Supplementary Information

Introducing I$^-$/Formic Acid as a *Green* Reagent for the Reduction of Sulfinates and Sulfoxides

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1. General experimental information

All reagents and solvents were purchased from commercial sources, and were used as received, unless noted otherwise. Thin layer chromatography (TLC) qualitative analysis was performed using glass or aluminum backed silica gel plates (F254). TLC plates were visualized through exposition to a UV light lamp (254 nm). Purifications were performed through flash column chromatography was performed on 230-400 mesh silica gel. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance III HD 400 and JEOL ECA 500 spectrometers. Chemical shifts of both ^{1}H and ^{13}C are reported in parts per million (ppm) on the δ scale referenced with respect to residual solvent ($CDCl_3$) at 7.26 ppm or from internal standard tetramethylsilane (TMS) at 0.00 ppm for ^{1}H NMR spectra and to residual solvent ($CDCl_3$) at 77.16 ppm for ^{13}C NMR spectra. ^{1}H NMR data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet or m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR data were collected with complete proton decoupling. Both ^{1}H and ^{13}C NMR data are reported in parts per million (ppm) on the δ scale. Infrared spectra were recorded on a Varian FT-IR 600IR spectrometer with an ATR sampling accessory. Mass spectra were obtained on an Agilent G1969A ESI-TOF or Jeol AccuTOF JMS-T100LC instruments.

2. Early optimizations for the reduction of sulfinate 1a

Due to the lack of reproducibility observed in the conversion of methyl sulfinate probe **1a** to its corresponding disulfide **2a** using formic acid under MW heating, we considered the possibility of ghost reactivity resulting from the glassware. It was noted that the personnel involved in the early stages of the project were also working in Lewis's acid-catalyzed epoxide ring-opening procedures. To investigate this further, substoichiometric amounts of transition metal salts were deliberately added, so the formation of **2a** from **1a** was evaluated **(Table S1)**. In general, most of the added salts resulted in low or no yield of the disulfide product **2a**, excepting for $MnBr_2$, which delivered 85% yield **(entry 14)** and complete conversion when the temperature was raised to 130 °C **(entry 17)**. Considering previous studies on the "saline effect" observed in the acceleration of various chemical processes,[1] an additional a saline additive (NaBr, 20% mol, **entry 18**) was introduced. The reaction kinetics were significantly improved, with complete conversion even at a lower temperature of 100 °C (*cf.* **entries 18 and 17**). However, when different salts (including bromide and chloride-based) were evaluated at a lower temperature to assess their impact on the reaction kinetics **(entries 19-24)**, it was found that sodium bromide exhibited superior performance and the bromide-based additives were superior in general. This led to the assumption that bromide, rather than Mn, played a crucial role in the reduction process. Consequently, all the bromide equivalents were replaced with NaBr, resulting in virtually the same outcome, with complete disappearance of the sulfinate starting material after 30 minutes at 90 °C. However, the yield of the recovered disulfide remained low, never exceeding 40%. A secondary pathway was deemed for the generation of the thiosulfonate intermediary **(4)** through dismutation,[2] leading to the wastage of sulfinate units as a non-reducible sulfonic species. As clear evidence emerged, indicating that the halide species played a crucial role in a mechanism involving nucleophilic attack on sulfur,[3] we decided to switch towards iodide, resulting in a significant improvement in the recovery of the disulfide product **(entries 27 and 28)**.

The enhanced nucleophilicity of iodide[4] favored the preferential formation of the thiosulfonate **(4)** through the iodide-catalyzed pathway, thereby minimizing the yield reduction caused by the dismutation pathway. Among the various iodide sources tested, potassium iodide (KI) exhibited the highest proficiency, achieving an excellent yield of 95% **(Table S2)**.

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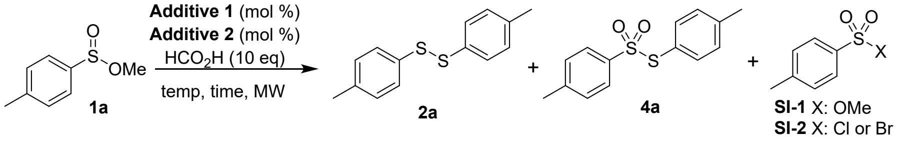
[1] Selected literature: a) P. Eckert, S. Sharif and M. G. Organ, *Angew. Chem. Int. Ed.*, 2021, **60**, 12224–12241. b) B. Zhang, J. Song, H. Liu, J. Shi, J. Ma, H. Fan, W. Wang, P. Zhang and B. Han, *Green Chem.*, 2014, **16**, 1198–1201. c) M. A. Mellmer, C. Sanpitakseree, B. Demir, K. Ma, W. A. Elliott, P. Bai, R. L. Johnson, T. W. Walker, B. H. Shanks, R. M. Rioux, M. Neurock and J. A. Dumesic, *Nat. Commun.*, 2019, **10**, 1–10.

[2] J. L. Kice and N. E. Pawlowski, *J. Am. Chem. Soc.*, 1964, **86**, 4898–4904.

[3] D. Landini, F. Montanari, H. Hogeveen and G. Maccagnani, *Tetrahedron Lett.* 1964, **5**, 2691–2696.

[4] A. J. Parker, *Chem. Rev.*, 1969, **69**, 1–32.

Table S1. Salt effect screening of diverse TM-based additives for reduction of methyl sulfinate **1a** to the disulfide **2a**.



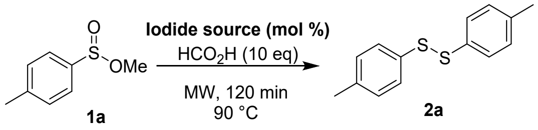
Entry	Additive 1 (% mol)	Additive 2 (% mol)	Temp. (°C)	Time (min)	Conversion (%)[a]			
					2a	4a	SI-1	SI-2[c]
1	$CoCl_2$ (5)	-	100	30	-	92	6	2
2	$InCl_3$ (5)	-	100	30	-	89	11	-
3	$PdCl_2$ (5)	-	100	30	15	83	2	-
4	Pd/C (5)	-	100	30	-	75	10	-
5	$CuCl_2$ (5)	-	100	30	3	75	8	6
6	$CrCl_3$ (5)	-	100	30	-	100	-	-
7	$CrCl_3 \cdot 6H_2O$ (5)	-	100	30	-	100	-	-
8	$Cr(acac)_3$ (5)	-	100	30	-	88	8	-
9	$FeCl_3$ (5)	-	100	30	9	85	5	1
10	FeO_2 (5)	-	100	30	-	94	6	-
11	$AlCl_3$ (5)	-	100	30	3	97	-	-
12	$MnSO_4$	-	100	30	-	95	3	
13	$MnCl_2$ (5)	-	100	30	-	95	5	-
14	**$MnBr_2$ (5)**	**-**	**100**	**30**	**85**	**15**	**-**	**-**
15	$MnBr_2$ (5)	-	110	30	88	12	-	-
16	$MnBr_2$ (5)	-	120	30	93	7	-	-
17	$MnBr_2$ (5)	-	130	30	100	-	-	-
18	**$MnBr_2$ (5)**	**NaBr (20)**	**100**	**30**	**100**	**-**	**-**	**-**
19	$MnBr_2$ (5)	NaBr (20)	90	30	82	12	-	6
20	$MnBr_2$ (10)	KBr (20)	90	30	60	27	-	13
21	$MnBr_2$ (10)	LiBr (20)	90	30	67	22	-	11
22	$MnBr_2$ (5)	NaCl (20)	90	30	19	68	-	13
23	$MnBr_2$ (5)	KCl (20)	90	30	10	80	-	10
24	$MnBr_2$ (10)	NaBr (20)	90	60	100 (37)	-	-	-
25	NaBr (30)	-	130	60	87	13	-	-
26	**-**	**NaBr (30)**	**90**	**60**	**100 (37)[b]**	**-**	**-**	**-**
27	-	**NaI (30)**	**90**	**120**	**100 (88)[b]**	**-**	**-**	**-**
28	-	**KI (20)**	**90**	**120**	**100 (95)[b]**	**-**	**-**	**-**

[a] Determined through ^{1}H-NMR

[b] Isolated yield.

[c] Collective sulfonyl halide yields.

Table S2. Iodide source screening for reduction of methyl sulfinate **1a** to the disulfide **2a**.

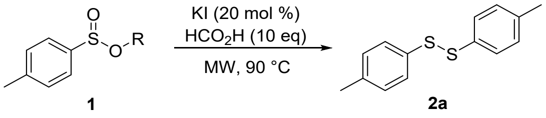


Entry	MI$_n$ (mol %)	Yield 2a (%)[a]
1	TBAI (20)	84
2	CuI (20)	35
3	ZnI$_2$ (10)	34
4	NaI (20)	88
5	**KI (20)**	**95**
6	K (15)	47[d]
7[b]	KI (15)	78
8[c]	KI (30)	88
8	HI (20)	50
8	I$_2$ (10)	39

[a] Isolated yields. [b] Reaction time 180 min [c] Reaction time 45 min [d] Determined by ^{1}H-NMR

Lastly, we investigated the influence of the alkyl substituent on the sulfinate **(Table S3)**. While the increasing steric demand of the alkyl group affects the reaction kinetics, the yield of the disulfide exceeds 90% in all cases after 2 hours.

Table S3. Influence of the steric demand from the sulfinate alkyl group for reduction of sulfinates **1** to the disulfide **2a**.

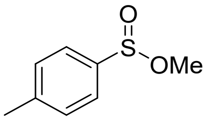


R	Time (min)	Yield 2a (%)[a]
Me	60	70
	120	**95**
Et	60	78
	120	91
***i*-Pr**	60	31
	120	90

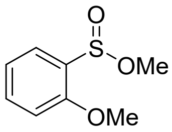
[a] Isolated yields.

3. General procedure for the synthesis of methyl sulfinates (1a-m) from thiols.

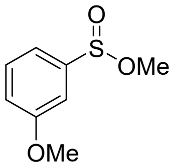
In a flask, the corresponding thiol (1 eq) was dissolved in MeOH: DCM (1:1 v/v, 0.3 M) and cooled at 0° C using an ice bath. *N*-bromosuccinimide (NBS, 2 eq) was then added in one portion. The reaction mixture was stirred for one hour. Subsequently, while maintaining the temperature at 0 °C, the mixture was treated with a saturated solution of NaHCO$_3$ until discoloration. The ice bath was removed, and the biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with DCM (4 times). The combined organic extracts were dried over Na$_2$SO$_4$ and concentrated under vacuum to obtain the crude sulfinate. The material was purified through SiO$_2$ column chromatography.[5]



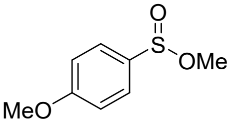
Methyl 4-methylbenzenesulfinate (1a) was synthesized from 4-methylbenzenethiol (2.20 g, 17.8 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (90:10 v/v) solvent system. Pure **1a** was obtained as a colorless oil with a yield of 94% (2.85 g). The spectral characteristics of the purified **1a** were similar to those of previously synthesized material.[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 3.46 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 140.8, 129.7, 125.4, 49.3, 21.5 ppm.



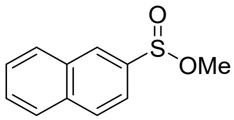
Methyl 2-methoxybenzenesulfinate (1b) was synthesized from 2-methoxybenzenethiol (1.04 g, 7.4 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (90:10 v/v) solvent system. Pure **1b** was obtained as a colorless oil with a yield of 30 % (0.42 g). The spectral characteristics of the purified **1b** were similar to those of previously synthesized material.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.74 – 7.42 (m, 1H), 7.06 (dd, *J* = 7.4, 0.6 Hz, 1H), 6.90 (d, *J* = 8.2, 1H), 3.84 (s, 3H), 3.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 134.1, 131.1, 126.2, 120.8, 111.4, 56.1, 50.4 ppm.



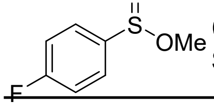
Methyl 3-methoxybenzenesulfinate (1c) was synthesized from 3-methoxybenzenethiol (0.38 g, 2.71 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (99:01 v/v) solvent system. Pure **1c** was obtained as a colorless oil with a yield of 43 % (126 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 -7.44 (m, 1H), 7.26 (s, 2H), 7.15 - 7.07 (m, 1H), 3.87 (s, 3H), 3.49 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 130.3, 118.9, 117.8, 109.8, 55.7, 49.8 ppm. IR (ATR) ν 1128 (-S=O). HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calculated for $C_8H_{11}O_3S$ 187.0; found 187.1.



Methyl 4-methoxybenzenesulfinate (1d) was synthesized from 4-methoxybenzenethiol (1.12 g, 7.98 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexaness:EtOAc (gradient 98:2 to 95:5 v/v) solvent system. Pure **1d** was obtained as a colorless oil with a yield of 92% (1.37 g). The spectral characteristics of the purified **1d** were similar to those of previously synthesized material.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.46 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 135.6, 127.3, 114.5, 55.7, 49.3 ppm.



Methyl naphthalene-2-sulfinate (1e) was synthesized from naphthalene-2-thiol (0.206 g, 1.2 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (99:1 v/v) solvent system. Pure **1e** was obtained as a colorless oil with a yield of 94% (0.249 g). The spectral characteristics of the purified **1e** were similar to those of previously synthesized material.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.17 (m,dd, *J* =1.8, 0.7 Hz, 1H), 7.89 – 7.87 (m, 2H), 7.83-7.80 (m, 1H), 7.59 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.55-7.48 (m, 2H), 3.40 (s, 3H) ppm. ^{13}C NMR (100Hz, $CDCl_3$), δ 141.1, 135.1, 132.6, 129.4, 129.1, 128.4, 128.1, 127.4, 126.6, 121.0, 49.7 ppm.



Methyl 4-fluorobenzenesulfinate (1f) was synthesized from 4-fluorobenzenethiol (0.8 g, 6.2 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (98:2 v/v) solvent system.

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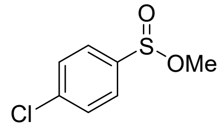
[5] J. A. Lujan-Montelongo, A. O. Estevez, F. F. Fleming, *Eur. J. Org. Chem.,* **2015**, 1602-1605.

[6] Y. Z. Ji, M. Wang, H. J. Li, Y. Liu, Y. C. Wu, *Eur. J. Org. Chem.,* 2016, **2016**, 4077-4083.

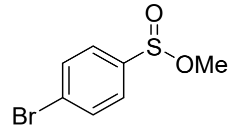
[7] J. L Garcia Ruano,. J. Alemán, C. Fajardo, A. Parra, *Org. Lett.,* **7**, 2005, 5493-5496.

[8] G. Zhang, Z. Sang, W. Wu, Q. Fan, C. Ding, *ChemistrySelect*, **7**, 2022, e202202833.

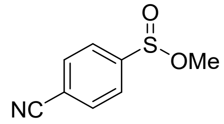
Pure **1f** was obtained as a colorless oil with a yield of 95% (1.03 g). The spectral characteristics of the purified **1f** were similar to those of previously synthesized material.[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 2H), 7.27 – 7.22 (m, 2H), 3.49 (s, 3H) ppm.^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0 (d, $J_{C\text{-}F}$ = 253.0 Hz), 139.7 (d, $J_{C\text{-}F}$ = 3.1 Hz), 127.9 (d, $J_{C\text{-}F}$ = 9.1 Hz), 116.4 (d, $J_{C\text{-}F}$ = 22.4 Hz), 49.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) 107.4 ppm.



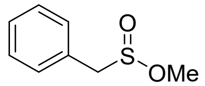
Methyl 4-chlorobenzenesulfinate (1g) was synthesized from 4-chlorobenzenethiol (0.532 g, 3.7 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (95:5 v/v) solvent system. Pure **1g** was obtained as a colorless oil with a yield of 85% (0.6 g). The spectral characteristics of the purified **1g** were similar to those of previously synthesized material.[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 3H), 3.49 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 138.7, 129.5, 127.0, 49.8 ppm.



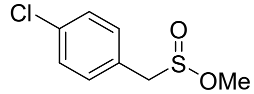
Methyl 4-bromobenzenesulfinate (1h) was synthesized from 4-bromobenzenethiol (0.51 g, 2.7 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (90:10 v/v) solvent system. Pure **1h** was obtained as a colorless oil with a yield of 88% (0.59 g). The spectral characteristics of the purified **1h** were similar to those of previously synthesized material.[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 3.41 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 132.4, 127.1, 127.0, 49.8 ppm.



Methyl 4-cyanobenzenesulfinate (1i) was synthesized from 4-cyanobenzenethiol[11] (0.42 g, 3.11 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (99:1 v/v) solvent system. Pure **1i** was obtained as an orange oil with a yield of 84% (0.47 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 4H), 3.54 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 133.0, 126.5, 117.7, 116.2, 50.6 ppm. IR (ATR) v (cm^{-1}) 2223 (-C≡N), 1131 (-S=O). HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calculated for $C_8H_8NO_2S$ 182.0270; found 182.0272.



Methyl phenylmethanesulfinate (1j) was synthesized from benzyl mercaptan (1.69 g, 13.6 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (gradient 90:10 to 80:20 v/v) solvent system. Pure **1j** was obtained as a colorless oil with a yield of 83% (1.91 g). The spectral characteristics of the purified **1j** were similar to those of previously synthesized material.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 -7.29 (m, 5H), 4.04 (d, *J* = 13.1, 2H), 3.95 (d, *J* = 13.1 Hz, 1H), 3.74 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.5, 129.0 128.9, 128.4, 64.2, 54.8 ppm.



Methyl (4-chlorophenyl) methanesulfinate (1k) was synthesized from (4-chlorophenyl) methanethiol (1.94 g, 12.2 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (70:30 v/v) solvent system. Pure **1k** was obtained as a colorless oil with a yield of 55% (1.38 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.6, 2H), 3.92 (d, *J* = 13.2 Hz, 1H), 3.84 (d, *J* = 13.2 Hz, 1H), 3.66 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5, 131.9, 129.0, 127.2, 63.1, 54.9 ppm. IR (ATR) ν 1124 (-S=O). HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calculated for $C_8H_{10}ClO_2S$ 205.0; found 205.0.

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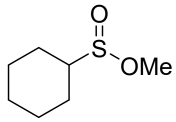
[9] R. Kowalczyk, A. J. Edmunds, R. G. Hall, C. Bolm, *Org. Lett.,* **13**, 2011, 768-771.

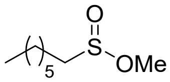
[10] B. Du, Z. Li, P. Qian, J. Han, Y. Pan, *Chem. Asian J.,* **11**, 2016, 478-481.

[11] C. Silva-Cuevas, C. Pérez-Arrieta, L. A. Polindara-García, J. A. Lujan-Montelongo, *Tetrahedron Lett.,* **58**, 2017, 2244-2247.

[12] L. A. T. Nguyen, T. N. Le, C. T. Duong, C. T. Vo, F. Duus, T. X. T. Luu, *J. Sulfur Chem.,* **42**, 2021, 519-528.



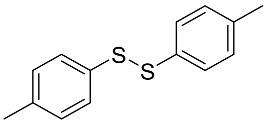
Methyl cyclohexanesulfinate (1l) was synthesized from cyclohexyl thiol (1.26 g, 10.8 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes: DCM:Et_2O (90:5:5 v/v/v) solvent system. Pure **1l** was obtained as a colorless oil with a yield of 84% (1.48 g). The spectral characteristics of the purified **1l** were similar to those of previously synthesized material.[5] ^1H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 2.56 (tt, J = 11.6, 3.7 Hz, 1H), 2.05-1.95 (m, 2H), 1.90 – 1.83 (m, 2H), 1.71 – 1.65 (m, 1H), 1.47 – 1.18 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.7, 55.1, 25.7, 25.3, 25.2, 24.6, 24.2 ppm.



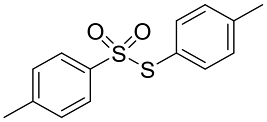
Methyl heptane-1-sulfinate (1m) was synthesized from heptanethiol (0.532 g, 3.7 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (gradient 95:5 v/v) solvent system. Pure **1m** was obtained as a colorless oil with a yield of 85% (0.6 g). ^1H NMR (400 MHz, $CDCl_3$) δ3.77 (s, 3H), 2.81 – 2.65 (m, 2H), 1.73 – 1.65 (m, 2H), 1.45 – 1.38 (m, 2H), 1.34 – 1.27 (m, 6H), 0.8 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.1, 54.5, 31.6, 29.0, 28.9, 22.7, 21.4, 14.2 ppm. IR (ATR) v 1127(-S=O). HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calculated for $C_8H_{19}O_2S$ 179.1100; found 179.1107.

4. General procedure for the synthesis of disulfides (2a-m) from sulfinates (1a-m).

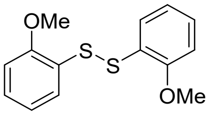
In a high-precision glass vial (Biotage®), formic acid (10 eq) and potassium iodide (20% mol) were sequentially added to the corresponding sulfinate (1 eq). The vial was properly sealed and subjected to microwave irradiation in a Biotage® reactor to the corresponding temperature for 120 minutes. After the required time, the mixture was cooled under ice bath and then was treated with a cold $NaHCO_3$ solution until pH= 8. The solution was dissolved in EtOAc and transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with EtOAc three times. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure, and the crude product was purified through SiO_2 column chromatography.



***p*-tolyldisulfide (2a)** was synthesized from methyl 4-methylbenzenesulfinate (**1a,** 220 mg, 1.2 mmol) using the general procedure at 90° C. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (99:01 v/v) solvent system. Pure **2a** was obtained as a white solid with a yield of 95% (151 mg). The spectral characteristics of the purified **2a** were similar to those of previously synthesized material.[13] ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.8 Hz, 4H), 7.09 (d, J = 7.8 Hz, 4H), 2.31 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 134.0, 129.9, 128.7, 21.2 ppm. Mp. 44 – 46 °C (lit.[13] 47 – 49 °C).



***S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (4a)**. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (99:01 v/v) solvent system. The spectral characteristics of the purified **4a** were similar to those of previously synthesized material.[14] ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.22 (dd, J = 11.5, 8.3 Hz, 4H), 7.14 (d, J = 8.2 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H) ppm.



bis (*o*-methoxyphenyl) disulfide (2b) was synthesized from methyl 2-methoxybenzenesulfinate (**1b**, 206 mg, 1.11 mmol) using the general procedure at 90° C. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (95:05 v/v) solvent system. Pure **2b** was obtained as a white solid

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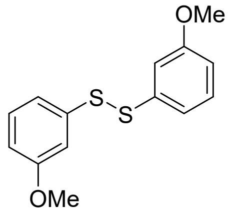
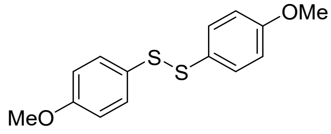
[13] J. L. G. Ruano, A. Parra, J. Alemán, *Green Chem.,* **10**, 2008, 706-711.

[14]. E. Jacobsen, M. K. Chavda, K. M. Zikpi, S. L. Waggoner, D. J. Passini, J. A. Wolfe,... & S. R. Hitchcock, *Tetrahedron Lett.,* **58**, 2017, 3073-3077.

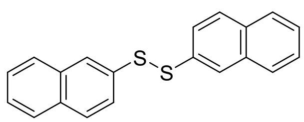
with a yield of 82% (126 mg). The spectral characteristics of the purified **2b** were similar to those of previously synthesized material.[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.13 (ddd, *J* = 8.3, 7.4, 1.6 Hz, 2H), 6.85 (td *J* = 7.8, 1.1 Hz 2H), 6.79 (d, *J* = 8.2 Hz, 2H), 3.84 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 127.9, 127.6, 124.6, 121.5, 110.6, 56.0 ppm. Mp. 118-119 °C (lit.[15] 120 – 121 °C).



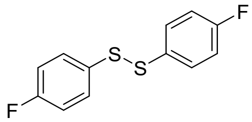
bis (*m*-methoxyphenyl) disulfide (2c) was synthesized from methyl 3-methoxybenzenesulfinate (**1c**, 210 mg, 1.13 mmol) using the general procedure at 90° C. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (95:05 v/v) solvent system. Pure **2c** was obtained as a yellow oil with a yield of 82% (129 mg). The spectral characteristics of the purified **2c** were similar to those of previously synthesized material.[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 -7.19 (m, 2H), 7.09 -7.07 (m, 4H), 6.77 -6.75 (m, 2H), 3.77 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 138.4, 130.0, 119.7, 113.3, 112.7, 55.5 ppm.



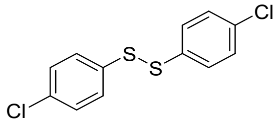
bis (*p*-methoxyphenyl) disulfide (2d) was synthesized from methyl 4-methoxybenzenesulfinate (**1d**, 208 mg, 1.12 mmol) using the general procedure at 100° C. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (95:05 v/v) solvent system. Pure **2d** was obtained as a white solid with a yield of 85% (132 mg). The spectral characteristics of the purified **2d** were similar to those of previously synthesized material.[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 4H), 6.83 (d, *J* = 8.4 Hz, 4H), 3.79 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 132.8, 128.6, 114.8, 55.5 ppm. Mp. 33 – 35 °C (lit.[13] 41 – 43 °C).



bis (2-naphthyl) disulfide (2e) was synthesized from methyl naphthalene-2-sulfinate (**1e**, 165 mg, 0.8 mmol) using the general procedure at 90° C. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (99:01 v/v) solvent system. Pure **2e** was obtained as a white solid with a yield of 77% (98 mg). The spectral characteristics of the purified **2e** were similar to those of previously synthesized material.[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 1.4 Hz, 2H), 7.75 – 7.66 (m, 4H), 7.64 (dd, *J* = 6.1, 3.1 Hz, 2H), 7.54 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.40 – 7.33 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 132.6, 129.1, 127.9, 127.6, 126.9, 126.7, 126.4, 125.8 ppm. mp. 138 – 140 °C (lit.[16] 136 – 137 °C).



bis (*p*-fluorophenyl) disulfide (2f) was synthesized from methyl 4-fluorobenzenesulfinate (**1f**, 206 mg, 1.14 mmol) using the general procedure at 90° C. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (98:02 v/v) solvent system. Pure **2f** was obtained as a colorless oil with a yield of 91% (130 mg). The spectral characteristics of the purified **2f** were similar to those of previously synthesized material.[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (dd, *J* =5.5, 2.3 Hz, 4H), 7.0 (t, *J* = 8.4 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 248.3 Hz), 132.3 (d, $J_{C\text{-}F}$ =3.2 Hz), 131.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 116.4 (d, $J_{C\text{-}F}$ = 22.2 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) 113.4 ppm.



bis (*p*-chlorophenyl) disulfide (2g) was synthesized from methyl 4-chlorobenzenesulfinate (**1g**, 199 mg, 1.4 mmol) using the general procedure at 90° C. The product was purified through SiO_2 column chromatography

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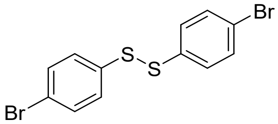
[15] X. Li, J. Du, Y. Zhang, H. Chang, W. Gao, W. Wei, *Org. Biomol. Chem.,* **17**, 2019, 3048-3055.

[16] M. Lin, L. Bian, Q. Chen, H. Xu, Z. Liu, K. Zhu, *Angew. Chem. Int. Ed.*, **62**, 2023 e202303035.

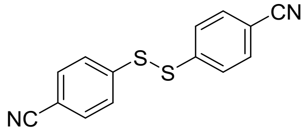
[17] H. Yue, J. Wang, Z. Xie, J. Tian, D. Sang, S. Liu, *ChemistrySelect*, **5**, 2020, 4273-4277.

[18] L. H. Zou, J. Reball, J. Mottweiler, C. Bolm, *Chem. Commun.,* **48**, 2012, 11307-11309.

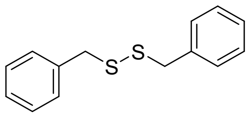
using a hexanes:EtOAc (94:06 v/v) solvent system. Pure **2g** was obtained as a white solid with a yield of 81% (120 mg). The spectral characteristics of the purified **2g** were similar to those of previously synthesized material.[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 4H), 7.27 (d, *J* = 8.5 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 133.8, 129.5, 129.4 ppm. Mp. 70 – 72 °C (lit.[17] 71 – 73 °C).



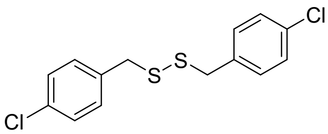
bis (*p*-bromophenyl) disulfide (2h) was synthesized from methyl 4-bromobenzenesulfinate (**1h**, 250 mg, 1.1 mmol) using the general procedure at 100° C. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (90:10 v/v) solvent system. Pure **2h** was obtained as a white solid with a yield of 84% (168 mg). The spectral characteristics of the purified **2h** were similar to those of previously synthesized material.[19] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 4H), 7.35 – 7.32 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.9, 132.4, 129.5, 121.7 ppm. Mp. 88 – 90 °C (lit.[18] 92 – 96 °C).



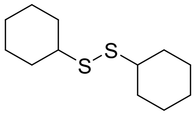
bis (*p*-cyanophenyl) disulfide (2i) was synthesized from methyl 4-cyanobenzenesulfinate (**1i**, 216 mg, 1.19 mmol) using the general procedure at 100° C. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (95:05 v/v) solvent system. Pure **2i** was obtained as a white solid with a yield of 76% (122 mg). The spectral characteristics of the purified **2i** were similar to those of previously synthesized material.[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 4H), 7.56 (d, *J* = 8.1 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 132.9, 126.6, 118.3, 111.0 ppm. Mp. 172 – 174 °C (lit.[19] 168 – 170 °C).



bis (benzyl) disulfide (2j) was synthesized from methyl phenylmethanesulfinate (**1i**, 214 mg, 1.26 mmol) using the general procedure at 110° C. The product was purified through SiO2 column chromatography using a hexanes:EtOAc (99:01 v/v) solvent system. Pure **2j** was obtained as a white solid with a yield of 80% (93 mg). The spectral characteristics of the purified **2j** were similar to those of previously synthesized material.[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 -7.22 (m, 10H), 3.60 (s, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 129.1, 128.6, 127.1, 35.7 ppm. Mp. 66 – 68 °C (lit.[16] 67 – 71 °C).



bis (4-chlorobenzyl) disulfide (2k) was synthesized from methyl (4-chlorophenyl) methanesulfinate (**1k**, 232 mg, 1.13 mmol) using the general procedure at 110° C. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (99:01 v/v) solvent system. Pure **2k** was obtained as a white solid with a yield of 78% (105 mg). The spectral characteristics of the purified **2k** were similar to those of previously synthesized material.[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* =8.5 Hz, 4H), 7.19 (d, *J* =8.5 Hz, 4H), 3.54 (s, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 133.0, 130.4, 128.8, 35.0 ppm. Mp. 61-62 °C (lit.[22] 62-63 °C).



bis (cyclohexyl) disulfide (2l) was synthesized from methyl cyclohexanesulfinate (**1k**, 197 mg, 1.21 mmol) using the general procedure at 120° C. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (99:01 v/v) solvent system. Pure **2l** was obtained as a colorless oil with a yield of 78% (109

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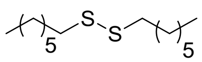
[19] A. Shard, R. Kumar, N. Sharma, A. K. Sinha, *Rsc Adv.*, **4**, 2014, 33399-33407.

[20] Y. Zheng, F. L. Qing, Y. Huang, X. H. Xu, *Adv. Synth. Catal.*, **358**, 2016, 3477-3481.

[21] H. Huang, J. Ash, J. Y. Kang, *Org. Biomol. Chem.,* **16**, 2018, 4236-4242.

[22] J. L. Howard, C. Schotten, S. T. Alston, D. L. Browne, *Chem. Commun.,* **52**, 2016, 8448-8451.

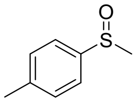
mg). The spectral characteristics of the purified **2l** were similar to those of previously synthesized material.[23] ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.71 – 2.65 (m, 2H), 2.07 – 2.02 (m, 4H), 1.82 – 1.77 (m, 4H), 1.63 – 1.55 (m, 2H), 1.37 – 1.23 (m, 10H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 50.1, 33.0, 26.2, 25.8 ppm.



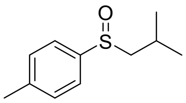
Bis (hepthyl) disulfide (2m) was synthesized from methyl heptane-1-sulfinate (**1m**, 223 mg, 1.36 mmol) using the general procedure at 110° C. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (99:1 v/v) solvent system. Pure **2m** was obtained as a colorless oil with a yield of 74% (132 mg). ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.68 (t, J =7.4 Hz, 4H), 1.67 (q, J = 7.5 Hz, 4H), 1.39 – 1.25 (m, 16H), 0.88 (t, J = 6.7 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 39.3, 31.9, 29.4, 29.1, 28.6, 22.8, 14.2 ppm. IR (ATR) v 1243 (-S-S-). HRMS (ESI/QTOF) m/z: [M/2]$^+$ Calculated for C$_7$H$_{15}$S 131.0889; found 131.0880.

5. General procedure for the synthesis of sulfoxides (5a-r) from sulfinates (1a-h).

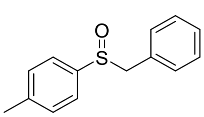
In a Schlenk flask, the corresponding methyl sulfinate (**1a-h**, 1 eq) was dissolved in anhydrous THF (0.3 M) and cooled at 0° C using an ice bath. Alkylmagnesium chloride (1.1 – 2.0 eq) was added slowly in one portion. The reaction mixture was warmed to room temperature and stirred overnight. Subsequently, the reaction was treated with a water-ice solution and DCM was added. The biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with DCM (4 times). The combined organic extracts were dried over Na$_2$SO$_4$ and concentrated under vacuum to obtain the crude sulfoxide. The material was purified through SiO$_2$ column chromatography.



1-methyl-4-(methylsulfinyl)benzene (5a) was synthesized from methyl 4-methylbenzenesulfinate (**1a**, 1.22 g, 7.2 mmol) and methyl magnesium bromide (2 eq) using the general procedure. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (80:20 v/v) solvent system. Pure **5a** was obtained as a colorless oil with a yield of 99% (1.10 g). The spectral characteristics of the purified **5a** were similar to those of previously synthesized material.[24] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 2.70 (s, 3H), 2.41 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.6, 141.6, 130.2, 123.7, 44.1, 21.5 ppm.



1-(isobutylsulfinyl)-4-methylbenzene (5b) was synthesized from methyl 4-methylbenzenesulfinate (**1a**, 505 mg, 2.9 mmol) and isobutylmagnesium chloride (1.1 eq) using the general procedure. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (70:30 v/v) solvent system. Pure **5b** was obtained as a colorless oil with a yield of 51% (295 mg). The spectral characteristics of the purified **5b** were similar to those of previously synthesized material.[25] ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 2.75 (dd, J =12.9, 5.0 Hz, 1H) 2.38 (dd, J = 12.9 9.2 Hz, 1H), 2.35 (s, 3H), 2.18 – 2.10 (m, 1H), 1.08 (d, J = 6.6 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$) δ 141.5, 141.4, 130.0, 124.0, 67.7, 24.3, 22.9, 21.8, 21.5 ppm.



1-(benzylsulfinyl)-4-methylbenzene (5c) was synthesized from methyl 4-methylbenzenesulfinate (**1a**, 500 mg, 2.94 mmol) and benzylmagnesium bromide (1.5 eq) using the general procedure. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (gradient 70:30 to 50:50 v/v) solvent system. Pure **5c** was obtained as a white solid with a yield of 47% (321 mg). The spectral

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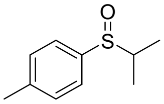
[23] D. Sarkar, M. K. Ghosh, N. Rout, *Tetrahedron Lett.,* **59**, 2018, 2360-2364.

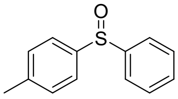
[24] P. G. Reddy, N. Mamidi, C. P. Pradeep, *CrystEngComm.,* **18**, 2016, 4272-4276.

[25] P. R. Blakemore, M. S. Burge, *J. Am. Chem. Soc.,* **129**, 2007, 3068-3069.

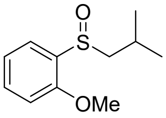
characteristics of the purified **5c** were similar to those of previously synthesized material[26] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.19 (m, 4H), 7.19 – 7.11 (m, 3H), 6.93 (dd, *J* = 7.8, 1.7 Hz, 2H), 4.02 (d, *J* = 12.5 Hz, 1H), 3.90 (d, *J* = 12.4 Hz, 1H), 2.33 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 139.8, 130.5, 129.7, 129.5, 128.6, 128.3, 124.6, 63.9, 21.6 ppm. Mp. 140 – 142 °C (lit[27] 140 – 141 °C).



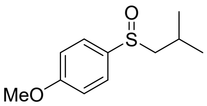
1-(isopropylsulfinyl)-4-methylbenzene (5d) was synthesized from methyl 4-methylbenzenesulfinate (**1a**, 601 mg, 3.5 mmol) and isopropylmagnesium chloride (1.1 eq) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (65:35 v/v) solvent system. Pure **5d** was obtained as a colorless oil with a yield of 64% (409 mg). The spectral characteristics of the purified **5d** were similar to those of previously synthesized material.[28] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 2H), 2.77 (hept, *J* = 6.9, 1H), 2.34 (s, 3H), 1.12 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 138.4, 129.6, 125.0, 54.5, 21.4, 15.8, 14.1 ppm.



1-(phenylsulfinyl)-4-methylbenzene (5e) was synthesized from methyl 4-methylbenzenesulfinate (**1a**, 601 mg, 3.5 mmol) and phenylmagnesium bromide (1.5 eq) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (65:35 v/v) solvent system. Pure **5e** was obtained as a white solid with a yield of 40% (510 mg). The spectral characteristics of the purified **5e** were similar to those of previously synthesized material.[29] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.42 (m, 3H), 7.26 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 142.6, 141.8, 131.0, 130.2, 129.4, 125.1, 124.8, 21.5 ppm.



1-(isobutylsulfinyl)-2-methoxybenzene (5i) was synthesized from methyl 2-methoxybenzenesulfinate (**1c**, 452 mg, 2.43 mmol) and isobutylmagnesium chloride (2 eq) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (80:20 v/v) solvent system. Pure **5i** was obtained as a colorless oil with a yield of 19% (96 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.45 – 7.45 – 7.41 (m, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 3.88 (s, 3H), 2.82 7 (dd, *J* = 12.9, 10.0 Hz, 1H), 2.63 (dd, *J* = 12.9, 4.2 Hz, 1H), 2.38 – 2.27 (m, 1H), 1.18 (d, *J* = 6.6 Hz, 3H) 1.04 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 132.4, 131.9, 125.1, 121.8, 110.7, 64.7, 55.8, 24.4, 23.1, 21.7 ppm. MS (ESI/SQ) m/z: $[M+H]^+$ Calculated for $C_{11}H_{17}O_2S$ 213.1; found 213.1.



1-(isobutylsulfinyl)-4-methoxybenzene (5k) was synthesized from methyl 4-methoxybenzenesulfinate (**1d**, 306 mg, 1.64 mmol) and isobutylmagnesium chloride (1.1 eq) using the general procedure. The product was purified through SiO_2 radial chromatography using a hexanes:EtOAc (80:20 v/v) solvent system. Pure **5k** was obtained as a colorless oil with a yield of 31% (109 mg). The spectral characteristics of the purified **5k** were similar to those of previously synthesized material.[30] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.9 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H), 2.81 (dd, *J* = 12.9, 5.2 Hz, 1H), 2.43 (dd, *J* = 12.9, 8.9 Hz, 1H), 2.19 – 2.12 (m, 1H), 1.12 (d, *J* = 6.6 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 135.7, 126.0, 114.9, 67.7, 55.6, 24.3, 22.9, 21.9 ppm.

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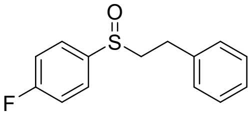
[26] M. Azizi, A. Maleki, F. Hakimpoor, R. Ghalavand, A. Garavand, *Catal. Lett.,* **147**, 2017, 2173-2177.

[27] C. Boudou, M. Berges, C. Sagnes, J. Sopková−de Oliveira Santos, S. Perrio, P. Metzner, *J. Org. Chem.,* **72**, 2007, 5403-5406.

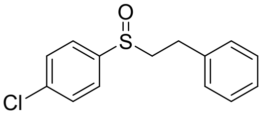
[28] D.C. Lenstra, V. Vedovato, E. Ferrer Flegeau, J. Maydom, M. C. Willis, *Org. Lett.,* **18**, 2016, 2086-2089.

[29] X. Li, J. Du, Y. Zhang, H. Chang, W. Gao, W. Wei, *Org. Biomol. Chem.,* **17**, 2019, 3048-3055.

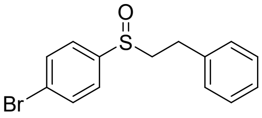
[30] S.Ruppenthal, R. Brückner, *J. Org. Chem.,* **80**, 2014, 897-910.



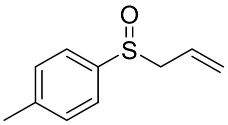
1-(phenethylsulfinyl)-4-fluorbenzene (5l) was synthesized from methyl 4-fluorbenzenesulfinate (**1f**, 744 mg, 3.2 mmol) and phenethylmagnesium chloride (2 eq) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (60:40 v/v) solvent system. Pure **5l** was obtained as a colorless oil with a yield of 64% (509 mg). The spectral characteristics of the purified **5l** were similar to those of previously synthesized material.[31] ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.16 (m, 5H), 3.13 – 2.98 (m, 3H), 2.93 – 2.86 (m, 1H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ 164.4 (d, *J* = 251.5 Hz), 139.2 (d, *J* = 3.1 Hz), 138.7, 128.9, 128.6, 126.9, 126.4 (d, *J* = 8.9 Hz), 116.7 (d, *J* = 22.6 Hz), 58.7, 28.3 ppm.



1-(phenethylsulfinyl)-4-chlorobenzene (5m) was synthesized from methyl 4-chlorobenzenesulfinate (**1g**, 869 mg, 3.4 mmol) and phenethylmagnesium chloride (2 eq) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (70:30 v/v) solvent system. Pure **5m** was obtained as a colorless oil with a yield of 27% (246 mg). The spectral characteristics of the purified **5m** were similar to those of previously synthesized material.[30] ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.31 – 7.22 (m, 3H), 7.18 – 7.16 (m, 2H), 3.14 – 2.99 (m, 3H), 2.91 – 2.84 (m, 1H) ppm. ^{13} C NMR (400 MHz, $CDCl_3$) δ 142.3, 138.6, 137.3, 129.7, 128.9, 128.6, 126.9, 125.6, 58.5, 28.2 ppm.



1-(phenethylsulfinyl)-4-bromobenzene (5n) was synthesized from methyl 4-bromobenzenesulfinate (**1h**, 446 mg, 1.90 mmol) and phenethylmagnesium chloride (2 eq) using the general procedure. The product was purified through SiO_2 radial chromatography using a hexanes:EtOAc (80:20 v/v) solvent system. Pure **5n** was obtained as a colorless oil with a yield of 51% (301 mg). The spectral characteristics of the purified **5n** were similar to those of previously synthesized material.[30] ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.22 (m, 3H), 7.17 (d, *J* = 8.3 Hz, 2H), 3.14 – 2.99 (m, 3H), 2.91 – 2.84 (m, 1H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ 143.0, 138.6, 132.6, 128.9, 128.7, 126.9, 125.8, 125.6, 58.4, 28.2 ppm.



1-(allylsulfinyl)-4-methylbenzene (5r) was synthesized from methyl 4-methylbenzenesulfinate (**1a**, 549 mg, 3.23 mmol) and allylmagnesium bromide (2 eq) using the general procedure. The product was purified through SiO_2 radial chromatography using a hexanes:EtOAc (70:30 v/v) solvent system. Pure **5r** was obtained as a colorless oil with a yield of 36% (210 mg). The spectral characteristics of the purified **5r** were similar to those of previously synthesized material.[27] ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.30 (dd, *J* = 8.5, 0.7 Hz, 2H), 5.62 (ddt, *J* = 17.6, 10.4, 7.5 Hz, 1H), 5.31 (ddt, *J* = 10.2, 1.4, 0.7 Hz, 1H), 5.19 (dq, *J* = 17.0, 1.2 Hz, 1H), 3.55 – 3.46 (m, 2H), 2.40 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 139.8, 129.8, 125.5, 124.5, 123.9, 61.0, 21.5 ppm.

6. General procedure for the synthesis of mesylated alcohols (SI-3a-b).

In a flask, the corresponding alcohol (1 eq) was dissolved in DCM (0.7 M) and cooled at 0 °C using an ice bath. Et_3N (1 eq) was added in one portion. The solution was stirred for 10 minutes and then, MsCl (1.25 eq) was slowly added. The reaction mixture was stirred for one hour. Subsequently, while maintaining the temperature at 0 °C, the mixture was treated with a saturated solution of $NaHCO_3$. The ice bath was removed, and the biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with DCM (4 times). The combined

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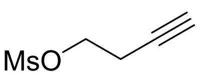
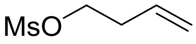
[31] H. L. Yue, M. Klussmann, *Synlett*, **27**, 2016, 2505-2509.

organic extracts were dried over Na_2SO_4 and concentrated under vacuum to obtain the crude mesylatel alcohols **(SI-3a-c)**. The material was purified through SiO_2 column chromatography.

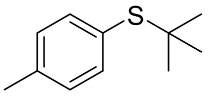


But-3-yn-1-yl methanesulfonate (SI-3a) was synthesized from but-3-yn-1-ol (0.19 g, 2.64 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (70:30 v/v) solvent system. Pure **SI-3a** was obtained as an oil with a yield of 83% (0.32 g). The spectral characteristics of the purified **SI-3a** were similar to those of previously synthesized material.[32] ^1H NMR (400 MHz, $CDCl_3$) δ 4.29 (t, *J* = 6. 7 Hz, 2H), 3.04 (s, 3H), 2.65 (td, *J* = 6.7, 2.7 Hz, 2H), 2.06 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 78.7, 71.1, 67.2, 37.8, 19.8 ppm.

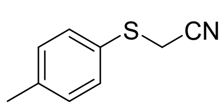


But-3-en-1-l methanesulfonate (SI-3b) was synthesized from but-3-en-1-ol (0.72 g, 9.92 mmol) using the general procedure. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (70:30 v/v) solvent system. Pure **SI-3b** was obtained as an oil with a yield of 90% (1.35 mg). The spectral characteristics of the purified **SI-3b** were similar to those of previously synthesized material.[33] ^1H NMR (400 MHz, $CDCl_3$) δ 5.73 (ddt, *J* =17.0, 10.3, 6.7 Hz, 1H), 5.15 – 5.07 (m, 2H), 4.20 (t, *J* = 6.7 Hz, 2H), 2.95 (s, 3H), 2.45 (qt, *J* =6.7, 1.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5, 118.5, 69.0, 37.5, 33.5 ppm.

7. General procedures for thioeter synthesis from thiols (SI-7f-v).



***tert*-butyl(*p*-tolyl)sulfane (SI-7f).**[34] In a flask, mix acetic acid (1 mL), perchloric acid (65%, 0.4 mL) and acetic anhydride (0.6 mL) in a in an ice bath and stir the mixture for 20 minutes. Add 4-methylbenzenethiol (700 mg, 5.6 mmol) and *tert*-butyl alcohol (568 mg) to the mixture and adjust the volume with acetic acid to 5 mL. Stir the reaction mixture at room temperature for 2 hours. Dilute the reaction mixture with brine (3 mL) and was added Et_2O. The biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 times). and transfer the mixture to a separatory funnel. Wash the organic layer with K_2CO_3 solution (3 times) and then wash with water. The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to obtain the crude thioether. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (90:10 v/v) solvent system. Pure **SI-7f** was obtained as an oil with a yield of 97.6% (0.992 g).



2-(*p*-tolylthio)acetonitrile (SI-7h).[35] In a flask, 4-methyl thiophenol (179 mg, 1.44 mmol) and chloroacetonitrile (1.0 eq) were dissolved in H_2O (1 M) at room temperature. Et_3N (1.1 eq) was added dropwise. The reaction was stirred for 1 hour at room temperature. Subsequently, to the mixture of reaction was added EtOAc and was treated with brine. The biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with EtOAc (4 times). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to obtain the crude thioether. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (90:10 v/v) solvent system. Pure **SI-7h** was obtained as an oil with a yield of 99.6% (0.235 g).

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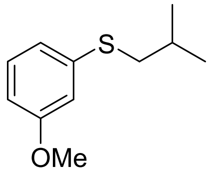
[32] F. K. Cheung, A. M. Hayes, D. J. Morris, M. Wills, *Org. Biomol. Chem.,* **5**, 2007, 1093-1103.

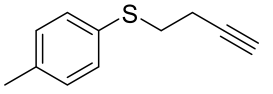
[33] J. M. Frost, D. A. DeGoey, L. Shi, R. J. Gum, M. M. Fricano, G. L. Lundgaard,... & M. E. *J.* Kort, *Med. Chem.* **59**, 2016, 3373-3391.

[34] Nawrot, D.; Kolenič, M.; Kuneš, J.; Kostelansky, F.; Miletin, M.; Novakova, V.; Zimcik, P. *Tetrahedron*, **2018**, *74*(5), 594-599.

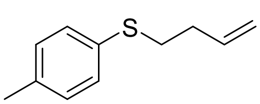
[35] Azizi, N.; Khajeh Amiri, A.; Bolourtchian, M.; Saidi, M. R. *J. Iranian Chem. Soc.* **2009**, *6*, 749-753.



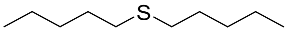
Isobutyl(3-methoxyphenyl)sulfane (SI-7j). In a flask, 3-methoxy thiophenol (500 mg, 3.57 mmol) were dissolved in EtOH (1 M) at room temperature. NaOH (1.2 eq) was added and stirred for 10 minutes. 1-Bromo-2-methylpropane (1.2 eq) was added, and the reaction was stirred for 12 hours at room temperature. Subsequently, EtOH was evaporated, and the crude was redissolved in DCM. Water was added and the biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with DCM (4 times). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to obtain the crude thioether. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (90:10 v/v) solvent system. Pure **SI-7j** was obtained as an oil with a yield of 84% (0.589 g).



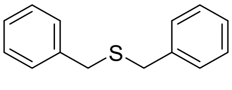
But-3-yn-1-yl(*p*-tolyl)sulfane (SI-7s). In a flask, 4-methyl thiophenol (188 mg, 1.44 mmol) was dissolved in acetone (0.67 M) at room temperature. K_2CO_3 (1.46 eq) was then added in one portion. The reaction was stirred for 15 minutes and but-3-yn-1-yl methanesulfonate (**SI-3a**, 1.02 eq) was added dropwise. The mixture was stirred for 6 hours at 60° C. The mixture of reaction was quenched with water and brine. The biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with EtOAc (4 times). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to obtain the crude thioether. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (98:02 v/v) solvent system. Pure **SI-7s** was obtained as an oil with a yield of 73% (0.187 g).



But-3-en-1-yl(*p*-tolyl)sulfane (SI-7t). In a flask, 4-methyl thiophenol (1.22 g, 9.79 mmol) was dissolved in DMF:THF (1:1 v/v, 2 M) and cooled at 0° C using an ice bath. NaH (60% mineral oil, 1.13 eq) was then added in one portion. The solution was stirred for 15 minutes and but-3-en-1-l methanesulfonate **(SI-3b)** in THF (1 M) was added dropwise. The ice bath was removed, and the mixture was stirred for 12 hours at 70° C. The reaction was quenched with water and a NaOH solution (1 N) and the biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with DCM (4 times). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to obtain the crude thioether. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (90:10 v/v) solvent system. Pure **SI-7t** was obtained as an oil with a yield of 91% (0.714 g).



di-*n*-pentylsulfane (SI-7u). In a flask, 1-pentanethiol[36] (0.22 g, 2.12 mmol) was dissolved in a solution NaOH (1.5 eq) in ethanol (10 mL) and the reaction was stirred at 0°C for 10 minutes. 1-bromopentane (1.2 eq) was added and the reaction was stirred for 12 h at room temperature. The solvent was removed under reduced pressure and the crude was redissolved in DCM. Water was added, and the biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with DCM (4 times). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to obtain the crude thioether. The product was purified through SiO_2 column chromatography using hexanes:EtOAc (100:0 - 99:01 v/v) solvent system. Pure **(SI-7u)** was obtained as a oil with a yield of 67% (0.25 g).



di-benzylsulfane (SI-7v). In a flask, benzyl mercaptan (0.65 g, 5.23 mmol) was dissolved in a solution NaOH (1.5 eq) in ethanol (10 mL) and the reaction was stirred at -10°C for 10 minutes. Benzyl bromide (1.2 eq) was added, and the reaction was stirred for 12 h at room temperature. The solvent was removed under reduced pressure and the crude was redissolved in DCM. Water was added, and the biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was

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[36] Synthetized according: Z. Li, Z. Wu, F. Luo, *J. Agric. Food Chem.,* **53**, 2015, 3872-3876.

extracted with DCM (4 times). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to obtain the crude thioether. The product was purified through SiO_2 column chromatography using hexanes:EtOAc (100:0 - 90:10 v/v) solvent system. Pure **(SI-7v)** was obtained as an oil with a yield of 73% (0.82 g).

8. General procedure for the synthesis of sulfoxides (5f-r) from thioethers.

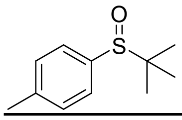
Procedure a.[37] In a flask, the corresponding thioether (1 eq) was dissolved in 2,2,2-trifluoroethanol (2 M) and cooled at 0° C using an ice bath. A solution of 30% H_2O_2 (1.7 eq) was then added slowly in one portion. The reaction mixture was warm at room temperature and stirred for 20 h. Sodium sulfite (1.7 eq) was added and the reaction was stirred for 30 minutes more. The mixture was filtered on celite, dry over Na_2SO4 and concentrated under reduced pressure. The material was purified through SiO_2 column chromatography.

Procedure b. In a flask, the corresponding thioether (1 eq) was dissolved in CH_3CN (0.05 M) and cooled at 0° C using an ice bath. Oxone® (0.9 eq) was then added slowly in one portion. The reaction mixture was stirred overnight. Subsequently, the mixture was cooled at 0 °C and was treated with a saturated solution of $NaHCO_3$ until pH=8. The ice bath was removed, and the biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous was extracted with EtOAc (4 times). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to obtain the crude sulfoxide. The material was purified through SiO_2 column chromatography.

Procedure c. In a flask, the corresponding thioether (1 eq) was dissolved in MeOH (0.5 M) and cooled at 0° C using an ice bath. A solution of 30% H_2O_2 (4 eq) was added dropwise. The mixture was stirred overnight at room temperature. Subsequently, the reaction was cooled at 0 °C, the mixture was treated with a saturated solution of $NaHCO_3$ until pH=8. The ice bath was removed, and the biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous was extracted with EtOAc (4 times). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to obtain the crude sulfoxide. The material was purified through SiO_2 column chromatography.

Procedure d. In a flask, the corresponding thioether (1 eq) was dissolved in DCM (0.1 M) and cooled at 0° C using an ice bath. *m*-CPBA (1.1 eq) was added slowly in one portion. The reaction mixture was stirred overnight. Subsequently, while maintaining the temperature at 0 °C, the mixture was treated with a saturated solution of $NaHCO_3$ until pH=8. The ice bath was removed, and the biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous was extracted with DCM (4 times). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to obtain the crude sulfoxide. The material was purified through SiO_2 column chromatography.

Procedure e. In a flask, the corresponding thioether (1 eq) was dissolved in AcOH (1 M) and cooled at 0° C using an ice bath. A solution of 30% H_2O_2 (4 eq) was then added dropwise. The reaction mixture was stirred for 30 minutes. Subsequently, while maintaining the temperature at 0 °C, the mixture was treated with a saturated solution of NaOH (1 N) until pH=8. The ice bath was removed, and the biphasic mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous was extracted with EtOAc (4 times). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to obtain the crude sulfoxide. The material was purified through SiO_2 column chromatography.



1-(*tert*-butylsulfinyl)-4-methylbenzene (5f) was synthesized from *tert*-butyl(p-tolyl)sulfane (1.19 g, 6.6 mmol) using the procedure a. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (80:20 v/v) solvent

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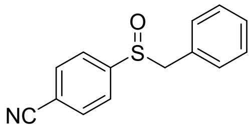
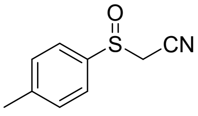
[37] F. Gelat, J. F. Lohier, A. C. Gaumont, S. Perrio, *Adv. Synth. Catal.*, **357**, 2015, 2011-2016.

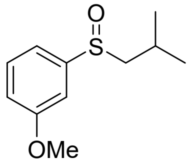
system. Pure **5f** was obtained as a solid with a yield of 98% (1.26 g). The spectral characteristics of the purified **5f** were similar to those of previously synthesized material.[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 1.16 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 136.7, 129.2, 126.4, 55.8, 22.9, 21.6 ppm.



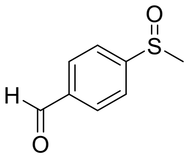
4-(benzylsulfinyl)benzonitrile (5g) was synthesized from 4-(benzylthio)benzonitrile[11] (0.51 g, 2.25 mmol) using the procedure b. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (80:20 v/v) solvent system. Pure **5g** was obtained as a solid with a yield of 12% (0.06 g). The spectral characteristics of the purified **5g** were similar to those of previously synthesized material.[38] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.24 (m, 3H), 6.95 (d, *J* = 6.9 Hz, 2H), 4.08 (dd, *J* = 12.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 132.4, 130.4, 128.8, 128.7, 128.1, 125.3, 117.9, 114.9, 63.2 ppm.



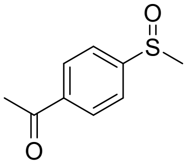
2-(*p*-tolylsulfinyl)acetonitrile (5h) was synthesized from 2-(*p*-tolylthio) acetonitrile (**SI-7h**, 0.29 g, 1.75 mmol) using the procedure c. The product was purified through SiO_2 radial chromatography using a hexanes:EtOAc (80:20 v/v) solvent system. Pure **5h** was obtained as a solid with a yield of 94% (0.29 g). The spectral characteristics of the purified **5h** were similar to those of previously synthesized material.[39] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 3.75 (d, *J* = 15.7 Hz, 1H), 3.65 (d, *J* = 15.7 Hz, 1H), 2.46 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 138.3, 130.6, 124.3, 111.2, 44.9, 21.7 ppm. Mp. 67 -69 °C (lit.[40] 72 – 73 °C).



1-(isobutylsulfinyl)-3-methoxybenzene (5j). was synthesized from Isobutyl(3-methoxyphenyl)sulfane using the procedure d. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (80:20 v/v) solvent system. Pure **5j** was obtained as a oil with a yield of 97% (0.58 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 1H), 7.26 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.13 (ddd, *J* = 7.6, 1.6, 0.9 Hz, 1H), 7.01 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 3.87 (s, 3H), 2.85 (dd, *J* = 12.9, 4.9 Hz, 1H), 2.47 (dd, *J* = 12.9, 9.3 Hz, 1H), 2.30 – 2.18 (m, 1H), 1.17 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 146.2, 130.3, 117.6, 116.1, 108.4, 67.7, 55.7, 24.4, 22.9, 21.8 ppm. IR (ATR) ν 1247 (-S=O). MS (ESI/SQ) m/z: $[M+H]^+$ Calculated for $C_{11}H_{17}O_2S$ 213.1; found 213.1.



4-(Methylsulfinyl)benzaldehyde (5o) was synthesized from 4-(benzylthio)benzonitrile (75 mg, 0.49 mmol) using the procedure c. The product was purified through SiO_2 radial chromatography using a hexanes:EtOAc (10:90 v/v) solvent system. Pure **5o** was obtained as a solid with a yield of 86% (71 mg). The spectral characteristics of the purified **5o** were similar to those of previously synthesized material.[41] ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 2.79 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 152.5, 138.3, 130.5, 124.3, 43.9 ppm. Mp. 84 – 86 °C (lit[36] 88 – 89 °C).



4-(Methylsulfinyl) phenyl)ethan-1-one (5p) was synthesized from 1-(4-(methylthio)phenyl)ethan-1-one (86 mg, 0.52 mmol) using the procedure e. The product was purified through SiO_2 radial chromatography using a hexanes:EtOAc (10:90 v/v) solvent system. Pure **5p** was obtained as a solid with a yield of 69% (66 mg). The spectral characteristics of the purified **5p** were similar to those of

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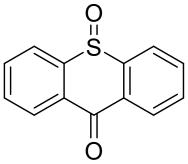
[38] I. Sorribes, A. Corma, *Chem. Sci.* 10, 2019, 3130-3142.

[39] M. Rodríguez Rivero, J. C. Carretero, *J. Org. Chem.*, **68**, 2003, 2975-2978.

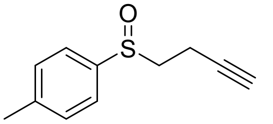
[40] T. Numata, O. Itoh, T. Yoshimura, S. Oae, *Bull. Chem. Soc. Jpn.,* **56**, 1983, 257-265

[41]. Y. Xie, Y. Li, S. Zhou, S. Zhou, Y. Zhang, M. Chen, Z. Li, *Synlett*, **29**, 2018, 340-343.

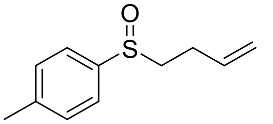
previously synthesized material.[42] ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 2.76 (s, 3H), 2.66 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.1, 151.1, 139.3, 129.3, 123.9, 44.0, 26.9 ppm. Mp. 126 – 128 °C (lit.[37] 128 – 130 °C).



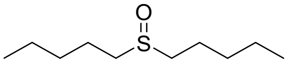
9*H*-thioxanthen-9-one 10-oxide (5q) was synthesized from 9*H*-thioxanthen-9-one (0.407 g, 1.92 mmol) using the procedure d. The product was purified through SiO$_2$ radial chromatography using a hexanes:EtOAc (70:30 v/v) solvent system. Pure **5q** was obtained as a solid with a yield of 69% (0.304 g). The spectral characteristics of the purified **5q** were similar to those of previously synthesized material.[43] ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.38 (ddd, *J* = 7.8, 1.4, 0.5 Hz, 2H), 8.19 (ddd, *J* = 7.8, 1.2, 0.5 Hz, 2H), 7.87 (ddd, *J* = 7.8, 7.4, 1.3 Hz, 2H), 7.74 (ddd, *J* = 7.8, 7.4, 1.2 Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$) δ 180.0, 145.1, 133.9, 131.5, 129.5,128.7, 127.2 ppm. Mp. 199 – 201 °C (lit[44] 199 – 201 °C).



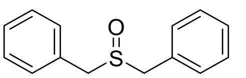
1-(but-3-yn-1-ylsulfinyl)-4-methylbenzene (5s) was synthesized from but-3-in-1-yl(p-tolyl)sulfane (**SI-7s**, 0.17 g, 0.97 mmol) using the procedure c. The product was purified through SiO$_2$ radial chromatography using a hexanes:Et$_2$O:DCM (70:15:15 v/v/v) solvent system. Pure **5s** was obtained as a solid with a yield of 78% (0.45 g). The spectral characteristics of the purified **5s** were similar to those of previously synthesized material.[40] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 3.02 – 2.88 (m, 2H), 2.75 – 2.67 (m, 1H), 2.44 – 2.36 (m, 1H), 2.42 (s, 3H), 2.02 (t, *J* = 2.67 Hz, 1H) p pm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.9, 139.8, 130.2, 124.2, 80.9, 70.5, 55.3, 21.6, 12.2 ppm. p. 42 – 44 °C.



1-(But-3-en-1-ylsulfinyl)-4-methylbenzene (5t) was synthesized from but-3-en-1-yl(p-tolyl)sulfane (**SI-7t**, 0.70 g, 3.93 mmol) using the procedure c. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (80:20 v/v) solvent system. Pure **5t** was obtained as an oil with a yield of 60% (0.45 g). The spectral characteristics of the purified **5t** were similar to those of previously synthesized material.[45] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.85 – 5.74 (ddt, 16.9, 10.0, 6.6 Hz, 1H), 5.13 – 5.05 (m, 2H), 2.86 – 2.82 (dd, *J* = 7.92 Hz, 2H), 2.56 – 2.43 (m, 1H), 2.42 (s, 3H), 2.38 – 2.28 (m, 1H) ppm. ^{13}C NRM (100 MHz, CDCl$_3$) δ 141.6, 140.6, 135.1,130.1, 124.2, 117.1, 56.3, 26.4, 21.5 ppm.



1-(pentylsulfinyl)pentane (5u) was synthesized from di-*n*-pentylsulfane (**SI-7u**, 0.24 g, 1.41 mmol) using the procedure e. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (100:00 - 80-20 v/v) solvent system. Pure **5u** was obtained as a oil with a yield of 78% (0.21 g). The spectral characteristics of the purified **5v** were similar to those of previously synthesized material.[46] ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.75 (t, *J* = 7.0 Hz, 4H), 1.78 (q, *J* = 7.0 Hz, 4H), 1.40 – 1.10 (m, 8H), 0.95 (t, *J* = 6.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.3, 31.3, 29.6, 22.5, 14.1 ppm.



(sulfinylbis(methylene))dibenzene (5v) was synthesized from di-benzylsulfane (**SI-7v**, 0.80 g, 3.73 mmol) using the procedure d. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (80:20 v/v) solvent system. Pure **5v** was obtained as a solid with a yield of 91% (0.79 g). The spectral characteristics of the purified **5v** were similar to those of previously synthesized material.[47] ^{1}H NMR

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[42]. S. Gan, J. Yin, Y. Yao, Y. Liu, D. Chang, D. Zhu, L. Shi, *Org. Biomol. Chem.,* **15**, 2017, 2647-2654.

[43]. S. Amriou, C. Wang, A. S. Batsanov, M. R. Bryce, D. F. Perepichka, E. Ortí, ... & C. Rovira, *Chem. Eur. J.,* **12**, 2006, 3389-3400.

[44] K. Bahrami, M. M. Khodaei, M. Sheikh Arabi, *J. Org. Chem.,* **75**, 2010, 6208-6213.

[45] C. R. Emerson, L. N. Zakharov, P. R. Blakemore, *Chem. Eur. J.,* **19**, 2013, 16342-16356.

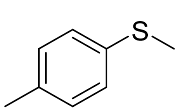
[46] A. Maercker, R. Schuhmacher, W. Buchmeier, H. D. Lutz, *Chem. Ber.*, **124**, 1991, 2489-2498.

[47] H. Yu, Z. Li, C. Bolm, *Org. Lett.,* **20**, 2018, 2076-2079.

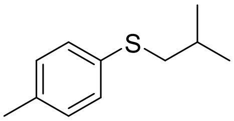
(400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 6H), 7.32 – 7.26 (m, 4H), 3.93 (d, *J* = 13.0 Hz, 2H), 3.87 (d, *J* = 13.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.3, 129.1, 128.5, 57.4 ppm. Mp. 132 – 134 °C (lit.[48] 128 – 130 °C).

9. General procedure for the synthesis of thioeters (6a-v) from sulfoxides (5a-v)

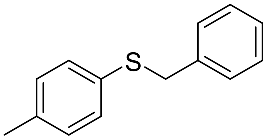
In a high-precision glass vial (Biotage®), formic acid (10 eq) and potassium iodide (20% mol) were sequentially added to the corresponding sulfoxide (1 eq). The vial was properly sealed and subjected to microwave irradiation in a Biotage® reactor to the corresponding temperature and time. After the required time, the mixture was cooled under ice bath and then was treated with a cold $Na_2S_2O_3$ solution until pH= 8. The solution was dissolved in EtOAc and transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with EtOAc three times. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure, and the crude product was purified through SiO_2 column chromatography.



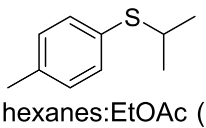
Methyl(*p*-tolyl)sulfane (6a) was synthesized from 1-(methylsulfinyl)-4-methylbenzene (**5a,** 206 mg, 1.34 mmol) using the general procedure at 100° C for 2 h. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (99:01 v/v) solvent system. Pure **6a** was obtained as a colorless oil with a yield of 81% (150 mg). The spectral characteristics of the purified **6a** were similar to those of previously synthesized material.[49] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H), 2.32 (s, 3H) ppm. ^{13}C NRM (100 MHz, $CDCl_3$) δ 135.2, 134.8, 129.7, 127.4, 21.0, 16.7 ppm.



Isobutyl(*p*-tolyl)sulfane (6b) was synthesized from 1-(isobutylsulfinyl)-4-methylbenzene (**5b,** 212 mg, 1.08 mmol) using the general procedure at 100° C for 2 h. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (99:01 v/v) solvent system. Pure **6b** was obtained as a colorless oil with a yield of 86% (168 mg). The spectral characteristics of the purified **6b** were similar to those of previously synthesized material.[50] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 2.79 (d, *J* = 6.9 Hz, 2H), 2.33 (s, 3H), 1.85 (nonet, *J* = 6.8 Hz, 1H), 1.04 (d, *J* = 6.7 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) 135.8, 133.7, 129.8, 129.7, 43.5, 28.4, 22.1, 21.2 ppm.



Benzyl(*p*-tolyl)sulfane (6c) was synthesized from 1-(benzylsulfinyl)-4-methylbenzene (**5c,** 115 mg, 0.50 mmol) using the general procedure at 100 °C for 2 h and using 20 eq of HCO_2H. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (99:01 v/v) solvent system. Pure **6c** was obtained as a colorless oil with a yield of 92% (98 mg). The spectral characteristics of the purified **6c** were similar to those of previously synthesized material.[43] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.13 (m, 7H), 7.00 – 6.99 (d, *J* = 8.0 Hz, 2H), 4.00 (s, 2H), 2.24 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 136.7, 132.6, 130.8, 129.7, 129.0, 128.5, 127.2, 39.9, 21.2 ppm.



Isopropyl(*p*-tolyl)sulfane (6d) was synthesized from 1-(isopropylsulfinyl)-4-methylbenzene (**5d,** 238 mg, 1.30 mmol) using the general procedure at 100° C for 3 h. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (98:02 v/v) solvent system. Pure **6d** was obtained as a colorless oil with a yield of

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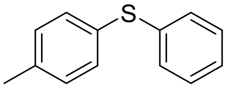
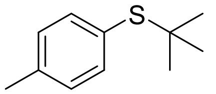
[48] A. A. Manesh, F. H. Eshbala, S. Hemmati, H. Veisi, *RSC Adv.*, **5**, 2015, 70265-70270.
[49] R. Ma, A. H. Liu, C. B. Huang, X. D. Li, L. N. He, *Green Chem.,* **15**, 2013, 1274-1279.
[50] P. R. Blakemore, M. S. Burge, *J. Am. Chem. Soc.*, **129**, 2007, 3068-3069.

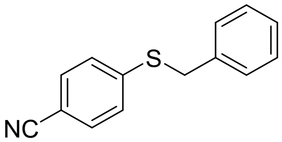
87% (190 mg). The spectral characteristics of the purified **6d** were similar to those of previously synthesized material.[51] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 2H), 7.02 – 7.00 (m, 2H), 3.20 (hept, J = 6.7 Hz, 1H), 2.24 (s, 3H), 1.18 (d, J = 6.7 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 132.9, 131.7, 129.7, 38.8, 23.3, 21.2 ppm.



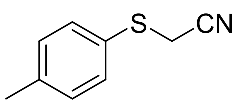
Phenyl(p-tolyl)sulfane (6e) was synthesized from 1-(phenylsulfinyl)-4-methylbenzene (**5e,** 76 mg, 0.35 mmol) following the general procedure at 100° C for 4 h and using 15 eq of HCO_2H. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (99:01 v/v) solvent system. Pure **6e** was obtained as a colorless oil with a yield of 99% (69 mg). The spectral characteristics of the purified **6e** were similar to those of previously synthesized material.[52] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.29 (m, 2H), 7.26 – 7.24 (m, 4H), 7.20 – 7.17 (m, 1H), 7.13 (d, J = 8.0 Hz, 2H), 2.33 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 137.3, 132.4, 131.4, 130.2, 129.9, 129.2, 126.5, 21.3 ppm.



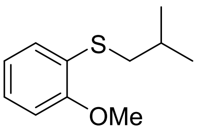
***tert*-butyl(*p*-tolyl)sulfane (6f)** was synthesized from 1-(*tert*-butylsulfinyl)-4-methylbenzene (**5f,** 273 mg, 1.39 mmol) using the general procedure at 100° C for 4 h. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (95:05 v/v) solvent system. Pure **6f** was obtained as a colorless oil with a yield of 88% (221 mg). The spectral characteristics of the purified **6f** were similar to those of previously synthesized material.[53] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 2.36 (s, 3H), 1.27 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 137.6, 129.4, 129.3, 45.7, 31.0, 21.4 ppm.



4-(benzylthio)benzonitrile (6g) was synthesized from 4-(benzylsulfinyl)benzonitrile (**5g,** 50 mg, 0.29 mmol) following the general procedure at 100° C for 4 h. The product was purified through SiO_2 radial chromatography using a hexanes:EtOAc (90:10 v/v) solvent system. Pure **6g** was obtained as a brown solid with a yield of 84% (40 mg). The spectral characteristics of the purified **6g** were similar to those of previously synthesized material.[34] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.5 Hz, 2H), 7.36 – 7.25 (m, 7H), 4.19 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 135.9, 132.4, 128.9, 128.8, 127.9, 127.5, 119.0, 108.7, 37.3 ppm. Mp. 81 – 82 °C (lit.[54] 74 – 75 °C).



2-(*p*-tolylthio)acetonitrile (6h) was synthesized from 2-(*p*-tolylsulfinyl)acetonitrile (**5h,** 56 mg, 0.31 mmol) following the general procedure at 100° C for 4 h. The product was purified through SiO_2 radial chromatography using a hexanes:EtOAc (90:10 v/v) solvent system. Pure **6h** was obtained as a colorless oil with a yield of 81% (42 mg). The spectral characteristics of the purified **6h** were similar to those of previously synthesized material.[55] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 3.51 (s, 2H), 2.36 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 133.4, 130.5, 128.5, 116.8, 22.2, 21.4 ppm.



Isobutyl(2-methoxyphenyl)sulfane (6i) was synthesized from 1-(isobutylsulfinyl)-2-methoxybenzene (**5i,** 42 mg, 0.20 mmol) following the general procedure at 100° C for 2 h. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (95:05 v/v) solvent system. Pure **6i** was

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[51] X. Zhao, X. Zheng, B. Yang, J. Sheng, K. Lu, *Org. Biomol. Chem.*, **16**, 2018, 1200-1204.

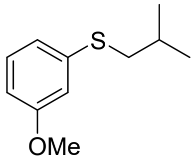
[52] K. D. Jones, D. J. Power, D. Bierer, K. M. Gericke, S. G. Stewart, *Org. Lett.,* **20**, 2017, 208-211.

[53] X. Zhao, X. Zheng, B. Yang, J. Sheng, K. Lu, *Org. Biomol. Chem.*, **16**, 2018, 1200-1204.

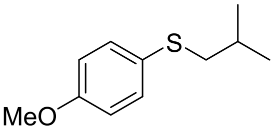
[54] G. A. Russell, J. M. Pecoraro, *J. Org. Chem.*, **44**, 1979, 3990-3991.

[55] N. P. Ramirez, B. König, J. C. Gonzalez-Gomez, *Org. Lett.,* **21**, 2019*,* 1368-1373.

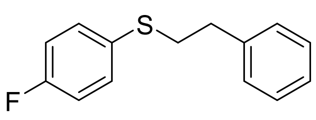
obtained as a solid with a yield of 84% (32 mg). The spectral characteristics of the purified **6i** were similar to those of previously synthesized material.[56] ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.24 (dd, J = 7.6, 1.6 Hz, 1H), 7.15 (td, J = 8.1, 1.7 Hz, 1H), 6.92 (td, J = 7.6, 1.2 1H), 6.84 (dd, J = 7.9, 1.1 Hz, 1H), 3.89 (s, 3H), 2.77 (d, J = 6.8 Hz, 2H), 1.93 – 1.83 (dhep, J = 13.4, 6.7 Hz, 1H), 1.05 (d, J = 6.7 Hz, 6H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$) δ 157.2, 128.7, 126.6, 125.7, 121.1, 110.5, 55.9, 41.0, 28.3, 22.4 ppm. Mp. 36 – 38 °C. IR (ATR) v 2868 (-C-S-). MS (ESI/SQ) m/z: [M+H]$^+$ Calculated for $C_{11}H_{17}OS$ 197.1; found 197.1.



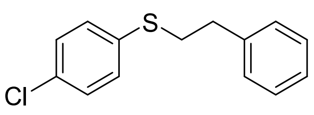
Isobutyl(3-methoxyphenyl)sulfane (6j) was synthesized from 1-(isobutylsulfinyl)-4-methoxybenzene (**5j,** 276 mg, 1.13 mmol) following the general procedure at 100° C for 2 h. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (90:10 v/v) solvent system. Pure **6j** was obtained as a colorless oil with a yield of 87% (223 mg). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.17 (t, J = 8.0 Hz, 1H), 6.90 – 6.86 (m, 2H), 6.69 (d, J = 8.0, 2.5 Hz, 1H), 3.79 (s, 3H), 2.80 (d, J = 6.8 Hz, 2H), 1.95 -1.83 (m, 1H), 1.03 (d, J = 6.7 Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ 159.9, 138.9, 129.7, 120.9, 114.2, 111.3, 55.4, 42.5, 28.4, 22.2 ppm. IR (ATR) v 2955 (-C-S-). MS (ESI/ QTOF) m/z: [M+H]$^+$ Calculated for $C_{11}H_{17}OS$ 197.1; found 197.1.



Isobutyl(4-methoxyphenyl)sulfane (6k) was synthesized from 1-(isobutylsulfinyl)-4-methoxybenzene (**5k,** 30 mg, 0.14 mmol) following the general procedure at 100° C for 2 h. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (95:05 v/v) solvent system. Pure **6k** was obtained as a colorless oil with a yield of 89% (24 mg). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H), 2.71 (d, J = 6.9 Hz, 2H), 1.78 (dhep, J = 13.4, 6.7 Hz, 1H), 1.00 (d, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 158.8, 132.9, 127.6, 114.6, 55.5, 45.1, 28.4, 22.1 ppm. MS (ESI/QTOF) m/z: [M+H]$^+$ Calculated for $C_{11}H_{17}OS$ 197.1; found 197.1.



(4-Fluorphenyl(phenethyl)sulfane (6l) was synthesized from 1-fluor-4-(phenethylsulfinyl)lbenzene (**5l,** 180 mg, 0.73 mmol) following the general procedure at 100° C for 2 h. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (95:05 v/v) solvent system. Pure **6l** was obtained as a colorless oil with a yield of 96% (162 mg). The spectral characteristics of the purified **6l** were similar to those of previously synthesized material..[57] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.34 (m, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 7.02 – 6.98 (m, 2H), 3.11 (dd, J = 9.0, 6.7 Hz , 2H), 2.88 (dd, J = 9.0, 6.7 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.9 (d, J = 246.3 Hz), 140.2, 132.5 (d, J = 9.0 Hz), 131.3 (d, J = 3.4 Hz), 128.7 (d, J = 2.2 Hz), 126.6, 116.2 (d, J = 21.9 Hz), 36.6, 35.9 ppm.



(4-Chlorophenyl(phenethyl)sulfane (6m) was synthesized from 1-chloro-4-(phenethylsulfinyl)lbenzene (**5m,** 126 mg, 0.48 mmol) following the general procedure at 100° C for 2 h. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (98:02 v/v) solvent system. Pure **6m** was obtained as a colorless oil with a yield of 100% (118 mg). The spectral characteristics of the purified **6m** were similar to those of previously synthesized material.[58] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.17 (m, 9H), 3.14 (dd, J = 8.9, 6.8 Hz, 2H), 2.91 (dd J = 8.9, 6.7 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.1, 135.1, 132.1, 130.7, 129.2, 128.7, 128.6, 126.7, 35.6, 35.3 ppm.

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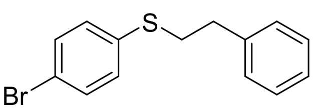
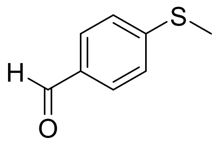
[56] K. D. Jones, D. J. Power, D. Bierer, K. M. Gericke, S. G. Stewart, *Org. Lett.,* **20**, 2017, 208-211.

[57] Y. Chen, R. He, H. Song, G. Yu, C. Li, Y. Liu, Q. Wang, *Eur. J. Org. Chem.,* 2021, 1179-1183.

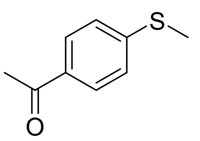
[58] B. Movassagh, A. Yousefi, *Monatsh. Chem.,* **146**, 2015, 135-142.



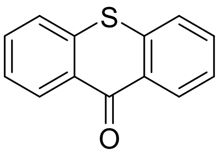
(4-Bromophenyl(phenethyl)sulfane (6n) was synthesized from 1-bromo-4-(phenethylsulfinyl)lbenzene (**5n,** 213 mg, 0.69 mmol) following the general procedure at 100° C for 2 h. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (98:02 v/v) solvent system. Pure **6n** was obtained as a colorless oil with a yield of 98% (198 mg). The spectral characteristics of the purified **6n** were similar to those of previously synthesized material.[59] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, J = 8.6 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.25 – 7.17 (m, 5H), 3.14 (dd, J = 9.0, 6.9 Hz, 2H), 2.91 (dd, J = 9.0, 6.9 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.0, 135.8, 132.1, 130.8, 128.7, 128.6, 126.7, 119.9, 35.6, 35.3 ppm.



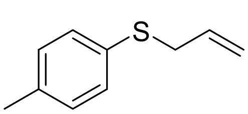
4-(Methylthio)benzaldenyde (6o) was synthesized from 4-(methylsulfinyl)benzaldehyde (**5o,** 52 mg, 0.31 mmol) following the general procedure at 100° C for 2 h. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (90:10 v/v) solvent system. Pure **6o** was obtained as an oil with a yield of 86% (40 mg). The spectral characteristics of the purified **6o** were similar to those of previously synthesized material.[60] ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.92 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 2.54(s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 191.4, 148.0, 133.1, 130.1, 125.3, 14.8 ppm.



1-(4-(methylthio)phenyl)ethan-1-one (6p) was synthesized from 1-(4-(methylsulfinyl)phenyl)ethan-1-one (**5p,** 66 mg, 0.36 mmol) following the general procedure at 100° C for 2h. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (90:10 v/v) solvent system. Pure **6p** was obtained as a colorless oil with a yield of 87% (52 mg). The spectral characteristics of the purified **6p** were similar to those of previously synthesized material.[61] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 2.57 (s, 3H), 2.52 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.3, 146.0, 133.7, 128.9, 125.1, 26.6, 14.9 ppm. Mp. 74 – 76 °C (lit.[62] 71 – 72 °C).



9*H*-thioxanthen-9-one (6q) was synthesized from 9*H*-thioxanthen-9-one-10-oxide (**5q,** 204 mg, 0.89 mmol) following the general procedure at 100° C for 2 h. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (99:01 v/v) solvent system. Pure **6q** was obtained as a colorless oil with a yield of 96% (190 mg). The spectral characteristics of the purified **6q** were similar to those of previously synthesized material.[43] ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.63 – 8.61 (m, 2H), 7.64 – 7.57 (m, 4H), 7.51 – 7.47 (m, 2H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$) δ 180.1, 137.4, 132.4, 130.0, 129.4,126.5, 126.1.ppm. mp. 214 – 216 °C (lit.[63] 213 – 214 °C).



Allyl(*p*-tolyl)sulfane (6r) was synthesized from 1-(Allylsulfinyl)-4-methylbenzene (**5r,** 172 mg, 0.96 mmol) following the general procedure at 100° C for 2 h and using 12 eq of HCO$_2$H. The product was purified through SiO$_2$ column chromatography using a hexanes:EtOAc (gradient 99:01 v/v) solvent system. Pure **6r** was obtained as a colorless oil with a yield of 2% (24 mg). The spectral characteristics of the purified **6r** were similar to those of previously synthesized material.[43] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 (d, J =8.1 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.92 – 5.81 (m, 1H), 5.11 – 5.03 (m, 2H), 3.50 (dt, J = 7.0, 1.1 Hz, 2H), 2.31 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.6, 134.0,

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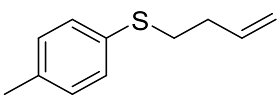
[59]. Y. Shi, Z. Ke, Y. Y. Yeung, *Green Chem.,* **20**, 2018, 4448-4452.

[60]. W. Yin, C. Chu, Q. Lu, J. Tao, X. Liang, R. Liu, *Adv. Synth. Catal.,* **352**, 2010, 113-118.

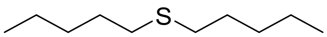
[61] B. Landers, C. Berini, C. Wang, O. Navarro, *J. Org. Chem.,* **76**, 2011, 1390-1397.

[62] J. F. Hooper, A. B. Chaplin, C. Gonzalez-Rodriguez, A. L. Thompson, A. S. Weller, M. C. Willis, *J. Am. Chem. Soc.,* **134**, 2012, 2906-2909.

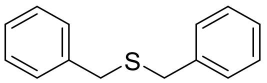
[63] W. E. Truce, J. A. Simms, *J. Org. Chem.,* **22**, 1957, 617-620.



But-3-en-1-yl(*p*-tolyl)sulfane (6t) was synthesized from 1-(but-3-en-1-ylsulfinyl)-4-methylbenzene (**5t,** 50 mg, 0.26 mmol) following the general procedure at 90° C for 2 h. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (95:05 v/v) solvent system. Pure **6t** was obtained as a colorless oil with a yield of 31% (14 mg). The spectral characteristics of the purified **6t** were similar to those of previously synthesized material.[40] ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 5.84 (ddt, 16.9, 10.2, 6.6 Hz, 1H), 5.10 – 5.02 (m, 2H), 2.86 – 2.82 (t, *J* = 7.9 Hz, 2H), 2.39 – 2.33 (m, 2H), 2.32 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 136.3, 132.7, 130.3, 129.8, 116.3, 33.3, 33.6, 21.2 ppm.



di-*n*-pentylsulfane (6u) was synthesized from 1-(pentylsulfinyl)pentane (**5u,** 205 mg, 1.08 mmol) following the general procedure at 100° C for 3 h. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (100:0 - 99:01 v/v) solvent system. Pure **6u** was obtained as a colorless oil with a yield of 91% (171 mg). The spectral characteristics of the purified **6u** were similar to those of previously synthesized material.[64] ^1H NMR (400 MHz, $CDCl_3$) δ 2.50 (t, *J* = 7.0 Hz, 4H), 1.57 (q, *J* = 7.0 Hz, 4H), 1.40 – 1.30 (m, 8H), 0.90 (t, *J* = 6.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.3, 31.3, 29.6, 22.5, 14.1 ppm.



di-benzylsulfane (6v) was synthesized from (sulfinylbis(methylene))dibenzene (**5v,** 272 mg, 1.18 mmol) following the general procedure at 100° C for 3 h. The product was purified through SiO_2 column chromatography using a hexanes:EtOAc (100:0 - 90:10 v/v) solvent system. Pure **6v** was obtained as a colorless oil with a yield of 95% (140 mg). The spectral characteristics of the purified **6v** were similar to those of previously synthesized material.[65] ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 10H), 3.60 (s, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 129.1, 128.6, 127.1, 35.8 ppm.

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[64] Wang, M. L., & Tseng, Y. H. (2004). Synthesis of thioether using dimethyloctyl (3-sulfopropyl) ammonium betaine and di-active site quaternary ammonium salt as new phase-transfer catalysts. *Reaction Kinetics and Catalysis Letters*, *82*, 81-87.

[65] M. L. Wang, Y. H. Tseng, *React. Kinet. Catal. Lett.*, **82**, 2004, 81-87.

10. NMR spectra of compounds.

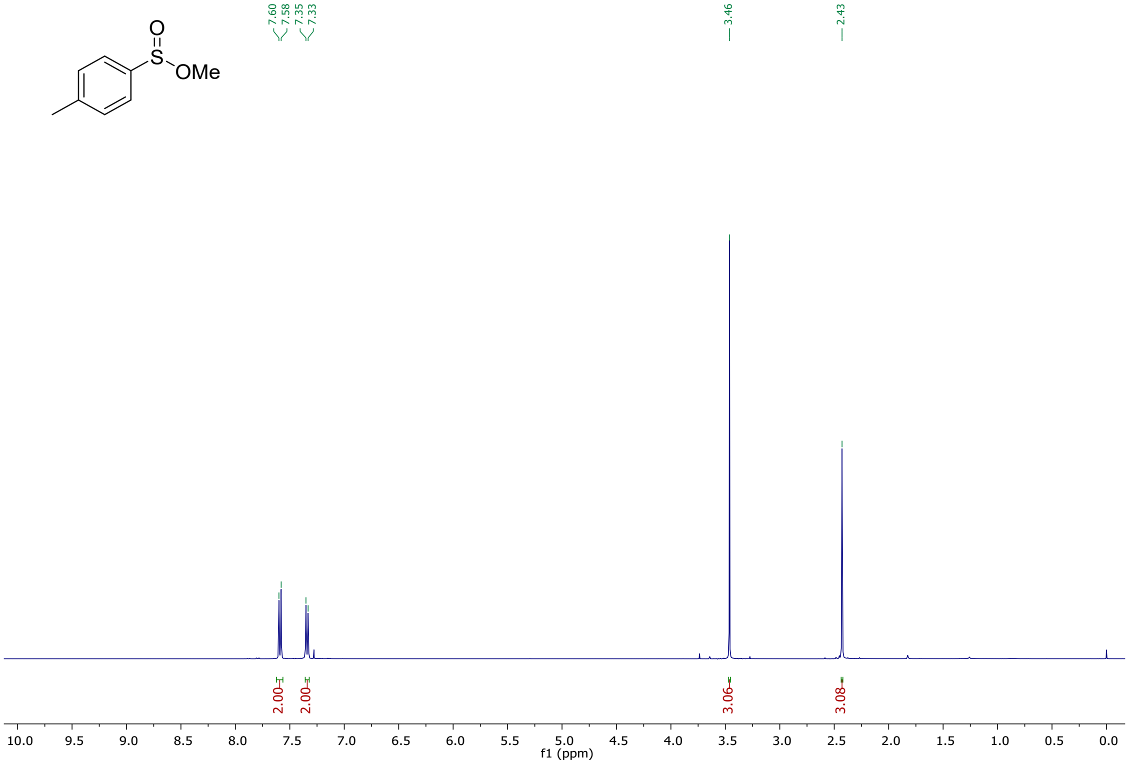

Figure S1. ^{1}H-NMR spectra of compound **1a**.

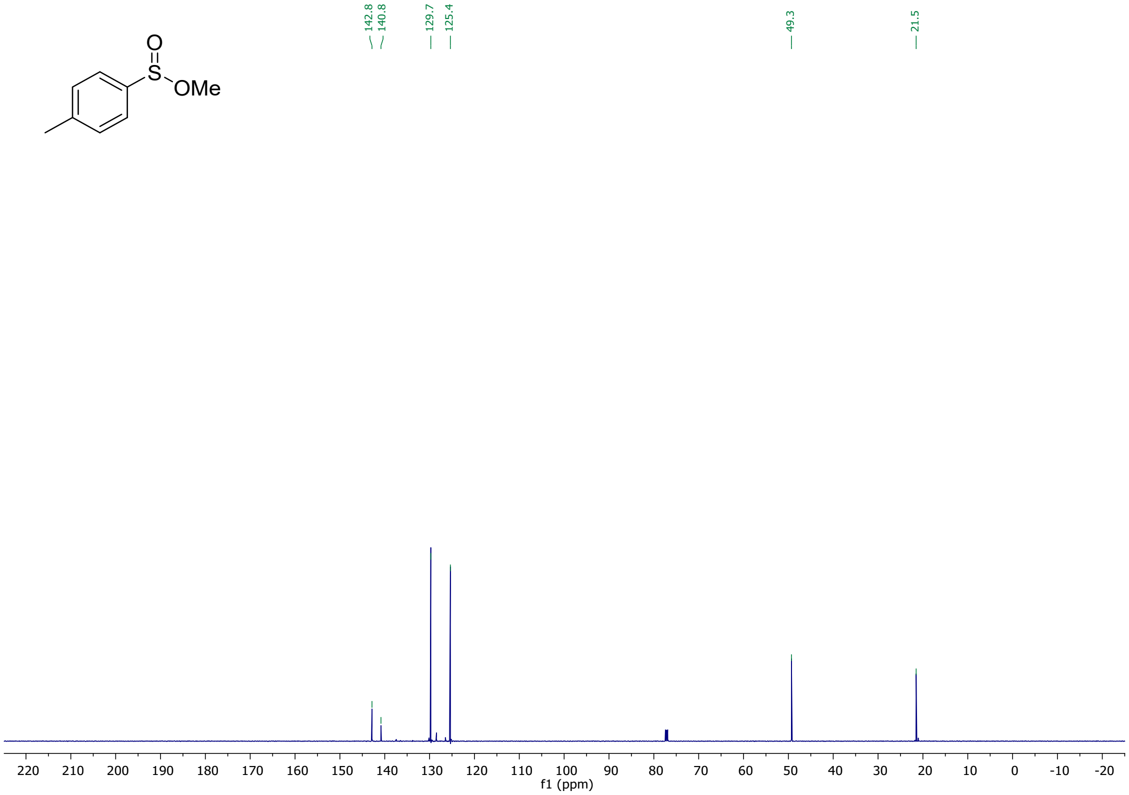

Figure S2. ^{13}C-NMR spectra of compound **1a**.

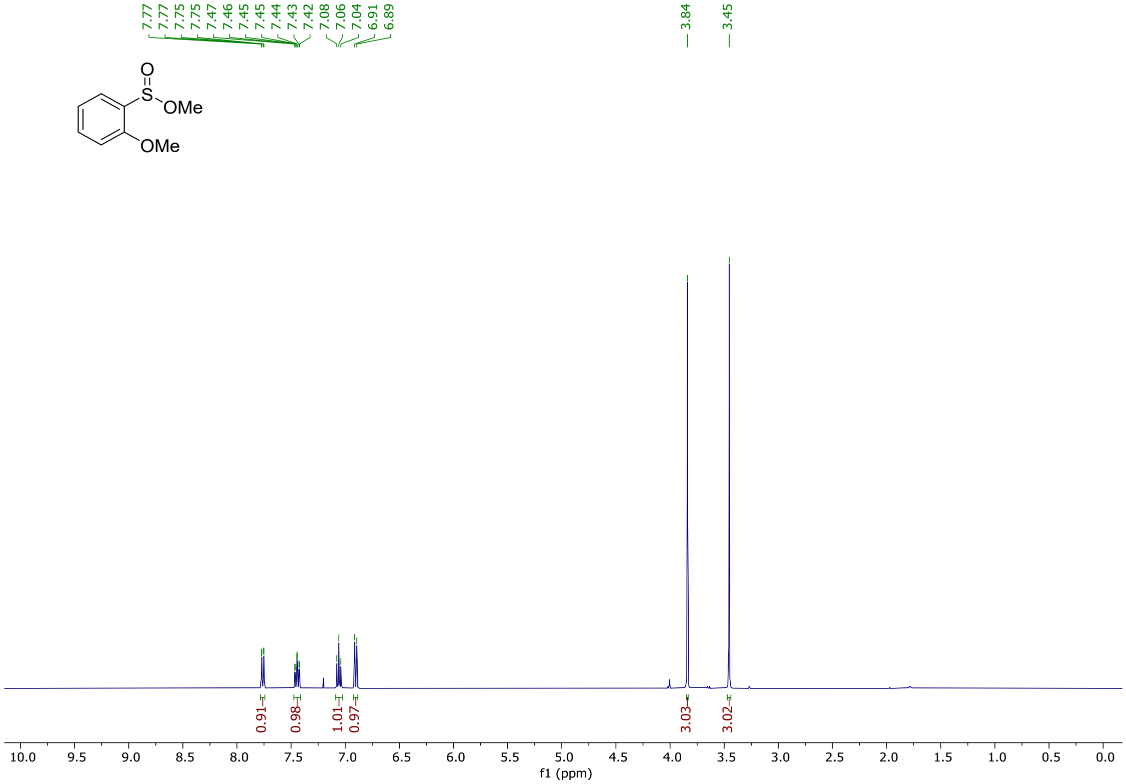

Figure S3. ^{1}H-NMR spectra of compound **1b**.

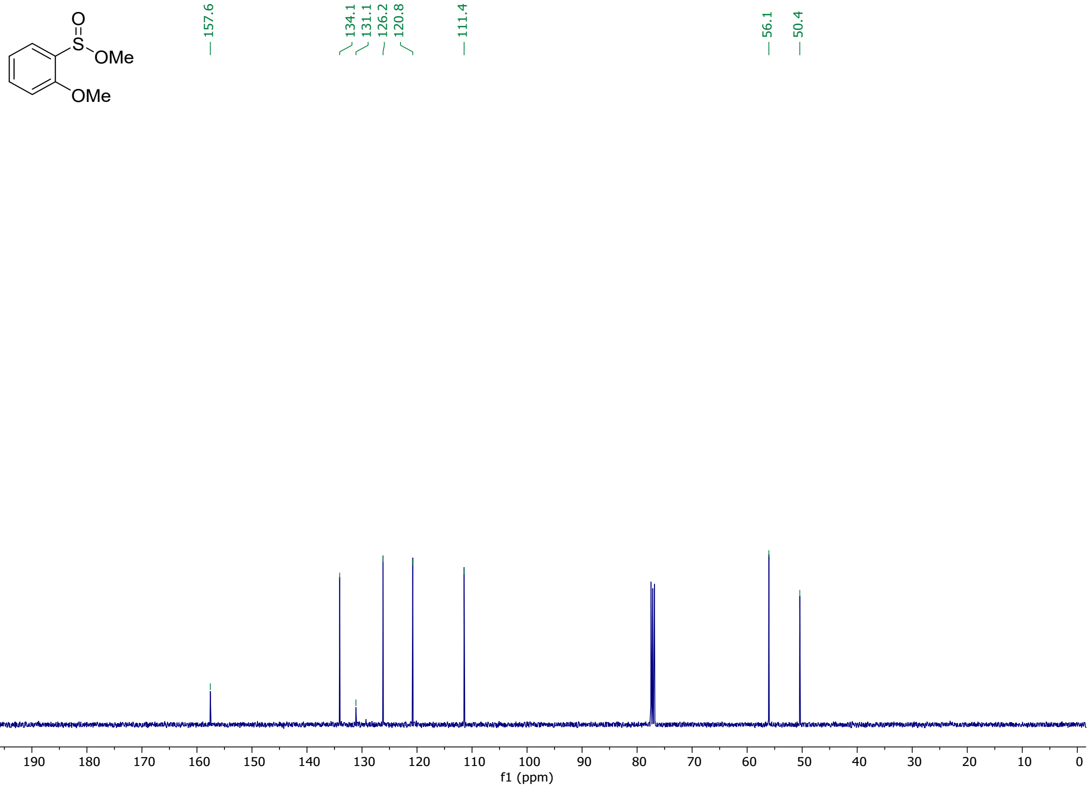

Figure S4. ^{13}C-NMR spectra of compound **1b**.

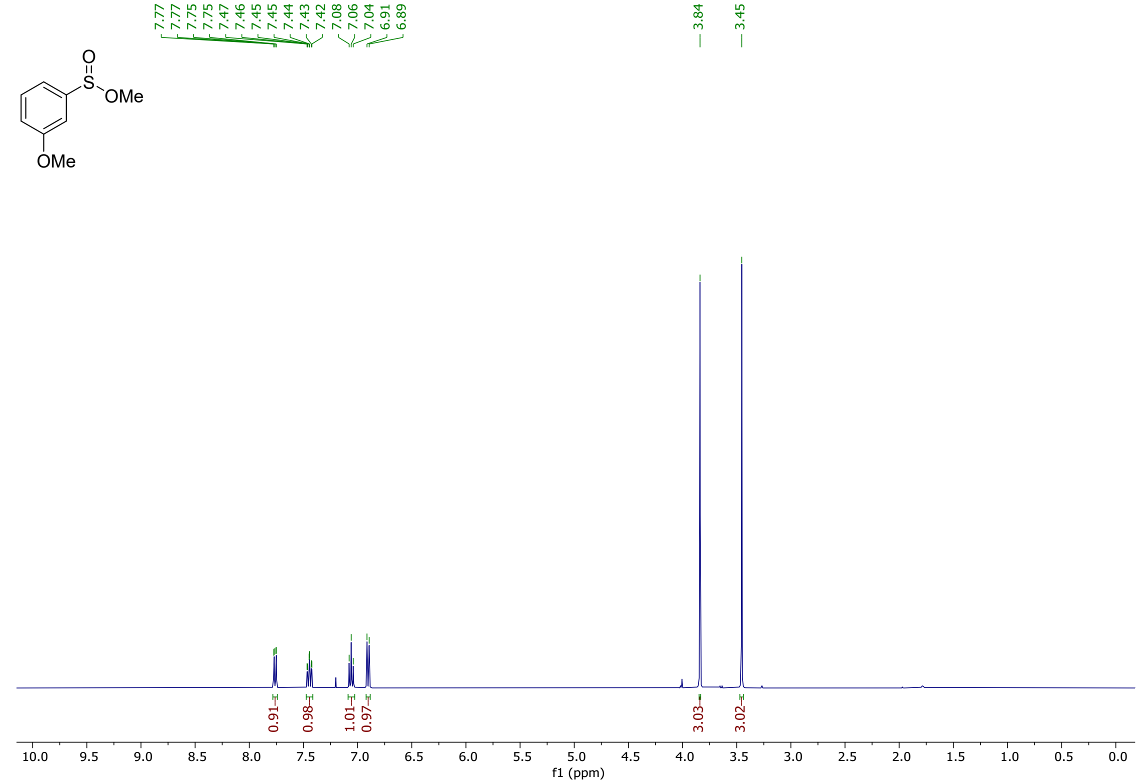

Figure S5. ^{1}H-NMR spectra of compound **1c**.

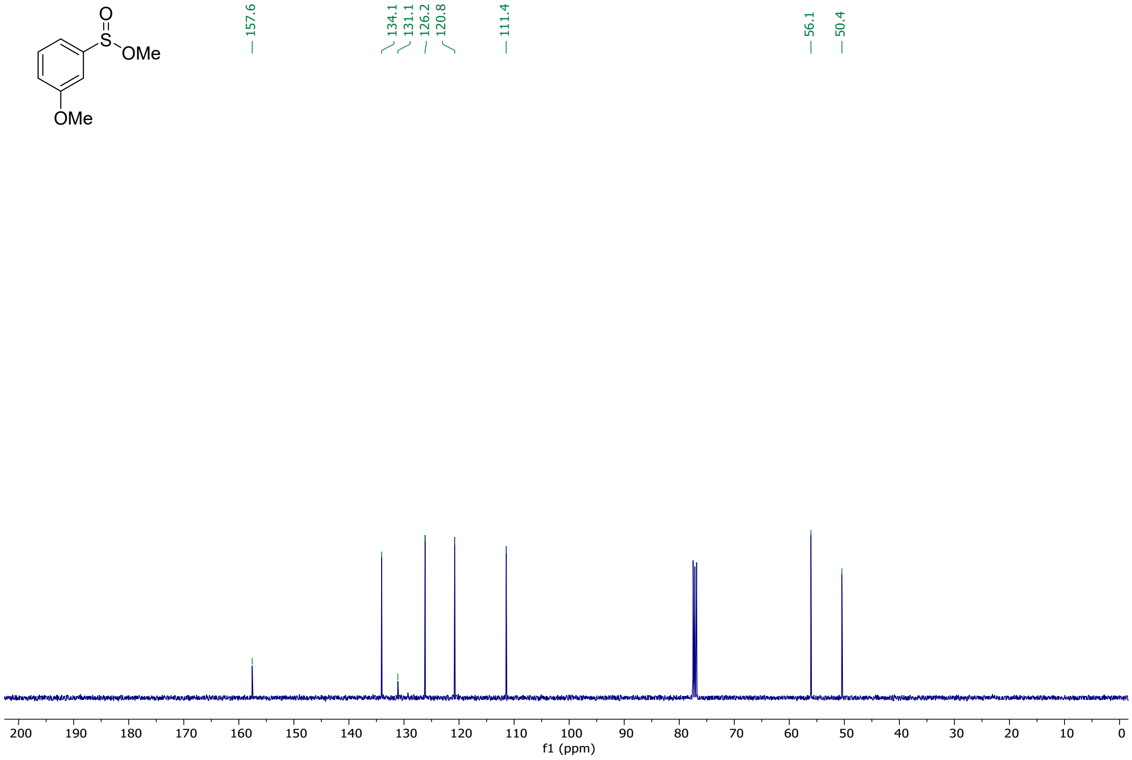

Figure S6. ^{13}C-NMR spectra of compound **1c**.

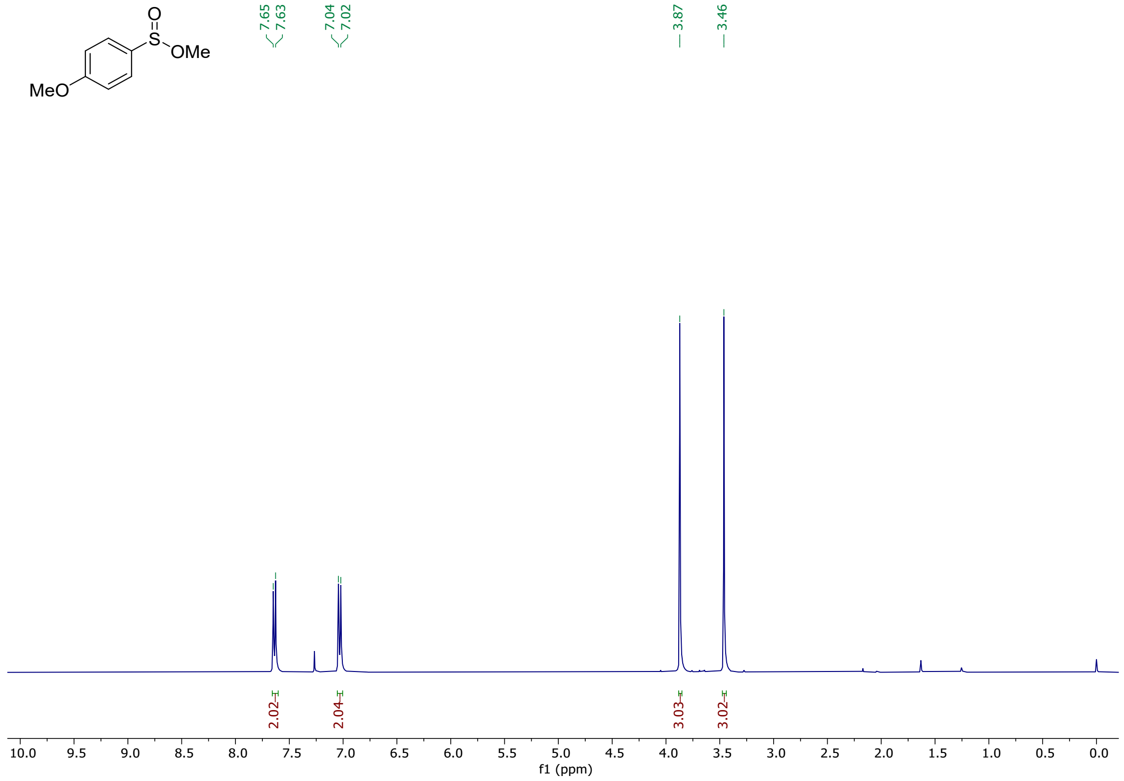

Figure S7. ^{1}H-NMR spectra of compound **1d**.

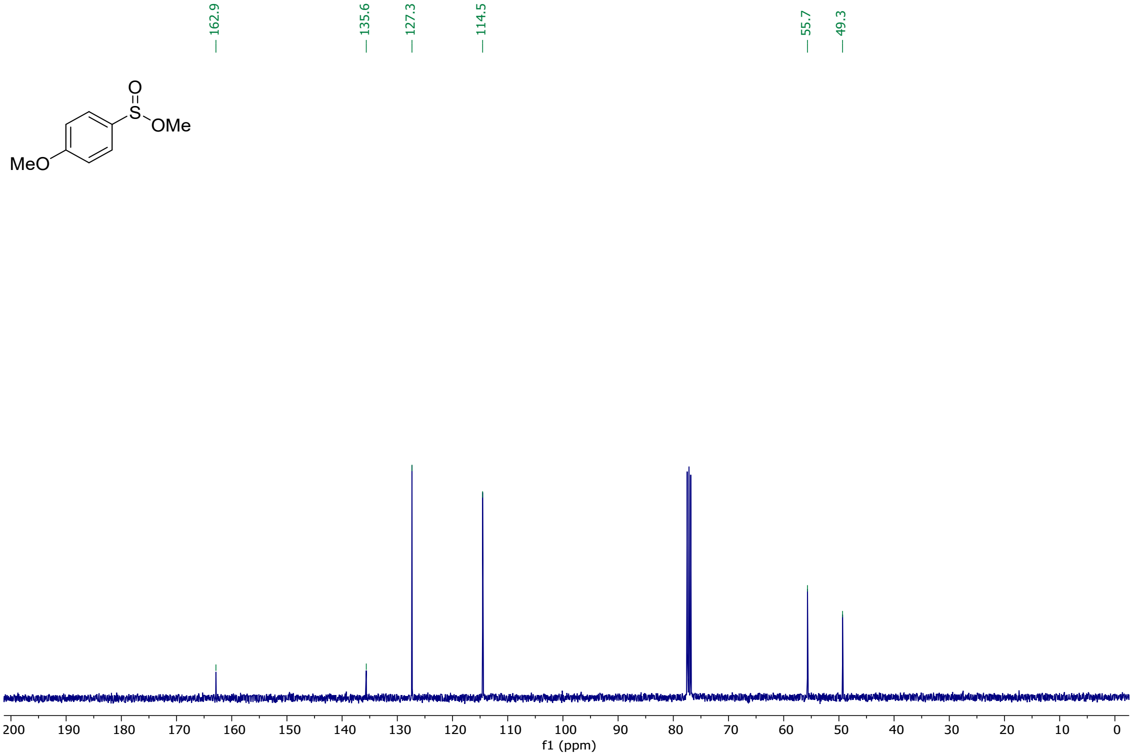

Figure S8. ^{13}C-NMR spectra of compound **1d**.

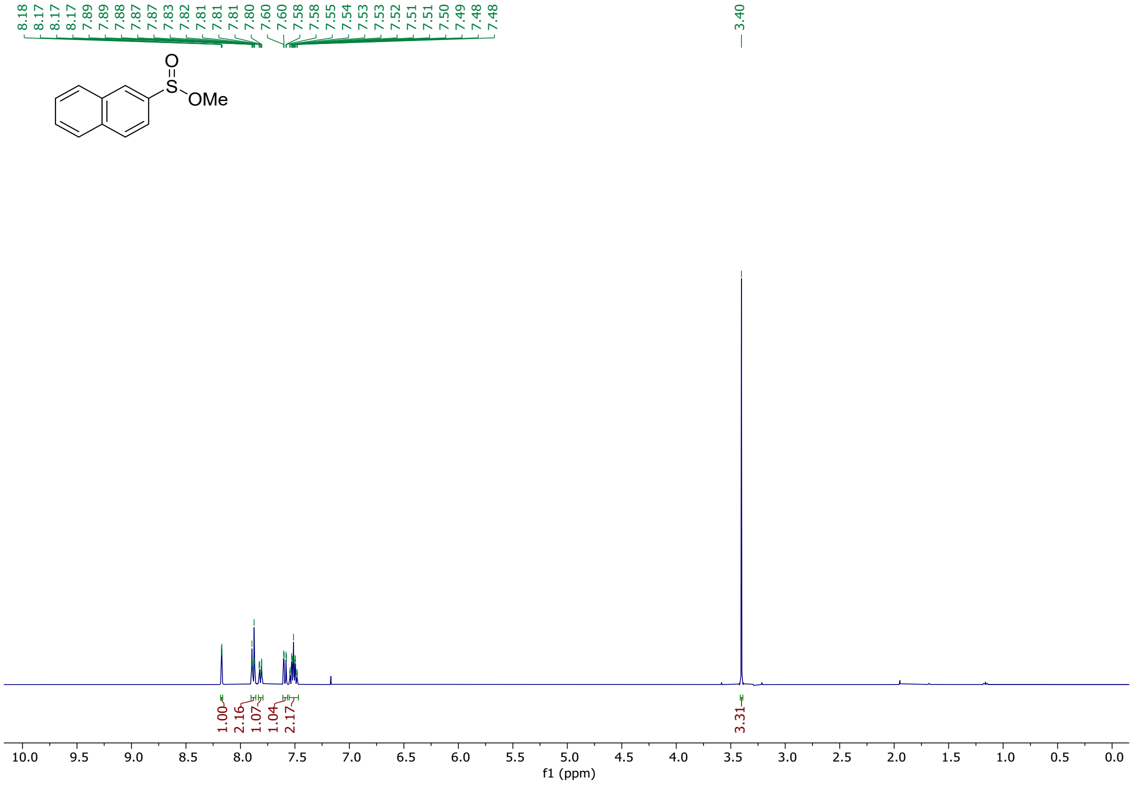

Figure S9. ^{1}H-NMR spectra of compound **1e**.

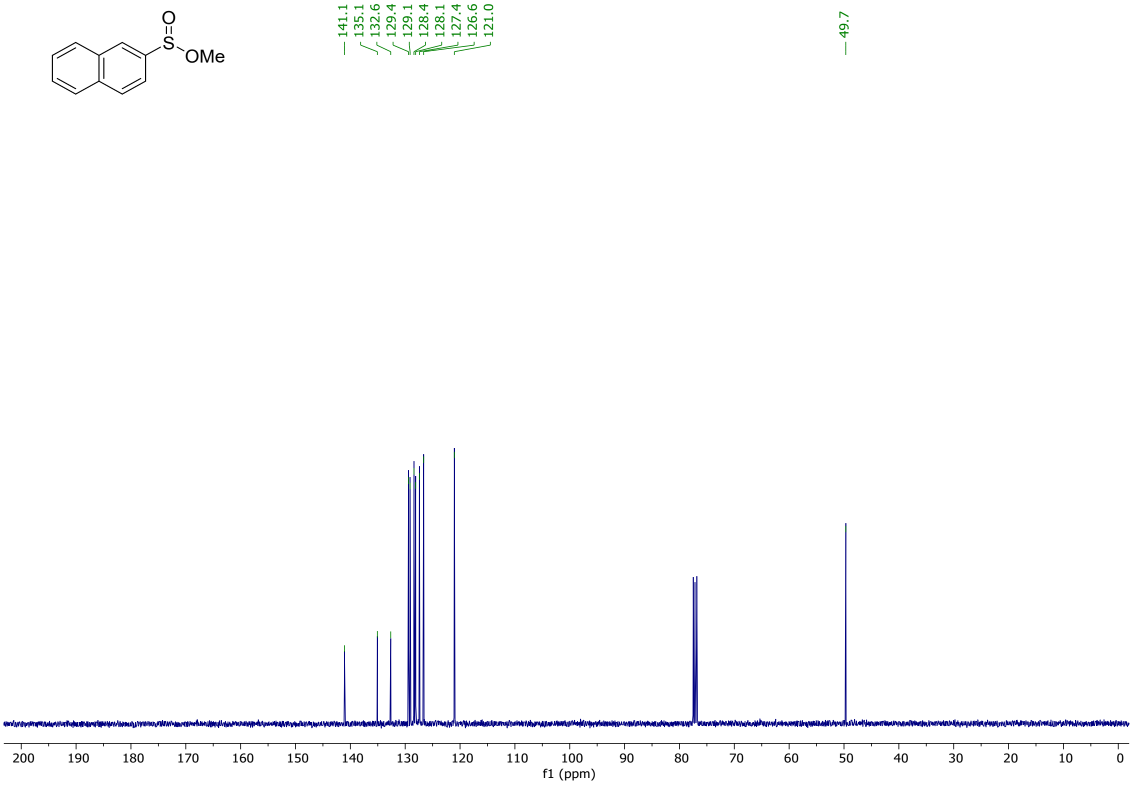

Figure S10. ^{13}C-NMR spectra of compound **1e**.

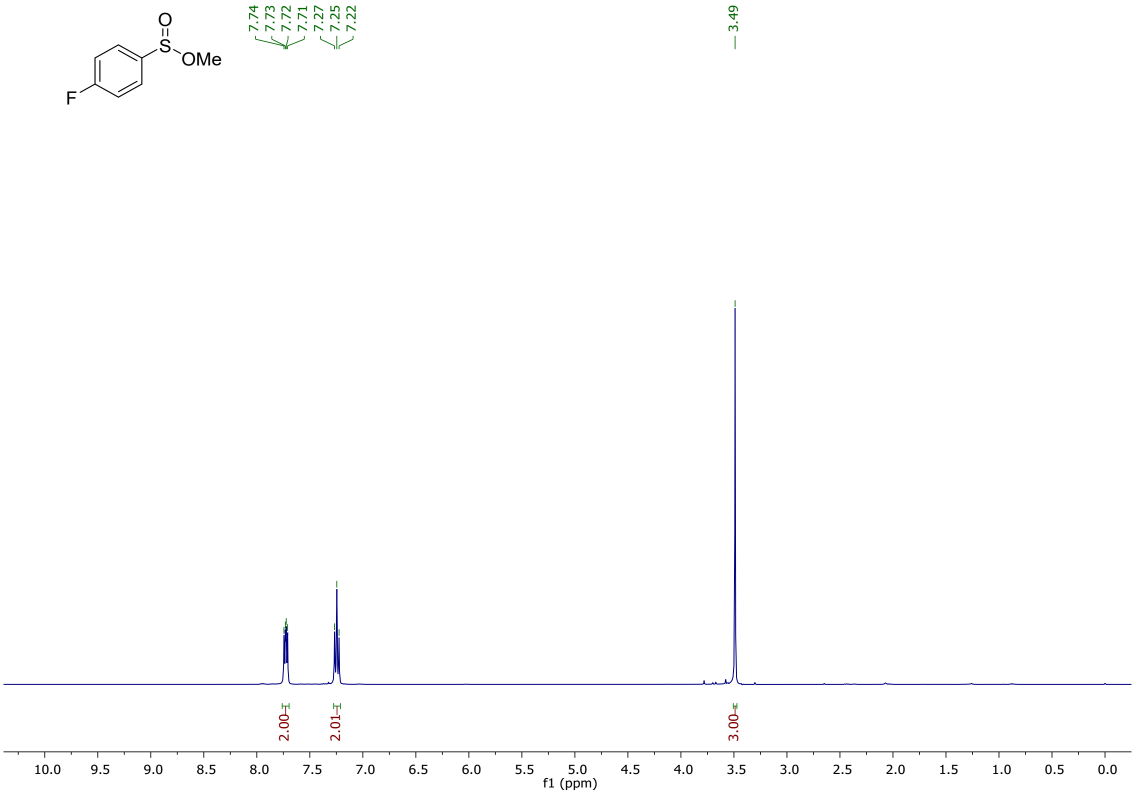

Figure S11. ^{1}H-NMR spectra of compound **1f**.

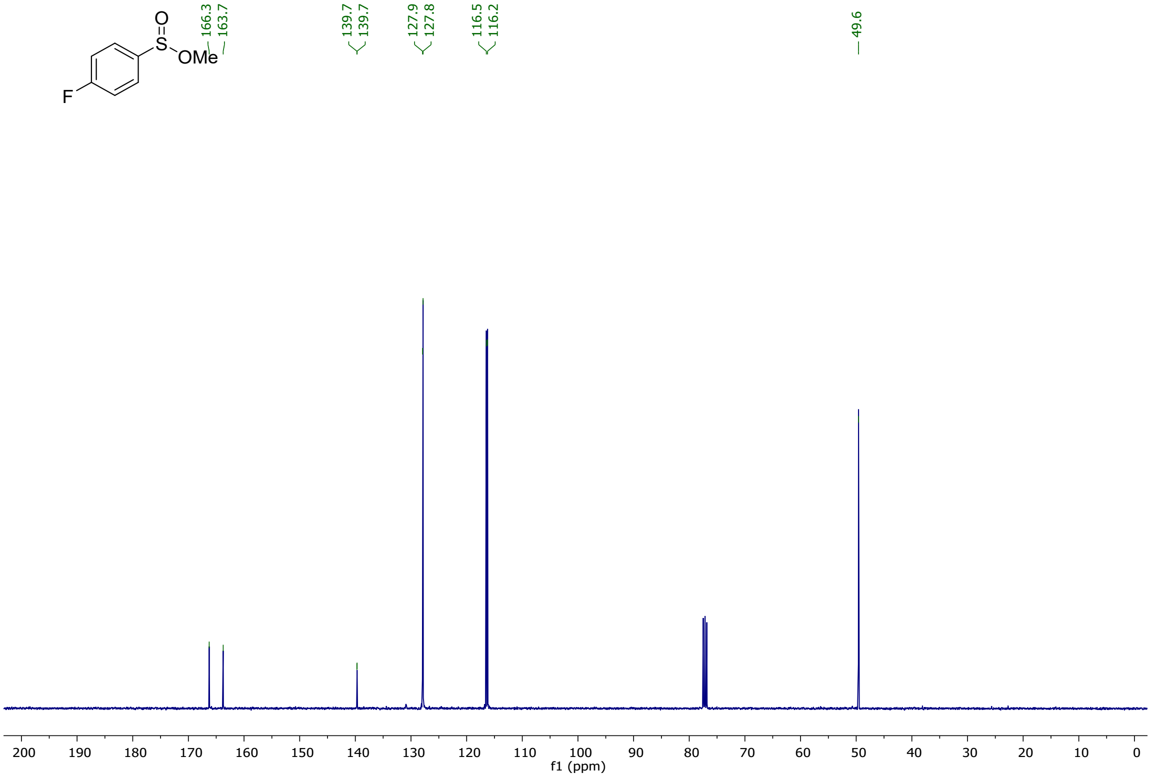

Figure S12. ^{13}C-NMR spectra of compound **1f**.

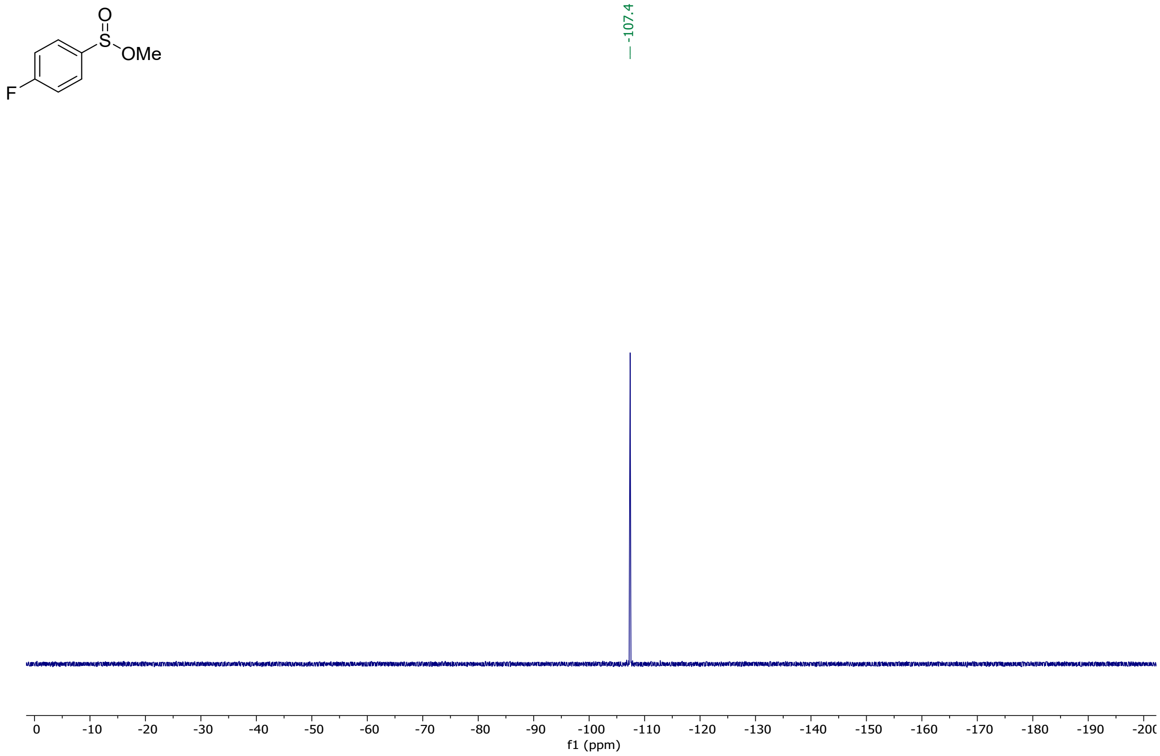

Figure S13. ^{19}F-NMR spectra of compound **1f**.

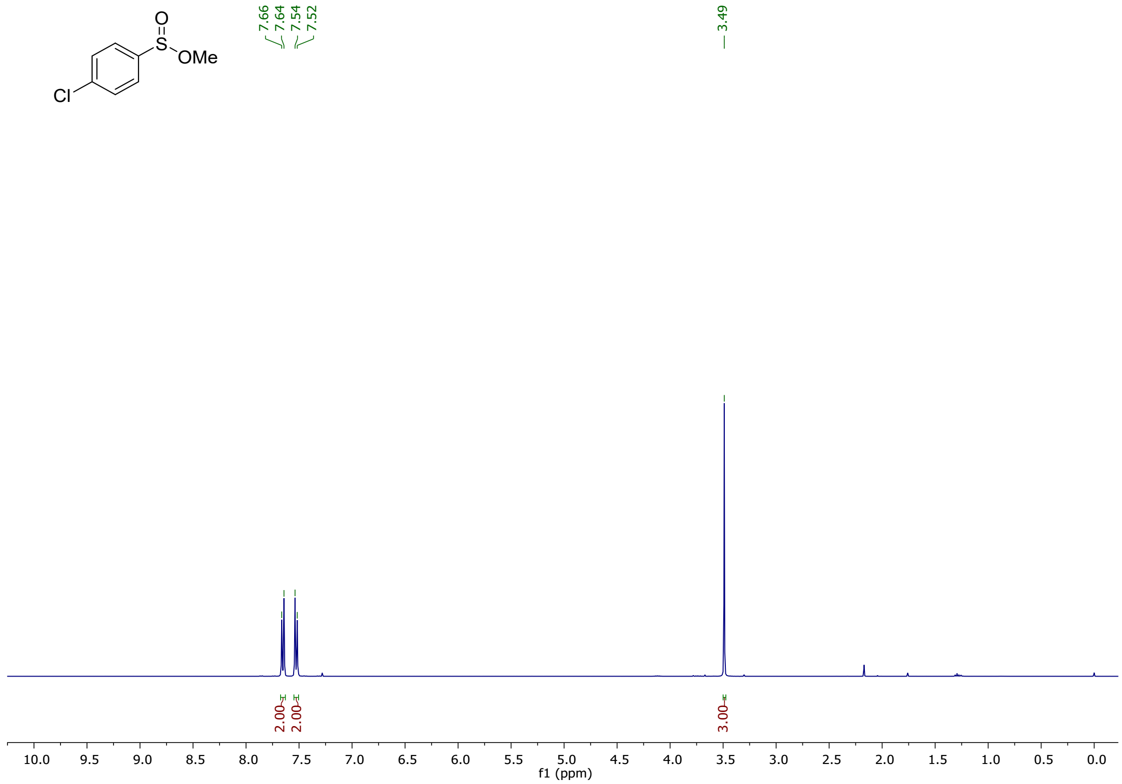

Figure S14. ^{1}H-NMR spectra of compound **1g**.

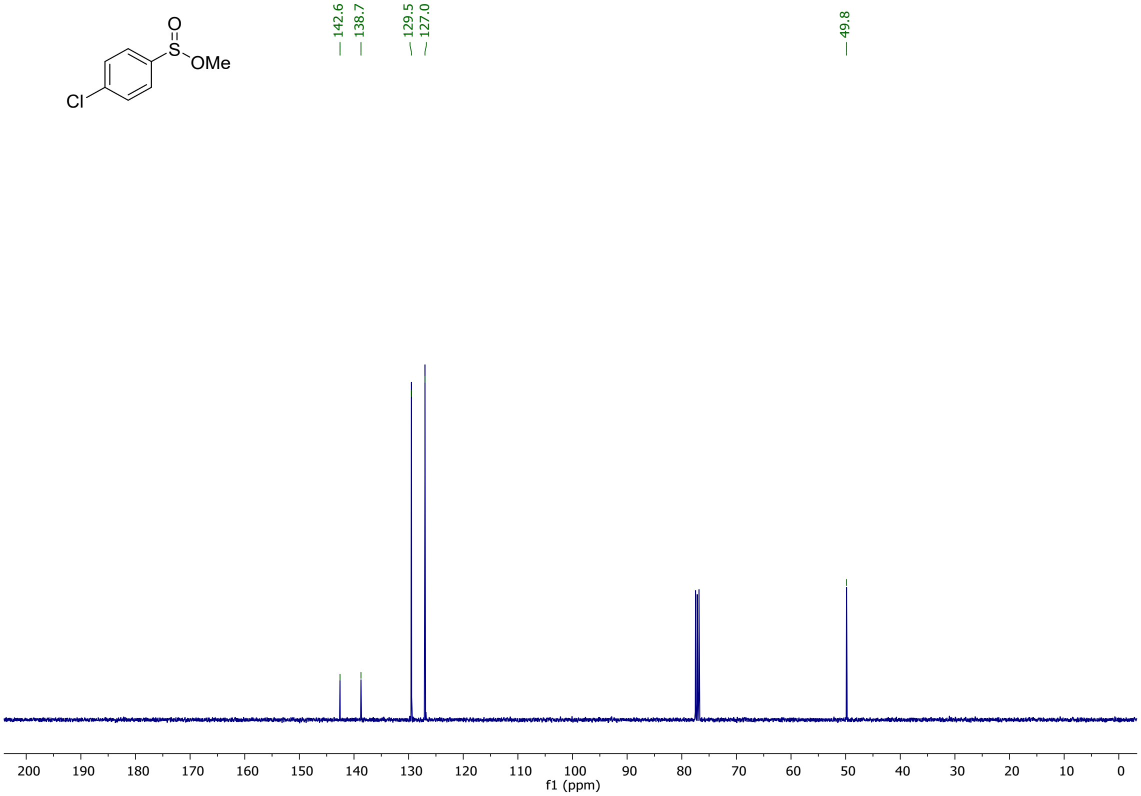

Figure S15. ^{13}C-NMR spectra of compound **1g**.

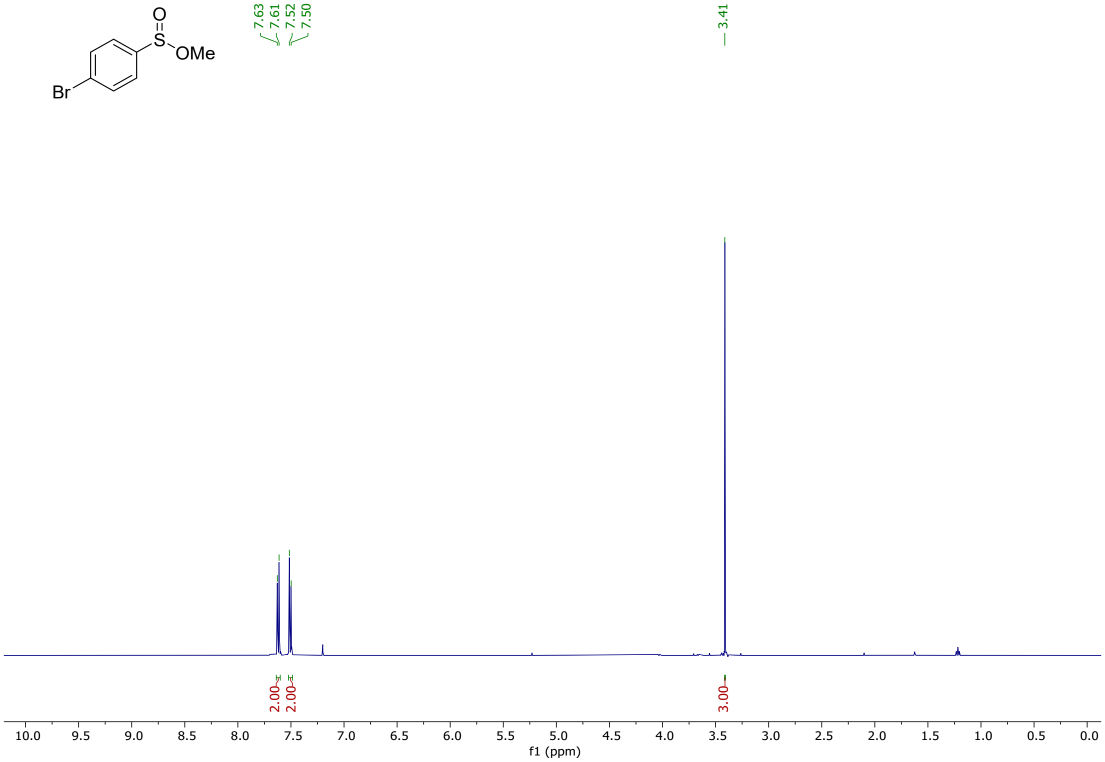

Figure S16. ^{1}H-NMR spectra of compound **1h**.

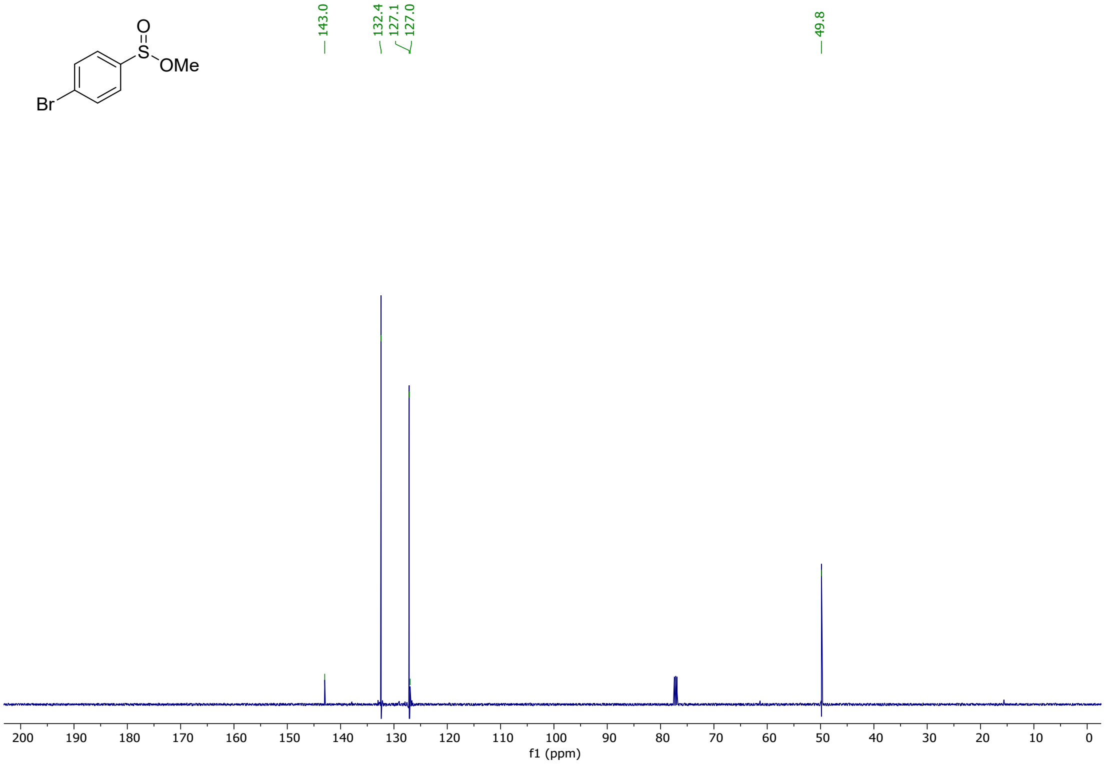

Figure S17. ^{13}C-NMR spectra of compound **1h**.

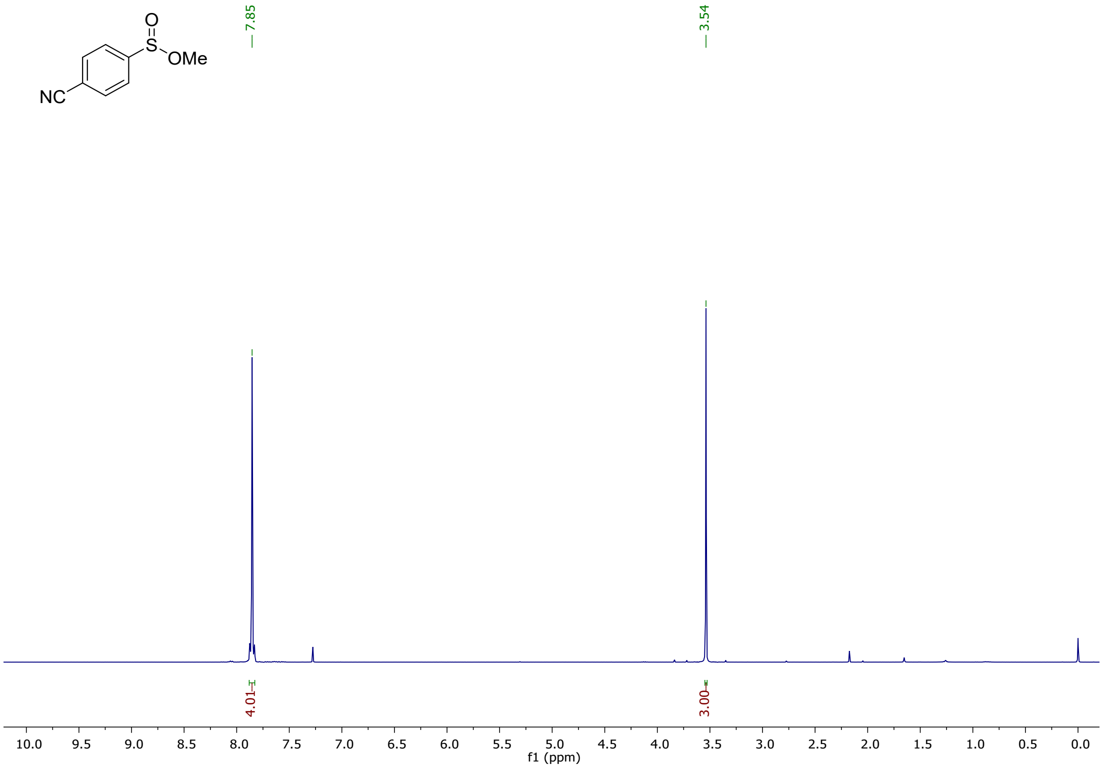

Figure S18. ^{1}H-NMR spectra of compound **1i**.

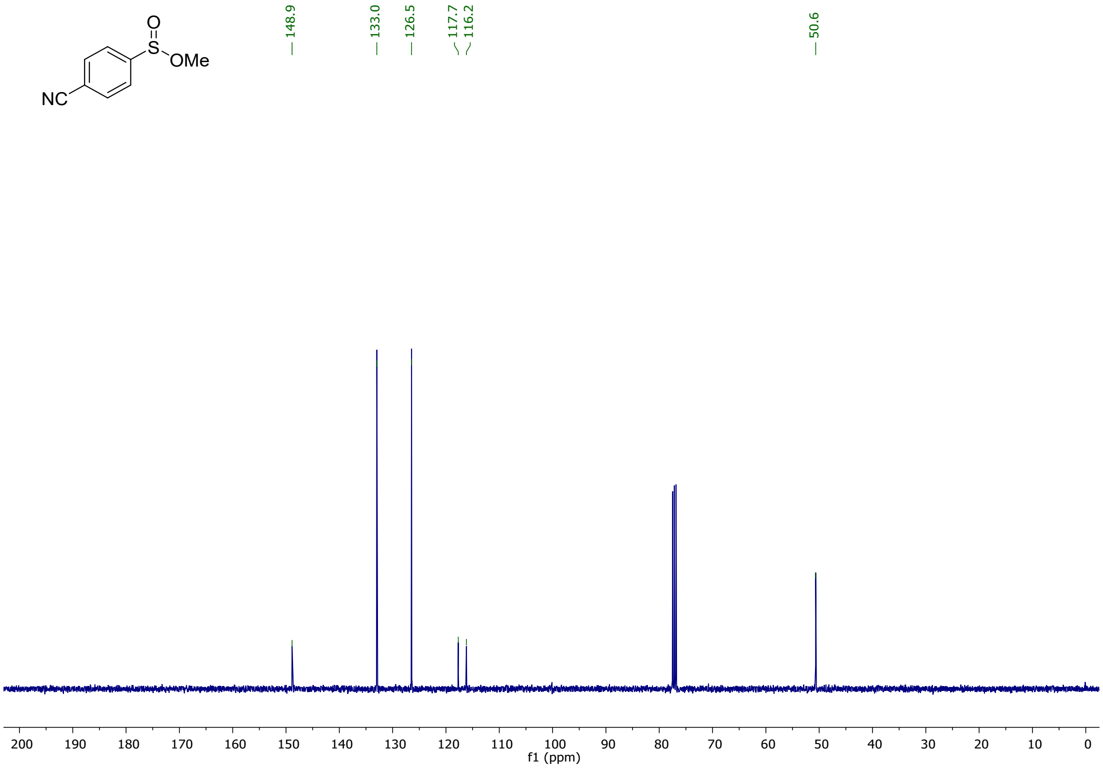

Figure S19. ^{13}C-NMR spectra of compound **1i**.

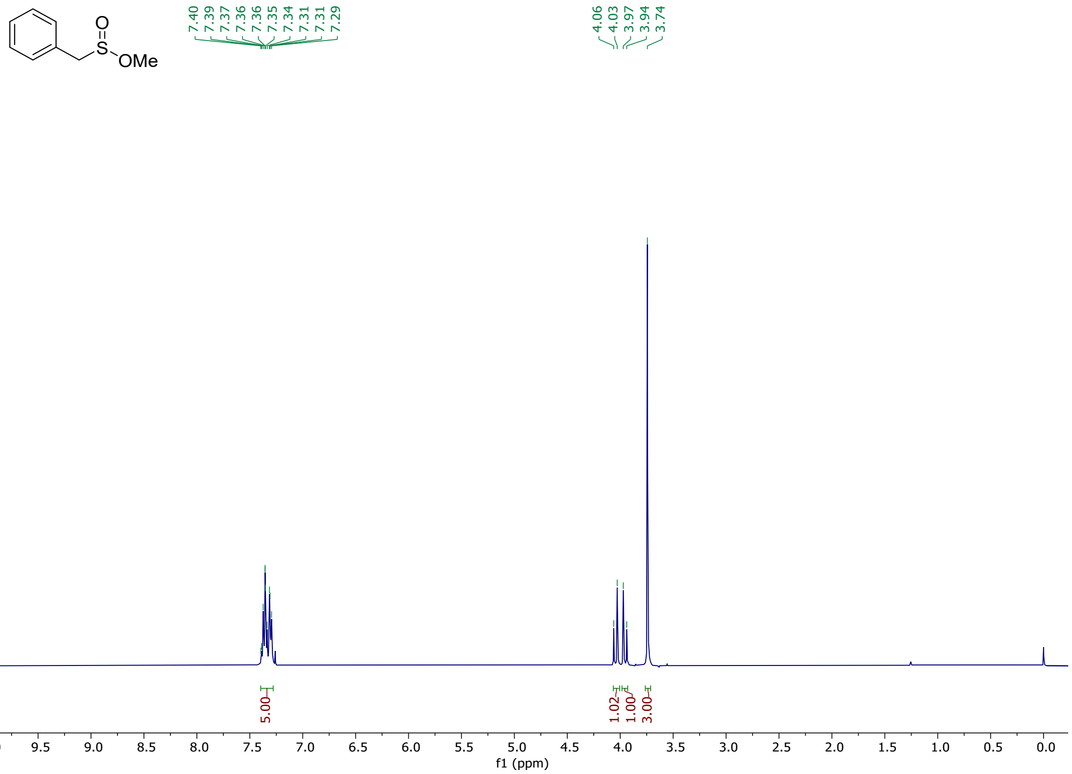

Figure S20. ^{1}H-NMR spectra of compound **1j**.

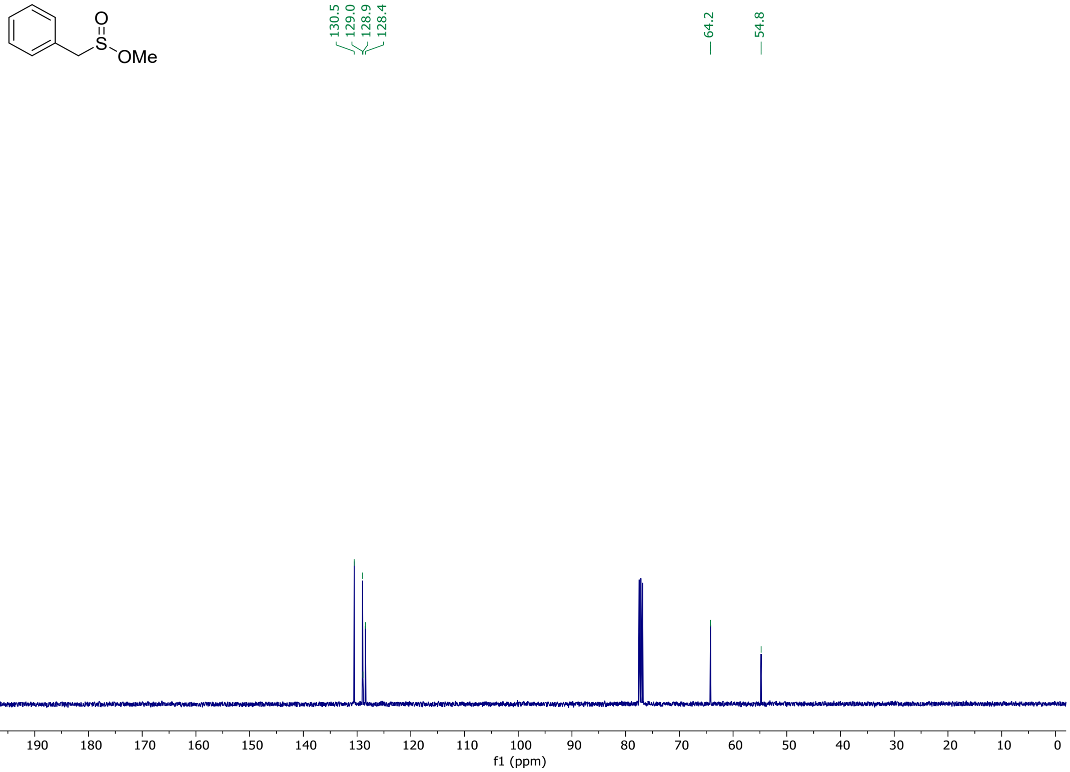

Figure S21. ^{13}C-NMR spectra of compound **1j**.

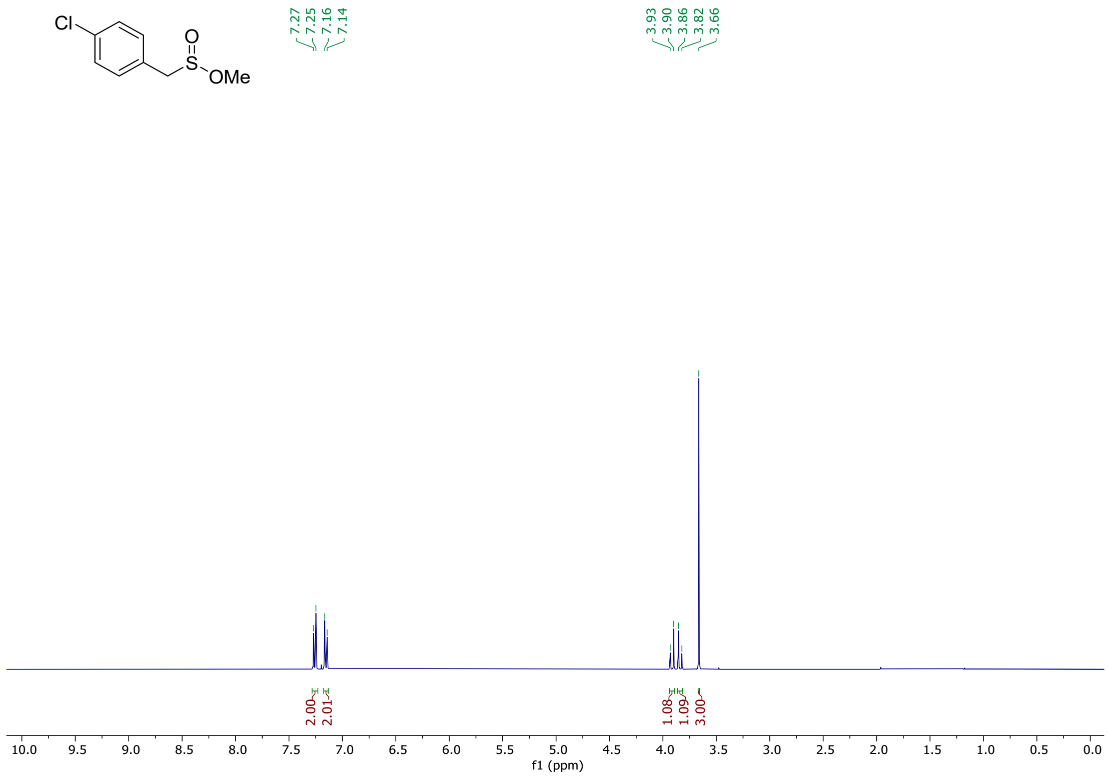

Figure S22. ^{1}H-NMR spectra of compound **1k**.

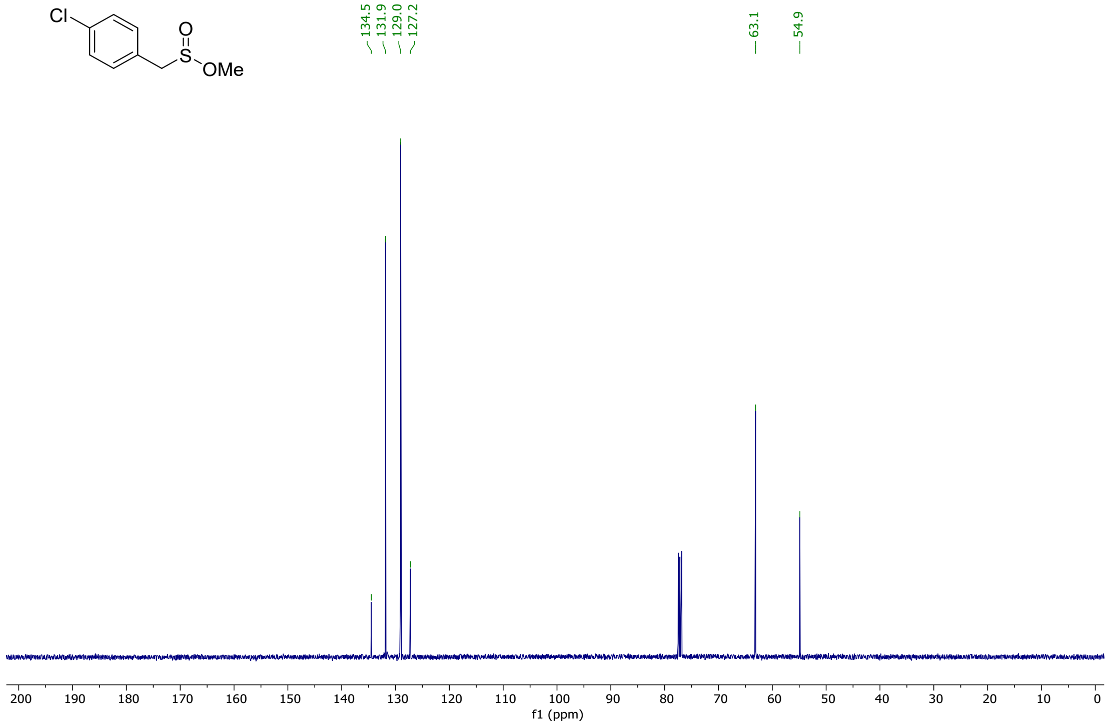

Figure S23. ^{13}C-NMR spectra of compound **1k**.

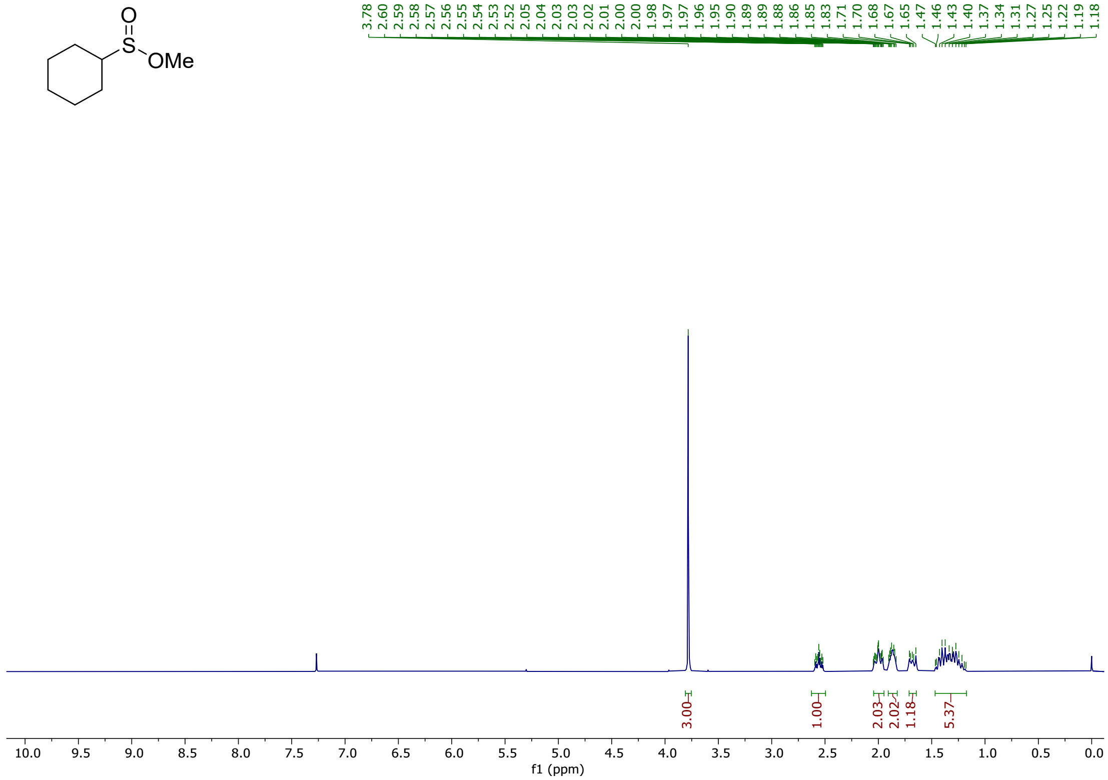

Figure S24. ^{1}H-NMR spectra of compound **1l**.

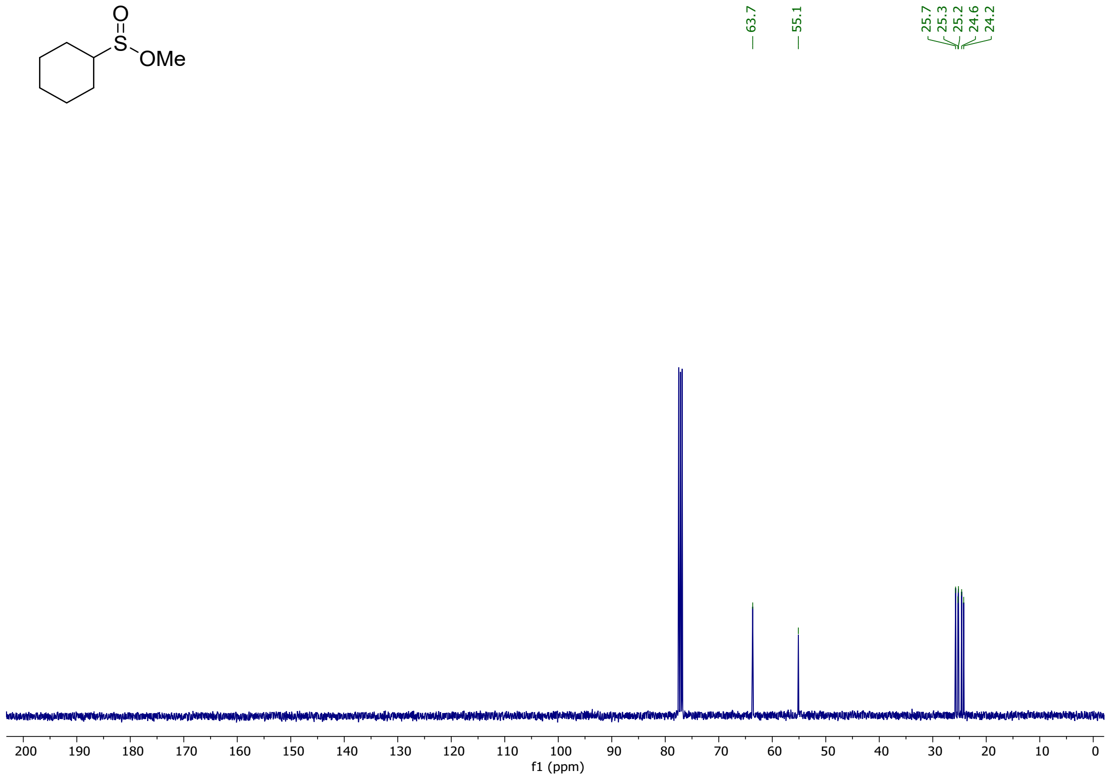

Figure S25. ^{13}C-NMR spectra of compound **1l**.

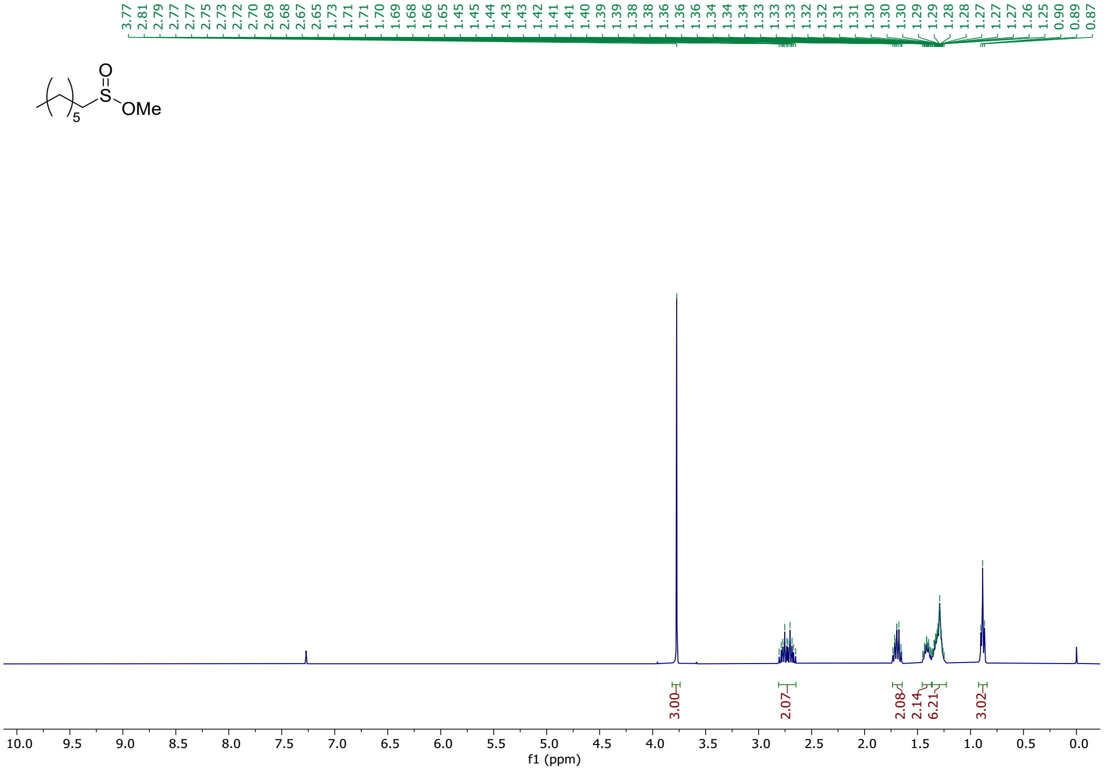

Figure S26. ^{1}H-NMR spectra of compound **1m**.

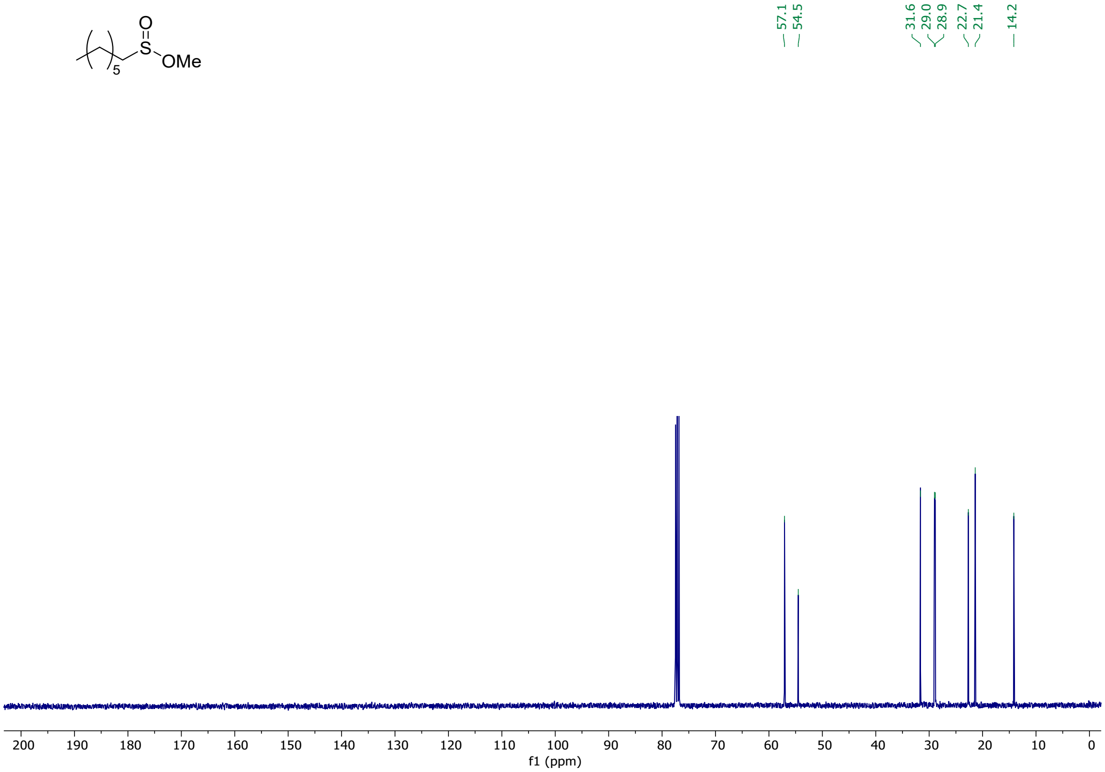

Figure S27. ^{13}C -NMR spectra of compound **1m**.

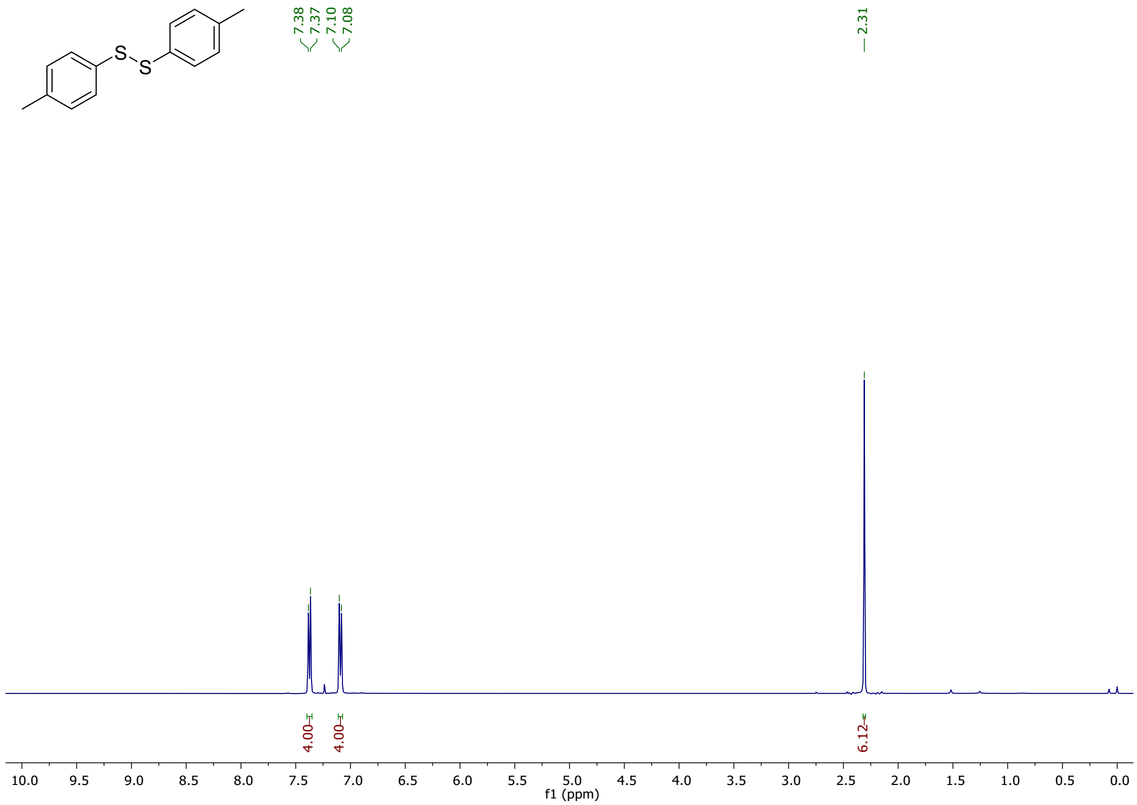

Figure S28. ^{1}H-NMR spectra of compound **2a**.

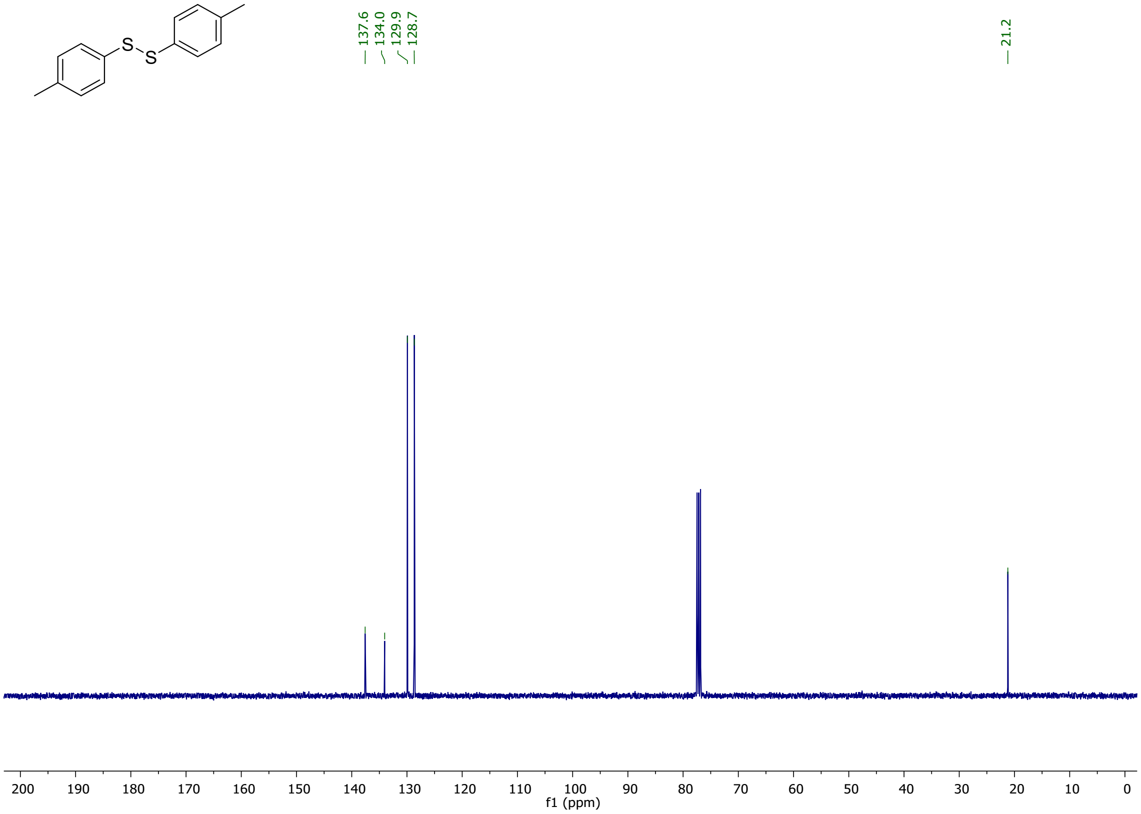

Figure S29. ^{13}C-NMR spectra of compound **2a**.

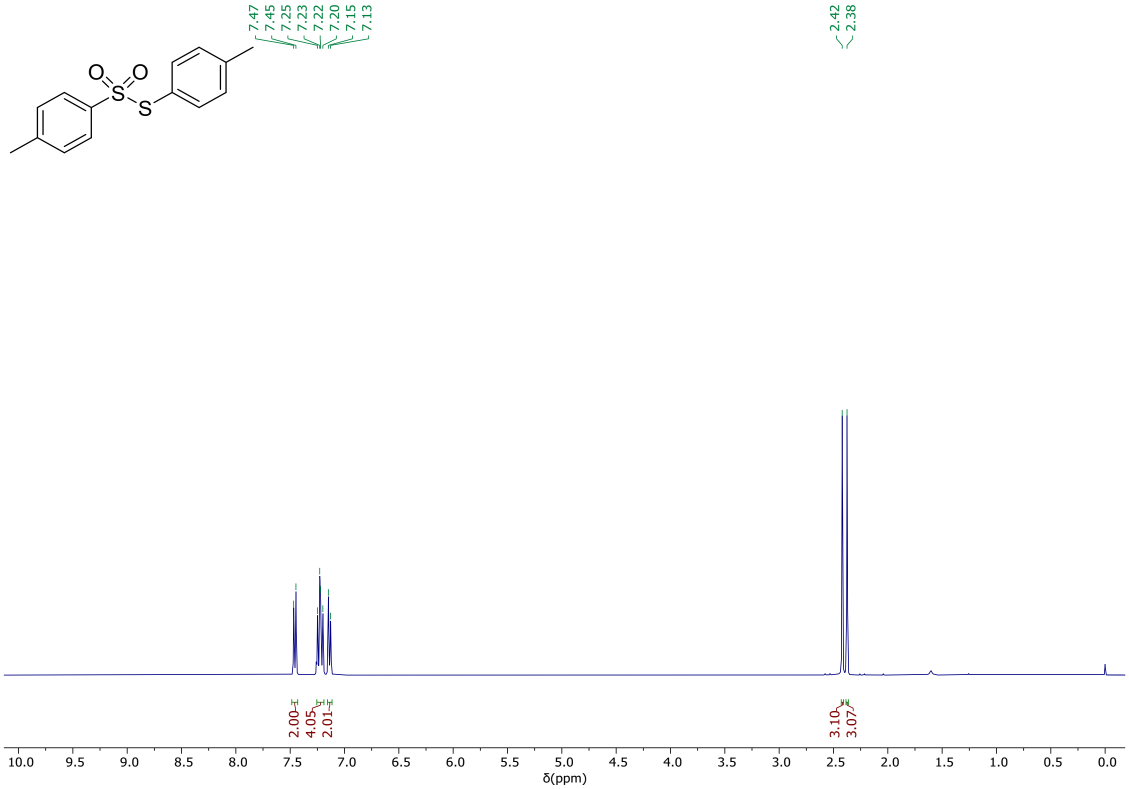

Figure S30. ^{1}H-NMR spectra of compound **4a**.

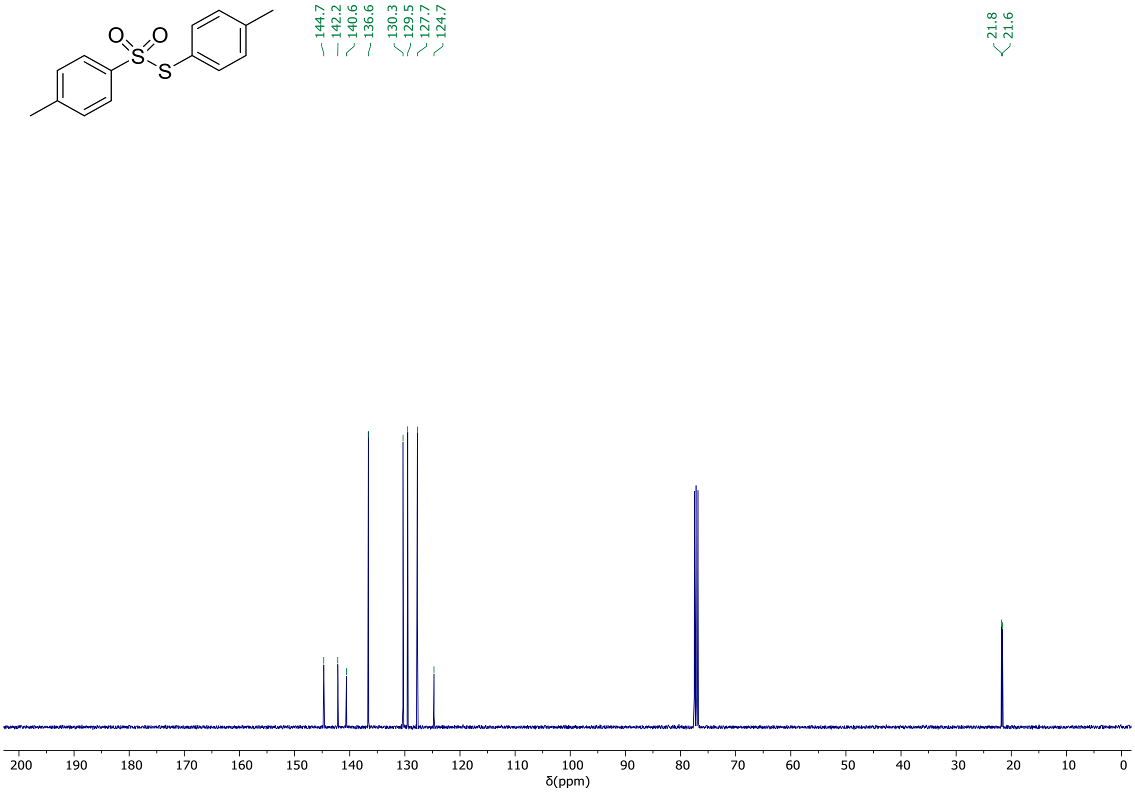

Figure S31. ^{13}C-NMR spectra of compound **4a**.

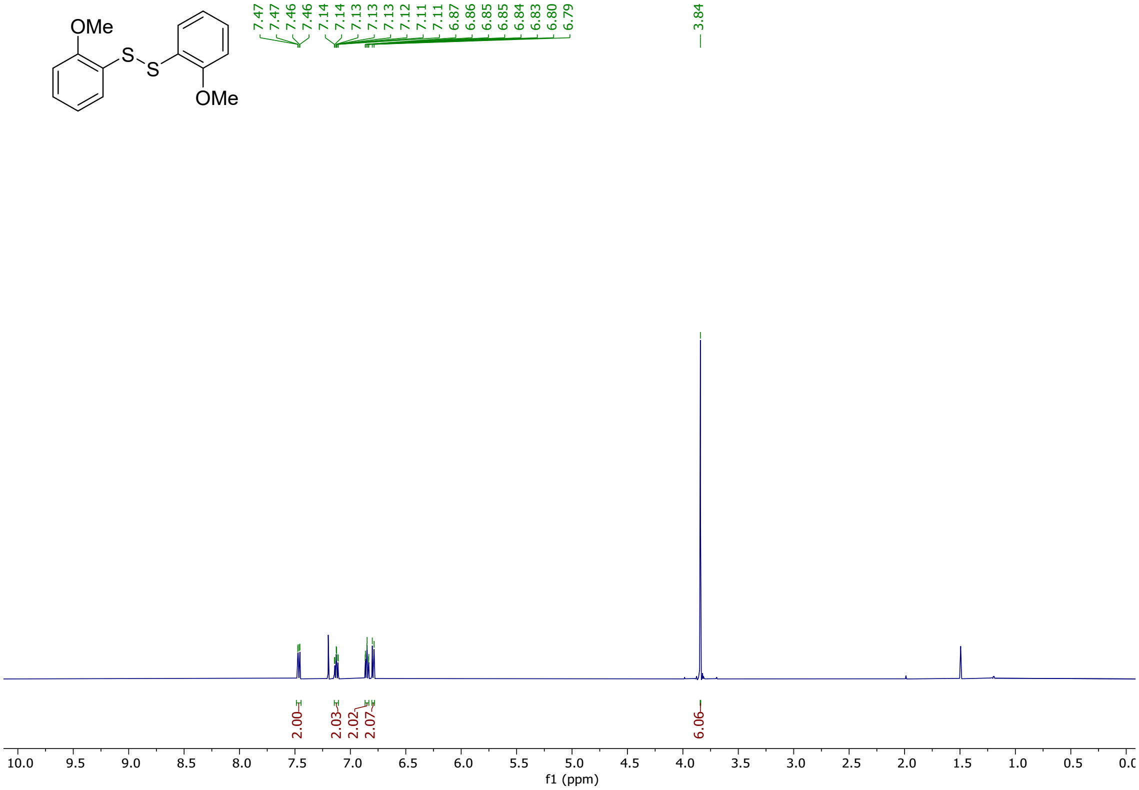

Figure S32. ^{1}H-NMR spectra of compound **2b**.

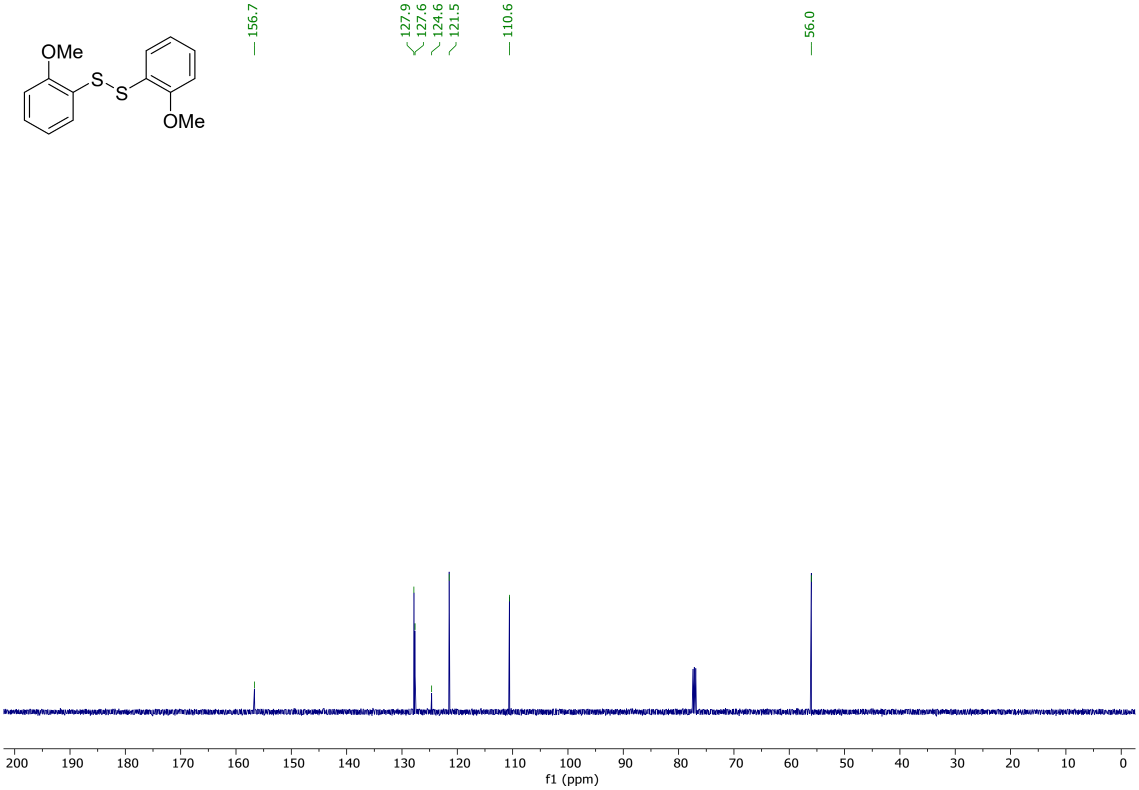

Figure S33. ^{13}C-NMR spectra of compound **2b**.

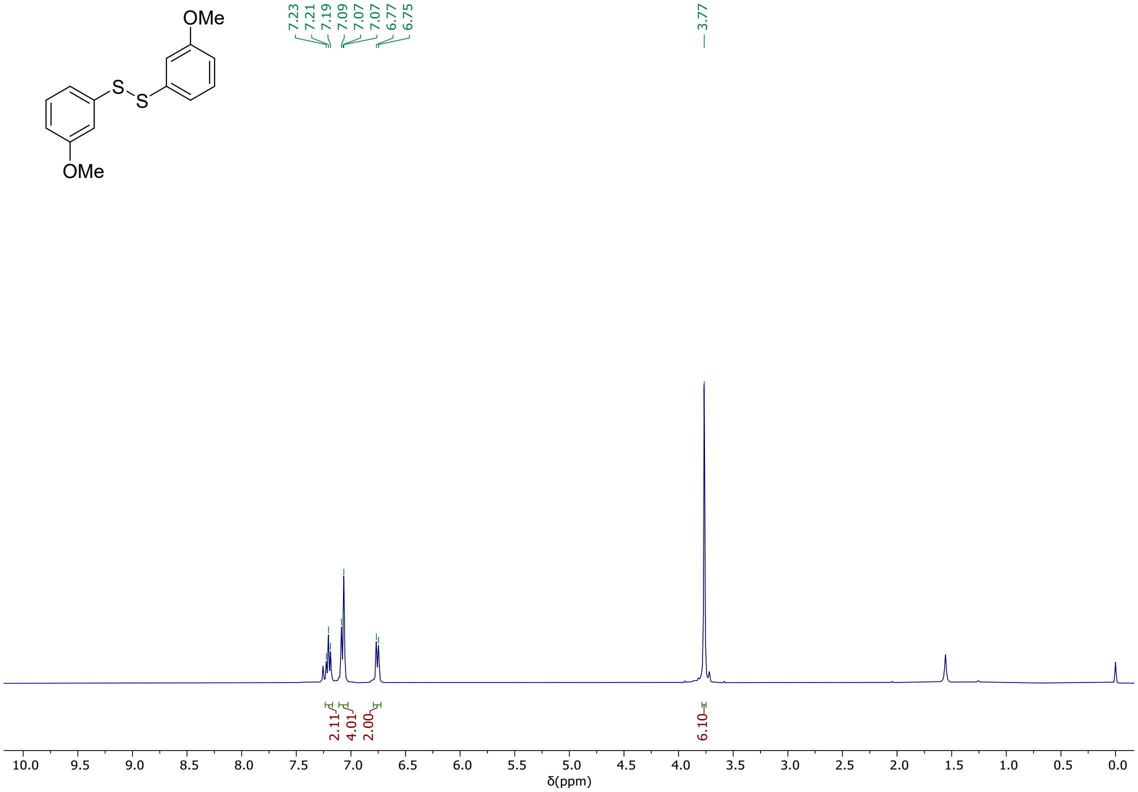

Figure S34. ^{1}H-NMR spectra of compound **2c**.

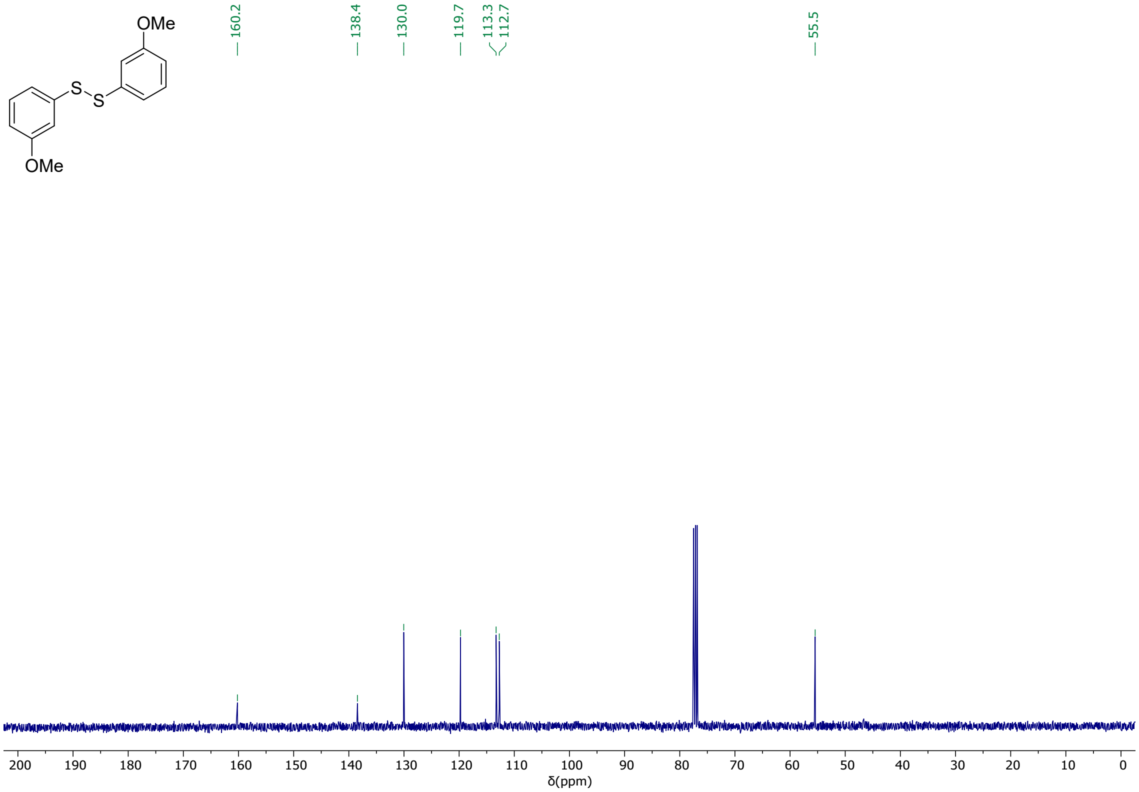

Figure S35. ^{13}C-NMR spectra of compound **2c**.

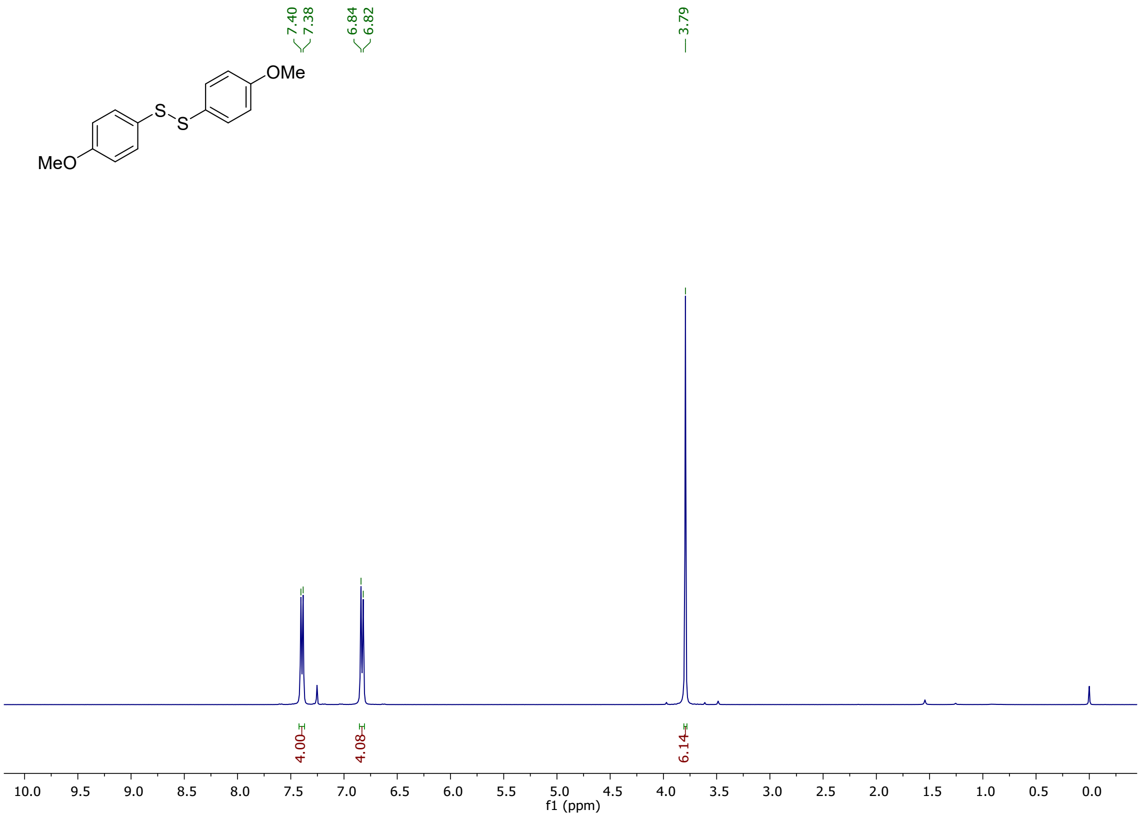

Figure S36. ^{1}H-NMR spectra of compound **2d**.

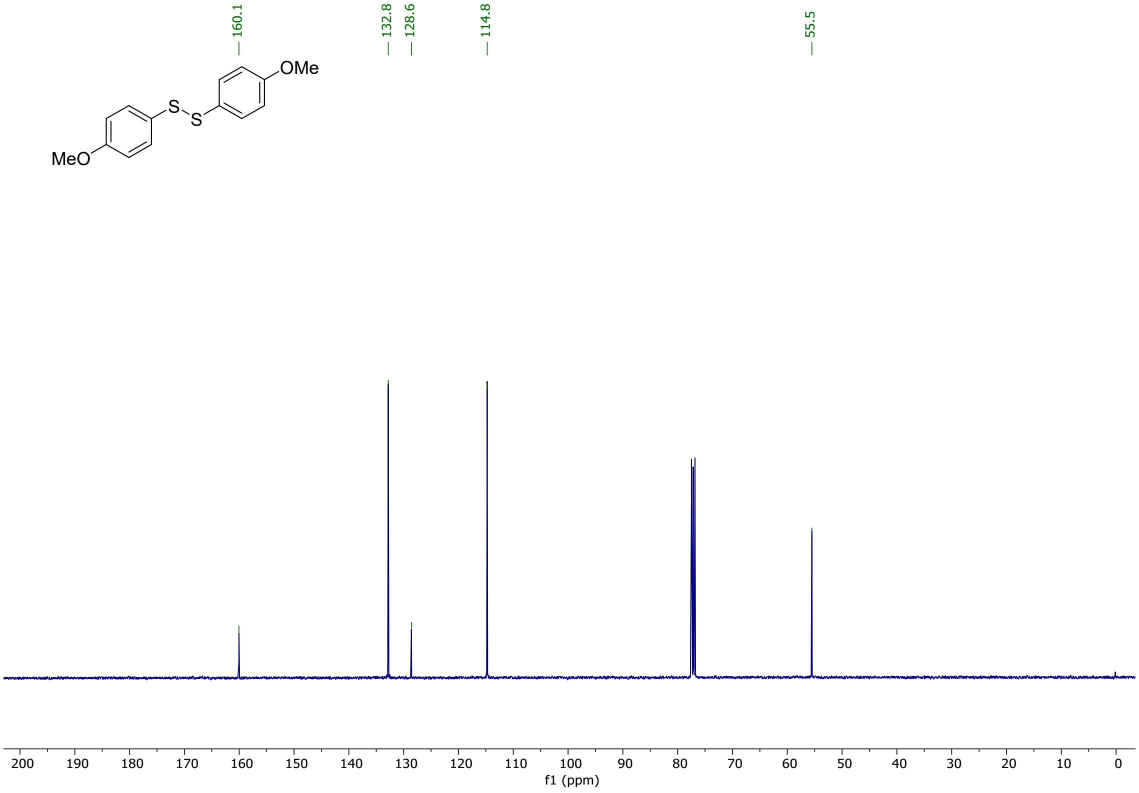

Figure S37. ^{13}C-NMR spectra of compound **2d**.

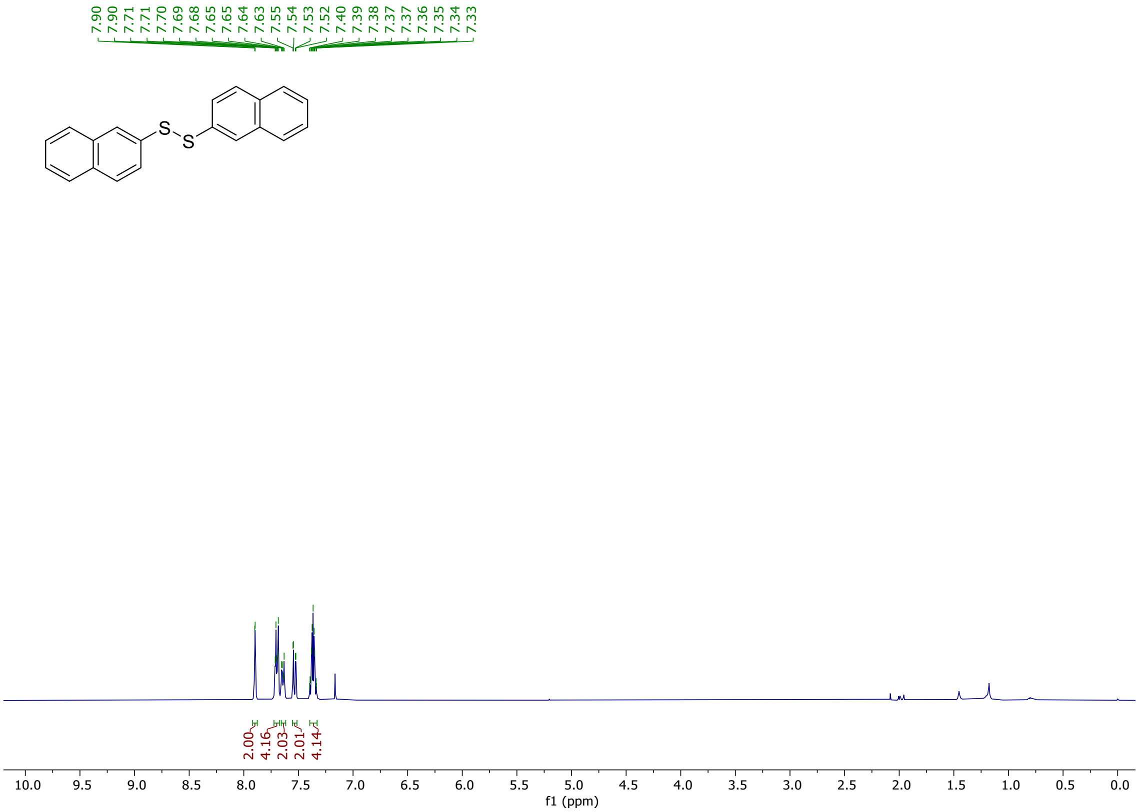

Figure S38. ^{1}H-NMR spectra of compound **2e**.

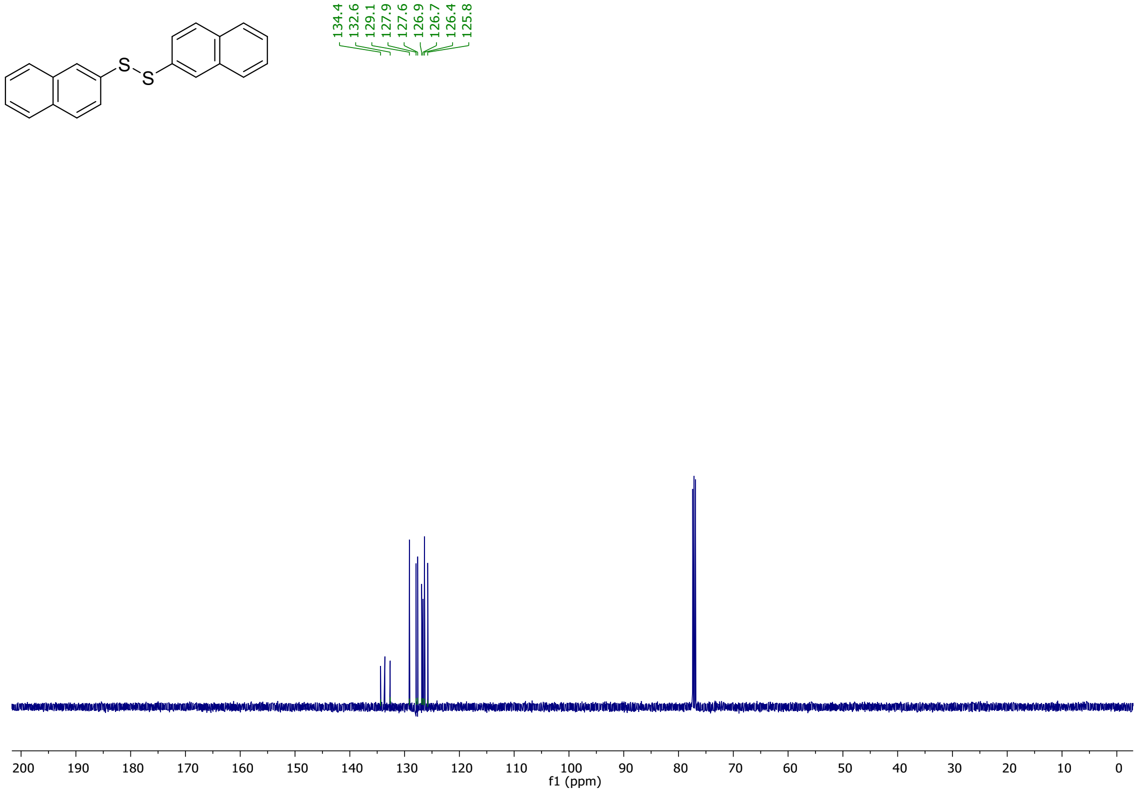

Figure S39. ^{13}C-NMR spectra of compound **2e**.

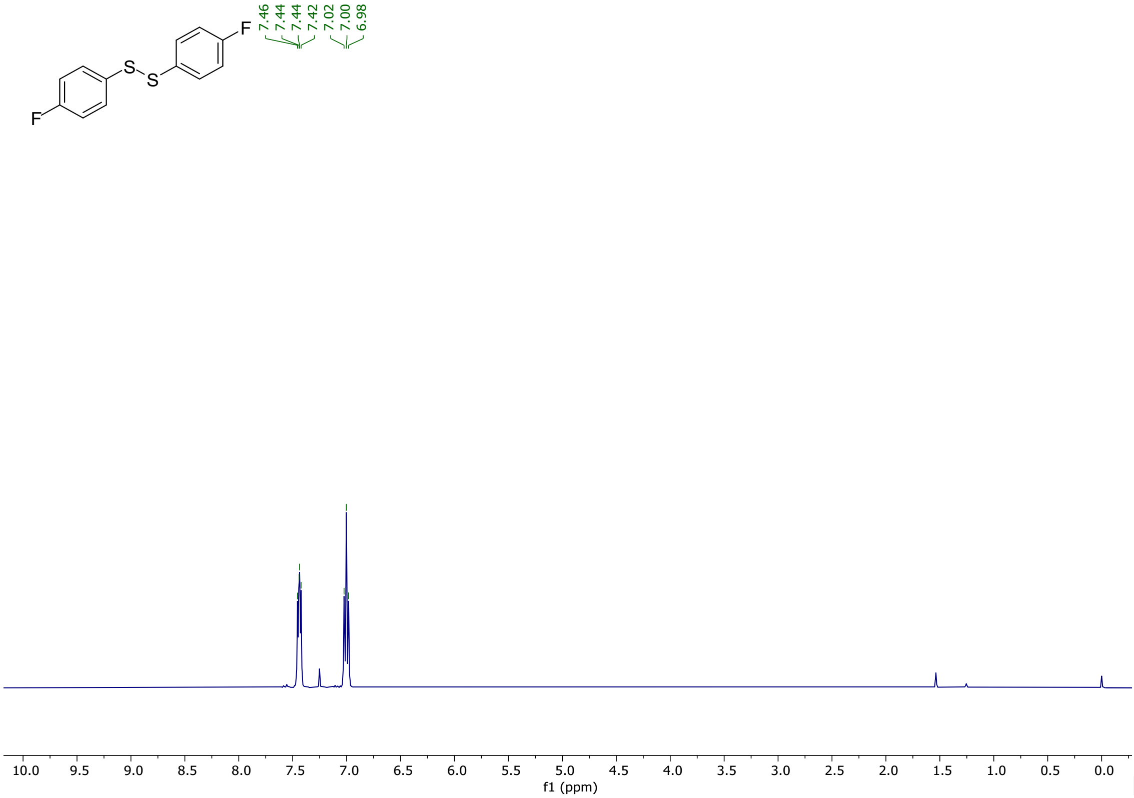

Figure S40. ^{1}H-NMR spectra of compound **2f**.

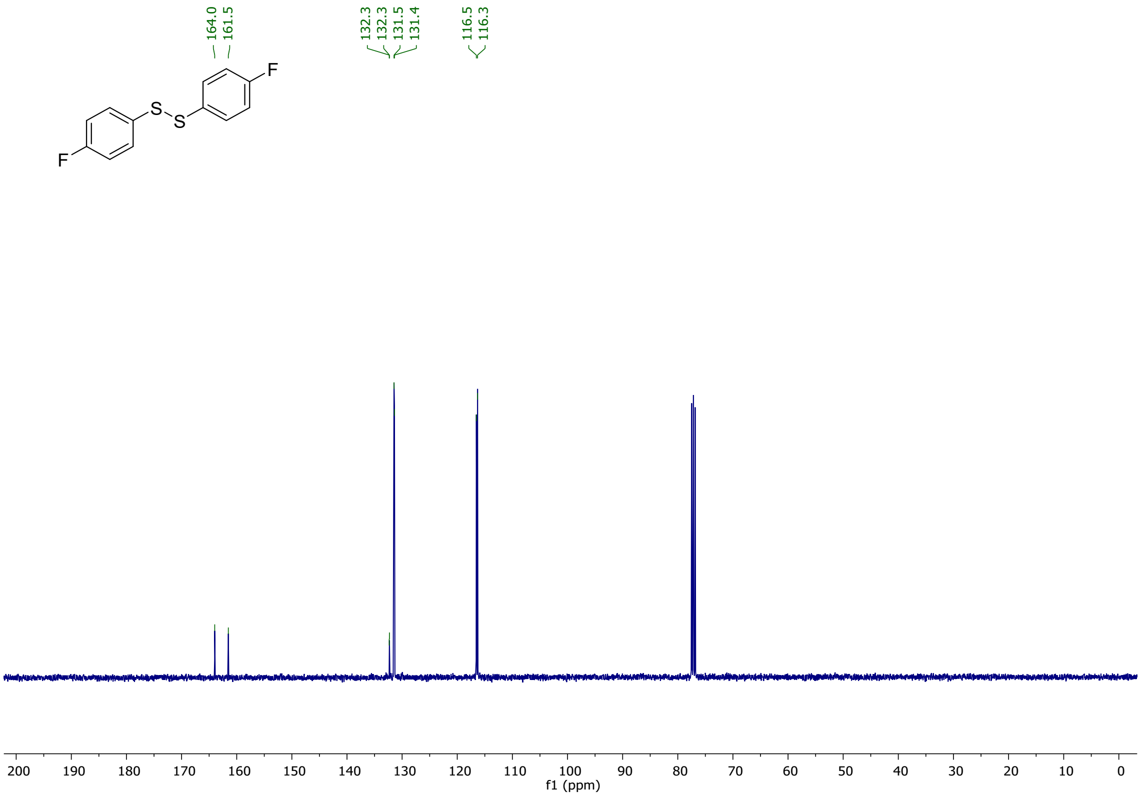

Figure S41. ^{13}C-NMR spectra of compound **2f**.

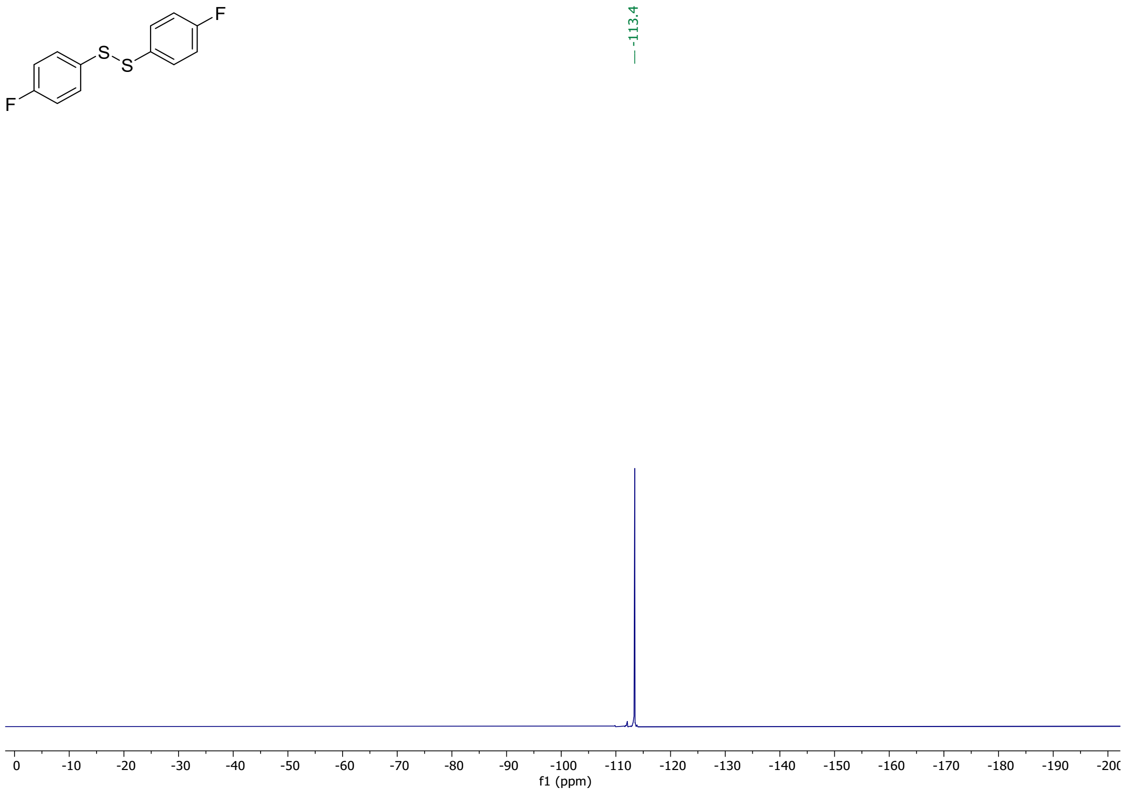

Figure S42. ^{19}F-NMR spectra of compound **2f**.

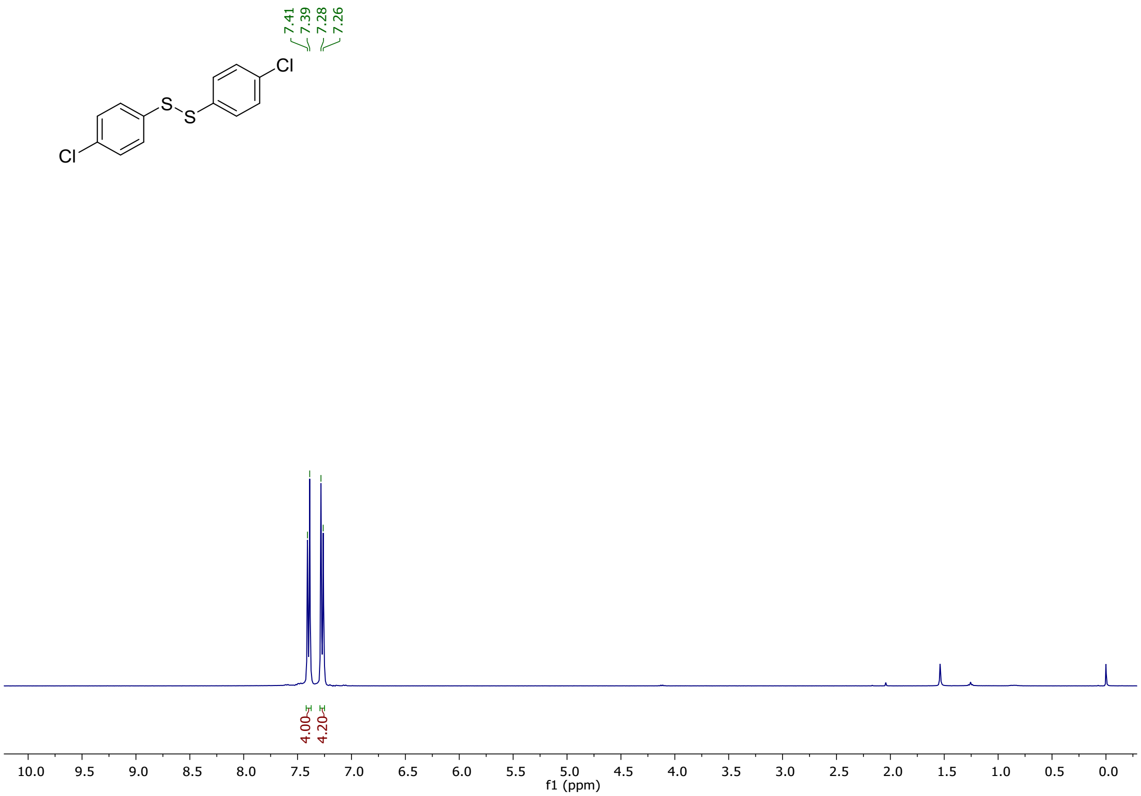

Figure S43. ^{1}H-NMR spectra of compound **2g**.

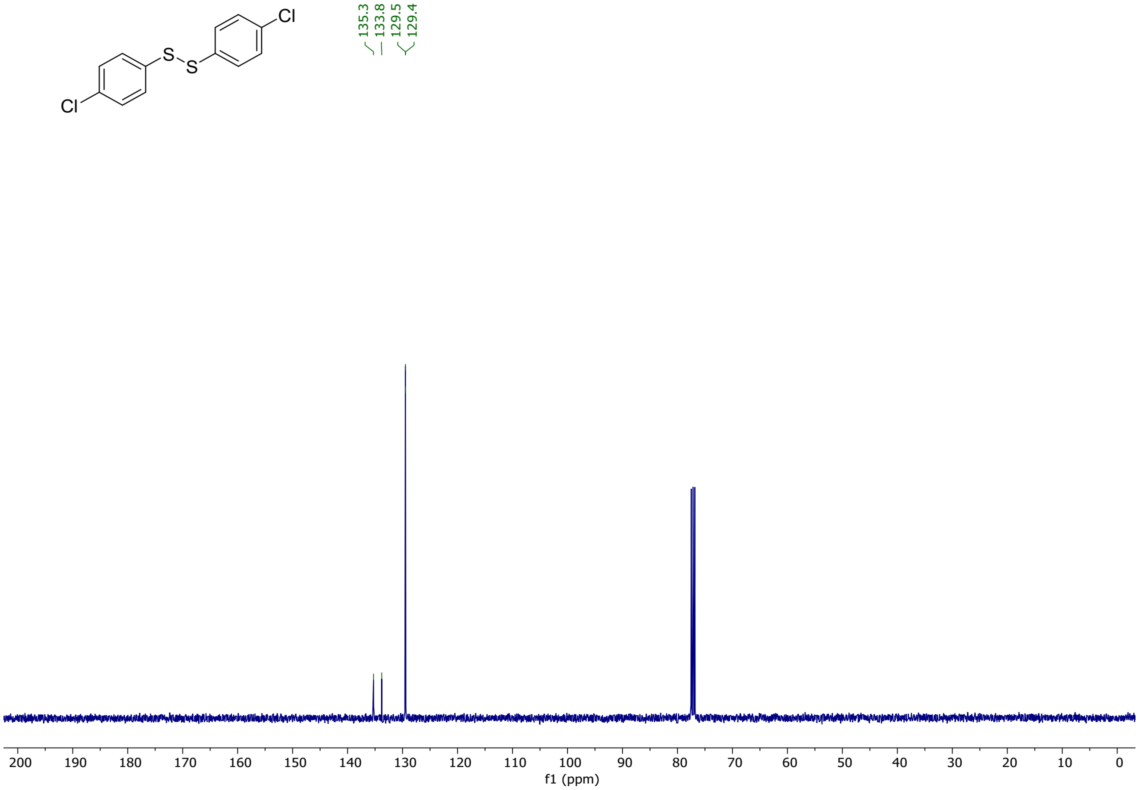

Figure S44. ^{13}C-NMR spectra of compound **2g**.

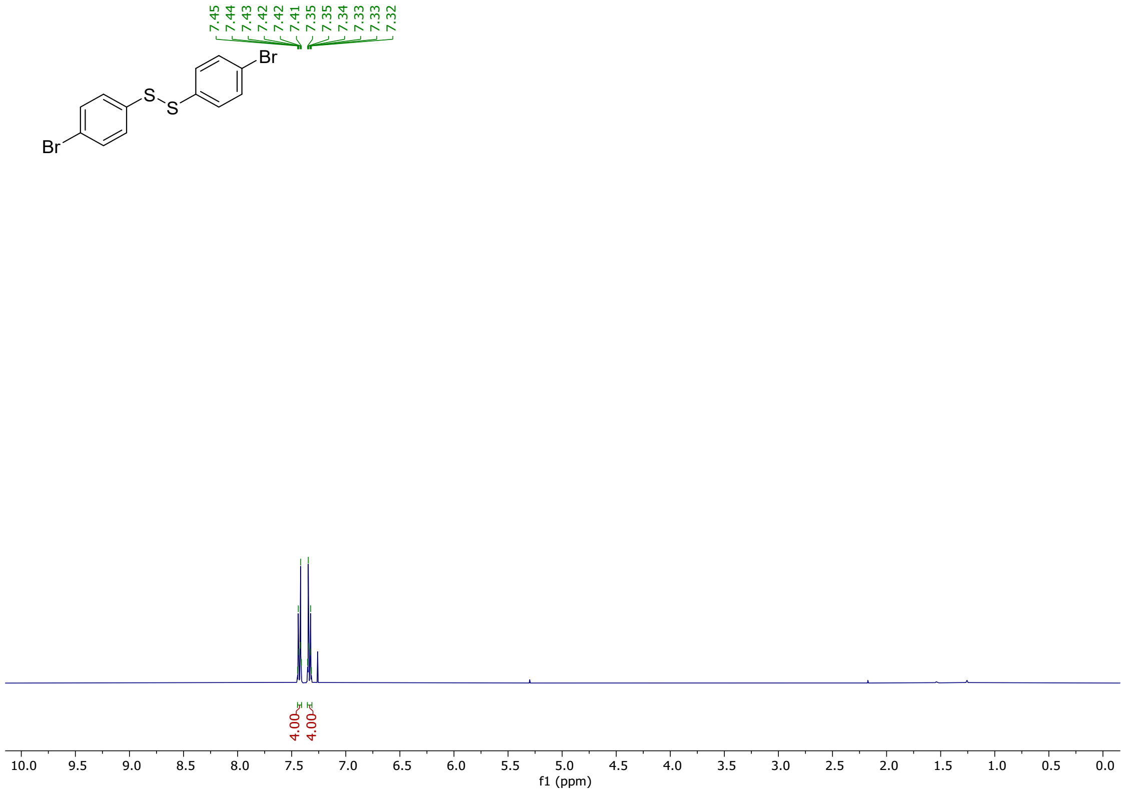

Figure S45. ^{1}H-NMR spectra of compound **2h**.

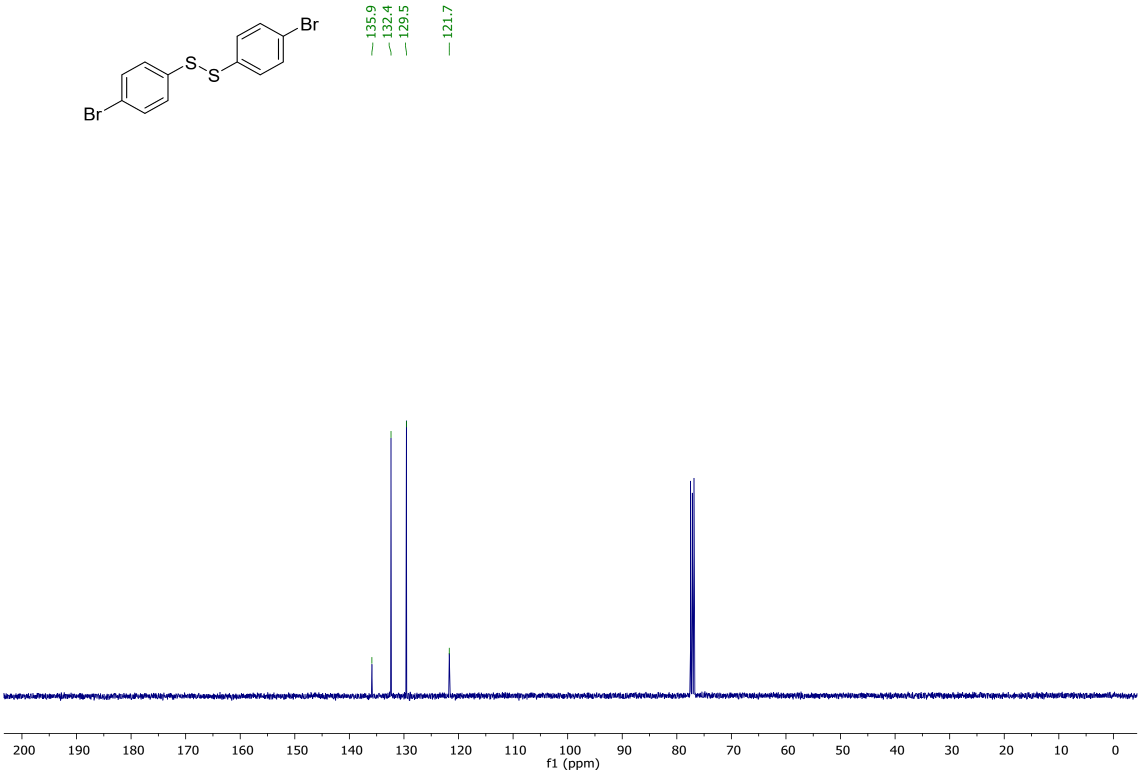

Figure S46. ^{13}C-NMR spectra of compound **2h**.

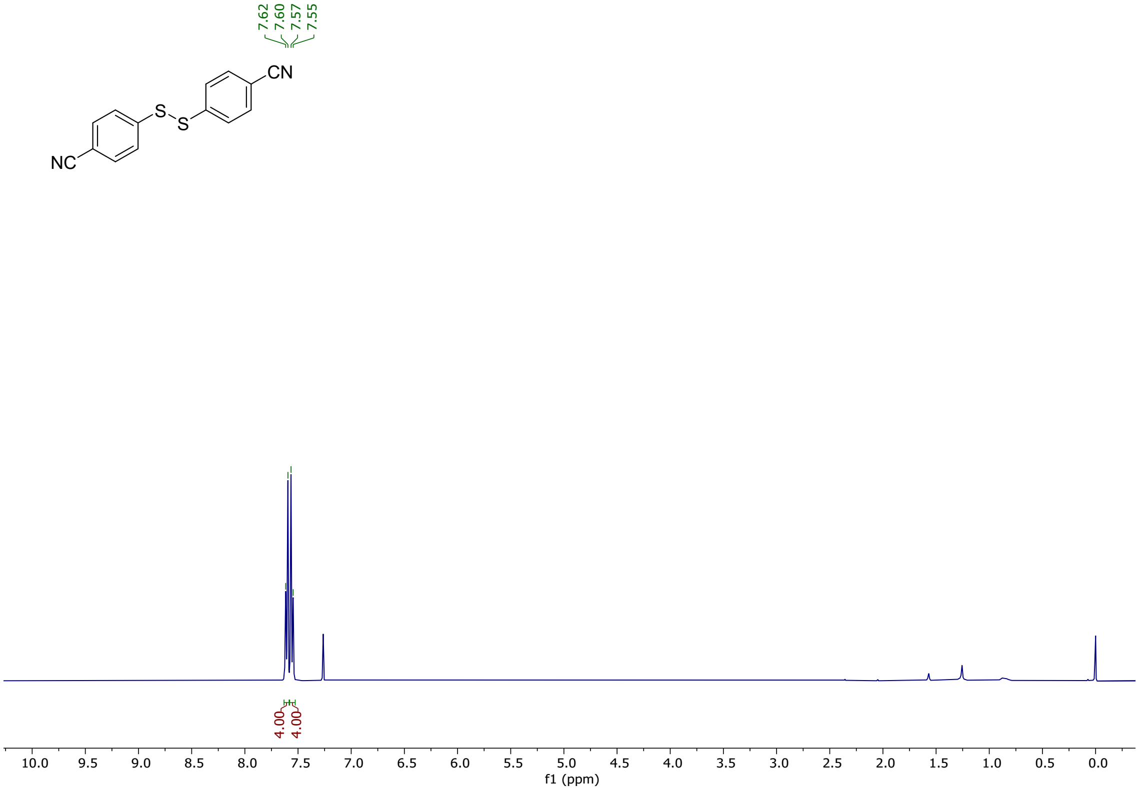

Figure S47. ^{1}H-NMR spectra of compound **2i**.

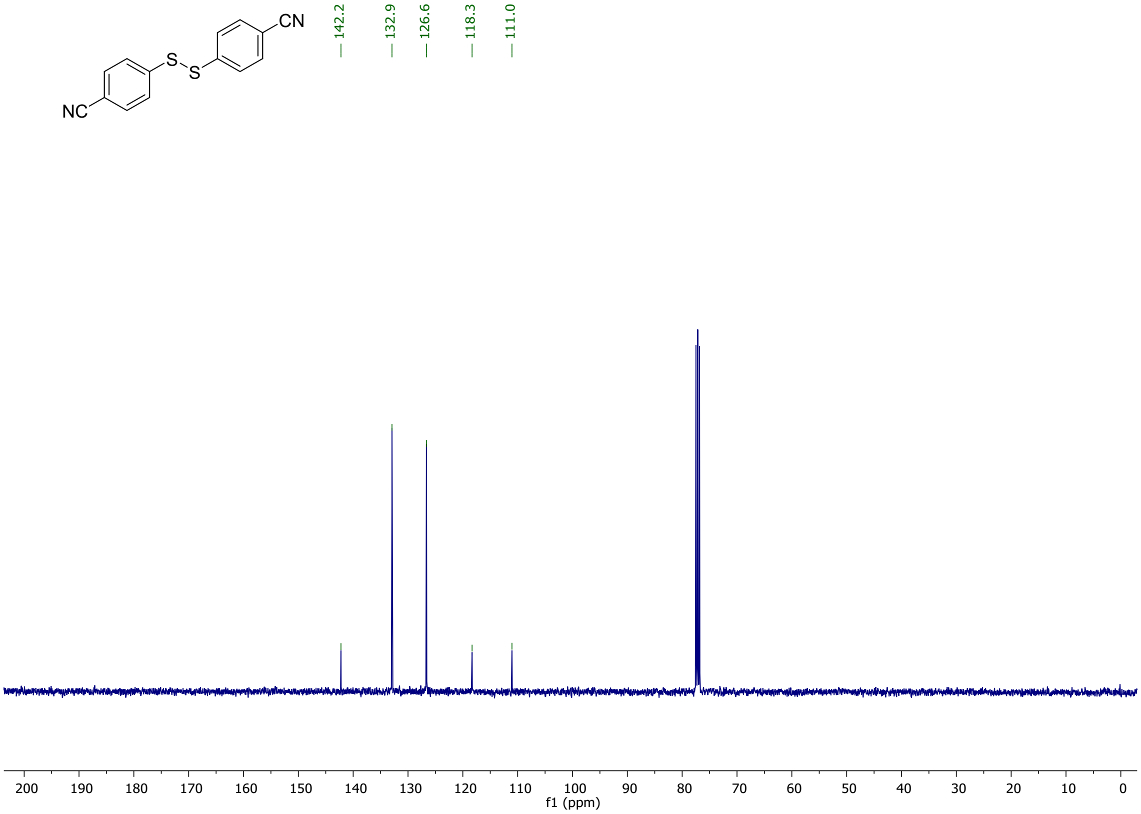

Figure S48. ^{13}C-NMR spectra of compound **2i**.

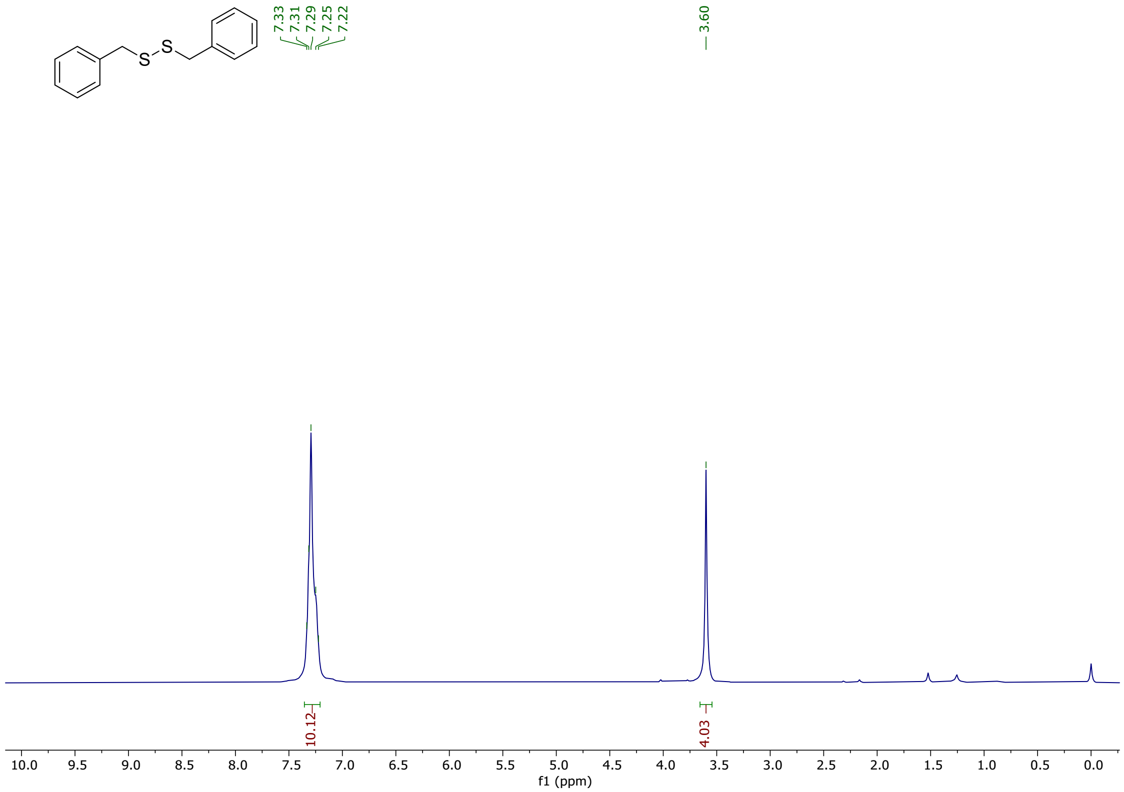

Figure S49. ^{1}H-NMR spectra of compound **2j**.

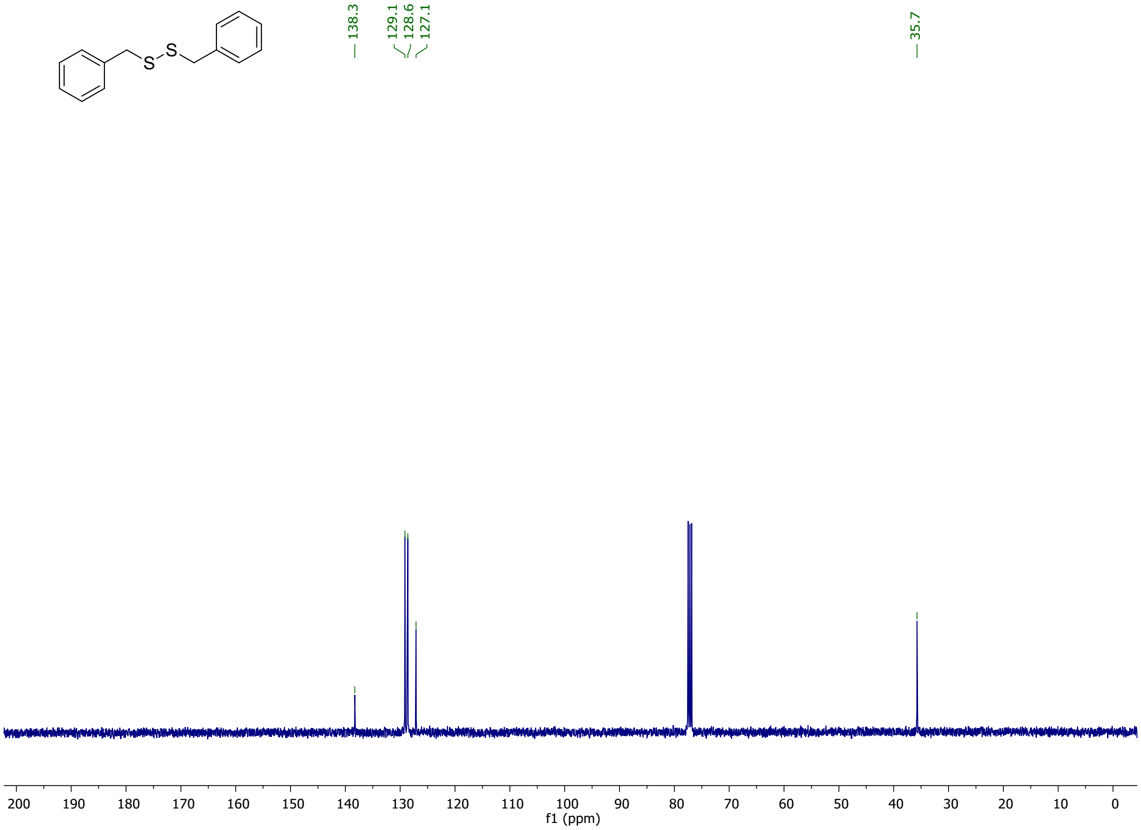

Figure S50. ^{13}C-NMR spectra of compound **2j**.

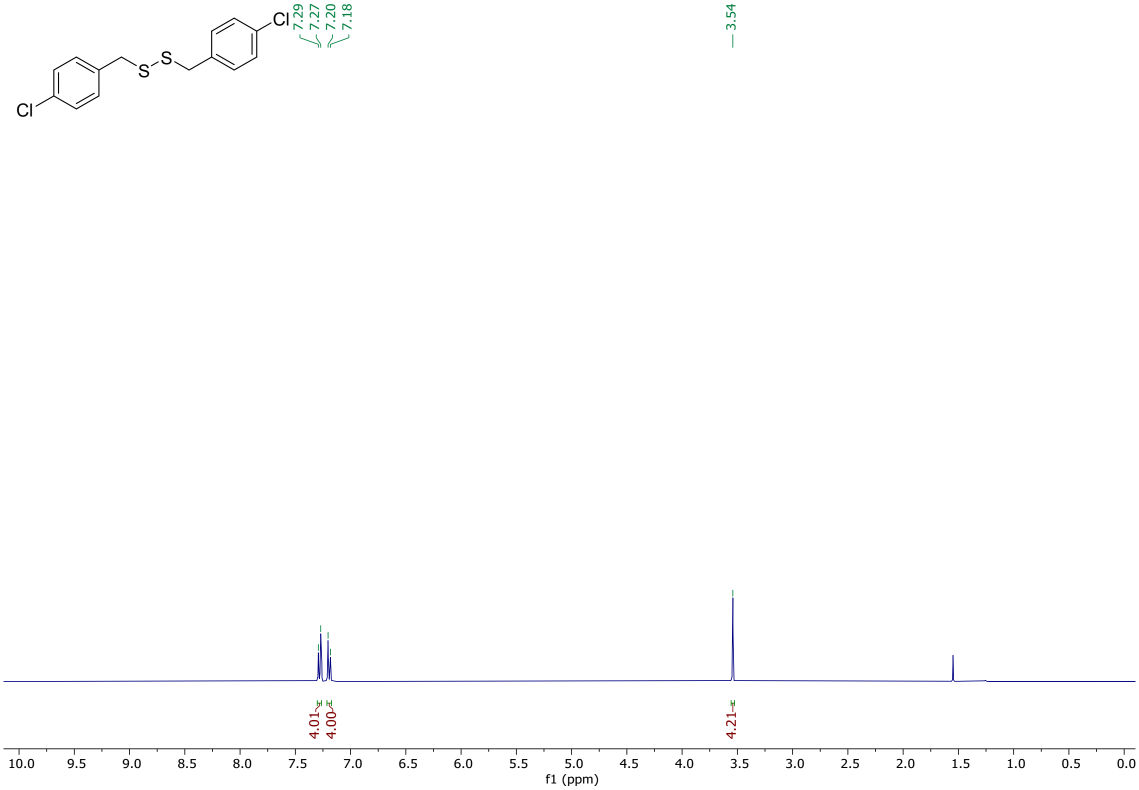

Figure S51. ^{1}H-NMR spectra of compound **2k**.

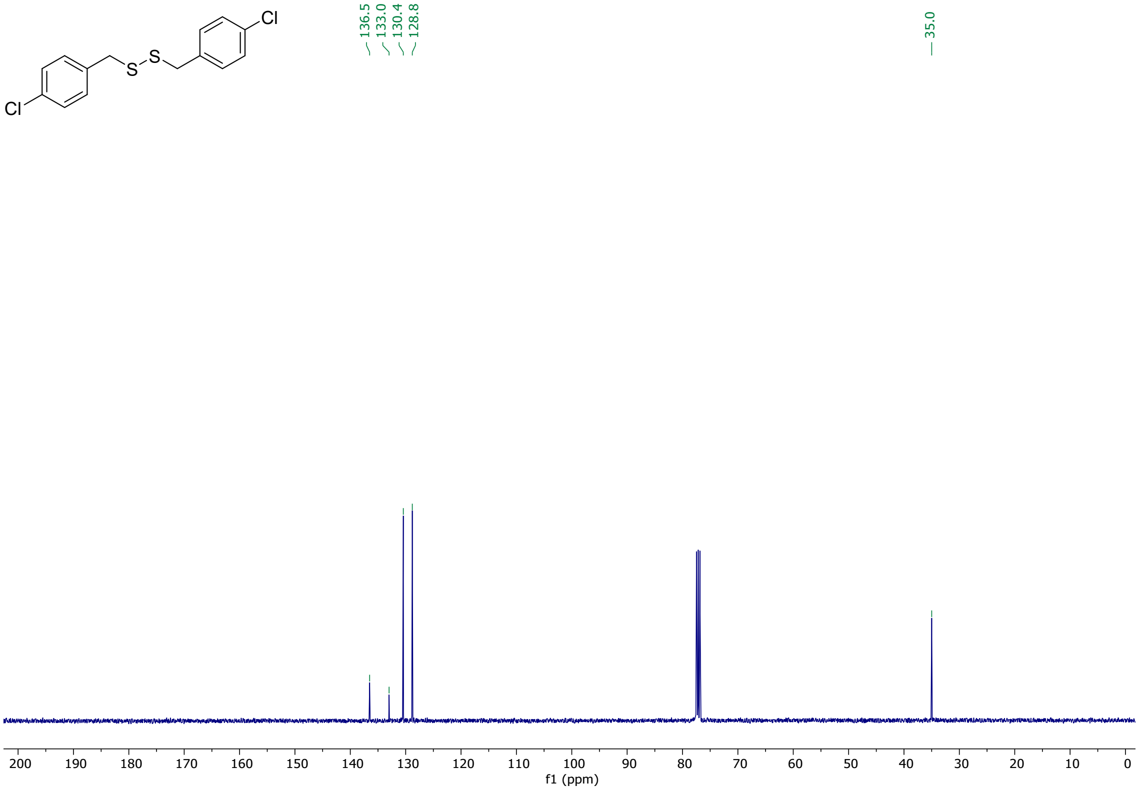

Figure S52. ^{13}C-NMR spectra of compound **2k**.

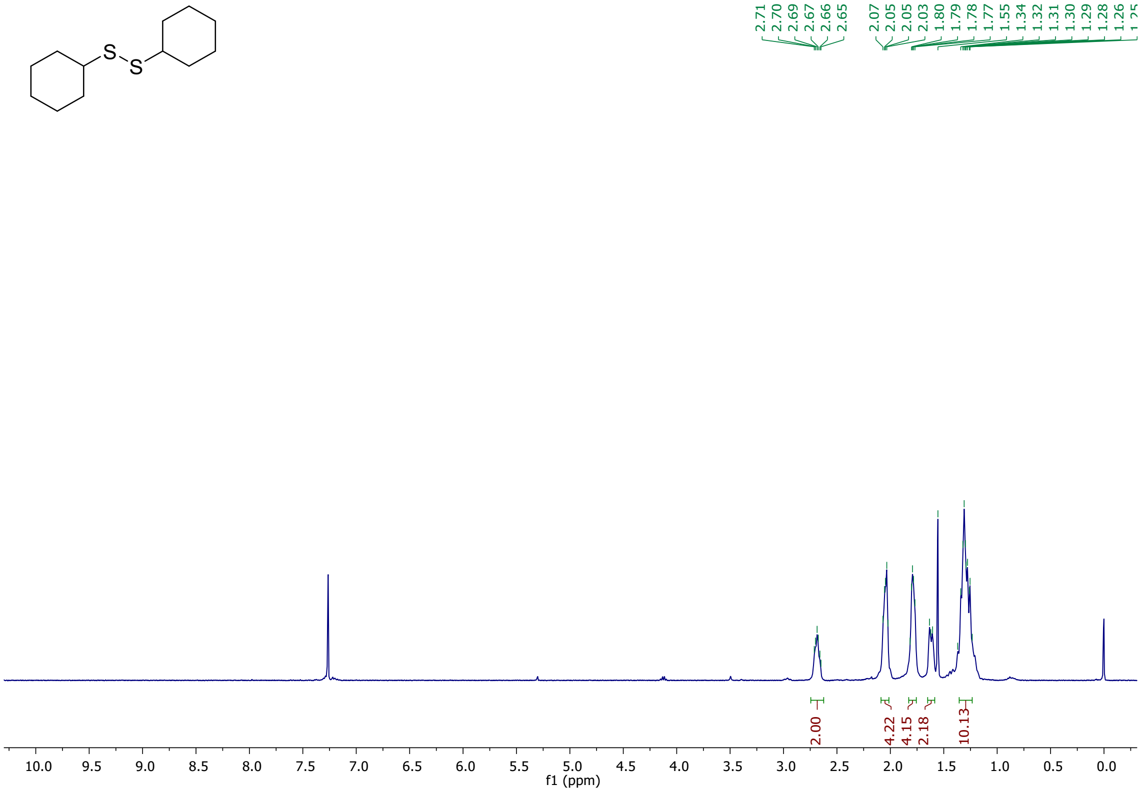

Figure S53. ^{1}H-NMR spectra of compound **2l**.

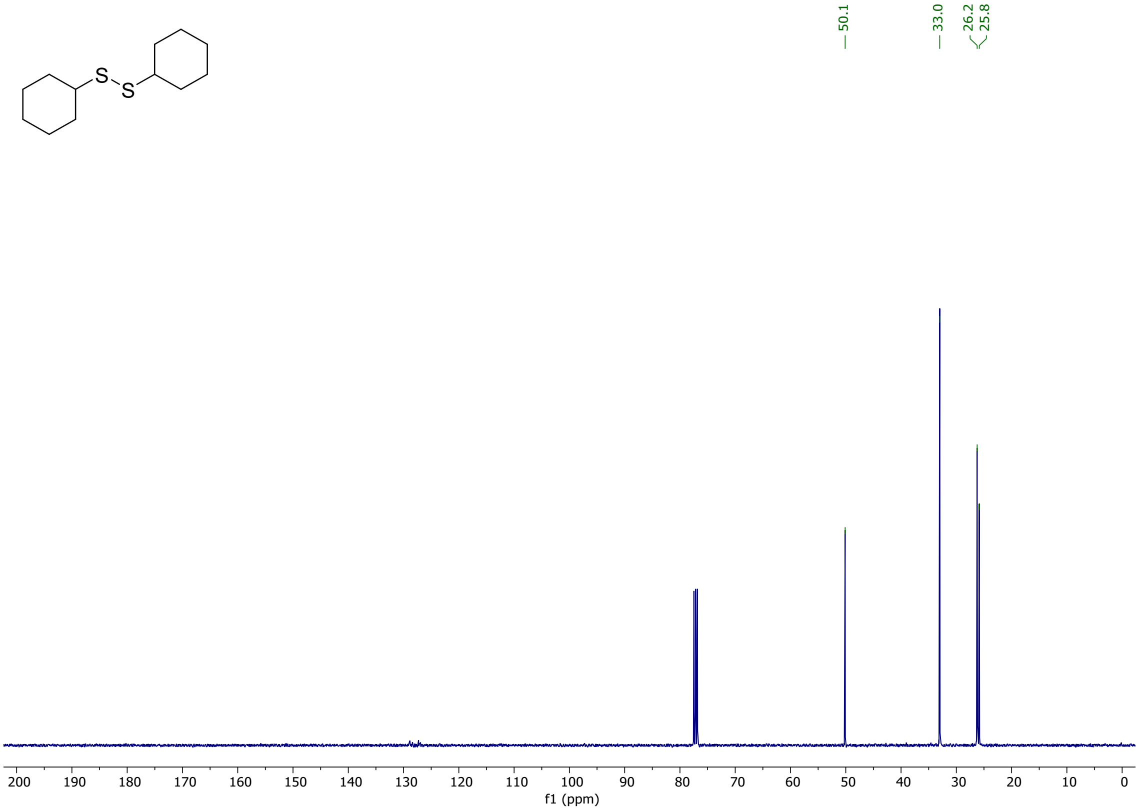

Figure S54. ^{13}C-NMR spectra of compound **2l**.

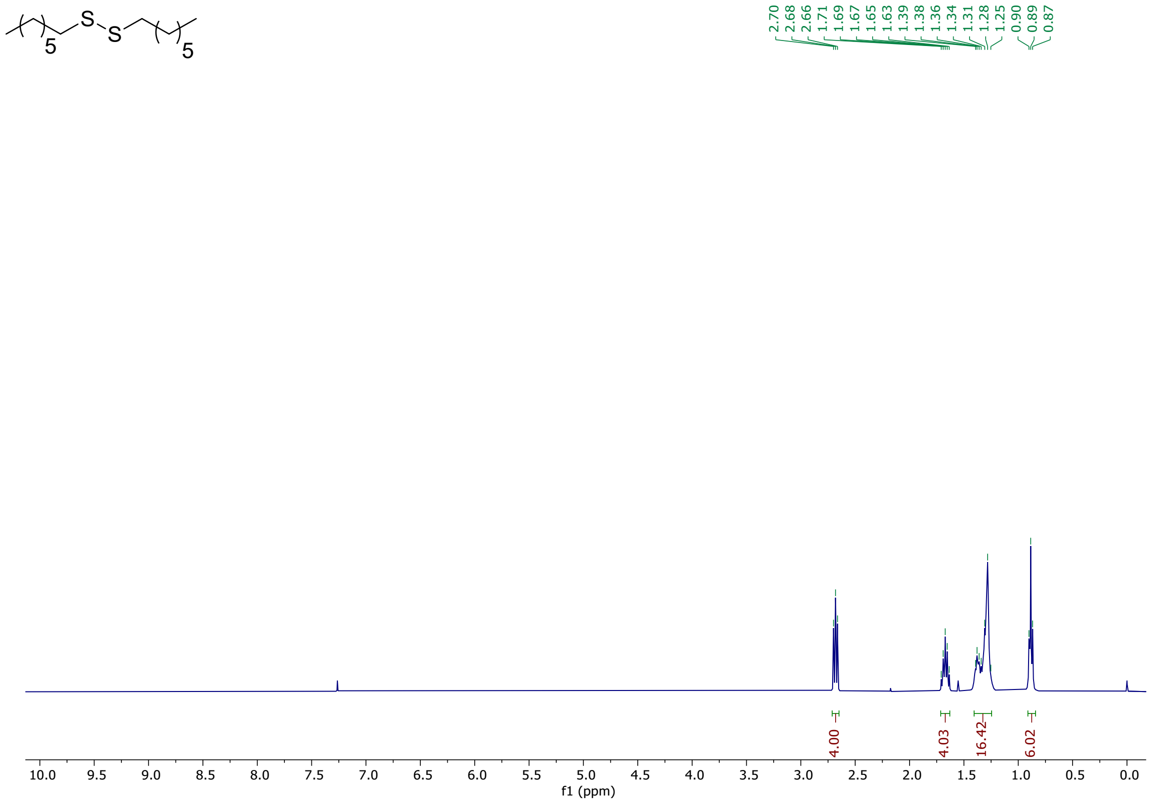

Figure S55. ^{1}H-NMR spectra of compound **2m**.

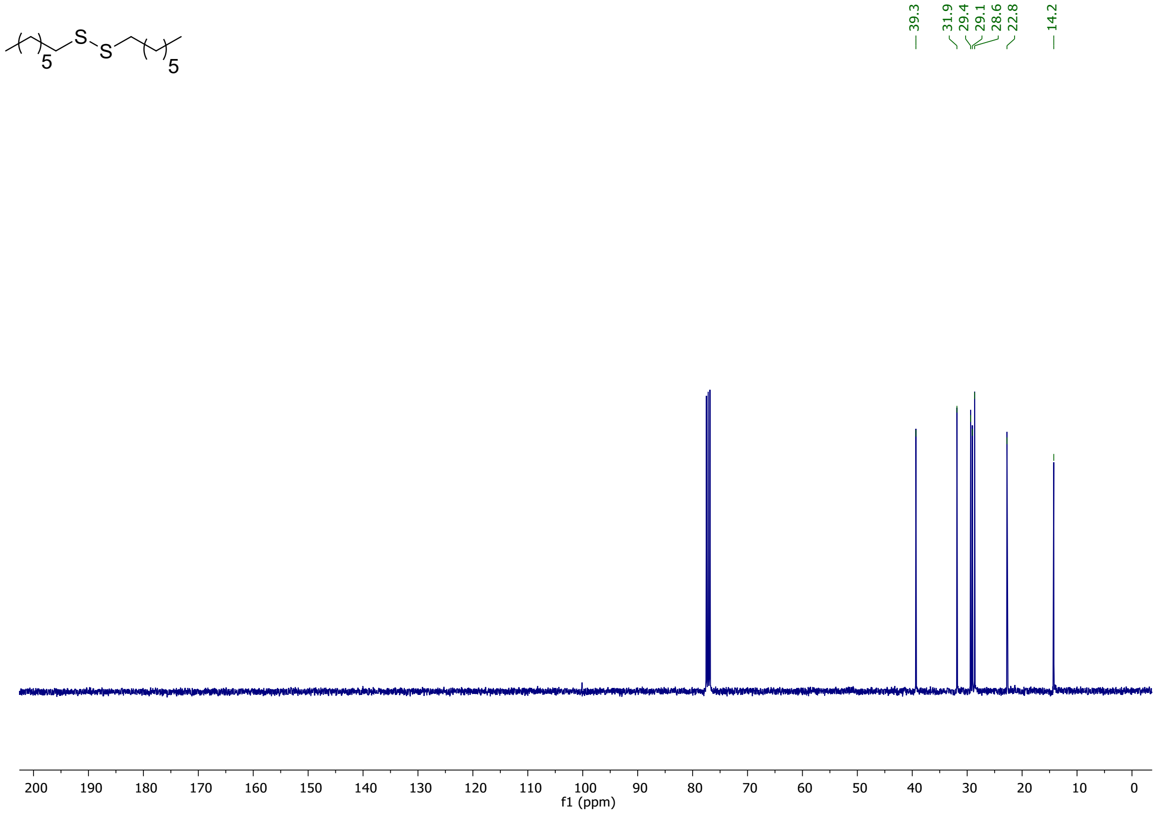

Figure S56. ^{1}H-NMR spectra of compound **2m**.

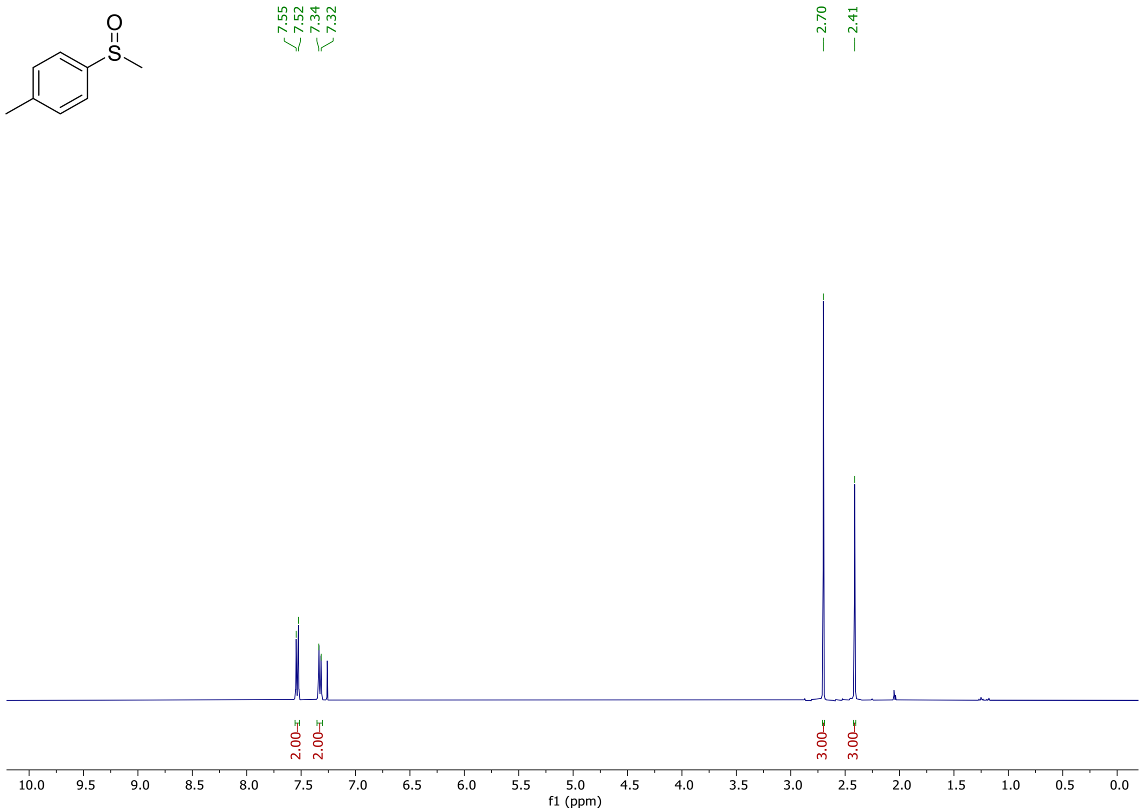

Figure S57. ^{1}H-NMR spectra of compound **5a**.

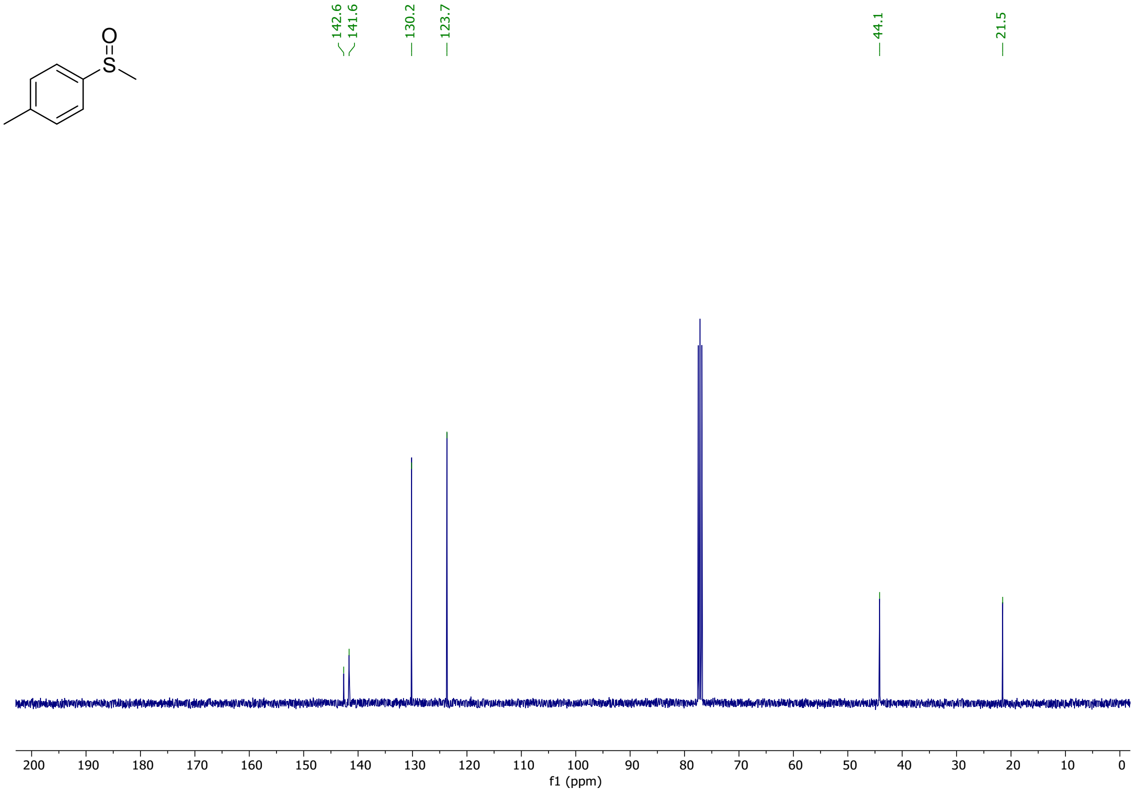

Figure S58. ^{1}H-NMR spectra of compound **5a**.

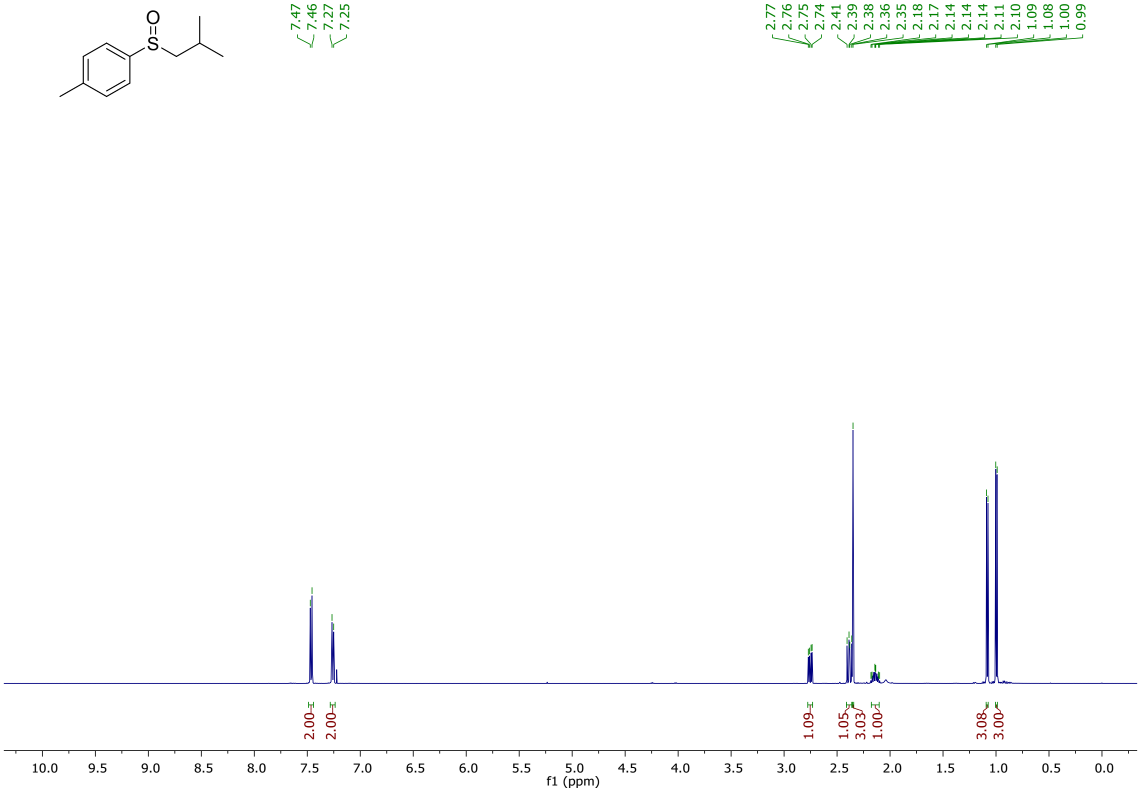

Figure S59. ^{1}H-NMR spectra of compound **5b**.

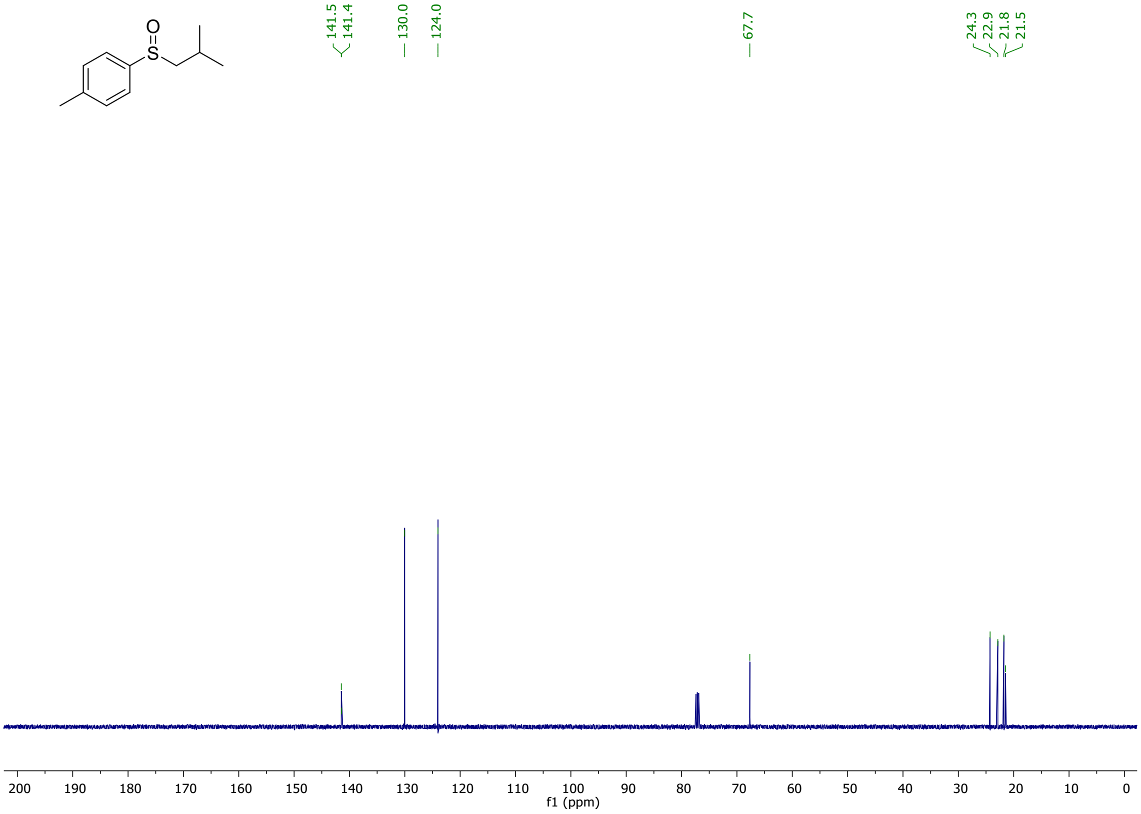

Figure S60. ^{13}C-NMR spectra of compound **5b**.

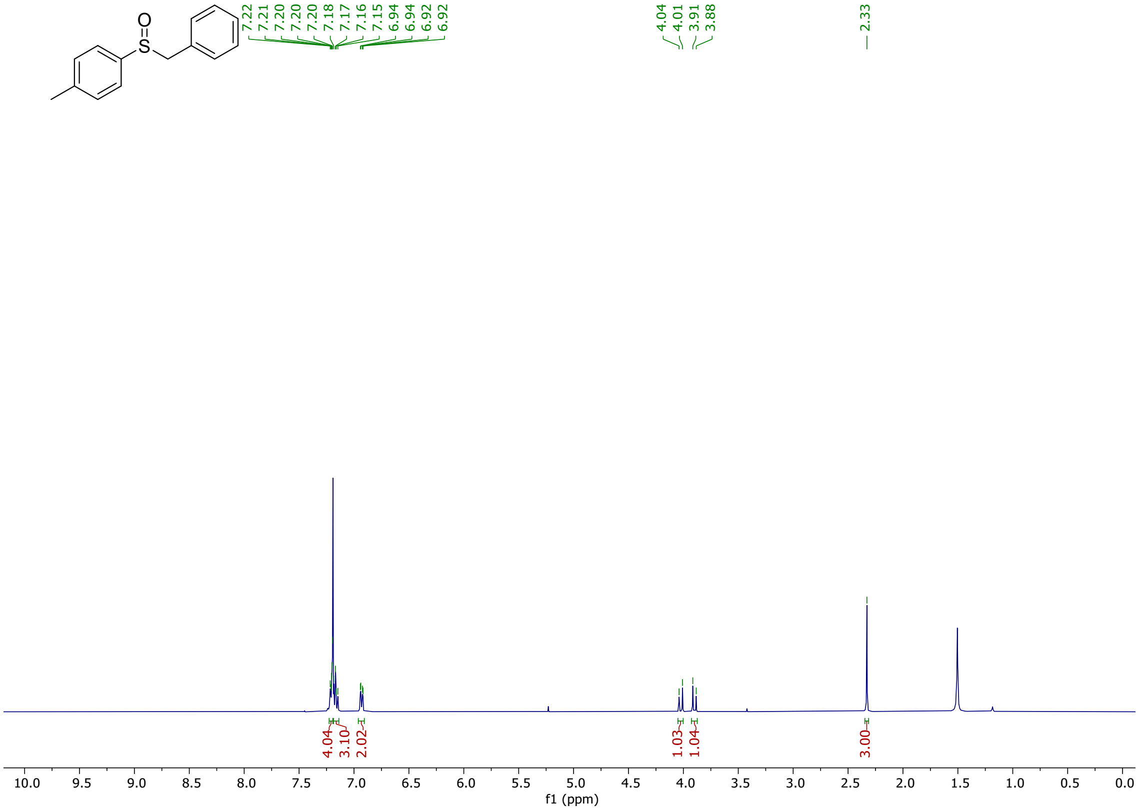

Figure S61. ^{1}H-NMR spectra of compound **5c**.

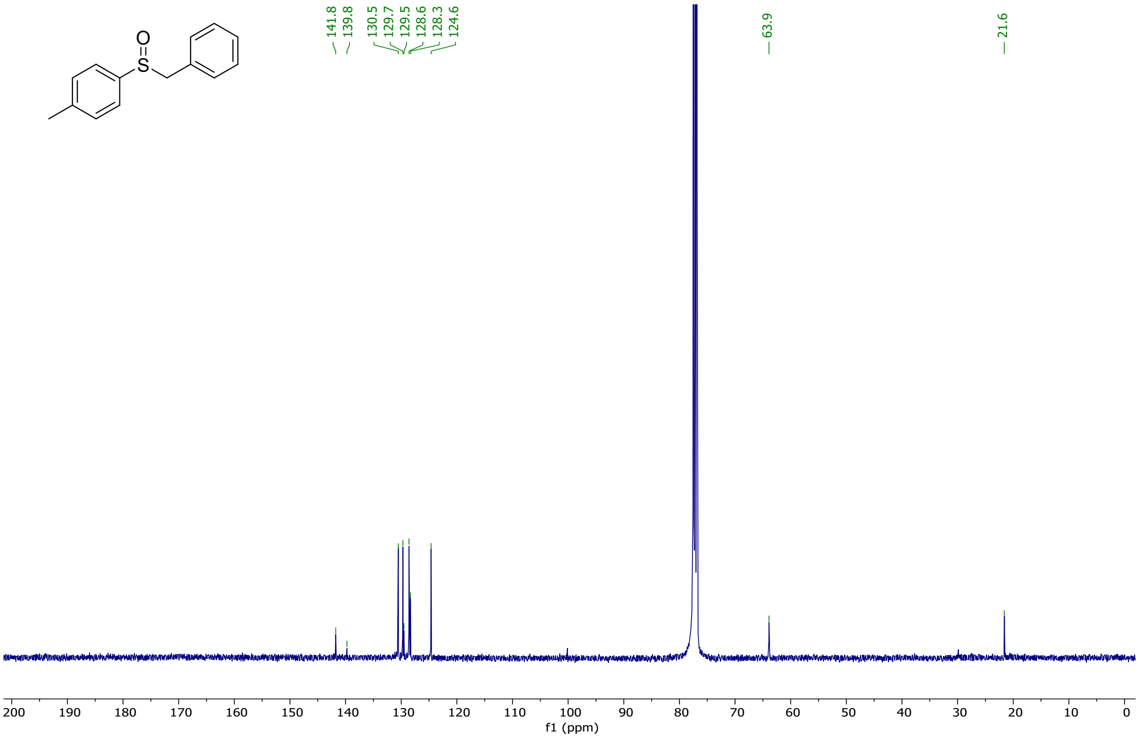

Figure S62. ^{13}C-NMR spectra of compound **5c**.

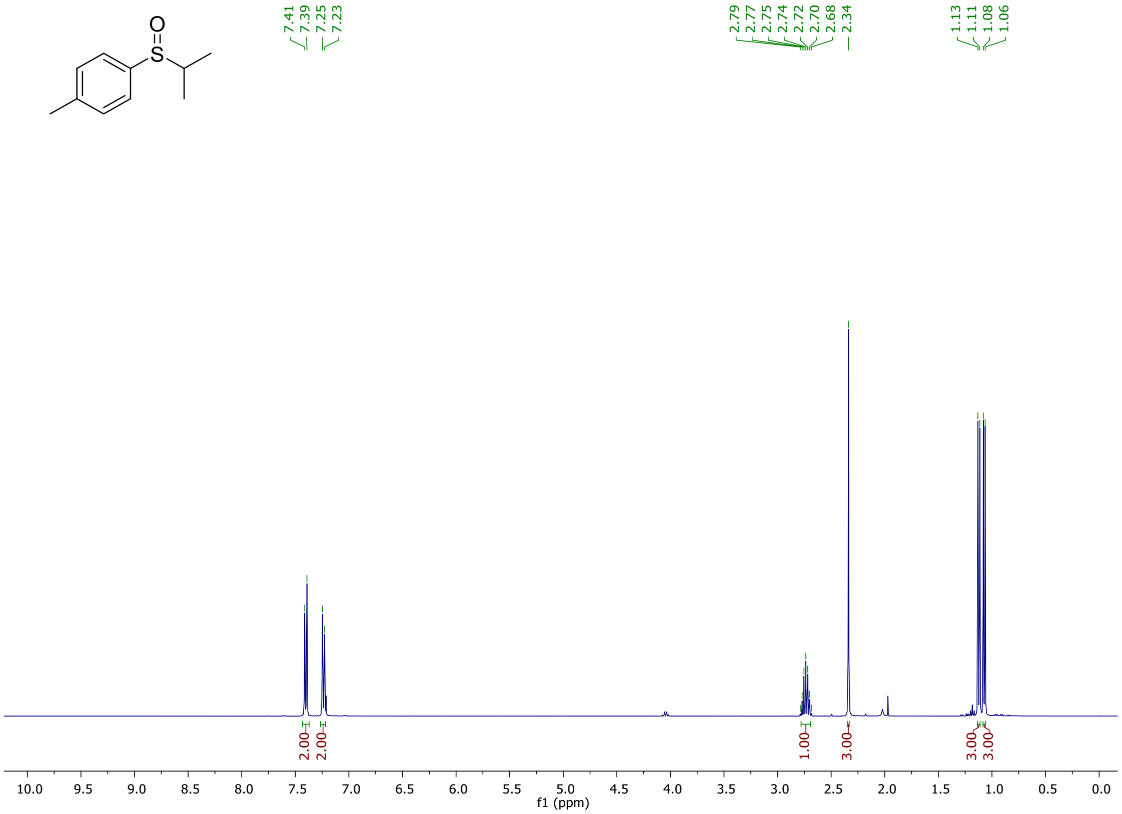

Figure S63. ^{1}H-NMR spectra of compound **5d**.

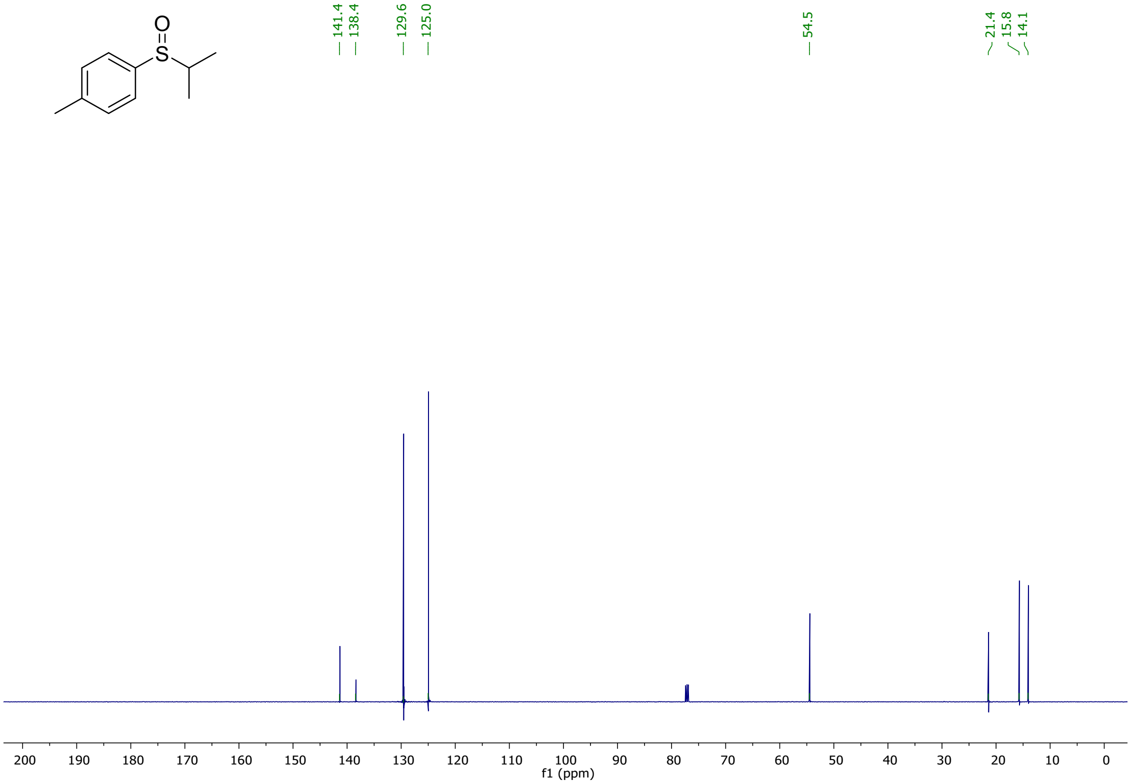

Figure S64. ^{13}C-NMR spectra of compound **5d**.

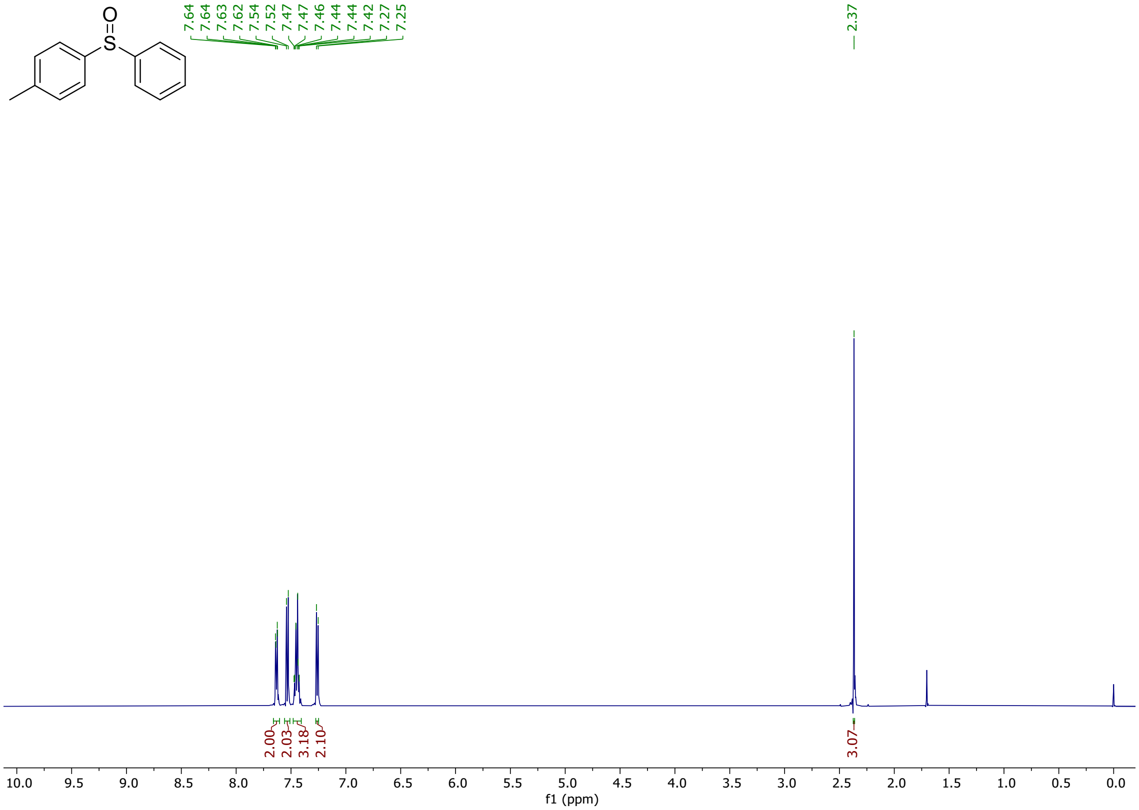

Figure S65. ^{1}H-NMR spectra of compound **5e**.

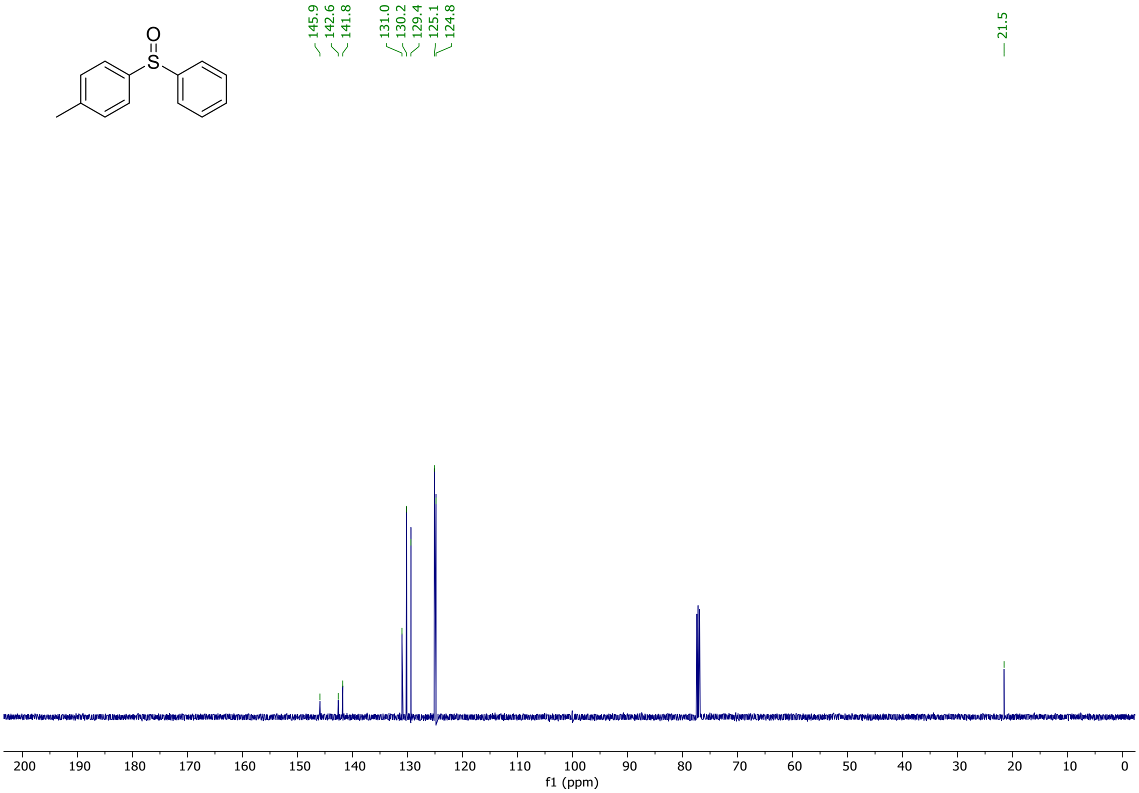

Figure S66. ^{13}C-NMR spectra of compound **5e**.

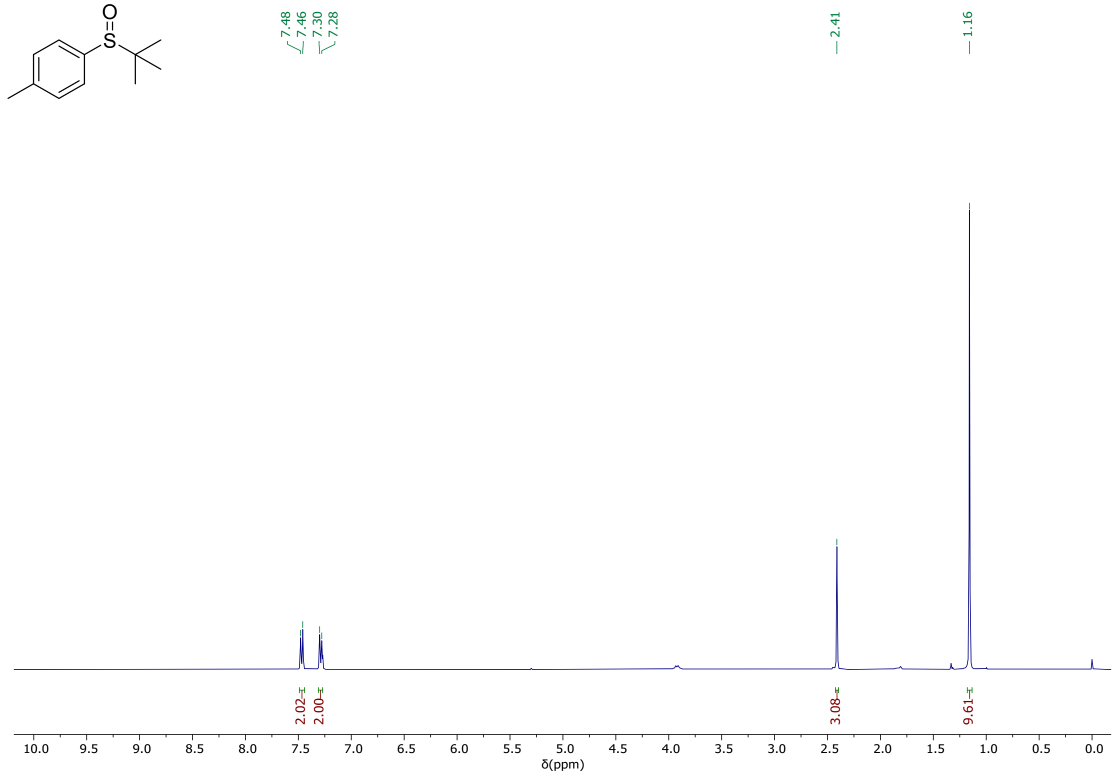

Figure S67. ^{1}H-NMR spectra of compound **5f**.

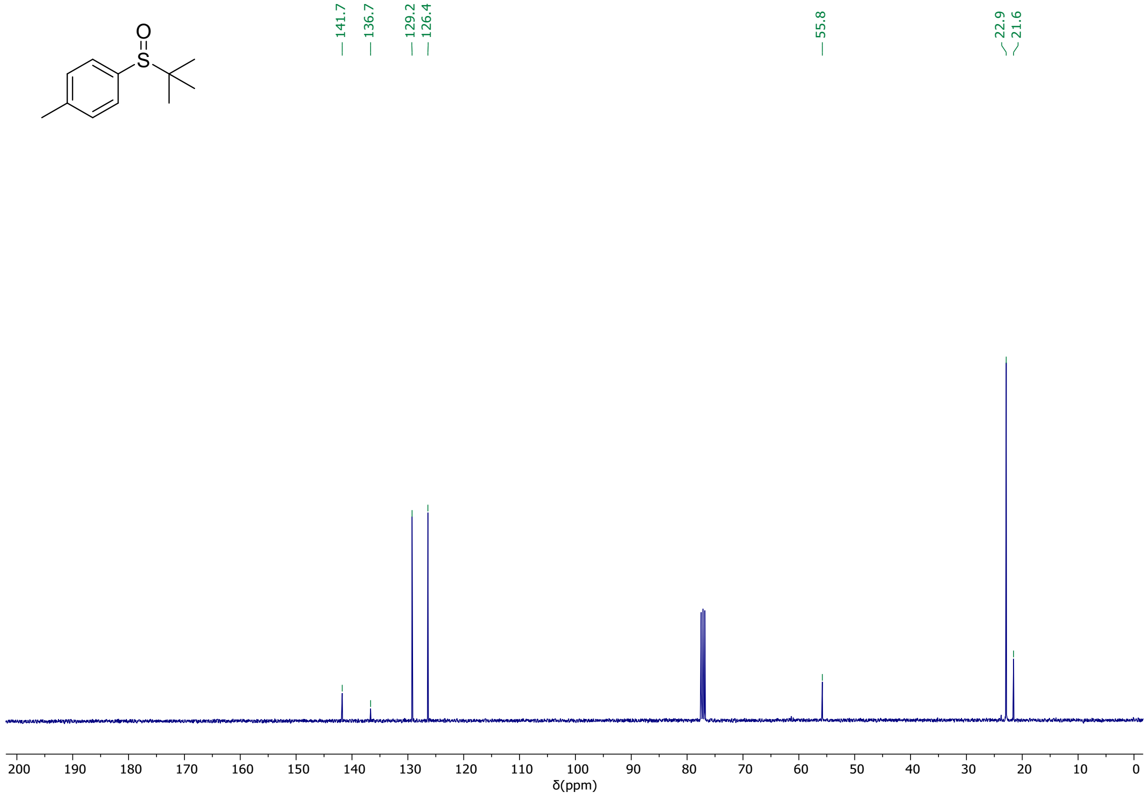

Figure S68. ^{1}H-NMR spectra of compound **5f**.

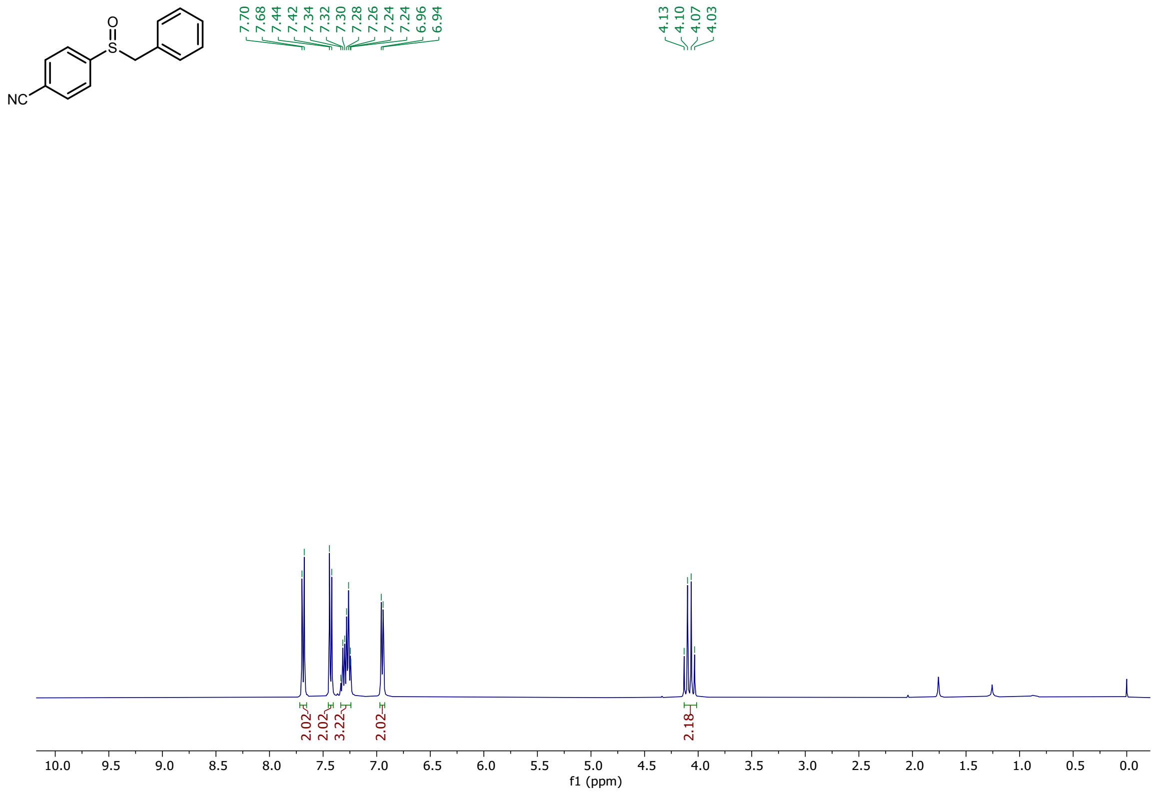

Figure S69. ^{1}H-NMR spectra of compound **5g**.

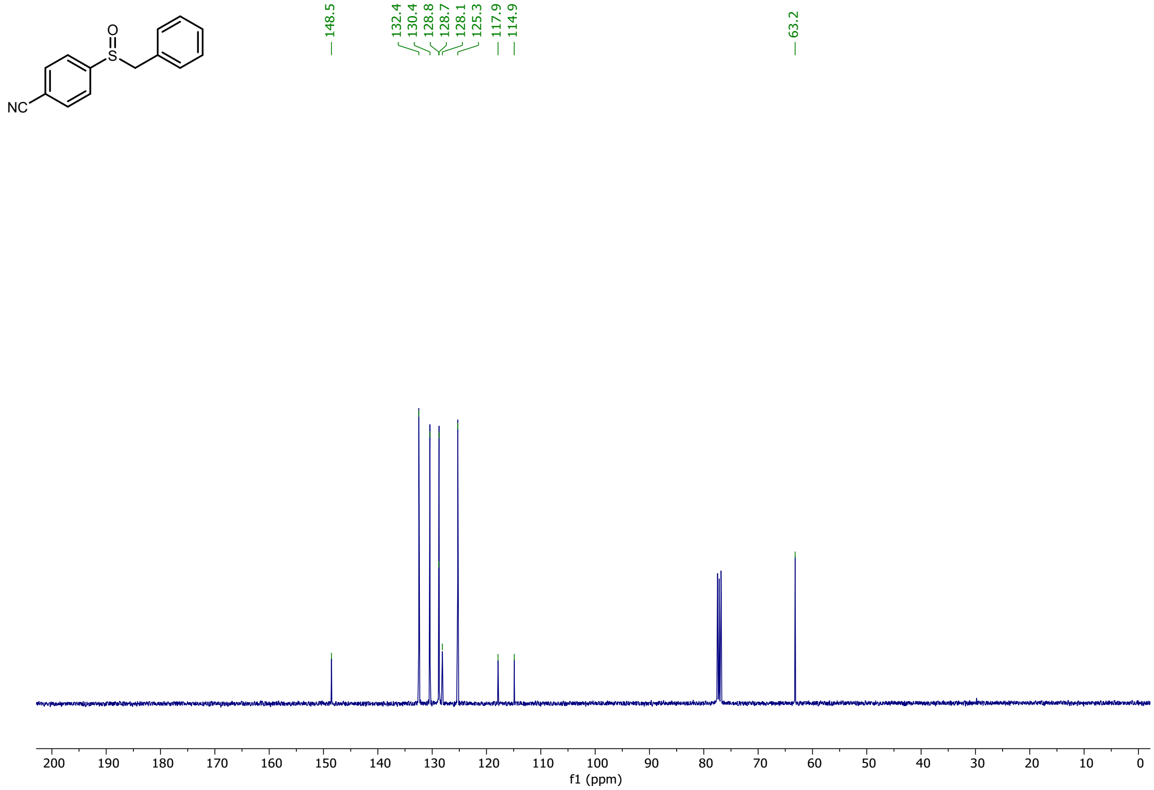

Figure S70. ^{13}C-NMR spectra of compound **5g**.

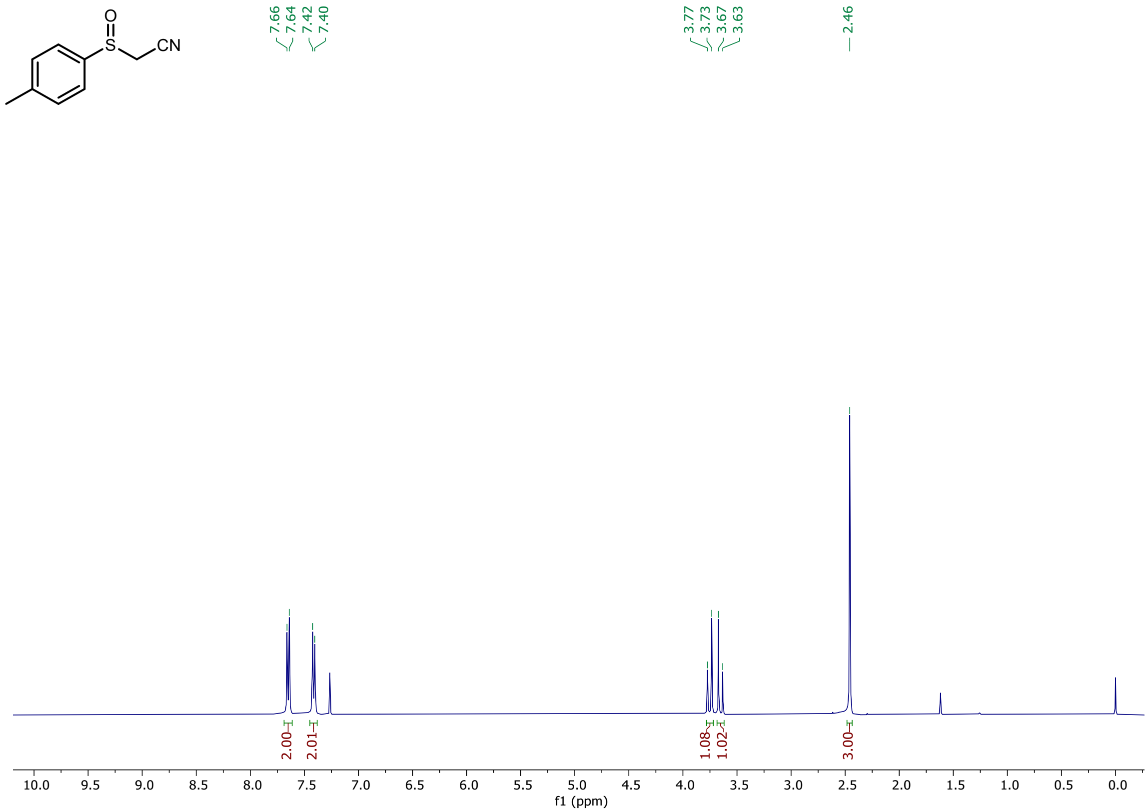

Figure S71. ^{1}H-NMR spectra of compound **5h**.

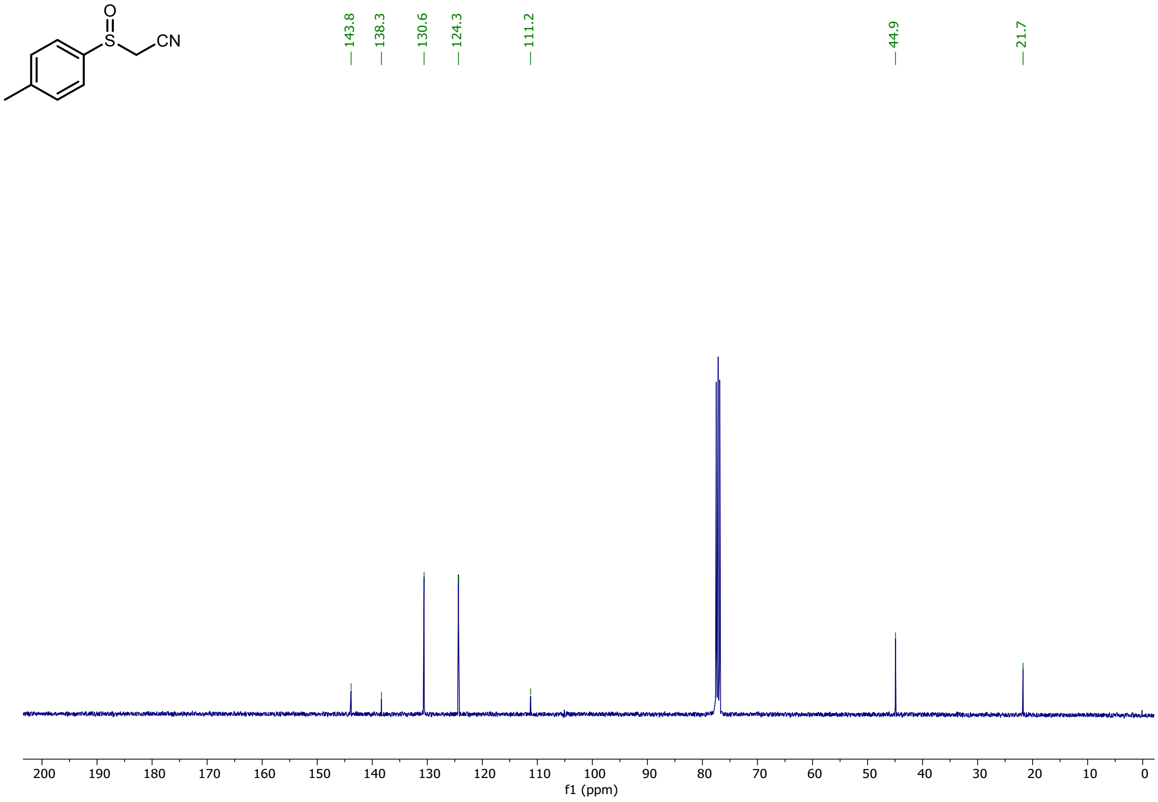

Figure S72. ^{13}C-NMR spectra of compound **5h**.

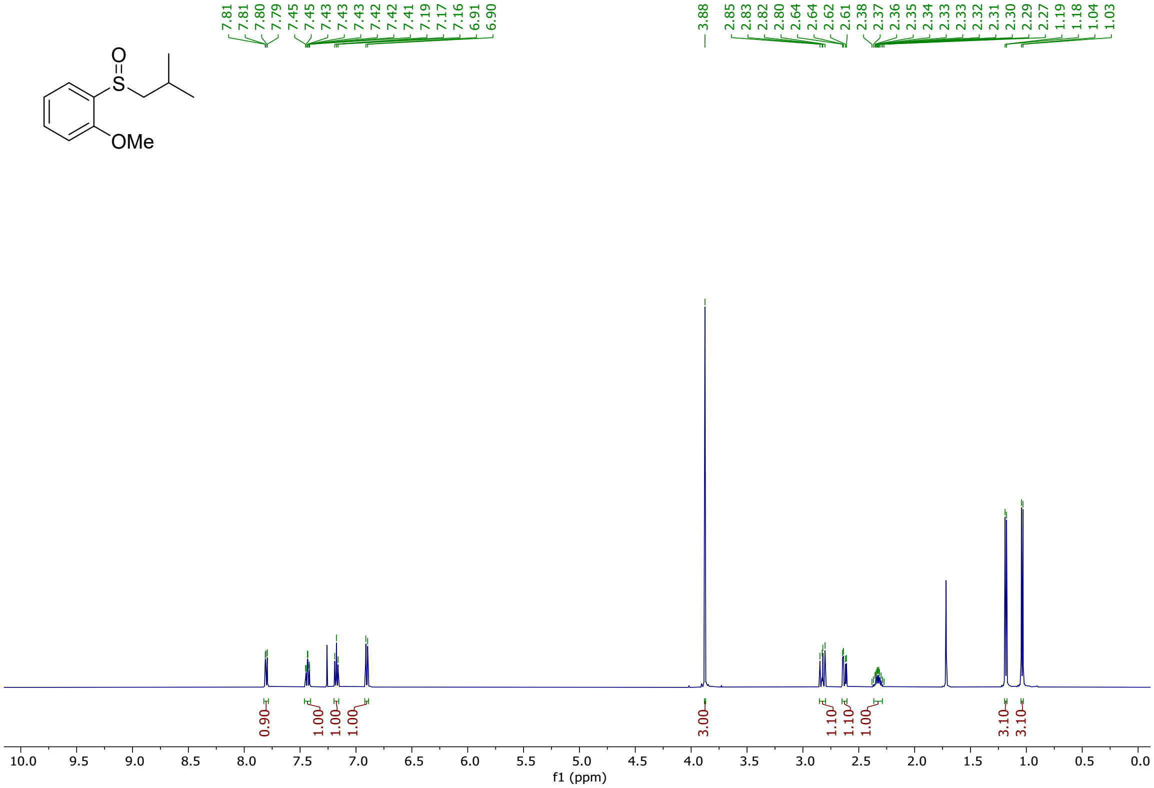

Figure S73. ^{1}H-NMR spectra of compound **5i**.

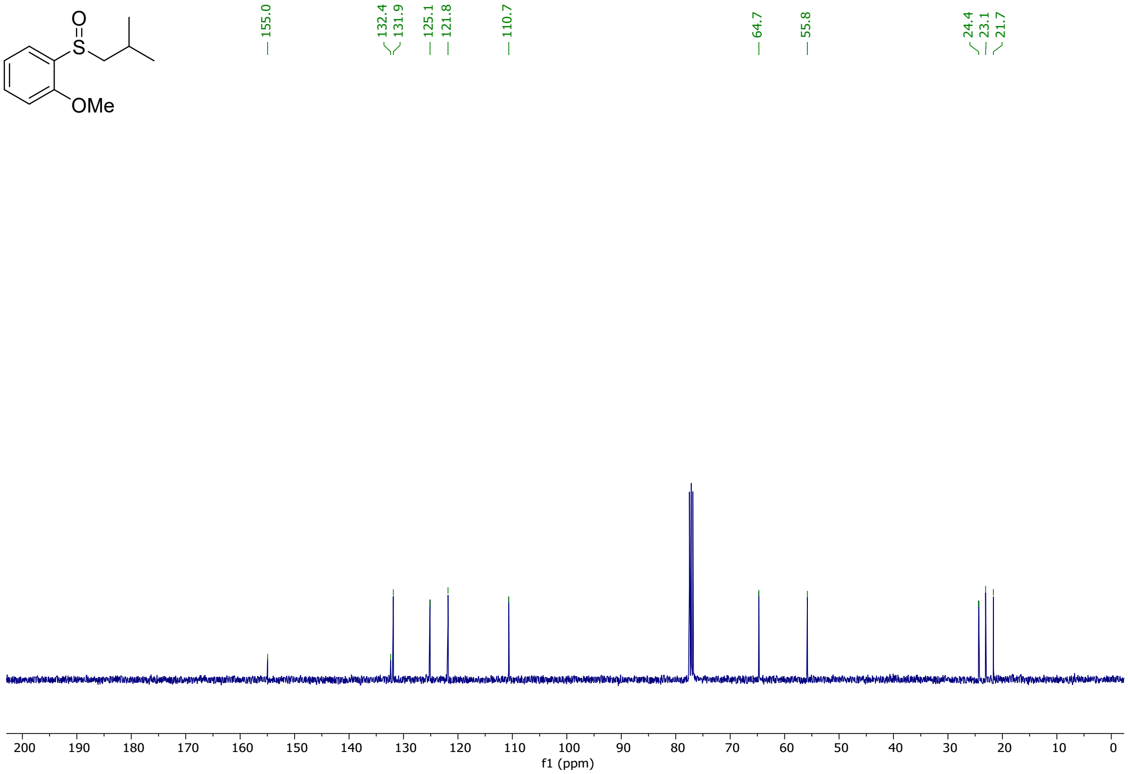

Figure S74. ^{13}C-NMR spectra of compound **5i**.

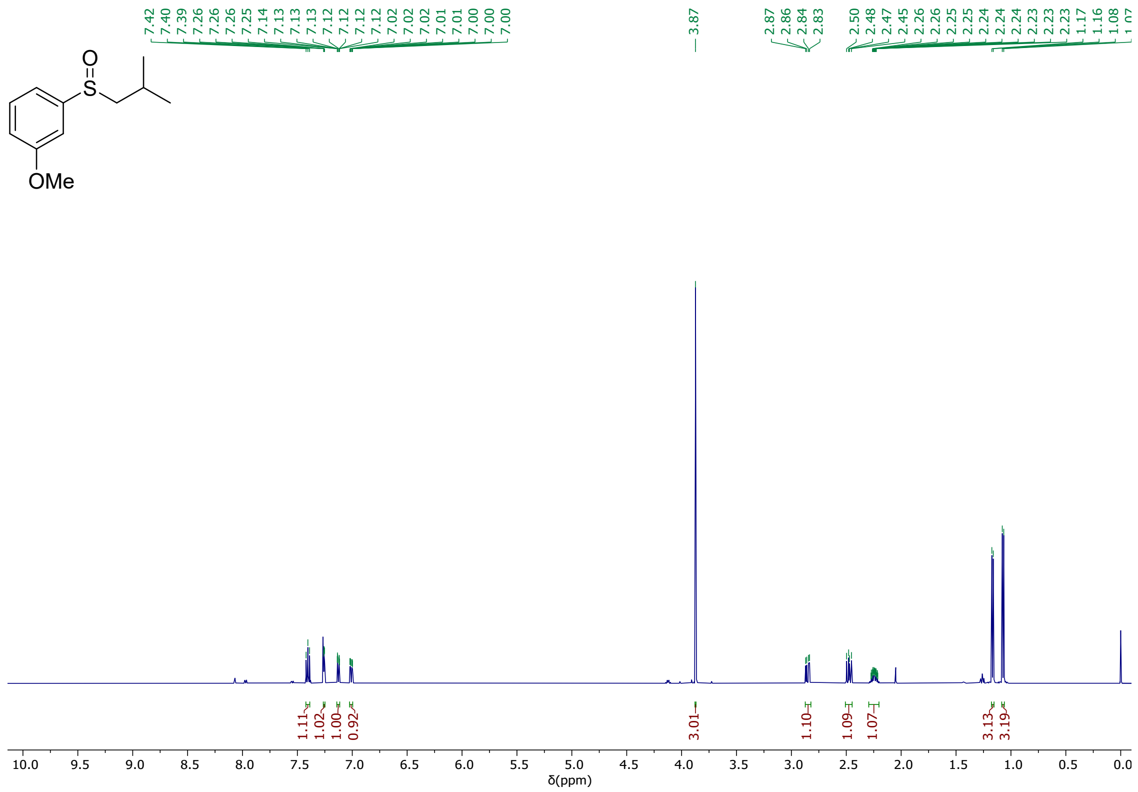

Figure S75. ^{1}H-NMR spectra of compound **5j**.

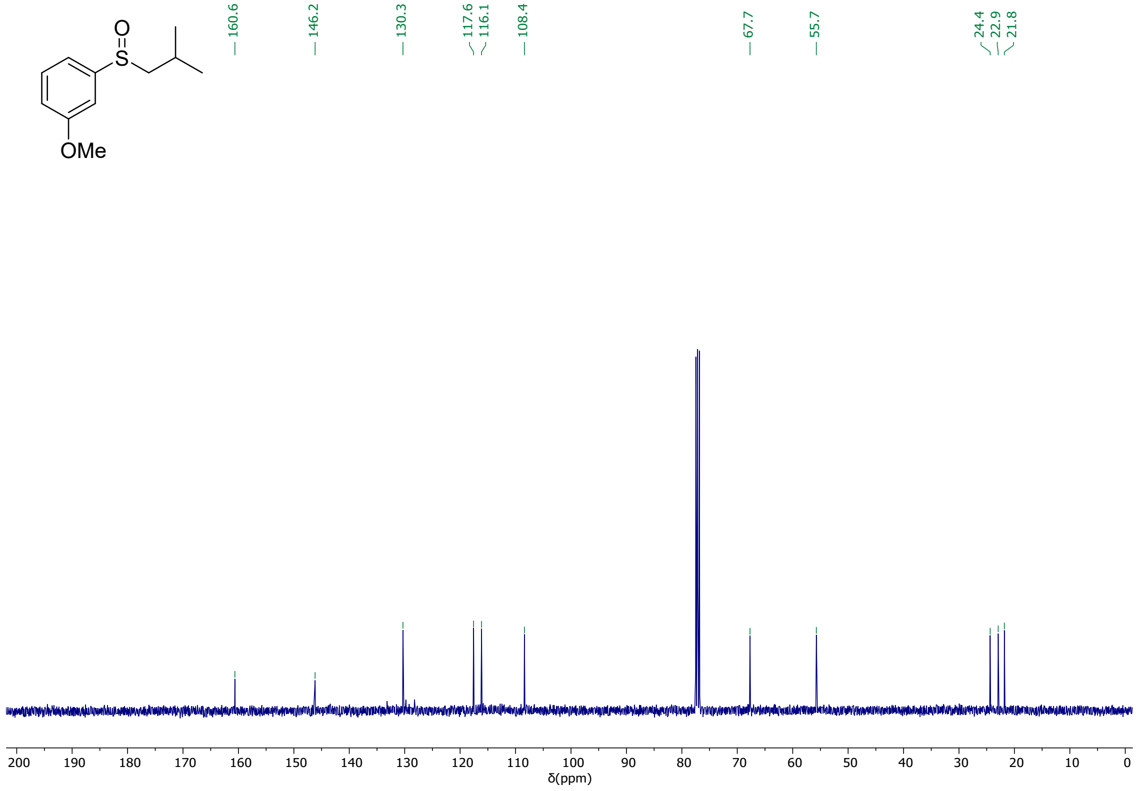

Figure S76. ^{13}C-NMR spectra of compound **5j**.

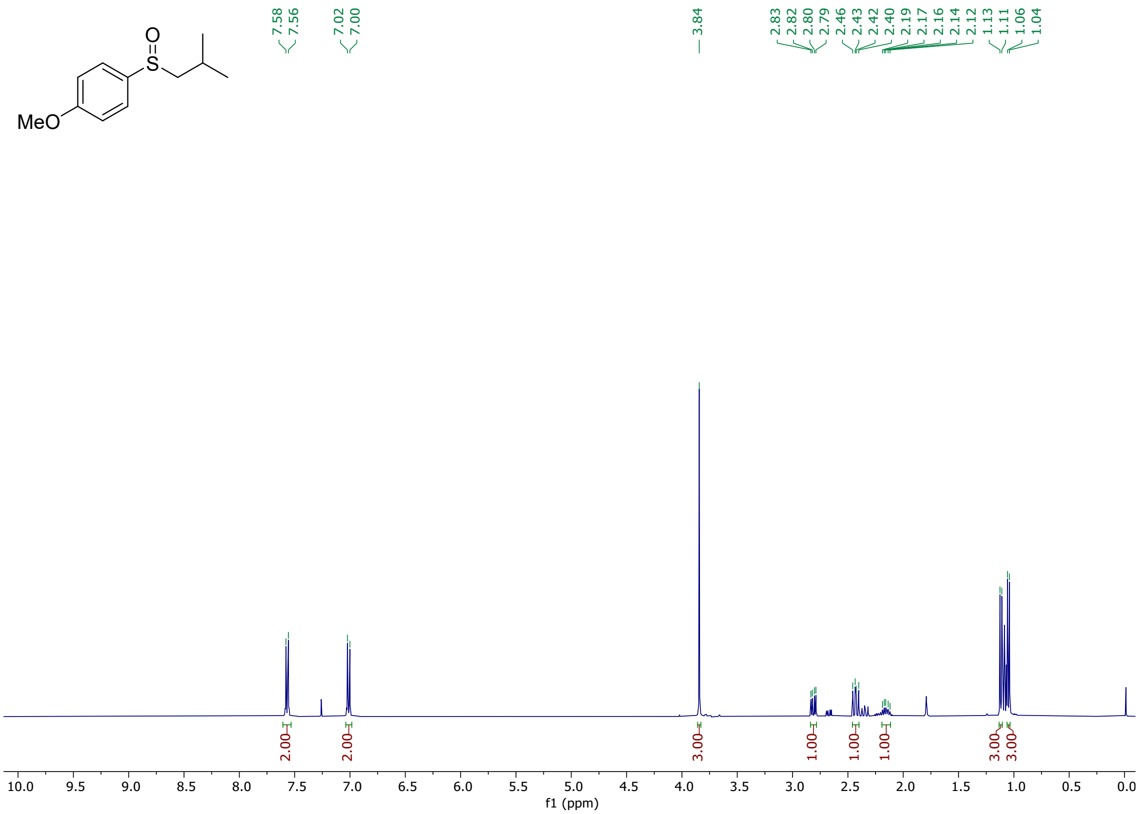

Figure S77. ^{1}H-NMR spectra of compound **5k**.

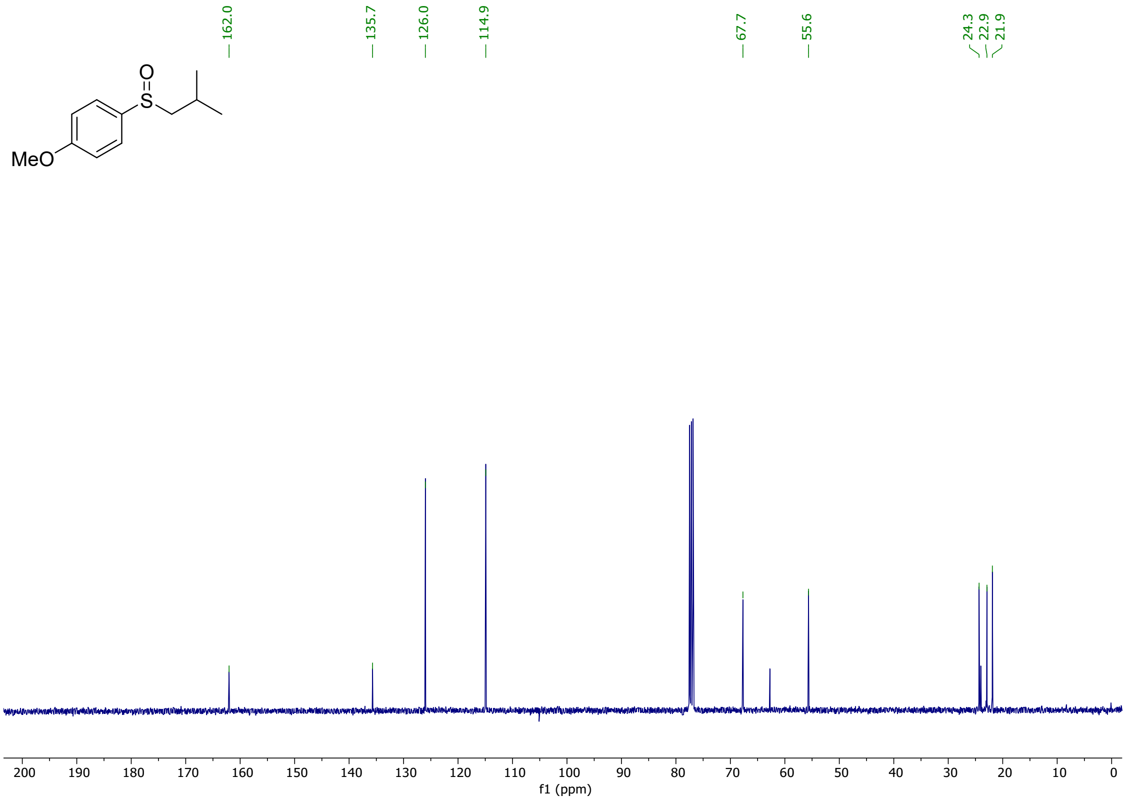

Figure S78. ^{13}C-NMR spectra of compound **5k**.

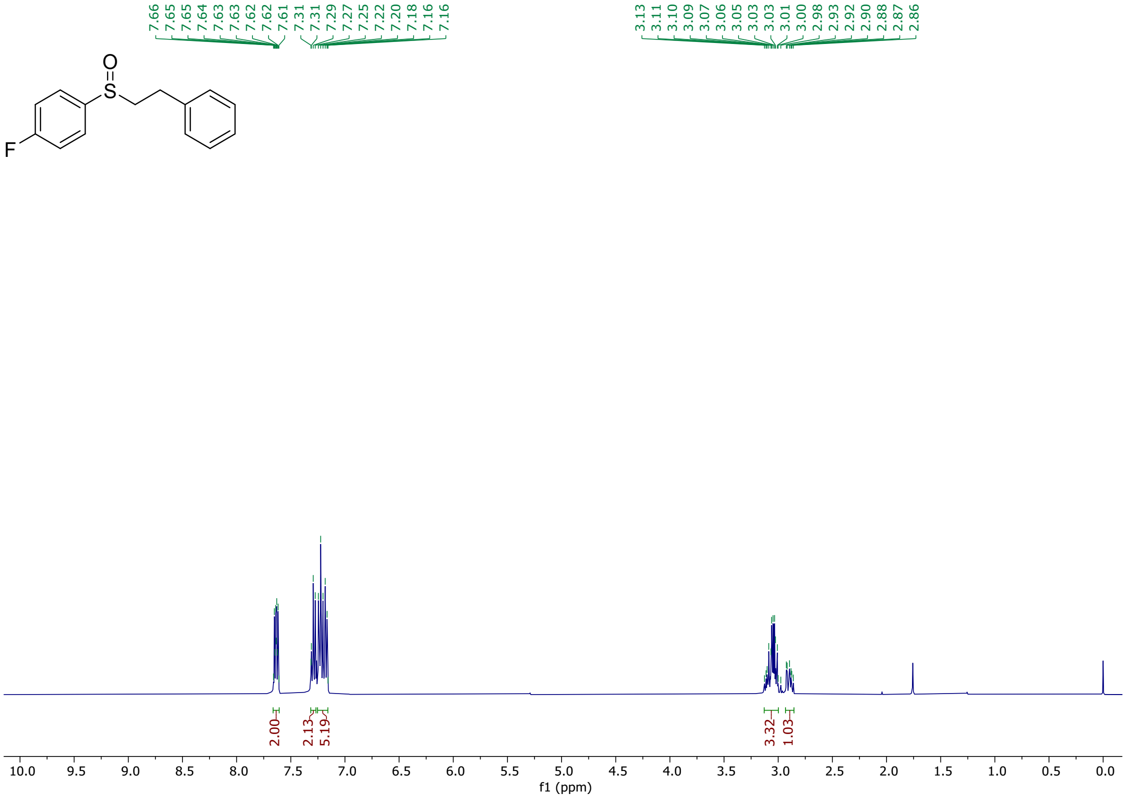

Figure S79. ^{1}H-NMR spectra of compound **5l**.

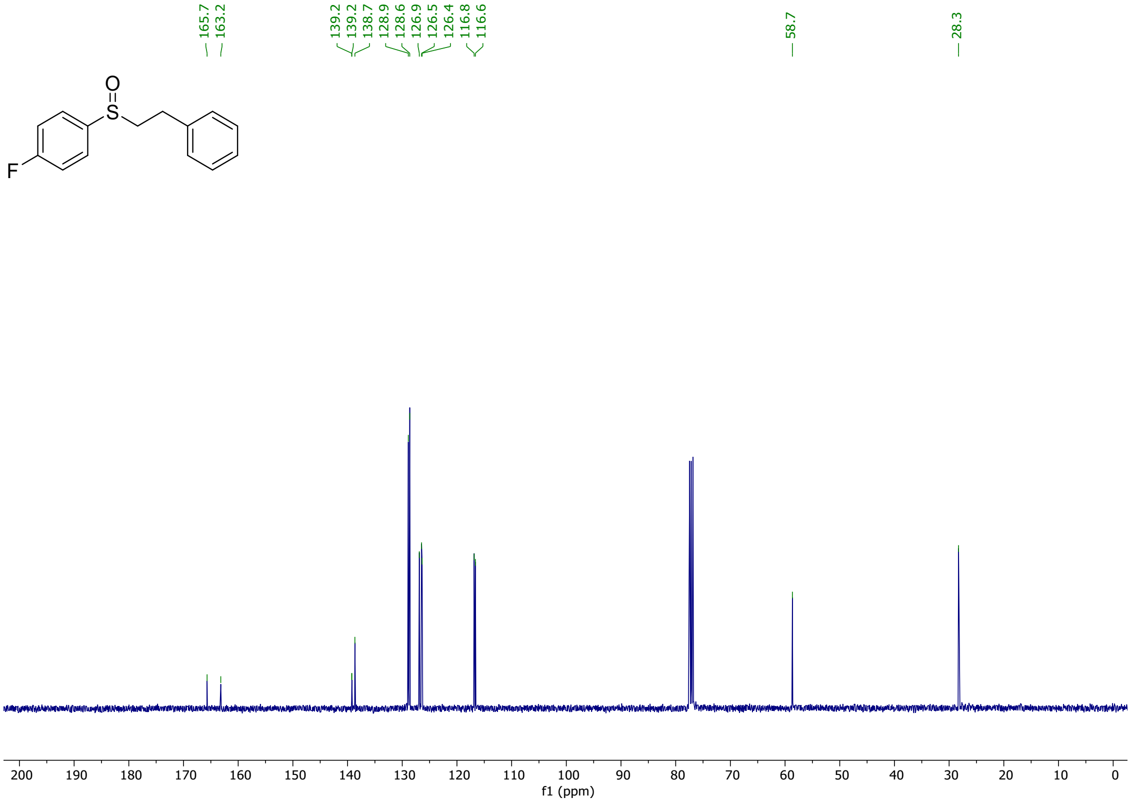

Figure S80. ^{13}C-NMR spectra of compound **5l**.

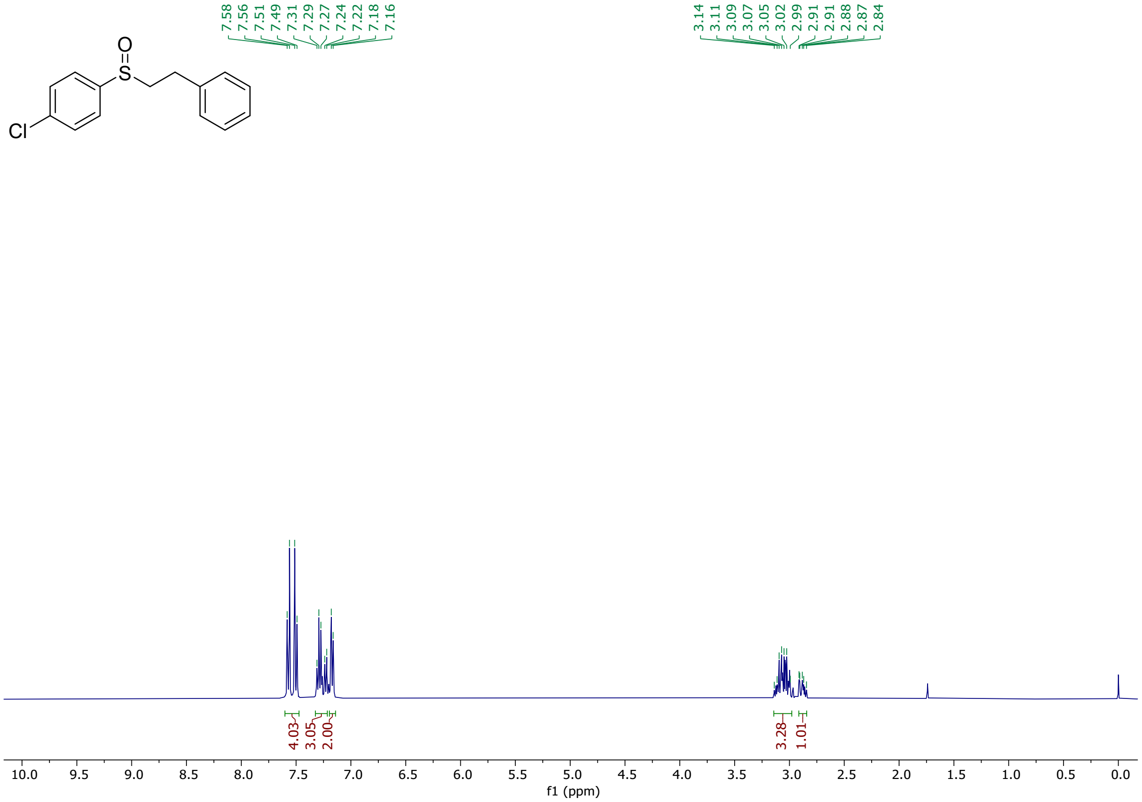

Figure S81. ^{1}H-NMR spectra of compound **5m**.

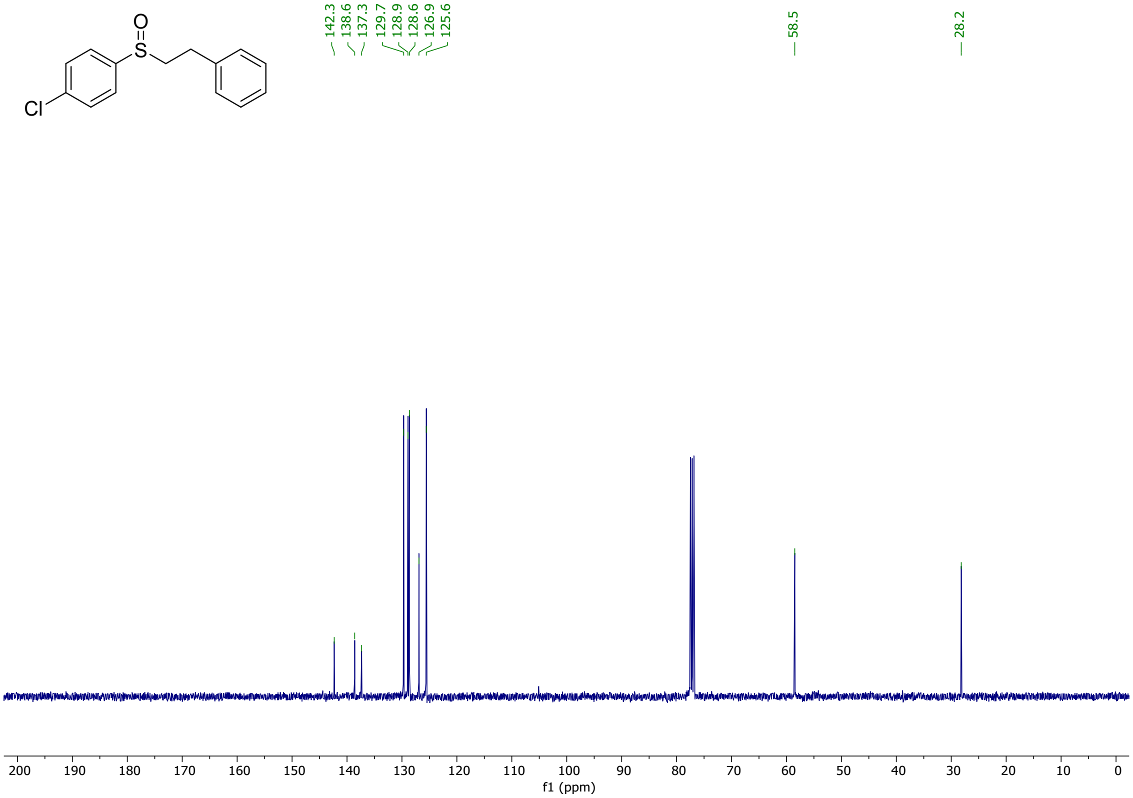

Figure S82. ^{13}C-NMR spectra of compound **5m**.

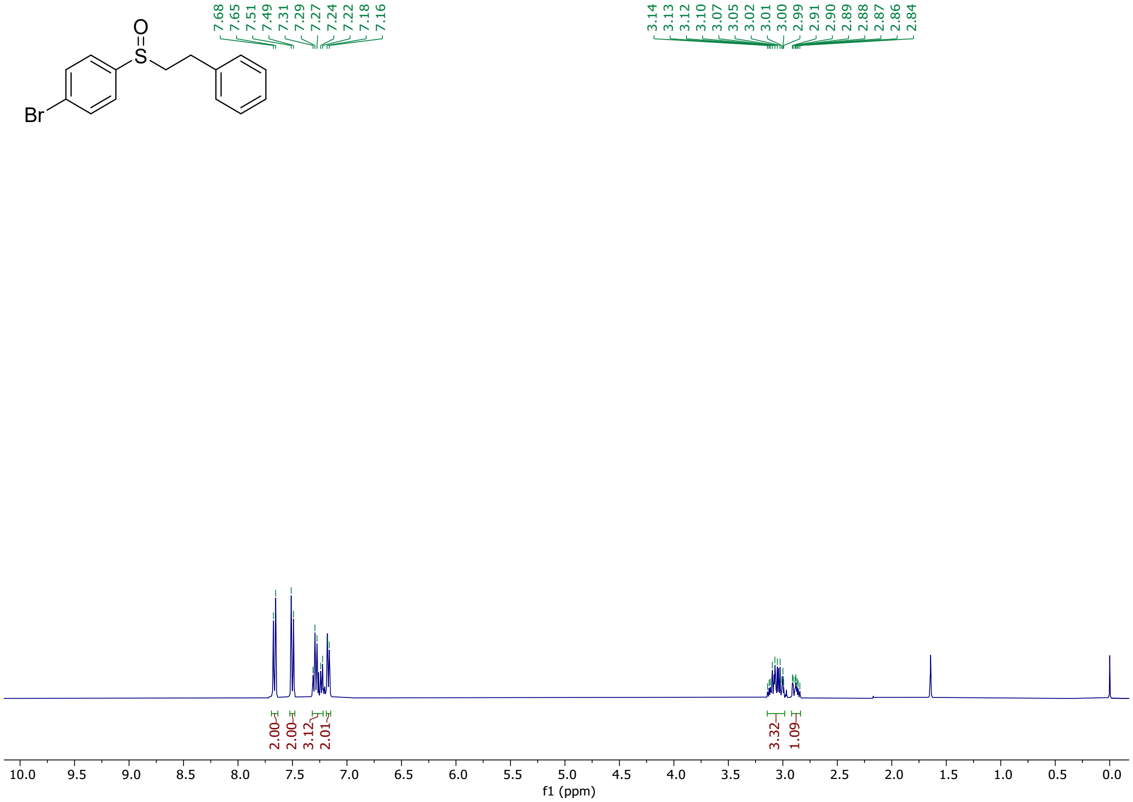

Figure S83. ^{1}H-NMR spectra of compound **5n**.

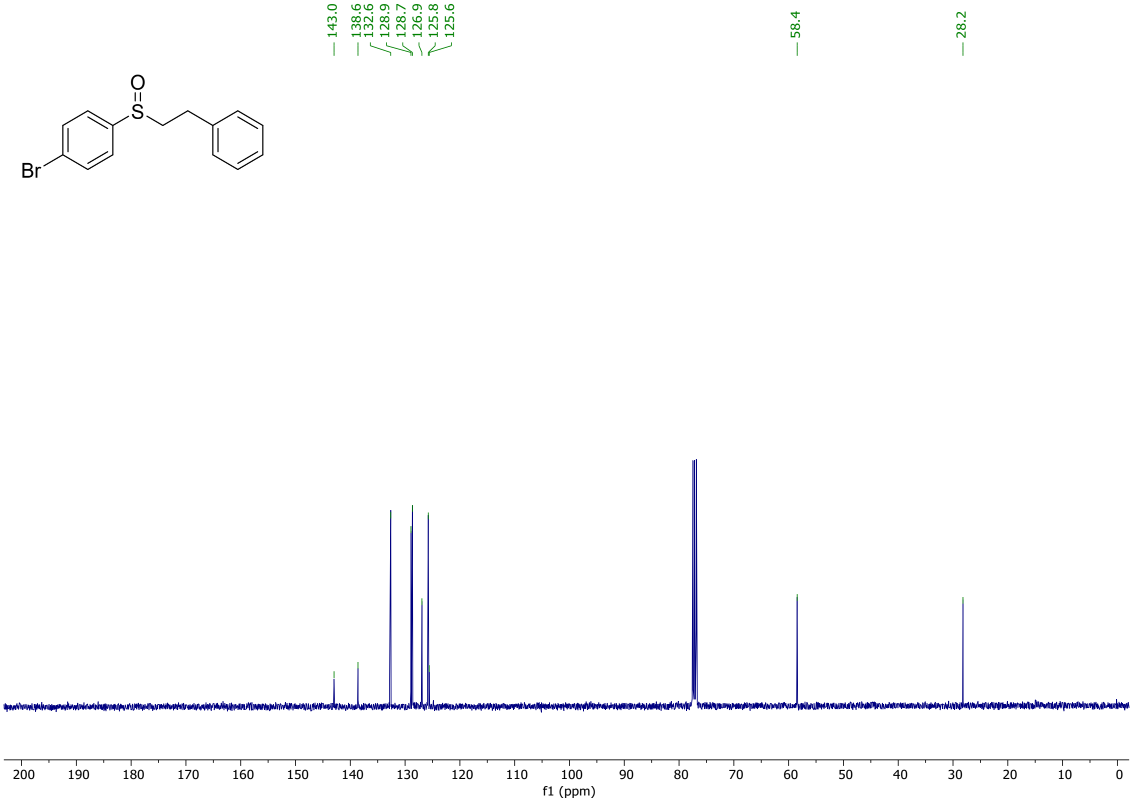

Figure S84. ^{13}C-NMR spectra of compound **5n**.

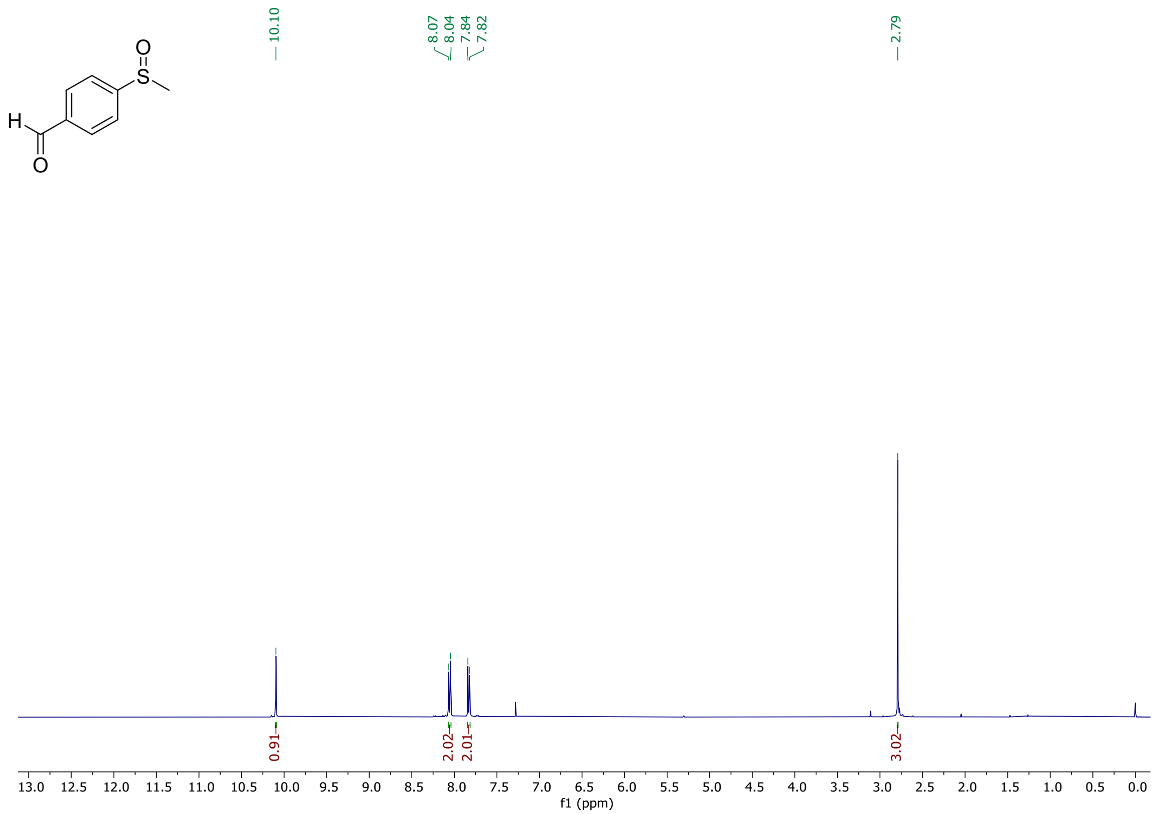

Figure S85. ^{1}H-NMR spectra of compound **5o**.

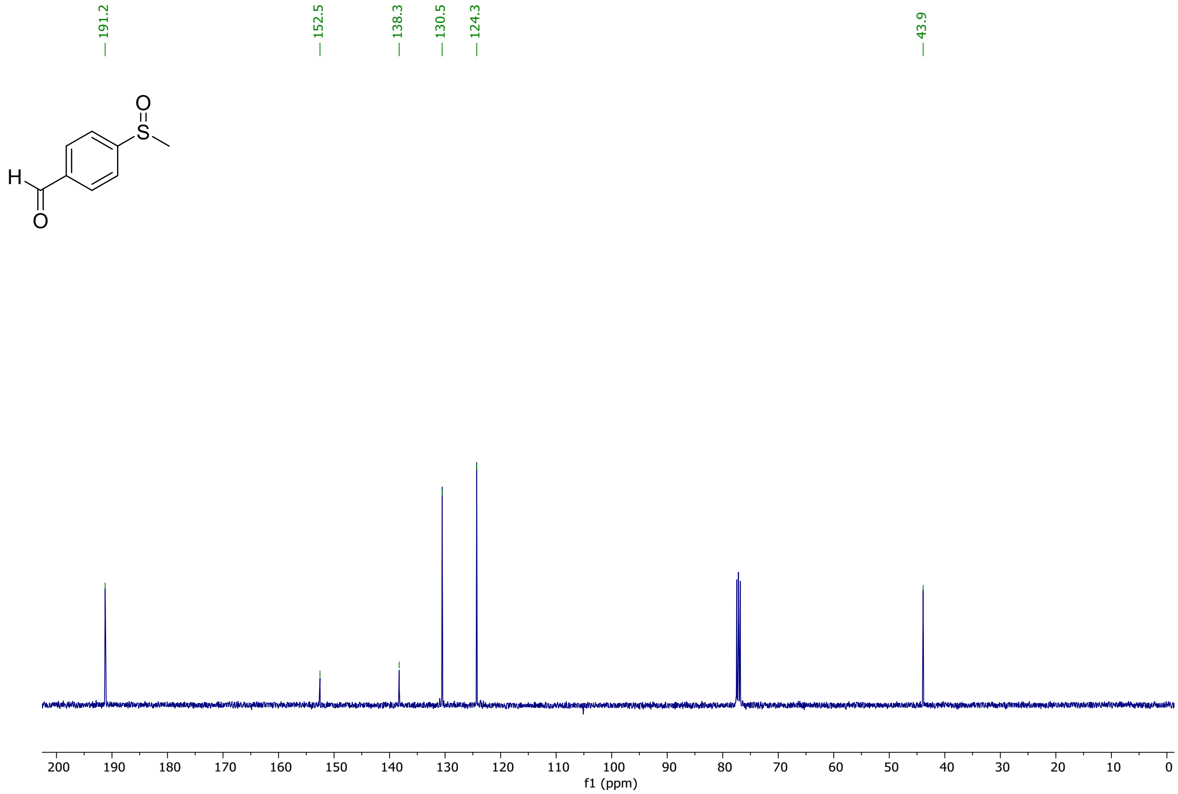

Figure S86. ^{13}C-NMR spectra of compound **5o**.

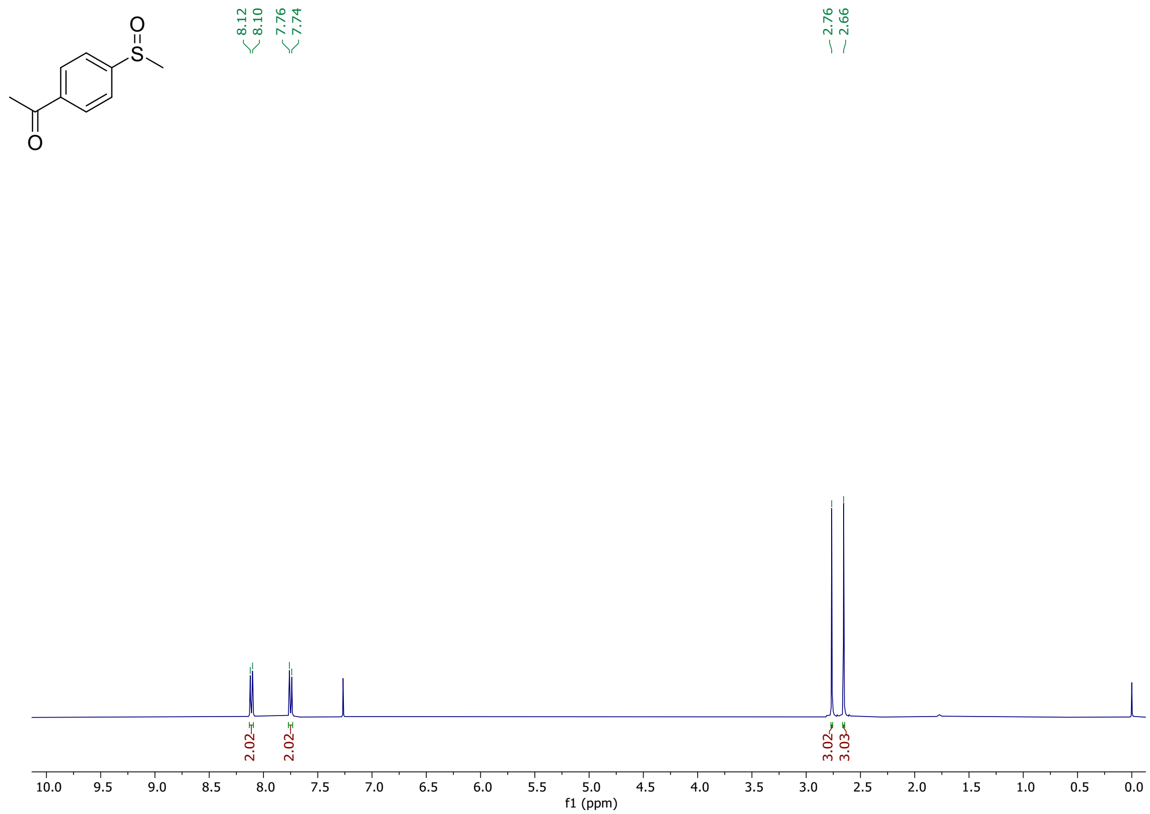

Figure S87. ^{1}H-NMR spectra of compound **5p**.

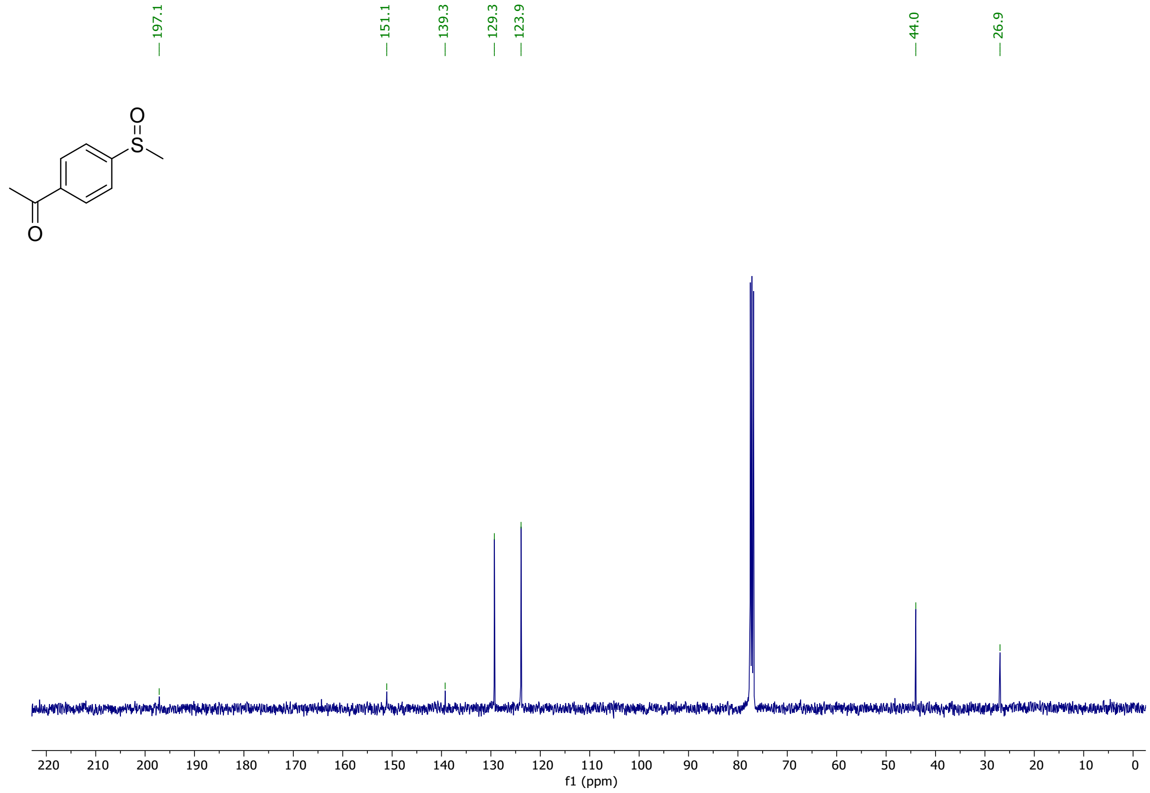

Figure S88. ^{13}C-NMR spectra of compound **5p**.

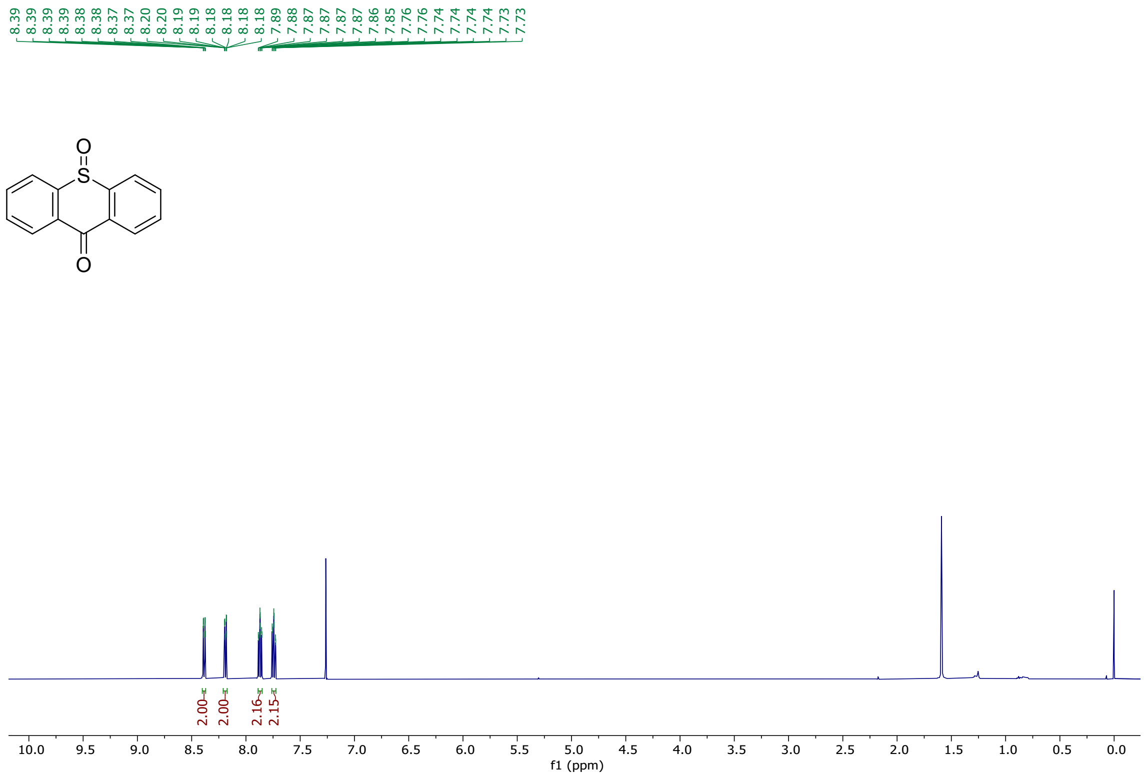

Figure S89. ^{1}H-NMR spectra of compound **5q**.

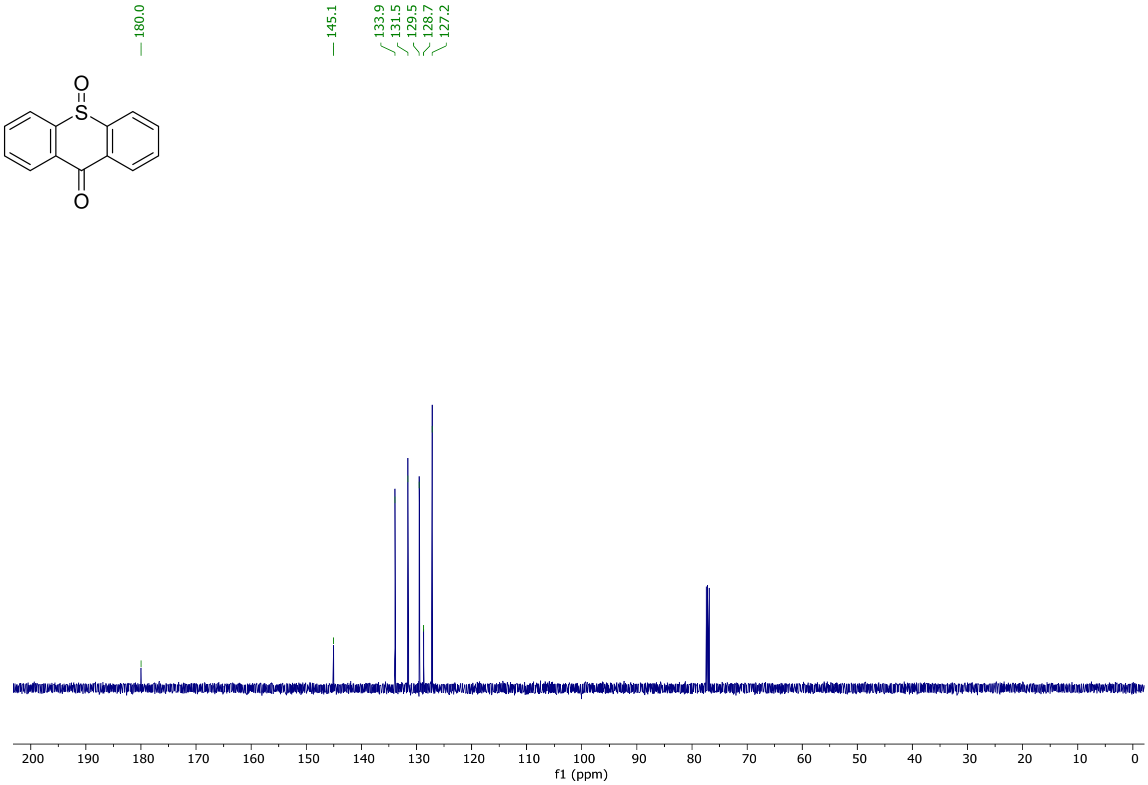

Figure S90. ^{13}C-NMR spectra of compound **5q**.

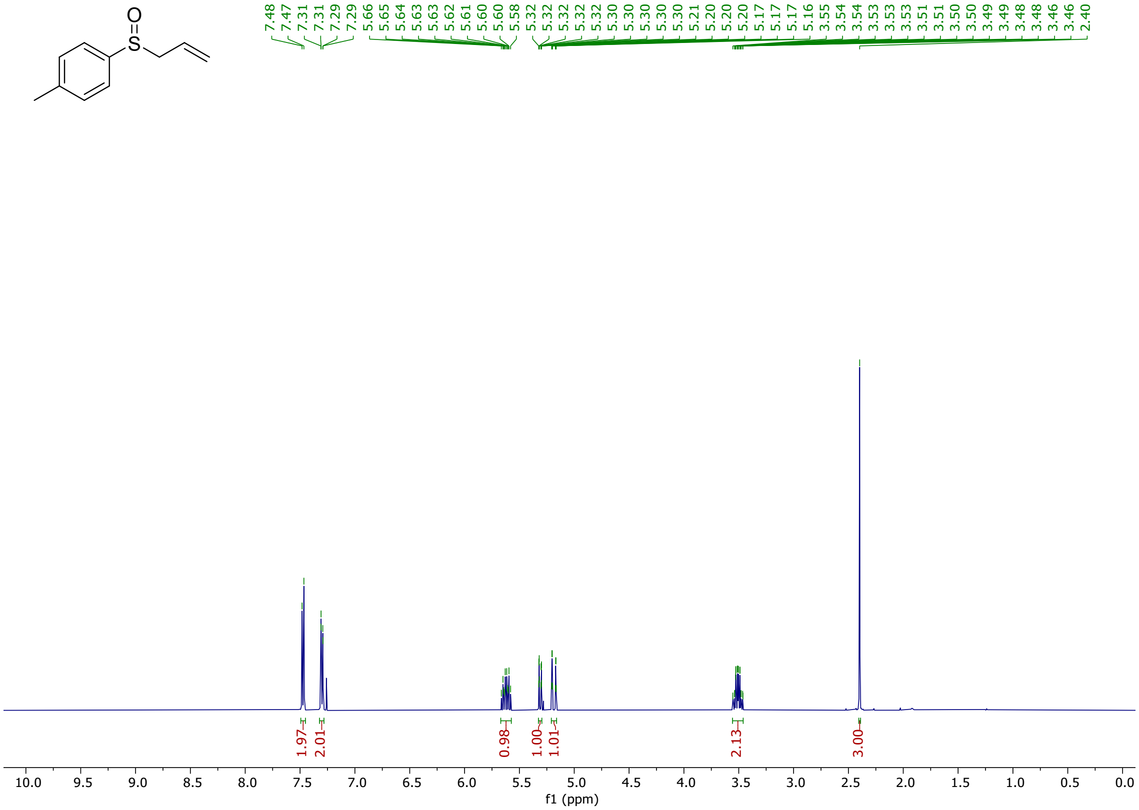

Figure S91. ^{1}H-NMR spectra of compound **5r**.

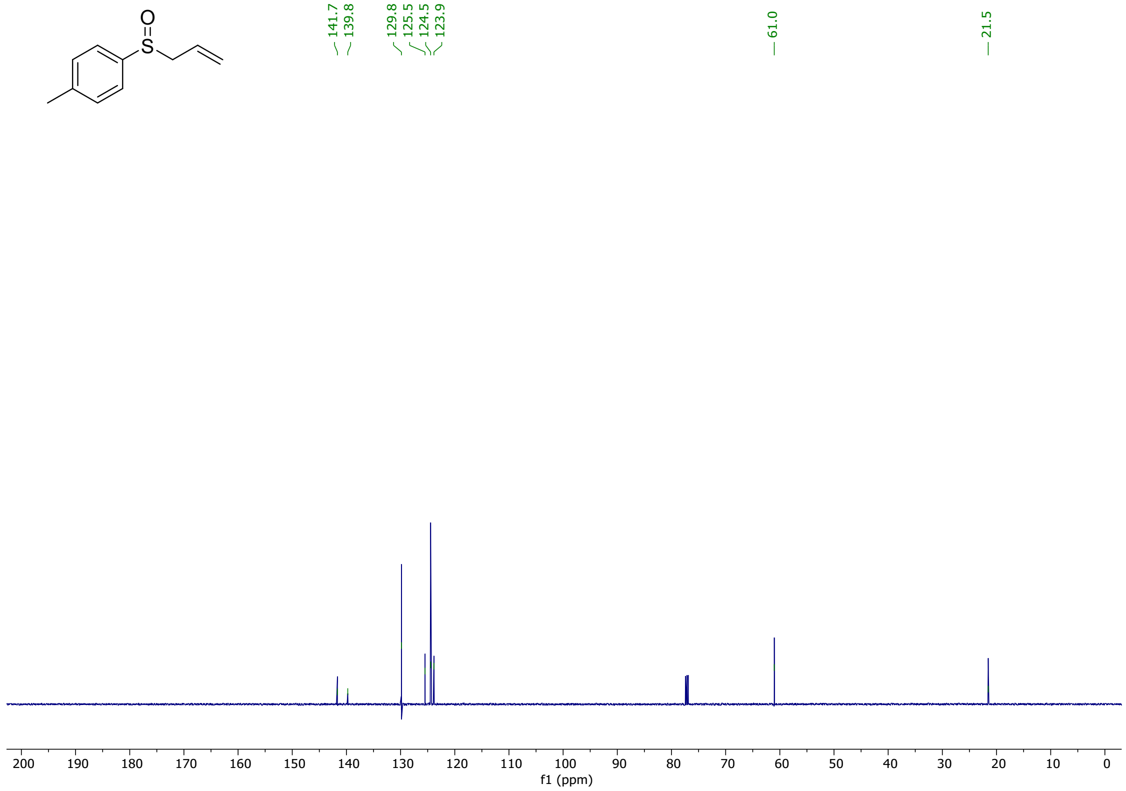

Figure S92. ^{13}C-NMR spectra of compound **5r**.

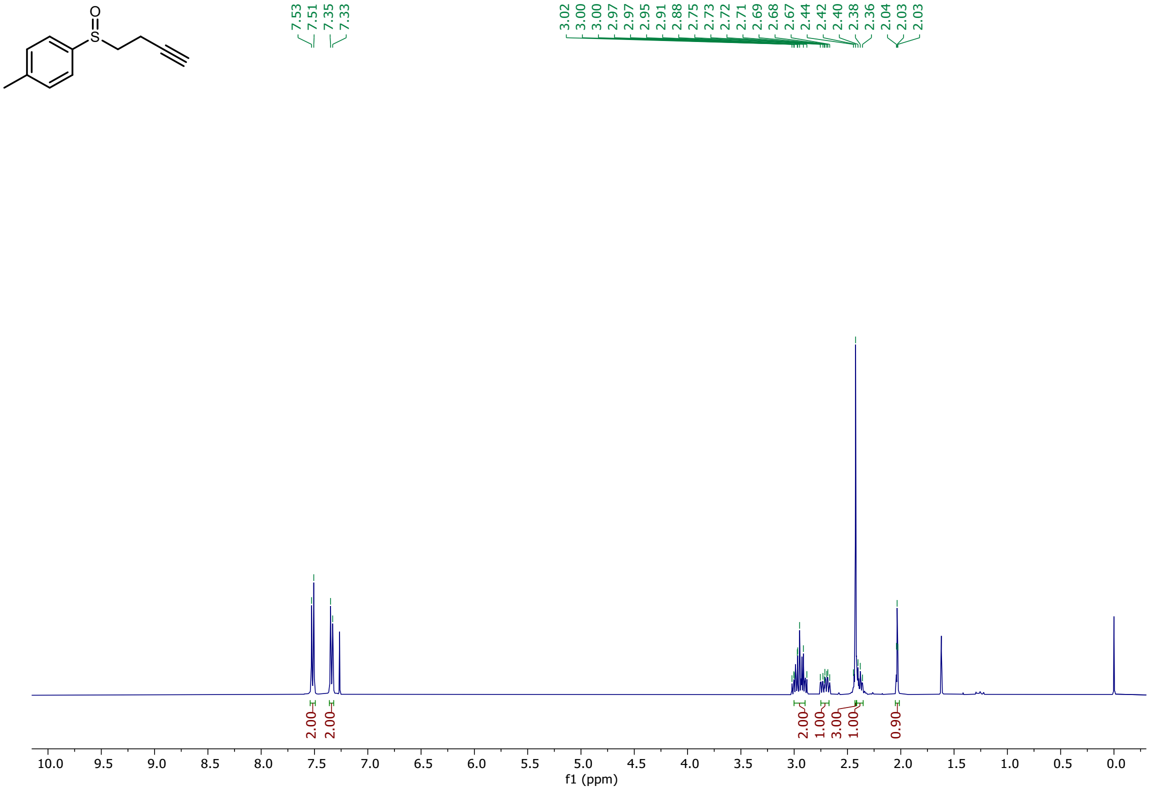

Figure S93. ^{1}H-NMR spectra of compound **5s**.

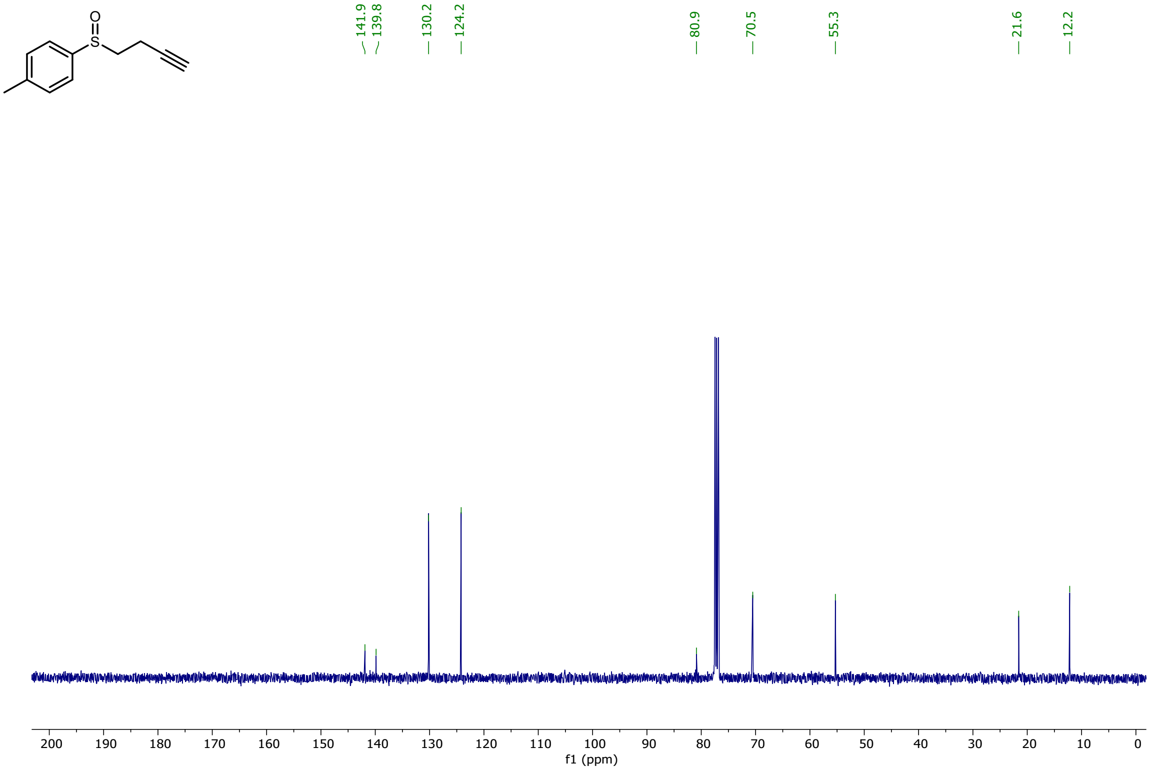

Figure S94. ^{13}C-NMR spectra of compound **5s**.

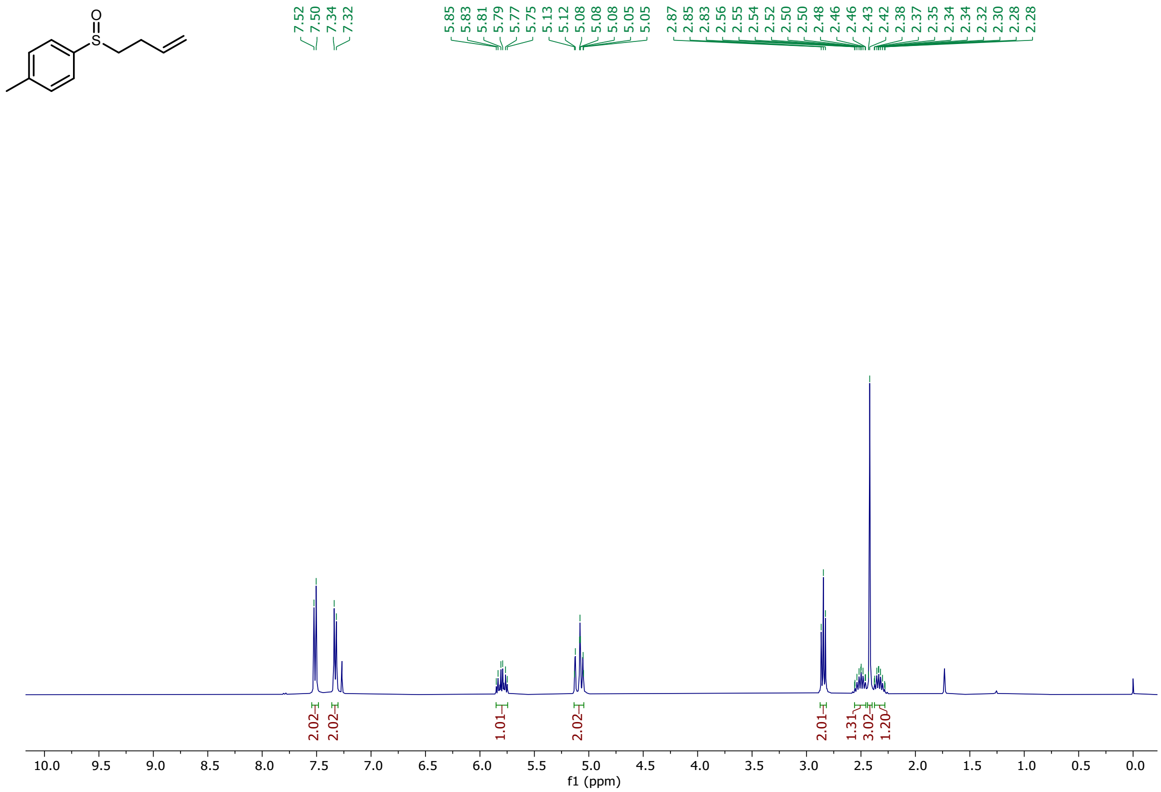

Figure S95. ^{1}H-NMR spectra of compound **5t**.

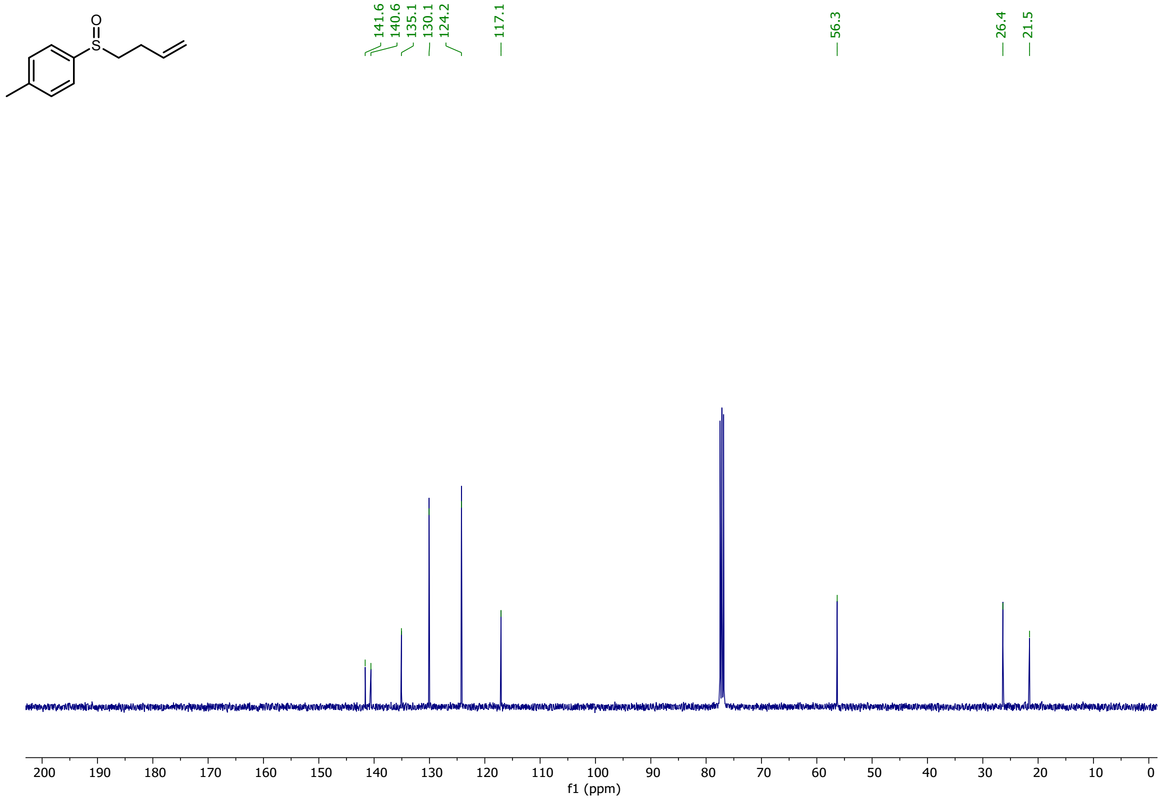

Figure S96. ^{13}C-NMR spectra of compound **5t**.

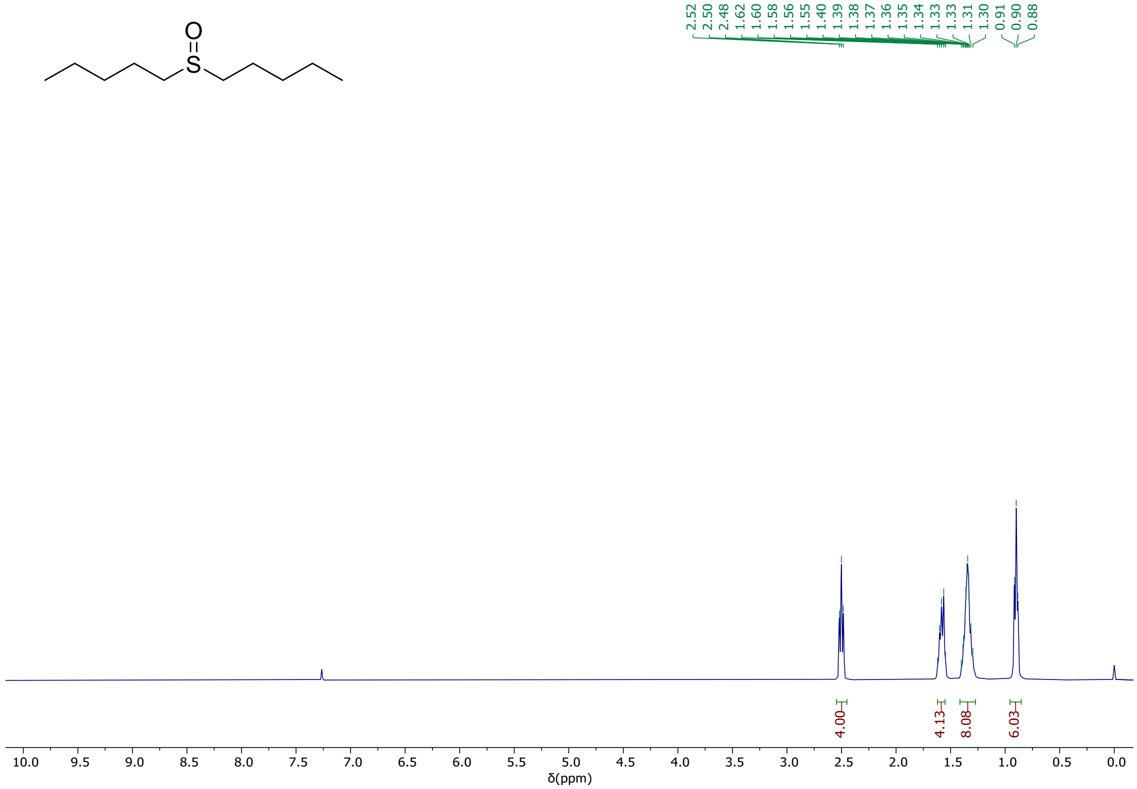

Figure S97. ^{1}H-NMR spectra of compound **5u**.

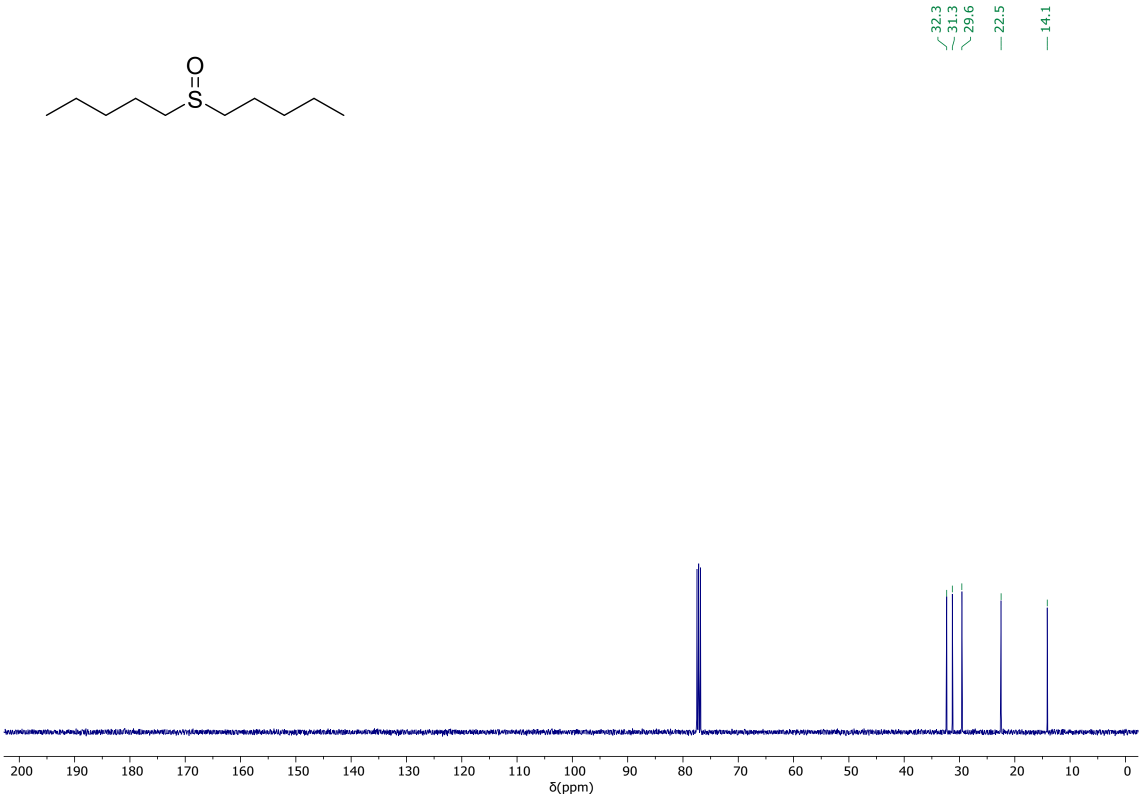

Figure S98. ^{1}H-NMR spectra of compound **5u**.

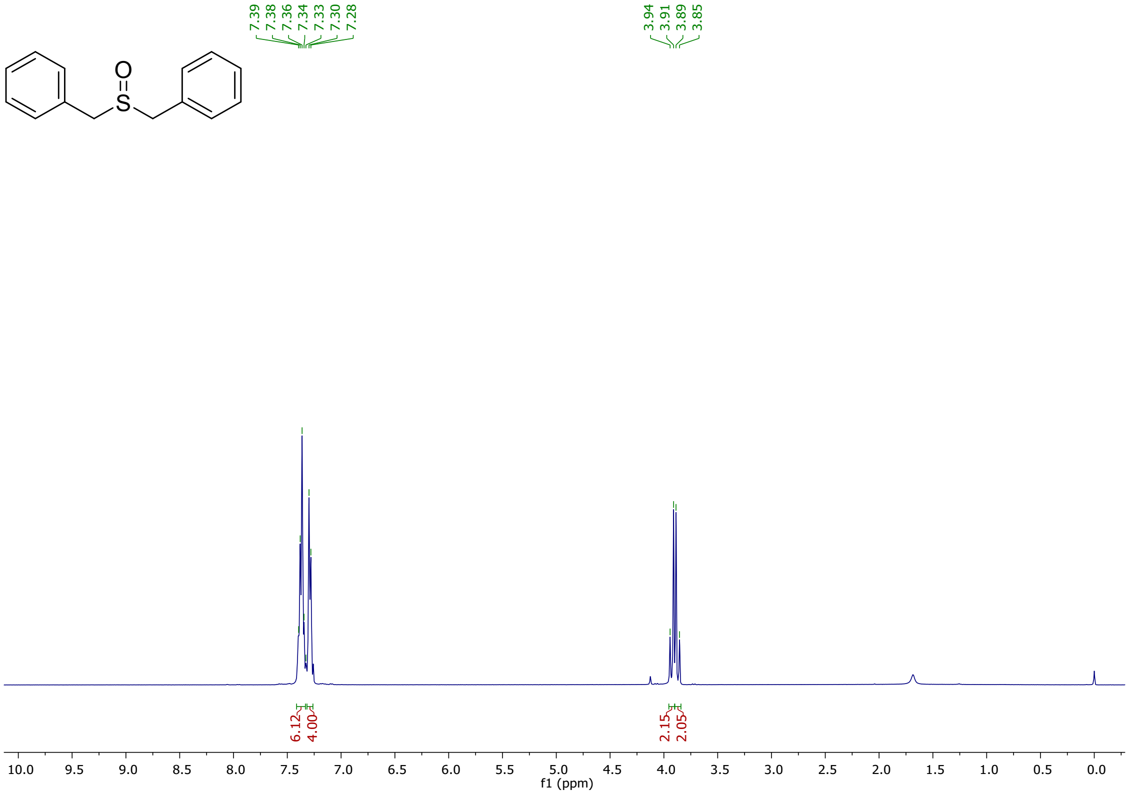

Figure S99. ^{13}C-NMR spectra of compound **5v**.

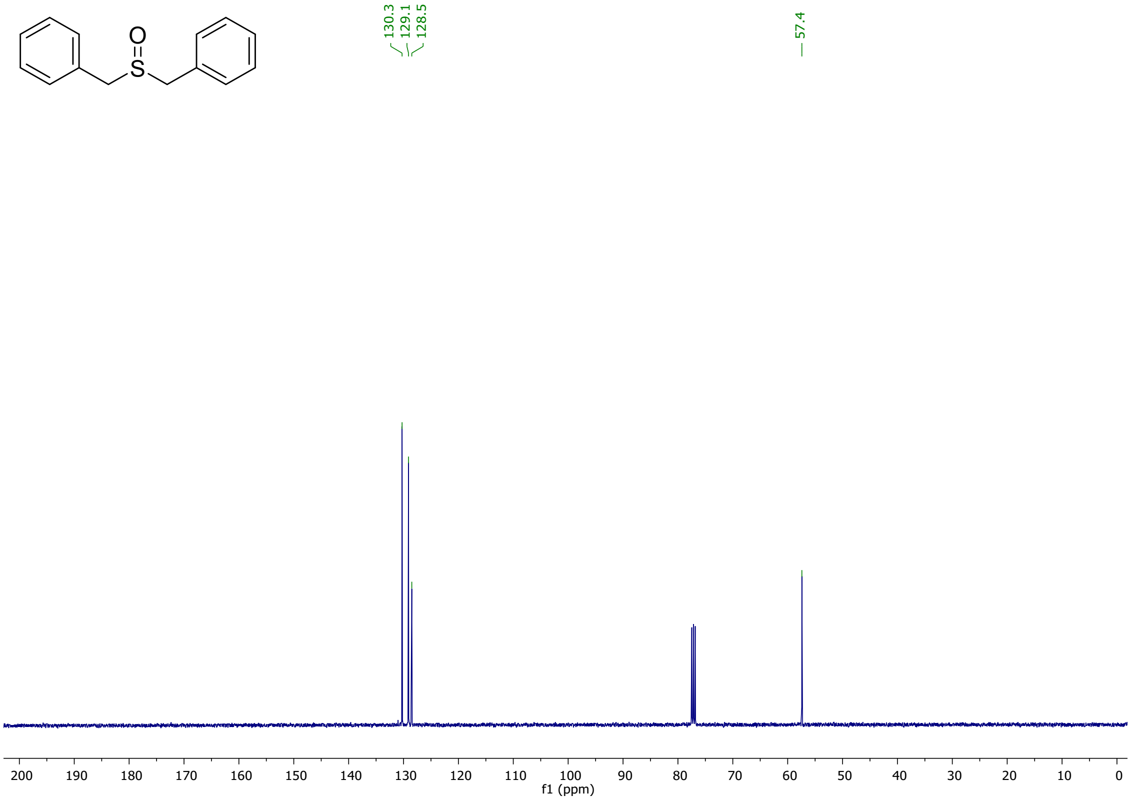

Figure S100. ^{13}C-NMR spectra of compound **5v**.

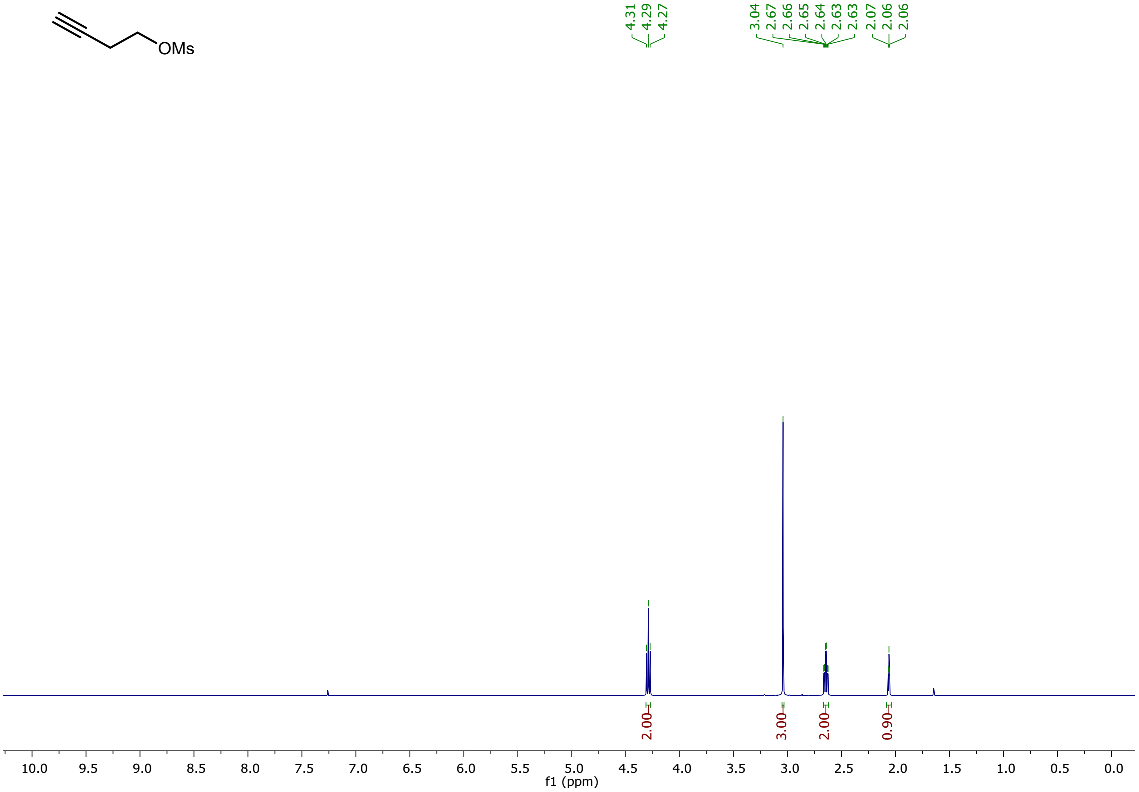

Figure S101. ^{1}H-NMR spectra of compound **SI-3a**.

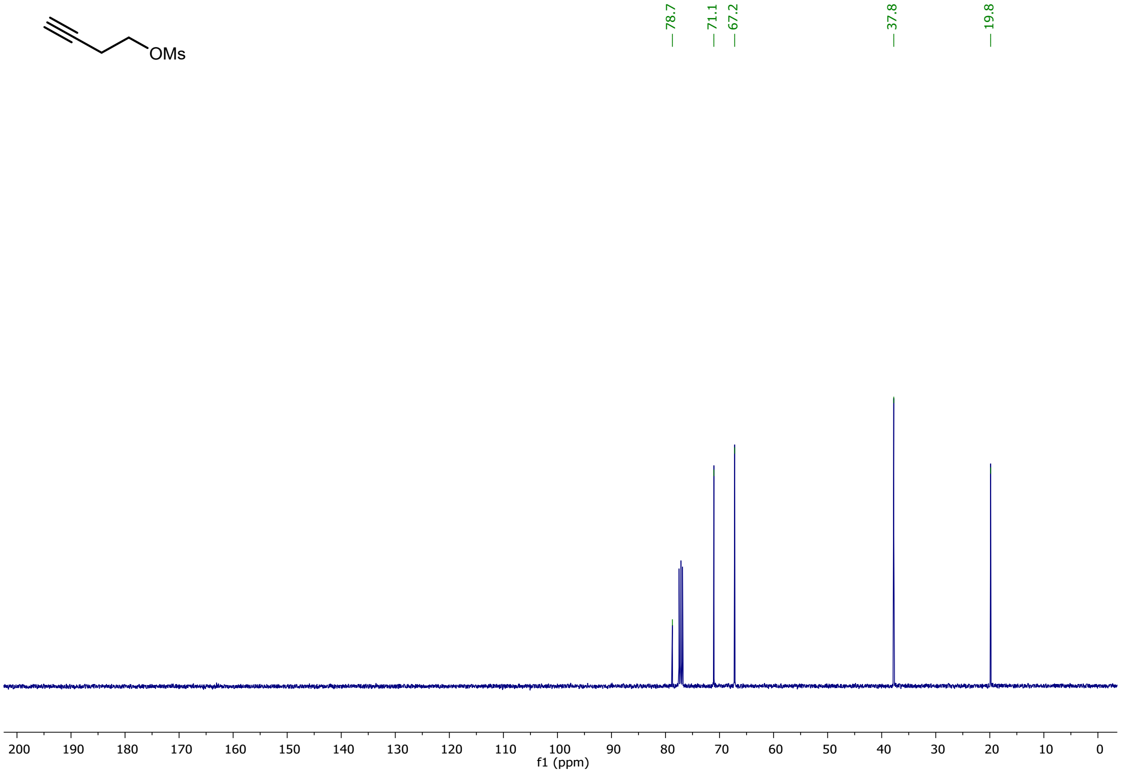

Figure S102. ^{13}C-NMR spectra of compound **SI-3a**.

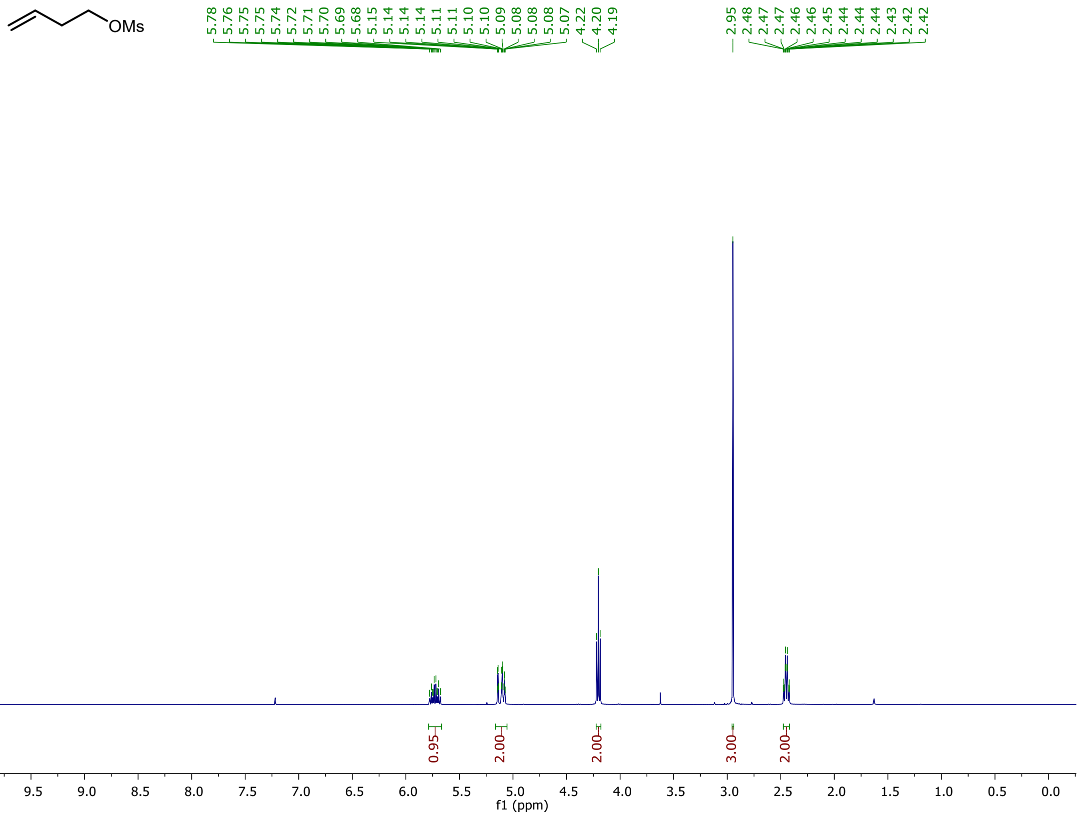

Figure S103. ^{1}H-NMR spectra of compound **SI-3b**.

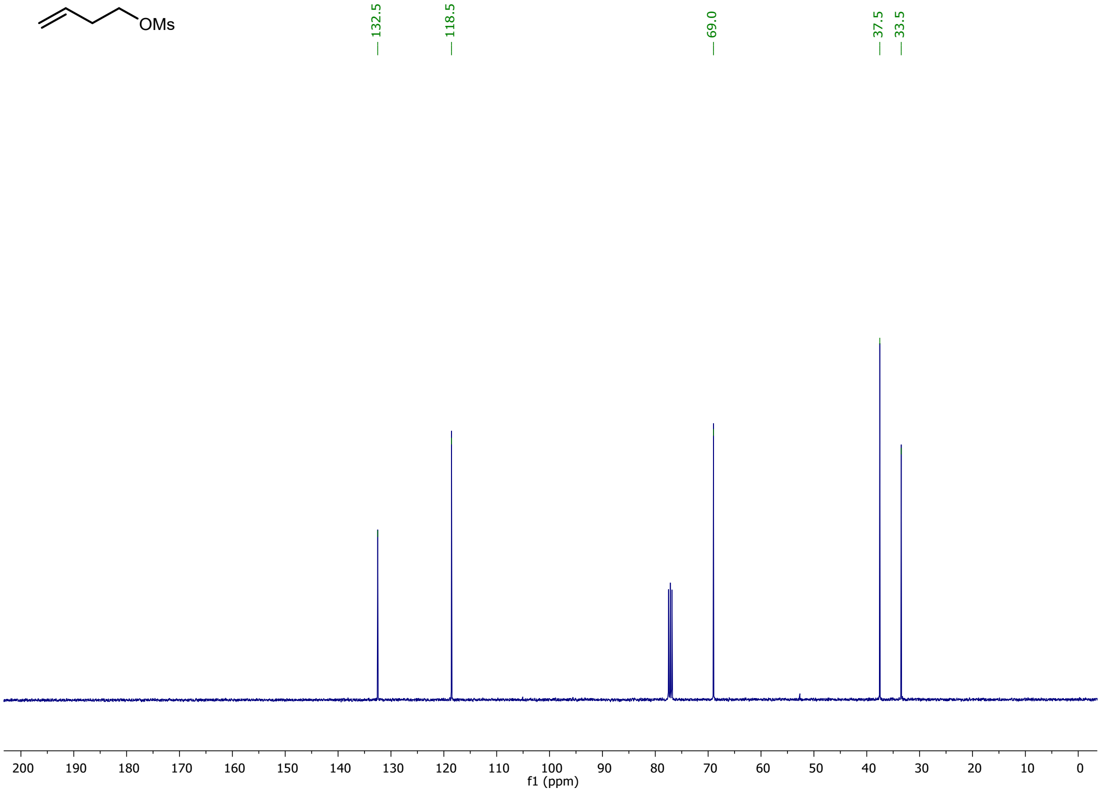

Figure S104. ^{13}C-NMR spectra of compound **SI-3b**.

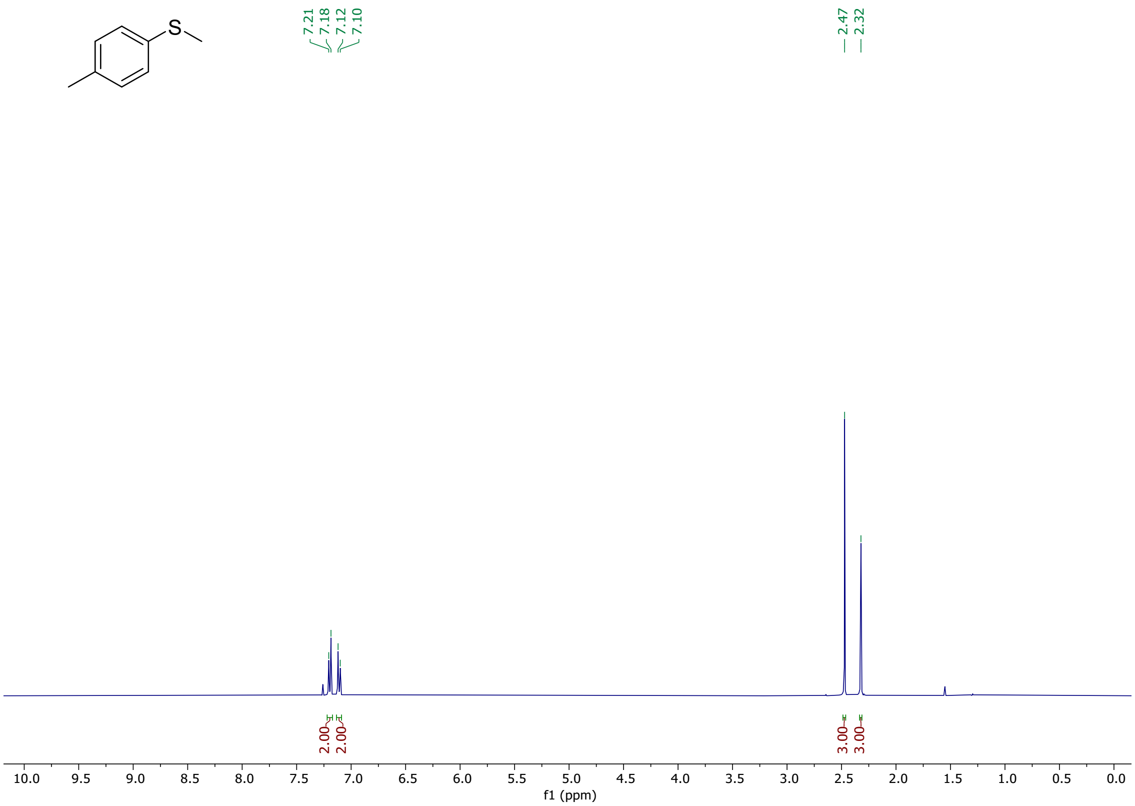

Figure S105. ^{1}H-NMR spectra of compound **6a**.

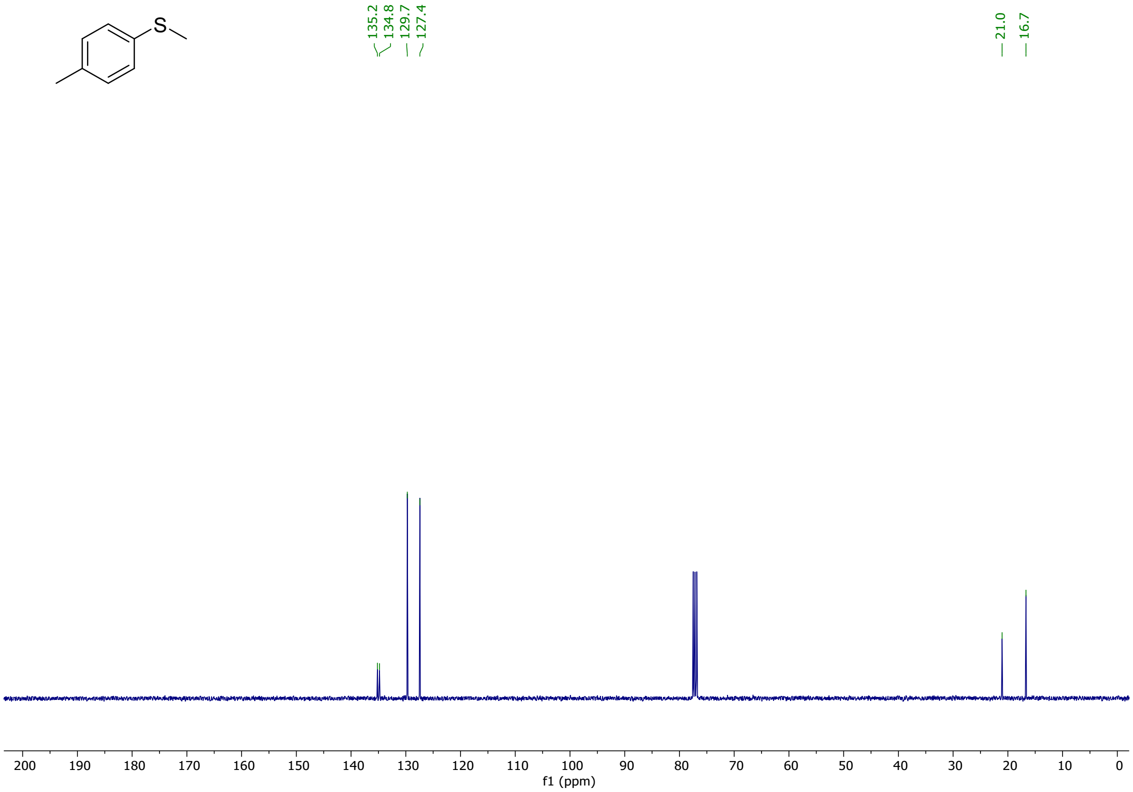

Figure S106. ^{13}C-NMR spectra of compound **6a.**

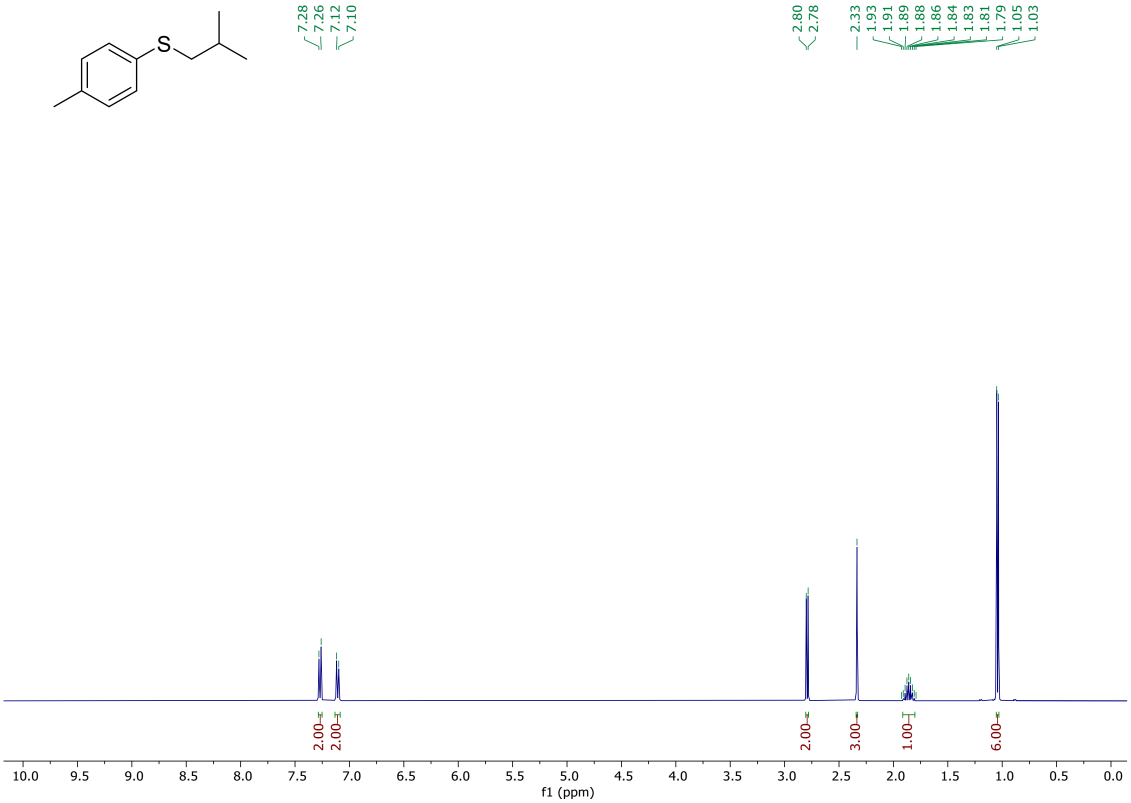

Figure S107. ^{1}H-NMR spectra of compound **6b**.

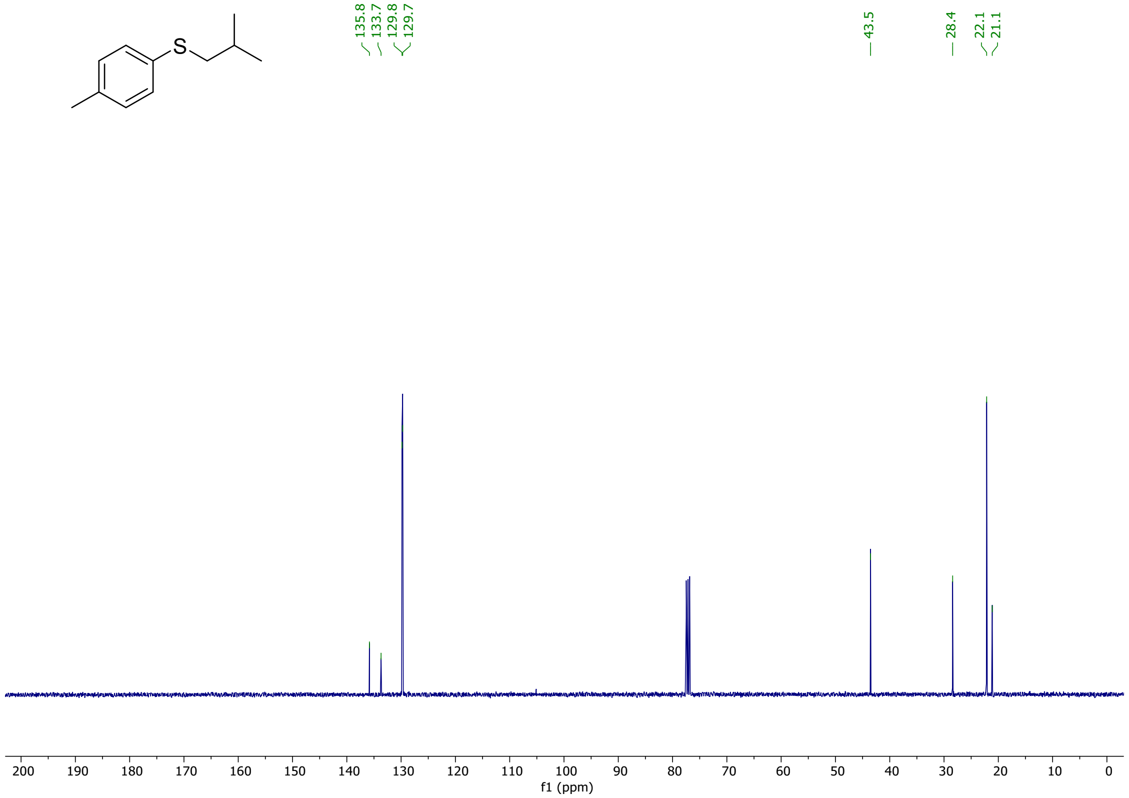

Figure S108. ^{13}C-NMR spectra of compound **6b**.

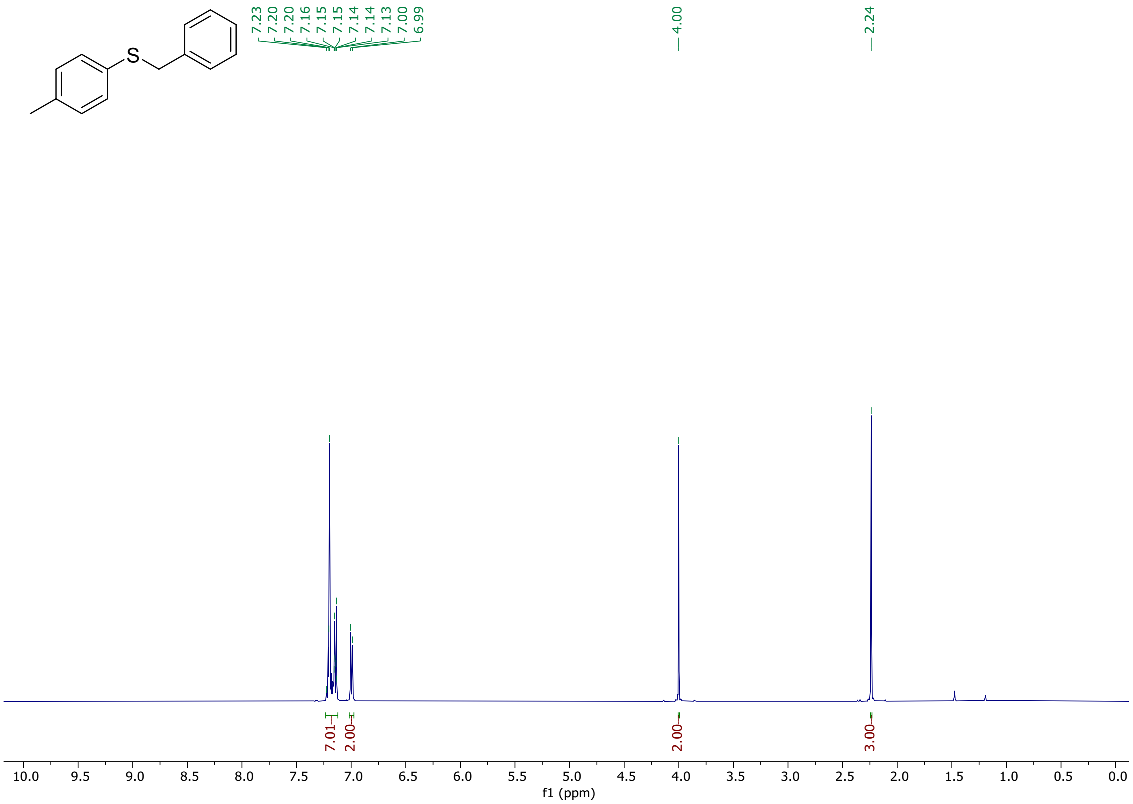

Figure S109. ^{1}H-NMR spectra of compound **6c**.

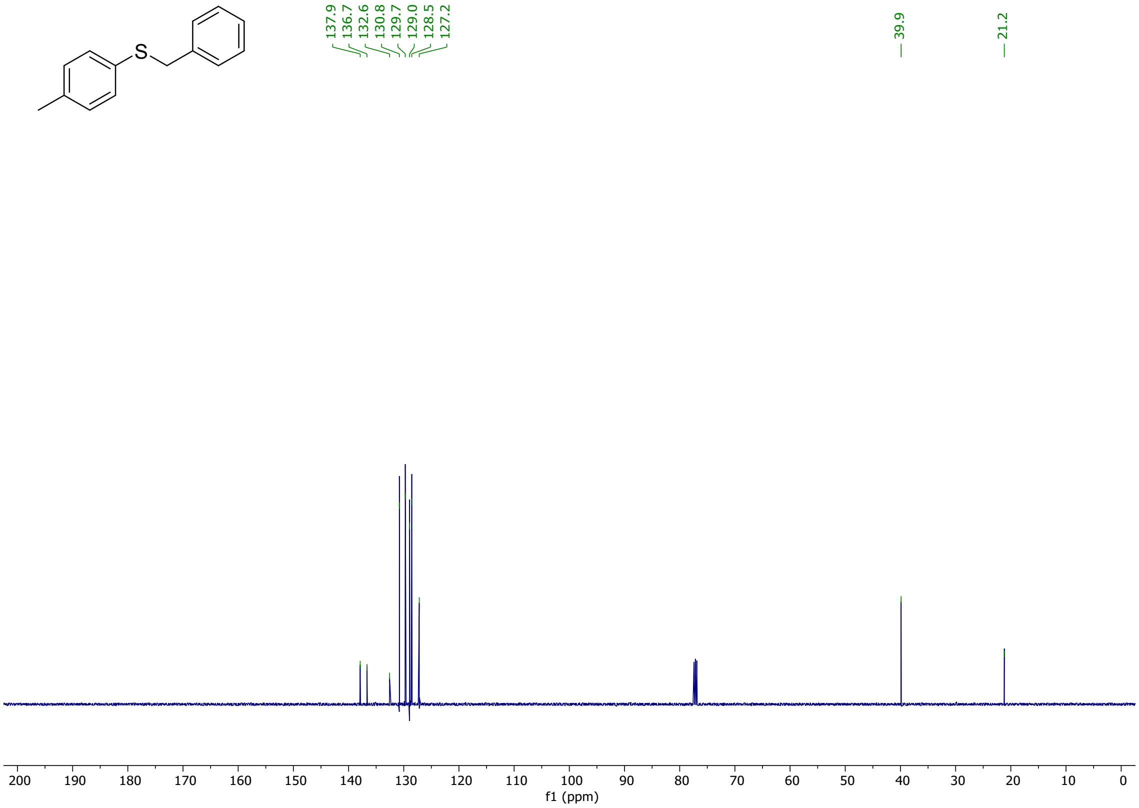

Figure S110. ^{13}C-NMR spectra of compound **6c**.

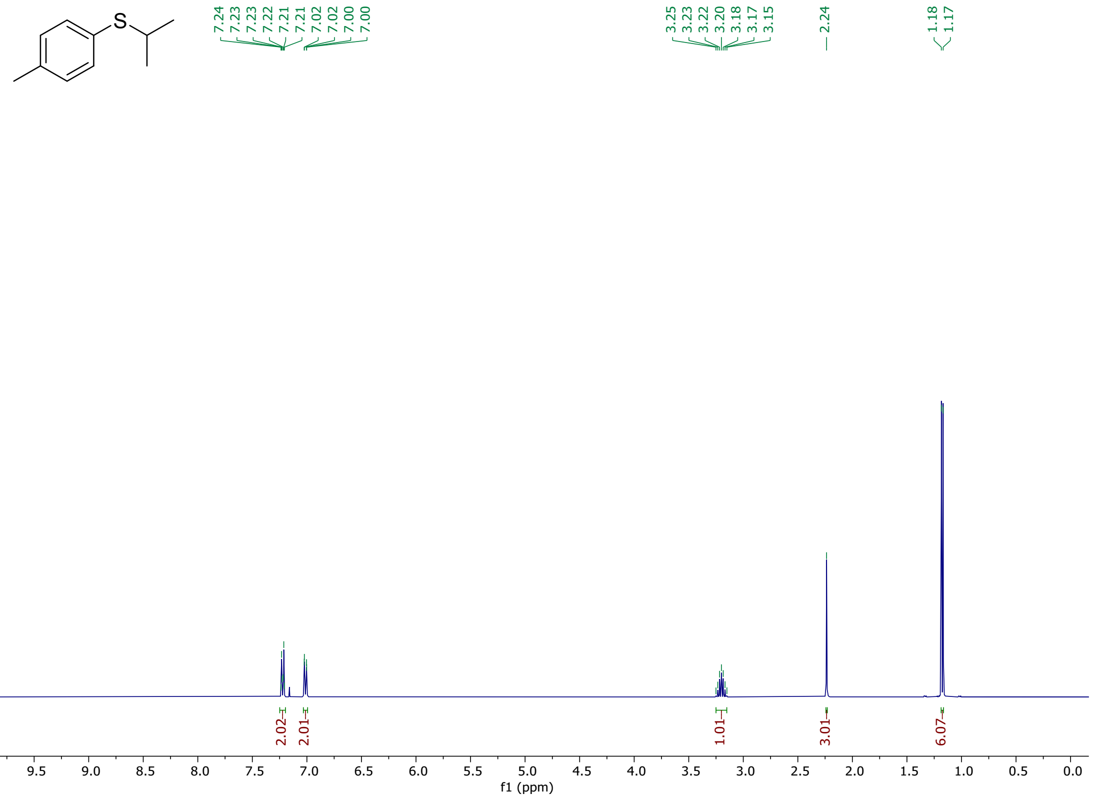

Figure S111. ^{1}H-NMR spectra of compound **6d**.

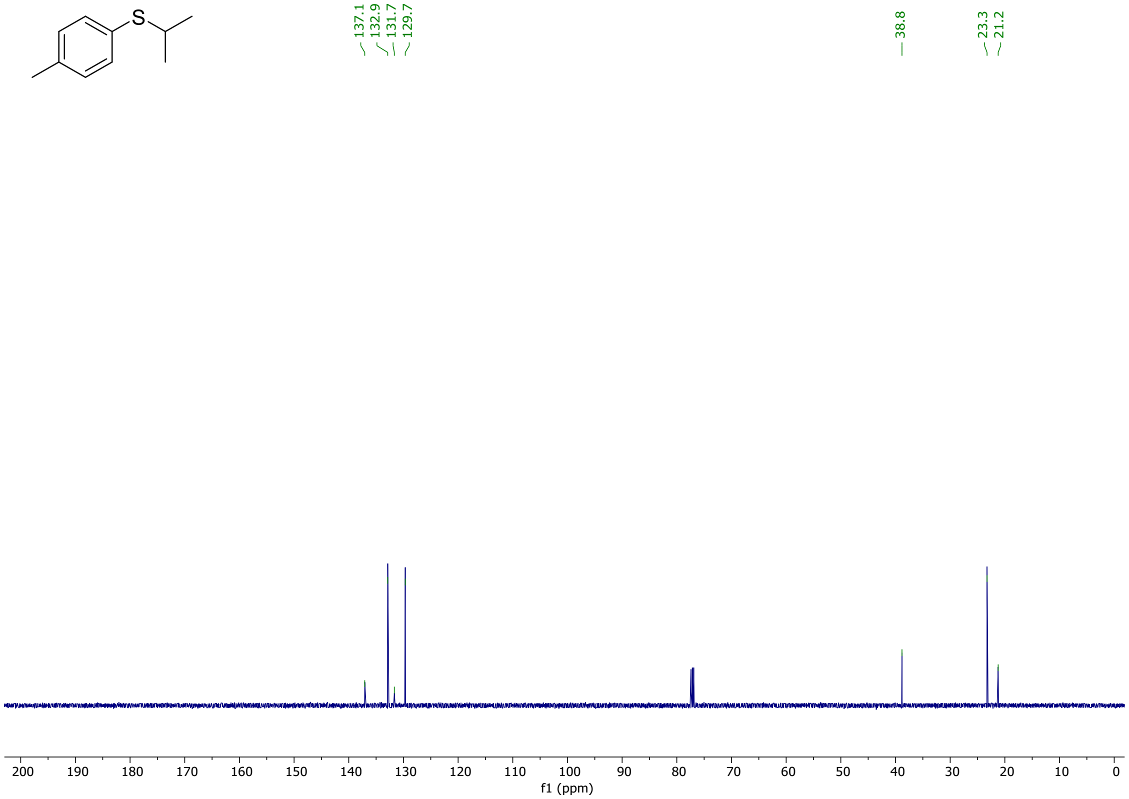

Figure S112. ^{13}C-NMR spectra of compound **6d**.

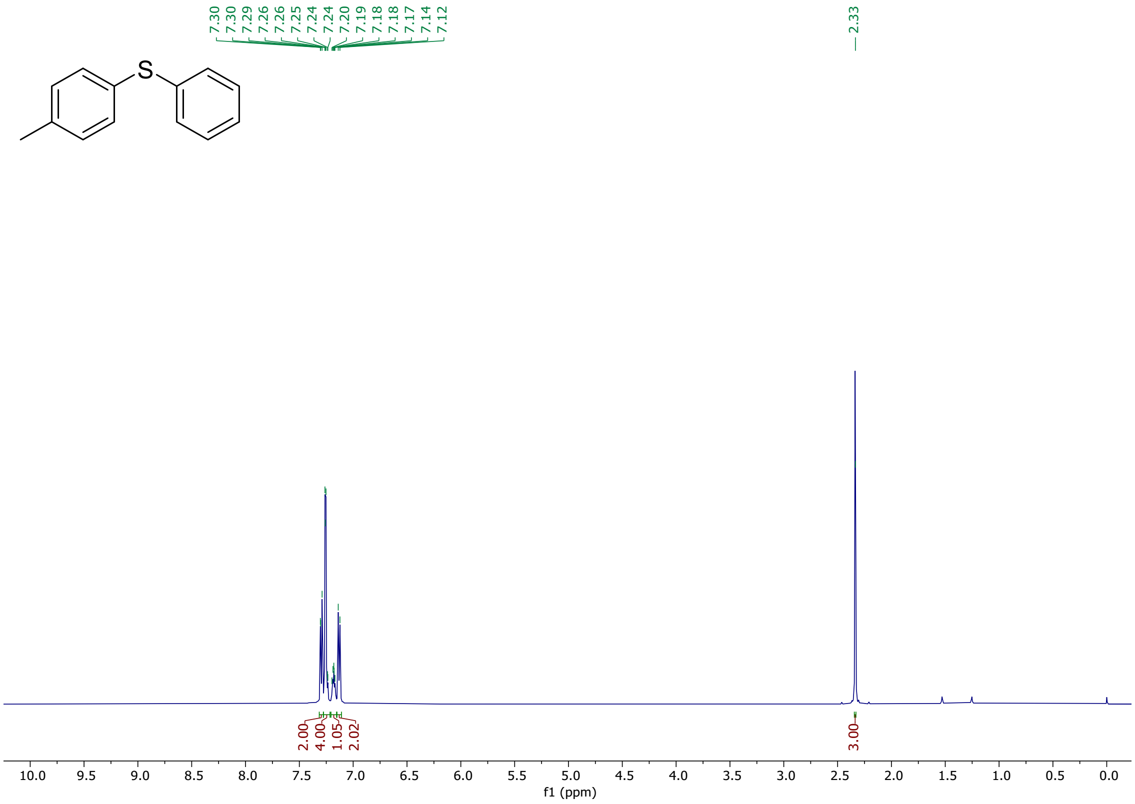

Figure S113. ^{1}H-NMR spectra of compound **6e**.

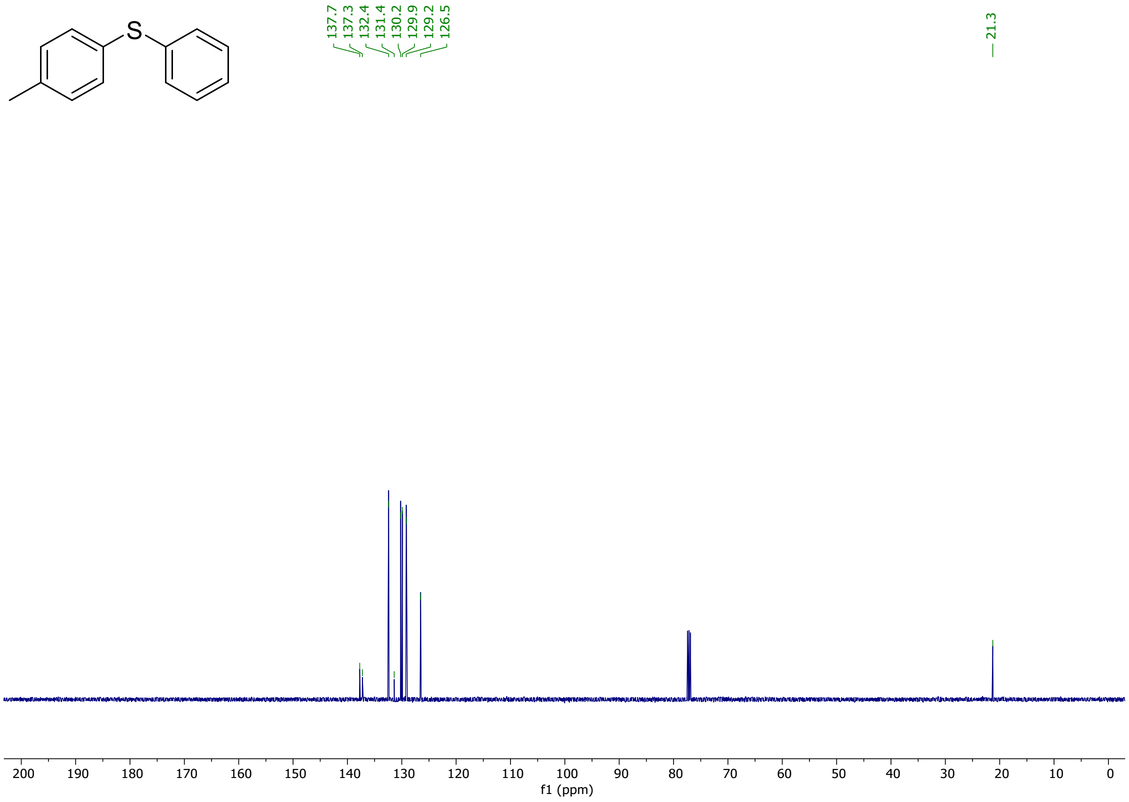

Figure S114. ^{13}C-NMR spectra of compound **6e**.

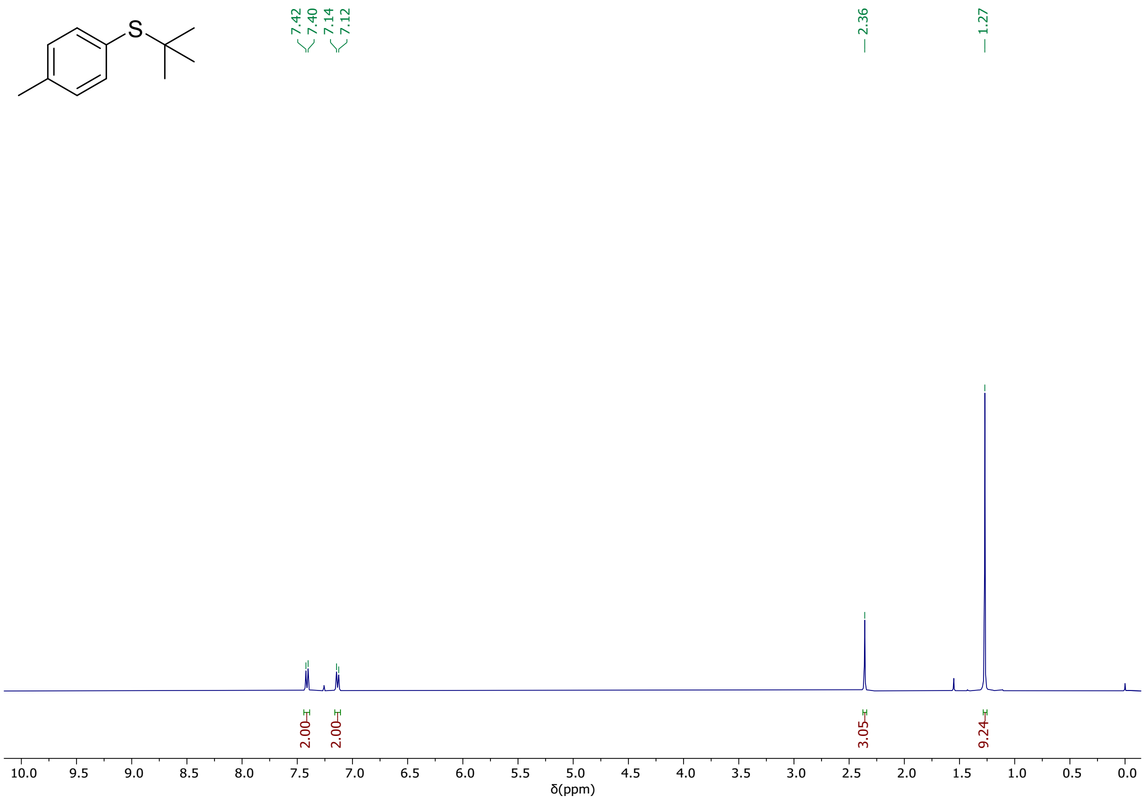

Figure S115. ^{1}H-NMR spectra of compound **6f**.

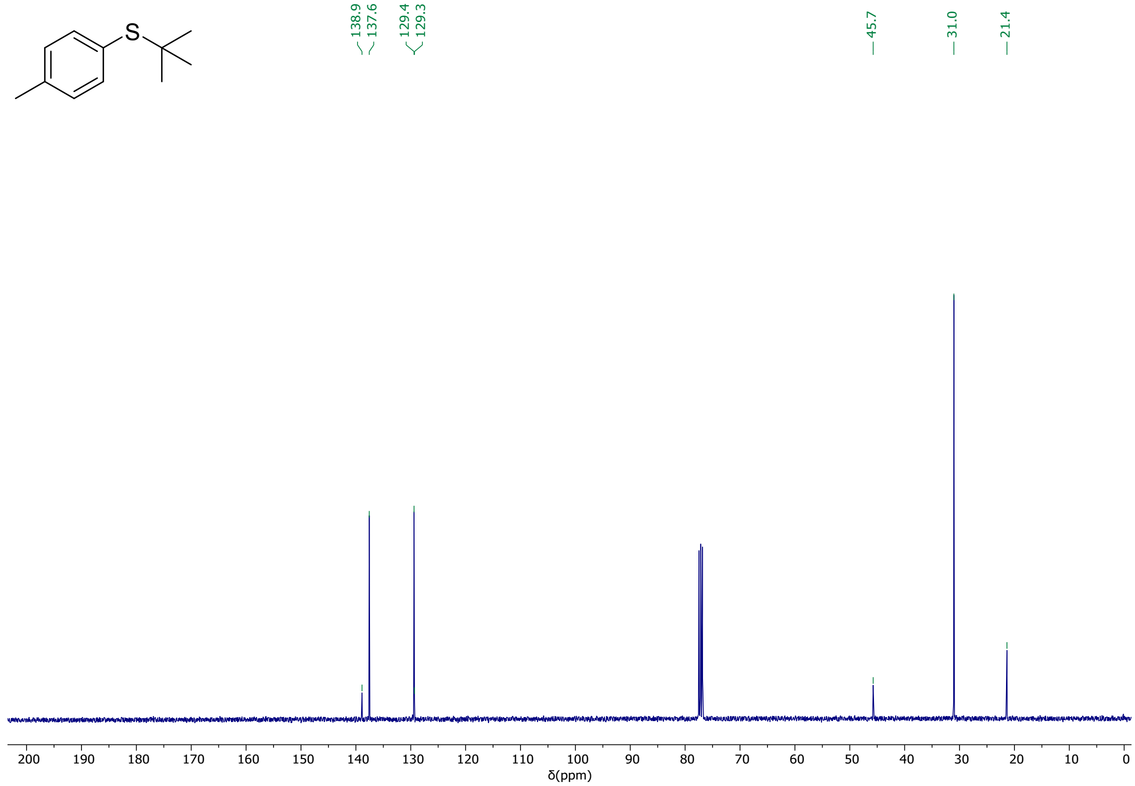

Figure S116. ^{13}C-NMR spectra of compound **6f**.

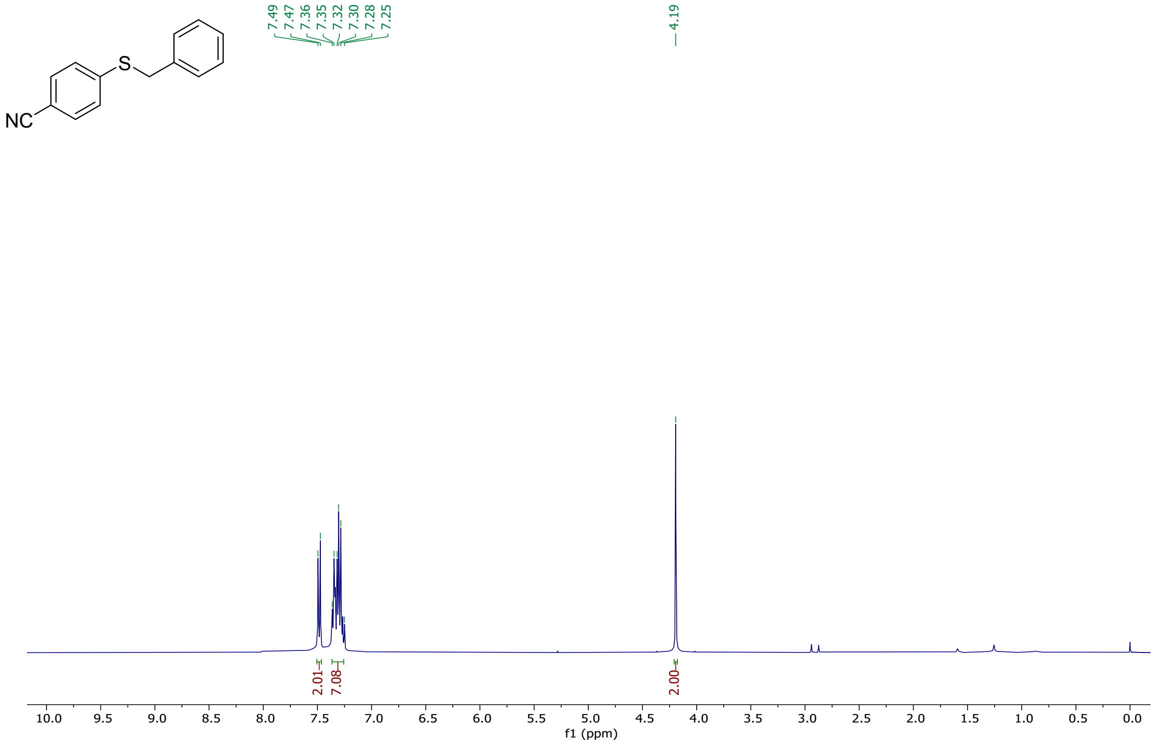

Figure S117. ^{1}H-NMR spectra of compound **6g**.

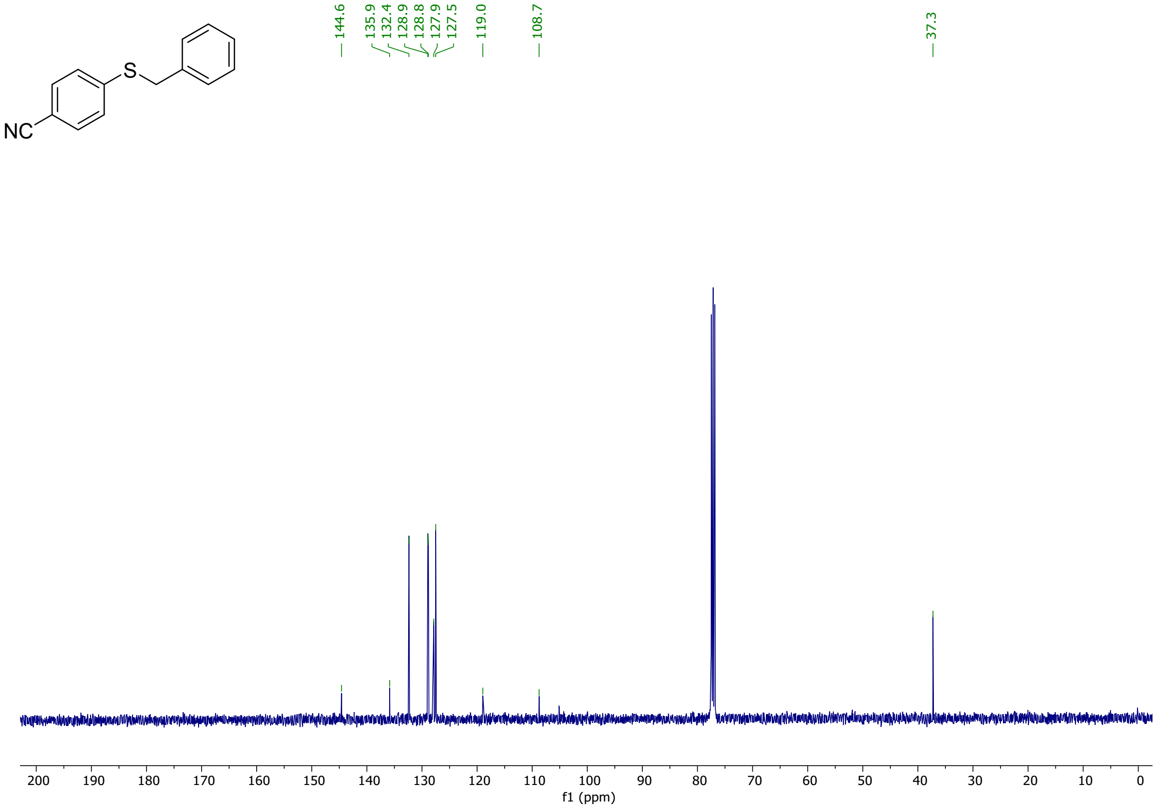

Figure S118. ^{13}C-NMR spectra of compound **6g**.

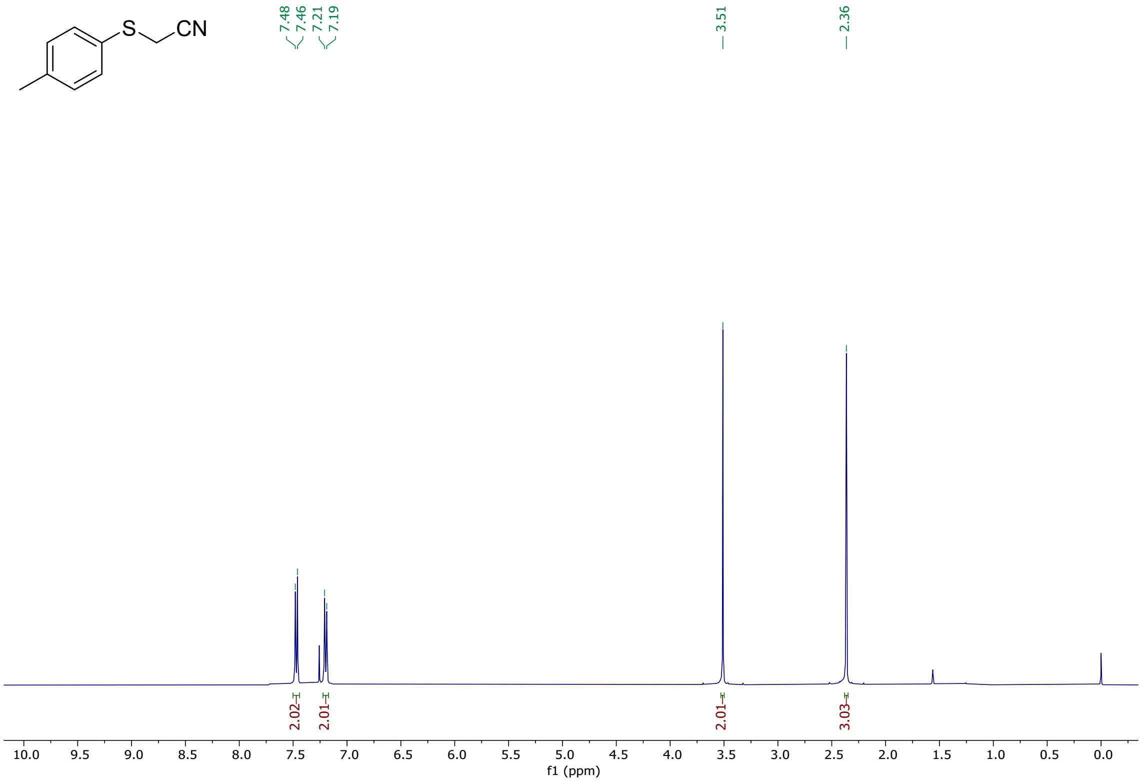

Figure S119. ^{1}H-NMR spectra of compound **6h**.

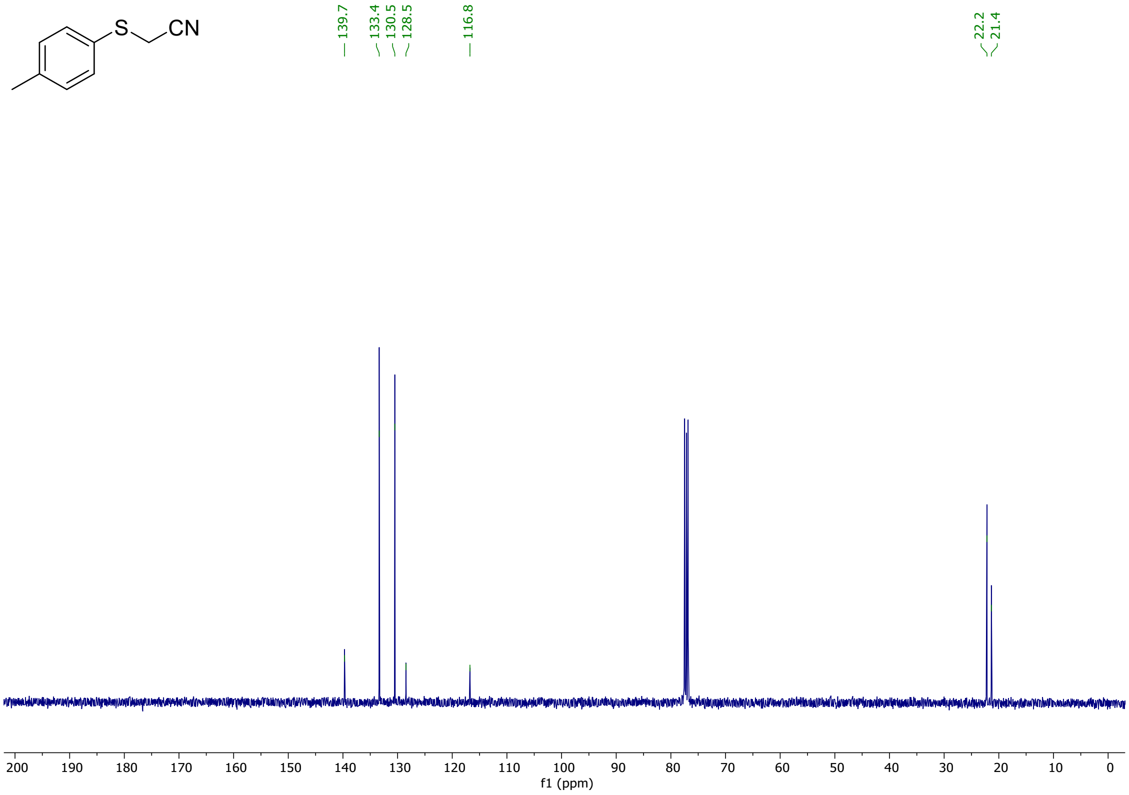

Figure S120. ^{13}C-NMR spectra of compound **6h**.

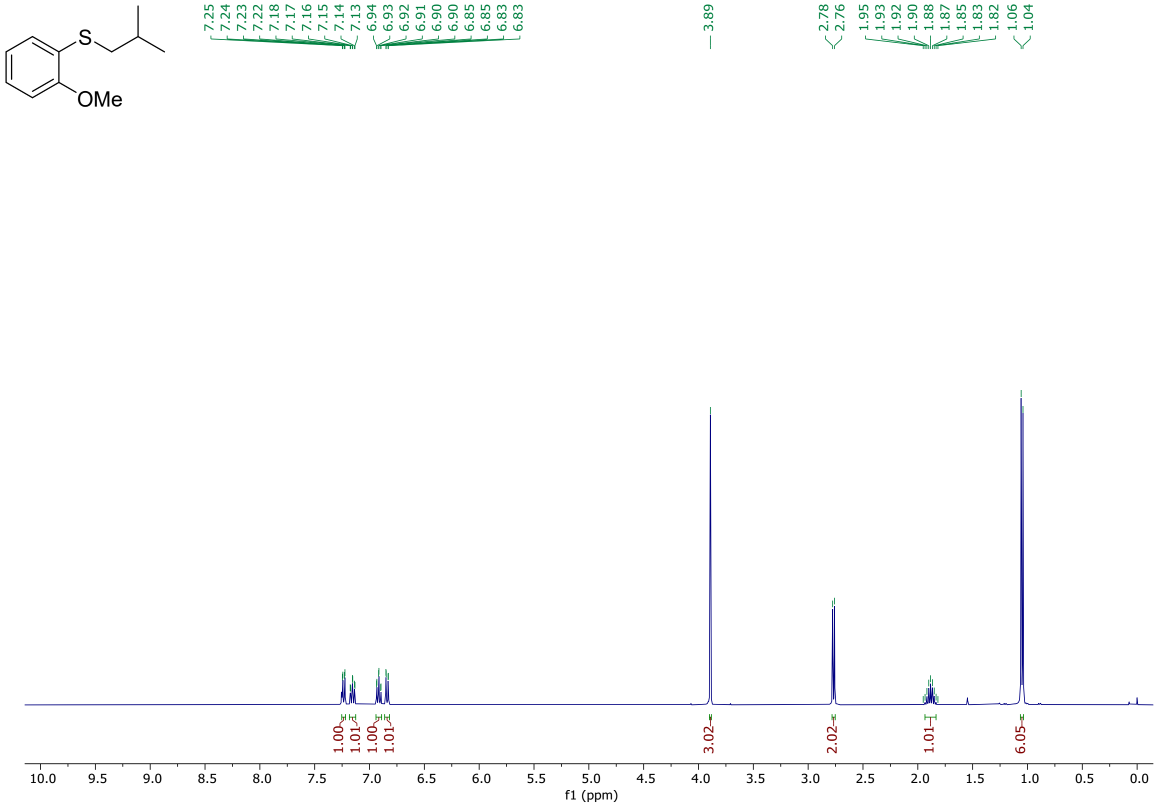

Figure S121. ^{1}H-NMR spectra of compound **6i**.

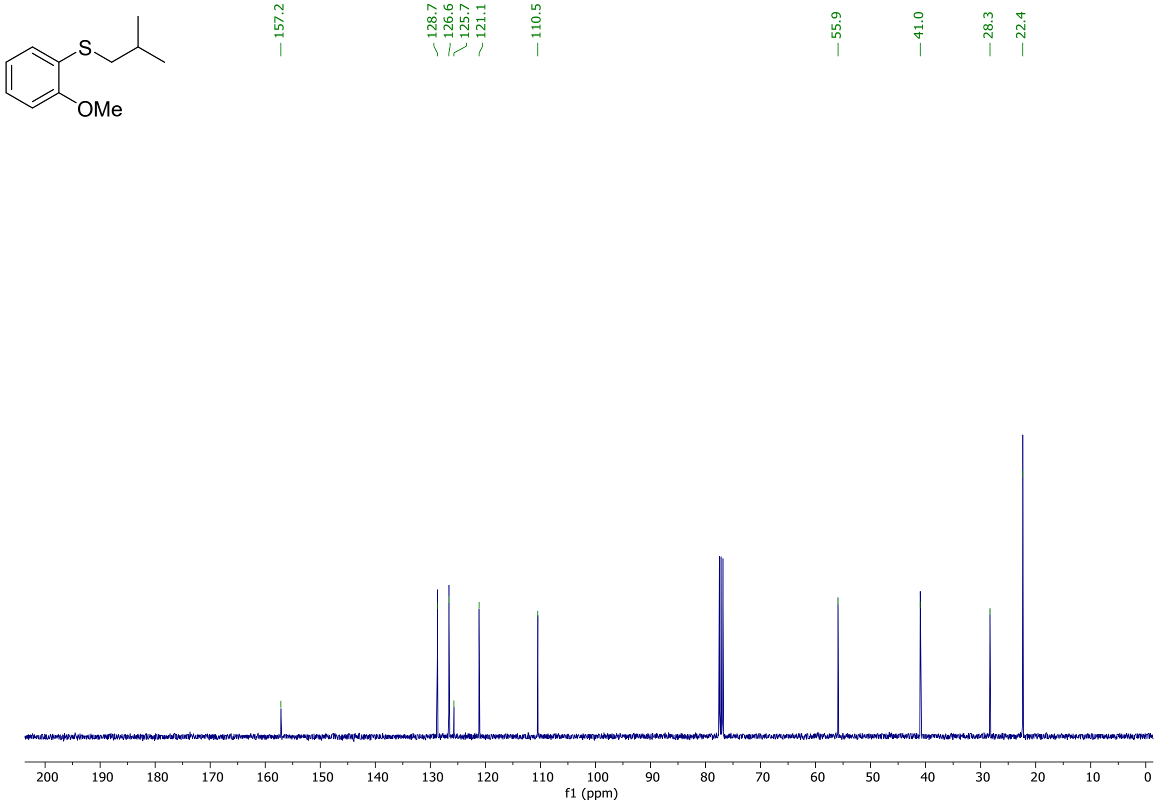

Figure S122. ^{1}H-NMR spectra of compound **6i**.

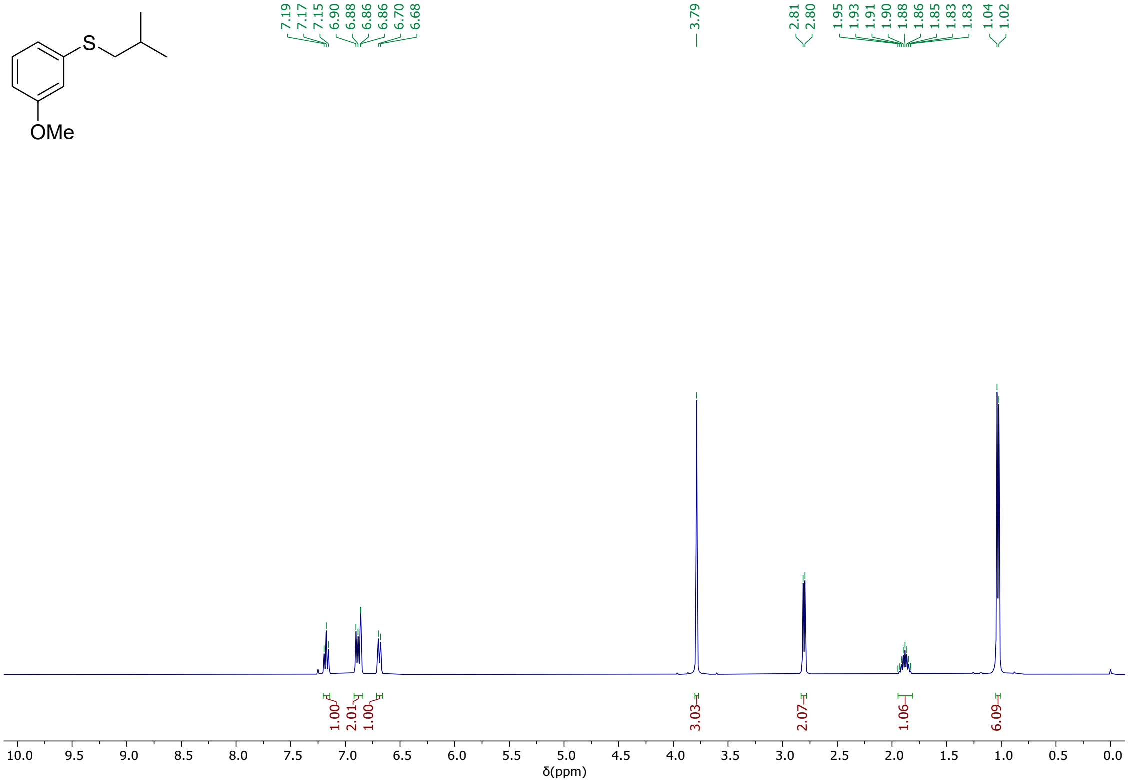

Figure S123. ^{1}H-NMR spectra of compound **6j**.

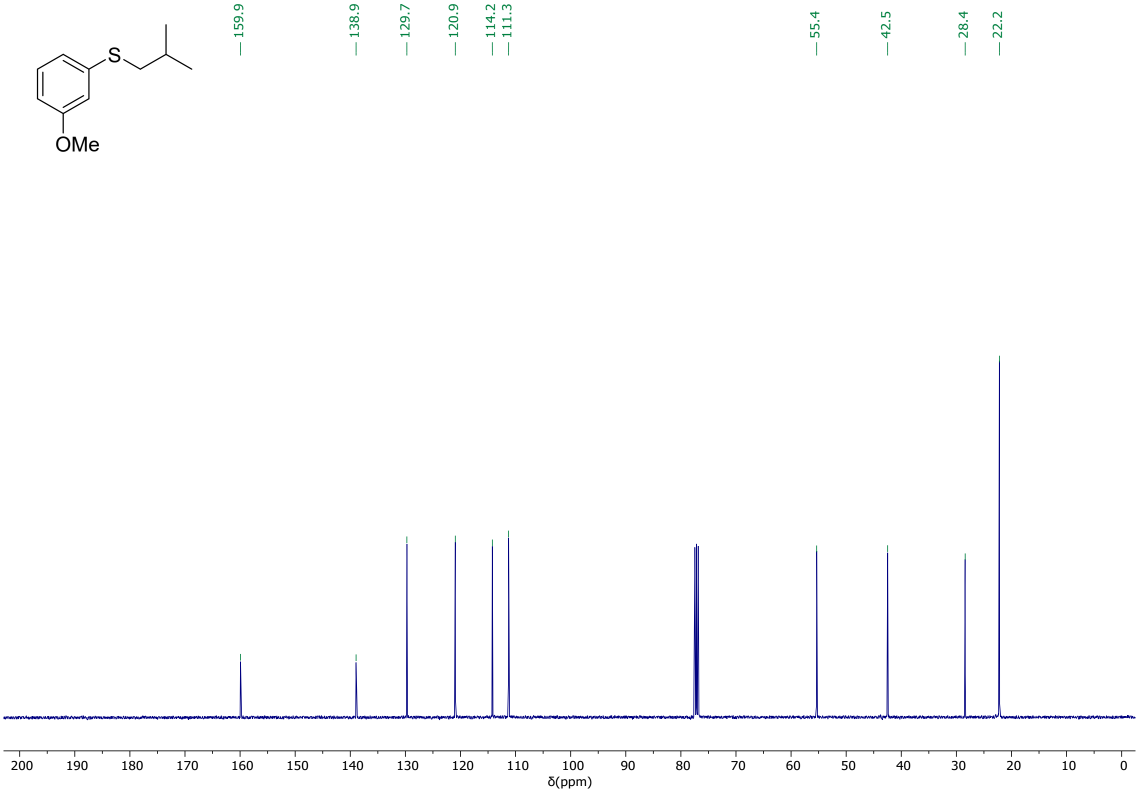

Figure S124. ^{1}H-NMR spectra of compound **6j**.

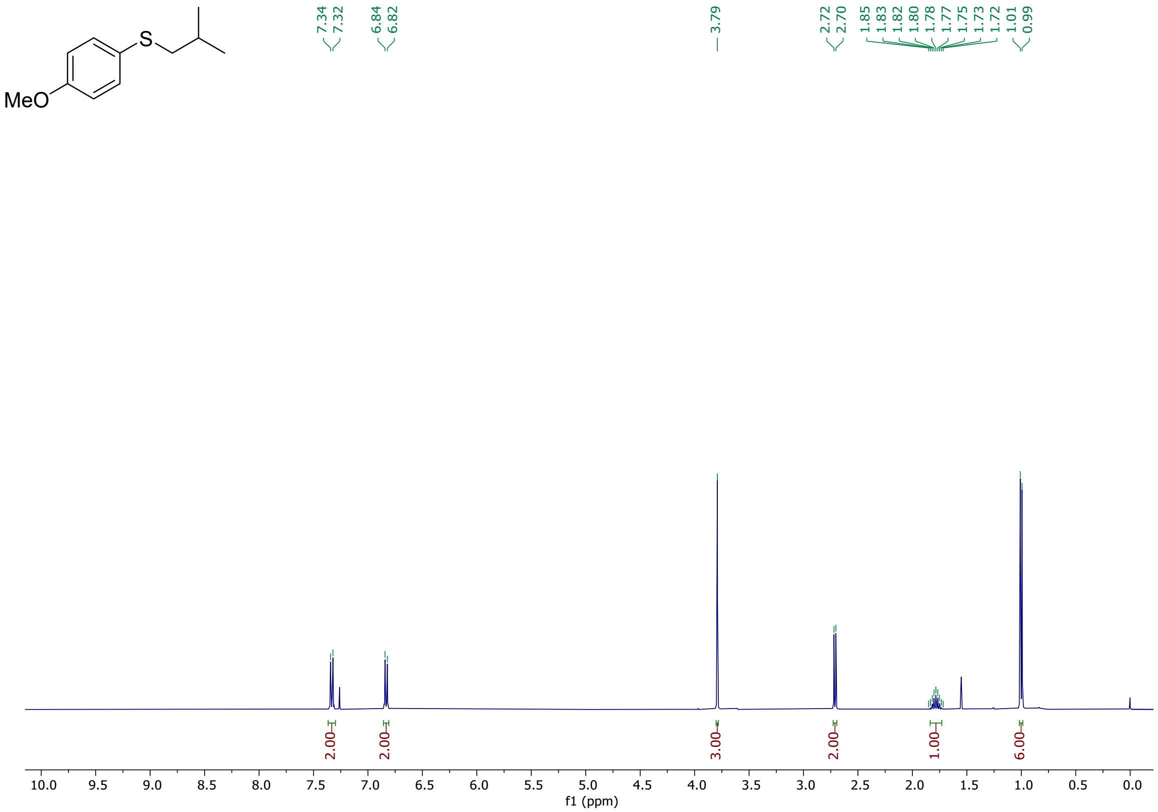

Figure S125. ^{1}H-NMR spectra of compound **6k**.

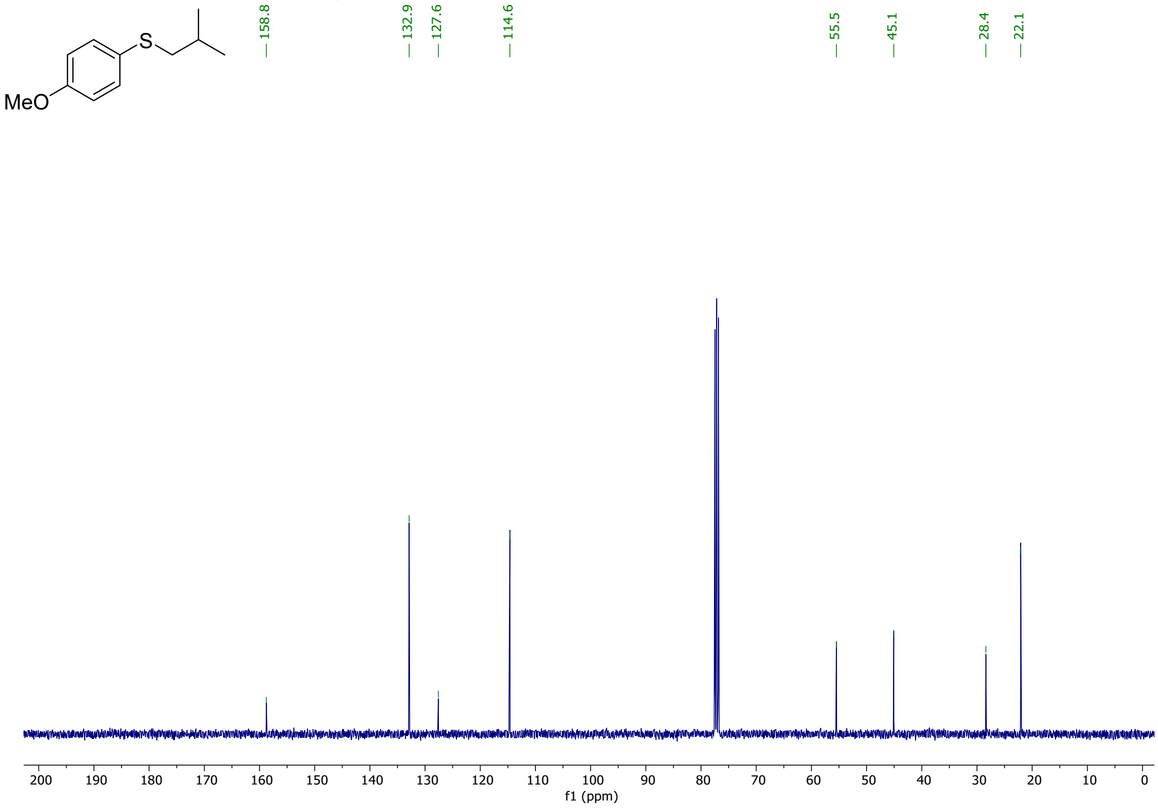

Figure S126. ^{13}C-NMR spectra of compound **6k**.

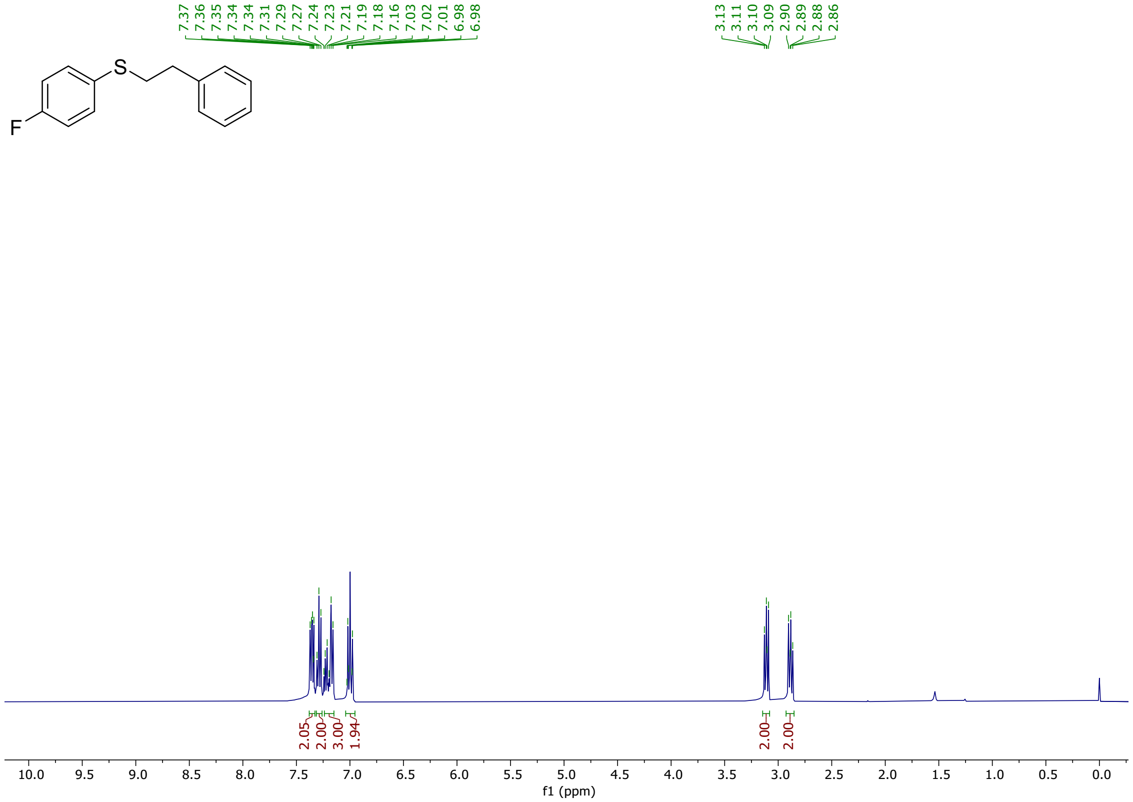

Figure S127. ^{1}H-NMR spectra of compound **6l**.

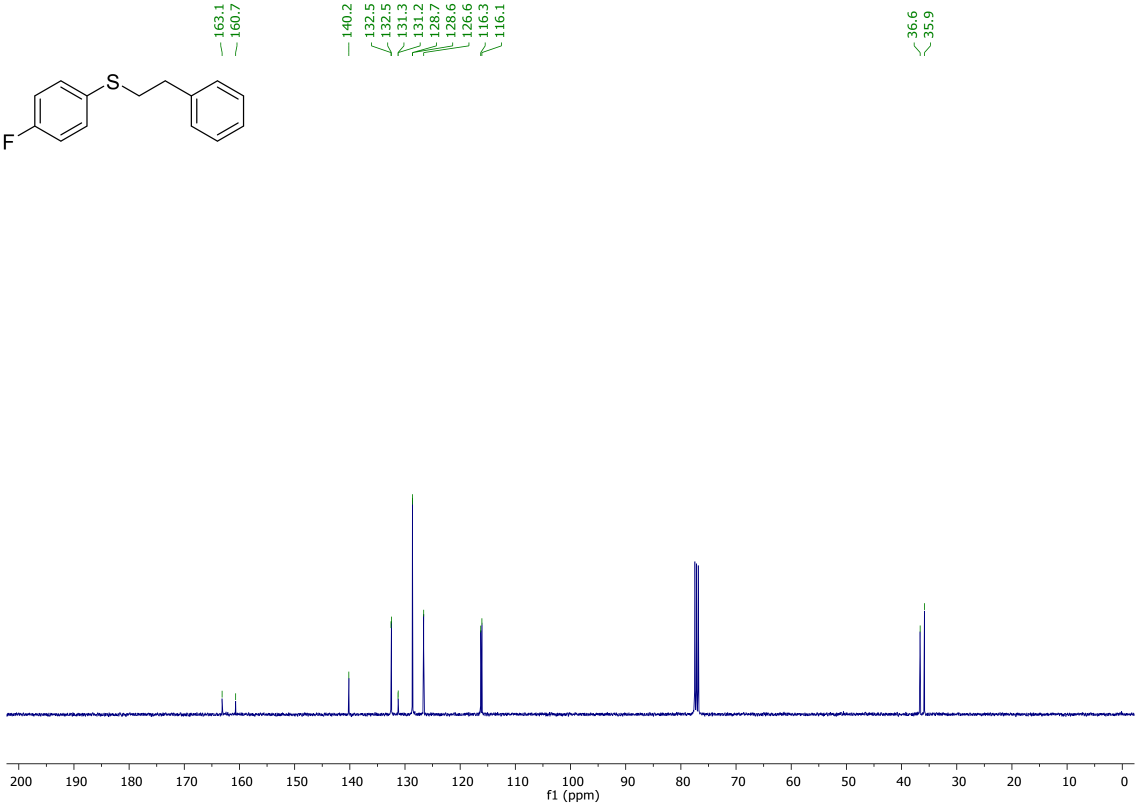

Figure S128. ^{13}C-NMR spectra of compound **6l**.

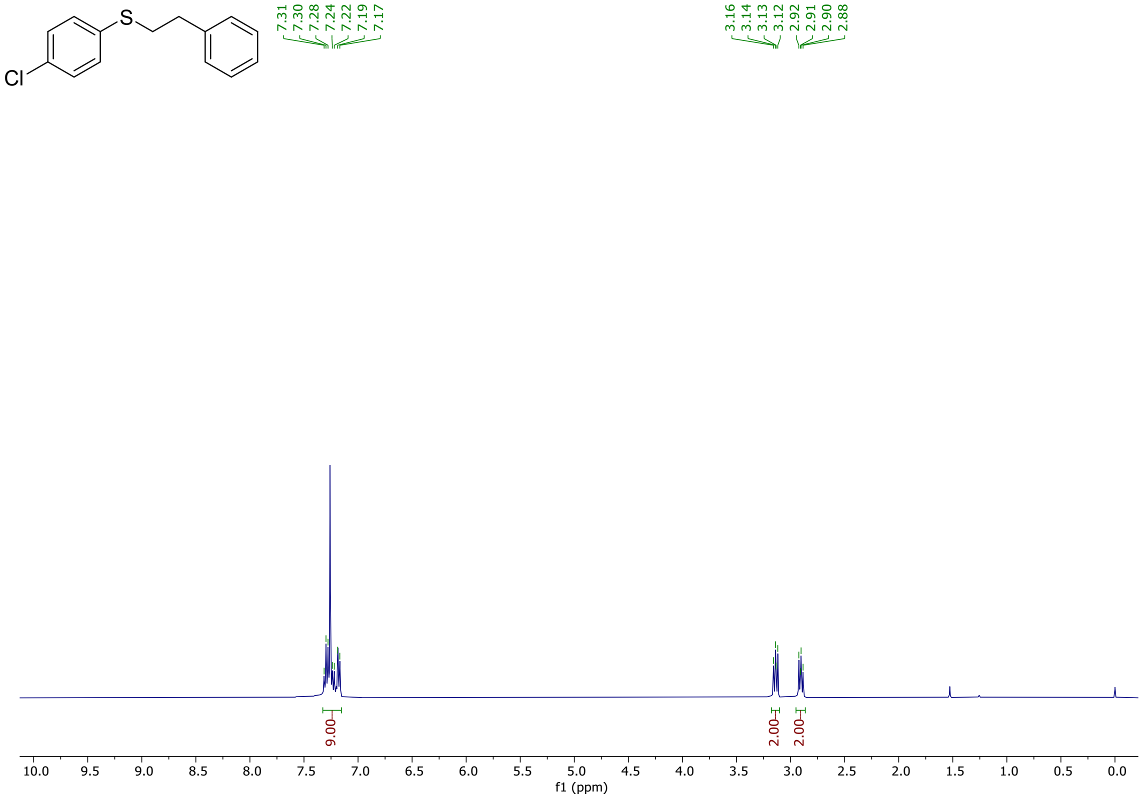

Figure S129. ^{1}H-NMR spectra of compound **6m.**

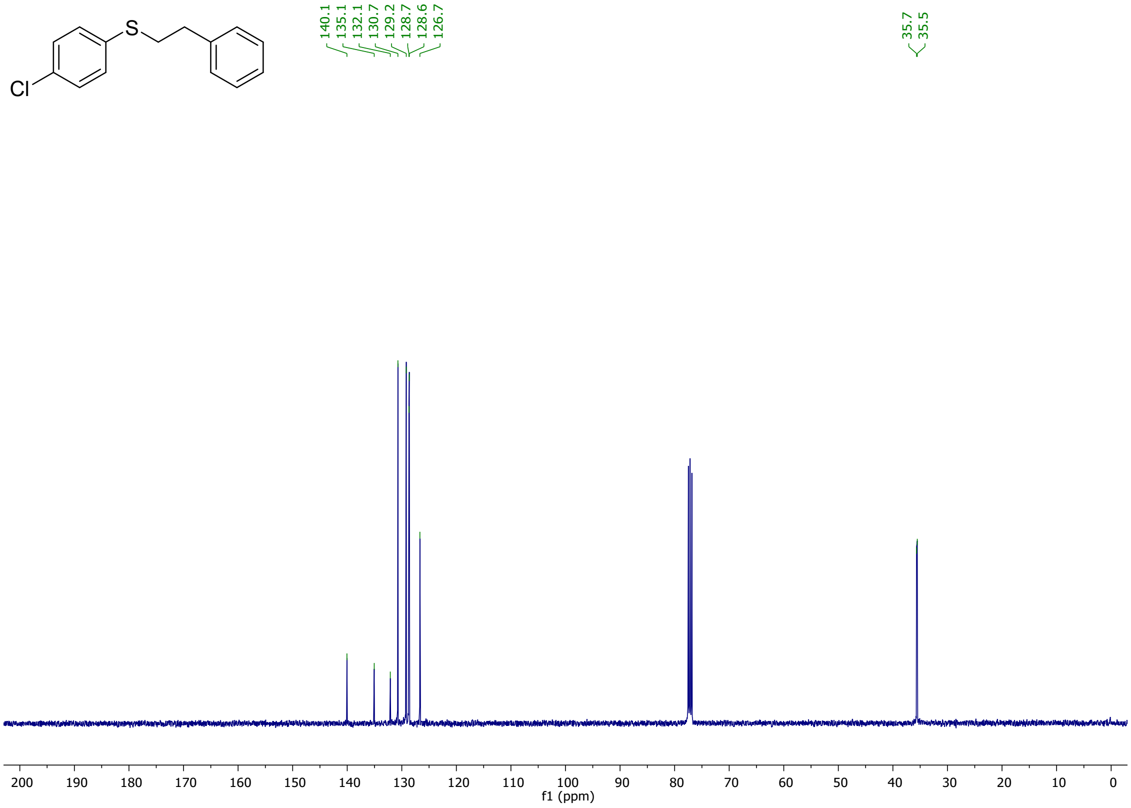

Figure S130. ^{13}C-NMR spectra of compound **6m.**

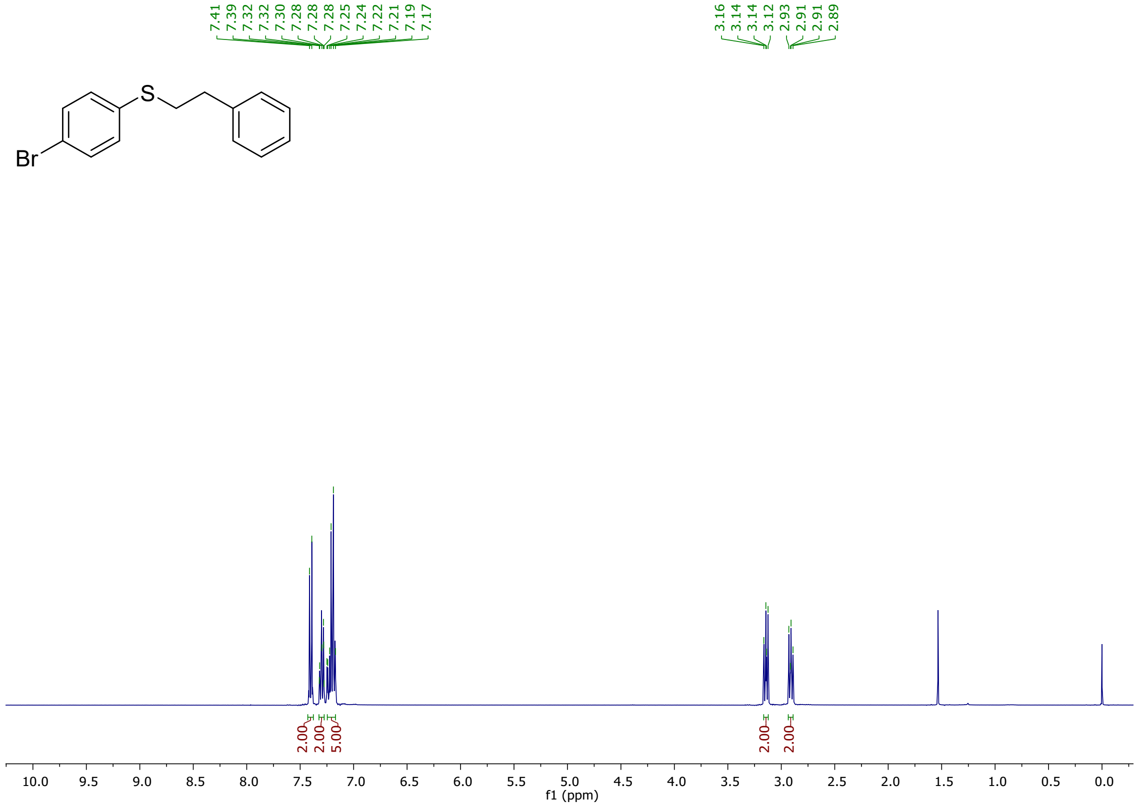

Figure S131. ^{1}H-NMR spectra of compound **6n**.

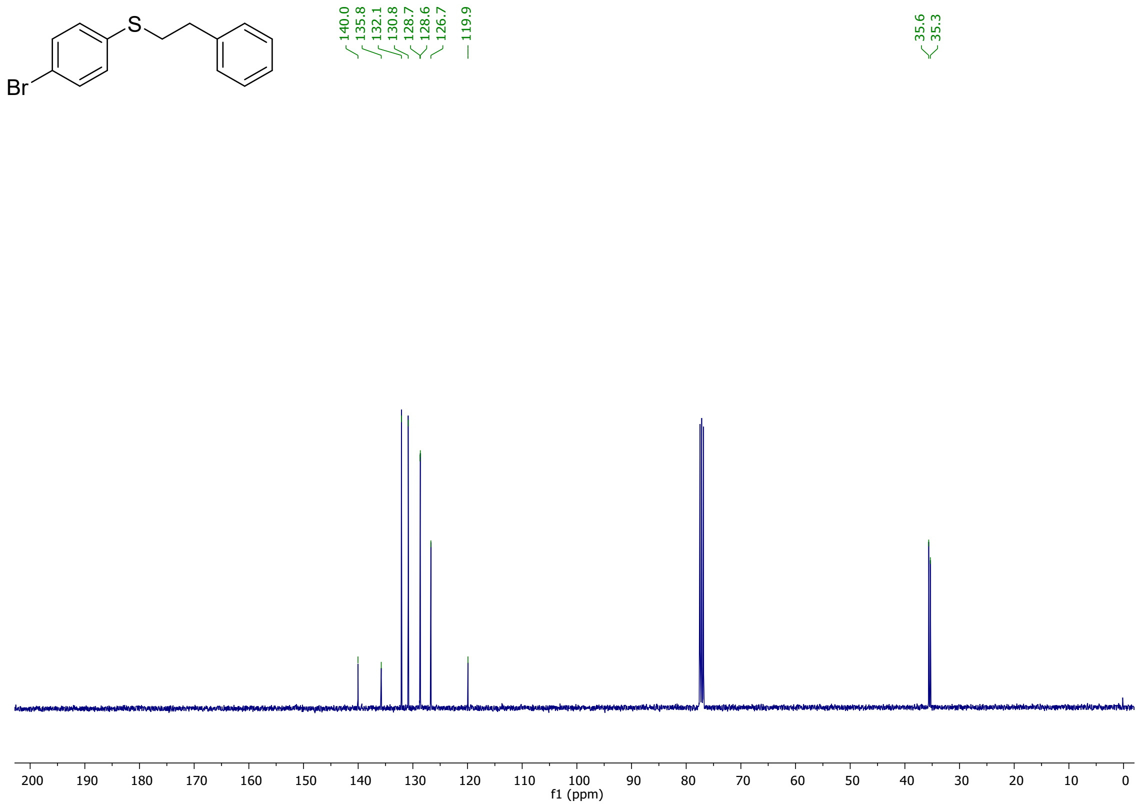

Figure S132. ^{13}C-NMR spectra of compound **6n**.

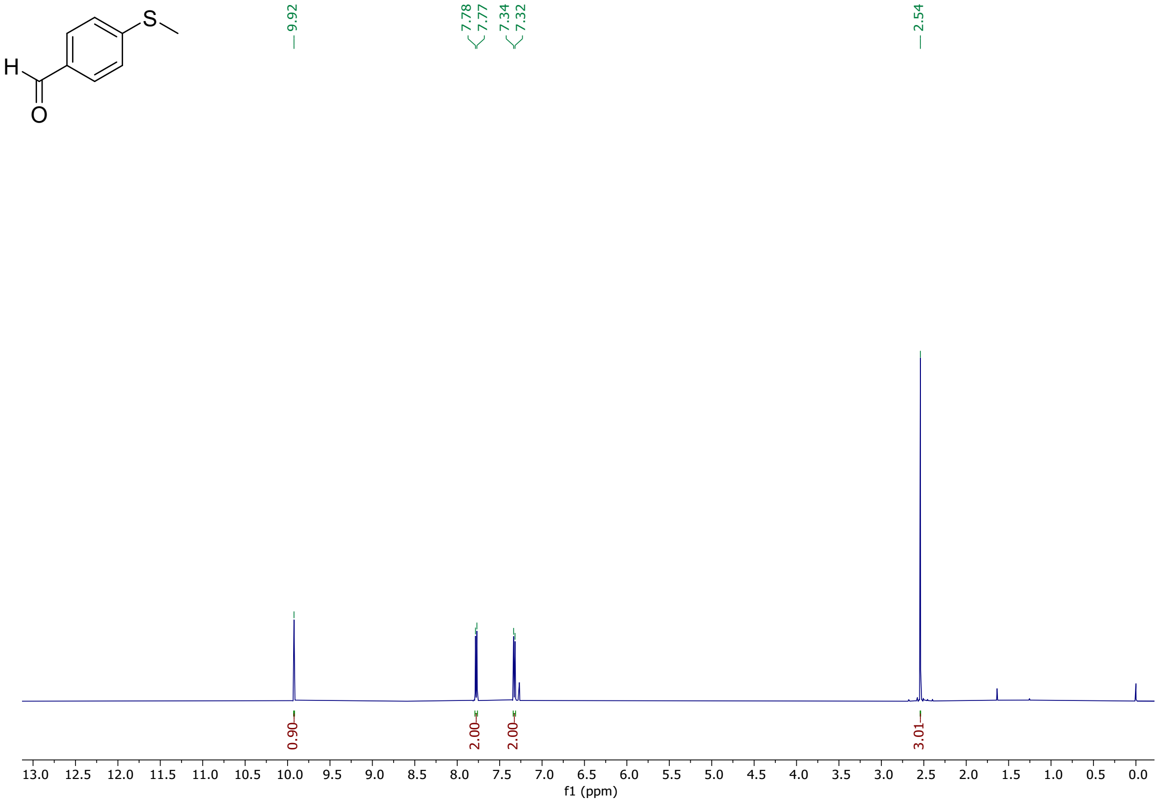

Figure S133. ^{1}H-NMR spectra of compound **6o**.

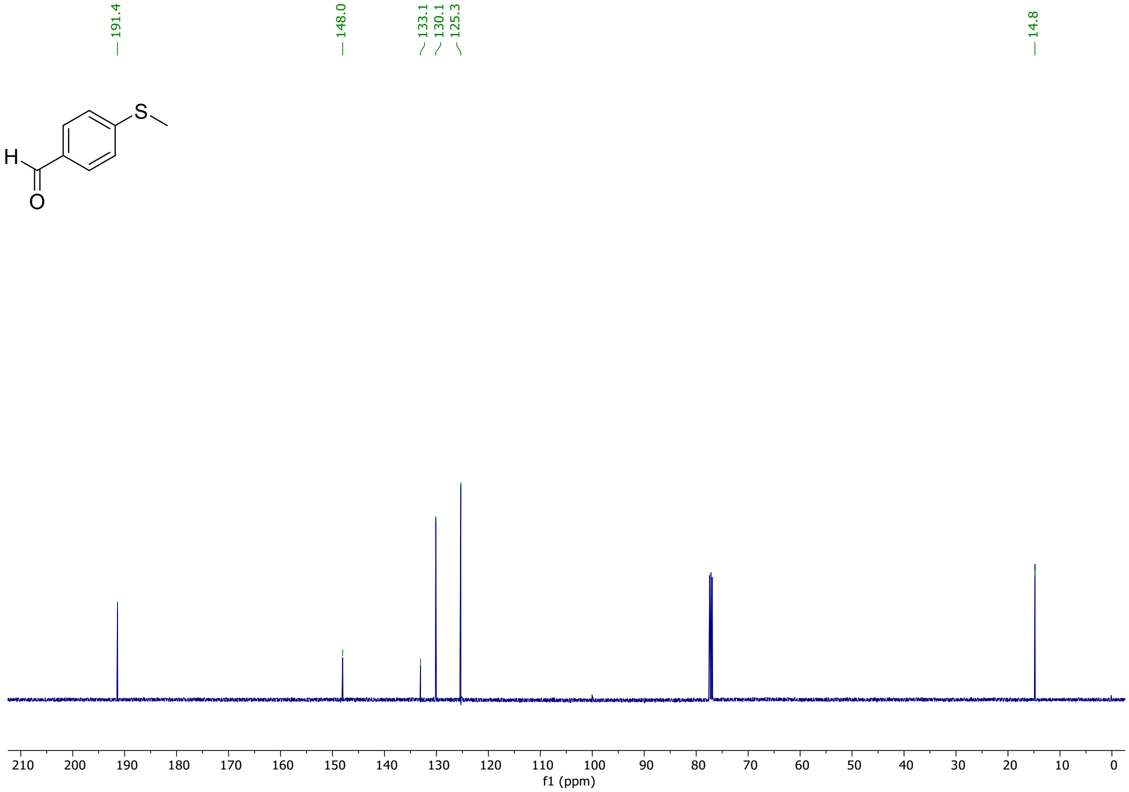

Figure S134. ^{13}C-NMR spectra of compound **6o**.

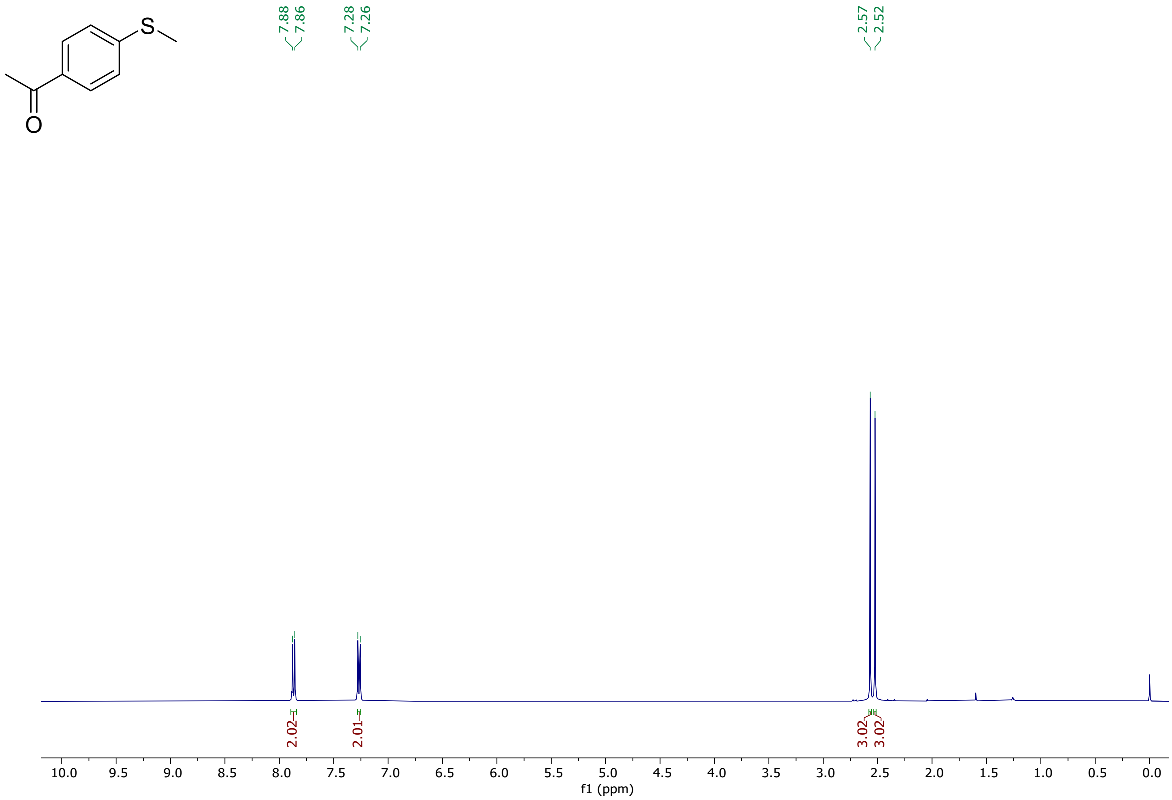

Figure S135. ^{1}H-NMR spectra of compound **6p**.

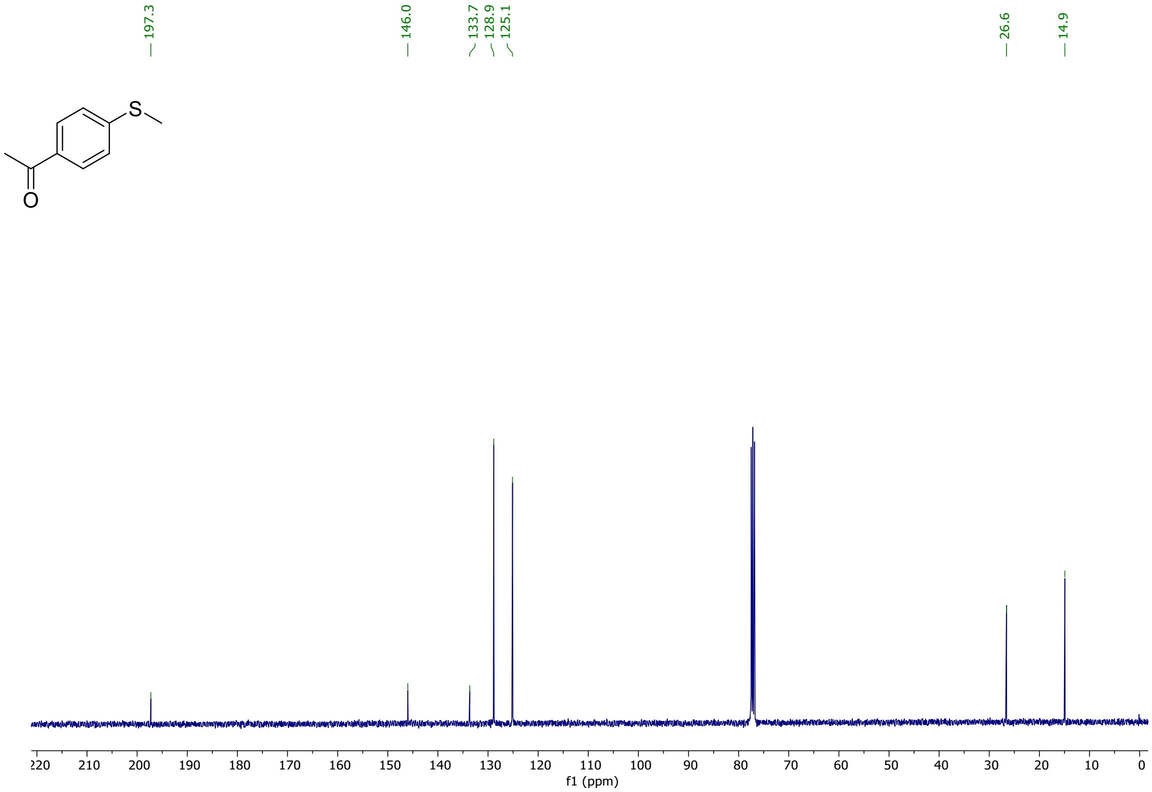

Figure S136. ^{13}C-NMR spectra of compound **6p**.

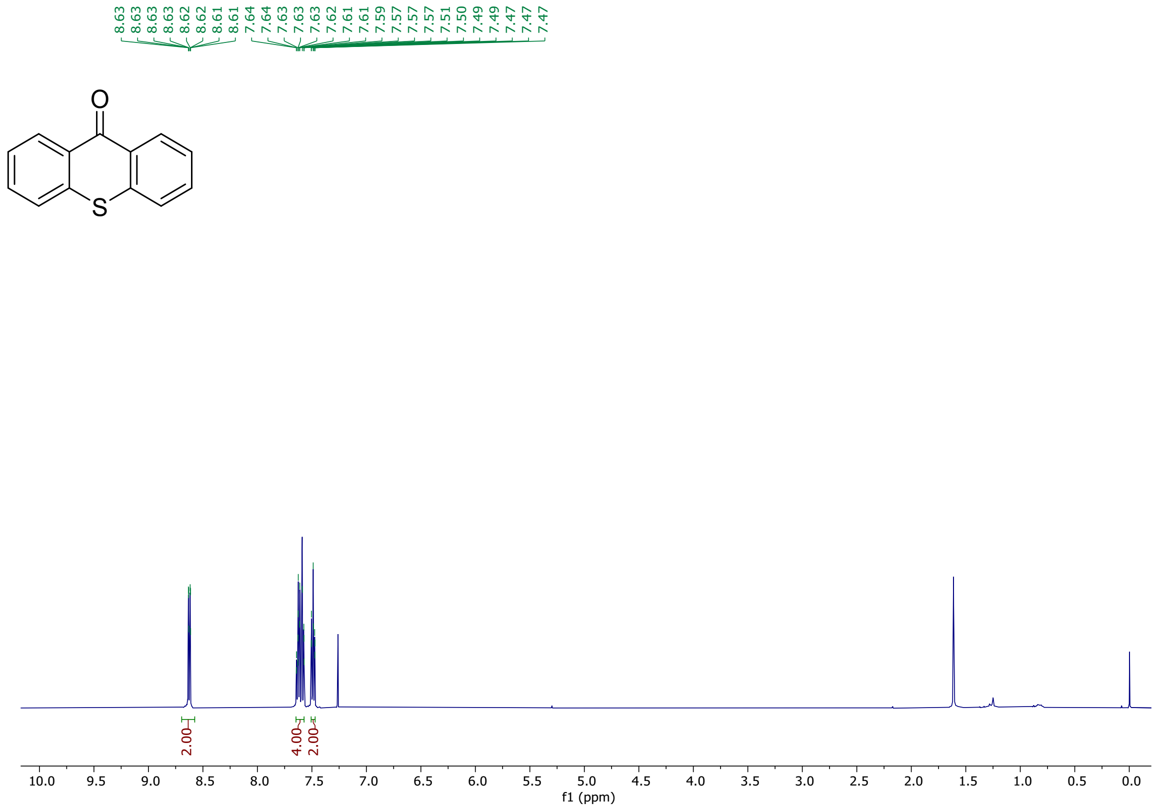

Figure S137. ^{1}H-NMR spectra of compound **6q**.

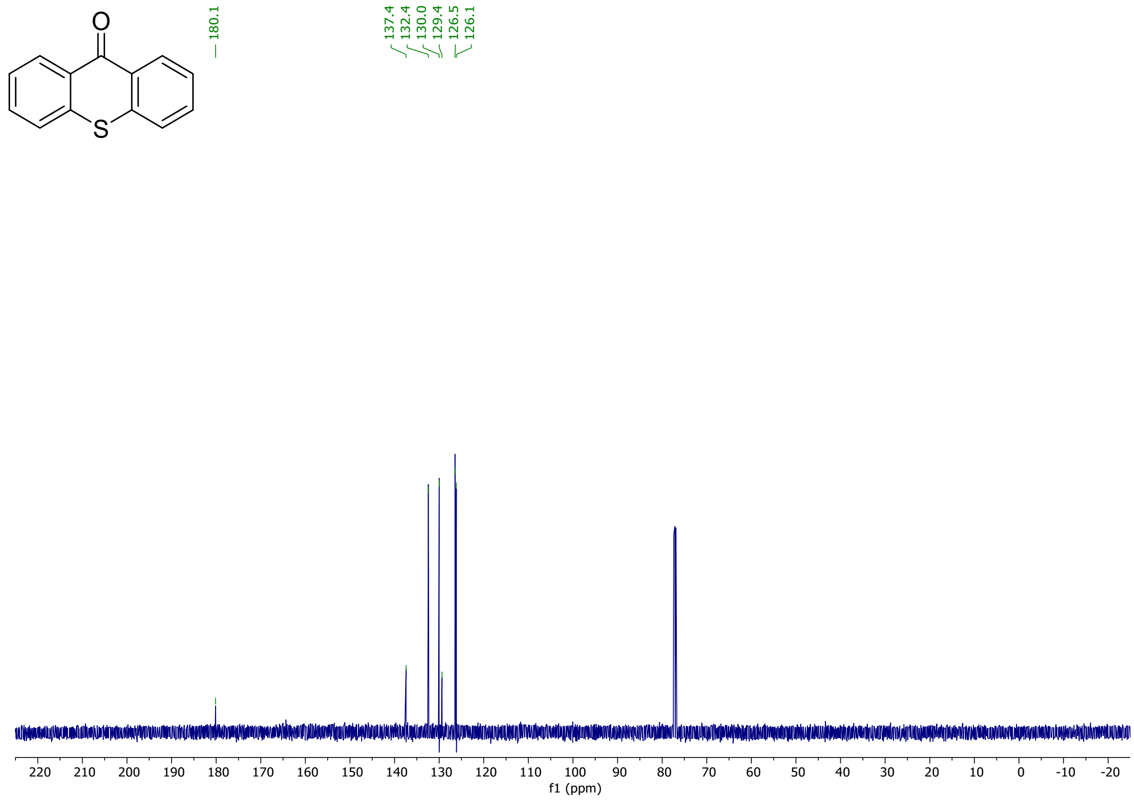

Figure S138. ^{13}C-NMR spectra of compound **6q**.

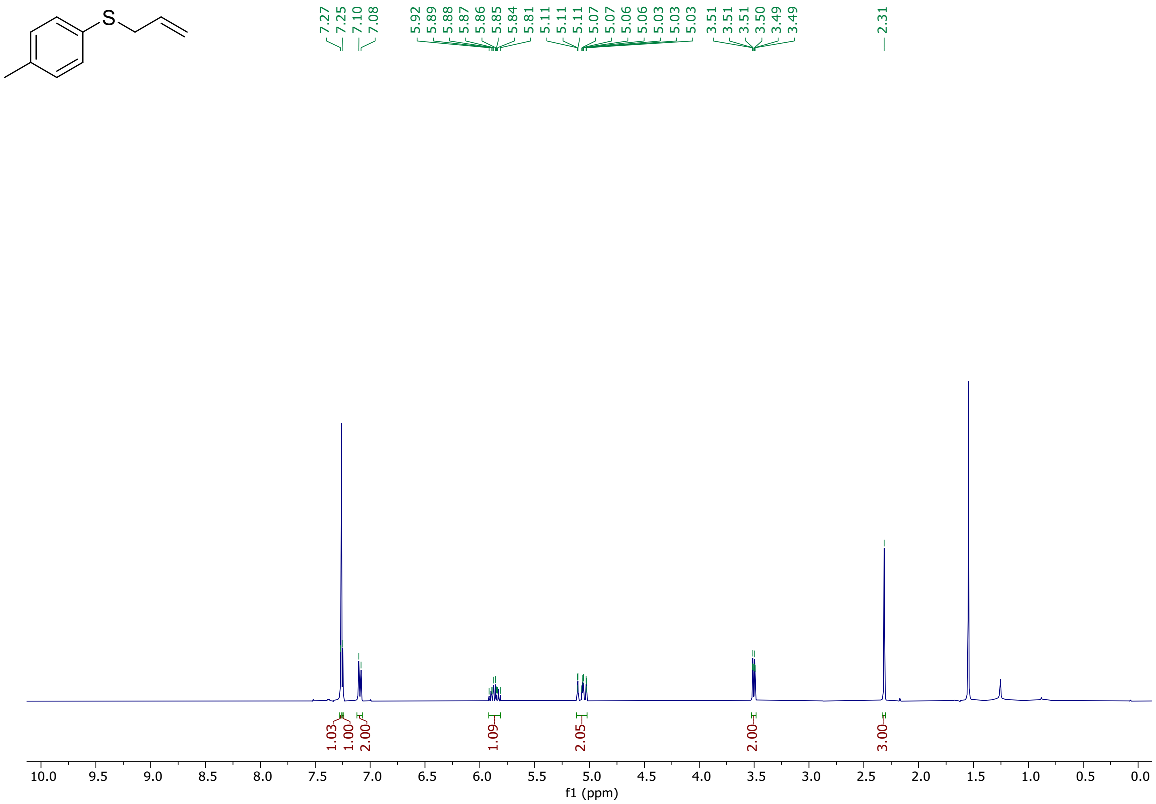

Figure S139. ^{1}H-NMR spectra of compound **6r**.

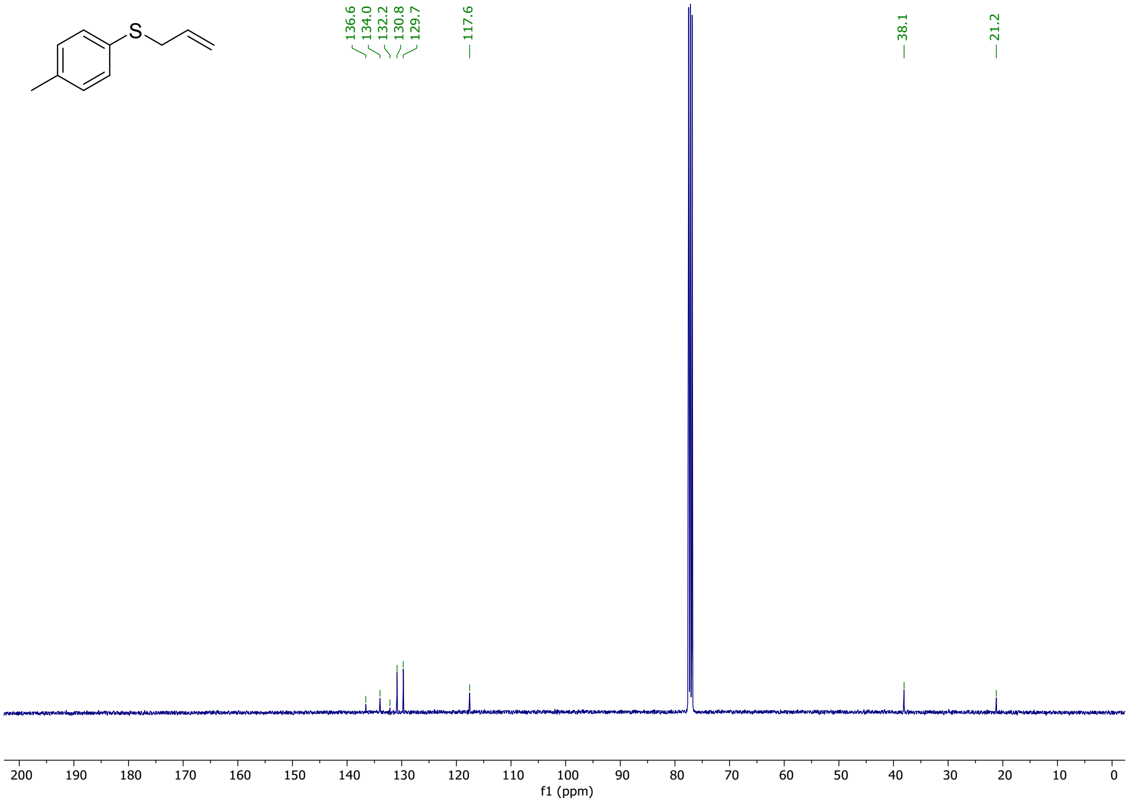

Figure S140. ^{13}C-NMR spectra of compound **6r**.

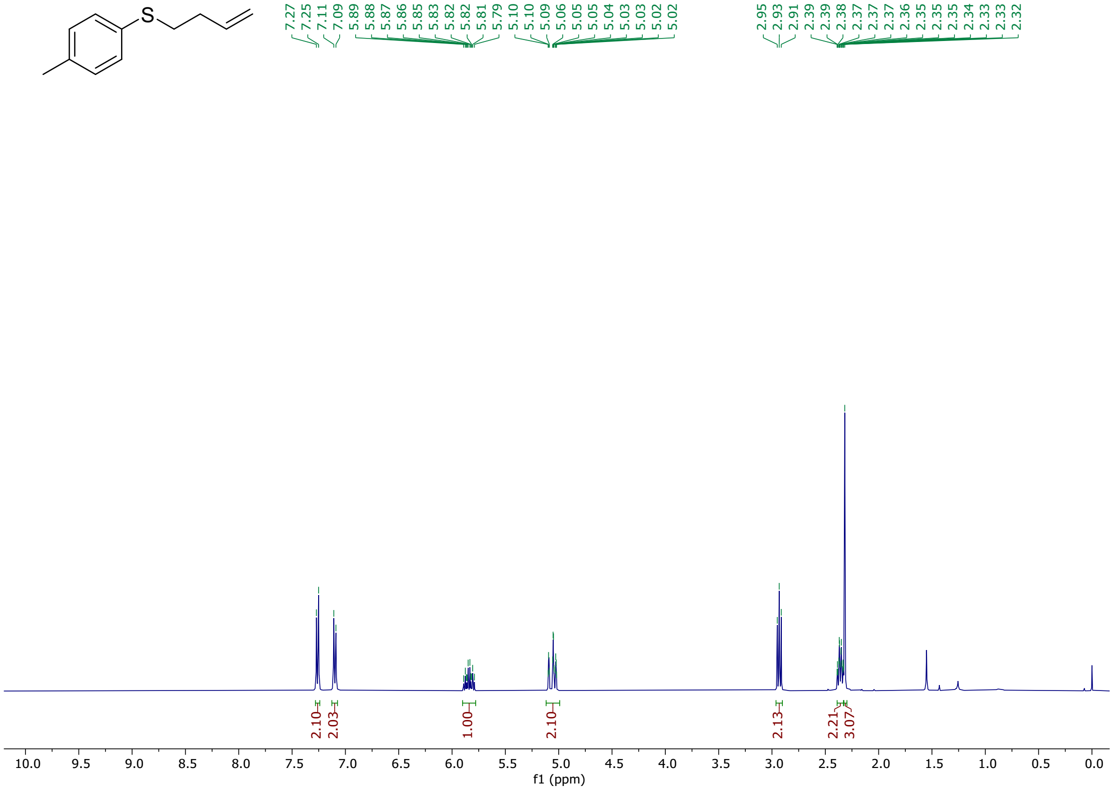

Figure S141. ^{1}H-NMR spectra of compound **6t**.

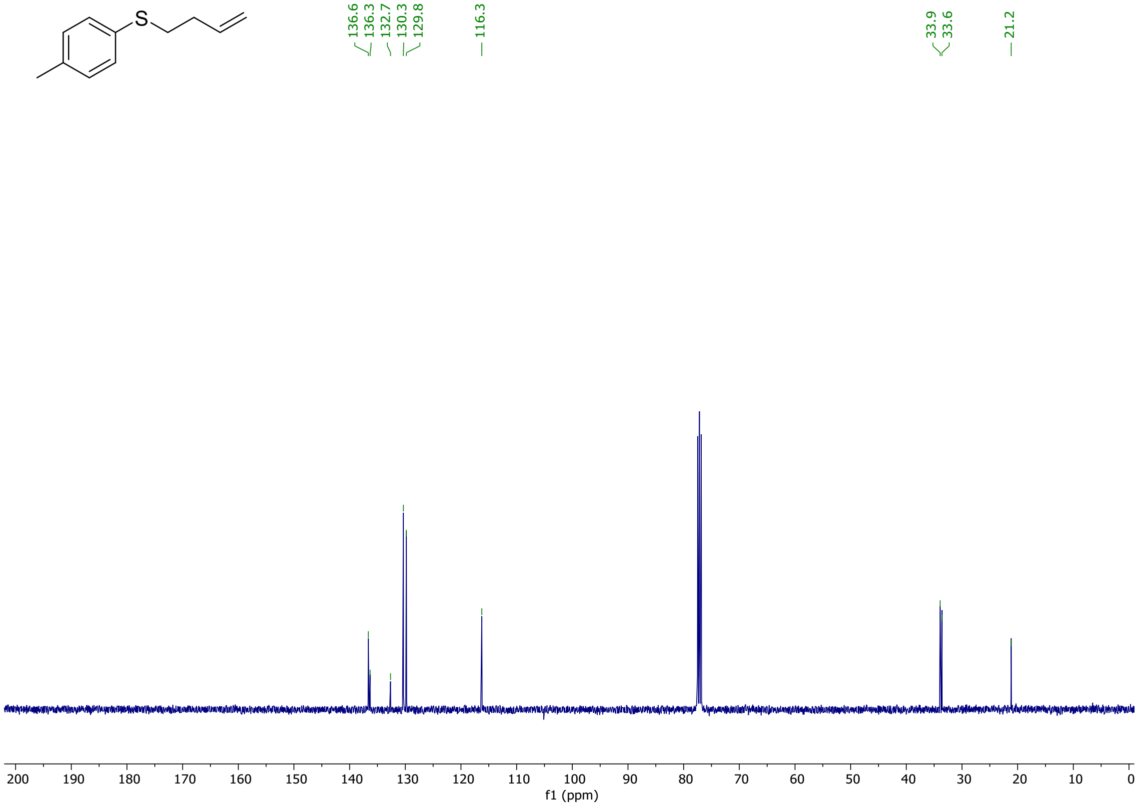

Figure S142. ^{13}C-NMR spectra of compound **6t**.

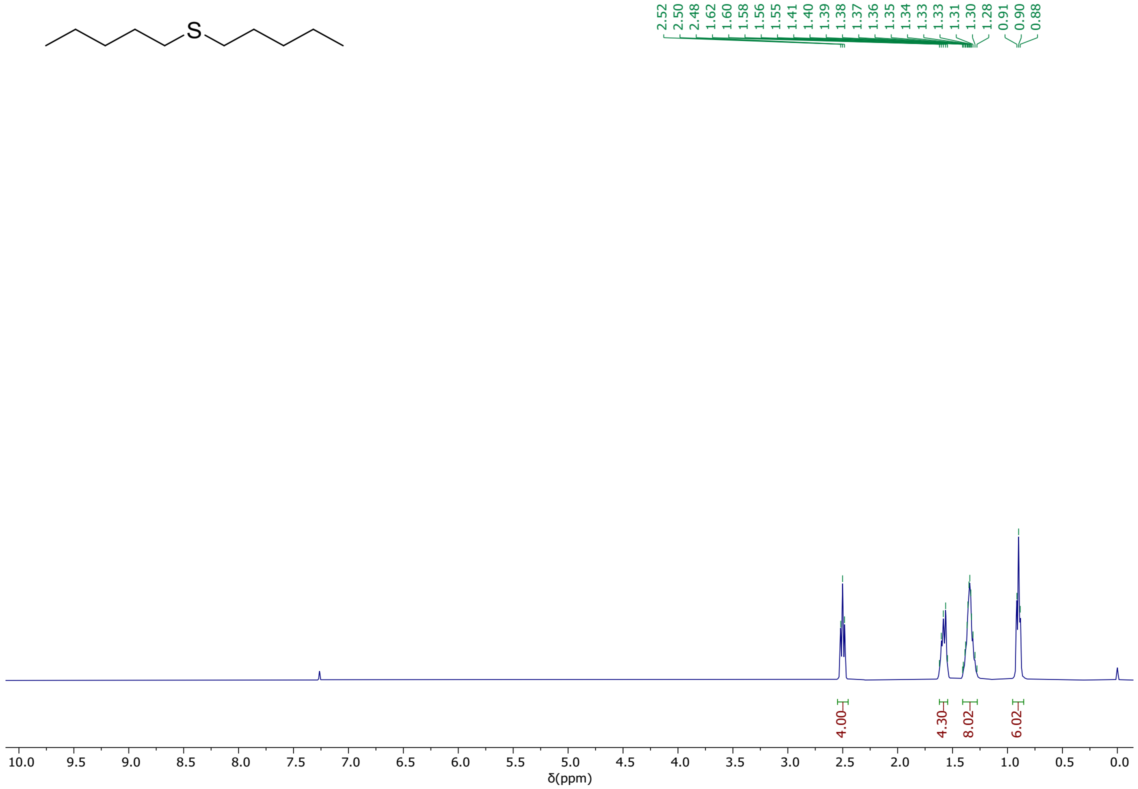

Figure S143. ^{1}H-NMR spectra of compound **6u**.

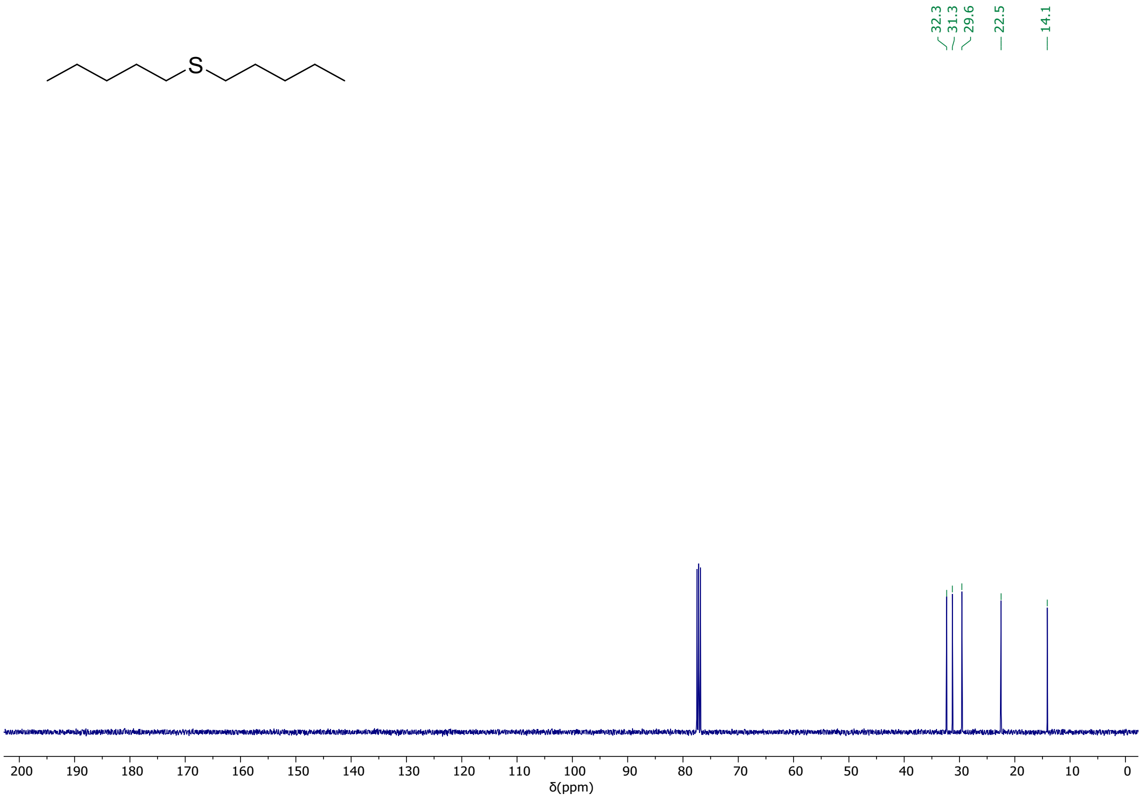

Figure S144. ^{1}H-NMR spectra of compound **6u**.

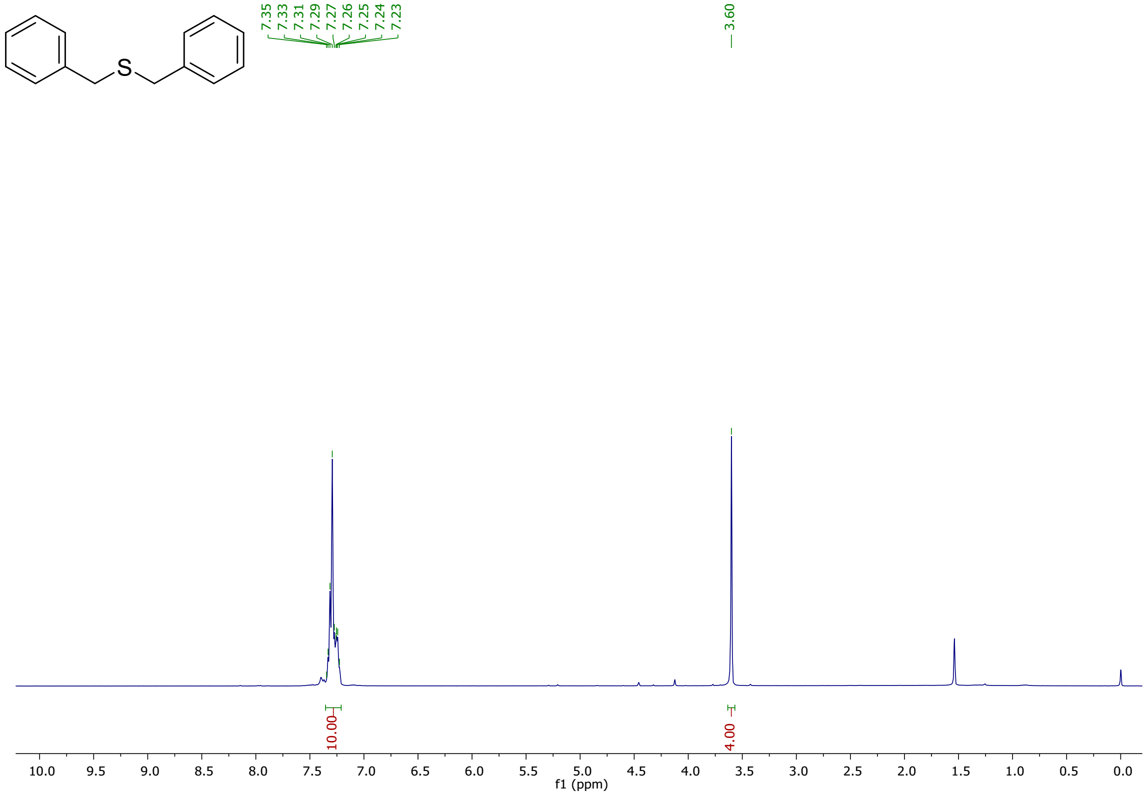

Figure S145. ^{1}H-NMR spectra of compound **6v**.

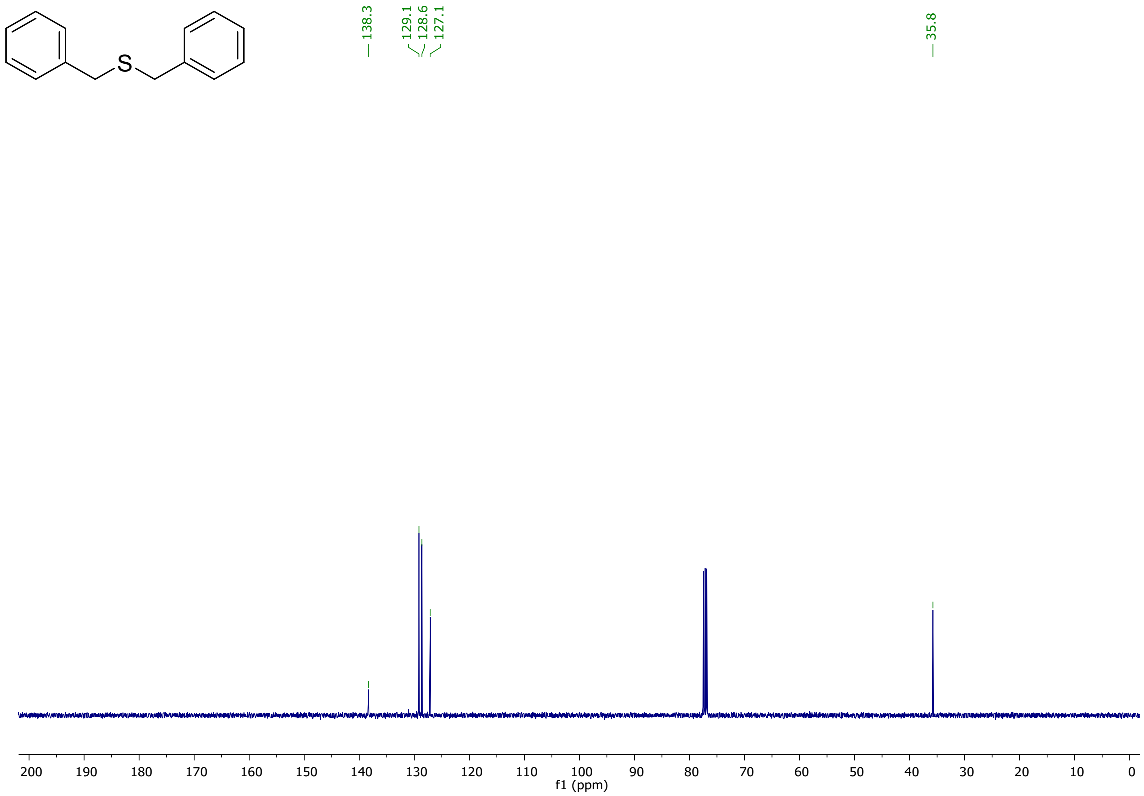

Figure S146. ^{1}H-NMR spectra of compound **6v**.

11. Computational details

All DFT calculations have been performed with Gaussian 09, Revision D.01 and GaussView 6 as visualizer. Geometry optimizations and frequency analyses were performed using the rage-separated DFA ωB97XD/def2tzvp, employing the SMD model for implicit solvation, using formic acid as the solvent. Optimization calculations included the option "opt=gdiis,verytight," and for transition states (TS) search, we used the keyword "opt=(ts,calcfc,noeigen,gdiis,verytight)." For the stationary states, minima and TSs, the thermodynamic properties were evaluated at 363.15 K. The GDIIS method was preferred in most cases for the convergence of optimized structures. Imaginary frequencies were inspected to determine the stationary points (no imaginary frequencies) or transition states (only one imaginary frequency). All transition states were confirmed by IRC calculations using the same theoretical methodology as that used in the geometry optimizations.

12. Optimized structures in cartesian coordinates and thermal corrections

A1

```
Zero-point correction=                           0.111202 (Hartree/Particle)
Thermal correction to Energy=                    0.130948
Thermal correction to Enthalpy=                  0.132098
Thermal correction to Gibbs Free Energy=         0.044609
Sum of electronic and zero-point Energies=       -21700.999200
Sum of electronic and thermal Energies=          -21700.979454
Sum of electronic and thermal Enthalpies=        -21700.978304
Sum of electronic and thermal Free Energies=     -21701.065793
-------------------------------------------------------------------------------------
O          0.000014994   -0.000005074   -0.000008323
K         -0.000011735   -0.000007809   -0.000002948
S          0.000003662    0.000001218   -0.000000080
I         -0.000012038    0.000013411    0.000014009
C          0.000012048    0.000013417    0.000007305
H          0.000018705    0.000014638    0.000006421
H          0.000016235    0.000013929    0.000006544
H          0.000005743    0.000018422    0.000013052
C         -0.000001830    0.000001765    0.000001922
H         -0.000006225   -0.000005481   -0.000002630
H          0.000005688    0.000004223    0.000001764
H         -0.000008143    0.000006810    0.000007684
I          0.000007256   -0.000021198   -0.000018941
H          0.000013074   -0.000010922   -0.000012112
I         -0.000032038   -0.000014946   -0.000002938
H         -0.000025396   -0.000022403   -0.000010727
```

A-TS

```
Zero-point correction=                           0.099580 (Hartree/Particle)
Thermal correction to Energy=                    0.119072
Thermal correction to Enthalpy=                  0.120222
Thermal correction to Gibbs Free Energy=         0.034856
Sum of electronic and zero-point Energies=       -2047.778571
Sum of electronic and thermal Energies=          -2047.759078
Sum of electronic and thermal Enthalpies=        -2047.757928
Sum of electronic and thermal Free Energies=     -2047.843295
```

```
-----------------------------------------------------------------------------------------
O        -0.000004645    0.000010346   -0.000014495
K         0.000036180   -0.000002768   -0.000001669
S         0.000000260   -0.000001572    0.000002364
I         0.000020816   -0.000022463    0.000029711
C        -0.000019871   -0.000004681    0.000010047
H        -0.000028847   -0.000000291    0.000004999
H        -0.000022322   -0.000003743    0.000009069
H        -0.000019332   -0.000012136    0.000020920
C         0.000001730   -0.000003128    0.000004302
H         0.000013415   -0.000000794   -0.000000958
H        -0.000009011    0.000000953    0.000000035
H         0.000001962   -0.000010668    0.000015370
I        -0.000002125    0.000009953   -0.000014244
H        -0.000007209    0.000012249   -0.000017040
I         0.000031504    0.000015275   -0.000027496
H         0.000007494    0.000013468   -0.000020913
```

B1 (B1-2FA)

```
Zero-point correction=                          0.152565 (Hartree/Particle)
Thermal correction to Energy=                    0.177571
Thermal correction to Enthalpy=                  0.178721
Thermal correction to Gibbs Free Energy=         0.082237
Sum of electronic and zero-point Energies=         -1830.556166
Sum of electronic and thermal Energies=            -1830.531160
Sum of electronic and thermal Enthalpies=          -1830.530010
Sum of electronic and thermal Free Energies=        -1830.626494
-----------------------------------------------------------------------------------------
O         0.000006389    0.000009402   -0.000005996
H         0.000003100    0.000006380   -0.000006007
O        -0.000002869    0.000000203   -0.000005818
C         0.000010150    0.000010142   -0.000000296
O         0.000008832    0.000006640    0.000004524
H         0.000013460    0.000013498   -0.000000194
O        -0.000000747   -0.000004041    0.000005831
C        -0.000002838   -0.000003397    0.000001204
O        -0.000003446   -0.000001036   -0.000004672
H        -0.000002285   -0.000003060    0.000001233
H        -0.000003705   -0.000000791   -0.000004709
K         0.000004985   -0.000002386    0.000013659
S        -0.000001847   -0.000002136   -0.000000234
I         0.000001526   -0.000008214    0.000018188
C        -0.000008634   -0.000007194   -0.000002328
H        -0.000009580   -0.000005735   -0.000007085
H        -0.000011218   -0.000010126   -0.000002036
H        -0.000008387   -0.000008974    0.000001256
C         0.000001109    0.000002140   -0.000001505
H         0.000005215    0.000005502   -0.000000685
H        -0.000000481    0.000002928   -0.000006397
H         0.000001271    0.000000255    0.000002069
```

B-TS (B-TS-2FA)

Zero-point correction= 0.146941 (Hartree/Particle)
Thermal correction to Energy= 0.171278
Thermal correction to Enthalpy= 0.172428
Thermal correction to Gibbs Free Energy= 0.081289
Sum of electronic and zero-point Energies= -1830.501527
Sum of electronic and thermal Energies= -1830.477190
Sum of electronic and thermal Enthalpies= -1830.476040
Sum of electronic and thermal Free Energies= -1830.567179

O	0.000002491	0.000000425	0.000026281
H	0.000007803	-0.000002871	0.000016764
O	0.000008704	-0.000003822	0.000008950
C	0.000003005	-0.000001897	0.000020620
O	-0.000003097	0.000002207	0.000010935
H	0.000014668	-0.000005760	0.000023440
O	-0.000025206	0.000012012	0.000007737
C	-0.000020951	0.000009604	0.000013393
O	-0.000007565	0.000004121	0.000014940
H	-0.000028096	0.000013350	0.000015824
H	0.000000576	0.000000042	0.000011981
K	-0.000025652	0.000012102	0.000013616
S	0.000001014	-0.000000559	-0.000009844
I	-0.000012618	0.000004601	-0.000031797
C	0.000001088	-0.000001187	-0.000020193
H	0.000009137	-0.000004667	-0.000014679
H	-0.000009360	0.000003599	-0.000019394
H	0.000003742	-0.000002801	-0.000032254
C	0.000017652	-0.000008513	-0.000013603
H	0.000019799	-0.000009907	-0.000025969
H	0.000017372	-0.000008255	-0.000009952
H	0.000025494	-0.000011824	-0.000006797

C1

Zero-point correction= 0.146463 (Hartree/Particle)
Thermal correction to Energy= 0.178629
Thermal correction to Enthalpy= 0.179779
Thermal correction to Gibbs Free Energy= 0.061463
Sum of electronic and zero-point Energies= -2728.381917
Sum of electronic and thermal Energies= -2728.349751
Sum of electronic and thermal Enthalpies= -2728.348601
Sum of electronic and thermal Free Energies= -2728.466917

O	0.000003808	-0.000002128	-0.000002914
H	0.000005187	-0.000003965	-0.000004284
O	0.000007496	-0.000007258	-0.000006845
C	0.000000023	0.000002338	0.000000987
O	-0.000001578	0.000004239	0.000002625
H	-0.000001377	0.000004430	0.000002635
K	-0.000010418	-0.000001536	0.000004623
S	0.000006514	-0.000003506	-0.000005006
I	-0.000002348	0.000012725	0.000006694

C	0.000010705	-0.000007645	-0.000008681
H	0.000015715	-0.000007674	-0.000011276
H	0.000007936	-0.000012721	-0.000009504
H	0.000010659	-0.000004863	-0.000007461
C	0.000012205	0.000004218	-0.000004354
H	0.000010371	0.000007261	-0.000002144
H	0.000017020	0.000003228	-0.000007229
H	0.000012420	0.000006886	-0.000003260
I	-0.000008613	-0.000017262	-0.000003134
H	-0.000000963	-0.000013891	-0.000005479
O	-0.000016856	0.000008505	0.000012343
C	-0.000022131	0.000005085	0.000013118
O	-0.000023339	-0.000000103	0.000011869
H	-0.000026676	0.000007439	0.000016767
K	-0.000005759	0.000016199	0.000009909

C-TS1

Zero-point correction= 0.146681 (Hartree/Particle)
Thermal correction to Energy= 0.177024
Thermal correction to Enthalpy= 0.178174
Thermal correction to Gibbs Free Energy= 0.065252
Sum of electronic and zero-point Energies= -2728.378971
Sum of electronic and thermal Energies= -2728.348628
Sum of electronic and thermal Enthalpies= -2728.347478
Sum of electronic and thermal Free Energies= -2728.460400

O	0.000005889	0.000000505	0.000003934
H	0.000005417	-0.000001793	0.000005918
O	0.000004060	-0.000006273	0.000009463
C	0.000003255	0.000003844	-0.000001422
O	0.000000512	0.000004347	-0.000003958
H	0.000003611	0.000006392	-0.000003703
K	-0.000010974	-0.000001546	-0.000006759
S	0.000003589	-0.000004252	0.000006972
I	-0.000002465	0.000007553	-0.000009463
C	0.000006136	-0.000008236	0.000012983
H	0.000010776	-0.000007871	0.000016103
H	0.000002603	-0.000012573	0.000014639
H	0.000006397	-0.000006677	0.000011556
C	0.000010300	0.000002357	0.000005402
H	0.000009365	0.000005286	0.000001779
H	0.000014487	0.000001900	0.000009063
H	0.000010784	0.000003793	0.000004361
I	-0.000009878	-0.000013260	0.000005813
H	-0.000002614	-0.000009934	0.000008002
O	-0.000011870	0.000008193	-0.000017223
C	-0.000017796	0.000005620	-0.000019184
O	-0.000020980	0.000000552	-0.000016431
H	-0.000020465	0.000008081	-0.000023650
K	-0.000000140	0.000013989	-0.000014197

C2 (C2-2FA)

```
Zero-point correction=                          0.152715 (Hartree/Particle)
Thermal correction to Energy=                   0.184023
Thermal correction to Enthalpy=                 0.185173
Thermal correction to Gibbs Free Energy=        0.071270
Sum of electronic and zero-point Energies=        -2728.392050
Sum of electronic and thermal Energies=           -2728.360742
Sum of electronic and thermal Enthalpies=         -2728.359592
Sum of electronic and thermal Free Energies=      -2728.473495
-----------------------------------------------------------------------------------
O      -0.000034565   -0.000013764   -0.000016535
H      -0.000025756   -0.000011118   -0.000023019
O      -0.000003147   -0.000003659   -0.000033025
C      -0.000030708   -0.000010821    0.000000497
O      -0.000017161   -0.000005665    0.000007426
H      -0.000040308   -0.000013690    0.000007862
K       0.000014893    0.000006319    0.000012815
S       0.000007961    0.000001452   -0.000016827
I       0.000025795    0.000011785    0.000030458
C       0.000023389    0.000006053   -0.000028222
H       0.000017196    0.000003026   -0.000037442
H       0.000032274    0.000008598   -0.000035487
H       0.000030335    0.000009374   -0.000017685
C      -0.000007374   -0.000003481   -0.000009285
H      -0.000018314   -0.000006784   -0.000002973
H      -0.000011286   -0.000005780   -0.000020992
H      -0.000001038   -0.000000322    0.000000710
I       0.000018066    0.000003606   -0.000034591
H       0.000001964   -0.000002425   -0.000035718
O      -0.000001457    0.000003867    0.000046630
C       0.000008937    0.000006350    0.000053921
O       0.000019127    0.000010907    0.000041575
H       0.000006677    0.000008061    0.000066100
K      -0.000015499   -0.000001890    0.000043807
```

C-TS2 (C-TS2-2FA)

```
Zero-point correction=                          0.148493 (Hartree/Particle)
Thermal correction to Energy=                   0.178532
Thermal correction to Enthalpy=                 0.179682
Thermal correction to Gibbs Free Energy=        0.071009
Sum of electronic and zero-point Energies=        -2728.358302
Sum of electronic and thermal Energies=           -2728.328263
Sum of electronic and thermal Enthalpies=         -2728.327113
Sum of electronic and thermal Free Energies=      -2728.435786
-----------------------------------------------------------------------------------
O       0.000013278   -0.000020658    0.000002215
H       0.000007720   -0.000012152    0.000001133
O       0.000002175   -0.000004716   -0.000002143
C       0.000012547   -0.000022370    0.000005950
O       0.000009369   -0.000013493    0.000004889
H       0.000018425   -0.000029140    0.000006759
K       0.000002967    0.000001780    0.000023658
```

S	-0.000003415	0.000004123	-0.000006757
I	-0.000009965	0.000014005	-0.000010957
C	-0.000010237	0.000013997	-0.000011788
H	-0.000008390	0.000010857	-0.000012013
H	-0.000013167	0.000020823	-0.000005351
H	-0.000012777	0.000015878	-0.000020668
C	-0.000000354	-0.000004967	-0.000019811
H	0.000004001	-0.000011619	-0.000017502
H	0.000000687	-0.000007398	-0.000022156
H	-0.000003831	-0.000001086	-0.000027024
I	-0.000003815	0.000013469	0.000024817
H	0.000001242	-0.000000725	0.000005462
O	0.000001817	0.000001700	0.000016936
C	-0.000002717	0.000010743	0.000021285
O	-0.000005718	0.000016730	0.000026141
H	-0.000005598	0.000014723	0.000018969
K	0.000005756	-0.000010502	-0.000002044

B1-3FA-HT

Zero-point correction= 0.188357 (Hartree/Particle)
Thermal correction to Energy= 0.218997
Thermal correction to Enthalpy= 0.220147
Thermal correction to Gibbs Free Energy= 0.109352
Sum of electronic and zero-point Energies= -2020.324907
Sum of electronic and thermal Energies= -2020.294268
Sum of electronic and thermal Enthalpies= -2020.293118
Sum of electronic and thermal Free Energies= -2020.403913

O	-0.000007207	0.000003529	0.000010464
H	-0.000003057	0.000001250	0.000009230
O	0.000003831	-0.000002253	0.000006976
C	-0.000012701	0.000006196	0.000009066
O	-0.000012176	0.000006407	0.000006202
H	-0.000017072	0.000008676	0.000010554
O	0.000001848	-0.000000615	-0.000010605
C	0.000004103	-0.000001666	-0.000011938
O	0.000005278	-0.000002615	-0.000006551
H	0.000005095	-0.000002025	-0.000017422
H	0.000004524	-0.000002381	-0.000001408
K	-0.000009477	0.000005263	-0.000004383
S	0.000002937	-0.000001900	0.000007717
I	-0.000004186	0.000002059	0.000003657
C	0.000010959	-0.000006080	0.000006544
H	0.000014360	-0.000008045	0.000010346
H	0.000012520	-0.000006662	0.000000670
H	0.000010726	-0.000005991	0.000007528
C	0.000001426	-0.000001377	0.000017402
H	-0.000003333	0.000001031	0.000018863
H	0.000005426	-0.000003651	0.000020615
H	0.000001185	-0.000001346	0.000018304
O	0.000001298	0.000000122	-0.000022975
H	0.000001643	-0.000000158	-0.000018494

C	-0.000004385	0.000003337	-0.000023421
O	-0.000008799	0.000005316	-0.000018605
H	-0.000004768	0.000003578	-0.000028334

B-TS-3FA-HT

Zero-point correction= 0.183473 (Hartree/Particle)
Thermal correction to Energy= 0.213208
Thermal correction to Enthalpy= 0.214358
Thermal correction to Gibbs Free Energy= 0.109006
Sum of electronic and zero-point Energies= -2020.276613
Sum of electronic and thermal Energies= -2020.246878
Sum of electronic and thermal Enthalpies= -2020.245728
Sum of electronic and thermal Free Energies= -2020.351079

O	0.000000954	-0.000007977	-0.000005032
H	-0.000000017	-0.000000631	-0.000003637
O	-0.000000955	0.000004837	-0.000002173
C	0.000002605	-0.000014795	-0.000003630
O	0.000002293	-0.000016160	-0.000001429
H	0.000003005	-0.000020661	-0.000005041
O	-0.000000583	0.000002333	-0.000008414
C	-0.000001742	0.000006847	-0.000014289
O	-0.000001752	0.000009089	-0.000014677
H	-0.000002077	0.000009678	-0.000018912
H	-0.000001124	0.000006156	-0.000007434
K	0.000002127	-0.000014238	-0.000003717
S	0.000000014	0.000001635	0.000006865
I	0.000001209	-0.000004282	0.000018425
C	-0.000001692	0.000012495	0.000008227
H	-0.000002412	0.000016477	0.000005356
H	-0.000001918	0.000013191	0.000004834
H	-0.000001713	0.000013872	0.000015033
C	0.000000369	0.000000704	0.000014148
H	0.000001390	-0.000006072	0.000014510
H	-0.000000331	0.000004352	0.000011445
H	0.000000129	0.000003145	0.000020406
O	-0.000000544	0.000001869	-0.000007273
H	-0.000000345	0.000001963	-0.000008072
C	0.000000814	-0.000005884	-0.000006454
O	0.000001564	-0.000011998	-0.000004013
H	0.000000732	-0.000005943	-0.000005052

B1-3FA-HH

Zero-point correction= 0.188762 (Hartree/Particle)
Thermal correction to Energy= 0.219357
Thermal correction to Enthalpy= 0.220507
Thermal correction to Gibbs Free Energy= 0.111962
Sum of electronic and zero-point Energies= -2020.324513
Sum of electronic and thermal Energies= -2020.293918
Sum of electronic and thermal Enthalpies= -2020.292768
Sum of electronic and thermal Free Energies= -2020.401313

O	0.000003507	0.000001092	0.000023500
H	0.000002535	-0.000004116	0.000014889
O	0.000000956	-0.000012905	0.000000767
C	0.000003583	0.000011327	0.000028349
O	0.000002559	0.000014388	0.000022950
H	0.000004677	0.000017005	0.000037995
O	-0.000004659	0.000009781	-0.000026356
C	-0.000004831	0.000007060	-0.000028711
O	-0.000003064	-0.000001967	-0.000020940
H	-0.000006519	0.000011909	-0.000037669
H	-0.000001539	-0.000006340	-0.000012857
K	-0.000002223	0.000026498	-0.000003183
S	0.000000736	-0.000011373	-0.000000056
I	-0.000002352	0.000018064	-0.000007619
C	-0.000000584	-0.000023842	-0.000014050
H	0.000000436	-0.000034641	-0.000012009
H	-0.000002436	-0.000019404	-0.000024323
H	-0.000000569	-0.000024309	-0.000014170
C	0.000003726	-0.000020772	0.000015534
H	0.000004760	-0.000014437	0.000025063
H	0.000004475	-0.000031858	0.000015701
H	0.000003677	-0.000021102	0.000015068
O	-0.000001216	0.000014721	-0.000001716
H	-0.000001983	0.000008967	-0.000009180
C	-0.000001225	0.000025673	0.000002980
O	-0.000002065	0.000028433	-0.000001384
H	-0.000000361	0.000032150	0.000011427

B-TS-3FA-HH

Zero-point correction= 0.182065 (Hartree/Particle)
Thermal correction to Energy= 0.211304
Thermal correction to Enthalpy= 0.212454
Thermal correction to Gibbs Free Energy= 0.108802
Sum of electronic and zero-point Energies= -2020.277520
Sum of electronic and thermal Energies= -2020.248281
Sum of electronic and thermal Enthalpies= -2020.247131
Sum of electronic and thermal Free Energies= -2020.350783

O	0.000022630	-0.000017714	0.000023136
H	-0.001035794	-0.000885950	0.002185876
O	0.000263674	-0.000467329	-0.002540968
C	0.000032621	-0.000014555	0.000018149
O	0.000027177	-0.000007132	0.000007134
H	0.000046725	-0.000020004	0.000023914
O	-0.000005859	0.000021859	-0.000031875
C	-0.000005461	0.000020255	-0.000028765
O	-0.000005159	0.000010048	-0.000014478
H	-0.000006165	0.000027061	-0.000039320
H	-0.000007698	-0.000000138	0.000001306
K	0.000023865	0.000014906	-0.000024969
S	0.000859119	0.001496189	0.000449846
I	-0.000133293	-0.000148468	-0.000081133

C	-0.000041815	0.000005361	-0.000002826
H	-0.000043731	0.000000305	0.000004816
H	-0.000041821	0.000014196	-0.000016003
H	-0.000053262	0.000004037	0.000000438
C	-0.000021254	-0.000012834	0.000021484
H	-0.000007447	-0.000015796	0.000024282
H	-0.000024381	-0.000018329	0.000030027
H	-0.000033706	-0.000011886	0.000021604
O	0.000030061	-0.000001042	-0.000002028
H	0.000017381	0.000003836	-0.000007744
C	0.000044003	0.000000460	-0.000006194
O	0.000042008	0.000007524	-0.000016011
H	0.000057584	-0.000004861	0.000000300

B1-4FA

Zero-point correction= 0.224511 (Hartree/Particle)
Thermal correction to Energy= 0.260988
Thermal correction to Enthalpy= 0.262138
Thermal correction to Gibbs Free Energy= 0.139744
Sum of electronic and zero-point Energies= -2210.093653
Sum of electronic and thermal Energies= -2210.057177
Sum of electronic and thermal Enthalpies= -2210.056027
Sum of electronic and thermal Free Energies= -2210.178421

O	0.000000749	-0.000001181	0.000002711
H	-0.000000526	-0.000001812	0.000001605
O	-0.000003258	-0.000002646	-0.000000572
C	0.000003929	0.000001868	0.000002329
O	0.000003245	0.000003675	-0.000000542
H	0.000005056	0.000002535	0.000003146
O	-0.000000541	-0.000000898	0.000000585
C	-0.000000787	-0.000003079	0.000003417
O	-0.000002151	-0.000005154	0.000004178
H	-0.000000301	-0.000004129	0.000005441
H	-0.000002699	-0.000003979	0.000002285
K	0.000004602	0.000004598	-0.000000442
S	-0.000003505	-0.000000154	-0.000004322
I	0.000000896	0.000007280	-0.000009201
C	-0.000006723	-0.000001748	-0.000006426
H	-0.000008843	-0.000003844	-0.000006335
H	-0.000006196	-0.000002450	-0.000004861
H	-0.000006927	-0.000000106	-0.000009152
C	-0.000004658	0.000000531	-0.000006995
H	-0.000002802	0.000001512	-0.000005872
H	-0.000006949	-0.000001591	-0.000006989
H	-0.000004866	0.000002285	-0.000009767
O	0.000002608	-0.000004367	0.000009691
H	0.000000884	-0.000004990	0.000008363
C	0.000005343	-0.000001495	0.000008992
O	0.000005104	0.000000497	0.000006387
H	0.000007054	-0.000000786	0.000010621
O	0.000002311	0.000002380	-0.000000189

H	0.000001334	0.000001085	0.000000069
C	0.000005300	0.000004399	0.000000154
O	0.000006743	0.000005595	0.000001480
H	0.000006573	0.000006170	0.000000212

B-TS-4FA

Zero-point correction= 0.218217 (Hartree/Particle)
Thermal correction to Energy= 0.253965
Thermal correction to Enthalpy= 0.255115
Thermal correction to Gibbs Free Energy= 0.135500
Sum of electronic and zero-point Energies= -2210.050968
Sum of electronic and thermal Energies= -2210.015220
Sum of electronic and thermal Enthalpies= -2210.014070
Sum of electronic and thermal Free Energies= -2210.133685

O	0.000003121	0.000002159	-0.000000507
H	0.000258058	-0.000406146	0.000207144
O	-0.000575736	0.000411233	-0.000059538
C	0.000009456	0.000003951	0.000002922
O	0.000011310	0.000003142	0.000006284
H	0.000013574	0.000006515	0.000002794
O	-0.000002057	0.000001371	-0.000004503
C	-0.000006060	0.000002368	-0.000010360
O	-0.000008447	0.000001653	-0.000011588
H	-0.000007644	0.000003987	-0.000014804
H	-0.000007061	-0.000001568	-0.000004601
K	0.000011581	0.000006333	0.000001062
S	0.000801538	-0.000041877	-0.000445570
I	-0.000490765	0.000018084	0.000323150
C	-0.000011313	-0.000010601	0.000006613
H	-0.000015125	-0.000011259	0.000003809
H	-0.000011541	-0.000008855	0.000003356
H	-0.000012181	-0.000014156	0.000011857
C	-0.000002404	-0.000009580	0.000014096
H	0.000003123	-0.000007374	0.000015981
H	-0.000005828	-0.000009970	0.000011197
H	-0.000004393	-0.000013365	0.000018555
O	-0.000001578	0.000008821	-0.000016901
H	-0.000004141	0.000006456	-0.000015447
C	0.000005386	0.000011663	-0.000014549
O	0.000008393	0.000011502	-0.000011215
H	0.000008258	0.000014197	-0.000015996
O	0.000001443	0.000002207	-0.000002324
H	0.000000027	0.000001946	-0.000003339
C	0.000008359	0.000004944	0.000000108
O	0.000012742	0.000006973	0.000001127
H	0.000009906	0.000005247	0.000001188

B1-4FAbis

Zero-point correction= 0.224152 (Hartree/Particle)
Thermal correction to Energy= 0.261023
Thermal correction to Enthalpy= 0.262173

Thermal correction to Gibbs Free Energy= 0.136742
Sum of electronic and zero-point Energies= -2210.088814
Sum of electronic and thermal Energies= -2210.051944
Sum of electronic and thermal Enthalpies= -2210.050794
Sum of electronic and thermal Free Energies= -2210.176224

O	-0.000005378	0.000002571	-0.000006610
H	-0.000002768	0.000002065	-0.000005738
O	0.000001400	0.000001062	-0.000004399
C	-0.000007302	0.000001864	-0.000003721
O	-0.000006576	0.000001047	-0.000000560
H	-0.000010232	0.000002511	-0.000004560
O	0.000005410	-0.000000667	-0.000000090
C	0.000007118	0.000000041	-0.000003093
O	0.000005095	0.000001229	-0.000006060
H	0.000008023	0.000000186	-0.000003705
H	0.000003998	0.000001308	-0.000005252
K	-0.000001358	-0.000000785	0.000003263
S	0.000001372	0.000000010	-0.000000400
I	0.000000298	-0.000003230	0.000010587
C	0.000005908	-0.000000732	0.000000227
H	0.000006476	-0.000000180	-0.000001851
H	0.000007977	-0.000000905	-0.000000001
H	0.000005978	-0.000001559	0.000002946
C	-0.000001391	0.000000209	-0.000000181
H	-0.000004296	0.000000704	-0.000000713
H	-0.000000399	0.000000705	-0.000002189
H	-0.000001293	-0.000000608	0.000002551
O	-0.000000506	0.000002920	-0.000009241
H	0.000001632	0.000002314	-0.000008415
C	-0.000002790	0.000002108	-0.000006479
O	-0.000001829	0.000001259	-0.000003143
H	-0.000005194	0.000002759	-0.000007193
O	-0.000002646	-0.000004344	0.000015277
H	-0.000005288	-0.000003858	0.000014939
C	-0.000001056	-0.000003517	0.000012119
O	-0.000002419	-0.000002477	0.000009224
H	0.000002036	-0.000004012	0.000012461

B-TS-4FAbis

Zero-point correction= 0.219222 (Hartree/Particle)
Thermal correction to Energy= 0.255202
Thermal correction to Enthalpy= 0.256352
Thermal correction to Gibbs Free Energy= 0.136117
Sum of electronic and zero-point Energies= -2210.040713
Sum of electronic and thermal Energies= -2210.004733
Sum of electronic and thermal Enthalpies= -2210.003583
Sum of electronic and thermal Free Energies= -2210.123817

O	0.000005860	-0.000008436	0.000008564
H	0.000000063	-0.000004799	0.000008090
O	-0.000003682	-0.000002080	0.000007289

C	0.000006903	-0.000006712	0.000003980
O	0.000008853	-0.000004809	-0.000000331
H	0.000012785	-0.000010228	0.000004599
O	-0.000005514	0.000004252	-0.000001390
C	-0.000007911	0.000002935	0.000002632
O	-0.000006967	-0.000000142	0.000006986
H	-0.000008607	0.000003543	0.000002620
H	-0.000005161	-0.000001344	0.000007305
K	0.000004218	0.000000793	-0.000005520
S	-0.000003417	0.000001551	0.000000862
I	-0.000002511	0.000006600	-0.000008706
C	-0.000010424	0.000004559	0.000002601
H	-0.000011707	0.000002854	0.000006767
H	-0.000011796	0.000006392	0.000000906
H	-0.000011541	0.000006113	0.000001117
C	-0.000001634	-0.000000890	0.000003095
H	0.000002542	-0.000002355	0.000001496
H	-0.000002586	-0.000002768	0.000007251
H	-0.000003631	0.000001101	0.000001743
O	0.000000621	-0.000006919	0.000011131
H	-0.000002566	-0.000004193	0.000009669
C	0.000004397	-0.000006833	0.000007326
O	0.000005225	-0.000004773	0.000002817
H	0.000008152	-0.000010034	0.000008952
O	0.000010436	0.000007991	-0.000023644
H	0.000013124	0.000006208	-0.000023669
C	0.000005457	0.000007749	-0.000019420
O	0.000007951	0.000004951	-0.000015729
H	0.000003071	0.000009722	-0.000019389

C2-3FA-FA

Zero-point correction= 0.187889 (Hartree/Particle)
Thermal correction to Energy= 0.225661
Thermal correction to Enthalpy= 0.226811
Thermal correction to Gibbs Free Energy= 0.095733
Sum of electronic and zero-point Energies= -2918.159479
Sum of electronic and thermal Energies= -2918.121707
Sum of electronic and thermal Enthalpies= -2918.120557
Sum of electronic and thermal Free Energies= -2918.251635

O	-0.000005214	0.000000977	-0.000004190
H	-0.000007745	0.000001355	-0.000005829
O	-0.000012227	0.000001171	-0.000007558
C	-0.000000934	-0.000001085	0.000001781
O	-0.000000354	-0.000002610	0.000004530
H	0.000001899	-0.000001515	0.000003634
K	0.000011944	0.000002221	0.000001105
S	-0.000009529	-0.000001770	-0.000001010
I	0.000003568	-0.000006482	0.000013670
C	-0.000014137	-0.000001739	-0.000002997
H	-0.000020077	-0.000002280	-0.000004621
H	-0.000011213	0.000001097	-0.000006969

H	-0.000013368	-0.000004034	0.000001696
C	-0.000015549	-0.000006230	0.000004722
H	-0.000013746	-0.000006305	0.000005749
H	-0.000021402	-0.000006359	0.000002424
H	-0.000014773	-0.000008534	0.000009429
I	0.000003076	0.000009110	-0.000015610
H	-0.000008375	0.000003804	-0.000010829
O	0.000017385	-0.000003203	0.000013049
C	0.000024681	-0.000001125	0.000014253
O	0.000025667	0.000001512	0.000007897
H	0.000028539	-0.000002482	0.000017105
K	0.000004737	-0.000008614	0.000018211
O	0.000005265	0.000009312	-0.000014526
H	0.000002070	0.000006726	-0.000011571
C	0.000012399	0.000009151	-0.000012401
O	0.000011970	0.000006012	-0.000005707
H	0.000015444	0.000011920	-0.000015436

C-TS2-3FA-FA

Zero-point correction= 0.184244 (Hartree/Particle)
Thermal correction to Energy= 0.220361
Thermal correction to Enthalpy= 0.221511
Thermal correction to Gibbs Free Energy= 0.098214
Sum of electronic and zero-point Energies= -2918.128302
Sum of electronic and thermal Energies= -2918.092185
Sum of electronic and thermal Enthalpies= -2918.091035
Sum of electronic and thermal Free Energies= -2918.214332

O	0.000001854	-0.000010161	0.000006529
H	-0.000000800	-0.000007953	-0.000000981
O	-0.000003426	-0.000005987	-0.000008451
C	0.000003851	-0.000009029	0.000012152
O	0.000003528	-0.000005994	0.000010418
H	0.000006276	-0.000010998	0.000018846
K	0.000003824	0.000013559	0.000008457
S	-0.000003670	-0.000003851	-0.000009584
I	-0.000003323	-0.000000207	-0.000009012
C	-0.000007861	-0.000002384	-0.000021195
H	-0.000008674	-0.000004520	-0.000023103
H	-0.000008018	0.000004926	-0.000022702
H	-0.000009212	-0.000006636	-0.000024265
C	-0.000003986	-0.000016204	-0.000008486
H	-0.000001561	-0.000017950	-0.000001554
H	-0.000005292	-0.000019335	-0.000011608
H	-0.000005240	-0.000018271	-0.000011631
I	-0.000002731	0.000018938	-0.000010376
H	-0.000003404	0.000000179	-0.000009329
O	0.000006271	0.000010287	0.000015747
C	0.000005308	0.000017321	0.000011990
O	0.000004347	0.000023542	0.000008241
H	0.000005717	0.000018652	0.000012860
K	0.000004786	-0.000007379	0.000014248

O	0.000002971	0.000003369	0.000007632
H	0.000002793	-0.000001925	0.000007940
C	0.000004754	0.000010632	0.000011338
O	0.000005991	0.000010708	0.000014864
H	0.000004926	0.000016672	0.000011011

C2-3FA-I

```
Zero-point correction=                           0.188686 (Hartree/Particle)
Thermal correction to Energy=                    0.225783
Thermal correction to Enthalpy=                  0.226933
Thermal correction to Gibbs Free Energy=         0.100201
Sum of electronic and zero-point Energies=          -2918.159780
Sum of electronic and thermal Energies=             -2918.122683
Sum of electronic and thermal Enthalpies=           -2918.121533
Sum of electronic and thermal Free Energies=        -2918.248265
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O	0.000011011	0.000006505	0.000000073
H	0.000004075	0.000007610	-0.000000266
O	-0.000010513	0.000008287	-0.000000972
C	0.000013668	-0.000000962	0.000000590
O	0.000008151	-0.000005737	0.000000829
H	0.000021460	-0.000002324	0.000001090
K	0.000004238	-0.000000397	0.000000210
S	-0.000014933	-0.000001098	-0.000000581
I	-0.000012632	-0.000021479	0.000000792
C	-0.000027611	0.000000464	-0.000001286
H	-0.000029670	0.000001889	-0.000001456
H	-0.000029529	0.000006593	-0.000001742
H	-0.000031049	-0.000006148	-0.000001004
C	-0.000012873	-0.000009628	0.000000030
H	-0.000005071	-0.000010625	0.000000440
H	-0.000016085	-0.000006836	-0.000000299
H	-0.000016393	-0.000016409	0.000000290
I	-0.000010884	0.000020406	-0.000001764
H	-0.000009805	0.000013434	-0.000001296
O	0.000017687	-0.000016061	0.000001730
C	0.000017500	-0.000015319	0.000001874
O	0.000012863	-0.000009179	0.000001122
H	0.000021730	-0.000020731	0.000002269
K	0.000010548	-0.000024568	0.000002003
O	0.000013202	0.000025929	-0.000001004
H	0.000006798	0.000024459	-0.000001235
C	0.000019538	0.000019042	-0.000000235
O	0.000017919	0.000012204	-0.000000080
H	0.000026661	0.000020679	-0.000000120

C-TS2-3FA-I

```
Zero-point correction=                           0.183330 (Hartree/Particle)
Thermal correction to Energy=                    0.219784
Thermal correction to Enthalpy=                  0.220934
Thermal correction to Gibbs Free Energy=         0.096644
Sum of electronic and zero-point Energies=          -2918.129257
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Sum of electronic and thermal Energies= -2918.092804
Sum of electronic and thermal Enthalpies= -2918.091654
Sum of electronic and thermal Free Energies= -2918.215944

O	0.000010384	-0.000011090	0.000011221
H	0.000005705	-0.000007921	0.000004216
O	0.000001496	-0.000006697	-0.000003280
C	0.000009095	-0.000009552	0.000014395
O	0.000006514	-0.000006080	0.000007668
H	0.000014070	-0.000011678	0.000020256
K	-0.000002988	0.000014360	0.000008132
S	-0.000002912	-0.000004329	-0.000011934
I	-0.000008567	-0.000000695	-0.000020487
C	-0.000008151	-0.000003151	-0.000022213
H	-0.000006553	-0.000004710	-0.000020175
H	-0.000012144	0.000004404	-0.000023637
H	-0.000008514	-0.000008347	-0.000028614
C	0.000002042	-0.000017392	-0.000013328
H	0.000005629	-0.000019041	-0.000006891
H	0.000003313	-0.000020623	-0.000013850
H	0.000000289	-0.000019844	-0.000020104
I	-0.000010447	0.000021093	-0.000002351
H	-0.000000832	0.000000105	-0.000001600
O	-0.000001969	0.000010397	0.000006312
C	-0.000006963	0.000018377	0.000002941
O	-0.000010158	0.000024735	0.000002315
H	-0.000008576	0.000019330	0.000000291
K	0.000004447	-0.000008116	0.000001936
O	0.000003927	0.000009055	0.000018337
H	-0.000000132	0.000012673	0.000012980
C	0.000006396	0.000008318	0.000024291
O	0.000004653	0.000011926	0.000022990
H	0.000010949	0.000004491	0.000030186

C2-4FA-I-I

Zero-point correction= 0.224595 (Hartree/Particle)
Thermal correction to Energy= 0.267675
Thermal correction to Enthalpy= 0.268825
Thermal correction to Gibbs Free Energy= 0.126435
Sum of electronic and zero-point Energies= -3107.924094
Sum of electronic and thermal Energies= -3107.881014
Sum of electronic and thermal Enthalpies= -3107.879864
Sum of electronic and thermal Free Energies= -3108.022254

O	0.000001808	0.000013990	0.000000397
H	0.000001093	0.000011012	0.000004102
O	-0.000000194	0.000003683	0.000010440
C	0.000001880	0.000011012	-0.000005319
O	0.000001148	0.000005632	-0.000005278
H	0.000002567	0.000014179	-0.000009489
K	0.000000026	-0.000005455	-0.000009318
S	-0.000000765	-0.000000264	0.000008692

I	-0.000001133	-0.000009094	-0.000000715
C	-0.000001787	-0.000004076	0.000016333
H	-0.000001593	-0.000000408	0.000020333
H	-0.000002404	-0.000007974	0.000017143
H	-0.000001997	-0.000006266	0.000015654
C	0.000000224	0.000006643	0.000008738
H	0.000000897	0.000009656	0.000004363
H	0.000000201	0.000009405	0.000013352
H	-0.000000056	0.000004656	0.000008309
I	-0.000001847	-0.000009435	0.000007666
H	-0.000000667	0.000000580	0.000009634
O	0.000000354	-0.000007892	-0.000016891
C	-0.000000864	-0.000014342	-0.000018399
O	-0.000000856	-0.000016850	-0.000014275
H	-0.000000641	-0.000017054	-0.000020486
K	0.000000981	0.000000359	-0.000012620
O	0.000000652	0.000007398	0.000004439
H	-0.000000023	0.000002891	0.000005194
C	0.000001118	0.000008683	-0.000001829
O	0.000001363	0.000005564	-0.000006332
H	0.000002035	0.000013699	-0.000002646
O	-0.000000378	-0.000004881	-0.000001817
H	-0.000000944	-0.000006468	0.000000647
C	-0.000000373	-0.000006039	-0.000008064
O	-0.000000156	-0.000008398	-0.000011014
H	0.000000332	-0.000004146	-0.000010944

C-TS2-4FA-I-I

Zero-point correction= 0.219833 (Hartree/Particle)
Thermal correction to Energy= 0.261740
Thermal correction to Enthalpy= 0.262890
Thermal correction to Gibbs Free Energy= 0.127591
Sum of electronic and zero-point Energies= -3107.894741
Sum of electronic and thermal Energies= -3107.852834
Sum of electronic and thermal Enthalpies= -3107.851683
Sum of electronic and thermal Free Energies= -3107.986982

O	0.000006517	0.000001532	-0.000000375
H	0.000001174	0.000001041	0.000000648
O	-0.000003890	-0.000000427	0.000000569
C	0.000008747	-0.000001283	-0.000000900
O	0.000007676	-0.000002789	-0.000003756
H	0.000013906	0.000000264	-0.000001849
K	0.000002591	0.000000977	0.000000416
S	-0.000004737	-0.000005853	-0.000004082
I	-0.000006074	-0.000013398	-0.000008975
C	-0.000012628	-0.000006404	-0.000002999
H	-0.000013170	-0.000003883	-0.000001046
H	-0.000014965	-0.000005650	-0.000002105
H	-0.000013882	-0.000009857	-0.000005389
C	-0.000002253	-0.000008721	-0.000006142
H	0.000002344	-0.000008595	-0.000006695

H	-0.000003195	-0.000006754	-0.000004548
H	-0.000004053	-0.000012233	-0.000008495
I	-0.000010438	0.000005460	0.000005525
H	-0.000005418	0.000002211	0.000002227
O	0.000006654	-0.000006980	-0.000006454
C	0.000002878	-0.000006967	-0.000005165
O	-0.000002038	-0.000005671	-0.000003999
H	0.000002906	-0.000010077	-0.000007867
K	0.000009709	-0.000010599	-0.000009141
O	0.000001188	0.000011011	0.000007953
H	-0.000001840	0.000009539	0.000007338
C	0.000006194	0.000009998	0.000006747
O	0.000007242	0.000008125	0.000004886
H	0.000009518	0.000011735	0.000007349
O	-0.000000298	0.000014616	0.000010917
H	-0.000003274	0.000012169	0.000009508
C	0.000003245	0.000012923	0.000009074
O	0.000003014	0.000008994	0.000006253
H	0.000006650	0.000015548	0.000010571

C2-4FA-I-FA

Zero-point correction= 0.224595 (Hartree/Particle)
Thermal correction to Energy= 0.267675
Thermal correction to Enthalpy= 0.268825
Thermal correction to Gibbs Free Energy= 0.126435
Sum of electronic and zero-point Energies= -3107.924094
Sum of electronic and thermal Energies= -3107.881014
Sum of electronic and thermal Enthalpies= -3107.879864
Sum of electronic and thermal Free Energies= -3108.022254

O	0.000001808	0.000013990	0.000000397
H	0.000001093	0.000011012	0.000004102
O	-0.000000194	0.000003683	0.000010440
C	0.000001880	0.000011012	-0.000005319
O	0.000001148	0.000005632	-0.000005278
H	0.000002567	0.000014179	-0.000009489
K	0.000000026	-0.000005455	-0.000009318
S	-0.000000765	-0.000000264	0.000008692
I	-0.000001133	-0.000009094	-0.000000715
C	-0.000001787	-0.000004076	0.000016333
H	-0.000001593	-0.000000408	0.000020333
H	-0.000002404	-0.000007974	0.000017143
H	-0.000001997	-0.000006266	0.000015654
C	0.000000224	0.000006643	0.000008738
H	0.000000897	0.000009656	0.000004363
H	0.000000201	0.000009405	0.000013352
H	-0.000000056	0.000004656	0.000008309
I	-0.000001847	-0.000009435	0.000007666
H	-0.000000667	0.000000580	0.000009634
O	0.000000354	-0.000007892	-0.000016891
C	-0.000000864	-0.000014342	-0.000018399
O	-0.000000856	-0.000016850	-0.000014275

H	-0.000000641	-0.000017054	-0.000020486
K	0.000000981	0.000000359	-0.000012620
O	0.000000652	0.000007398	0.000004439
H	-0.000000023	0.000002891	0.000005194
C	0.000001118	0.000008683	-0.000001829
O	0.000001363	0.000005564	-0.000006332
H	0.000002035	0.000013699	-0.000002646
O	-0.000000378	-0.000004881	-0.000001817
H	-0.000000944	-0.000006468	0.000000647
C	-0.000000373	-0.000006039	-0.000008064
O	-0.000000156	-0.000008398	-0.000011014
H	0.000000332	-0.000004146	-0.000010944

C-TS2-4FA-I-FA

Zero-point correction= 0.219852 (Hartree/Particle)
Thermal correction to Energy= 0.261842
Thermal correction to Enthalpy= 0.262992
Thermal correction to Gibbs Free Energy= 0.126128
Sum of electronic and zero-point Energies= -3107.894830
Sum of electronic and thermal Energies= -3107.852840
Sum of electronic and thermal Enthalpies= -3107.851690
Sum of electronic and thermal Free Energies= -3107.988554

O	-0.000000819	-0.000005509	-0.000001219
H	-0.000002181	-0.000003942	-0.000002893
O	-0.000003796	-0.000002204	-0.000004575
C	0.000001390	-0.000006050	0.000001339
O	0.000002058	-0.000005191	0.000002141
H	0.000002792	-0.000007361	0.000002846
K	0.000003129	0.000002586	0.000003883
S	-0.000002607	-0.000002716	-0.000003400
I	-0.000000784	-0.000003495	-0.000001053
C	-0.000005556	-0.000000798	-0.000006660
H	-0.000006788	-0.000000496	-0.000008096
H	-0.000005252	0.000001926	-0.000006122
H	-0.000006307	-0.000002746	-0.000007626
C	-0.000003286	-0.000007691	-0.000004304
H	-0.000001631	-0.000009102	-0.000002439
H	-0.000004797	-0.000007894	-0.000006147
H	-0.000003683	-0.000008881	-0.000004874
I	-0.000002690	0.000007818	-0.000002767
H	-0.000003615	0.000000466	-0.000004246
O	0.000005987	-0.000000749	0.000007513
C	0.000005051	0.000001448	0.000005636
O	0.000004233	0.000004894	0.000005294
H	0.000006284	0.000001684	0.000007584
K	0.000004548	-0.000007627	0.000005013
O	-0.000001216	0.000000528	-0.000001419
H	-0.000001020	-0.000001983	-0.000001325
C	0.000000465	0.000002563	0.000000797
O	0.000002318	0.000001952	0.000002816
H	0.000000319	0.000005412	0.000000661

O	0.000002049	0.000011503	0.000003041
H	0.000000785	0.000010721	0.000001496
C	0.000004135	0.000010531	0.000005664
O	0.000004870	0.000008981	0.000006176
H	0.000005615	0.000011422	0.000007264