

Supporting Information

Reduction of CO₂ into Methylenes Coupled with the Formation of C-S Bonds under NaBH₄/I₂ System

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General Information

All solvents were dried and distilled before use according to the standard methods. Unless otherwise noted, the starting materials were commercially available and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh neutral alumina in hexane and ethyl acetate.

¹H NMR, ¹³C NMR, ¹⁹F NMR, ¹¹B NMR data were recorded with 600 MHz, 400 MHz spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.16 ppm, chloroform), respectively.

General procedure for the reductive functionalization of CO₂ with thiophenols to dithioacetals

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added NaBH₄ (1.5 mmol), the tube was evacuated and filled CO₂ for three times. Then the thiol (0.5 mmol) and 1,4-dioxane (1.0 mL) were added to the tube under a positive CO₂ atmosphere. The reaction tube was sealed and stirred at 80 °C for 30 min, After the reaction mixture allowed to room temperature, I₂ (0.5 mmol) was added under a positive CO₂ atmosphere, the reaction tube was sealed again and stirred for 24 h at 100 °C. After completion, the residue was carefully quenched with water and the mixture was extracted with ethyl acetate (3 x 10 mL). The yields were determined by ¹H NMR technique using trichloroethylene (45 μ L, 0.5 mmol) as an internal standard. The reaction mixture was purified by neutral alumina column chromatography with hexane/ethyl acetate as the eluent to afford the desired dithioacetals. All of the products were characterized by NMR techniques.

Typical example of preparation of 2a in 1 mmol scale:

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added NaBH₄ (113.4 mg, 3.0 mmol), the tube was evacuated and filled CO₂ for three times. Then the 4-

methylbenzenethiol **1a** (124.2 mg, 1.0 mmol) and 1,4-dioxane (2.0 mL) were added to the tube under a positive CO₂ atmosphere. The reaction tube was sealed and stirred at 80 °C for 30 min. After the reaction mixture cooled down to room temperature, I₂ (253.8 mg, 1.0 mmol) was added under CO₂ atmosphere, the reaction tube was sealed again and stirred for 24 h at 100 °C. After reaction completed, the residue was carefully quenched with water and the mixture was extracted with ethyl acetate (3 x 10 mL). The yield was determined by ¹H NMR using trichloroethylene (90 µL, 1.0 mmol) as an internal standard. The reaction mixture was purified by neutral alumina column chromatography with hexane/ethyl acetate as the eluent to afford the colorless oil bis(*p*-tolylthio)methane at 92% yield (119.6 mg).

ORTEP diagram of compound 2p

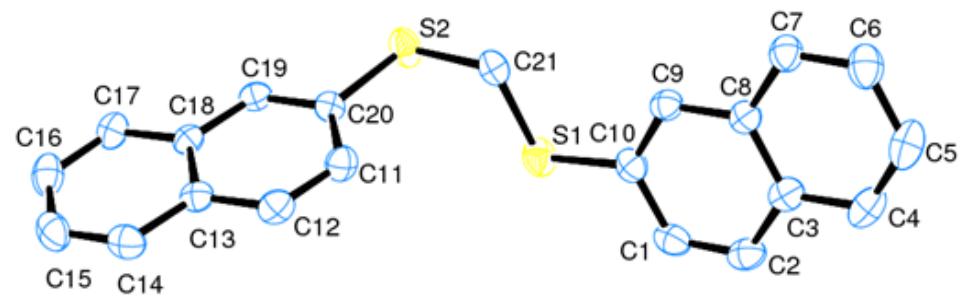


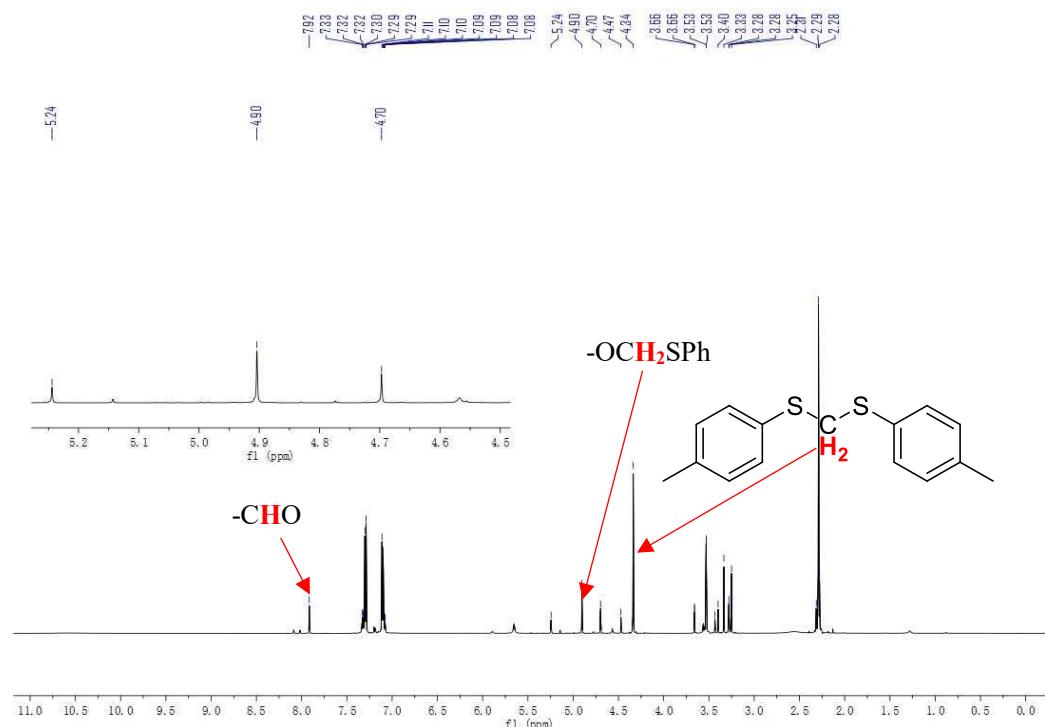
Figure S1. ORTEP diagram of compound **2p** with thermal ellipsoids at 30% probability (H not shown for clarity)

Crystal data and structure refinement details of 2p

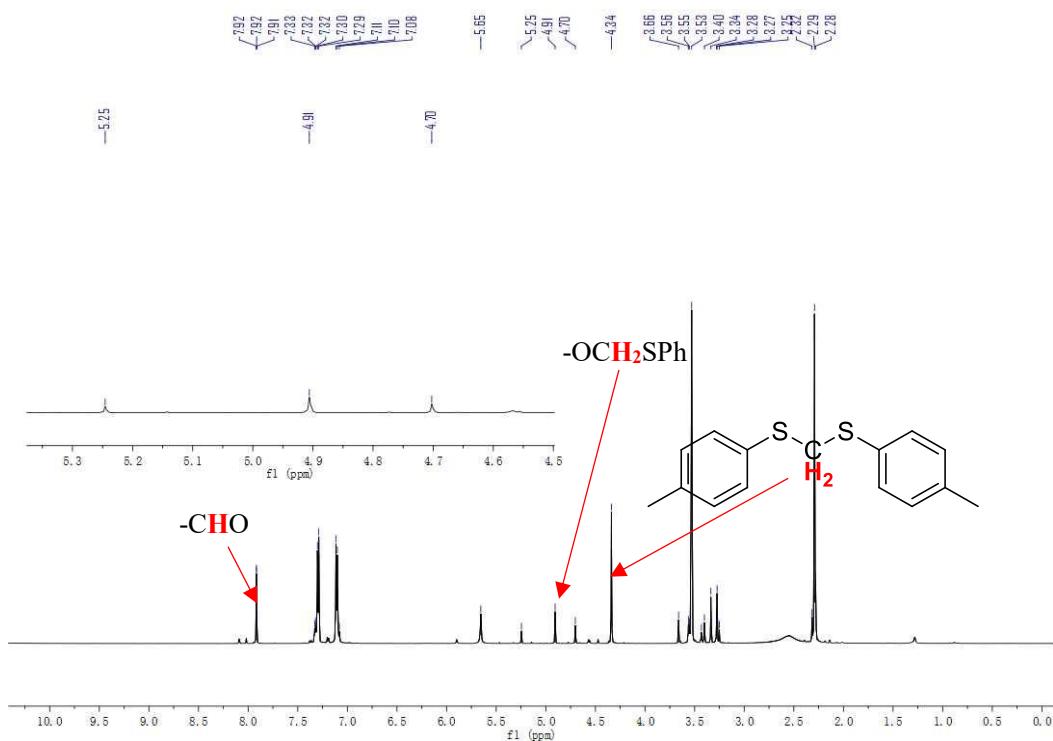
Table S1. Single crystal X-ray data and structure refinement details for 2p

Identification code	2p
Empirical formula	C ₂₁ H ₁₆ S ₂
Formula weight	332.46
Temperature	200 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P 21/c
Unit cell dimensions	a = 16.6265(19) Å α= 90° b = 5.9931(6) Å β= 104.15° c = 16.6263(19) Å γ = 90°
Volume	1606.4 (3) Å ³
Z	4
Density (calculated)	1.375 g/cm ³
Absorption coefficient	0.328mm ⁻¹
F(000)	696
Crystal size	0.16 x 0.16 x 0.15 mm ³
Theta range for data collection	2.52 to 25.04°.
Index ranges	-19<=h<=17, -7<=k<=7, -19<=l<=19
Reflections collected	8507
Independent reflections	2799 [R(int) = 0.0384]
Completeness to theta= 25.04°	98.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6609
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2799/0/208
Goodness-of-fit on F2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0361, wR2 = 0.0824
R indices (all data)	R1 = 0.0539, wR2 = 0.0910
Largest diff. peak and hole	0.19 and -0.22 e.Å ⁻³

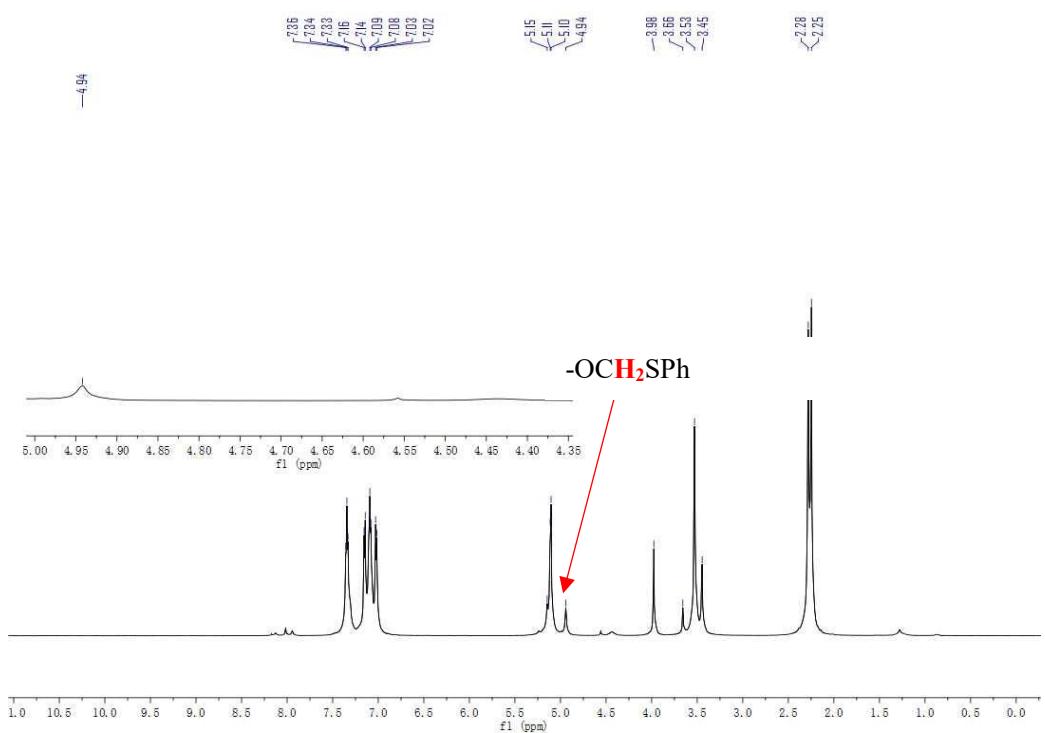
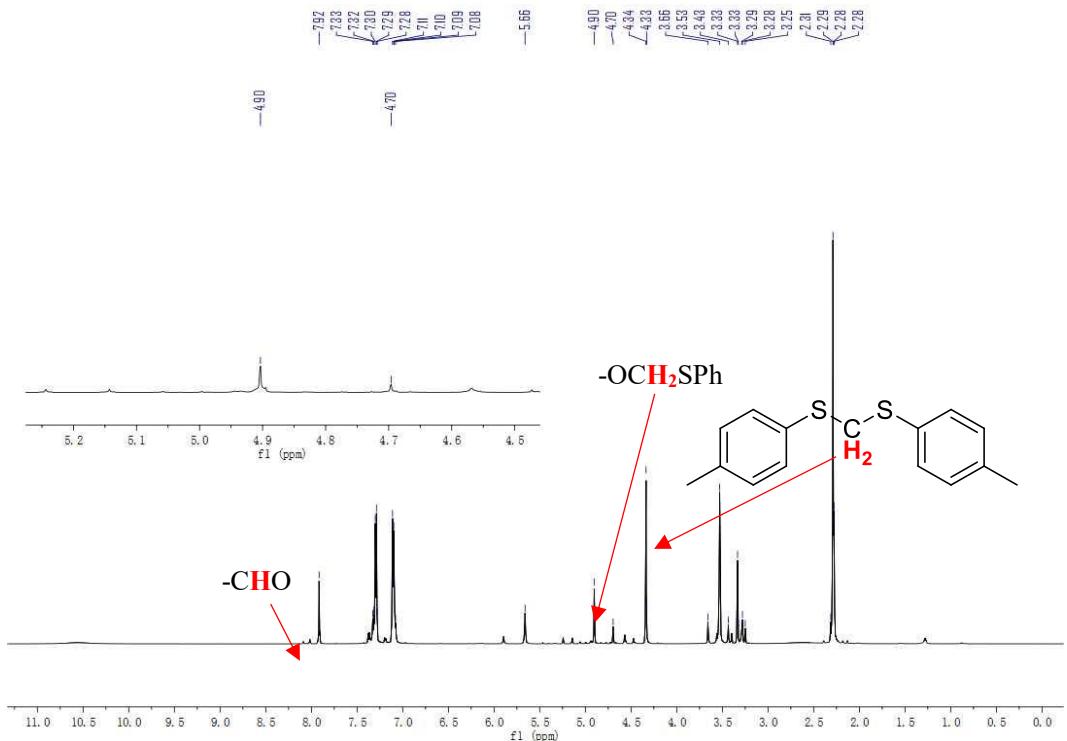
Monitoring the reaction process by NMR in 1,4-dioxane-d₈

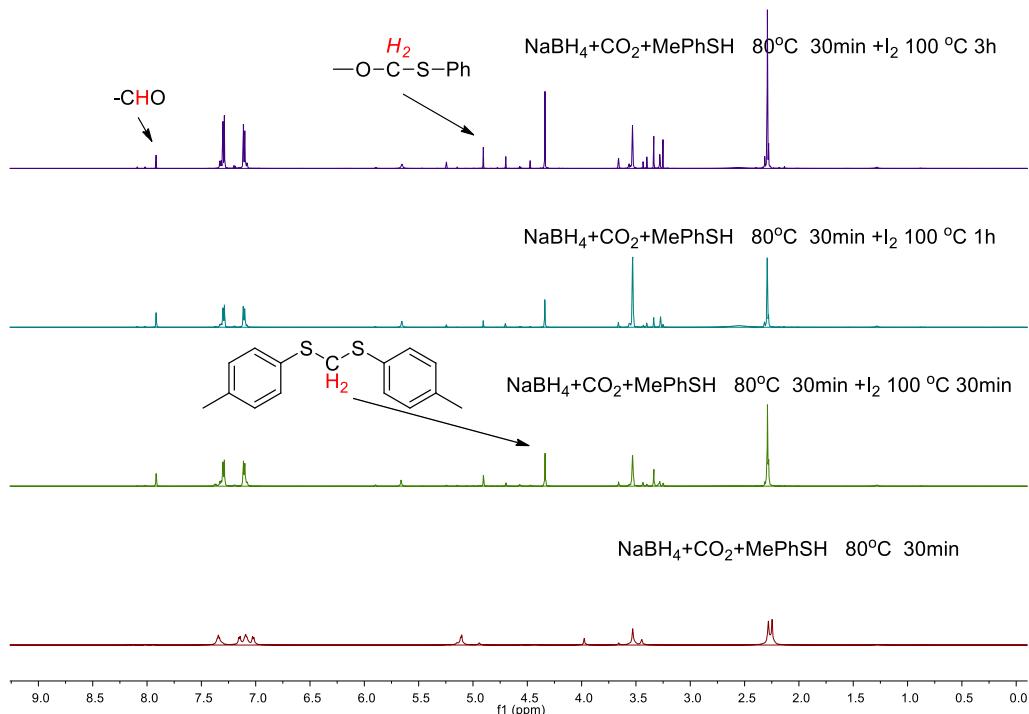


¹H NMR (NaBH₄ + CO₂ + MePhSH 80 °C 30 min + I₂ 100 °C 3 h)



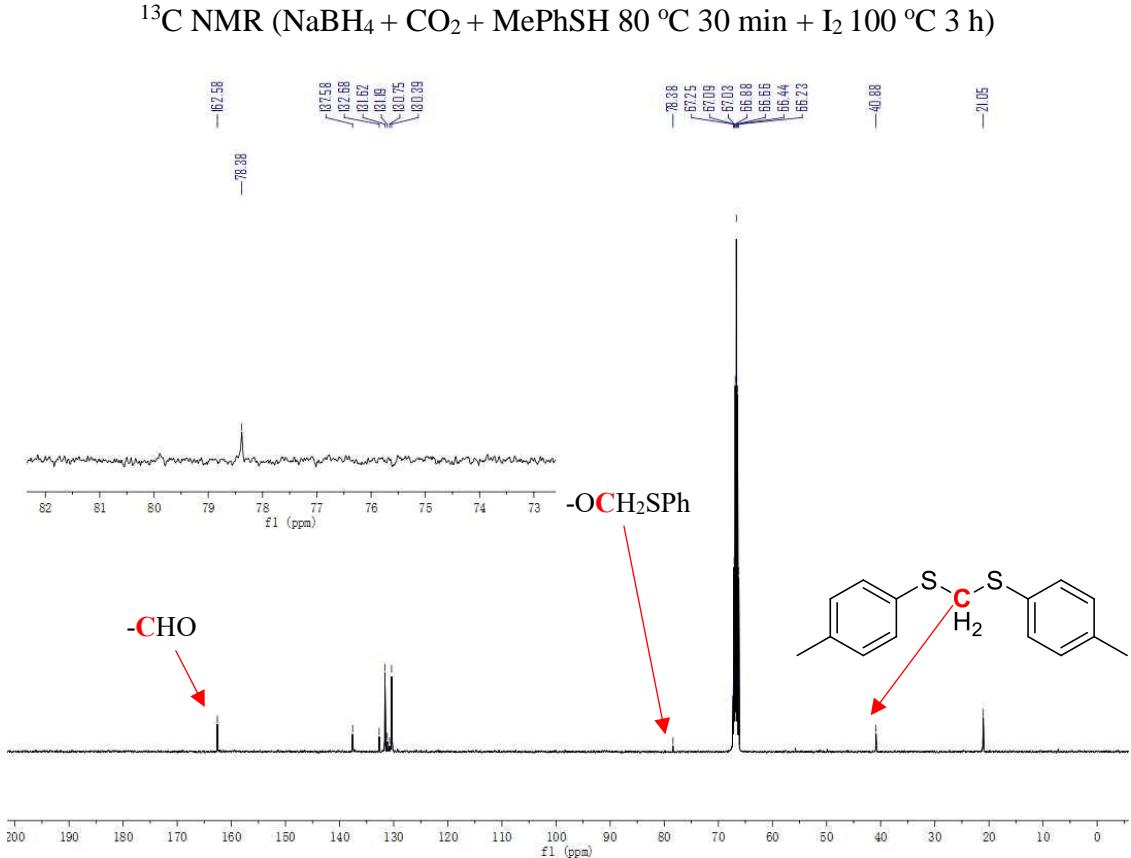
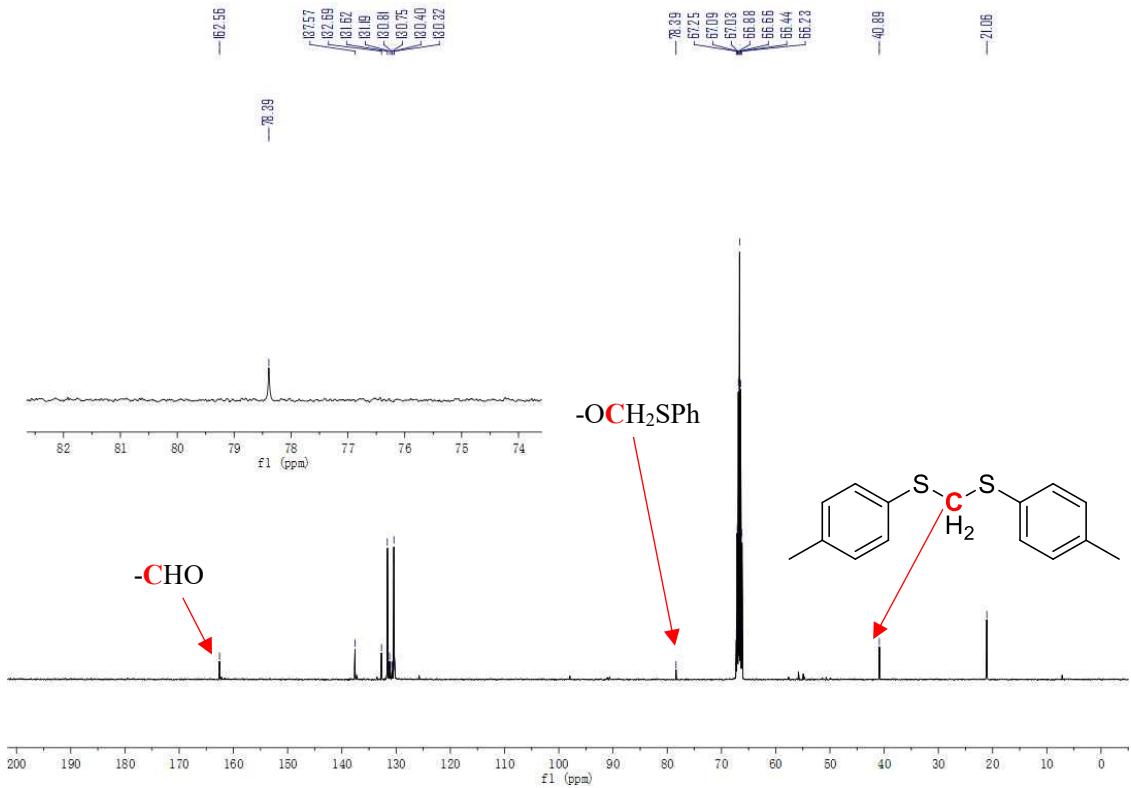
¹H NMR (NaBH₄ + CO₂ + MePhSH 80 °C 30 min + I₂ 100 °C 1 h)

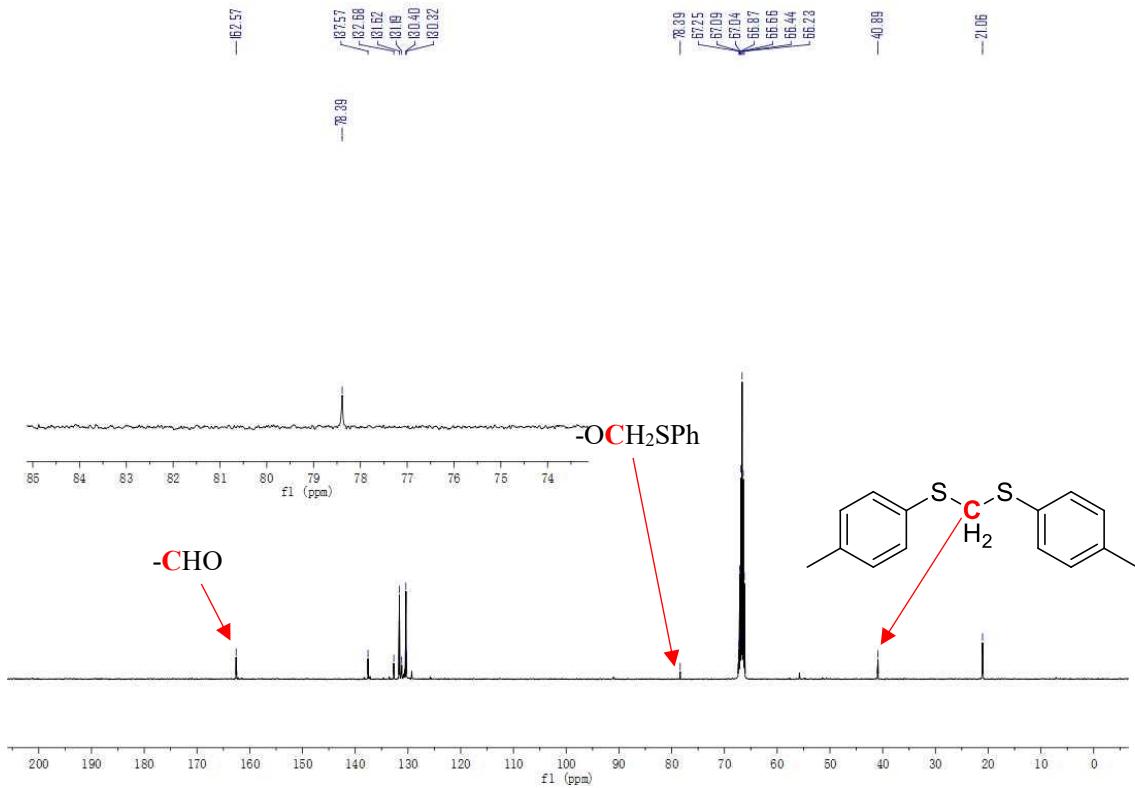




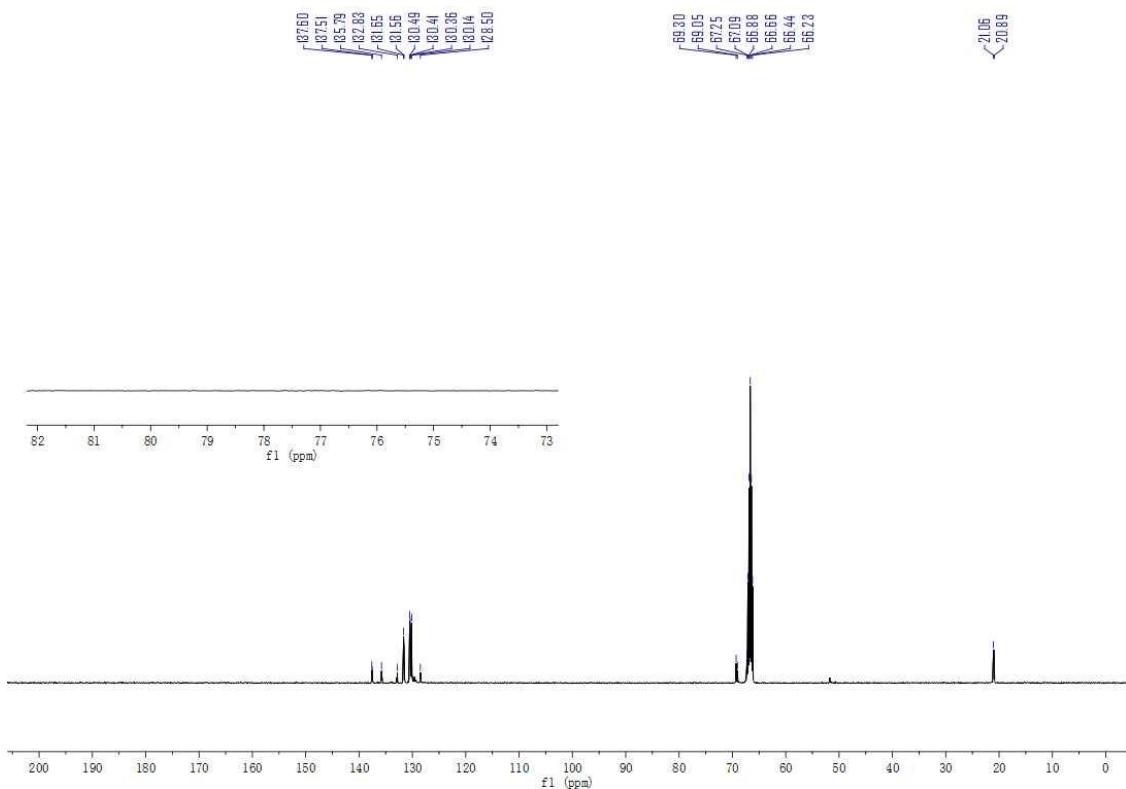
¹H NMR spectrum for the reaction process in 1,4-dioxane-d₈ in comparison

Figure S2. ¹H NMR spectrum for the reaction process in 1,4-dioxane-d₈

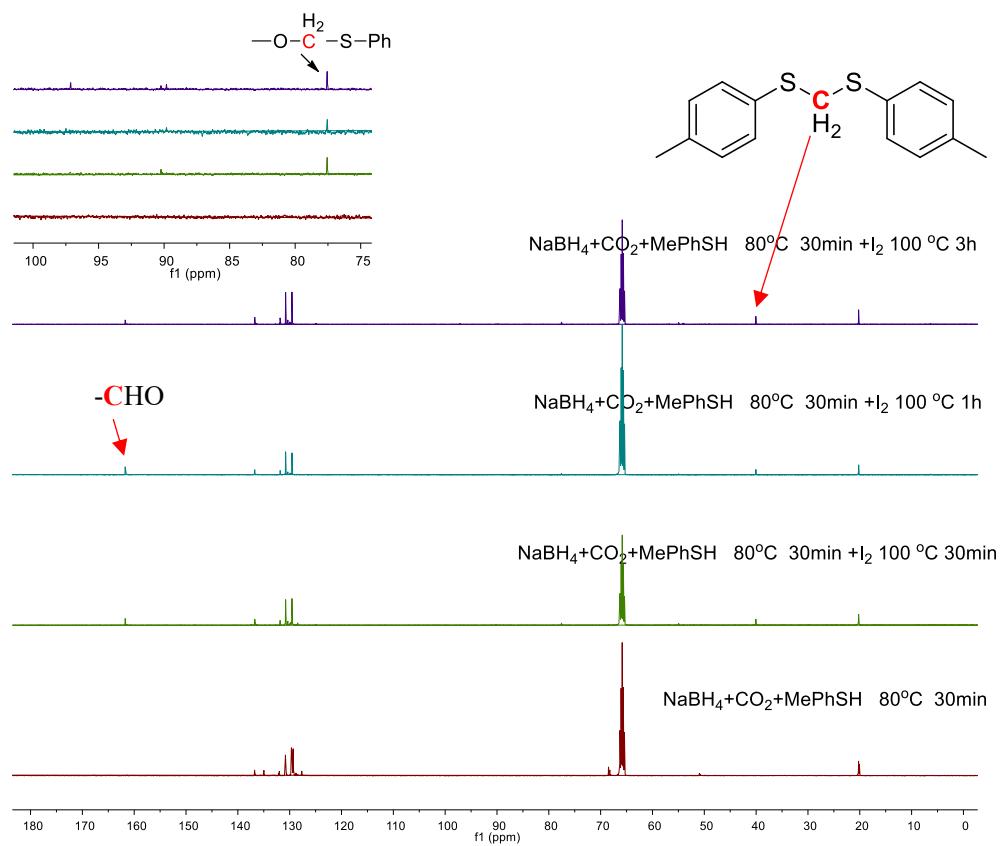




¹³C NMR (NaBH₄ + CO₂ + MePhSH 80 °C 30 min + I₂ 100 °C 30 min)



¹³C NMR (NaBH₄ + CO₂ + MePhSH 80 °C 30 min)



^{13}C NMR spectrum for the reaction process in 1,4-dioxane-d₈ in comparison

Figure S3. ^{13}C NMR spectrum for the reaction process in 1,4-dioxane-d₈

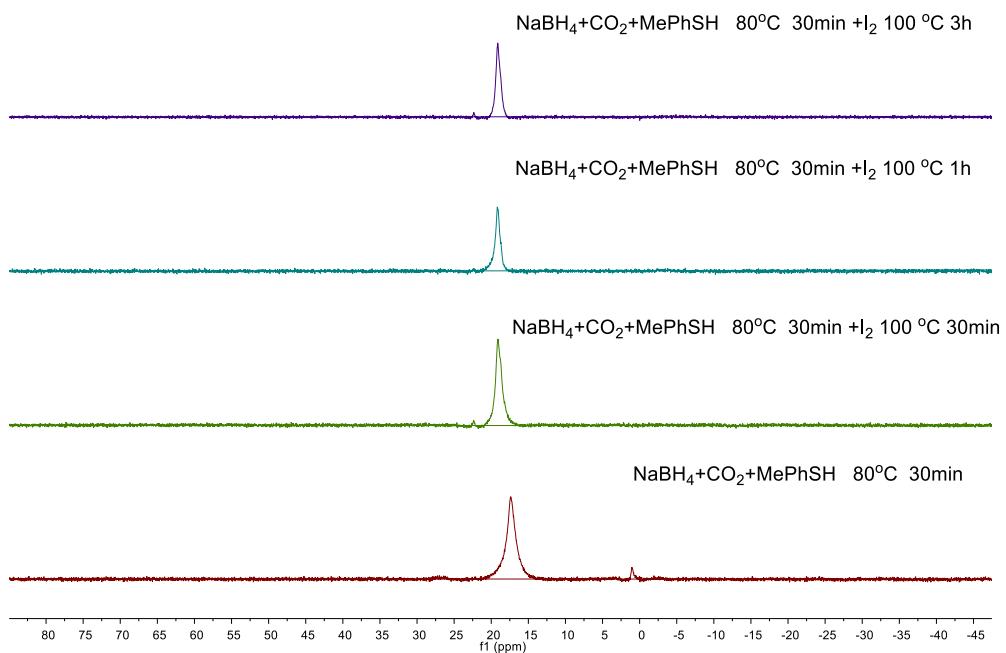


Figure S4. ^{11}B NMR spectrum for the reaction process in 1,4-dioxane- d_8

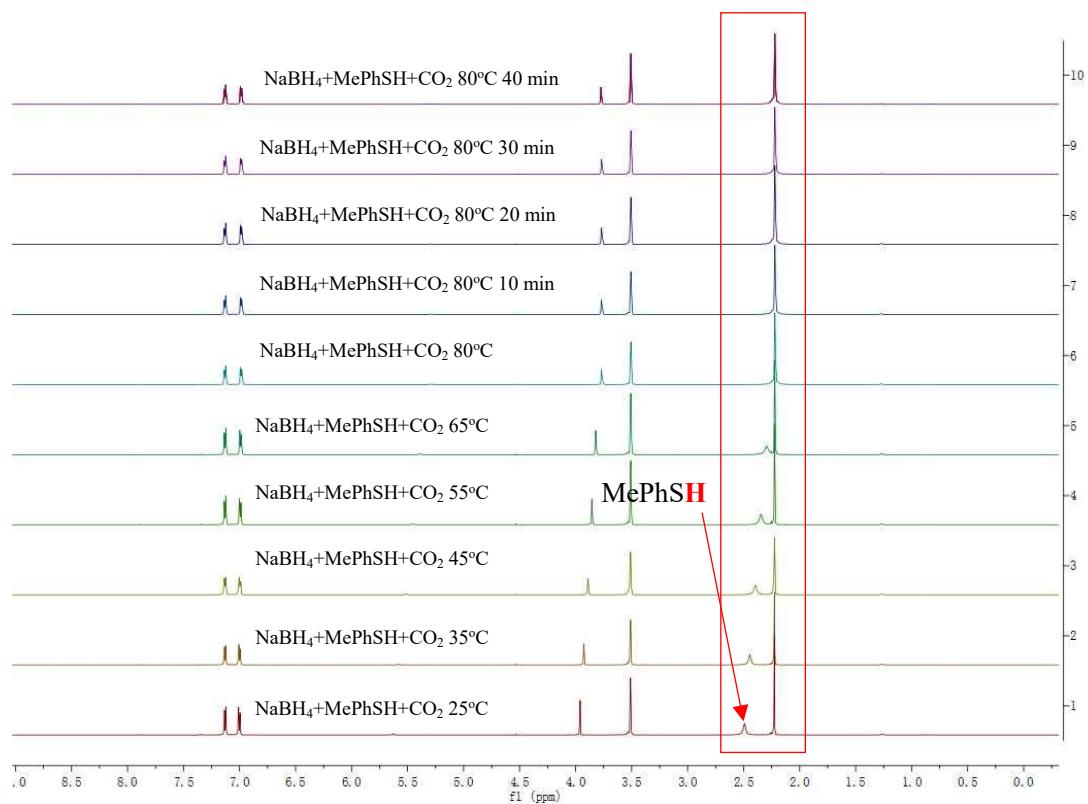


Figure S5. ¹H NMR monitoring of the reaction before I_2 addition

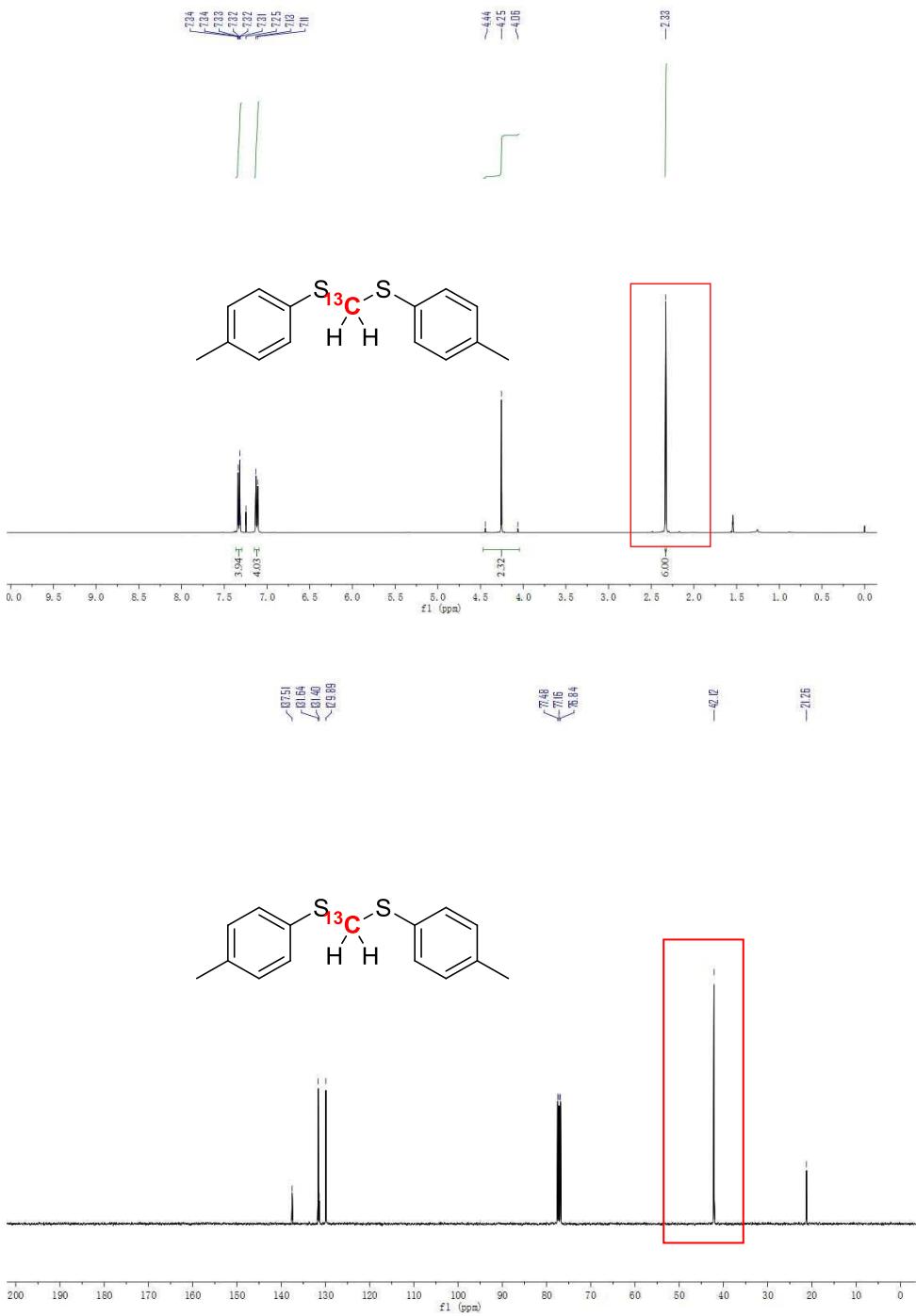
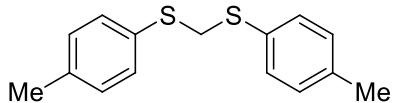


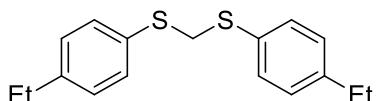
Figure S6. ^1H NMR and ^{13}C spectrum for ^{13}C -labelled **2a**

Characterization data of dithioacetals

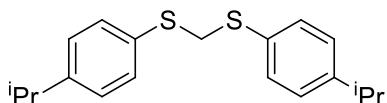
(Some dithioacetals were identified through comparisons with reported literatures for the corresponding compounds of ^1H NMR and ^{13}C NMR data.)



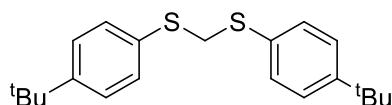
Bis(p-tolylthio)methane (2a)¹ Yellow oil (60 mg, 92%): ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.33 (d, $J = 8.0$ Hz, 4H), 7.11 (d, $J = 6.8$ Hz, 4H), 4.25 (s, 2H), 2.33 (s, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 137.46, 131.59, 131.37, 129.86, 42.07, 21.23. GC-MS: 260.



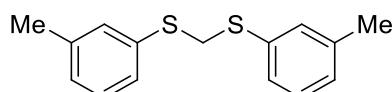
Bis((4-ethylphenyl)thio)methane (2b)¹ Colorless oil (62 mg, 86%): ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.35 (d, $J = 8.2$ Hz, 4H), 7.13 (d, $J = 8.1$ Hz, 4H), 4.27 (s, 2H), 2.88 (m, 1H), 2.62 (q, $J = 7.6$ Hz, 4H), 1.22 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 143.74, 131.63 (d, $J = 16.4$ Hz), 128.68, 41.97, 28.60, 15.56. GC-MS: 288.



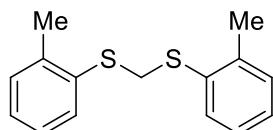
Bis((4-isopropylphenyl)thio)methane (2c) Colorless oil (70 mg, 88%): ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.36 (d, $J = 8.2$ Hz, 4H), 7.17 (d, $J = 8.2$ Hz, 4H), 4.28 (s, 2H), 2.88 (hept, $J = 6.9$ Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 148.32, 131.93, 131.42, 127.27, 41.84, 33.89, 24.02. GC-MS: 316. HRMS (APCI), m/z : [M + H]⁺ calcd. for C₁₉H₂₅S₂⁺ 317.1392; found 317.1389.



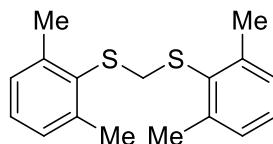
Bis((4-(tert-butyl)phenyl)thio)methane (2d)¹ Colorless oil (71 mg, 90%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.38-7.30 (m, 8H), 4.29 (s, 2H), 1.30 (s, 18H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 150.50, 131.73, 130.91, 126.16, 41.48, 34.66, 31.34. GC-MS: 344.



Bis(m-tolylthio)methane (2e)¹ Colorless oil (51 mg, 78%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.24-7.16 (m, 6H), 7.04 (d, *J* = 7.5 Hz, 2H), 4.33 (s, 2H), 2.32 (s, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 138.90, 134.95, 131.37, 128.94, 128.07, 127.75, 40.62, 21.47. GC-MS: 260.

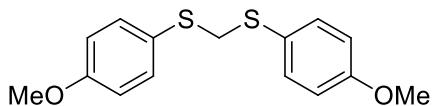


Bis(o-tolylthio)methane (2f)¹ Colorless oil (57 mg, 88%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.43-7.37 (m, 2H), 7.20-7.11 (m, 6H), 4.29 (s, 2H), 2.35 (s, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 138.65, 134.61, 130.26, 129.97, 126.97, 126.64, 38.69, 20.57. GC-MS: 260.

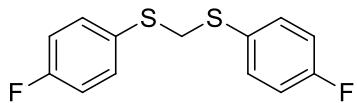


Bis((2,6-dimethylphenyl)thio)methane (2g) Colorless oil (41 mg, 57%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.14-7.05 (m, 6H), 3.84 (s, 2H), 2.43 (s, 12H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 143.34, 133.29, 128.84, 128.26, 41.76, 22.05. GC-

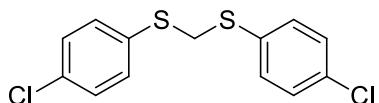
MS: 288. HRMS (APCI), *m/z*: [M + H]⁺ calcd. for C₁₇H₂₁S₂⁺ 289.1079; found 289.1071.



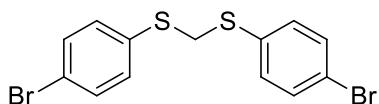
Bis((4-methoxyphenyl)thio)methane (2h)¹ White solid (65 mg, 89%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.40 (d, *J* = 8.8 Hz, 4H), 6.85 (d, *J* = 8.7 Hz, 4H), 4.15 (s, 2H), 3.80 (s, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 159.71, 134.57, 125.37, 114.71, 55.46, 44.63. GC-MS: 292.



Bis((4-fluorophenyl)thio)methane (2i)¹ Colorless oil (42 mg, 63%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.41 (dd, *J* = 8.8, 5.2 Hz, 4H), 7.01 (t, *J* = 8.7 Hz, 4H), 4.21 (s, 2H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 163.86, 161.40, 134.17 (d, *J* = 8.3 Hz), 129.65 (d, *J* = 3.1 Hz), 116.39, 116.18, 43.28. GC-MS: 268.

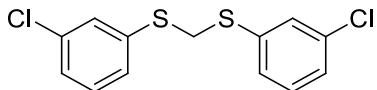


Bis((4-chlorophenyl)thio)methane (2j)¹ White solid (54 mg, 72%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.32 (d, *J* = 8.6 Hz, 4H), 7.27 (d, *J* = 8.7 Hz, 4H), 4.26 (s, 2H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 133.68, 133.09, 132.49, 129.32, 41.31. GC-MS: 301.

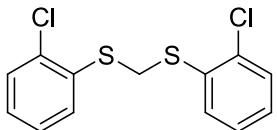


Bis((4-bromophenyl)thio)methane (2k)¹ White solid (75 mg, 77%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.43 (d, *J* = 8.5 Hz, 4H), 7.26 (d, *J* = 8.5 Hz, 4H), 4.27 (s, 2H).

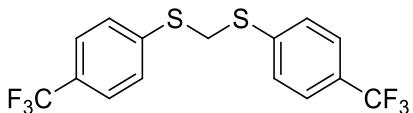
¹³C NMR (101 MHz, CHLOROFORM-D) δ 133.75, 132.63, 132.26, 121.56, 40.92. GC-MS: 390.



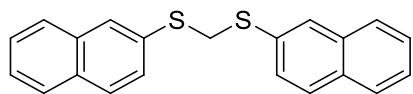
Bis((3-chlorophenyl)thio)methane (2l)¹ Colorless oil (60 mg, 80%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.37 (s, 2H), 7.29-7.20 (m, 7H), 4.33 (s, 2H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 136.68, 134.84, 130.24 (d, *J* = 15.5 Hz), 128.72, 127.53, 40.18. GC-MS: 301.



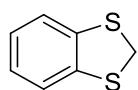
Bis((2-chlorophenyl)thio)methane (2m)¹ White solid (46 mg, 61%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.47 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.38 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.21 (dtd, *J* = 16.9, 7.4, 1.5 Hz, 4H), 4.40 (s, 2H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 135.06, 133.86, 131.24, 130.01, 128.22, 127.37, 37.26. GC-MS: 301.



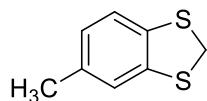
Bis((4-trifluoromethylphenyl)thio)methane (2n) White solid (49mg, 53%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.55 (d, *J* = 8.5 Hz, 4H), 7.45 (d, *J* = 8.4 Hz, 4H), 4.43 (s, 2H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 139.78, 129.53, 129.27, 128.95, 128.62, 128.15, 126.02 (d, *J* = 3.6 Hz), 125.44, 122.73, 120.03, 38.30 (s). ¹⁹F NMR (565 MHz, CHLOROFORM-D) δ -62.55. GC-MS: 368. HRMS (APCI), *m/z*: [M + H]⁺ calcd. for C₁₅H₁₁F₆S₂⁺ 369.0201; found 369.0195.



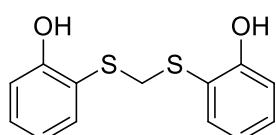
Bis(naphthalen-2-ylthio)methane (2p)¹ Colorless oil (70 mg, 84%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.87 (d, *J* = 1.5 Hz, 2H), 7.76 (dt, *J* = 17.5, 7.9 Hz, 6H), 7.51-7.42 (m, 6H), 4.53 (s, 2H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 133.77, 132.41 (d, *J* = 1.2 Hz), 129.54, 128.74, 128.36, 127.86, 127.52, 126.75, 126.31, 40.65 (s). GC-MS: 332.



1,3-Benzodithiole (2q)² Colorless oil (45mg, 58%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.20 (dd, *J* = 5.9, 3.2 Hz, 1H), 7.00 (dd, *J* = 5.7, 3.3 Hz, 1H), 4.48 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 138.30, 125.64, 122.46, 36.09. GC-MS: 154.

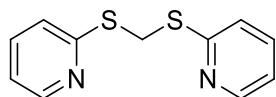


5-Methyl-1,3-benzodithiole (2r)³ Colorless oil (51mg, 61%): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.09 (d, *J* = 7.9 Hz, 1H), 7.04 (s, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 4.46 (s, 2H), 2.25 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 138.39, 135.70, 134.80, 126.52, 123.23, 122.17, 36.34, 20.99. GC-MS: 168.

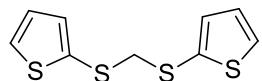


2,2'-(Methylenedithio)di-phenol (2s) Colorless oil (39 mg, 59%): ¹H NMR (400 MHz,

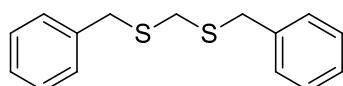
CHLOROFORM-D) δ 7.46 (dd, $J = 7.7, 1.6$ Hz, 2H), 7.34-7.27 (m, 2H), 7.00 (dd, $J = 8.2, 1.3$ Hz, 2H), 6.89 (td, $J = 7.5, 1.2$ Hz, 2H), 6.45 (s, 2H), 3.94 (s, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 157.02, 136.22, 132.12, 121.21, 117.82, 115.55, 44.30. GC-MS: 264. HRMS (APCI), m/z : [M + H] $^+$ calcd. for $\text{C}_{13}\text{H}_{13}\text{O}_2\text{S}_2^+$ 265.0351; found 265.0344.



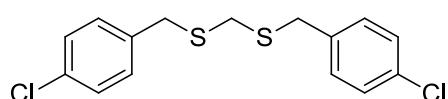
Bis(pyridin-2-ylthio)methane (2t)⁴ The yield is low for getting desired product, so we could not isolate pure compound.



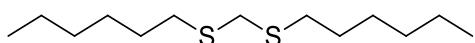
Bis(thiophen-2-ylthio)methane (2u)⁴ Colorless oil (19 mg, 30%): ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.43-7.40 (m, 2H), 7.22 (dd, $J = 3.5, 1.0$ Hz, 2H), 7.02 (dd, $J = 5.4, 3.6$ Hz, 2H), 4.05 (s, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 135.24, 132.35, 130.66, 127.75, 49.28. GC-MS: 244.



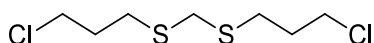
Bis(benzylthio)methane (2v)⁴ White solid (28 mg, 43%): ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.29 (d, $J = 4.4$ Hz, 8H), 7.23 (dt, $J = 5.5, 4.2$ Hz, 2H), 3.83 (s, 4H), 3.37 (s, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 137.81, 129.25, 128.55, 127.18, 34.57, 33.56. GC-MS: 260.



Bis(4-chloro-benzylthio)methane (2w**)** Colorless oil (60 mg, 73%): ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.29-7.24 (m, 4H), 7.24-7.19 (m, 4H), 3.77 (s, 4H), 3.32 (s, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 136.21, 133.03, 130.55, 128.83, 33.76, 33.30. GC-MS: 329. HRMS (APCI), m/z : [M + H] $^+$ calcd. for $\text{C}_{15}\text{H}_{15}\text{Cl}_2\text{S}_2^+$ 328.9987; found 328.9973.



Bis-(hexylmercapto)methane (2x**)⁵** Colorless oil (36 mg, 58%): ^1H NMR (400 MHz, CHLOROFORM-D) δ 3.66 (s, 2H), 2.66-2.59 (m, 4H), 1.62-1.56 (m, 4H), 1.40 (dd, $J = 14.6, 7.6$ Hz, 4H), 1.29 (d, $J = 4.1$ Hz, 8H), 0.89 (t, $J = 6.9$ Hz, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 35.58, 31.57, 31.02, 29.21, 28.74, 22.70, 14.18. GC-MS: 248.



Bis((3-chloropropyl)thio)methane (2y**)** Colorless oil (36 mg, 62%): ^1H NMR (400 MHz, CHLOROFORM-D) δ 3.68 (s, 2H), 3.66 (t, $J = 7.0$ Hz, 4H), 2.80 (t, $J = 7.0$ Hz, 4H), 2.10-2.03 (m, 4H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 43.56, 35.61, 31.79, 27.95. GC-MS: 233. HRMS (APCI), m/z : [M + H] $^+$ calcd. for $\text{C}_7\text{H}_{15}\text{Cl}_2\text{S}_2^+$ 232.9987; found 232.9979.

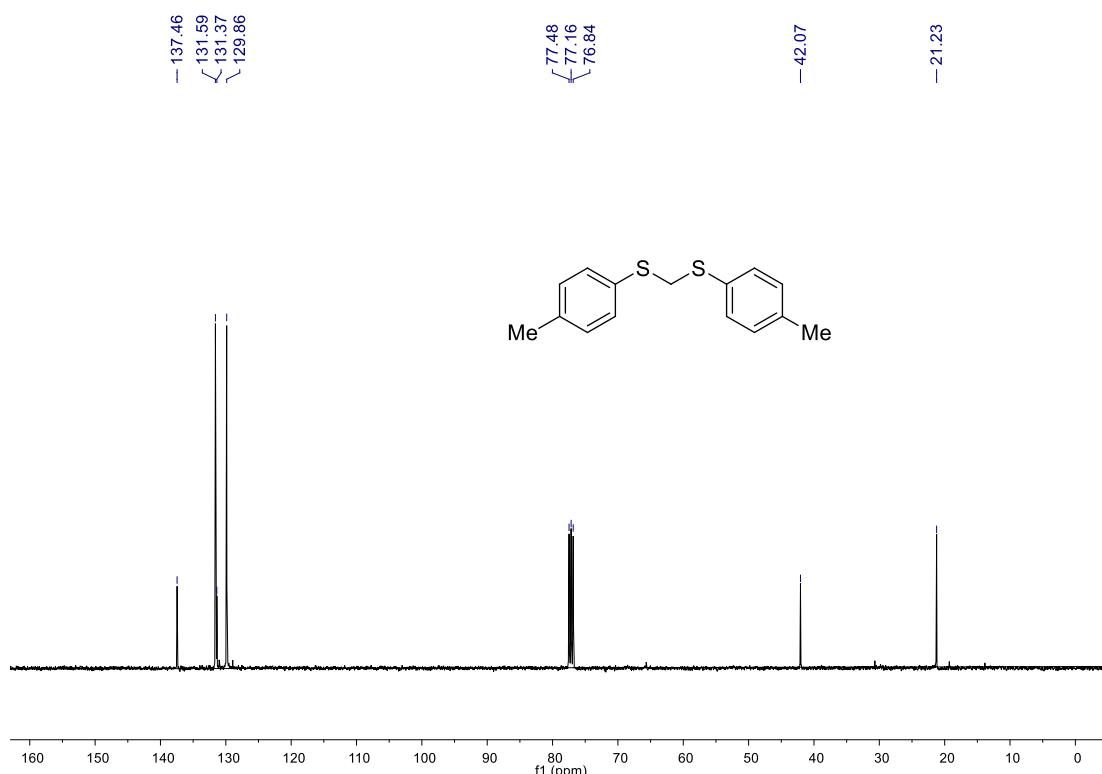
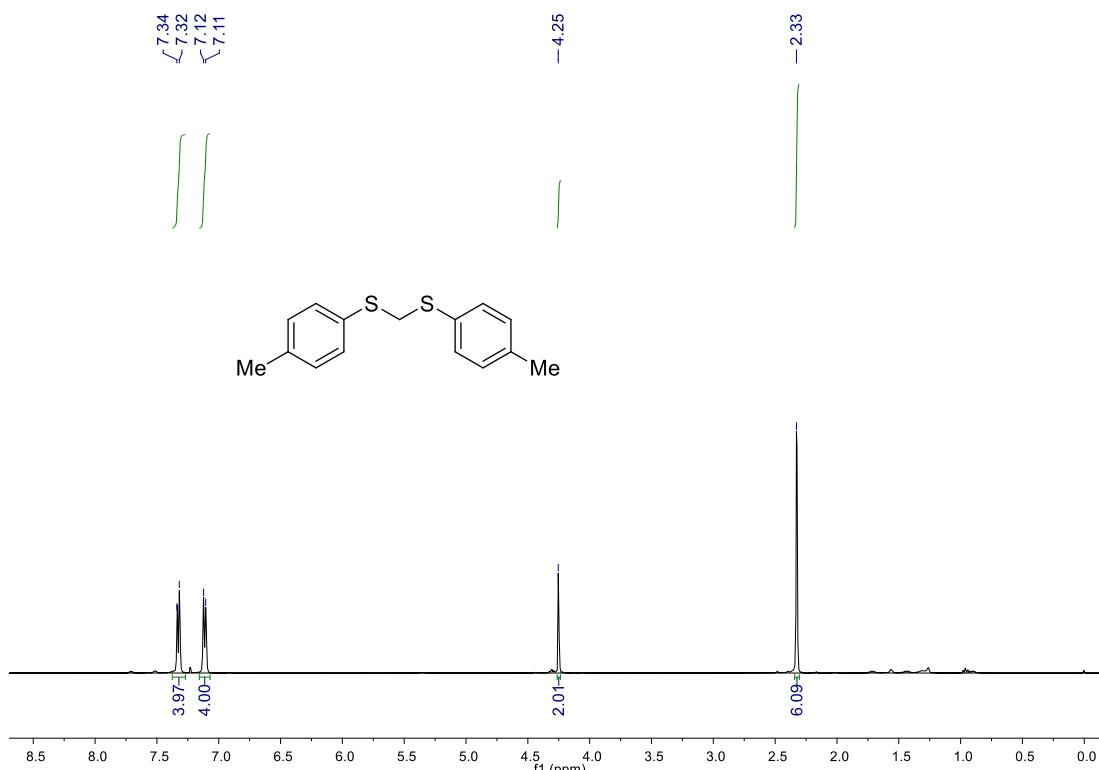


1,3-Dithiane (2z**)⁶** White solid (36 mg, 60%): ^1H NMR (400 MHz, CHLOROFORM-D) δ 3.78 (s, 2H), 2.86-2.79 (m, 4H), 2.11-2.04 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 32.07, 30.04, 26.69. GC-MS: 120.

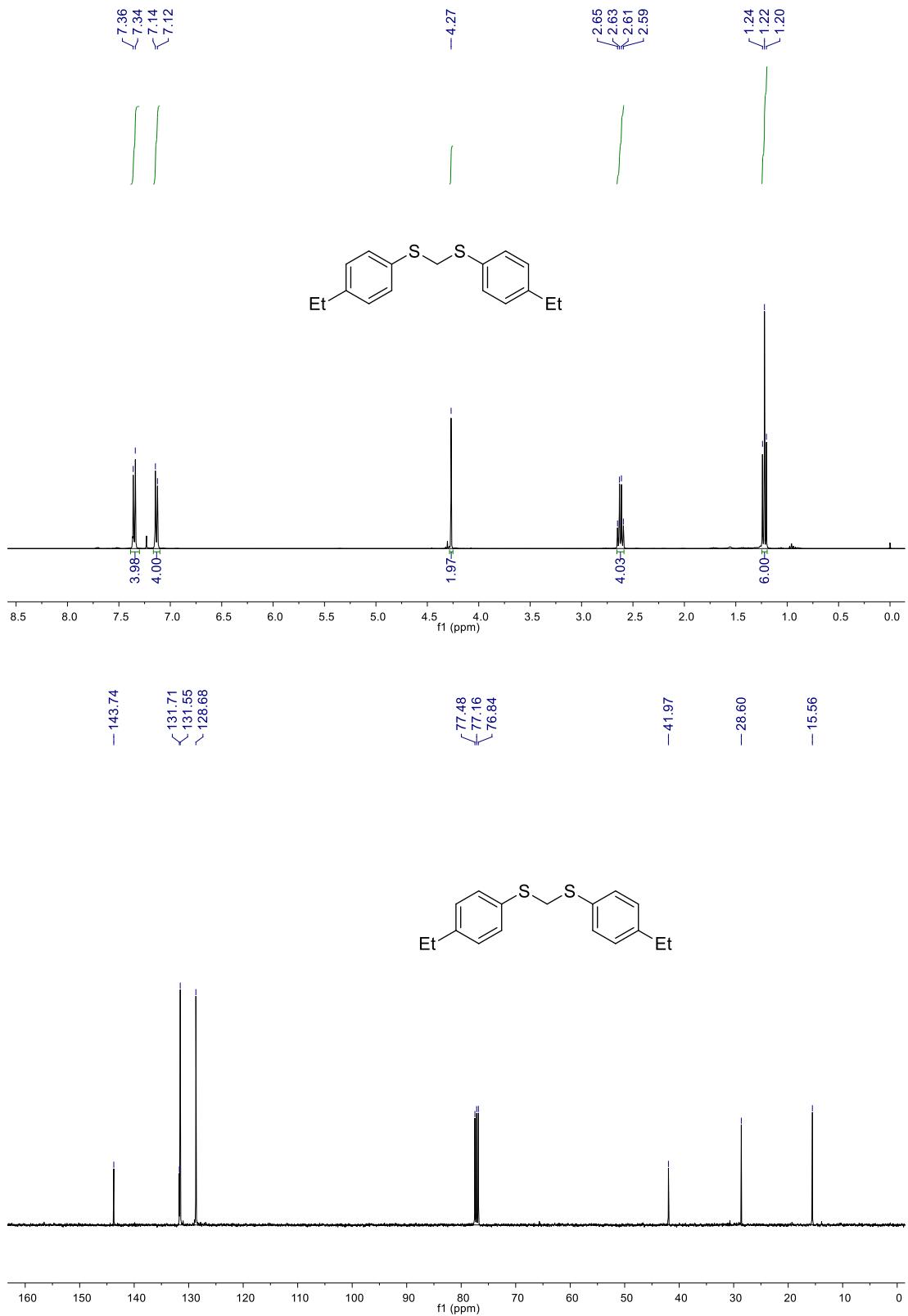
References

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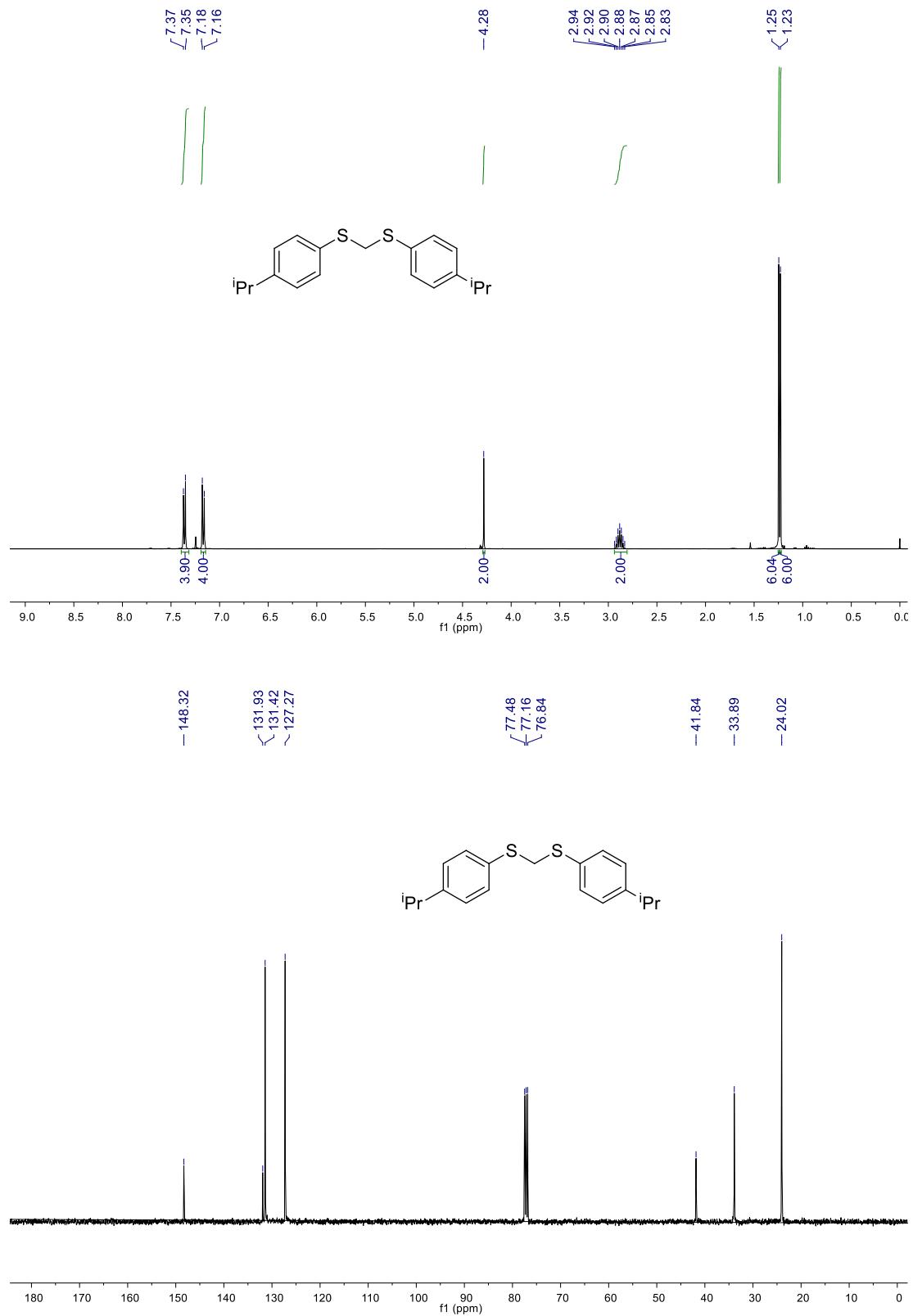
¹H and ¹³C NMR Spectrum of Dithioacetals



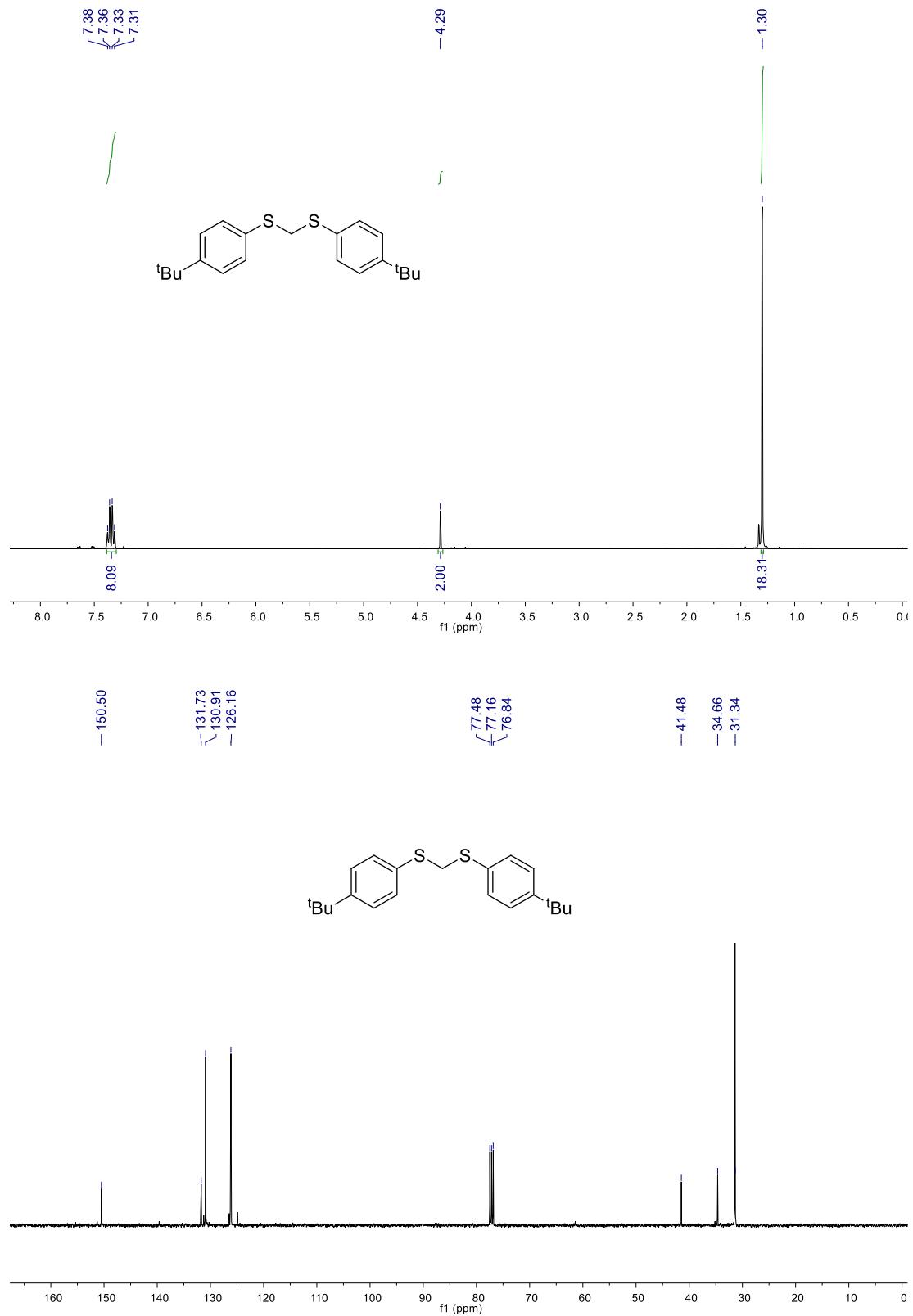
¹H and ¹³C NMR Spectrum of 2a



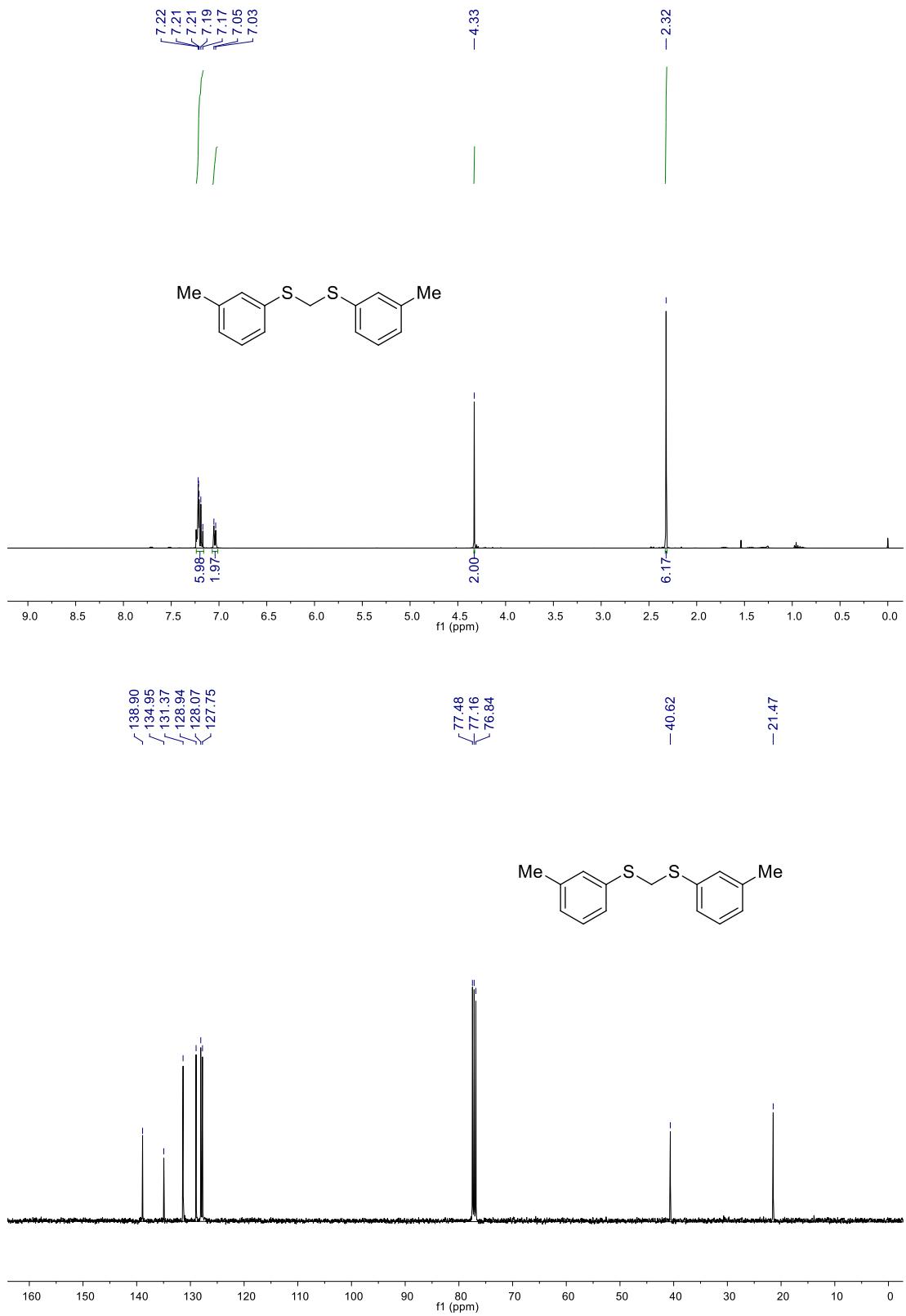
¹H and ¹³C NMR Spectrum of **2b**



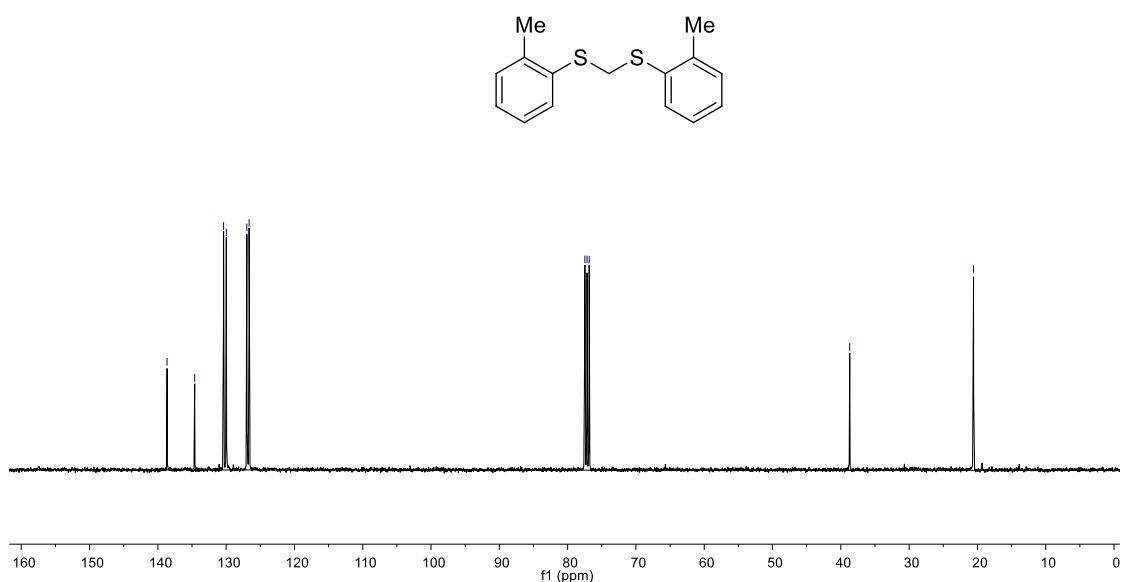
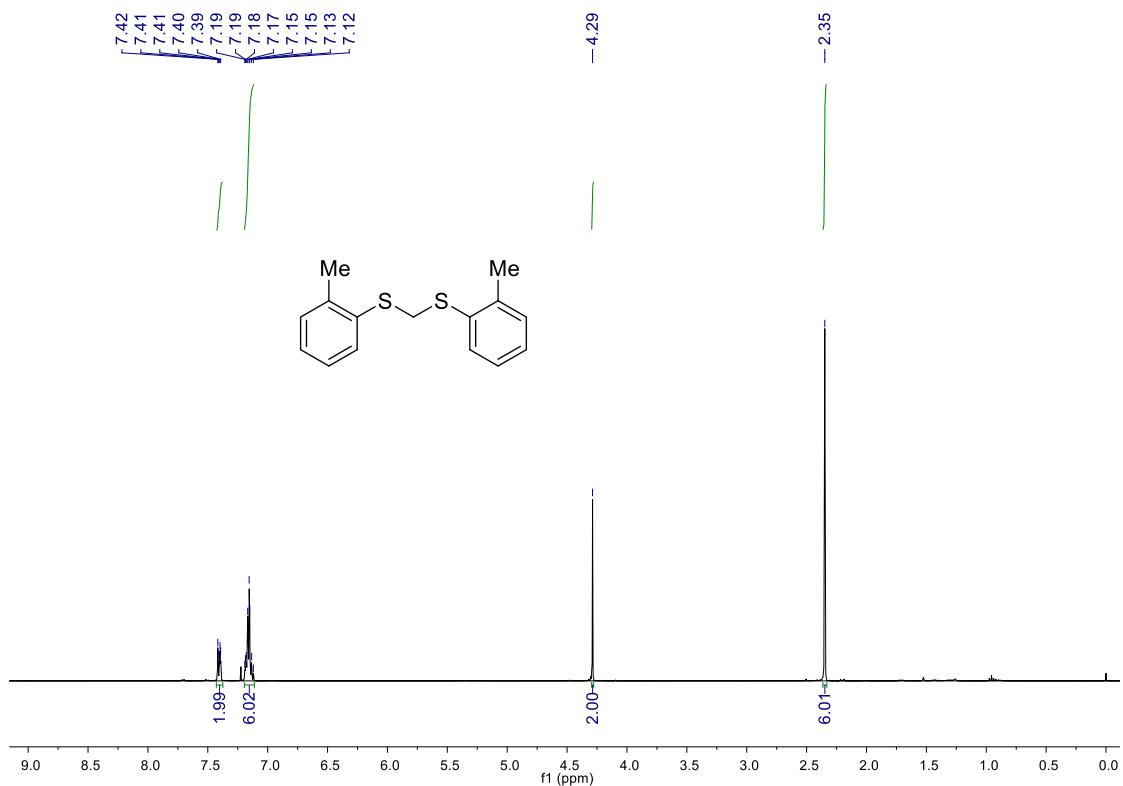
¹H and ¹³C NMR Spectrum of **2c**



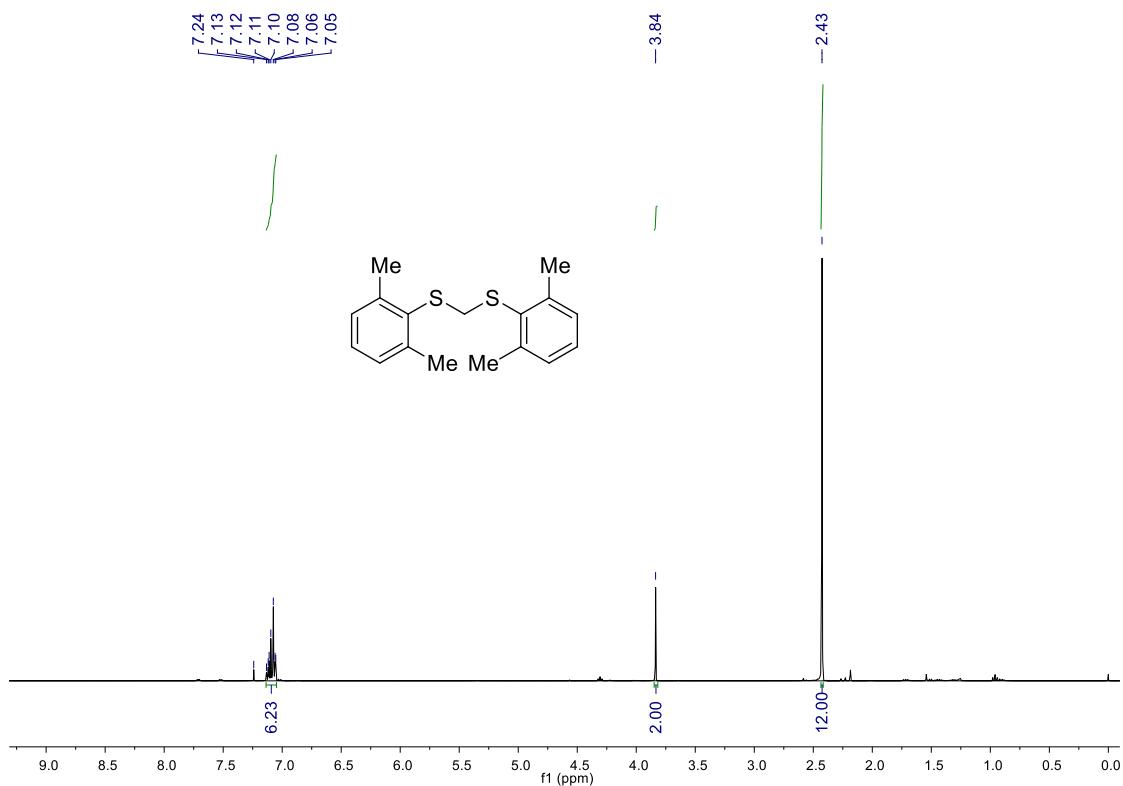
¹H and ¹³C NMR Spectrum of **2d**



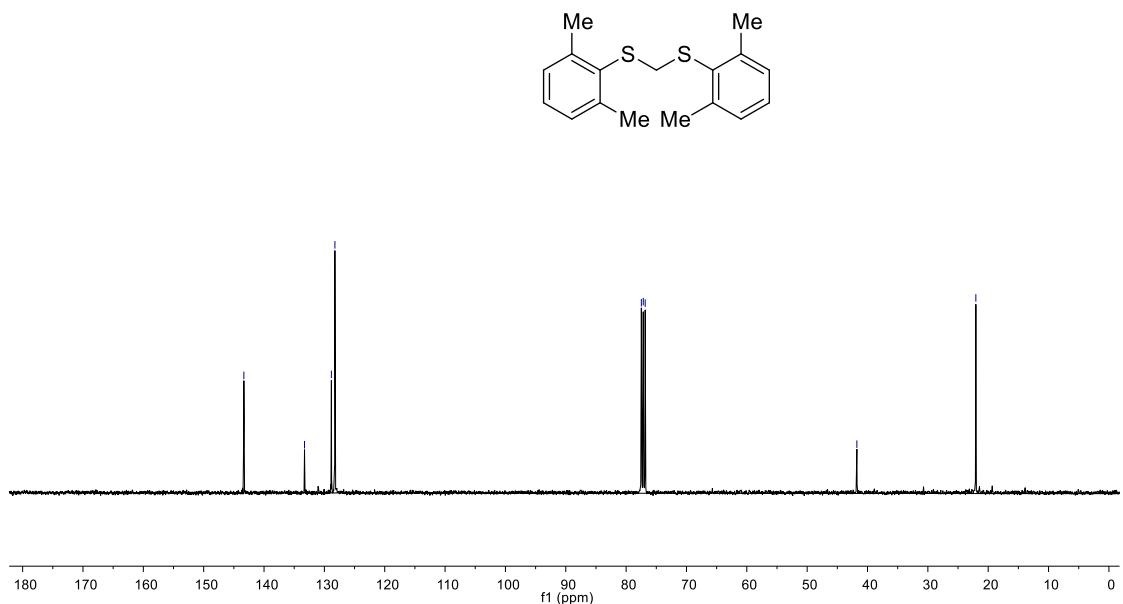
¹H and ¹³C NMR Spectrum of **2e**



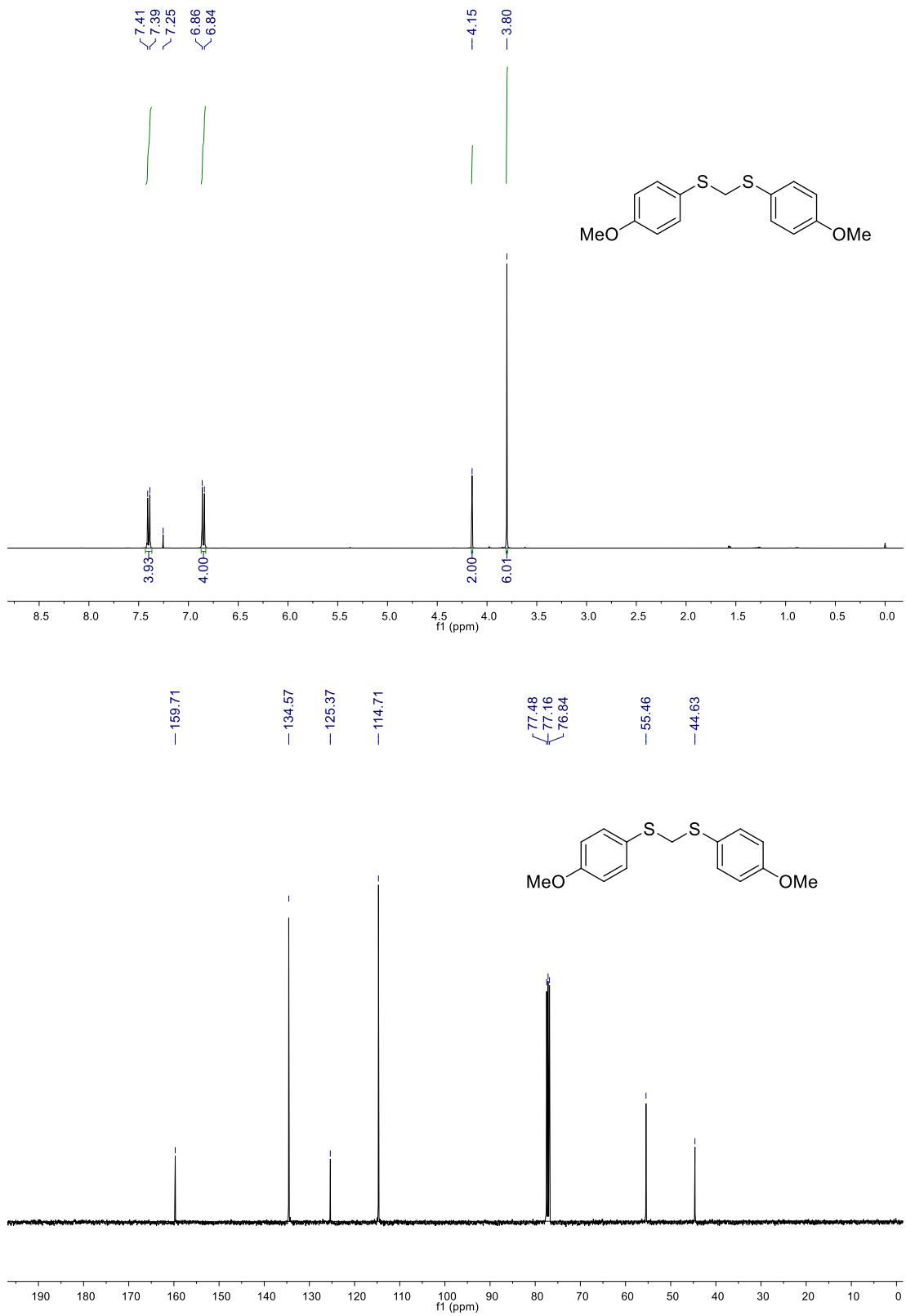
¹H and ¹³C NMR Spectrum of **2f**



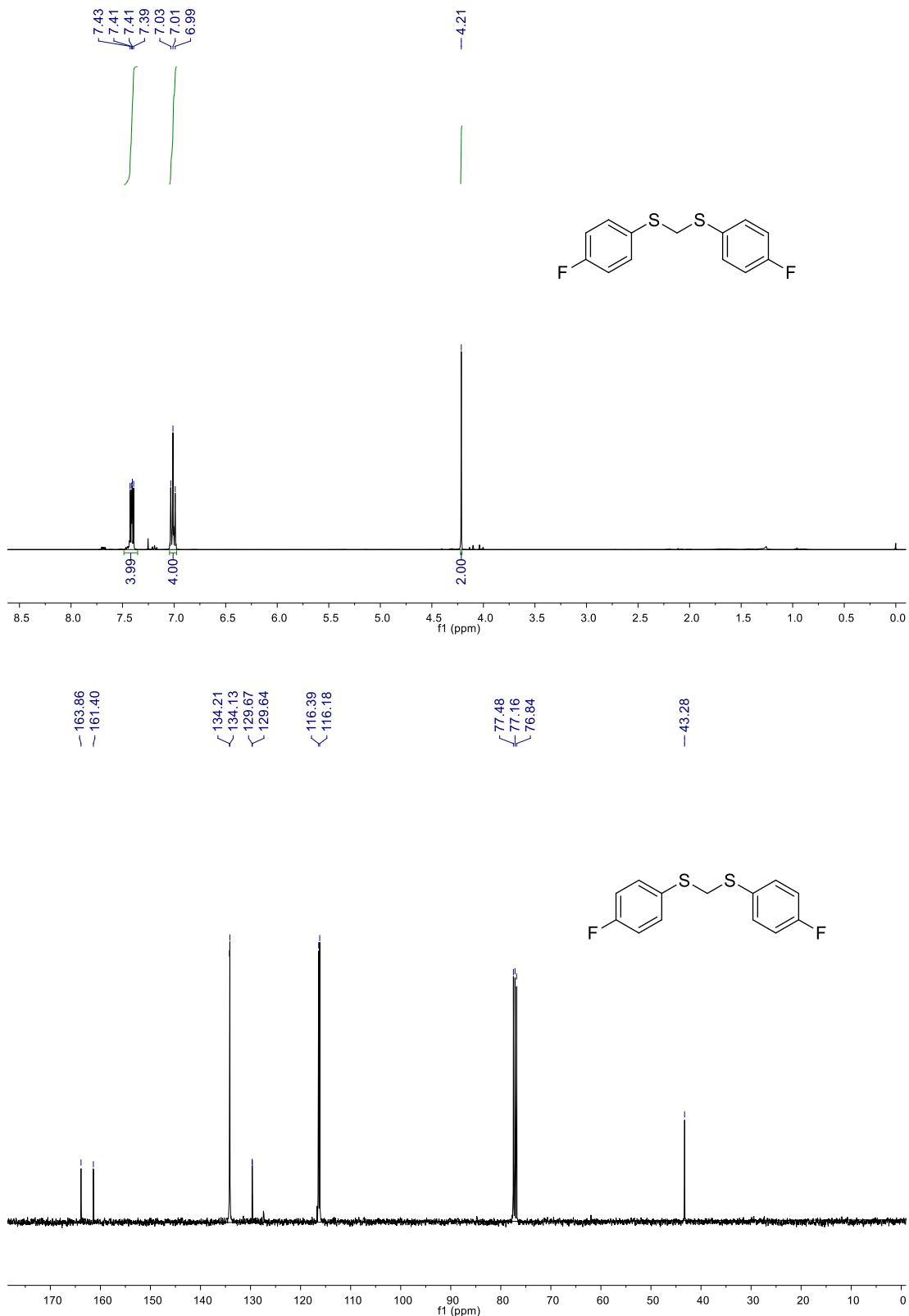
— 143.34
 — 133.29
 — 128.84
 — 128.26
 — 77.48
 — 77.16
 — 76.84
 — 41.76
 — 22.05



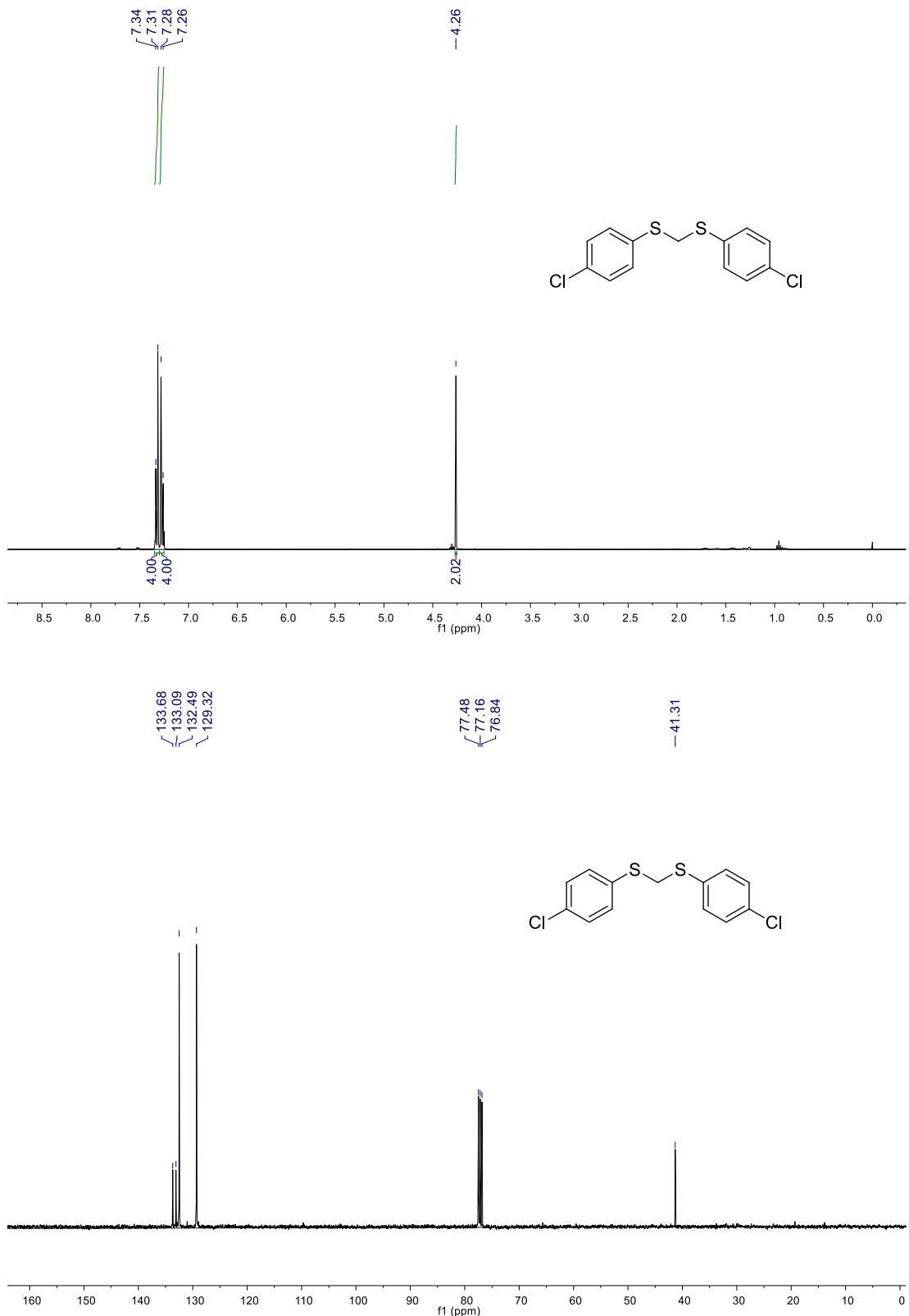
¹H and ¹³C NMR Spectrum of **2g**



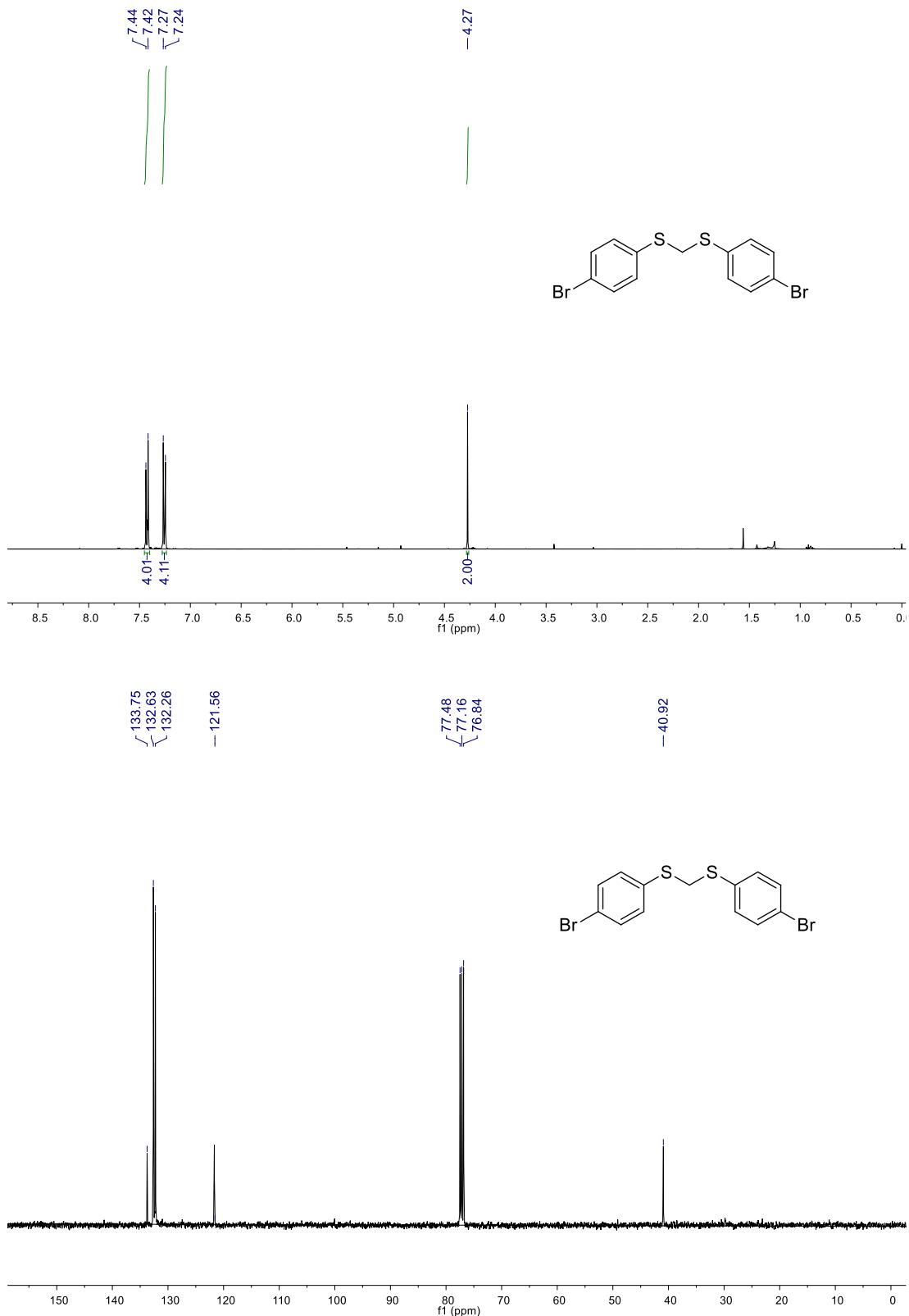
¹H and ¹³C NMR Spectrum of **2h**



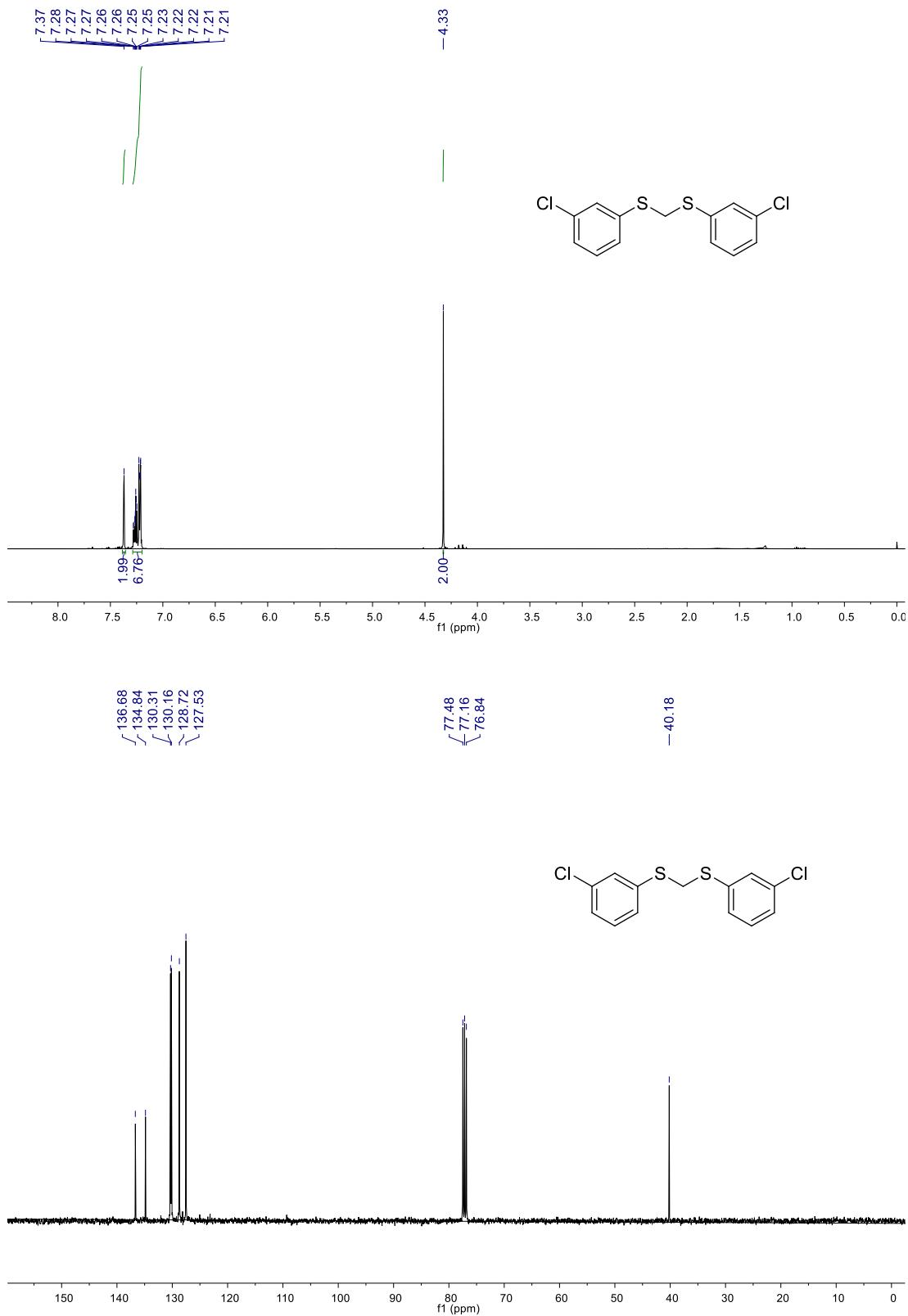
¹H and ¹³C NMR Spectrum of **2i**



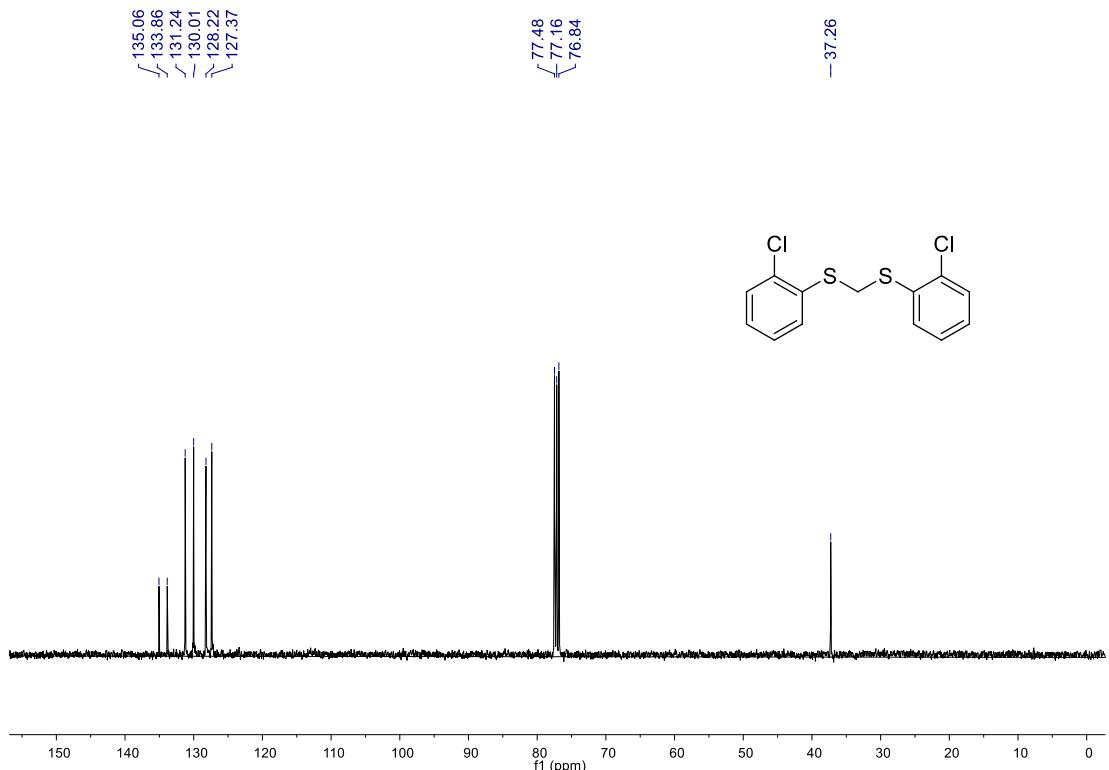
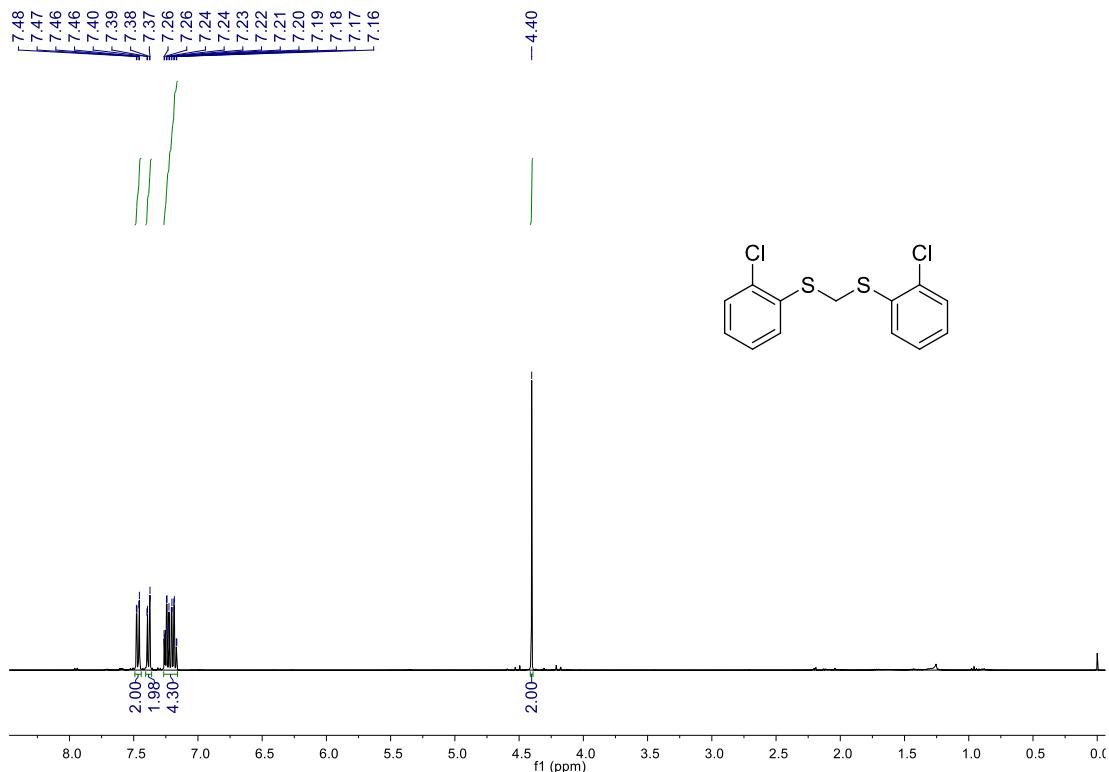
¹H and ¹³C NMR Spectrum of **2j**



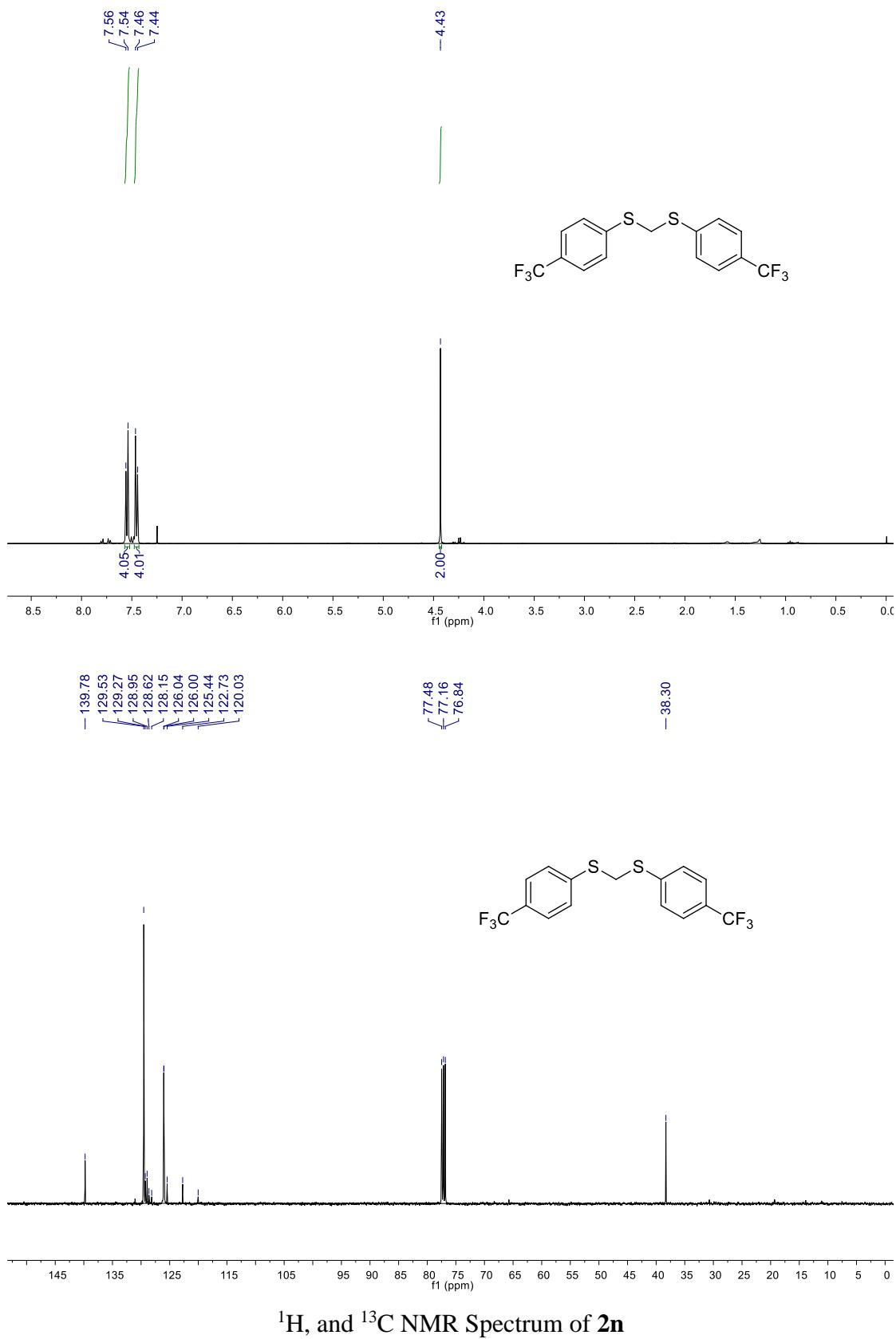
¹H and ¹³C NMR Spectrum of **2k**

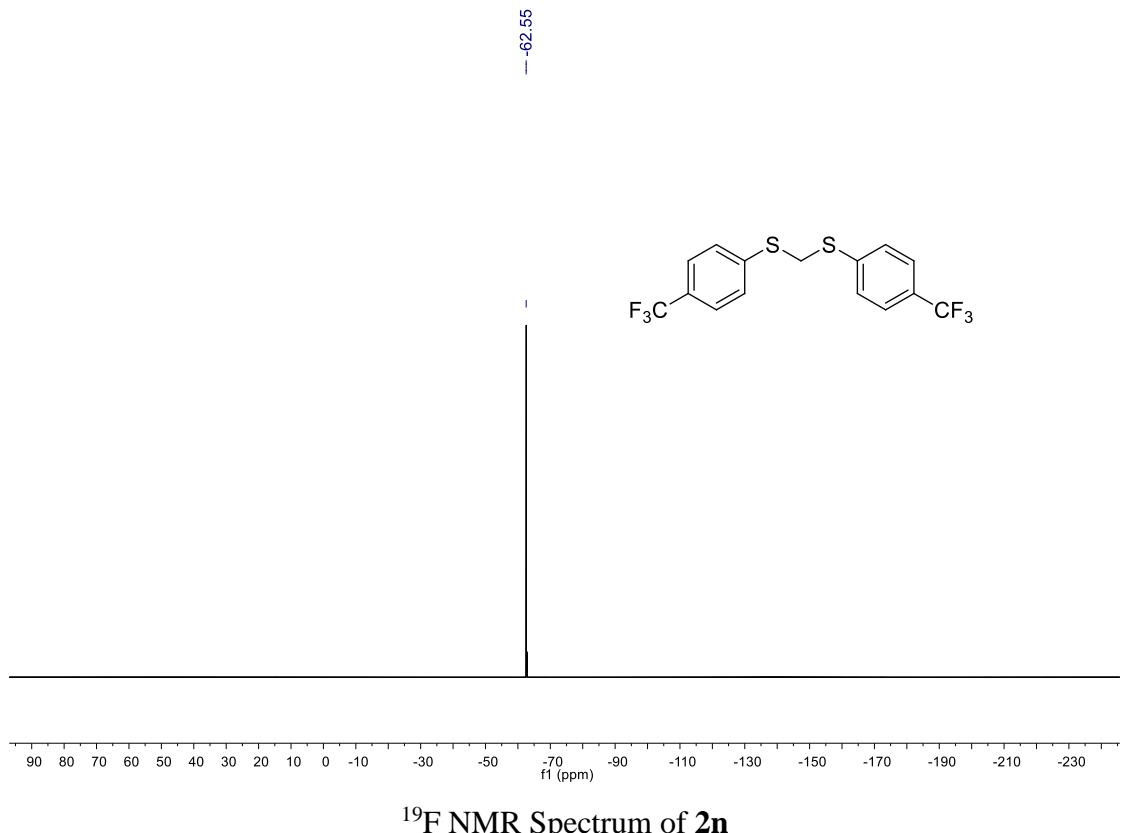


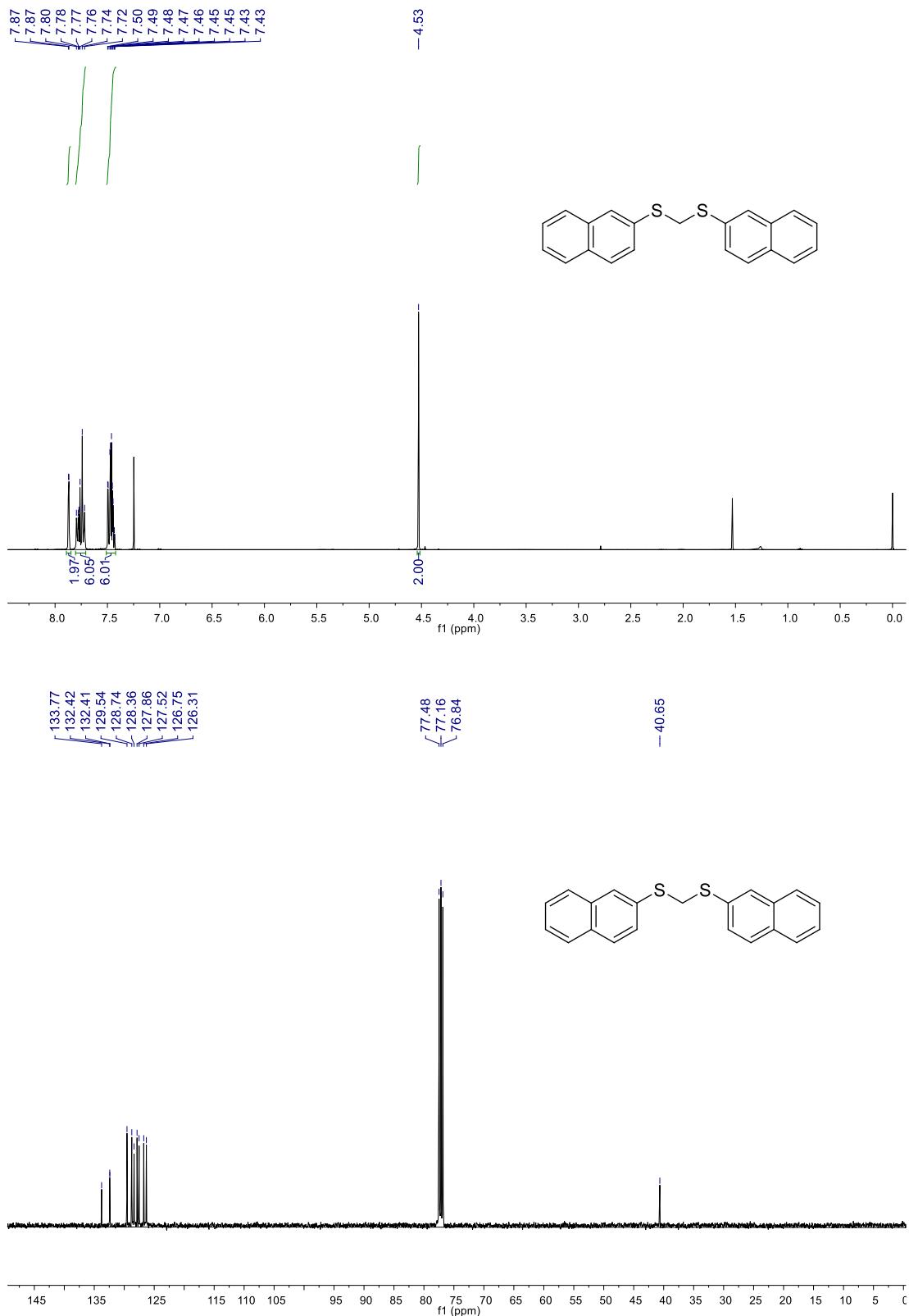
¹H and ¹³C NMR Spectrum of **2l**



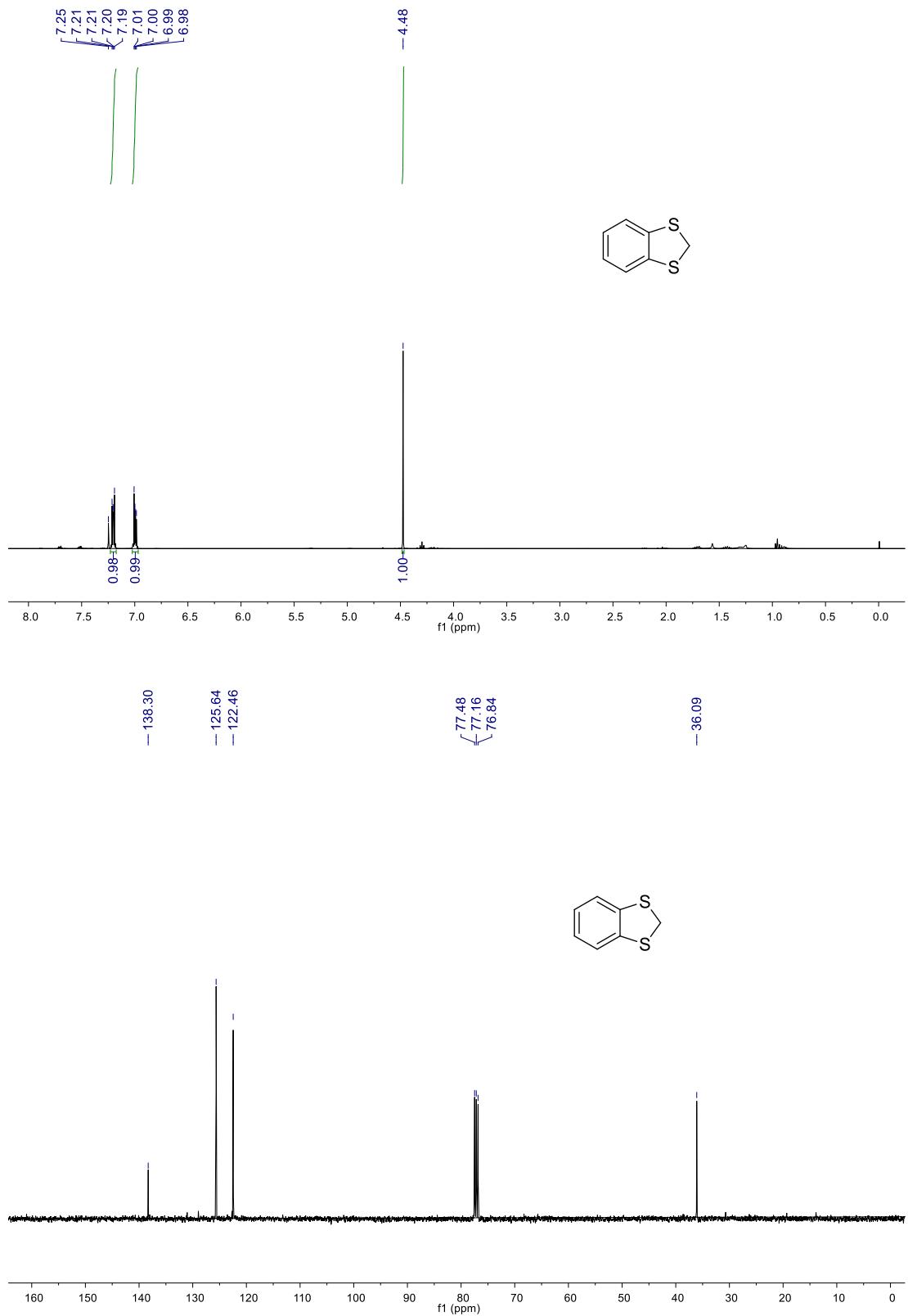
¹H and ¹³C NMR Spectrum of **2m**



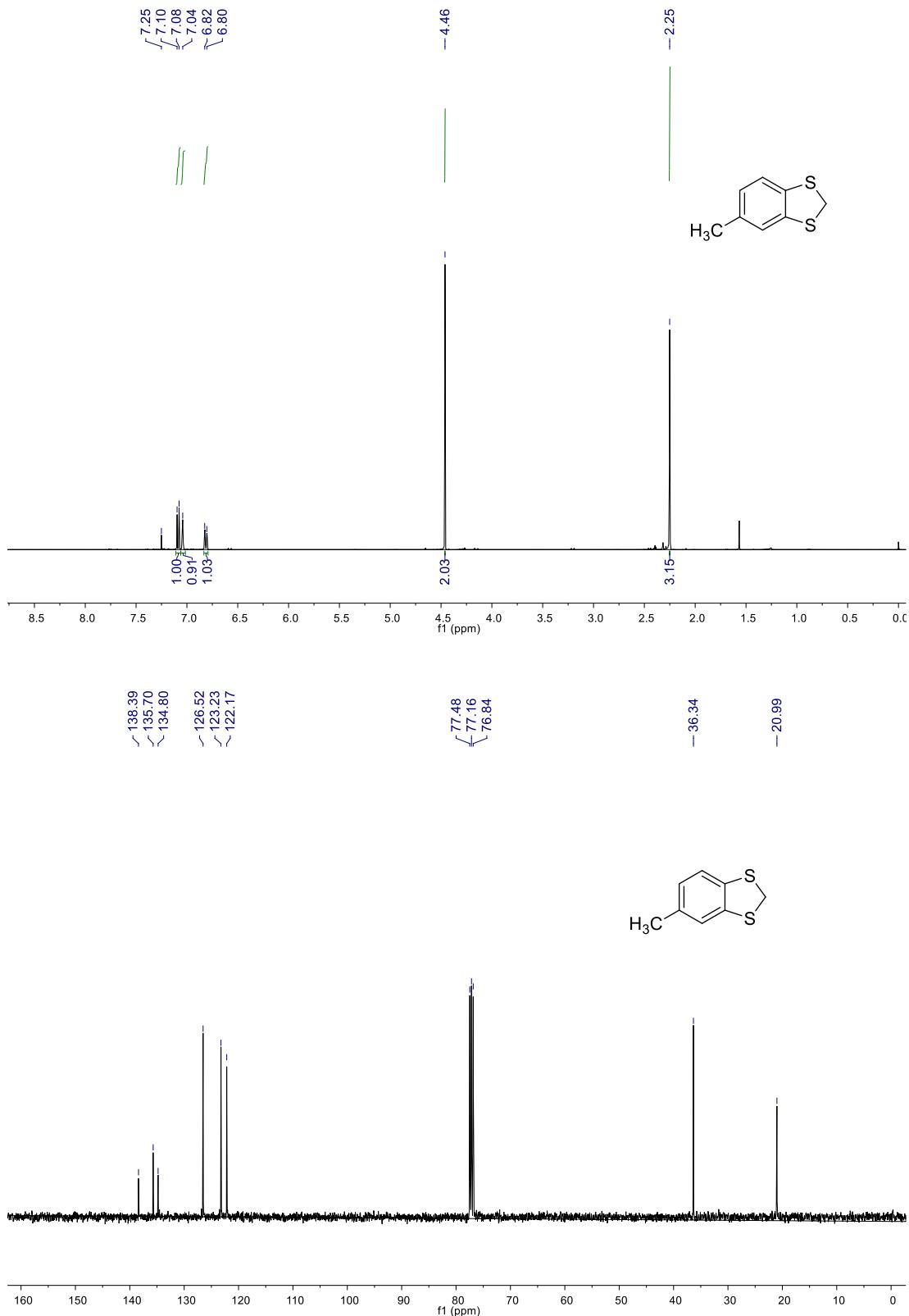


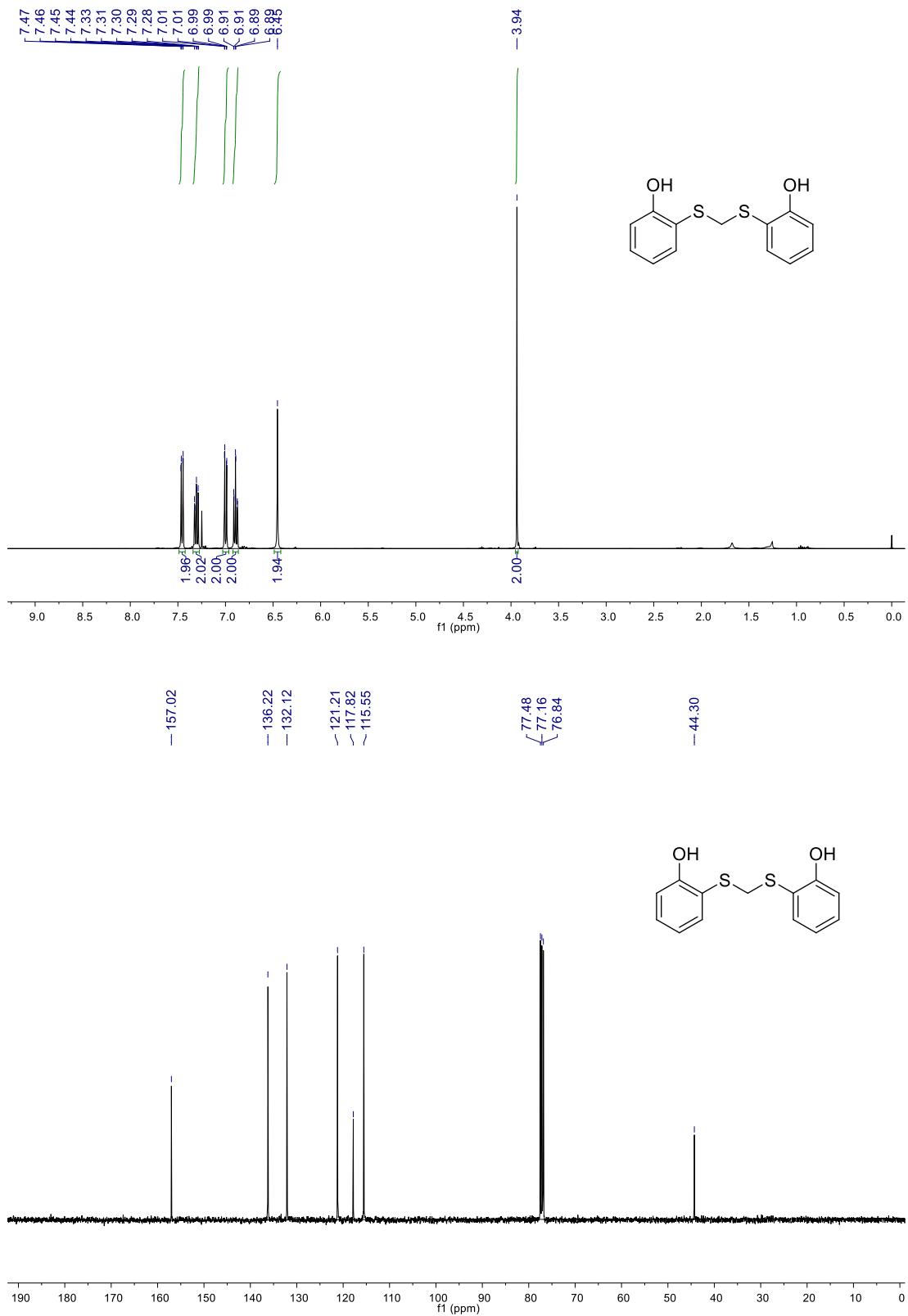


¹H and ¹³C NMR Spectrum of **2p**

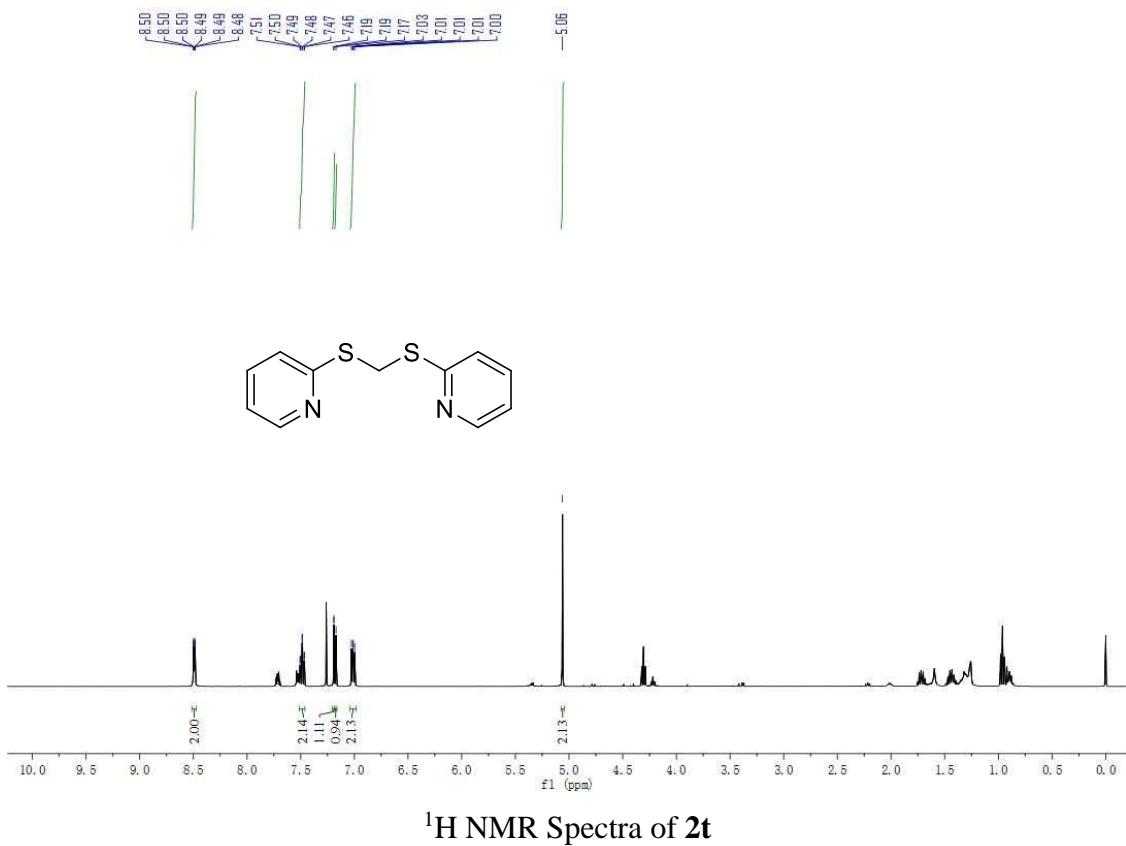


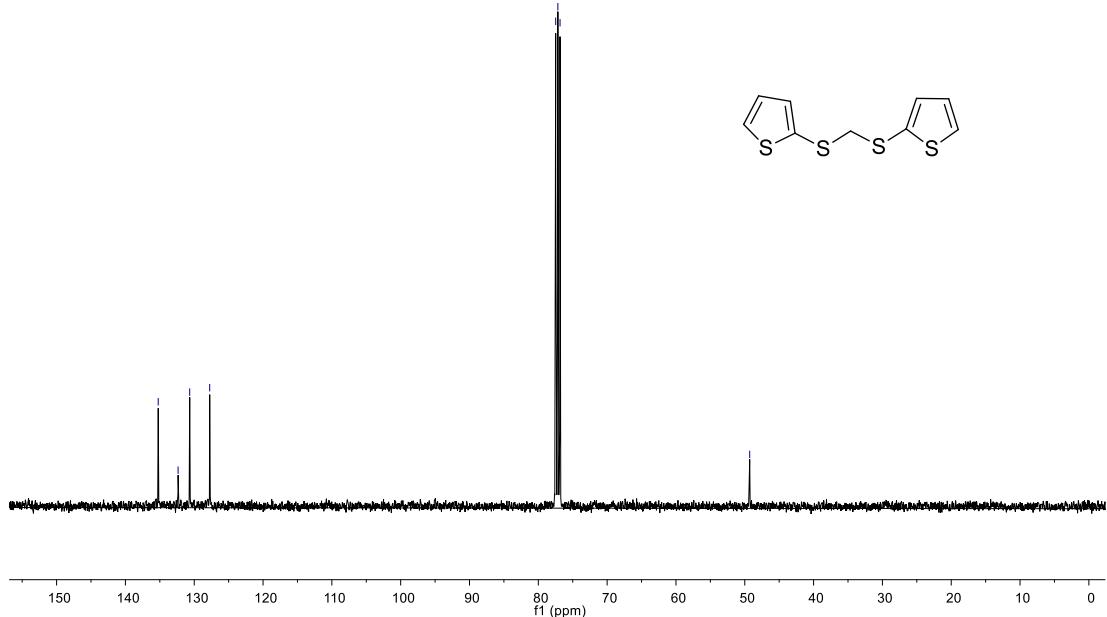
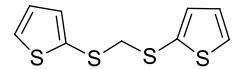
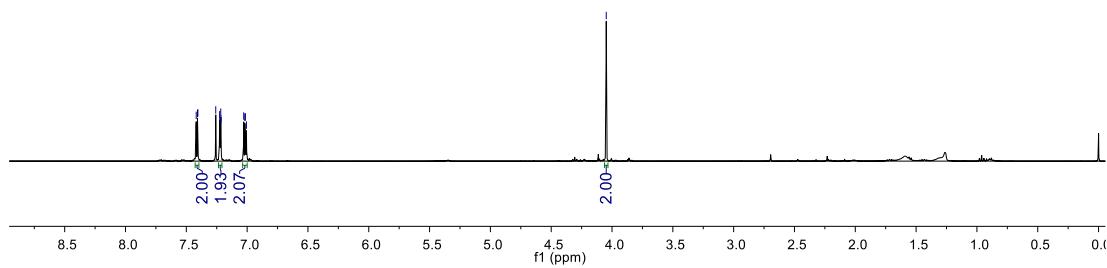
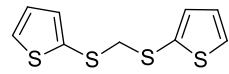
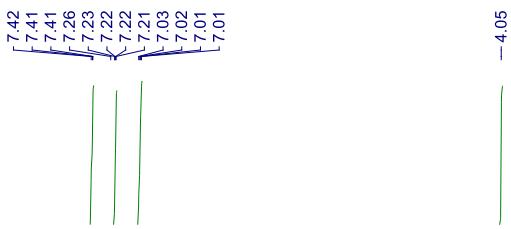
¹H and ¹³C NMR Spectrum of **2q**



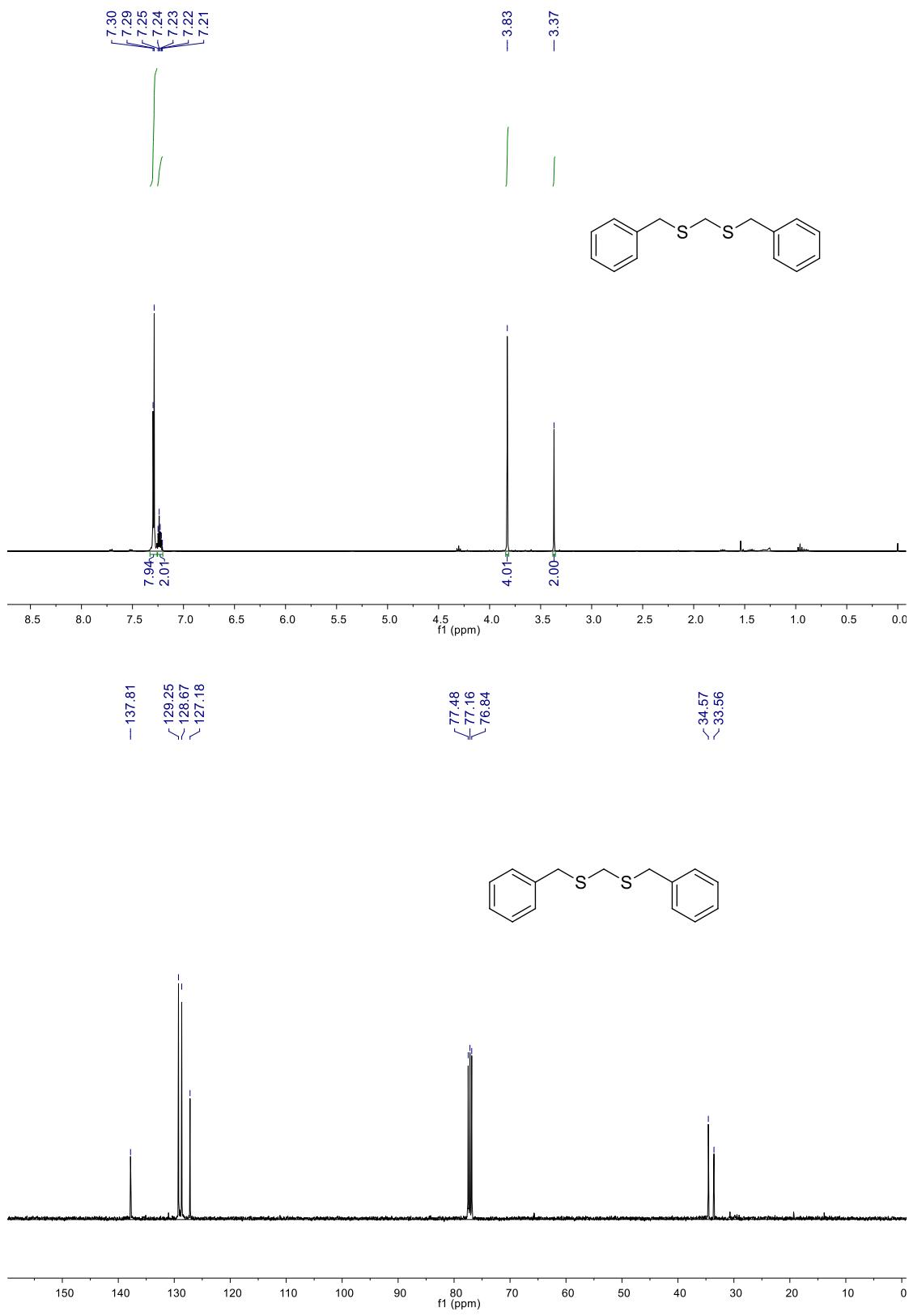


¹H and ¹³C NMR Spectrum of **2s**

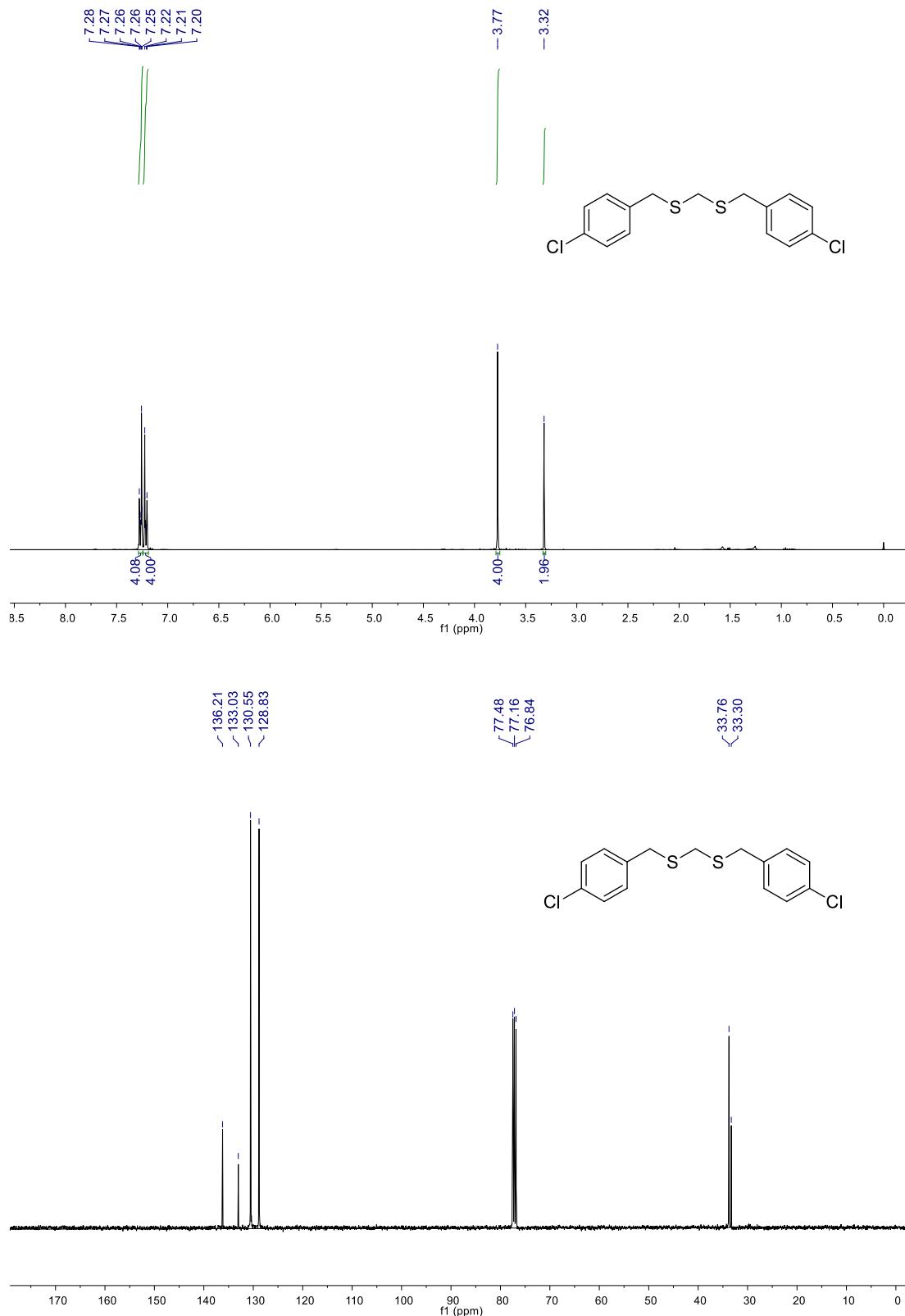




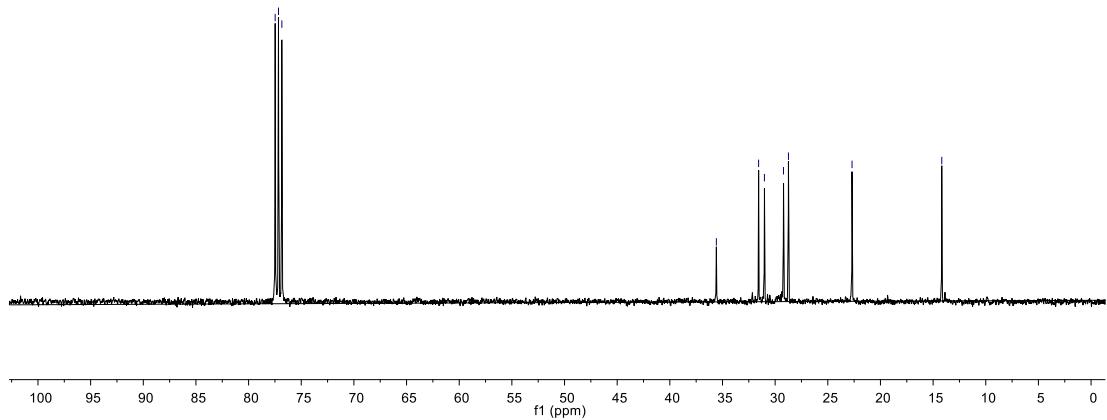
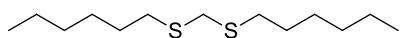
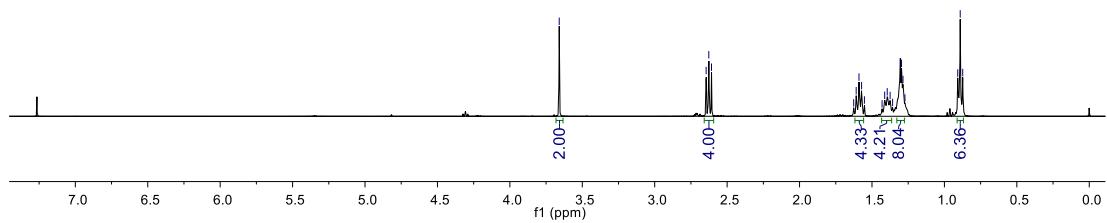
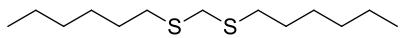
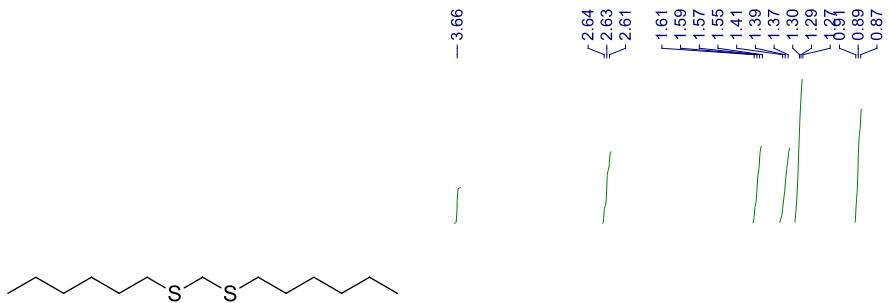
¹H and ¹³C NMR Spectrum of **2u**



¹H and ¹³C NMR Spectrum of **2w**

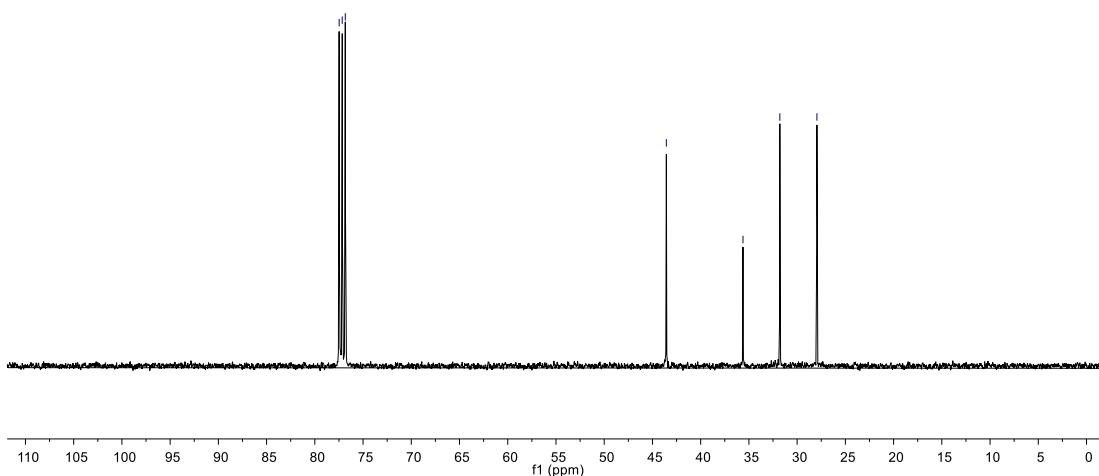
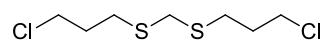
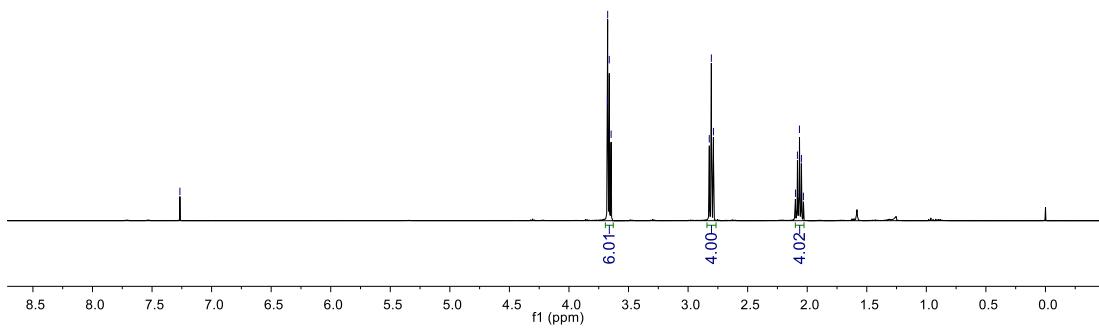
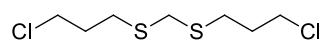
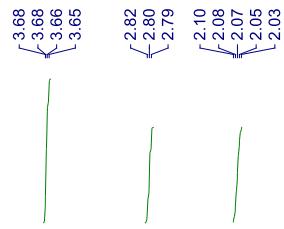


¹H and ¹³C NMR Spectrum of **2w**

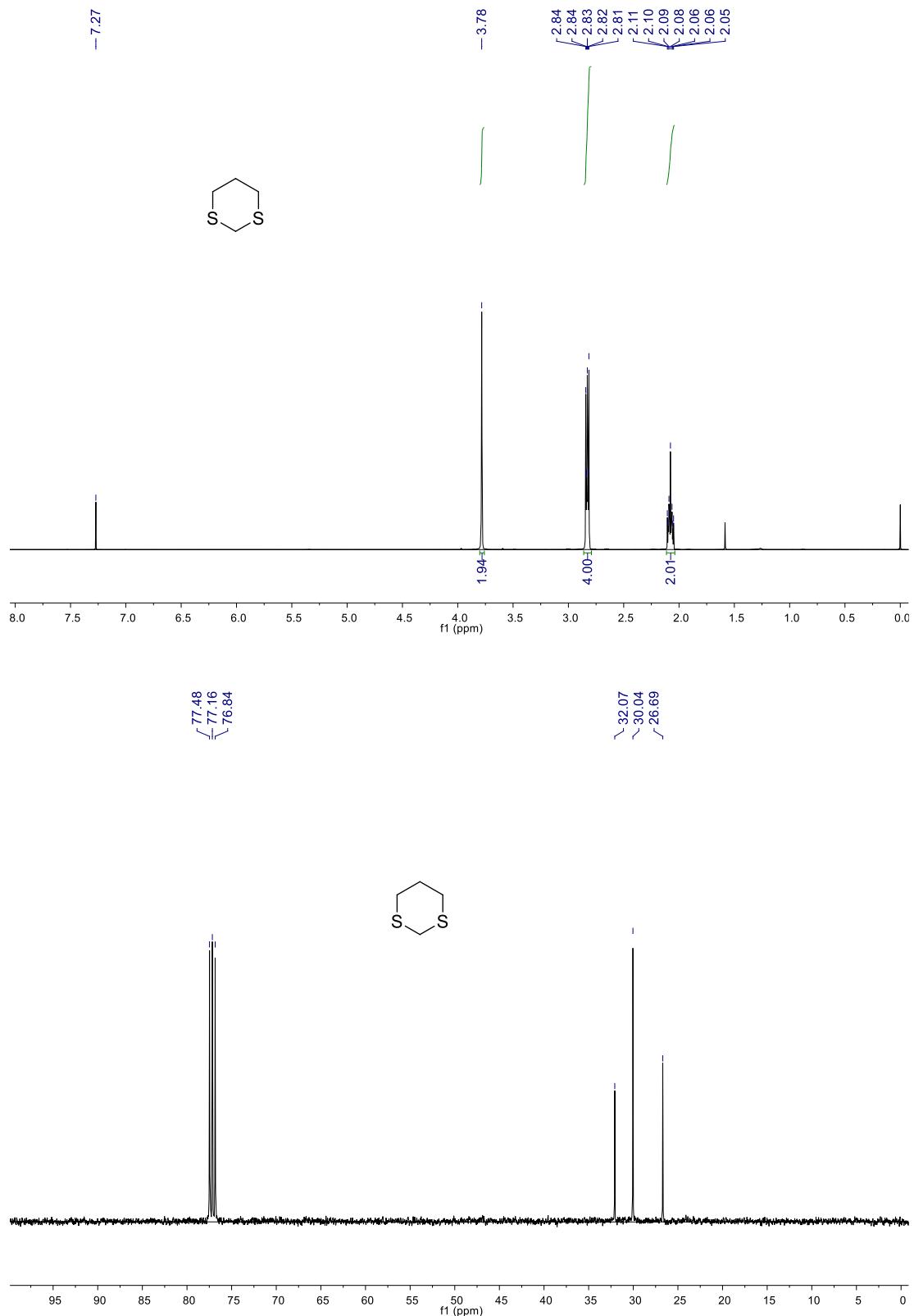


¹H and ¹³C NMR Spectrum of **2x**

- 7.27



^1H and ^{13}C NMR Spectrum of 2y



^1H and ^{13}C NMR Spectrum of **2z**