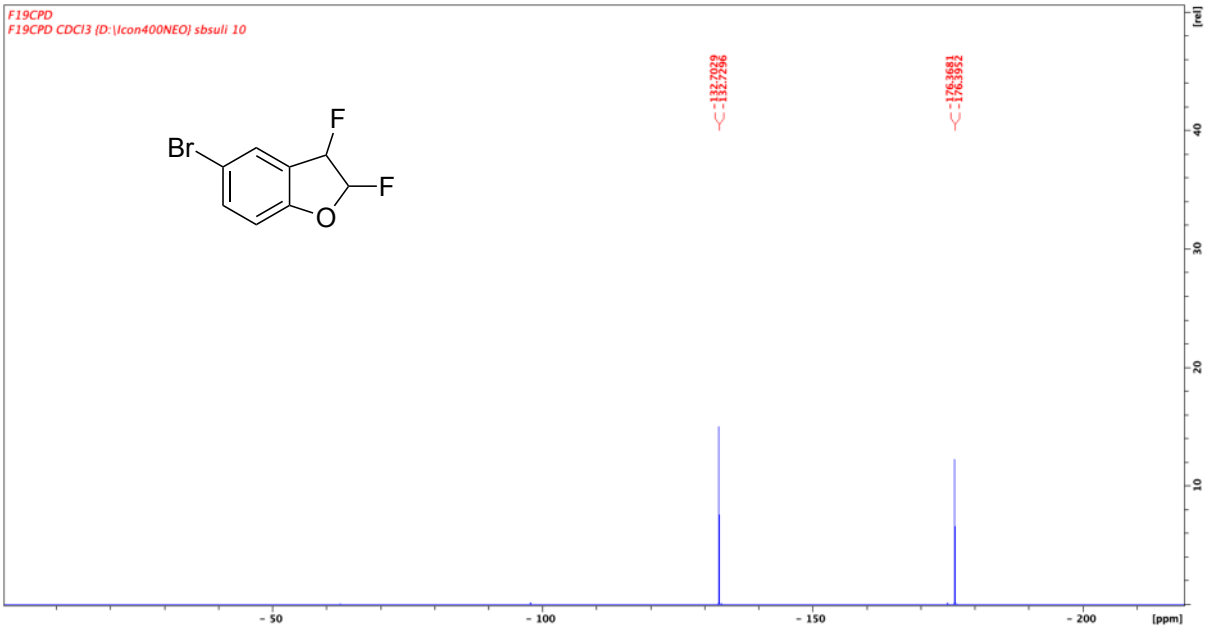
^{19}F NMR spectrum of **6n** (Crude reaction mixture)



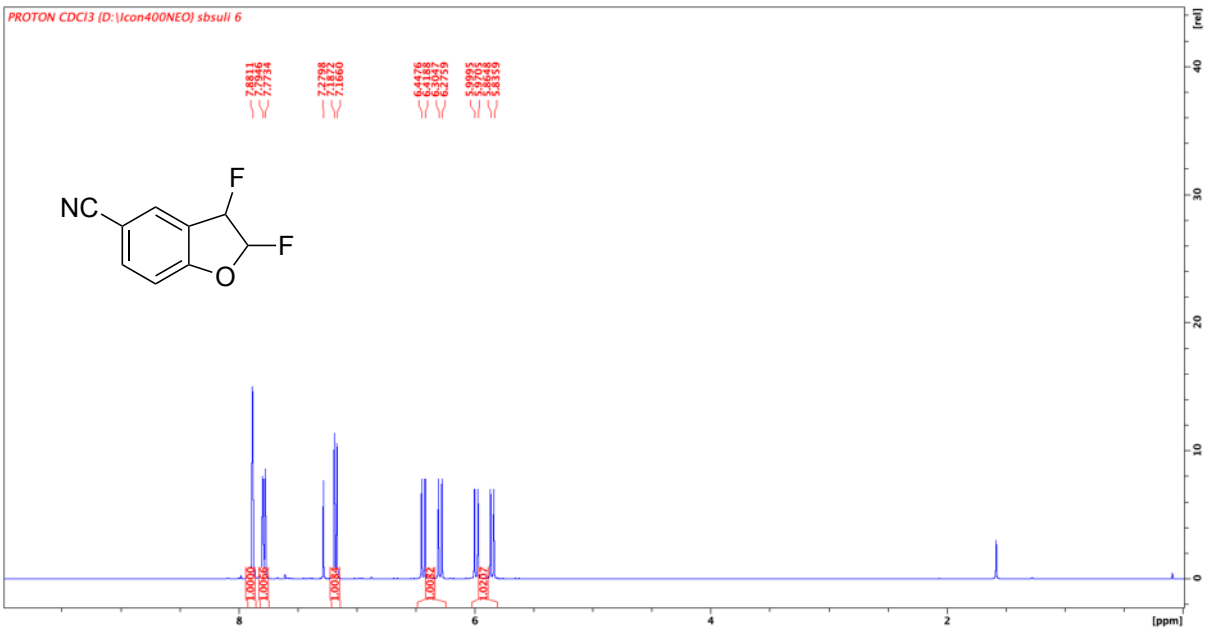
^{1}H NMR spectrum of **6j**



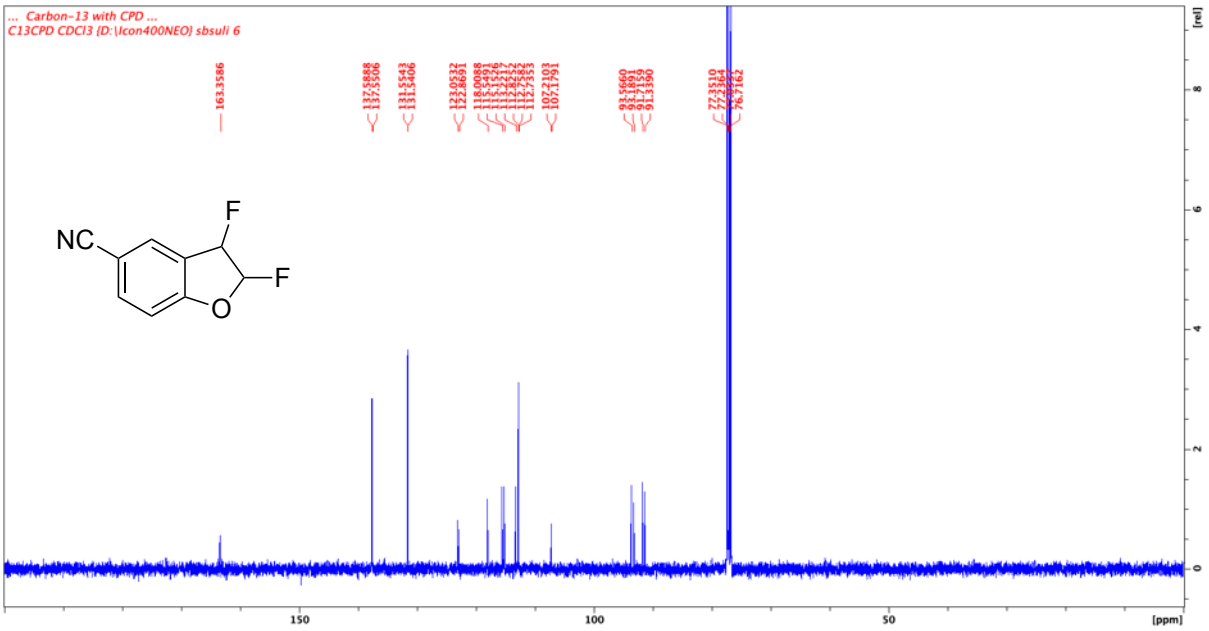
^{13}C NMR spectrum of **6j**



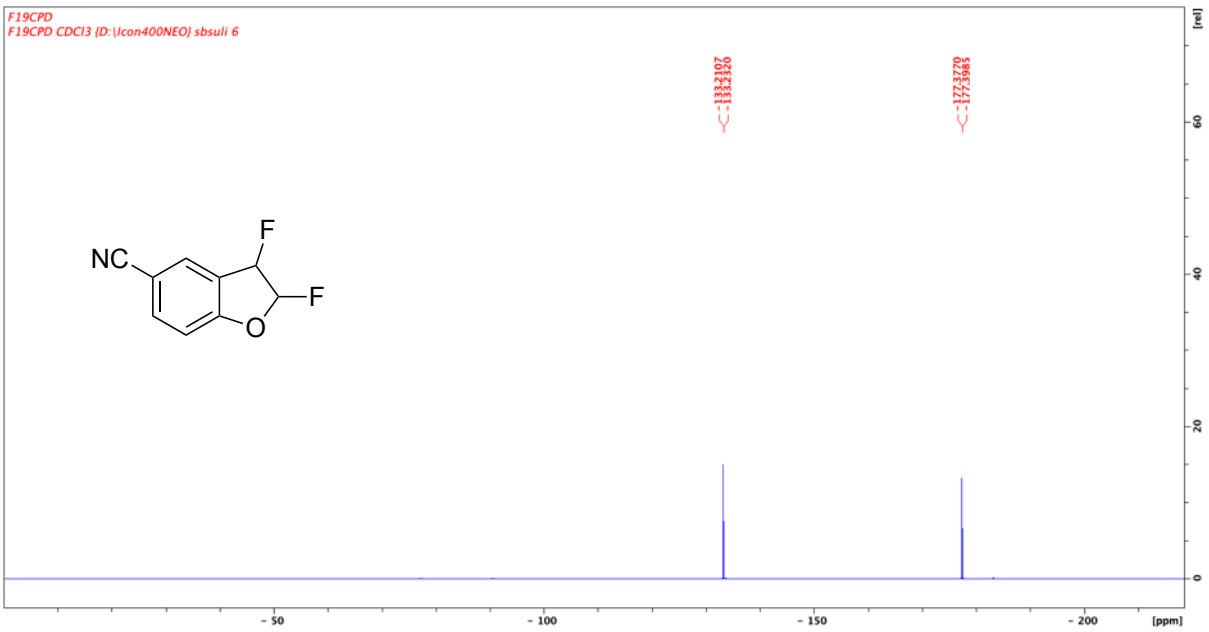
^{19}F NMR spectrum of **6j**



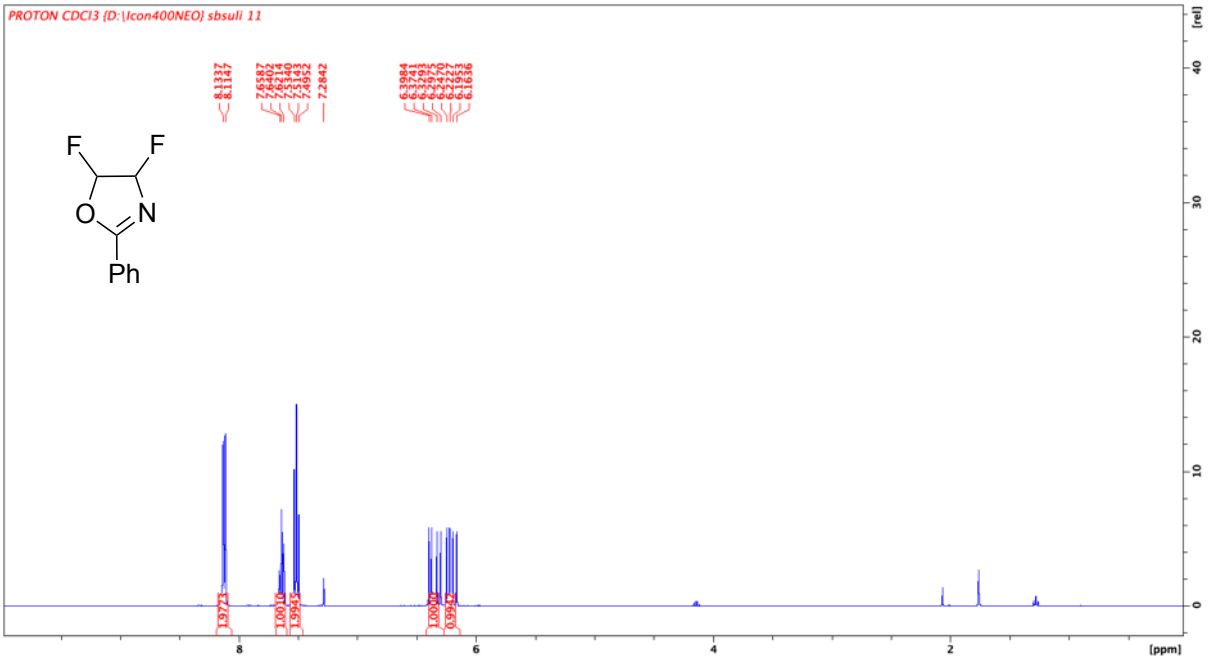
^{1}H NMR spectrum of **6k**



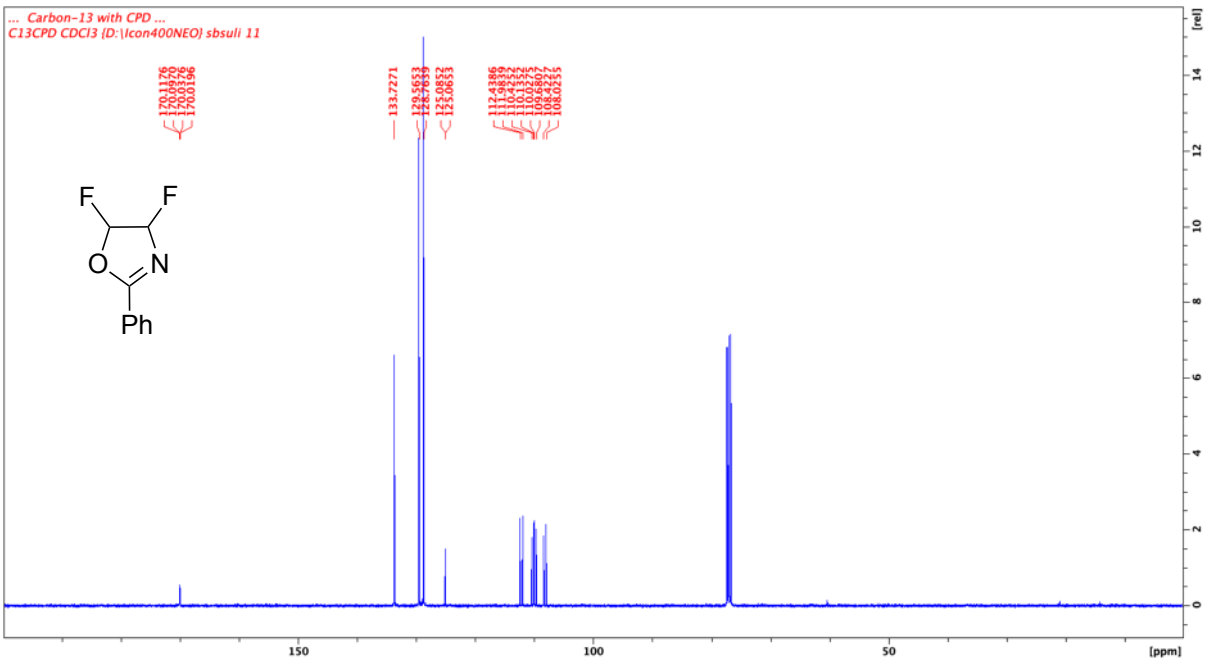
^{13}C NMR spectrum of **6k**



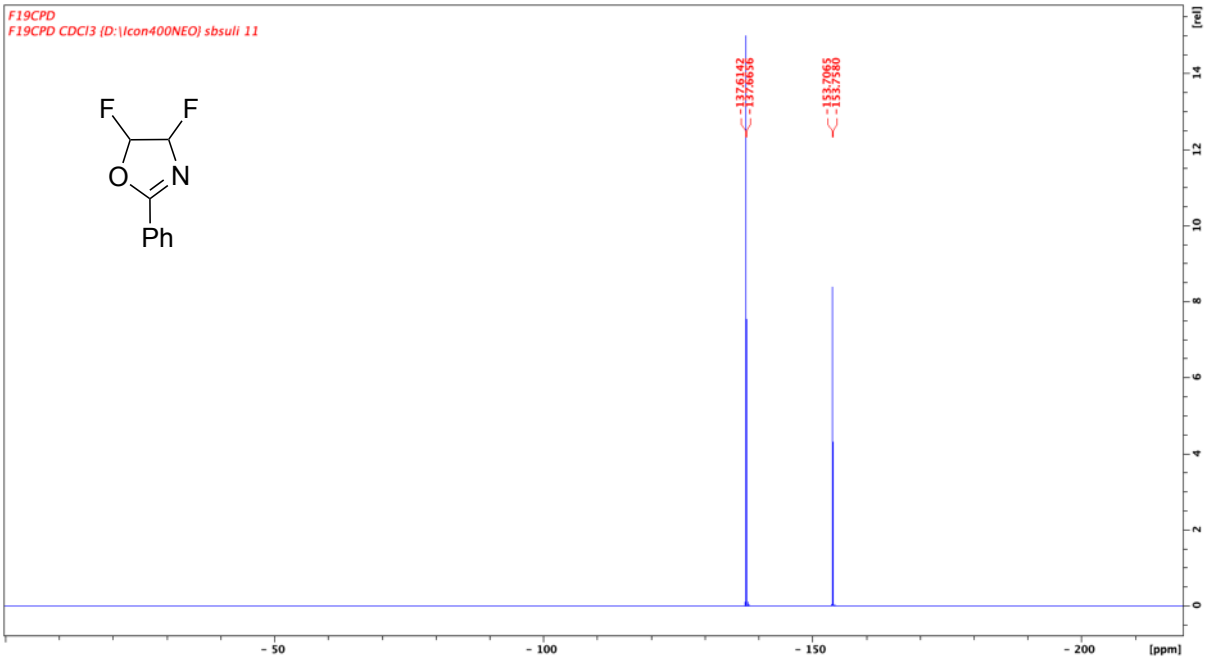
^{19}F NMR spectrum of **6k**



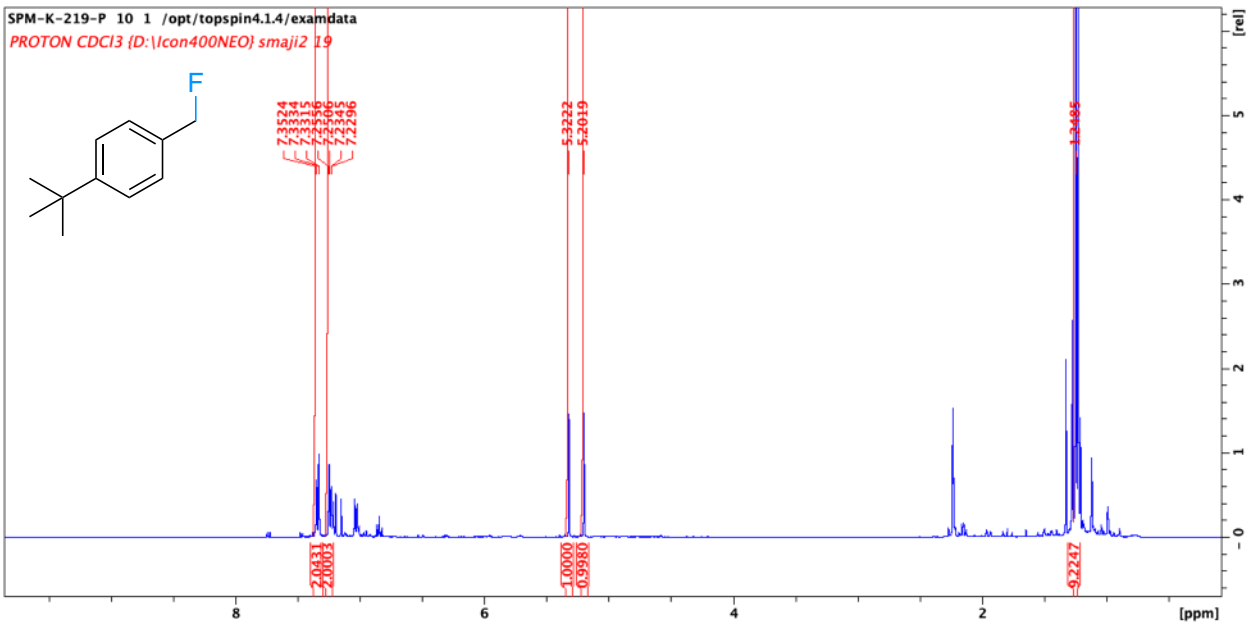
^{1}H NMR spectrum of **6x**



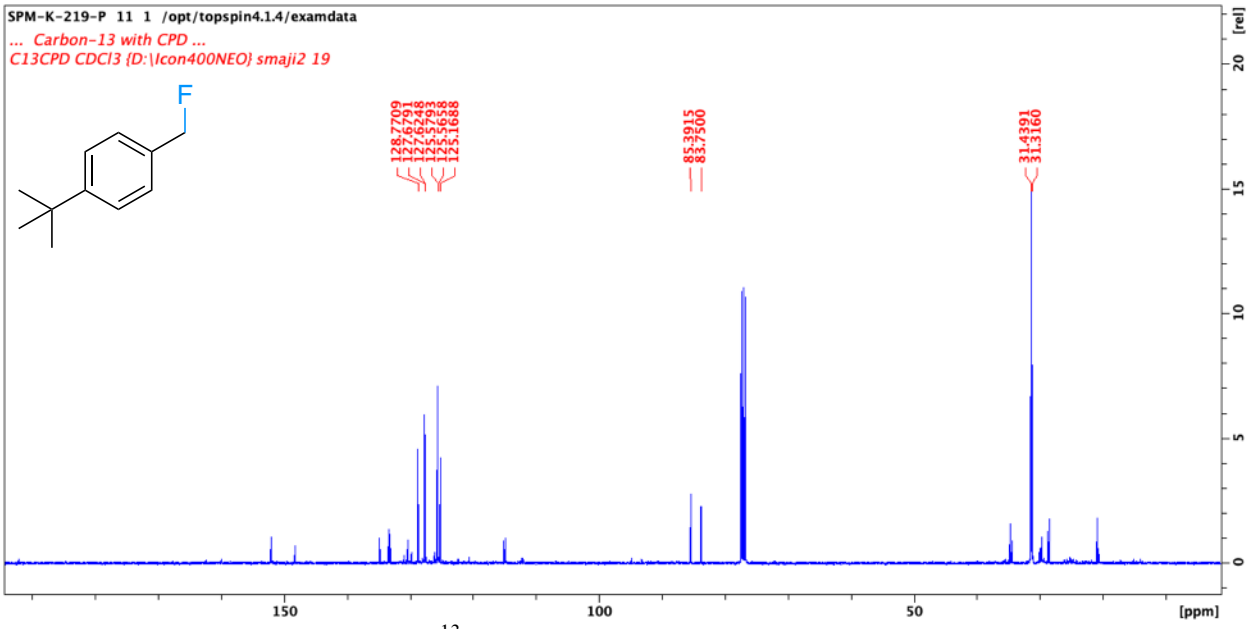
^{13}C NMR spectrum of **6x**



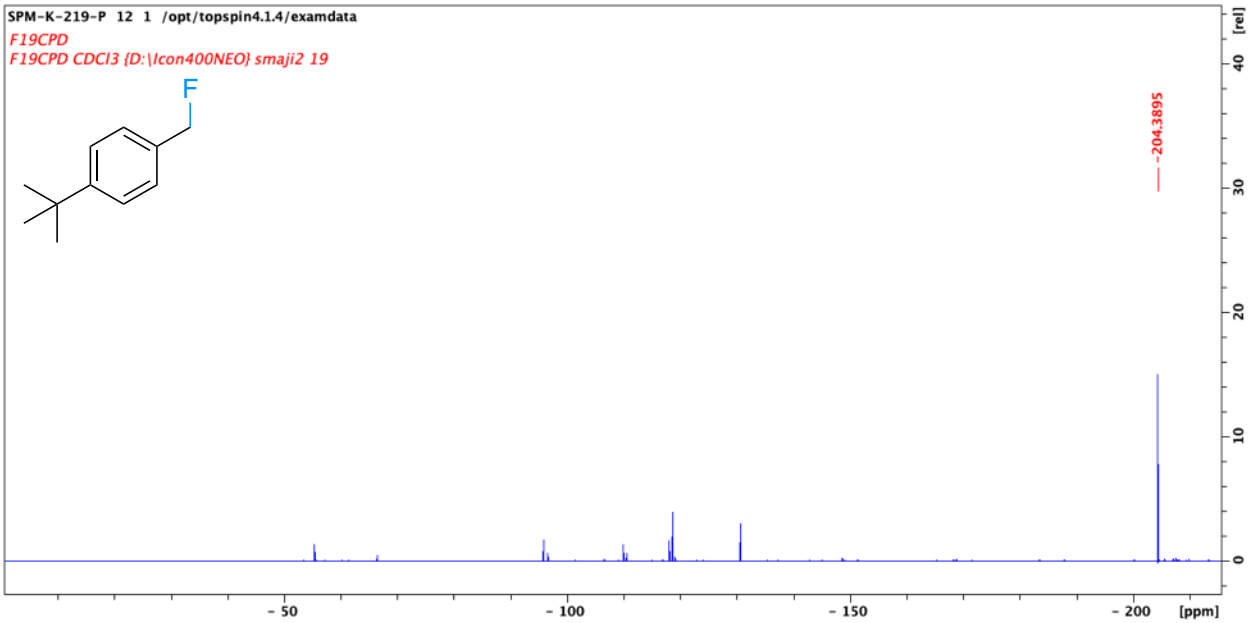
^{19}F NMR spectrum of **6x**



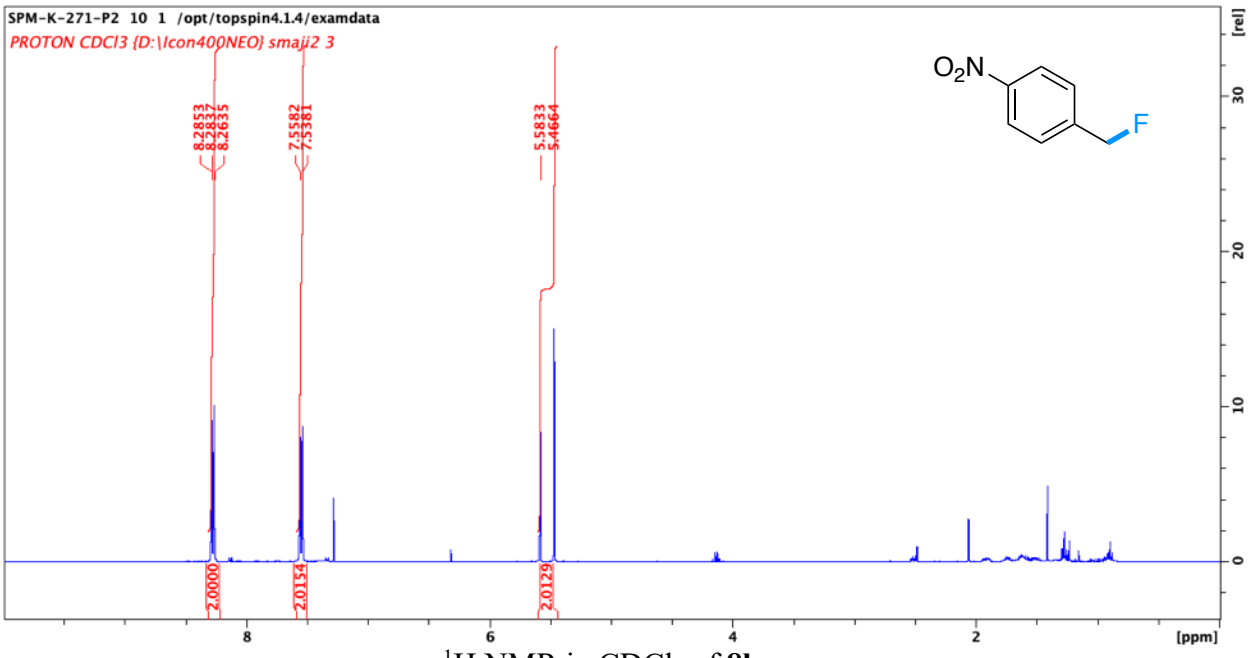
^{1}H NMR in $CDCl_3$ of **8a**



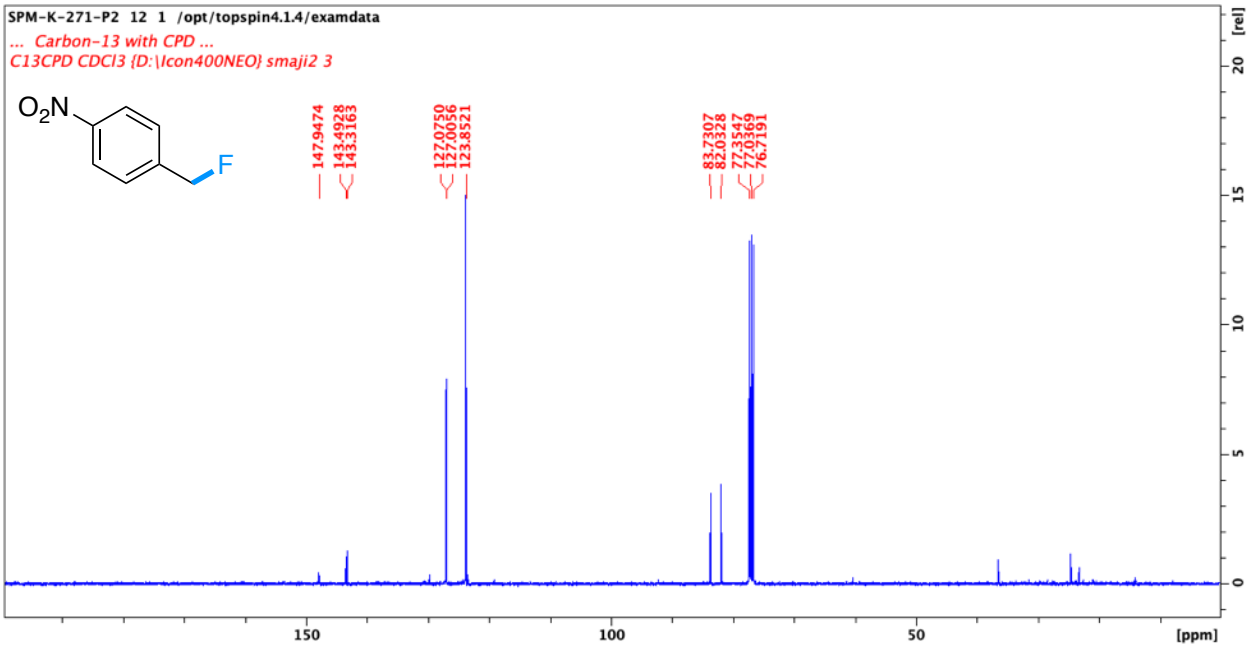
^{13}C NMR spectrum of **8a**



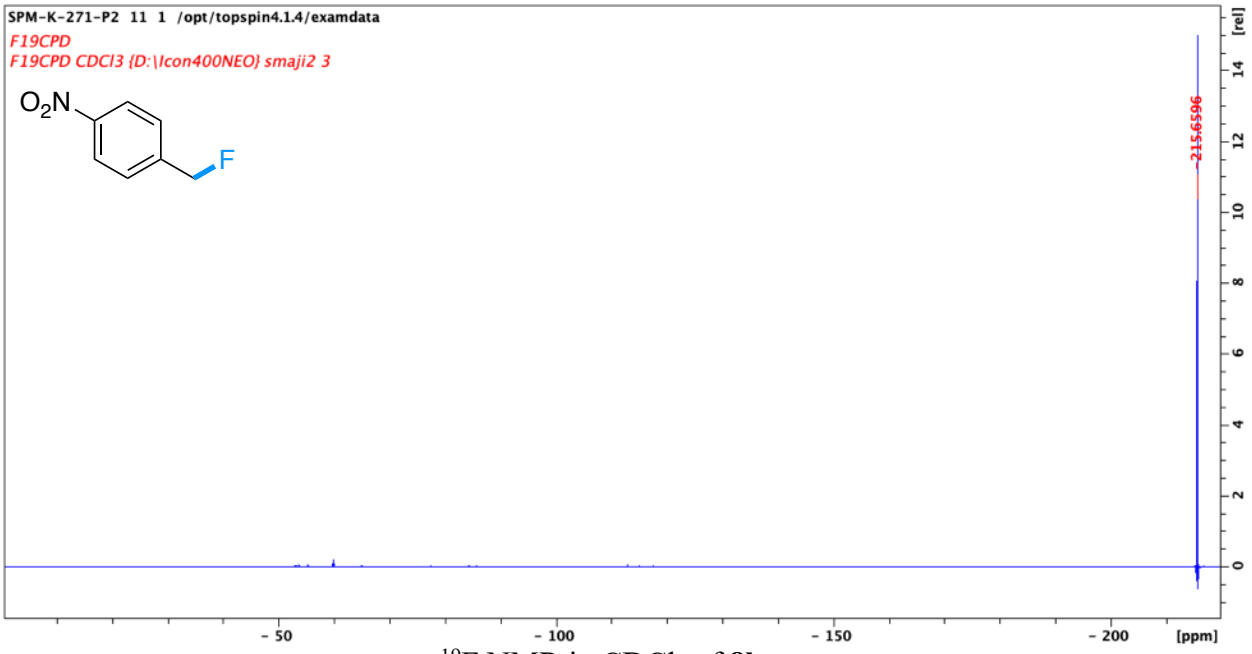
^{19}F NMR in $CDCl_3$ of **8a**



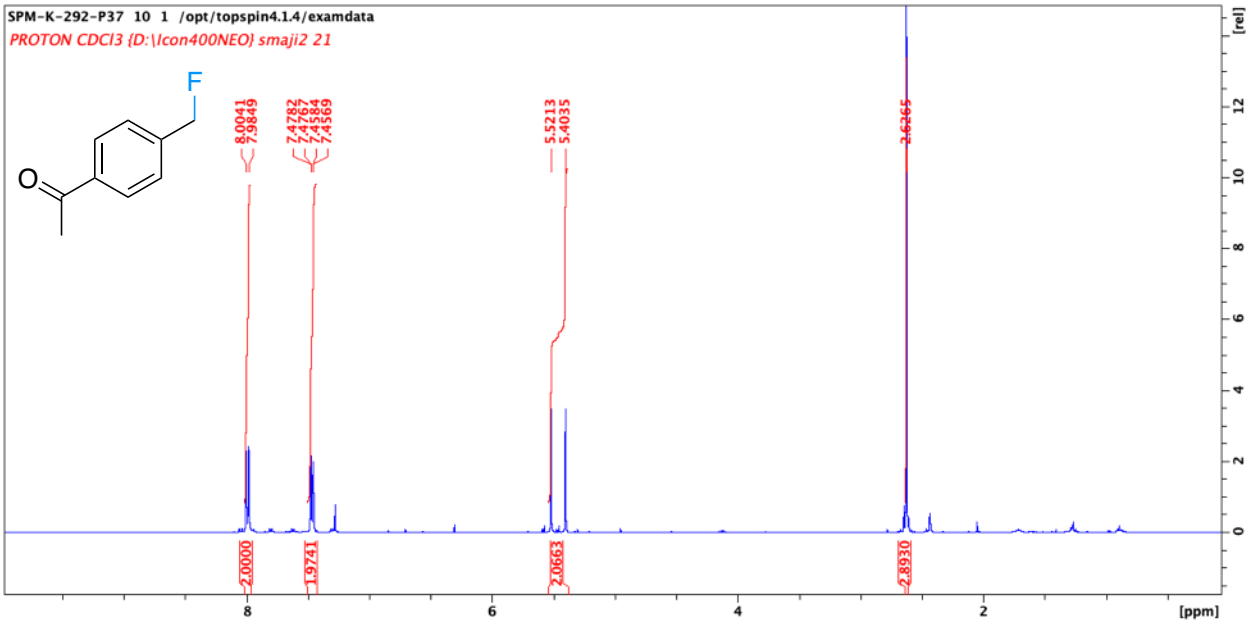
^{1}H NMR in $CDCl_3$ of **8b**



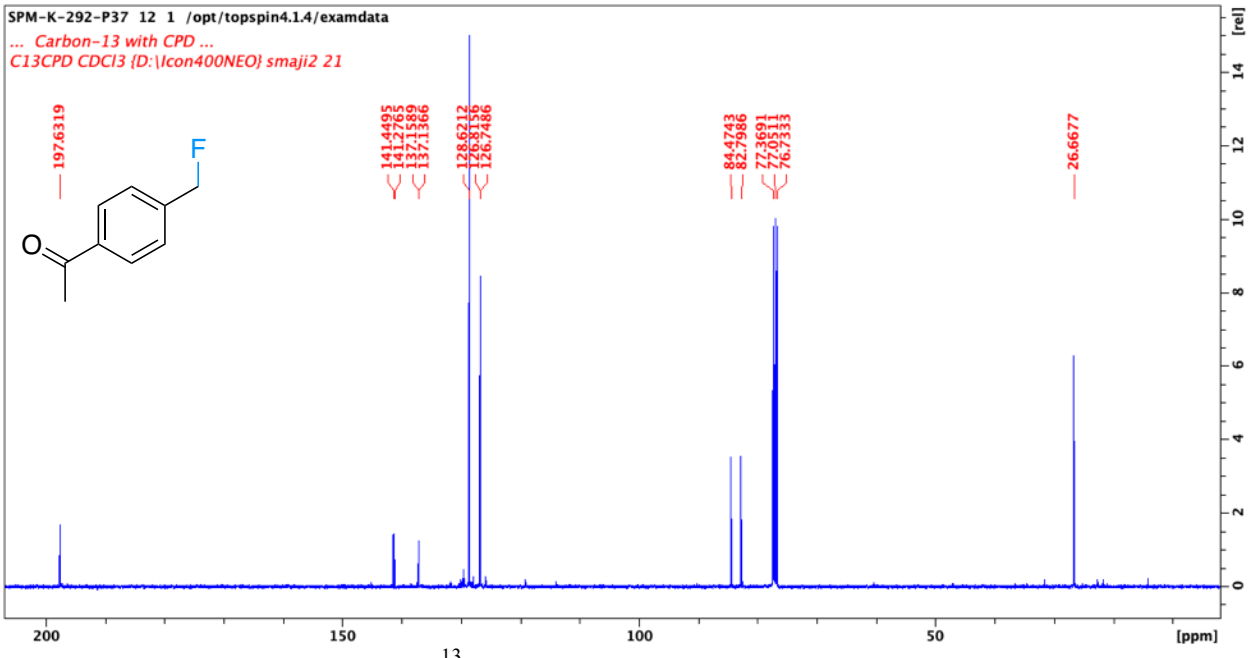
^{13}C NMR spectrum of **8b**



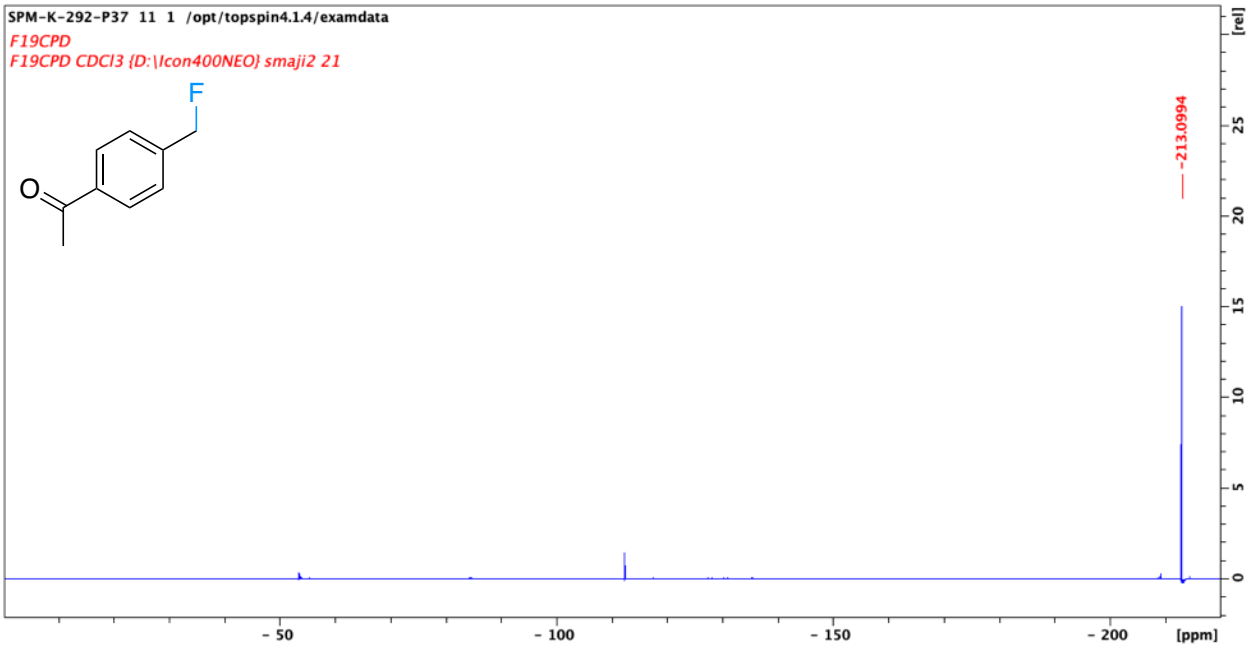
^{19}F NMR in $CDCl_3$ of **8b**



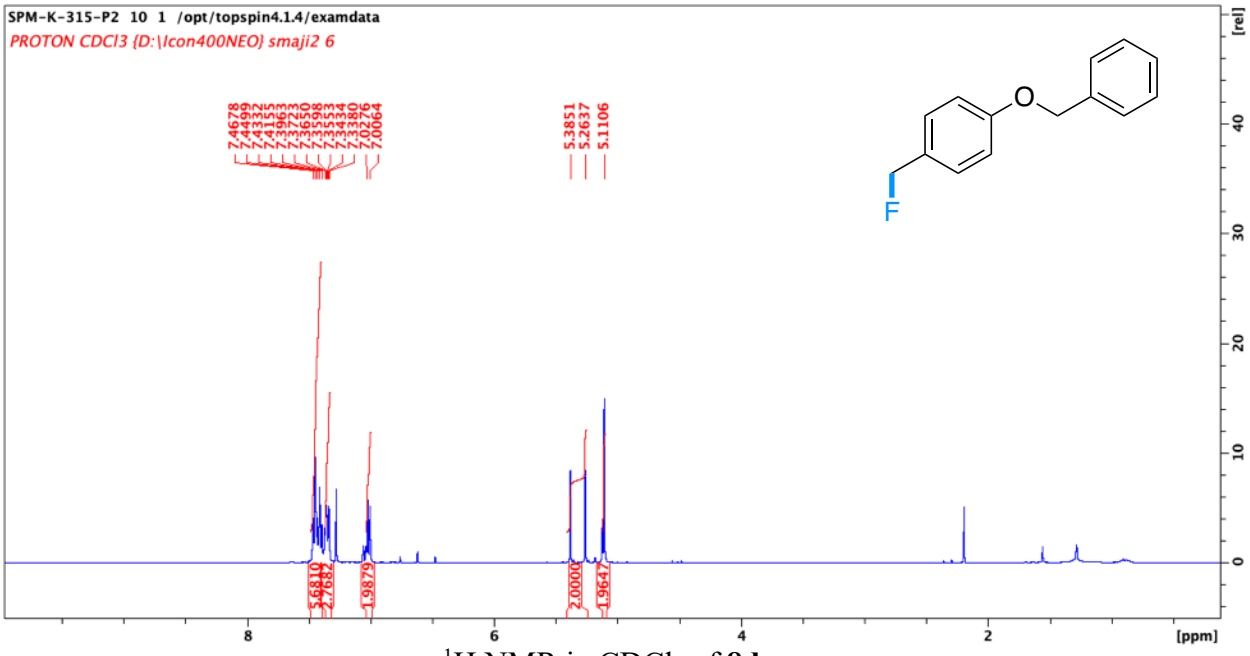
^{1}H NMR in $CDCl_3$ of **8c**



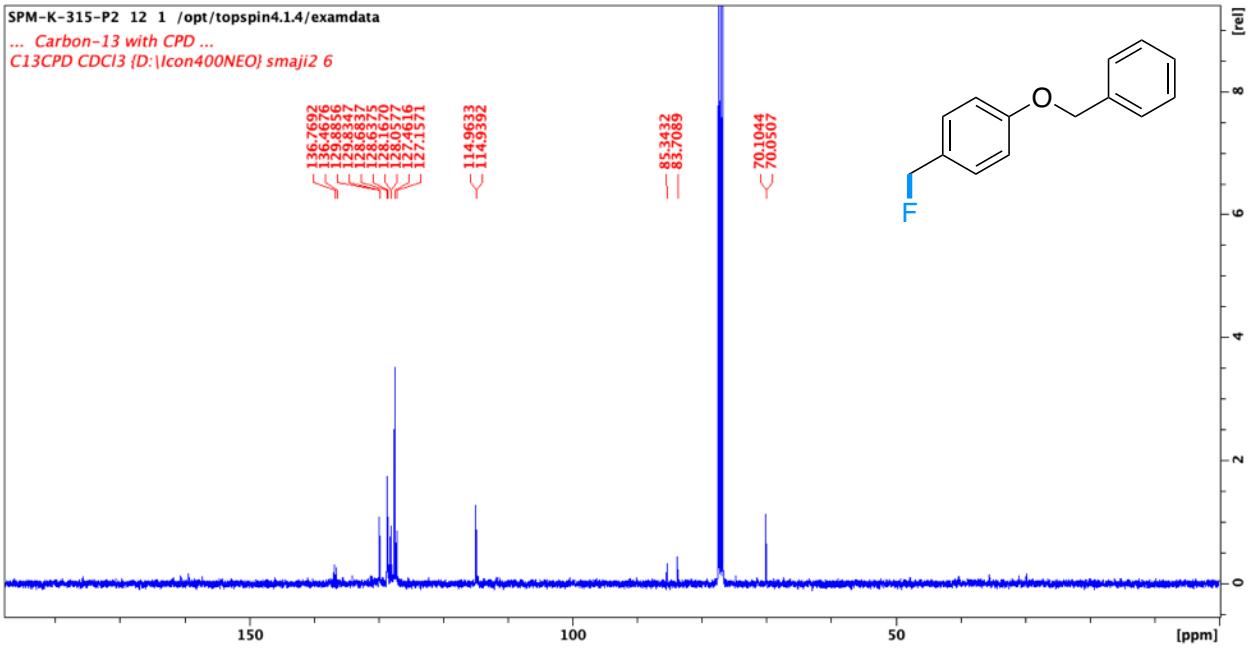
^{13}C NMR spectrum of **8c**



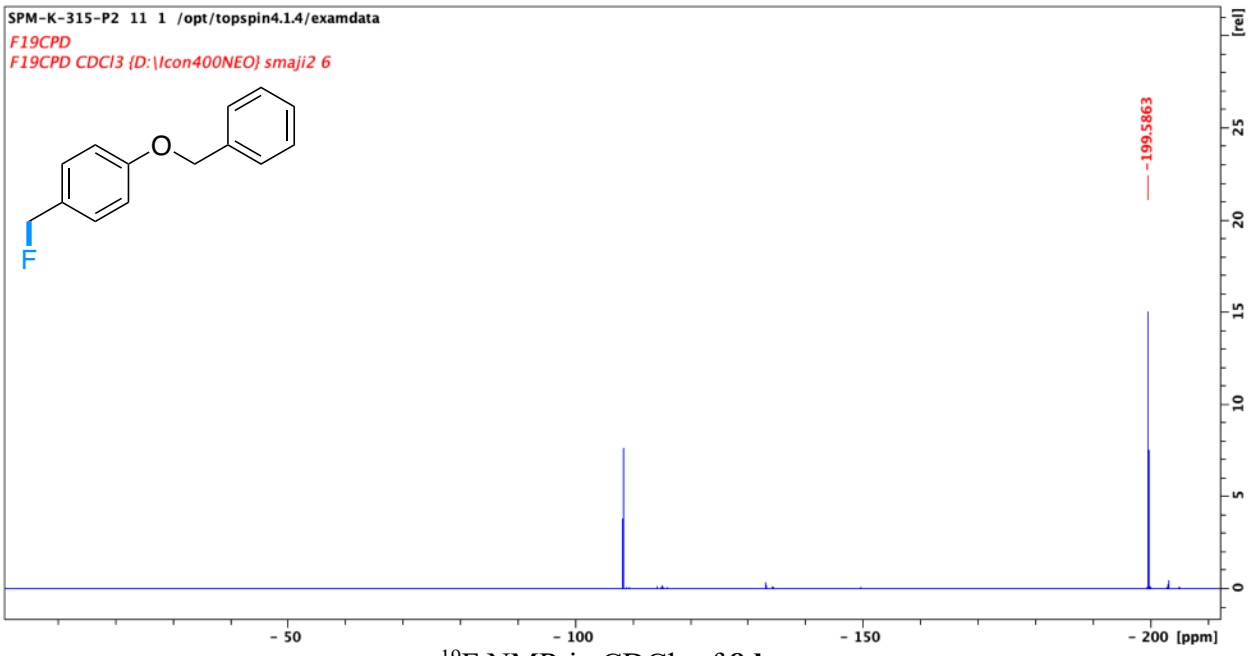
^{19}F NMR in $CDCl_3$ of **8c**



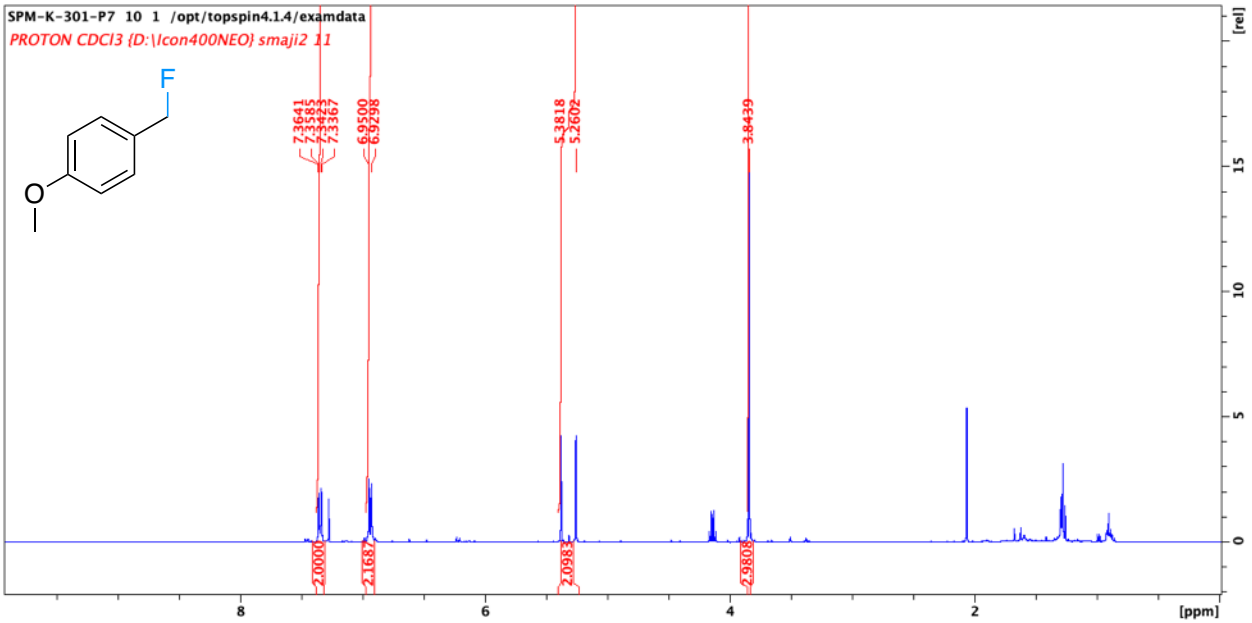
^{1}H NMR in $CDCl_3$ of **8d**



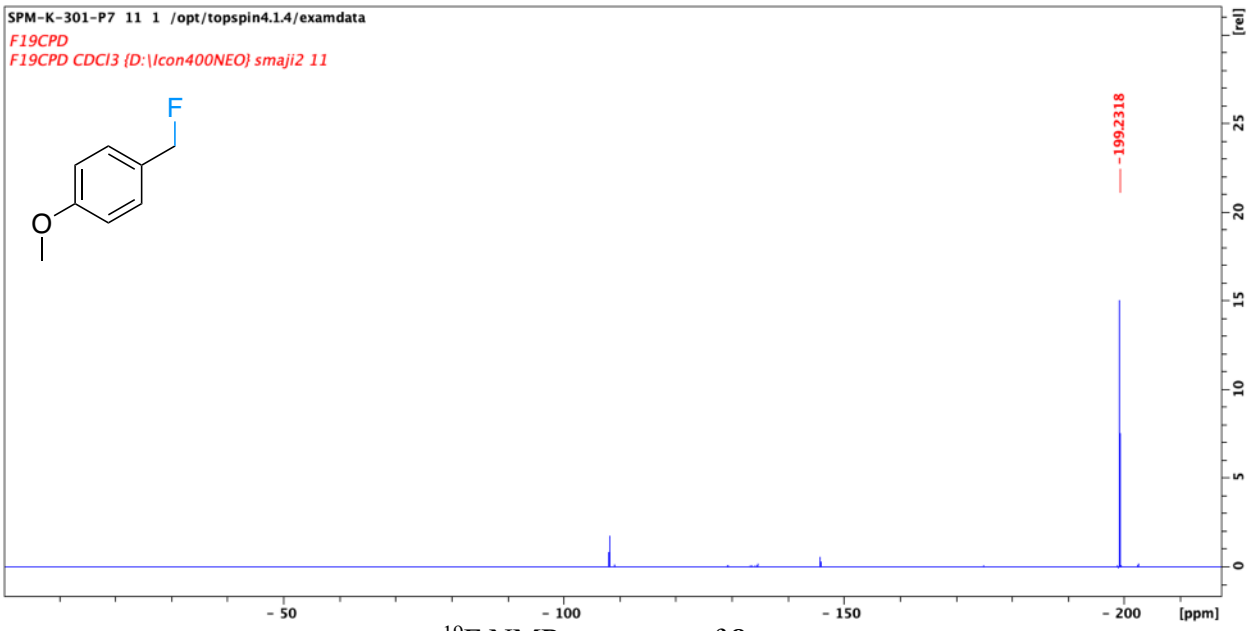
^{13}C NMR spectrum of **8d**



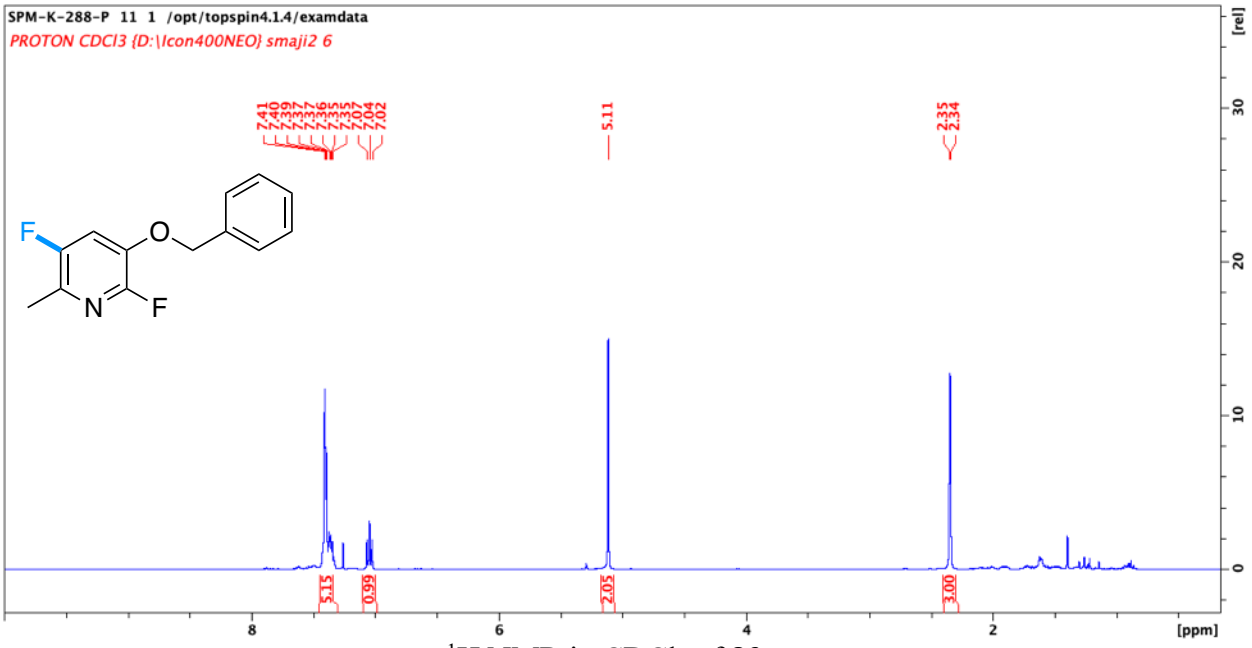
^{19}F NMR in $CDCl_3$ of **8d**



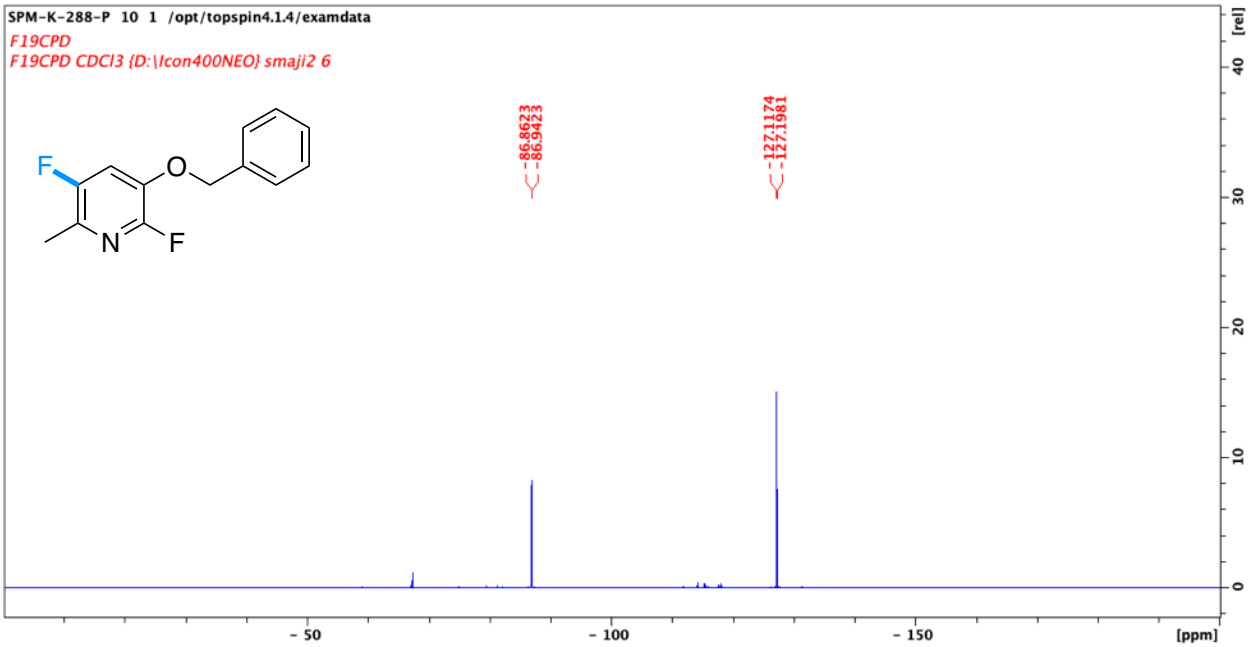
^{1}H NMR in $CDCl_3$ of **8e**



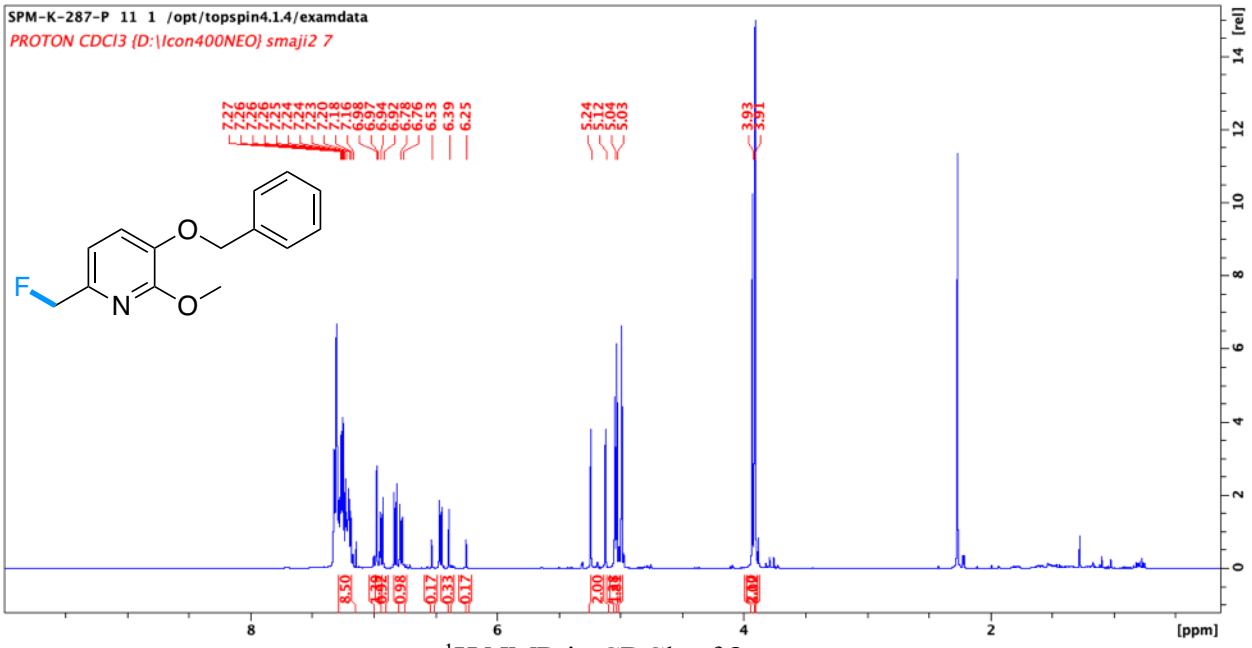
^{19}F NMR spectrum of **8e**



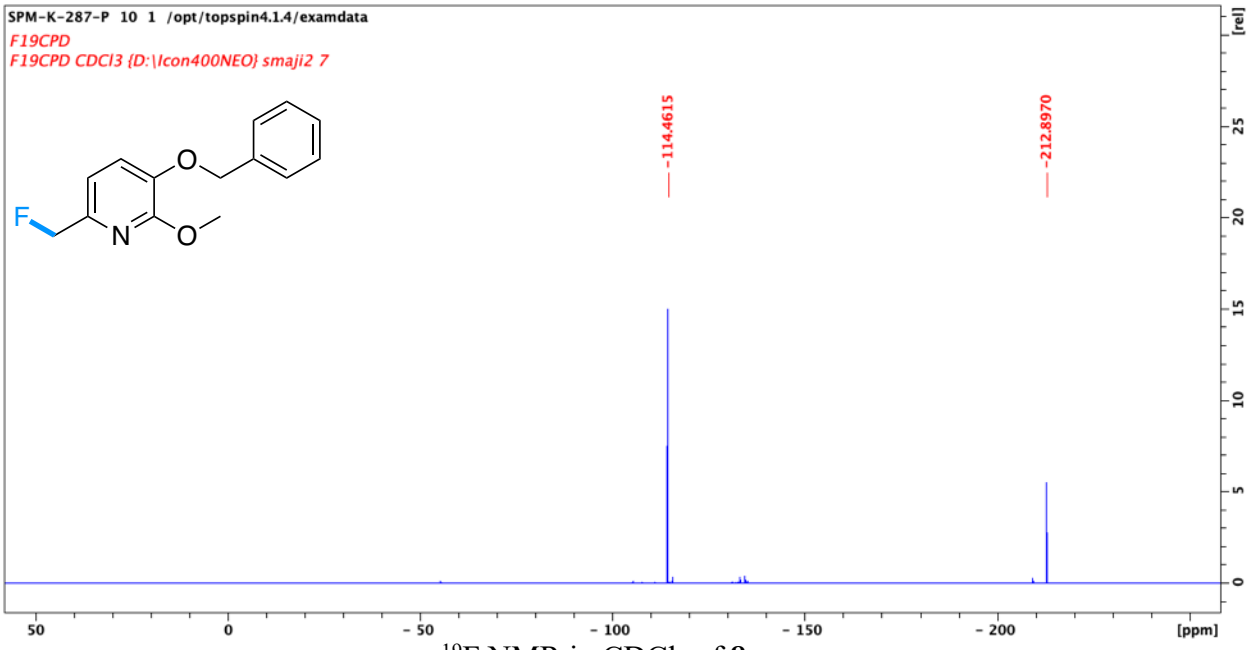
^{1}H NMR in $CDCl_3$ of **8f**



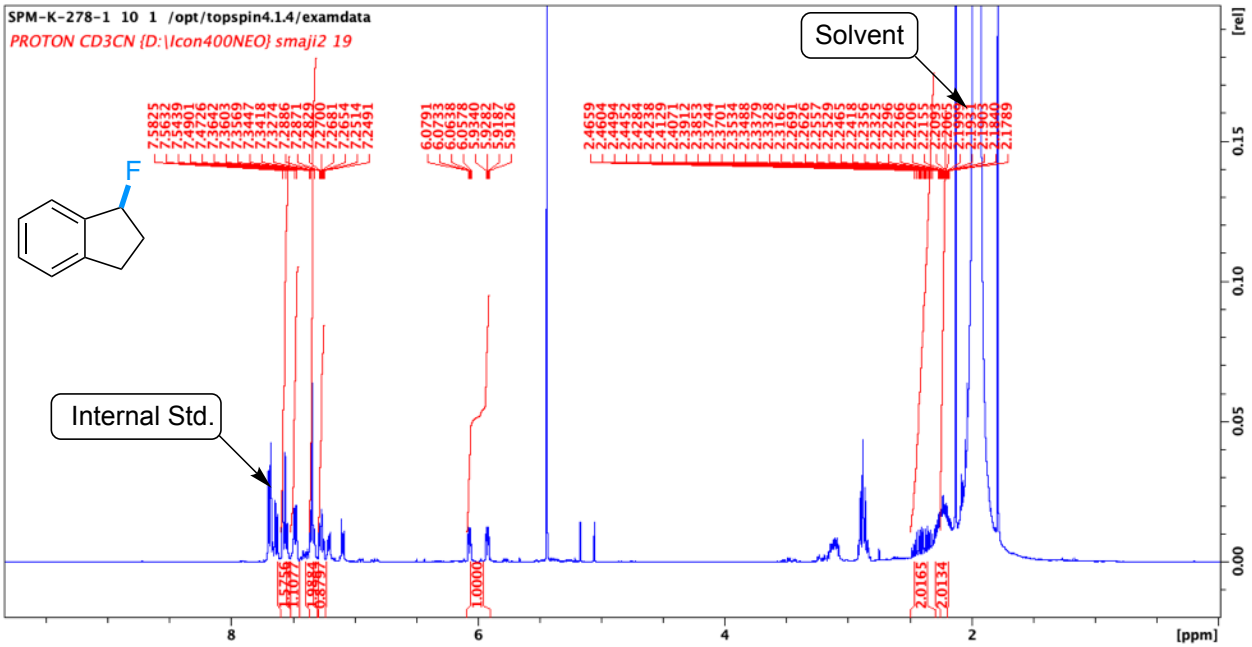
^{19}F NMR in $CDCl_3$ of **8f**



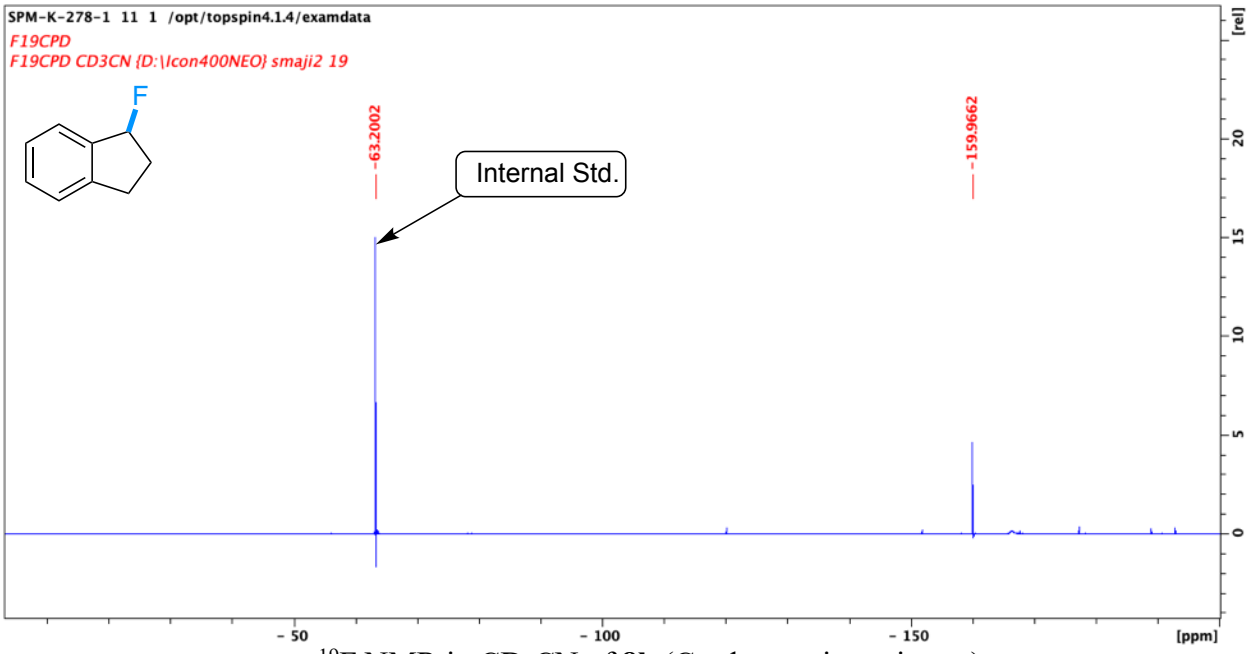
^{1}H NMR in $CDCl_3$ of **8g**



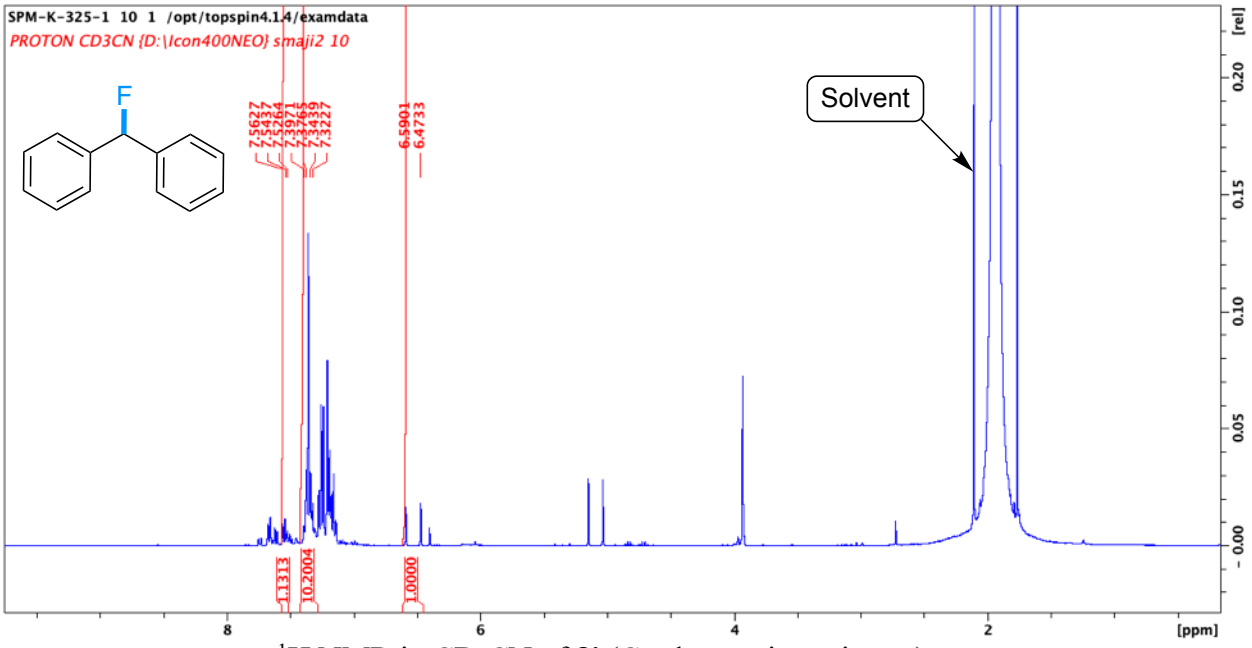
^{19}F NMR in $CDCl_3$ of **8g**



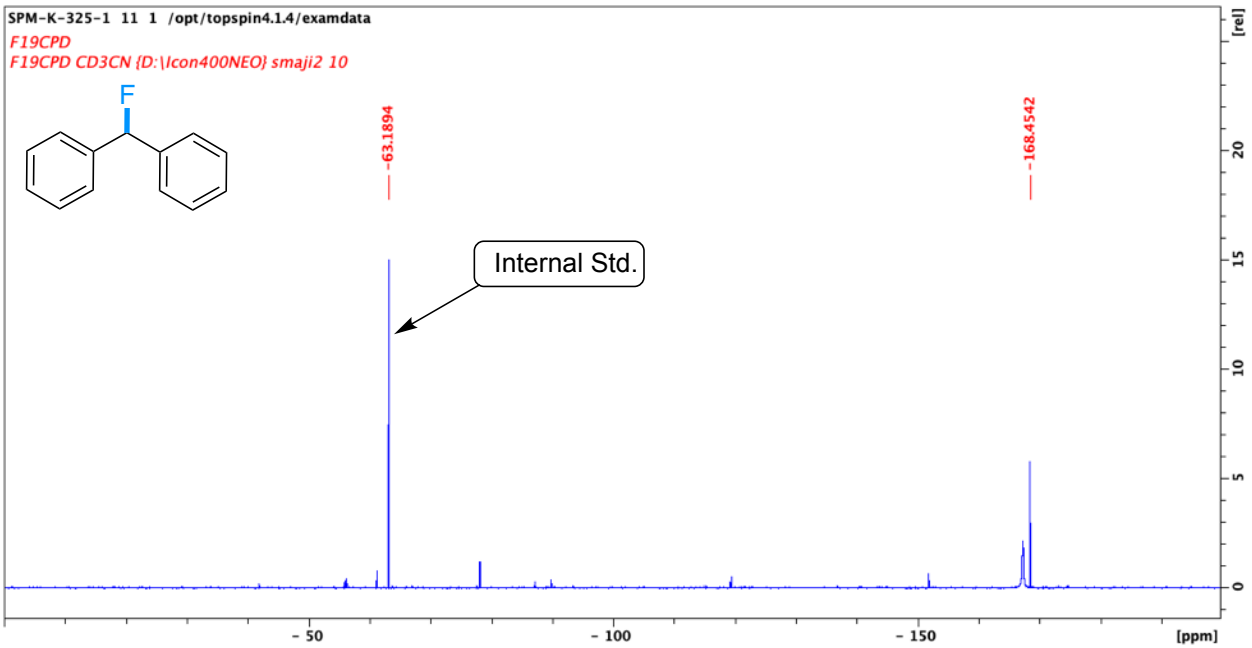
^{1}H NMR in CD_3CN of **8h** (Crude reaction mixture)



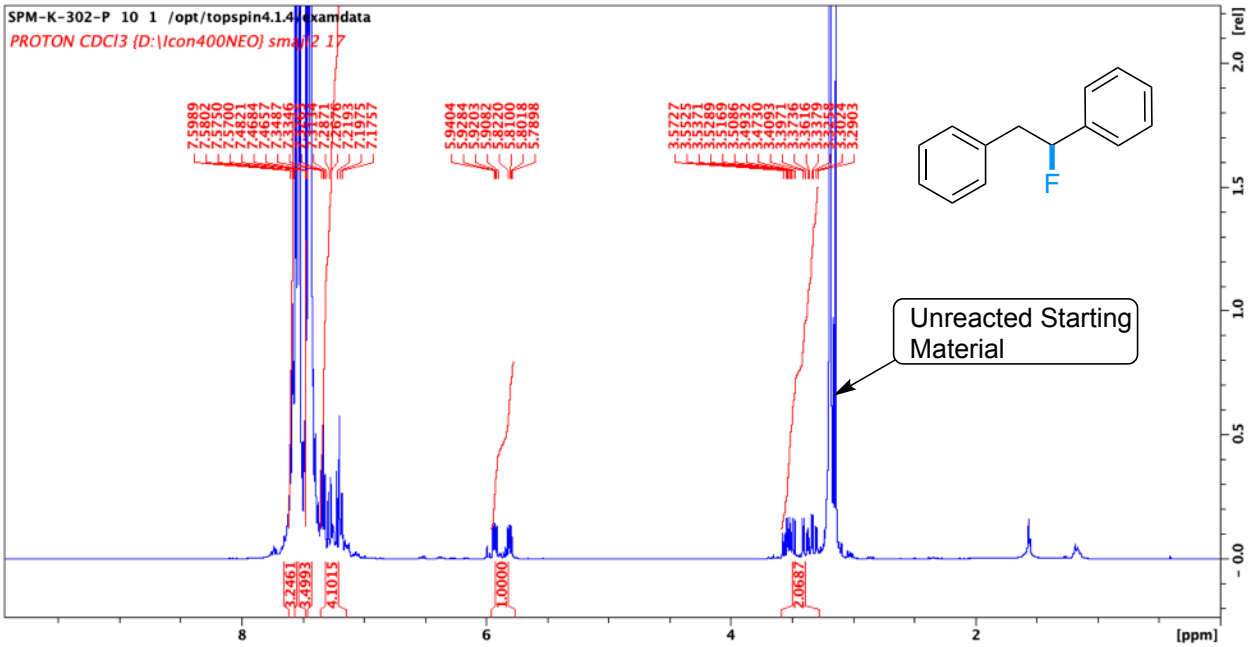
^{19}F NMR in CD_3CN of **8h** (Crude reaction mixture)



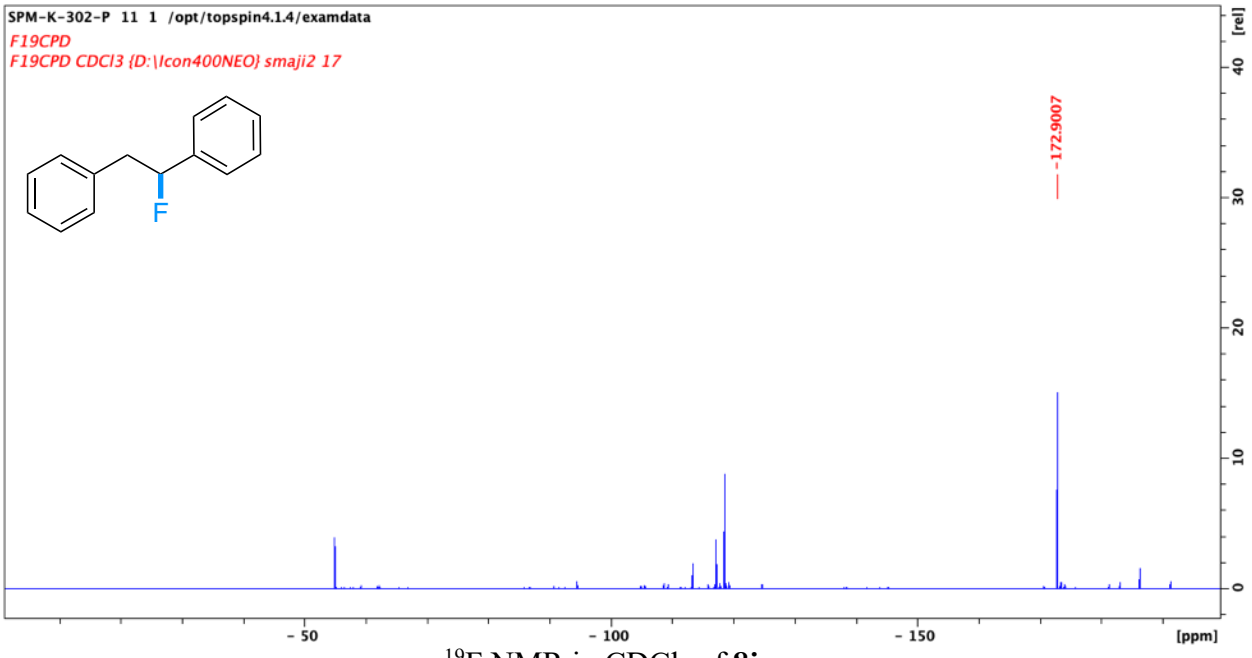
^{1}H NMR in CD_3CN of **8i** (Crude reaction mixture)



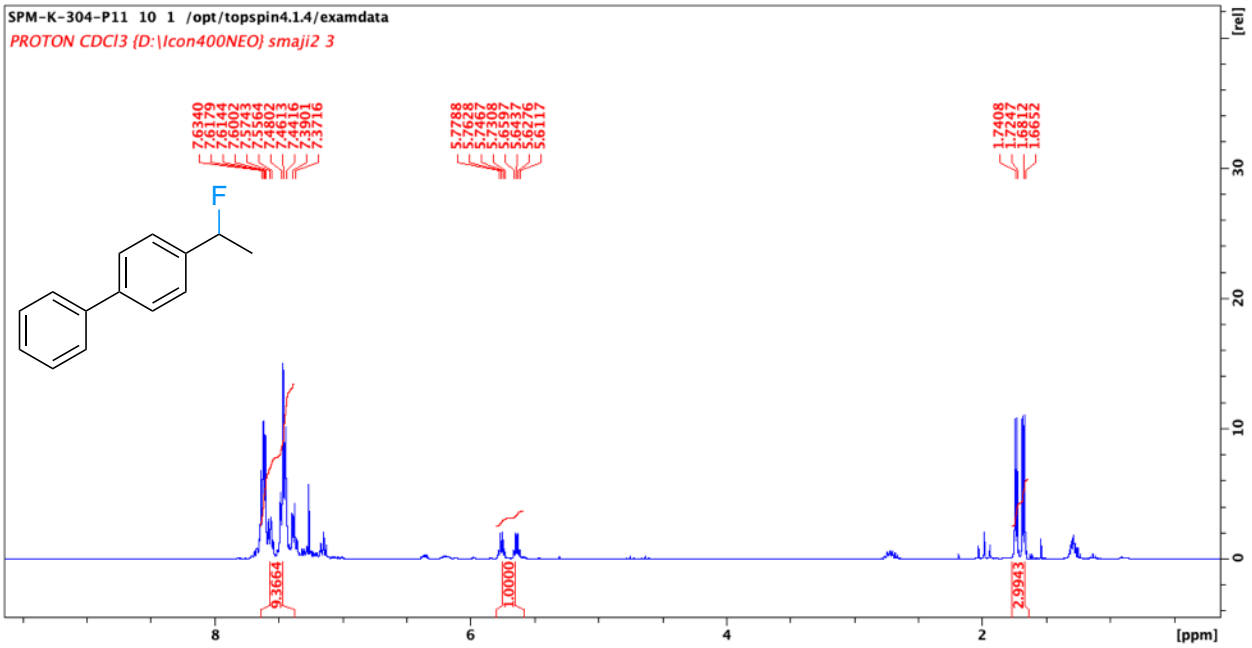
^{19}F NMR in CD_3CN of **8i** (Crude reaction mixture)



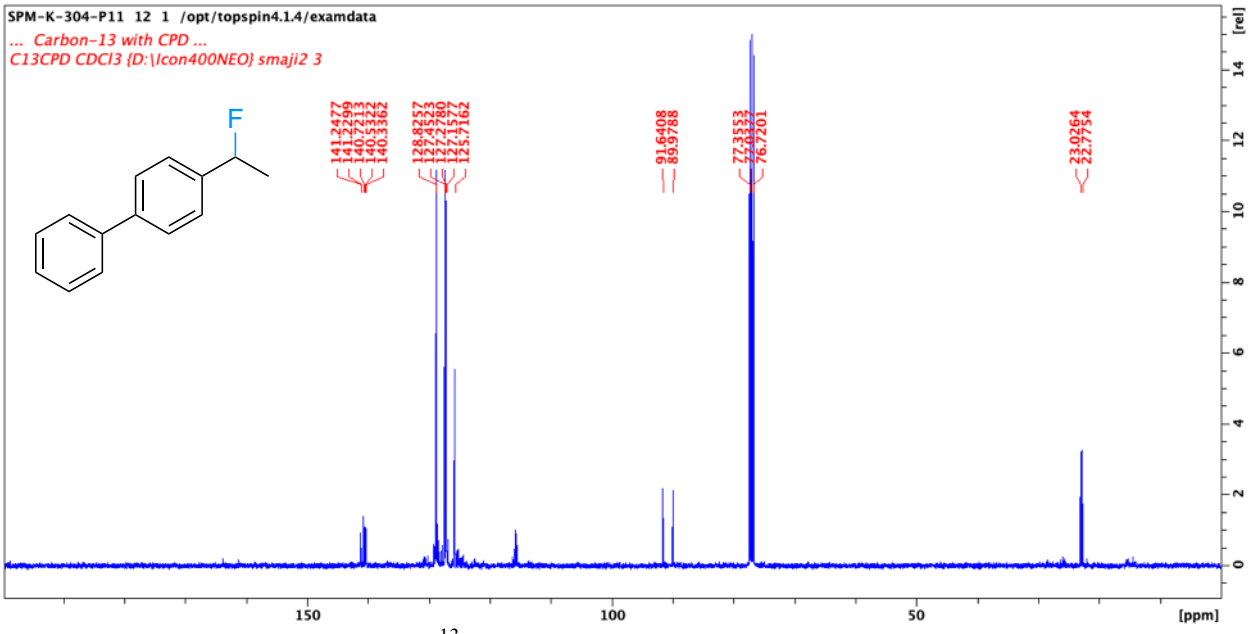
^{1}H NMR in $CDCl_3$ of **8j**



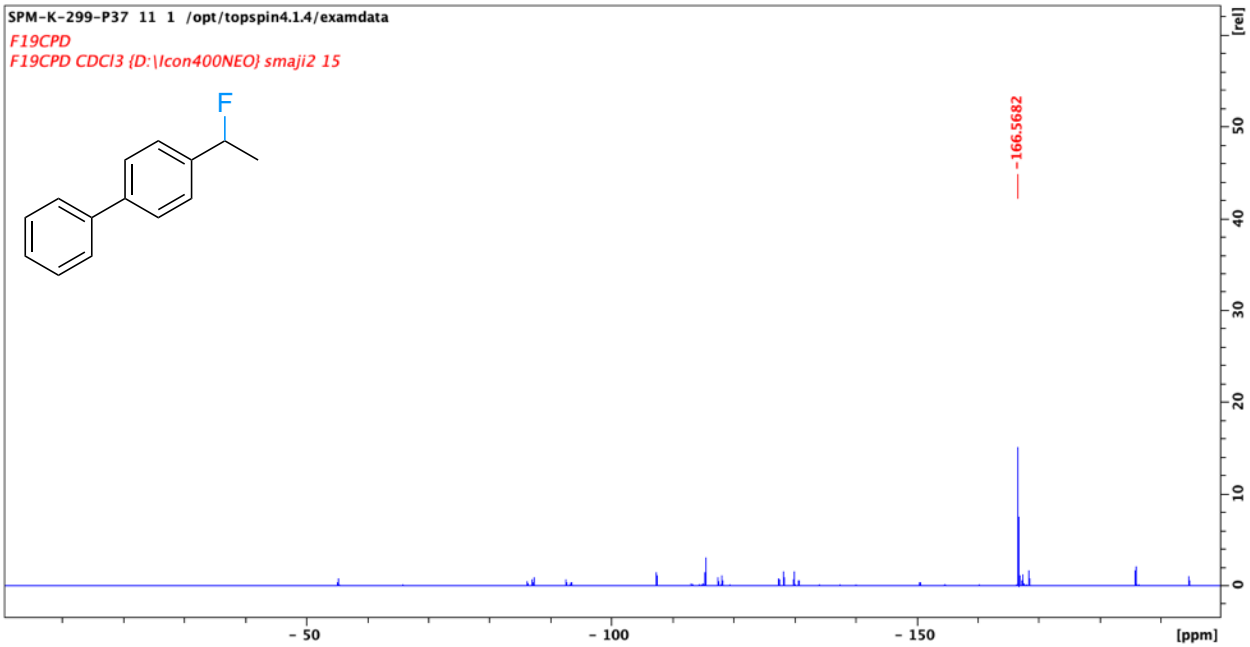
^{19}F NMR in $CDCl_3$ of **8j**



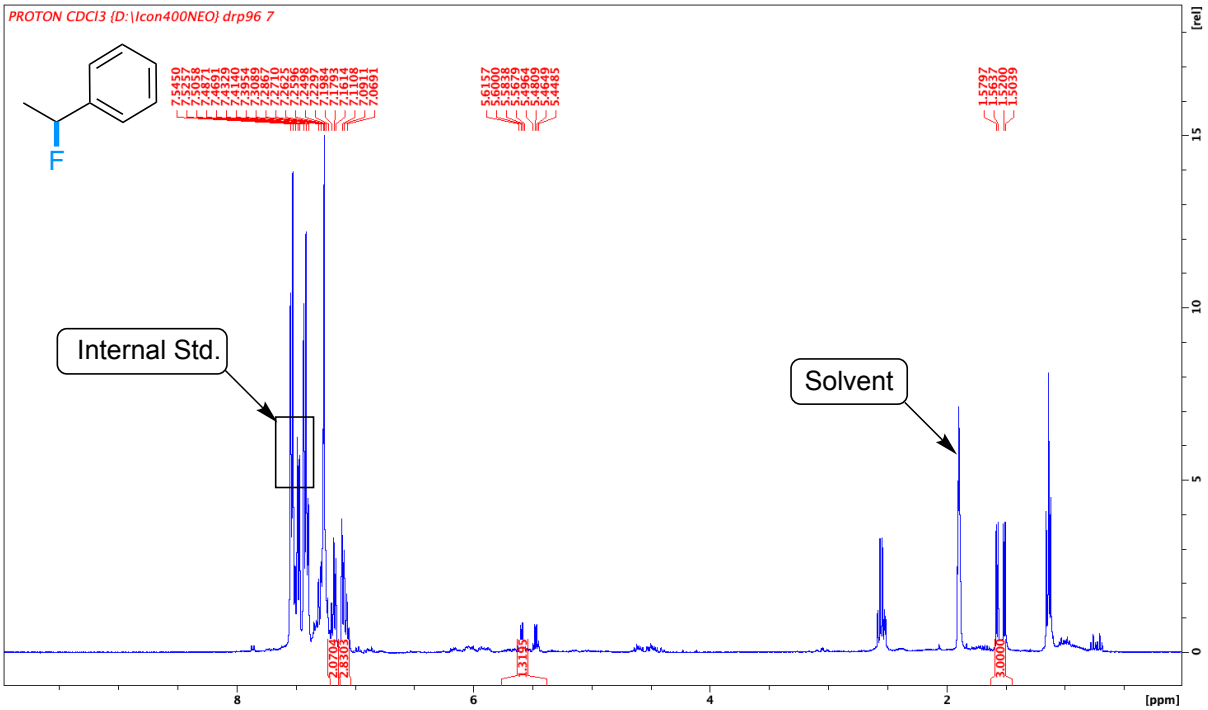
^{1}H NMR in $CDCl_3$ of **8k**



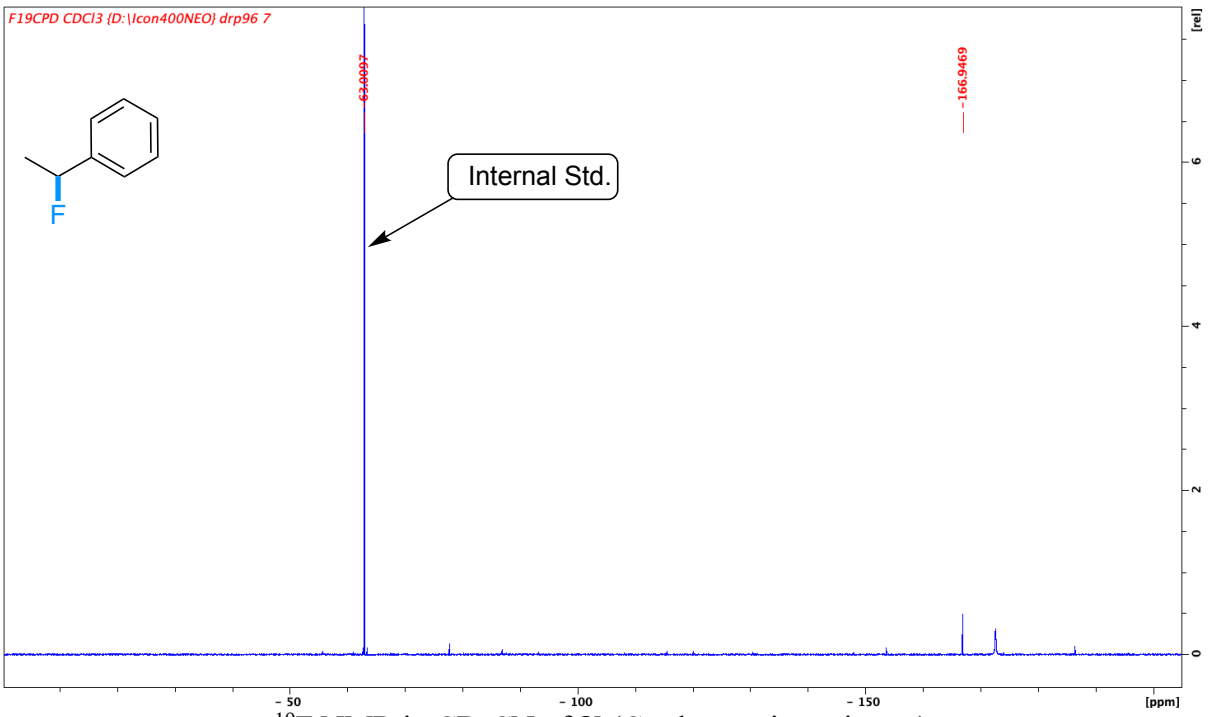
^{13}C NMR spectrum of **8k**



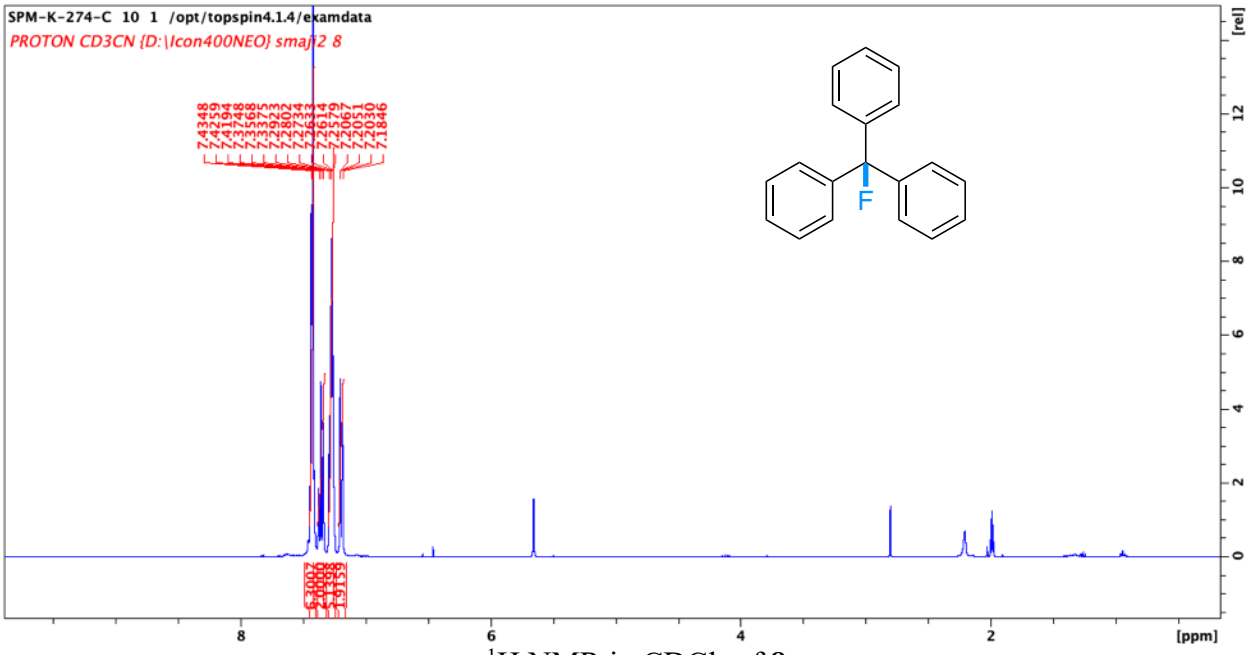
^{19}F NMR in $CDCl_3$ of **8k**



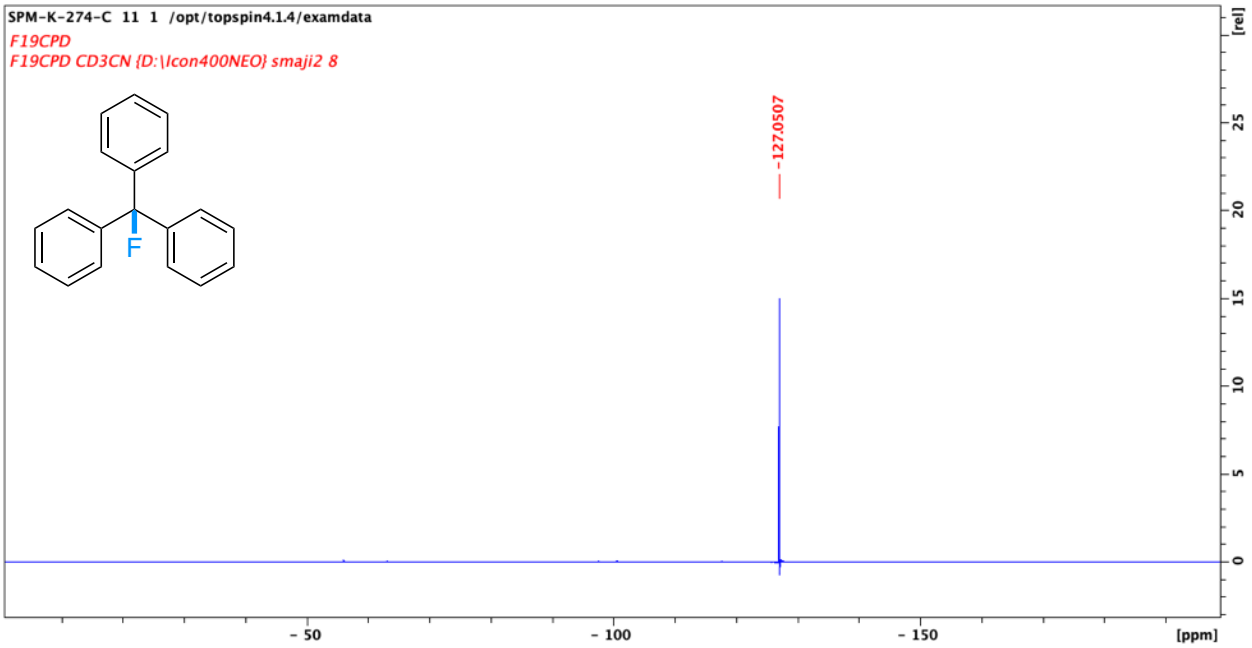
^{1}H NMR in $CDCl_3$ of **8l** (Crude reaction mixture in CD_3CN)



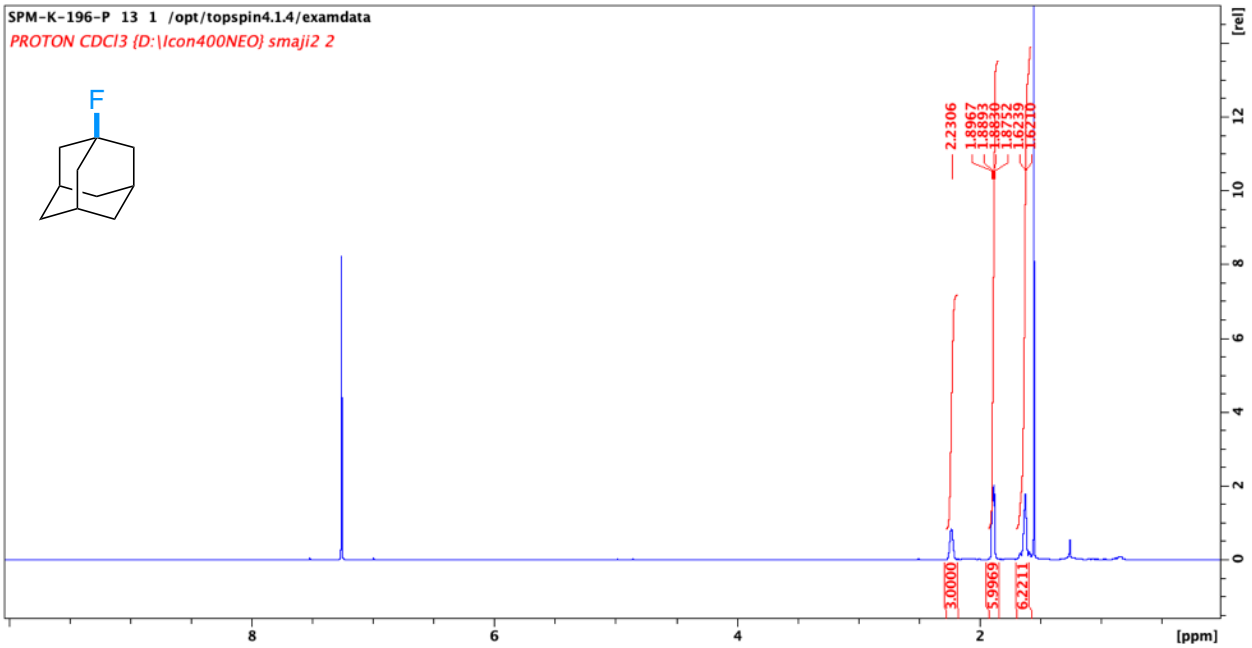
^{19}F NMR in CD_3CN of **8l** (Crude reaction mixture)



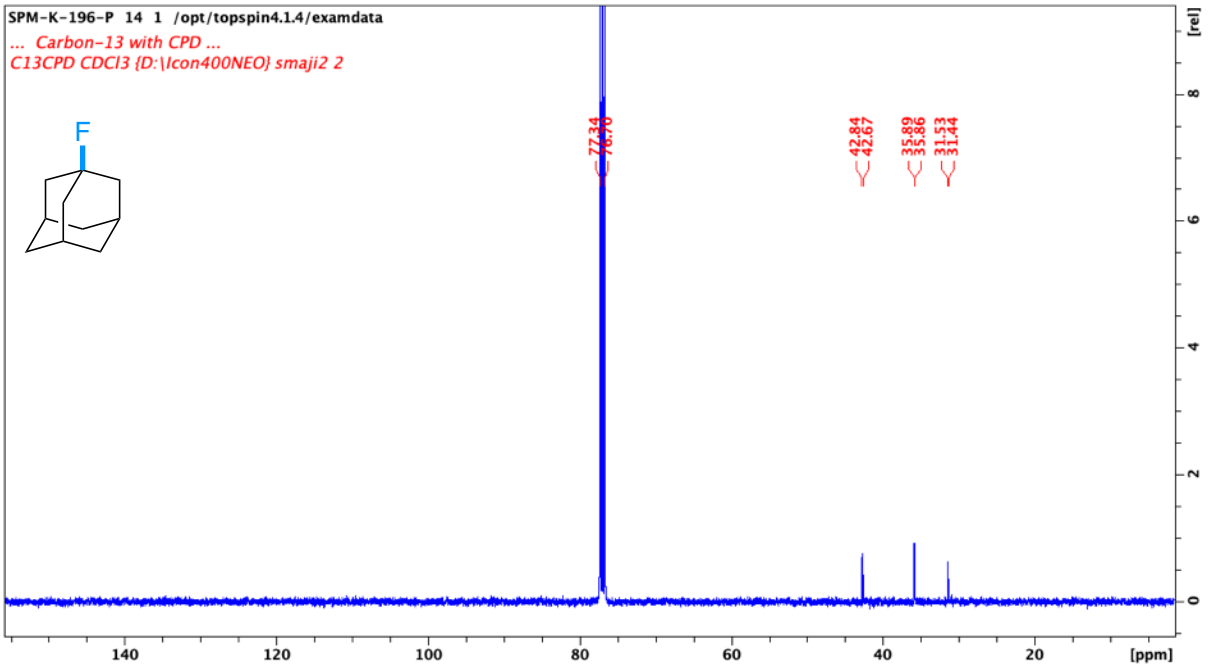
^{1}H NMR in $CDCl_3$ of **8m**



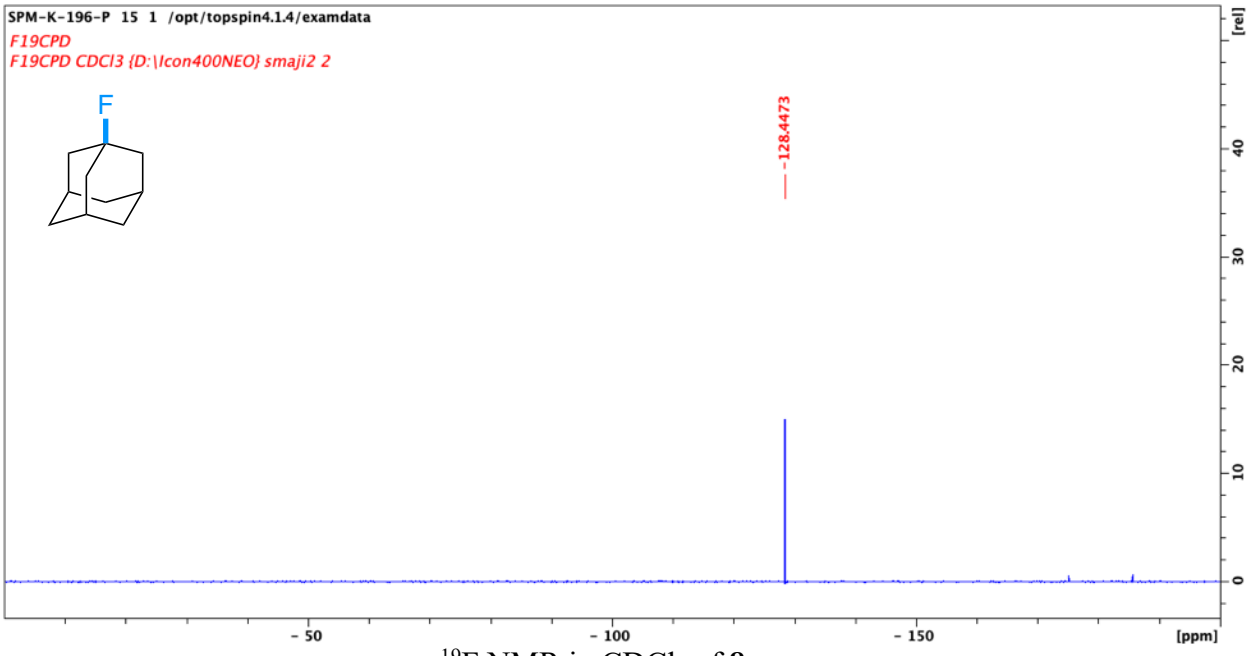
^{13}C NMR spectrum of **8m**



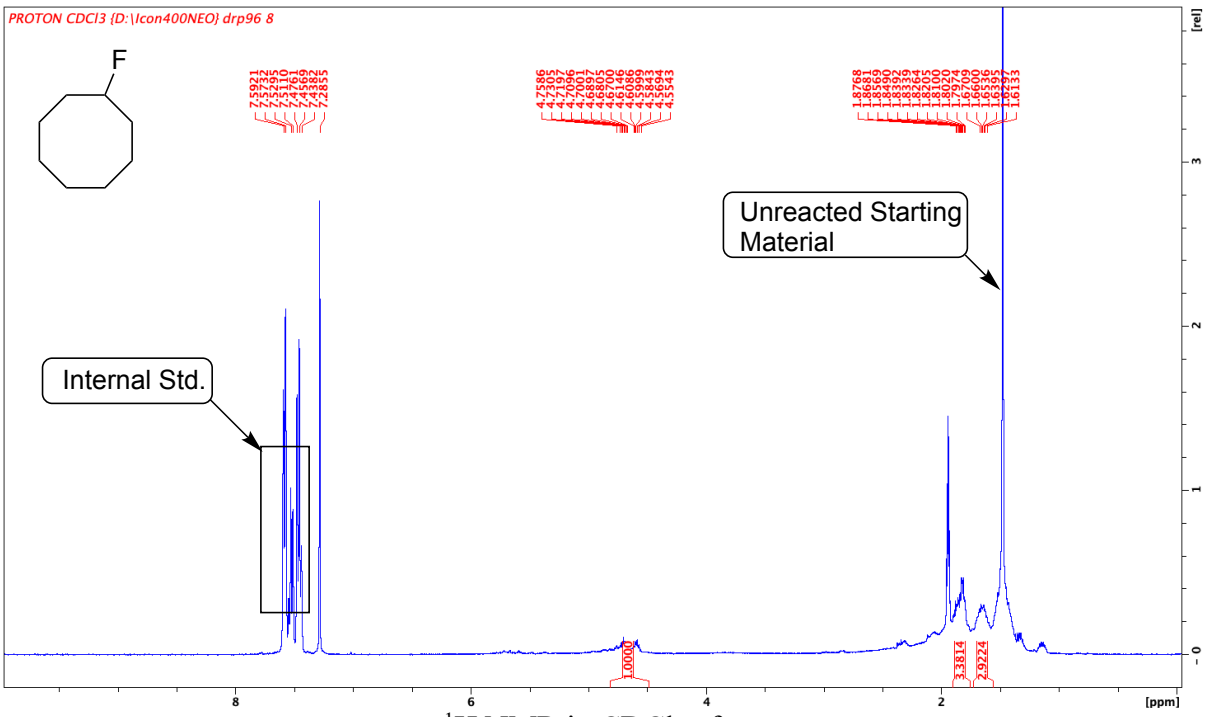
^{1}H NMR in $CDCl_3$ of **8n**



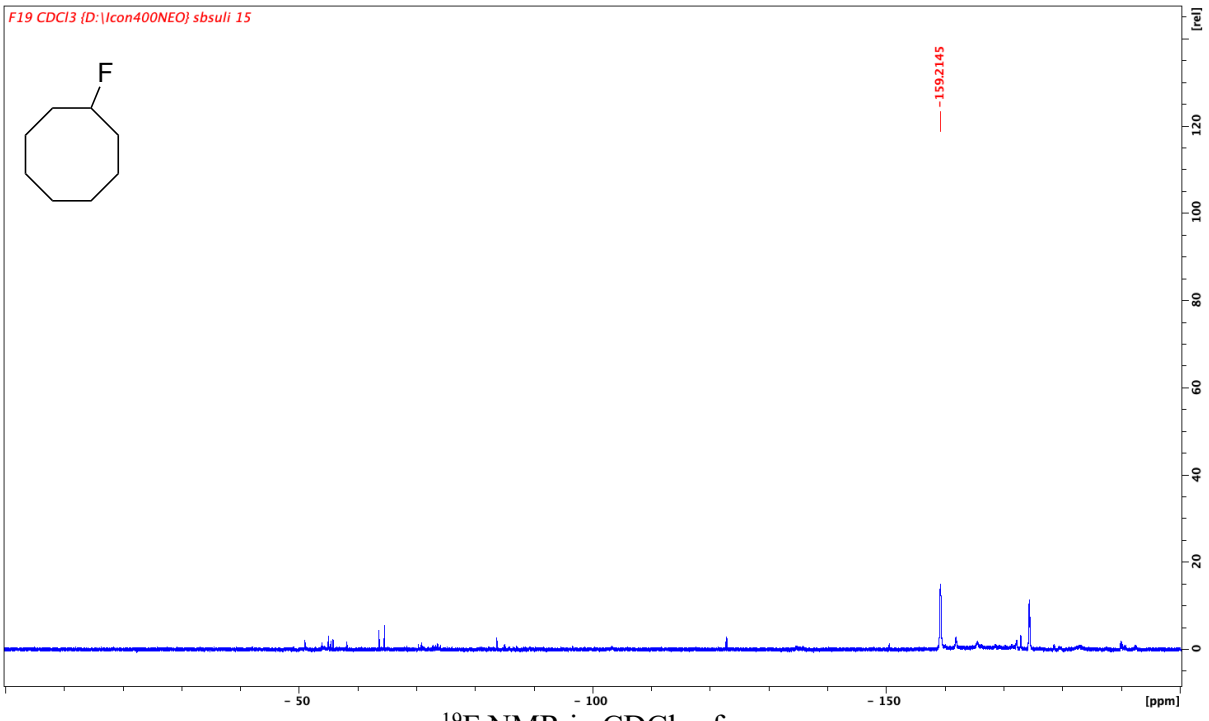
^{13}C NMR spectrum of **8n**



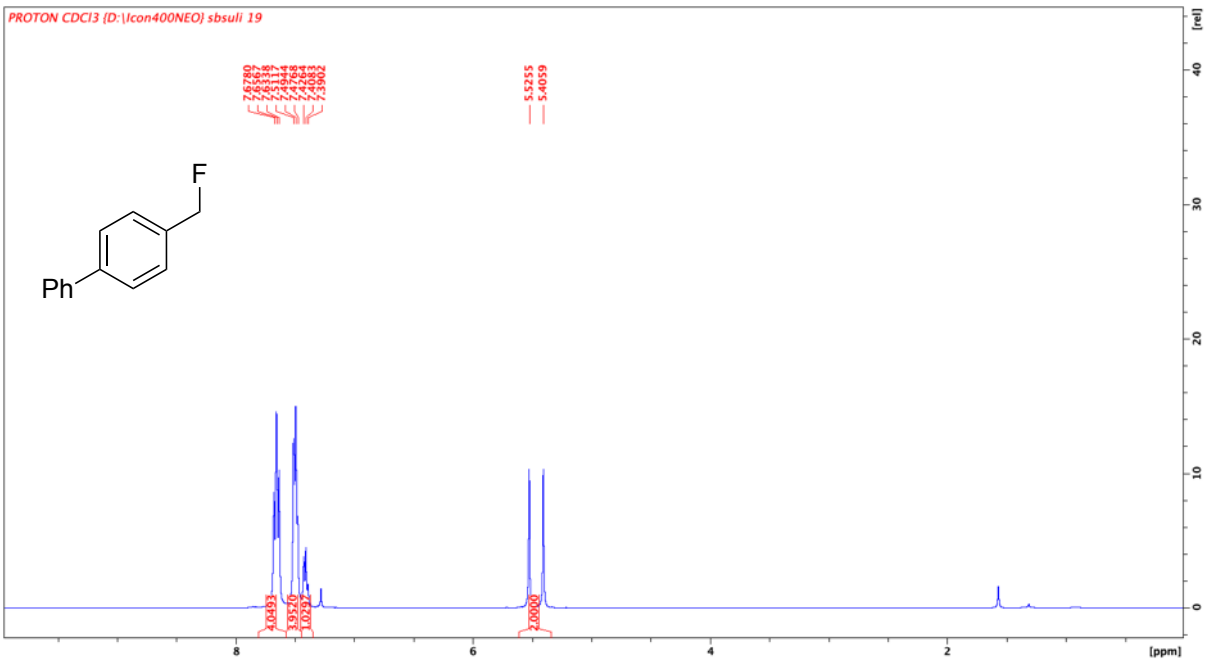
^{19}F NMR in $CDCl_3$ of **8n**



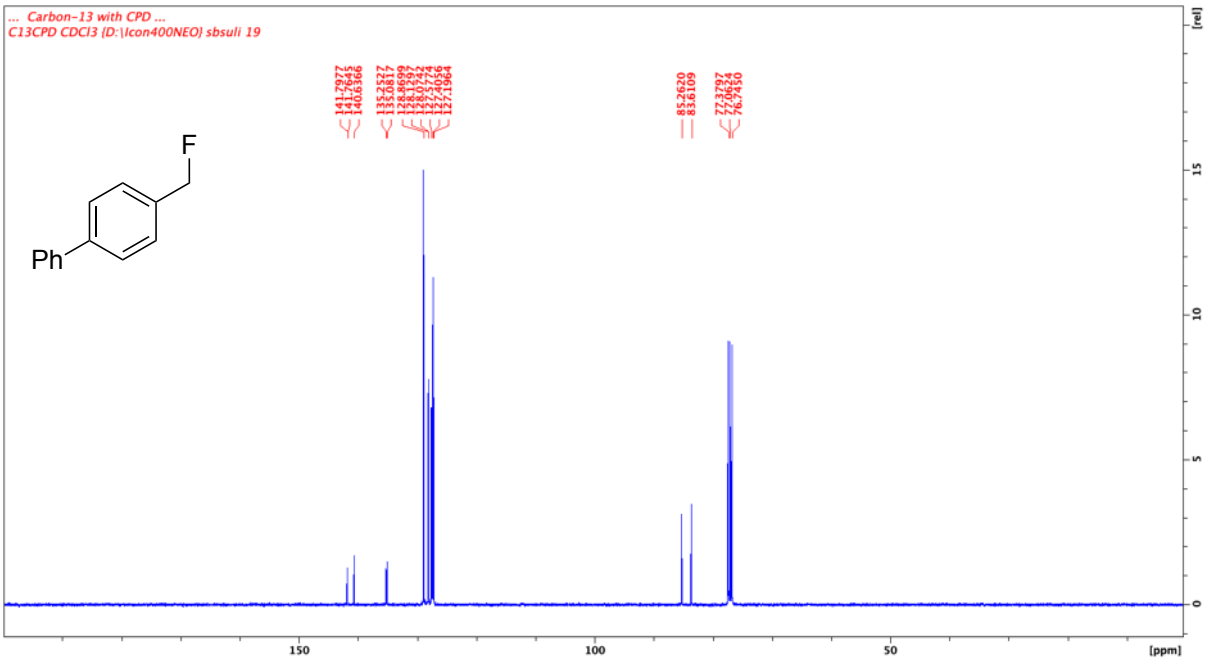
^{1}H NMR in $CDCl_3$ of **xx**



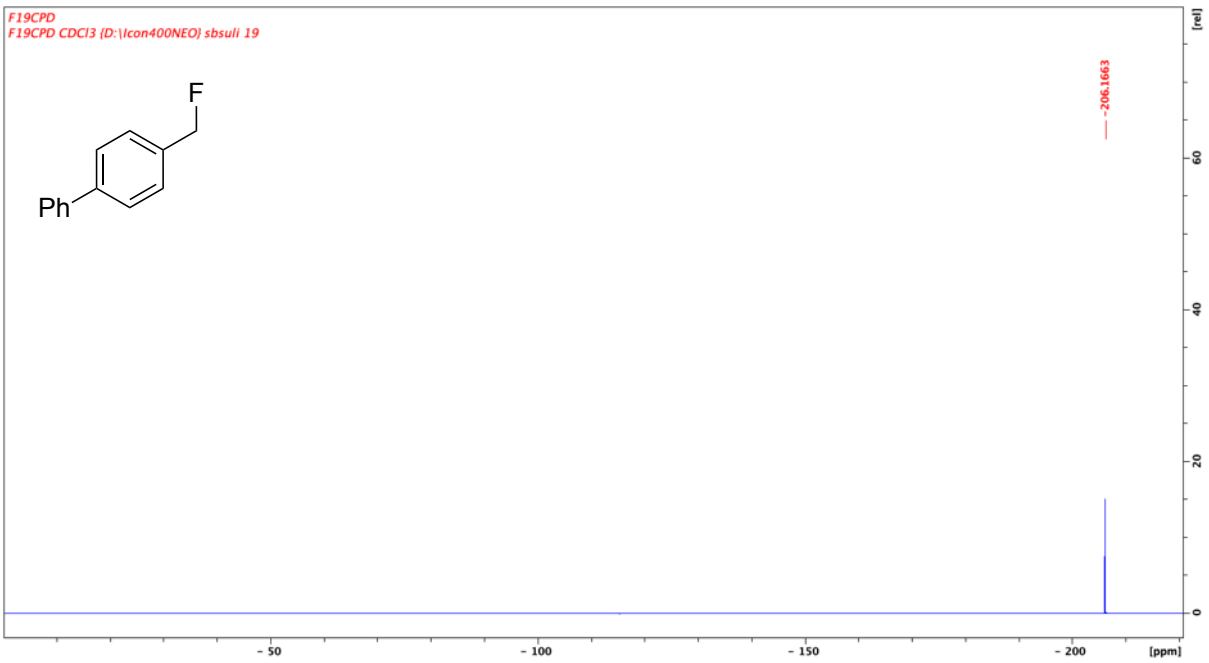
^{19}F NMR in $CDCl_3$ of **xx**



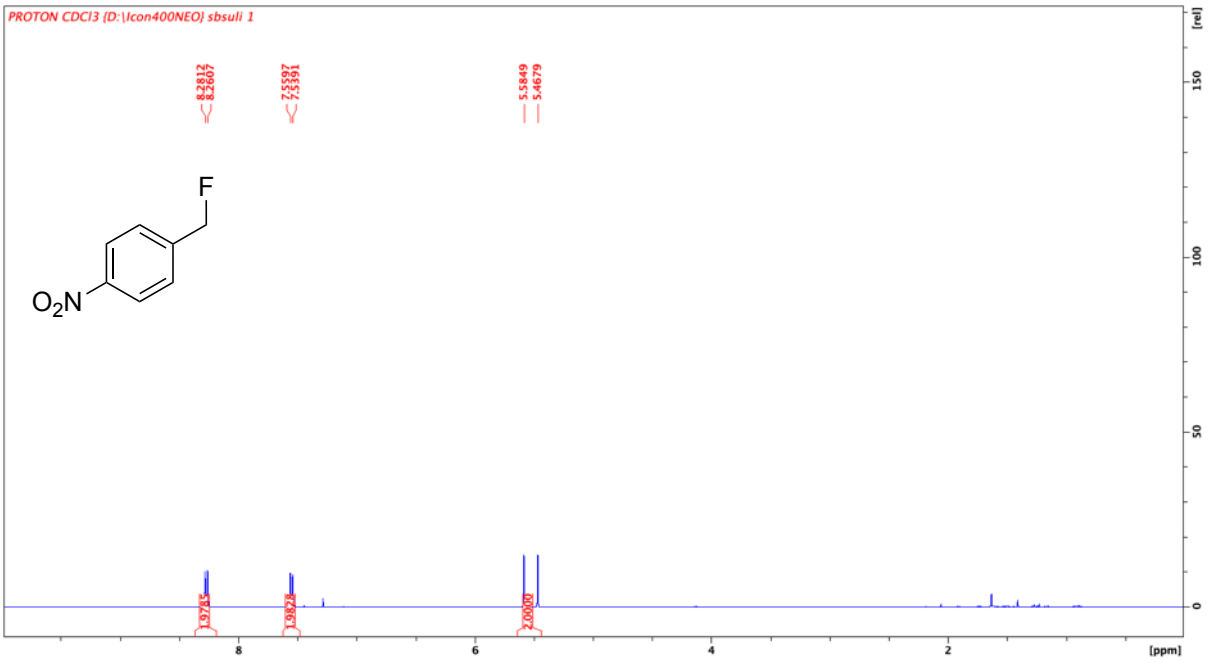
^{1}H NMR in $CDCl_3$ of **10a**



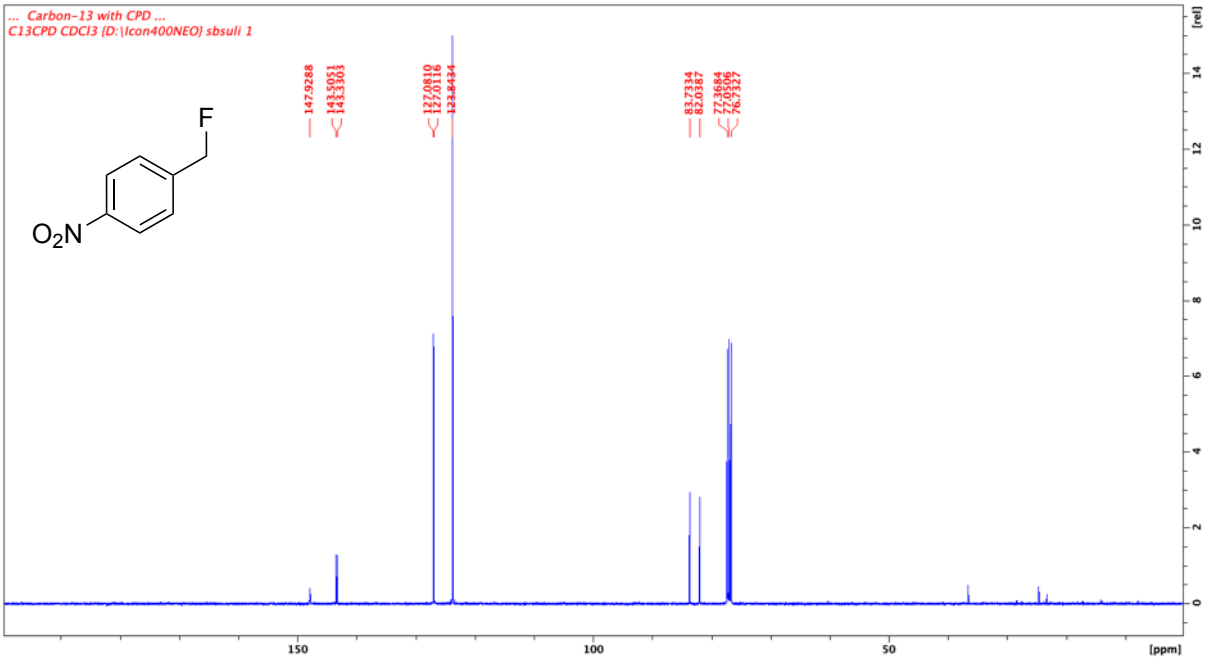
^{13}C NMR in $CDCl_3$ of **10a**



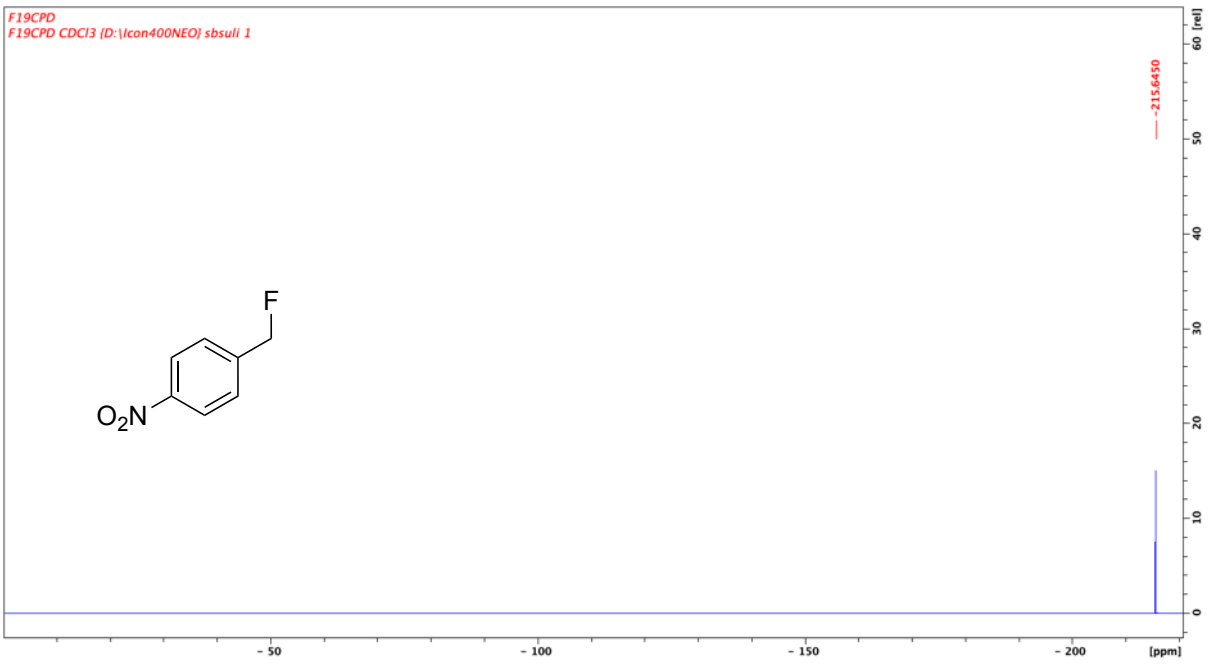
^{19}F NMR in $CDCl_3$ of **10a**



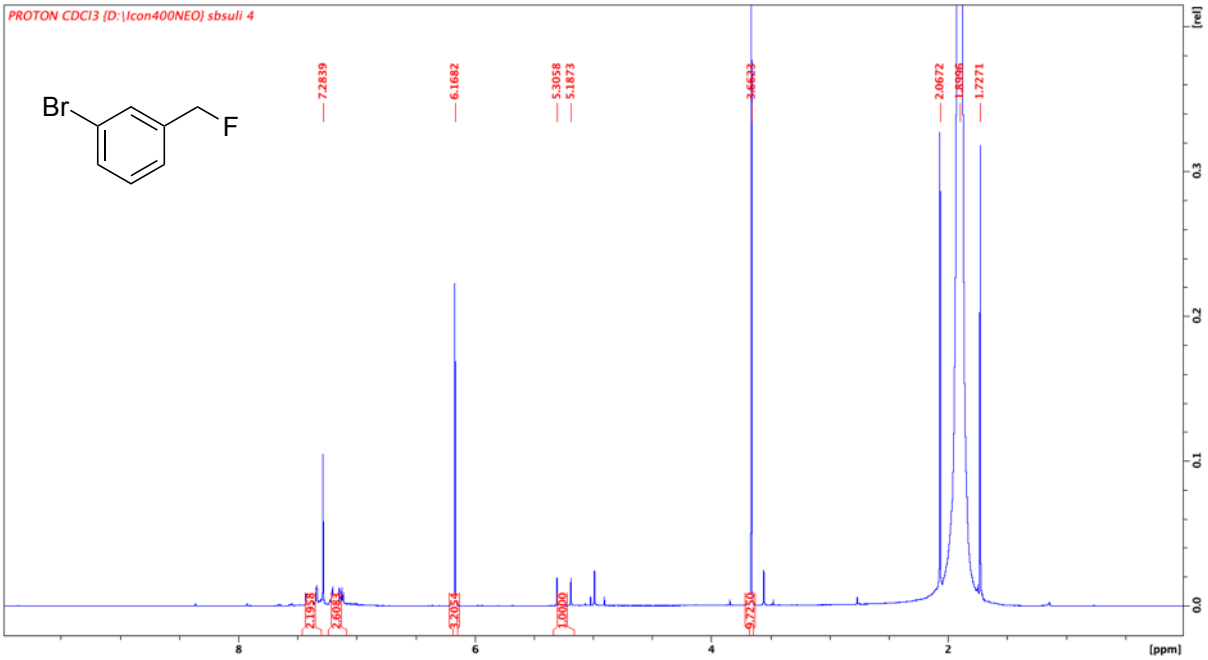
^{1}H NMR in $CDCl_3$ of **10b**



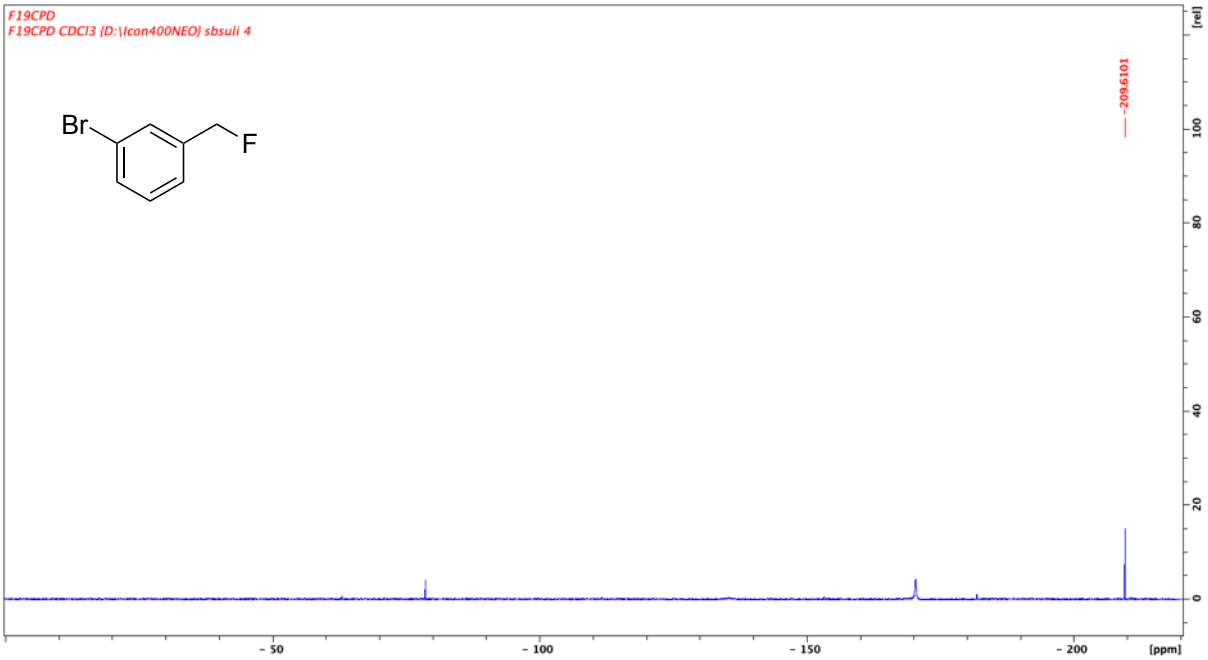
^{13}C NMR in $CDCl_3$ of **10b**



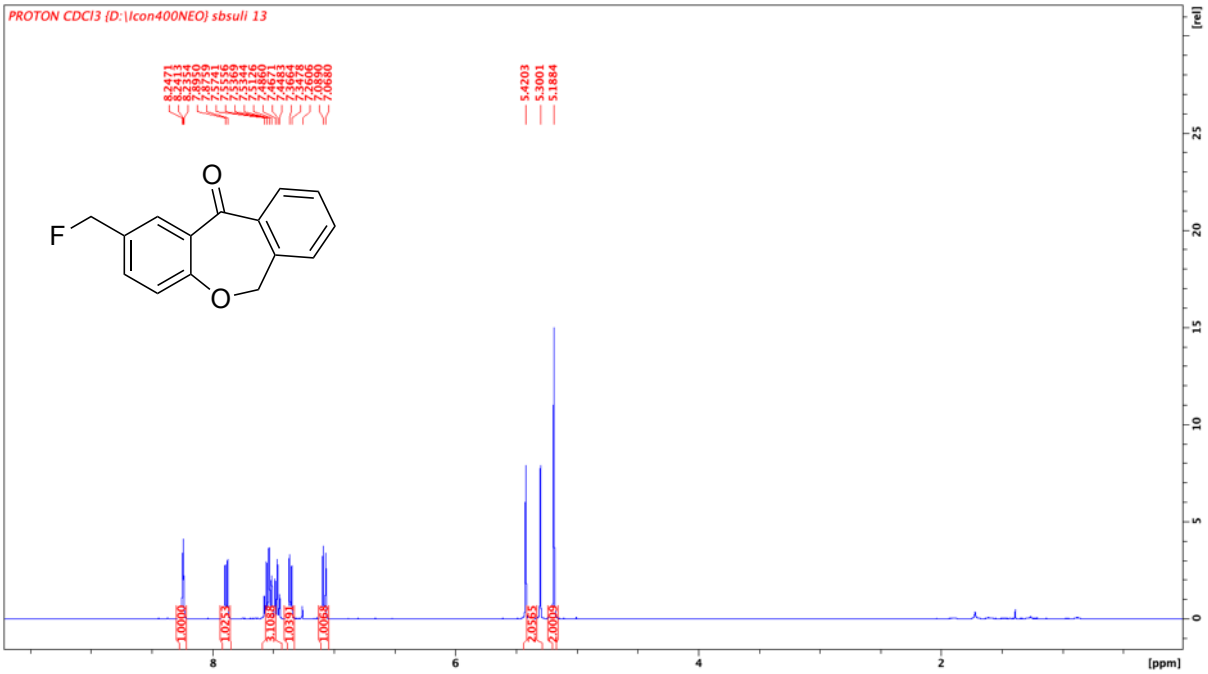
^{19}F NMR in $CDCl_3$ of **10b**



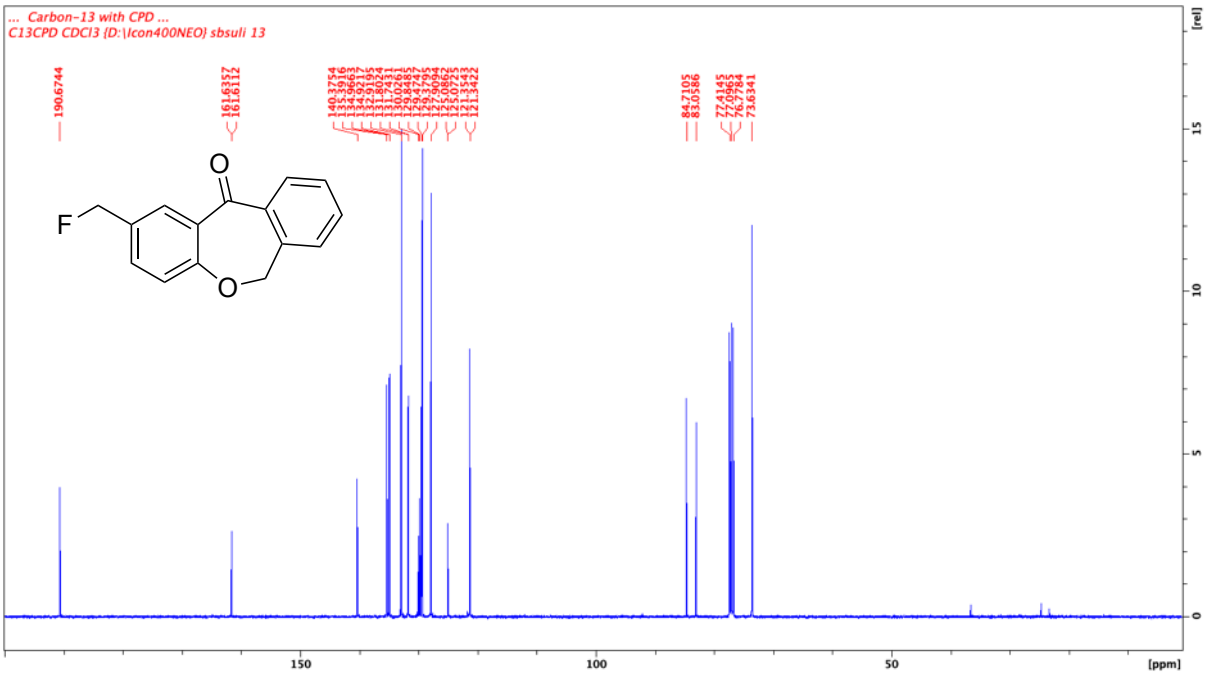
^{1}H NMR in $CDCl_3$ of **10c** (Crude reaction mixture)



^{19}F NMR in $CDCl_3$ of **10c** (Crude reaction mixture)

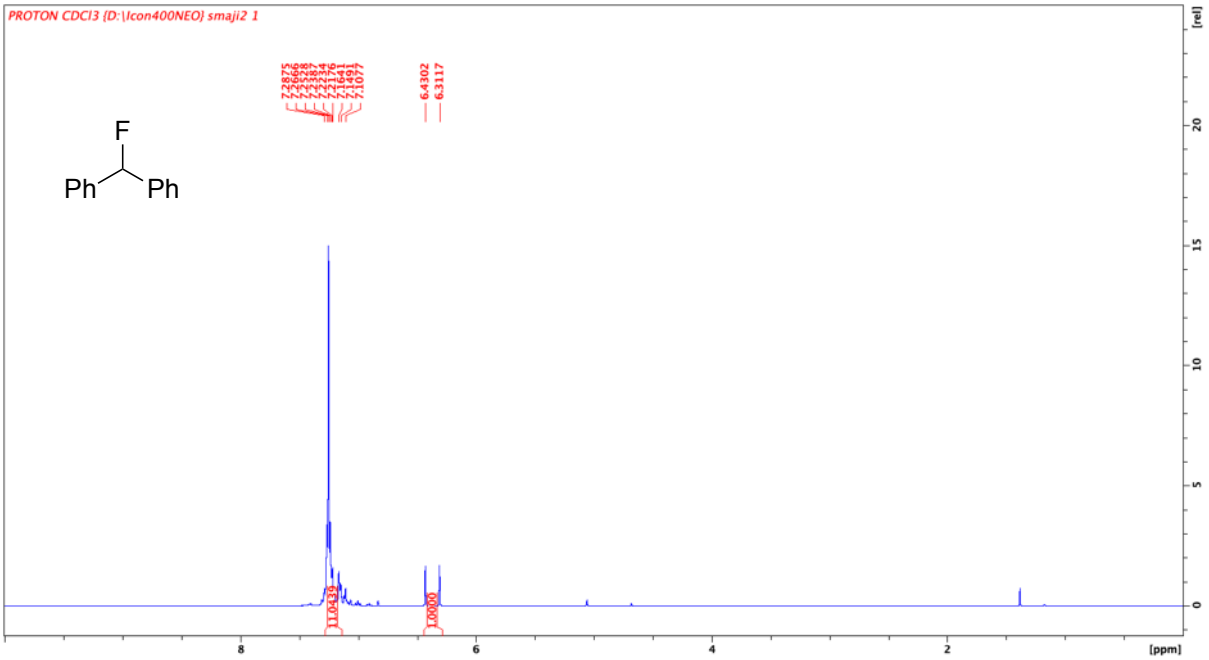


^{1}H NMR in $CDCl_3$ of **10d**

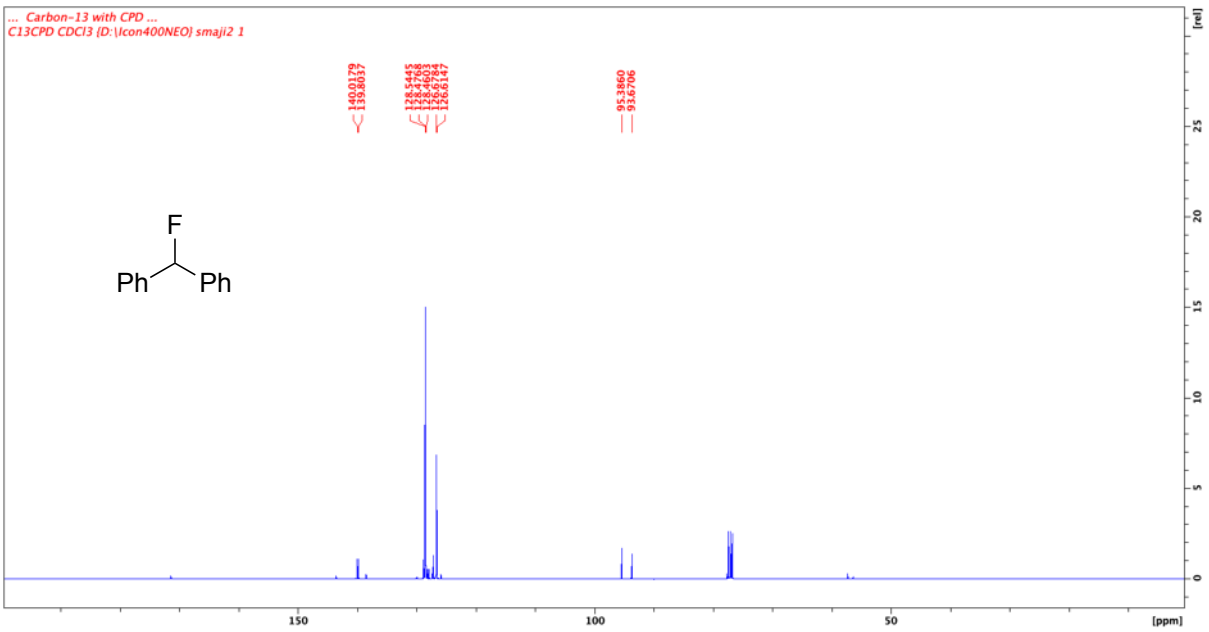


^{13}C NMR in $CDCl_3$ of **10d**

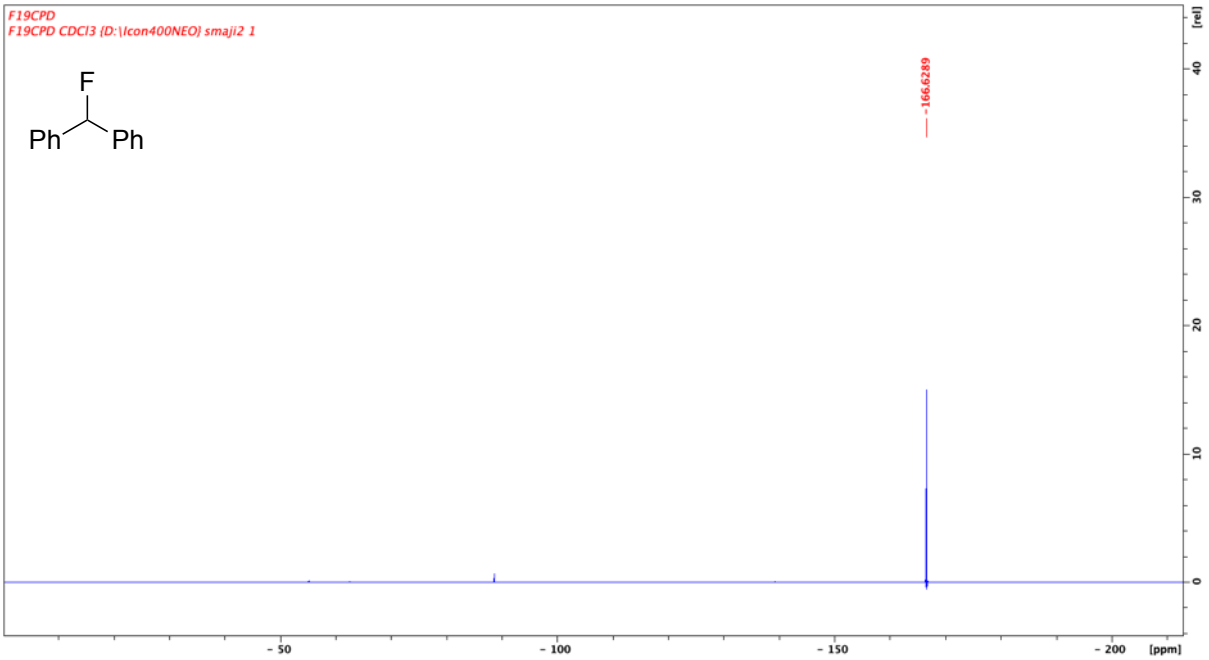
^{19}F NMR in $CDCl_3$ of **10d**



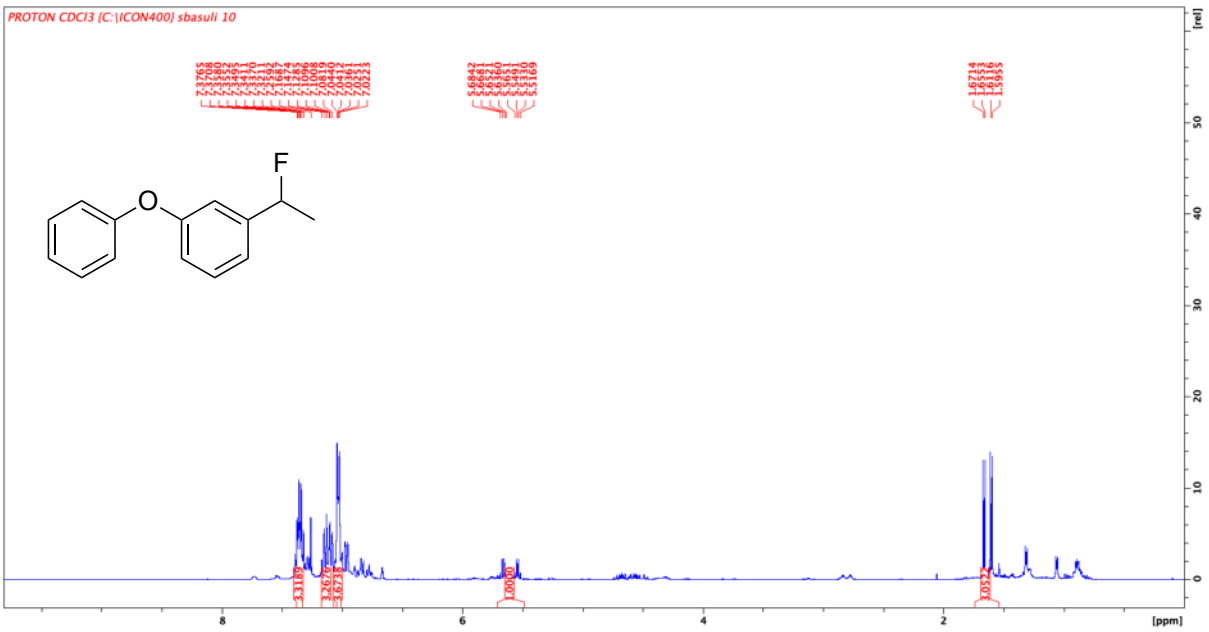
^{1}H NMR in $CDCl_3$ of **10e**



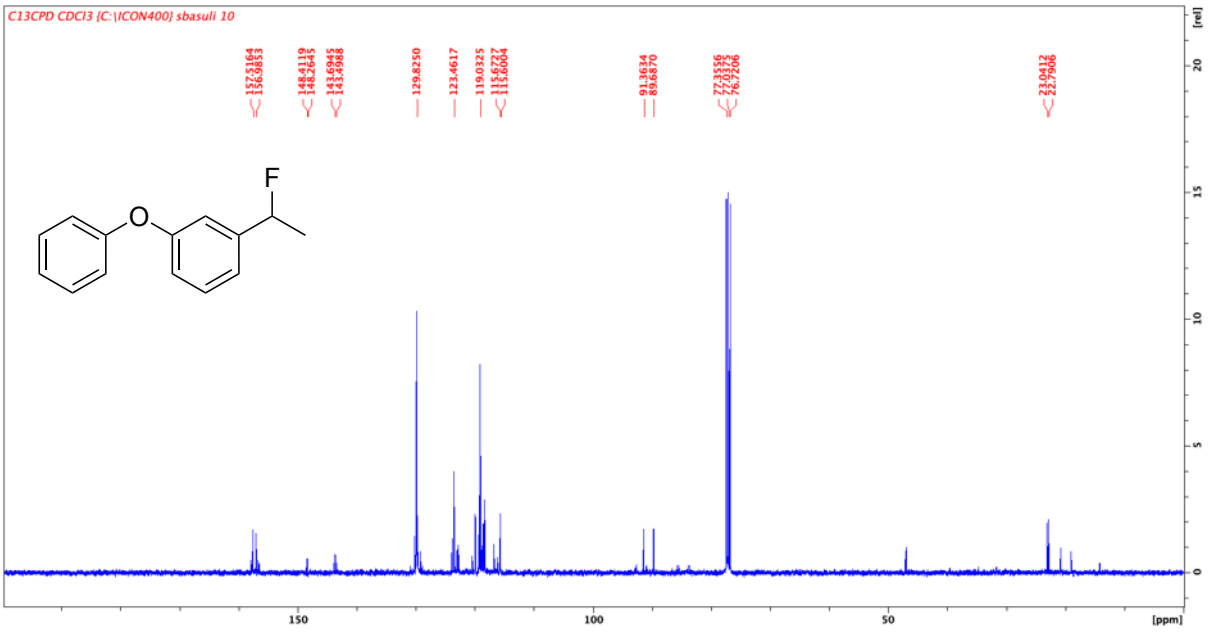
^{13}C NMR in $CDCl_3$ of **10e**



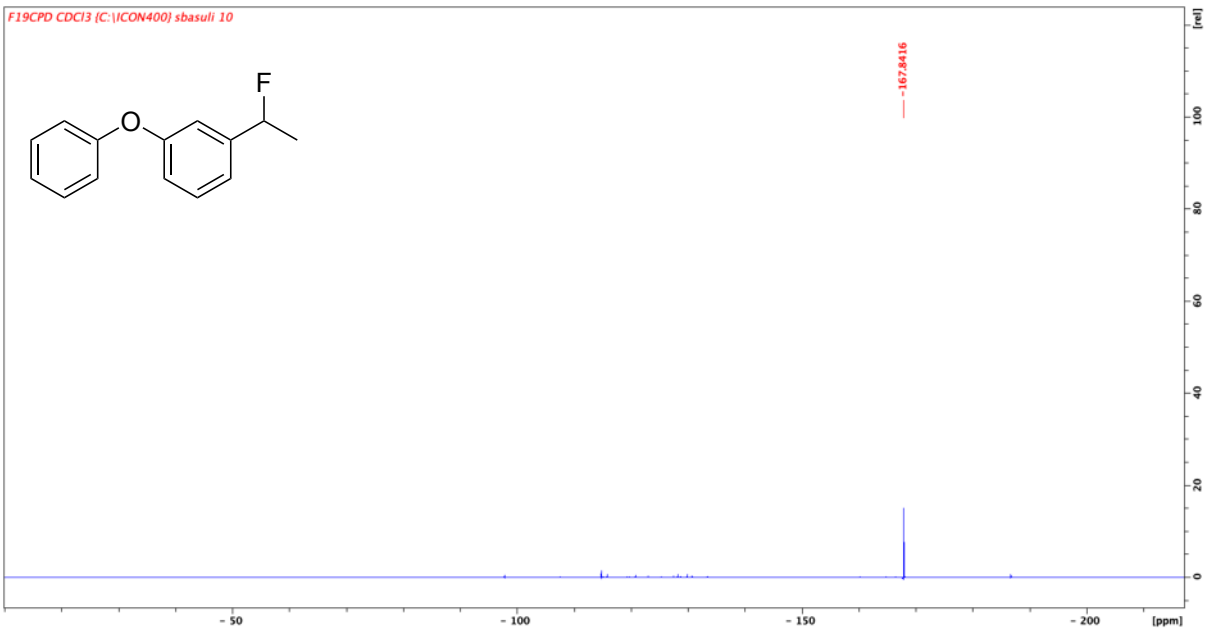
^{19}F NMR in $CDCl_3$ of **10e**



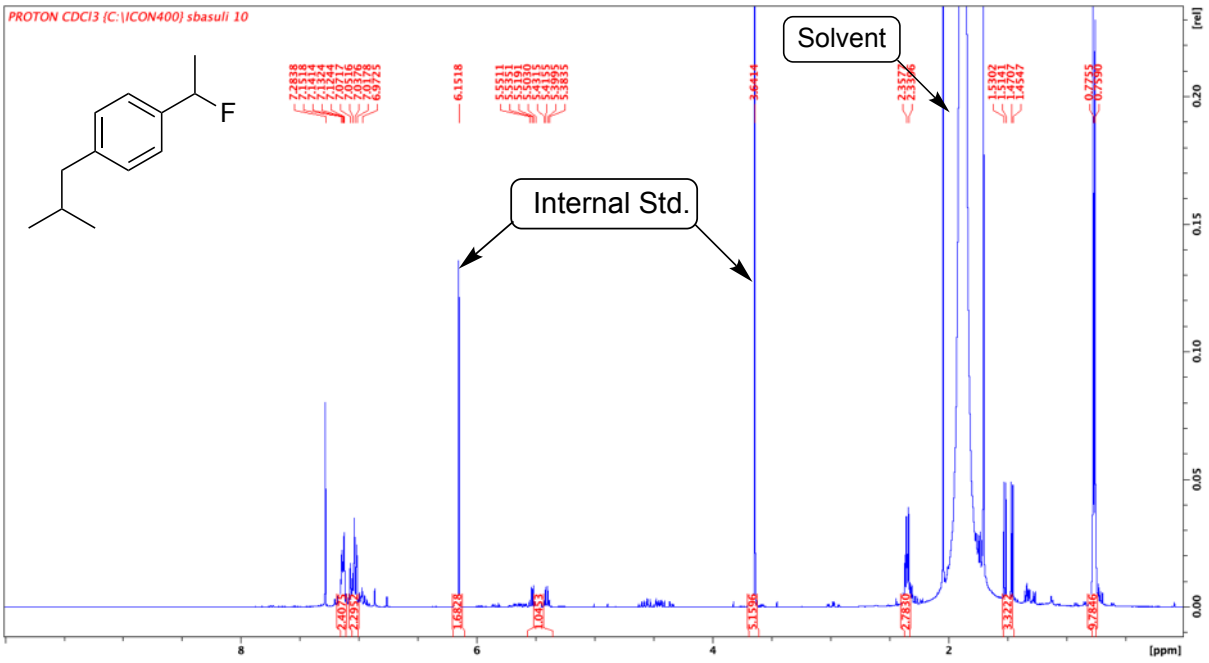
^{1}H NMR in $CDCl_3$ of **10f**



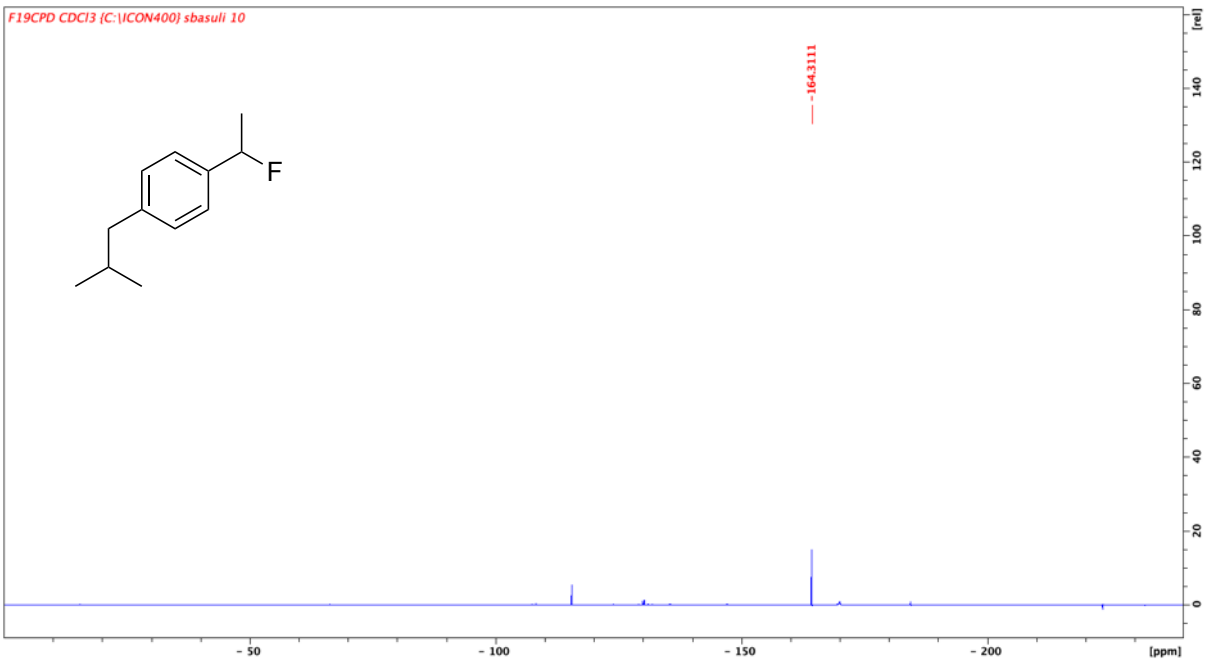
^{13}C NMR in $CDCl_3$ of **10f**



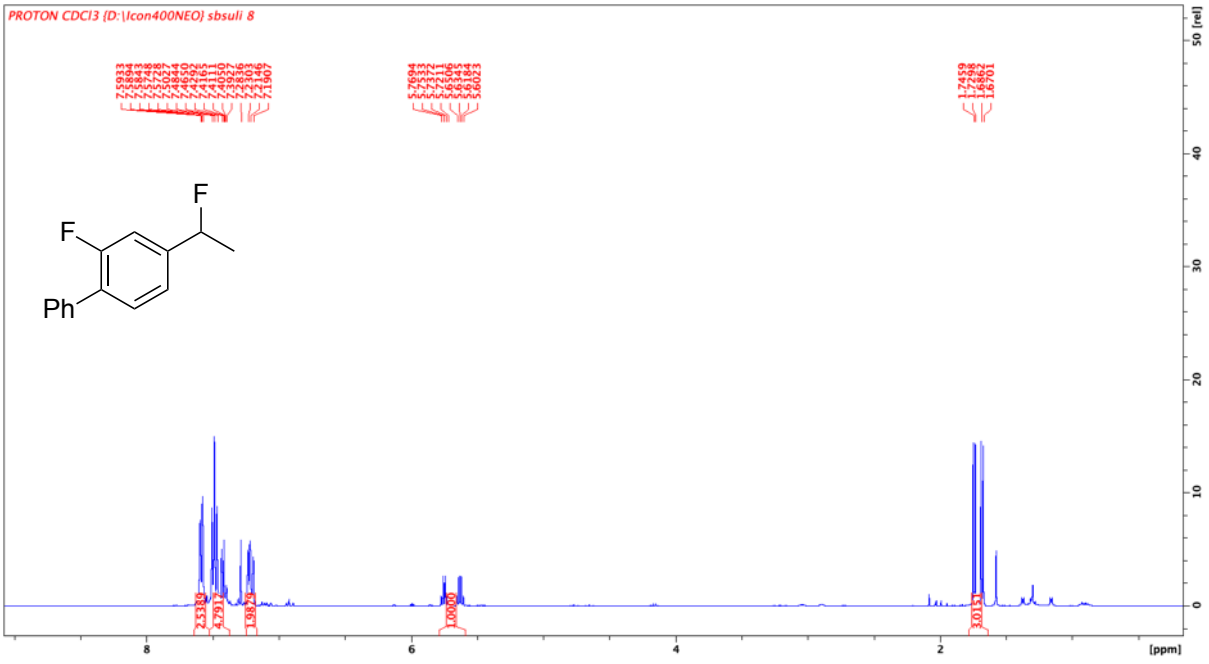
^{19}F NMR in $CDCl_3$ of **10f**



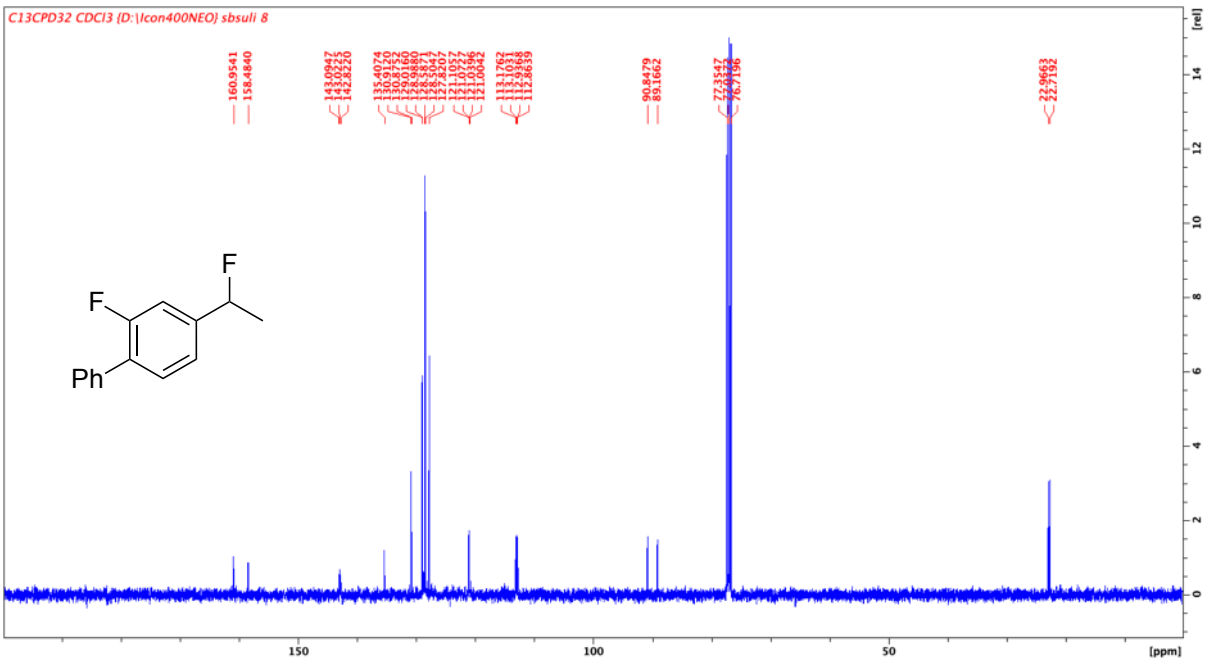
^{1}H NMR in $CDCl_3$ of **10g** (Crude reaction mixture)



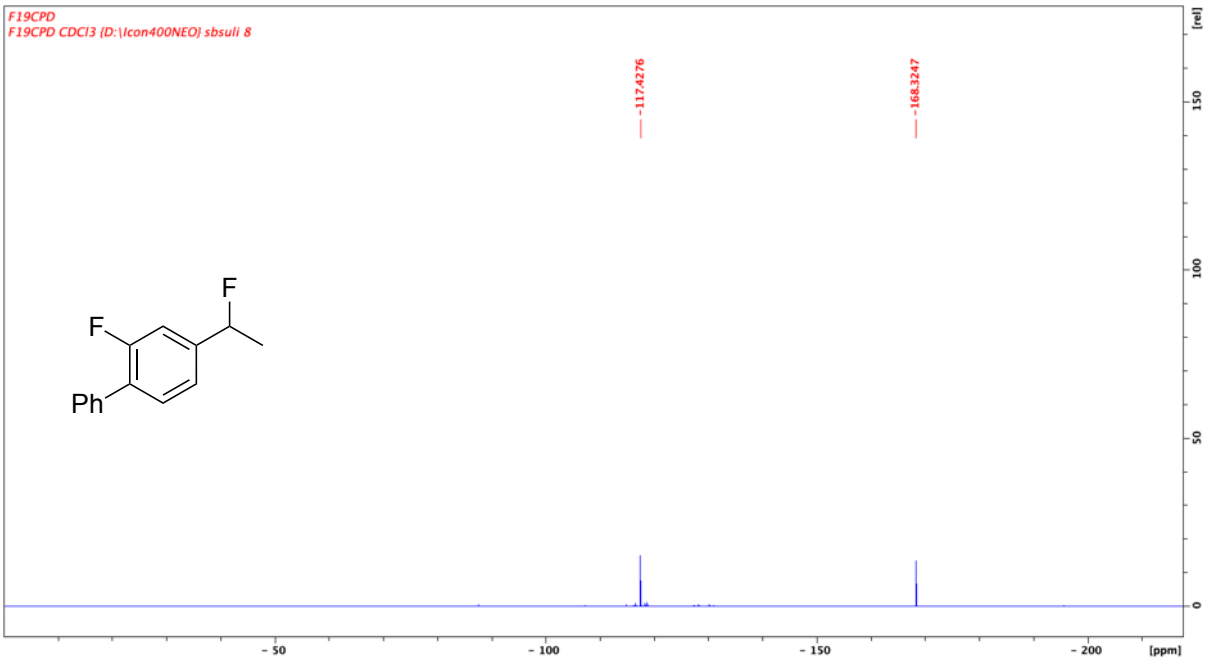
^{19}F NMR in $CDCl_3$ of **10g** (Crude reaction mixture)



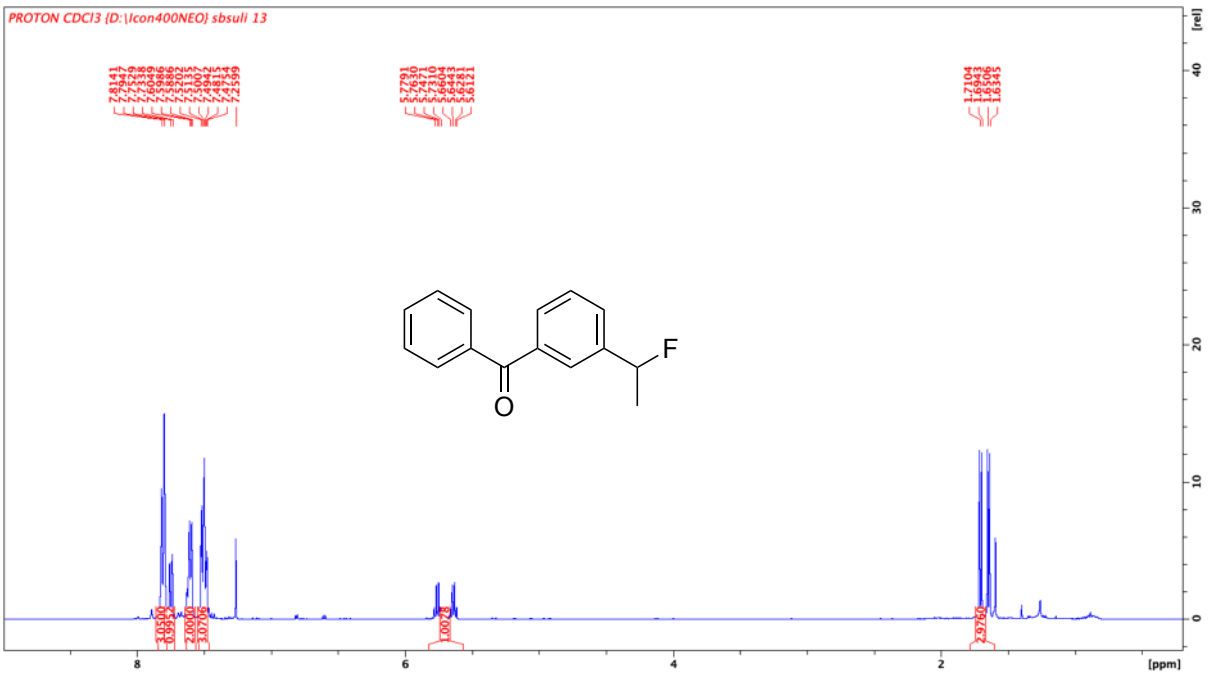
^{1}H NMR in $CDCl_3$ of **10h**



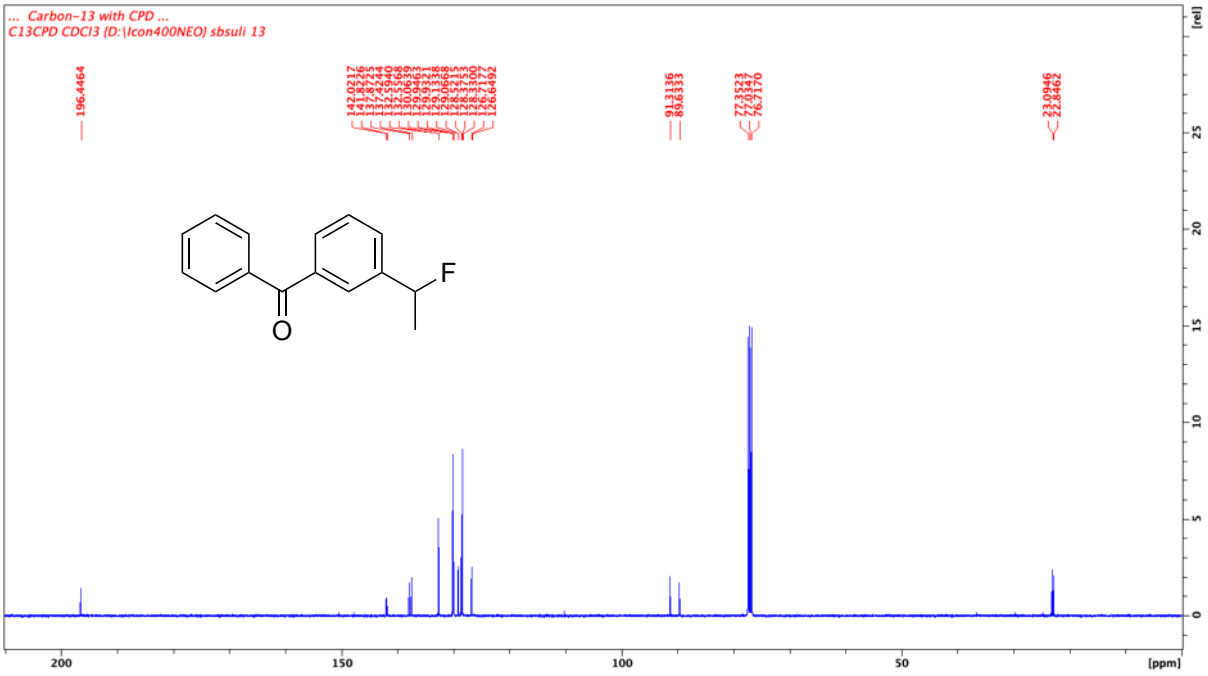
^{13}C NMR in $CDCl_3$ of **10h**



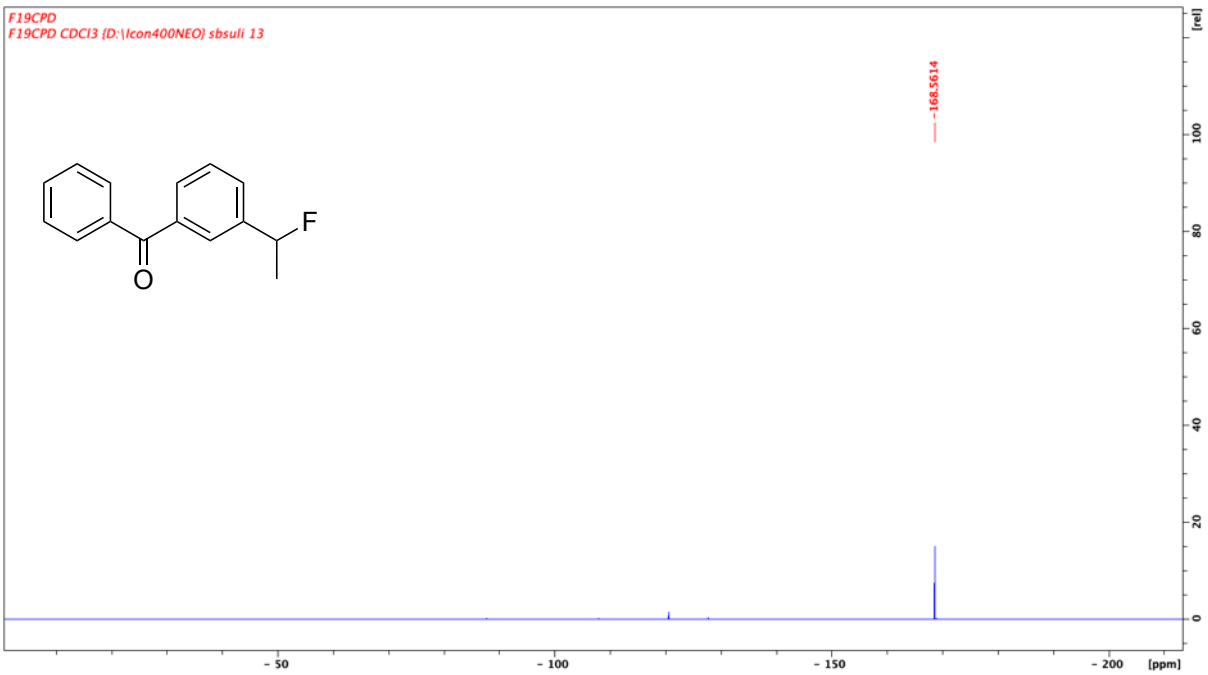
^{19}F NMR in $CDCl_3$ of **10h**



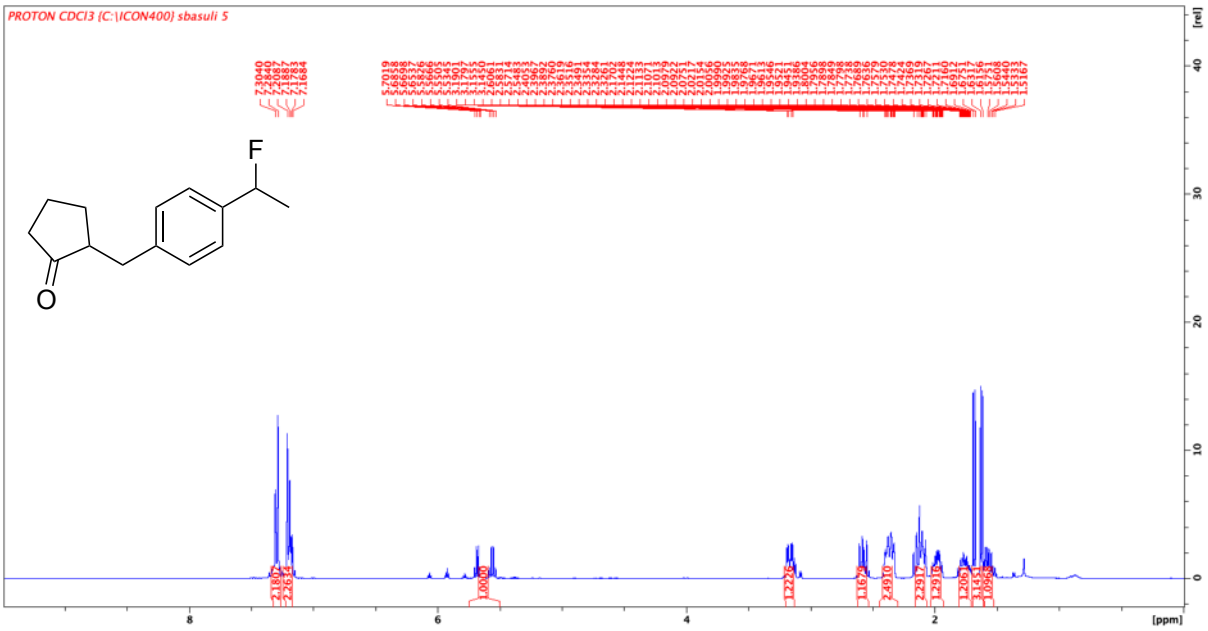
^{1}H NMR in $CDCl_3$ of **10i**



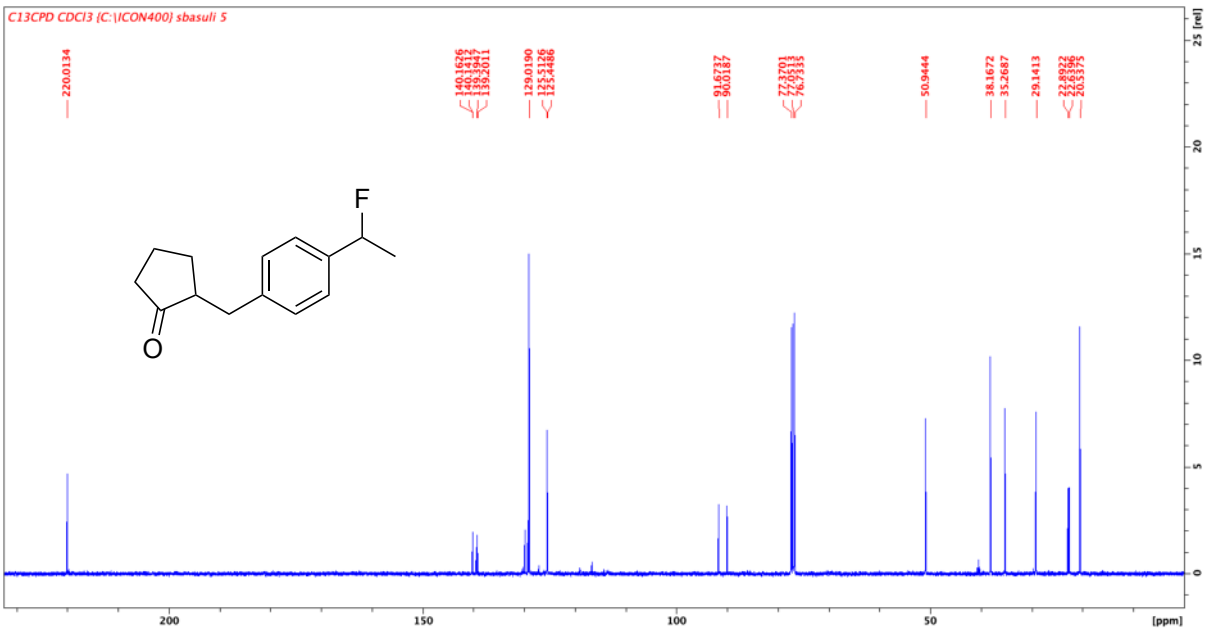
^{13}C NMR in $CDCl_3$ of **10i**



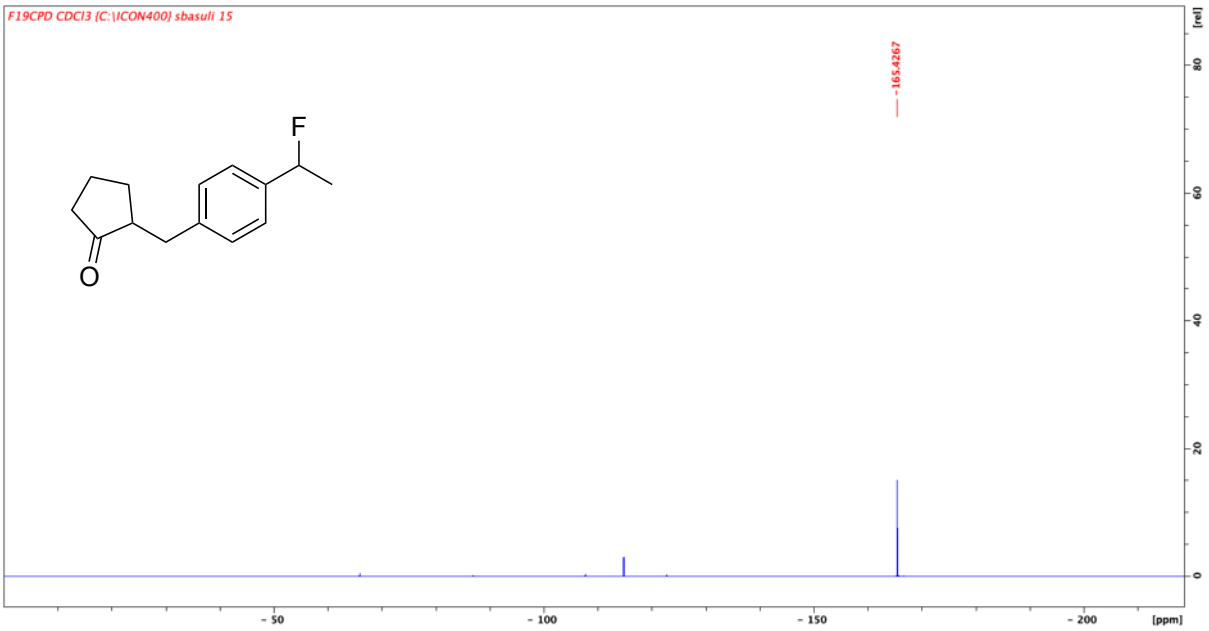
^{19}F NMR in $CDCl_3$ of **10i**



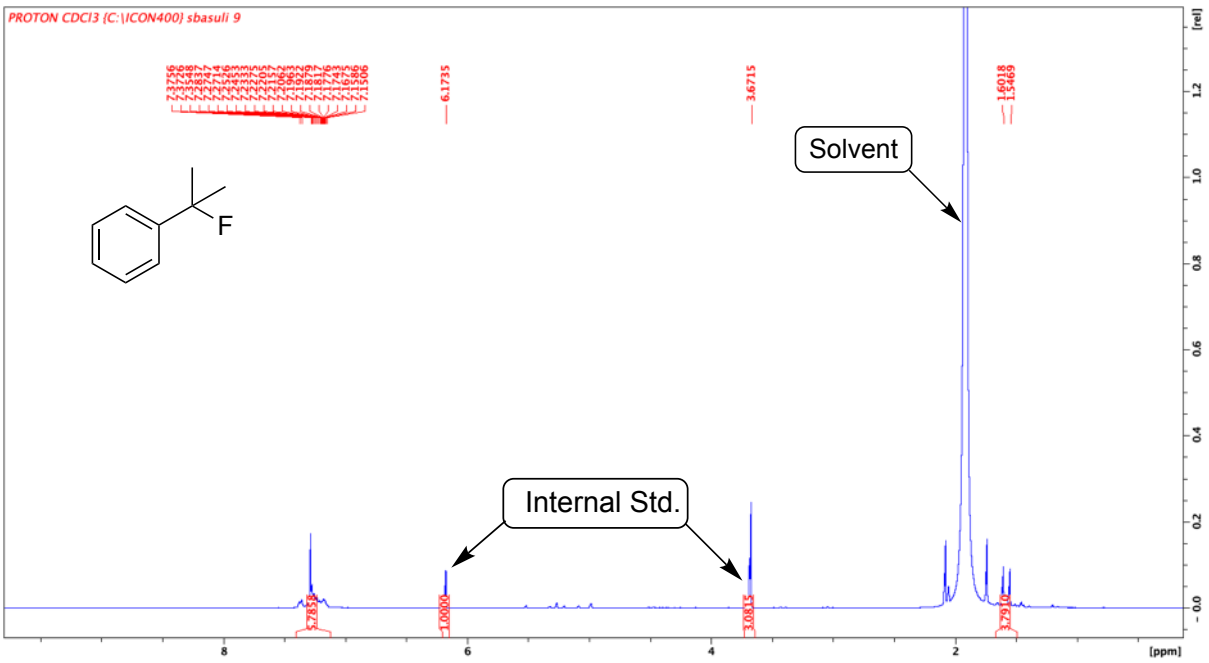
^{1}H NMR in $CDCl_3$ of **10j**



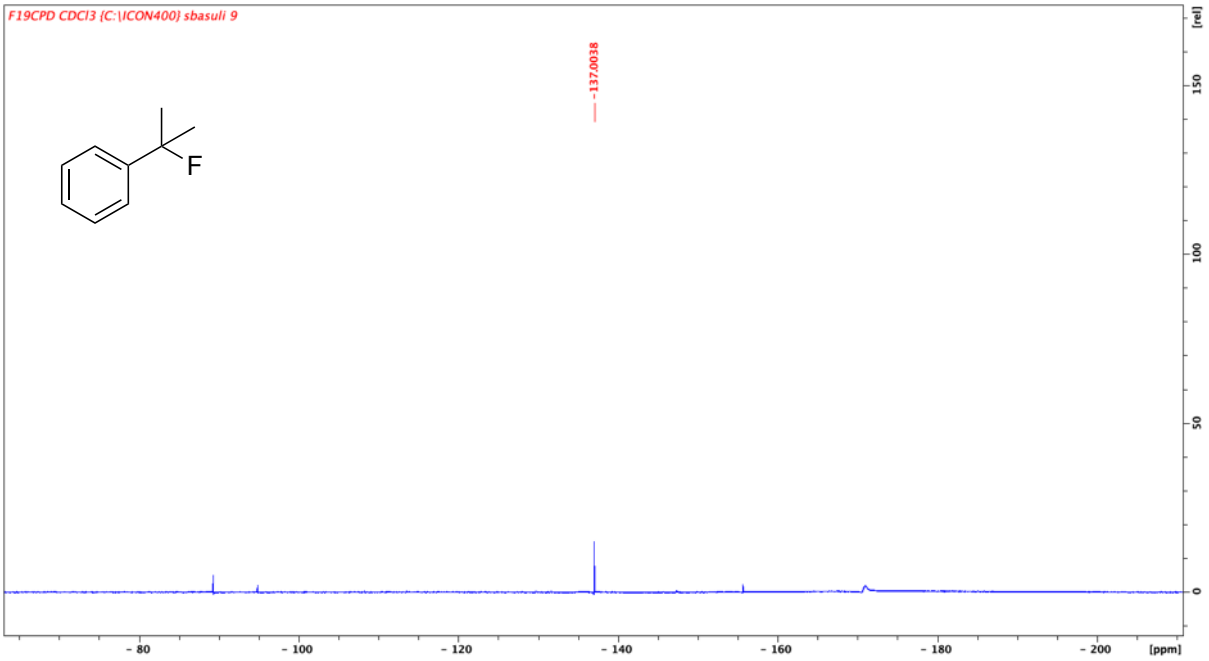
^{13}C NMR in $CDCl_3$ of **10j**



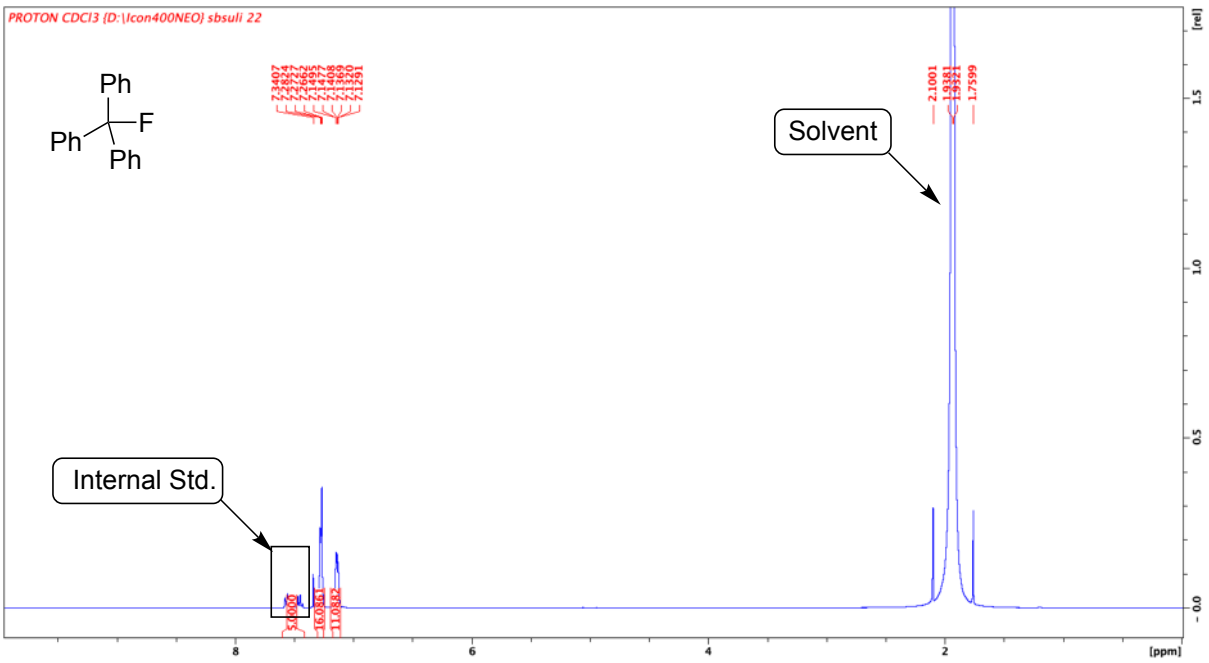
^{19}F NMR in $CDCl_3$ of **10j**



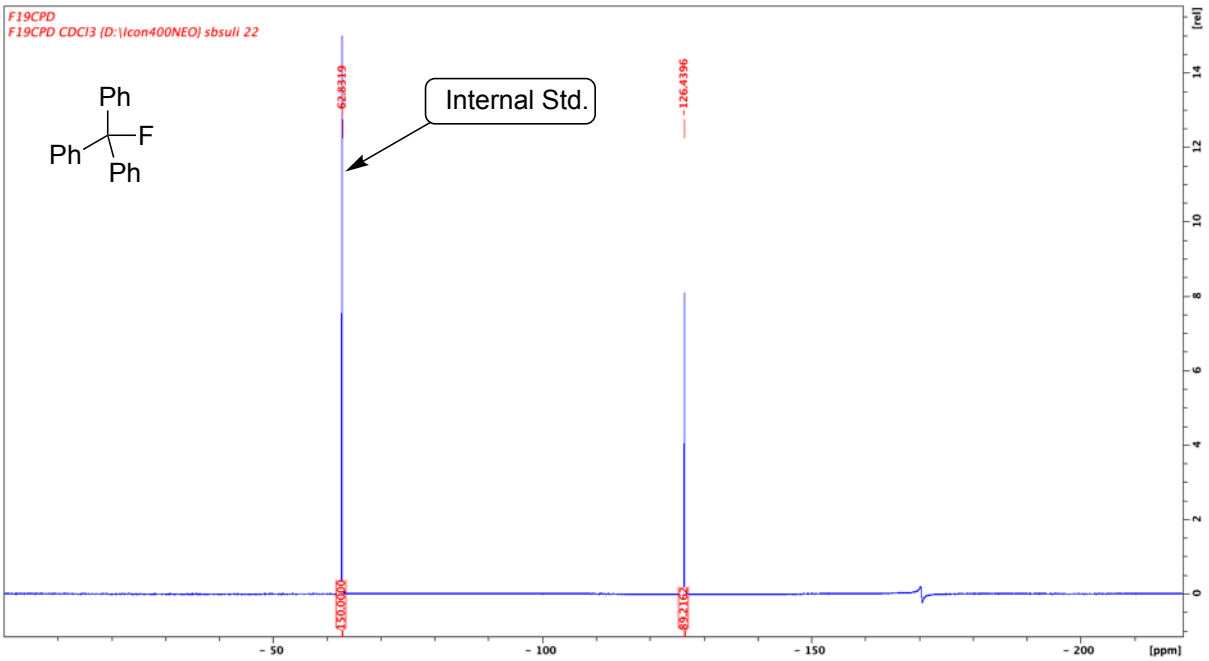
^{1}H NMR in $CDCl_3$ of **10k** (Crude reaction mixture)



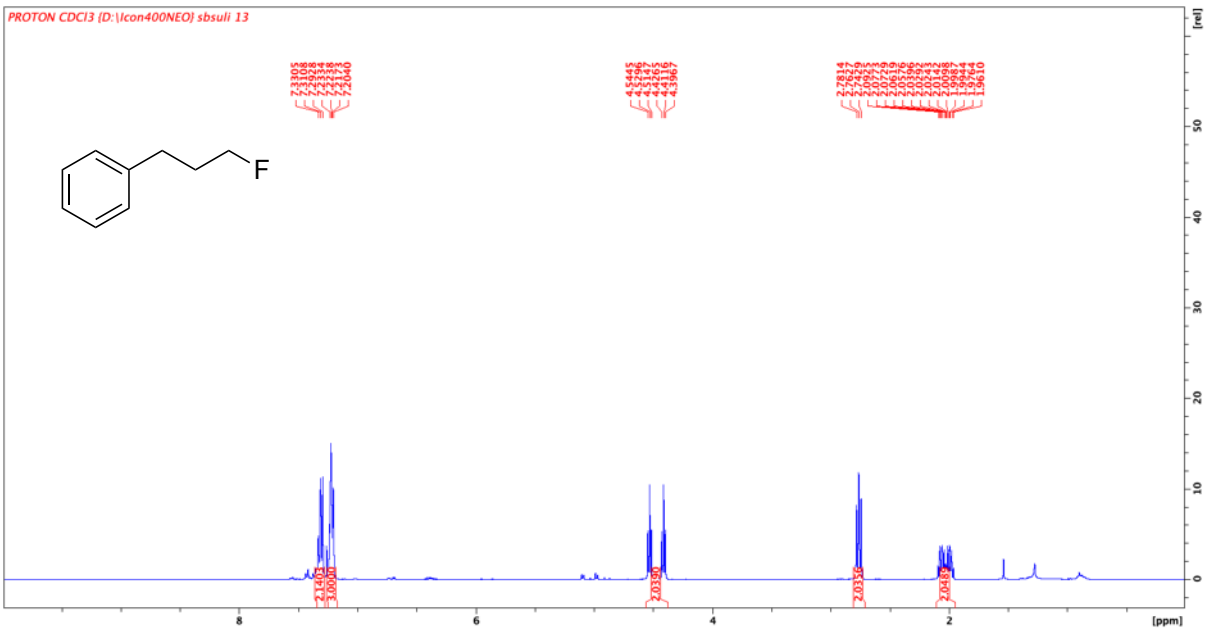
^{19}F NMR in $CDCl_3$ of **10k** (Crude reaction mixture)



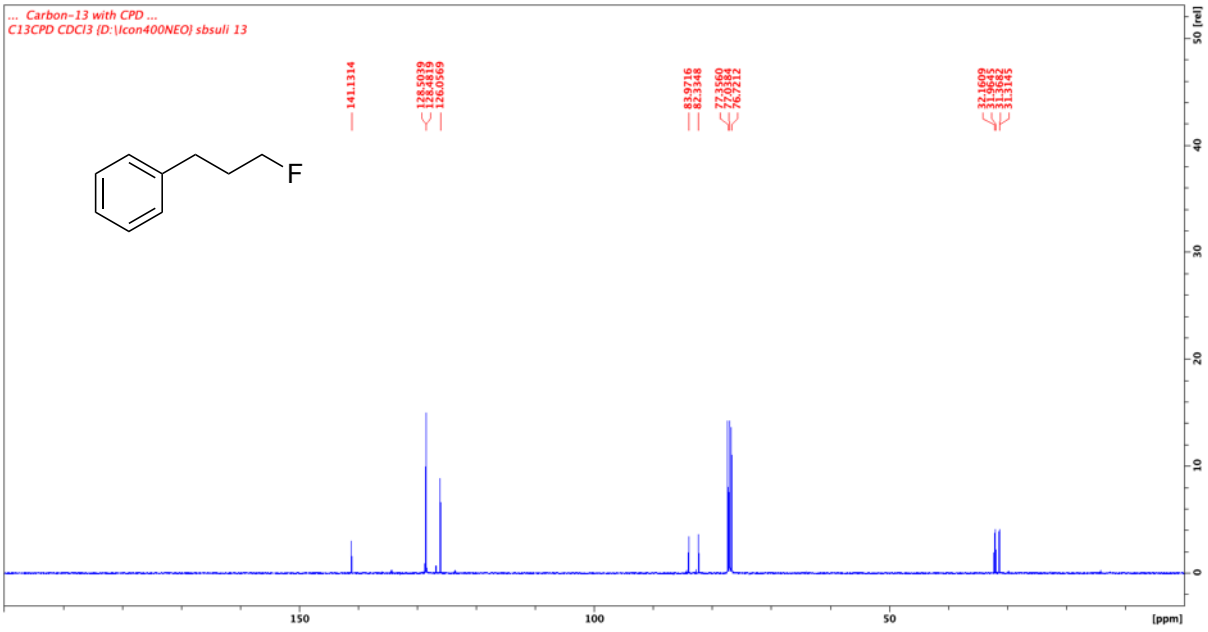
^{1}H NMR in $CDCl_3$ of **10l** (Crude reaction mixture)



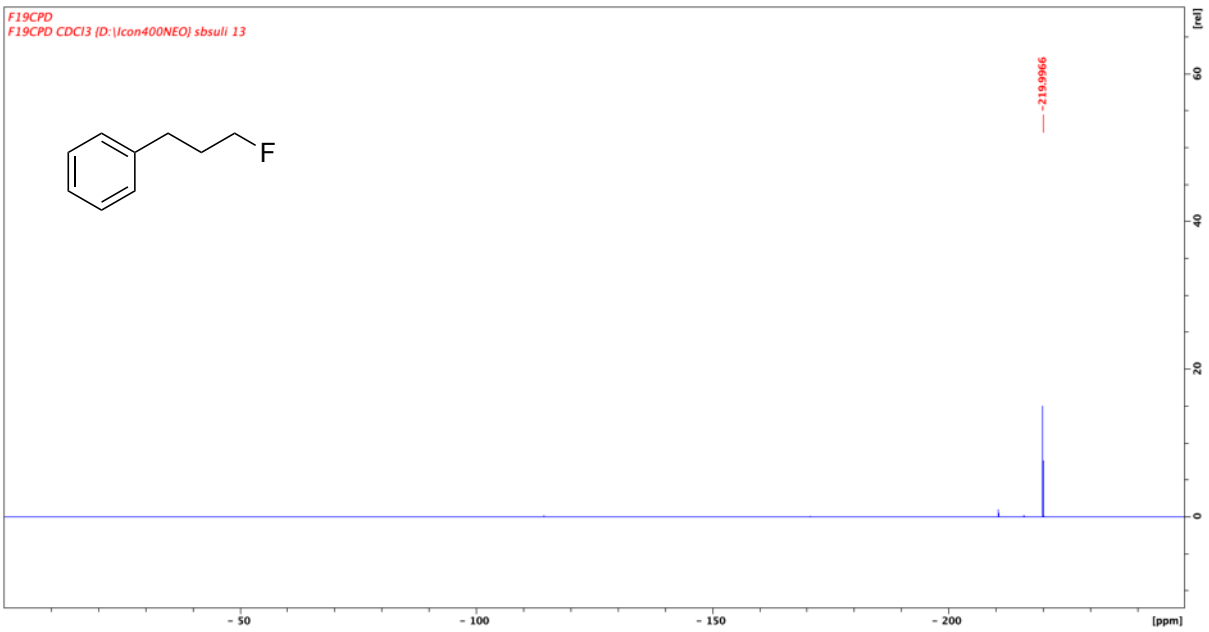
^{19}F NMR in $CDCl_3$ of **10l** (Crude reaction mixture)



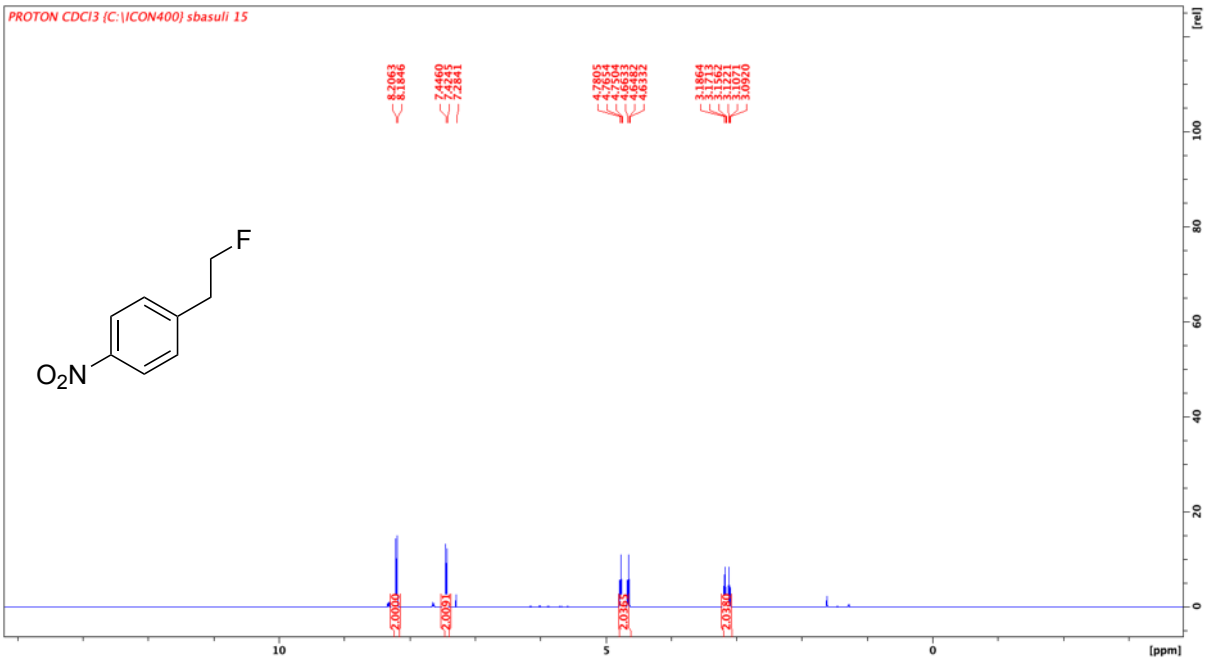
^{1}H NMR in $CDCl_3$ of **10m**



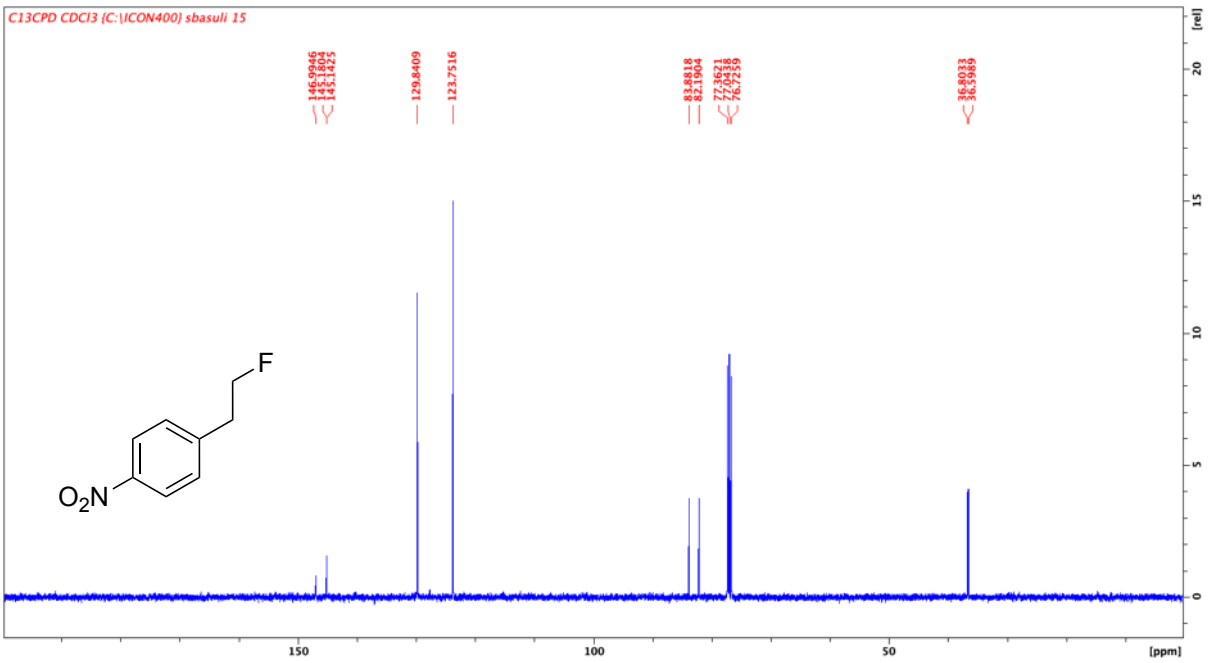
^{13}C NMR in $CDCl_3$ of **10m**



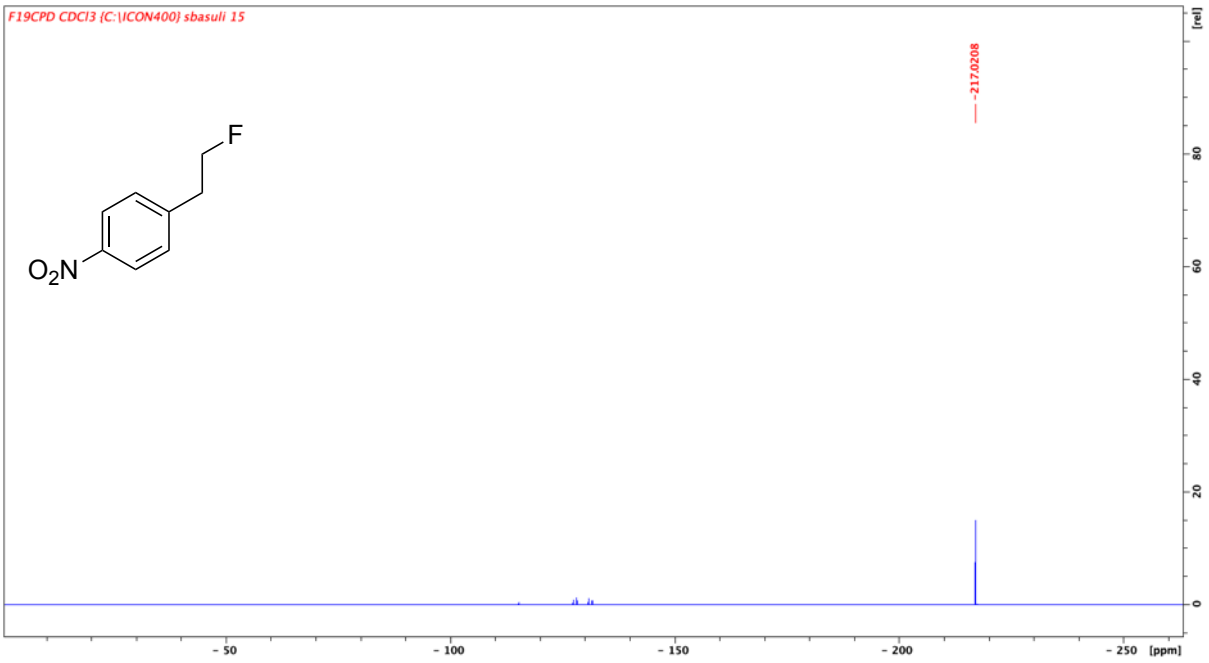
^{19}F NMR in $CDCl_3$ of **10m**



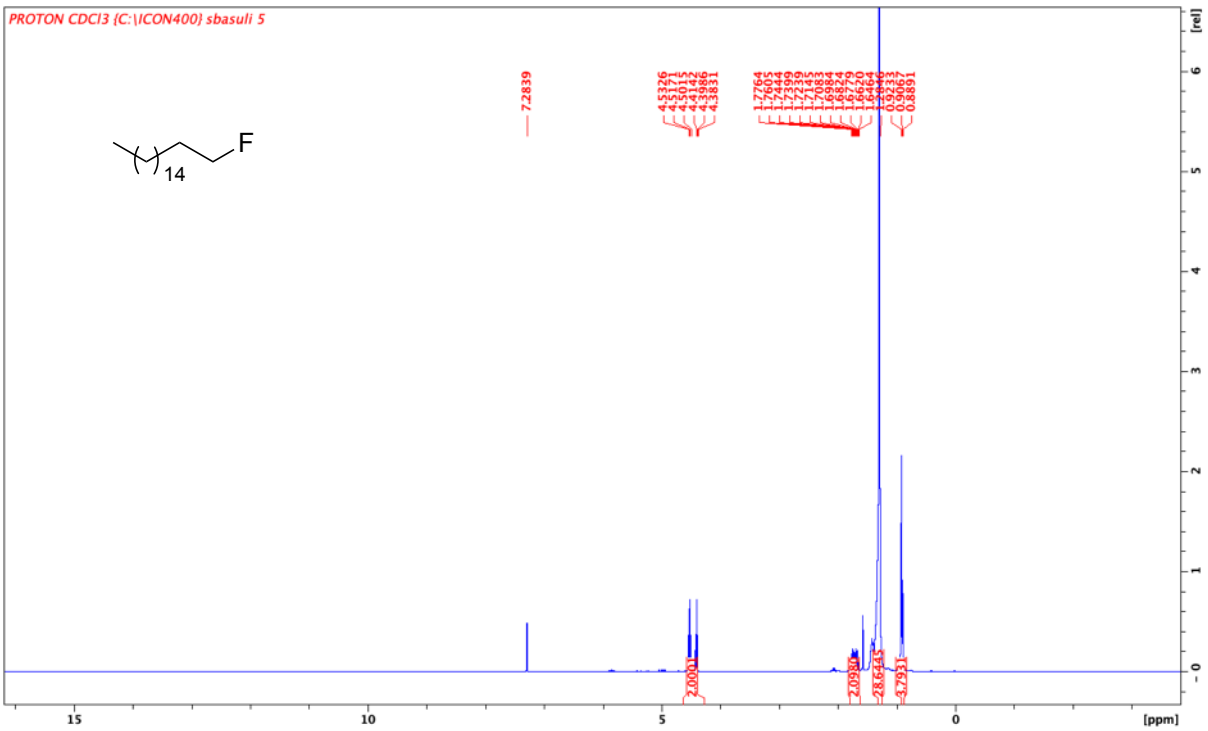
^{1}H NMR in $CDCl_3$ of **10n**



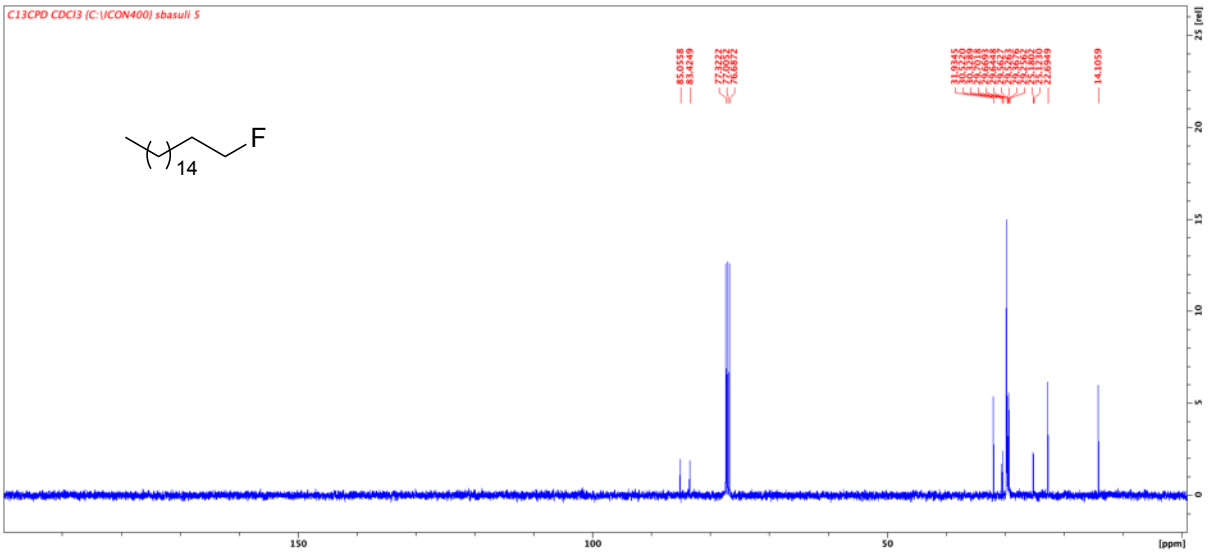
^{13}C NMR in $CDCl_3$ of **10n**



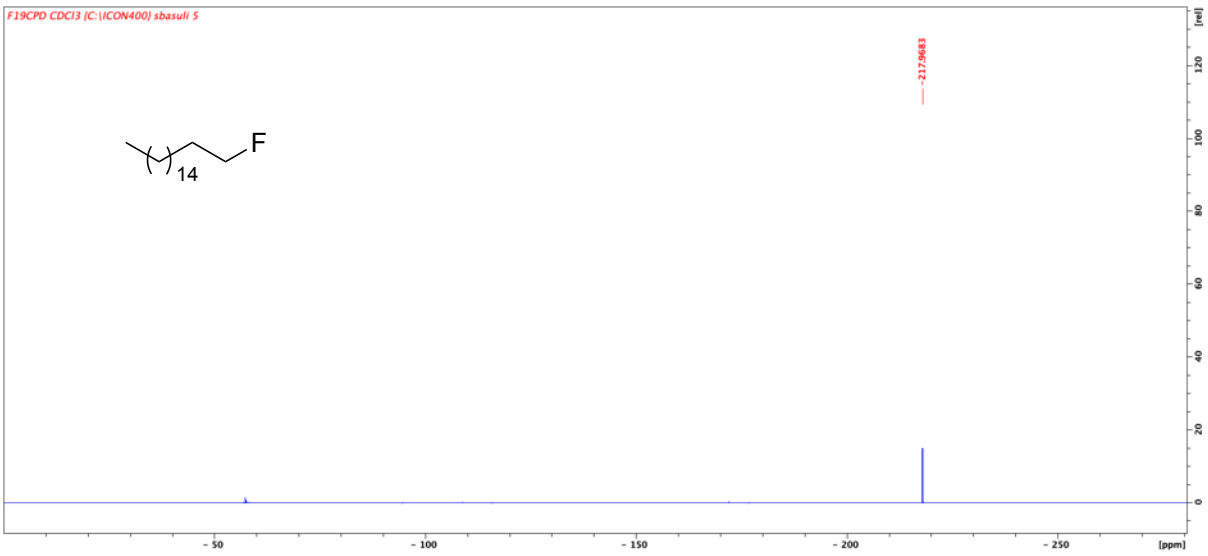
^{19}F NMR in $CDCl_3$ of **10n**



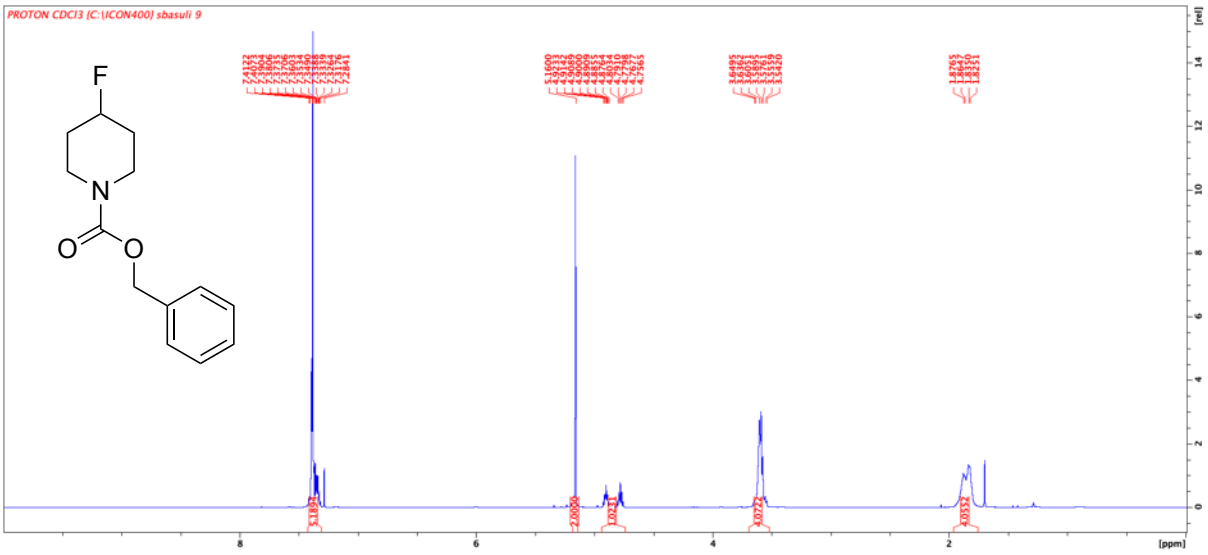
^{1}H NMR in $CDCl_3$ of **10o**



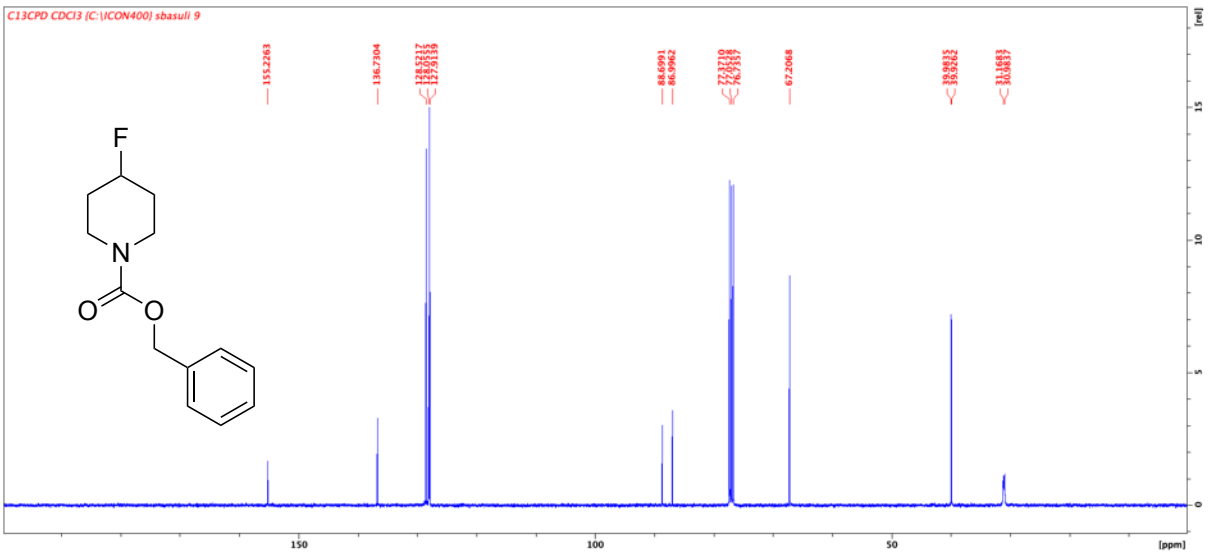
^{13}C in $CDCl_3$ of **10o**



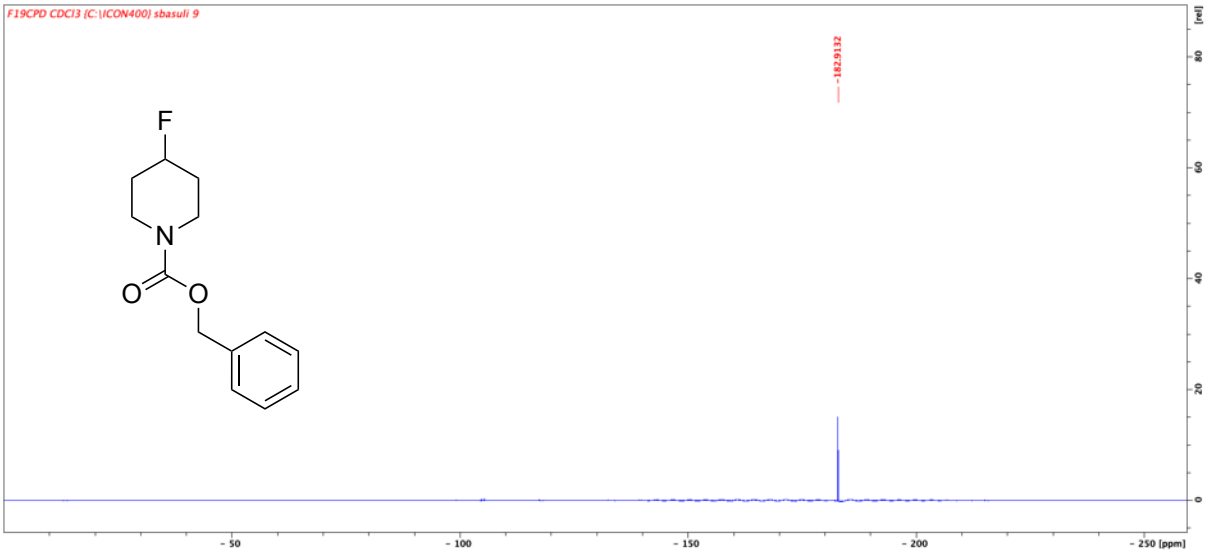
^{19}F NMR in $CDCl_3$ of **10o**



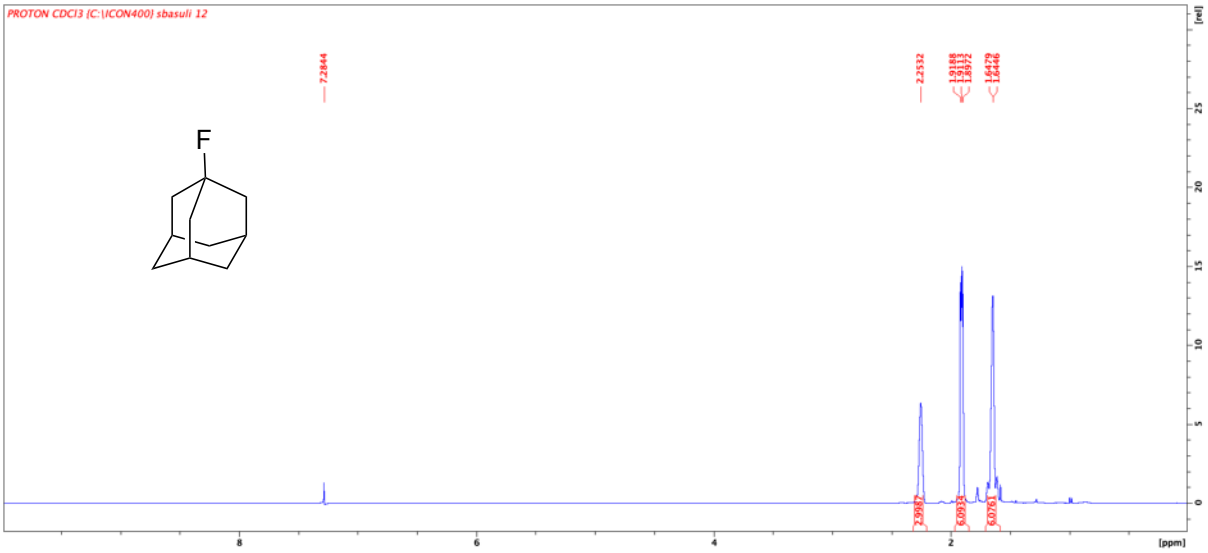
^{1}H NMR in $CDCl_3$ of **10p**



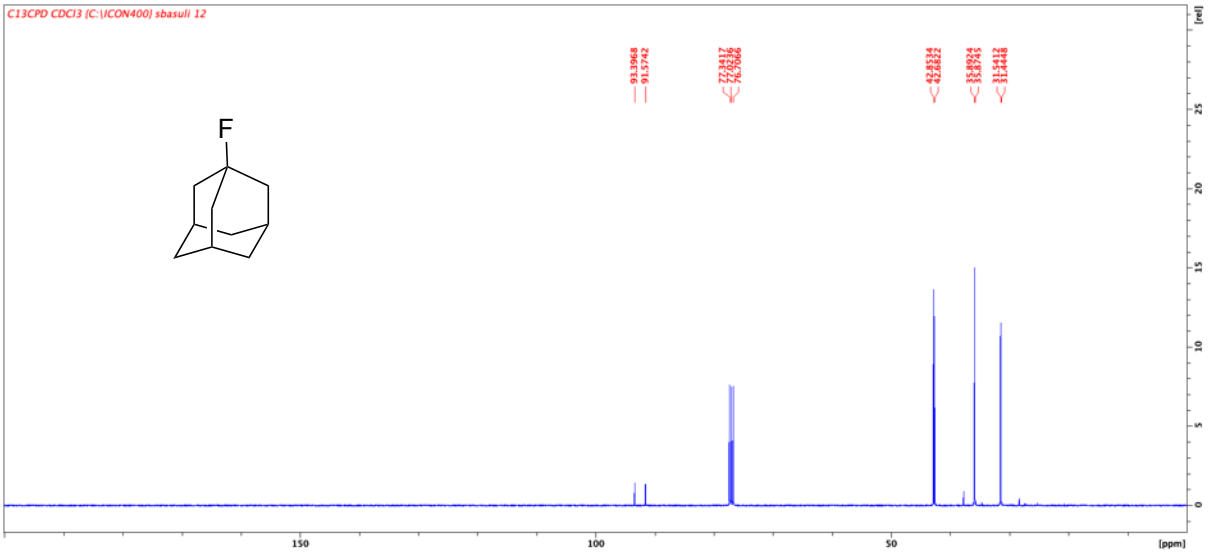
^{13}C NMR in $CDCl_3$ of **10p**



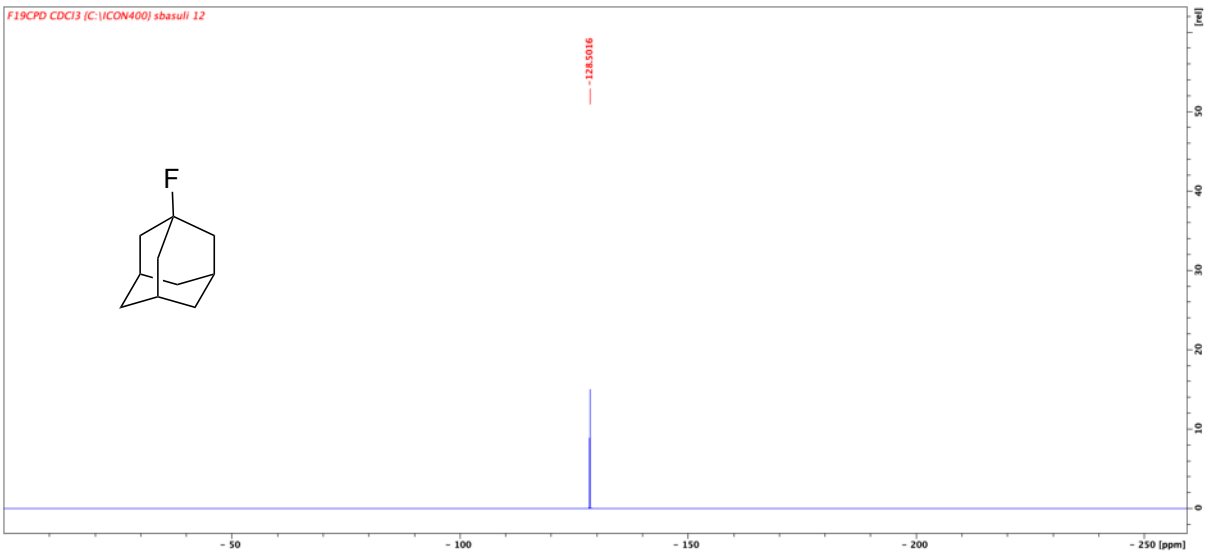
^{19}F NMR in $CDCl_3$ of **10p**



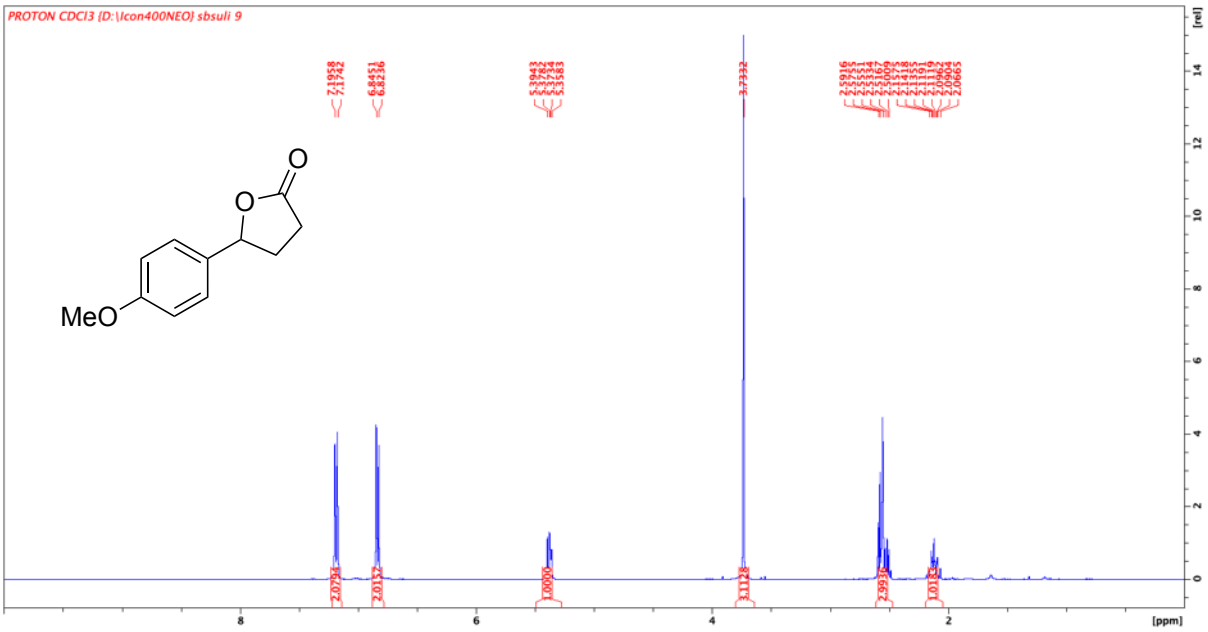
^{1}H NMR in $CDCl_3$ of **10q**



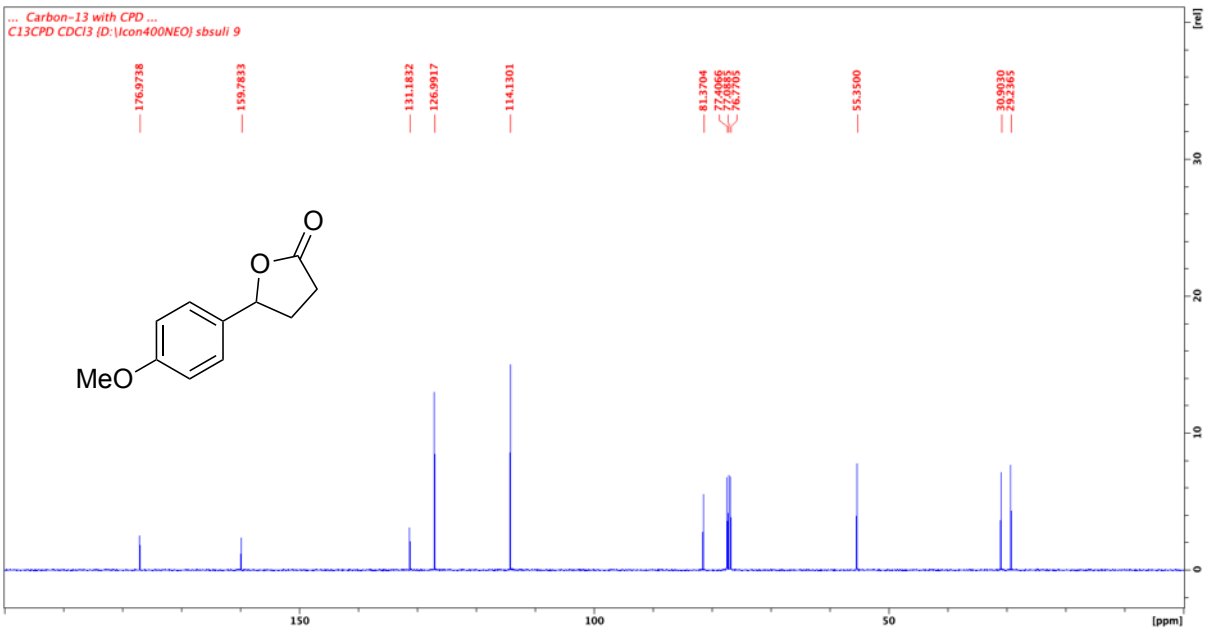
^{13}C NMR in $CDCl_3$ of **10q**



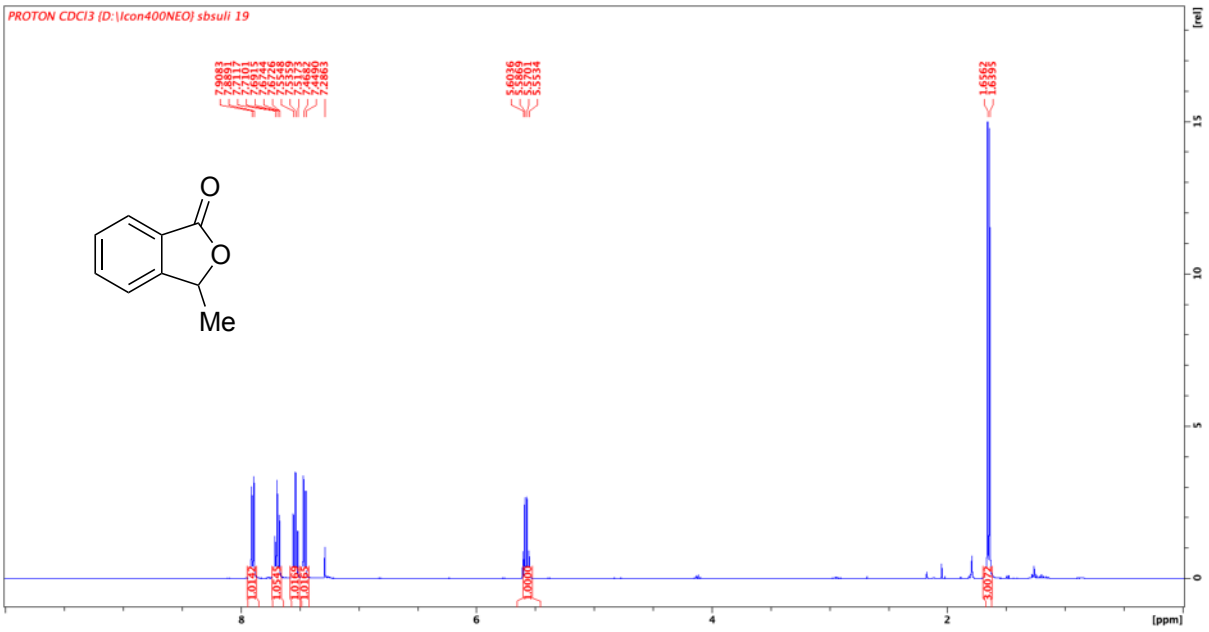
^{19}F NMR in $CDCl_3$ of **10q**



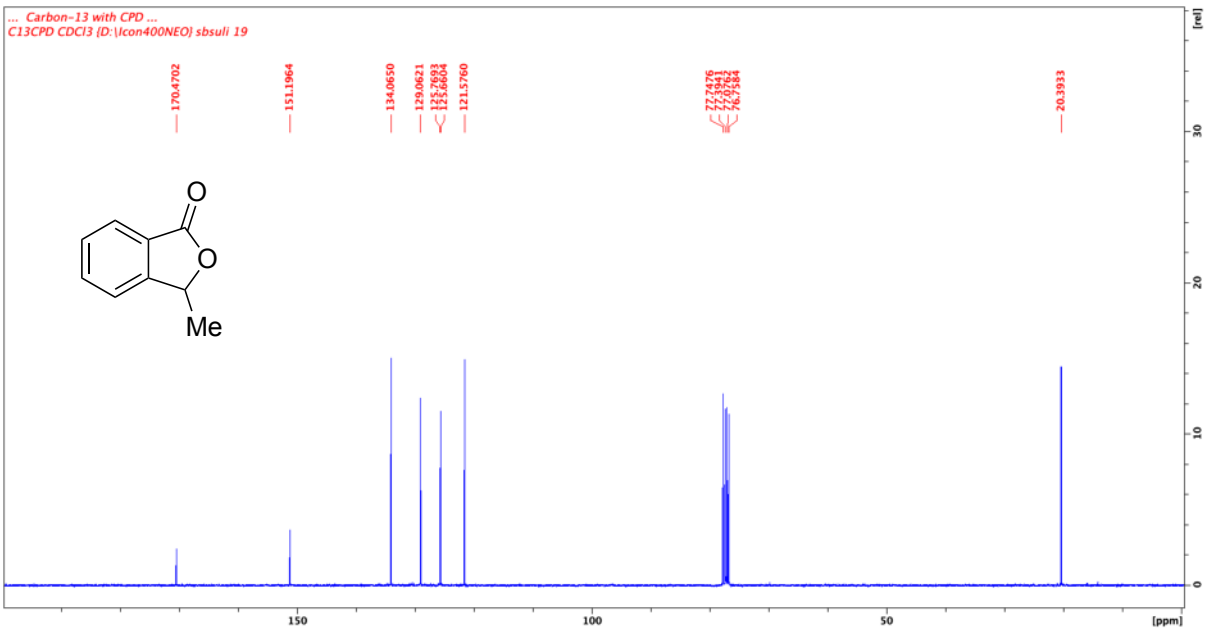
^{1}H NMR in $CDCl_3$ of **10r′**



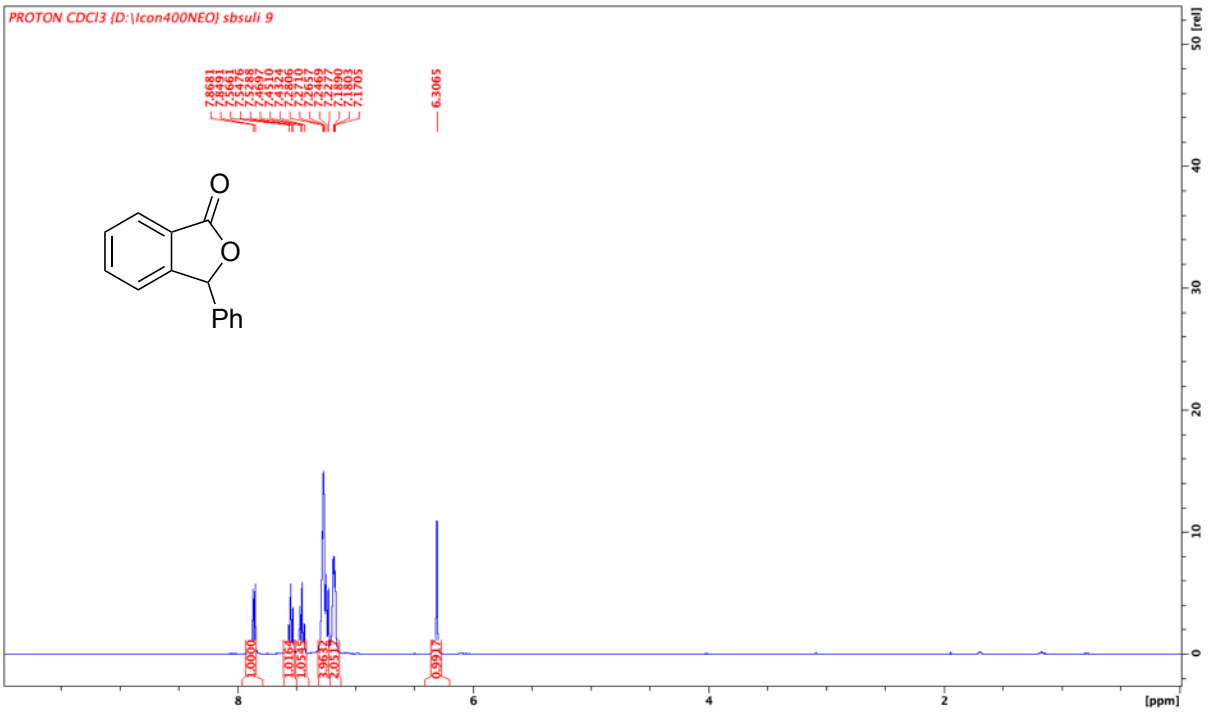
^{13}C NMR spectrum of **10r′**



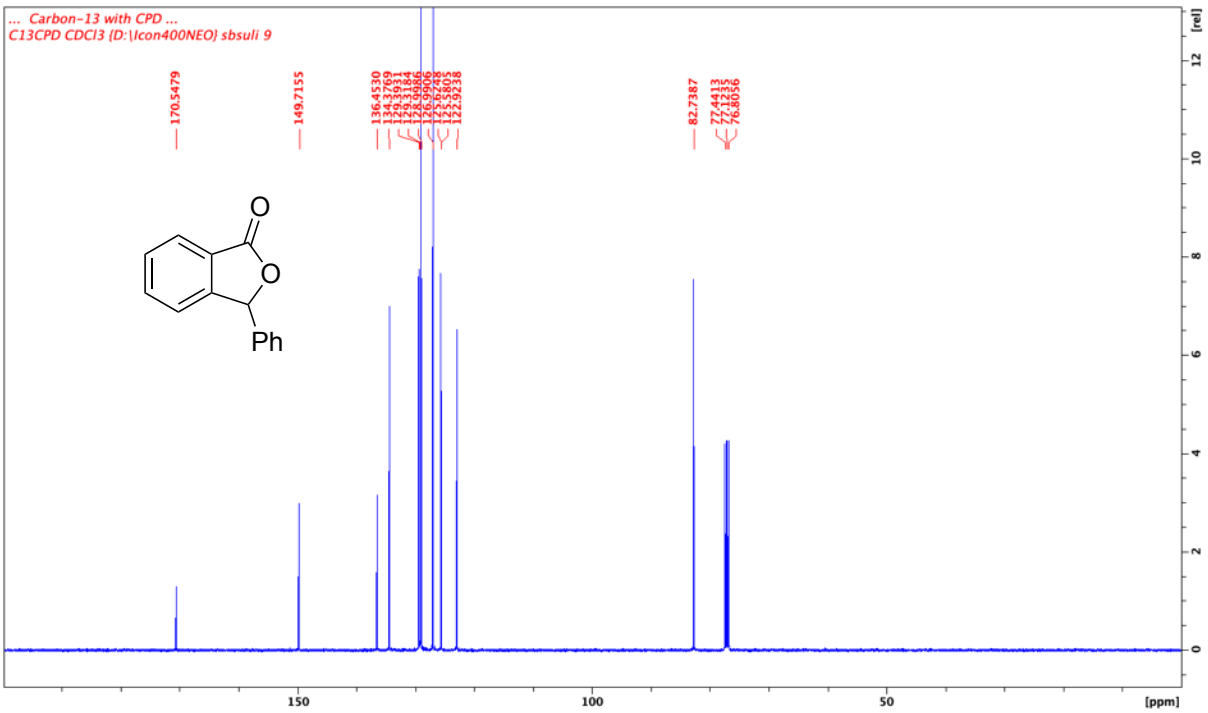
^{1}H NMR in $CDCl_3$ of **10s′**



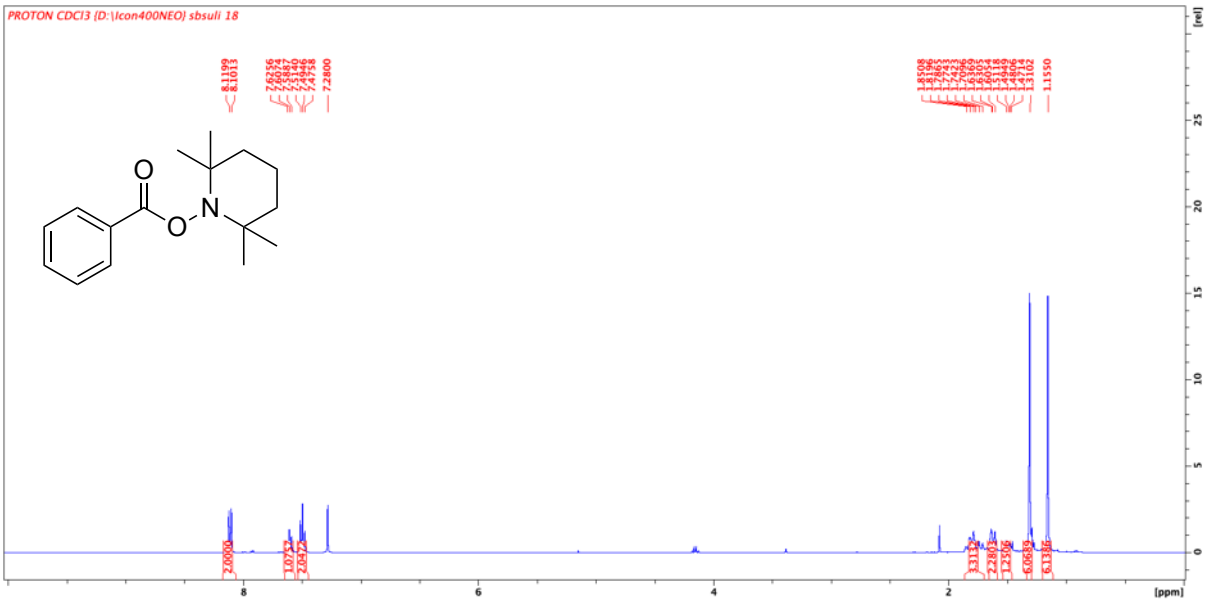
^{13}C NMR spectrum of **10s′**



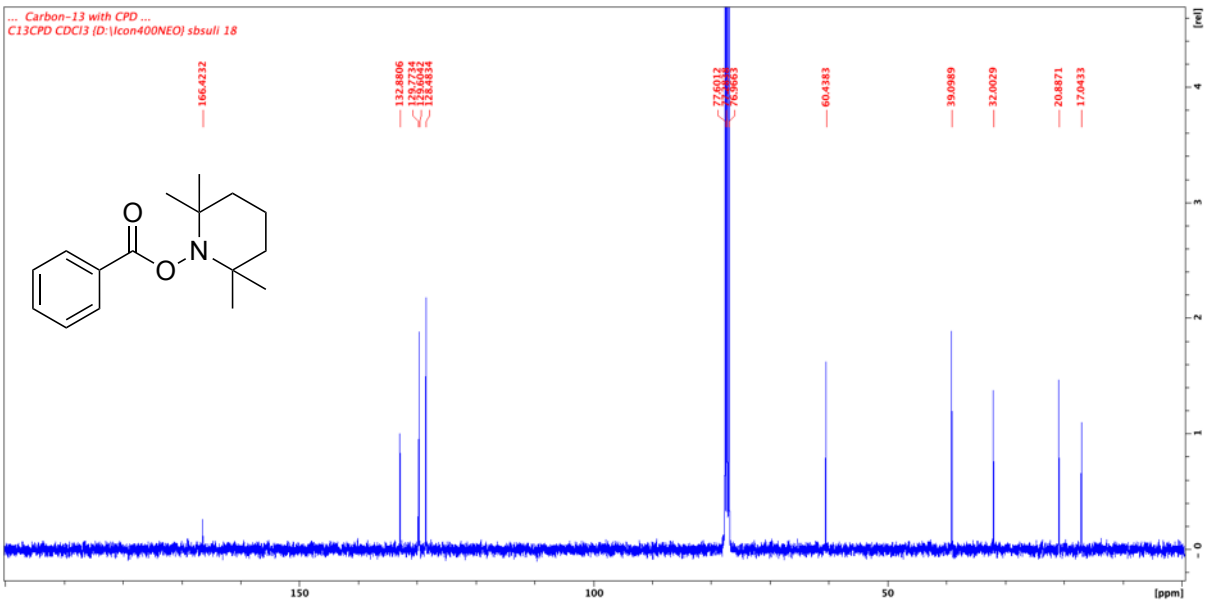
^{1}H NMR in $CDCl_3$ of **10t′**



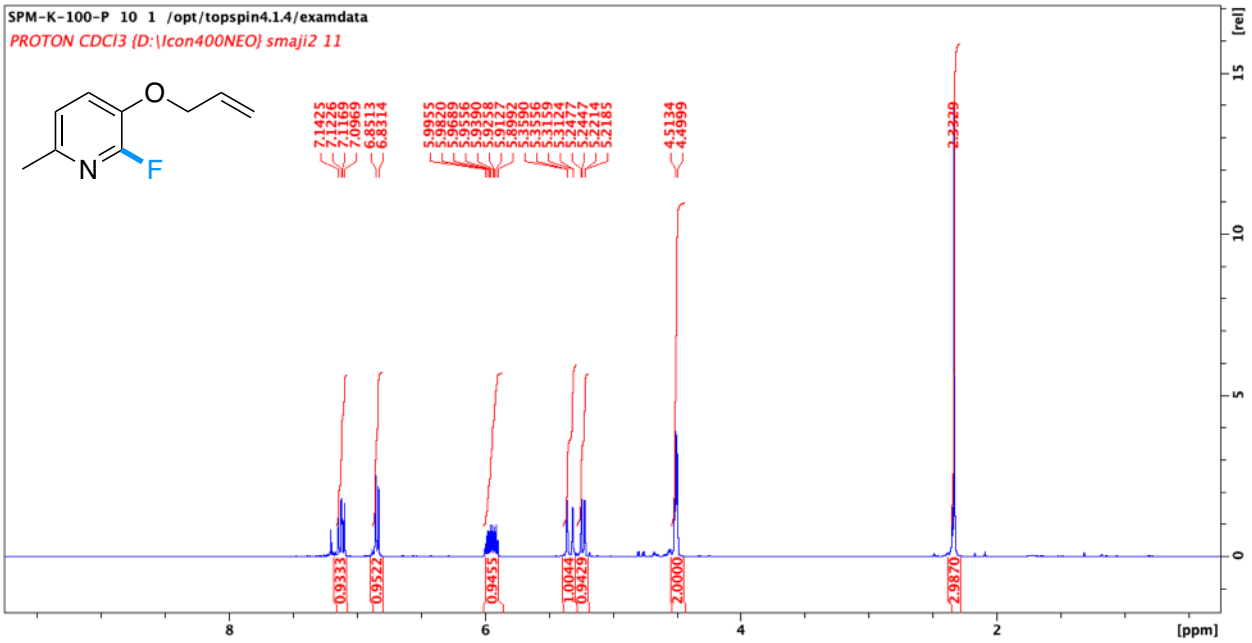
^{13}C NMR spectrum of **10t′**



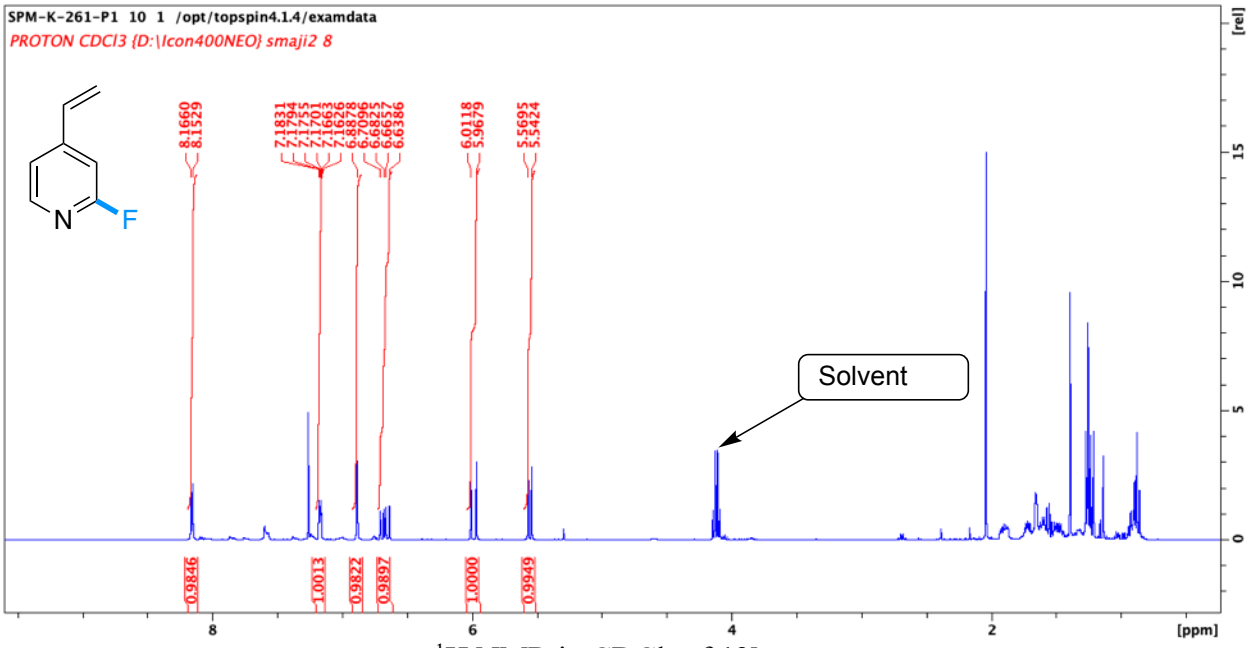
^{1}H NMR in $CDCl_3$ of TEMPO adduct



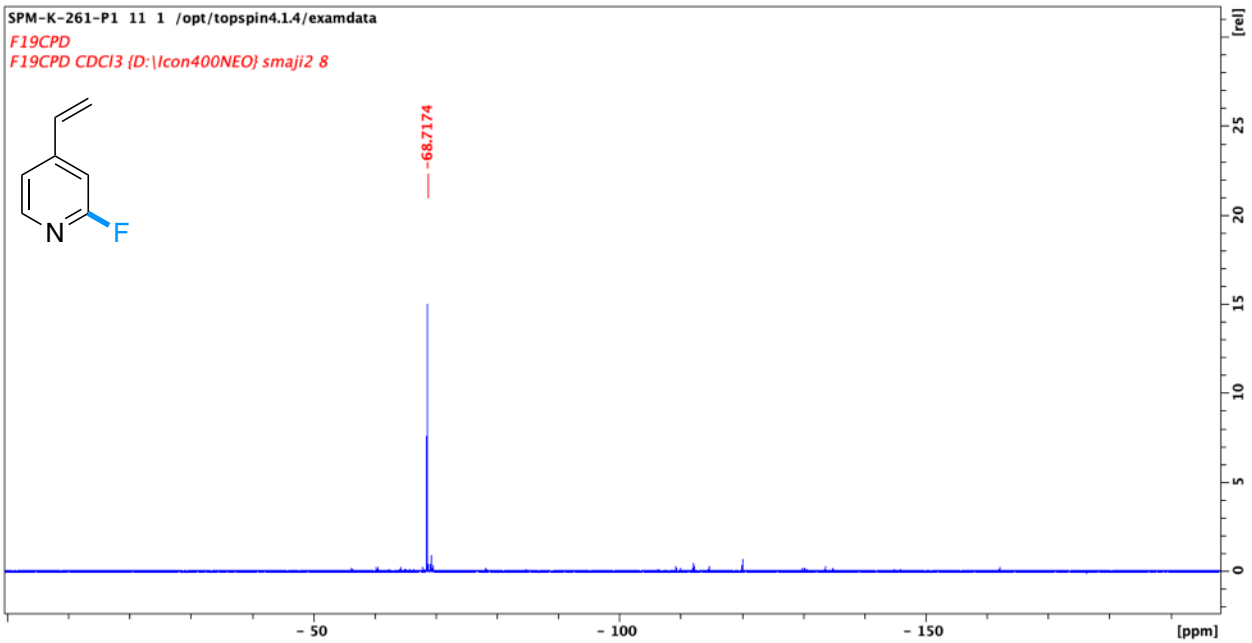
^{13}C NMR spectrum of TEMPO adduct



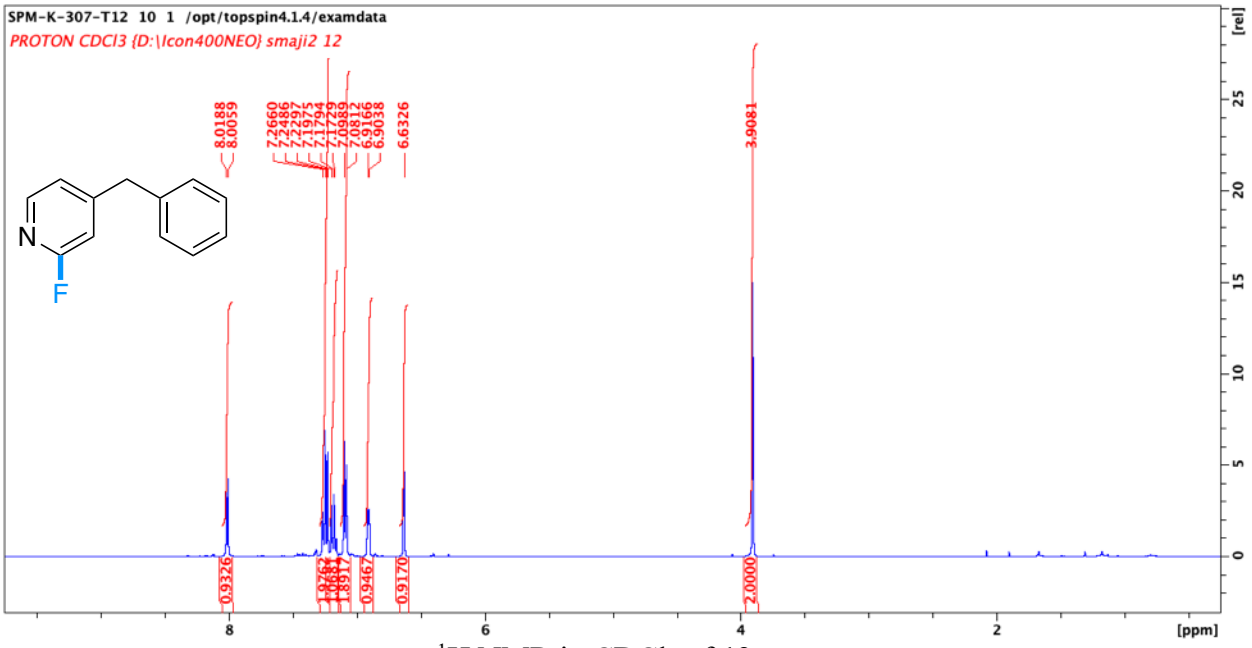
^{1}H NMR in $CDCl_3$ of **12a**



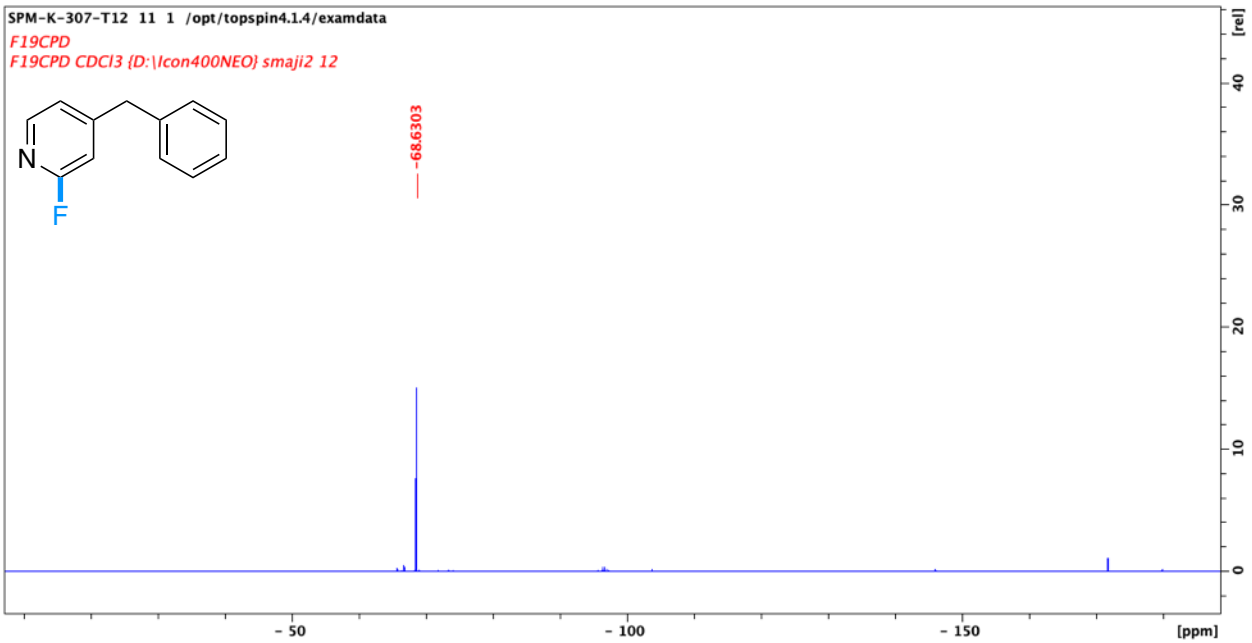
^{1}H NMR in $CDCl_3$ of **12b**



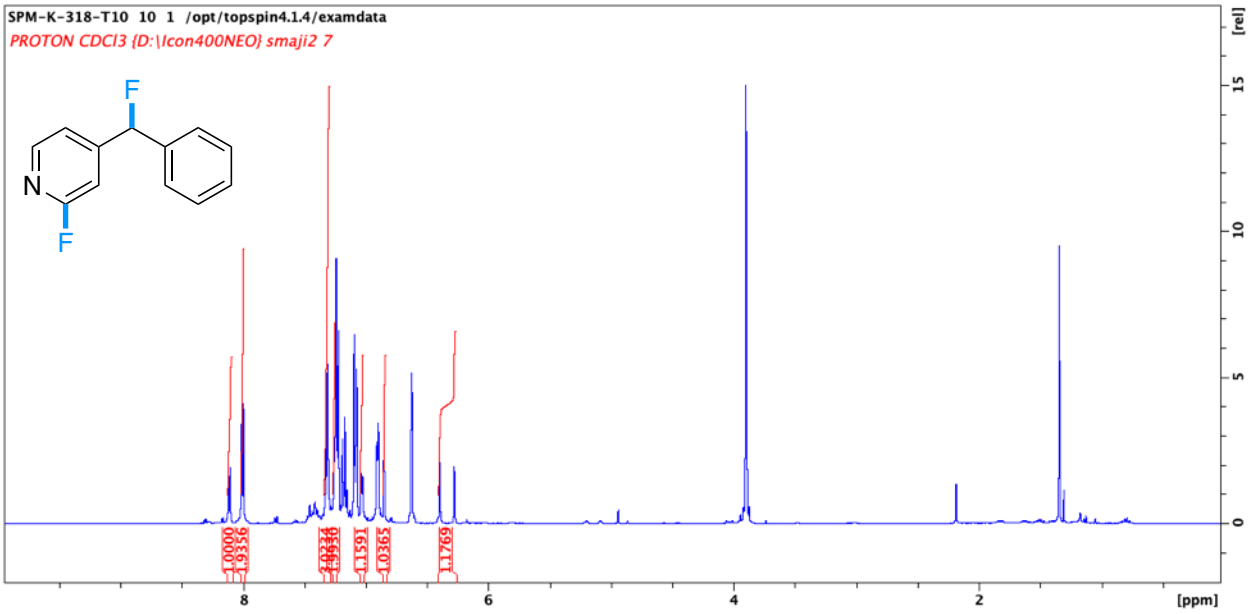
^{19}F NMR in $CDCl_3$ of **12b**



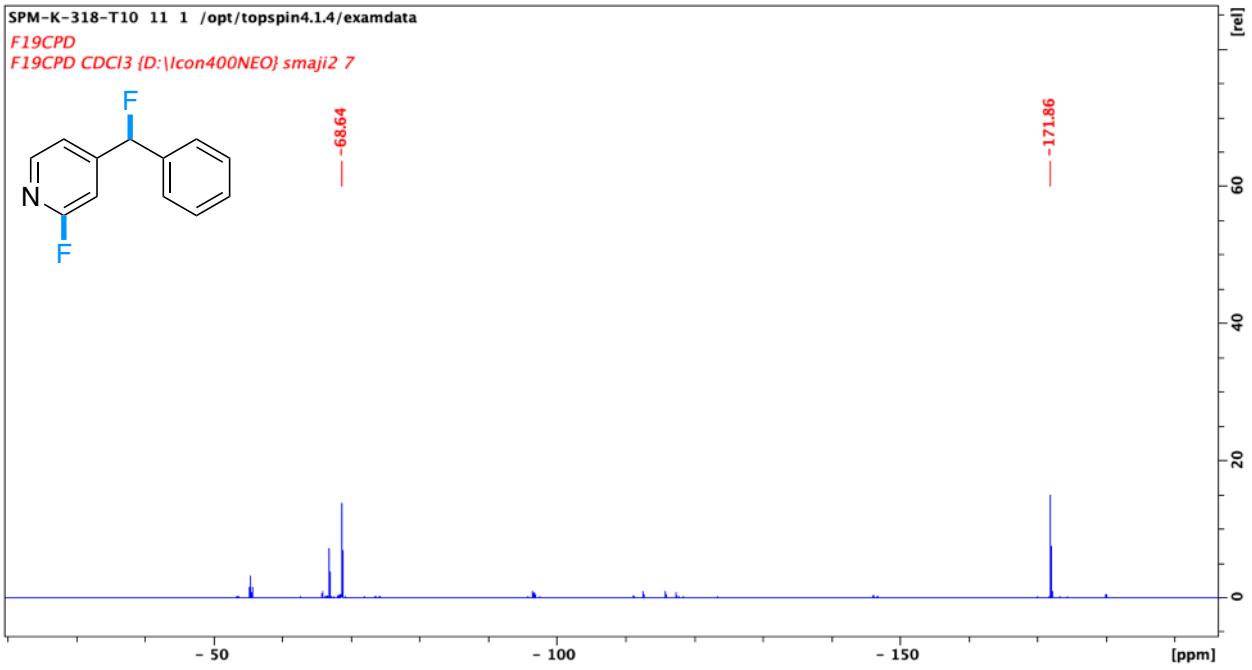
^{1}H NMR in $CDCl_3$ of **12c**



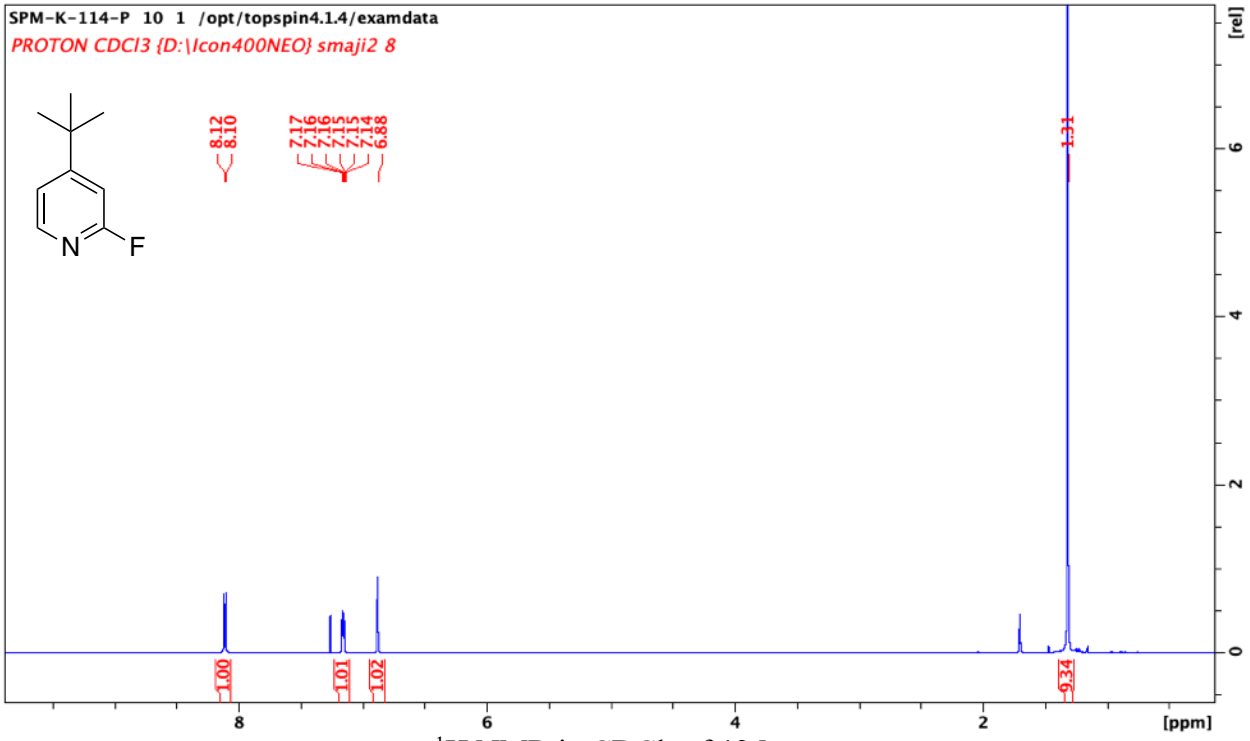
^{19}F NMR in $CDCl_3$ of **12c**



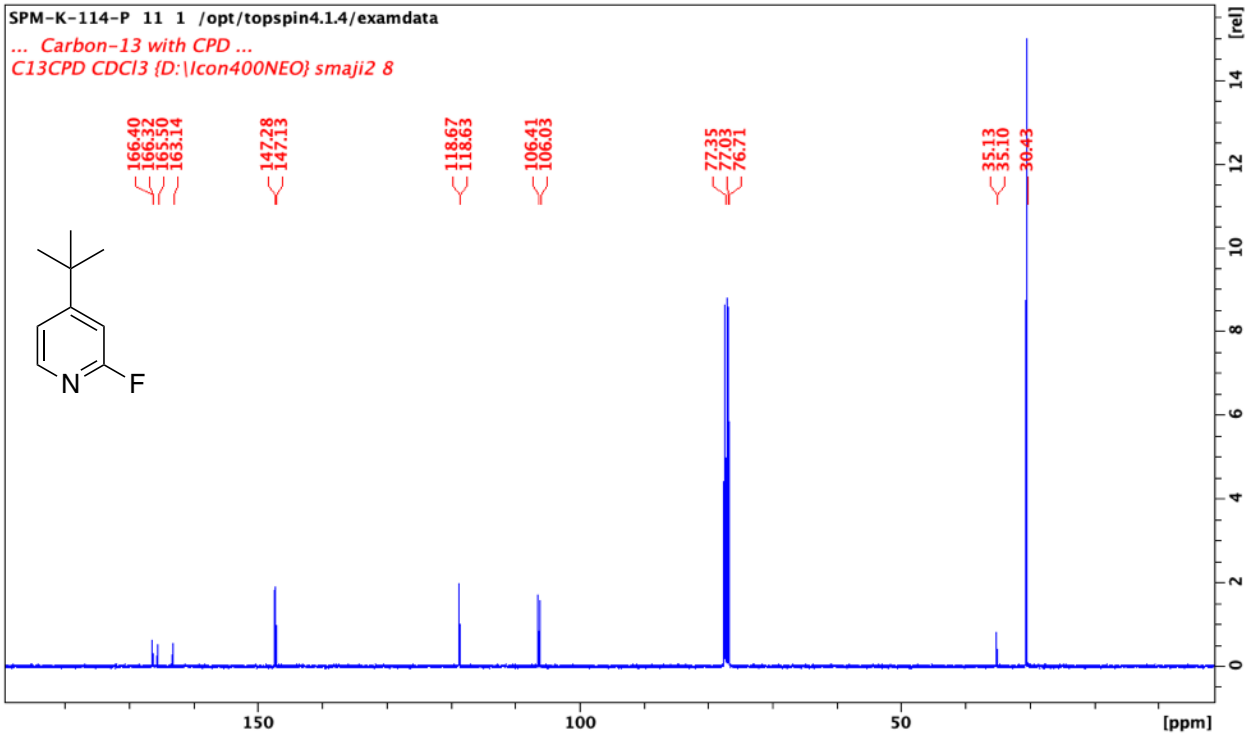
^{1}H NMR in $CDCl_3$ of **12c′**



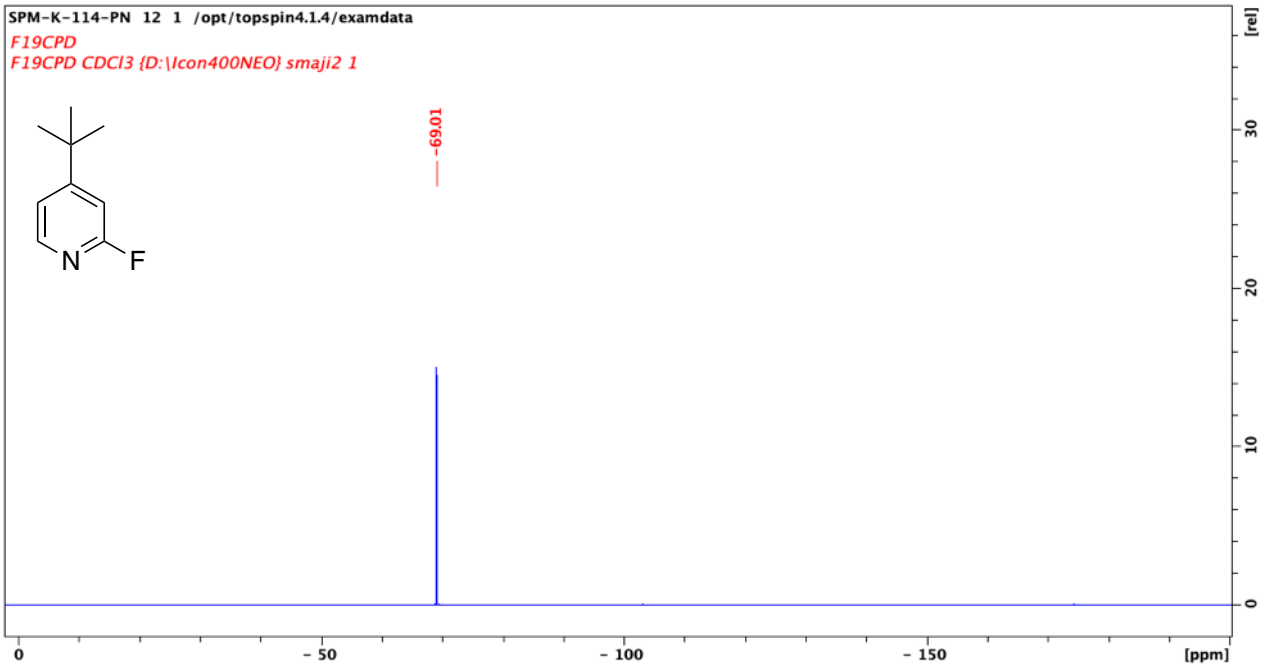
^{19}F NMR in $CDCl_3$ of **12c′**



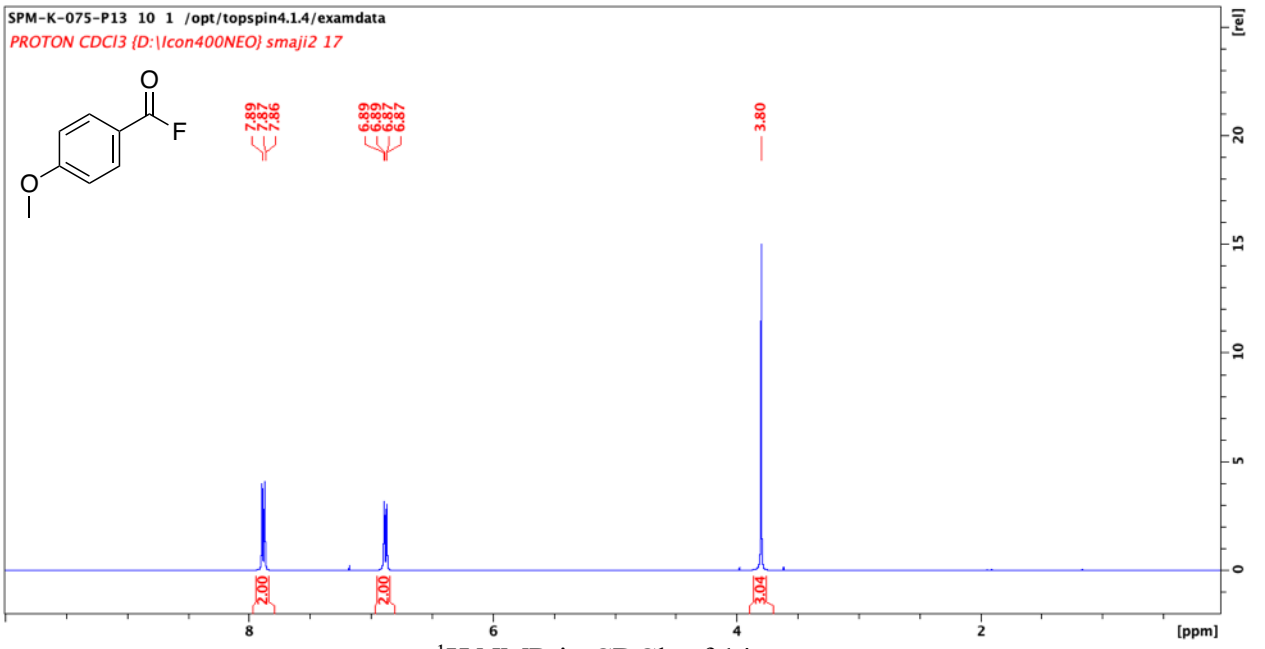
^{1}H NMR in $CDCl_3$ of **12d**



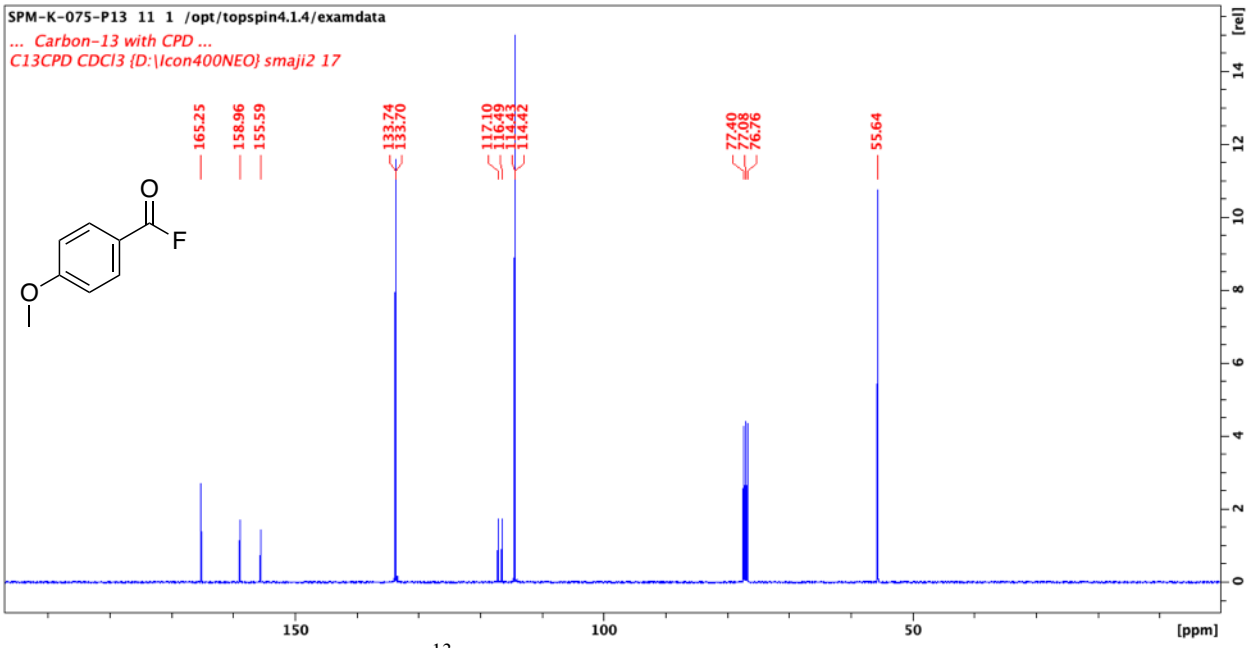
^{13}C NMR in $CDCl_3$ of **12d**



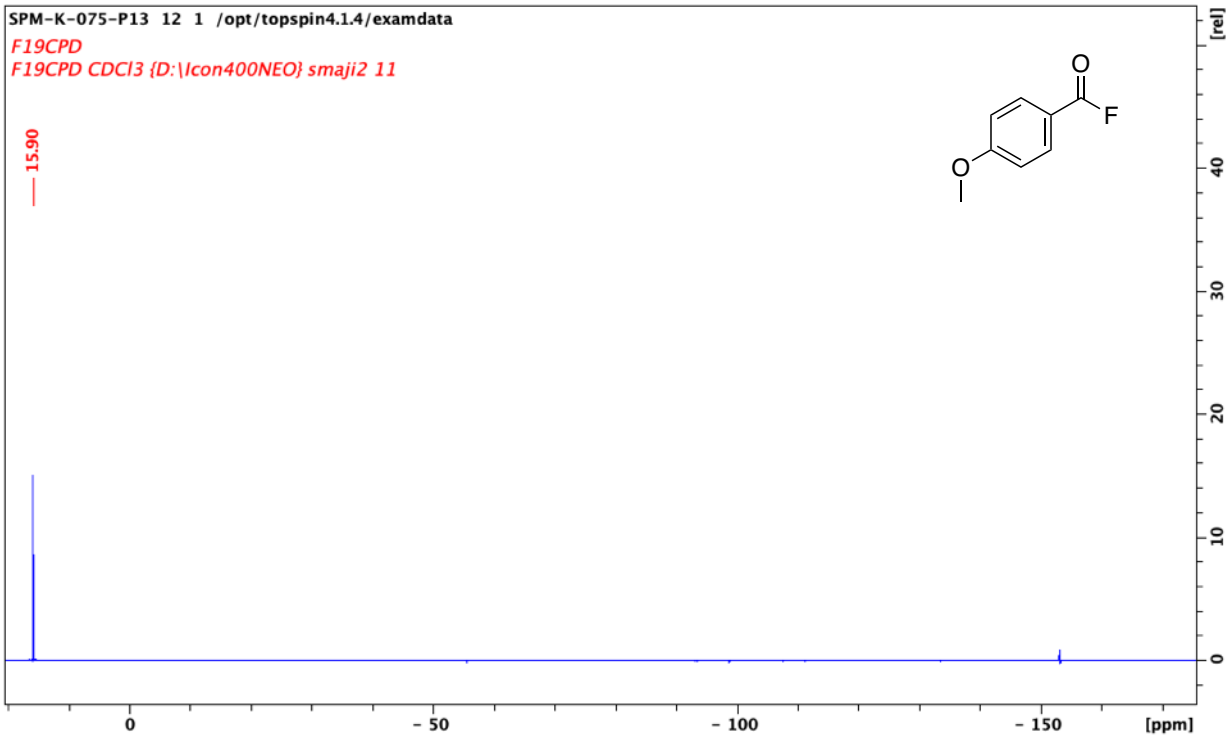
^{19}F NMR in $CDCl_3$ of **12d**



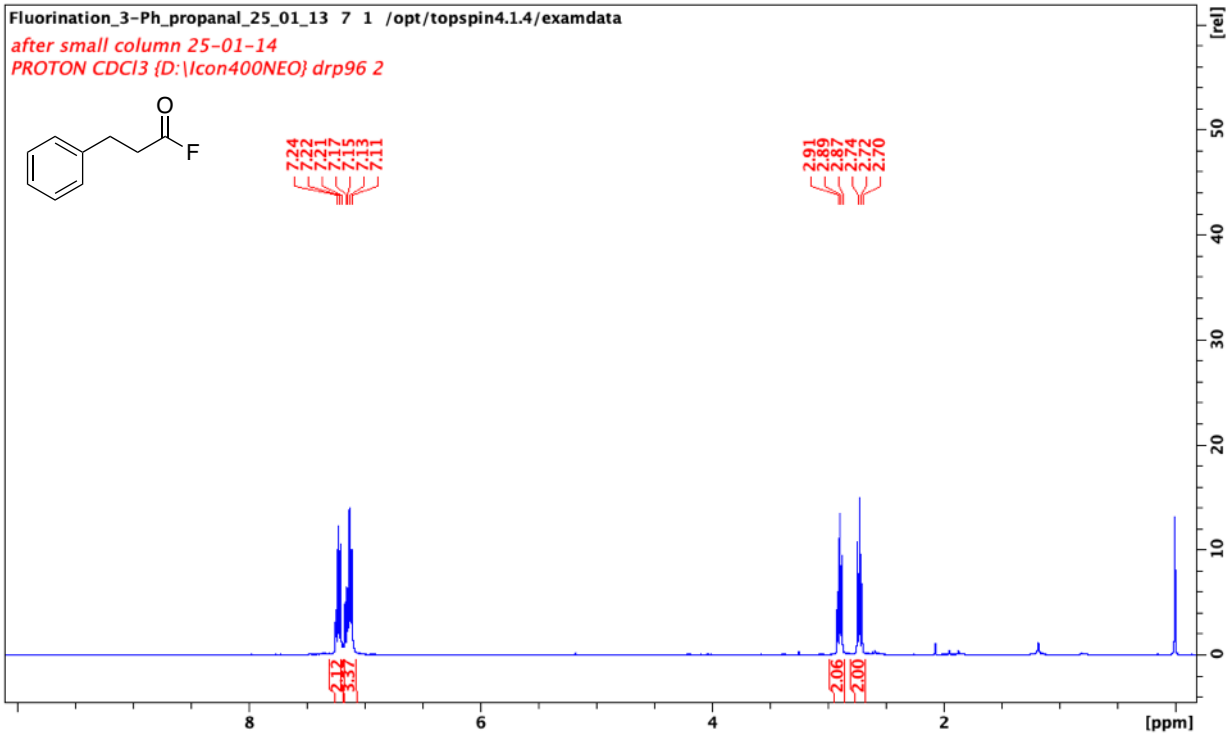
^{1}H NMR in $CDCl_3$ of **14a**



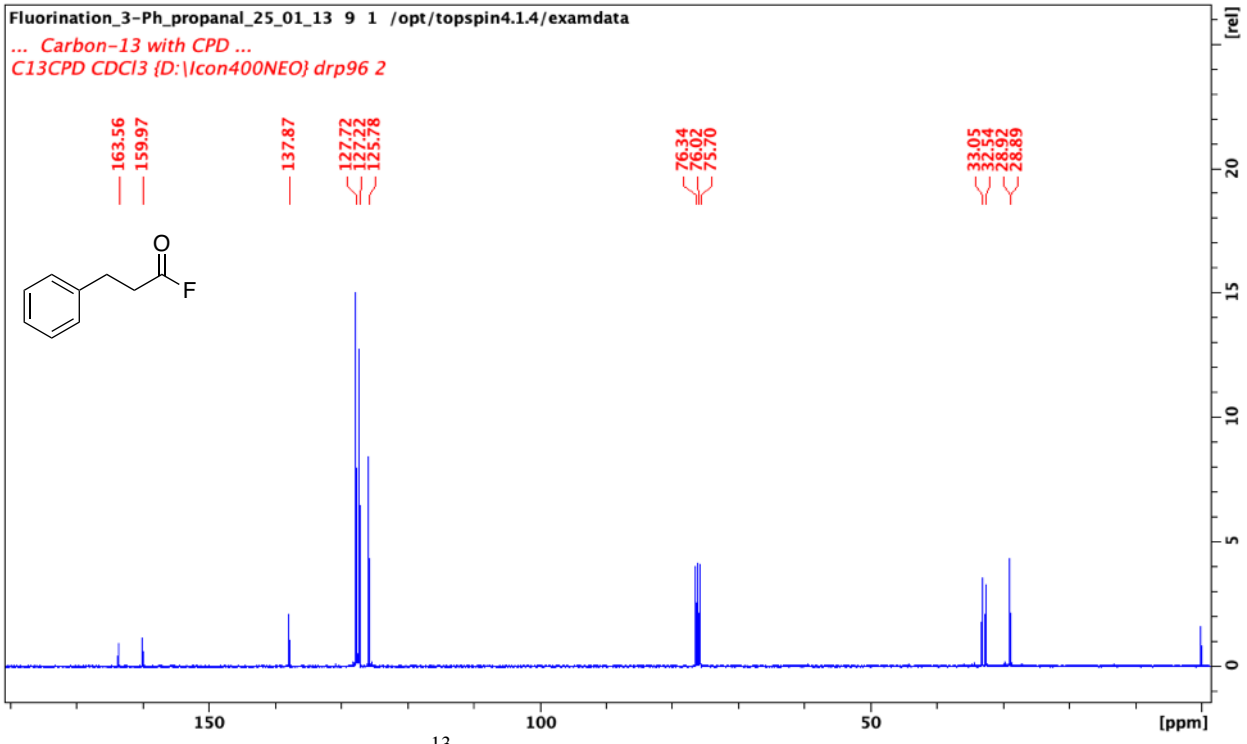
^{13}C NMR in $CDCl_3$ of **14a**



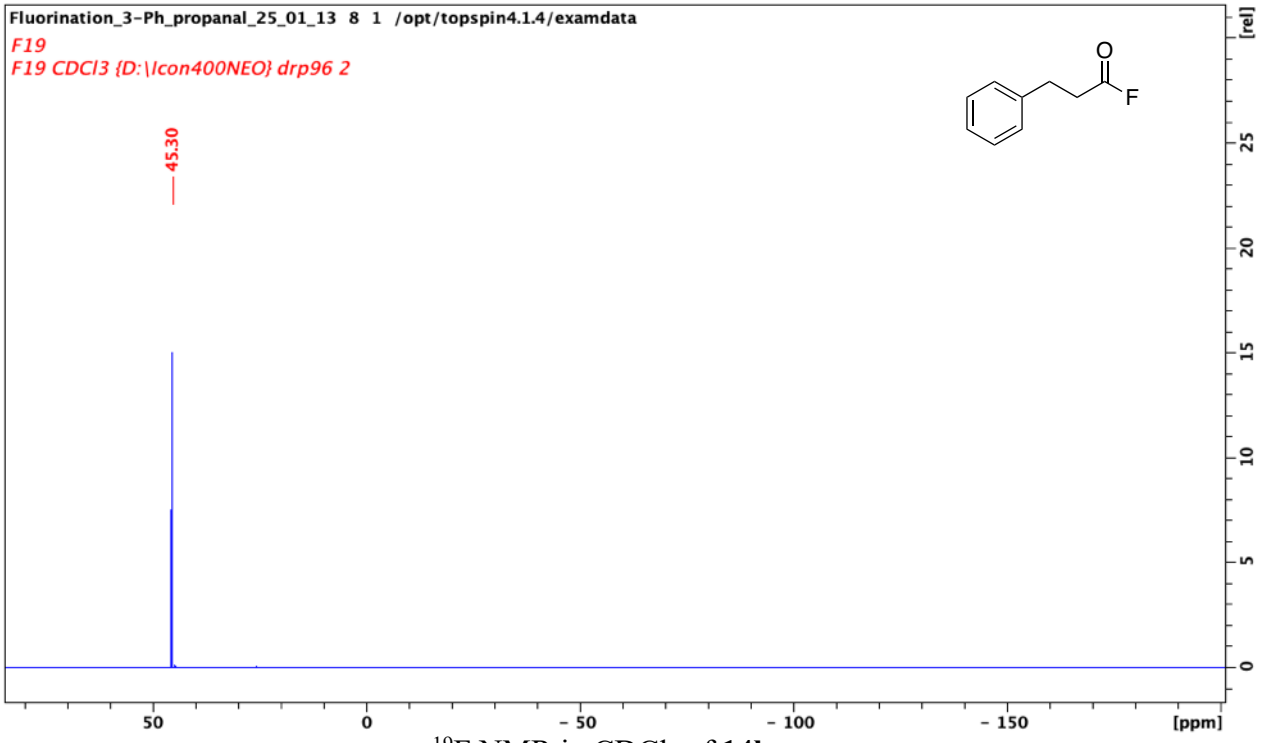
^{19}F NMR in $CDCl_3$ of **14a**



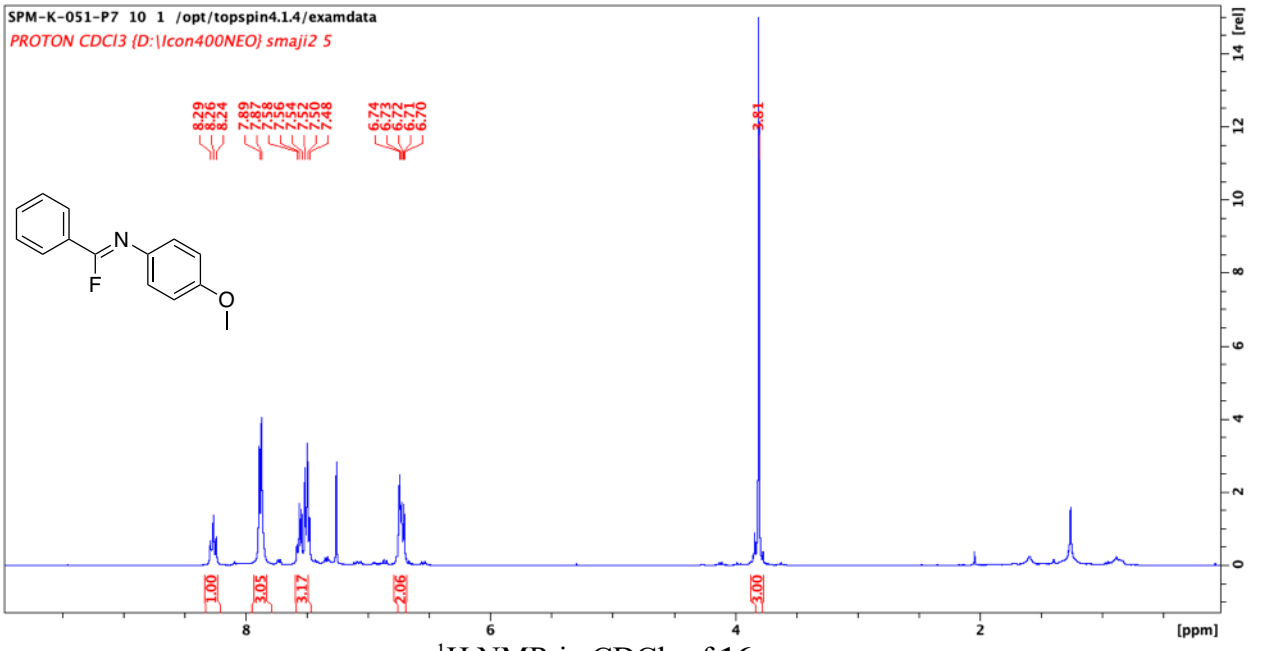
^{1}H NMR in $CDCl_3$ of **14b**



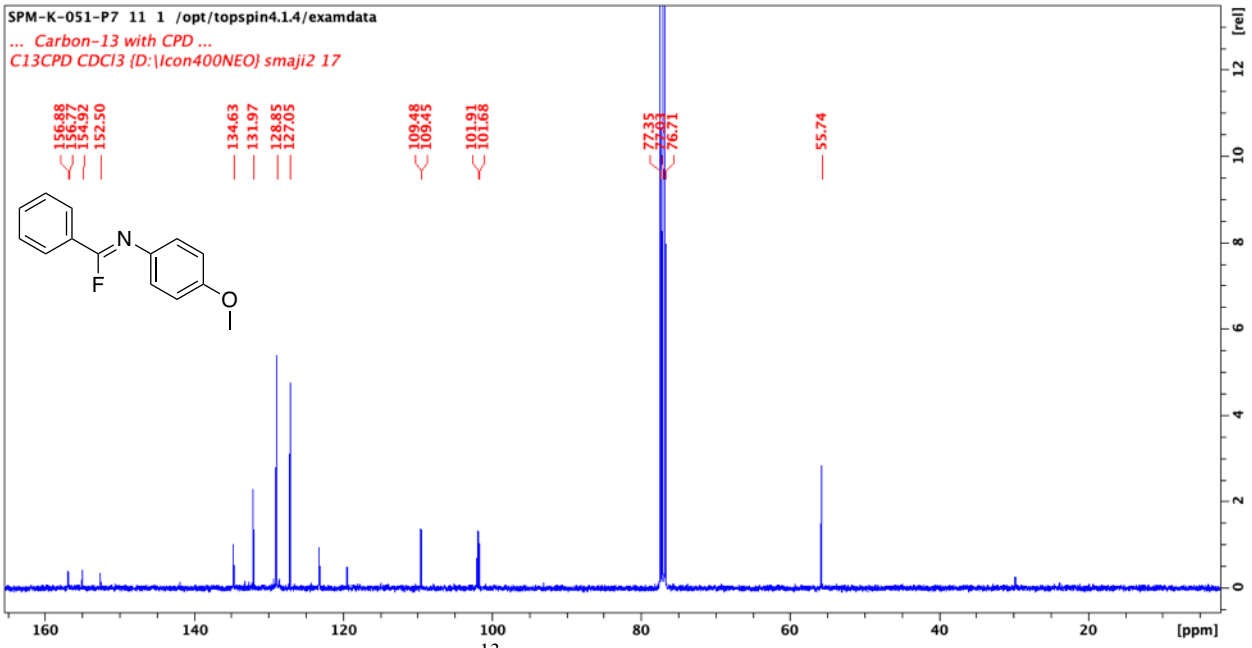
^{13}C NMR in $CDCl_3$ of **14b**



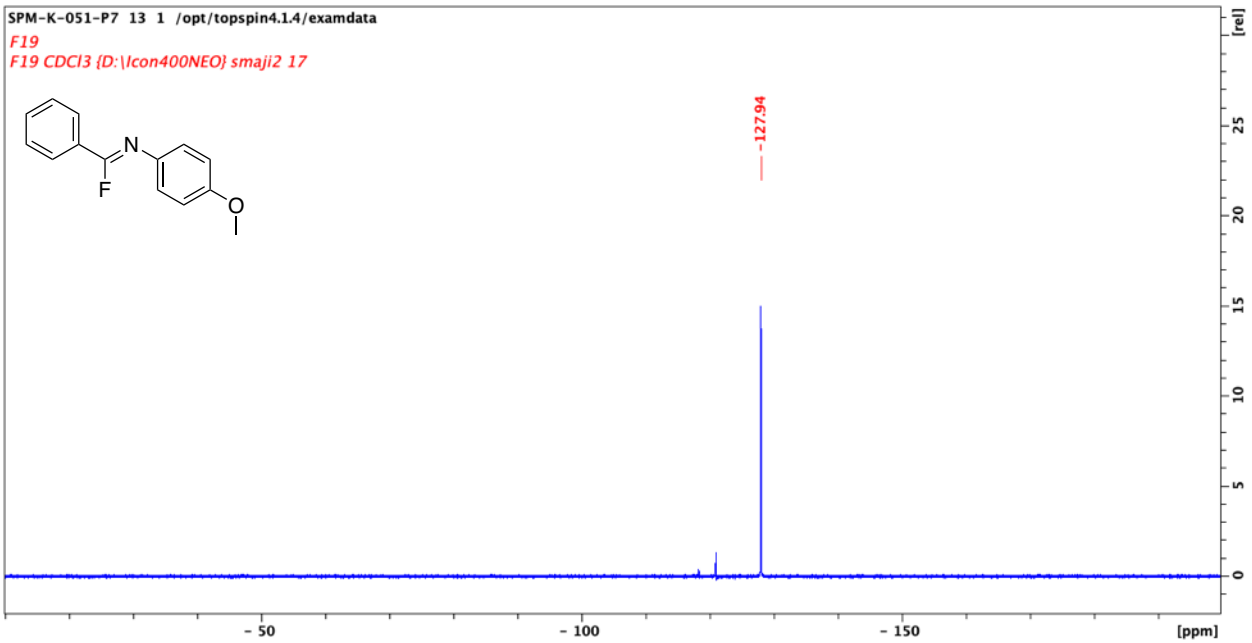
^{19}F NMR in $CDCl_3$ of **14b**



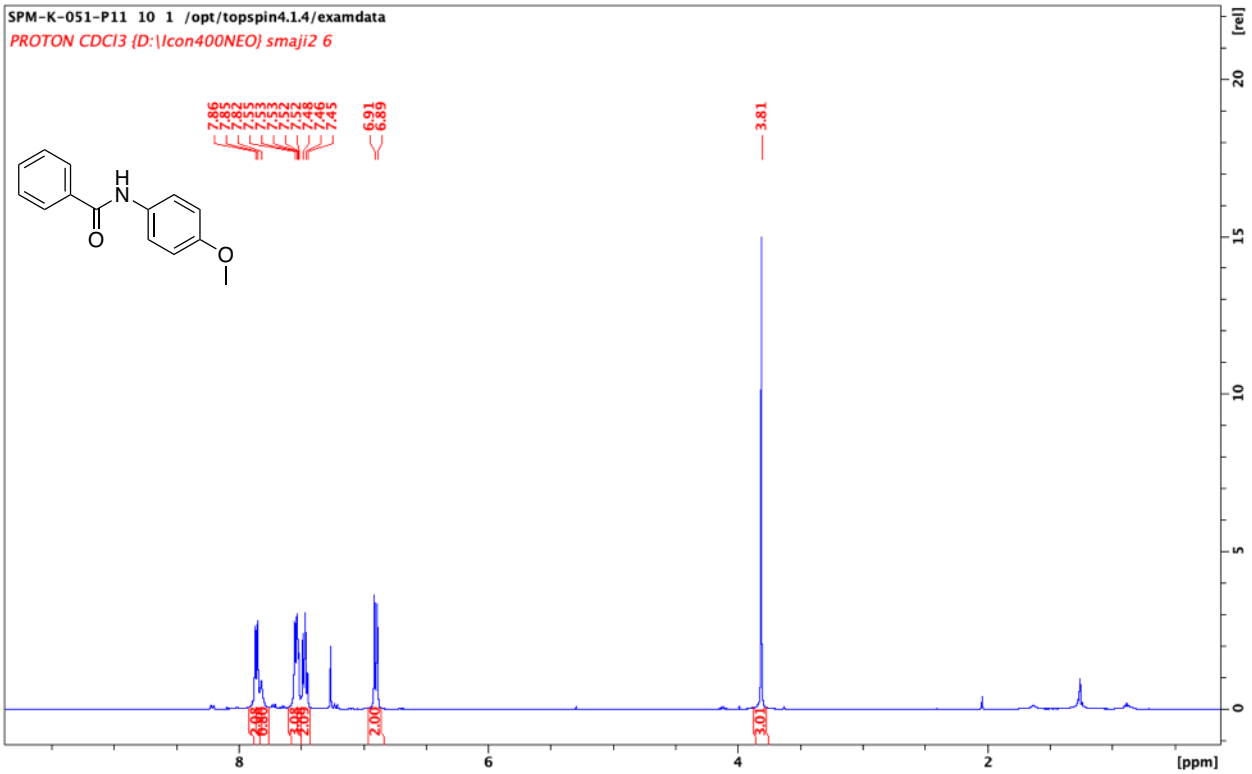
^{1}H NMR in $CDCl_3$ of **16a**



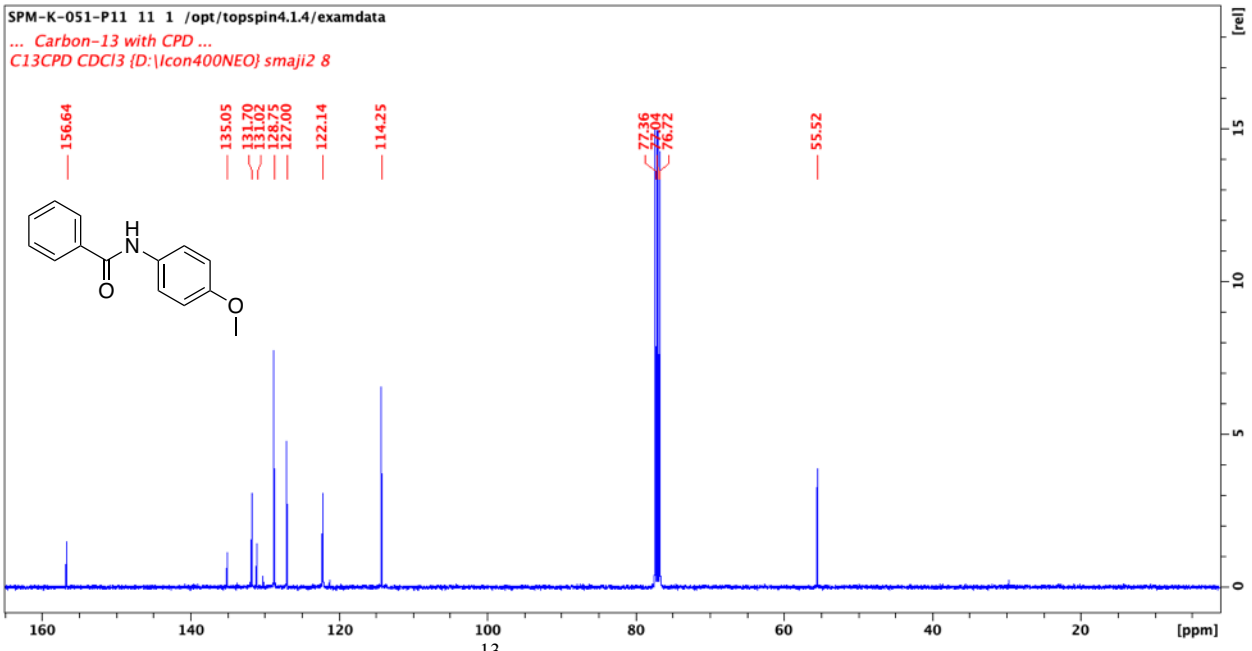
^{13}C NMR in $CDCl_3$ of **16a**



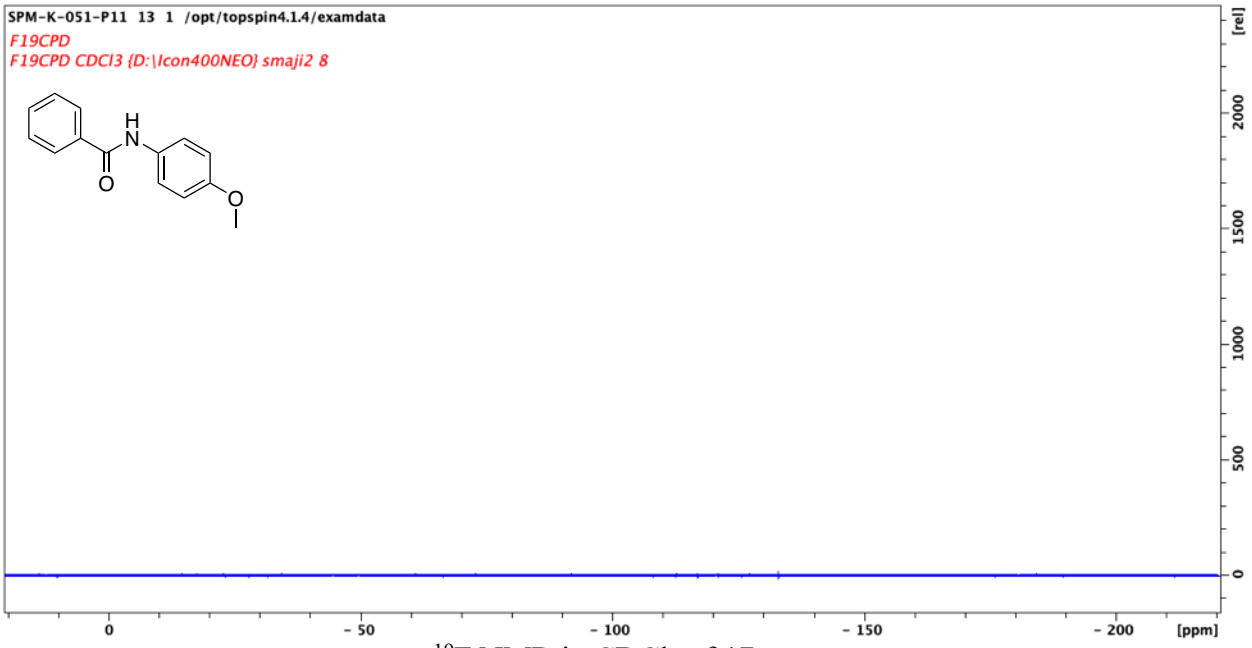
^{19}F NMR in $CDCl_3$ of **16a**



^{1}H NMR in $CDCl_3$ of **17a**



^{13}C NMR in $CDCl_3$ of **17a**



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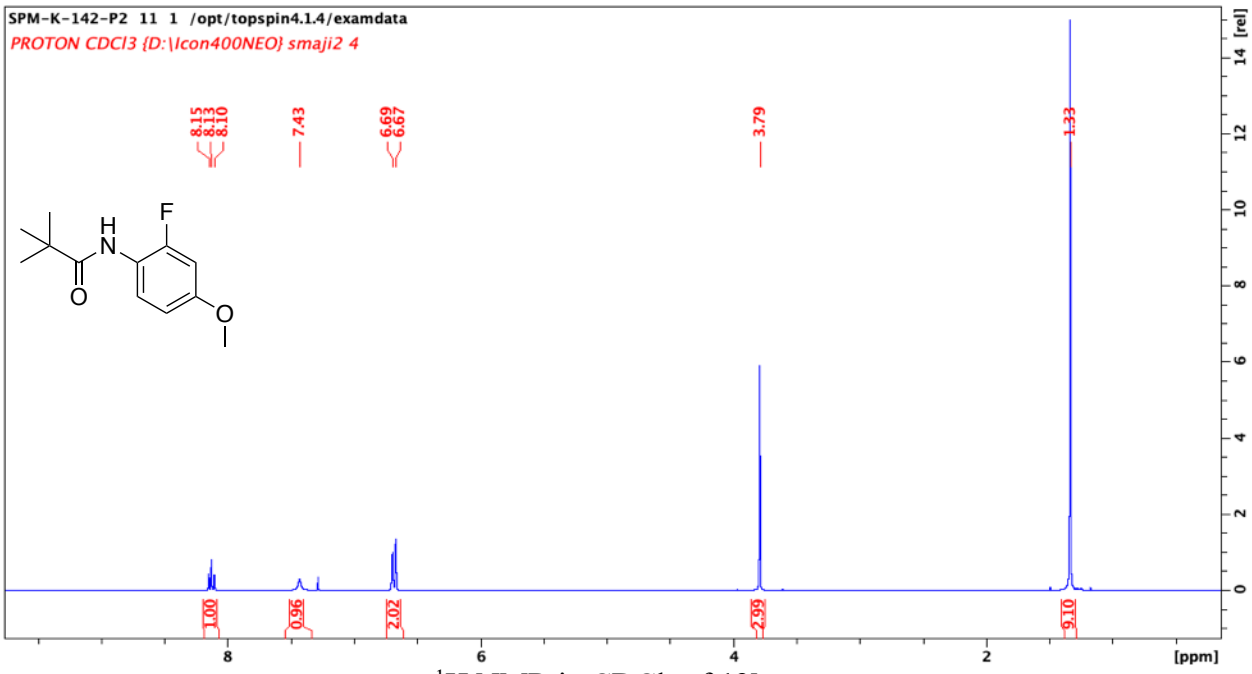
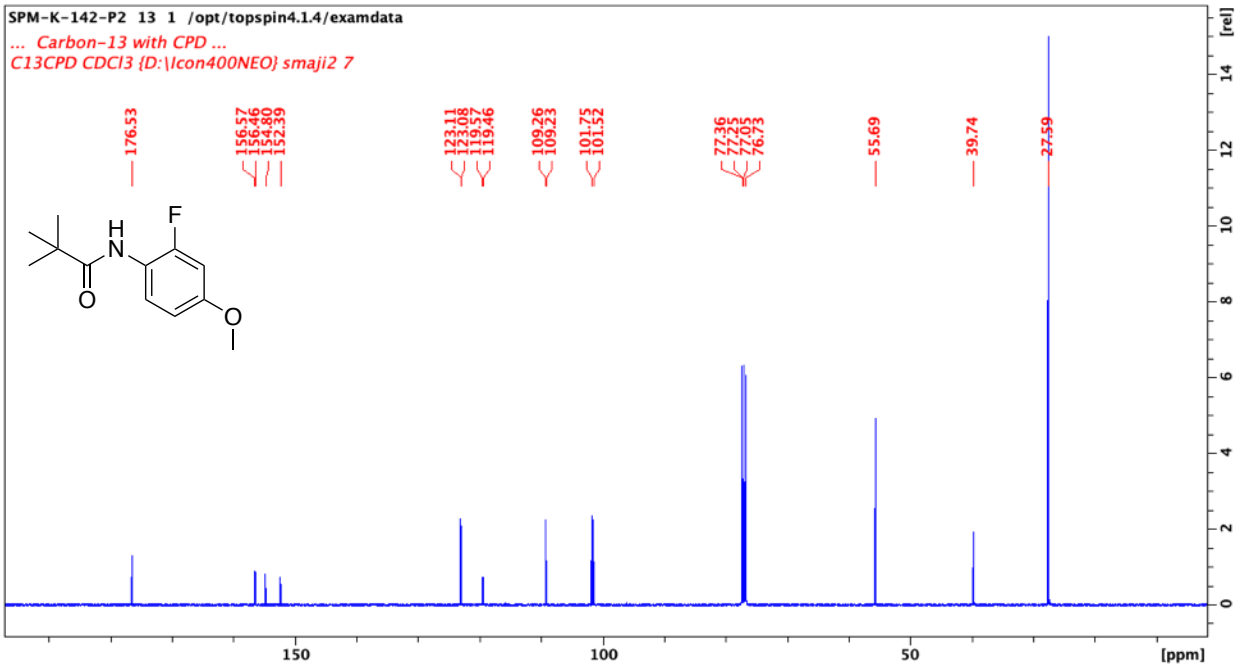
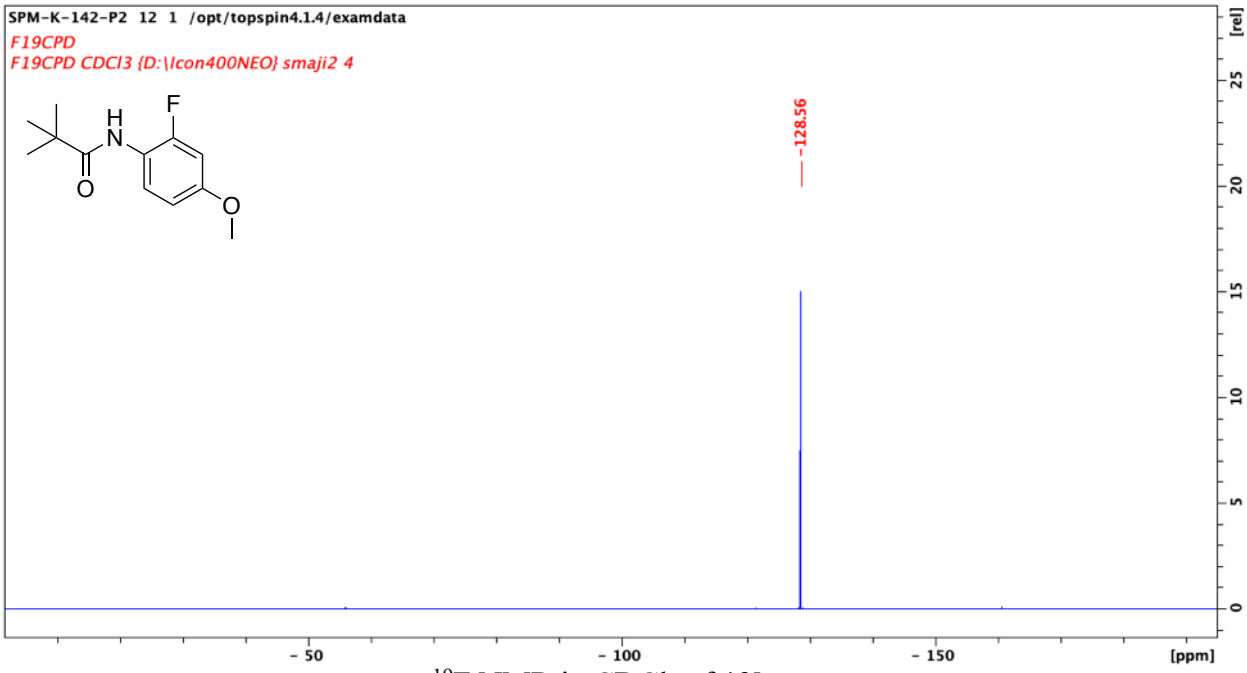


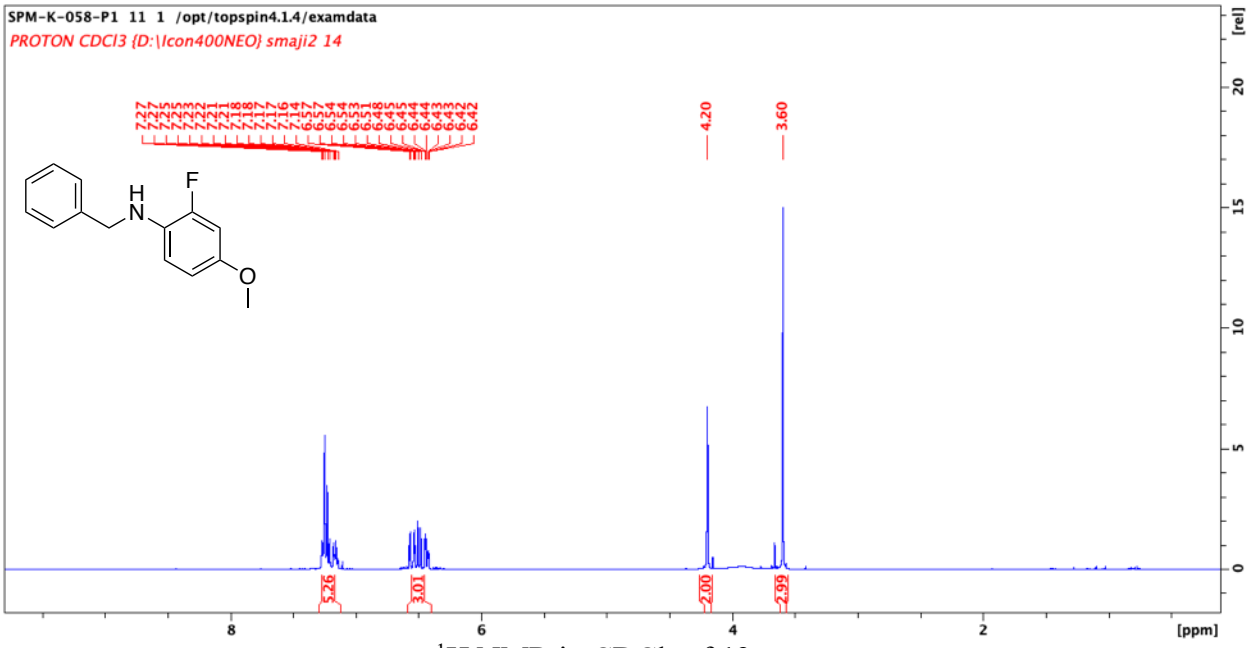
^{1}H NMR in $CDCl_3$ of **19b**



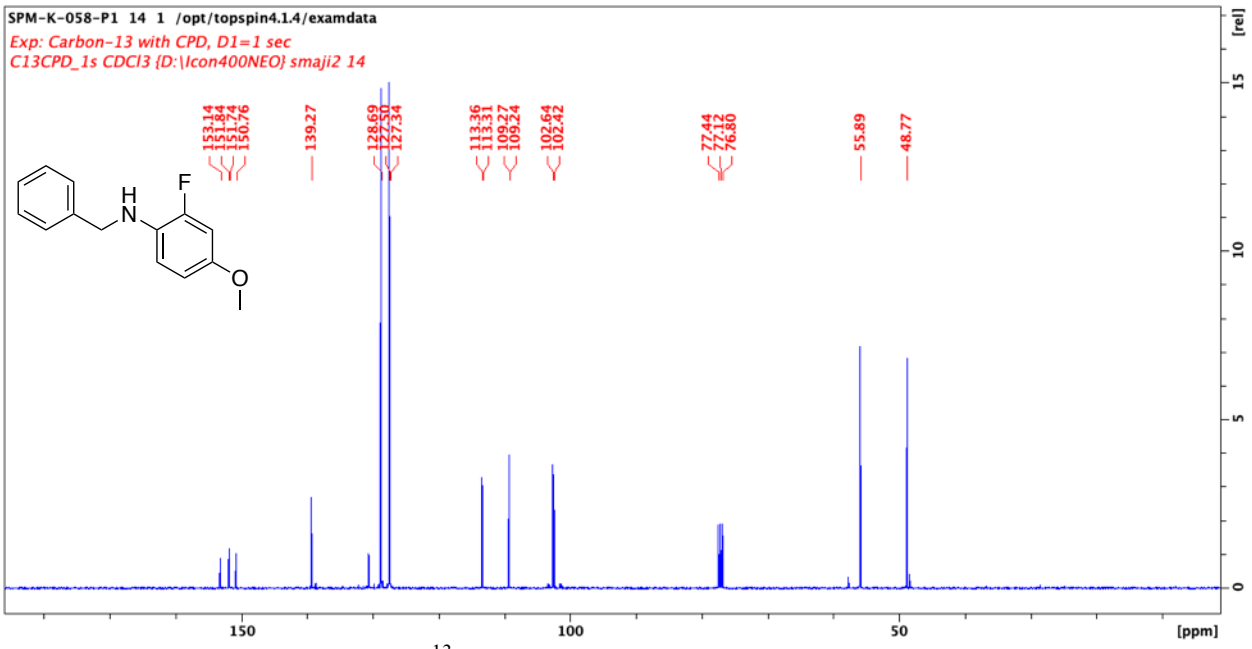
^{13}C NMR in $CDCl_3$ of **19b**



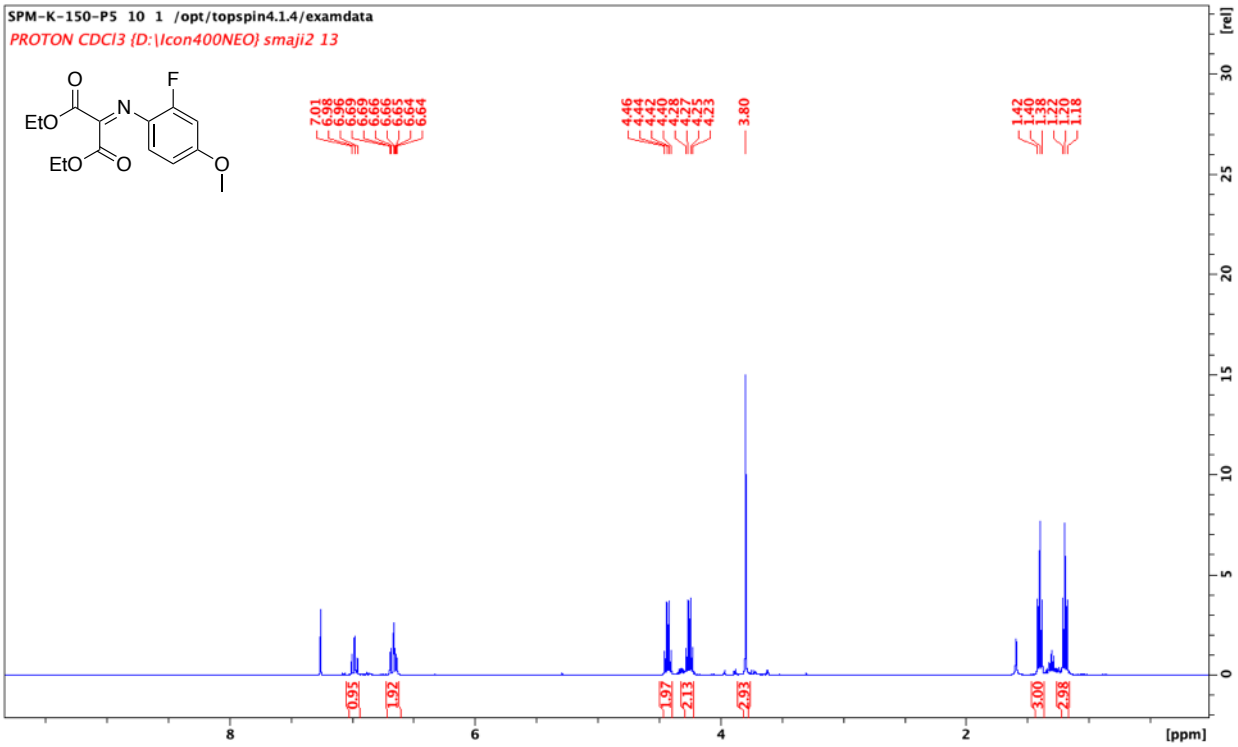
^{19}F NMR in $CDCl_3$ of **19b**



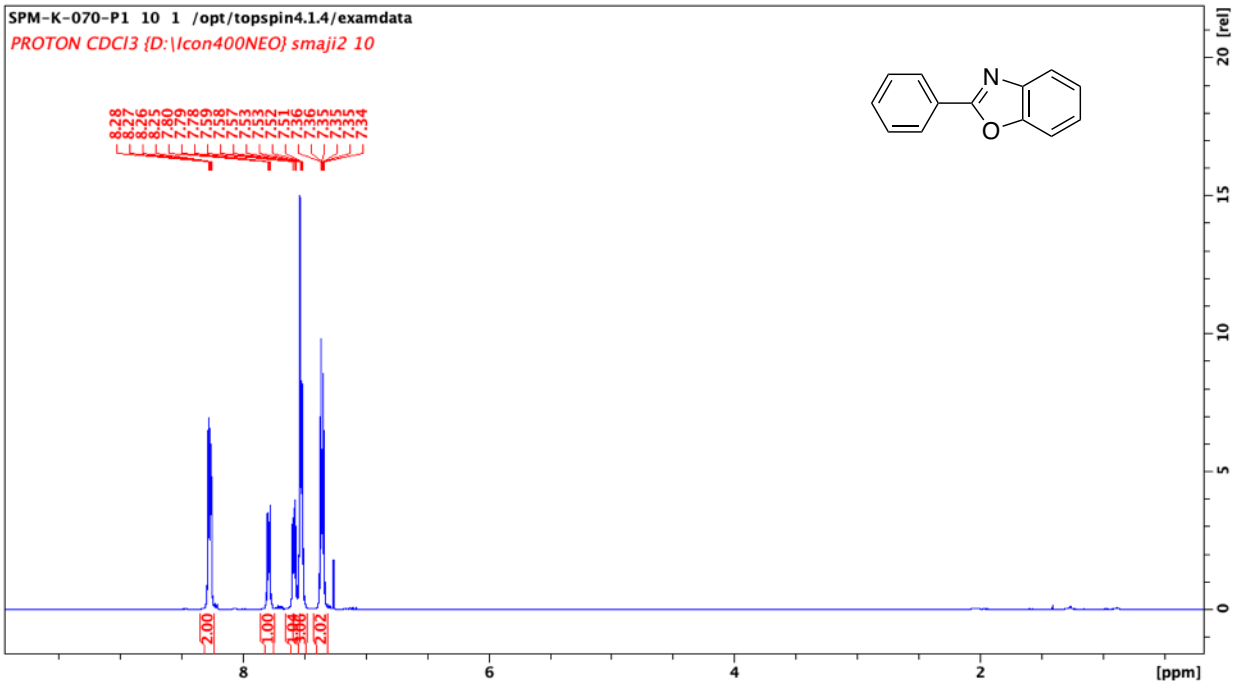
^{1}H NMR in $CDCl_3$ of **19a**



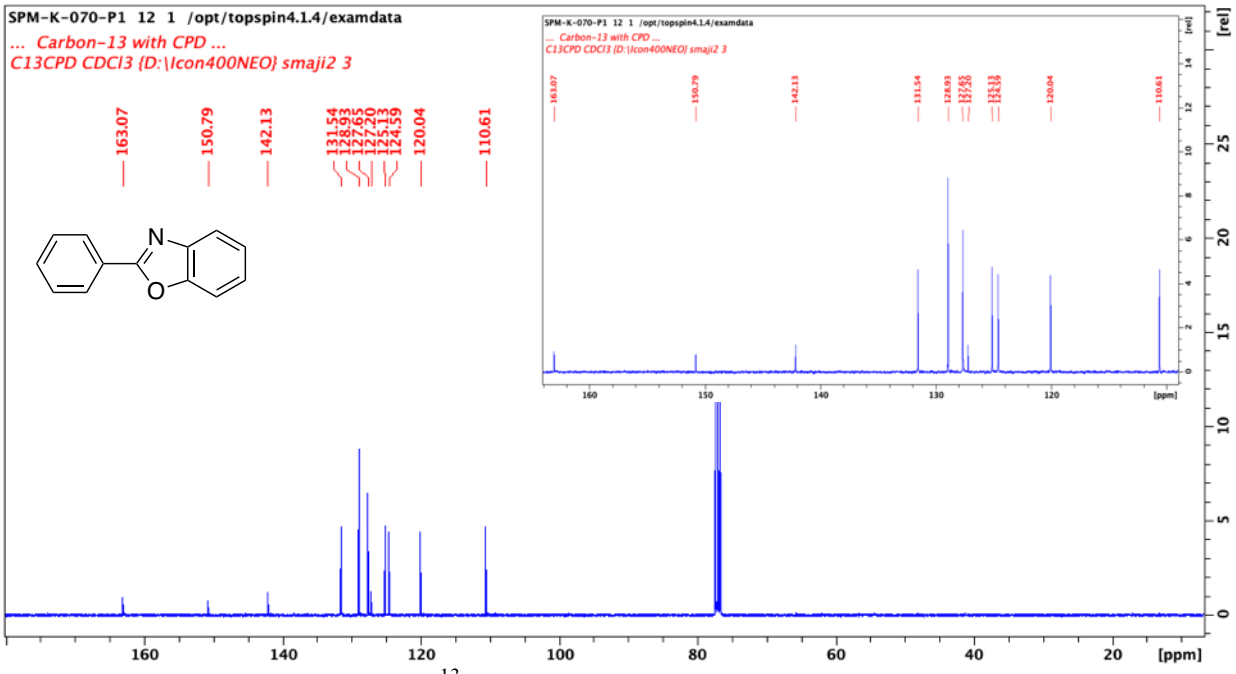
^{13}C NMR in $CDCl_3$ of **19a**



^{1}H NMR in $CDCl_3$ of **21**



^{1}H NMR in $CDCl_3$ of **23**



^{13}C NMR in $CDCl_3$ of **23**

Computational Methods

All the calculations discussed in the manuscript and ESI were conducted using the full quantum mechanical density functional theory (DFT) approach with the Gaussian 16[1] package employing the B3LYP[2] and M06-2X[3] functional. The def2-TZVP[4,5] basis set has been employed for finding energy minima structures and transition state calculations. Solvent corrections were incorporated with full optimization calculations using the polarizable continuum model (PCM),[6,7] with acetonitrile ($\varepsilon = 37.5$) as the solvent. Harmonic frequency calculations were performed to validate stationary points as local minima or transition state structures. All starting geometries and intermediates were verified as true minima, and all the transition structures were characterized by one imaginary frequency. An ultrafine grid was employed to reduce the errors associated with low frequency modes in computing thermal corrections and kinetic isotope effects. The values reported are ΔG values, with zeropoint energy corrections, internal energy, and entropic contributions included at the 298.15K considering the experimental reaction temperature. The Gibbs free energies were further corrected using Grimme's quasi-rigid rotor harmonic oscillator approximation[8] approach with 100 cm^{-1} frequency cut-offs at 298.15K. The perl code used for computing the free energy corrections is reported at the end of the ESI. Intermediates along the reaction coordinate were located by performing a quick reaction coordinate analysis (QRC) from the respective transition structures. ISOEFF code developed by Paneth and coworkers[9-10] was used to compute the KIEs. We have used the experimental temperature (298.15 K) and frequency scale factor (0.963) corresponding to our DFT level of theory (B3LYP/def2-TZVP) for the KIE predictions. Further, single point energies were computed at the TPSS[11]/def2-TZVP, wB97X-D[12]/def2-QZVP and M062X/6-311+g(d,p)[13]/SDD[14](for silver atom) level of theory. Molecular graphics were generated using CYLView package.[15]

Mechanistic Investigation of 2-Fluorination of Pyridine

1. Original Hartwig-Fier model

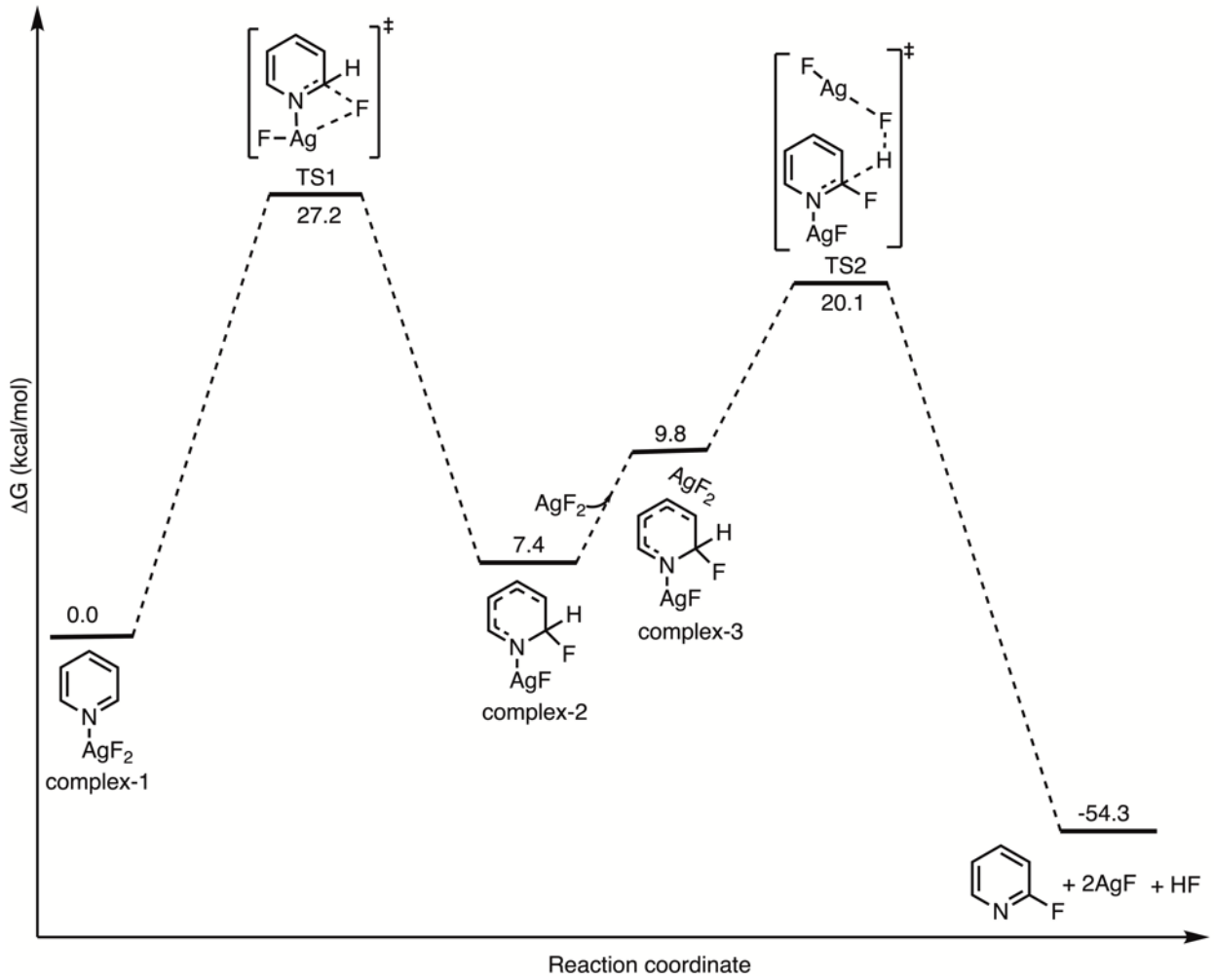
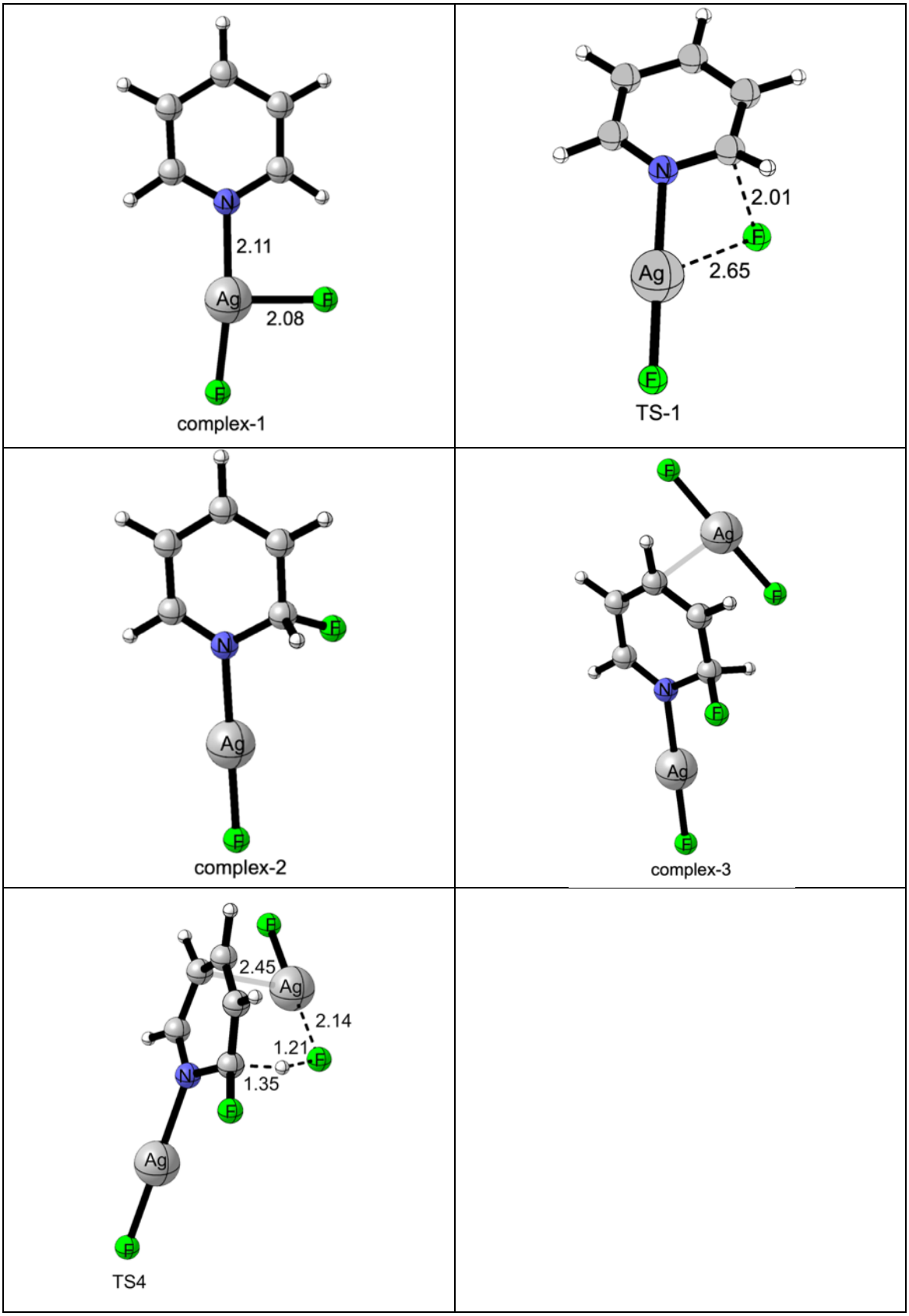


Figure S1. Free energy profile for the formation of fluoropyridine at the 2-position *via* nucleophilic attack followed by rearomatization involving hydrogen atom transfer (HAT), calculated at the B3LYP/def2-TZVP/PCM (acetonitrile) level of theory.

Computational prediction of k_H/k_D at the B3LYP/def2-TZVP/PCM(acetonitrile) level of theory.

Geometry	Frequency	Corrected Frequency	KIE	Wigner Correction	Wigner Corrected KIE
TS1	-519.1391	-511.8372	1.090	1.0057	1.096
TS2	-643.8568	-525.6501	4.127	1.1031	4.553

CLYview generated molecular structures for the important intermediates and transitions states for the energy profile in Figure S1.



3. Fluorination of pyridine involving two molecules of silver fluorides (AgF_2) as coordinating/resting state complex.

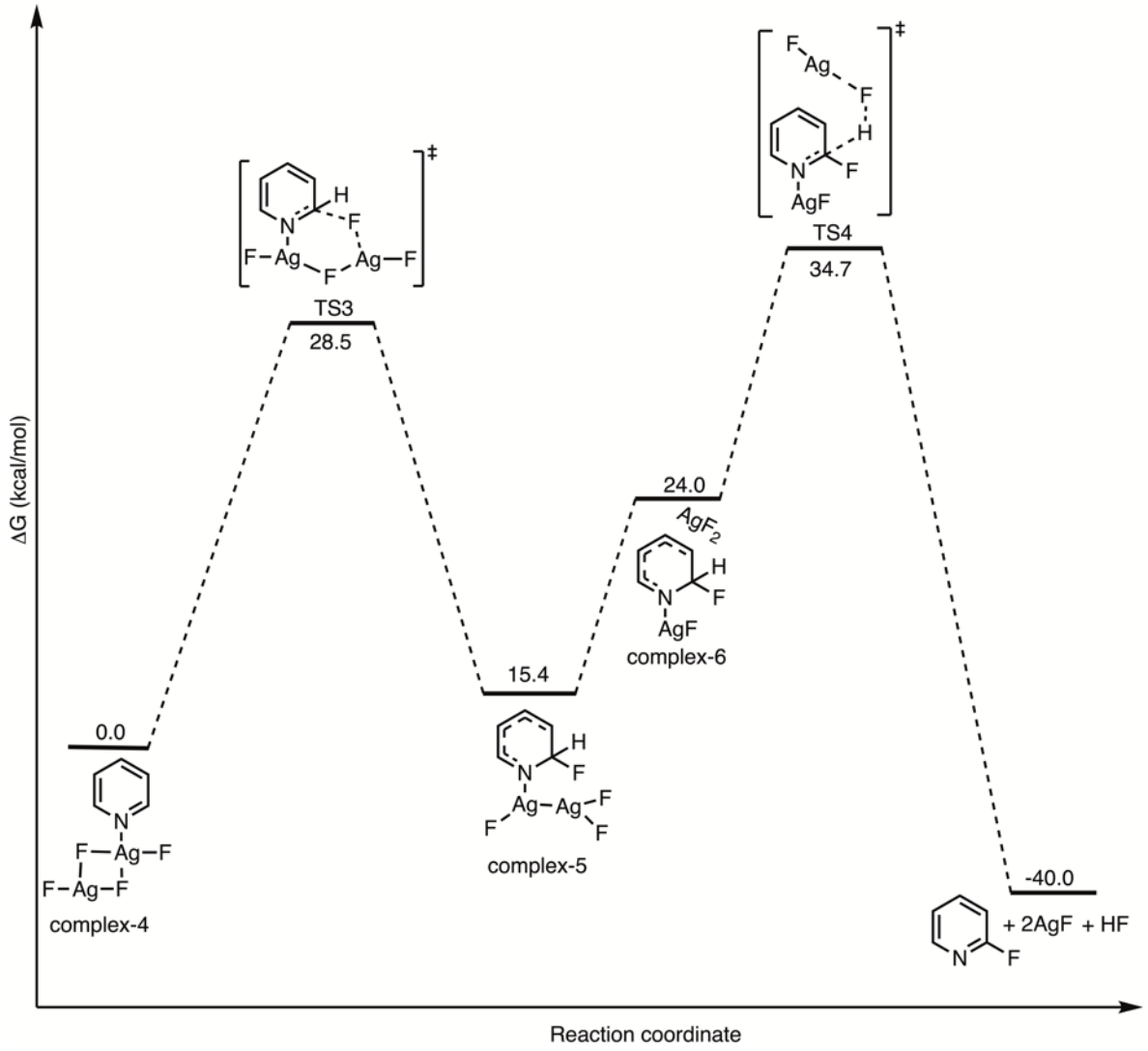
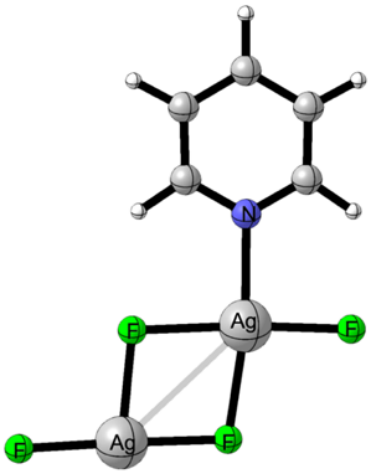


Figure S3. Free energy profile for the formation of fluoropyridine at the 2-position *via* nucleophilic attack followed by rearomatization involving hydrogen atom transfer (HAT), calculated at the B3LYP/def2-TZVP/PCM (acetonitrile) level of theory.

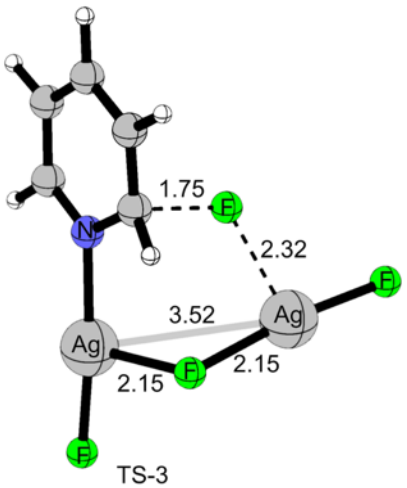
Computational prediction of k_H/k_D at the B3LYP/def2-TZVP/PCM(acetonitrile) level of theory.

Geometry	Frequency	Corrected Frequency	KIE	Wigner Correction	Wigner Corrected KIE
TS3	-564.7563	-562.7016	0.805621	1.0017	0.807
TS4	-643.8568	-525.6501	4.127	1.1031	4.553

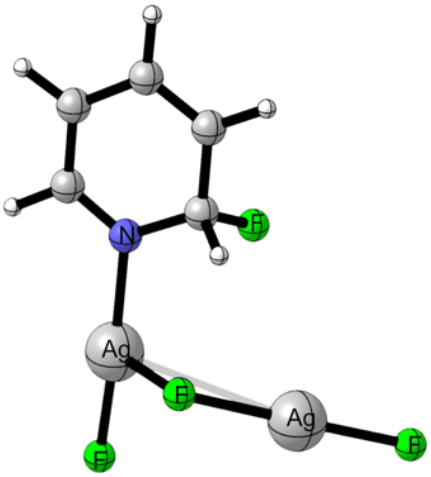
CLYview generated molecular structures for the important intermediates and transitions states for the energy profile in Figure S3.



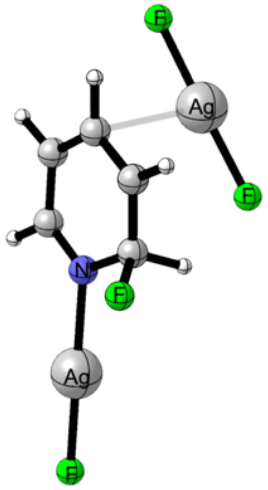
complex-4



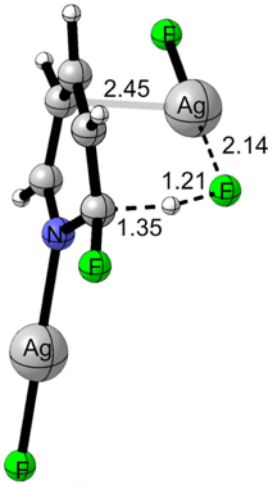
TS-3



complex-5



complex-6



TS4

5. Fluorination of pyridine involving one silver fluoride (AgF_2) molecule as coordinating complex.

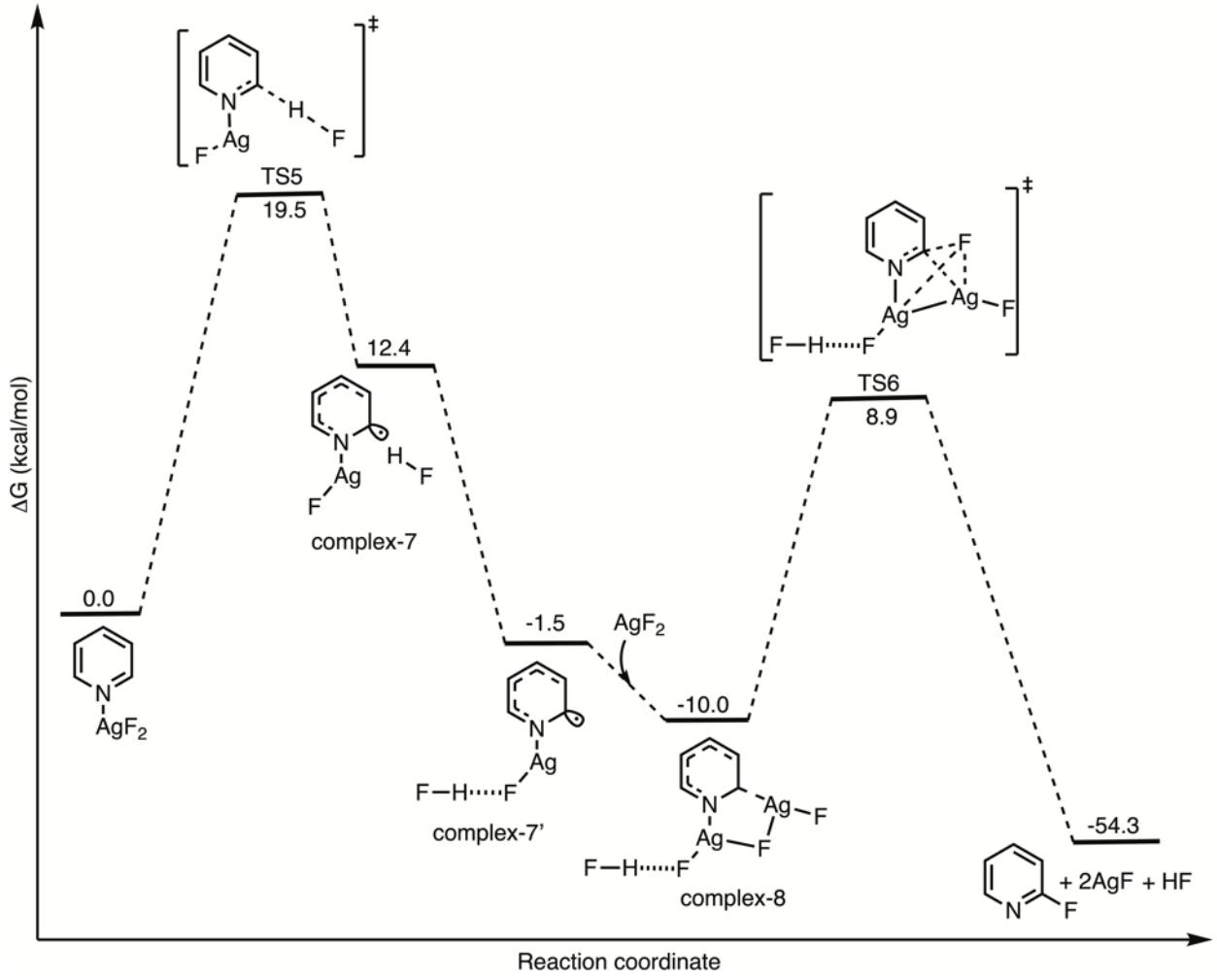
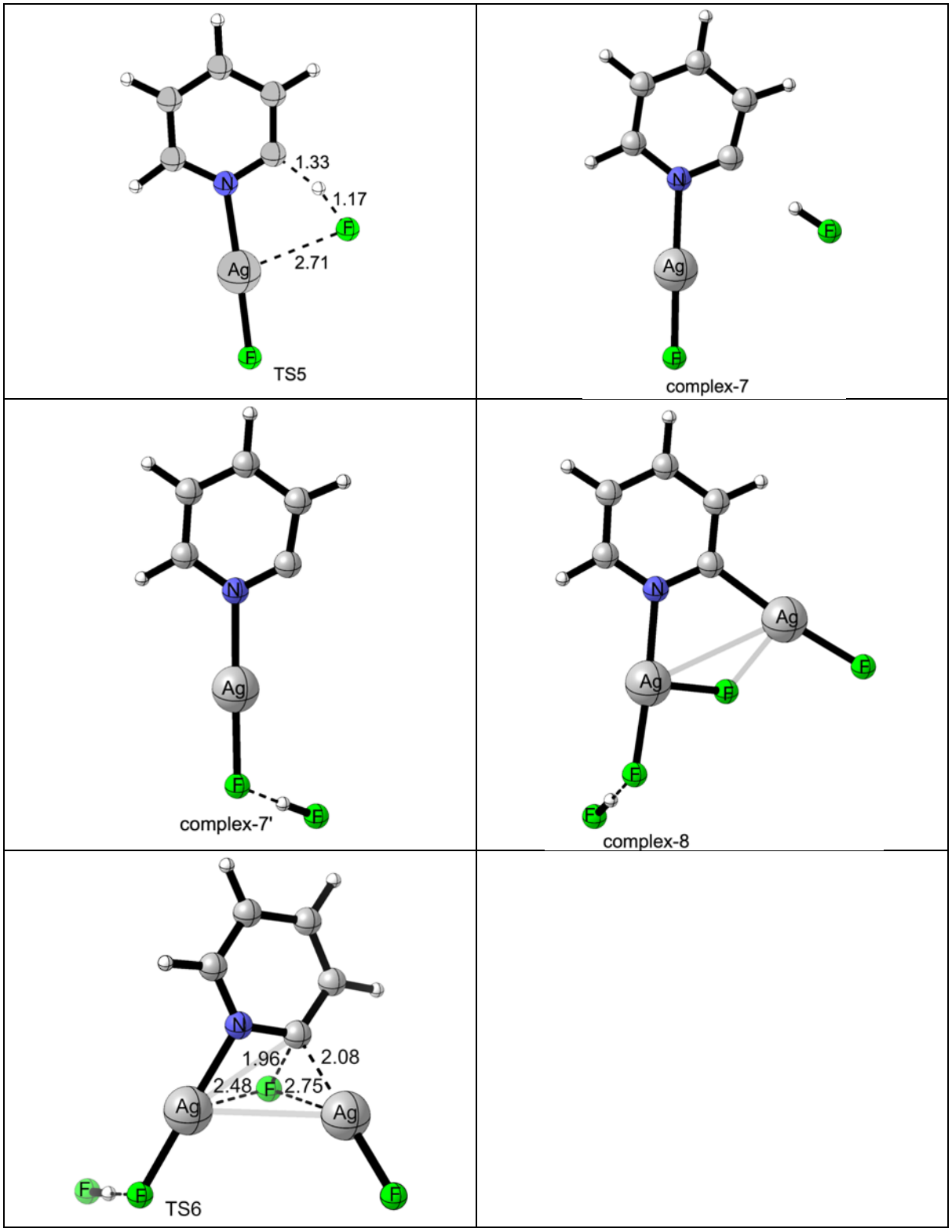


Figure S5. Free energy profile for the formation of fluoropyridine at the 2-position *via* C-H activation followed by reductive elimination, calculated at the B3LYP/def2-TZVP/PCM (acetonitrile) level of theory.

Computational prediction of k_H/k_D at the B3LYP/def2-TZVP/PCM(acetonitrile) level of theory.

Geometry	Frequency	Corrected Frequency	KIE	Wigner Correction	Wigner Corrected KIE
TS5	-1510.5171	-1109.7132	5.48616	1.4575	7.996
TS6	-311.3114	-309.3841	1.579	1.0010	1.581

CLYview generated molecular structures for the important intermediates and transitions states for the energy profile in Figure S5.



6. Fluorination of pyridine involving two silver fluorides (AgF_2) molecules as coordinating complex initiated by C-H activation.

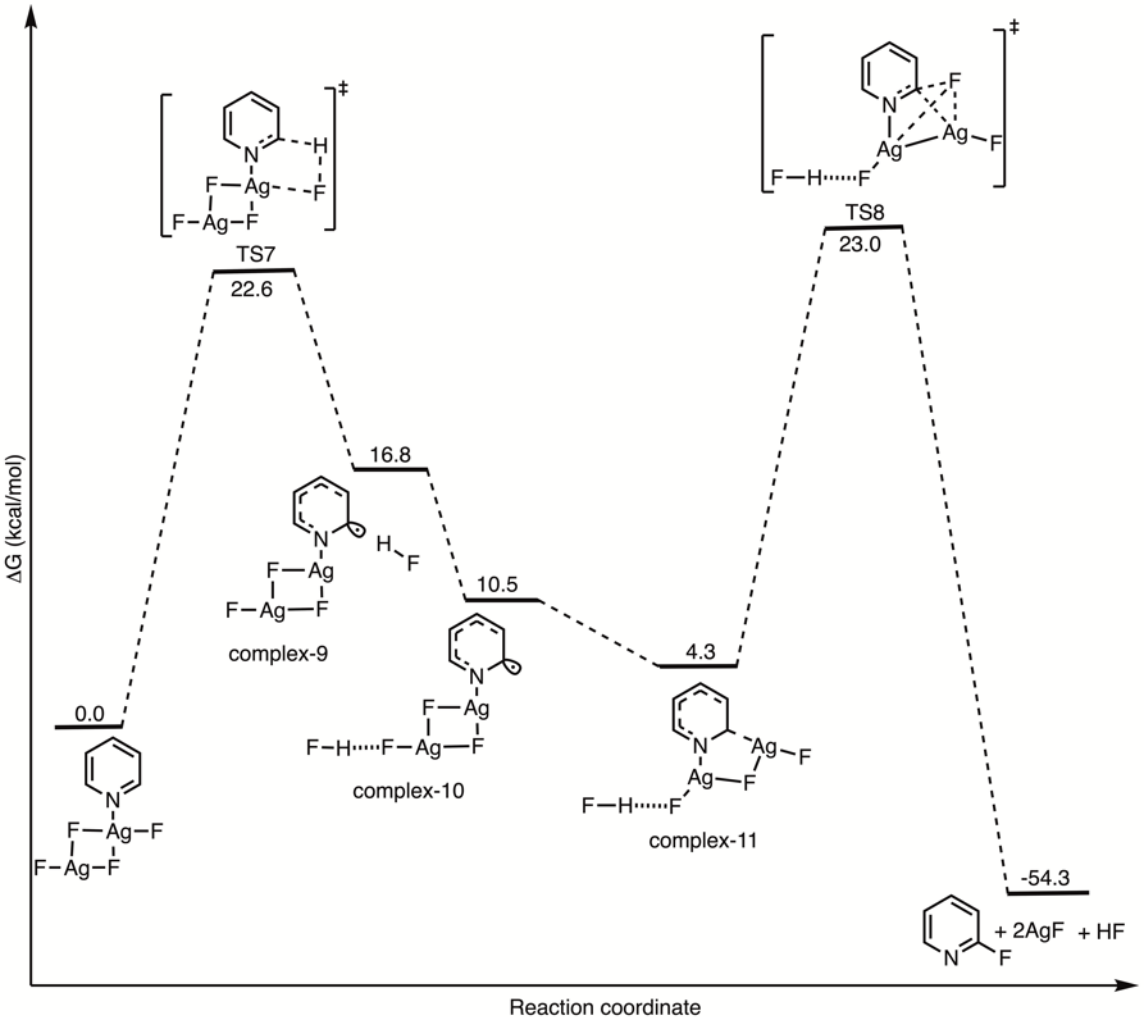


Figure S6. Free energy profile for the formation of fluoropyridine *via* C-H activation followed by bimetallic reductive elimination at the 2-position considering two molecules of AgF_2 as resting state complex, calculated at the B3LYP/def2-TZVP/PCM (acetonitrile) level of theory.

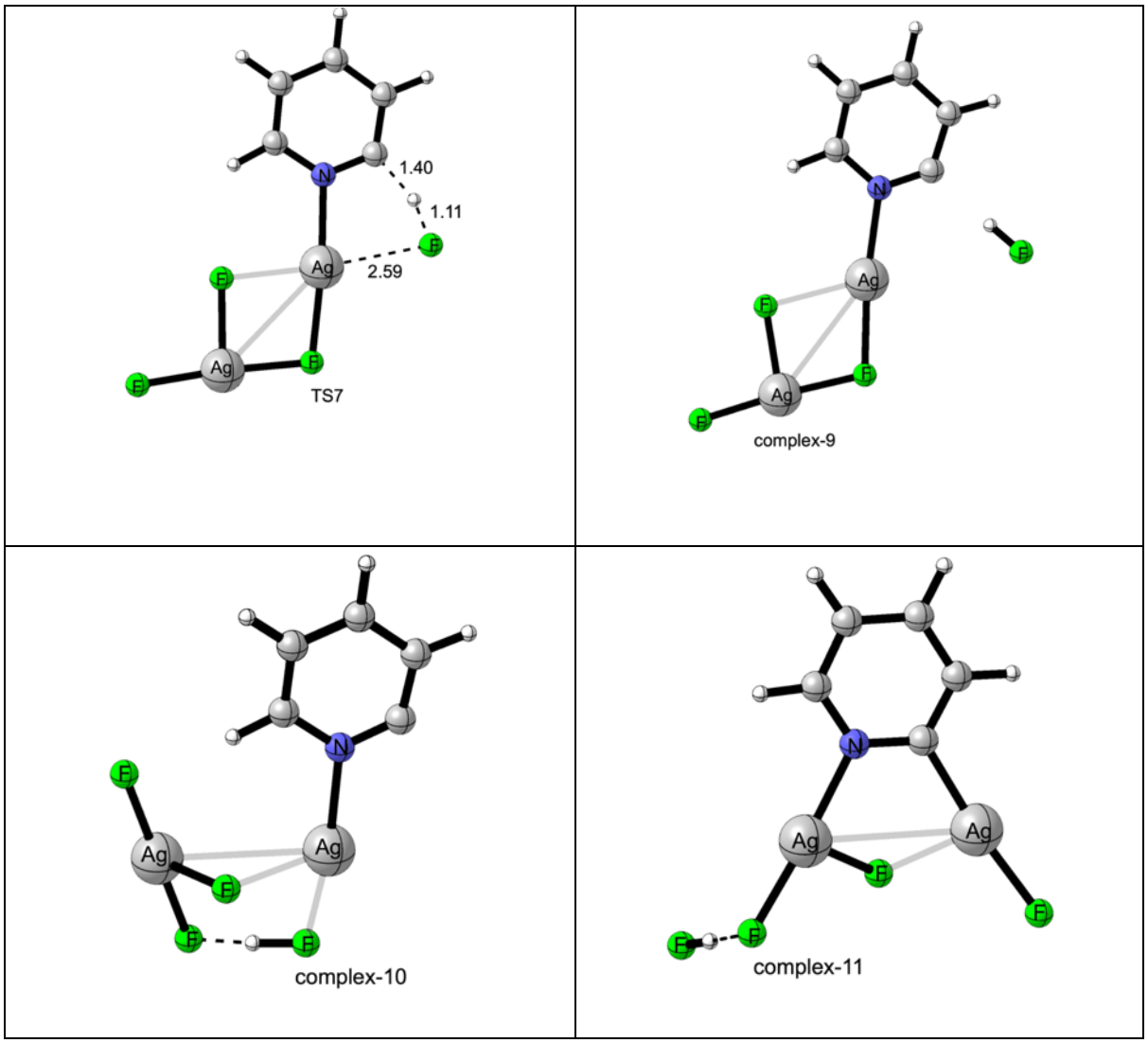
Computational prediction of k_H/k_D at the B3LYP/def2-TZVP/PCM(acetonitrile) level of theory.

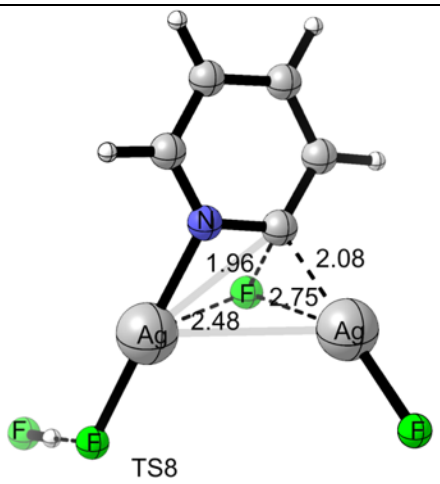
Geometry	Frequency	Corrected Frequency	KIE	Wigner Correction	Wigner Corrected KIE
TS7	-1279.4702	-1250.6427	6.1212	1.0278	6.291
TS8	-311.3114	-309.3841	1.579	1.0010	1.581

Weighted prediction of k_H/k_D at the B3LYP/def2-TZVP/PCM(acetonitrile) level of theory.

Geometry	Relative Free Energy	Population %	Energy weighted KIE
TS7	0.0	33	3.13
TS8	0.4	67	

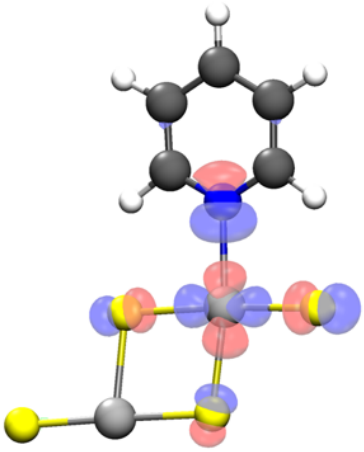
CLYview generated molecular structures for the important intermediates and transitions states for the energy profile in Figure S6.



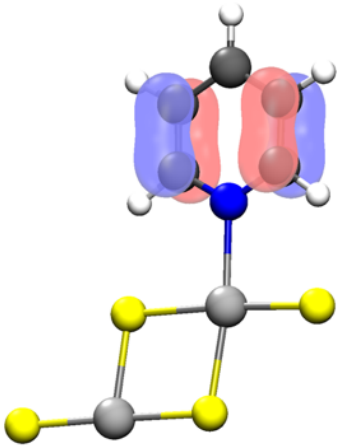


TS8

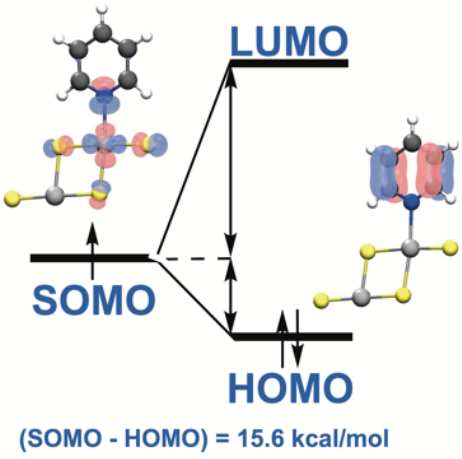
SOMO-HOMO orbitals and their energy gap for pyridine 2AgF2 complex (complex-4) geometry.



SOMO

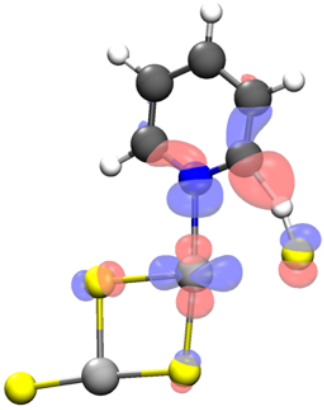


HOMO

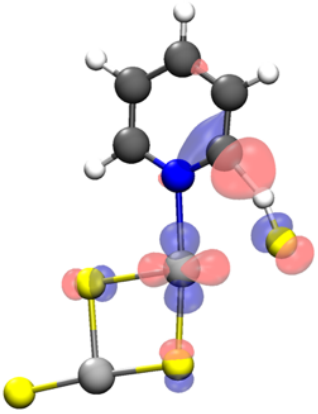


SOMO-HOMO

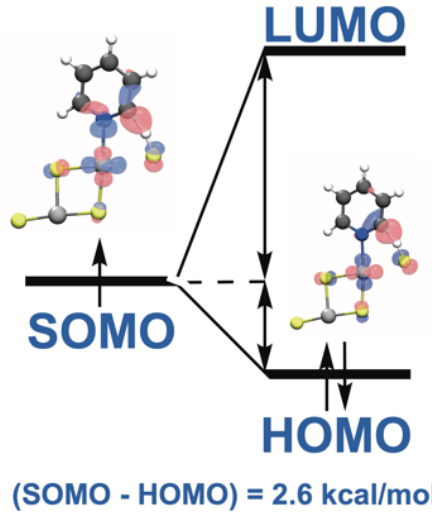
SOMO-HOMO orbitals and their energy gap for the transition state (TS-7) geometry.



SOMO



HOMO



SOMO-HOMO

7. Fluorination of pyridine involving two molecules of silver fluorides (AgF_2) and two molecules of acetonitrile (CH_3CN) coordinating with each silver (Ag) complex.

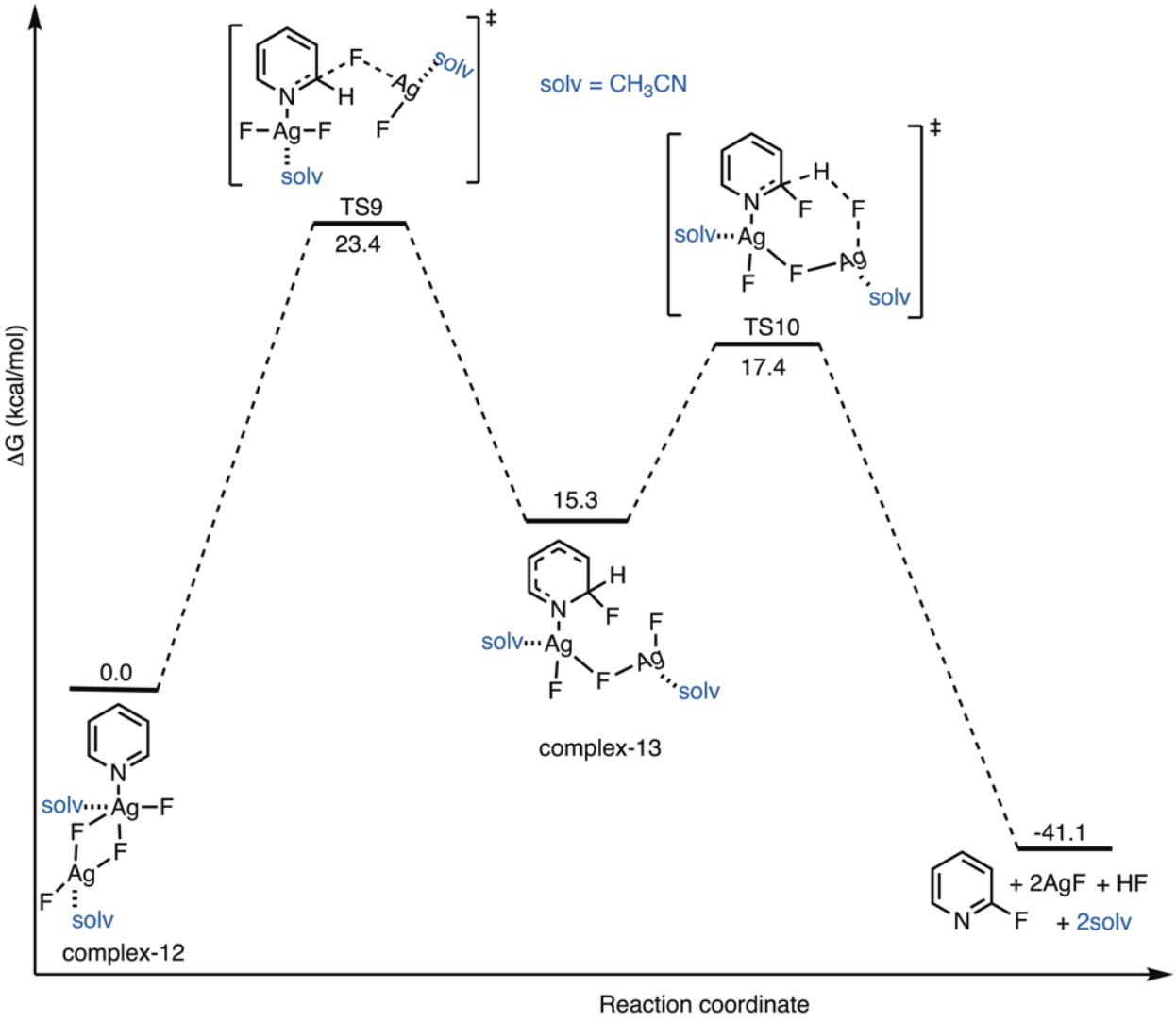
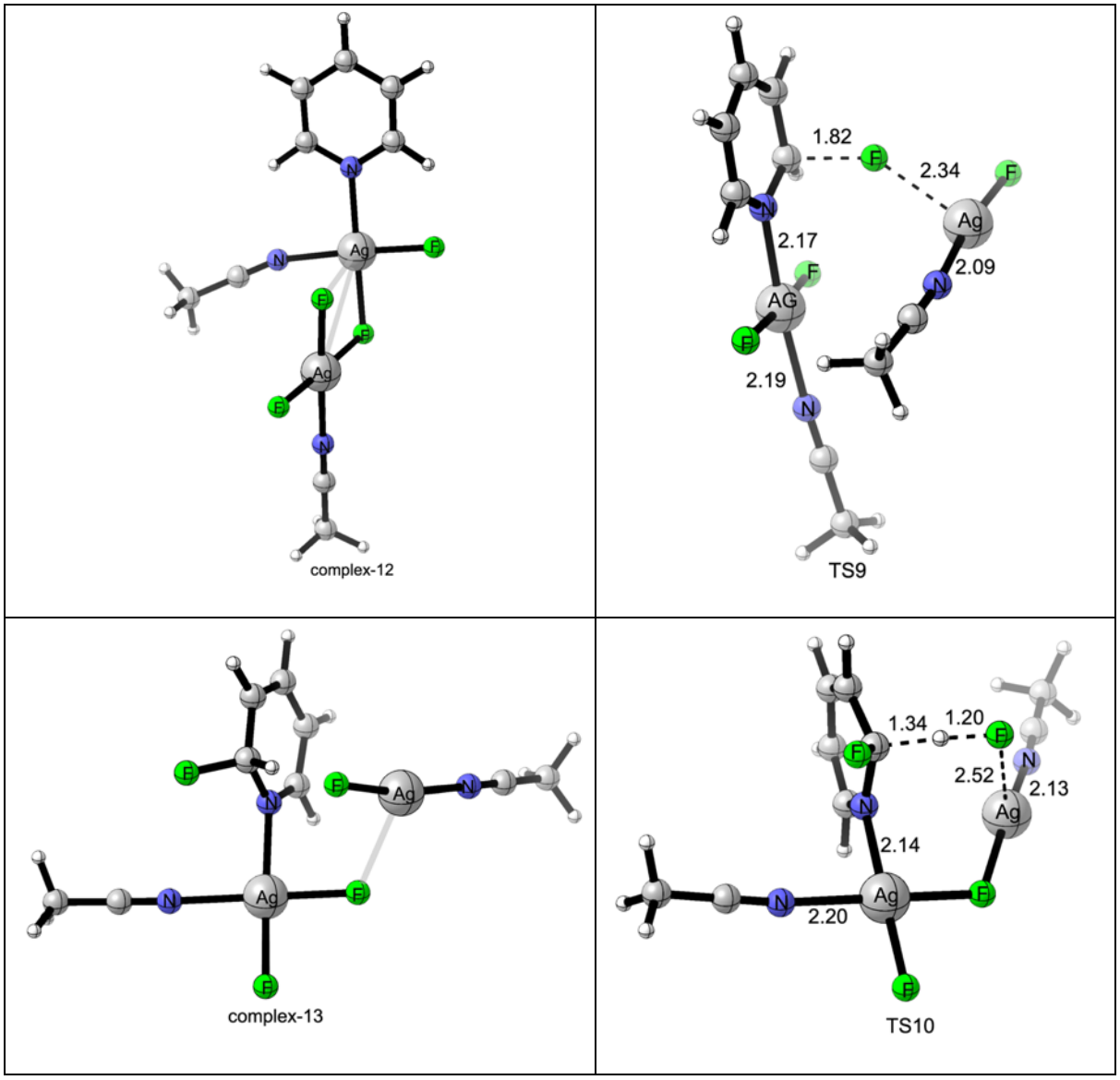


Figure 7. Free energy profile for the formation of fluoropyridine at the 2-position *via* nucleophilic attack followed by rearomatization involving hydrogen atom transfer pathway, calculated at the B3LYP/def2-TZVP/PCM (acetonitrile) level of theory.

Table S18. CLYview generated molecular structures for the important intermediates and transitions states for the energy profile in Figure 7.



8. Fluorination of pyridine involving two molecules of silver fluorides (AgF_2) and two molecules of acetonitrile (CH_3CN) coordinating with each silver (Ag) complex.

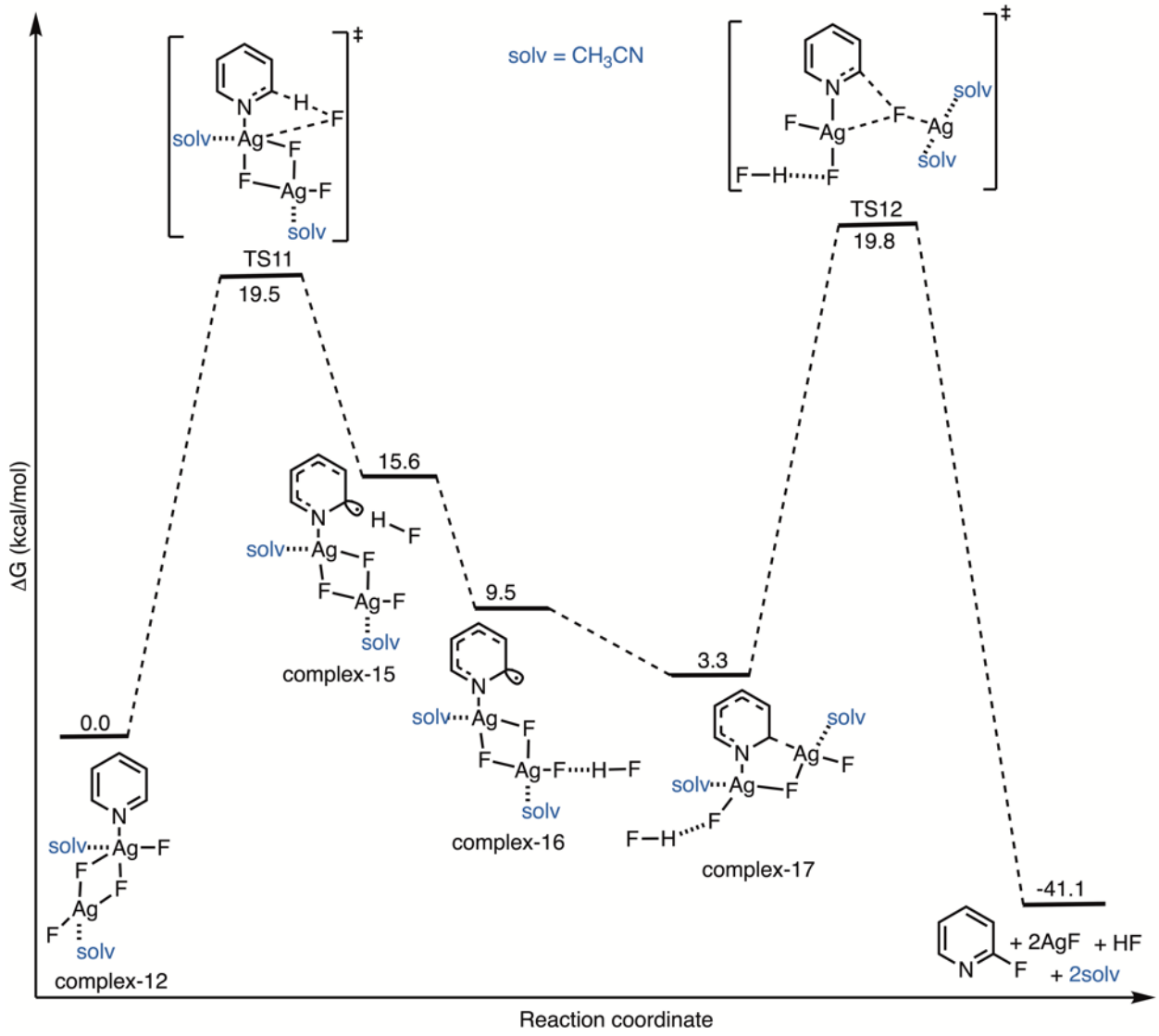


Figure 8. Free energy profile for the formation of fluoropyridine at the 2-position *via* C-H activation followed by reductive elimination, calculated at the B3LYP/def2-TZVP/PCM (acetonitrile) level of theory.

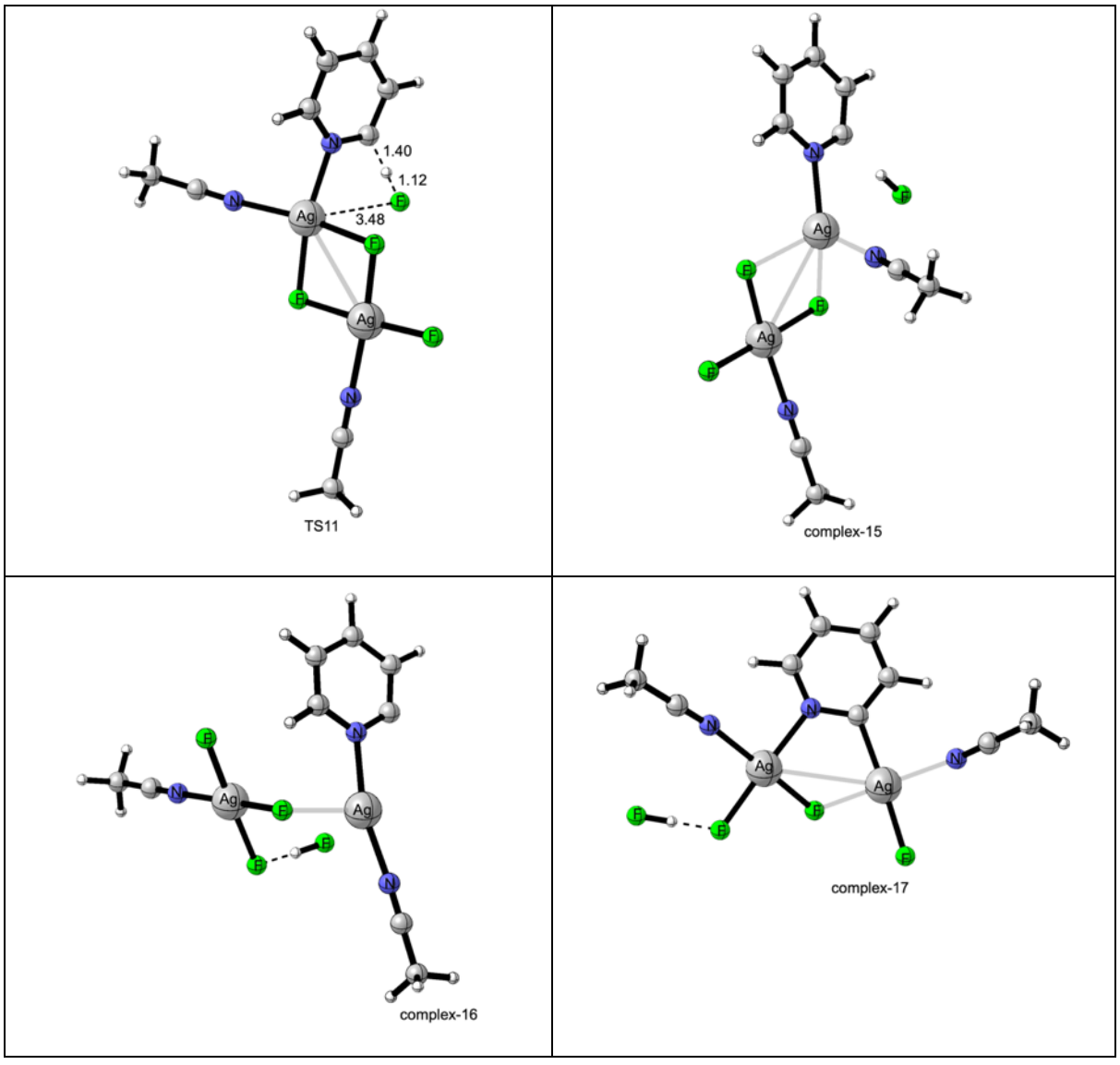
Table S19. Computational prediction of k_H/k_D at the B3LYP/def2-TZVP/PCM(acetonitrile) level of theory.

Geometry	Frequency	Corrected Frequency	KIE	Wigner Correction	Wigner Corrected KIE
TS11	-953.6053	-709.7433	5.219957	1.2587	6.570
TS12	-276.7302	-275.2895	1.475964	1.0007	1.477

Table S20. Weighted prediction of k_H/k_D at the B3LYP/def2-TZVP/PCM(acetonitrile) level of theory.

Geometry	Relative Free Energy	Population %	Energy weighted KIE
TS11	0.0	37	3.36
TS12	0.3	63	

Table S21. CLYview generated molecular structures for the important intermediates and transitions states for the energy profile in Figure 8.



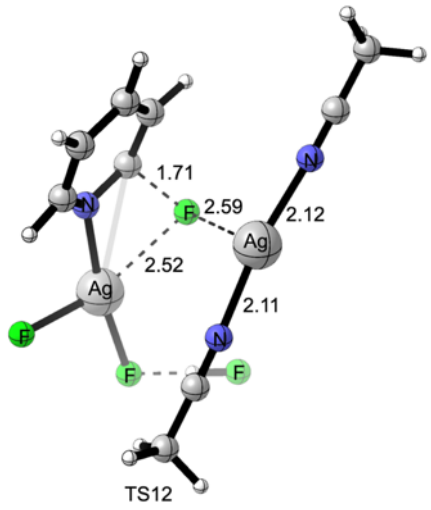
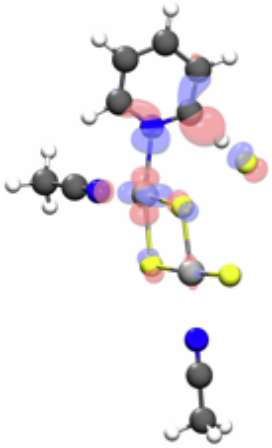
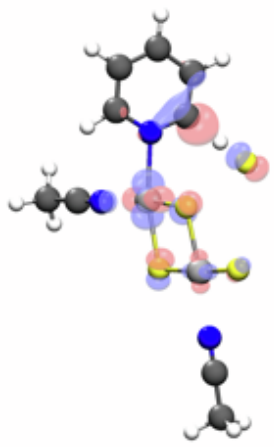


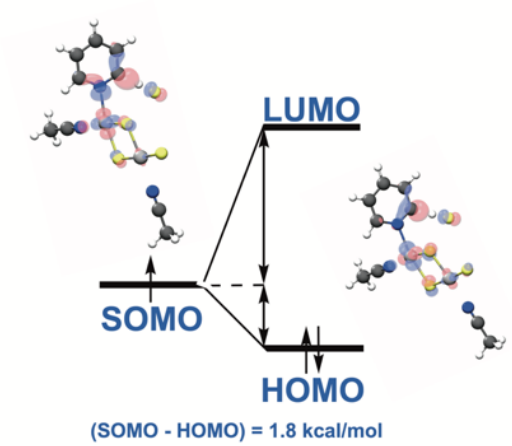
Table S22. SOMO-HOMO orbitals and their energy gap for the C-H activation transition state (TS-11) geometry.



SOMO

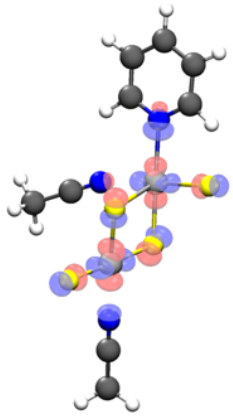
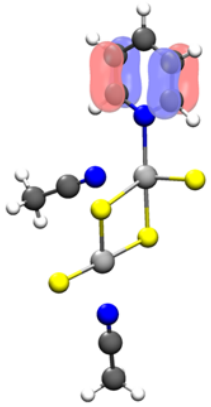


HOMO



SOMO-HOMO

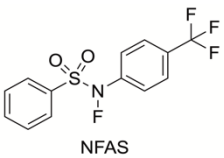
Table S23. SOMO-HOMO orbitals and their energy gap for the pyridine-2AgF_2 complex with involvement of acetonitrile.

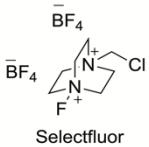
 SOMO	 HOMO

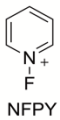
BDE calculations

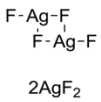
Table S24. Bond dissociation enthalpy computed and compared with experimental values.

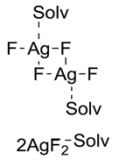
Substrate	BDE at DLPNO(CCSTD)-def2qzvpp (gas phase)	BDE in experimental conditions
F_2	36.0	36.7
CF_3OF	45.1	43.5
AgF_2	57.3	55.2
$2AgF_2$	**35.9**	-
$2AgF_2$---Solv	**37.7**	-
NFAS	52.2	53.0
NFSI	60.1	63.0
Selectfluor	64.2	62.0
XeF_2	58.8	64.0
NFPY	78.0	76.0
CuF_2	78.2	85.6











Calculation of redox potential

We calculated the redox potentials of the AgF_2 monomer and dimer complex with and without solvent(acetonitrile) bound and benchmarked them using only hybrid functionals against experimentally reported values from the literature. We have employed two different levels of theory. Based on the agreement between experiment and theory we identified B3LYP/6-311++G(d,p)LANL2DZ(Ag)//B3LYP/6-31+G(d,p)LANL2DZ(Ag)+PCM(acetonitrile) as the appropriate levels of theory. Further the Nernst equation was used to compute the redox potentials (1) where n is the number of electrons (1 for all the species as the reactions reported here involved single electron transfer), F is the Faraday constant (23.061 kcal/mol-V), E^0_{cell} is the computed redox potential, and $\Delta G^{\#}$ is the free energy difference between the reduced form and the oxidized form of the species. The computed E^0_{cell} was further corrected by subtracting the absolute value for the standard hydrogen electrode (4.281 V) and saturated calomel electrode (0.141 V).

$$\Delta G = -n.\ F.\ E^0_{cell} \qquad (1)$$

2. Reduction potential calculated at the B3LYP/6-311++G(d,p)LANL2DZ(Ag)//B3LYP/6-31+G(d,P)LANL2DZ(Ag)+PCM(acetonitrile) level of theory.

Entries	Experimental Reduction Potential	Calculated Reduction Potential
AgF_2	1.98	1.96
$AgF_2(CH_3CN)$	-	1.70
$2AgF_2$		2.08
$2AgF_2(CH_3CN)_2$	-	1.55

Predicted k_H/k_D for C-sp^3(H) activation TSs in manuscript

Computational prediction of k_H/k_D at the B3LYP/def2-TZVP/PCM(acetonitrile) level of theory at 323.15 K.

Geometry	**Frequency**	**Corrected Frequency**	**KIE**	**Wigner Correction**	**Wigner Corrected KIE**
Toluene_$2AgF_2$_TS (**TS-CH** in manuscript)	-415.7149	-356.8987	3.748	3.922	3.891

Computational prediction of k_H/k_D at the B3LYP/def2-TZVP/PCM(acetonitrile) level of theory at 323.15 K.

Geometry	**Frequency**	**Corrected Frequency**	**KIE**	**Wigner Correction**	**Wigner Corrected KIE**
Toluene_$2AgF_2(CH_3CN)_2$_TS (**TS-CH$_{CH3CN}$** in manuscript)	-773.6665	-627.717	4.009	5.107	4.471

QRRHO Perl code

Perl code used for computing Grimme's quasi rigid rotor harmonic oscillator corrected free energy corrections:

```
#!/usr/bin/perl -w

use strict;
use Math::Trig;

#Based on Gaussian Thermochemistry white paper, calculate: E + ZPVE, H (0K), H(Temp), G(Temp) (http://www.gaussian.com/g_whitepap/thermo/thermo.pdf)
#Usage: thermo.pl [log file] [temp in Kelvin]
#Default to T = 298.15
#Originally written by Paul Cheong.
#Modified version: In addition to "normal" analysis, also prints results using Grimme's rotor/harmonic oscillator interpolation approach
#See Grimme, S. Chem. Eur. J. 2012, 18, 9955
#Now reading vibrational frequencies and rotational constants to avoid truncation problem that arose when I was using Vibrational and Rotational Temps directly

use strict;
my $T = 298.15;
my $v0 = 100; #cutoff for quasi-RRHO (in cm-1)
my $P = 1*101317; #1 ATM
if($ARGV[1]) {
	$T = $ARGV[1];
}

my $infile;
if($ARGV[0]) {
	$infile = $ARGV[0];
} else {
	die "Must at least supply a Gaussian log file";
}

open INFILE, $infile or die "Can't open $infile";

#CONSTANTS
my $h = 6.62606957E-34; #J.s
my $kb = 1.380662E-23; #J/K
my $c = 29979245800; #cm/s

my $R = 1.987204; #kcal/mol
my $cm2kcal = 0.0028591459;
my $cm2hartree = 4.5563352812122E-06;
my $kcal2hartree = 0.0015936;
my $amu2kg = 1.66053886E-27;
```

```
my $mass; #molecular mass
my $mult; #Spin multiplicity
my @rottemps; #rotational temperatures (Kelvin)
my @vibtemps; #vibrational temperatures (Kelvin)
my @Truhlar_vibtemps;   #vibrational temperatures (Kelvin) with frequencies below $v0
shifted to $v0
my @vibfreqs; #vibrational frequencies (cm-1)

my $sigmar = 1; #Rotational symmetry number
my $ZPVE; #Zero point energy read from G09 output
my $Elec_zpve; #Sum of electronic and zero-point Energies read from G09 output

while (<INFILE>) {# read in data from Gaussian log file
	my $line = $_;
	if($line =~ / Harmonic frequencies/) { #reset everything if new frequency calculation is
found
		@vibtemps = ();
		@vibfreqs = ();
		@Truhlar_vibtemps = ();
	}
	if($line =~ /^ Frequencies --/) {
		chomp;
		$line =~ s/^\s+//;
		my @array= split(/\s+/o,$line);
		foreach my $freq (2..$#array) {
			if($array[$freq] > 0 ) {
				push(@vibfreqs, $array[$freq]);
				push(@vibtemps, $array[$freq]*$c*$h/$kb);
				if($array[$freq] < $v0 ) {
					push(@Truhlar_vibtemps, $v0*$c*$h/$kb);
				} else {
					push(@Truhlar_vibtemps, $array[$freq]*$c*$h/$kb);
				}
			}
		}
	}
	if($line =~ /^ Rotational constants \(GHZ\):\s+(\S+)\s+(\S+)\s+(\S+)/) {
		@rottemps = ($1, $2, $3);
		foreach my $rot (0..$#rottemps) {
			$rottemps[$rot] *= $h*(10**9)/($kb);
		}
	}
	if($line =~ /^ Molecular mass:\s+(\S+)/) {
		$mass = $1*$amu2kg;
	}
	if($line =~ /^ Sum of electronic and zero-point Energies=\s+(\S+)/) {
		$Elec_zpve = $1;
	}
	if($line =~ /^ Zero-point correction=\s+(\S+)/) {
```

```
            $ZPVE = $1;
        }
        if($line =~ / Multiplicity = (\d+)/) {
            $mult = $1;
        }
        if($line =~ / Rotational symmetry number\s+(\d+)/) {
            $sigmar = $1;
        }
}

#Calculate average moment of inertia for Grimme's quasi-RRHO approach
my $Bav = ($h**2/(24*pi**2*$kb))*(1/$rottemps[0] + 1/$rottemps[1] + 1/$rottemps[2]);

if ($#rottemps!=2) {
        die "Problem reading Rotational constants";
}

#Translational component of Entropy
my $qt = (2*pi*$mass*$kb*$T/($h*$h))**(3/2)*$kb*$T/$P;
my $St = $R*(log($qt) + 5/2);

#Translation component of Energy
my $Et = 3*$R*$T/2;

#Electronic component of Entropy
my $Se = $R*(log($mult));

#Rotational component of Entropy
my $qr = (sqrt(pi)/$sigmar)*($T**(3/2)/sqrt($rottemps[0]*$rottemps[1]*$rottemps[2]));
my $Sr = $R*(log($qr) + 3/2);

#Rotational component of Energy
my $Er = 3*$R*$T/2;

#Vibrational component of Entropy and Energy
my $Ev = 0;
my $Ev_Truhlar = 0;
my $Sv = 0;
my $Sv_quasiRRHO = 0;
my $Sv_Truhlar = 0;

foreach my $i (0..$#vibtemps) {
        my $Sv_temp = $vibtemps[$i]/($T*(exp($vibtemps[$i]/$T)-1)) - log(1-exp(-
$vibtemps[$i]/$T));

        $Sv += $Sv_temp;
        $Sv_Truhlar += $Truhlar_vibtemps[$i]/($T*(exp($Truhlar_vibtemps[$i]/$T)-1)) -
log(1-exp(-$Truhlar_vibtemps[$i]/$T));
        $Ev += $vibtemps[$i]*(1/2 + 1/(exp($vibtemps[$i]/$T) - 1));
        $Ev_Truhlar += $Truhlar_vibtemps[$i]*(1/2 + 1/(exp($Truhlar_vibtemps[$i]/$T) - 1));
```

```
        #calculate quasi-RRHO contribution to Sv
        my $mu = $h/(8*pi**2*$vibfreqs[$i]*$c);
        my $mu_prime = $mu*$Bav/($mu + $Bav);
        my $Sr = 1/2 + log(sqrt(8*pi**3*$mu_prime*$kb*$T/$h**2));

        my $weight = 1/(1+($v0/$vibfreqs[$i])**4);

        $Sv_quasiRRHO += $weight*$Sv_temp + (1-$weight)*$Sr;
}

$Sv *= $R;
$Ev *= $R;
$Ev_Truhlar *= $R;
$Sv_quasiRRHO *= $R;
$Sv_Truhlar *= $R;

#Grab Electronic energy from $Elec_zpve and $ZPVE
my $E_e = $Elec_zpve - $ZPVE;
my $Etot = $Et + $Er + $Ev;
my $Etot_Truhlar = $Et + $Er + $Ev_Truhlar;
my $Hcorr = $Etot + $R*$T;
my $Stot = $St + $Sr + $Sv + $Se;
my $Stot_quasiRRHO = $St + $Sr + $Sv_quasiRRHO + $Se;
my $Stot_Truhlar = $St + $Sr + $Sv_Truhlar + $Se;
my $Gcorr = $Hcorr - $T*$Stot;
my $Gcorr_quasiRRHO = $Hcorr - $T*$Stot_quasiRRHO;
my $Gcorr_Truhlar = $Hcorr - $T*$Stot_Truhlar;
$Etot *= $kcal2hartree/1000;
$Etot_Truhlar *= $kcal2hartree/1000;
$Hcorr *= $kcal2hartree/1000;
$Gcorr *= $kcal2hartree/1000;
$Gcorr_quasiRRHO *= $kcal2hartree/1000;
$Gcorr_Truhlar *= $kcal2hartree/1000;
printf("\ File Name: $infile \n");
printf("\nRRHO Thermochemistry (T = $T)\n");
printf(" Zero-point correction (RRHO)=                    %10.6f (Hartree/Particle)\n",
$ZPVE);
printf(" Thermal correction to Energy (RRHO)=             %10.6f\n", $Etot);
printf(" Thermal correction to Enthalpy (RRHO)=           %10.6f\n", $Hcorr);
printf(" Thermal correction to Gibbs Free Energy (RRHO)=  %10.6f\n", $Gcorr);

printf(" Sum of electronic and zero-point Energies (RRHO)=      %10.6f\n", $Elec_zpve);
printf(" Sum of electronic and thermal Energies (RRHO)=         %10.6f\n", $E_e + $Etot);
printf(" Sum of electronic and thermal Enthalpies (RRHO)=       %10.6f\n", $E_e +
$Hcorr);
printf(" Sum of electronic and thermal Free Energies (RRHO)=    %10.6f\n\n\n", $E_e +
$Gcorr);

printf("\nQuasi-RRHO Thermochemistry (T = $T, v0 = $v0 cm-1)\n");
```

```
printf(" Zero-point correction (QRRHO)=                %10.6f (Hartree/Particle)\n",
$ZPVE);
printf(" Thermal correction to Energy (QRRHO)=             %10.6f\n", $Etot);
printf(" Thermal correction to Enthalpy (QRRHO)=           %10.6f\n", $Hcorr);
printf(" Thermal correction to Gibbs Free Energy (QRRHO)=  %10.6f\n",
$Gcorr_quasiRRHO);

printf(" Sum of electronic and zero-point Energies (QRRHO)=      %10.6f\n",
$Elec_zpve);
printf(" Sum of electronic and thermal Energies (QRRHO)=         %10.6f\n", $E_e +
$Etot);
printf(" Sum of electronic and thermal Enthalpies (QRRHO)=       %10.6f\n", $E_e +
$Hcorr);
printf(" Sum of electronic and thermal Free Energies (QRRHO)=    %10.6f\n\n\n", $E_e +
$Gcorr_quasiRRHO);

printf("\nQuasi-harmonic Thermochemistry (T = $T, cutoff = $v0 cm-1)\n");
printf(" Zero-point correction (QHO)=                  %10.6f (Hartree/Particle)\n", $ZPVE);
printf(" Thermal correction to Energy (QHO)=               %10.6f\n", $Etot_Truhlar);
printf(" Thermal correction to Enthalpy (QHO)=             %10.6f\n", $Hcorr);
printf(" Thermal correction to Gibbs Free Energy (QHO)=    %10.6f\n", $Gcorr_Truhlar);

printf(" Sum of electronic and zero-point Energies (QHO)=        %10.6f\n", $Elec_zpve);
printf(" Sum of electronic and thermal Energies (QHO)=           %10.6f\n", $E_e +
$Etot_Truhlar);
printf(" Sum of electronic and thermal Enthalpies (QHO)=         %10.6f\n", $E_e +
$Hcorr);
printf(" Sum of electronic and thermal Free Energies (QHO)=      %10.6f\n\n\n", $E_e +
$Gcorr_Truhlar);
```

References for computational section

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Coordinates of calculated structures

1. AgF_2

Ag	0.0000000	-0.0000000	-0.0000000
F	0.0000000	-0.0000000	-1.9586040
F	-0.0000000	0.0000000	1.9586040

2. $2AgF_2$ Triplet Complex

Ag	-1.6015520	-0.3011890	-0.0008720
F	-3.2900200	0.6967970	0.1192970
F	0.1655030	-1.3690890	-0.1147480
Ag	1.6016060	0.3013140	-0.0008360
F	-0.1656250	1.3687620	-0.1148340
F	3.2898580	-0.6971270	0.1192050

3. Pyridine

C	0.0002000	1.3785870	-0.0000000
C	-1.1938690	0.6696680	0.0000080
C	-1.1417390	-0.7190740	-0.0000030
N	-0.0002110	-1.4129570	-0.0000050
C	1.1940650	0.6693240	-0.0000040
C	1.1415380	-0.7194040	0.0000030
H	-2.0580130	-1.2994010	-0.0000130
H	0.0003550	2.4607240	-0.0000180
H	-2.1486310	1.1776760	0.0000170
H	2.1489750	1.1770540	-0.0000080
H	2.0576140	-1.2999550	0.0000320

4. $2AgF_2$ Singlet Complex

Ag	-1.4413550	-0.3236620	0.0018760
F	-3.1026770	0.7046240	0.1581640
F	0.1608920	-1.5541560	-0.1679320
Ag	1.4413460	0.3236320	0.0018070
F	-0.1609530	1.5541510	-0.1677980
F	3.1027880	-0.7044620	0.1583310

5. $2AgF_2$ Open Shell Singlet Complex

Ag	-1.6155070	-0.3009820	-0.0014580
F	-3.3011480	0.7021100	0.1144800
F	0.1639430	-1.3501500	-0.1068560
Ag	1.6155370	0.3009450	-0.0015020

F	-0.1641810	1.3502230	-0.1067540
F	3.3012280	-0.7019890	0.1145870

6. $AgFAgF_2$ complex

C	0.0000000	-0.0000000	0.2787220
N	0.0000000	-0.0000000	1.4291700
C	-0.0000000	0.0000000	-1.1735610
H	-0.0000000	1.0244750	-1.5450530
H	0.8872210	-0.5122380	-1.5450530
H	-0.8872210	-0.5122380	-1.5450530

7. $AgFAgF_2$ complex

Ag	-1.4024970	0.2409170	0.0000760
F	-3.0801190	-0.8258390	-0.0006980
F	0.2064430	1.4941690	0.0002710
Ag	1.9569000	-0.1092860	-0.0001590
F	-0.0215420	-1.3557340	0.0008610

8. AgF_2……solv

Ag	0.8839490	0.0116490	-0.0026350
F	0.9588210	2.0032010	-0.0087330
F	1.1214050	-1.9670980	-0.0103040
N	-1.3186490	-0.0548610	0.0685240
C	-2.4626730	-0.0433480	0.0245160
C	-3.9076770	-0.0268840	-0.0320290
H	-4.2408460	0.8750310	-0.5446610
H	-4.2614710	-0.9033120	-0.5740240
H	-4.3126720	-0.0387290	0.9792900

9. CH_3CN

C	0.0000000	-0.0000000	0.2787220
N	0.0000000	-0.0000000	1.4291700
C	-0.0000000	0.0000000	-1.1735610
H	-0.0000000	1.0244750	-1.5450530
H	0.8872210	-0.5122380	-1.5450530
H	-0.8872210	-0.5122380	-1.5450530

10. $2AgF_2$……solv triplet complex

Ag	1.5089150	-0.6446710	-0.0323400
F	2.2457550	-2.5315150	0.0332250
F	0.5311830	1.2716510	-0.1135680
Ag	-1.5029340	0.6298130	-0.0323740
F	-0.5256720	-1.2873340	-0.1095360
F	-2.2374410	2.5179060	0.0274400
C	-5.8785390	-1.1671300	0.1415350
H	-6.5931420	-0.3446960	0.1636410
H	-5.9988230	-1.7766170	1.0367480
H	-6.0583890	-1.7805680	-0.7409780
C	-4.5345610	-0.6366670	0.0943670
N	-3.4709860	-0.2160880	0.0554570
C	5.8440230	1.2492730	0.1439630
H	5.7737000	2.3300300	0.0235570
H	6.4547680	0.8339460	-0.6572660
H	6.3033880	1.0204300	1.1052740
C	4.5203050	0.6704220	0.0917960
N	3.4717860	0.2138080	0.0506270

11. $2AgF_2$……solv singlet complex

Ag	1.5089150	-0.6446710	-0.0323400
F	2.2457550	-2.5315150	0.0332250

F	0.5311830	1.2716510	-0.1135680
Ag	-1.5029340	0.6298130	-0.0323740
F	-0.5256720	-1.2873340	-0.1095360
F	-2.2374410	2.5179060	0.0274400
C	-5.8785390	-1.1671300	0.1415350
H	-6.5931420	-0.3446960	0.1636410
H	-5.9988230	-1.7766170	1.0367480
H	-6.0583890	-1.7805680	-0.7409780
C	-4.5345610	-0.6366670	0.0943670
N	-3.4709860	-0.2160880	0.0554570
C	5.8440230	1.2492730	0.1439630
H	5.7737000	2.3300300	0.0235570
H	6.4547680	0.8339460	-0.6572660
H	6.3033880	1.0204300	1.1052740
C	4.5203050	0.6704220	0.0917960
N	3.4717860	0.2138080	0.0506270

12. AgF

Ag	0.0000000	0.0000000	0.3371220
F	0.0000000	0.0000000	-1.7605260

13. AgF_2AgFH

H	0.9761620	-1.4558830	0.3424390
Ag	1.7321140	-0.0101380	0.0205520
F	-0.1151920	1.2184760	-0.0024910
Ag	-1.7892140	0.0991860	-0.0072240
F	3.7165060	-0.5435980	-0.0911310
F	-3.4115850	-0.9781420	-0.0140280

14. $AgFAgF_2$……solv complex

Ag	1.6043790	-0.5177240	-0.0007360
F	2.8350260	-2.1520920	-0.0051540
F	0.2368930	1.0672940	0.0031610
Ag	-1.7995370	-0.1345170	0.0035040
F	-0.1472930	-1.6830820	-0.0012890
C	-6.3318580	1.1534640	-0.0093760
H	-6.4793230	1.9308310	-0.7587000
H	-6.9657990	0.2993390	-0.2461840
H	-6.6031360	1.5428910	0.9716050
N	-3.8454320	0.4167740	0.0027560
C	-4.9442740	0.7427260	-0.0022230
C	5.3463300	2.4316500	-0.0014480
H	4.9928360	3.4623660	-0.0011740
H	5.9523150	2.2566990	0.8870830
H	5.9509780	2.2567240	-0.8908970
N	3.3166170	0.8205580	0.0000560
C	4.2139020	1.5315070	-0.0006180

15. $2AgF_2$……solv open singlet complex

Ag	1.6043790	-0.5177240	-0.0007360
F	2.8350260	-2.1520920	-0.0051540
F	0.2368930	1.0672940	0.0031610
Ag	-1.7995370	-0.1345170	0.0035040
F	-0.1472930	-1.6830820	-0.0012890
C	-6.3318580	1.1534640	-0.0093760
H	-6.4793230	1.9308310	-0.7587000
H	-6.9657990	0.2993390	-0.2461840
H	-6.6031360	1.5428910	0.9716050
N	-3.8454320	0.4167740	0.0027560
C	-4.9442740	0.7427260	-0.0022230

C	5.3463300	2.4316500	-0.0014480
H	4.9928360	3.4623660	-0.0011740
H	5.9523150	2.2566990	0.8870830
H	5.9509780	2.2567240	-0.8908970
N	3.3166170	0.8205580	0.0000560
C	4.2139020	1.5315070	-0.0006180

16. HF

F	0.0000000	0.0000000	0.0928170
H	0.0000000	0.0000000	-0.8353560

17. 2-fluoro pyrdine

C	0.8871250	-0.0197400	-0.0000370
F	2.2375630	-0.0360840	0.0000170
N	0.3082260	-1.1908440	0.0000340
C	-1.0332010	-1.2036580	-0.0000180
H	-1.5015690	-2.1802360	-0.0000810
H	-2.8752350	-0.1070930	0.0000010
C	-1.7963480	-0.0480130	0.0000050
H	-1.7012540	2.1055810	0.0000830
C	-1.1403660	1.1807910	0.0000230
C	0.2449600	1.2093460	-0.0000260
H	0.8093970	2.1300530	-0.0000830

18. pyrdine-2AgF_2 triplet complex

Ag	0.4187770	-0.8008530	-0.0360740
C	3.4461800	-0.5006240	0.1139710
H	3.3298550	-1.5727570	0.1849600
F	1.3249600	-2.6262080	0.0425340
F	-0.6804090	1.0740090	-0.0932120
N	2.3141810	0.2014250	-0.0050630
C	2.3454540	1.5354720	-0.1030940
H	3.5393980	3.3047740	-0.1671000
C	3.5441740	2.2275790	-0.0851610
C	4.7291260	1.5141370	0.0390270
H	5.6792810	2.0304690	0.0565060
C	4.6787560	0.1301440	0.1404820
H	5.5780630	-0.4603300	0.2390610
H	1.3897660	2.0326100	-0.1936570
Ag	-2.6716450	0.2520320	0.0197450
F	-3.6911990	1.9368280	0.1375030
F	-1.6525700	-1.5391210	-0.0810710

19. pyrdine-2AgF_2 open singlet complex

Ag	0.4426550	-0.7979670	0.0327580
C	3.4595150	-0.4902340	-0.1184610
H	3.3436440	-1.5620480	-0.1922740
F	1.3550640	-2.6183140	-0.0068080
F	-0.6958370	1.0354260	0.0451370
N	2.3280090	0.2116910	0.0075340
C	2.3609600	1.5457440	0.1126640
H	3.5563890	3.3131250	0.1827630
C	3.5605200	2.2364130	0.0945890
C	4.7444140	1.5230960	-0.0376710
H	5.6950530	2.0384850	-0.0558400
C	4.6923820	0.1395130	-0.1461170
H	5.5906640	-0.4514190	-0.2505980
H	1.4073130	2.0446970	0.2086800
Ag	-2.7061170	0.2449620	-0.0179880

F	-3.7467440	1.9197270	-0.1071660
F	-1.6250560	-1.5146900	0.0610930

20. pyrdine-2AgF_2 singlet complex

Ag	0.5451000	-0.6194240	-0.0576850
C	3.4444620	-0.5873770	0.3228250
H	3.2318040	-1.6259950	0.5232690
F	1.3103040	-2.3848660	-0.1826660
F	-0.2619490	1.1321880	0.0777610
N	2.4035460	0.1888200	-0.0049910
C	2.5518980	1.4897540	-0.2894870
H	3.9059820	3.1184150	-0.4886440
C	3.8064540	2.0693720	-0.2526670
C	4.9036290	1.2908740	0.0891150
H	5.8921240	1.7270190	0.1279800
C	4.7182970	-0.0532040	0.3812230
H	5.5436920	-0.6942440	0.6530170
H	1.6573210	2.0421740	-0.5305970
Ag	-2.9061640	0.1676050	0.0341770
F	-4.4933680	1.4890800	0.1462730
F	-1.2921150	-1.3375300	-0.1137350

21. pyr-AgF_2

Ag	-0.5471530	0.0257640	0.1437670
C	2.3129710	1.1491350	-0.0363570
H	1.7184280	2.0495490	0.0331430
F	-0.4879120	2.0952260	0.1624000
F	-0.5352160	-2.0441150	0.2340330
N	1.6286280	0.0013880	0.0175540
C	2.2654910	-1.1718580	-0.0620120
H	4.1280930	-2.1980240	-0.2720890
C	3.6416320	-1.2354500	-0.2061150
C	4.3660640	-0.0522340	-0.2662830
H	5.4414420	-0.0734620	-0.3814250
C	3.6911930	1.1584100	-0.1776370
H	4.2187320	2.1005810	-0.2187780
H	1.6332980	-2.0474050	-0.0084830
N	-2.7500060	0.0018010	0.0230500
C	-3.8758970	-0.0130240	-0.1853660
C	-5.2995410	-0.0554800	-0.4402950
H	-5.6829750	-1.0471910	-0.2001820
H	-5.8061420	0.6872870	0.1754520
H	-5.4883410	0.1584680	-1.4923960

22. TS1

Ag	-1.298999	-1.060796	-0.225749
F	-2.581435	0.873525	1.044034
C	-1.584538	1.815084	-0.422554
C	-1.353279	3.155874	-0.063972
C	-0.067783	3.552004	0.262977
C	0.963446	2.624682	0.198185
C	0.662560	1.299535	-0.144199
H	1.977930	2.885573	0.460771
H	0.135147	4.576921	0.541231
H	-2.169253	3.861593	-0.111802
H	-2.468088	1.555979	-0.986347
N	-0.569006	0.915760	-0.429887
F	-2.008531	-2.931980	0.075110
H	1.424139	0.532442	-0.117610

23. Int0

Ag	-1.447896	-0.294217	-0.028104
F	0.715118	2.002489	0.494220
C	1.283841	1.024855	-0.349874
C	2.763935	1.091805	-0.232437
C	3.492432	-0.017195	0.067136
C	2.828089	-1.230359	0.299864
C	1.413939	-1.266848	0.254830
H	3.367025	-2.131992	0.548597
H	4.570455	0.034274	0.135135
H	3.223215	2.051205	-0.425462
H	0.966659	1.303453	-1.361557
N	0.663303	-0.237378	-0.022752
F	-3.488369	-0.353590	-0.047527
H	0.903748	-2.194059	0.482458

24. Int1

F	4.684933	-1.102780	-0.338153
Ag	2.846909	-0.333834	0.097242
N	0.929077	0.425736	0.550587
C	0.425496	1.486852	-0.293258
H	0.344795	1.093349	-1.312598
F	-1.460270	-0.003415	-2.093749
Ag	-2.882151	0.061708	-0.715697
F	-4.328656	0.074161	0.625541
C	-0.877574	2.086005	0.104810
H	-2.571451	1.964583	1.401826
C	-1.630578	1.523192	1.102978
H	-1.674466	-0.048192	2.611018
C	-1.115596	0.410070	1.810243
C	0.179124	-0.064864	1.498226
F	1.396963	2.497554	-0.323822
H	0.598230	-0.870617	2.086305
H	-1.209168	2.955650	-0.444541

25. TS2

F	-3.111518	-4.316980	-0.428106
Ag	-2.073066	-2.618400	0.032340
N	-1.045298	-0.832611	0.520618
C	0.176406	-0.529635	-0.121039
H	-0.276816	0.240834	-1.132279
F	-0.867609	1.099128	-1.752145
Ag	-1.744625	2.525632	-0.425172
F	-2.601247	3.871625	0.772917
C	1.084833	0.417713	0.510592
H	1.128498	2.169687	1.717341
C	0.527614	1.387041	1.276769
H	-1.333363	2.027633	2.246224
C	-0.886960	1.339378	1.544709
C	-1.563943	0.124592	1.259288
F	0.766605	-1.644781	-0.634654
H	-2.539852	-0.057299	1.688752
H	2.135339	0.379756	0.263679

26. $TS1_{CH3CN}$

Ag	-0.868959	-0.383317	0.035414
F	1.228904	-0.912796	-1.424143
C	2.017549	-0.440155	0.372247

C	3.326637	0.050264	0.213294
C	3.566290	1.400071	0.410334
C	2.515667	2.225104	0.785708
C	1.227274	1.679450	0.898943
H	2.652835	3.286774	0.928869
H	4.563778	1.801188	0.295084
H	4.127314	-0.643957	0.005464
H	1.858025	-1.492927	0.550311
N	0.998084	0.396114	0.686644
F	-2.664296	-1.026068	-0.685507
H	0.366004	2.309111	1.081137
N	-1.886245	3.087351	0.576053
C	-2.749423	2.575390	0.011864
C	-3.823559	1.904396	-0.695833
H	-3.583577	0.839113	-0.782533
H	-4.758110	2.026463	-0.148192
H	-3.935672	2.336426	-1.690278

27. Int0$_{CH3CN}$

Ag	-0.957250	-0.326427	0.336940
F	1.902872	-1.481945	-0.574021
C	2.098176	-0.450823	0.371423
C	3.463582	0.108840	0.195057
C	3.653582	1.443685	0.013035
C	2.538668	2.292722	-0.039947
C	1.237816	1.741813	0.060756
H	2.644943	3.356340	-0.191457
H	4.650833	1.846749	-0.099134
H	4.285838	-0.590992	0.247619
H	2.007320	-0.941338	1.347410
N	0.997145	0.471692	0.233202
F	-2.880087	-1.042164	0.443554
H	0.375226	2.391700	-0.029083
N	-1.870309	3.187415	-0.265025
C	-2.841262	2.572299	-0.197870
C	-4.053921	1.781464	-0.109298
H	-4.679012	2.157859	0.700709
H	-4.607404	1.851975	-1.045875
H	-3.788238	0.735133	0.084881

28. Int1$_{CH3CN}$

F	3.221592	-0.437419	-1.587328
Ag	1.679094	0.636964	-0.723920
N	0.059503	1.539118	0.291026
C	-0.898026	2.269161	-0.513071
H	-1.228861	1.596655	-1.314218
F	-2.047963	-0.163057	-1.917380
Ag	-2.400988	-1.149357	-0.207035
F	-3.041370	-1.918473	1.515582
C	-2.078791	2.818534	0.200141
H	-3.178895	2.903759	2.017685
C	-2.298848	2.530293	1.511847
H	-1.489614	1.514570	3.254718
C	-1.359756	1.756769	2.210833
C	-0.190943	1.313922	1.547444
F	-0.208382	3.325360	-1.155055
H	0.554945	0.751080	2.093938
H	-2.769104	3.412374	-0.382699
N	2.536615	-0.538655	2.611461
C	3.504165	-0.482836	1.989905

C	4.705739	-0.419315	1.179718
H	5.362265	-1.254778	1.424489
H	4.420412	-0.467444	0.123080
H	5.231549	0.515230	1.374001
N	-0.473209	-2.183145	-0.230652
C	0.610412	-2.554327	-0.244402
C	1.984750	-2.994868	-0.278651
H	2.359365	-3.087223	0.739925
H	2.047352	-3.960185	-0.780614
H	2.572156	-2.244504	-0.823243

28. $TS2_{CH3CN}$

F	5.005601	0.307370	0.410585
Ag	3.038056	0.896685	0.290892
N	1.000101	1.464972	0.228284
C	0.463890	2.043162	-0.940293
H	-0.068974	0.952837	-1.521067
F	-0.693725	-0.071281	-1.703741
Ag	-2.001214	-0.456256	0.018167
F	-3.194347	-0.721483	1.651786
C	-0.734472	2.857589	-0.825207
H	-2.553675	3.039425	0.264931
C	-1.602432	2.535531	0.167744
H	-1.840918	1.357559	1.997297
C	-1.227555	1.532100	1.126046
C	0.138545	1.161422	1.178771
F	1.443497	2.559327	-1.744979
H	0.525431	0.632821	2.041066
H	-0.944597	3.594982	-1.585771
N	1.997846	-0.463525	3.534011
C	3.127195	-0.650873	3.411286
C	4.549271	-0.879082	3.240461
H	4.760618	-1.946349	3.309661
H	4.858741	-0.503796	2.257234
H	5.101081	-0.357084	4.022470
N	-2.689191	-2.291461	-0.949027
C	-3.028247	-3.272687	-1.431551
C	-3.454461	-4.512396	-2.041723
H	-2.978858	-5.350219	-1.532345
H	-4.536914	-4.606305	-1.959676
H	-3.168408	-4.518269	-3.093097

29. pyr-$(2AgF_2)_2$

Ag	0.4187770	-0.8008530	-0.0360740
C	3.4461800	-0.5006240	0.1139710
H	3.3298550	-1.5727570	0.1849600
F	1.3249600	-2.6262080	0.0425340
F	-0.6804090	1.0740090	-0.0932120
N	2.3141810	0.2014250	-0.0050630
C	2.3454540	1.5354720	-0.1030940
H	3.5393980	3.3047740	-0.1671000
C	3.5441740	2.2275790	-0.0851610
C	4.7291260	1.5141370	0.0390270
H	5.6792810	2.0304690	0.0565060
C	4.6787560	0.1301440	0.1404820
H	5.5780630	-0.4603300	0.2390610
H	1.3897660	2.0326100	-0.1936570
Ag	-2.6716450	0.2520320	0.0197450
F	-3.6911990	1.9368280	0.1375030
F	-1.6525700	-1.5391210	-0.0810710

30. TS1’

Ag	-1.178026	1.373260	0.092164
C	1.725551	1.369880	-0.029883
H	1.148819	2.647562	-0.013379
F	0.371898	3.442650	0.014468
F	-2.409571	-0.607328	0.156429
N	0.769691	0.498382	0.015629
C	0.962675	-0.832558	0.015587
H	2.441477	-2.366979	-0.037339
C	2.260421	-1.301755	-0.036180
C	3.314298	-0.389109	-0.086068
H	4.335268	-0.746701	-0.126865
C	3.061089	0.976126	-0.083694
H	3.858077	1.703194	-0.121642
H	0.091577	-1.469654	0.056113
Ag	-4.313363	0.319981	0.230067
F	-5.449163	-1.303532	0.287750
F	-3.266044	2.096682	0.175264

31. Int2

F	-0.755911	2.865200	-1.206018
Ag	0.417392	1.342150	-0.709234
F	-0.511398	0.927381	1.180319
Ag	-2.361708	-0.123475	0.928704
F	0.179198	-1.867009	-0.741912
C	1.162436	-1.454973	0.180692
N	1.742009	-0.236728	-0.333246
C	2.114650	-2.575426	0.397322
C	3.447145	-2.429036	0.160351
C	3.931775	-1.202437	-0.312584
C	3.022373	-0.144107	-0.547326
H	0.616687	-1.206758	1.095986
H	1.689600	-3.503576	0.752659
H	4.127555	-3.253041	0.324687
H	4.979180	-1.044803	-0.519470
F	-4.122544	-1.164872	0.714494
H	3.391387	0.801251	-0.926555

32. TS4

F	-3.111518	-4.316980	-0.428106
Ag	-2.073066	-2.618400	0.032340
N	-1.045298	-0.832611	0.520618
C	0.176406	-0.529635	-0.121039
H	-0.276816	0.240834	-1.132279
F	-0.867609	1.099128	-1.752145
Ag	-1.744625	2.525632	-0.425172
F	-2.601247	3.871625	0.772917
C	1.084833	0.417713	0.510592
H	1.128498	2.169687	1.717341
C	0.527614	1.387041	1.276769
H	-1.333363	2.027633	2.246224
C	-0.886960	1.339378	1.544709
C	-1.563943	0.124592	1.259288
F	0.766605	-1.644781	-0.634654
H	-2.539852	-0.057299	1.688752
H	2.135339	0.379756	0.263679

33. TS3

F	0.412931	-2.974326	-1.069770

Ag	0.406517	-0.998918	-0.865361
F	-1.684391	-0.814153	-1.332379
Ag	-2.789636	-0.348796	0.456069
F	-1.631659	1.649121	0.262735
C	-0.426970	1.895467	-0.985514
N	0.606403	1.072998	-0.594727
C	-0.258419	3.314175	-0.889592
C	0.831925	3.827743	-0.229280
C	1.795498	2.954339	0.270551
C	1.645470	1.582746	0.049230
H	-1.062292	1.485885	-1.755065
H	-1.026165	3.947372	-1.308257
H	0.950098	4.896123	-0.113323
H	2.668814	3.310676	0.795631
F	-3.946656	-0.111800	2.116993
H	2.407423	0.890640	0.382048

34. TS3’

Ag	1.012461	-1.143066	-0.076863
C	1.799707	1.605889	0.048509
H	2.855563	0.804540	0.036775
F	3.533615	-0.147493	0.011735
F	1.266781	-3.149855	-0.152365
N	0.694679	0.918603	-0.000465
C	-0.523033	1.492498	-0.000966
H	-1.584090	3.339288	0.052700
C	-0.611260	2.869340	0.052640
C	0.557926	3.625524	0.105633
H	0.502360	4.705675	0.147959
C	1.795379	2.995764	0.104257
H	2.718525	3.553722	0.144517
H	-1.388510	0.849129	-0.043566

35. Int 2’

Ag	1.339218	-0.198452	0.399327
C	-1.418573	0.855609	0.286768
H	3.964760	0.852375	-0.230287
F	4.339186	1.554457	-0.836368
F	3.432615	-0.095669	0.585966
N	-0.778516	-0.266878	0.192787
C	-1.483626	-1.400720	-0.043204
H	-3.407005	-2.258106	-0.366045
C	-2.855999	-1.348025	-0.178398
C	-3.512670	-0.122231	-0.071724
H	-4.588601	-0.068332	-0.176496
C	-2.780217	1.035974	0.170576
H	-3.245533	2.005938	0.260529
H	-0.925285	-2.321649	-0.117175

36. Int 2’

Ag	1.339218	-0.198452	0.399327
C	-1.418573	0.855609	0.286768
H	3.964760	0.852375	-0.230287
F	4.339186	1.554457	-0.836368
F	3.432615	-0.095669	0.585966
N	-0.778516	-0.266878	0.192787
C	-1.483626	-1.400720	-0.043204
H	-3.407005	-2.258106	-0.366045
C	-2.855999	-1.348025	-0.178398
C	-3.512670	-0.122231	-0.071724

H	-4.588601	-0.068332	-0.176496
C	-2.780217	1.035974	0.170576
H	-3.245533	2.005938	0.260529
H	-0.925285	-2.321649	-0.117175

37. Int0’

Ag	1.446719	0.029881	2.086347
F	0.096234	-1.102783	3.018595
C	-2.719662	-0.279204	-1.554313
Ag	-0.081140	0.985864	-0.743844
F	0.119712	1.579299	1.685658
F	2.971941	1.009157	1.039261
F	2.042802	1.824157	-0.914904
H	2.496297	1.482462	-0.040679
C	-3.901216	-0.990723	-1.592917
H	-4.550072	-0.991932	-2.455795
H	-5.105383	-2.294347	-0.384364
C	-4.196915	-1.708029	-0.437631
C	-3.320544	-1.668302	0.646665
H	-3.533670	-2.220081	1.550991
C	-2.164883	-0.916003	0.568399
N	-1.889766	-0.222384	-0.565423
H	-1.453270	-0.852890	1.381335

38. Int 1’

C	-2.616353	1.565962	0.396929
C	-1.445311	0.829646	0.244757
N	-0.315826	1.438372	-0.121505
C	-0.272396	2.762462	-0.355334
C	-1.402084	3.542249	-0.220469
C	-2.591947	2.933493	0.162851
Ag	-1.423762	-1.194012	0.571044
Ag	1.422999	0.301753	-0.347051
F	3.162686	-0.703584	-0.712376
F	-1.618104	-3.203795	0.818651
F	0.773919	-1.011156	1.199932
H	0.680492	3.178088	-0.651402
H	-1.344023	4.603669	-0.411418
H	-3.494001	3.519537	0.279097
H	-3.530647	1.071686	0.692865
H	4.162202	-0.480553	0.283166
F	4.835902	-0.304866	0.970973

39. $TS3_{CH3CN}$

C	-1.033249	-2.737233	0.741044
Ag	-1.288617	2.265696	0.195154
F	-2.383942	3.268079	-1.200352
H	-0.179566	-3.001127	1.351638
C	-2.308951	-3.278508	0.966235
N	-0.794560	-1.891628	-0.241546
F	-2.214013	0.169700	-0.273714
H	-2.451258	-3.973008	1.781067
C	-3.351666	-2.931251	0.114978
H	-4.333204	-3.365836	0.243862
C	-3.111515	-2.033988	-0.904133
H	-3.885369	-1.731727	-1.593902
C	-1.820040	-1.441768	-1.028201
H	-1.502260	-0.970894	-1.945807
N	-0.061414	1.486900	1.698918
C	0.640276	0.935028	2.417637

C	1.531185	0.197930	3.281141
H	1.023551	-0.044799	4.214406
H	1.810919	-0.719647	2.750140
H	2.416592	0.796465	3.494273
Ag	1.177261	-1.042462	-0.523345
F	0.534122	-0.196064	-2.301077
F	1.795199	-2.025660	1.212505
N	3.114787	-0.033882	-0.673187
C	4.100269	0.548249	-0.699667
C	5.346502	1.282079	-0.733889
H	6.144075	0.630290	-1.089512
H	5.250298	2.134825	-1.405338
H	5.589088	1.636027	0.267733

40. Int 3’

C	-2.616353	1.565962	0.396929
C	-1.445311	0.829646	0.244757
N	-0.315826	1.438372	-0.121505
C	-0.272396	2.762462	-0.355334
C	-1.402084	3.542249	-0.220469
C	-2.591947	2.933493	0.162851
Ag	-1.423762	-1.194012	0.571044
Ag	1.422999	0.301753	-0.347051
F	3.162686	-0.703584	-0.712376
F	-1.618104	-3.203795	0.818651
F	0.773919	-1.011156	1.199932
H	0.680492	3.178088	-0.651402
H	-1.344023	4.603669	-0.411418
H	-3.494001	3.519537	0.279097
H	-3.530647	1.071686	0.692865
H	4.162202	-0.480553	0.283166
F	4.835902	-0.304866	0.970973

41. TS2’

C	-2.205416	1.532438	0.932144
C	-1.193916	0.753354	0.326090
N	-0.327659	1.322853	-0.535795
C	-0.413129	2.606681	-0.876384
C	-1.432641	3.401989	-0.363110
C	-2.333881	2.850985	0.553503
Ag	-1.496056	-1.278605	0.014367
Ag	1.416022	0.198004	-0.468821
F	3.126204	-0.933136	-0.354724
F	-1.798892	-3.271963	-0.332864
F	0.141463	0.209153	1.654259
H	0.305603	2.981583	-1.590829
H	-1.517505	4.429047	-0.685815
H	-3.117653	3.464112	0.977447
H	-2.847253	1.089042	1.678401
H	4.007753	-0.455602	0.642749
F	4.604826	-0.099652	1.337268

42. Int 0’

Ag	1.446719	0.029881	2.086347
F	0.096234	-1.102783	3.018595
C	-2.719662	-0.279204	-1.554313
Ag	-0.081140	0.985864	-0.743844
F	0.119712	1.579299	1.685658
F	2.971941	1.009157	1.039261
F	2.042802	1.824157	-0.914904
H	2.496297	1.482462	-0.040679

C	-3.901216	-0.990723	-1.592917
H	-4.550072	-0.991932	-2.455795
H	-5.105383	-2.294347	-0.384364
C	-4.196915	-1.708029	-0.437631
C	-3.320544	-1.668302	0.646665
H	-3.533670	-2.220081	1.550991
C	-2.164883	-0.916003	0.568399
N	-1.889766	-0.222384	-0.565423
H	-1.453270	-0.852890	1.381335

44. $TS4_{CH3CN}$

F	-2.814115	-2.689275	-0.208652
Ag	-1.736101	-0.950834	-0.163641
N	-0.585276	0.855037	-0.119896
C	-0.401273	1.498281	1.114030
H	0.491968	0.755871	1.785337
F	1.285133	0.035889	2.321933
Ag	1.981407	-0.982331	0.121982
F	0.075964	-2.055413	0.083941
H	0.096956	3.429146	1.989761
C	0.131437	2.847840	1.078649
H	1.231144	4.267358	-0.054762
C	0.755359	3.295481	-0.045665
H	1.228164	2.828620	-2.126673
C	0.749126	2.501201	-1.216629
C	0.029950	1.316356	-1.204492
F	-1.566281	1.375951	1.902713
H	-0.077883	0.726329	-2.106050
N	3.872951	-0.187826	-0.433151
C	4.857885	0.328034	-0.710720
C	6.101131	0.980127	-1.061214
H	5.899035	1.814106	-1.732969
H	6.585906	1.353070	-0.159330
H	6.760768	0.268949	-1.557735
N	-3.567082	0.222081	-0.525567
C	-4.462177	0.925957	-0.645660
C	-5.592254	1.816675	-0.796106
H	-5.597246	2.233319	-1.802959
H	-6.517561	1.266454	-0.628080
H	-5.516175	2.626437	-0.070842

45. py-$(2AgF_2)_2$-CH3CN

Ag	-1.014377	-0.552142	0.860586
C	-3.483844	-2.359692	0.941586
H	-2.696135	-2.995604	1.320465
F	-0.644445	-2.421438	1.613869
F	1.058788	0.021007	1.164986
N	-3.114609	-1.114902	0.618503
C	-4.016874	-0.251646	0.138991
H	-6.044165	0.113899	-0.424735
C	-5.342732	-0.609693	-0.035266
C	-5.738879	-1.898237	0.297625
H	-6.768285	-2.205294	0.172056
C	-4.793677	-2.785701	0.793385
H	-5.058714	-3.797591	1.063993
H	-3.661751	0.738300	-0.105327
Ag	1.893047	0.157945	-0.813204
F	2.634273	0.271813	-2.722284
F	0.177550	-0.813268	-1.415174
N	3.640093	1.162233	-0.030905

C	4.577154	1.683885	0.369207
C	5.762003	2.341670	0.874686
H	6.425043	1.602618	1.323794
H	6.279371	2.841156	0.056059
H	5.478580	3.077368	1.626810
N	-1.305201	1.521834	0.216986
C	-1.116768	2.559481	-0.229908
C	-0.874701	3.866750	-0.796956
H	-0.116334	4.383067	-0.208944
H	-0.523728	3.756304	-1.822773
H	-1.796507	4.447615	-0.789763

46. Int1'$_{CH3CN}$

C	1.954526	2.114163	-0.840824
C	1.096023	1.048239	-0.572133
N	-0.226506	1.254057	-0.585488
C	-0.752453	2.461021	-0.852599
C	0.052843	3.545133	-1.134734
C	1.431819	3.365738	-1.128769
Ag	1.798311	-0.886683	-0.209580
Ag	-1.526935	-0.421601	-0.192388
F	-2.739305	-2.117747	0.164791
F	2.401114	-2.839630	0.132257
F	-0.124553	-1.613357	-1.213903
H	-1.829640	2.540320	-0.837095
H	-0.394745	4.504023	-1.352639
H	2.092173	4.195331	-1.345662
H	3.022375	1.954886	-0.824247
H	-4.095543	-1.888223	0.055539
F	-5.070205	-1.726806	-0.035385
N	3.800591	-0.137668	0.664086
C	4.670381	0.291504	1.277029
C	5.770761	0.837501	2.043335
H	5.555308	0.744805	3.105732
H	6.685678	0.293830	1.814717
H	5.902380	1.888533	1.792307
N	-3.014067	0.785996	0.827863
C	-3.890045	1.328655	1.323888
C	-4.997594	2.016463	1.949595
H	-5.094685	1.690624	2.982023
H	-4.821069	3.090658	1.926089
H	-5.918043	1.785241	1.411911

47. Int0'$_{CH3CN}$

Ag	1.528263	-0.826278	-0.684554
F	2.463006	0.574971	-1.861115
C	-1.332606	3.036912	0.993095
Ag	-1.906694	0.266278	-0.026715
F	-0.236795	-0.496082	-1.710115
F	0.530093	-2.240122	0.577635
F	-0.616496	-1.024707	2.227640
H	-0.125841	-1.564260	1.531104
C	-0.810693	4.285289	1.263392
H	-1.234312	4.942748	2.007664
H	0.776705	5.599095	0.658933
C	0.304316	4.636782	0.507631
C	0.807923	3.746266	-0.439819
H	1.674465	3.999432	-1.033591
C	0.195866	2.521651	-0.623697
N	-0.887187	2.191852	0.121605

H	0.552052	1.790466	-1.334839
N	-3.322350	-1.335667	0.030906
C	-4.031012	-2.234011	0.093962
C	-4.923633	-3.370184	0.176295
H	-4.385042	-4.229848	0.574618
H	-5.759019	-3.131562	0.834269
H	-5.303317	-3.611030	-0.816402
N	3.367540	-1.183968	0.405429
C	4.335410	-1.347197	0.994441
C	5.558588	-1.555924	1.737971
H	6.355789	-1.847627	1.054482
H	5.838250	-0.633178	2.246222
H	5.407299	-2.343812	2.475576

48. Int2$_{CH3CN}$

F	-2.255392	-2.986426	0.052975
Ag	-1.510441	-1.086009	-0.205476
N	-0.651719	0.899483	-0.491652
C	-0.739696	1.852322	0.586967
H	-0.298264	1.373578	1.480372
F	0.877840	0.358897	2.577401
Ag	2.160621	-0.177898	1.014209
F	0.445704	-1.784805	-0.107723
H	-0.227771	3.920862	1.103969
C	-0.095493	3.166528	0.340864
H	1.158794	4.330972	-0.920302
C	0.663758	3.381602	-0.767983
H	1.374343	2.493971	-2.621773
C	0.784862	2.363390	-1.726786
C	0.083834	1.150453	-1.535023
F	-2.107096	2.050171	0.878034
H	0.150053	0.374153	-2.286575
N	3.665466	-0.451231	-0.425933
C	4.461959	-0.587197	-1.238870
C	5.474184	-0.753044	-2.261605
H	5.093264	-0.387902	-3.215637
H	6.365181	-0.187357	-1.989921
H	5.731343	-1.808425	-2.356147
N	-3.566814	-0.346196	-0.433104
C	-4.627910	0.075535	-0.517224
C	-5.967197	0.614848	-0.618214
H	-6.348616	0.461340	-1.627156
H	-6.617575	0.109471	0.095008
H	-5.947026	1.681416	-0.396368

49. TS1'$_{CH3CN}$

Ag	-0.049536	-0.101939	1.063316
C	-2.699142	-0.078215	-0.275940
H	-2.181177	-1.310387	-0.688384
F	-1.785742	-2.309750	-0.992312
F	1.995205	-1.030119	1.136654
N	-2.020347	0.657589	0.552799
C	-2.450865	1.829866	1.049651
H	-4.041472	3.250014	1.050434
C	-3.685456	2.307315	0.660291
C	-4.447517	1.554646	-0.233244
H	-5.419434	1.912038	-0.549343
C	-3.959612	0.348786	-0.711010
H	-4.532265	-0.256186	-1.399217
H	-1.807414	2.357229	1.738697

Ag	2.593794	-0.779127	-0.881530
F	3.049874	-0.473792	-2.847190
F	0.779117	0.286652	-1.009331
N	4.417223	-1.895771	-0.564261
C	5.384253	-2.484666	-0.396198
C	6.605660	-3.229138	-0.182175
H	6.383701	-4.295851	-0.166203
H	7.307956	-3.017952	-0.988007
H	7.048241	-2.937490	0.769913
N	-0.497194	-0.267602	3.244250
C	-0.793667	-0.325041	4.349745
C	-1.164920	-0.396708	5.746536
H	-0.742450	-1.296992	6.191885
H	-0.782648	0.478620	6.271035
H	-2.250550	-0.425301	5.835256

50. TS2'$_{CH3CN}$

Ag	1.324447	-1.195441	0.557777
F	0.481856	0.252519	-1.422319
C	0.653883	1.892086	-0.952785
Ag	-1.857382	0.709781	-0.610683
F	-3.271145	1.554682	0.647752
F	-1.777430	-2.771720	-1.811402
F	-3.090847	-0.892673	-1.172613
H	-2.330006	-1.991947	-1.552894
C	1.958386	2.210258	-0.526957
H	2.800936	1.988757	-1.166594
H	3.101796	3.122782	1.020867
C	2.115363	2.820179	0.692648
C	0.999211	3.050030	1.525897
H	1.106018	3.521220	2.491494
C	-0.238152	2.649602	1.087558
N	-0.396980	2.110212	-0.139944
H	-1.138800	2.753596	1.677162
N	3.350375	-0.989141	-0.040312
C	4.413486	-0.819525	-0.431690
C	5.754274	-0.596168	-0.926022
H	6.353919	-1.494529	-0.781784
H	5.715980	-0.354192	-1.987958
H	6.208663	0.232227	-0.382996
N	-0.554410	-1.688915	1.392966
C	-1.660480	-1.923157	1.581694
C	-3.063910	-2.196421	1.785732
H	-3.215339	-3.266989	1.920298
H	-3.418181	-1.664603	2.668217
H	-3.604219	-1.851965	0.902565

XYZ coordinates for Figure 5 calculations

Toluene

H	-1.064888	2.468480	0.020525
H	-1.239643	3.395158	1.506498
C	-1.482028	2.442254	1.027699
H	-0.976048	1.657093	1.590371
C	-2.970153	2.221747	0.997944
C	-3.740835	2.676680	-0.073494
H	-3.254026	3.172608	-0.905009
H	-5.697846	2.859369	-0.932404
C	-5.120084	2.500248	-0.090020
C	-5.755857	1.860678	0.968970

H	-6.828922	1.719720	0.956841
C	-4.999489	1.398837	2.041037
H	-5.482751	0.894868	2.868601
C	-3.620543	1.578028	2.052226
H	-3.039270	1.211195	2.890021

Toluene_2AgF_2_QRCR

C	1.429498	-1.081885	1.364485
H	1.129316	-0.161155	1.863080
C	2.699398	-0.961989	0.668064
C	3.148798	0.322117	0.204843
C	3.482582	-2.123490	0.383121
C	4.325480	0.421557	-0.486509
H	2.540195	1.198841	0.427209
C	4.652258	-2.009009	-0.307720
H	3.131180	-3.085772	0.728773
C	5.083982	-0.733489	-0.751350
H	4.678400	1.381874	-0.835106
H	5.256206	-2.878772	-0.523368
H	6.010065	-0.651795	-1.304252
Ag	-2.382408	-1.136169	-0.234727
F	-0.481282	-1.518252	-0.797449
F	-4.270750	-1.001393	0.371518
H	1.375411	-1.951148	2.018647
H	0.661568	-1.254132	0.555773
Ag	-0.399664	1.809959	0.025293
F	-2.212844	0.945568	-0.700389
F	1.338837	2.630035	0.800563

Toluene_2AgF_2_TS

C	-1.695417	2.336868	-1.120430
H	-2.201622	3.133540	-0.581311
C	-1.808607	1.028356	-0.562415
C	-2.148395	0.850172	0.814523
C	-1.525805	-0.122060	-1.358912
C	-2.237926	-0.416534	1.336866
H	-2.345307	1.723957	1.432723
C	-1.617967	-1.378107	-0.820673
H	-1.248569	0.018237	-2.395111
C	-1.973969	-1.534251	0.531107
H	-2.508085	-0.558162	2.374338
H	-1.417709	-2.250647	-1.426642
H	-2.038284	-2.527855	0.953942
Ag	1.151966	4.999833	-0.970707
F	0.805008	2.958992	-0.772622
F	1.545525	6.897324	-1.388246
H	-1.764575	2.405515	-2.203772
H	-0.499894	2.606604	-0.929273
Ag	-0.888745	4.313366	1.924977
F	0.783844	5.351674	1.087248
F	-2.543478	3.293361	2.635049

Toluene_2$AgF_2(CH_3CN)_2$_QRCR

C	-1.252523	3.517289	-0.010798
H	-1.122669	4.342146	0.692621

C	-2.431267	2.671595	0.366369
C	-2.545644	2.164001	1.680104
C	-3.422087	2.339194	-0.545941
C	-3.631185	1.346441	2.045993
H	-1.858947	2.503670	2.444892
C	-4.495123	1.524396	-0.181286
H	-3.359531	2.714778	-1.559278
C	-4.601412	1.018638	1.107968
H	-3.709912	0.998046	3.066846
H	-5.249886	1.280702	-0.917690
H	-5.433846	0.385788	1.382307
Ag	1.976527	-0.801472	0.512792
F	0.945205	1.003695	0.542788
F	2.905108	-2.618999	0.500429
H	-1.367260	3.929164	-1.012350
H	-0.339650	2.916088	0.017753
Ag	-1.133065	0.112780	1.597614
F	0.320276	-1.576671	1.602722
F	-0.659059	0.652813	3.479286
N	-1.764987	-0.520682	-0.322252
C	-2.100154	-0.786630	-1.382550
C	-2.538281	-1.105630	-2.721571
H	-1.675293	-1.342184	-3.343252
H	-3.210046	-1.963019	-2.692181
H	-3.063666	-0.247721	-3.141002
N	3.624743	0.107734	-0.584605
C	4.464177	0.607389	-1.181472
C	5.524152	1.238451	-1.937076
H	5.232631	1.307393	-2.984820
H	5.705542	2.239221	-1.546205
H	6.435097	0.646532	-1.853641

Toluene_2AgF$_2$(CH$_3$CN)$_2$_TS

C	-0.111833	2.538305	-0.535728
H	0.568990	2.764994	0.280094
C	-1.459865	2.235525	-0.144918
C	-1.768773	1.860237	1.200193
C	-2.524058	2.293449	-1.083709
C	-3.084396	1.667180	1.592317
H	-0.958209	1.793297	1.911945
C	-3.817448	2.073721	-0.685289
H	-2.298531	2.541384	-2.112315
C	-4.107552	1.772945	0.659686
H	-3.308322	1.420311	2.620693
H	-4.624471	2.139376	-1.402391
H	-5.133625	1.611856	0.961173
Ag	2.184405	-0.822143	-0.290370
F	0.875074	0.379457	-1.567000
F	3.495819	-2.039607	0.726549
H	-0.022318	3.209772	-1.387980
H	0.344307	1.496656	-0.999361
Ag	-1.007864	-0.782497	0.623937
F	0.713809	-2.296002	-0.351721
F	0.654469	0.023978	1.621412
N	-2.830252	-1.352596	-0.266001

C	-3.830075	-1.541036	-0.791789
C	-5.095604	-1.770911	-1.452397
H	-4.923819	-2.239075	-2.421415
H	-5.715266	-2.425307	-0.839530
H	-5.607911	-0.819693	-1.596779
N	3.618479	0.806999	-0.291211
C	4.340390	1.694343	-0.248503
C	5.252894	2.815741	-0.194911
H	5.756400	2.923394	-1.155348
H	4.698342	3.727289	0.026333
H	5.994779	2.645597	0.584848