Supporting Information
for

Visible-Light-Induced Thiol–Disulfide Transformation via an Oxidant-Free Radical Pathway

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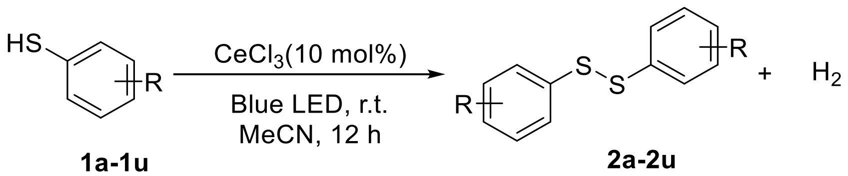
1. General Information

^{1}H NMR spectra were recorded on Varian Inova-400 or 600 MHz spectrometers. ^{1}H NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm or $CDCl_3$ (δ = 7.26 ppm ^{1}H), Chemical shifts are reported in ppm, and coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 F254 plates and viewed by UV LED (254 nm). Column chromatographic purification was performed using 200-300 mesh silica gel.

Cerium trichloride ($CeCl_3$, 99.99%)， Cerium dioxide (CeO_2, 99.99%) were purchased from Aldrich. All the other chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

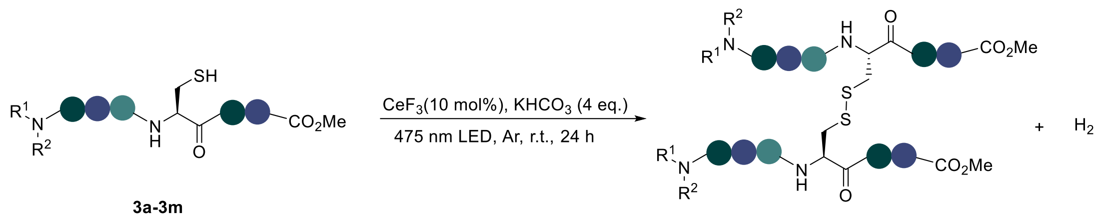
2. General procedure for the synthesis of substrates

synthesis of disulfide and substrate scope



Under an argon atmosphere, cerium(III) chloride (4.9 mg, 0.02 mmol, 0.1 equiv) was added to a dry 10 mL Schlenk tube equipped with a stir bar. Thiophenols(0.2mmol, 1 equiv) and deoxygenated acetonitrile (2.0 mL) were then injected via syringe. An aluminum foil gas-collection bag was attached to the Schlenk tube via latex tubing. The system was evacuated and refilled with argon using a double-manifold line until no gas evolution was observed. The stopcock was tightened, the latex tubing section was filled with argon, and the assembly was connected to the Schlenk tube. The reaction mixture was irradiated with a 50 W blue LED (λ = 475 nm) for 12 hours. After completion of the reaction, the stopcock of the Schlenk tube and the valve of the collection bag were opened. DCM was injected via syringe until the Schlenk tube was filled with liquid, followed by closing the collection bag valve. The combined organic layers were washed with saturated sodium hydroxide (NaOH) solution (15 mL), dried over anhydrous magnesium sulfate ($MgSO_4$), filtered, and concentrated under reduced pressure to afford the crude product. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) yielded the disulfide product(**2a-2u**) The structure of the disulfide products was confirmed by NMR spectroscopy, and the spectroscopic data were consistent with those reported in the refenrences[1-8]. The collected gas in the aluminum bag was subsequently analyzed by GC.

synthesis of cysteine-derived substrates and substrate scope



Under an argon atmosphere, cerium(III) fluoride (CeF_3, 3.9 mg, 0.02 mmol, 0.1 equiv) was added to a dry 10 mL Schlenk tube equipped with a magnetic stir bar. Cysteine-derived substrates (0.2 mmol, 1 equiv) and deoxygenated acetonitrile (2.0 mL) were then added via syringe. An aluminum foil gas-collection bag was connected to the Schlenk tube via latex tubing. The reaction system was evacuated and backfilled with argon using a double-manifold line until no further gas evolution was observed. The stopcock of the Schlenk tube was then tightened, the latex tubing section was filled with argon, and the assembly was reconnected to the Schlenk tube.

The reaction mixture was irradiated with a 50 W blue LED (λ = 475 nm) for 24 h. After completion of the reaction, the stopcock of the Schlenk tube and the valve of the gas-collection bag were opened. Dichloromethane (DCM) was injected via syringe until the Schlenk tube was completely filled with liqui d, after which the valve of the collection bag was closed. The combined organ ic layers were washed with saturated aqueous sodium hydroxide solution (15 m L), dried over anhydrous magnesium sulfate ($MgSO_4$), filtered, and concentrated under reduced pressure to afford the crude product(**4a-4m**). Purification by col umn chromatography (silica gel, dichloromethane/methanol = 30:1) yielded the cysteine-derived disulfide product. The gas collected in the aluminum foil bag was subsequently analyzed by GC.

3. Detailed description of the photoirradiation setup

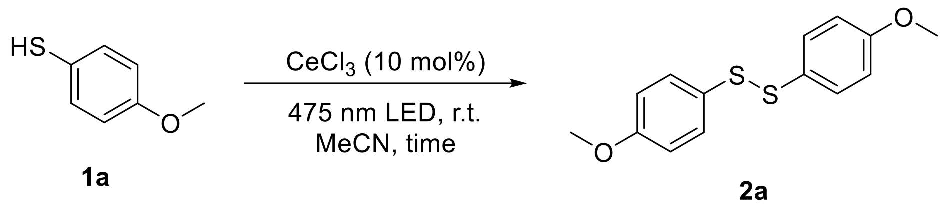
To improve reproducibility, the photoirradiation setup used in this work is described as follows. All photoirradiation experiments were performed in a circular photoreactor equipped with blue LEDs (475 nm, 50 W). The reactions were conducted in 10 mL Schlenk tubes placed in the designated slots of the photoreactor and irradiated from the side by the surrounding LED light source. The photoreactor was positioned on a magnetic stirrer, and all reactions were carried out under continuous magnetic stirring at room temperature during irradiation. A representative photograph of the photoirradiation setup is shown in **Figure S1**.

Fig S1 Representative photograph of the photoirradiation setup used in this work.

4. Optimization of reaction conditions

4.1 Optimization for disulfide and substrate scope

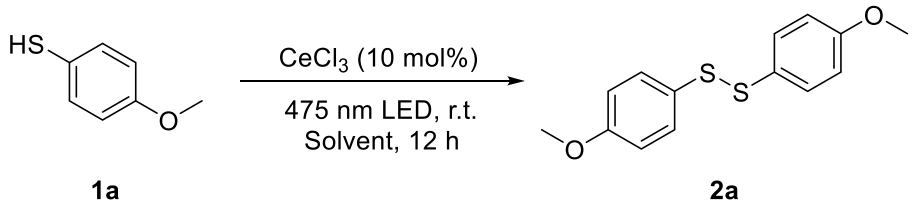
Table S1 Screening of reaction time [a]



Entry	Time (h)	Yield [b] (%)
1	1	10
2	3	51
3	6	65
4	12	80
5	24	82

[a] Reaction conditions: **1a** (0.2 mmol), $CeCl_3$ (0.02 mmol), MeCN (2 mL) at room temperature (25 °C), Blue LED (475 nm, 50 W). [b] isolated yield.

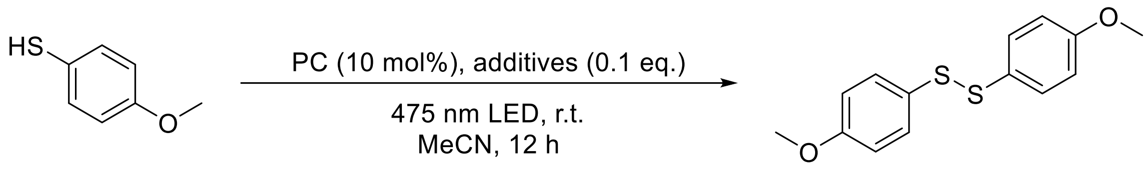
Table S2 Screening of solvent [a]



Entry	Solvent	Yield [b] (%)
1	Acetone	n.r.
2	MeOH	60
3	Toluene	49
4	EA	65
5	DMF	n.r.
6	DCE	68
7	DCM	74
8	MeCN	80

[a] Reaction conditions: **1a** (0.2 mmol), $CeCl_3$ (0.02 mmol), MeCN (2 mL) at room temperature (25 °C), Blue LED (475 nm, 50 W) for 12 h. [b] isolated yield.

Table S3 Screening of photocatalysts [a]

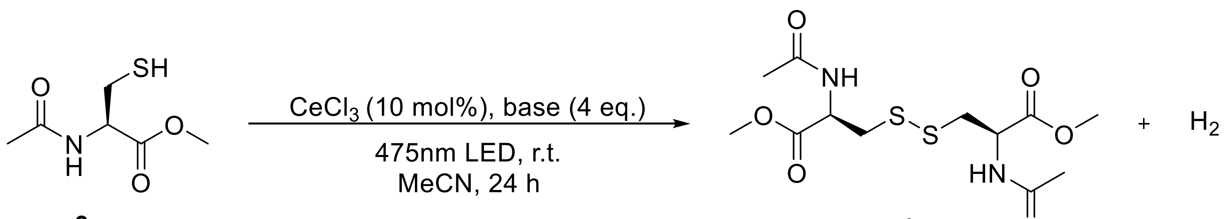


Entry	Photocatalysts	additives	Yield [b] (%)
1	CeO_2	-	28
2	$Ce(SO_4)_2$	-	52
3	$CeCl_3$	-	80
4	$CeCl_3$	MeOH	59
5	$CeCl_3$	EtOH	54
6	$CeCl_3·7H_2O$	-	47

[a] Reaction conditions: **1a** (0.2 mmol), PC (0.02 mmol), additives (0.02 mmol), MeCN (2 mL) at room temperature (25 °C), Blue LED (475 nm, 50 W) for 12 h. [b] isolated yield.

4.2 Optimization for cysteine-derived substrates and substrate scope

Table S4 Screening of base[a]

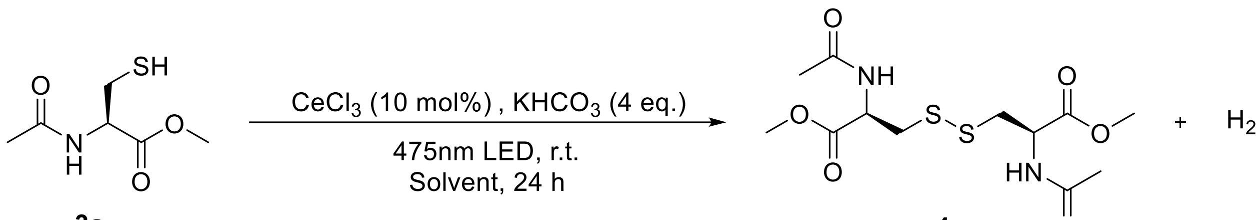


Entry	base	Yield [b] (%)
1	-	n.r.[c]
2	Na_2CO_3	35
3	$NaHCO_3$	27
4	K_3PO_4	trace[d]

5	K_2HPO_4	n.r.
6	NaOH	n.r.
7	Na_2CO_3	35
8	$KHCO_3$	38

[a] Reaction conditions: **3a** (0.2 mmol), $CeCl_3$ (0.02 mmol), base (0.8 mmol), MeCN (2 mL) at room temperature (25 °C), Blue LED (475 nm, 50 W) for 24 h. [b] isolated yield. [c] n.r.=no reaction. [d] Trace≤1%.

Table S5 Screening of solvent[a]

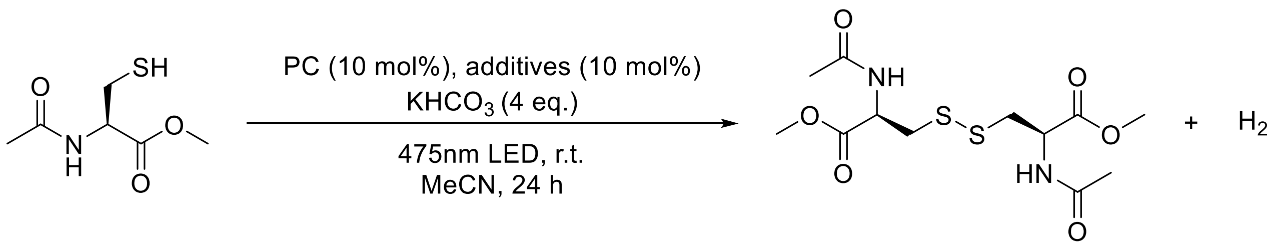


3a **4a**

Entry	Solvent	Yield [b] (%)
1	THF	n.r.[c]
2	DMF	29
3	DMA	n.r.
4	MTBE	trace[d]
5	NMP	n.r.

[a] Reaction conditions: **3a** (0.2 mmol), $CeCl_3$ (0.02 mmol), $KHCO_3$ (0.8 mmol), Solvent (2 mL) at room temperature (25 °C), Blue LED (475 nm, 50 W) for 24 h. [b] isolated yield. [c] n.r.=no reaction. [d] Trace≤1%.

Table S6 Screening of photocatalysts[a]



3a **4a**

Entry	Photocatalysts	additives	Yield [b] (%)
1	$CeCl_3$	MeOH	24
2	$CeCl_3$	EtOH	7

3	$CeCl_3$	*t*-BuOH	34
4	$CeCl_3$	TCE	n.r.[c]
5	$CeCl_3$	TFE	13
6	$CeCl_3$	*i*-PrOH	33
7	$CeCl_3$	HFIP	26
8	$CeCl_3$	CyOH	trace[d]
9	CeF_3	-	62
10	$Ce(CF_3SO_3)_3$	-	n.r.
11	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	-	trace

[a] Reaction conditions: **3a** (0.2 mmol), PC (0.02 mmol), additives (0.1 mmol), MeCN (2 mL) at room temperature (25 °C), Blue LED (475 nm, 50 W) for 24 h. [b] isolated yield. [c] n.r.=no reaction. [d] Trace≤1%.

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(1) Dai, W.-T.; Wen, C.-C.; Lin, H.-J.; Huang, M.-H. Photocatalyzed Aerobic Oxidation of Thiols to Disulfides Using Cu_2O Polyhedra. *ACS Appl. Mater. Interfaces* **2025**, *17*, 18268-18274.

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(6) Yang, L.-T.; Li, S.-D.; Dou, Y.-C.; Zhen, S.; Li, H.; Zhang, P.-K.; Yuan, B.-X.; Yang, G.-Y. TEMPO-Catalyzed Aerobic Oxidative Coupling of Thiols for Metal-Free Formation o f S–N/S–S Bonds. *Asian J. Org. Chem.* **2017**, *6*, 265-268.

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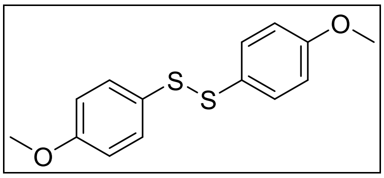
Novel Approach to Access Aryl Iodides and Disulfides via Dehydrazination of Arylhydrazines and Arylsulfonylhydrazides. *ChemistrySelect* **2018**, 3, 2800-2804.
(8) Veladi, P.; Prabhu, G.; Basavaprabhu; Panguluri, N. R.; Sureshbabu, V. V. Alternative Protocol for the Synthesis of Symmetrical Dibenzyl Diselenides and Disulfides. *Synthesis* **2016**, 48, 1711–1718.

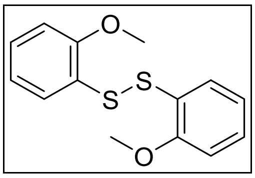
5. Characterization data of the products

Bis(4–methoxyphenyl) disulfide (2a)[1]



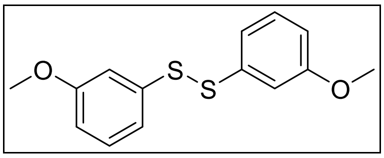
Yellow oil; 22.3 mg, 80% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 – 7.36 (m, 4H), 6.89 – 6.79 (m, 4H), 3.80 (s, 6H).

Bis(2–methoxyphenyl) disulfide (2b)[1]



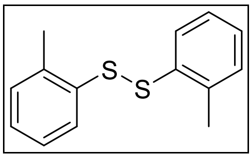
Pale yellow oil; 13.9 mg, 50% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.19 (td, *J* = 7.8, 1.6 Hz, 2H), 6.99 – 6.77 (m, 4H), 3.90 (s, 6H).

1–methoxy–3–[(3–methoxyphenyl)disulfanyl]benzene (2c)[5]



Pale yellow oil; 12.5 mg, 45% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.21 (t, *J* = 8.1 Hz, 2H), 7.11 – 7.04 (m, 4H), 6.76 (ddd, *J* = 8.2, 2.4, 1.1 Hz, 2H), 3.77 (s, 6H).

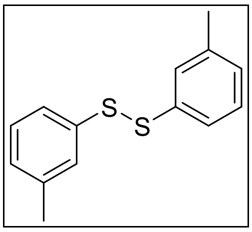
1–methyl–2–[(2–methylphenyl)disulfanyl]benzene (2d)[6]



Pale yellow oil; 11.3 mg, 46% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54

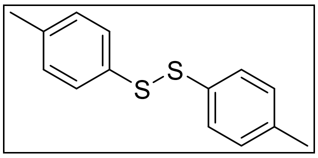
– 7.48 (m, 2H), 7.18 – 7.14 (m, 4H), 7.14 – 7.10 (m, 2H), 2.43 (s, 6H).

1–methyl–3–[(3–methylphenyl)disulfanyl]benzene (2e)[3]



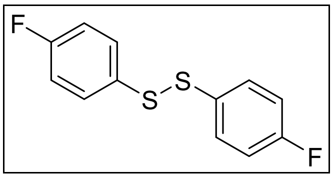
Pale yellow oil; 10.3 mg, 42% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 – 7.47 (m, 2H), 7.18 – 7.14 (m, 4H), 7.14 – 7.10 (m, 2H), 2.43 (s, 6H).

1–methyl–4–[(4–methylphenyl)disulfanyl]benzene (2f)[1]



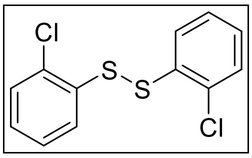
Pale yellow oil; 17.7 mg, 72% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (d, 4H), 7.11 (d, *J* = 8.1 Hz, 4H), 2.33 (s, 6H).

Bis(4–fluorophenyl) disulfide (2g)[1]



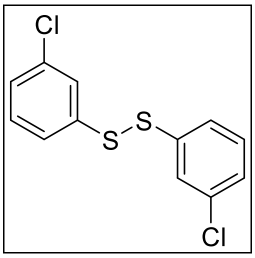
White oil; 18.0 mg, 71% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 – 7.46 (m, 4H), 7.20 – 7.14 (m, 4H).

Bis(2–chlorophenyl) disulfide (2h)[4]



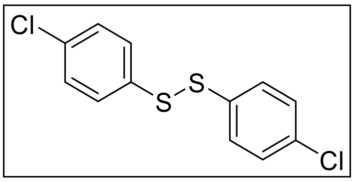
Pale yellow oil; 17.8 mg, 62% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.36 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.22 (td, *J* = 7.6, 1.5 Hz, 2H), 7.16 (td, *J* = 7.6, 1.7 Hz, 2H).

Bis(3–chlorophenyl) disulfide (2i)[4]



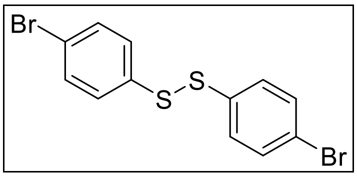
Pale yellow oil; 14.6 mg, 51% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 – 7.47 (m, 2H), 7.35 (dt, *J* = 7.4, 1.7 Hz, 2H), 7.25 – 7.19 (m, 4H).

Bis(4–chlorophenyl) disulfide (2j)[1]



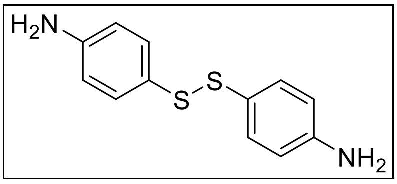
White oil; 19.5 mg, 68% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 – 7.36 (m, 4H), 7.30 – 7.26 (m, 4H).

Bis(4–bromophenyl) disulfide (2k)[1]



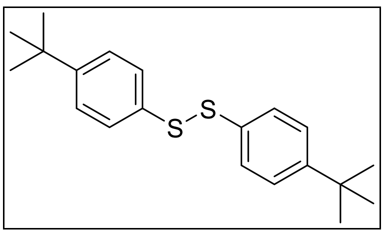
White oil; 24.8 mg, 66% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.46 – 7.40 (m, 4H), 7.36 – 7.31 (m, 4H).

4–Aminophenyl disulfide (2l)[6]



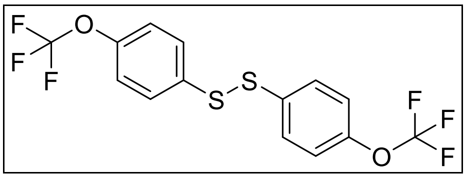
Pale yellow oil; 9.2 mg, 40% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.25 (m, 4H), 6.59 (d, *J* = 8.6 Hz, 4H), 3.76 – 3.57 (m, 4H).

Bis[4–(1,1–dimethylethyl)phenyl] disulfide (2m)[1]



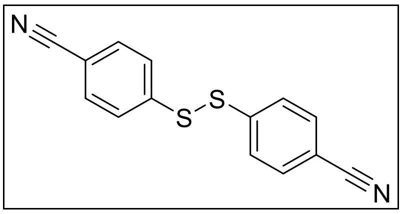
White oil; 15.6 mg, 47% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 – 7.40 (m, 4H), 7.36 – 7.29 (m, 4H), 1.30 (s, 18H).

Disulfide, bis[4–(trifluoromethoxy)phenyl] (2n)[3]



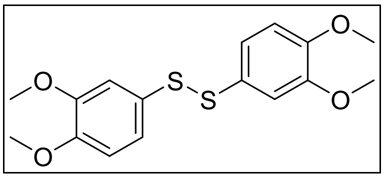
White oil; 27.4 mg, 75% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 – 7.46 (m, 4H), 7.20 – 7.14 (m, 4H).

4–[(4–cyanophenyl)disulfanyl]benzonitrile (2o)[3]



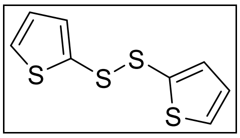
Yellow oil; 10.5 mg, 62% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 – 7.59 (m, 4H), 7.57 – 7.53 (m, 4H).

Bis(3,4–dimethoxyphenyl) disulfide (2p)[7]



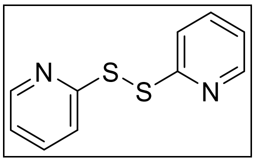
Pale yellow oil; 15.5 mg, 46% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.04 (dd, *J* = 8.3, 2.1 Hz, 2H), 7.00 (d, *J* = 2.1 Hz, 2H), 6.77 (d, *J* = 8.3 Hz, 2H), 3.85 (s, 6H), 3.81 (s, 6H).

2,2'–Dithienyl Disulfide (2q)[6]



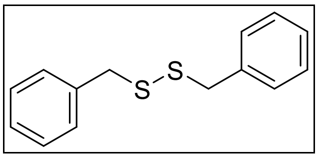
Yellow oil; 14.7 mg, 64% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (dd, *J* = 5.3, 1.3 Hz, 2H), 7.16 (dd, *J* = 3.6, 1.3 Hz, 2H), 7.01 (dd, *J* = 5.3, 3.6 Hz, 2H).

2,2′–Dipyridyl Disulfide (2r)[1]



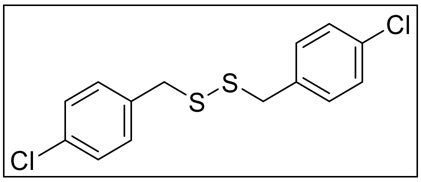
White oil; 7.9 mg, 40% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.50 – 8.44 (m, 2H), 7.68 – 7.56 (m, 4H), 7.11 (ddd, *J* = 6.8, 4.8, 2.1 Hz, 2H).

Dibenzyl disulfide (2s)[2]



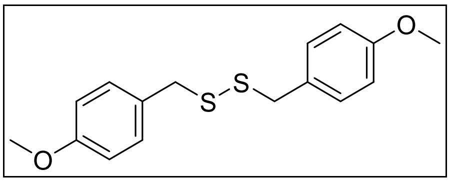
White oil; 12.3 mg, 50% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.3 Hz, 4H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 4H), 3.81 (d, *J* = 12.1 Hz, 4H).

Bis(4–chlorobenzyl) disulfide (2t)[2]



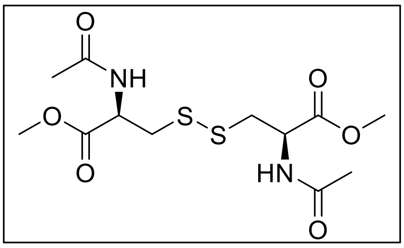
White oil; 15.4 mg, 49% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 4H), 7.19 – 7.07 (m, 4H), 3.58 (s, 4H).

Bis[(4–methoxyphenyl)methyl] disulfide (2u)[8]



White oil; 12.9 mg, 42% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.15 (m, 4H), 6.92 – 6.77 (m, 4H), 3.80 (s, 6H), 3.71 (d, *J* = 7.3 Hz, 4H).

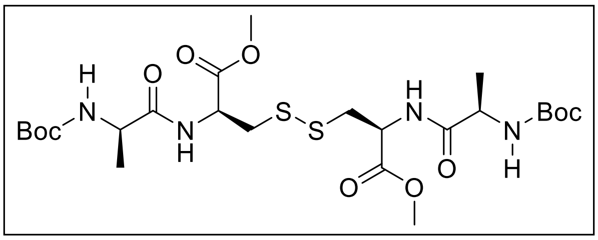
***N*-Ac-Cys-OMe disulfide (4a)**



White solid; 21.8 mg, 62% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.58 (d, *J*

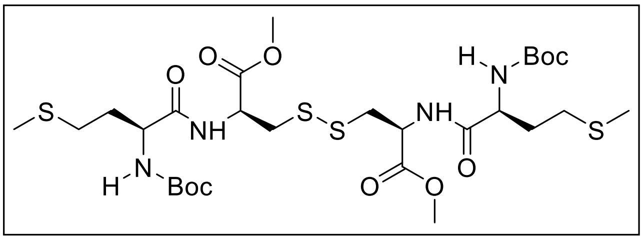
= 7.5 Hz, 2H), 4.87 (dt, *J* = 7.5, 5.0 Hz, 2H), 3.77 (s, 6H), 3.28–3.13 (m, 4H), 2.06 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.94, 170.14, 52.84, 51.74, 40.73, 29.33, 23.14. HRMS (ESI) m/z calculated for $C_{12}H_{20}N_2O_6S_2$ ($[M+H]^+$): 353.0836, found 353.0850.

***N*-Boc-Ala-Cys-OMe disulfide (4b)**



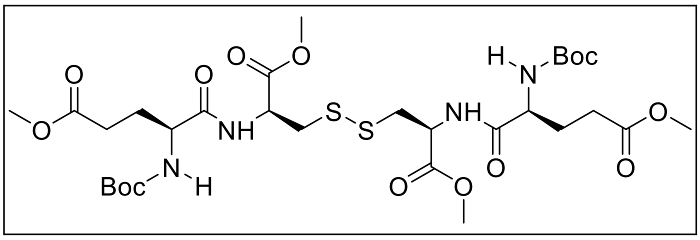
White solid; 32.3 mg, 56% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.99 (d, *J* = 7.4 Hz, 2H), 4.98 (s, 2H), 4.85 (dt, *J* = 8.0, 4.1 Hz, 2H), 4.23–4.15 (m, 2H), 3.79 (s, 6H), 3.01 (ddd, *J* = 10.0, 6.0, 4.2 Hz, 4H), 1.45 (s, 18H), 1.38 (d, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.16, 170.55, 155.76, 80.10, 52.80, 52.09, 49.84, 40.81, 29.70, 28.35, 18.09. HRMS (ESI) m/z calculated for $C_{24}H_{42}N_4O_{10}S_2$ ($[M+H]^+$): 611.2415, found 611.2454.

***N*-Boc-Met-Cys-OMe disulfide (4c)**



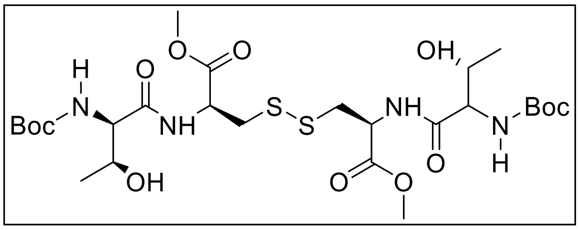
White solid; 58.4 mg, 80% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.04 (d, *J* = 7.7 Hz, 2H), 5.19 (d, *J* = 8.0 Hz, 2H), 4.87 (dt, *J* = 8.0, 4.2 Hz, 2H), 4.32 (q, *J* = 7.6 Hz, 2H), 3.79 (s, 6H), 3.01 (dd, *J* = 9.1, 4.2 Hz, 4H), 2.67–2.55 (m, 4H), 2.12 (s, 6H), 2.13–2.00 (m, 2H), 1.45 (s, 18H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.17, 170.43, 155.98, 80.17, 53.39, 52.79, 52.23, 40.00, 31.82, 30.05, 28.35, 15.32. HRMS (ESI) m/z calculated for $C_{28}H_{50}N_4O_{10}S_4$ ($[M+H]^+$): 731.2483, found 731.2462.

***N*-Boc-Glu-OMe-Cys-OMe disulfide (4d)**



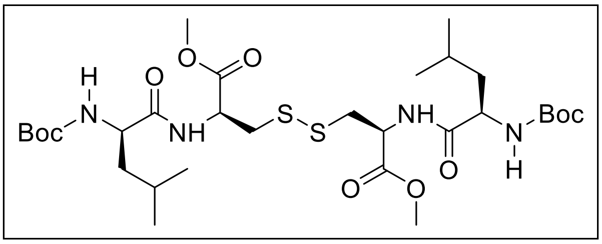
Yellow solid; 37.7 mg, 50% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.7 Hz, 2H), 5.66 (d, *J* = 8.5 Hz, 2H), 4.86 (dt, *J* = 7.7, 5.5 Hz, 2H), 4.32 (q, *J* = 7.7 Hz, 2H), 3.75 (s, 6H), 3.67 (s, 6H), 3.12-3.05 (m, 4H), 2.55–2.39 (m, 4H), 2.14 (dt, *J* = 13.9, 6.8 Hz, 4H), 1.42 (s, 18H). **^{13}C NMR (**101 MHz, Chloroform-*d*) δ 173.65, 172.03, 170.46, 155.97, 53.56, 52.82, 52.20, 51.83, 40.21, 30.22, 28.33, 27.65. HRMS (ESI) m/z calculated for $C_{30}H_{50}N_4O_{14}S_2$ ($[M+H]^+$): 755.2838, found 755.2837.

***N*-Boc-Thr-Cys-OMe disulfide (4e)**



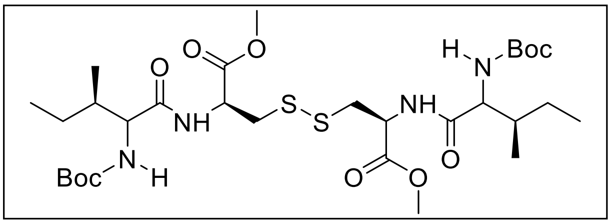
Yellow solid; 20.2 mg, 30% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.8 Hz, 2H), 5.70 (d, *J* = 8.5 Hz, 2H), 4.85 (dt, *J* = 7.8, 5.8 Hz, 2H), 4.43–4.06 (m, 4H), 3.76 (s, 6H), 3.20–3.06 (m, 4H), 1.45 (s, 18H), 1.28–1.17 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.60, 170.42, 156.59, 80.61, 66.76, 58.74, 52.89, 52.03, 41.10, 29.71, 28.31, 22.70, 18.51. HRMS (ESI) m/z calculated for $C_{26}H_{46}N_4O_{12}S_2$ ($[M+H]^+$): 671.2626, found 671.2623.

***N*-Boc-Leu-Cys-OMe disulfide (4f)**



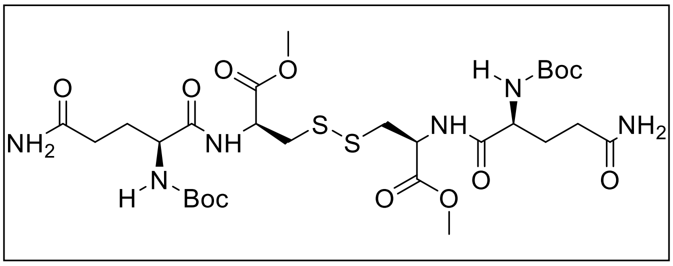
White solid; 90% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.01 (d, *J* = 7.6 Hz, 2H), 4.97 (d, *J* = 8.0 Hz, 2H), 4.83 (dt, *J* = 8.0, 4.2 Hz, 2H), 4.12-4.02 (m, 2H), 3.77 (s, 6H), 2.99 (ddd, *J* = 14.3, 9.1, 4.4 Hz, 4H), 1.65–1.50 (m, 6H), 1.43 (s, 18H), 1.29–1.21 (m, 2H), 0.93 (d, *J* = 6.2 Hz, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.48, 170.34, 155.73, 80.28, 53.69, 53.19, 52.83, 40.81, 28.31, 26.66, 24.72, 22.89, 22.02. HRMS (ESI) m/z calculated for $C_{30}H_{54}N_4O_{10}S_2$ ($[M+H]^+$): 695.3354, found 695.3355.

***N*-Boc-Ile-Cys-OMe disulfide (4g)**



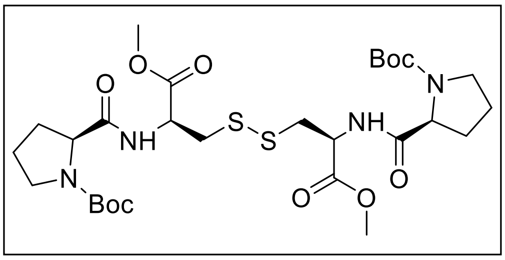
Yellow solid; 22% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.5 Hz, 2H), 5.33 (d, *J* = 9.1 Hz, 2H), 4.90 (td, *J* = 7.3, 4.1 Hz, 2H), 4.14 (t, *J* = 8.4 Hz, 2H), 3.73 (s, 6H), 3.12 (dd, *J* = 14.1, 4.2 Hz, 2H), 3.00 (dd, *J* = 14.2, 7.2 Hz, 2H), 1.63–1.53 (m, 2H), 1.41 (s, 18H), 1.35–1.26 (m, 2H), 1.26–1.23 (m, 2H), 1.23–1.11 (m, 2H), 0.98 (d, *J* = 6.7 Hz, 6H), 0.89 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.54, 170.64, 156.19, 79.86, 58.89, 52.64, 39.37, 37.13, 28.34, 24.85, 15.30, 11.02. HRMS (ESI) m/z calculated for $C_{30}H_{54}N_4O_{10}S_2$ ($[M+H]^+$): 695.3354, found 695.3354.

***N*-Boc-Gln-Cys-OMe disulfide (4h)**



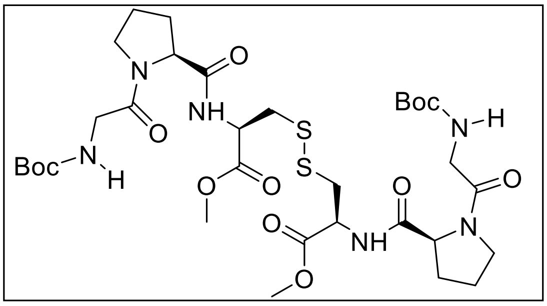
White soild; 63% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90–7.75 (br d, *J* = 8.0 Hz, 2H), 6.80–6.30 (br s, 4H), 5.85 (d, *J* = 8.4 Hz, 2H), 4.90–4.75 (m, 2H), 4.35–4.20 (m, 2H), 3.76 (s, 6H), 3.20–3.05 (m, 4H), 2.45–2.30 (m, 4H), 1.90–1.60 (m, 4H), 1.43 (s, 18H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.75, 172.18, 170.82, 156.01, 80.14, 53.51, 52.87, 52.32, 40.70, 31.85, 29.03, 28.36. HRMS (ESI) m/z calculated for $C_{28}H_{48}N_6O_{12}S_2$ ($[M+H]^+$): 725.2844, found 725.2866.

***N*-Boc-Pro-Cys-OMe disulfide (4i)**



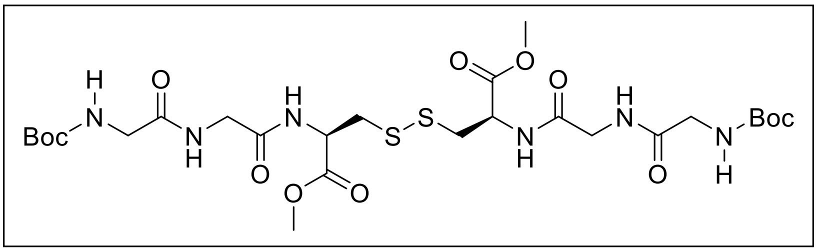
White solid; 51%**;** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (br d, *J* = 7.5 Hz, 2H), 4.95–4.80 (m, 4H), 4.35–4.20 (m, 2H), 3.76 (s, 6H), 3.55–3.10 (m, 8H), 2.20–1.95 (m, 4H), 1.70–1.55 (m, 4H), 1.45 (s, 18H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.63, 170.66, 154.80, 80.76, 61.13, 59.87, 52.72, 51.29, 47.08, 40.30, 31.03, 28.34, 24.51, 23.71. HRMS (ESI) m/z calculated for $C_{28}H_{46}N_4O_{10}S_2$ ([M+H]$^+$): 663.2728, found 663.2736.

***N*-Boc-Gly-Pro-Cys-OMe disulfide (4j)**



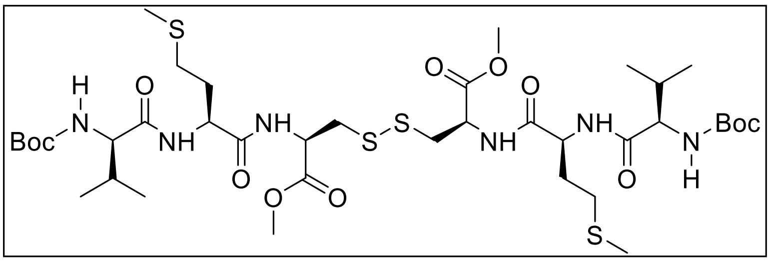
White solid; 50%**;** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.8 Hz, 2H), 5.44 (t, *J* = 4.6 Hz, 2H), 4.77 (dt, *J* = 8.2, 4.4 Hz, 2H), 4.55 (dd, *J* = 8.1, 2.9 Hz, 2H), 3.97–3.89 (m, 4H), 3.76 (s, 6H), 3.64–3.41 (m, 4H), 3.01 (ddd, *J* = 14.2, 8.6, 4.4 Hz, 2H), 2.91 (ddd, *J* = 14.0, 9.5, 4.4 Hz, 2H), 2.31–2.14 (m, 4H), 1.99 (m, 4H), 1.63 (t, *J* = 9.0 Hz, 2H), 1.40 (s, 18H), 1.24 (d, *J* = 12.3 Hz, 2H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.88, 170.44, 168.53, 155.82, 79.79, 60.13, 53.96, 52.80, 46.37, 43.09, 29.69, 28.34, 27.85, 26.53, 24.95, 22.38. HRMS (ESI) m/z calculated for $C_{32}H_{52}N_6O_{12}S_2$ ([M+H]$^+$): 777.3157, found 777.3117.

***N*-Boc-Gly-Gly-Cys-OMe disulfide (4k)**



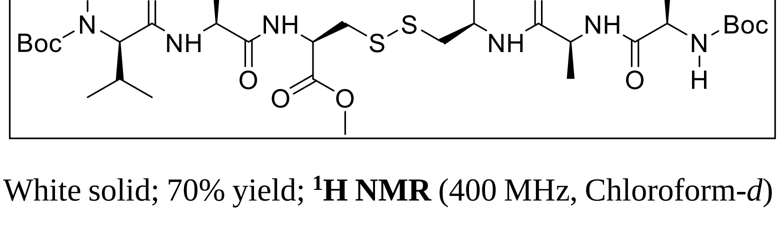
White liquid; 80% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.53 (br s, 2H), 5.79 (br s, 2H), 4.82 (td, *J* = 8.2, 4.5 Hz, 2H), 4.15–3.95 (m, 4H), 3.95–3.78 (m, 4H), 3.72 (s, 6H), 3.17 (dd, *J* = 14.3, 4.5 Hz, 4H), 3.04–2.92 (m, 4H), 1.41 (s, 18H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.91, 170.75, 169.53, 156.44, 80.25, 52.82, 52.26, 44.08, 42.98, 40.57, 28.35. HRMS (ESI) m/z calculated for $C_{26}H_{44}N_6O_{12}S_2$ ([M+H]$^+$): 697.2531, found 697.2514.

***N*-Boc-Val-Met-Cys-Ome disulfide (4l)**



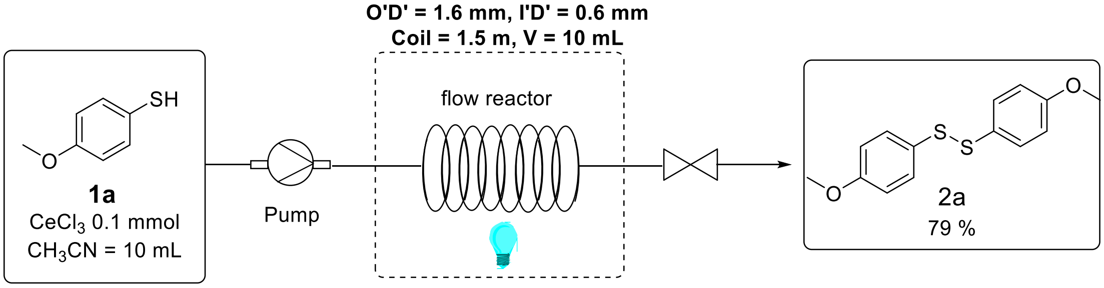
White solid; 90% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.8–7.10 (br s , 2H), 5.40 (d, *J* = 8.7 Hz, 2H), 4.87 (d, *J* = 6.0 Hz, 2H), 4.82 (dt, *J* = 14.5, 6.8 Hz, 4H), 3.99 (t, *J* = 7.7 Hz, 2H), 3.75 (s, 6H), 3.17–3.02 (m, 6H), 2.58 (t, *J* = 7.3 Hz, 6H), 2.09 (s, 6H), 2.04–1.94 (m, 4H), 1.91–1.20 (m, 14H), 1.43 (s, 18H), 0.95–0.85 (m, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.33, 171.36, 170.31,151.11, 60.04, 52.81, 52.34, 52.10, 40.11, 31.34, 30.88, 29.92, 29.71, 28.39, 22.71, 19.41, 17.99, 15.29, 14.15. HRMS (ESI) m/z calculated for $C_{38}H_{68}N_6O_{12}S_4$ ([M+H]$^+$): 929.3851, found 929.3823.

N-Boc-Val-Ala-Cys-OMe disulfide (4m)



White solid; 70% yield; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 5.40 – 5.30 (m, 2H), 4.88 (q, J = 6.3 Hz, 2H), 4.68 (t, J = 7.3 Hz, 2H), 4.05 – 3.96 (m, 2H), 3.75 (s, 6H), 3.20 – 2.99 (m, 4H), 2.11 (hept, J = 6.5 Hz, 2H), 1.42 (s, 18H), 1.29 – 1.23 (m, 12H), 0.93 (d, J = 6.8 Hz, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.49, 172.08, 170.36, 155.94, 59.85, 52.82, 52.37, 48.59, 31.94, 31.52, 31.06, 30.13, 29.71, 28.37, 22.71, 19.44, 18.05, 17.78, 14.15. HRMS (ESI) m/z calculated for $C_{34}H_{60}N_6O_{12}S_2$ ($[M+H]^+$): 809.3783, found 809.3763.

6. Scale-up reaction in continuous-flow reactor [a]

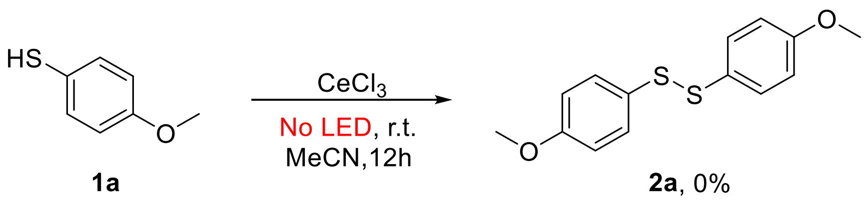


Entry	Rate (mL/min)	Residue time	Yield [b] (%)
1	2	5	46
2	1	10	60
3	0.5	20	79
4	0.25	40	73

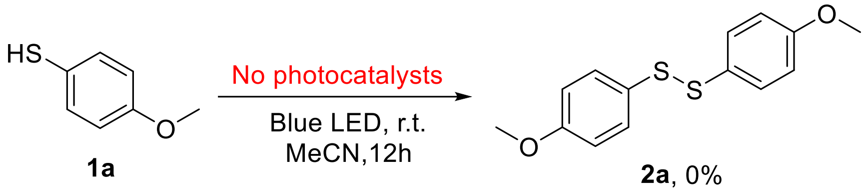
[a] Reaction conditions: **1a** (1 mmol), $CeCl_3$ (0.1 mmol) at room temperature (25 °C), Blue LED (475 nm, 50 W) for 12 h. [b] isolated yield.

7. Mechanistic studies

Control Experiments

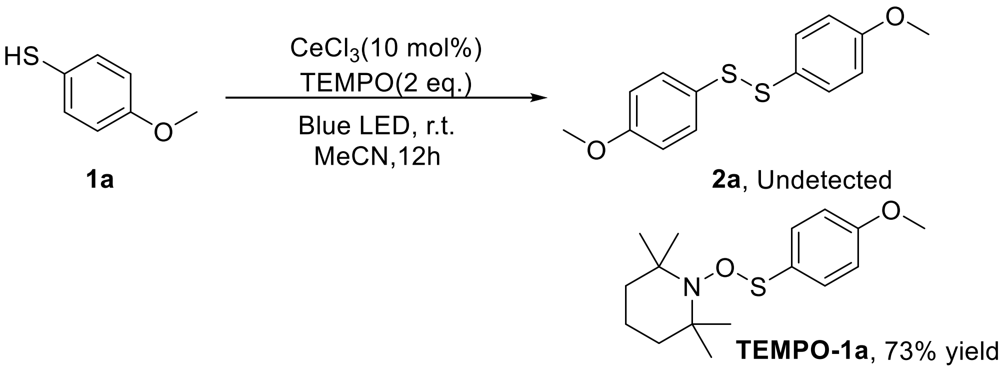


A light-proof experiment was performed in contrast to standard reaction conditions, where the reaction tube was wrapped in tin foil to prevent external light sources from affecting the reaction. After the reaction was completed under the condition of no light source, the disulfide product formation was not detected by TLC detection.



After that, experiments without photocatalysts were carried out, and compared with the standard reaction conditions, no photocatalysts were involved. After the reaction was completed, the disulfide product formation was not detected by TLC detection.

Radical Trapping Experiment Using TEMPO



In an argon atmosphere, add 1a (0.20 mmol, 1.0 equivalent), $CeCl_3$ (0.02 mmol, 0.1 equivalent), and CH_3CN (2 mL) to a 10 mL Schlenk tube fitted with a rubber stopper and magnetic stir bar. The free radical scavenger 2,2,6,6-tetramethyl-1-piperidine oxy (TEMPO) (0.40 mmol, 2.0 equivalent) was added to the reaction mixture. The reaction mixture is thawed and degassed by double row tubes and liquid nitrogen three times. The reaction mixture is then stirred and irradiated with blue LEDs at temperature. After 12 h, TLC analysis showed that no disulfide product was formed; instead, a new spot was observed. The reaction mixture was purified by silica gel column chromatography (PE/EA = 30:1) to afford the TEMPO–*p*-methoxyphenylthiyl radical adduct in 73% yield. The formation of this adduct suggests that the reaction involves a free radical process. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.75 (m, 2H), 6.95 – 6.87 (m, 2H), 3.84 (s, 3H), 1.64 (d, 6H), 1.57 (s, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.66, 139.35, 128.09, 113.60, 60.66, 55.53, 43.90, 31.08, 16.75. HRMS (ESI) m/z calculated for $C_{16}H_{26}NO_2S$ ($[M+H]^+$): 296.1640, found 296.1642.

Fluorescence quenching experiment

In order to elucidate the energy transfer path of the photocatalytic system, the Stern-Volmer fluorescence quenching kinetics method was used in this study. The results obtained are shown in Figure S2, and the experimental results show that the fluorescence intensity of the excited cerium chloride decreases linearly as the concentration of 4-methoxyphenylthiophenol increases from 0 mM to 0.5 mM, confirming the existence of a dynamic quenching mechanism in the system.

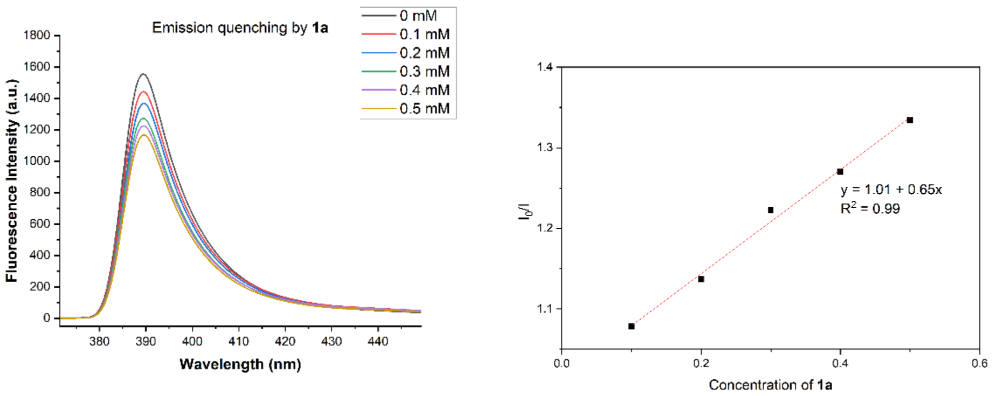


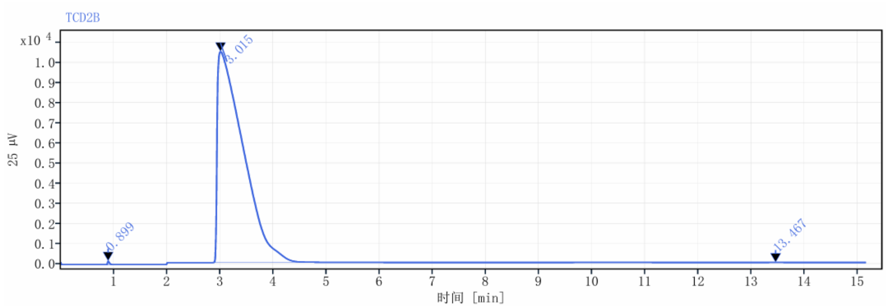
Fig S2 Fluorescence quenching effect of reactant **1a**

Hydrogen detection

In order to verify that the reaction is a coupled hydrogen evolution reaction, the gas produced by the reaction is collected and tested by the gas phase. The collection device used is shown in **Figure S3.**

Fig S3 Hydrogen collection unit for disulfide synthesis

Before the reaction, the argon gas in the foil gas sampling bag is replaced three times and then connected to the front end of the Schlenk tube. The gas produced by the reaction is collected with an aluminum foil gas sampling bag. After the reaction is completed, the collected gas is fed into the gas phase to detect the gas composition, and the results are shown in Figure S3. The peak at 0.899 min was H_2, the peak at 3-4 min was mainly argon, and the peak at 13.467 min was CO_2 brought into the air during injection. Since the detected amount of hydrogen collected in the air pocket far exceeds the amount of hydrogen carried in the air at the time of injection, it is assumed that hydrogen is formed in this reaction.

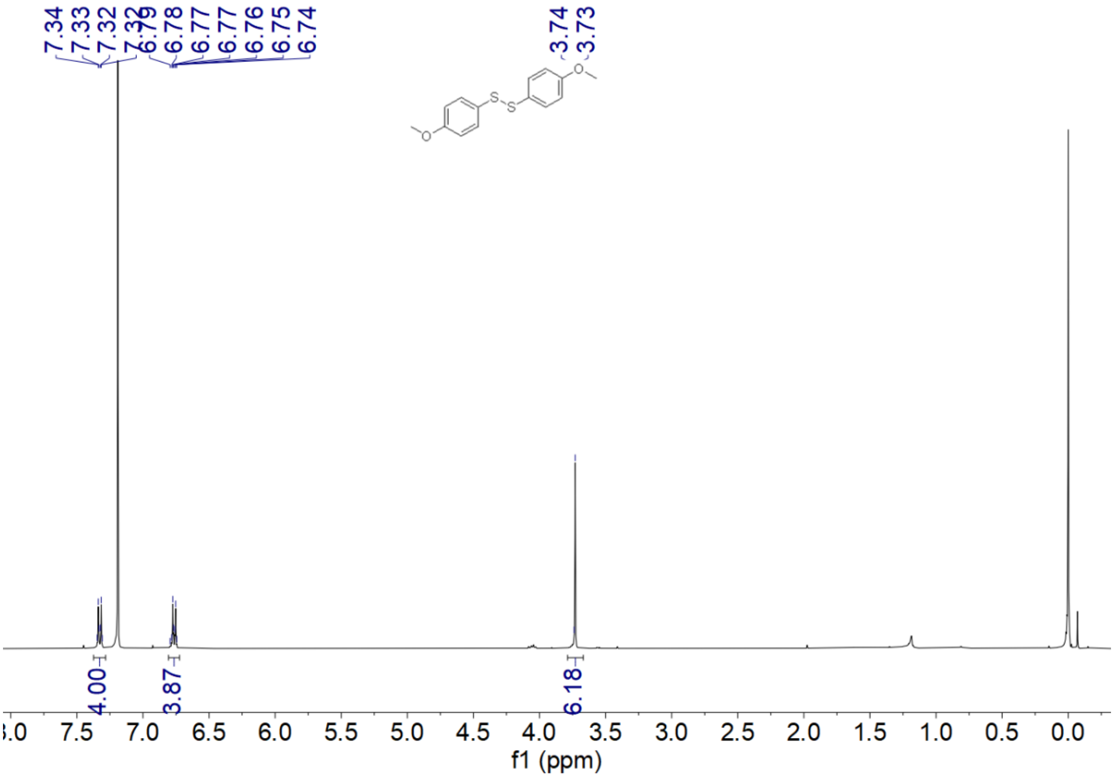


信号: TCD2B

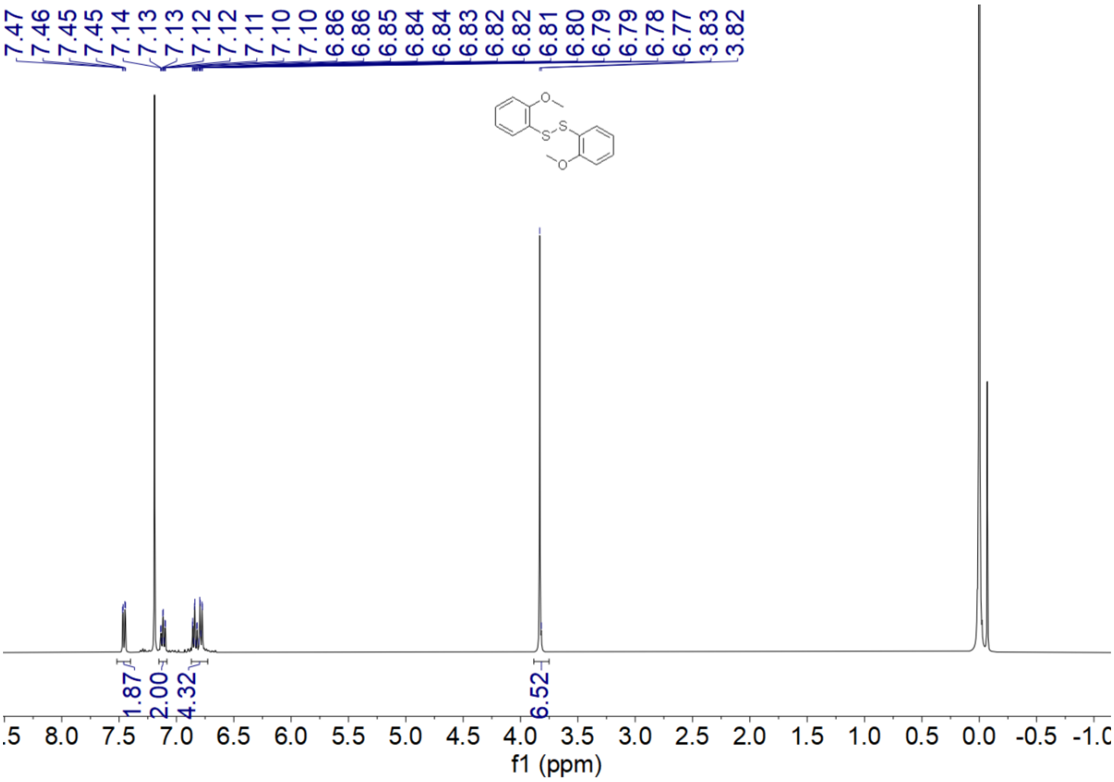
名称	保留时间 [min]	响应因子	峰面积	含量 [%]	浓度 []	ISTD 名称	组
H2	0.899	35.548	409.777	11.527	11.527		
CO2	13.467	4529.845	49.202	0.011	0.011		
		总计(不含 ISTD):		11.538			

Fig S3 Disulfide reaction to collect gas gas phase results

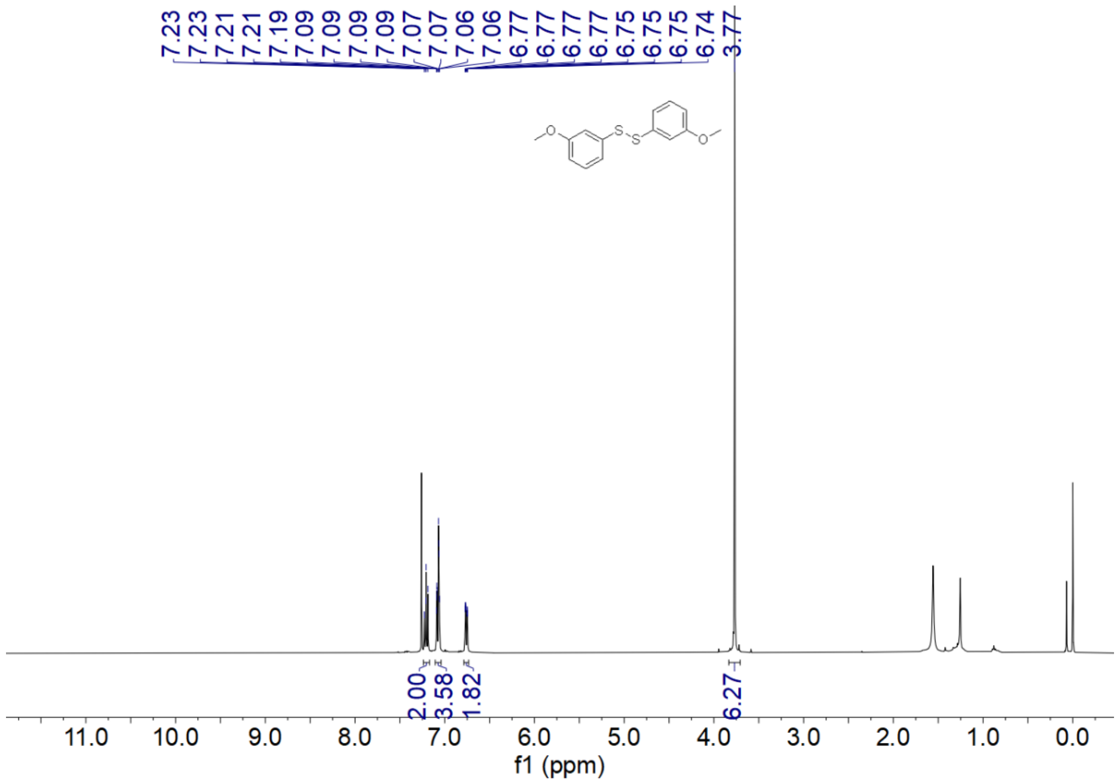
8. ^{1}H NMR spectra of the products



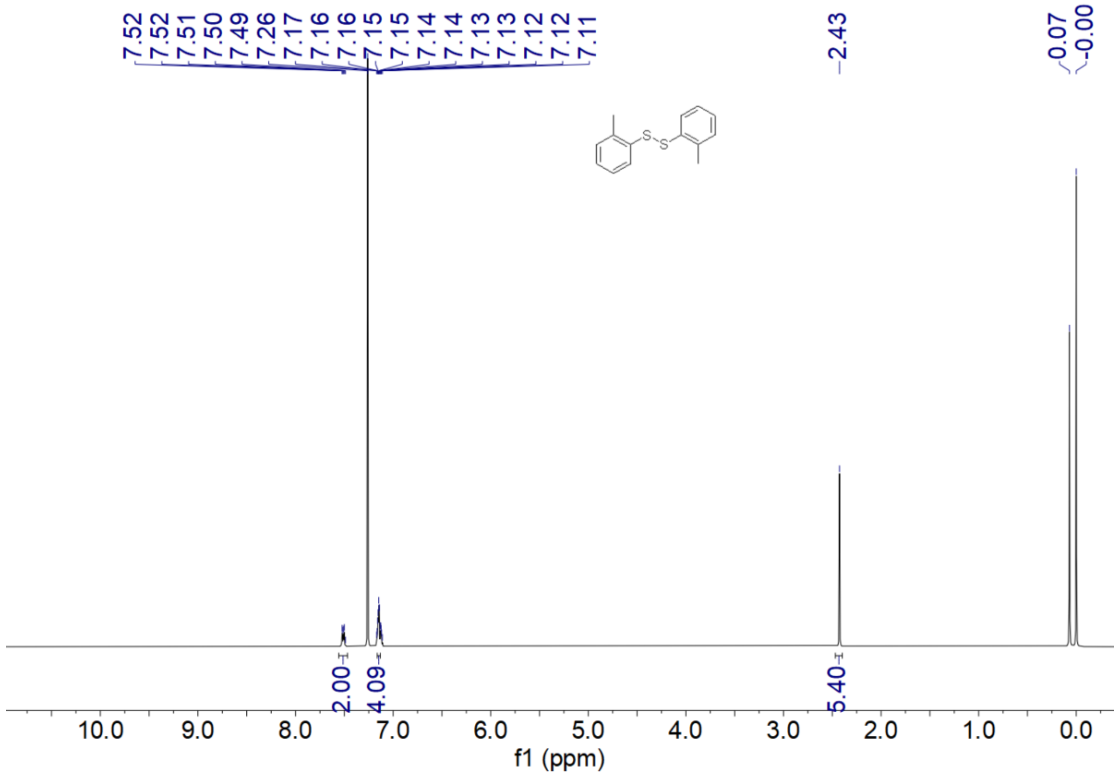
^{1}**H NMR** (400 MHz, $CDCl_3$) of compound **2a**



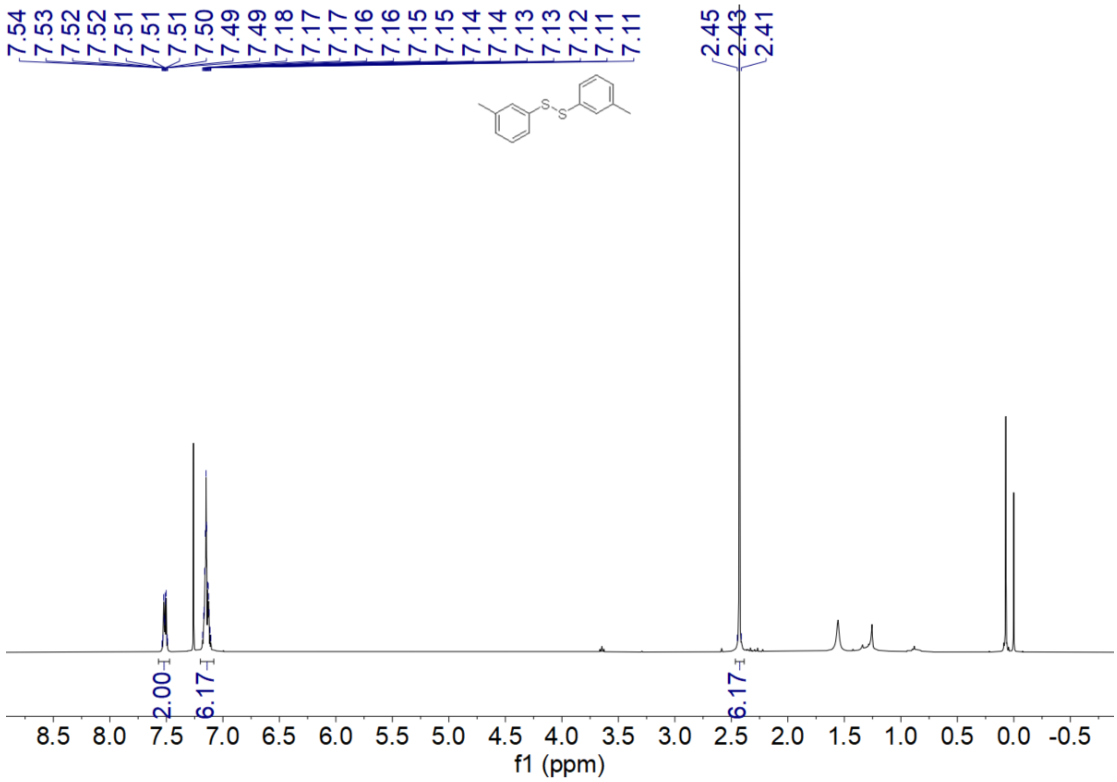
^{1}**H NMR** (400 MHz, $CDCl_3$) of compound **2b**



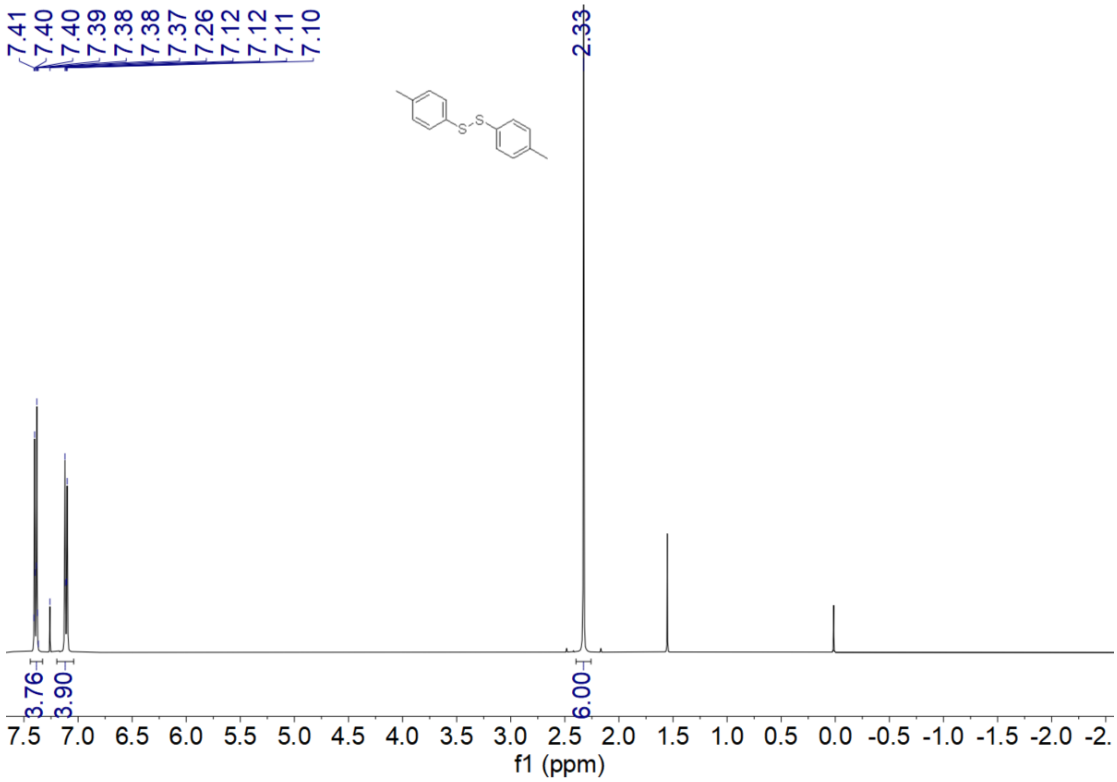
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2c**



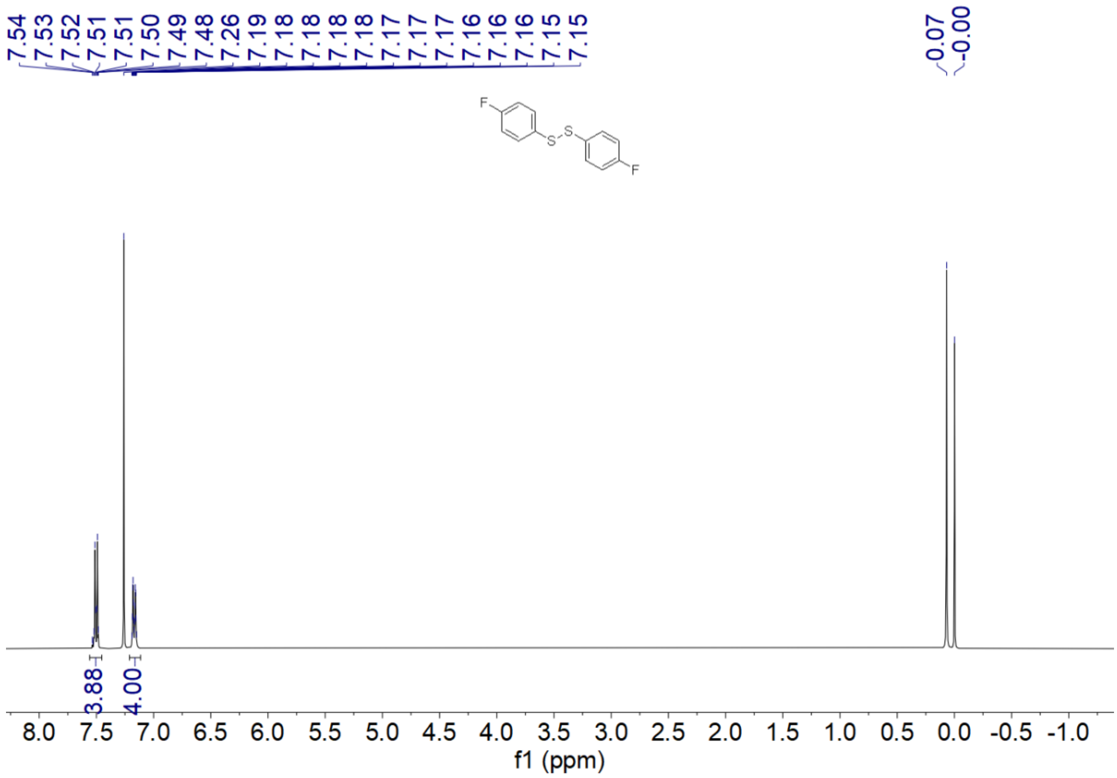
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2d**



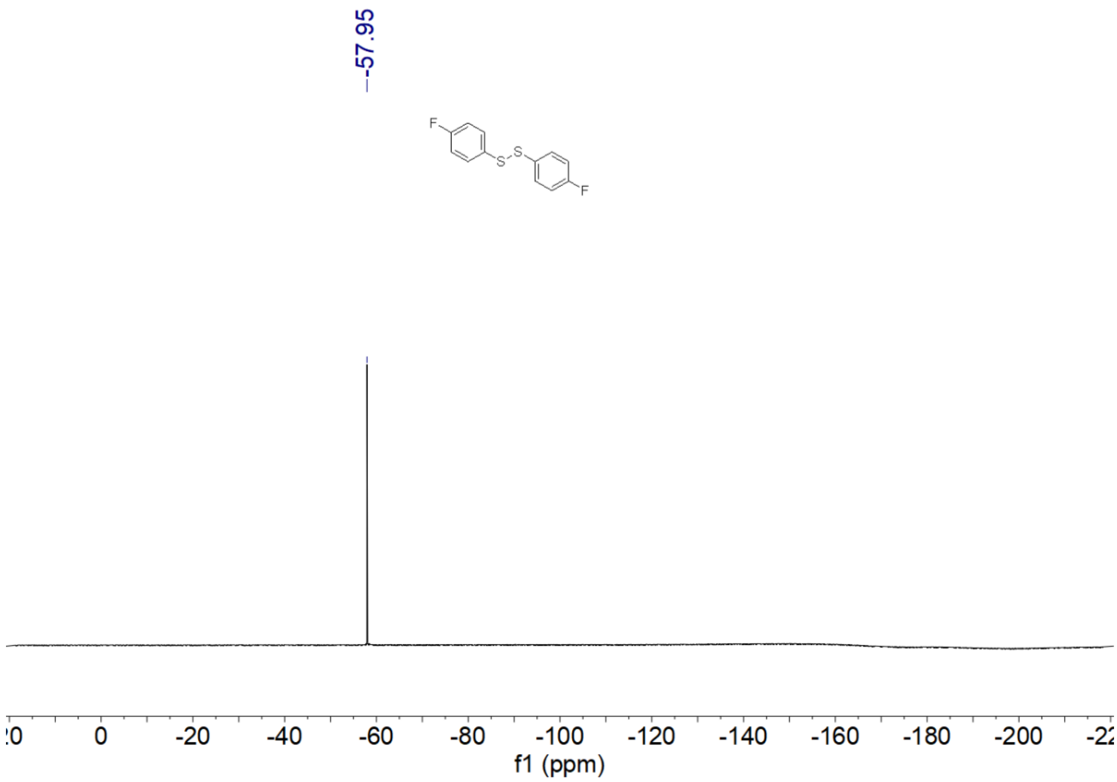
^{1}**H NMR** (400 MHz, $CDCl_3$) of compound **2e**



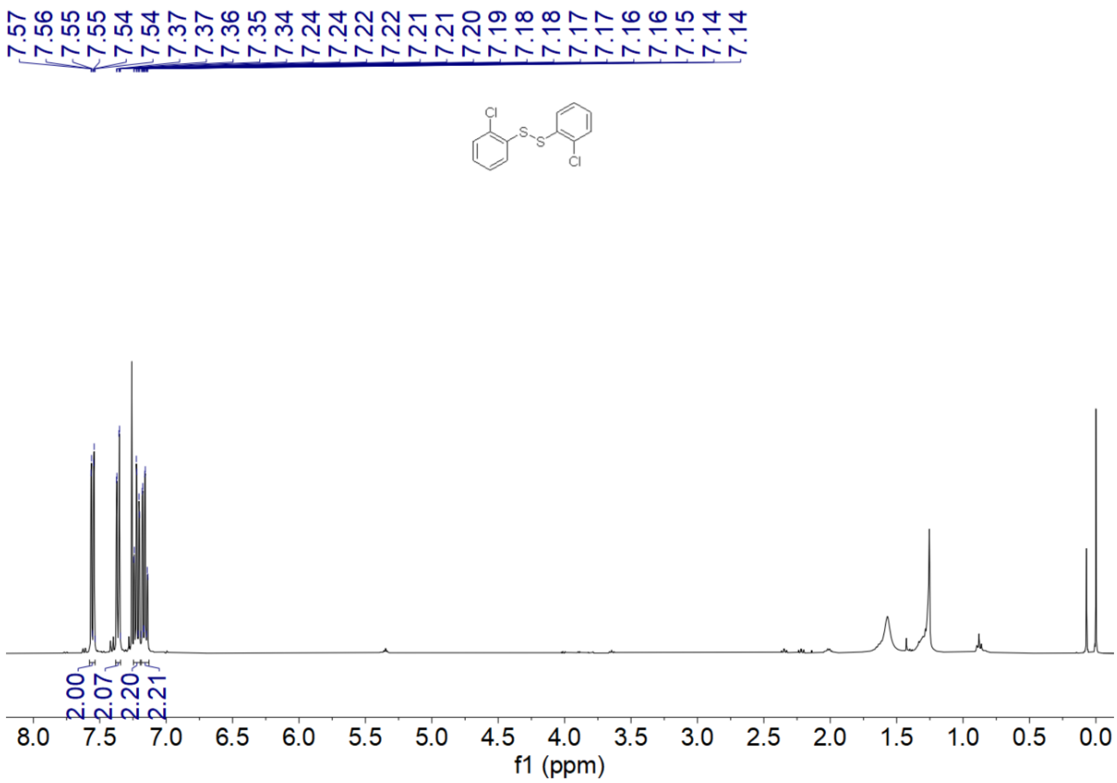
^{1}**H NMR** (400 MHz, $CDCl_3$) of compound **2f**



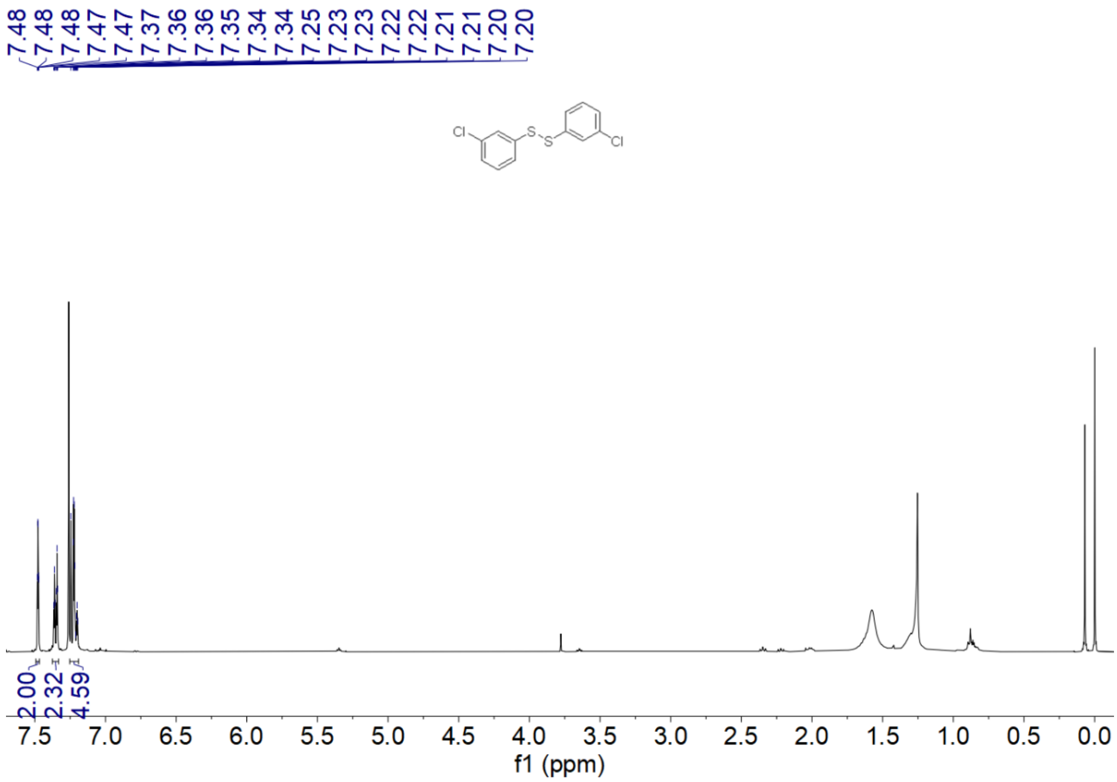
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2g**



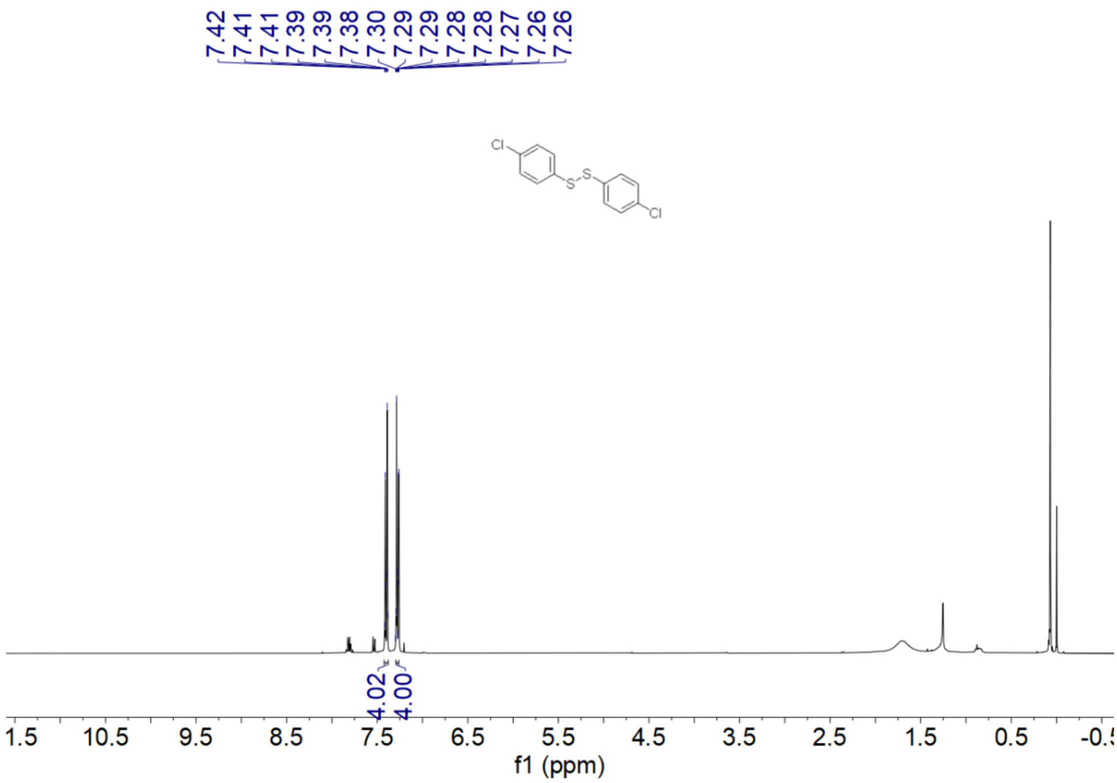
^{19}F NMR (400 MHz, $CDCl_3$) of compound **2g**



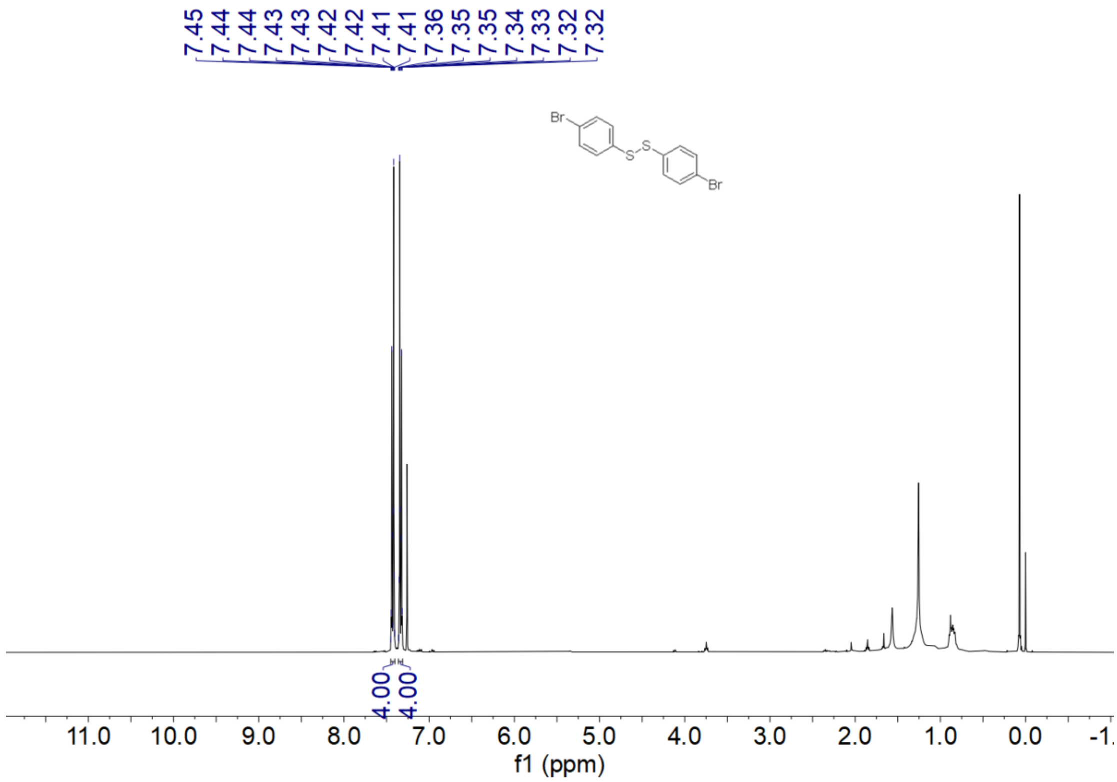
^{1}**H NMR** (400 MHz, $CDCl_3$) of compound **2h**



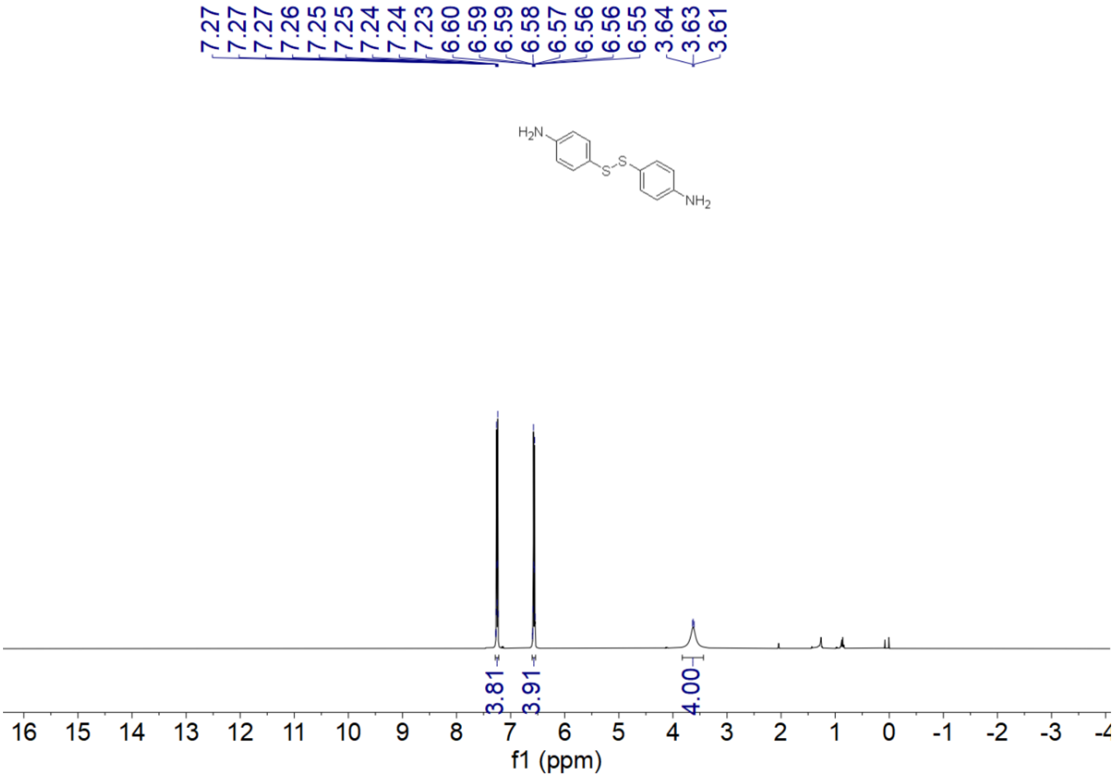
^{1}**H NMR** (400 MHz, $CDCl_3$) of compound **2i**



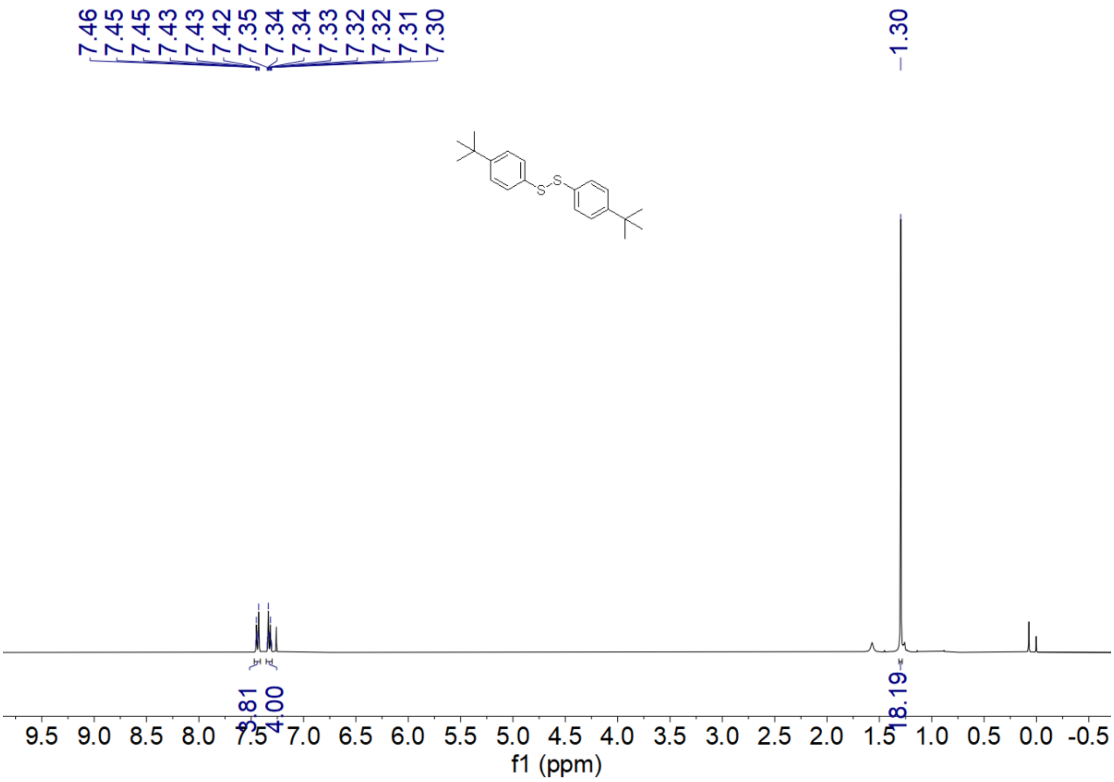
¹H NMR (400 MHz, $CDCl_3$) of compound **2j**



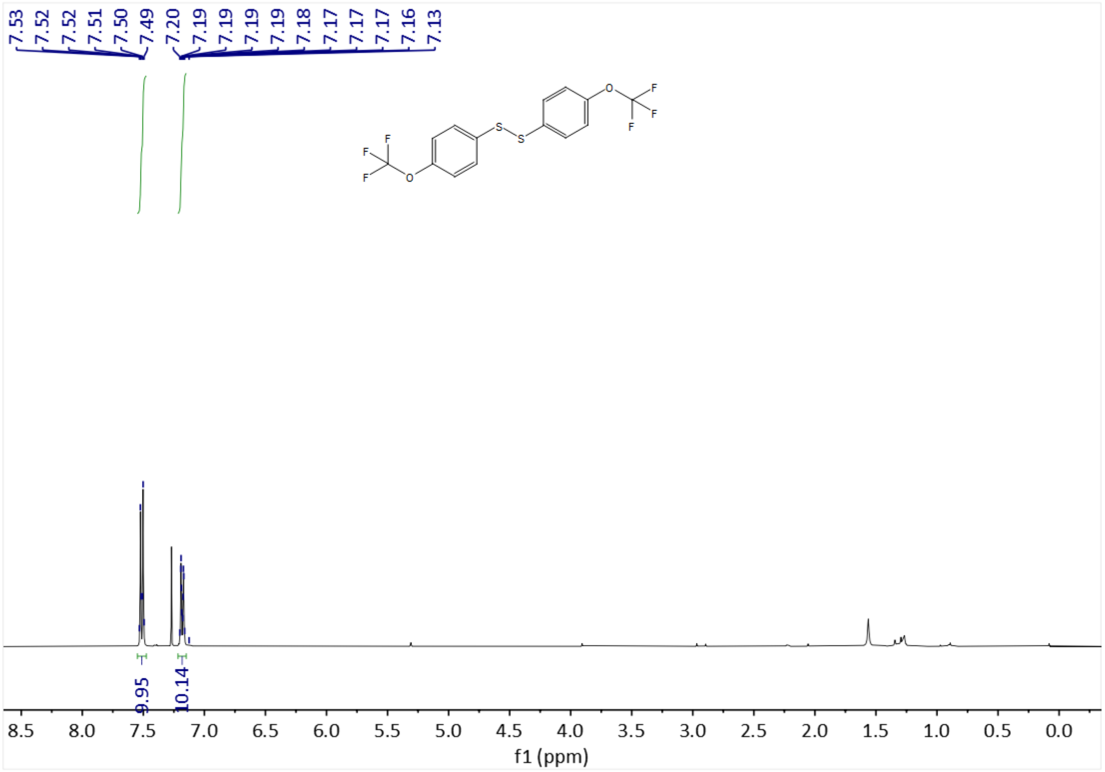
¹H NMR (400 MHz, $CDCl_3$) of compound **2k**



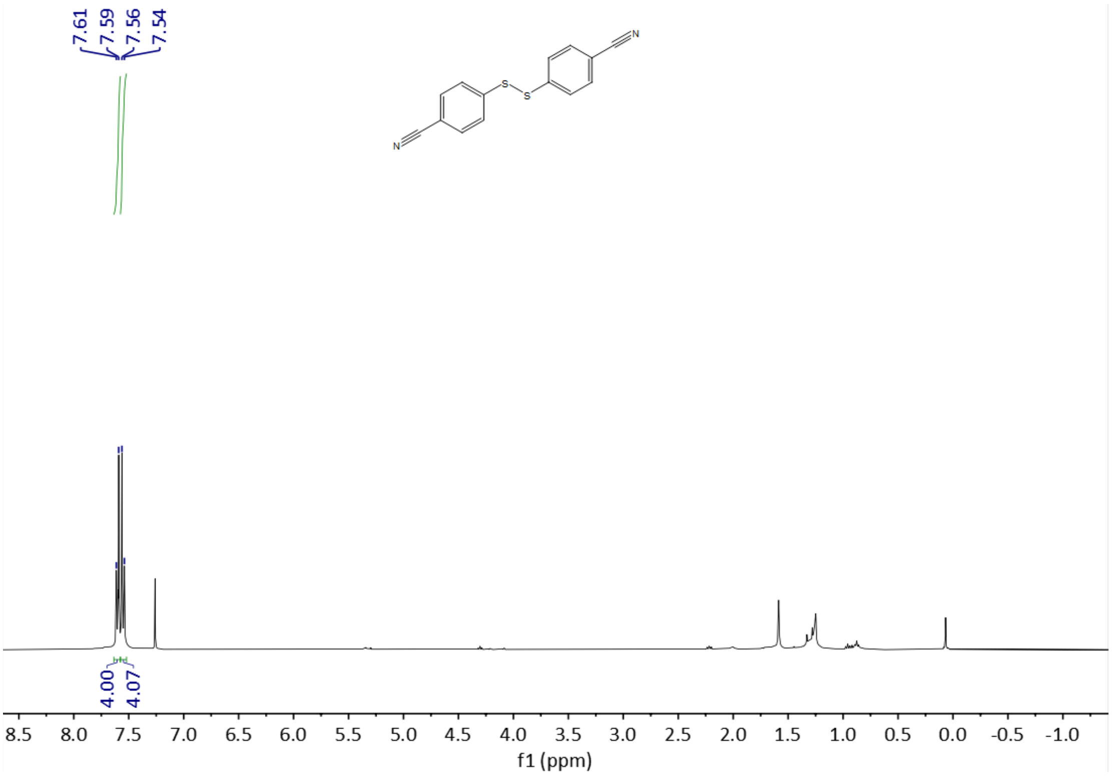
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2l**



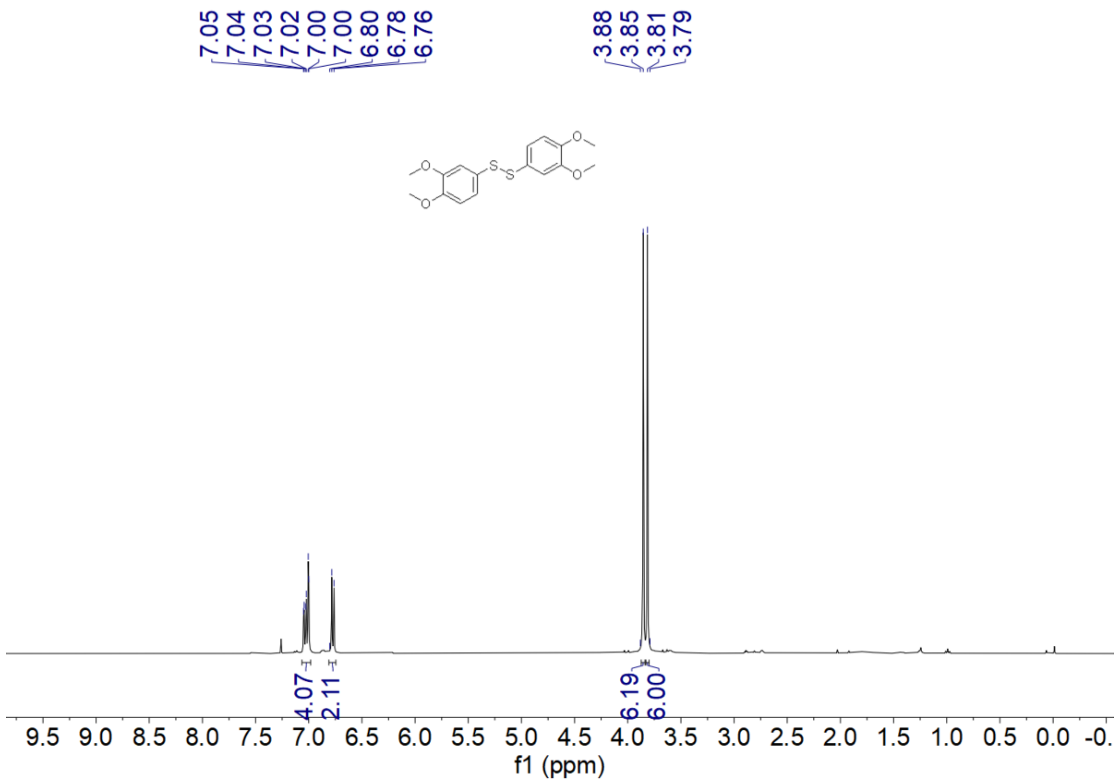
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2m**



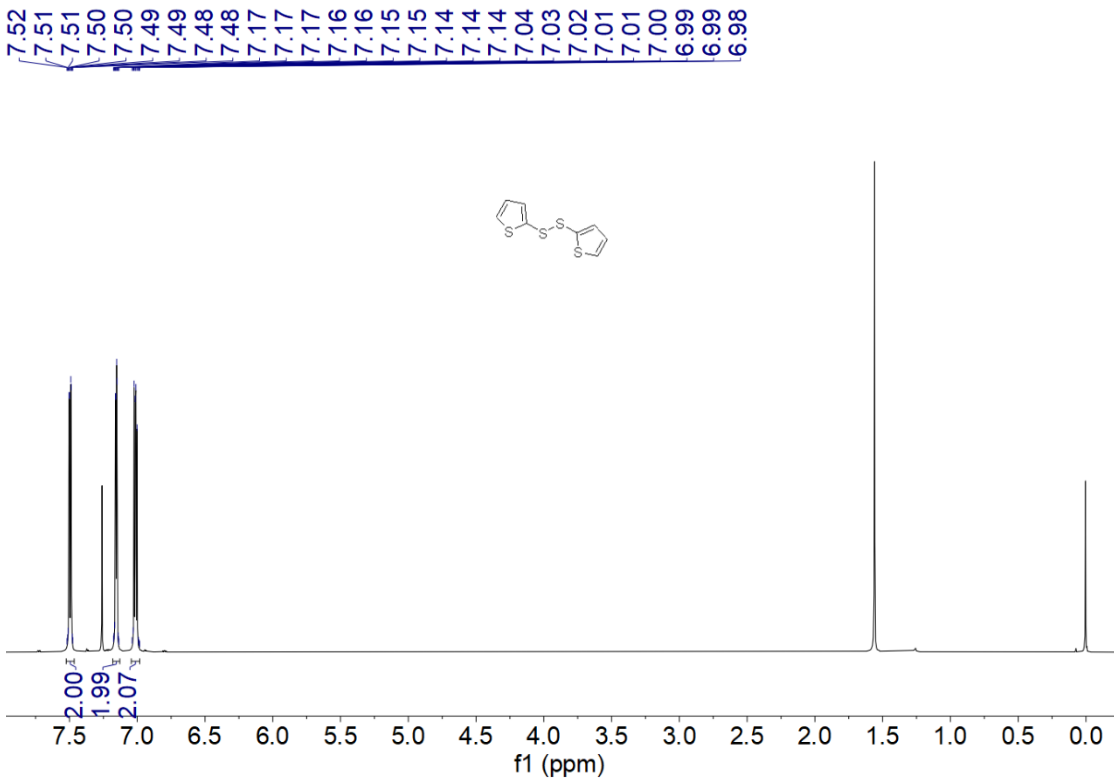
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2n**



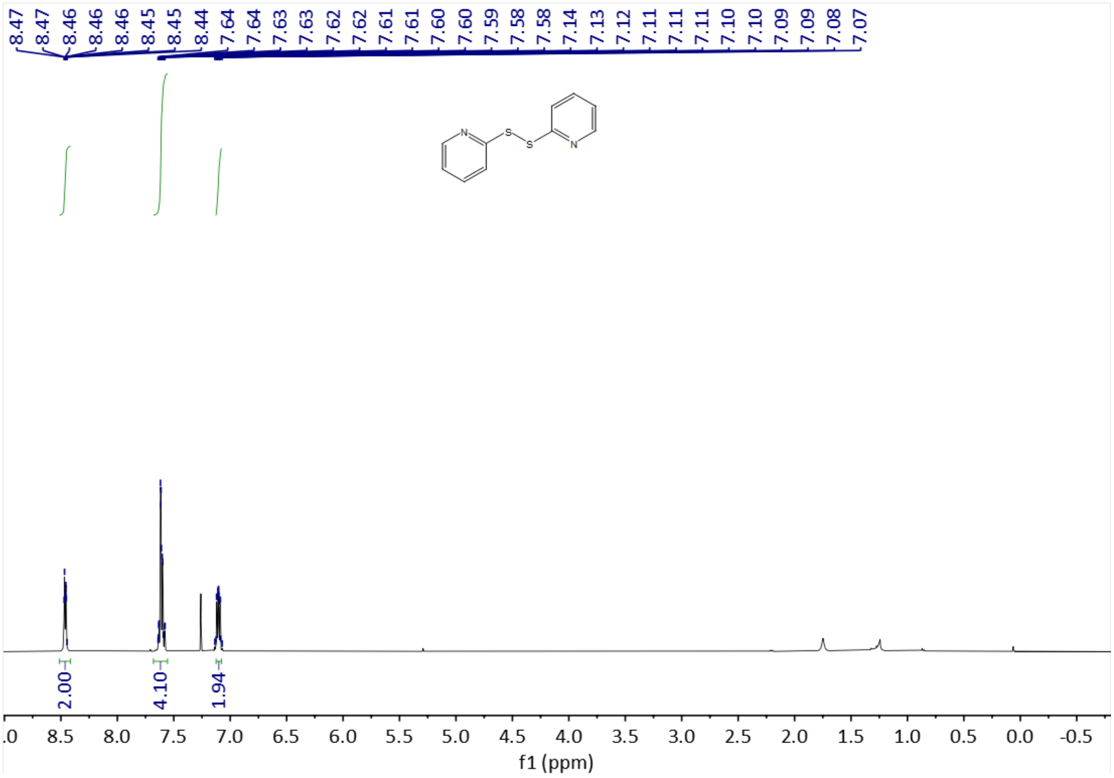
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2o**



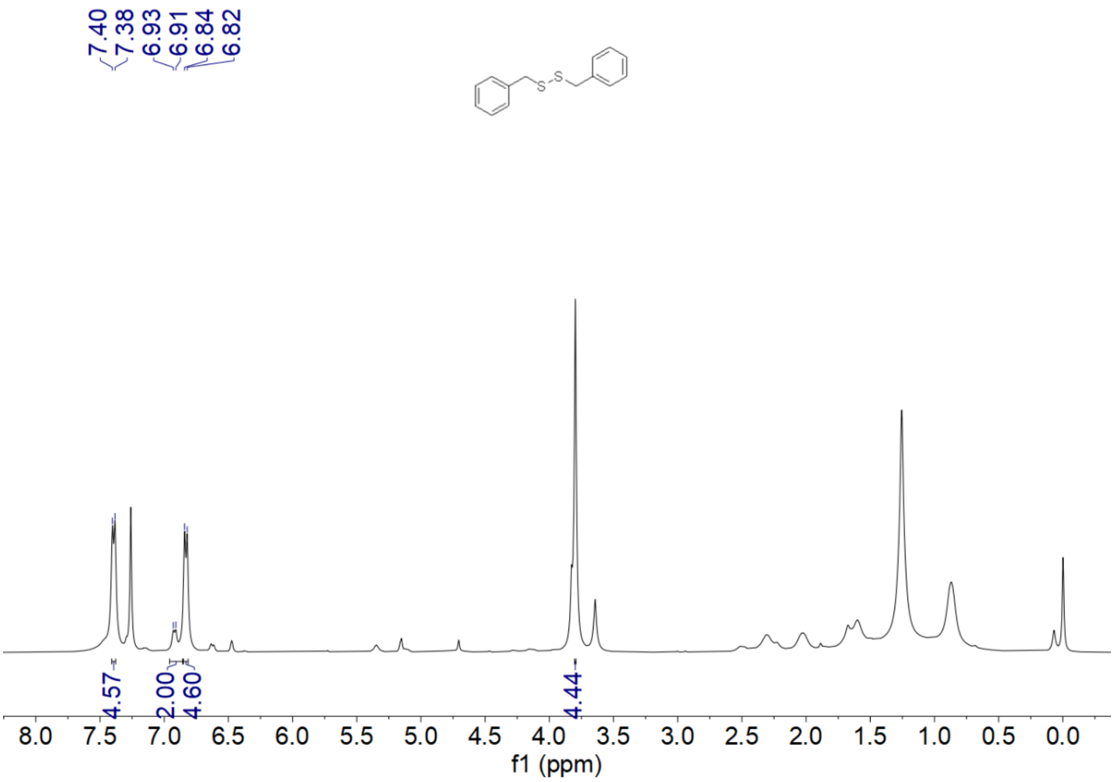
[1]**H NMR** (400 MHz, $CDCl_3$) of compound **2p**



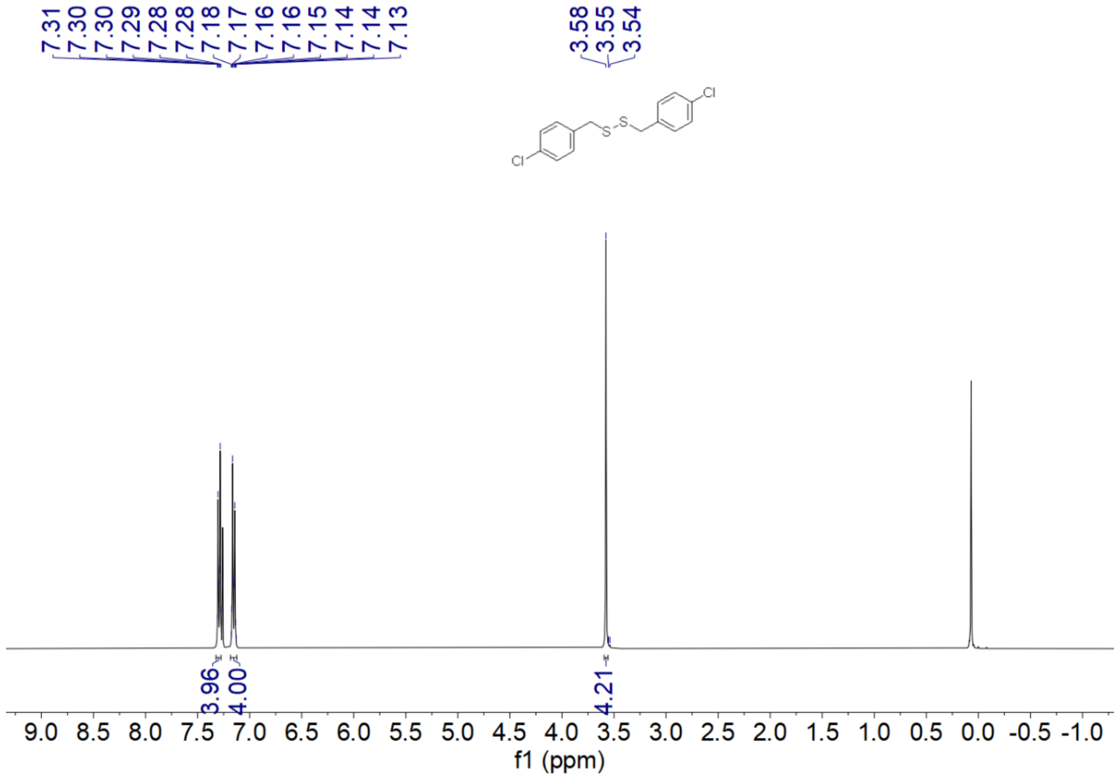
[1]**H NMR** (400 MHz, $CDCl_3$) of compound **2q**



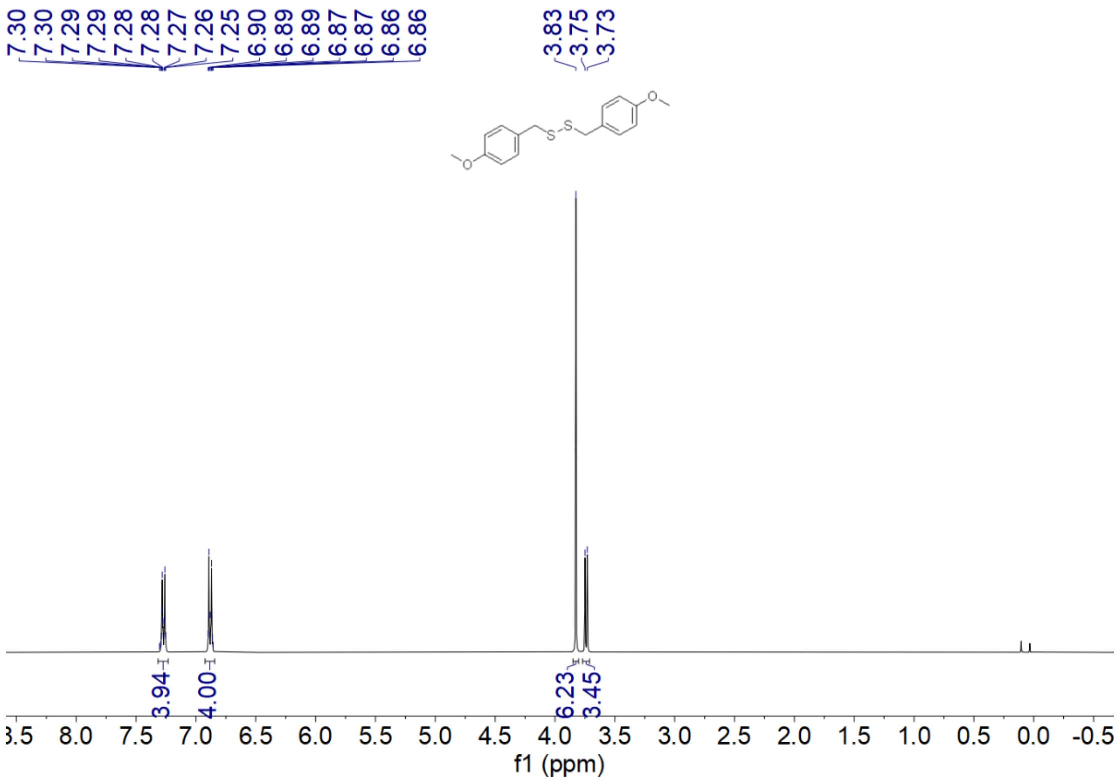
^{1}**H NMR** (400 MHz, $CDCl_3$) of compound **2r**



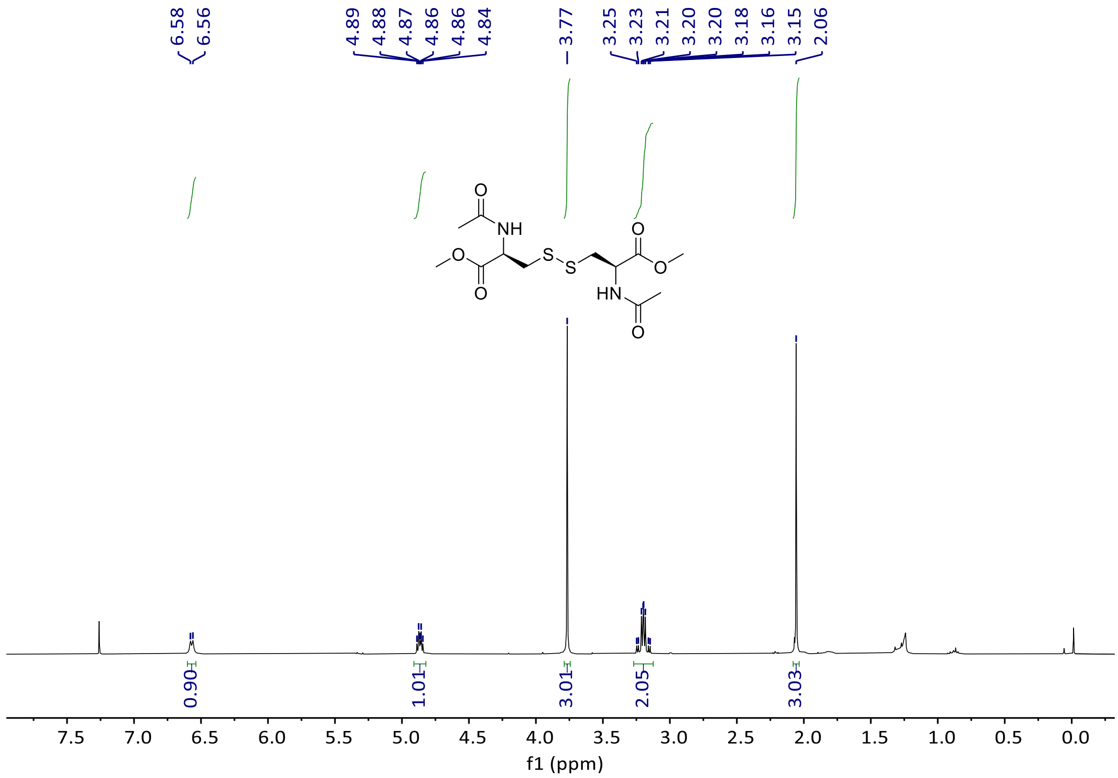
^{1}**H NMR** (400 MHz, $CDCl_3$) of compound **2s**



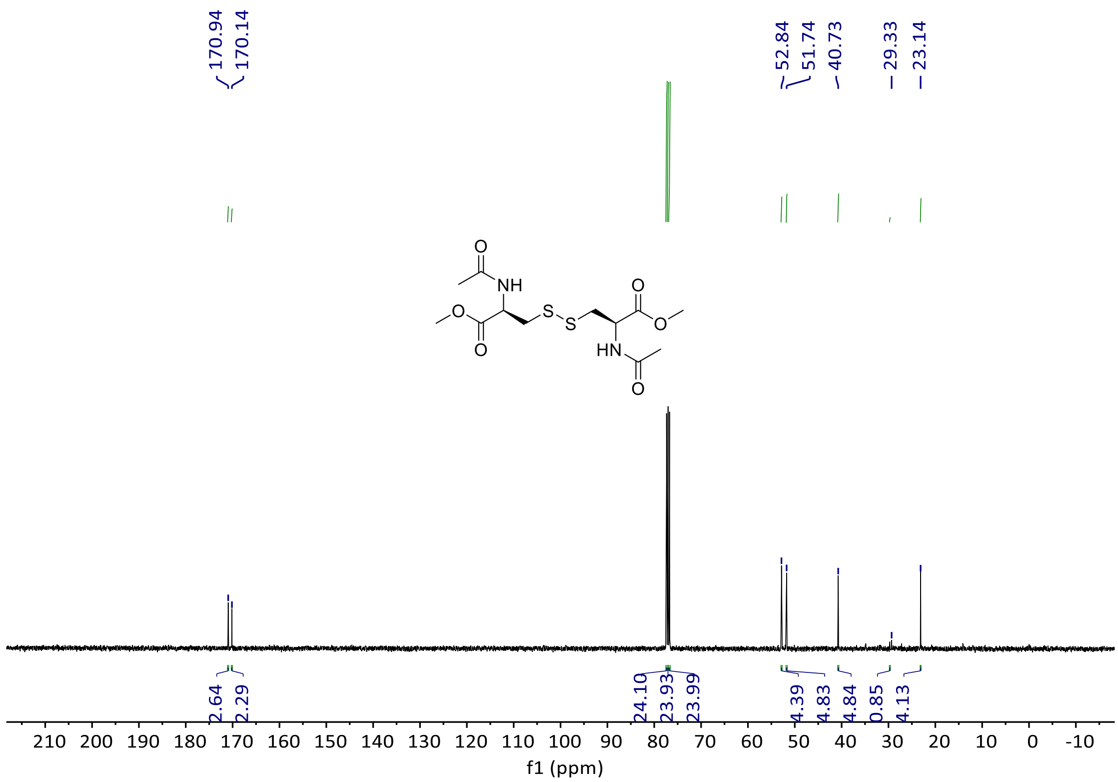
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2t**



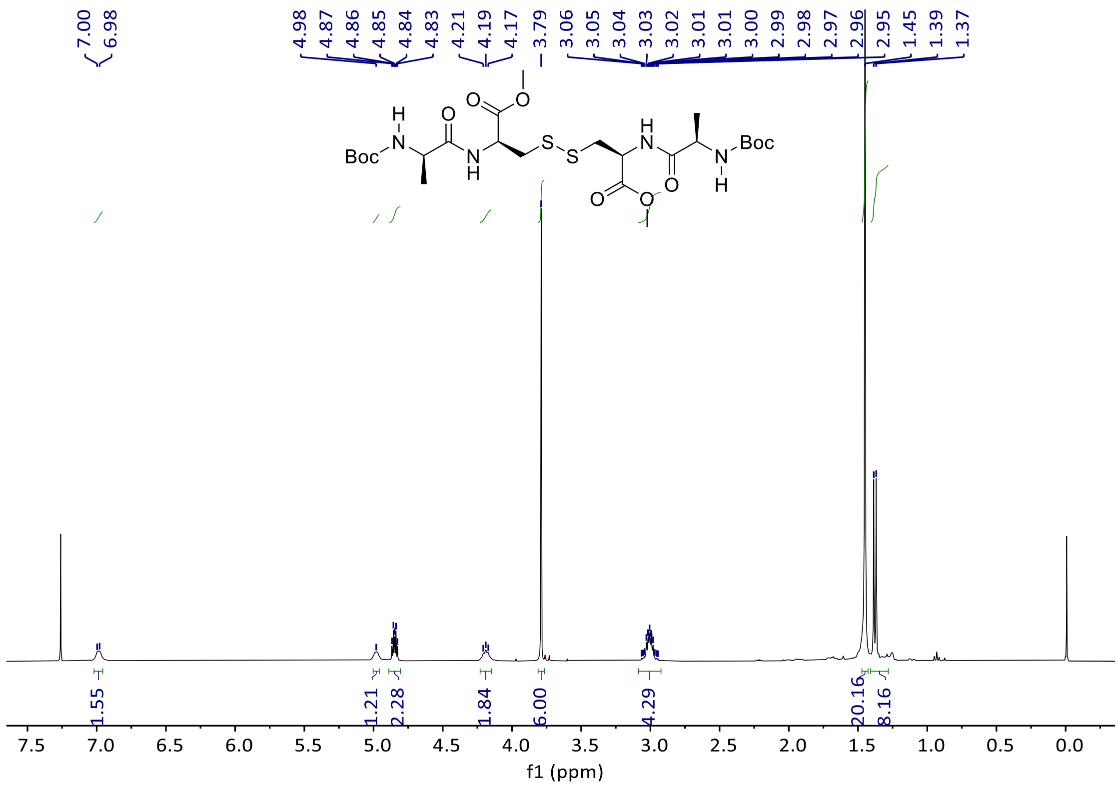
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2u**



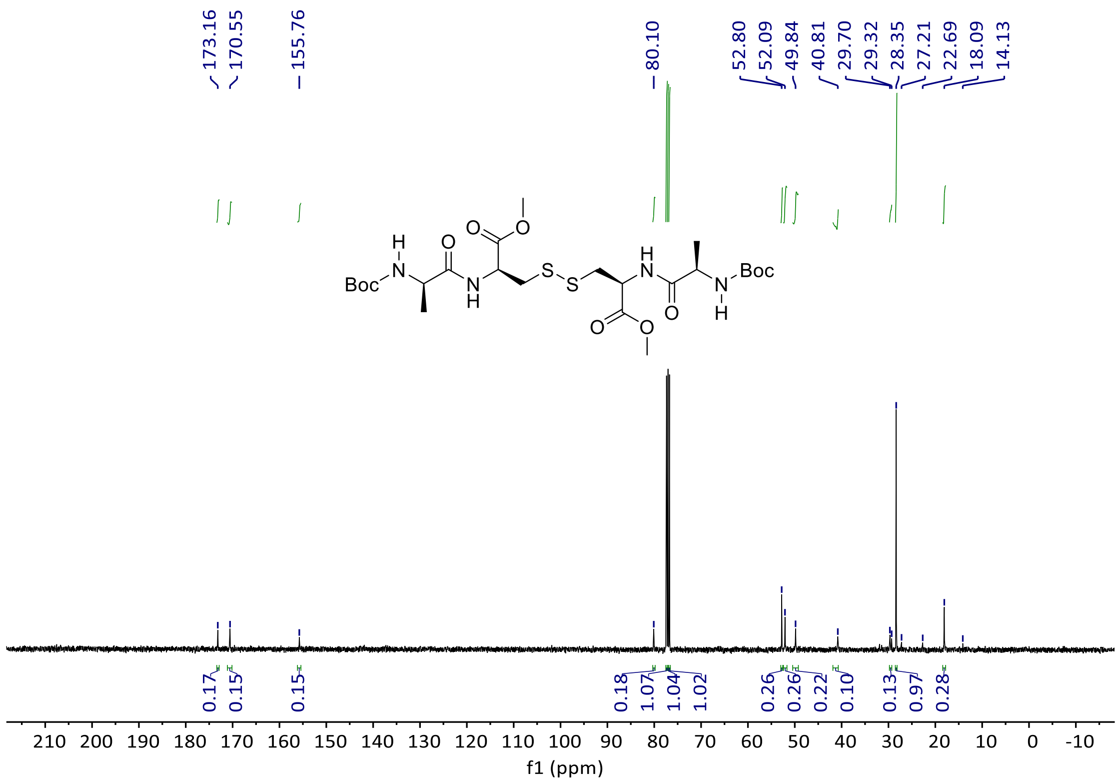
^{1}**H NMR** (400 MHz, $CDCl_3$) of compound **4a**



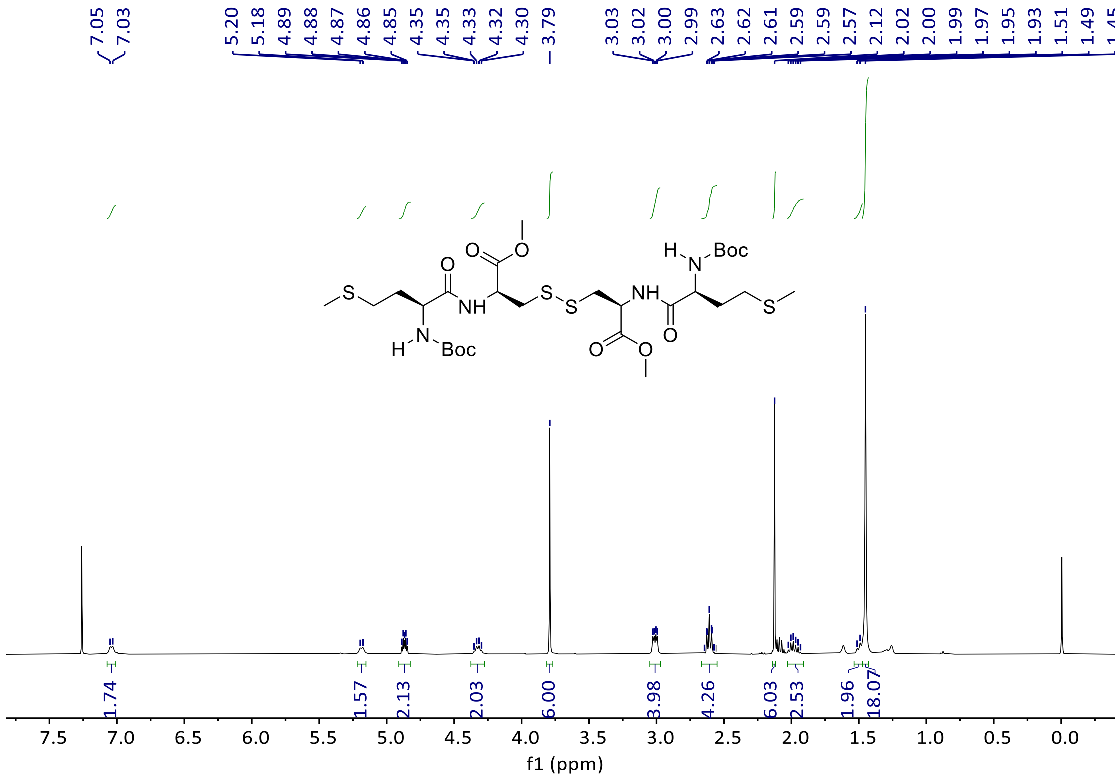
^{13}**C NMR** (101 MHz, $CDCl_3$) of compound **4a**



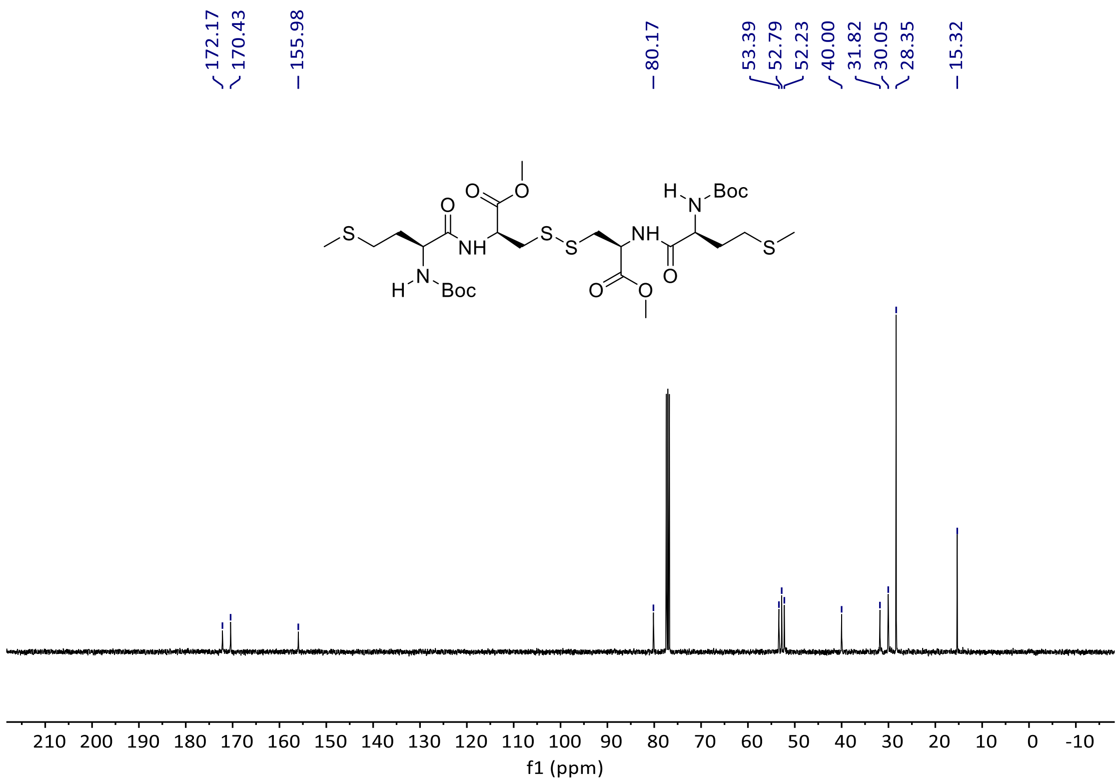
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4b**



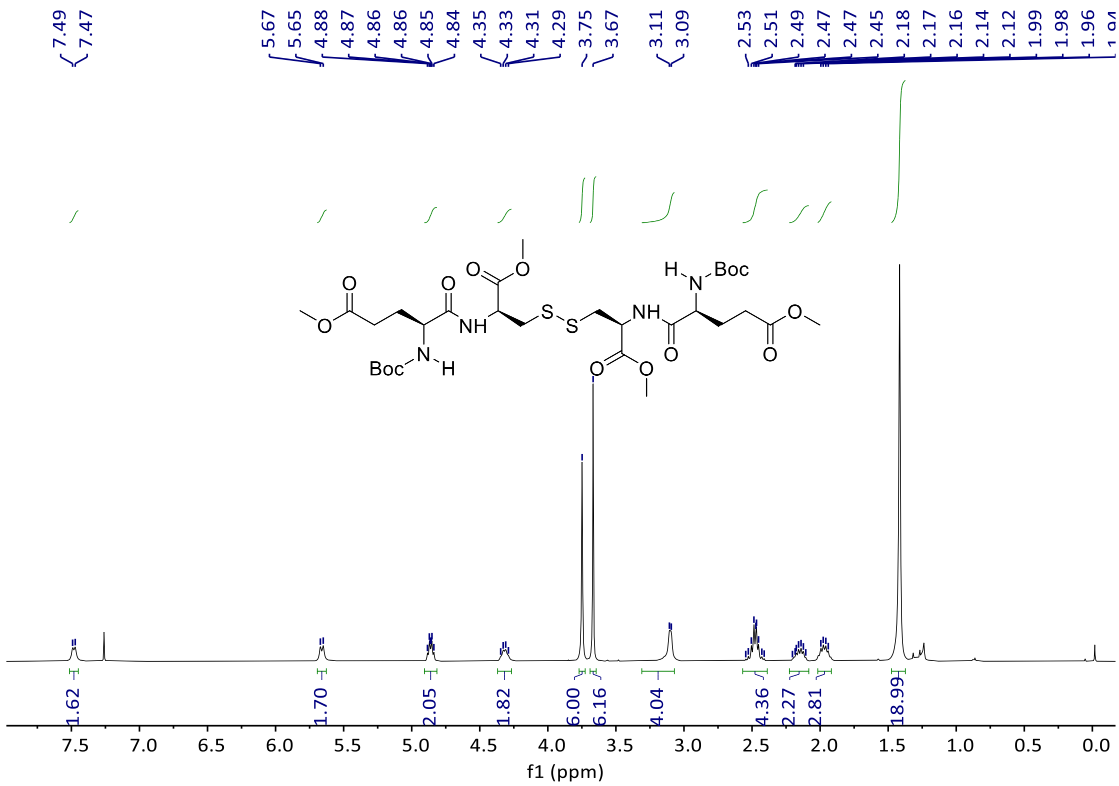
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4b**



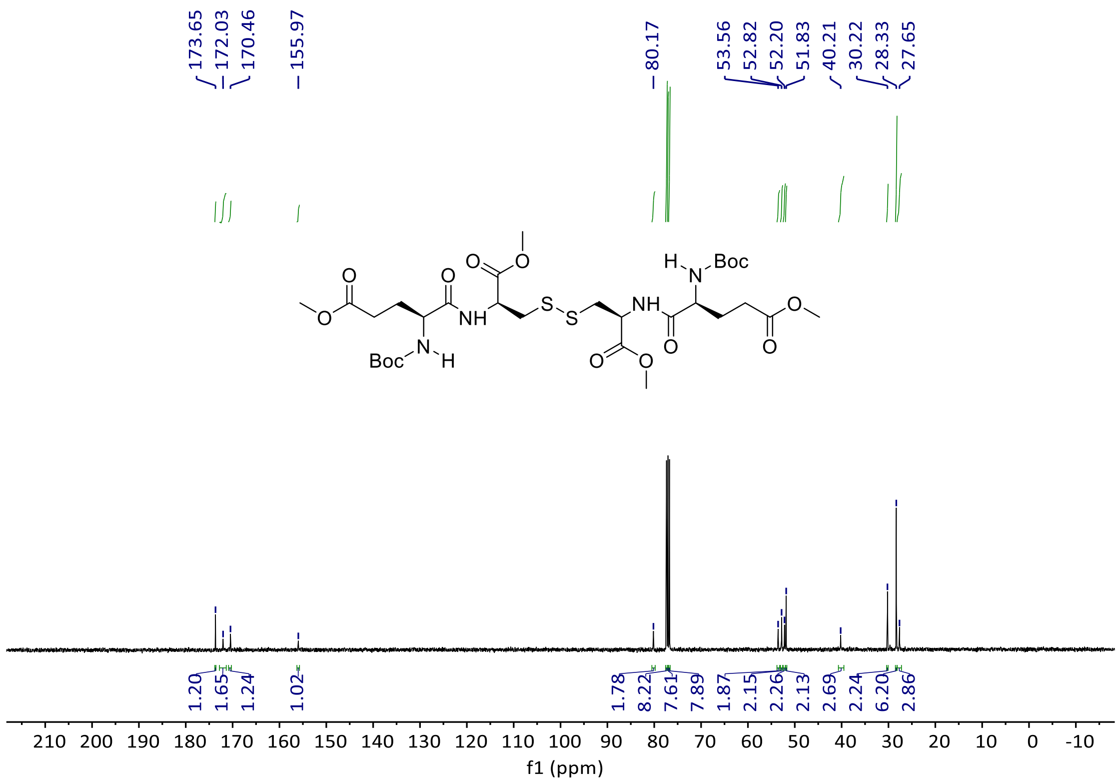
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4c**



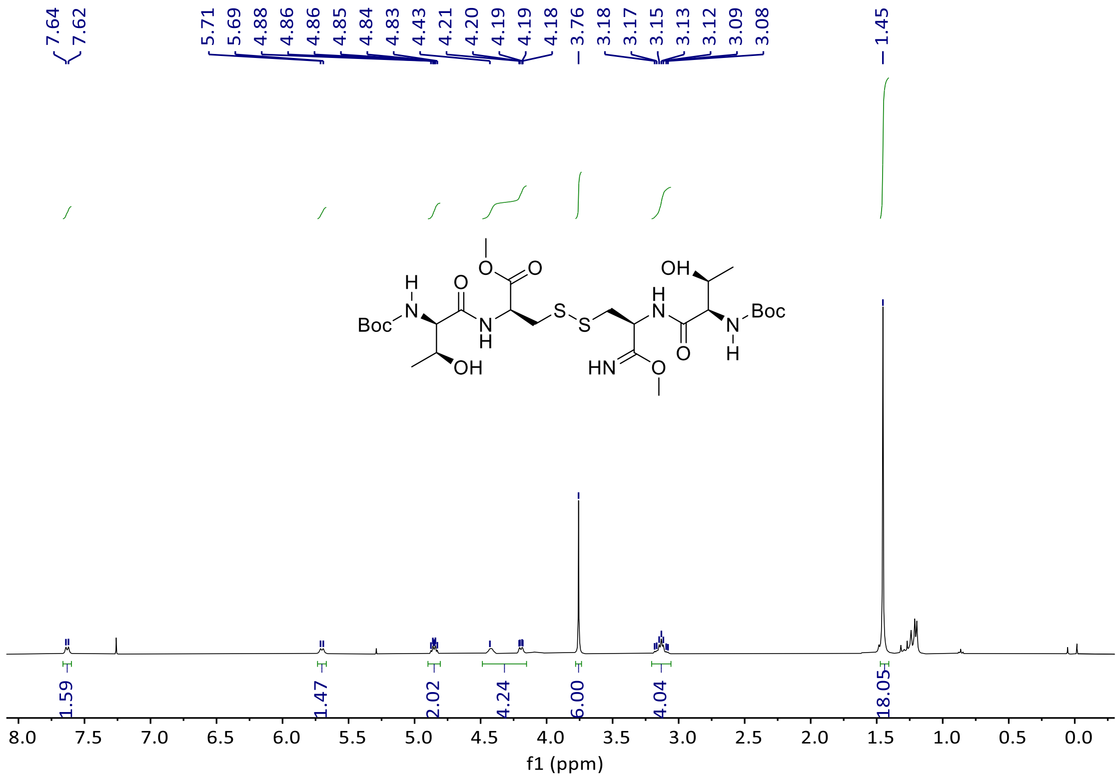
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4c**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **4d**



^{13}C NMR (101 MHz, $CDCl_3$) of compound **4d**



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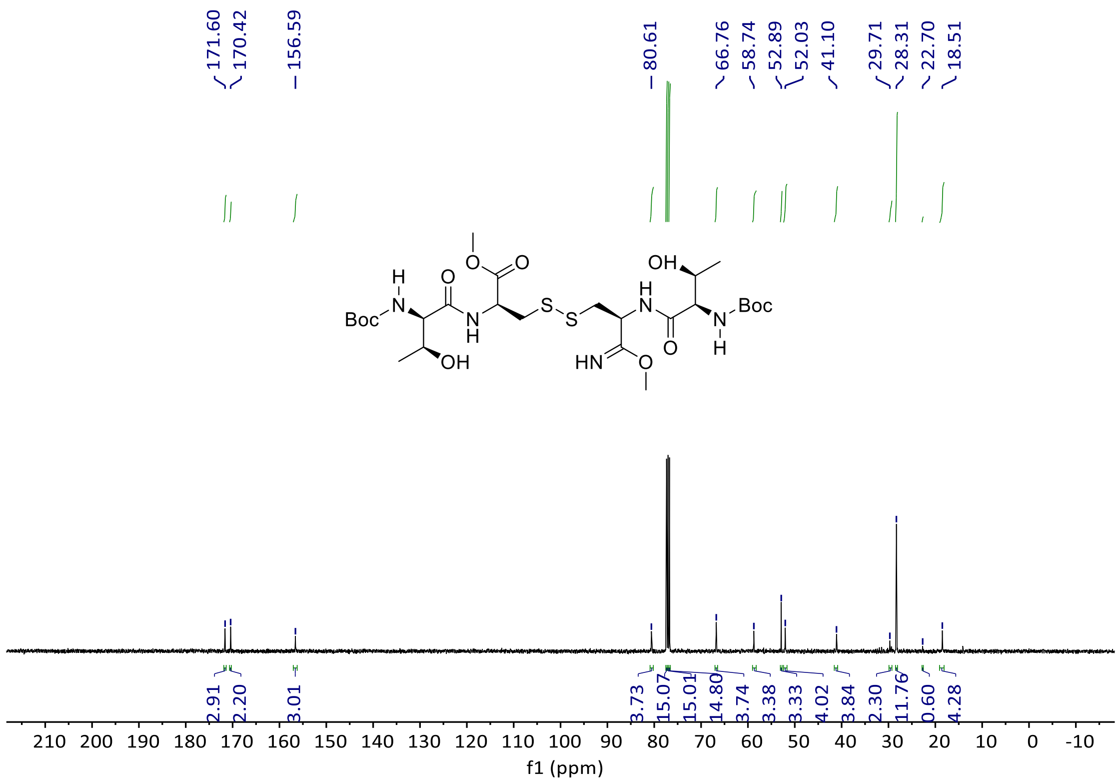

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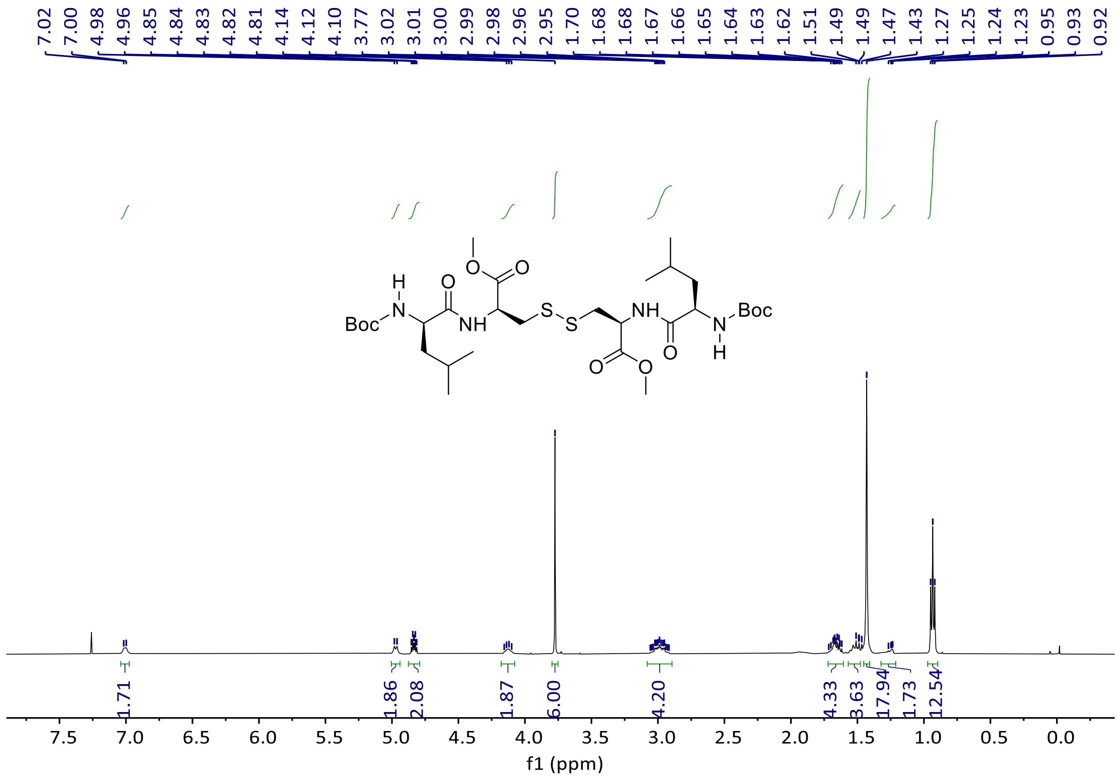
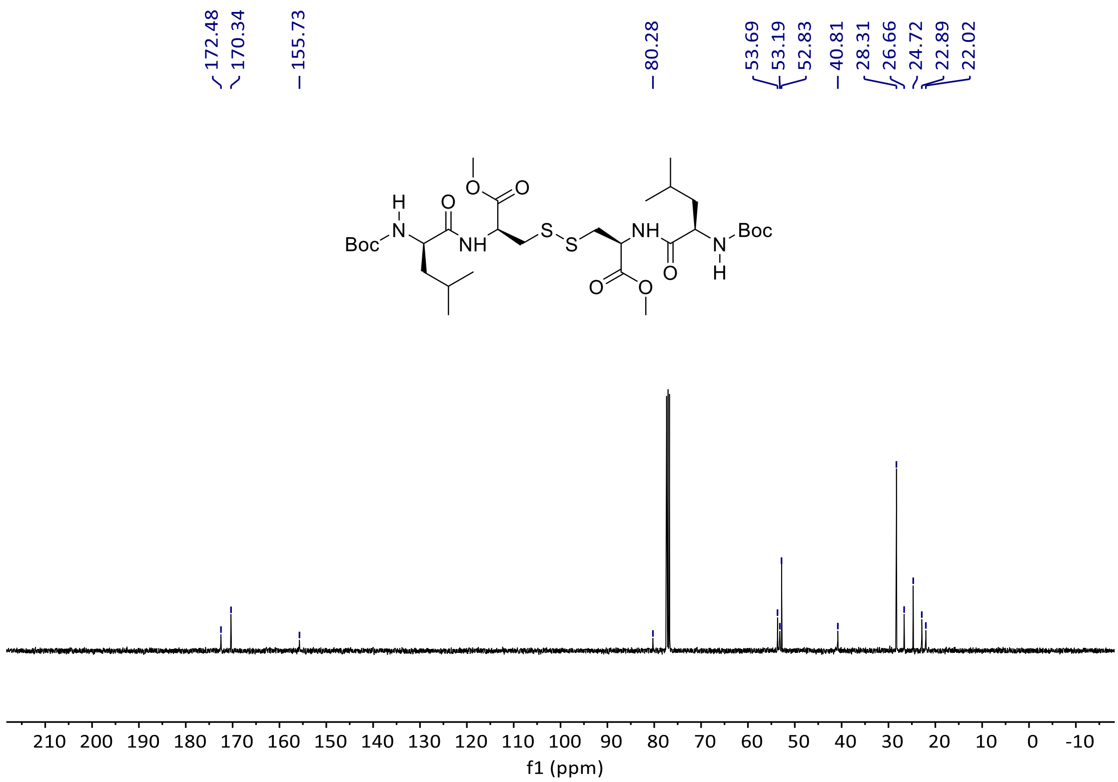
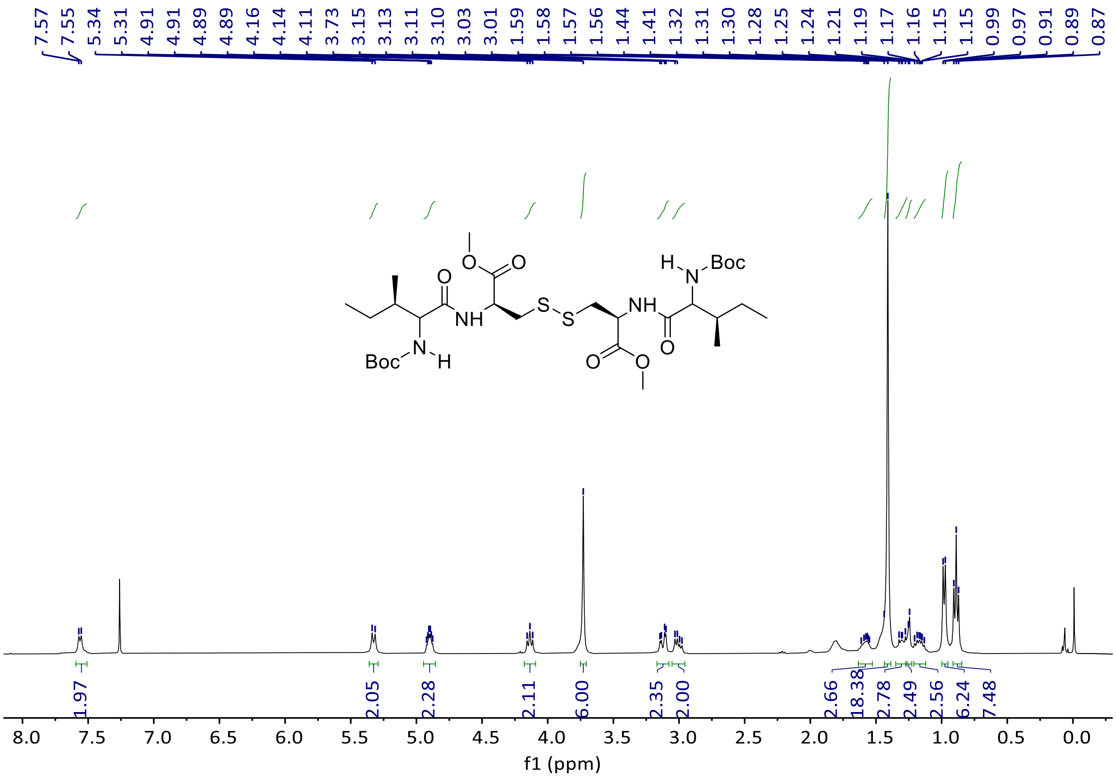


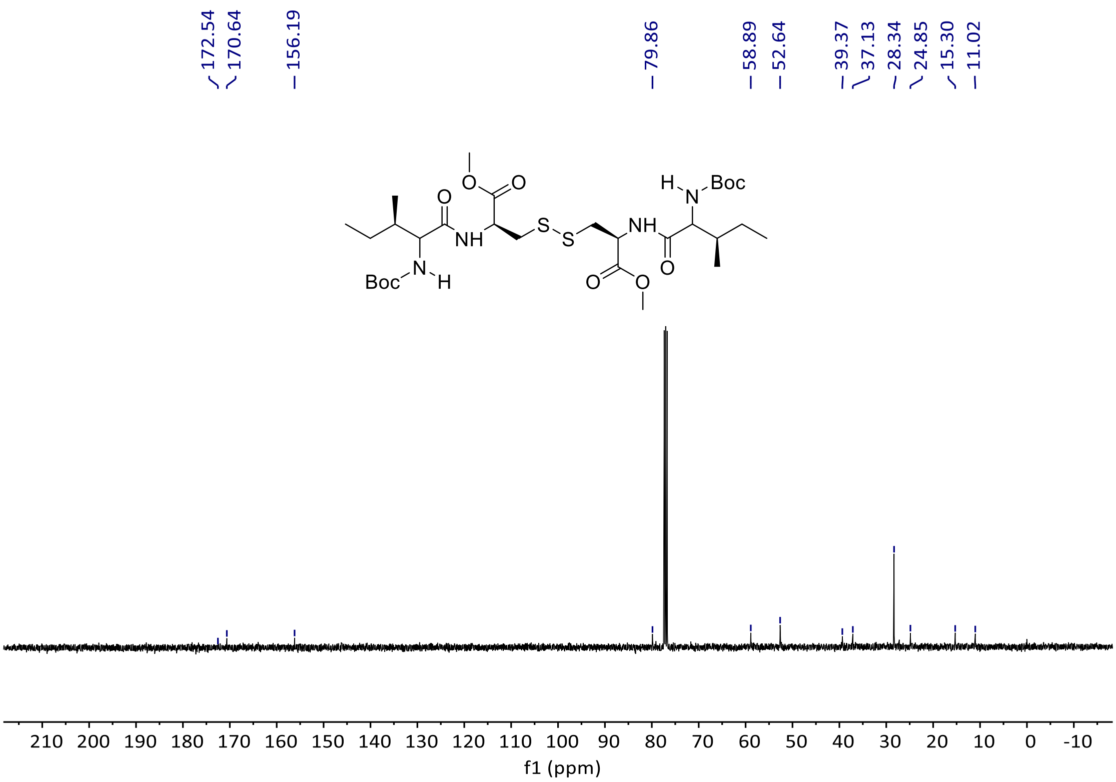
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4f**



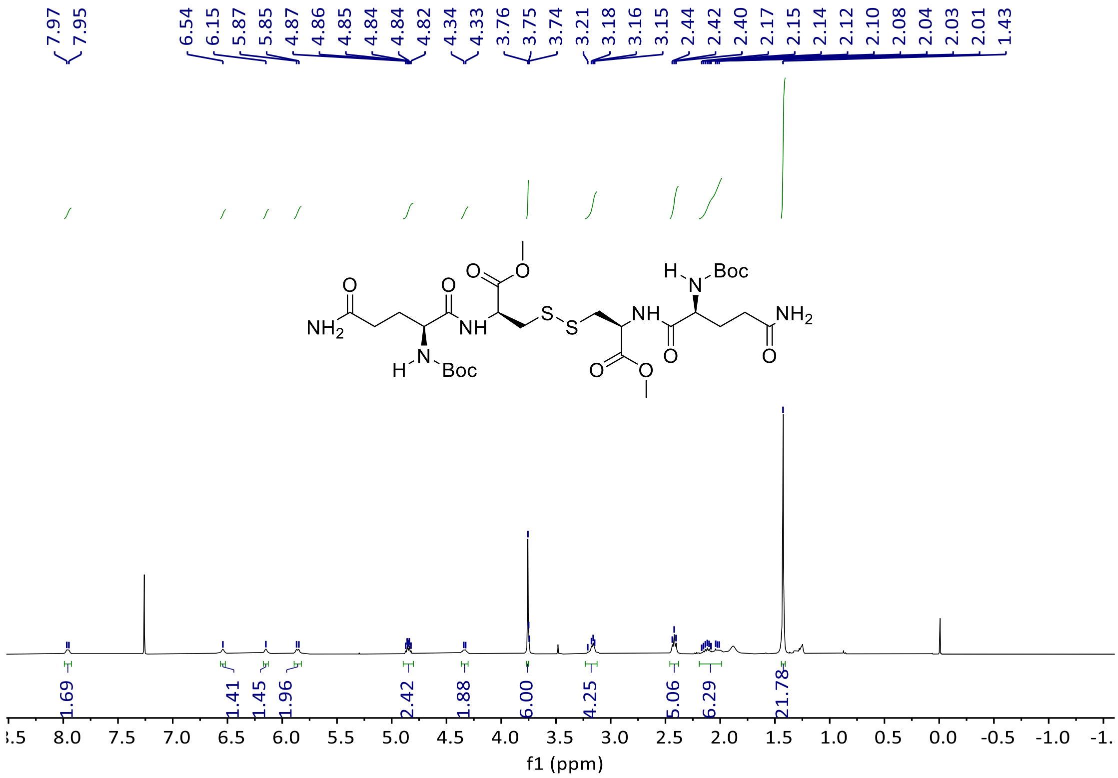
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4f**



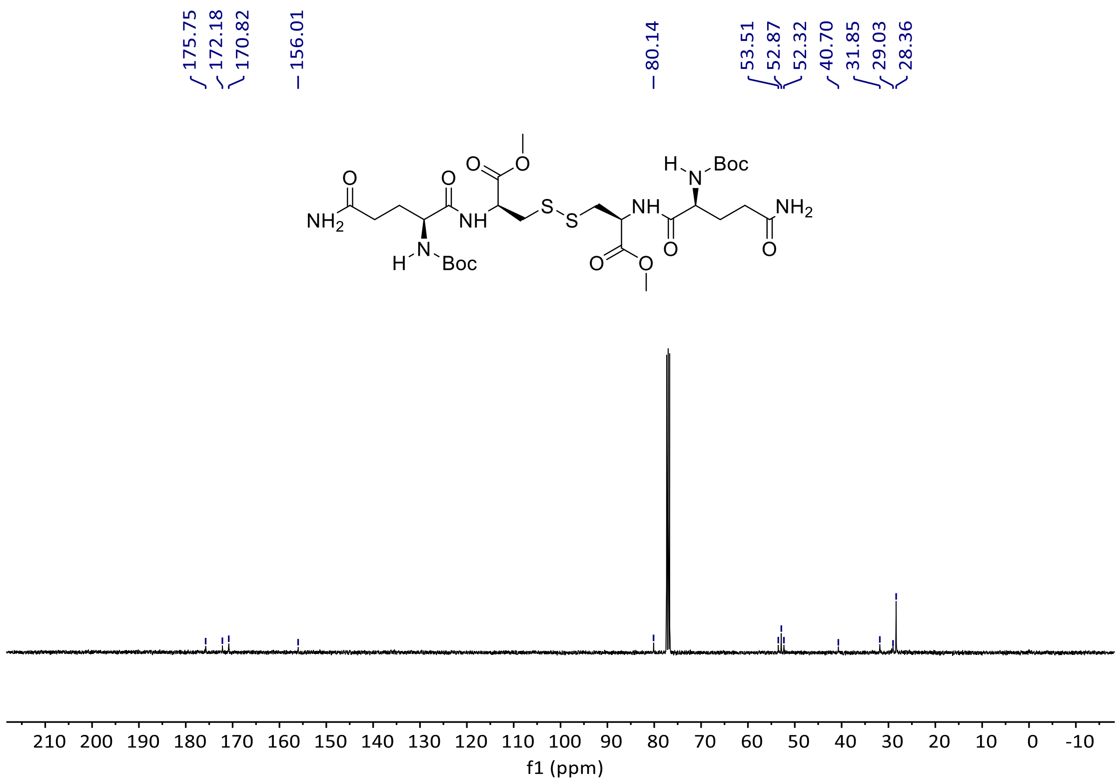
[1]H NMR (400 MHz, $CDCl_3$) of compound **4g**



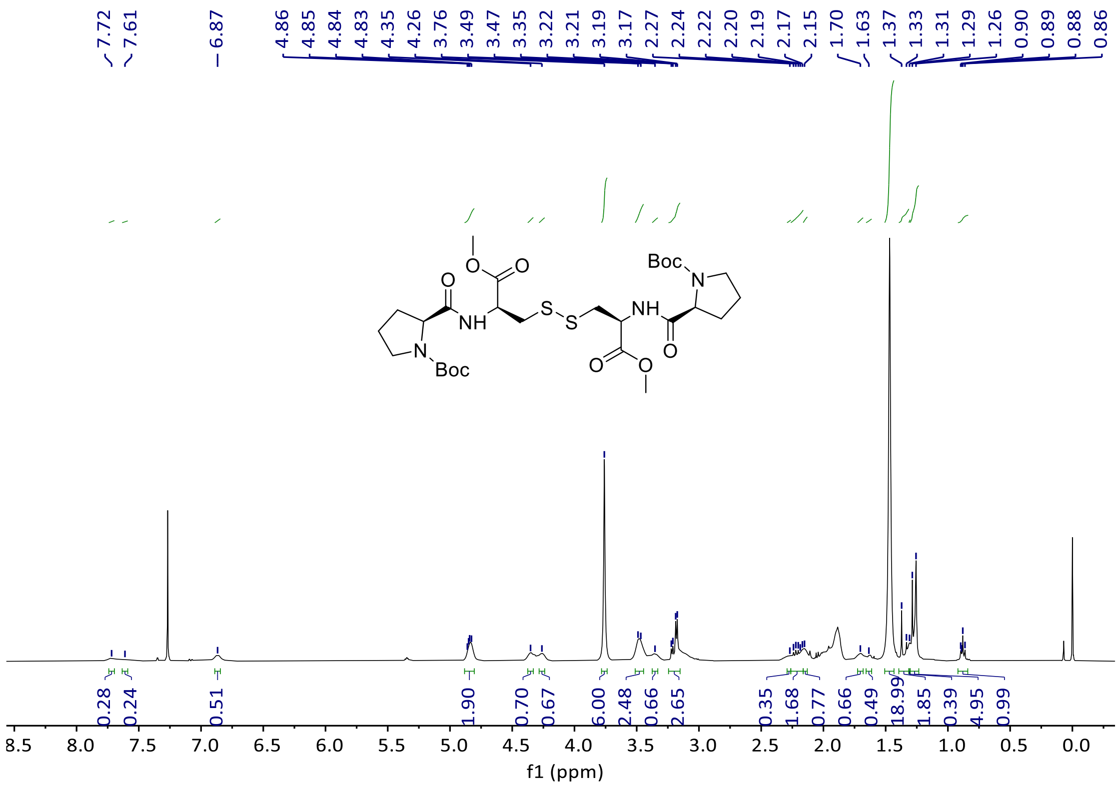
[13]C NMR (101 MHz, $CDCl_3$) of compound **4g**



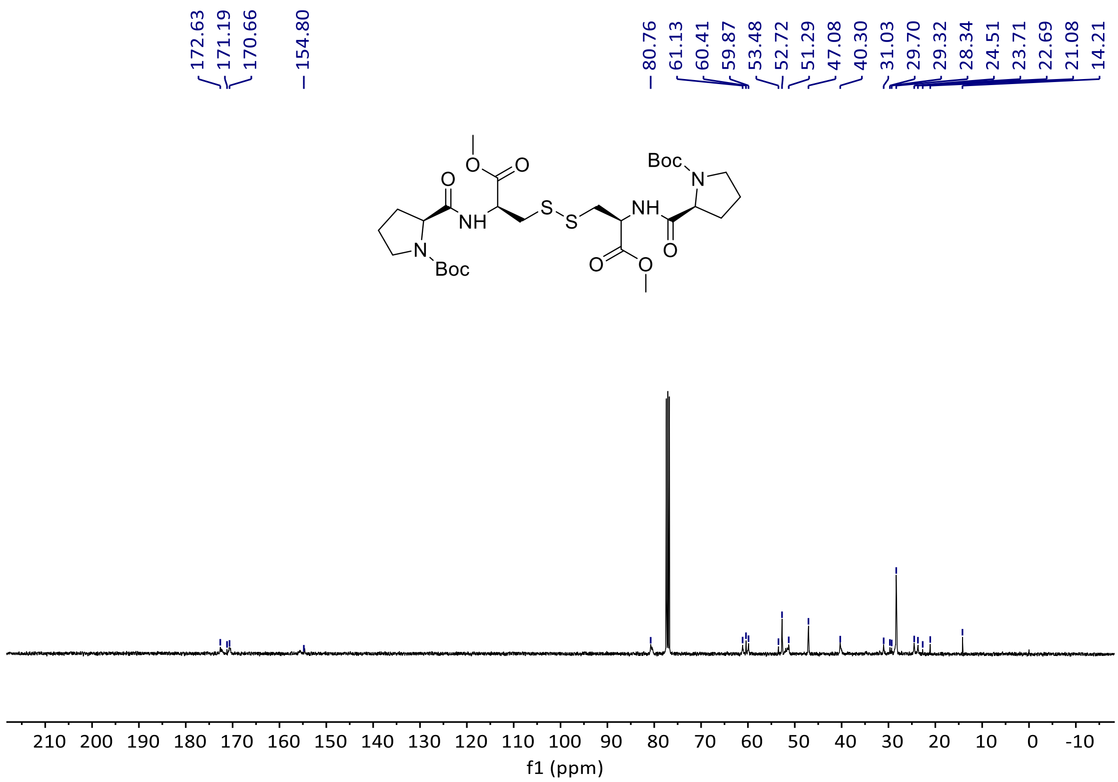
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4h**



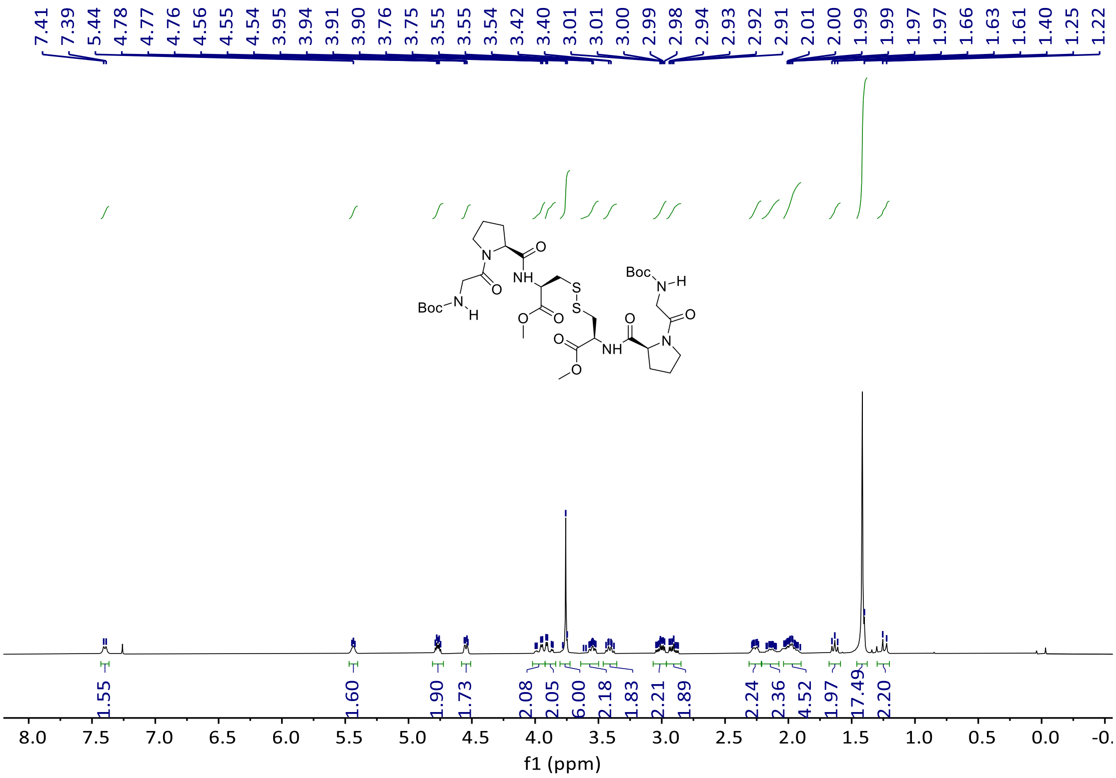
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4h**



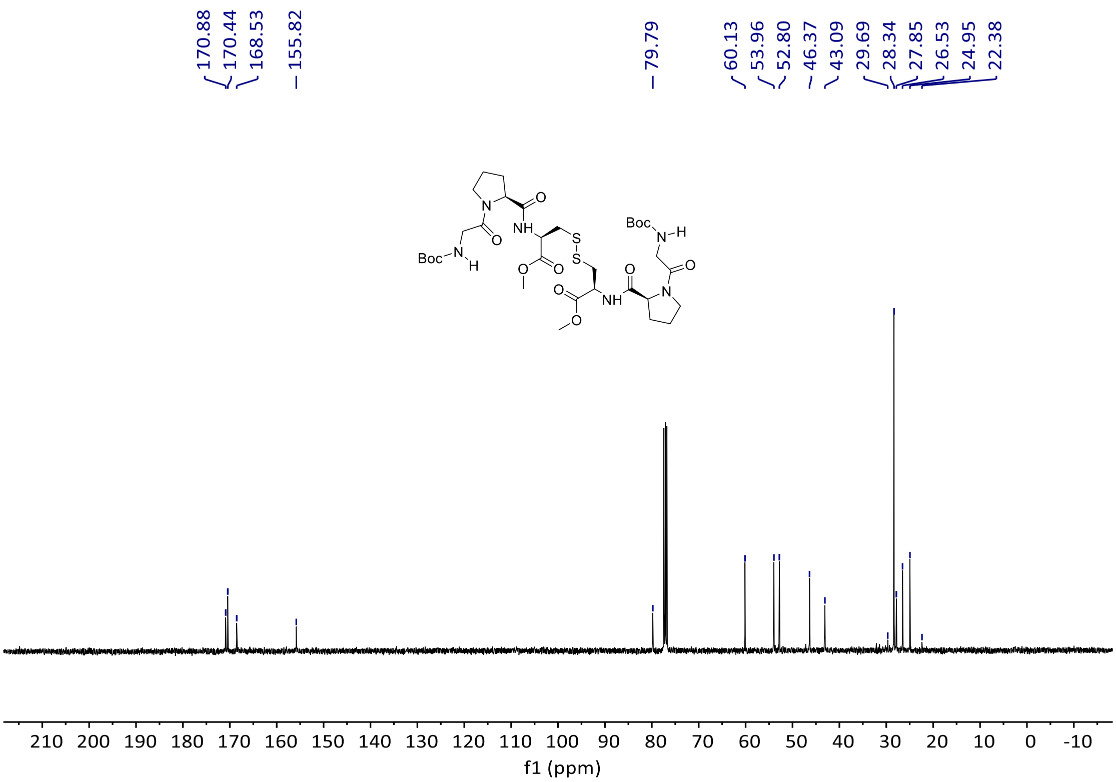
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4i**



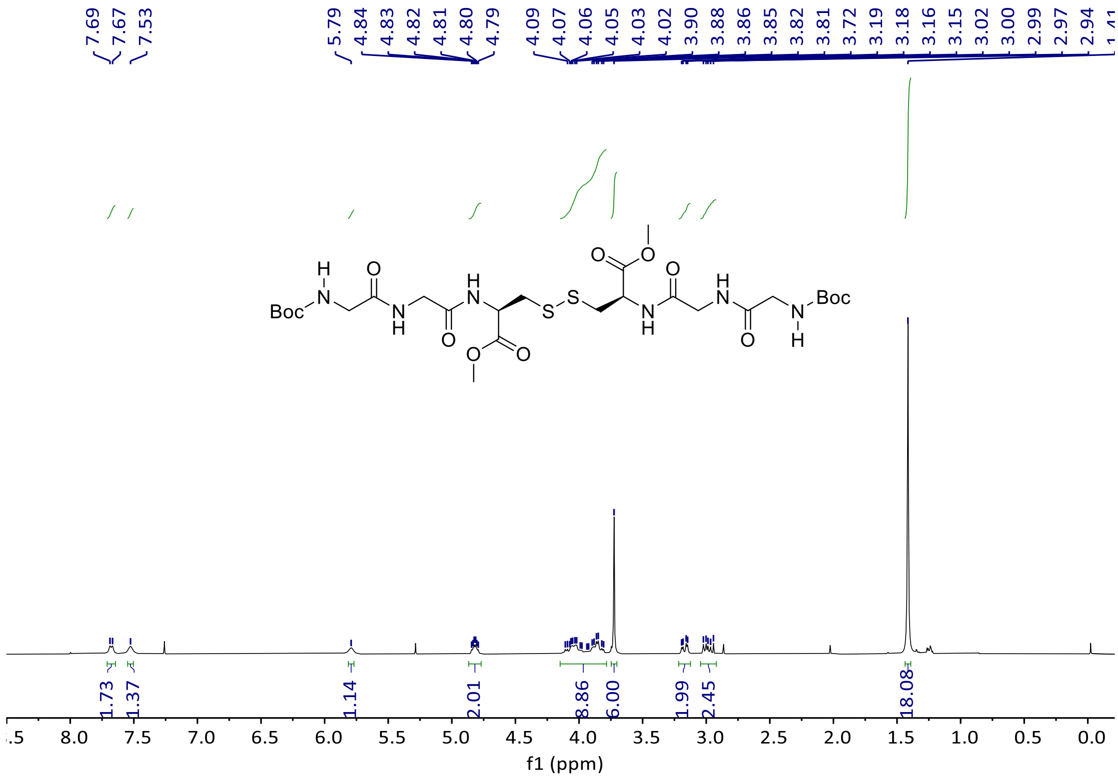
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4i**



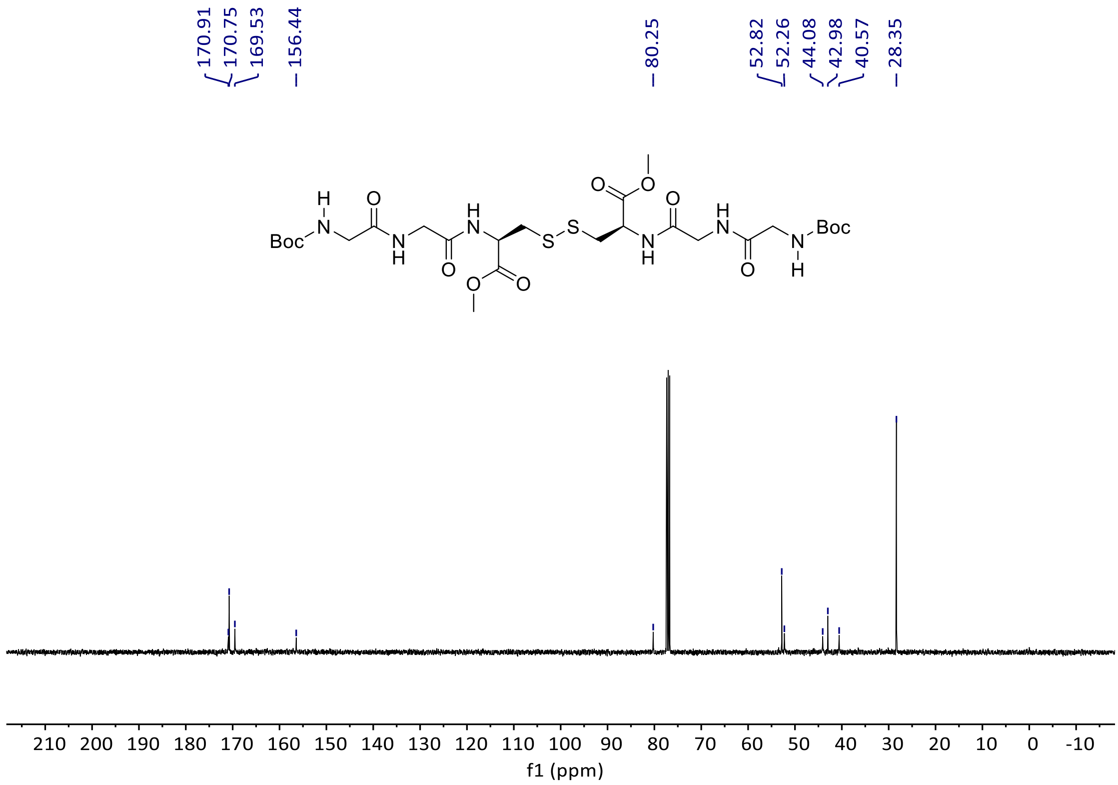
[1]H NMR (400 MHz, $CDCl_3$) of compound **4j**



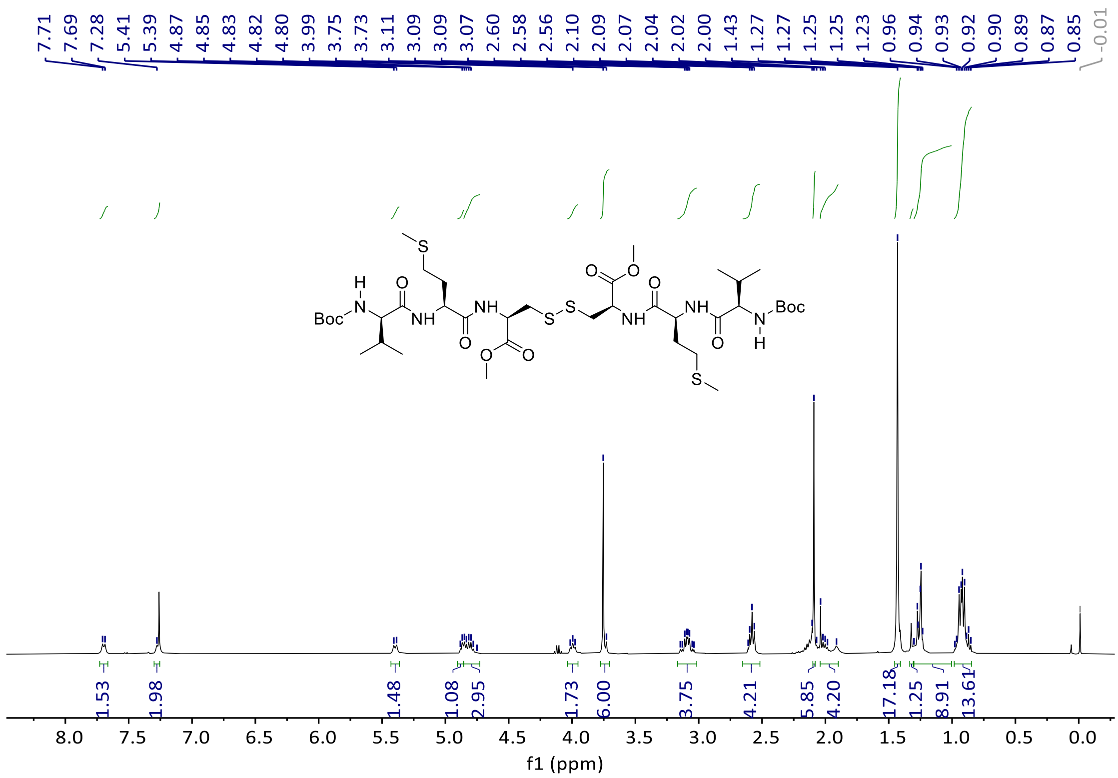
[13]C NMR (101 MHz, $CDCl_3$) of compound **4j**



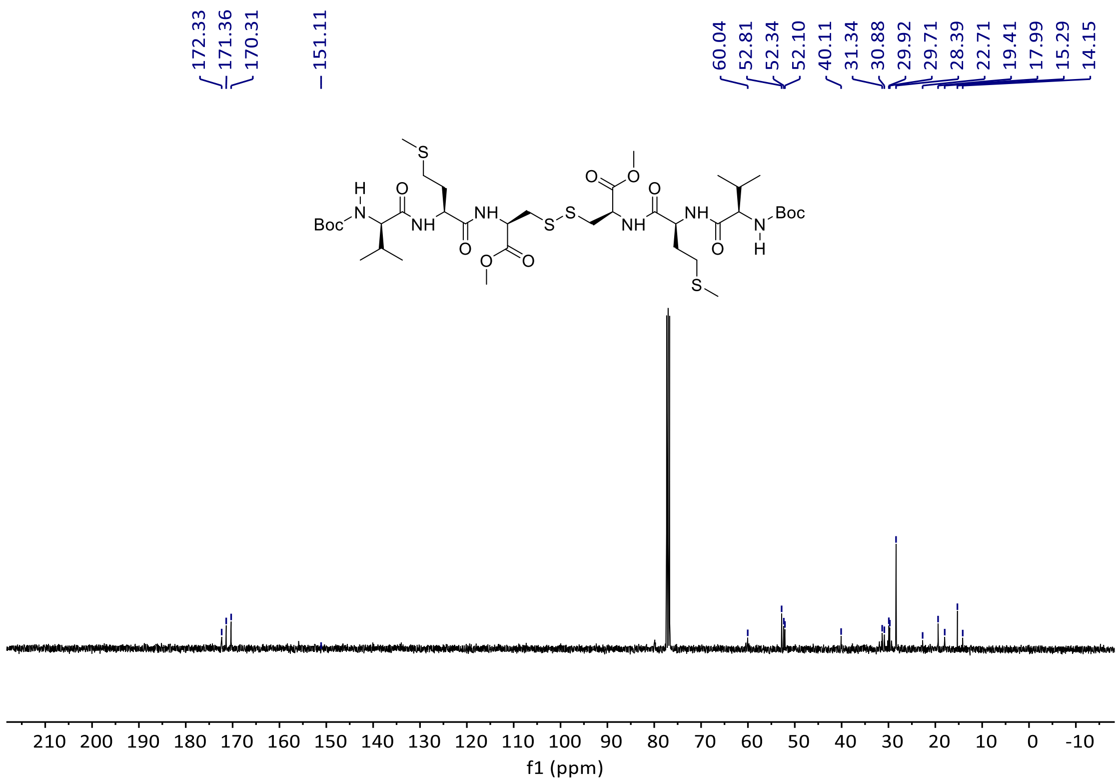
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4k**



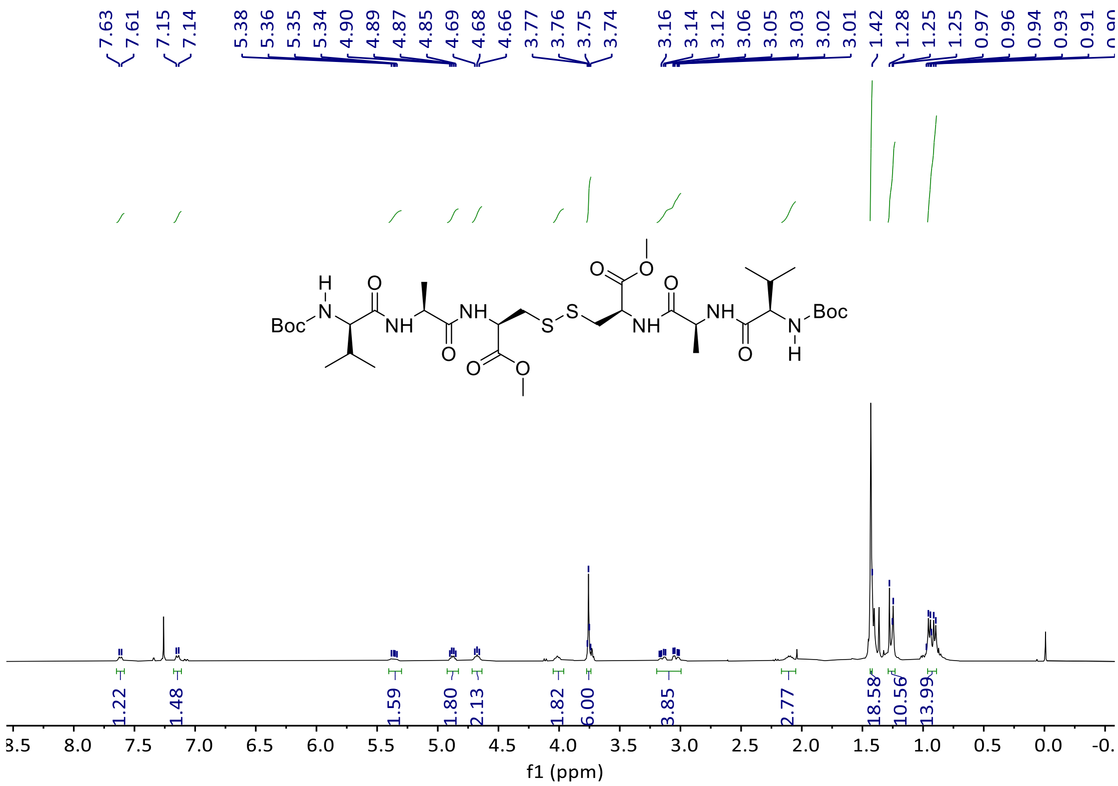
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4k**



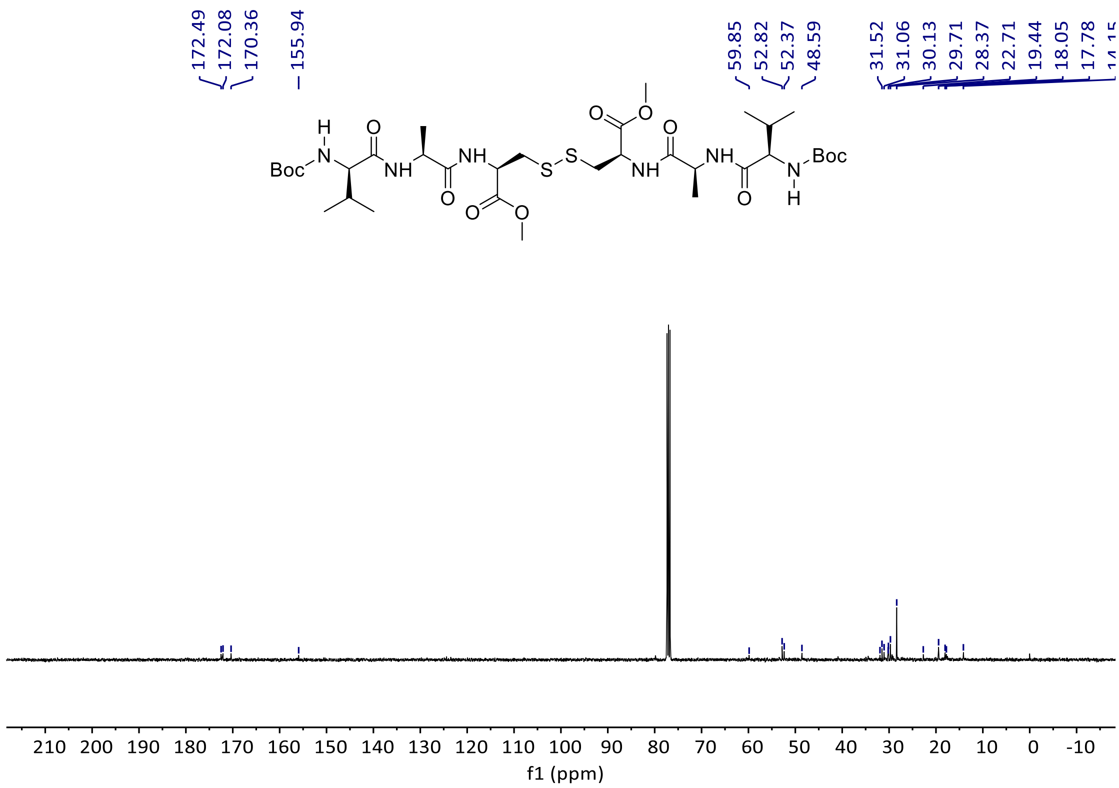
^{1}**H NMR** (400 MHz, $CDCl_3$) of compound **4l**



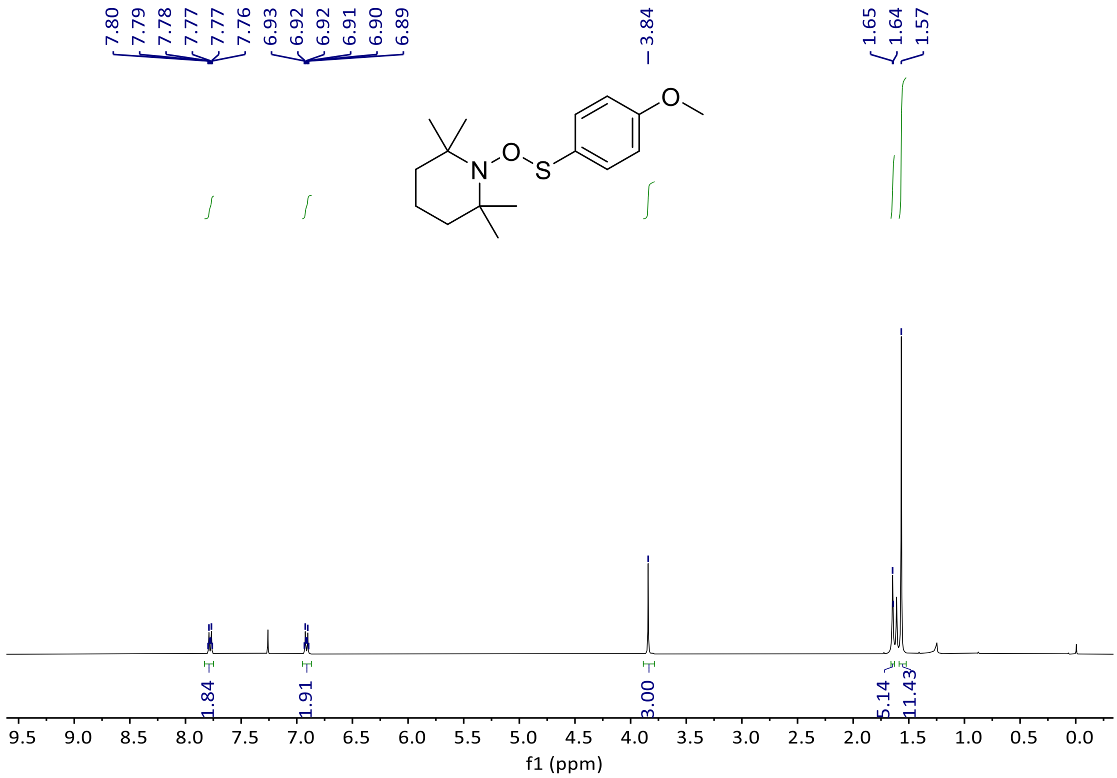
^{13}**C NMR** (101 MHz, $CDCl_3$) of compound **4l**



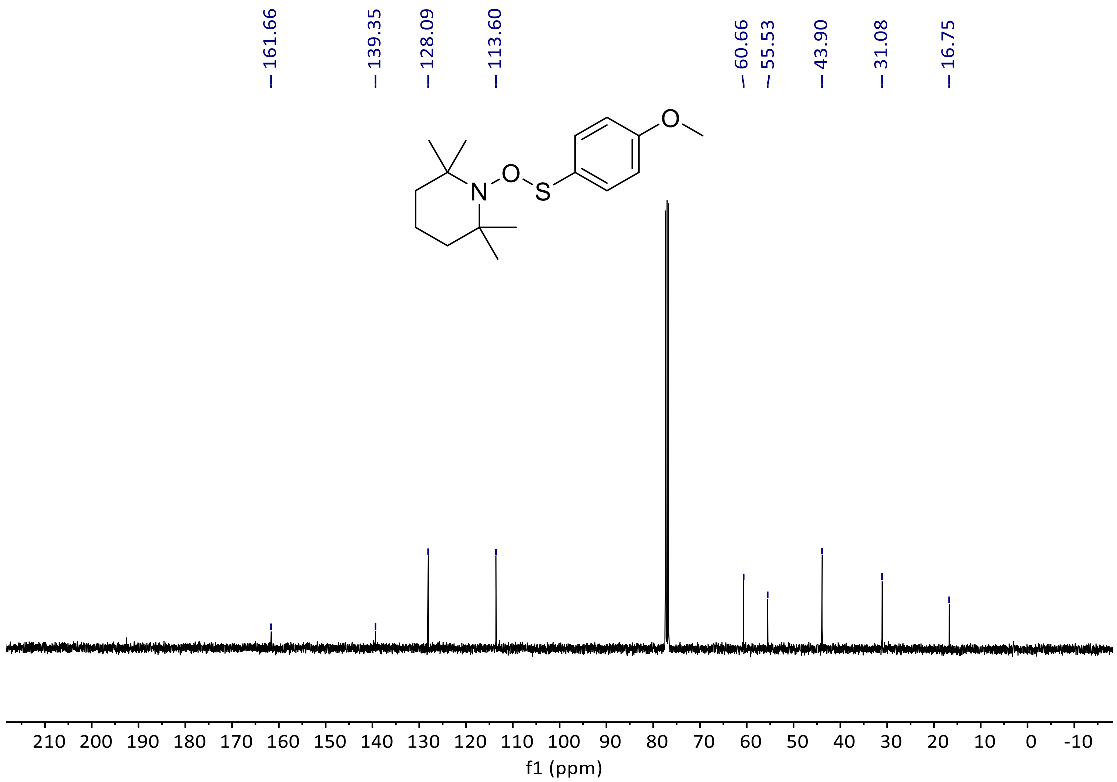
¹H NMR (400 MHz, $CDCl_3$) of compound **4m**



¹³C NMR (101 MHz, $CDCl_3$) of compound **4m**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **Tempo-1a**



^{13}C NMR (101 MHz, $CDCl_3$) of compound **Tempo-1a**