

Supporting Information for

The Thiolation of Pentafluorobenzene with Disulfides by C–H, C–F Bond Activation and C-S Bond Formation

1) General Information

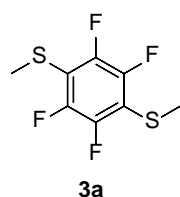
Unless otherwise noted, all starting materials were commercially available and were used without further purification. All reactions were carried out under room temperature and air atmosphere.

^1H , ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AV400 Spectrometer (FT, 400 MHz for ^1H ; 100 MHz for ^{13}C ; 376 MHz for ^{19}F) at room temperature and CDCl_3 as the solvent with tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). GC analyses were recorded on TECHCOMP GC7900 spectrometer using FID. Melting points were detected by YUHUA X-4 Micromelting Point Apparatus.

2) Synthesis of Starting Materials

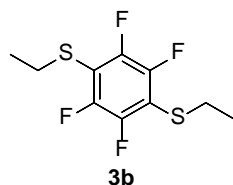
Preparation of 3a~q

0.4 mmol pentafluorobenzene, 0.8 mmol disulfides, 0.8 mmol KOH and 2 mL DMF were added to a grinding tube. After that the mixture was stirred at room temperature (25°C) for 10 h. The reaction mixture was quenched with water and extracted with ethyl acetate. The extraction was washed with brine and dried over Na_2SO_4 . The solvent was then evaporated in vacuo and the residue was purified by using silicon gel column with petroleum ether to afford the final products.

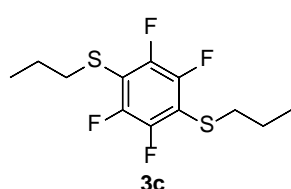


1,4-bis(methylmercapto)-2,3,5,6-tetrafluorobenzene¹ (**3a**): White solid, m.p. $90 \sim 91^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ : 2.52 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 147.90 ~ 147.63 (m), 145.41 ~ 145.15 (m), 115.68 ~ 115.42 (m), 17.72; ^{19}F NMR (376 MHz, CDCl_3) δ : -134.84 (s,

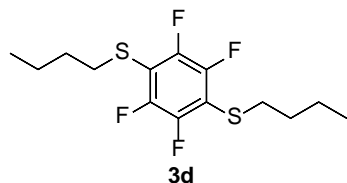
4F).



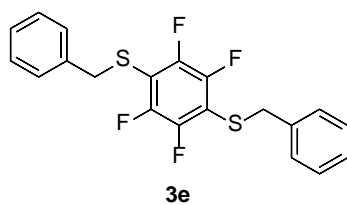
1,4-bis(ethylthio)-2,3,5,6-tetrafluorobenzene² (**3b**): White solid, m.p. 43 ~ 44 °C. ¹H NMR (400 MHz, CDCl₃) δ: 2.97 (q, *J* = 7.2 Hz, 4H), 1.26 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ: 148.26 ~ 148.00 (m), 145.78 ~ 145.52 (m), 114.36 ~ 113.94 (m), 28.82, 15.00. ¹⁹F NMR (376 MHz, CDCl₃) δ: -134.00 (s, 4F).



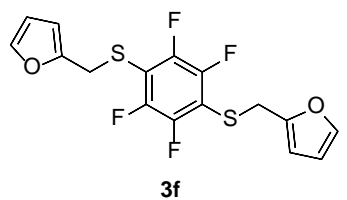
1,4-bis(propylthio)-2,3,5,6-tetrafluorobenzene³ (**3c**): White solid, m.p. 38 ~ 39 °C. ¹H NMR (400 MHz, CDCl₃) δ: 2.90 (t, *J* = 7.2 Hz, 4H), 1.63 ~ 1.54 (m, 4H), 1.00 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ: 148.31 ~ 148.04 (m), 145.83 ~ 145.56 (m), 114.67 ~ 114.11 (m), 36.61, 23.20, 12.95. ¹⁹F NMR (376 MHz, CDCl₃) δ: -134.02 (s, 4F).



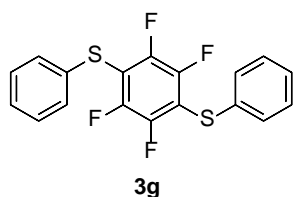
1,4-bis(butylthio)-2,3,5,6-tetrafluorobenzene³ (**3d**): Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ: 2.94 (t, *J* = 7.2 Hz, 4H), 1.59 ~ 1.51 (m, 4H), 1.47 ~ 1.38 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ: 148.27 ~ 148.01 (m), 145.79 ~ 145.53 (m), 114.65 ~ 114.23 (m), 34.35, 31.85, 21.54, 13.53. ¹⁹F NMR (376 MHz, CDCl₃) δ: -134.03 (s, 4F).



1,4-bis(benzylthio)-2,3,5,6-tetrafluorobenzene (**3e**): White solid, m.p. 140 ~ 143 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.25 ~ 7.22 (m, 6H), 7.21 ~ 7.19 (m, 4H), 4.09 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ: 148.23 ~ 147.97 (m), 145.74 ~ 145.48 (m), 136.42, 128.77, 128.64, 127.77, 114.22 ~ 113.80 (m), 38.88. ¹⁹F NMR (376 MHz, CDCl₃) δ: -133.38 (s, 4F). HRMS (ESI) calcd for C₂₀H₁₅F₄S₂ [M+H]⁺ 395.0551; found 395.0556.

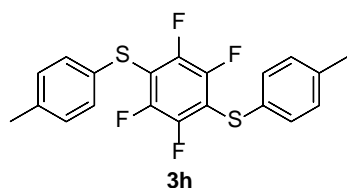


1,4-bis(furfurylthio)-2,3,5,6-tetrafluorobenzene (**3f**): Yellow solid, m.p. 93 ~ 95 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.31 (dd, *J* = 1.2 Hz, 0.8 Hz, 2H), 6.22 (dd, *J* = 2 Hz, 1.2 Hz, 2H), 6.03 (d, *J* = 2.8 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ: 149.50, 148.29 ~ 148.03 (m), 145.79 ~ 145.53 (m), 142.92, 113.95 ~ 113.64 (m), 110.50, 108.57, 31.15. ¹⁹F NMR (376 MHz, CDCl₃) δ: -133.31 (s, 4F). HRMS



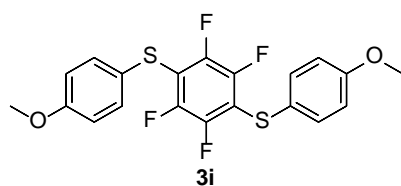
(ESI) calcd for $C_{16}H_{11}F_4O_2S_2$ $[M+H]^+$ 375.0131; found 375.0130.

1,4-bis(phenylthio)-2,3,5,6-tetrafluorobenzene⁴ (**3g**): White solid, m.p. 109 ~ 111 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.41 ~ 7.38 (m, 4H), 7.33 ~ 7.28 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.36 ~ 148.10 (m), 145.86 ~ 145.55 (m), 132.59, 131.00, 129.41, 128.10, 115.44 ~ 115.03 (m). ¹⁹F NMR (376 MHz, CDCl₃) δ: -131.96 (s, 4F).



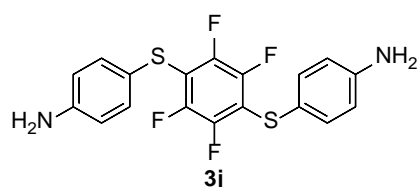
1,4-bis(*p*-tolylthio)-2,3,5,6-tetrafluorobenzene⁴ (**3h**):

White solid, m.p. 121 ~ 124 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.35 (d, *J* = 8.0 Hz, 4H), 7.13 (d, *J* = 8.0 Hz, 4H), 2.34 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.24 ~ 147.99 (m), 145.74 ~ 145.48 (m), 138.58, 131.81, 130.17, 128.92, 116.00 ~ 115.52 (m), 21.15. ¹⁹F NMR (376 MHz, CDCl₃) δ: -130.67 (s, 4F).



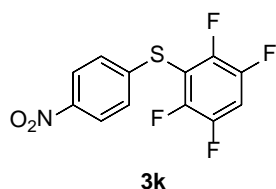
1,4-bis(4-methoxyphenylthio)-2,3,5,6-tetrafluorobenzene⁴ (**3i**): White solid, m.p. 110 ~ 112 °C.

¹H NMR (400 MHz, CDCl₃) δ: 7.44 (d, *J* = 8.0 Hz, 4H), 6.82 (d, *J* = 8.0 Hz, 4H), 3.78 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 160.25, 148.00 ~ 147.75 (m), 145.50 ~ 145.25 (m), 134.80, 122.55, 116.46 ~ 116.13 (m), 114.93, 55.37. ¹⁹F NMR (376 MHz, CDCl₃) δ: -133.36 (s, 4F).

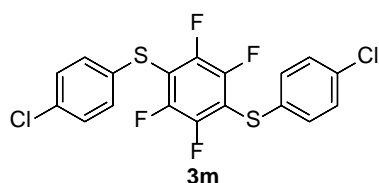


1,4-bis(4-aminophenylthio)-2,3,5,6-tetrafluorobenzene (**3j**): Yellow solid, m.p. 205 ~ 208 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.24 (d, *J* = 8.4 Hz, 4H), 6.57 (d, *J* = 8.4 Hz, 4H), 5.77 (s, 4H). ¹³C NMR

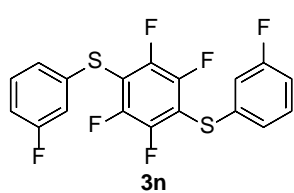
(100 MHz, CDCl₃) δ: 147.90 ~ 147.64 (m), 147.13, 145.45 ~ 145.15 (m), 135.38, 119.11, 115.40, 115.16 ~ 114.95 (m). ¹⁹F NMR (376 MHz, CDCl₃) δ: -133.87 (s, 4F). HRMS (ESI) calcd for $C_{18}H_{13}F_4N_2S_2$ $[M+H]^+$ 397.0451; found 397.0444.



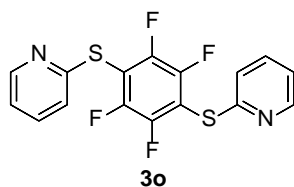
(4-nitrophenyl)(2,3,5,6-tetrafluorophenyl)sulfane⁴ (**3k**): Yellow solid, m.p. 94 ~ 96 °C. ¹H NMR (400 MHz, CDCl₃) δ: 8.13 ~ 8.10 (m, 2H), 7.30 ~ 7.28 (m, 2H), 7.25 ~ 7.21 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.40 ~ 148.20 (m), 147.69 ~ 147.39 (m), 146.58, 145.95 ~ 145.72 (m), 145.18 ~ 144.89 (m), 142.64, 127.97, 124.42, 111.69 ~ 111.29 (m), 108.87 ~ 108.42 (m). ¹⁹F NMR (376 MHz, CDCl₃) δ: -131.27 ~ -131.37 (m, 2F), -135.95 ~ -136.05 (m, 2F).



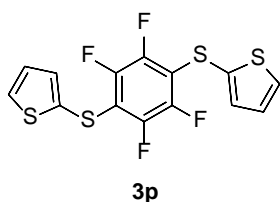
1,4-bis(4-chlorophenylthio)-2,3,5,6-tetrafluorobenzene⁴ (**3m**): White solid, m.p. 164 ~ 167 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.35 (d, *J* = 8.4 Hz, 4H), 7.28 (d, *J* = 8.4 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.24 ~ 147.99 (m), 145.72 ~ 145.47 (m), 134.63, 132.67, 130.79, 129.64, 115.44 ~ 115.17 (m). ¹⁹F NMR (376 MHz, CDCl₃) δ: -131.77 (s, 4F).



1,4-bis(3-fluorophenylthio)-2,3,5,6-tetrafluorobenzene⁴ (**3n**): White solid, m.p. 75 ~ 76 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.29 ~ 7.23 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.06 ~ 7.03 (m, 2H), 6.99 ~ 76.94 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 162.8 (d, *J* = 248.4 Hz), 148.42 ~ 148.17 (m), 145.90 ~ 145.65 (m), 134.56 (d, *J* = 7.8 Hz), 130.73 (d, *J* = 8.4 Hz), 126.12 (d, *J* = 3.1 Hz), 117.25 (d, *J* = 23.3 Hz), 115.21 (d, *J* = 21.0 Hz), 115.01 ~ 114.76 (m). ¹⁹F NMR (376 MHz, CDCl₃) δ: -110.91 (s, 2F), -131.21 (s, 4F).



2,3,5,6-tetrafluoro-1,4-bis(2-pyridylsulfenyl)benzene (**3o**): White solid, m.p. 155 ~ 158 °C. ¹H NMR (400 MHz, CDCl₃) δ: 8.43 (d, *J* = 4.4 Hz, 2H), 7.60 ~ 7.55 (m, 4H), 7.09 ~ 7.06 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 155.47, 150.11, 148.70 ~ 148.45 (m), 146.19 ~ 145.93 (m), 137.07, 121.92, 121.19, 112.69 ~ 112.26 (m). ¹⁹F NMR (376 MHz, CDCl₃) δ: -130.68 (s, 4F)



2,3,5,6-tetrafluoro-1,4-bis(2-thienylsulfenyl)benzene (**3p**):

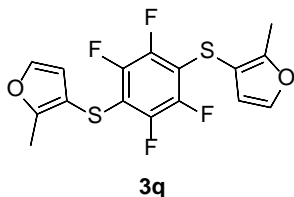
Yellow solid, m.p. 115 ~ 117 °C. ¹H NMR (400 MHz, CDCl₃)

δ: 7.40 (dd, *J* = 5.2, 1.2 Hz, 2H), 7.36 (dd, *J* = 3.8, 0.8 Hz, 2H),

6.97 (dd, *J* = 5.2, 3.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ:

147.93 ~ 147.65 (m), 145.39 ~ 145.14 (m), 136.69, 131.56,

128.69, 127.68, 116.80 ~ 116.39 (m). ¹⁹F NMR (376 MHz, CDCl₃) δ: -133.02 (s, 4F).



2,3,5,6-tetrafluoro-1,4-bis(2-methyl-3-furyl)sulfenyl)benzene (**3q**):

Yellow solid, m.p. 100 ~ 102 °C. ¹H NMR (400 MHz, CDCl₃)

δ: 7.24 (d, *J* = 2 Hz, 2H), 6.38 (d, *J* = 1.6 Hz, 2H), 2.41 (s,

6H). ¹³C NMR (100 MHz, CDCl₃) δ: 157.30, 147.95 ~ 147.66

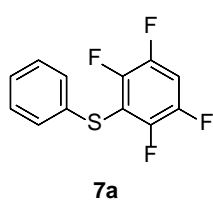
(m), 145.45 ~ 145.23 (m), 140.84, 115.24, 111.86 ~ 111.68 (m), 107.09, 11.86. ¹⁹F NMR

(376 MHz, CDCl₃) δ: -133.97 (s, 4F). HRMS (ESI) calcd for C₁₆H₁₁F₄O₂S₂ [M+H]⁺

375.0131; found 375.0129.

Preparation of 7a and 7b

5 mmol pentafluorobenzene, 5 mmol arylthiols sodium and 25 mL DMF were added to a round bottomed flask. After that the mixture was stirred at room temperature (25 °C) for 10 h. The reaction mixture was quenched with water and extracted with ethyl acetate. The extraction was washed with brine and dried over Na₂SO₄. The solvent was then evaporated in vacuo and the residue was purified by using silicon gel column with petroleum ether to afford the final products.



1-phenylthio-2,3,5,6-tetrafluorobenzene⁵ (**7a**): Colorless liquid. ¹H

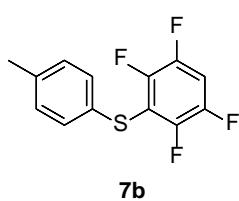
NMR (400 MHz, CDCl₃) δ: 7.42 ~ 7.39 (m, 2H), 7.35 ~ 7.29 (m,

3H), 7.18 ~ 7.09 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.26 ~

148.07 (m), 147.47 ~ 147.17 (m), 145.81 ~ 145.61 (m), 144.98 ~

144.68 (m), 133.04, 130.55, 129.36, 127.85, 115.08 ~ 114.68 (m), 107.24 ~ 106.79 (m).

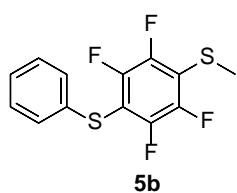
¹⁹F NMR (376 MHz, CDCl₃) δ: -132.63 ~ -132.72 (m, 2F), -137.50 ~ -137.60 (m, 2F).



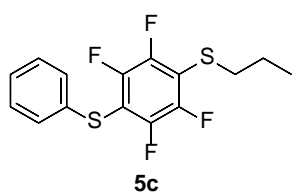
1-phenylthio-2,3,5,6-tetrafluorobenzene (**7b**): Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ : 7.32 (d, $J = 8$ Hz, 2H), 7.11 (d, $J = 8$ Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 148.13 ~ 147.94 (m), 147.41 ~ 147.15 (m), 145.68 ~ 145.48 (m), 144.92 ~ 144.62 (m), 138.35, 131.44, 130.12, 129.25, 115.68 (t, $J = 20$ Hz), 106.67 (t, $J = 22.6$ Hz), 21.13. ^{19}F NMR (376 MHz, CDCl_3) δ : -133.03 ~ -133.13 (m, 2F), -137.71 ~ -137.81 (m, 2F).

Preparation of 5b and 5h

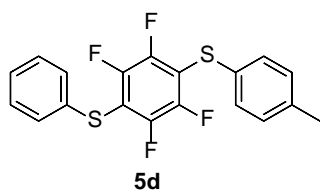
0.4 mmol pentafluorobenzene, 0.4 mmol arylsulfane tetrafluorobenzene and 2 mL DMF were added to a grinding tube. After that the mixture was stirred at room temperature (25 °C) for 10 h. The reaction mixture was quenched with water and extracted with ethyl acetate. The extraction was washed with brine and dried over Na_2SO_4 . The solvent was then evaporated in vacuo and the residue was purified by using silicon gel column with petroleum ether to afford the final products.



1-methylmercapto-4-phenylmercapto-2,3,5,6-tetrafluorobenzene (**5b**): Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ : 7.41 ~ 7.39 (m, 2H), 7.35 ~ 7.29 (m, 3H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 148.32 ~ 147.61 (m), 145.82 ~ 145.19 (m), 133.09, 130.58, 129.35, 127.86, 118.17 ~ 117.72 (m), 113.19 ~ 112.64 (m), 17.47 (t, $J = 4.3$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ : -132.85 ~ -132.95 (m, 2F), -134.12 ~ -134.23 (m, 2F).



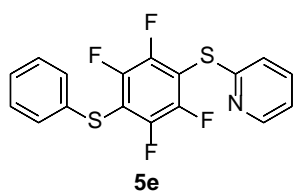
propyl(2,3,5,6-tetrafluoro-4-(p-tolylthio)phenyl)-sulfane (**5c**): Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ : 7.37 ~ 7.35 (m, 2H), 7.30 ~ 7.24 (m, 3H), 2.93 (t, $J = 7.2$ Hz, 2H), 1.64 ~ 1.55 (m, 2H), 1.00 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 148.31 ~ 148.02 (m), 145.90 ~ 145.66 (m), 133.02, 130.60, 129.37, 127.88, 129.21, 116.38 (t, $J = 20$ Hz), 113.29 (t, $J = 20$ Hz), 36.52 (t, $J = 3.1$ Hz), 23.26, 13.02. ^{19}F NMR (376 MHz, CDCl_3) δ : -133.15 ~ -133.26 (m, 2F), -133.34 ~ -133.45 (m, 2F). HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{13}\text{F}_4\text{S}_2$ $[\text{M}+\text{H}]^+$ 333.0395; found 333.0398.



phenyl(2,3,5,6-tetrafluoro-4-(*p*-tolylthio)phenyl)-sulfane

(5d): White solid, m.p. 78 ~ 79 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.40 ~ 7.28 (m, 7H), 7.13 (d, *J* = 8 Hz 2H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.30 ~ 148.06

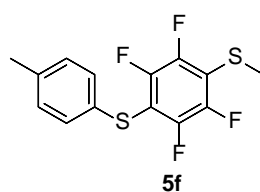
(m), 145.83 ~ 145.44 (m), 138.67, 132.70, 131.90, 130.90, 130.20, 129.83, 129.41, 128.76, 128.53, 128.05, 116.21 (t, *J* = 20 Hz), 114.78 (t, *J* = 20 Hz), 21.19. ¹⁹F NMR (376 MHz, CDCl₃) δ: -132.09 ~ -132.20 (m, 2F), -132.31 ~ -132.42 (m, 2F).



2-((2,3,5,6-tetrafluoro-4-(phenylthio)phenyl)thio)-pyridine

(5e): White solid, m.p. 114 ~ 115 °C. ¹H NMR (400 MHz, CDCl₃) δ: 8.38 ~ 8.37 (m, 1H), 7.62 ~ 7.58 (m, 1H), 7.46 ~ 7.44 (m, 2H), 7.37 ~ 7.31 (m, 3H), 7.28 ~ 7.24 (m, 1H), 7.12

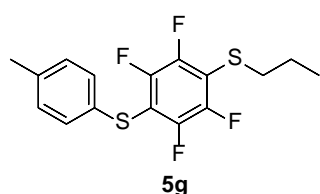
~ 7.09 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 155.39, 150.11, 148.61 ~ 148.11 (m), 146.16 ~ 145.63 (m), 137.05, 132.55, 131.03, 129.43, 128.12, 121.91, 121.19, 116.14 (t, *J* = 20 Hz), 111.56 (t, *J* = 20 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ: -130.54 ~ -130.66 (m, 2F), -132.04 ~ -132.16 (m, 2F). HRMS (ESI) calcd for C₁₇H₁₀F₄NS₂ [M+H]⁺ 368.0185; found 368.0180.



methyl(2,3,5,6-tetrafluoro-4-(*p*-tolylthio)phenyl)sulfane **(5f)**:

Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ: 7.33 (d, *J* = 8 Hz, 2H), 7.12 (d, *J* = 8 Hz, 2H), 2.55 (s, 3H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.19 ~ 147.63 (m), 145.73 ~

145.11 (m), 138.39, 131.48, 130.13, 129.27, 117.42 (t, *J* = 20 Hz), 113.80 (t, *J* = 20 Hz), 21.13, 17.53 (t, *J* = 4.3 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ: -133.19 ~ -133.29 (m, 2F), -134.23 ~ -134.34 (m, 2F).

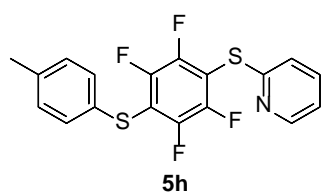


propyl(2,3,5,6-tetrafluoro-4-(*p*-tolylthio)phenyl)-sulfane

(5g): Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ: 7.32 (d, *J* = 8 Hz, 2H), 7.11 (d, *J* = 8 Hz, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.63 ~ 1.58 (m, 2H), 1.01 (t, *J* = 7.2 Hz,

3H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.36 ~ 147.93 (m), 145.85 ~ 145.42 (m), 138.41, 131.53, 131.45, 130.13, 129.21, 115.88 (t, *J* = 20 Hz), 114.22 (t, *J* = 20 Hz), 36.54 (t, *J* = 2.9 Hz), 23.25, 21.14, 13.01. ¹⁹F NMR (376 MHz, CDCl₃) δ: -133.15 ~ -133.26 (m,

2F), -133.34 ~ -133.45 (m, 2F). HRMS (ESI) calcd for C₁₆H₁₅F₄S₂ [M+H]⁺ 347.0551; found 347.0555.



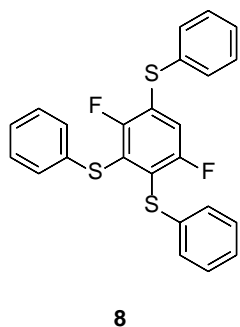
2-((2,3,5,6-tetrafluoro-4-(p-tolylthio)phenyl)thio)-pyridine

(**5h**): White solid, m.p. 89 ~ 90 °C. ¹H NMR (400 MHz, CDCl₃) δ: 8.36 ~ 8.35 (m, 1H), 7.59 ~ 7.55 (m, 1H), 7.38 (d, *J* = 7.6 Hz 2H), 7.21 (d, *J* = 8 Hz 1H), 7.13 (d, *J* = 8 Hz 2H),

7.10 ~ 7.06 (m, 1H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 155.49, 150.09, 148.57 ~ 148.17 (m), 146.13 ~ 145.51 (m), 138.60, 137.03, 131.89, 130.19, 128.71, 121.84, 121.15, 117.03 (t, *J* = 20 Hz), 111.07 (t, *J* = 20 Hz), 21.17. ¹⁹F NMR (376 MHz, CDCl₃) δ: -130.78 ~ -130.90 (m, 2F), -132.45 ~ -132.56 (m, 2F). HRMS (ESI) calcd for C₁₈H₁₂F₄NS₂ [M+H]⁺ 382.0342; found 382.0345.

Preparation of 8

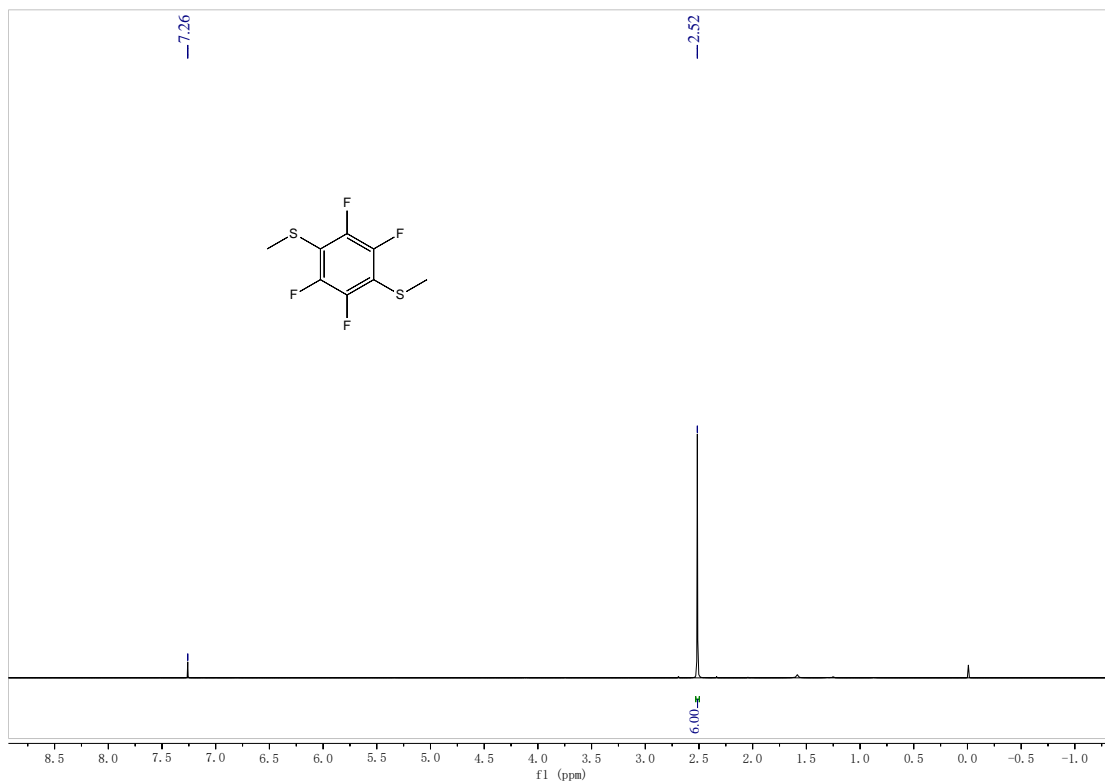
0.4 mmol pentafluorobenzene, 2.4 mmol sodium thiophenolate and 2 mL DMF were added to a grinding tube. After that the mixture was stirred at room temperature (25 °C) for 10 h. The reaction mixture was quenched with water and extracted with ethyl acetate. The extraction was washed with brine and dried over Na₂SO₄. The solvent was then evaporated in vacuo and the residue was purified by using silicon gel column with petroleum ether to afford the final products.



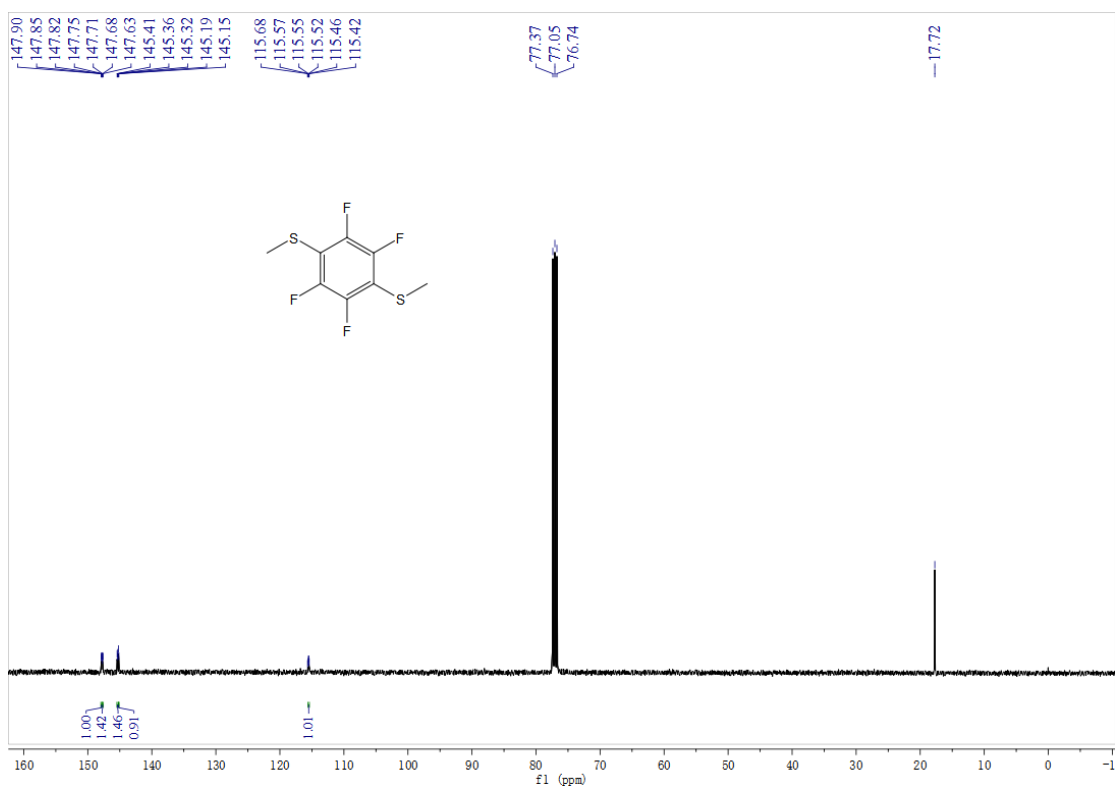
1,2,4-tris(phenylthio)-3,6-difluorobenzene⁶ (**8**): White solid. m.p. 93 - 95 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.57-7.54 (m, 2H), 7.48-7.46 (m, 3H), 7.28-7.19 (m, 10H), 6.65 (dd, *J* = 8.4, 6.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 159.27 (dd, *J* = 246.8, 2.9 Hz), 155.51 (dd, *J* = 243.4, 2.8 Hz), 135.31 (dd, *J* = 55.7, 1.6 Hz), 134.45, 130.26 - 130.18 (m), 129.98, 129.54, 129.43, 129.03,

128.98, 128.78, 128.10 (d, *J* = 18.9 Hz), , 126.85, 126.55, 123.82 (d, *J* = 19.5 Hz), 116.11 (dd, *J* = 29.2, 2.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ: -102.75 (d, *J* = 14.7 Hz, 1F), -104.38 (d, *J* = 14.7 Hz, 1F).

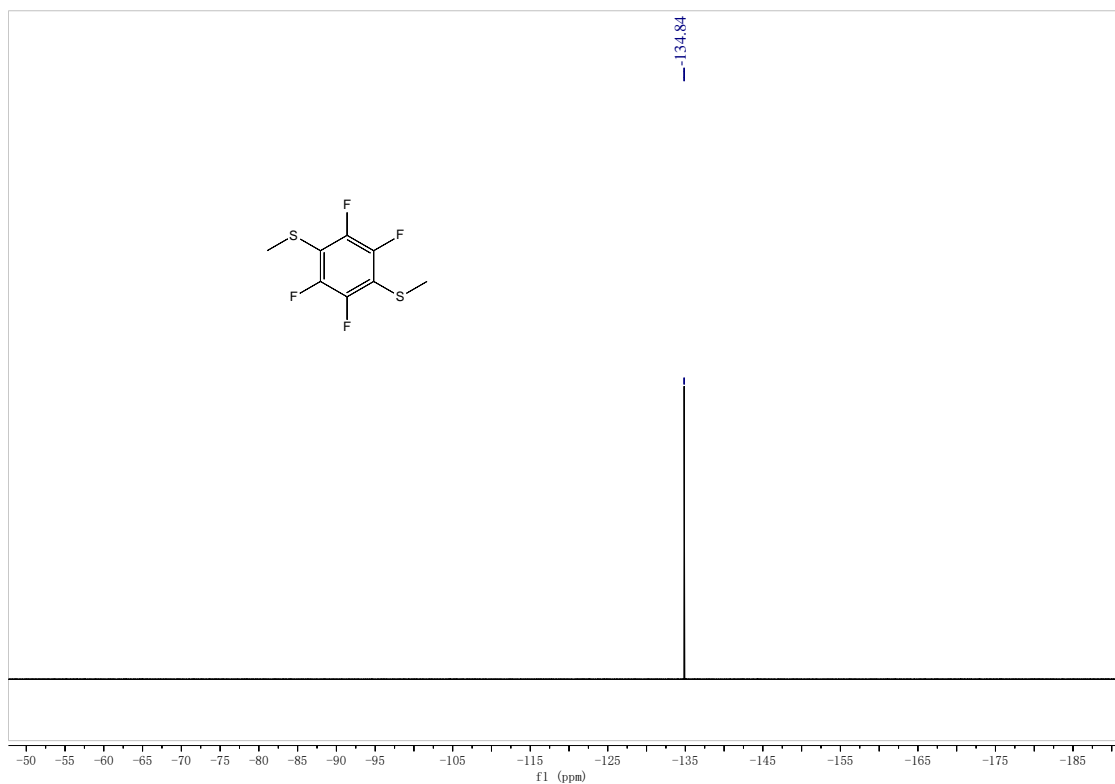
3) Scanned ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra



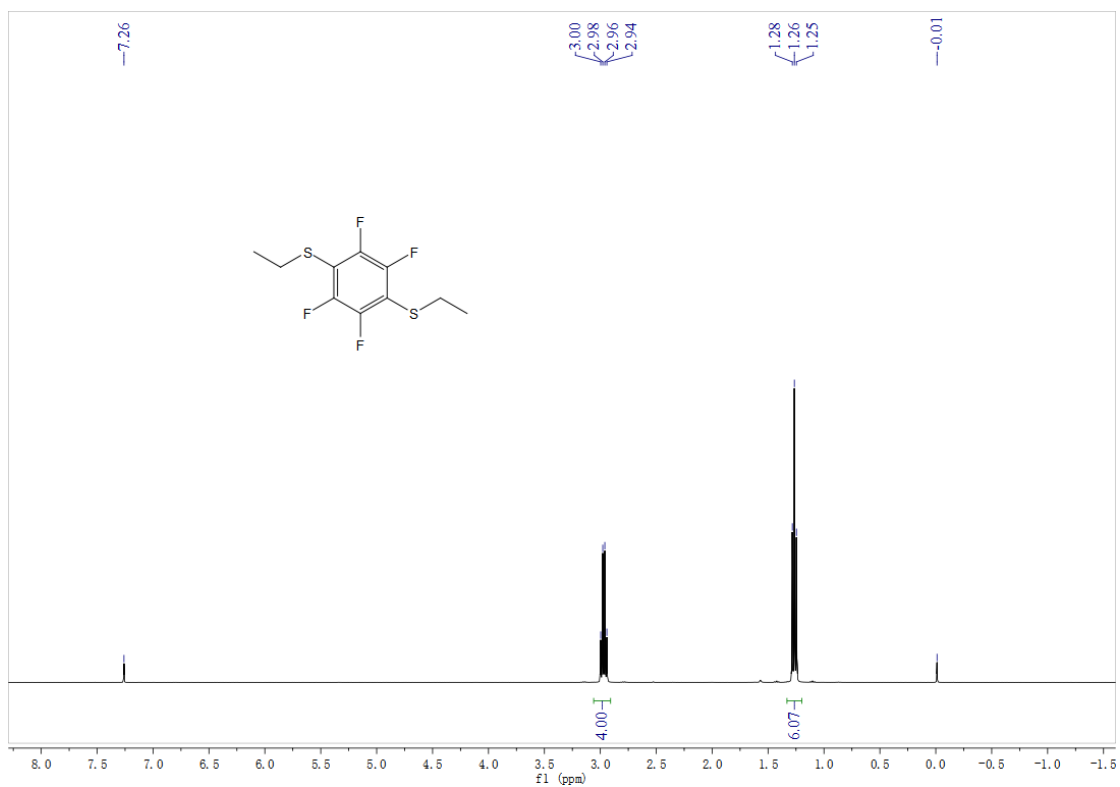
^1H NMR (400 MHz, CDCl_3): 1,4-bis(methylmercapto)-2,3,5,6-tetrafluorobenzene (**3a**)



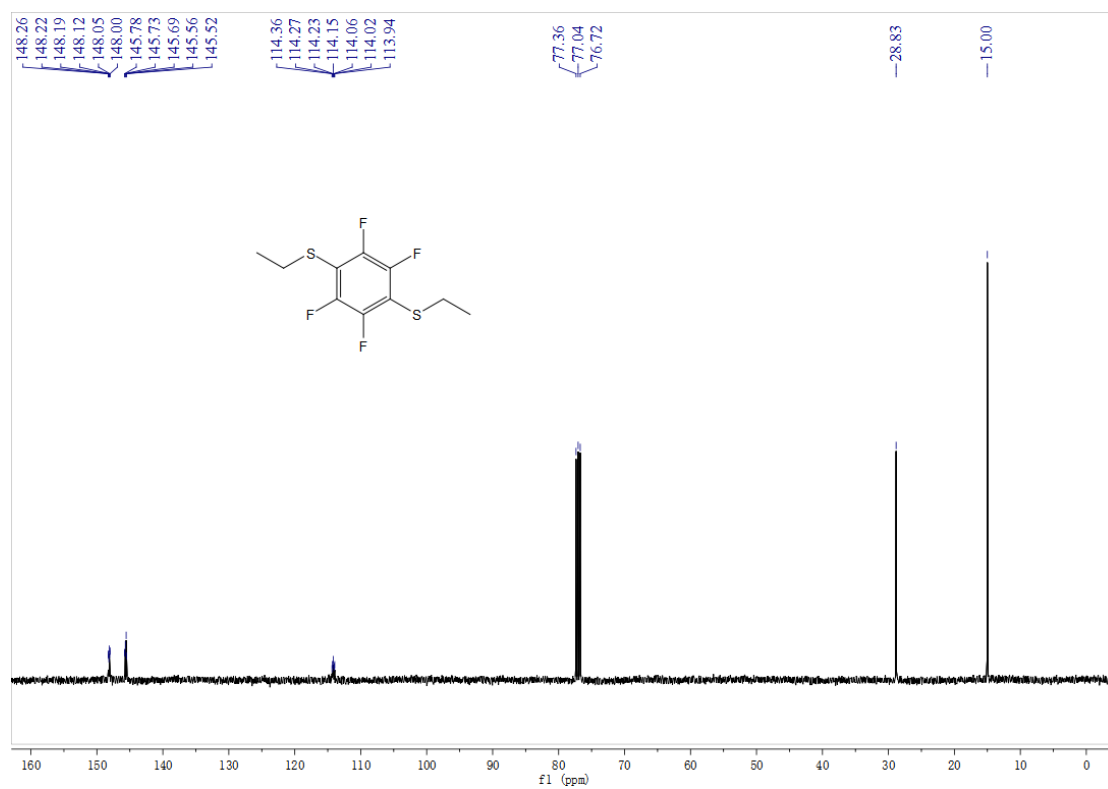
^{13}C NMR (100 MHz, CDCl_3): 1,4-bis(methylmercapto)-2,3,5,6-tetrafluorobenzene (**3a**)



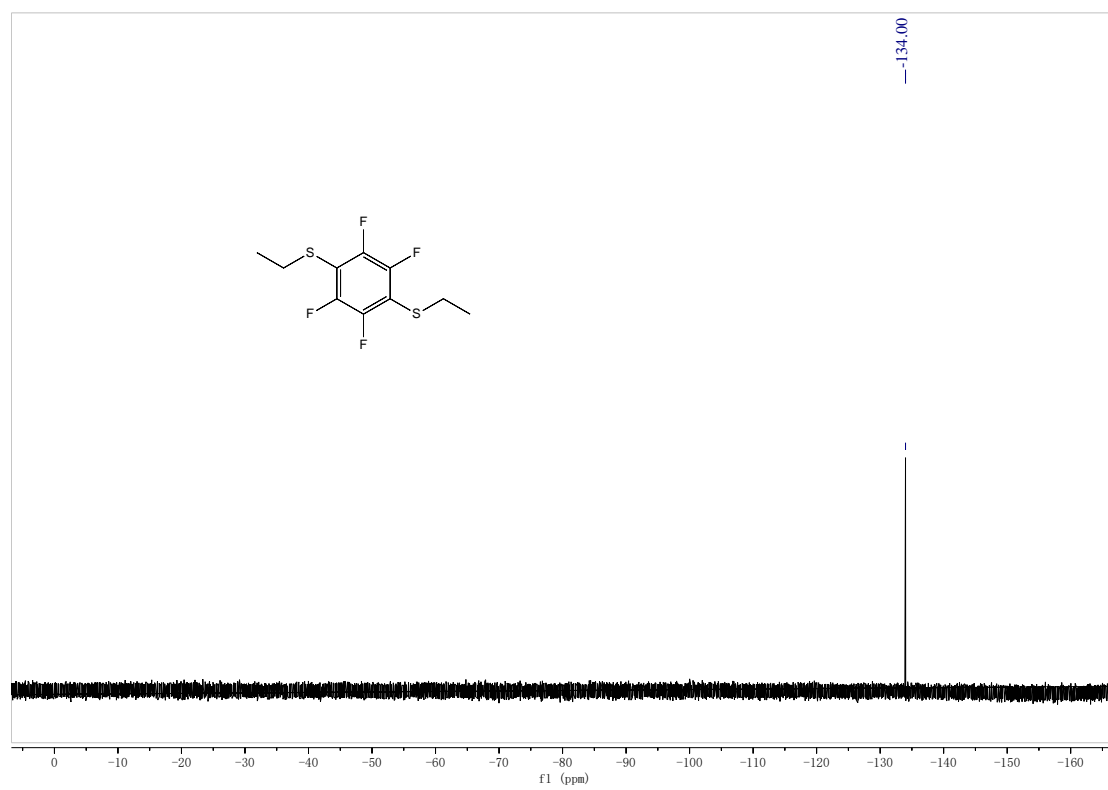
^{19}F NMR (376 MHz, CDCl_3): 1,4-bis(methylmercapto)-2,3,5,6-tetrafluorobenzene (**3a**)



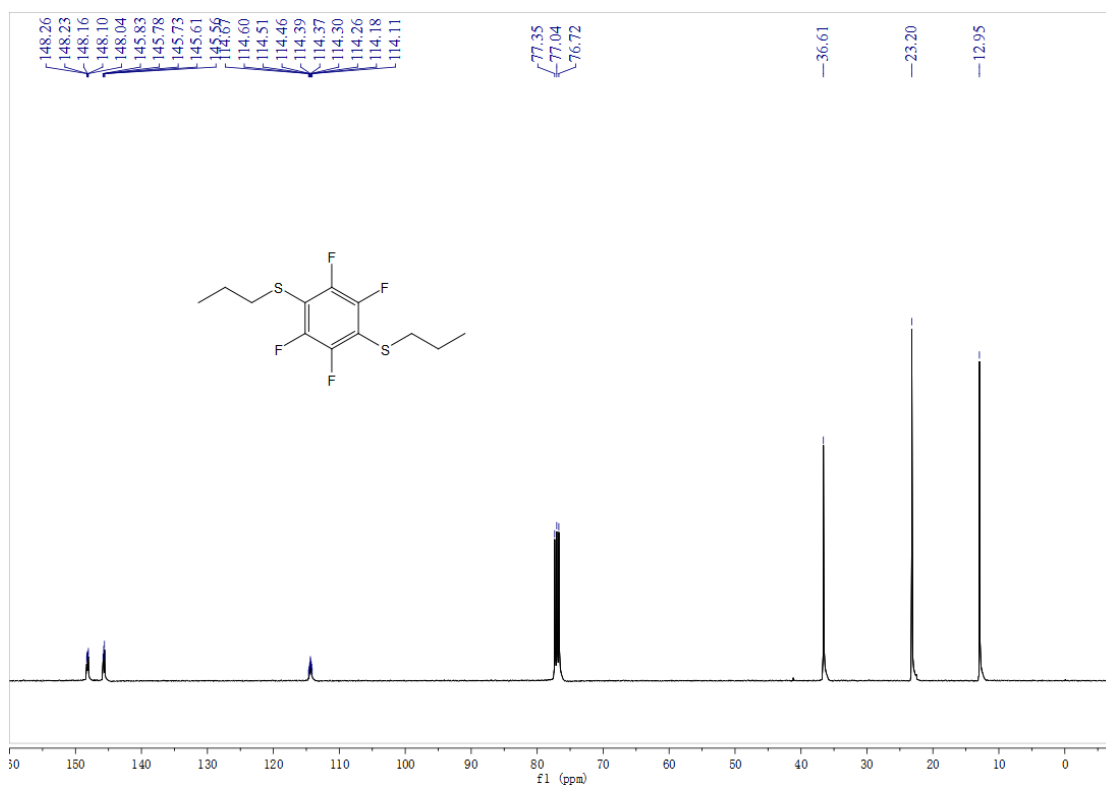
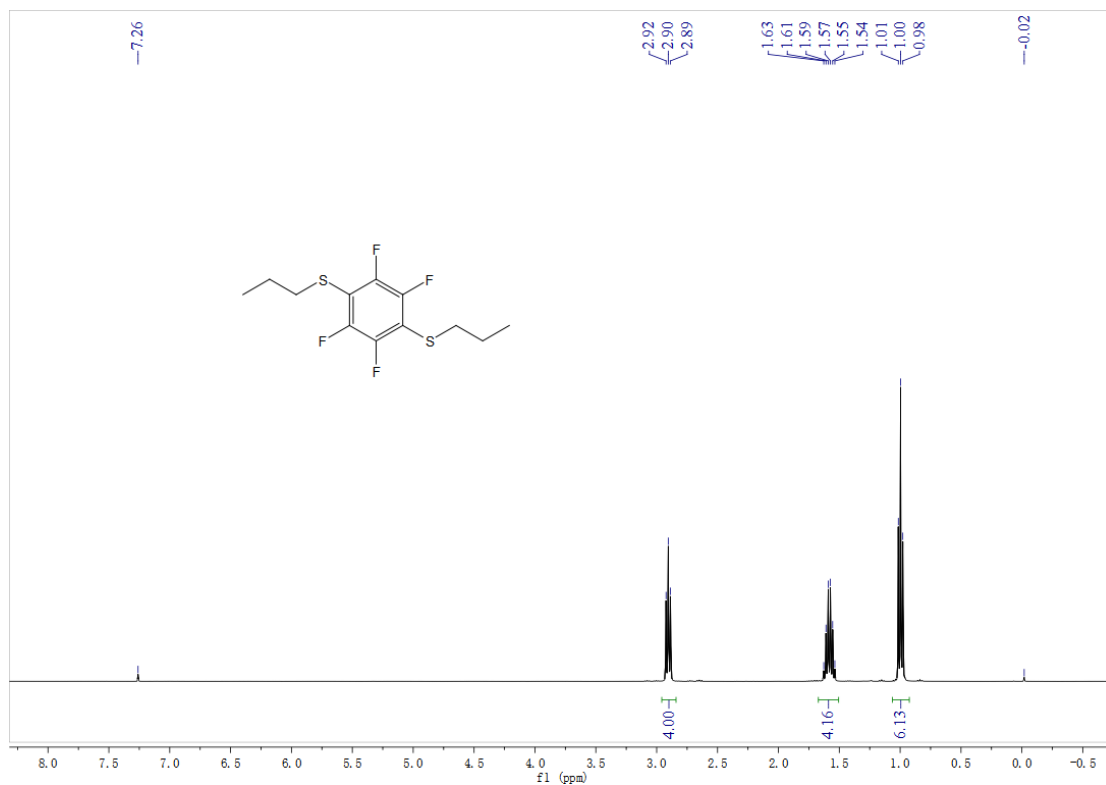
^1H NMR (400 MHz, CDCl_3): 1,4-bis(ethylthio)-2,3,5,6-tetrafluorobenzene (**3b**)

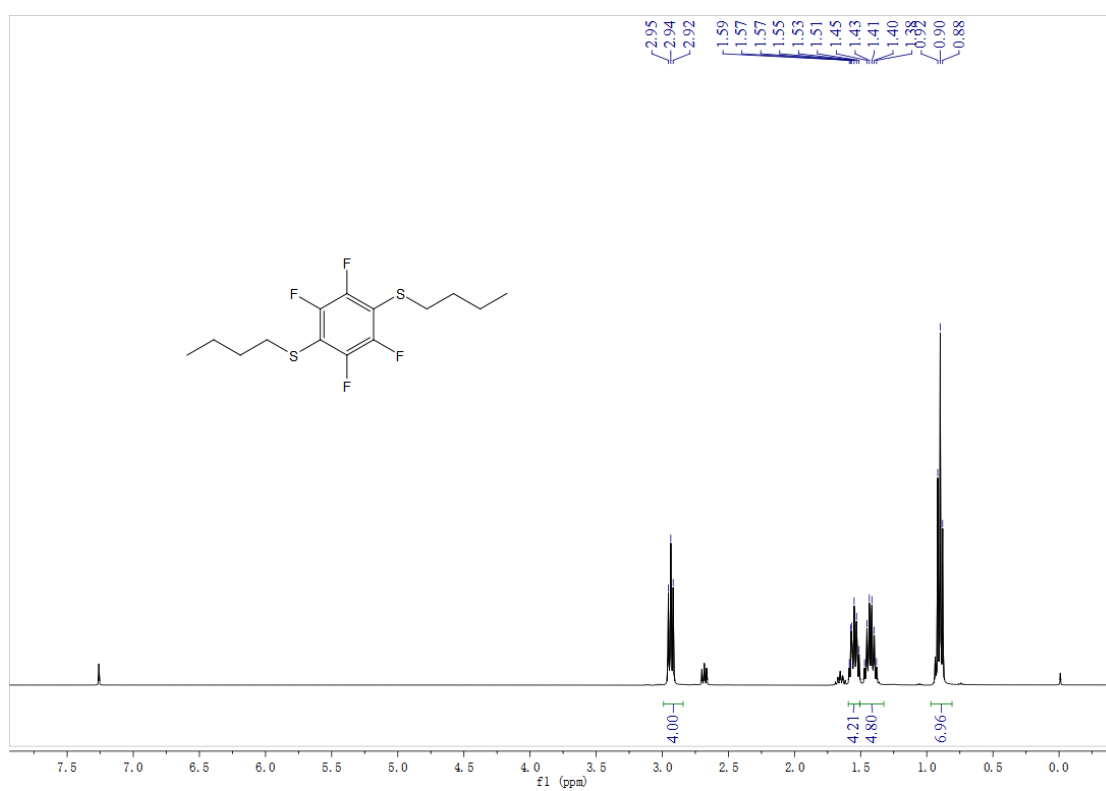
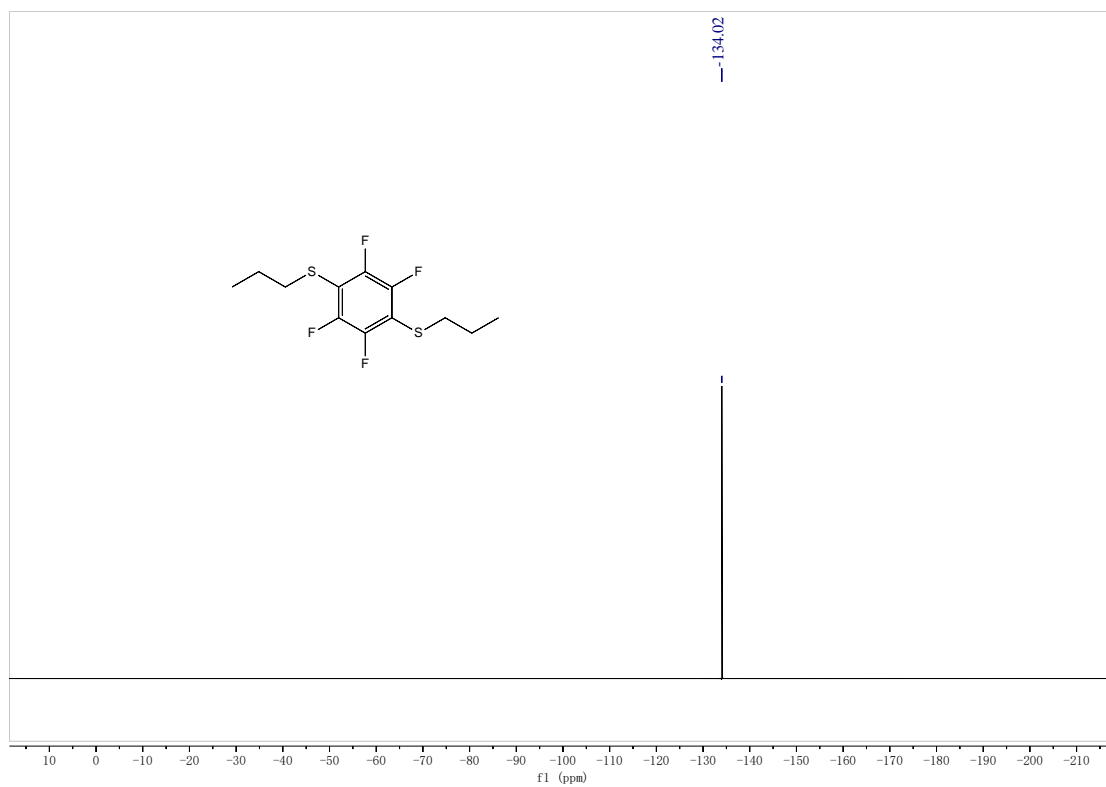


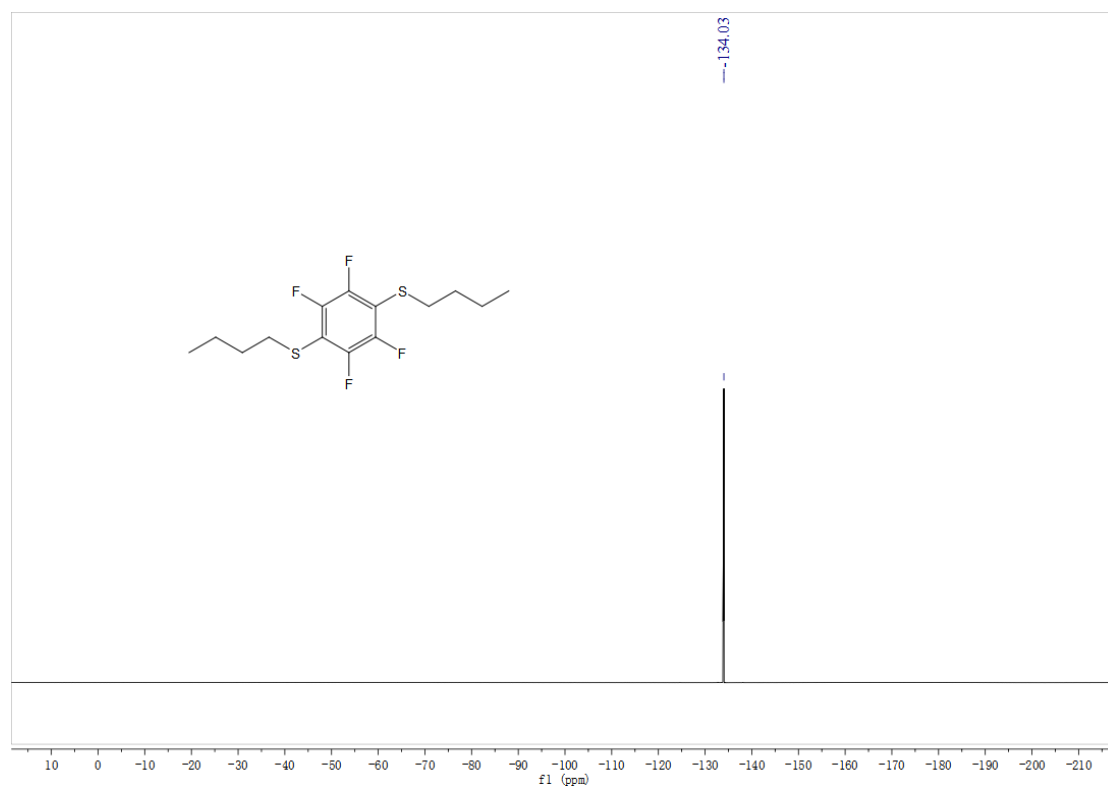
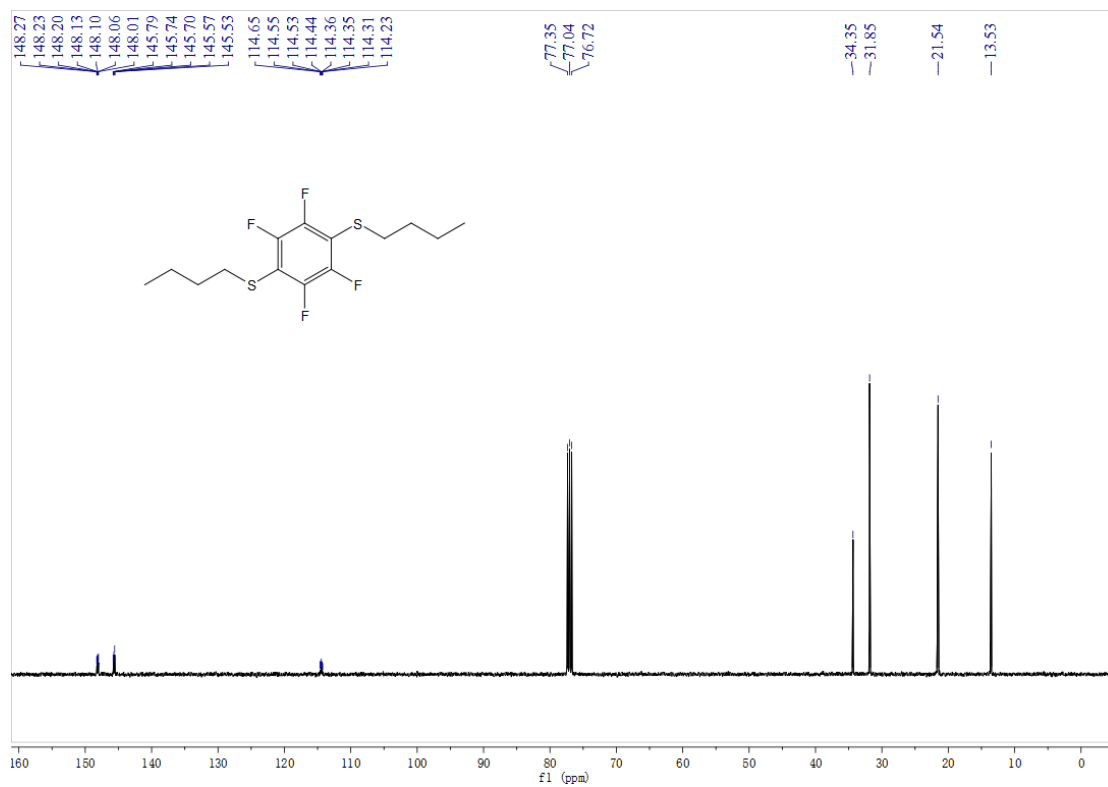
¹³C NMR (100 MHz, CDCl₃): 1,4-bis(ethylthio)-2,3,5,6-tetrafluorobenzene (**3b**)

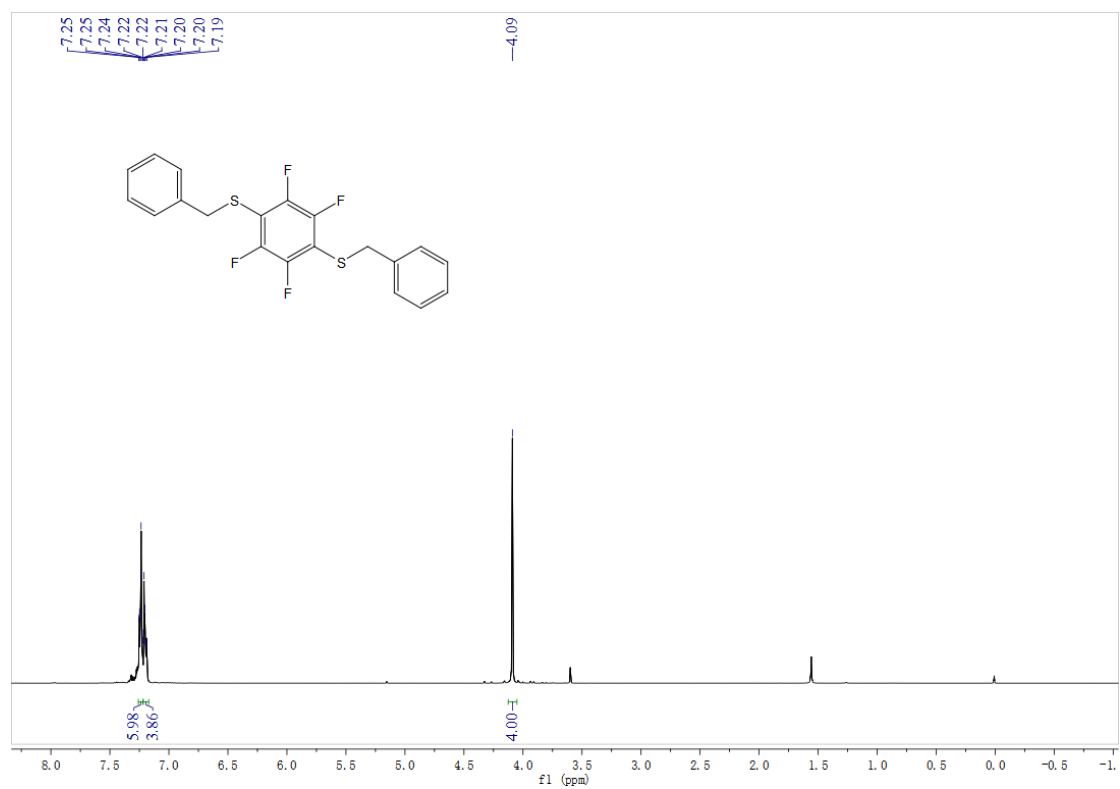


¹⁹F NMR (376 MHz, CDCl₃): 1,4-bis(ethylthio)-2,3,5,6-tetrafluorobenzene (**3b**)

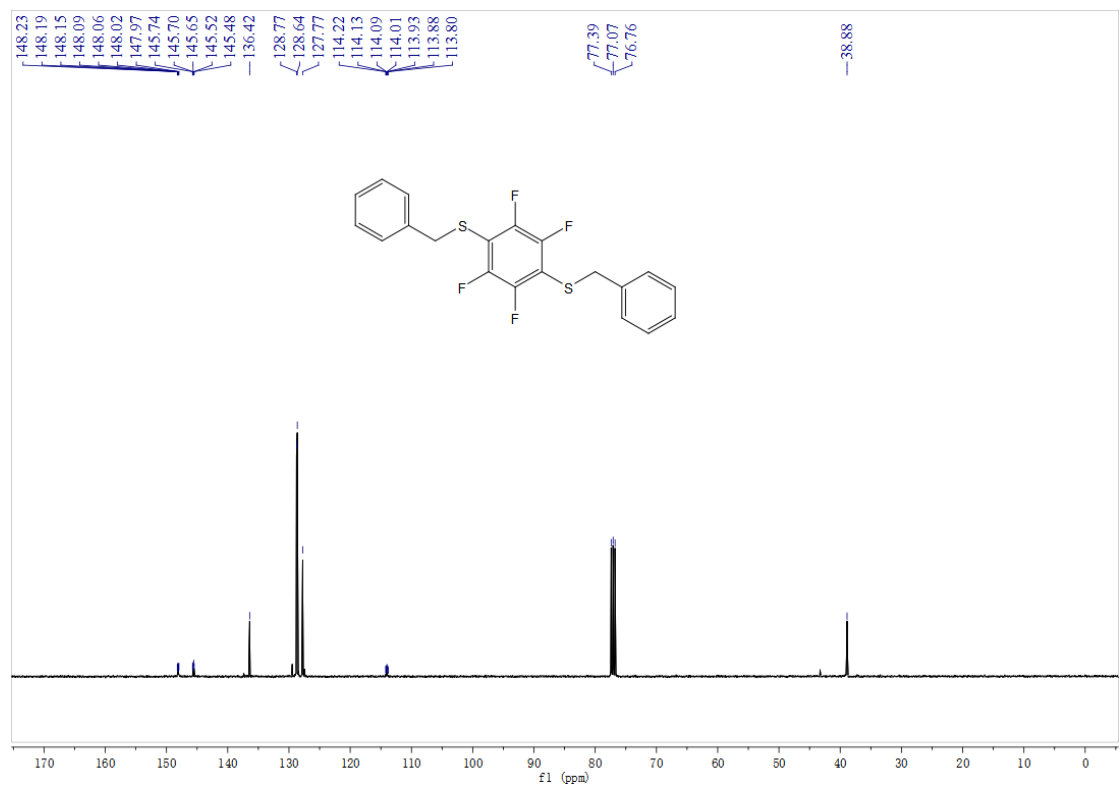




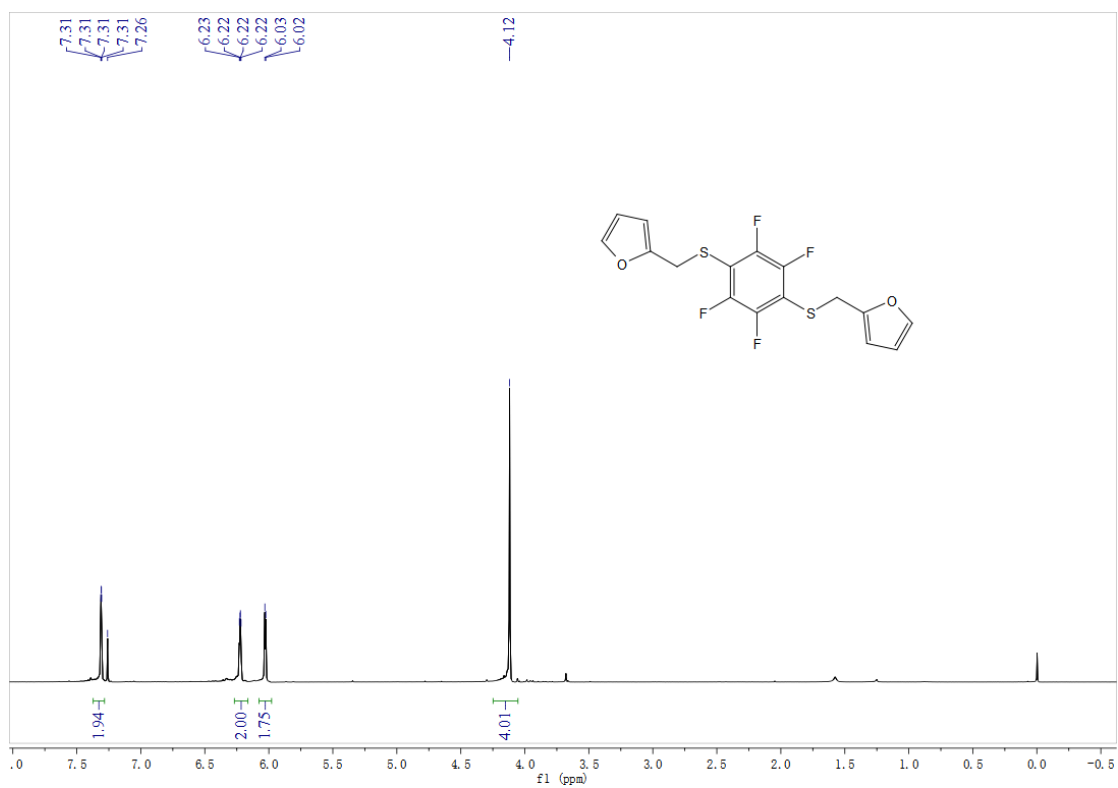
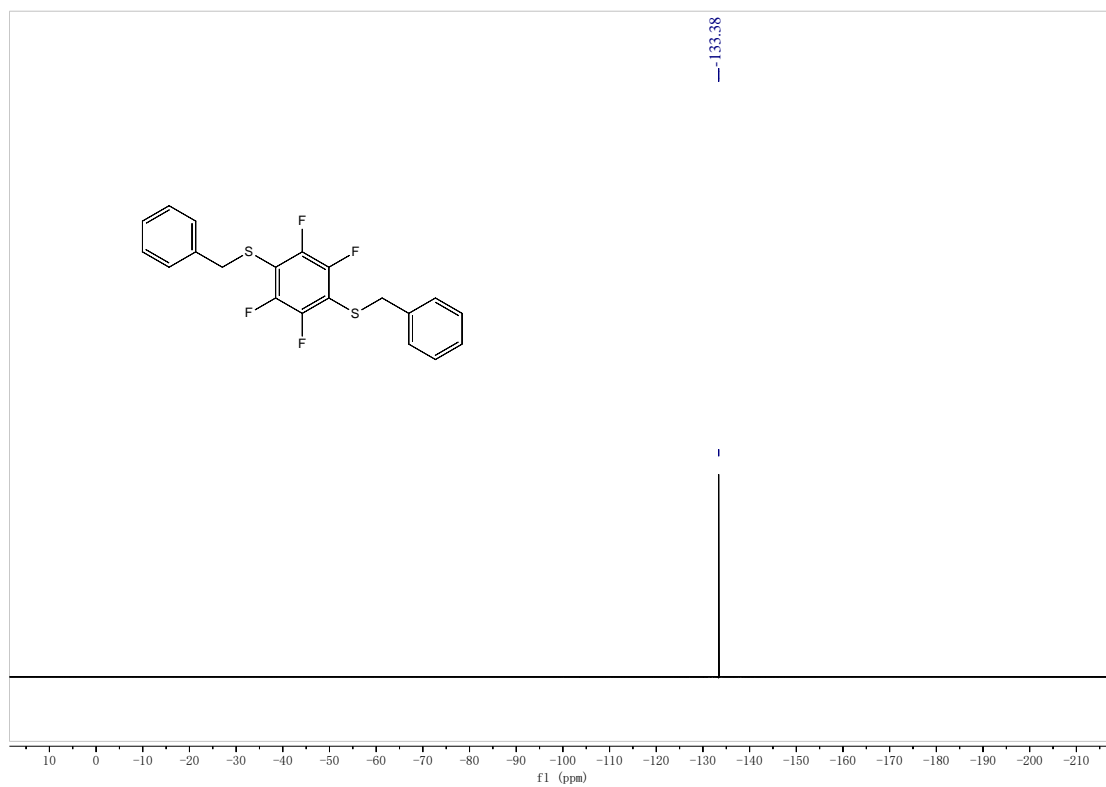


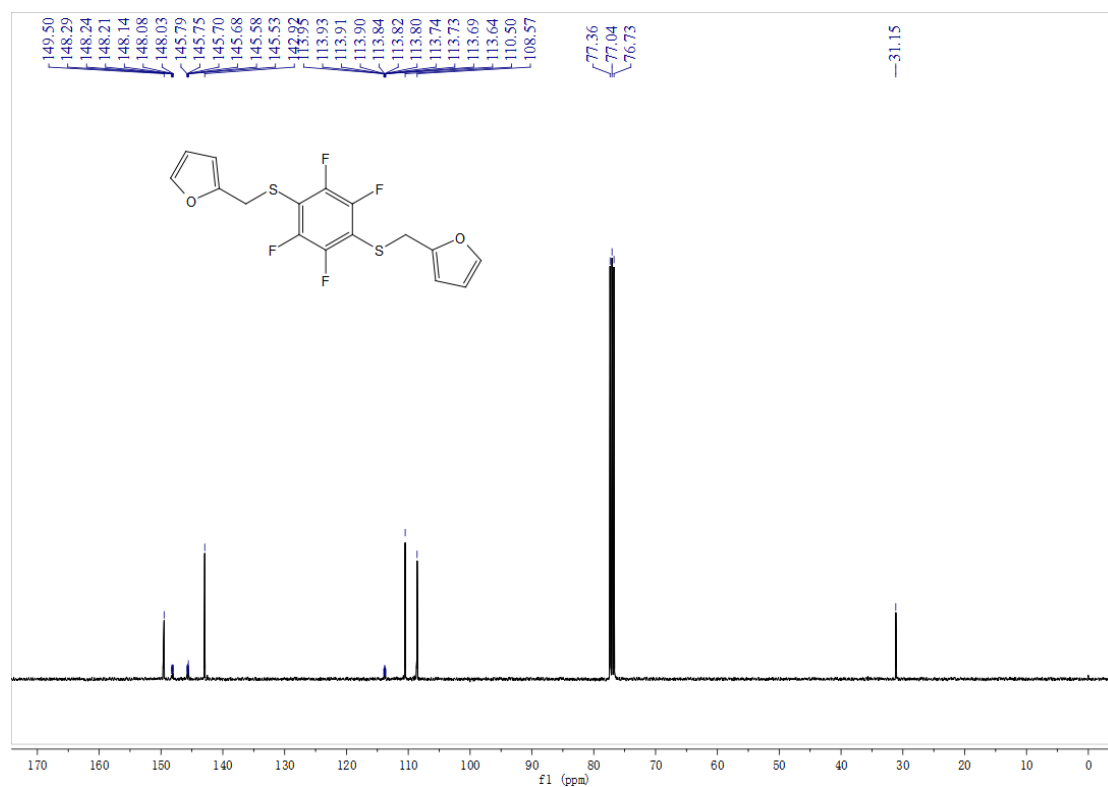


¹H NMR (400 MHz, CDCl₃): 1,4-bis(benzylthio)-2,3,5,6-tetrafluorobenzene (**3e**)

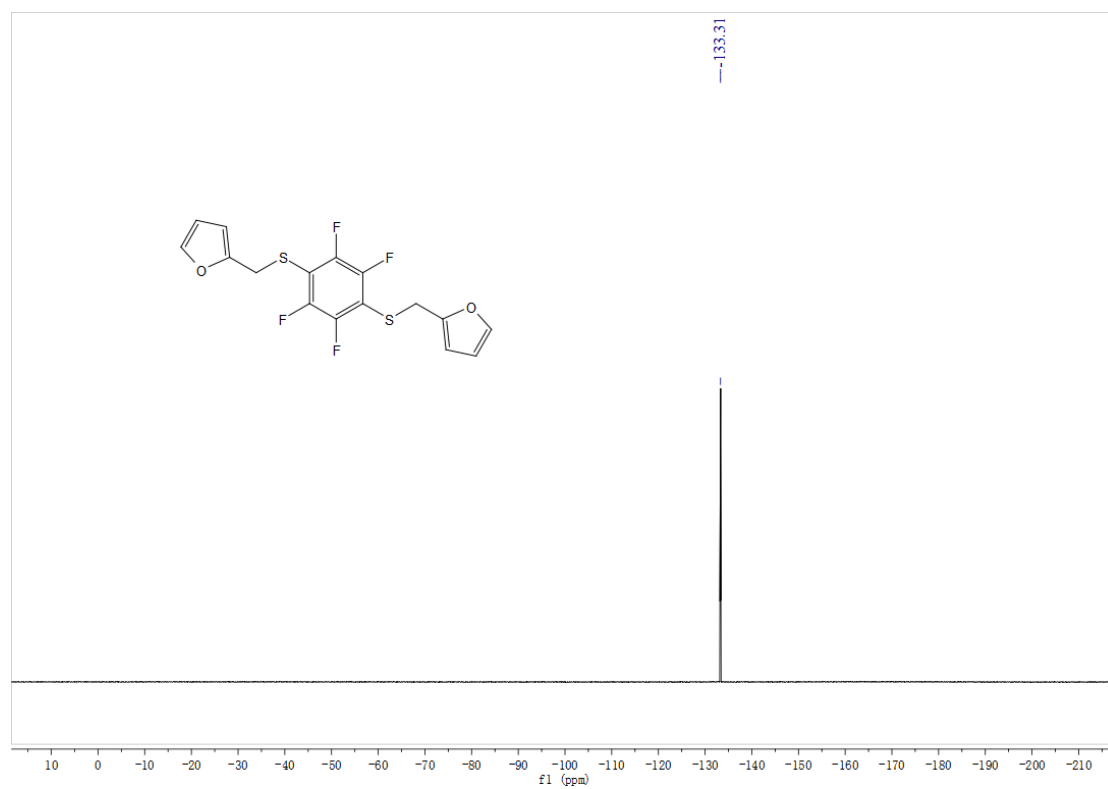


¹³C NMR (100 MHz, CDCl₃): 1,4-bis(benzylthio)-2,3,5,6-tetrafluorobenzene (**3e**)

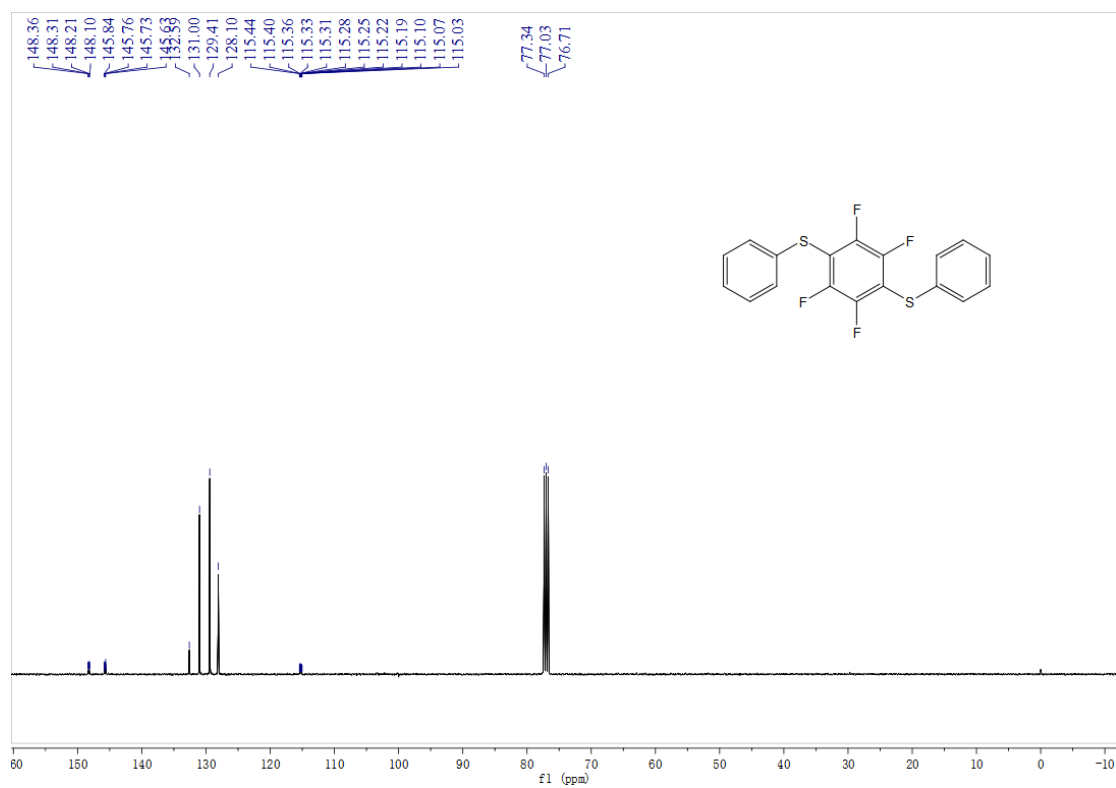
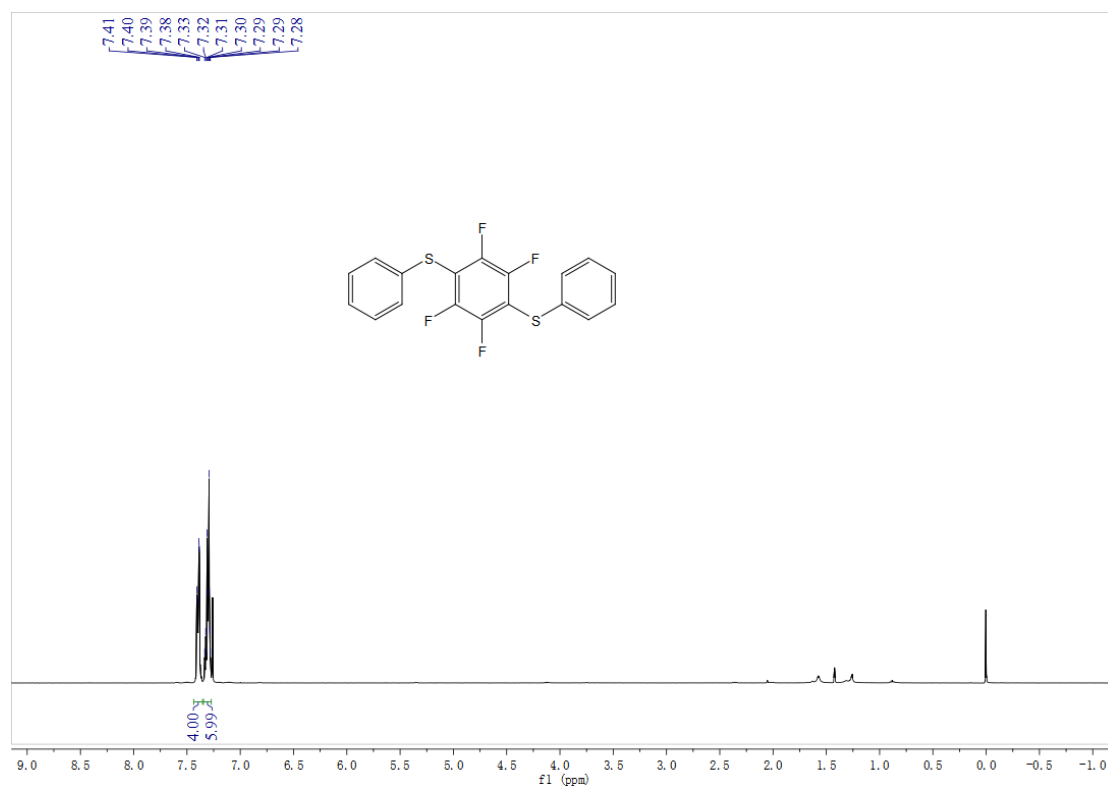




¹³C NMR (100 MHz, CDCl₃): 1,4-bis(furfurylthio)-2,3,5,6-tetrafluorobenzene (3f)



¹⁹F NMR (376 MHz, CDCl₃): 1,4-bis(furfurylthio)-2,3,5,6-tetrafluorobenzene (3f)

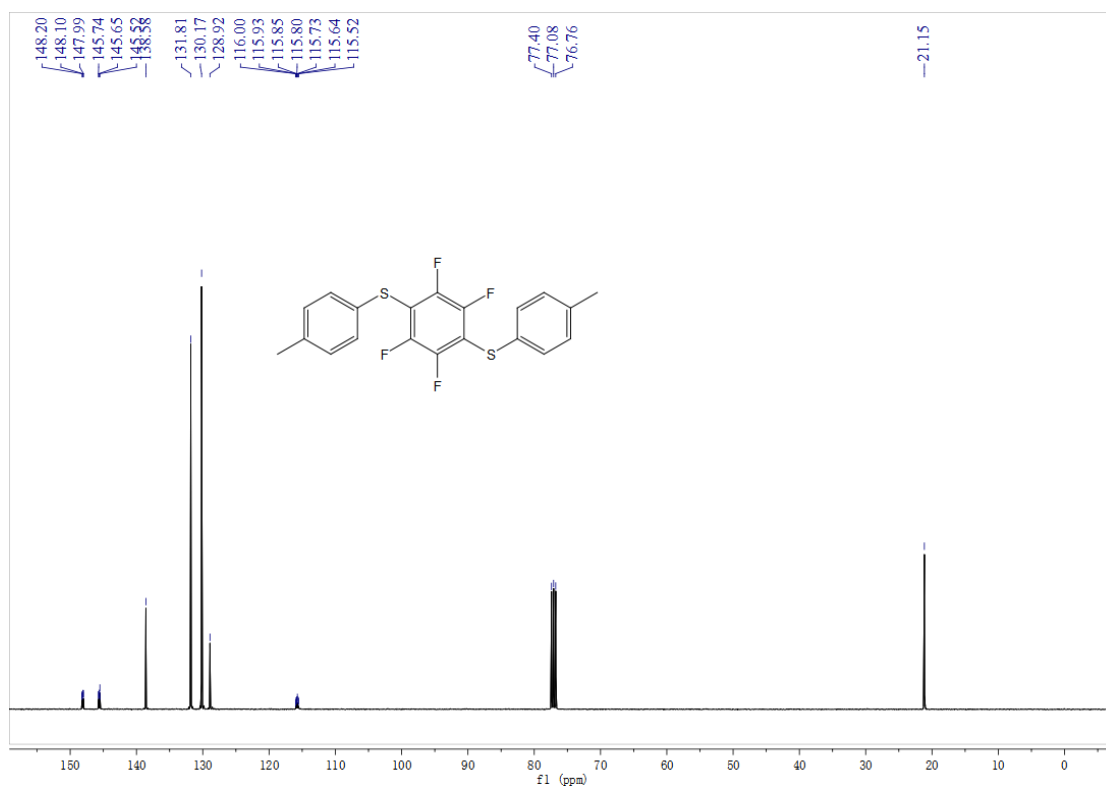




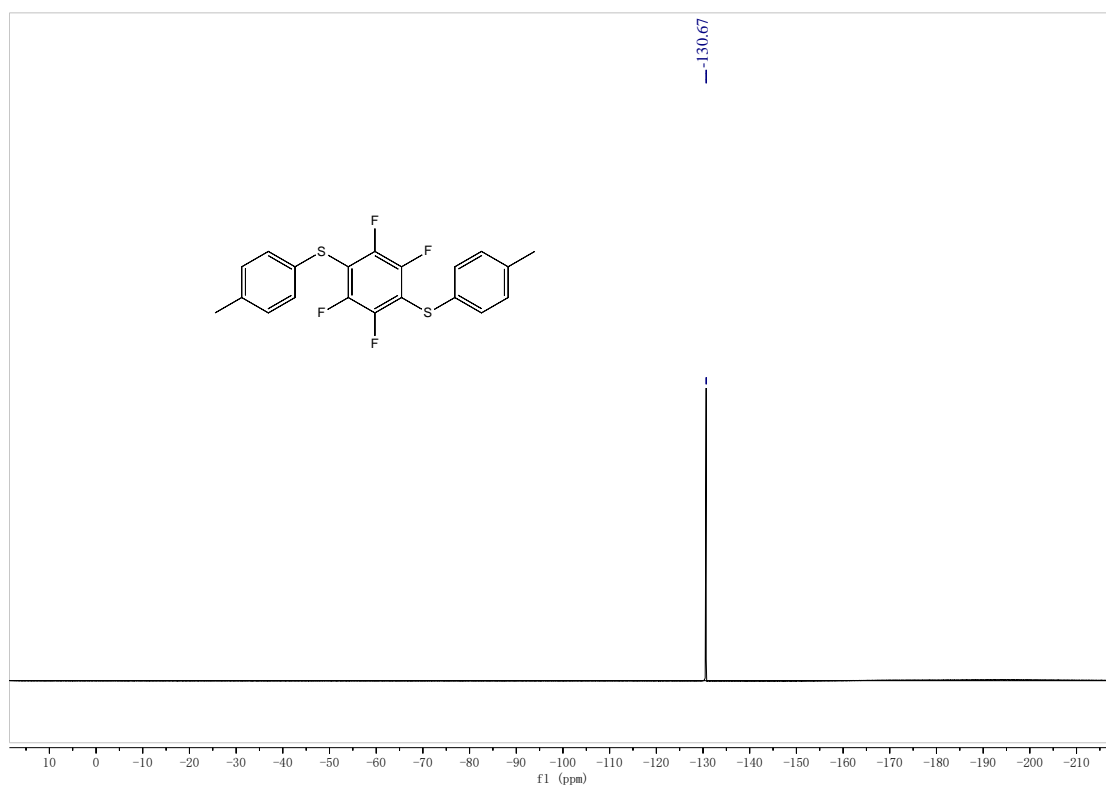
^{19}F NMR (376 MHz, CDCl_3): 1,4-bis(phenylthio)-2,3,5,6-tetrafluorobenzene (**3g**)



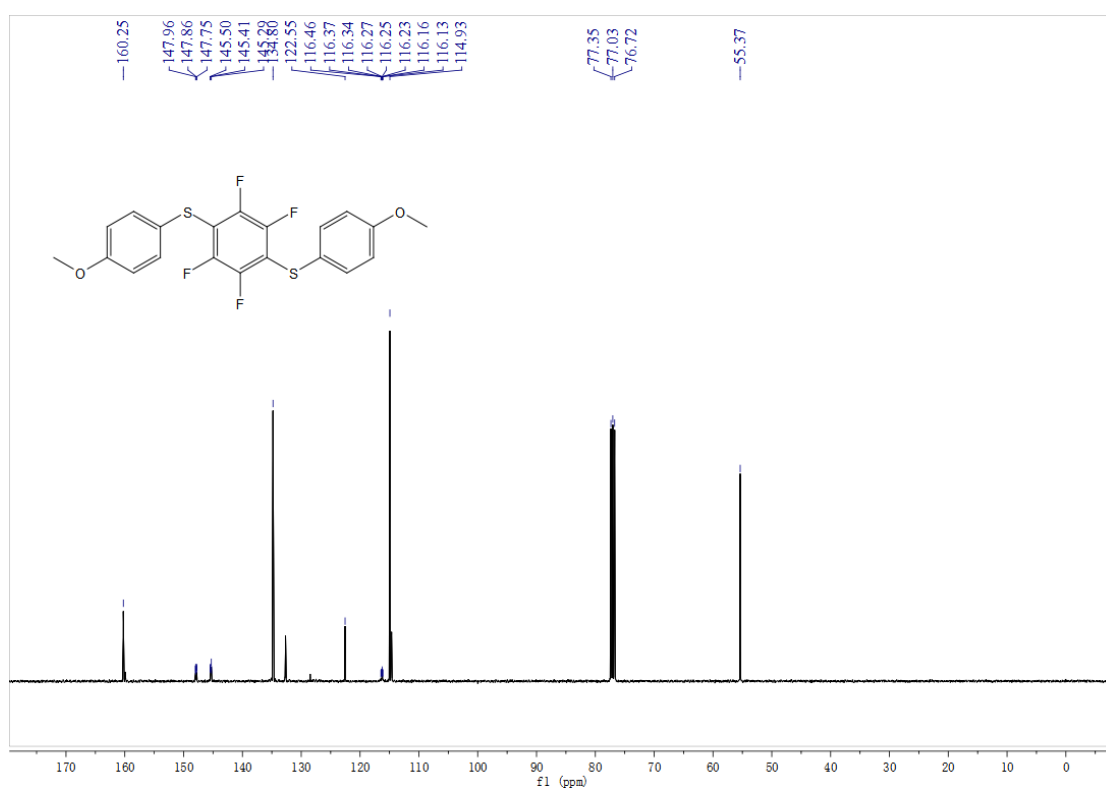
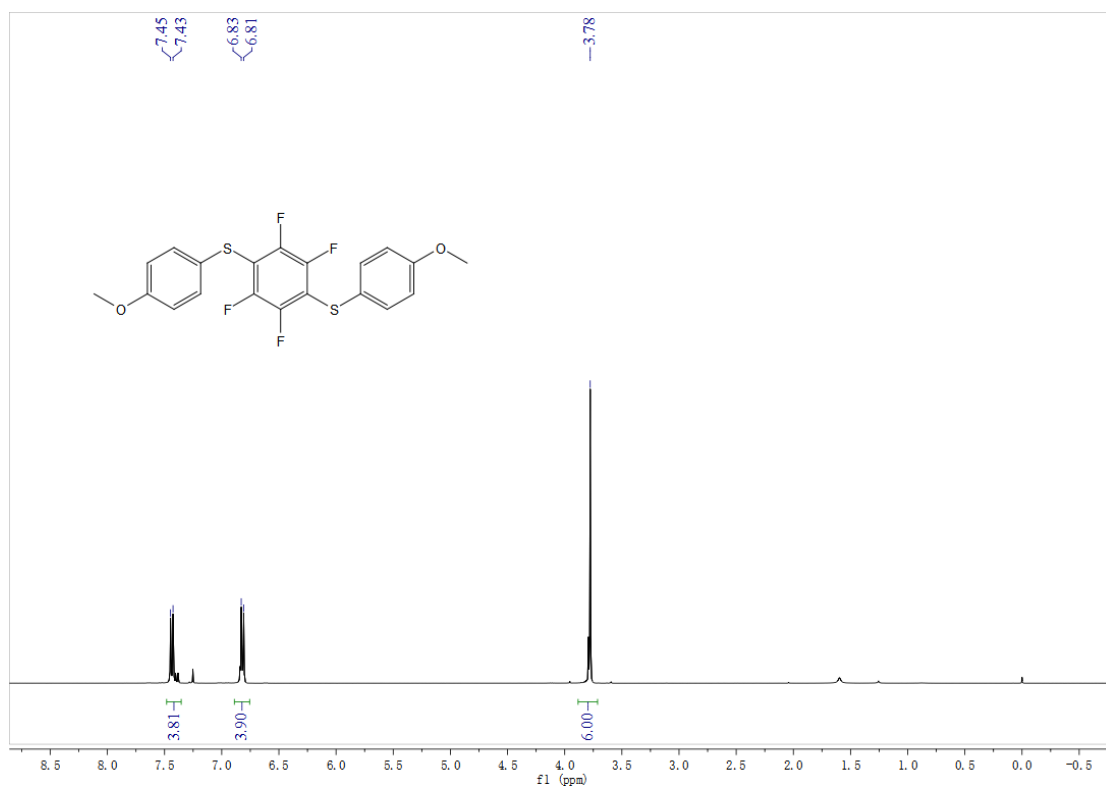
^1H NMR (400 MHz, CDCl_3): 1,4-bis(*p*-tolylthio)-2,3,5,6-tetrafluorobenzene (**3h**)

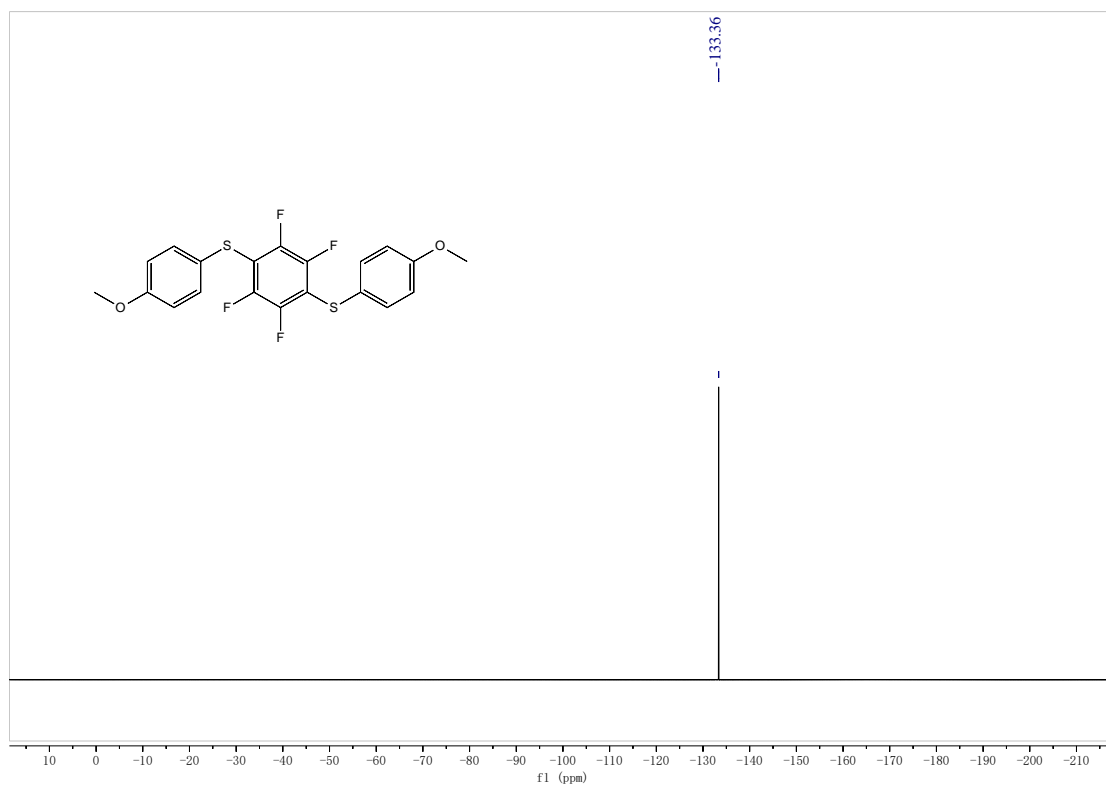


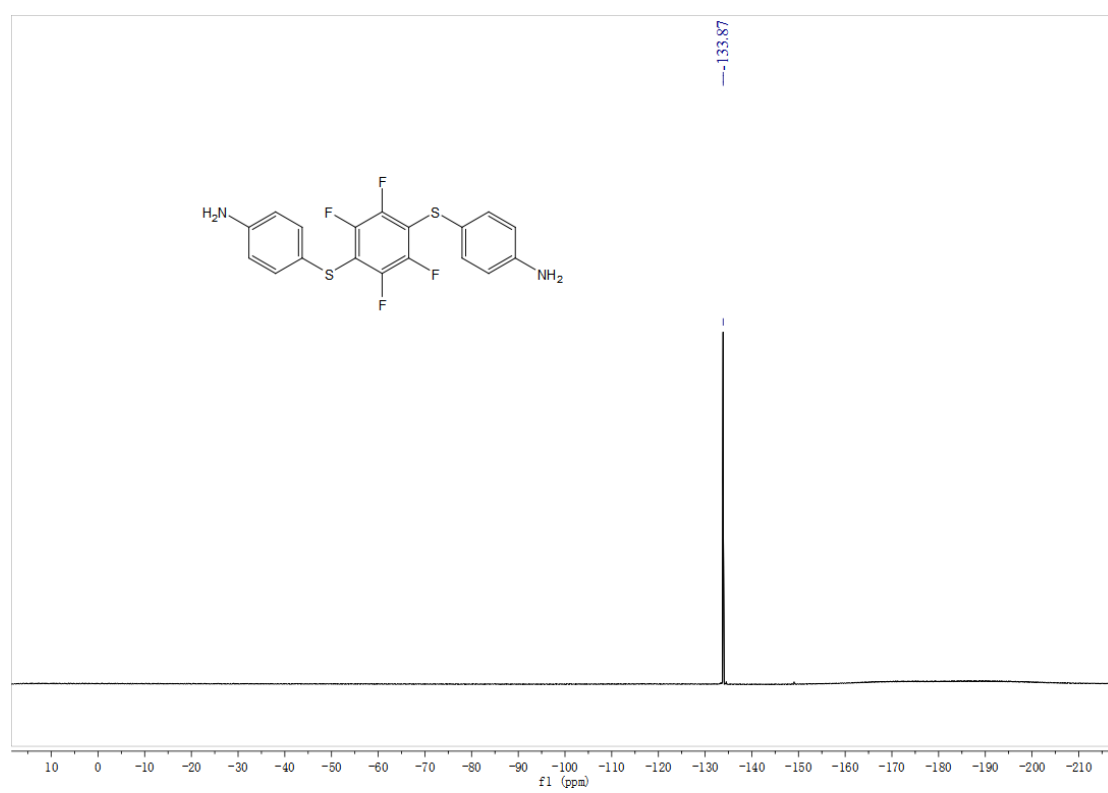
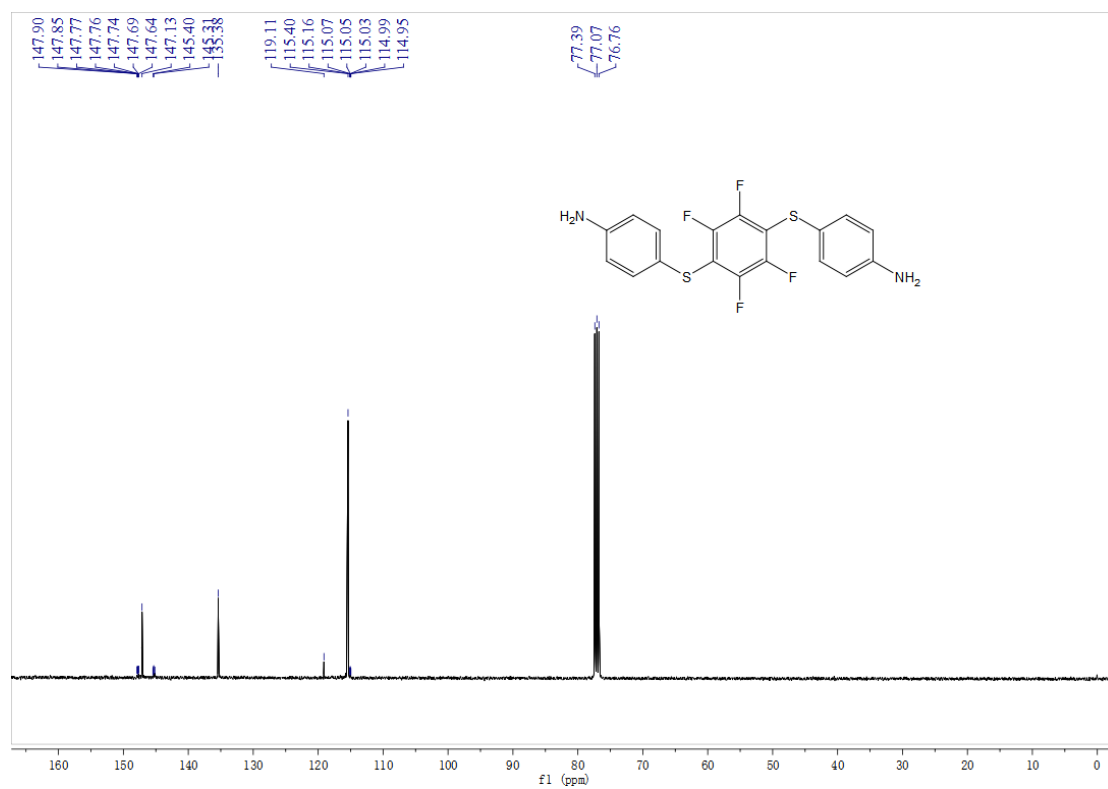
¹³C NMR (100 MHz, CDCl₃): 1,4-bis(*p*-tolylthio)-2,3,5,6-tetrafluorobenzene (**3h**)

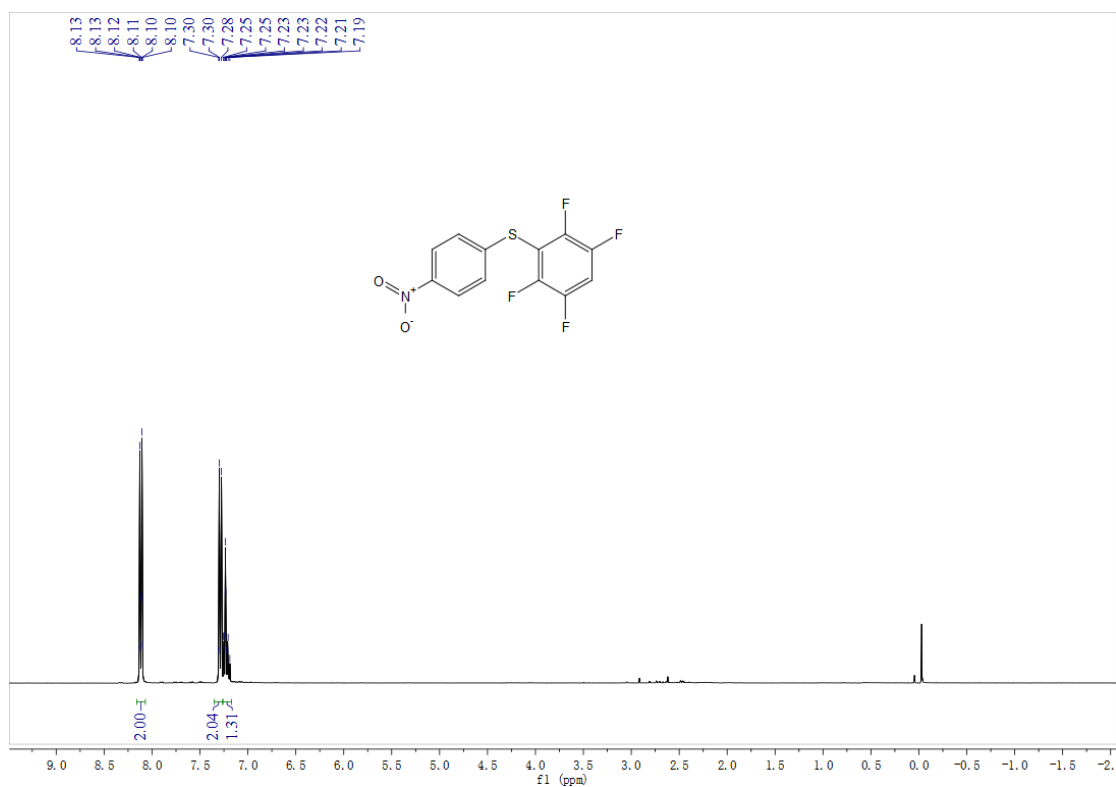


¹⁹F NMR (376 MHz, CDCl₃): 1,4-bis(*p*-tolylthio)-2,3,5,6-tetrafluorobenzene (**3h**)

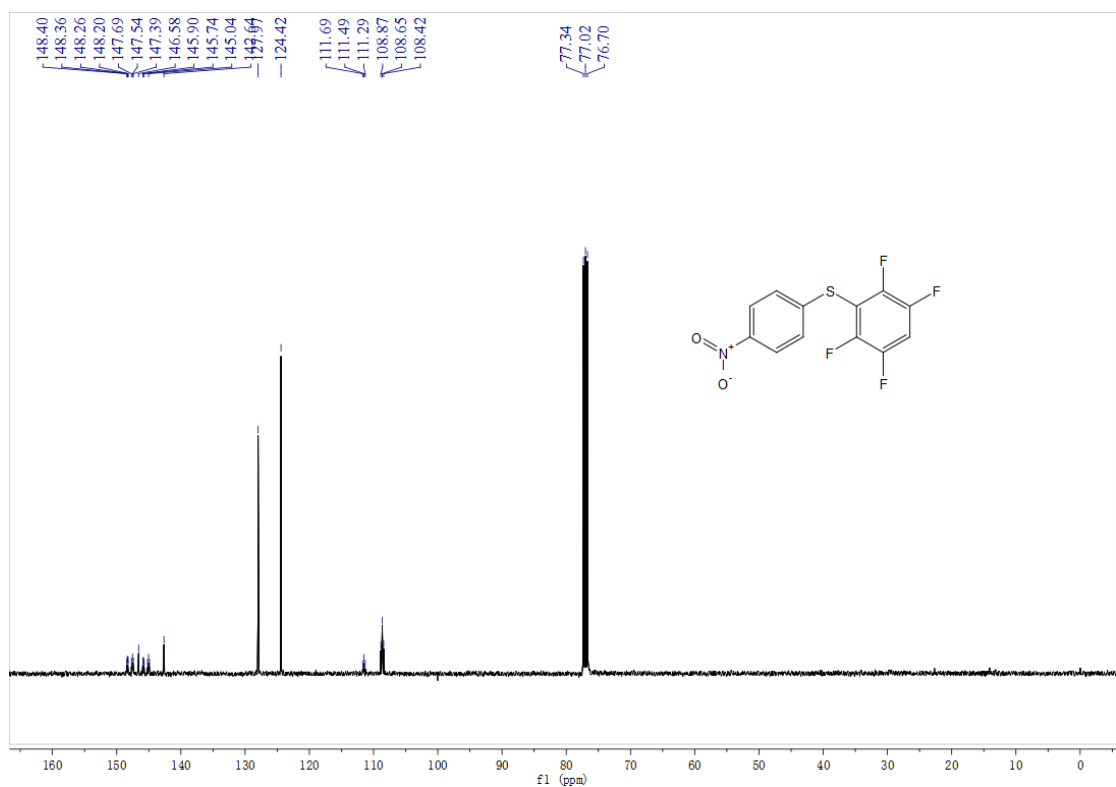








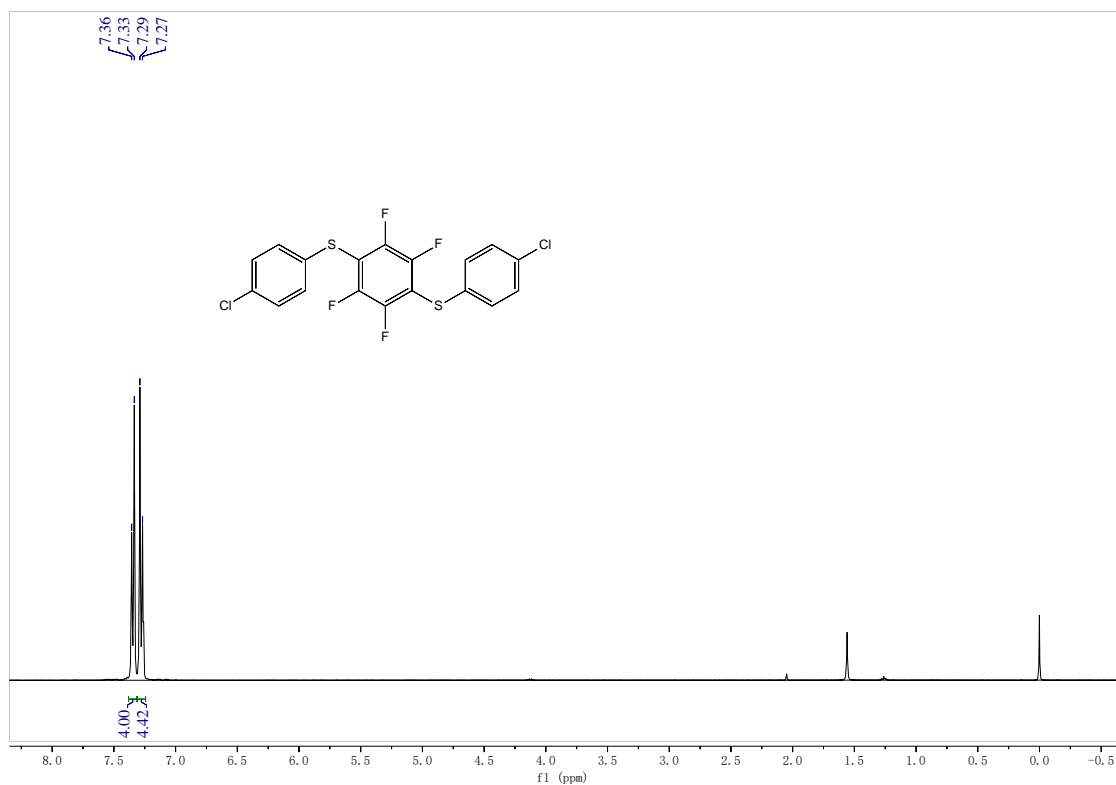
¹H NMR (400 MHz, CDCl₃): (4-nitrophenyl)(2,3,5,6-tetrafluorophenyl)sulfane (**3k**)



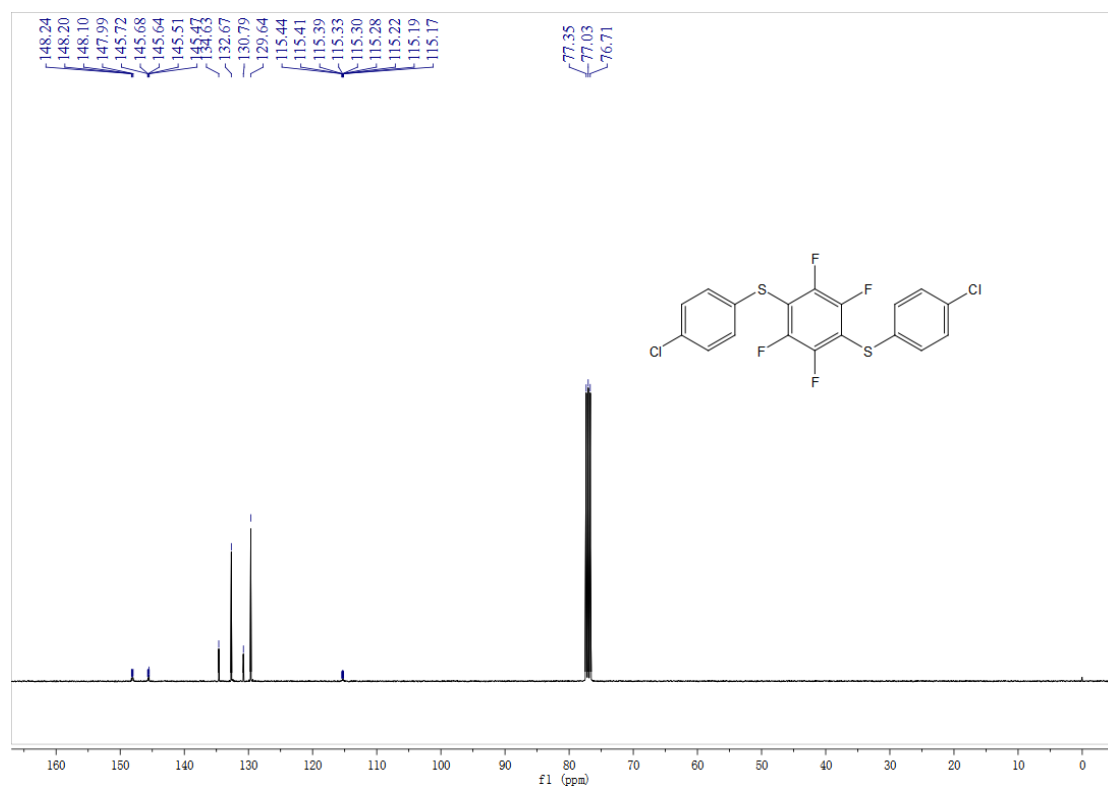
¹³C NMR (100 MHz, CDCl₃): (4-nitrophenyl)(2,3,5,6-tetrafluorophenyl)sulfane (**3k**)



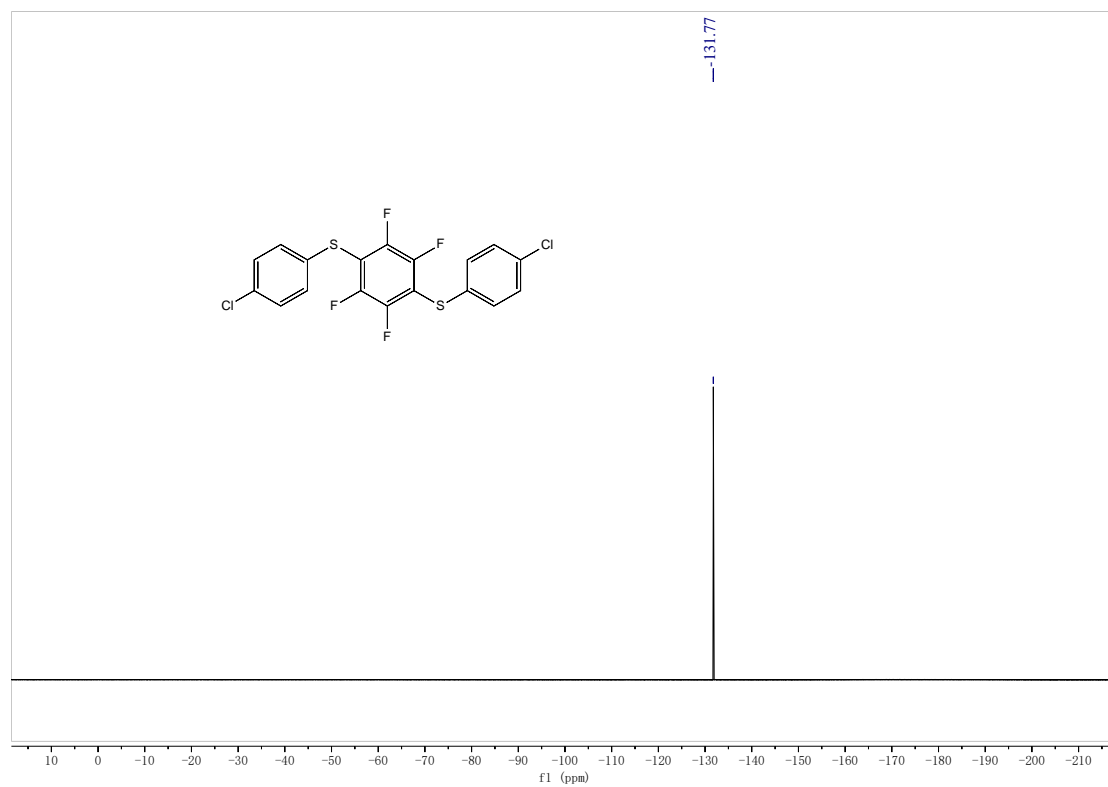
¹⁹F NMR (376 MHz, CDCl₃): (4-nitrophenyl)(2,3,5,6-tetrafluorophenyl)sulfane (**3k**)



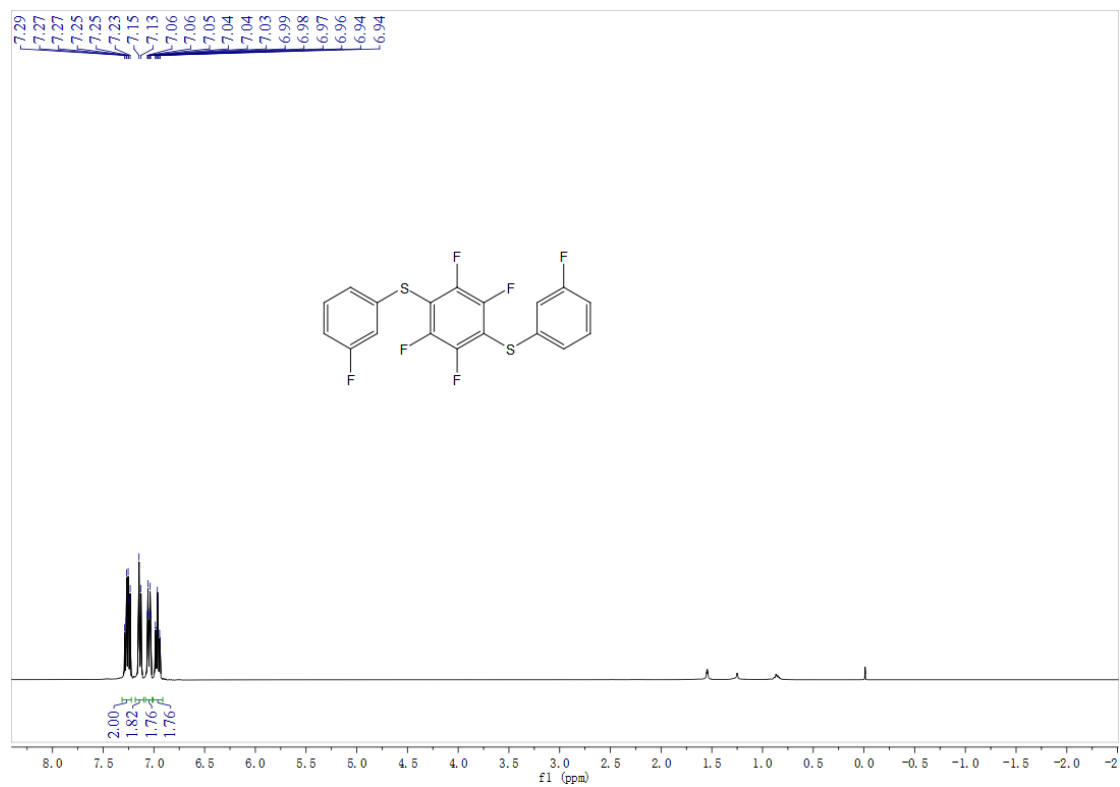
¹H NMR (400 MHz, CDCl₃): 1,4-bis(4-chlorophenylthio)-2,3,5,6-tetrafluoro-benzene (**3m**)



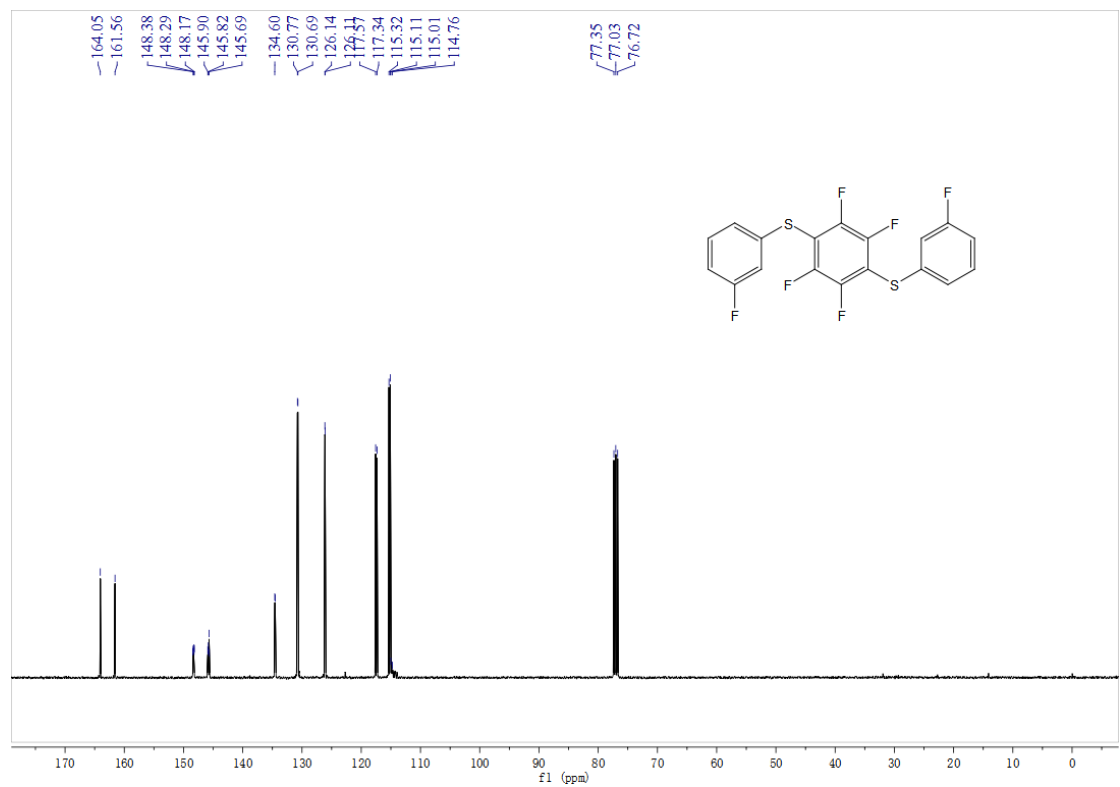
¹³C NMR (100 MHz, CDCl₃): 1,4-bis(4-chlorophenylthio)-2,3,5,6-tetrafluoro-benzene (**3m**)



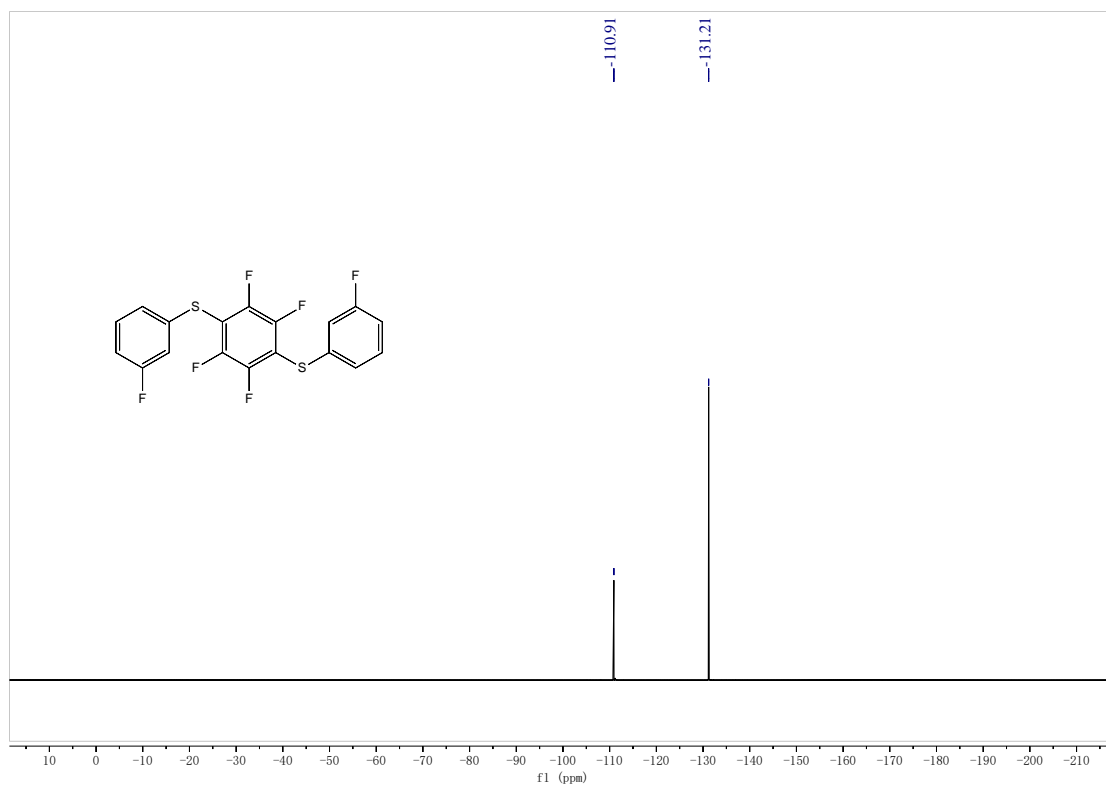
¹⁹F NMR (376 MHz, CDCl₃): 1,4-bis(4-chlorophenylthio)-2,3,5,6-tetrafluoro-benzene (**3m**)



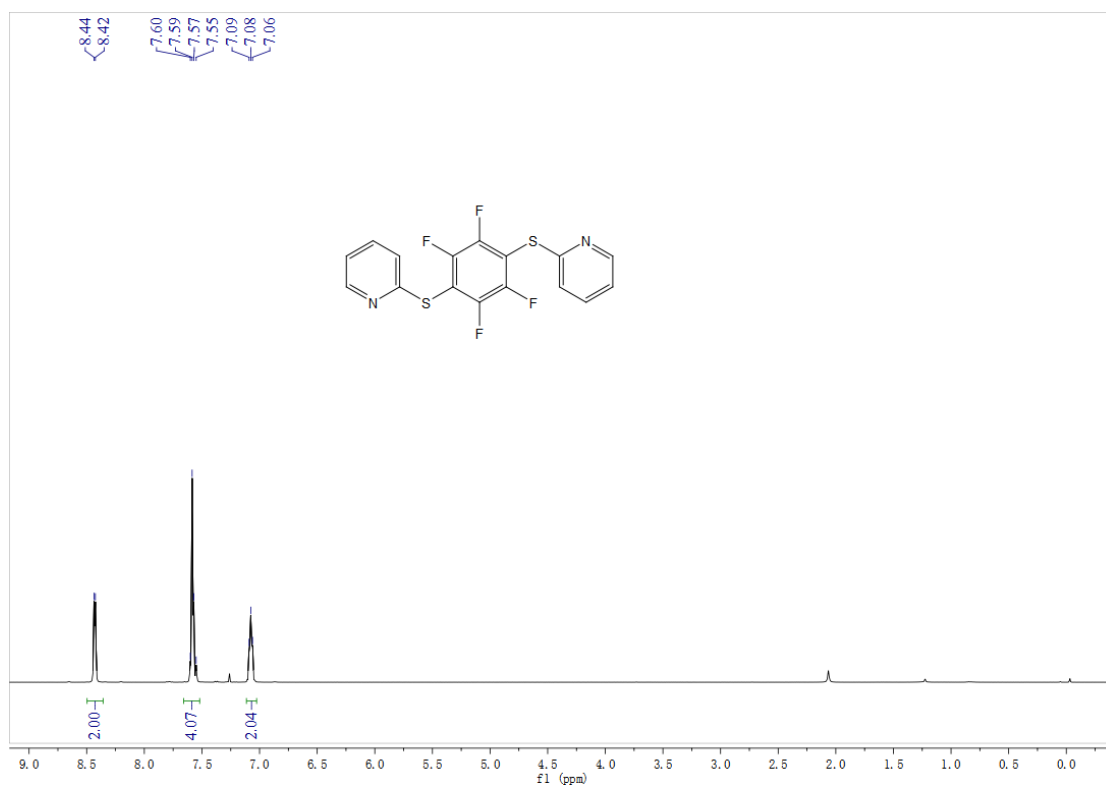
¹H NMR (400 MHz, CDCl₃): 1,4-bis(3-fluorophenylthio)-2,3,5,6-tetrafluorobenzene (**3n**)



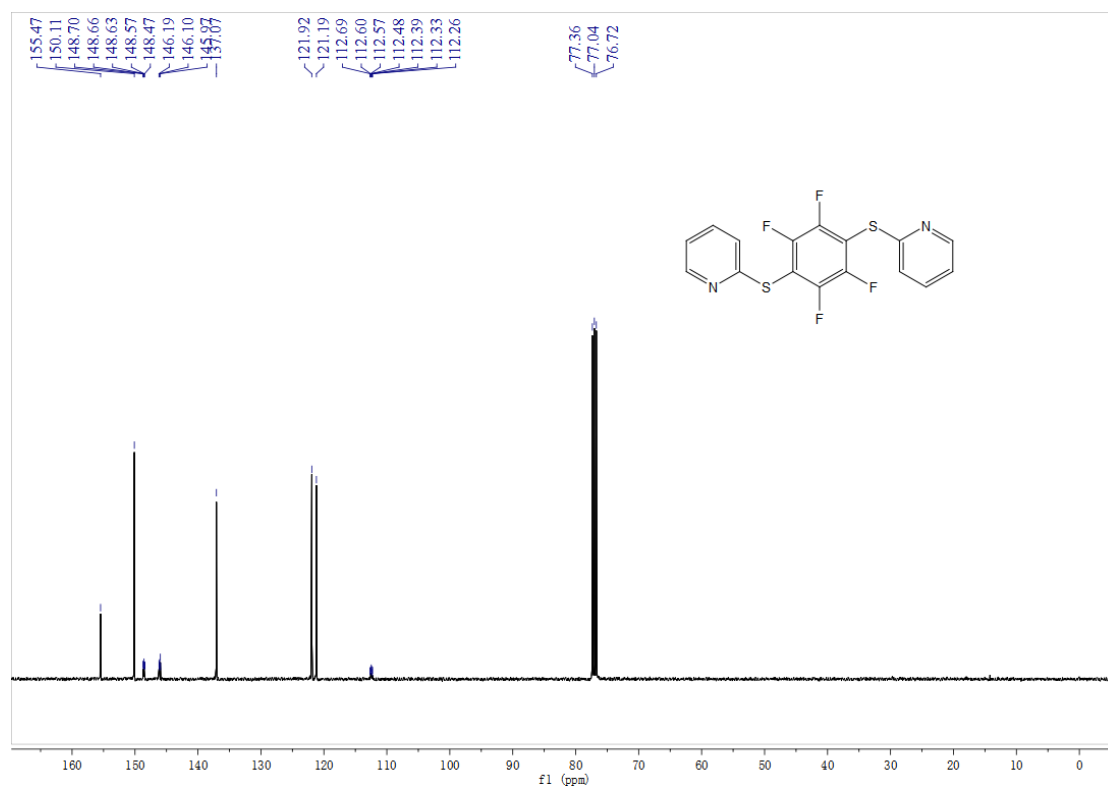
¹³C NMR (100 MHz, CDCl₃): 1,4-bis(3-fluorophenylthio)-2,3,5,6-tetrafluorobenzene (**3n**)



^{19}F NMR (376 MHz, CDCl_3): 1,4-bis(3-fluorophenylthio)-2,3,5,6-tetrafluorobenzene (**3n**)



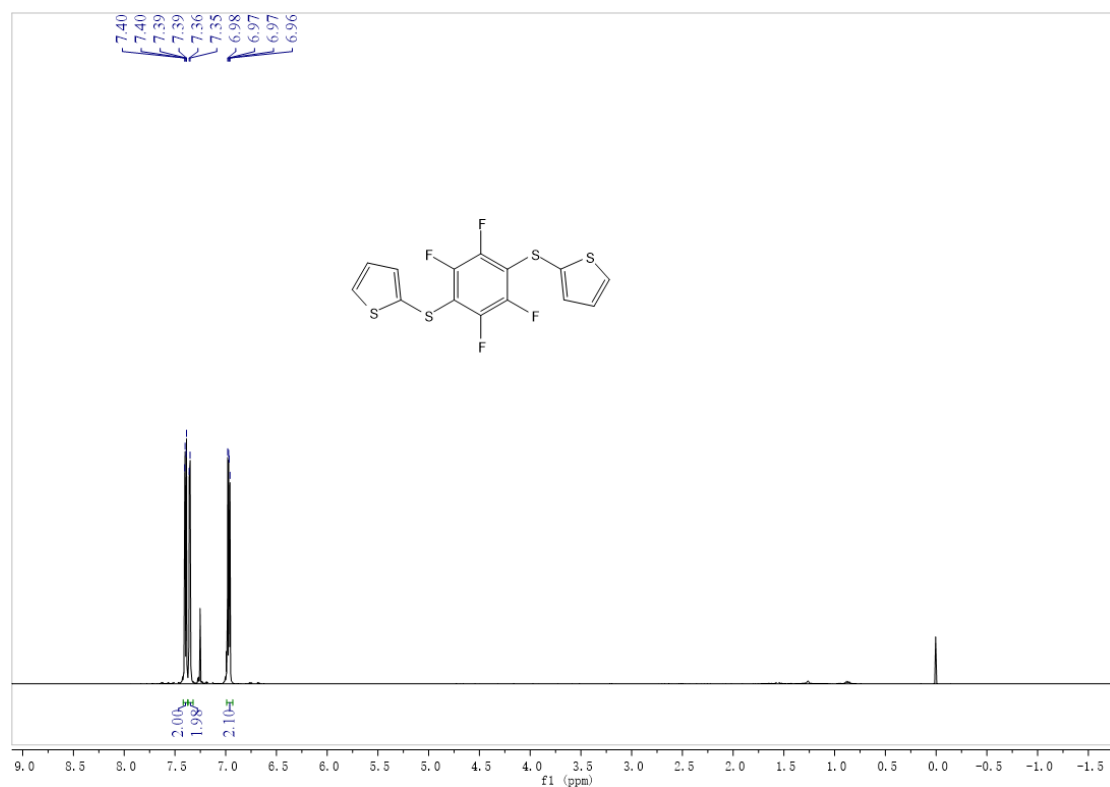
^1H NMR (400 MHz, CDCl_3): 2,3,5,6-tetrafluoro-1,4-bis(2-pyridylsulfenyl)benzene (**3o**)



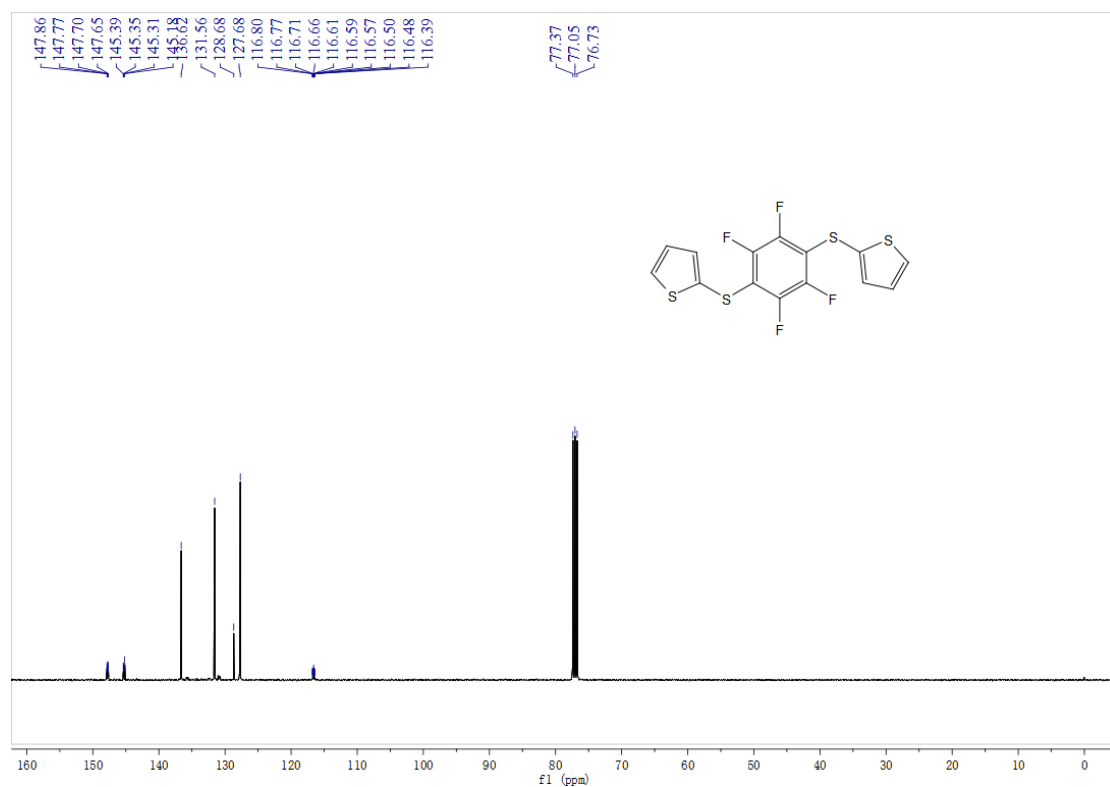
¹³C NMR (100 MHz, CDCl₃): 2,3,5,6-tetrafluoro-1,4-bis(2-pyridylsulfenyl)benzene (**30**)



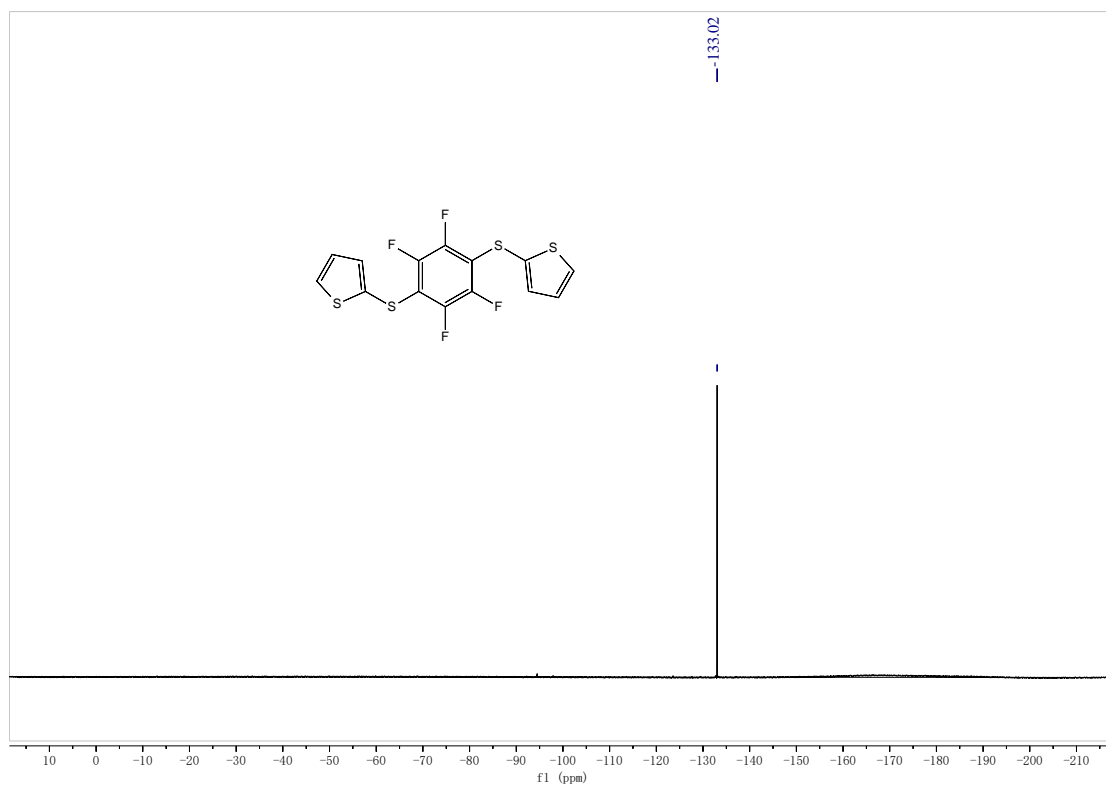
¹⁹F NMR (376 MHz, CDCl₃): 2,3,5,6-tetrafluoro-1,4-bis(2-pyridylsulfenyl)benzene (**30**)



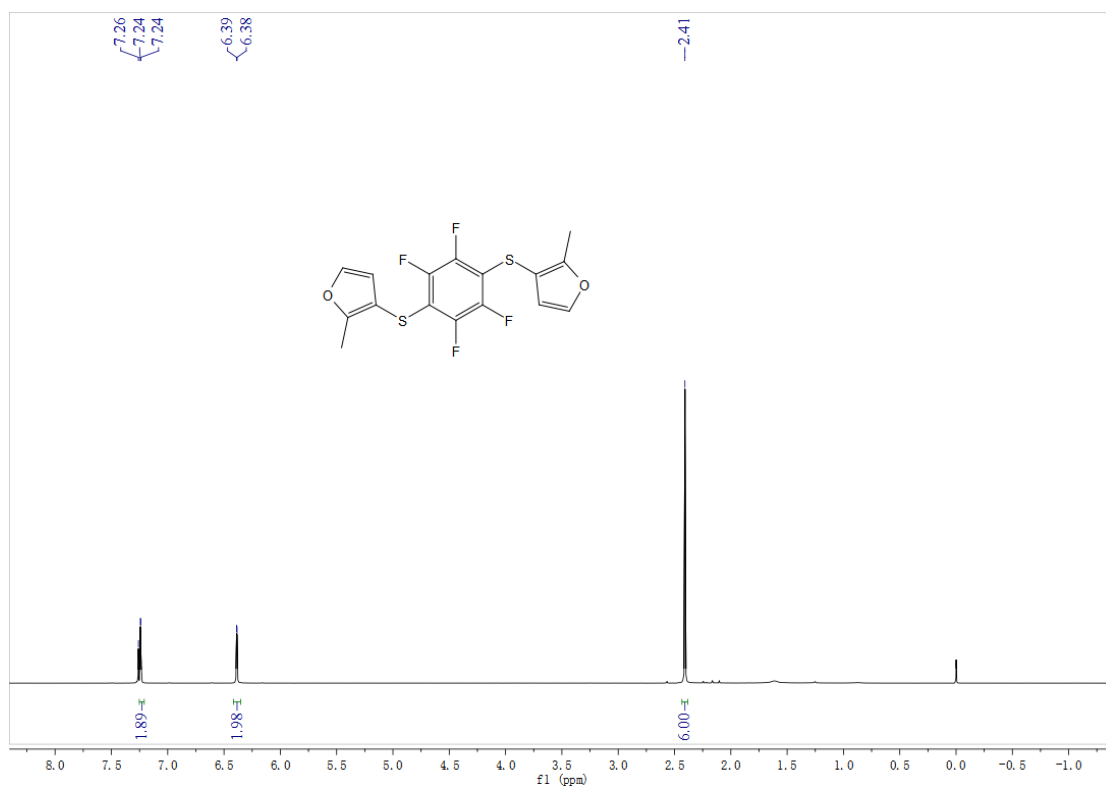
¹H NMR (400 MHz, CDCl₃): 2,3,5,6-tetrafluoro-1,4-bis(2-thienylsulfenyl)benzene (**3p**)



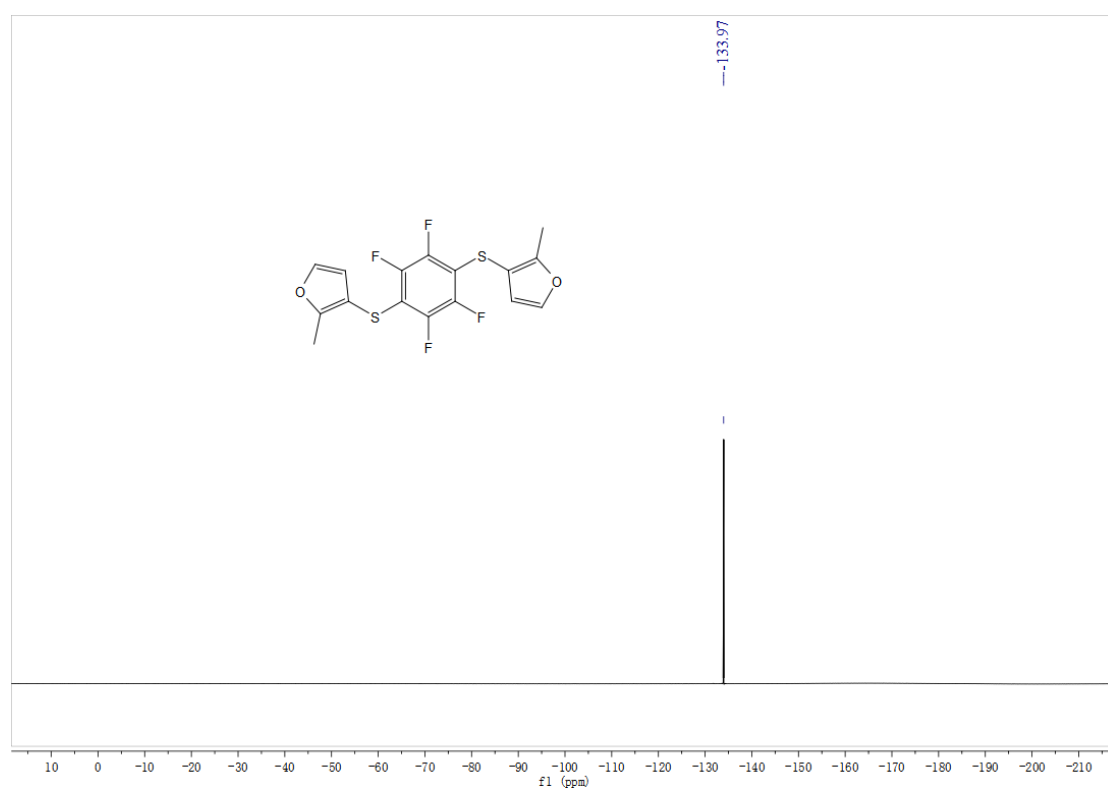
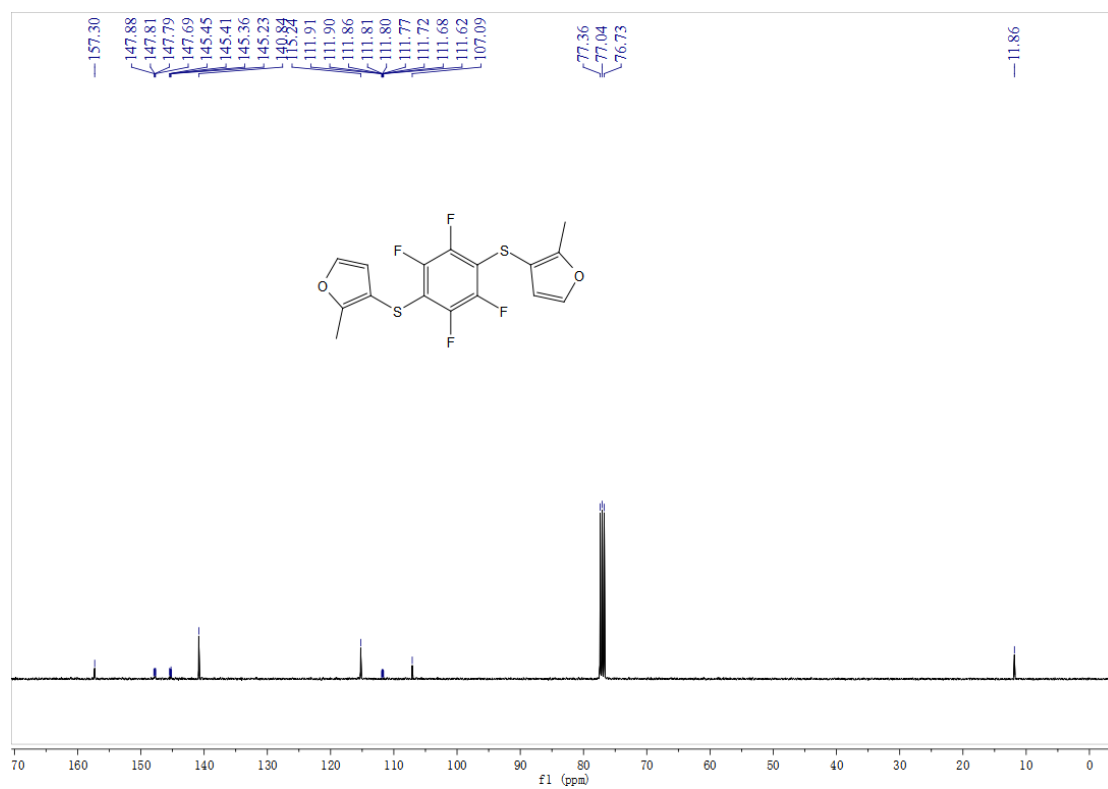
¹³C NMR (100 MHz, CDCl₃): 2,3,5,6-tetrafluoro-1,4-bis(2-thienylsulfenyl)benzene (**3p**)

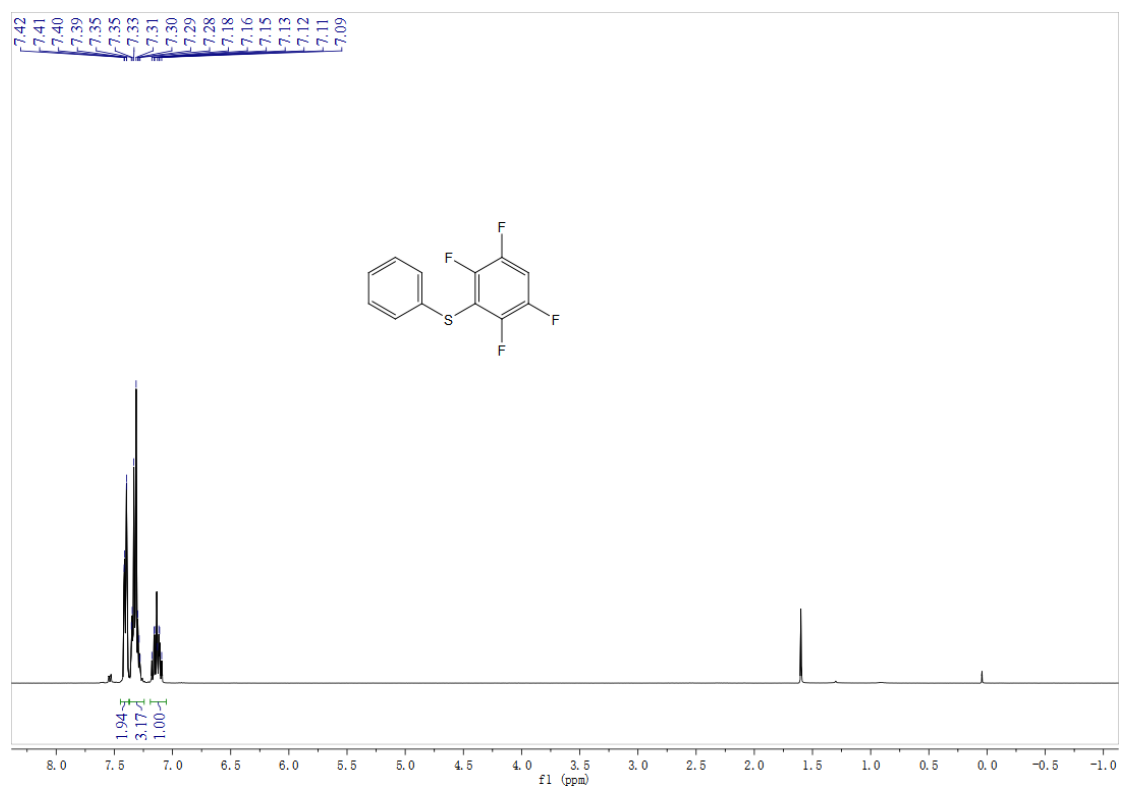


^{19}F NMR (376 MHz, CDCl_3): 2,3,5,6-tetrafluoro-1,4-bis(2-thienylsulfenyl)benzene (**3p**)

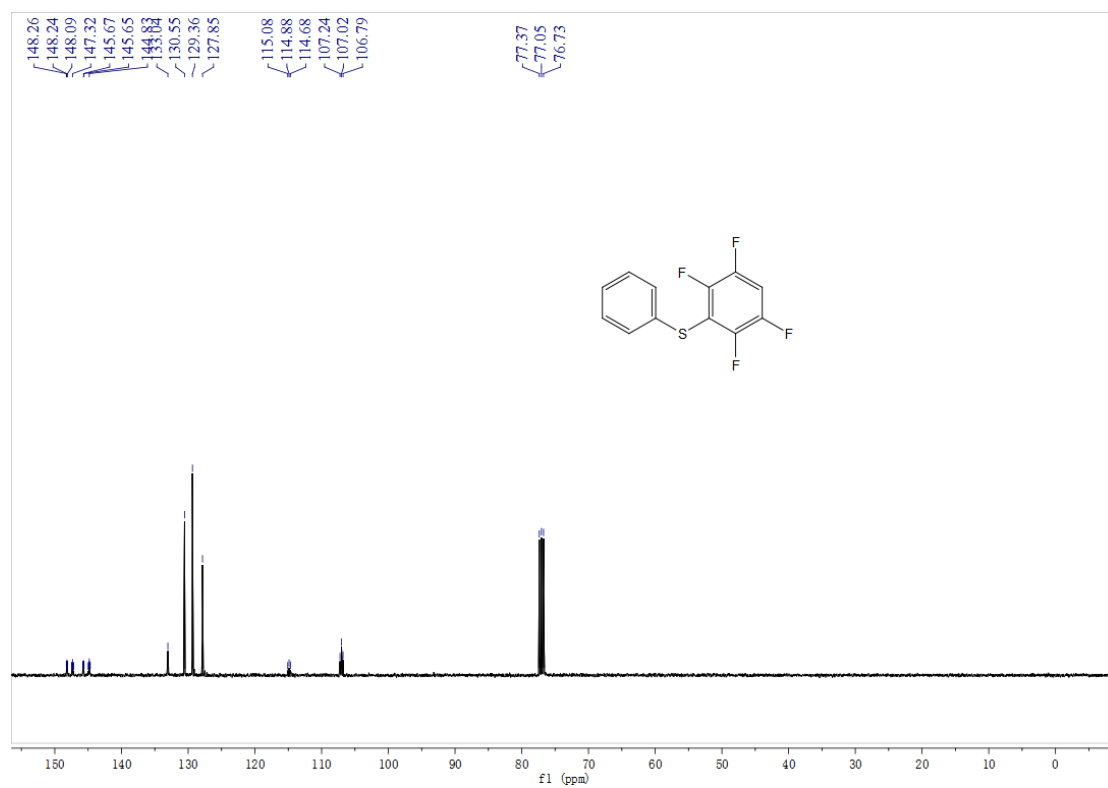


^1H NMR (400 MHz, CDCl_3): 2,3,5,6-tetrafluoro-1,4-bis(2-methyl-3-furyl)benzene (**3q**)

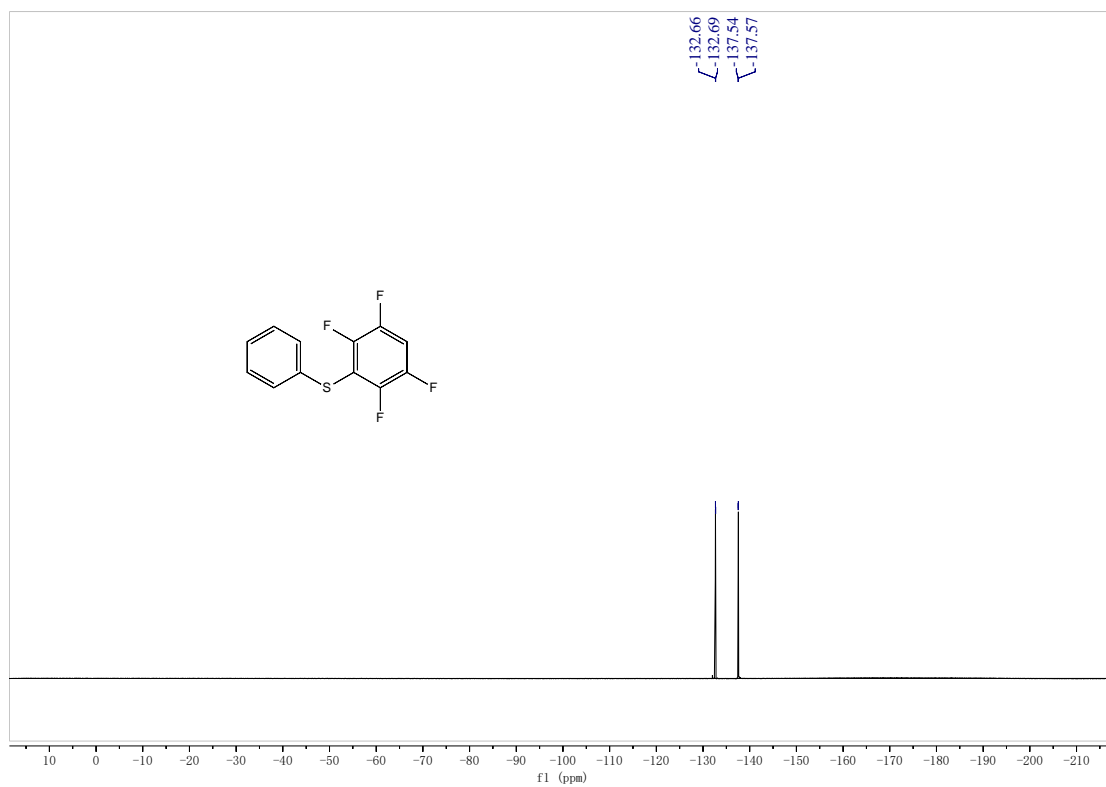


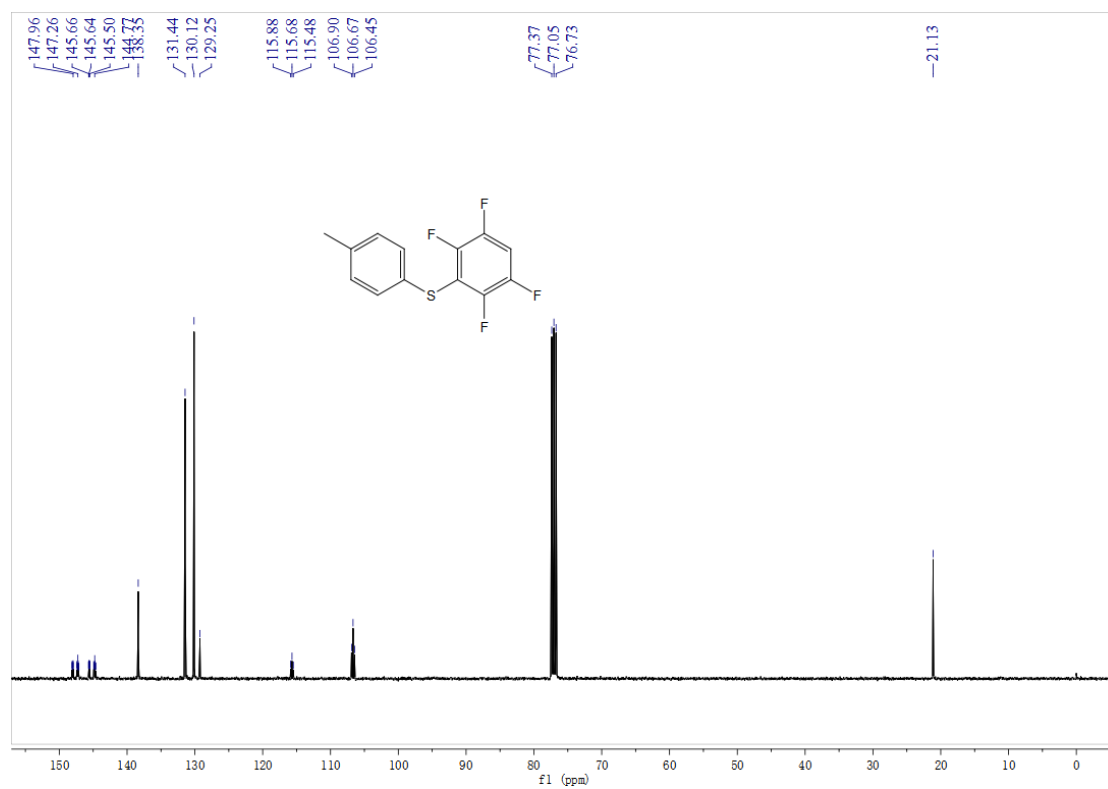


^1H NMR (400 MHz, CDCl_3): 1-phenylthio-2,3,5,6-tetrafluorobenzene (**7a**)

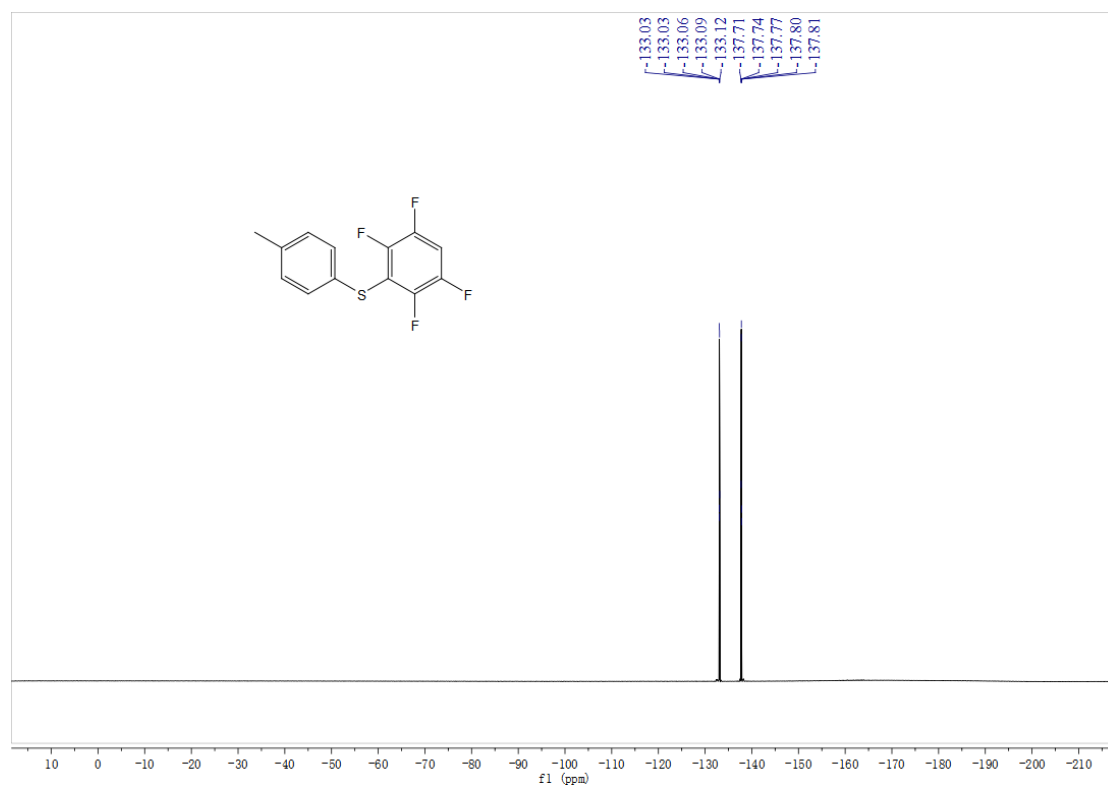


^{13}C NMR (100 MHz, CDCl_3): 1-phenylthio-2,3,5,6-tetrafluorobenzene (**7a**)

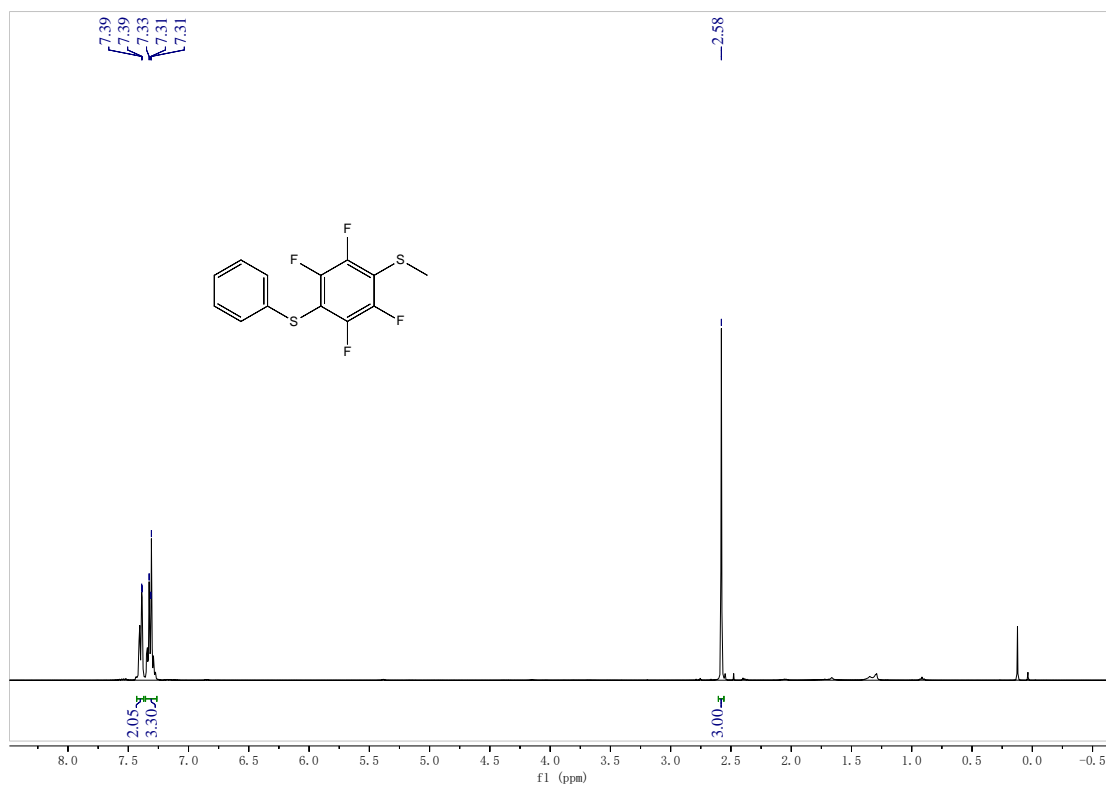




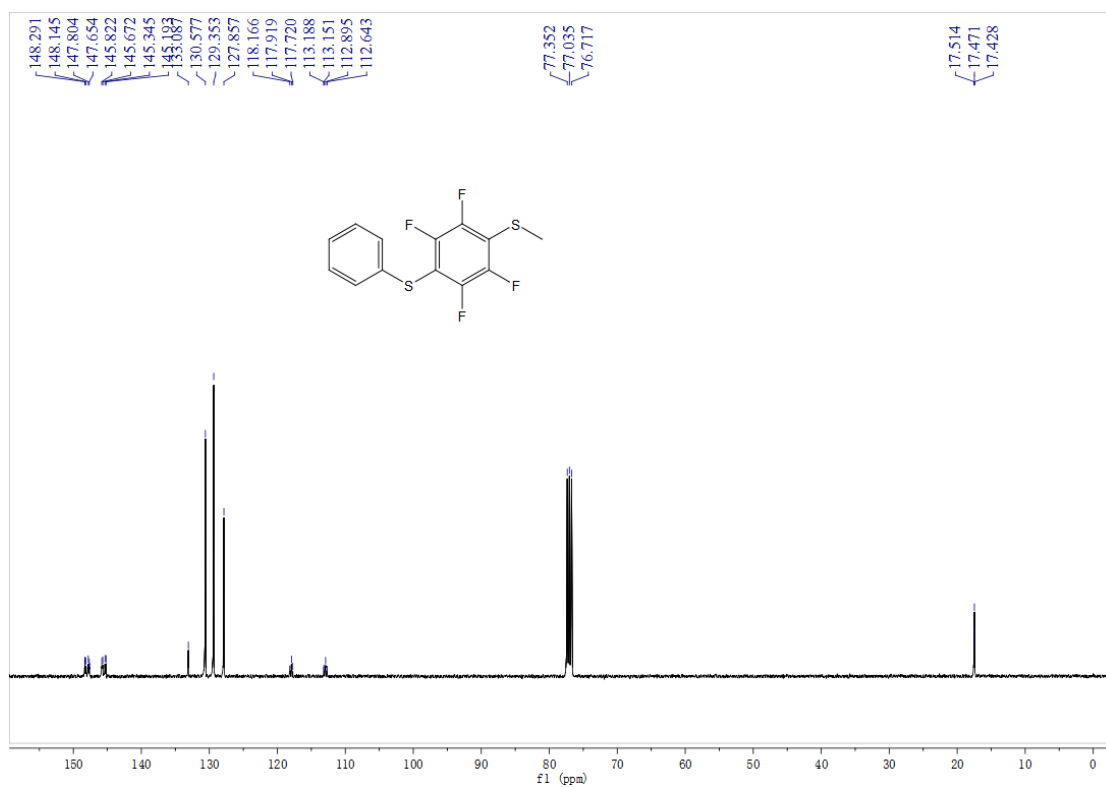
¹³C NMR (100 MHz, CDCl₃): 2,3,5,6-tetrafluoro-1-(*p*-tolylthio)benzene (**7b**)



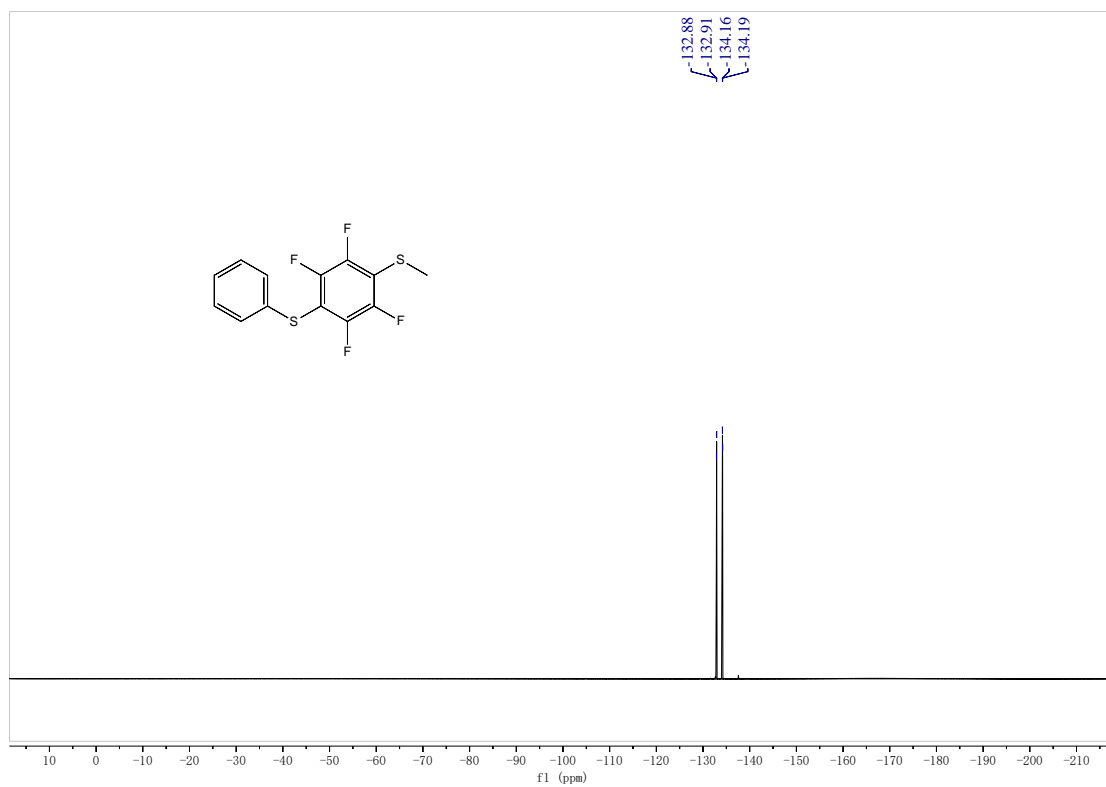
¹⁹F NMR (376 MHz, CDCl₃): 2,3,5,6-tetrafluoro-1-(*p*-tolylthio)benzene (**7b**)



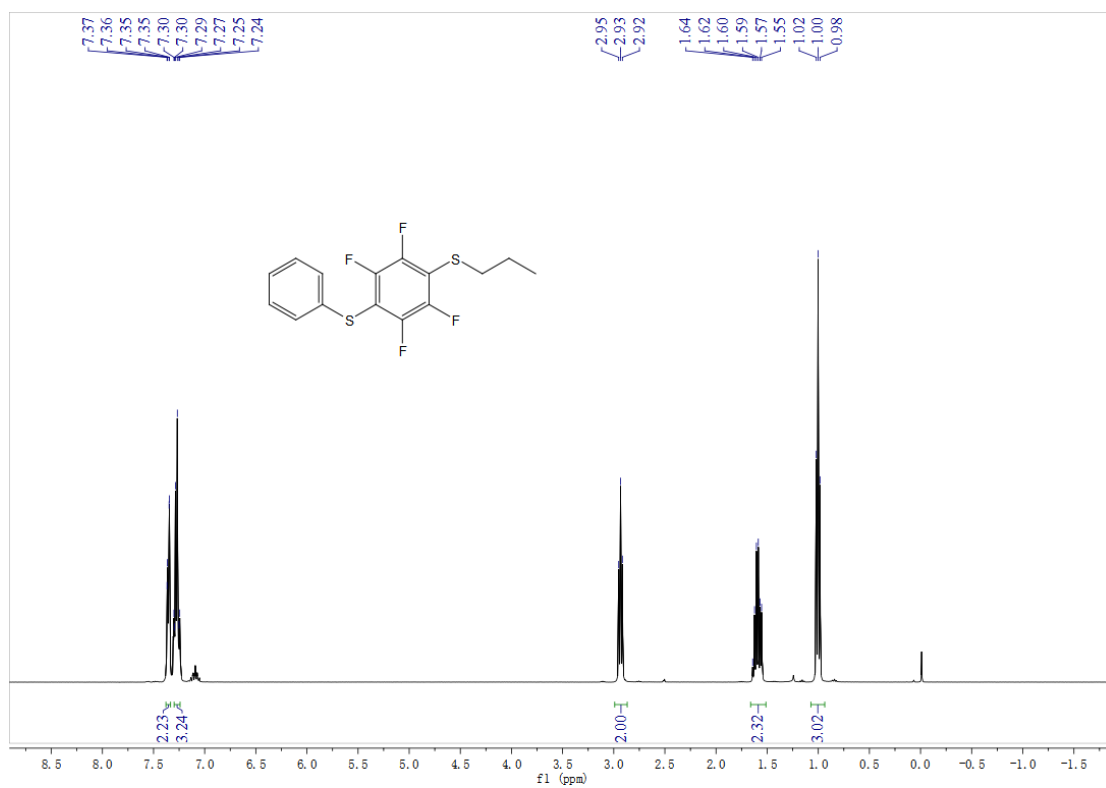
¹H NMR (400 MHz, CDCl₃): 1-methylmercapto-4-phenylmercapto-2,3,5,6-tetrafluor-benzol (**5b**)



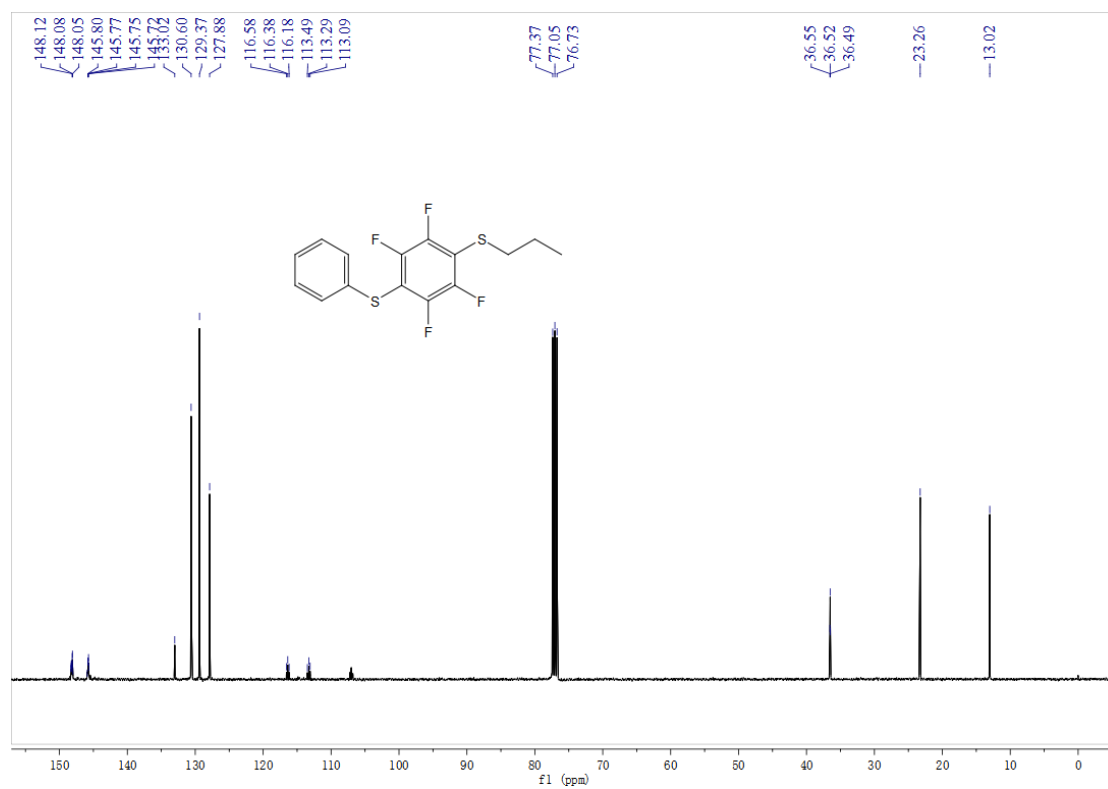
¹³C NMR (100 MHz, CDCl₃): 1-methylmercapto-4-phenylmercapto-2,3,5,6-tetrafluor-benzol (**5b**)



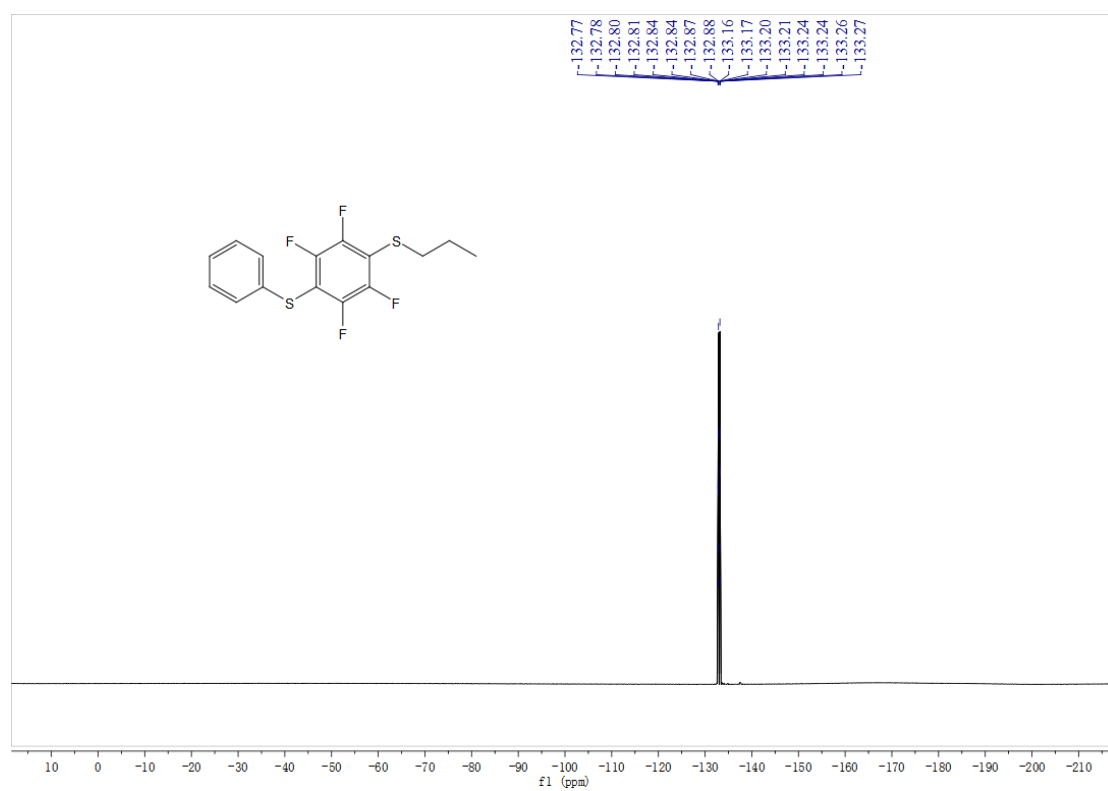
^{19}F NMR (376 MHz, CDCl_3): 1-methylmercapto-4-phenylmercapto-2,3,5,6-tetrafluor-benzol (**5b**)



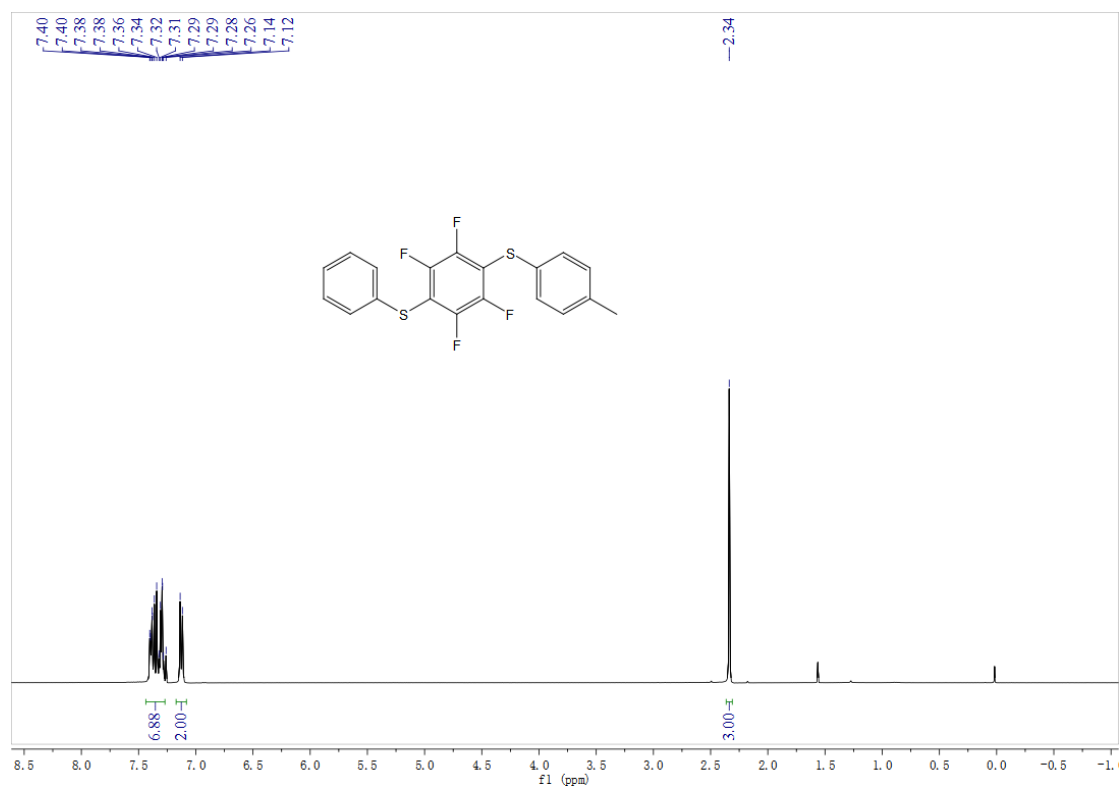
^1H NMR (400 MHz, CDCl_3): phenyl(2,3,5,6-tetrafluoro-4-(propylthio)phenyl)sulfane (**5c**)



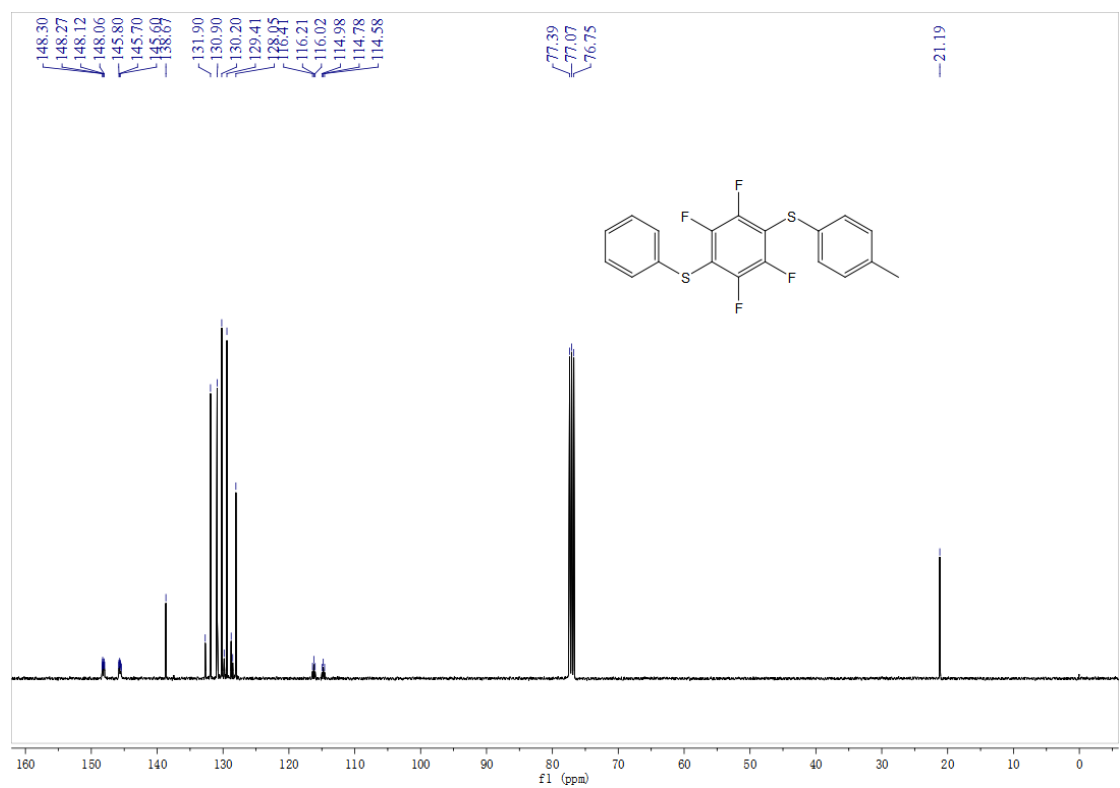
¹³C NMR (100 MHz, CDCl₃): phenyl(2,3,5,6-tetrafluoro-4-(propylthio)phenyl)sulfane (**5c**)



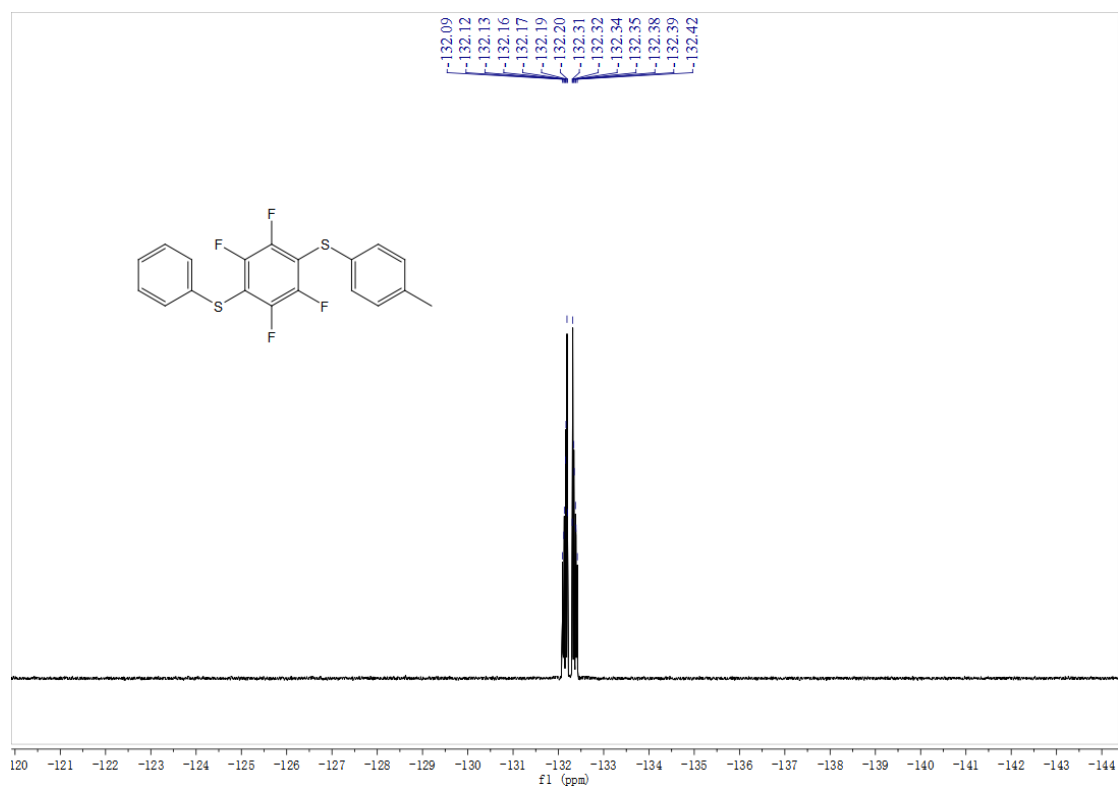
¹⁹F NMR (376 MHz, CDCl₃): phenyl(2,3,5,6-tetrafluoro-4-(propylthio)phenyl)sulfane (**5c**)



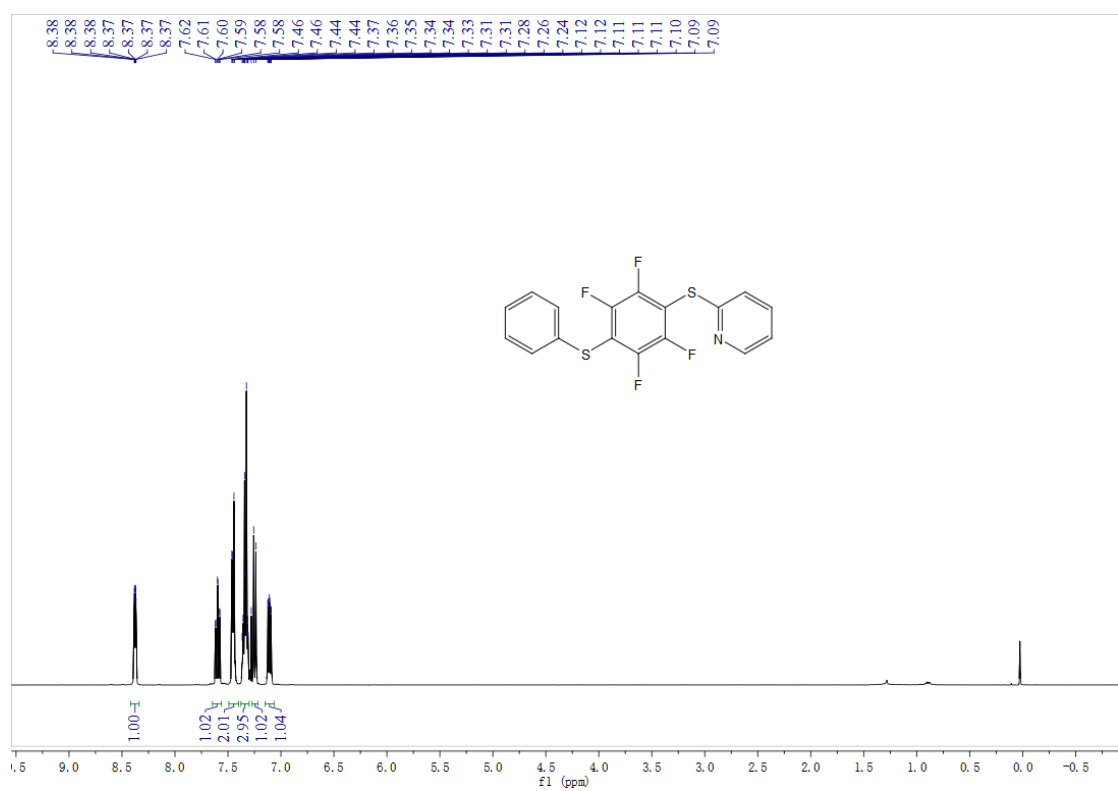
¹H NMR (400 MHz, CDCl₃): phenyl(2,3,5,6-tetrafluoro-4-(*p*-tolylthio)phenyl)sulfane (**5d**)



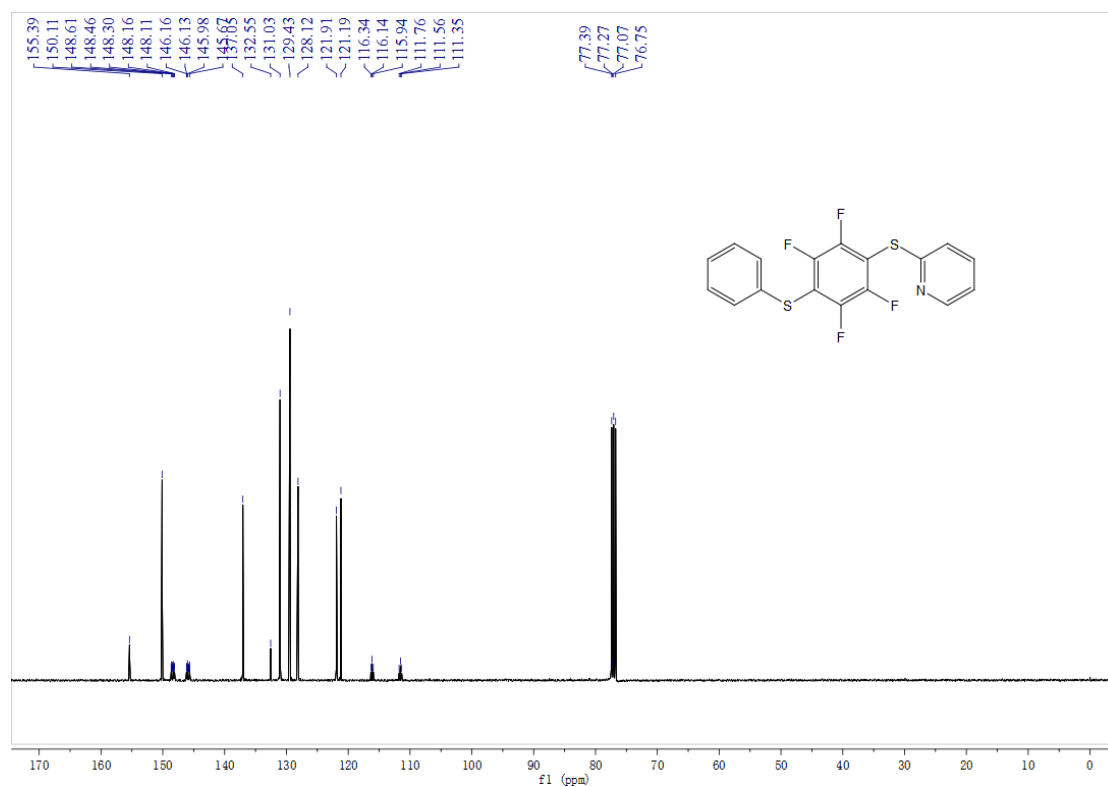
¹³C NMR (100 MHz, CDCl₃): phenyl(2,3,5,6-tetrafluoro-4-(*p*-tolylthio)phenyl)sulfane (**5d**)



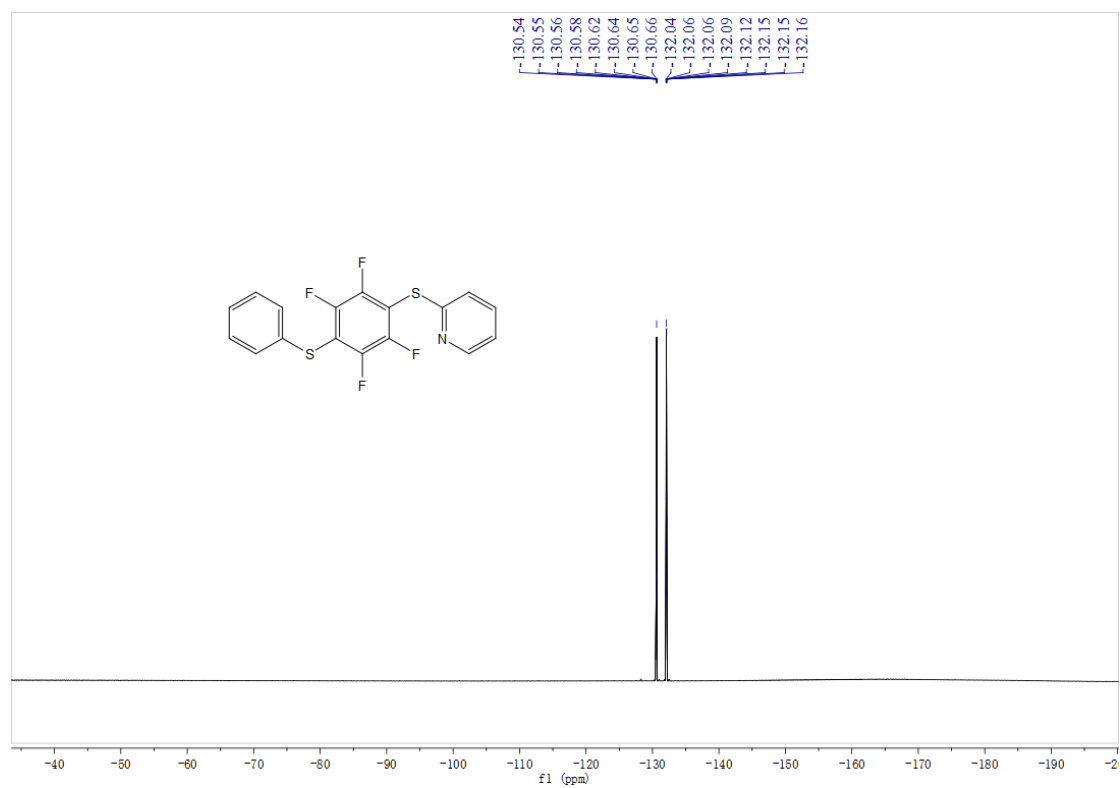
^{19}F NMR (376 MHz, CDCl_3): phenyl(2,3,5,6-tetrafluoro-4-(p-tolylthio)phenyl)sulfane (**5d**)



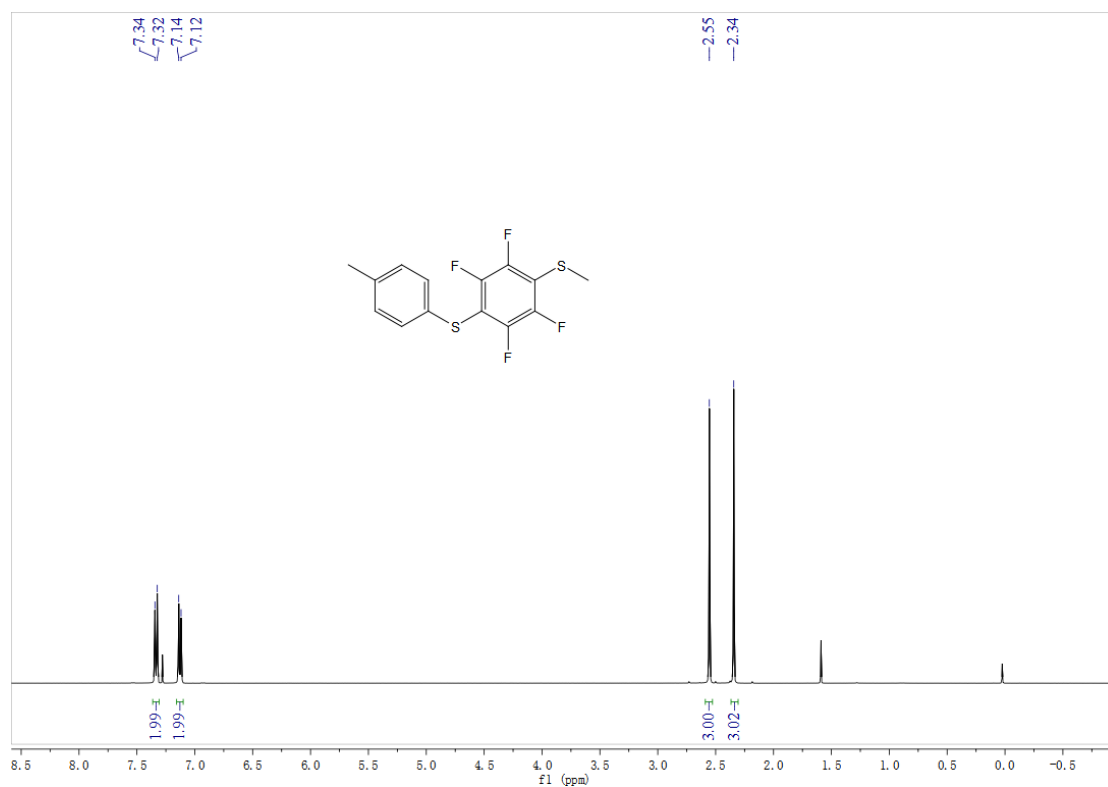
^1H NMR (400 MHz, CDCl_3): 2-((2,3,5,6-tetrafluoro-4-(phenylthio)phenyl)thio)pyridine (**5e**)



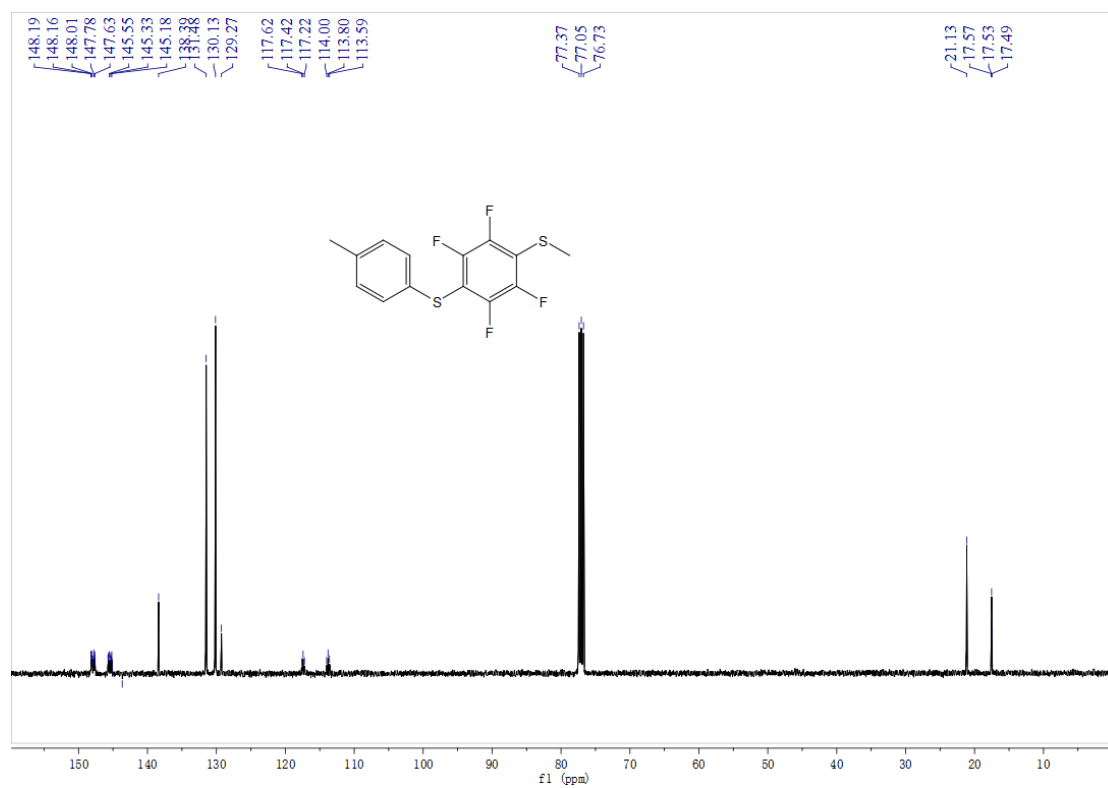
¹³C NMR (100 MHz, CDCl₃): 2-((2,3,5,6-tetrafluoro-4-(phenylthio)phenyl)thio)pyridine(5e)



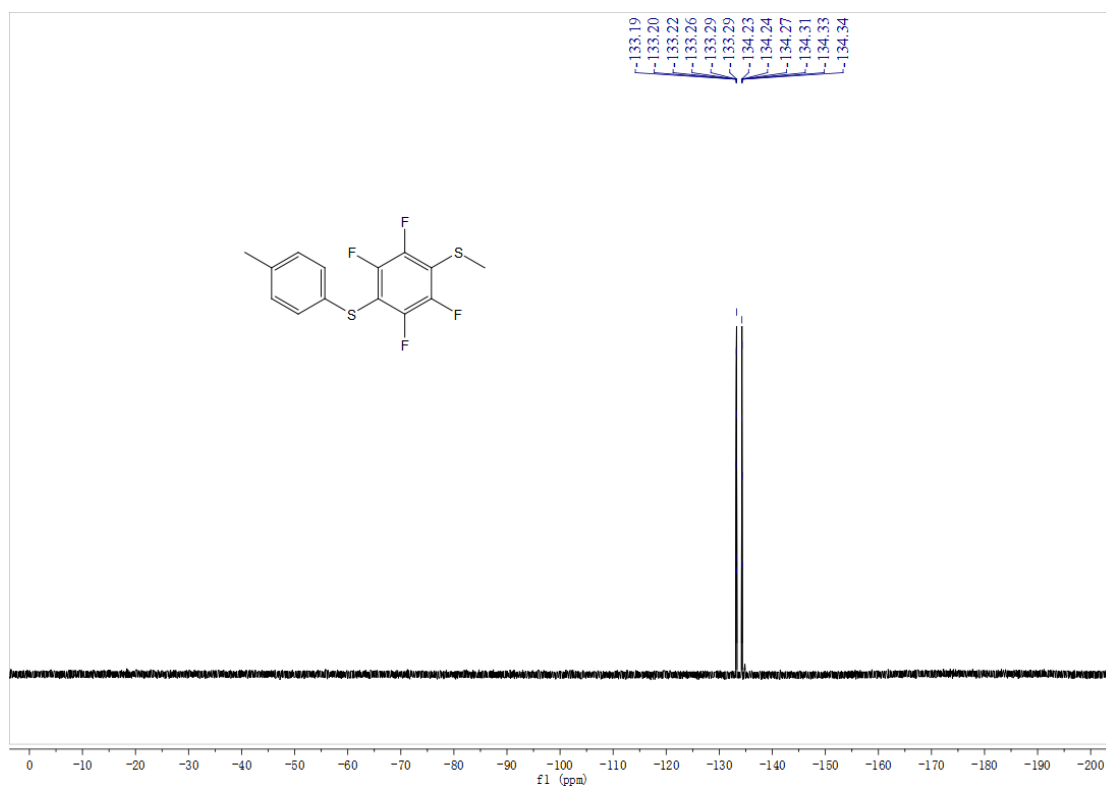
¹⁹F NMR (376 MHz, CDCl₃): 2-((2,3,5,6-tetrafluoro-4-(phenylthio)phenyl)thio)pyridine(5e)



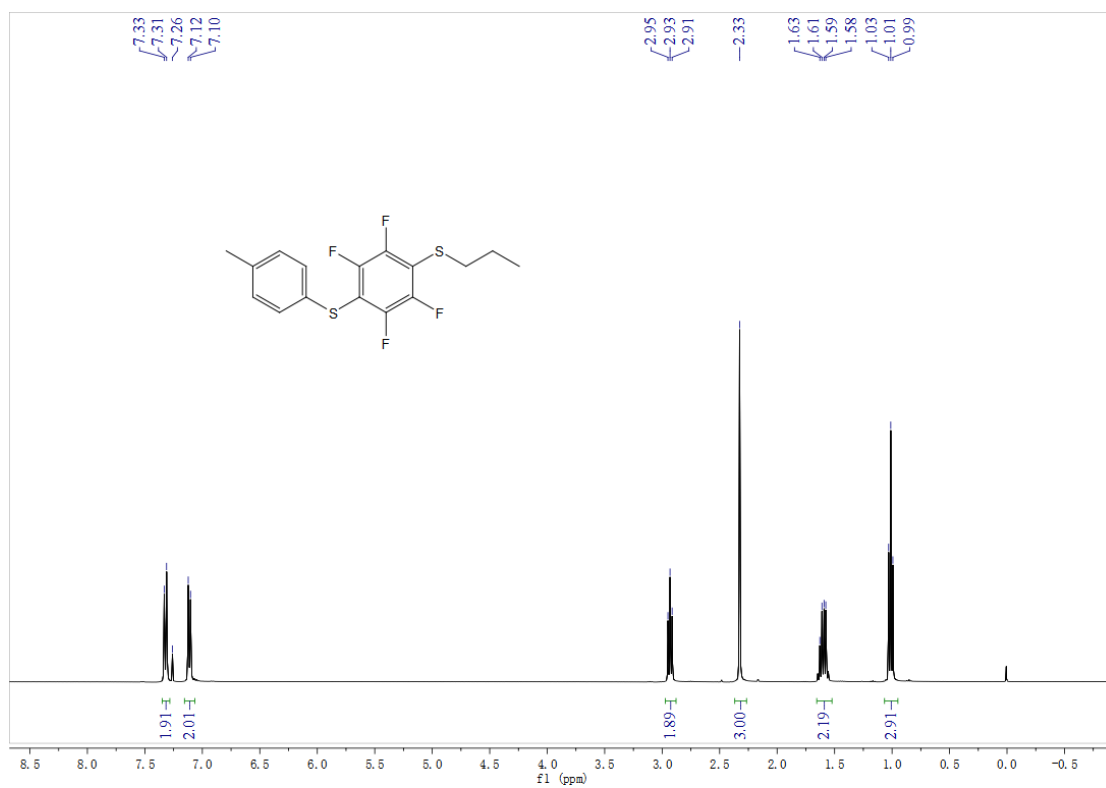
¹H NMR (400 MHz, CDCl₃): methyl(2,3,5,6-tetrafluoro-4-(p-tolylthio)phenyl)sulfane (**5f**)



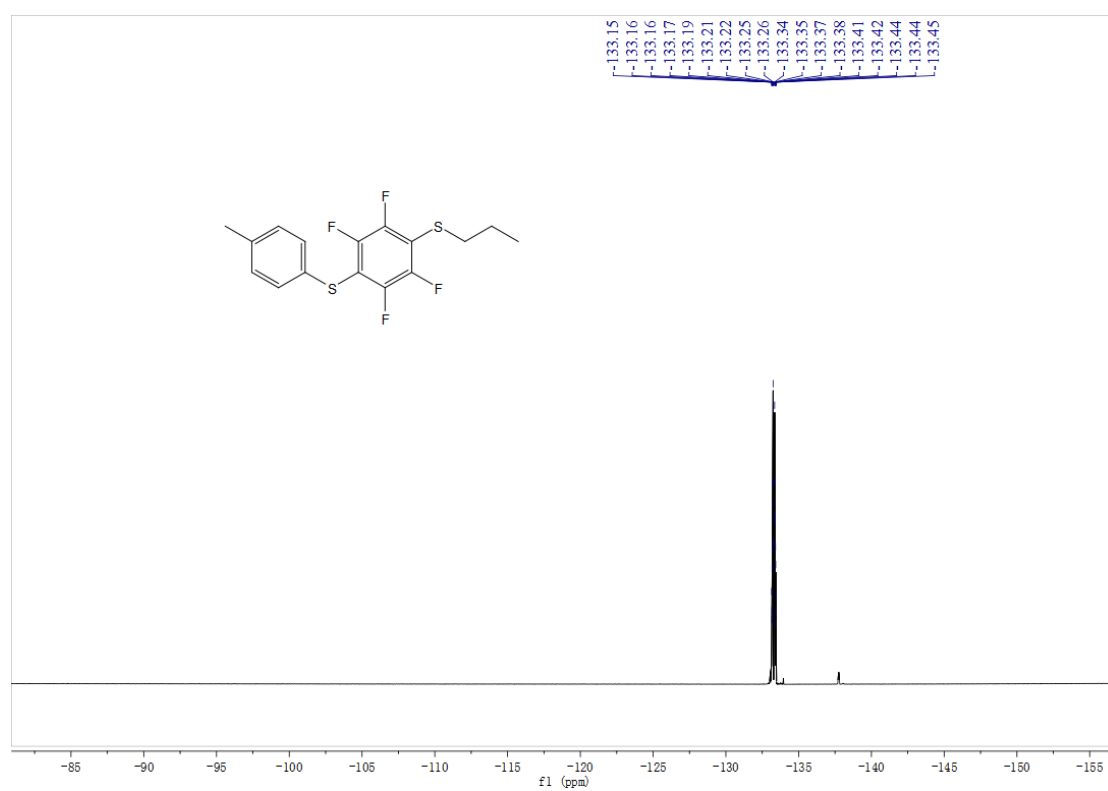
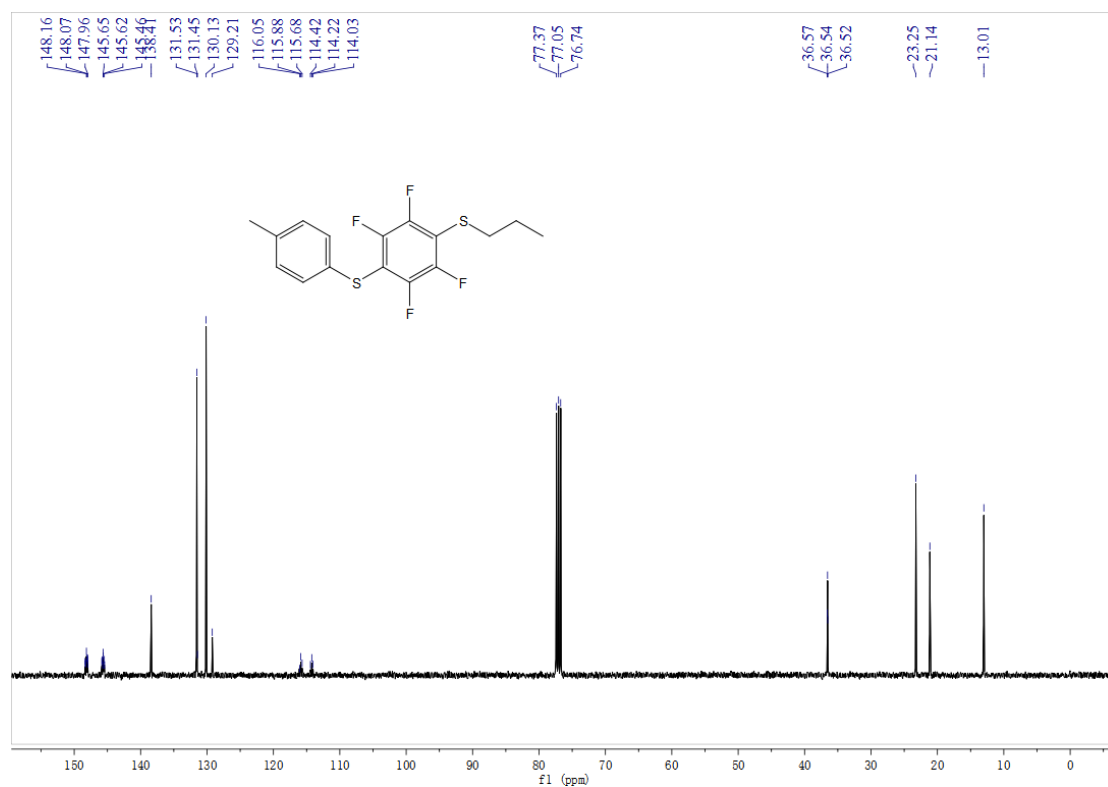
¹³C NMR (100 MHz, CDCl₃): methyl(2,3,5,6-tetrafluoro-4-(p-tolylthio)phenyl)sulfane (**5f**)

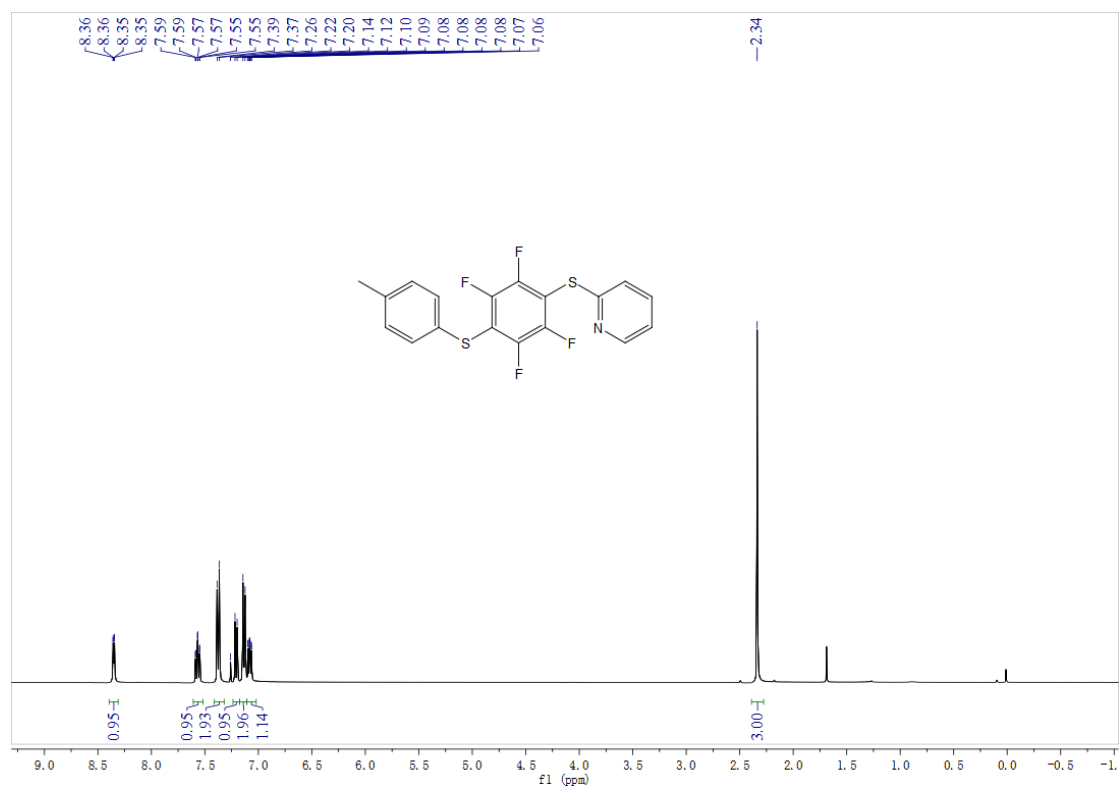


^{19}F NMR (376 MHz, CDCl_3): methyl(2,3,5,6-tetrafluoro-4-(p-tolylthio)phenyl)sulfane (5f)

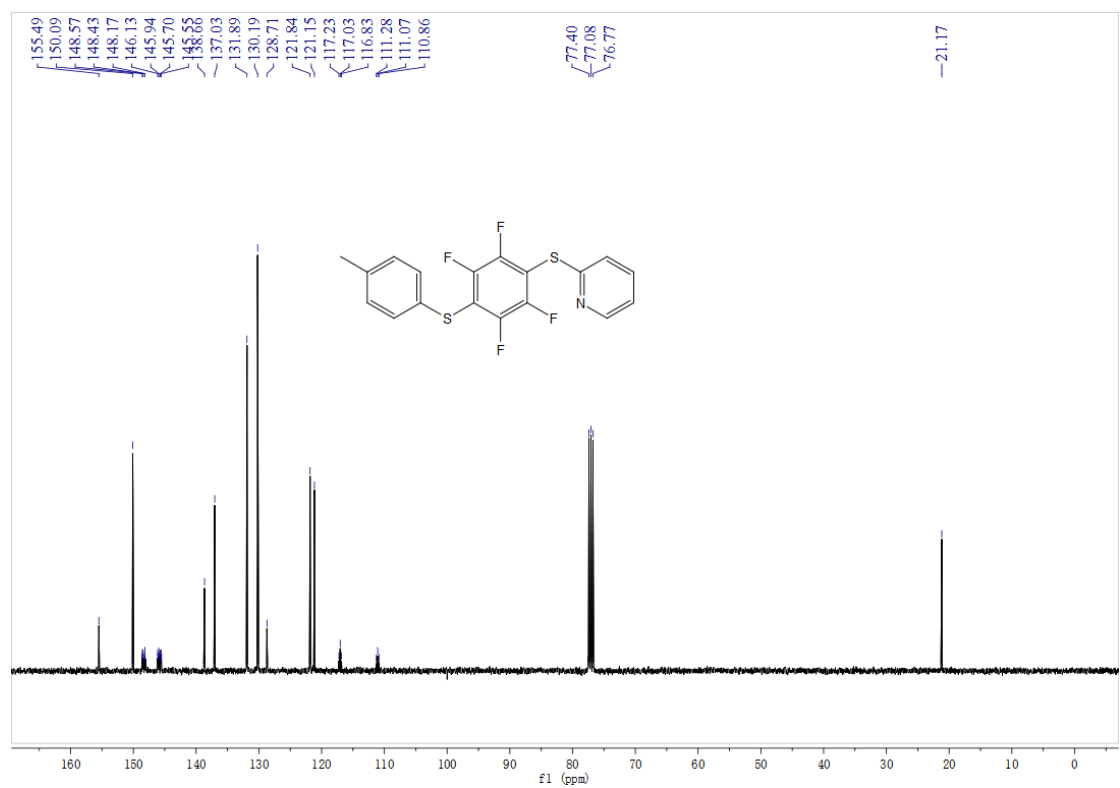


^1H NMR (400 MHz, CDCl_3): propyl(2,3,5,6-tetrafluoro-4-(p-tolylthio)phenyl)sulfane (5g)

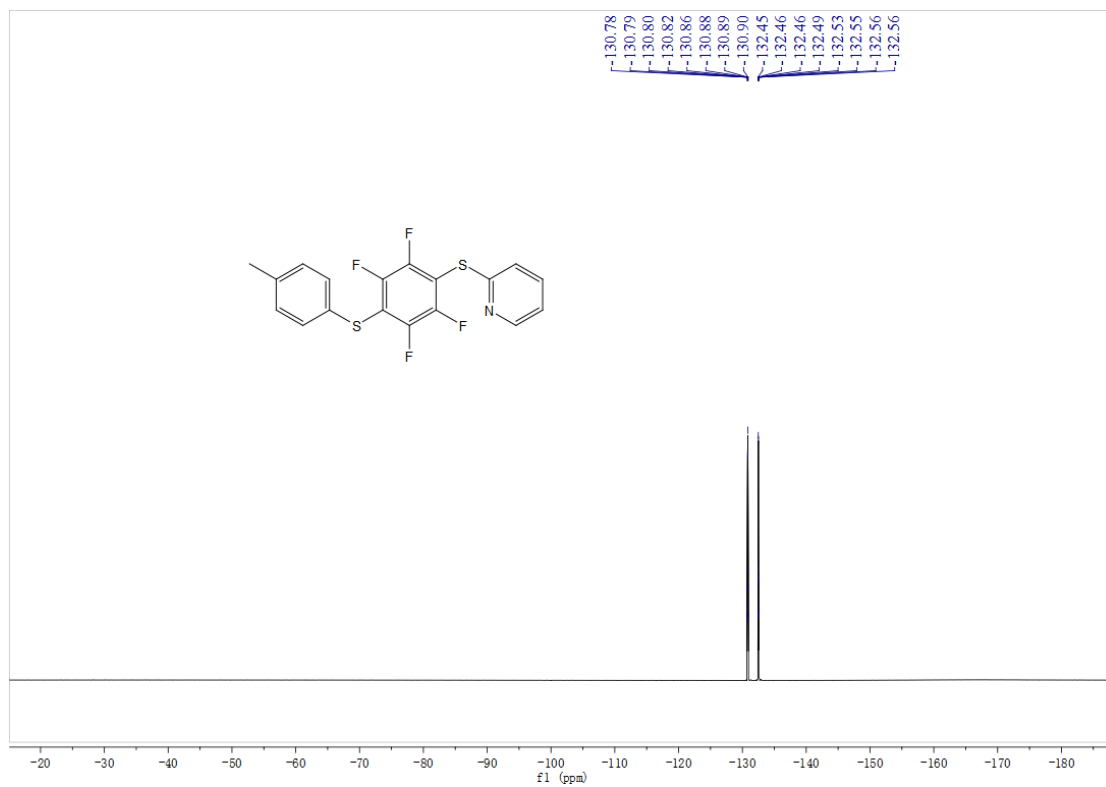




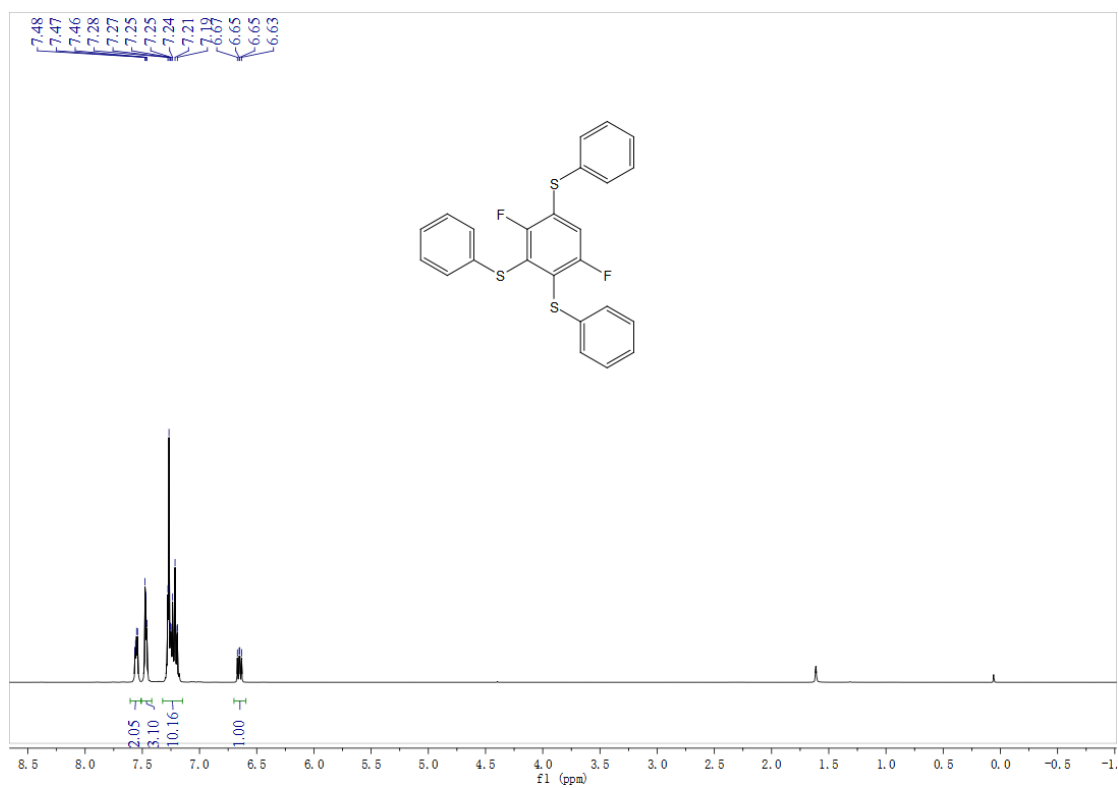
¹H NMR (400 MHz, CDCl₃): 2-((2,3,5,6-tetrafluoro-4-(p-tolylthio)phenyl)thio)pyridine (**5h**)



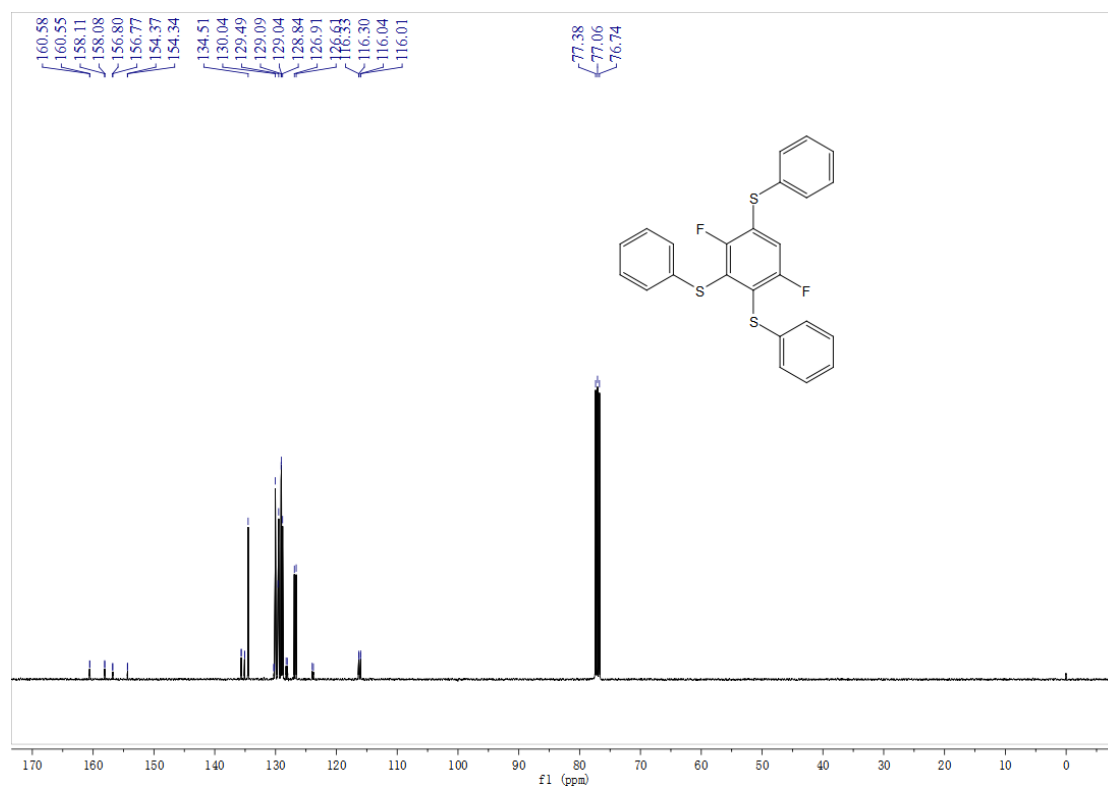
¹³C NMR (100 MHz, CDCl₃): 2-((2,3,5,6-tetrafluoro-4-(p-tolylthio)phenyl)thio)pyridine (**5h**)



¹⁹F NMR (376 MHz, CDCl₃): 2-((2,3,5,6-tetrafluoro-4-(p-tolylthio)phenyl)thio)pyridine (**5h**)



¹H NMR (400 MHz, CDCl₃): 1,2,4-tris(phenylthio)-3,6-difluorobenzene (**8**)



¹³C NMR (100 MHz, CDCl₃): 1,2,4-tris(phenylthio)-3,6-difluorobenzene (**8**)



¹⁹F NMR (376 MHz, CDCl₃): 1,2,4-tris(phenylthio)-3,6-difluorobenzene (**8**)

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