

Visible-Light-Promoted S-Trifluoromethylation of Thiophenols with Trifluoromethyl Phenyl Sulfone

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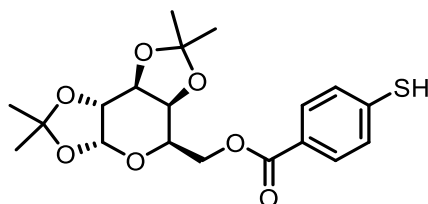
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1. General Information

Unless otherwise mentioned, all solvents and reagents are purchased from commercial sources and used as received. Tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF) were dried by passing through a solvent purification system. ^1H NMR spectra were recorded at 400 MHz. ^{19}F NMR spectra were recorded at 376 MHz. ^{13}C NMR spectra were recorded at 101 MHz. ^1H NMR chemical shifts were determined relative to internal $(\text{CH}_3)_4\text{Si}$ (TMS) at δ 0.00 ppm or to the signal of the residual protonated solvent: CDCl_3 at δ 7.26 ppm. ^{19}F NMR chemical shifts were determined relative to internal or external CFCl_3 at δ 0.00 ppm. ^{13}C NMR chemical shifts were determined relative to the signal of the solvent: CDCl_3 at δ 77.16 ppm. Data for ^1H , ^{13}C , ^{19}F NMR were recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, qt = quartet of triplets, tq = triplet of quartets, br = broad, hept = heptet). Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer. The LEDs were manufactured by Zhejiang Gulinwa Electronic Corporation.

2. Synthesis of Substrate (1x)



Colorless oil. The synthesis of this compound refers to this literature.¹

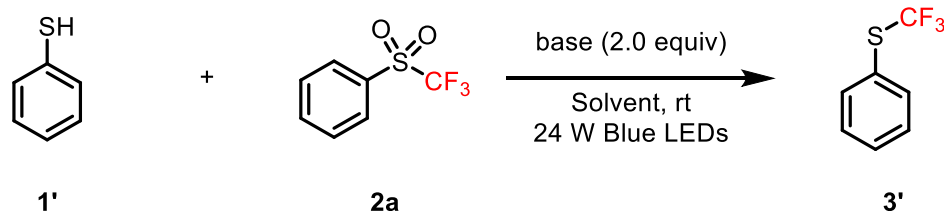
((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-mercaptobenzoate (1x). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.3$ Hz, 2H), 5.54 (d, $J = 5.0$ Hz, 1H), 4.63 (dd, $J = 7.9, 2.5$ Hz, 1H), 4.49 (dd, $J = 11.5, 4.8$ Hz, 1H), 4.38 (dd, $J = 11.5, 7.6$ Hz, 1H), 4.33 (dd, $J = 5.0, 2.5$ Hz, 1H), 4.29 (dd, $J = 7.9, 1.9$ Hz, 1H), 4.14 (ddd, $J = 7.1, 4.8, 1.9$ Hz, 1H), 3.59 (s, 3H), 1.49 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.9, 138.4, 130.3, 128.1, 127.0, 109.7, 108.8, 96.3, 71.1, 70.7, 70.5, 66.2, 63.9, 26.02, 25.98, 25.0, 24.5. **MS** (ESI, m/z): 397.0 (M+H⁺). **HRMS** (ESI): Calcd for C₁₉H₂₅O₇S⁺ (M+H⁺) 397.1316, found 397.1309. **IR** (film): 2987, 2934, 2558, 1716, 1595, 1404, 1382, 1273, 1212, 1007, 1069, 1007, 918, 899, 758, 733, 689, 512, 481 cm⁻¹.

3. Optimization of the Reaction Conditions

Typical procedures for optimization of the reaction conditions

Under dry N₂ atmosphere, to sealed tube were added PhSO₂CF₃ (**2a**) (0.6 mmol, 126.0 mg, 1.2 equiv), Cs₂CO₃ (1.0 mmol, 325.0 mg, 2.0 equiv) and dry DMAc (5.0 mL), then PhSH (0.5 mmol, 55.0 mg, 1.0 equiv) was added. The mixture was irradiated by a 24 W blue LED for 24 h.

Table 1 Survey of reaction conditions for trifluoromethylation of Arylthiophenol^a



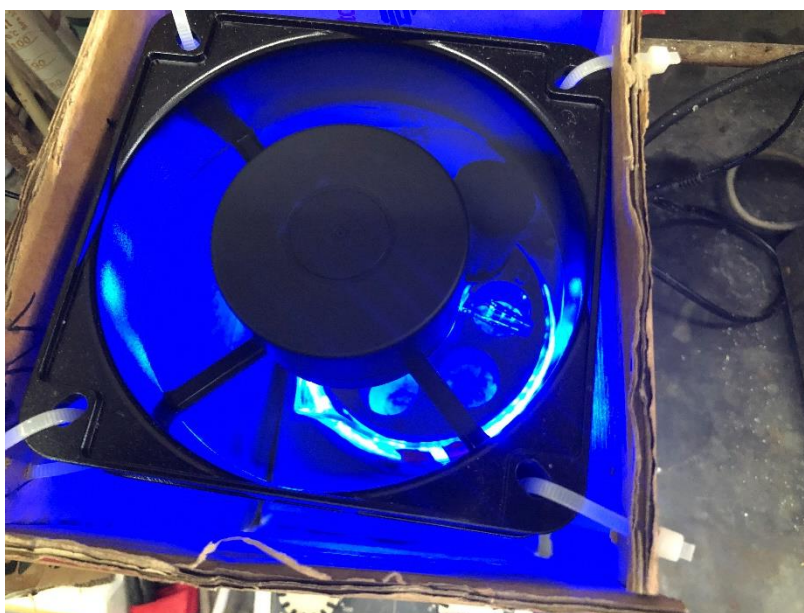
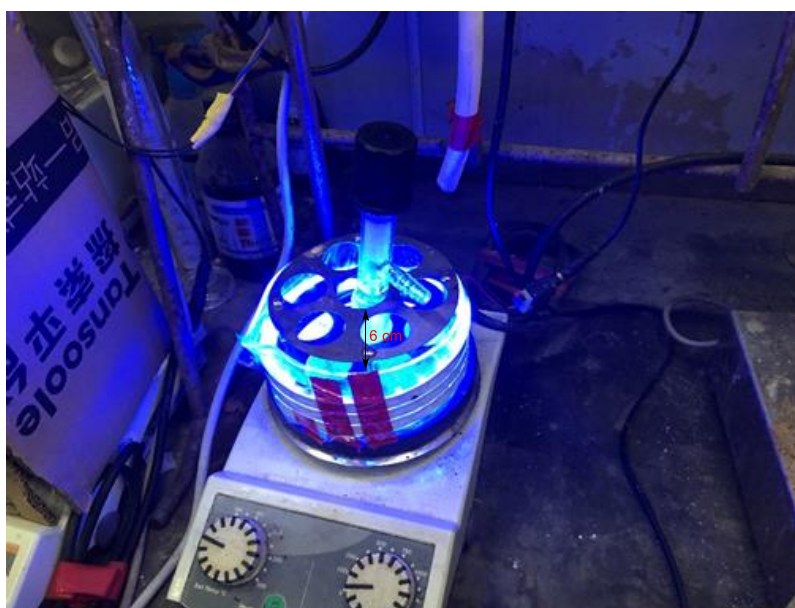
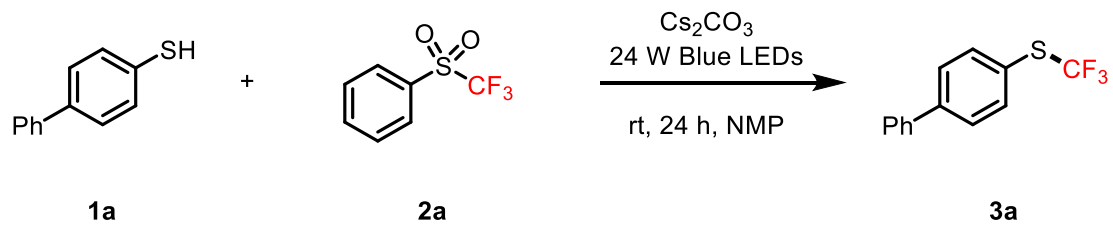
Entry	Solvent	Time (h)	Base	Yield (%) ^[b]
1 ^[c]	DMF	12	Cs ₂ CO ₃	Trace
2	DMF	12	Cs ₂ CO ₃	61
3	DMAc	12	Cs ₂ CO ₃	72
4	DMSO	12	Cs ₂ CO ₃	33
5	NMP	12	Cs ₂ CO ₃	72
6	DMPU	12	Cs ₂ CO ₃	52
7	CH ₃ CN	12	Cs ₂ CO ₃	3
8	DMAc	12	K ₃ PO ₄	64
9	DMAc	12	K ₂ CO ₃	54
10	DMAc	12	Na ₂ CO ₃	58
11	DMAc	12	NaH	61
12	DMAc	18	Cs ₂ CO ₃	72
13	NMP	18	Cs ₂ CO ₃	80
14	NMP	24	Cs ₂ CO ₃	81
15 ^[d]	NMP	24	Cs ₂ CO ₃	81
16 ^[e]	NMP	24	Cs ₂ CO ₃	72

^aReaction conditions : **1'** (0.5 mmol, 1.0 equiv), **2a** (0.6 mmol, 1.2 equiv), solvent (5.0 mL);

^bDetermined by ¹⁹F NMR spectroscopy using trifluoromethoxybenzene as an internal standard.

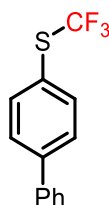
^cIn dark environment; ^d**2a** (0.55 mmol, 1.1 equiv); ^eUnder white light irradiation.

4. Perfluoroalkylation of Thiophenols with Perfluoroalkyl phenyl Sulfones

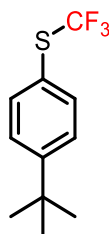


Typical procedures

Under dry N₂ atmosphere, to sealed tube were added **1a** (0.50 mmol, 93.1 mg, 1.0 equiv), **2a** (0.55 mmol, 115.5 mg, 1.1 equiv), Cs₂CO₃ (1.00 mmol, 325.0 mg, 2.0 equiv), dry NMP (5.00 mL). The mixture was irradiated by a 24 W blue LED for 24 h. After the completion of the reaction, the mixture was quenched by saturated NH₄Cl solution, then the mixture was extracted with Et₂O for 3 times. The organic phase was combined and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel by using petroleum ether as an eluent to provide **3a** as white solid (103.0 mg, 81%).

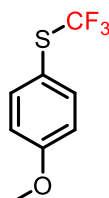


[1,1'-Biphenyl]-4-yl(trifluoromethyl)sulfane (3a) The product (103.2 mg, 81% yield) was purified with silica gel chromatography (Petroleum ether) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.65–7.59 (m, 4H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.43–7.39 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -42.72 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 143.9, 139.7, 136.7, 129.7 (q, *J* = 309.4 Hz), 129.0, 128.19, 128.17, 127.3, 123.1 (q, *J* = 2.2 Hz). All the characterization data are consistent with previous report.²

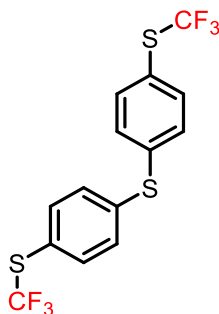


(4-(tert-Butyl)phenyl)(trifluoromethyl)sulfane (3b) The product (82.9 mg, 71% yield) was purified with silica gel chromatography (*n*-pentane) as a colorless liquid.

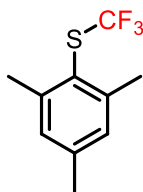
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.3$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H), 1.32 (s, 9H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -43.03 (s, 3F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.4, 136.1, 129.7 (q, $J = 307.9$ Hz), 126.6, 120.9 (q, $J = 2.2$ Hz), 34.9, 31.1. All the characterization data are consistent with previous report.²



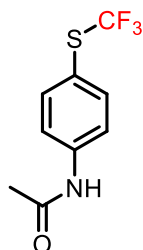
(4-Methoxyphenyl)(trifluoromethyl)sulfane (3c) The product (78.1 mg, 75% yield) was purified with silica gel chromatography (*n*-pentane) as a colorless liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56 (d, $J = 8.8$ Hz, 2H), 6.91 (d, $J = 8.8$ Hz, 2H), 3.82 (s, 3H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -43.99 (s, 3F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.9, 138.3, 129.6 (q, $J = 308.2$ Hz), 115.0, 114.8 (q, $J = 2.3$ Hz), 55.4. All the characterization data are consistent with previous report.²



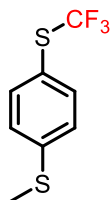
Bis(4-((trifluoromethyl)thio)phenyl)sulfane (3d) The product (187.4 mg, 97% yield) was purified with silica gel chromatography (Petroleum ether) as a colorless liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.3$ Hz, 4H), 7.36 (d, $J = 8.4$ Hz, 4H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -42.65 (s, 6F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.7, 137.0, 131.6, 129.4 (q, $J = 308.3$ Hz), 123.55 (q, $J = 2.3$ Hz). **MS** (EI, m/z): 386 (M^+). **HRMS** (EI): Calcd for $\text{C}_{14}\text{H}_{28}\text{F}_6\text{S}_3^+$ (M^+) 385.9687, found 385.9693. **IR** (film): 2927, 2852, 1571, 1476, 1391, 1119, 1088, 1013, 817, 756, 579, 504 cm^{-1} .



Mesityl(trifluoromethyl)sulfane (3e) The product (79.1 mg, 72% yield) was purified with silica gel chromatography (Petroleum ether) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.99 (s, 2H), 2.52 (s, 6H), 2.29 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -41.99 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 145.3, 141.4, 130.2 (q, $J = 309.3$ Hz), 129.6, 120.1 (q, $J = 1.7$ Hz), 22.1, 21.1.³

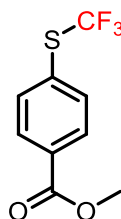


N-(4-((Trifluoromethyl)thio)phenyl)acetamide (3f) The product (88.0 mg, 75% yield) was purified with silica gel chromatography (PE:EA = 3:1) as a white solid. ^1H NMR (400 MHz, CD_3COCD_3) δ 9.47 (s, 1H), 7.79 (d, $J = 8.7$ Hz, 2H), 7.62 (d, $J = 8.7$ Hz, 2H), 2.10 (s, 3H). ^{19}F NMR (376 MHz, CD_3COCD_3) δ -44.66 (s, 3F). ^{13}C NMR (101 MHz, CD_3COCD_3) δ 168.6, 142.6, 137.3, 129.9 (q, $J = 307.0$ Hz), 119.8, 116.4 (q, $J = 2.2$ Hz), 23.5. All the characterization data are consistent with previous report.²

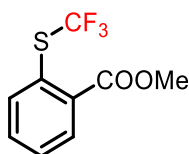


Methyl(4-((trifluoromethyl)thio)phenyl)sulfane (3g) The product (104.0 mg, 93% yield) was purified with silica gel chromatography (*n*-pentane) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 2.48 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -43.30 (s, 3F). ^{13}C NMR (101

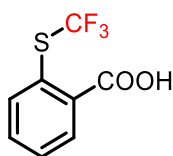
MHz, CDCl₃) δ 143.3, 136.7, 129.5 (q, J = 308.3 Hz), 126.3, 119.7 (q, J = 2.3 Hz), 15.0. All the characterization data are consistent with previous report.²



Methyl 4-((trifluoromethyl)thio)benzoate (3h) The product (107.7 mg, 91% yield) was purified with silica gel chromatography (PE:EA = 40:1) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 3.92 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -41.88 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 166.1, 135.6, 132.2, 130.4, 129.9, 129.3 (q, J = 309.1 Hz), 52.5. All the characterization data are consistent with previous report.⁴

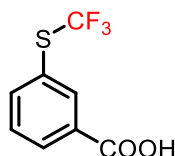


Methyl 2-((trifluoromethyl)thio)benzoate (3i) The product (91.3 mg, 77% yield) was purified with silica gel chromatography (PE:EA = 40:1) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 7.7 Hz, 1H), 7.73–7.71 (m, 1H), 7.54–7.50 (m, 1H), 7.44–7.40 (m, 1H), 3.92 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -41.41 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 166.7, 132.72, 132.69 (q, J = 2.4 Hz), 132.5, 130.9, 129.5 (q, J = 310.1 Hz), 128.7, 128.3 (q, J = 2.3 Hz), 52.6. All the characterization data are consistent with previous report.⁵

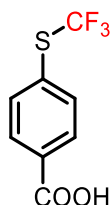


2-((Trifluoromethyl)thio)benzoic acid (3j) The product (63.4 mg, 57% yield) was purified with silica gel chromatography (PE:EA = 3:1) as a white solid. ¹H NMR

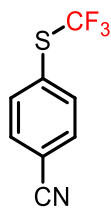
(400 MHz, CDCl₃) δ 8.11 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.59 (td, $J = 7.7, 1.7$ Hz, 1H), 7.46 (td, $J = 7.6, 1.2$ Hz, 1H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -41.23 (s, 3F). **¹³C NMR** (101 MHz, CDCl₃) δ 171.2, 133.50, 132.1, 132.0 (q, $J = 2.3$ Hz), 130.4, 130.0 (q, $J = 2.3$ Hz), 129.5 (q, $J = 310.1$ Hz), 128.44. All the characterization data are consistent with previous report.⁶



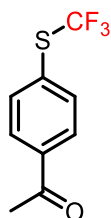
2-((Trifluoromethyl)thio)benzoic acid (3k) The product (90.2 mg, 81% yield) was purified with silica gel chromatography (PE:EA = 3:1) as a white solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.40 (s, 1H), 8.23 (d, $J = 7.8$ Hz, 1H), 7.90 (d, $J = 7.9$ Hz, 1H), 7.56 (t, $J = 7.8$ Hz, 1H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -42.46 (s, 3F). **¹³C NMR** (101 MHz, CDCl₃) δ 171.0, 141.3, 137.8, 132.5, 130.8, 129.8, 129.4 (q, $J = 310.7$ Hz), 125.4 (q, $J = 2.2$ Hz). All the characterization data are consistent with previous report.⁷



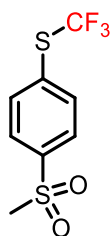
4-((Trifluoromethyl)thio)benzoic acid (3l) The product (90.1 mg, 81% yield) was purified with silica gel chromatography (PE:EA = 3:1) as a white solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.14 (d, $J = 8.4$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 2H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -41.65 (s, 3F). **¹³C NMR** (101 MHz, CDCl₃) δ 171.0, 135.5, 131.19, 131.16 (q, $J = 2.3$ Hz), 131.0, 129.3 (q, $J = 308.5$ Hz). All the characterization data are consistent with previous report.²



4-((Trifluoromethyl)thio)benzonitrile (3m) The product (90.1 mg, 81% yield) was purified with silica gel chromatography (PE:EA = 3:1) as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (d, $J = 8.1$ Hz, 2H), 7.70 (d, $J = 8.6$ Hz, 2H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -41.56 (s, 3F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 136.0, 132.9, 130.5, 129.0 (q, $J = 309.9$ Hz), 117.6, 114.6. All the characterization data are consistent with previous report.²

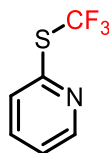


1-(4-((Trifluoromethyl)thio)phenyl)ethan-1-one (3n) The product (76.3 mg, 69% yield) was purified with silica gel chromatography (PE:EA = 40:1) as a colorless liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.3$ Hz, 2H), 7.73 (d, $J = 8.1$ Hz, 2H), 2.61 (s, 3H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -41.80 (s, 3F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 197.0, 138.5, 135.7, 130.8, 129.3 (q, $J = 309.4$ Hz), 129.1, 26.7. All the characterization data are consistent with previous report.⁴

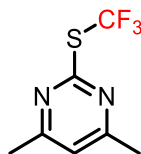


(4-(Methylsulfonyl)phenyl)(trifluoromethyl)sulfane (3o) The product (123.5 mg, 96% yield) was purified with silica gel chromatography (PE:EA = 4:1) as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, $J = 7.9$ Hz, 2H), 7.81 (d, $J = 8.2$ Hz,

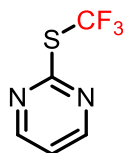
2H), 3.06 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -41.47 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 142.7, 136.2, 131.4 (q, $J = 2.3$ Hz), 129.1 (q, $J = 309.1$ Hz), 128.3, 44.3. All the characterization data are consistent with previous report.⁸



2-((Trifluoromethyl)thio)pyridine (3p) The product (72.4 mg, 81% yield) was purified with silica gel chromatography (*n*-pentane:Et₂O = 20:1) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.61–8.59 (m, 1H), 7.71 (td, $J = 7.7, 1.9$ Hz, 1H), 7.57 (d, $J = 7.9$ Hz, 1H), 7.30 (ddd, $J = 7.6, 4.8, 1.1$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -40.22 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 150.7, 149.5 (q, $J = 2.8$ Hz), 137.7, 129.4 (q, $J = 309.1$ Hz), 128.2 (q, $J = 1.9$ Hz), 123.80. All the characterization data are consistent with previous report.⁶

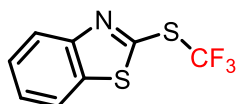


4,6-Dimethyl-2-((trifluoromethyl)thio)pyrimidine (3q) The product (89.3 mg, 86% yield) was purified with silica gel chromatography (PE:EA = 30:1) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 6.84 (s, 1H), 2.42 (s, 6H). ^{19}F NMR (376 MHz, CDCl_3) δ -40.85 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 168.2, 164.5 (q, $J = 3.1$ Hz), 128.4 (q, $J = 307.5$ Hz), 118.1, 23.8. All the characterization data are consistent with previous report.⁹

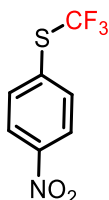


2-((Trifluoromethyl)thio)pyrimidine (3r) The product (83.1 mg, 92% yield) was purified with silica gel chromatography (*n*-pentane:Et₂O = 20:1) as a colorless

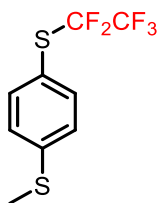
liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.62 (d, $J = 4.9$ Hz, 2H), 7.16 (t, $J = 4.9$ Hz, 1H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -41.10 (s, 3F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.9 (q, $J = 3.2$ Hz), 158.0, 128.3 (q, $J = 307.8$ Hz), 119.0. All the characterization data are consistent with previous report.²



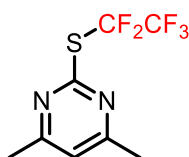
2-((Trifluoromethyl)thio)benzo[d]thiazole (3s) The product (88.3 mg, 75% yield) was purified with silica gel chromatography (PE) as a colorless liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.11 (dd, $J = 8.1, 1.0$ Hz, 1H), 7.85 (d, $J = 1.3$ Hz, 1H), 7.53 (ddd, $J = 8.3, 7.2, 1.3$ Hz, 1H), 7.46 (ddd, $J = 8.2, 7.2, 1.3$ Hz, 1H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -40.22 (s, 3F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.1, 151.7 (q, $J = 3.0$ Hz), 137.9, 128.2 (q, $J = 312.1$ Hz), 127.0, 126.7, 124.1, 121.3. All the characterization data are consistent with previous report.²



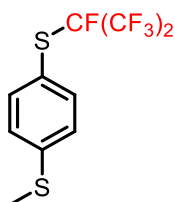
(4-Nitrophenyl)(trifluoromethyl)sulfane (3t) The product (40.0 mg, 36% yield) was purified with silica gel chromatography (PE) as a light yellow solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.26 (d, $J = 8.8$ Hz, 2H), 7.81 (d, $J = 8.7$ Hz, 2H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -41.39 (s, 3F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.2, 136.1, 132.6 (q, $J = 2.4$ Hz), 129.0 (q, $J = 308.8$ Hz), 124.4. All the characterization data are consistent with previous report.²



Methyl(4-((perfluoroethyl)thio)phenyl)sulfane (3u) The product (132.7 mg, 97% yield) was purified with silica gel chromatography (Petroleum ether) as a colorless liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 (d, $J = 8.5$ Hz, 2H), 7.23 (d, $J = 8.5$ Hz, 2H), 2.48 (s, 3H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -82.50 (t, $J = 3.5$ Hz, 3F), -92.31 (q, $J = 3.7$ Hz, 2F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.7, 137.4, 126.2, 123.1–119.4 (m), 118.0 (t, $J = 3.1$ Hz), 117.7–114.1 (m), 14.9. All the characterization data are consistent with previous report.¹⁰

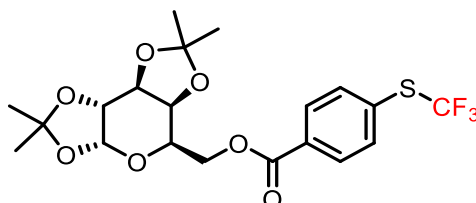


4,6-Dimethyl-2-((perfluoroethyl)thio)pyrimidine (3v) The product (84.1 mg, 65% yield) was purified with silica gel chromatography (PE:EA = 50:1) as a colorless liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.88 (s, 1H), 2.43 (s, 6H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -82.86 (t, $J = 3.3$ Hz, 3F), -92.73 (q, $J = 3.5$ Hz, 2F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.3, 163.6, 123.5–119.6 (m), 118.6, 117.7–113.9 (m), 23.8. All the characterization data are consistent with previous report.⁹



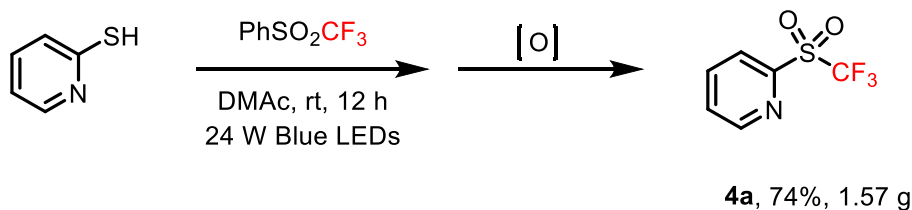
Methyl(4-((perfluoropropan-2-yl)thio)phenyl)sulfane (3w) The product (82.8 mg, 51% yield) was purified with silica gel chromatography (Petroleum ether) as a colorless liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 2.48 (s, 3H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -73.86 (d, $J = 11.4$ Hz, 6F), -157.58 (hept, $J = 11.2$ Hz, 1F). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.9, 137.7, 126.1, 120.3 (qd, $J = 287.8$ Hz, 30.2 Hz), 118.1, 99.6–96.5 (m), 14.9. **MS** (EI, m/z): 324 (M^+). **HRMS** (EI): Calcd for $\text{C}_{11}\text{H}_7\text{F}_7\text{S}_2^+$ (M^+) 323.9872, found 323.9871. **IR** (film): 2925, 2848, 1578, 1478, 1284, 1223, 1187, 1105, 1074, 1013, 960, 941, 813, 754, 716, 509

cm⁻¹.



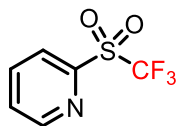
((3aR,5R,5aS,8aS,8bR)-2,2,7,7-Tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-((trifluoromethyl)thio)benzoate (3x) The product (210.8 mg, 91% yield) was purified with silica gel chromatography (PE:EA = 10:1) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 5.54 (d, *J* = 4.9 Hz, 1H), 4.63 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.51 (dd, *J* = 11.6, 4.6 Hz, 1H), 4.42 (dd, *J* = 11.6, 7.7 Hz, 1H), 4.33 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.29 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.15 (ddd, *J* = 7.0, 4.7, 1.9 Hz, 1H), 1.48 (s, 3H), 1.44 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -41.88 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 165.4, 135.5, 132.1, 130.5, 129.9 (q, *J* = 2.3 Hz), 129.3 (q, *J* = 309.5 Hz), 109.7, 108.8, 96.3, 71.1, 70.7, 70.5, 66.0, 64.4, 25.99, 25.95, 24.9, 24.5. MS (ESI, m/z): 465.0 (M+H⁺). HRMS (ESI): Calcd for C₂₀H₂₄F₃O₇S⁺ (M+H⁺) 465.1189, found 465.1184. IR (film): 2989, 2936, 1727, 1399, 1383, 1273, 1212, 1165, 1116, 1071, 1008, 919, 898, 857, 764, 693, 511 cm⁻¹.

5. Preparation of Trifluoromethyl-heteroaryl Sulfones



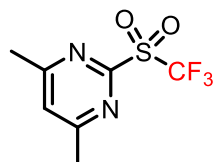
Typical procedures

Under dry N₂ atmosphere, to sealed tube were added **pyridine-2-thiol** (10.0 mmol, 1.11 g, 1.0 equiv), **2a** (11.0 mmol, 2.31 g, 1.1 equiv), Cs₂CO₃ (20.0 mmol, 6.5 g, 2.0 equiv), dry DMAc (50.0 mL). The mixture was irradiated by a 24 W blue LED for 12 h. After the completion of the reaction, the mixture was quenched by saturated NH₄Cl solution, then the mixture was extracted with Et₂O for 3 times. The organic phase was combined and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to give a brown liquid. To a 100 mL, three-neck flask were added the above obtained brown liquid, and NaIO₄ (25.0 mmol, 5.33 g, 2.5 equiv), RuCl₃ · xH₂O (1.0 mg), CCl₄ (10.0 mL), CH₃CN (10.0 mL) and H₂O (20.0 mL) were added, The mixture was stirred at room temperature overnight. After the completion of the reaction, the mixture was extracted with dichloromethane (DCM) for 3 times. Then the organic phase was combined and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel by using a 10:1 mixture of PE/ethyl acetate (EA) as an eluent to provide **4a** as white solid (1.57 g, 74%).

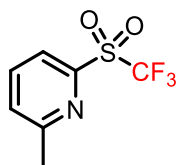


2-((Trifluoromethyl)sulfonyl)pyridine (4a) The product (1.57 g, 74% yield) was purified with silica gel chromatography (PE:EA = 10:1) as white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.85 (d, *J* = 4.8 Hz, 1H), 8.29 – 8.16 (m, 1H), 8.08 (td, *J* = 7.8, 1.7 Hz, 1H), 7.73 (ddd, *J* = 7.8, 4.7, 1.3 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -75.83 (s,

3F). ^{13}C NMR (101 MHz, CDCl_3) δ 151.4, 151.1, 138.8, 129.7, 126.3, 119.8 (q, $J = 327.6$ Hz). All the characterization data are consistent with previous report.¹¹



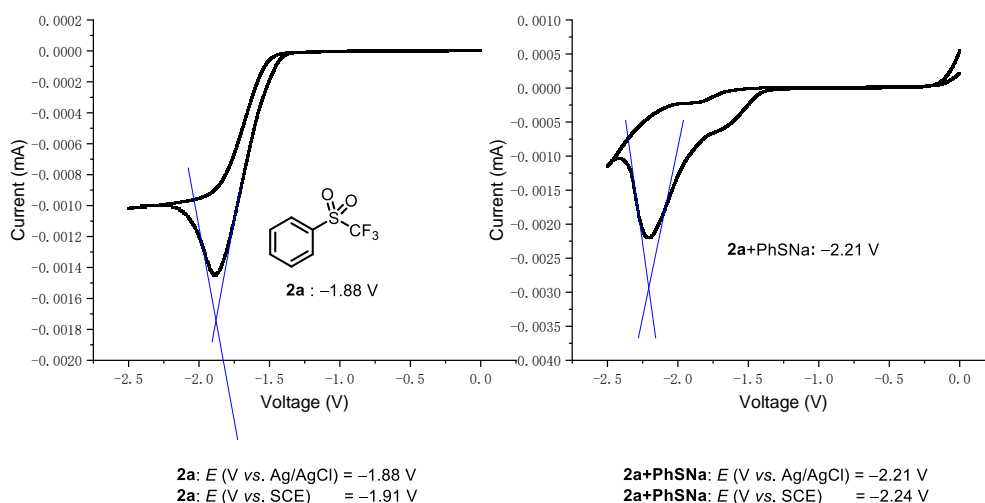
4,6-Dimethyl-2-((trifluoromethyl)sulfonyl)pyrimidine (4b) The product (1.96 g, 82% yield) was purified with silica gel chromatography (PE:EA = 3:1) as white solid. Mp: 38 – 39 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.35 (s, 1H), 2.63 (s, 6H). ^{19}F NMR (376 MHz, CDCl_3) δ – 73.69 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 170.2, 161.0, 124.7, 119.9 (q, $J = 327.9$ Hz), 23.9. MS (DART, m/z): 241.0 ($\text{M}+\text{H}^+$). HRMS (DART): Calcd for $\text{C}_7\text{H}_8\text{F}_3\text{N}_2\text{O}_2\text{S}^+$ ($\text{M}+\text{H}^+$) 241.0253, found 241.0252. IR (film): 2936, 1597, 1510, 1436, 1371, 1205, 1114, 633, 608, 563, 521 cm^{-1} .

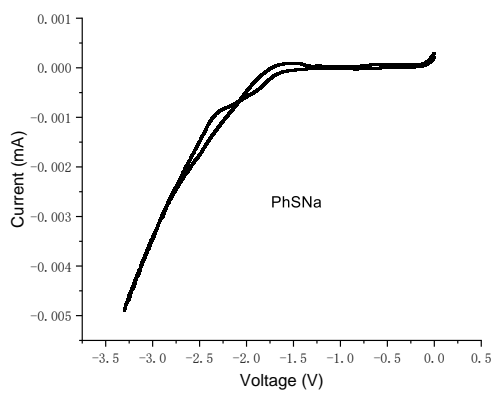


2-Methyl-6-((trifluoromethyl)sulfonyl)pyridine (4c) The product (1.34 g, 74% yield) was purified with silica gel chromatography (PE:EA = 10:1) as white solid. Mp: 70 – 71 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 7.7$ Hz, 1H), 7.93 (t, $J = 7.8$ Hz, 1H), 7.56 (d, $J = 7.8$ Hz, 1H), 2.67 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ –75.75 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 161.6, 150.4 (q, $J = 2.0$ Hz), 138.5, 129.1, 123.4, 119.8 (q, $J = 327.8$ Hz), 24.2. MS (FI, m/z): 225 (M^+). HRMS (DART): Calcd for $\text{C}_7\text{H}_8\text{F}_3\text{NO}_2\text{S}^+$ (M^+) 225.0066, found 225.0072. IR (film): 3114, 3061, 2919, 1593, 1456, 1367, 1254, 1215, 1173, 1147, 1102, 985, 911, 867, 975, 762, 618, 589, 546, 524, 511 cm^{-1} .

6. Cyclic Voltammetry Study

The cyclic voltammetry measurements were performed on an EG & G-Princeton Applied Research CHI660E A18407 electrochemical workstation, using a standard three-electrode setup with two platinum wire electrode (a working electrode and a counter electrode) and a Ag/AgCl (3 M KCl) system in anhydrous CH₃CN as the reference electrode. All solutions of the compounds under the study were in the supporting electrolyte *n*-Bu₄NPF₆ (0.2 M) with the voltage scan rate of 0.05 V s⁻¹. Solutions (5 mL) were thoroughly bubbled with dry nitrogen for 15 min to remove oxygen before any experiment and kept under positive pressure of nitrogen. Under these experimental conditions, the [FeCp₂]/[FeCp₂]⁺ couple was located at $E_{1/2} = +0.42$ V in CH₃CN. The first reduction potentials of fluoroalkyl sulfones: cathodic peak potential *vs.* SCE (the saturated calomel electrode). E (V *vs.* SCE) = E (V *vs.* Ag/AgCl) - 0.03 V (potentials for reference electrode: Ag/AgCl (3 M KCl): +0.21 V, SCE: +0.24 V)

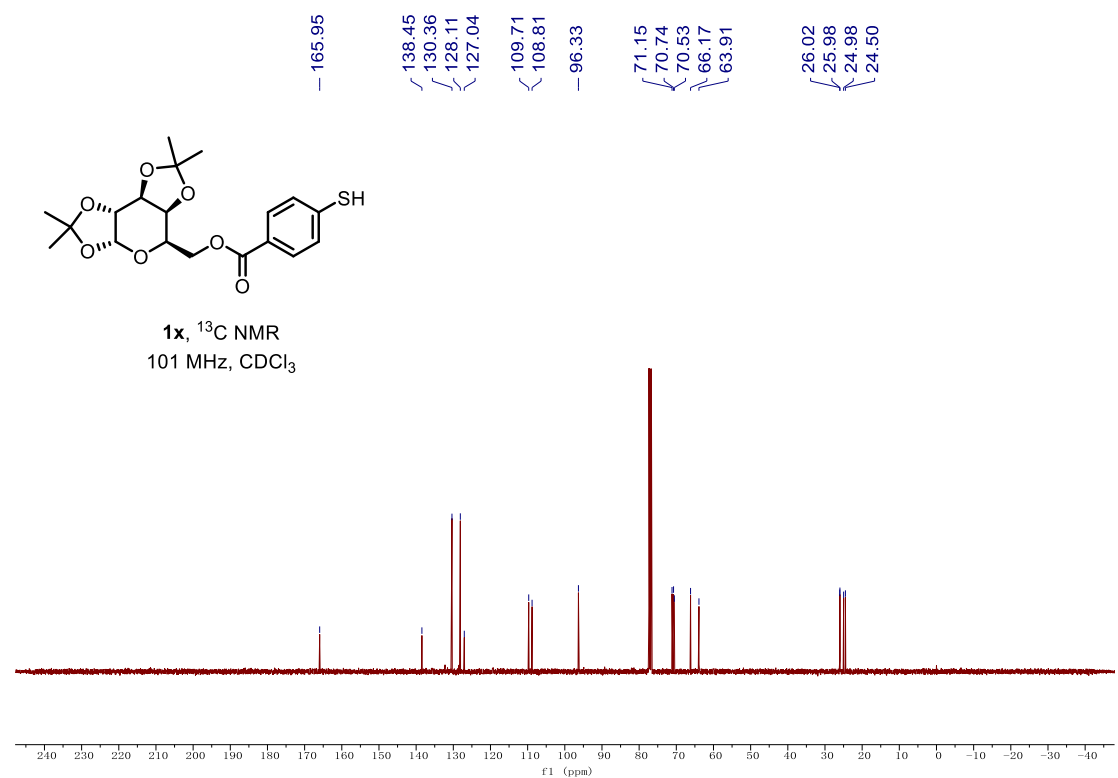
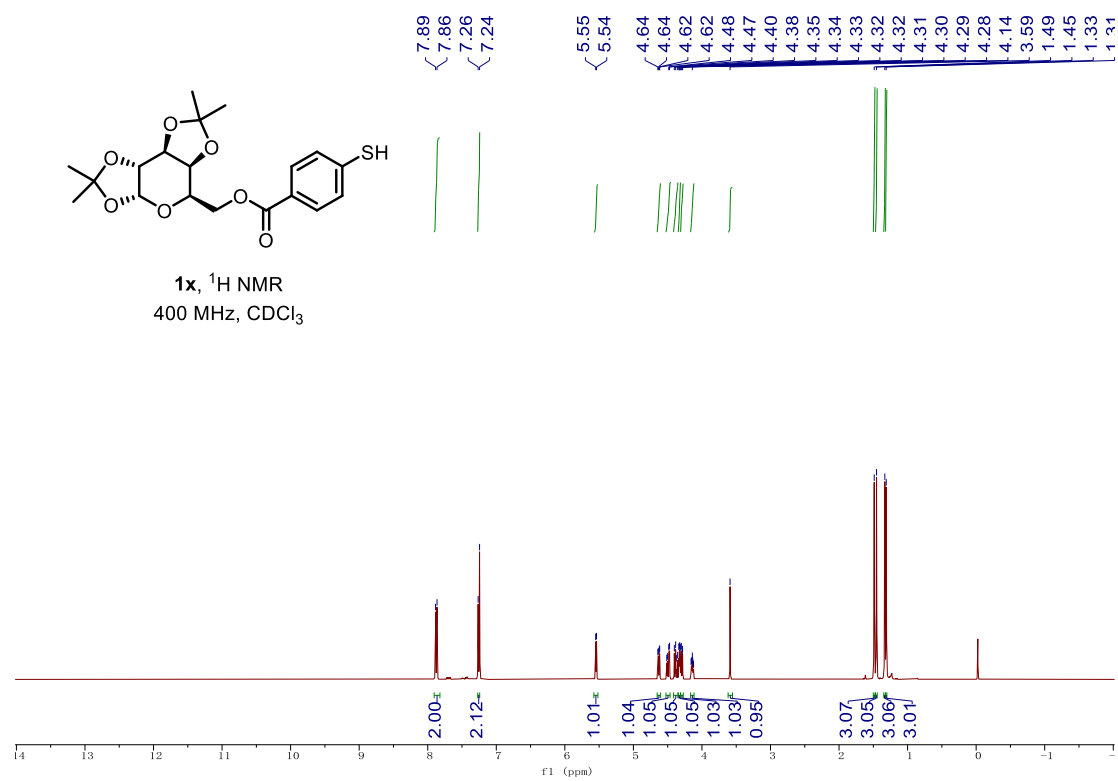


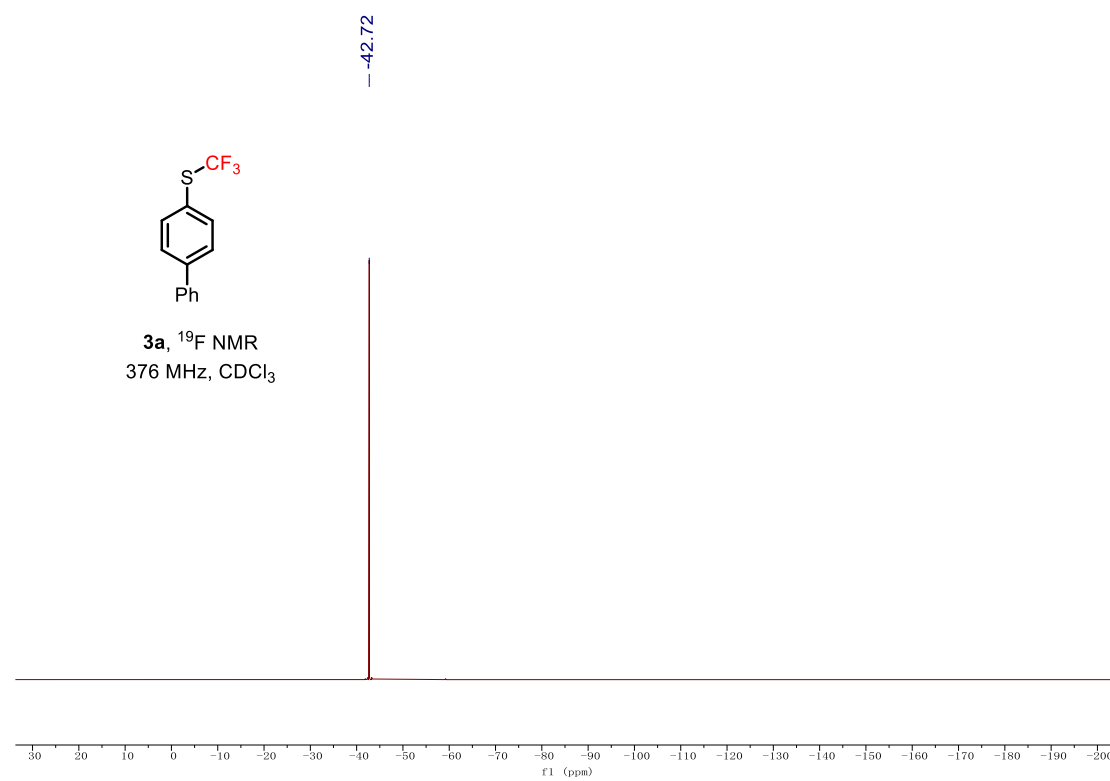
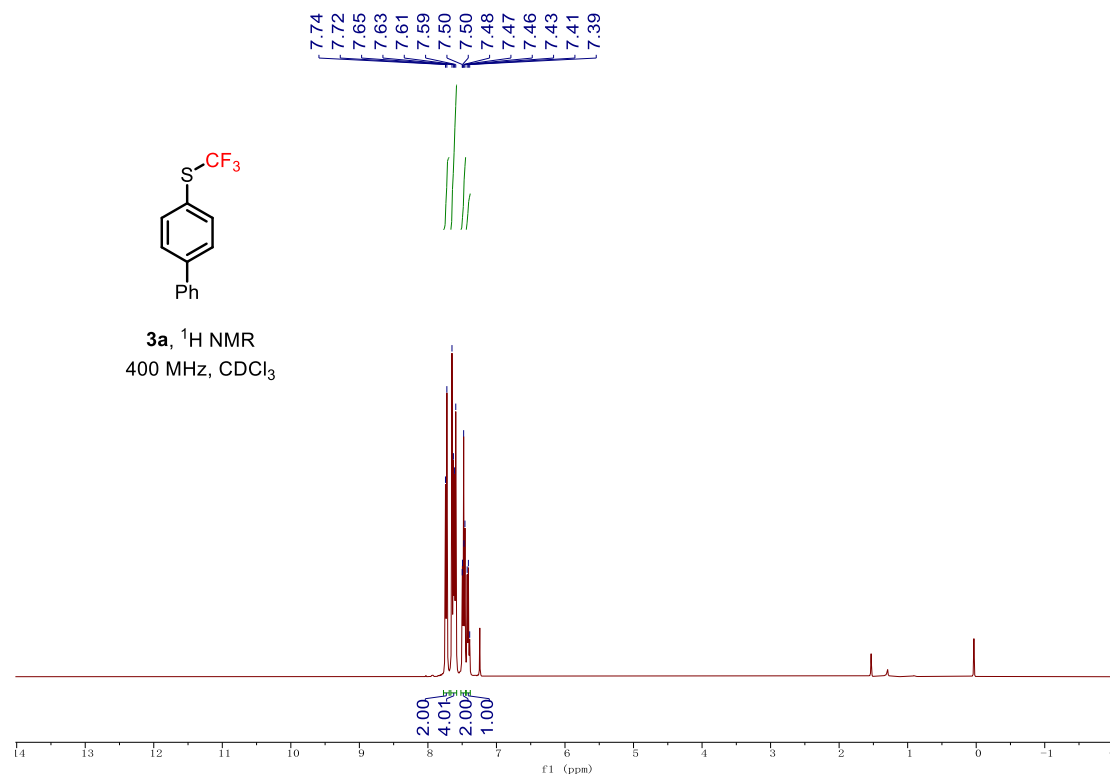


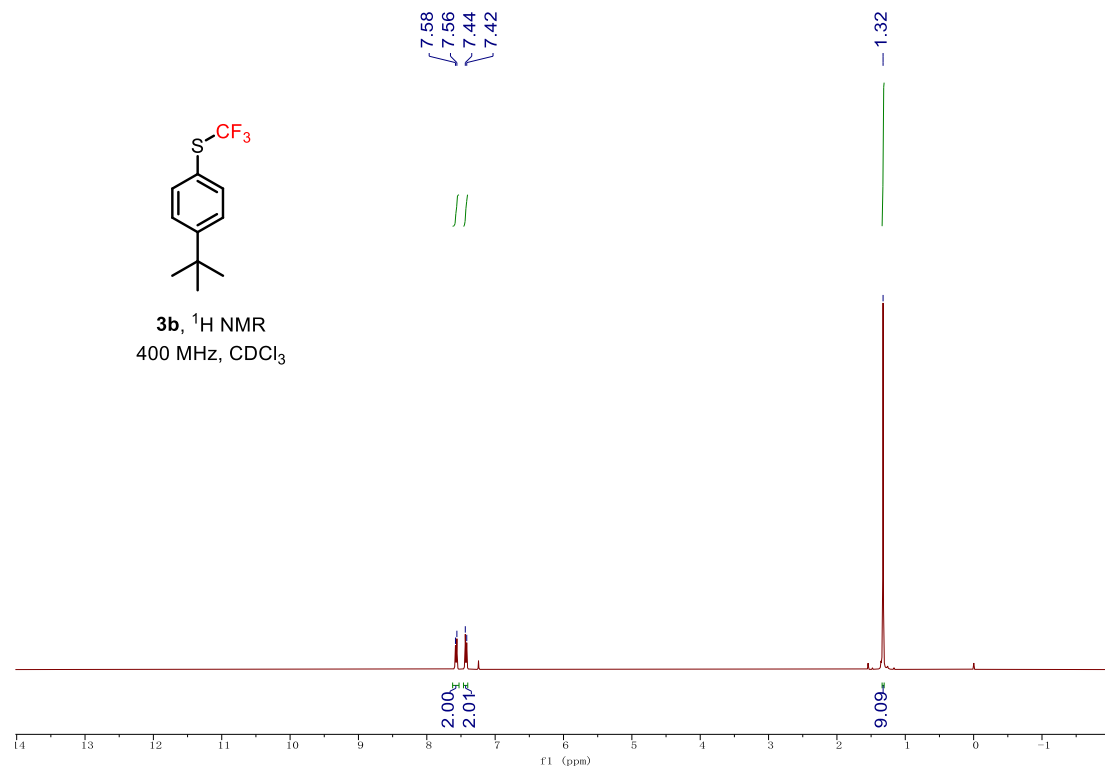
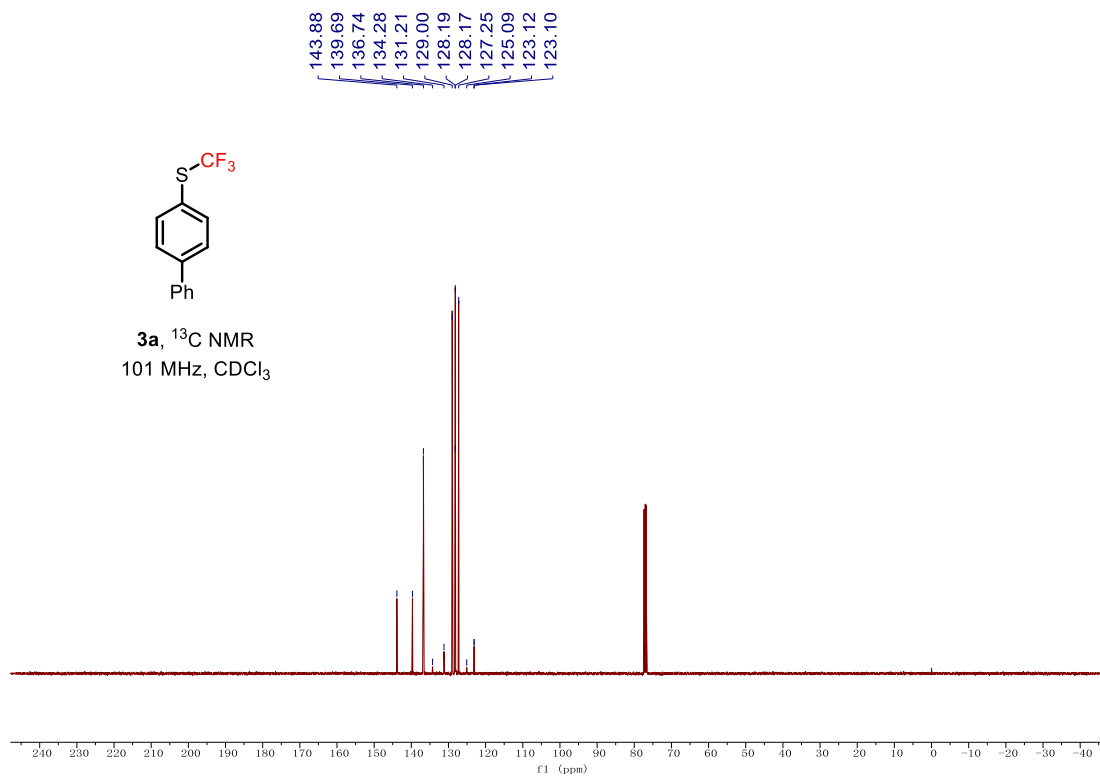
7. References

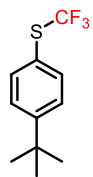
- (1) Y. Jiang, Y. Qin, S. Xie, X. Zhang, J. Dong, D. Ma, *Org. Lett.* **2009**, *11*, 22.
- (2) N. J. W. Straathof, B. J. P. Tegelbeckers, V. Hessel, X. Wang, T. Noel, *Chem. Sci.* **2014**, *5*, 4768.
- (3) M. Horvat, M. Jereb, J. Iskra, *Eur. J. Org. Chem.* **2018**, 3837.
- (4) X. Xiao, X. Wang, T. Yang, L. Lu, Q. Shen, *Angew. Chem. Int. Ed.* **2013**, *52*, 3457.
- (5) W. Zhong, X. Liu, *Tetrahedron Letters* **2014**, *55*, 4909.
- (6) J. Ma, W. Yi, G. Lu, C. Cai, *Catal. Sci. Technol.* **2016**, *6*, 417.
- (7) G. Danoun, B. Bayarmagnai, M. F. Gruenberg, L. Goossen, *Chem. Sci.* **2014**, *5*, 1312.
- (8) C. Chen, Y. Xie, L. Chu, R. Wang, X. Zhang, F. Qing, *Angew. Chem. Int. Ed.* **2012**, *51*, 2492.
- (9) Sipyagin, Enshov, *Chemistry of Heterocyclic Compounds*, **2003**, *39*, 1172.
- (10) J. Xiang, X. Xu, F. Qing, *Journal of Fluorine Chemistry* **2017**, *203*, 110.
- (11) J. Rong, L. Deng, P. Tan, C. Ni, Y. Gu, J. Hu, *Angew. Chem. Int. Ed.* **2016**, *55*, 2743.

8. ^1H , ^{19}F and ^{13}C NMR Spectra of Isolated Compounds

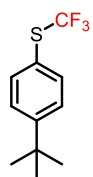
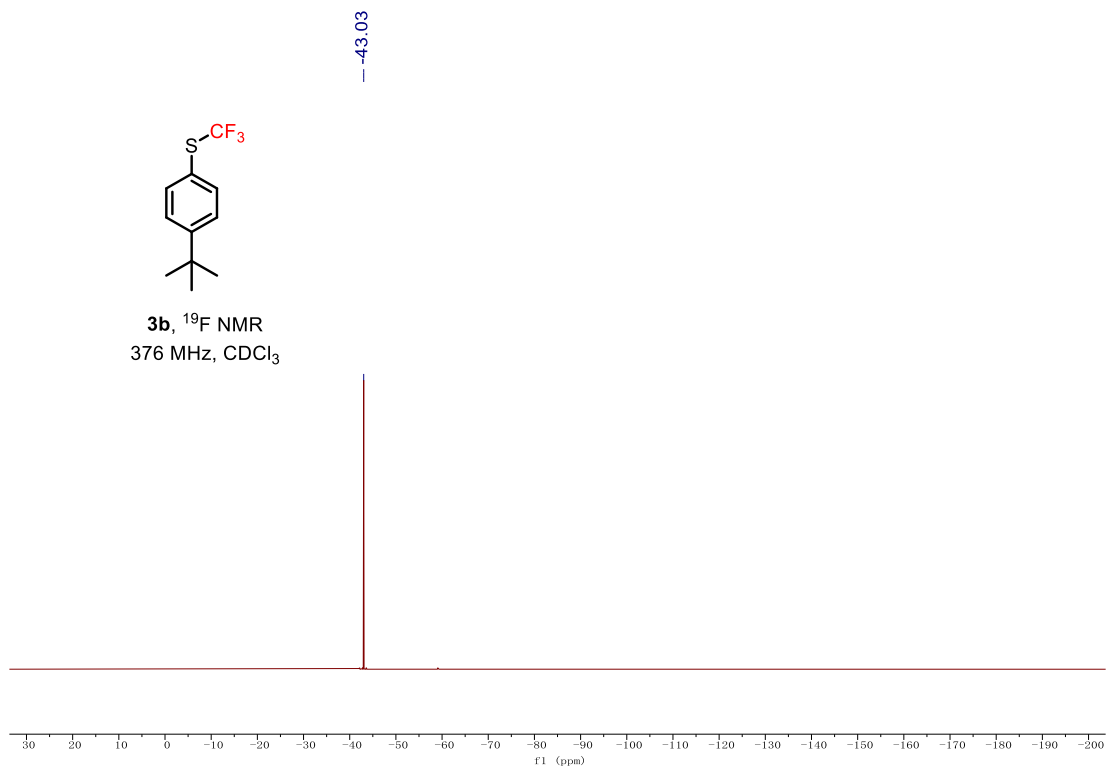




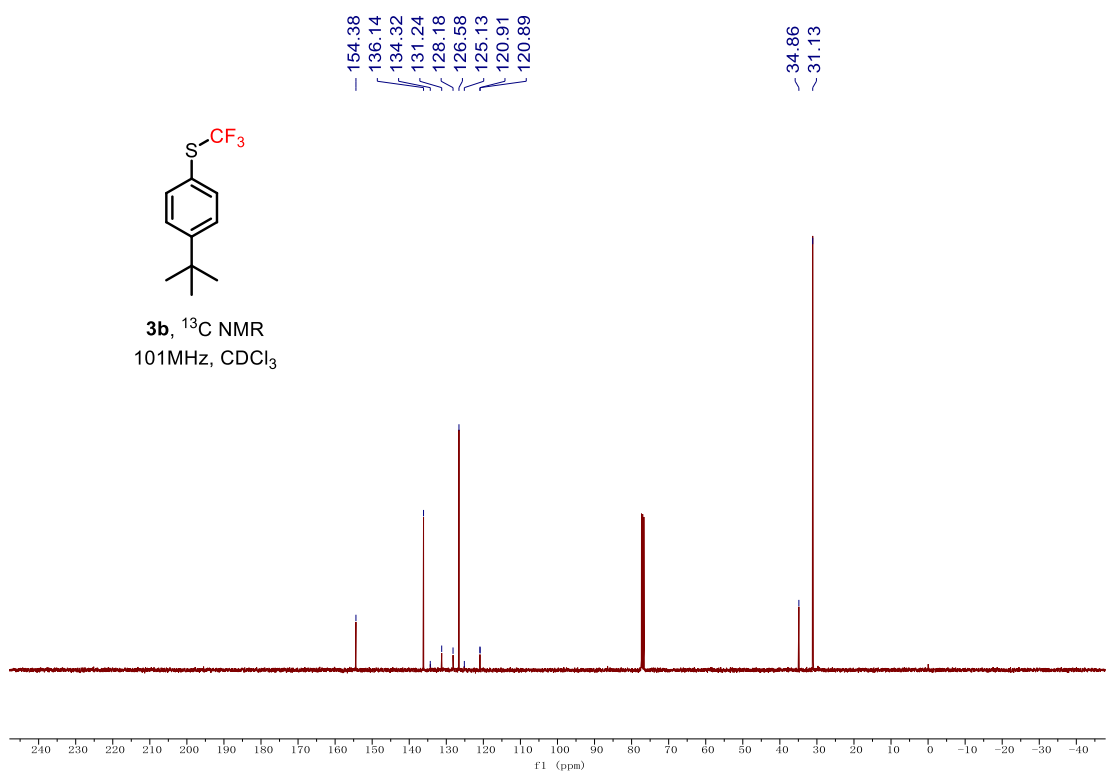


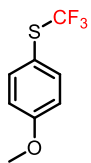


3b, ^{19}F NMR
376 MHz, CDCl_3

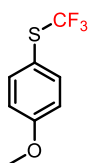
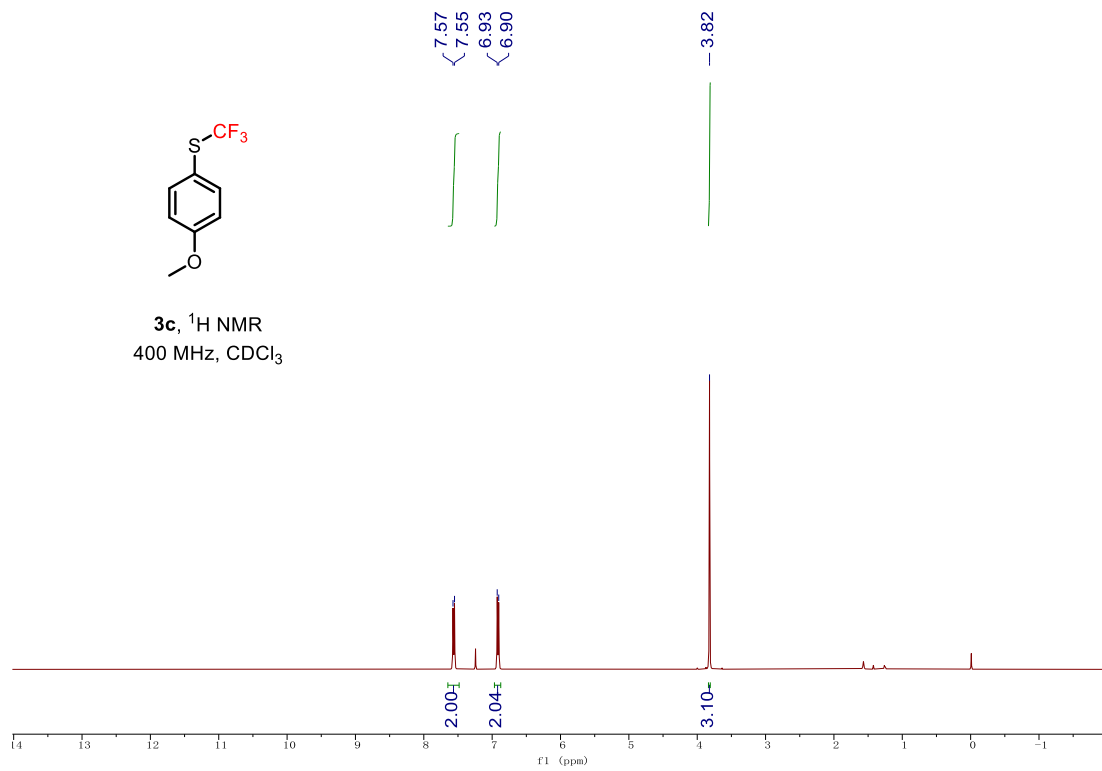


3b, ^{13}C NMR
101 MHz, CDCl_3

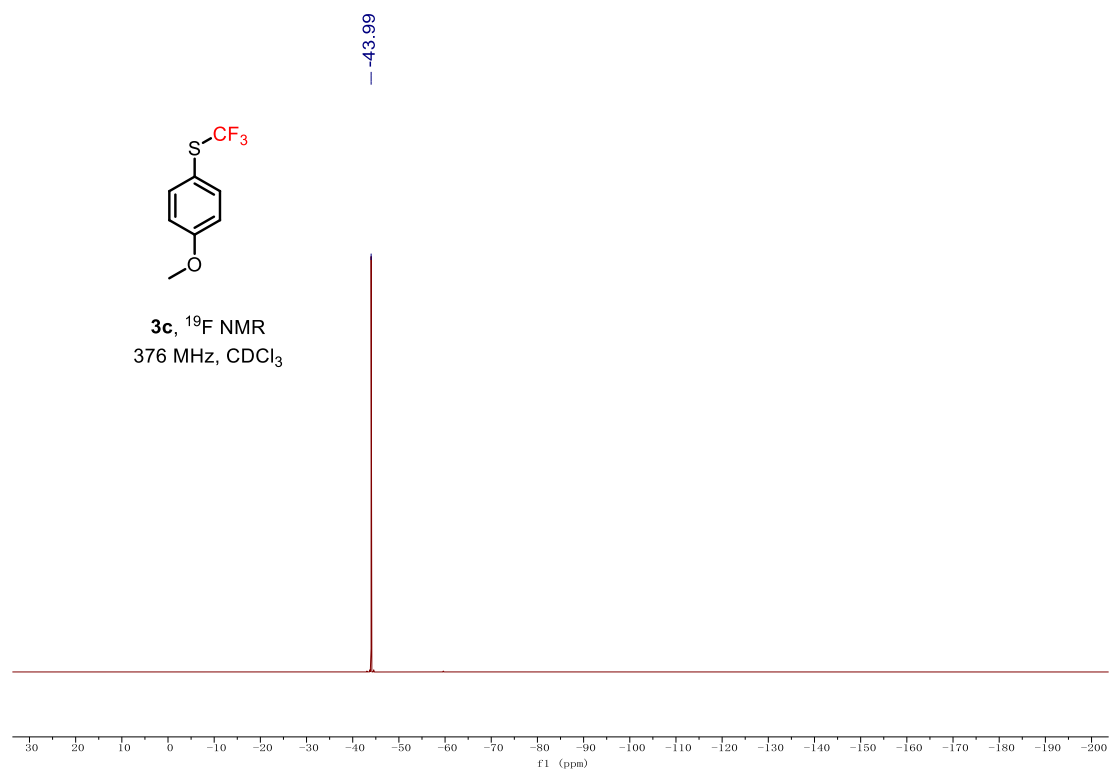


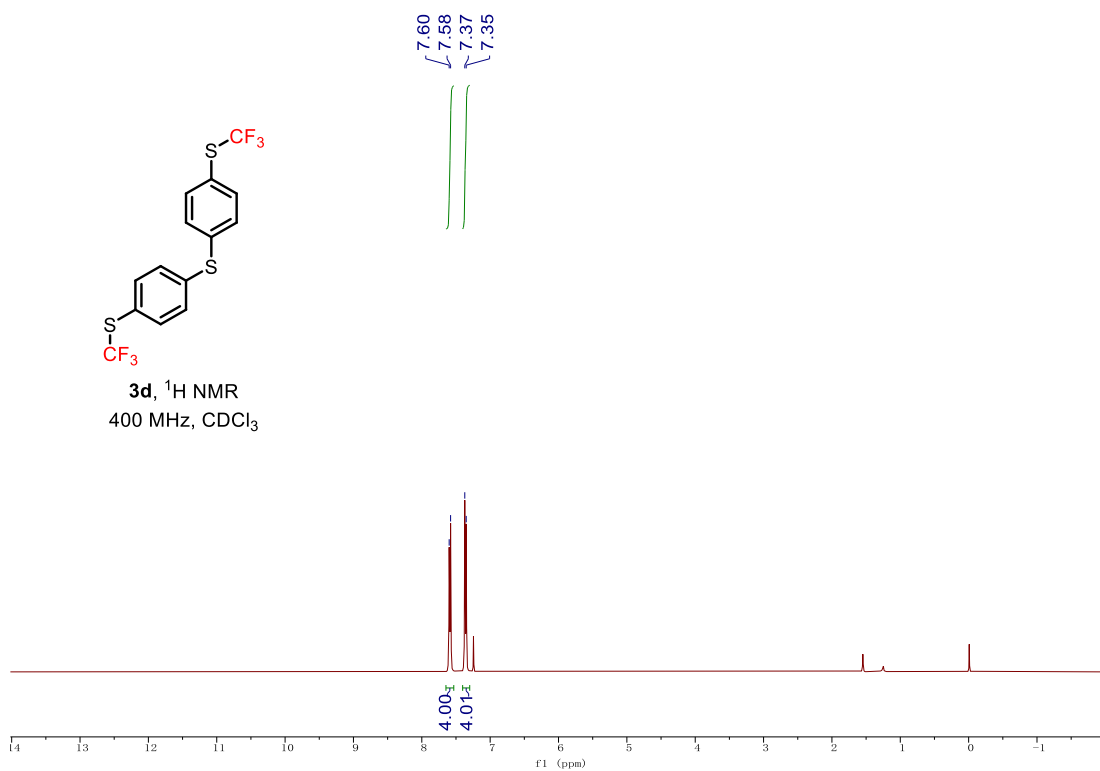
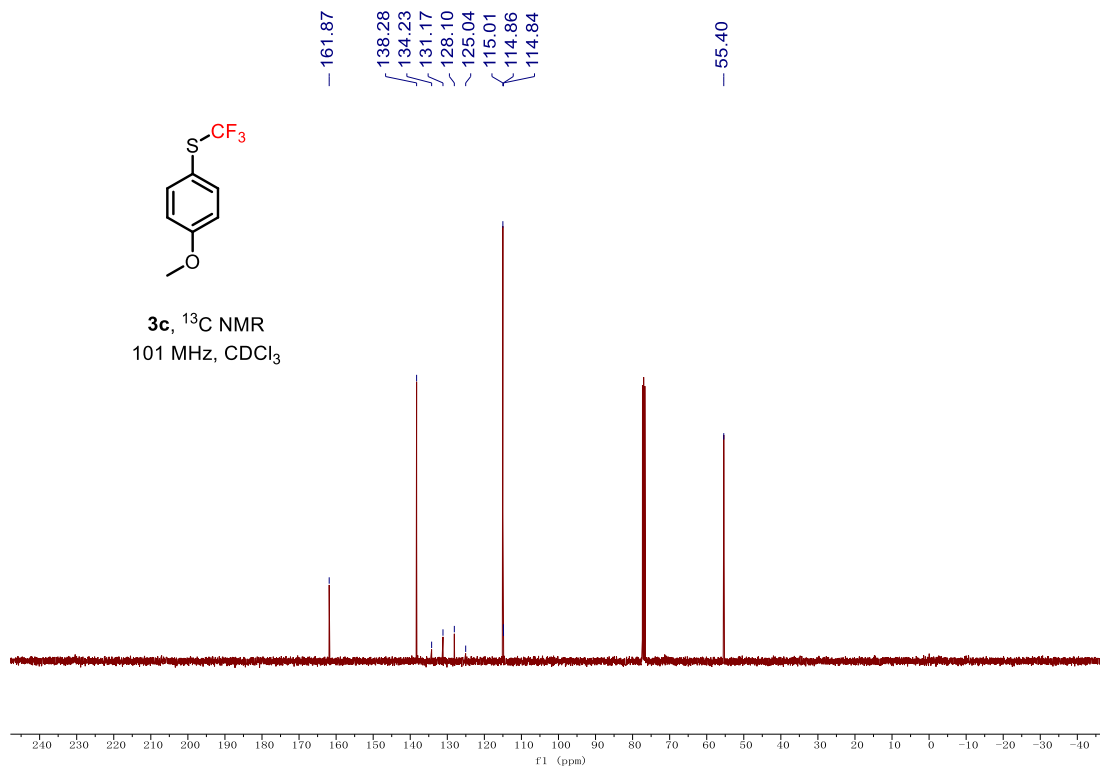


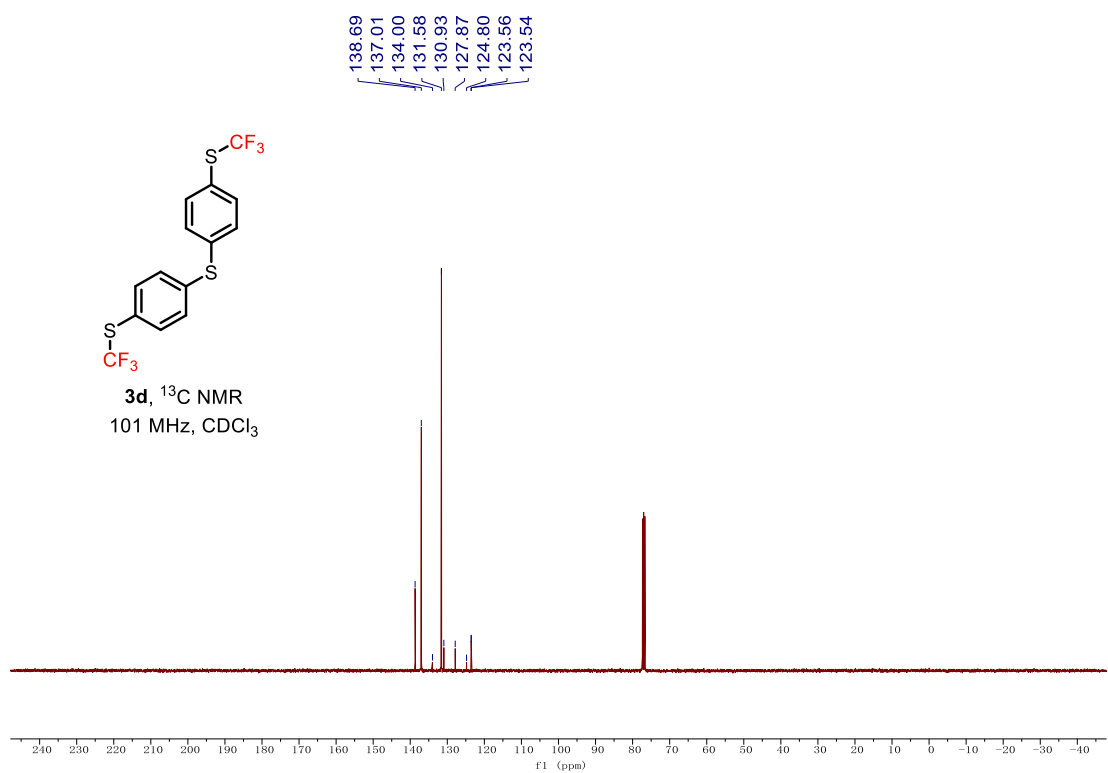
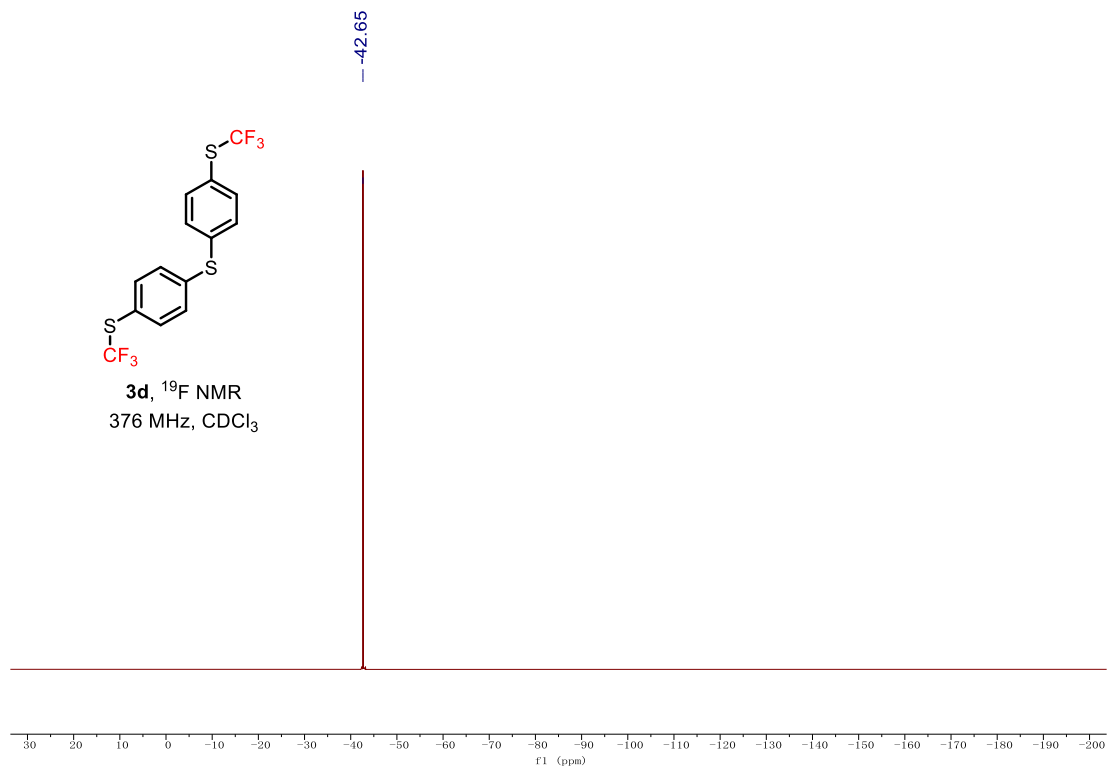
3c, ^1H NMR
400 MHz, CDCl_3



3c, ^{19}F NMR
376 MHz, CDCl_3

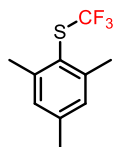
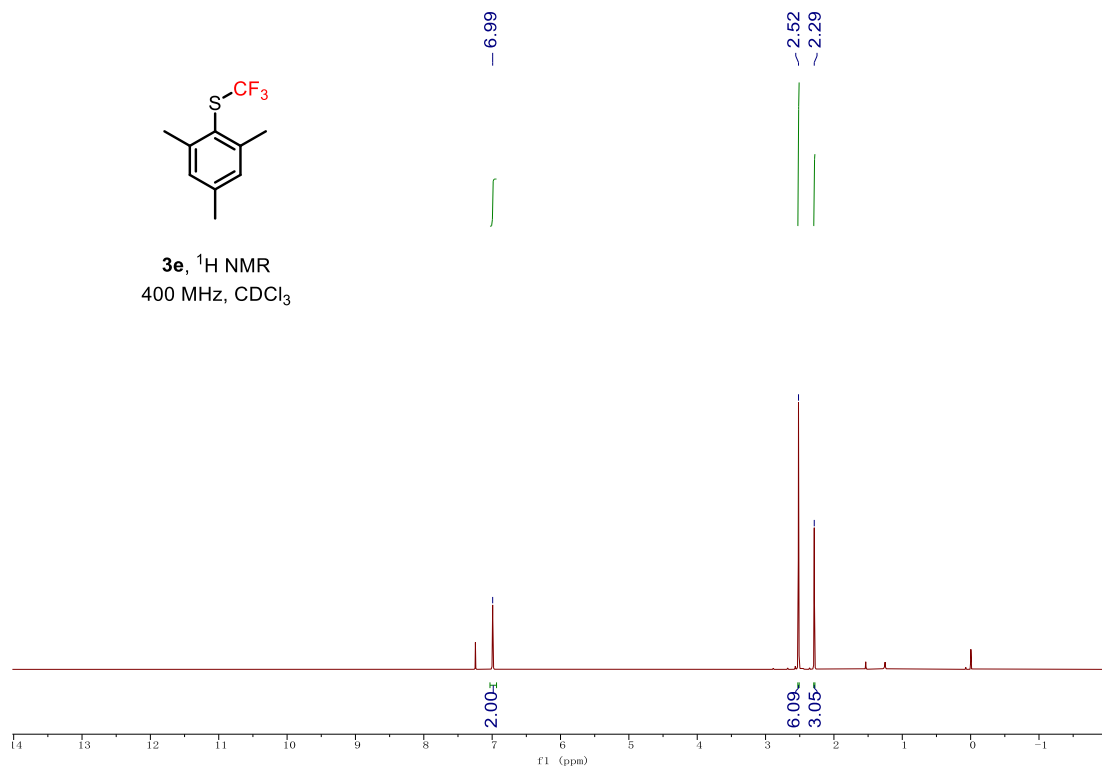




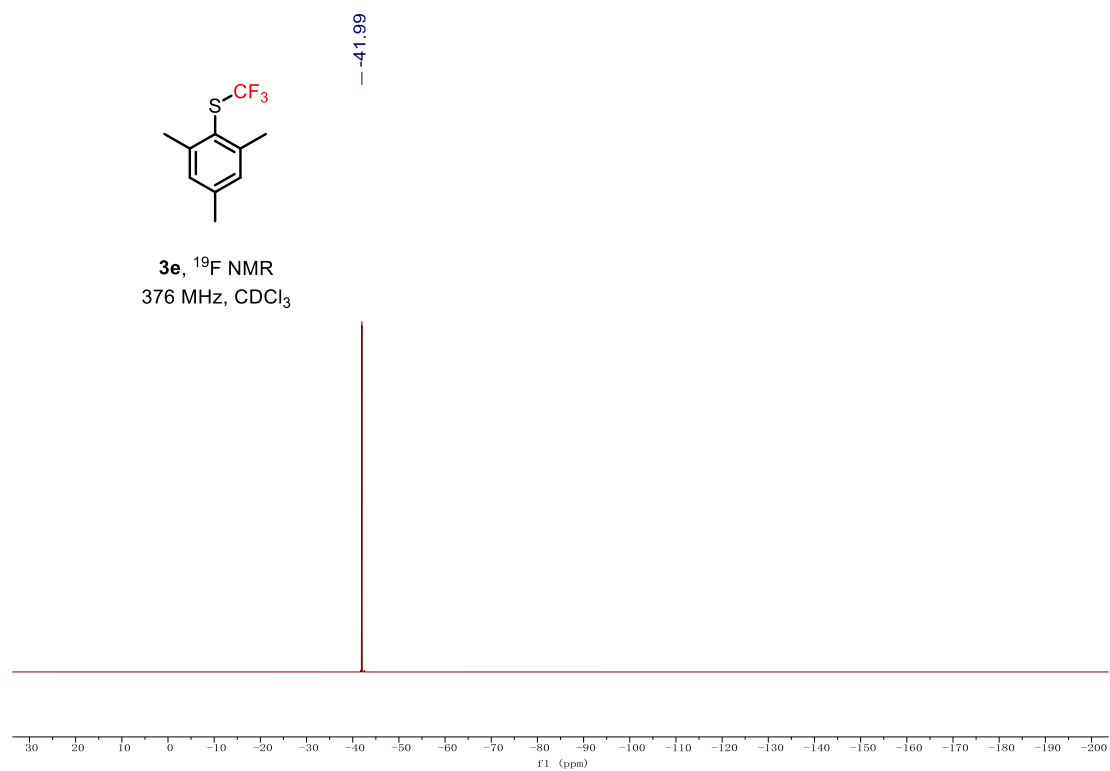


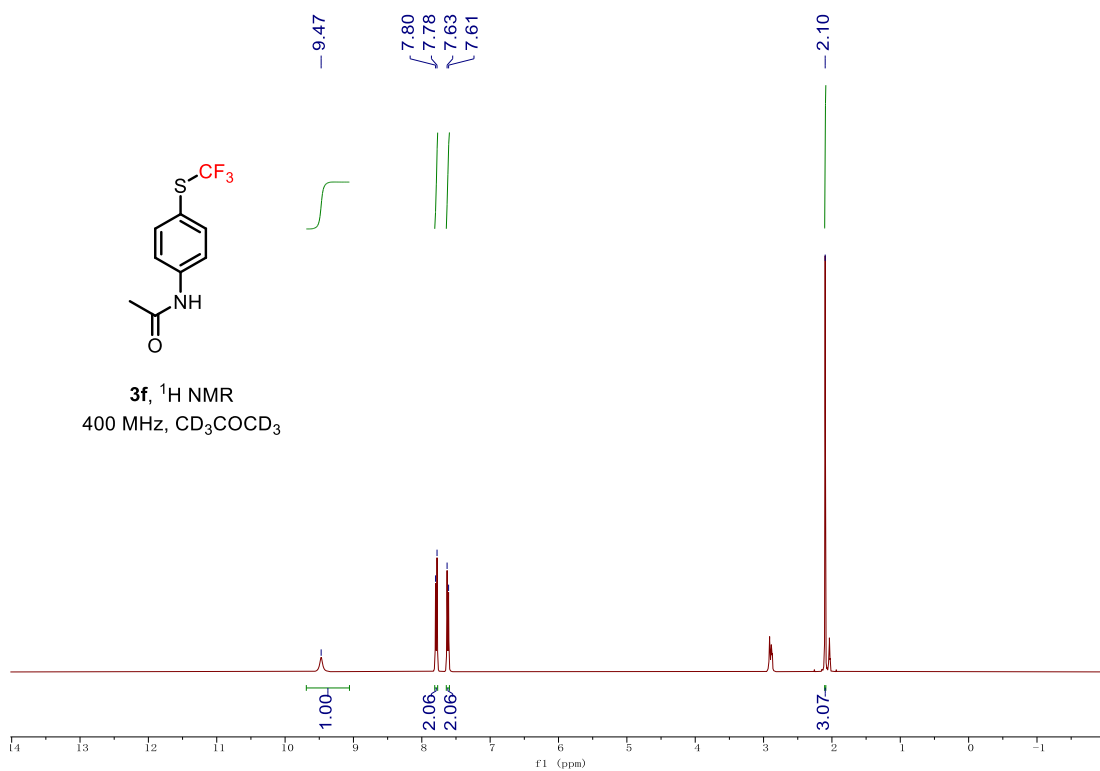
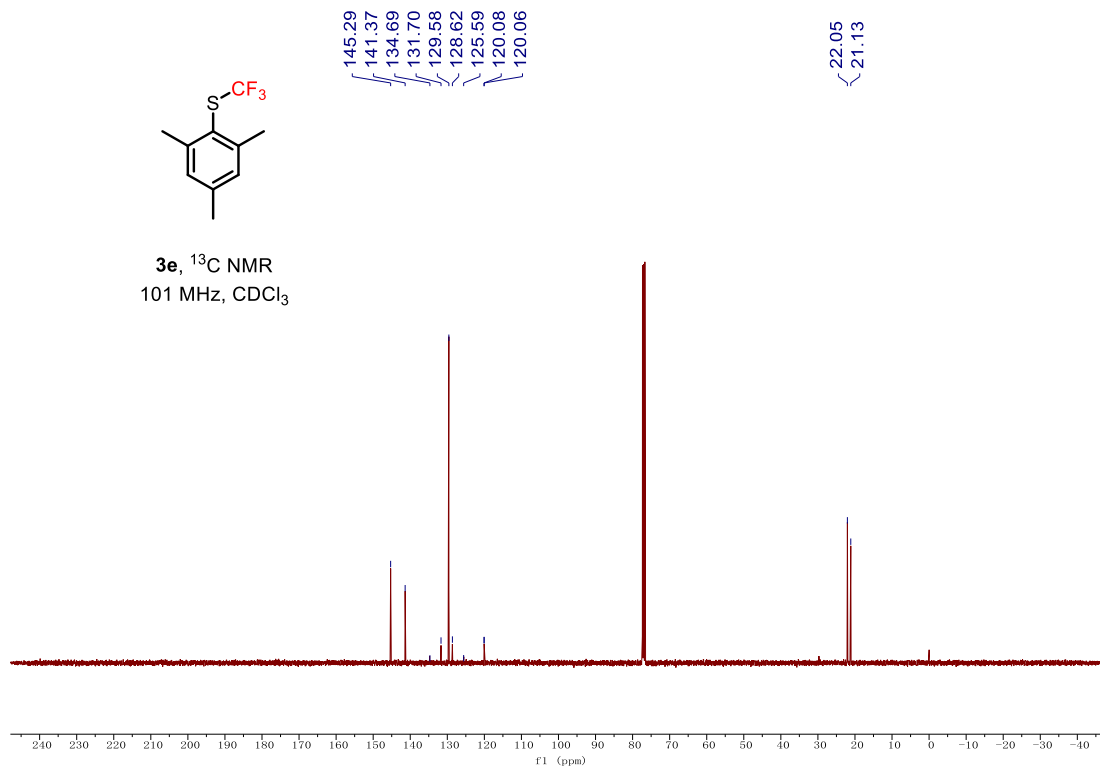


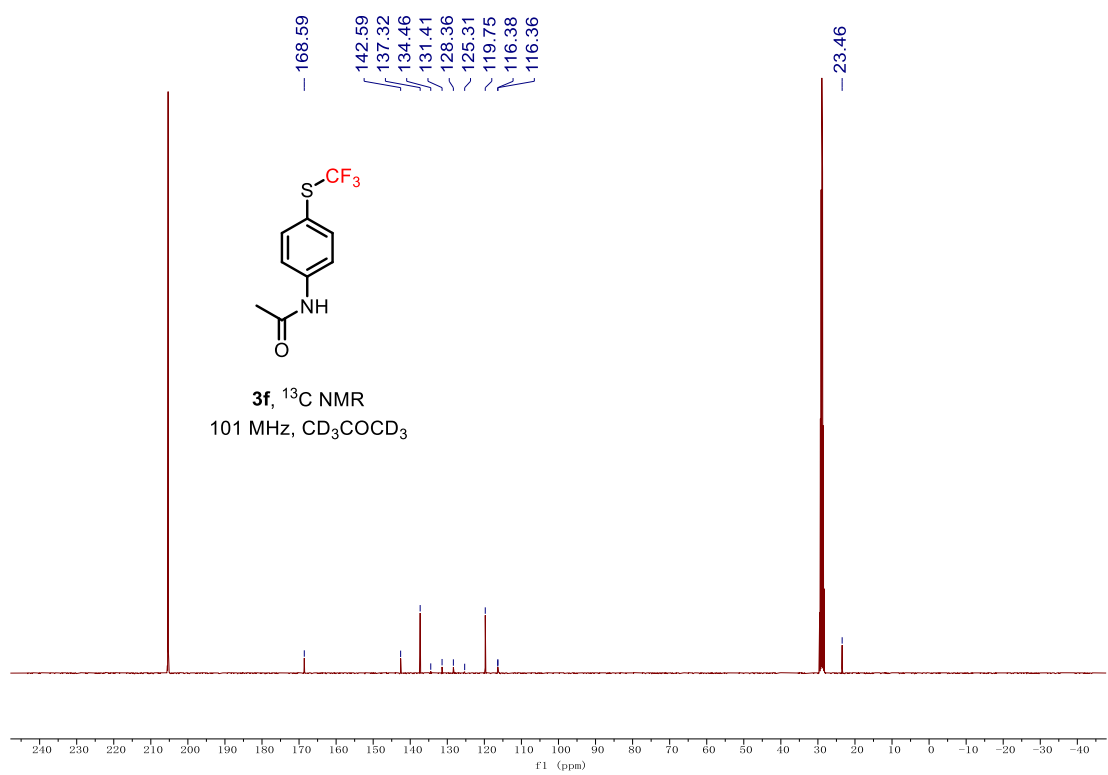
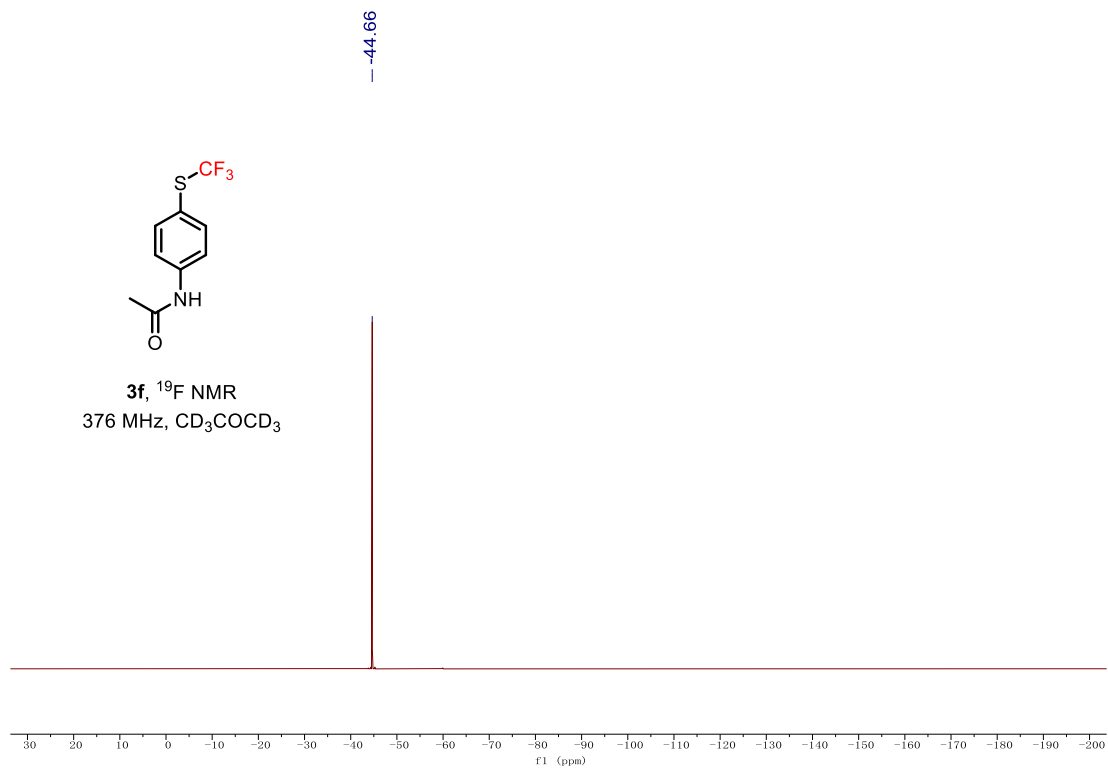
3e, ^1H NMR
400 MHz, CDCl_3

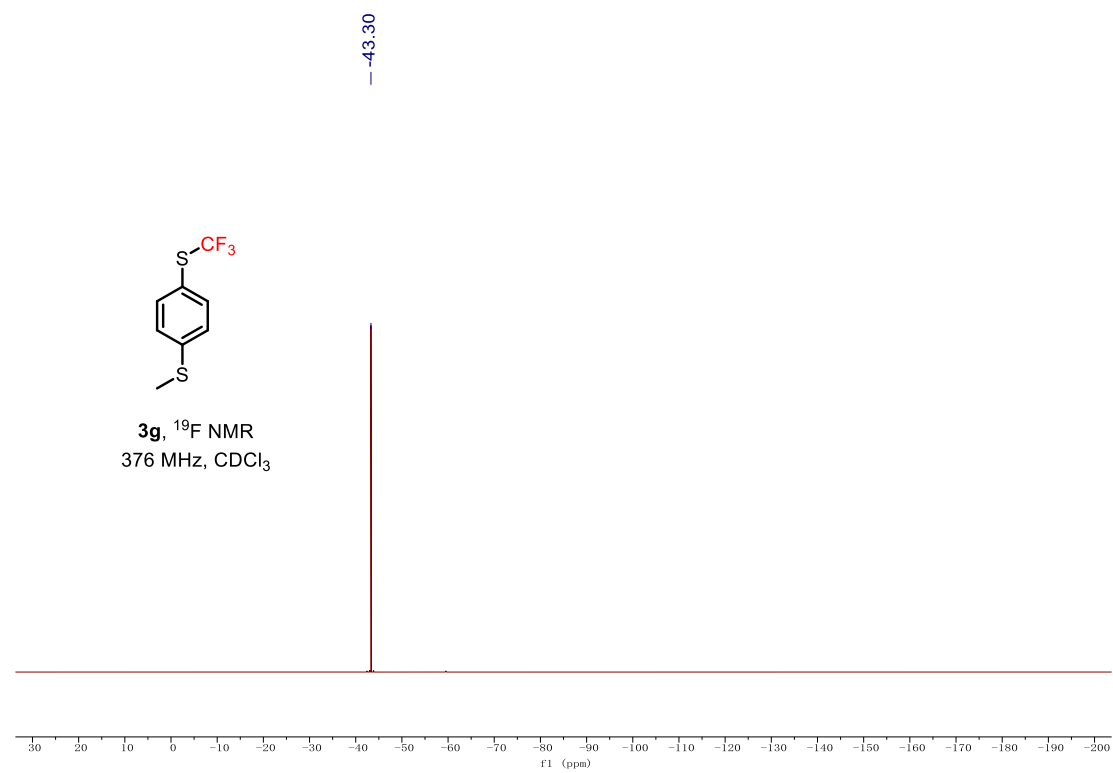
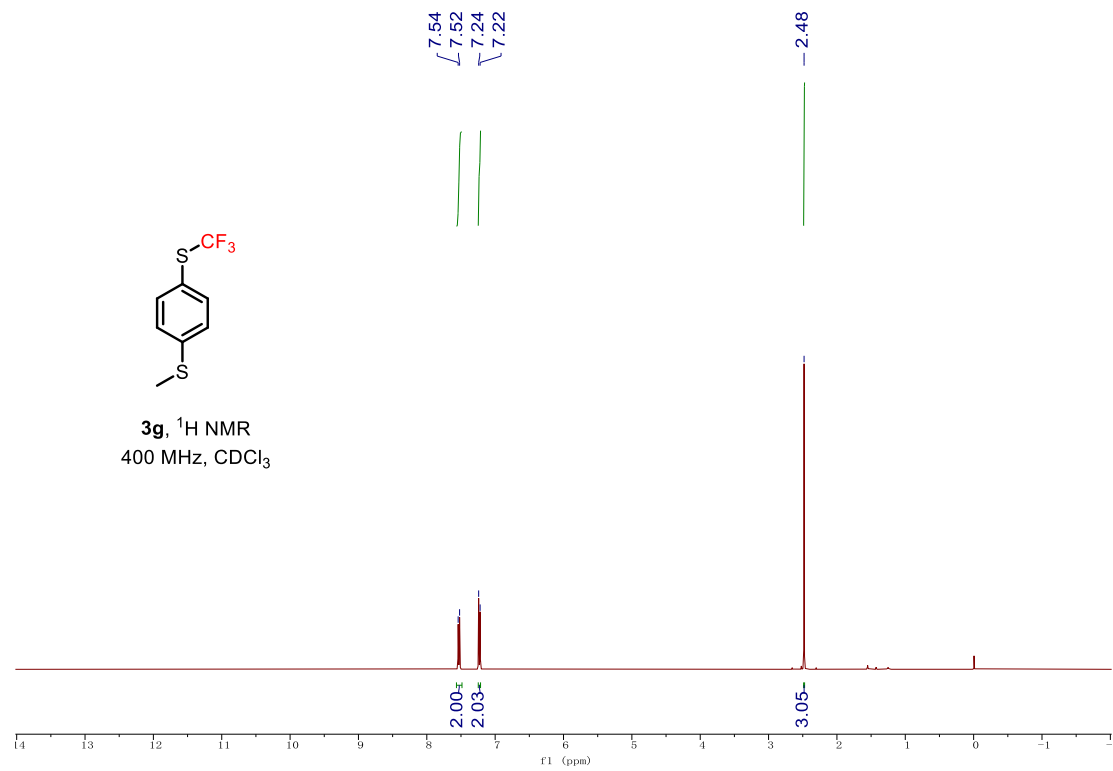


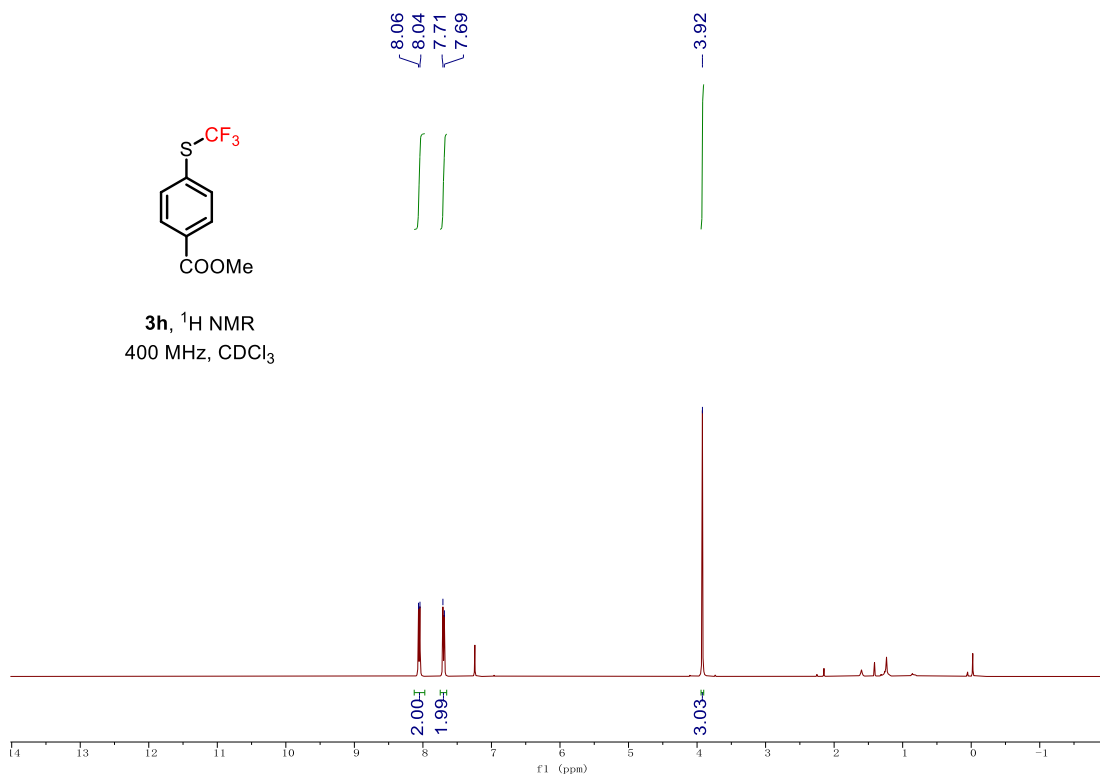
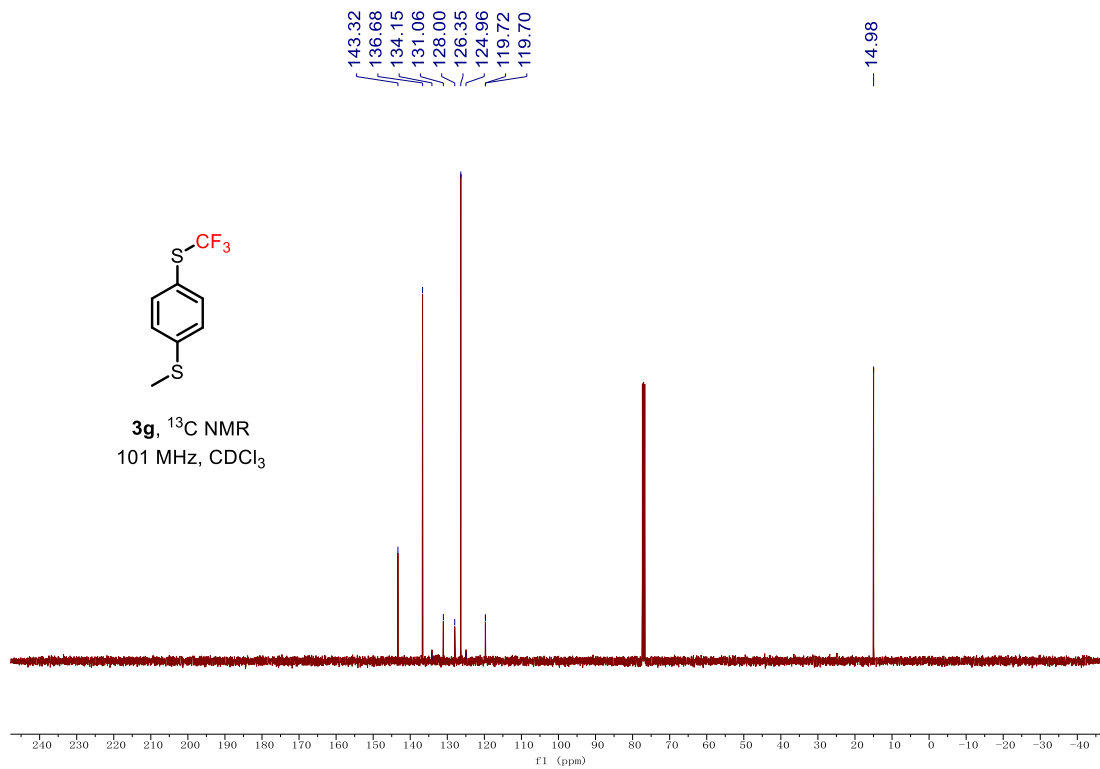
3e, ^{19}F NMR
376 MHz, CDCl_3

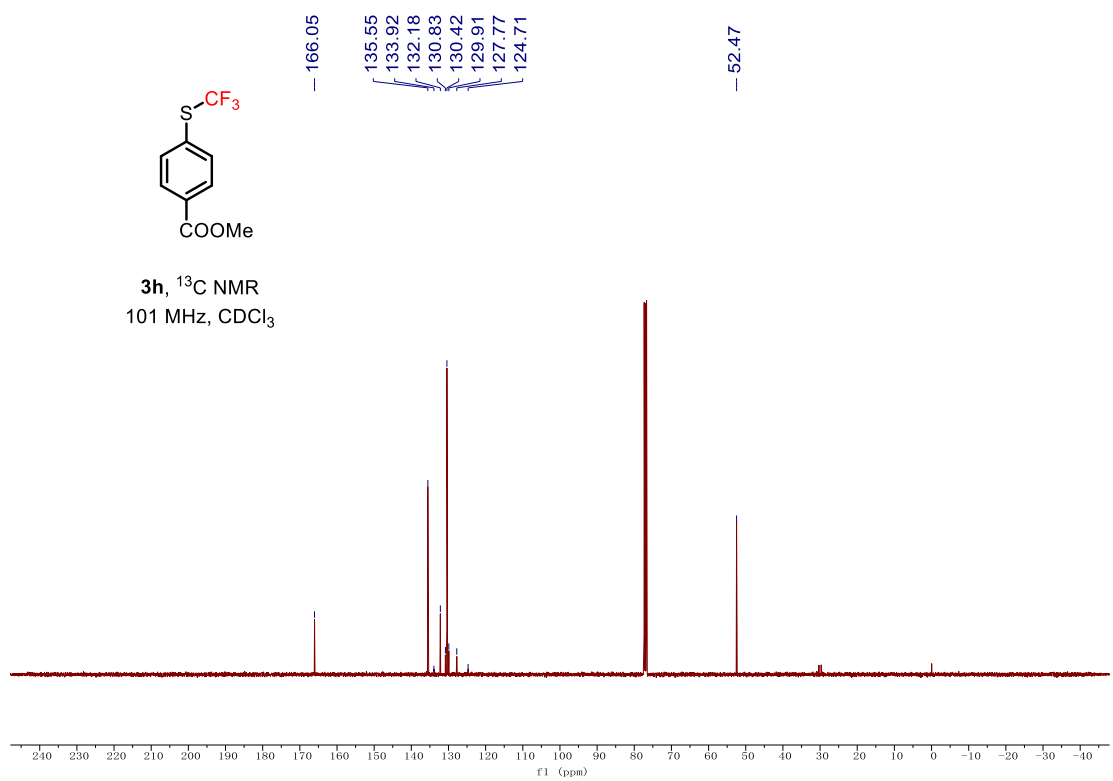
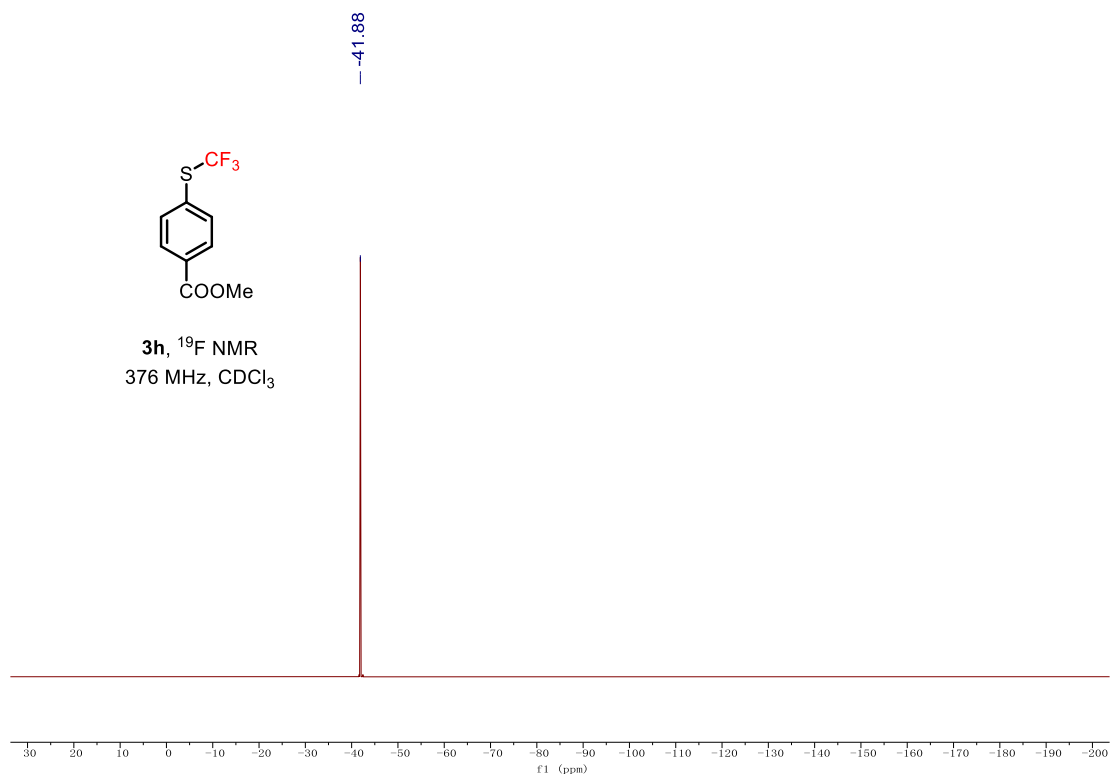


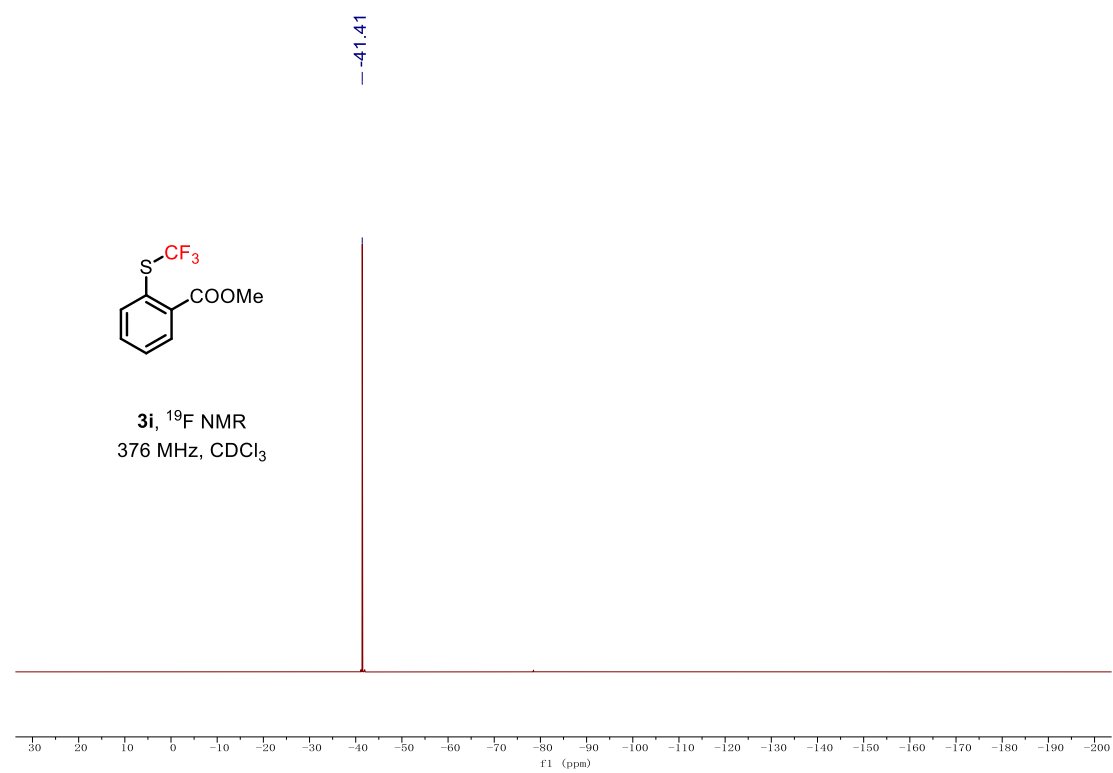
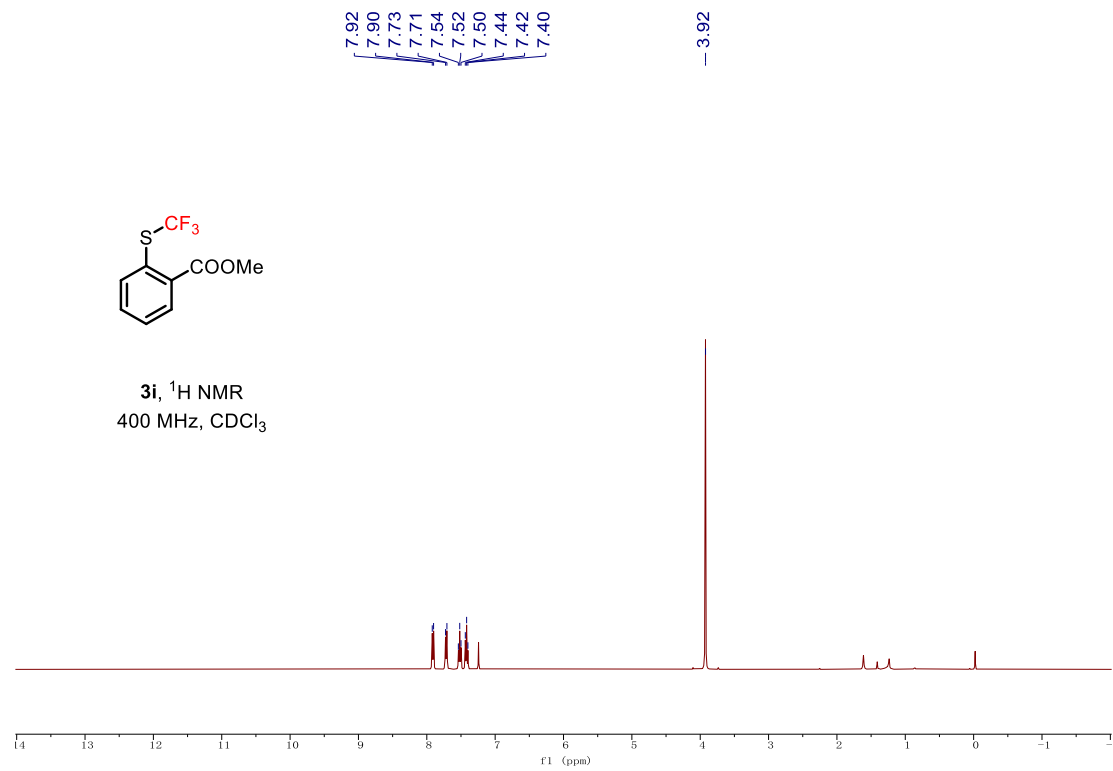


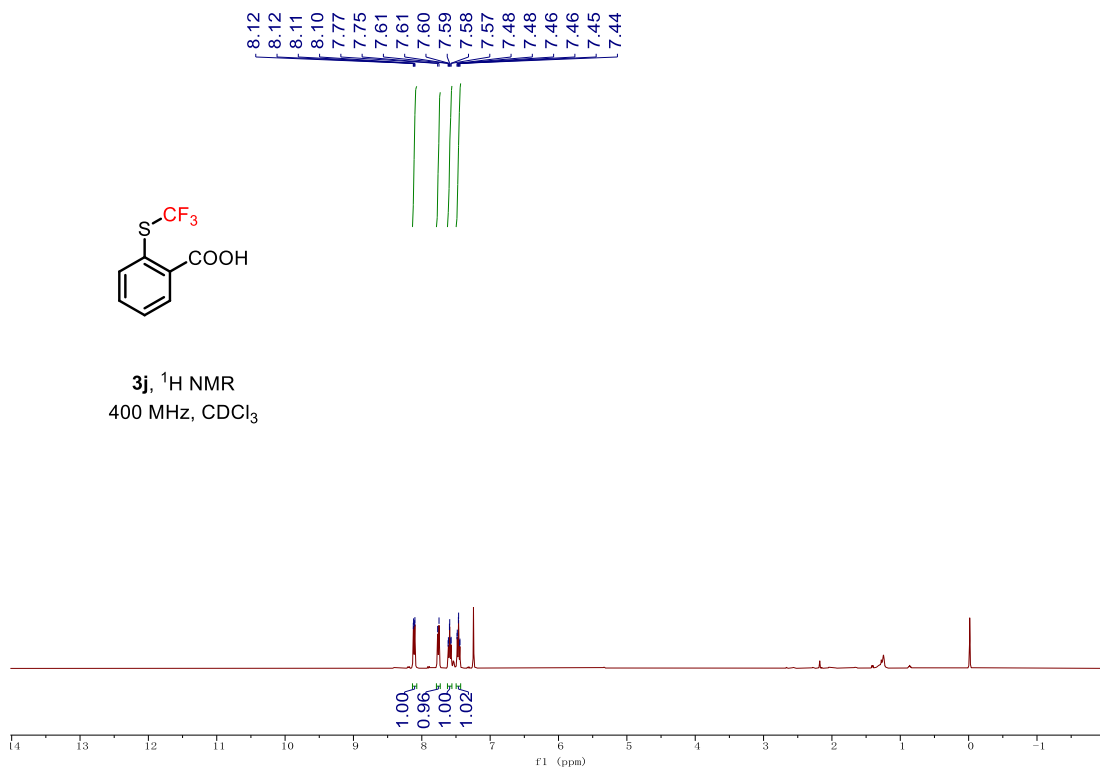
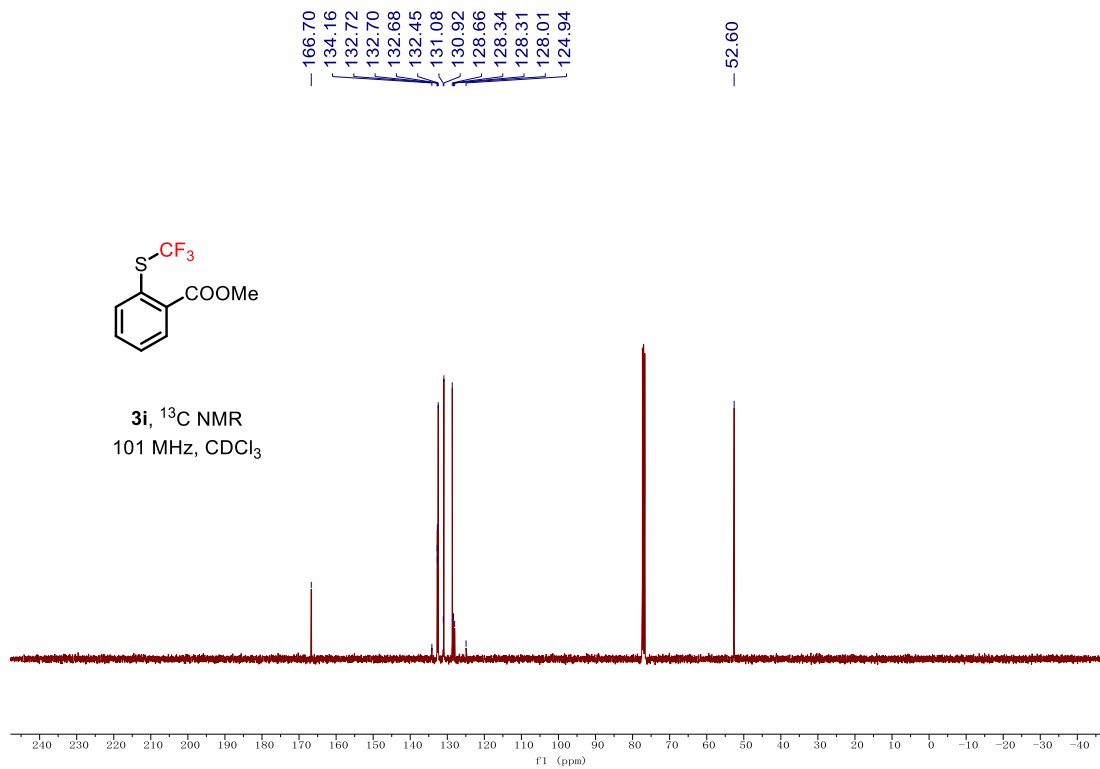


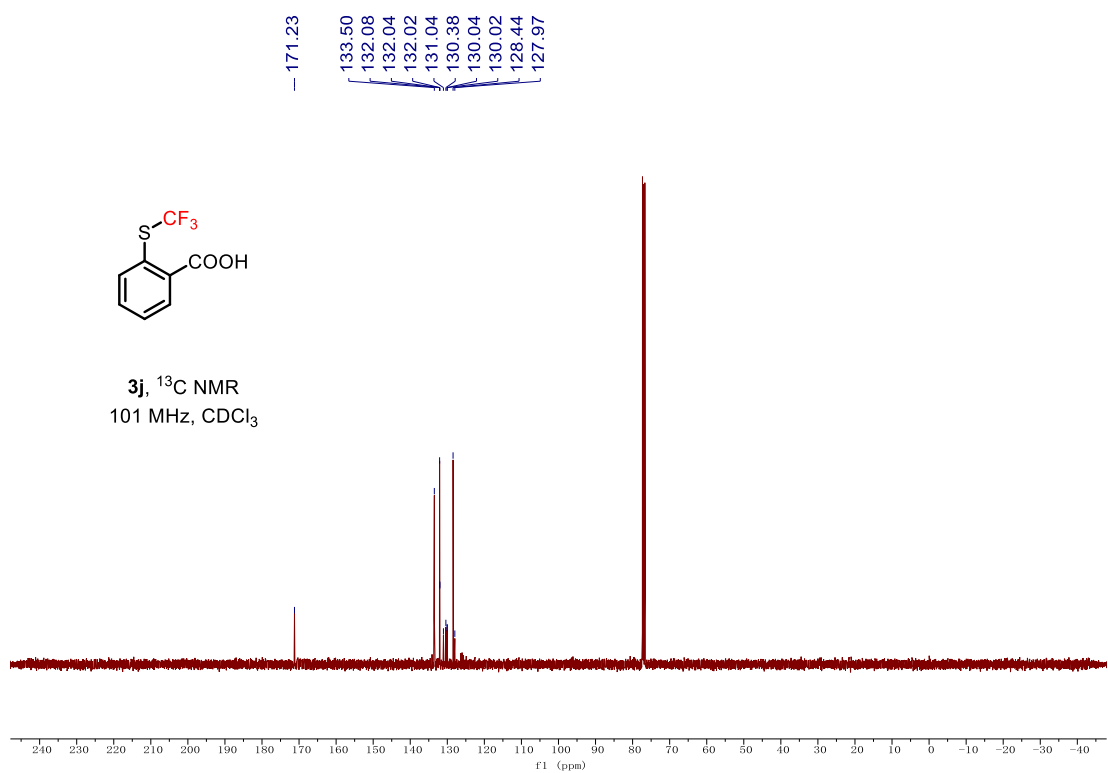
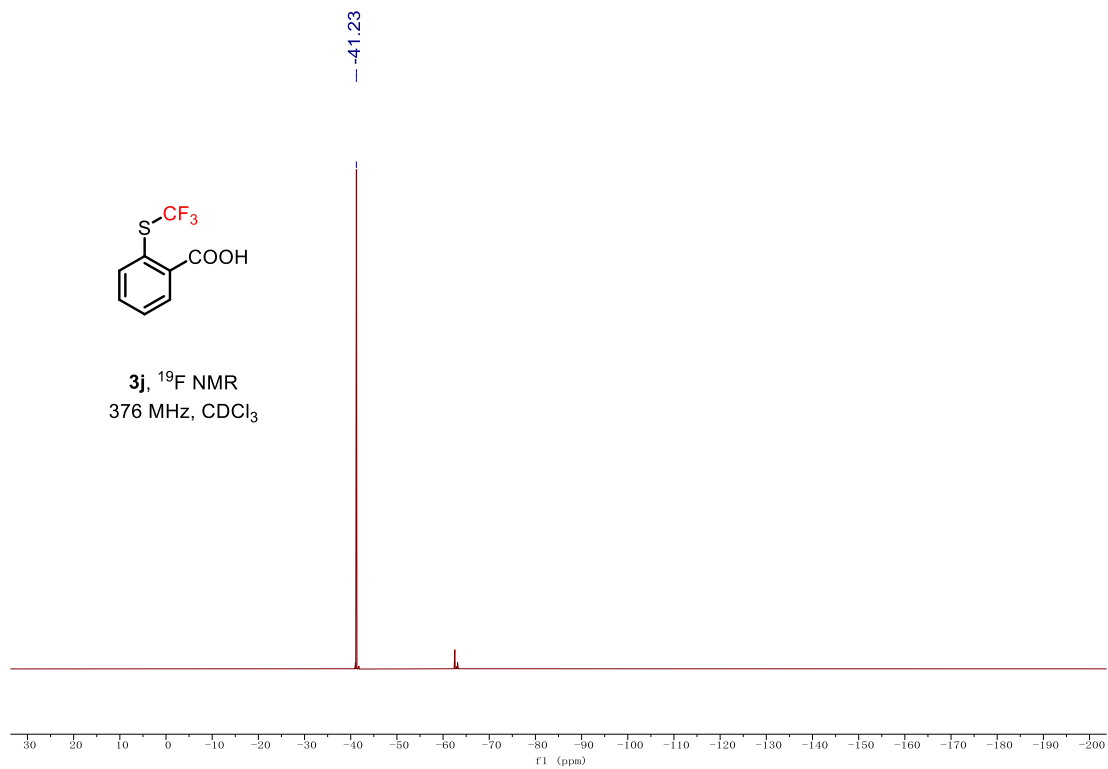


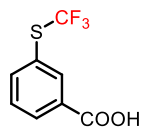




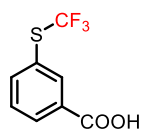
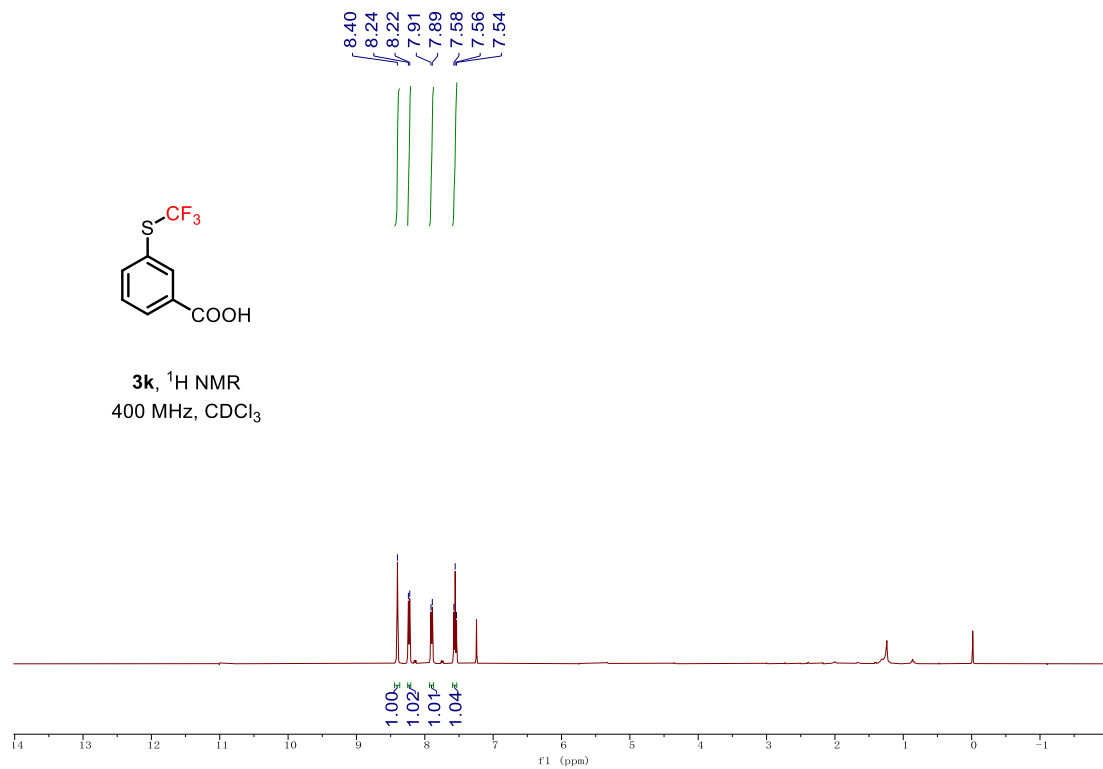




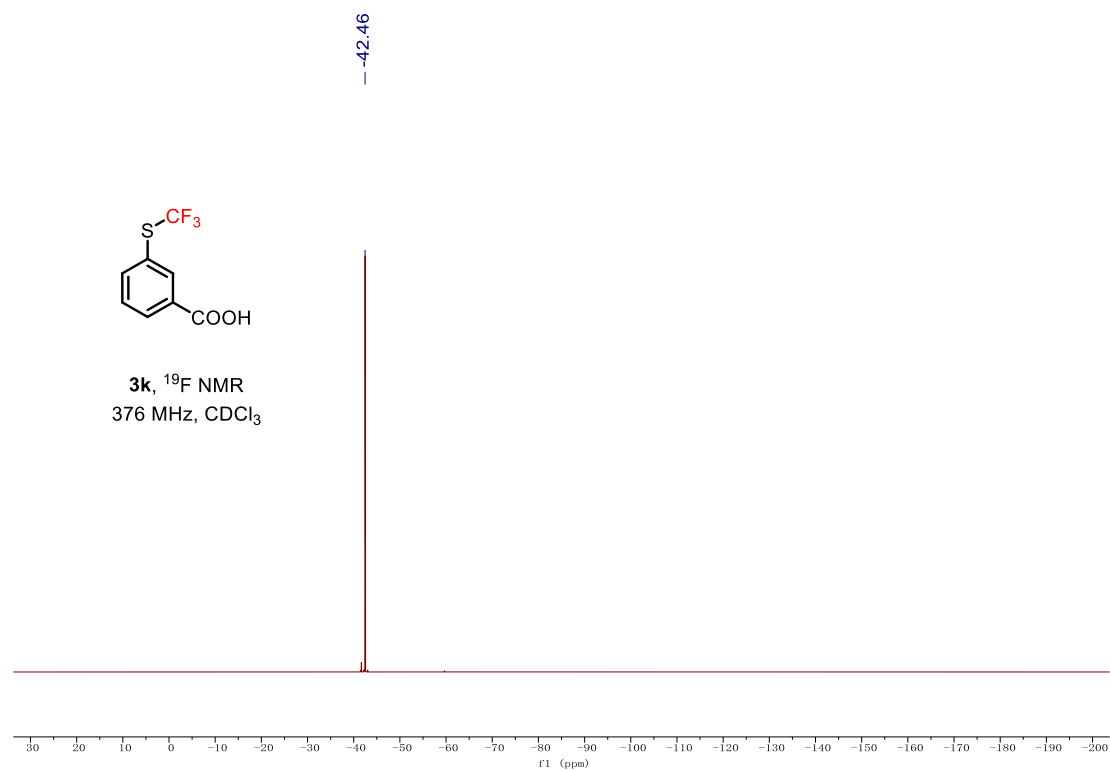




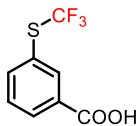
3k, ^1H NMR
400 MHz, CDCl_3



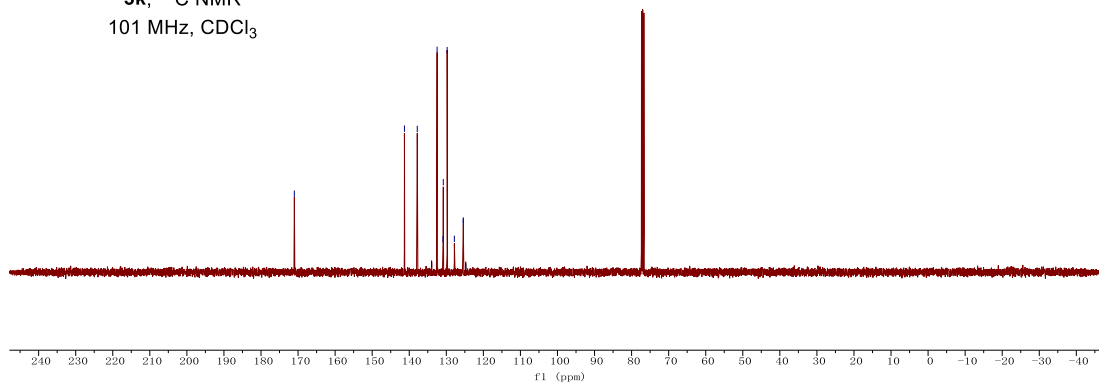
3k, ^{19}F NMR
376 MHz, CDCl_3



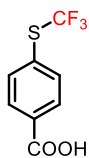
171.00
141.29
137.83
133.97
132.48
130.89
130.81
129.77
127.82
125.44
125.42
124.73



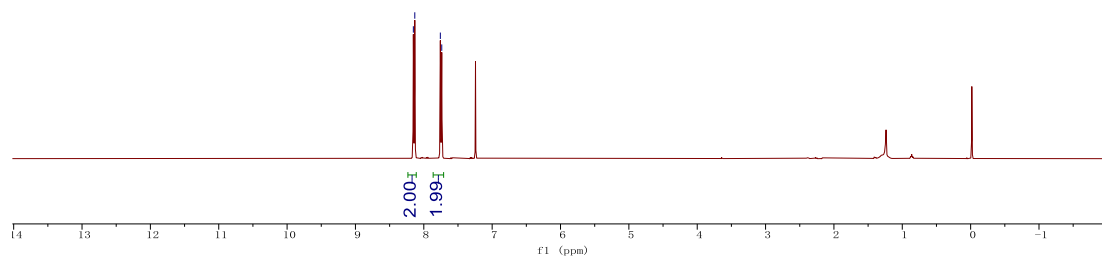
3k, ^{13}C NMR
101 MHz, CDCl_3

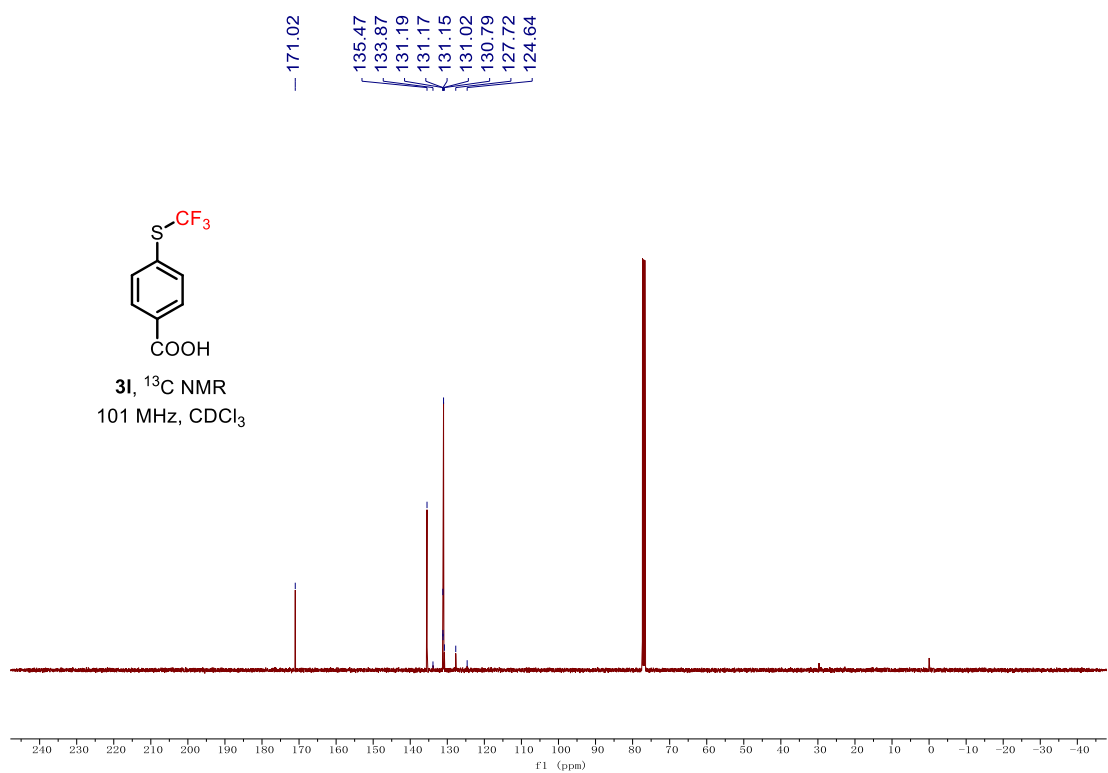
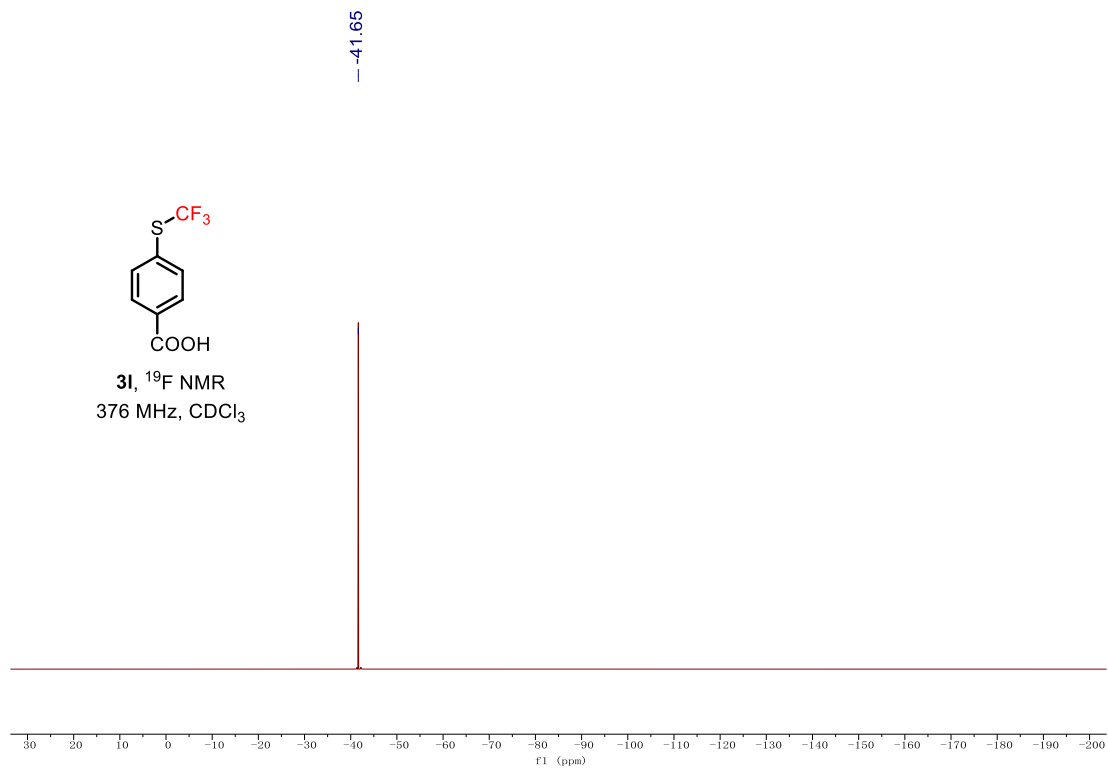


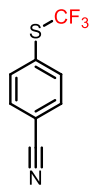
8.15
8.13
7.76
7.74



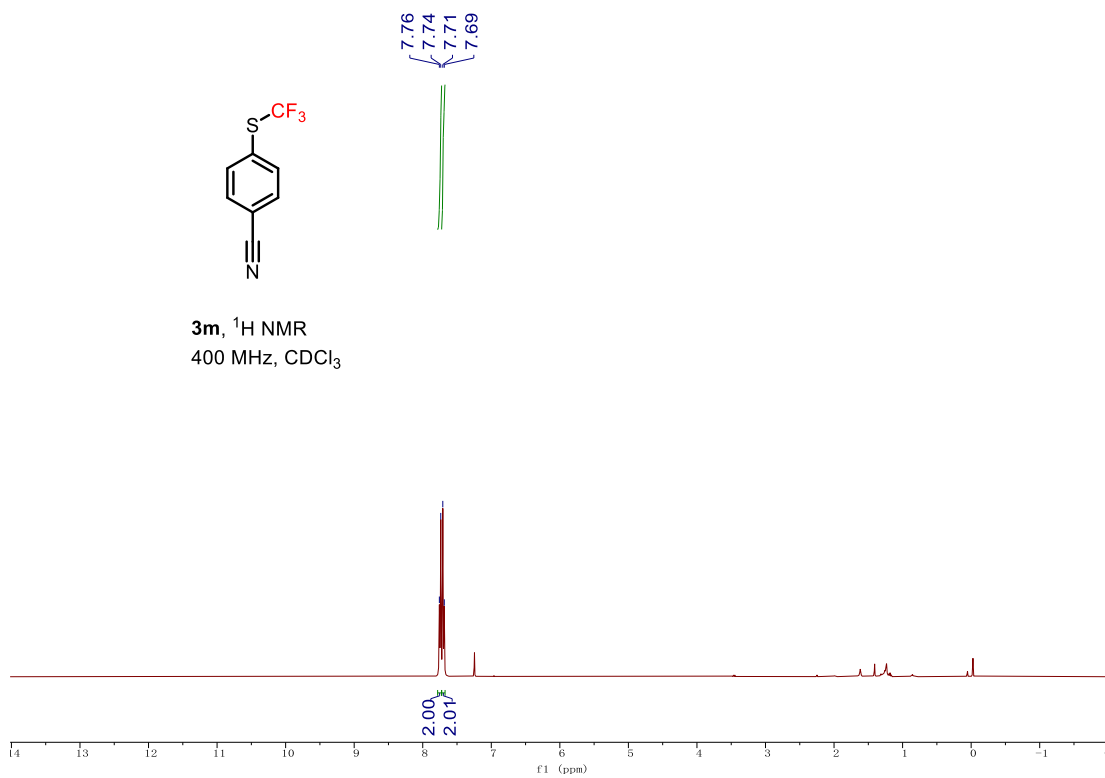
3l, ^1H NMR
400 MHz, CDCl_3



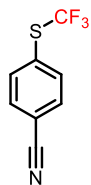




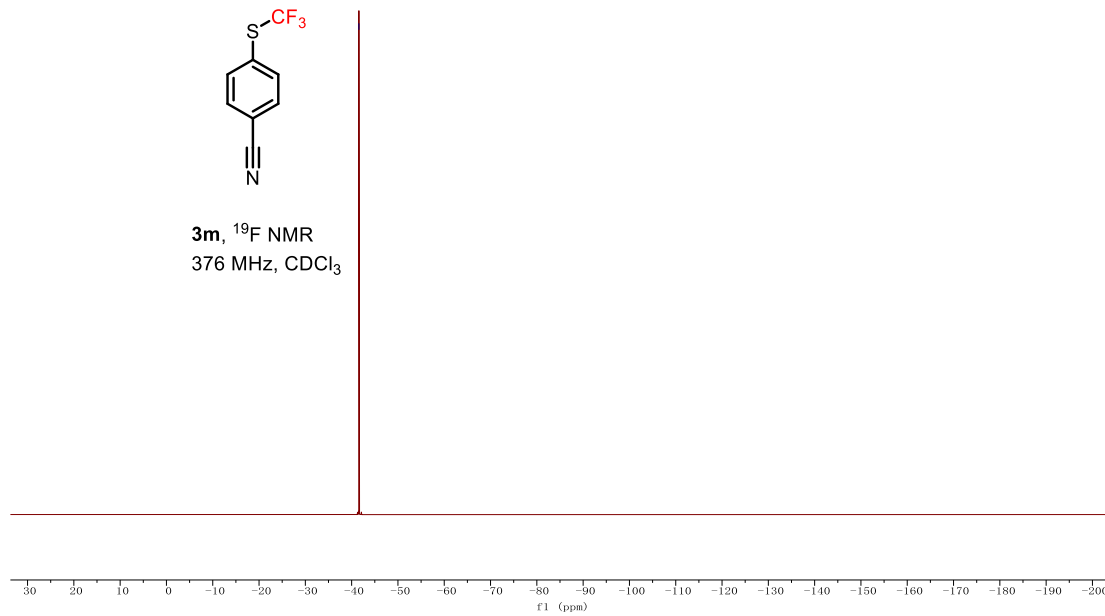
3m, ^1H NMR
400 MHz, CDCl_3



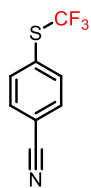
-41.56



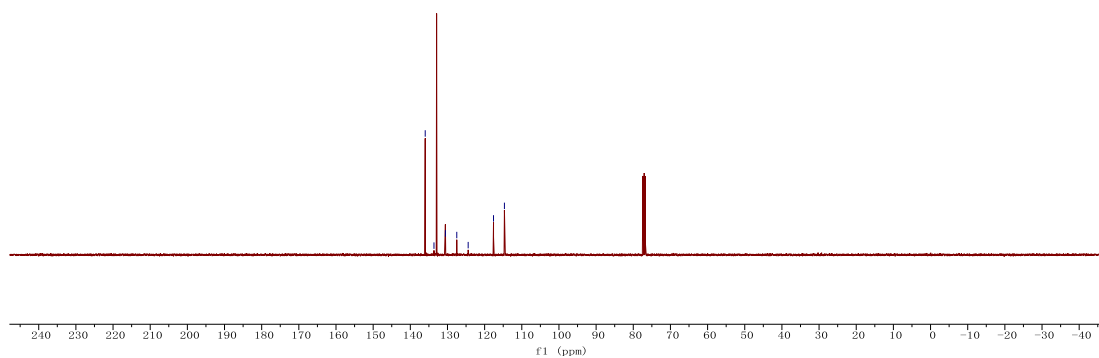
3m, ^{19}F NMR
376 MHz, CDCl_3



135.99
133.64
130.55
127.50
124.43
117.61
114.68

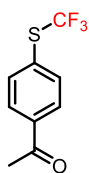


3m, ^{13}C NMR
101 MHz, CDCl_3

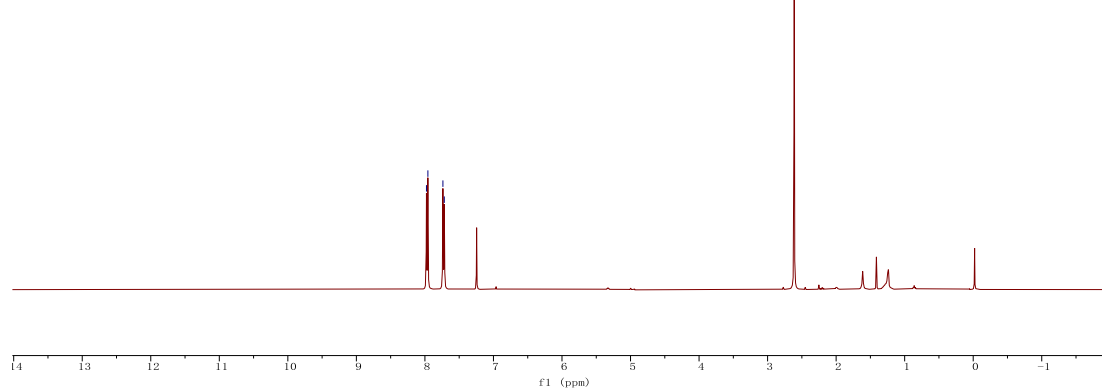


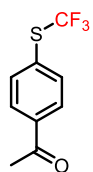
7.98
7.96
7.74
7.72

2.61

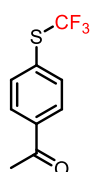
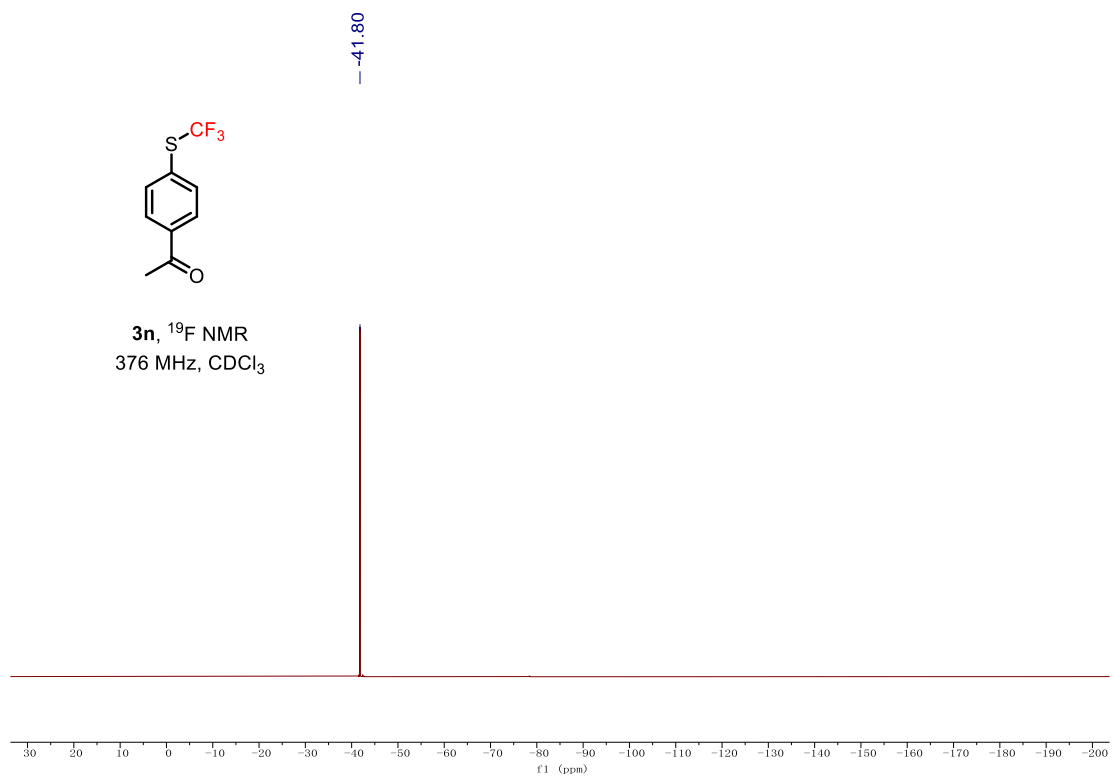


3n, ^1H NMR
400 MHz, CDCl_3

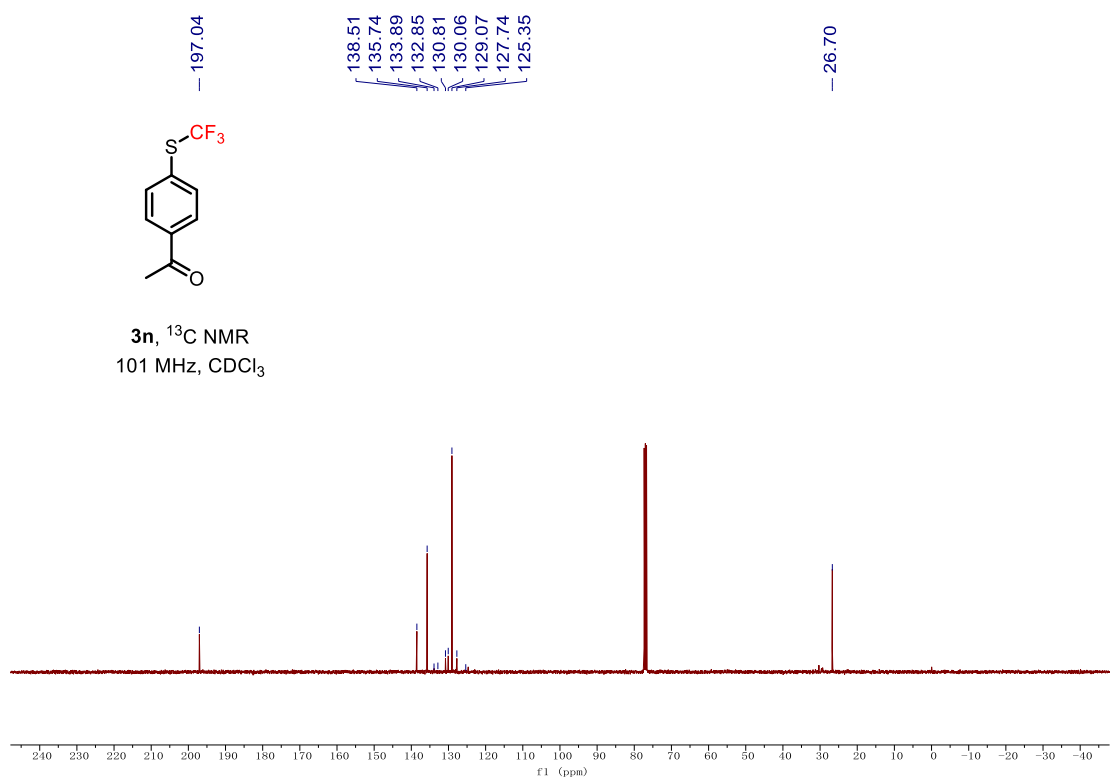


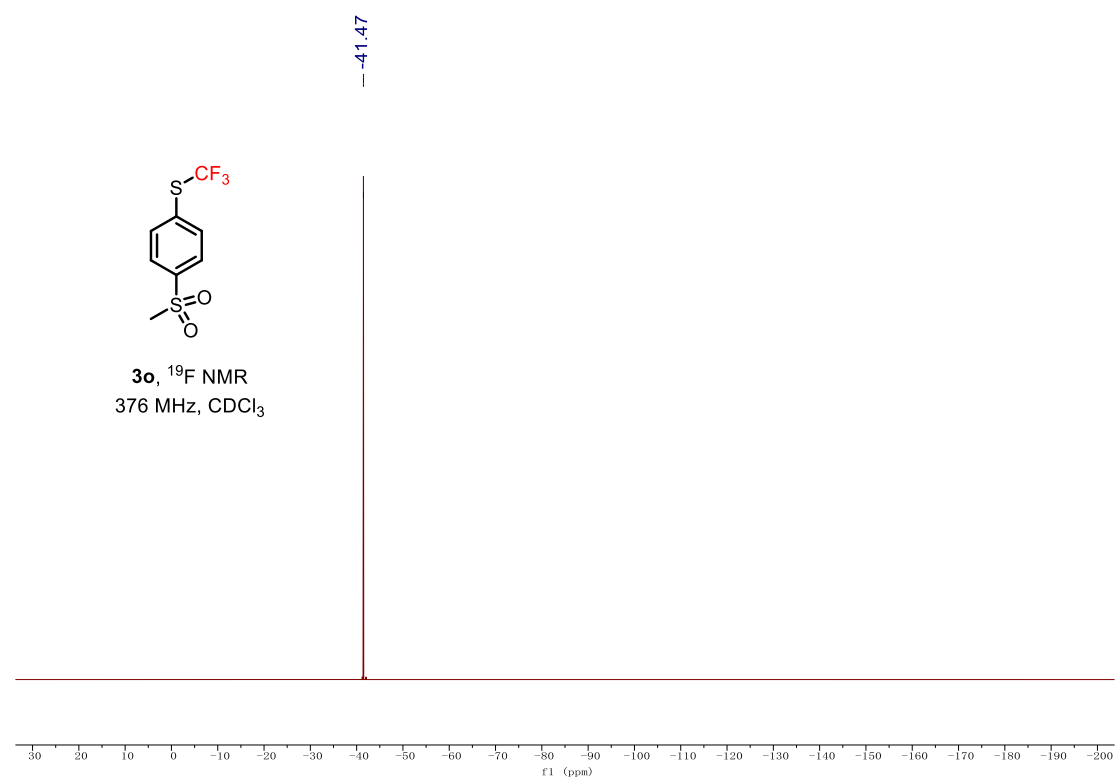
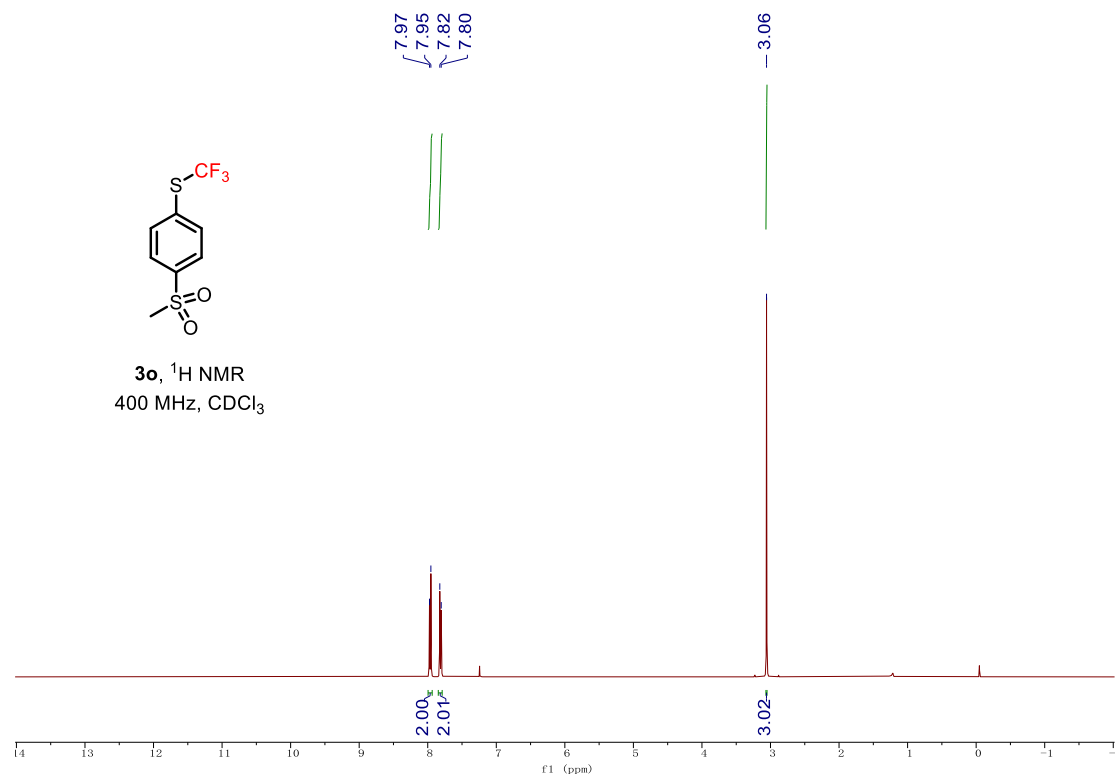


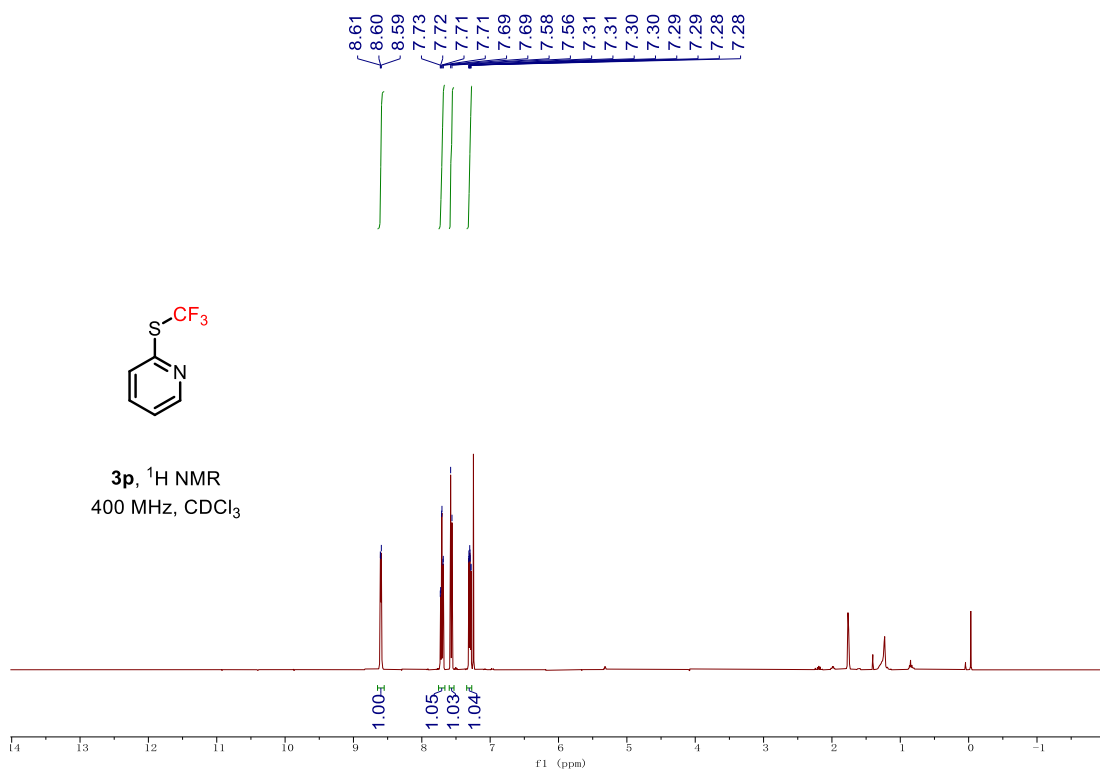
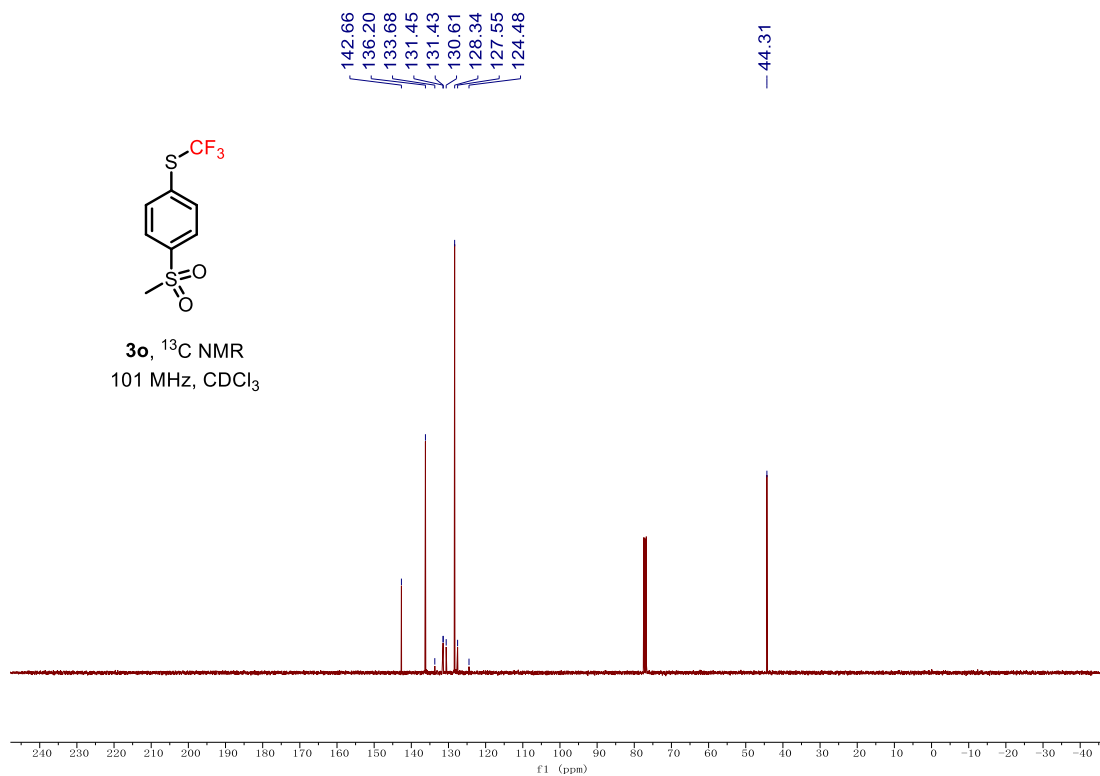
3n, ^{19}F NMR
376 MHz, CDCl_3

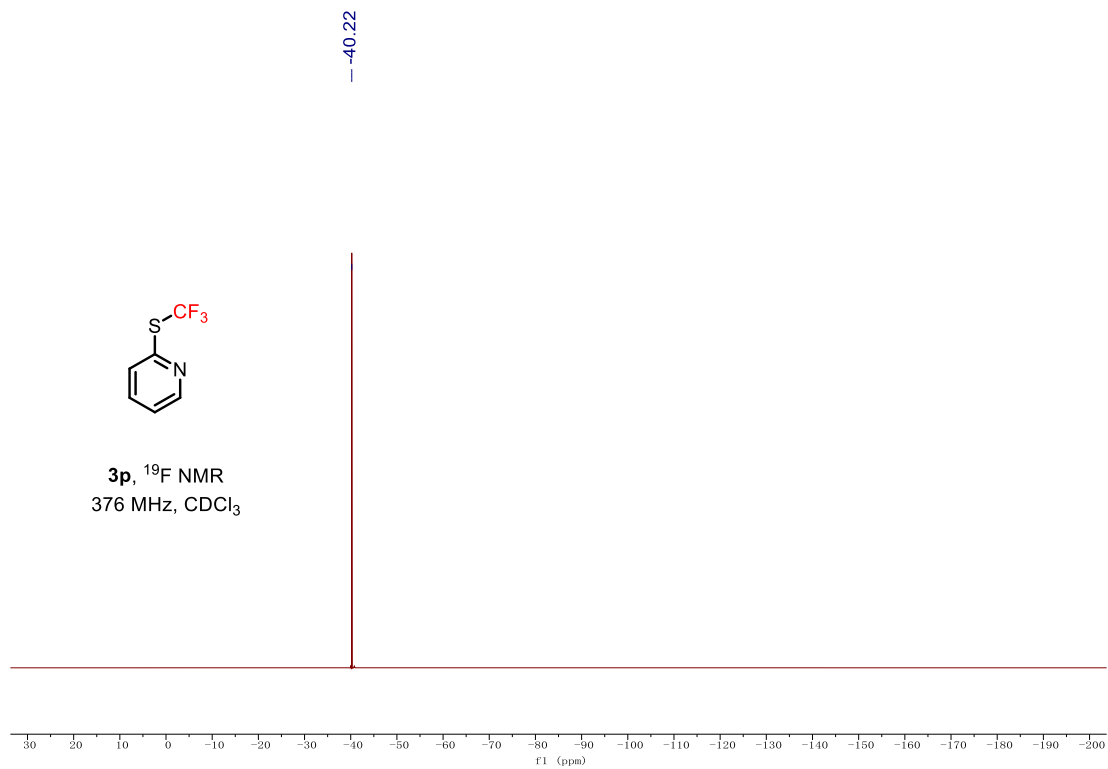


3n, ^{13}C NMR
101 MHz, CDCl_3

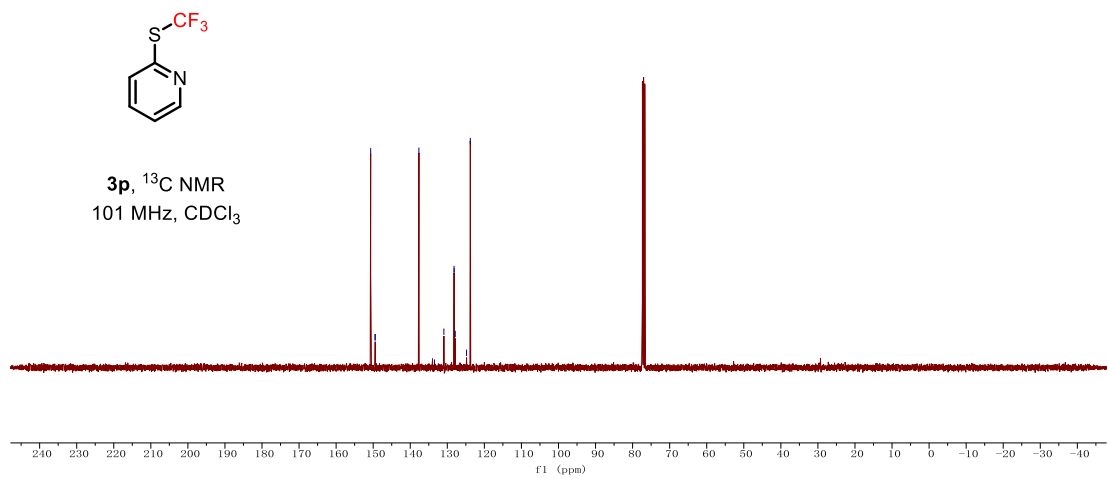


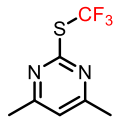




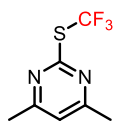
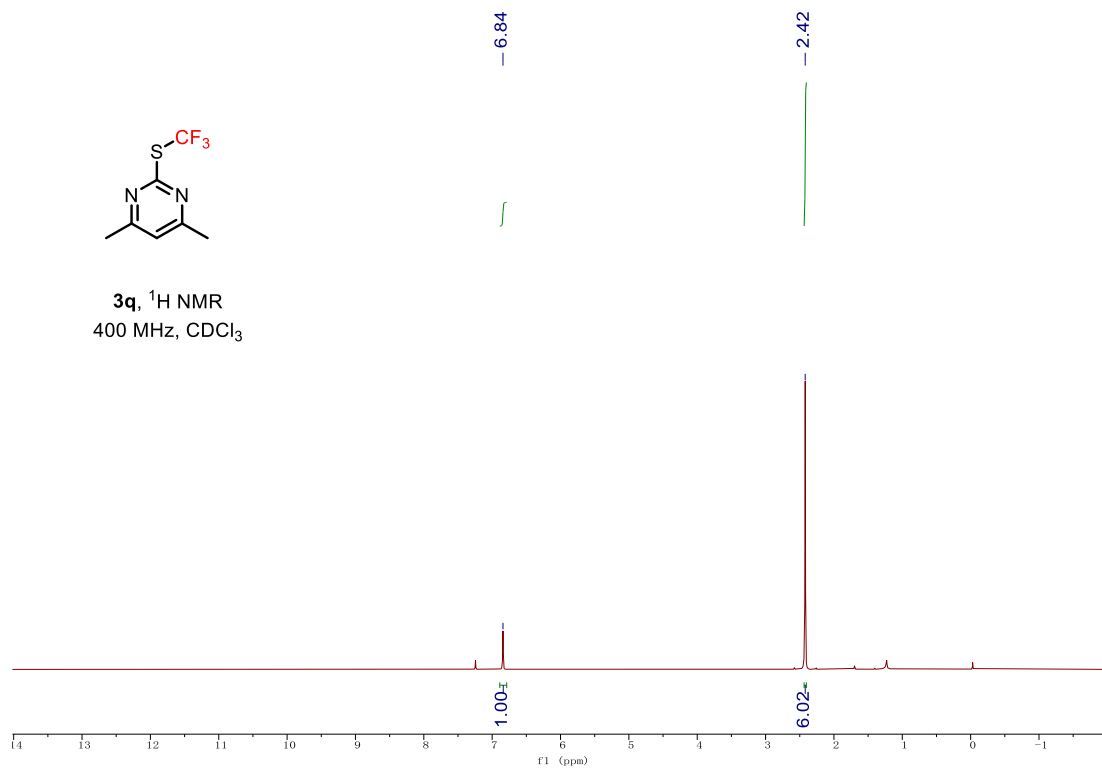


150.68
149.49
149.46
137.66
133.44
130.92
128.18
127.86
124.80
123.80

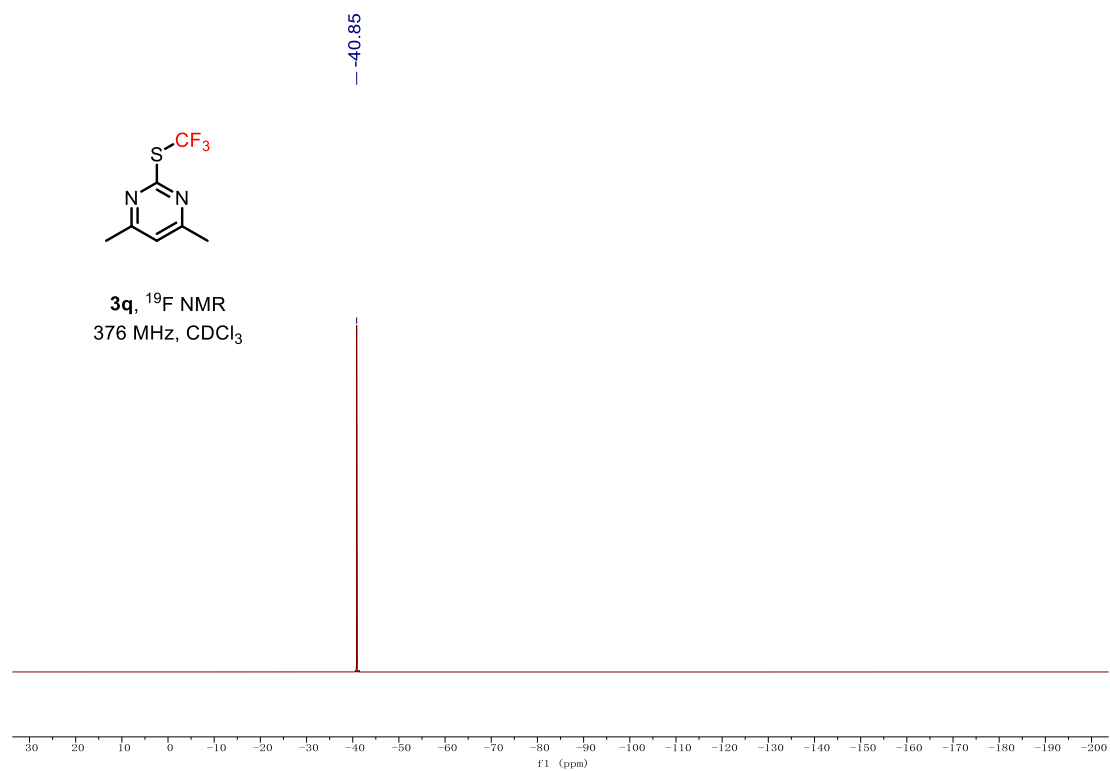


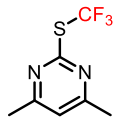


3q, ^1H NMR
400 MHz, CDCl_3

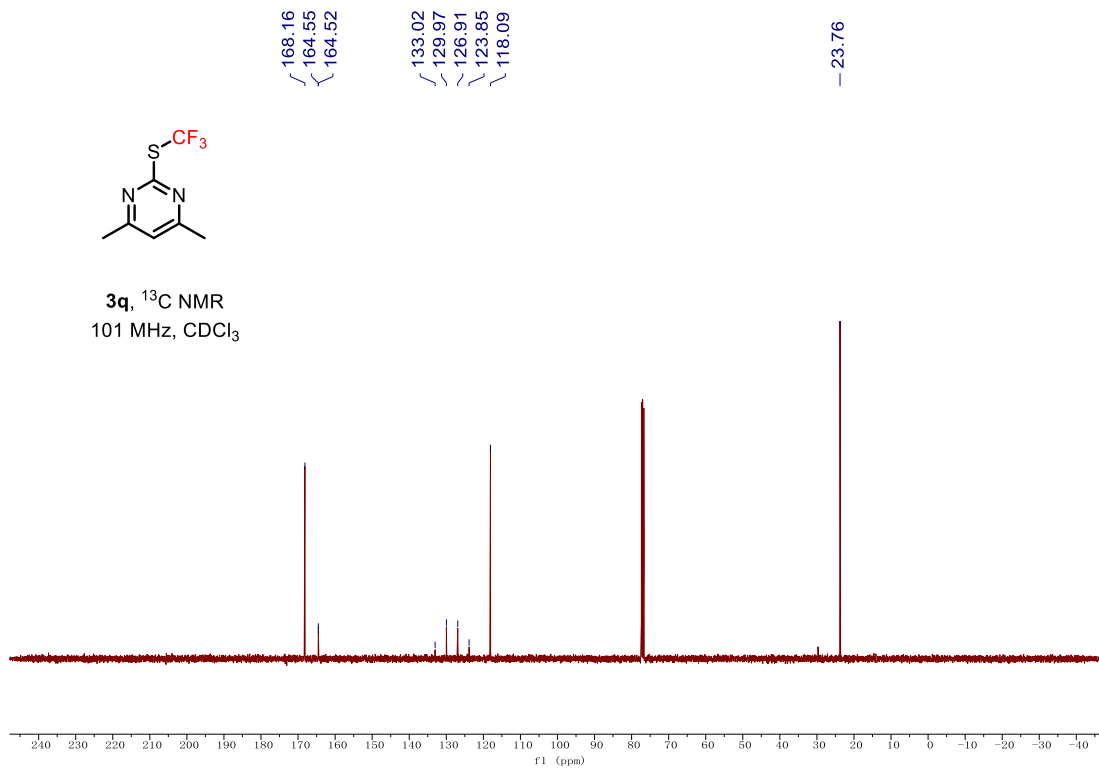


3q, ^{19}F NMR
376 MHz, CDCl_3

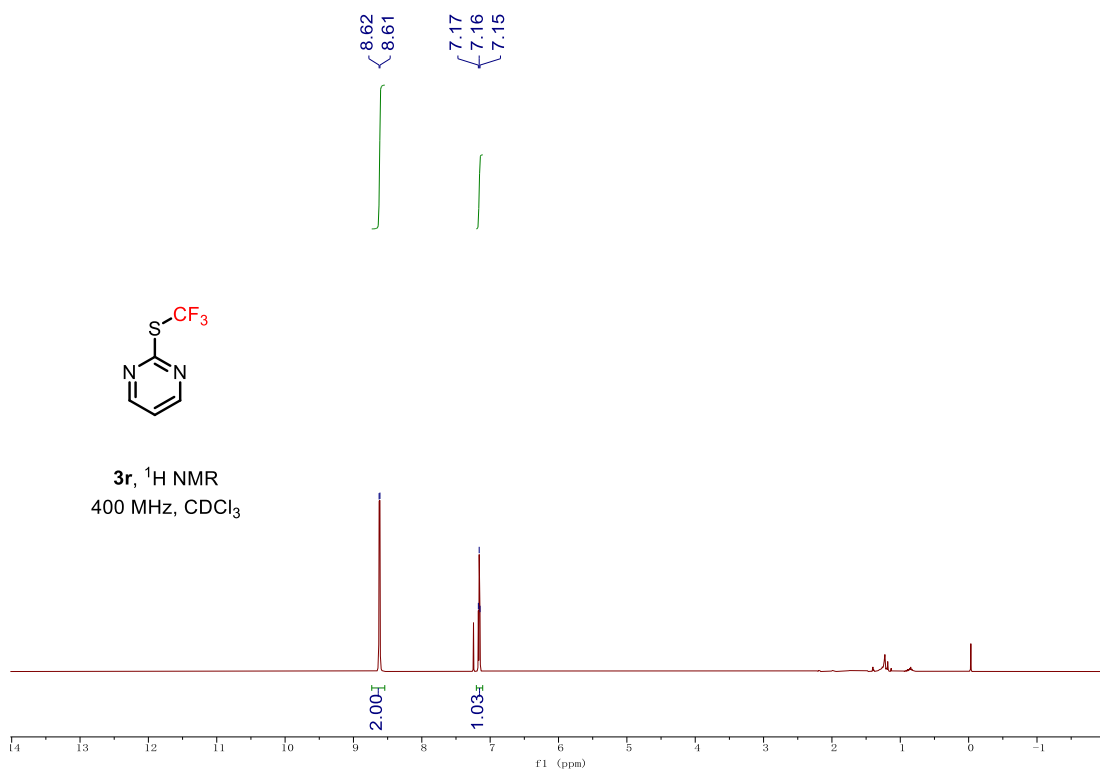


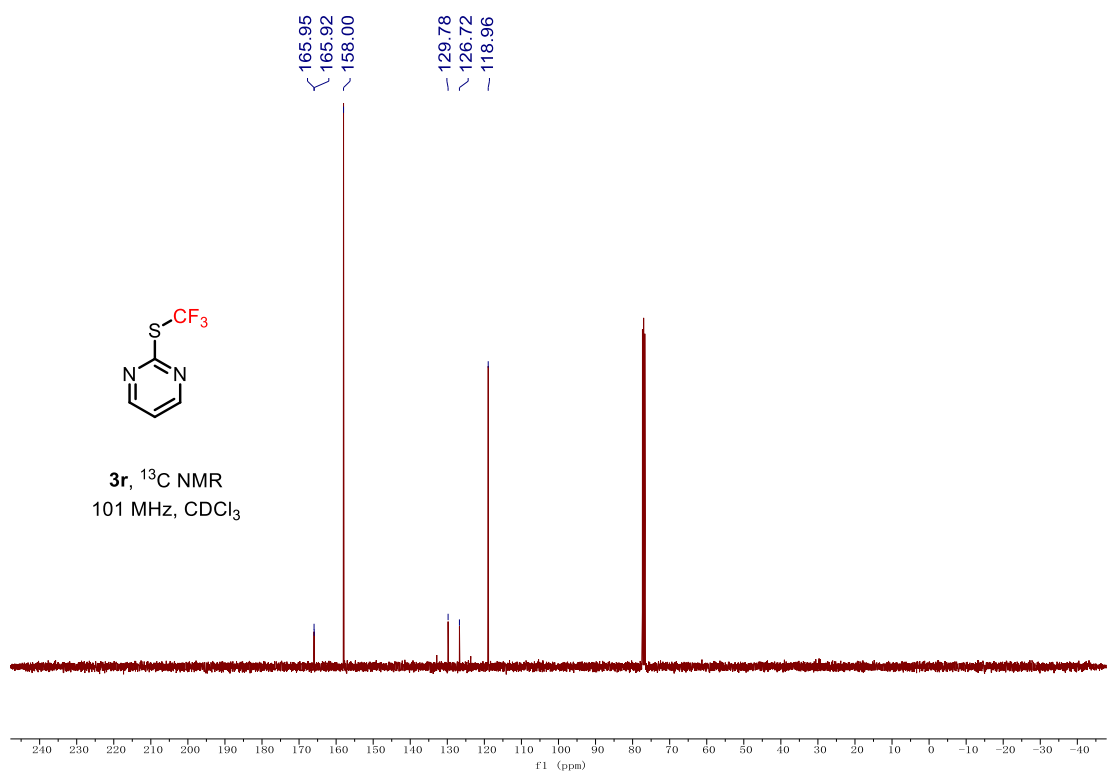
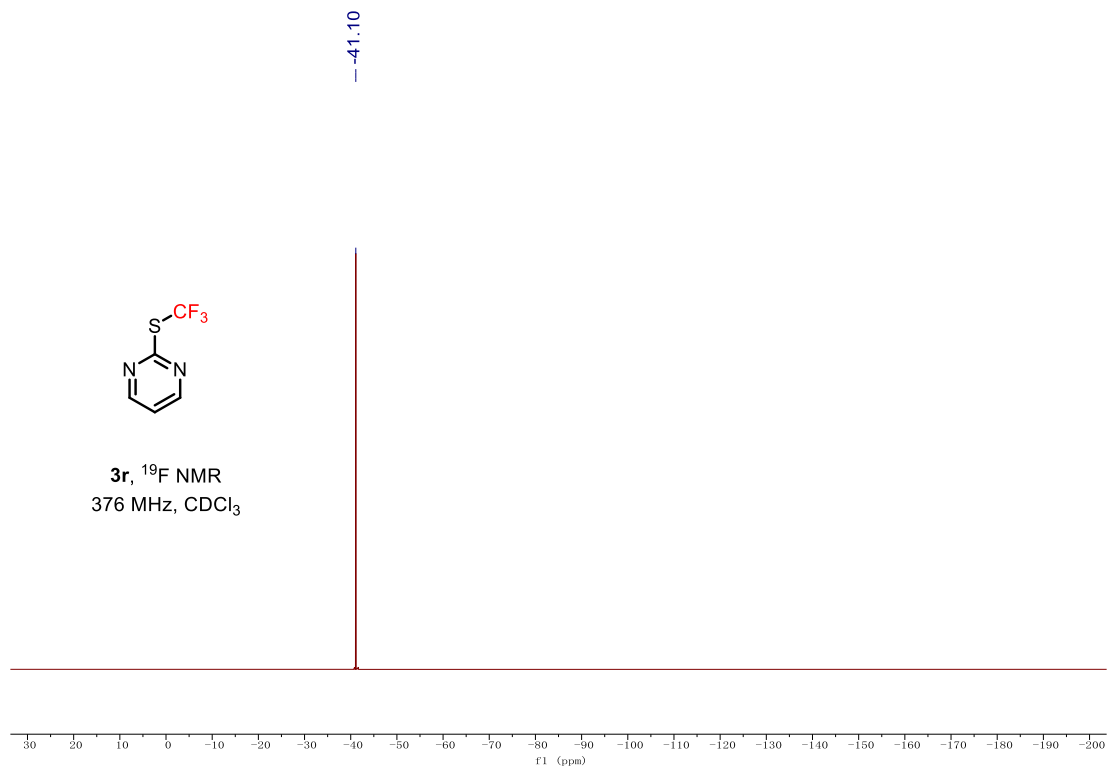


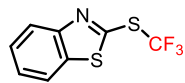
3q, ^{13}C NMR
101 MHz, CDCl_3



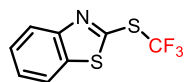
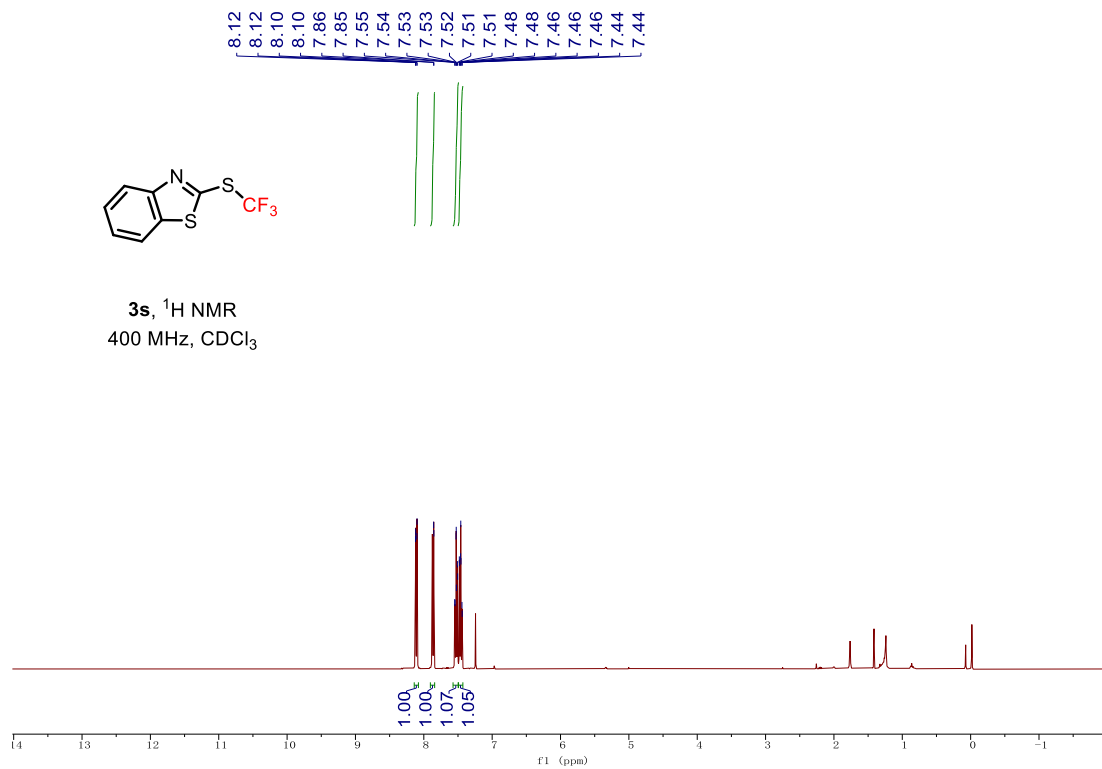
3r, ^1H NMR
400 MHz, CDCl_3



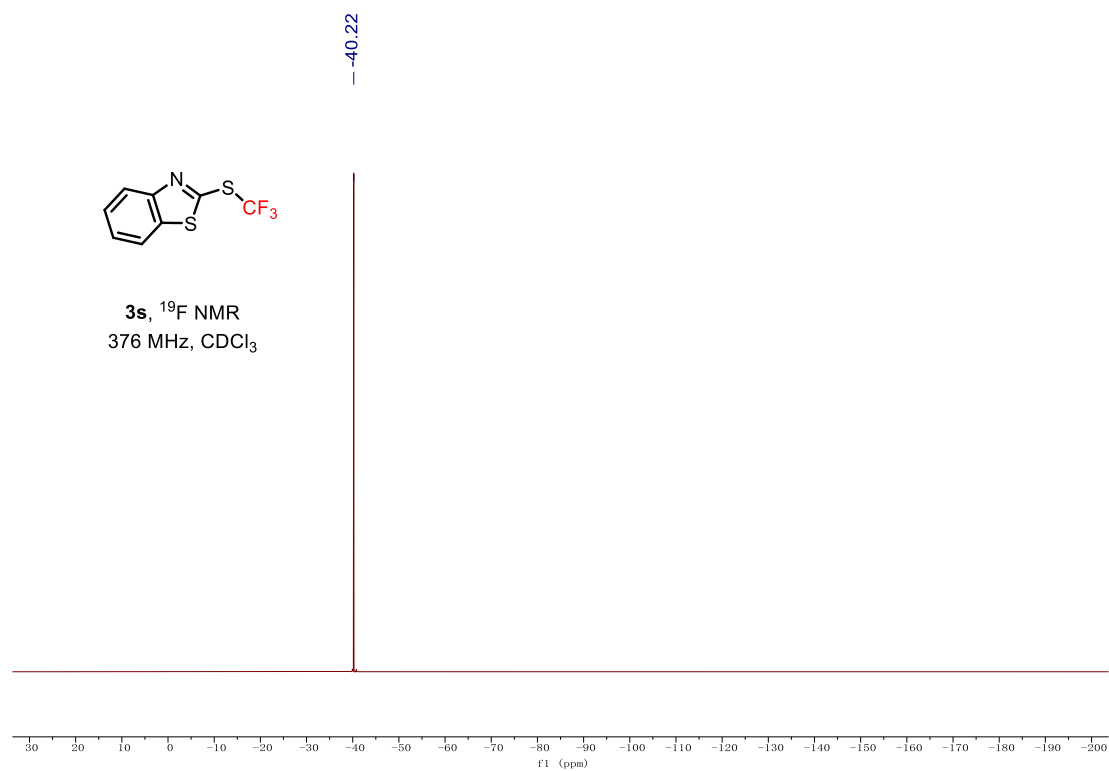


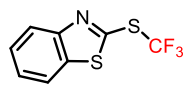


3s, ^1H NMR
400 MHz, CDCl_3

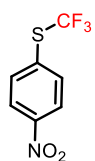
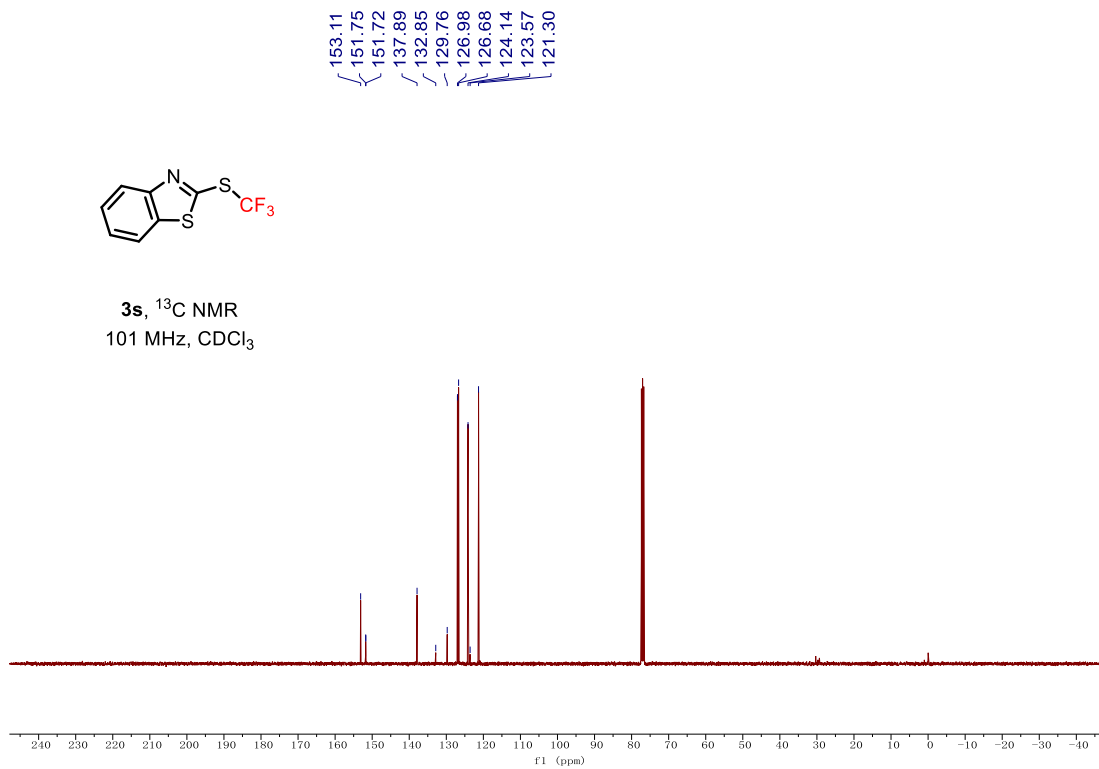


3s, ^{19}F NMR
376 MHz, CDCl_3

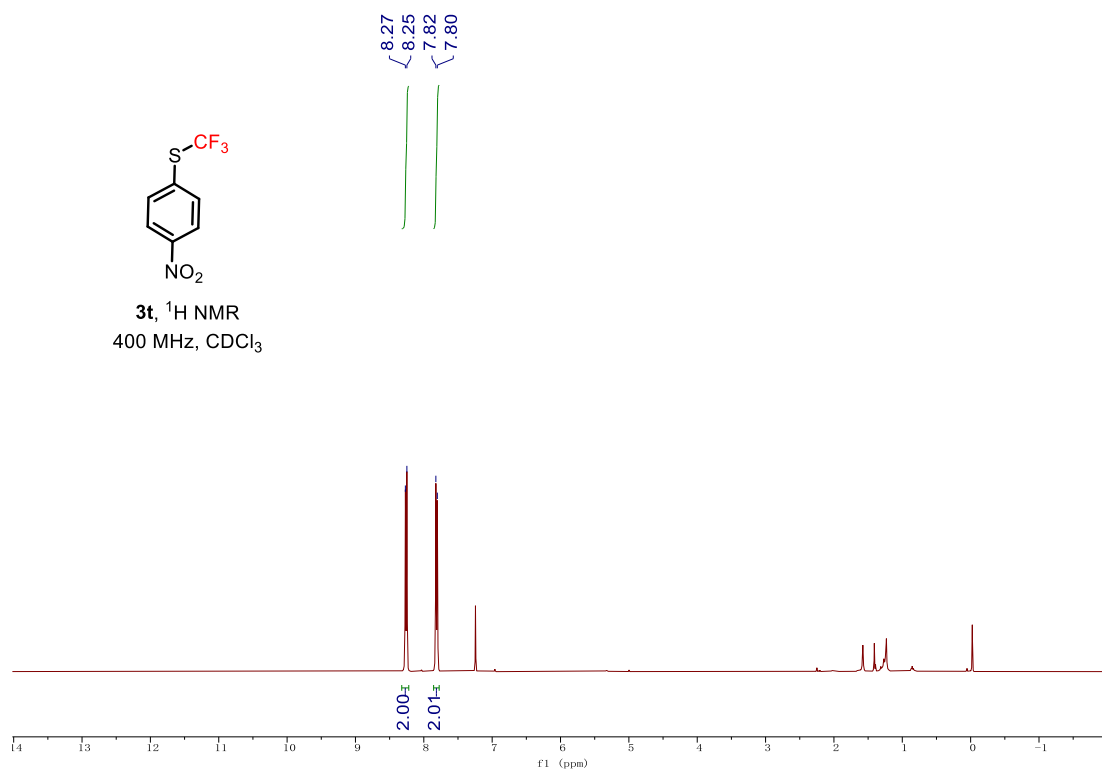


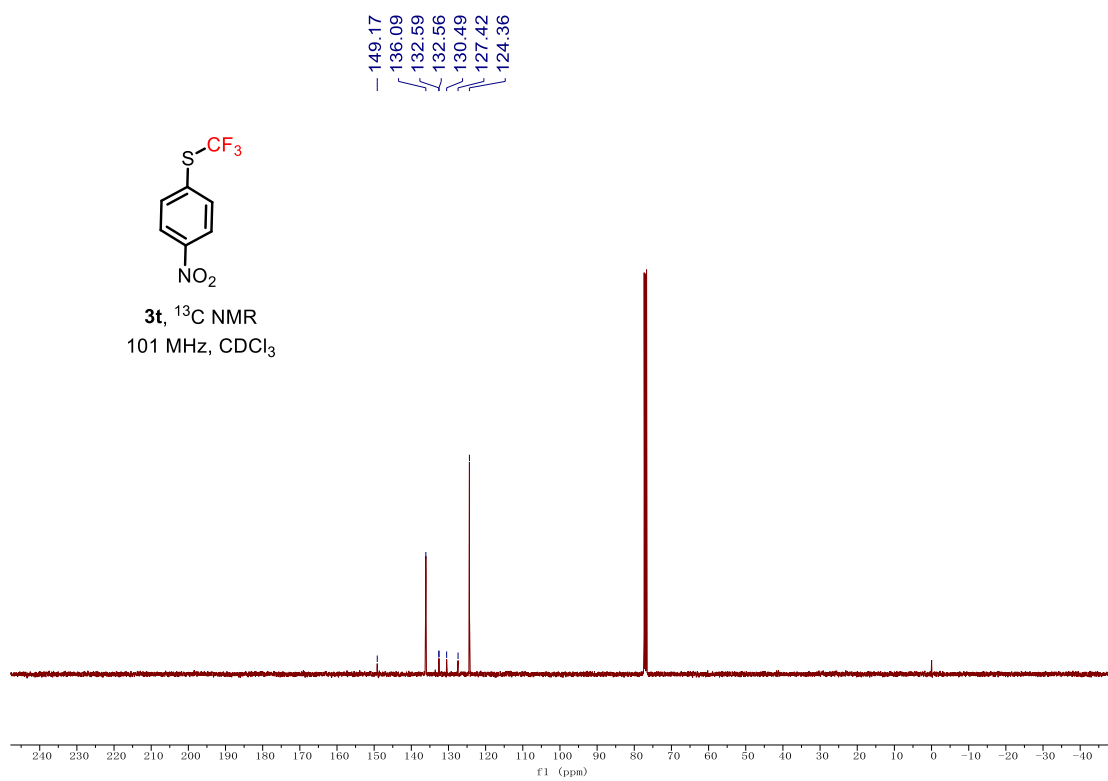
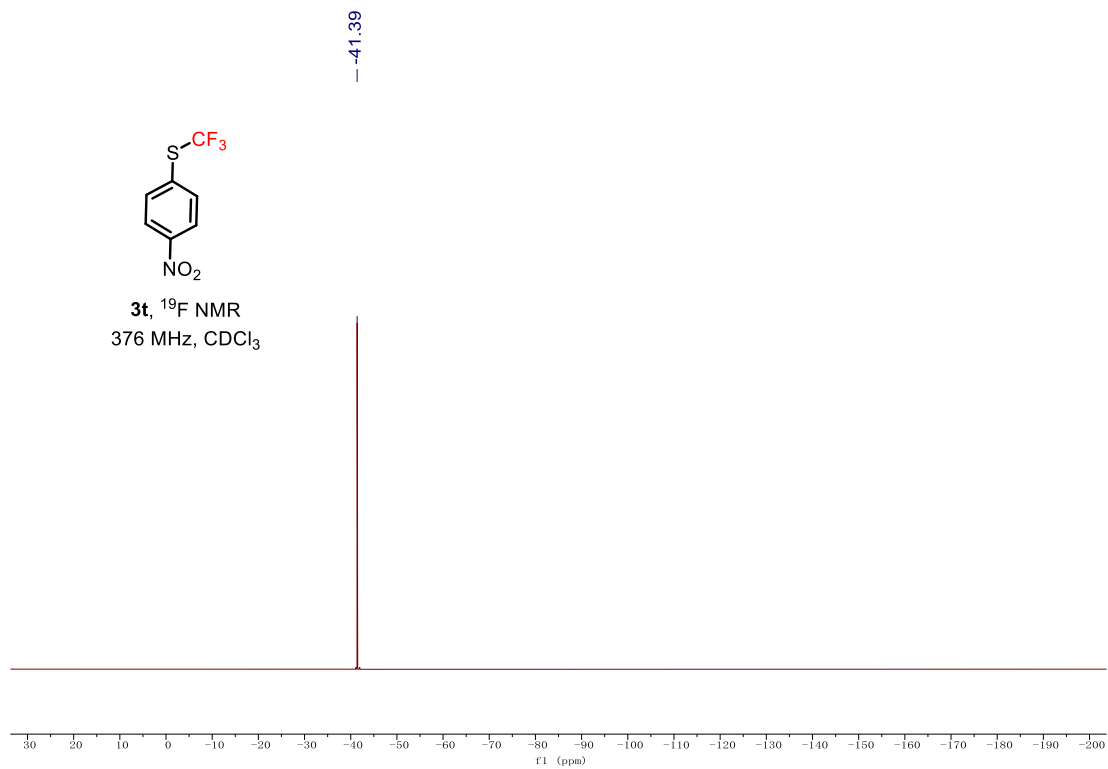


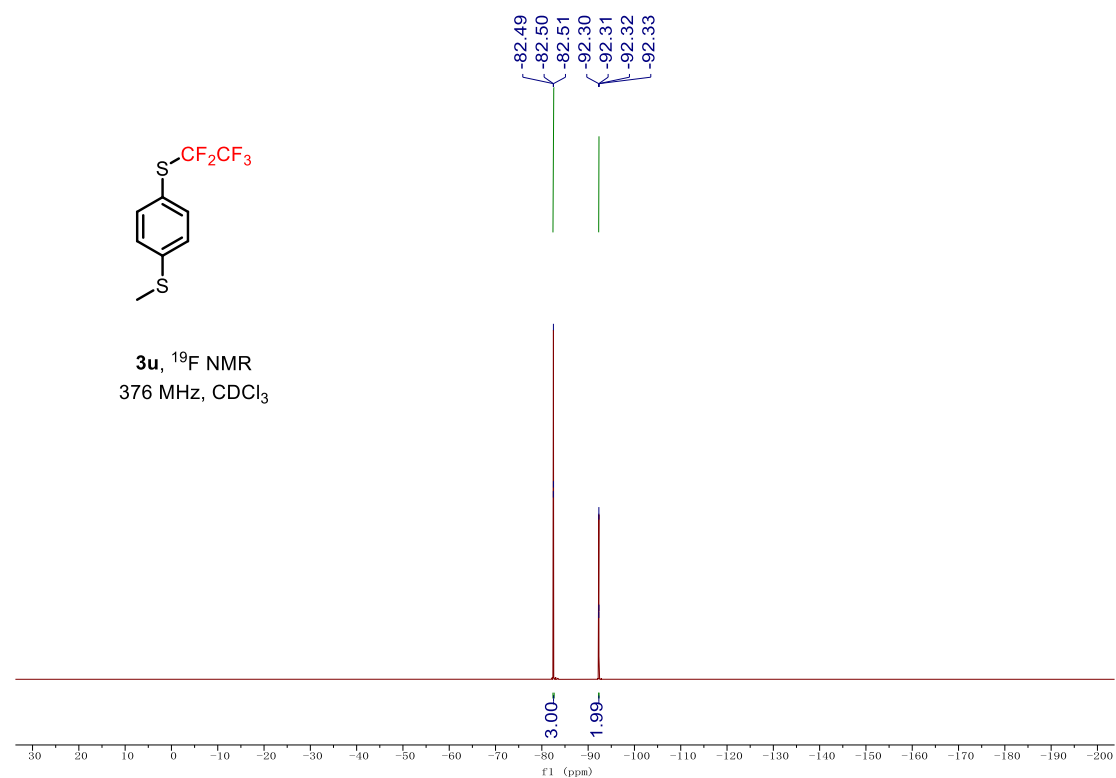
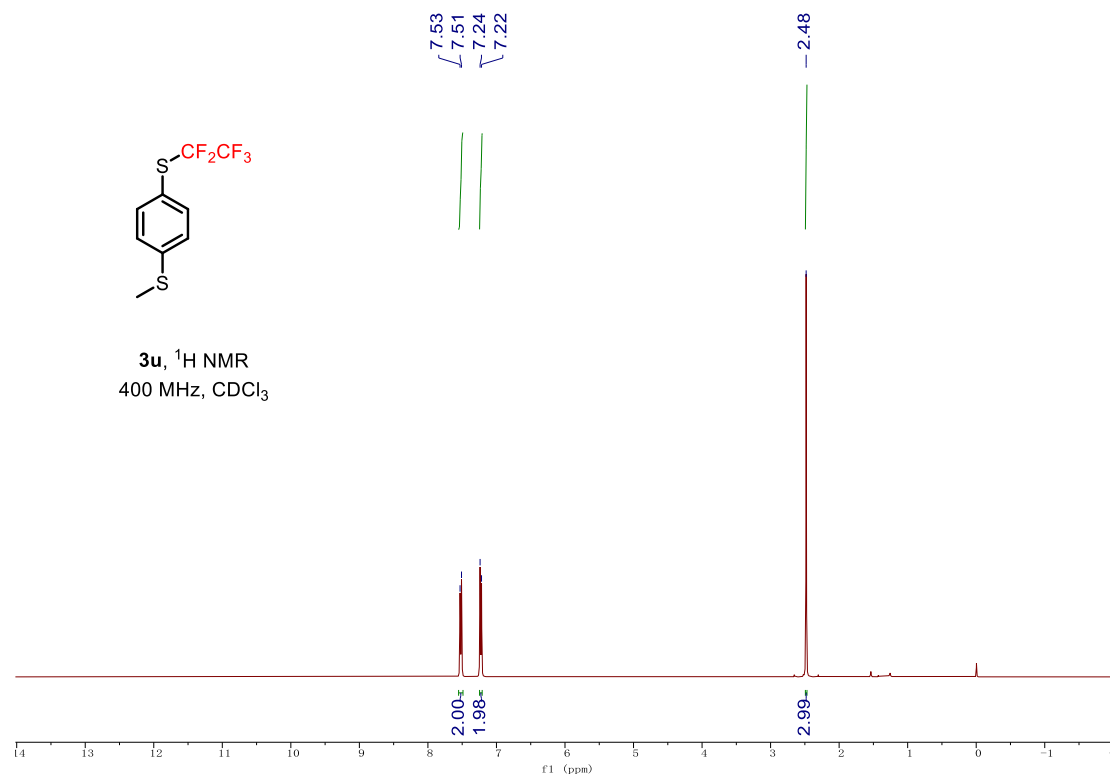
3s, ^{13}C NMR
101 MHz, CDCl_3

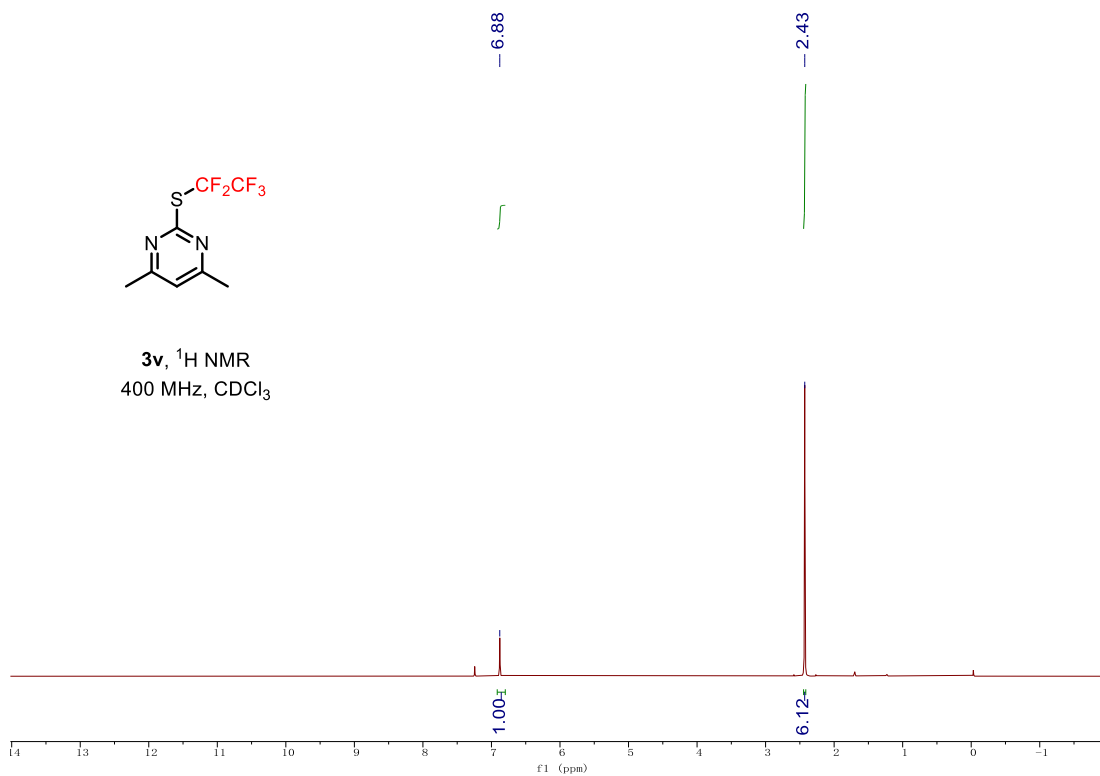
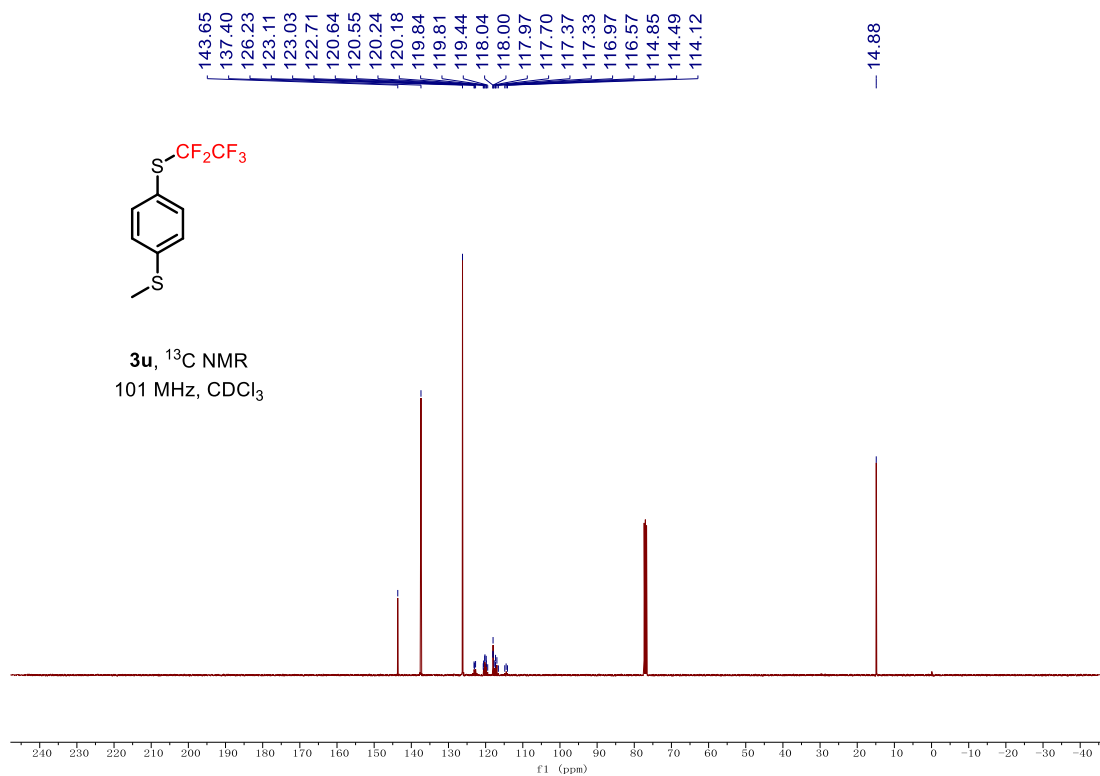


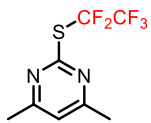
3t, ^1H NMR
400 MHz, CDCl_3



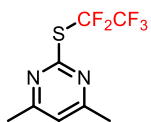
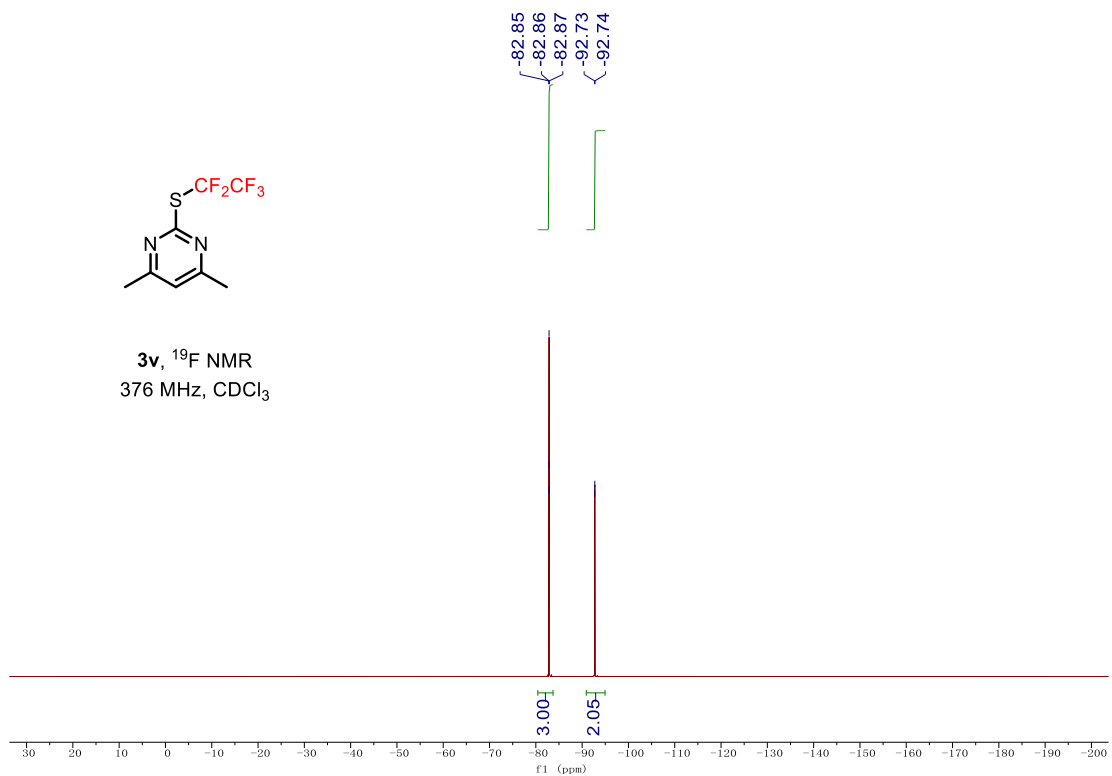




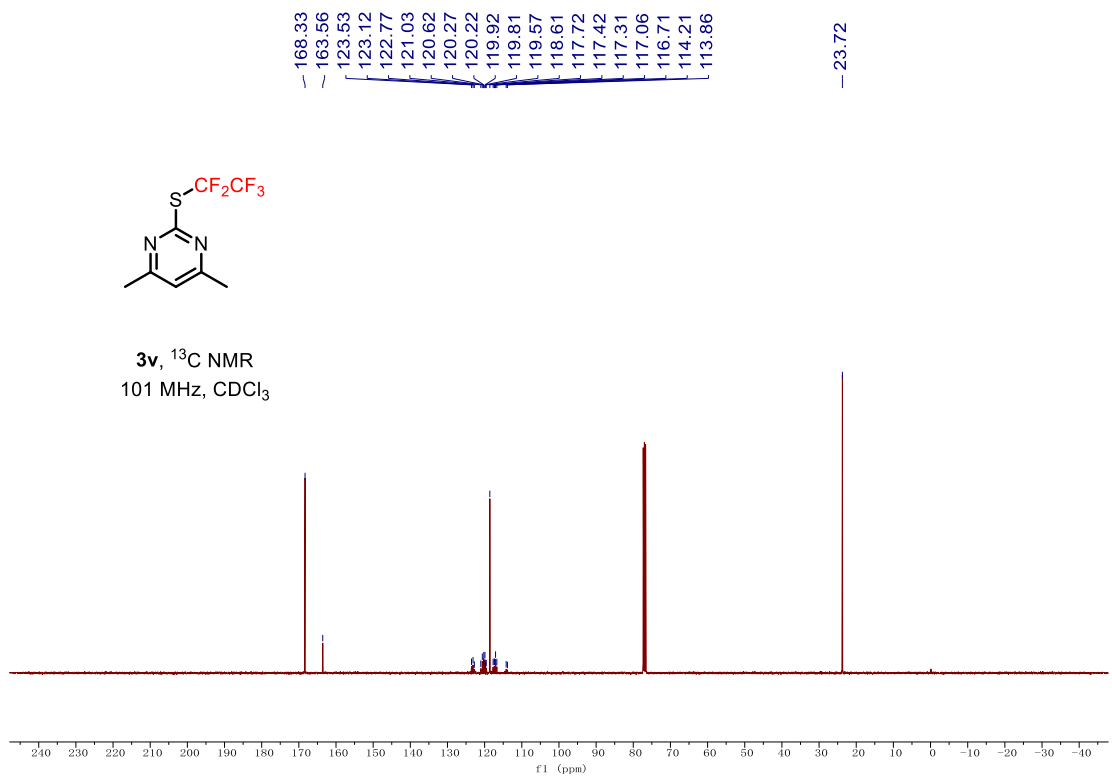


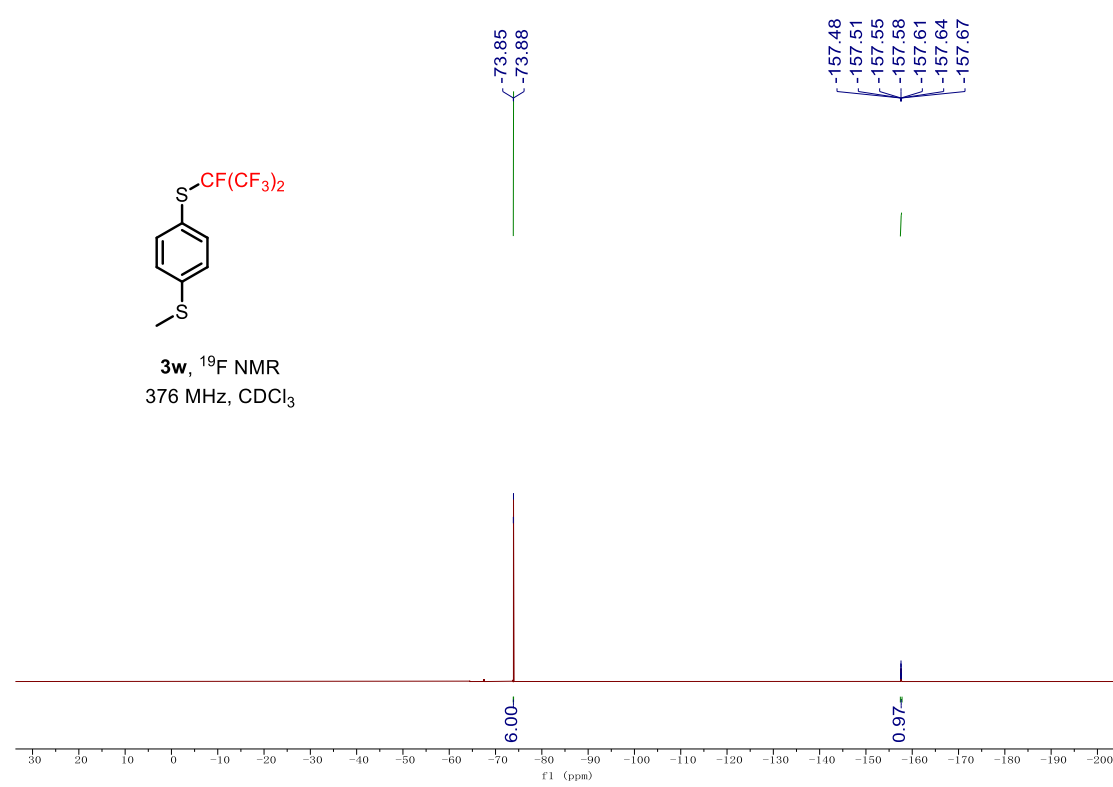
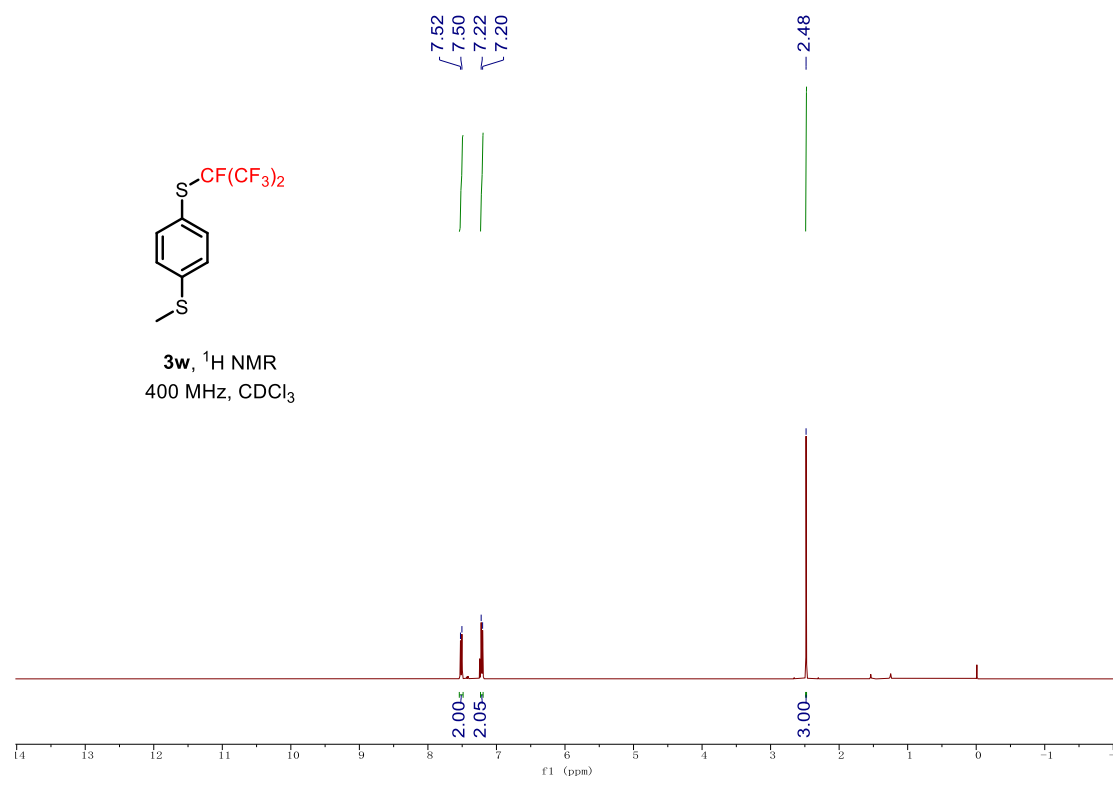


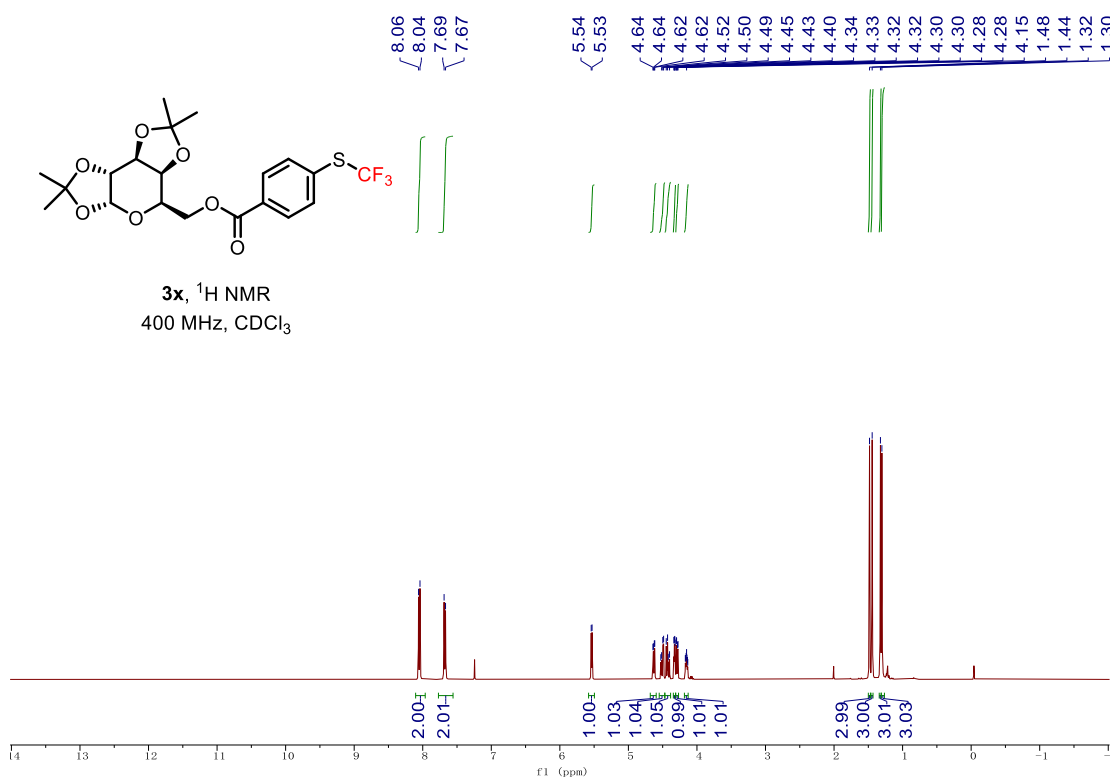
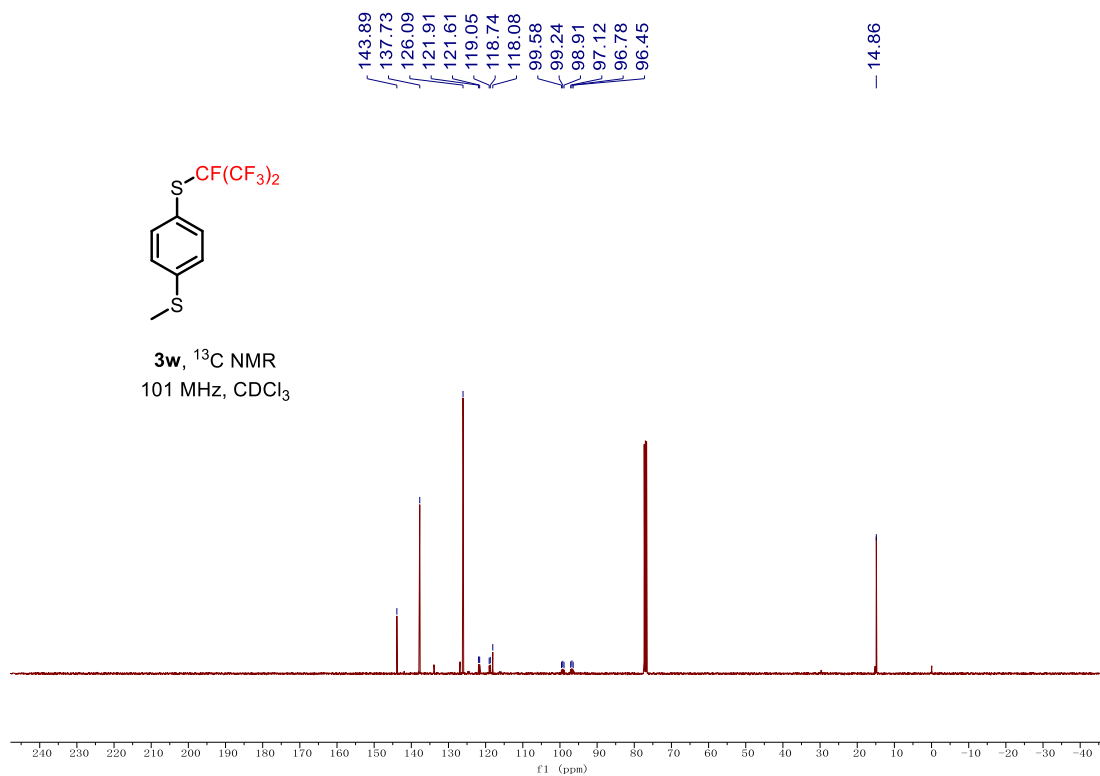
3v, ^{19}F NMR
376 MHz, CDCl_3

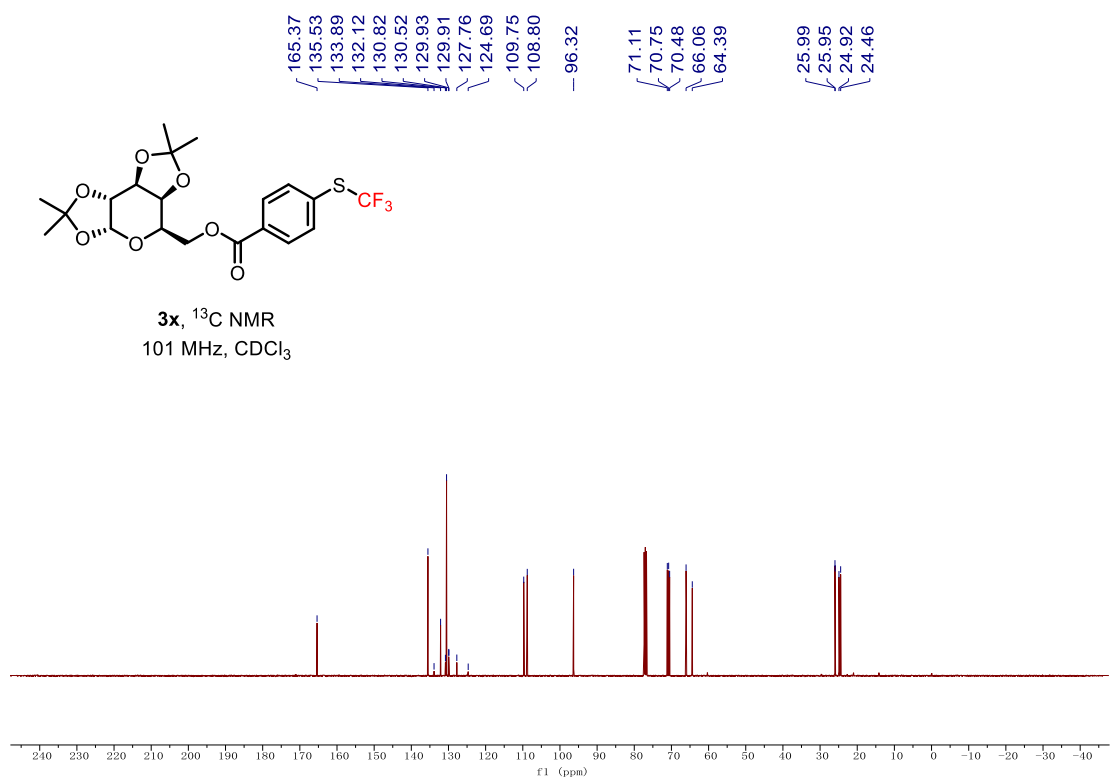
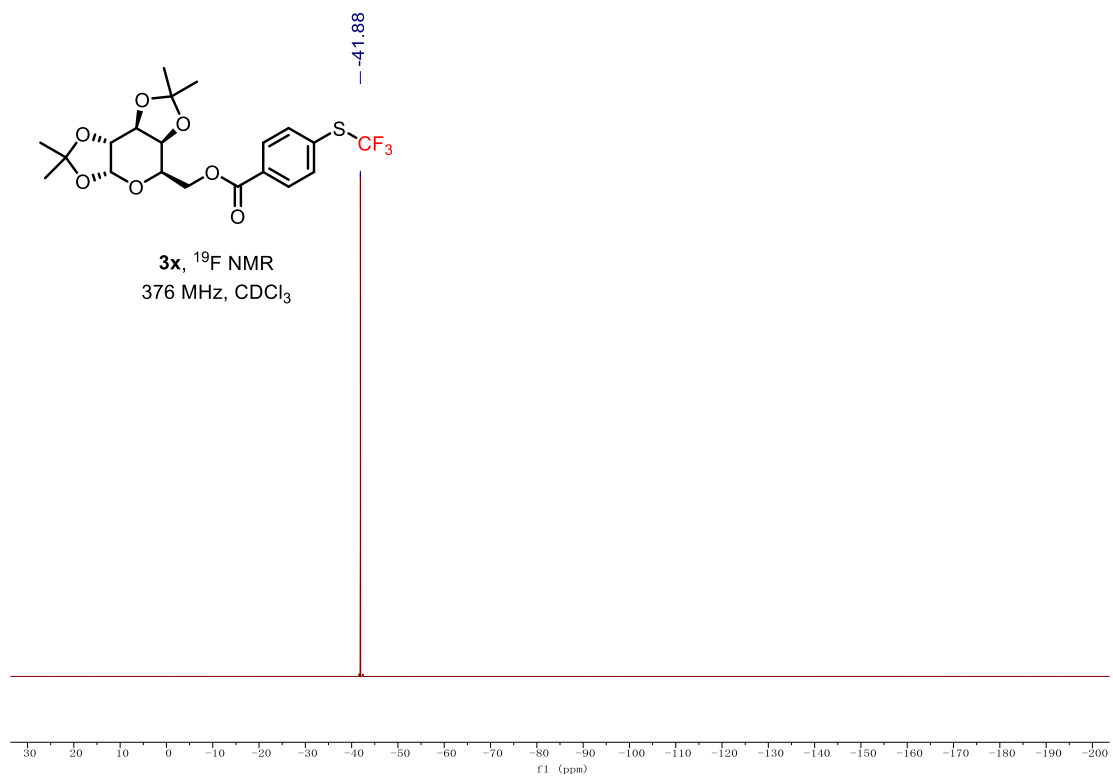


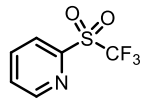
3v, ^{13}C NMR
101 MHz, CDCl_3



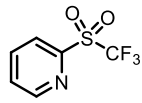
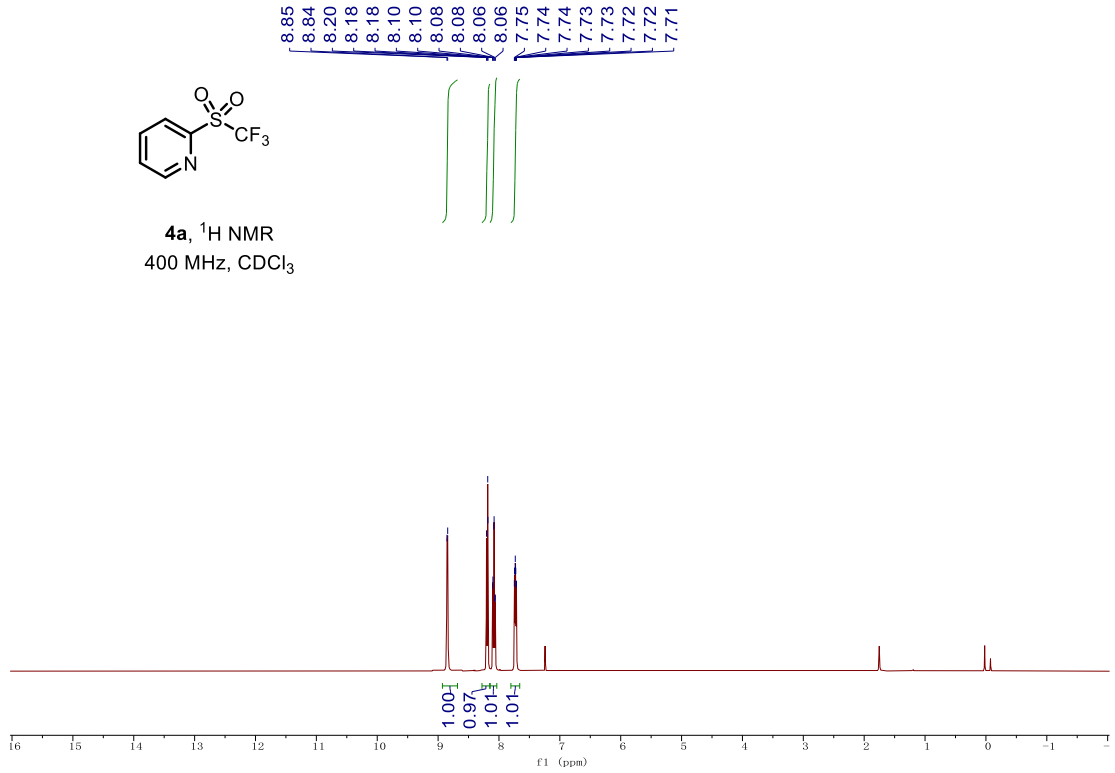




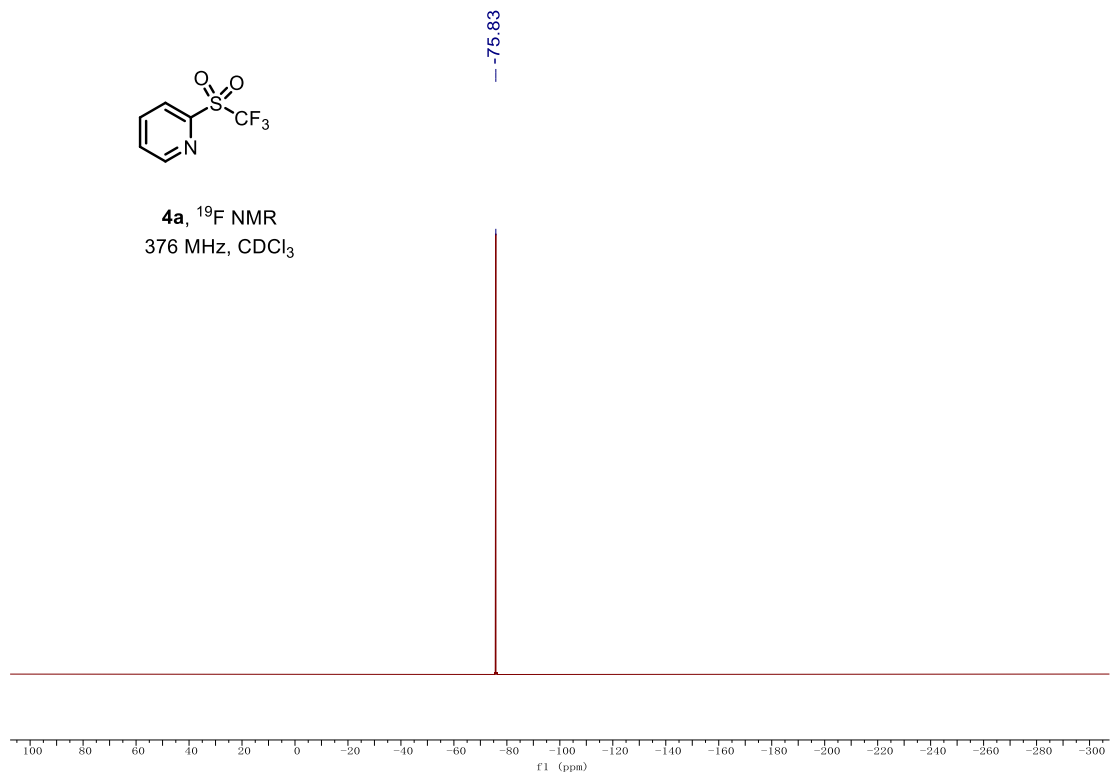


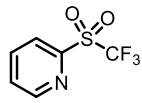


4a, ^1H NMR
400 MHz, CDCl_3

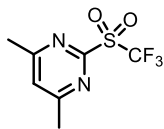
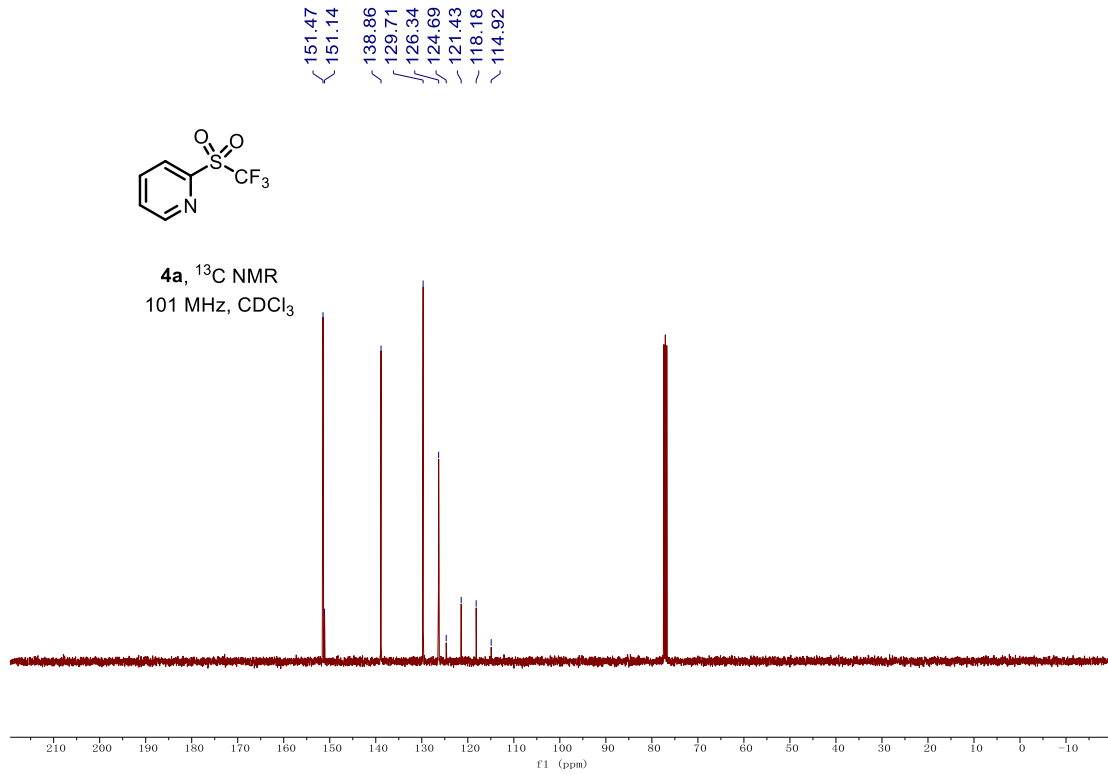


4a, ^{19}F NMR
376 MHz, CDCl_3

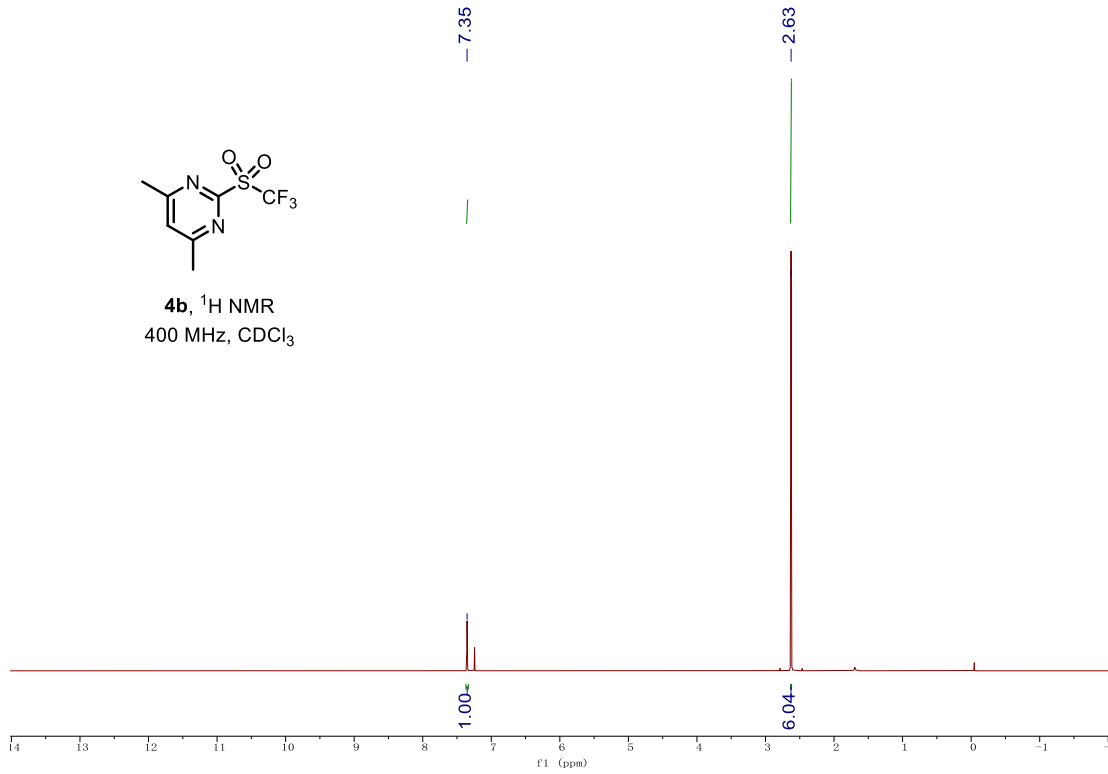


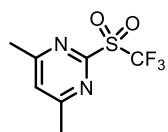


4a, ^{13}C NMR
101 MHz, CDCl_3

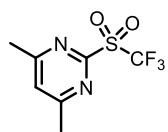
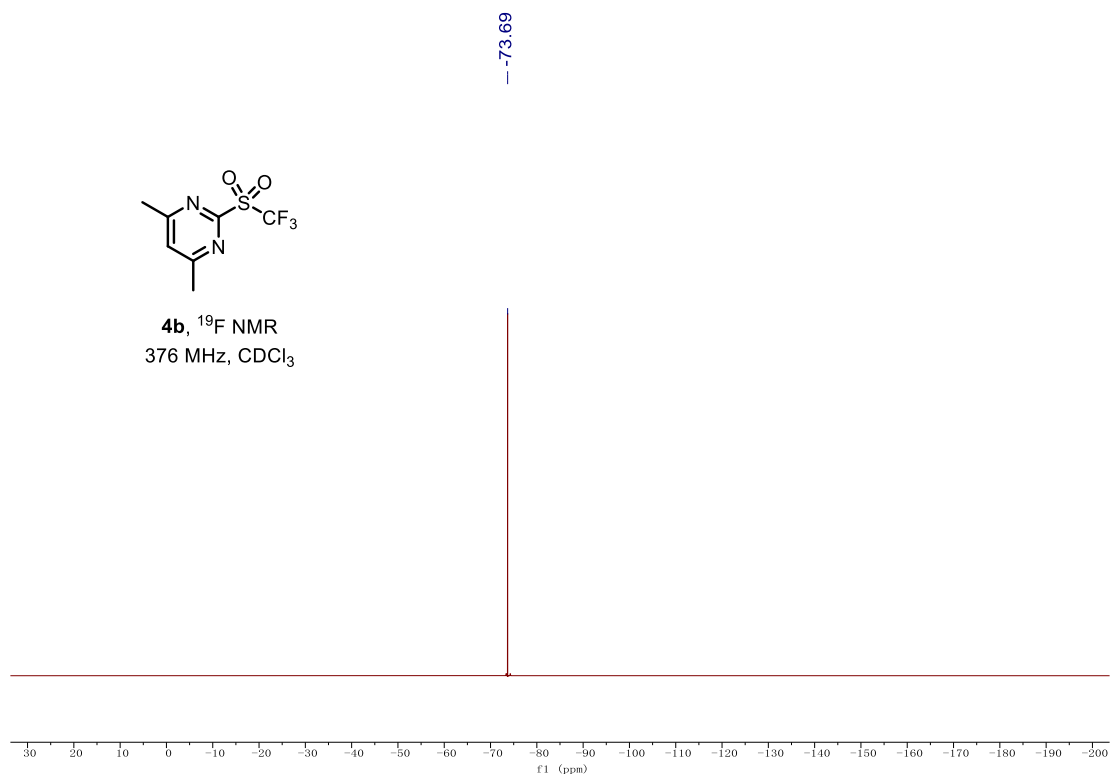


4b, ^1H NMR
400 MHz, CDCl_3

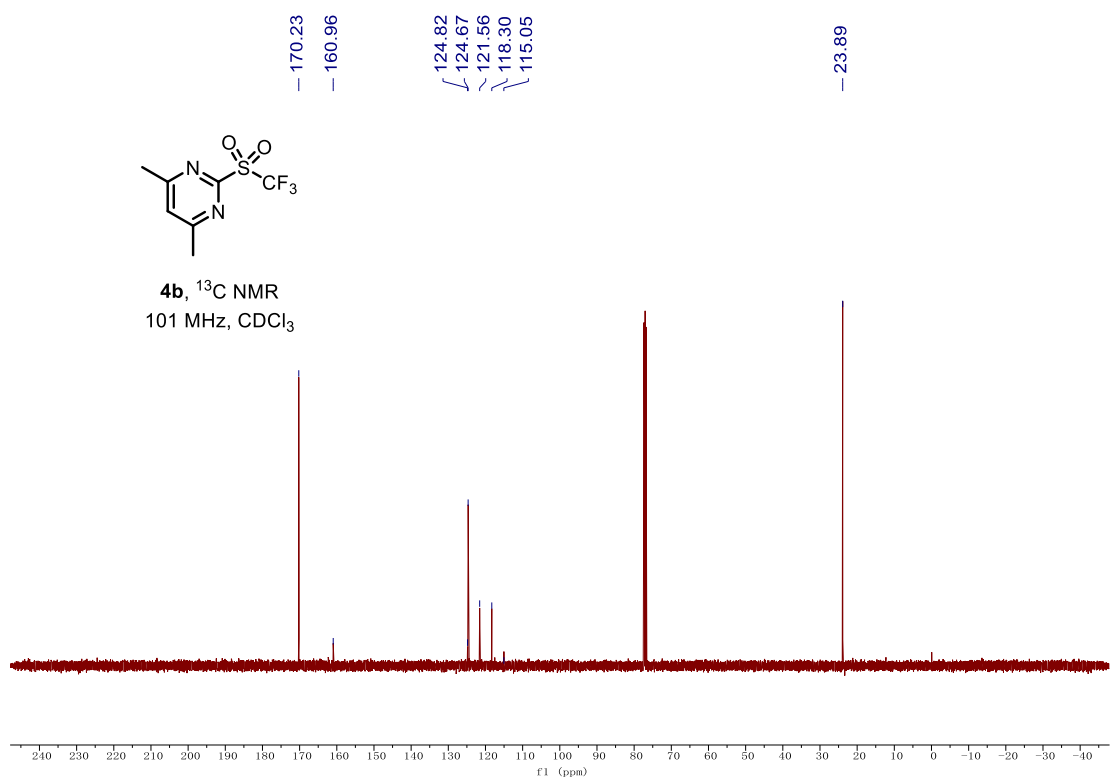


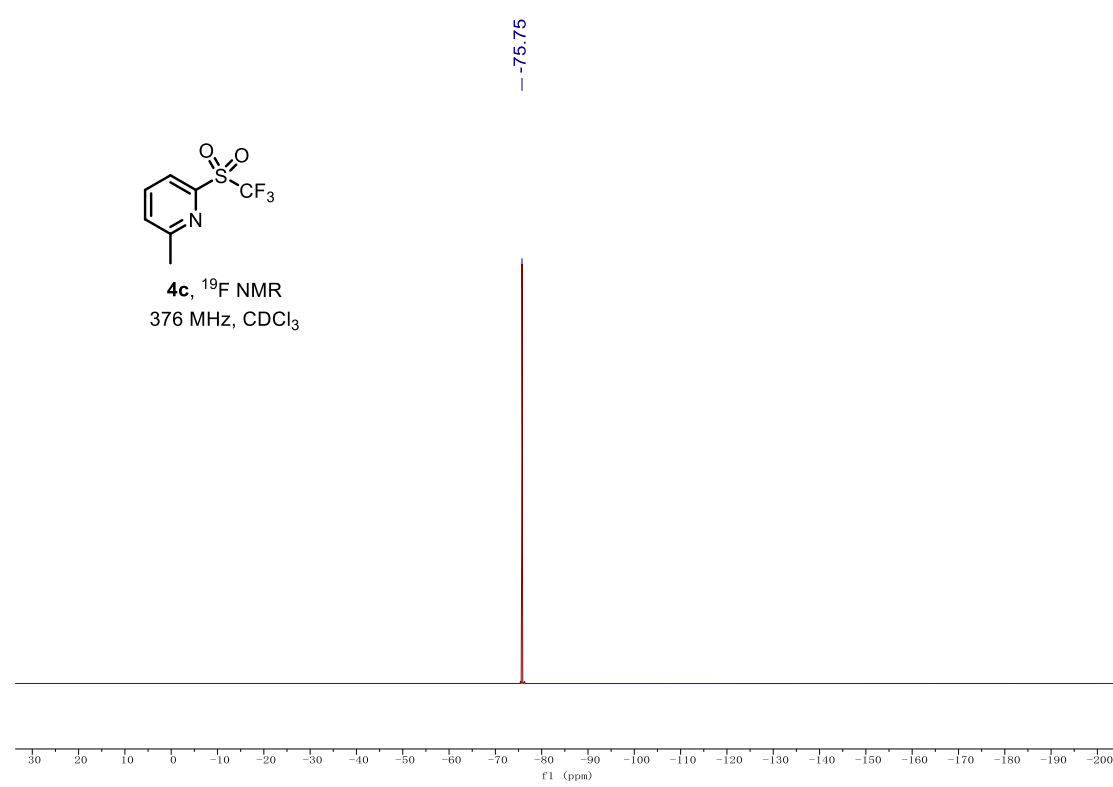
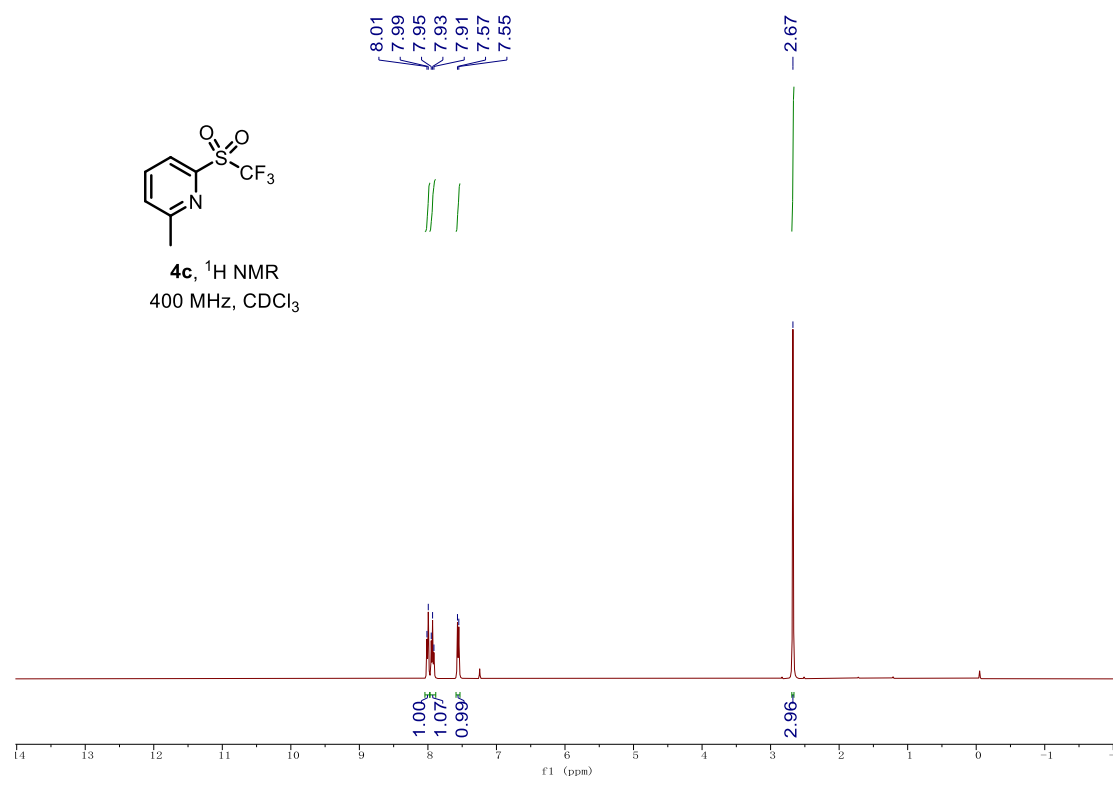


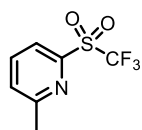
4b, ^{19}F NMR
376 MHz, CDCl_3



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







4c, ^{13}C NMR
101 MHz, CDCl_3

161.68
150.42
150.40
138.58
129.71
124.74
123.44
121.49
118.23
114.97

24.28

