Supporting Information

Disulfide Metathesis *via* Sulfur···Iodine Interaction and Photoswitchability

Ashis Mathuri, Milan Pramanik, Amarchand Parida and Prasenjit Mal*

School of Chemical Sciences, National Institute of Science Education and Research (NISER) Bhubaneswar, HBNI, PO Bhimpur-Padanpur, Via Jatni, District Khurda, Odisha 752050, India.

*Corresponding author: Prasenjit Mal, Tel.: +91 9439613856, E-mail: pmal@niser.ac.in

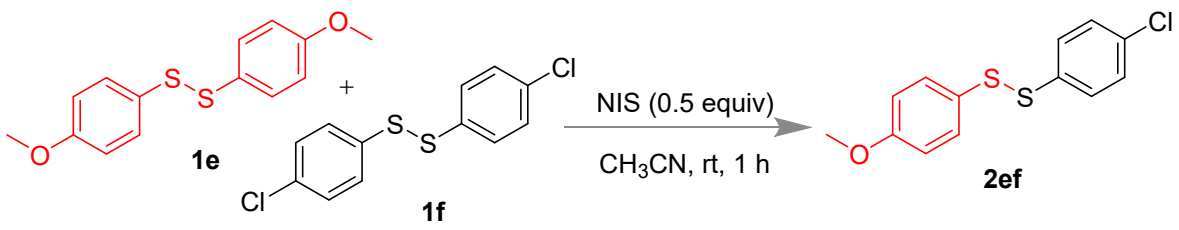
Content

EXPERIMENTAL SECTION

General Aspects. All the chemicals were purchased from commercial sources and used as received. All the reactions were generally carried out under an open atmosphere unless otherwise noted. The reactions were monitored by TLC on aluminum sheets pre-coated with silica gel. Chromatographic purifications of the compounds were performed using silica gel (Mess 230-400) and ethyl acetate/hexane as eluent. The ^{1}H and ^{13}C spectra of the compounds were recorded on Bruker 400 MHz and 700 MHz instruments at 25 ºC. The chemical shift value (δ, ppm) were reported with respect to the residual chloroform (7.26 for ^{1}H and 77.16 ppm for ^{13}C). Mass spectra were recorded as ESI-TOF (HRMS). Infrared spectra were recorded on neat solids using KBr pellets and described in wavenumber (cm^{-1}). Digital melting point apparatus was used to record the compound's melting point in degree centigrade (°C) and are uncorrected.

Synthesis

Representative procedure for the synthesis of unsymmetrical diaryldisulfide (2ef)

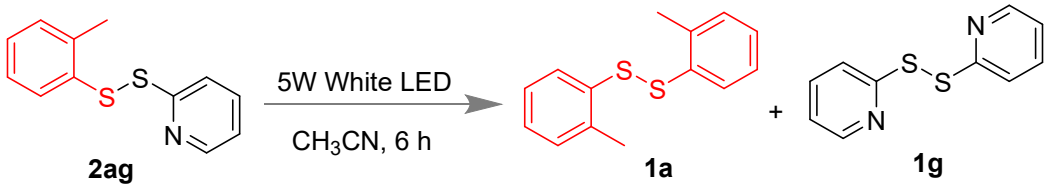


Scheme S1

In a 10 mL round-bottomed flask, a solution of compound **1e** (58 mg, 0.209 mmol) and **1f** (60 mg, 0.209 mmol) were prepared in 1.5 mL CH_3CN. Next, *N*-iodosuccinimide (NIS) (24 mg, 0.105 mmol) was added to the solution, and content was allowed to stir at room temperature

for 1 h. After completion, the reaction mixture was concentrated under reduced pressure. After that, the crude mixture was diluted in DCM, and organic content was washed with saturated $(NH_4)_2S_2O_8$ solution, dried over Na_2SO_4, and evaporated to dryness. The crude mixture was further purified by column chromatography using the hexane-EtOAc mixture as eluent.

Procedure for the synthesis of symmetrical diaryldisulfide using visible light.



Scheme S2

In an oven dried quartz tube unsymmetrical disulfide **2ag** (0.2439 mmol, 60 mg) was dissolved in 0.5 mL acetonitrile (CH_3CN) solvent. Then the reaction mixture was irradiated by 5W white LEDs light for 6 h. After completion of the reaction, acetonitrile (CH_3CN) was removed under reduced pressure. Then, the crude mixture purified by silica-gel column chromatography using distilled ethyl acetate and hexane as the eluent to afford **1a** with 38% (16 mg) and **1g** with 45% (17 mg) yields, respectively.

EPR Experiments. EPR spectra was recorded at 298 K using EPR spectrometer derived at 9.4335 GHz. Typical spectrometer parameters are shown as follows, g = 2.9898; scan range: 100 G; center field set: 3480.00 G; time constant: 0.16 ms; scan time: 122.88 s; modulation amplitude: 20.0 G; modulation frequency: 100 kHz; receiver gain: 2.00×10^2; microwave power: $7.14e^{-001}$ mW.

Experiment in presence DMPO.[1] A mixture compound **1e** (58 mg, 0.209 mmol) , **1f** (60 mg, 0.209 mmol) , N-iodosuccinimide (NIS) (24 mg, 0.105 mmol) and DMPO (20 µL) were stirred in 1.0 mL CH_3CN for 60 min. Afterwards, 300 µL solution was quickly transferred into EPR tube to analyze EPR. Appearance of sharp signal indicated the presence of radical intermediate. A similar experiment was conducted without NIS but no signal was observed.

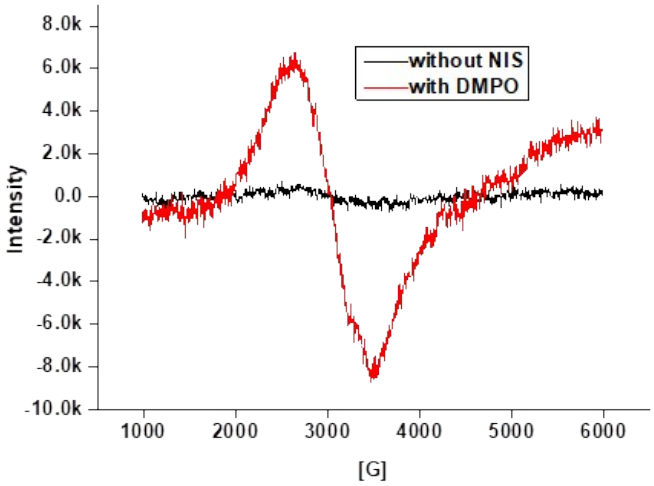


Fig. S1. a) EPR spectrum of the reaction under the standard condition with DMPO (red); b) EPR spectrum of the reaction without NIS and with DMPO.

UV experiment. UV experiments were carried out for the solution of disulfide **1f (**2×10^{-4} M in MeCN which shows absorption at 245 nm. Following addition of NIS (2×10^{-4} M in MeCN) showed significant red shift from 245 nm to 360 nm.

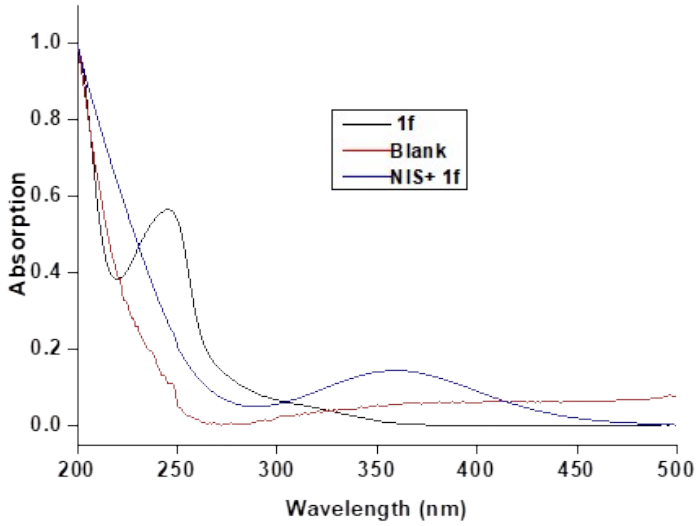


Fig. S2. UV spectrum of disulfide **1f** and NIS in MeCN.

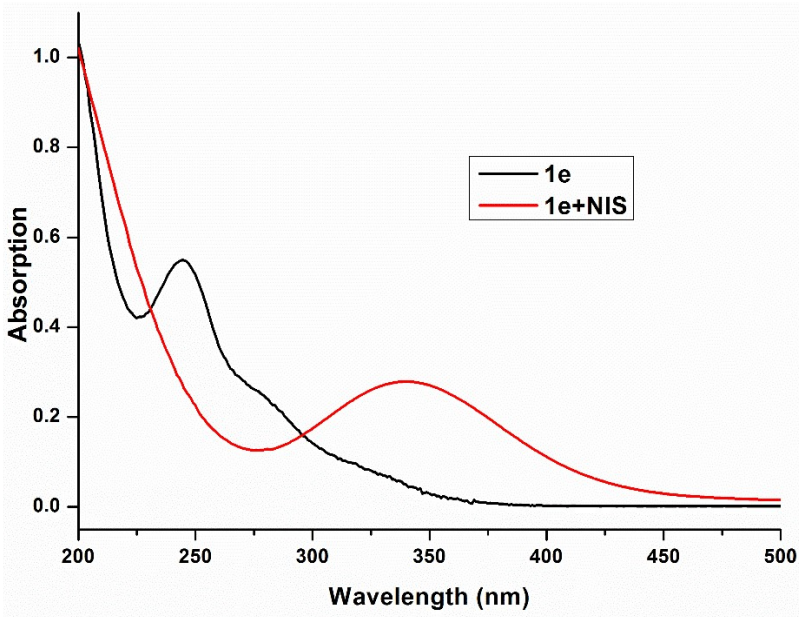


Fig. S3. UV spectrum of disulfide **1e** and NIS in MeCN.

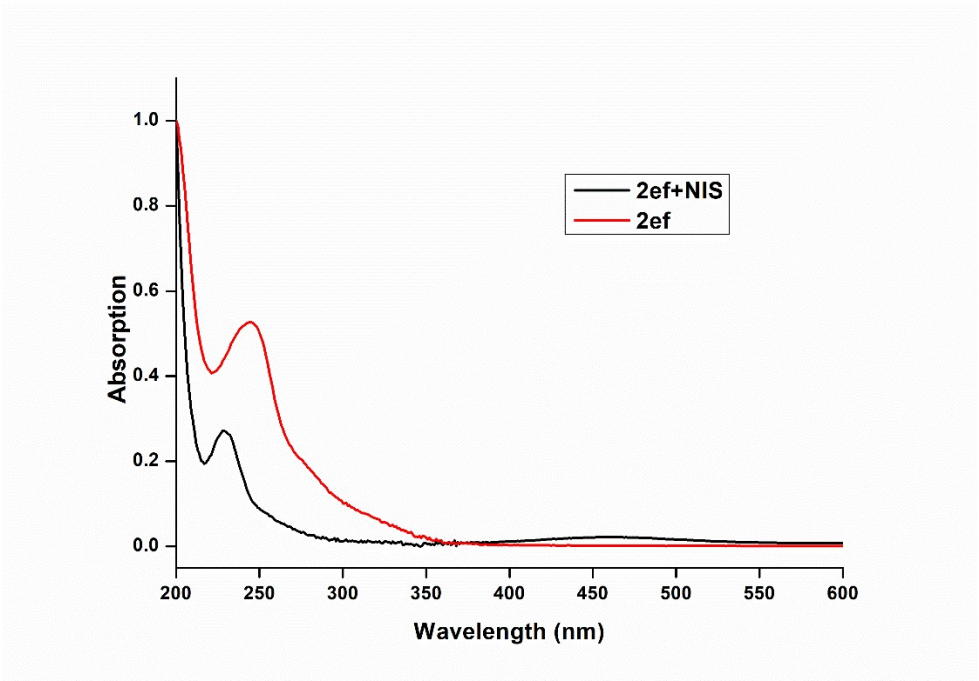


Fig. S4. UV spectrum of disulfide **2ef** and NIS in MeCN.

Fluorescence quenching studies. The addition of NIS (2×10^{-4} M in MeCN) to disulfide at 360 nm in room temperature shows maximum emission at 418 nm. Following gradual decrese in fluorescence intensity was observed with every 10 mins time intervals.

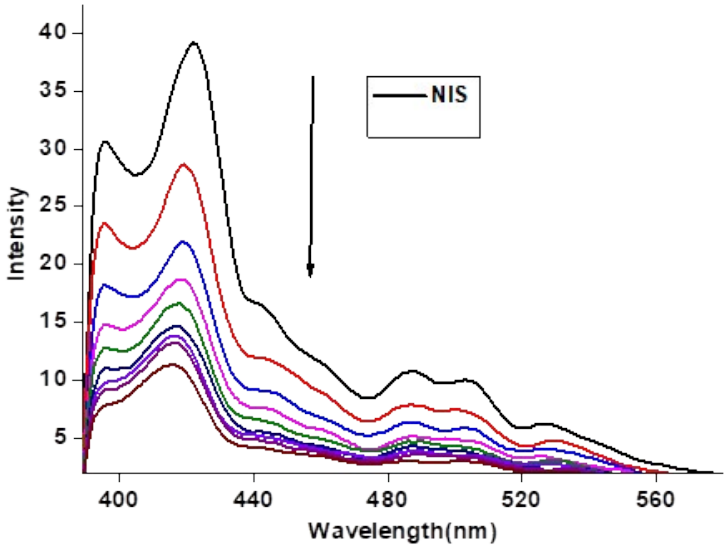


Fig. S5. Time-dependent Fluorescence spectrum of disulfide **1f** and NIS in MeCN (every 10 min intervals).

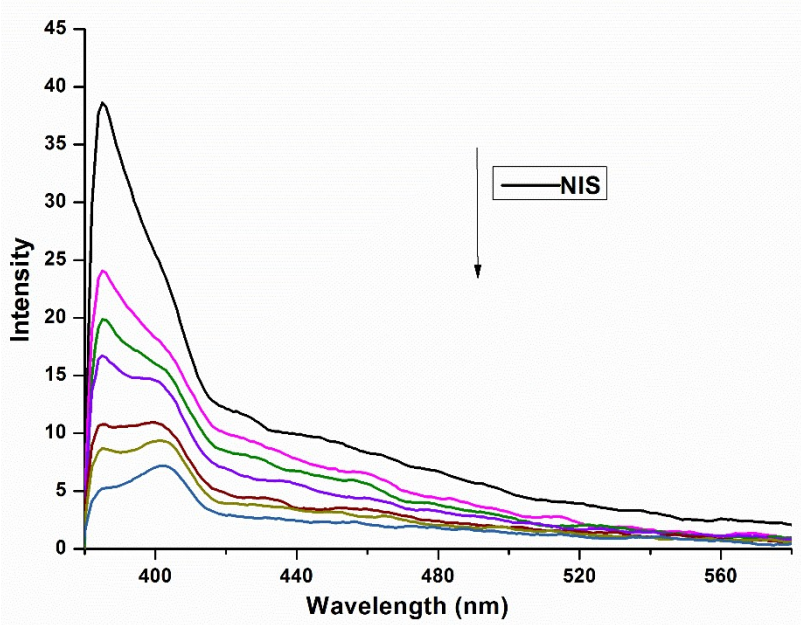


Fig. S6. Time-dependent Fluorescence spectrum of disulfide **1e** and NIS in MeCN (every 10 min intervals).

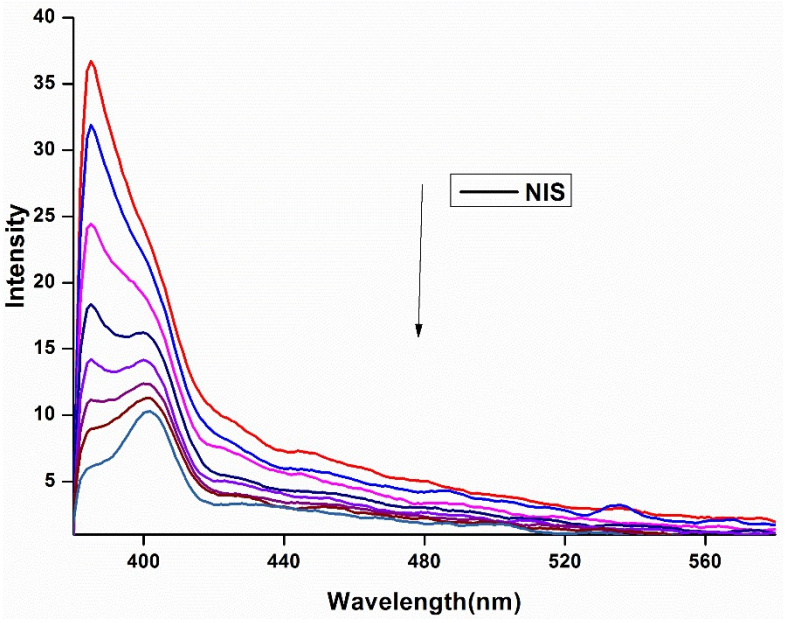


Fig. S7. Time-dependent Fluorescence spectrum of disulfide **2ef** and NIS in MeCN (every 10 min intervals).

Theoretical Investigations

All calculations were performed using software package Gaussian 09 ver. D01. The geometry of all the disulfides and NIS were optimized by density functional theory (DFT) at RB3LYP/LanL2DZ level.

XYZ Coordinates and Thermochemical Data of disulfide (2bu) (Energies in Hartree)

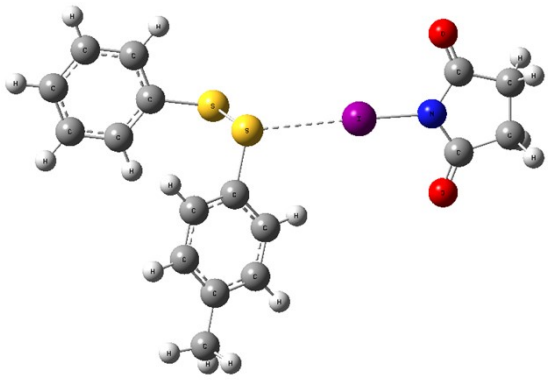


Fig. S8.

Sum of electronic and zero-point Energies = -893.805937

Sum of electronic and thermal Energies = -893.781657

Sum of electronic and thermal Enthalpies = -893.780713

Sum of electronic and thermal Free Energies = -893.870846

C	1.32174	-0.74962	0.53955
C	0.48047	-1.28147	-0.45272
C	-0.45653	-0.45079	-1.1036
C	-0.54465	0.91155	-0.74608
C	0.30111	1.43388	0.24737
C	1.24375	0.61311	0.90857
H	2.0446	-1.39785	1.03071
H	0.54869	-2.32989	-0.72871

H	-1.26533	1.55093	-1.24784
H	0.22869	2.48712	0.51094
C	-4.42945	-2.49561	-2.5101
C	-4.33294	-3.85822	-2.86647
C	-5.36111	-1.6578	-3.16046
C	-5.17259	-4.38136	-3.86743
H	-3.61075	-4.49378	-2.36223
C	-6.19849	-2.1858	-4.16077
H	-5.42552	-0.61017	-2.88117
C	-6.10525	-3.54666	-4.51507
H	-5.09855	-5.43139	-4.13929
H	-6.91702	-1.53987	-4.65929
H	-6.75304	-3.95273	-5.28861
C	2.13165	1.17468	2.00336
H	2.34199	2.23872	1.84398
H	1.6474	1.07972	2.98612
H	3.08835	0.64193	2.05758
S	-1.50173	-1.11995	-2.45323
S	-3.387	-1.82713	-1.1526
C	4.05329	-3.4161	-6.12757
C	3.40354	-4.80669	-5.94098
H	4.15726	-3.12518	-7.17805
H	5.04473	-3.33711	-5.66963
H	3.14432	-5.29309	-6.88716
H	4.03164	-5.50551	-5.37874

I	0.47354	-2.29966	-3.86624
N	2.03239	-3.16751	-4.90577
C	3.11481	-2.42194	-5.43614
C	2.11529	-4.56136	-5.1489
O	1.28708	-5.40317	-4.7795
O	3.25302	-1.1958	-5.34396

XYZ Coordinates and Thermochemical Data of disulfide (1b) (Energies in Hartree)

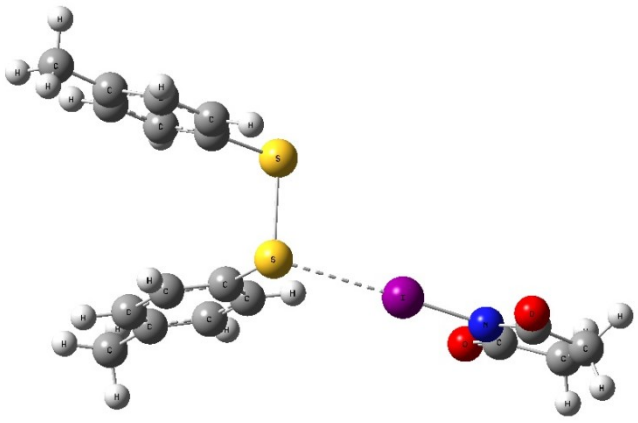


Fig. S9.

Sum of electronic and zero-point Energies = -933.091097

Sum of electronic and thermal Energies = -933.064908

Sum of electronic and thermal Enthalpies = -933.063964

Sum of electronic and thermal Free Energies = -933.159256

C	-2.13394	1.47759	0.62612
C	-1.86543	0.12961	0.33917
C	-2.74246	-0.60445	-0.48848
C	-3.88788	0.0244	-1.01881
C	-4.14703	1.37656	-0.72633
C	-3.27622	2.12441	0.09664
H	-1.4509	2.03412	1.26528
H	-0.9854	-0.35616	0.75118
H	-4.56456	-0.54041	-1.65366
H	-5.03278	1.85181	-1.14285
C	-5.11935	-3.60468	0.33783
C	-5.59572	-4.65313	-0.47878
C	-6.01972	-2.6283	0.81185
C	-6.95834	-4.72124	-0.81054
H	-4.90126	-5.40279	-0.84747
C	-7.38405	-2.70671	0.47468
H	-5.65357	-1.81984	1.43815
C	-7.87538	-3.75221	-0.33774
H	-7.3148	-5.53401	-1.4408
H	-8.0698	-1.94888	0.84805
C	-3.54191	3.58876	0.39315
H	-4.56884	3.87152	0.13584
H	-3.3821	3.81767	1.45446
H	-2.86554	4.23542	-0.18391

S	-2.36639	-2.3483	-0.92888
S	-3.35211	-3.5426	0.83722
C	-9.34997	-3.85102	-0.68235
H	-9.83646	-4.64785	-0.10179
H	-9.87744	-2.91526	-0.46564
H	-9.49803	-4.08683	-1.74378
C	1.49807	-8.6358	0.49859
C	0.28196	-9.59005	0.53336
H	2.09623	-8.73119	-0.41358
H	2.17712	-8.76964	1.34704
H	0.20033	-10.21886	-0.35937
H	0.28089	-10.2577	1.40126
I	-1.76452	-5.72287	0.7107
N	-0.49282	-7.34697	0.61641
C	0.91743	-7.2192	0.55587
C	-0.95352	-8.68731	0.60956
O	-2.13945	-9.03711	0.65676
O	1.54002	-6.14991	0.55166

XYZ Coordinates and Thermochemical Data of disulfide (1u) (Energies in Hartree)

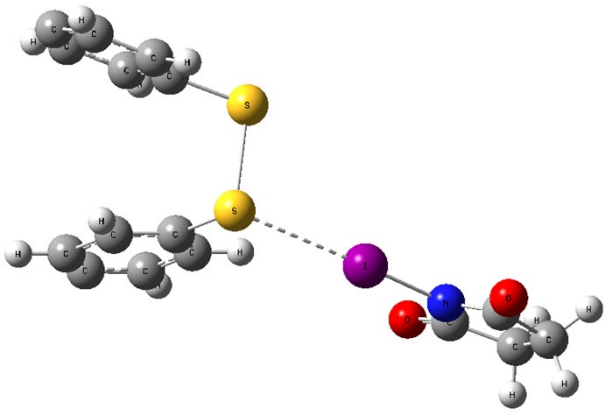


Fig. S10.

Sum of electronic and zero-point Energies = -853.095286

Sum of electronic and thermal Energies = -853.072786

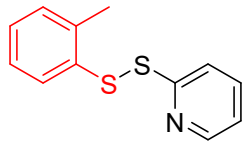
Sum of electronic and thermal Enthalpies = -853.071841

Sum of electronic and thermal Free Energies = -853.156339

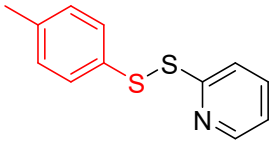
C	-3.274	0.49583	0.80713
C	-2.68306	-0.75716	0.4972
C	-3.28851	-1.60611	-0.45573
C	-4.47771	-1.22385	-1.11605
C	-5.08049	0.02952	-0.82638
C	-4.45008	0.8074	0.13477
H	-2.81567	1.15468	1.54066
H	-1.76863	-1.06479	0.99845
H	-4.93327	-1.88745	-1.84638
H	-5.99227	0.33288	-1.33543
C	-5.18064	-4.63308	0.31353
C	-5.65375	-5.56403	-0.63769

C	-6.06349	-3.72795	0.94412
C	-7.03212	-5.59335	-0.97597
H	-4.96273	-6.25385	-1.11593
C	-7.44794	-3.7465	0.62585
H	-5.68549	-3.01639	1.67353
C	-7.84604	-4.66851	-0.33216
H	-7.40453	-6.30547	-1.70846
H	-8.13404	-3.05712	1.1119
S	-2.50694	-3.21505	-0.88498
S	-3.40121	-4.61553	0.77974
C	1.76608	-8.80892	-1.05608
C	0.45292	-9.62497	-1.03578
H	2.36833	-8.98165	-1.95408
H	2.40953	-9.00356	-0.1918
H	0.32114	-10.25387	-1.92243
H	0.36197	-10.27612	-0.16015
I	-1.16381	-5.55641	-0.94855
N	-0.07473	-7.3101	-0.99621
C	1.34198	-7.33701	-1.0282
C	-0.67828	-8.59249	-0.99677
O	-1.89593	-8.81082	-0.97066
O	2.07717	-6.34176	-1.03198

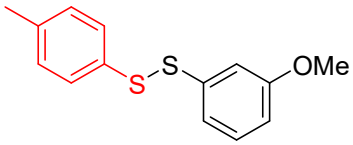
CHARATERIZATION DATA

2-(*o*-Tolyldisulfaneyl)pyridine (2ag). R_f = 0.5 (5% ethyl acetate in hexane); colorless liquid; 

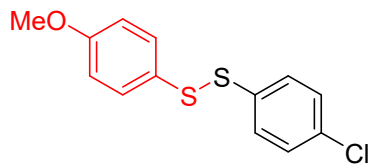
yield 75% (43 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 4.8, 0.4 Hz, 1H), 7.62-7.56 (m, 3H), 7.17-7.13 (m, 3H), 7.01-6.99 (m, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 149.6, 137.3, 136.7, 134.6, 130.5, 127.4, 127.3, 126.9, 120.9, 119.8, 20.0; IR (KBr) ῡ 3046, 2921, 2348, 1573, 1445, 674, 484; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{12}NS_2$ 234.0406; found 234.0381.

2-(*p*-Tolyldisulfaneyl)pyridine (2bg).[2] R_f = 0.5 (5% ethyl acetate in hexane); colorless liquid; 

yield 74% (42 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.2 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.61-7.57 (m, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 7.08-7.05 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 149.6, 137.7, 137.3, 132.8, 130.0, 128.2, 120.8, 119.7, 21.1.

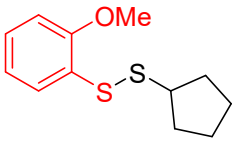
1-(3-Methoxyphenyl)-2-(*p*-tolyl)disulfane (2bd).[3] R_f = 0.5 (2% ethyl acetate in hexane); 

colorless liquid; yield 82% (44 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.23-7.18 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.09-7.07 (m, 2H), 6.77-6.74 (m, 1H), 3.77(s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 138.7, 137.7, 133.7, 130.0(×2), 128.6, 119.7, 113.2, 112.6, 55.4, 21.2.

1-(4-Chlorophenyl)-2-(4-methoxyphenyl)disulfane (2ef).[4] R_f = 0.5 (2% ethyl acetate in hexane); colorless liquid; yield 80% (35 mg); ^{1}H NMR (400 

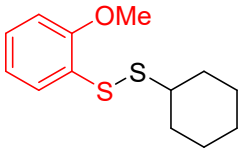
MHz, $CDCl_3$) δ 7.45-7.38 (m, 4H), 7.29-7.26 (m, 2H), 6.85-6.82 (m, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 136.2, 133.6, 132.3, 130.0, 129.3, 127.7, 114.9, 55.5.

1-Cyclopentyl-2-(2-methoxyphenyl)disulfane (2ch).[2] R_f = 0.6 (2% ethyl acetate in hexane);



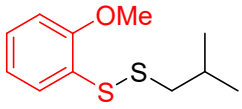
colorless liquid; yield 70% (36 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.21-7.17 (m, 1H), 7.01-6.97 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 3.89 (s, 3H), 3.36-3.30 (m, 1H), 1.98-1.91 (m, 2H), 1.77-1.66 (m, 4H), 1.61-1.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 127.5,127.4, 126.0, 121.2, 110.7, 56.0, 50.0, 32.9, 24.8.

1-Cyclohexyl-2-(2-methoxyphenyl)disulfane (2ci). R_f = 0.5 (in hexane); colorless liquid;



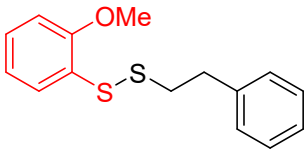
yield 64% (35 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.20-7.16 (m, 1H), 6.99 (td, *J* = 7.6, 1.0 Hz, 1H), 6.85-6.83 (m, 1H), 3.89 (s, 3H), 2.83-2.76 (m, 1H), 2.06-2.02 (m, 2H), 1.78-1.75 (m, 2H), 1.45-1.31 (m, 3H), 1.29-1.24 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 127.3, 127.2, 126.4, 121.3, 110.6, 56.0, 49.7, 32.8, 26.2, 25.7. IR (KBr) ῡ 2925, 2348, 1236, 746, 588; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{18}OS_2Na$ 277.0691; found 277.0668.

1-Isobutyl-2-(2-methoxyphenyl)disulfane (2cn). R_f = 0.7 (hexane); colorless liquid; yield



84% (41 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.23-7.19 (m, 1H), 7.02-6.98 (m, 1H), 6.86 (dd, *J* = 8.0, 0.5 Hz, 1H), 3.89 (s, 3H), 2.64 (d, *J* = 6.8 Hz, 2H), 2.04-1.90 (m, 1H), 1.01 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 127.8, 127.7, 125.7, 121.3, 110.8, 56.0, 48.1, 28.2, 21.9; IR (KBr) ῡ 3085, 2957, 1473, 748, 674; HRMS (ESI/Q-TOF) m/z: $[M]^+$ calcd for $C_{11}H_{16}OS_2$ 228.0637; found 228.0619.

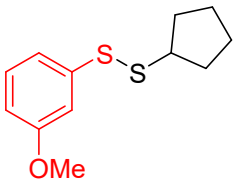
1-(2-Methoxyphenyl)-2-phenethyldisulfane (2cl). R_f = 0.3 (in hexane); colorless liquid; yield



75% (45 mg) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.31-7.28 (m, 2H), 7.26-7.23 (m, 1H), 7.22-7.18 (m, 3H),

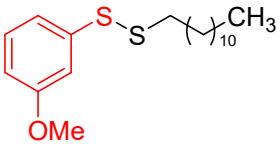
7.01-6.97 (m, 1H), 6.88 (dd, J = 8.0, 0.8 Hz, 1H), 3.91 (s, 3H), 3.05-2.96 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 140.1, 128.8, 128.6, 128.3, 128.0, 126.5, 125.3, 121.4, 110.9, 56.0, 39.8, 35.5; IR (KBr) ῡ 3061, 2929, 2348, 1602, 699; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}OS_2Na$ 299.0535; found 299.0544.

1-Cyclopentyl-2-(3-methoxyphenyl)disulfane (2dh). R_f = 0.5 (in hexane); colorless liquid;



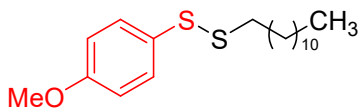
yield 77% (40 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, J = 7.8 Hz, 1H), 7.14-7.09 (m, 2H), 6.75-6.72 (m, 1H), 3.82 (s, 3H), 3.37-3.30 (m, 1H), 1.97-1.90 (m, 2H), 1.78-1.64 (m, 4H), 1.61-1.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 139.6, 129.9, 119.3, 112.5, 112.2, 55.5, 50.5, 32.9, 24.8; IR (KBr) ῡ 2955, 2347, 1588, 684; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{17}OS_2$ 241.0715; found 241.0744.

1-Dodecyl-2-(3-methoxyphenyl)disulfane (2do).[5] R_f = 0.6 (in hexane); colorless liquid; yield



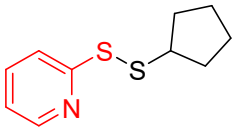
71% (36 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, J = 7.8 Hz, 1H), 7.13-7.12 (m, 1H), 7.11-7.09 (m, 1H), 6.75 (dd, J = 8.2, 0.8 Hz, 1H), 3.82 (s, 3H), 2.75 (t, J = 7.2 Hz, 2H), 1.71-1.63 (m, 2H), 1.31-1.26 (m, 18H), 0.91-0.87 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 139.3, 129.9, 119.6, 112.7, 112.6, 55.5, 39.3, 32.1, 29.8, 29.74, 29.71, 29.6, 29.5, 29.3, 29.0, 28.6, 22.8, 14.2.

1-Dodecyl-2-(4-methoxyphenyl)disulfane (2eo).[6] R_f = 0.4 (5% ethyl acetate in hexane);

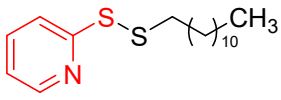


colorless liquid; yield 82% (26 mg); NMR (400 MHz, $CDCl_3$) δ 7.49-7.45 (m, 2H), 6.88-6.84 (m, 2H), 3.80 (s, 3H), 2.73 (t, J = 7.2, 2H), 1.69-1.62 (m, 2H), 1.33-1.24 (m, 18H), 0.90-0.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 131.8, 128.7, 114.8, 55.5, 39.0, 32.1, 29.79, 29.78, 29.73, 29.6, 29.5, 29.3, 28.9, 28.6, 22.8, 14.3.

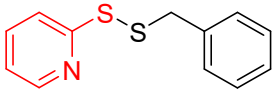
2-(Cyclopentyldisulfaneyl)pyridine (2gh).[3] R_f = 0.6 (5% ethyl acetate in hexane); colorless liquid; yield 86% (50 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.41 (m, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.63-7.59 (m, 1H), 7.05-7.02 (m, 1H), 3.40-3.33 (m, 1H), 1.97-1.90 (m, 2H), 1.79-1.63 (m, 2H), 1.60-1.54 (m, 2H), 1.27-1.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 149.5, 137.0, 120.5, 119.6, 50.4, 32.9, 24.8.



2-(Dodecyldisulfaneyl)pyridine (2go).[7] R_f = 0.7 (5% ethyl acetate in hexane); colorless liquid; yield 92% (43 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.07-7.04 (m, 1H), 2.78 (t, *J* = 7.2, 2H), 1.71-1.64 (m, 2H), 1.41-1.24 (m, 18H), 0.88-0.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 149.7, 137.0, 120.6, 119.7, 39.2, 32.0, 30.3, 29.7, 29.7, 29.6, 29.5, 29.3, 29.1, 28.6, 22.8, 14.2.

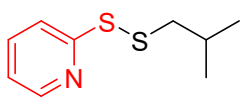


2-(Benzyldisulfaneyl)pyridine (2gj).[8] R_f = 0.3 (2% ethyl acetate in hexane); colorless liquid; yield 95% (54 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.41 (m, 1H), 7.50-7.48 (m, 2H), 7.31-7.26 (m, 3H), 7.24-7.18 (m, 2H), 7.03-6.99 (m, 1H), 4.01 (s, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 149.5, 136.8, 136.6, 129.4, 128.6, 127.7, 120.5, 119.6, 43.9.



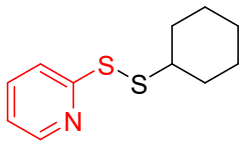
2-((4-(*tert*-Butyl)benzyl)disulfaneyl)pyridine (2gk). R_f = 0.5 (5% ethyl acetate in hexane); colorless liquid; yield 87% (42 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41-8.39 (m, 1H), 7.47-7.46 (m, 2H), 7.27-7.21(m, 4H), 7.01-6.97 (m, 1H), 4.00 (s, 2H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 150.7, 149.5, 136.8, 133.5, 129.2, 125.6, 120.5, 119.6, 43.6, 31.4, 29.8; IR (KBr) ῡ 2960, 2924, 2348, 1574, 758; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{20}NS_2$ 290.1032; found 290.1051.

2-(Isobutyldisulfaneyl)pyridine (2gn).[9] R_f = 0.7 (5% ethyl acetate in hexane); colorless



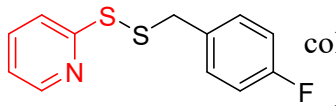
liquid; yield 72% (39 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* =4.6 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.62-7.58 (m, 1H), 7.04-7.01 (m, 1H), 2.67 (d, *J* = 6.8 Hz, 2H), 1.98-1.89 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 149.6, 137.0, 120.5, 119.6, 48.4, 28.2, 21.8.

2-(Cyclohexyldisulfaneyl)pyridine (2gr).[10] R_f = 0.6 (5% ethyl acetate in



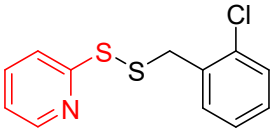
hexane); colorless liquid; yield 83% (49 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 4.6 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.06-7.03 (m, 1H), 2.87-2.81 (m, 1H), 2.05 (d, *J* = 11.3 Hz, 2H), 1.77-1.74 (m, 2H), 1.44-1.35 (m, 3H), 1.34-1.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 149.4, 137.0, 120.4, 119.5, 50.1, 32.8, 26.2, 25.6.

2-((4-Fluorobenzyl)disulfaneyl)pyridine(2gq). R_f = 0.55 (5% ethyl acetate in hexane);



colorless liquid; yield 56% (30 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.42 (d, *J* = 4.2 Hz, 1H), 7.51 (dd, *J* = 7.9, 7.5 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.25-7.23 (m, 2H), 7.04-7.01 (m, 1H), 6.91 (t, *J* = 8.6 Hz, 2H), 3.98 (s, 2H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 162.37 (d, $^1J_{CF}$ = 246.5 Hz), 159.9, 149.6, 136.8, 132.5 (d, $^4J_{CF}$ = 3.2 Hz), 131.1 (d, $^3J_{CF}$ = 8.2 Hz), 120.7, 119.7, 115.5 (d, $^2J_{CF}$ = 21.5 Hz), 42.8, IR (KBr) ῡ 2923, 2352, 1508, 759; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{10}ClNS_2Na$ 289.9835; found 289.9815.

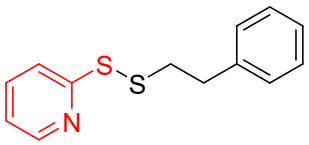
2-((2-Chlorobenzyl)disulfaneyl)pyridine (2gp). R_f = 0.5 (5% ethyl acetate in hexane);



colorless liquid; yield 62% (31 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.39 (d, *J* = 4.5 Hz, 1H), 7.51-7.47 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.13-

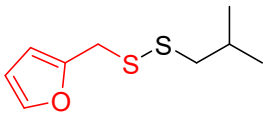
7.10 (m, 2H), 7.07 (t, J = 7.4 Hz, 1H), 7.02-6.97 (m, 1H), 4.13 (s, 2H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.2, 149.5, 136.9, 134.4, 131.9, 129.7, 129.2, 126.8, 120.6, 119.4, 41.5; IR (KBr) ῡ 2927, 2348, 1518, 749; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C12H_{10}ClNS_2Na$ 289.9835; found 289.9815.

2-(Phenethyldisulfaneyl)pyridine (2gl).[8] R_f = 0.3 (2% ethyl acetate in hexane); colorless



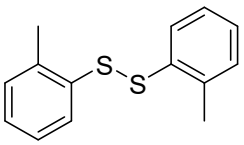
liquid; yield 70% (38 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48-8.46 (m, 1H), 7.68-7.66 (m, 1H), 7.63-7.59 (m, 1H), 7.30-7.27 (m, 2H), 7.23-7.17 (m, 3H), 7.09-7.06 (m, 1H), 3.08-2.99 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 149.7, 139.7, 137.1, 128.7, 128.6, 126.6, 120.7, 119.7, 40.1, 35.4.

2-((Isobutyldisulfaneyl)methyl)furan (2mn). R_f = 0.5 (2% ethyl acetate in hexane);colorless



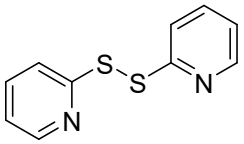
liquid; yield 54% (29 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 1.4 Hz, 1H), 6.33-6.32 (m, 1H), 6.27 (d, J = 3.0, 1H), 3.89 (s, 2H), 2.34 (d, J = 6.8 Hz, 2H), 1.89-1.79 (m, 1H), 0.94 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 142.5, 110.9, 108.5, 48.4, 36.0, 28.1, 21.8; IR (KBr) ῡ 2956, 2924, 2348, 1463, 736; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{15}OS_2$ 203.0559; found 203.0543.

1,2-Di-o-tolyldisulfane (1a).[11] R_f = 0.7 (hexane); white solid; yield 38% (16 mg); ^{1}H NMR



(700 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.17 (d, J = 7.0 Hz, 3H), 7.16-7.12 (m, 3H), 2.44 (s, 6H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 137.5, 135.6, 130.4, 128.8, 127.5, 126.8, 20.1.

1,2-Di(pyridin-2-yl)disulfane (1g).[11] R_f = 0.5 (5% ethyl acetate in hexane); white solid; yield



45% (17 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.43 (d, J = 4.8 Hz, 2H),

7.60-7.56 (m, 4H), 7.09-7.07 (m, 2H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 158.9, 149.6, 137.5, 121.2, 119.7.

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NMR SPECTRA

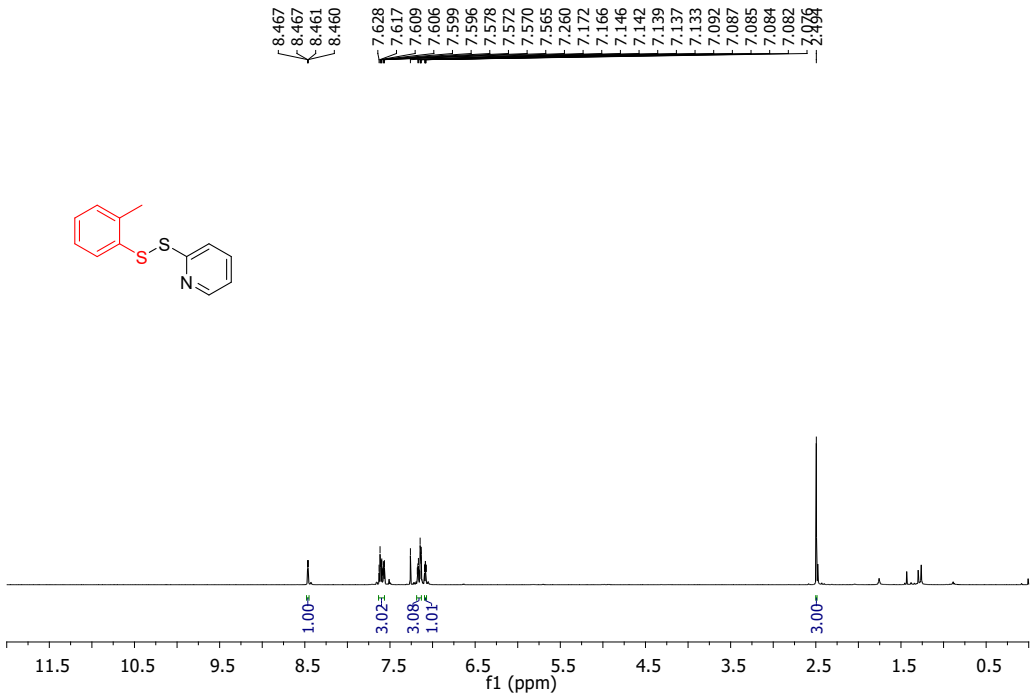

Fig. S11. ^{1}H NMR spectrum of 2-(o-tolyldisulfaneyl)pyridine **(2ag)**

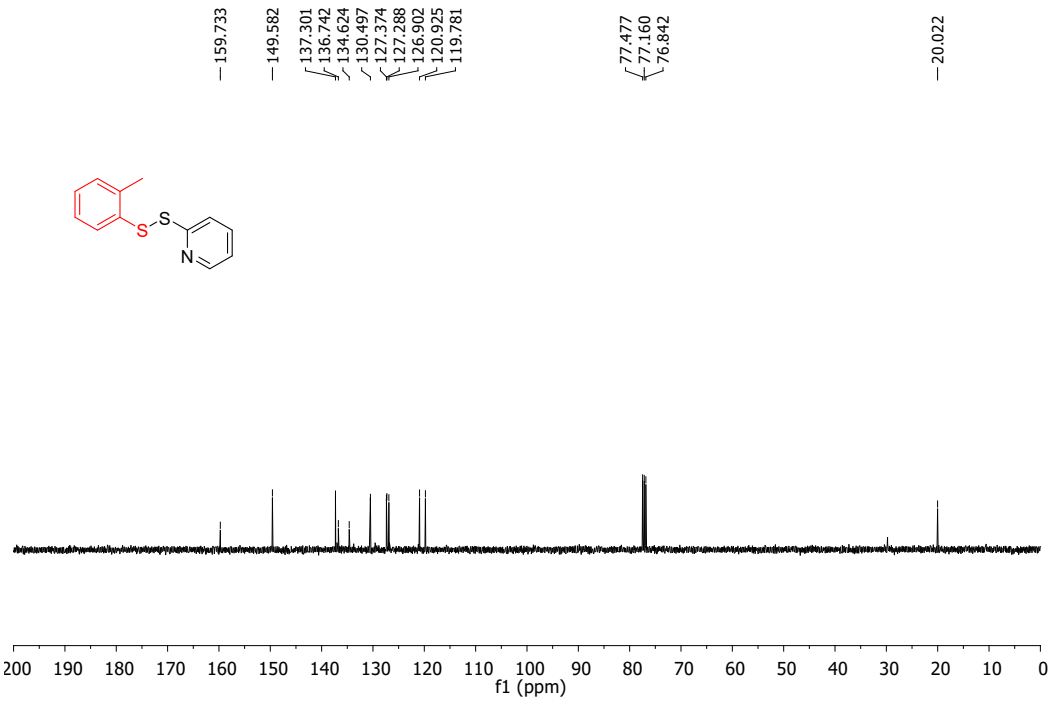

Fig. S12. ^{13}C NMR spectrum of 2-(o-tolyldisulfaneyl)pyridine **(2ag)**

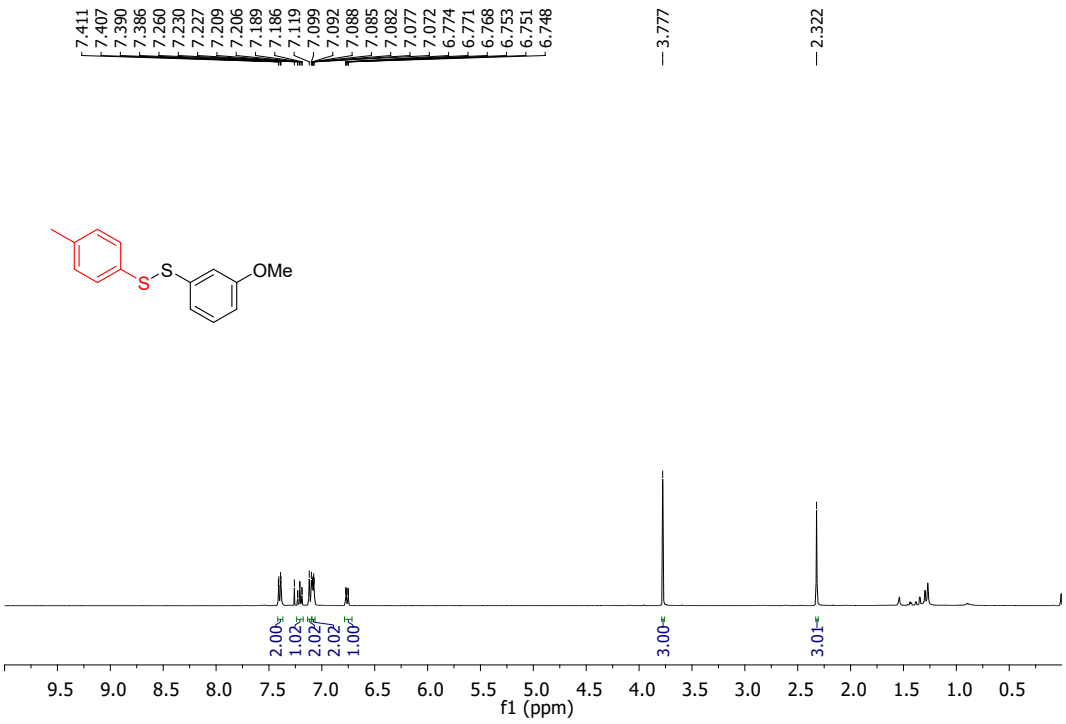

Fig. S13. ^{1}H NMR spectrum of 1-(3-methoxyphenyl)-2-(p-tolyl)disulfane **(2bd)**

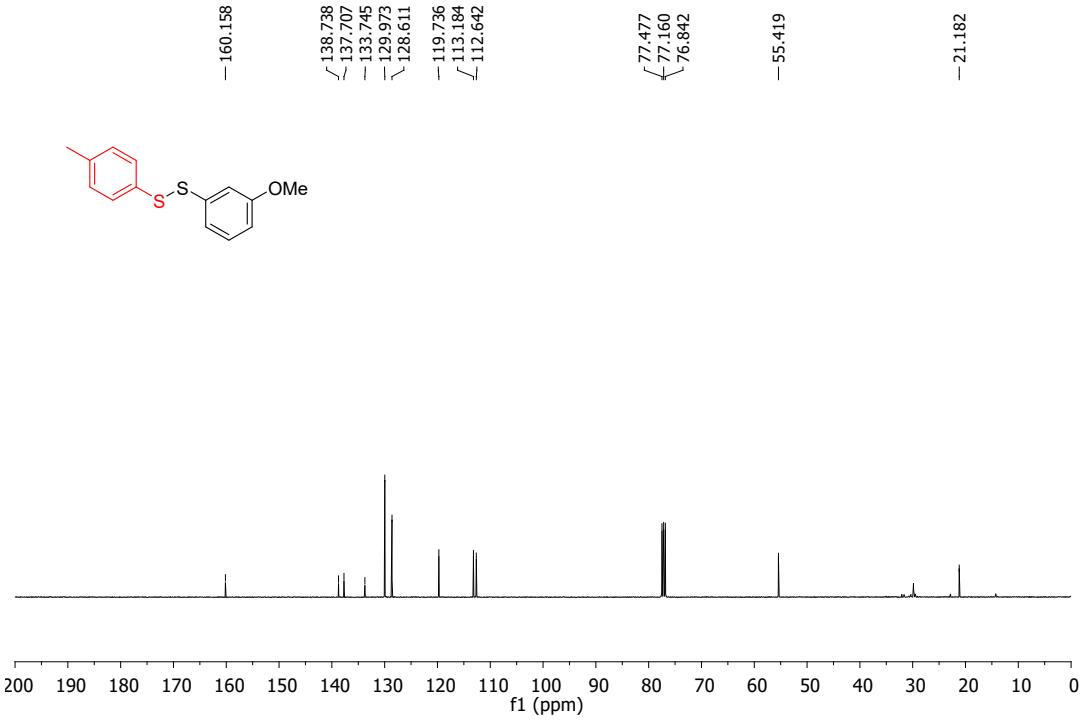

Fig. S14. ^{13}C NMR spectrum of 1-(3-methoxyphenyl)-2-(p-tolyl)disulfane **(2bd)**

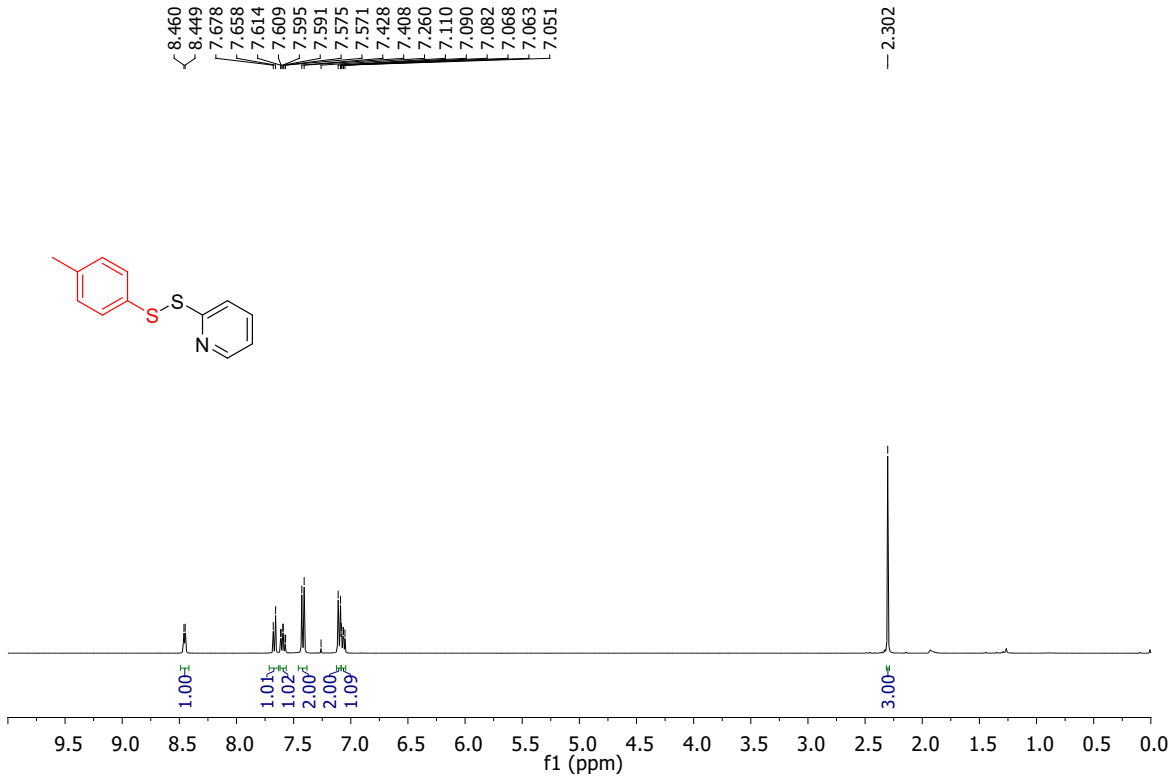

Fig. S15. ^{1}H NMR spectrum of 2-(p-tolyldisulfaneyl)pyridine **(2bg)**

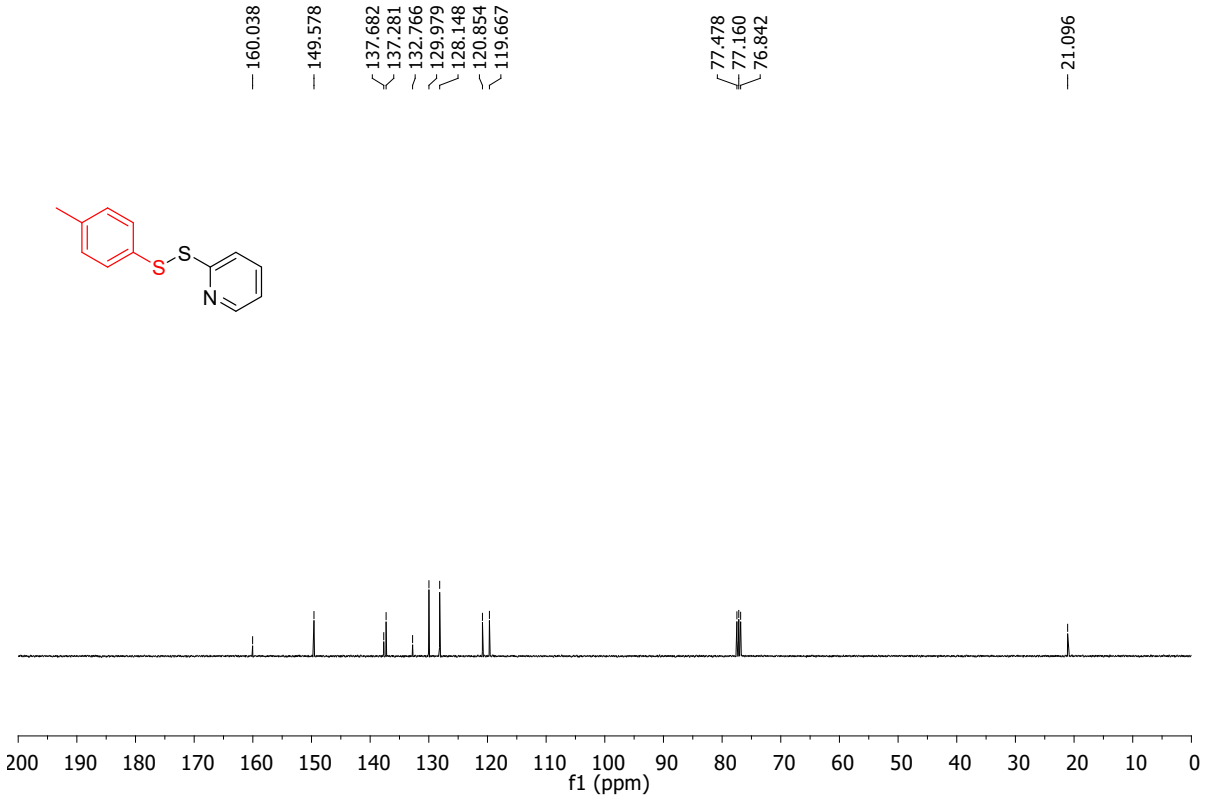

Fig. S16. ^{13}C NMR spectrum of 2-(p-tolyldisulfaneyl)pyridine **(2bg)**

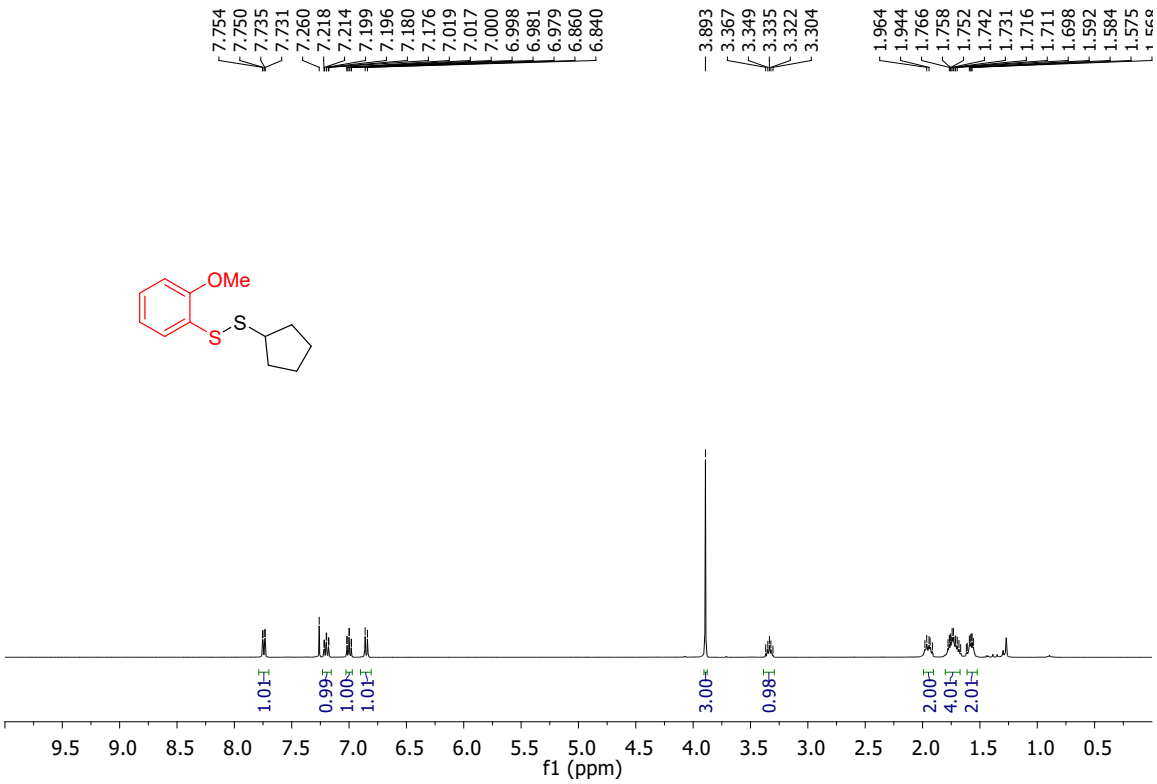

Fig. S17. [1]H NMR spectrum of1-cyclopentyl-2-(2-methoxyphenyl)disulfane **(2ch)**

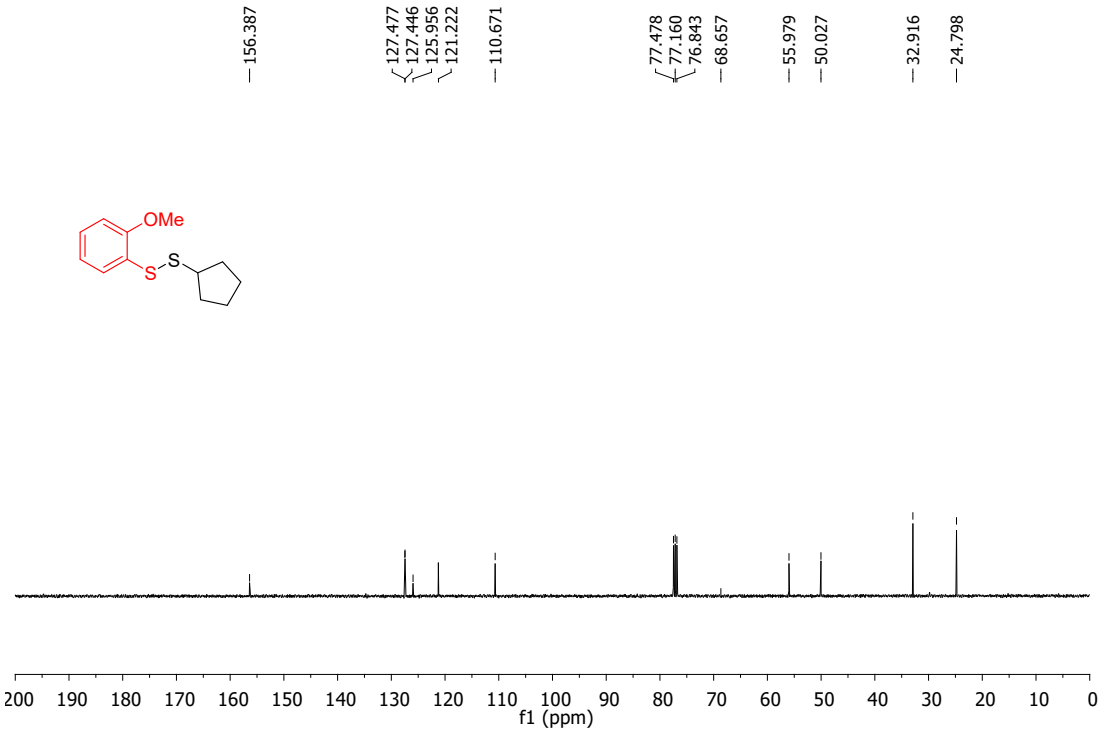

Fig. S18. [13]C NMR spectrum of 1-cyclopentyl-2-(2-methoxyphenyl)disulfane **(2ch)**

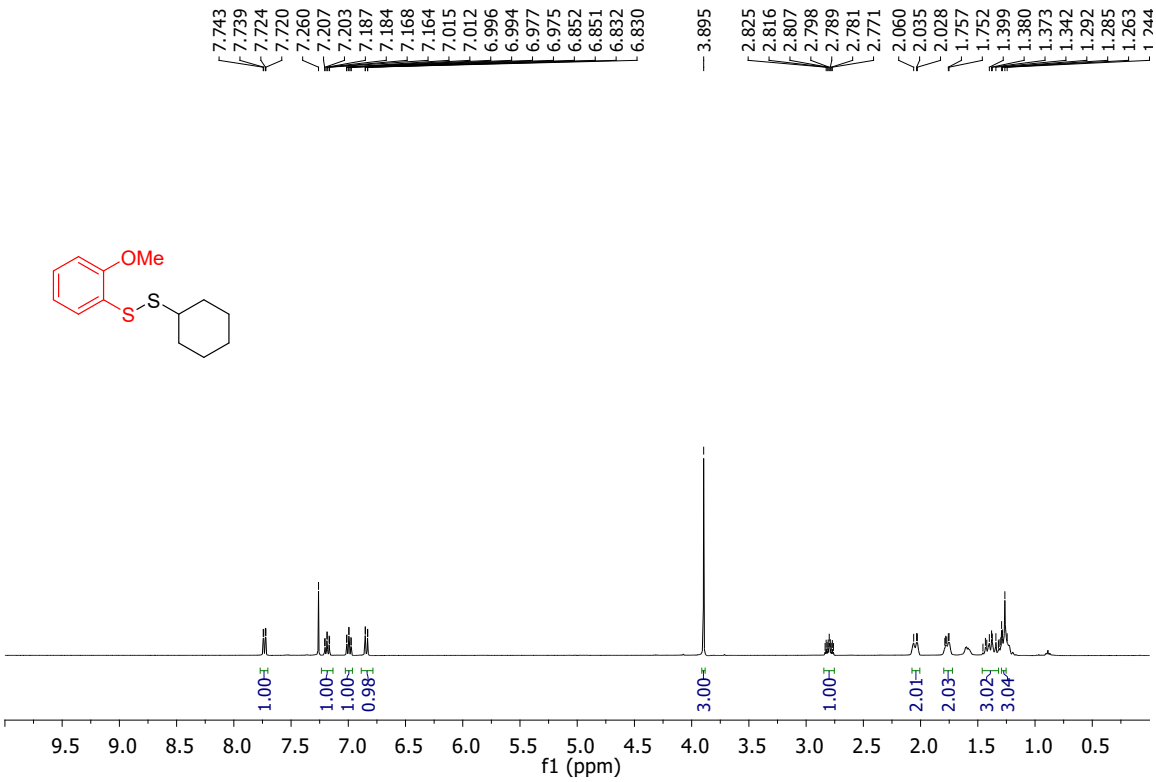

Fig. S19. [1]H NMR spectrum of 1-cyclohexyl-2-(2-methoxyphenyl)disulfane **(2ci)**

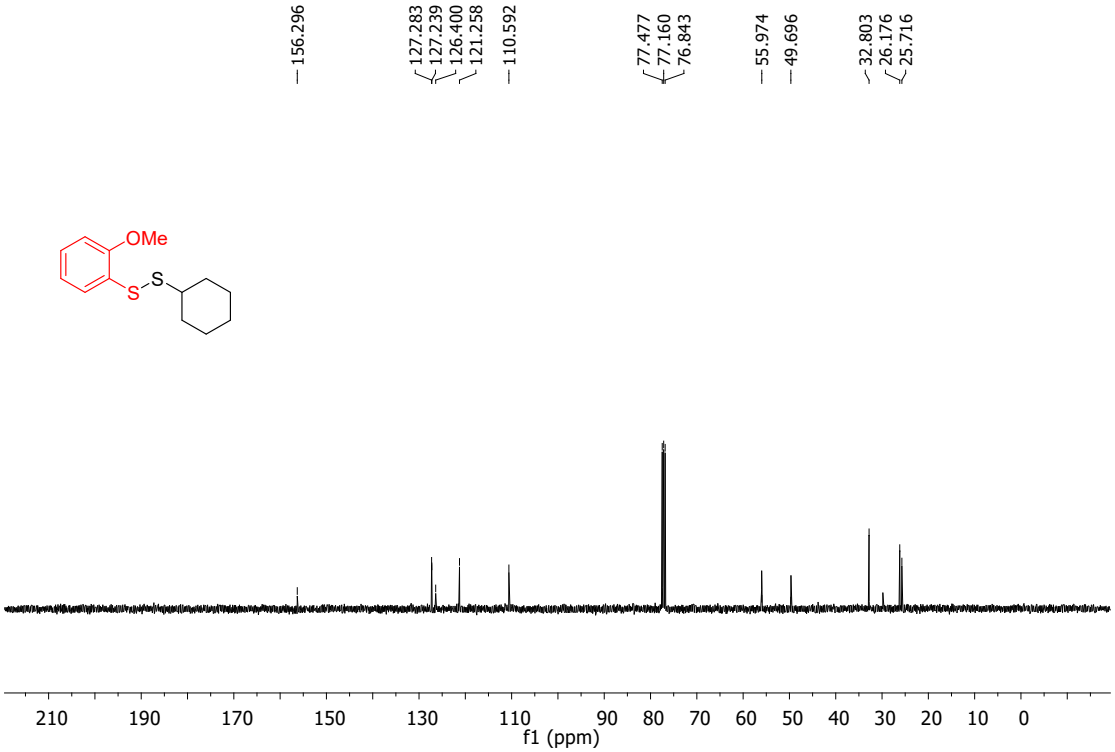

Fig. S20. [13]C NMR spectrum of 1-cyclohexyl-2-(2-methoxyphenyl)disulfane (**2ci)**

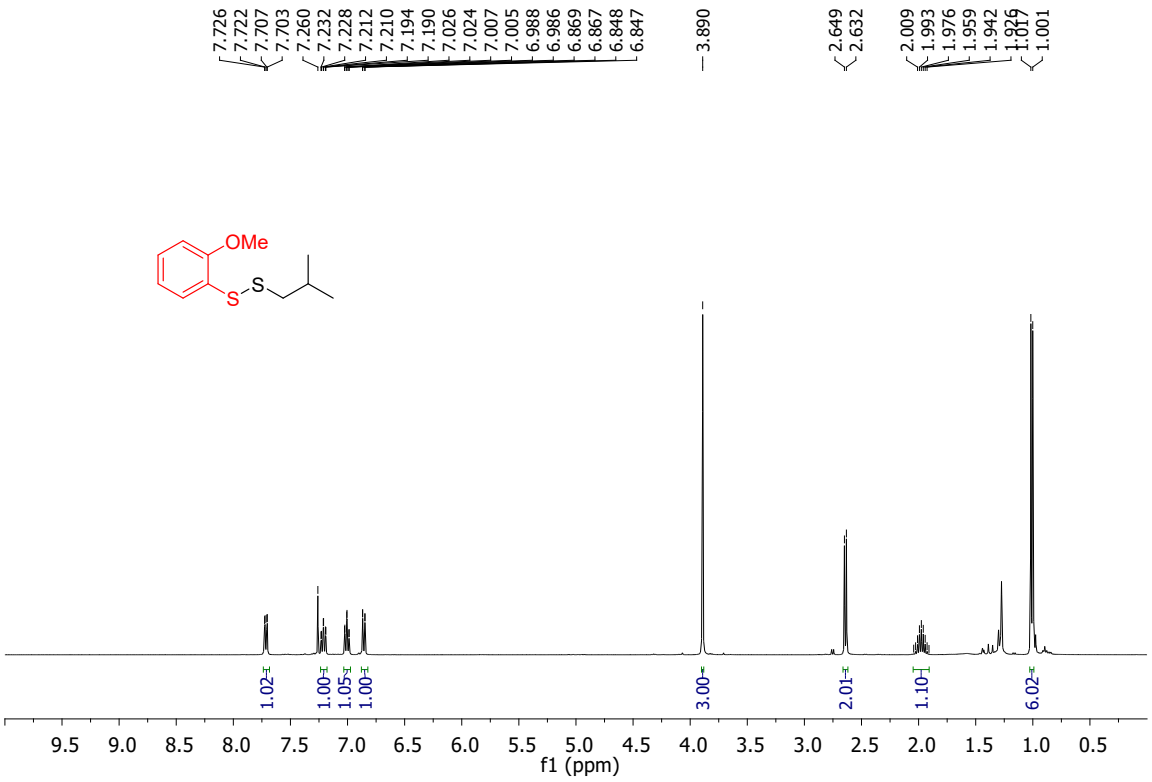

Fig. S21. ^{1}H NMR spectrum of 1-isobutyl-2-(2-methoxyphenyl)disulfane **(2cn)**

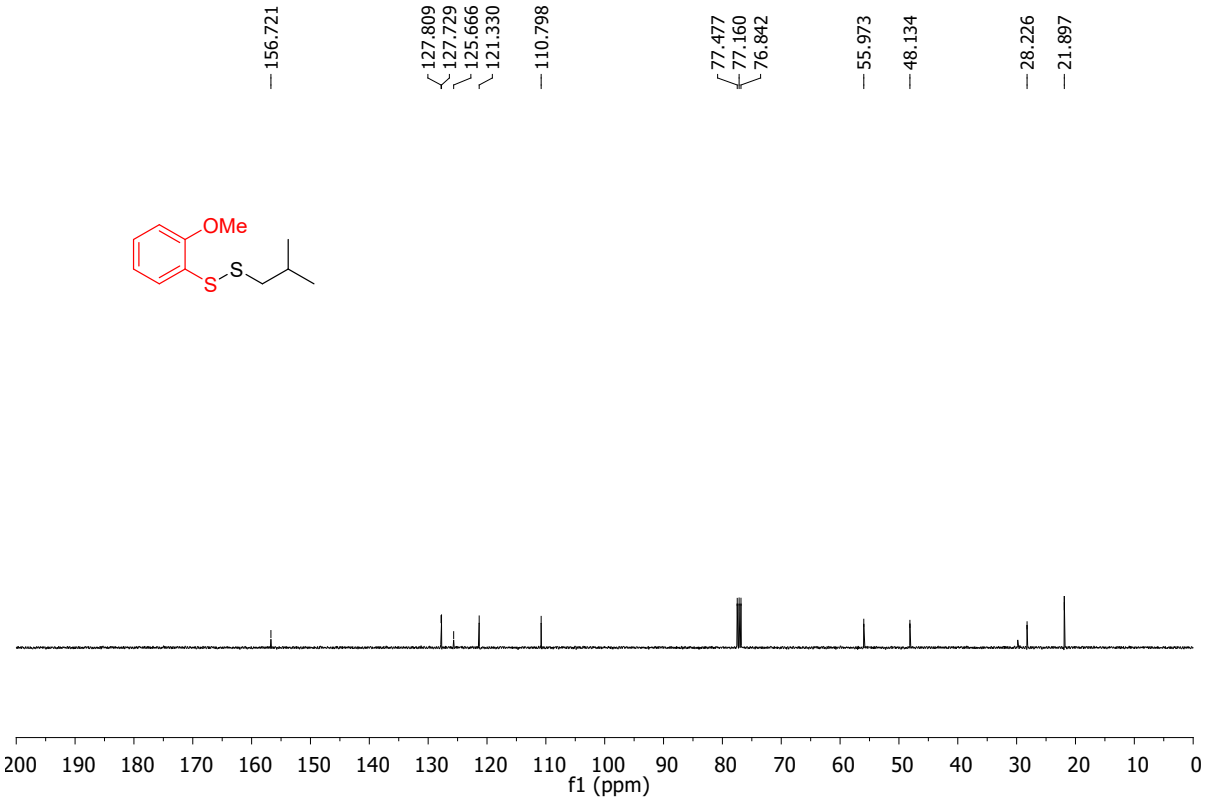

Fig. S22. ^{13}C NMR spectrum of 1-isobutyl-2-(2-methoxyphenyl)disulfane **(2cn)**

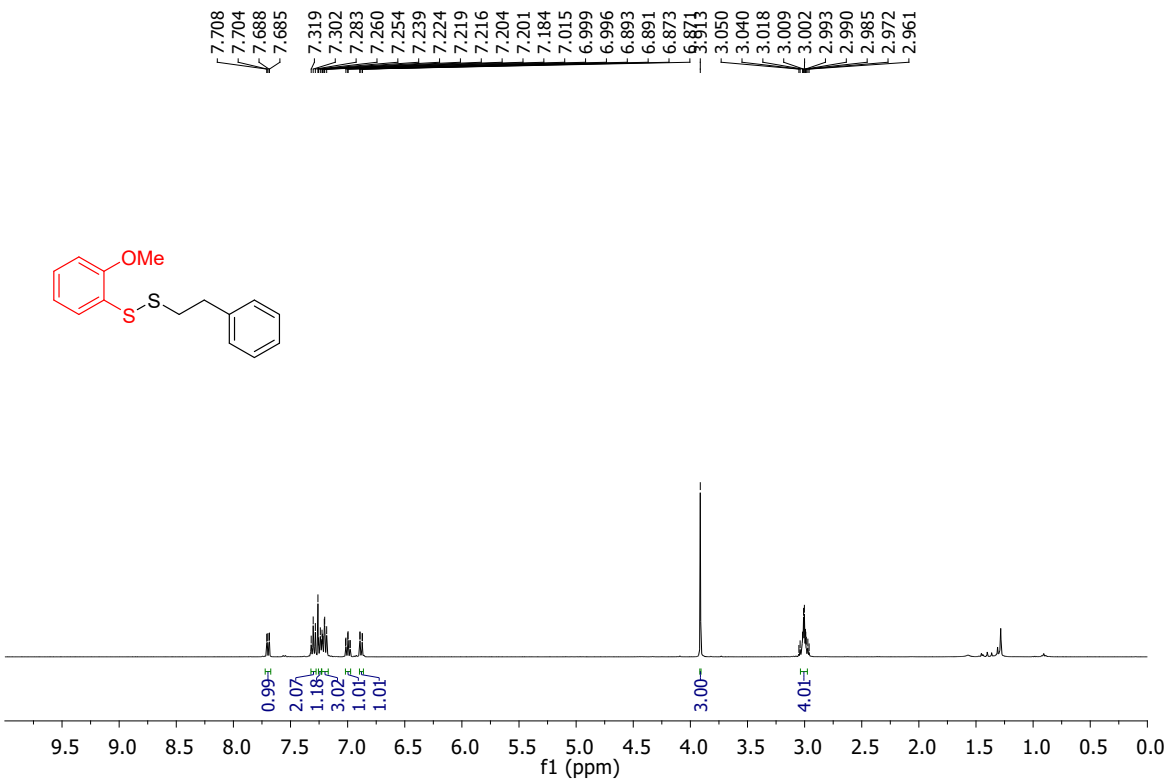

Fig. S23. [1]H NMR spectrum of 1-(2-methoxyphenyl)-2-phenethyldisulfane **(2cl)**

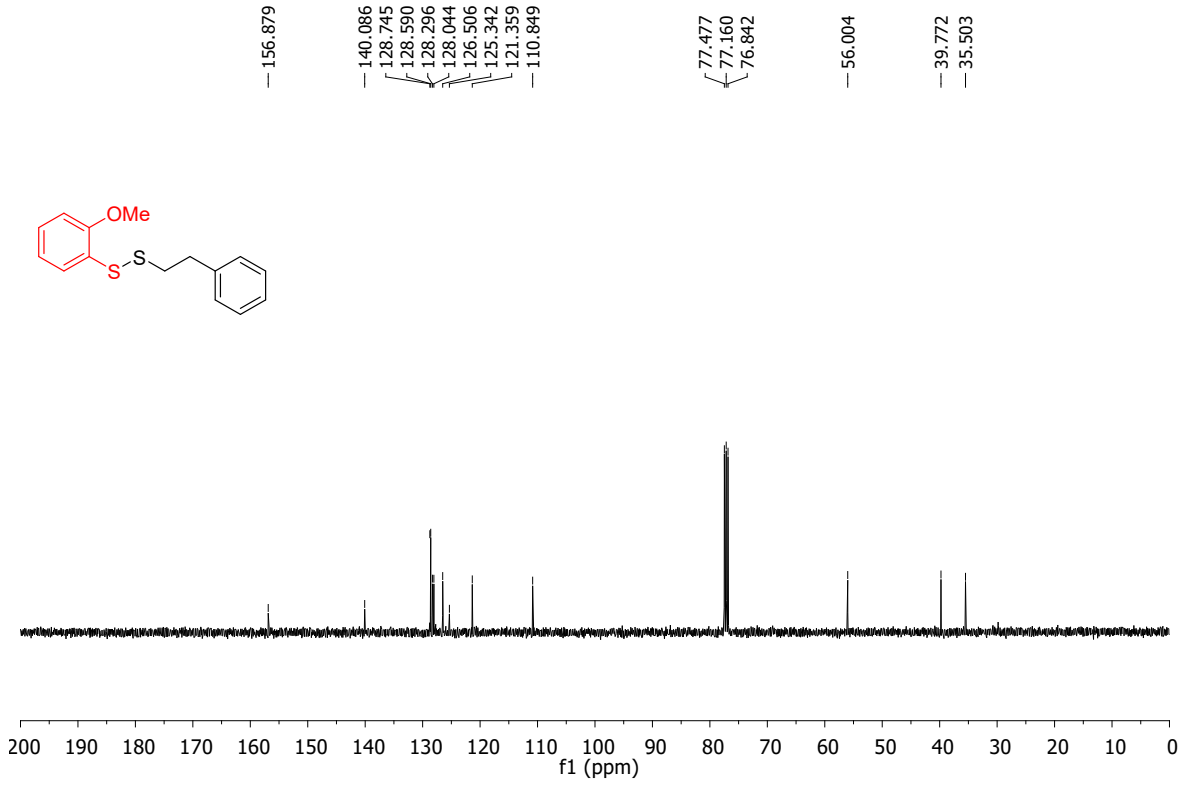

Fig. S24. [13]C NMR spectrum of 1-(2-methoxyphenyl)-2-phenethyldisulfane **(2cl)**

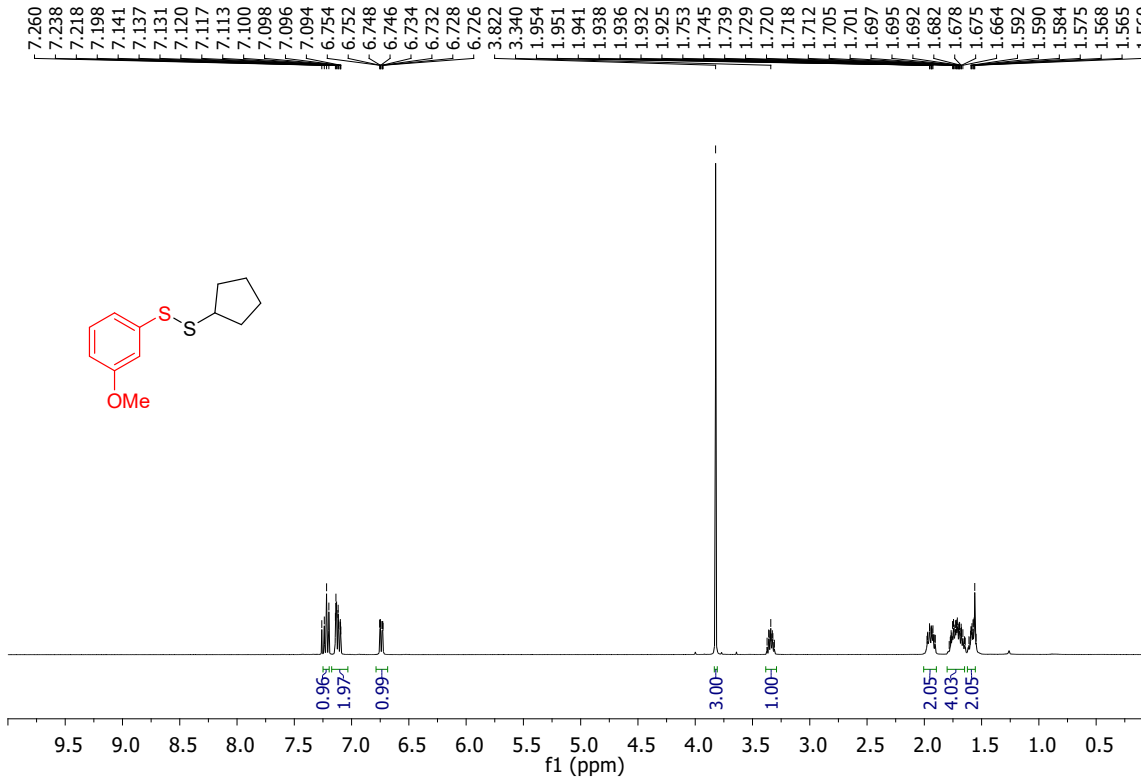

Fig. S25. ^{1}H NMR spectrum of 1-cyclopentyl-2-(3-methoxyphenyl)disulfane **(dh)**

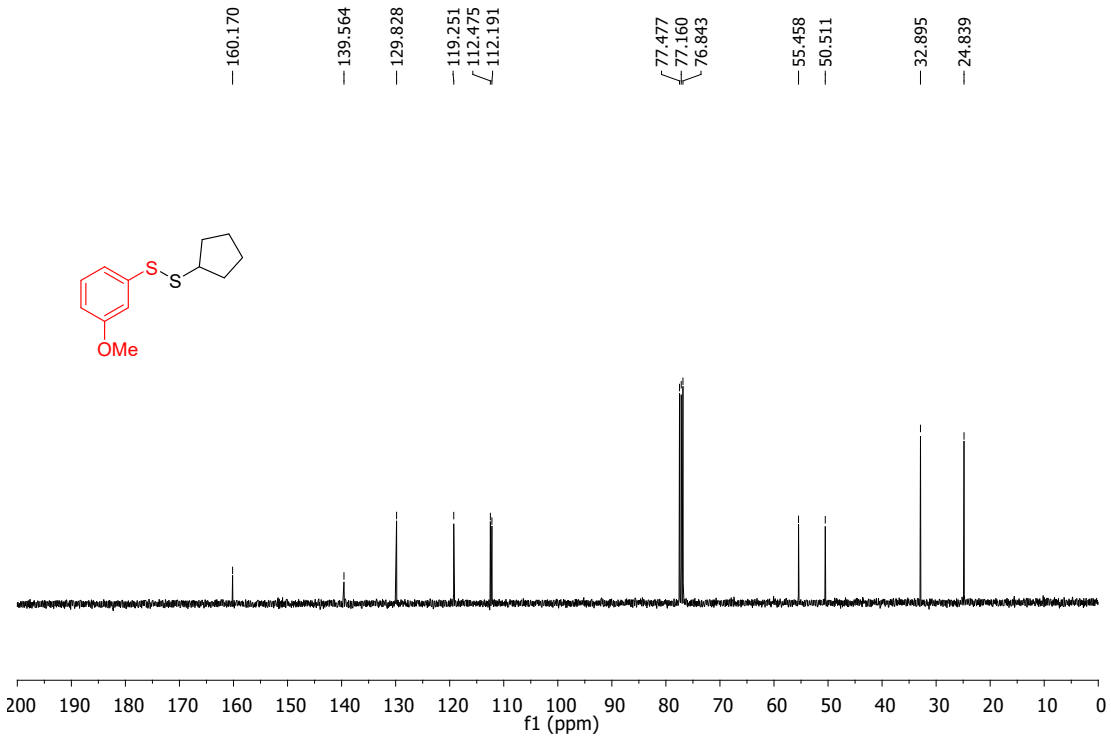

Fig. S26. ^{13}C NMR spectrum of 1-cyclopentyl-2-(3-methoxyphenyl)disulfane **(dh)**

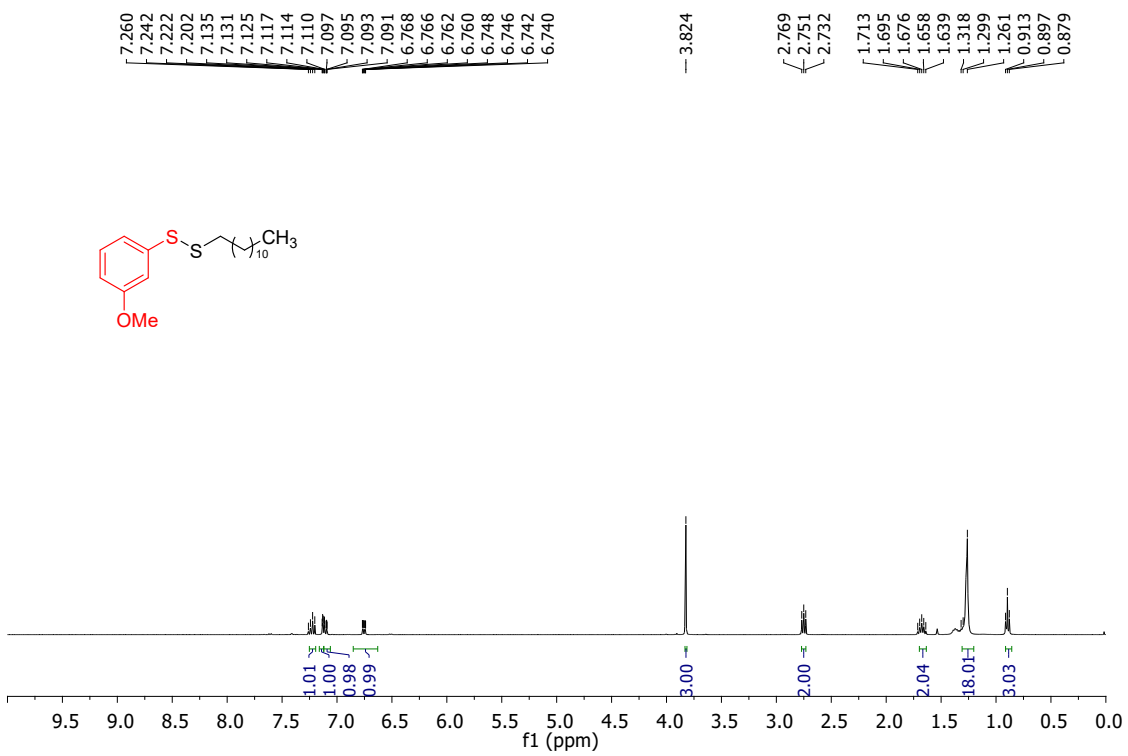

Fig. S27. [1]H NMR spectrum of 1-dodecyl-2-(3-methoxyphenyl)disulfane **(2do)**

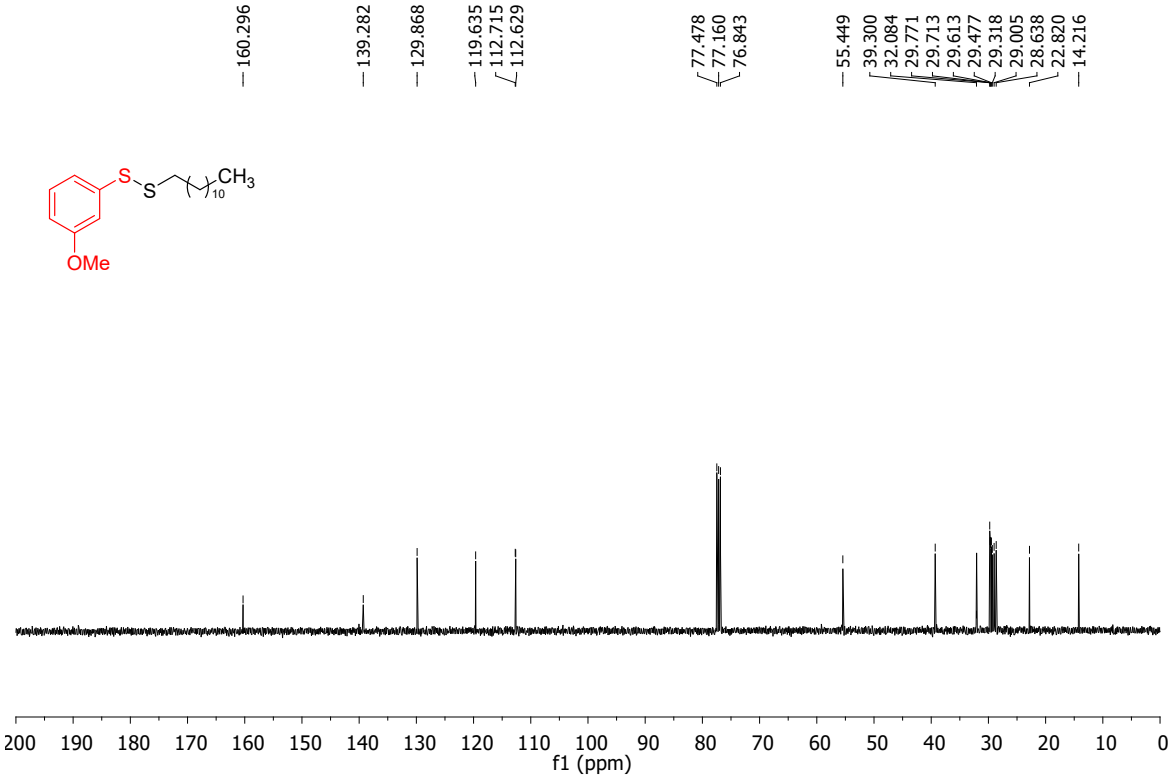

Fig. S28. [13]C NMR spectrum of 1-dodecyl-2-(3-methoxyphenyl)disulfane **(2do)**

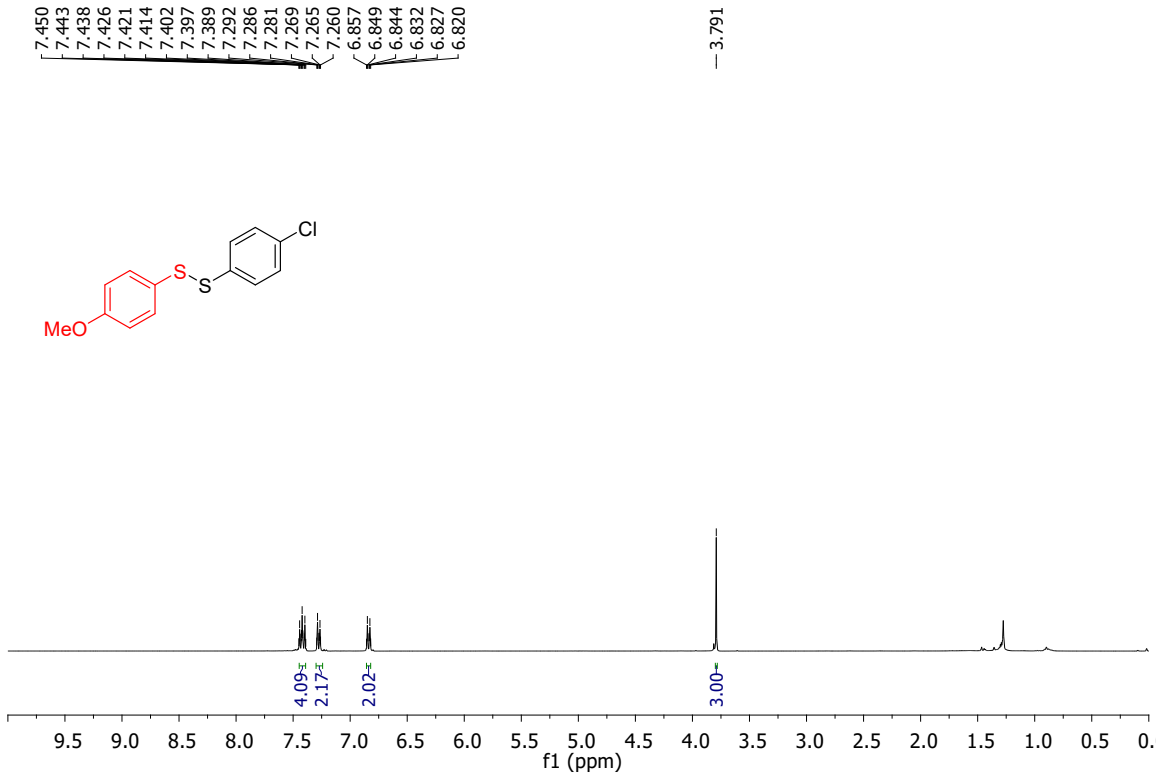

Fig. S29. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-2-(4-methoxyphenyl)disulfane **(2ef)**

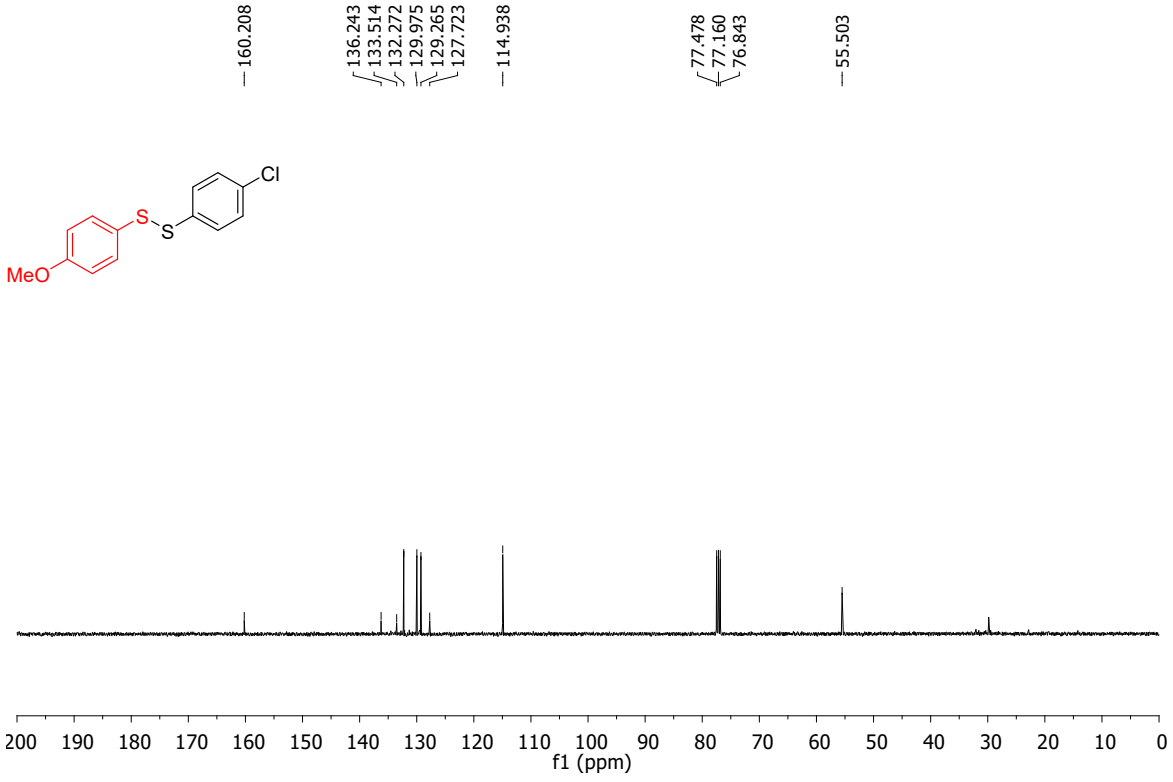

Fig. S30. ^{13}C NMR spectrum of 1-(4-chlorophenyl)-2-(4-methoxyphenyl)disulfane **(2ef)**

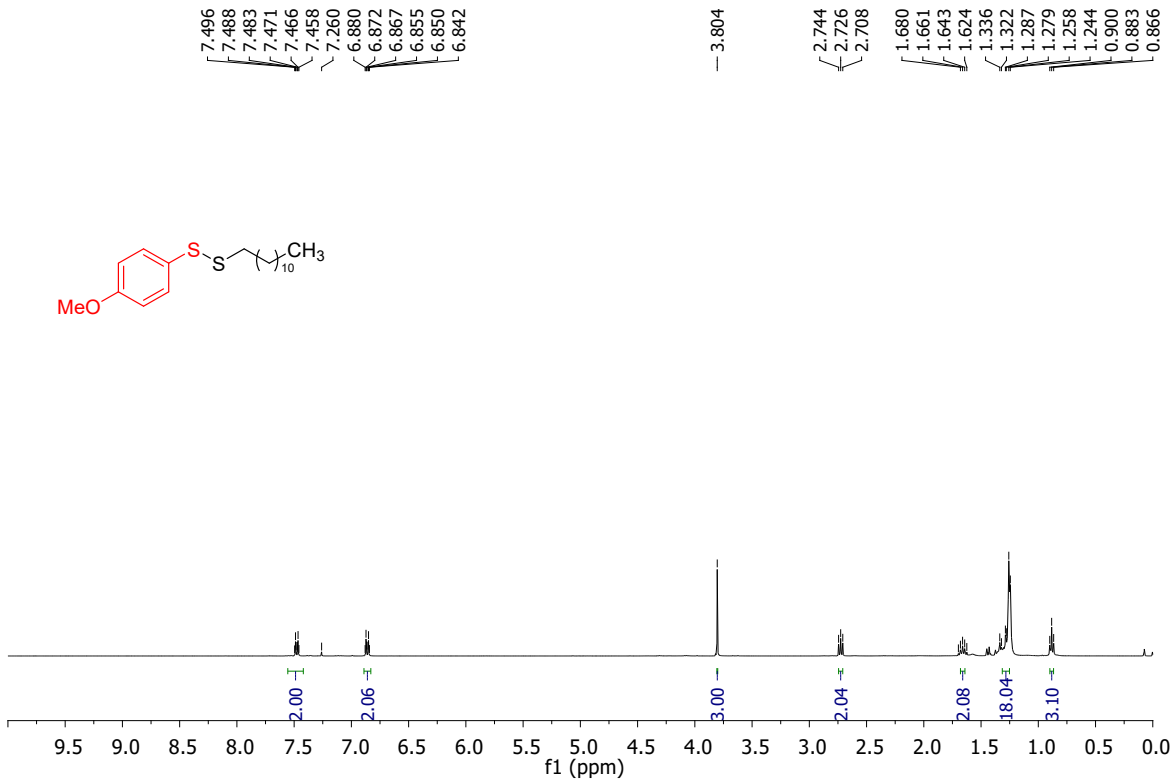

Fig. S31. [1]H NMR spectrum of 1-dodecyl-2-(4-methoxyphenyl)disulfane **(2eo)**

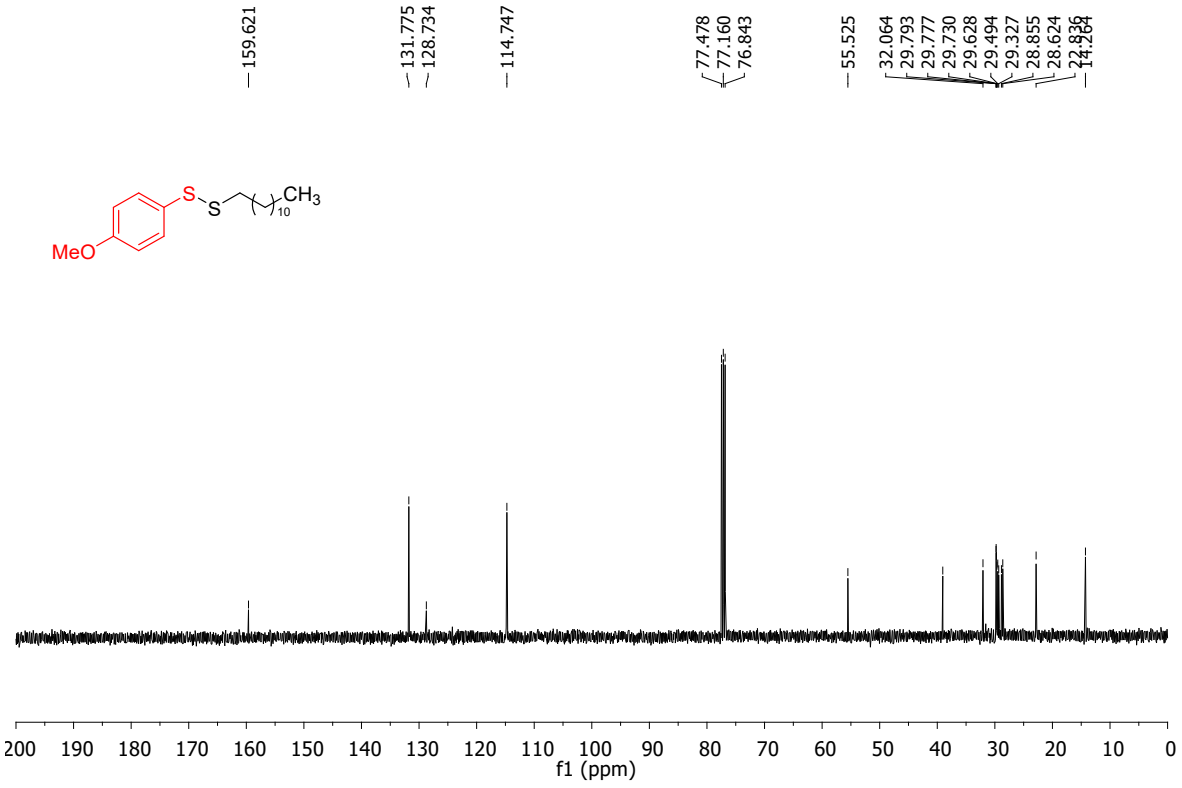

Fig. S32. [13]C NMR spectrum of 1-dodecyl-2-(4-methoxyphenyl)disulfane **(2eo)**

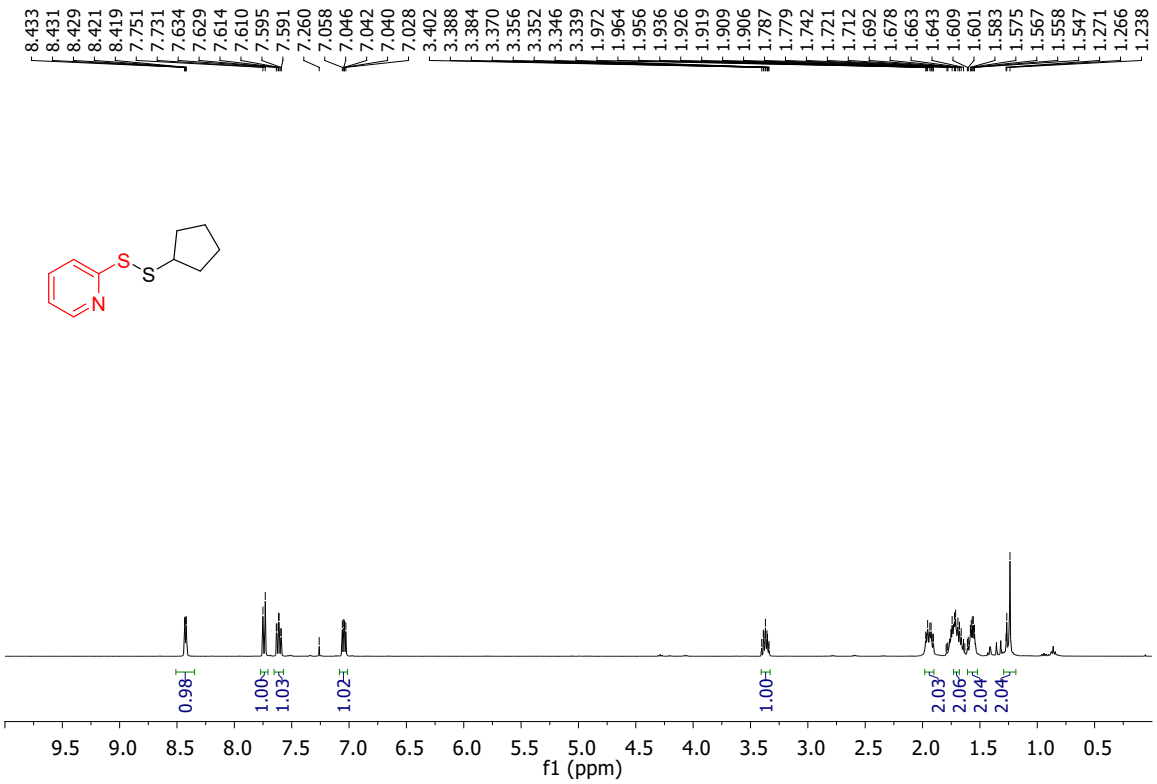

Fig. S33. ^{1}H NMR spectrum of 2-(cyclopentyldisulfaneyl)pyridine **(2gh)**

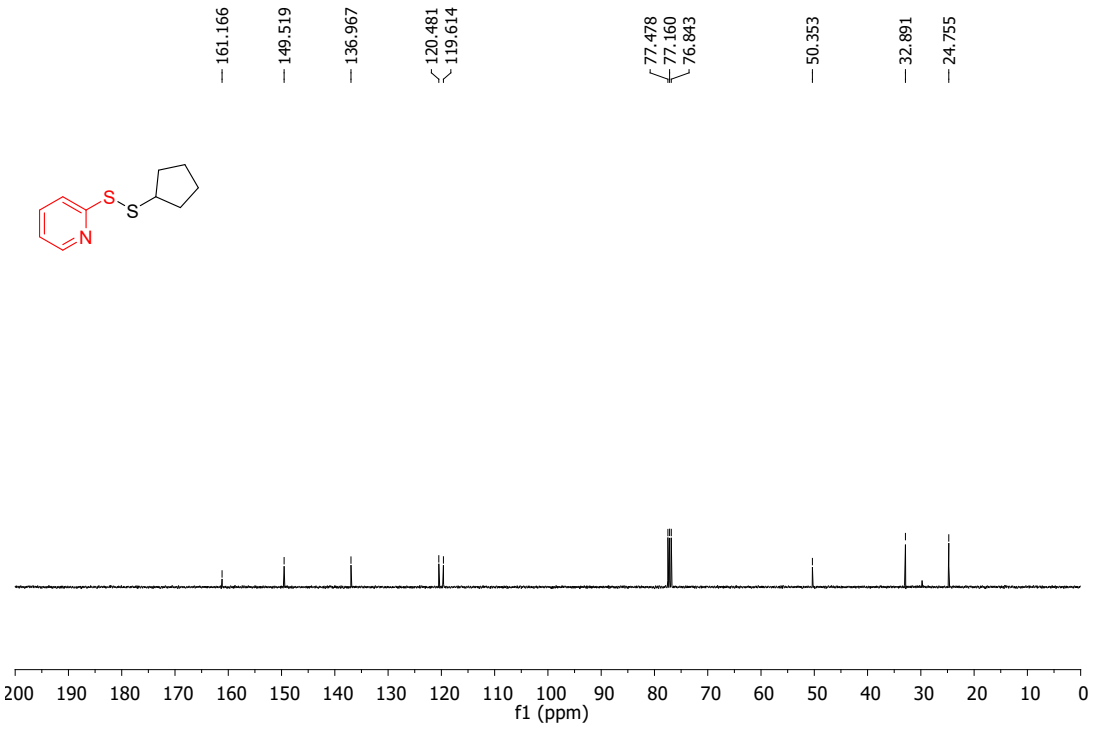

Fig. S34. ^{13}C NMR spectrum of 2-(cyclopentyldisulfaneyl)pyridine **(2gh)**

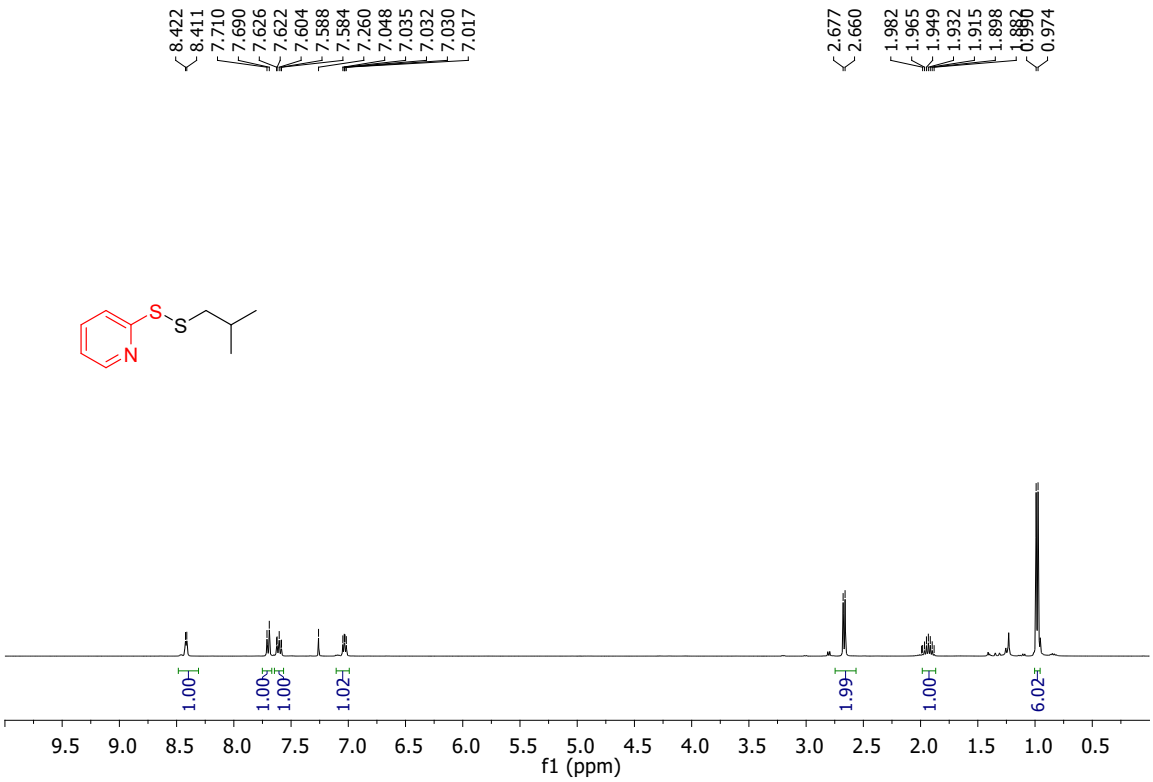

Fig. S35. [1]H NMR spectrum of 2-(isobutyldisulfaneyl)pyridine **(2gn)**

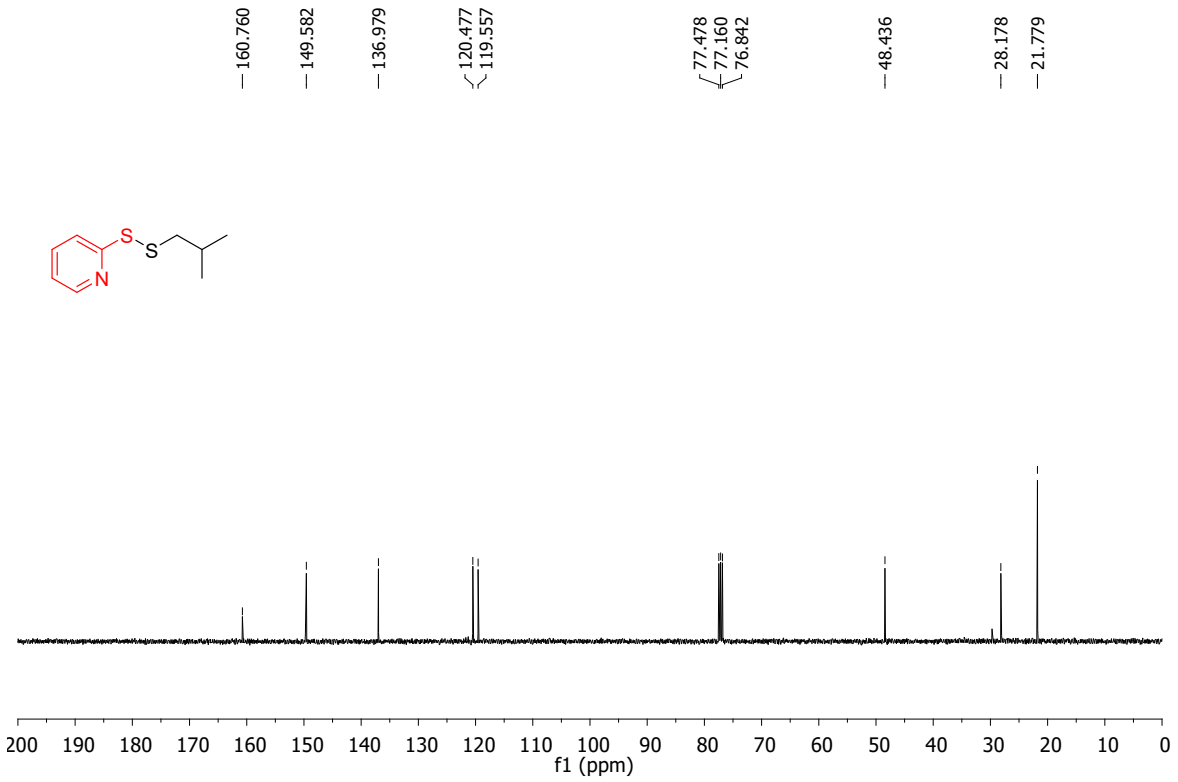

Fig. S36. [13]C NMR spectrum of 2-(isobutyldisulfaneyl)pyridine **(2gn)**

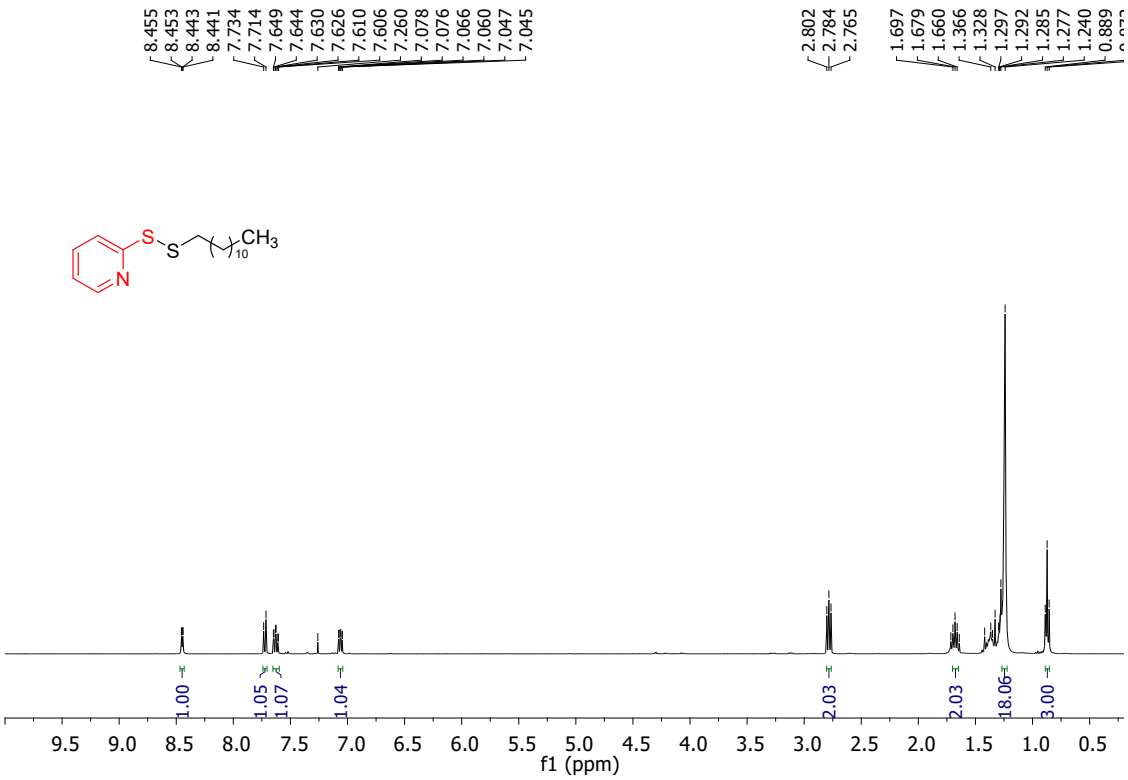

Fig. S37. ^{1}H NMR spectrum of 2-(dodecyldisulfaneyl)pyridine **(2go)**

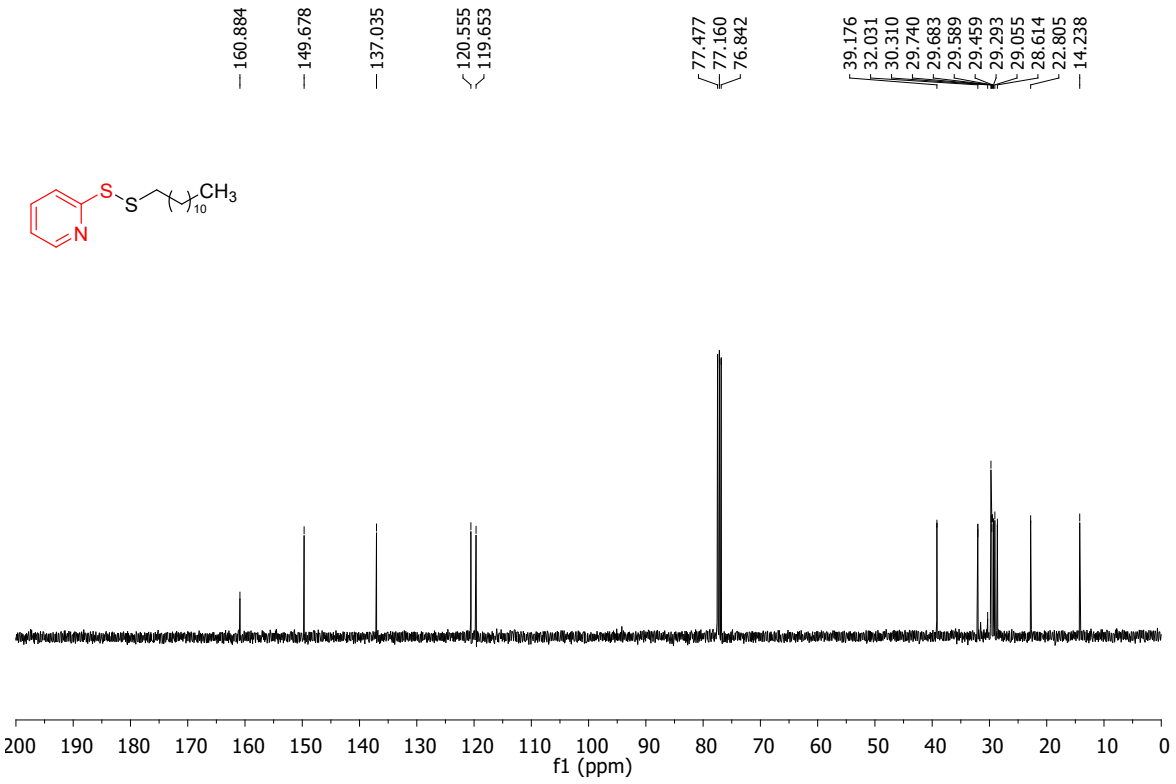

Fig. S38. ^{13}C NMR spectrum of 2-(dodecyldisulfaneyl)pyridine **(2go)**

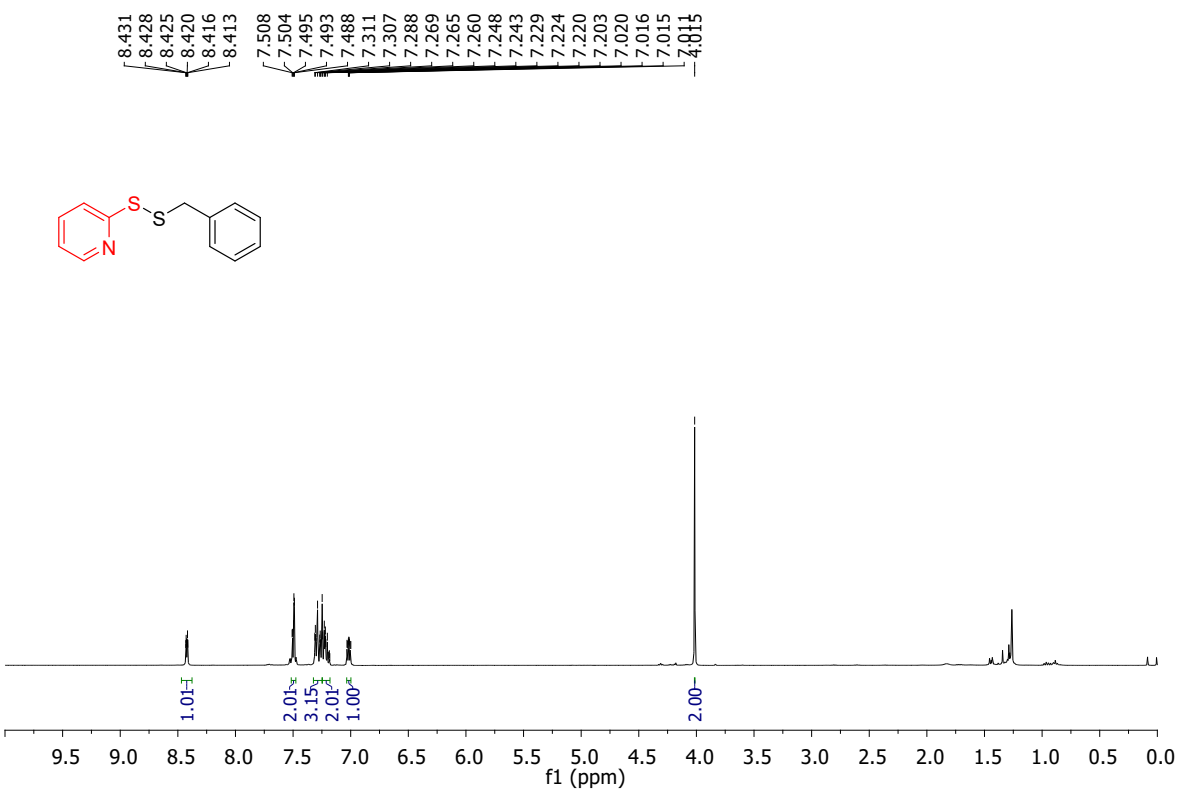

Fig. S39. ^{1}H NMR spectrum of 2-(benzyldisulfaneyl)pyridine **(2gj)**

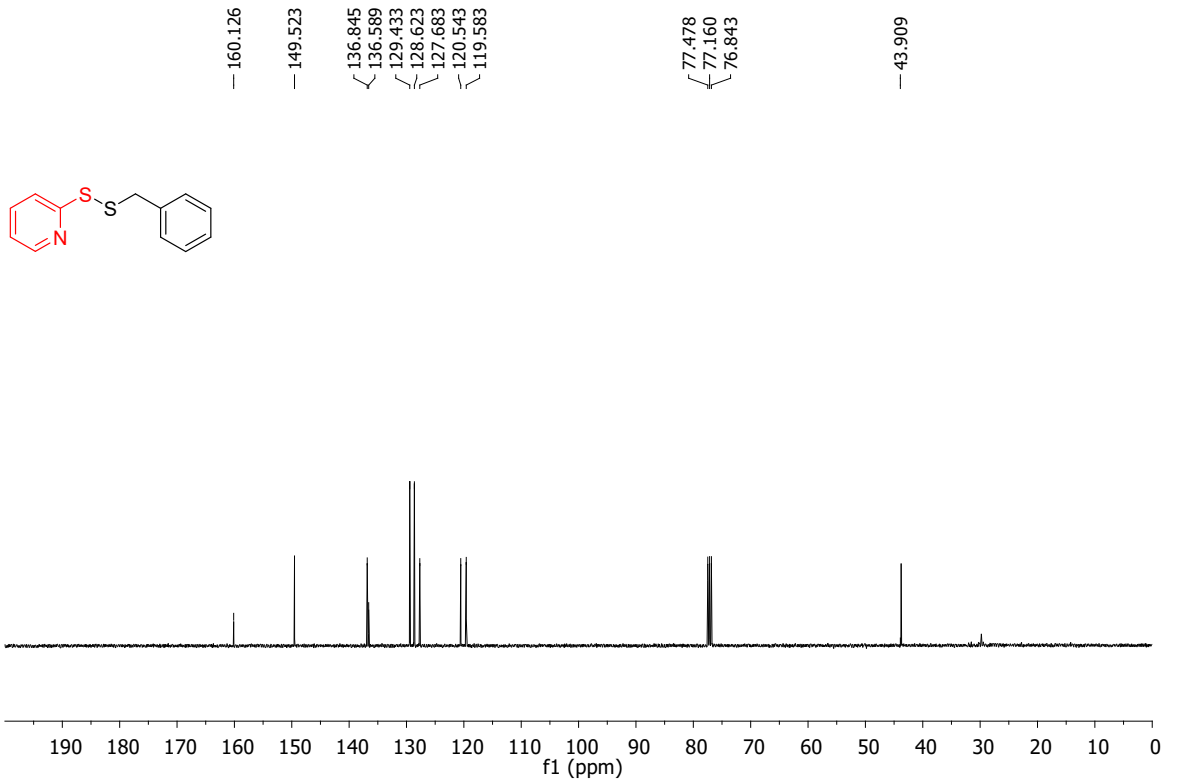

Fig. S40. ^{13}C NMR spectrum of 2-(benzyldisulfaneyl)pyridine **(2gj)**

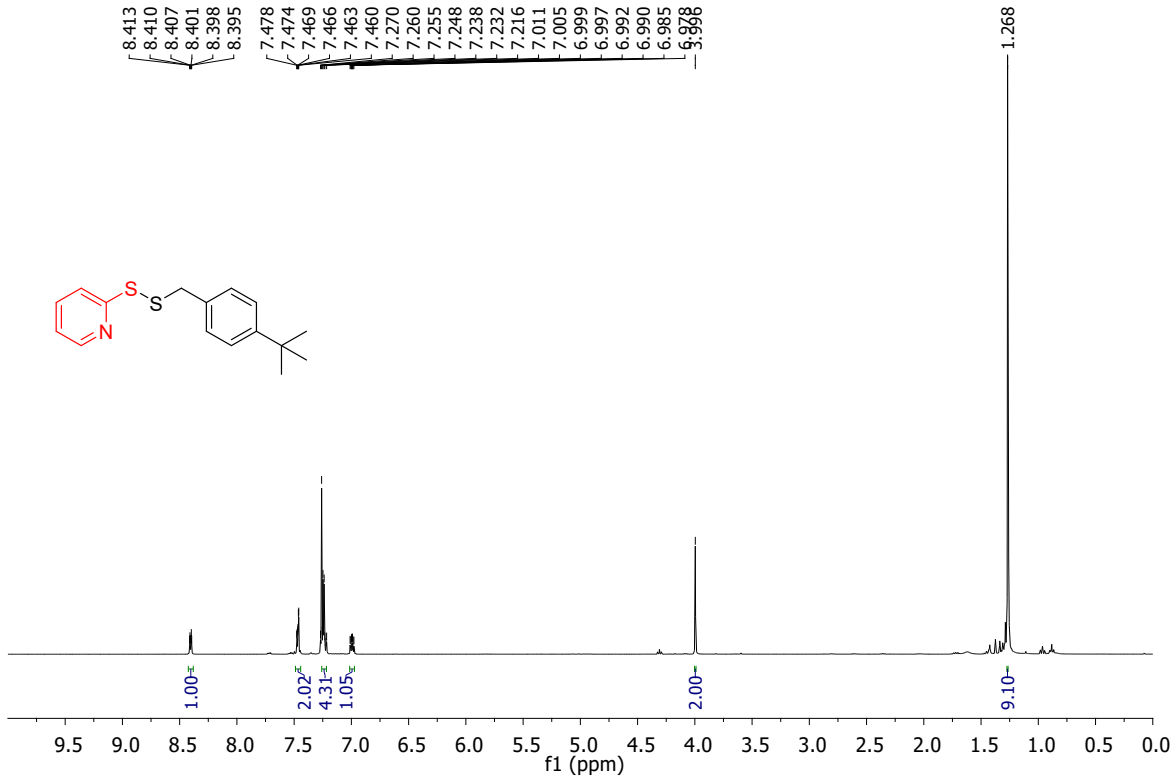

Fig. S41. [1]H NMR spectrum of 2-((4-(tert-butyl) benzyl)disulfaneyl)pyridine **(2gk)**

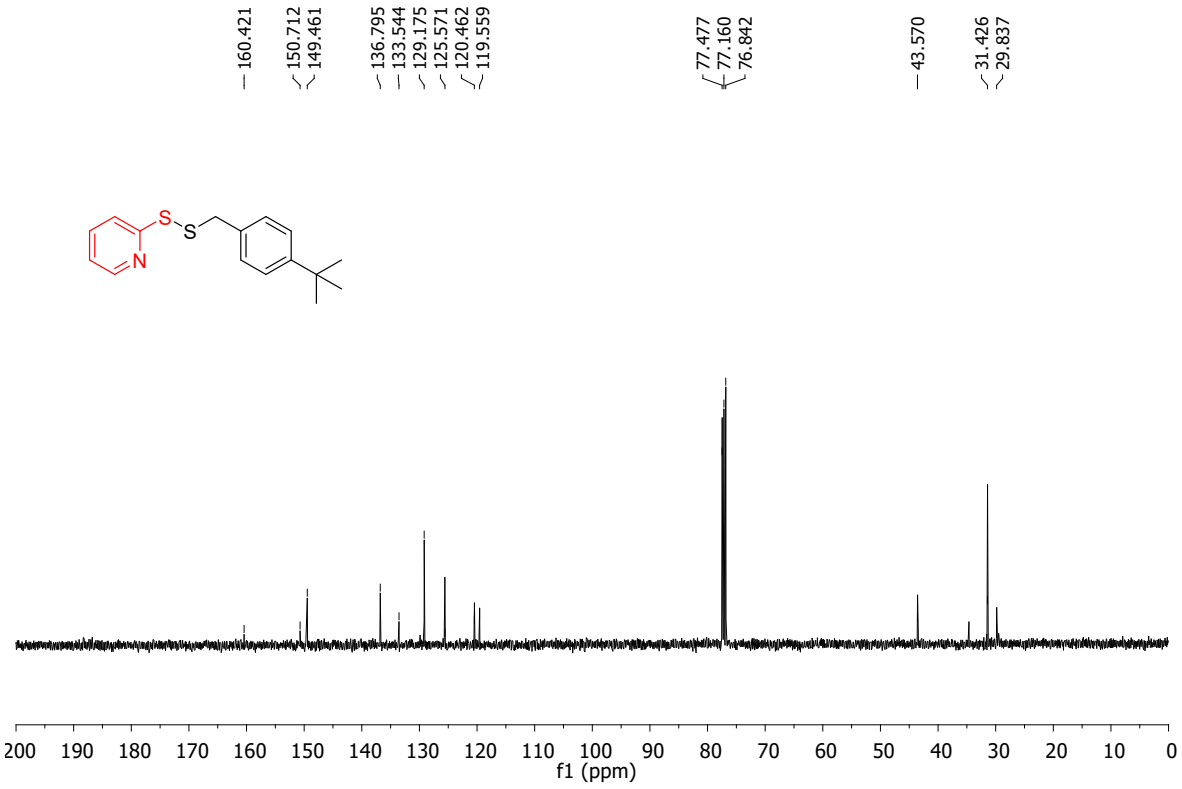

Fig. S42. [13]C NMR spectrum of 2-((4-(tert-butyl)benzyl)disulfaneyl)pyridine **(2gk)**

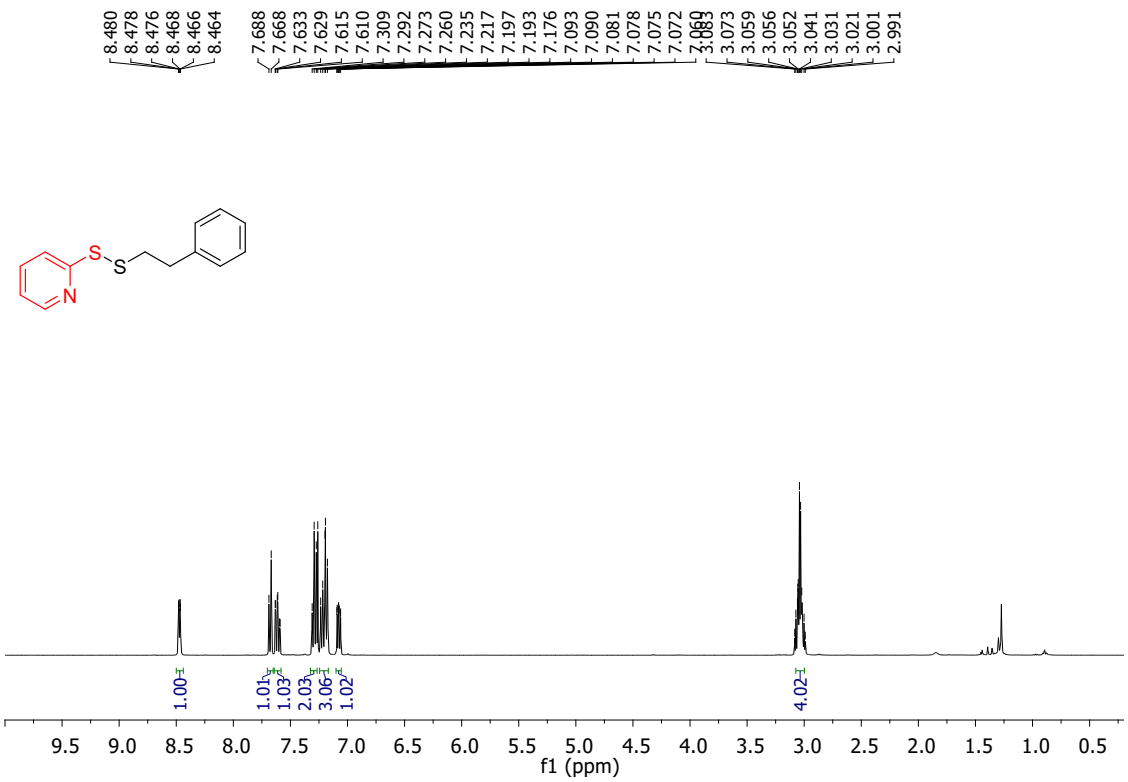

Fig. S43. [1]H NMR spectrum of 2-(phenethyldisulfaneyl) pyridine **(2gl)**

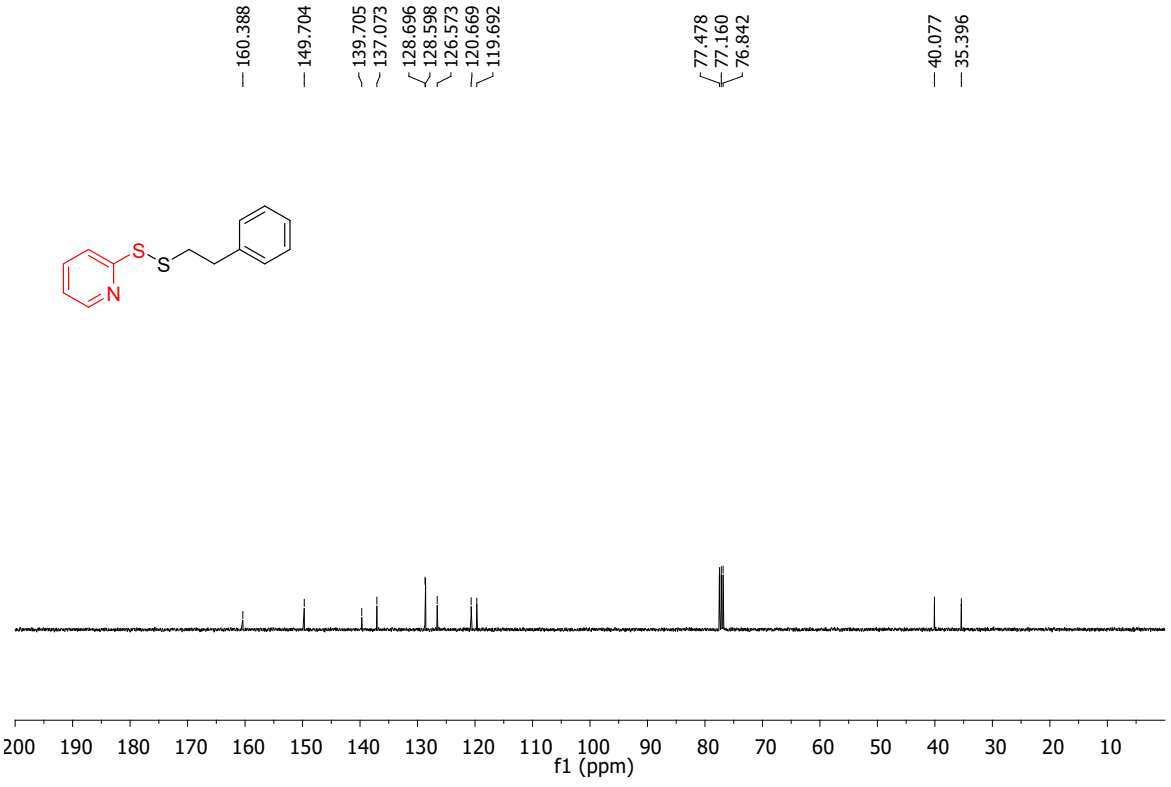

Fig. S44. [13]C NMR spectrum of 2-(phenethyldisulfaneyl) pyridine **(2gl)**

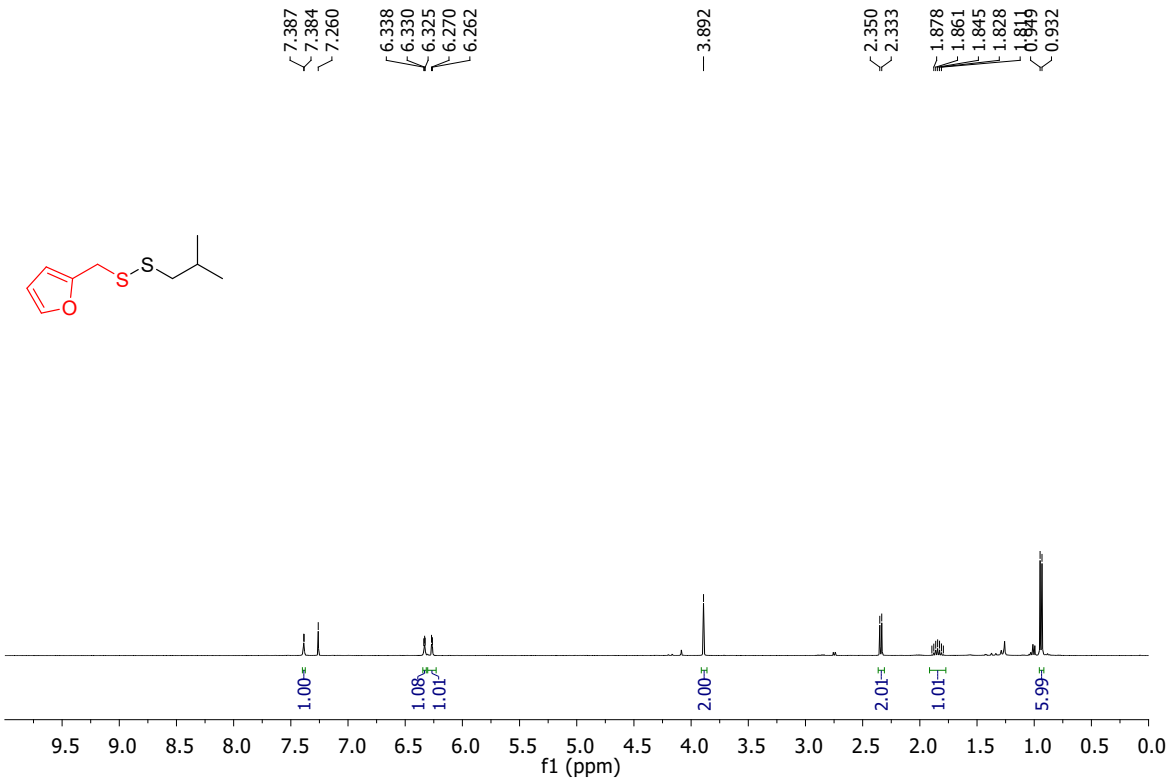

Fig. S45. [1]H NMR spectrum of 2-((isobutyldisulfaneyl) methyl) furan **(2mn)**

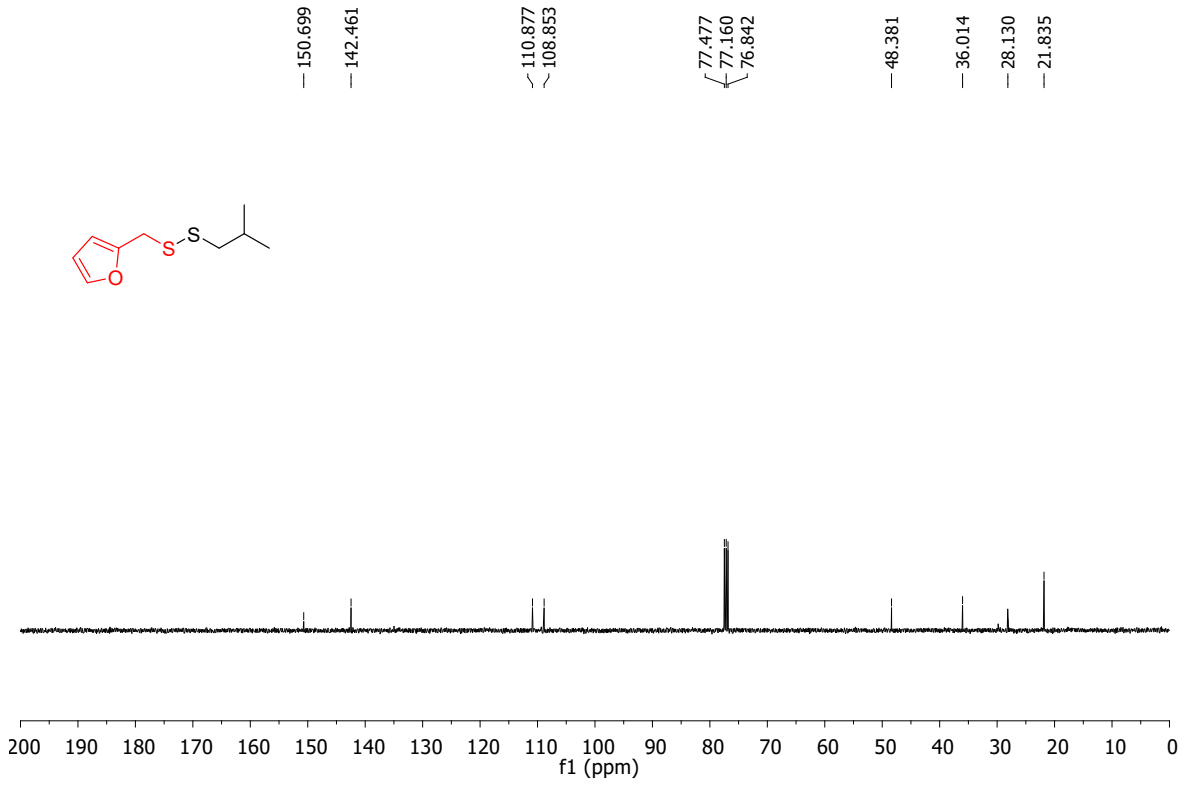

Fig. S46. [13]C NMR spectrum of 2-((isobutyldisulfaneyl) methyl)furan **(2mn)**

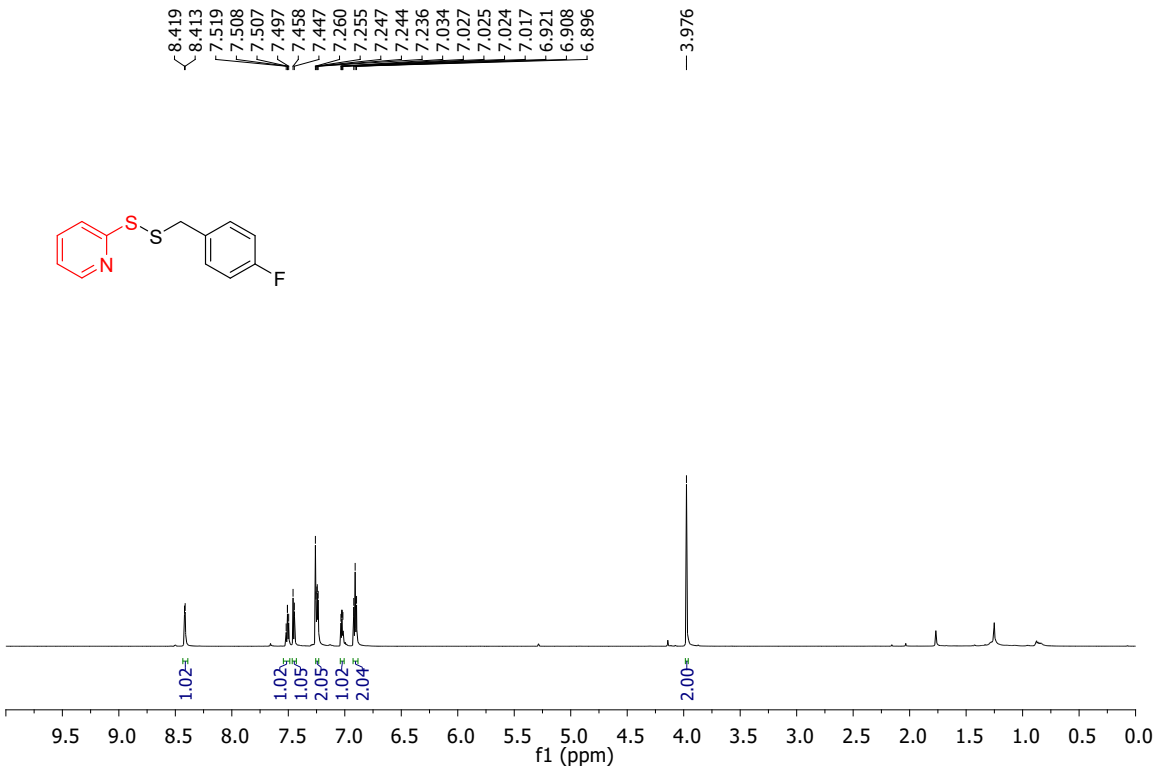

Fig. S47. [1]H NMR spectrum of 2-((4-fluorobenzyl)disulfaneyl)pyridine **(2gq)**

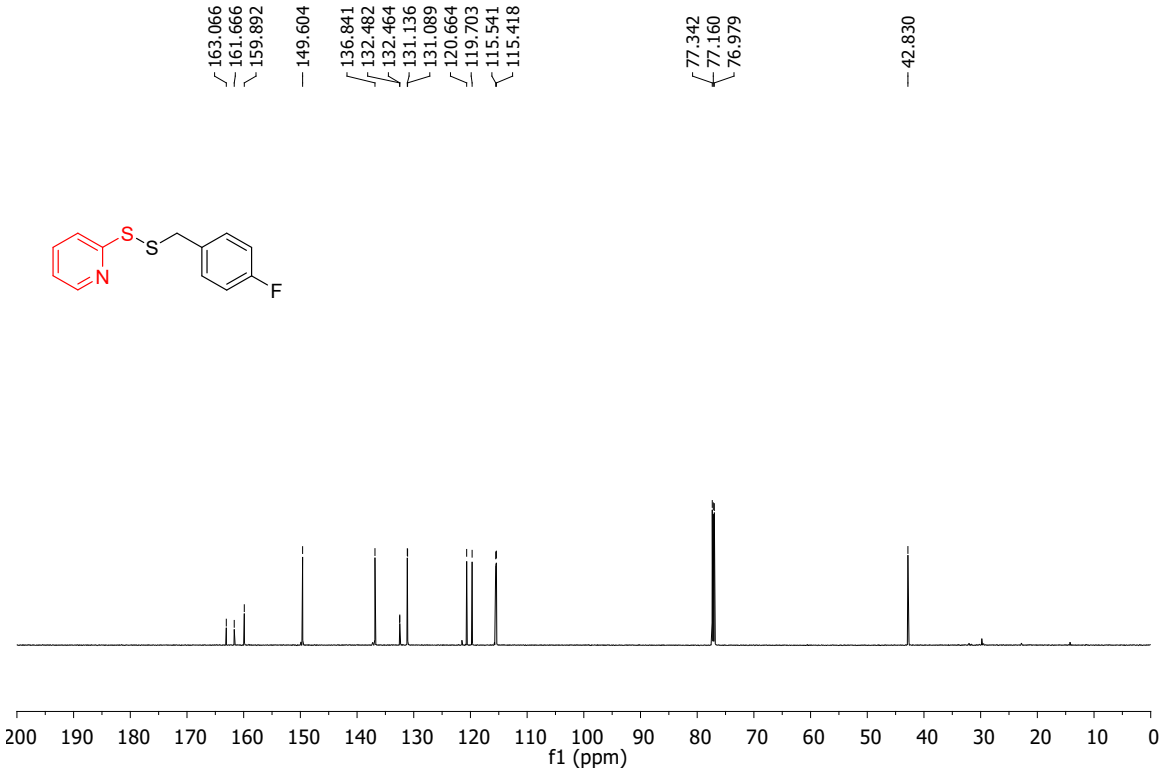

Fig. S48. [13]C NMR spectrum of 2-((4-fluorobenzyl)disulfaneyl)pyridine **(2gq)**

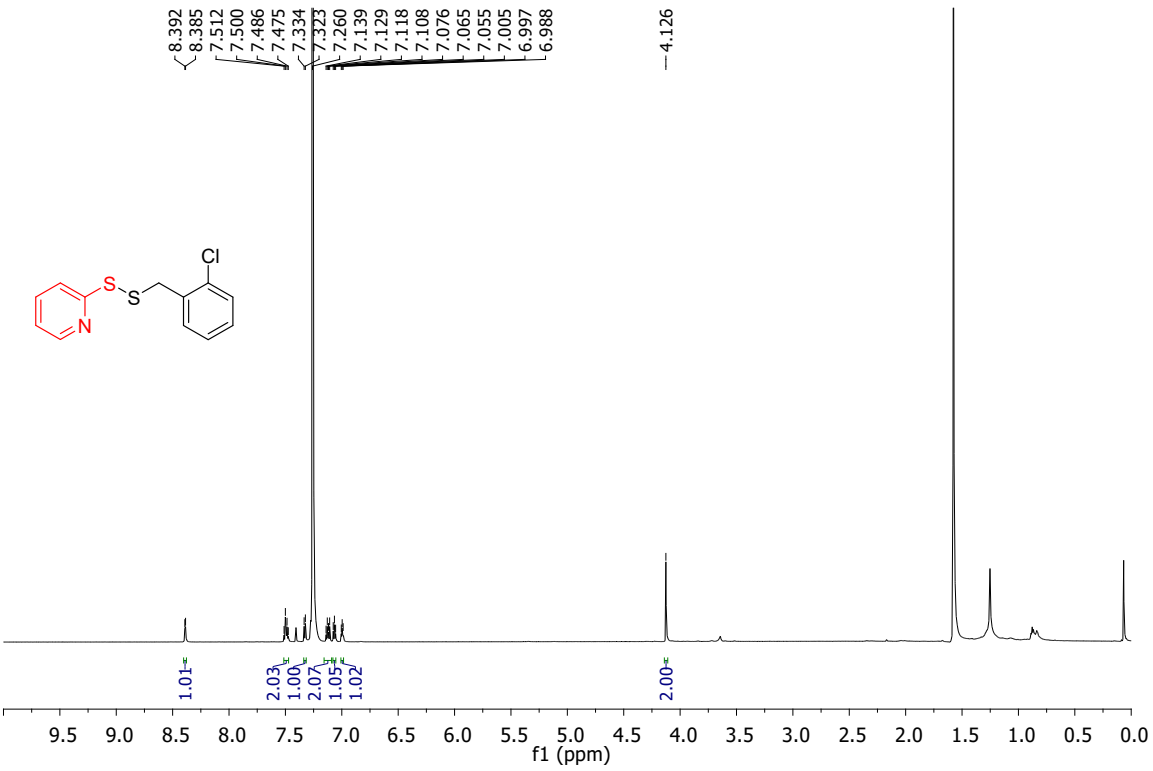

Fig. S49. ^{1}H NMR spectrum of 2-((2-chlorobenzyl)disulfaneyl)pyridine **(2gp)**

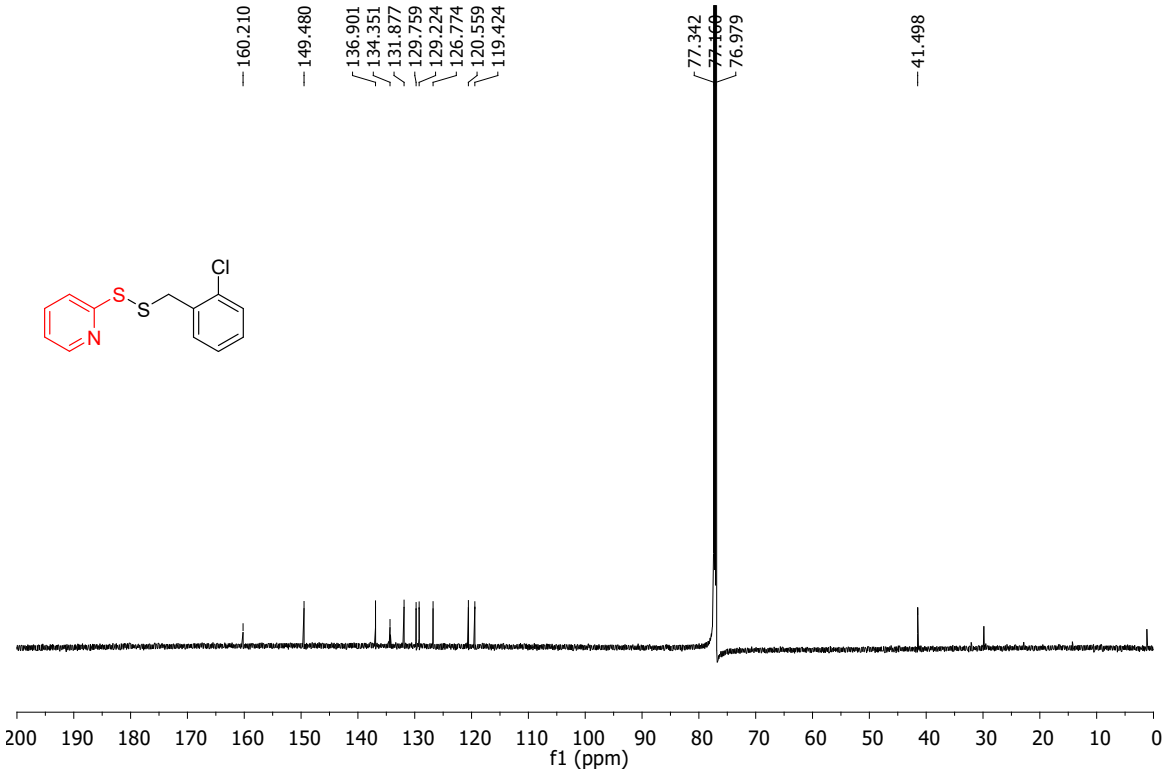

Fig. S50. ^{13}C NMR spectrum of 2-((2-chlorobenzyl)disulfaneyl)pyridine **(2gp)**

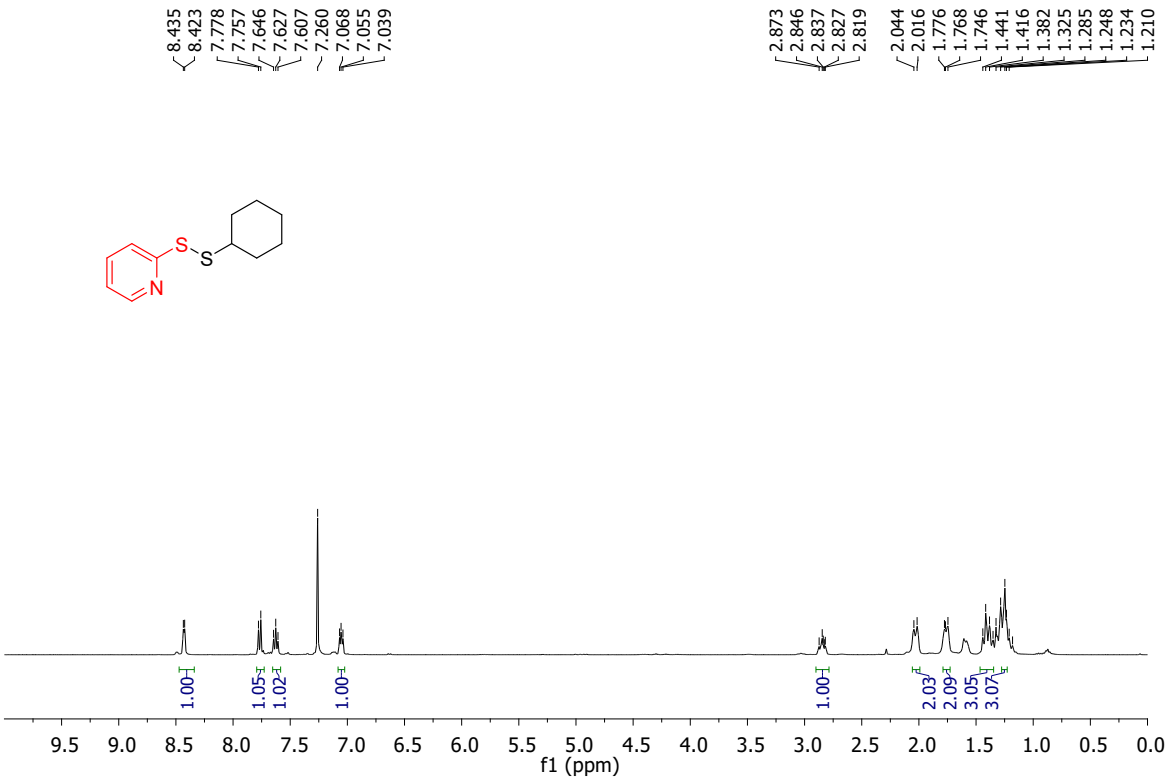

Fig. S51. ^{1}H NMR spectrum of 2-(cyclohexyldisulfaneyl)pyridine **(2gr)**

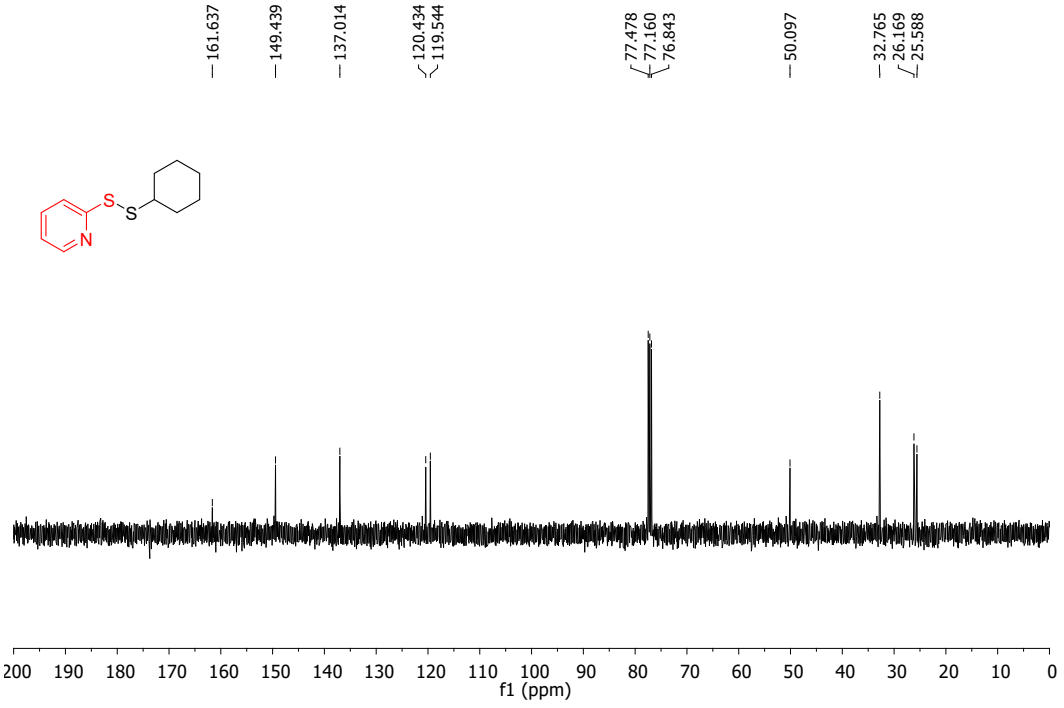

Fig. S52. ^{13}C NMR spectrum of 2-(cyclohexyldisulfaneyl)pyridine **(2gr)**

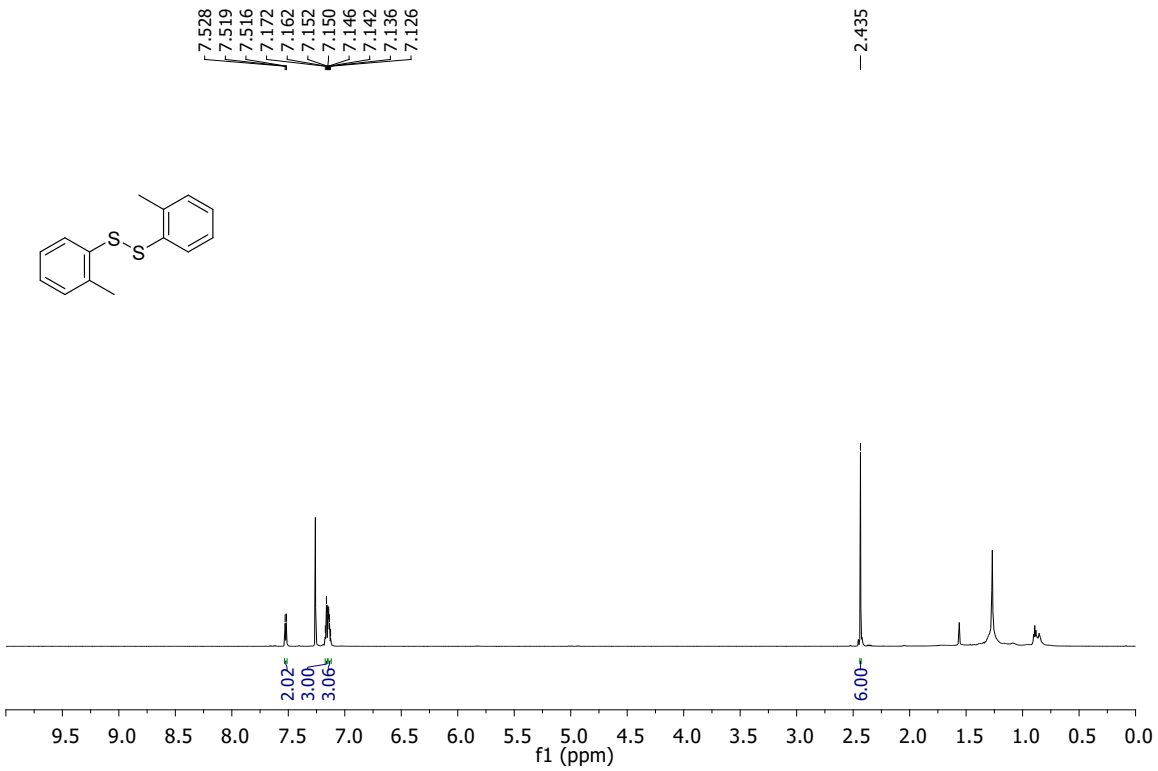

Fig. S53. ^{1}H NMR spectrum of 1,2-di-o-tolyldisulfane **(1a)**

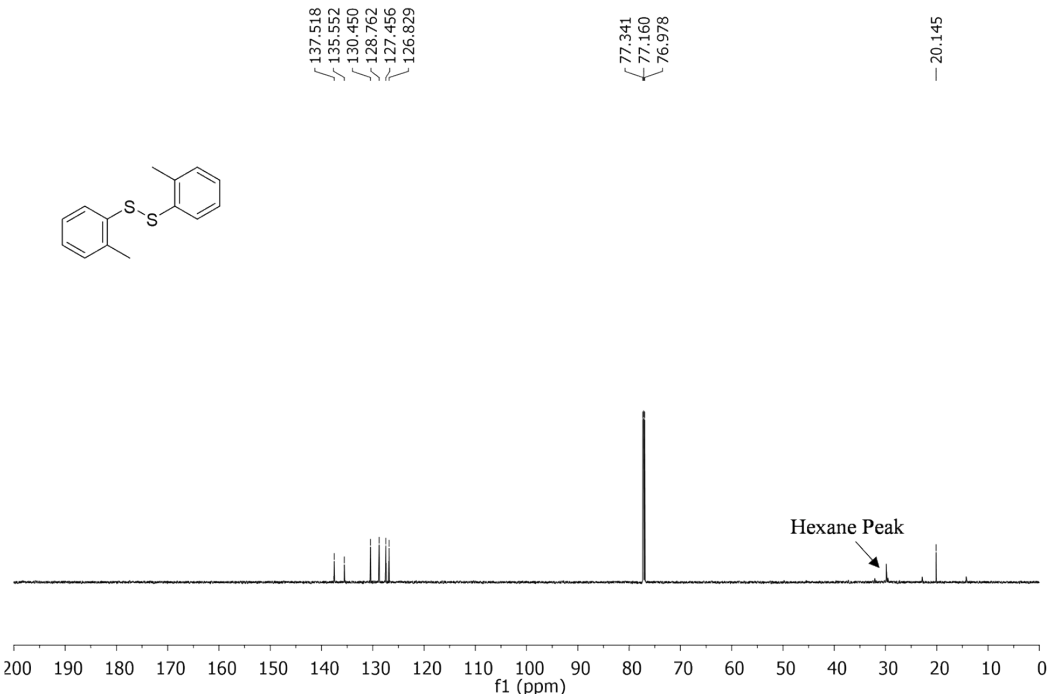

Fig. S54. ^{13}C NMR spectrum of 1,2-di-o-tolyldisulfane **(1a)**

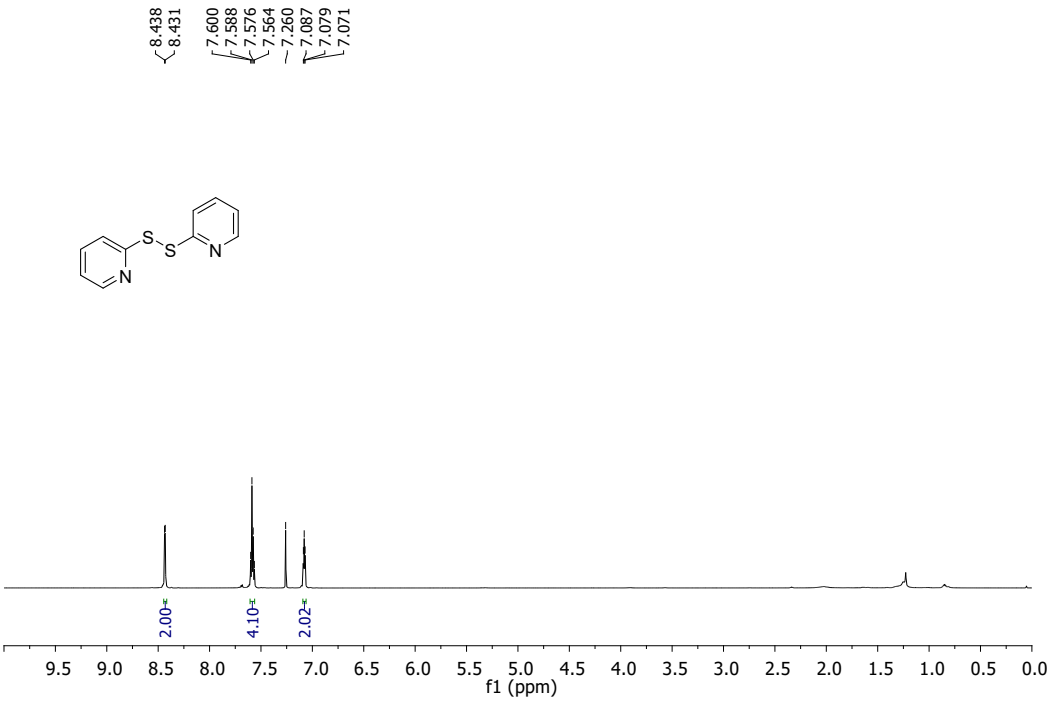

Fig. S55. ^{1}H NMR spectrum of 1,2-di(pyridin-2-yl)disulfane **(1g)**

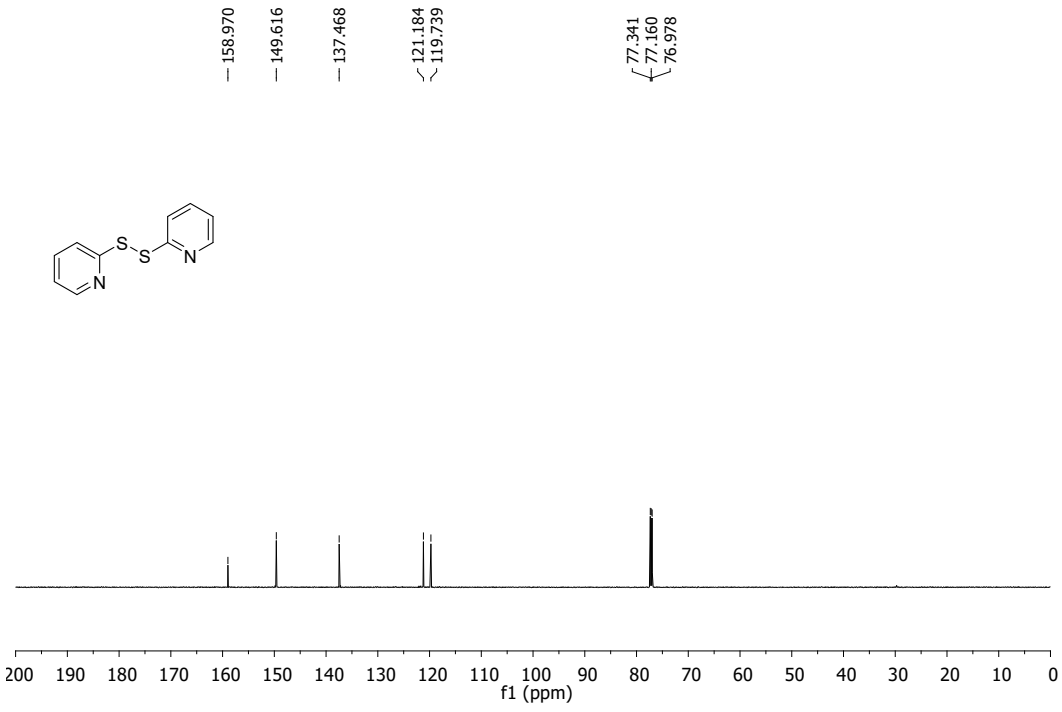

Fig. S56. ^{13}C NMR spectrum of 1,2-di(pyridin-2-yl)disulfane **(1g).**