Supporting Information

for

Deoxyfluorination of alcohols with aryl fluorosulfonates

Xiu Wang,[a,‡] Min Zhou,[a,‡] Qinghe Liu,[a,‡] Chuanfa Ni,[a] Zhongbo Fei,[b,†] Wei Li,[b] and Jinbo Hu[a,*]

[a] *Key Laboratory of Organofluorine Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Ling-Ling Road, Shanghai 200032, China*

E-mail: jinbohu@sioc.ac.cn

[b] *Chemical and Analytical Development, Suzhou Novartis Pharma Technology Co., Ltd. Changshu, Jiangsu Province 215537, P.R. China*

[†] *Current Address: Suli Pharmaceutical Technology Jiangyin Co., Ltd. Pudong District, Shanghai, 201318, P.R. China. Orcid.org/0000-0002-5980-4017*

[‡] These authors contributed equally to this work.

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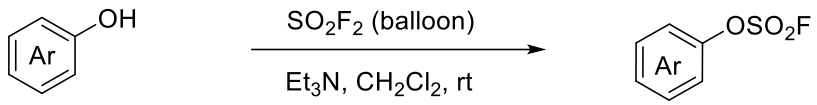
1. General Information

Unless otherwise mentioned, reagents were purchased from commercial sources and used without further purification. Toluene ($PhCH_3$) was dried by passing through a solvent purification system. Tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) and Me_4NF was purchased from Sigma-aldrich. NMR spectra were obtained on a Bruker AV400 or Agilent MR400 (400 MHz for ^1H; 376 MHz for ^{19}F; 101 MHz for ^{13}C), or an Agilent MR500 (500 MHz for ^1H; 126 MHz for ^{13}C) spectrometer. ^1H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ at δ 0.00 ppm or to the signal of a residual protonated solvent: $CDCl_3$ at δ 7.26 ppm. ^{13}C NMR chemical shifts were determined relative to internal $CDCl_3$ at δ 77.0 ppm. ^1H, ^{13}C and ^{19}F multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), triplet of quartets (tq), triplet of triplets (tt), triplet of multiplets (tm), quartet of triplets (qt), multiplet (m), and broad resonance (br). Flash chromatography was performed using 230-400 mesh SiliaFlash® P60 (Silicycle Inc.). All the melting points were uncorrected. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode. All reactions were monitored by TLC and ^{19}F NMR spectroscopy.

2. Preparation of Aryl Fluorosulfonates (2)

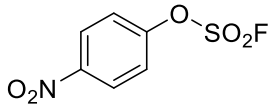


1 **2**

Experimental procedures[1]**:**

To a 50-mL Schlenk tube equipped with a stir bar were added phenol (10 mmol), CH_2Cl_2 (10 mL) and Et_3N (2.1 mL, 15 mmol, 1.5 equiv). The mixture was stirred at room temperature for 10 min. The reaction flask was then sealed with a septum, the atmosphere above the solution was removed with gentle vacuum, and SO_2F_2 gas was introduced by a needle from a balloon filled with the gas. The reaction mixture was vigorously stirred at room temperature for 6 hours, monitoring by GC-MS and TLC. After completion, the solvent was removed by rotary evaporation, the residue was dissolved in ethyl acetate, washed with 1M HCl and brine solution. Then the organic phase was dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography using petroleum ether and ethyl acetate as the eluent to give the target products **2**.

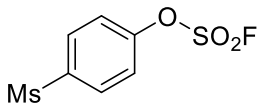
4-Nitrophenyl sulfurofluoridate (2a)[1]



2a was obtained as a yellow oil (1.9 g, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 9.2 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 39.47 (s); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 153.4, 147.3, 126.2, 122.1.

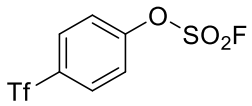
4-(Methylsulfonyl)phenyl sulfurofluoridate (2b) [2]



2b was obtained as a white solid (2.1 g, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50–7.90 (m, 2H), 7.76–7.44 (m, 2H), 3.10 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 39.35 (s); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 153.0, 141.1, 130.3, 122.2, 44.5.

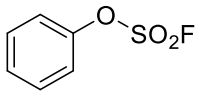
4-((Trifluoromethyl)sulfonyl)phenyl sulfurofluoridate (2c)



2c was obtained as a yellow solid (1.8 g, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 40.29 (s), −7.88 (s); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 155.0, 133.7, 132.0, 122.7, 119.6 (q, *J* = 325.8 Hz). **MS** (ESI, m/z): 308.0 ($[M+H]^+$). **HRMS** (ESI) m/z: $[M]^+$ Calcd. for $C_7H_4O_5F_4S_2$: 307.9431; Found: 307.9424.

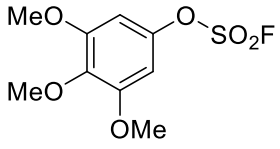
4-Nitrophenyl sulfurofluoridate (2d)[1]



2d was obtained as a colorless oil (1.5 g, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 37.49 (s); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 150.1, 130.4, 128.7, 120.9.

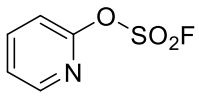
3,4,5-Trimethoxyphenyl sulfurofluoridate (2e)



2e was obtained as a white solid (2.3 g, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (s, 2H), 3.87 (s, 6H), 3.84 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 37.18 (s); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 153.9, 145.8, 138.0, 98.6, 61.0, 56.4. **MS** (ESI, m/z): 267.0 ($[M+H]^+$). **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_9H_{12}FO_6S$: 267.0333; Found: 267.0332.

Pyridin-2-yl sulfurofluoridate (2f)[2]



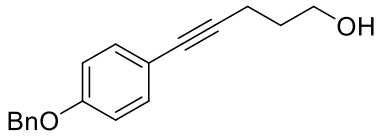
2f was obtained as a colorless oil (1.5 g, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (dd, *J* = 4.9, 2.0 Hz, 1H), 7.93 (tdd, *J* = 7.3, 2.0, 0.6 Hz, 1H), 7.41 (dd, *J* = 7.4, 4.9 Hz, 1H), 7.20 (dd, *J* = 8.2, 0.9 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 44.40 (s); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.3, 148.6, 141.2, 124.2, 114.2 (d, *J* = 2.5 Hz).

3. Synthesis of Alcohol

Modification of literature's method[3]: To a 50-mL Schlenk tube A equipped with a stir bar were added $PdCl_2(PPh_3)_2$ (1.5 mol%, 0.075 mmol, 0.0527 g) and copper(I) iodide (3 mol%, 0.15 mol, 0.0286 g), 1-(benzyloxy)-4-(5-iodopent-1-yn-1-yl)benzene (1 equiv., 5 mmol, 1.5507 g), THF (5 mL) and Et_3N (9 mL). To another Schlenk tube B equipped with a stir bar were added 4-pentyn-1-ol (1.1 equiv., 5.5 mmol, 0.4626 g), THF (2 mL), this solution from Schlenk tube B was dropwise introduced to the stirring solution A via syringe. The mixture was stirred at room temperature until consumption of starting material was observed by TLC. After completion, the solvent was removed by rotary evaporation, the residue was dissolved in ethyl acetate, washed with 1M HCl and brine solution. Then the organic phase was dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography using petroleum ether and ethyl acetate as the eluent to give the alcohol **3o**.

5-(4-(benzyloxy)phenyl)pent-4-yn-1-ol (3o)



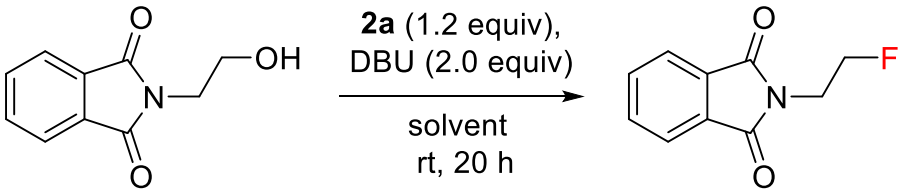
3o was obtained as a yellow solid (1.1 g, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (q, *J* = 7.9 Hz, 4H), 7.35 (d, *J* = 8.3 Hz, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.05 (s, 2H), 3.81 (t, *J* = 6.2 Hz, 2H), 2.53 (t, *J* = 6.9 Hz, 2H), 1.93-1.81 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.3, 136.7, 132.9, 128.6, 128.1, 127.5, 116.2, 114.8, 87.9, 80.9, 70.0, 61.9, 31.5, 16.0. **MS** (ESI, m/z): 267.1 ($[M+H]^+$). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{19}O_2^+$: 267.1380; Found: 267.1379.

4. Details for Deoxyfluorination of Alcohols

4.1 Optimization the Reaction Conditions of Deoxyfluorination

Table S1. Optimization the solvent

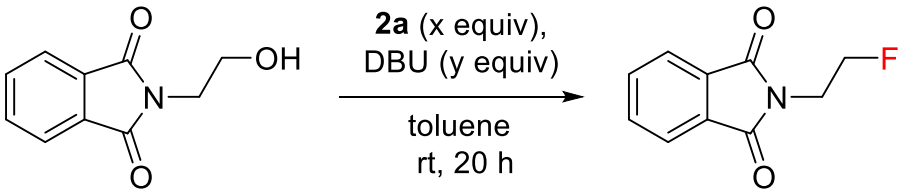


3a
(0.5 mmol)

4a

entry	solvent	**4a** (%)
1	THF	10
2	DCM	20
3	acetone	11
4	Bu_2O	0
5	toluene	40

Table S2. Optimization the amount of **2a**, **3a** and DBU

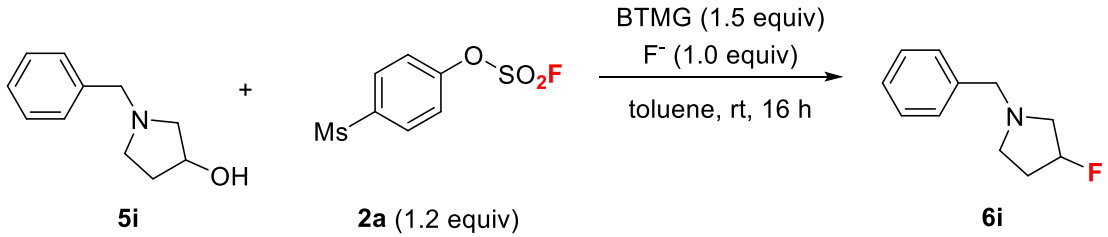


3a
(0.5 mmol)

4a

entry	x	y	**4a** (%)
1	1.2	2.0	40
2	1.2	1.1	45
3	1.2	1.3	51
4	1.2	1.5	73
5	1.2	1.8	44
6	1.4	1.5	65
7	1.4	1.75	42

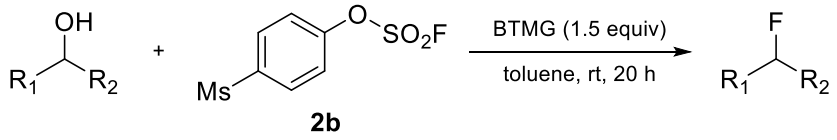
Table S3. Optimization the external fluoride source



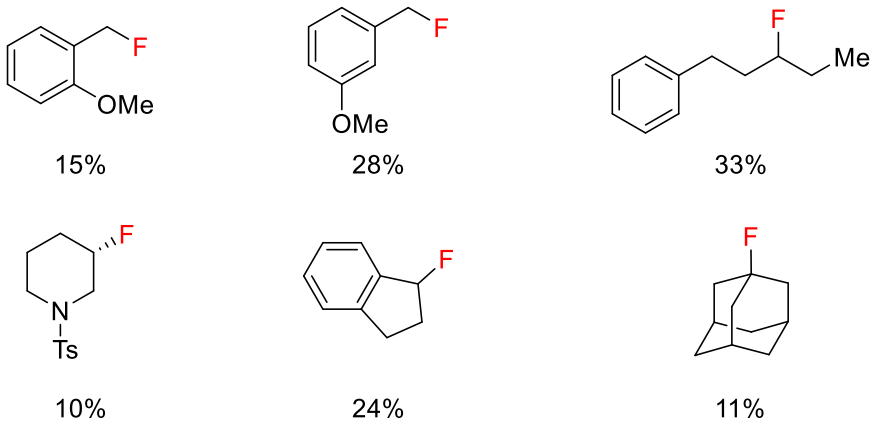
5i **2a** (1.2 equiv) **6i**

entry	F^-	**6i** (%)
1	TBAF	4
2	TBAT	14
3	TASF	53
4	KF/18-c-6	32
5	CsF/18-c-6	35
6	TBAF(^{t}BuOH)$_4$	23
7	KHF_2	33
8	$Et_3N(HF)_3$	42
9	TMAF	16

Table S4. Unsuccessful examples in deoxyfluorination of alcohols with aryl fluorosulfonates[ab]



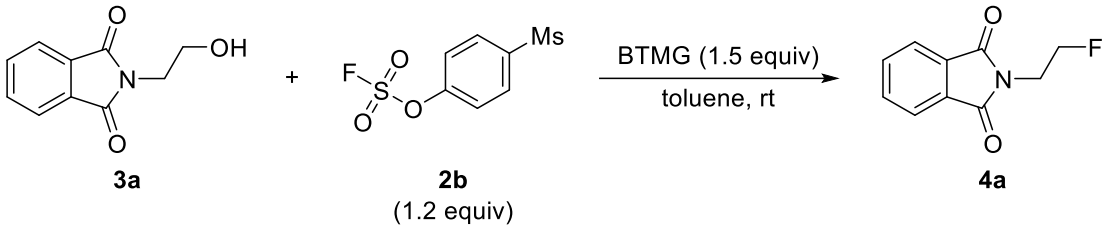
2b



[a] Reaction conditions: alcohol (0.5 mmol), **2b** (1.2 equiv, 0.6 mmol, 2 equiv of 2b was added for secondary or tertiary alcohols), BTMG (1.5 equiv, 0.75 mmol), TASF (1 equiv, 0.5 mmol, for secondary or tertiary alcohol), toluene (5 mL), rt, 20 h. [b]

Determined by ^{19}F NMR analysis of the crude mixture, using fluorobenzene as an internal standard.

4.2 Time Course Experiments



3a + **2b** (1.2 equiv) → **4a**

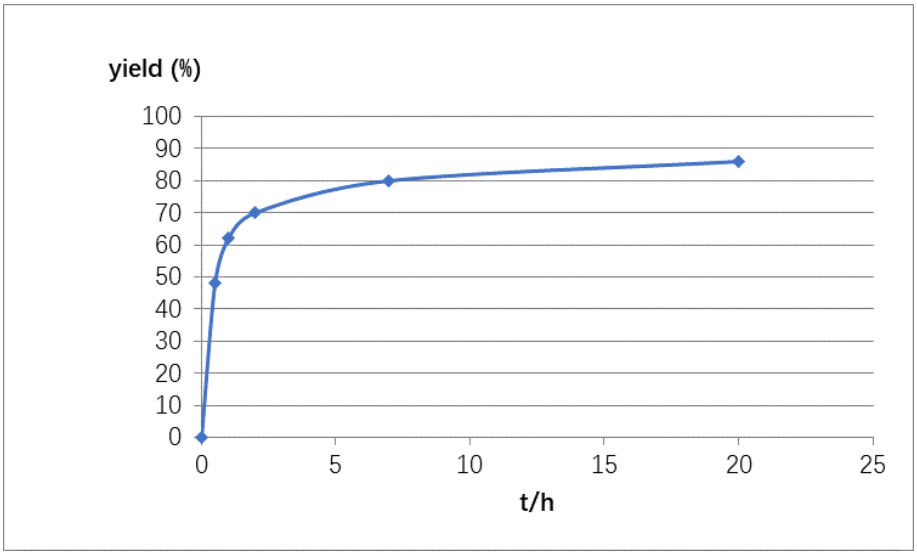
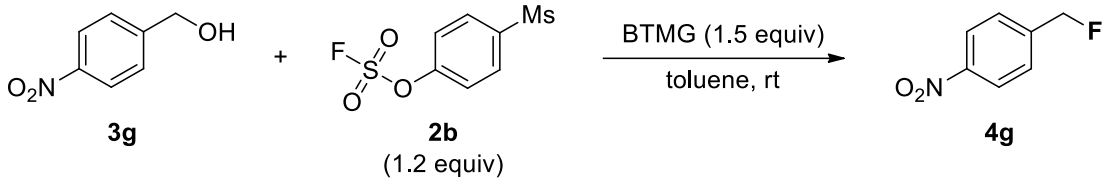


Figure S1. Time course reaction of **3a** monitored by ^{19}F NMR analysis



3g + **2b** (1.2 equiv) → **4g**

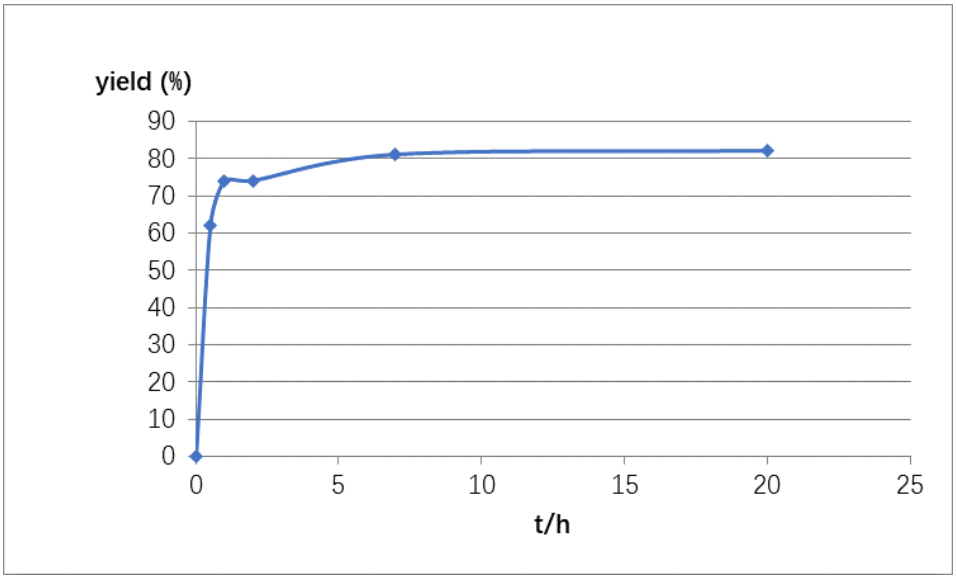
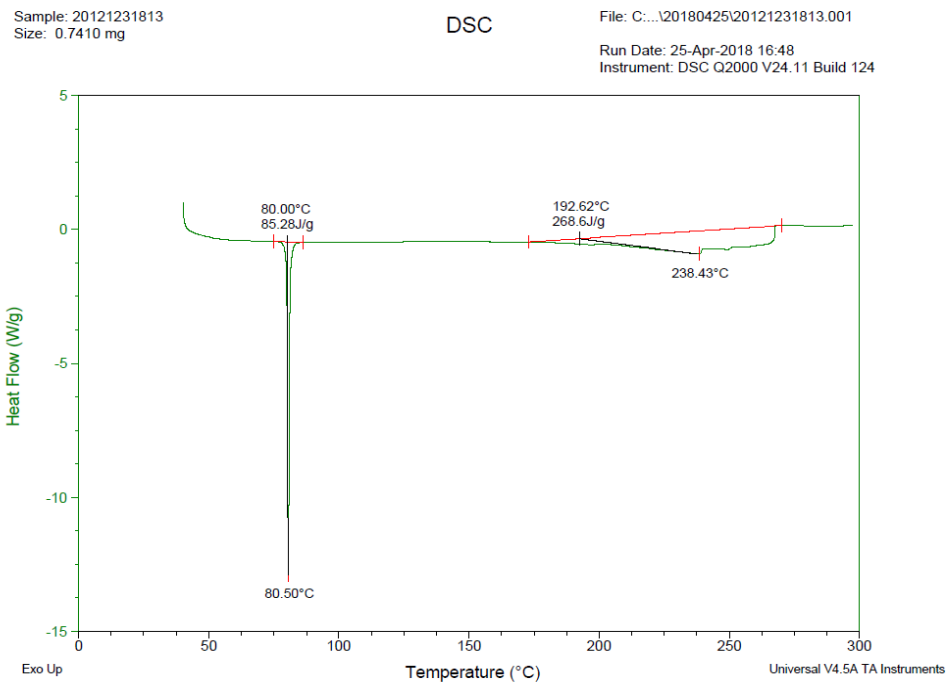


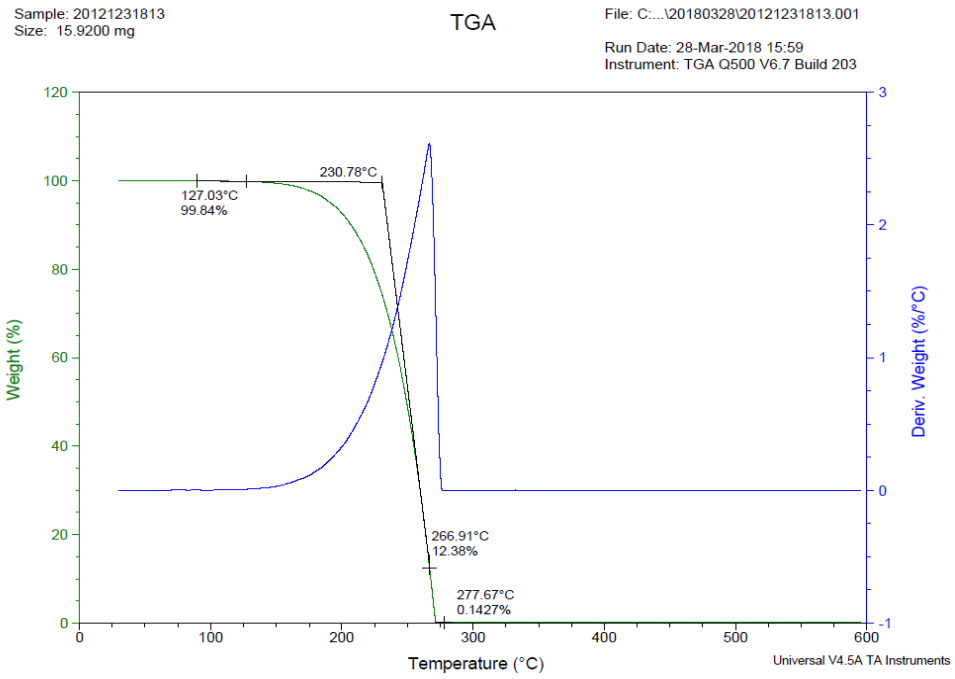
Figure S2. Time course reaction of **3g** monitored by ^{19}F NMR analysis

4.3 Stability of Aryl Fluorosulfonate (2b)

The stability of fluorination reagent has typically been assessed by differential scanning calorimetry (DSC). Here, we report DSC data for the newly-disclosed reagent **2b** (**Scheme S1**). Measurements were performed in crimped Tzero aluminum pans using the indicated sample masses. Sharp endotherms attributed melting were observed for **2b** (85.3J/g at 80 ^{o}C). A number of other artifacts were observed, potentially corresponding to impurities or endothermic decomposition. Crimped Tzero aluminum pans are not airtight, so the highest temperature artifact likely arises from premature evaporation, which would occur well below the actual boiling point. Importantly, no exothermic decomposition was observed on between 0 and 300 ^{o}C, indicating that this reagent has considerable thermal stability. And we also conducted the thermo gravimetric analysis (TGA) for **2b** (**Scheme S2**). This reagent hardly decomposed below 127 ^{o}C, further indicating its thermal stability.



Scheme S1. DSC of **2b**

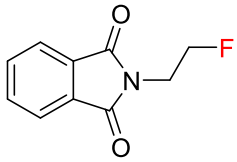


Scheme S2. TGA of **2b**

5. Deoxyfluorination of Alcohols with 2b

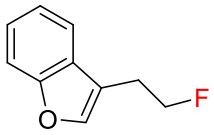
General Procedure 1: To a 25-mL polytetrafluoroethylene (PTFE) tube were sequentially added alcohol (**3**, 0.5 mmol), 4-(methylsulfonyl)phenyl fluorosulfonate (**2b**, 1.2 equiv., 0.6 mmol, 0.153 g), toluene (5 mL) and 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (BTMG, 1.5 equiv., 0.75 mmol, 155 uL). The mixture was stirred at room temperature for 20 h. The reaction mixture was concentrated under vacuum and purified by chromatography on silica gel to afford the desired alkyl fluorides **4**.

2-(2-Fluoroethyl)isoindoline-1,3-dione (4a)[4]



Follow the ***General Procedure 1***, product **4a** was obtained as a white solid (83.1 mg, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.76 (m, 2H), 7.76-7.57 (m, 2H), 4.61 (dt, *J* = 46.9, 5.2 Hz, 2H), 3.98 (dt, *J* = 24.1, 5.2 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –224.7 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.0, 134.1, 131.9, 123.4, 80.4 (d, *J* = 171.7 Hz), 38.2 (d, *J* = 22.3 Hz).

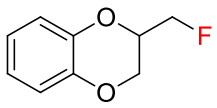
3-(2-Fluoroethyl)benzofuran (4b)[5]



Follow the ***General Procedure 1***, product **4b** was obtained as a colorless liquid (59.5 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.6, 0.5 Hz, 1H), 7.54 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.36-7.30 (m, 1H), 7.30-7.25 (m, 1H), 4.73 (dt, *J* = 47.0, 6.3 Hz, 2H), 3.10 (dt, *J* = 23.9, 6.3 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –214.5 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.3, 142.2, 127.9, 124.4, 122.5, 119.5,

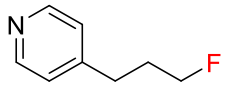
115.8, 111.6, 82.8 (d, *J* = 168.9 Hz), 25.1 (d, *J* = 21.8 Hz).

2-(Fluoromethyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (4c)[6]



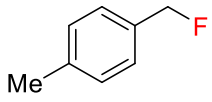
Follow the ***General Procedure 1***, product **4c** was obtained as a pale-yellow liquid (55.5 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08-6.71 (m, 4H), 4.76-4.55 (m, 2H), 4.42 (ddtd, *J* = 18.1, 7.1, 4.7, 2.4 Hz, 1H), 4.34 (ddd, *J* = 11.5, 2.3, 1.4 Hz, 1H), 4.14 (dd, *J* = 11.5, 7.1 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –233.4 (td, *J* = 46.7, 17.9 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0, 142.8, 121.9, 121.7, 117.5, 117.3, 81.3 (d, *J* = 172.5 Hz), 71.3, 64.3 (d, *J* = 6.9 Hz).

4-(3-Fluoropropyl)pyridine (4d)[5]



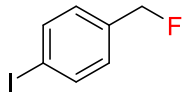
Follow the ***General Procedure 1***, product **4d** was obtained as a light yellow liquid (23.0 mg, 33% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (s, 2H), 7.14 (d, J = 2.4 Hz, 2H), 4.45 (dt, J = 47.1, 5.8 Hz, 2H), 2.76-2.73 (m, 2H), 2.01 (dddd, J = 15.2, 13.3, 10.0, 5.9 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –220.89 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1, 149.8, 124.1, 82.7 (d, J = 165.8 Hz), 30.4 (d, J= 75 Hz), 30.8.

1-(fluoromethyl)-4-methylbenzene (4e)[7]



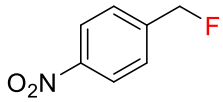
Follow the ***General Procedure 1***, the yield of product **4e** was measured by ^{19}F NMR using fluorobenzene as an internal standard (72%). **^{19}F NMR** (376 MHz, $CDCl_3$): –201.74 (t, *J* = 48.3 Hz).

1-(fluoromethyl)-4-iodobenzene (4f)[8]



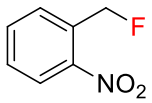
Follow the ***General Procedure 1***, product **4f** was obtained as a white solid (77.9 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$**)**: δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.4 Hz, 2H), 5.32 (d, *J* = 47.5 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ –208.87 (t, *J* = 47.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 137.70, 129.12, 129.06, 94.42, 83.80 (d, *J* = 167.4 Hz).

1-(Fluoromethyl)-4-nitrobenzene (4g)[8]



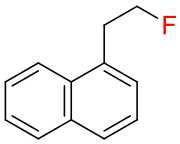
Follow the ***General Procedure 1***, product **4g** was obtained as a pale-yellow solid (63.6 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 5.50 (d, *J* = 46.8 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -215.7 (t, *J* = 46.8 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 138.6 (d, *J* = 17.7 Hz), 122.3 (d, *J* = 7.0 Hz), 119.0, 78.1 (d, *J* = 170.6 Hz).

1-(Fluoromethyl)-2-nitrobenzene (4h)[9]



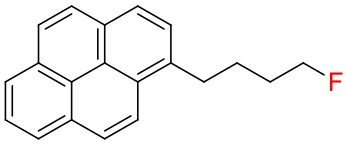
Follow the ***General Procedure 1***, product **4h** was obtained as a pale-yellow solid (58.2 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.64-7.42 (m, 1H), 5.85 (d, *J* = 47.9 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -219.2 (t, *J* = 47.9 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.38, 134.36, 134.2 (d, *J* = 19.3 Hz), 128.5, 126.8 (d, *J* = 17.6 Hz), 124.8, 81.2 (d, *J* = 172.7 Hz).

1-(2-Fluoroethyl)naphthalene (4i)[5]



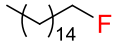
Following the ***General Procedure 1***, product **4i** was obtained as a colorless liquid (64.4 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 1H), 7.99-7.88 (m, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.64-7.52 (m, 2H), 7.52-7.39 (m, 2H), 4.82 (dt, *J* = 47.0, 6.9 Hz, 2H), 3.56 (dt, *J* = 20.4, 6.9 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -213.3 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.0, 132.9 (d, *J* = 7.3 Hz), 132.1, 129.0, 127.7, 127.3, 126.3, 125.8, 125.6 123.5, 83.6 (d, *J* = 169.8 Hz), 33.9 (d, *J* = 20.9 Hz).

1-(4-Fluorobutyl)pyrene (4j)



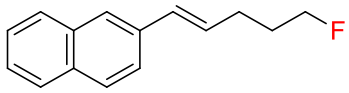
Follow the ***General Procedure 1***, product **4j** was obtained as a yellow solid (89.9 mg, 59% yield). m.p. 50-51 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 9.2 Hz, 1H), 8.21 (d, *J* = 7.7 Hz, 2H), 8.14 (s, 1H), 8.12 (d, *J* = 3.4 Hz, 1H), 8.10-7.99 (m, 3H), 7.87 (d, *J* = 7.8 Hz, 1H), 4.54 (dt, *J* = 47.5, 5.9 Hz, 2H), 3.38 (t, *J* = 7.6 Hz, 2H), 2.09-1.96 (m, 2H), 1.96-1.79 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -218.0 (tt, *J* = 47.4, 25.1 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.3 131.5, 131.0, 130.0, 128.7, 127.6, 127.4, 127.3, 126.7, 125.9, 125.2, 125.1, 125.0, 124.9, 124.8, 123.3, 84.1 (d, *J* = 164.5 Hz), 33.0, 30.5 (d, *J* = 19.9 Hz), 27.4 (d, *J* = 4.7 Hz). **MS** (EI, m/z): 276 (M^+). **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{20}H_{17}F$: 276.1309; Found: 276.1320.

1-Fluorohexadecane (4k)[5]



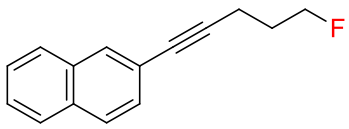
Following the ***General Procedure 1***, product **4k** was obtained as a white solid (81.4 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.44 (dt, *J* = 47.4, 6.2 Hz, 2H), 1.81-1.59 (m, 2H), 1.50-1.17 (m, 26H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -218.0 (tt, *J* = 47.3, 24.8 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 84.1 (d, *J* = 164.5 Hz), 71.0, 32.0, 30.5 (d, *J* = 19.3 Hz), 29.73, 29.70, 29.68, 29.59, 29.56, 29.4, 29.3, 26.2, 25.2 (d, *J* = 5.5 Hz), 22.7, 14.1.

(*E*)-2-(5-Fluoropent-1-en-1-yl)naphthalene (4l)[5]



Follow the ***General Procedure 1***, product **4l** was obtained as a white solid (52.3 mg, 49% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (t, *J* = 8.4 Hz, 3H), 7.70 (s, 1H), 7.60 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.52-7.40 (m, 2H), 6.61 (d, *J* = 15.8 Hz, 1H), 6.42-6.29 (m, 1H), 4.54 (dt, *J* = 47.2, 6.0 Hz, 2H), 2.42 (q, *J* = 7.0 Hz, 2H), 2.06-1.80 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -219.4 (tt, *J* = 47.3, 25.3 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.1 133.8, 132.8, 131.0, 129.7, 128.2, 127.9, 127.7, 126.3, 125.7, 125.6, 123.6, 83.4 (d, *J* = 164.9 Hz), 30.2 (d, *J* = 19.9 Hz), 28.8 (d, *J* = 5.5 Hz).

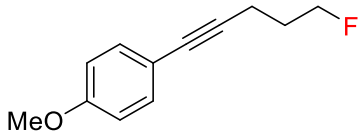
2-(5-Fuoropent-1-yn-1-yl)naphthalene (4m)[5]



Following the ***General Procedure 1***, product **4m** was obtained as a colorless liquid (72.8 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.91-7.70 (m, 3H), 7.55-7.48 (m, 3H), 4.68 (dt, *J* = 47.1, 5.8 Hz, 2H), 2.66 (t, *J* = 7.0 Hz, 2H), 2.13-1.99 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -221.3 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.1, 132.6, 131.3, 128.7, 128.0, 127.8, 127.7, 126.52, 126.5, 121.1, 89.0, 82.6 (d,

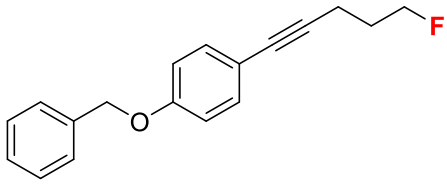
J = 165.3 Hz), 81.7, 29.7 (d, *J* = 20.1 Hz), 15.6 (d, *J* = 5.6 Hz).

1-(5-Fluoropent-1-yn-1-yl)-4-methoxybenzene (4n)



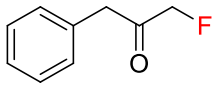
Follow the ***General Procedure 1***, product **4n** was obtained as a colorless liquid (70.2 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.30 (m, 2H), 6.95-6.73 (m, 2H), 4.60 (dt, *J* = 47.2, 5.8 Hz, 2H), 3.79 (s, 3H), 2.55 (t, *J* = 7.0 Hz, 2H), 2.16-1.80 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -221.5 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.20, 132.90, 115.82, 113.86, 86.86, 82.59 (d, *J* = 165.2 Hz), 81.00, 55.21, 29.70 (d, *J* = 20.0 Hz), 15.41 (d, *J* = 5.6 Hz). **MS** (EI, m/z): 192 (M^+). **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{12}H_{13}FO$: 192.0945; Found: 192.0954.

1-(benzyloxy)-4-(5-fluoropent-1-yn-1-yl)benzene (4o)



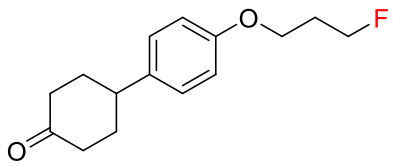
Following the ***General Procedure 1***, product **4o** was obtained as a white solid (108.7 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.35 (m, 7H), 6.96-6.91 (m, 2H), 5.08 (s, 2H), 4.70 (t, *J* = 5.8 Hz, 1H), 4.58 (t, *J* = 5.8 Hz, 1H), 2.59 (t, *J* = 7.0 Hz, 2H), 2.08-1.94 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -221.82 (tt, *J* = 47.2, 25.6 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.43, 136.75, 132.99, 128.65, 128.09, 127.52, 116.17, 114.85, 87.07, 82.63 (d, *J* = 165.1 Hz), 81.06, 70.01, 29.74 (d, *J* = 20.1 Hz), 15.48 (d, *J* = 5.9 Hz). **MS** (EI, m/z): 268 (M^+). **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{18}H_{17}FO$: 268.1258; Found: 268.1265.

1-Fluoro-3-phenylpropan-2-one (4p)[10]



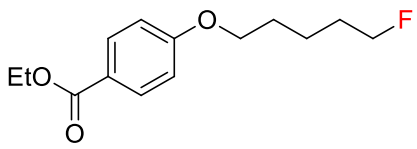
Follow the ***General Procedure 1***, product **4p** was obtained as a colorless liquid (46.1 mg, 61% yield). **^{1}H NMR** (400 MHz, C_6D_6) δ 7.13-6.99 (m, 5H), 4.87 (s, 2H), 4.17 (d, *J* = 47.1 Hz, 2H). **^{19}F NMR** (376 MHz, C_6D_6) δ -229.4 (t, *J* = 47.0 Hz, 1F). **^{13}C NMR** (101 MHz, C_6D_6) δ 166.9 (d, *J* = 21.9 Hz), 135.3, 128.4, 128.3, 77.0 (d, *J* = 182.6 Hz), 66.3.

4-(4-(3-Fuoropropoxy)phenyl)cyclohexan-1-one (4q)



Follow the ***General Procedure 1***, product **4q** was obtained as a white solid (70.6 mg, 56% yield). m.p. 62-63 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.63 (dt, *J* = 47.1, 5.8 Hz, 2H), 4.08 (t, *J* = 6.1 Hz, 2H), 2.98 (tt, *J* = 12.1, 3.3 Hz, 1H), 2.49 (dd, *J* = 11.6, 5.7 Hz, 4H), 2.28-2.15 (m, 3H), 2.12 (dt, *J* = 11.9, 6.0 Hz, 1H), 1.89 (qd, *J* = 12.3, 6.1 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -222.3 (tt, *J* = 47.1, 25.9 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.2, 157.4, 137.2, 127.6, 114.6, 80.7 (d, *J* = 164.4 Hz), 63.5 (d, *J* = 5.4 Hz), 41.9, 41.4, 34.2, 30.4 (d, *J* = 20.0 Hz). **MS** (EI, m/z): 250 (M^+). **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{15}H_{19}FO_2$: 250.1364; Found: 250.1376.

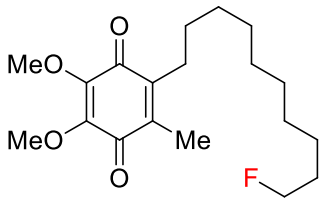
Ethyl 4-((5-fluoropentyl)oxy)benzoate (4r)



Follow the ***General Procedure 1***, product **4r** was obtained as a white solid (85.5 mg, 67% yield). m.p. 30-32 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.9 Hz, 2H),

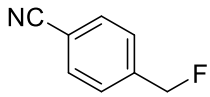
6.88 (d, *J* = 8.9 Hz, 2H), 4.45 (dt, *J* = 47.3, 6.0 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.99 (t, *J* = 6.3 Hz, 2H), 1.90-1.68 (m, 4H), 1.65-1.53 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -218.6 (tt, *J* = 47.3, 25.2 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 162.7, 131.5, 122.8, 114.0, 83.8 (d, *J* = 164.5 Hz), 67.8, 60.6, 30.1 (d, *J* = 20.0 Hz), 28.7, 21.9 (d, *J* = 5.4 Hz), 14.4. **MS** (EI, m/z): 254 (M^+). **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{14}H_{19}FO_3$: 254.1313; Found: 254.1318.

2-(10-Fluorodecyl)-5,6-dimethoxy-3-methylcyclohexa-2,5-diene-1,4-dione (4s)[5]



Follow the ***General Procedure 1***, product **4s** was obtained as an orange solid (68 mg, 40% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.40 (dt, *J* = 47.4, 6.2 Hz, 2H), 3.96 (d, *J* = 1.2 Hz, 6H), 2.51-2.33 (m, 2H), 1.98 (s, 3H), 1.82-1.52 (m, 2H), 1.48-1.16 (m, 14H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -218.1 (tt, *J* = 47.4, 24.9 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.7, 184.1, 144.3, 143.0, 138.6, 84.2 (d, *J* = 164.2 Hz), 61.1, 30.4 (d, *J* = 19.2 Hz), 29.8, 29.4, 29.4, 29.3, 29.2 28.7, 26.4, 25.1 (d, *J* = 5.5 Hz), 11.9.

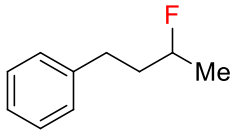
4-(fluoromethyl)benzonitrile (4t)[11]



Follow the ***General Procedure 1***, product **4t** was obtained as a light yellow oil (41 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75-7.61 (m, 2H), 7.46 (d, *J* = 5.8 Hz, 2H), 5.44 (dt, *J* = 46.9, 4.6 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -215.02 (t, *J* = 46.9 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ141.6 (d, *J* = 17.7 Hz), 132.5, 127.1 (d, *J* = 7.1 Hz), 118.6, 112.5 (d, *J* = 2.4 Hz), 83.2 (d, *J* = 170.3 Hz).

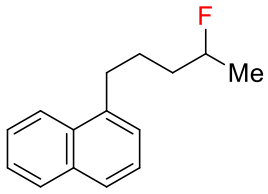
General Procedure 2: To a 25-mL polytetrafluoroethylene (PTFE) tube were sequentially added alcohol (**5**, 0.5 mmol), 4-(methylsulfonyl)phenyl fluorosulfonate (**2b**, 254 mg, 1.0 mmol, 2.0 equiv). The tube was moved into the glove box, and TASF (138 mg, 0.5 mmol, 1.0 equiv), toluene (5.0 mL), 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (BTMG, 0.155 mL, 0.75 mmol, 1.5 equiv) were added. The mixture was stirred at room temperature for 20 h. The reaction mixture was concentrated under vacuum and purified by chromatography on silica gel to afford the desired alkyl fluorides **6**.

(3-Fluorobutyl)benzene (6a)[8]



Follow the ***General Procedure 2***, product **6a** was obtained as a colorless liquid (37.4 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 2H), 7.26-7.18 (m, 3H), 4.81-4.56 (m, 1H), 2.90-2.67 (m, 2H), 2.13-1.95 (m, 1H), 1.94-1.75 (m, 1H), 1.38 (dd, *J* = 23.9, 6.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -174.3 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 128.5, 126.0, 90.1, 89.2, 38.7 (d, *J* = 20.7 Hz), 31.4 (d, *J* = 4.6 Hz), 21.0 (d, *J* = 22.6 Hz).

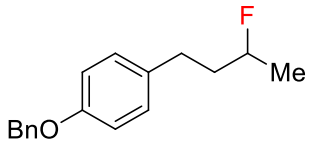
1-(4-Fluoropentyl)naphthalene (6b)[5]



Follow the ***General Procedure 2***, product **6b** was obtained as a colorless liquid (70.5 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.65-7.51 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 6.8 Hz, 1H), 4.92-4.19 (m, 1H), 3.17 (t, *J* = 7.4 Hz, 2H), 2.13-1.58 (m,

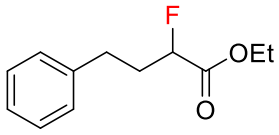
4H), 1.39 (dd, *J* = 23.9, 6.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -177.6 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.1, 133.9, 131.8, 128.8, 126.6, 125.9, 125.7, 125.5, 125.4, 123.7, 90.8 (d, *J* = 164.7 Hz), 36.8 (d, *J* = 20.7 Hz), 32.7, 26.2 (d, *J* = 4.6 Hz), 21.0(d, *J* = 22.8 Hz).

1-(Benzyloxy)-4-(3-fluorobutyl)benzene (6c)



Follow the ***General Procedure 2***, product **6c** was obtained as a white solid (68.5 mg, 53% yield). m.p. 30 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.34 (m, 5H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.99-6.94 (m, 2H), 5.09 (s, 2H), 4.80-4.61 (m, 1H), 2.84-2.64 (m, 2H), 2.08-1.73 (m, 2H), 1.39 (dd, *J* = 23.9, 6.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -174.2 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1, 137.2, 133.9, 129.4, 128.6, 127.99, 127.5, 114.9, 90.0 (d, *J* = 164.9 Hz), 70.1, 38.9 (d, *J* = 20.8 Hz), 30.5 (d, *J* = 4.9 Hz), 21.0 (d, *J* = 22.7 Hz). **MS** (EI, m/z): 258 (M^+). **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{17}H_{19}FO$: 258.1414; Found: 258.1421.

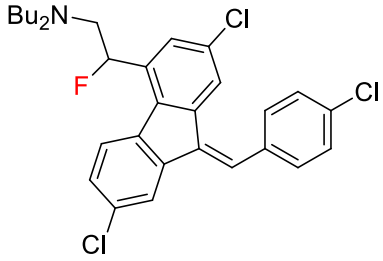
Ethyl-2-fluoro-4-phenylbutanoate (6d)[12]



Follow the ***General Procedure 2***, product **6d** was obtained as a colorless liquid (48.5 mg, 46% yield). **^{1}H NMR** (400 MHz, C_6D_6) δ 7.10 (t, *J* = 7.4 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.3 Hz, 2H), 4.61 (ddd, *J* = 49.0, 7.7, 4.6 Hz, 1H), 3.86 (q, *J* = 7.1 Hz, 2H), 2.88-2.43 (m, 2H), 2.16-1.84 (m, 2H), 0.86 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, C_6D_6) δ -192.7 (ddd, *J* = 48.8, 27.5, 21.1 Hz, 1F). **^{13}C NMR** (101 MHz, C_6D_6) δ 169.1 (d, *J* = 23.6 Hz), 140.3, 128.4, 126.1, 87.9 (d, *J* = 185.2 Hz), 60.7, 34.1

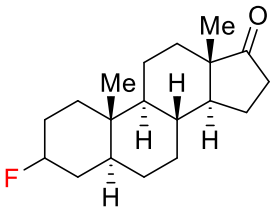
(d, *J* = 21.3 Hz), 30.4 (d, *J* = 3.2 Hz), 13.6.

(*Z*)-*N*-Butyl-*N*-(2-(2,7-dichloro-9-(4-chlorobenzylidene)-9H-fluoren-4-yl)-2-fluoro ethyl)butan-1-amine (6e)[13]



Follow the ***General Procedure 2***, product **6e** was obtained as a yellow solid (156.7 mg, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 14.4, 5.0 Hz, 2H), 7.52 (s, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.43 (s, 4H), 7.32 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.09 (dd, *J* = 48.2, 6.4 Hz, 1H), 3.05-2.75 (m, 2H), 2.61 (tdd, *J* = 20.2, 13.3, 7.2 Hz, 4H), 1.56-1.23 (m, 9H), 0.94 (t, *J* = 7.2 Hz, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -180.1 (ddd, *J* = 48.2, 33.8, 21.2 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3, 138.3, 136.0, 135.8, 135.6, 134.8, 134.6, 134.5, 134.5, 134.0, 133.3, 132.8, 130.6, 129.1, 128.6, 128.1, 125.8, 125.7, 124.4, 124.4, 123.6, 120.6, 92.0 (d, *J* = 176.0 Hz), 59.3 (d, *J* = 22.2 Hz), 54.3, 29.0, 20.7, 14.2.

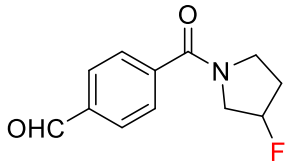
(5S,8R,9S,10S,13S,14S)-3-Fluoro-10,13-dimethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-one (6f)[5]



Follow the ***General Procedure 2***, product **6f** was obtained as a white solid (105.6 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.77 (dt, *J* = 48.9, 2.7 Hz, 1H), 2.39 (ddd, *J* = 19.1, 8.9, 1.1 Hz, 1H), 2.02 (dt, *J* = 19.2, 9.0 Hz, 1H), 1.93-1.73 (m, 4H), 1.69-1.60 (m, 2H), 1.60-1.35 (m, 6H), 1.33-1.13 (m, 6H), 0.98 (qd, *J* = 12.6, 4.7 Hz,

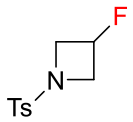
1H), 0.82 (s, 3H), 0.81-0.74 (m, 4H). **^{19}F NMR (**376 MHz, $CDCl_3$) δ -181.1 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 221.2, 89.2 (d, *J* = 165.6 Hz), 54.2, 51.4, 47.7, 39.4, 35.8, 35.8, 35.0, 33.8 (d, *J* = 21.5 Hz), 32.4, 31.5, 30.7, 28.0, 27.0 (d, *J* = 21.8 Hz), 21.7, 20.0, 13.8, 11.1.

4-(3-fluoropyrrolidine-1-carbonyl)benzaldehyde (6g)[5]



Follow the ***General Procedure 2***, product **6g** was obtained as a white solid (61.8 mg, 56% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) [mixture of 2 rotamers] δ 10.02 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.64 (dd, *J* = 17.8, 7.9 Hz, 2H), 5.26 (t, *J* = 51.4 Hz, 1H), 4.08-3.72 (m, 2H), 3.72-3.43 (m, 2H), 2.47-1.86 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) [mixture of 2 rotamers] δ –177.5 [–178.4] (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) for one rotamer: δ 191.6, 168.5, 141.9, 137.2, 129.8, 127.8, 92.8 (d, *J* = 95.3 Hz), 53.0 (d, *J* = 23.5 Hz), 46.9, 33.1 (d, *J* = 21.7 Hz); for another rotamer: δ 191.6 168.7, 142.0, 137.2, 129.8, 127.7, 91.0 (d, *J* = 92.6 Hz), 55.4 (d, *J* = 23.4 Hz), 44.0, 31.0 (d, *J* = 21.6 Hz).

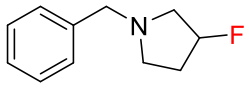
3-Fluoro-1-tosylazetidine (6h)



Follow the ***General Procedure 2***, product **6h** was obtained as a white solid (59.5 mg, 51% yield). m.p. 108-109 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 5.24-4.93 (m, 1H), 4.15-3.97 (m, 2H), 3.80 (ddd, *J* = 23.5, 10.4, 4.3 Hz, 2H), 2.44 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -179.82 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 131.1, 129.9, 128.4, 80.1 (d, *J* = 208.0 Hz), 58.2, 57.9, 21.6. **MS** (ESI, m/z): 229.9 ($[M+H]^+$). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for

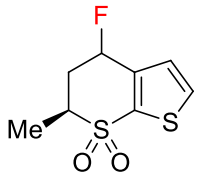
$C_{10}H_{13}FNO_2S^+$: 230.0646; Found: 230.0645.

1-Benzyl-3-fluoropyrrolidine (6i)[14]



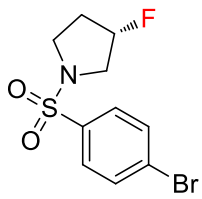
Follow the ***General Procedure 2***, product **6i** was obtained as a pale-yellow solid (53.8 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 4H), 7.27-7.21 (m, 1H), 5.33-4.98 (m, 1H), 3.79-3.56 (m, 2H), 2.99-2.61 (m, 3H), 2.47 (dd, *J* = 14.2, 8.4 Hz, 1H), 2.25-1.95 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -168.3 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.6, 128.8, 128.3, 127.1, 93.5 (d, *J* = 175.3 Hz), 60.5 (d, *J* = 23.1 Hz), 60.2, 52.2, 32.8 (d, *J* = 22.4 Hz).

4-Fluoro-6-methyl-5,6-dihydro-4H-thieno[2,3-*b*]thiopyran 7,7-dioxide (6j)[13]



Follow the ***General Procedure 2***, product **6j** was obtained as a white solid (93.5 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 5.0 Hz, 1H), 7.11 (d, *J* = 5.0 Hz, 1H), 5.59 (dt, *J* = 48.8, 3.0 Hz, 1H), 3.84-3.63 (m, 1H), 2.77-2.51 (m, 2H), 1.51 (d, *J* = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -161.6 (ddd, *J* = 48.9, 37.7, 15.1 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.5 (d, *J* = 19.9 Hz), 139.0 (d, *J* = 6.1 Hz), 131.1 (d, *J* = 2.5 Hz), 82.2, 80.5, 52.2, 36.4 (d, *J* = 22.4 Hz), 10.3.

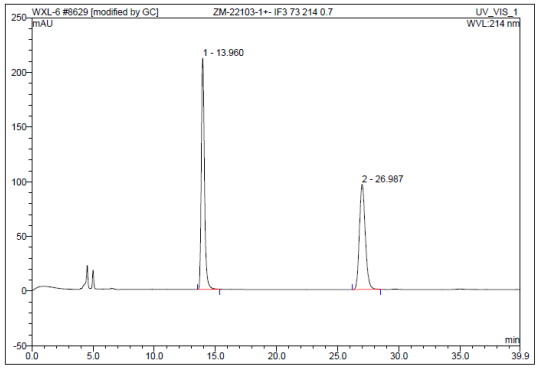
(S)-1-((4-Bromophenyl)sulfonyl)-3-fluoropyrrolidine (6k)[5]



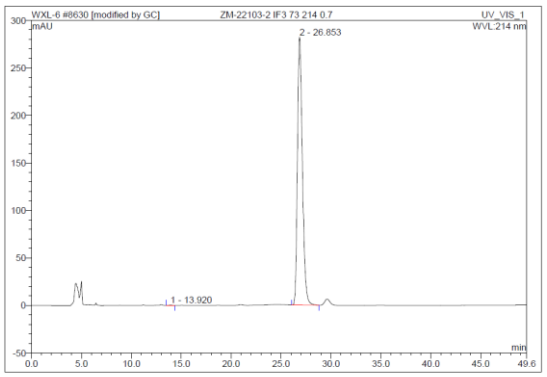
Follow the ***General Procedure 1***, product **6k** was obtained as a white solid (106.6 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.60 (m, 4H), 5.24-5.02 (m, 1H), 3.58-3.42 (m, 3H), 3.31-3.19 (m, 1H), 2.26-2.07 (m, 1H), 2.05-1.83 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -176.0 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.7, 132.4, 129.0, 127.9, 92.1 (d, *J* = 178.3 Hz), 54.4 (d, *J* = 23.6 Hz), 45.9, 32.5 (d, *J* = 22.3 Hz).

HPLC Traces for Measuring Enantiomeric Excess: A racemic sample of compound **6k** was obtained through deoxyfluorination of racemic alcohol **5k** with 4-(methylsulfonyl)phenyl fluorosulfonate (**2b**). The racemic and optically active **6k** was analyzed with HPLC (CHIRALPAK IF3 (0.46×25 cm, 3 um), hexane/IPA = 70/30 (v/v), λ = 214 nm, 0.70mL/min) to determine the retention time and enantiomeric excesses. For (S)-**6k**, e.e. =99.5%. [e.s.% = 99.5/99.9∗100% = 99.6%].

Racemic **5k** optically active **5k**

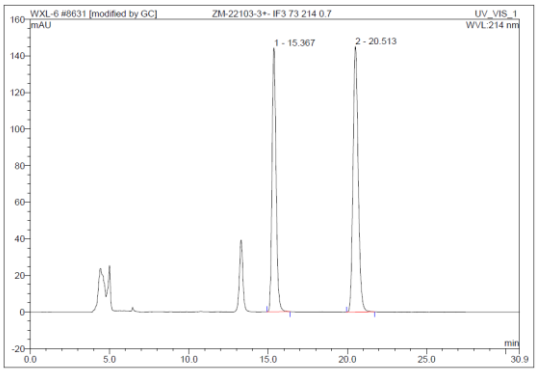


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.96	n.a.	211.557	63.745	54.31	n.a.	BMB
2	26.99	n.a.	96.178	53.620	45.69	n.a.	BMB
Total:			307.735	117.365	100.00	0.000	

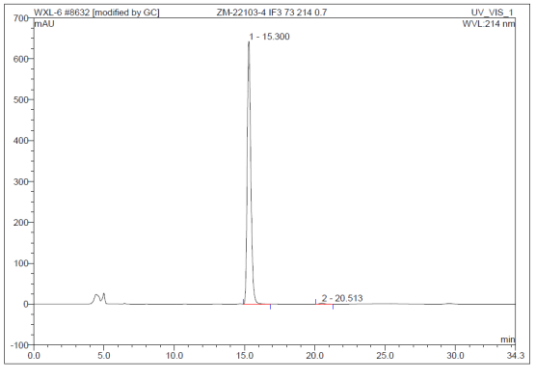


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.92	n.a.	0.319	0.092	0.06	n.a.	BMB*
2	26.85	n.a.	281.976	162.257	99.94	n.a.	BMB
Total:			282.295	162.349	100.00	0.000	

Racemic **6k** optically active **6k**



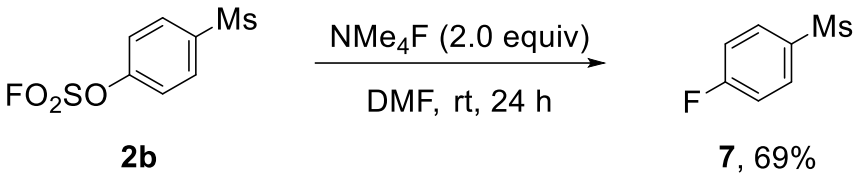
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.37	n.a.	144.285	42.427	43.54	n.a.	BMB
2	20.51	n.a.	145.092	55.011	56.46	n.a.	BMB
Total:			289.377	97.439	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.30	n.a.	642.789	192.384	99.50	n.a.	BMB
2	20.51	n.a.	2.533	0.968	0.50	n.a.	BMB
Total:			645.322	193.353	100.00	0.000	

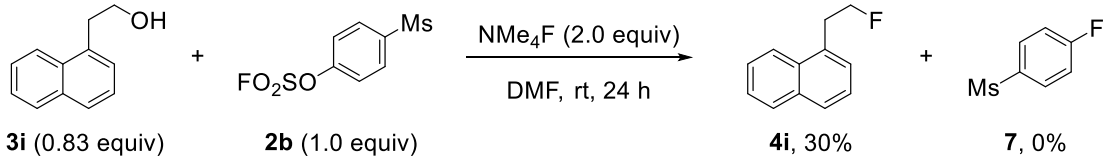
Large-Scale Synthetic Procedure for 4a: To a 500-mL polytetrafluoroethylene (PTFE) tube were sequentially added alcohol (**3**, 20 mmol), 4-(methylsulfonyl)phenyl fluorosulfonate (**2b**, 1.2 equiv., 24 mmol, 6.1 g), toluene (200 mL) and 2-*tert*-butyl-1,1,3,3- tetramethylguanidine (BTMG, 1.5 equiv., 30 mmol, 6 mL). The mixture was stirred at room temperature for 20 h. The reaction mixture was concentrated under vacuum and purified by chromatography on silica gel to afford the desired alkyl fluorides **4a** with 76% yield (2.9363 g).

6. Control Experiments of 2b and Me_4NF[15]



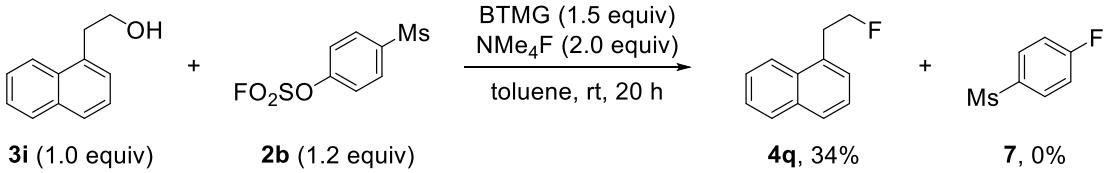
2b **7**, 69%

To a 4-mL vial were sequentially added **2b** (0.5 mmol, 127 mg), Me_4NF (93 mg, 1.0 mmol, 2.0 equiv) and DMF (2.5 mL) in the glove box. Then the vial was sealed with a cap and the mixture was stirred at room temperature for 24 h. The reaction mixture was dilute with ethyl ether and washed with water for 3 times, dried over $MgSO_4$. The crude product was purified by chromatography on silica gel to afford **7**[16] as a white solid (60 mg, 69% yield). M.p. 49-50 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.7, 5.1 Hz, 2H), 7.25 (dd, *J* = 10.6, 6.4 Hz, 2H), 3.06 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.5 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8 (d, *J* = 256.2 Hz), 136.7 (d, *J* = 3.2 Hz), 130.3 (d, *J* = 9.4 Hz), 116.7 (d, *J* = 22.7 Hz), 44.7. **MS** (EI, m/z): 174 (M^+). **HRMS** (EI) m/z: $[M]^+$ Calcd. For $C_7H_7FO_2S$: 174.0145; Found: 174.0154.



3i (0.83 equiv) **2b** (1.0 equiv) **4i**, 30% **7**, 0%

To a 4-mL vial were sequentially added **2b** (0.5 mmol, 127 mg), Me_4NF (93 mg, 1.0 mmol, 2.0 equiv), 1-(2-naphthyl)ethanol (71.8 mg, 0.413 mmol, 0.83 equiv) and DMF (2.5 mL) in the glove box. Then the vial was sealed with a cap and the mixture was stirred at room temperature for 24 h. The yield was determined by ^{19}F NMR of the reaction mixture with PhF as the internal standard.



3i (1.0 equiv) **2b** (1.2 equiv) **4q**, 34% **7**, 0%

To a 25-mL polytetrafluoroethylene (PTFE) tube were sequentially added **2b** (153 mg 0.6 mmol, 1.2 equiv), Me_4NF (93 mg, 1.0 mmol, 2.0 equiv), 1-(2-naphthyl)ethanol (86 mg, 0.5 mmol, 1.0 equiv) and toluene (5.0 mL) in the glove box. Then the tube was sealed with a cap and the mixture was stirred at room temperature for 24 h. The yield was determined by ^{19}F NMR of the reaction mixture with PhF as the internal standard.

7. References

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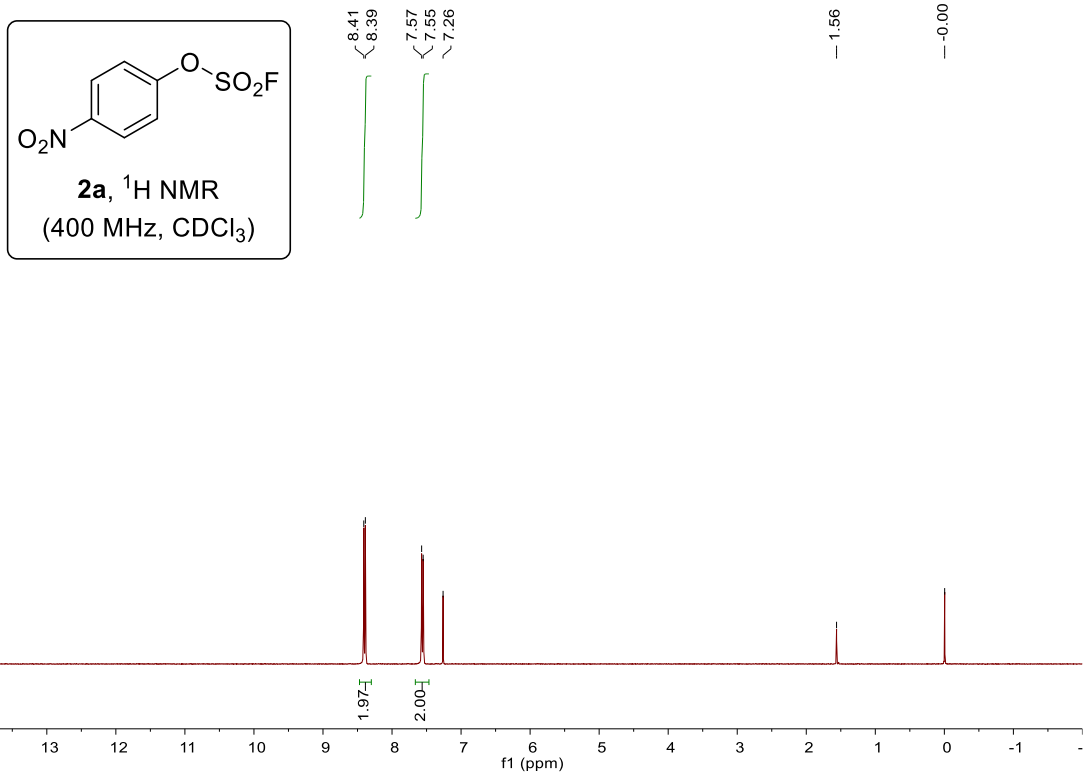
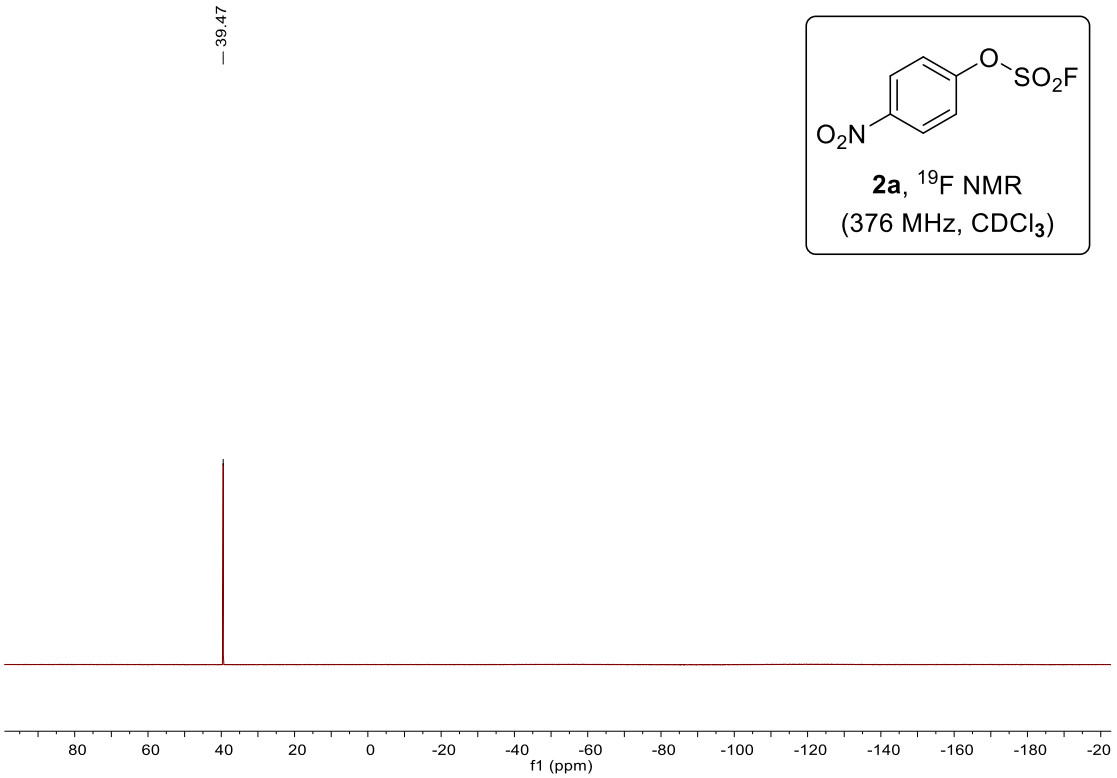
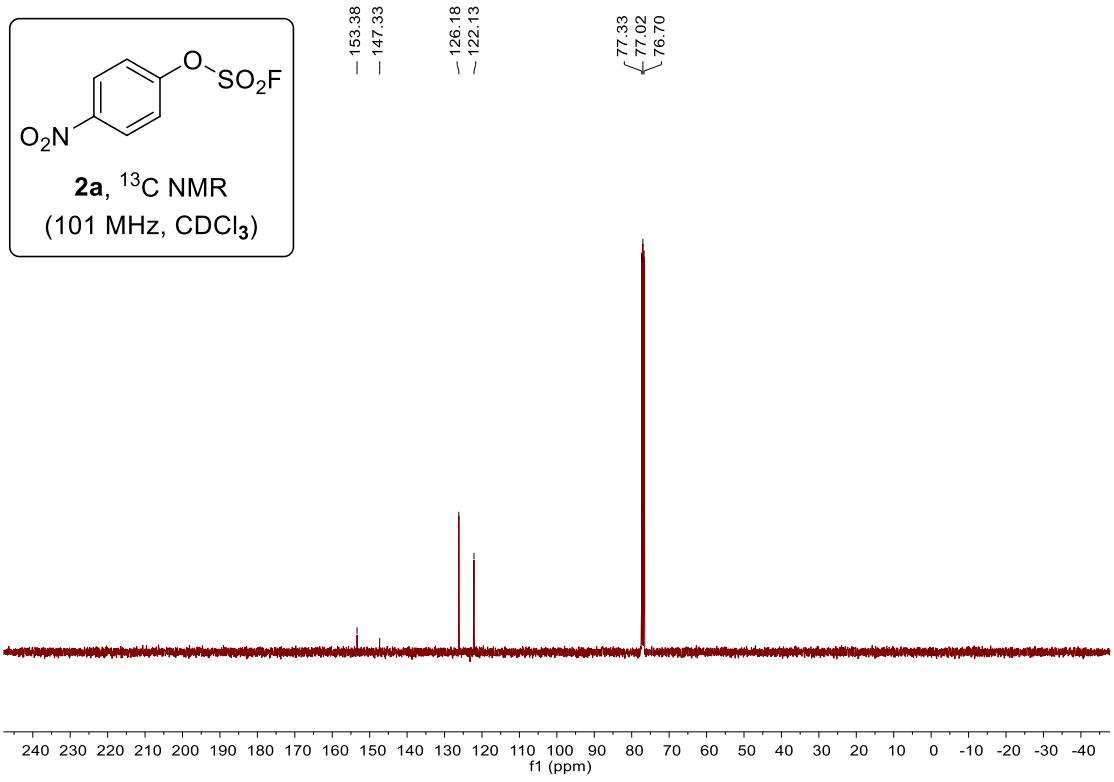
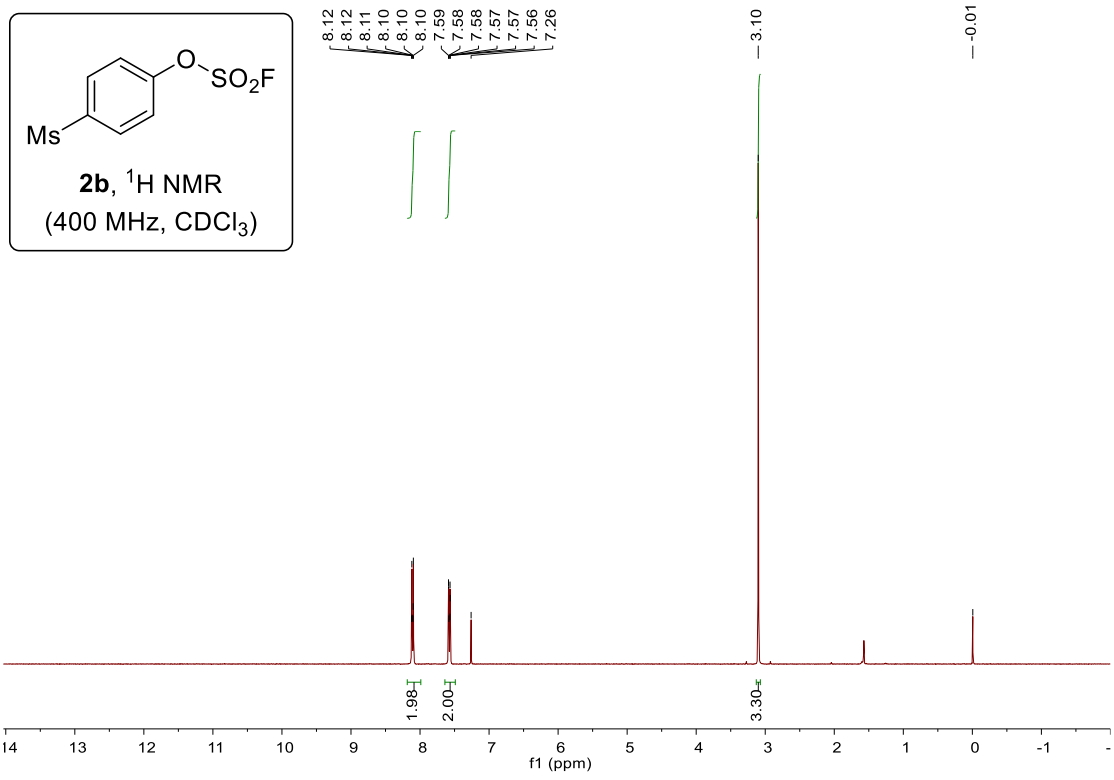
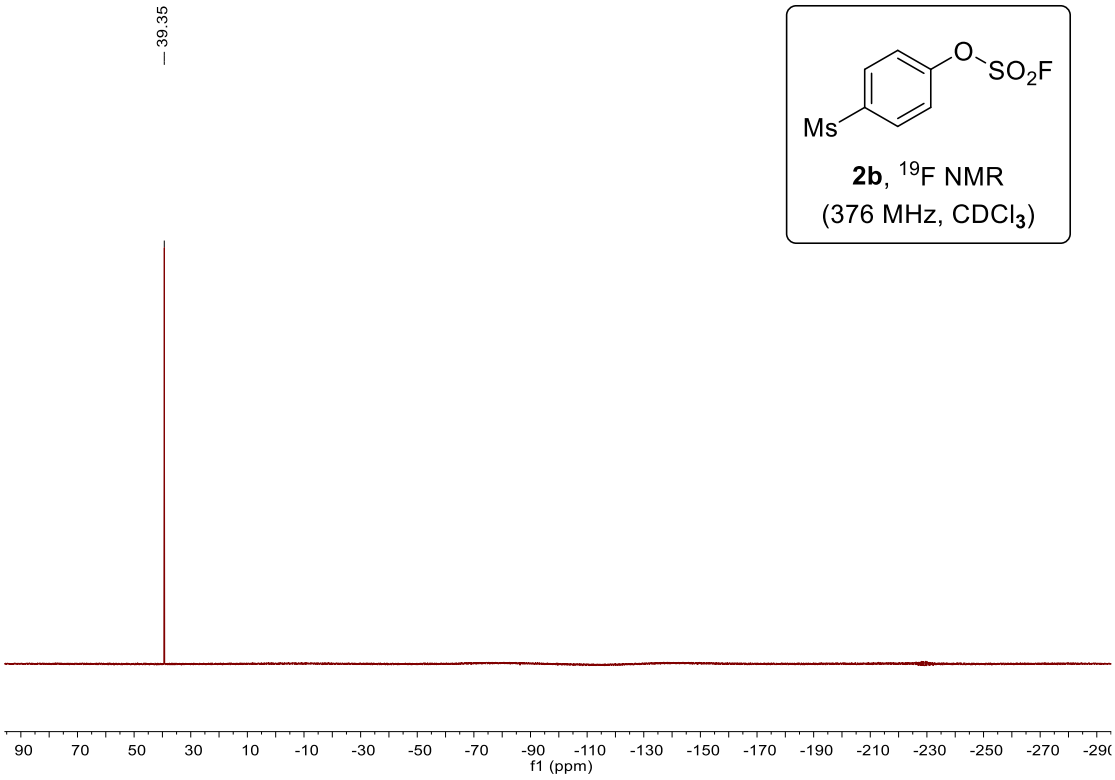
8. Copies of Spectra

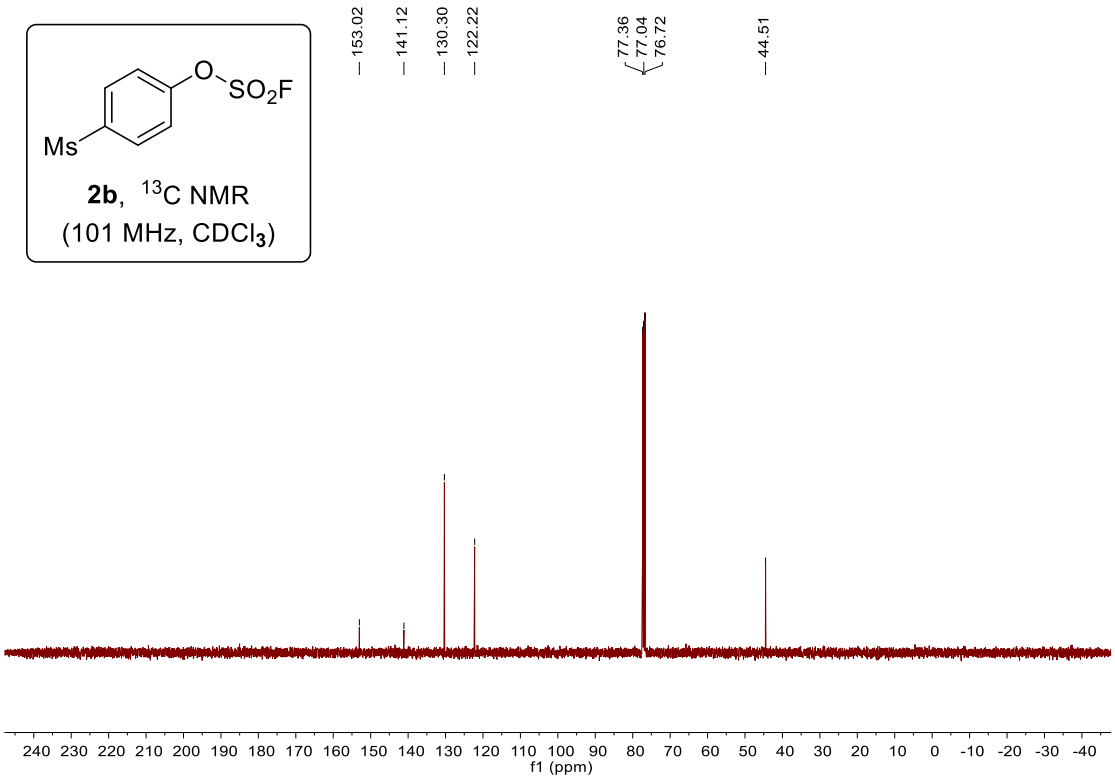


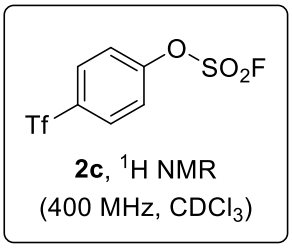



O
SO2F
O2N
2a, 13C NMR
(101 MHz, CDCl3)
153.38
147.33
126.18
122.13
77.33
77.02
76.70
f1 (ppm)

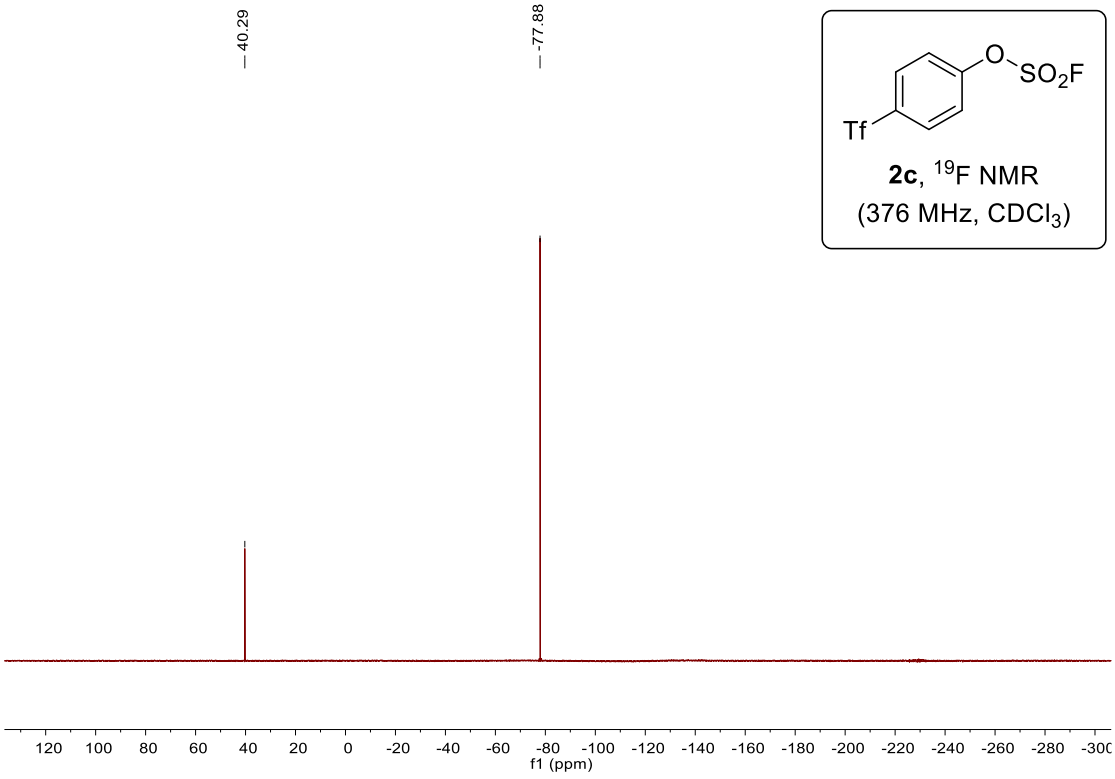

O
SO2F
Ms
2b, 1H NMR
(400 MHz, CDCl3)
8.12
8.12
8.11
8.10
8.10
8.10
7.59
7.58
7.58
7.57
7.57
7.56
7.26
3.10
-0.01
1.98
2.00
3.30
f1 (ppm)


39.35
O
SO2F
Ms
2b, 19F NMR
(376 MHz, CDCl3)
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

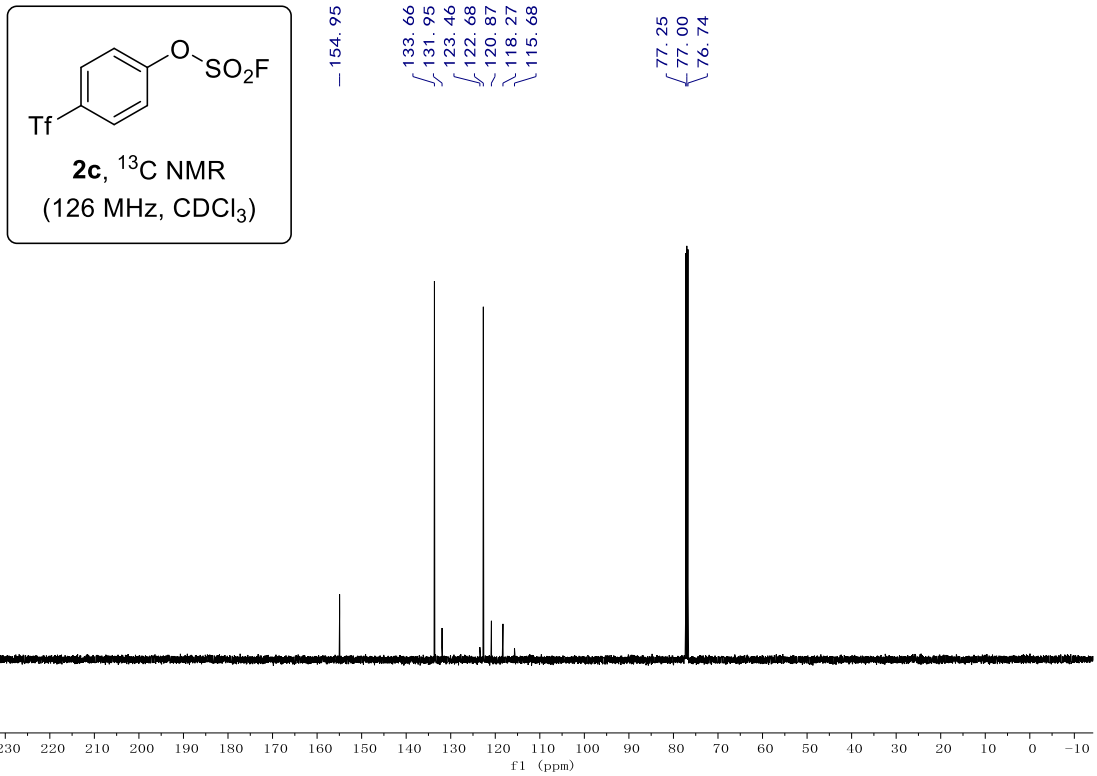

153.02
141.12
130.30
122.22
77.36
77.04
76.72
44.51
O
SO2F
Ms
2b, 13C NMR
(101 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

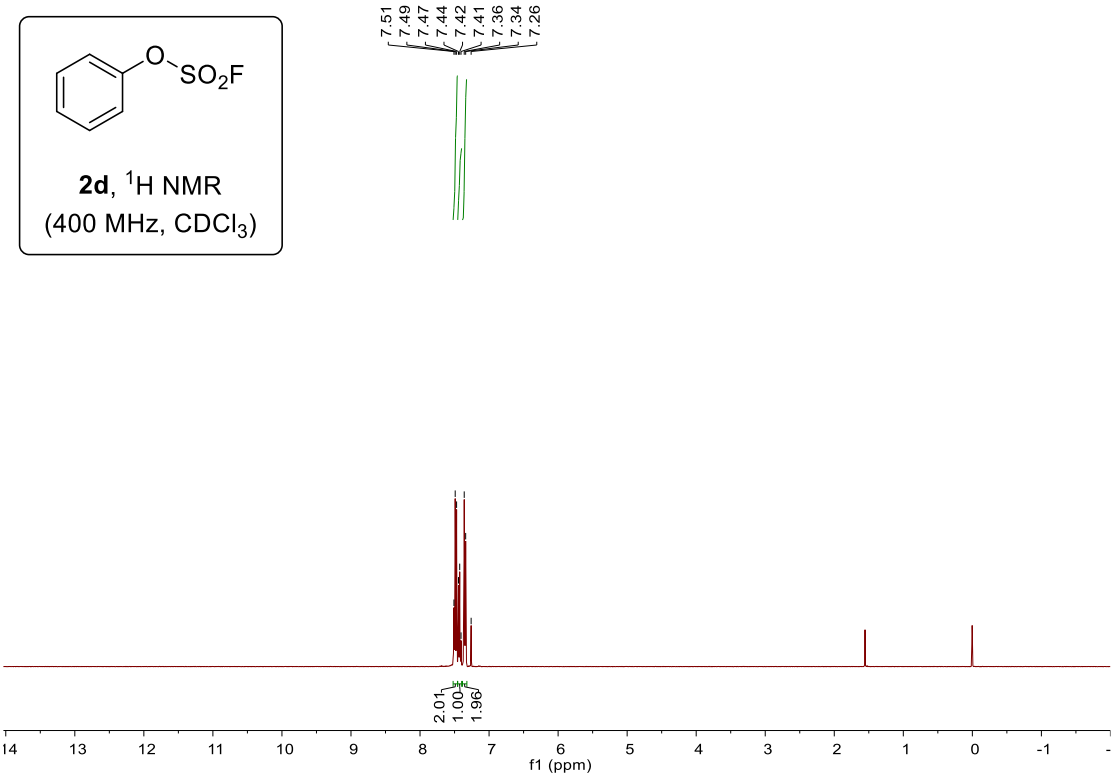


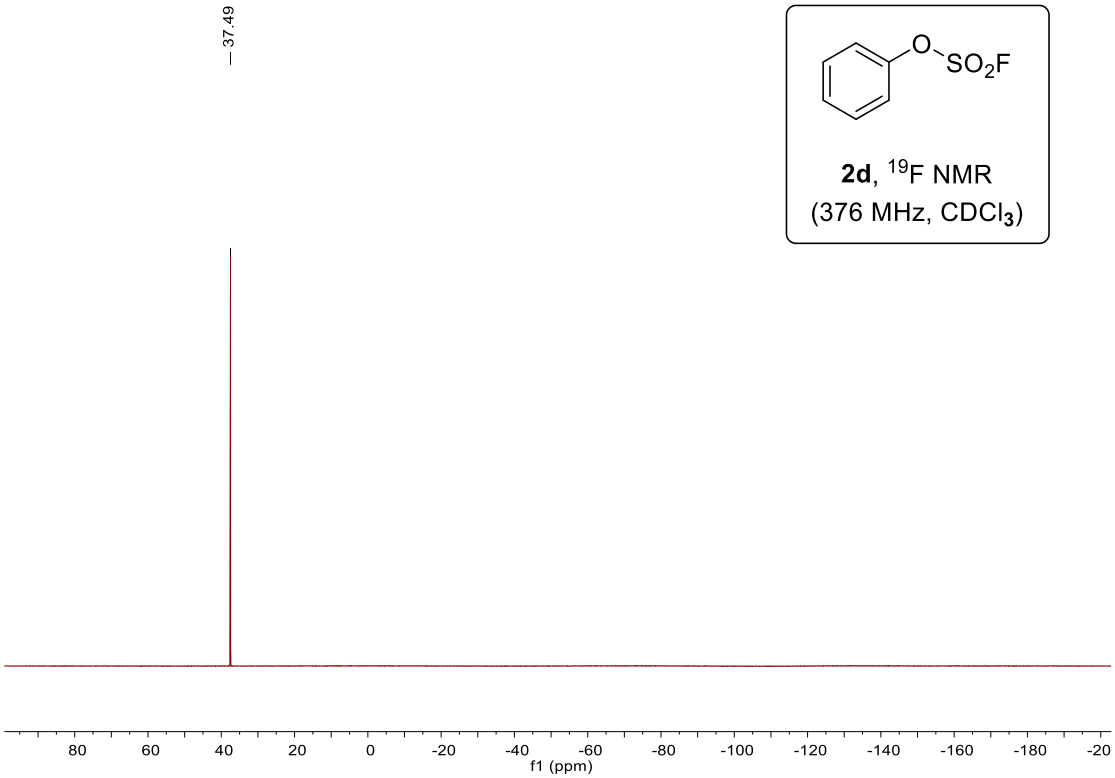
2c, ^{1}H NMR
(400 MHz, $CDCl_3$)

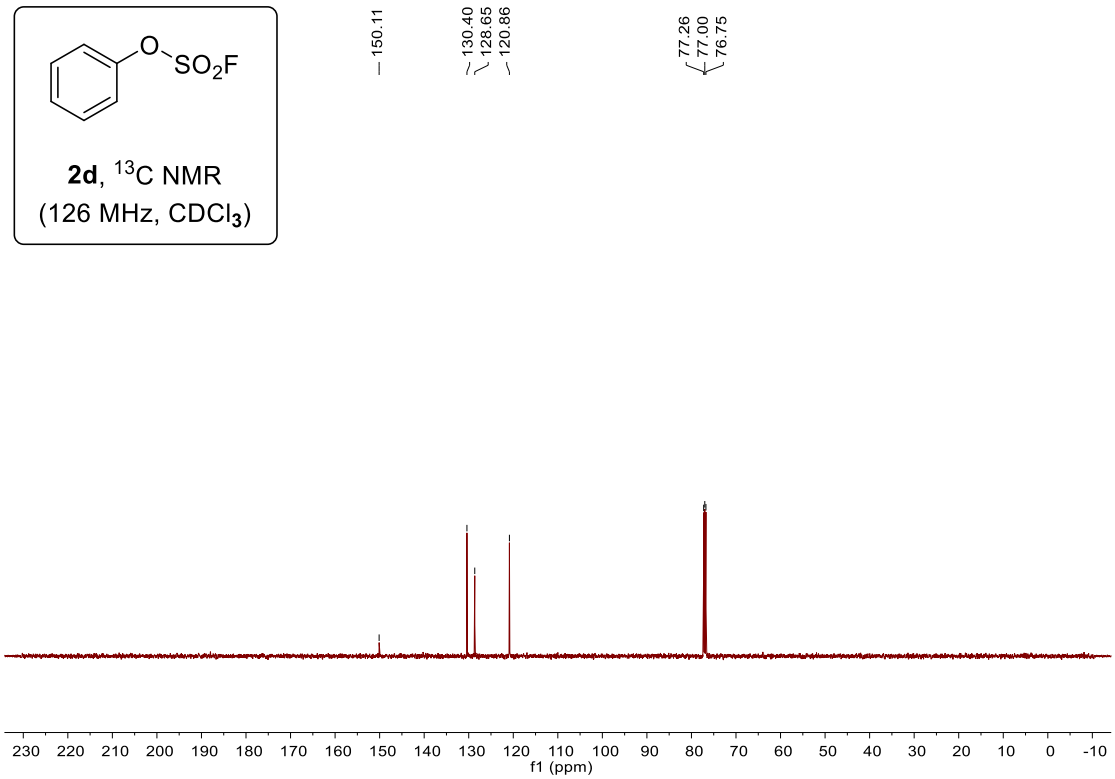


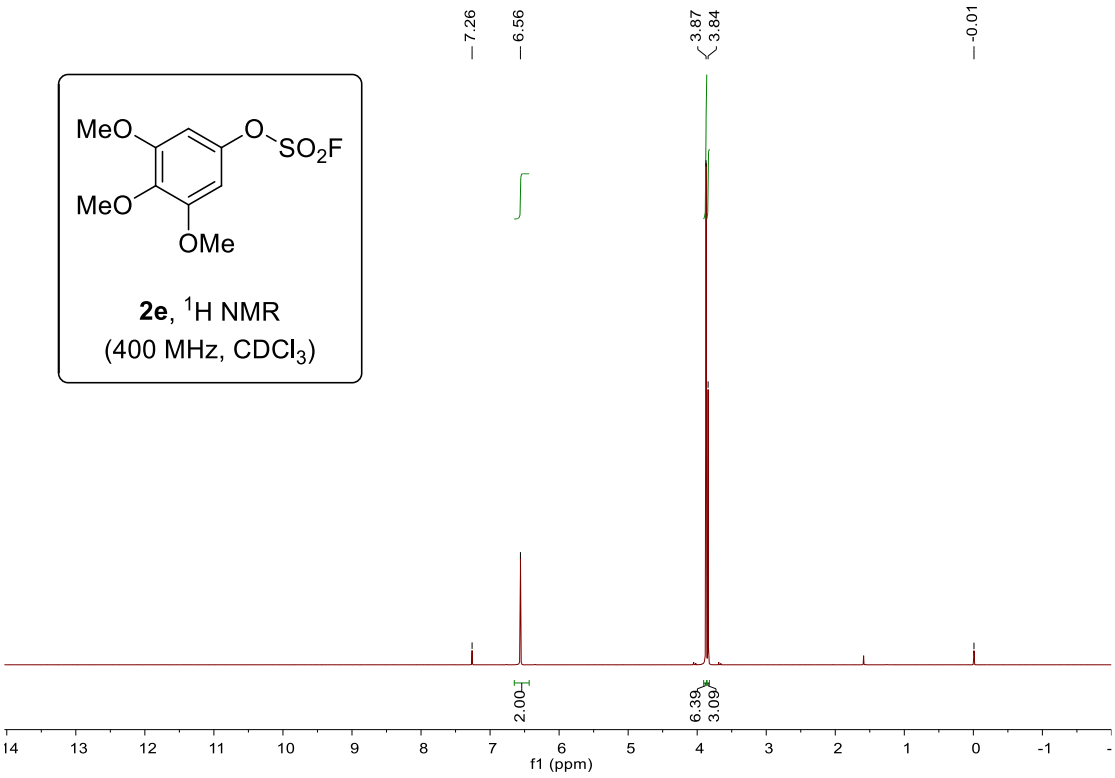
2c, ^{19}F NMR
(376 MHz, $CDCl_3$)

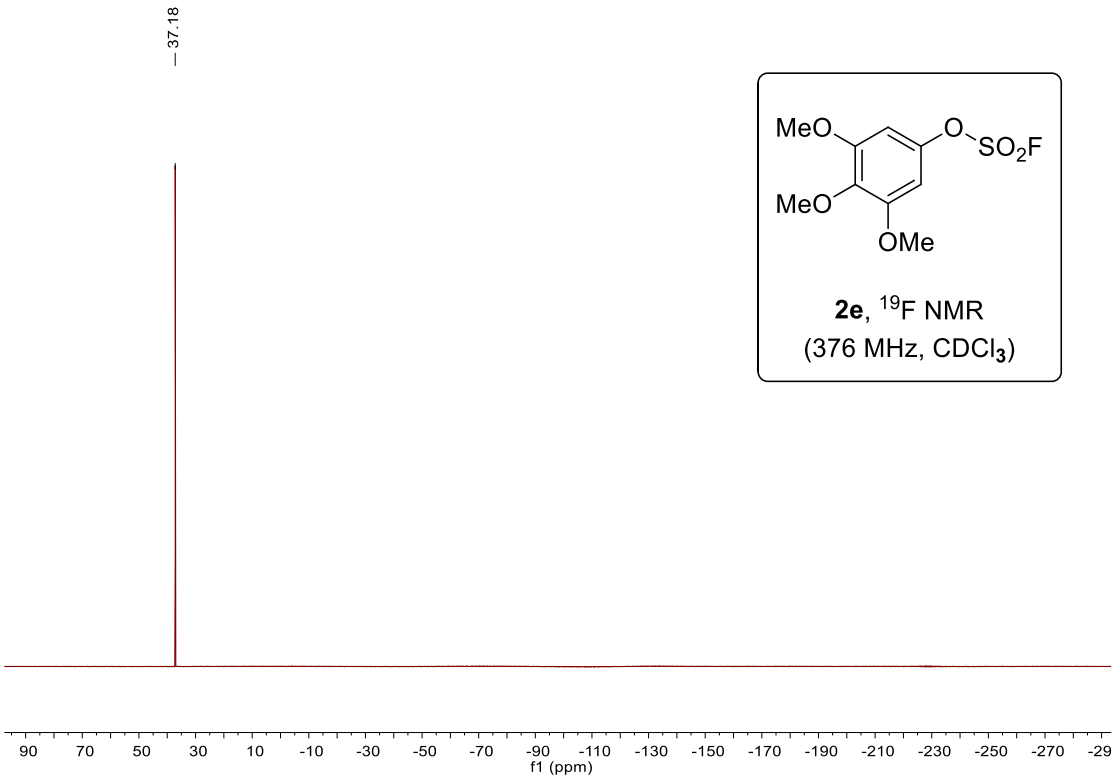

Tf
O
SO2F
2c, 13C NMR
(126 MHz, CDCl3)
154.95
133.66
131.95
123.46
122.68
120.87
118.27
115.68
77.25
77.00
76.74
f1 (ppm)

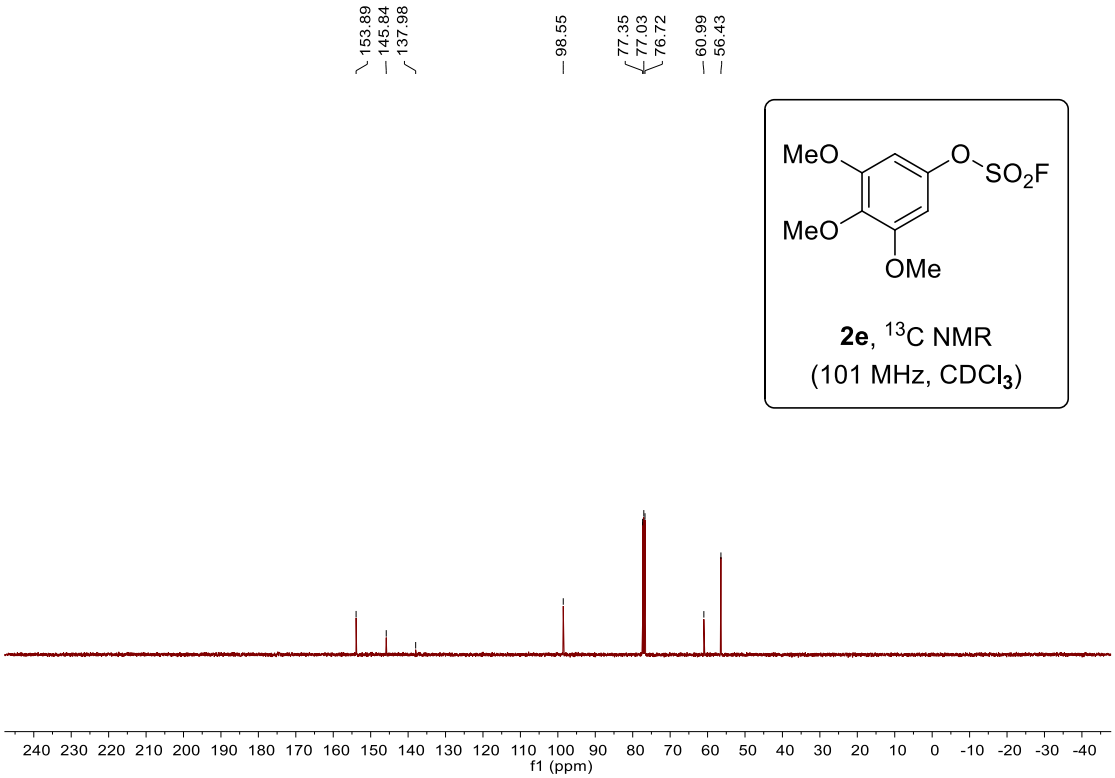

O
SO2F
2d, 1H NMR
(400 MHz, CDCl3)
7.51
7.49
7.47
7.44
7.42
7.41
7.36
7.34
7.26
2.01
1.00
1.96
f1 (ppm)

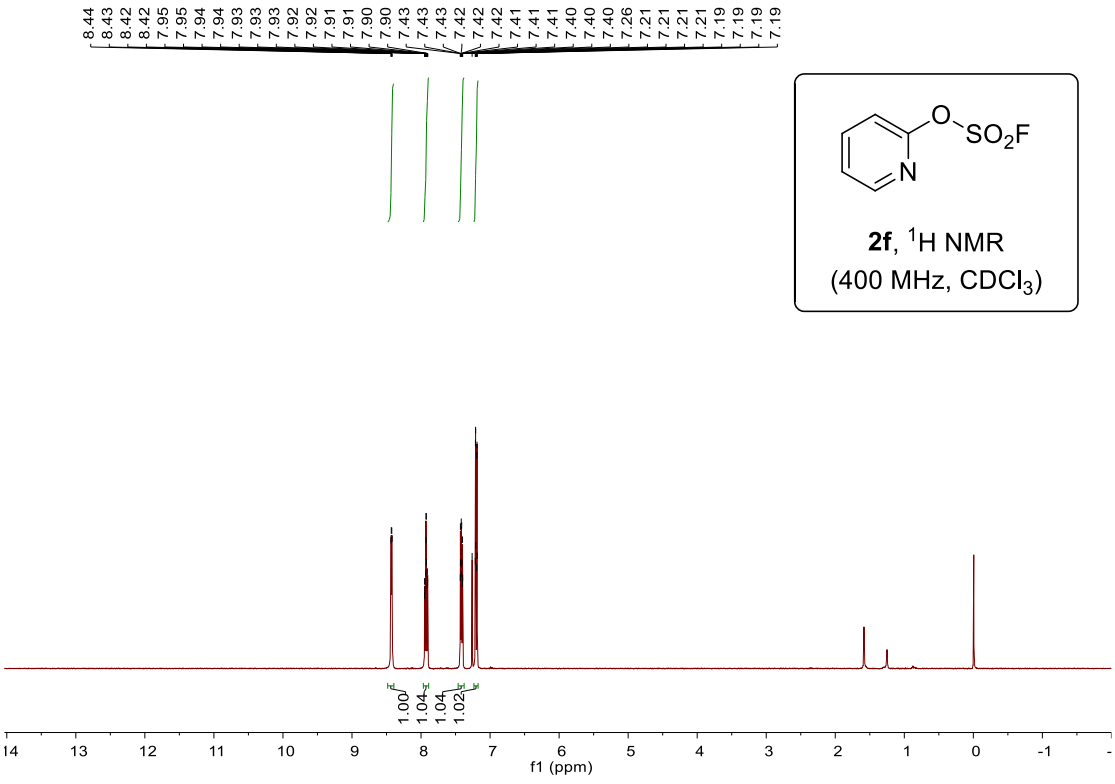

37.49
O
SO2F
2d, 19F NMR
(376 MHz, CDCl3)
80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -20
f1 (ppm)

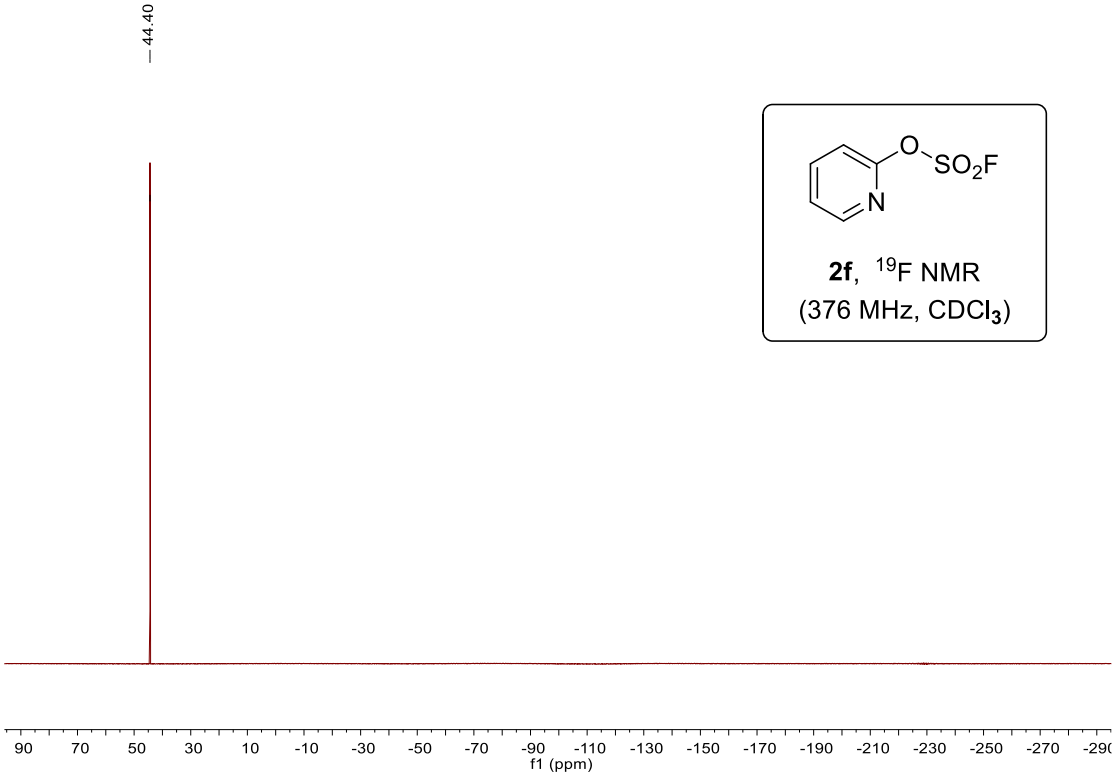

O
SO2F
2d, 13C NMR
(126 MHz, CDCl3)
150.11
130.40
128.65
120.86
77.26
77.00
76.75
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

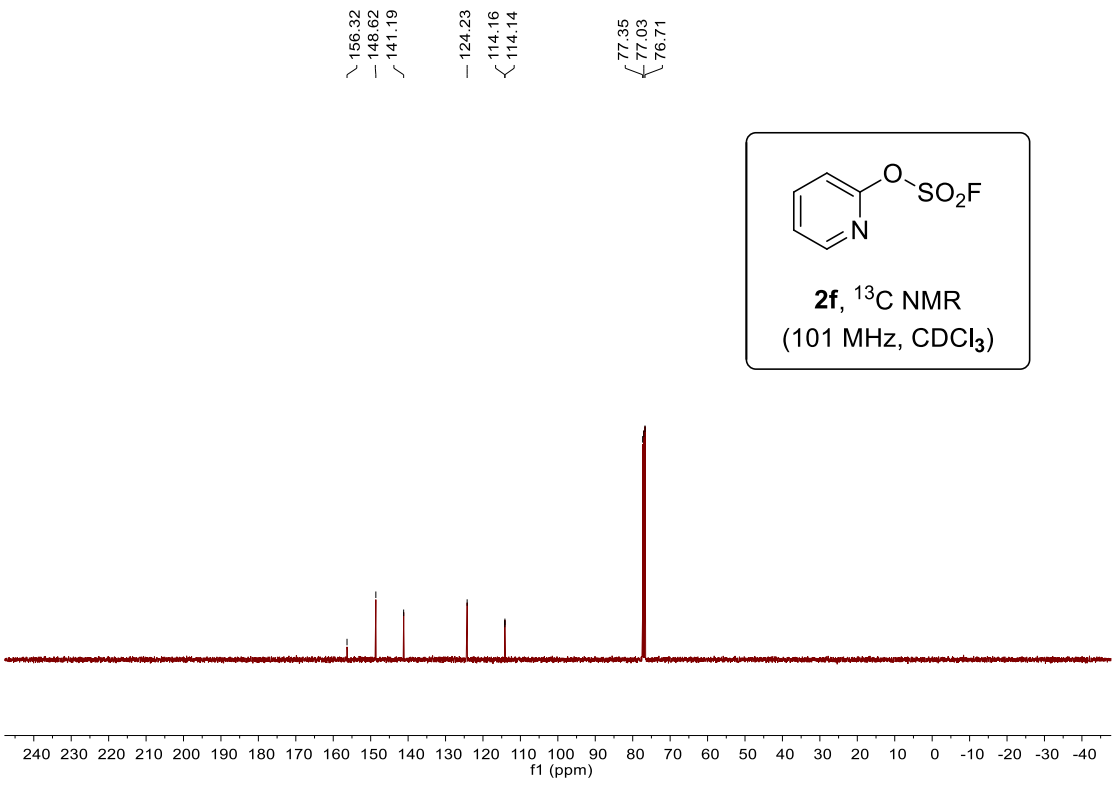

7.26
6.56
3.87
3.84
-0.01
MeO
O
SO2F
MeO
OMe
2e, 1H NMR
(400 MHz, CDCl3)
2.00
6.39
3.09
f1 (ppm)

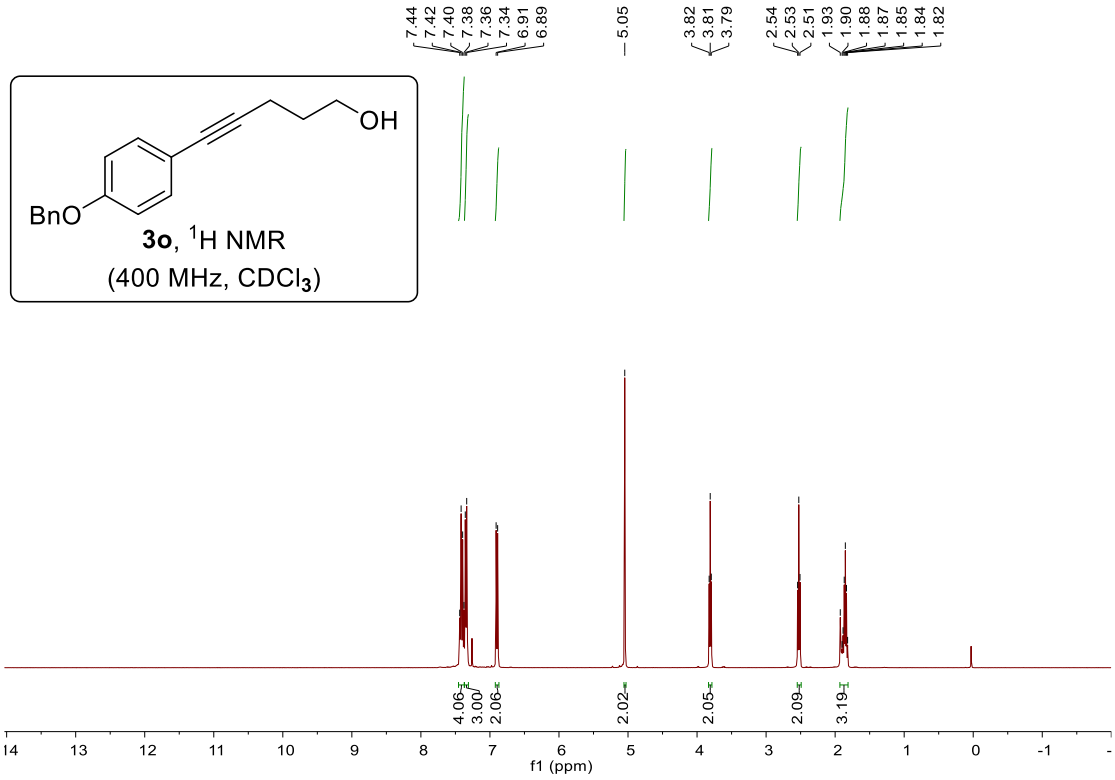

37.18
MeO
O
SO2F
MeO
OMe
2e, 19F NMR
(376 MHz, CDCl3)
f1 (ppm)

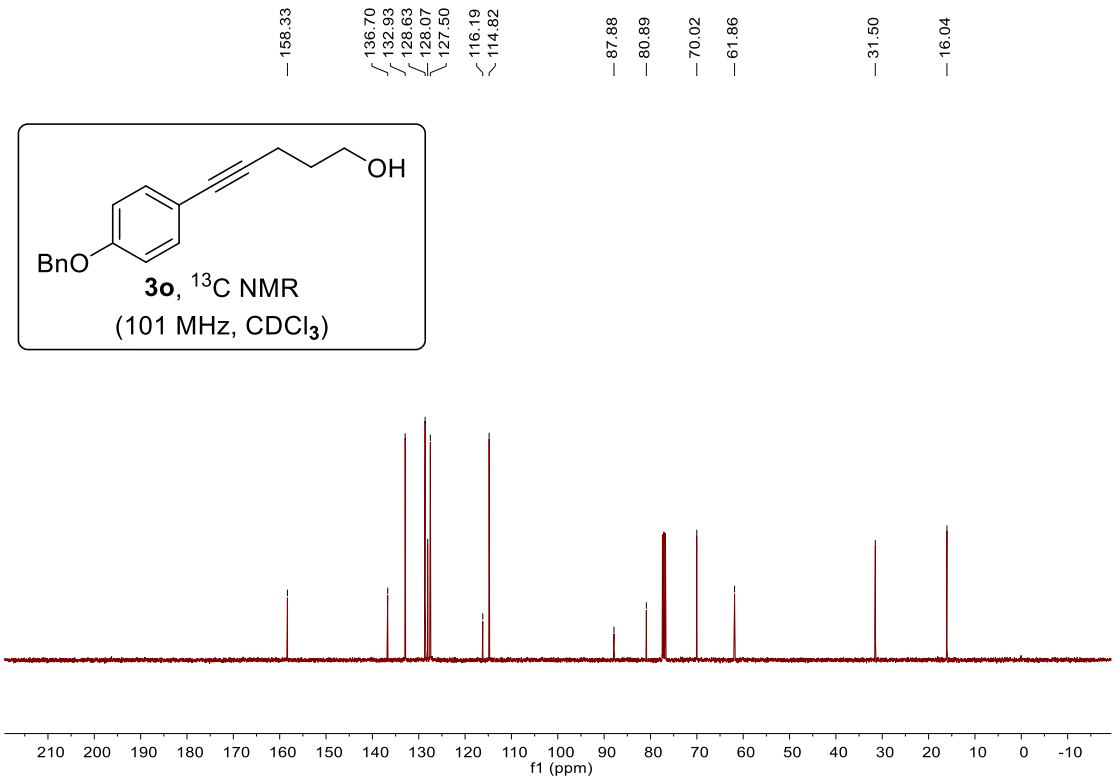

153.89
145.84
137.98
98.55
77.35
77.03
76.72
60.99
56.43
MeO
MeO
OMe
O
SO2F
2e, 13C NMR
(101 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

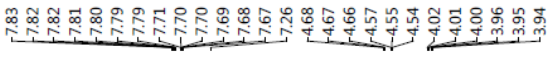

8.44
8.43
8.42
8.42
8.42
7.95
7.95
7.94
7.94
7.93
7.93
7.93
7.92
7.92
7.91
7.91
7.90
7.90
7.43
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.26
7.21
7.21
7.21
7.19
7.19
7.19
7.19
O
SO2F
N
2f, 1H NMR
(400 MHz, CDCl3)
1.00
1.04
1.04
1.02
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

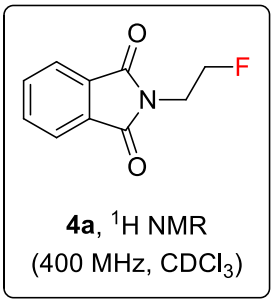

44.40
O
SO2F
N
2f, 19F NMR
(376 MHz, CDCl3)
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)


156.32
148.62
141.19
124.23
114.16
114.14
77.35
77.03
76.71
O
SO2F
N
2f, 13C NMR
(101 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

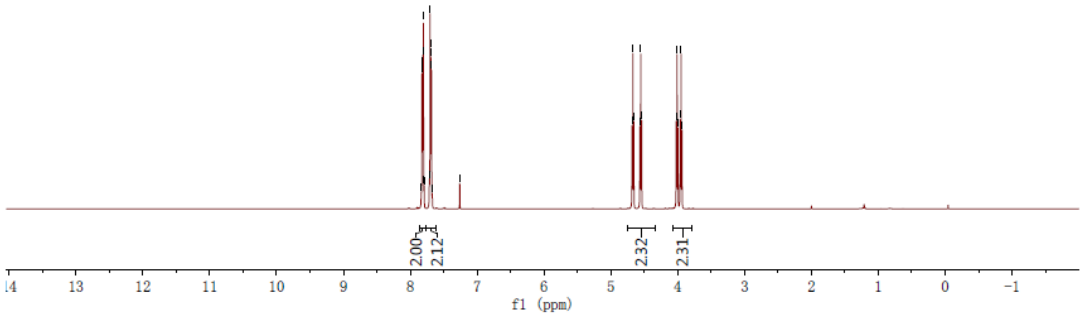

7.44
7.42
7.40
7.38
7.36
7.34
6.91
6.89
5.05
3.82
3.81
3.79
2.54
2.53
2.51
1.93
1.90
1.88
1.87
1.85
1.84
1.82
OH
BnO
3o, 1H NMR
(400 MHz, CDCl3)
4.06
3.00
2.06
2.02
2.05
2.09
3.19
f1 (ppm)

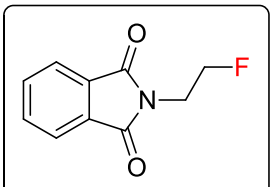

158.33
136.70
132.93
128.63
128.07
127.50
116.19
114.82
87.88
80.89
70.02
61.86
31.50
16.04
OH
BnO
3o, 13C NMR
(101 MHz, CDCl3)
f1 (ppm)



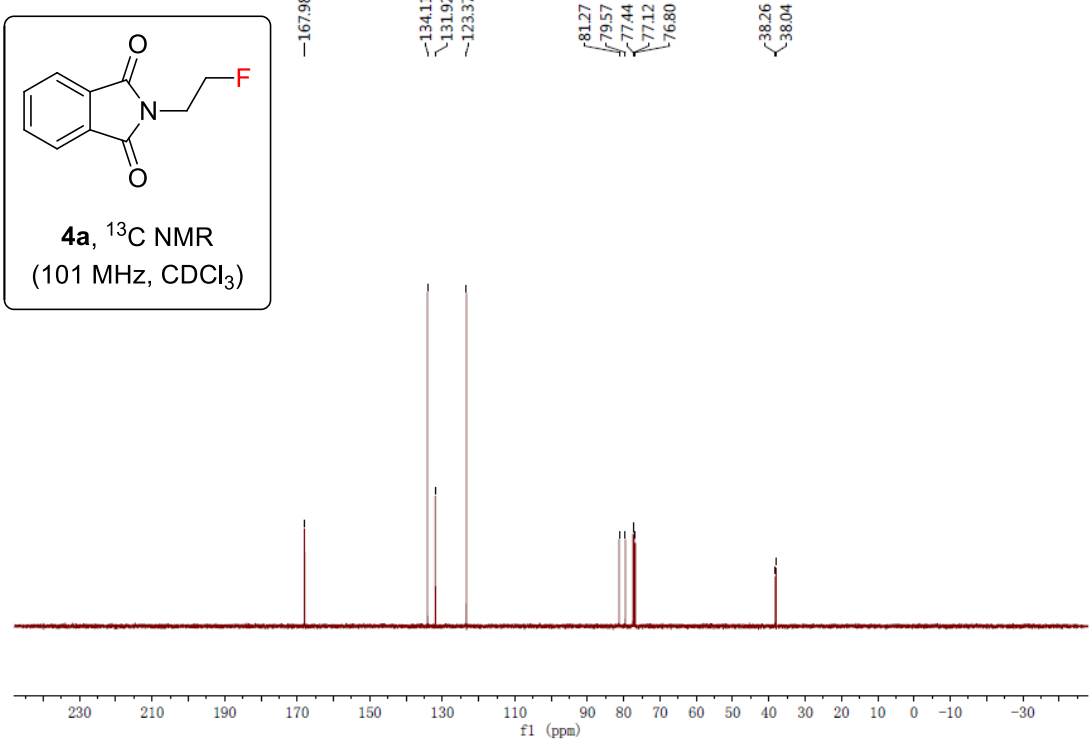


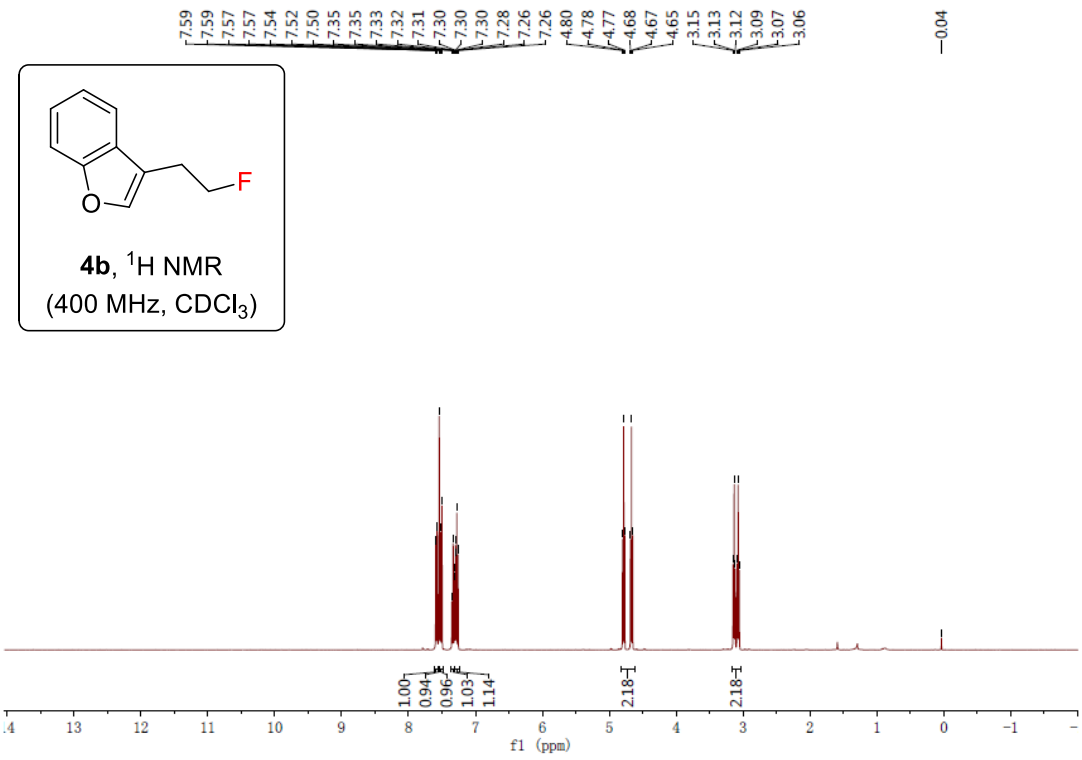
4a, ^{1}H NMR
(400 MHz, $CDCl_3$)

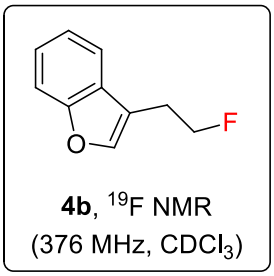




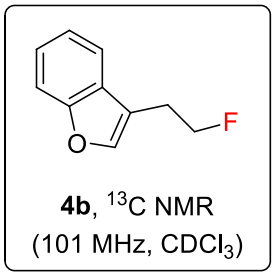
4a, ^{19}F NMR
(376 MHz, $CDCl_3$)


O
N
F
O
4a, 13C NMR
(101 MHz, CDCl3)
167.98
134.11
131.92
123.37
81.27
79.57
77.44
77.12
76.80
38.26
38.04
f1 (ppm)

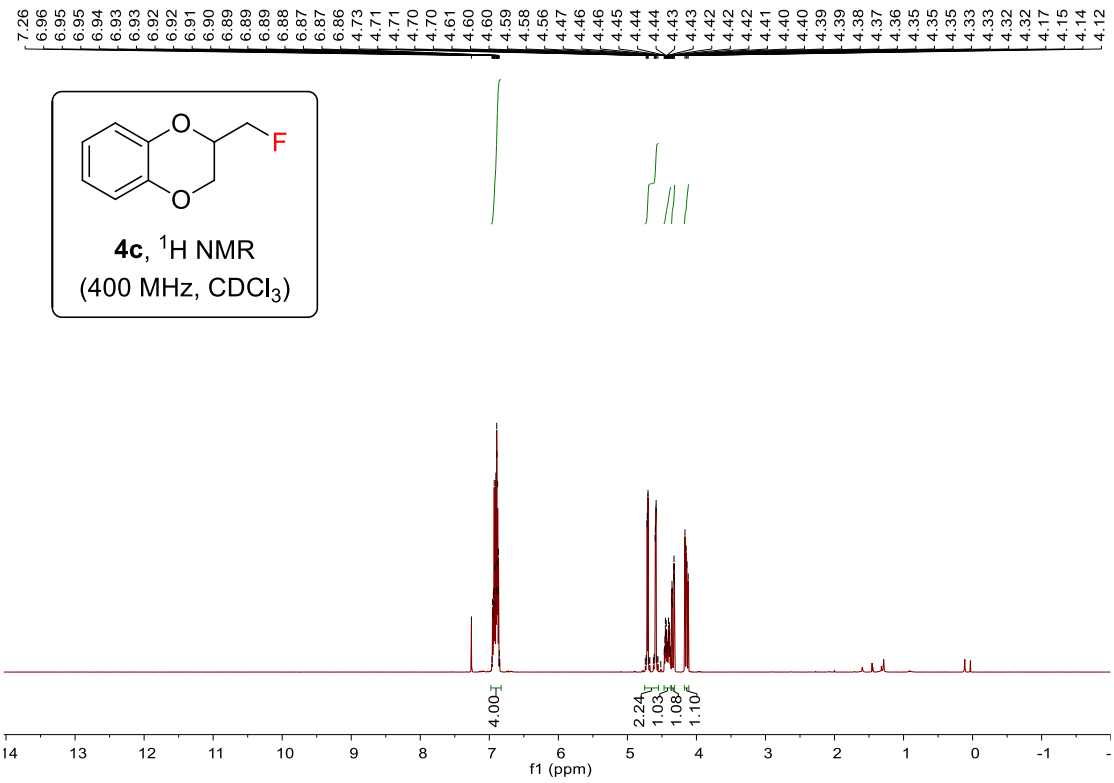

7.59
7.59
7.57
7.57
7.54
7.52
7.50
7.35
7.35
7.33
7.32
7.31
7.30
7.30
7.30
7.28
7.26
7.26
4.80
4.78
4.77
4.68
4.67
4.65
3.15
3.13
3.12
3.09
3.07
3.06
0.04
O
F
4b, 1H NMR
(400 MHz, CDCl3)
1.00
0.94
0.96
1.03
1.14
2.18
2.18
f1 (ppm)

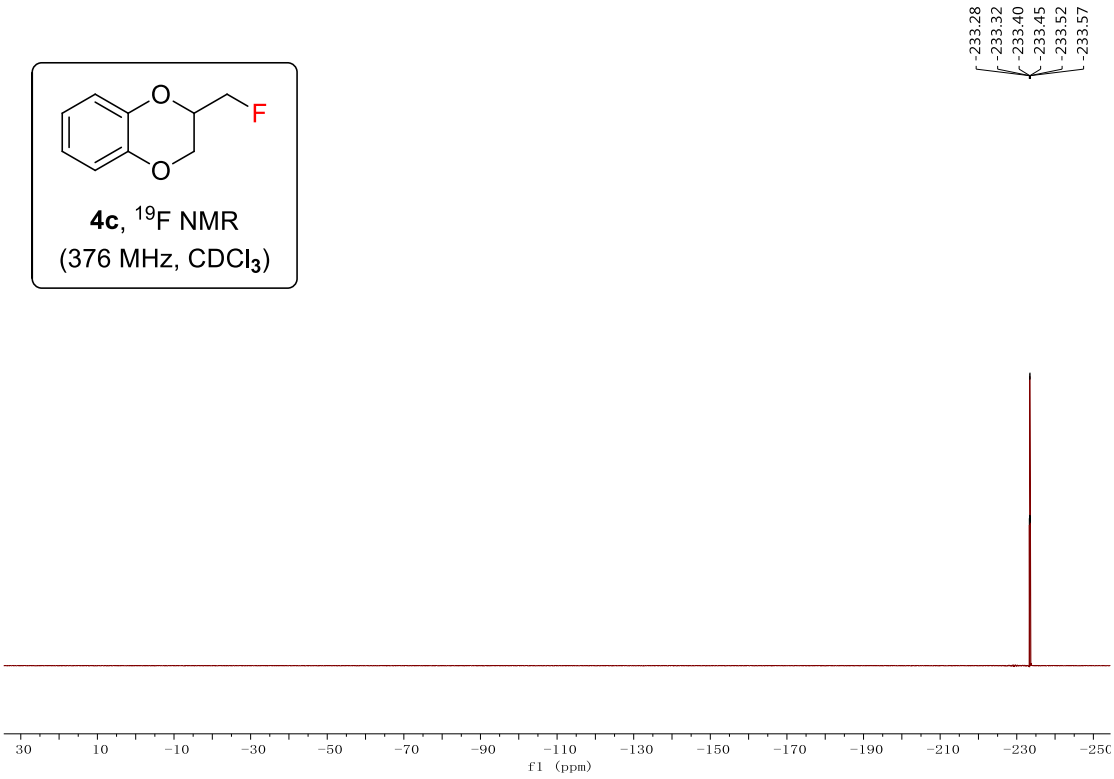


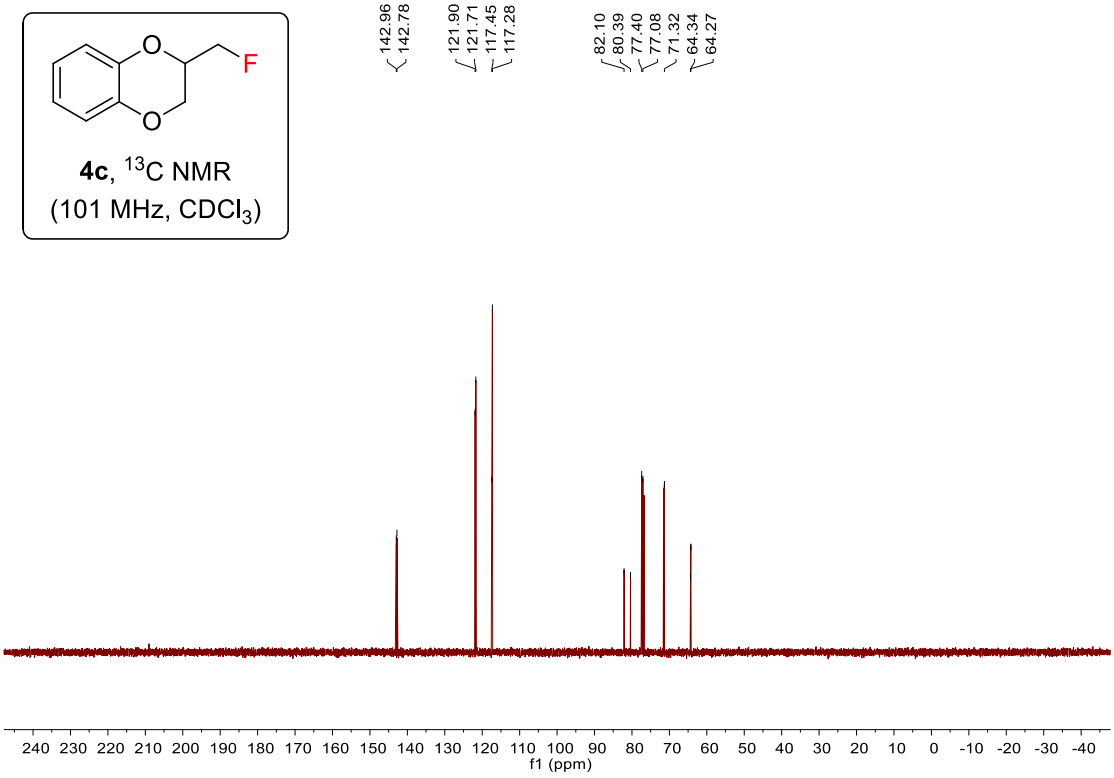
4b, ^{19}F NMR
(376 MHz, $CDCl_3$)

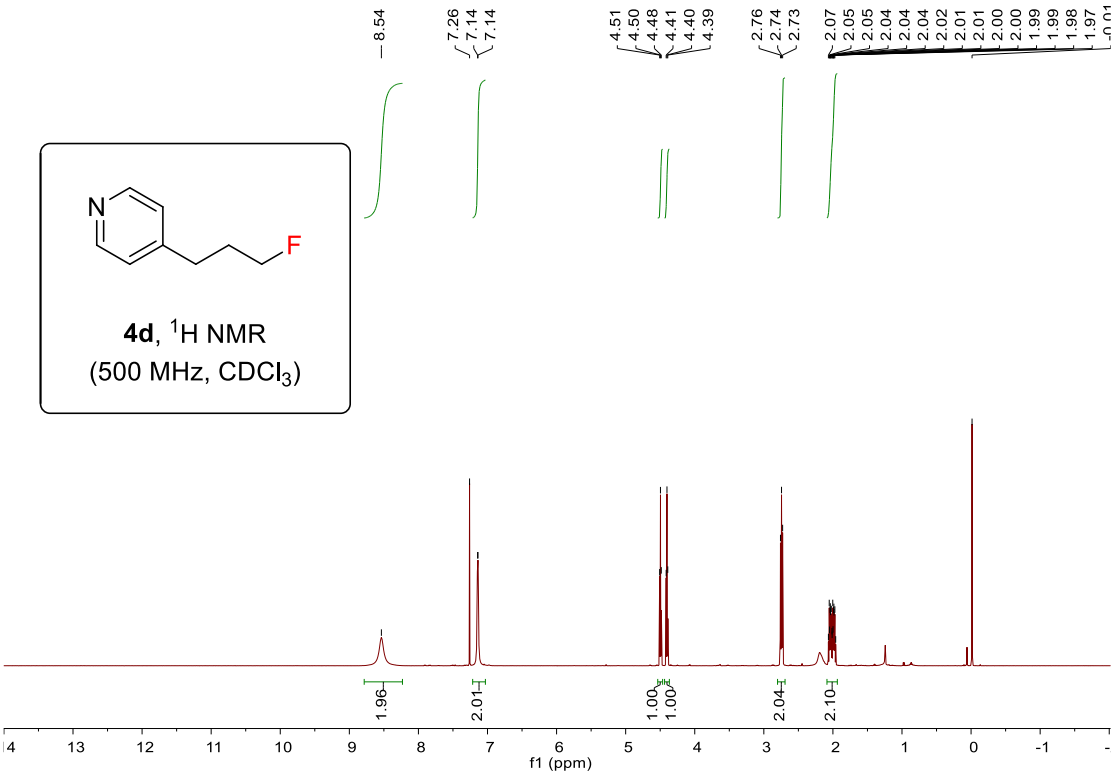


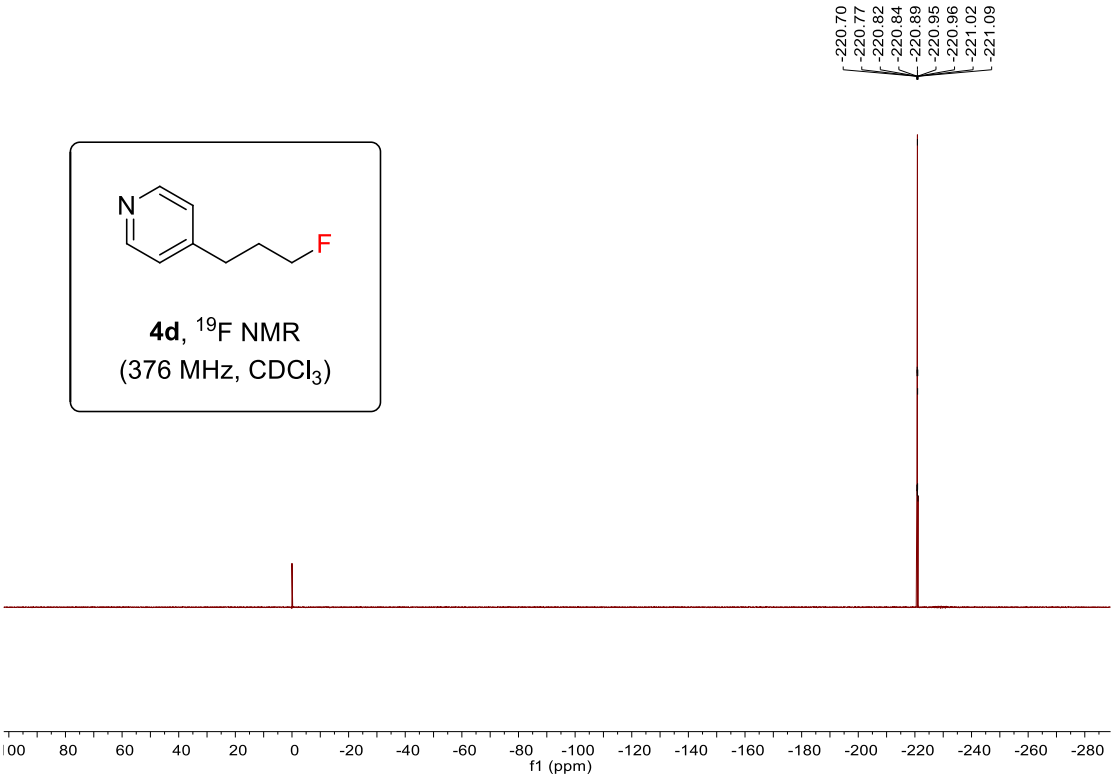
4b, ^{13}C NMR
(101 MHz, $CDCl_3$)

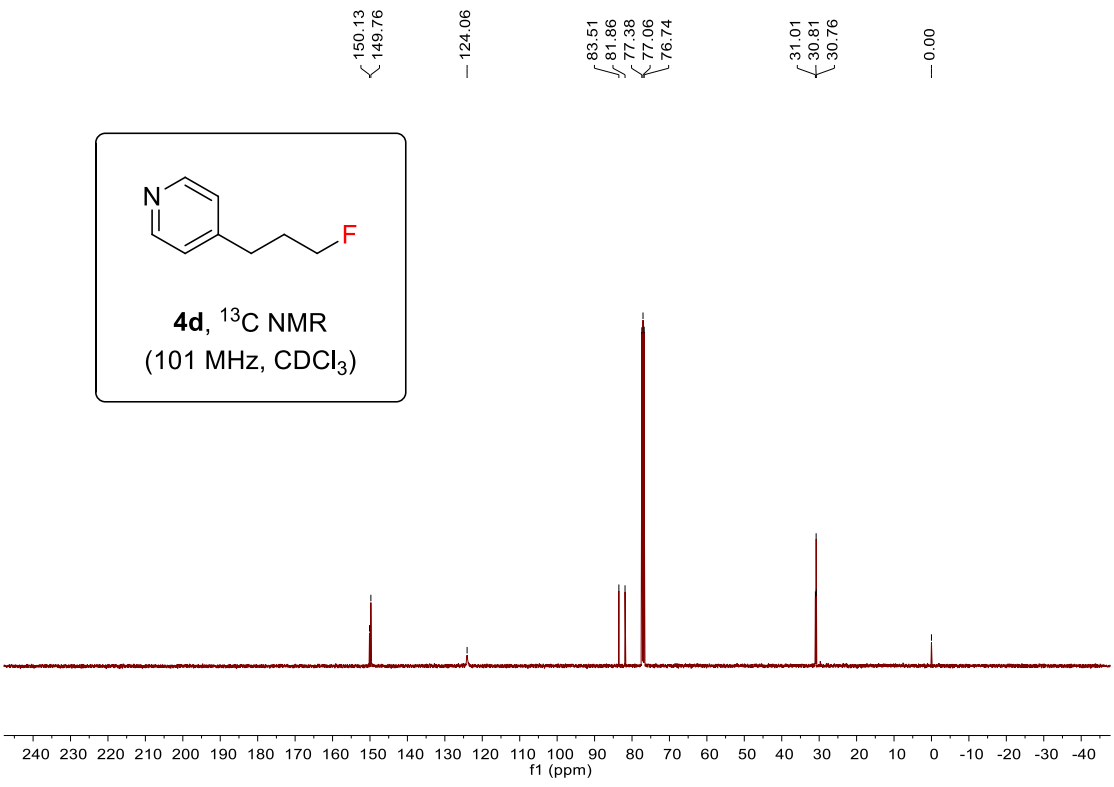

7.26
6.96
6.95
6.95
6.94
6.93
6.93
6.92
6.92
6.91
6.90
6.89
6.89
6.89
6.88
6.87
6.87
6.86
4.73
4.71
4.71
4.70
4.70
4.61
4.60
4.60
4.59
4.58
4.56
4.47
4.46
4.46
4.45
4.44
4.44
4.43
4.43
4.42
4.42
4.42
4.41
4.40
4.40
4.39
4.39
4.38
4.37
4.36
4.35
4.35
4.33
4.33
4.32
4.32
4.17
4.15
4.14
4.12
O
O
F
4c, 1H NMR
(400 MHz, CDCl3)
4.00
2.24
1.03
1.08
1.10
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

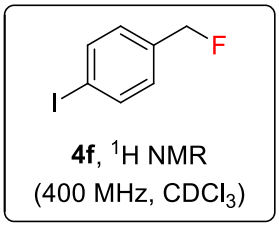

-233.28
-233.32
-233.40
-233.45
-233.52
-233.57
O
O
F
4c, 19F NMR
(376 MHz, CDCl3)
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)


O
F
O
4c, 13C NMR
(101 MHz, CDCl3)
142.96
142.78
121.90
121.71
117.45
117.28
82.10
80.39
77.40
77.08
71.32
64.34
64.27
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

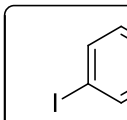

N
F
4d, 1H NMR
(500 MHz, CDCl3)
8.54
7.26
7.14
7.14
4.51
4.50
4.48
4.41
4.40
4.39
2.76
2.74
2.73
2.07
2.05
2.05
2.04
2.04
2.04
2.02
2.01
2.01
2.00
2.00
1.99
1.99
1.98
1.97
1.96
2.01
1.00
1.00
2.04
2.10
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


-220.70
-220.77
-220.82
-220.84
-220.89
-220.95
-220.96
-221.02
-221.09
N
F
4d, 19F NMR
(376 MHz, CDCl3)
f1 (ppm)

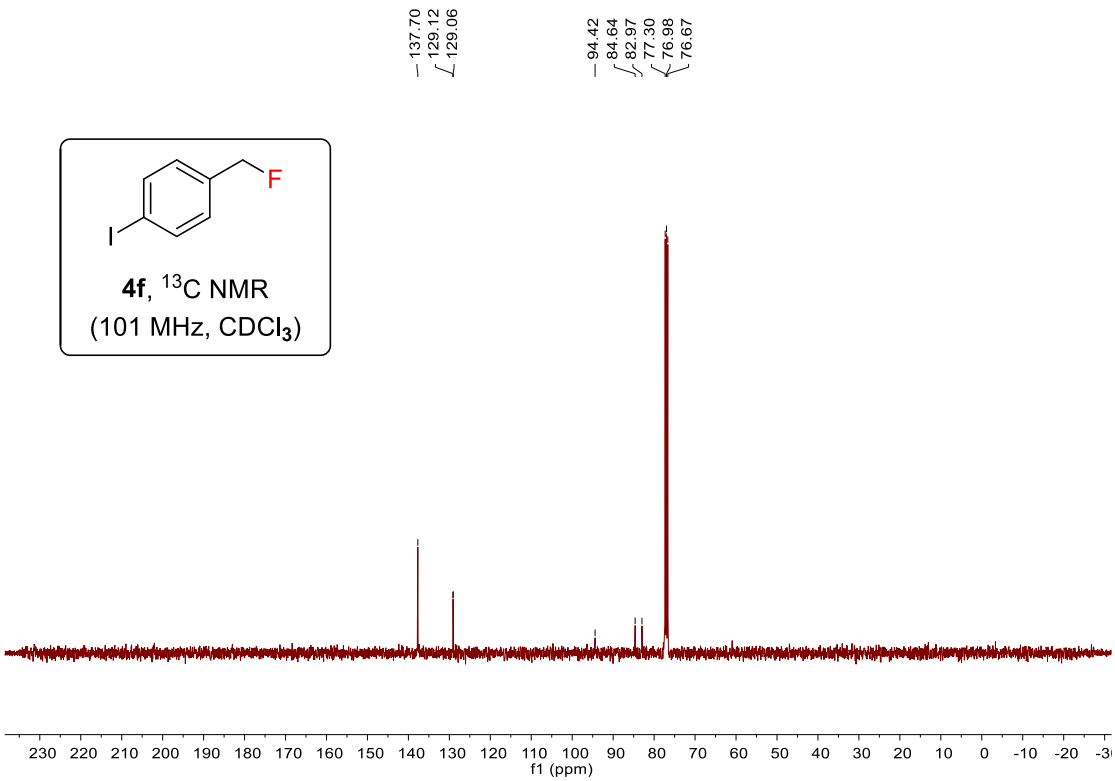

150.13
149.76
124.06
83.51
81.86
77.38
77.06
76.74
31.01
30.81
30.76
0.00
N
F
4d, 13C NMR
(101 MHz, CDCl3)
f1 (ppm)



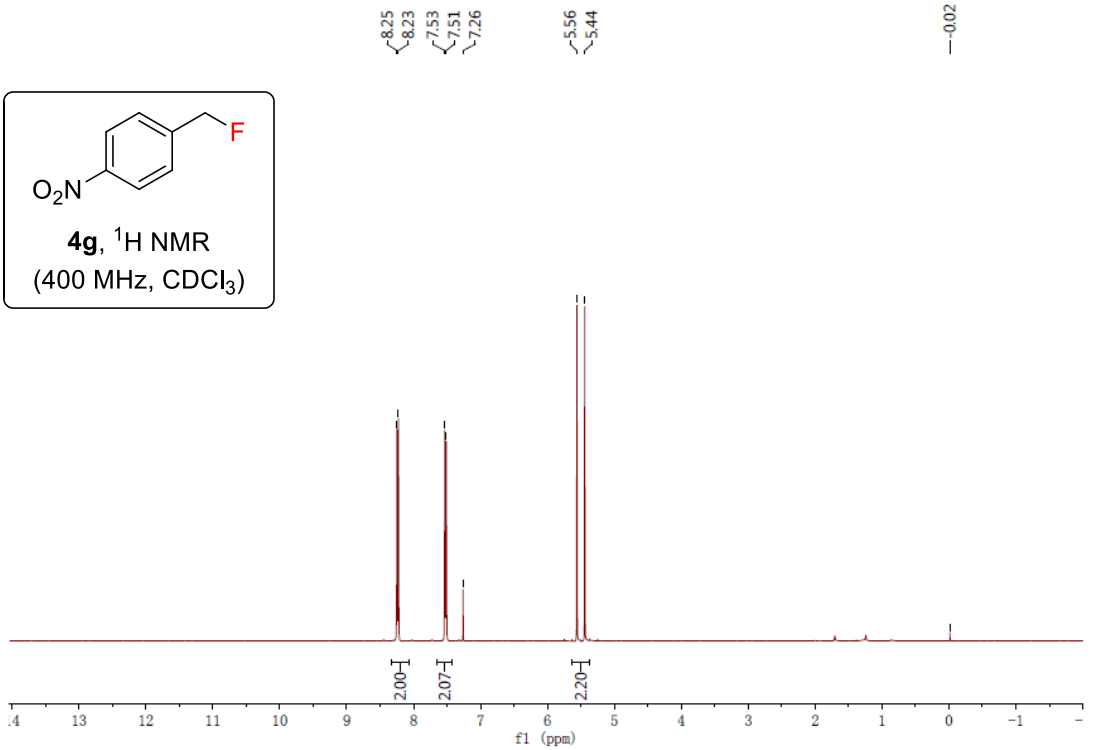
4f, ^{1}H NMR
(400 MHz, $CDCl_3$)



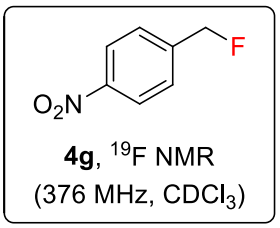
4f, ^{19}F NMR
(376 MHz, $CDCl_3$)



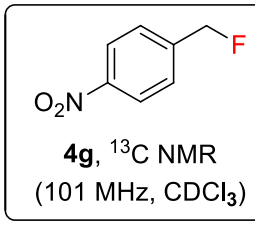
4f, ^{13}C NMR
(101 MHz, $CDCl_3$)



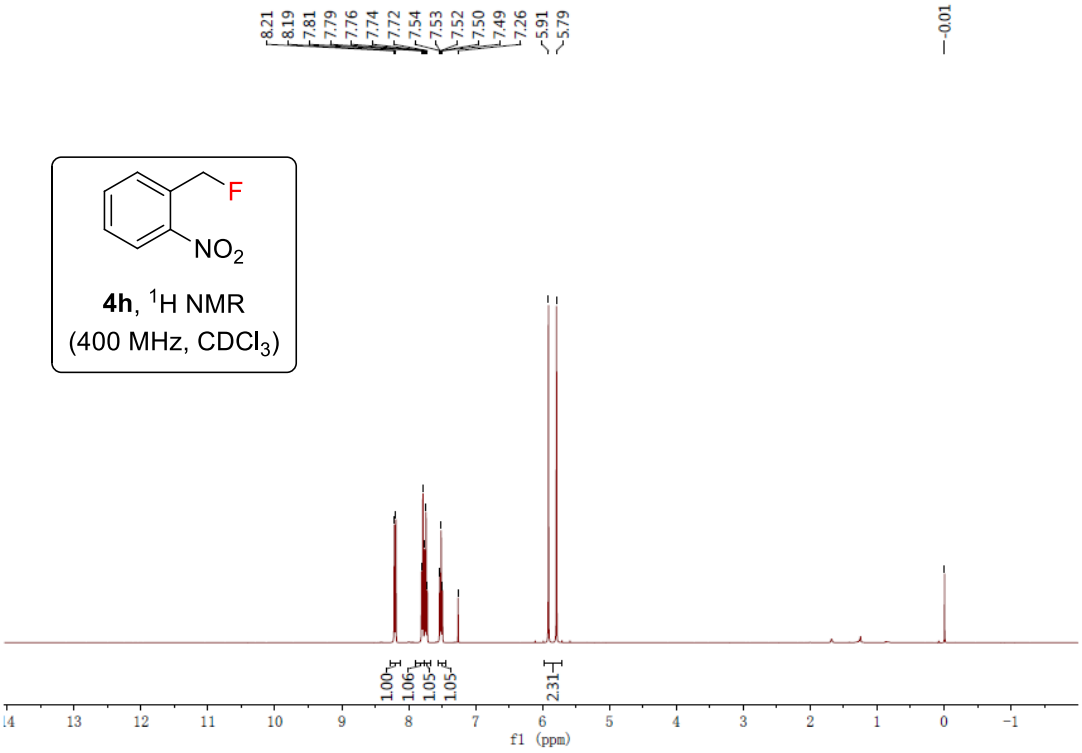
4g, ^{1}H NMR
(400 MHz, $CDCl_3$)

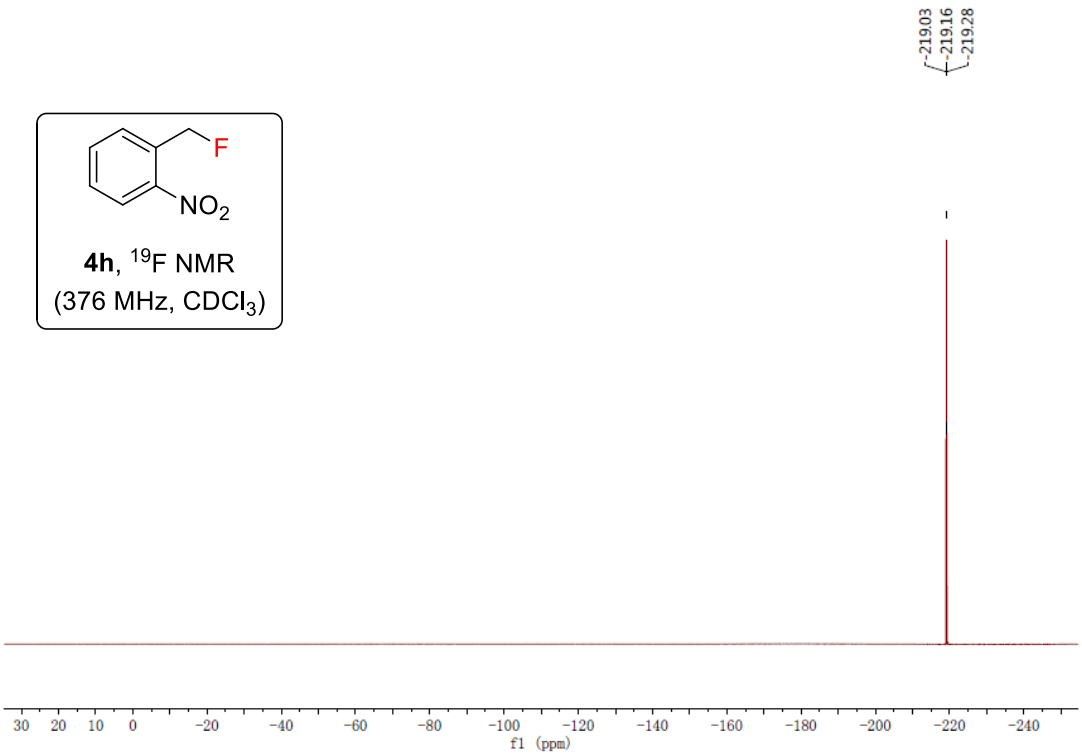


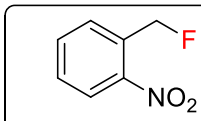
4g, ^{19}F NMR
(376 MHz, $CDCl_3$)



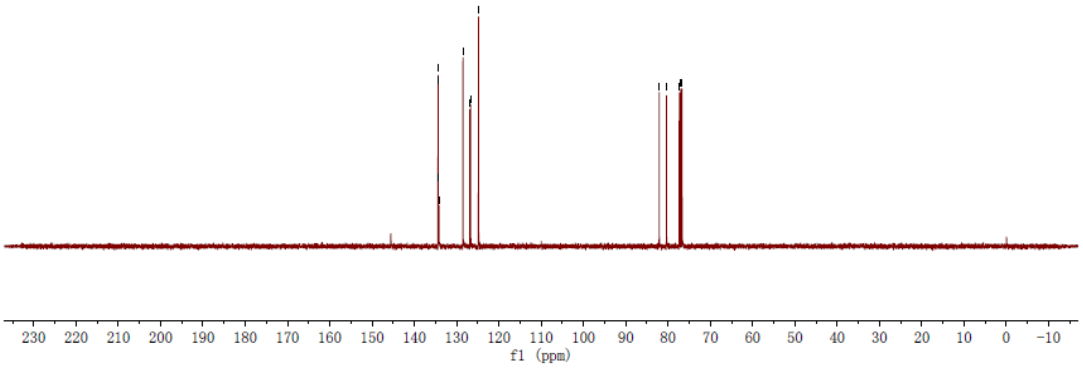
4g, ^{13}C NMR
(101 MHz, $CDCl_3$)

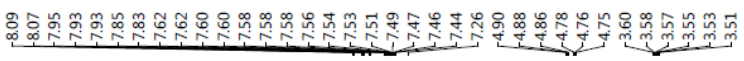

8.21
8.19
7.81
7.79
7.76
7.74
7.72
7.54
7.53
7.52
7.50
7.49
7.26
5.91
5.79
0.01
F
NO2
4h, 1H NMR
(400 MHz, CDCl3)
1.00
1.06
1.05
1.05
2.31
f1 (ppm)

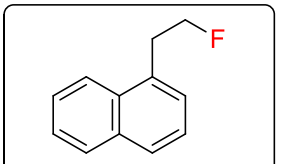

219.03
219.16
219.28
F
NO2
4h, 19F NMR
(376 MHz, CDCl3)
f1 (ppm)



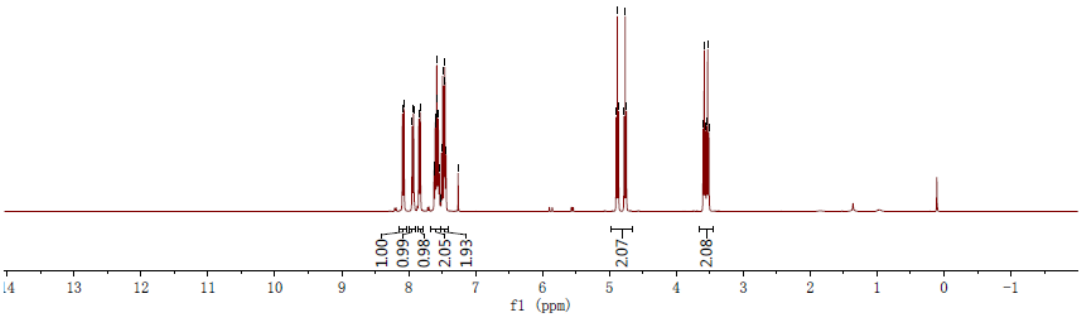
4h, ^{13}C NMR
(101 MHz, $CDCl_3$)

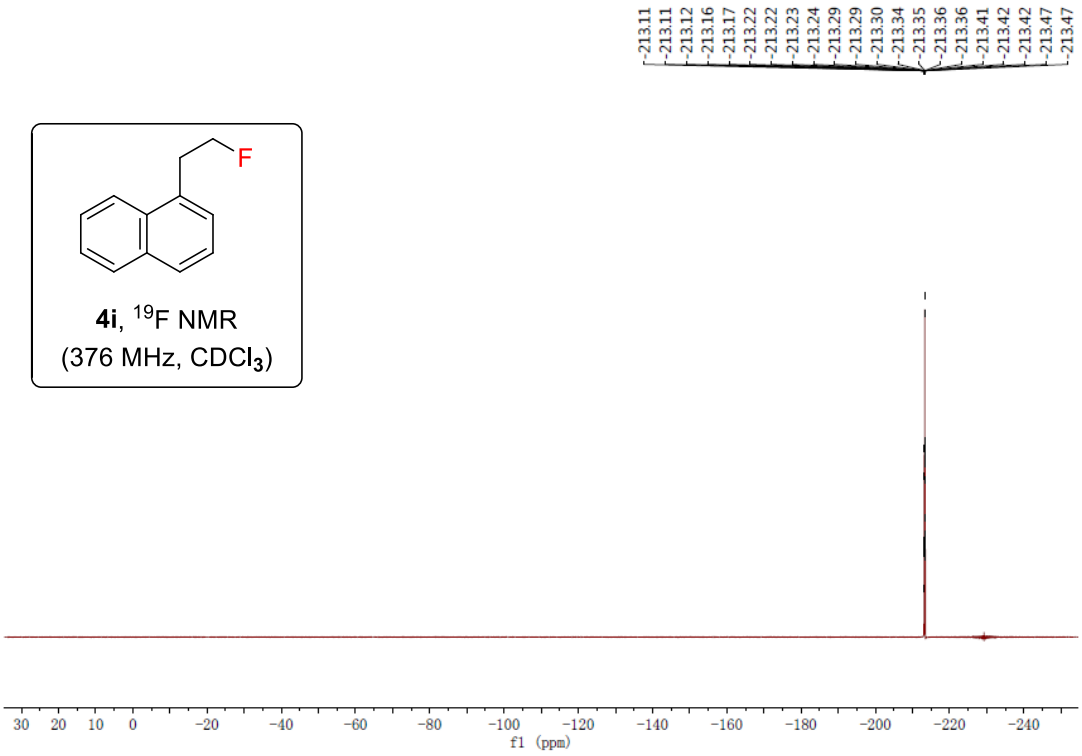


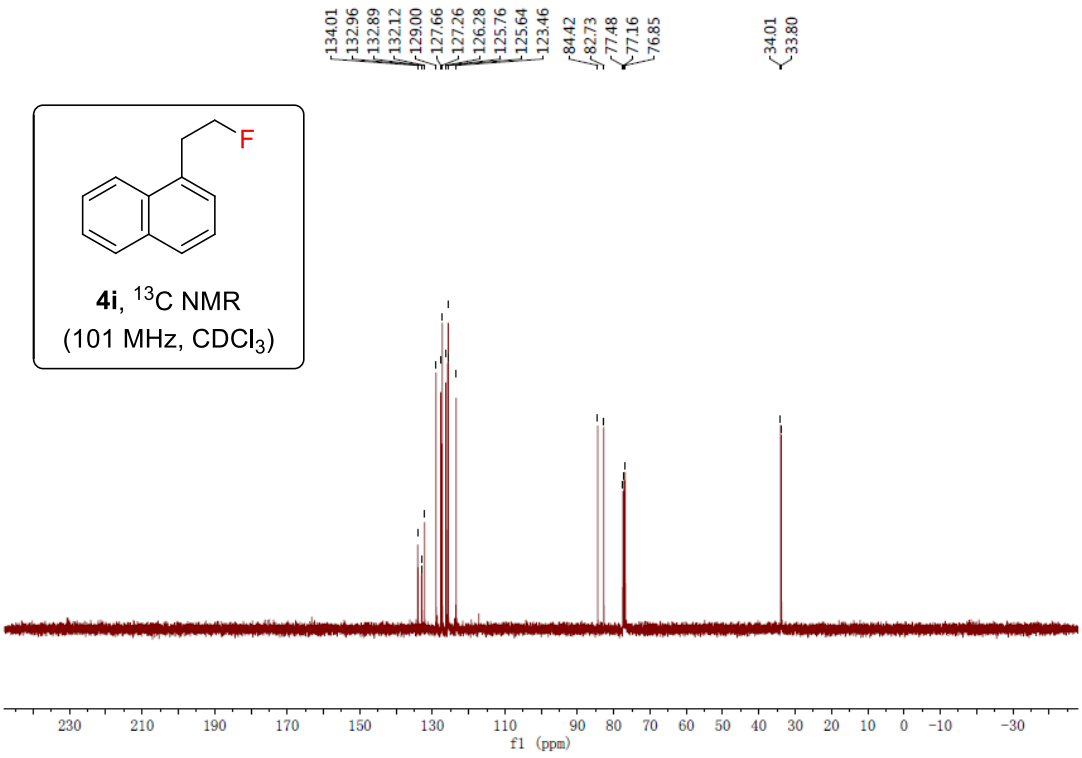


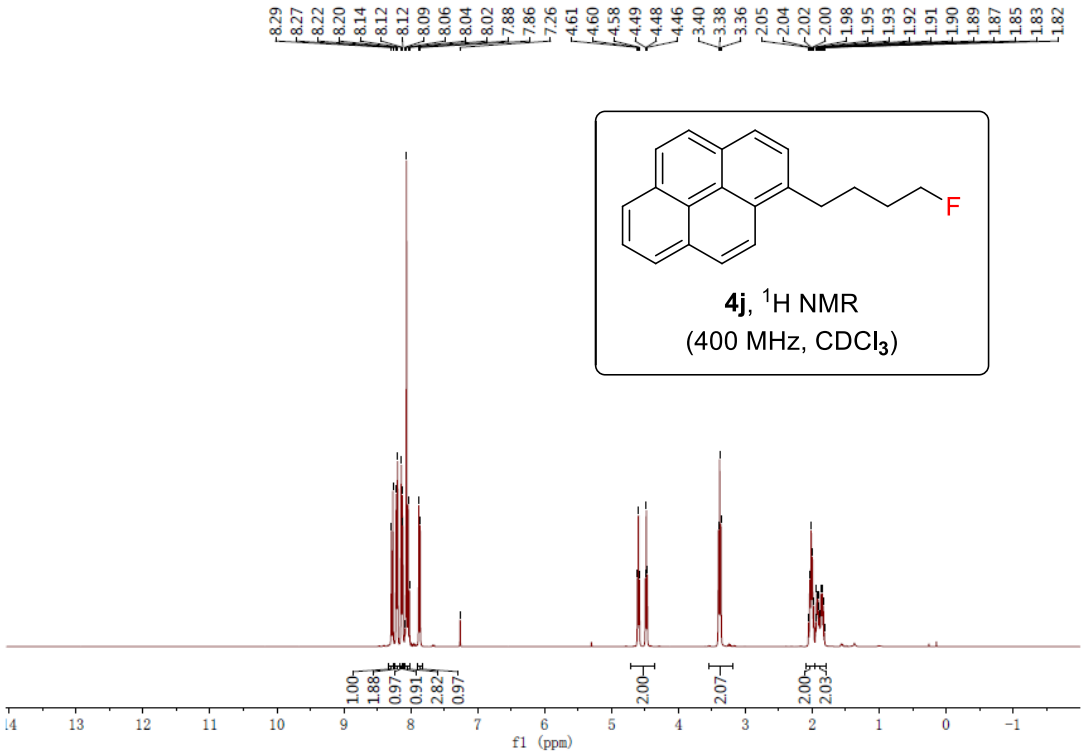


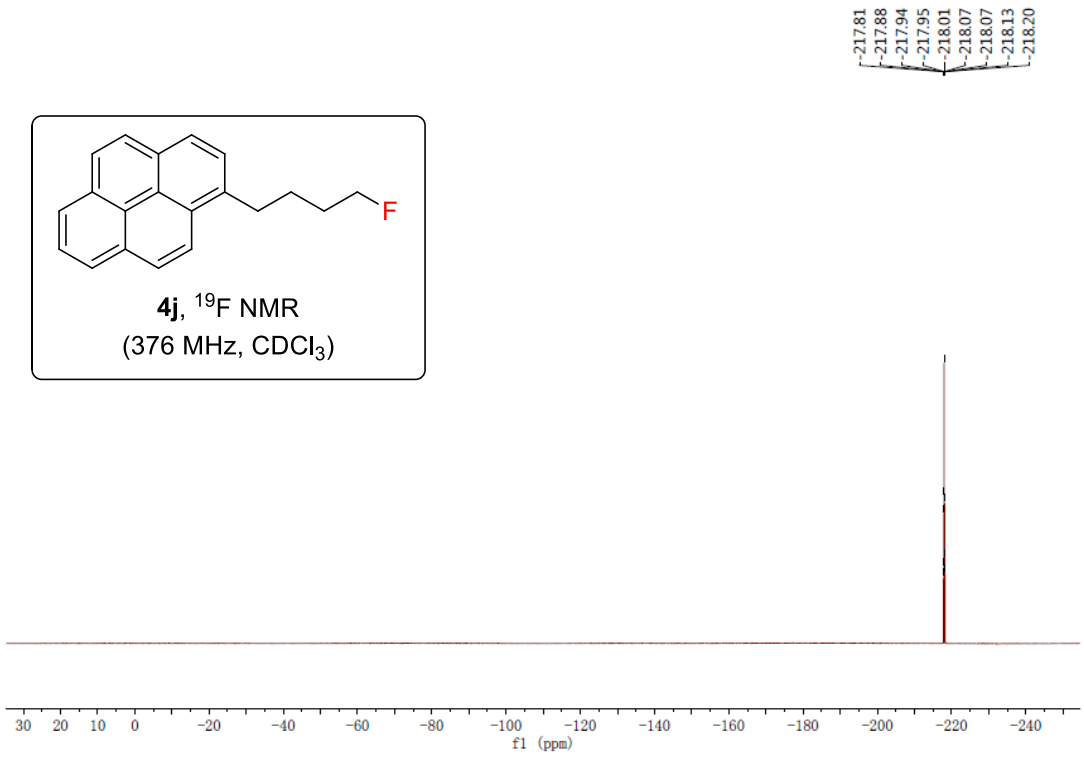
4i, ^{1}H NMR
(400 MHz, $CDCl_3$)

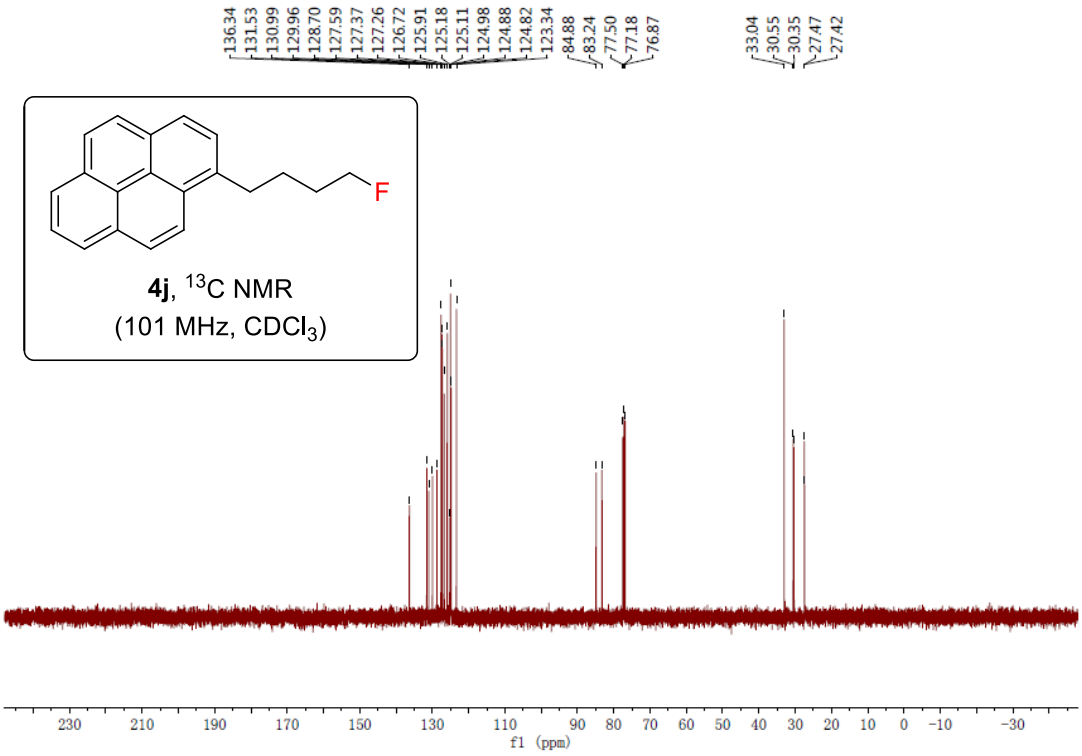


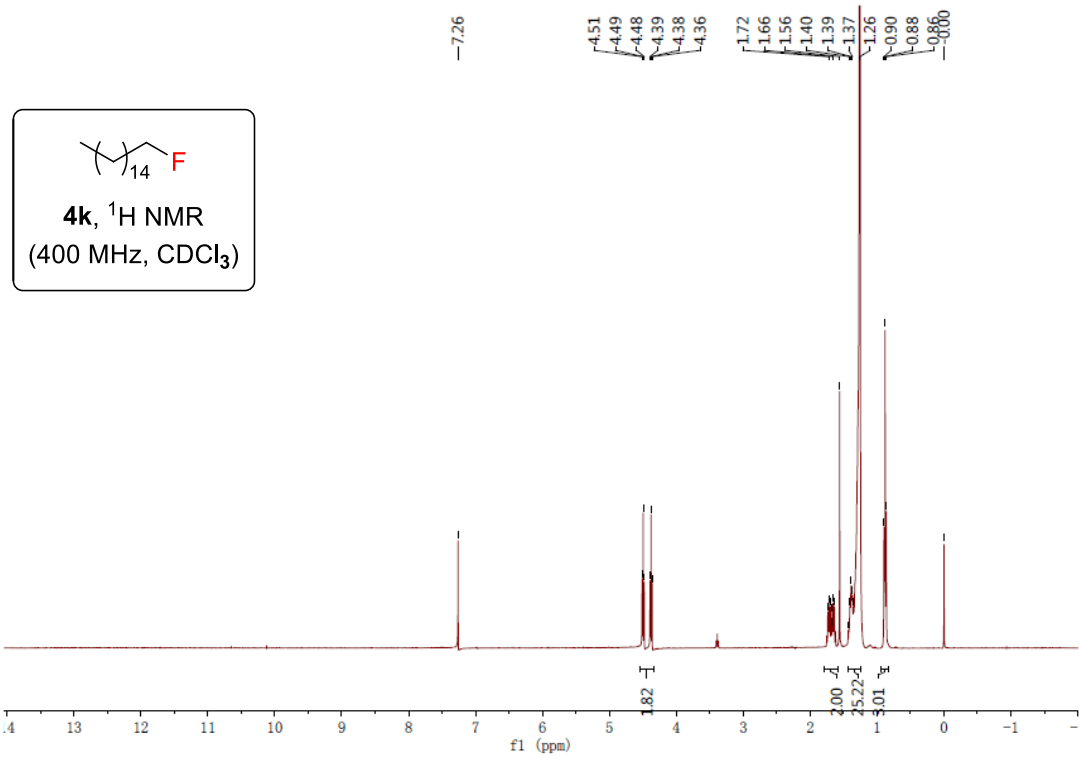

-213.11
-213.11
-213.12
-213.16
-213.17
-213.22
-213.22
-213.23
-213.24
-213.29
-213.29
-213.30
-213.34
-213.35
-213.36
-213.36
-213.41
-213.42
-213.42
-213.47
-213.47
F
4i, 19F NMR
(376 MHz, CDCl3)
30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

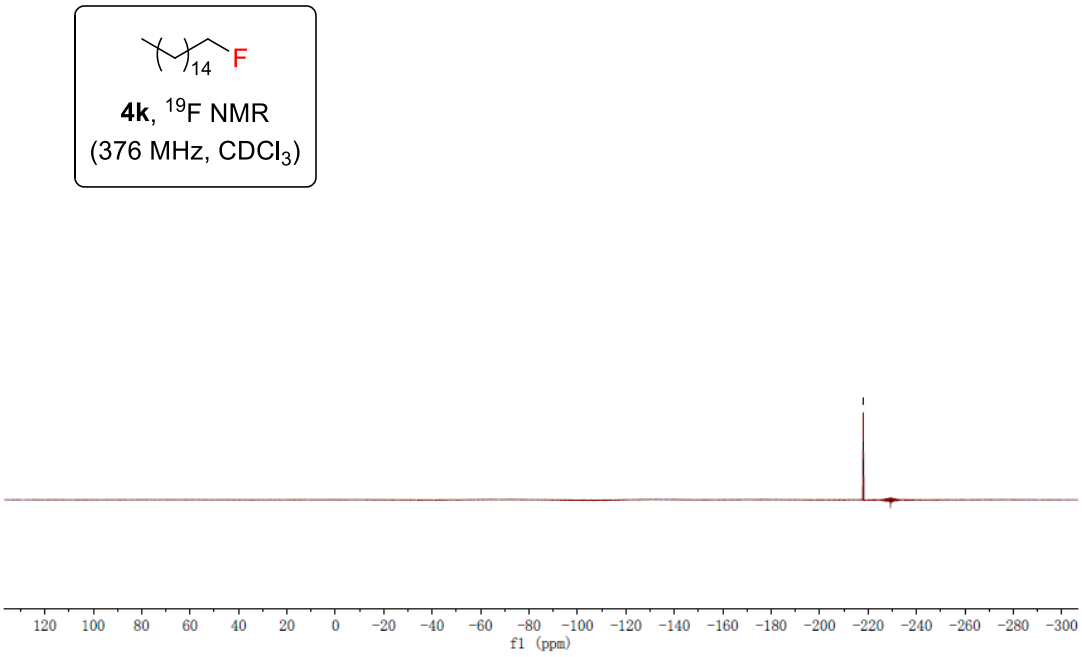

134.01
132.96
132.89
132.12
129.00
127.66
127.26
126.28
125.76
125.64
123.46
84.42
82.73
77.48
77.16
76.85
34.01
33.80
F
4i, 13C NMR
(101 MHz, CDCl3)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30
f1 (ppm)

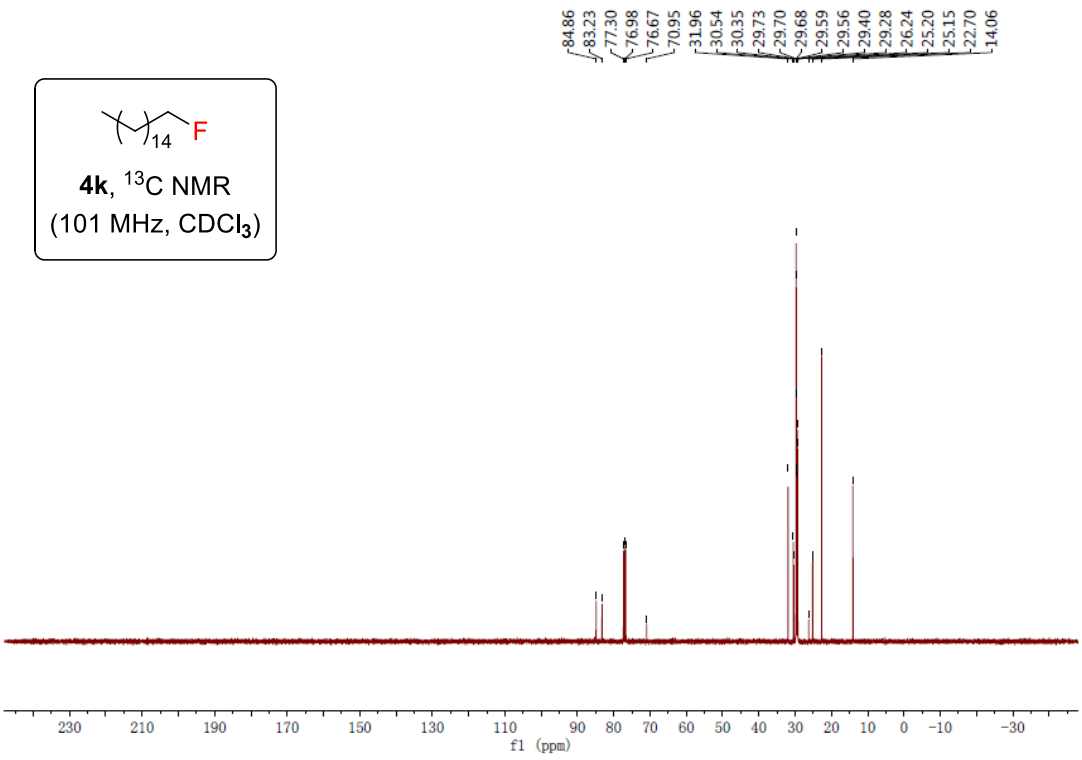

8.29
8.27
8.22
8.20
8.14
8.12
8.12
8.09
8.06
8.04
8.02
7.88
7.86
7.26
4.61
4.60
4.58
4.49
4.48
4.46
3.40
3.38
3.36
2.05
2.04
2.02
2.00
1.98
1.95
1.93
1.92
1.91
1.90
1.89
1.87
1.85
1.83
1.82
F
4j, 1H NMR
(400 MHz, CDCl3)
1.00
1.88
0.97
0.91
2.82
0.97
2.00
2.07
2.00
2.03
f1 (ppm)

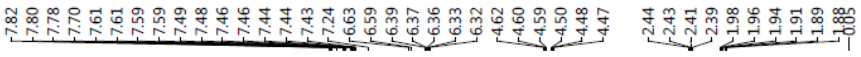

217.81
217.88
217.94
217.95
218.01
218.07
218.07
218.13
218.20
F
4j, 19F NMR
(376 MHz, CDCl3)
f1 (ppm)

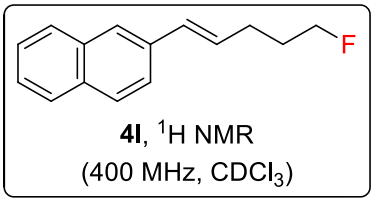

136.34
131.53
130.99
129.96
128.70
127.59
127.37
127.26
126.72
125.91
125.18
125.11
124.98
124.88
124.82
123.34
84.88
83.24
77.50
77.18
76.87
33.04
30.55
30.35
27.47
27.42
F
4j, 13C NMR
(101 MHz, CDCl3)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
−10
−30
f1 (ppm)


7.26
4.51
4.49
4.48
4.39
4.38
4.36
1.72
1.66
1.56
1.40
1.39
1.37
1.26
0.90
0.88
0.86
0.00
F
14
4k, 1H NMR
(400 MHz, CDCl3)
1.82
2.00
25.22
3.01
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

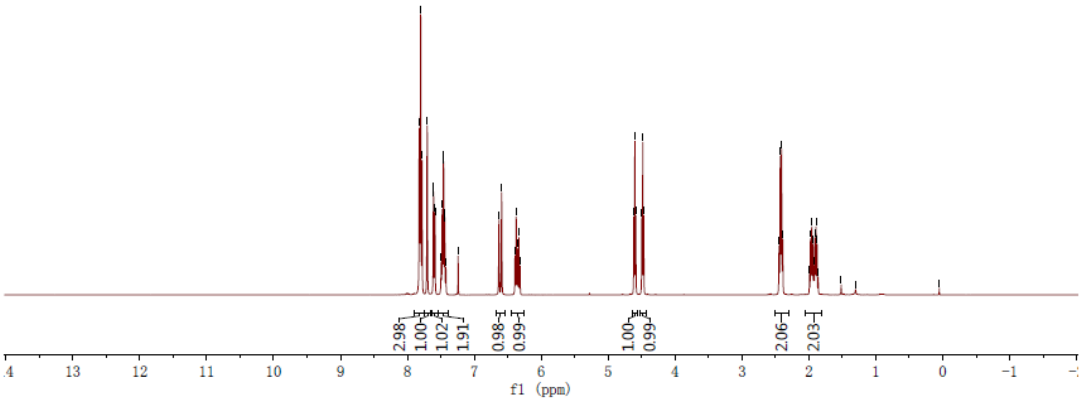

-217.81
-217.88
-217.94
-217.94
-218.00
-218.06
-218.07
-218.13
-218.19
14
F
4k, 19F NMR
(376 MHz, CDCl3)
120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

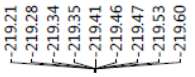

84.86
83.23
77.30
76.98
76.67
70.95
31.96
30.54
30.35
29.73
29.70
29.68
29.59
29.56
29.40
29.28
26.24
25.20
25.15
22.70
14.06
14
F
4k, 13C NMR
(101 MHz, CDCl3)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30
f1 (ppm)

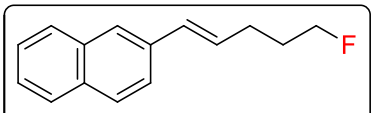




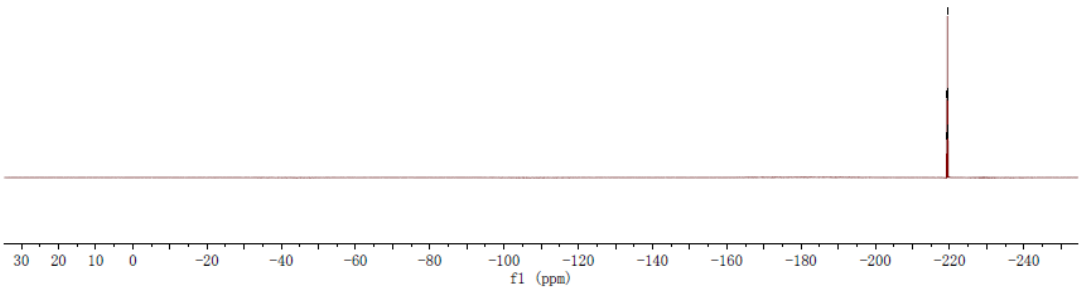
4l, ^{1}H NMR
(400 MHz, $CDCl_3$)

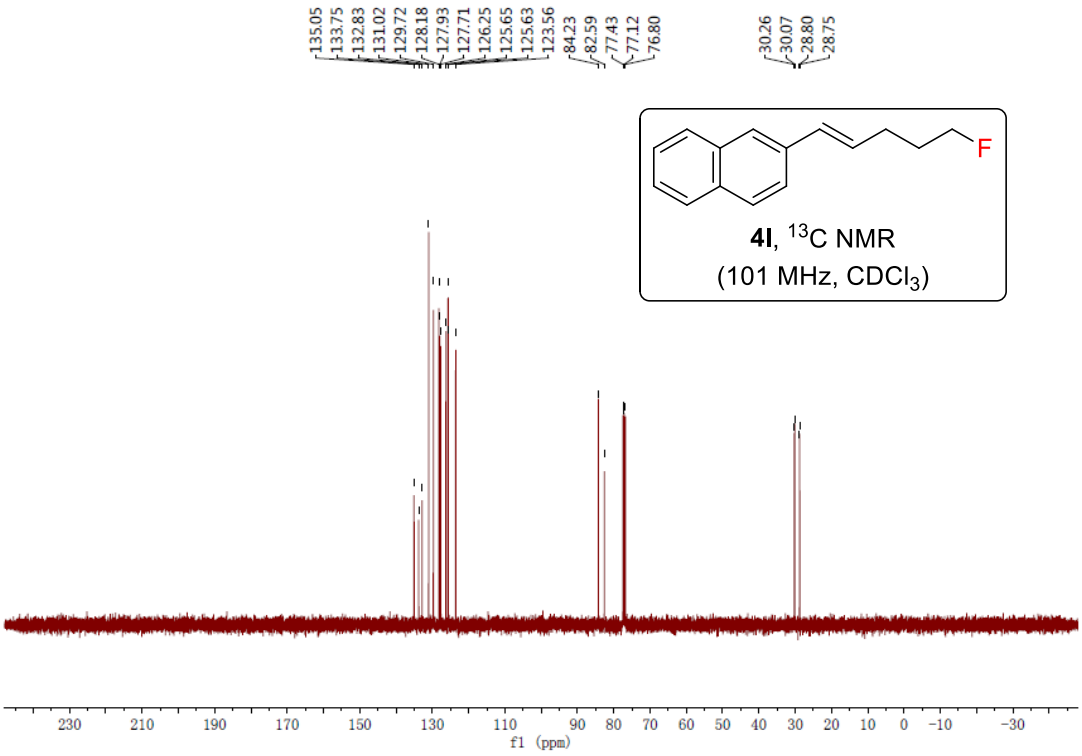


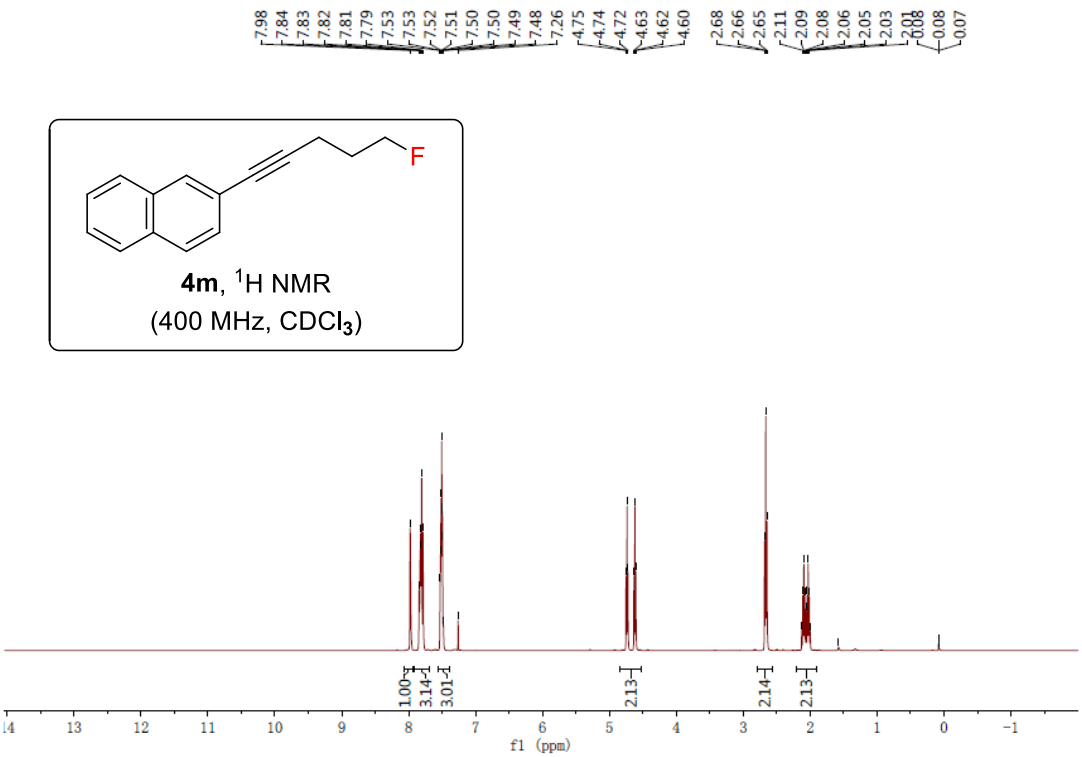


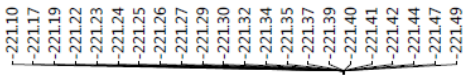


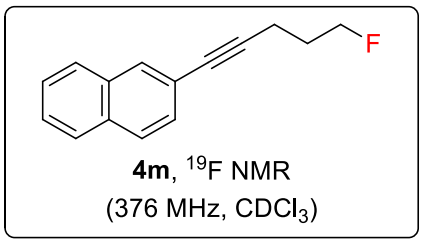
4l, ^{19}F NMR
(376 MHz, $CDCl_3$)



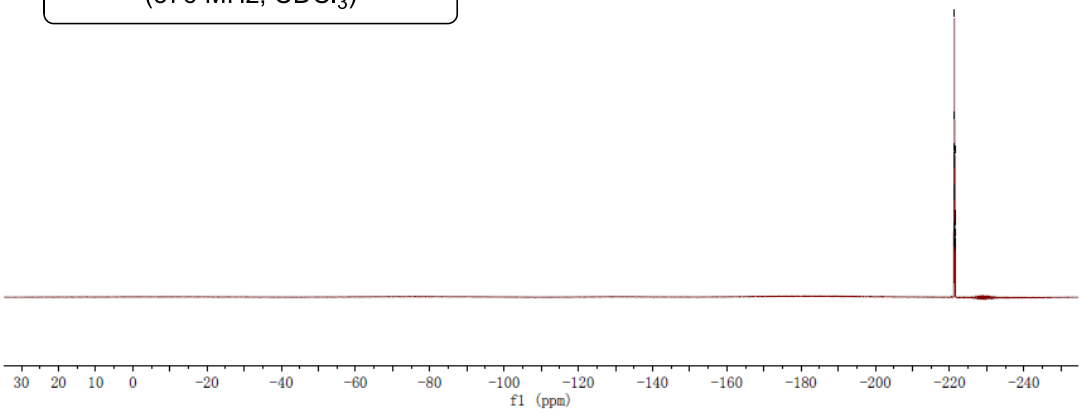

135.05
133.75
132.83
131.02
129.72
128.18
127.93
127.71
126.25
125.65
125.63
123.56
84.23
82.59
77.43
77.12
76.80
30.26
30.07
28.80
28.75
F
4l, 13C NMR
(101 MHz, CDCl3)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 −10 −30
f1 (ppm)

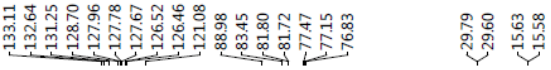

7.98
7.84
7.83
7.82
7.81
7.79
7.53
7.53
7.52
7.51
7.50
7.50
7.49
7.48
7.26
4.75
4.74
4.72
4.63
4.62
4.60
2.68
2.66
2.65
2.11
2.09
2.08
2.06
2.05
2.03
2.01
0.08
0.08
0.07
F
4m, 1H NMR
(400 MHz, CDCl3)
1.00
3.14
3.01
2.13
2.14
2.13
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

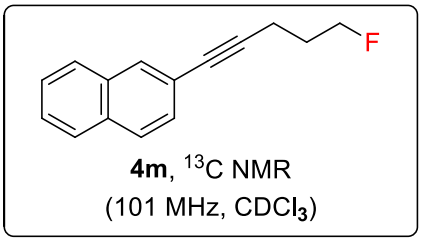




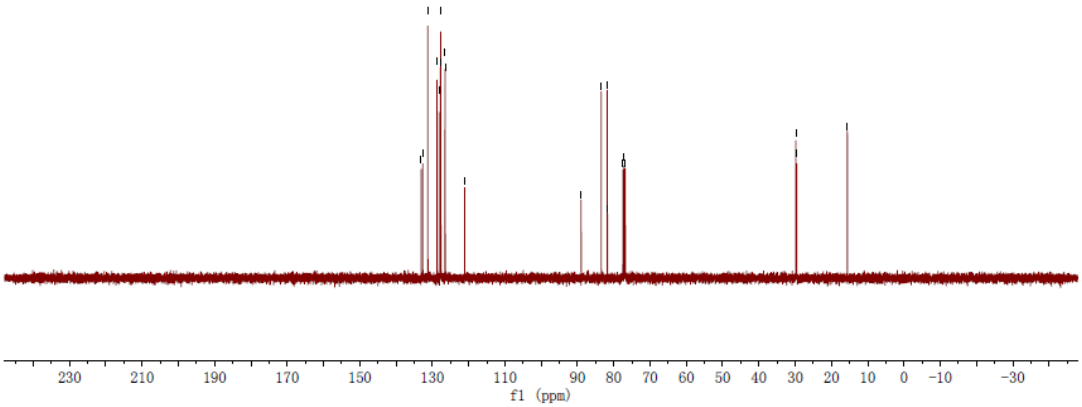
4m, ^{19}F NMR
(376 MHz, $CDCl_3$)

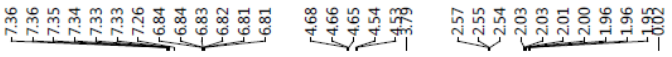


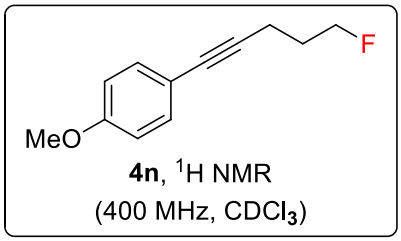




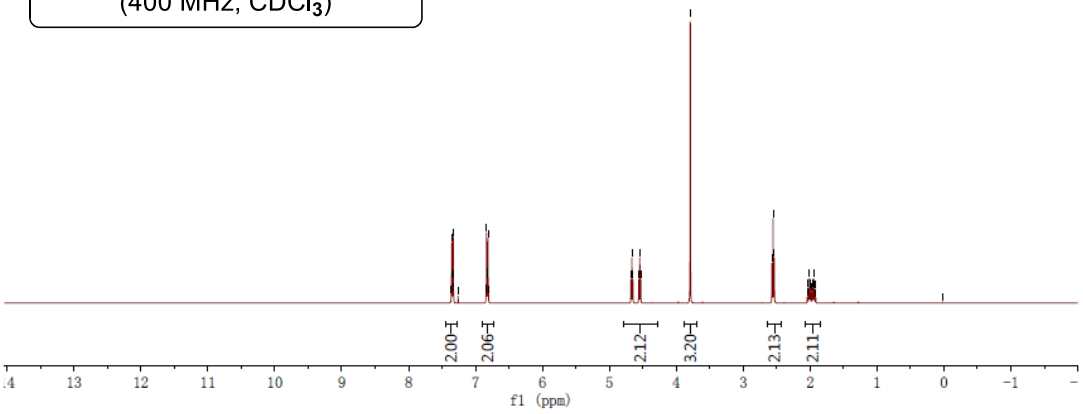
4m, ^{13}C NMR
(101 MHz, $CDCl_3$)

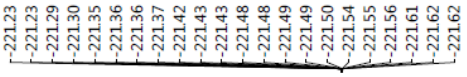


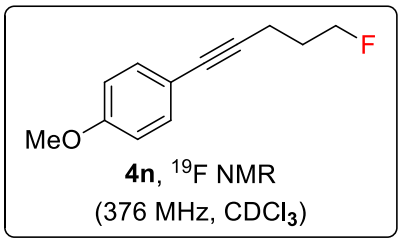




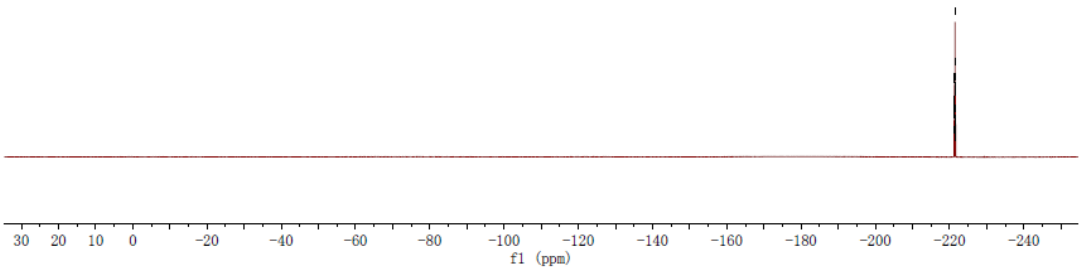
4n, ^{1}H NMR
(400 MHz, $CDCl_3$)

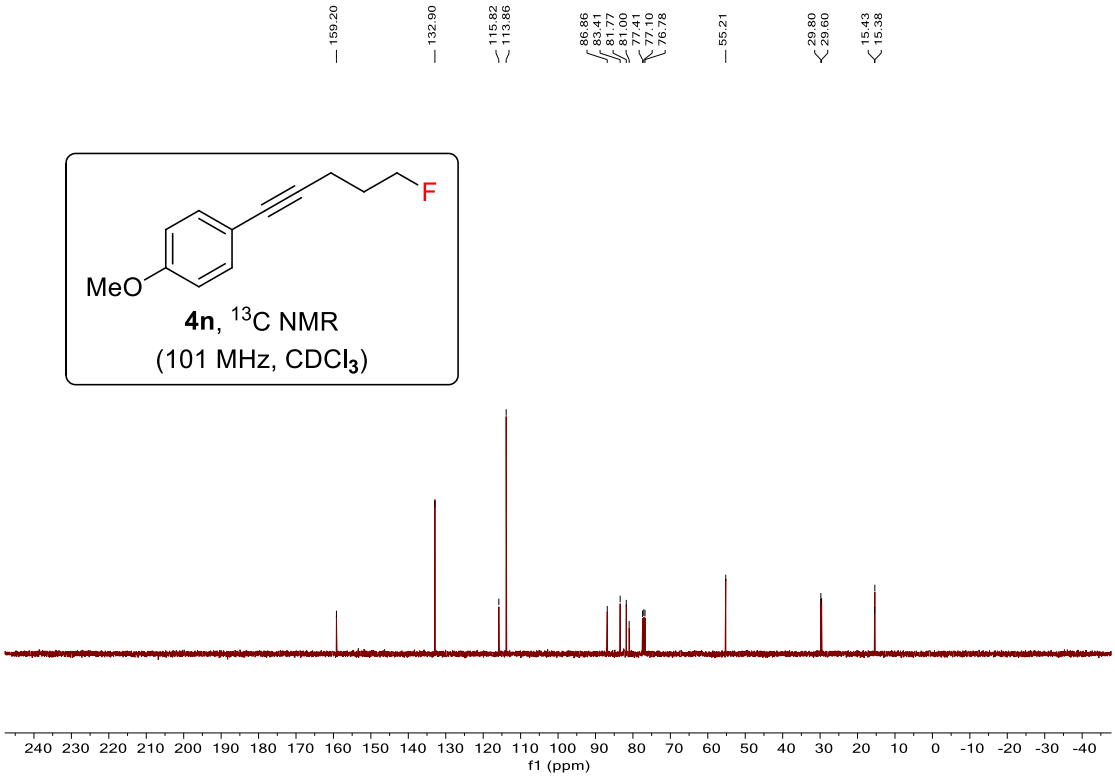


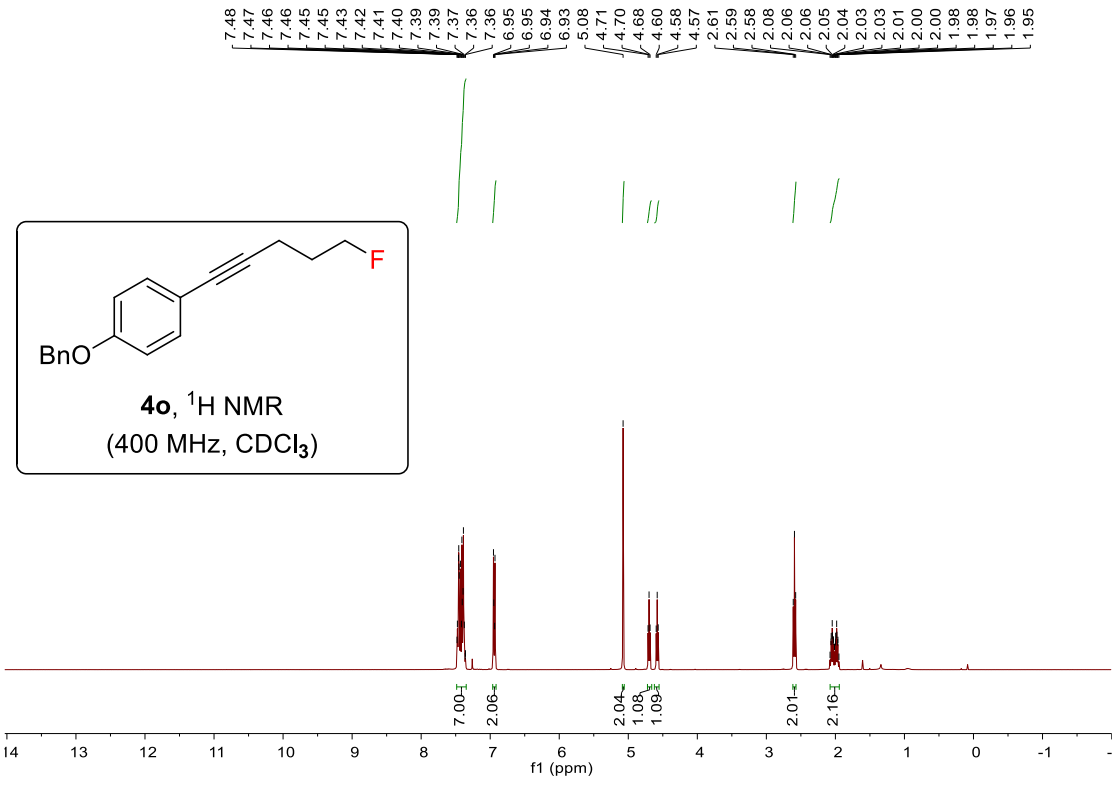




4n, ^{19}F NMR
(376 MHz, $CDCl_3$)




159.20
132.90
115.82
113.86
86.86
83.41
81.77
81.00
77.41
77.10
76.78
55.21
29.80
29.60
15.43
15.38
F
MeO
4n, 13C NMR
(101 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


7.48
7.47
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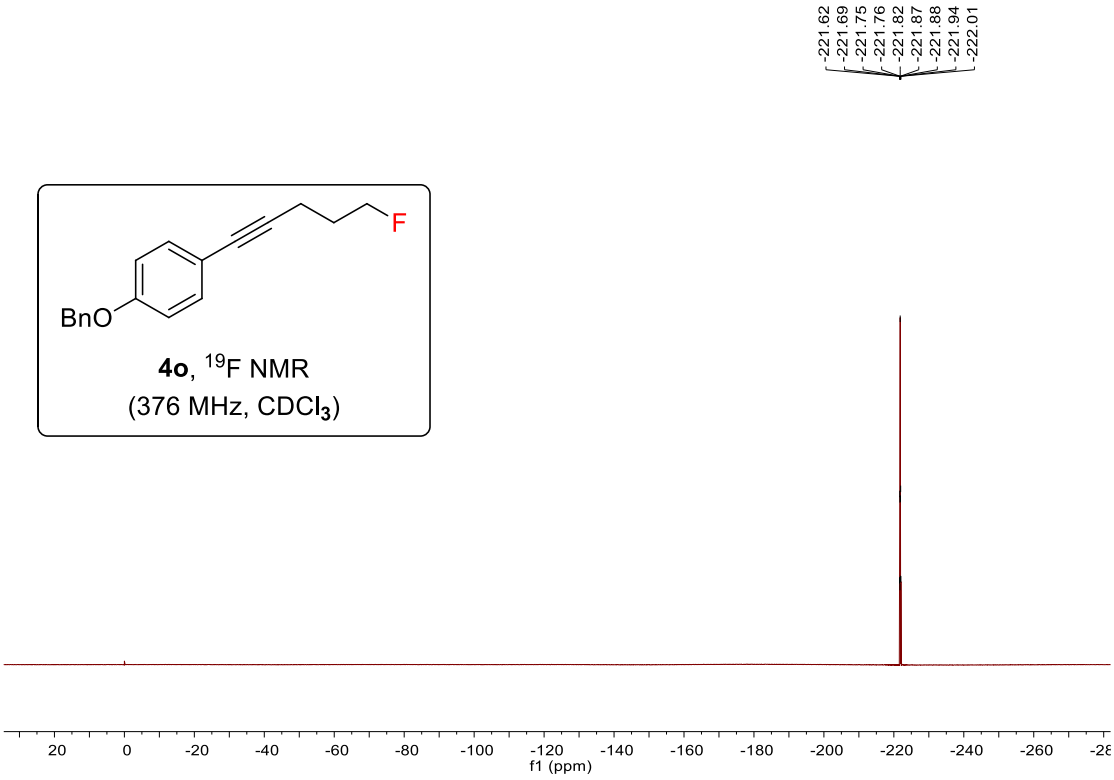
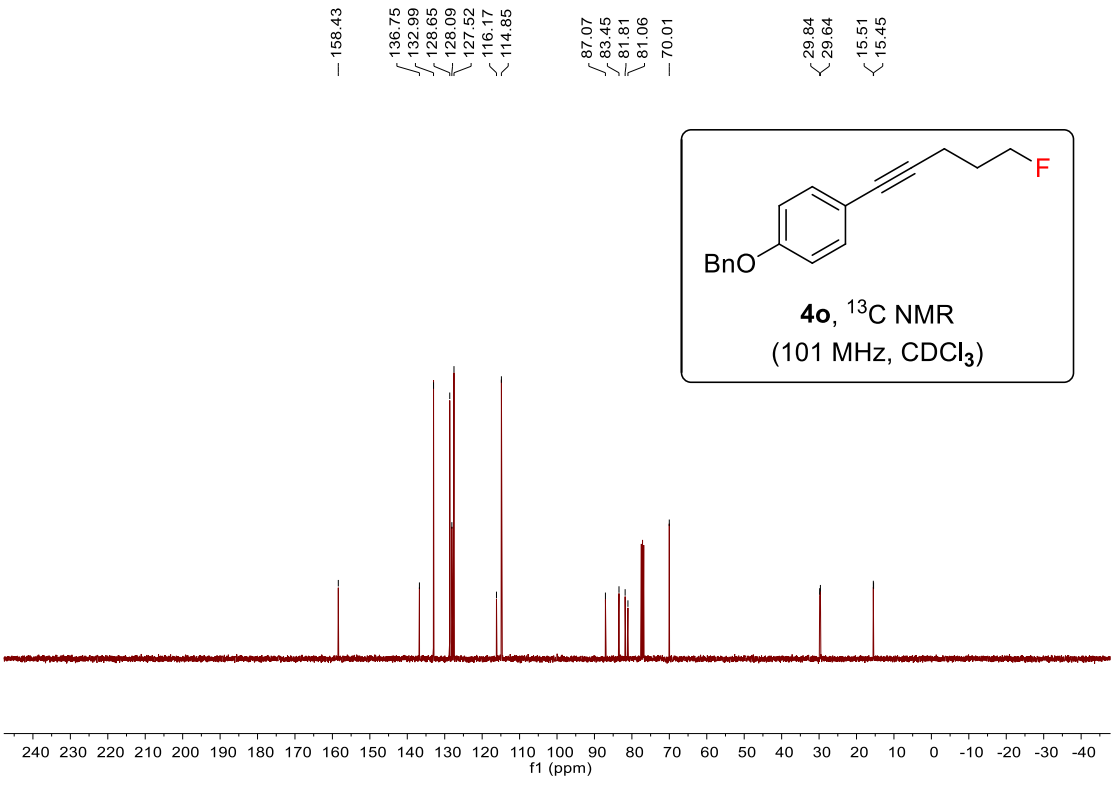
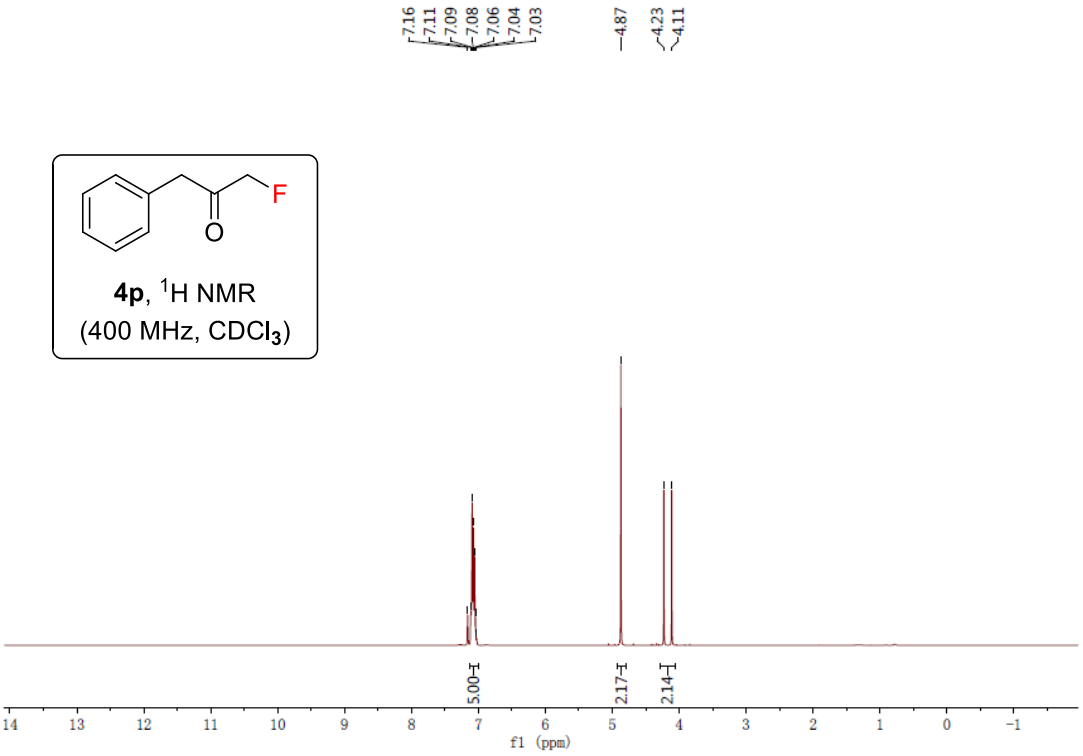
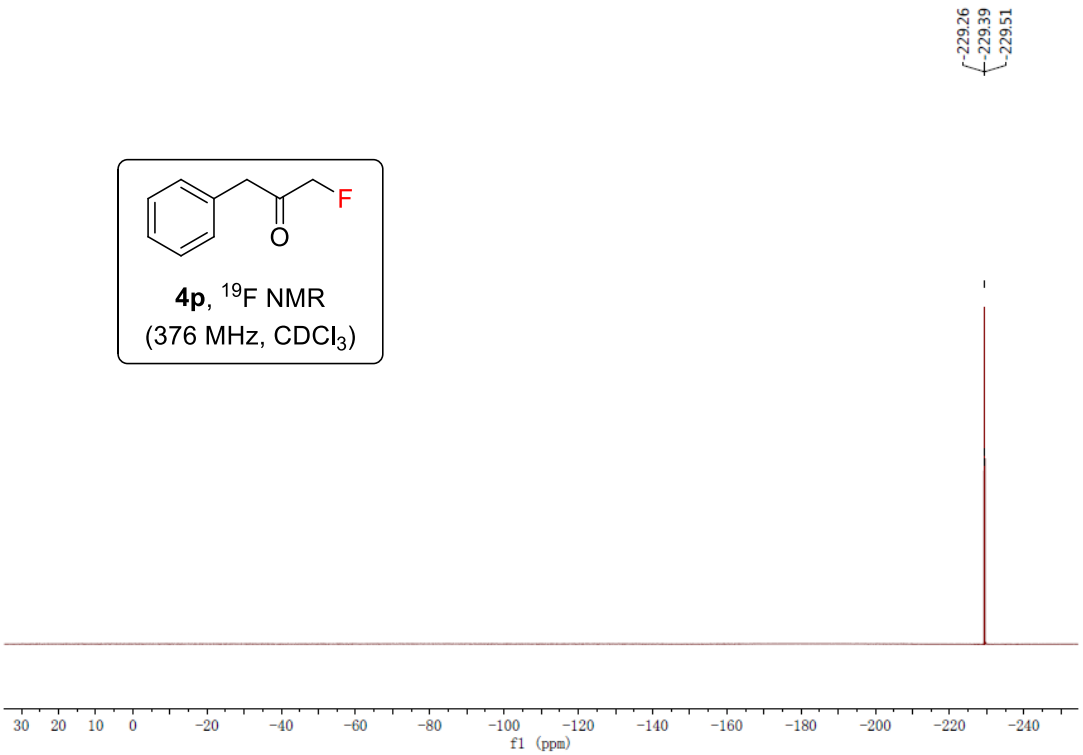
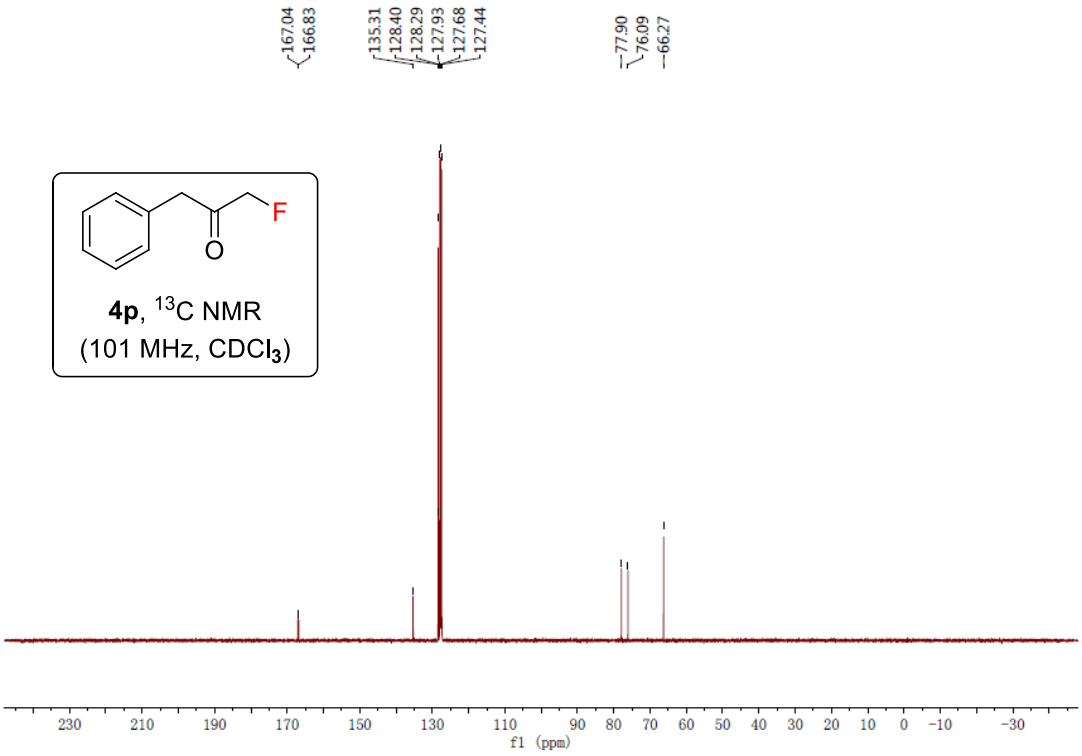
7.46
7.45
7.45
7.43
7.42
7.41
7.40
7.39
7.39
7.37
7.36
7.36
6.95
6.95
6.94
6.93
5.08
4.71
4.70
4.68
4.60
4.58
4.57
2.61
2.59
2.58
2.08
2.06
2.06
2.05
2.04
2.03
2.03
2.01
2.00
2.00
1.98
1.98
1.97
1.96
1.95
F
BnO
4o, 1H NMR
(400 MHz, CDCl3)
7.00
2.06
2.04
1.08
1.09
2.01
2.16
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

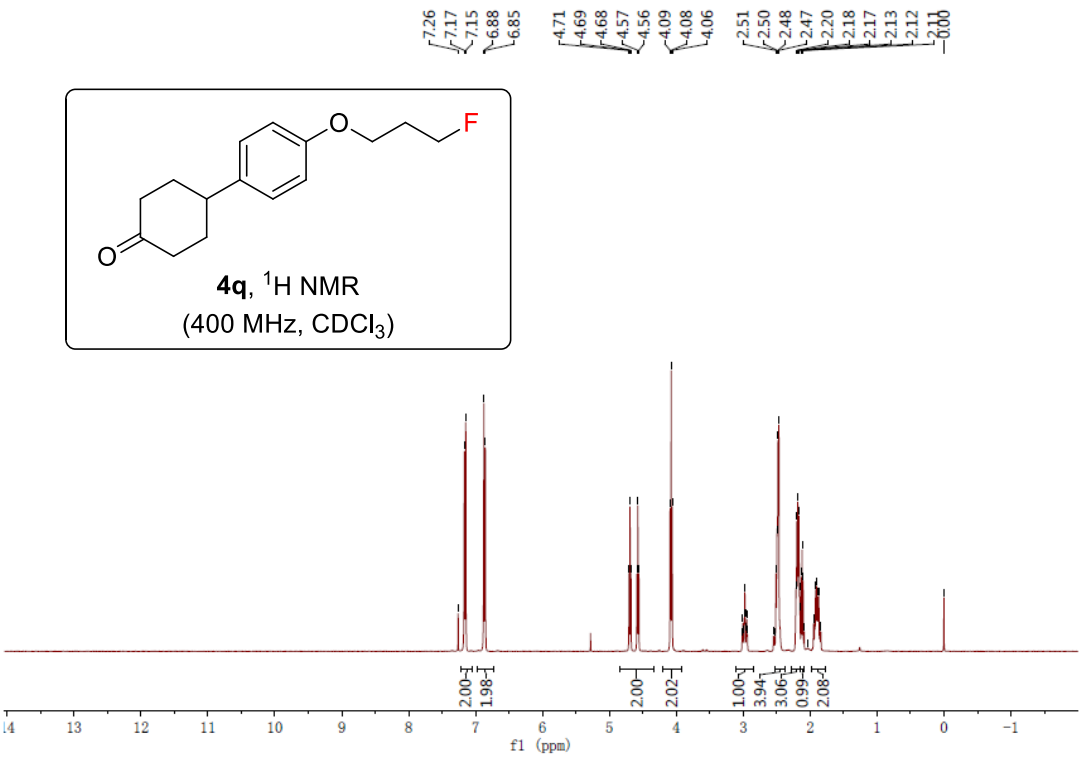

-221.62
-221.69
-221.75
-221.76
-221.82
-221.87
-221.88
-221.94
-222.01
F
BnO
4o, 19F NMR
(376 MHz, CDCl3)
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

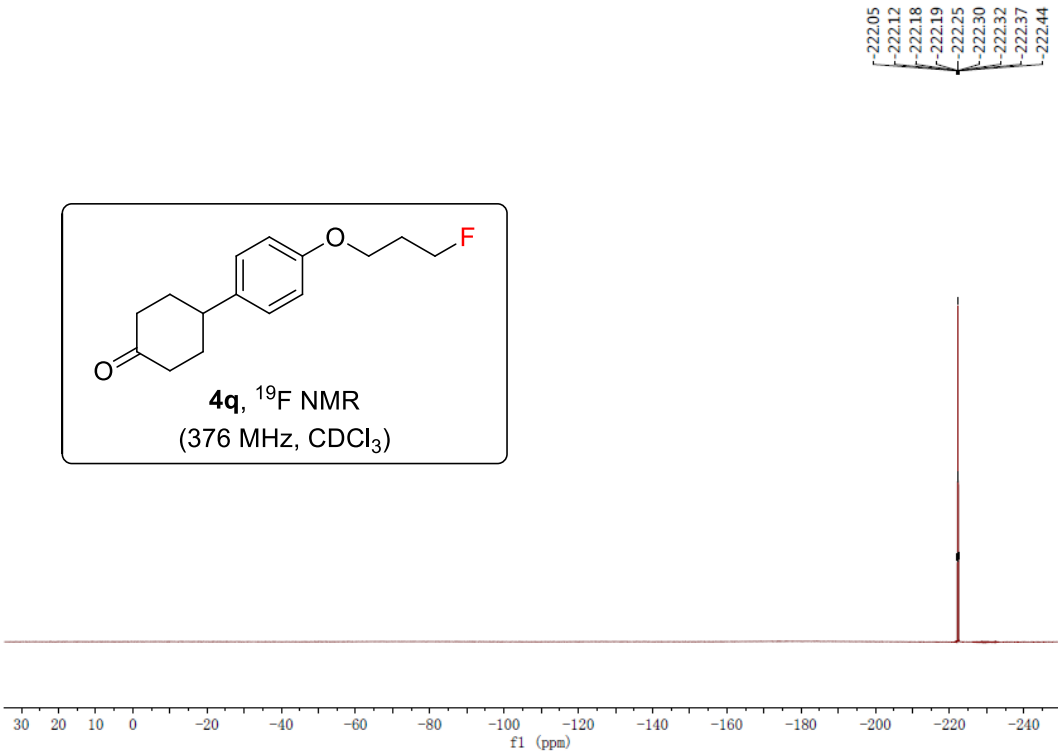

158.43
136.75
132.99
128.65
128.09
127.52
116.17
114.85
87.07
83.45
81.81
81.06
70.01
29.84
29.64
15.51
15.45
F
BnO
4o, 13C NMR
(101 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

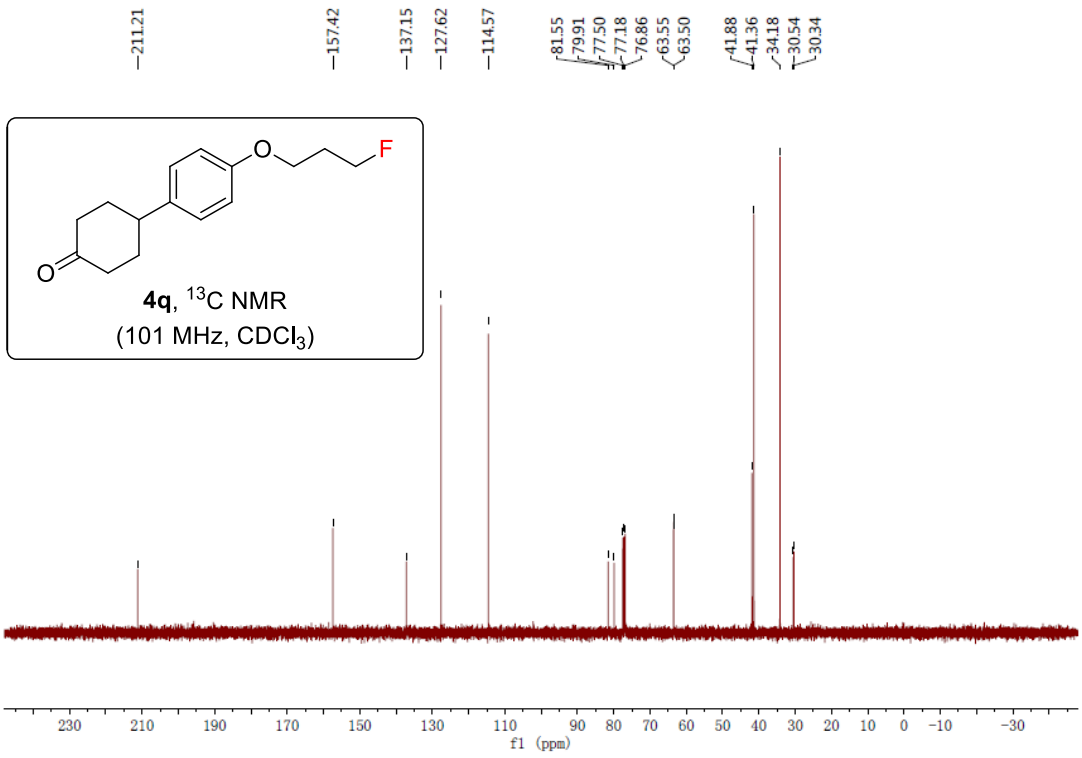

7.16
7.11
7.09
7.08
7.06
7.04
7.03
4.87
4.23
4.11
F
O
4p, 1H NMR
(400 MHz, CDCl3)
5.00
2.17
2.14
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

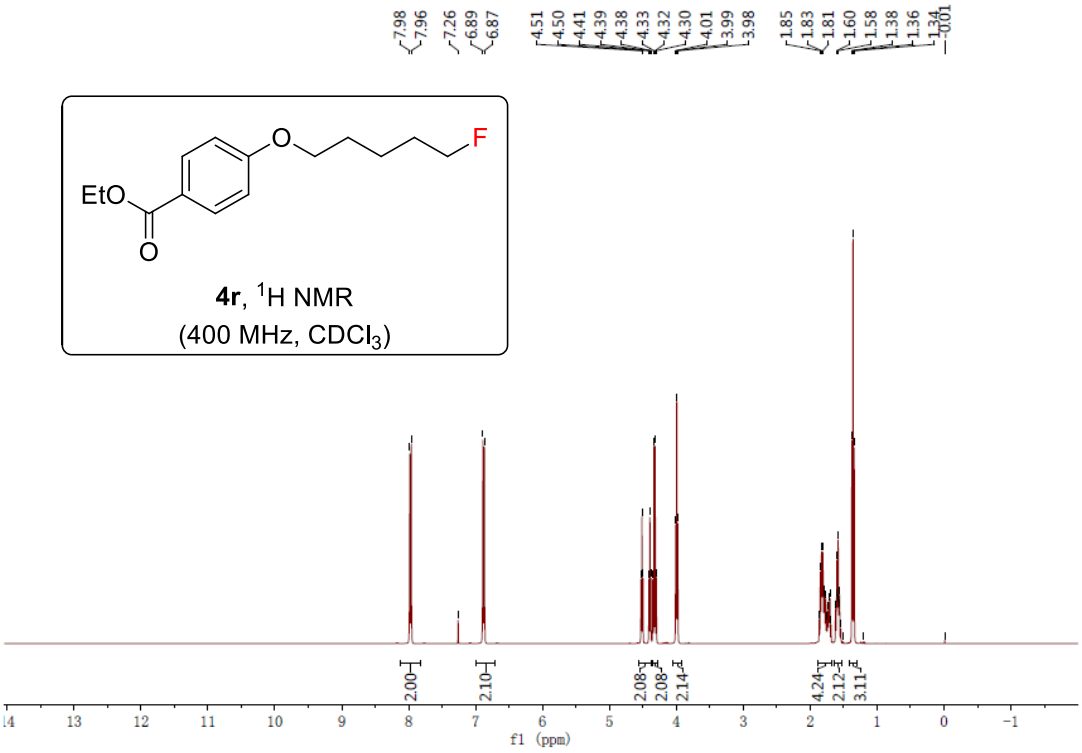

-229.26
-229.39
-229.51
F
O
4p, 19F NMR
(376 MHz, CDCl3)
30 20 10 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240
f1 (ppm)

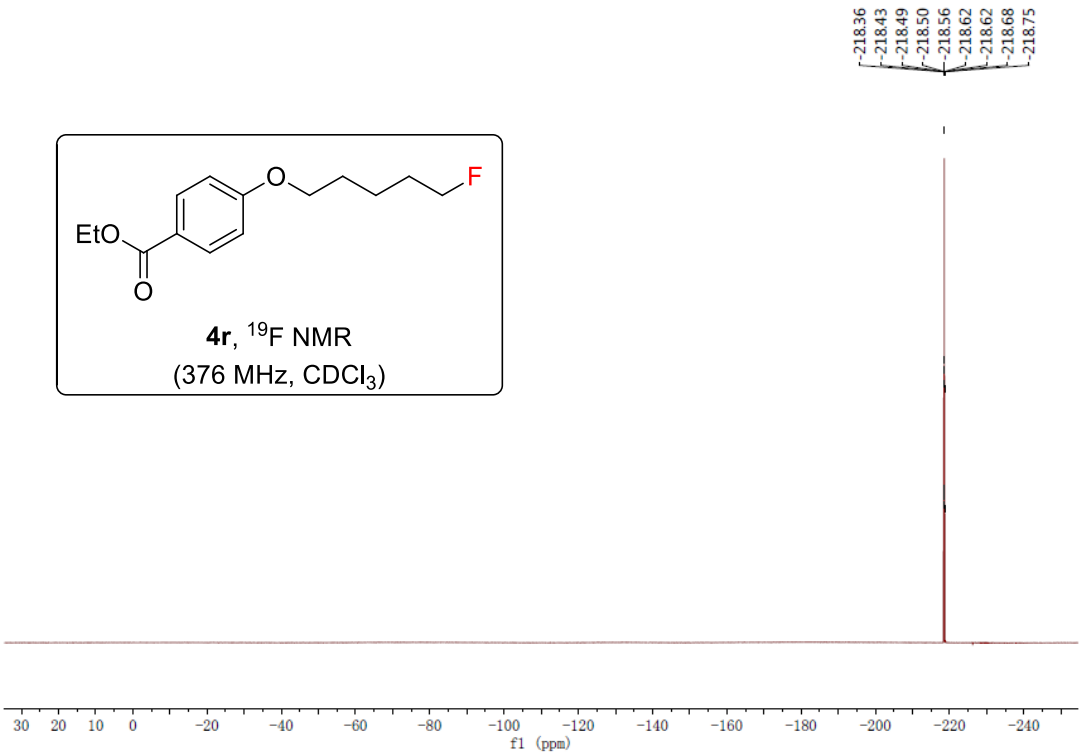

167.04
166.83
135.31
128.40
128.29
127.93
127.68
127.44
77.90
76.09
66.27
F
O
4p, 13C NMR
(101 MHz, CDCl3)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)

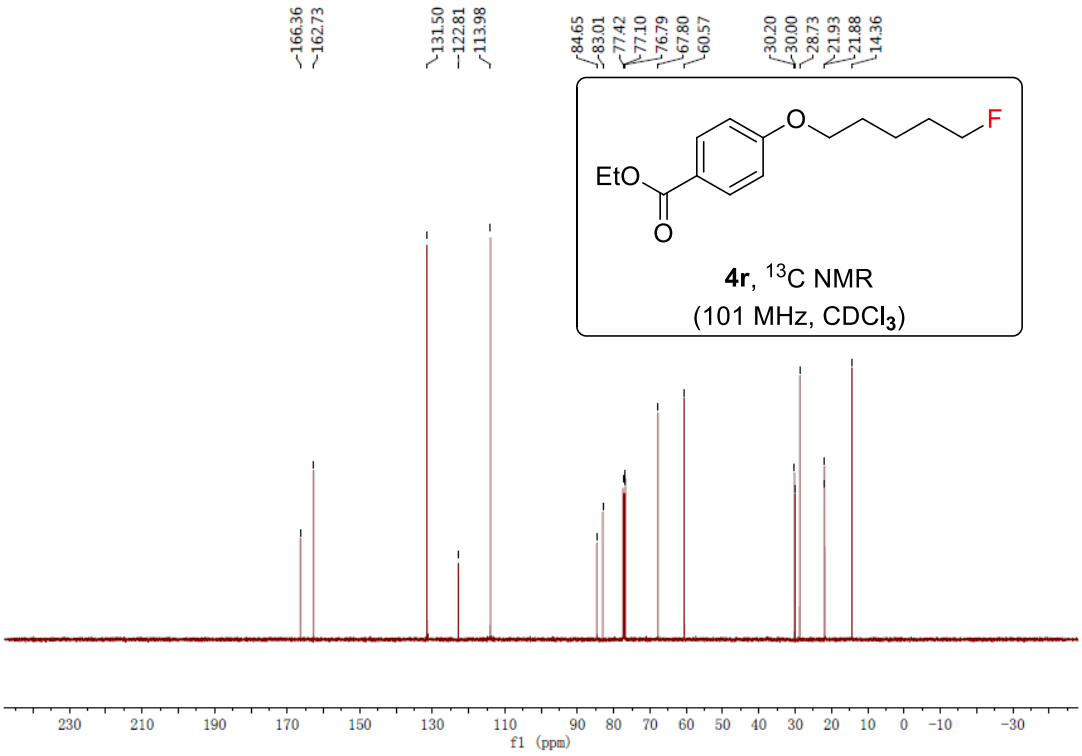

7.26
7.17
7.15
6.88
6.85
4.71
4.69
4.68
4.57
4.56
4.09
4.08
4.06
2.51
2.50
2.48
2.47
2.20
2.18
2.17
2.13
2.12
2.11
0.00
O
F
O
4q, 1H NMR
(400 MHz, CDCl3)
2.00
1.98
2.00
2.02
1.00
3.94
3.06
0.99
2.08
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

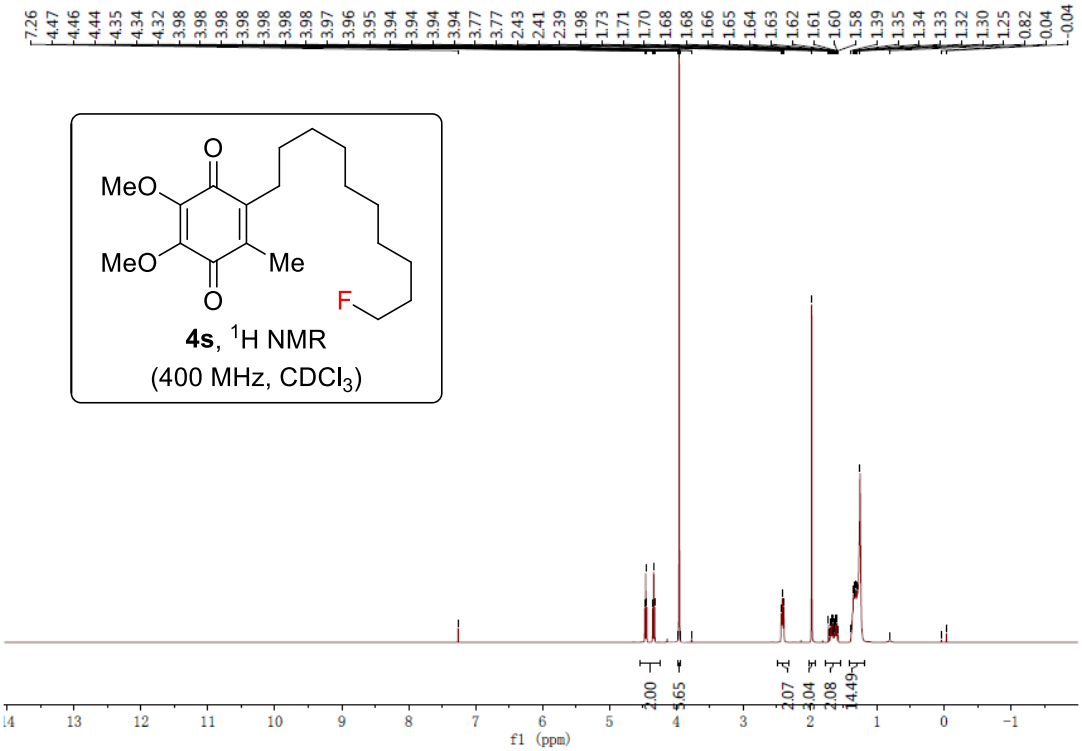

-222.05
-222.12
-222.18
-222.19
-222.25
-222.30
-222.32
-222.37
-222.44
O
F
O
4q, 19F NMR
(376 MHz, CDCl3)
30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

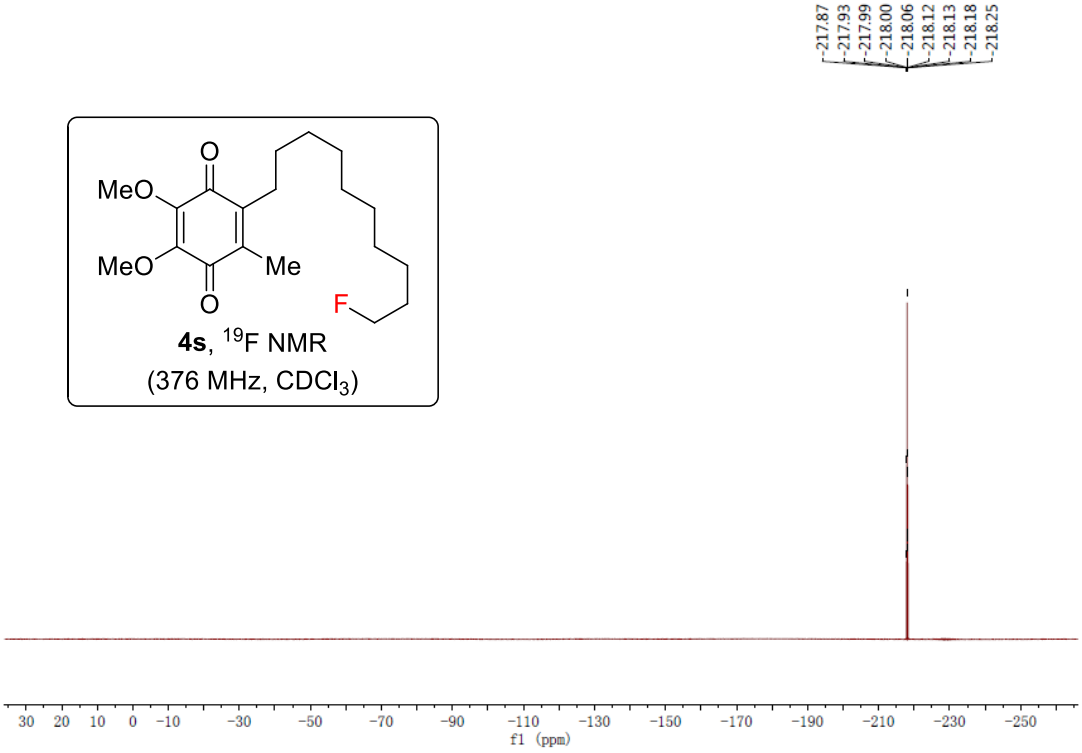

211.21
157.42
137.15
127.62
114.57
81.55
79.91
77.50
77.18
76.86
63.55
63.50
41.88
41.36
34.18
30.54
30.34
O
F
O
4q, 13C NMR
(101 MHz, CDCl3)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30
f1 (ppm)

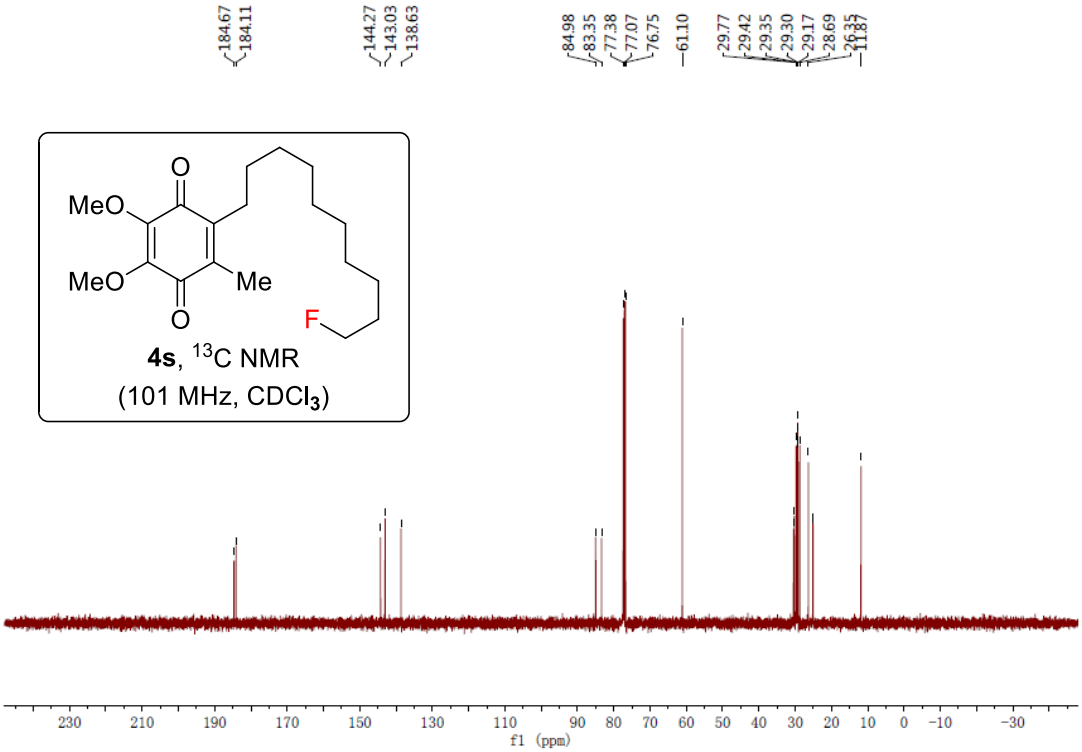

7.98
7.96
7.26
6.89
6.87
4.51
4.50
4.41
4.39
4.38
4.33
4.32
4.30
4.01
3.99
3.98
1.85
1.83
1.81
1.60
1.58
1.38
1.36
1.34
0.01
EtO
O
O
F
4r, 1H NMR
(400 MHz, CDCl3)
2.00
2.10
2.08
2.08
2.14
4.24
2.12
3.11
f1 (ppm)

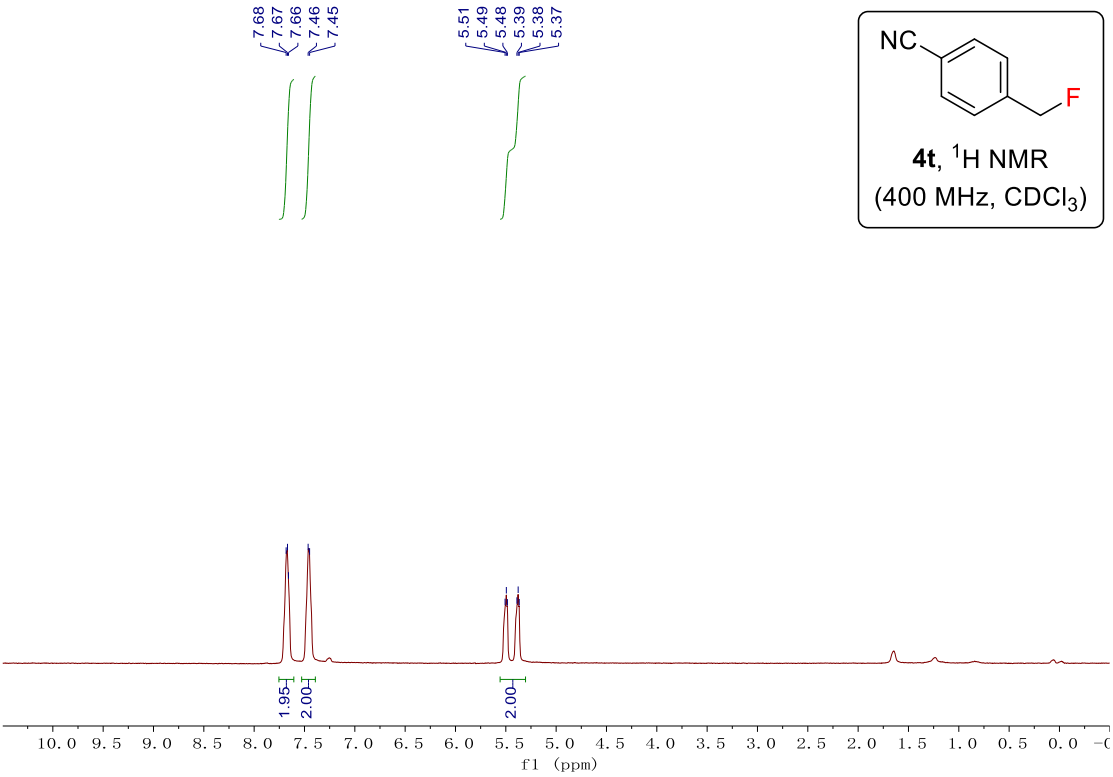

218.36
218.43
218.49
218.50
218.56
218.62
218.62
218.68
218.75
EtO
O
O
F
4r, 19F NMR
(376 MHz, CDCl3)
f1 (ppm)

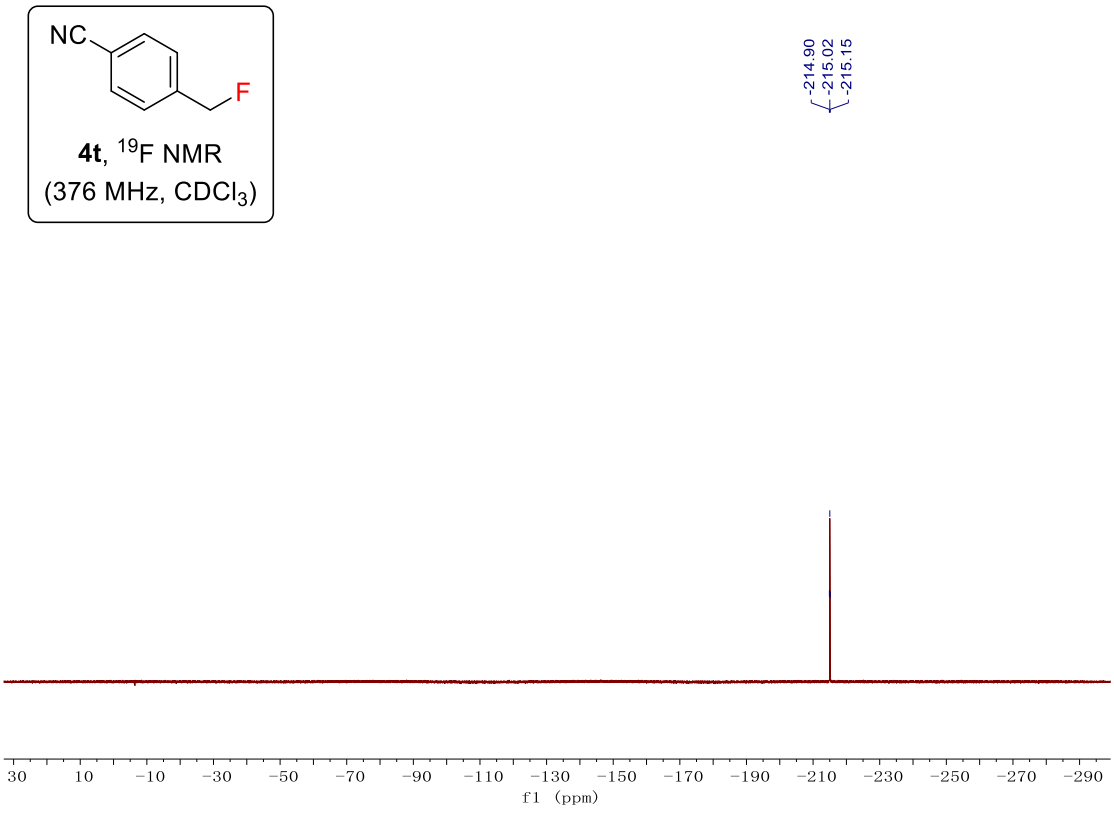

166.36
162.73
131.50
122.81
113.98
84.65
83.01
77.42
77.10
76.79
67.80
60.57
30.20
30.00
28.73
21.93
21.88
14.36
EtO
O
O
F
4r, 13C NMR
(101 MHz, CDCl3)
f1 (ppm)

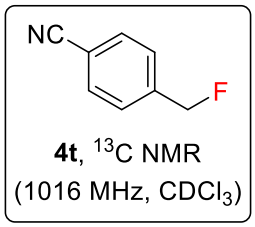

MeO
MeO
Me
O
O
O
F
4s, 1H NMR
(400 MHz, CDCl3)
f1 (ppm)


-217.87
-217.93
-217.99
-218.00
-218.06
-218.12
-218.13
-218.18
-218.25
MeO
MeO
Me
O
O
F
4s, 19F NMR
(376 MHz, CDCl3)
30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250
f1 (ppm)

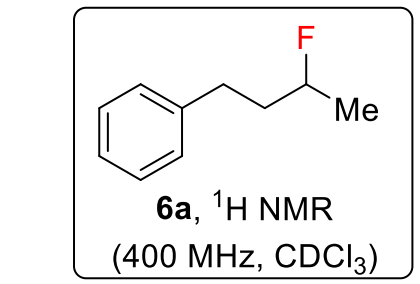

184.67
184.11
144.27
143.03
138.63
84.98
83.35
77.38
77.07
76.75
61.10
29.77
29.42
29.35
29.30
29.17
28.69
26.35
11.87
MeO
MeO
Me
O
O
F
4s, 13C NMR
(101 MHz, CDCl3)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30
f1 (ppm)


7.68
7.67
7.66
7.46
7.45
5.51
5.49
5.48
5.39
5.38
5.37
NC
F
4t, 1H NMR
(400 MHz, CDCl3)
1.95
2.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

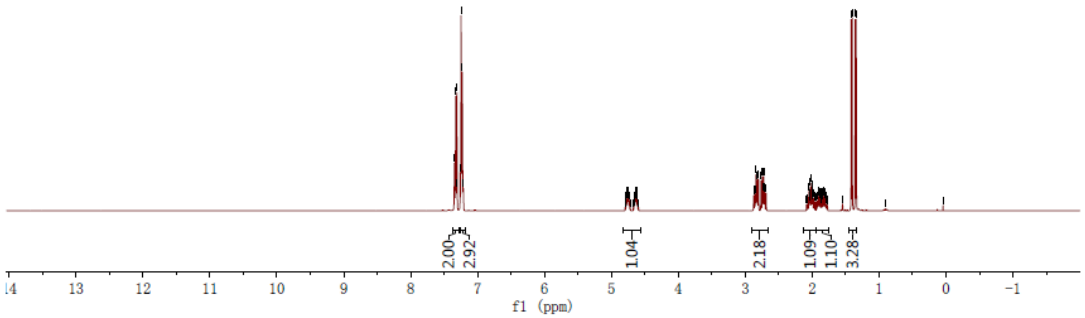

NC
F
4t, 19F NMR
(376 MHz, CDCl3)
-214.90
-215.02
-215.15
30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

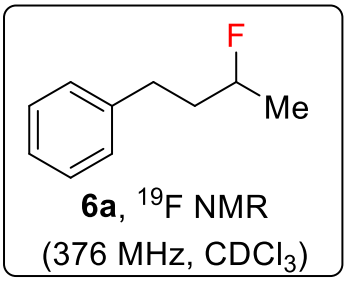


4t, ^{13}C NMR
(1016 MHz, $CDCl_3$)

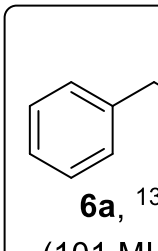


6a, ^{1}H NMR
(400 MHz, $CDCl_3$)

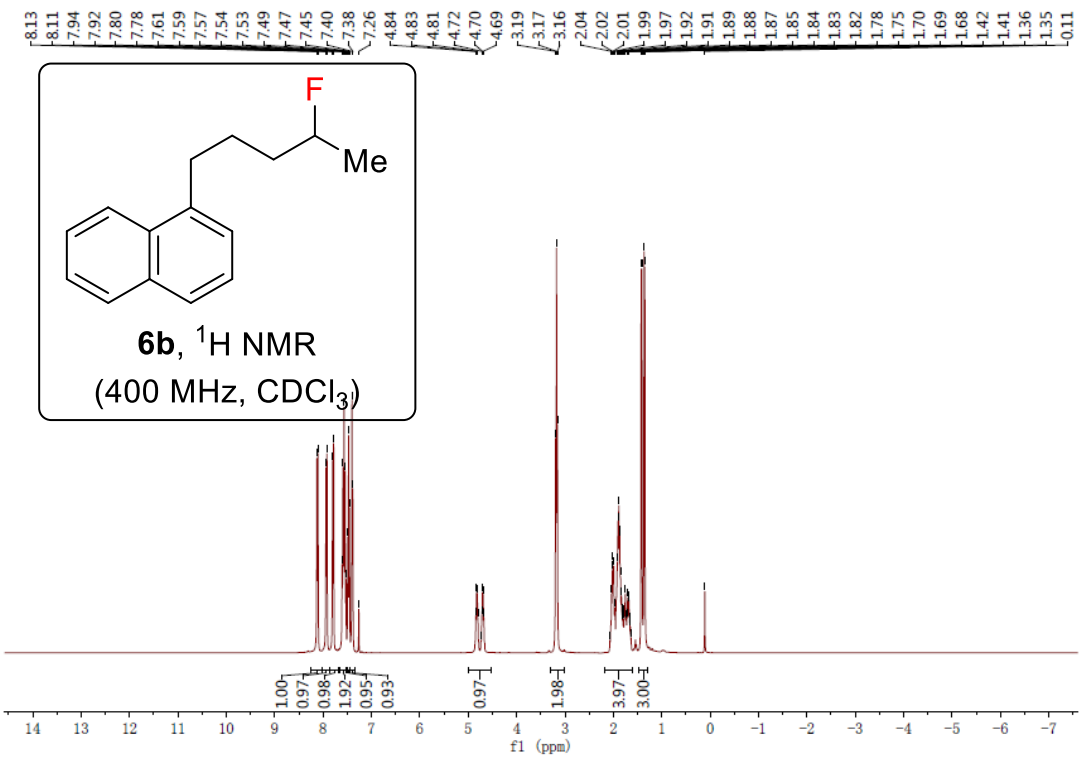


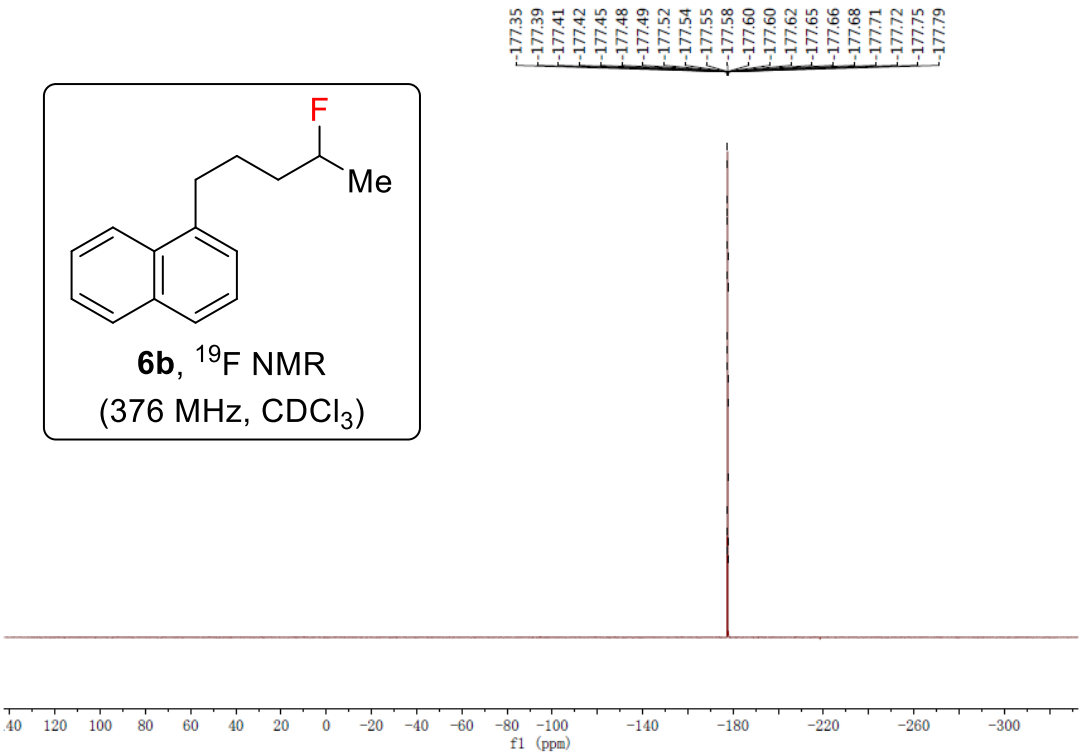


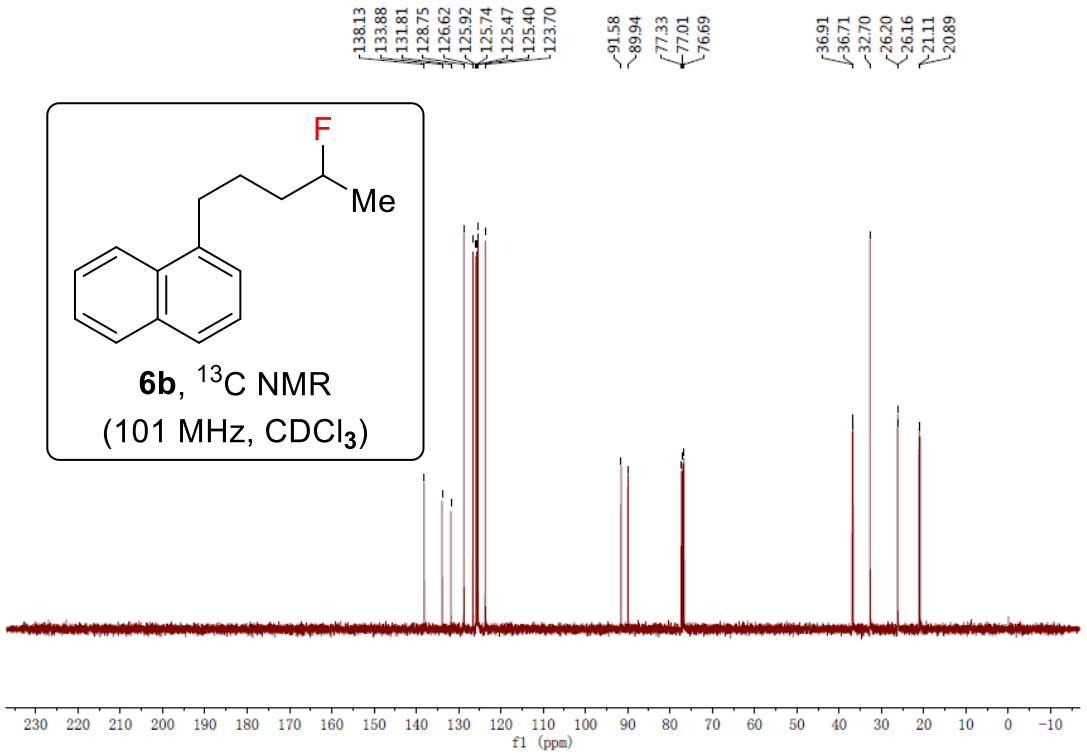
6a, ^{19}F NMR
(376 MHz, $CDCl_3$)

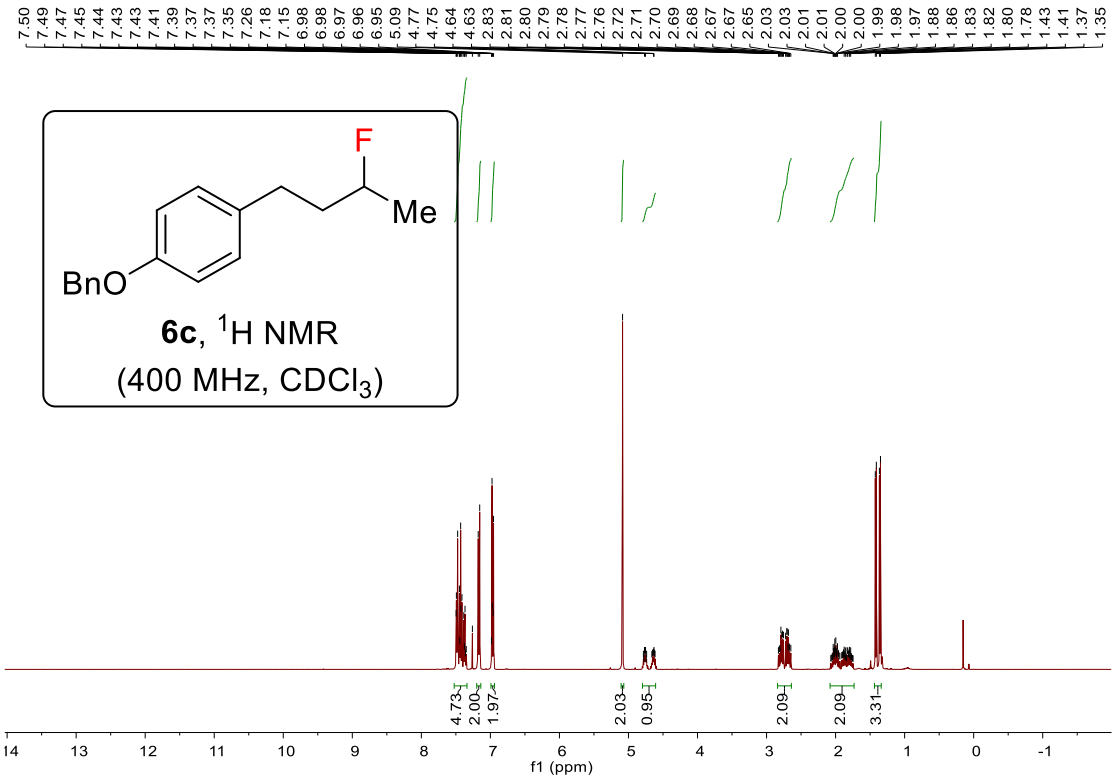


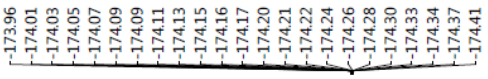
6a, ^{13}C NMR
(101 MHz, $CDCl_3$)

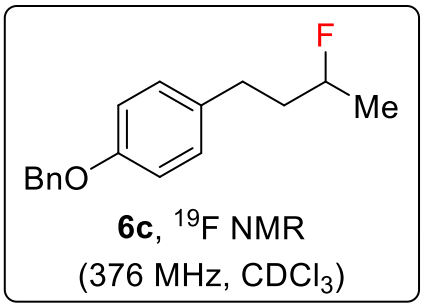

F
Me
6b, 1H NMR
(400 MHz, CDCl3)
f1 (ppm)


F
Me
6b, 19F NMR
(376 MHz, CDCl3)
f1 (ppm)

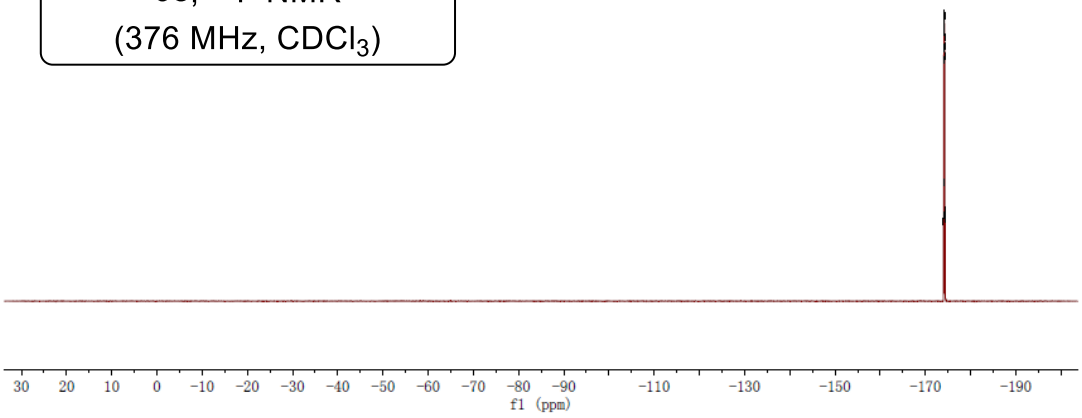

F
Me
6b, 13C NMR
(101 MHz, CDCl3)
f1 (ppm)

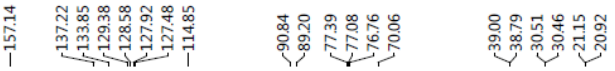

F
Me
BnO
6c, 1H NMR
(400 MHz, CDCl3)
f1 (ppm)

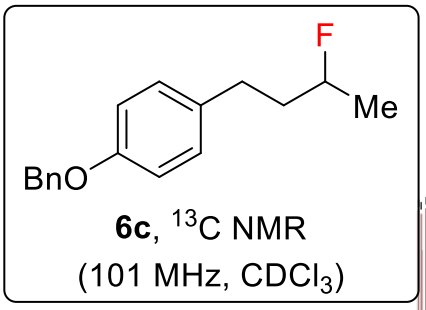




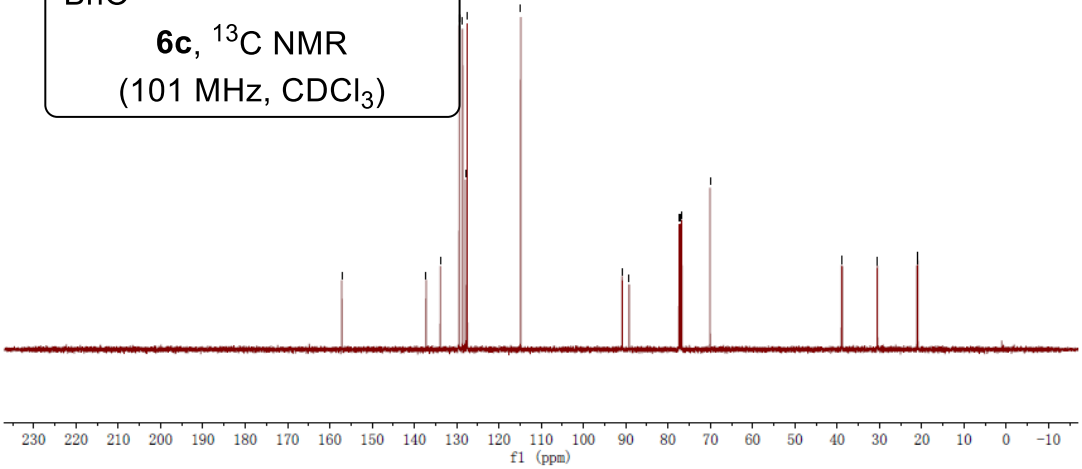
6c, ^{19}F NMR
(376 MHz, $CDCl_3$)

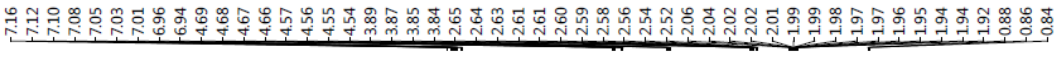


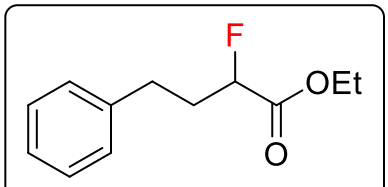




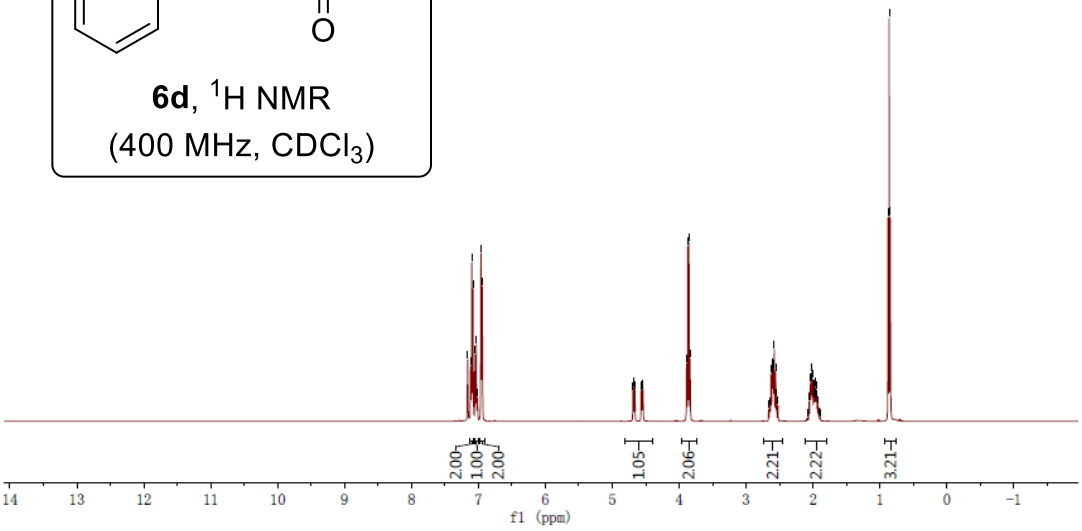
6c, ^{13}C NMR
(101 MHz, $CDCl_3$)

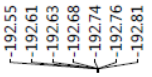


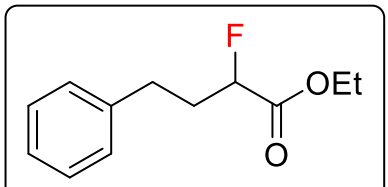




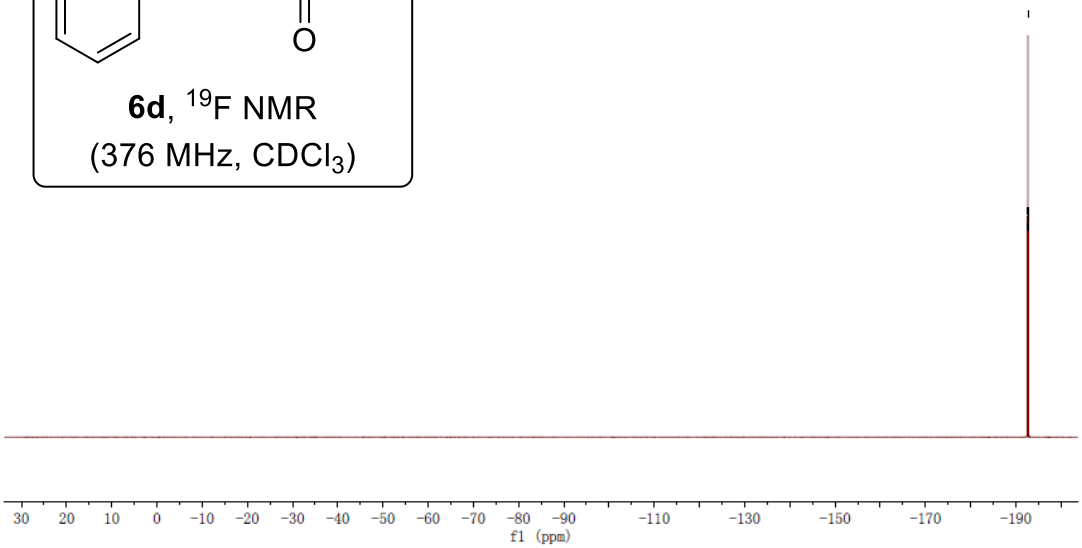
6d, ^{1}H NMR
(400 MHz, $CDCl_3$)

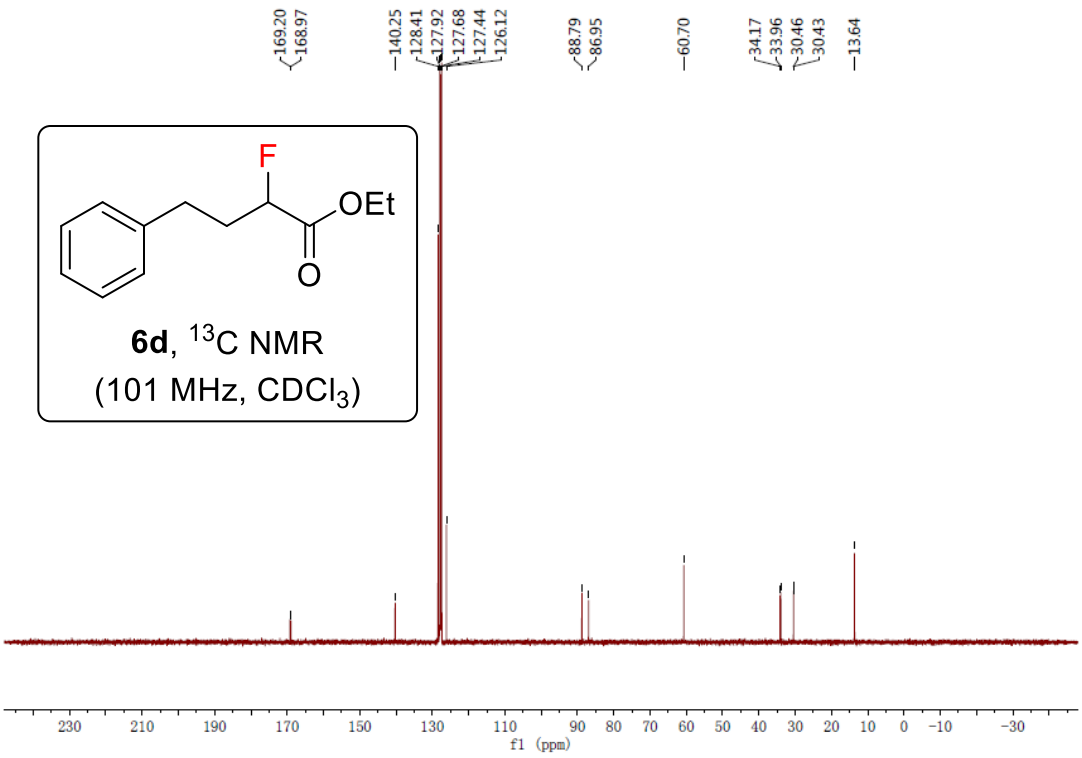




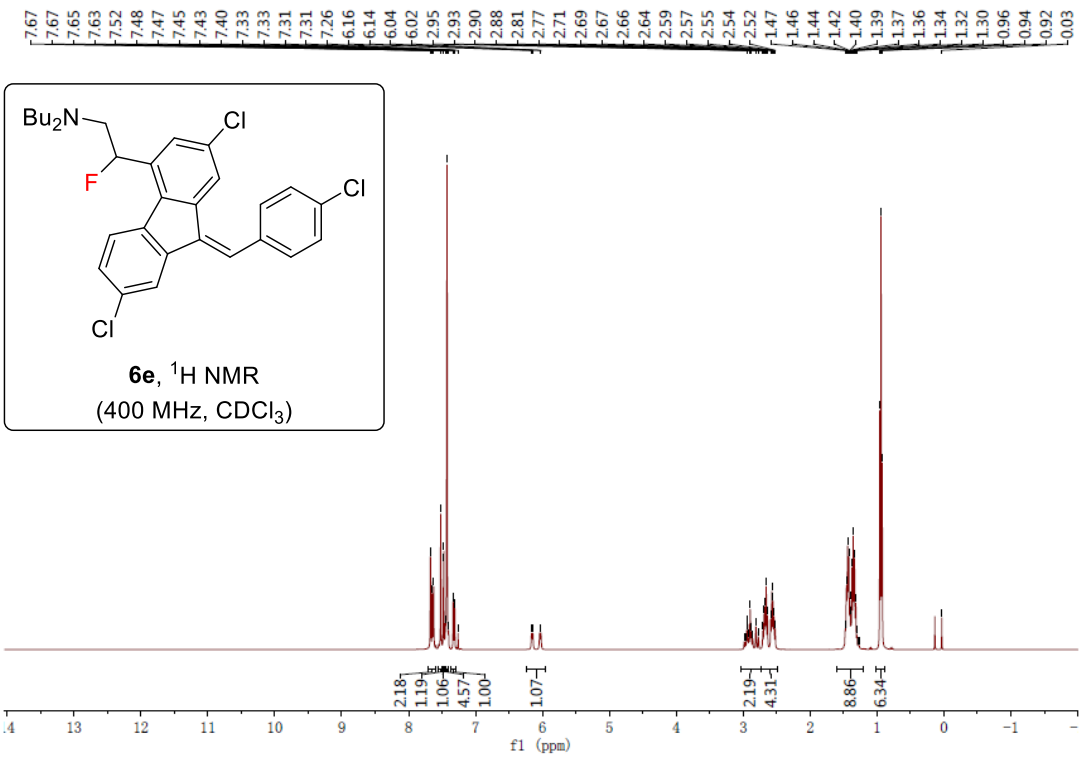


6d, ^{19}F NMR
(376 MHz, $CDCl_3$)

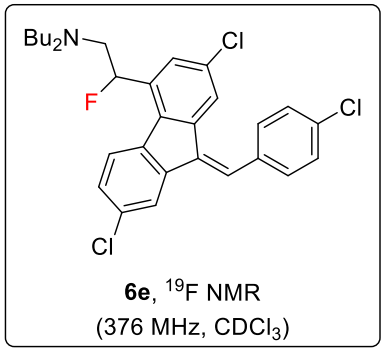




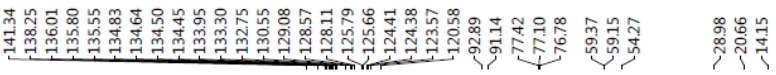
6d, ^{13}C NMR
(101 MHz, $CDCl_3$)

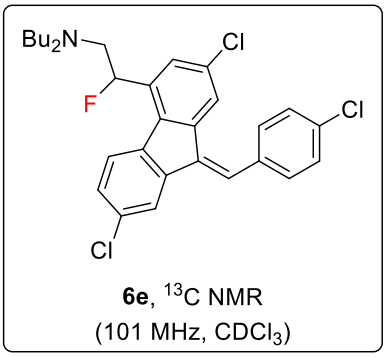


6e, ^{1}H NMR
(400 MHz, $CDCl_3$)

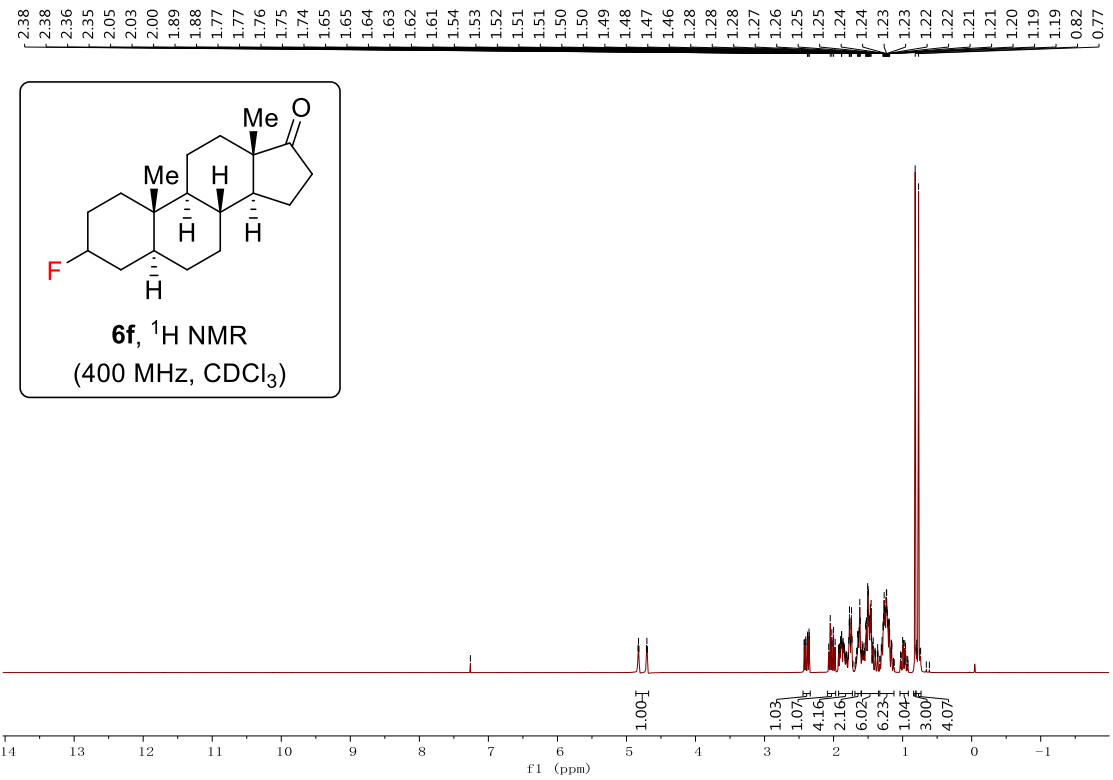


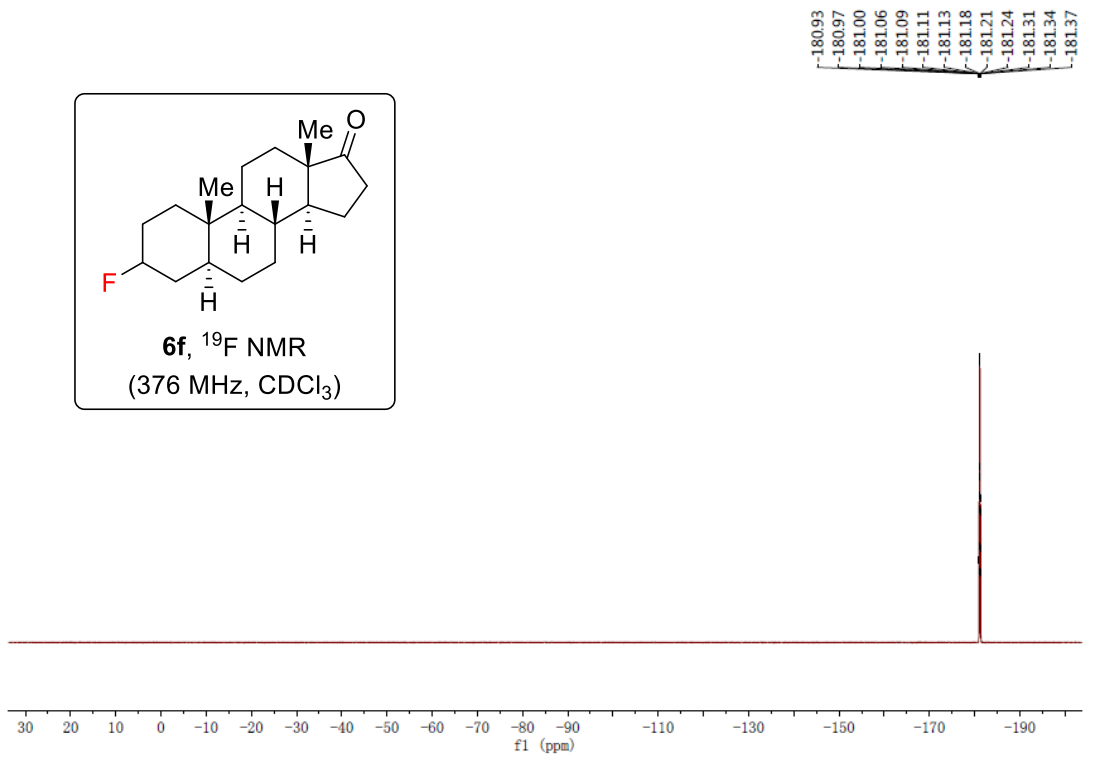
6e, ^{19}F NMR
(376 MHz, $CDCl_3$)

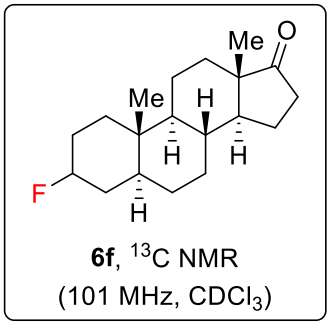




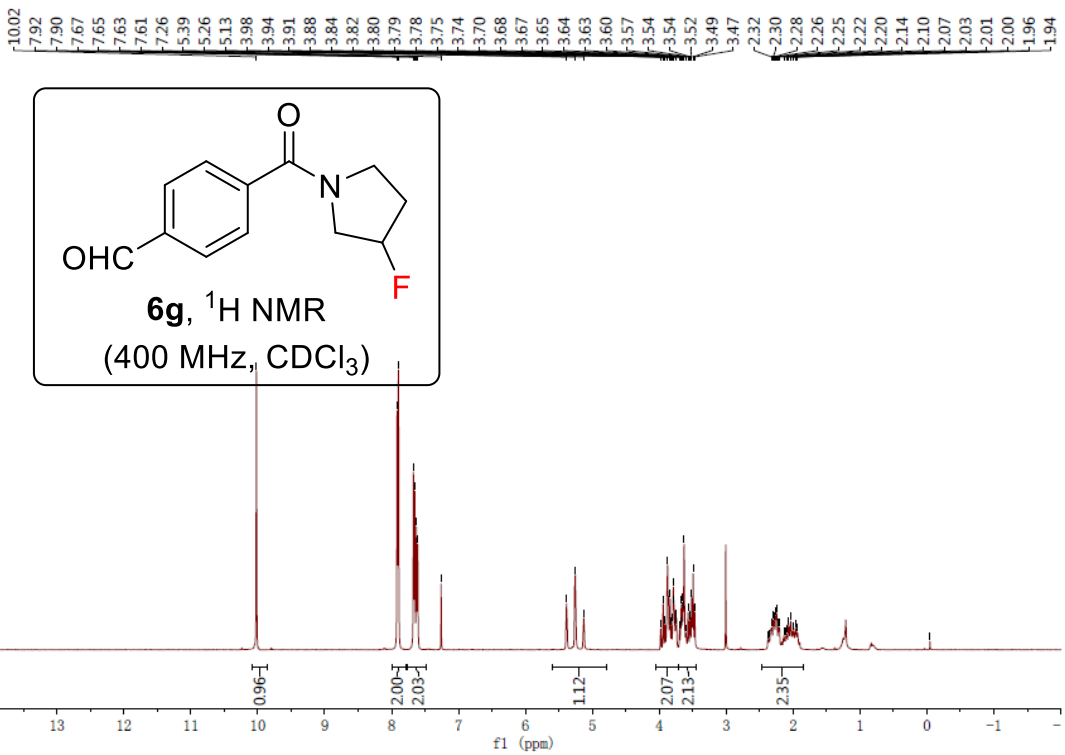
6e, ^{13}C NMR
(101 MHz, $CDCl_3$)


Me
O
Me
H
H
H
F
H
6f, 1H NMR
(400 MHz, CDCl3)
f1 (ppm)

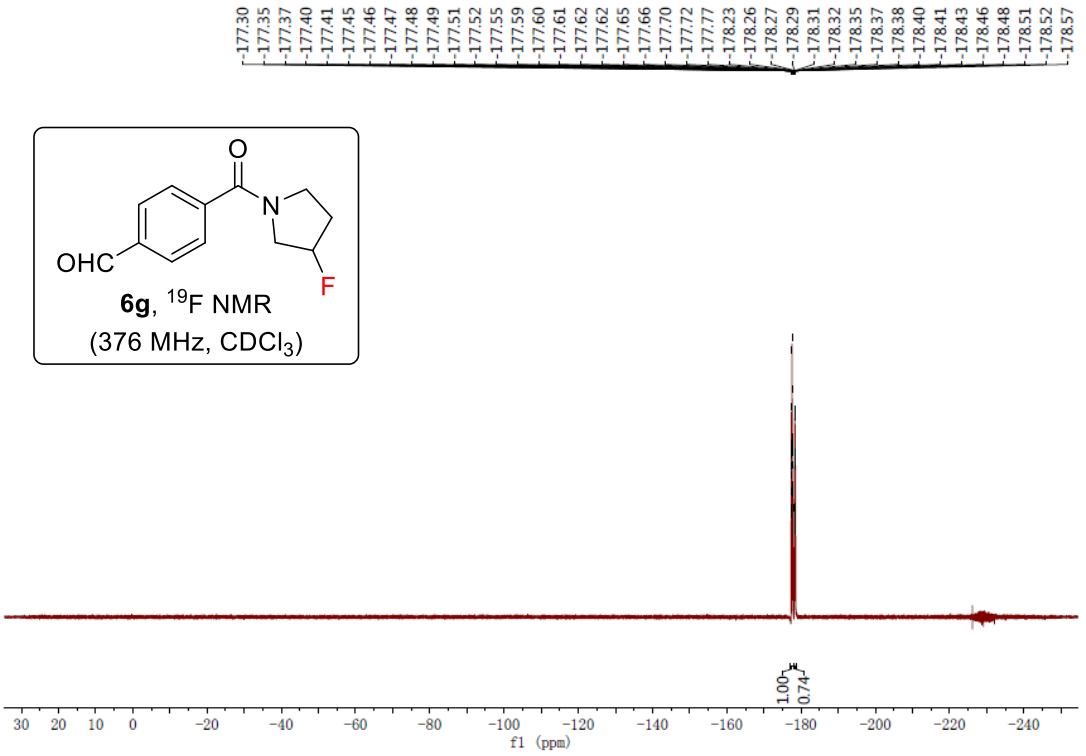

Me
O
Me
H
H
H
F
H
6f, 19F NMR
(376 MHz, CDCl3)
f1 (ppm)

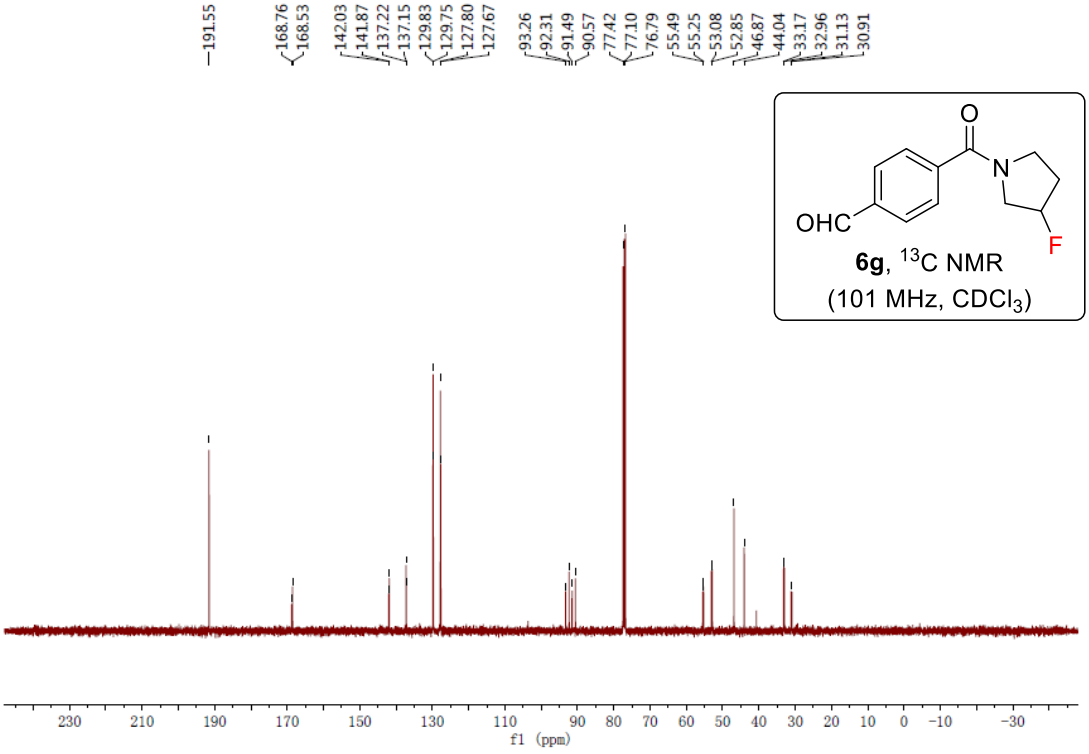


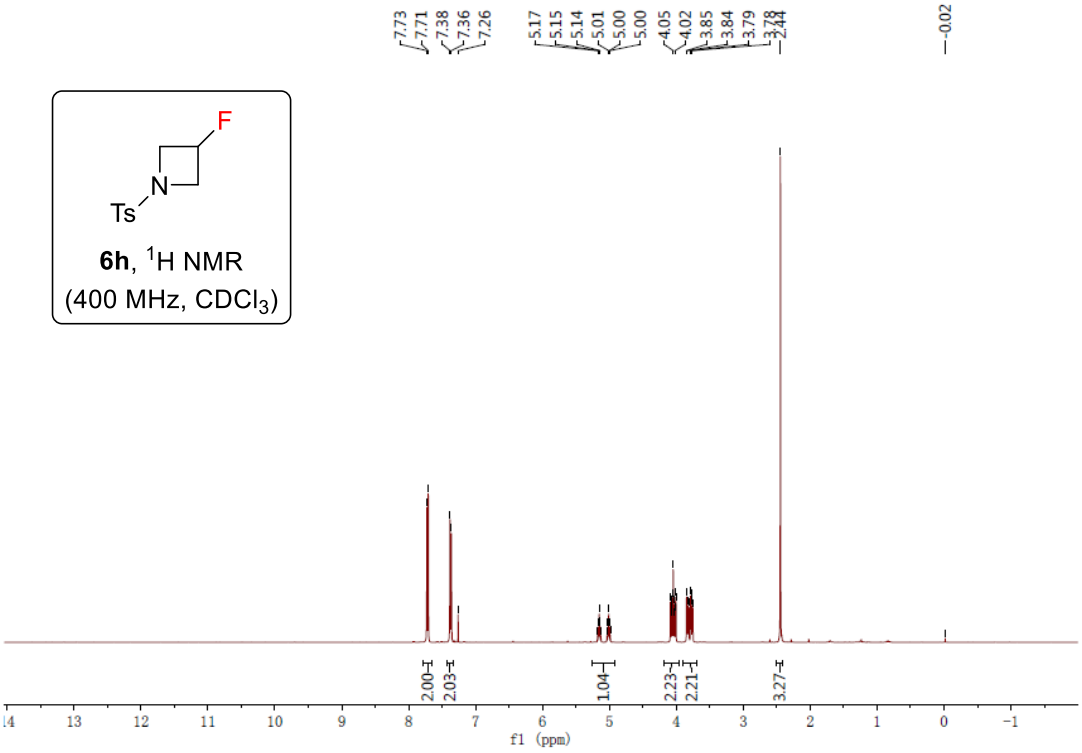
6f, ^{13}C NMR
(101 MHz, $CDCl_3$)

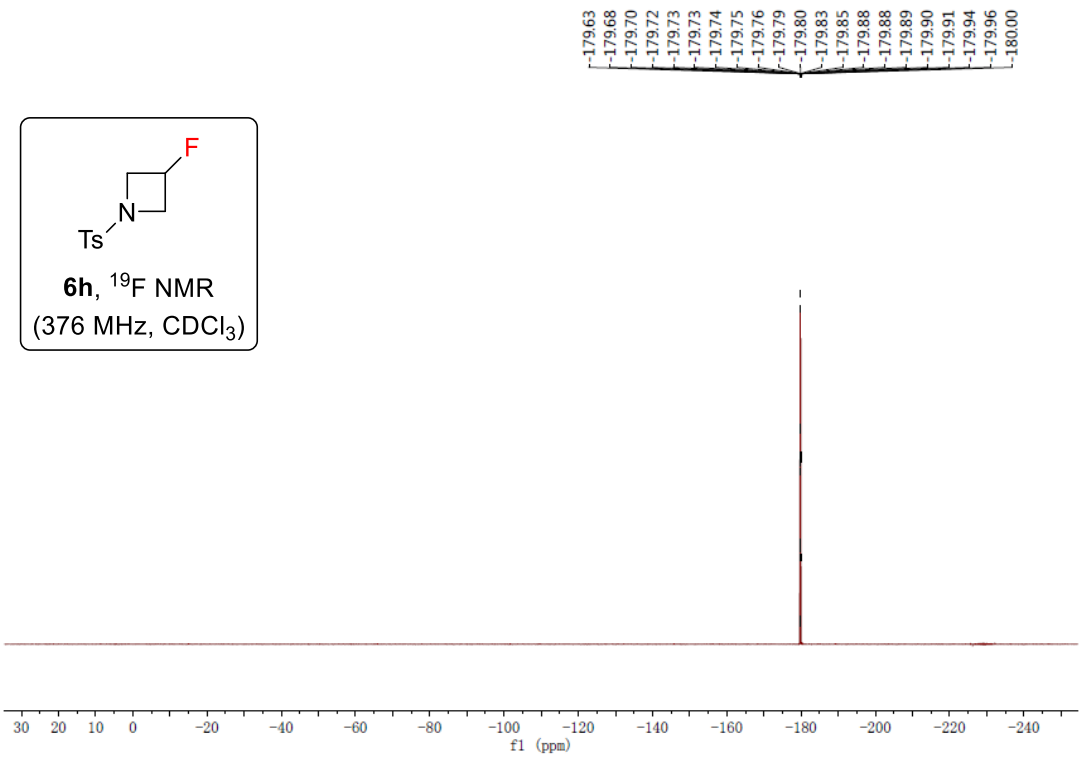


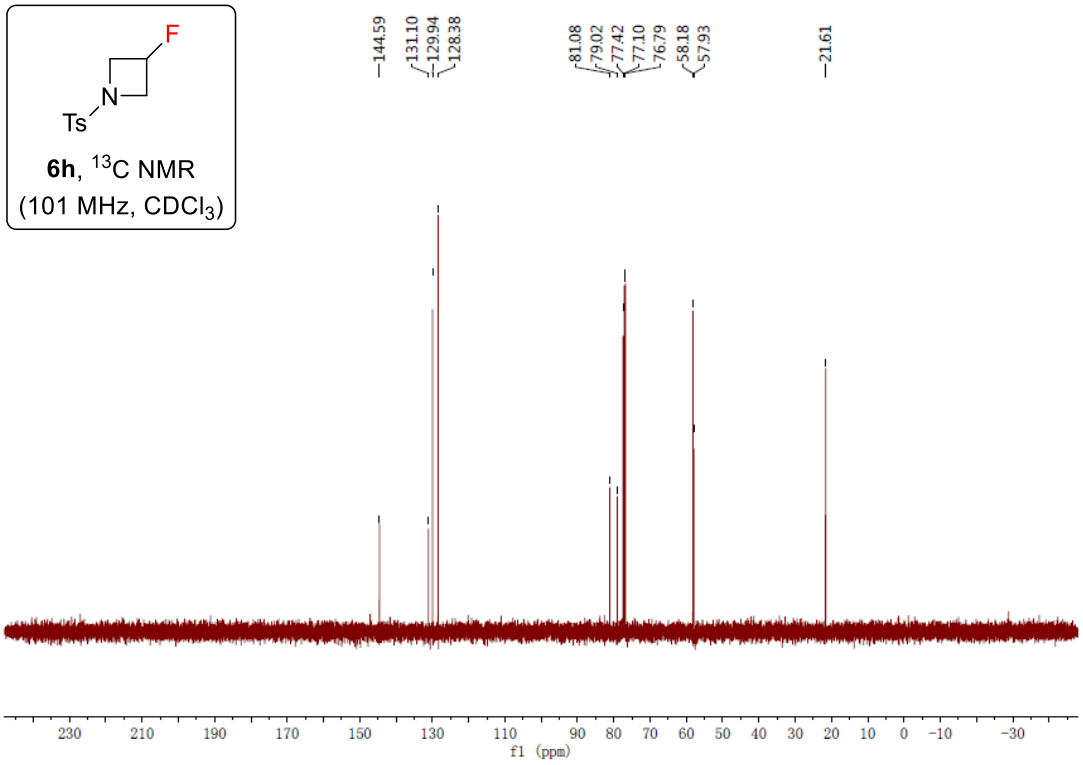
6g, ^{1}H NMR
(400 MHz, $CDCl_3$)

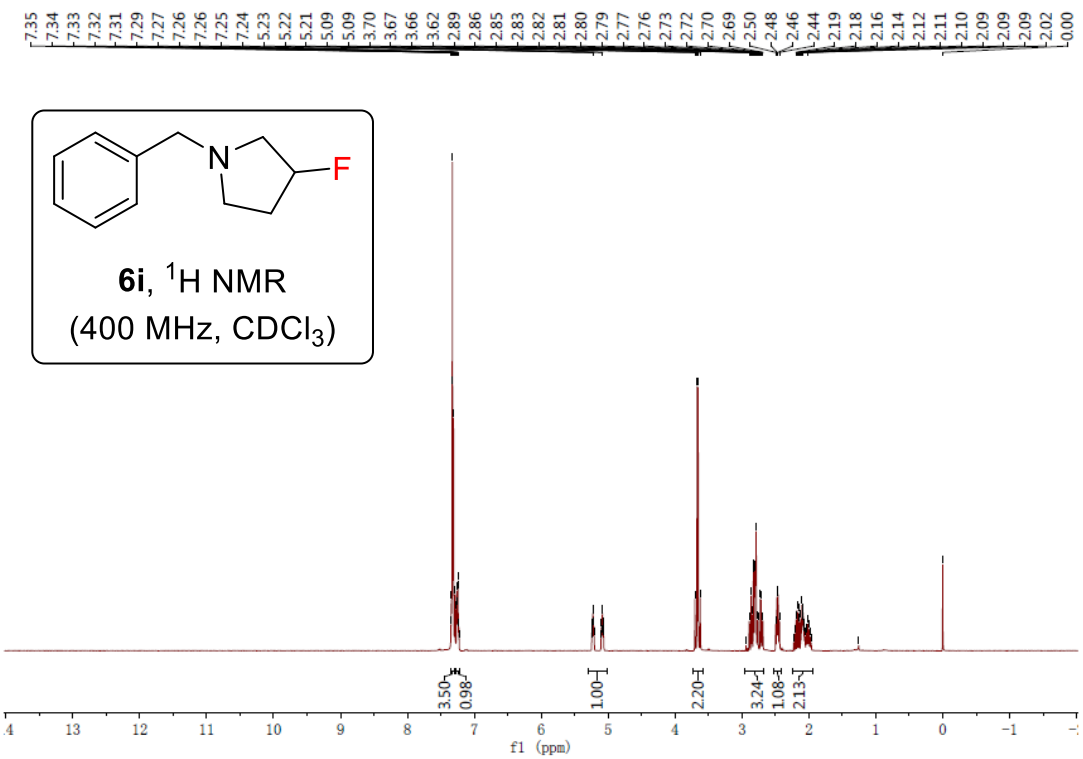

-177.30
-177.35
-177.37
-177.40
-177.41
-177.45
-177.46
-177.47
-177.48
-177.49
-177.51
-177.52
-177.55
-177.59
-177.60
-177.61
-177.62
-177.62
-177.65
-177.66
-177.70
-177.72
-177.77
-178.23
-178.26
-178.27
-178.29
-178.31
-178.32
-178.35
-178.37
-178.38
-178.40
-178.41
-178.43
-178.46
-178.48
-178.51
-178.52
-178.57
O
N
OHC
F
6g, 19F NMR
(376 MHz, CDCl3)
1.00
0.74
30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

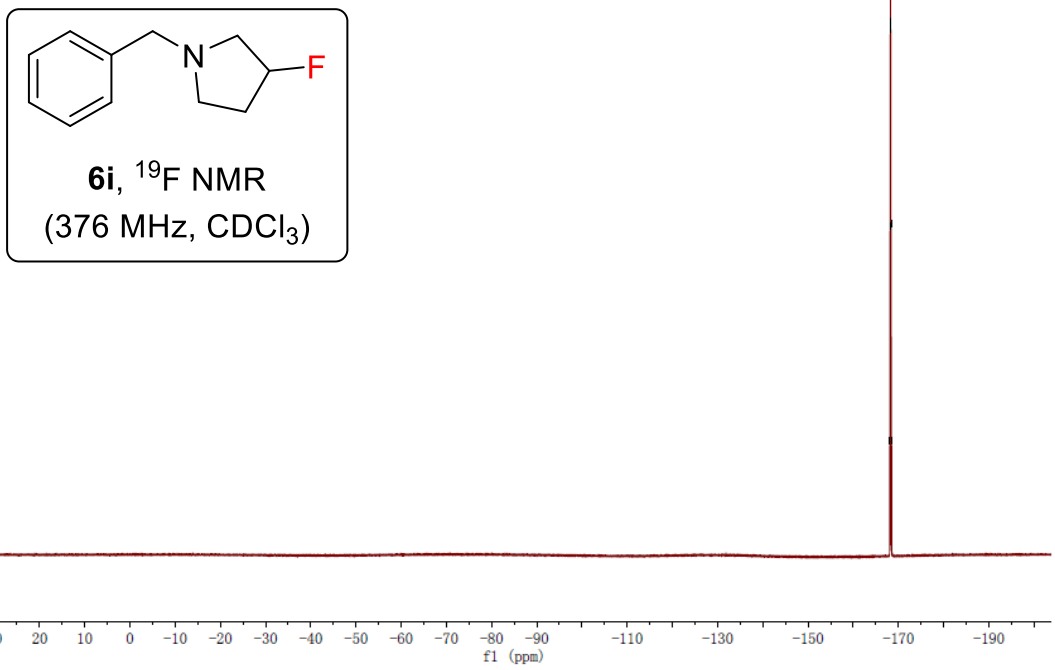

191.55
168.76
168.53
142.03
141.87
137.22
137.15
129.83
129.75
127.80
127.67
93.26
92.31
91.49
90.57
77.42
77.10
76.79
55.49
55.25
53.08
52.85
46.87
44.04
33.17
32.96
31.13
30.91
O
N
OHC
F
6g, 13C NMR
(101 MHz, CDCl3)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30
f1 (ppm)

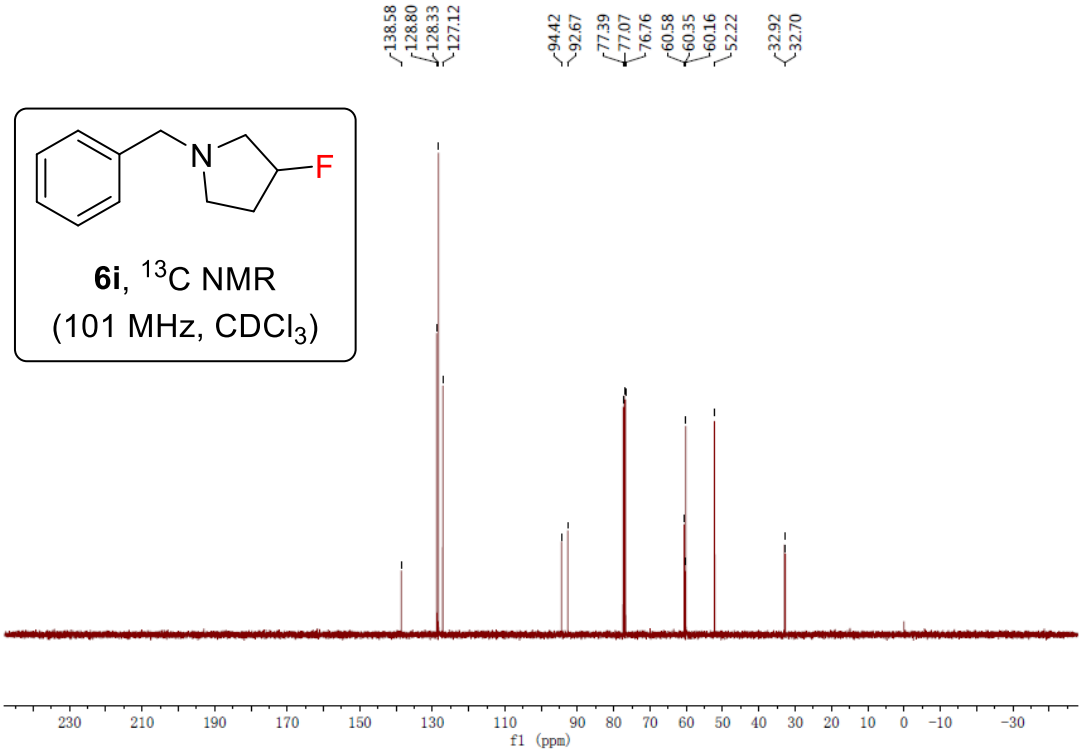

F
N
Ts
6h, 1H NMR
(400 MHz, CDCl3)
7.73
7.71
7.38
7.36
7.26
5.17
5.15
5.14
5.01
5.00
5.00
4.05
4.02
3.85
3.84
3.79
3.78
3.77
2.44
0.02
2.00
2.03
1.04
2.23
2.21
3.27
f1 (ppm)

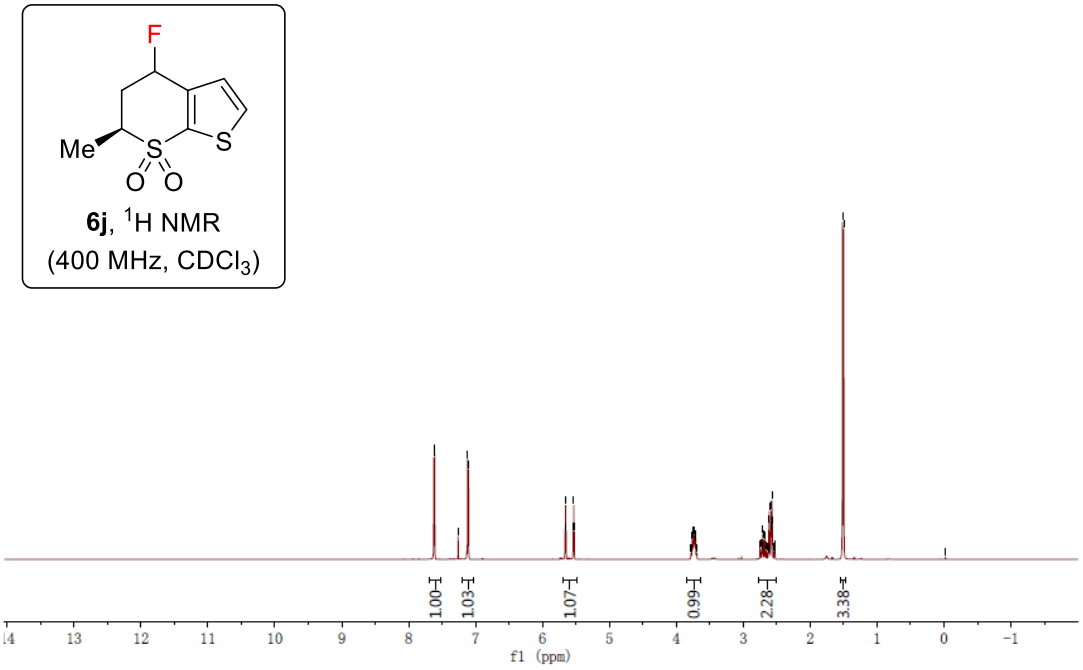

F
N
Ts
6h, 19F NMR
(376 MHz, CDCl3)
-179.63
-179.68
-179.70
-179.72
-179.73
-179.73
-179.74
-179.75
-179.76
-179.79
-179.80
-179.83
-179.85
-179.88
-179.88
-179.89
-179.90
-179.91
-179.94
-179.96
-180.00
f1 (ppm)


F
N
Ts
6h, 13C NMR
(101 MHz, CDCl3)
144.59
131.10
129.94
128.38
81.08
79.02
77.42
77.10
76.79
58.18
57.93
21.61
f1 (ppm)

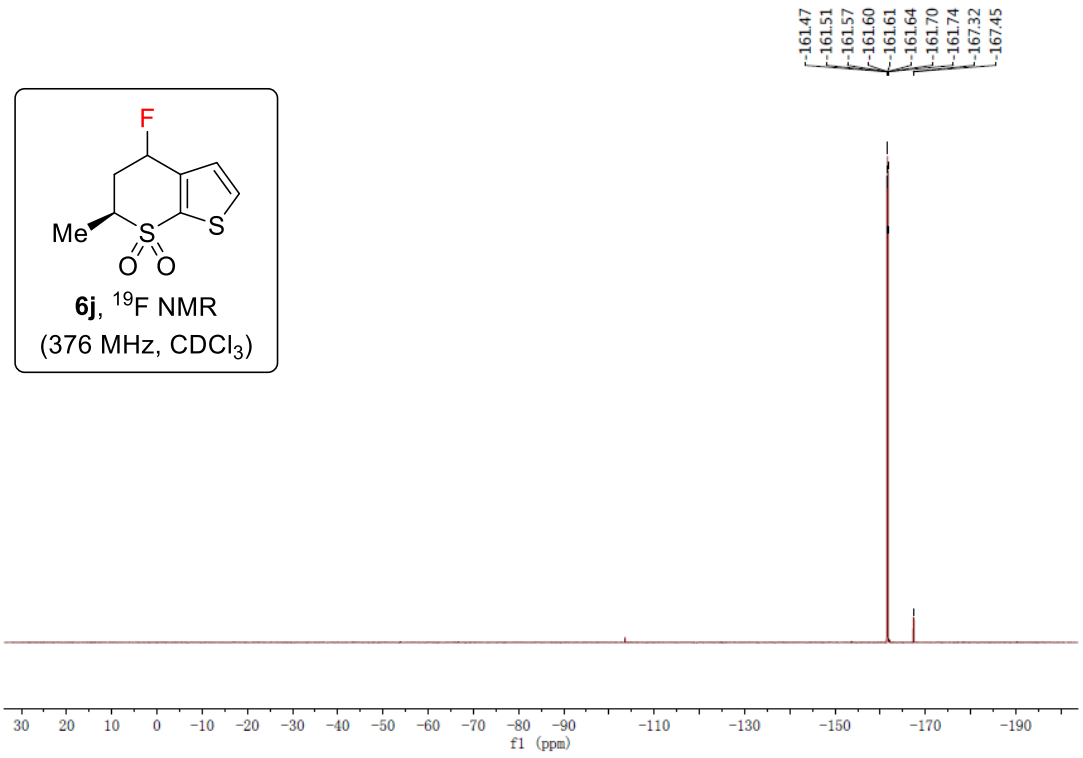

7.35
7.34
7.33
7.32
7.31
7.29
7.27
7.26
7.26
7.25
7.24
5.23
5.22
5.21
5.09
5.09
3.70
3.67
3.66
3.62
2.89
2.86
2.85
2.83
2.82
2.81
2.80
2.79
2.77
2.76
2.73
2.72
2.70
2.69
2.50
2.48
2.46
2.44
2.19
2.18
2.16
2.14
2.12
2.11
2.10
2.09
2.09
2.09
2.02
0.00
N
F
6i, 1H NMR
(400 MHz, CDCl3)
3.50
0.98
1.00
2.20
3.24
1.08
2.13
f1 (ppm)


-168.04
-168.12
-168.19
-168.27
-168.35
-168.42
-168.50
N
F
6i, 19F NMR
(376 MHz, CDCl3)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)

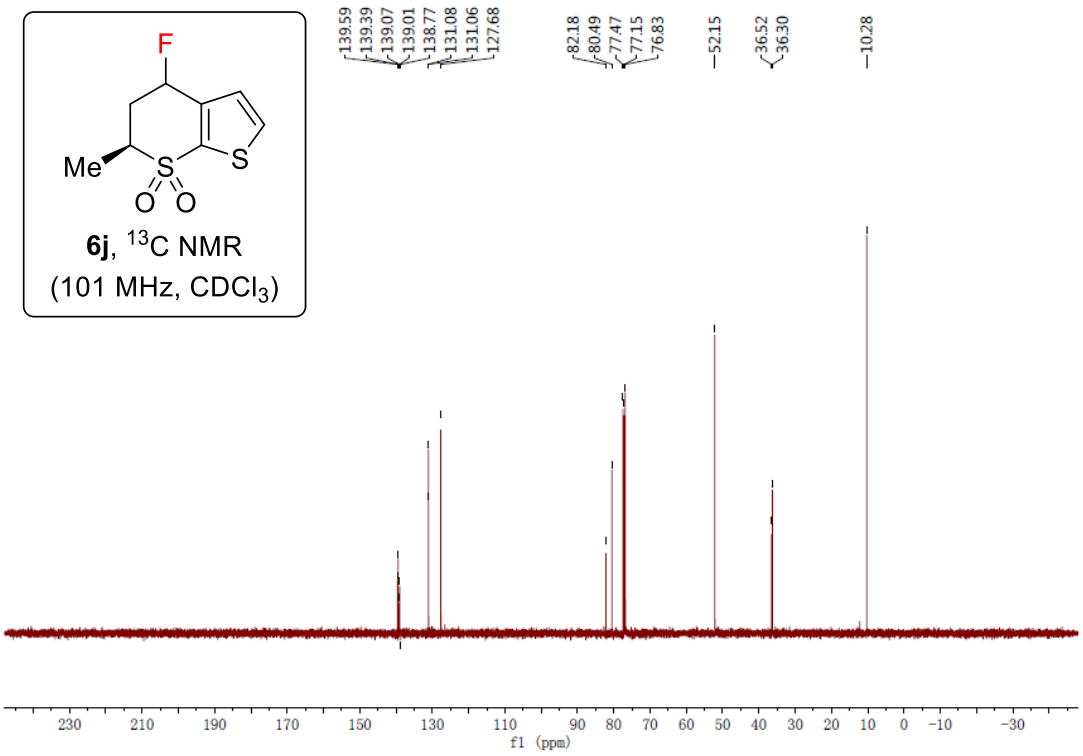

138.58
128.80
128.33
127.12
94.42
92.67
77.39
77.07
76.76
60.58
60.35
60.16
52.22
32.92
32.70
N
F
6i, 13C NMR
(101 MHz, CDCl3)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30
f1 (ppm)

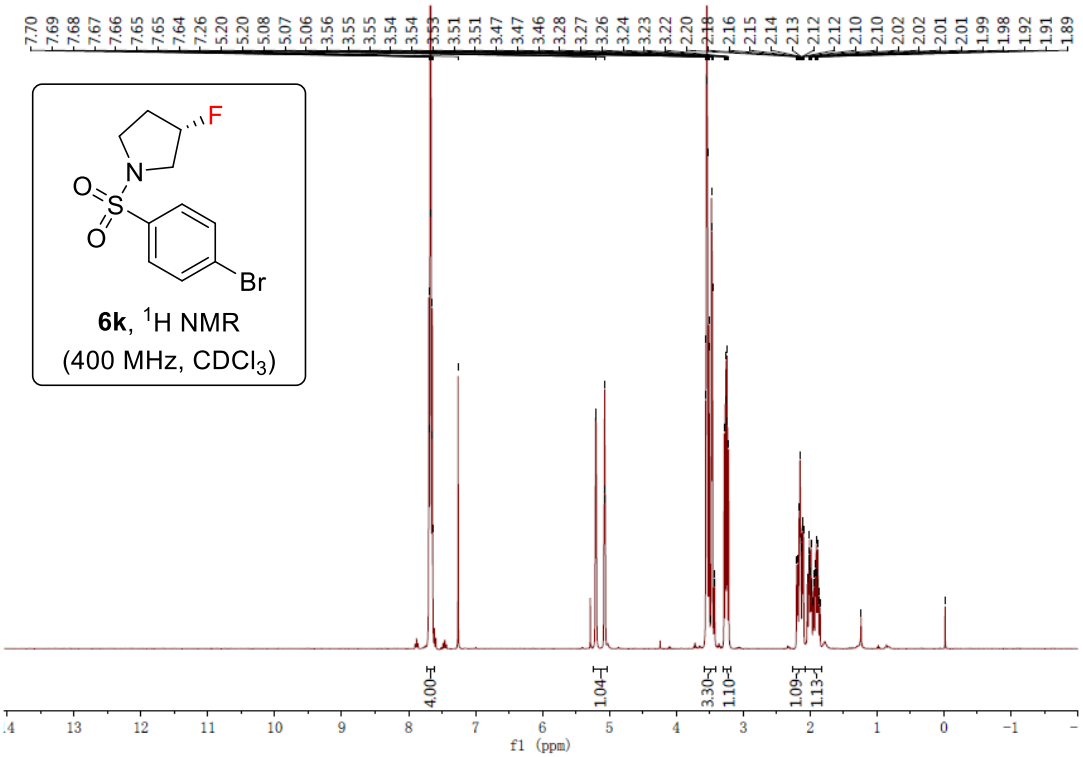


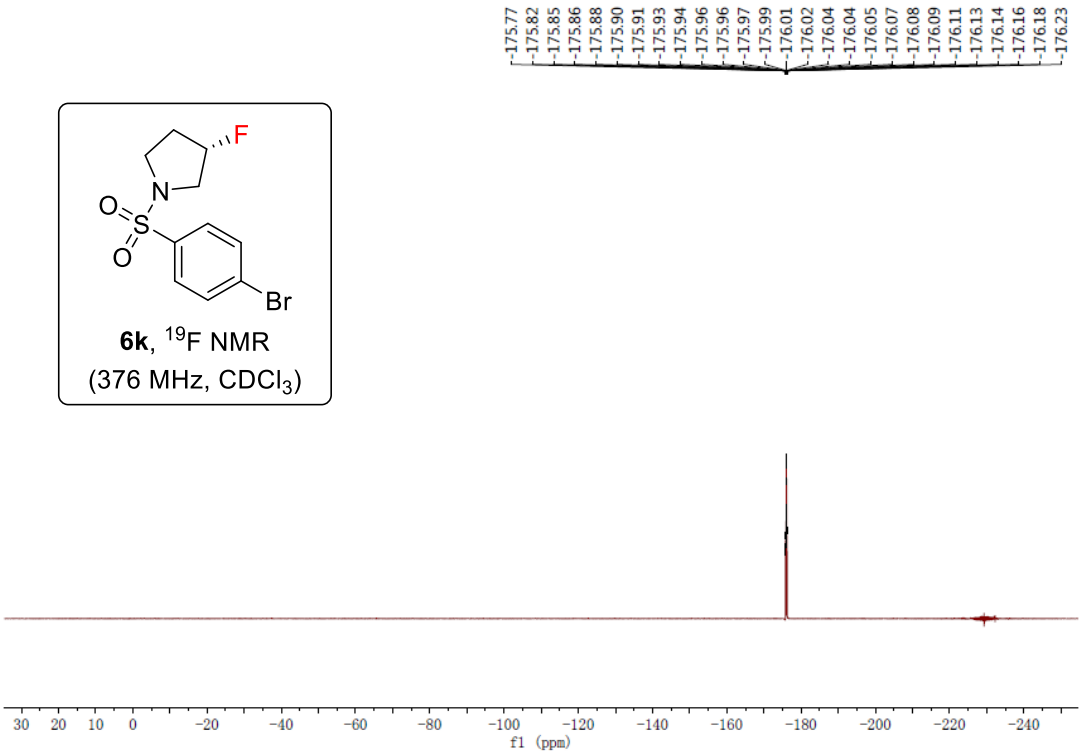
6j, ^{1}H NMR
(400 MHz, $CDCl_3$)

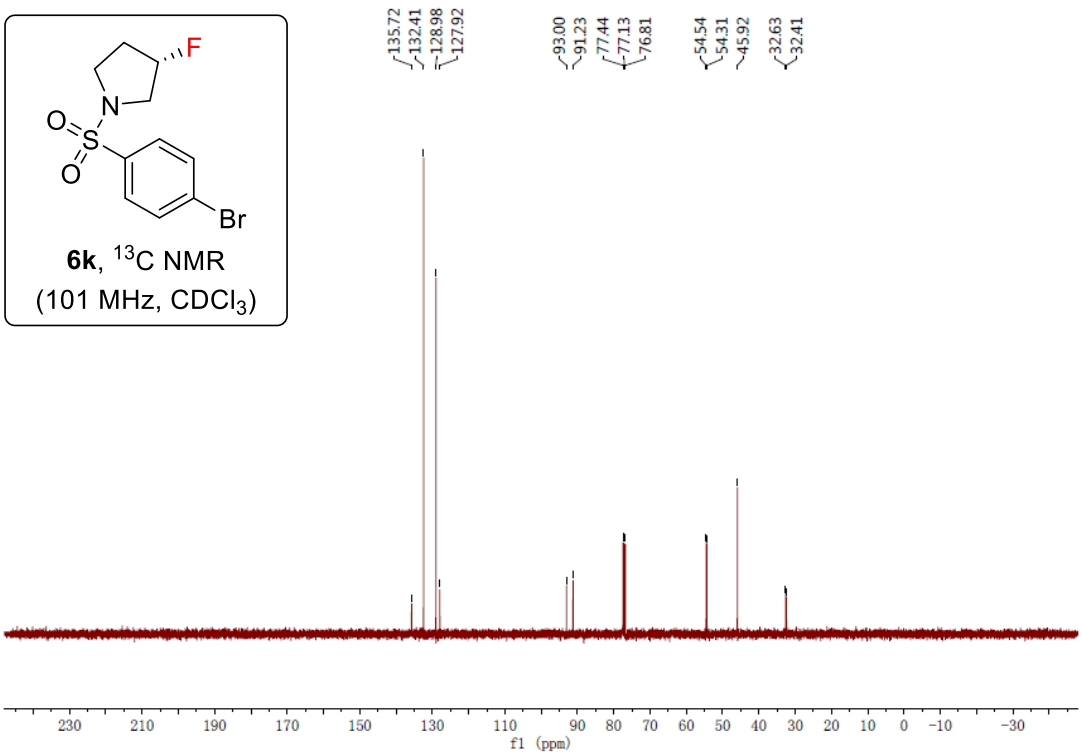


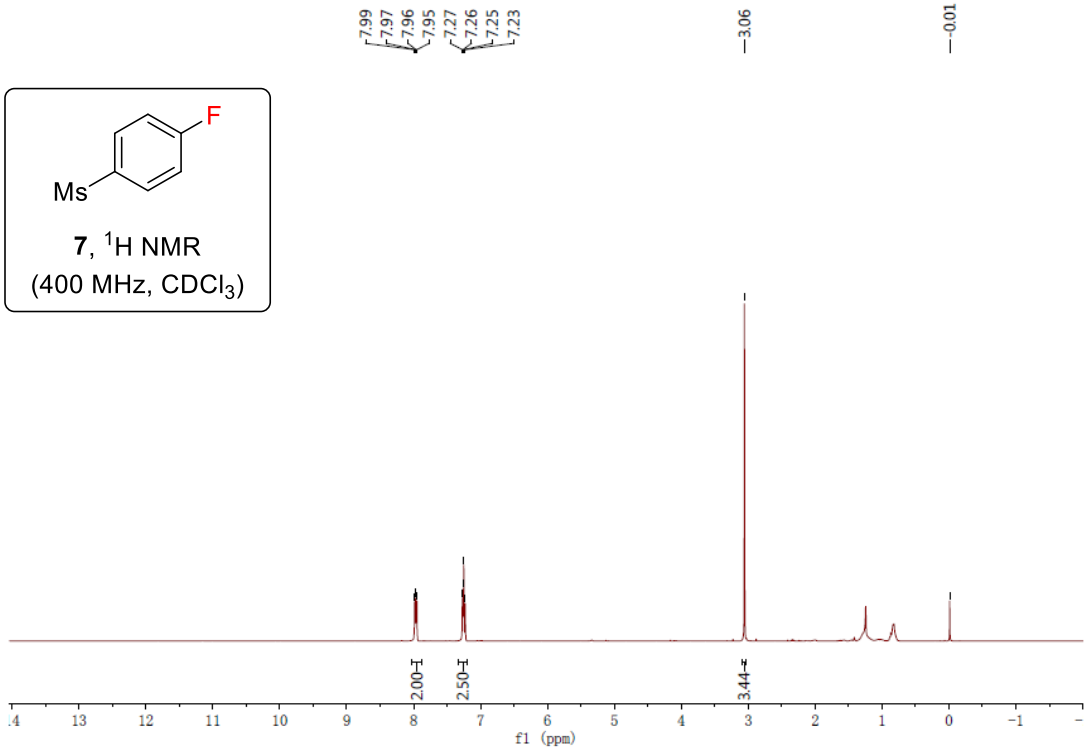
6j, ^{19}F NMR
(376 MHz, $CDCl_3$)

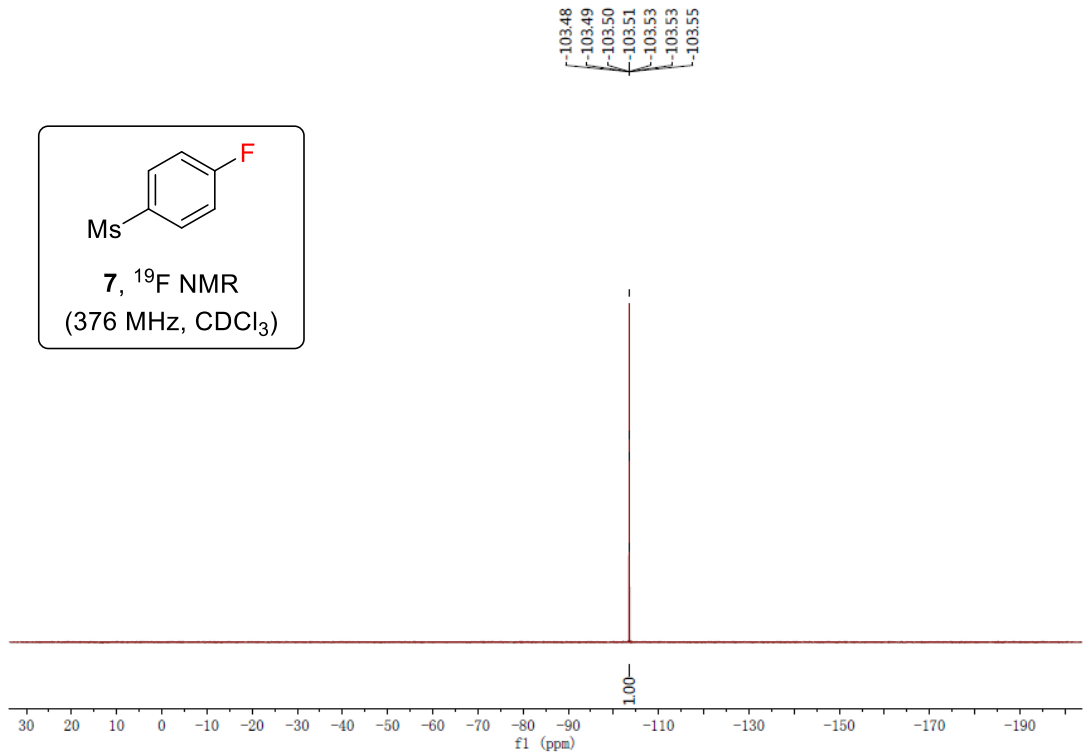

F
Me
S
S
O
O
6j, 13C NMR
(101 MHz, CDCl3)
139.59
139.39
139.07
139.01
138.77
131.08
131.06
127.68
82.18
80.49
77.47
77.15
76.83
52.15
36.52
36.30
10.28
f1 (ppm)

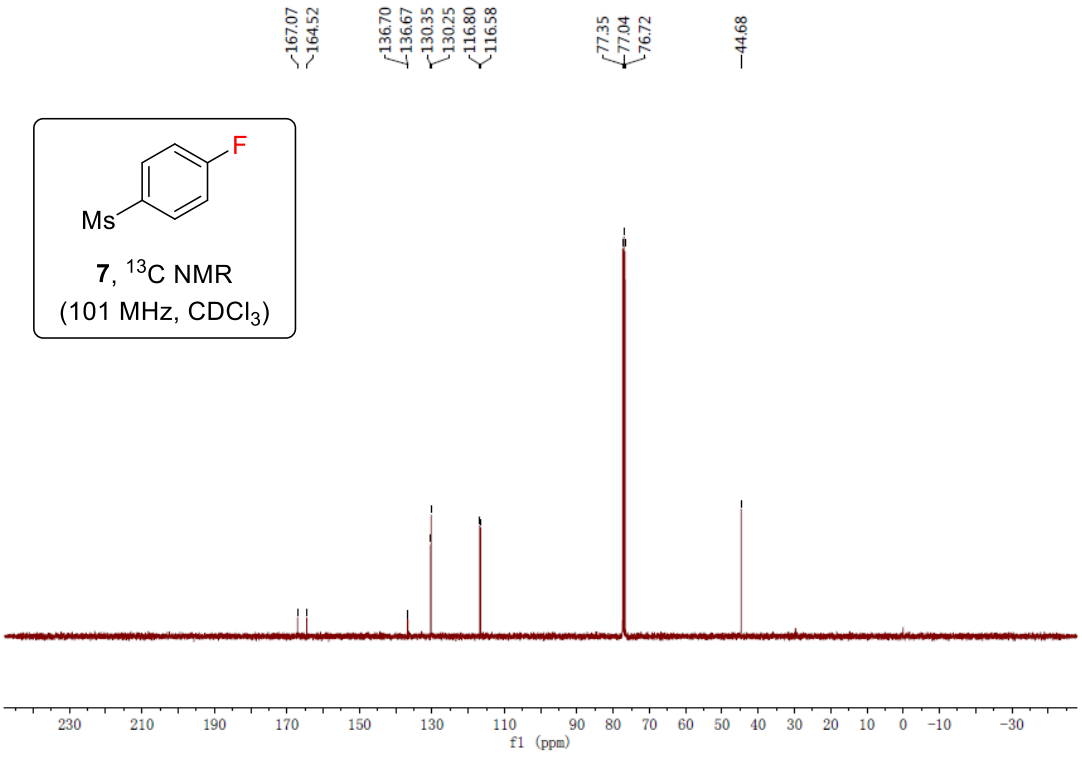

F
N
O
S
O
Br
6k, 1H NMR
(400 MHz, CDCl3)
4.00
1.04
3.30
1.10
1.09
1.13
f1 (ppm)


-175.77
-175.82
-175.85
-175.86
-175.88
-175.90
-175.91
-175.93
-175.94
-175.96
-175.96
-175.97
-175.99
-176.01
-176.02
-176.04
-176.04
-176.05
-176.07
-176.08
-176.09
-176.11
-176.13
-176.14
-176.16
-176.18
-176.23
F
N
O
S
O
Br
6k, 19F NMR
(376 MHz, CDCl3)
30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

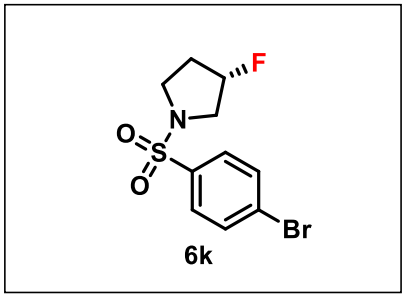

135.72
132.41
128.98
127.92
93.00
91.23
77.44
77.13
76.81
54.54
54.31
45.92
32.63
32.41
F
N
O
S
O
Br
6k, 13C NMR
(101 MHz, CDCl3)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30
f1 (ppm)

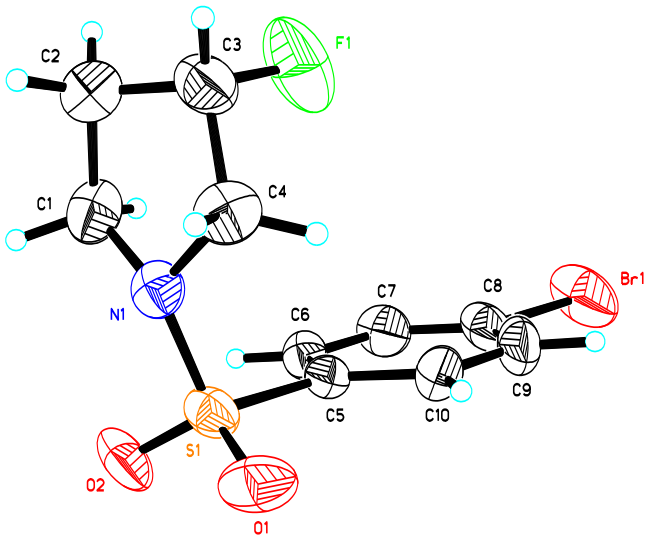

7.99
7.97
7.96
7.95
7.27
7.26
7.25
7.23
3.06
0.01
F
Ms
7, 1H NMR
(400 MHz, CDCl3)
2.00
2.50
3.44
f1 (ppm)


103.48
103.49
103.50
103.51
103.53
103.53
103.55
F
Ms
7, 19F NMR
(376 MHz, CDCl3)
1.00
f1 (ppm)


167.07
164.52
136.70
136.67
130.35
130.25
116.80
116.58
77.35
77.04
76.72
44.68
F
Ms
7, 13C NMR
(101 MHz, CDCl3)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
−10
−30
f1 (ppm)

9. X-ray Structure of 6k (CCDC 2084521)





Identification code	mo_d8v19081_0m	
Empirical formula	C10 H11 Br F N O2 S	
Formula weight	308.17	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.1604(8) Å	= 90°.
	b = 10.1970(10) Å	= 90°.
	c = 11.8624(13) Å	= 90°.
Volume	1229.0(2) $Å^3$	
Z	4	
Density (calculated)	1.665 Mg/m^3	
Absorption coefficient	3.512 mm^{-1}	
F(000)	616	
Crystal size	0.200 x 0.170 x 0.130 mm^3	

Theta range for data collection	2.634 to 25.999°.
Index ranges	-12<=h<=12, -12<=k<=12, -14<=l<=14
Reflections collected	10977
Independent reflections	2414 [R(int) = 0.0461]
Completeness to theta = 25.242°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.3777
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2414 / 0 / 146
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0439, wR2 = 0.1073
R indices (all data)	R1 = 0.0654, wR2 = 0.1181
Absolute structure parameter	0.036(9)
Extinction coefficient	0.033(6)
Largest diff. peak and hole	0.470 and -0.570 e.$Å^{-3}$