Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

For

Cyanofluorination of vinyl ethers enabled by electron donor-acceptor complexes

Jia-Li Liu,[a] Ze-Fan Zhu[a] and Feng Liu*[a,b]

[a]Jiangsu Key Laboratory of Neuropsychiatric Diseases and Department of Medicinal Chemistry, College of Pharmaceutical Sciences, Soochow University, 199 Ren-Ai Road, Suzhou, Jiangsu 215123, People's Republic of China.

E-mail: fliu2@suda.edu.cn

[b]Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China.

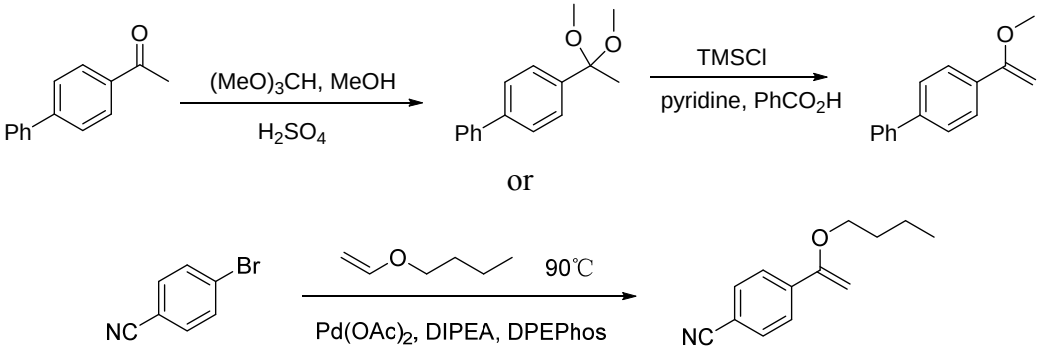
Table of Contents

1. General remarks

^{1}H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for ^{13}C NMR, 564 MHz for ^{19}F NMR) agilent NMR spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) or 77.16 ppm (for ^{13}C NMR). ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.00 ppm. HRMS was recorded on a GCT Premier^{TM} (CI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, ν_{max} in cm^{-1}. Melting points were measured using SGW, X-4B and values are uncorrected. All commercially available reagents and solvents were used as received unless otherwise specified. The substrates we are readily prepared according to known methods. (*Angew. Chem., Int. Ed.* **2011**, 50, 12605; *Org. Process. Res. Dev.* **2016**, 20, 1203; *J. Org. Chem.* **1995**, 60, 1880.)

2. Synthesis of vinyl ethers

Synthetic Scheme:



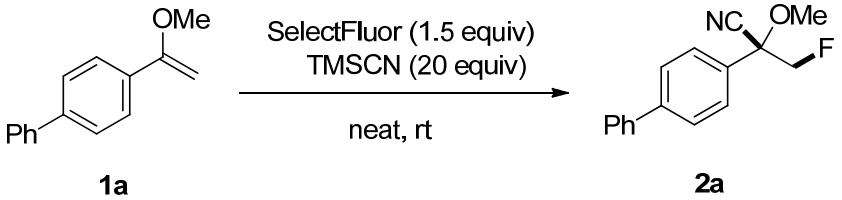
Typical synthetic procedures:

1: Ketone (0.98 g, 5 mmol), $(MeO)_3CH$ (0.8 g, 7.5 mmol), and H_2SO_4 (40 μL, 3.44 mmol) in MeOH (1 mL) were stirred at 40 ℃ for 2 h. Et_3N (9 mL) was added, and the solution was poured into Et_2O (10 mL), washed with saturated $NaHCO_3$ solution (40 mL × 2), and dried over $MgSO_4$. After evaporation of the solvent, the resulting crude material (1.09 g) was used for the next step without further purification.

Acetal (1.09 g, 4.5 mmol), pyridine (2 mL), TMSCl (3.59 g, 33 mmol), and $PhCO_2H$ (50 mg, 0.4 mmol) were heated at 65 ºC for 2 h. After cooling to the room temperature, 15% NaOH solution (2 mL) was added and the mixture was extracted with Et_2O (10 mL × 3). The combined organic phases were washed with saturated $NaHCO_3$ solution (10 mL × 2), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by flash column chromatography with petroleum ether on Al_2O_3 to afford 0.66 g (3.2 mmol, 70%) of **1a** as a colorless oil. (*Angew. Chem. Int. Ed.* **2011**, 50, 12605; *J. Org. Chem.* **1995**, 60, 1880.)

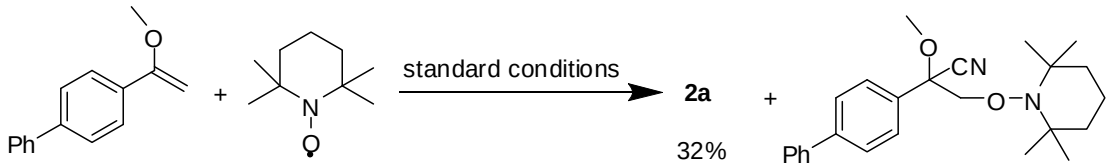
2: A solution of 4-bromobenzonitrile (0.91 g, 5 mmol), DIPEA (2 mL, 15 mmol), $Pd(OAc)_2$ (25 mg, 2 mol%), DPEDhos (65 mg, 2.4 mol%) and *n*-Butyl vinyl ether in *n*-BuOH was stirred at 95 °C for 1 h. The solution was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 200:1 to 100:1) to afford 0.54 g (2.7 mmol, 54%) of **1u** as a colorless oil. (*Org. Process. Res. Dev.* **2016**, 20, 1203.)

3. Typical experimental procedures



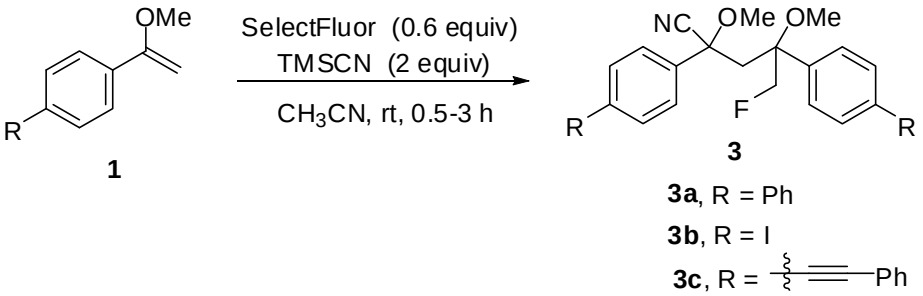
1a **2a**

To a mixture of vinyl ether **1a** (42 mg, 0.2 mmol) and TMS-CN (0.5 ml, 4.0 mmol) was stirred for 10 minutes and then added Selectfluor (106.3 mg, 0.3 mmol) at rt under argon atmosphere. The resulting mixture was stirred for 1.5 h. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 75:1) to give **2a** as a white solid (92% yield, 47 mg).



(2.0 equiv) **4,** 46%

Procedures for control experiment: (1) To a mixture of vinyl ether **1a** (42 mg, 0.2 mmol) and TMS-CN (0.5 mL, 4.0 mmol) was added Selectfluor (106.3 mg, 0.3 mmol) and TEMPO (62.5 mg, 0.4 mmol) at rt under argon atmosphere. The resulting mixture was stirred for 8 h. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 150:1 to 75:1) to give **2a** (32% yield, 16 mg) and **4** as a white solid (46% yield, 36 mg).



Procedures for synthesis of dimerized products: To a solution of vinyl ether **1** (0.2 mmol) and TMS-CN (53 μl, 0.4 mmol) in CH_3CN (2 mL) was added Selectfluor (43 mg, 0.12 mmol) at rt under argon atmosphere. The resulting mixture was stirred for 3 h. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 50:1) to give **3a/b/c** as a white solid (the major isomer, ca. 50% yield). However, we can't isolate the other isomer from the resulting messy mixture.

2,4-Di([1,1'-biphenyl]-4-yl)-5-fluoro-2,4-dimethoxypentanenitrile (3a): One isomer; White solid; m.p. 54-56 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 8H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.41 (m, 6H), 7.40 – 7.34 (m, 2H), 4.99 (dd, *J* = 46.2, 10.2 Hz, 1H), 4.86 (dd, *J* = 48.0, 10.3 Hz, 1H), 3.24 (s, 3H), 3.16 (s, 3H), 2.83 (d, *J* = 15.1 Hz, 1H), 2.56 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.2, 141.1, 140.7, 140.1, 137.4 (d, J_{C-F} = 3.4 Hz), 136.6, 129.0, 128.9, 127.9, 127.54, 127.52, 127.25, 127.24, 127.20, 126.7, 117.1, 84.0 (d, J_{C-F} = 178.0 Hz), 79.0, 78.98 (d, J_{C-F} = 16.8 Hz), 53.5, 51.4, 49.5 (d, J_{C-F} = 4.2 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -226.67 (t, *J* = 47.1 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3028, 2935, 2831, 1481, 732; HRMS (CI) calcd $C_{31}H_{29}FNO_2$ $[M + H]^+$: 466.2182, found: 466.2180.

5-Fluoro-2,4-bis(4-iodophenyl)-2,4-dimethoxypentanenitrile (3b): One isomer; White solid; m.p. 69-71 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.66 (m, 4H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 4.92 – 4.62 (m, 2H), 3.17 (s, 3H), 3.08 (s, 3H), 2.61 (d, *J* = 15.1 Hz, 1H), 2.39 (d, *J* = 15.1 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2 (d, J_{C-F} = 3.6 Hz), 138.1, 137.7, 137.5, 129.0, 128.0, 116.5, 95.3, 94.3, 83.9 (d, J_{C-F} = 179.4 Hz), 78.8 (d, J_{C-F} = 17.1 Hz), 78.7, 53.6, 51.4 (d, J_{C-F} = 2.6 Hz), 49.0 (d, J_{C-F} = 4.4 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -226.38 (t, *J* = 47.1 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2929, 2831, 1483, 995, 814; HRMS (CI) calcd $C_{19}H_{19}FI_2NO_2$ $[M + H]^+$: 565.9489, found: 565.9476.

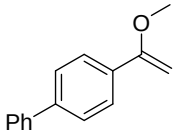
5-Fluoro-2,4-dimethoxy-2,4-bis(4-(phenylethynyl)phenyl)pentanenitrile (3c): One isomer; White solid; m.p. 124-126 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 8H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.33 (m, 6H), 4.89 (dd, *J* = 46.3, 10.3 Hz, 1H), 4.76 (dd, *J* = 47.7, 10.3 Hz, 1H), 3.20 (s, 3H), 3.12 (s, 3H), 2.70 (d, *J* = 15.2 Hz, 1H), 2.47 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.7 (d, J_{C-F} = 3.5 Hz), 137.7, 132.1, 131.81, 131.78, 128.7, 128.54, 128.48, 128.46, 127.2, 126.3, 124.6, 123.4, 123.3, 123.0, 116.7, 90.8, 90.1, 89.2, 88.5, 84.1 (d, J_{C-F} =

178.9 Hz), 79.0 (d, J_{C-F} = 17.0 Hz), 78.9, 53.6, 51.4 (d, J_{C-F} = 2.4 Hz), 49.1 (d, J = 4.2 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -226.38 (t, J = 47.0 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2956, 2828, 1504, 751, 683; HRMS (CI) calcd $C_{35}H_{29}FNO_2$ $[M + H]^+$: 514.2182, found: 514.2183.

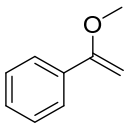
4. References for known products

Enyry	Reference	Compound
1	J.-L. Liu, Z.-F. Zhu; F. Liu. *Org. Lett.*, **2018** , 20, 720-723.	**4**

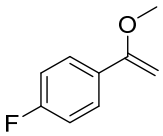
5. Characterization of the substrates and products



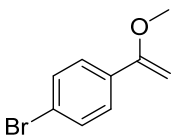
4-(1-Methoxyvinyl)-1,1'-biphenyl (1a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2H), 7.67 – 7.57 (m, 4H), 7.46 (t, J = 7.4 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 4.74 (d, J = 1.6 Hz, 1H), 4.28 (s, 1H), 3.79 (s, 3H).



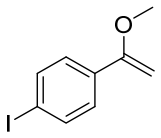
(1-Methoxyvinyl)benzene (1b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 6.7 Hz, 2H), 7.37 – 7.29 (m, 3H), 4.66 (d, J = 2.4 Hz, 1H), 4.22 (d, J = 2.3 Hz, 1H), 3.75 (s, 3H).



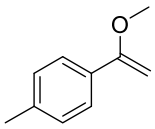
1-Fluoro-4-(1-methoxyvinyl)benzene (1c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.64 (d, J = 2.6 Hz, 1H), 4.23 (d, J = 2.6 Hz, 1H), 3.74 (s, 3H).



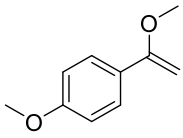
1-Bromo-4-(1-methoxyvinyl)benzene (1d): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 4H), 4.63 (d, J = 3.0 Hz, 1H), 4.21 (d, J = 3.0 Hz, 1H), 3.70 (s, 3H).



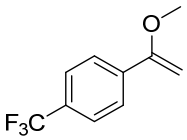
1-Iodo-4-(1-methoxyvinyl)benzene (1e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 4.66 (d, *J* = 2.7 Hz, 1H), 4.23 (d, *J* = 2.6 Hz, 1H), 3.73 (s, 3H).



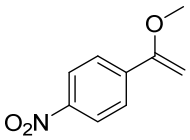
1-(1-Methoxyvinyl)-4-methylbenzene (1f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.66 (d, *J* = 2.2 Hz, 1H), 4.21 (d, *J* = 2.1 Hz, 1H), 3.77 (s, 3H), 2.39 (s, 3H).



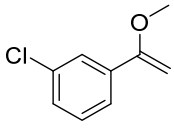
1-Methoxy-4-(1-methoxyvinyl)benzene (1g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.55 (d, *J* = 2.4 Hz, 1H), 4.14 (d, *J* = 2.3 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H).



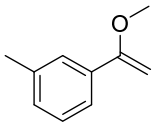
1-(1-Methoxyvinyl)-4-(trifluoromethyl)benzene (1h): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 4.76 (d, *J* = 3.1 Hz, 1H), 4.34 (d, *J* = 3.1 Hz, 1H), 3.77 (s, 3H).



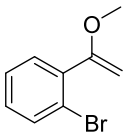
1-(1-Methoxyvinyl)-4-nitrobenzene (1i): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H), 4.83 (d, *J* = 3.4 Hz, 1H), 4.42 (d, *J* = 3.4 Hz, 1H), 3.77 (s, 3H).



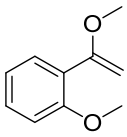
1-Chloro-3-(1-methoxyvinyl)benzene (1j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.49 (d, *J* = 6.8 Hz, 1H), 7.31 – 7.22 (m, 2H), 4.67 (d, *J* = 2.7 Hz, 1H), 4.25 (d, *J* = 2.7 Hz, 1H), 3.73 (s, 3H).



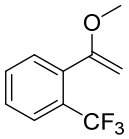
1-(1-Methoxyvinyl)-3-methylbenzene (1k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.34 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 6.7 Hz, 1H), 4.63 (s, 1H), 4.19 (s, 1H), 3.73 (s, 3H), 2.35 (s, 3H).



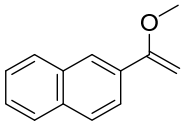
1-Bromo-2-(1-methoxyvinyl)benzene (1l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 4.41 (s, 1H), 4.31 (s, 1H), 3.73 (s, 3H).



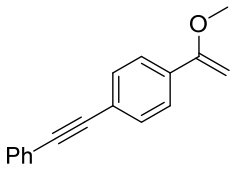
1-Methoxy-2-(1-methoxyvinyl)benzene (1m): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 11.4, 4.2 Hz, 1H), 7.05 – 6.87 (m, 2H), 4.66 (d, *J* = 1.6 Hz, 1H), 4.46 (d, *J* = 1.4 Hz, 1H), 3.87 (s, 3H), 3.74 (s, 3H).



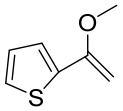
1-(1-Methoxyvinyl)-2-(trifluoromethyl)benzene (1n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.40 (m, 3H), 4.36 (s, 1H), 4.28 (d, *J* = 1.9 Hz, 1H), 3.72 (s, 3H).



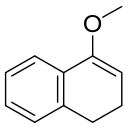
2-(1-Methoxyvinyl)naphthalene (1o): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.93 – 7.87 (m, 1H), 7.86 – 7.80 (m, 2H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.54 – 7.42 (m, 2H), 4.86 (d, *J* = 2.1 Hz, 1H), 4.37 (d, *J* = 2.1 Hz, 1H), 3.84 (s, 3H).



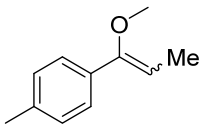
1-(1-Methoxyvinyl)-4-(phenylethynyl)benzene (1p): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.2 Hz, 2H), 7.60 – 7.48 (m, 4H), 7.43 – 7.30 (m, 3H), 4.73 (d, *J* = 2.6 Hz, 1H), 4.29 (d, *J* = 2.5 Hz, 1H), 3.77 (s, 3H).



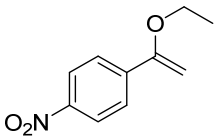
2-(1-Methoxyvinyl)thiophene (1q): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 6.99 – 6.93 (m, 1H), 4.63 (d, *J* = 2.8 Hz, 1H), 4.16 (d, *J* = 2.8 Hz, 1H), 3.71 (s, 3H).



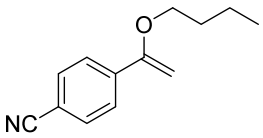
4-Methoxy-1,2-dihydronaphthalene (1r): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.1 Hz, 1H), 7.25 – 7.11 (m, 3H), 5.01 (t, *J* = 4.4 Hz, 1H), 3.73 (s, 3H), 2.78 (t, *J* = 7.8 Hz, 2H), 2.40 – 2.32 (m, 2H).



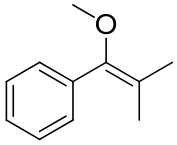
1-(1-Methoxyprop-1-en-1-yl)-4-methylbenzene (1s): Two isomers (1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.19 (m, 4H), 5.37 (q, *J* = 6.8 Hz, 1H)/4.82 (q, *J* = 7.0 Hz, 1H), 3.66 (s, 3H)/3.58 (s, 3H), 2.40 (s, 3H)/2.39 (s, 3H), 1.83 (d, *J* = 6.9 Hz, 3H)/1.74 (d, *J* = 7.0 Hz, 3H).



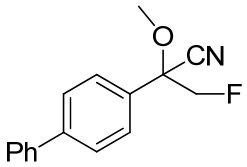
1-(1-Ethoxyvinyl)-4-nitrobenzene (1t): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 4.81 (s, 1H), 4.39 (s, 1H), 3.94 (q, *J* = 6.8 Hz, 2H), 1.44 (t, *J* = 6.8 Hz, 3H).



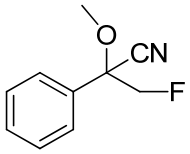
4-(1-Butoxyvinyl)benzonitrile (1u): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 4.75 (d, *J* = 2.8 Hz, 1H), 4.35 (d, *J* = 2.8 Hz, 1H), 3.86 (t, *J* = 6.3 Hz, 2H), 1.89 – 1.68 (m, 2H), 1.55 – 1.45 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).



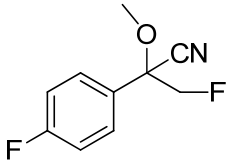
(1-Methoxy-2-methylprop-1-en-1-yl)benzene (1v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.14 (m, 5H), 3.23 (s, 3H), 1.77 (s, 3H), 1.59 (s, 3H).



2-([1,1'-Biphenyl]-4-yl)-3-fluoro-2-methoxypropanenitrile (2a): White solid; m.p. 55-57 ℃; 92% yield (47 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.67 – 7.57 (m, 4H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 4.65 (dd, *J* = 47.2, 9.6 Hz, 1H), 4.50 (dd, *J* = 46.6, 9.6 Hz, 1H), 3.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.4, 139.9, 131.1 (d, J_{C-F} = 2.4 Hz), 129.1, 128.1, 128.0, 127.3, 127.1, 116.1 (d, J_{C-F} = 2.2 Hz), 86.2 (d, J_{C-F} = 190.8 Hz), 80.90 (d, J_{C-F} = 18.8 Hz), 54.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -217.58 (t, *J* = 46.8 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2959, 2834, 1480, 1049, 763; HRMS (CI) calcd $C_{16}H_{15}FNO$ $[M + H]^+$: 256.1138, found: 256.1135.

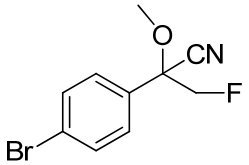


3-Fluoro-2-methoxy-2-phenylpropanenitrile (2b): Colorless oil; 70% yield (25 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.50 – 7.46 (m, 3H), 4.59 (dd, *J* = 47.2, 9.6 Hz, 1H), 4.44 (dd, *J* = 46.5, 9.6 Hz, 1H), 3.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 132.3, 130.4, 129.4, 126.6, 116.1 (d, J_{C-F} = 2.1 Hz), 86.2 (d, J_{C-F} = 190.8 Hz), 81.1 (d, J_{C-F} = 18.8 Hz), 54.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -217.58 (t, *J* = 46.8 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2962, 2837, 1447, 1049, 695; HRMS (CI) calcd $C_{10}H_{10}FNO$ $[M]^+$: 179.0746, found: 179.0743.

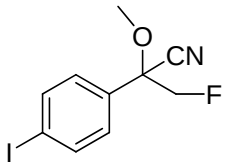


3-Fluoro-2-(4-fluorophenyl)-2-methoxypropanenitrile (2c): Colorless oil; 82% yield (32 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.19 – 7.14 (m, 2H), 4.58 (dd, *J* = 47.1, 9.6 Hz, 1H), 4.43 (dd, *J* = 46.5, 9.6 Hz, 1H), 3.40 (s, 3H); ^{13}C

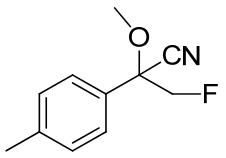
NMR (150 MHz, $CDCl_3$) δ 163.8 (d, J_{C-F} = 250.4 Hz), 128.7 (d, J_{C-F} =8.6 Hz), 128.3 (t, J_{C-F} = 2.7 Hz), 116.5 (d, J_{C-F} = 22.1 Hz), 116.0 (d, J_{C-F} = 2.2 Hz), 86.1 (d, J_{C-F} = 190.7 Hz), 80.5 (d, J_{C-F} = 19.2 Hz), 54.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ -110.46 – -110.53 (m, 1F), -218.11 (t, J = 46.7 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2923, 2852, 1301, 1141, 1034; HRMS (CI) calcd $C_{10}H_{10}F_2NO$ $[M + H]^+$: 198.0730, found: 198.0731.



2-(4-Bromophenyl)-3-fluoro-2-methoxypropanenitrile (2d): Colorless oil; 93% yield (48 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 4.57 (dd, J = 47.0, 9.6 Hz, 1H), 4.42 (dd, J = 46.4, 9.6 Hz, 1H), 3.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 132.6, 131.6 (d, J_{C-F} = 2.1 Hz), 128.3, 124.8, 115.7 (d, J_{C-F} = 2.4 Hz), 85.9 (d, J_{C-F} = 190.8 Hz), 80.5 (d, J_{C-F} = 19.4 Hz), 54.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -218.48 (t, J = 46.8 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2959, 2837, 1486, 1049, 820; HRMS (CI) calcd $C_{10}H_{10}{}^{79}BrFNO$ $[M + H]^+$: 257.9930, found: 257.9927.

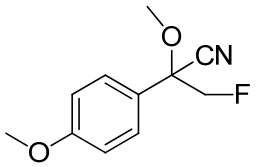


3-Fluoro-2-(4-iodophenyl)-2-methoxypropanenitrile (2e): Colorless oil; 85% yield (52 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 4.57 (dd, J = 47.0, 9.6 Hz, 1H), 4.42 (dd, J = 46.4, 9.6 Hz, 1H), 3.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5, 132.3 (d, J_{C-F} = 2.4 Hz), 128.4, 115.7 (d, J_{C-F} = 2.5 Hz), 96.6, 85.8 (d, J_{C-F} = 190.8 Hz), 80.6 (d, J_{C-F} = 19.4 Hz), 54.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -218.44 (t, J = 46.7 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2960, 2834, 1391, 1052, 813; HRMS (CI) calcd $C_{10}H_{10}FINO$ $[M + H]^+$: 305.9791, found: 305.9792.

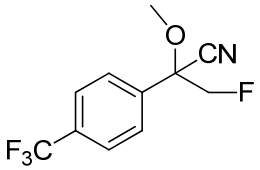


3-Fluoro-2-methoxy-2-(p-tolyl)propanenitrile (2f): Colorless oil; 87% yield (34 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 4.57 (dd, J = 47.3, 9.7 Hz, 1H), 4.41 (dd, J = 46.6, 9.6 Hz, 1H), 3.37 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.5, 130.0, 129.2 (d, J_{C-F} = 2.8 Hz), 126.5, 116.2 (d, J_{C-F} = 2.1 Hz), 86.2 (d, J_{C-F} = 190.6 Hz), 80.9 (d, J_{C-F} = 18.6 Hz), 54.3, 21.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -217.25 (t, J = 46.9 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2974, 2902, 1046, 639, 617; HRMS (CI) calcd $C_{11}H_{13}FNO$ $[M + H]^+$: 194.0981,

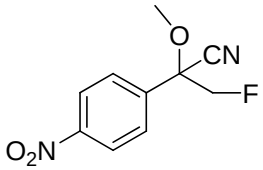
found: 194.0979.



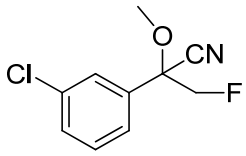
3-Fluoro-2-methoxy-2-(4-methoxyphenyl)propanenitrile (2g): Colorless oil; 91% yield (38 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 4.57 (dd, J = 47.3, 9.6 Hz, 1H), 4.40 (dd, J = 46.6, 9.6 Hz, 1H), 3.83 (s, 3H), 3.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 128.0, 123.9 (d, J_{C-F} = 3.1 Hz), 116.3 (d, J_{C-F} = 2.3 Hz), 114.7, 86.2 (d, J_{C-F} = 190.7 Hz), 80.7 (d, J_{C-F} = 18.7 Hz), 55.5, 54.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -216.99 (t, J = 47.0 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2962, 2840, 1513, 1251, 837; HRMS (CI) calcd $C_{11}H_{13}FNO_2$ $[M + H]^+$: 210.0930, found: 210.0934.



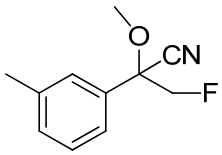
3-Fluoro-2-methoxy-2-(4-(trifluoromethyl)phenyl)propanenitrile (2h): Colorless oil; 70% yield (35 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 4.62 (dd, J = 46.9, 9.5 Hz, 1H), 4.47 (dd, J = 46.3, 9.5 Hz, 1H), 3.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.7, 132.7 (q, J_{C-F} = 32.9 Hz), 127.2, 126.4 (dd, J_{C-F} = 7.2, 3.5 Hz), 123.7 (q, J_{C-F} =269.2 Hz), 115.6 (d, J_{C-F} = 2.6 Hz), 85.9 (d, J_{C-F} = 190.8 Hz), 80.5 (d, J_{C-F} = 19.7 Hz), 54.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.02 (s, 3F), -219.29 (t, J = 46.6 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2941, 2837, 1319, 1123, 840; HRMS (CI) calcd $C_{11}H_9F_4NO$ $[M]^+$: 247.0620, found: 247.0627.



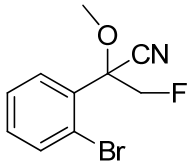
3-Fluoro-2-methoxy-2-(4-nitrophenyl)propanenitrile (2i): Colorless oil; 90% yield (40 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H), 4.64 (dd, J = 46.7, 9.5 Hz, 1H), 4.49 (dd, J = 46.3, 9.5 Hz, 1H), 3.46 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.2, 139.6 (d, J_{C-F} = 1.4 Hz), 127.9, 124.5, 115.3 (d, J_{C-F} = 2.8 Hz), 85.6 (d, J_{C-F} = 190.7 Hz), 80.2 (d, J_{C-F} = 20.3 Hz), 55.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ -220.20 (t, J = 46.4 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2923, 2849, 1519, 1034, 855; HRMS (CI) calcd $C_{10}H_{10}FN_2O_3$ $[M + H]^+$: 225.0675, found: 225.0672.



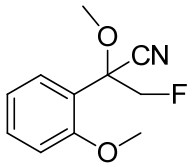
2-(3-Chlorophenyl)-3-fluoro-2-methoxypropanenitrile (2j): Colorless oil; 86% yield (37 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.47 – 7.36 (m, 3H), 4.59 (dd, *J* = 47.0, 9.6 Hz, 1H), 4.44 (dd, *J* = 46.4, 9.6 Hz, 1H), 3.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.6, 134.6, 130.7, 130.6, 126.7, 124.9, 115.6 (d, J_{C-F} = 2.4 Hz), 85.9 (d, J_{C-F} = 190.8 Hz), 80.4 (d, J_{C-F} = 19.4 Hz), 54.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -218.54 (t, *J* = 46.7 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2962, 2837, 1058, 790, 698; HRMS (CI) calcd $C_{10}H_{10}{}^{35}ClFNO$ $[M + H]^+$: 214.0435, found: 214.0439.



3-Fluoro-2-methoxy-2-(m-tolyl)propanenitrile (2k): Colorless oil; 90% yield (35 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 3H), 7.27 (d, *J* = 7.7 Hz, 1H), 4.58 (dd, *J* = 47.3, 9.6 Hz, 1H), 4.42 (dd, *J* = 46.5, 9.6 Hz, 1H), 3.39 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.3, 132.1 (d, J_{C-F} = 2.4 Hz), 131.1, 129.2, 127.1, 123.6, 116.2 (d, J_{C-F} = 2.1 Hz), 86.3 (d, J_{C-F} = 190.7 Hz), 81.1 (d, J_{C-F} = 18.6 Hz), 54.5, 21.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -217.33 (t, *J* = 46.9 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2959, 2831, 1049, 784, 698; HRMS (CI) calcd $C_{11}H_{12}FNO$ $[M]^+$: 193.0903, found: 193.0906.

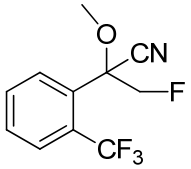


2-(2-Bromophenyl)-3-fluoro-2-methoxypropanenitrile (2l): Colorless oil; 89% yield (46 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 4.85 (dd, *J* = 46.3, 9.5 Hz, 1H), 4.79 (dd, *J* = 46.7, 9.5 Hz, 1H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 131.7, 130.8 (d, J_{C-F} = 0.6 Hz), 130.0 (d, J_{C-F} = 3.0 Hz), 128.2, 120.6, 115.1 (d, J_{C-F} = 3.0 Hz), 83.5 (d, J_{C-F} = 188.7 Hz), 81.6 (d, J_{C-F} = 19.7 Hz), 54.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -220.57 (t, *J* = 46.5 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2965, 2843, 1257, 1084, 614; HRMS (CI) calcd $C_{10}H_9{}^{79}BrFNO$ $[M]^+$: 256.9852, found: 256.9859.

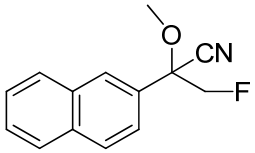


3-Fluoro-2-methoxy-2-(2-methoxyphenyl)propanenitrile (2m): Colorless oil; 80%

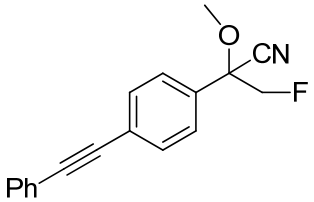
yield (33 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 8.2 Hz, 1H), 4.76 (dd, J = 46.9, 9.5 Hz, 1H), 4.55 (dd, J = 47.3, 9.5 Hz, 1H), 3.92 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.0, 131.5, 128.1, 121.2, 119.7 (d, J_{C-F} =3.4 Hz), 115.6 (d, J_{C-F} = 3.3 Hz), 112.3, 84.3 (d, J_{C-F} = 188.6 Hz), 78.3 (d, J_{C-F} = 18.8 Hz), 55.9, 54.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ -219.28 (t, J = 47.1 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2974, 2849, 1031, 1016, 766; HRMS (CI) calcd $C_{11}H_{12}FNO_2$ $[M]^+$: 209.0852, found: 209.0861.



3-Fluoro-2-methoxy-2-(2-(trifluoromethyl)phenyl)propanenitrile (2n): Colorless oil; 67% yield (33 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.68 (t, J = 7.7 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 4.79 (dd, J = 46.7, 9.6 Hz, 1H), 4.62 (dd, J = 46.2, 9.6 Hz, 1H), 3.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 132.6, 131.2, 130.9, 130.6, 129.2 (q, J_{C-F} = 6.7 Hz), 128.3 (q, J_{C-F} = 32.2 Hz), 123.7 (q, J_{C-F} = 273.4 Hz), 115.8 (d, J_{C-F} = 1.8 Hz), 85.2 (dq, J_{C-F} = 187.7, 4.0 Hz), 82.4 (d, J_{C-F} = 19.6 Hz), 55.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -56.05 (s, 3F), -217.96 (t, J = 46.5 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2971, 2843, 1129, 1037, 769; HRMS (CI) calcd $C_{11}H_9F_4NO$ $[M]^+$: 247.0620, found: 247.0628.

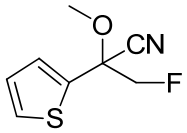


3-Fluoro-2-methoxy-2-(naphthalen-2-yl)propanenitrile (2o): Colorless oil; 88% yield (40 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.96 (d, J = 8.6 Hz, 1H), 7.95 – 7.92 (m, 1H), 7.92 – 7.88 (m, 1H), 7.61 – 7.57 (m, 2H), 7.57 – 7.54 (m, 1H), 4.71 (dd, J = 47.1, 9.7 Hz, 1H), 4.54 (dd, J = 46.4, 9.7 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.0, 133.0, 129.6, 128.5, 127.9, 127.7, 127.4, 127.3, 122.5, 116.2 (d, J_{C-F} = 2.2 Hz), 86.1 (d, J_{C-F} = 190.6 Hz), 81.3 (d, J_{C-F} = 18.9 Hz), 54.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -217.89 (t, J = 46.8 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2959, 2938, 1046, 817, 748; HRMS (CI) calcd $C_{14}H_{12}FNO$ $[M]^+$: 229.0903, found: 229.0914.

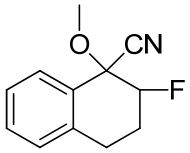


3-Fluoro-2-methoxy-2-(4-(phenylethynyl)phenyl)propanenitrile (2p): White solid;

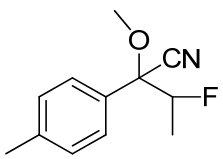
m.p. 73-75 ℃; 88% yield (49 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.58 – 7.52 (m, 4H), 7.40 – 7.35 (m, 3H), 4.60 (dd, J = 47.1, 9.6 Hz, 1H), 4.45 (dd, J = 46.4, 9.6 Hz, 1H), 3.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 132.4, 132.1 (d, J_{C-F} = 2.3 Hz), 131.8, 128.8, 128.5, 126.6, 125.7, 122.8, 115.9 (d, J_{C-F} = 2.3 Hz), 91.4, 88.2, 86.0 (d, J_{C-F} = 191.0 Hz), 80.8 (d, J_{C-F} = 19.1 Hz), 54.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -218.07 (t, J = 46.8 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2923, 2858, 1049, 840, 760; HRMS (CI) calcd $C_{18}H_{15}FNO$ $[M + H]^+$: 280.1138, found: 280.1142.



3-Fluoro-2-methoxy-2-(thiophen-2-yl)propanenitrile (2q): Colorless oil; 80% yield (30 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 5.1 Hz, 1H), 7.38 (d, J = 3.5 Hz, 1H), 7.08 (t, J = 4.3 Hz, 1H), 4.70 (dd, J = 46.9, 9.5 Hz, 1H), 4.55 (dd, J = 46.3, 9.5 Hz, 1H), 3.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.7 (d, J_{C-F} = 2.4 Hz), 129.3, 128.6, 127.3, 115.6 (d, J_{C-F} = 2.0 Hz), 86.1 (d, J_{C-F} = 191.3 Hz), 77.5, 54.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ -216.94 (t, J = 46.6 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2920, 2855, 1266, 1025, 801; HRMS (CI) calcd C_8H_9FNOS $[M + H]^+$: 186.0389, found: 186.0390.

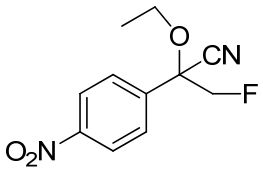


2-Fluoro-1-methoxy-1,2,3,4-tetrahydronaphthalene-1-carbonitrile (2r): Colorless oil; 85% yield (35 mg); Two isomers (1:1.1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, J = 7.6 Hz, 1H), 7.40 – 7.27 (m, 2H), 7.20 (d, J = 7.4 Hz, 1H), 5.20 – 4.98 (m, 1H), 3.51 (s, 1.4H)/3.49 (s, 1.6H), 3.18 – 2.77 (m, 2H), 2.54 – 2.10 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.8, 135.4, 130.4, 130.2, 129.8, 129.6 (d, J_{C-F} = 2.1 Hz), 129.42, 129.38, 129.3, 129.1, 126.6, 117.12, 117.08 (d, J_{C-F} = 3.6 Hz), 90.6 (d, J_{C-F} = 192.1 Hz), 90.3 (d, J_{C-F} = 183.1 Hz), 76.7 (d, J_{C-F} = 22.6 Hz), 76.5 (d, J_{C-F} = 18.4 Hz), 54.2 (d, J_{C-F} = 1.5 Hz), 54.1, 26.0 (d, J_{C-F} = 10.5 Hz), 24.3 (d, J_{C-F} = 6.5 Hz), 23.9 (d, J_{C-F} = 19.7 Hz), 22.9 (d, J_{C-F} = 19.5 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -186.06 – -186.39 (m), -188.80 – -189.13 (m); FT-IR (thin film, KBr): ν (cm^{-1}) 2962, 2840, 1450, 1063, 760; HRMS (CI) calcd $C_{12}H_{12}FNO$ $[M]^+$: 205.0903, found: 205.0913.

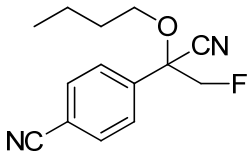


3-Fluoro-2-methoxy-2-(p-tolyl)butanenitrile (2s): Colorless oil; 92% yield (38 mg); Two isomers (1:1.2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, J = 8.1 Hz, 1H)/7.38 (d, J

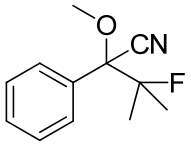
= 8.1 Hz, 1H), 7.26 (d, J = 7.3 Hz, 2H), 4.80 (dq, J = 47.3, 6.4 Hz, 0.45H)/4.69 (dq, J = 45.9, 6.2 Hz, 0.55H), 3.34 (s, 1.4H)/3.33 (s, 1.6H), 2.39 (s, 3H), 1.53 (dd, J = 24.1, 6.2 Hz, 1.6H)/1.20 (dd, J = 23.6, 6.4 Hz, 1.4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.3, 140.0, 130.6, 129.9, 129.73 (d, J_{C-F} = 2.3 Hz), 129.69, 126.9, 126.8, 116.3, 116.0 (d, J_{C-F} = 2.1 Hz), 92.6 (d, J_{C-F} = 187.9 Hz), 92.4 (d, J_{C-F} = 182.2 Hz), 85.1 (d, J_{C-F} = 18.5 Hz), 84.2 (d, J_{C-F} = 24.1 Hz), 54.4, 54.2, 21.2, 16.2 (d, J_{C-F} = 22.2 Hz), 16.0 (d, J_{C-F} = 22.5 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -177.51 – -177.78 (m), -179.96 – -180.25 (m);FT-IR (thin film, KBr): ν (cm^{-1}) 2926, 2858, 1084, 817, 608; HRMS (CI) calcd $C_{12}H_{14}FNO$ $[M]^+$: 207.1059, found: 207.1065.



2-Ethoxy-3-fluoro-2-(4-nitrophenyl)propanenitrile (2t): White solid; m.p. 84-86 ℃; 98% yield (47 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 4.64 (dd, J = 46.7, 9.3 Hz, 1H), 4.48 (dd, J = 46.2, 9.3 Hz, 1H), 3.79 (p, J = 7.0 Hz, 1H), 3.44 (p, J = 7.0 Hz, 1H), 1.31 (t, J = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.1, 140.4 (d, J_{C-F} = 1.3 Hz), 127.8, 124.4, 115.7 (d, J_{C-F} = 2.7 Hz), 85.7 (d, J_{C-F} = 190.5 Hz), 79.3 (d, J_{C-F} = 20.4 Hz), 63.7, 15.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ -220.10 (t, J = 46.5 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2920, 2855, 1513, 1049, 855; HRMS (CI) calcd $C_{11}H_{12}FN_2O_3$ $[M + H]^+$: 239.0832, found: 239.0841.



4-(1-Butoxy-1-cyano-2-fluoroethyl)benzonitrile (2u): Colorless oil; 80% yield (39 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 4.61 (dd, J = 46.8, 9.4 Hz, 1H), 4.45 (dd, J = 46.3, 9.4 Hz, 1H), 3.69 (dd, J = 14.7, 6.6 Hz, 1H), 3.35 (dd, J = 14.8, 6.6 Hz, 1H), 1.71 – 1.58 (m, 2H), 1.46 – 1.32 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.6, 133.0, 127.4, 117.9, 115.7 (d, J_{C-F} = 2.6 Hz), 114.3, 85.7 (d, J_{C-F} = 190.4 Hz), 79.4 (d, J_{C-F} = 20.2 Hz), 67.6, 31.4, 19.2, 13.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ -218.48 – -220.93 (m, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2965, 2878, 2227, 1049, 840; HRMS (CI) calcd $C_{14}H_{16}FN_2O$ $[M + H]^+$: 247.1247, found: 247.1248.

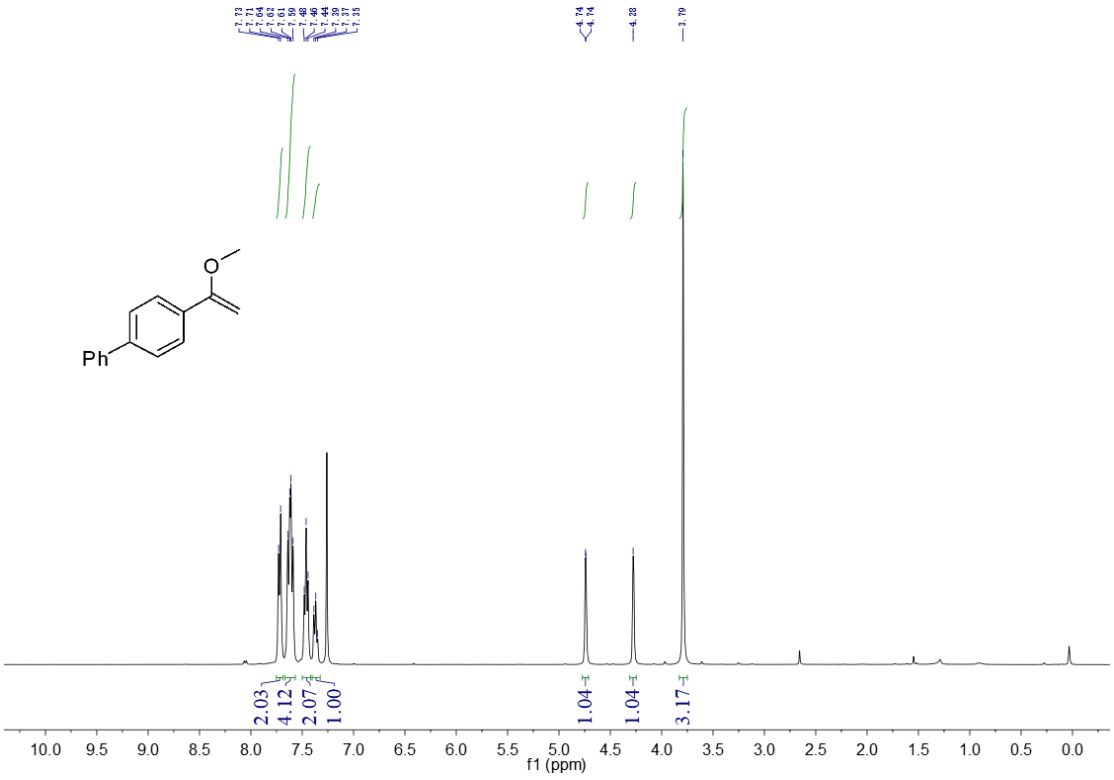


3-Fluoro-2-methoxy-3-methyl-2-phenylbutanenitrile (2v): Colorless oil; 81% yield

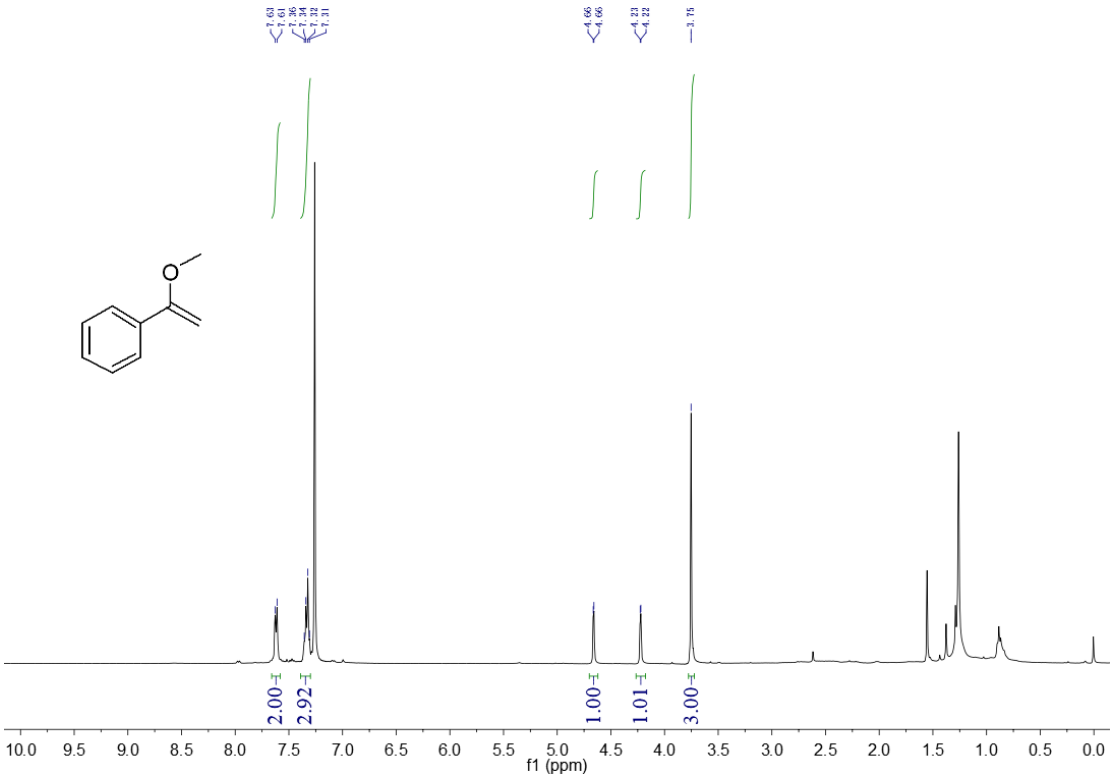
(33.6 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.46 – 7.42 (m, 3H), 3.43 (s, 3H), 1.52 (d, J = 21.6 Hz, 3H), 1.36 (d, J = 21.7 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 132.7, 129.7, 128.5, 127.9 (d, J_{C-F} = 1.0 Hz), 117.4 (d, J_{C-F} = 3.2 Hz), 96.6 (d, J_{C-F} = 183.4 Hz), 86.7 (d, J_{C-F} = 24.7 Hz), 55.1, 23.2 (d, J_{C-F} = 23.4 Hz), 22.5 (d, J_{C-F} = 23.4 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -147.03 – -147.31 (m, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2988, 2943, 1102, 751, 700; HRMS (ESI) calcd $C_{12}H_{14}FNNaO$ $[M + Na]^+$: 230.0952, found: 230.0946.

5. NMR Spectra for the substrates and products

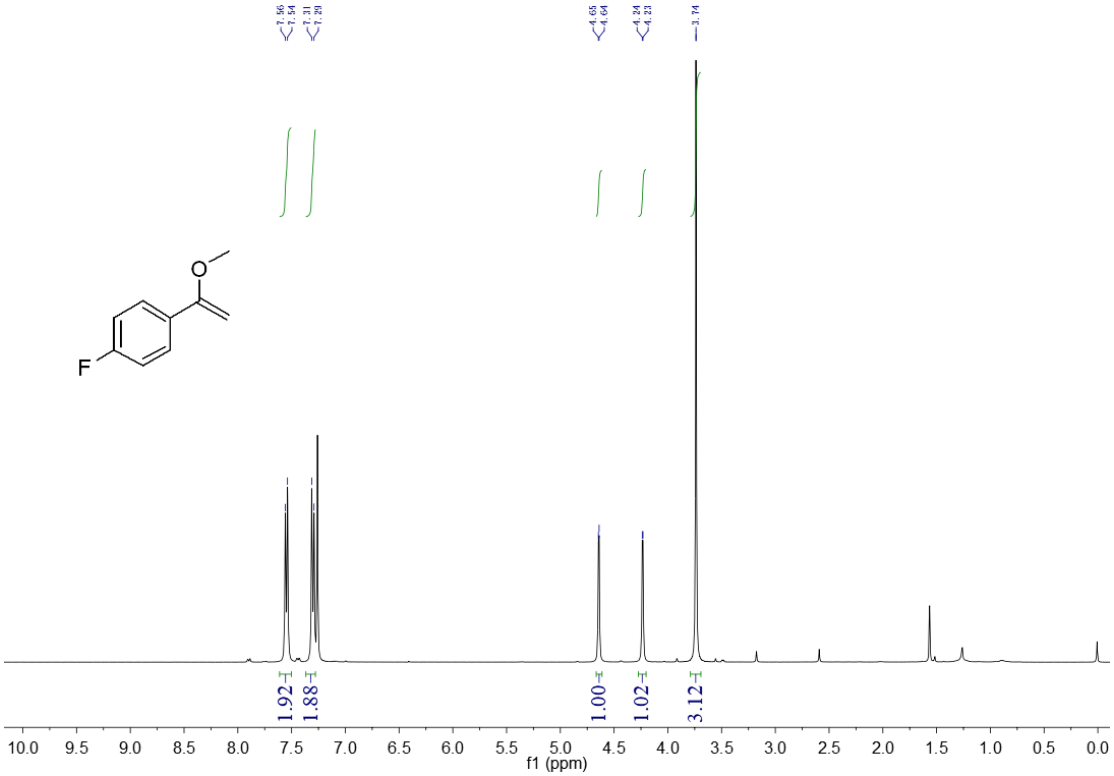
^{1}H NMR of **1a**



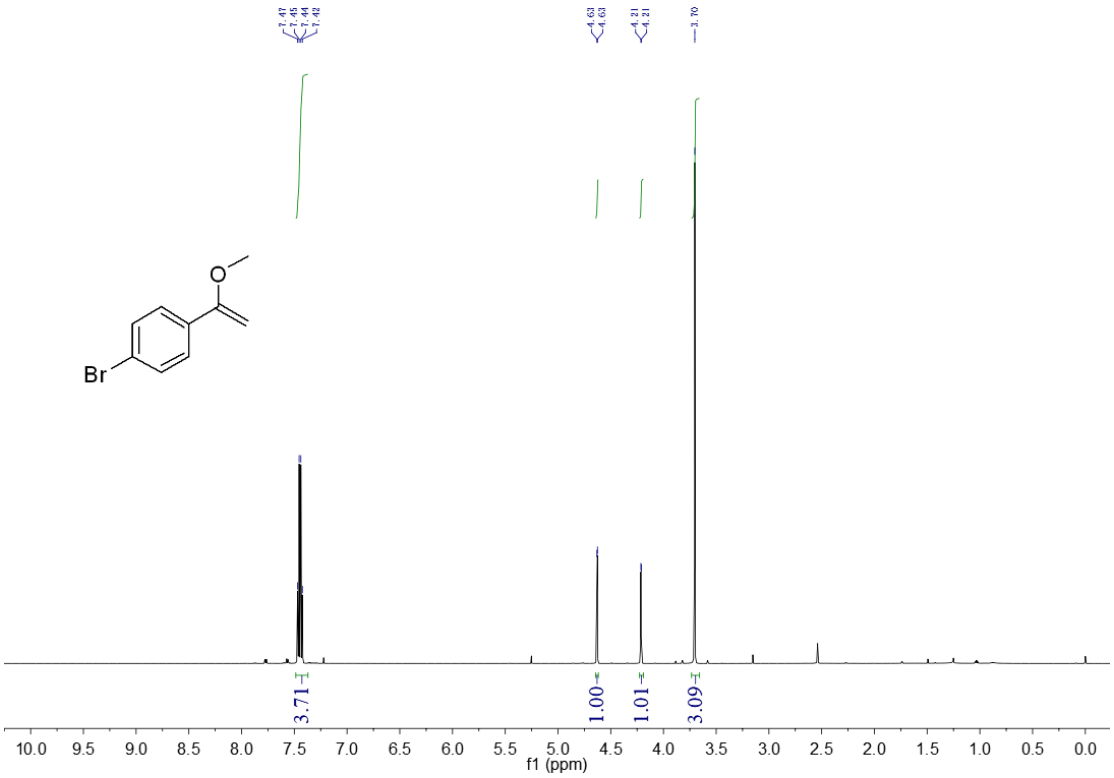
^{1}H NMR of **1b**



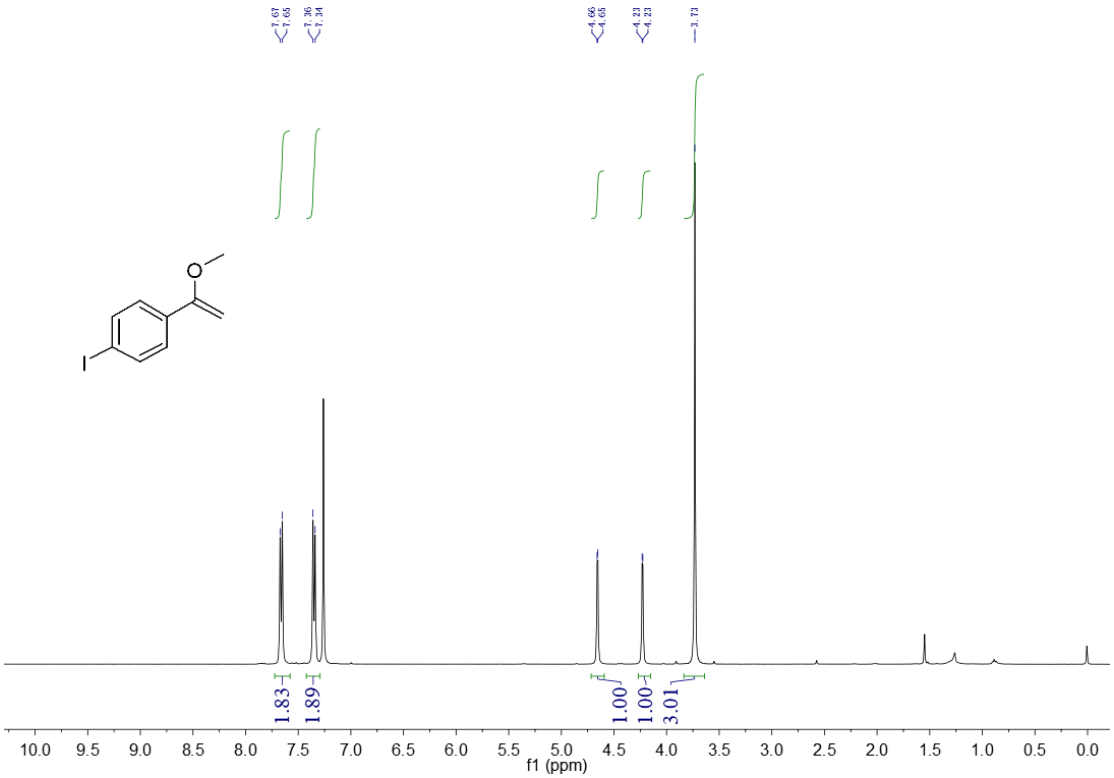
^{1}H NMR of **1c**



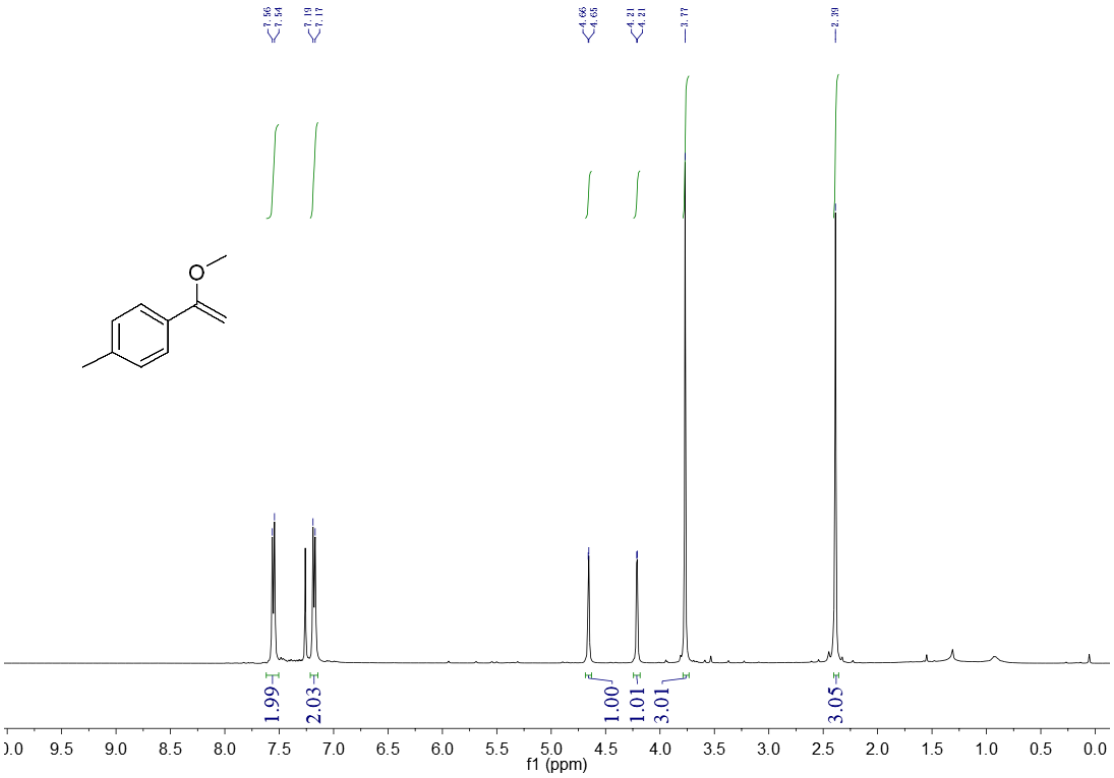
^{1}H NMR of **1d**



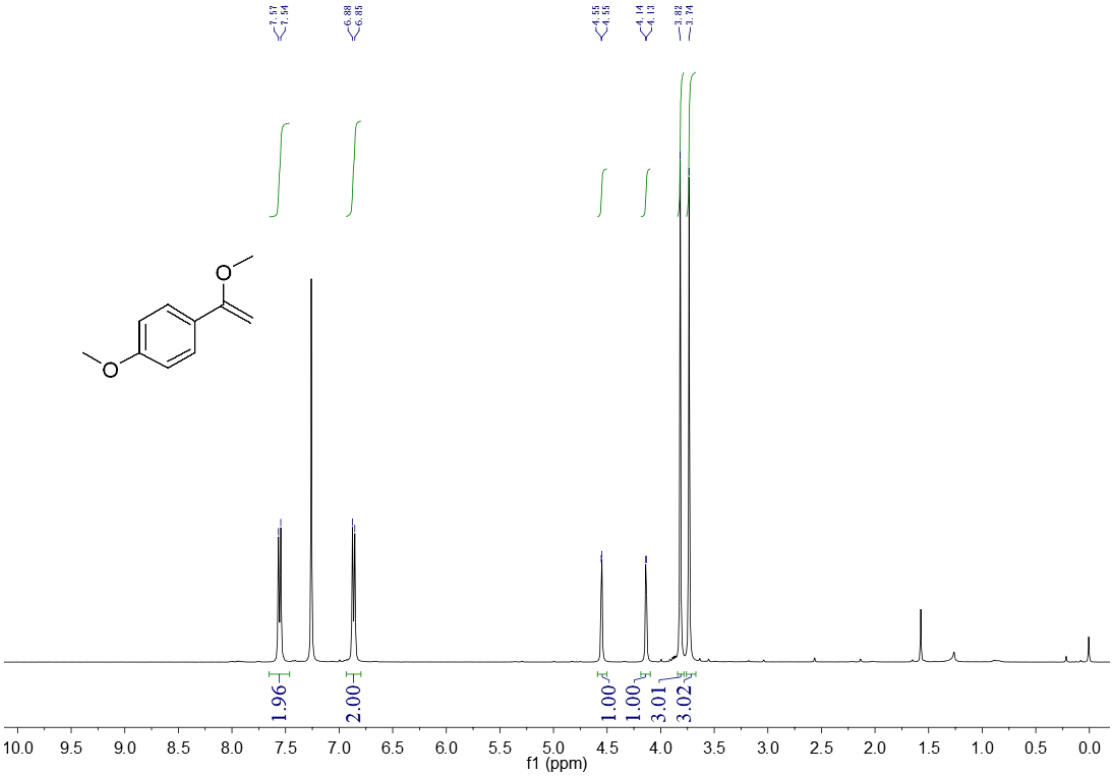
^{1}H NMR of **1e**



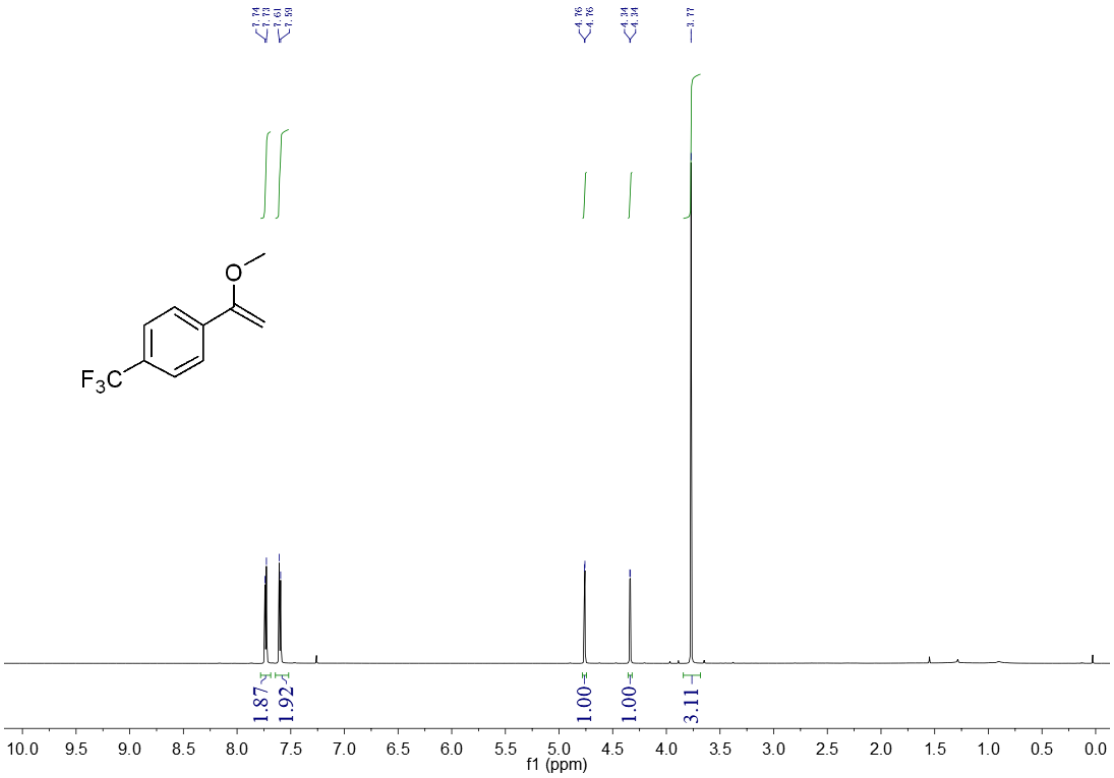
^{1}H NMR of **1f**



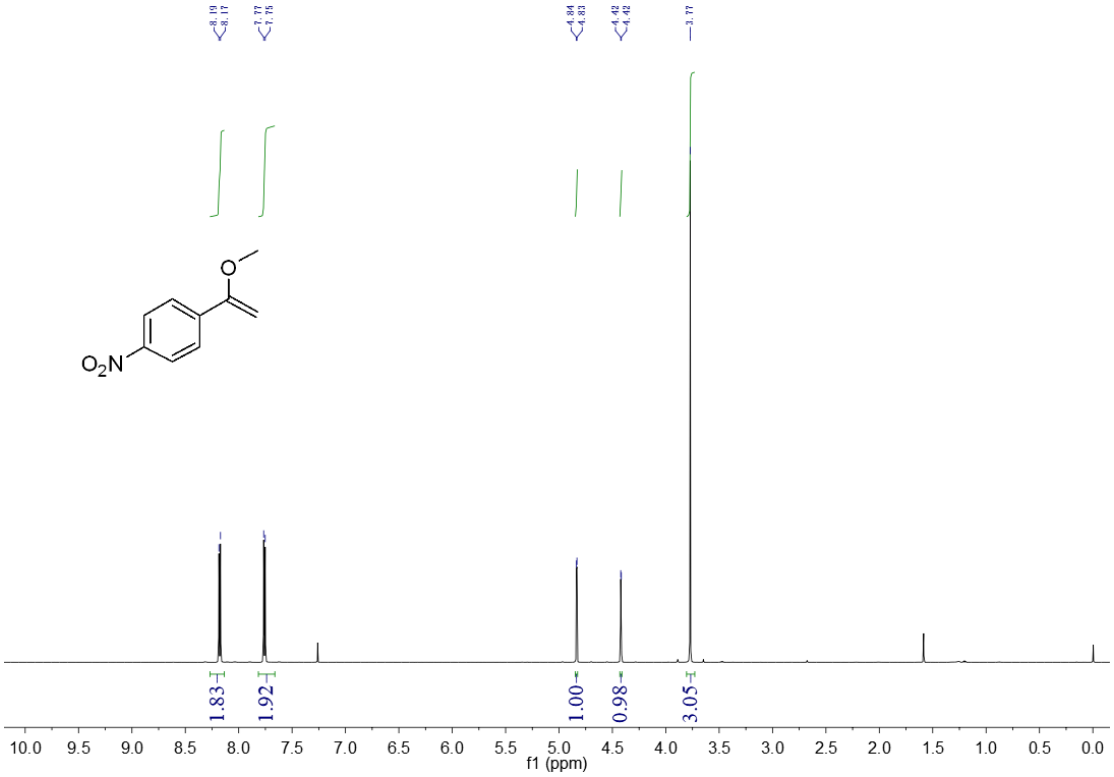
^{1}H NMR of **1g**



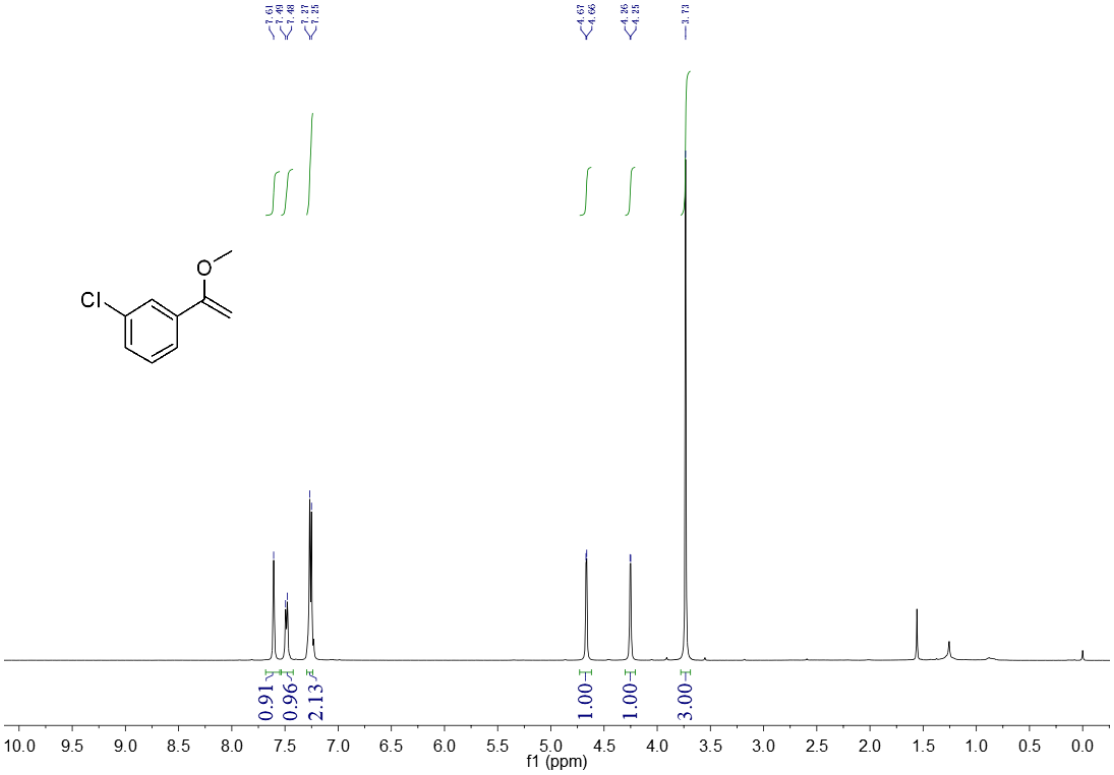
^{1}H NMR of **1h**



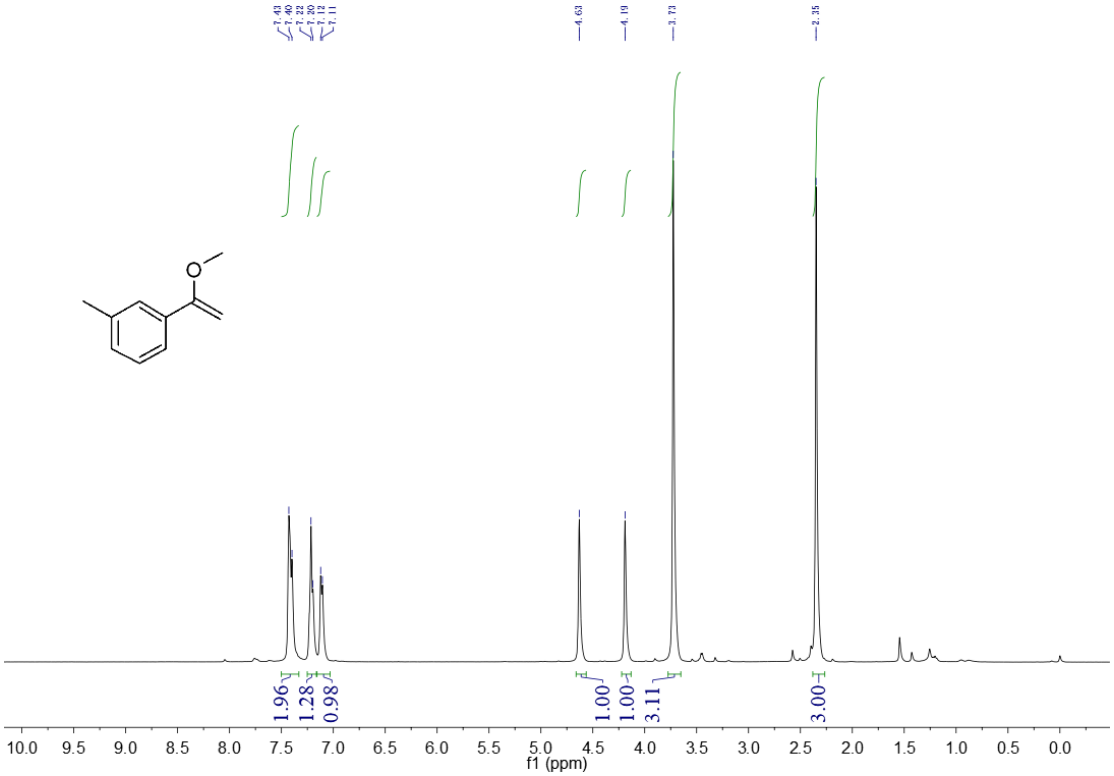
^{1}H NMR of **1i**



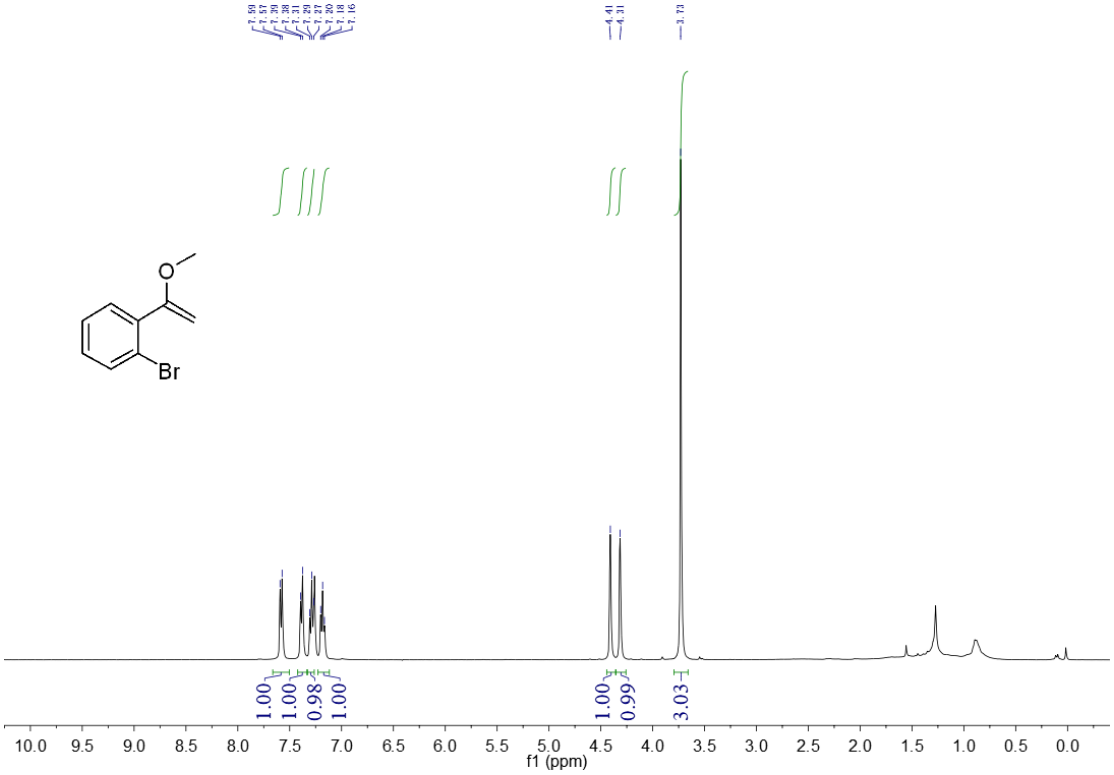
^{1}H NMR of **1j**



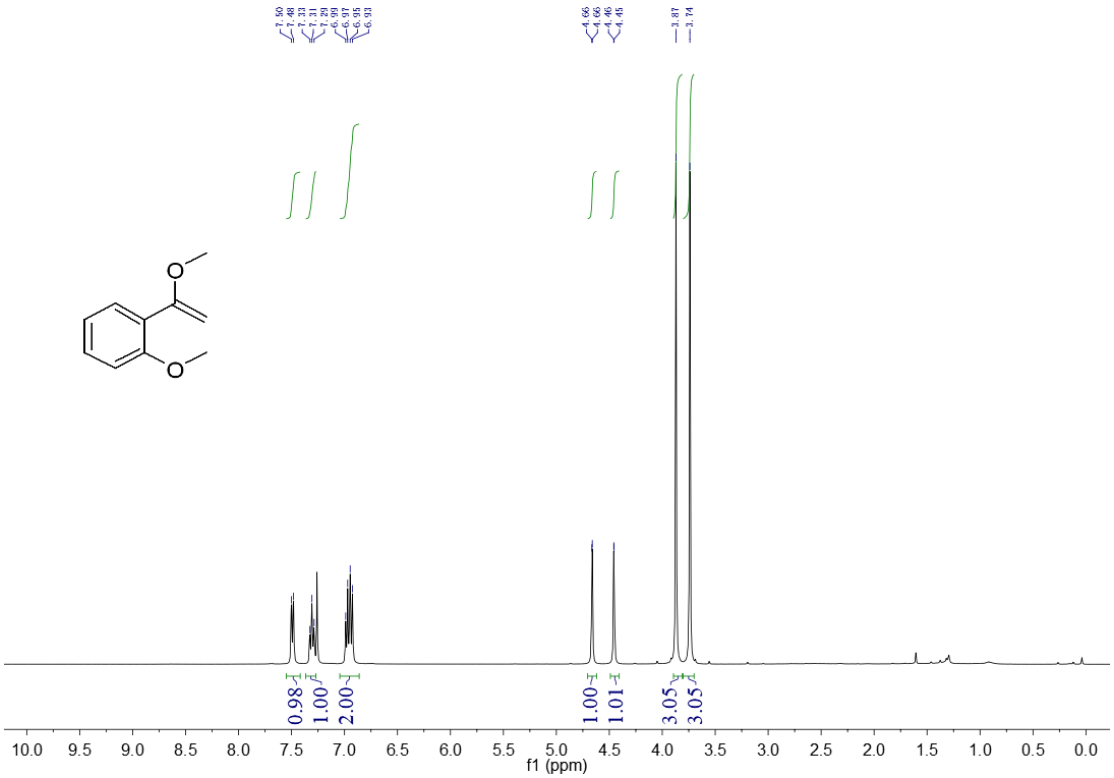
^{1}H NMR of **1k**



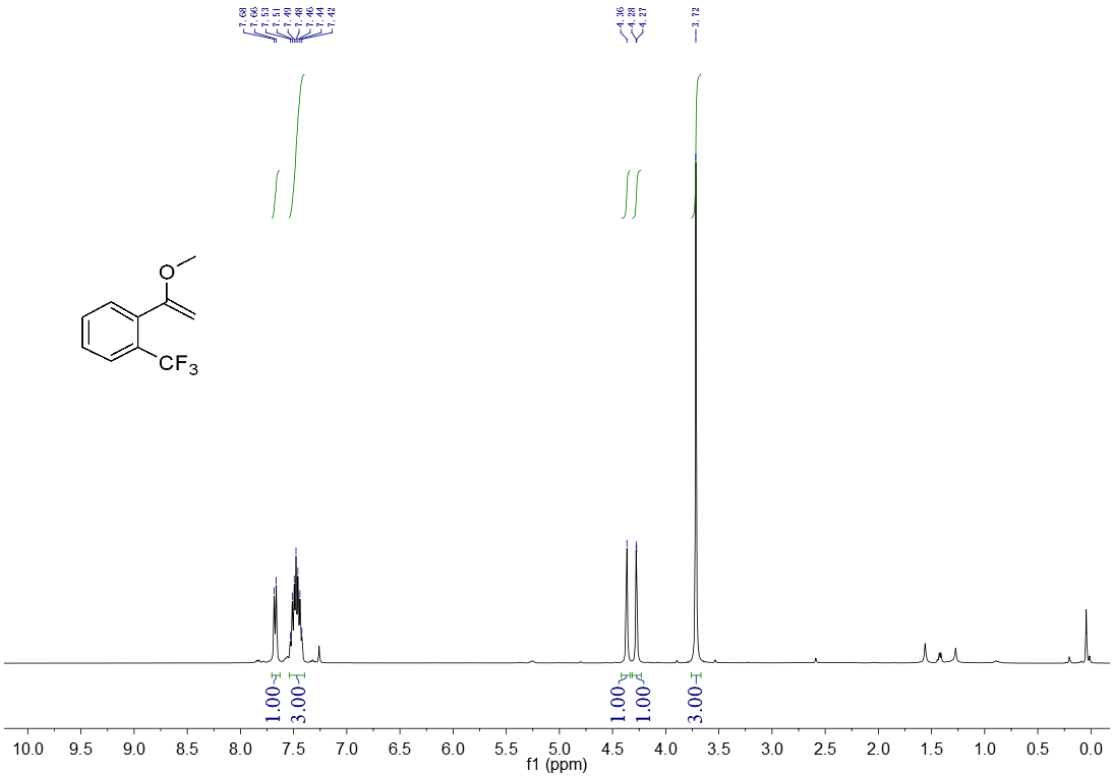
^{1}H NMR of **1l**



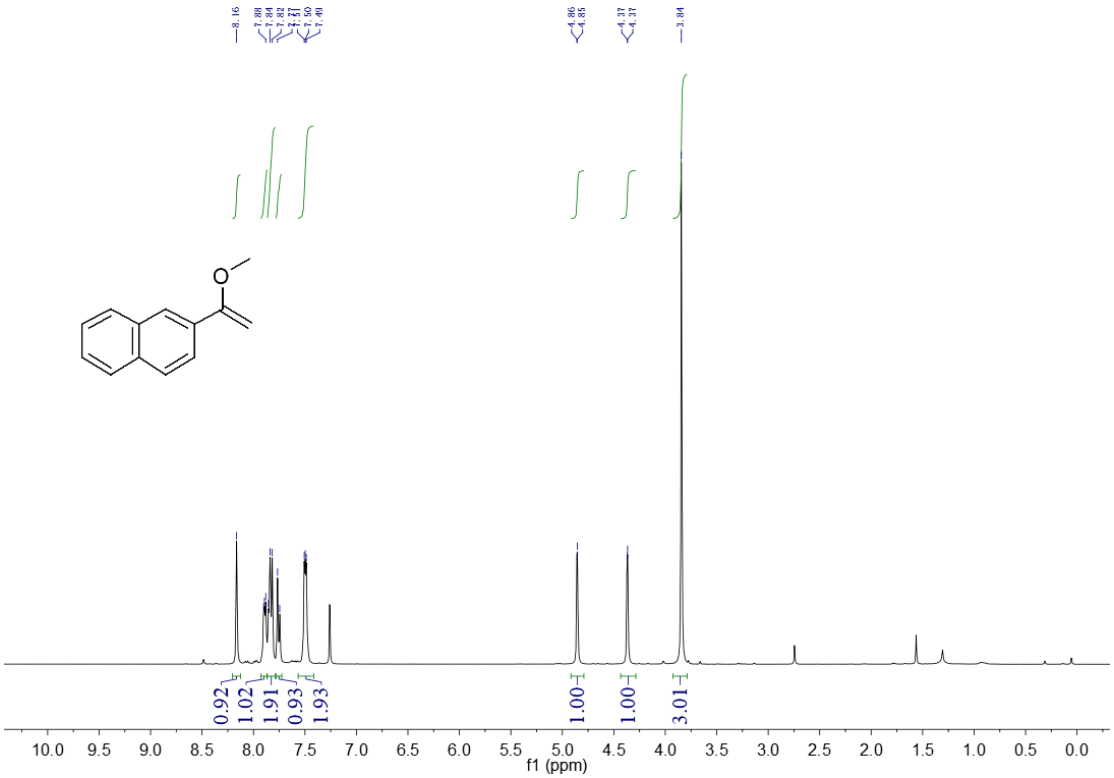
^{1}H NMR of **1m**



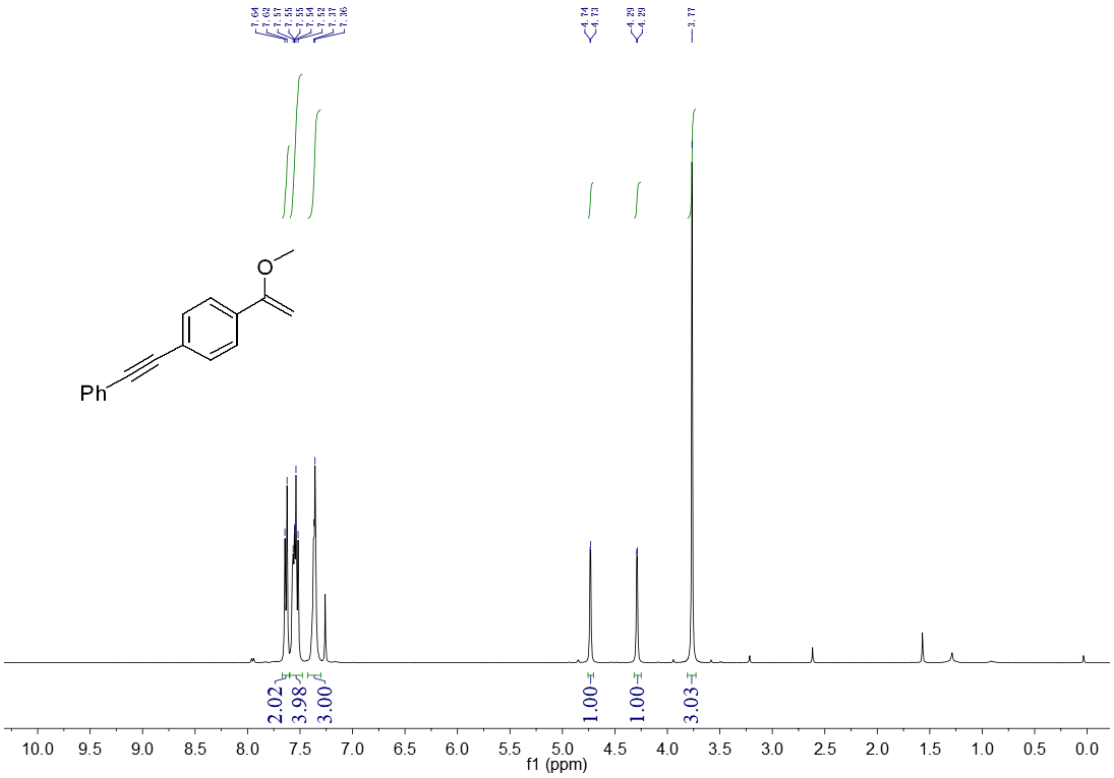
^{1}H NMR of **1n**



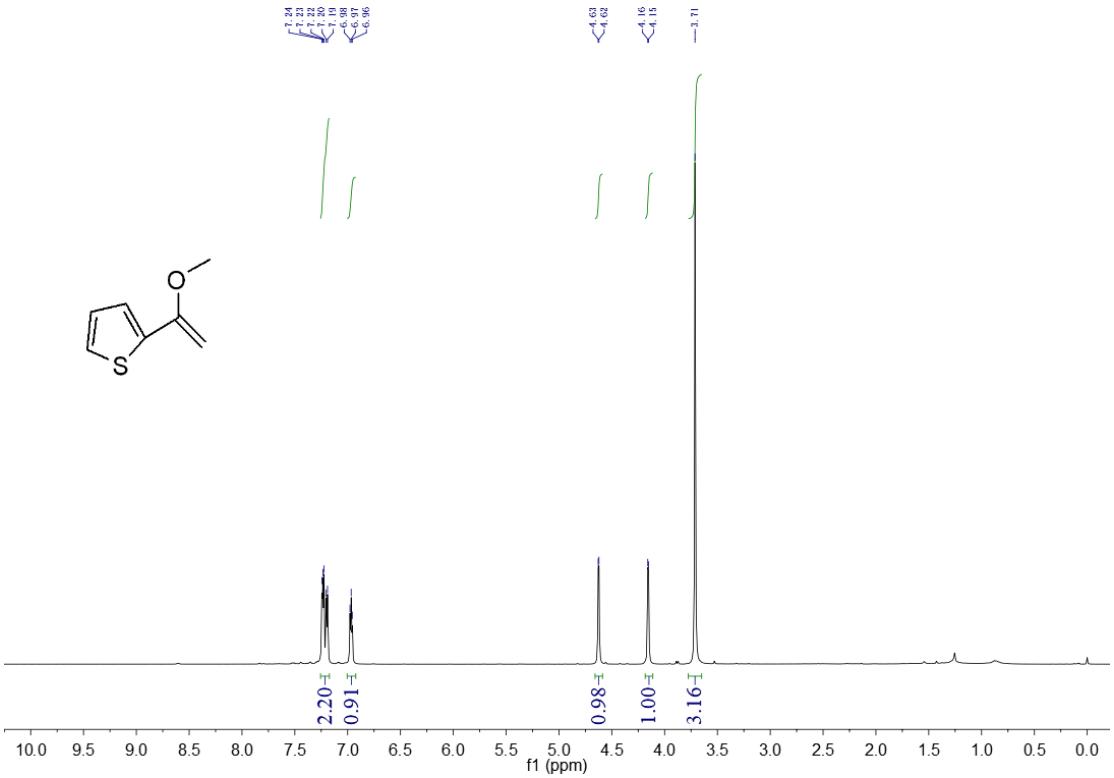
^{1}H NMR of **1o**



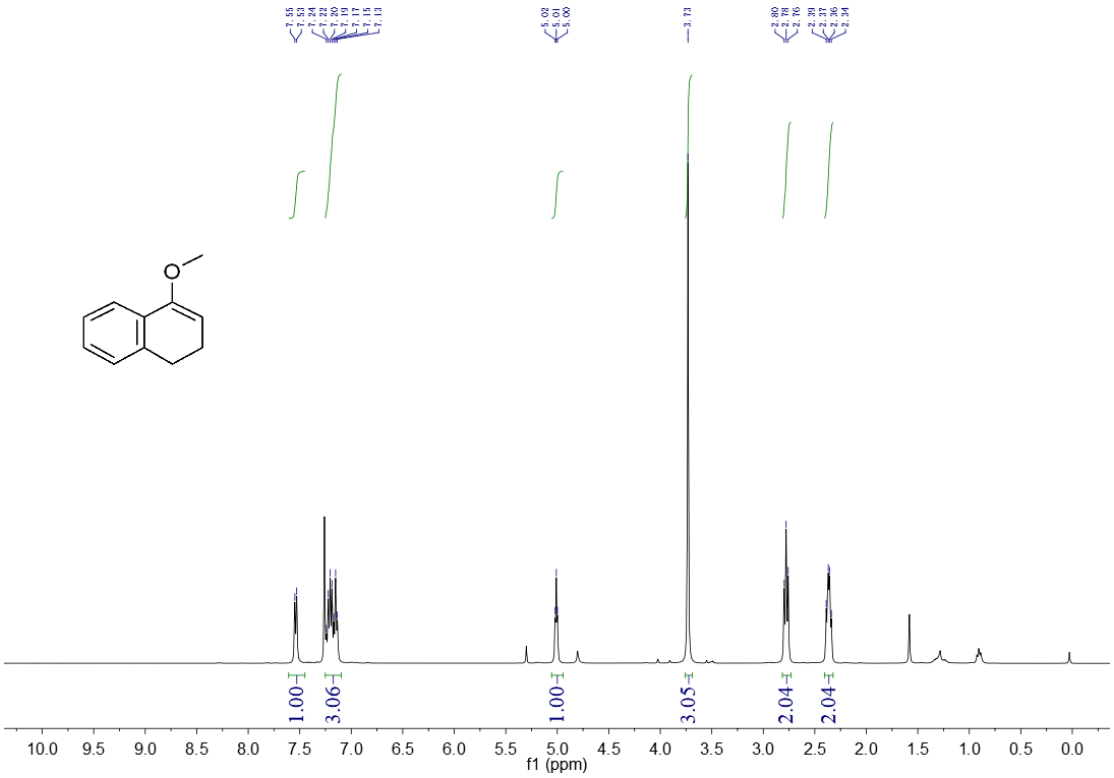
^{1}H NMR of **1p**



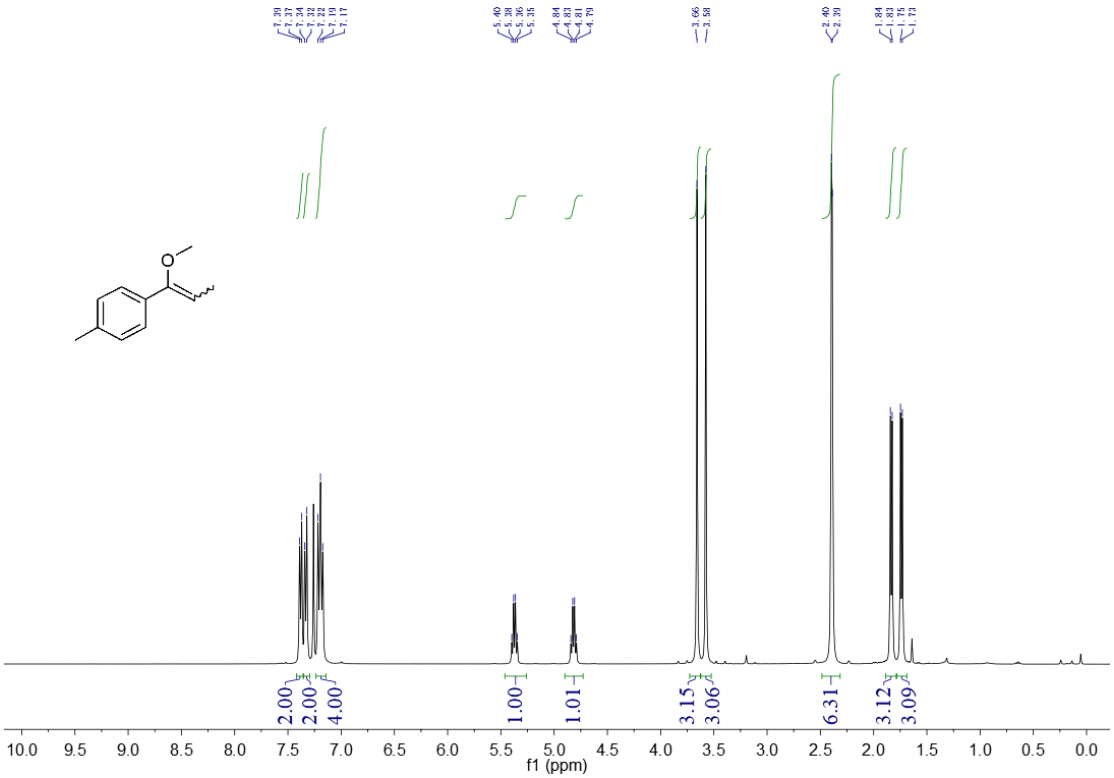
^{1}H NMR of **1q**



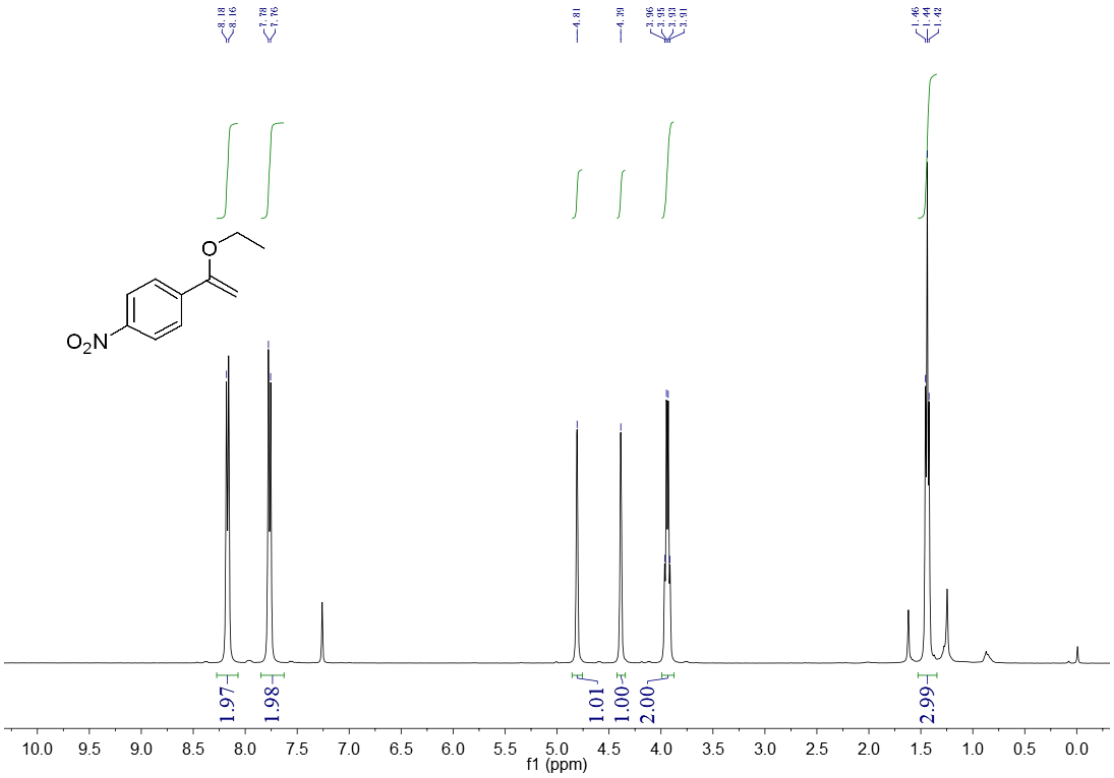
^{1}H NMR of **1r**



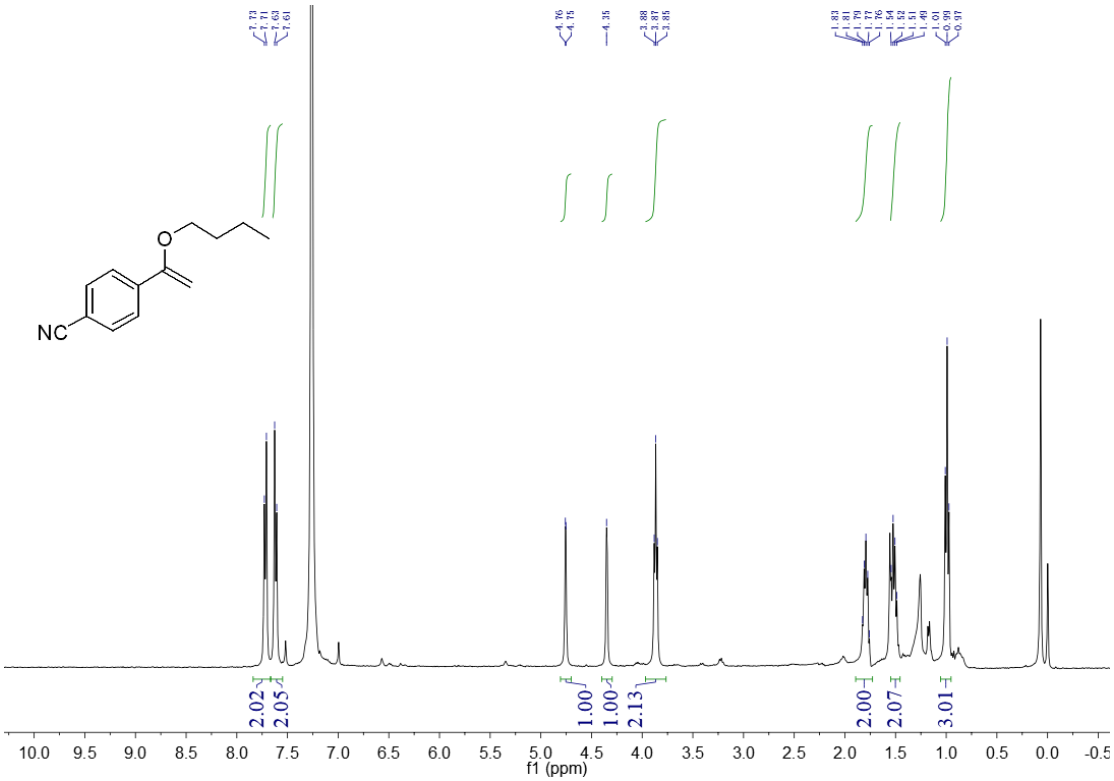
^{1}H NMR of **1s**



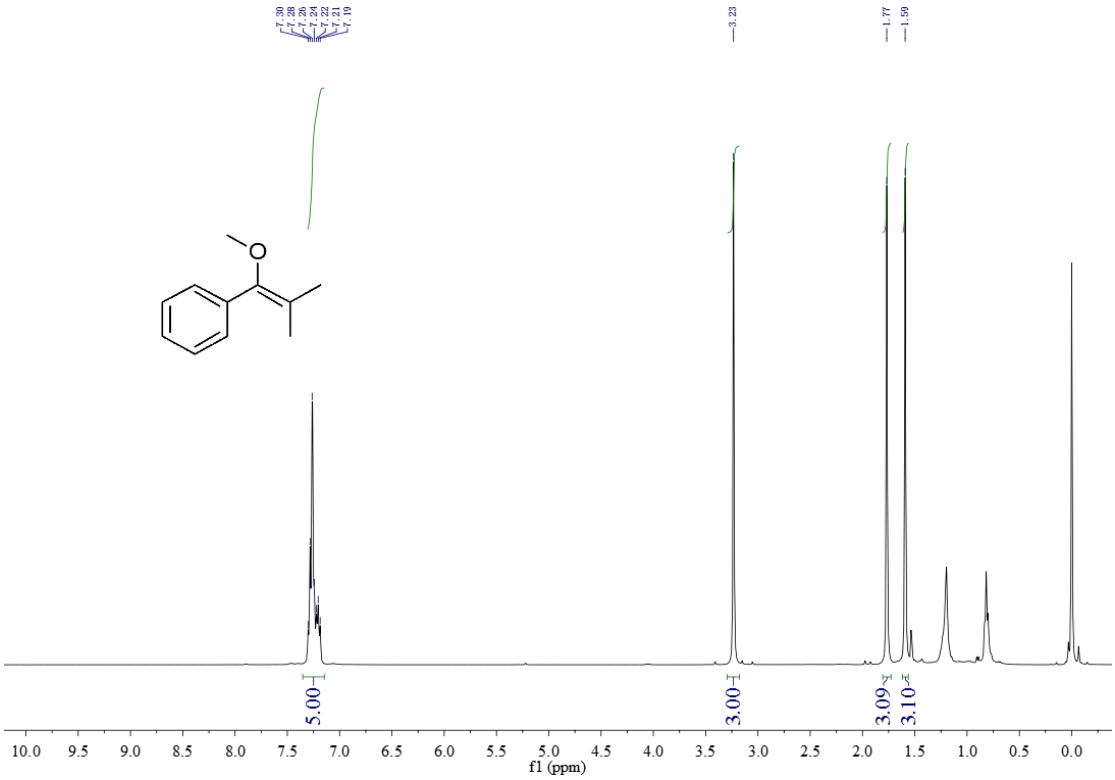
^{1}H NMR of **1t**



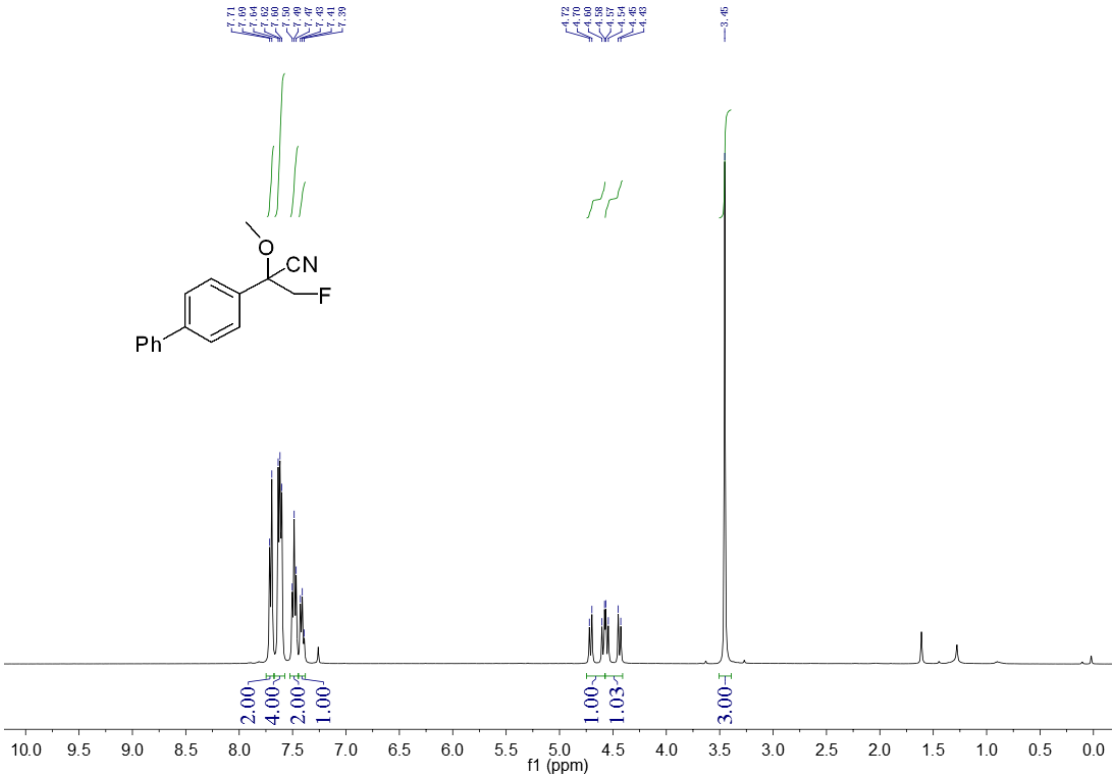
^{1}H NMR of **1u**



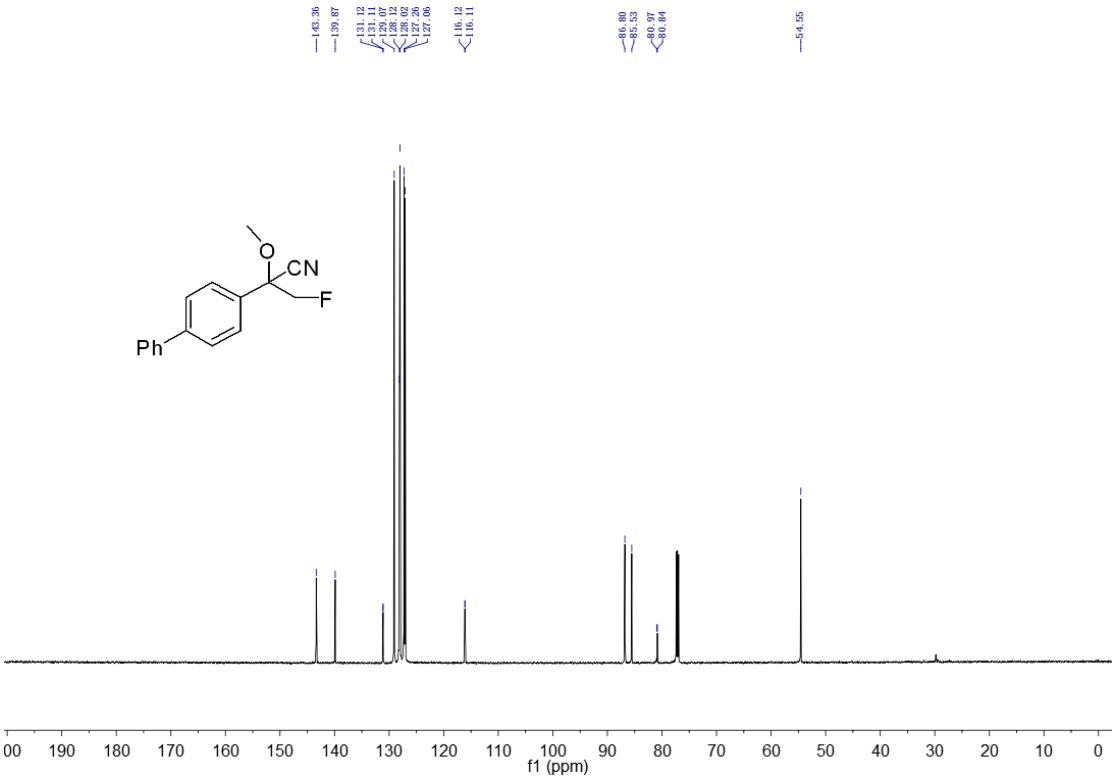
^{1}H NMR of **1v**



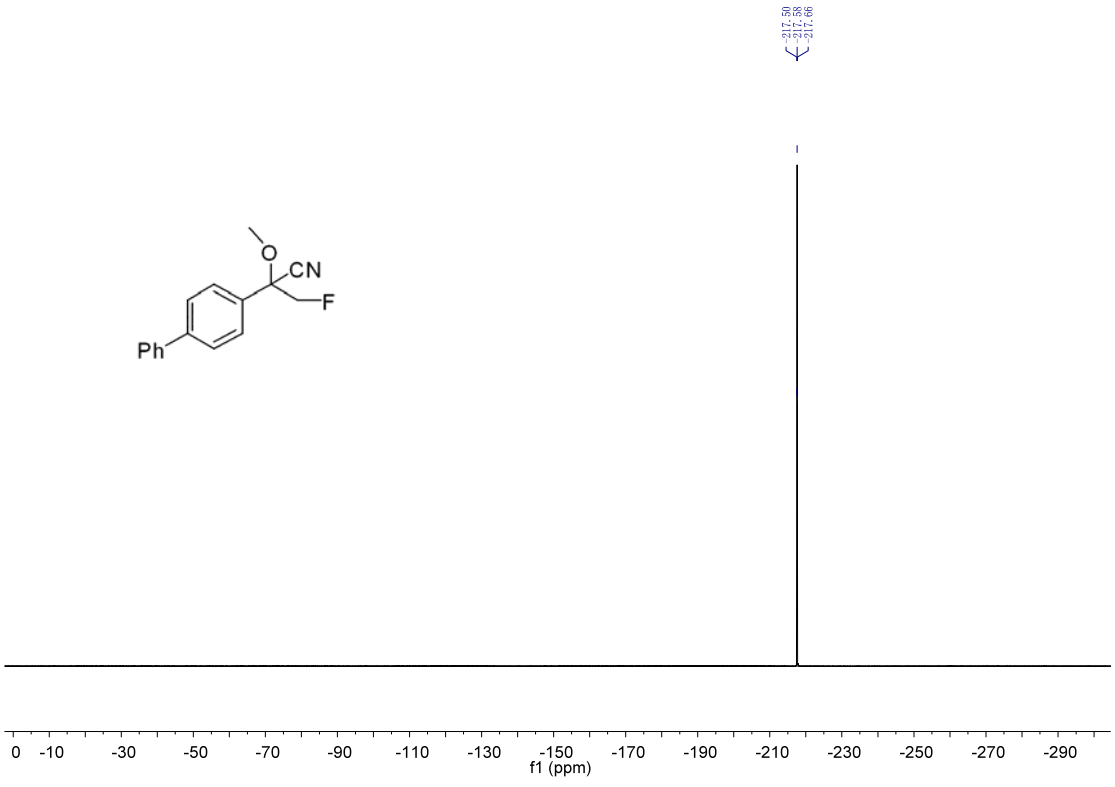
^{1}H NMR of **2a**



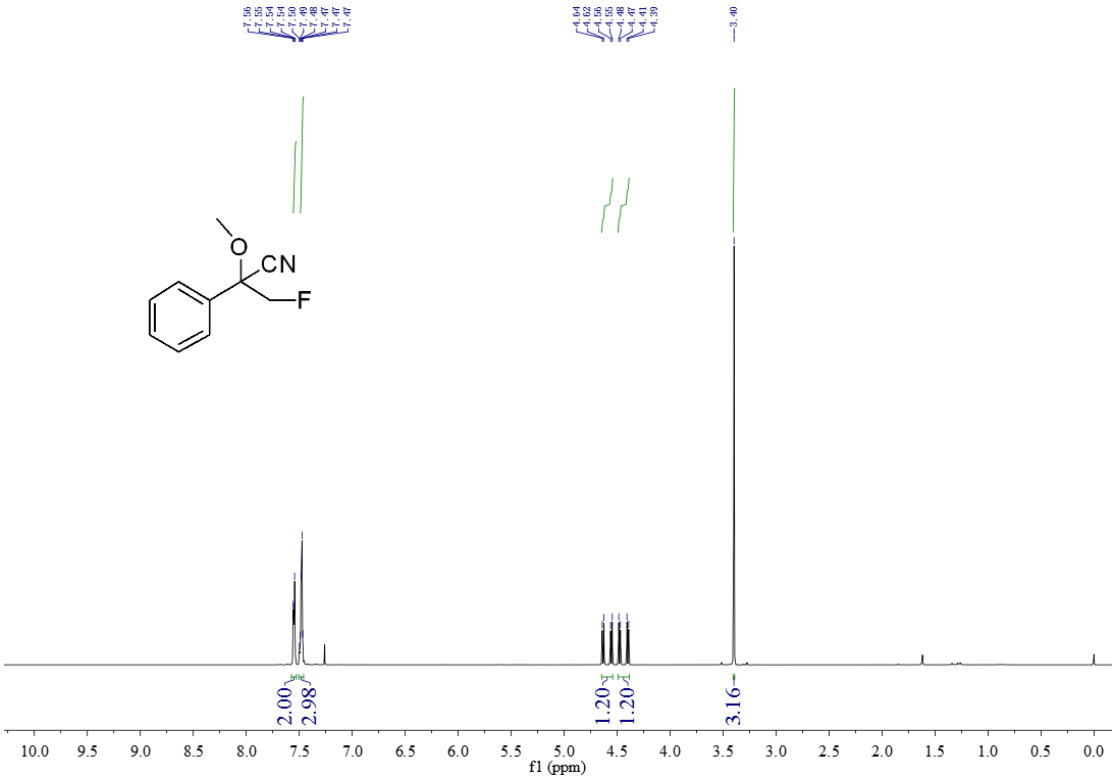
^{13}C NMR of **2a**



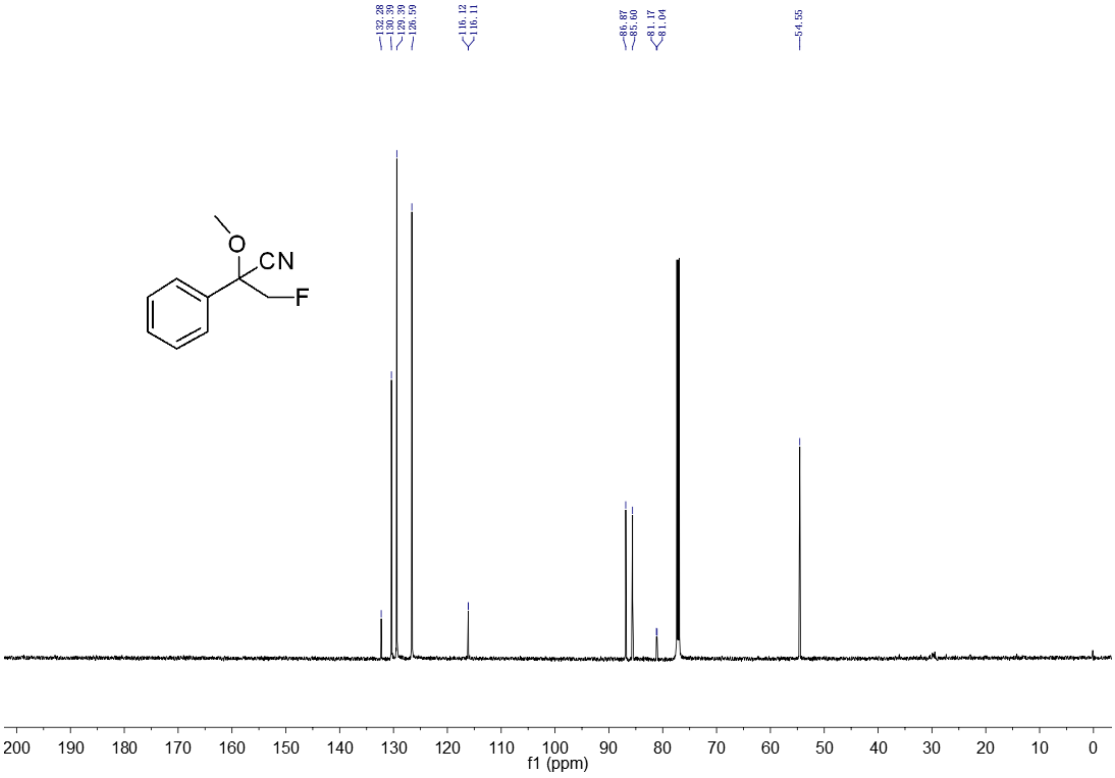
^{19}F NMR of **2a**



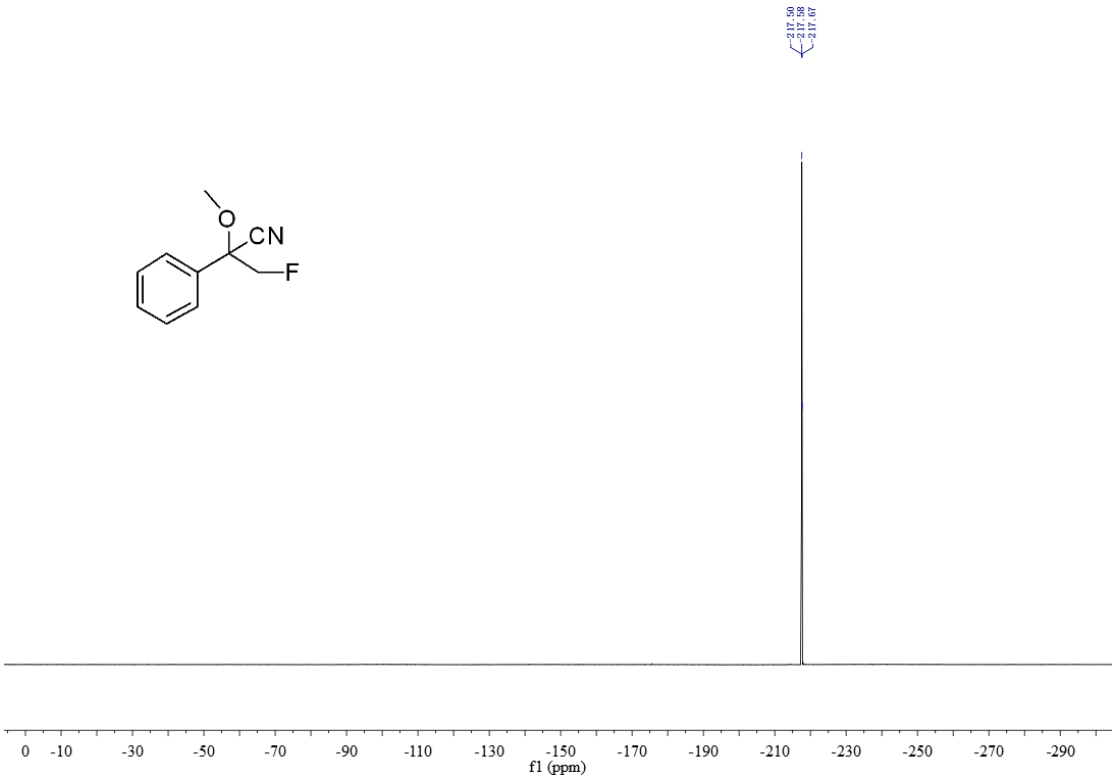
^{1}H NMR of **2b**



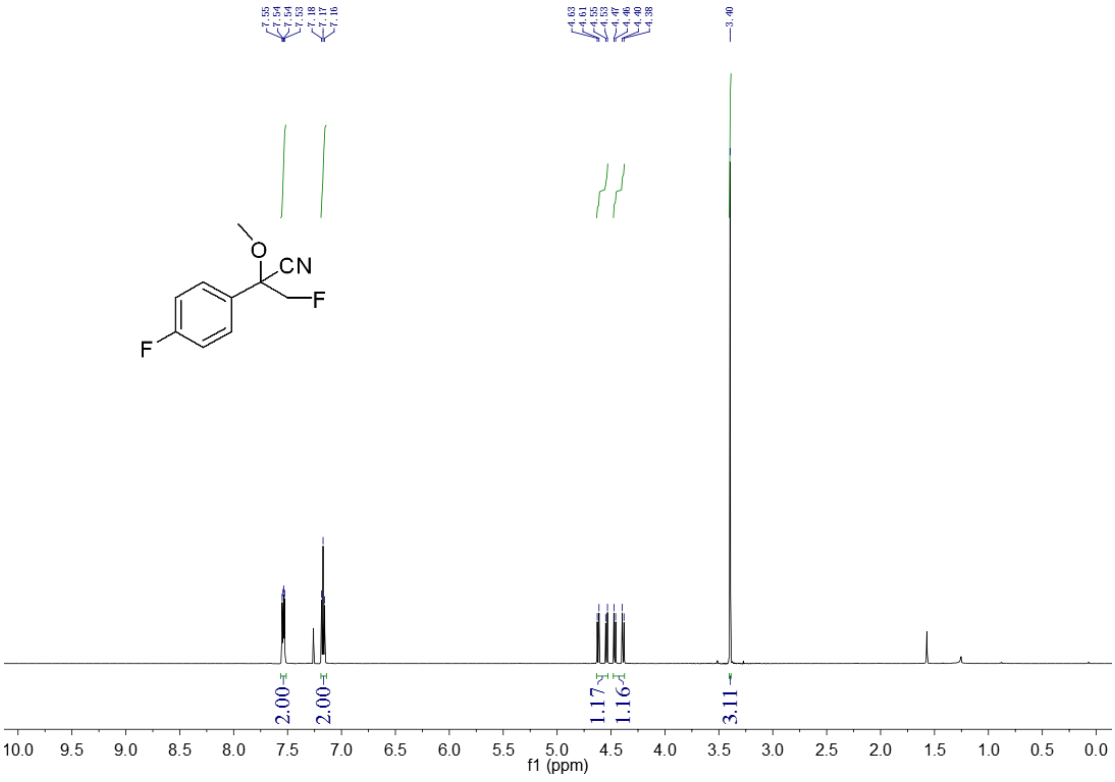
^{13}C NMR of **2b**



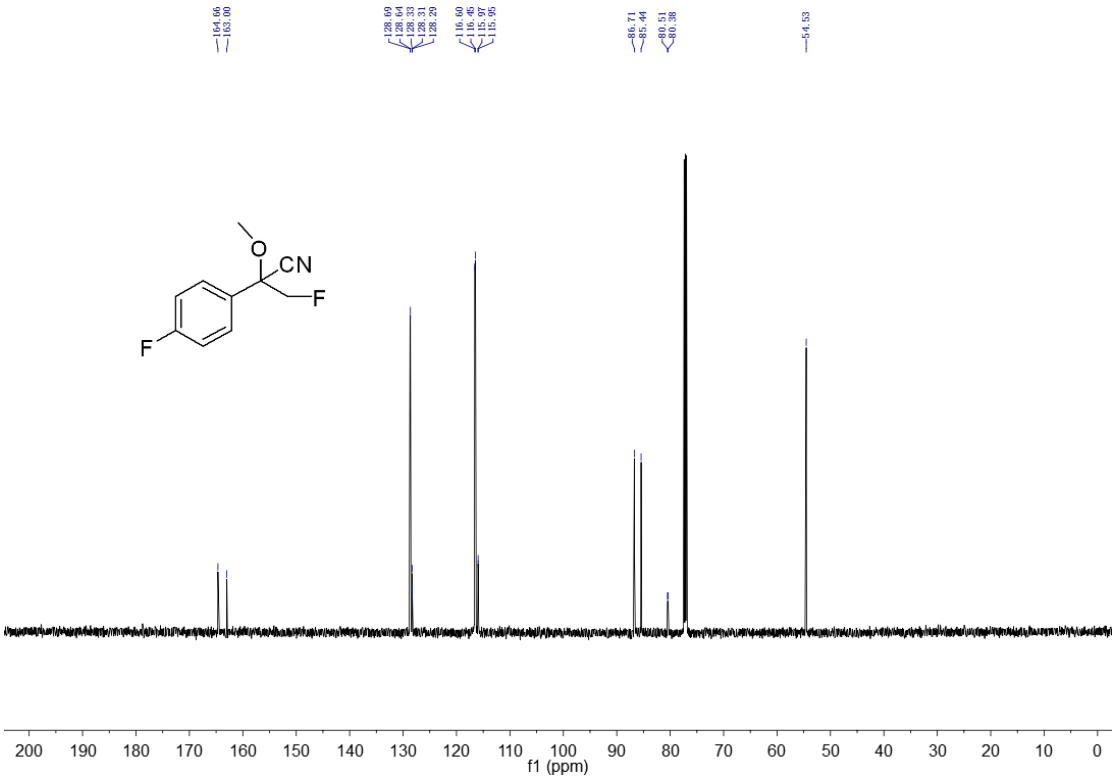
^{19}F NMR of **2b**



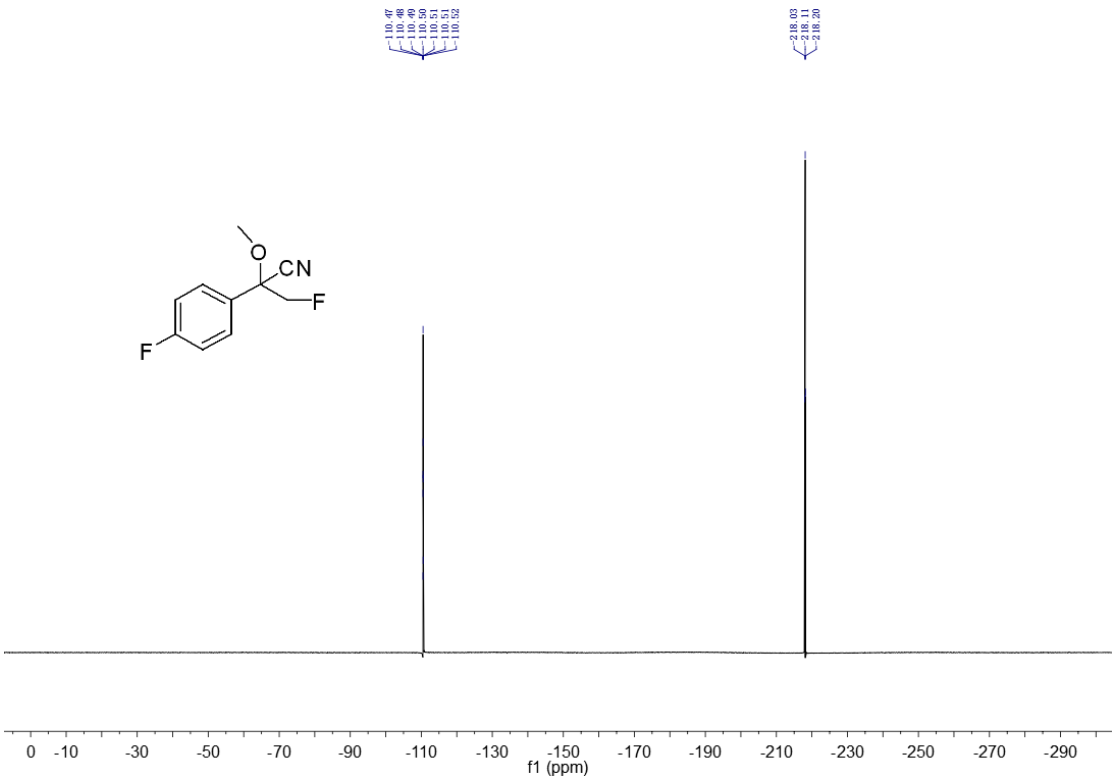
^{1}H NMR of **2c**



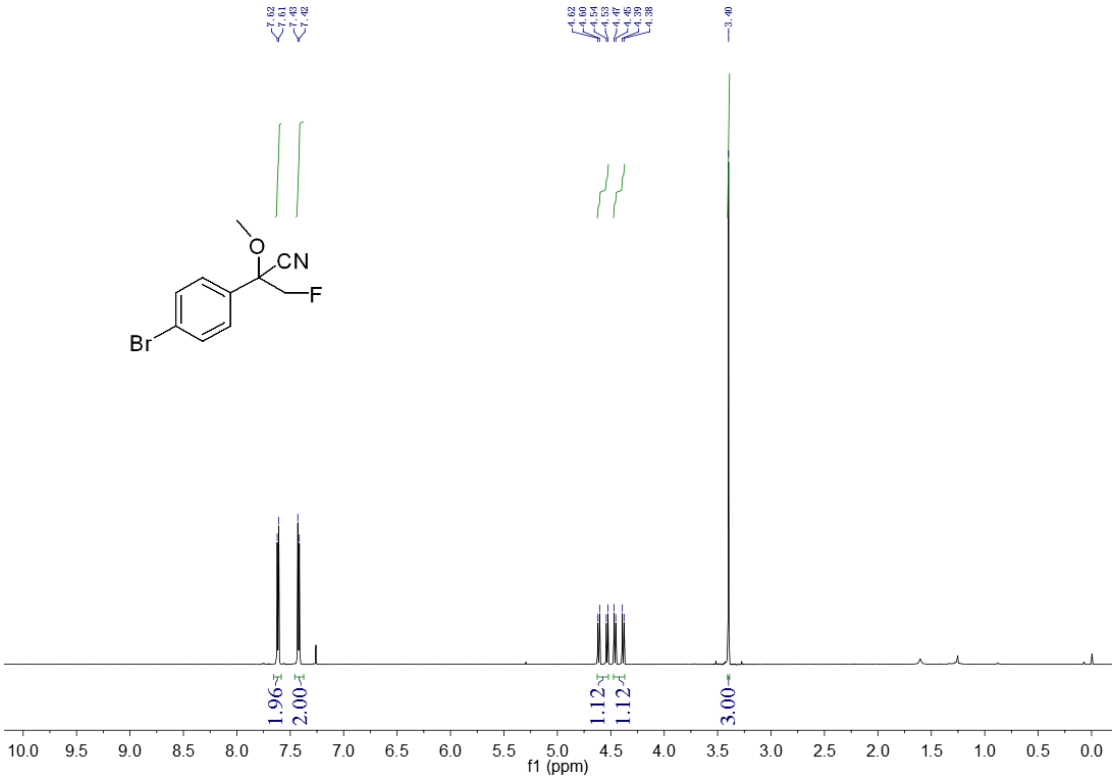
^{13}C NMR of **2c**



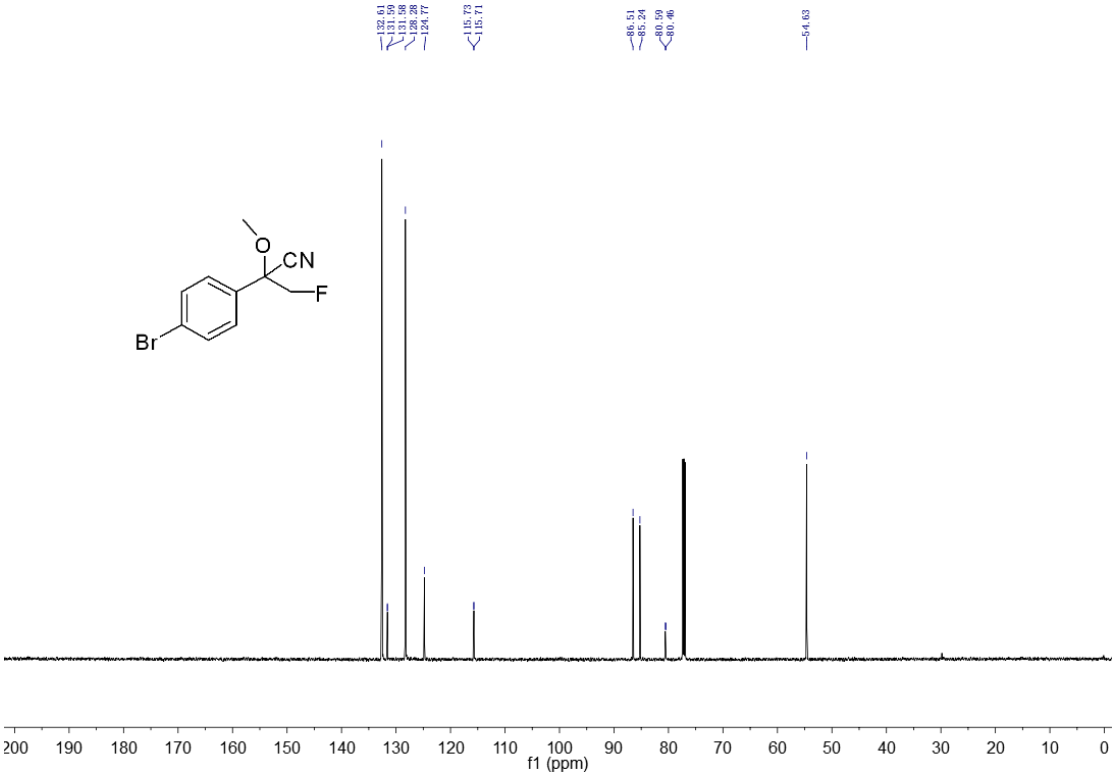
^{19}F NMR of **2c**



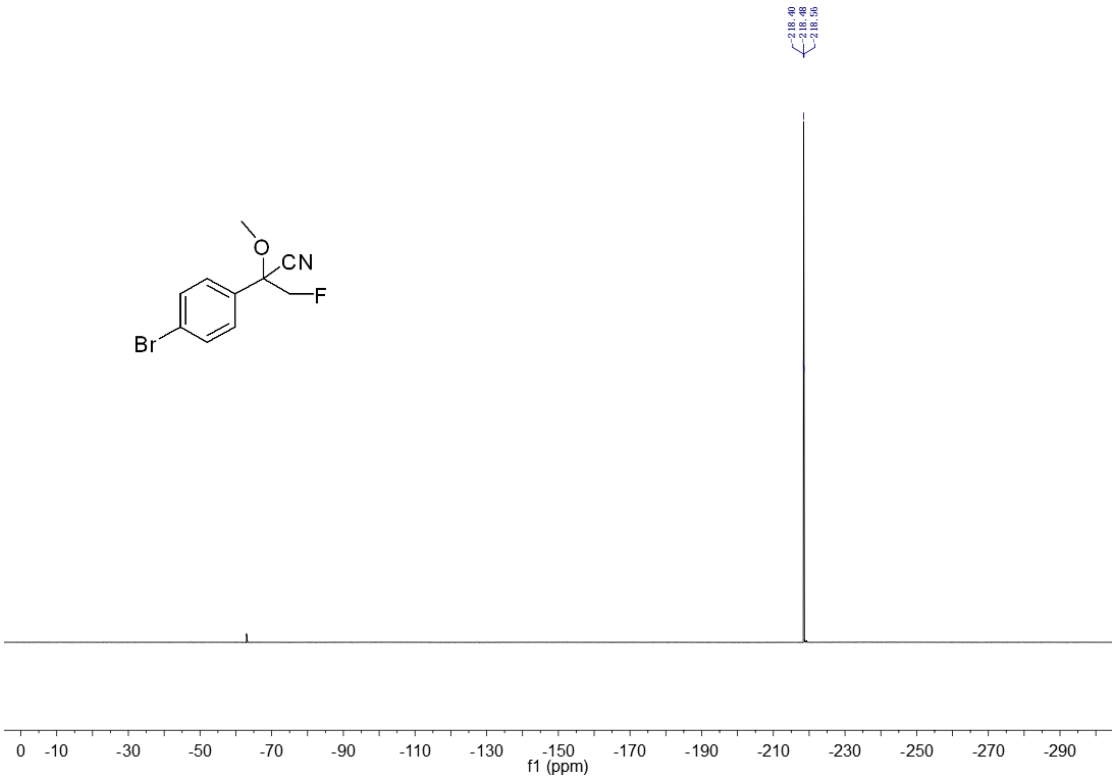
^{1}H NMR of **2d**



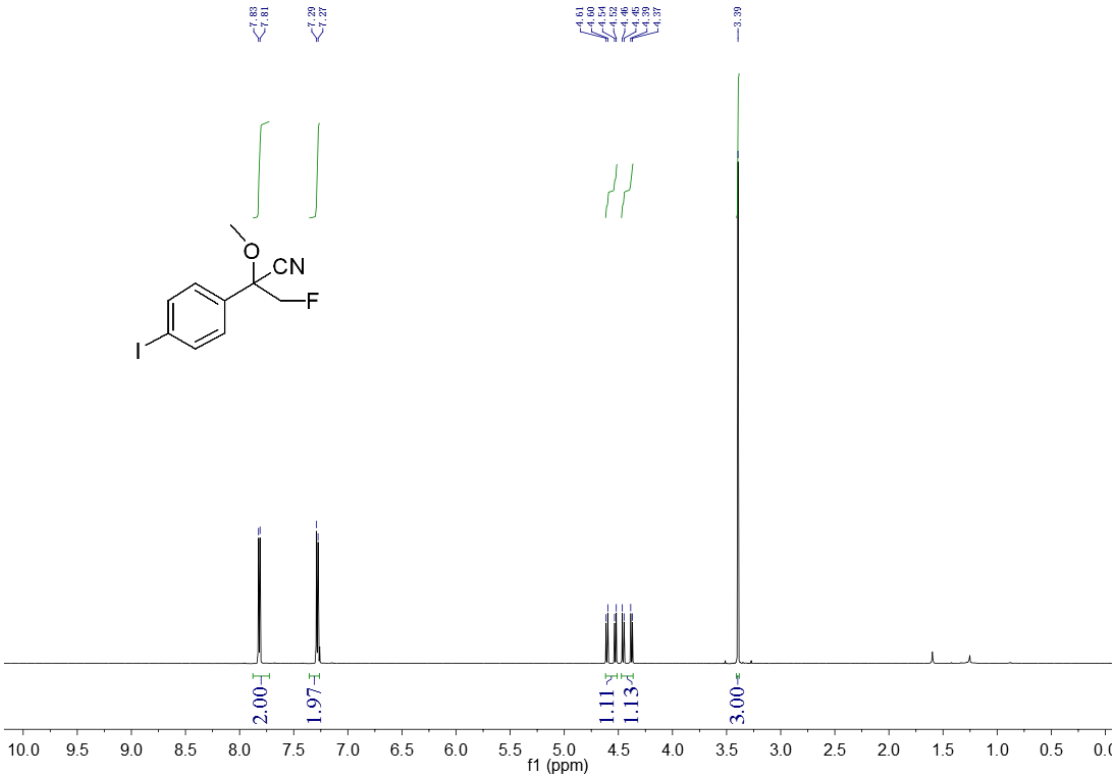
^{13}C NMR of **2d**



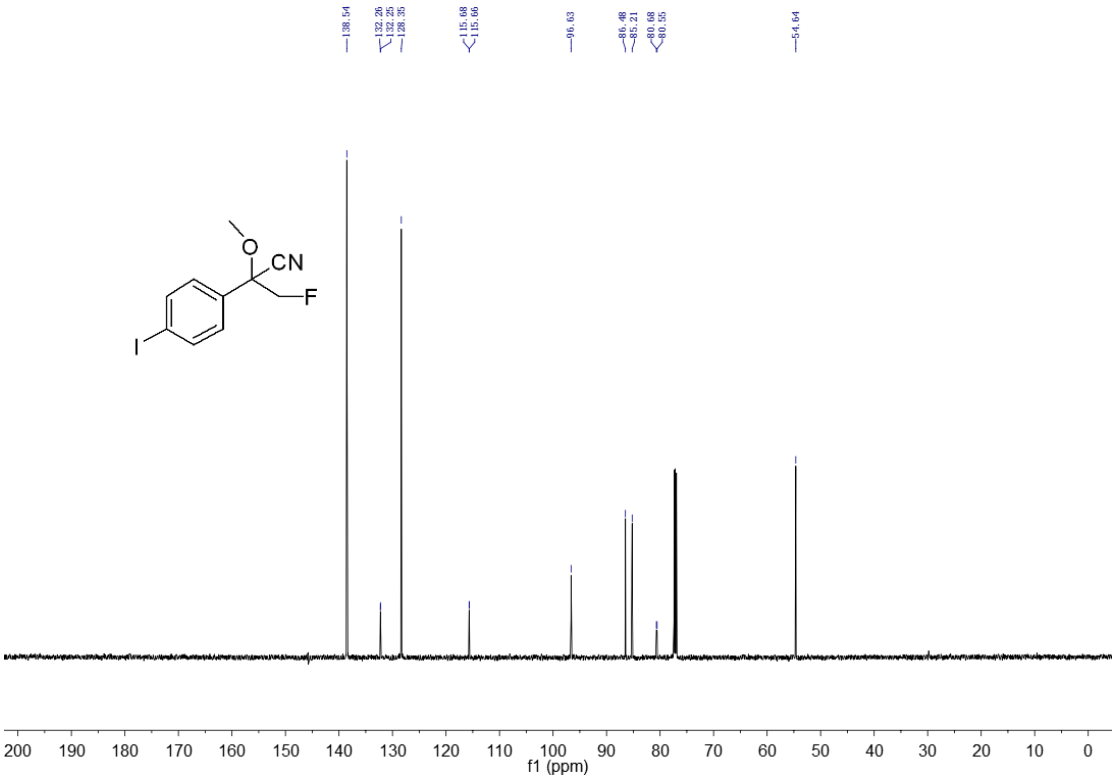
^{19}F NMR of **2d**



^{1}H NMR of **2e**

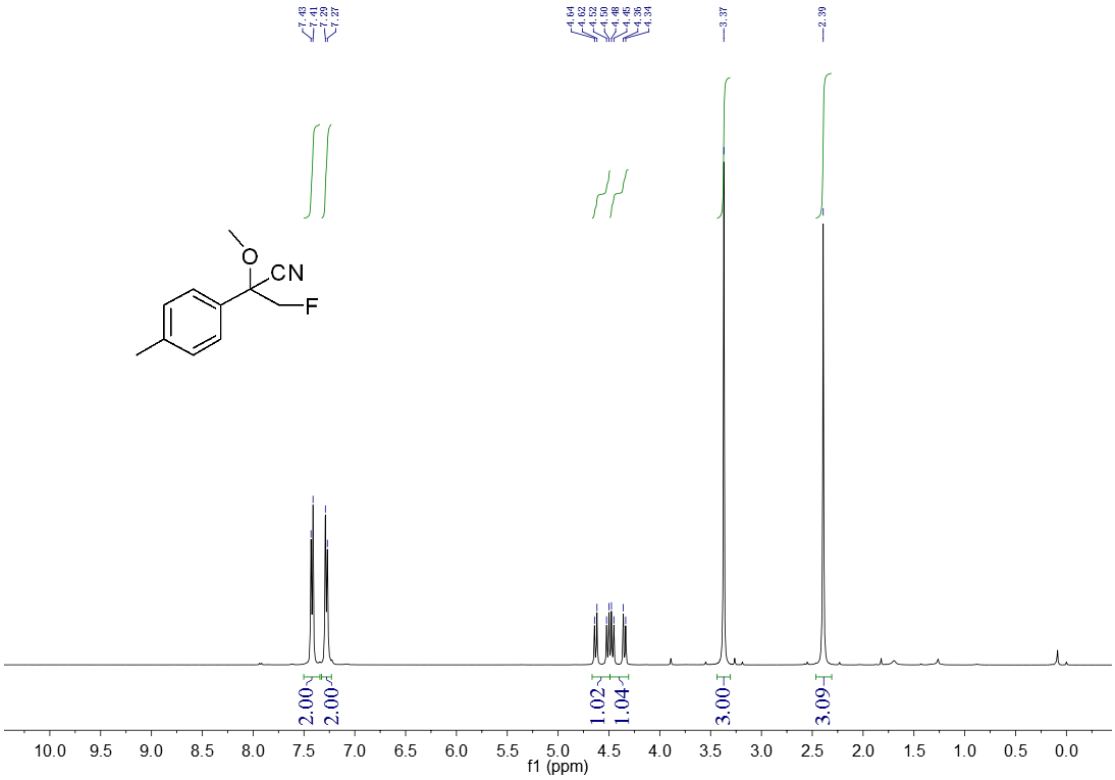


^{13}C NMR of **2e**

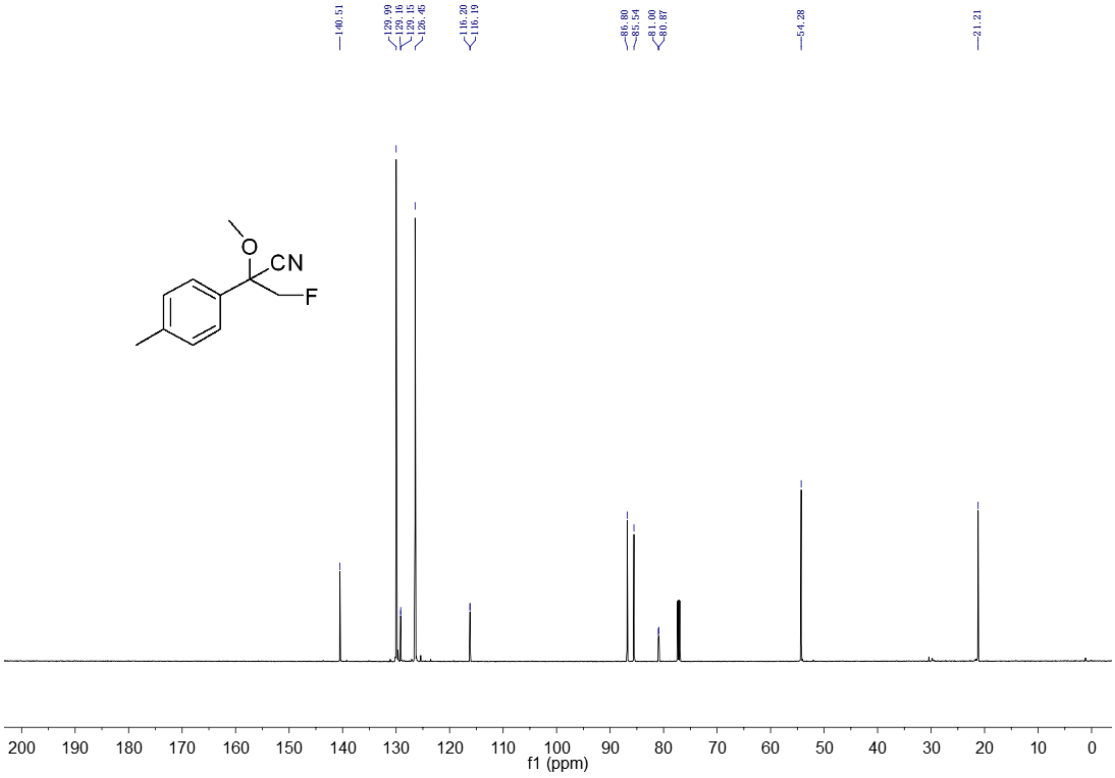


^{19}F NMR of **2e**

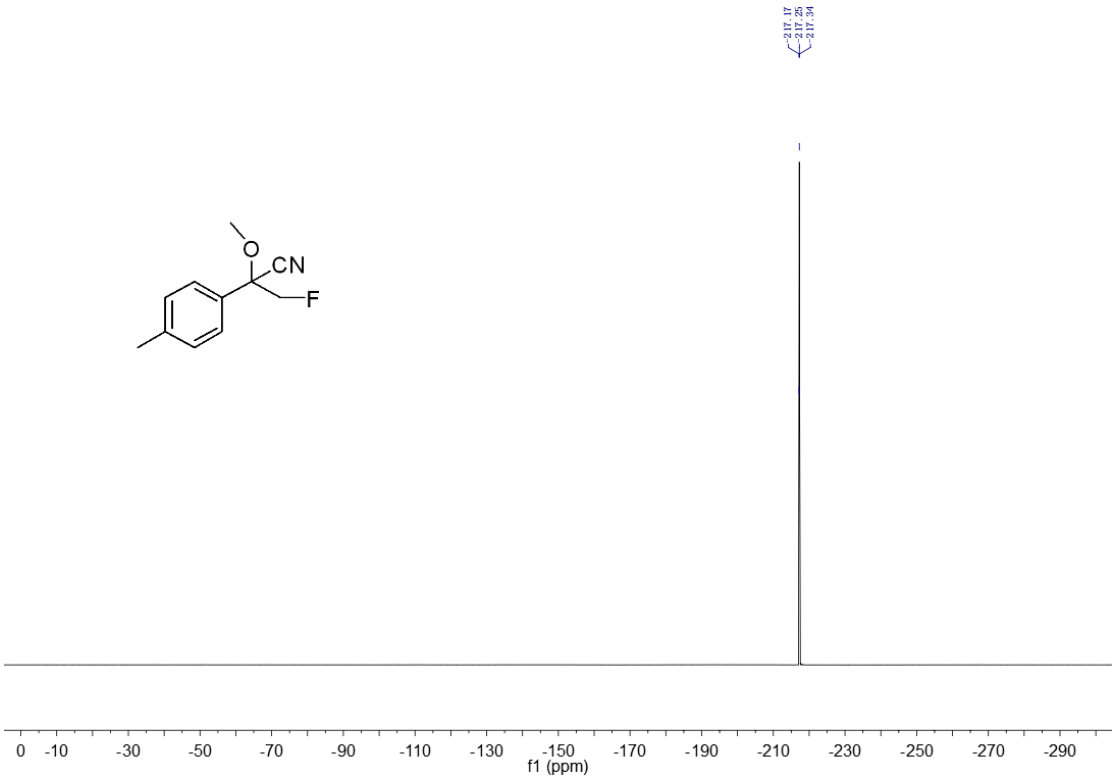
^{1}H NMR of **2f**



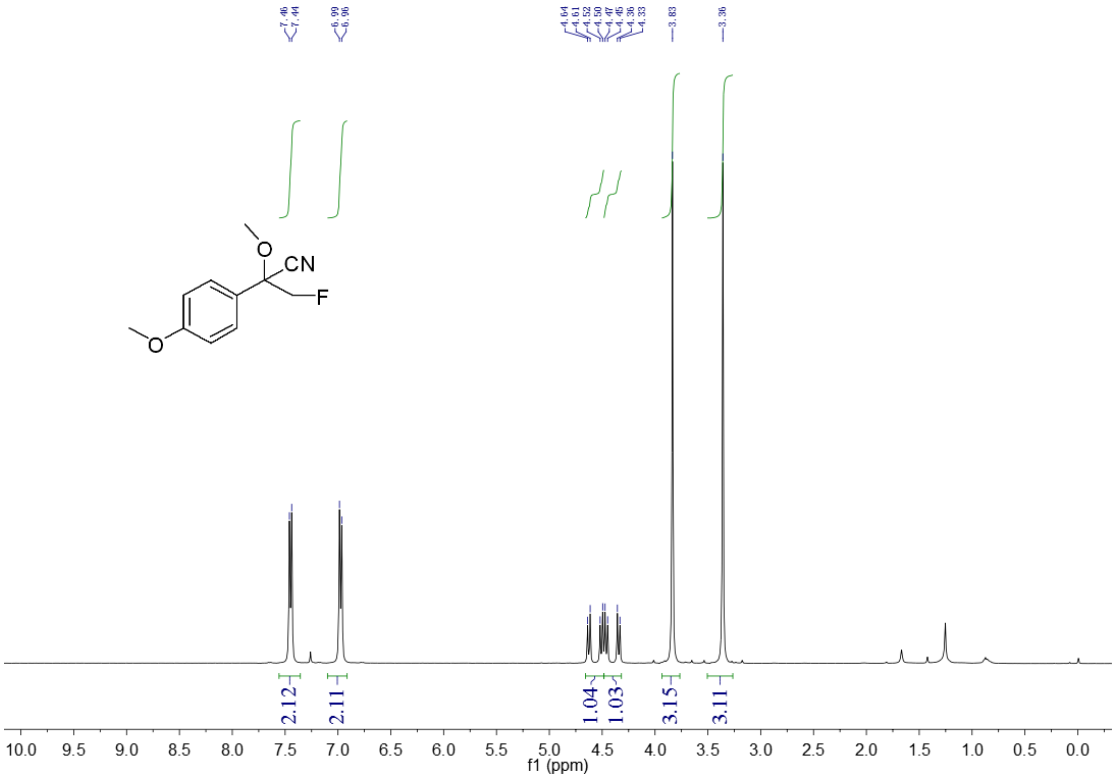
^{13}C NMR of **2f**



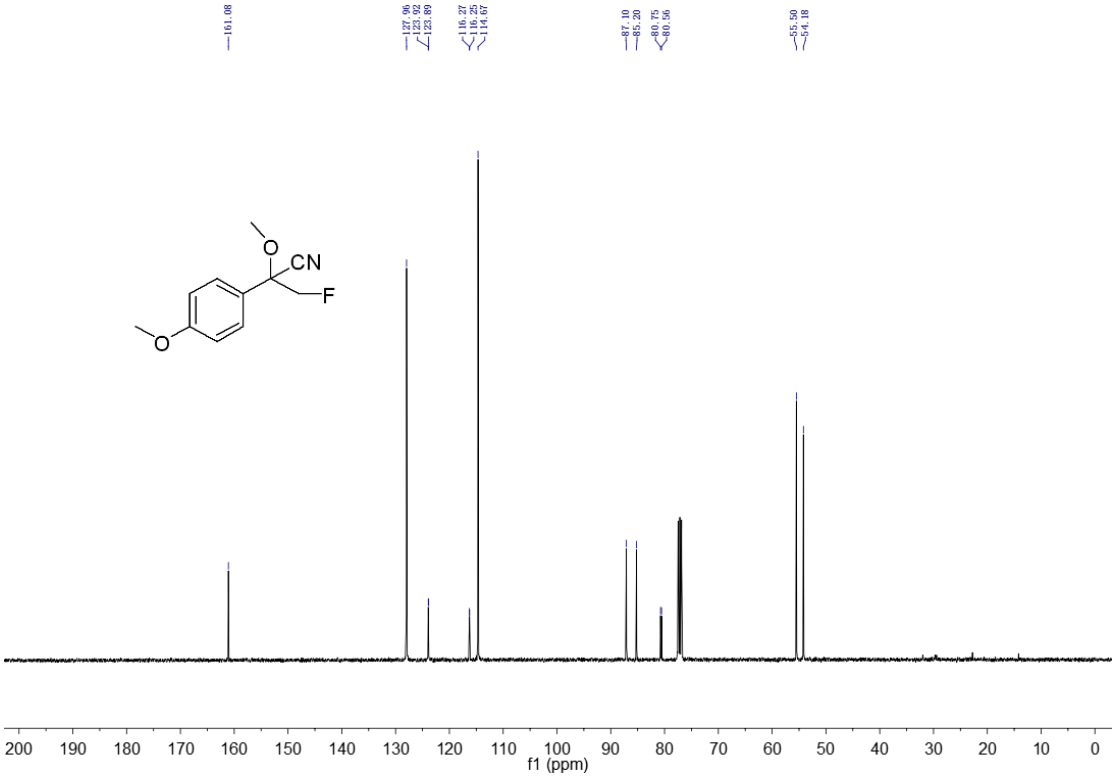
^{19}F NMR of **2f**



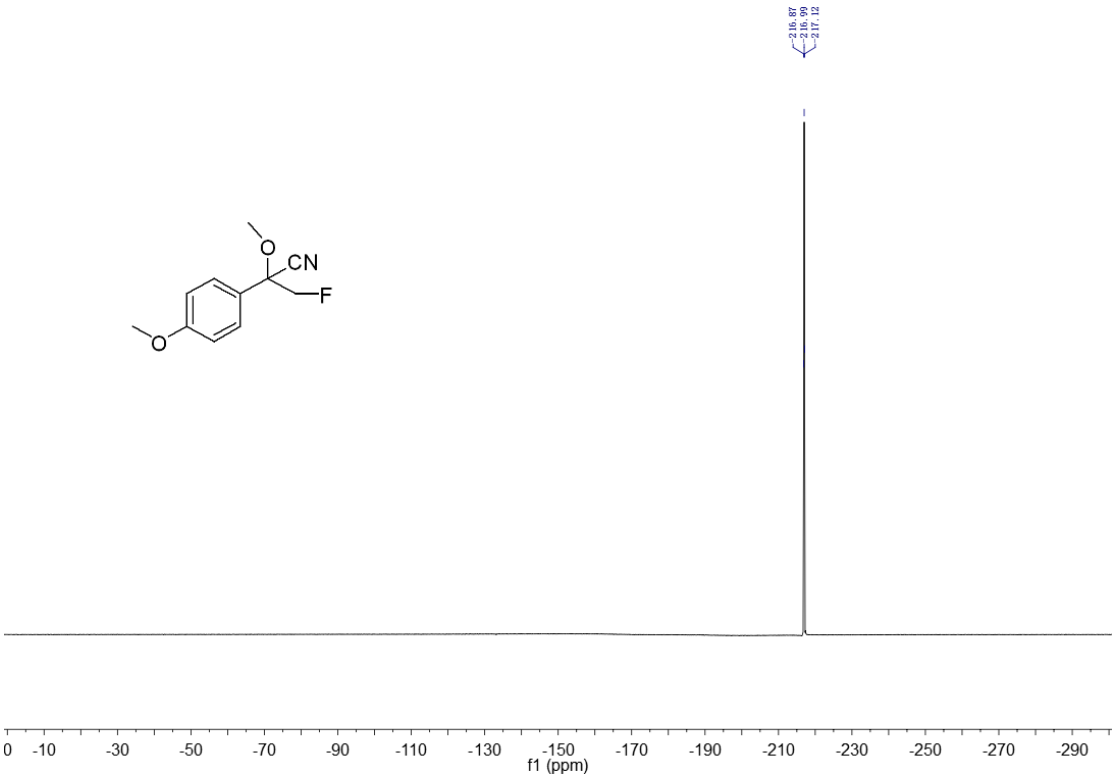
^{1}H NMR of **2g**



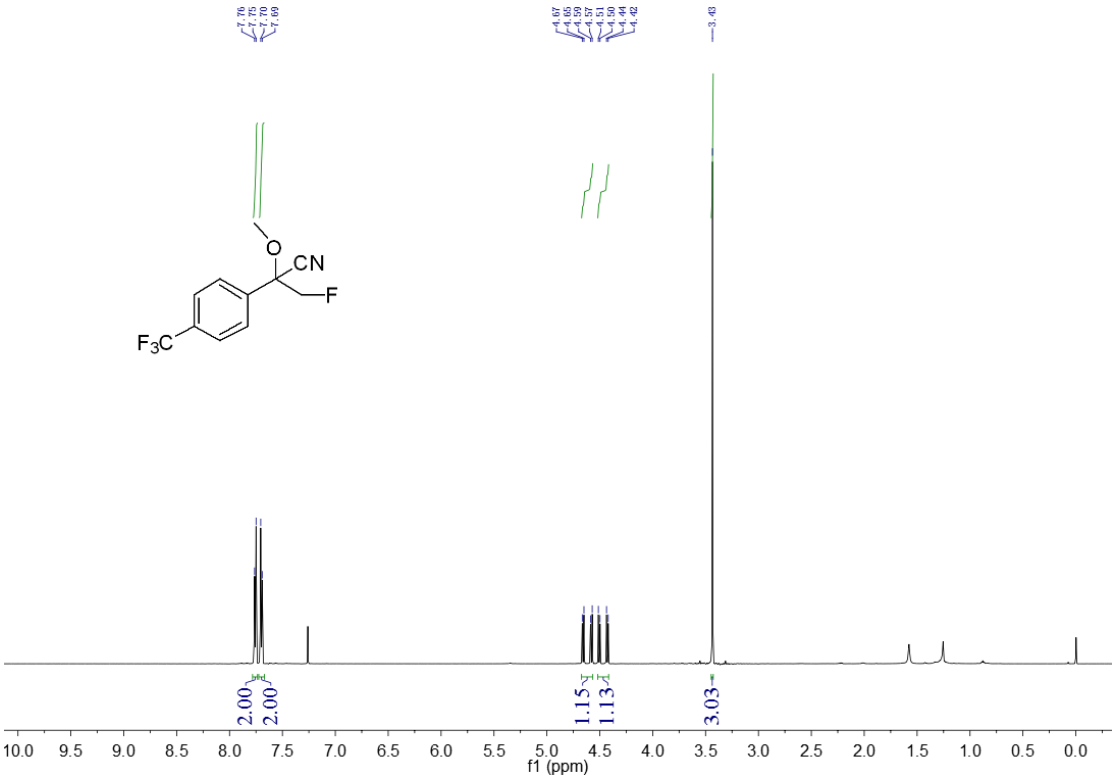
^{13}C NMR of **2g**



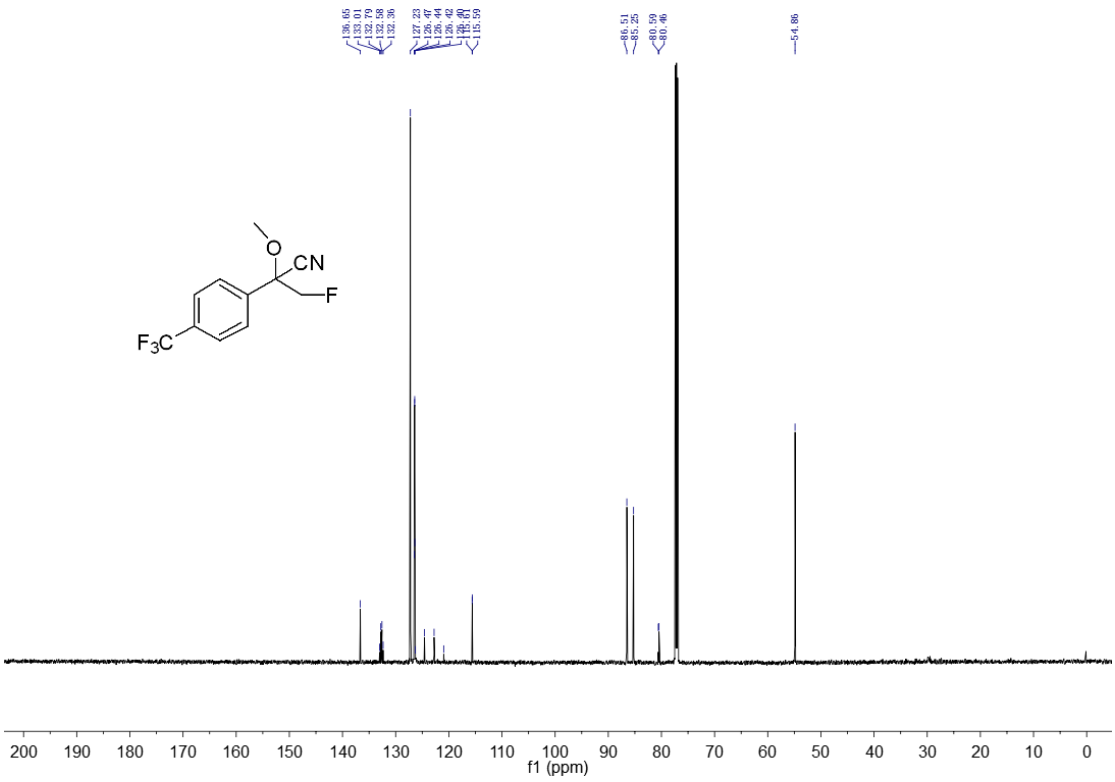
^{19}F NMR of **2g**



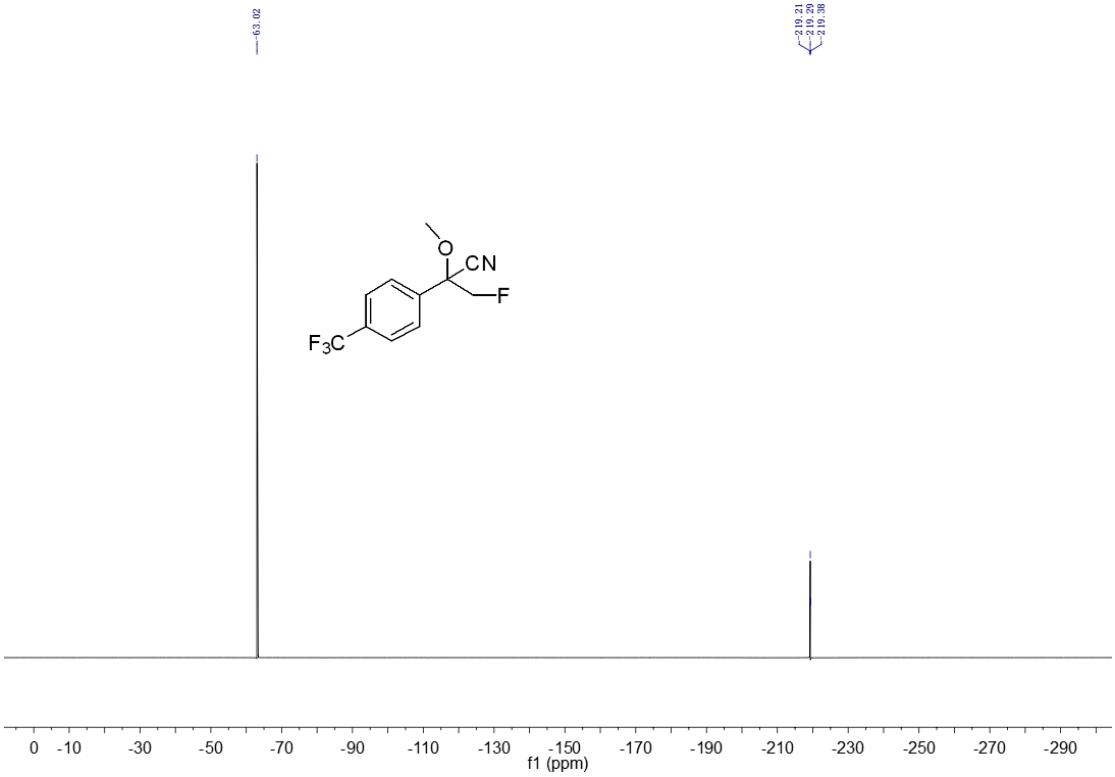
^{1}H NMR of **2h**



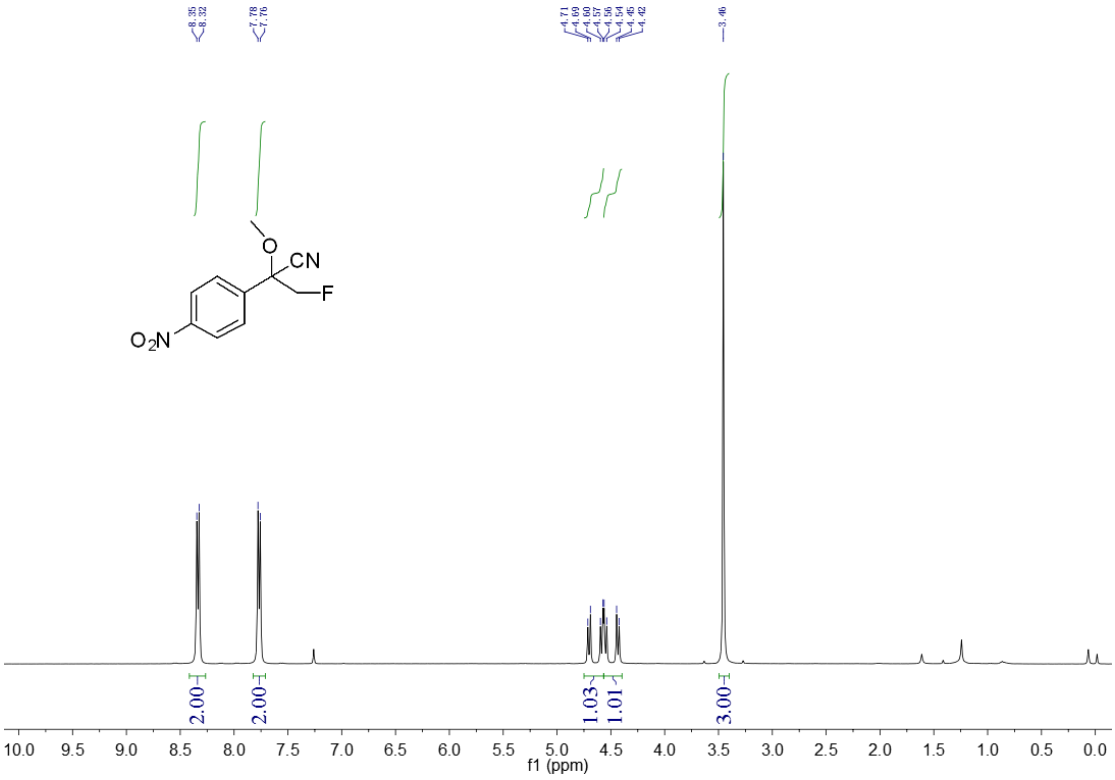
^{13}C NMR of **2h**



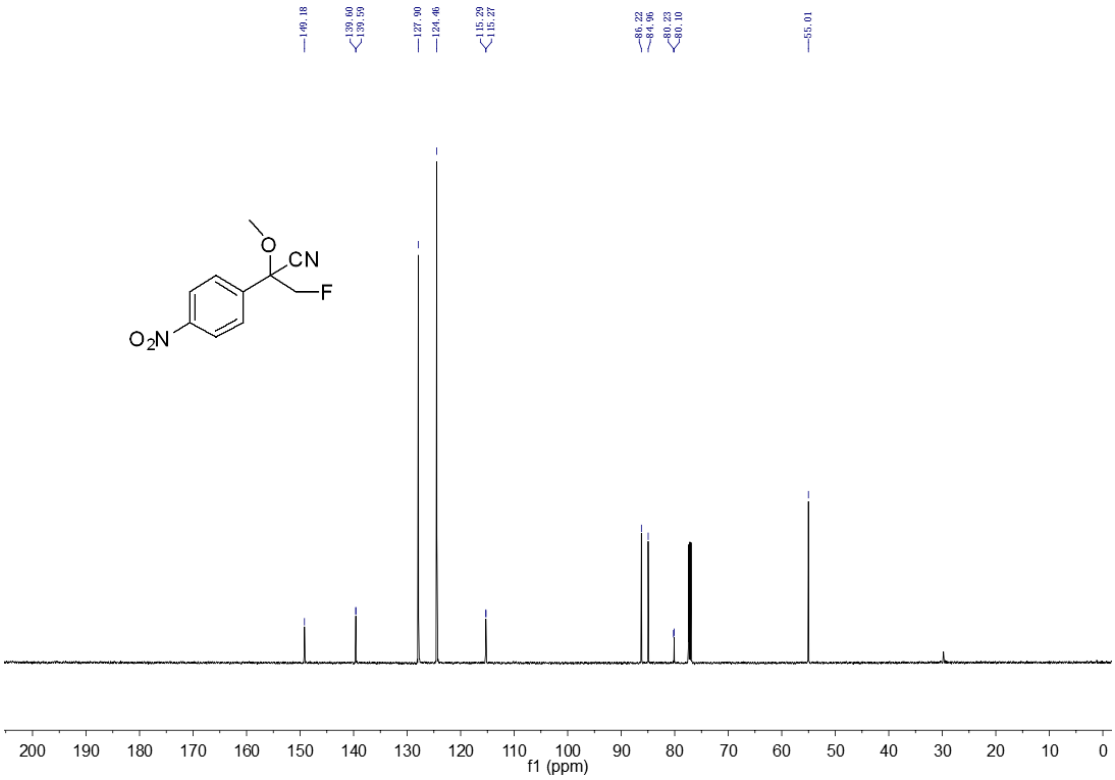
^{19}F NMR of **2h**



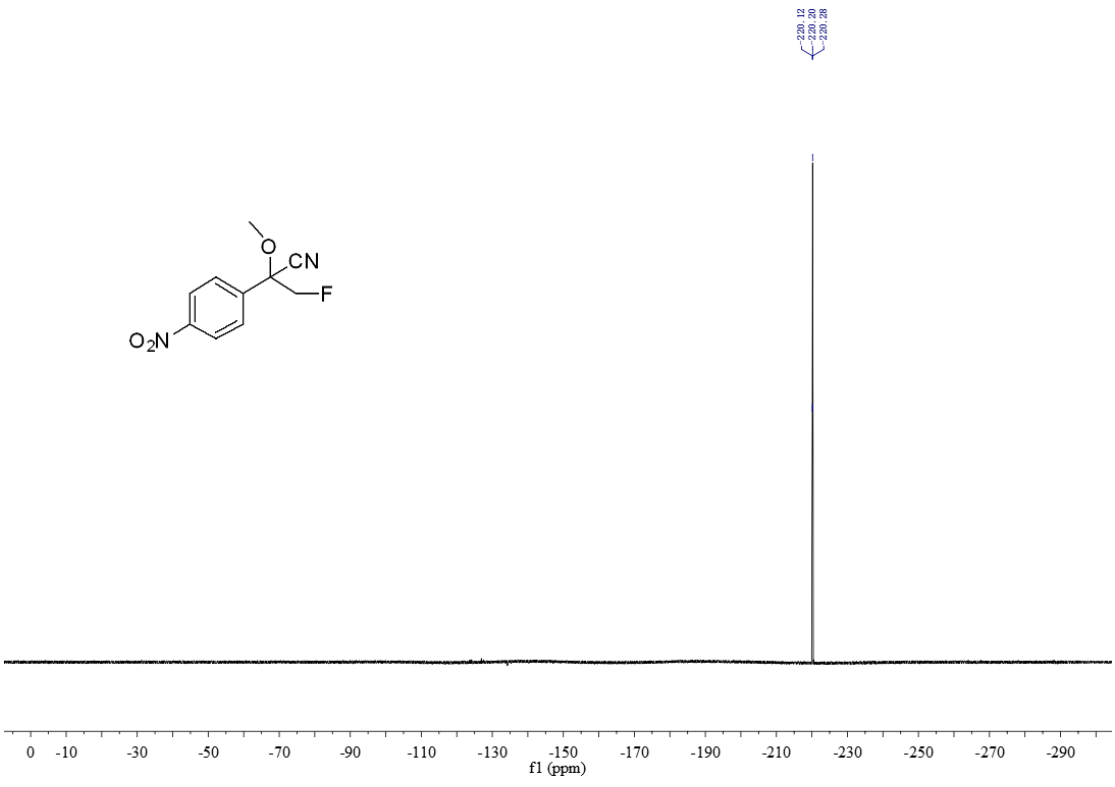
^{1}H NMR of **2i**



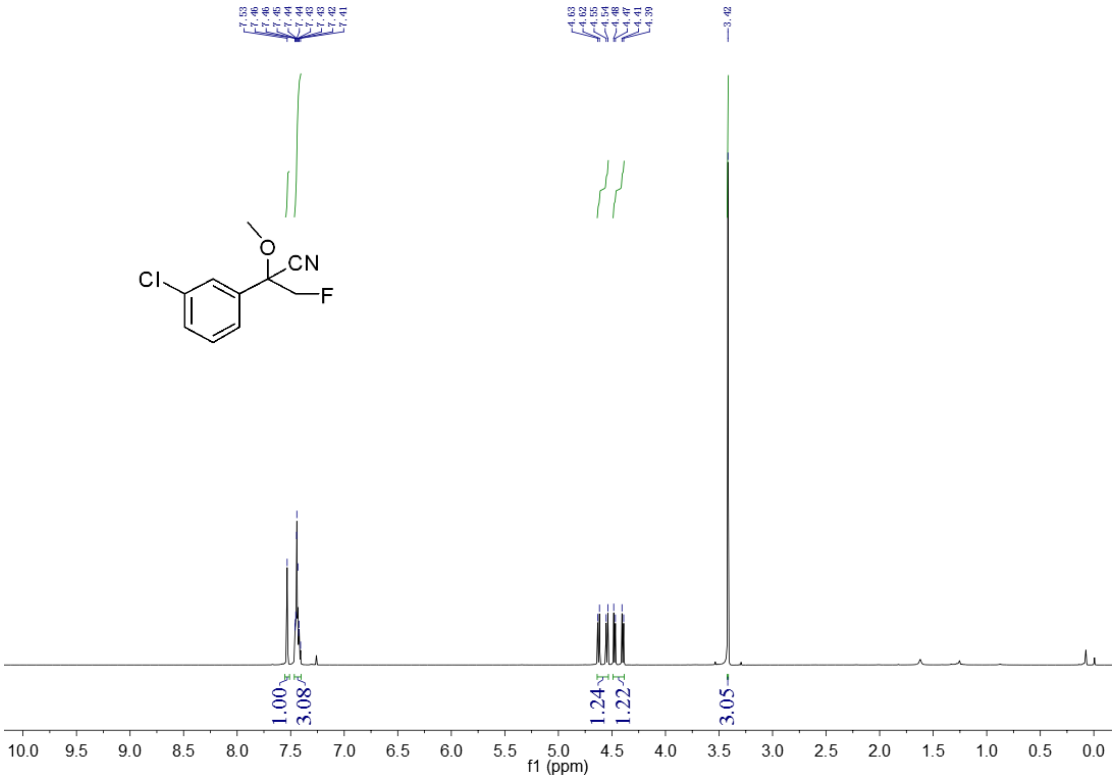
^{13}C NMR of **2i**



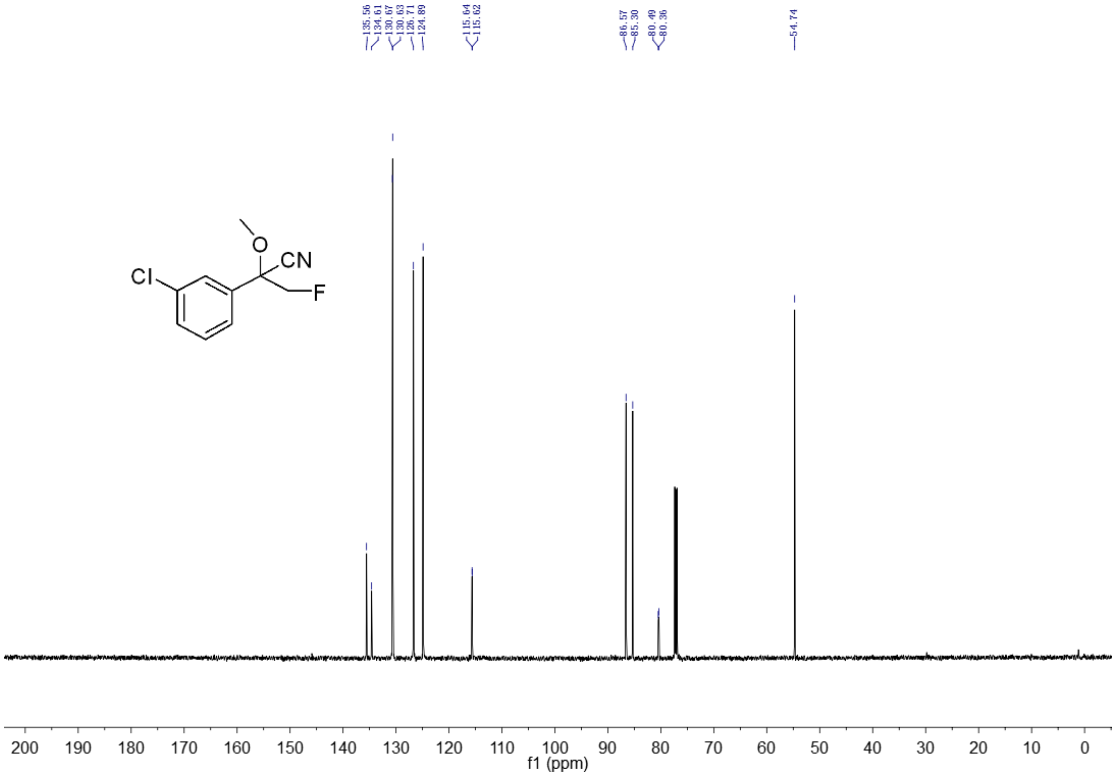
^{19}F NMR of **2i**



^{1}H NMR of **2j**

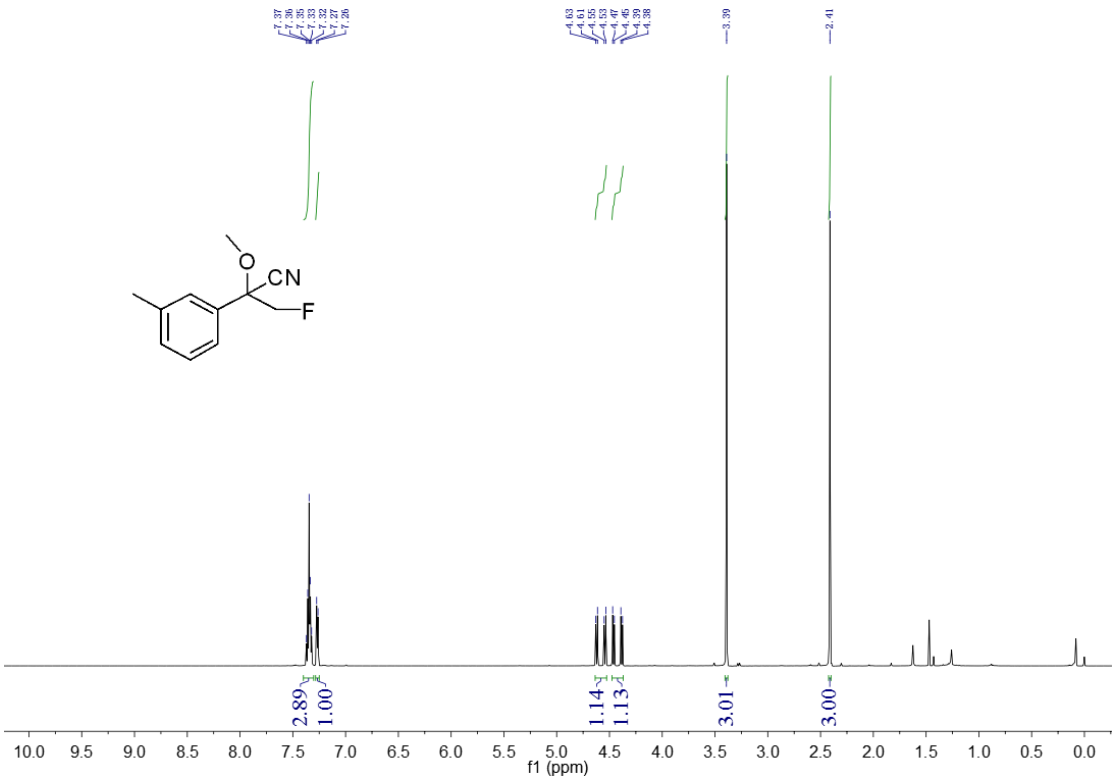


^{13}C NMR of **2j**

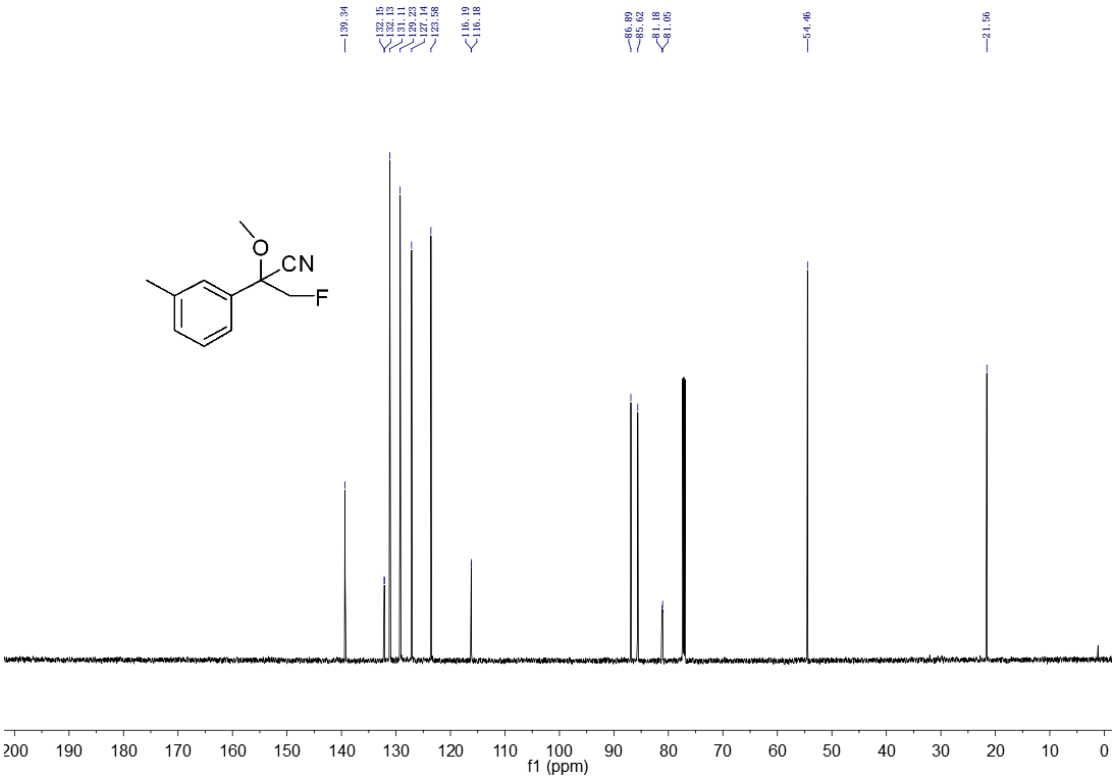


^{19}F NMR of **2j**

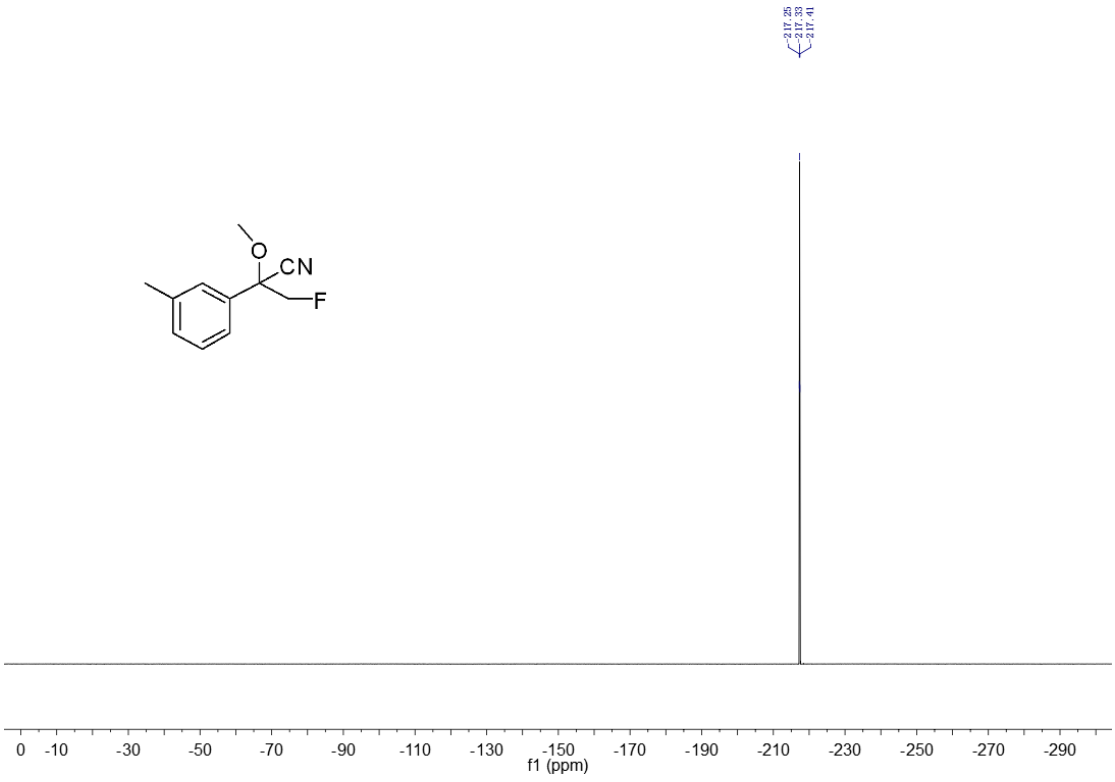
^{1}H NMR of **2k**



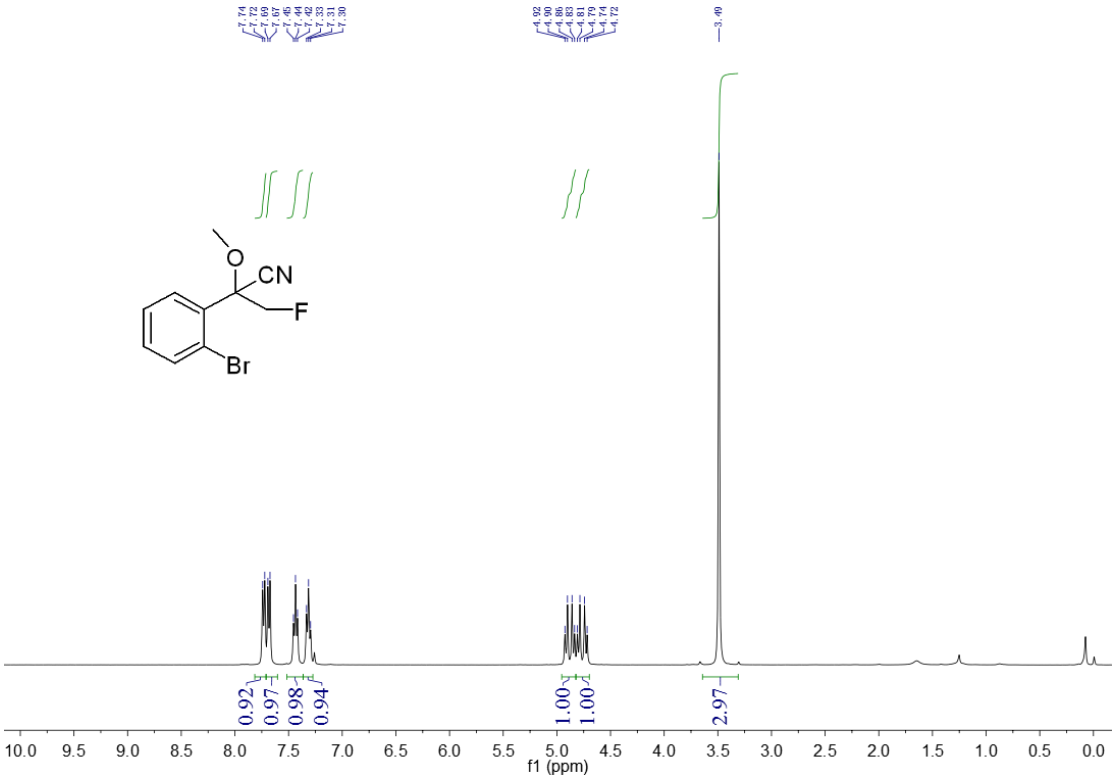
^{13}C NMR of **2k**



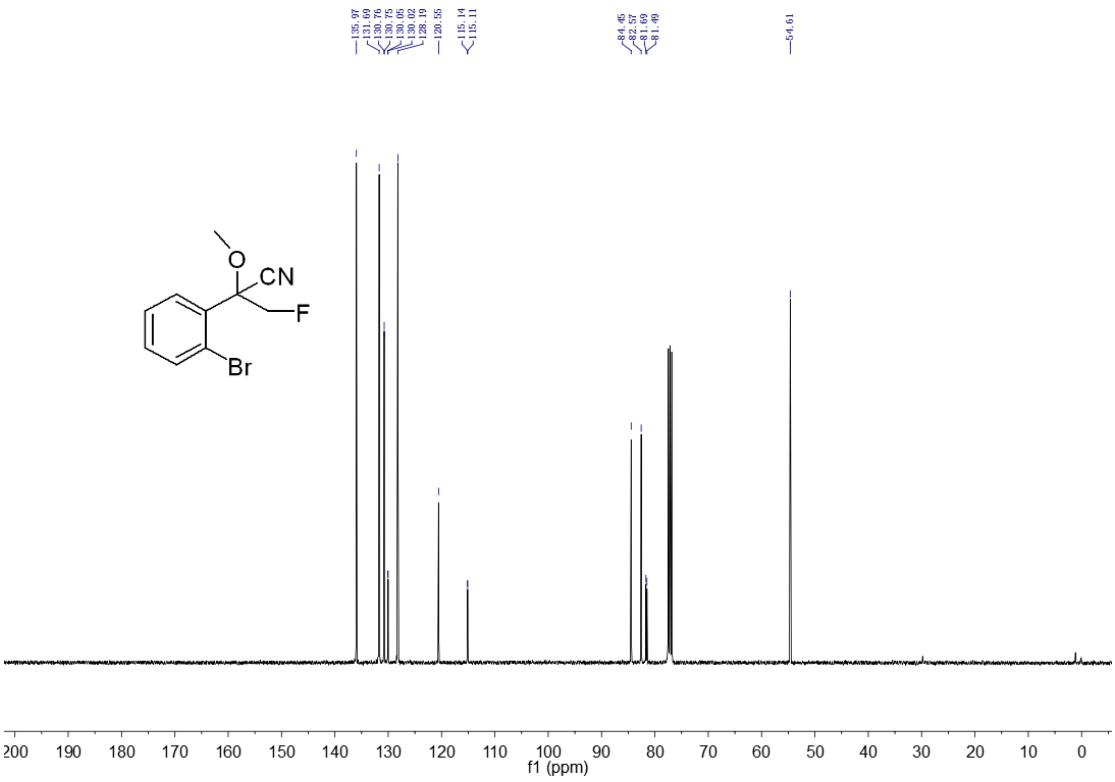
^{19}F NMR of **2k**



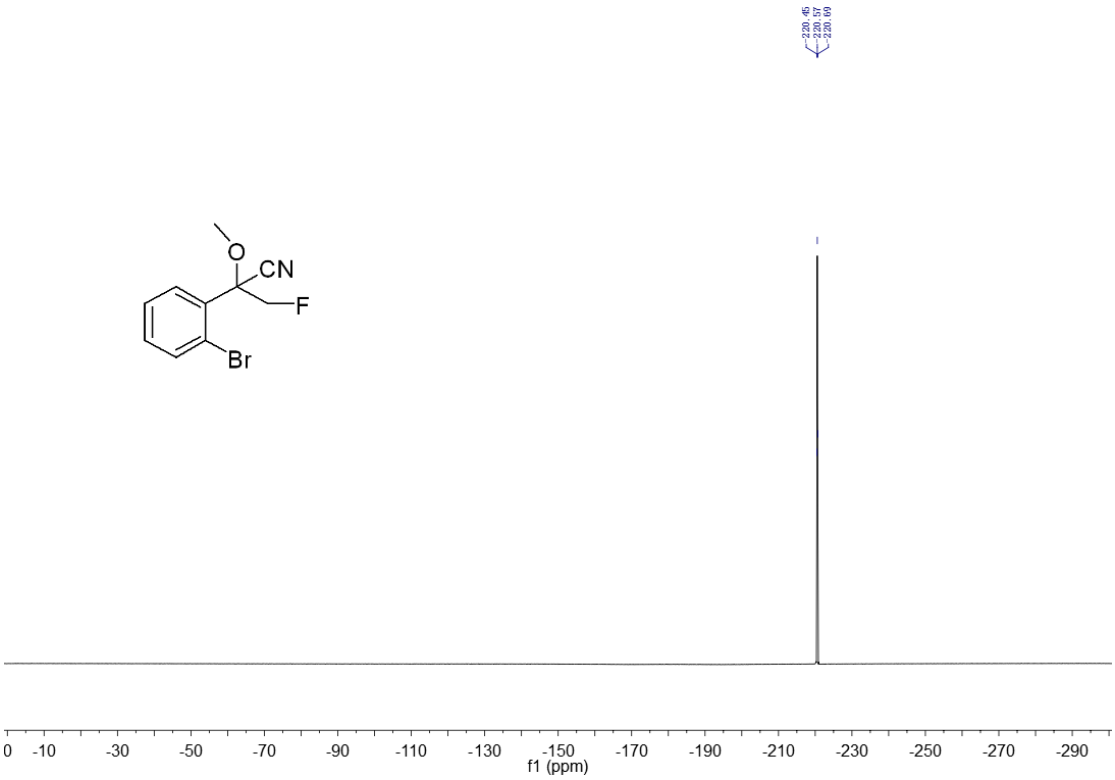
^{1}H NMR of **2l**



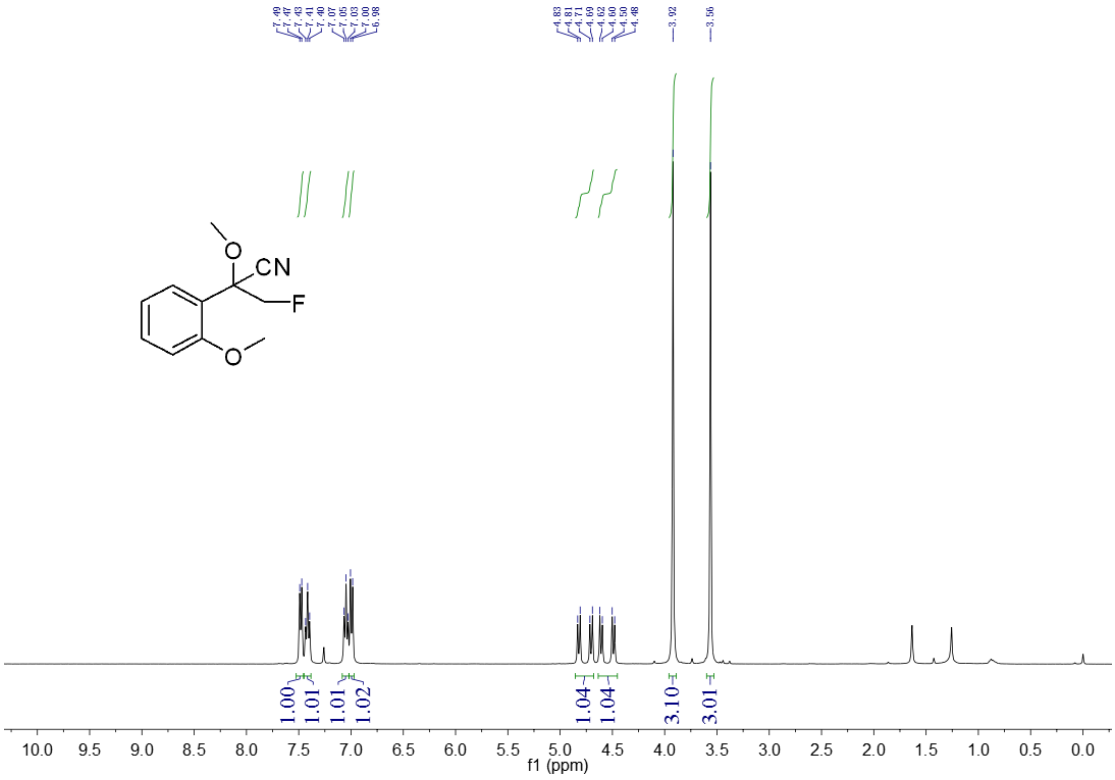
^{13}C NMR of **2l**



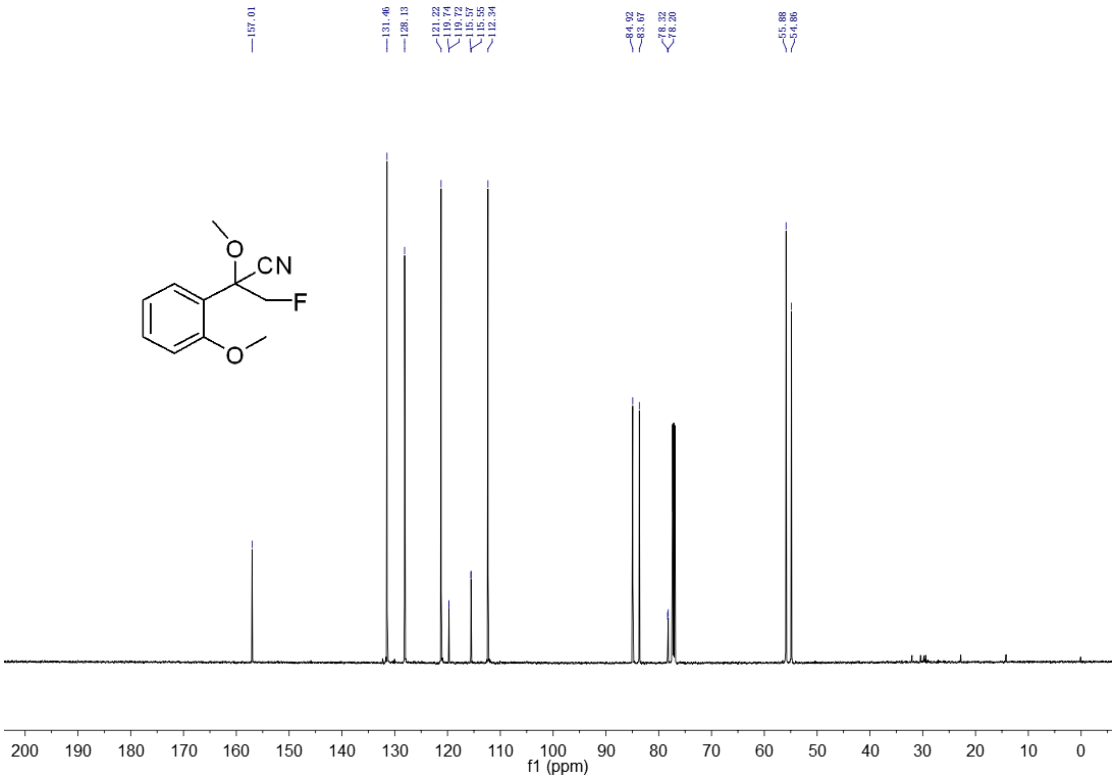
^{19}F NMR of **2l**



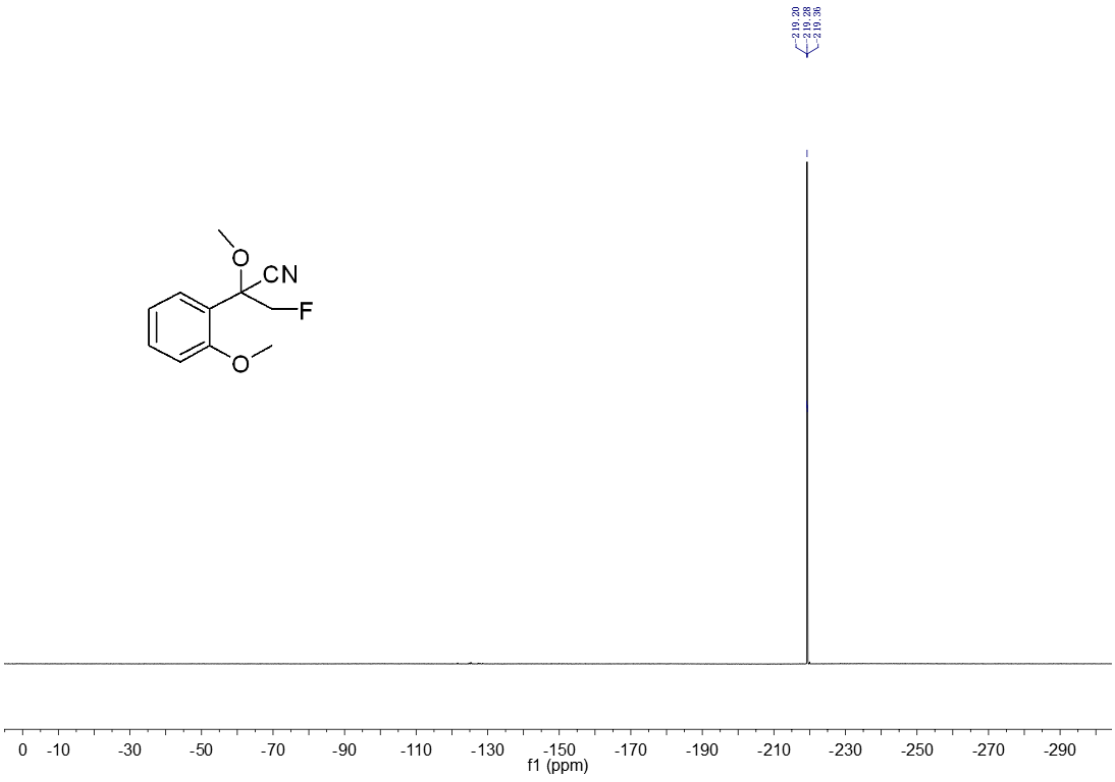
^{1}H NMR of **2m**



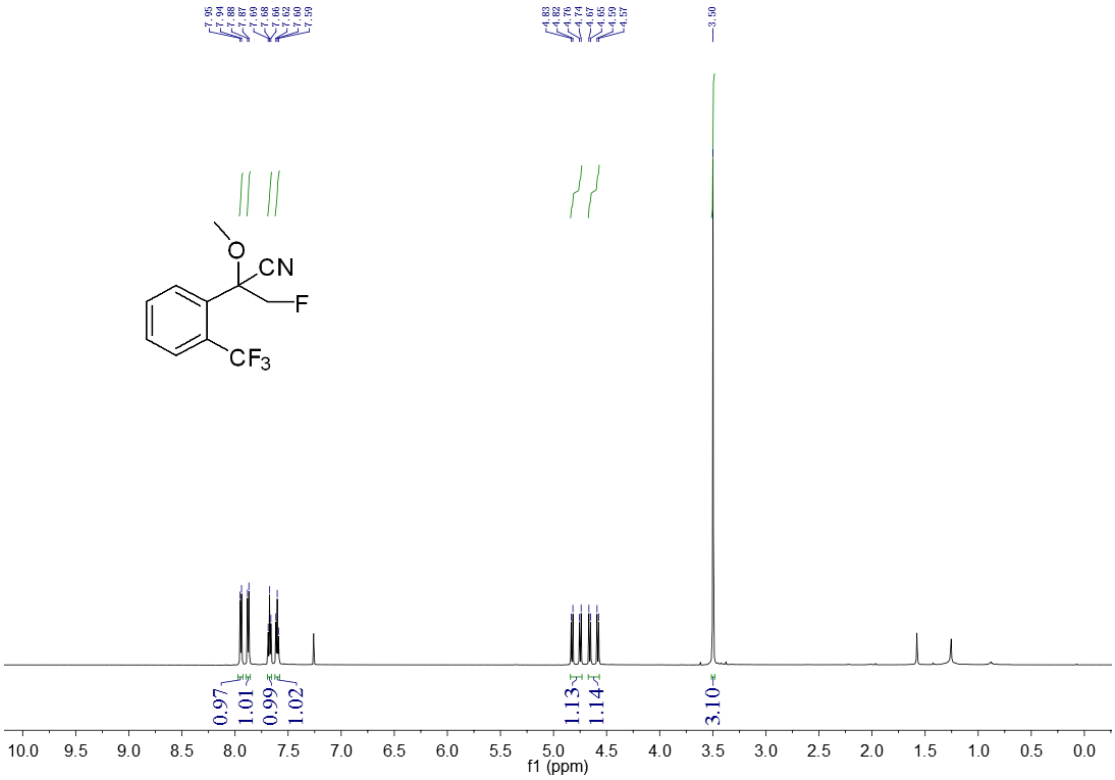
^{13}C NMR of **2m**



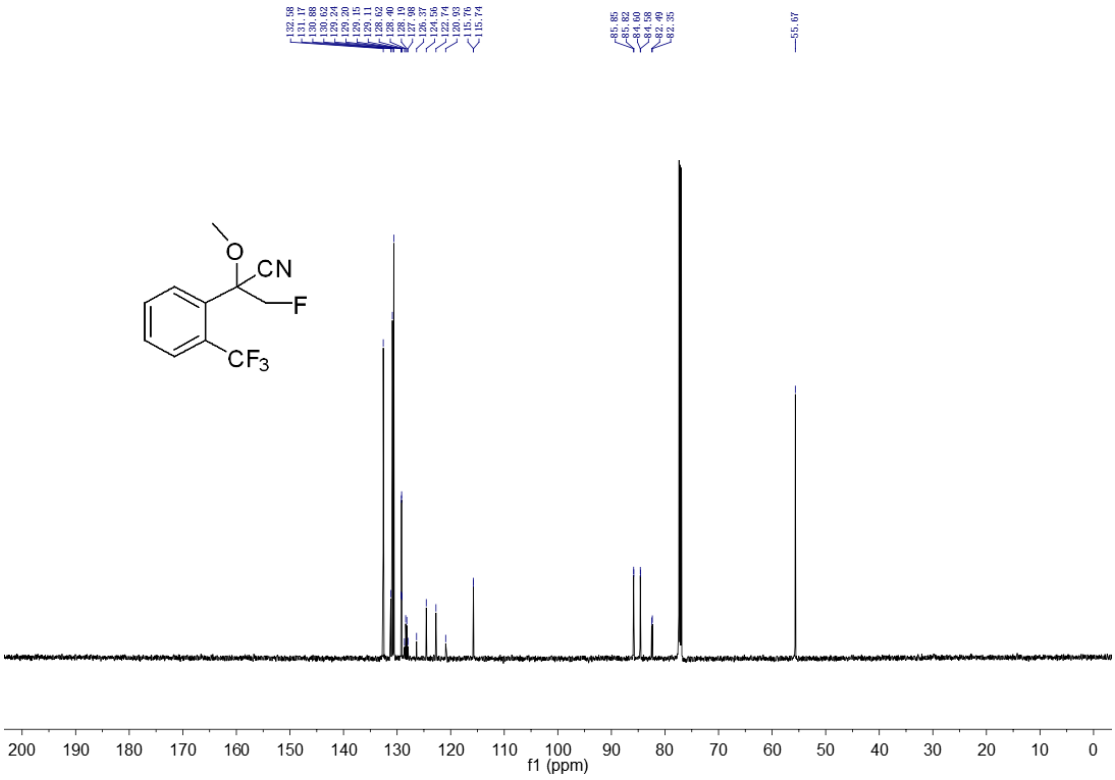
^{19}F NMR of **2m**



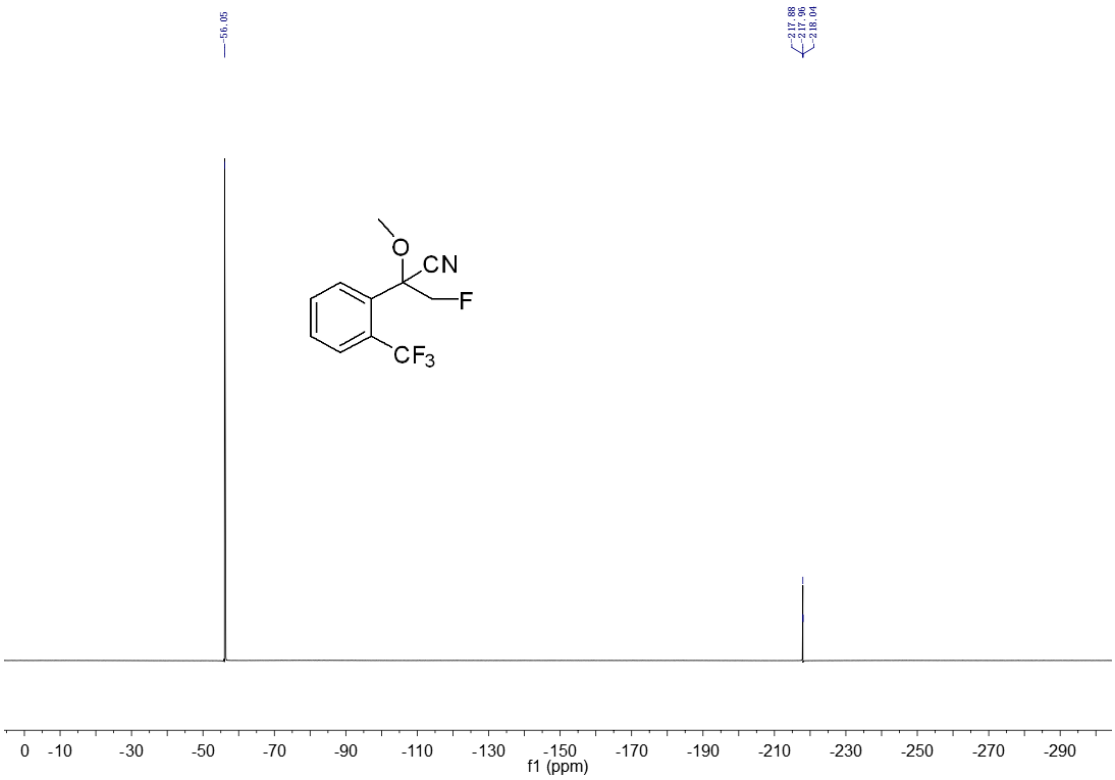
^{1}H NMR of **2n**



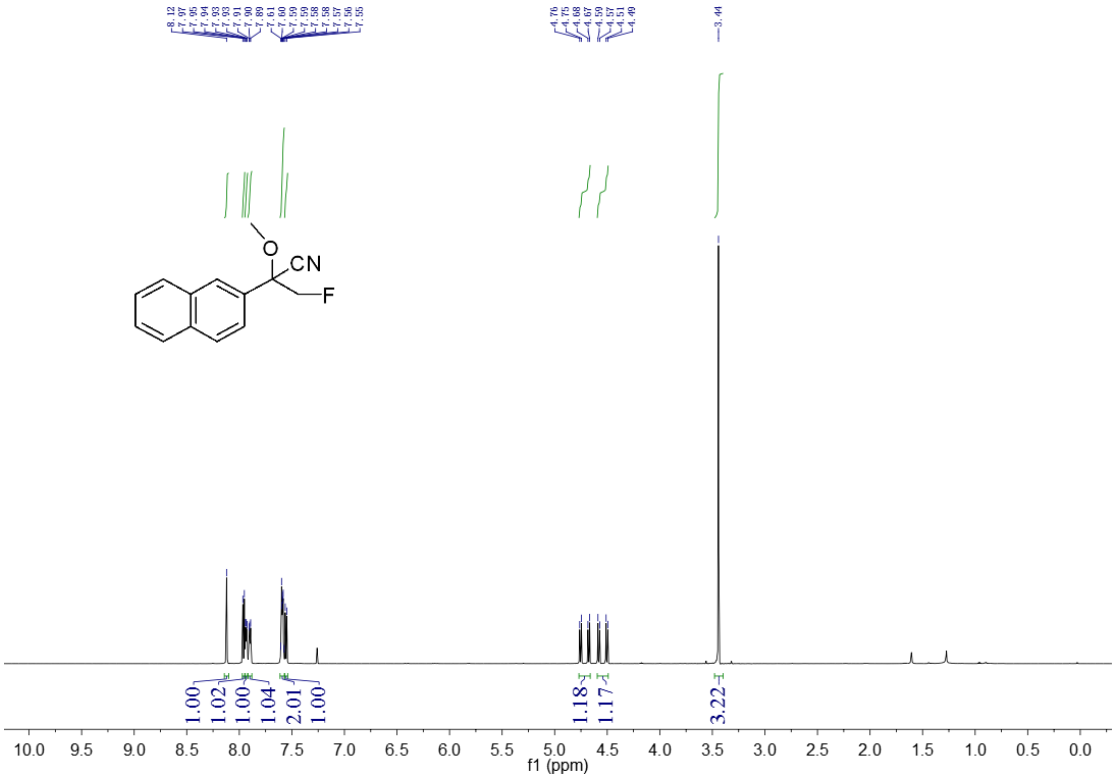
^{13}C NMR of **2n**



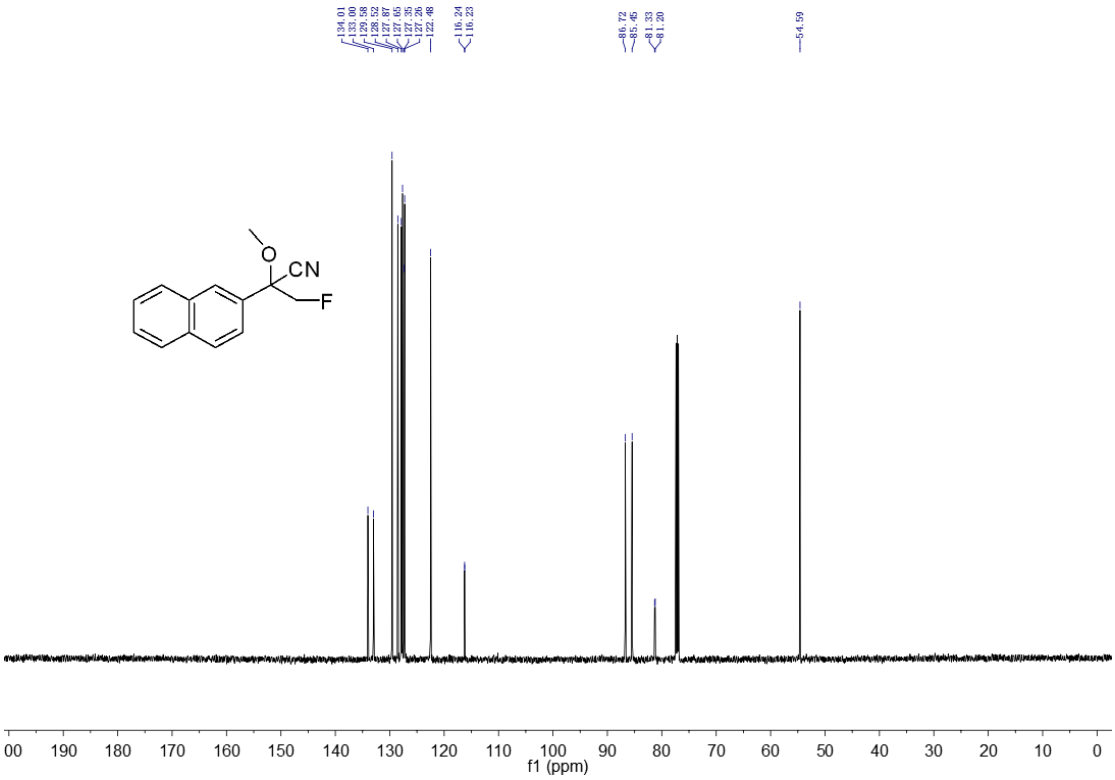
^{19}F NMR of **2n**



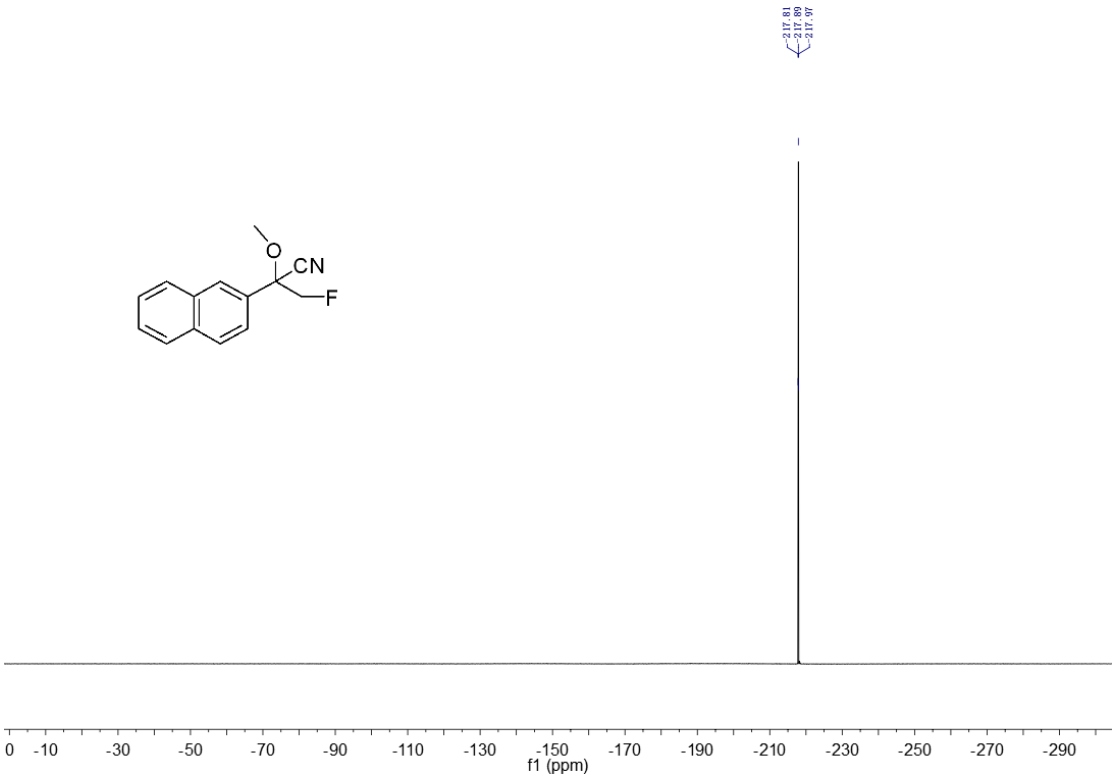
^{1}H NMR of **2o**



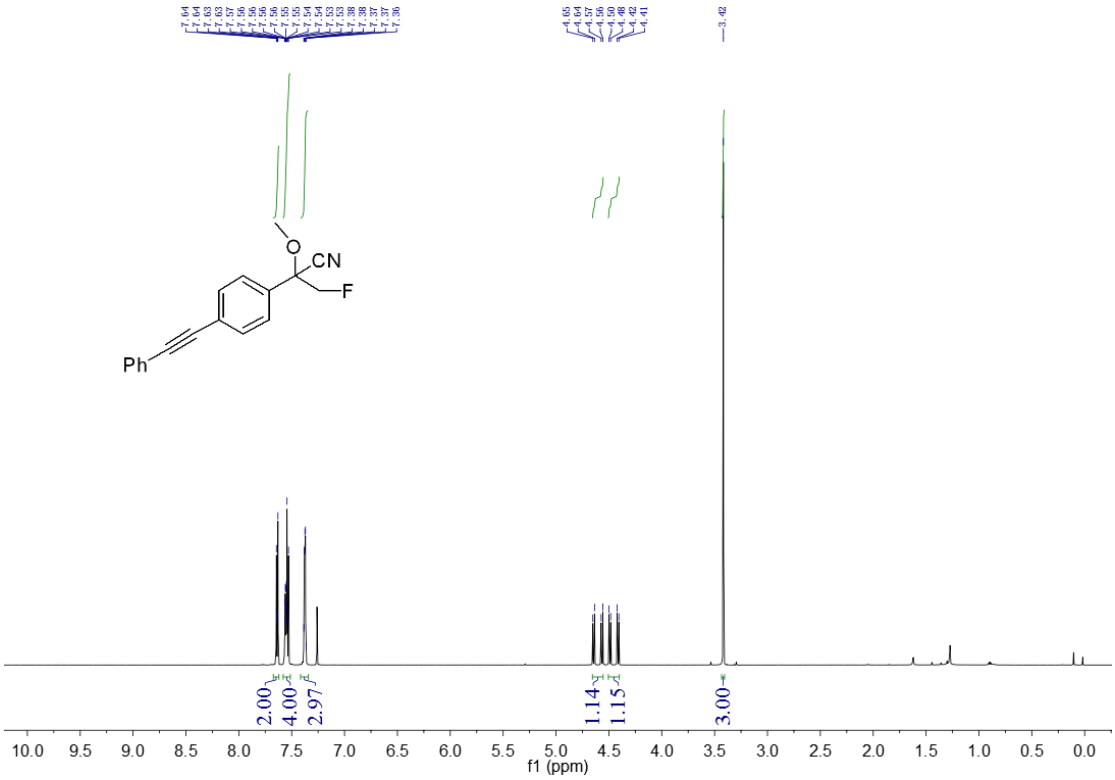
^{13}C NMR of **2o**



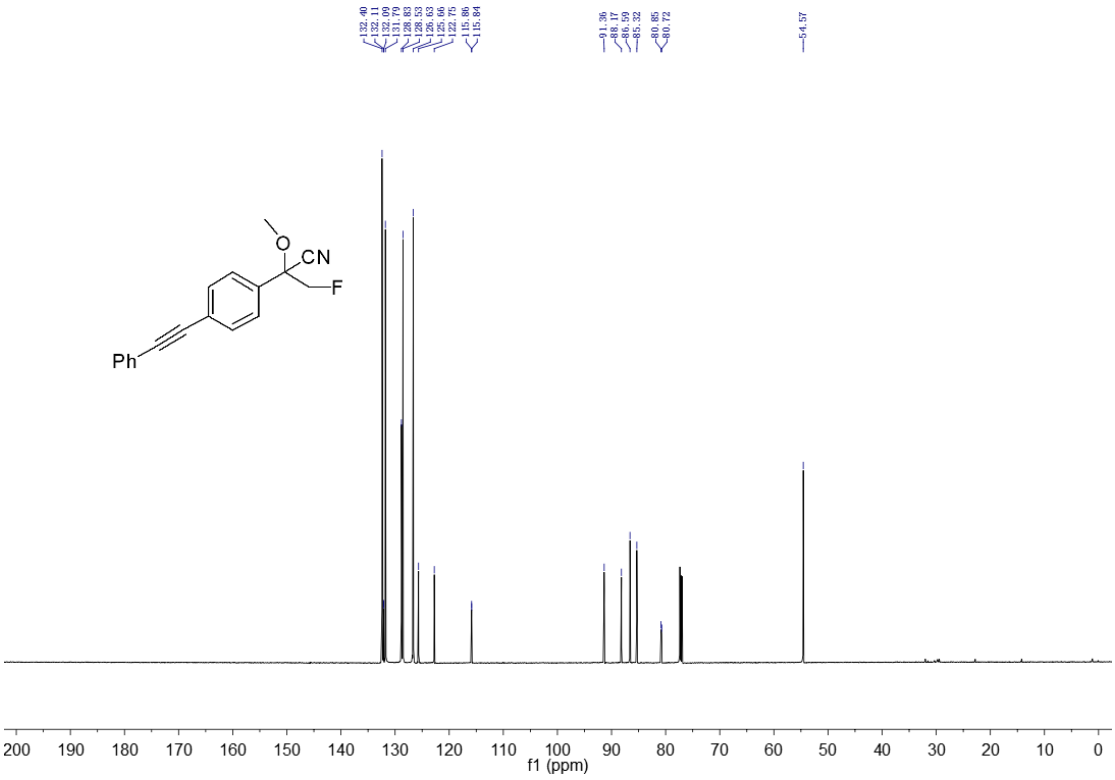
^{19}F NMR of **2o**



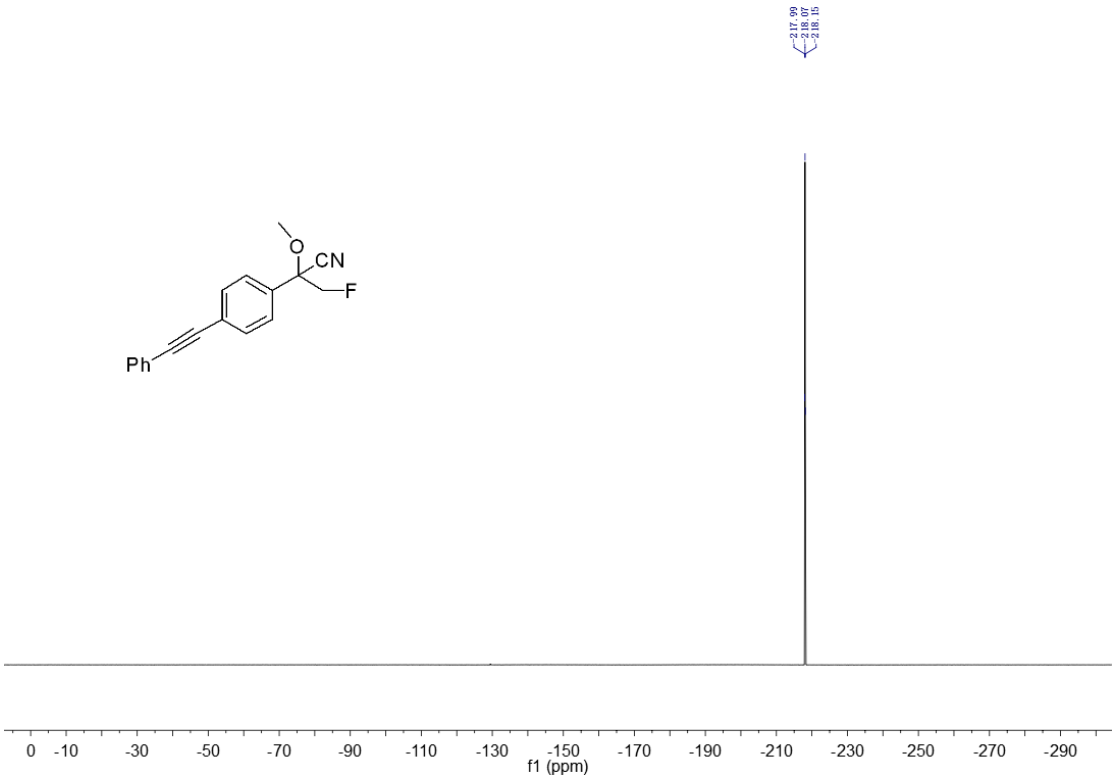
^{1}H NMR of **2p**



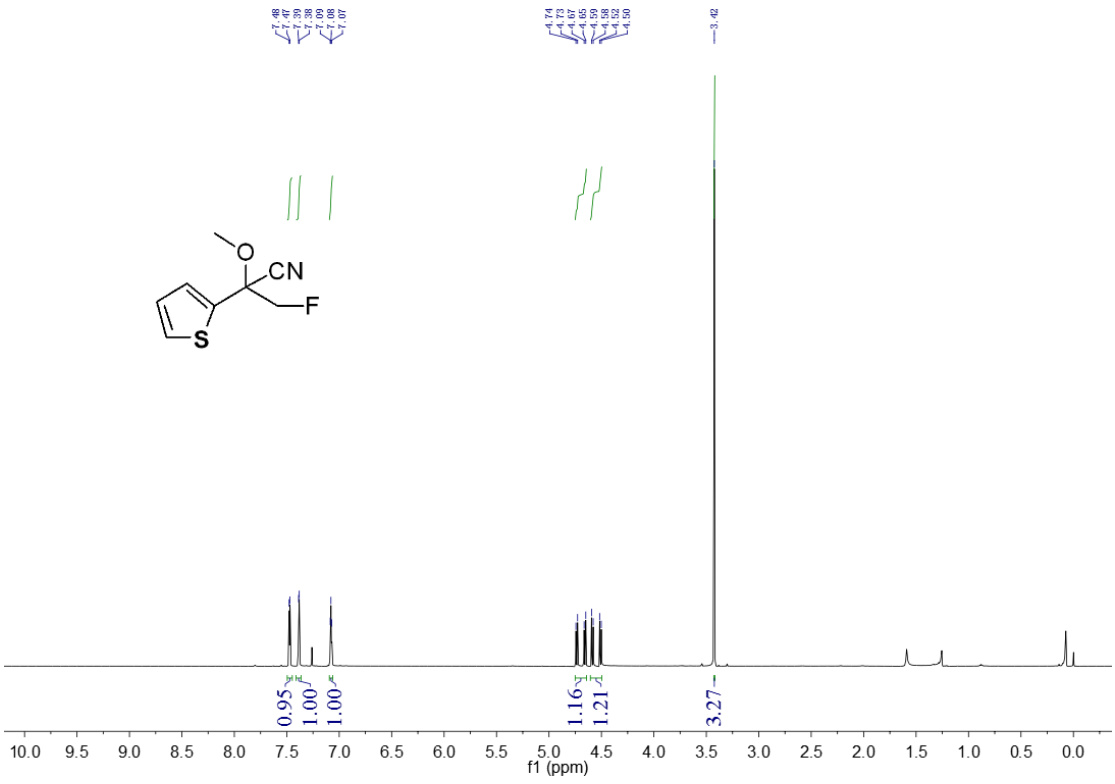
^{13}C NMR of **2p**



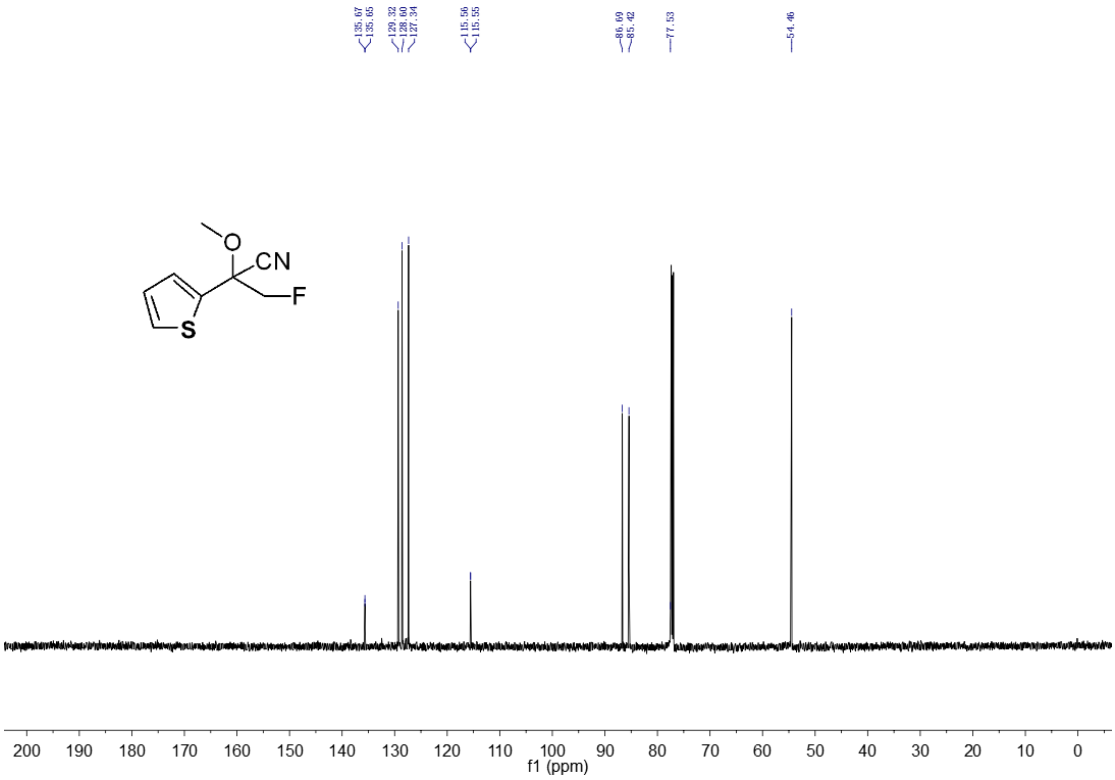
^{19}F NMR of **2p**



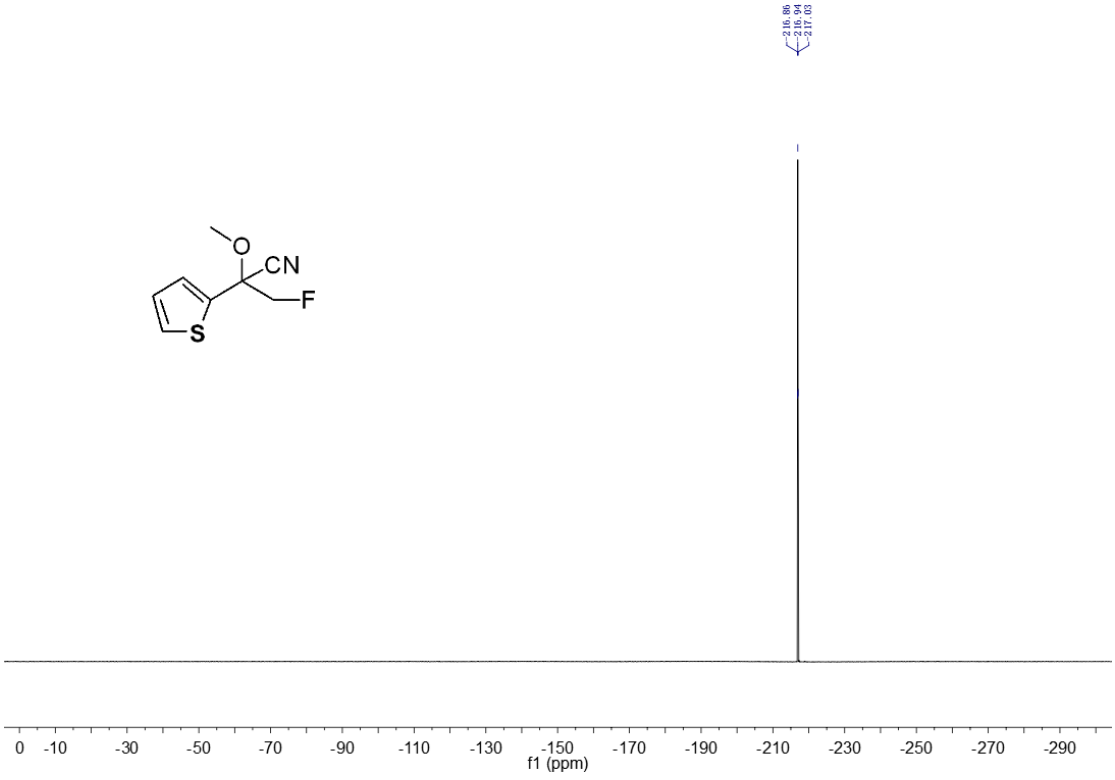
^{1}H NMR of **2q**



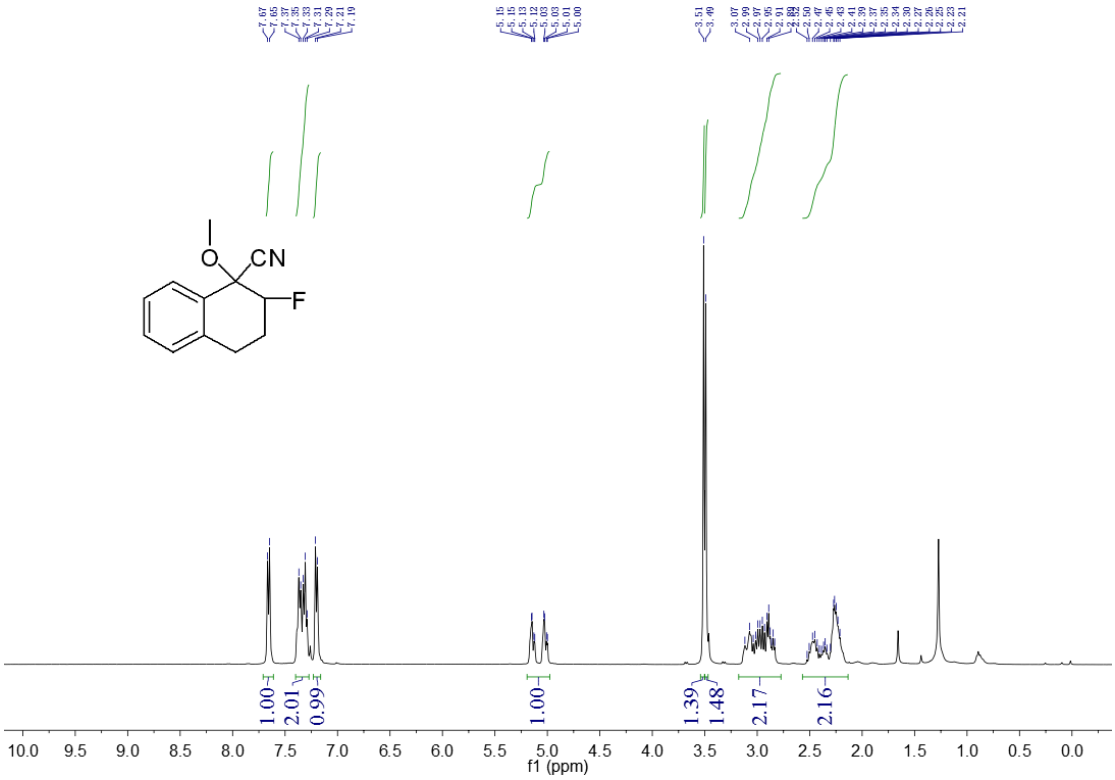
^{13}C NMR of **2q**



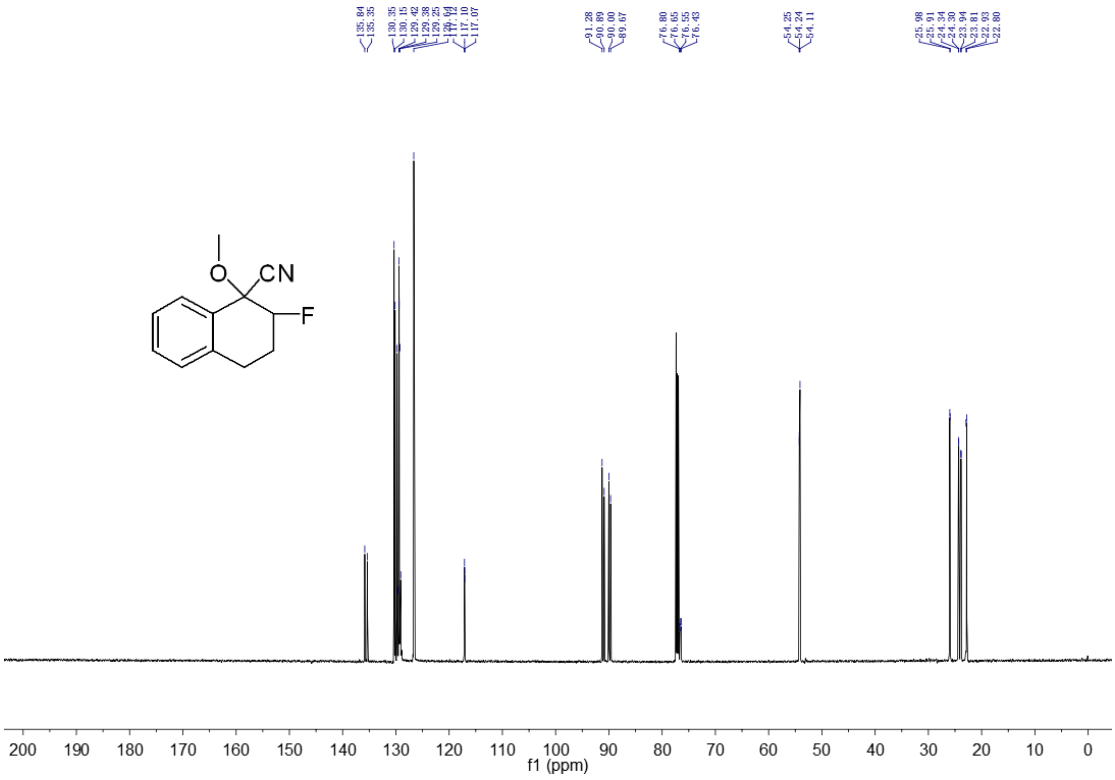
^{19}F NMR of **2q**



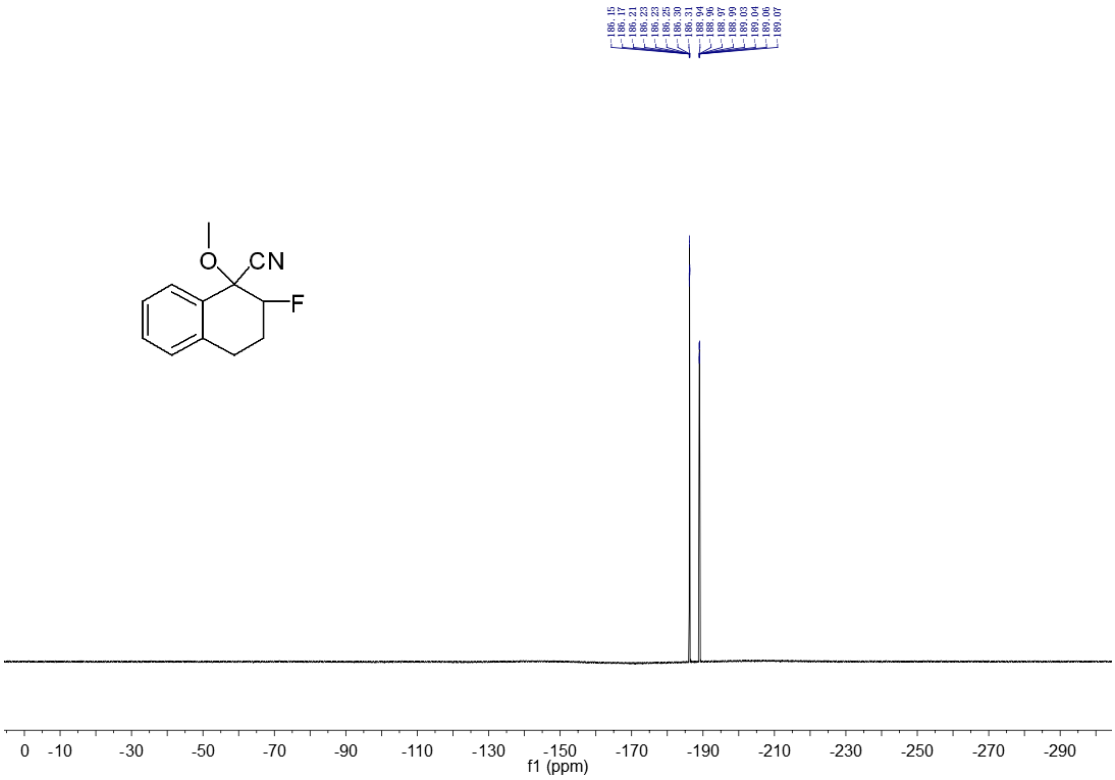
^{1}H NMR of **2r**



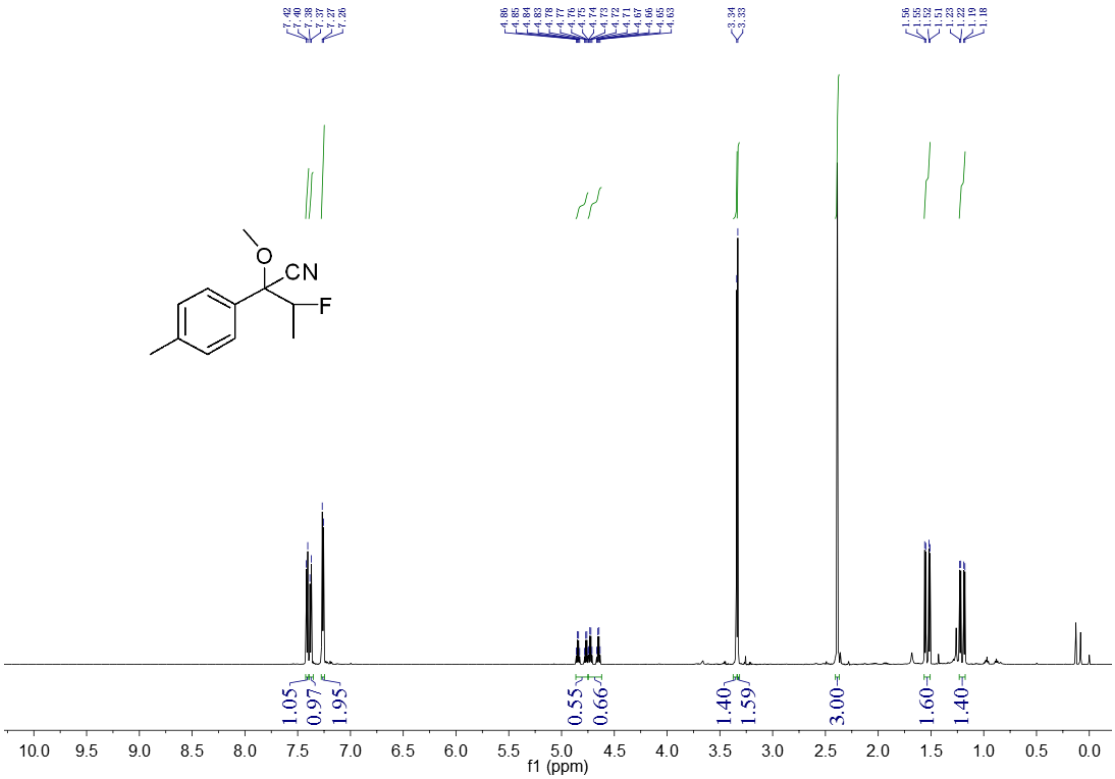
^{13}C NMR of **2r**



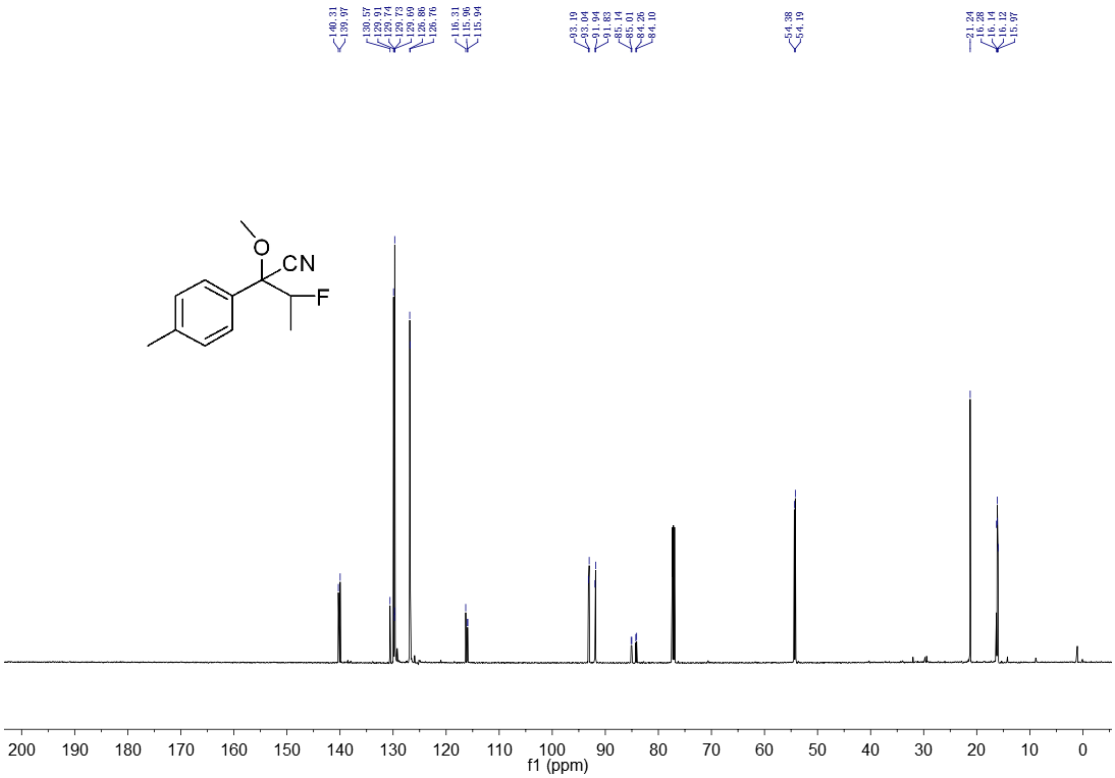
^{19}F NMR of **2r**



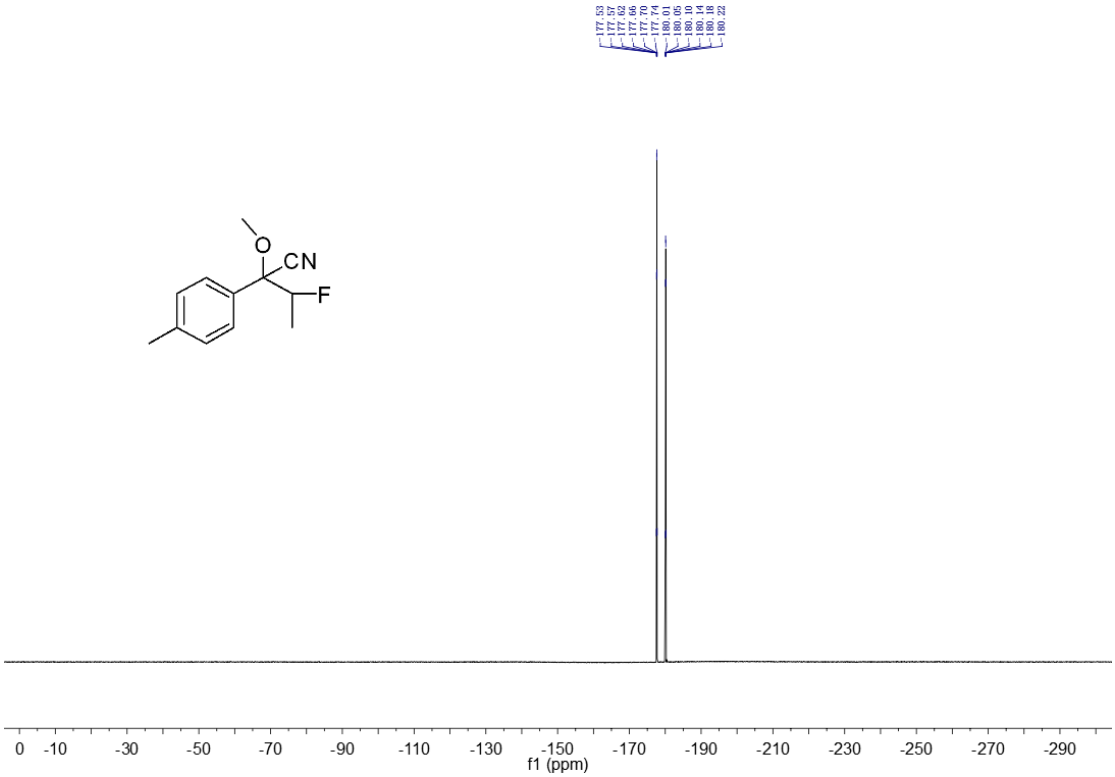
^{1}H NMR of **2s**



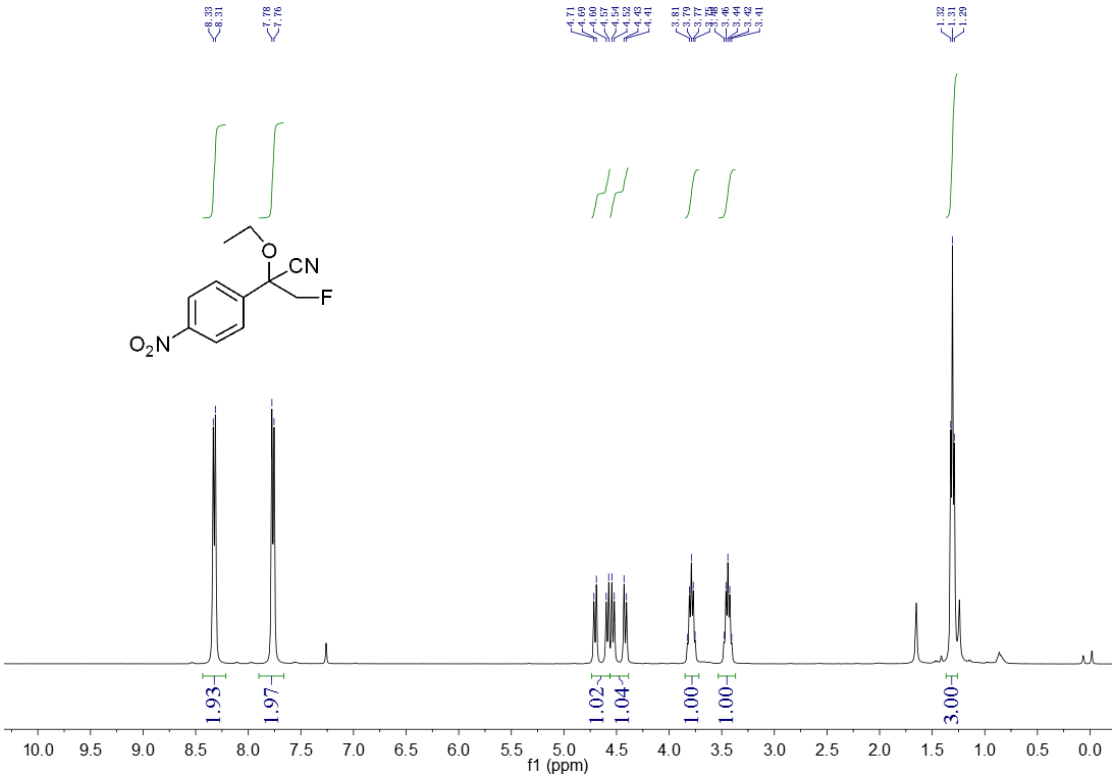
^{13}C NMR of **2s**



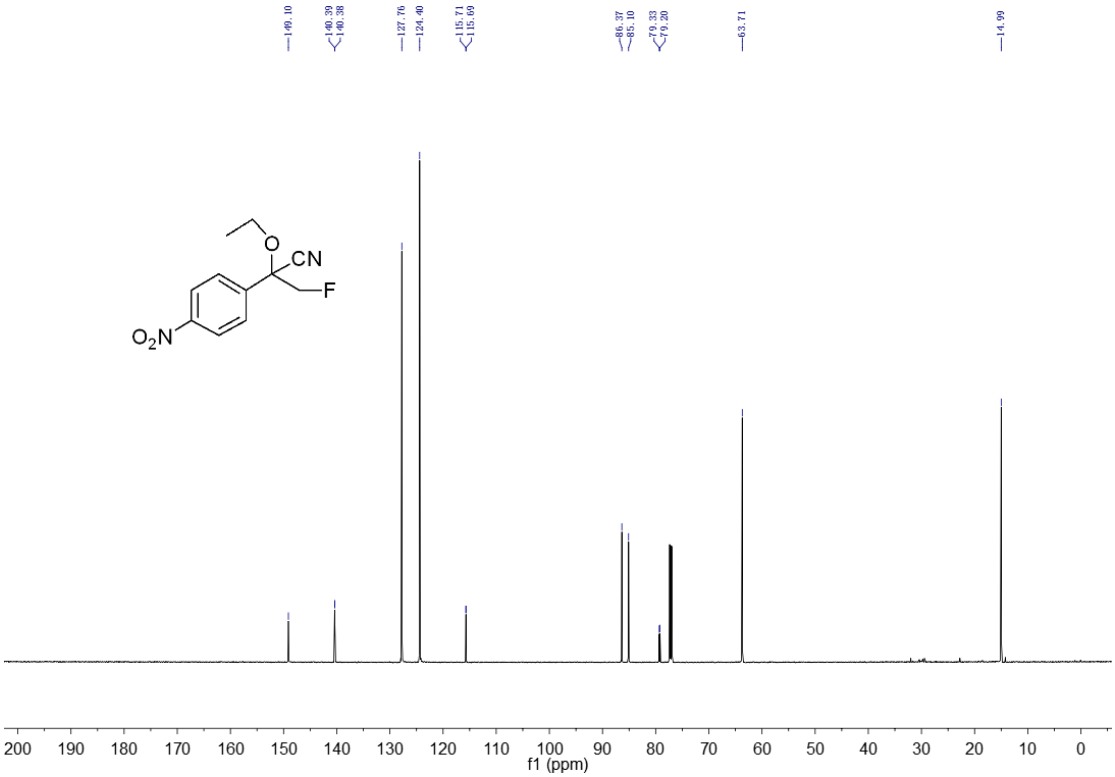
^{19}F NMR of **2s**



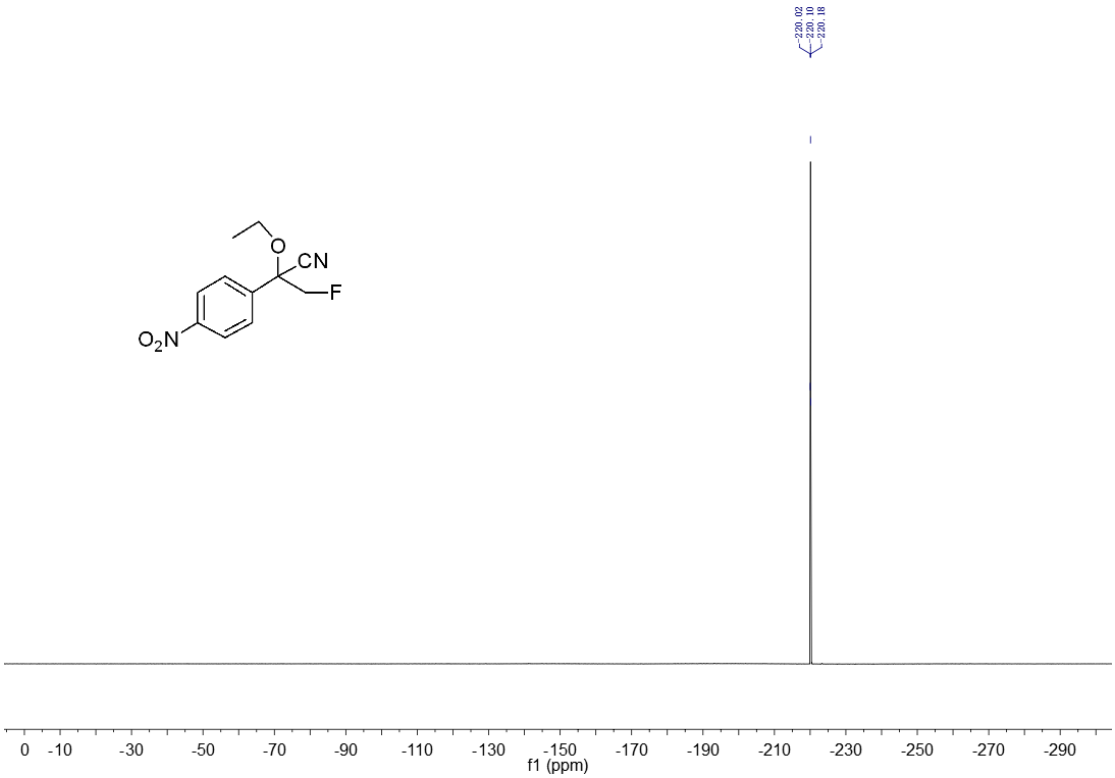
^{1}H NMR of **2t**



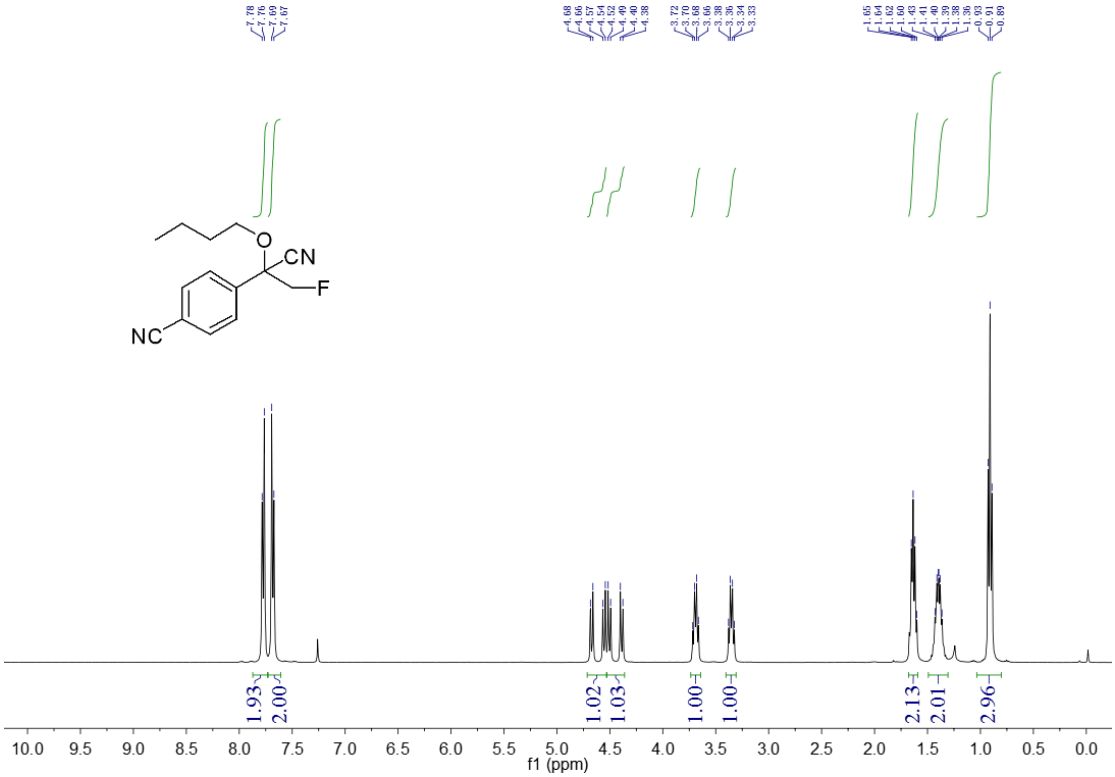
^{13}C NMR of **2t**



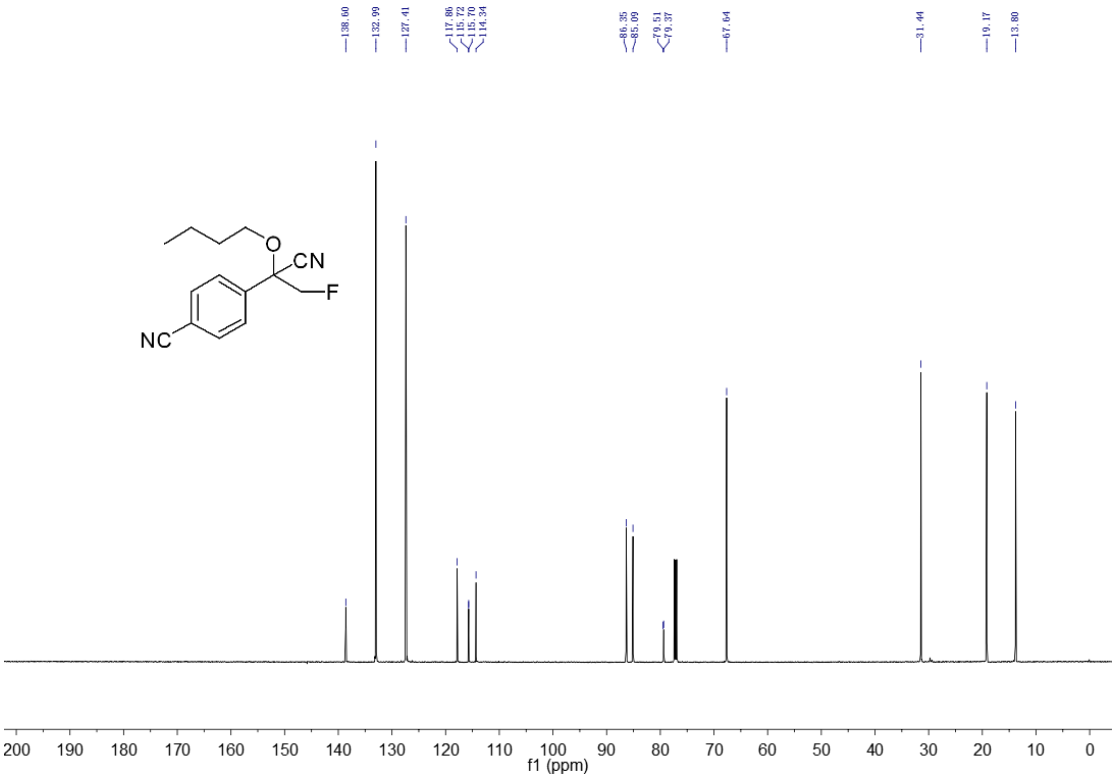
^{19}F NMR of **2t**



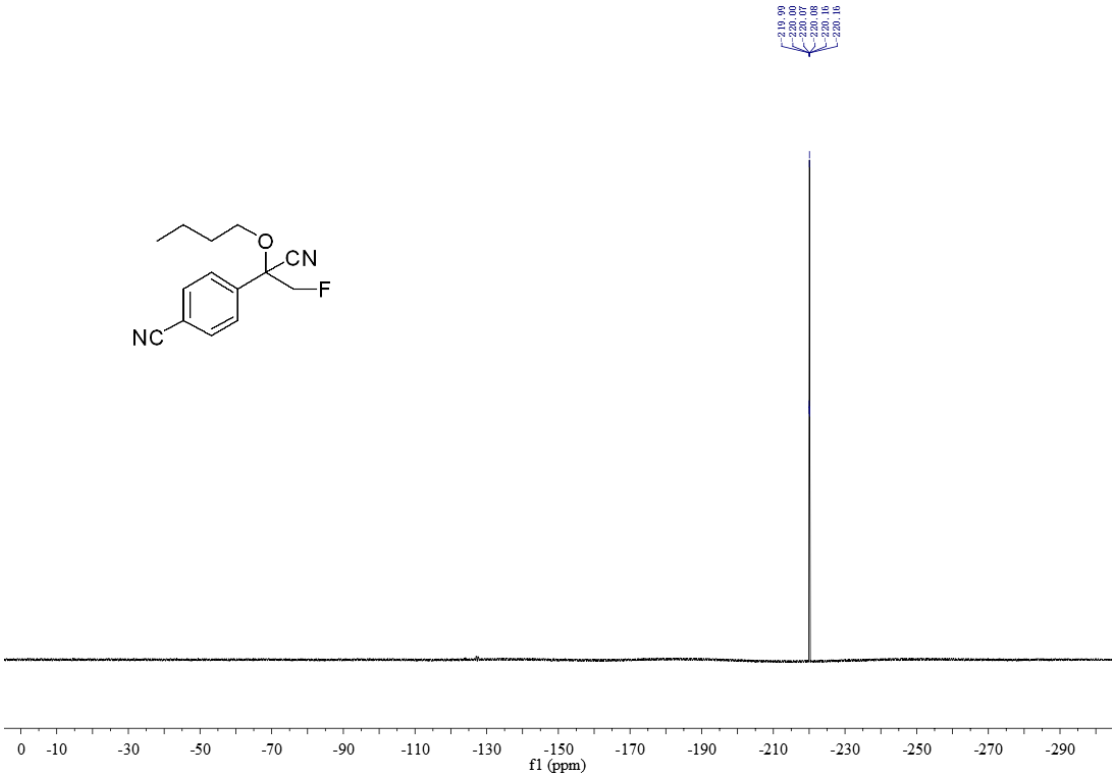
^{1}H NMR of **2u**



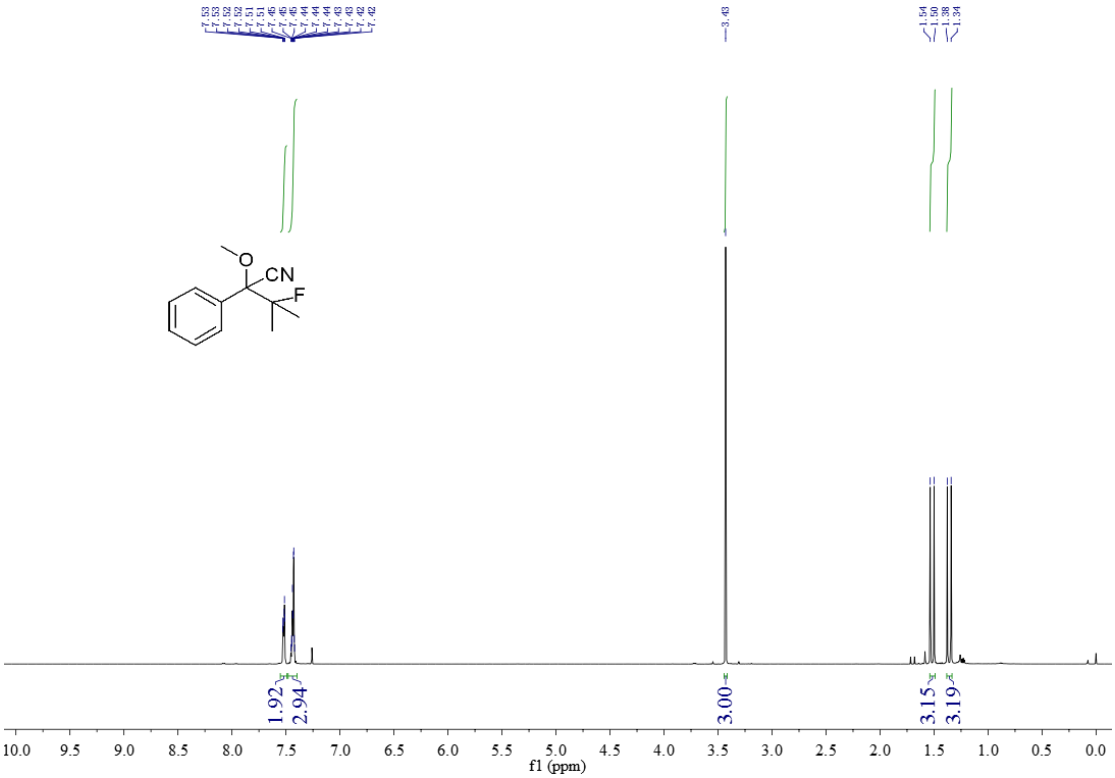
^{13}C NMR of **2u**



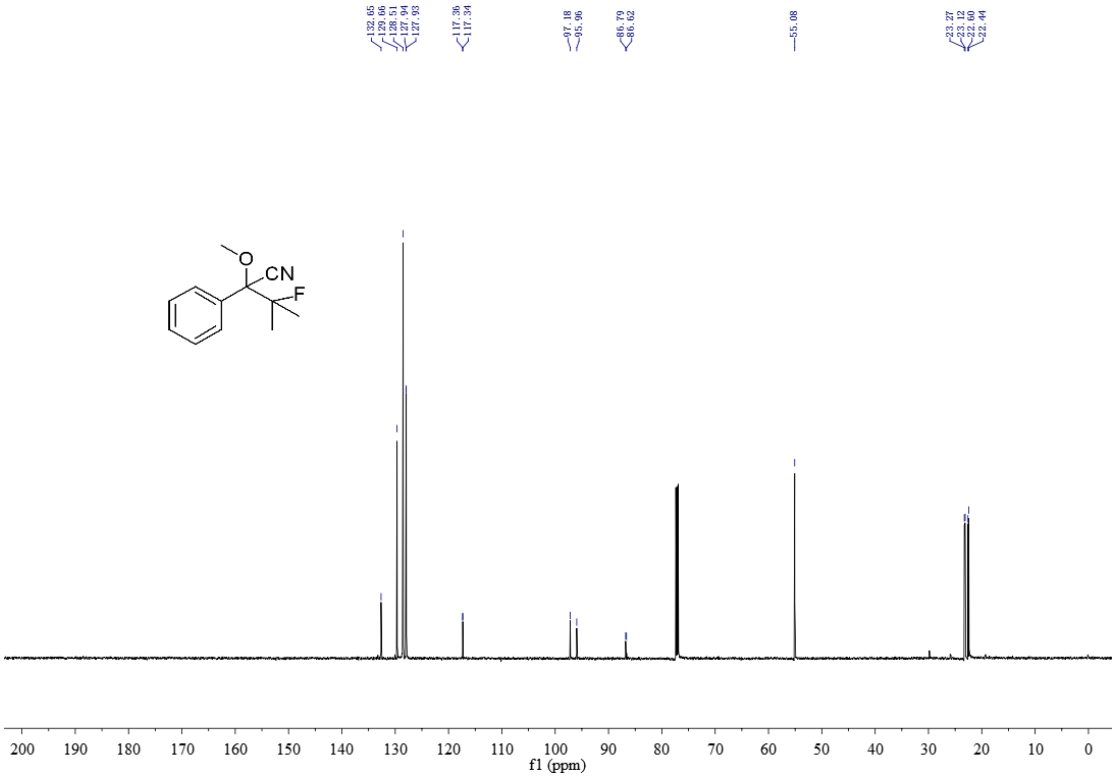
^{19}F NMR of **2u**



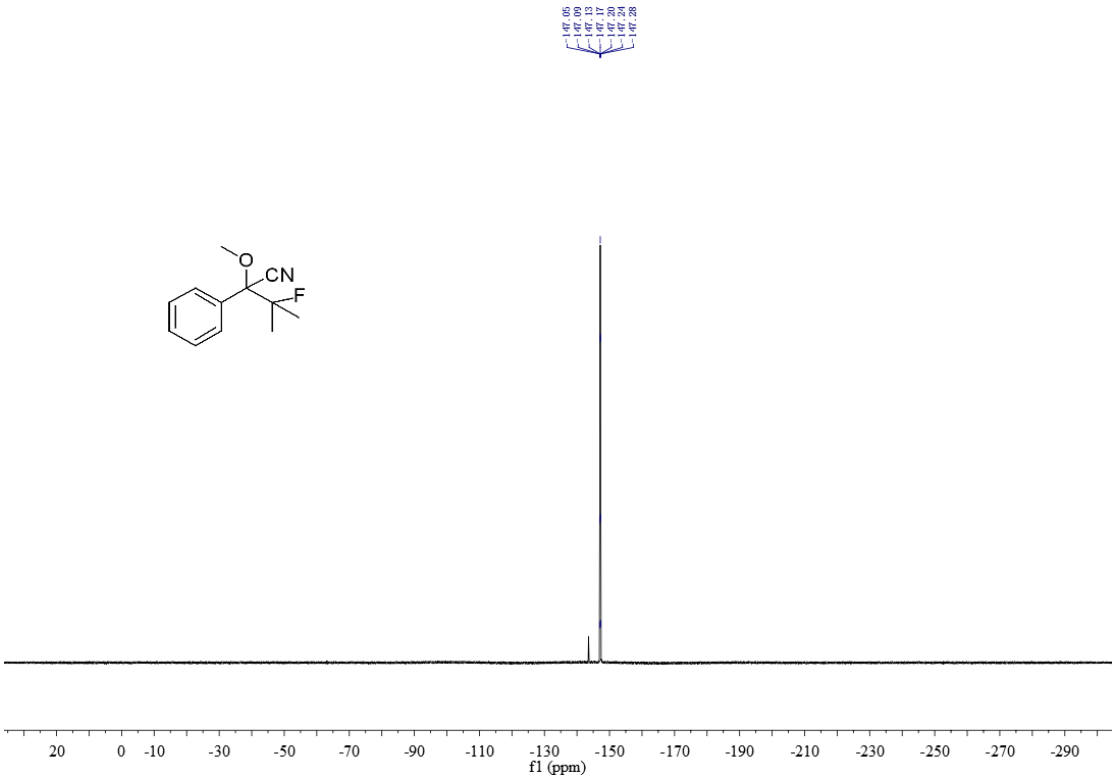
^{1}H NMR of **2v**



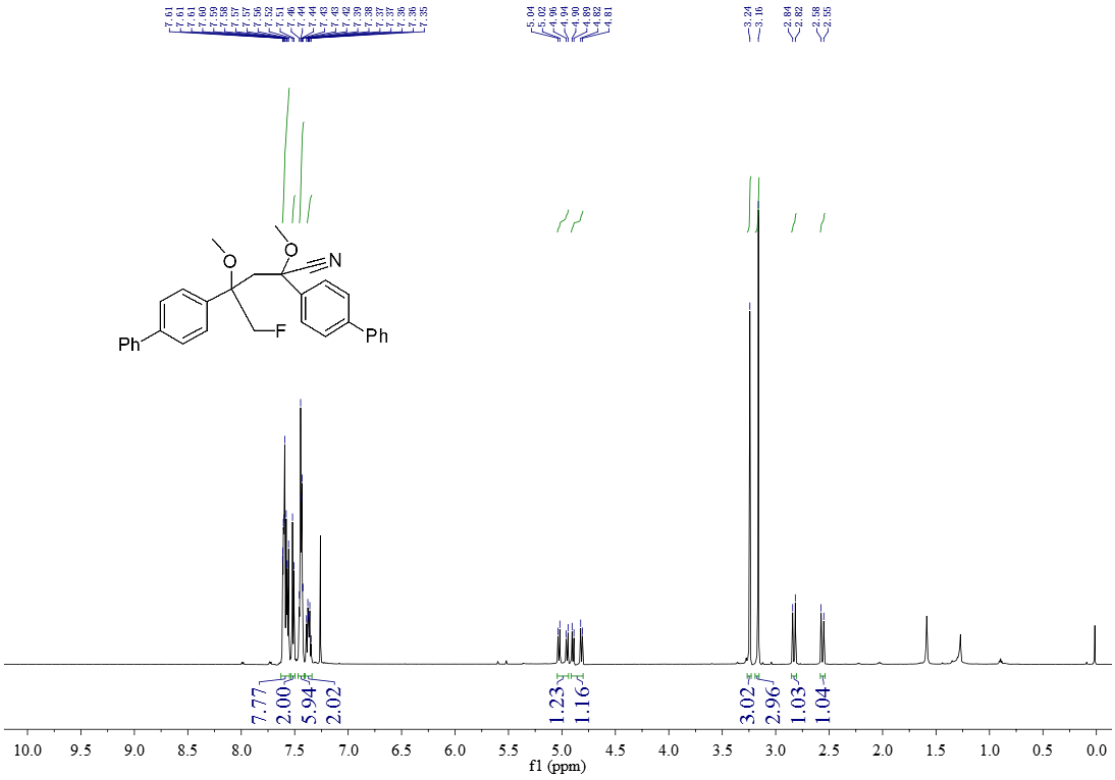
^{13}C NMR of **2v**



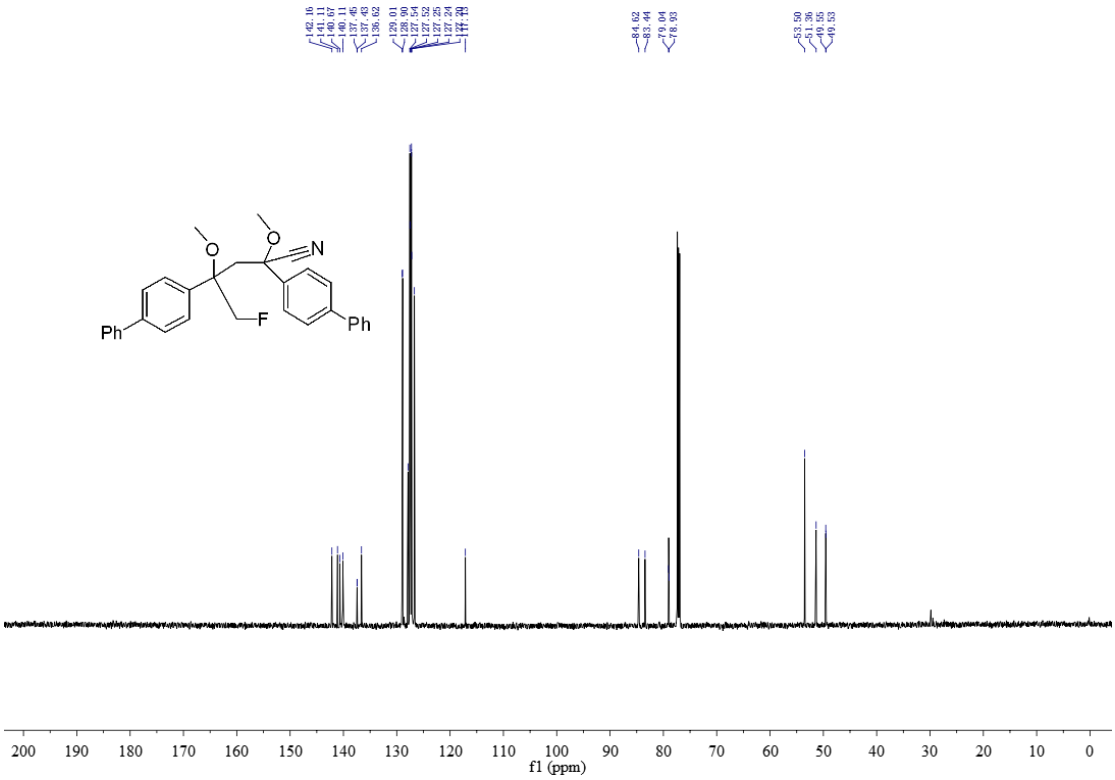
^{19}F NMR of **2v**



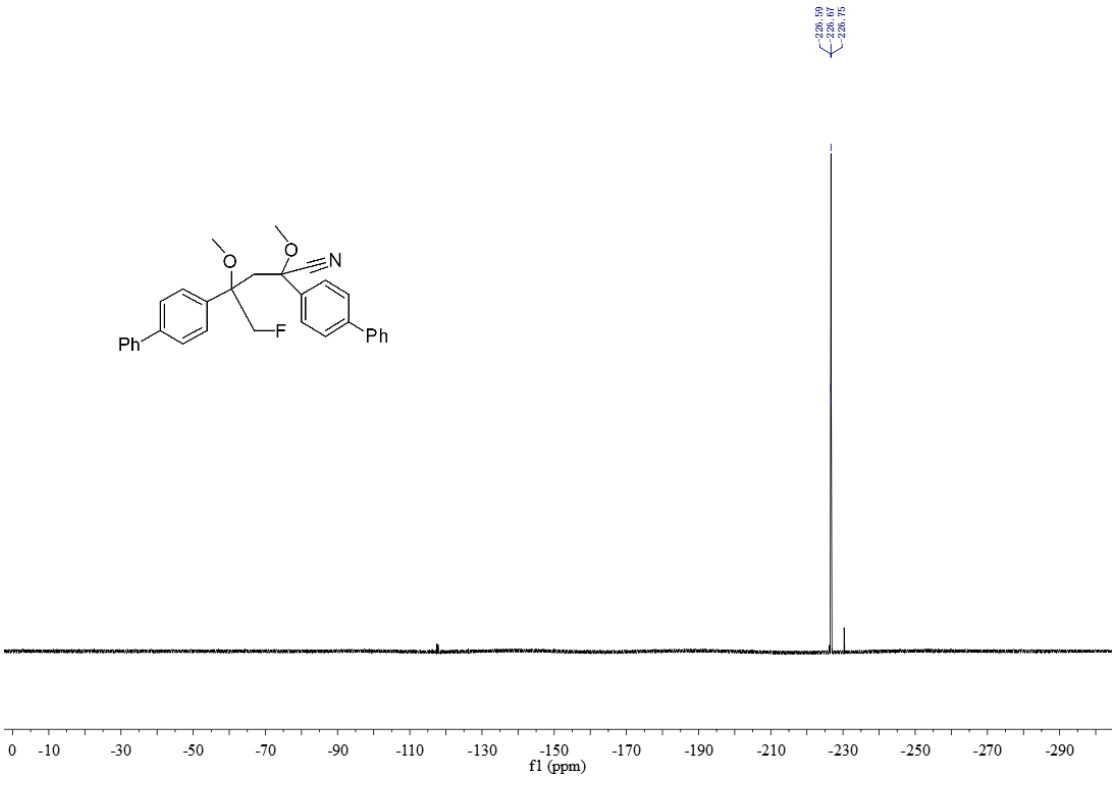
^{1}H NMR of **3a**



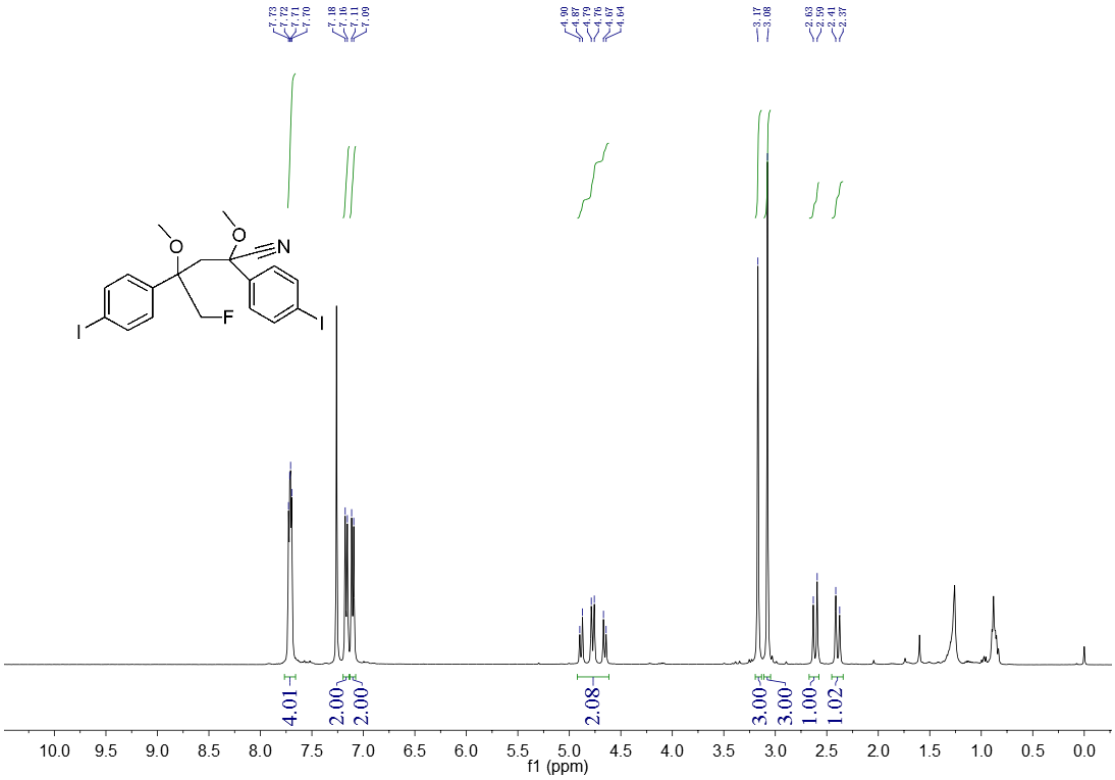
^{13}C NMR of **3a**



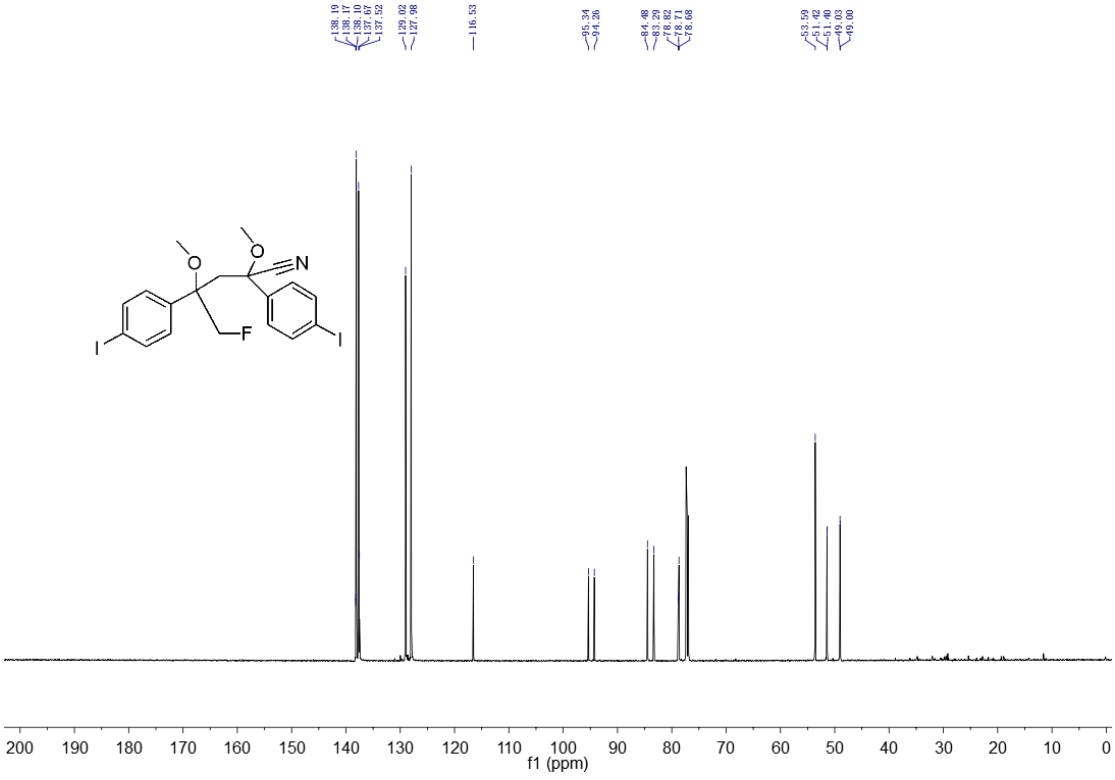
^{19}F NMR of **3a**



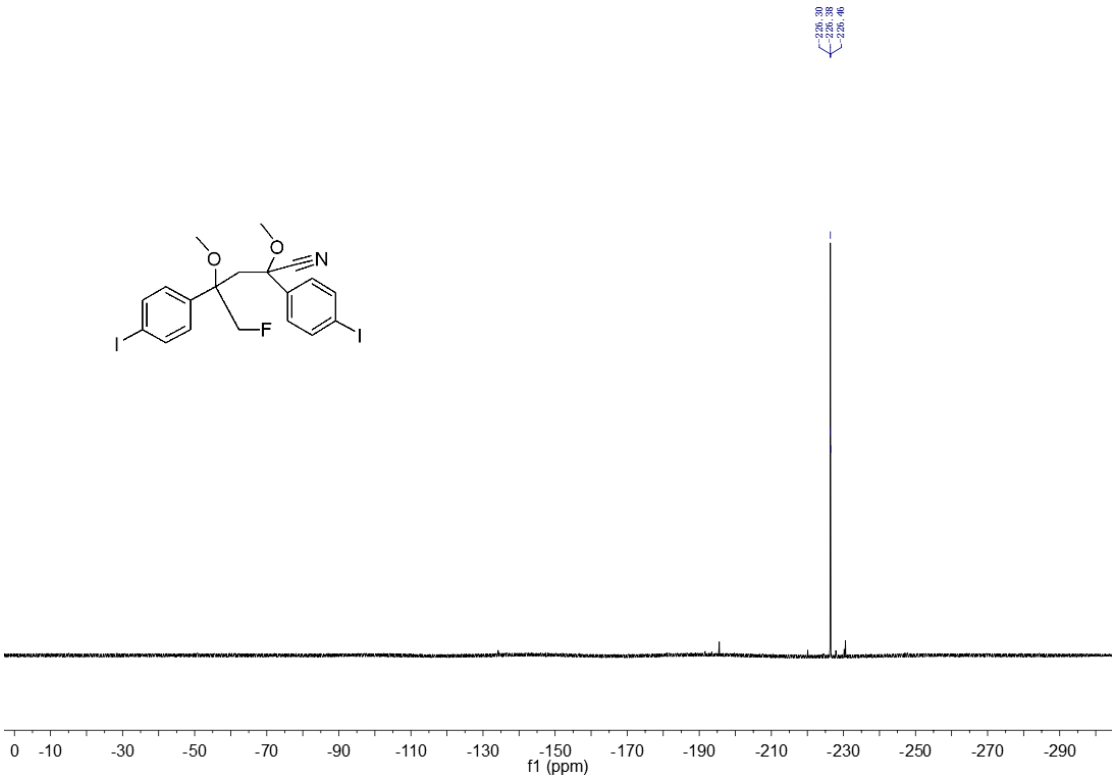
^{1}H NMR of **3b**



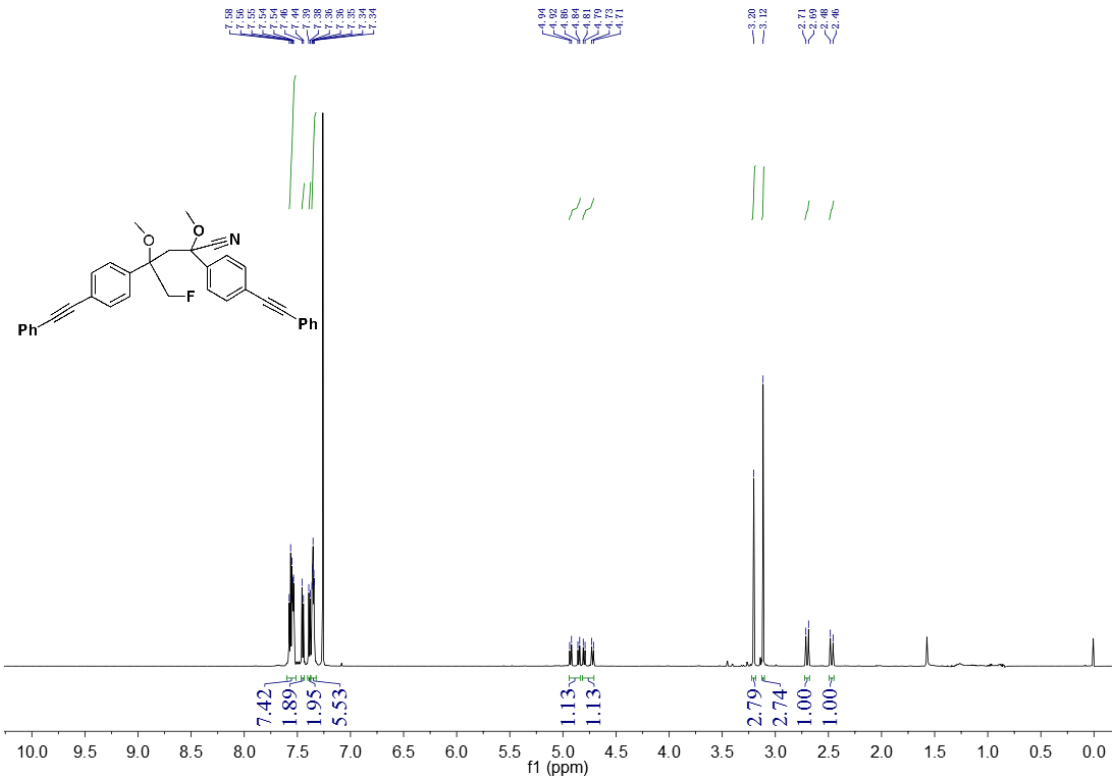
^{13}C NMR of **3b**



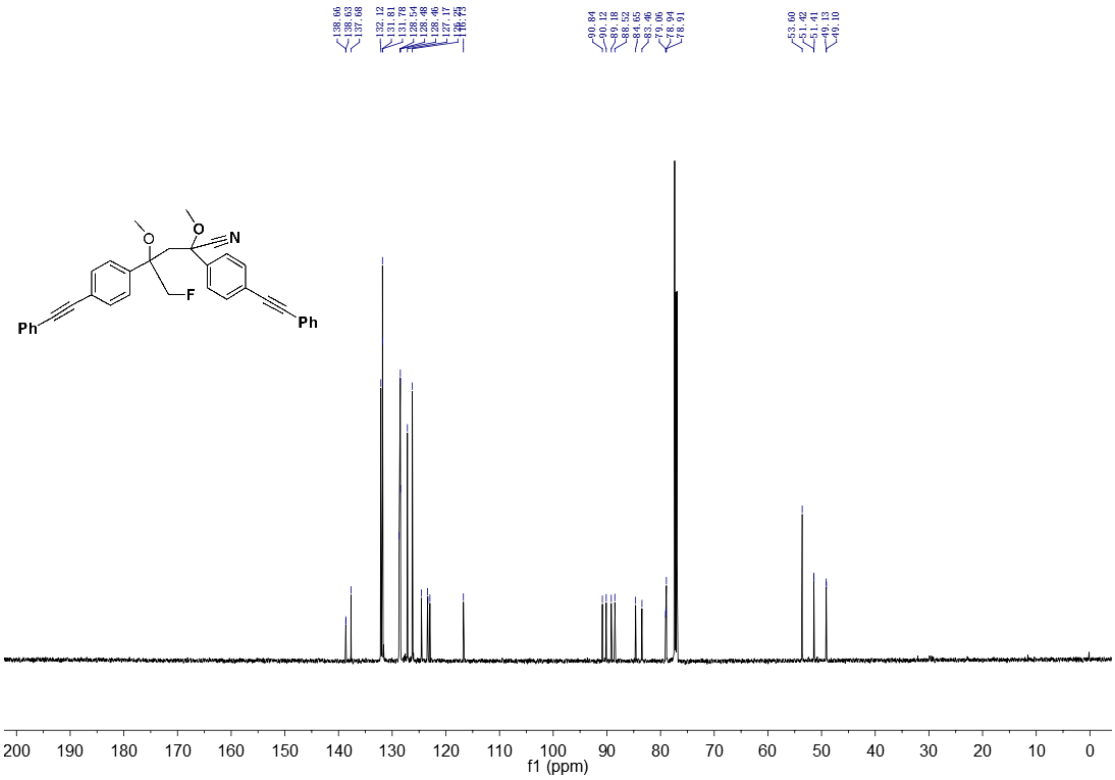
^{19}F NMR of **3b**



^{1}H NMR of **3c**



^{13}C NMR of **3c**



^{19}F NMR of **3c**