SUPPORTING INFORMATION

ORGANOCATALYTIC CS_2 INSERTION INTO EPOXIDES IN NEAT CONDITIONS: A STRAIGHTFORWARD APPROACH FOR THE EFFICIENT SYNTHESIS OF DI- AND TRI-THIOCARBONATES

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1. GENERAL CONSIDERATIONS:

All commercially available reagents and solvents were used without further purification excepting cyclohexene oxide **1e**, which was distilled under reduced pressure. Choline chloride (*ChCl*) and tetrabutylammonium chloride (TBACl) were dried under high vacuum before being used. α-Methylstyrene oxide **1d** was prepared from the reaction of acetophenone and trimethylsulfoxonium oxide.[1] (1*R**,2*R**,6*S**)-7-Oxabicyclo[4.1.0]heptan-2-ol (**1f**) was obtained upon reaction of *m*CPBA with 2-cyclohexen-1-ol.[2] *O*-Benzyl-(1*S**,2*R**,6*S**)-7-oxabicyclo[4.1.0]heptan-2-ol (**1g**) was obtained by benzylation of **1f** employing benzyl bromide and sodium hydride.[3] Furfuryl glycidyl ether (**1h**) was obtained from the nucleophilic attack of furfuryl alcohol to epichlorohydrin.[4]

Flash chromatography of reaction products was carried out using Silica gel 60, particle size 400-630 micron (VWR). Analytical thin layer chromatography (TLC) was performed on DC-Alufolien Kieselgel Silica Gel 60 F254 0.2 mm plates (Merck) and compounds were visualized by UV fluorescence or using either $KMnO_4$ or vanillin stains followed by heating.

^{1}H-NMR and proton-decoupled ^{13}C-NMR spectra were obtained using a Bruker AV-300 (^{1}H, 300.13 MHz and ^{13}C, 75.5 MHz) spectrometer using the δ scale (ppm) for chemical shifts. Calibration was made on the residual signal of the solvent (^{13}C: $CDCl_3$, 77.16 ppm; ^{1}H: $CDCl_3$, 7.26 ppm).[5] Coupling constants (*J*-values) are given in hertzs (Hz). The DEPT-135 technique was used to assign methylene (CH_2) signals. Chemical shifts are reported as follows: value (description of absorption, coupling constant(s) where applicable, number of protons).

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[1] K. Zhang, B.-H. Ren, X.-F. Liu, L.-L. Wang, M. Zhang, W.-M. Ren, X.-B. Lu, W.-Z. Zhang, *Angew. Chem. Int. Ed.*, 2022, **61**, e202207660.

[2] I. Fujimori, T. Mita, K. Maki, M. Shiro, A. Sato, S. Furusho, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.*, 2006, **128**, 16438.

[3] A. M. Al-Etaibi, N. A. Al-Awadi, M. R. Ibrahim, Y. A. Ibrahim, *Molecules,* 2010, **15**, 407.

[4] C. G. de Almeida, S. G. Reis, A. M. de Almeida, C. G. Diniz, V. L. da Silva, M. Le Hyaric, *Chem. Biol. Drug. Des.*, 2011, **78**, 876.

[5] H. E. Gojlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512.

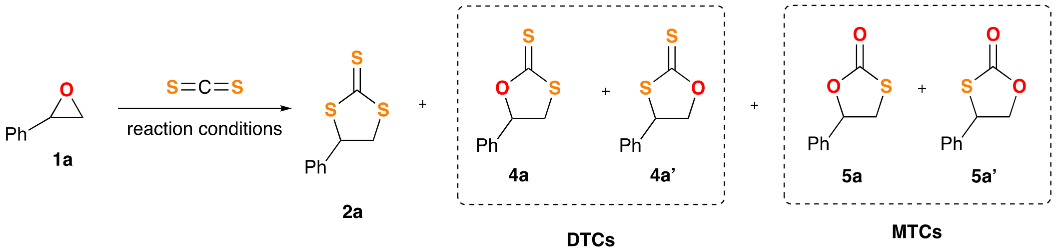
High resolution mass spectra (HRMS) experiments were carried out by ESI^+ using a Micro TOF Q spectrometer. IR spectra were recorded using NaCl plates or KBr pellets.

Optical rotations were measured using a Perkin-Elmer 241 polarimeter.

High-performance liquid chromatography (HPLC) analyses were carried out for the measurement of enantiomeric excesses (see Section 7), using a Hewlett Packard 1100 LC liquid chromatograph.

2. OPTIMISATION OF THE EXPERIMENTAL PROCEDURES:

Styrene oxide **1a** was adopted as the model substrate. It was treated with CS_2 and subjected to different reactions conditions. Conversion of **1a** into tri-thiocarbonate **2a**, di-thiocarbonates (**4a** and **4a'**), and mono-thiocarbonates (**5a** and **5a'**) was inferred by ^{1}H-NMR spectroscopy from crude reactions mixtures.



The following characteristic ^{1}H-NMR resonance signals were considered:

2a: 4.17 ppm (dd, J = 12.0, 10.3 Hz, 1H).[6]

4a: 6.07 ppm (dd, J = 9.8, 6.7 Hz, 1H).[7]

4a': 5.23 ppm (t, J = 6.8 Hz, 1H).[7]

5a: 3.58 ppm (dd, J = 11.2, 9.5 Hz, 1H).[8]

5a': 5.18 ppm (t, J = 7.4 Hz, 1H).[9]

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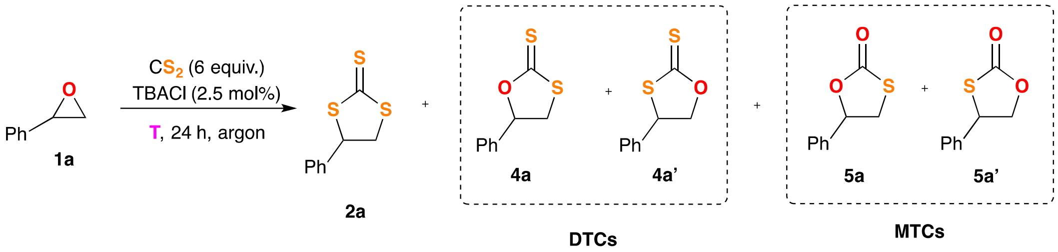
[6] C. Mei, X. Li, L. Liu, C. Cao, G. Pang, Y. Shi, *Tetrahedron*, 2017, **73**, 5706.

[7] J. Diebler, A. Spannenberg, T. Werner, *Org. Biomol. Chem.*, 2016,**14**, 7480.

[8] Y. Nishiyama, C. Katahira, N. Sonoda, *Tetrahedron,* 2006, **62**, 5803.

[9] W. Mahy, S. Cabezas-Hayes, G. Kociok-Köhn, C. G. Frost, *Eur. J. Org. Chem.*, 2017, **2017**, 6441.

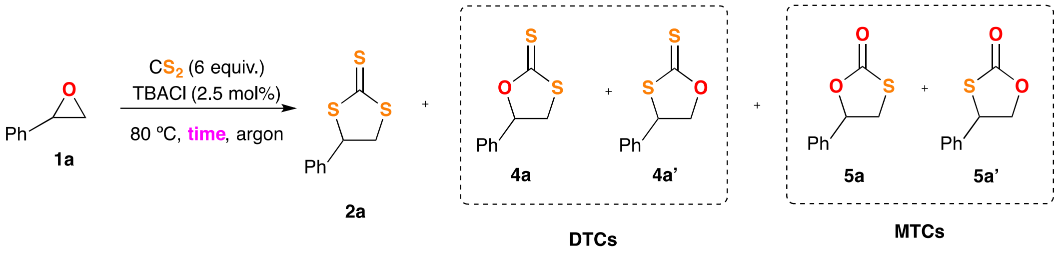
Table SI_1. Influence of temperature on the insertion of CS_2 into epoxide **1a**.[a]



entry	T (°C)	**2a** (%)[b]	**4a** (%)[b]	**4a'** (%)[b]	**5a** (%)[b]	**5a'** (%)[b]
1	40	18	0	0	0	0
2	50	66	0	0	21	0
3	60	74	1	0	7	2
4	80	88	0	0	9	2
5	90	84	0	0	8	1

[a] General conditions: styrene oxide **1a** (100 µL, 106 mg, 0.88 mmol) was dissolved in CS_2 (6 equiv., 0.32 mL, 402 mg, 5.28 mmol) and treated with dry TBACl (6.0 mg, 22 µmol). The mixture was stirred at the stated temperature for 24 h, inside a 10 mL sealed tube under an argon atmosphere. [b] Conversion of styrene oxide into the stated product was determined by ^1H NMR spectroscopy from crude reaction mixtures, using $CHBr_3$ (40 µL, 0.457 mmol) as an analytical internal standard.

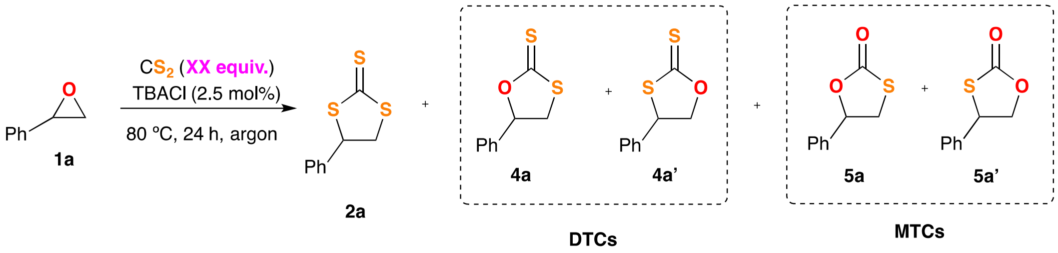
Table SI_2. Influence of reaction time on the insertion of CS_2 into epoxide **1a**.[a]



entry	t (h)	**2a** (%)[b]	**4a** (%)[b]	**4a'** (%)[b]	**5a** (%)[b]	**5a'** (%)[b]
1	6	76	2	0	9	2
2	24	88	0	0	9	2
3	48	87	0	0	8	2

[a] General conditions: styrene oxide **1a** (100 µL, 106 mg, 0.88 mmol) was dissolved in CS_2 (6 equiv., 0.32 mL, 402 mg, 5.28 mmol) and treated with dry TBACl (6.0 mg, 22 µmol). The mixture was stirred at 80 ºC for the stated time, inside a 10 mL sealed tube under an argon atmosphere. [b] Conversion of styrene oxide into the stated product was determined by ^{1}H NMR spectroscopy from crude reaction mixtures, using $CHBr_3$ (40 µL, 0.457 mmol) as an analytical internal standard.

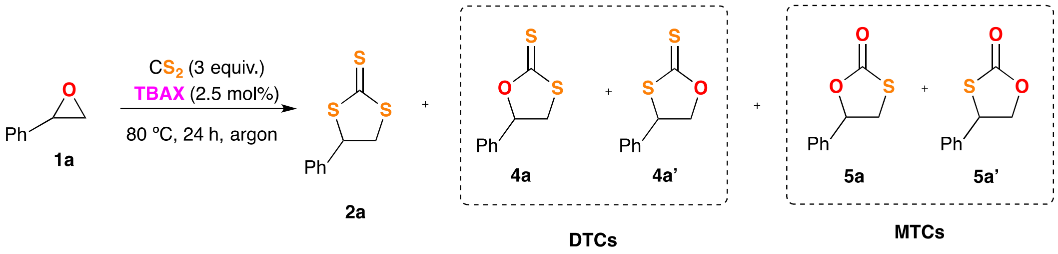
Table SI_3. Influence of the equivalents of CS_2 on the insertion of CS_2 into epoxide **1a**.[a]



entry	equiv. CS_2	**2a** (%)[b]	**4a** (%)[b]	**4a'** (%)[b]	**5a** (%)[b]	**5a'** (%)[b]
1	6	88	0	0	9	2
2	3	85	0	0	7	1

[a] General conditions: styrene oxide **1a** (100 µL, 106 mg, 0.88 mmol) was dissolved in the indicated amount of CS_2 and treated with dry TBACl (6.0 mg, 22 µmol). The mixture was stirred at 80 ºC for 24 h inside a 10 mL sealed tube under an argon atmosphere. [b] Conversion of styrene oxide into the stated product was determined by ^1H NMR spectroscopy from crude reaction mixtures, using $CHBr_3$ (40 µL, 0.457 mmol) as an analytical internal standard.

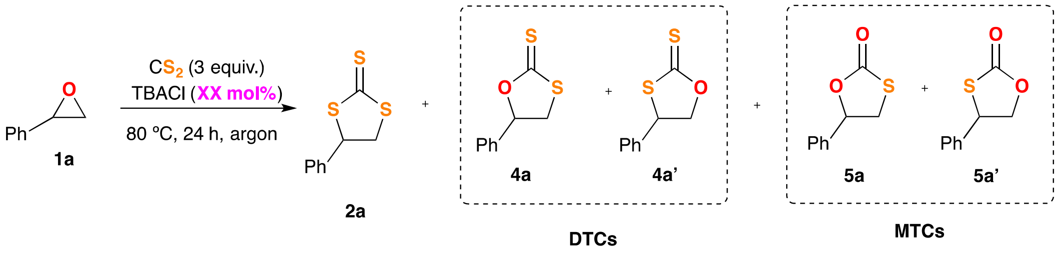
Table SI_4. Influence of the nature of salts TBAX on the insertion of CS_2 into epoxide **1a**.[a]



entry	X	**2a** (%)[b]	**4a** (%)[b]	**4a'** (%)[b]	**5a** (%)[b]	**5a'** (%)[b]
1[c]	--	0	0	0	0	0
2	Cl	85	0	0	7	1
3	Br	72	0	0	9	0
4	I	65	0	0	9	0

[a] General conditions: styrene oxide **1a** (100 µL, 106 mg, 0.88 mmol) was dissolved in CS_2 (3 equiv., 0.16 mL, 201 mg, 2.64 mmol) and treated with the indicated dry salt TBAX (22 µmol). The mixture was stirred at 80 °C for 24 h inside a 10 mL sealed tube under an argon atmosphere. [b] Conversion of styrene oxide into the stated product was determined by ^1H NMR spectroscopy from crude reaction mixtures, using $CHBr_3$ (40 µL, 0.457 mmol) as an analytical internal standard. [c] Blank experiment without the participation of the halide catalyst.

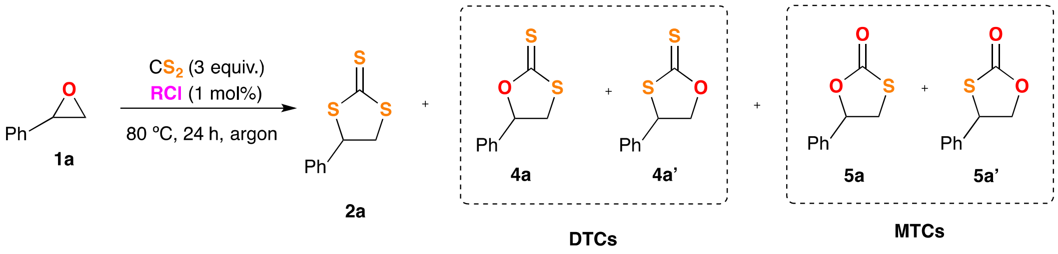
Table SI_5. Influence of the catalytic charge of TBACl on the insertion of CS_2 into epoxide **1a**.[a]

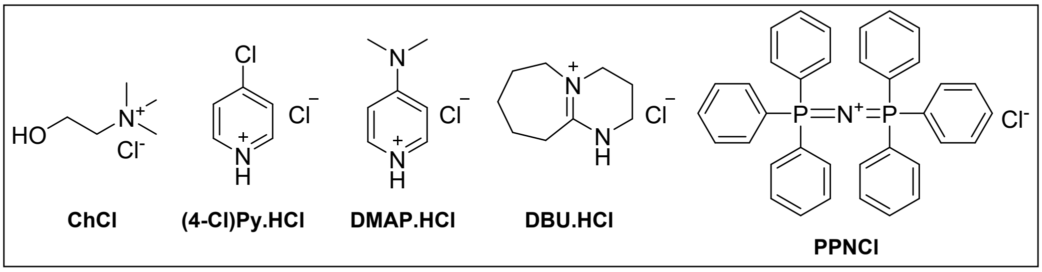


entry	TBACl mol %	**2a** (%)[b]	**4a** (%)[b]	**4a'** (%)[b]	**5a** (%)[b]	**5a'** (%)[b]
1	1	88	0	0	5	1
2	2.5	85	0	0	7	1
3	5	89	0	0	9	1

[a] General conditions: styrene oxide **1a** (100 µL, 106 mg, 0.88 mmol) was dissolved in CS_2 (3 equiv., 0.16 mL, 201 mg, 2.64 mmol) and treated with the stated catalytic amount of dry TBACl. The mixture was stirred at 80 ºC for 24 h inside a 10 mL sealed tube under an argon atmosphere. [b] Conversion of styrene oxide into the stated product was determined by ^1H NMR spectroscopy from crude reaction mixtures, using $CHBr_3$ (40 µL, 0.457 mmol) as an analytical internal standard.

Table SI_6. Influence of the nature of the cation of chloride salts of general form RCl on the insertion of CS_2 into epoxide **1a**.[a]



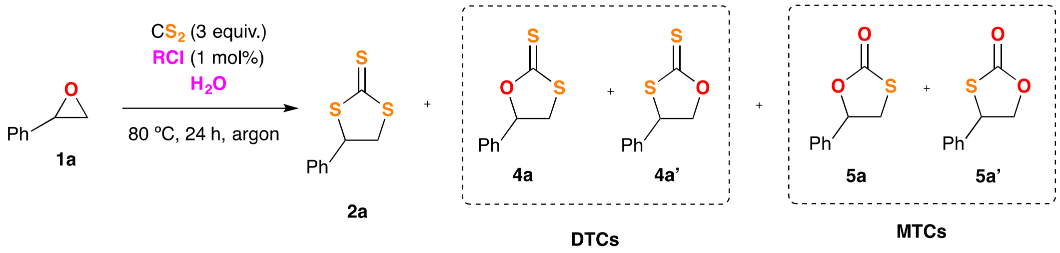


entry	RCl	**2a** (%)[b]	**4a** (%)[b]	**4a'** (%)[b]	**5a** (%)[b]	**5a'** (%)[b]
1	TBACl	88	0	0	5	1
2	NaCl	0	0	0	0	0
3	LiCl	4	17	6	0	0
4	NH_4Cl	0	0	0	0	0
5	NMe_4Cl	4	6	0	0	0
6	*ChCl*	51	1	0	6	2
7	(4-Cl)Py·HCl	0	0	0	0	0
8	DMAP·HCl	45	0	0	7	2
9	DBU·HCl	50	0	0	11	4
10	PPNCl	58	10	7	0	0

[a] General conditions: styrene oxide **1a** (100 µL, 106 mg, 0.88 mmol) was dissolved in CS_2 (3 equiv., 0.16 mL, 201 mg, 2.64 mmol) and treated with a dry chloride salt RCl (1 mol%). The mixture was stirred at 80 ºC for 24 h inside a 10 mL sealed tube under an argon atmosphere. [b] Conversion of styrene oxide into the stated product was determined by ^1H NMR spectroscopy from crude reaction mixtures, using $CHBr_3$ (40 µL, 0.457 mmol) as an analytical internal standard.

Entry 6 indicates that, upon individual optimization, the salt *ChCl* might become an optimum catalyst for the insertion of CS_2 into epoxide **1a**. Moreover, this salt is particularly interesting, as is rather cheap, non-toxic, and participates in the formation of most of the deep eutectic solvents reported.

Table SI_7. Influence of the presence of water on the insertion of CS_2 into epoxide **1a**.[a]

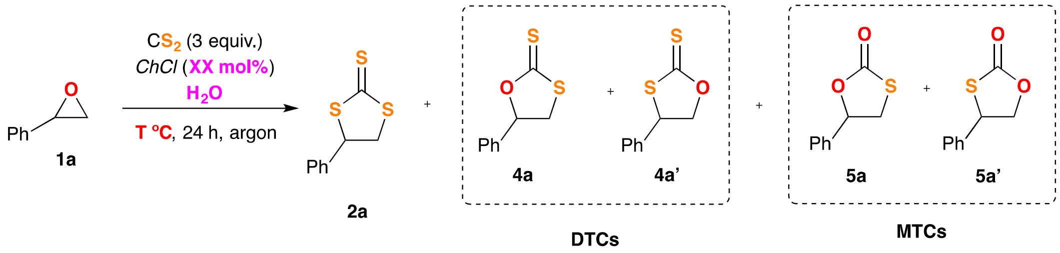


entry	RCl	equiv. H_2O	**2a** (%)[b]	**4a** (%)[b]	**4a'** (%)[b]	**5a** (%)[b]	**5a'** (%)[b]
1	TBACl	--	88	0	0	5	1
2	TBACl	1	88	0	0	6	0
3	*ChCl*	--	51	1	0	6	2
4	*ChCl*	1	55	1	0	4	1

[a] General conditions: styrene oxide **1a** (100 µL, 106 mg, 0.88 mmol) was dissolved in CS_2 (3 equiv., 0.16 mL, 201 mg, 2.64 mmol) and treated with a dry chloride salt RCl (1 mol%). In entries 2 and 4 H_2O (1 equiv., 16 µL, 16 mg, 0.88 mmol) was also added to the reaction medium. The mixtures were stirred at 80 ºC for 24 h inside a 10 mL sealed tube under an argon atmosphere. [b] Conversion of styrene oxide into the stated product was determined by ^1H NMR spectroscopy from crude reaction mixtures, using $CHBr_3$ (40 µL, 0.457 mmol) as an analytical internal standard.

Distilled water was used as an additive because the chloride salts under study (TBACl and *ChCl*) are sparingly soluble in CS_2. The addition of 1 equiv. of water ensures the formation of homogeneous reaction mixtures.

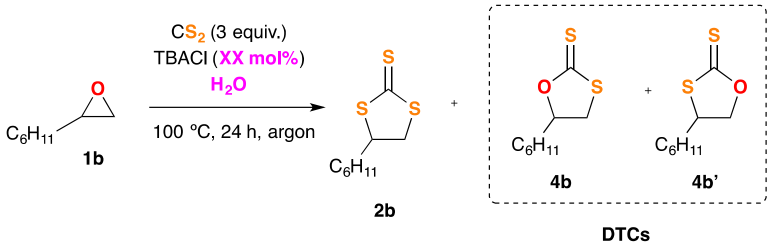
Table SI_8. Optimisation of *ChCl* as the catalyst for the insertion of CS_2 into epoxide **1a**.[a]



entry	T (°C)	*ChCl* mol%	equiv. H_2O	**2a** (%)[b]	**4a** (%)[b]	**4a'** (%)[b]	**5a** (%)[b]	**5a'** (%)[b]
1	80	1	-	51	1	0	6	2
2	80	1	1	55	1	0	4	1
3	80	1	2	66	0	0	0	0
4	80	2.5	1	64	0	0	4	0
5	80	2.5	2	78	0	0	2	0
6	80	2.5	3	70	0	0	0	0
7	100	2.5	2	93	0	0	5	0
8	100	5	2	78	0	0	0	0
9	100	5	4	75	3	2	5	0

[a] General conditions: styrene oxide **1a** (100 μL, 106 mg, 0.88 mmol) was dissolved in CS_2 (3 equiv., 0.16 mL, 201 mg, 2.64 mmol) and treated with the stated catalytic amount of *ChCl* and H_2O. The mixtures were stirred at 80 ºC (100 ºC in entries 7-9) for 24 h inside a 10 mL sealed tube under an argon atmosphere. [b] Conversion of styrene oxide into the stated product was determined by ^1H NMR spectroscopy from crude reaction mixtures, using $CHBr_3$ (40 μL, 0.457 mmol) as an analytical internal standard.

Table SI_9. Optimisation of TBACl as the catalyst for the insertion of CS_2 into epoxide **1b**.[a]



entry	TBACl mol %	equiv. H_2O	**2b** (%)[b]	**4b** (%)[b]	**4b'** (%)[b]
1	2.5	1	58	31	4
2[c]	2.5	1	0	0	0
3	5	1	73	7	7
4	7.5	1	75	2	7
5	10	1	79	5	7
6	15	1	75	0	2
7	2.5	2	63	30	4
8	5	2	71	13	7
9	7.5	2	77	6	8

[a] General conditions: 1,2-epoxyoctane **1b** (134 µL, 113 mg, 0.88 mmol) was dissolved in CS_2 (3 equiv., 0.16 mL, 201 mg, 2.64 mmol) and treated with the stated catalytic amount of TBACl and H_2O. The mixtures were stirred at 100 ºC for 24 h inside a 10 mL sealed tube under an argon atmosphere. [b] Conversion of 1,2-epoxyoctane **1b** oxide into the stated product, as determined by ^{1}H NMR spectroscopy from crude reaction mixtures, using $CHBr_3$ (40 µL, 0.457 mmol) as an analytical internal standard. [c] *ChCl* was used as the catalyst.

The following characteristic ^{1}H-NMR resonance signals were considered:

2b: 4.43-4.34 ppm (m, 1H).[10]

4b: 5.14-5.05 ppm (m, 1H).[10]

Compound **4b'** displays a characteristic resonance at δ = 4.72-4.60 ppm (m, 1H). Unfortunately, it can't be separated by flash chromatography from its regioisomer **4b**.

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[10] M. Okada, R. Nishiyori, S. Kaneko, K. Igawa, S. Shirakawa, *Eur. J. Org. Chem.*, 2018, **2018**, 2022.

3. EXPERIMENTAL PROCEDURES:

Standard procedure for the synthesis of TTCs or DTCs using TBACl as the catalyst (SP1)

In a 10 mL high-pressure close-capped tube are added sequentially tetrabutylammonium chloride (TBACl, 0.088 mmol, 10 mol%), the corresponding epoxide (0.88 mmol, 1 equiv.), carbon disulfide (160 μL, 2.64 mmol, 3 equiv.) and distilled water (0.88 mmol, 1 equiv.). The resulting mixture is purged with an argon stream before the tube is sealed and it is stirred at 100 °C for 24 hours, using an oil bath. Then, the reaction vessel is allowed to reach room temperature and it is opened inside a fume hood as smelly vapors are released. The crude mixture is diluted with 10 mL of CH_2Cl_2, transferred into a funnel, mixed with 10 mL of brine and extracted. The aqueous phase is washed with CH_2Cl_2 (2 x 10 mL) and the organic layers are combined, dried with $MgSO_4$ and filtered. Solvents and volatiles are removed under vacuum. For achieving analytical pure products, a flash chromatography on silica gel is performed.

In the particular case of **1a**, a greener procedure was performed and the *E*-factor value (see Section 4) calculated following the next protocol:

In a 10 mL high-pressure close-capped tube are added sequentially tetrabutylammonium chloride (TBACl, 6 mg, 0.022 mmol, 2.5 mol%), **1a** (100 μL, 0.88 mmol, 1 equiv.), carbon disulfide (160 μL, 2.64 mmol, 3 equiv.) and distilled water (0.88 mmol, 1 equiv.). The resulting mixture is purged with an argon stream before the tube is sealed and it is stirred at 100 °C for 24 hours, using an oil bath. Then, the reaction vessel is allowed to reach room temperature and it is opened inside a fume hood as smelly vapors are released. The crude mixture is washed with 1 mL of distilled water (stir for 30 min and then decant the aqueous phase), and finally a second treatment with 1 mL of hot distilled water (60 °C, stir for 10 min and decant the aqueous phase). Solvents and volatiles are removed under vacuum, affording **2a** (86% conversion, determined by ^{1}H-NMR using $CHBr_3$ as an internal standard) as a yellow solid.

Standard procedure for the synthesis of TTCs or DTCs using *ChCl* as the catalyst (SP2)

In a 10 mL high-pressure close-capped tube are added sequentially choline chloride (*ChCl*, 0.022 mmol, 2.5 mol%), the corresponding epoxide (0.88 mmol, 1 equiv.), carbon disulfide (160 μL, 2.64 mmol, 3 equiv.) and distilled water (1.76 mmol, 2 equiv.). The resulting mixture is purged with an argon stream before the tube is sealed and it is stirred at 100 ^{o}C for 24 hours, using an oil bath. Then, the reaction vessel is allowed to reach room temperature and it is opened inside a fume hood as smelly vapors are released. The crude mixture is diluted with 10 mL of CH_2Cl_2, transferred into a funnel, mixed with 10 mL of brine and extracted. The aqueous phase is washed with CH_2Cl_2 (2 x 10 mL) and the organic layers are combined, dried with $MgSO_4$ and filtered. Solvents and volatiles are removed under vacuum. For achieving analytical pure products, a flash chromatography on silica gel is performed.

4. *E*-FACTOR CALCULATION

According to its original definition, the Sheldon *E*-factor value is defined as the quotient between total mass of waste (understanding waste as everything but the product except for water) and mass of product. *E*-factor was calculated for the insertion of CS_2 into epoxide **1a** according protocol described in page SI_14.[11]

E-Factor: (mass of waste [g]) / (mass of final product [g])

Mass of waste = total amount of reactants [g] – mass of final product [g].

Amount of reactants [g]: 105.7 mg styrene oxide + 201.0 mg CS2 + 6.1 mg TBACl = 0.3128 g

Mass of final product = 0.1608 g

E- factor: (0.3128 – 0.1608) / (0.1608) = 0.945

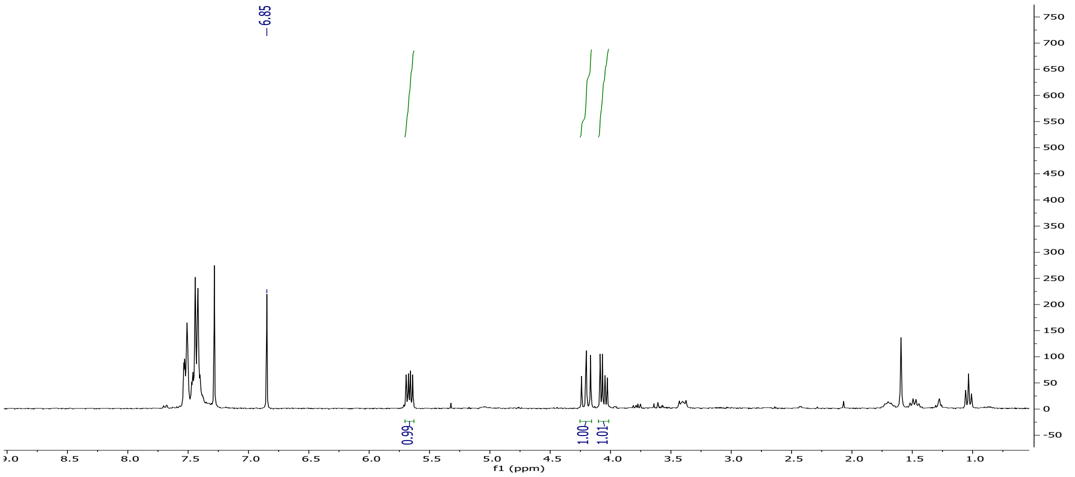

Figure SI_1. ^{1}H-NMR for crude product **2a** using TBACl (2.5 mol%) as catalyst.

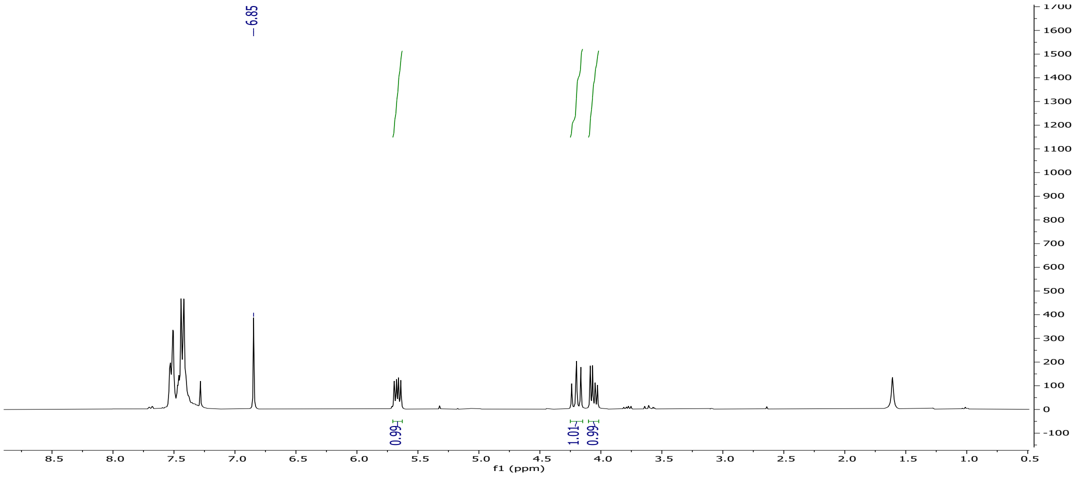

Figure SI_2. ^{1}H-NMR for purified product **2a** after treatment with water (as detailed in page SI_14)

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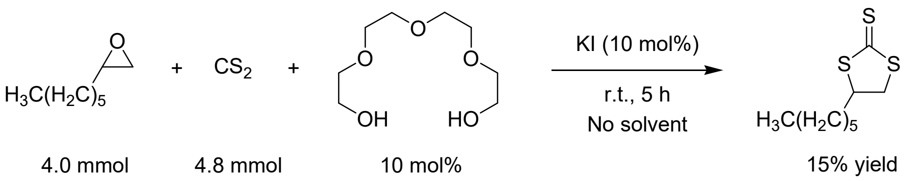
[11] R. A. Sheldon, *Green Chem.*, 2007, **9**, 1273.

E-Factor calculation for other reactions previously described in literature without taking account the downstream process:



Scheme SI_01. Synthesis of cyclic trithiocarbonates using KI-tetraethylene glycol complex as catalyst.[12]

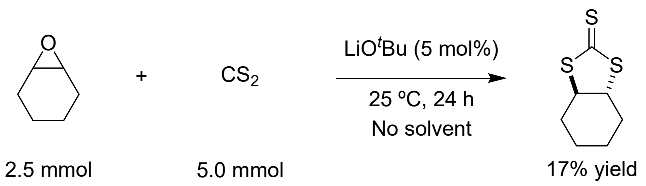
E-Factor: (mass of waste [g]) / (mass of final product [g])

Mass of waste = total amount of reactants [g] – mass of final product [g].

Amount of reactants [g]: 512.8 mg 2-hexyloxirane + 365.5 mg CS_2 + 77.7 mg tetraethylene glycol + 66.4 mg KI = 1.022 g

Mass of final product = 0.132 g

E- factor: (1.022 – 0.132) / (0.132) = 6.74



Scheme SI_02. Synthesis of cyclic trithiocarbonates using LiOtBu as catalyst.[13]

E-Factor: (mass of waste [g]) / (mass of final product [g])

Mass of waste = total amount of reactants [g] – mass of final product [g].

Amount of reactants [g]: 245.4 mg cyclohexene oxide + 380.7 mg CS_2 + 10.0 mg lithium *tert*-butoxide = 0.6361 g

Mass of final product = 0.0808 g

E- factor: (0.6361 – 0.0808) / (0.0808) = 6.87

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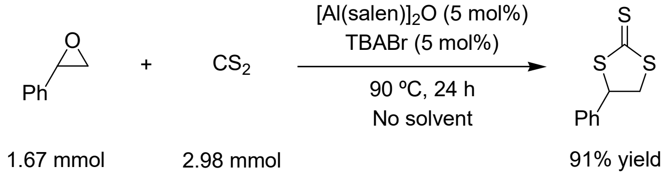
[12] M. Okada, R. Nishiyori, S. Kaneko, K. Igawa and S. Shirakawa, *Eur. J. Org. Chem*. 2018, **2018**, 2022.

[13] J. Diebler, A. Spannenberg and T. Werner, *Org. Biomol. Chem.*, 2016, **14**, 7480.



Scheme SI_03. Synthesis of cyclic trithiocarbonates using a bimetallic aluminon(salen) complex as catalyst.[14]

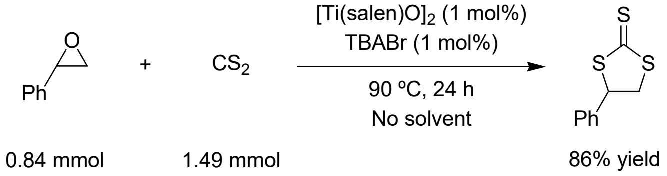
E-Factor: (mass of waste [g]) / (mass of final product [g])

Mass of waste = total amount of reactants [g] – mass of final product [g].

Amount of reactants [g]: 200.6 mg styrene oxide + 226.9 mg CS_2 + 47.5 mg bimetallic aluminum(salen) complex + 26.8 mg TBABr= 0.5018 g

Mass of final product = 0.3227 g

E- factor: (0.5018 – 0.3227) / (0.3227) = 0.55



Scheme SI_04. Synthesis of cyclic trithiocarbonates using a titanium(salen) catalyst.[15]

E-Factor: (mass of waste [g]) / (mass of final product [g])

Mass of waste = total amount of reactants [g] – mass of final product [g].

Amount of reactants [g]: 100.9 mg styrene oxide + 113.4 mg CS_2 + 10.0 mg titanium(salen) complex + 2.8 mg TBABr= 0.2271 g

Mass of final product = 0.1534 g

E- factor: (0.2271 – 0.1534) / (0.1534) = 0.48

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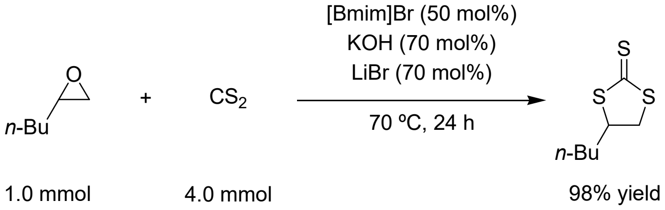
[14] W. Clegg, R. W. Harrington, M. North and P. Villuendas, *J. Org. Chem.*, 2010, **75**, 6201.

[15] C. Beattie and M. North, *ChemCatChem*, 2014, **6**, 1252.



Scheme SI_05. Synthesis of cyclic trithiocarbonates using N-heterocyclic carbene/LiBr complex as catalyst.[16]

E-Factor: (mass of waste [g]) / (mass of final product [g])

Mass of waste = total amount of reactants [g] – mass of final product [g].

Amount of reactants [g]: 100.2 mg 2-butyloxirane + 304.6 mg CS_2 + 109.6 mg [Bmim]Br + 39.3 mg KOH + 60.8 mg LiBr = 0.6145 g

Mass of final product = 0.1885 g

E- factor: (0.6145 – 0.1885) / (0.1885) = 2.26

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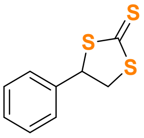
[16] C. Mei, X. Li, L. Liu, C. Cao, G. Pang and Y. Shi, *Tetrahedron*, 2017, **73**, 5706.

5. CHARACTERISATION OF CYCLIC TRITHIOCARBONATES 2a-j AND DITHIOCARBONATES 4h-k

4-Phenyl-1,3-dithiolane-2-thione (2a)



Prepared according to protocols **SP1** and **SP2**. Yellow solid (151 mg, 81% yield and 153 mg, 82% yield respectively). Purified by flash chromatography (Hexane/EtOAc, 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51-7.47 (m, 2H), 7.45-7.37 (m, 3H), 5.64 (dd, *J* = 10.4, 5.7 Hz, 1H), 4.18 (dd, *J* = 12.0, 10.4 Hz, 1H), 4.03 (dd, *J* = 12.1, 5.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 227.5 (C), 135.2 (C), 129.3 (2×CH), 129.3 (CH), 127.6 (2×CH), 64.3 (CH), 49.9 (CH_2).[6]

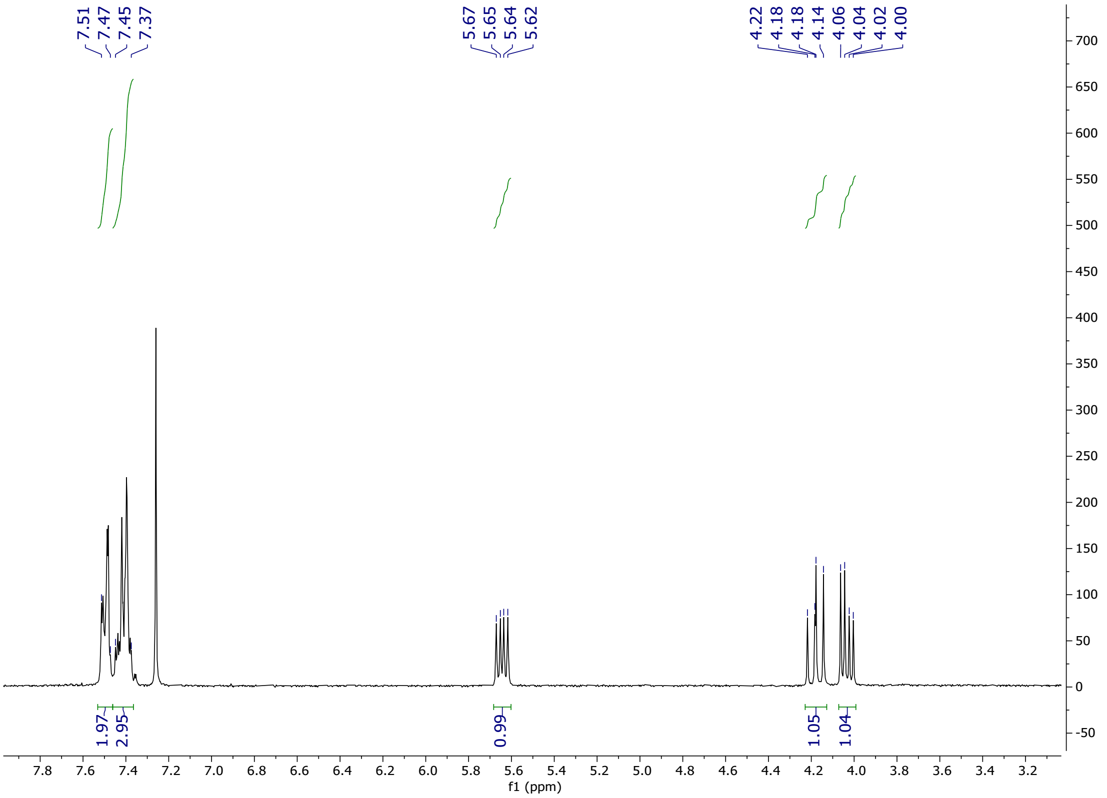


Figure SI_3. ^{1}H-NMR for **2a** in $CDCl_3$ (300 MHz).

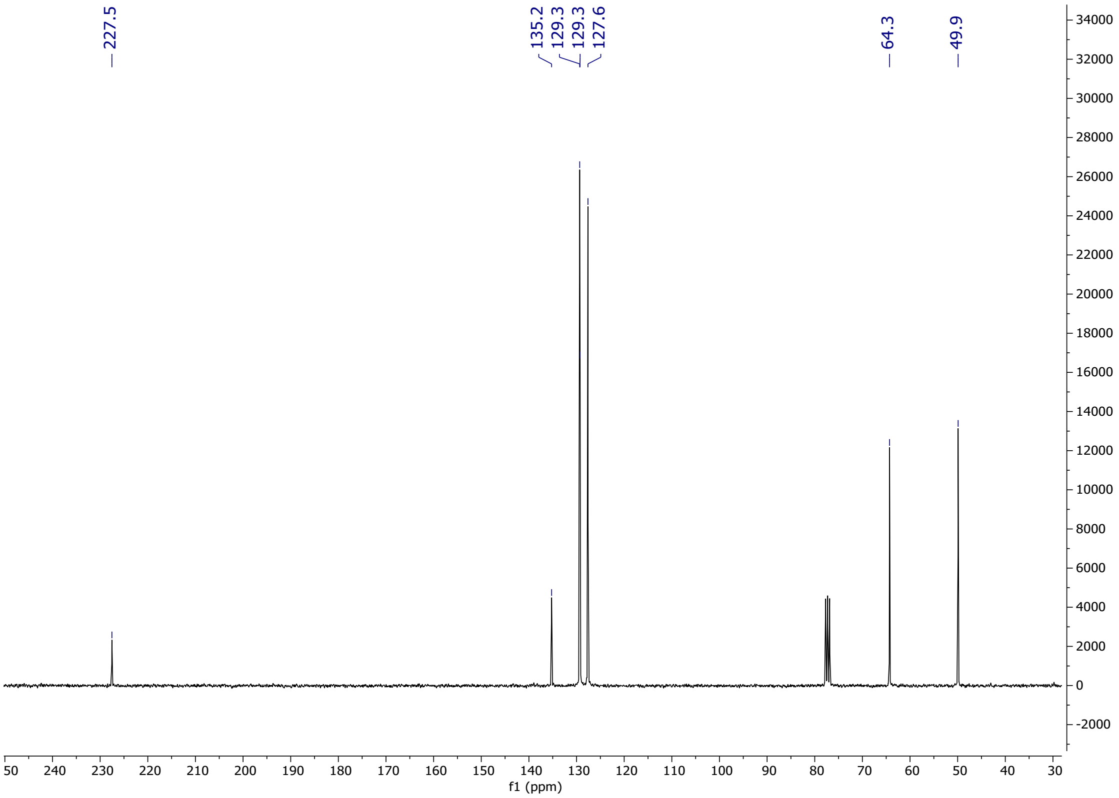


Figure SI_4. ^{13}C-NMR for **2a** in $CDCl_3$ (75 MHz).

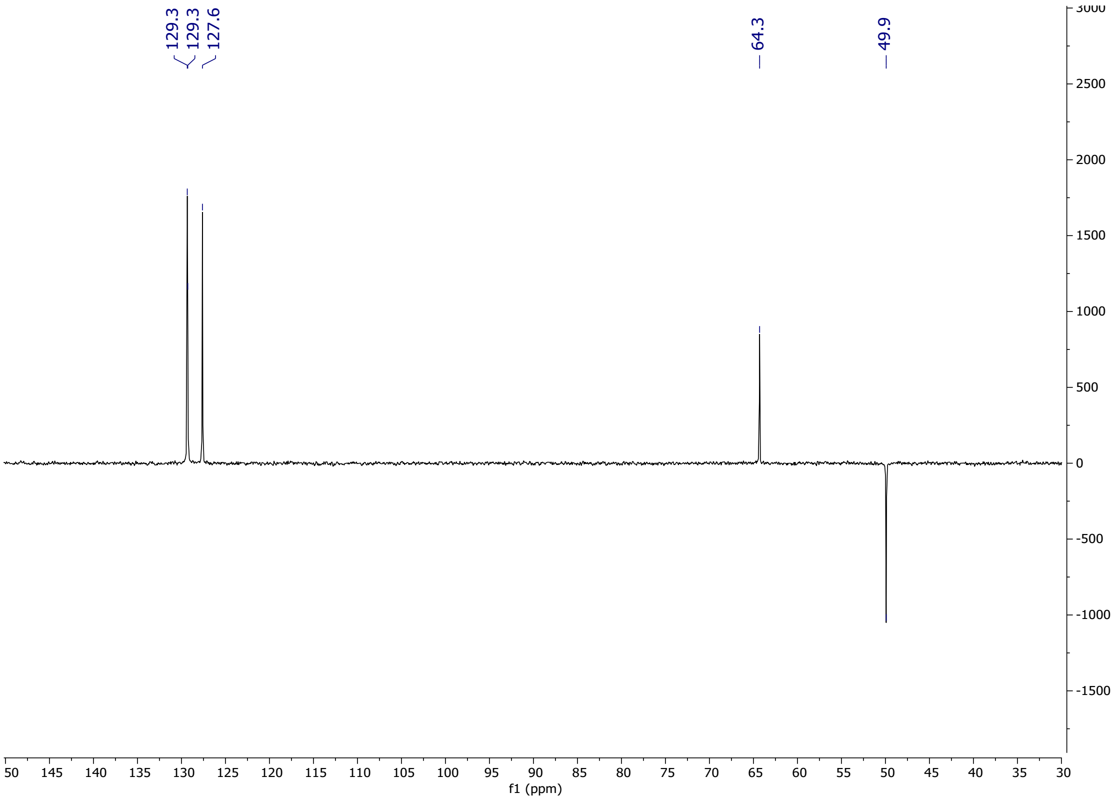
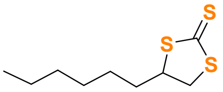


Figure SI_5. DEPT-135 NMR for **2a** in $CDCl_3$ (75 MHz).

4-Hexyl-1,3-dithiolane-2-thione (2b)



Prepared according to protocol **SP1**. Yellow oil (135 mg, 70% yield). Purified by flash chromatography (Hexane/EtOAc, 10:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.44-4.34 (m, 1H), 3.96 (dd, *J* = 11.9, 5.4 Hz, 1H), 3.70 (dd, *J* = 11.9, 7.9 Hz, 1H), 2.02-1.83 (m, 2H), 1.45-1.28 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 228.2 (C), 61.1 (CH), 48.3 (CH$_2$), 33.5 (CH$_2$), 31.5 (CH$_2$), 28.9 (CH$_2$), 28.3 (CH$_2$), 22.5 (CH$_2$), 14.1 (CH$_3$).[10]

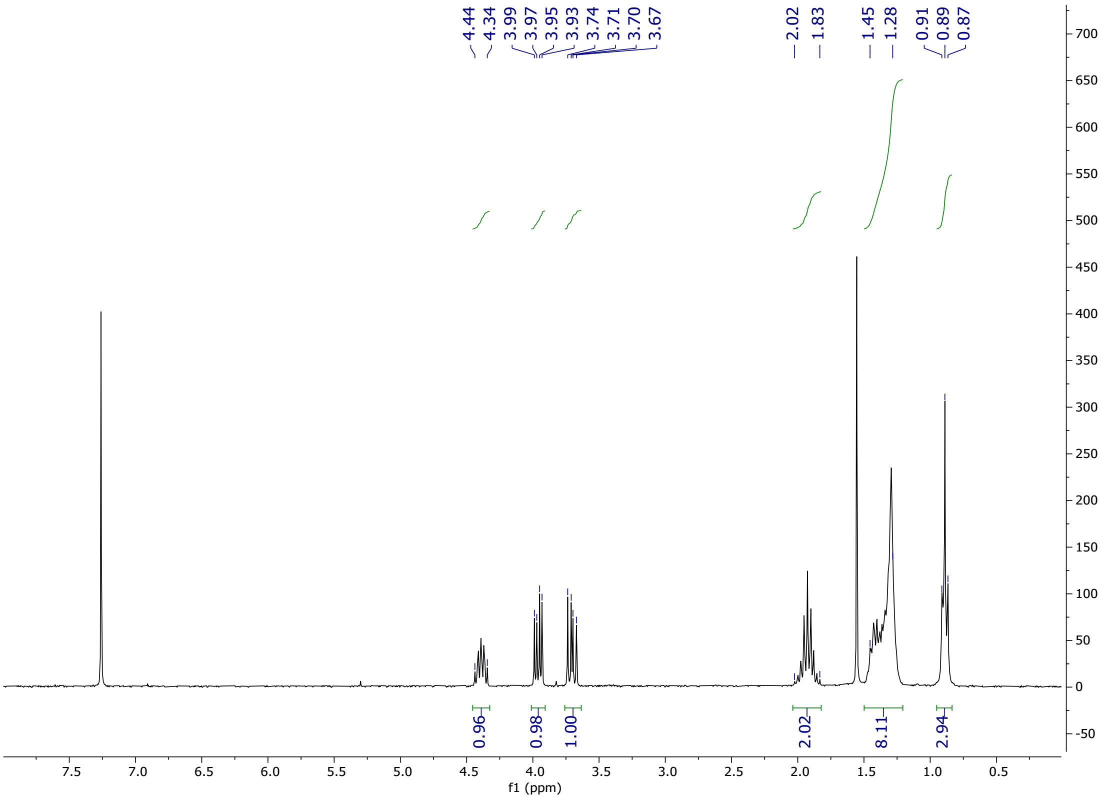


Figure SI_6. ^{1}H-NMR for **2b** in CDCl$_3$ (300 MHz).

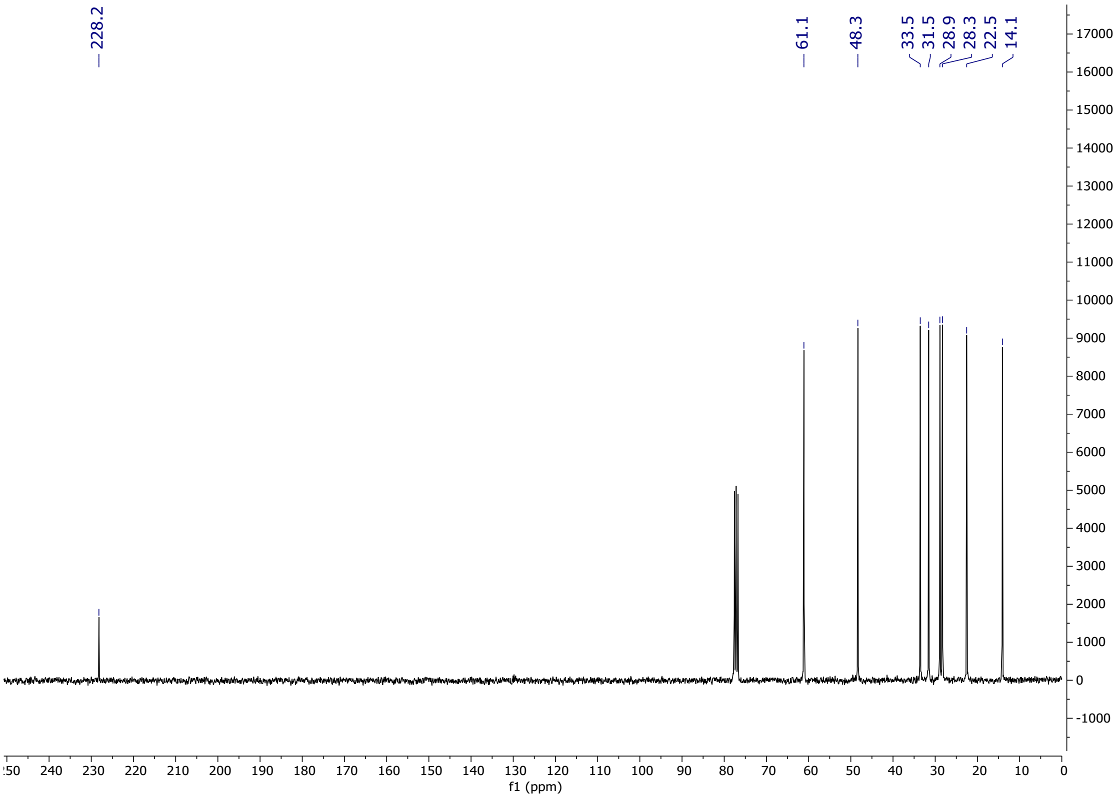


Figure SI_7. ^{13}C-NMR for **2b** in $CDCl_3$ (75 MHz).

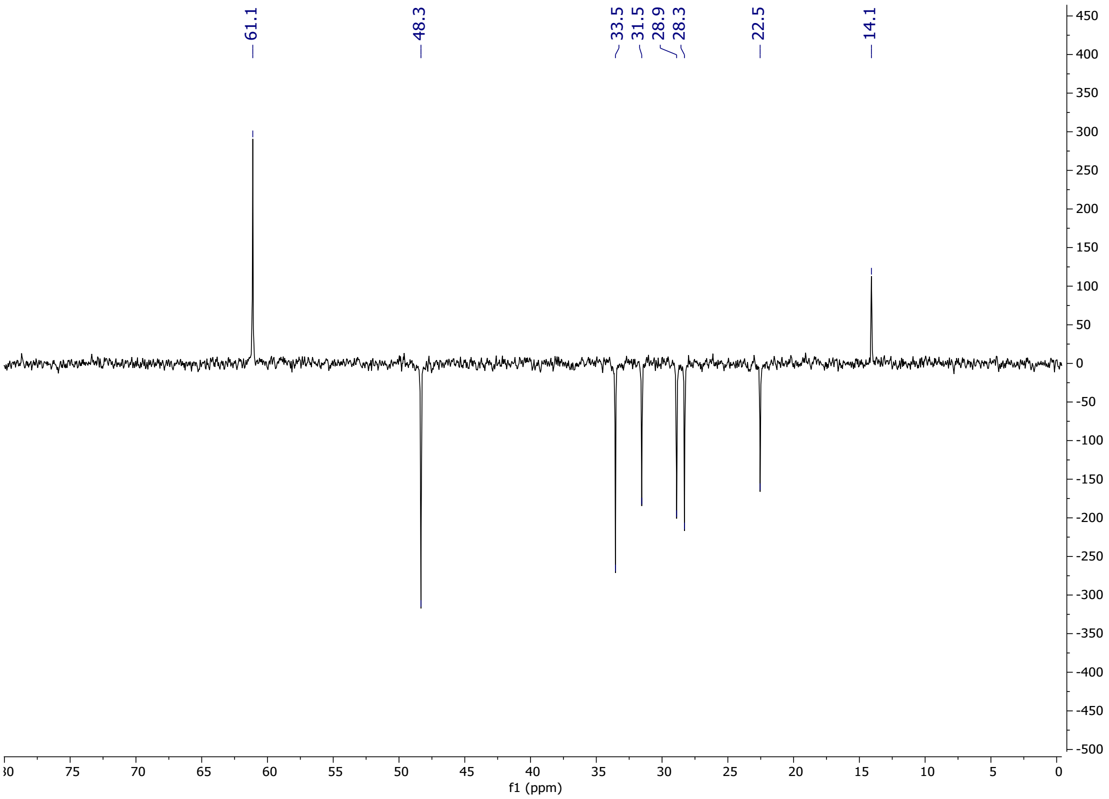
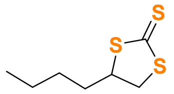


Figure SI_8. DEPT-135 NMR for **2b** in $CDCl_3$ (75 MHz).

4-Butyl-1,3-dithiolane-2-thione (2c)



Prepared according to protocol **SP1**. Yellow oil (103 mg, 61% yield). Purified by flash chromatography (Hexane/EtOAc, 10:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.44-4.34 (m, 1H), 3.96 (dd, *J* = 11.9, 5.4 Hz, 1H), 3.71 (dd, *J* = 11.9, 7.9 Hz, 1H), 2.01-1.86 (m, 2H), 1.46-1.35 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 228.2 (C), 61.1 (CH), 48.4 (CH$_2$), 33.3 (CH$_2$), 30.4 (CH$_2$), 22.4 (CH$_2$), 13.9 (CH$_3$).[6]

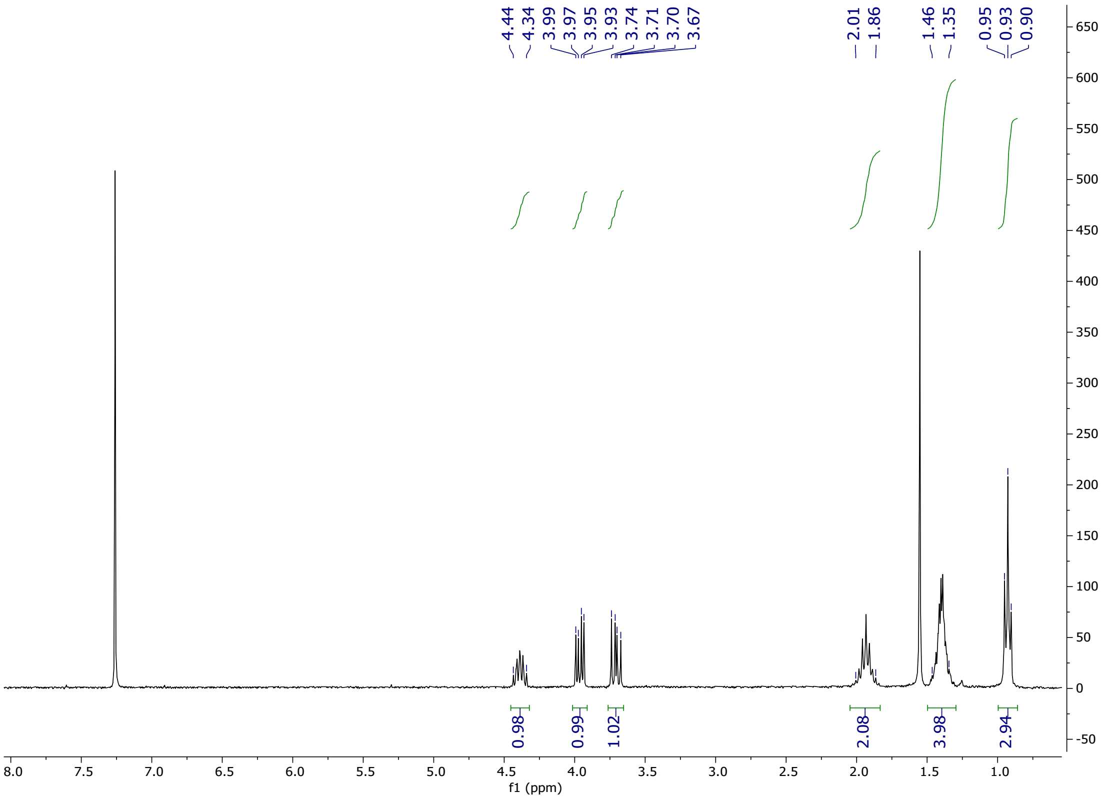


Figure SI_9. ^{1}H-NMR for **2c** in CDCl$_3$ (300 MHz).

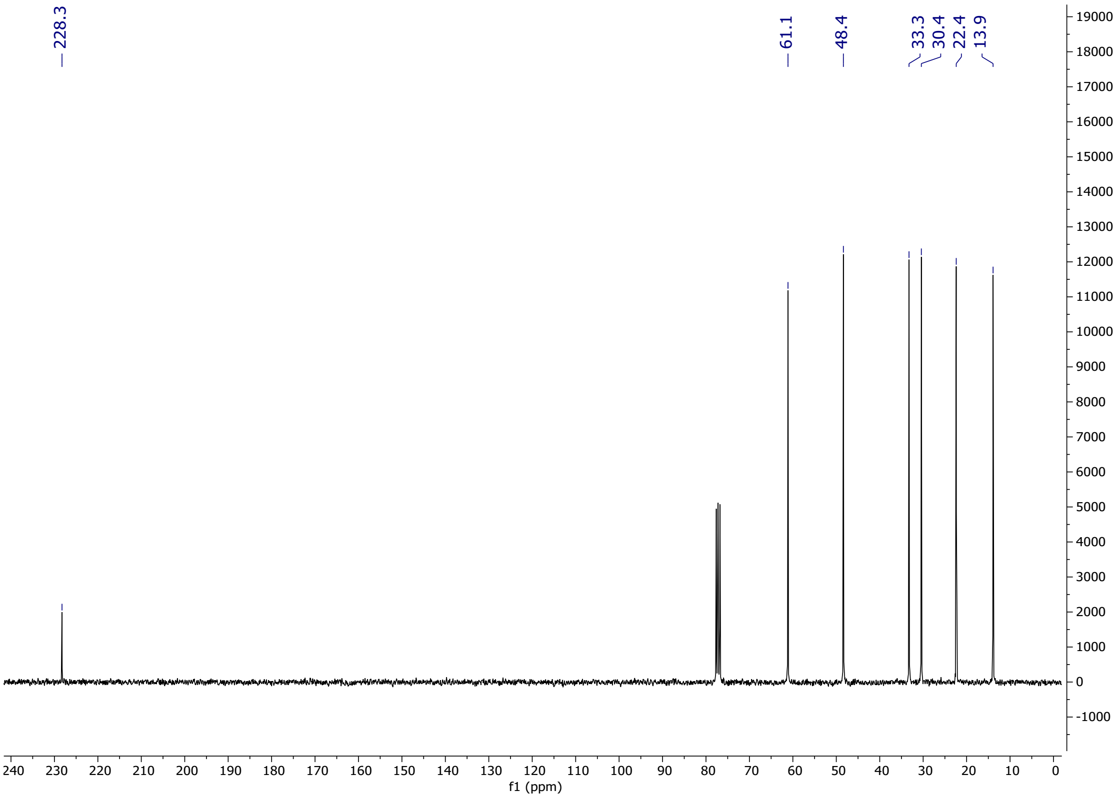


Figure SI_10. ^{13}C-NMR for **2c** in $CDCl_3$ (75 MHz).

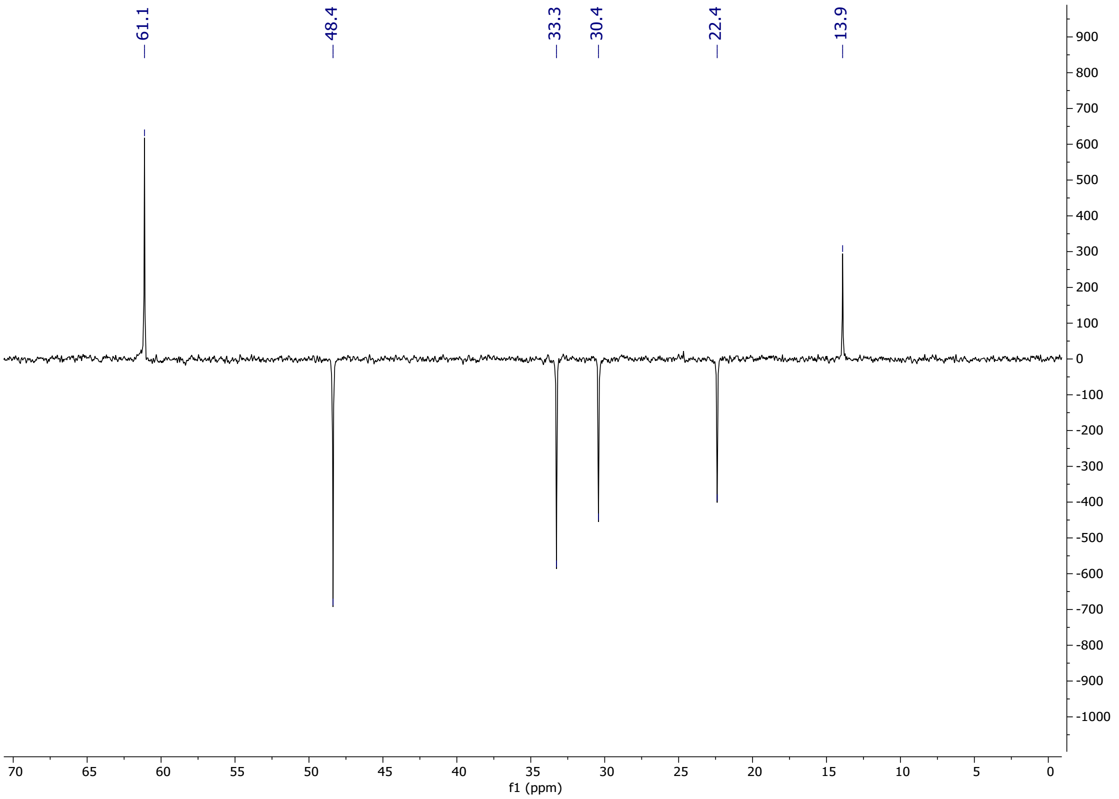
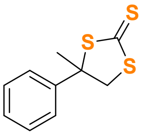


Figure SI_11. DEPT-135 NMR for **2c** in $CDCl_3$ (75 MHz).

4-Methyl-4-phenyl-1,3-dithiolane-2-thione (2d)



Prepared according to protocol **SP1**. Yellow oil (69 mg, 35% yield). Purified by flash chromatography (Hexane/EtOAc, 10:1). IR (NaCl): ν 3480, 3085, 3058, 3029, 2969, 2922, 2860, 2825, 1952, 1802, 1742, 1647, 1599, 1581, 1494, 1445, 1421, 1378, 1334, 1267, 1222, 1189, 1158, 1130, 1075, 1059, 1025, 1000, 925, 908, 886, 859, 762, 728, 696, 633, 618, 580 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56-7.51(m, 2H), 7.45-7.33 (m, 3H), 4.42 (d, *J* = 12.2 Hz, 1H), 3.85 (d, *J* = 12.1 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 226.4 (C), 140.6 (C), 129.1 (2×CH), 128.5 (CH), 126.1 (2×CH), 71.7 (C), 55.1 (CH_2), 28.0 (CH_3).

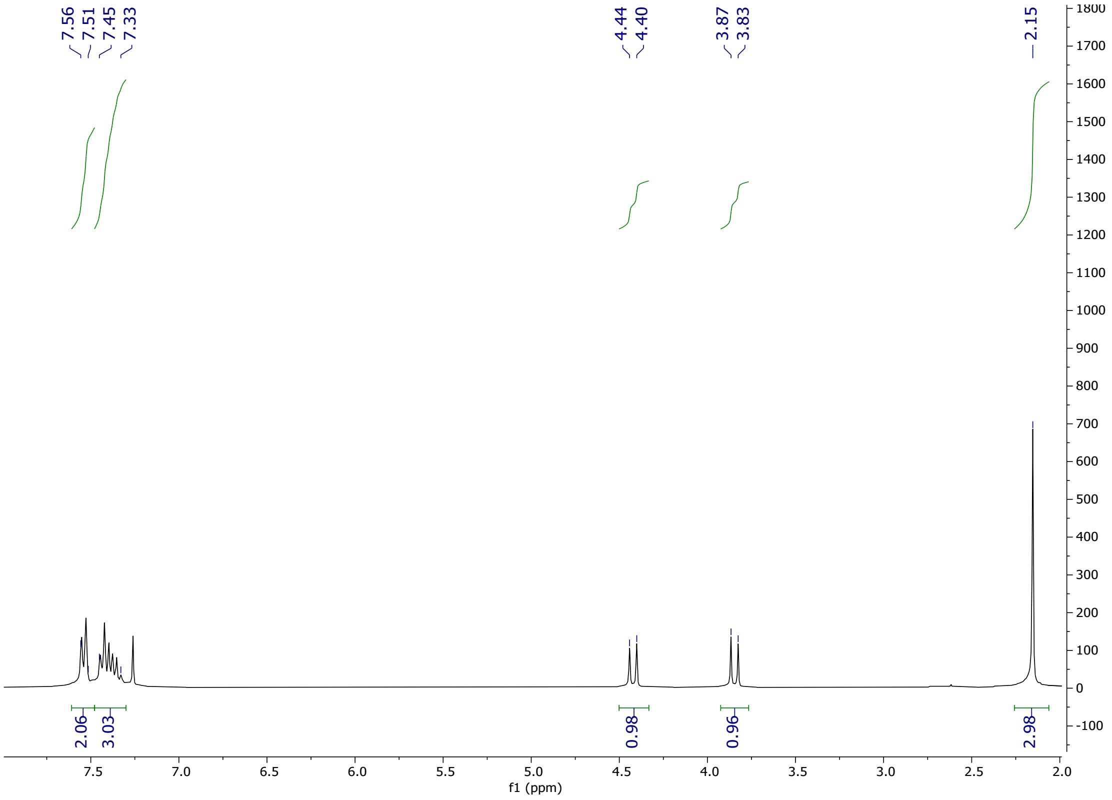


Figure SI_12. ^{1}H-NMR for **2d** in $CDCl_3$ (300 MHz).

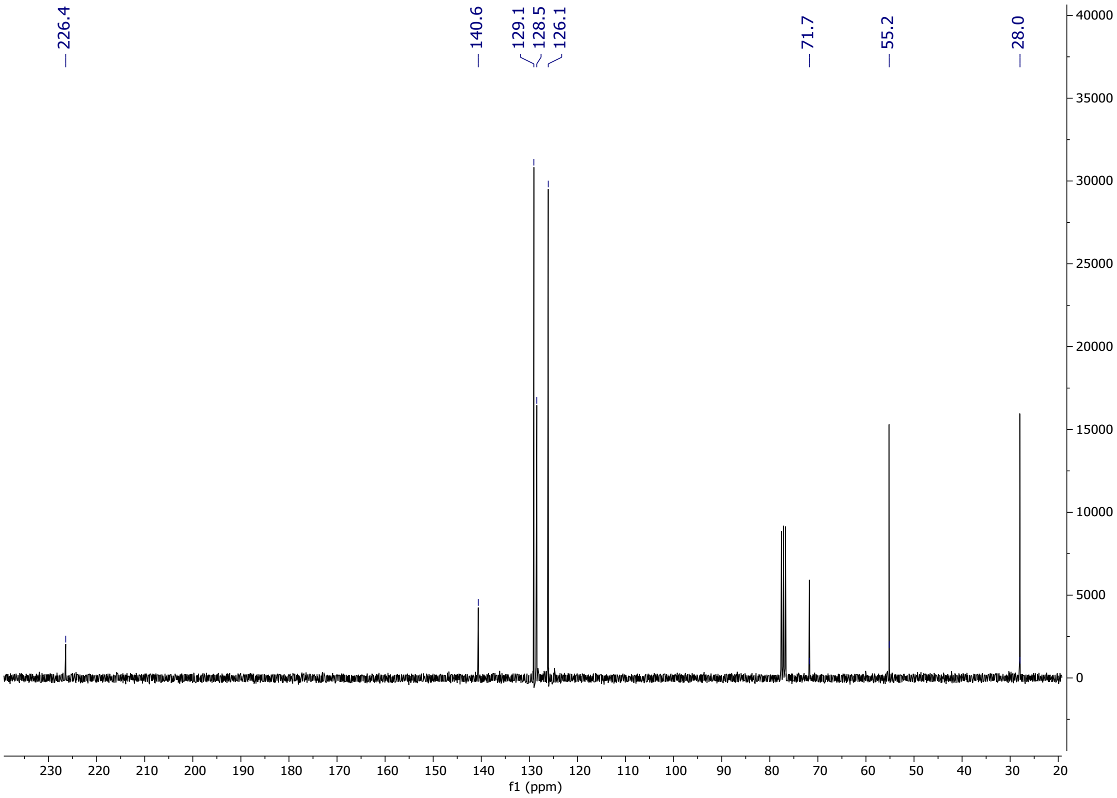


Figure SI_13. ^{13}C-NMR for **2d** in $CDCl_3$ (75 MHz).

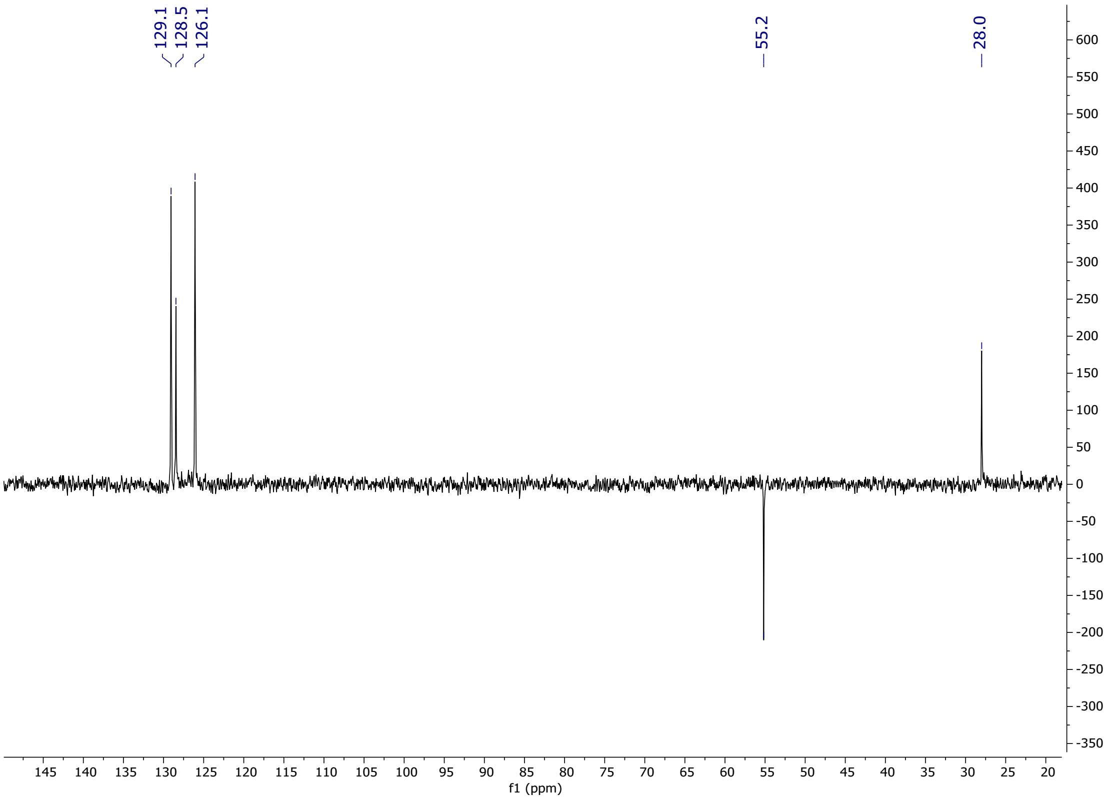
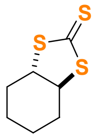


Figure SI_14. DEPT-135 NMR for **2d** in $CDCl_3$ (75 MHz).

trans-Hexahydrobenzo[d][1,3]dithiole-2-thione (2e)



Prepared according to protocols **SP1** and **SP2**. Yellow solid (87 mg, 52% yield and 119 mg, 71% yield respectively). Purified by flash chromatography (Hexane/EtOAc, 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.14-4.04 (m, 2H), 2.26-2.18 (m, 2H), 2.05-1.89 (m, 2H), 1.79-1.66 (m, 2H), 1.54-1.42 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 227.3 (C), 64.6 (2×CH), 29.1 (2×CH_2), 25.1 (2×CH_2).[10]

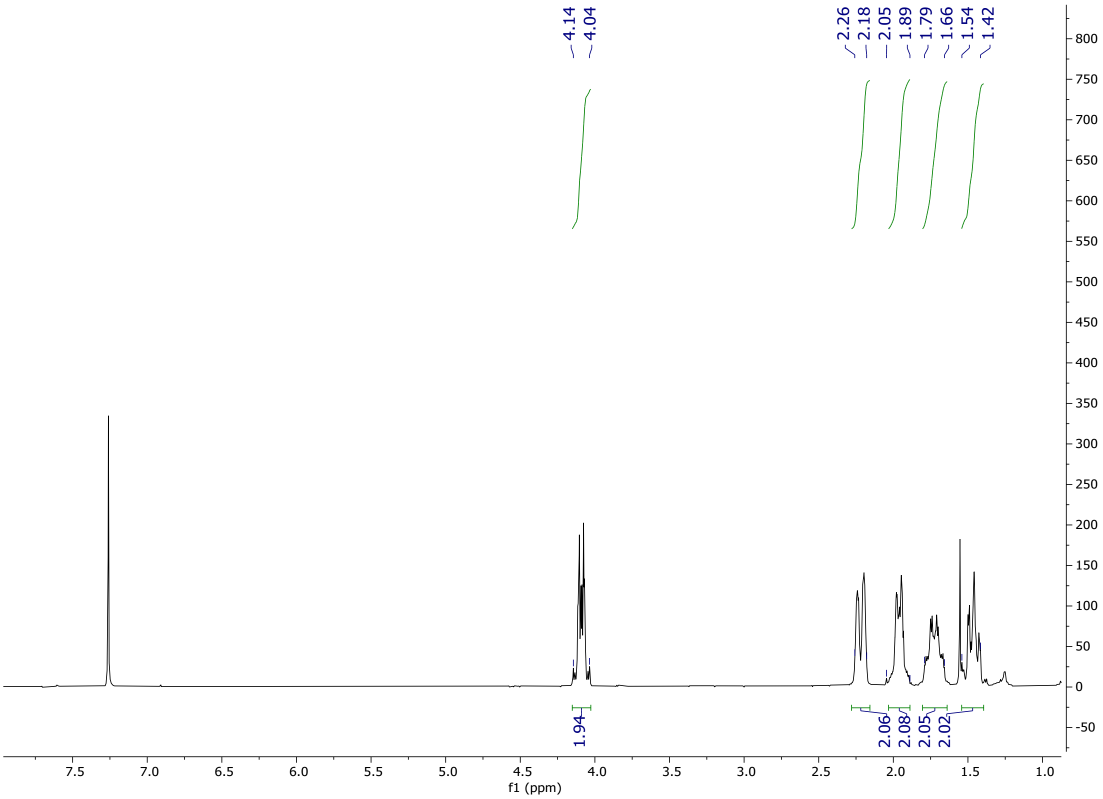


Figure SI_15. ^{1}H-NMR for **2e** in $CDCl_3$ (300 MHz).

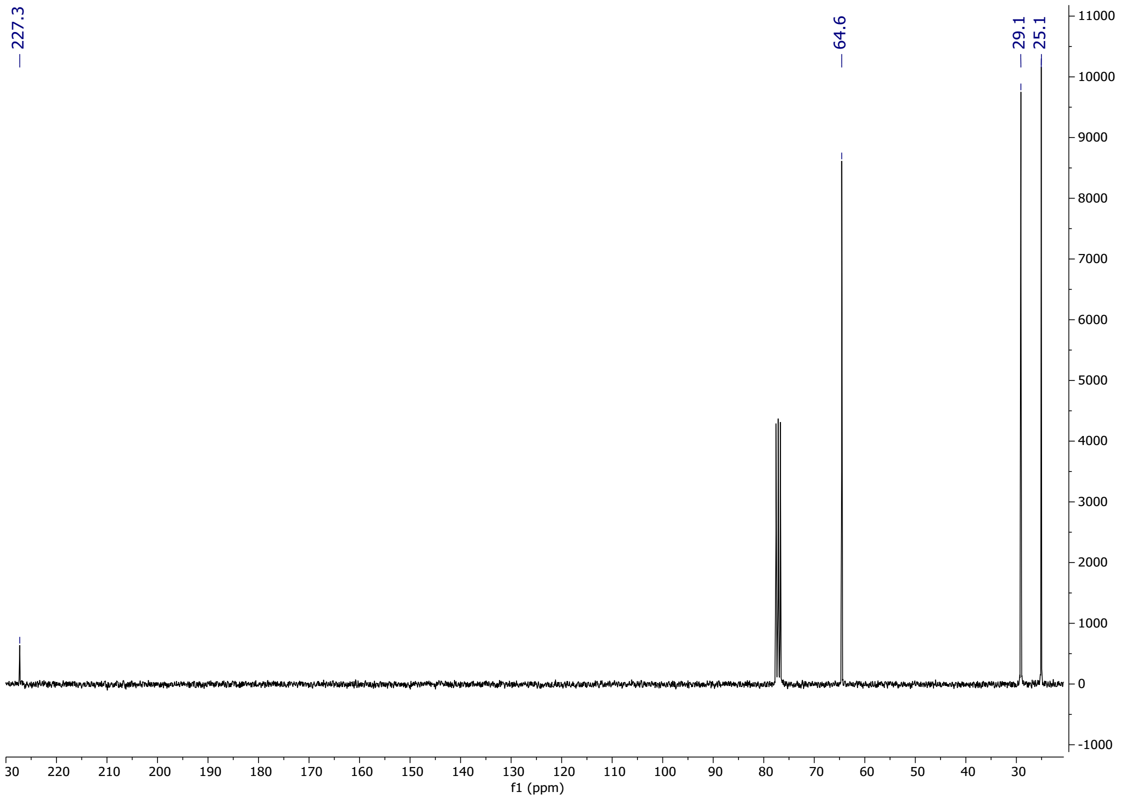


Figure SI_16. ^{13}C-NMR for **2e** in $CDCl_3$ (75 MHz).

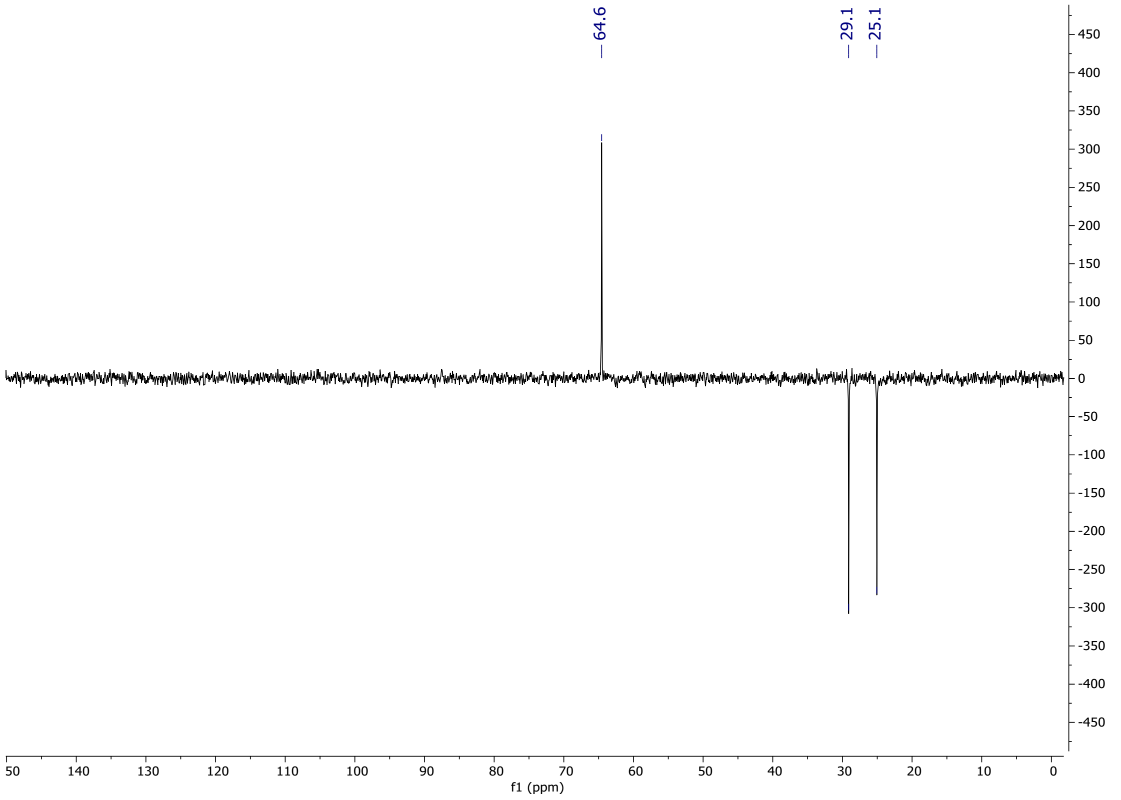
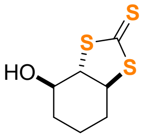


Figure SI_17. DEPT-135 NMR for **2e** in $CDCl_3$ (75 MHz).

***trans,cis*-4-Hydroxyhexahydrobenzo[d][1,3]dithiolane-2-thione (2f)**



Prepared according to protocols **SP1** and **SP2**. Yellow solid (93 mg, 51% yield and 81 mg, 45% yield respectively). Purified by flash chromatography (Hexane/EtOAc, 3:1). IR (KBr): ν 3246, 2944, 2922, 2855, 1714, 1655, 1454, 1443, 1404, 1359, 1338, 1331, 1326, 1277, 1258, 1245, 1224, 1993, 1128, 1097, 1072, 1057, 1034, 1013, 971, 965, 958, 909, 901, 866, 856, 842, 775, 748, 687, 626, 570, 532, 507, 502, 464, 454 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.20-4.09 (m, 2H), 4.02-3.95 (m, 1H), 2.21-2.12 (m, 2H), 2.07-2.00 (m, 1H), 1.93 (d, J = 5.3 Hz, 1H), 1.73-1.41 (m, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 226.7 (C), 72.4 (CH), 71.6 (CH), 61.7 (CH), 34.8 (CH$_2$), 28.1 (CH$_2$), 23.7 (CH$_2$).

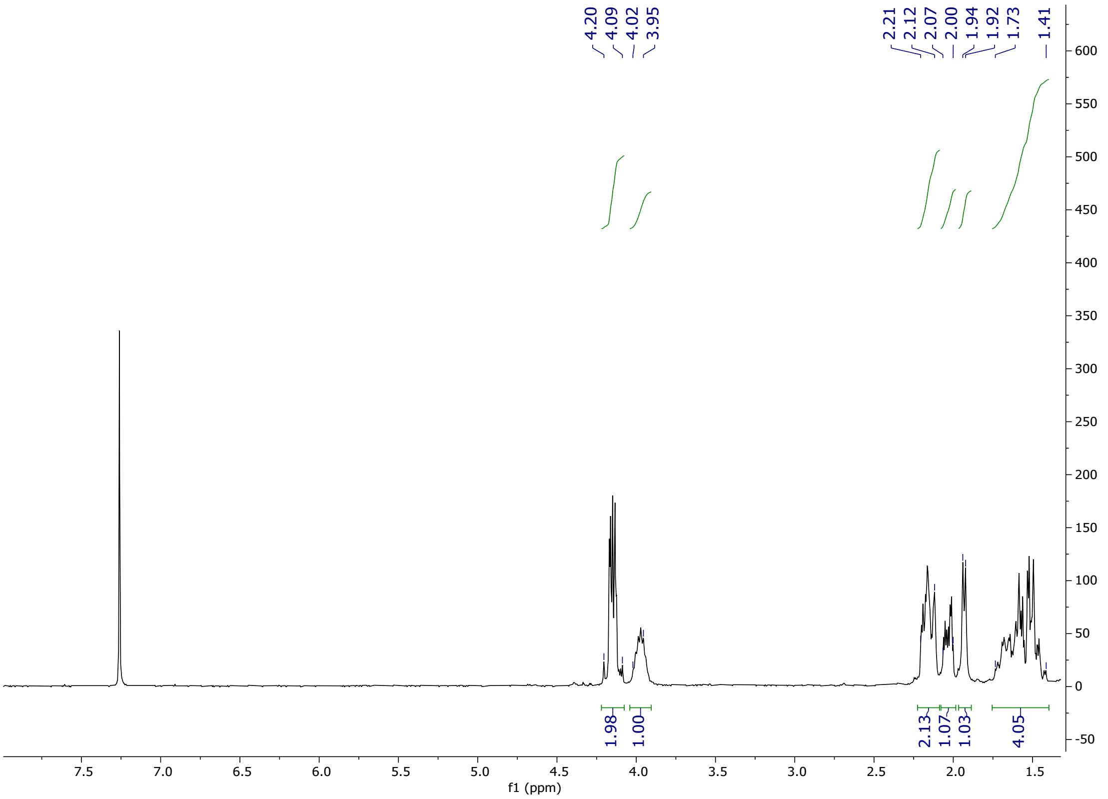


Figure SI_18. ^{1}H-NMR for **2f** in CDCl$_3$ (300 MHz).

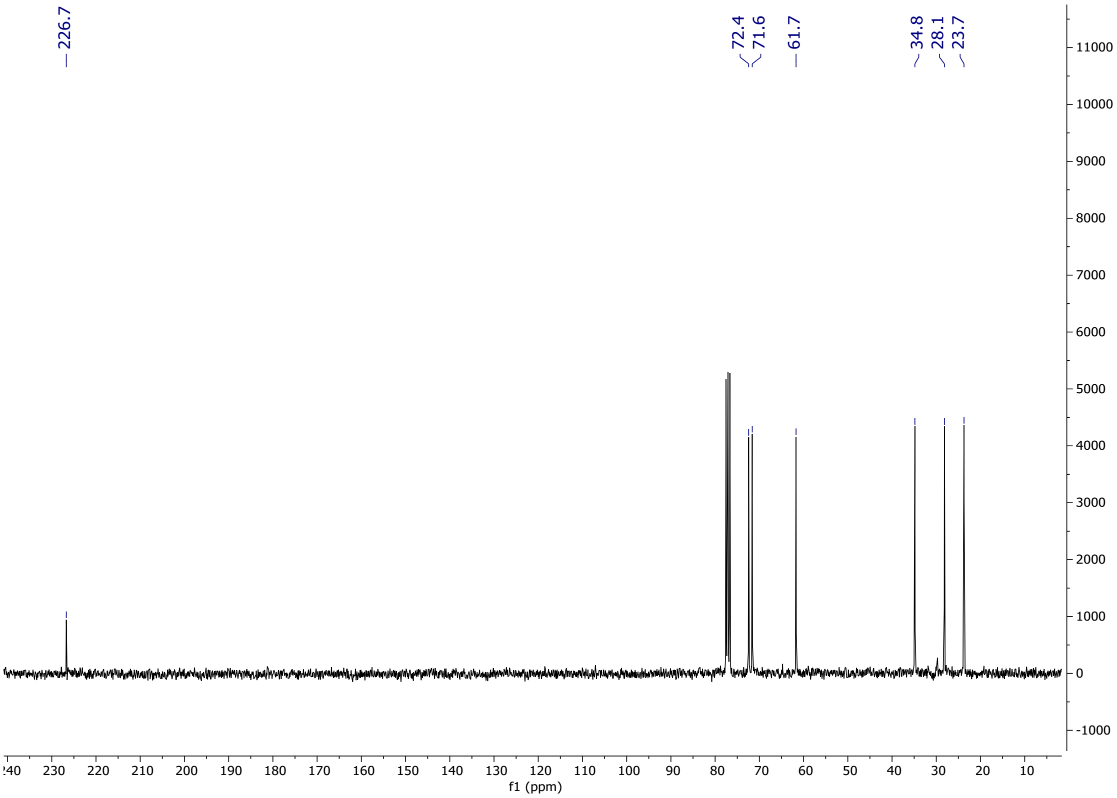


Figure SI_19. ^{13}C-NMR for **2f** in CDCl$_3$ (75 MHz).

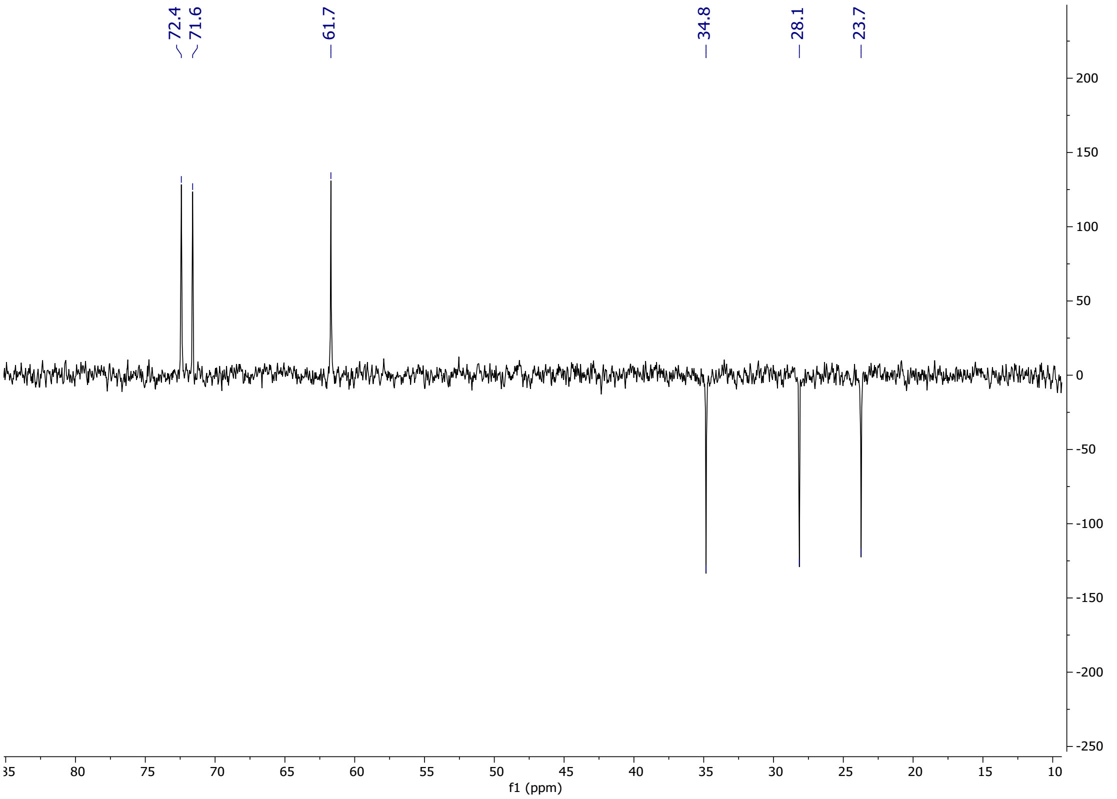
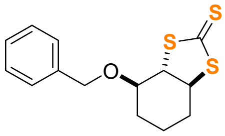


Figure SI_20. DEPT-135 NMR for **2f** in CDCl$_3$ (75 MHz).

trans,cis-4-(Benzyloxy)hexahydrobenzo[d][1,3]dithiolane-2-thione (2g)



Prepared according to protocol **SP1**. Yellow solid (151 mg, 58% yield). Purified by flash chromatography (Hexane/EtOAc, 10:1). Crystallized for X-Ray diffraction analysis using THF/Hexanes. IR (KBr): ν 3083, 3057, 3024, 2942, 2928, 2893, 2861, 1978, 1959, 1899, 1879, 1816, 1759, 1715, 1658, 1600, 1495, 1469, 1453, 1442, 1398, 1362, 1347, 1337, 1328, 1308, 1282, 1268, 1242, 1233, 1211, 1188, 1175, 1159, 1132, 1106, 1074, 1059, 1051, 1027, 1005, 991, 974, 947, 929, 912, 865, 859, 845, 826, 777, 743, 699, 624, 520, 505, 477, 460 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39-7.28 (m, 5H), 4.65 (d, *J* = 11.7 Hz, 1H), 4.50 (d, *J* = 11.8 Hz, 1H), 4.25 (dd, *J* = 12.6, 9.9 Hz, 1H), 4.11 (td, *J* = 12.0, 3.5 Hz, 1H), 3.73-3.65 (m, 1H), 2.39-2.30 (m, 1H), 2.17-2.01 (m, 2H), 1.74-1.60 (m, 1H), 1.53-1.36 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 226.8 (C), 137.5 (C), 128.6 (2×CH), 128.0 (CH), 127.7 (2×CH), 78.7 (CH), 70.8 (CH_2), 69.7 (CH), 61.7 (CH), 30.9 (CH_2), 28.4 (CH_2), 23.6 (CH_2).

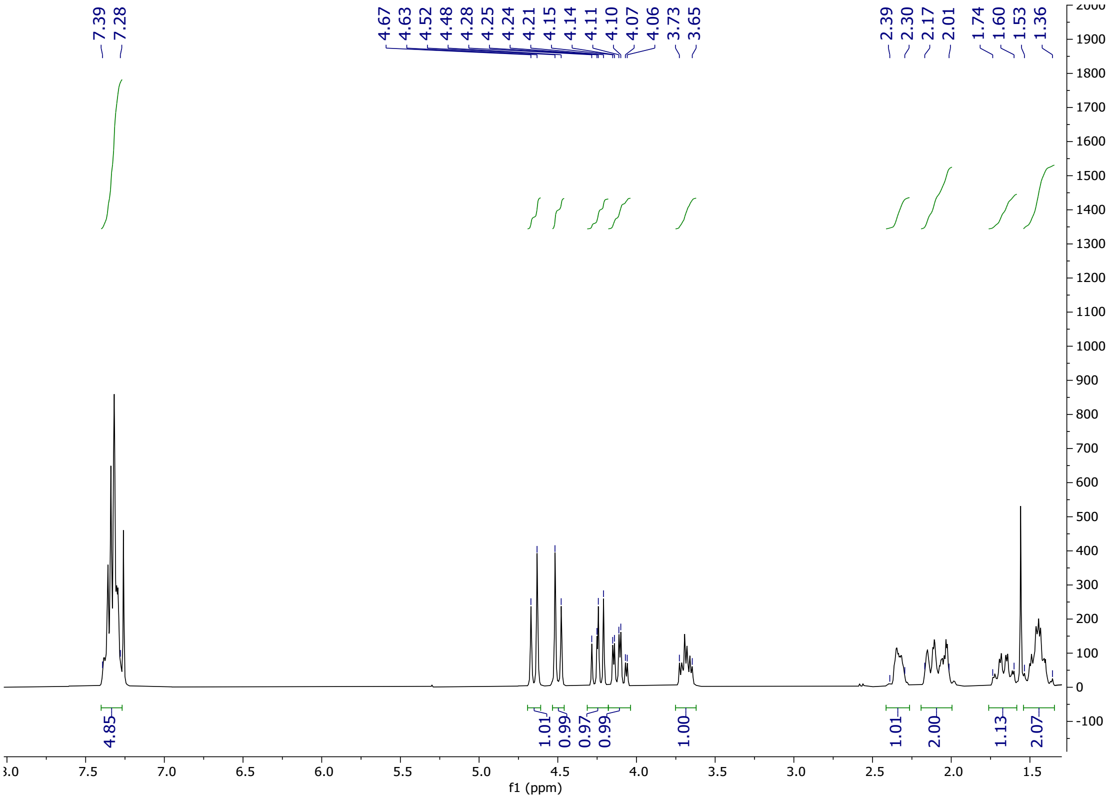


Figure SI_21. ^{1}H-NMR for **2g** in $CDCl_3$ (300 MHz).

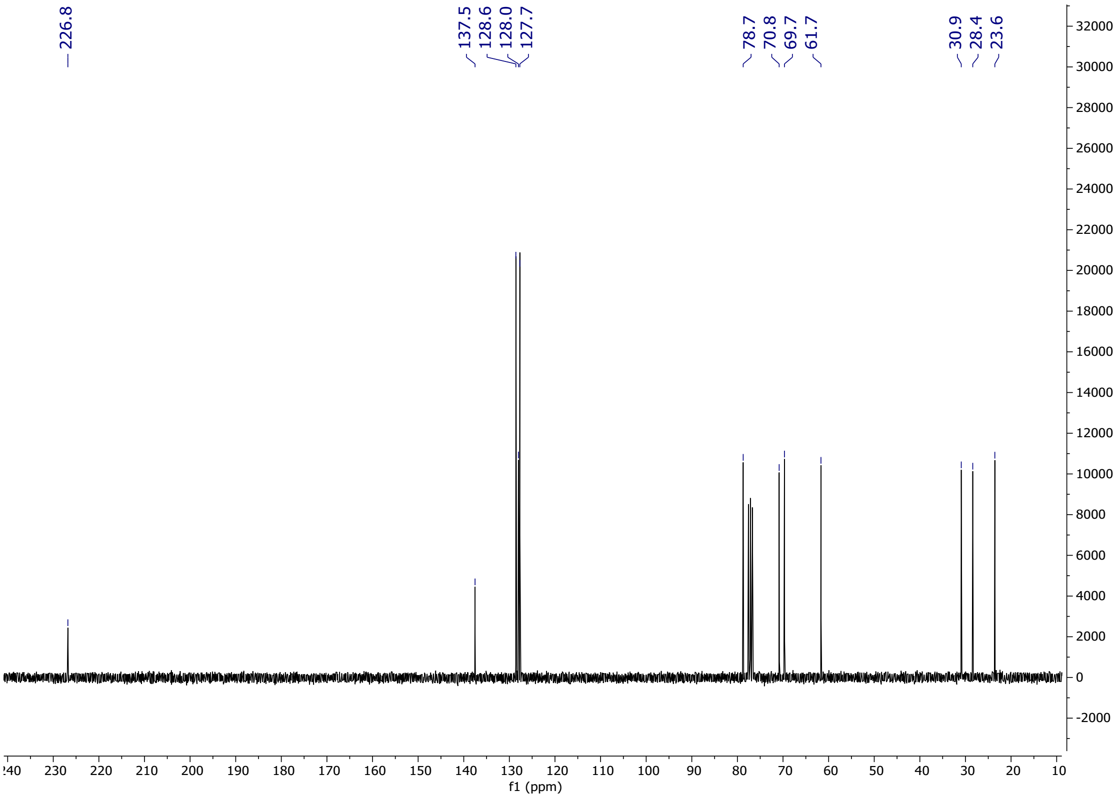


Figure SI_22. ^{13}C-NMR for **2g** in $CDCl_3$ (75 MHz).

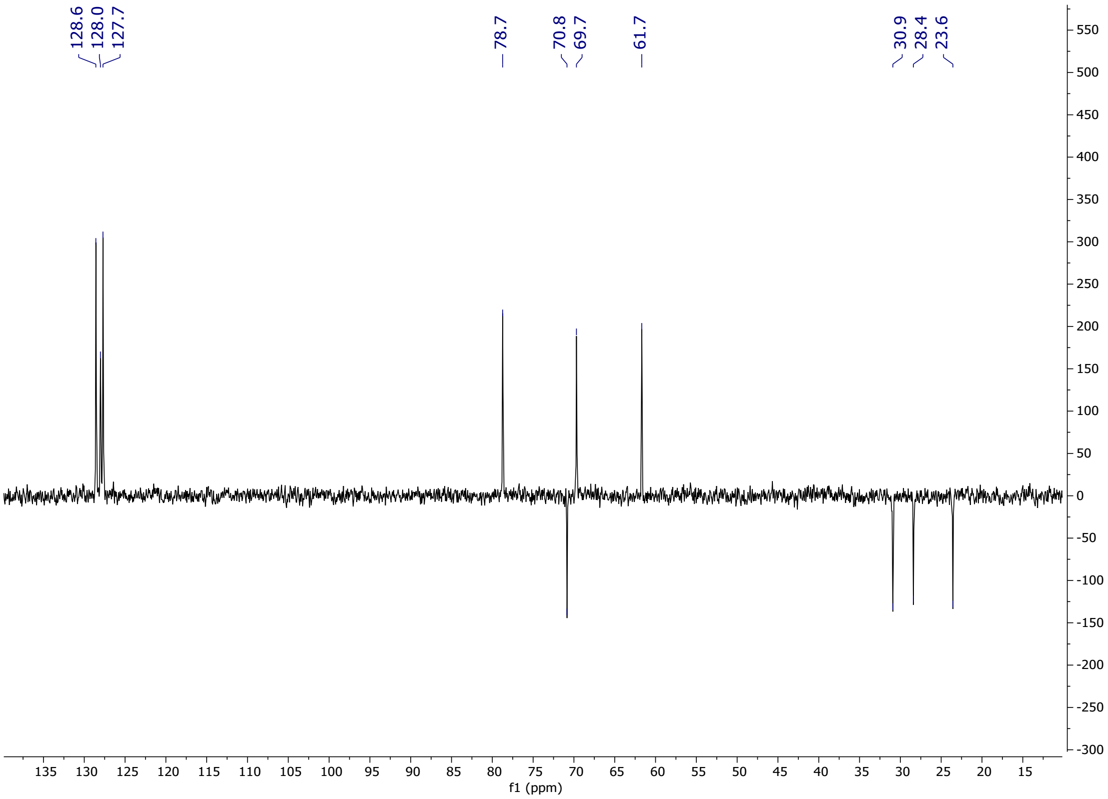
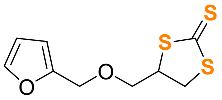


Figure SI_23. DEPT-135 NMR for **2g** in $CDCl_3$ (75 MHz).

4-((Furan-2-ylmethoxy)methyl)-1,3-dithiolane-2-thione (2h)



Prepared according to protocol **SP1**. Yellow oil (106 mg, 49% yield). Purified by flash chromatography (Hexane/EtOAc, 7:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (s, 1H), 6.36 (s, 2H), 4.52 (s, 2H), 4.44-4.36 (m, 1H), 4.07 (dd, *J* = 12.1, 5.6 Hz, 1H), 3.92 (dd, *J* = 12.1, 4.3 Hz, 1H), 3.85 (t, *J* = 9.5 Hz, 1H), 3.67 (dd, *J* = 9.8, 5.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 227.5 (C), 150.8 (C), 143.2 (CH), 110.5 (CH), 110.1 (CH), 68.6 (CH_2), 65.1 (CH_2), 58.0 (CH), 45.0 (CH_2).[6]

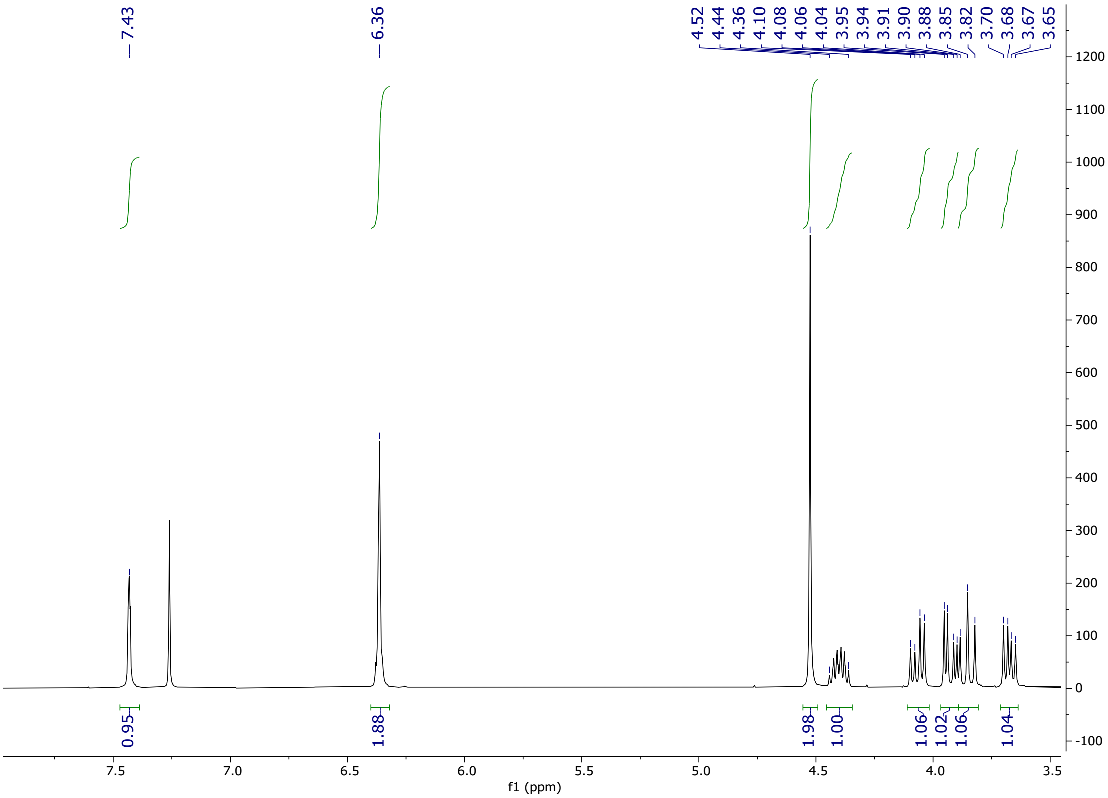


Figure SI_24. ^{1}H-NMR for **2h** in $CDCl_3$ (300 MHz).

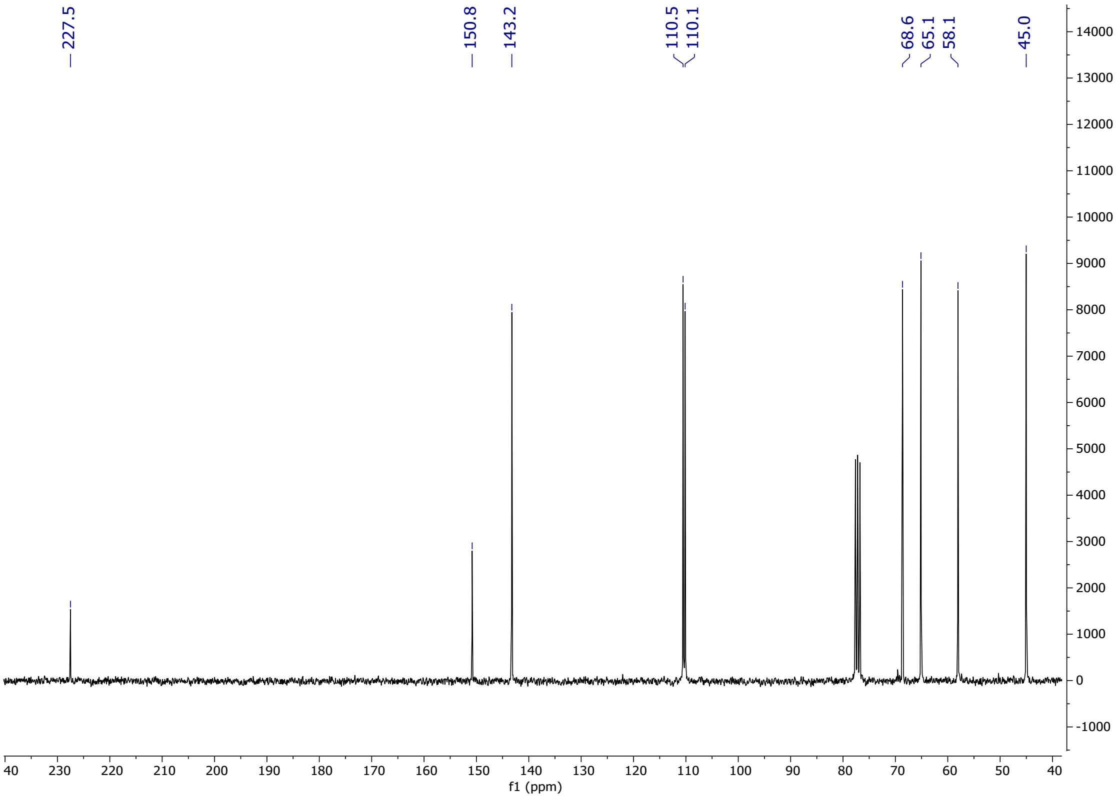


Figure SI_25. ^{13}C-NMR for **2h** in $CDCl_3$ (75 MHz).

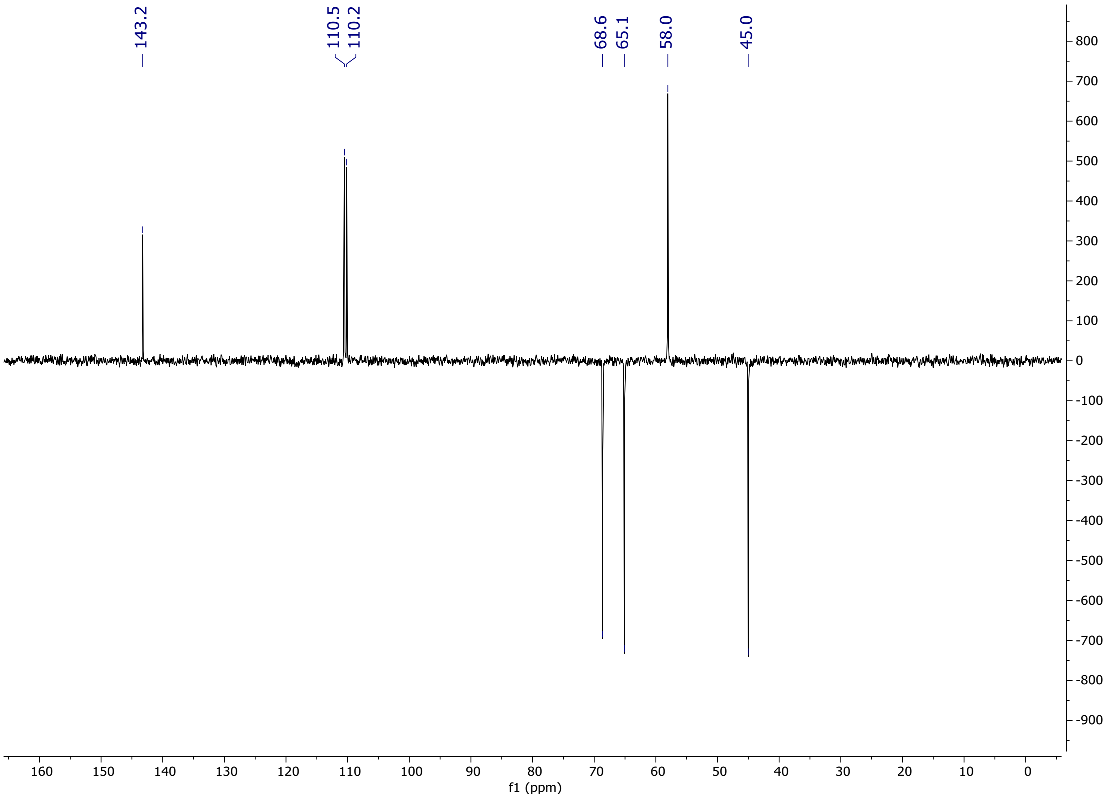
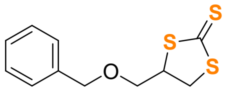


Figure SI_26. DEPT-135 NMR for **2h** in $CDCl_3$ (75 MHz).

4-((Benzyloxy)methyl)-1,3-dithiolane-2-thione (2i)



Prepared according to protocol **SP1**. Yellow oil (112 mg, 50% yield). Purified by flash chromatography (Hexane/EtOAc, 10:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.40-7.30 (m, 5H), 4.59 (s, 2H), 4.52-4.44 (m, 1H), 4.08 (dd, *J* = 12.1, 5.6 Hz, 1H), 3.96 (dd, *J* = 12.1, 4.7 Hz, 1H), 3.86 (t, *J* = 9.2 Hz, 1H), 3.68 (dd, *J* = 9.7, 5.8 Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 227.6 (C), 137.3 (C), 128.7 (2×CH), 128.2 (CH), 127.9 (2×CH), 73.5 (CH$_2$), 69.1 (CH$_2$), 58.4 (CH), 45.1 (CH$_2$).[6]

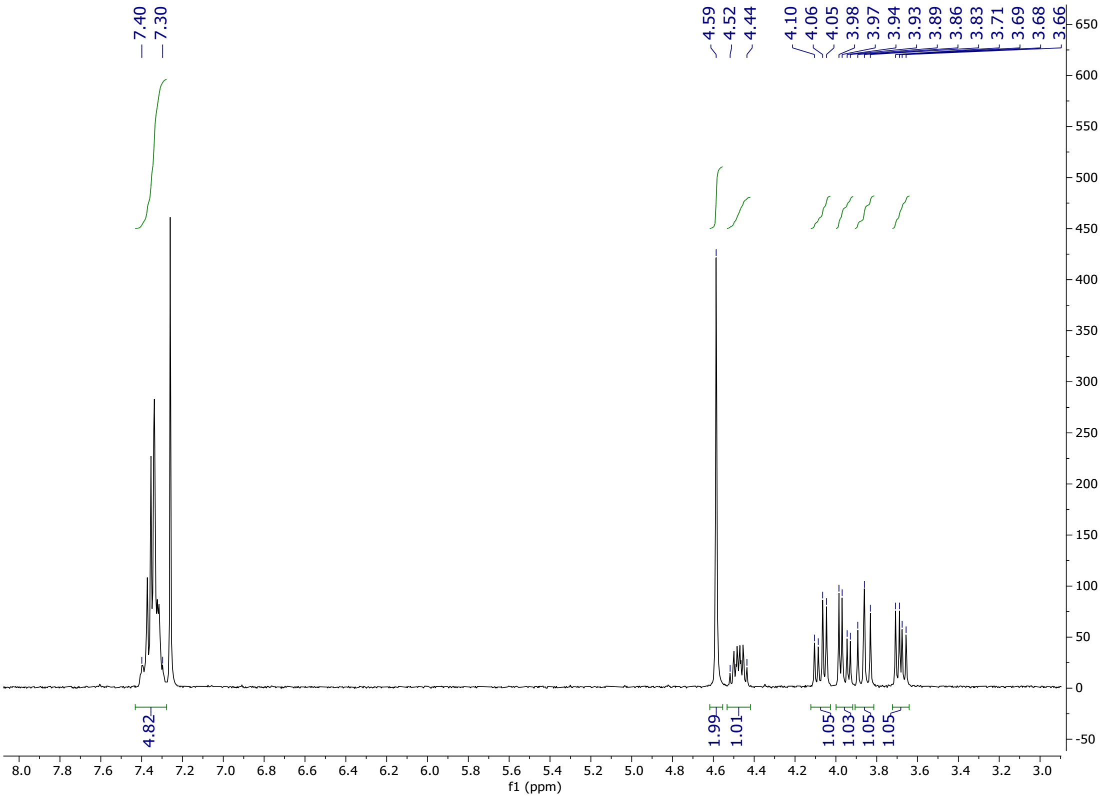


Figure SI_27. ^{1}H-NMR for **2i** in CDCl$_3$ (300 MHz).

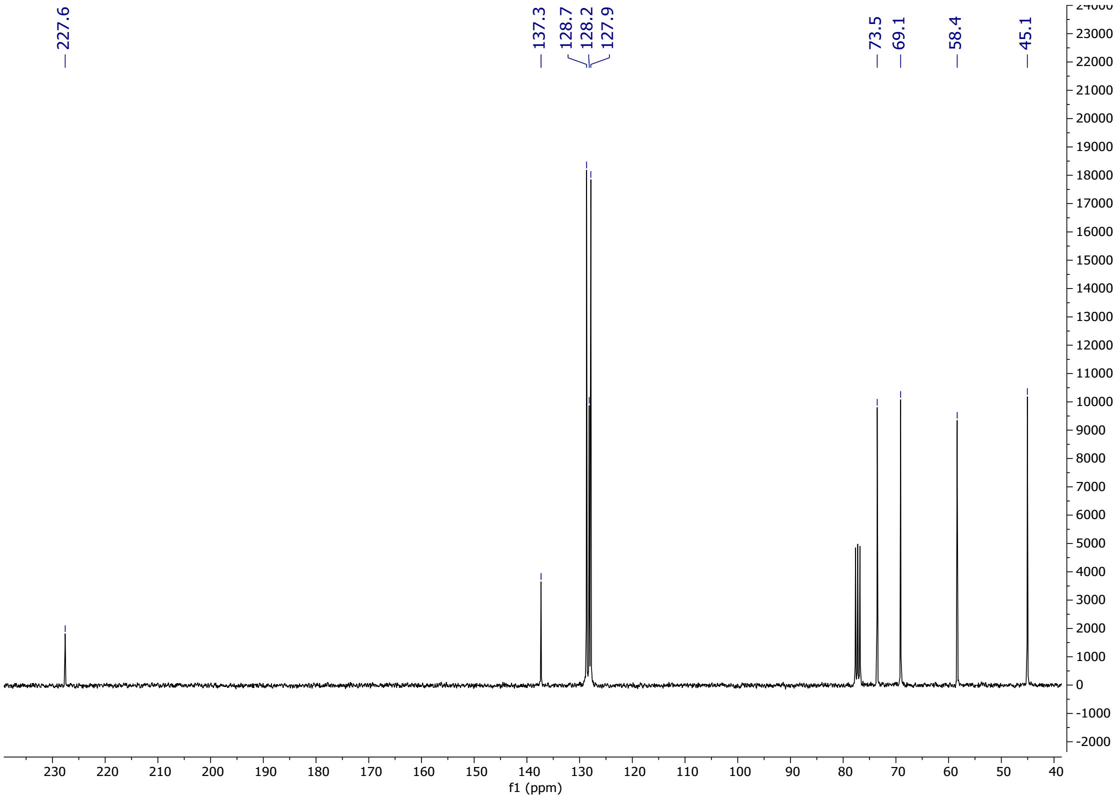


Figure SI_28. ^{13}C-NMR for **2i** in $CDCl_3$ (75 MHz).

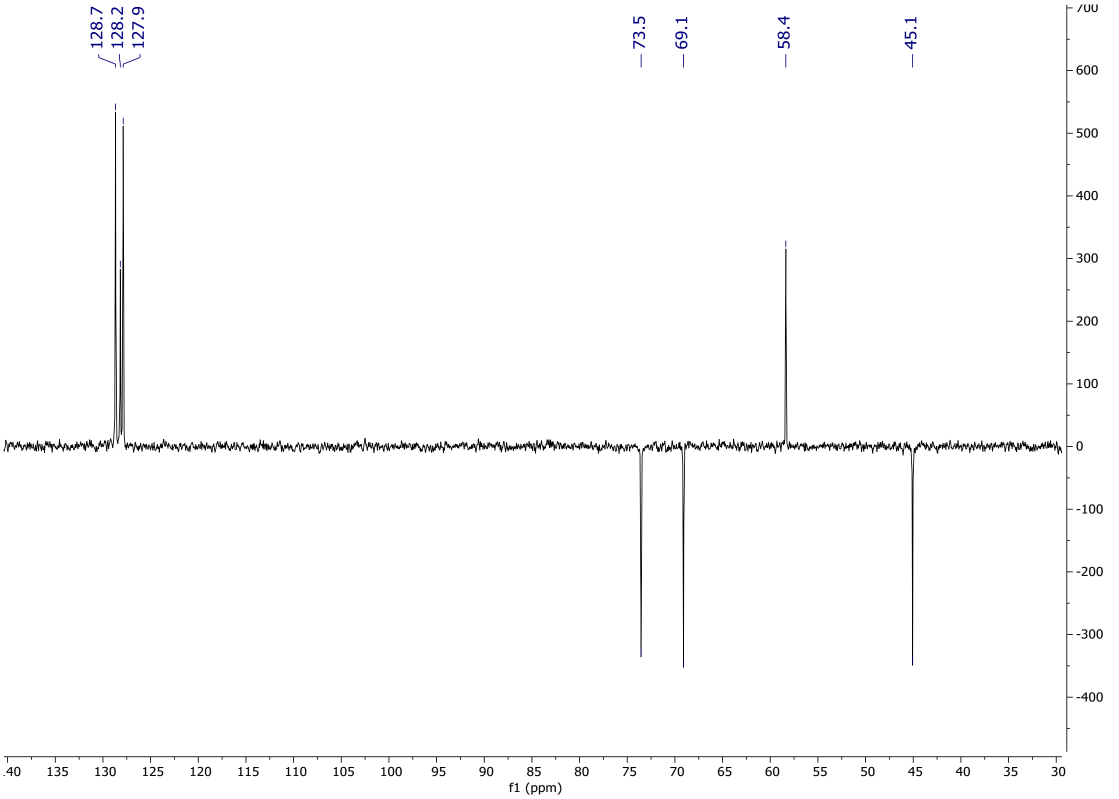
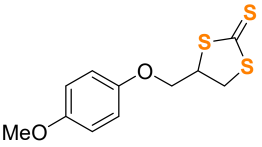


Figure SI_29. DEPT-135 NMR for **2i** in $CDCl_3$ (75 MHz).

4-((4-Methoxyphenoxy)methyl)-1,3-dithiolane-2-thione (2j)



Prepared according to protocol **SP1**. Yellow oil (135 mg, 56% yield). Purified by flash chromatography (Hexane/EtOAc, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.85 (s, 4H), 4.66-4.56 (m, 1H), 4.32 (t, *J* = 9.4 Hz, 1H), 4.24-4.04 (m, 3H), 3.78 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 227.0 (C), 154.6 (C), 151.9 (C), 115.9 (2×CH), 114.9 (2×CH), 67.5 (CH_2), 57.6 (CH), 55.8 (CH_3), 45.1 (CH_2).[6]

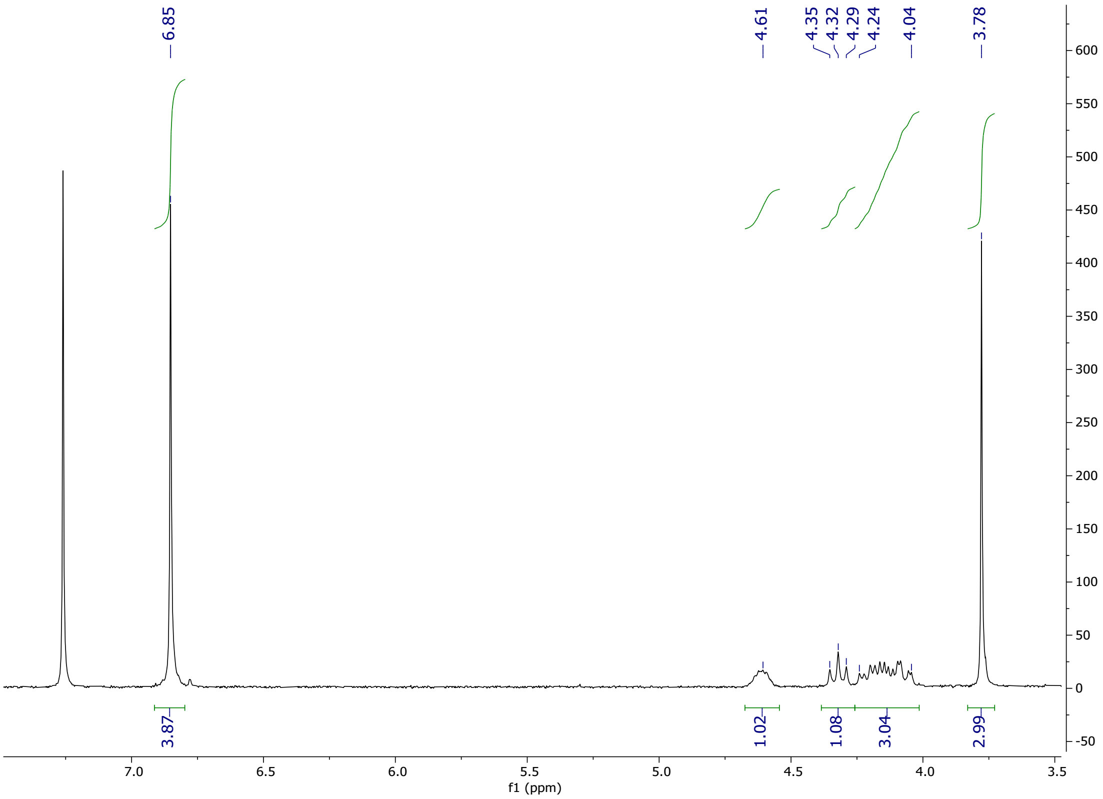


Figure SI_30. ^{1}H-NMR for **2j** in $CDCl_3$ (300 MHz).

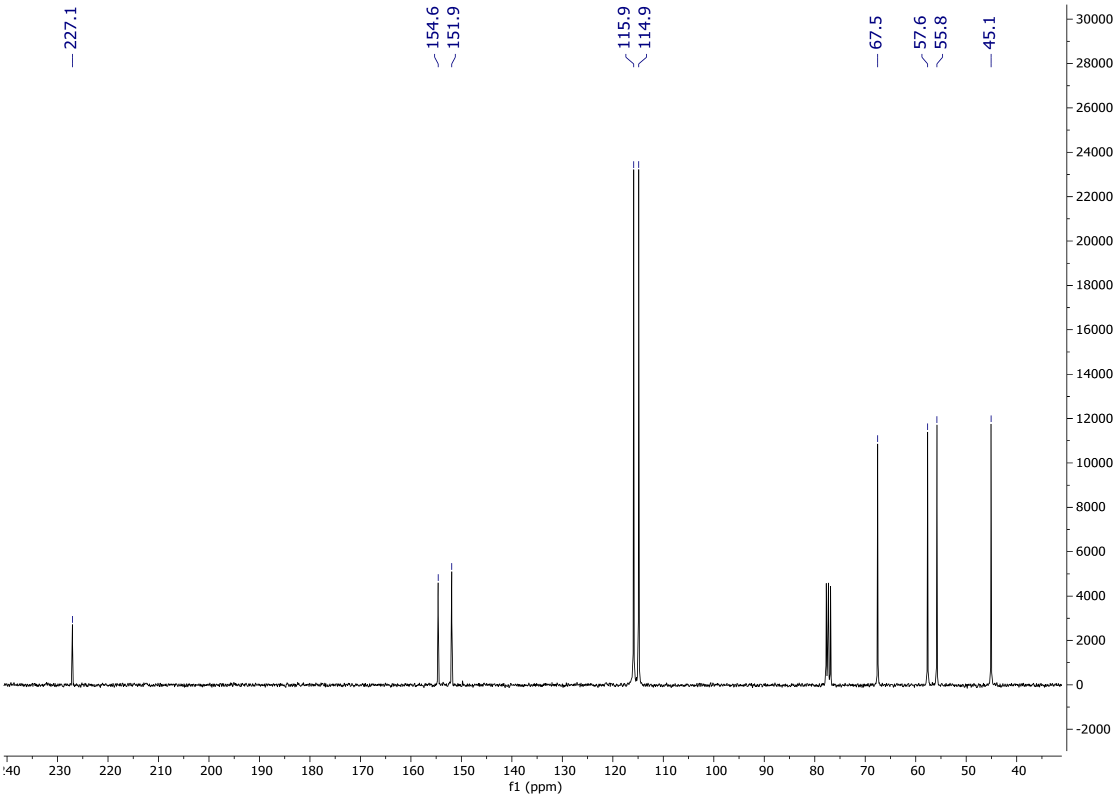


Figure SI_31. ^{13}C-NMR for **2j** in CDCl$_3$ (75 MHz).

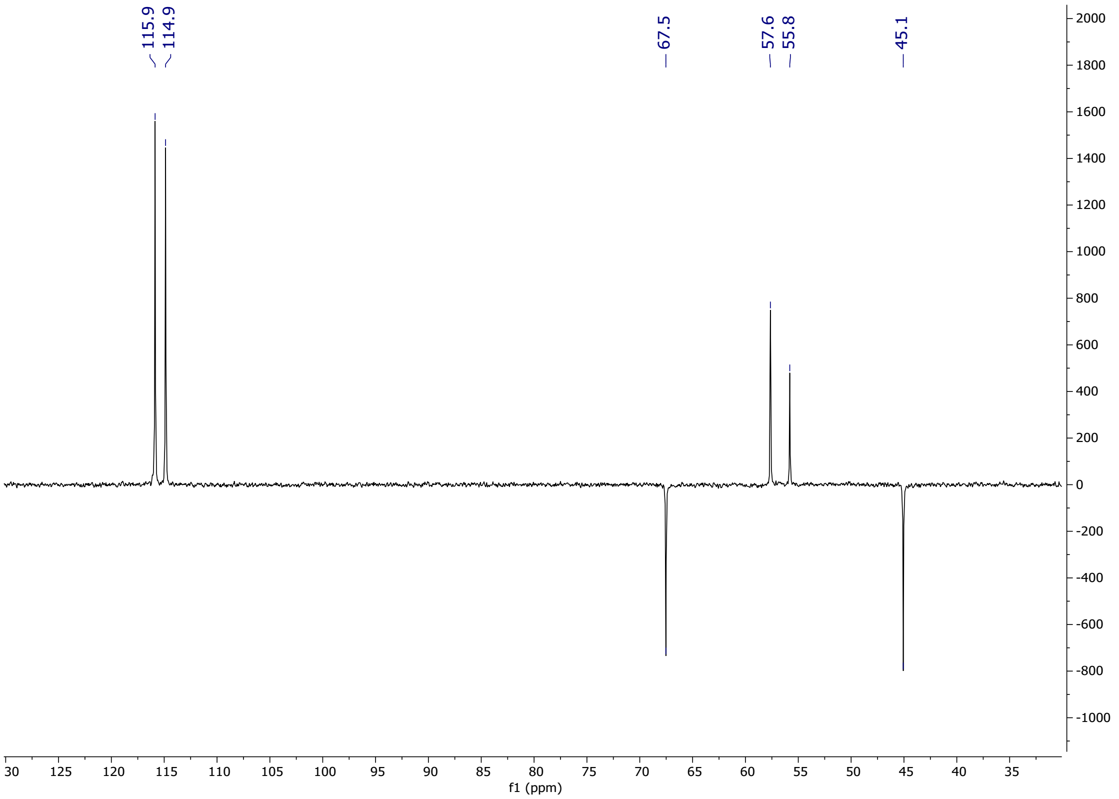
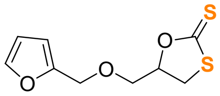


Figure SI_32. DEPT-135 NMR for **2j** in CDCl$_3$ (75 MHz).

5-((Furan-2-ylmethoxy)methyl)-1,3-oxathiolane-2-thione (4h)



Prepared according protocol **SP2**. Yellow oil (145 mg, 71% yield). Purified by flash chromatography (Hexane/EtOAc, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (t, *J* = 1.4 Hz, 1H), 6.37 (d, *J* = 1.4 Hz, 2H), 5.24-5.16 (m, 1H), 4.60-4.51(m, 2H), 3.86-3.76 (m, 2H), 3.68-3.54 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.0 (C), 150.7 (C), 143.2 (CH), 110.5 (CH), 110.3 (CH), 89.1 (CH), 68.2 (CH_2), 65.3 (CH_2), 36.1 (CH_2).[6]

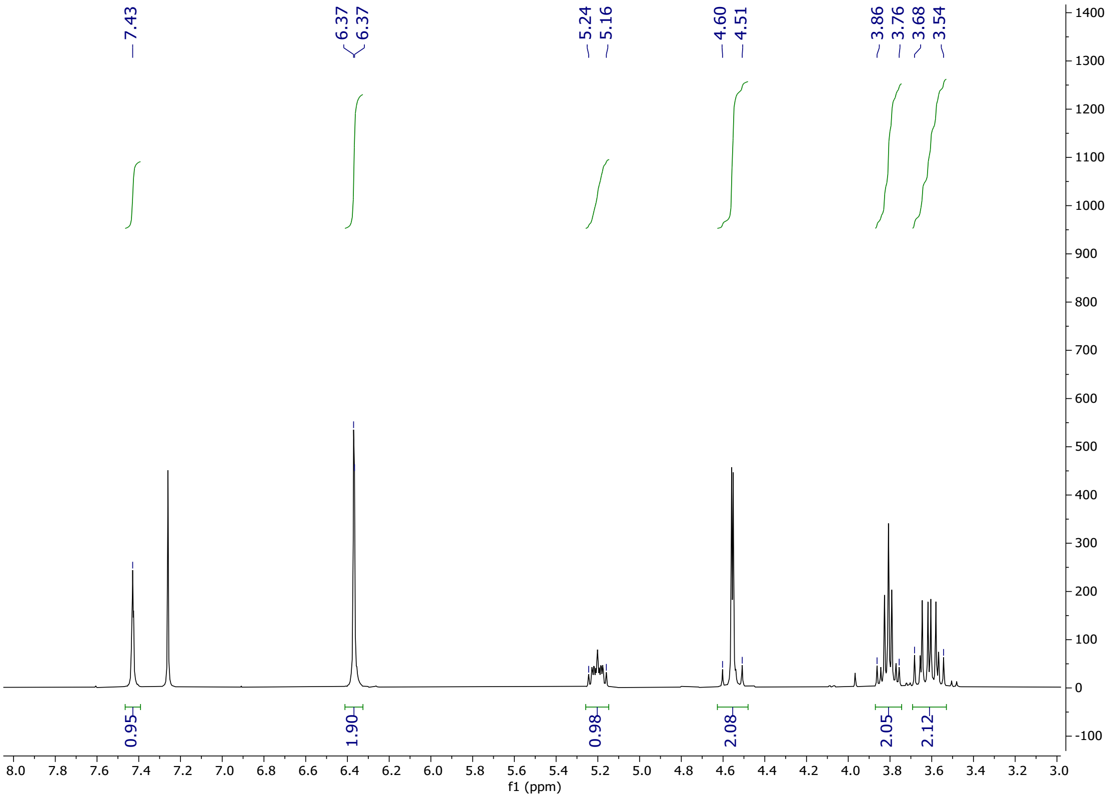


Figure SI_33. ^{1}H-NMR for **4h** in $CDCl_3$ (300 MHz).

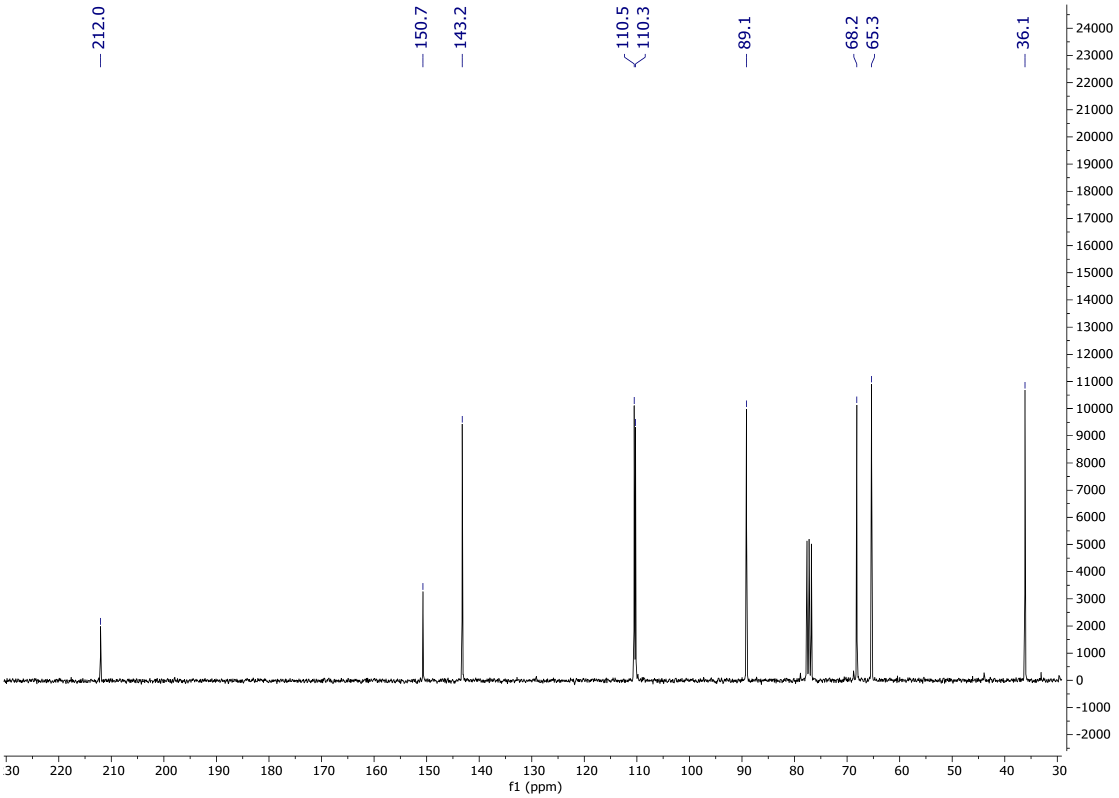


Figure SI_34. ^{13}C-NMR for **4h** in $CDCl_3$ (75 MHz).

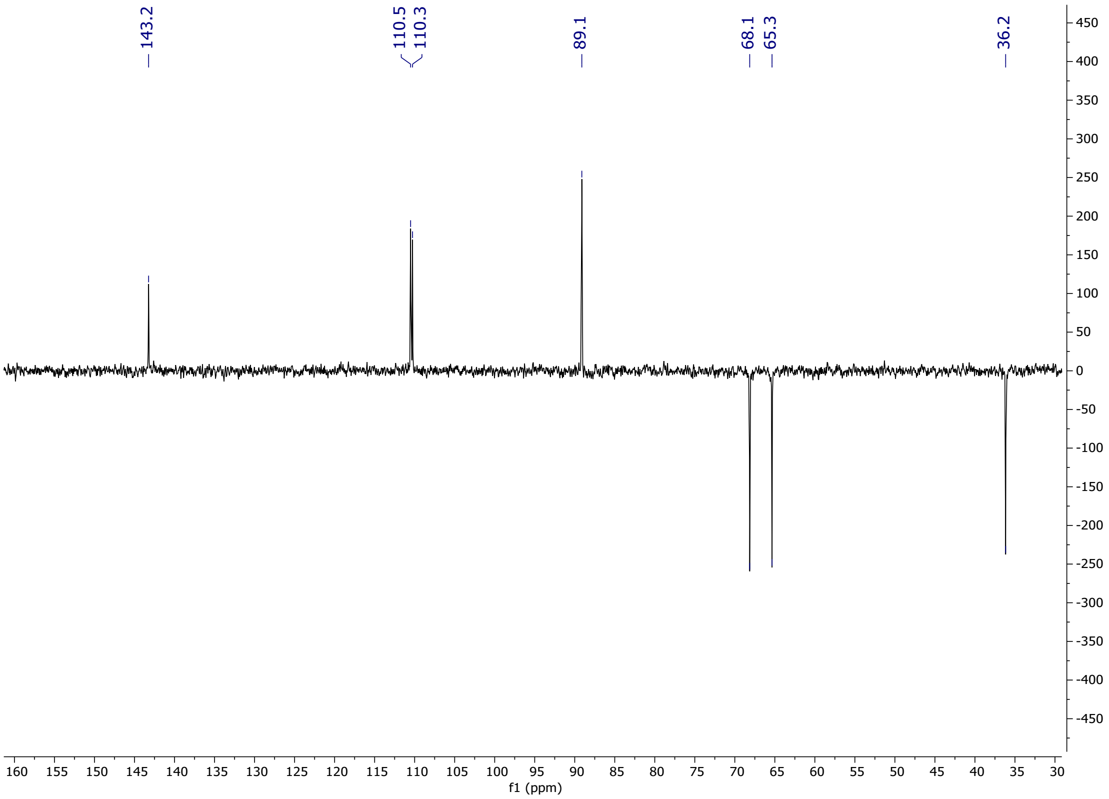
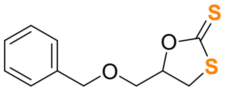


Figure SI_35. DEPT-135 NMR for **4h** in $CDCl_3$ (75 MHz).

5-((Benzyloxy)methyl)-1,3-oxathiolane-2-thione (4i)



Prepared according to protocol **SP2**. Yellow oil (171 mg, 81% yield). Purified by flash chromatography (Hexane/EtOAc, 4:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.41-7.30 (m, 5H), 5.30-5.20 (m, 1H), 4.66-4.56 (m, 2H), 3.87-3.76 (m, 2H), 3.73-3.57 (m, 2H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 212.0 (C), 137.2 (C), 128.6 (2×CH), 128.1 (CH), 127.9 (2×CH), 89.2 (CH), 73.8 (CH$_2$), 68.6 (CH$_2$), 36.2 (CH$_2$).[6]

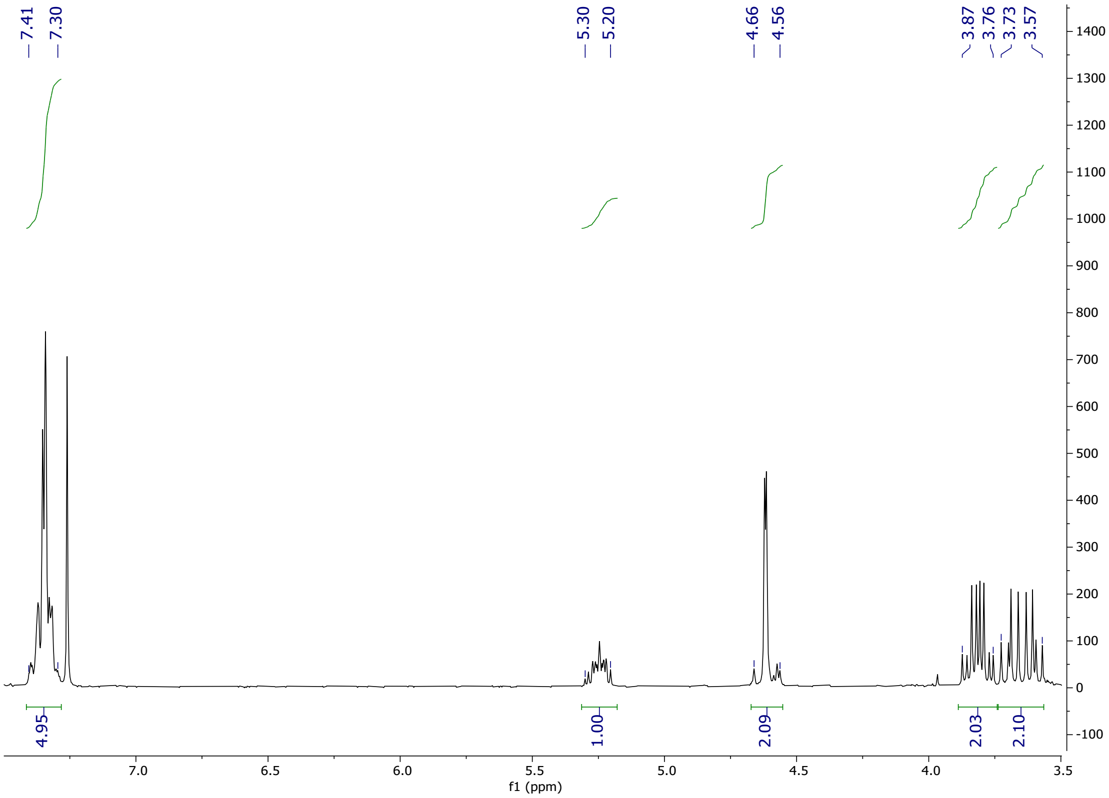


Figure SI_36. ^{1}H-NMR for **4i** in CDCl$_3$ (300 MHz).

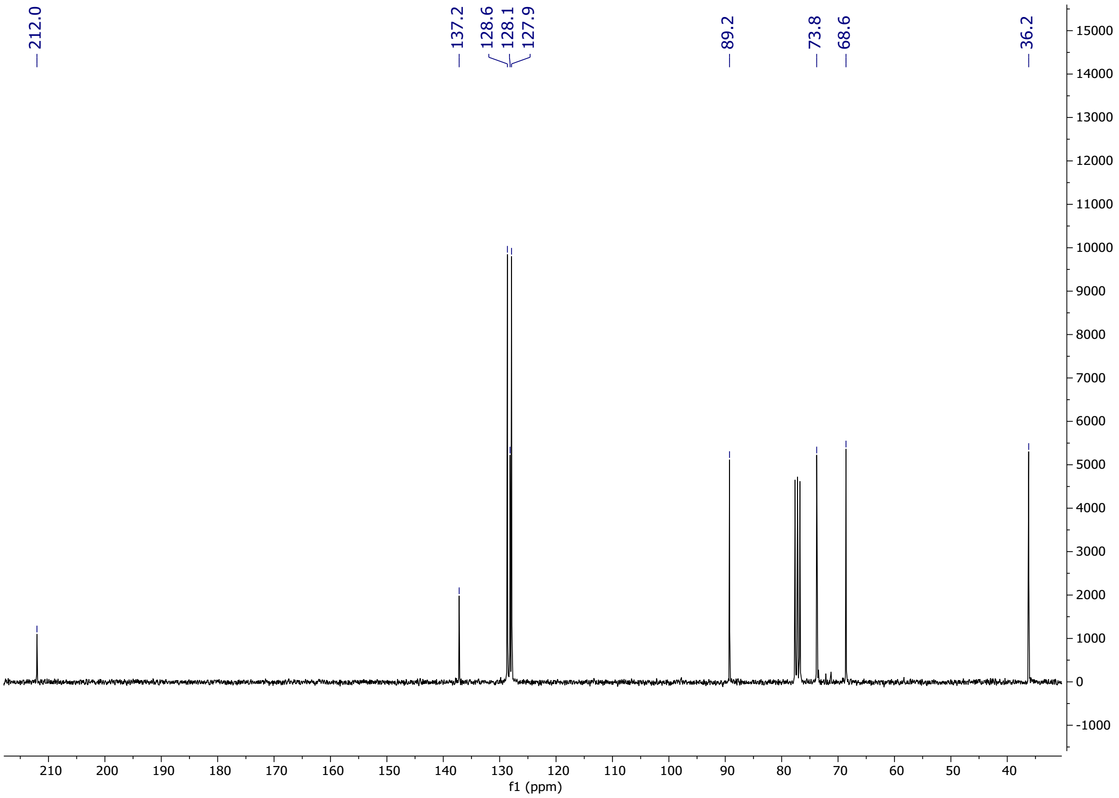


Figure SI_37. ^{13}C-NMR for **4i** in $CDCl_3$ (75 MHz).

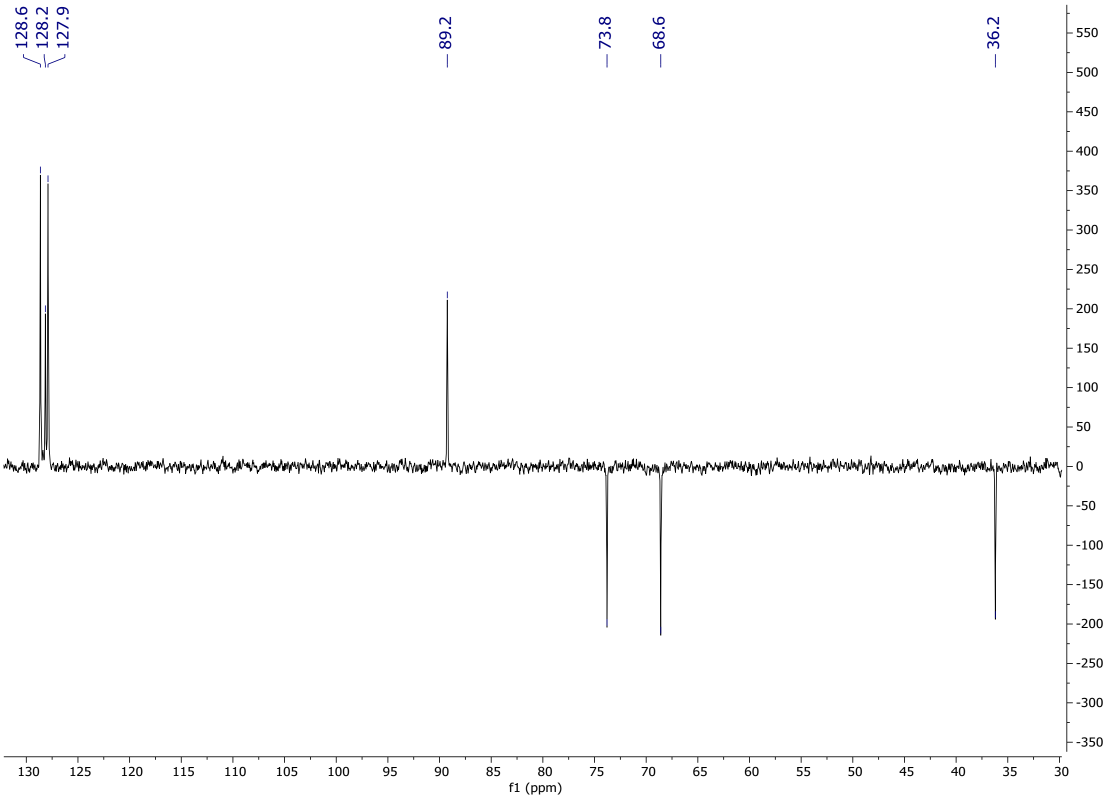
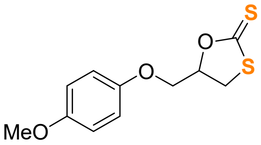


Figure SI_38. DEPT-135 NMR for **4i** in $CDCl_3$ (75 MHz).

5-((4-Methoxyphenoxy)methyl)-1,3-oxathiolane-2-thione (4j)



Prepared according to protocol **SP2**. Pale-yellow oil (165 mg, 73% yield). Purified by flash chromatography (Hexane/EtOAc, 4:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.89-6.82 (m, 4H), 5.46-5.38 (m, 1H), 4.31-4.22 (m, 2H), 3.84-3.70 (m, 5H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 211.7 (C), 154.6 (C), 151.9 (C), 115.8 (2×CH), 114.8 (2×CH), 88.2 (CH), 67.3 (CH$_2$), 55.8 (CH$_3$), 36.2 (CH$_2$).[6]

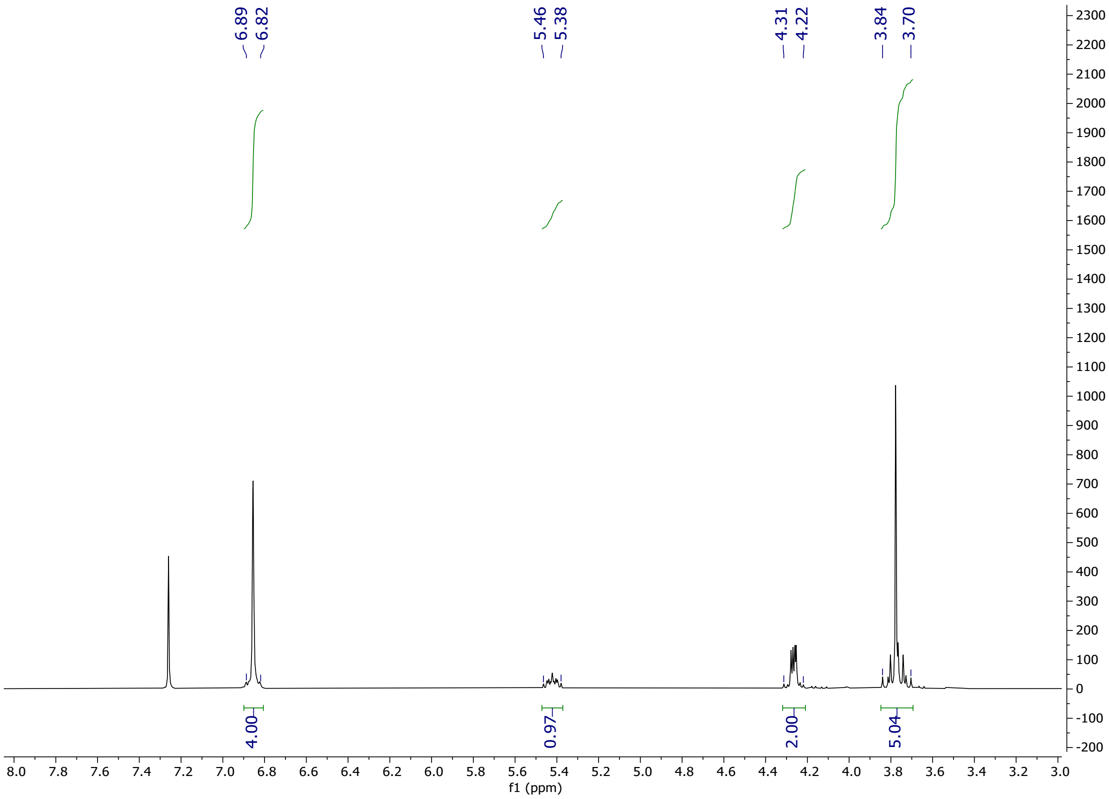


Figure SI_39 ^{1}H-NMR for **4j** in CDCl$_3$ (300 MHz).

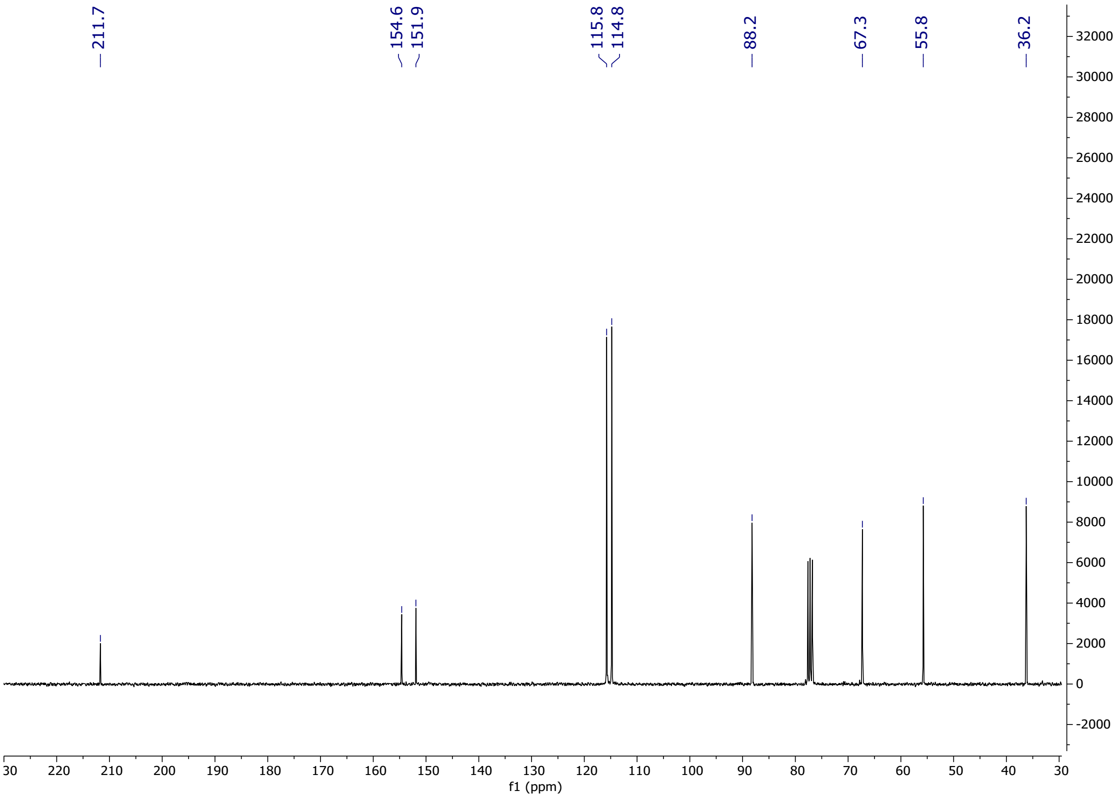


Figure SI_40. ^{13}C-NMR for **4j** in CDCl$_3$ (75 MHz).

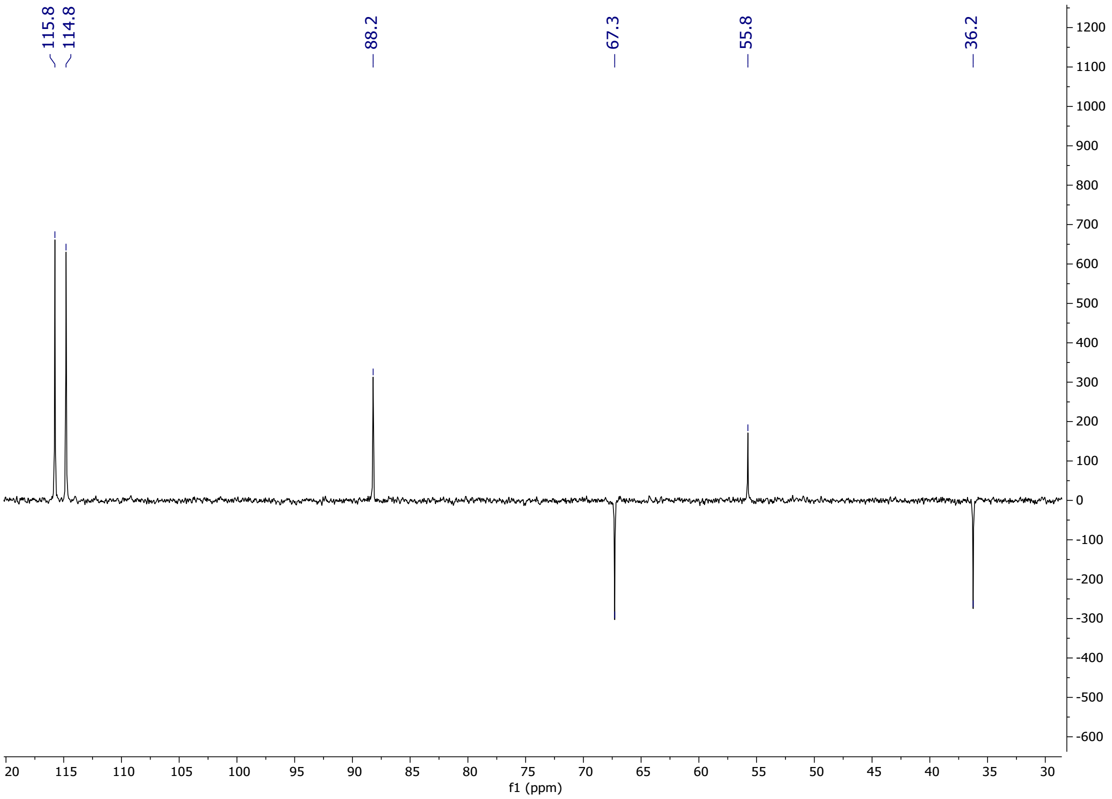
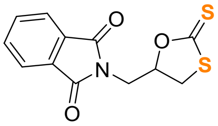


Figure SI_41. DEPT-135 NMR for **4j** in CDCl$_3$ (75 MHz).

5-(Phthalimidylmethyl)-1,3-oxathiolane-2-thione (4k)



Prepared according to protocols **SP1** and **SP2**. Pale brown solid (128 mg, 52% and 175 mg, 71% yield respectively). Purified by flash chromatography (Hexane/EtOAc, 4:1, to EtOAc). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.91-7.87 (m, 2H), 7.80-7.74 (m, 2H), 5.48-5.39 (m, 1H), 4.27 (dd, *J* = 14.2, 6.7 Hz, 1H), 4.05 (dd, *J* = 14.2, 5.7 Hz, 1H), 3.73 (dd, *J* = 11.4, 7.0 Hz, 1H), 3.58 (dd, *J* = 11.4, 7.1 Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 210.6 (C), 167.8 (2×C), 134.5 (2×CH), 131.6 (2×C), 123.8 (2×CH), 86.8 (CH), 39.5 (CH$_2$), 37.4 (CH$_2$).[10]

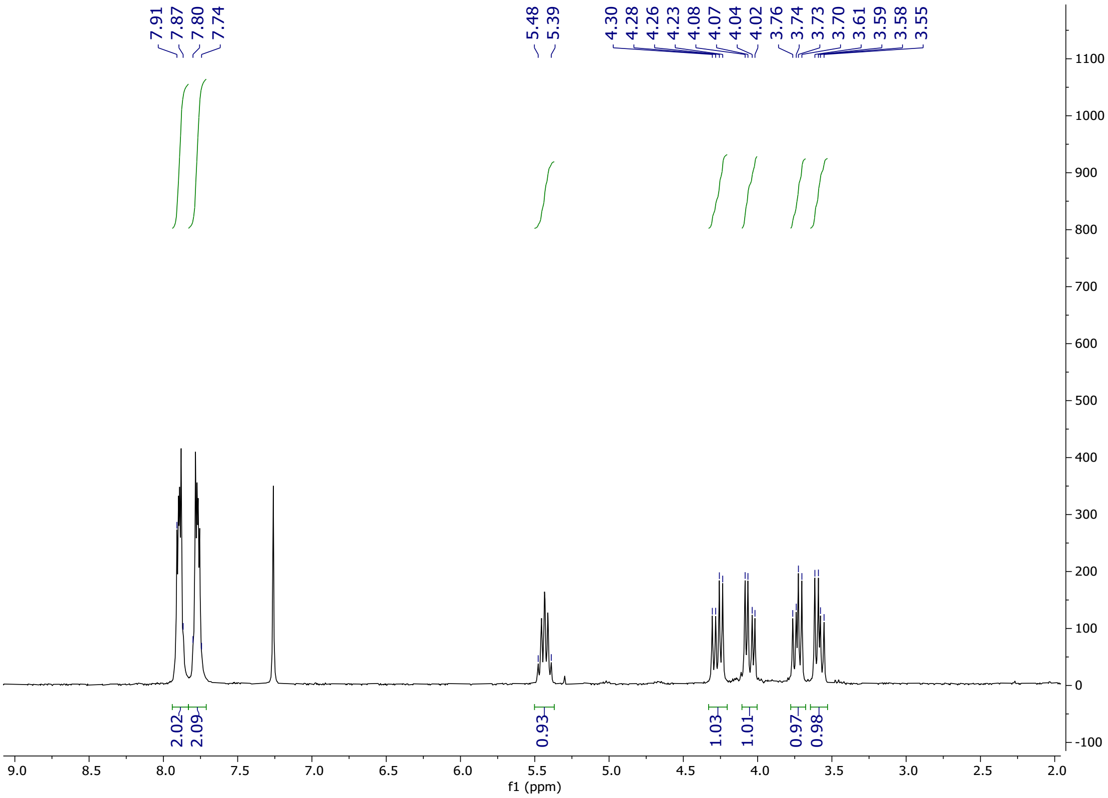


Figure SI_42. ^{1}H-NMR for **4k** in CDCl$_3$ (300 MHz).

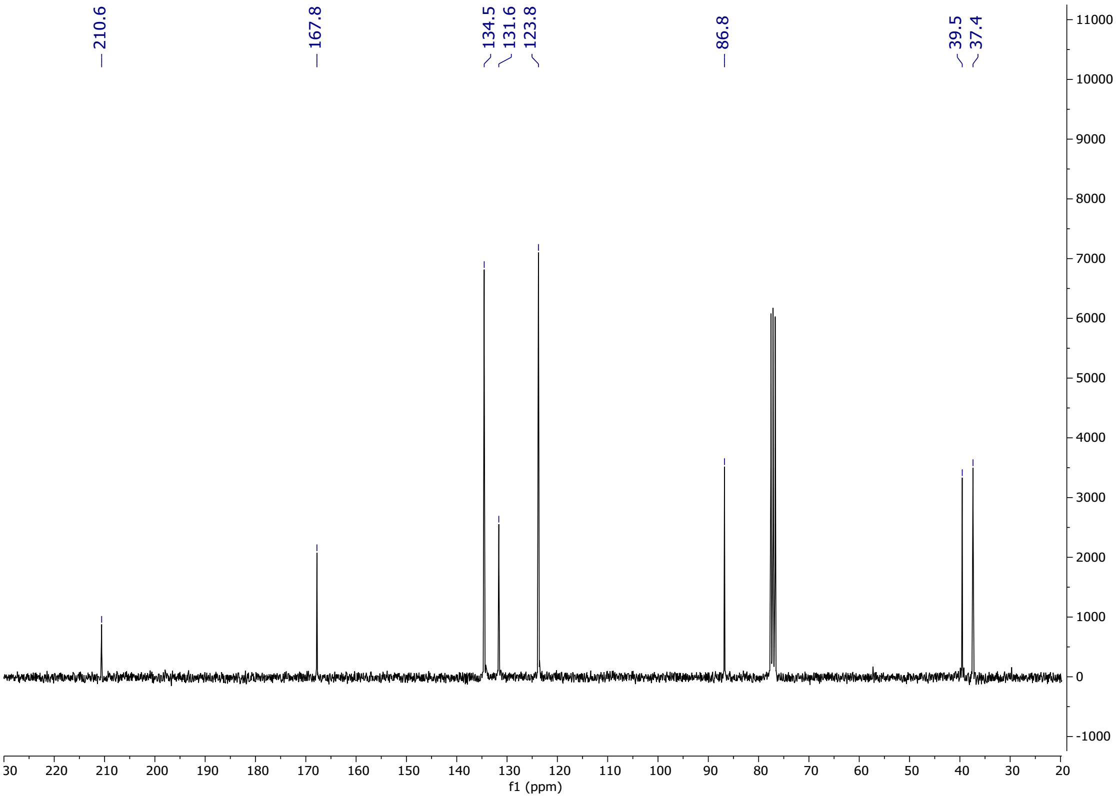


Figure SI_43. ^{13}C-NMR for **4k** in CDCl$_3$ (75 MHz).

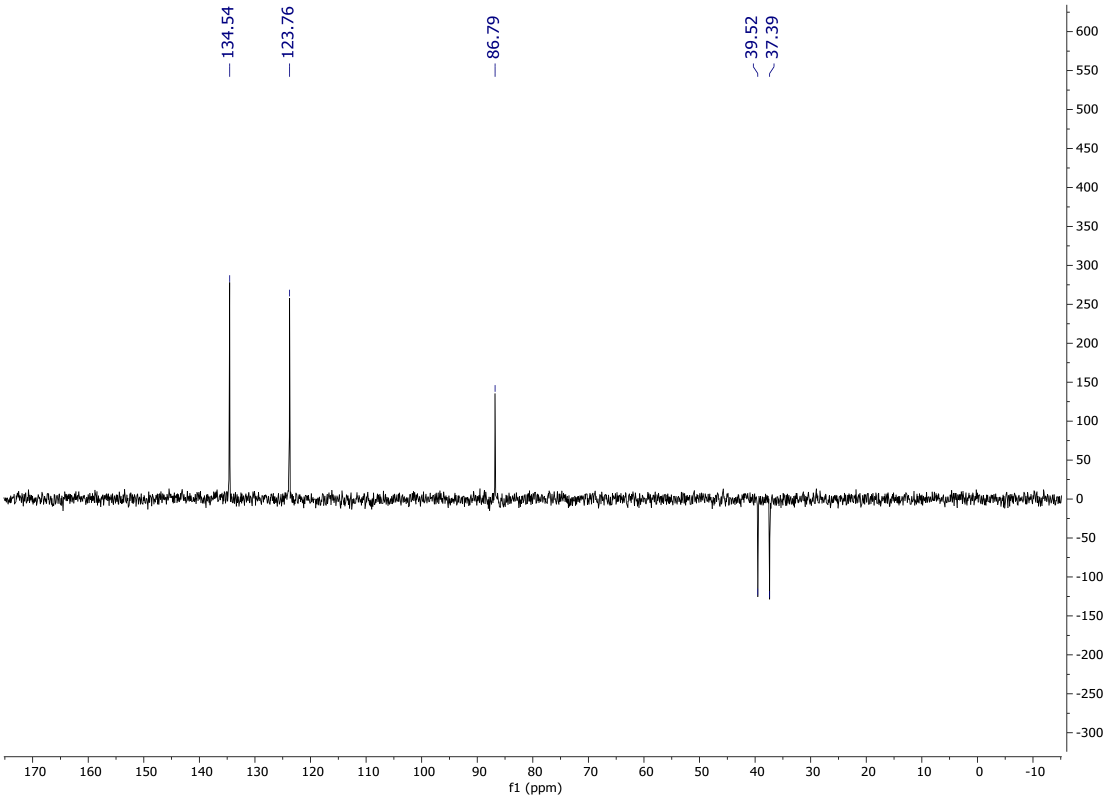
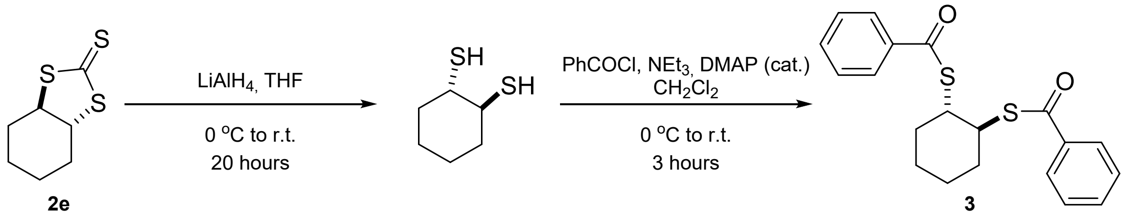


Figure SI_44. DEPT-135 NMR for **4k** in CDCl$_3$ (75 MHz).

6. SYNTHESIS AND CHARACTERISATION OF BIS-THIOESTER 3

Product **3** was prepared according to the following synthetic sequence:



2e

3

A solution of compound **2e** (167 mg, 0.88 mmol, 1 equiv.) in dry THF (5 mL) was cooled to 0 ºC and $LiAlH_4$ (42 mg, 1.1 mmol, 5 equiv.) was carefully added by portions during 15 min. The resulting solution was stirred for 20 h at room temperature and then the reaction was quenched with HCl 6N at 0 ºC (the aqueous solution was dropped until no effervescence was observed). Salts were filtered off through Celite®, and the filtrate washed with EtOAc (2 x 5 mL). Organic phases were combined, dried over Na_2SO_4 and the solvent evaporated under reduced pressure, obtaining a reaction crude that was purified by flash chromatography (Hex:EtOAc, 99:1). *trans*-1,2-Cyclohexanedithiol was afforded as a colourless oil (67 mg, 51% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.75-2.64 (m, 2H), 2.23-2.15 (m, 2H), 2.00 (d, *J* = 5.9 Hz, 2H), 1.78- 1.73 (m, 2H), 1.48-1.29 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 48.3 (2×CH), 36.9 (2×CH_2), 26.5 (2×CH_2).[17]

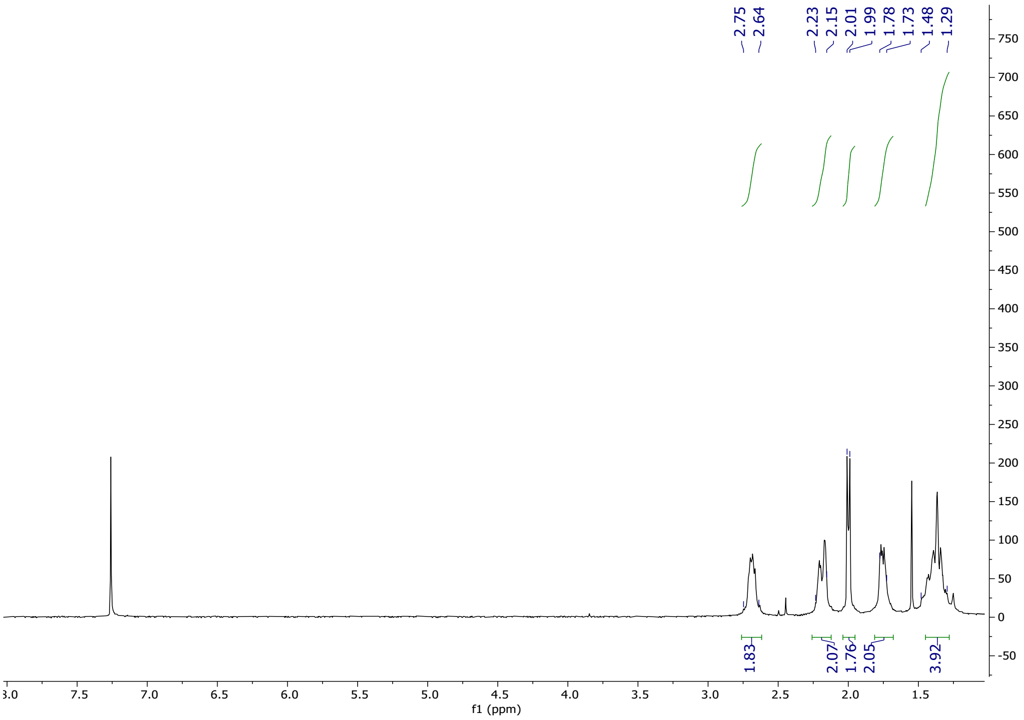


Figure SI_45. ^{1}H-NMR for *trans*-1,2-cyclohexanedithiol in $CDCl_3$ (300 MHz).

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[12] J. Houk, G. M. Whitesides, *J. Am. Chem. Soc.*, 1987, **109**, 6825.

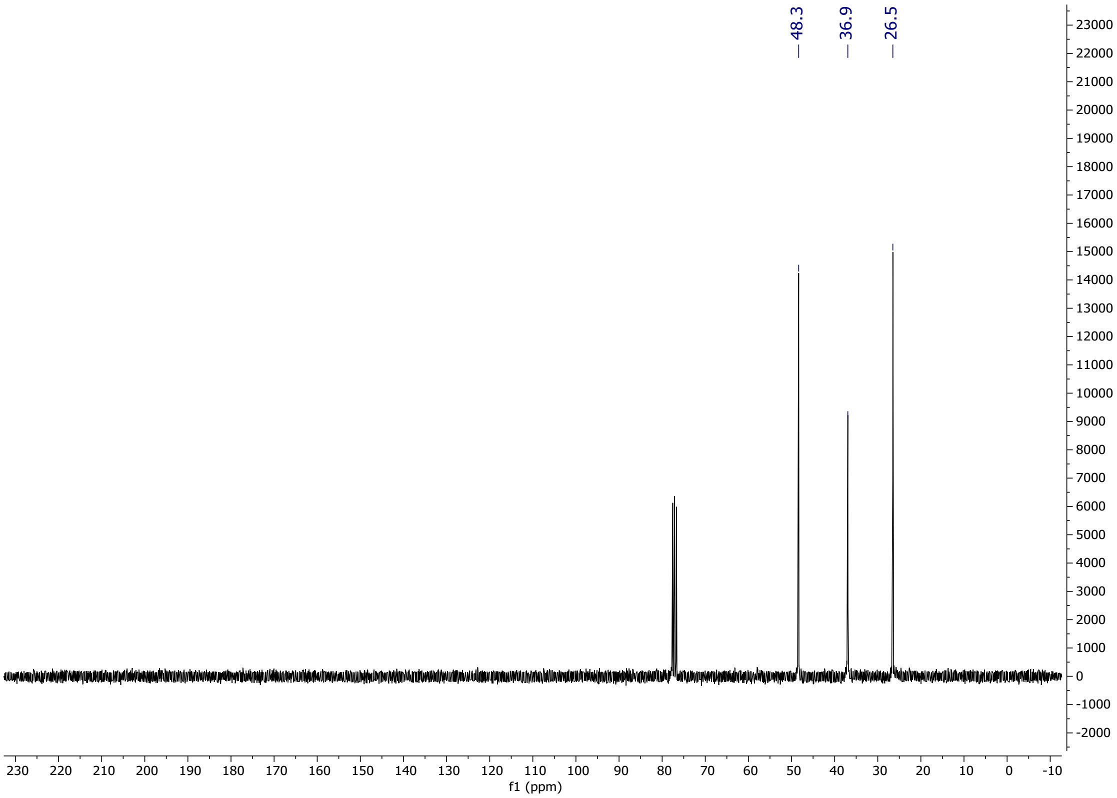


Figure SI_46. ^{13}C-NMR for *trans*-1,2-cyclohexanedithiol in $CDCl_3$ (75 MHz).

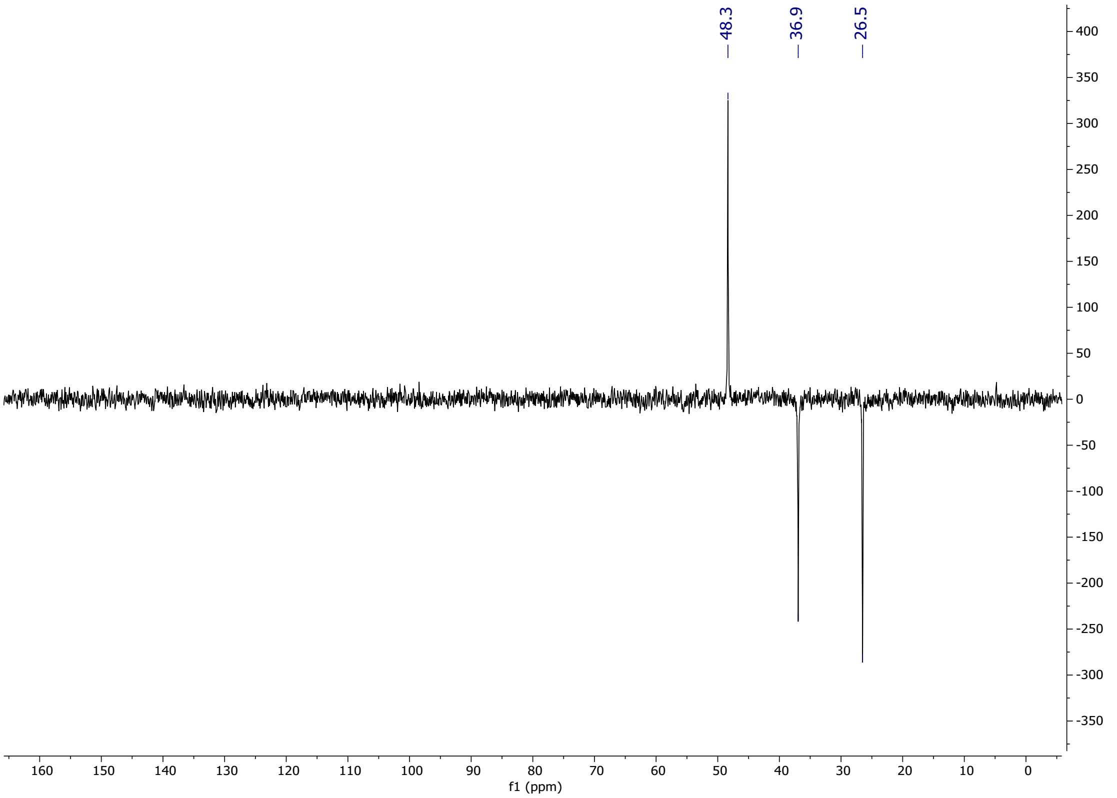


Figure SI_47. DEPT-135 NMR for *trans*-1,2-cyclohexanedithiol in $CDCl_3$ (75 MHz).

trans-(Cyclohexane-1,2-diyl)-dibenzothioate (3)

To a solution of *trans*-1,2-cyclohexanedithiol (33 mg, 0.22 mmol) in dry CH_2Cl_2 (2 mL), dry Et_3N (368 µL, 2.64 mmol, 6 equiv.) and DMAP (27 mg, 0.22 mg, 0.5 equiv.) were successively added under argon atmosphere and the resulting mixture was cooled to 0 ºC. Then, benzoyl chloride (154 µL, 1,32 mmol, 3 equiv.) was added dropwise and the reaction mixture stirred for 3 h at room temperature. Sequently, the crude was diluted with 10 mL of CH_2Cl_2 and quenched with 10 mL 1N HCl, the phases were separated and the aqueous phase extracted with CH_2Cl_2 (3 x 10 mL). Organic phases were combined, dried over Na_2SO_4 and the solvent evaporated under reduced pressure, obtaining a reaction crude that was purified by flash chromatography (Hex:EtOAc, 30:1), affording *trans*-(cyclohexane-1,2-diyl)-dibenzothioate **3** as a white solid (59 mg, 75% yield). The product was crystallized for X-Ray analysis from THF/Hexanes. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98-7.94 (m, 4H), 7.56 (t, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 4H), 3.97-3.95 (m, 2H), 2.30-2.26 (m, 2H), 1.86-1.70 (m, 4H), 1.62-1.54 (m, 2H + H_2O). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.0 (2×C=O), 137.0 (2×C), 133.3 (2×CH), 128.6 (4×CH), 127.3 (4×CH), 46.4 (2×CH), 33.7 (2×CH_2), 25.3 (2×CH_2). HMRS (ESI$^+$) calculated for $C_{20}H_{20}NaO_2S_2$ [(M+Na)$^+$]: 379.0797; found: 379.0784.

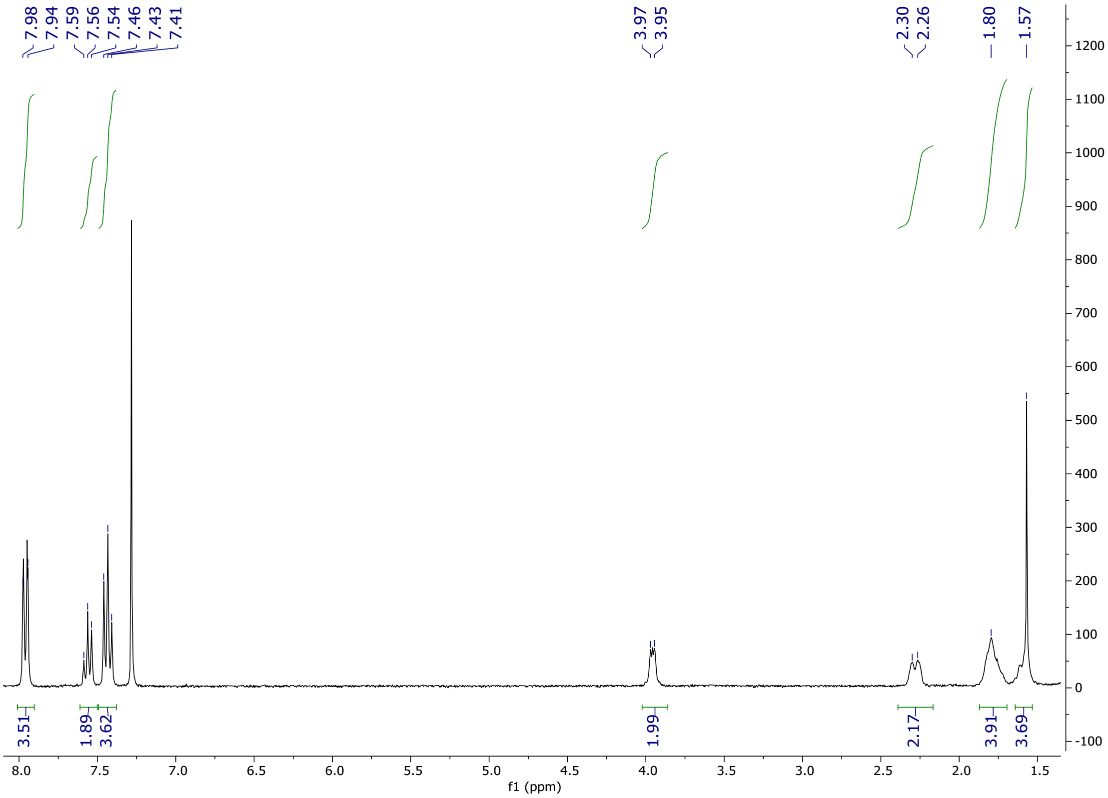


Figure SI_48. ^{1}H-NMR for **3** in $CDCl_3$ (300 MHz).

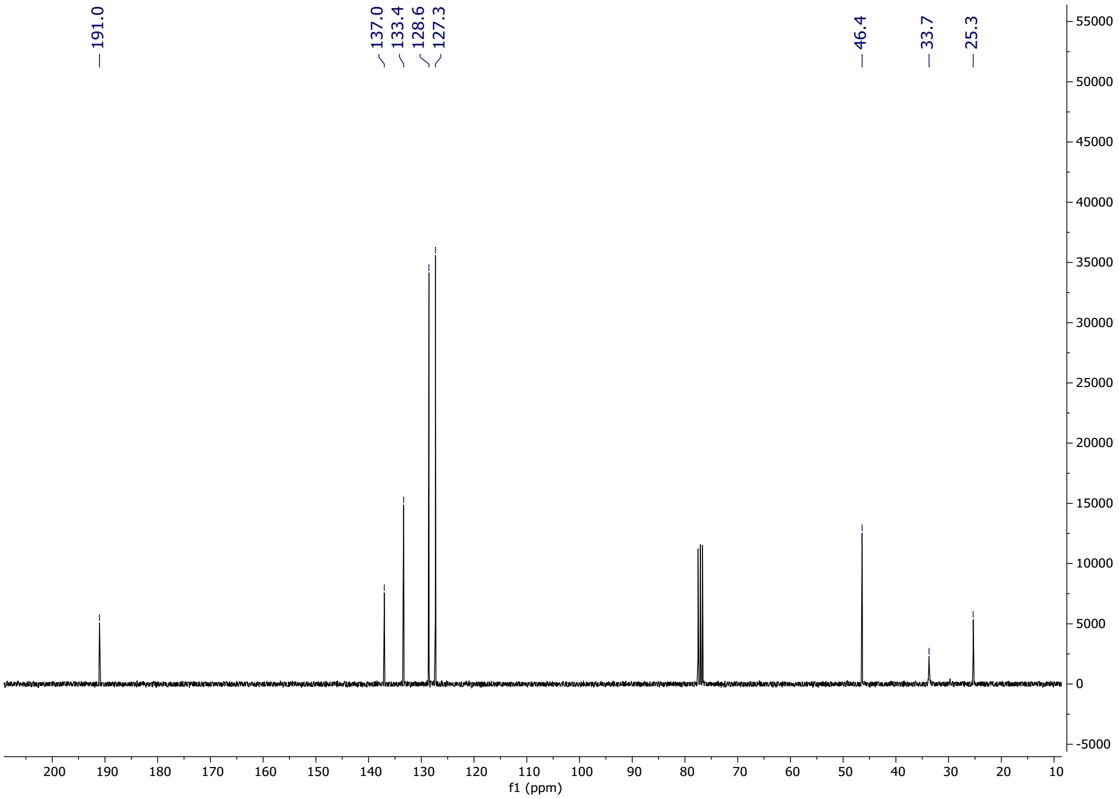


Figure SI_49. ^{13}C-NMR for **3** in $CDCl_3$ (75 MHz).

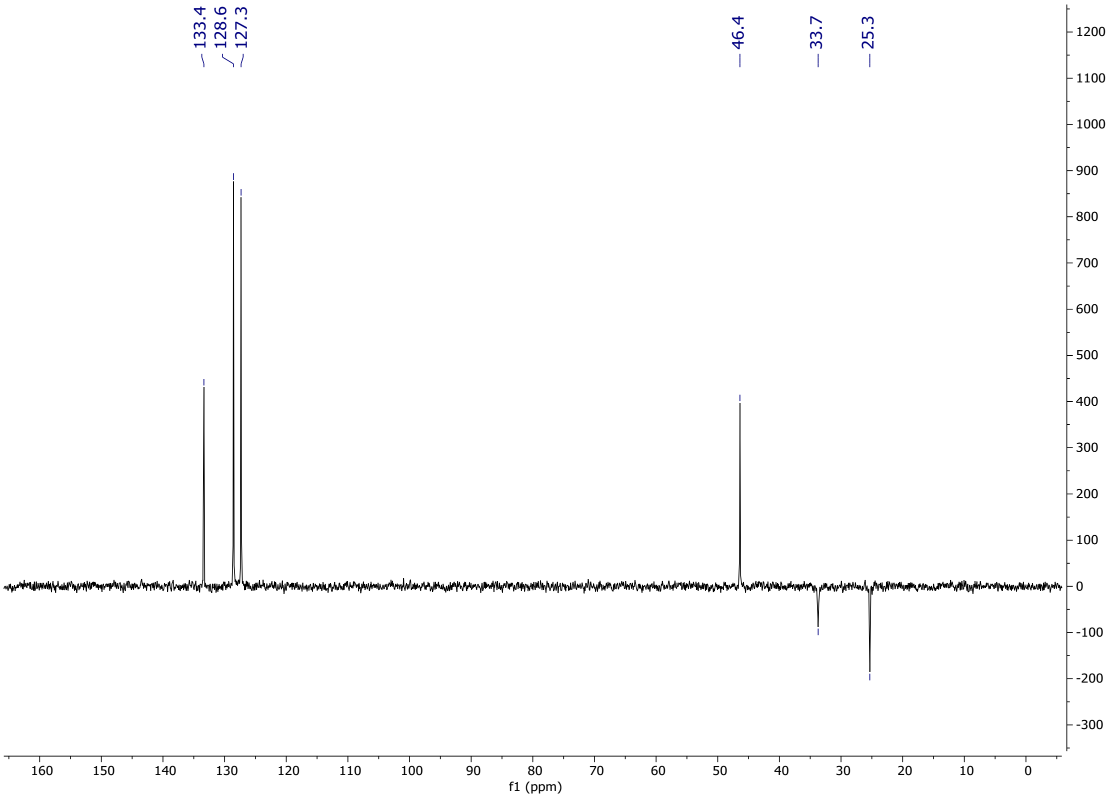
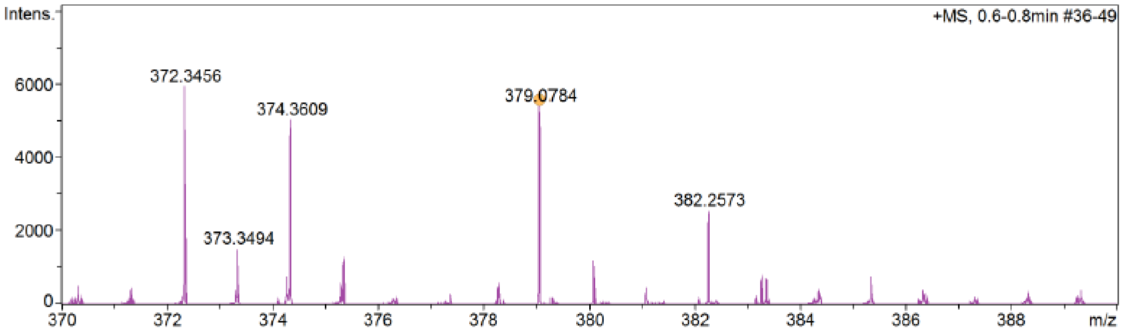


Figure SI_50. DEPT-135 NMR for **3** in $CDCl_3$ (75 MHz).

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.4 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	250 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
379.0784	1	C20H20NaO2S2	379.0797	3.5	n.a.	1	100.00	11.0	even	ok	M+Na

Figure SI_51. HRMS (ESI$^+$) spectrum for **3**.

7. HPLC ANALYSIS FOR DETERMINATION OF ENANTIOMERIC EXCESS

Optical purity of **2i** was measured by HPLC on a chiralcel OJ-H column (hexane/2-propanol 75:25), flow rate 0.8 mL/min, 40°C. The absolute configuration was assigned comparing the experimental specific rotation values obtained with those reported in the literature values.[10]

Experimental: $[\alpha]_D^{19}$= +142.0 (c=0.5, $CHCl_3$), for >99% *ee*.
Literature: $[\alpha]_D^{28}$= +154.3 (c=0.7, $CHCl_3$), for 98% *ee* of (*R*)-enantiomer.

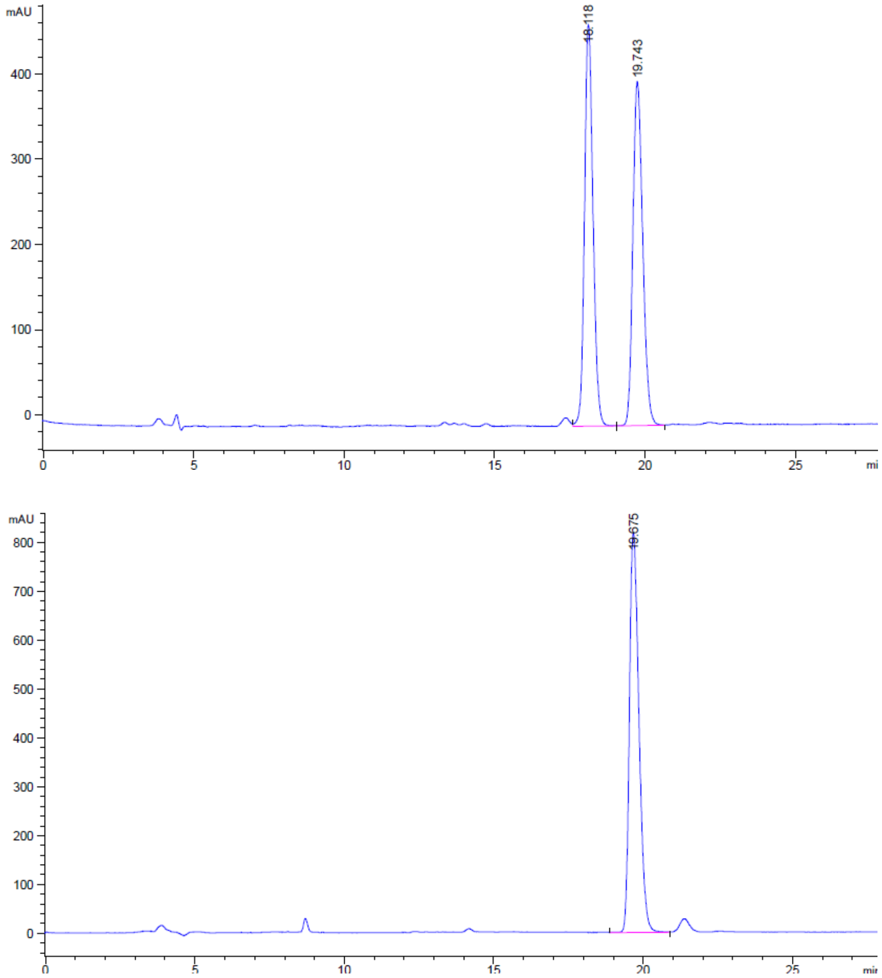


Figure SI_52. HPLC chromatograms for (±)-**2i** and (*R*)-**2i**, obtained after purification.

Optical purity of **4i** was measured by HPLC on a chiralcel AD-H column (hexane/2-propanol 95:5), flow rate 0.8 mL/min, 40°C. The absolute configuration was assigned comparing the experimental specific rotation values obtained with those reported in the literature values.[10]

Experimental: $[\alpha]_D^{19}$= +37.9 (c=1, $CHCl_3$), for >99% *ee*
Literature: $[\alpha]_D^{27}$= +39.6 (c=1.3, $CHCl_3$), for 99% *ee* of (*S*)-enantiomer.

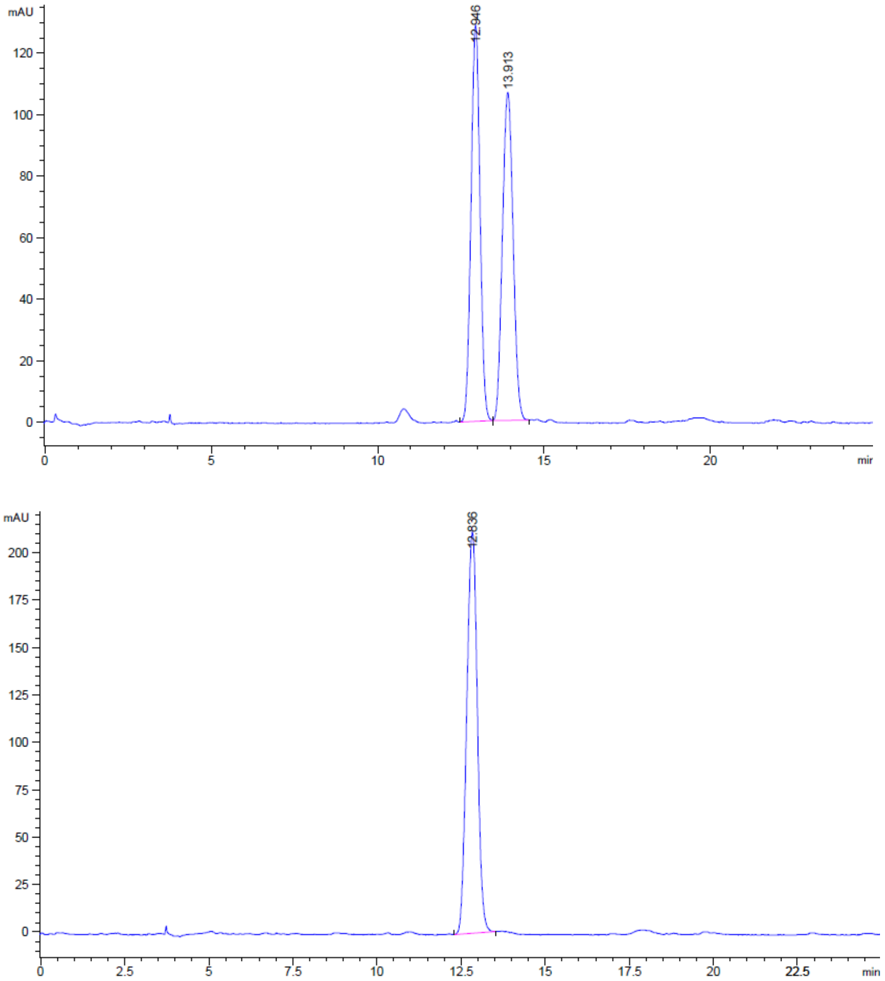


Figure SI_53. HPLC chromatograms for (±)-**4i** and (*S*)-**4i**, obtained after purification.

8. X-RAY ANALYSIS

Crystals of **2f**, **2g** and **3** were analysed by X-ray diffraction. A selection of crystal, measurement and refinement data is given in Table SI_10. Diffraction data were collected on a Oxford Diffraction Xcalibur Onyx Nova Geminy single crystal diffractometer. Empirical absorption corrections were applied using the SCALE3 ABSPACK algorithm as implemented in Chrysalis RED.[18] The structures were solved with SIR-2019.[19] Isotropic and full matrix anisotropic least square refinements were carried out using SHELXL.[20] All non-H atoms were refined anisotropically. All H atoms were set in calculated positions and were refined riding on their parent atoms. One of the two molecules found in the asymmetric unit of **2f** was partially disordered over two positions with a 54:46 occupancy ratio, requiring restraints on its geometrical and thermal parameters. The WINGX program system [21] was used throughout the structure determinations. The molecular plots were made with MERCURY.[22] The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers 2386775– 2386777 for **2f**, **2g** and **3**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif

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[18] *CrysAlisPro RED*, version 1.171.38.46: Oxford Diffraction Ltd., Oxford, UK, 2015.

[19] *SIR-2019*: Burla, M. C.; Caliandro, R.; Carroxxini, B.; Cascarano, G. L.; Cuocci, C.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G. Crystal structure determination and refinement via SIR2014. *J. Appl. Crystallogr.* 2015, **48**, 306.

[20] *SHELXL-2018*: Sheldrick, G. M. A short history of SHELX. *Acta Cryst.* 2008, **A64**, 112.

[21] *WINGX*, version 2021.3: Farrugia, L. WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* 2012, **45**, 849.

[22] *MERCURY*, version 2024.1.0 (build 401958): Cambridge Crystallographic Data Centre, Cambridge, UK, 2024.

Table SI_10. Crystal, measurement and refinement data for the compounds studied by X-ray diffraction.

	2f	**2g**	**3**
formula	$C_{14}H_{20}O_2S_6$	$C_{14}H_{16}OS_3$	$C_{20}H_{20}O_2S_2$
fw	412.66	296.45	356.48
cryst syst	triclinic	monoclinic	monoclinic
space group	*P*–1	*P*21/c	*C*2/c
a, Å	7.5479(4)	12.7687(3)	23.7180(5)
b, Å	11.0961(8)	8.3272(2)	5.8719(1)
c, Å	12.0292(8)	14.0444(4)	27.5681(5)
α, deg	103.921(6)	90	90
β, deg	97.793(5)	103.571(3)	106.489(2)
γ, deg	98.661(5)	90	90
V, $Å^3$	951.1(1)	1451.61(7)	3681.50(13)
Z	2	4	8
F(000)	432	624	1504
D_{calcd}, g cm^{-3}	1.441	1.356	1.286
μ, mm^{-1} (CuKα)	6.666	4.542	2.686
cryst size, mm	0.26 x 0.17 x 0.14	0.40 x 0.25 x 0.16	0.35 x 0.23 x 0.18
T, K	297(2)	297(2)	297(2)
θ range, deg	3.85 to 69.52	3.56 to 69.43	3.34 to 69.65
min./max. *h*, *k*, *l*	–9/8, –11/13, –14/14	–15/15, –10/8, –17/15	–28/28, –7/7, –29/33
no. collected reflns	10237	10722	15871
no. unique reflns	3533	2709	3431
no. reflns with $I > 2\sigma(I)$	2668	2362	3226
no. params/restraints	281/98	163/0	218/0
GOF (on F^2)	1.053	1.074	1.094
R_1 (on F, $I > 2\sigma(I)$)	0.053	0.045	0.037
wR_2 (on F^2, all data)	0.163	0.125	0.108
min./max. $\Delta\rho$, e $Å^{-3}$	–0.370/0.444	–0.314/0.342	–0.285/0.196
CCDC dep. no.	2386775	2386777	2386776

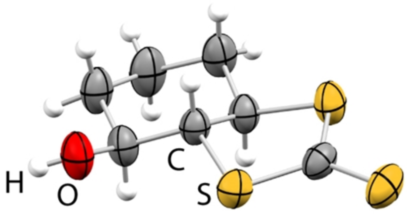

Figure SI_54. SCXRD molecular structure of **2f** (30% displacement ellipsoids; only the non-disorder molecule of the two found in the asymmetric unit is shown).

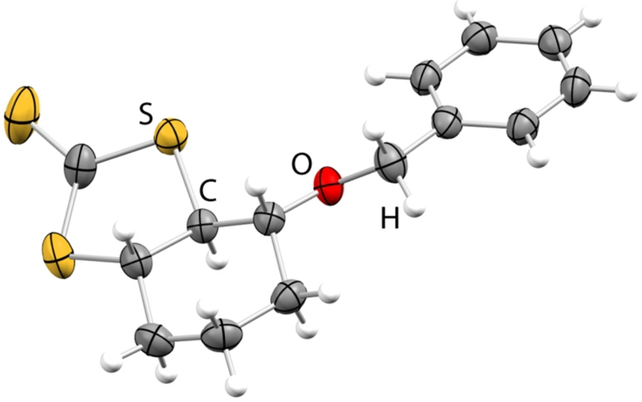

Figure SI_55. SCXRD molecular structure of **2g** (30% displacement ellipsoids).

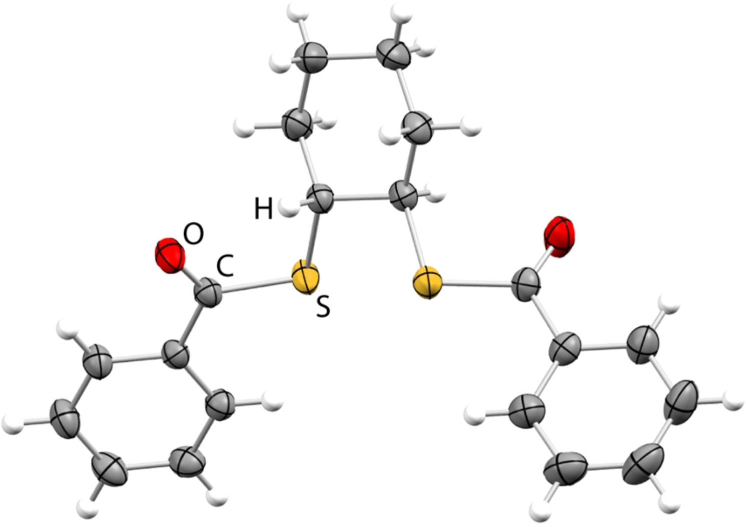

Figure SI_56. SCXRD molecular structure of **3** (30% displacement ellipsoids)

9. IR ANALYSIS

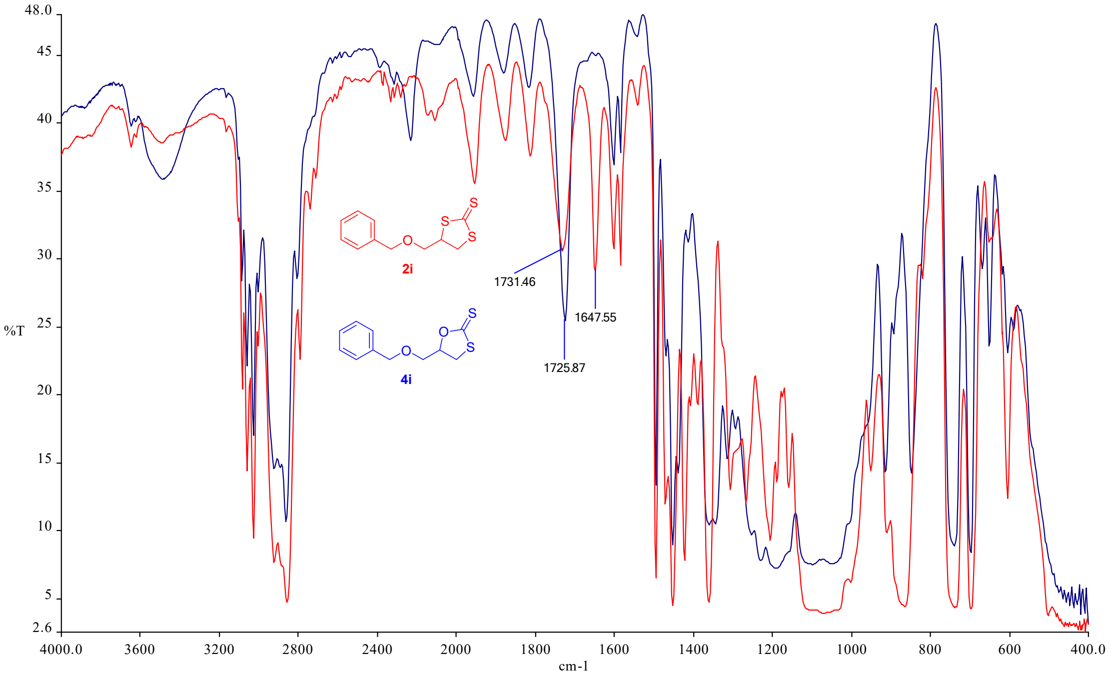

Figure SI_57. Overlay IR spectra for trithiocarbonate **2i** (red line) and dithiocarbonate **4i** (blue line)