Supplementary Information
For

Visible Light Induced Photocatalytic Deoxyfluorination of Benzyl Alcohol Using SF_6 as Fluorinating Reagent

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1. General Information

1.1 Instrumentation and methods

NMR spectra were recorded on Bruker-400 MHz, Bruker-500 MHz or Bruker-600 MHz NMR spectrometer (400 MHz, 500 MHz or 600 MHz for ^{1}H; 126 MHz or 151 MHz for ^{13}C and 376 MHz, 471 MHz or 565 MHz for ^{19}F {^{1}H, ^{13}C decoupled}). ^{1}H NMR spectra were referenced relative to internal $Si(Me)_4$(TMS) at δ 0.00 ppm or $CDCl_3$ at δ 7.26 ppm. ^{13}C NMR spectra were recorded at ambient temperature on Bruker-400 (101 MHz) or Bruker-500 (126 MHz) spectrometers and are referenced relative to $CDCl_3$ at δ 77.36 ppm. The ^{13}C NMR spectra were obtained with ^{1}H decoupling. Data for ^{1}H, ^{13}C, ^{19}F NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, quint = quintet, br = broad), integration, and coupling constant (Hz). High resolution mass spectra were recorded on P-SIMSGly of BrukerDaltonics Inc. using ESI-TOF (electrospray ionization-time of flight). Luminescence quenching experiments were done by Hitachi Fluorescence Spectrophotometer F-4600.

1.2 Reagents

Sulfur hexafluoride (SF_6) was purchased from Nanjing Special Gas Plant Co., Ltd., 4CzIPN was purchased from Leyan.com, N,N-diisopropylethylamine (DIPEA) was purchased from Aladdin and all solvents were purchased from *J&K* Chemical. benzyl alcohol derivants were commercially available or synthesized via following methods described in this supplementary information.

1.3 Information of the photocatalytic reactor

Photosyn-10™ Parallel Light Reaction Instrument

Parameters:

Peak wavelength: 448.1 nm

Half-peak breadth: 19.5 nm

Light output: 1.5 W * 12 blue LED, central-convergent removable lamp cup

Photoelectric efficiency: 76.262 %, 67.631 % at 988.1, 2066 mW input

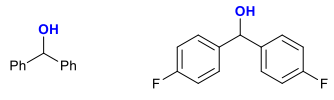
Detailed information of the light source used in this work can be found on the website:

http://en.hsly-greenlab.com/products_details/210.html

2. Supplementary Methods

2.1 Preparation of substrates

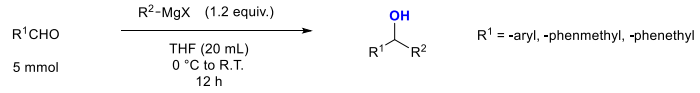
Commercial available substrates

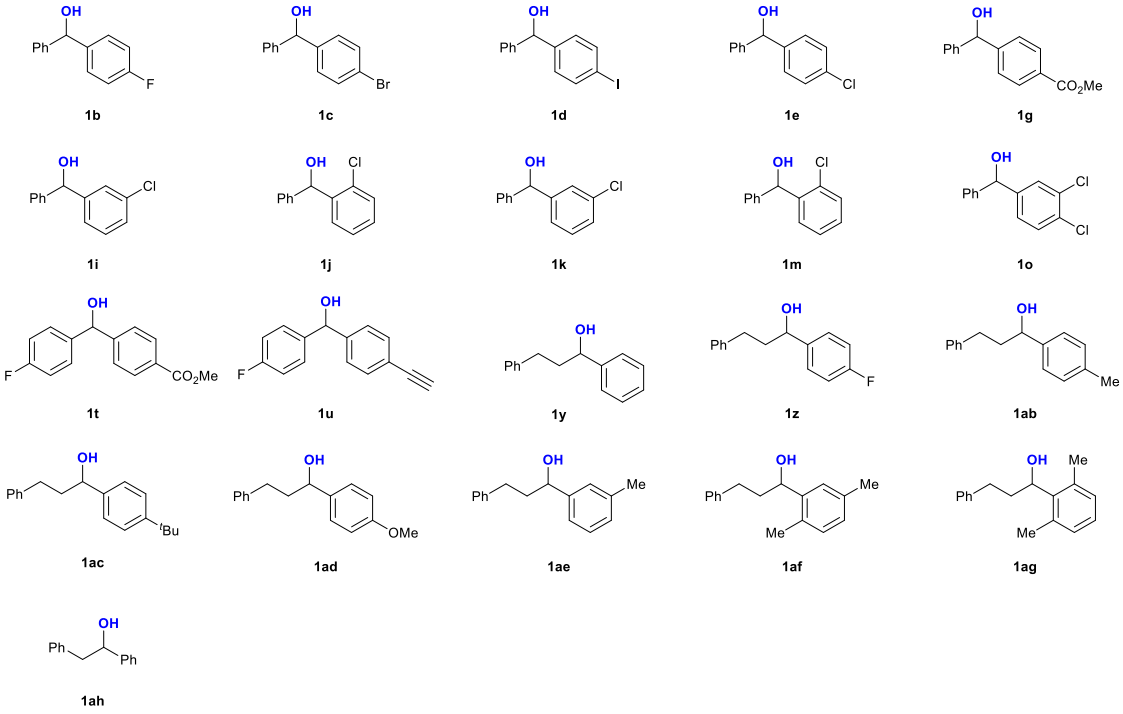


1a **1r**

The substrates **1a** and **1r** were commercially available and used without further purification. Other substrates were prepared according to General procedure A, General procedure B and General procedure C.

General procedure A





1b **1c** **1d** **1e** **1g**

1i **1j** **1k** **1m** **1o**

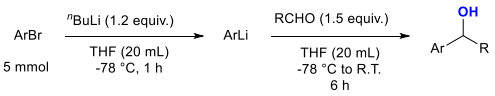
1t **1u** **1y** **1z** **1ab**

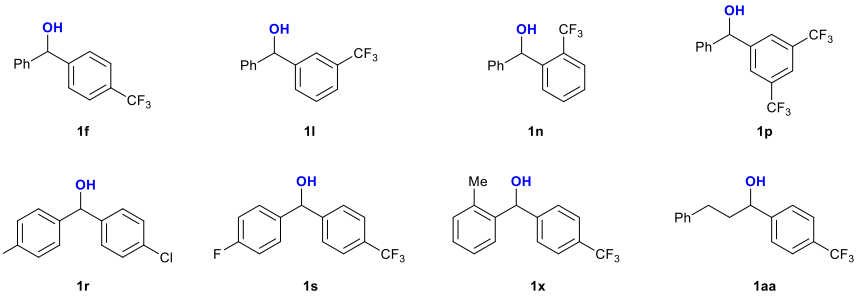
1ac **1ad** **1ae** **1af** **1ag**

1ah

Substrates **1b-1ah** were prepared through the General procedure A. An oven-dried, argon purged round bottom flask containing the aldehyde (5 mmol) in THF (20 mL) was cooled to 0 °C and stirred for 10 minutes. Then Grignard reagent (6 mL, 6 mmol, 1.2 equiv., 1.0 M solution in THF) was added dropwise over 5 minutes. The reaction was then allowed to warm to room temperature and left to stir for 6 hours. After completion, the reaction was cooled to 0 °C and water (1 mL) was then added dropwise in 2 minutes. The mixture was extracted with ethyl acetate and water for 3 times. The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel to give the desired product (R_f = 0.2-0.6, PE/EA = 1/1).

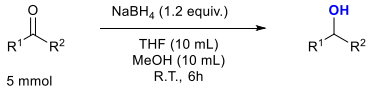
General procedure B

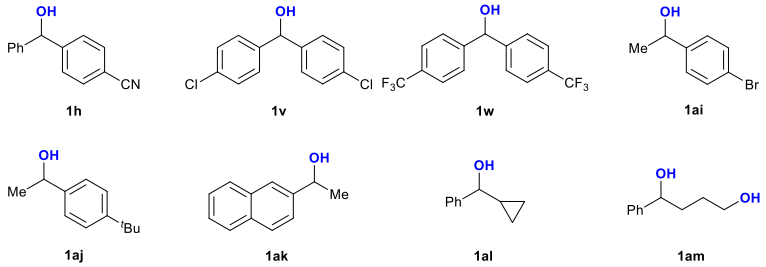




Substrates in **1f-1aa** were prepared through the General procedure B. An oven-dried, argon purged round bottom flask containing the aryl halide (5 mmol) in THF (15 mL) was cooled to -78 ˚C and stirred for 1 hour. n-butyllithium (2.5 mL, 6 mmol, 1.2 equiv., 2.4 M solution in hexane) was added to the reaction tube dropwise. After that, the reaction was stirred at -78 ˚C for 1 hour. Then the solution of alkyl aldehyde (7.5 mmol, 1.5 equiv.) in THF (10 mL) was added dropwise. The resulting mixture was warmed to room temperature and stirred for 6 hours. The mixture was quenched with NH_4Cl (saturated solution) and extracted with ethyl acetate and water for 3 times. The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give the desired product (Rf = 0.2-0.6, PE/EA = 1/1).

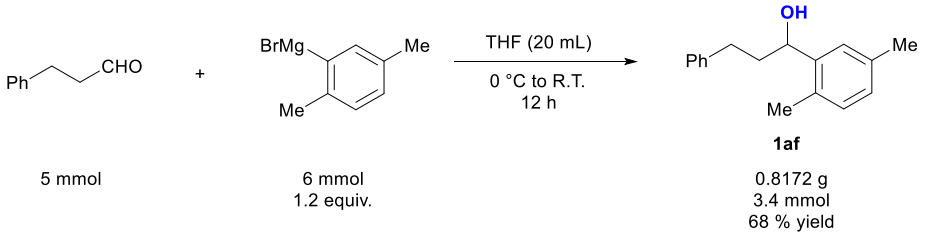
General procedure C





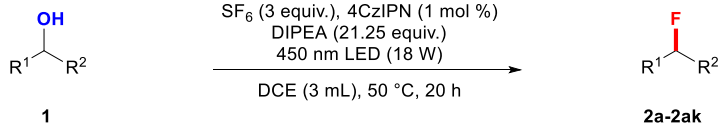
Substrates in **1h-1am** were prepared through the General procedure C. An oven-dried, argon purged round bottom flask containing the aryl halide (5 mmol) in THF (10 mL) was cooled to 0 ˚C and stirred for 10 minutes. $NaBH_4$ (0.2270 g, 6 mmol, 1.2 equiv.) was dissolved in MeOH (10 mL) and then cooled to 0 ˚C, added dropwise into aryl halide solution over 2 minutes, and the mixture was stirred at 0 ˚C for 30 minutes and allowed to warm up to room temperature and stirred for 6 hours. The resulting mixture was cooled to 0 ˚C before quenched with water (5 mL) added dropwise. The mixture was extracted with ethyl acetate for three time and water for 3 times. The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give the desired product (Rf = 0.2-0.6, PE/EA = 1/1).

Synthesis of 1-(2,5-dimethylphenyl)-3-phenylpropan-1-ol (1af)



An oven-dried, argon purged round bottom flask containing phenylpropyl aldehyde (5 mmol) in THF (20 mL) was cooled to 0 °C and stirred for 10 minutes. Then (2,5-dimethylphenyl)magnesium bromide (6 mL, 6 mmol, 1.2 equiv., 1.0 M solution in THF) was added dropwise over 5 minutes. The reaction was then allowed to warm to room temperature and left to stir for 6 hours. At completion, the reaction was cooled to 0 °C and water (1 mL) was then added dropwise in 2 minutes. The mixture was extracted with ethyl acetate and water for 3 times. The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel to give the desired product (Rf = 0.4, PE/EA = 1/1).

2.2 General procedure for dehydroxyfluorination of benzyl alcohol



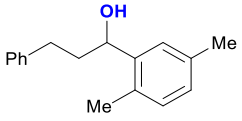
Products **2a-2al** were prepared through this procedure. In a 20 mL glass vial, 4CzIPN (4.74 mg, 0.006 mmol, 1 mol %) and DIPEA (1.6476 g, 12.75 mmol, 21.25 equiv.) were dissolved in DCE (18 mL). The solution was subjected to a 30-second sonication dispersion and then dispensed in equal volumes into 6 glass vials of 10 mL volume directly on bench. Benzyl alcohol **1** (0.1 mmol, 1.0 equiv.) was added and dissolved in each vial. For each glass vial, an oven-dried 10 mL Schlenk tube was evacuated and backfilled with SF_6 (repeated for 5 times), followed by filling in the solution via syringe. The tube was sealed with a Teflon lined cap and stirred under visible light source (450 nm, 18 W) at 50 ˚C for 20 h. The reaction mixture was concentrated *in vacuo*, then dissolved in $CDCl_3$ (0.5 mL) to measure ^1H NMR yield with CH_2Br_2 (17.4 mg, 0.1 mmol) as the internal standard substance. After NMR measurement, the sample was returned back into mixture, extracted with ethyl acetate, water and brine, dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The product was obtained by dual-step flash column chromatography on silica gel (Rf = 0.3-0.7, n-hexane, 40 ˚C). The purified product was then subject to NMR and HRMS characterization.

2.3 Dual-step flash column chromatography purification of benzyl fluorides

After extraction of reaction mixture by ethyl acetate-water system, the organic solvent is removed *in vacro*, and the residue is dissolved in n-hexane (2 mL). In a 3 cm diameter, 30 cm length glass column chromatography vessel with a ceramic sieve plate, 200 mesh column chromatography silica gel is filled to a height of 3 cm together with 0.5 cm height of quartz sand on top. The silica gel is rinsed 3 times with n-hexane preheated to 40 °C. After compressing the liquid level to the top of the silica gel, the reaction mixture is transferred into the vessel and pressed into the silica gel layer. 150 ml of n-hexane preheated to 40 °C is added and rinsed quickly downward to collect the first 50 ml of solution, which is then concentrated *in vacro* to obtain the first-step product. Switch to a 1 cm diameter, 20 cm length glass column chromatography vessel with ceramic sieve plate and add silica gel to a height of 10 cm together with 0.5 cm height of quartz sand. The second-step purified benzyl fluorides can be obtained by rapid rinsing with n-hexane preheated to 40 °C.

2.4 Characterization data for substrates and isolated products

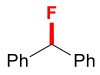
1-(2,5-dimethylphenyl)-3-phenylpropan-1-ol



1af

The substrate **1af** was purified with silica gel chromatography (PE/EA = 2/1, Rf = 0.3) as a white solid (0.8172 g, 68 % yield). **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.28 (dd, *J* = 13.5, 5.5 Hz, 3H), 7.19 (dd, *J* = 16.7, 7.7 Hz, 3H), 6.98 (q, *J* = 7.2, 6.8 Hz, 2H), 4.88 (dd, *J* = 8.5, 4.3 Hz, 1H), 2.92 – 2.65 (m, 2H), 2.32 (s, 3H), 2.18 (s, 3H), 2.10 – 1.92 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 142.82, 142.18, 136.1, 131.6, 130.7, 128.8 (d, *J* = 10.9 Hz), 128.3, 126.1 (d, *J* = 14.3 Hz), 70.3, 39.8, 32.7, 21.5, 18.8. **HRMS** (EI): m/z calcd. for $C_{17}H_{20}O$ [M]: 240.1514, found: 240.1505.

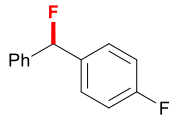
fluorodiphenylmethane



2a

The product **2a** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (95 % ^{1}H NMR yield, 9.5 mg, 51 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 10H), 6.47 (d, *J* = 47.4 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 140.2 (d, *J* = 21.6 Hz), 128l.8, 128.7 (d, *J* = 2.3 Hz), 126.9 (d, *J* = 6.3 Hz), 94.8 (d, *J* = 172.8 Hz). **^{19}F NMR** (376 MHz, Chloroform-d) δ -166.71 (d, *J* = 47.8 Hz). **HRMS** (EI): m/z calcd. for $C_{13}H_{11}F$ [M]: 186.0845, found: 186.0839.

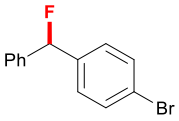
1-fluoro-4-(fluoro(phenyl)methyl)benzene



2b

The product **2b** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (85 % ^{1}H NMR yield, 12.9 mg, 63 % isolated yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 – 7.30 (m, 7H), 7.05 (td, *J* = 8.7, 0.9 Hz, 2H), 6.45 (d, *J* = 47.4 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 164.0 (d, *J* = 2.7 Hz), 162.1 (d, *J* = 2.8 Hz), 139.9 (d, *J* = 22.0 Hz), 136.0 (dd, *J* = 22.2, 3.4 Hz), 129.0, 128.9, 128.9, 128.9, 128.9, 126.8 (d, *J* = 6.4 Hz), 115.8 (d, *J* = 21.1 Hz), 94.2 (d, *J* = 172.8 Hz). **^{19}F NMR** (376 MHz, Chloroform-d) δ -113.43 (tt, *J* = 8.6, 4.3 Hz), -165.01 (dd, *J* = 47.3, 5.1 Hz). **HRMS** (EI): m/z calcd. for $C_{13}H_{10}F_2$ [M]: 204.0751, found: 204.0745.

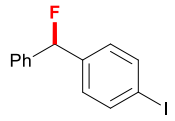
1-bromo-4-(fluoro(phenyl)methyl)benzene



2c

The product **2c** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (74 % ^{1}H NMR yield, 13.0 mg, 49 % isolated yield). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.31 (m, 5H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.42 (d, *J* = 47.3 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 139.5 (d, *J* = 21.3 Hz), 139.2 (d, *J* = 22.4 Hz), 132.0, 129.0 (d, *J* = 2.3 Hz), 128.9, 128.5 (d, *J* = 6.4 Hz), 126.9 (d, *J* = 6.0 Hz), 122.8 (d, *J* = 2.7 Hz), 94.2 (d, *J* = 173.5 Hz). **^{19}F NMR** (565 MHz, Chloroform-d) δ -166.88 (d, *J* = 47.6 Hz). **HRMS** (EI): m/z calcd. for $C_{13}H_{10}BrF$ [M]: 263.9950, found: 263.9950.

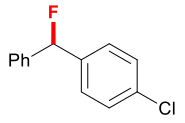
1-iodo-4-(fluoro(phenyl)methyl)benzene



2d

The product **2d** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (69 % ^{1}H NMR yield, 11.9 mg, 38 % isolated yield). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.31 (m, 6H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.41 (d, *J* = 47.3 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 139.9 (d, *J* = 22.3 Hz), 139.5 (d, *J* = 21.3 Hz), 137.9, 129.0, 128.9, 128.7 (d, *J* = 6.4 Hz), 126.9 (d, *J* = 6.0 Hz), 94.8, 94.6, 93.6. **^{19}F NMR** (565 MHz, Chloroform-d) δ -167.34 (d, *J* = 48.3 Hz). **HRMS** (EI): m/z calcd. for $C_{13}H_{10}FI$ [M]: 311.9811, found: 311.9811.

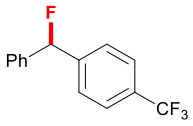
1-chloro-4-(fluoro(phenyl)methyl)benzene



2e

The product **2e** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (77 % ^{1}H NMR yield, 9.7 mg, 44 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.38 – 7.25 (m, 9H), 6.42 (d, *J* = 47.3 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 139.6 (d, *J* = 22.0 Hz), 138.7 (d, *J* = 23.0 Hz), 134.6 (d, *J* = 2.7 Hz), 129.0, 129.0, 128.9, 128.3 (d, *J* = 6.4 Hz), 126.9 (d, *J* = 6.4 Hz), 94.1 (d, *J* = 173.7 Hz). **^{19}F NMR** (471 MHz, Chloroform-d) δ -166.59 (d, *J* = 47.0 Hz). **HRMS** (EI): m/z calcd. for $C_{13}H_{10}ClF$ [M]: 220.0455, found: 220.0453.

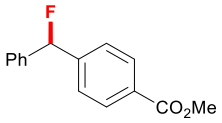
1-(fluoro(phenyl)methyl)-4-(trifluoromethyl)benzene



2f

The product **2f** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.2) as a light yellow oily liquid (71 % ^{1}H NMR yield, 13.5 mg, 53 % isolated yield). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.33 (m, 5H), 6.51 (d, *J* = 47.2 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 144.1 (d, *J* = 22.4 Hz), 139.3 (d, *J* = 21.2 Hz), 130.8 (q, *J* = 32.5 Hz), 129.3 (d, *J* = 2.4 Hz), 129.1, 127.1 (d, *J* = 6.2 Hz), 126.9 (d, *J* = 6.7 Hz), 125.8 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.2 Hz), 94.1 (d, *J* = 174.5 Hz). **^{19}F NMR** (565 MHz, Chloroform-d) δ -62.50, -168.52 (d, *J* = 47.5 Hz). **HRMS** (EI): m/z calcd. for $C_{14}H_{10}F_4$ [M]: 254.0719, found: 254.0718.

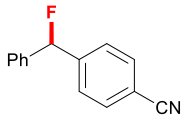
methyl 4-(fluoro(phenyl)methyl)benzoate



2g

The product **2g** was purified with silica gel chromatography (PE/EA = 10:1, Rf = 0.3) as a light yellow oily liquid (59 % ^{1}H NMR yield, 10.5 mg, 43 % isolated yield). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.04 (dt, *J* = 7.9, 0.9 Hz, 2H), 7.42 (dq, *J* = 7.6, 0.8 Hz, 2H), 7.39 – 7.31 (m, 5H), 6.49 (d, *J* = 47.2 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 167.0, 145.0 (d, *J* = 22.3 Hz), 139.4 (d, *J* = 21.4 Hz), 130.3, 130.1, 129.1 (d, *J* = 2.7 Hz), 129.0, 127.1 (d, *J* = 6.0 Hz), 126.4 (d, *J* = 7.0 Hz), 94.2 (d, *J* = 174.5 Hz), 52.5. **^{19}F NMR** (565 MHz, Chloroform-d) δ -168.49 (d, *J* = 47.6 Hz). **HRMS** (EI): m/z calcd. for $C_{15}H_{13}FO_2$ [M]: 244.0900, found: 244.0893.

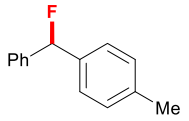
4-(fluoro(phenyl)methyl)benzonitrile



2h

The product **2h** was purified with silica gel chromatography (PE/EA = 10:1, Rf = 0.3) as a light yellow oily liquid (45 % ^{1}H NMR yield, 6.8 mg, 32 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.33 – 7.30 (m, 2H), 6.49 (d, *J* = 47.0 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 145.3 (d, *J* = 22.9 Hz), 138.8 (d, *J* = 21.0 Hz), 132.7, 129.5 (d, *J* = 2.4 Hz), 129.2, 127.1 (dd, *J* = 8.3, 6.4 Hz), 118.8, 112.5, 93.9 (d, *J* = 175.8 Hz). **^{19}F NMR** (471 MHz, Chloroform-d) δ -169.39 (d, *J* = 47.4 Hz). **HRMS** (EI): m/z calcd. for $C_{14}H_{10}FN$ [M]: 211.0797, found: 211.0791.

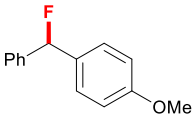
1-(fluoro(phenyl)methyl)-4-methylbenzene



2i

The product **2i** was obtained in the crude reaction mixture (89 % ^{1}H NMR yield). **Crude ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.44 (d, *J* = 47.5 Hz, 1H). **Crude ^{19}F NMR** (376 MHz, Chloroform-*d*) δ -165.80 (d, *J* = 47.5 Hz). **HRMS** (ESI): m/z calcd. for $C_{14}H_{13}FNa^{+}$ [M + Na^{+}]: 223.0893, found: 223.0870.

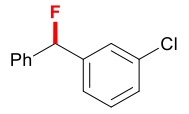
1-(fluoro(phenyl)methyl)-4-methoxybenzene



2j

The product **2j** was obtained in the crude reaction mixture (98 % ^{1}H NMR yield). **Crude ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.44 (d, *J* = 47.7 Hz, 1H). **Crude ^{19}F NMR** (376 MHz, Chloroform-*d*) δ -163.45 (d, *J* = 47.6 Hz). **HRMS** (ESI): m/z calcd. for $C_{14}H_{14}FO^{+}$ [M + H^{+}]: 217.1023, found: 217.1039.

1-chloro-3-(fluoro(phenyl)methyl)benzene

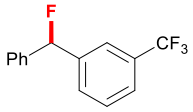


2k

The product **2k** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (84 % ^{1}H NMR yield, 13.5 mg, 61 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.39 – 7.19 (m, 9H), 6.41 (d, *J* = 47.2 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 142.2 (d, *J* = 22.5 Hz), 139.4 (d, *J* = 21.2 Hz), 134.8, 130.1, 129.1 (d, *J* = 2.3 Hz), 129.0, 128.8 (d, *J* = 1.8 Hz), 127.0 (d, *J* = 6.1 Hz), 126.8 (d, *J* = 6.9 Hz), 124.9 (d, *J* = 6.4 Hz), 94.0 (d, *J* = 174.4

Hz). **^{19}F NMR** (471 MHz, Chloroform-d) δ -167.56 (d, *J* = 47.0 Hz). **HRMS** (EI): m/z calcd. for $C_{13}H_{10}ClF$ [M]: 220.0455, found: 220.0452.

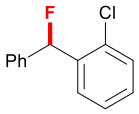
1-(fluoro(phenyl)methyl)-3-(trifluoromethyl)benzene



2l

The product **2l** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (56 % ^{1}H NMR yield, 11.9 mg, 47 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.56 (s, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.33 – 7.24 (m, 5H), 6.42 (d, *J* = 47.1 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.3 (d, *J* = 22.9 Hz), 139.2 (d, *J* = 21.2 Hz), 131.3 (q, *J* = 32.4 Hz), 130.0 (d, *J* = 6.4 Hz), 129.4, 129.3 (d, *J* = 2.3 Hz), 129.1, 127.1 (d, *J* = 6.0 Hz), 125.5 (dt, *J* = 5.5, 2.8 Hz), 124.3 (q, *J* = 272.4 Hz), 123.5 (dq, *J* = 7.6, 3.9 Hz), 94.1 (d, *J* = 174.5 Hz). **^{19}F NMR** (471 MHz, Chloroform-d) δ -62.64, -167.70 (d, *J* = 47.4 Hz). **HRMS** (ESI): m/z calcd. for $C_{14}H_{11}F_4^+$ [M + H^+]: 255.0791, found: 255.0774.

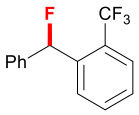
1-chloro-2-(fluoro(phenyl)methyl)benzene



2m

The product **2m** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.4) as a light yellow oily liquid (56 % ^{1}H NMR yield, 4.9 mg, 22 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.38 – 7.29 (m, 7H), 7.25 (td, *J* = 7.6, 1.8 Hz, 1H), 6.82 (d, *J* = 46.4 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 138.6 (d, *J* = 21.6 Hz), 137.7 (d, *J* = 23.4 Hz), 132.4 (d, *J* = 5.5 Hz), 129.9 (d, *J* = 3.0 Hz), 129.0 (d, *J* = 2.7 Hz), 128.8, 127.9 (d, *J* = 9.1 Hz), 127.4, 127.4, 127.4, 91.5 (d, *J* = 172.5 Hz). **^{19}F NMR** (471 MHz, Chloroform-d) δ -168.56 (d, *J* = 46.7 Hz). **HRMS** (EI): m/z calcd. for $C_{13}H_{10}ClF$ [M]: 220.0455, found: 220.0451.

1-(fluoro(phenyl)methyl)-2-(trifluoromethyl)benzene

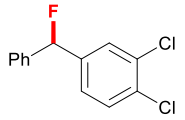


2n

The product **2n** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (41 % ^{1}H NMR yield, 7.6 mg, 30 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.56 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.39 – 7.27 (m, 5H), 6.90 (d, *J* = 46.7 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 139.5 (d, *J* = 22.2 Hz), 138.5 – 138.0 (m), 132.6, 129.5 (d, *J* = 8.1 Hz), 129.0 (d, *J* = 2.5 Hz), 128.9 (d, *J* = 2.8 Hz), 128.8, 127.0 (d, *J* = 6.7 Hz), 126.1 (q, *J* = 6.0 Hz), 124.4 (q, *J* = 273.6 Hz), 90.1 (dd, *J* = 171.4, 2.8 Hz).

^{19}F NMR (471 MHz, Chloroform-d) δ -57.87, -163.39 (d, *J* = 46.9 Hz). **HRMS** (EI): m/z calcd. for $C_{14}H_{10}F_4$ [M]: 254.0719, found: 254.0711.

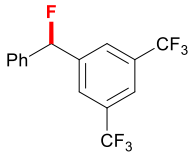
1,2-dichloro-4-(fluoro(phenyl)methyl)benzene



2o

The product **2o** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (48 % ^{1}H NMR yield, 9.4 mg, 37 % isolated yield). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.47 – 7.31 (m, 8H), 7.19 – 7.14 (m, 1H), 6.41 (d, *J* = 47.1 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.4 (d, *J* = 23.0 Hz), 139.0 (d, *J* = 21.1 Hz), 133.1, 132.8, 130.9, 129.3 (d, *J* = 2.2 Hz), 129.1, 128.7 (d, *J* = 7.1 Hz), 127.0 (d, *J* = 6.3 Hz), 126.0 (d, *J* = 6.4 Hz), 93.5 (d, *J* = 174.9 Hz). **^{19}F NMR** (565 MHz, Chloroform-d) δ -167.26 (d, *J* = 47.9 Hz). **HRMS** (EI): m/z calcd. for $C_{13}H_9Cl_2F$ [M]: 254.0065, found: 254.0058.

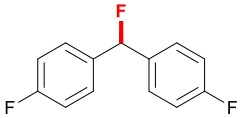
1-(fluoro(phenyl)methyl)-3,5-bis(trifluoromethyl)benzene



2p

The product **2p** was purified with silica gel chromatography (PE/EA = 100/1, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (37 % ^{1}H NMR yield, 9.3 mg, 29 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.85 (s, 1H), 7.80 (s, 1H), 7.46 – 7.38 (m, 3H), 7.36 – 7.30 (m, 3H), 6.54 (d, *J* = 46.8 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 142.9 (d, *J* = 23.6 Hz), 138.2 (d, *J* = 20.7 Hz), 132.3 (q, *J* = 33.5 Hz), 129.8 (d, *J* = 2.3 Hz), 129.4, 127.2 (d, *J* = 5.9 Hz), 126.9 – 126.3 (m), 123.5 (q, *J* = 272.8 Hz), 123.1 – 122.5 (m), 93.5 (d, *J* = 176.4 Hz). **^{19}F NMR** (471 MHz, Chloroform-d) δ -62.90, -168.30 (d, *J* = 46.8 Hz). **HRMS** (ESI): m/z calcd. for $C_{15}H_9F_7Na^+$ [M + Na^+]: 345.0485, found: 345.0505.

4,4'-(fluoromethylene)bis(fluorobenzene)

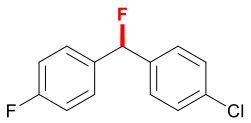


2q

The product **2q** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (96 % ^{1}H NMR yield, 20.2 mg, 91 % isolated yield). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 8.3, 5.4 Hz, 4H), 7.06 (t, *J* = 8.5 Hz, 4H), 6.43 (d, *J* = 47.4 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 163.9 (d, *J* = 2.4 Hz), 162.3 (d, *J* = 2.6 Hz), 135.8 (dd, *J* = 22.3, 3.3 Hz), 128.8 (dd, *J* = 8.3, 6.1 Hz), 115.9 (d, *J* = 21.7 Hz), 93.6 (d, *J* = 173.3 Hz). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -113.04, -163.16 (d, *J* = 47.8 Hz). **HRMS** (EI): m/z calcd. for $C_{14}H_{10}F_4$

[M]: 186.0845, found: 186.0839. **HRMS** (EI): m/z calcd. for $C_{13}H_9F_3$ [M]: 222.0656, found: 222.0651.

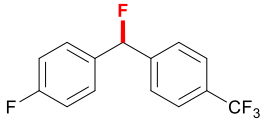
1-chloro-4-(fluoro(4-fluorophenyl)methyl)benzene



2r

The product **2r** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (86 % ^{1}H NMR yield, 18.6 mg, 78 % isolated yield). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.28 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.25 (d, *J* = 3.6 Hz, 2H), 7.06 (t, *J* = 8.5 Hz, 2H), 6.42 (d, *J* = 47.3 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 164.0 (d, *J* = 2.8 Hz), 162.3 (d, *J* = 2.7 Hz), 138.4 (d, *J* = 22.4 Hz), 135.5 (dd, *J* = 22.2, 3.3 Hz), 134.8 (d, *J* = 2.5 Hz), 129.1, 129.0 (dd, *J* = 8.5, 5.9 Hz), 128.1 (d, *J* = 6.3 Hz), 115.9 (d, *J* = 21.7 Hz), 93.5 (d, *J* = 173.6 Hz). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -112.75, -164.77 (d, *J* = 47.5 Hz). **HRMS** (EI): m/z calcd. for $C_{13}H_9ClF_2$ [M]: 238.0361, found: 238.0359.

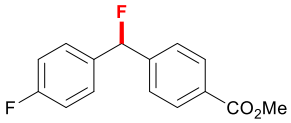
1-fluoro-4-(fluoro(4-(trifluoromethyl)phenyl)methyl)benzene



2s

The product **2s** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (59 % ^{1}H NMR yield, 13.9 mg, 51 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.30 (ddd, *J* = 8.8, 5.2, 1.6 Hz, 2H), 7.07 (t, *J* = 8.5 Hz, 2H), 6.48 (d, *J* = 47.2 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 164.0 (d, *J* = 2.7 Hz), 162.0 (d, *J* = 2.6 Hz), 143.5 (d, *J* = 22.7 Hz), 134.9 (dd, *J* = 21.6, 3.2 Hz), 131.4 – 130.0 (m), 128.9 (dd, *J* = 8.4, 5.8 Hz), 126.5 (d, *J* = 6.8 Hz), 125.6 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.2 Hz), 115.8 (d, *J* = 21.8 Hz), 93.1 (d, *J* = 175.0 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.67, -112.41 (tq, *J* = 9.4, 5.1 Hz), -166.80 (d, *J* = 47.3 Hz). **HRMS** (ESI): m/z calcd. for $C_{14}H_{10}F_5^+$ [M + H$^+$]: 273.0697, found: 273.0702.

methyl 4-(fluoro(4-fluorophenyl)methyl)benzoate

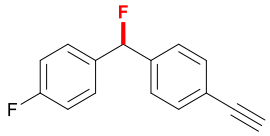


2t

The product **2t** was purified with silica gel chromatography (PE/EA = 10:1, Rf = 0.3) as a light yellow oily liquid (72 % ^{1}H NMR yield, 15.7 mg, 60 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.18 (m, 2H), 6.96 (t, *J* = 8.5 Hz, 2H), 6.39 (d, *J* = 47.2 Hz, 1H), 3.82 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.9, 164.2 (d, *J* = 2.7 Hz), 162.2 (d, *J* = 2.7 Hz), 144.7 (d, *J* = 22.4 Hz), 135.3 (dd, *J* = 21.6, 3.2 Hz), 130.5 (d, *J* = 1.8 Hz), 130.1, 129.2 (dd, *J* = 8.5, 5.7 Hz), 126.3 (d, *J* = 6.8 Hz), 116.0 (d, *J* = 21.8

Hz), 93.6 (d, *J* = 174.6 Hz), 52.5. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -112.56 (tq, *J* = 9.0, 4.8 Hz), -166.81 (d, *J* = 47.5 Hz). **HRMS** (EI): m/z calcd. for $C_{15}H_{12}F_2O_2$ [M]: 262.0805, found: 262.0797.

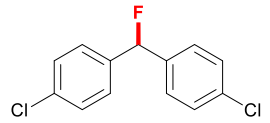
1-ethynyl-4-(fluoro(4-fluorophenyl)methyl)benzene



2u

The product **2u** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (69 % ^{1}H NMR yield, 10.5 mg, 46 % isolated yield). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.9 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.05 (t, *J* = 8.5 Hz, 1H), 6.43 (d, *J* = 47.3 Hz, 1H), 3.09 (s, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 164.0 (d, *J* = 2.6 Hz), 162.4, 140.5 (d, *J* = 22.2 Hz), 135.5 (dd, *J* = 21.8, 3.4 Hz), 132.6, 129.1 (dd, *J* = 8.4, 5.9 Hz), 126.6 (d, *J* = 6.6 Hz), 122.6, 115.9 (d, *J* = 21.7 Hz), 93.7 (d, *J* = 173.8 Hz), 83.4, 78.2. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -112.74, -165.73 (d, *J* = 47.7 Hz). **HRMS** (EI): m/z calcd. for $C_{15}H_{10}F_2$ [M]: 228.0751, found: 228.0749.

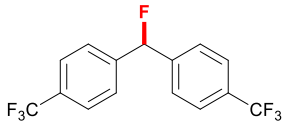
4,4'-(fluoromethylene)bis(chlorobenzene)



2v

The product **2v** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.4) as a light yellow oily liquid (82 % ^{1}H NMR yield, 18.4 mg, 72 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.55 – 7.15 (m, 8H), 6.40 (d, *J* = 47.2 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 138.1 (d, *J* = 22.1 Hz), 134.9 (d, *J* = 2.7 Hz), 129.1, 128.2 (d, *J* = 6.1 Hz), 93.4 (d, *J* = 174.4 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -166.49 (d, *J* = 47.1 Hz). **HRMS** (EI): m/z calcd. for $C_{13}H_9Cl_2F$ [M]: 254.0065, found: 254.0064.

4,4'-(fluoromethylene)bis((trifluoromethyl)benzene)

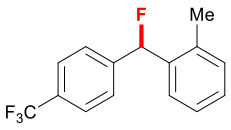


2w

The product **2w** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.5) as a light yellow oily liquid (43 % ^{1}H NMR yield, 11.9 mg, 37 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.1 Hz, 4H), 7.46 (d, *J* = 8.0 Hz, 4H), 6.55 (d, *J* = 46.9 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 143.1 (d, *J* = 21.5 Hz), 131.4 (q, *J* = 33.4 Hz), 129.6, 127.1 (d, *J* = 6.9 Hz), 126.1 (q, *J* = 4.0 Hz), 124.2 (q, *J* = 272.2 Hz), 93.3 (d, *J* = 176.1 Hz). **^{19}F NMR** (471

MHz, Chloroform-*d*) δ -62.77, -170.84 (d, *J* = 46.9 Hz). **HRMS** (ESI): m/z calcd. for $C_{15}H_9F_7$ [M]: 322.0592, found: 322.0586.

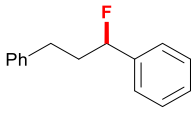
1-(fluoro(4-(trifluoromethyl)phenyl)methyl)-2-methylbenzene



2x

The product **2x** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (61 % ^{1}H NMR yield, 13.1 mg, 49 % isolated yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.08 (m, 4H), 6.58 (d, *J* = 47.0 Hz, 1H), 2.18 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.4 (d, *J* = 22.1 Hz), 137.0 (d, *J* = 19.5 Hz), 136.2 (d, *J* = 4.2 Hz), 131.2, 130.8 (qd, *J* = 32.4, 2.2 Hz), 129.3 (d, *J* = 2.2 Hz), 127.4 (dd, *J* = 7.2, 4.8 Hz), 126.6, 125.8 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.2 Hz), 92.1 (d, *J* = 173.0 Hz), 19.6. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.58, -169.49 (d, *J* = 46.8 Hz). **HRMS** (EI): m/z calcd. for $C_{15}H_{12}F_4$ [M]: 268.0875, found: 268.0868.

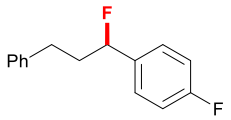
(1-fluoropropane-1,3-diyl)dibenzene



2y

The product **2y** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (58 % ^{1}H NMR yield, 10.1 mg, 47 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.39 – 7.26 (m, 8H), 7.22 – 7.17 (m, 3H), 5.43 (ddd, *J* = 47.9, 8.5, 4.4 Hz, 1H), 2.86 – 2.70 (m, 2H), 2.35 – 2.25 (m, 1H), 2.20 – 2.02 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.5, 140.5 (d, *J* = 19.8 Hz), 128.8, 128.6 (d, *J* = 1.9 Hz), 126.4, 125.9 (d, *J* = 6.7 Hz), 94.0 (d, *J* = 170.9 Hz), 39.2 (d, *J* = 23.9 Hz), 31.7 (d, *J* = 4.3 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -175.98 (ddd, *J* = 46.8, 30.1, 16.1 Hz). **HRMS** (ESI): m/z calcd. for $C_{15}H_{16}F^+$ [M + H^+]: 215.1231, found: 215.1260.

1-fluoro-4-(1-fluoro-3-phenylpropyl)benzene

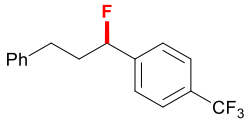


2z

The product **2z** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (57 % ^{1}H NMR yield, 11.4 mg, 49 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 4H), 7.23 – 7.18 (m, 3H), 7.06 (t, *J* = 8.6 Hz, 2H), 5.40 (ddd, *J* = 47.6, 8.6, 4.4 Hz, 1H), 2.85 – 2.69 (m, 2H), 2.37 – 2.01 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 164.0, 162.0, 141.3, 136.3 (dd, *J* = 20.2, 3.2 Hz), 128.8 (d, *J* = 9.1 Hz), 127.8 (dd, *J* = 8.2, 6.5 Hz), 126.5, 115.8 (d, *J* = 21.5 Hz), 93.4 (d, *J* = 171.0 Hz), 39.1 (d, *J* = 23.9 Hz), 31.6 (d, *J* = 4.2

Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -113.69 (td, *J* = 8.7, 4.7 Hz), -173.80 (ddd, *J* = 46.2, 29.8, 15.3 Hz). **HRMS** (EI): m/z calcd. for $C_{15}H_{14}F_2$ [M]: 232.1064, found: 232.1055.

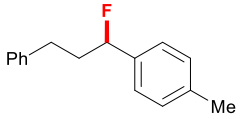
1-(1-fluoro-3-phenylpropyl)-4-(trifluoromethyl)benzene



2aa

The product **2aa** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (38 % ^{1}H NMR yield, 9.3 mg, 33 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.19 (m, 2H), 7.16 – 7.10 (m, 3H), 5.41 (ddd, *J* = 47.7, 8.7, 4.1 Hz, 1H), 2.77 – 2.65 (m, 2H), 2.29 – 1.97 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 144.6 (d, *J* = 19.9 Hz), 141.0, 130.8 (q, *J* = 32.6 Hz), 128.9 (dd, *J* = 15.2, 4.8 Hz), 126.6, 126.0 (d, *J* = 7.4 Hz), 125.8 (q, *J* = 3.8 Hz), 93.0 (d, *J* = 173.2 Hz), 39.2 (d, *J* = 23.2 Hz), 31.4 (d, *J* = 4.1 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.60, -180.18 (ddd, *J* = 47.6, 30.8, 16.8 Hz). **HRMS** (EI): m/z calcd. for $C_{16}H_{14}F_4$ [M]: 282.1032, found: 282.1023.

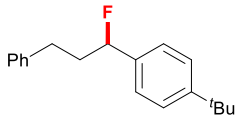
1-(1-fluoro-3-phenylpropyl)-4-methylbenzene



2ab

The product **2ab** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (68 % ^{1}H NMR yield, 14.4 mg, 63 % isolated yield). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.37 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.33 – 7.23 (m, 7H), 5.47 (ddd, *J* = 47.9, 8.5, 4.5 Hz, 1H), 2.93 – 2.77 (m, 2H), 2.43 (s, 3H), 2.41 – 2.34 (m, 1H), 2.25 – 2.11 (m, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.5, 138.4 (d, *J* = 2.1 Hz), 137.4 (d, *J* = 20.0 Hz), 129.5, 128.8, 126.3, 126.0 (d, *J* = 6.4 Hz), 93.9 (d, *J* = 169.9 Hz), 39.0 (d, *J* = 24.2 Hz), 31.7 (d, *J* = 4.3 Hz), 21.5. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -173.52 (ddd, *J* = 46.8, 29.8, 14.4 Hz). **HRMS** (ESI): m/z calcd. for $C_{16}H_{18}F^+$ [M + H$^+$]: 229.1387, found: 229.1402.

1-(tert-butyl)-4-(1-fluoro-3-phenylpropyl)benzene

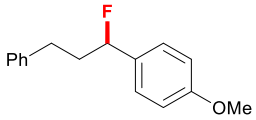


2ac

The product **2ac** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (67 % ^{1}H NMR yield, 11.9 mg, 44 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.34 – 7.30 (m, 2H), 7.22 – 7.18 (m, 4H), 7.15 – 7.12 (m, 3H), 5.33 (ddd, *J* = 47.9, 8.6, 4.4 Hz, 1H), 2.79 – 2.65 (m, 2H), 2.32 – 2.18 (m, 1H), 2.12 – 1.99 (m, 1H), 1.25 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.6, 137.4 (d, *J* = 19.9 Hz), 128.8 (d, *J* = 1.9 Hz), 126.3, 125.8 (d, *J* = 6.4 Hz), 125.7, 94.0 (d, *J* = 169.8 Hz), 38.9 (d, *J* = 24.1 Hz), 31.8 – 31.2 (m). **^{19}F NMR** (471

MHz, Chloroform-*d*) δ -173.90 (ddd, *J* = 46.8, 30.1, 15.4 Hz). **HRMS** (EI): m/z calcd. for $C_{19}H_{23}F$ [M]: 270.1784, found: 270.1776.

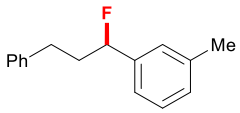
1-(1-fluoro-3-phenylpropyl)-4-methoxybenzene



2ad

The product **2ad** was obtained in the crude reaction mixture (44 % ^{1}H NMR yield). **Crude ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.36 (ddd, *J* = 47.8, 8.4, 4.8 Hz, 1H). **Crude ^{19}F NMR** (376 MHz, Chloroform-*d*) δ -170.10 (ddd, *J* = 48.0, 28.6, 14.6 Hz). **HRMS** (ESI): m/z calcd. for $C_{16}H_{18}FO^+$ [M + H^+]: 245.1336, found: 245.1344.

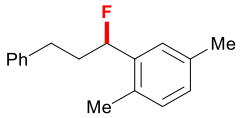
1-(1-fluoro-3-phenylpropyl)-3-methylbenzene



2ae

The product **2ae** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (72 % ^{1}H NMR yield, 14.6 mg, 64 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.25 – 7.01 (m, 9H), 5.31 (ddd, *J* = 47.9, 8.6, 4.4 Hz, 1H), 2.78 – 2.61 (m, 2H), 2.28 (s, 3H), 2.27 – 2.15 (m, 1H), 2.11 – 1.94 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.5, 140.4 (d, *J* = 19.4 Hz), 138.5, 129.4 (d, *J* = 2.2 Hz), 128.8, 128.7, 126.6 (d, *J* = 6.8 Hz), 126.4, 123.0 (d, *J* = 6.7 Hz), 94.1 (d, *J* = 170.7 Hz), 39.1 (d, *J* = 23.9 Hz), 31.7 (d, *J* = 4.2 Hz), 21.8. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -175.55 (ddd, *J* = 46.9, 30.1, 15.7 Hz). **HRMS** (ESI): m/z calcd. for $C_{16}H_{17}FNa^+$ [M + Na^+]: 251.1206, found: 251.1256.

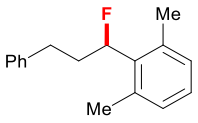
2-(1-fluoro-3-phenylpropyl)-1,4-dimethylbenzene



2af

The product **2af** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (57 % ^{1}H NMR yield, 10.4 mg, 43 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.24 – 7.19 (m, 2H), 7.16 – 7.11 (m, 4H), 6.94 (d, *J* = 1.2 Hz, 2H), 5.52 (ddd, *J* = 47.6, 9.1, 3.5 Hz, 1H), 2.82 (ddd, *J* = 14.3, 9.7, 4.9 Hz, 1H), 2.71 (ddd, *J* = 13.9, 9.4, 7.3 Hz, 1H), 2.25 (s, 3H), 2.23 – 2.14 (m, 1H), 2.09 (s, 3H), 2.05 – 1.90 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.5, 138.5 (d, *J* = 18.4 Hz), 136.0, 131.4 (d, *J* = 5.2 Hz), 130.7, 129.1 (d, *J* = 2.0 Hz), 128.8 (d, *J* = 2.5 Hz), 126.4, 126.1 (d, *J* = 8.3 Hz), 91.4 (d, *J* = 169.4 Hz), 38.3 (d, *J* = 24.2 Hz), 32.0 (d, *J* = 3.2 Hz), 21.4, 18.6. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -179.42 (ddd, *J* = 48.5, 33.3, 16.2 Hz). **HRMS** (ESI): m/z calcd. for $C_{17}H_{20}F^+$ [M + H^+]: 243.1544, found: 243.1537.

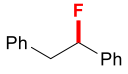
2-(1-fluoro-3-phenylpropyl)-1,3-dimethylbenzene



2ag

The product **2ag** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (60 % ^{1}H NMR yield, 13.8 mg, 57 % isolated yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.10 (m, 3H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 2H), 5.71 (ddd, *J* = 47.5, 10.2, 3.5 Hz, 1H), 2.89 (ddd, *J* = 14.0, 9.3, 4.7 Hz, 1H), 2.71 (dt, *J* = 13.8, 8.3 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.22 (s, 6H), 1.96 – 1.79 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.4, 136.3 (d, *J* = 17.5 Hz), 135.9 (d, *J* = 3.5 Hz), 129.5, 128.8 (d, *J* = 6.0 Hz), 128.1, 126.4, 92.0 (d, *J* = 170.5 Hz), 36.5 (d, *J* = 23.4 Hz), 32.3 (d, *J* = 3.2 Hz), 20.6 (d, *J* = 3.8 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -183.92 (ddd, *J* = 47.2, 34.1, 12.1 Hz). **HRMS** (ESI): m/z calcd. for $C_{17}H_{20}F^{+}$ [M + H^{+}]: 243.1544, found: 243.1591.

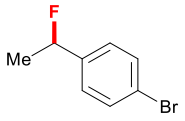
(1-fluoroethane-1,2-diyl)dibenzene



2ah

The product **2ah** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.3) as a light yellow oily liquid (47 % ^{1}H NMR yield, 6.6 mg, 33 % isolated yield). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.41 – 7.30 (m, 7H), 7.29 – 7.25 (m, 1H), 7.21 (d, *J* = 8.6 Hz, 2H), 5.69 (dd, *J* = 8.2, 4.8 Hz, 1H), 3.30 (ddd, *J* = 17.4, 14.3, 8.2 Hz, 1H), 3.14 (ddd, *J* = 28.8, 14.3, 4.8 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.1 (d, *J* = 20.1 Hz), 137.0 (d, *J* = 4.1 Hz), 129.8, 128.7 (d, *J* = 2.8 Hz), 127.0, 126.0 (d, *J* = 6.6 Hz), 95.2 (d, *J* = 174.1 Hz), 44.3 (d, *J* = 24.4 Hz). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -173.01 (ddd, *J* = 47.8, 29.0, 17.3 Hz). **HRMS** (EI): m/z calcd. for $C_{14}H_{13}F$ [M]: 200.0992, found: 200.1001.

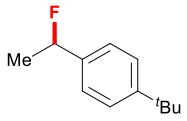
1-bromo-4-(1-fluoroethyl)benzene



2ai

The product **2ai** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.6) as a light yellow oily liquid (41 % ^{1}H NMR yield, 5.9 mg, 29 % isolated yield). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.52 – 7.47 (m, 2H), 7.24 – 7.19 (m, 2H), 5.57 (dq, *J* = 47.5, 6.4 Hz, 1H), 1.61 (dd, *J* = 23.9, 6.4 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.8 (d, *J* = 20.1 Hz), 132.0, 127.3 (d, *J* = 6.6 Hz), 122.4 (d, *J* = 2.6 Hz), 90.6 (d, *J* = 168.6 Hz), 23.2 (d, *J* = 25.2 Hz). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -167.92 (dq, *J* = 49.2, 25.3 Hz). **HRMS** (ESI): m/z calcd. for $C_{8}H_{9}BrF^{+}$ [M + H^{+}]: 202.9866, found: 202.9827.

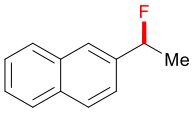
1-(tert-butyl)-4-(1-fluoroethyl)benzene



2aj

The product **2aj** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.5) as a light yellow oily liquid (77 % ^{1}H NMR yield, 9.9 mg, 55 % isolated yield). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.44 – 7.39 (m, 2H), 7.30 (dd, *J* = 8.4, 1.5 Hz, 2H), 5.61 (dq, *J* = 47.8, 6.4 Hz, 1H), 1.65 (dd, *J* = 23.8, 6.4 Hz, 3H), 1.33 (s, 9H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 151.6, 138.7 (d, *J* = 19.5 Hz), 125.7, 125.5 (d, *J* = 6.4 Hz), 91.2 (d, *J* = 166.2 Hz), 34.9, 31.7, 23.0 (d, *J* = 25.4 Hz). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -164.81 (dq, *J* = 49.8, 25.1 Hz). **HRMS** (EI): m/z calcd. for $C_{12}H_{17}F$ [M]: 180.1314, found: 180.1305.

2-(1-fluoroethyl)naphthalene



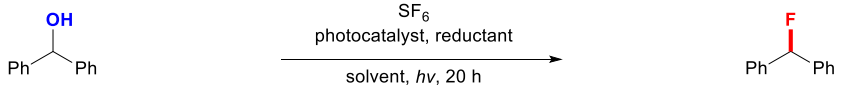
2ak

The product **2ak** was purified with silica gel chromatography (n-hexane, 40 ˚C, Rf = 0.6) as a light yellow oily liquid (67 % ^{1}H NMR yield, 9.0 mg, 52 % isolated yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 – 7.74 (m, 4H), 7.55 – 7.43 (m, 3H), 5.79 (dq, *J* = 47.6, 6.4 Hz, 1H), 1.72 (dd, *J* = 23.8, 6.4 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 137.8 (d, *J* = 19.3 Hz), 132.2, 132.1, 127.4, 127.1, 126.7, 125.2 (d, *J* = 14.8 Hz), 123.1 (d, *J* = 7.9 Hz), 122.1 (d, *J* = 5.8 Hz), 90.1 (d, *J* = 167.8 Hz), 21.9 (d, *J* = 25.3 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -166.98 (dq, *J* = 47.5, 23.9 Hz). HRMS (ESI): m/z calcd. for C12H12F^{+} [M + H^{+}]: 175.0918, found: 175.0910.

3. Additional experiments

3.1 Condition screening

Table SI-1. Control Experiments

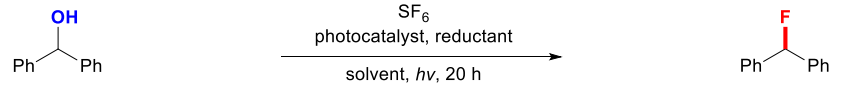


1a **2a**

entry	photocatalyst	reductant	atmosphere	yield
1	w/o	DIPEA	SF_6	N.D.
2	4CzIPN	w/o	SF_6	trace
3	4CzIPN	DIPEA	N_2	N.D.
4[b]	4CzIPN	DIPEA	N_2	19 %
5[b]	w/o	w/o	N_2	40 %

a. Unless otherwise noted, the reaction conditions were as follows: **1a** (0.1 mmol, 1.0 equiv.), SF_6 (0.3 mmol, 3.0 equiv., 7 mL), 4CzIPN (5 mol %), DIPEA (1 mmol, 10 equiv.), DCE (3.0 mL), 450 nm (18 W), 50 °C, 20 h, ^1H NMR yield, CH_2Br_2 as internal standard substance. b. DAST (0.2 mmol, 2.0 equiv.) was added.

Table SI-2. Fine Condition Screening



1a **2a**

entry	DIPEA	4CzIPN	DIPEA : 4CzIPN	**2a**
1	5.0 equiv	5 mol %	100	38 %
2	15.0 equiv.	5 mol %	300	83 %
3	15.0 equiv.	10 mol %	100	62 %
4	10.0 equiv.	1 mol %	1000	77 %
5	12.5 equiv.	1 mol %	1250	85 %
6	15.0 equiv.	1 mol %	1500	86 %
7	17.5 equiv.	1 mol %	1750	88 %
8	21.25 equiv.	1 mol %	2125	95 %
9	12.5 equiv.	0.5 mol %	2500	88 %
10	15.0 equiv.	0.5 mol %	3000	83 %
11	17.5 equiv.	0.5 mol %	3500	79 %

a. Unless otherwise noted, the reaction conditions were as follows: **1a** (0.1 mmol, 1.0 equiv.), SF_6 (0.3 mmol, 3.0 equiv., 7 mL), 4CzIPN (5 mol %), DIPEA (1 mmol, 10 equiv.), DCE (3.0 mL), 450 nm (18 W), 50 °C, 20 h, ^1H NMR yield, CH_2Br_2 as internal standard substance. b. DAST (0.2 mmol, 2.0 equiv.) was added.

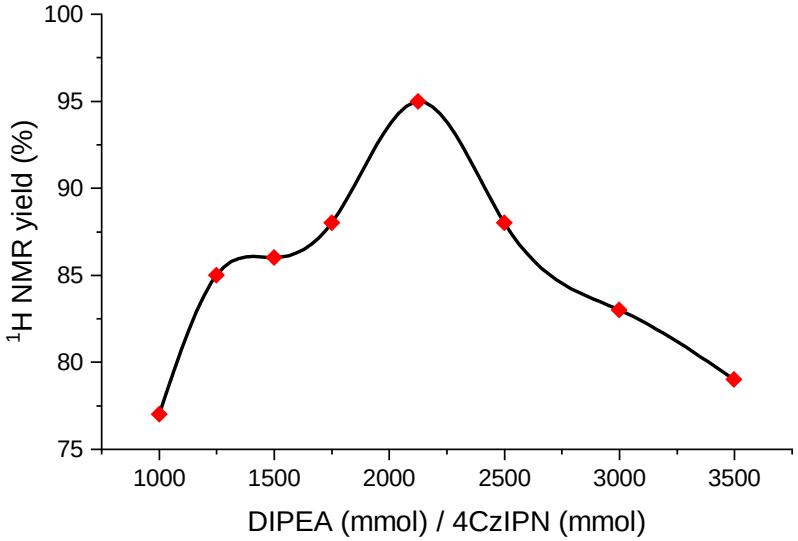
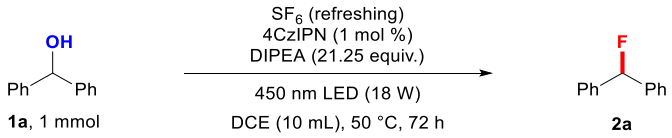


Figure SI-1. Photocatalyst / reductant ratio - yield plot.

3.2 Synthetic Utility

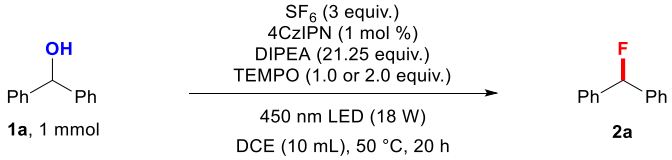
1 mmol scale reaction



In a 20 mL glass vial, 4CzIPN (7.9 mg, 0.01 mmol, 1 mol %), DIPEA (2.7460 g, 21.25 mmol, 21.25 equiv.) and benzyl alcohol **1** (0.1842 g, 1.0 mmol, 1.0 equiv.) were dissolved in DCE (10 mL). An oven-dried 50 mL Schlenk tube was evacuated and backfilled with SF_6 (repeated for 5 times), followed by filling in the mixture solution via syringe. The tube was sealed with a Teflon lined cap and stirred under visible light source (450 nm, 18 W) at 50 ˚C for 72 h. SF_6 was supplemented by balloon and syringe every 12 h until reaction time reached 72 h. The reaction mixture was concentrated *in vacuo*, then dissolved in $CDCl_3$ (0.5 mL) to measure ^{1}H NMR yield with CH_2Br_2 (87.0 mg, 0.5 mmol) as the internal standard substance. The result showed a 92 % yield in ^{1}H NMR spectrum.

3.3 Mechanistic study

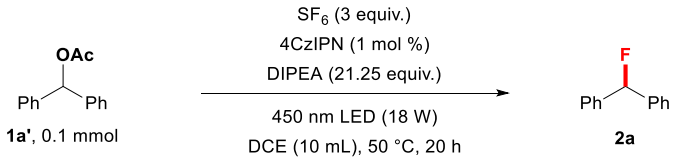
Radical trapping with TEMPO



In a 10 mL glass vial, 4CzIPN (0.79 mg, 0.001 mmol, 1 mol %), DIPEA (0.2746 g, 2.125 mmol, 21.25 equiv.) **1a** (0.0184 g, 0.1 mmol, 1.0 equiv.) and TEMPO (0.1 mmol, 1.0 equiv.; 0.2 mmol, 2.0 equiv.) were dissolved in DCE (3 mL). An oven-dried 10 mL Schlenk tube was evacuated and backfilled with SF_6 (repeated for 5 times), followed by filling in the mixture solution via syringe.

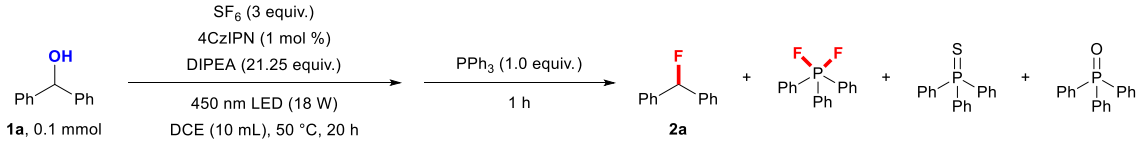
The tube was sealed with a Teflon lined cap and stirred under visible light source (450 nm, 18 W) at 50 ˚C for 20 h. The reaction mixture was concentrated *in vacuo*, then dissolved in $CDCl_3$ (0.5 mL) to measure ^1H NMR yield with CH_2Br_2 (17.4 mg, 0.1 mmol) as the internal standard substance. The yield did not show a significant reduction in the presence of the radical trapping agent (97 %, 89 % ^1H NMR yield).

Hydroxyl protection

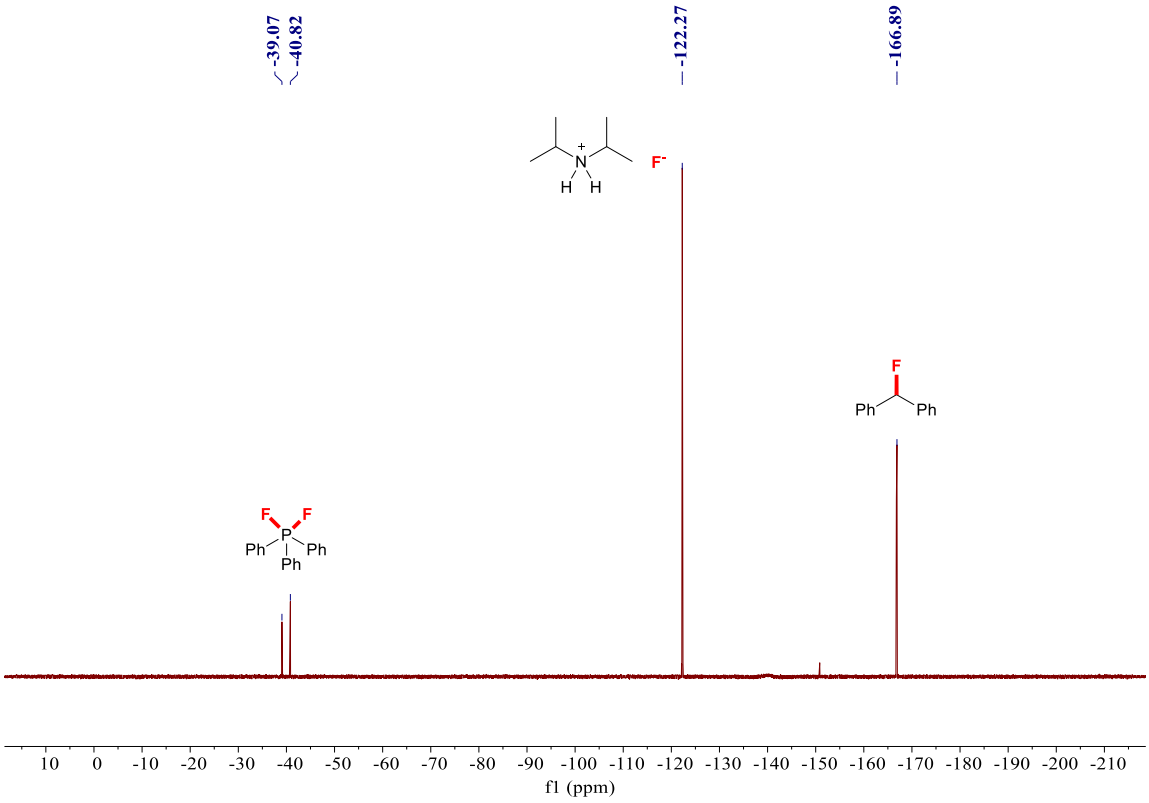


In a 10 mL glass vial, 4CzIPN (0.79 mg, 0.001 mmol, 1 mol %), DIPEA (0.2746 g, 2.125 mmol, 21.25 equiv.) and **1a'** (0.0226 g, 0.1 mmol, 1.0 equiv.) were dissolved in DCE (3 mL). An oven-dried 10 mL Schlenk tube was evacuated and backfilled with SF_6 (repeated for 5 times), followed by filling in the mixture solution via syringe. The tube was sealed with a Teflon lined cap and stirred under visible light source (450 nm, 18 W) at 50 ˚C for 20 h. The reaction mixture was concentrated *in vacuo*, then dissolved in $CDCl_3$ (0.5 mL) to measure ^1H NMR and ^{19}F NMR was conducted with CH_2Br_2 and $PhCF_3$ as the internal standard substance. The result showed no signal of expected product was detected.

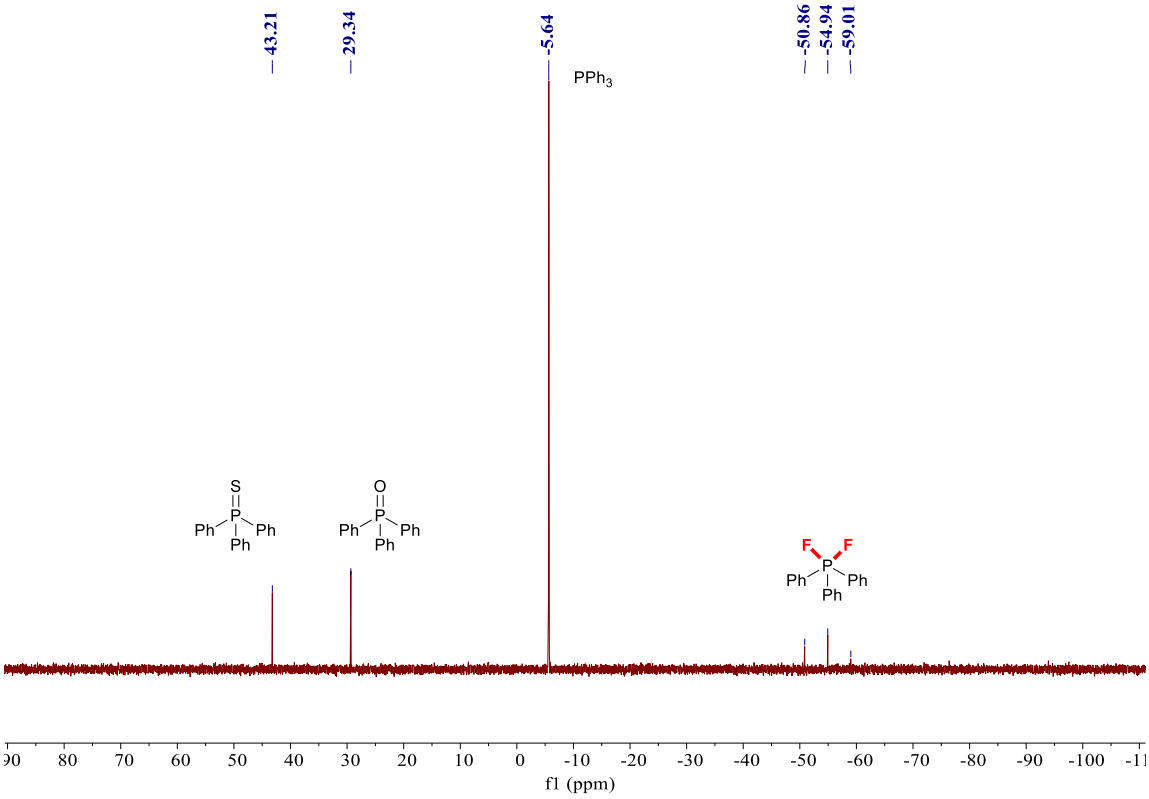
Fluorination reagent capture



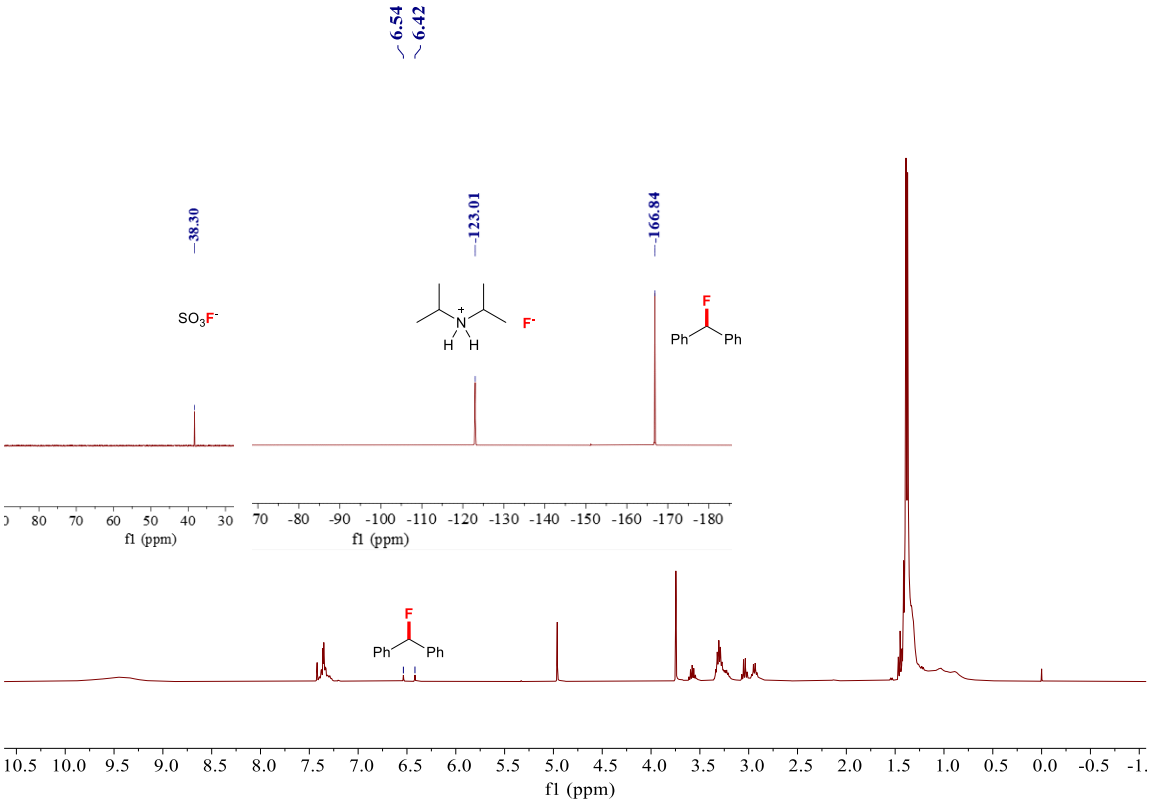
In a 10 mL glass vial, 4CzIPN (0.79 mg, 0.001 mmol, 1 mol %), DIPEA (0.2746 g, 2.125 mmol, 21.25 equiv.) and **1a** (0.0184 g, 0.1 mmol, 1.0 equiv.) were dissolved in DCE (3 mL). An oven-dried 10 mL Schlenk tube was evacuated and backfilled with SF_6 (repeated for 5 times), followed by filling in the mixture solution via syringe. The tube was sealed with a Teflon lined cap and stirred under visible light source (450 nm, 18 W) at 50 ˚C for 20 h. After completion, PPh_3 (0.1 mmol, 1.0 equiv.) was added into the mixture and stirred for another 1 h. The mixture was concentrated *in vacuo*, then dissolved in $CDCl_3$ (0.5 mL) for ^{19}F NMR and ^{31}P NMR analysis to detect possible derivatives from PPh_3. The result indicated that the *in situ* generated active species were smoothly captured. Another blank experiment without adding PPh_3 was conducted to analysis the NMR signals of the crude reaction mixture. SO_3F^- was deduced according to previous report (P. Nagorny, *Org. Lett.*, **2020**, 23, 190-194).



Crude ^{19}F NMR (376 MHz, $CDCl_3$) of products deriving from PPh_3

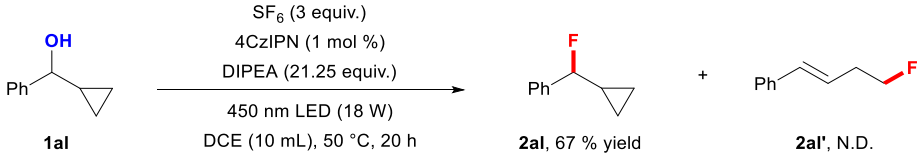


Crude ^{31}P NMR (162 MHz, $CDCl_3$) of products deriving from PPh_3



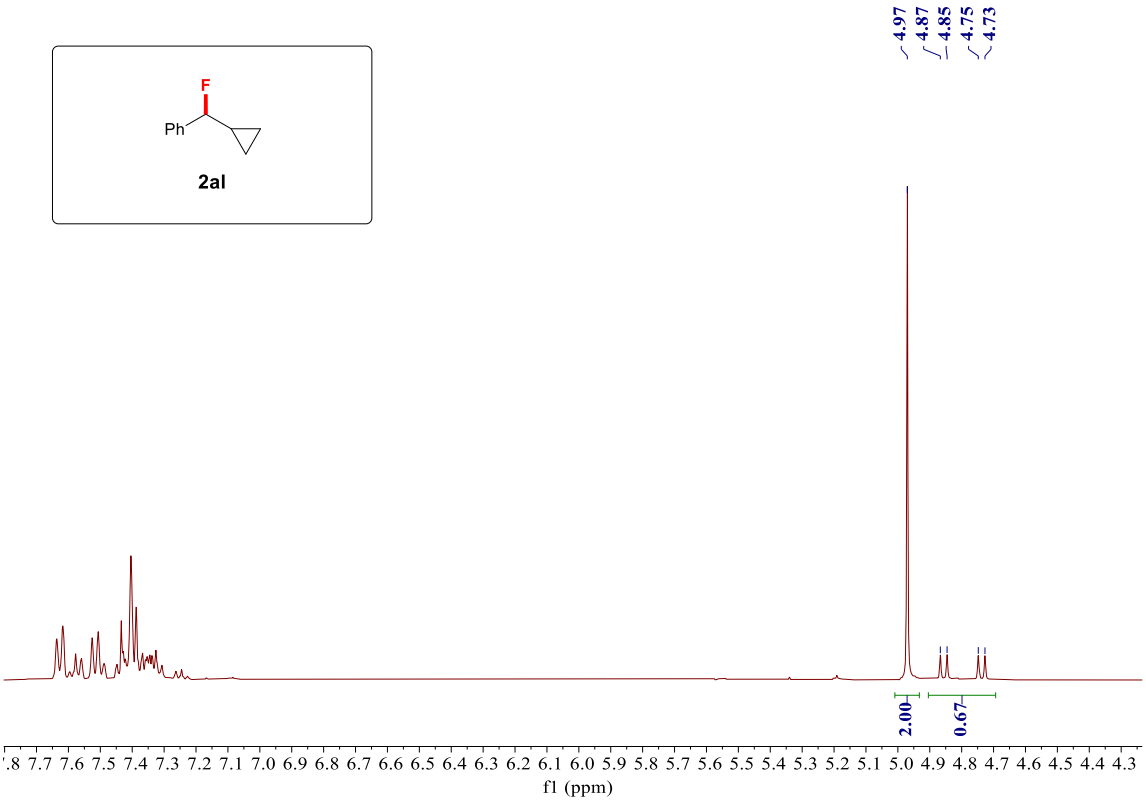
Crude ^{1}H, ^{19}F NMR analysis of reaction without PPh_3 addition

Radical clock experiment

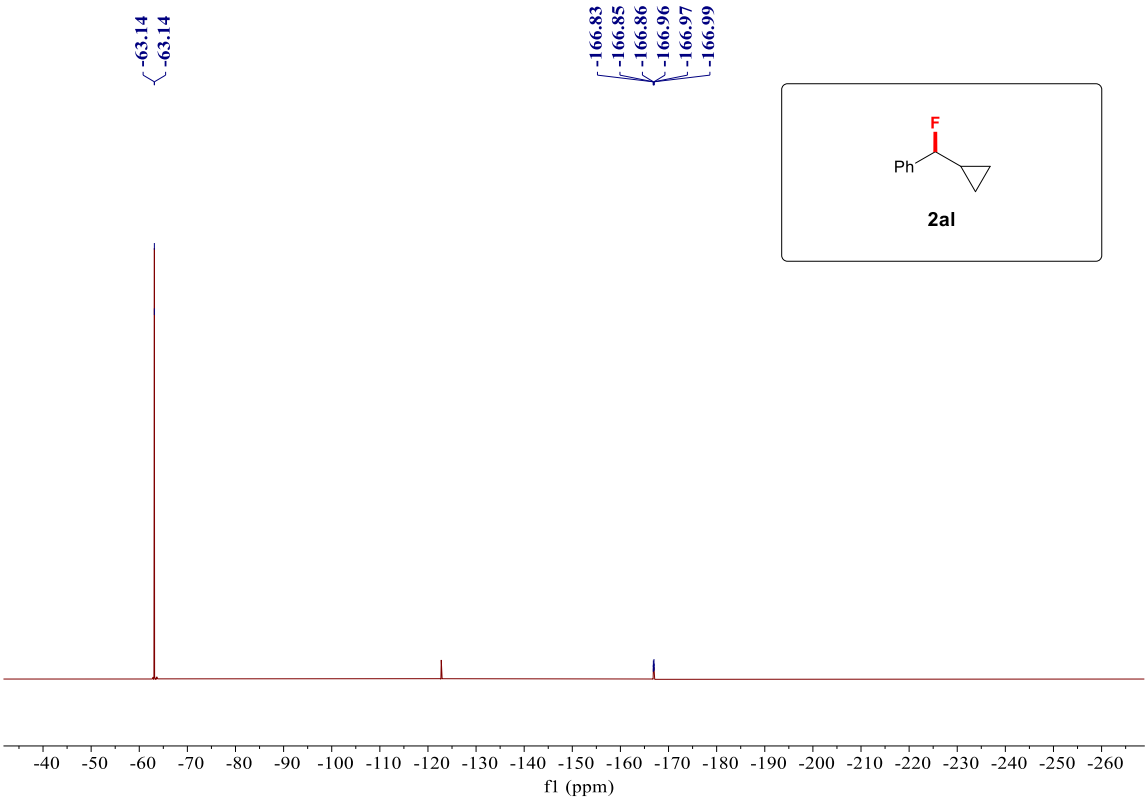


1al **2al**, 67 % yield **2al'**, N.D.

In a 10 mL glass vial, 4CzIPN (0.79 mg, 0.001 mmol, 1 mol %), DIPEA (0.2746 g, 2.125 mmol, 21.25 equiv.) and **1ai** (0.0148 g, 0.1 mmol, 1.0 equiv.) were dissolved in DCE (3 mL). An oven-dried 10 mL Schlenk tube was evacuated and backfilled with SF_6 (repeated for 5 times), followed by filling in the mixture solution via syringe. The tube was sealed with a Teflon lined cap and stirred under visible light source (450 nm, 18 W) at 50 ˚C for 20 h. The reaction mixture was concentrated *in vacuo*, then dissolved in $CDCl_3$ (0.5 mL) to measure ^{1}H NMR yield with CH_2Br_2 and as the internal standard substance. The result showed a 67 % ^{1}H NMR yield, and no signal of ring-opening product was detected.

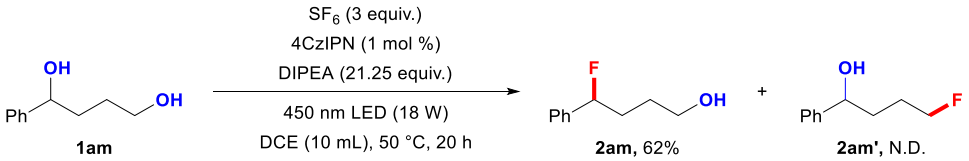


Crude ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2ai** reaction mixture

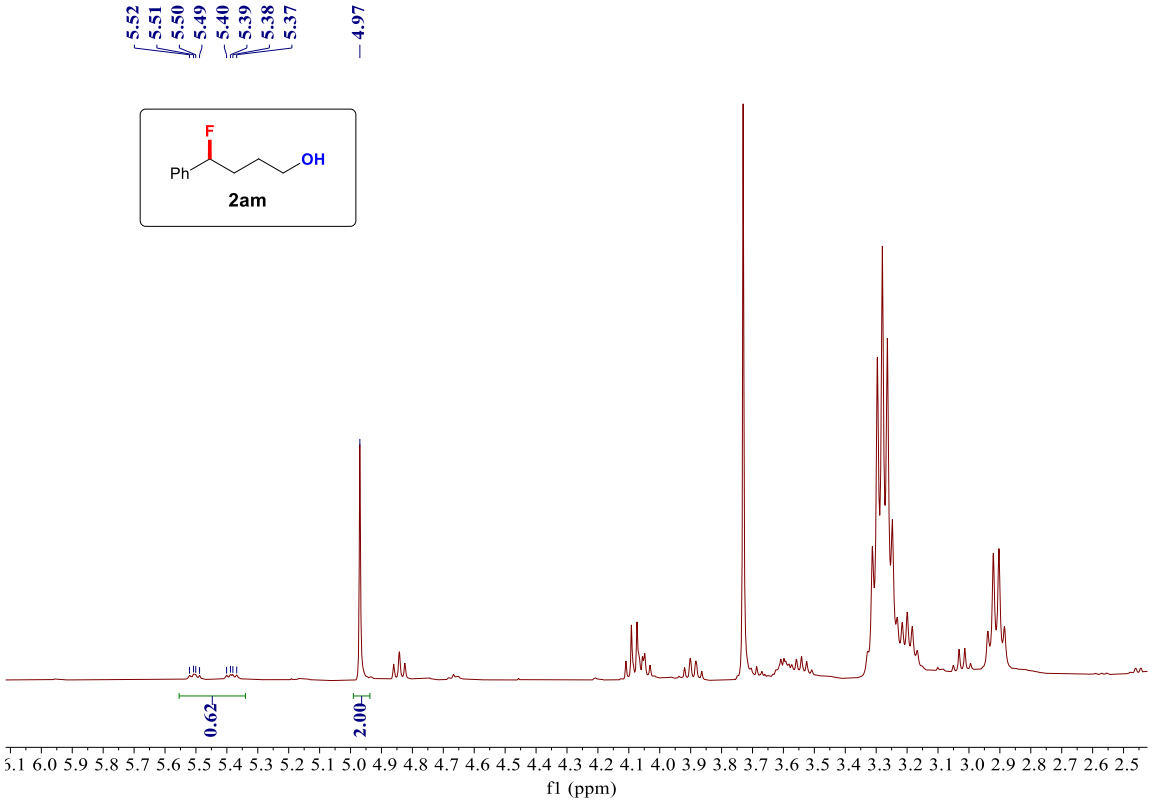


Crude ^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **2ai** reaction mixture

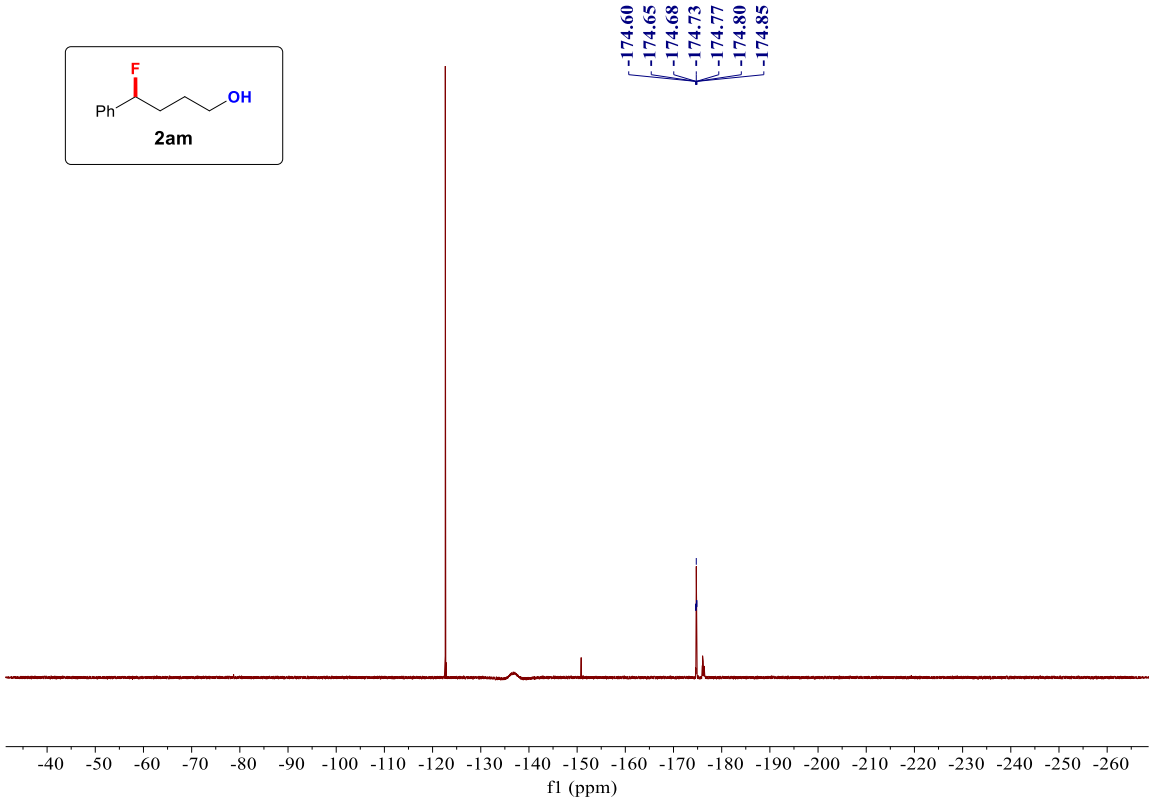
Regioselectivity experiment



In a 10 mL glass vial, 4CzIPN (0.79 mg, 0.001 mmol, 1 mol %), DIPEA (0.2746 g, 2.125 mmol, 21.25 equiv.) and **1am** (0.0166 g, 0.1 mmol, 1.0 equiv.) were dissolved in DCE (3 mL). An oven-dried 10 mL Schlenk tube was evacuated and backfilled with SF_6 (repeated for 5 times), followed by filling in the mixture solution via syringe. The tube was sealed with a Teflon lined cap and stirred under visible light source (450 nm, 18 W) at 50 ˚C for 20 h. The reaction mixture was concentrated *in vacuo*, then dissolved in $CDCl_3$ (0.5 mL) to measure ^1H NMR yield with CH_2Br_2 and as the internal standard substance. The result showed a 62 % ^1H NMR yield for benzyl fluoride, and no crude ^{19}F NMR signal of terminal alkyl fluoride was detected.



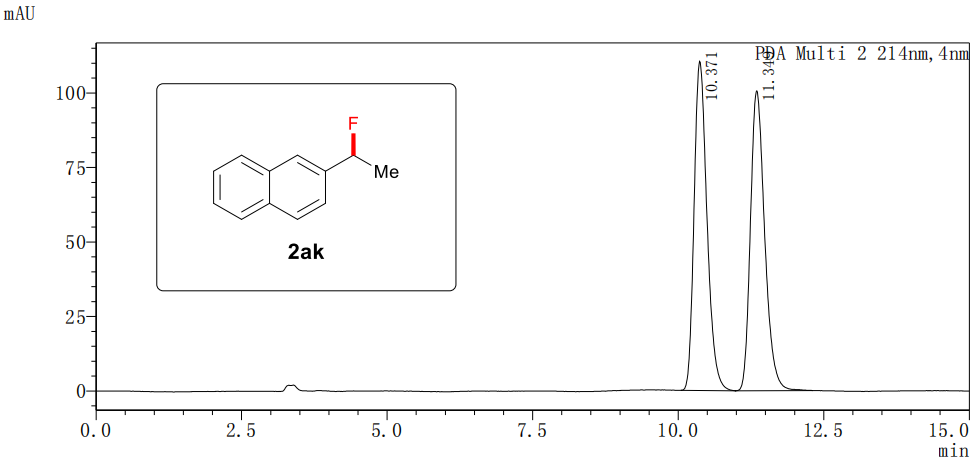
The Yield of **2am** Based on ^1H NMR (400 MHz, $CDCl_3$) Spectrum



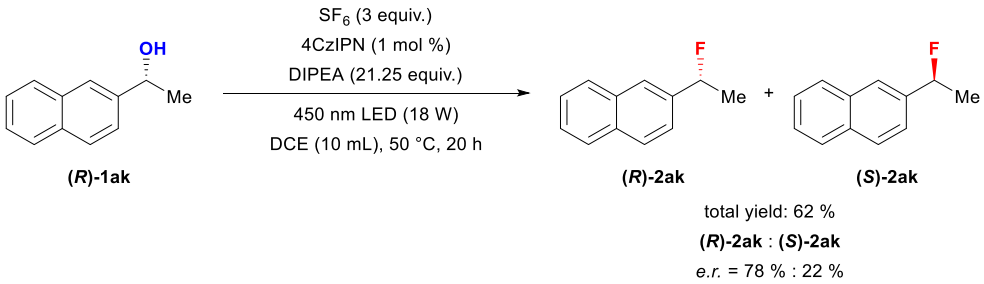
Crude ^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **2am** reaction mixture

Chiral substitution experiment

In a 10 mL glass vial, 4CzIPN (0.79 mg, 0.001 mmol, 1 mol %), DIPEA (0.2746 g, 2.125 mmol, 21.25 equiv.) and **1ak** (0.0172 g, 0.1 mmol, 1.0 equiv.) were dissolved in DCE (3 mL). An oven-dried 10 mL Schlenk tube was evacuated and backfilled with SF_6 (repeated for 5 times), followed by filling in the mixture solution via syringe. The tube was sealed with a Teflon lined cap and stirred under visible light source (450 nm, 18 W) at 50 ˚C for 20 h. The reaction mixture was concentrated *in vacuo*, then dissolved in $CDCl_3$ (0.5 mL) to measure ^1H NMR yield with CH_2Br_2 (17.4 mg, 0.1 mmol) as the internal standard substance. Then the product was obtained by dual-step flash column chromatography on silica gel (Rf = 0.6, n-hexane, 40 ˚C), then subject to chiral HPLC analysis for determination of the retention time.



Peak#	Ret. Time	Area	Area%
1	10.371	1706093	49.840
2	11.349	1717029	50.160
Total		3423122	100.000



In a 10 mL glass vial, 4CzIPN (0.79 mg, 0.001 mmol, 1 mol %), DIPEA (0.2746 g, 2.125 mmol, 21.25 equiv.) and **(*R*)-1ak** (0.0172 g, 0.1 mmol, 1.0 equiv.) were dissolved in DCE (3 mL). An oven-dried 10 mL Schlenk tube was evacuated and backfilled with SF_6 (repeated for 5 times), followed by filling in the mixture solution via syringe. The tube was sealed with a Teflon lined cap and stirred under visible light source (450 nm, 18 W) at 50 ˚C for 20 h. The reaction mixture was concentrated *in vacuo*, then dissolved in $CDCl_3$ (0.5 mL) to measure ^1H NMR yield with CH_2Br_2 (7.0 mg, 0.04 mmol) as the internal standard substance. Then the product was obtained by dual-step flash column chromatography on silica gel (Rf = 0.6, n-hexane, 40 ˚C), then subject to chiral HPLC analysis for determination of the *e.r.* value. we found that the reaction obtained 78 % chiral retention and 22 % chiral flip.

Upon analysis, we proposed the explanation for this reaction based on reported literatures (H. M. Bell et al., *J. Fluorine Chem.*, **1980**, 15, 191; A.I. Burmakov et al., *J. Fluorine Chem.*, **1981**, 19, 151). when SF_4 is used for alcohol deoxyfluorination, a C-O-S-F four-membered cyclic intermediate is often formed, thus completing the substitution via the S_Ni mechanism. In addition, a minority amount of racemization occurred probably through the S_N2 mechanism in which the fluorine ion attacks from the backside.

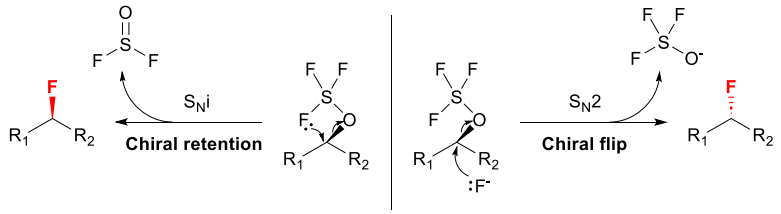
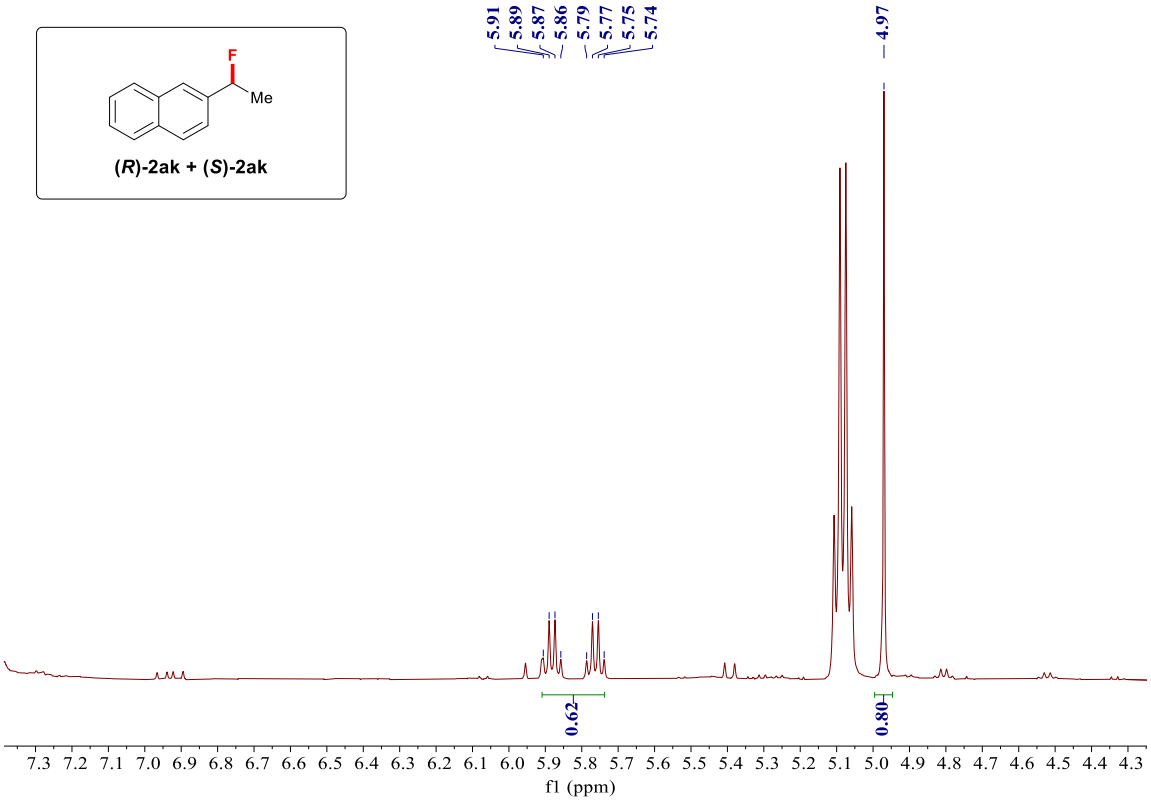
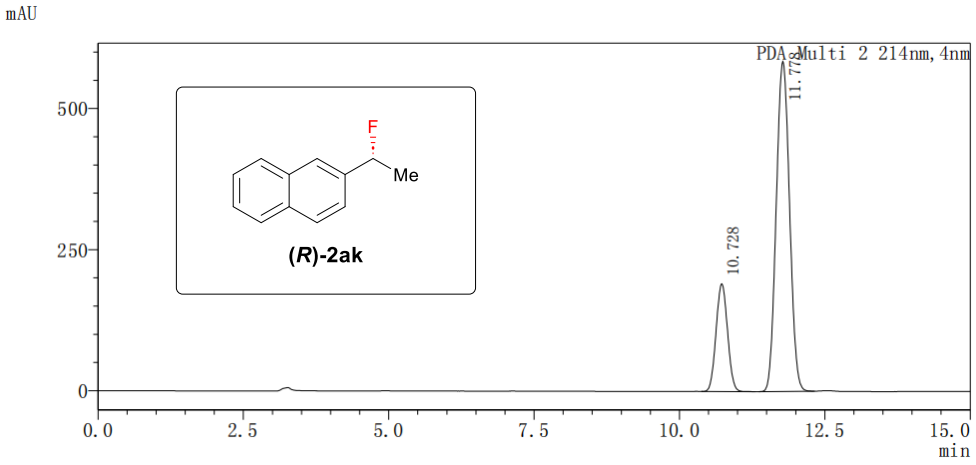


Figure SI-2. Proposed S_Ni mechanism for substitution with chiral retention



The Total Yield of **(*R*)-2ak** and **(*S*)-2ak** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



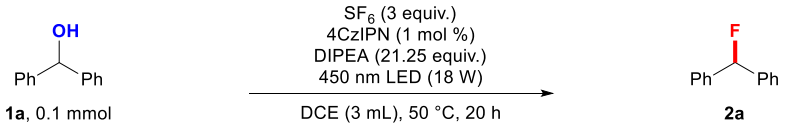
Peak#	Ret. Time	Area	Area%
1	10.728	2615300	21.940
2	11.778	9304954	78.060
Total		11920254	100.000

Optical Rotation: $[\alpha]_D^{20}$ = +15.8 (c 1.000, CHCl3).

HPLC analysis condition: Daicel Chiralpak OJ-H, n-hexane/iso-propanol = 49/1, 1.0 mL/min, λ = 214 nm. The assignment of the absolute configurations was confirmed according to previous report (*ACS Catal.*, **2020**, 10, 3, 1954).

3.4 Photochemistry experiments

Light on/off experiment



In a 20 mL glass vial, 4CzIPN (4.74 mg, 0.006 mmol, 1 mol %), DIPEA (1.6476 g, 12.75 mmol, 21.25 equiv.) and **1a** (0.1105 g, 0.6 mmol, 1.0 equiv.) were dissolved in DCE (18 mL). The mixture solution was sonicated and equally divided into 6 glass vials of the same size to ensure equal volume. Six oven-dried 10 mL Schlenk tubes numbered #1-#6 were evacuated and backfilled with SF_6 (repeated for 5 times), followed by filling in the separated solution via syringe. The tubes were sealed with Teflon lined caps and stirred under visible light source (450 nm, 18 W) at 50 ˚C to perform 6 parallel experiments. At the 6 h, the light was turned off and tube #1 was opened to measure ^1H NMR yield with CH_2Br_2 as the internal standard substance. After 3 h, tube #2 was subject to yield measurement and the light was turned on for another 6 h, and the rest of experiment was done in the same manner. The results showed obvious suspension of reaction process when light source was extracted.

Luminescence quenching experiments

To gain further insight for the process, we conducted Stern-Volmer studies on the photocatalytic system. The experiments were performed according to the following procedure. In the quartz cuvette, 4CzIPN (0.1 mM) was dissolved in DCE (3 mL). After completing the blank test, DIPEA was pipetted into each portion of solution using a 10 μL microsampler. The luminescence quenching effect of the sample was observed on Hitachi Fluorescence Spectrophotometer F-4600 with excitation wavelength at 378 nm, emission wavelength ranging from 400-750 nm. Emission intensity peak height at 535 nm was recorded.

First, we measured the emission intensity in the presence of various possible quenchers. 4CzIPN (0.1 mM) in DCE and sparged with SF_6 for 60 seconds before testing (line 1), 4CzIPN (0.1 mM) in DCE (line 2), 4CzIPN (0.1 mM) with substrate **1a** (10 mM) in DCE (line 3) and 4CzIPN (0.1 mM) with DIPEA (10 mM) in DCE (line 4). The study revealed that the excited state of 4CzIPN is quenched by the reductant DIPEA (**Figure SI-3**).

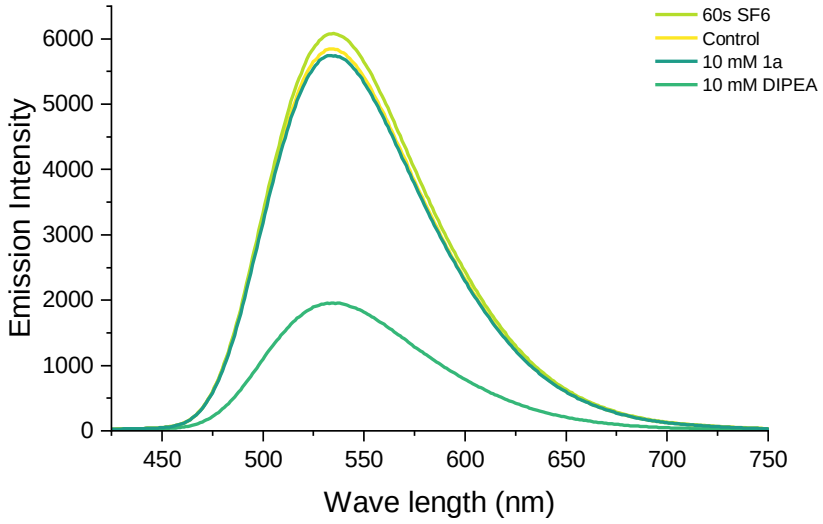


Figure SI-3. Luminescence quenching of excited 4CzIPN with various quenchers

Then, we added different concentrations of DIPEA to the system, measured the emission intensity of the 4CzIPN (0.1 mM) as below (**Figure SI-4**).

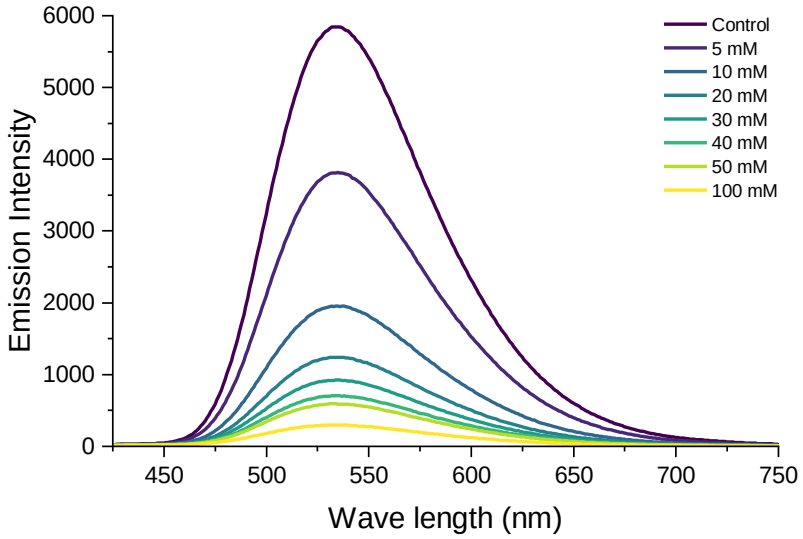


Figure SI-4. 4CzIPN emission quenching by different concentrations of DIPEA

In addition, the Stern-Volmer plot and a linear fit (**Figure SI-5**) were drawn according to the equation:

$$\frac{I_0}{I} - 1 = K_q[Q]$$

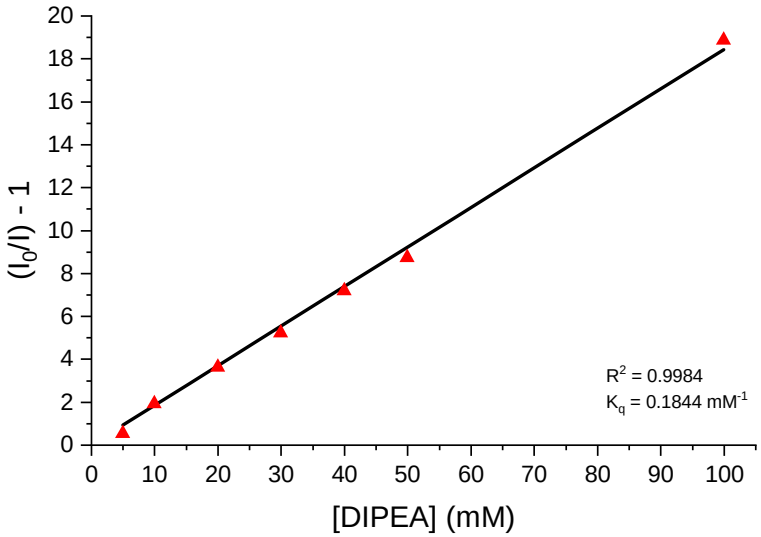
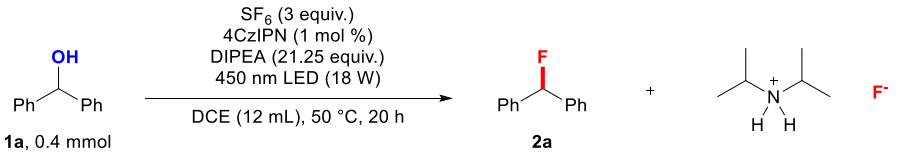


Figure SI-5. Stern-Volmer plot of 0.1 mM 4CzIPN quenched by different concentration of DIPEA

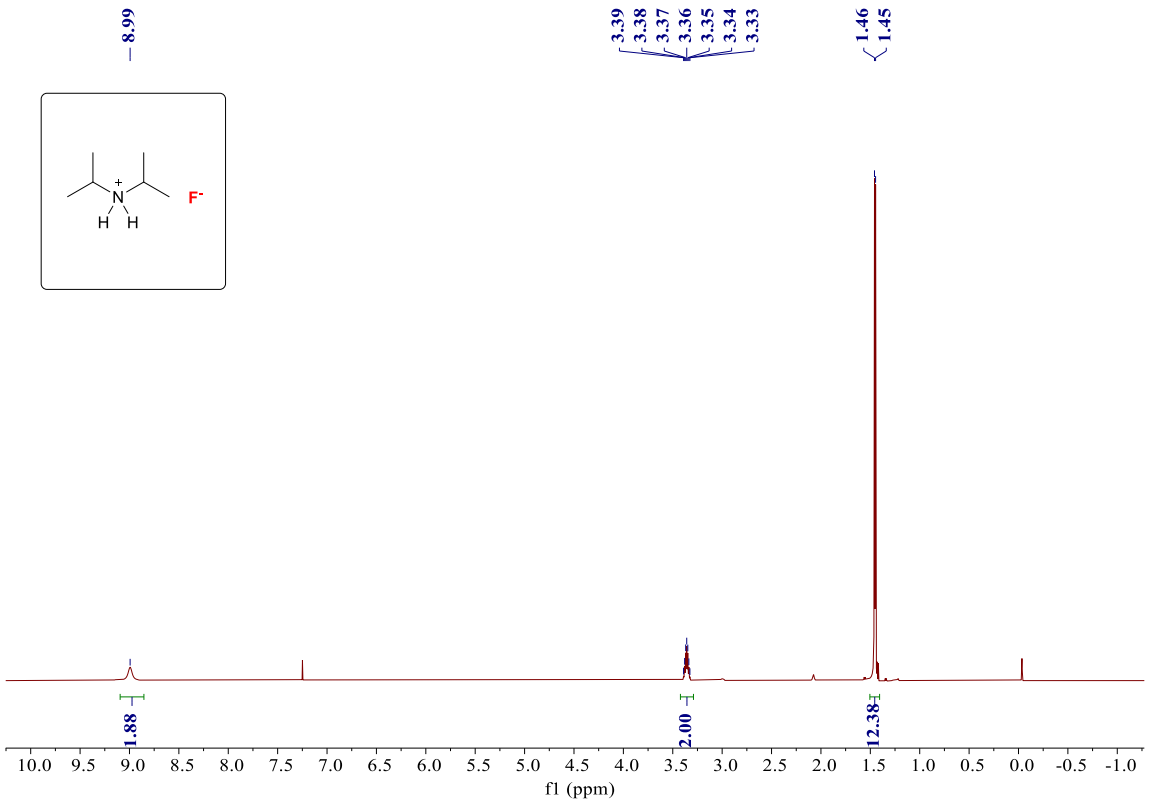
4. By-product salt preparation and analysis

4.1 Preparation and NMR analysis

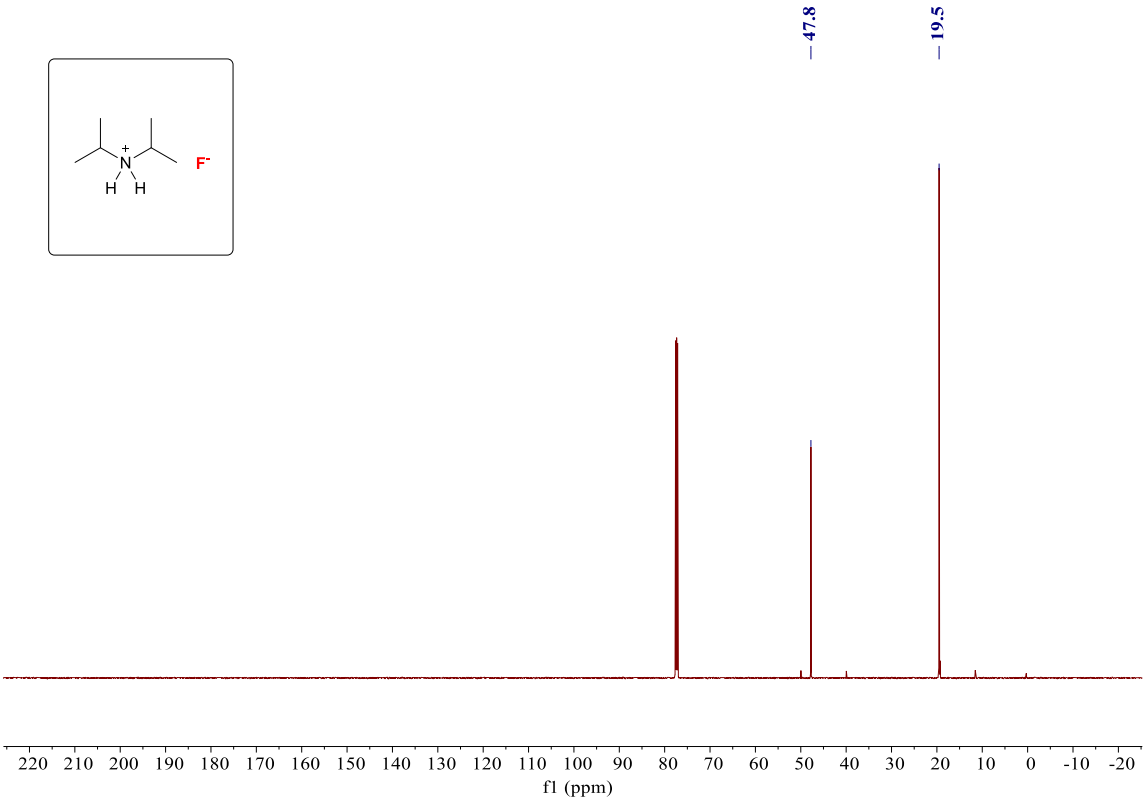


In a 20 mL glass vial, 4CzIPN (3.16 mg, 0.004 mmol, 1 mol %) and DIPEA (1.0984 g, 8.5 mmol, 21.25 equiv.) were dissolved in DCE (12 mL). The solution was subjected to a 30-second sonication dispersion and then dispensed in equal volumes into 4 glass vials of 10 mL volume directly on bench. **1a** (0.0184 g, 0.1 mmol, 1.0 equiv.) was added and dissolved in each vial. For each glass vial, an oven-dried 10 mL Schlenk tube was evacuated and backfilled with SF_6 (repeated for 5 times), followed by filling in the solution via syringe. The tube was sealed with a Teflon lined cap and stirred under visible light source (450 nm, 18 W) at 50 ˚C for 20 h. The reaction mixture was concentrated *in vacuo*, and the by-product salt was obtained by flash column chromatography on silica gel (from PE to DCM). The purified product was then subject to further characterization.

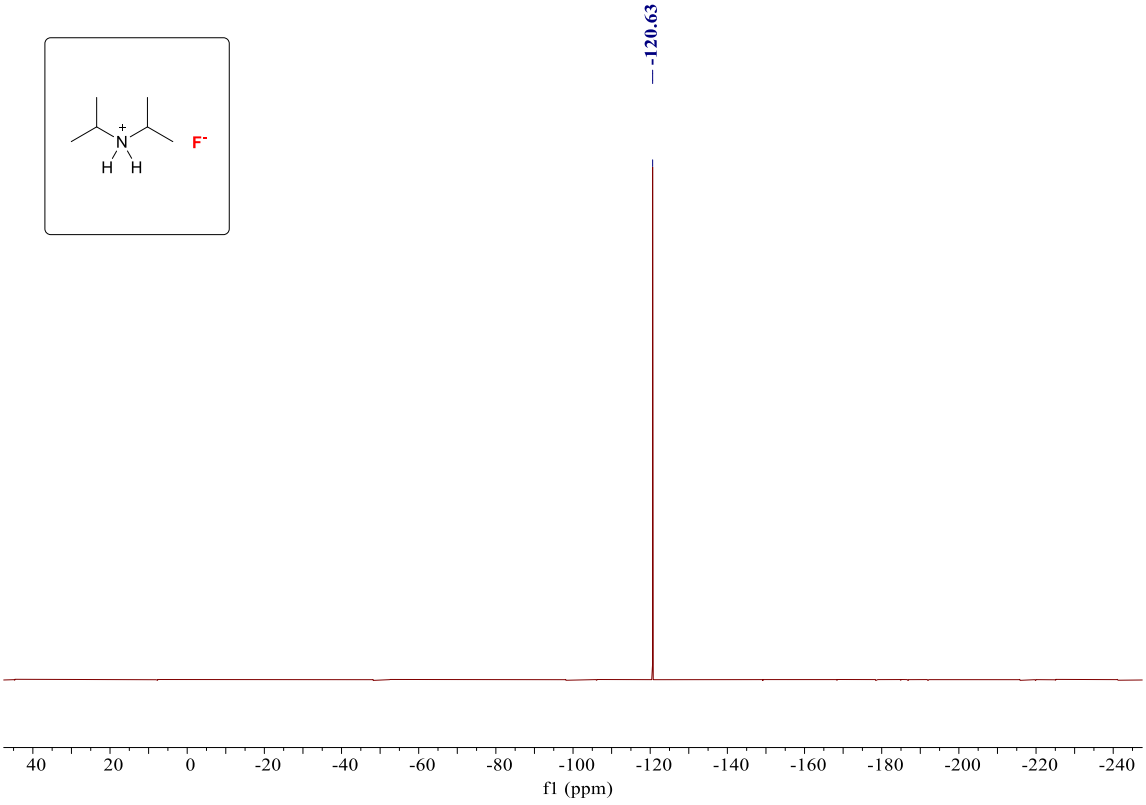
^{1}H NMR (600 MHz, Chloroform-d) δ 8.99 (s, 2H), 3.36 (hept, *J* = 6.4 Hz, 2H), 1.45 (d, *J* = 6.6 Hz, 12H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 47.8, 19.5. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -120.63.



^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of by-product salt



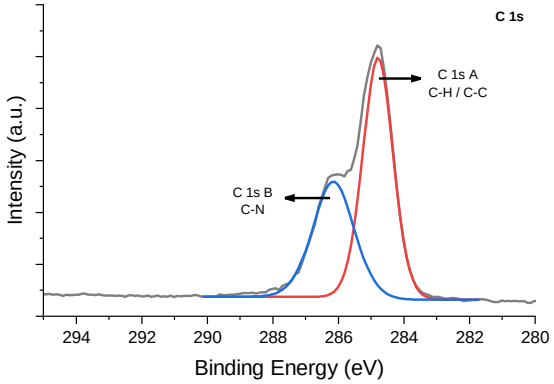
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of by-product salt

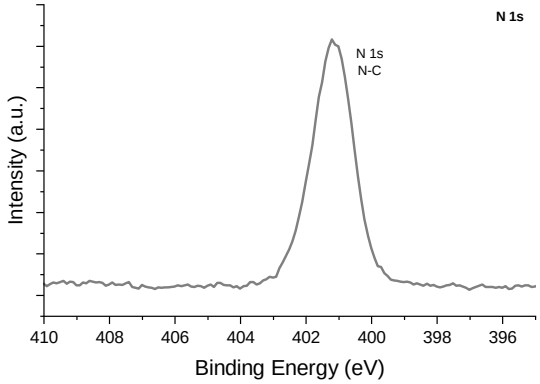


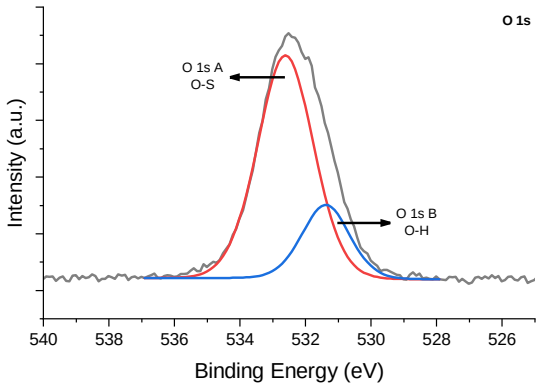
^{19}F NMR (500 MHz, $CDCl_3$) Spectrum of by-product salt

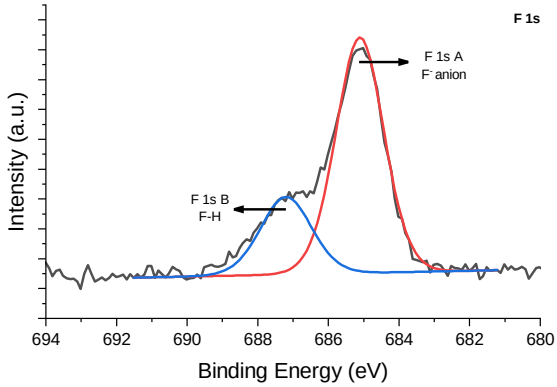
4.2 XPS analysis detail of by-product salt

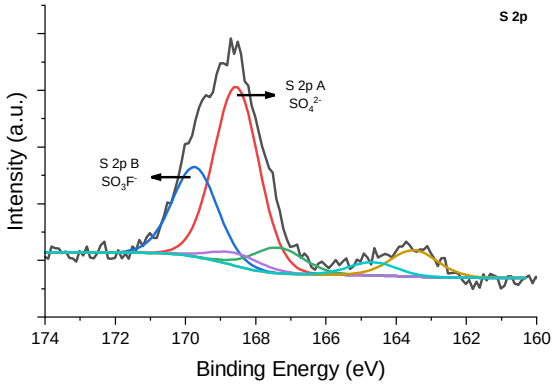
XPS elemental analysis further revealed the composition of the by-product salt. As C-O bonds were not detected and nitrogen formed C-N bond, it is suggested that the salt was derived from the reductant amine DIPEA. S-O and O-H bonds indicated the presence of partially protonated sulfur containing acid anion. Flourine signals were inferred as anions with or without hydrogen bond.

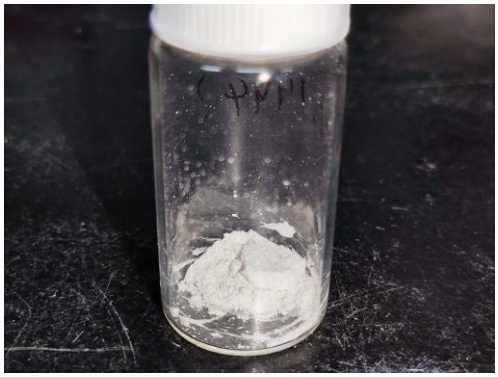






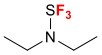
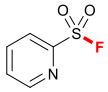
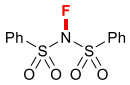
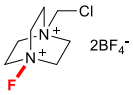
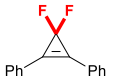




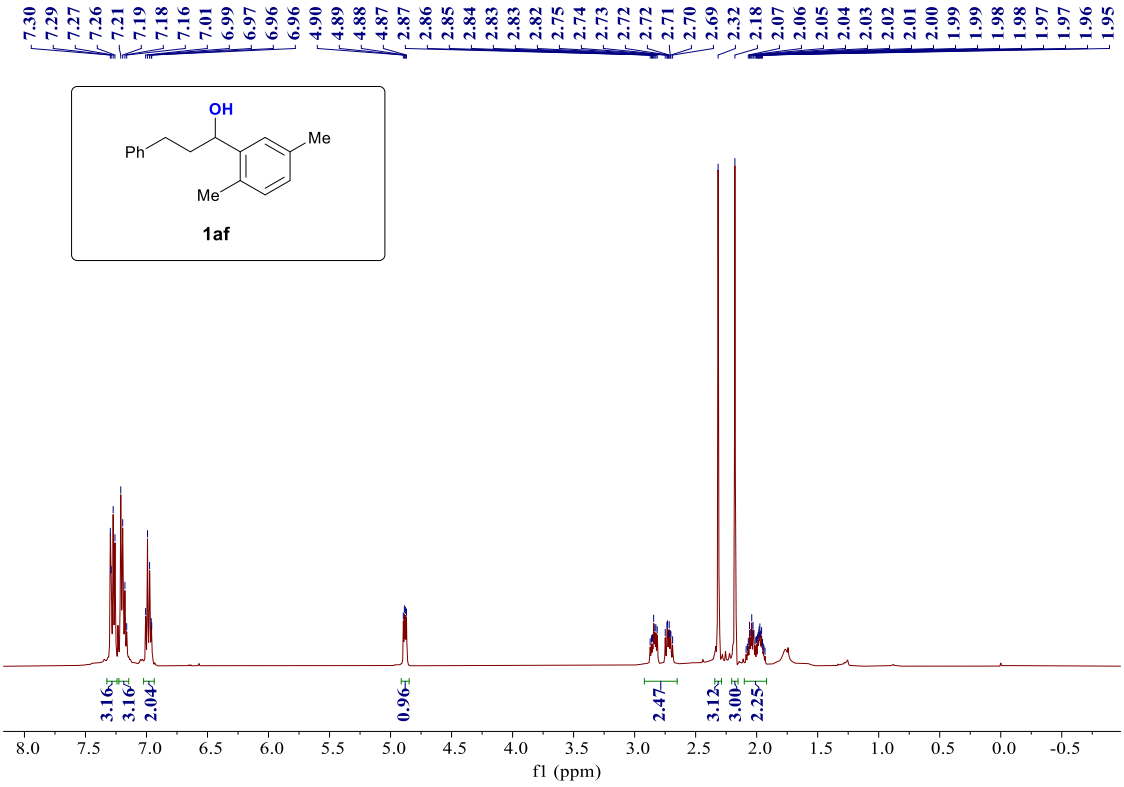


5. Additional information

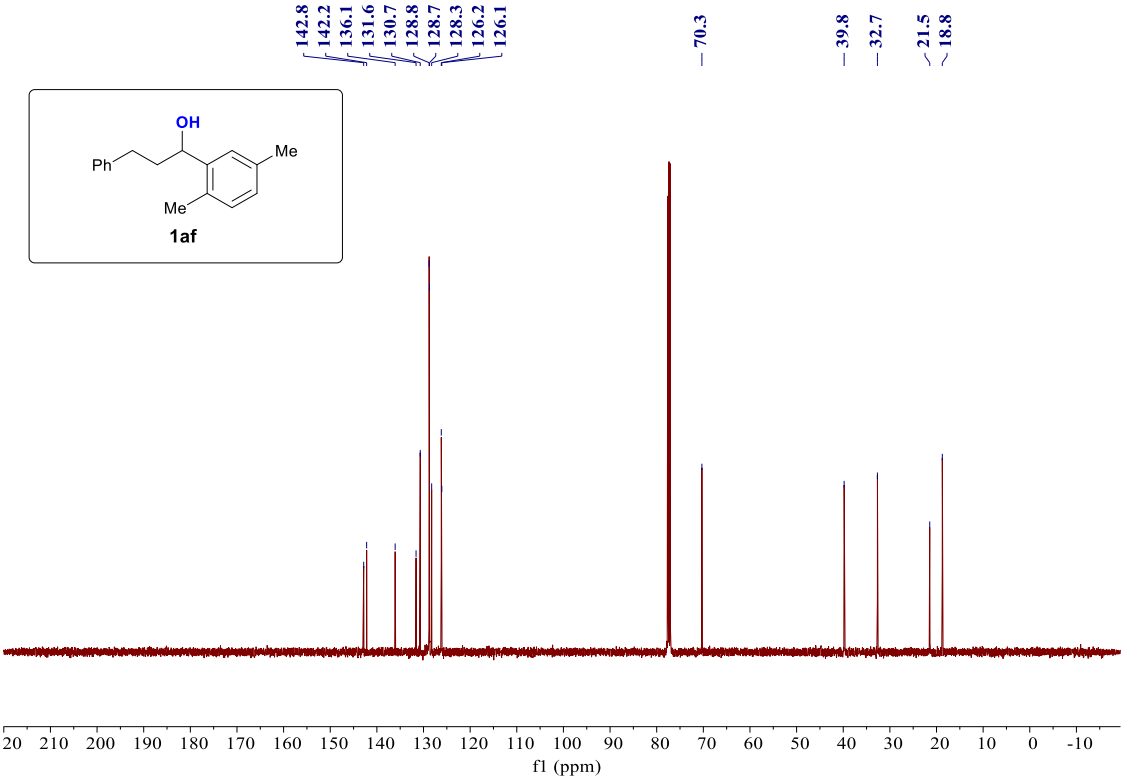
Table SI-3. Comparison Between SF_6 and Other Deoxyfluorination Reagents

	Fluorine content by		Commercial cost by		Source
	weight (%)	mole (%)	1 mol fluorine ($)	1 mol reagent ($)	
SF_6	**78**	**86**	**0.44**	**2.66**	Nanjing Special Gas Plant Co., Ltd. https://www.njtq.cn/product/781.html
SO_2F_2	37	40	9.86	19.71	Sichuan Shangfu Technology Co., Ltd. http://www.shangfluoro.com/2699-79-8.html
 DAST	35	16	15.79	47.37	Shanghai Haohong Scientific Co.,Ltd. https://www.leyan.com/38078-09-0.html
 PyFluor	12	7.1	186.99	186.99	Shanghai Haohong Scientific Co.,Ltd. https://www.leyan.com/878376-35-3.html
 NFSI	6.0	3.3	29.15	29.15	Shanghai Haohong Scientific Co.,Ltd. https://www.leyan.com/133745-75-2.html
 Selectfluor	5.3	2.9	32.27	32.27	Shanghai Haohong Scientific Co.,Ltd. https://www.leyan.com/140681-55-6.html
 CpFluor	17	7.4	7990.87	15981.74	DAICEL Chiral Technologies (China) Co., Ltd. https://www.daicelchiraltech.cn/reagents/detail/201223.html

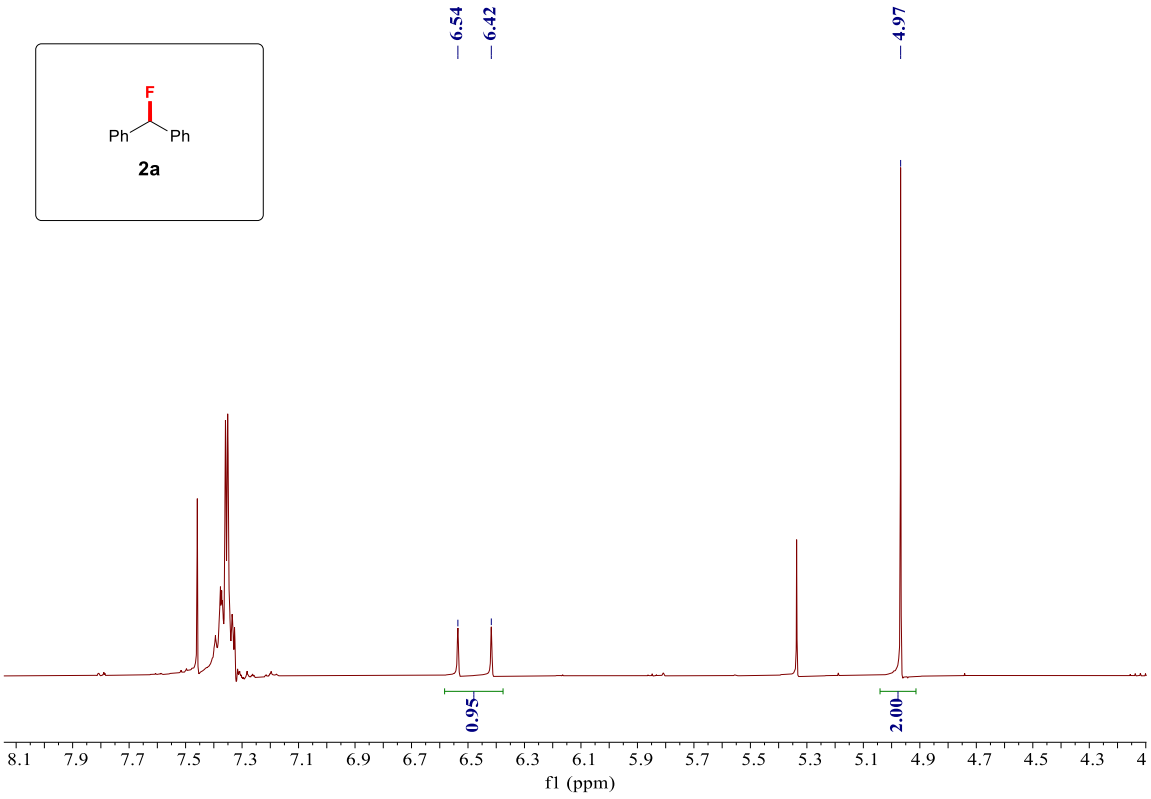
6. NMR Spectrum



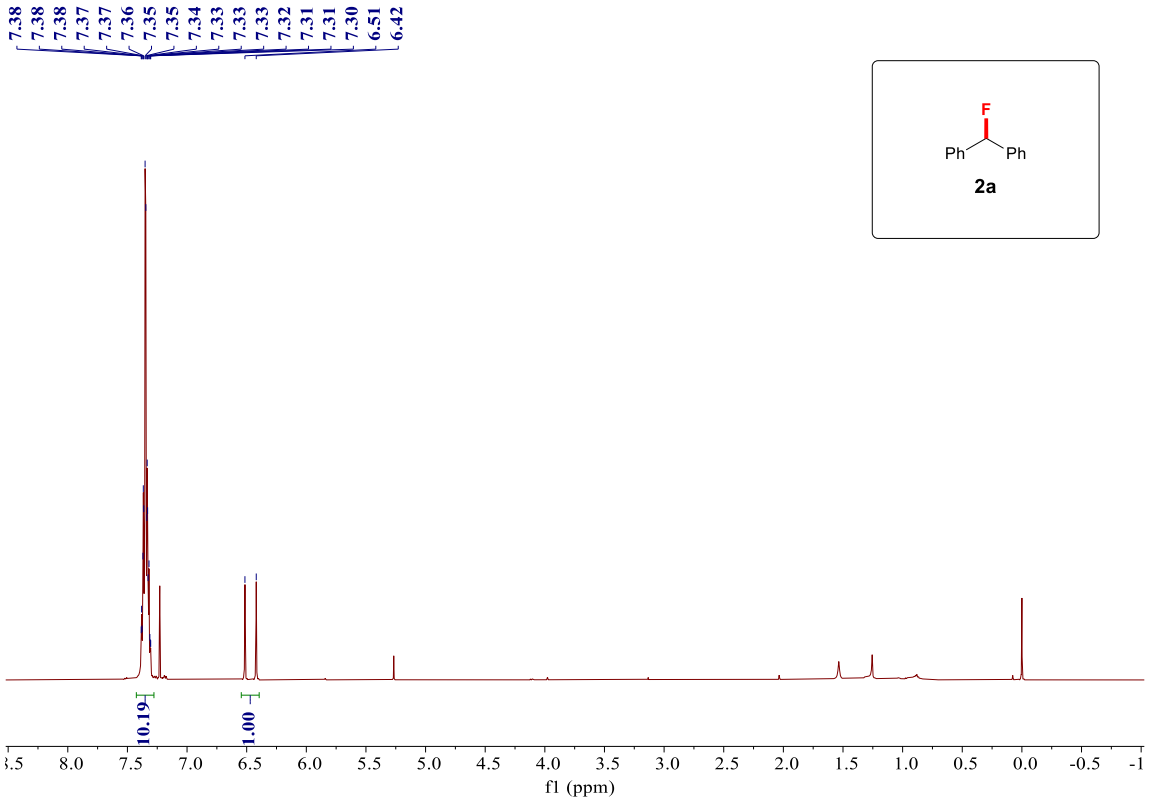
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **1af**



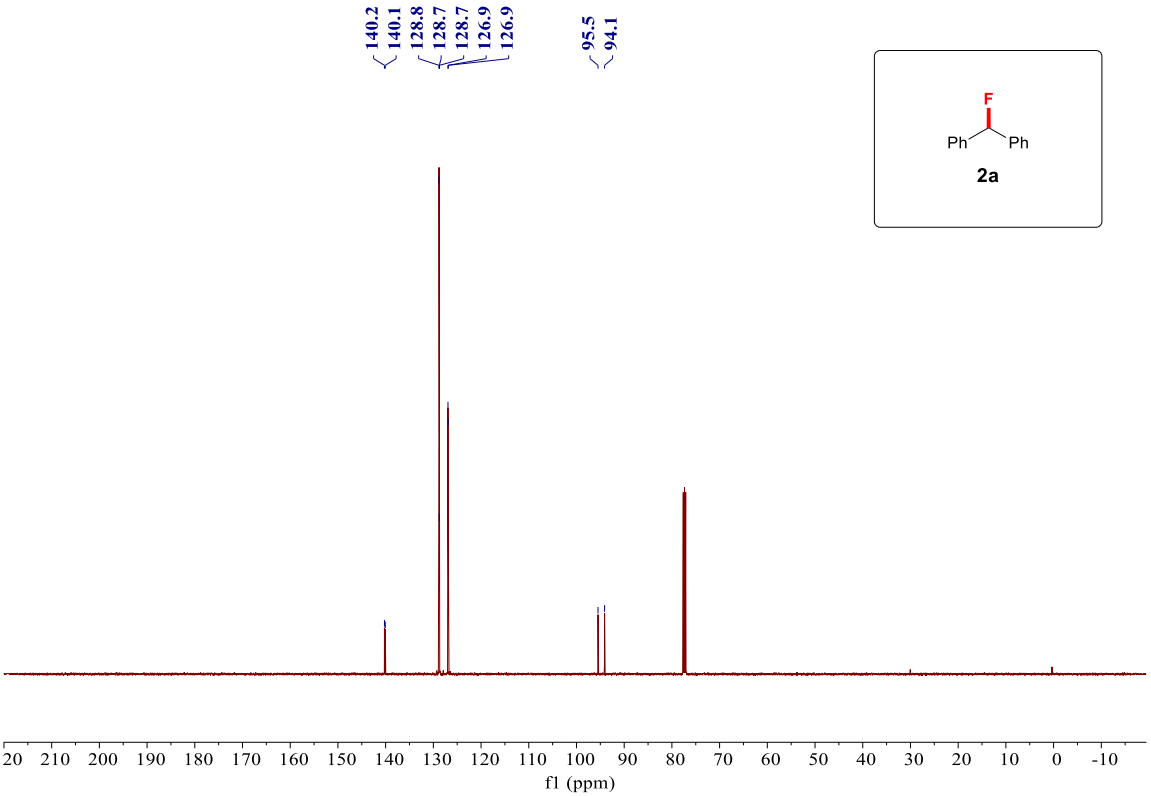
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **1af**



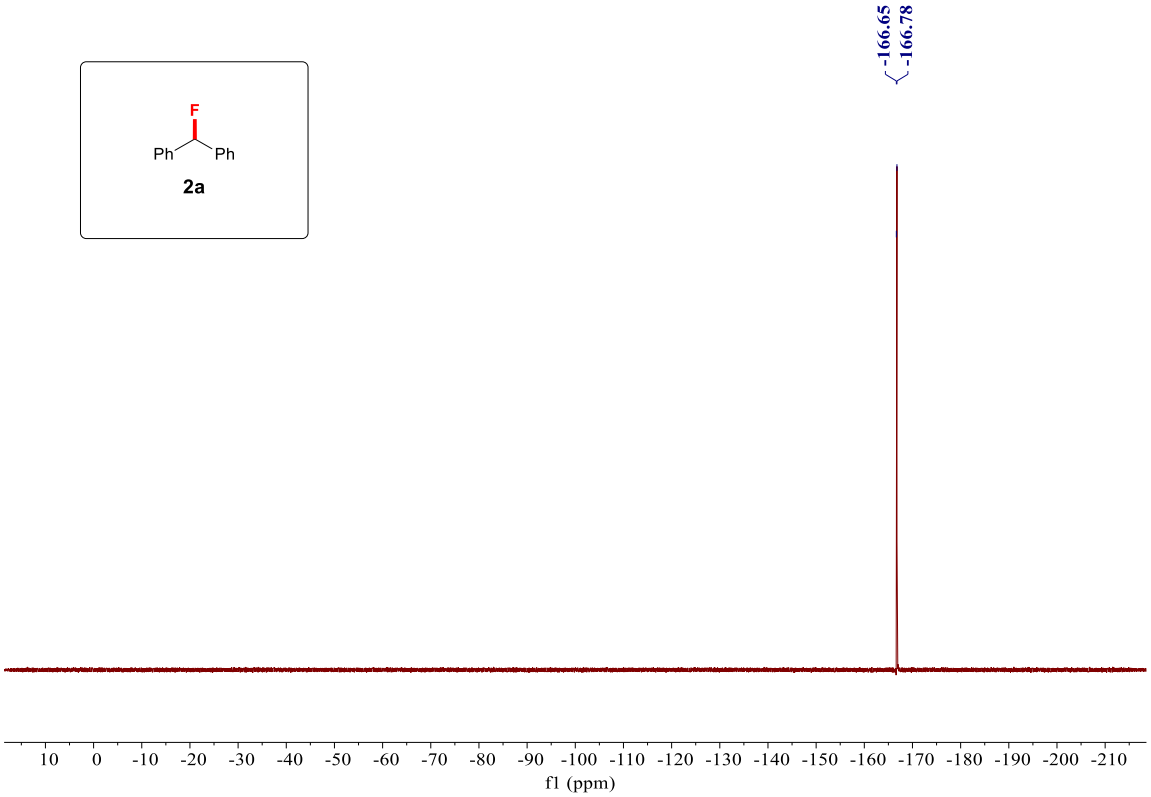
The Yield of **2a** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



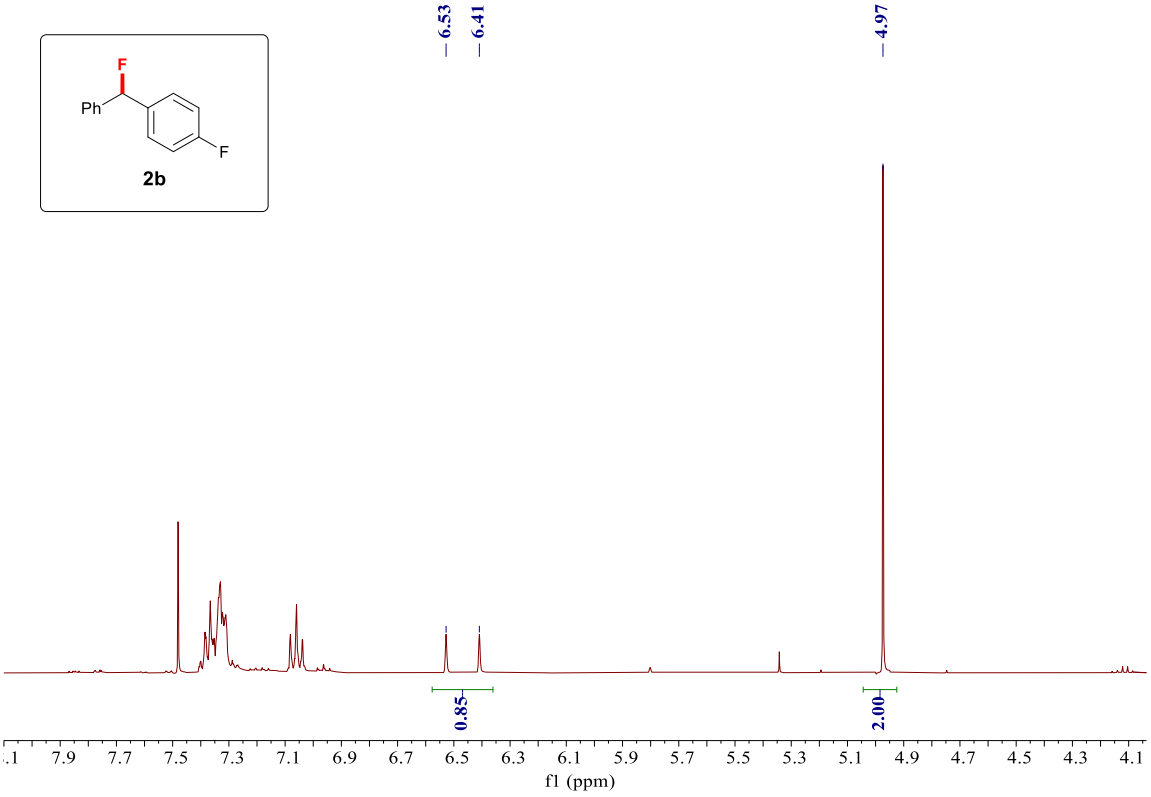
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2a**



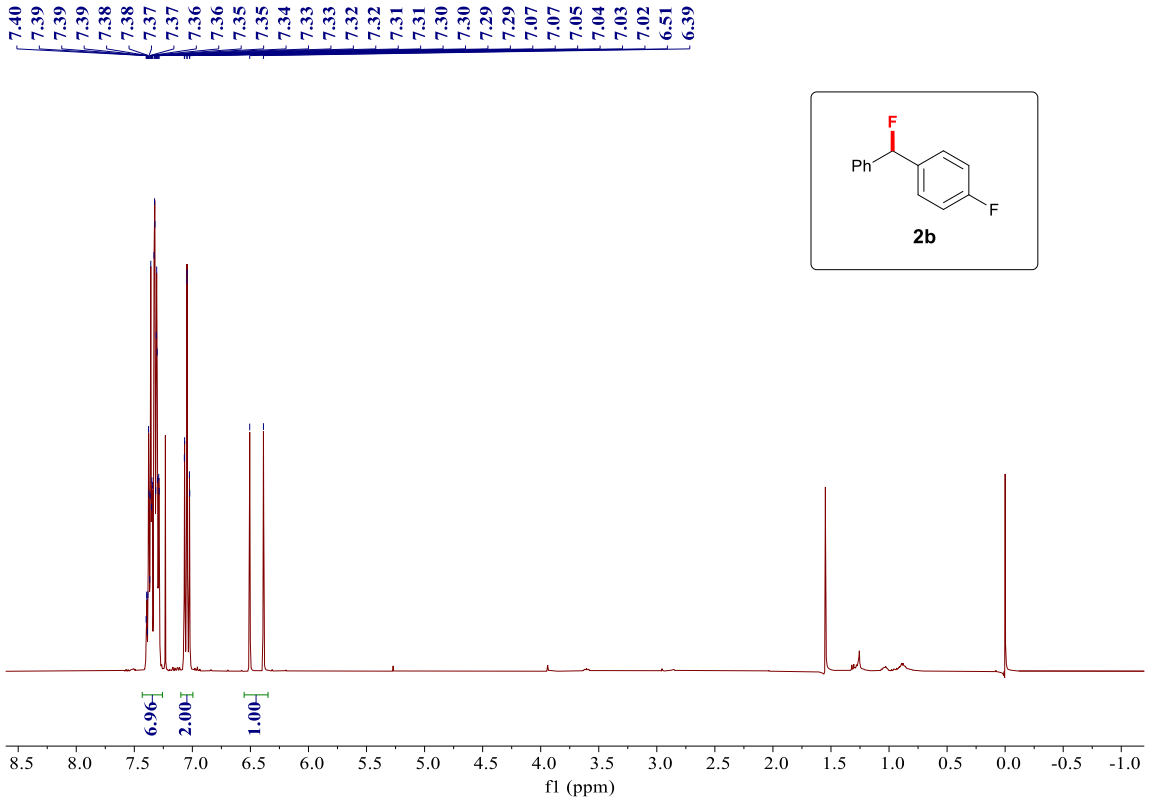
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2a**



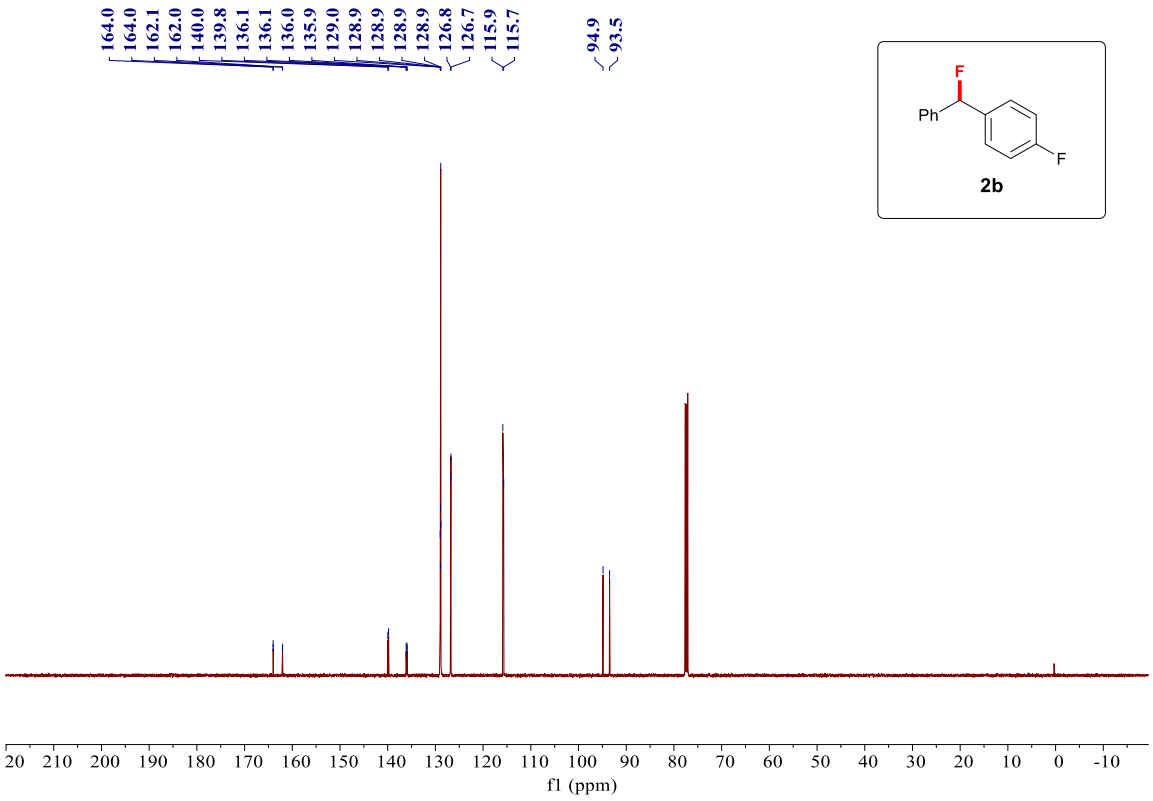
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **2a**



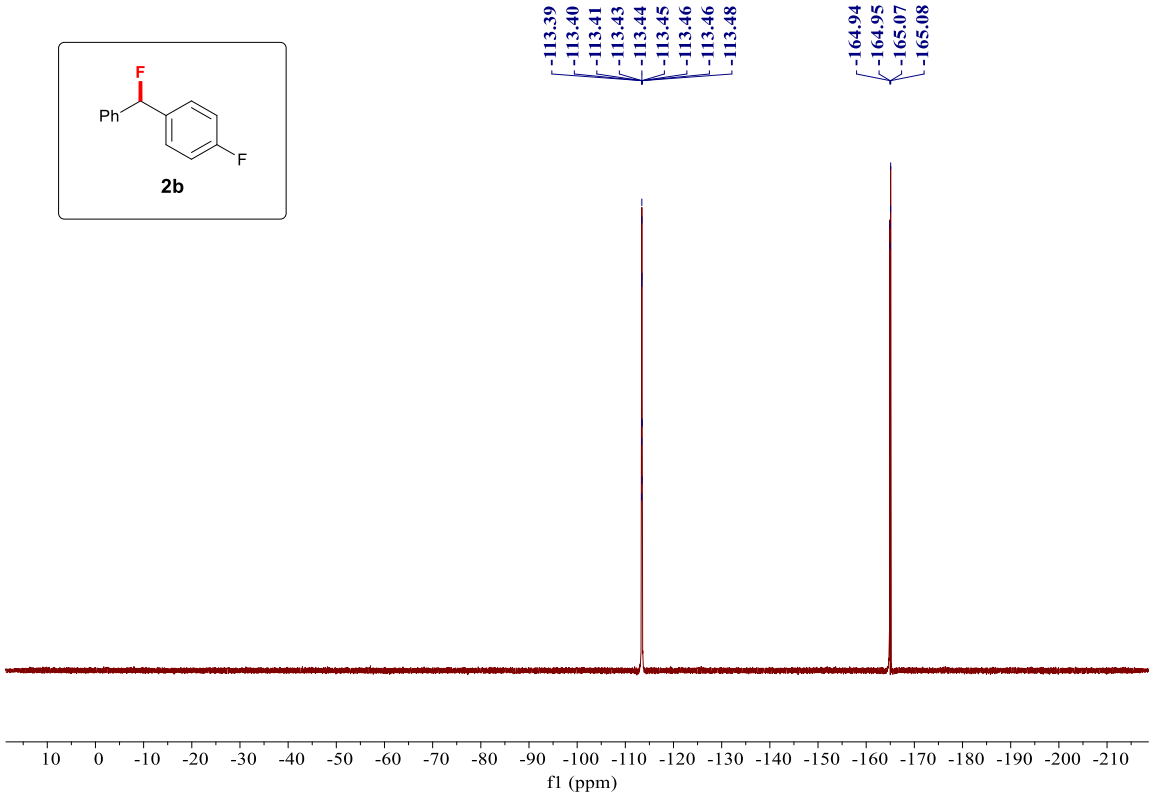
The Yield of **2b** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



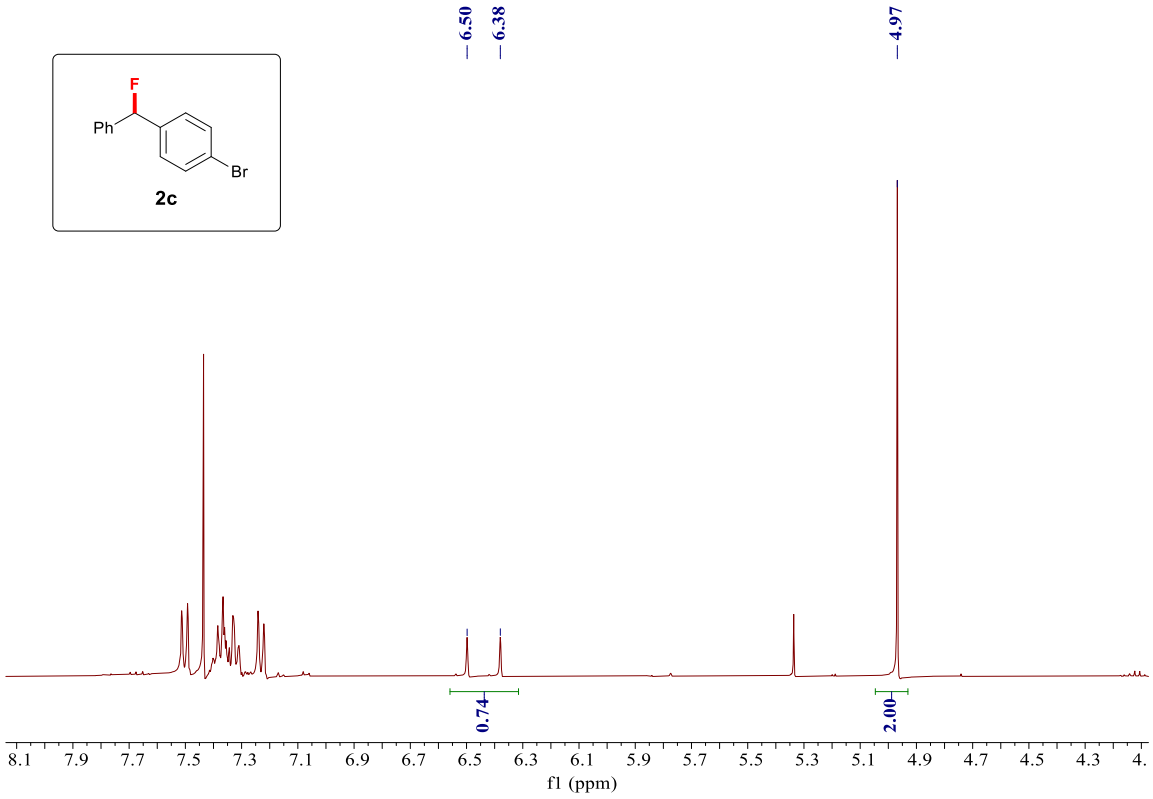
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **2b**



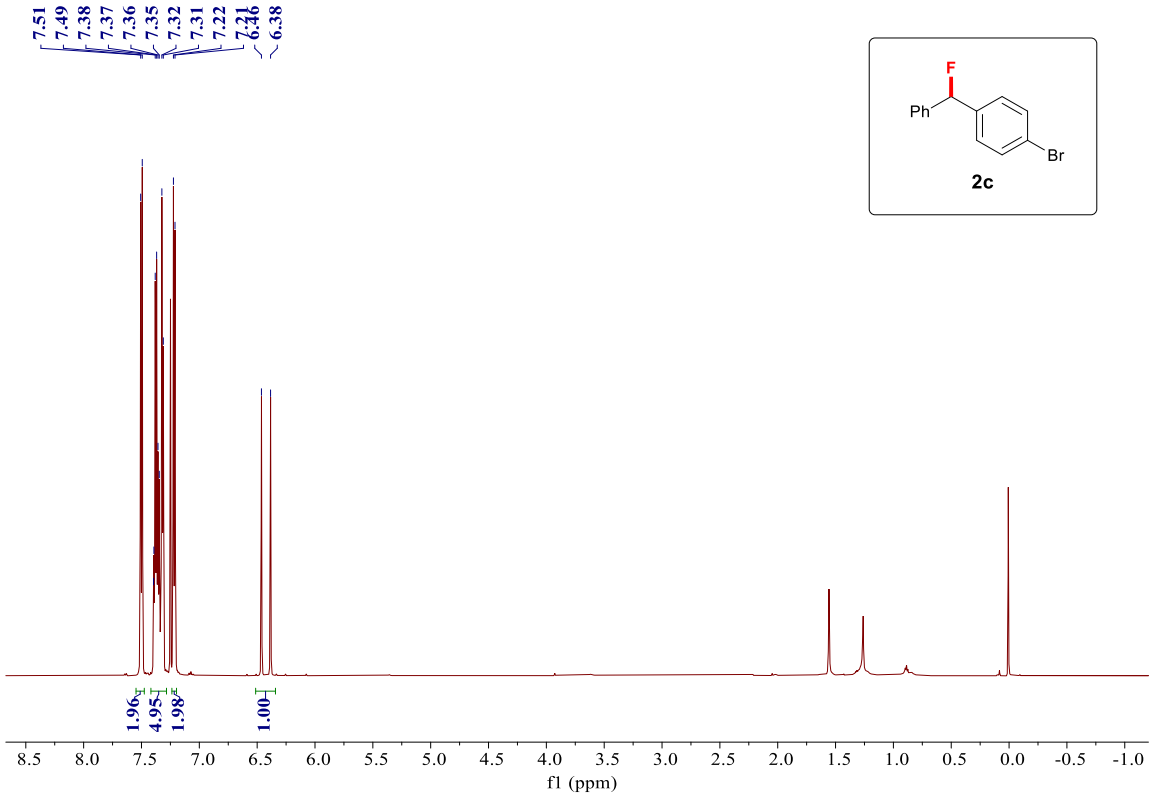
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2b**



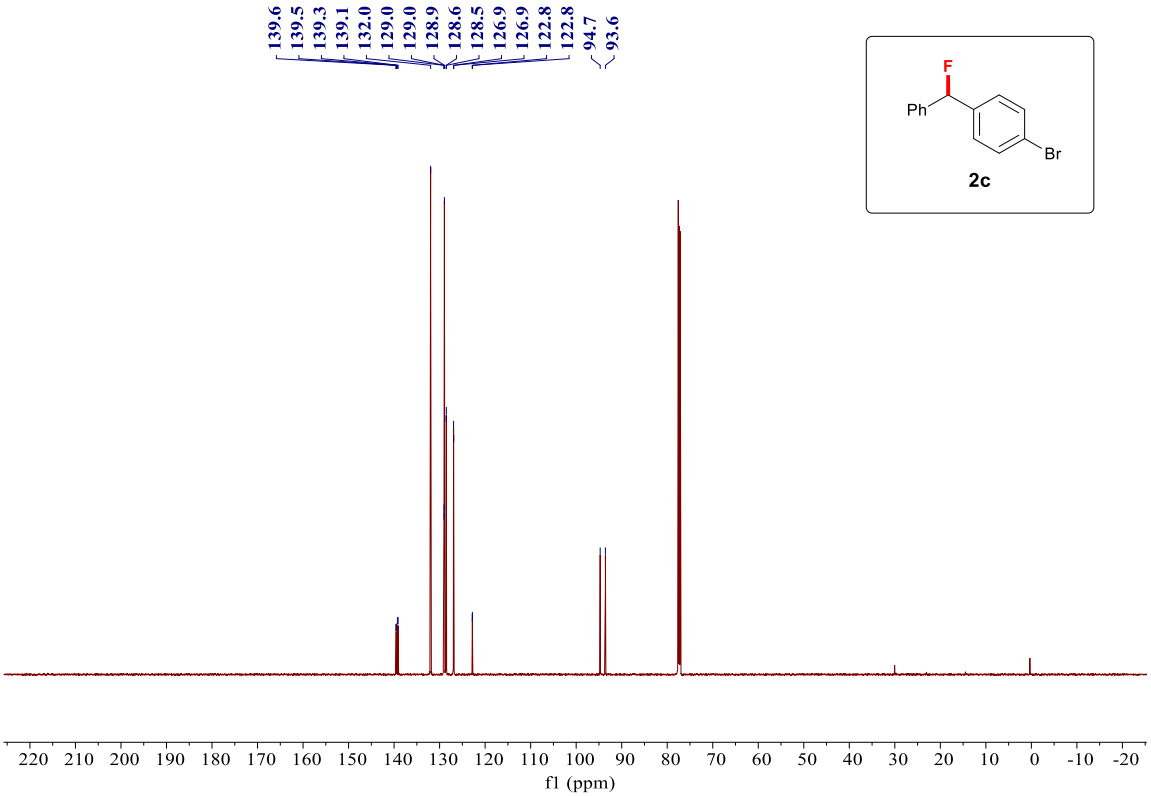
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **2b**



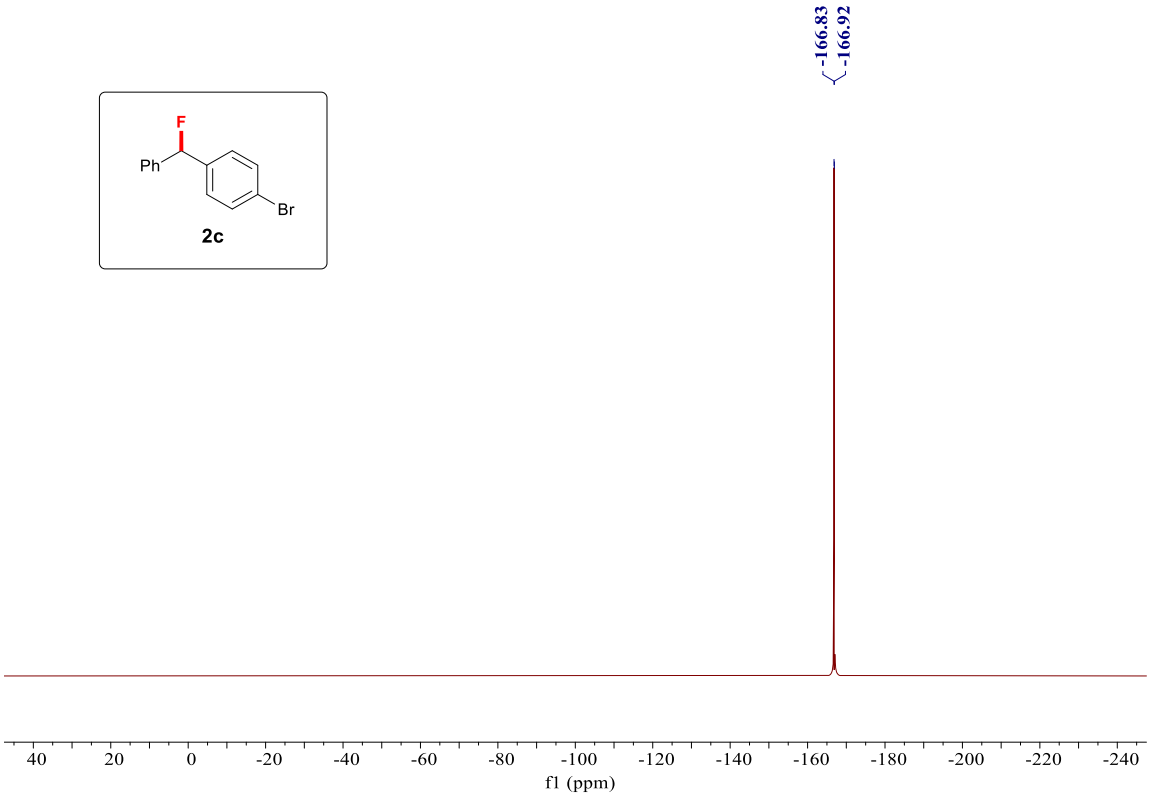
The Yield of **2c** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



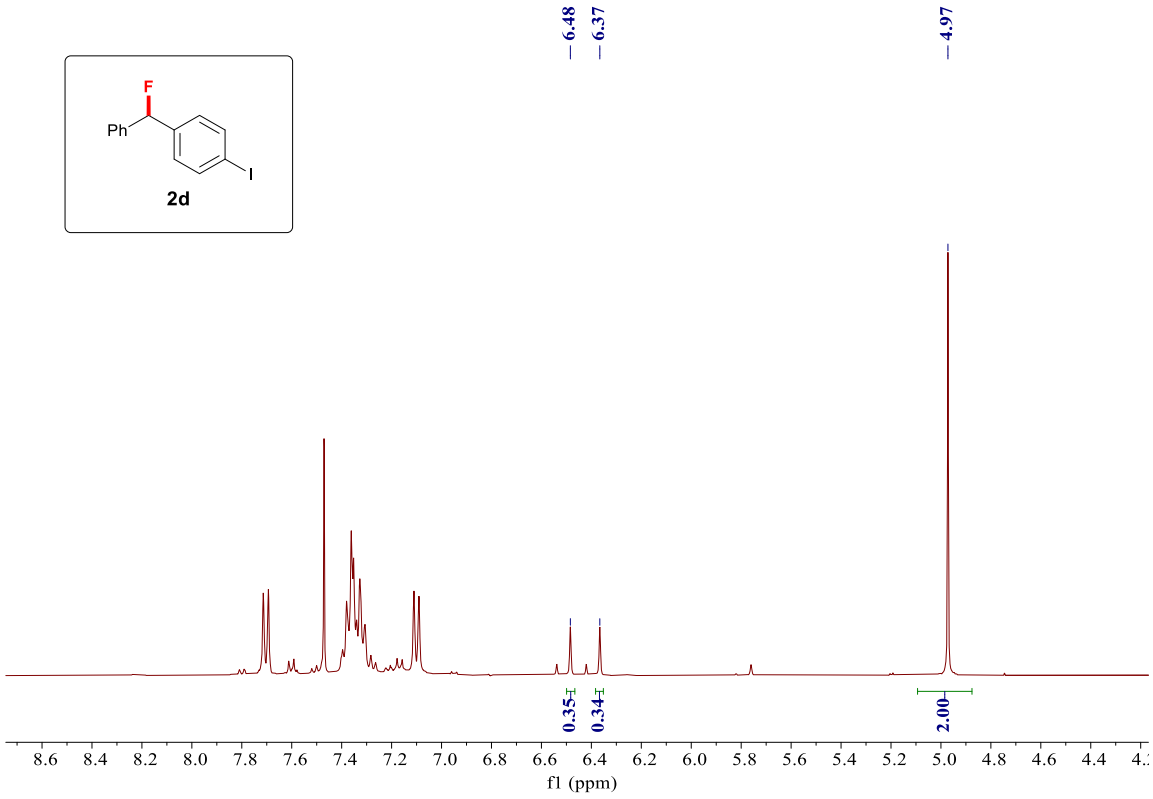
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **2c**



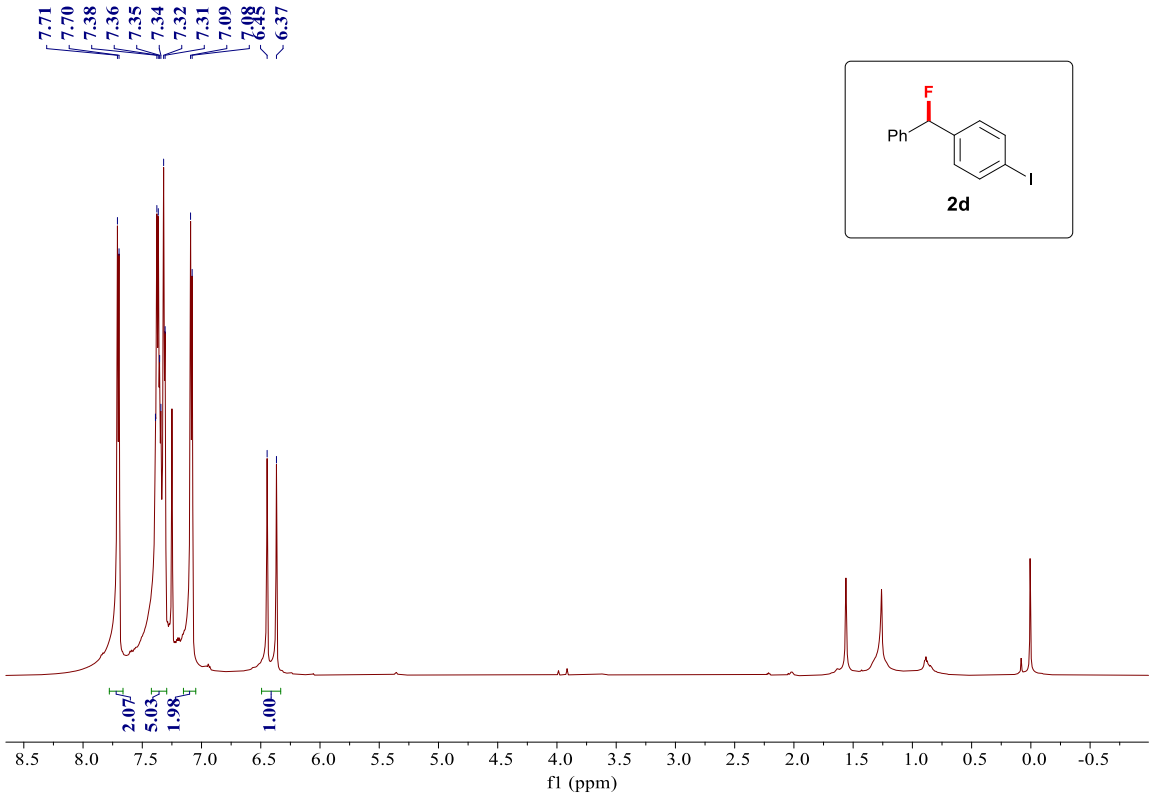
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of Compound **2c**



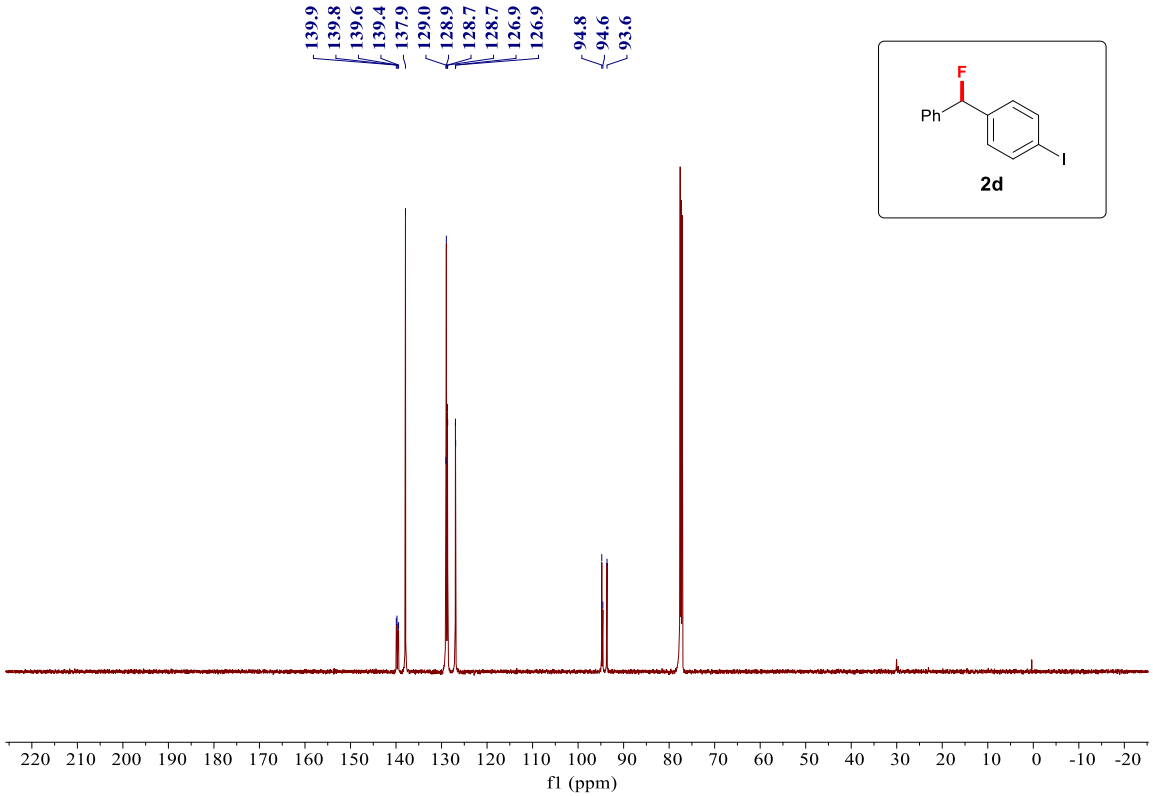
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of Compound **2c**



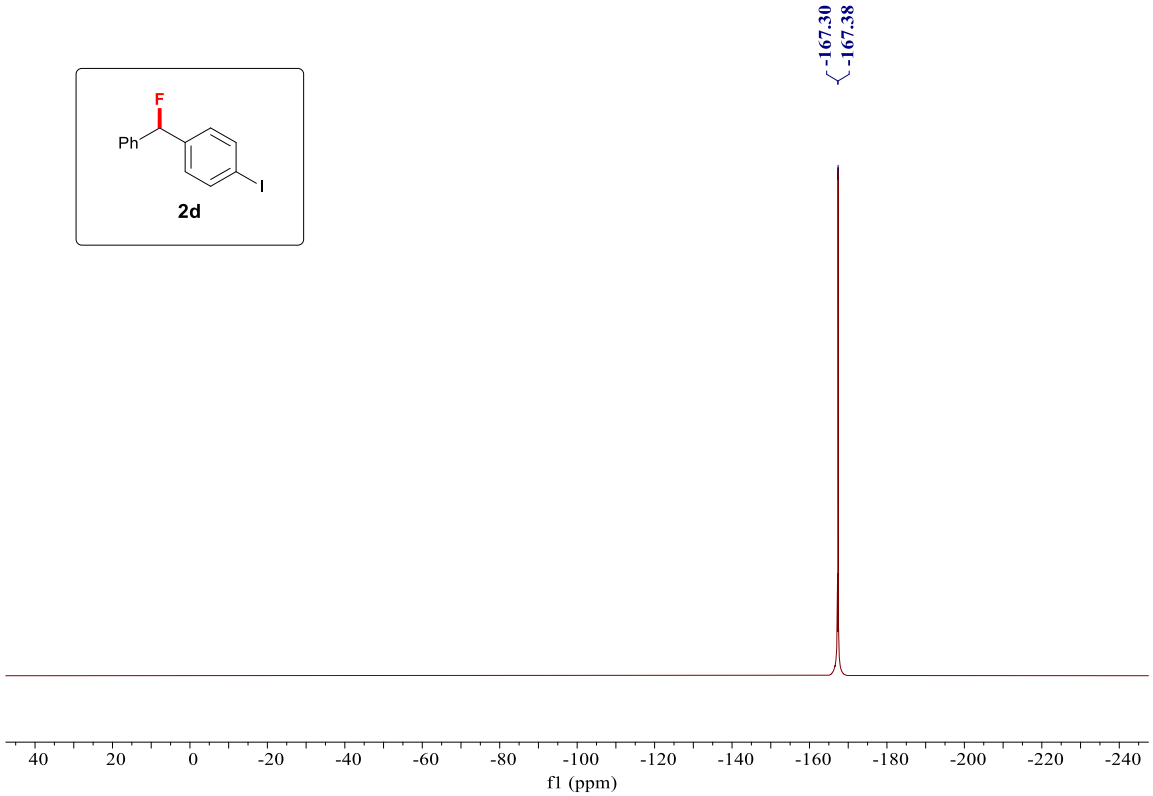
The Yield of **2d** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



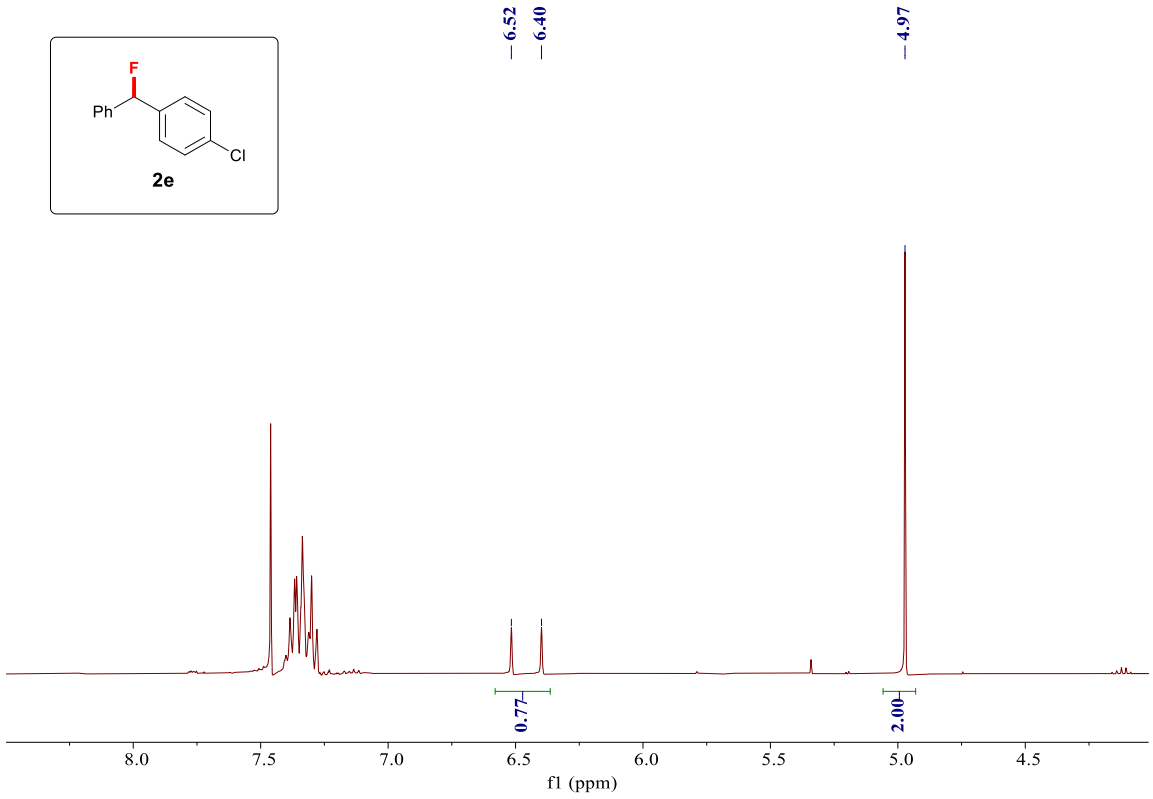
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **2d**



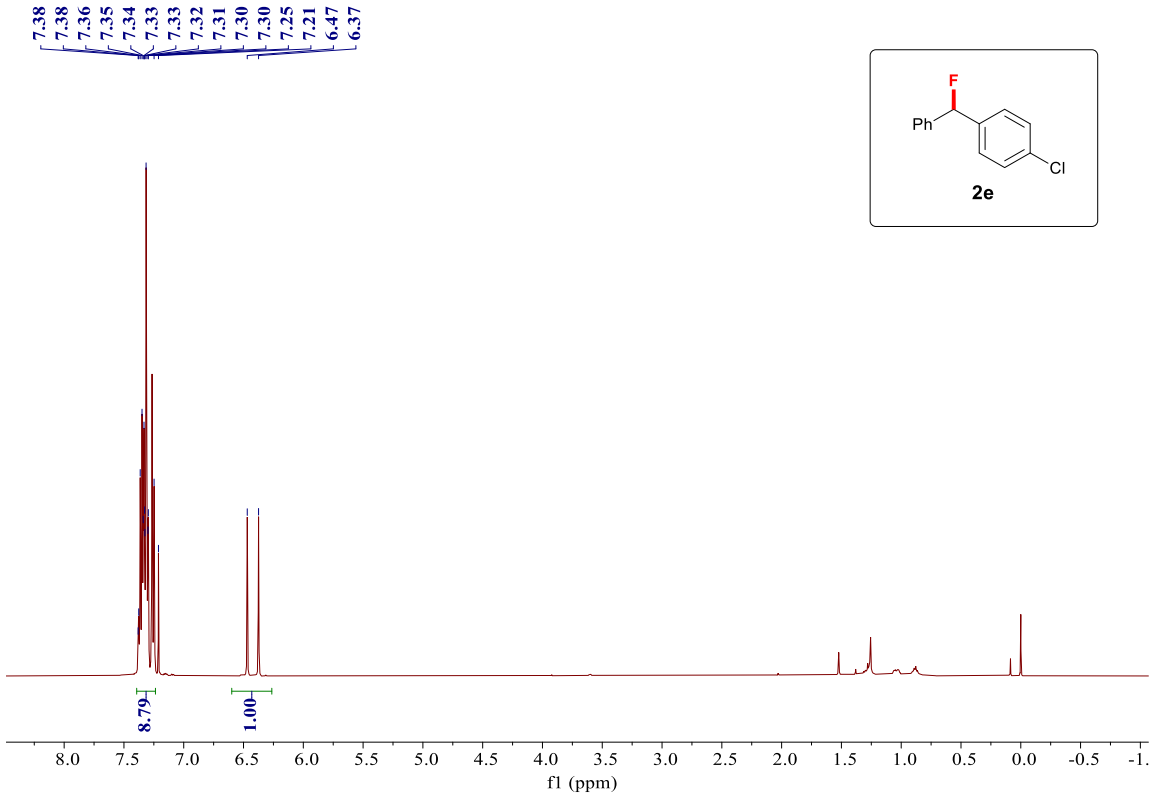
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of Compound **2d**



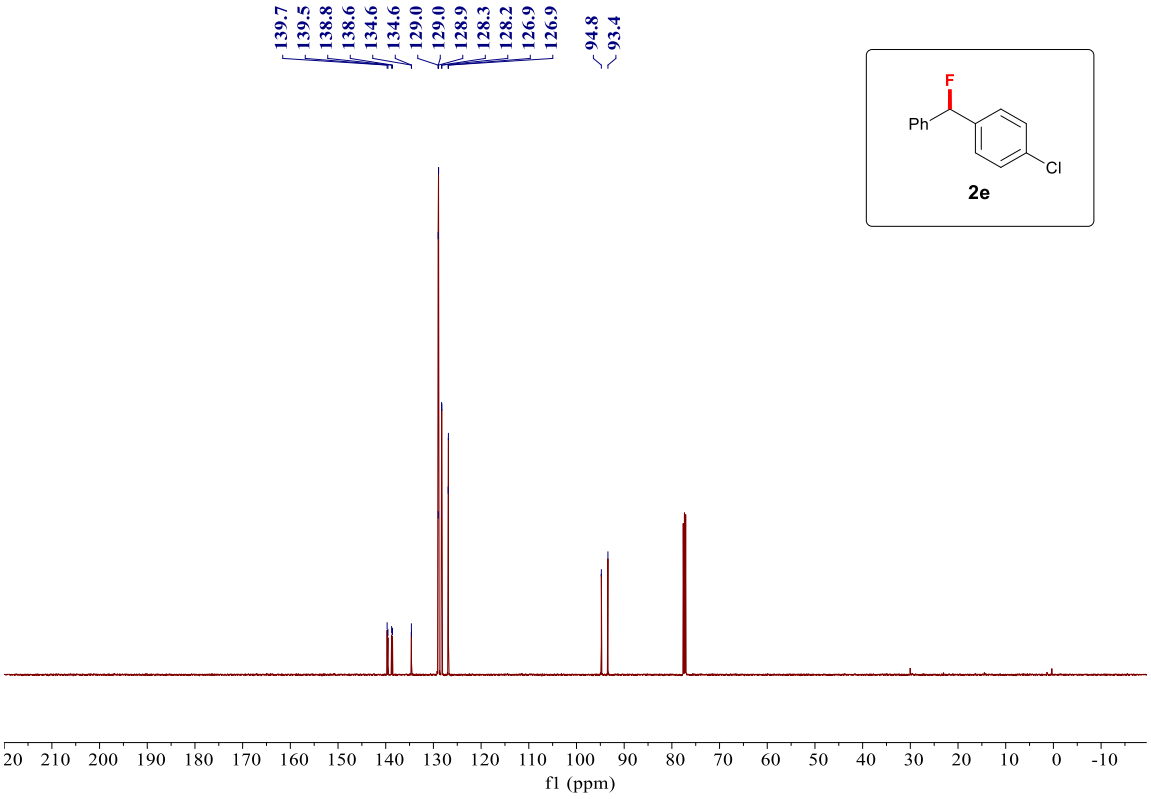
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of Compound **2d**



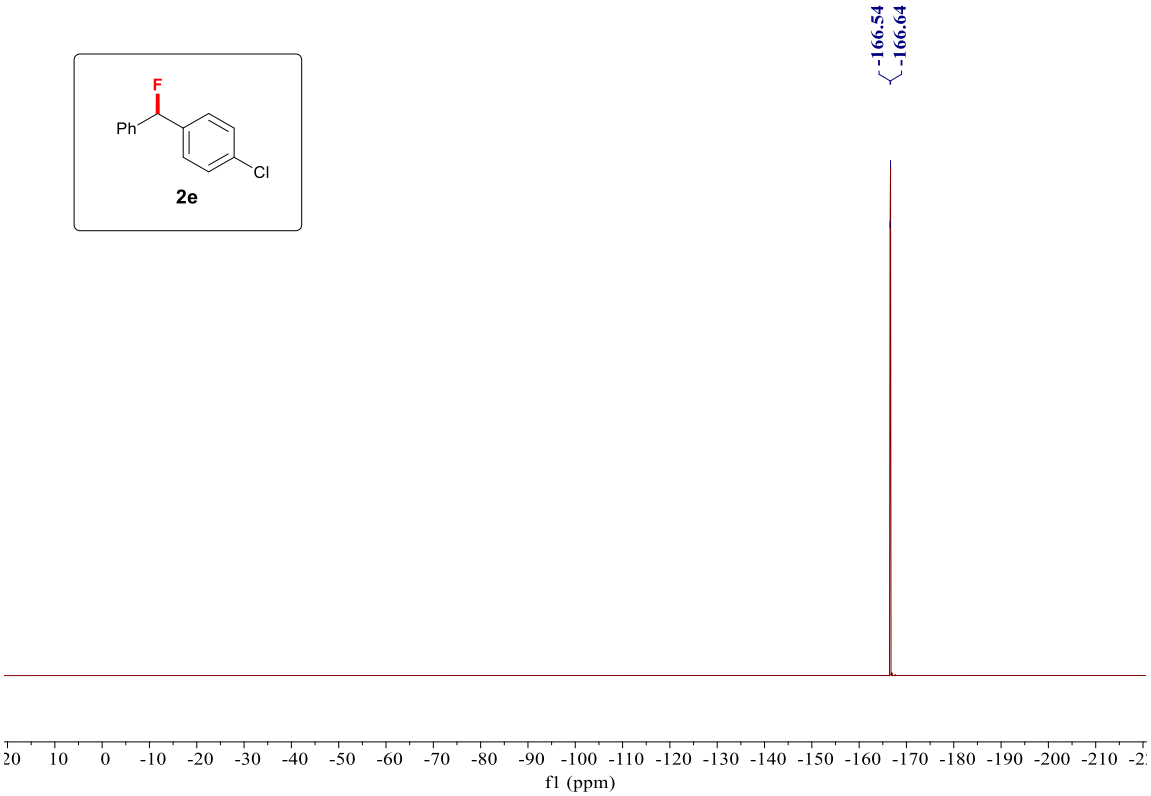
The Yield of **2e** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



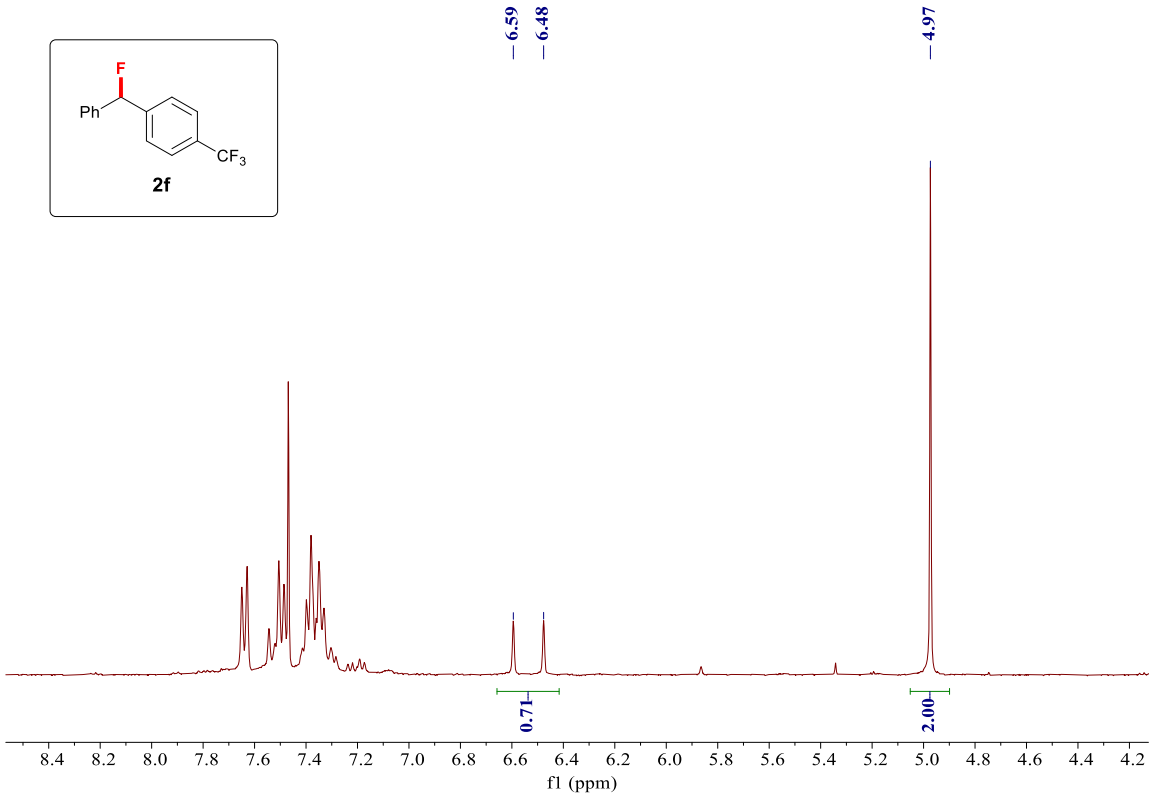
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2e**



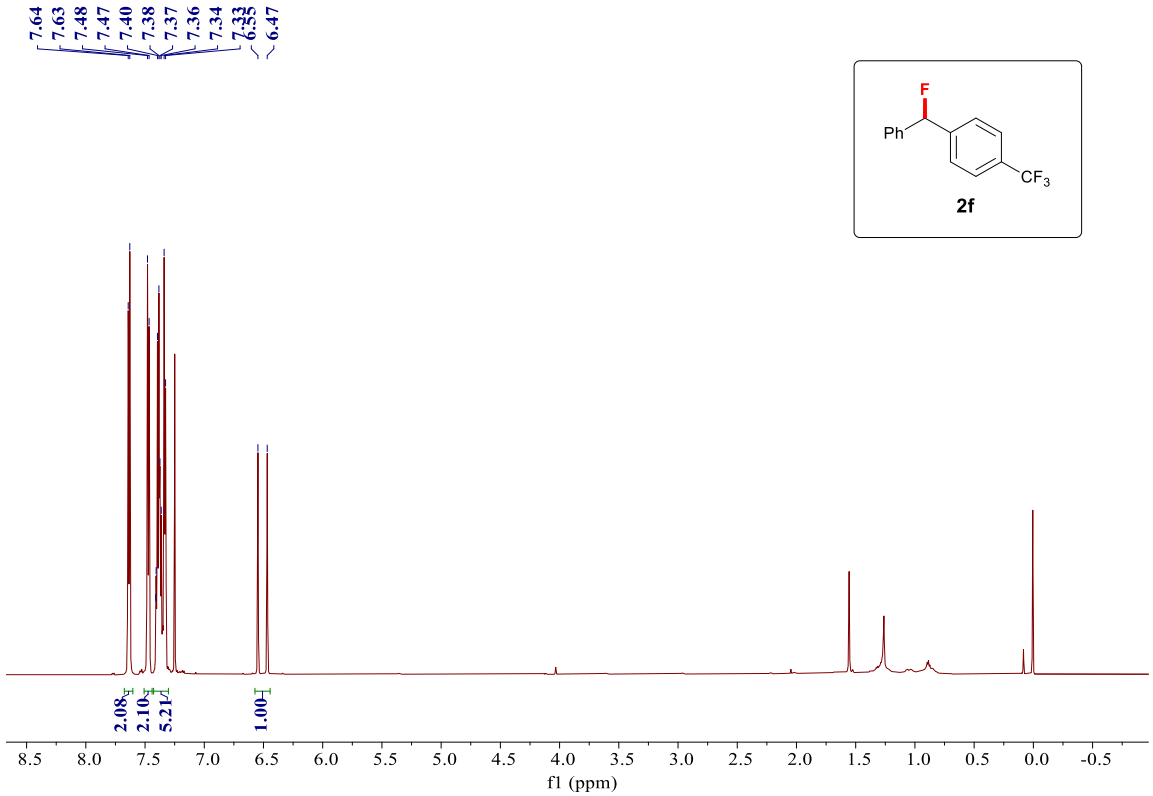
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2e**



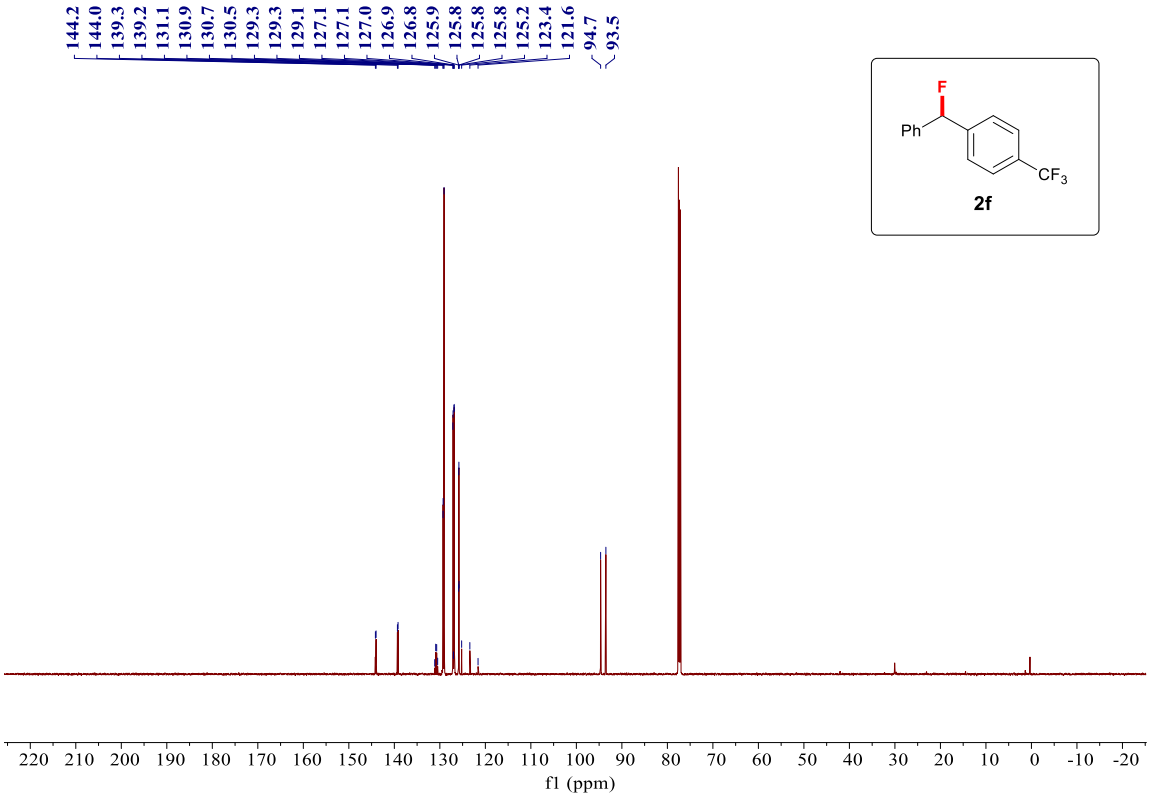
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2e**



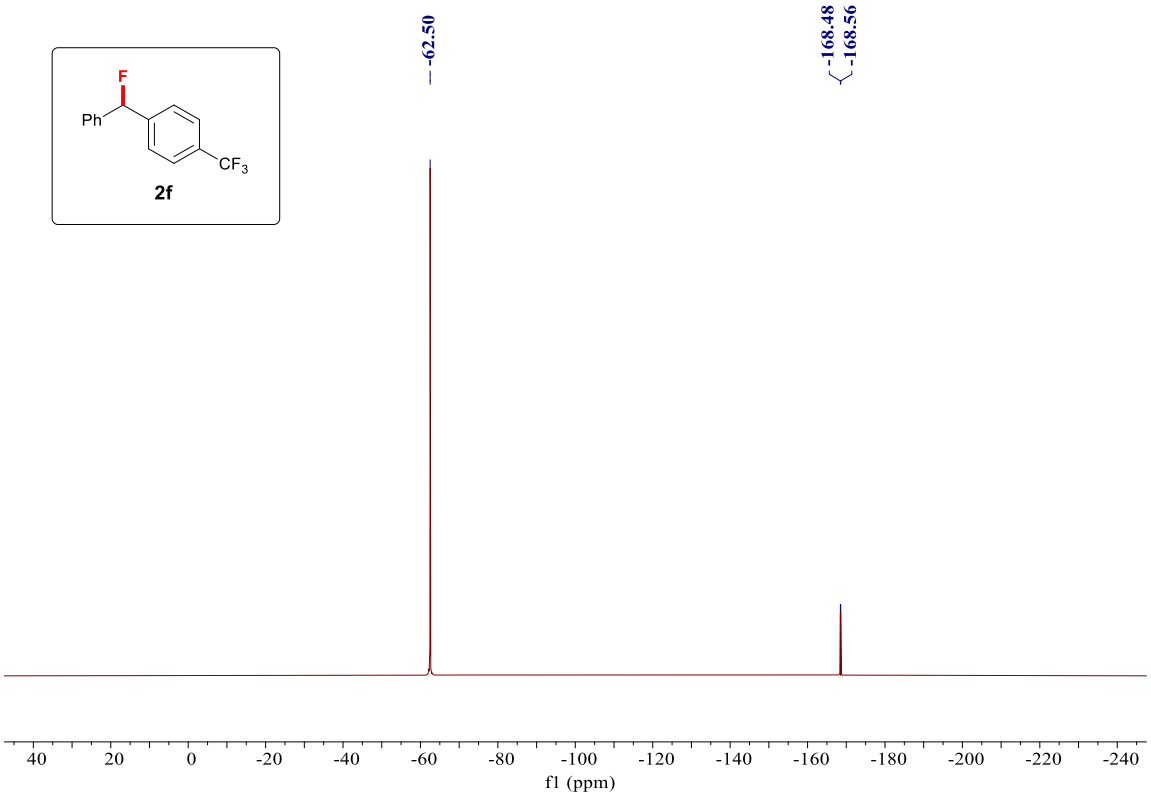
The Yield of **2f** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



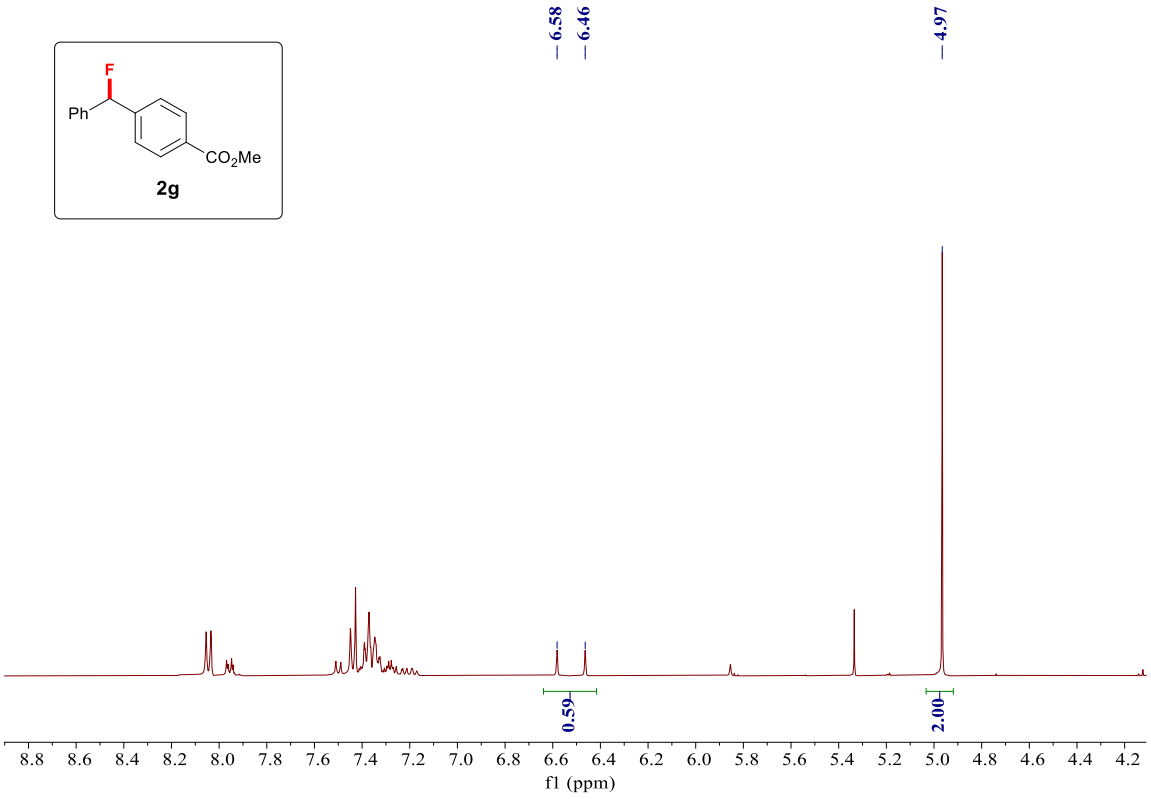
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **2f**



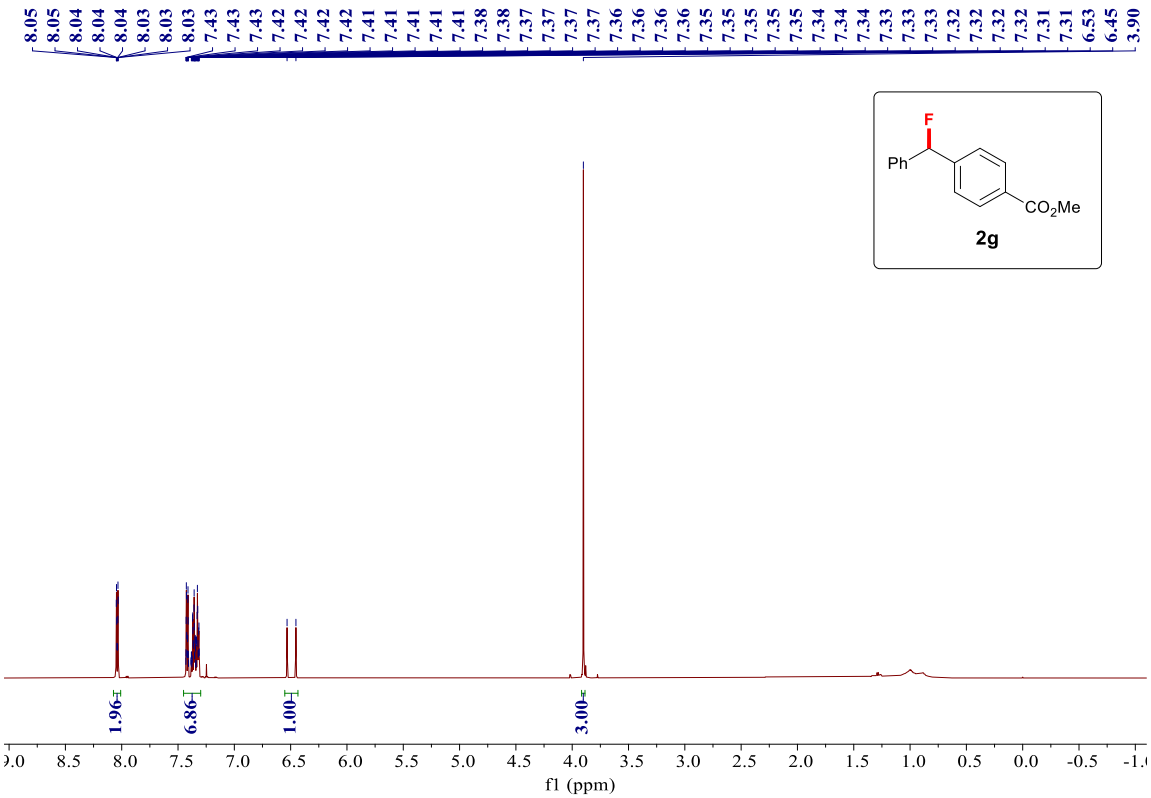
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of Compound **2f**



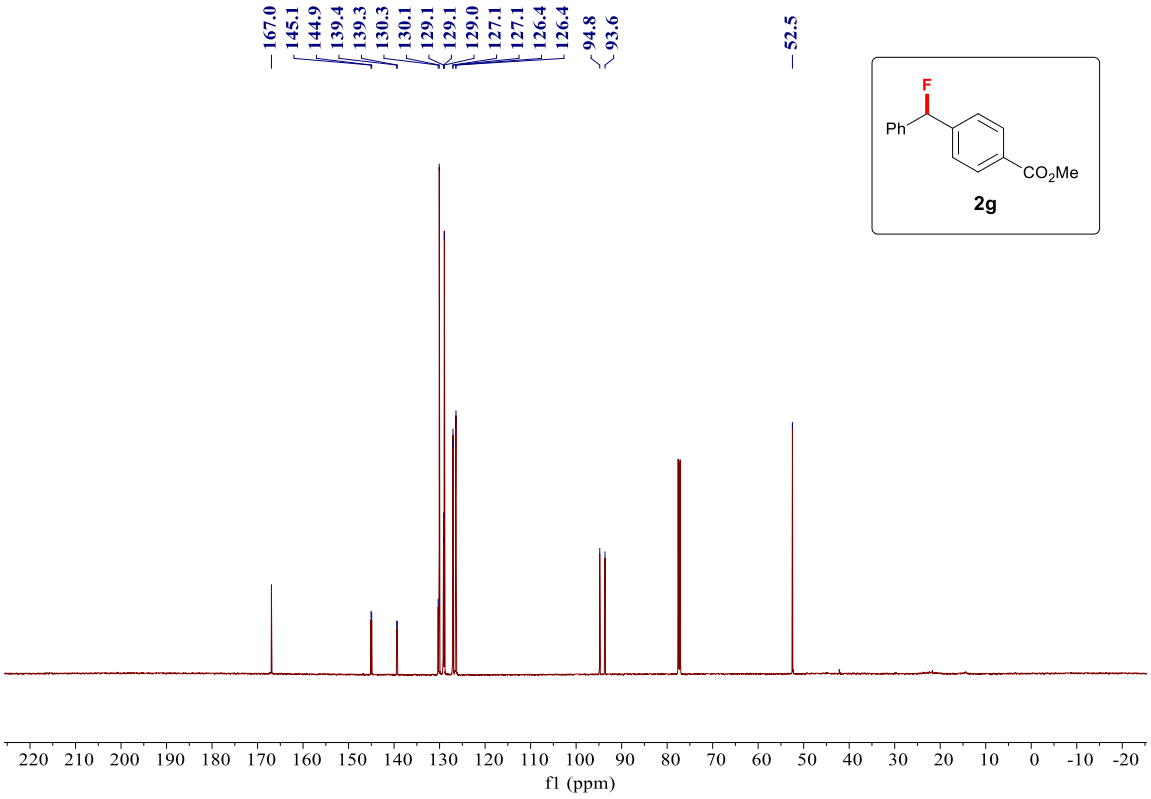
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of Compound **2f**



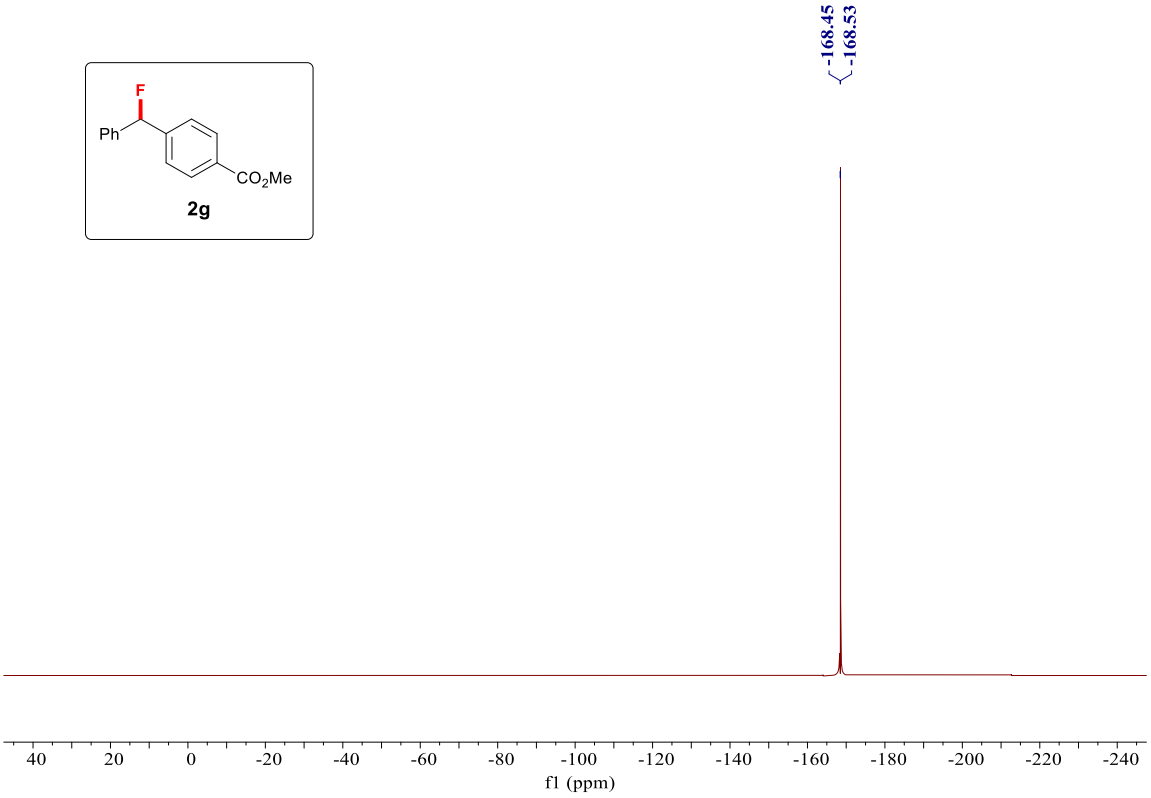
The Yield of **2g** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



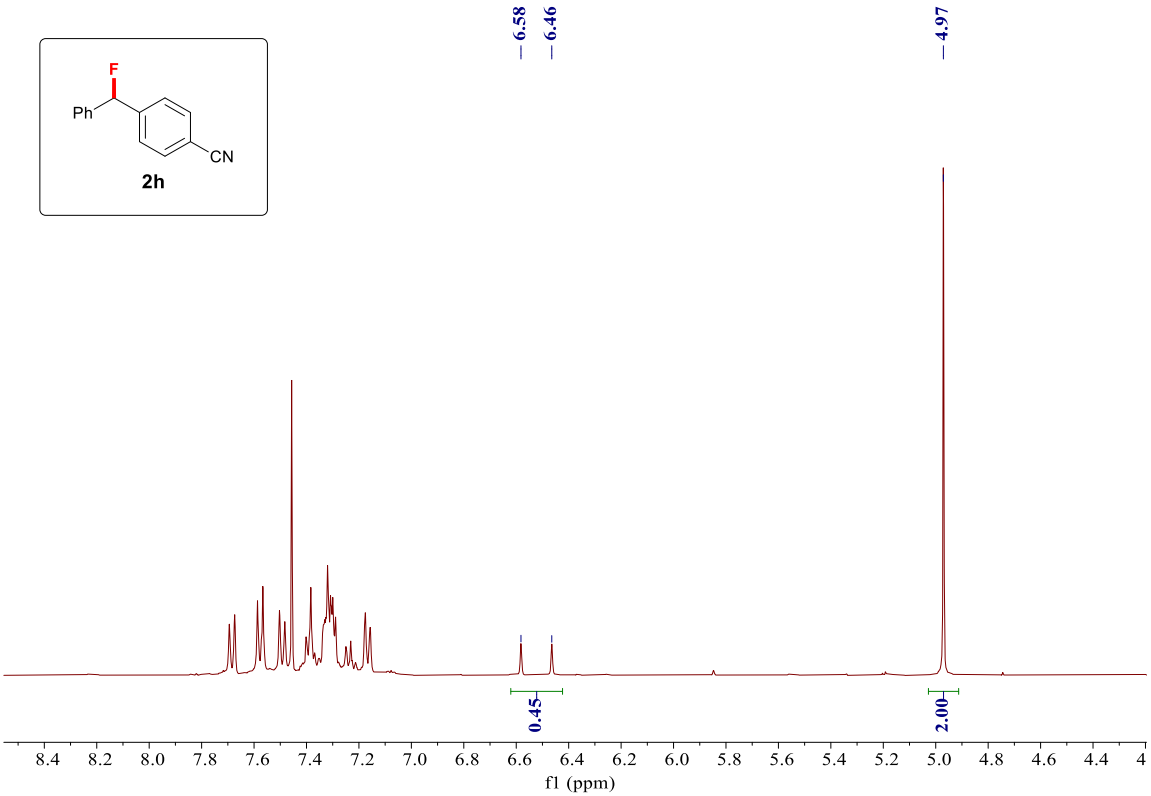
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **2g**



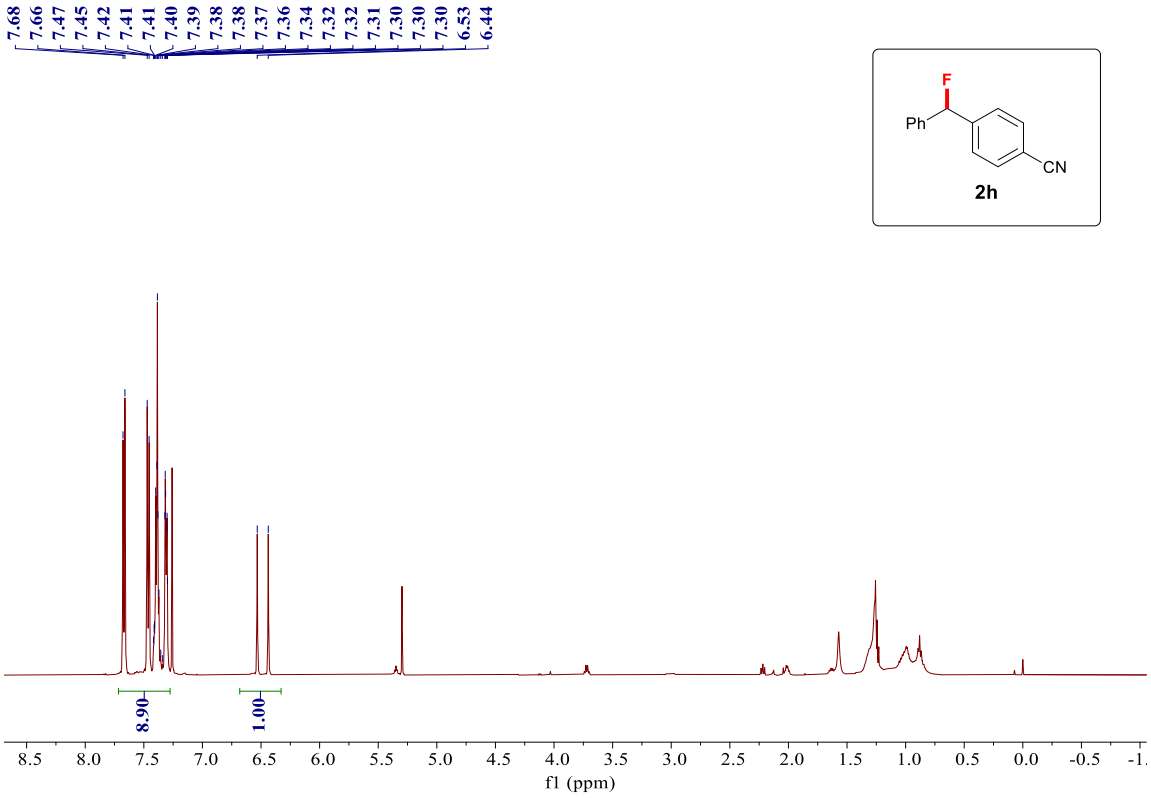
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of Compound **2g**



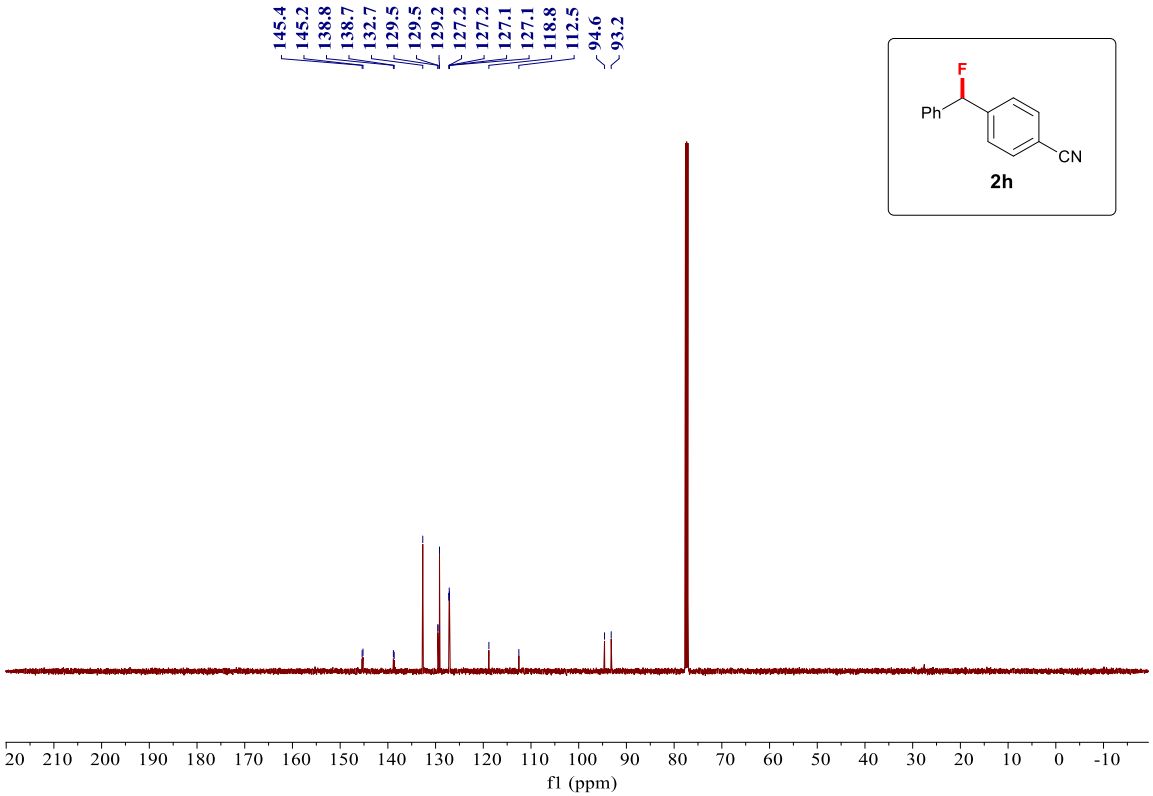
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of Compound **2g**



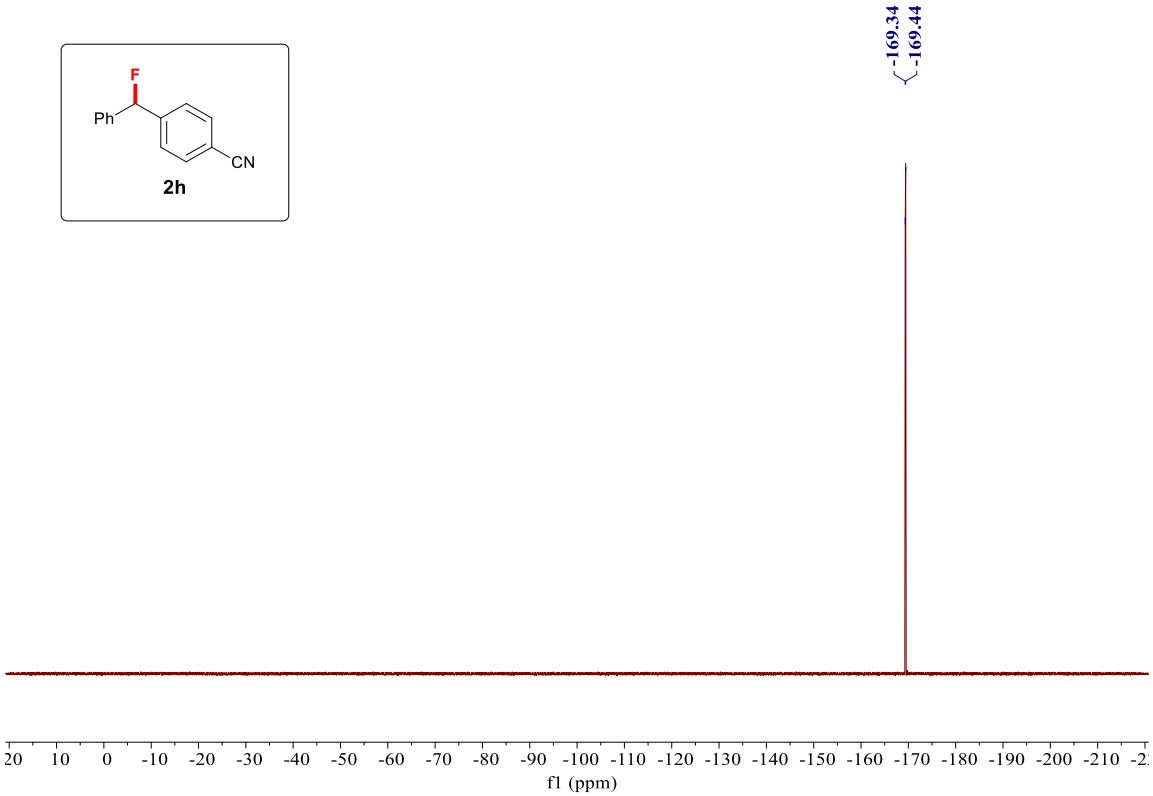
The Yield of **2h** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



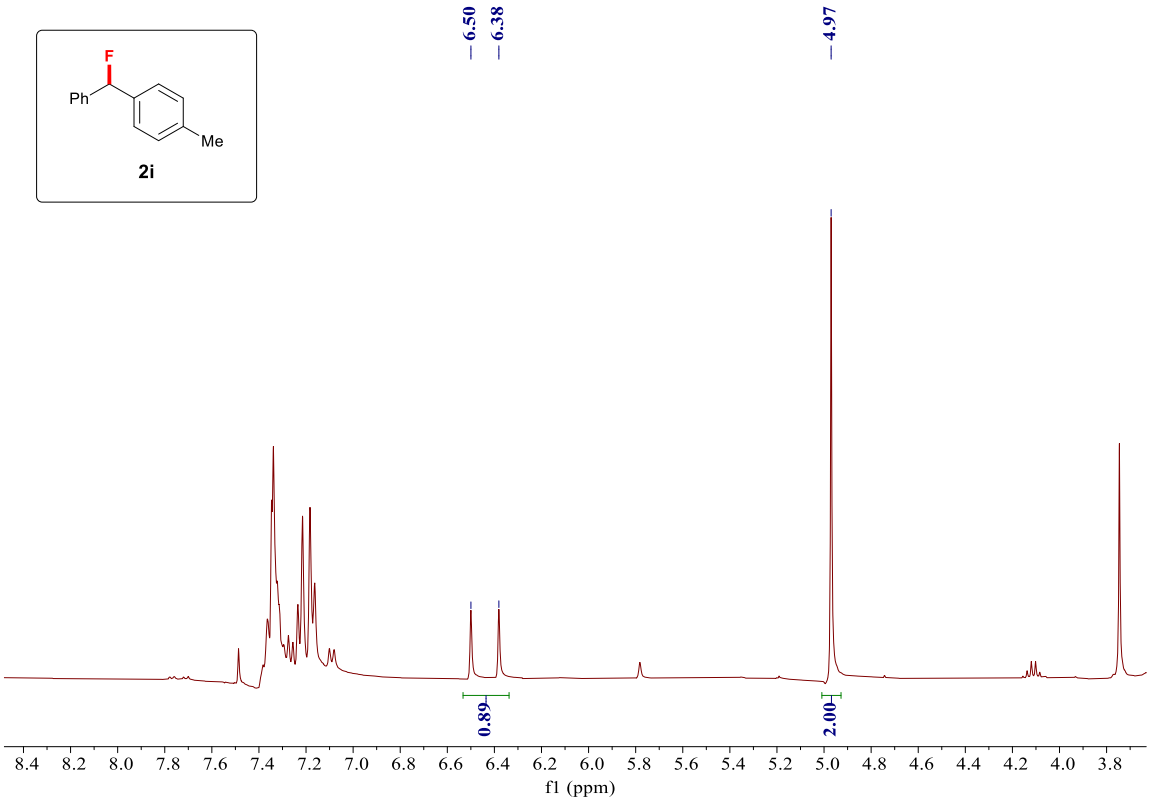
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2h**



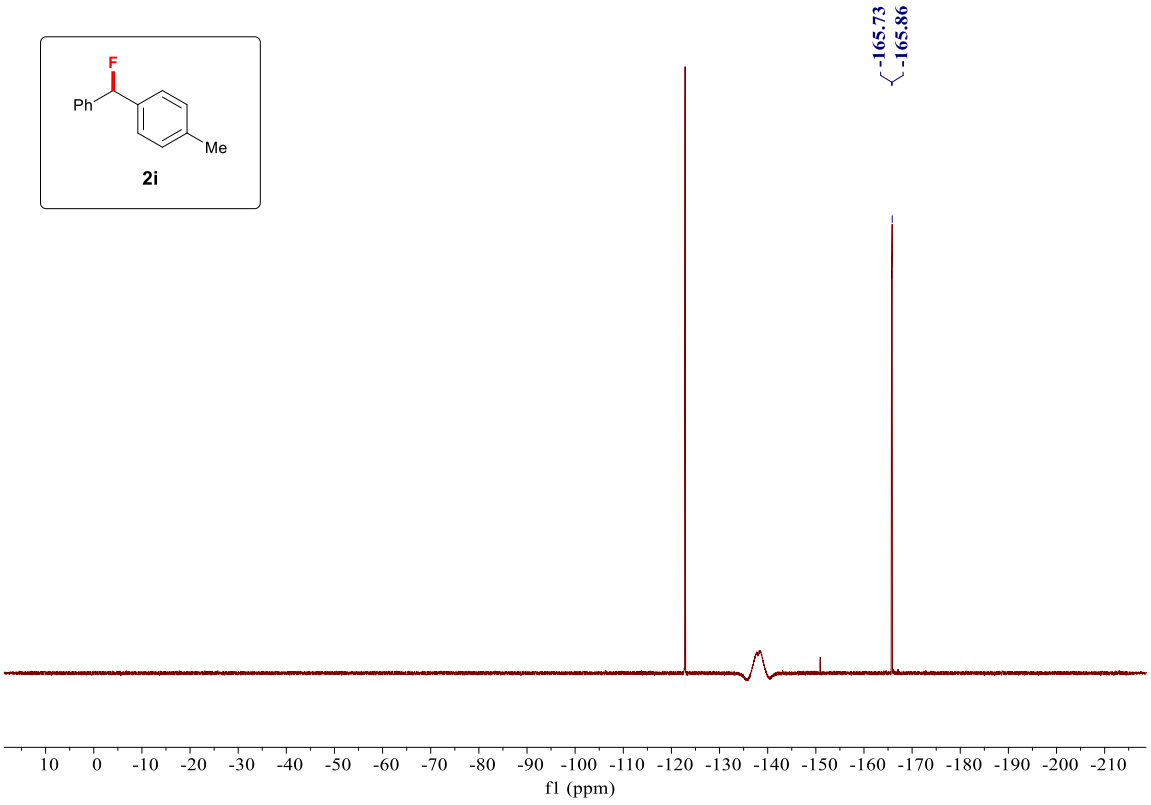
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2h**



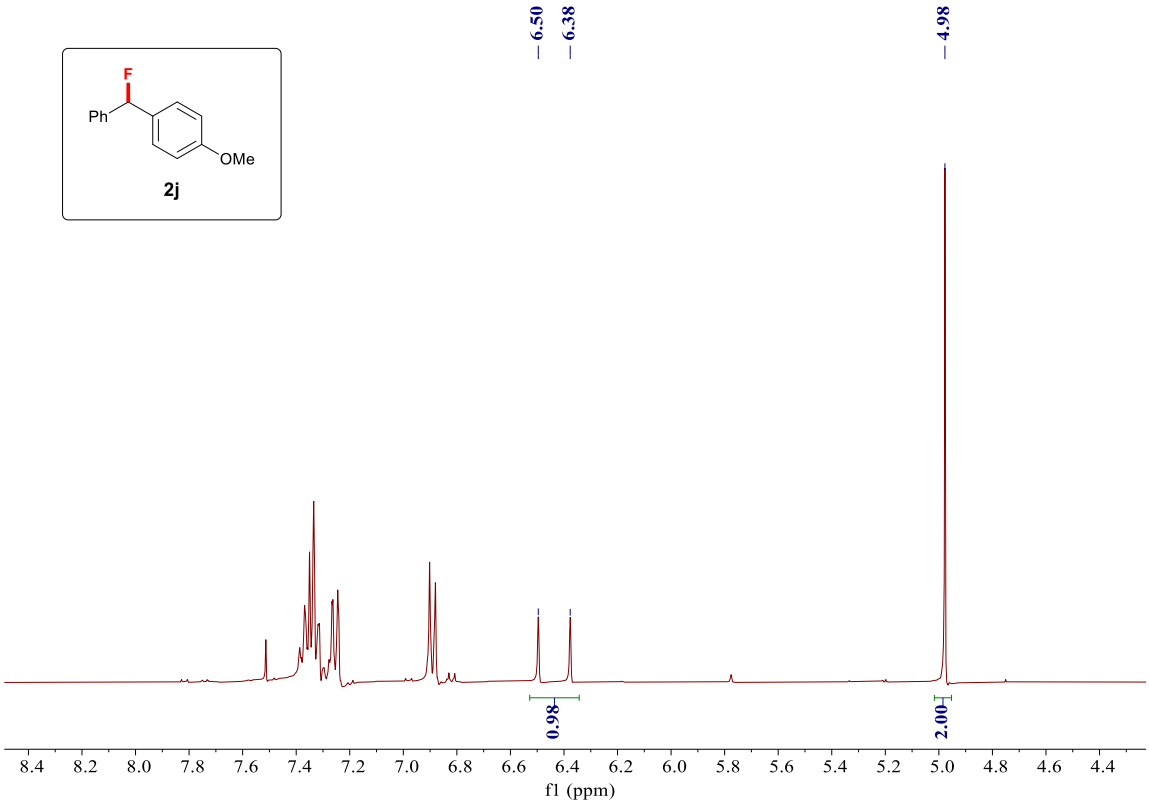
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2h**



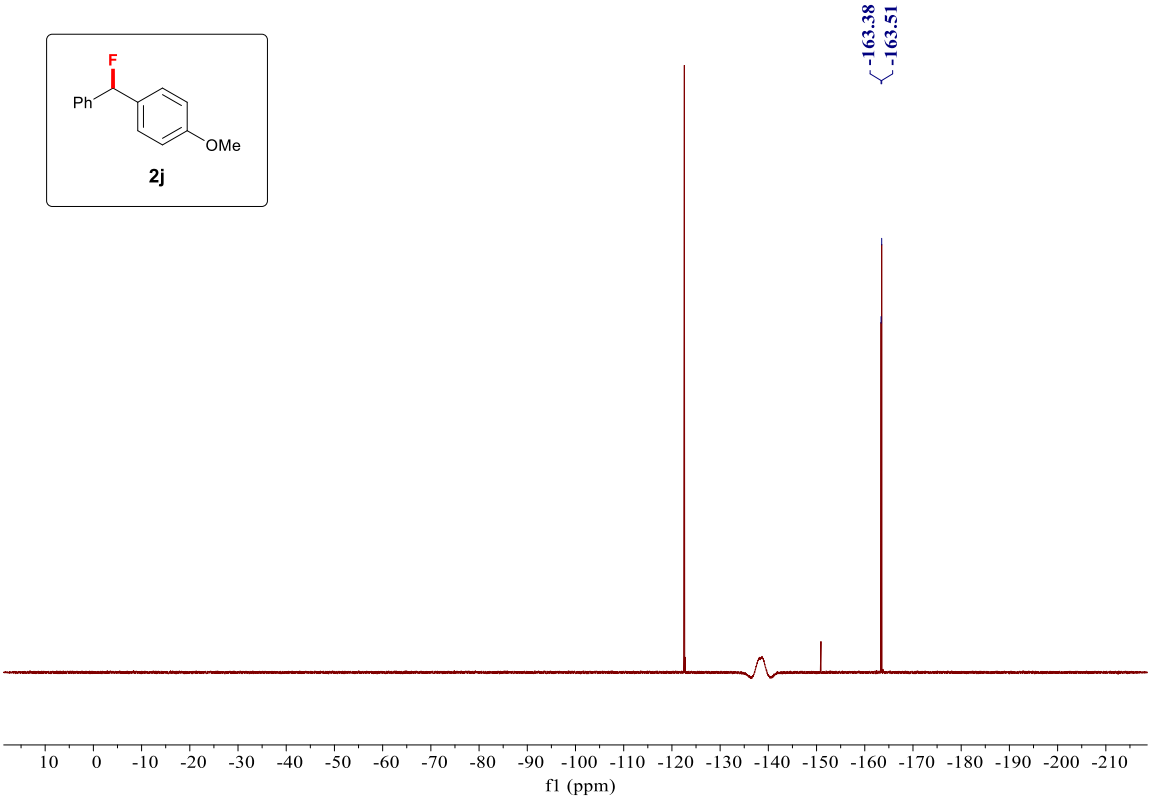
The Yield of **2i** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



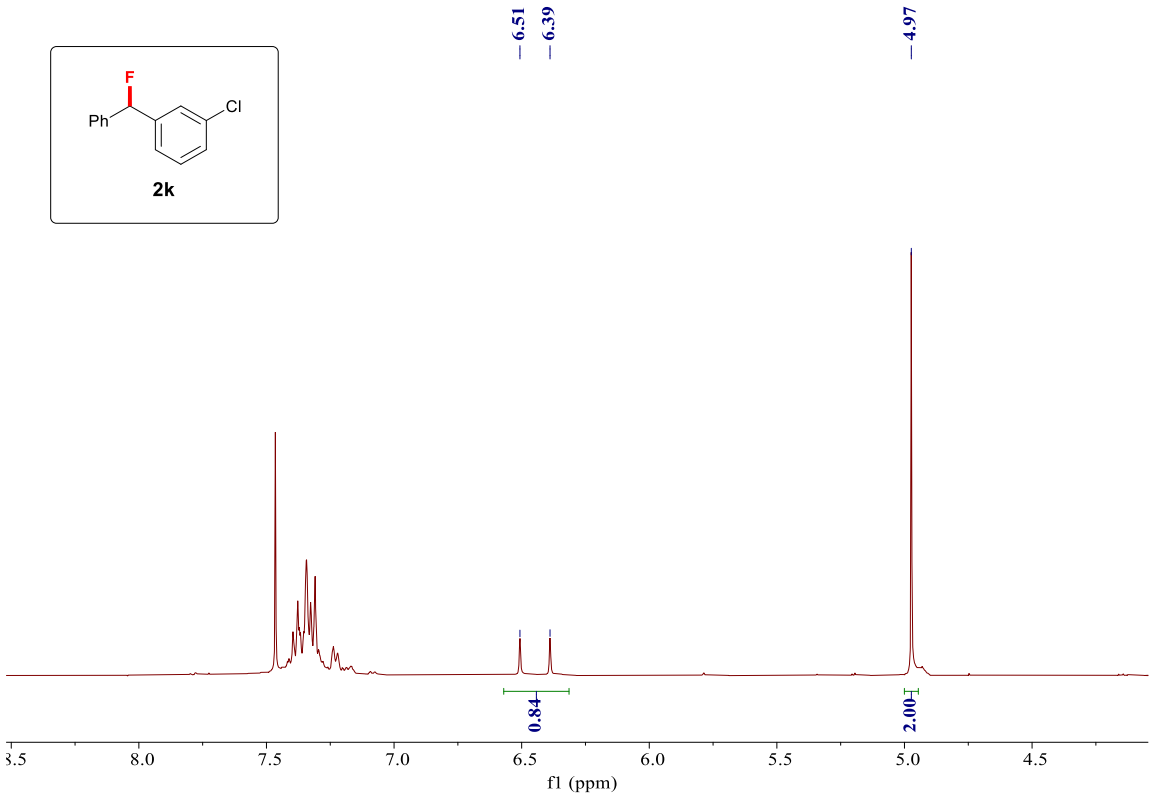
Crude ^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **2i** Reaction Mixture



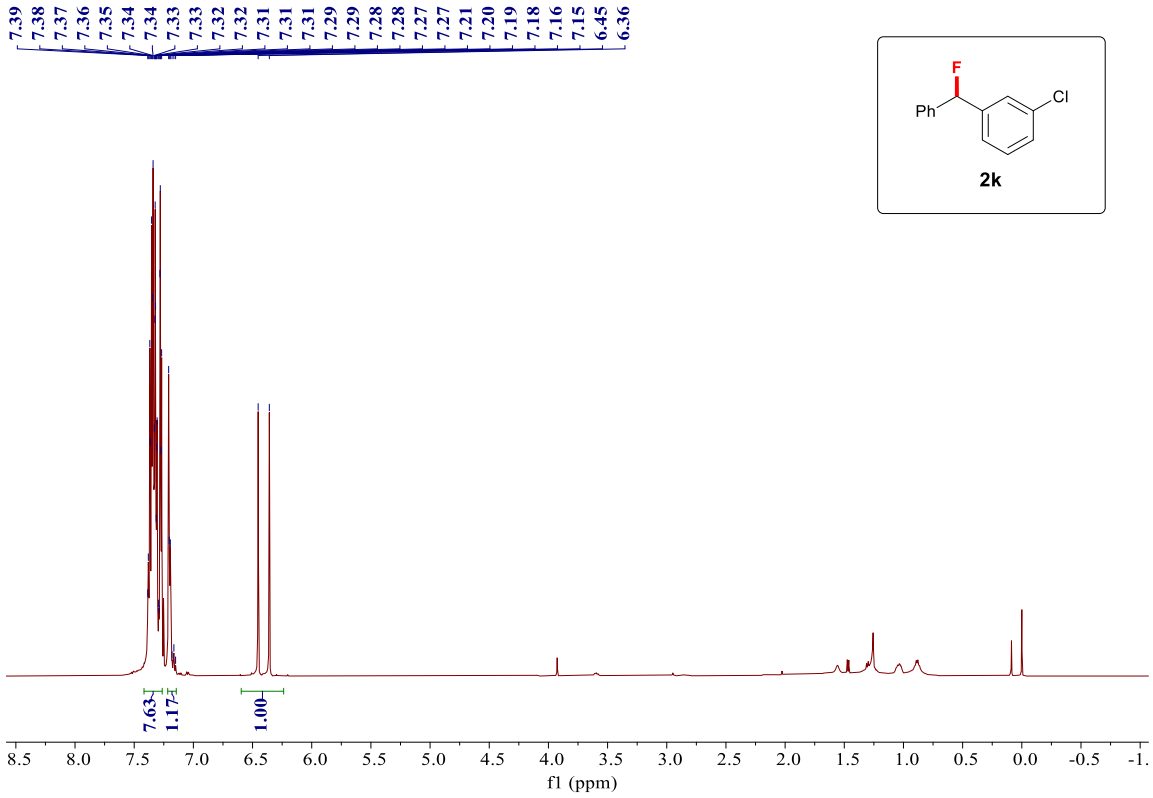
The Yield of **2j** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



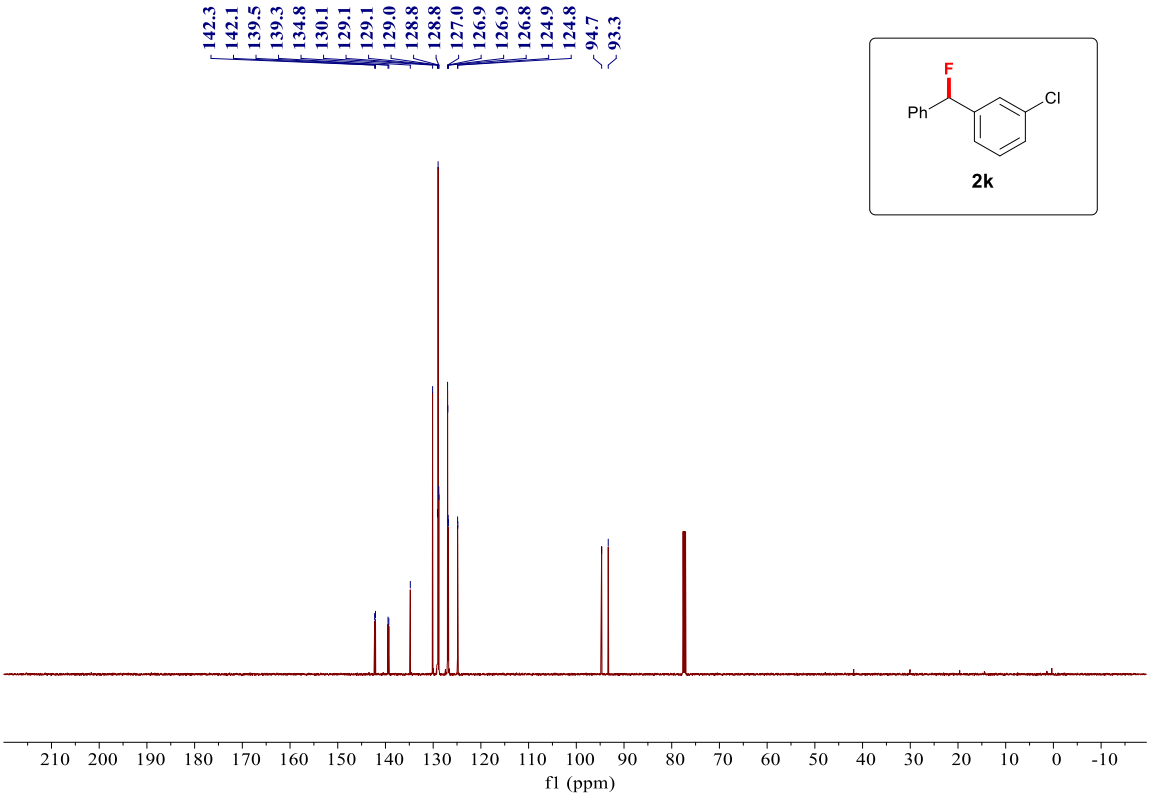
Crude ^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **2j** Reaction Mixture



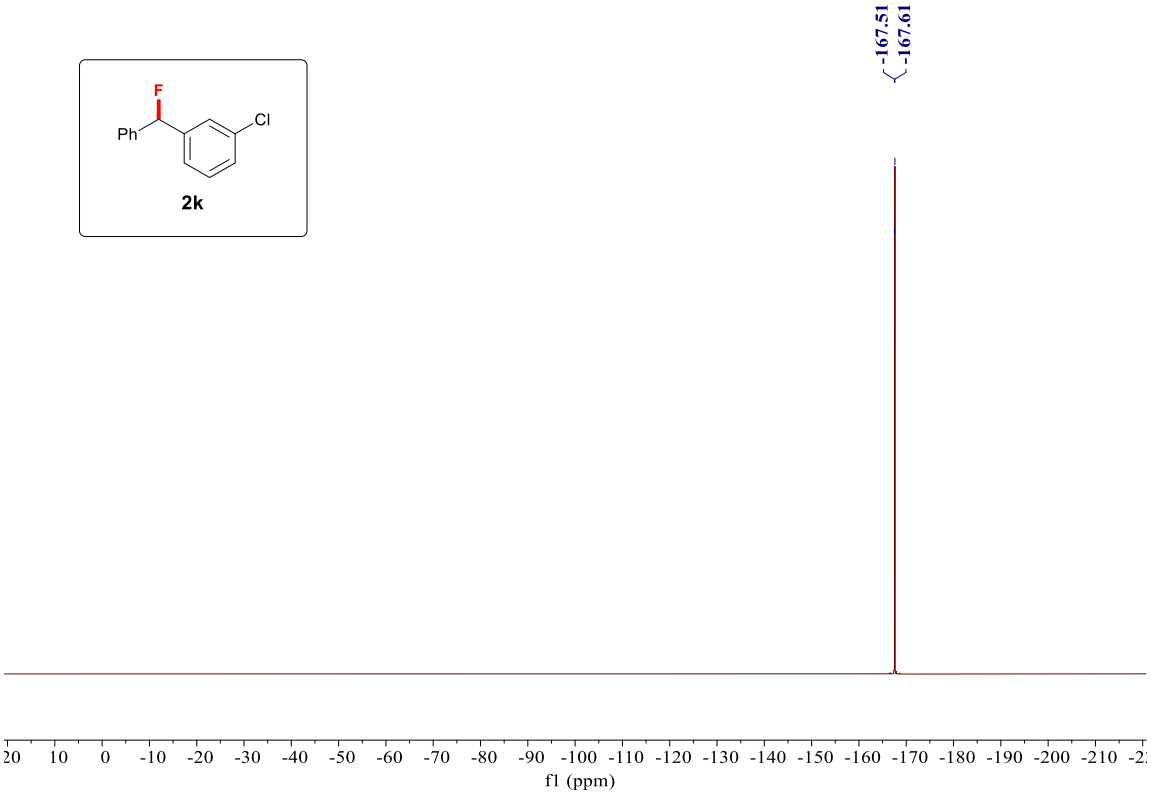
The Yield of **2k** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



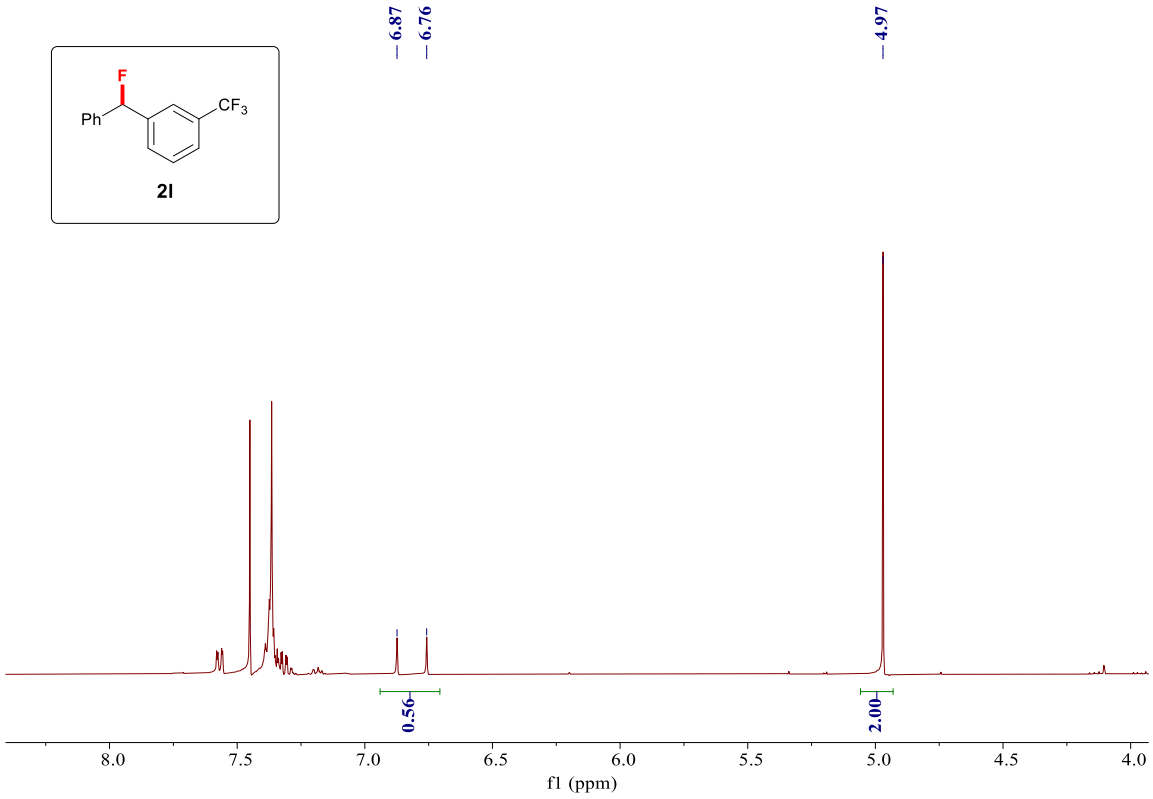
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2k**



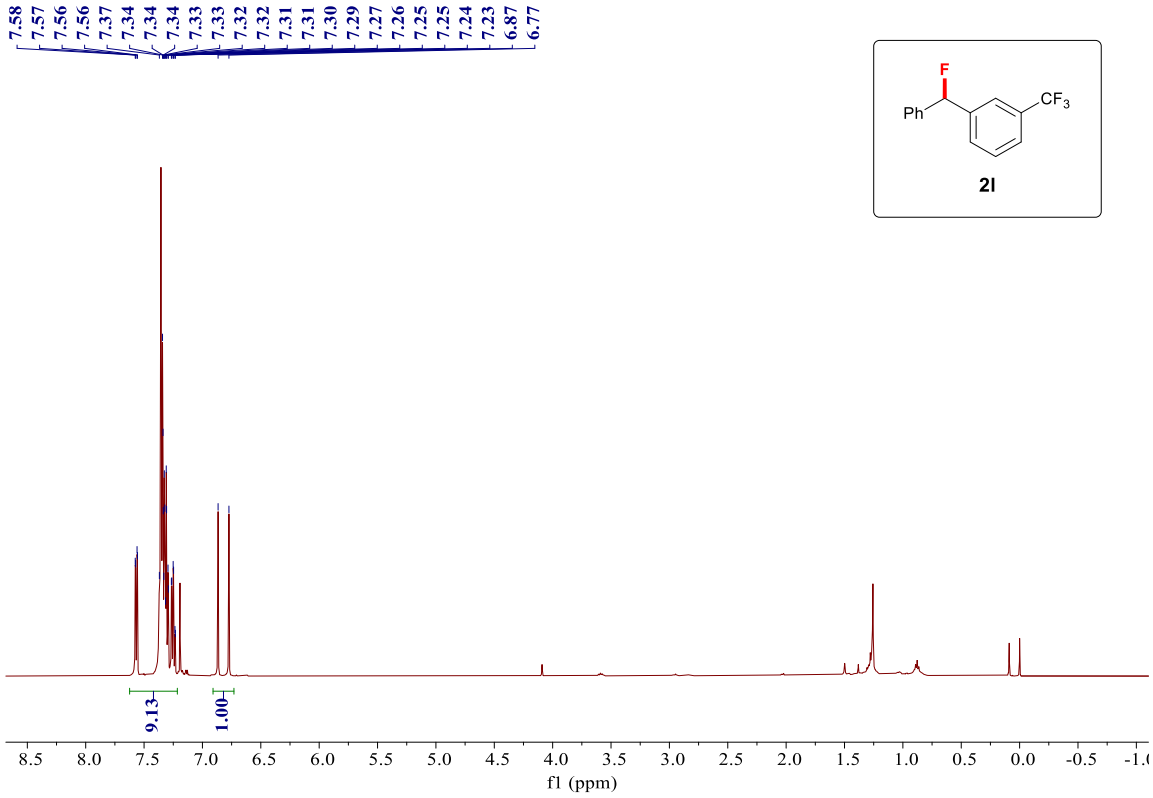
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2k**



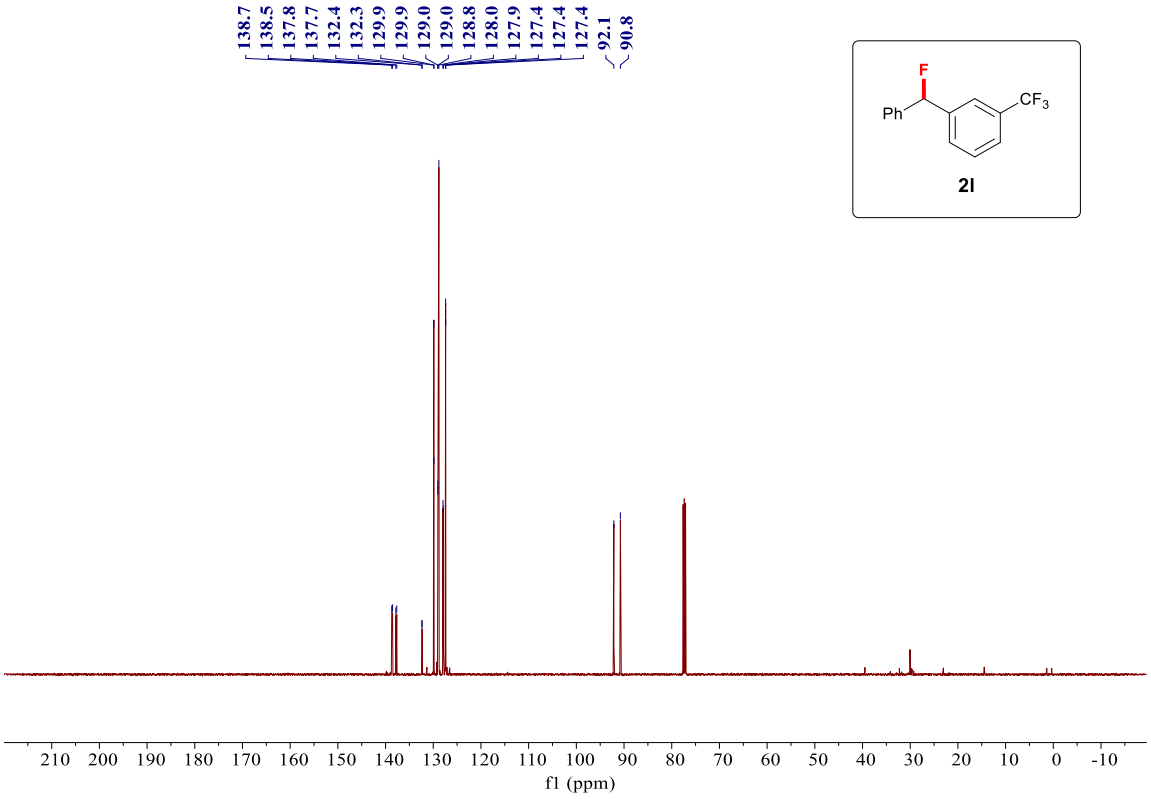
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2k**



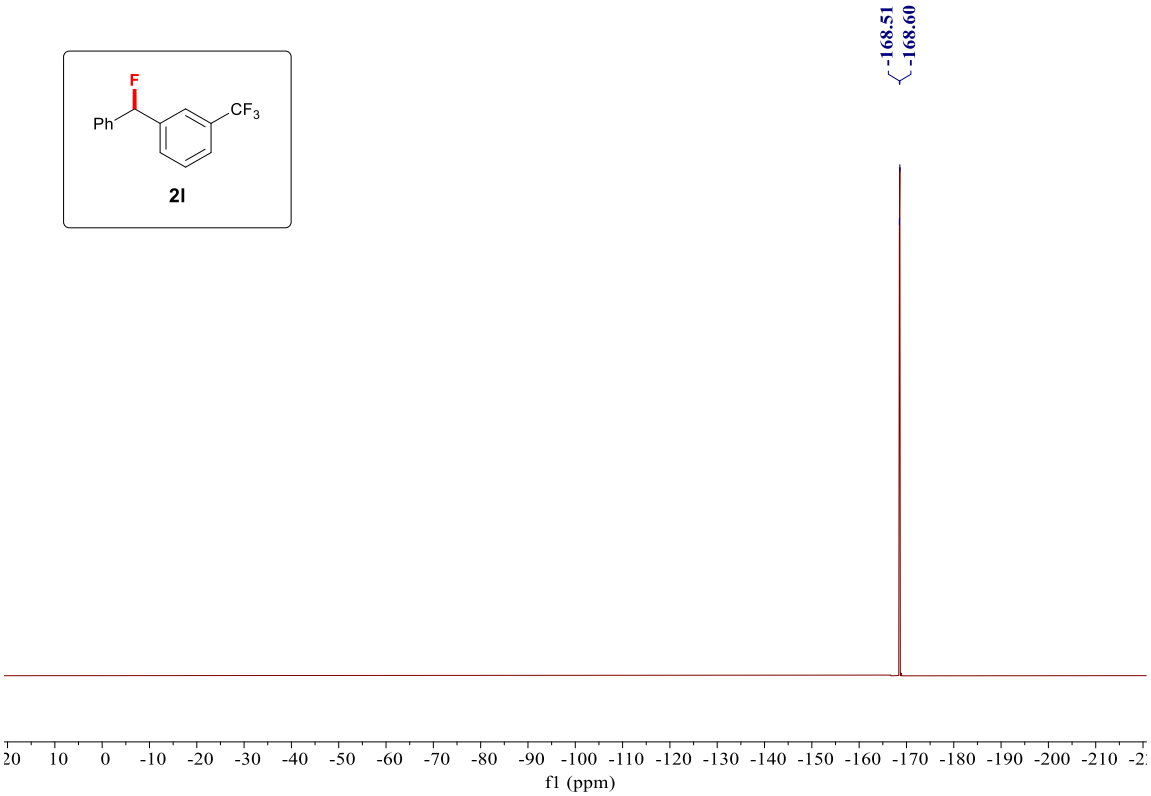
The Yield of **2l** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



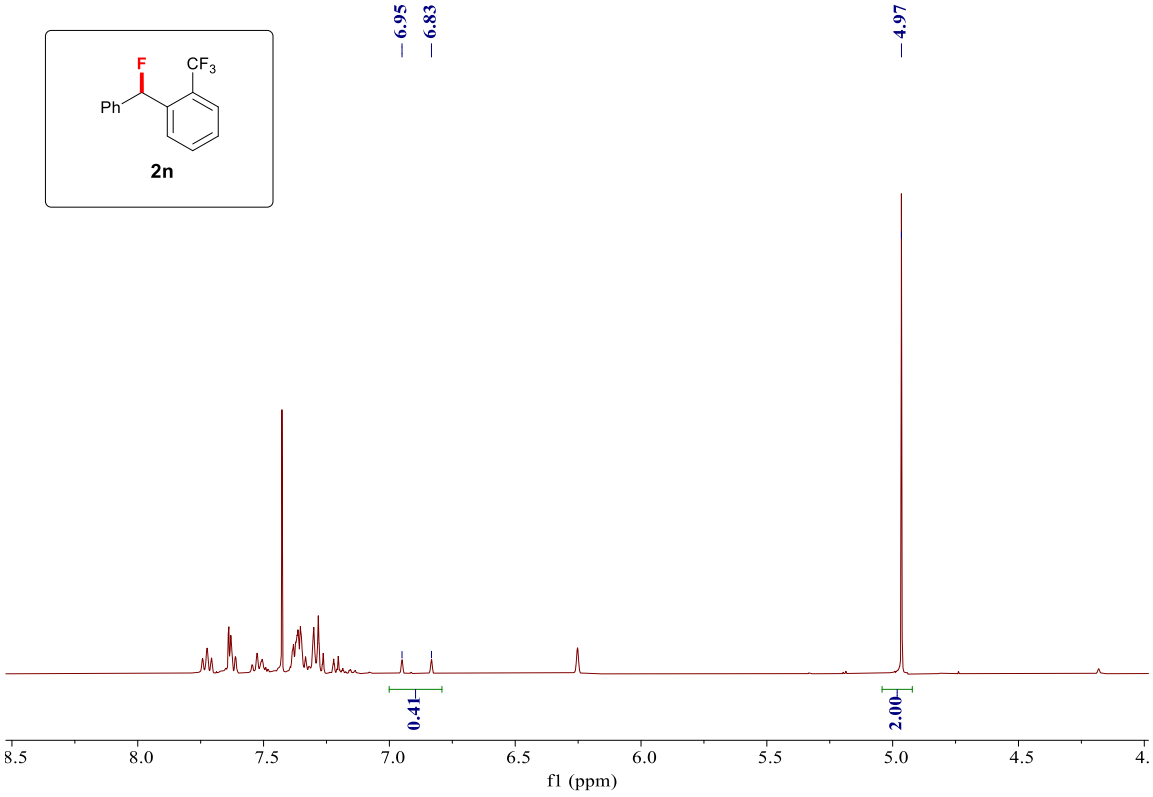
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2l**



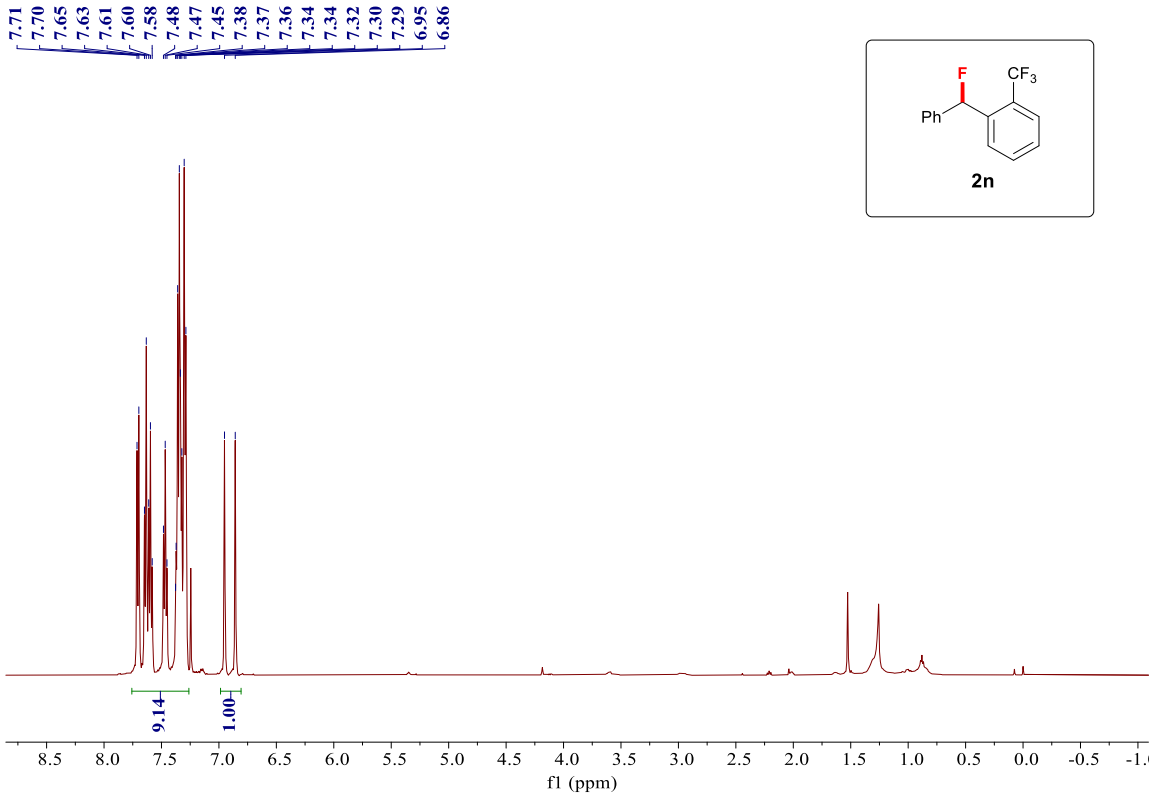
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2l**



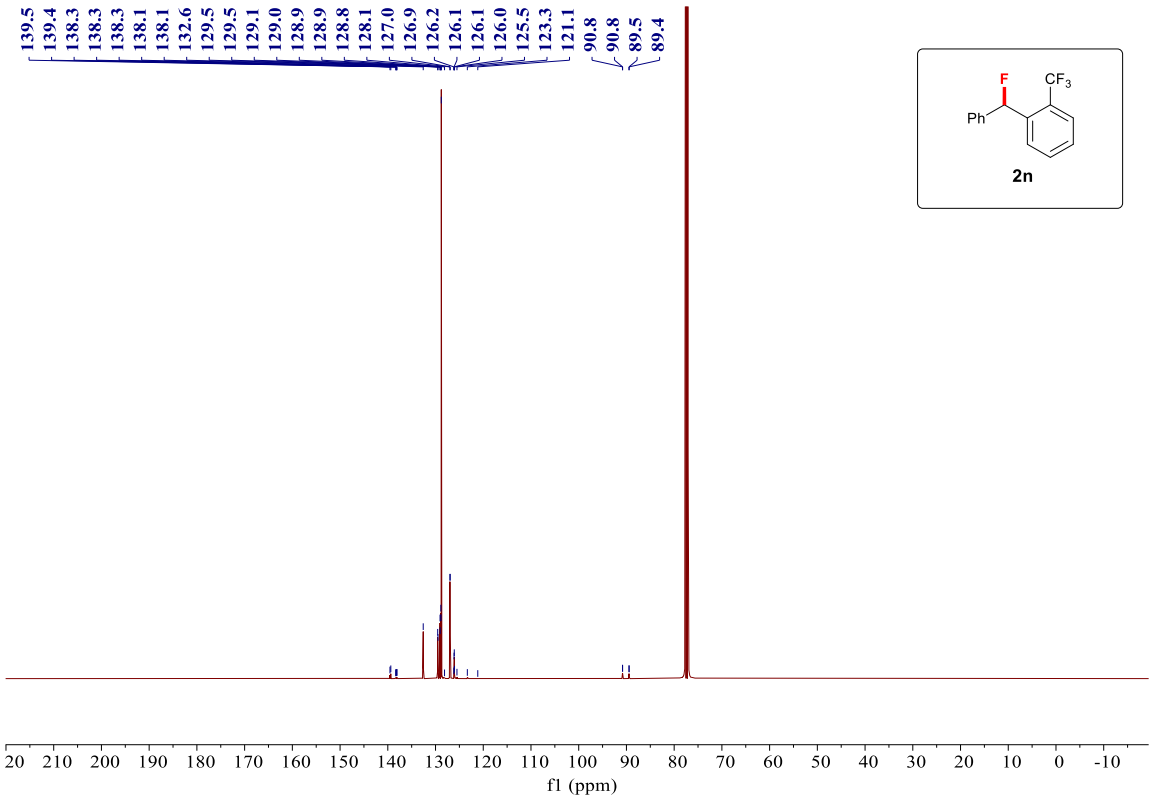
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2l**



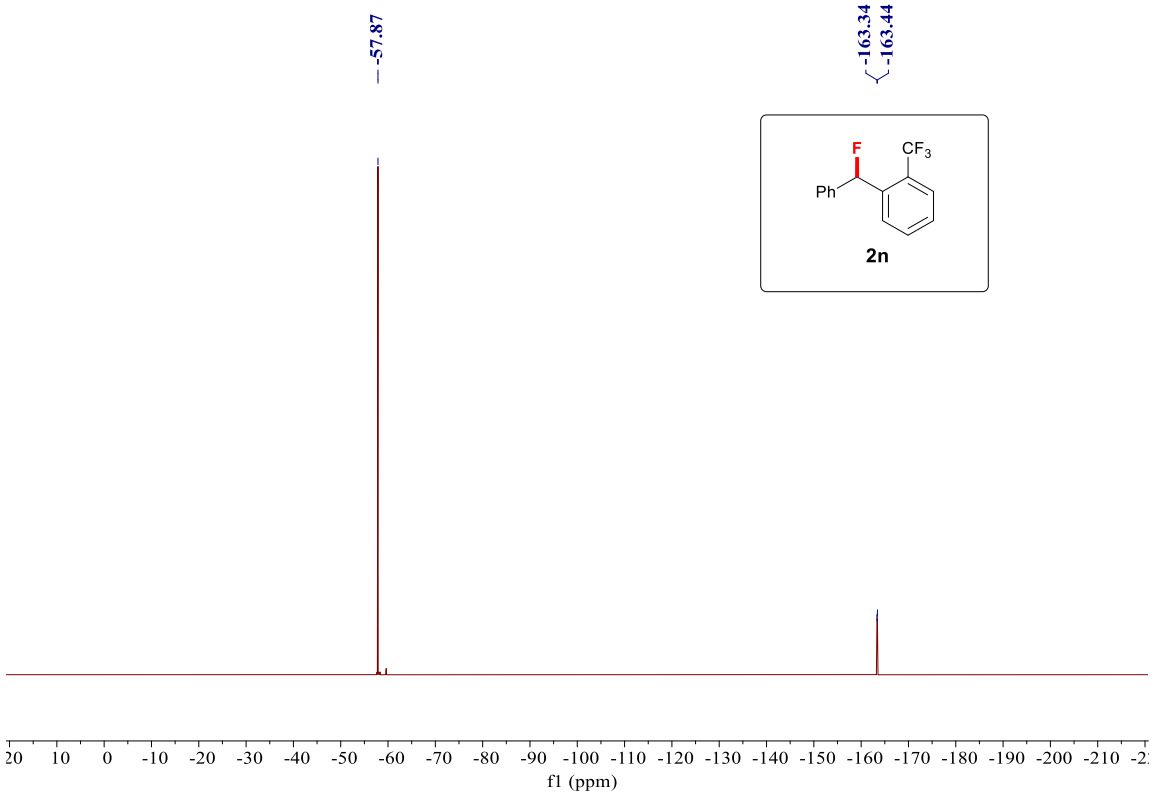
The Yield of **2n** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



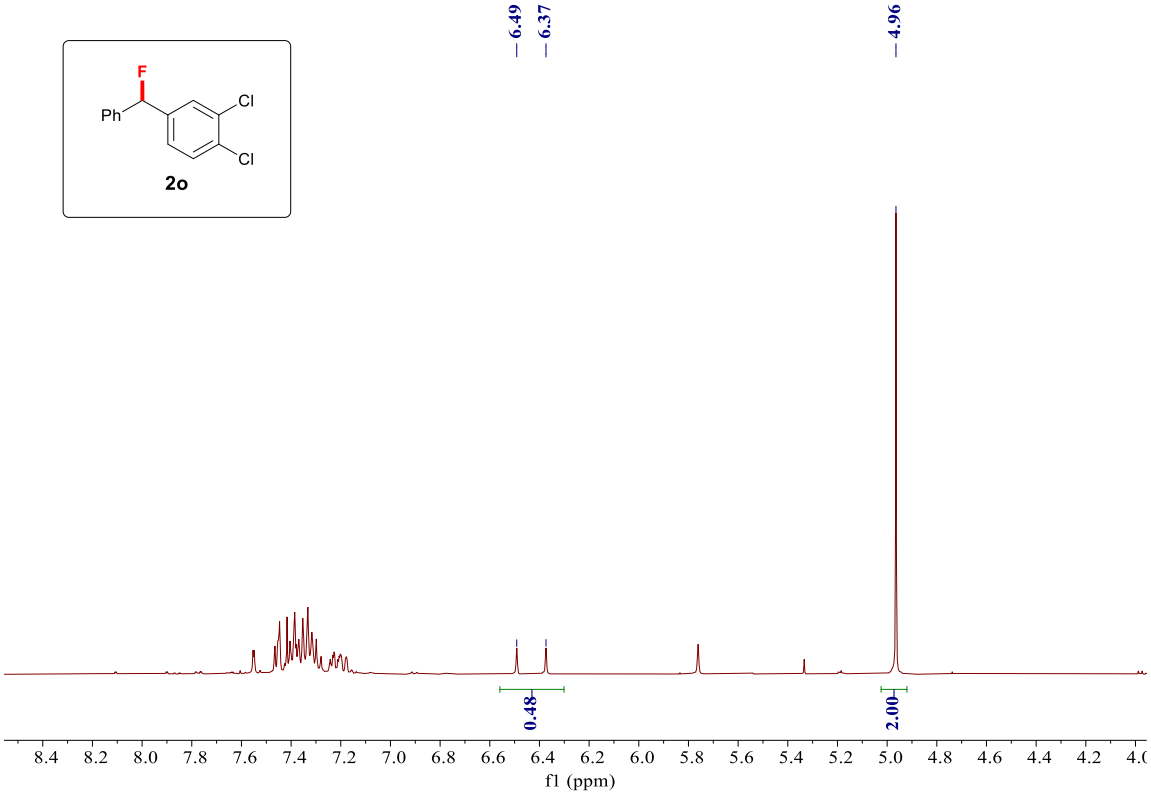
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2n**



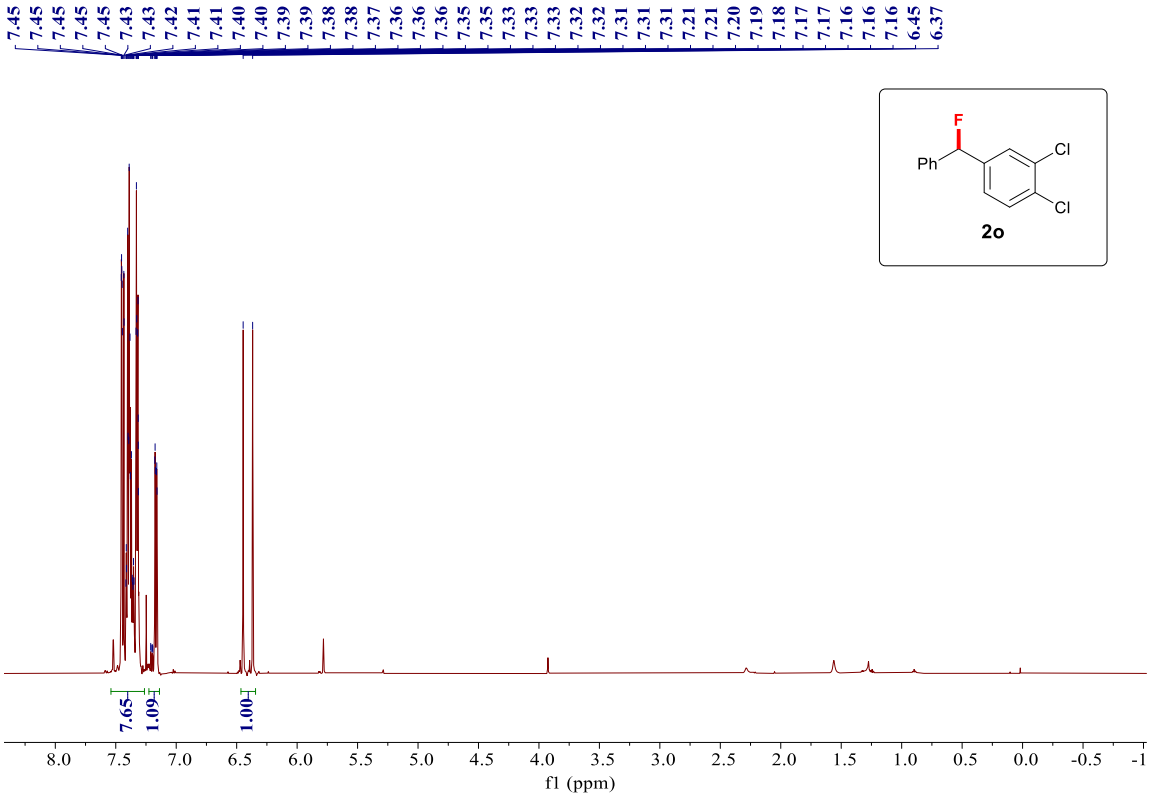
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2n**



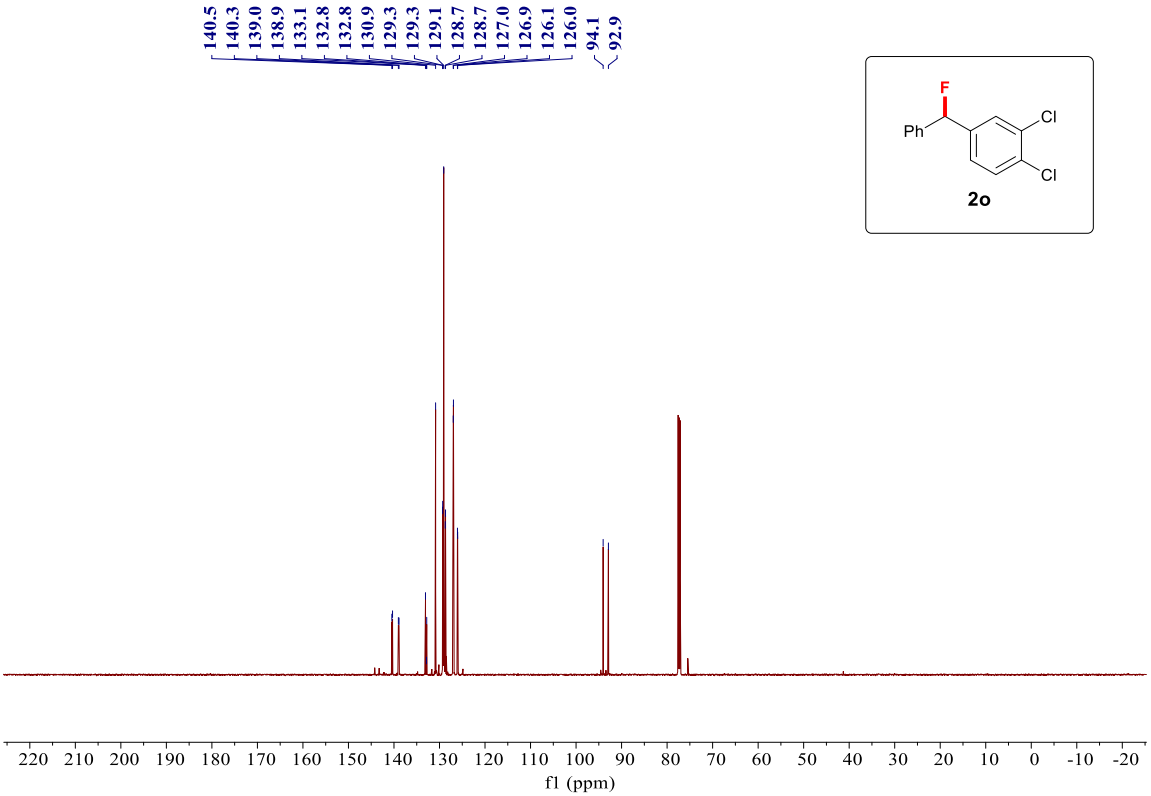
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2n**



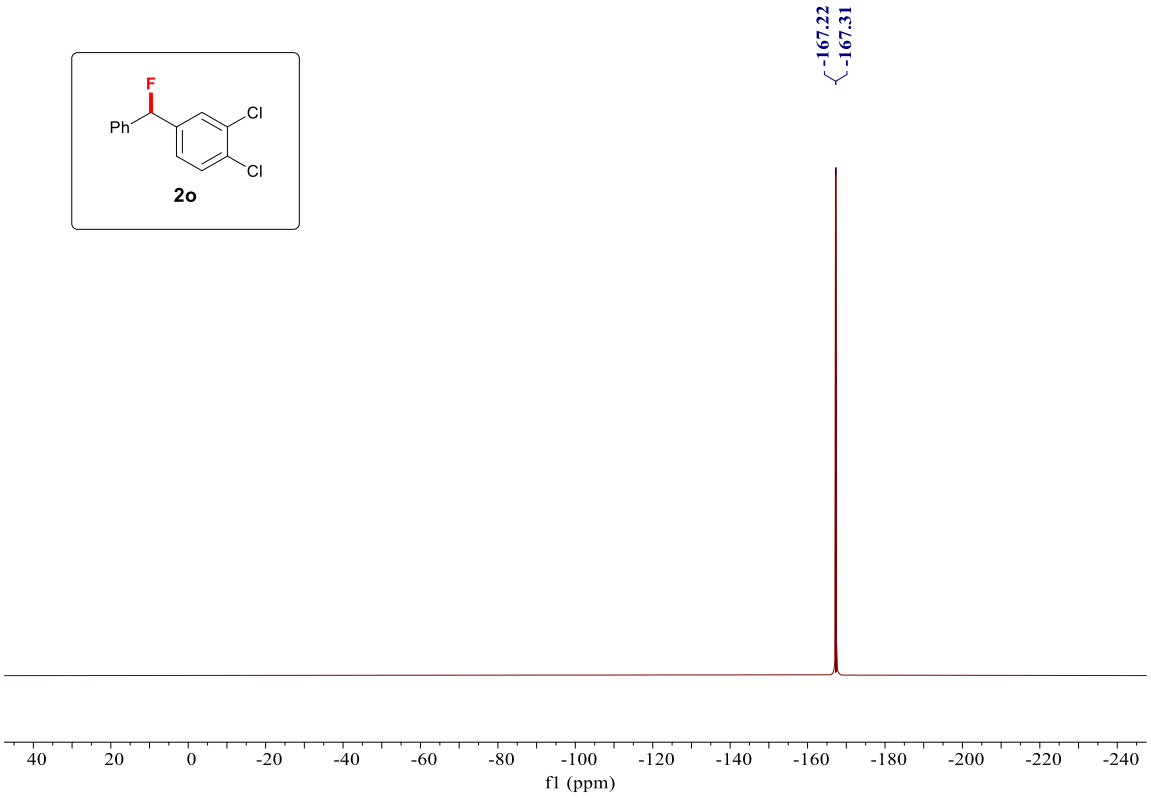
The Yield of **2o** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



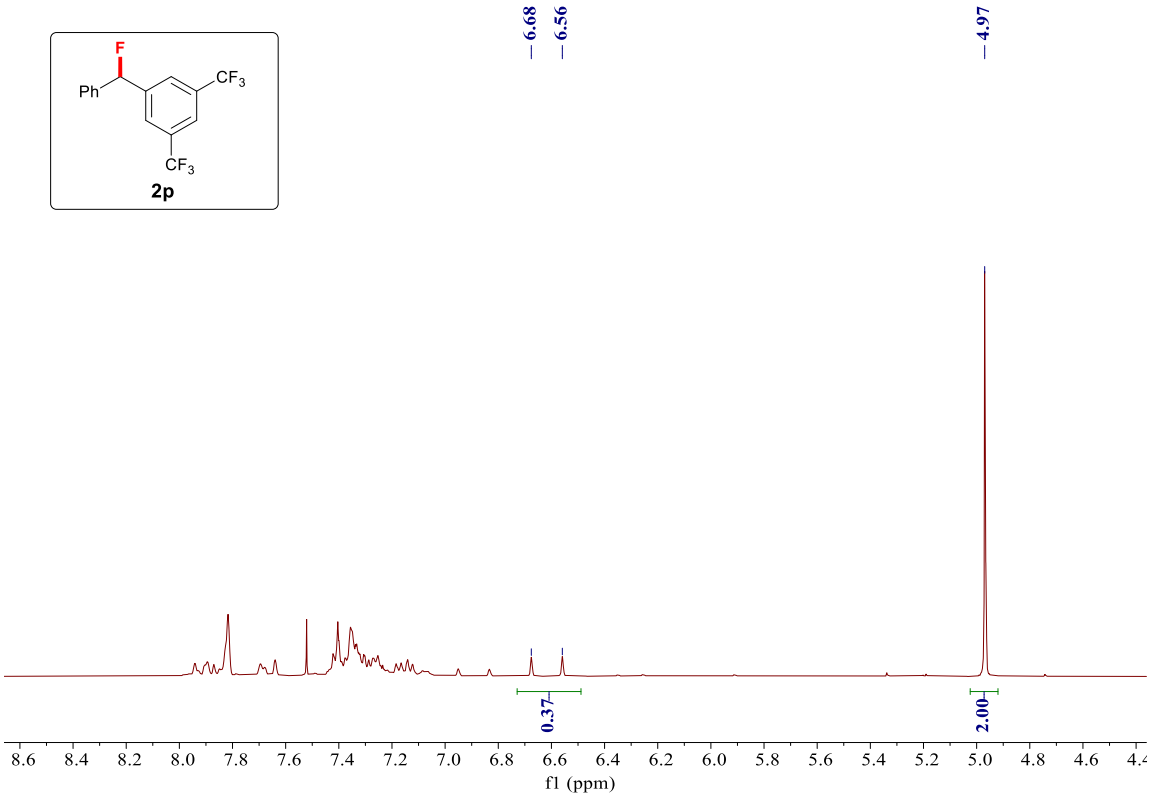
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **2o**



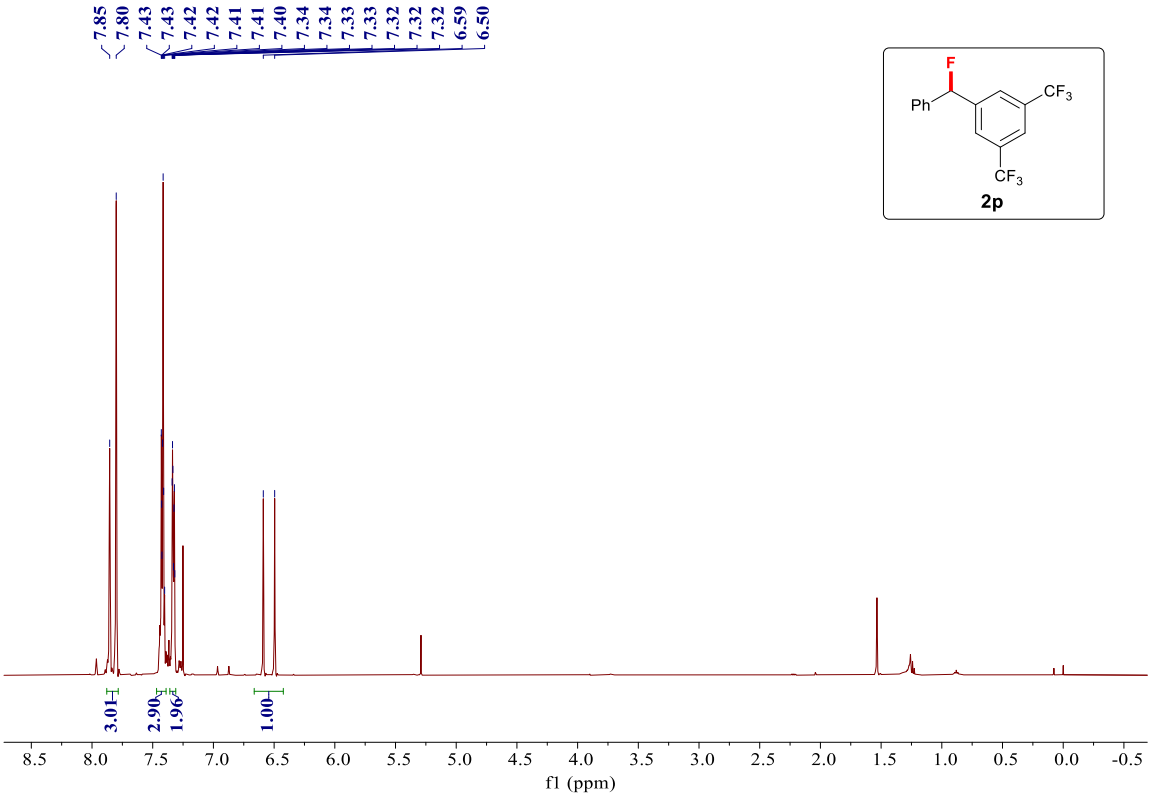
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of Compound **2o**



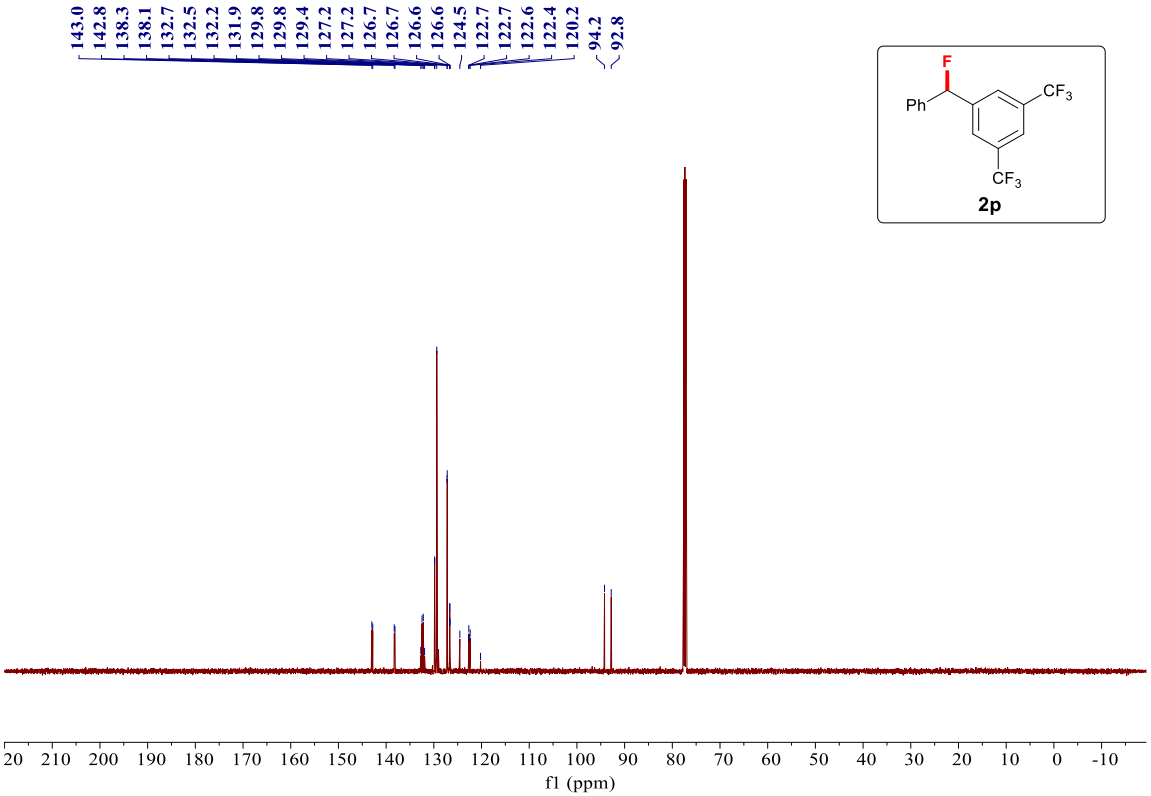
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of Compound **2o**



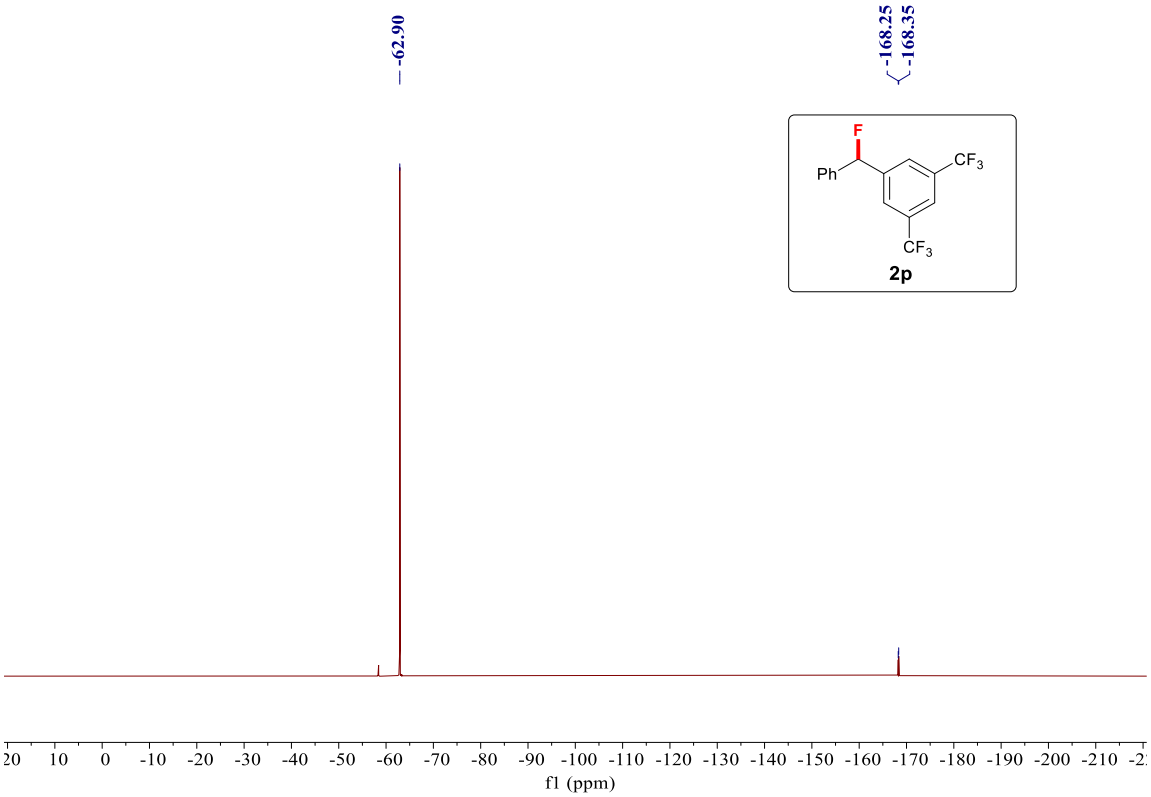
The Yield of **2p** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



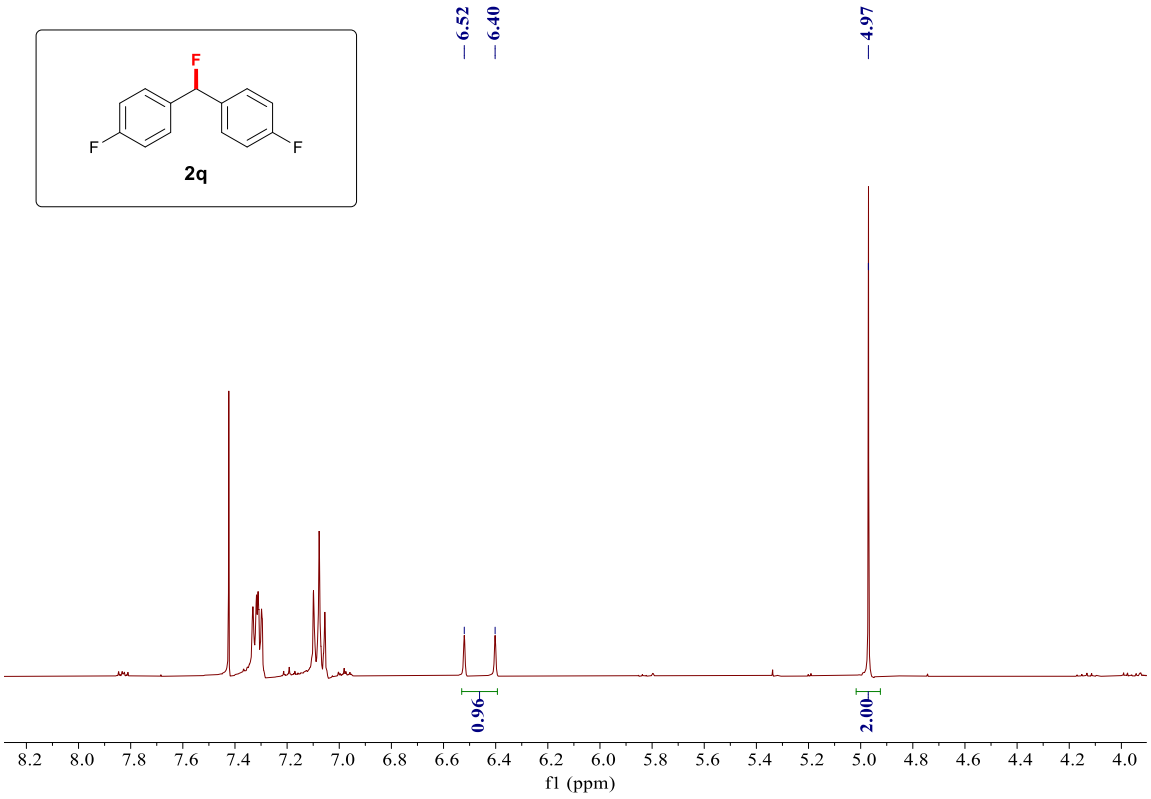
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2p**



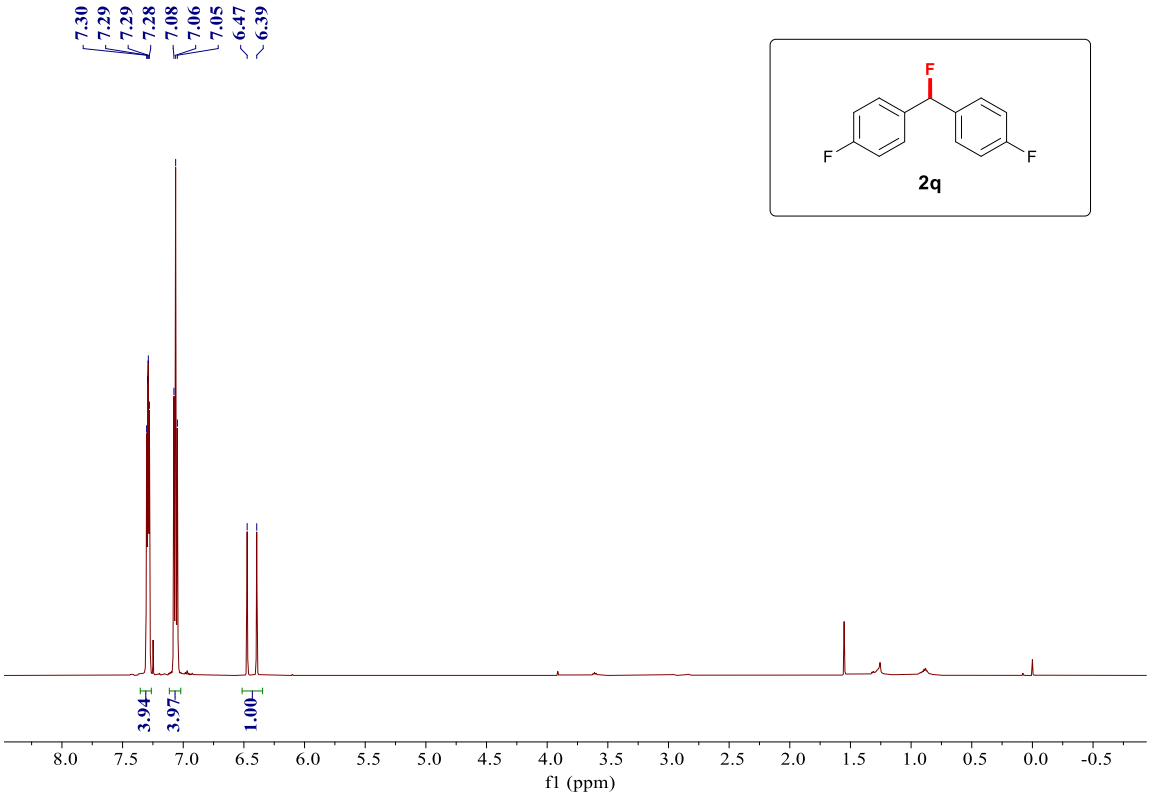
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2p**



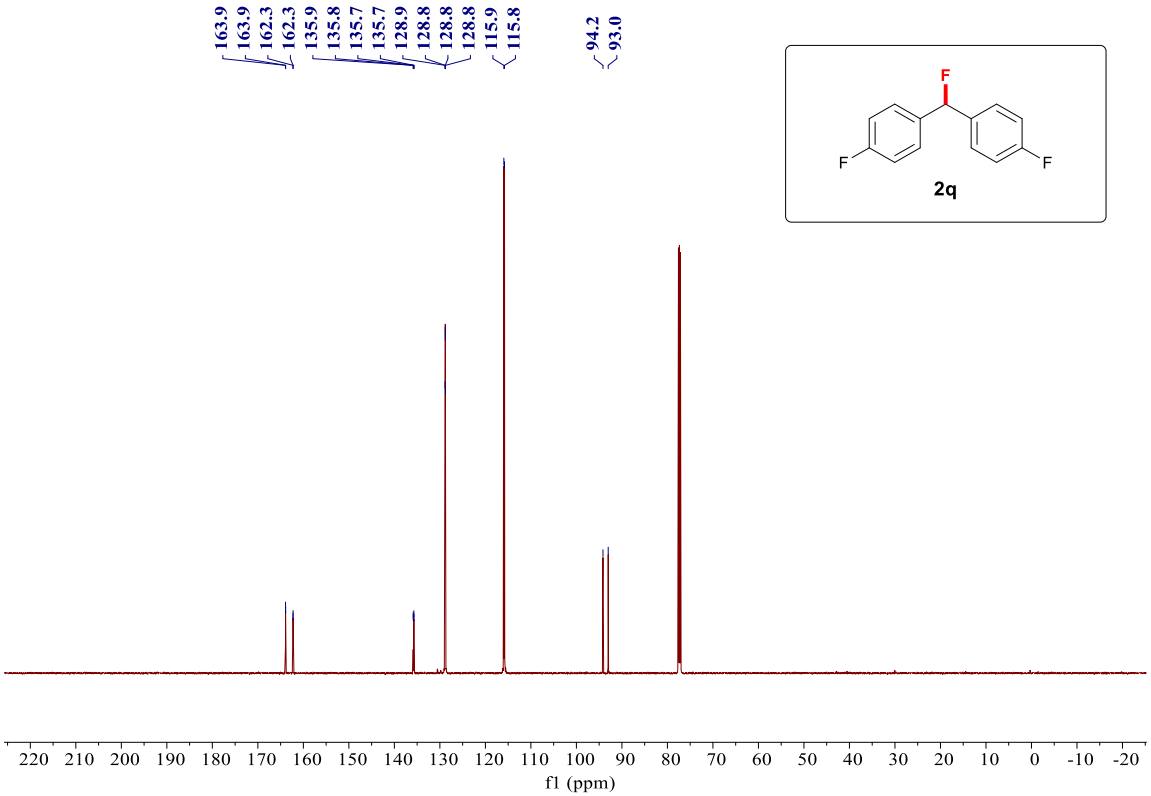
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2p**



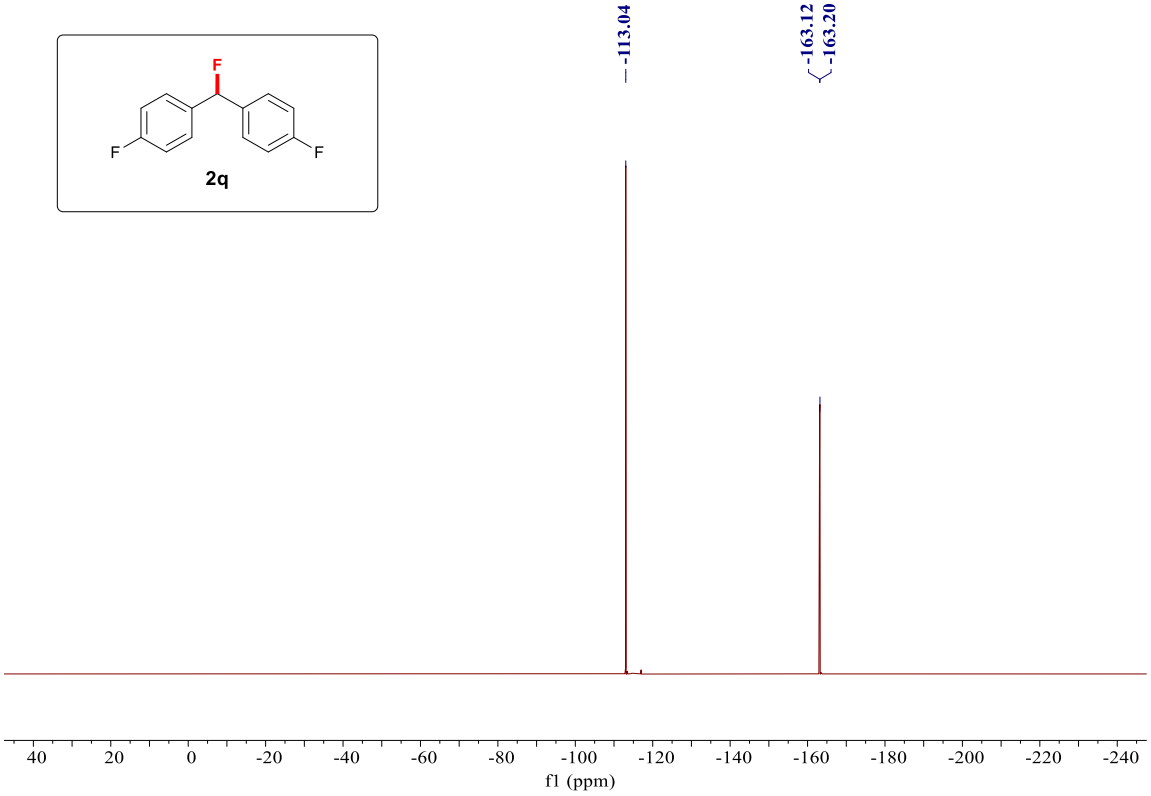
The Yield of **2q** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



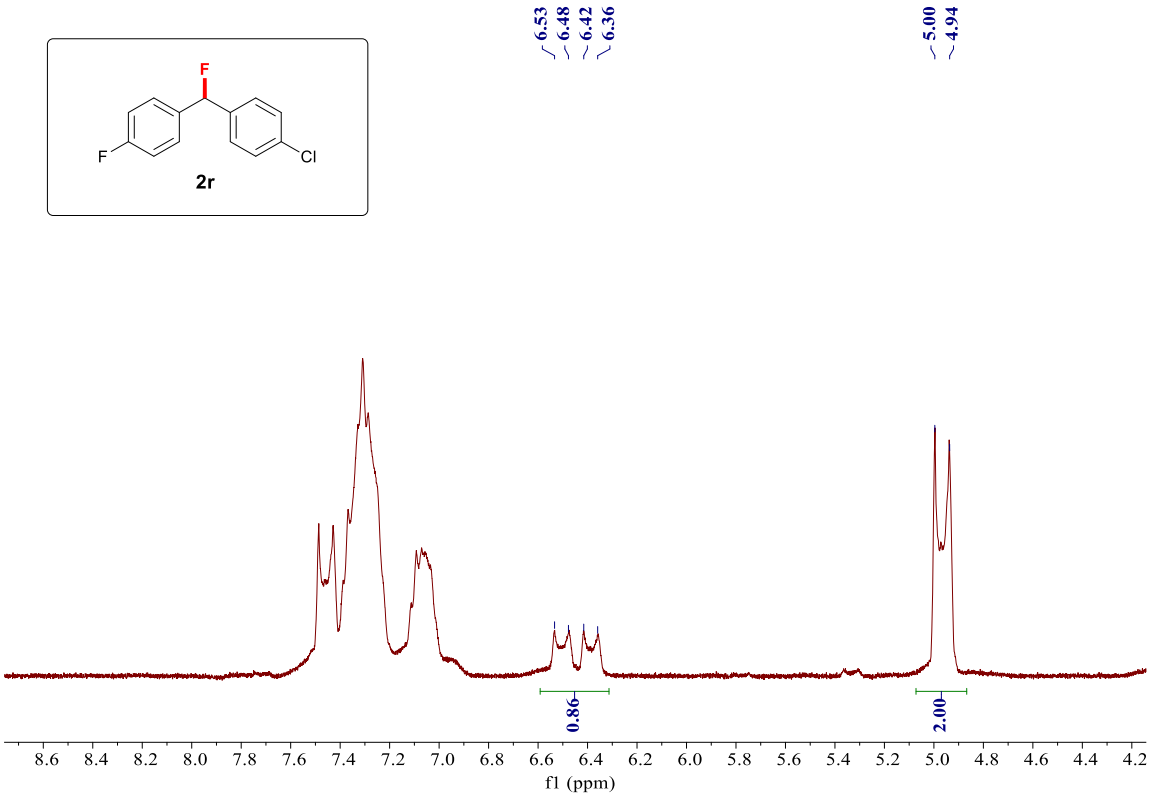
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **2q**



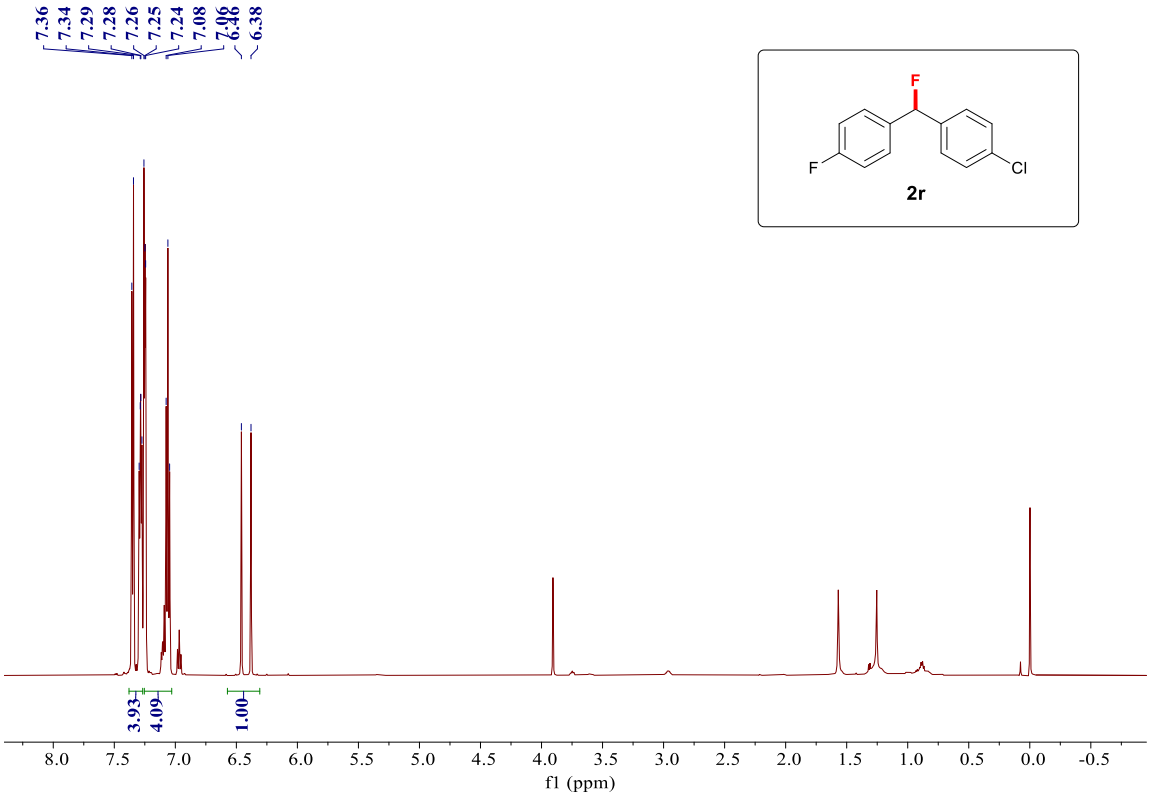
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of Compound **2q**



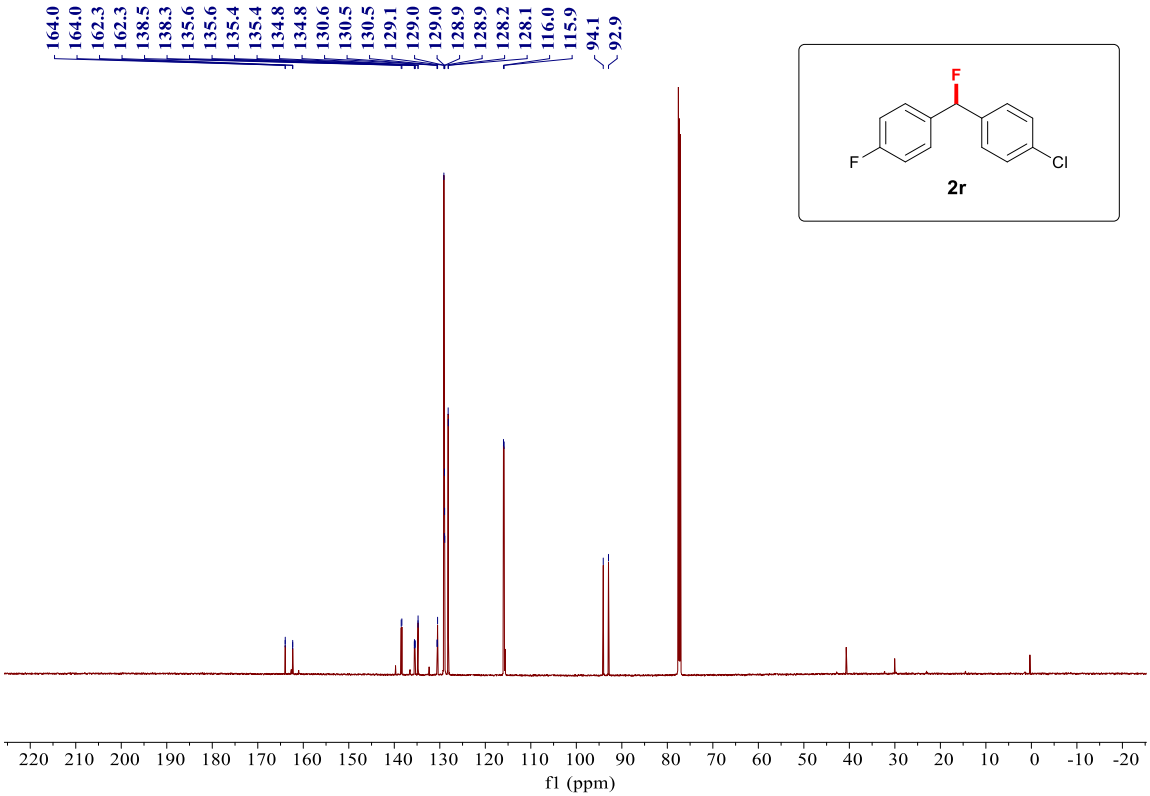
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of Compound **2q**



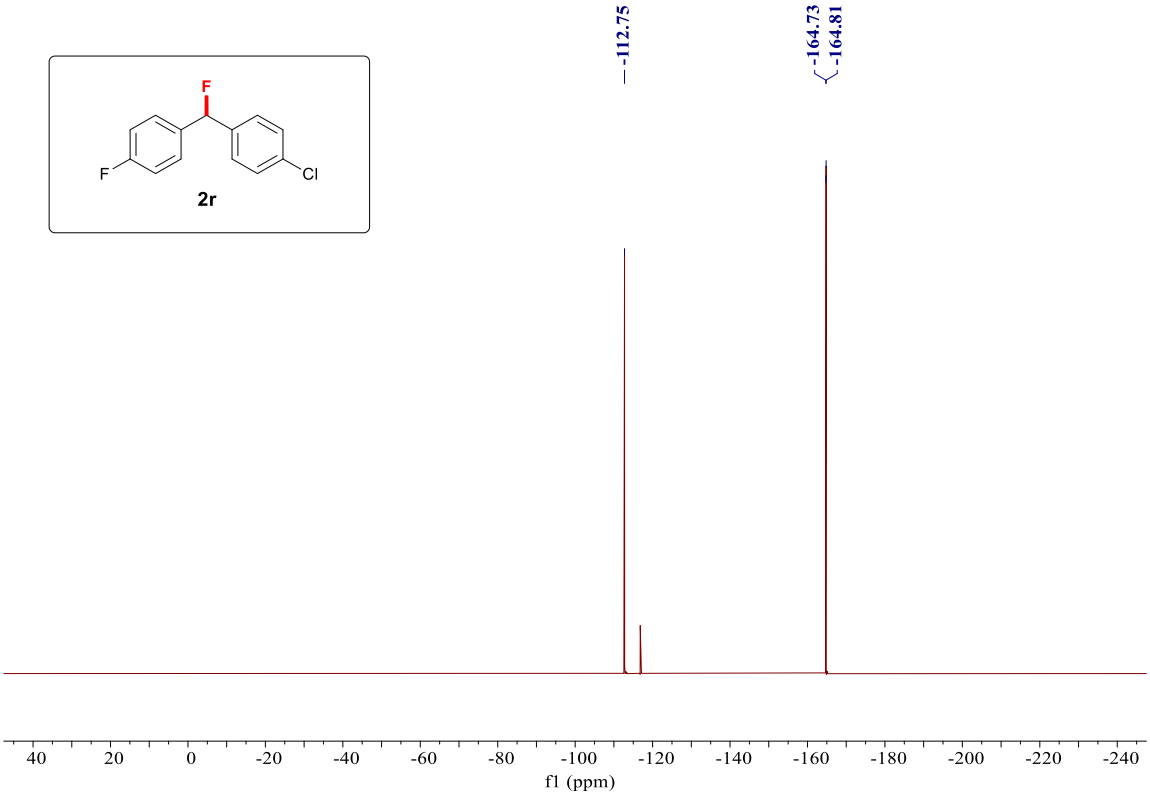
The Yield of **2r** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



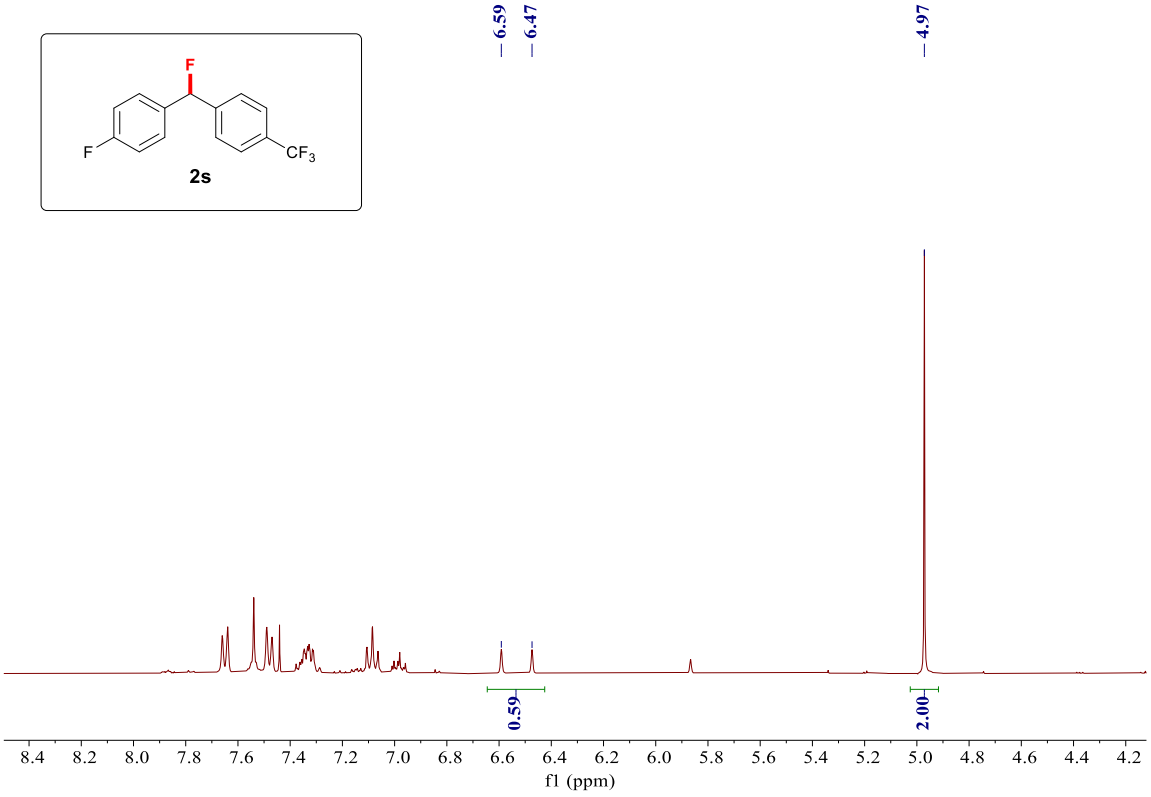
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **2r**



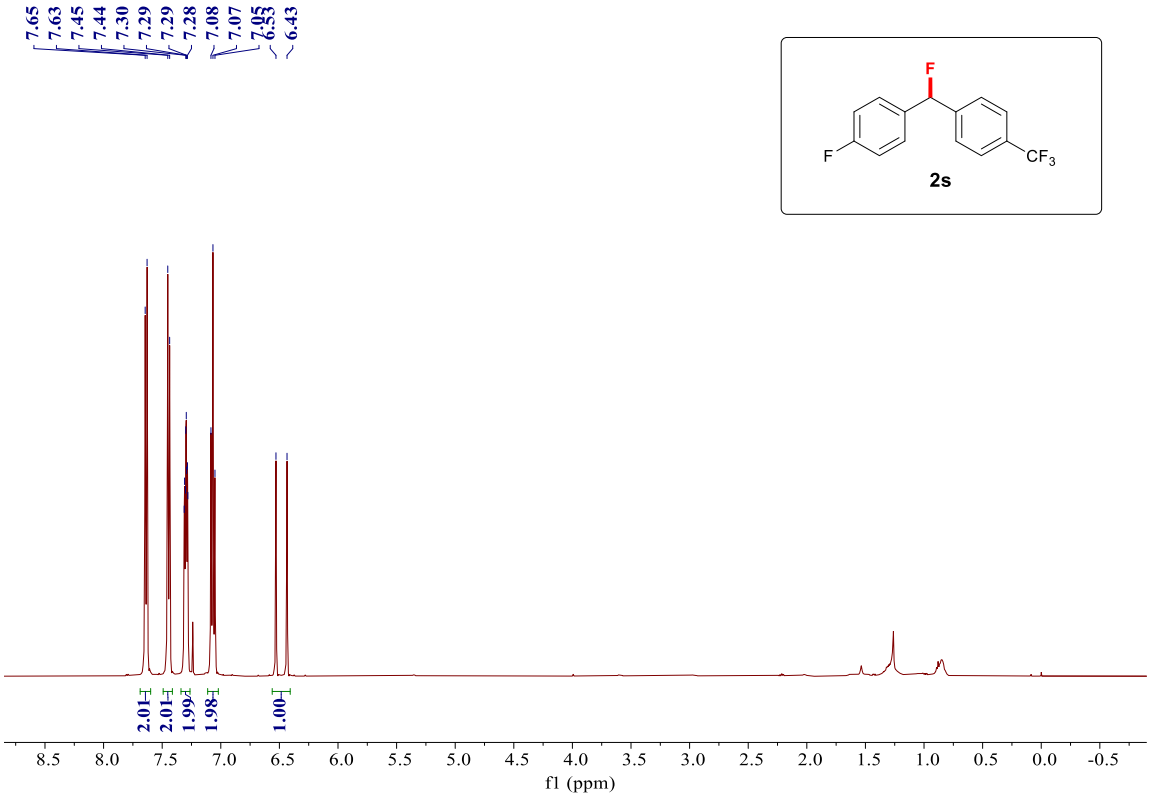
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of Compound **2r**



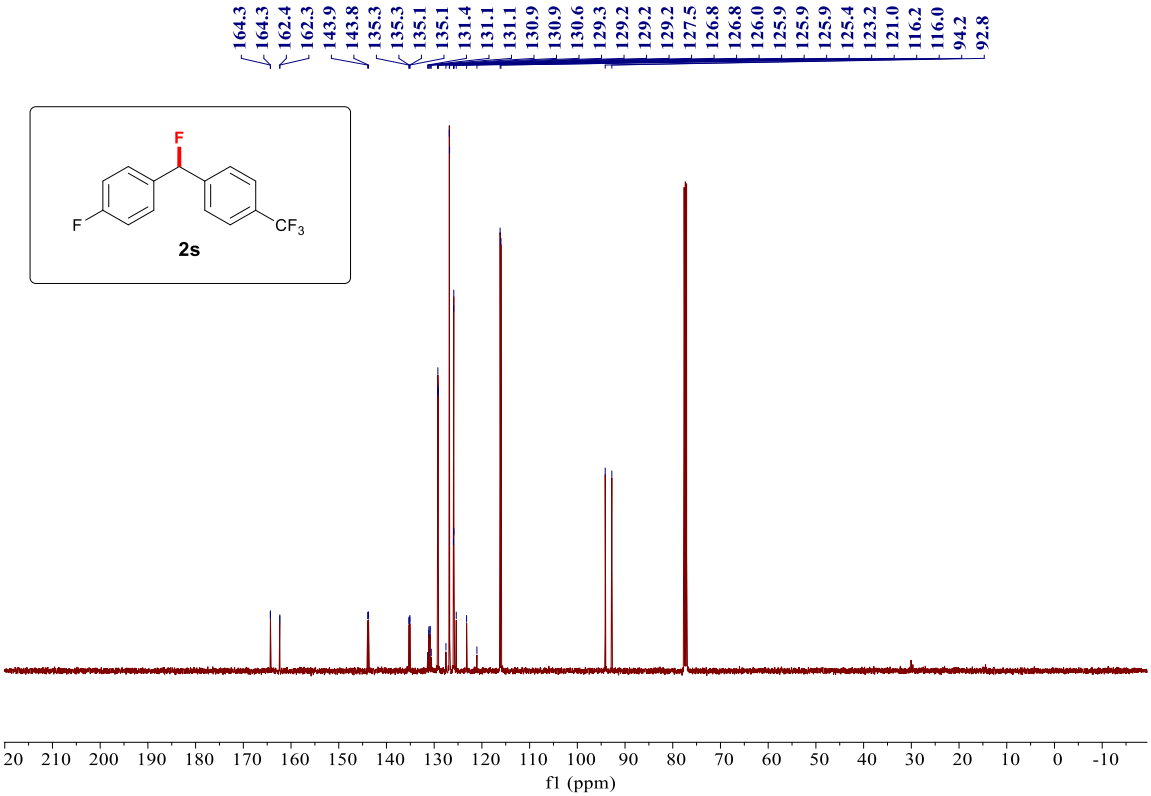
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of Compound **2r**



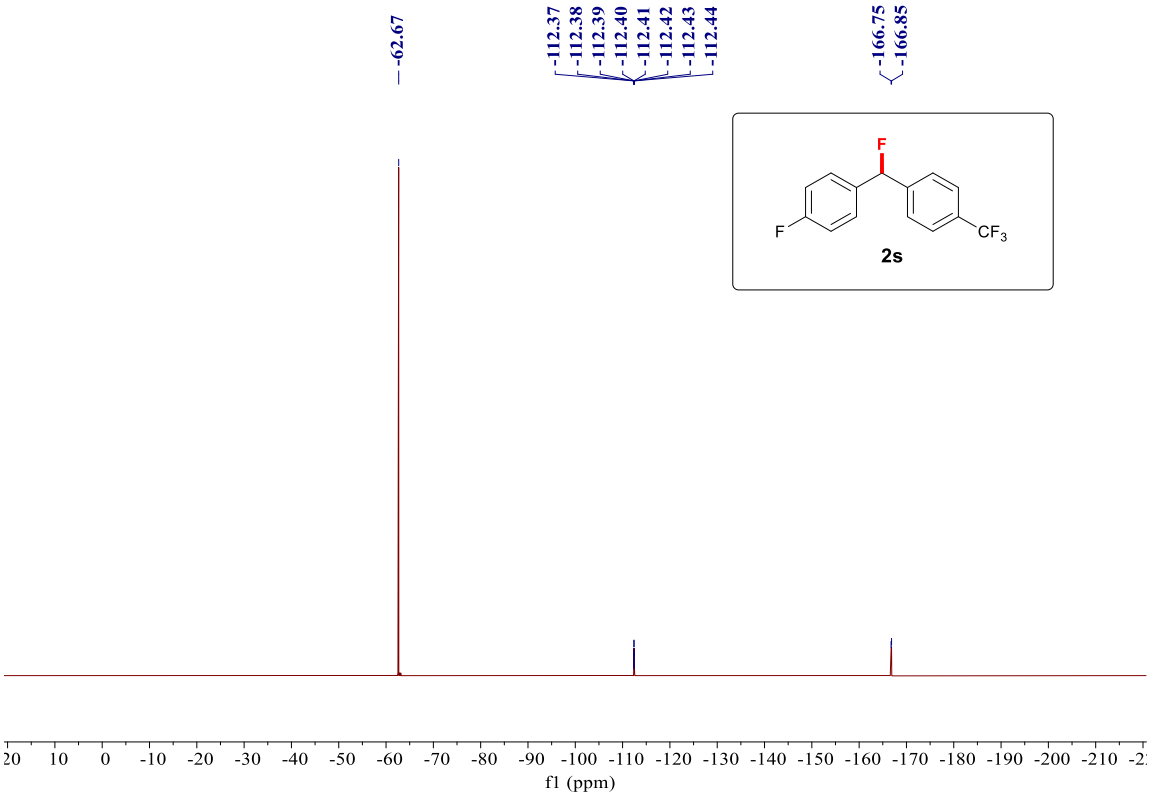
The Yield of **2s** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



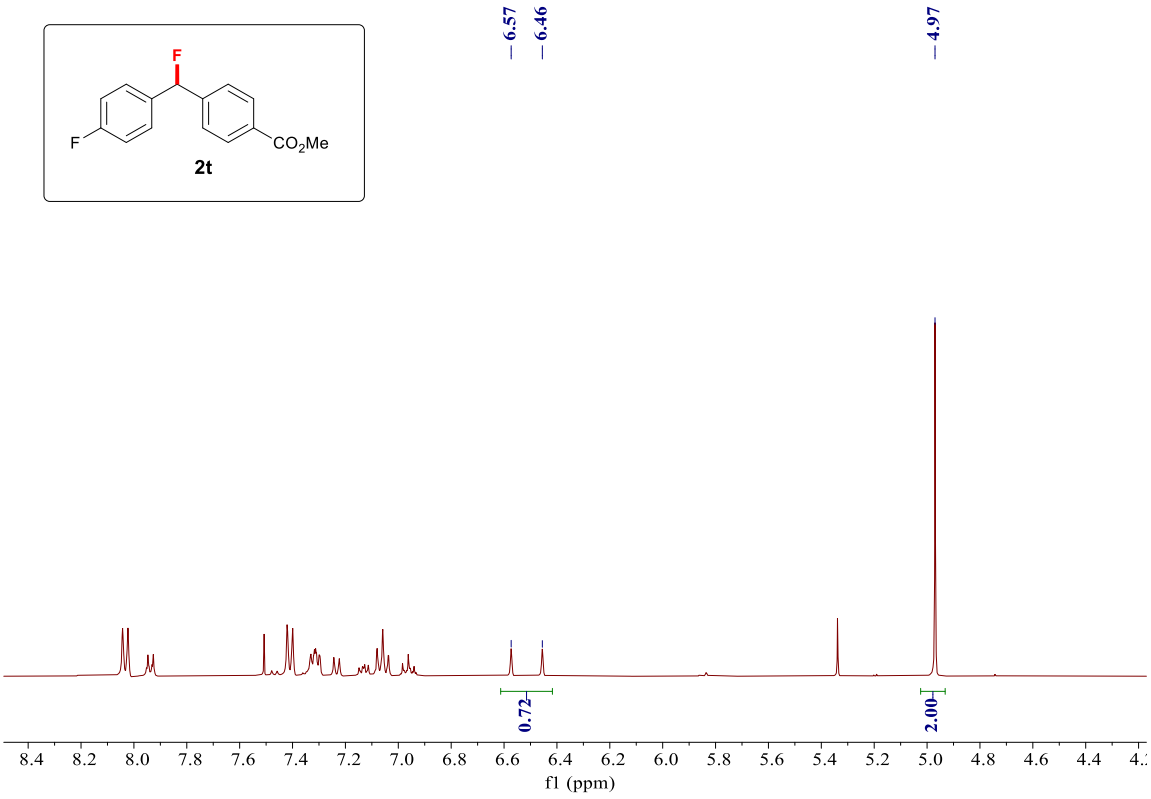
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2s**



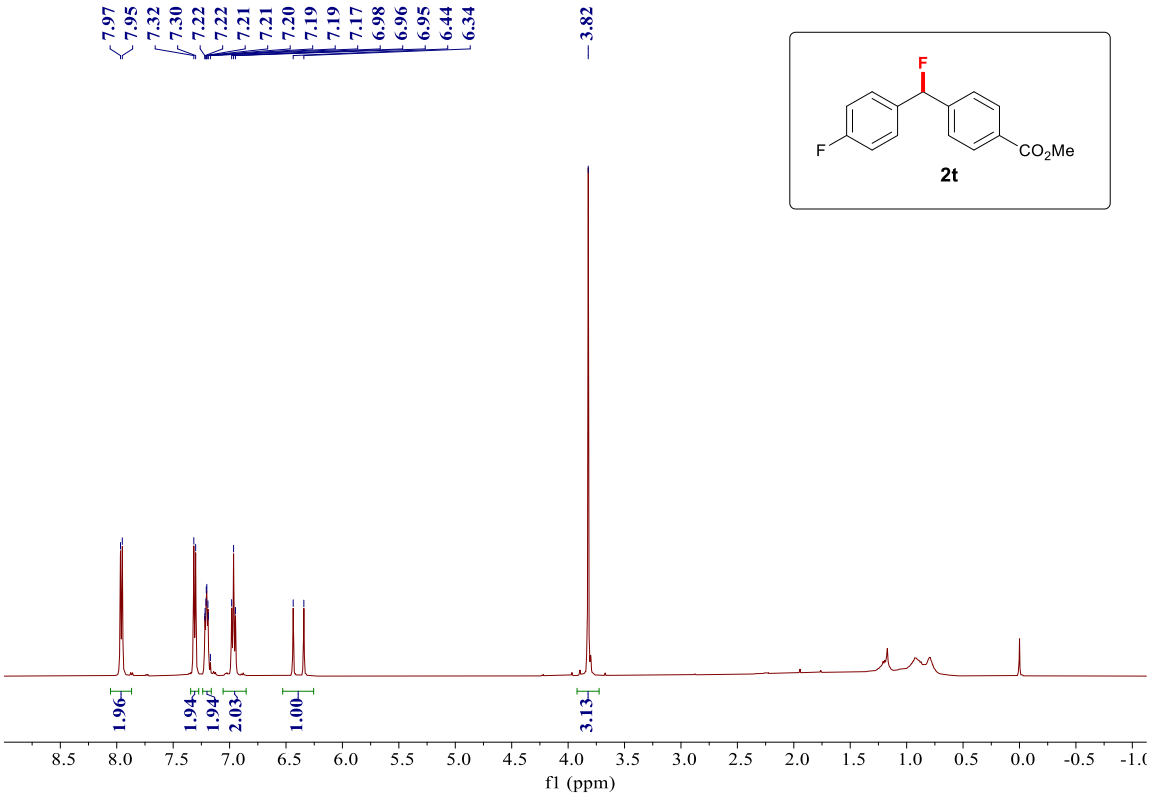
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2s**



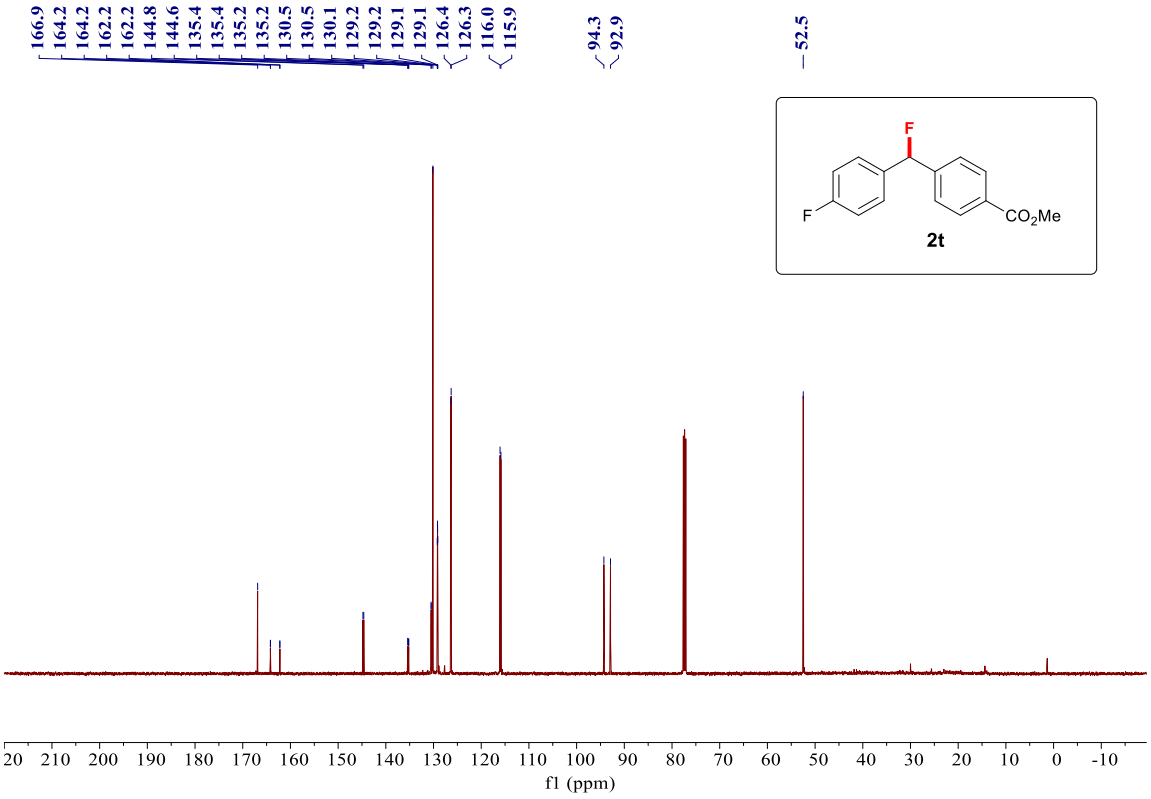
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2s**



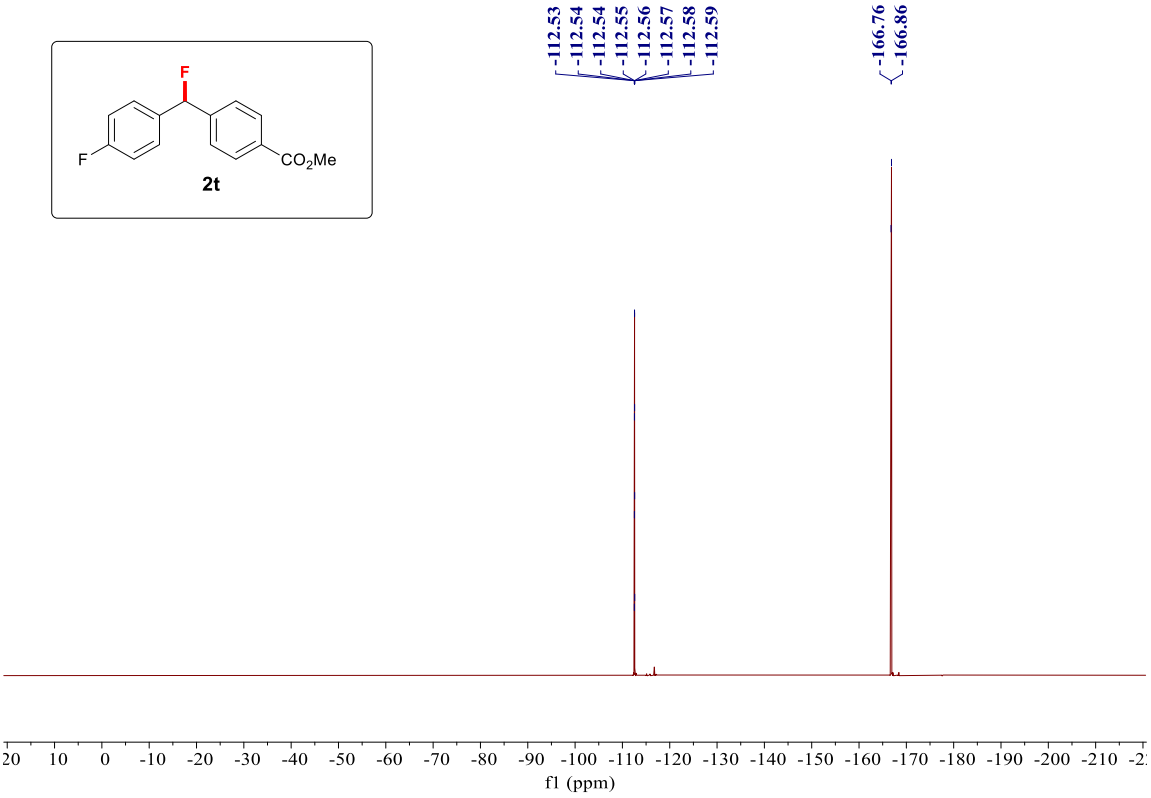
The Yield of **2t** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



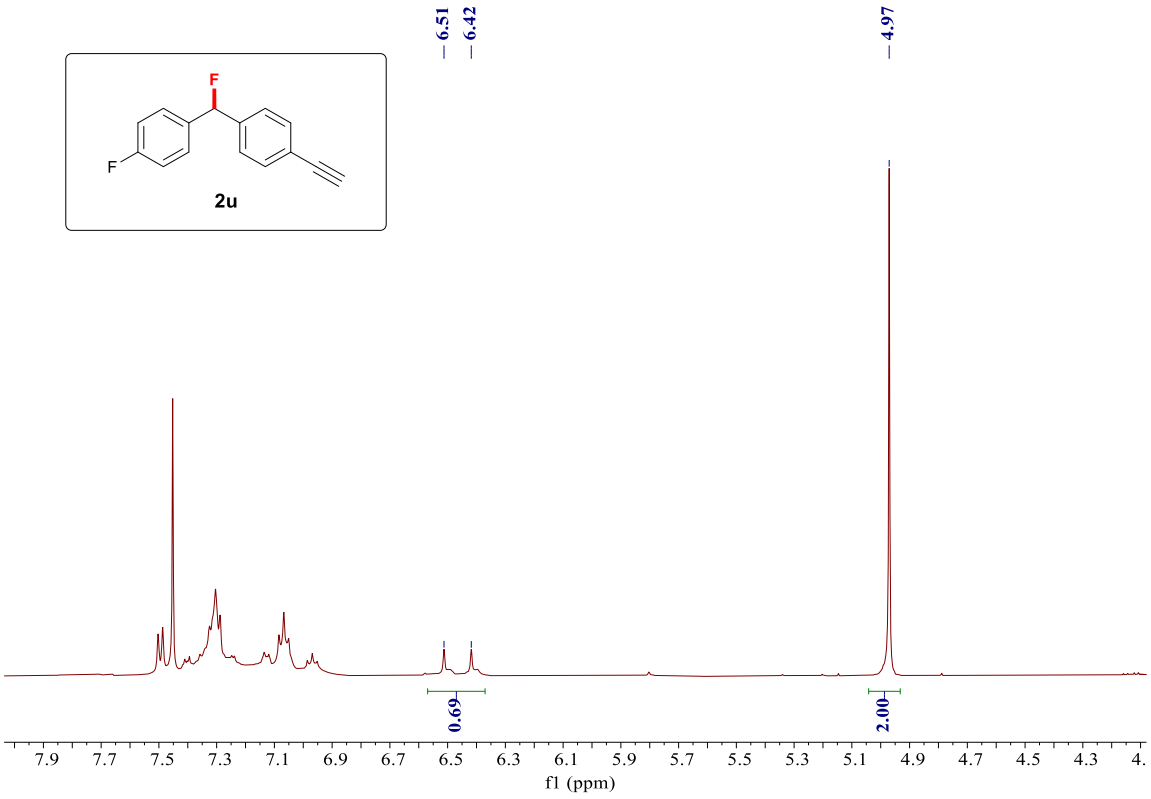
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2t**



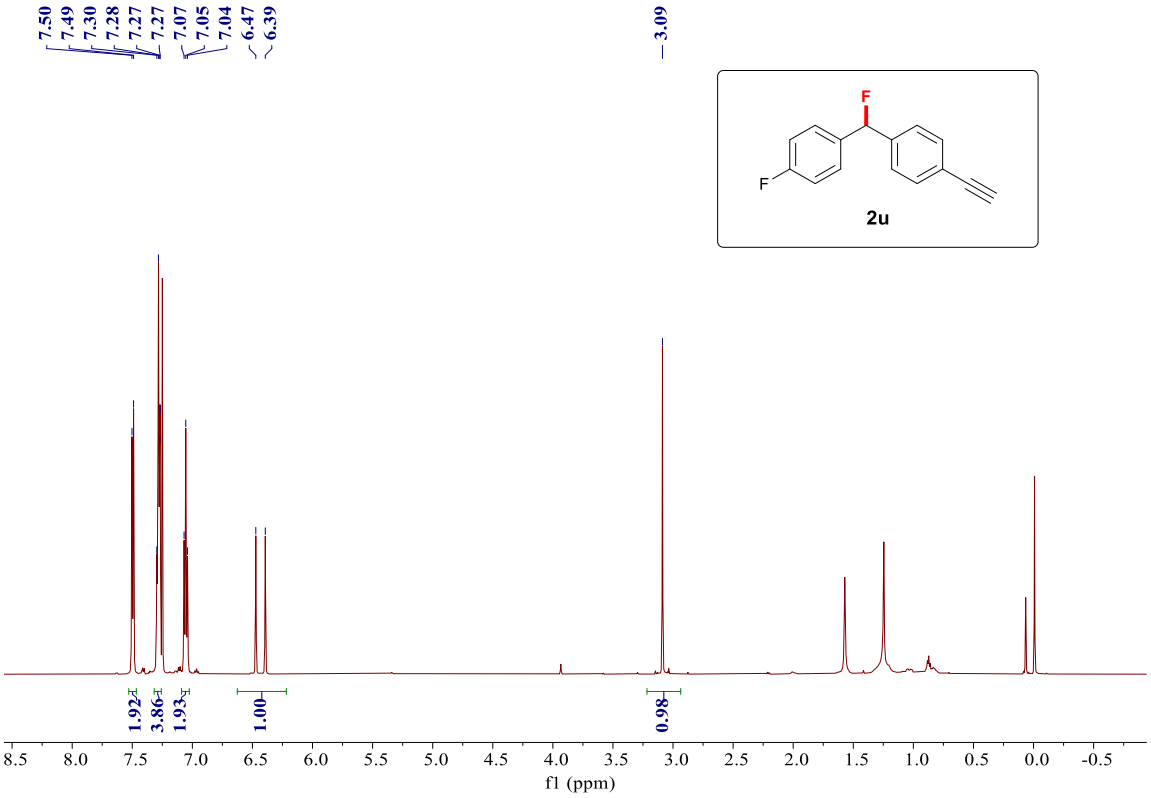
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2t**



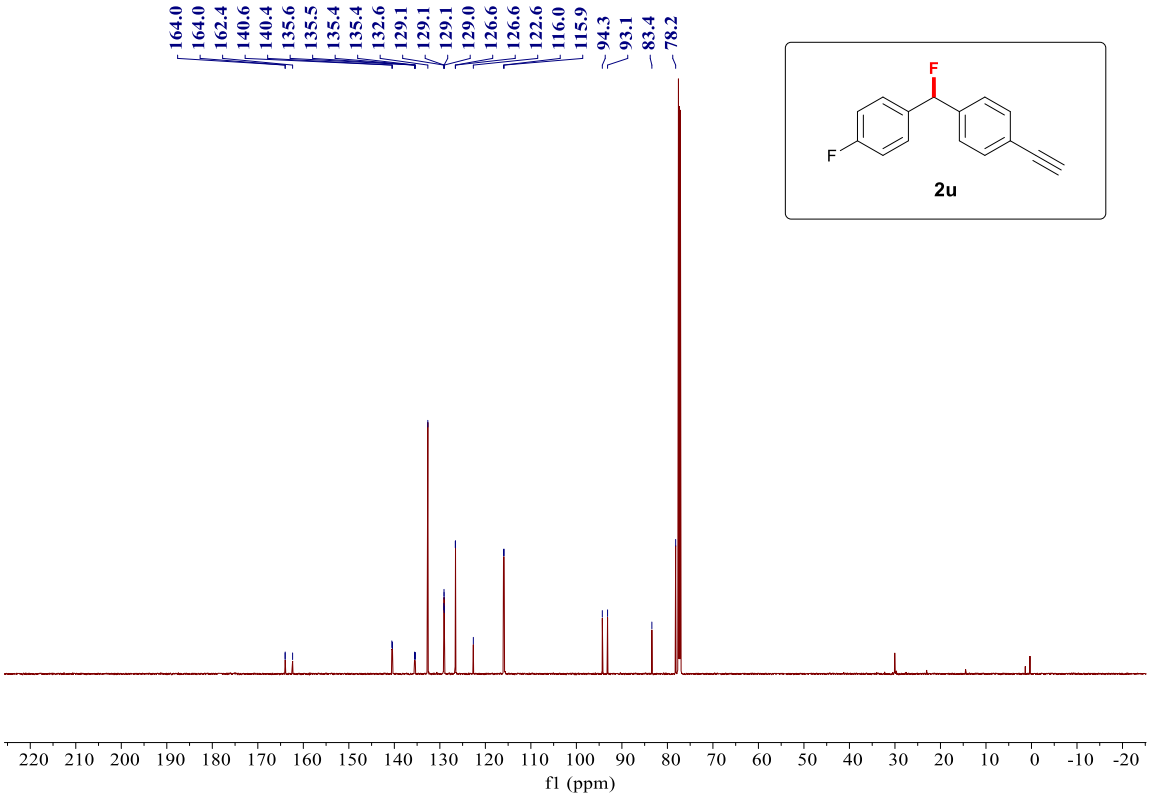
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2t**



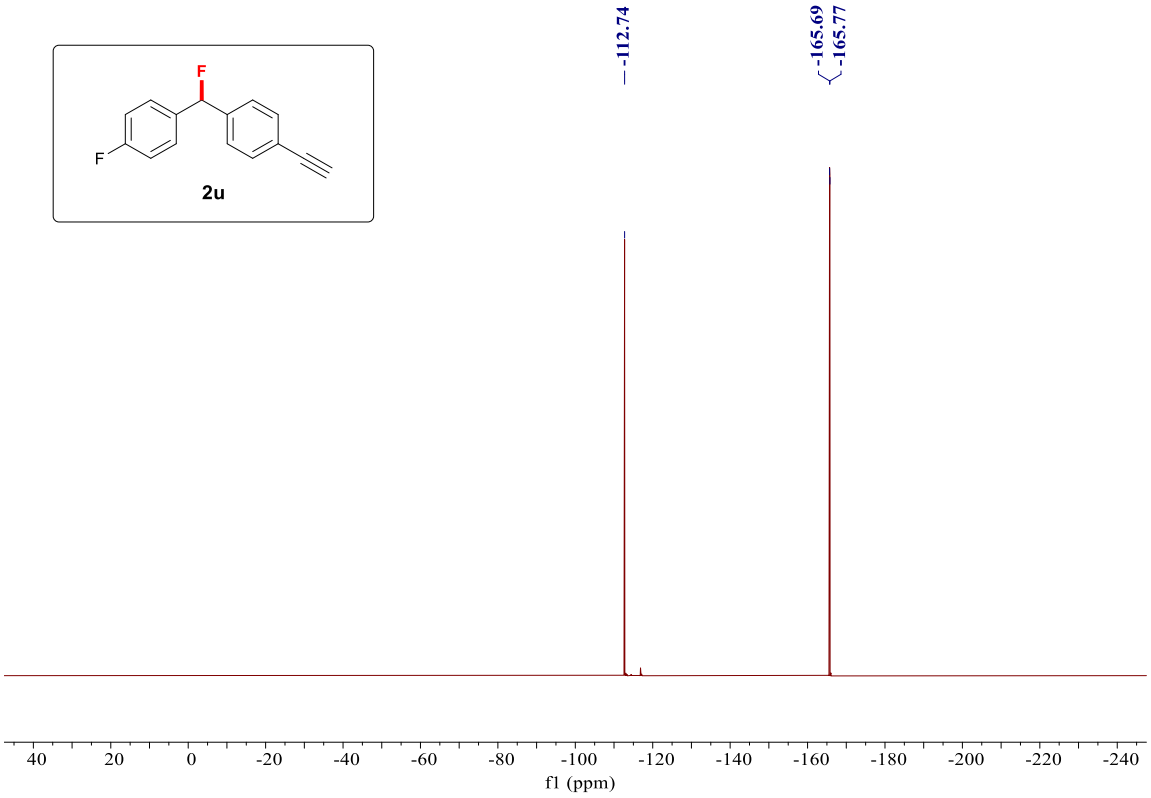
The Yield of **2u** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



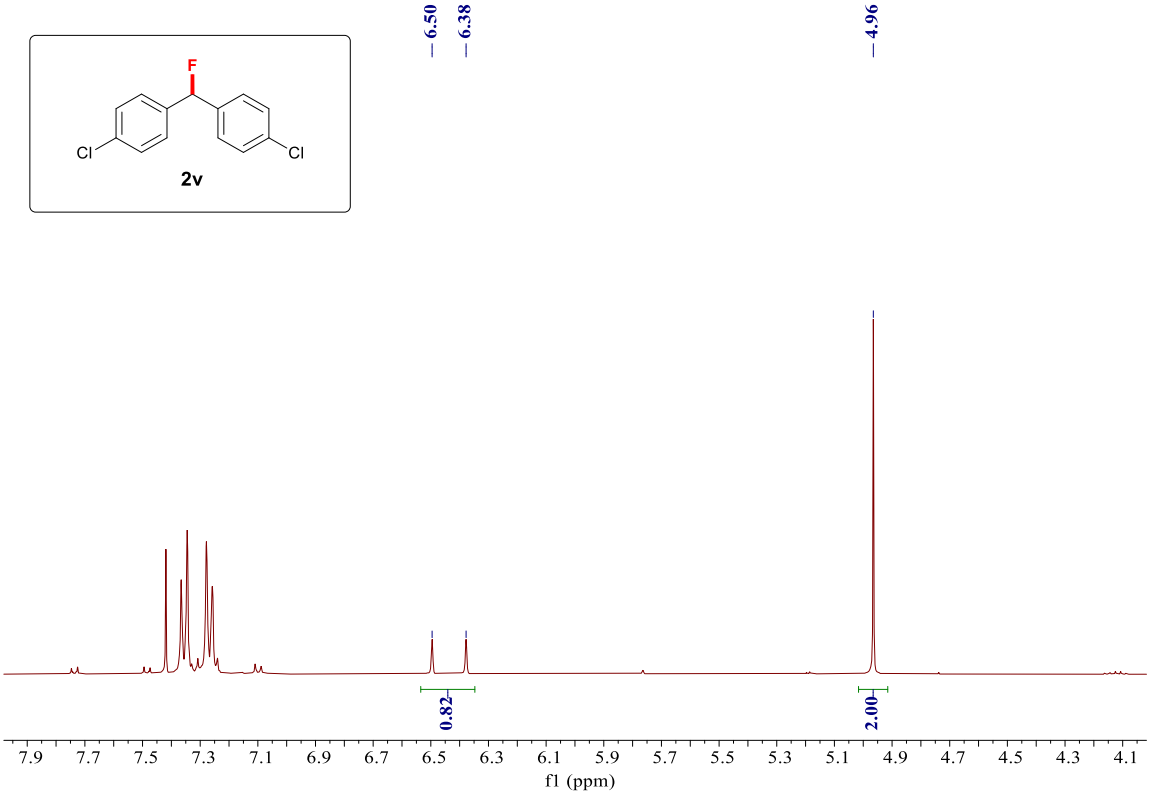
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **2u**



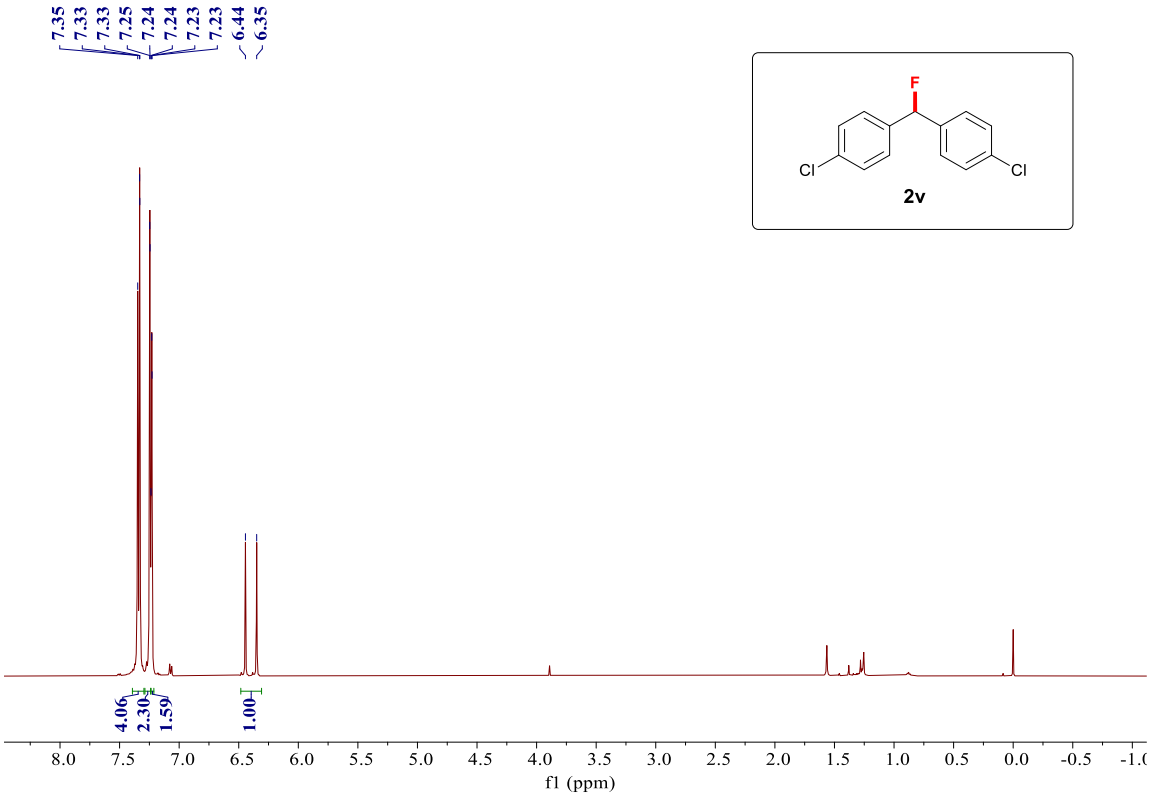
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of Compound **2u**



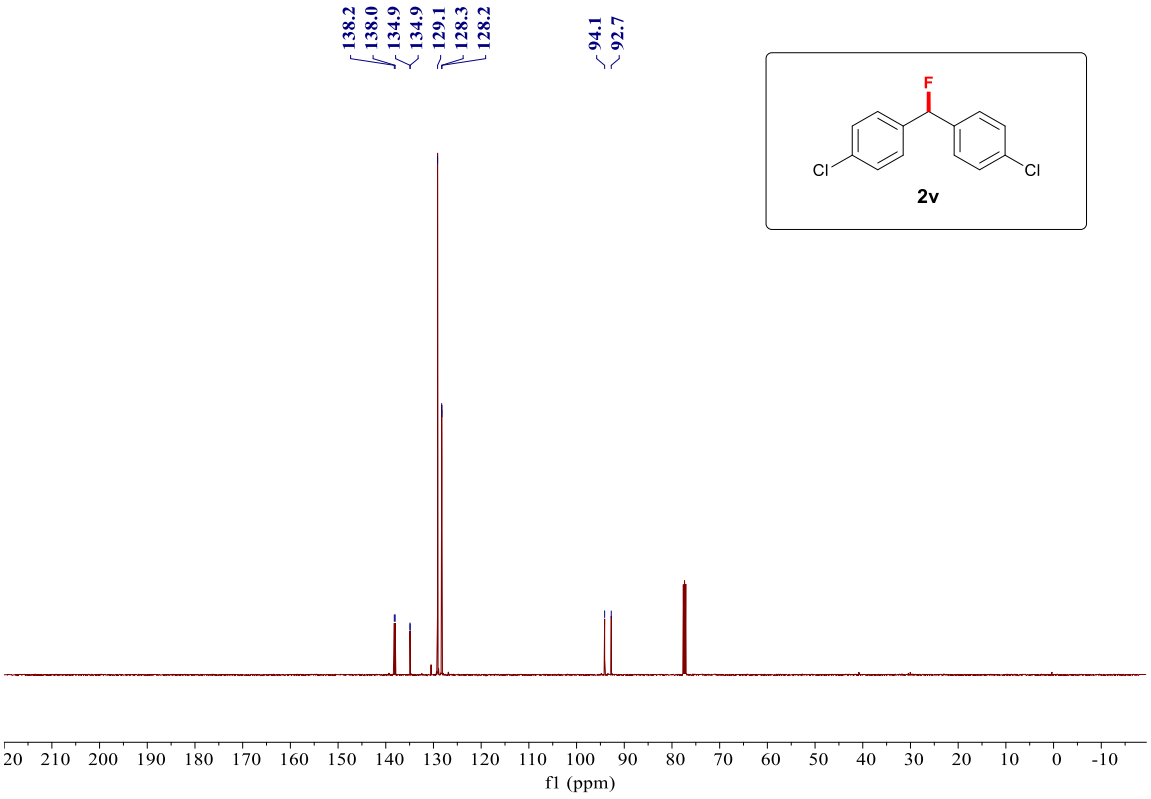
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of Compound **2u**



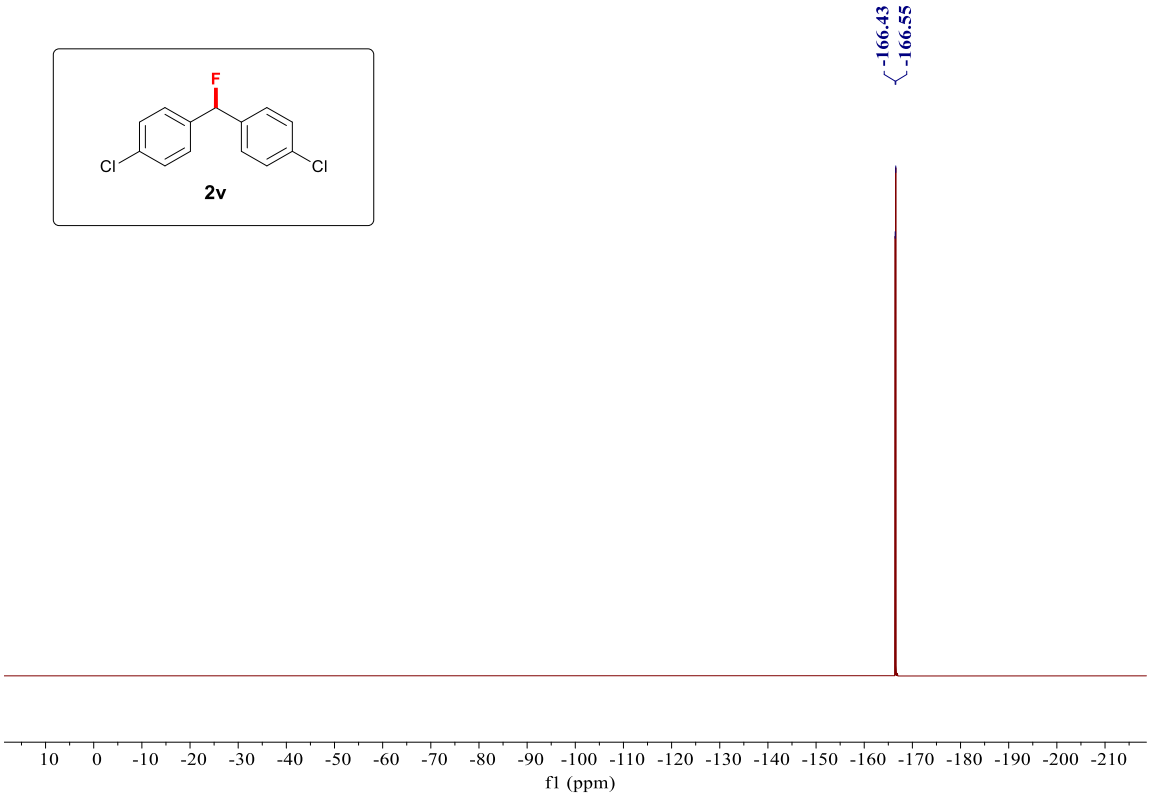
The Yield of **2v** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



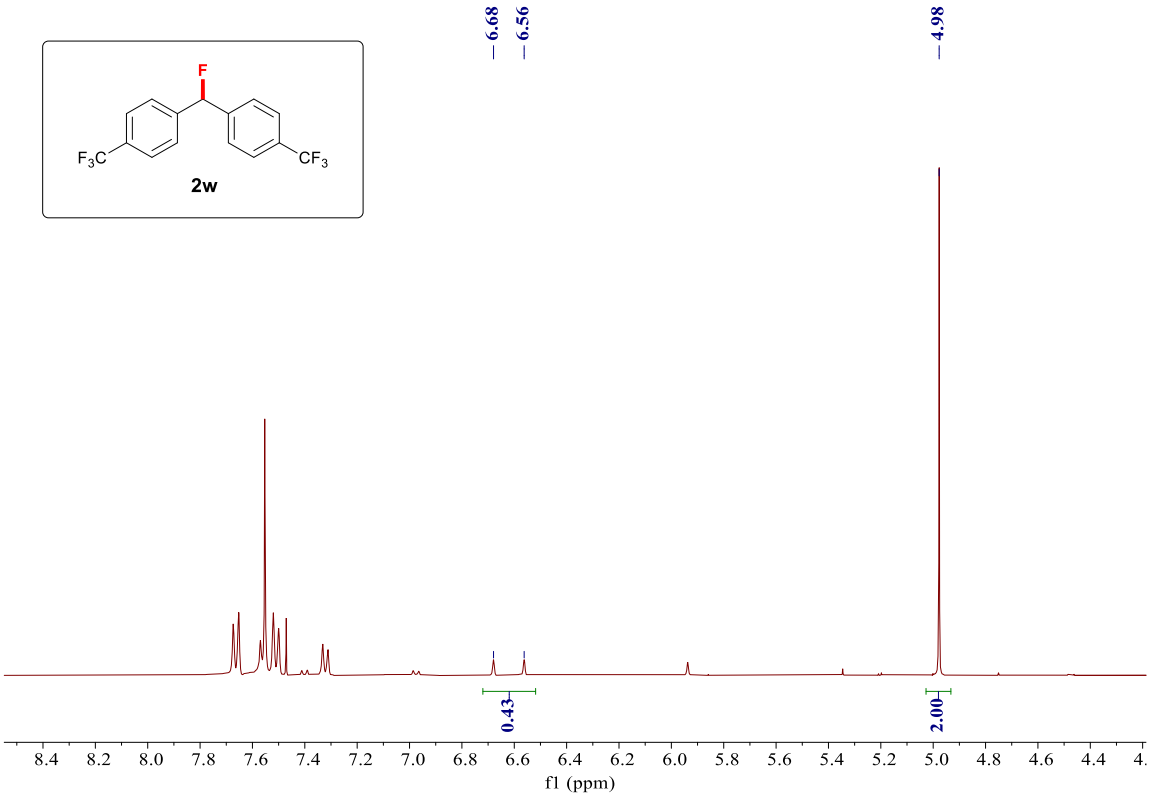
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2v**



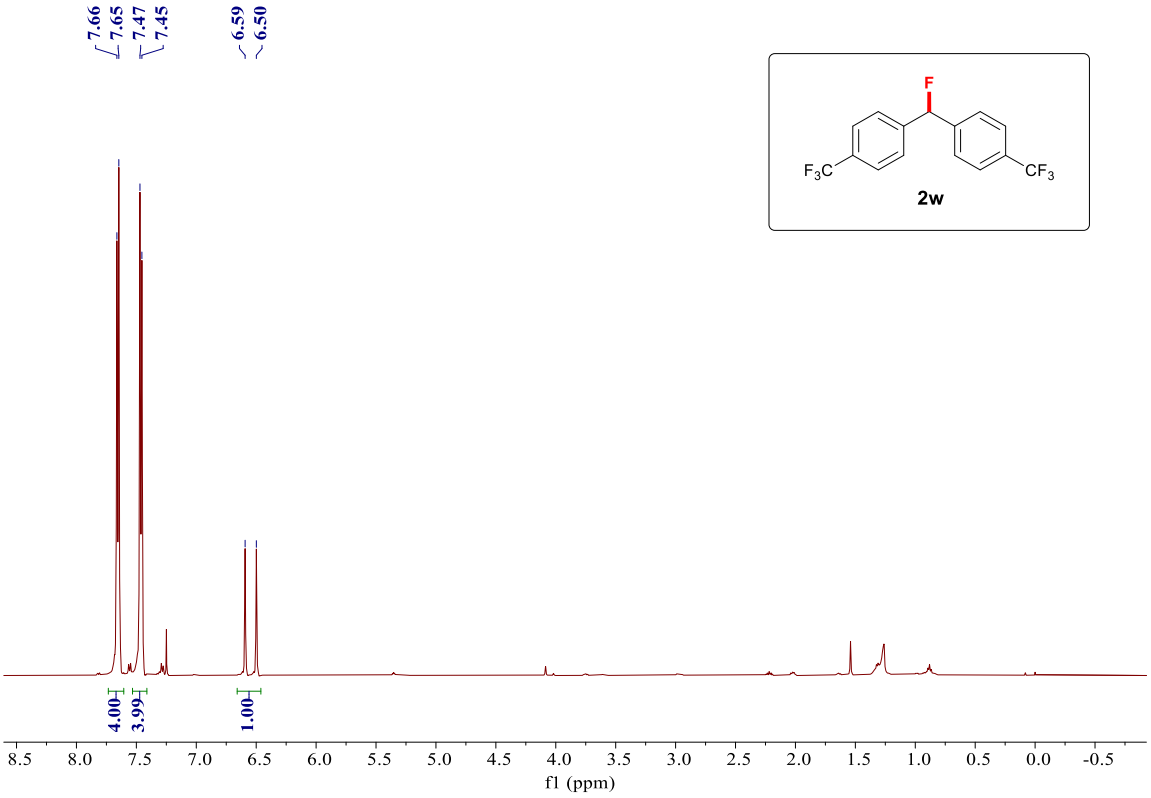
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2v**



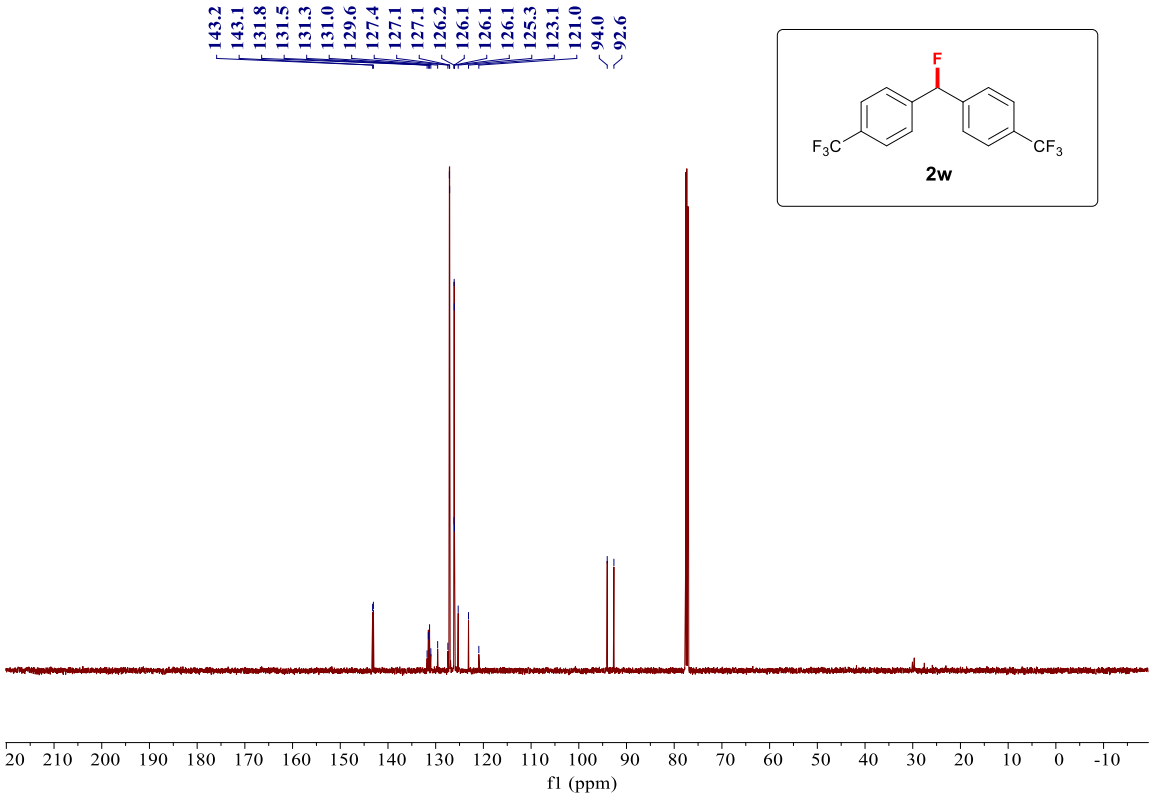
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **2v**



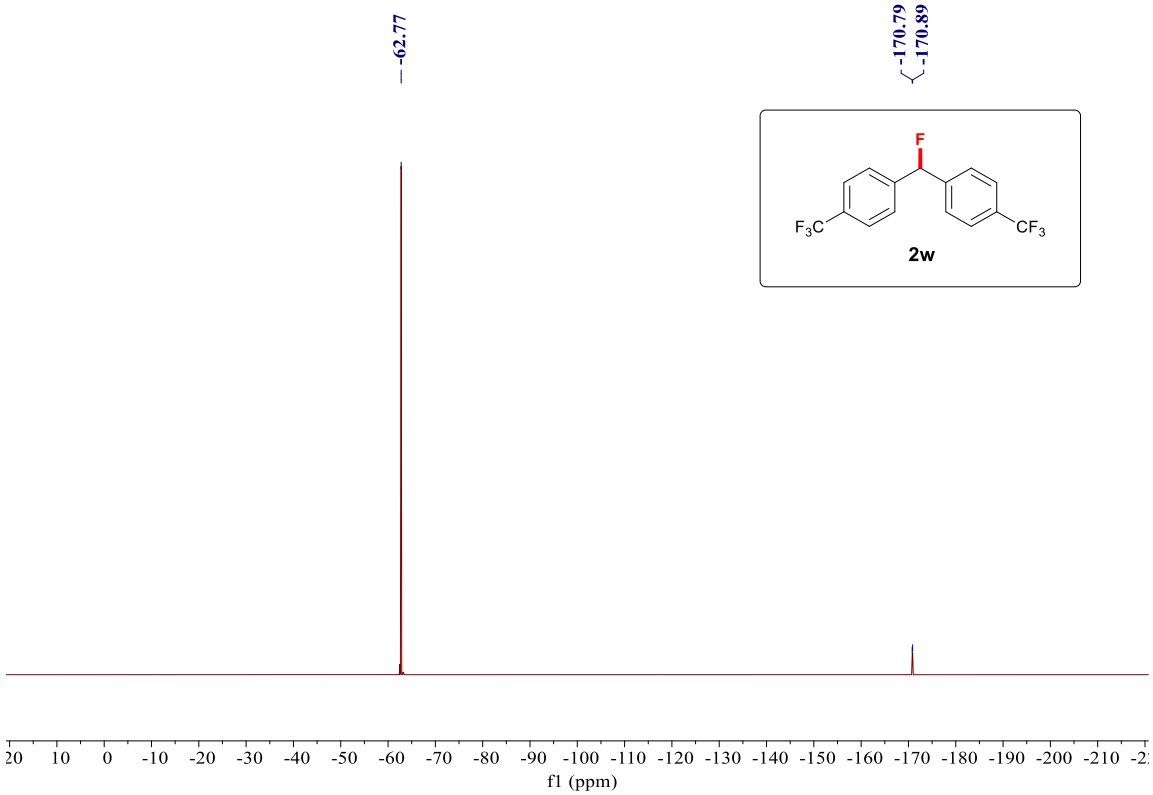
The Yield of **2w** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



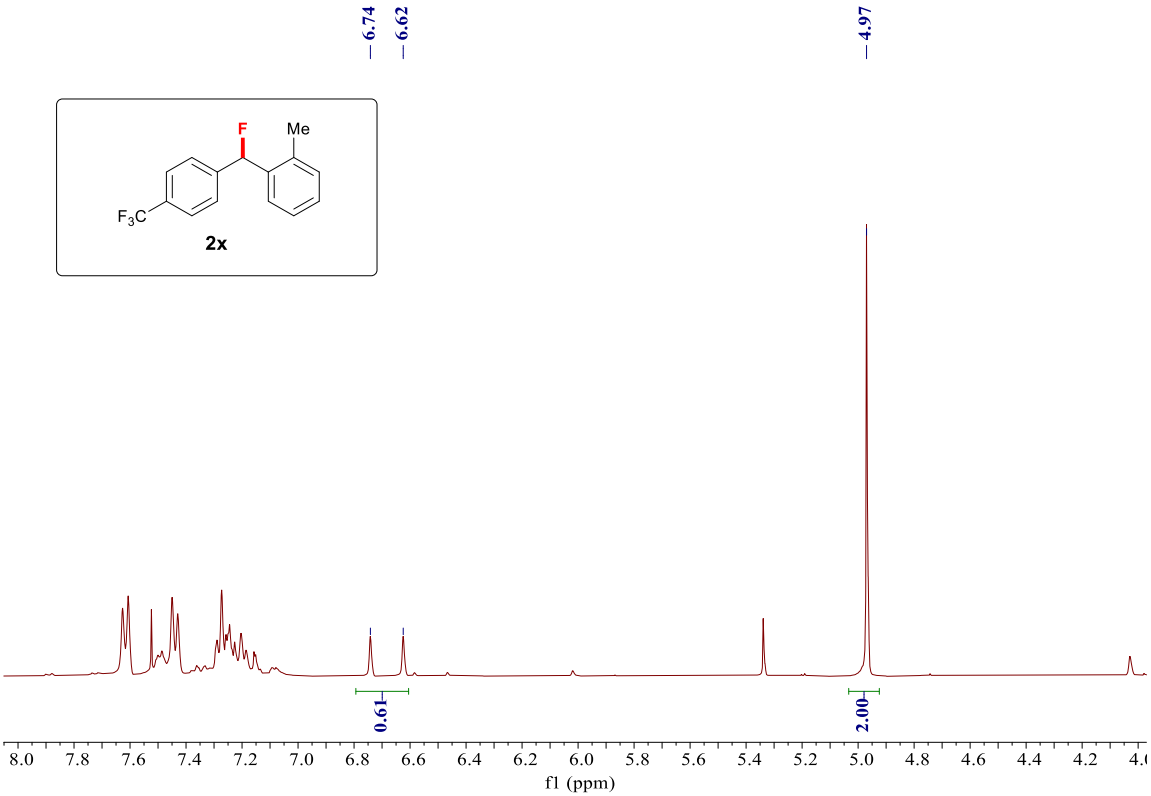
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2w**



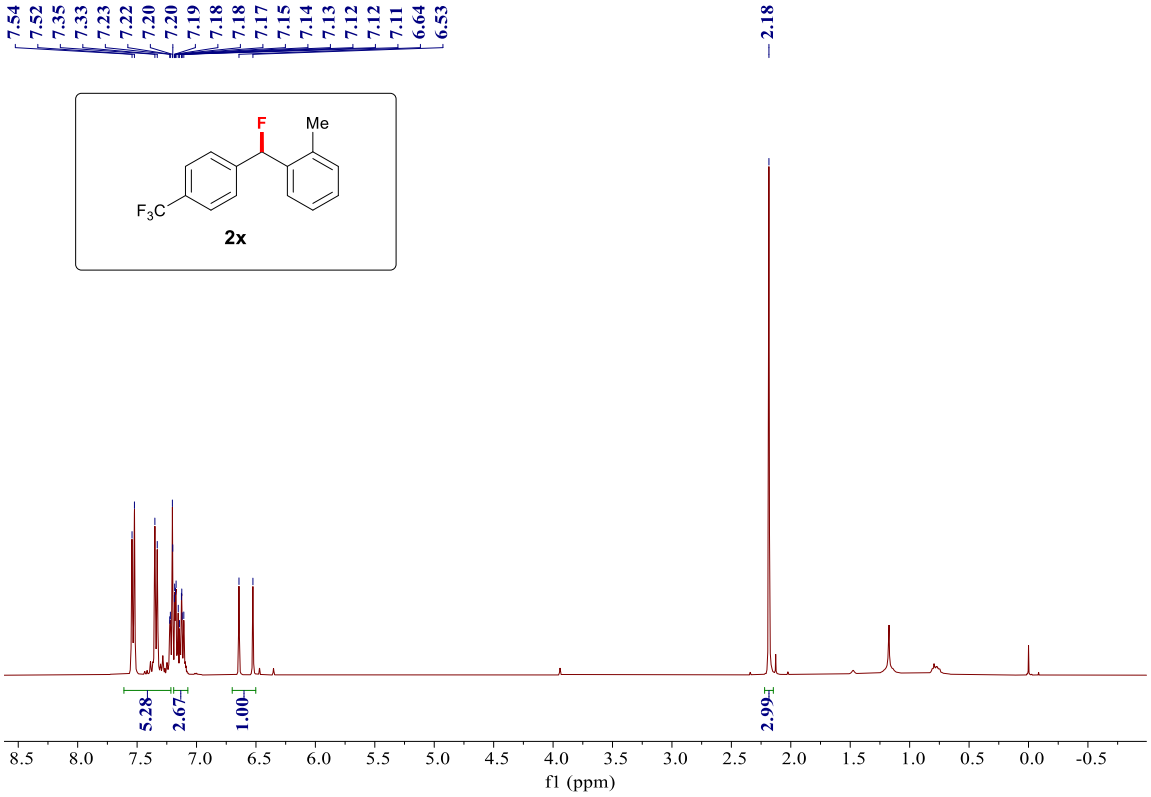
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2w**



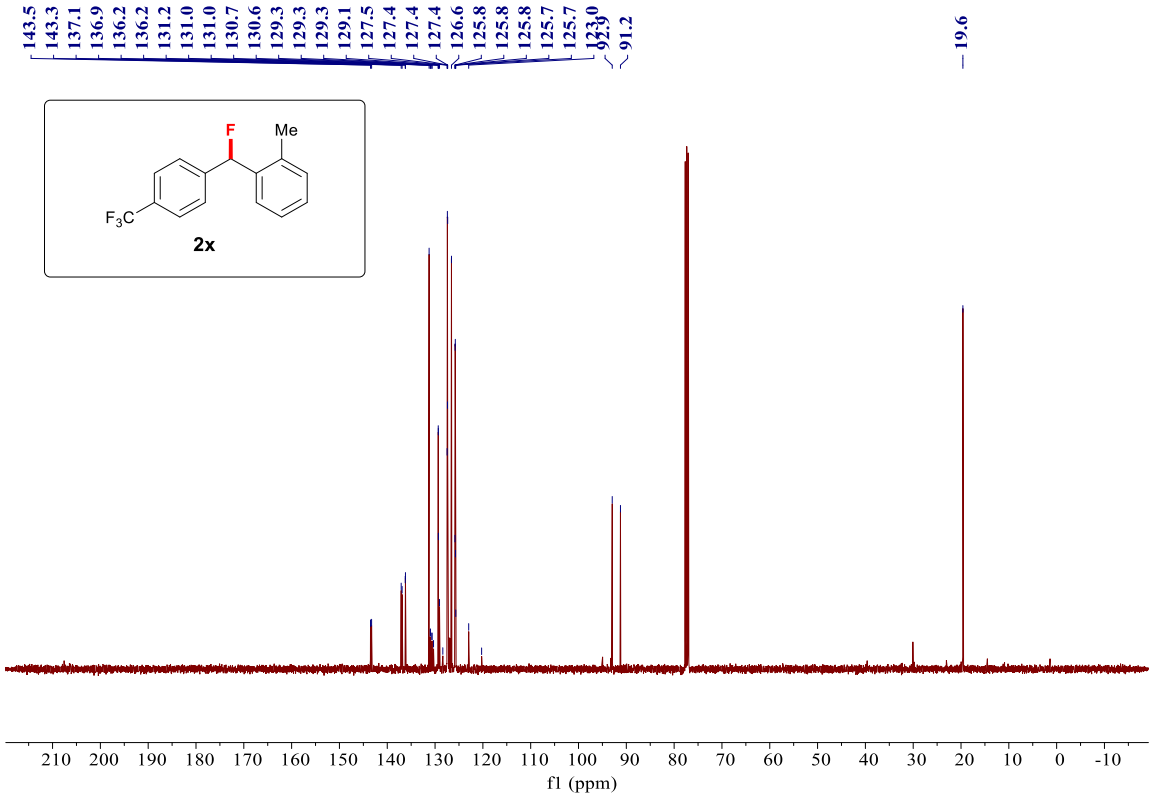
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2w**



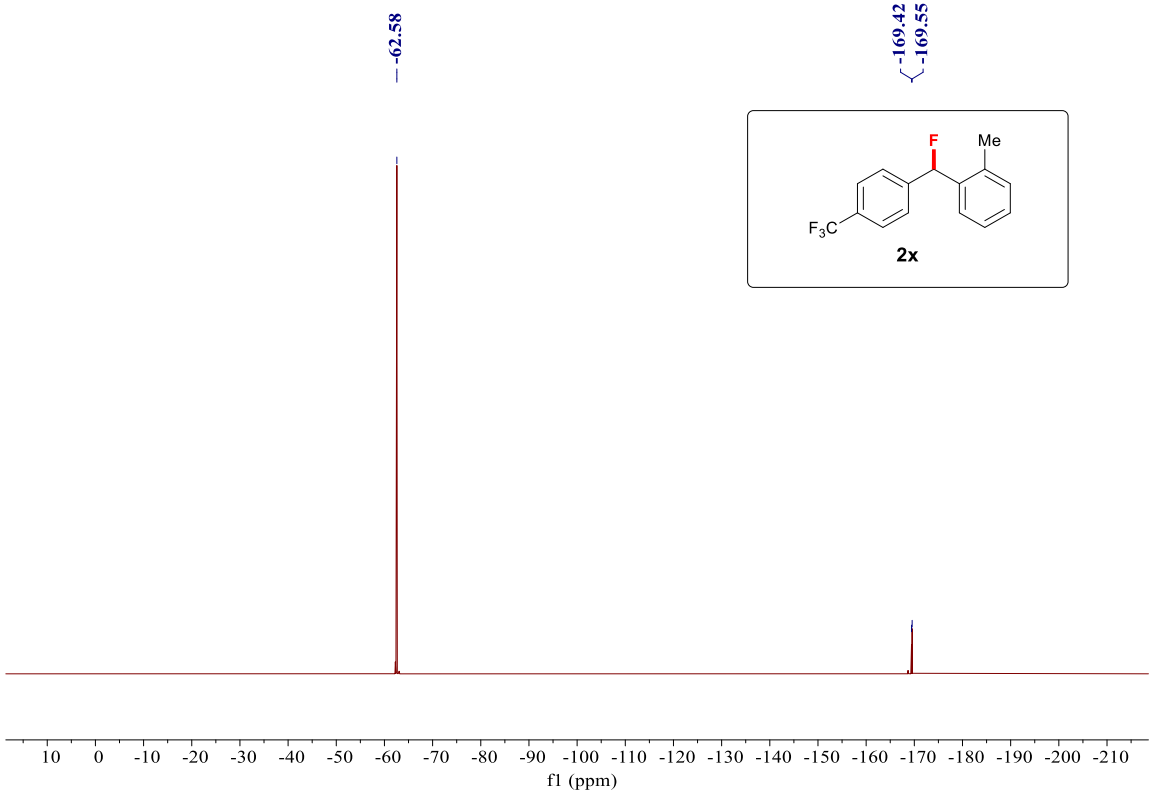
The Yield of **2x** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



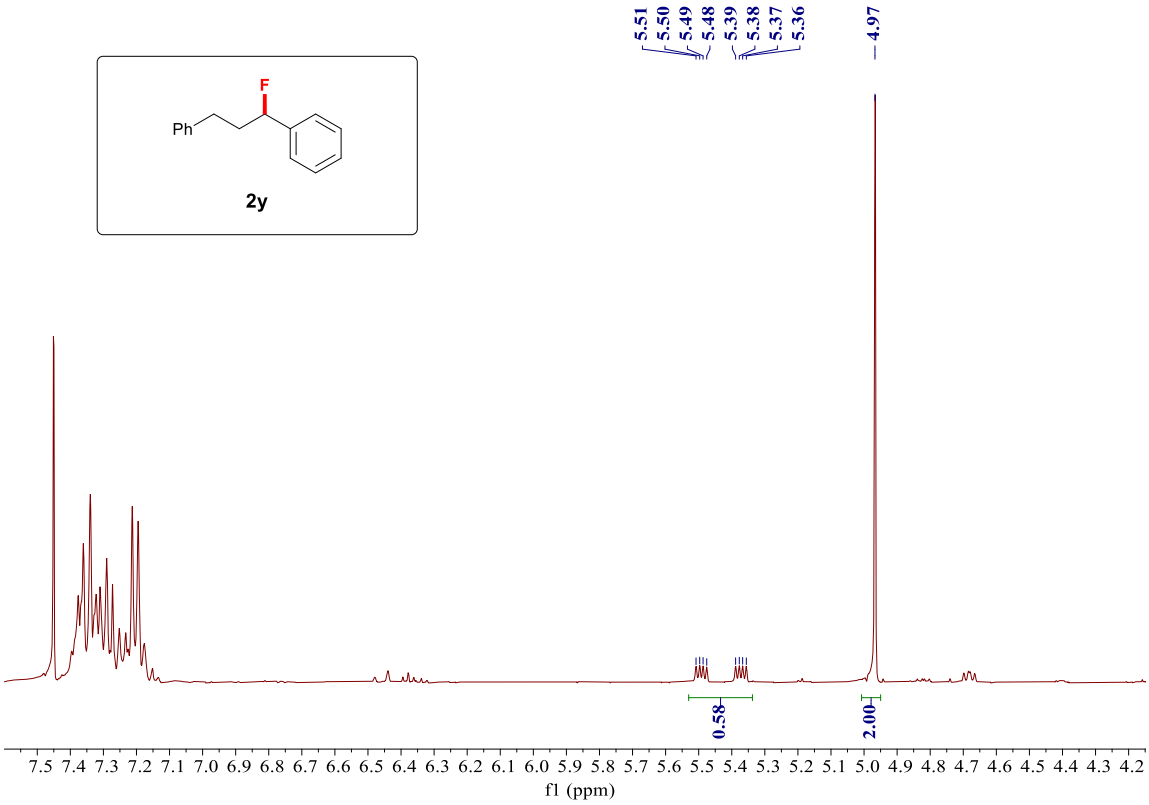
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **2x**



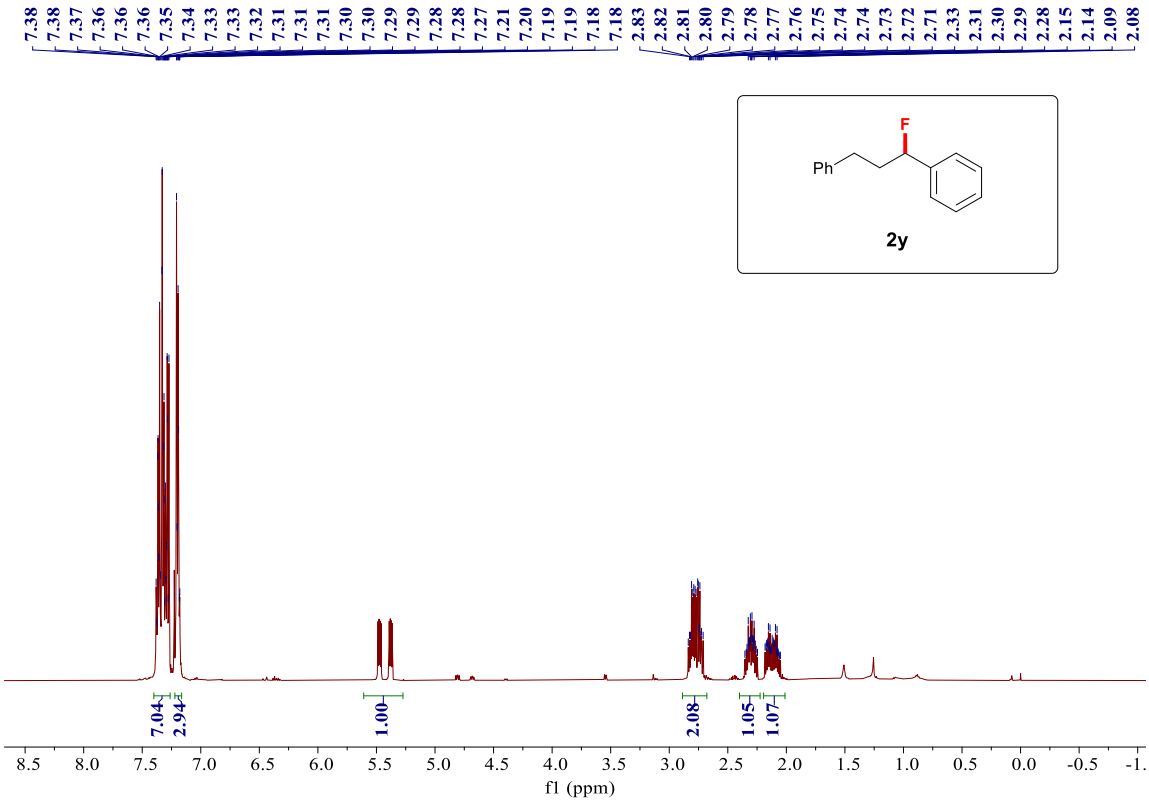
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **2x**



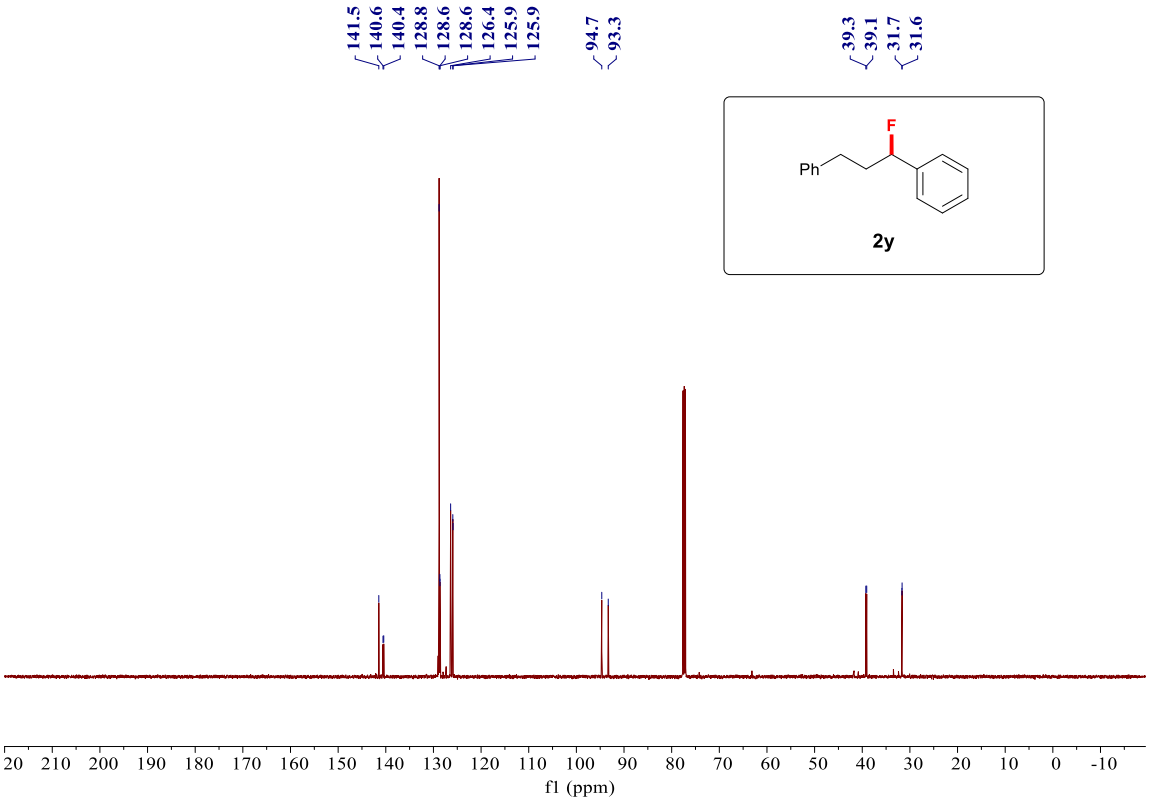
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **2x**



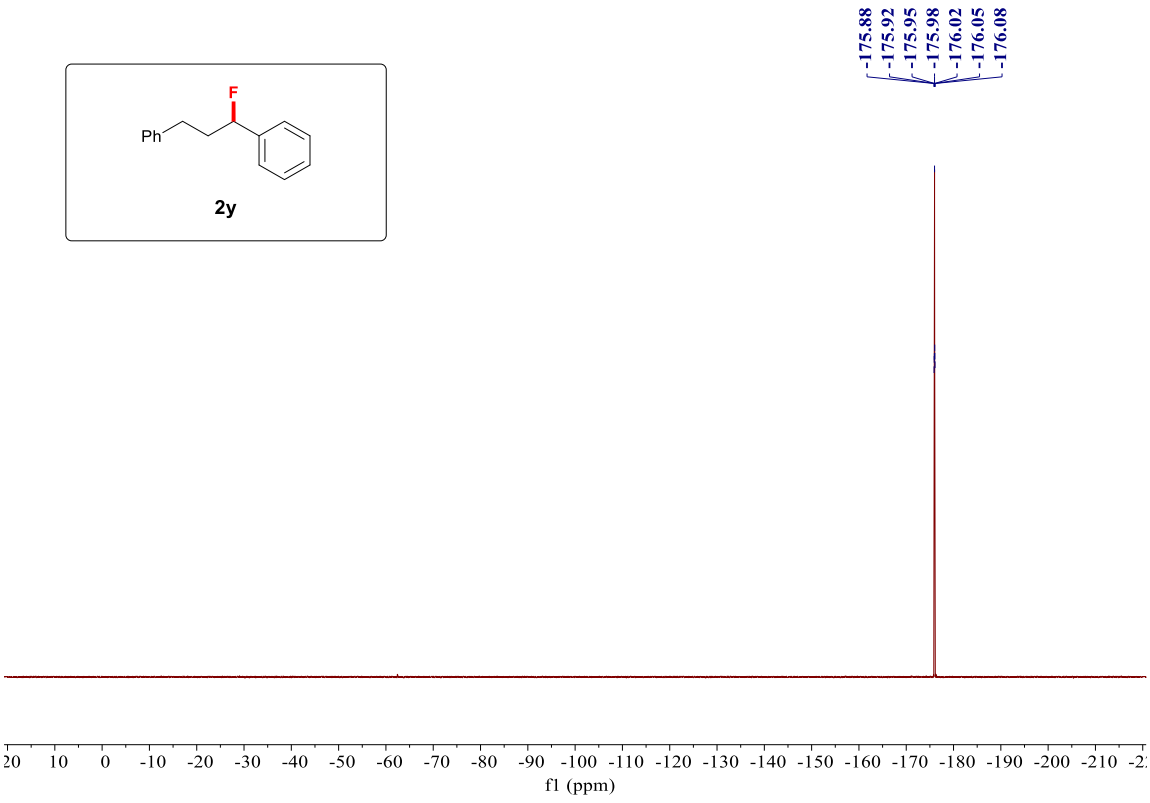
The Yield of **2y** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



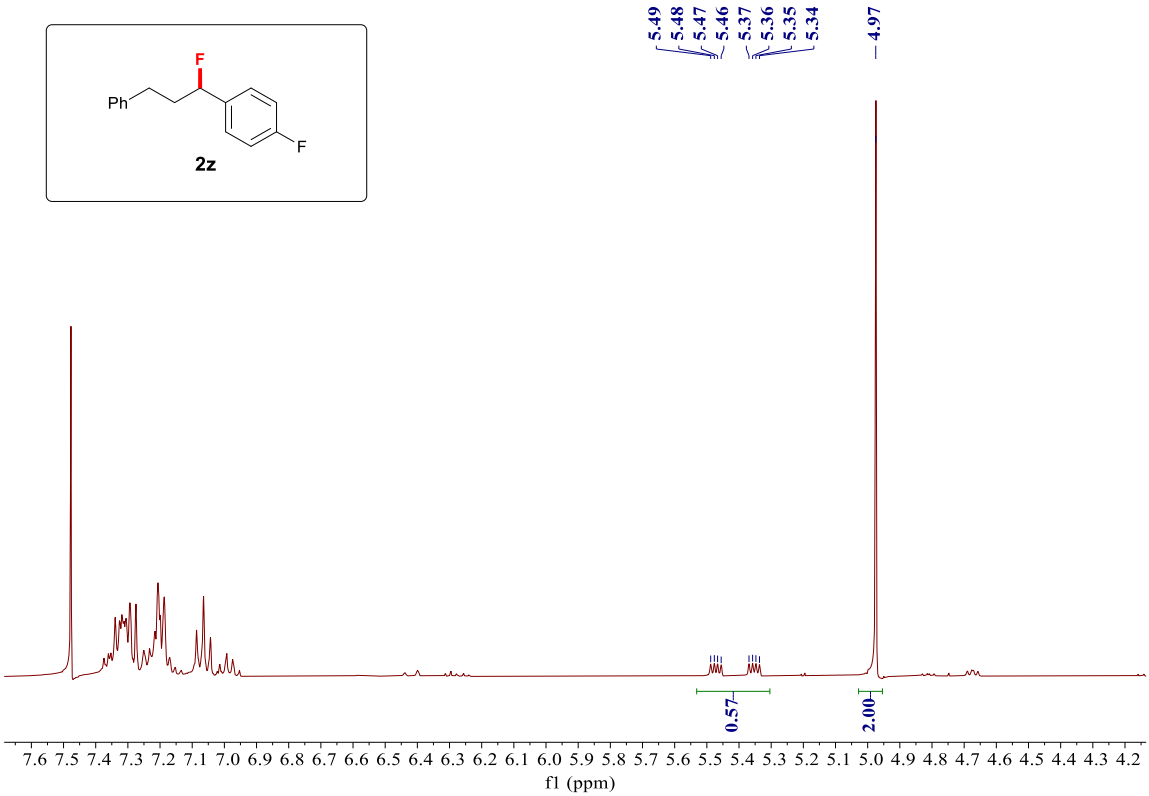
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2y**



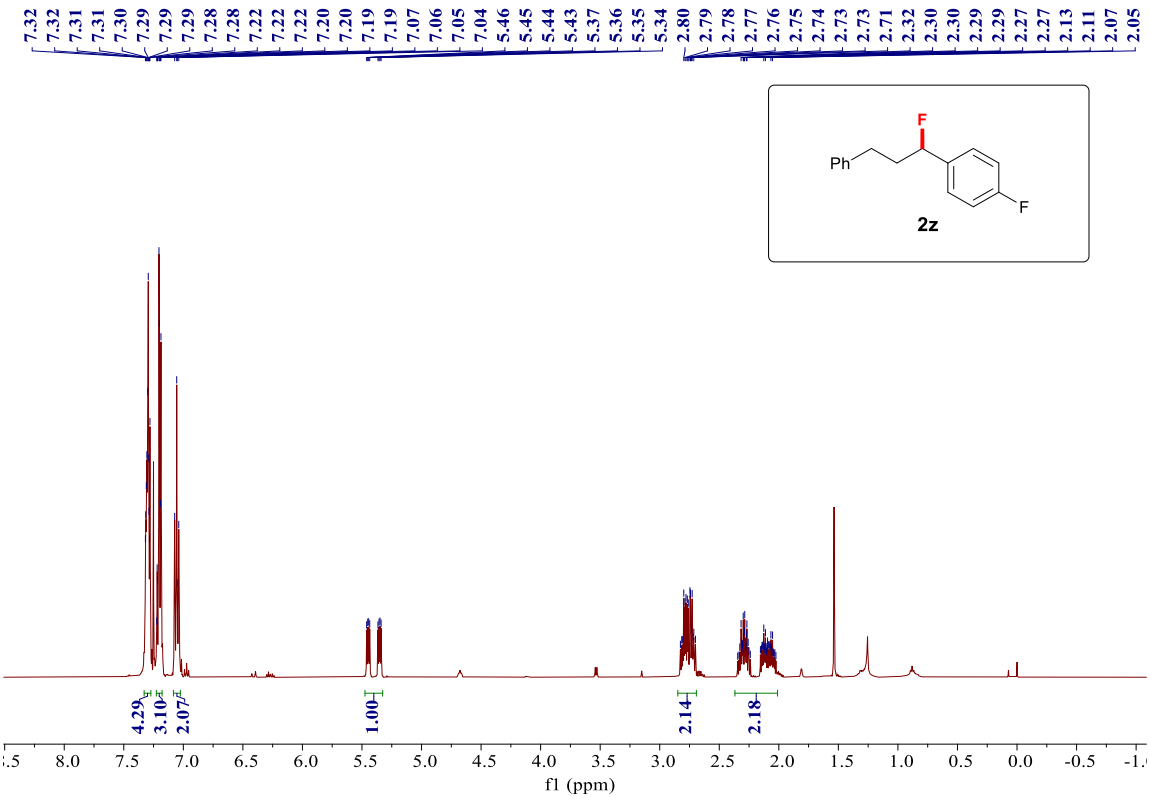
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2y**



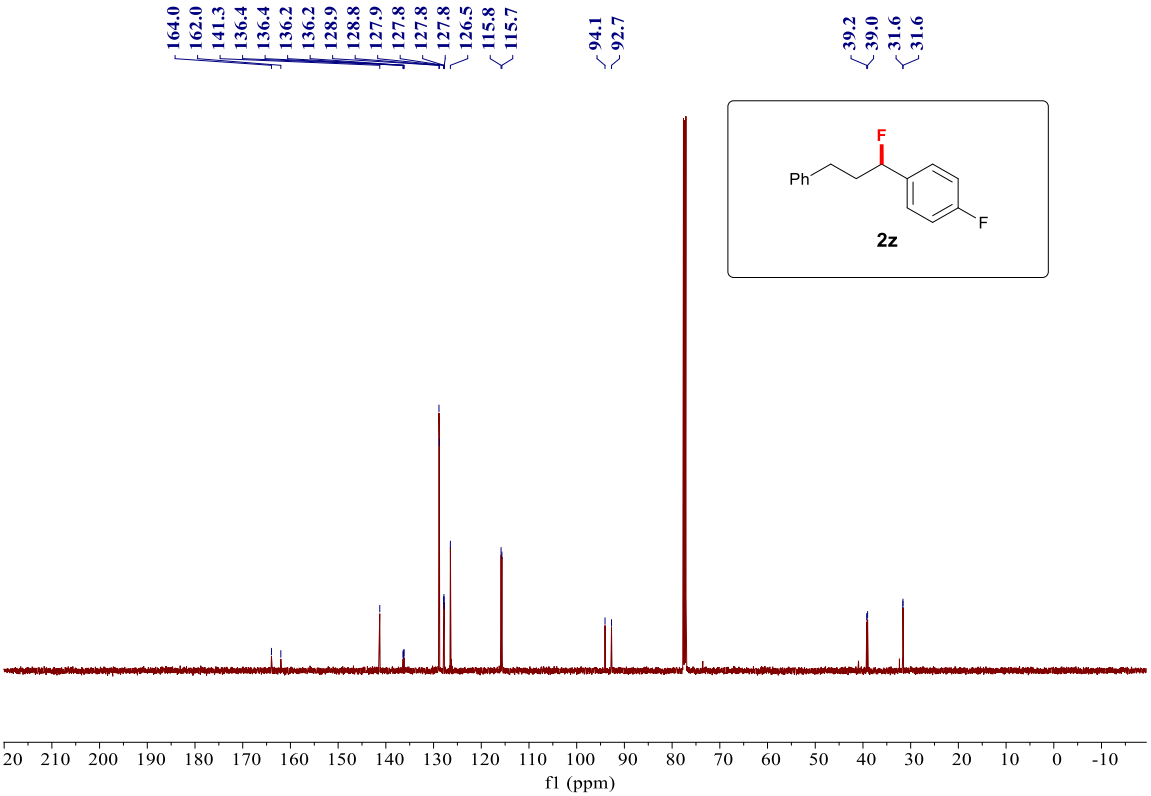
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2y**



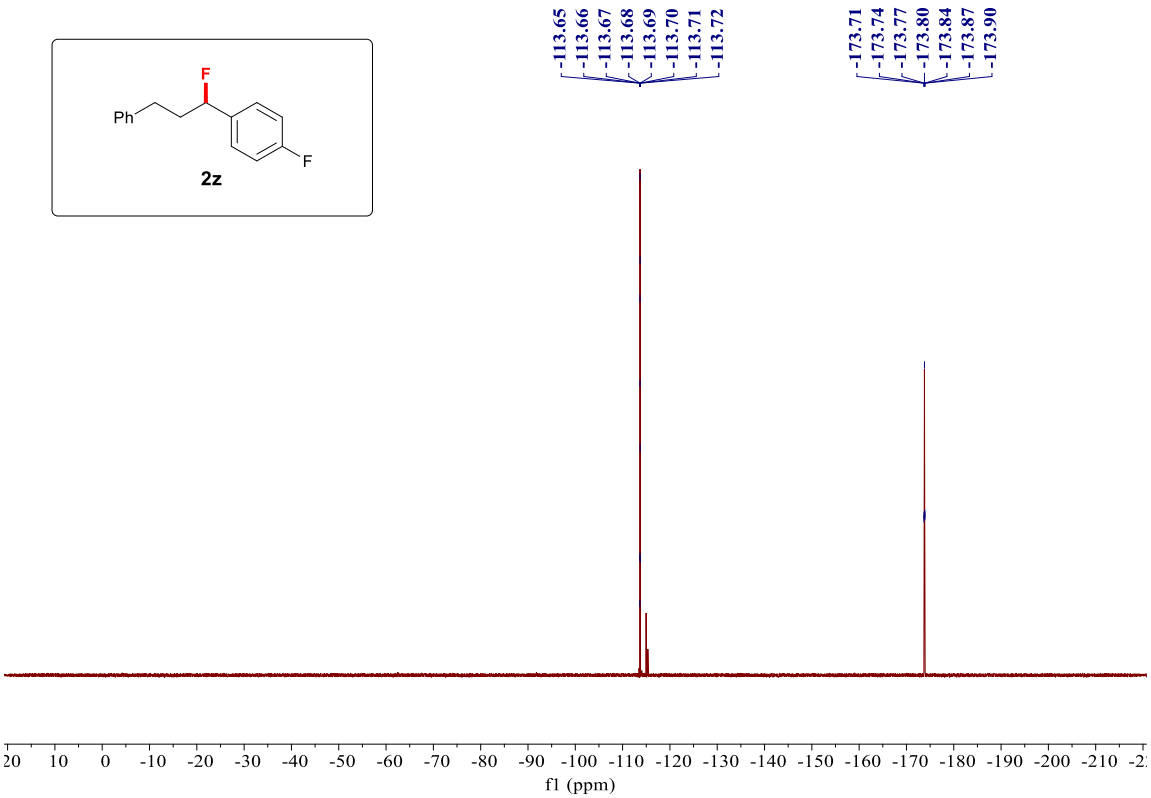
The Yield of **2z** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



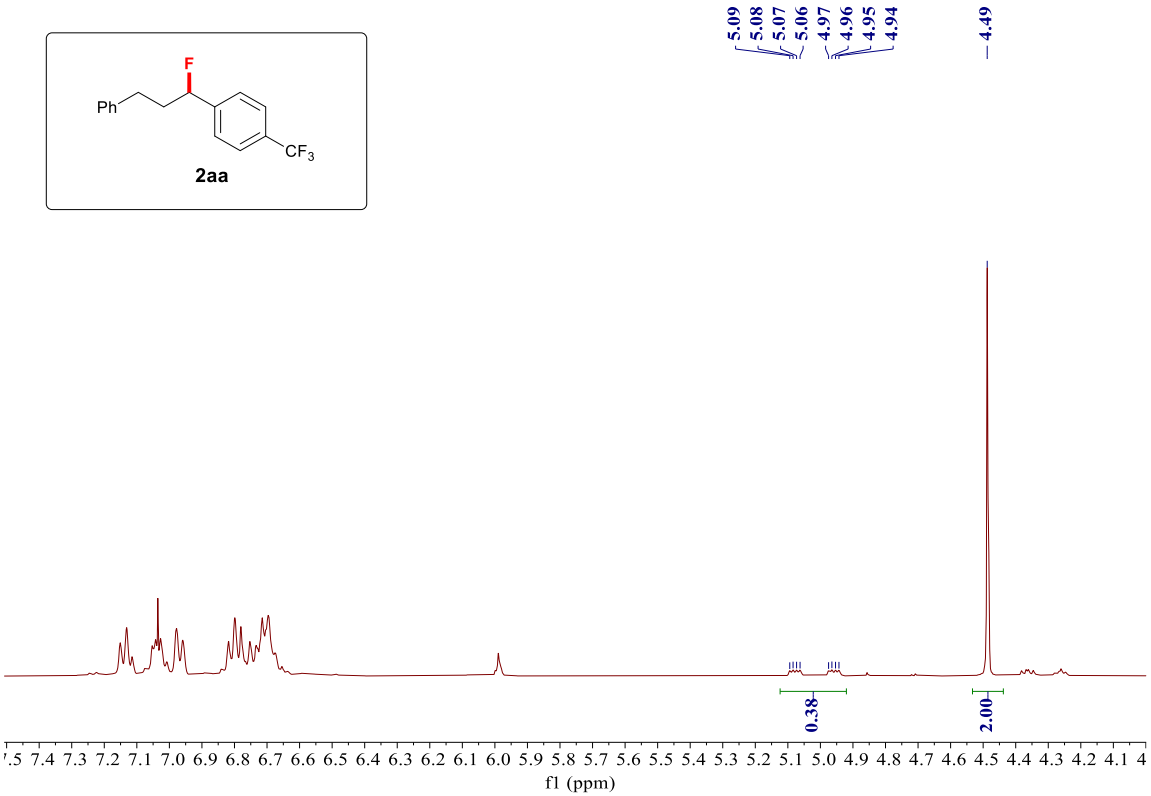
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2z**



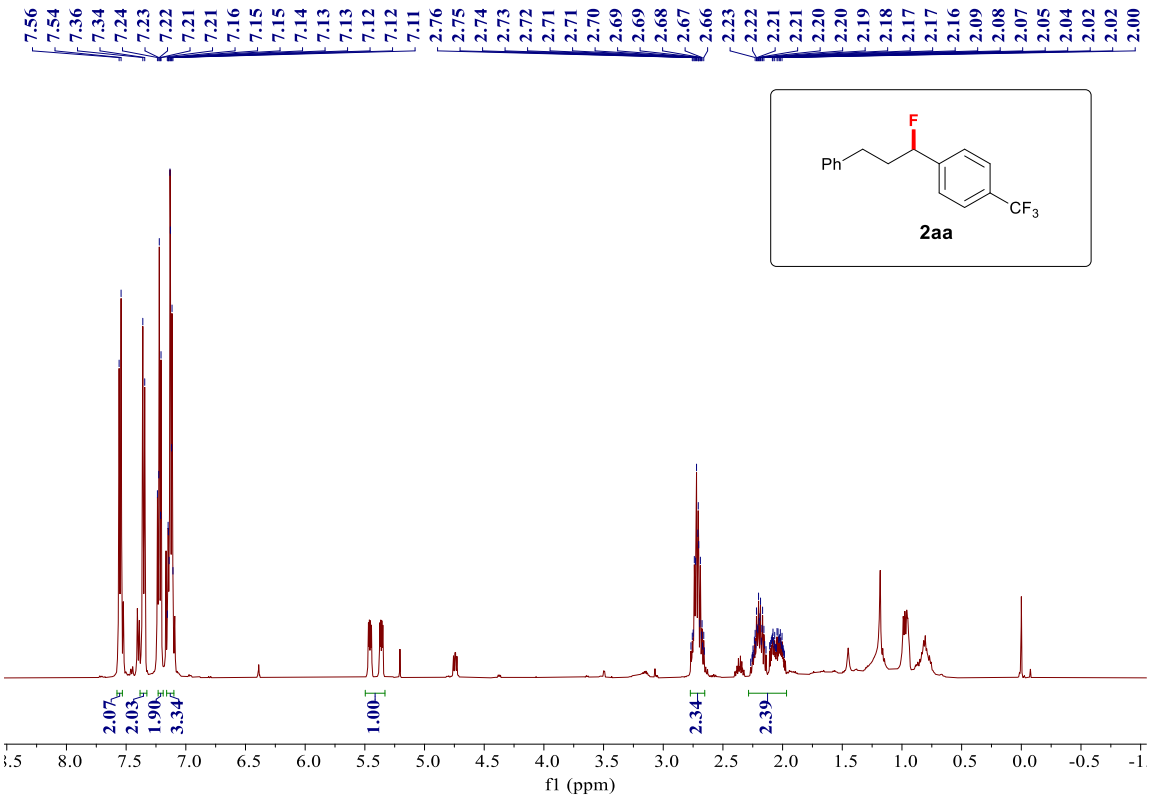
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2z**



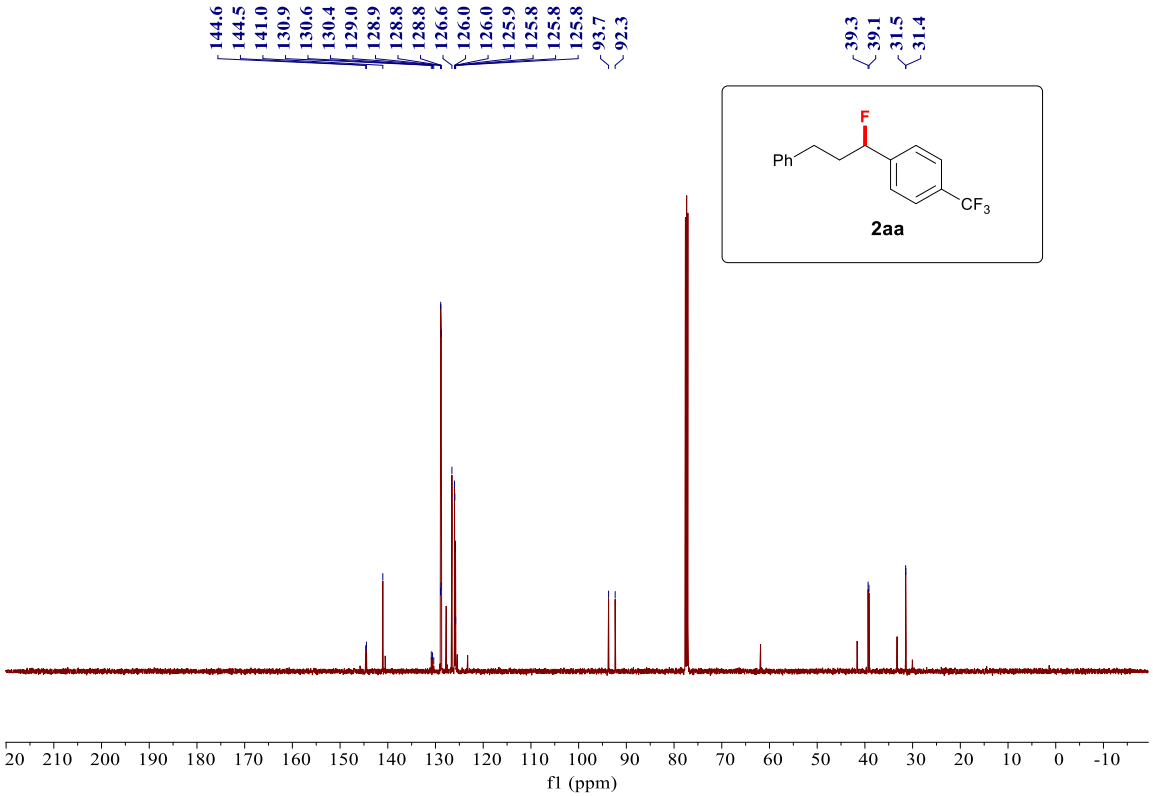
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2z**



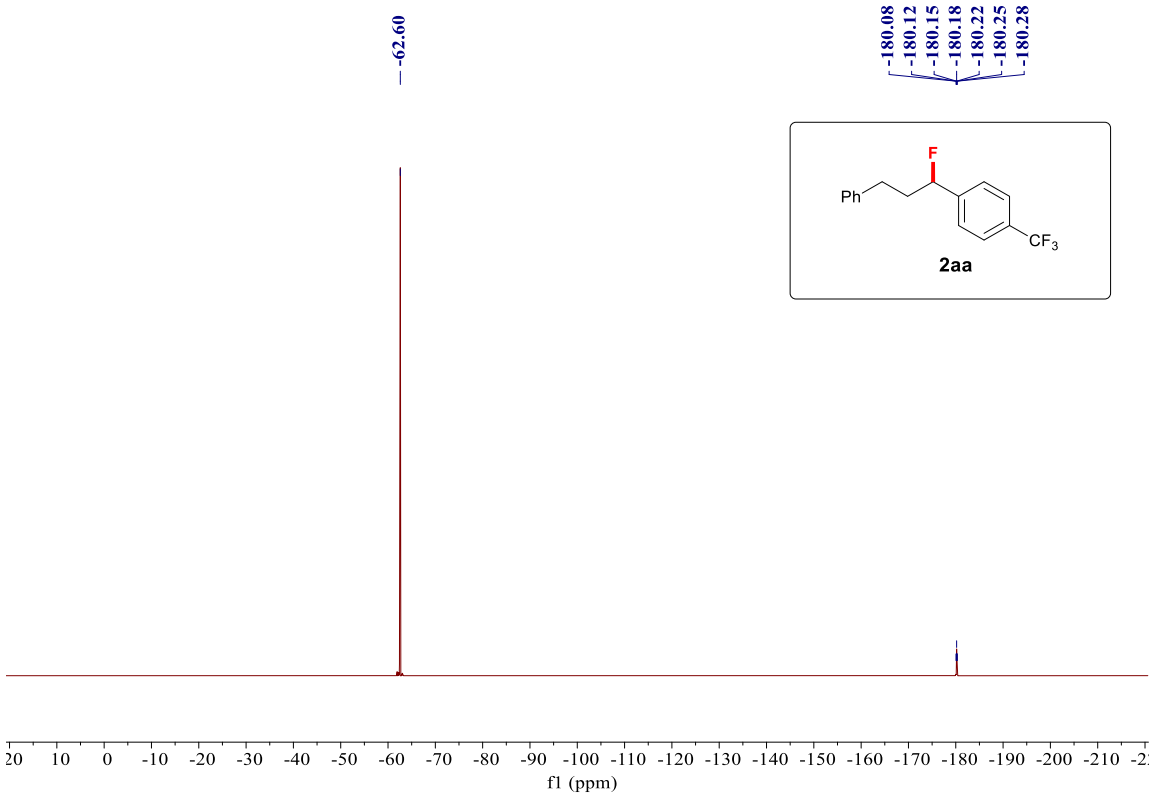
The Yield of **2aa** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



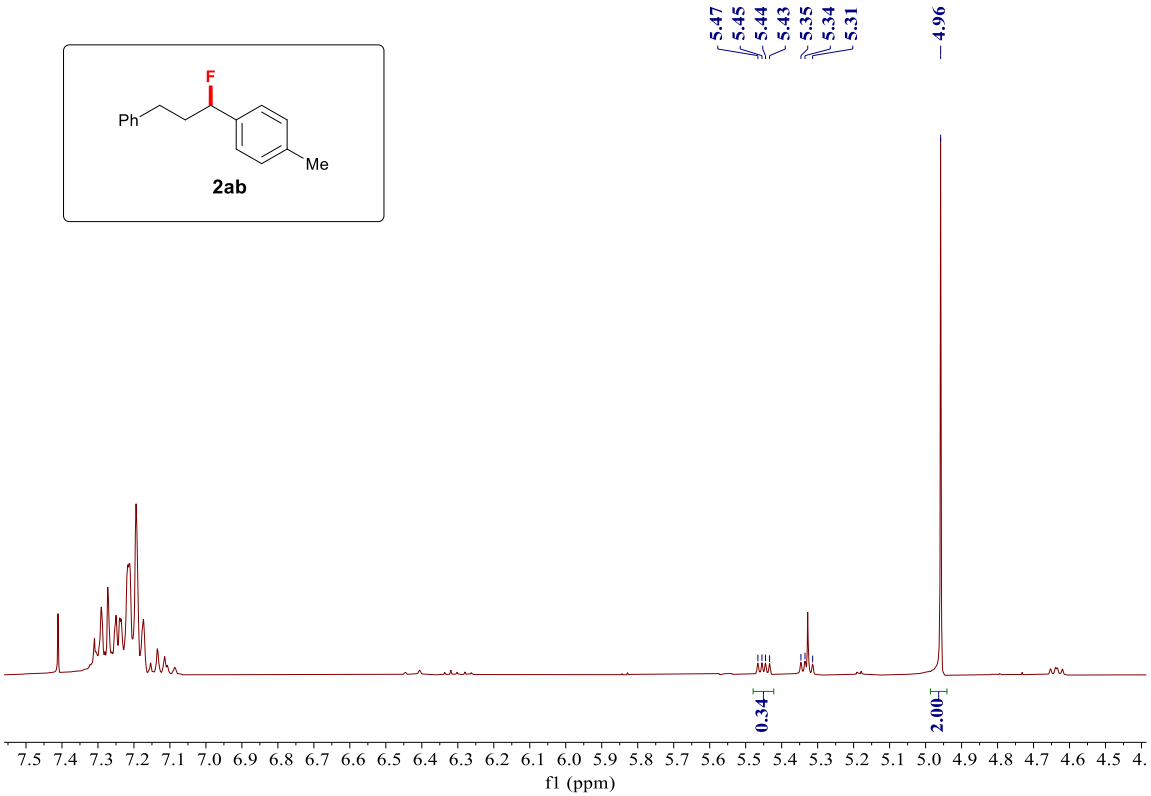
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2aa**



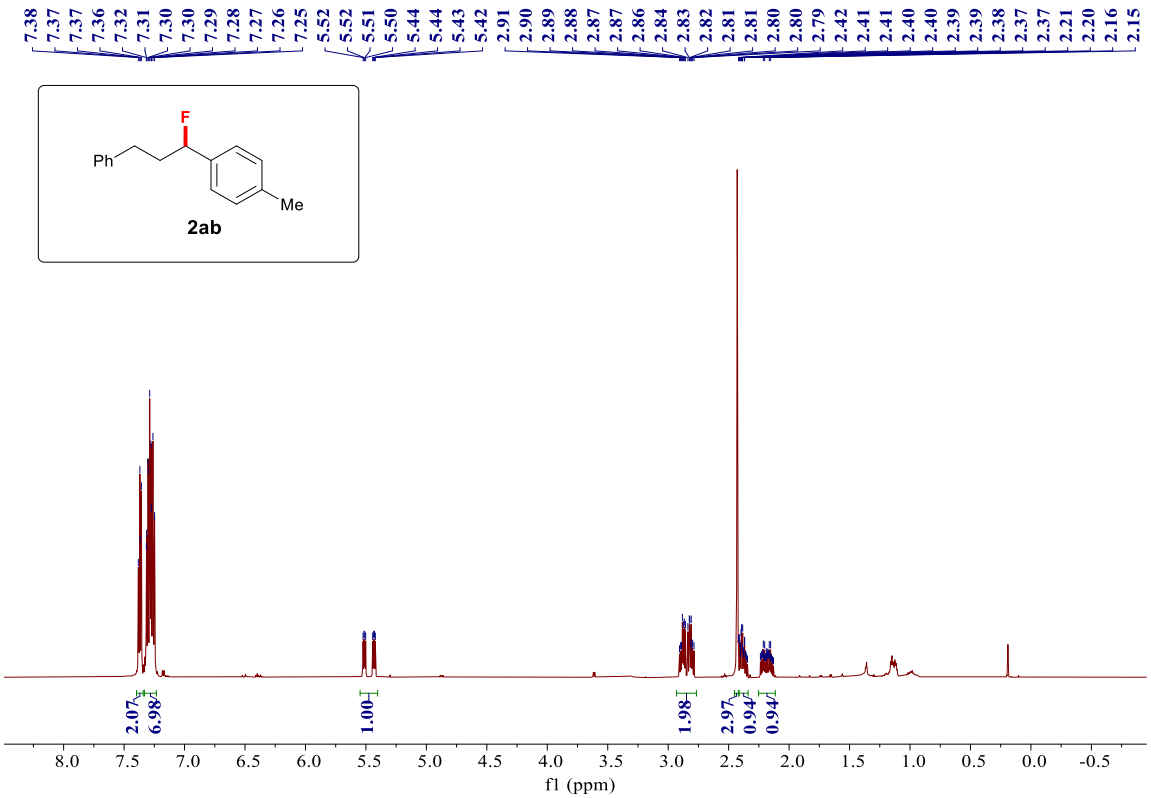
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2aa**



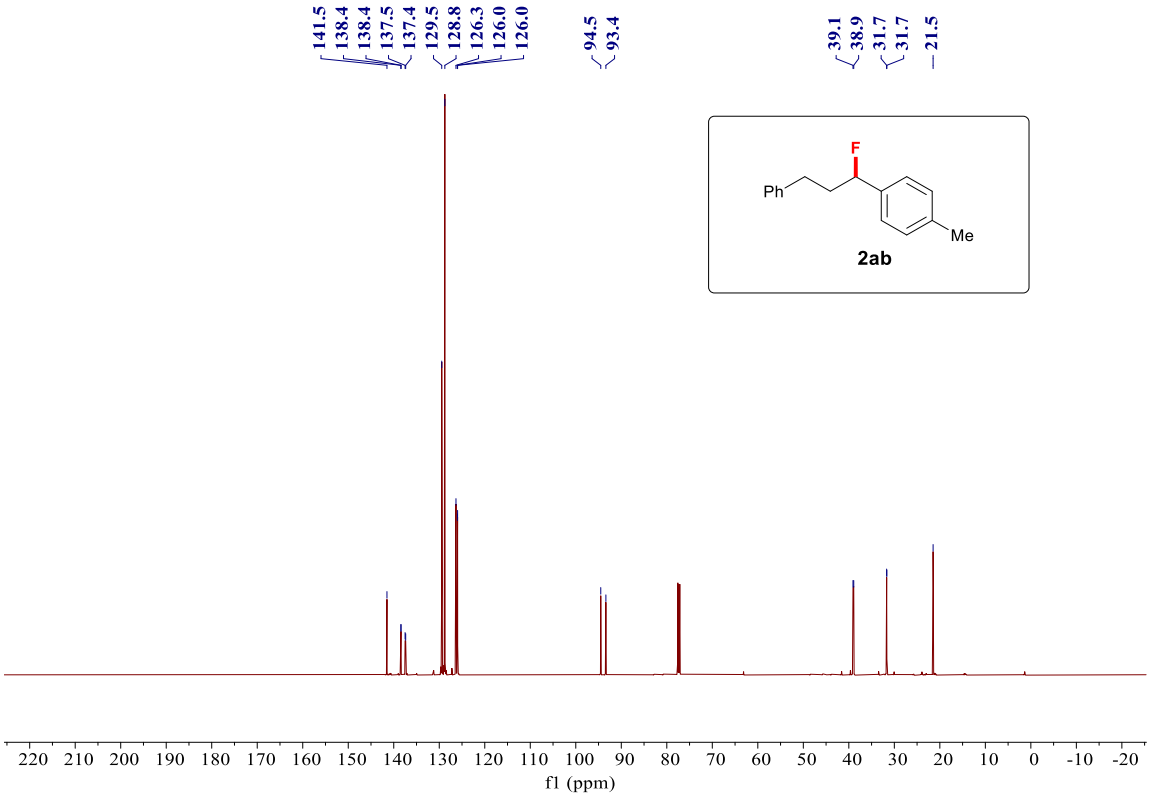
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2aa**



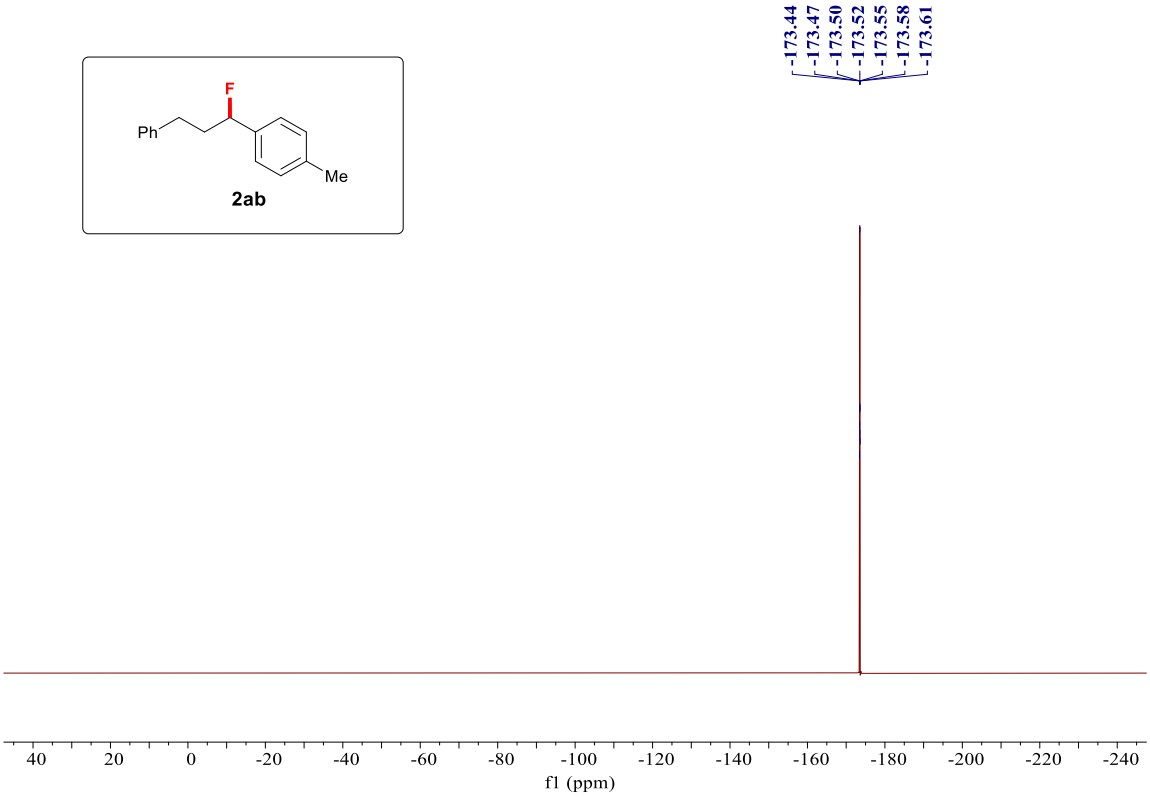
The Yield of **2ab** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



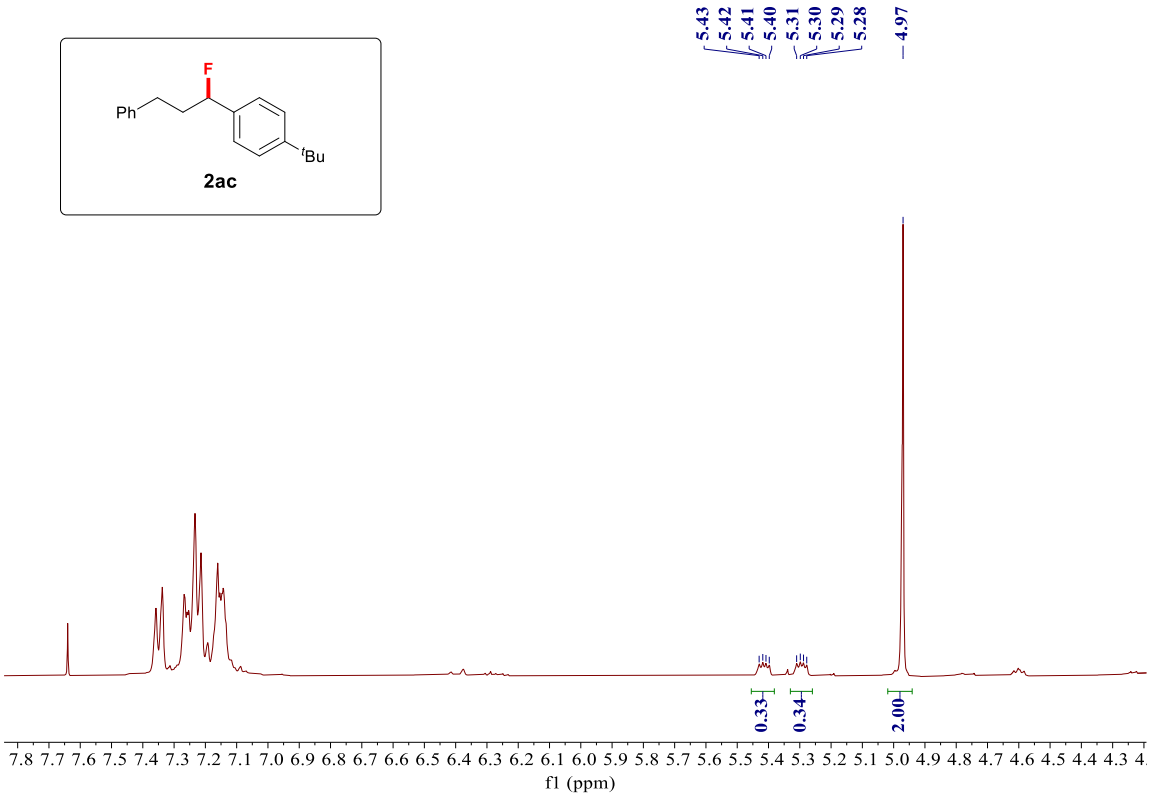
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **2ab**



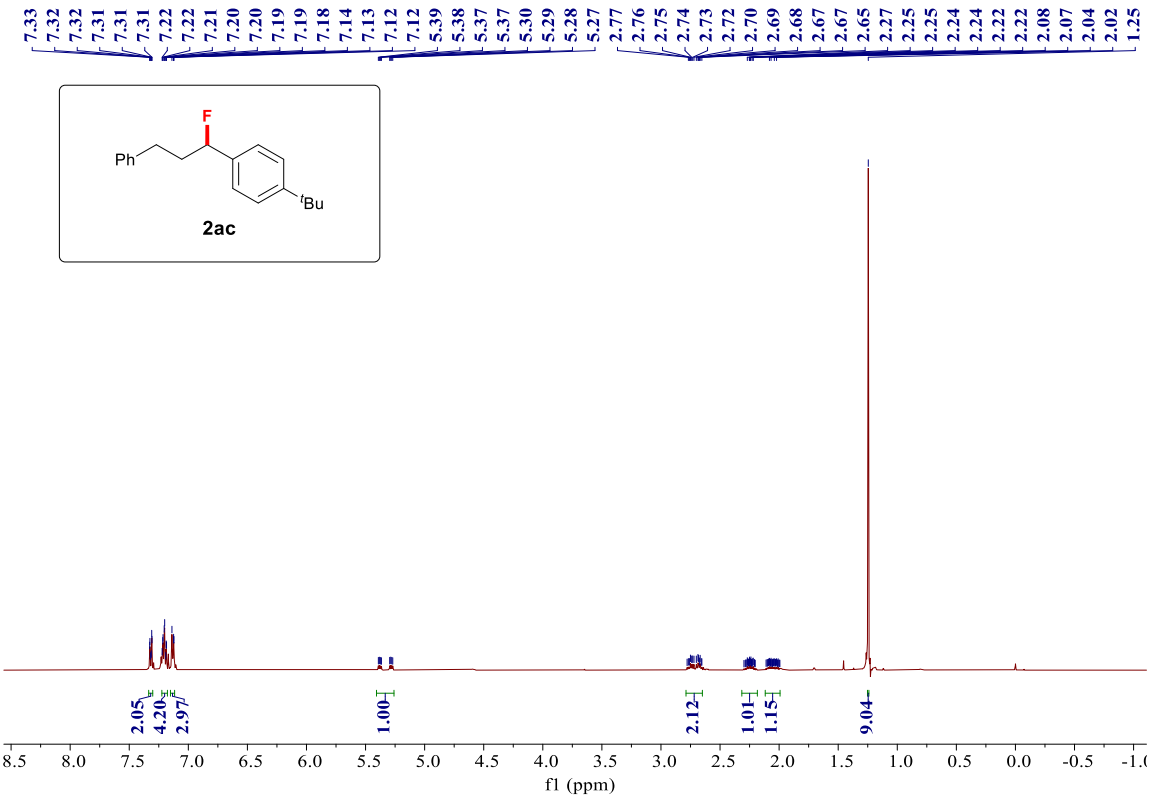
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of Compound **2ab**



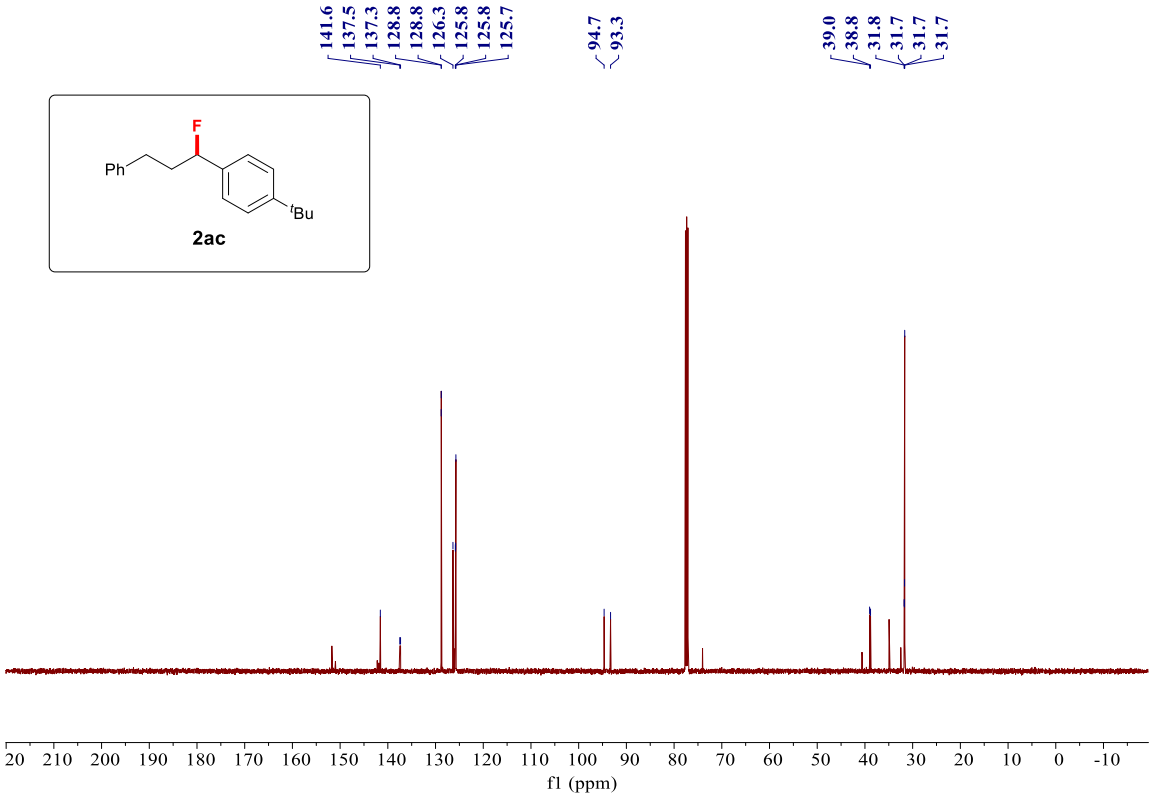
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of Compound **2ab**



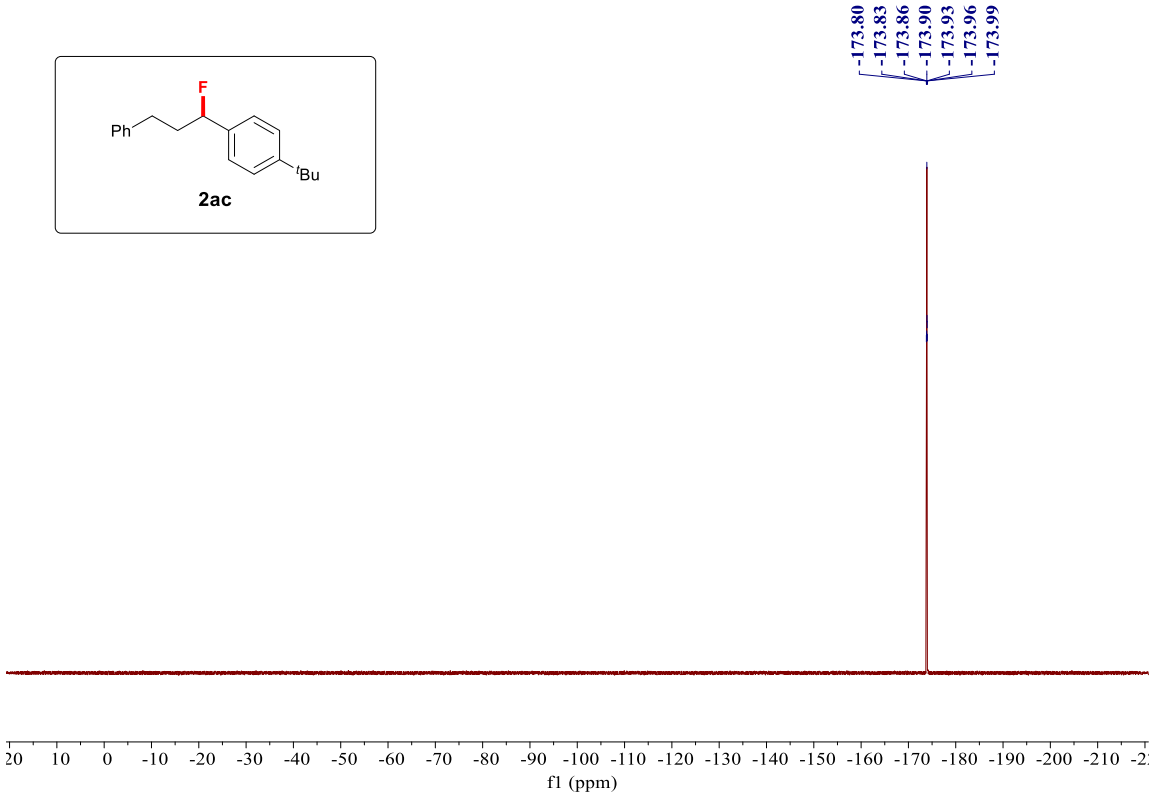
The Yield of **2ac** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



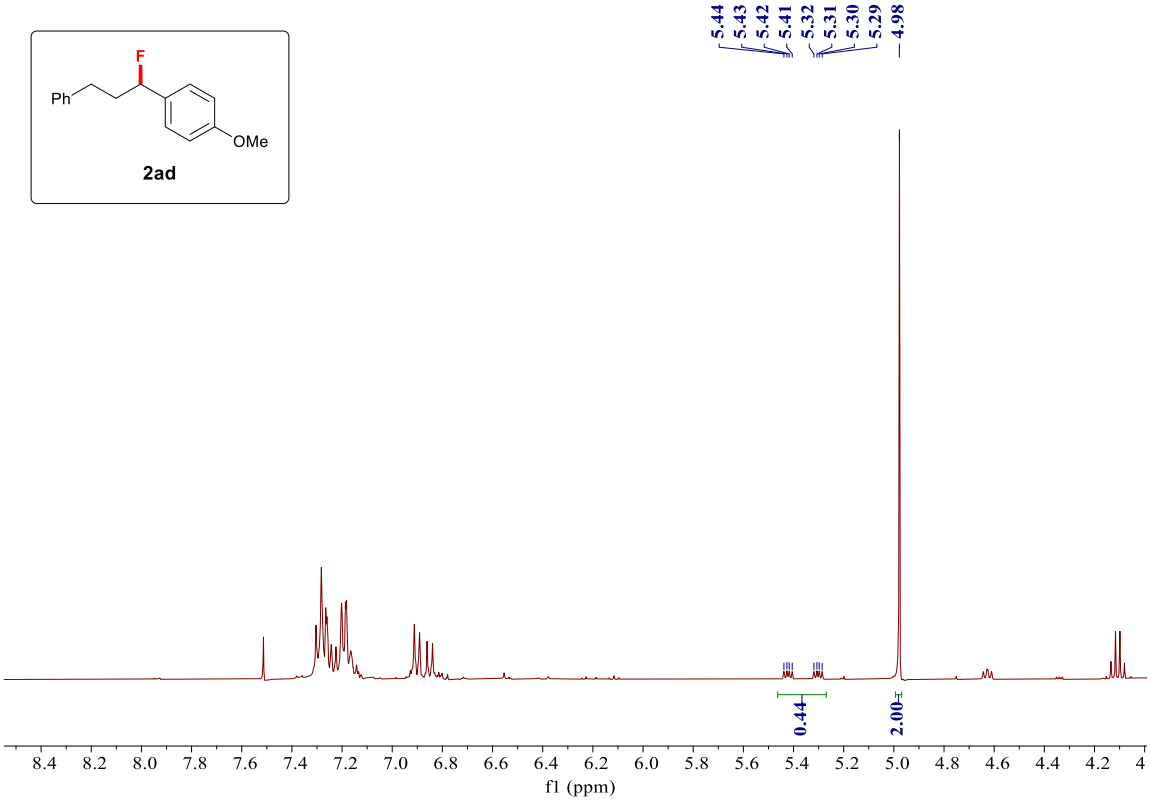
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2ac**



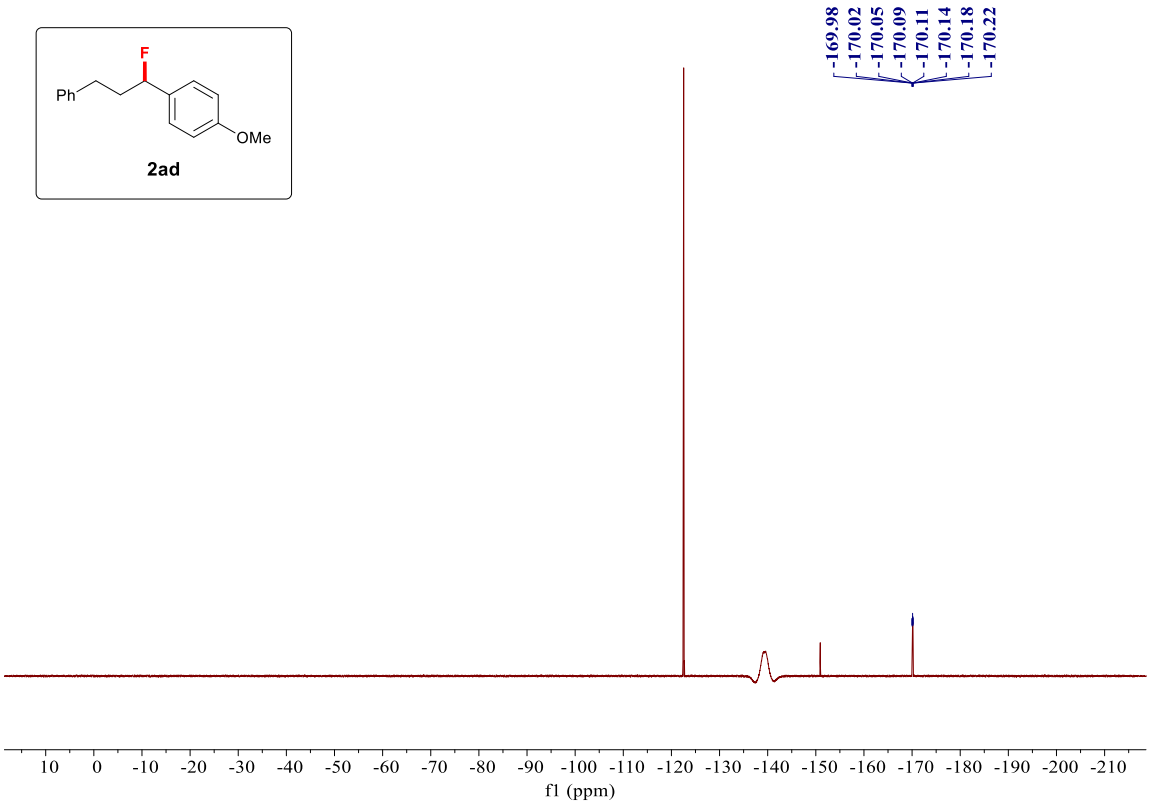
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2ac**



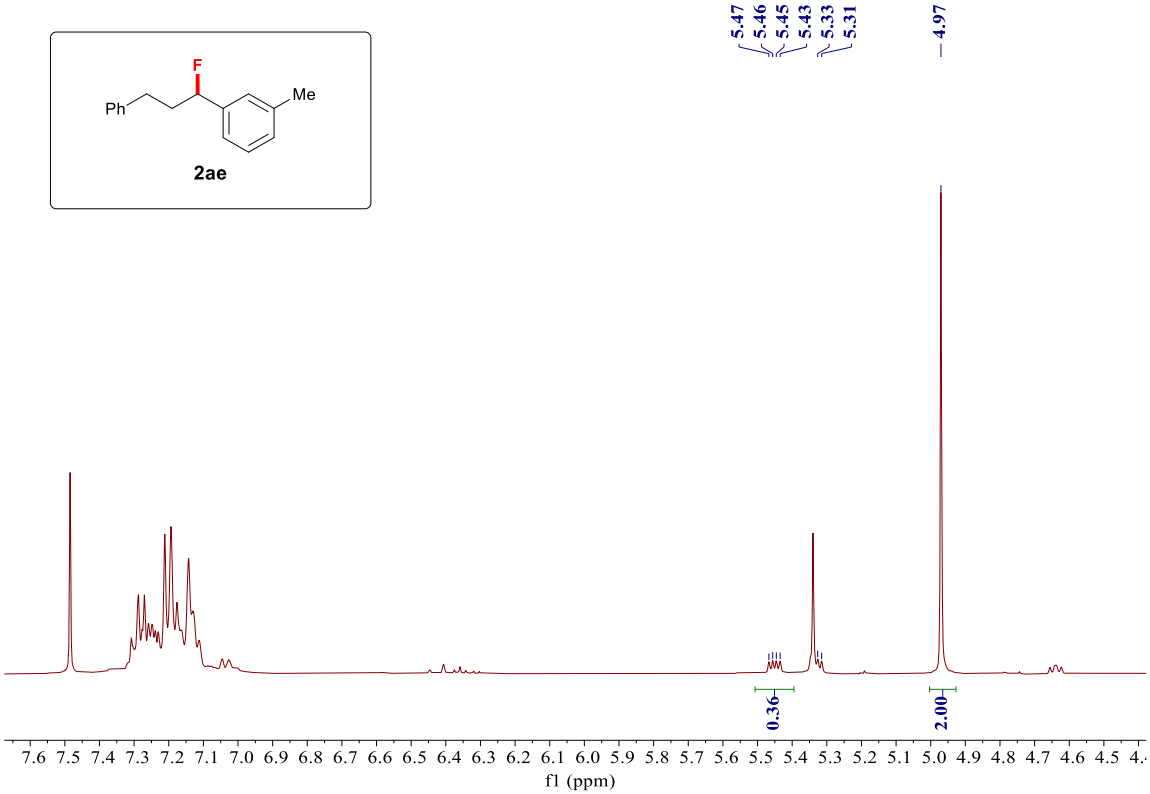
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2ac**



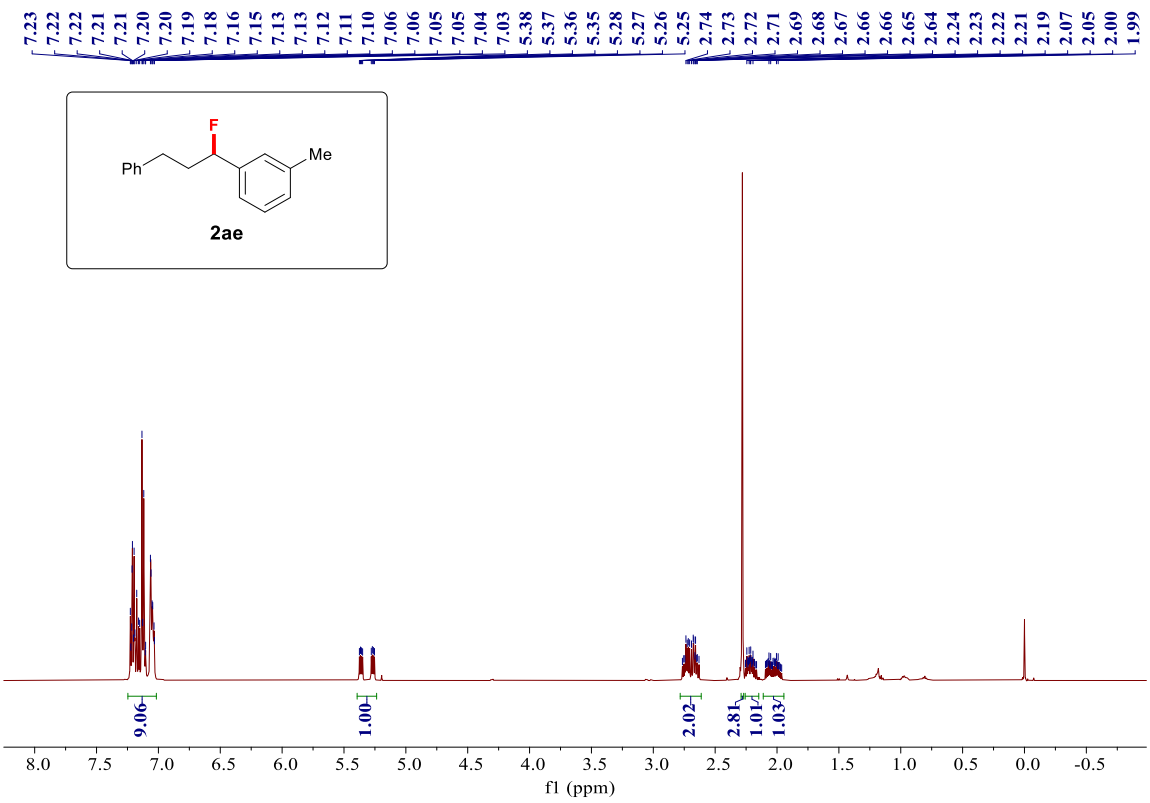
The Yield of **2ad** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



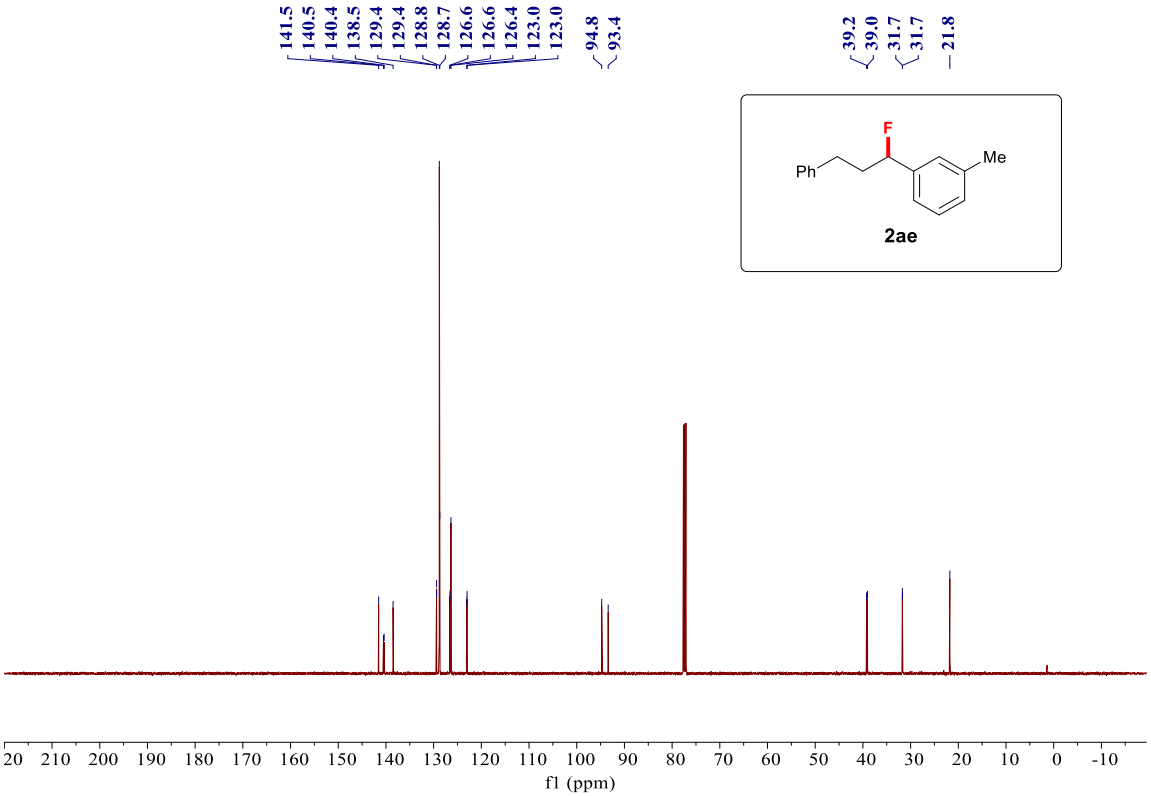
Crude ^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **2ad** Reaction Mixture



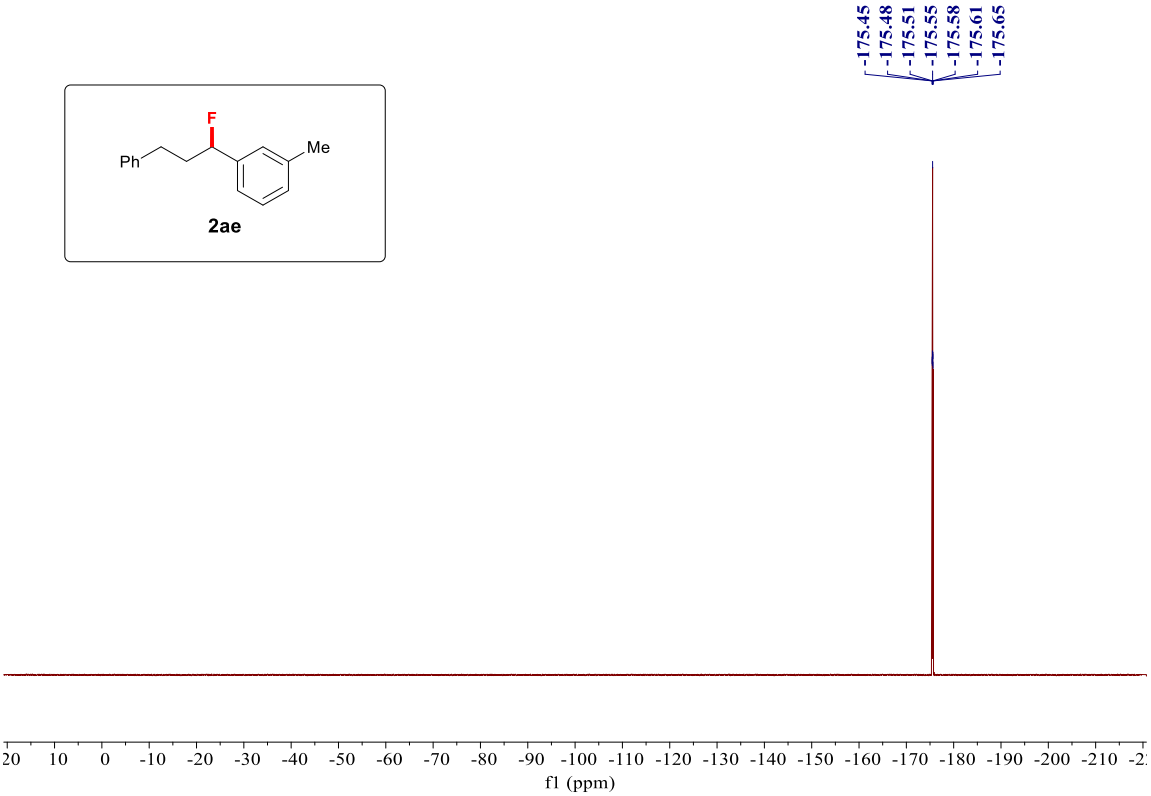
The Yield of **2ae** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



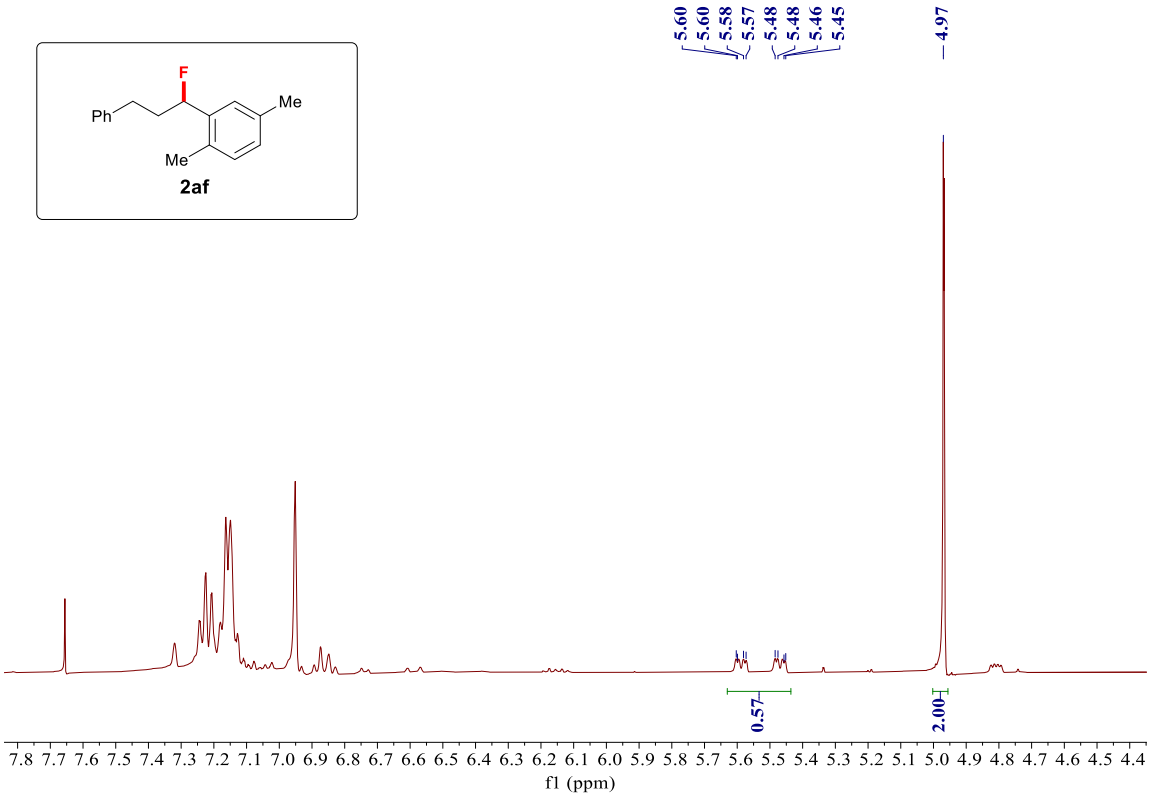
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2ae**



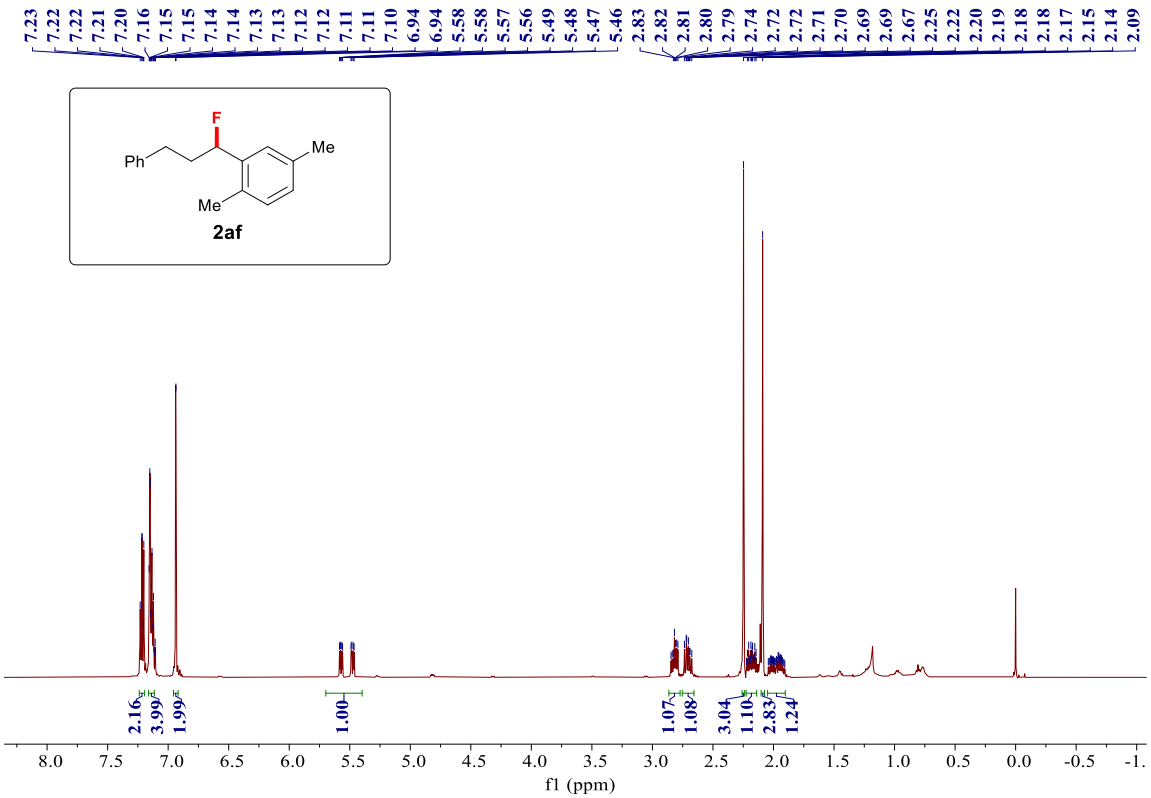
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2ae**



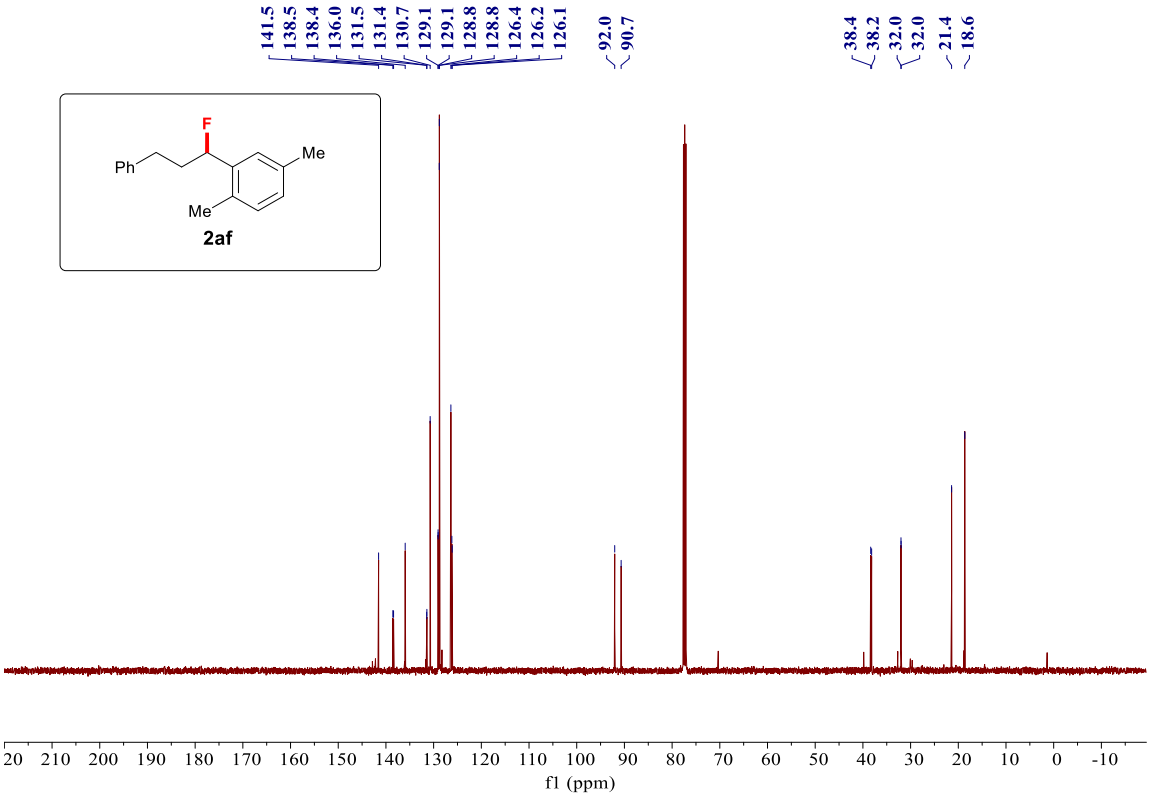
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2ae**



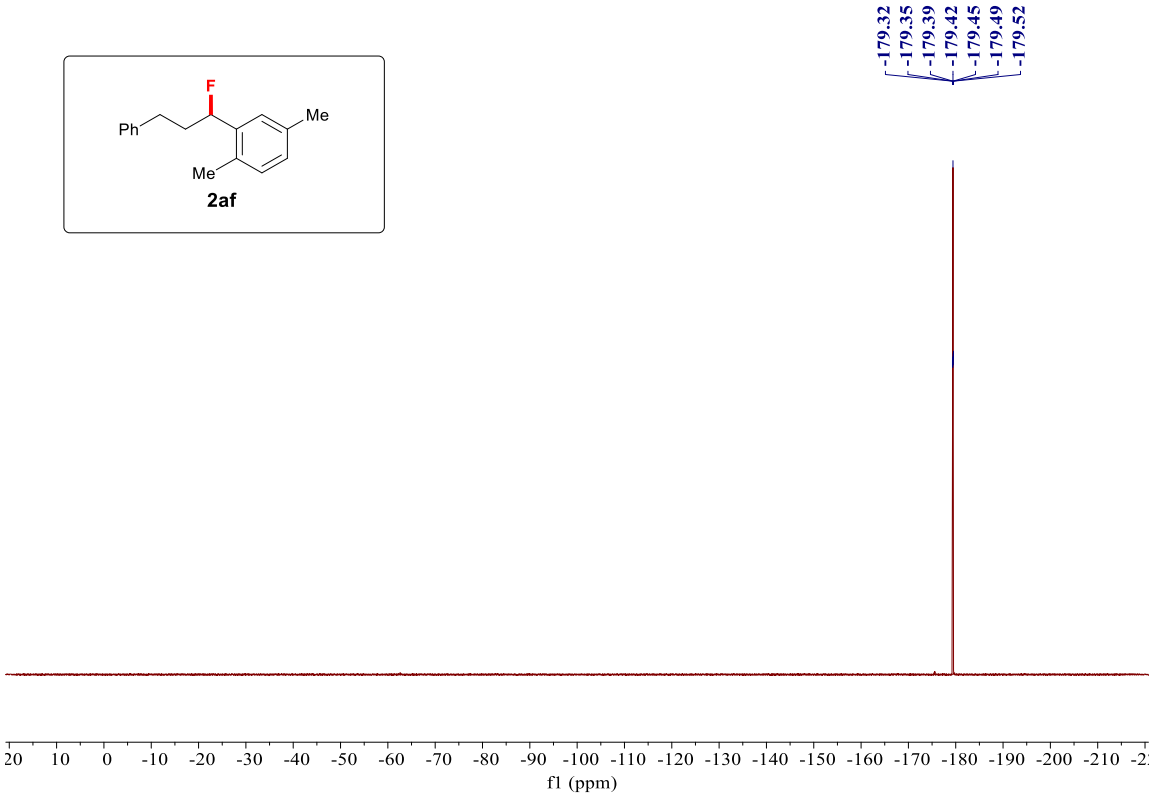
The Yield of **2af** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



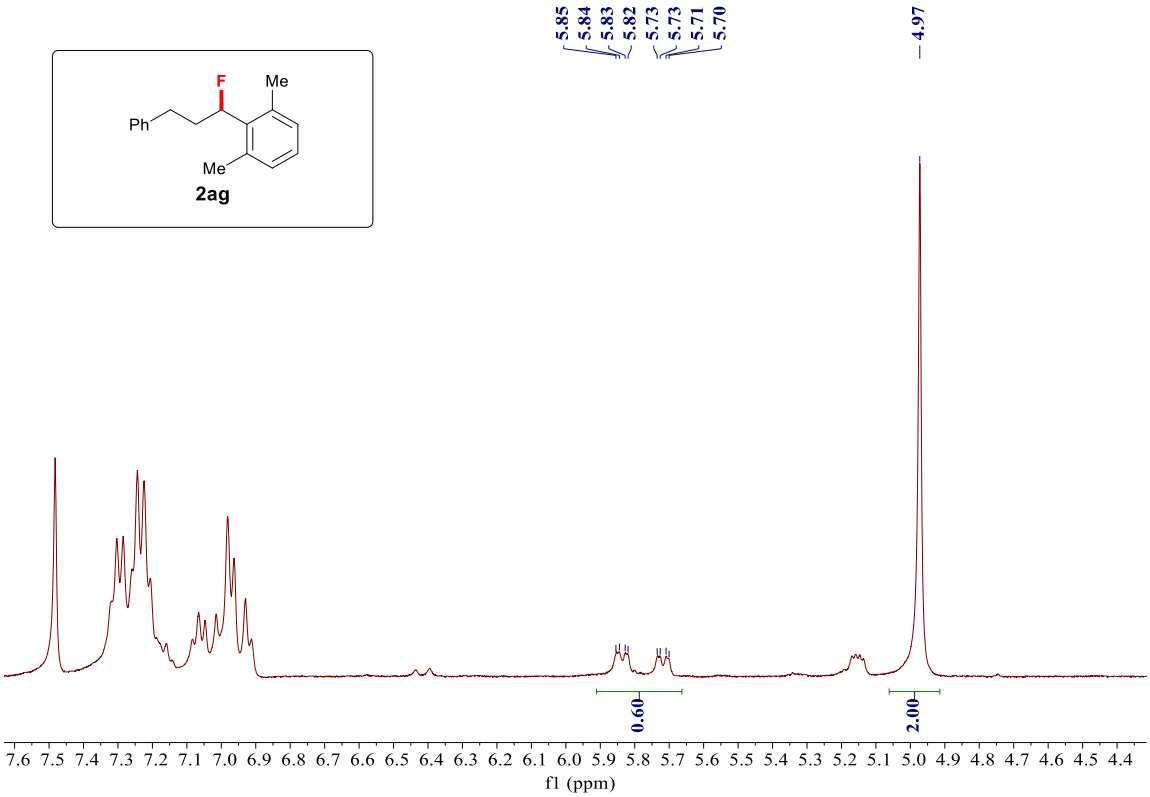
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2af**



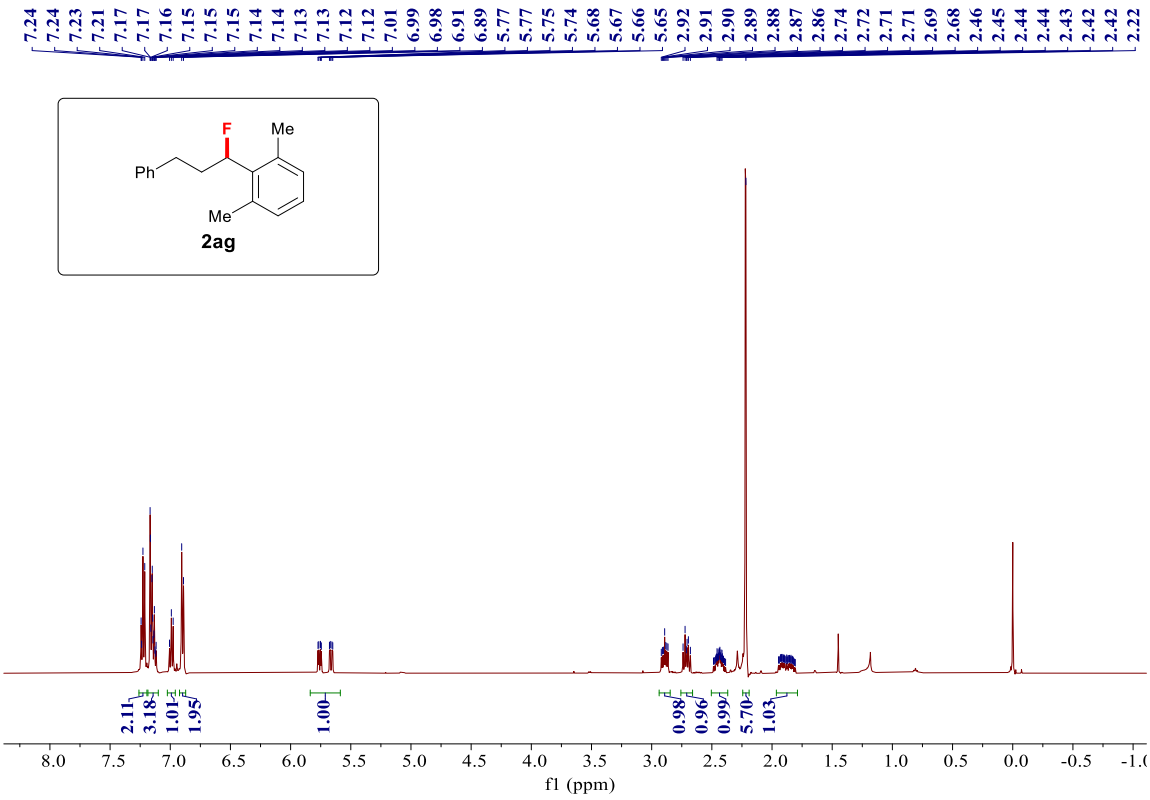
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2af**



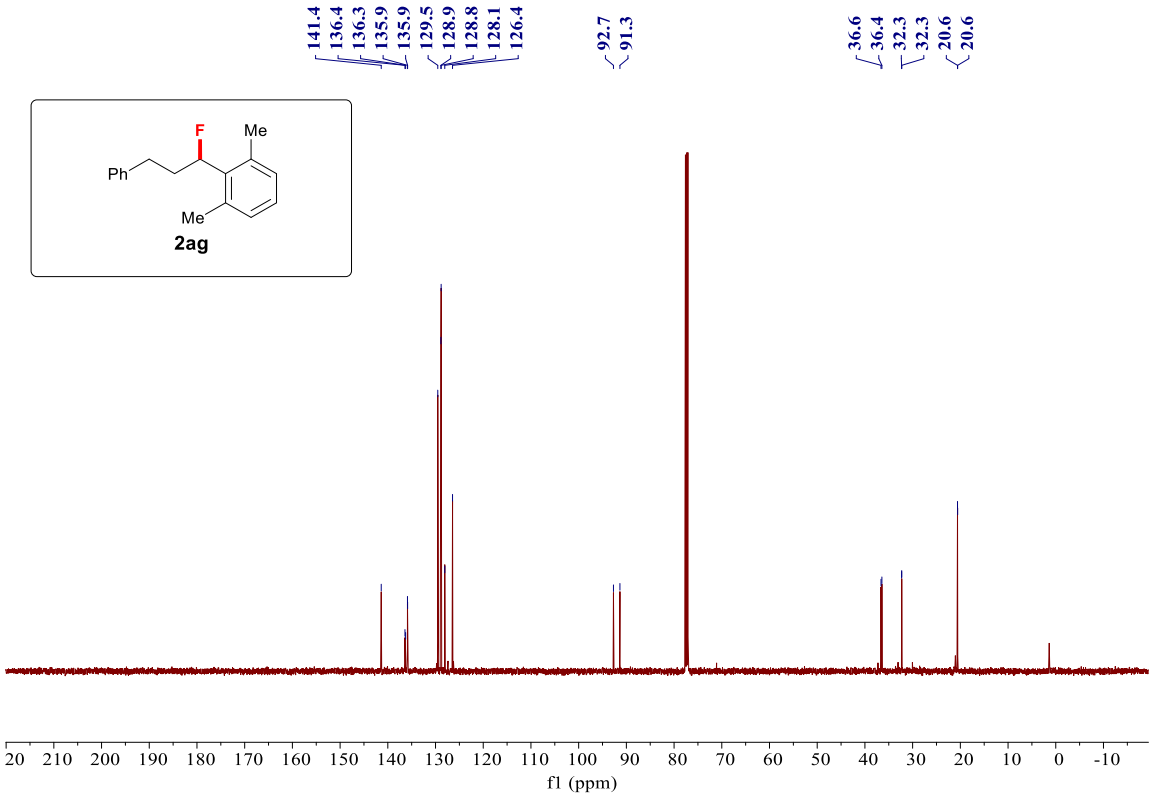
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2af**



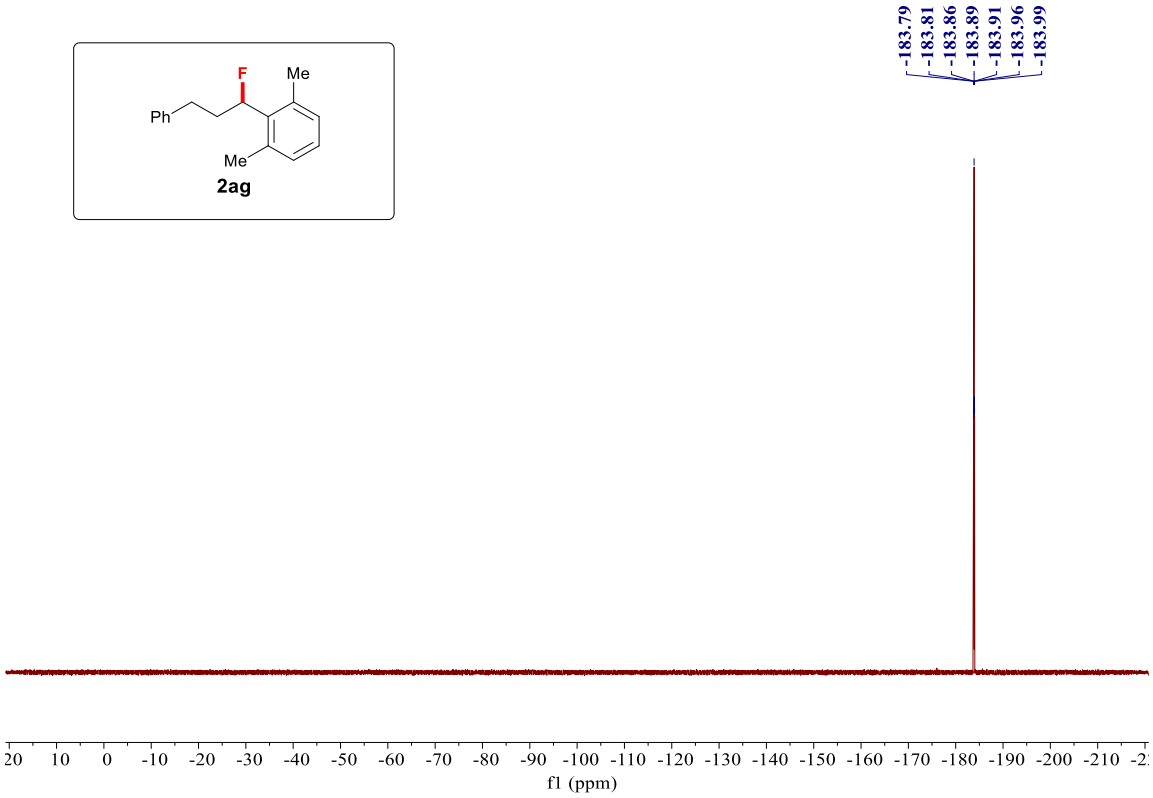
The Yield of **2ag** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



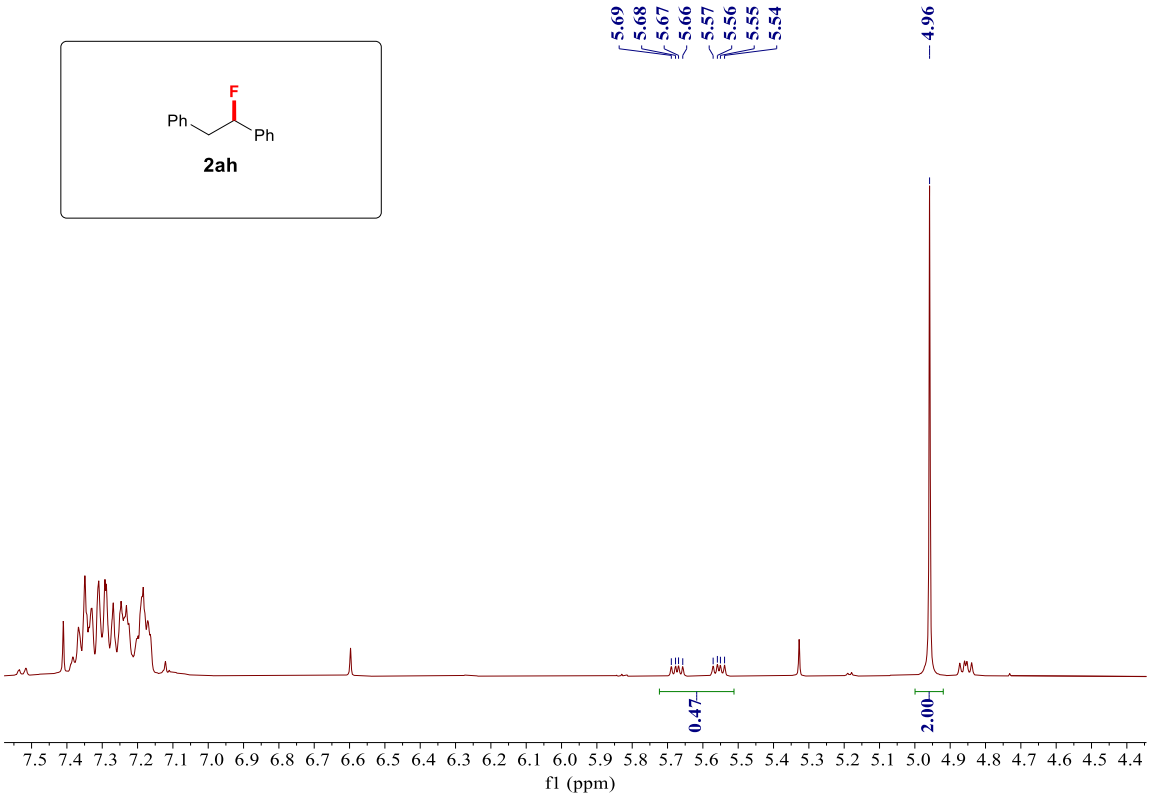
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **2ag**



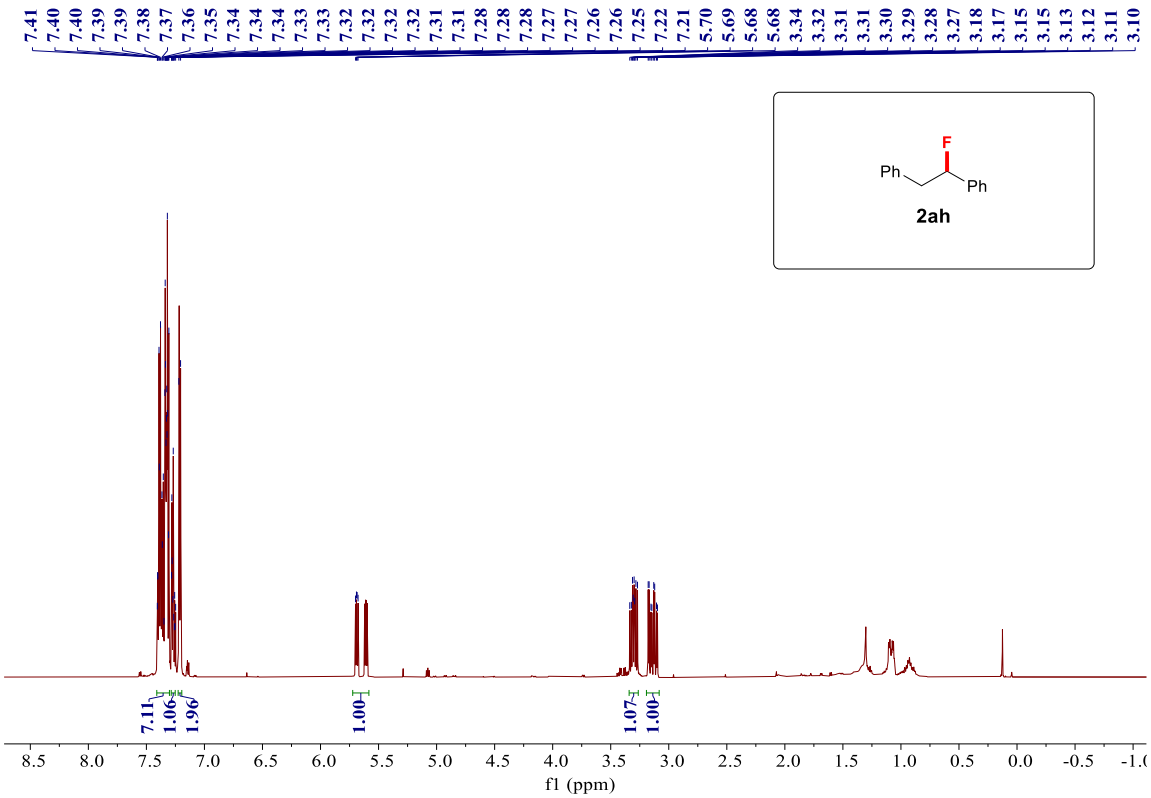
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2ag**



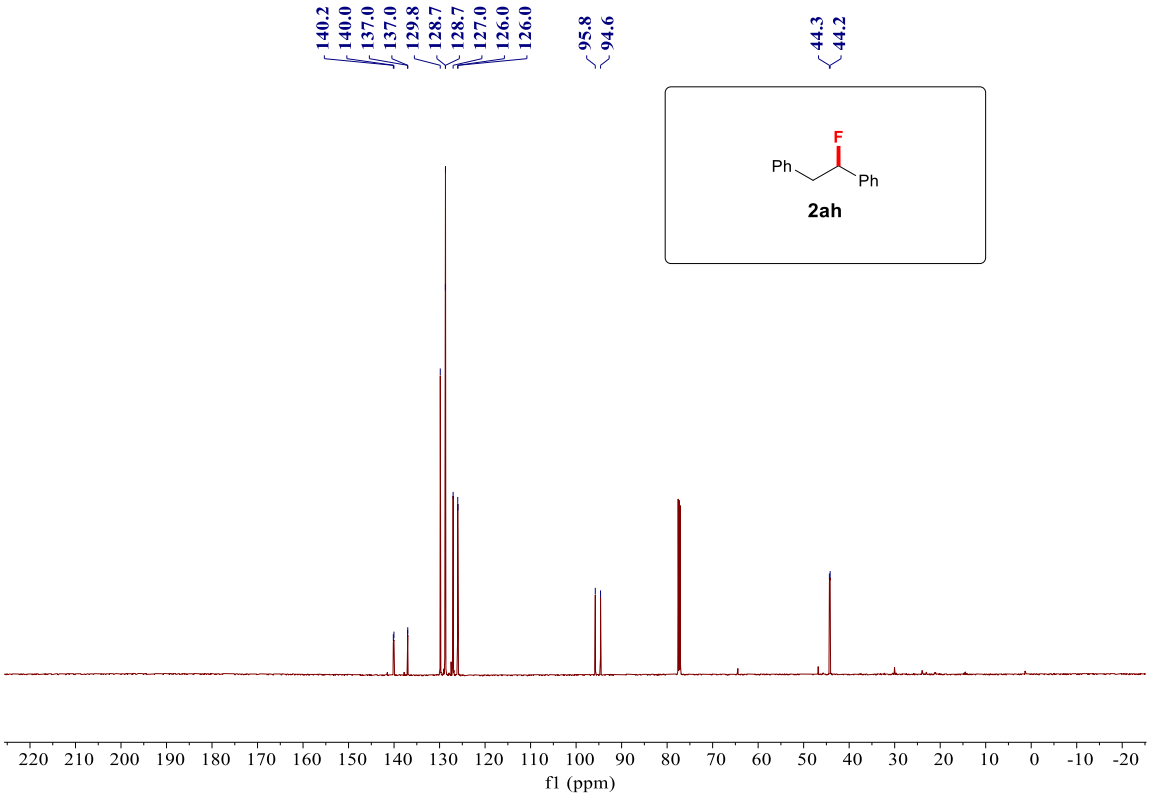
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **2ag**



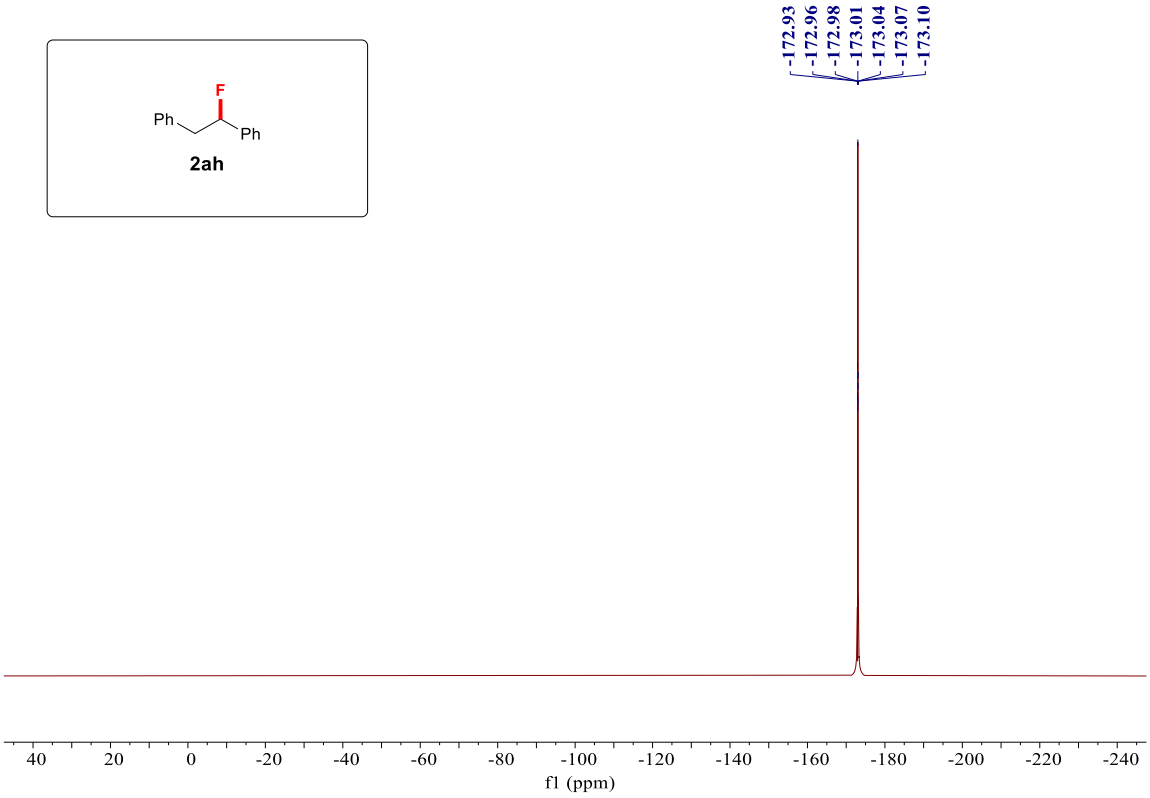
The Yield of **2ah** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



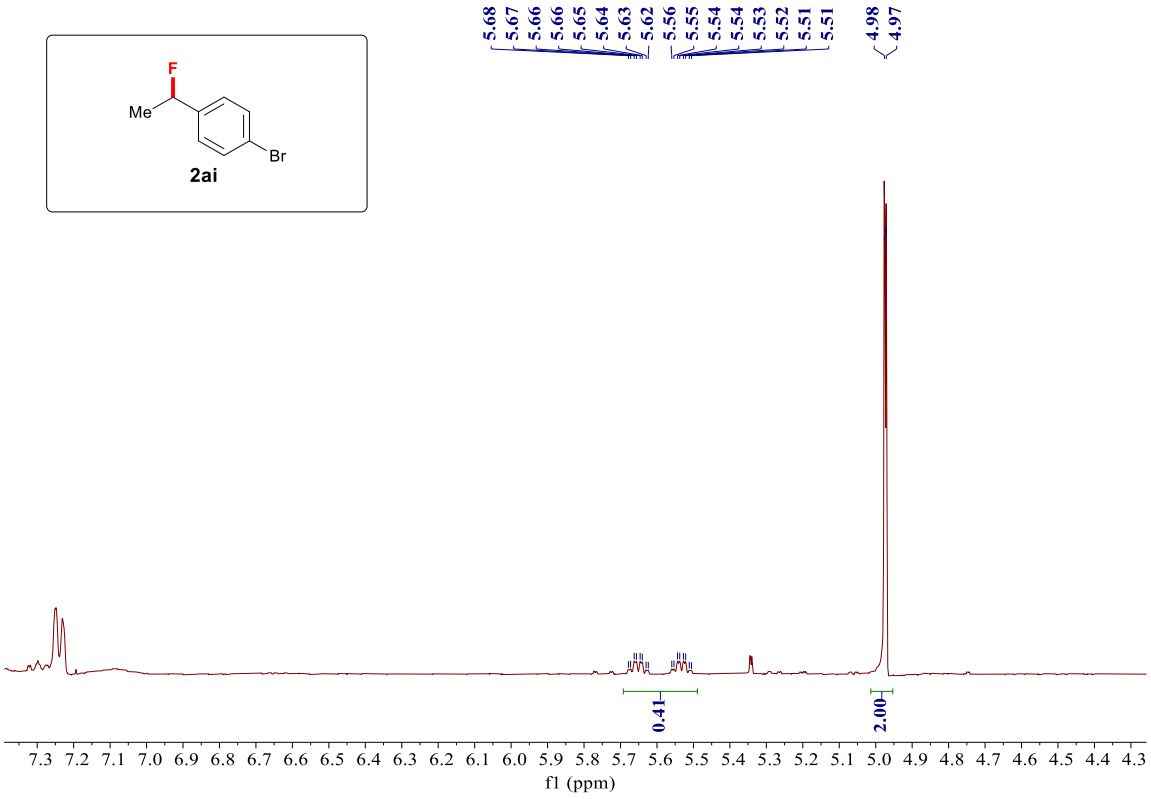
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **2ah**



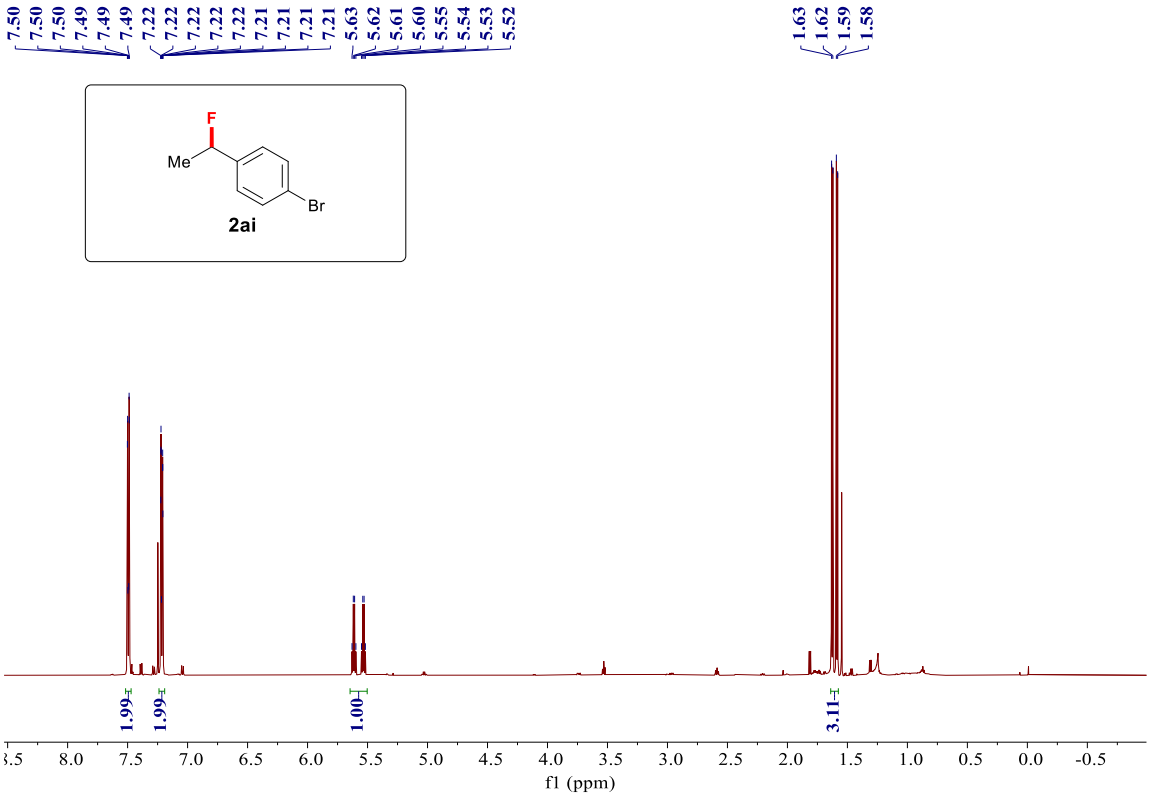
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of Compound **2ah**



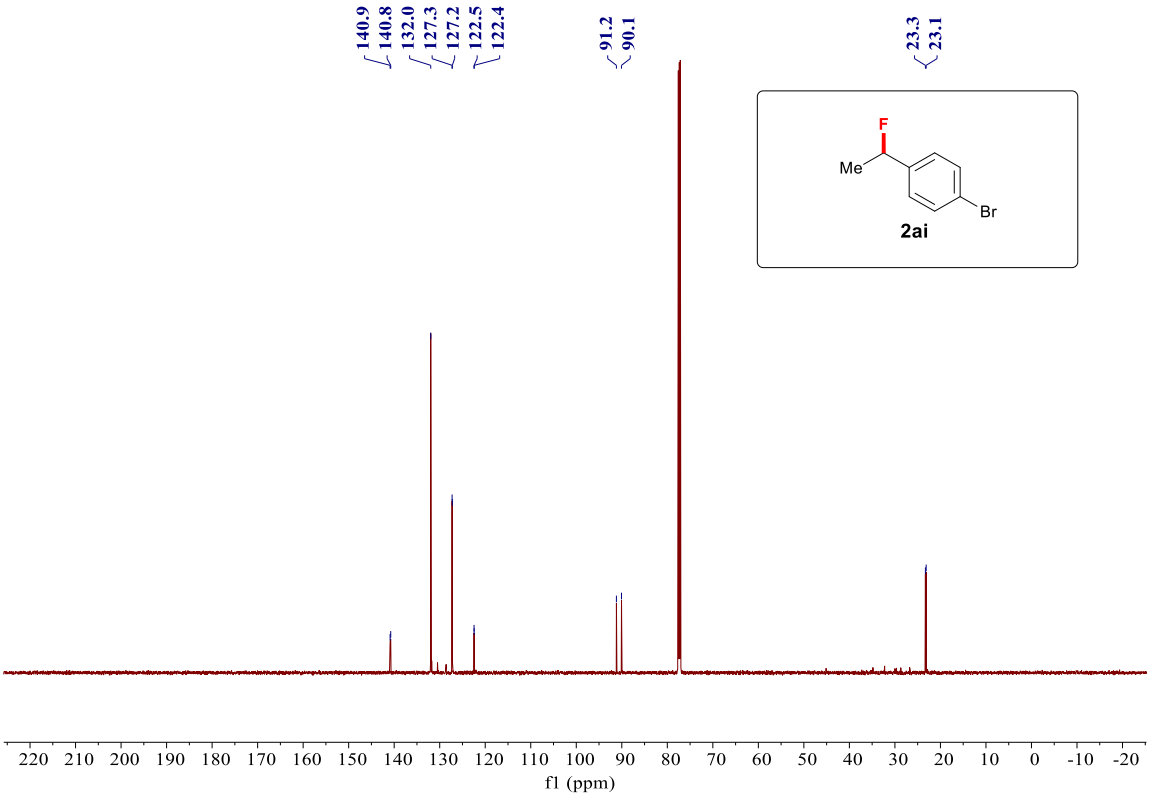
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of Compound **2ah**



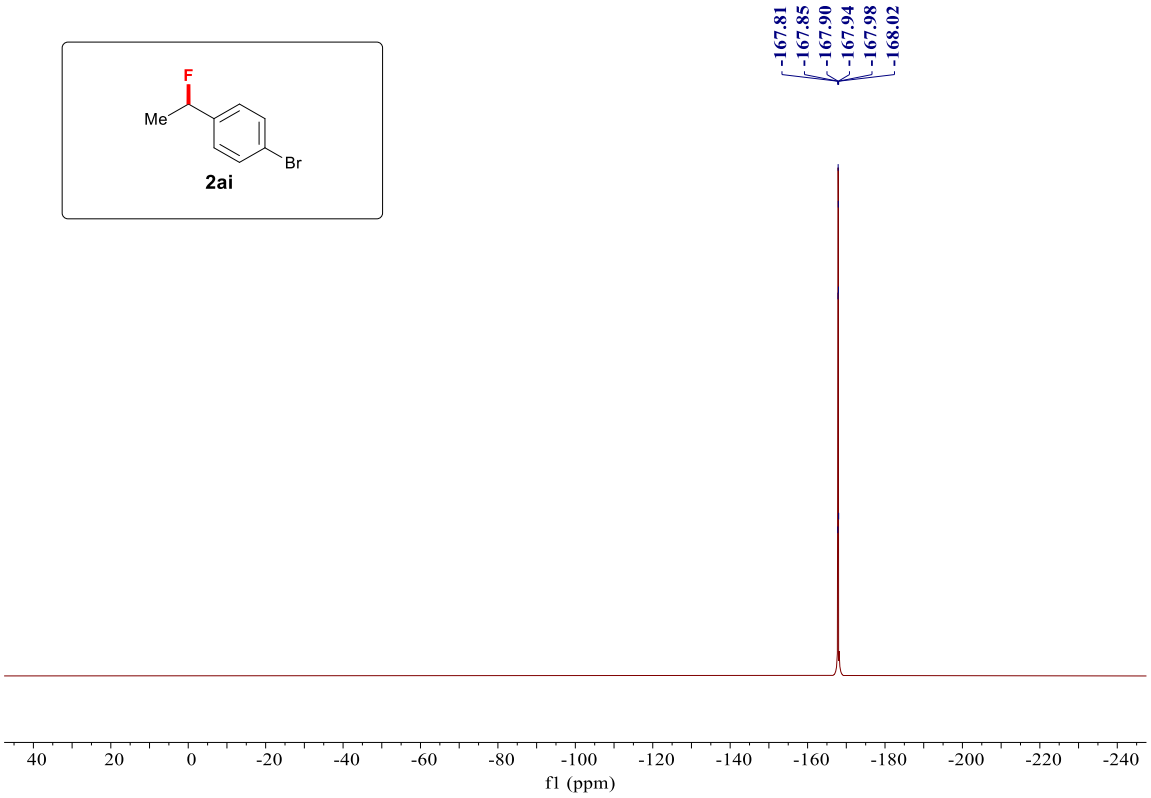
The Yield of **2ai** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



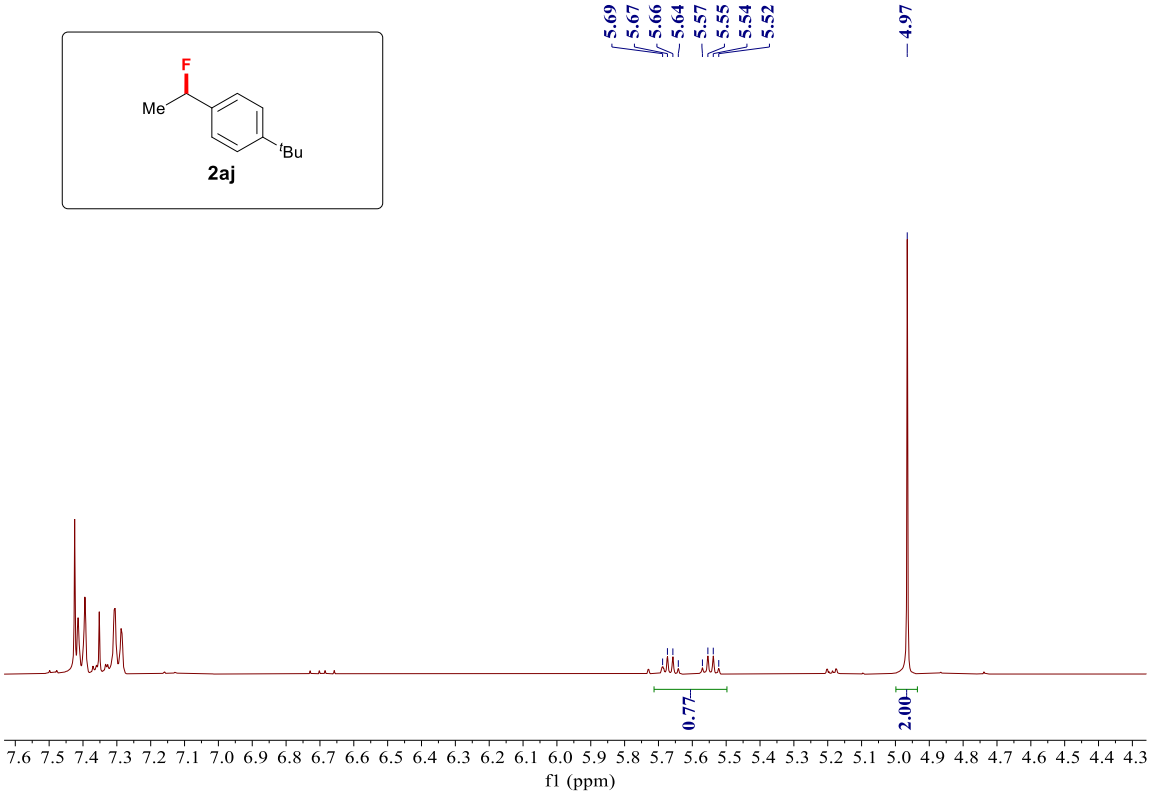
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **2ai**



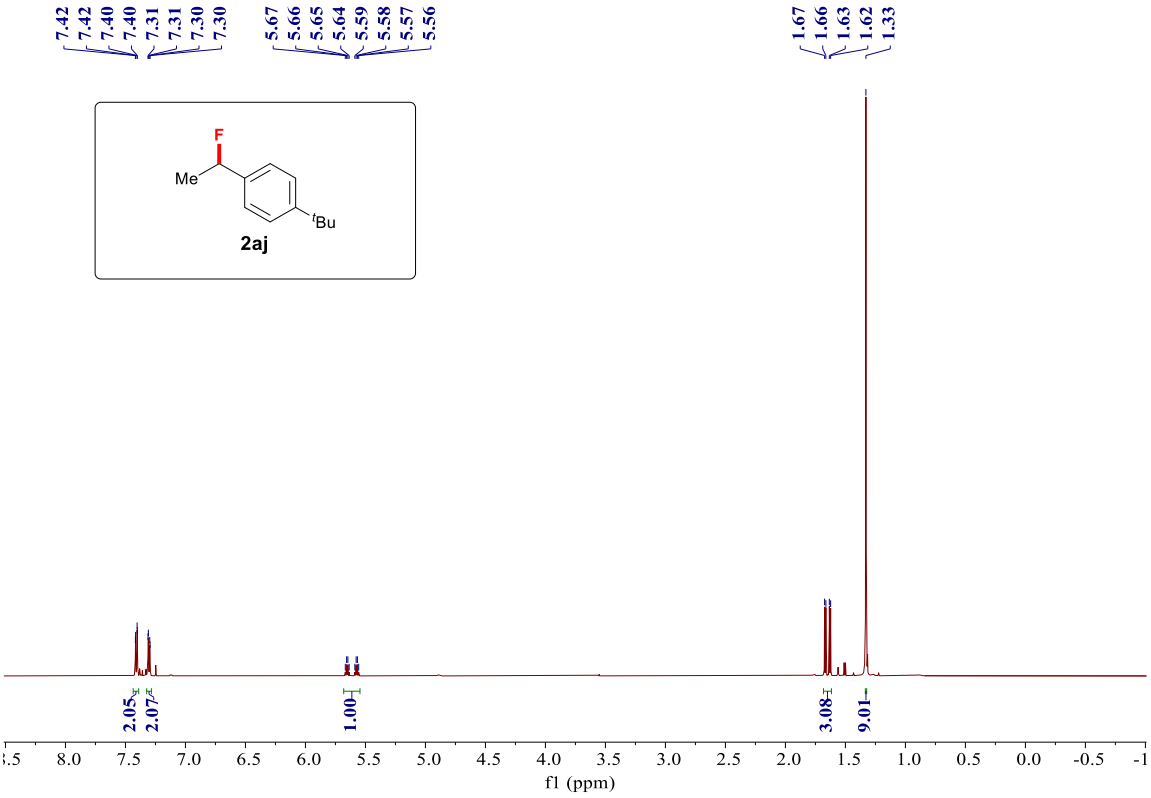
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of Compound **2ai**



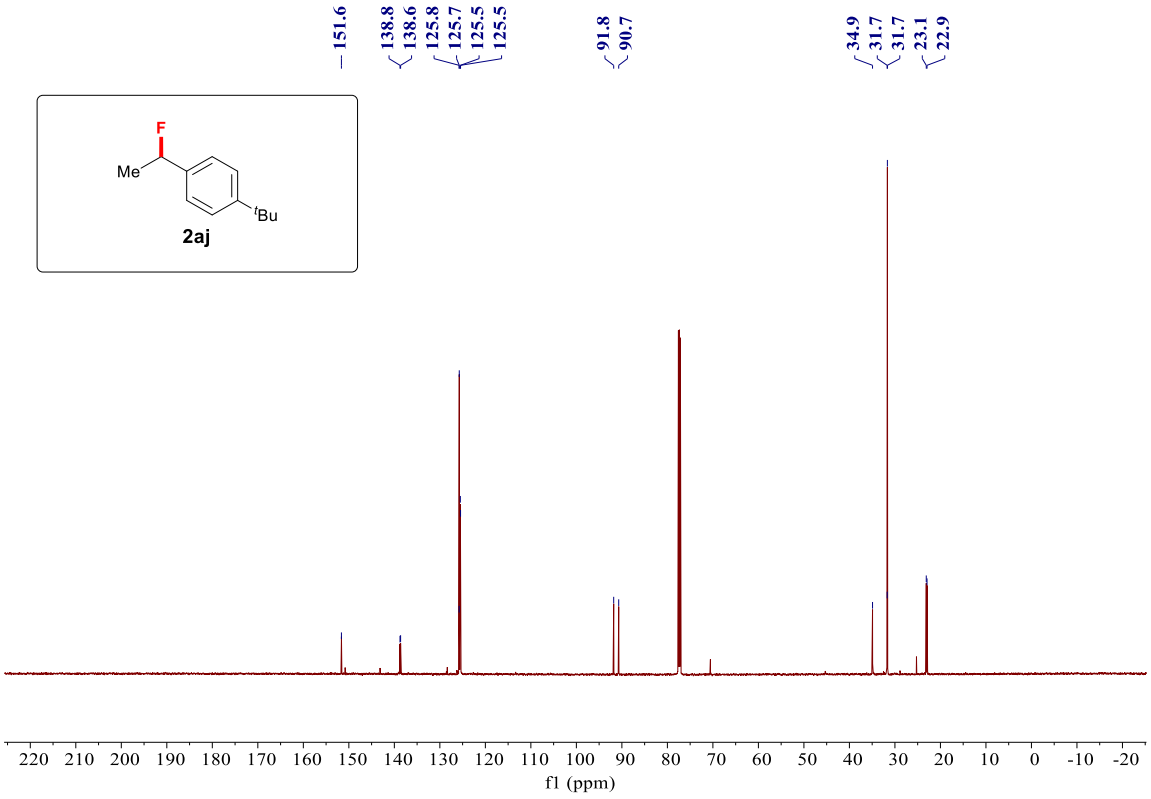
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of Compound **2ai**



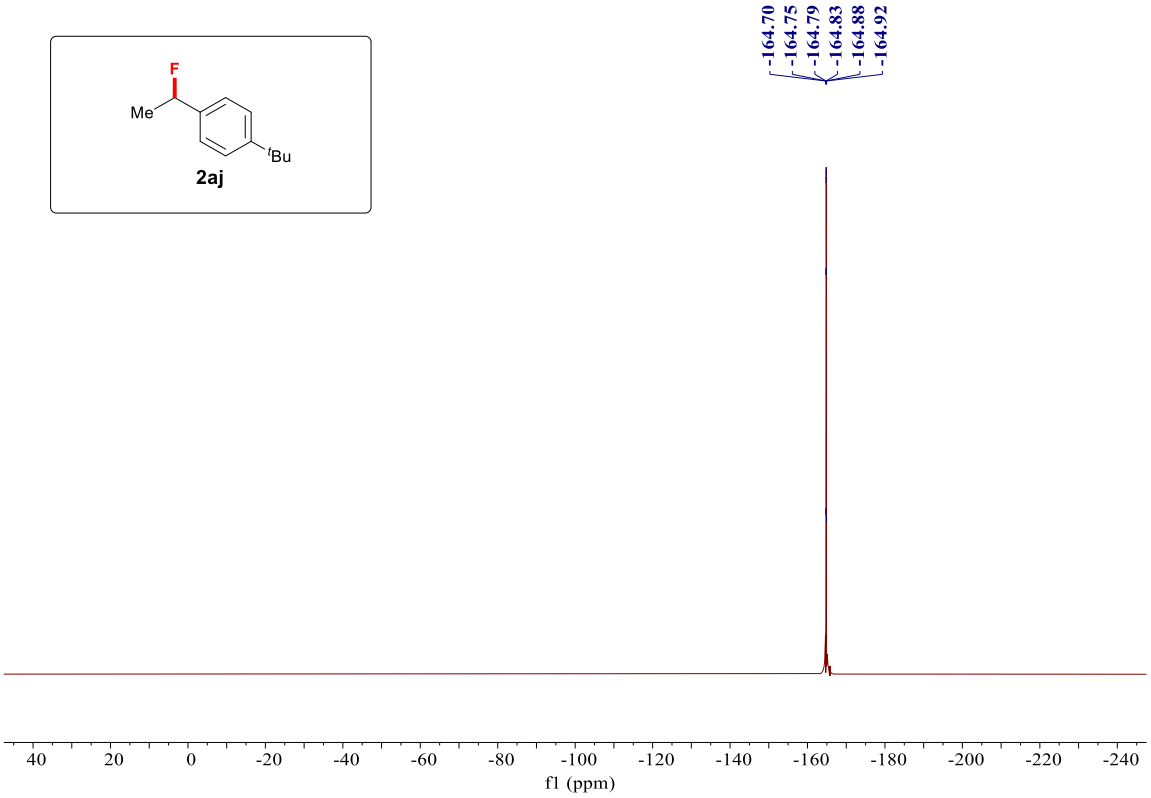
The Yield of **2aj** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



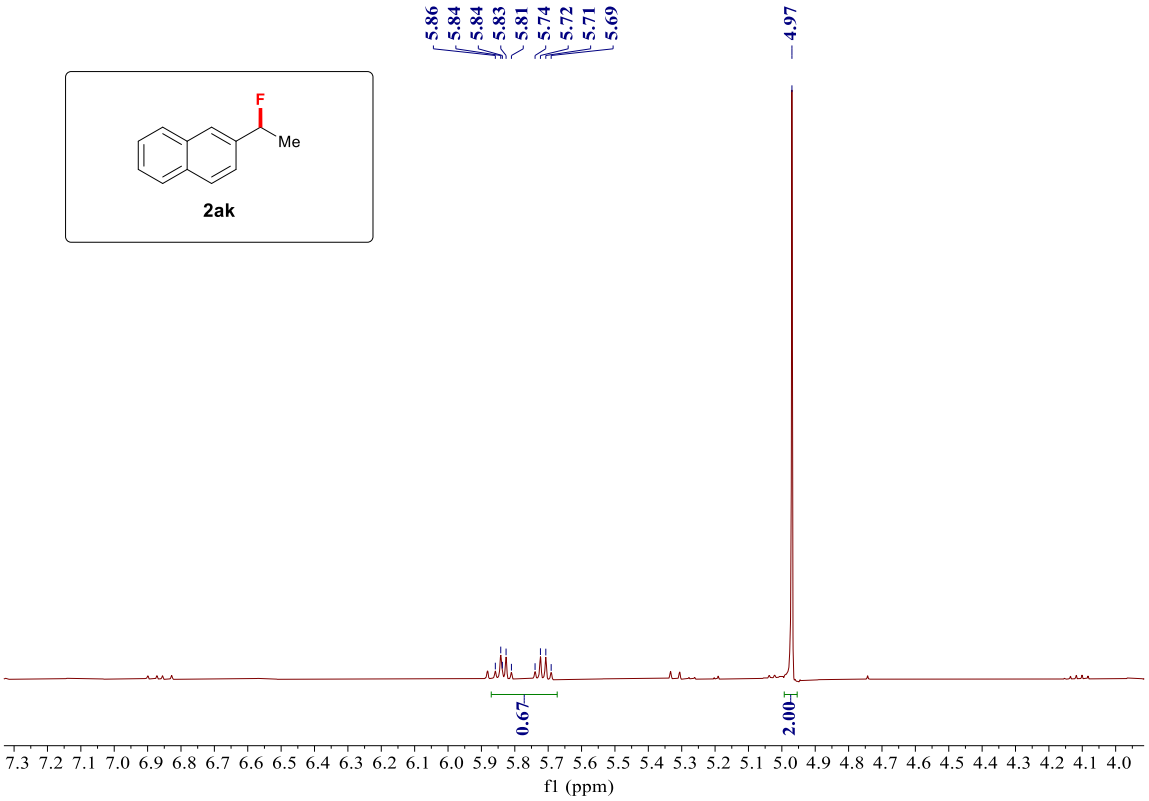
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **2aj**



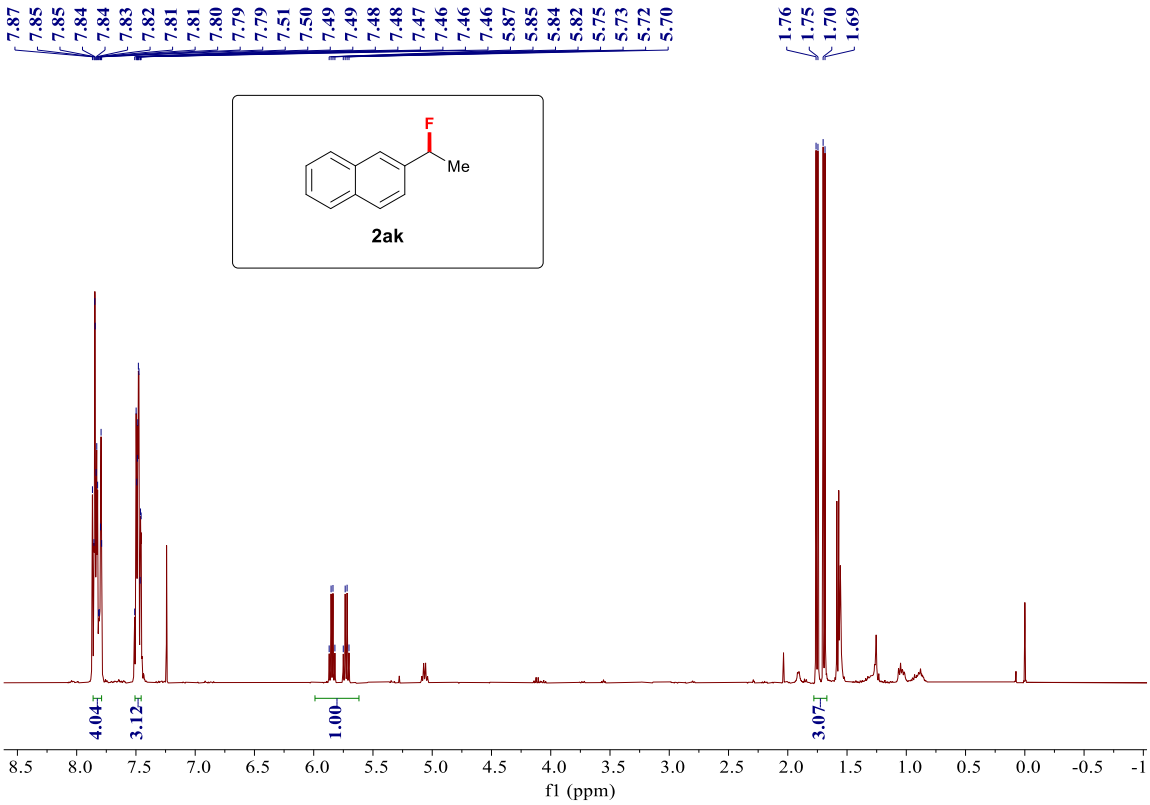
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of Compound **2aj**



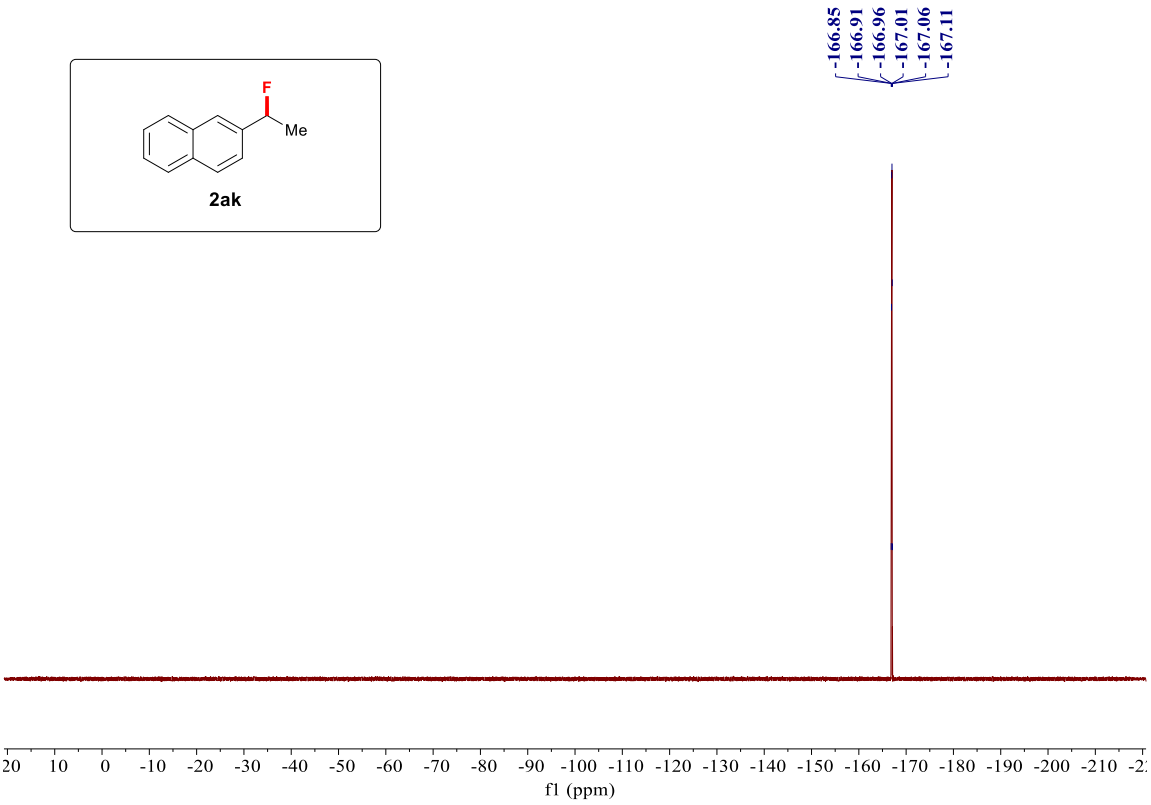
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of Compound **2aj**



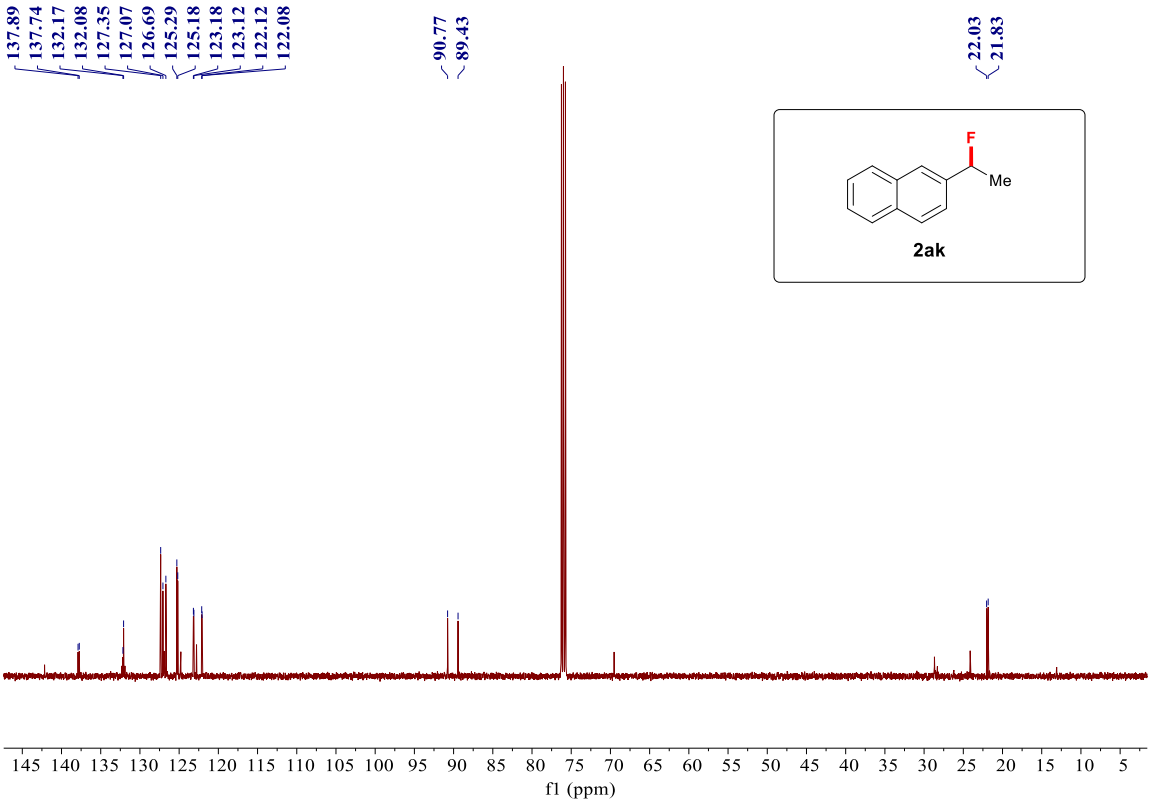
The Yield of **2ak** Based on ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **2ak**



^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **2ak**



^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **2ak**