Supporting Information

Hydrogenation of sulfoxides to sulfides mediated by incomplete cubane-type Mo_3S_4 clusters: synthetic applications and mechanistic insights

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1. Materials and methods

All reactions were performed under free atmosphere, unless otherwise stated. Cluster complexes employed in this work were prepared according to the published procedures. All other reagents were obtained from commercial sources and used as received or prepared according to the literature.

Elemental analyses were performed with a Euro EA 3000 Elemental Analyzer. Mass spectra were registered in a QTOF Premier instrument operated in the V-mode at a resolution of *ca*. 10000 (FWHM) equipped with an orthogonal Z-spray-electrospray interface (Waters, Manchester, UK). The temperature of the source block was set to 100 °C, and the desolvation temperature was set to 120 °C. A capillary voltage of 3.3 kV was used in the positive scan mode, and the cone voltage was set to Uc = 20 V. Sample solutions in CH_3CN or CH_3OH (0.1 % formic acid for organic compounds) were injected with a syringe pump directly connected to the ESI source at a flow rate of 10 μLmin^{-1}. The observed isotopic pattern of each compound perfectly matched the theoretical isotope pattern calculated from their elemental composition by using the MassLynx 4.1 program.[1] ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance III HD 300 MHz or 400 MHz spectrometer. Gas chromatography analyses were performed on an Agilent 7820A GC System equipped with a FID and a capillary column Agilent (HP-5, 30m x 0.32mm x 0.25 μm). The GC yields were determined by GC-FID using *n*-hexadecane as an internal standard.

2. General procedures for the catalytic reactions

2·1. General procedure for the catalytic hydrogenation of sulfoxides (0.1 mmol). General procedure A:

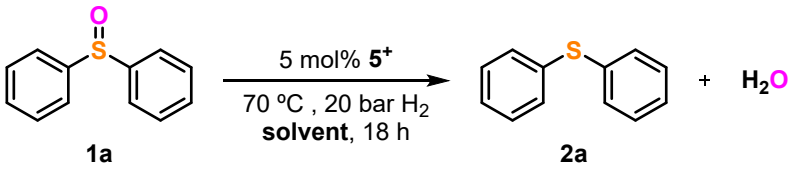
A 4 mL glass vial containing a stirring bar was charged with the molybdenum catalyst (0.0050 mmol of $[Mo_3S_4Cl_3(dmen)_3]Cl$), sulfoxide (0.1 mmol), internal standard (20 μL of hexadecane) and 3 mL of CH_3CN. Afterwards, the reaction vial was capped with a septum equipped with a syringe and set in the alloy plate and then introduced into a 300 mL autoclave. Once sealed, the autoclave was purged three times with 20 bar of hydrogen, then pressurized to 6 bar of hydrogen and placed into an aluminium block preheated at 50 °C. After 12 h, the autoclave was cooled to room temperature and the hydrogen was released. Ethyl acetate (2 mL) was then added, and a sample was taken to be analyzed by GC.

2·2. General procedure for the catalytic hydrogenation of sulfoxides (0.3 mmol). General procedure B:

A 8 mL glass vial containing a stirring bar was charged with the molybdenum catalyst (0.0050 mmol of $[Mo_3S_4Cl_3(dmen)_3]Cl$), sulfoxide (0.3 mmol) and 6 mL of CH_3CN. Afterwards, the reaction vial was capped with a septum equipped with a syringe and set in the alloy plate and then introduced into a 300 mL autoclave. Once sealed, the autoclave was purged three times with 20 bar of hydrogen, then pressurized to 6 bar of hydrogen and placed into an aluminium block preheated at 50 °C. After 18 h, the autoclave was cooled to room temperature and the hydrogen was released. To determine the isolated yields of the sulfide product, after completion of the reaction the mixture was taken to dryness and purified by flash silica gel chromatography (pentane/ethyl acetate mixtures) to give the corresponding pure product.

3. Conditions optimization for the hydrogenation of diphenyl sulfoxide

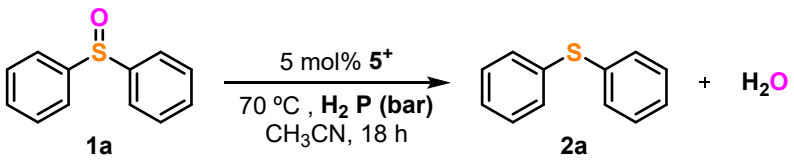
Table S1. Influence of the solvent in the hydrogenation of diphenyl sulfoxide (**1**)[a]



Entry	Solvent	Conversion (%)[b]	Yield (%)[b]
1	CH_3CN	>99	>99
2	H_2O	23	19
3	Triglyme	28	14
4	Glicerol	10	8
5	Propilene carbonate	49	45
6	CH_3OH	57	56

[a] Reaction conditions: diphenyl sulfoxide (0.1 mmol), catalyst (5 mol%), 70 ºC, H_2 pressure (20 bar), solvent (3 mL), 18 h. [b] Determined by GC using hexadecane as an internal standard.

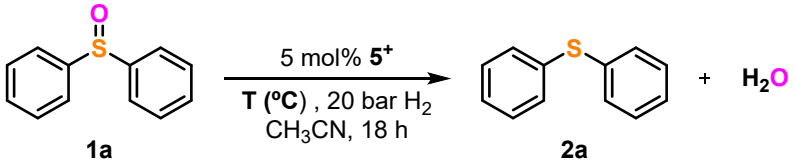
Table S2. Influence of the pressure in the hydrogenation of diphenyl sulfoxide (**1**)[a]



Entry	H_2 Pressure (bar)	Conversion (%)[b]	Yield (%)[b]
1	20	>99	>99
2	10	>99	>99
3	6	>99	>99
4	1-2	15	10

[a] Reaction conditions: diphenyl sulfoxide (0.1 mmol), catalyst (5 mol %), 70 ºC, H_2 pressure, CH_3CN (3 mL), 18 h. [b] Determined by GC using hexadecane as an internal standard.

Table S3. Influence of the temperature in the

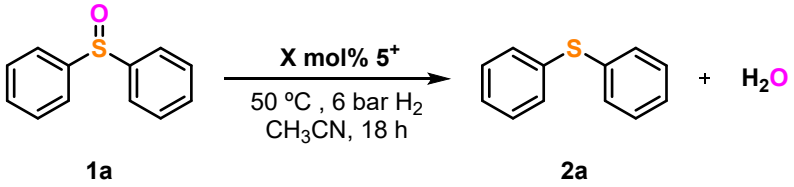


hydrogenation of diphenyl sulfoxide (**1**)[a]

Entry	Temperature (ºC)	Conversion (%)[b]	Yield (%)[b]
1	70	>99	>99
2	60	>99	>99
3	50	>99	>99
4	40	75	73

[a] Reaction conditions: diphenyl sulfoxide (0.1 mmol), catalyst (5 mol %), T (ºC), 6 bar H_2, CH_3CN (3 mL), 18 h. [b] Determined by GC using hexadecane as an internal standard.

Table S4. Influence of the catalyst loading in the



hydrogenation of diphenyl sulfoxide (**1**)[a]

Entry	X mol %	Conversion (%)[b]	Yield (%)[b]
1	0	3	0
2	1	19	14
3	3	72	72
4	5	>99	>99

[a] Reaction conditions: diphenyl sulfoxide (0.1 mmol), catalyst (X mol %), 70 ºC, 6 bar H_2, CH_3CN (3 mL), 18 h. [b] Determined by GC using hexadecane as an internal standard.

4. Cluster monitoring

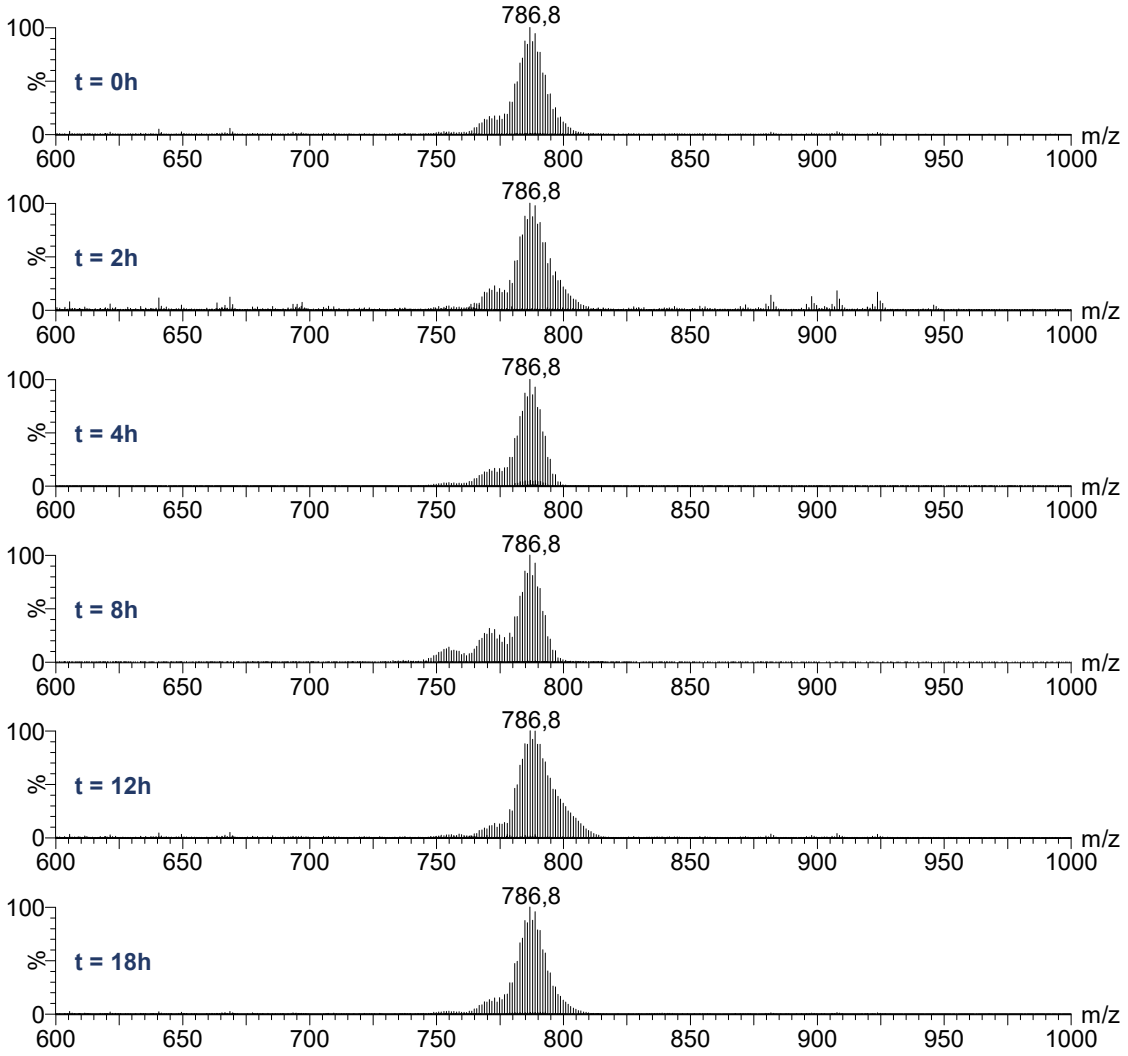


Figure S1. HRMS (ESI-TOF) spectra of catalyst $\mathbf{5}^{+}$ after diphenyl sulfoxide hydrogenation at different times. Spectra registered from different batch experiments at 20 V in CH_3CN.

5. Recycling experiments

Recycling experiments were performed by successive additions of diphenyl sulfoxide to the reaction mixture. After the fifth run, the reaction crude was concentrated under reduced pressure and the solid residue was washed three times with 5 mL of ethyl acetate and dried under vacuum. After that, the solid sample was analyzed by HRMS spectrometry and ^{1}H-NMR spectroscopy to confirm the integrity of the cluster catalyst.

Recycling experiments were also conducted by sample evaporation. Then, 5 mL of ethyl acetate were added to remove organics and the catalyst was dried under vacuum. Finally, the catalyst was redissolved in acetonitrile and the mixture was transferred to the reaction vial with diphenyl sulfoxide for the next run.

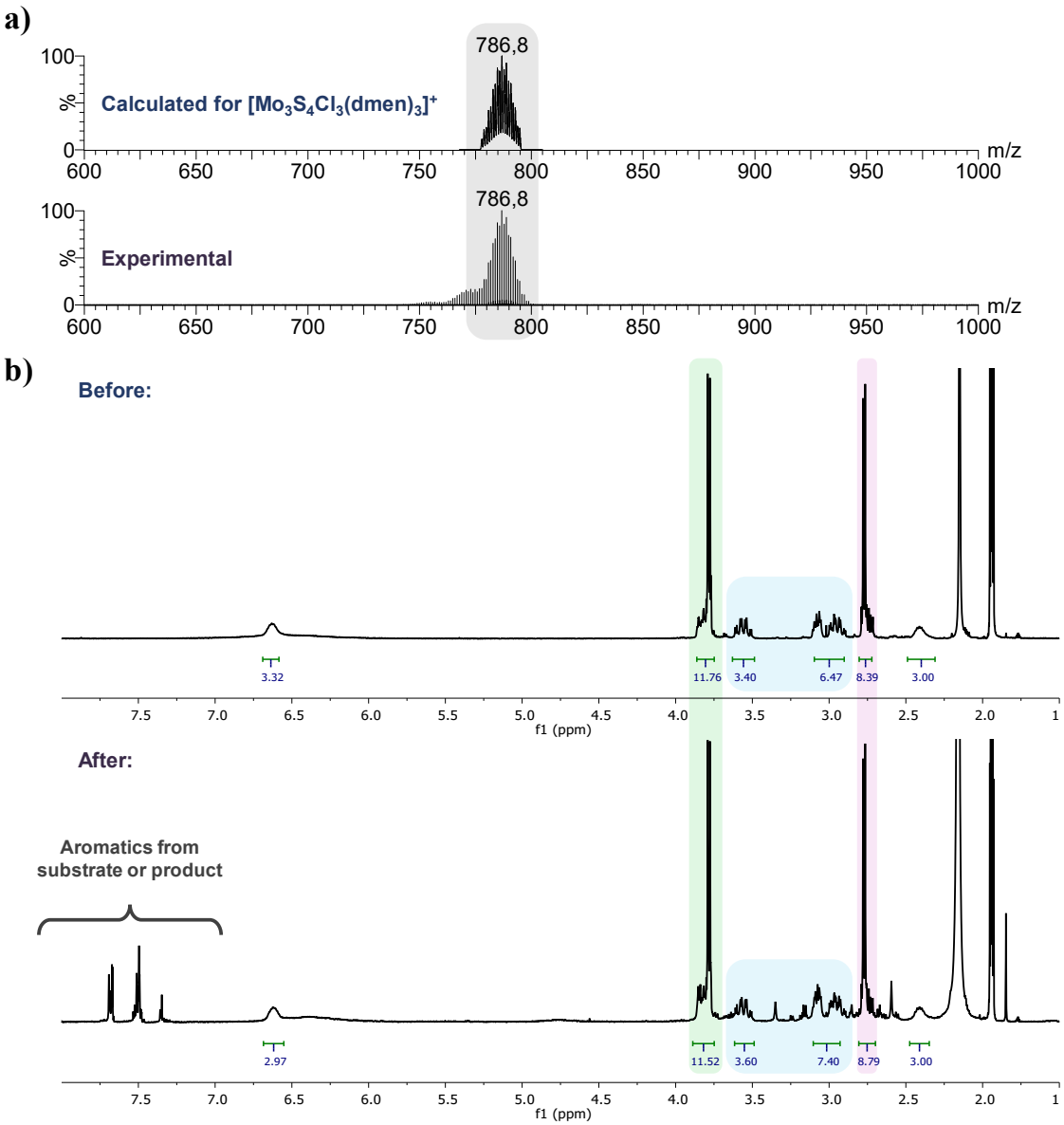
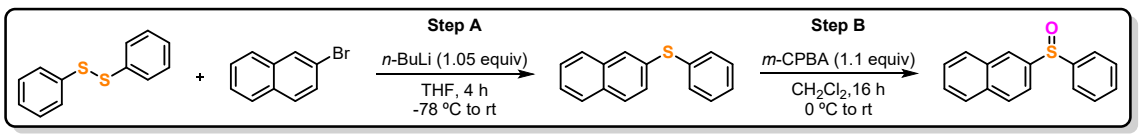


Figure S2. HRMS (ESI-TOF) spectrum of catalyst $\mathbf{5}^{+}$ after recycling experiments. Spectrum registered at 20 V in CH_3CN (a). ^{1}H-NMR (400 MHz, CD_3CN) spectra of catalyst $\mathbf{5}^{+}$ before and after recycling experiments.

6. Synthesis of sulfoxides

6.1 Synthesis of diaryl sulfoxides

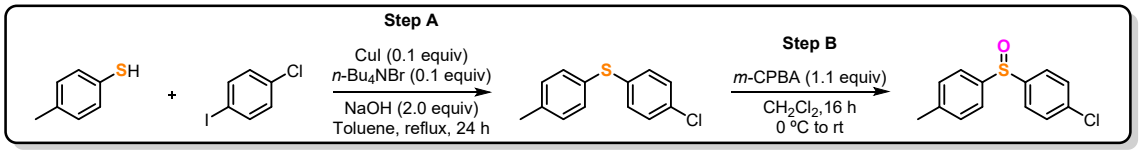
Bis(4-trifluoromethylphenyl) sulfoxide (1d)



Step A: The synthesis of this compound was adapted from the literature.[2] A mixture of 4-trifluoromethylbenzenethiol (0.95 g, 5 mmol), 4-iodobenzotrifluoride (1.43 g, 5 mmol), *n*-Bu_4NBr (0.18 g, 0.5 mmol) and NaOH (0.43 g, 10 mmol) and CuI (110.3 mg, 0.5 mmol) in toluene (6 mL) was stirred under reflux for 72 h. The reaction mixture was allowed to reach room temperature, then 10 mL of NH_4Cl (sat. aqueous solution) were added. The aqueous phase was separated and extracted with EtOAc (3 x 10 mL), the combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane) to give the corresponding sulfide as a white solid (520.0 mg, 31%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.62(d, J = 9.0 Hz, 4H), 6.48 (d, J = 9.0 Hz, 4H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 139.7, 131.1, 129.9 (q, J = 37.5 Hz), 125.8 (q, J = 3.7 Hz), 122.7 (q, J = 270.1 Hz). **^{19}F-NMR** (282 MHz, $CDCl_3$): δ = -62.8.

Step B: To a solution of bis(4-(trifluoromethyl)phenyl)sulfide (404.0 mg, 1.25 mmol) in CH_2Cl_2 (2 mL) was added *m*-CPBA (300.9 mg, 1.38 mmol) slowly at 0 °C and the mixture was stirred at this temperature for 4 h. Then the mixture was warmed to room temperature and stirred overnight. After that, the mixture was quenched with 4 mL of $NaHCO_3$ (sat. aqueous solution). The aqueous layer was then extracted with CH_2Cl_2 (3×10 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane:EtOAc = 9:1) to give the title compound **1d** as a white solid. (192.1 mg, 45%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.71(d, J = 8.8 Hz, 4H), 6.57 (d, J = 8.8 Hz, 4H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 144.5, 137.4, 134.0 (q, J = 32.4 Hz), 130.8 (q, J = 3.8 Hz), 128.7 (q, J = 270.2 Hz). **^{19}F-NMR** (282 MHz, $CDCl_3$): δ = -63.0.

3-(phenylsulfinyl)pyridine (1l)

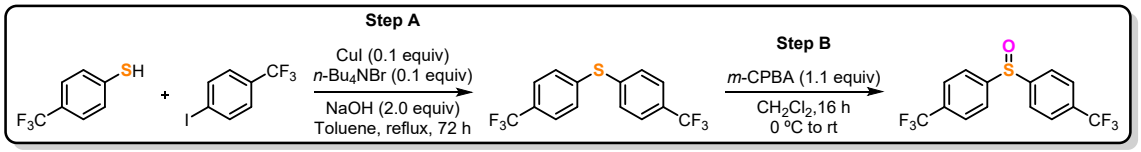


Step A: The synthesis of this compound was adapted from the literature.[3] A mixture of 3-bromopyridine (960 mg, 6.0 mmol), K_2CO_3 (1.61 g, 12.0 mmol) and thiophenol (650.0 mg, 6.0 mmol) in DMSO (4 mL) was stirred at 110 ºC for 72 h in a screw-capped tube. The reaction mixture was allowed to reach room temperature, then CH_2Cl_2 (5 mL) and H_2O (10 mL) were added. The aqueous phase was separated and extracted with CH_2Cl_2 (3 x 5 mL), the combined organic phase was washed with H_2O (3 x 5 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane:EtOAc = 9:1) to give the corresponding sulfide as a brown liquid (520.0 mg, 47%). **^{1}H-**

NMR (300 MHz, $CDCl_3$): δ = 8.56 (m, 1H), 8.45 (d, J = 4.4 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.39-7.28 (m, 5H), 7.22-7.18 (m, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 151.17, 147.96, 138.00, 134.05, 133.72, 131.86, 129.61, 127.96, 123.99.

Step B: To a solution of 3-phenylthiopyridine (220.0 mg, 1.17 mmol) in CH_2Cl_2 (2 mL) was added *m*-CPBA (279.6 mg, 1.29) slowly at 0 °C and the mixture was stirred at this temperature for 4 h. Then the mixture was warmed to room temperature and stirred overnight. After that, the mixture was quenched with 4 mL of $NaHCO_3$ (sat. aqueous solution). The aqueous layer was then extracted with CH_2Cl_2 (3×10 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane:EtOAc = 9:1) to give the title compound **1l** as a white solid. (187.5 mg, 79%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 8.78 (d, J = 1.7 Hz, 1H), 8.66 (dd, J = 4.8 Hz, J = 1.6 Hz, 1H), 8.00-7.96 (m, 1H), 7.68-7.64 (m, 2H), 7.51-7.47 (m, 3H), 7.42-7.37 (m, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 151.98, 146.47, 144.60, 142.44, 132.44, 131.65, 129.67, 124.69, 124.30.

2-(phenylsulfinyl)naphthalene (1m)

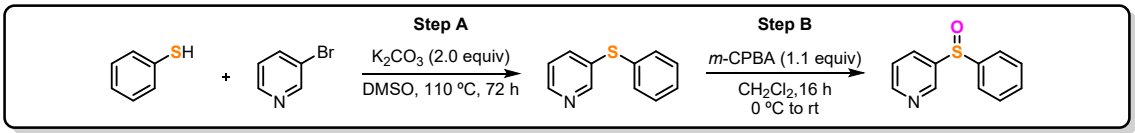


Step A: The synthesis of this compound was adapted from the literature.[2] To a solution of 2-bromonaphthalene (1.13 g, 5.0 mmol) in THF (28 mL) was added *n*-BuLi (2.5 M in hexane, 2.1 mL, 5.25 mmol) at -78 ºC. The mixture was stirred for 30 min, then to a solution of phenyl disulfie (1.22 g, 5.0 mmol) in THF (10 mL) was added dropwise. After stirring for 30 min, the mixture was warmed to 0 ºC and stirred for 1 h, then warmed to room temperature and stirred for 2.5 h. After that, the mixture was taken to dryness and the crude residue was dissolved in CH_2Cl_2 (20 mL) and washed with brine. The aqueous layer was washed with CH_2Cl_2 (20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (Hexane) to give the corresponding sulfide as a white solid (270.0 mg, 23%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 8.00 (s, 1H), 7.92-7.81 (m, 3H), 7.59-7.53 (m, 5H), 7.45-7.37 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 136.0, 133.8, 133.1, 132.3, 131.0, 129.9, 129.3, 128.9, 128.8, 127.8, 127.5, 127.1, 126.6, 126.2.

Step B: To a solution of 2-(phenylthio)naphthalene (270.0 mg, 1.14 mmol) in CH_2Cl_2 (2 mL) was added *m*-CPBA (278.1 mg, 1.26 mmol) slowly at 0 °C and the mixture was stirred at this temperature for 4 h. Then the mixture was warmed to room temperature and stirred overnight. After that, the mixture was quenched with 4 mL of $NaHCO_3$ (sat. aqueous solution). The aqueous

layer was then extracted with CH_2Cl_2 (3×10 mL). The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane:EtOAc = 8:2) to give the title compound **1m** as a white solid. (239.3 mg, 83%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 8.29 (s, 1H), 7.89-7.65 (m, 5H), 7.50-7.33 (m, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 145.3, 142.4, 134.2, 132.6, 130.9, 129.6, 129.2, 128.4, 127.9, 127.7, 125.1, 124.8, 124.8, 120.5.

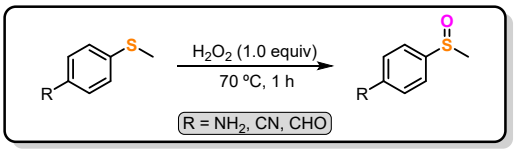
Bis(4-trifluoromethylphenyl) sulfoxide (1n)



Step A: The synthesis of this compound was adapted from the literature.[2] A mixture of *p*-toluenethiol (2.03 g, 16 mmol), 1-chloro-4-iodobenzene (3.77 g, 16 mmol), *n*-Bu_4NBr (0.53 g, 1.60 mmol) and NaOH (1.30 g, 32 mmol) and CuI (324.6 mg, 1.6 mmol) in toluene (11 mL) was stirred under reflux for 24 h. The reaction mixture was allowed to reach room temperature, then 10 mL of NH_4Cl (sat. aqueous solution) were added. The aqueous phase was separated and extracted with EtOAc (3 x 10 mL), the combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The mixture was recrystalized from ethanol to give the corresponding sulfide as a white solid (1.79 g, 48%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.28-7.10 (m, 8H), 2.33 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 138.1, 136.0, 132.5, 132.3, 130.8, 130.6, 130.2, 129.1, 21.3.

Step B: To a solution of (4-chlor-phenyl)(*p*-tolyl) sulfide (1.01 g, 4.06 mmol) in CH_2Cl_2 (15 mL) was added *m*-CPBA (1.05 g, 4.47 mmol) slowly at 0 °C and the mixture was stirred at this temperature for 4 h. Then the mixture was warmed to room temperature and stirred overnight. After that, the mixture was quenched with 10 mL of $NaHCO_3$ (sat. aqueous solution). The aqueous layer was then extracted with CH_2Cl_2 (3×10 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane:EtOAc = 9:1) to give the title compound **1n** as a white solid. (871.2 mg, 86%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.86-7.80 (m, 4H), 7.64 (d, J = 9.0 Hz, 2H), 7.50 (d, J = 9.0 Hz, 2H), 2.58 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 144.2, 141.8, 141.4, 136.5, 129.7, 129.0, 125.5, 124.4, 20.9.

6.2 Synthesis of thioanisole oxide derivatives



The procedure described in the literature was followed.[4] A mixture of the corresponding sulfide (2.0 mmol) and H_2O_2 30% (2.0 mmol, 200mL) were vigorously stirred at 70 ºC for 1 h. Then the mixture was cooled to room temperature, extracted with CH_2Cl_2 (3×10 mL), the combined organic phase was dried over anhydrous Na_2SO_4 concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the corresponding sulfoxide.

4-(methylsulfinyl)aniline (1t)

The sulfoxide **1t** was prepared following the procedure for thioanisole oxide derivatives described above (CH_2Cl_2 to CH_2Cl_2:Acetone = 9:1) and it was isolated as a brown solid (279.0 mg, 94%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H), 4.05 (brs, 2H), 2.66 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 149.7, 133.4, 125.8, 115.1, 43.9.

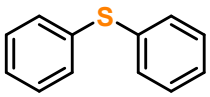
4-methanesulfinylbenzonitrile (1u)

The sulfoxide **1u** was prepared following the procedure for thioanisole oxide derivatives described above (Hexane:EtOAc = 2:8) and it was isolated as a white solid (265.1 mg, 78%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.68 (q, J = 7.9 Hz, 4H), 2.64 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 151.2, 132.7, 124.1, 117.5, 114.2, 43.4.

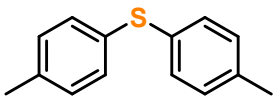
4-methylsulfinylbenzaldehyde (1v)

The sulfoxide **1t** was prepared following the procedure for thioanisole oxide derivatives described above (Hexane:EtOAc = 3:7) and it was isolated as a white solid (268.0 mg, 66%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 9.84 (s, 1H), 7.80 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 2.57 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 149.7, 133.4, 125.8, 115.1, 43.9.

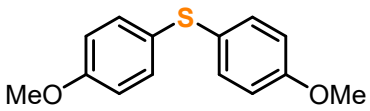
7. Characterization data of isolated compounds



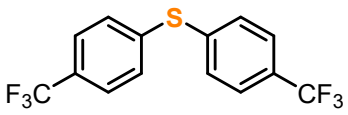
Diphenyl sulfide (2a). According to general procedure B, the desired product (**2a**, 52.4 mg, 95%) was isolated as a pale-yellow liquid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.37-7.24 (m, 10H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 136.4, 131.6, 129.8, 127.7. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_{12}H_{11}S$: 187.0582. Found: 187.0587. **Elemental analysis** Calc. (%) for $C_{12}H_{10}S$: C 77.38, H 5.41, S 17.21. Found: C 76.96, H 5.02, S 17.12.



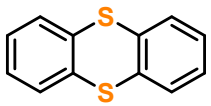
Bis(4-methylphenyl) sulfide (2b). According to general procedure B, the desired product (**2b**, 51.2 mg, 80%) was isolated as a white solid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.25 (d, J = 12.0 Hz, 4H), 7.13 (d, J = 12.0 Hz, 4fH), 2.34 (s, 6H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 137.7, 133.2, 131.6, 130.5, 21.4. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_{14}H_{15}S$: 215.0894. Found: 215.0816. **Elemental analysis** Calc. (%) for $C_{14}H_{14}S$: C 78.45, H 6.58, S 14.96. Found: C 78.34, H 6.34, S 14.70.



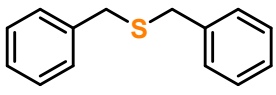
Bis(4-methoxyphenyl) sulfide (2c). According to general procedure B, the desired product (**2c**, 76.7 mg, 98%) was isolated as a white solid (Pentane:EtOAc = 9:1). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.32 (d, J = 9.0 Hz, 4H), 6.87 (d, J = 9.0 Hz, 4H), 3.79 (s, 6H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 159.7, 133.3, 128.0, 115.3, 55.9. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_{14}H_{15}SO_2$: 247.0793. Found: 247.0795. **Elemental analysis** Calc. (%) for $C_{14}H_{14}SO_2$: C 68.26, H 5.73, S 13.02. Found: C 68.75, H 5.81, S 13.22.



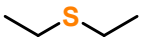
Bis(4-(trifluoromethyl)phenyl)sulfide (2d). According to general procedure B, the desired product (**2d**, 89.3 mg, 93%) was isolated as a white solid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.61 (d, J = 9.0 Hz, 4H), 6.48 (d, J = 9.0 Hz, 4H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 140.3, 131.7, 129.6 (q, J = 37.5 Hz), 126.9 (q, J = 3.8 Hz), 124.7 (q, J = 270.0 Hz). **^{19}F-NMR** (282 MHz, CD_2Cl_2): δ = -63.0. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_{14}H_9SF_6$: 323.0329. Found: 323.0318. **Elemental analysis** Calc. (%) for $C_{14}H_8SF_6$: C 52.18, H 2.50, S 9.95. Found: C 52.18, H 2.71, S 10.09.



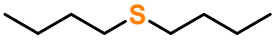
Thianthrene (2e). According to general procedure B, the desired product (**2e**, 46.6 mg, 75%) was isolated as a white solid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.52-7.46 (m, 4H), 7.29-7.23 (m, 4H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 136.1, 129.2, 128.3. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_{12}H_9S_2$: 217.0146. Found: 217.0141. **Elemental analysis** Calc. (%) for $C_{12}H_8S_2$: C 66.63, H 3.73, S 29.65. Found: C 67.00, H 3.79, S 29.54.



Bis(4-methoxyphenyl) sulfide (2f). According to general procedure B, the desired product (**2f**, 56.6 mg, 90%) was isolated as a white solid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.38-7.24 (m, 10H), 3.65 (s, 4H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 139.0, 129.5, 129.0, 127.5, 36.3. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_{14}H_{15}S$: 215.0894. Found: 215.0889. **Elemental analysis** Calc. (%) for $C_{14}H_{14}S$: C 78.45, H 6.58, S 14.96. Found: C 77.23, H 6.54, S 14.45.

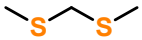


Diethyl sulfide (2h). According to general procedure B, the desired product (**2h**, 27.2 mg, 94%) was isolated as a colorless liquid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 2.53 (q, J = 7.4 Hz, 4H), 1.22 (t, J = 7.4 Hz, 6H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 25.9, 15.7. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_4H_{11}S$: 91.0581. Found: 91.0579. **Elemental analysis** Calc. (%) for $C_4H_{10}S$: C 53.27, H 11.18, S 35.55. Found: C 54.12, H 11.13, S 36.75.

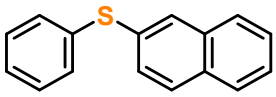


Dibuthyl sulfide (2i). According to general procedure B, the desired product (**2i**, 44.9 mg, 98%) was isolated as a colorless liquid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 2.49 (t, J = 7.3 Hz, 4H), 1.55 (m, 4H), 1.40 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 32.5, 32.3, 22.6, 14.1. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_8H_{19}S$: 147.1207. Found: 147.1212. **Elemental analysis** Calc. (%) for $C_8H_{18}S$: C 65.68, H 12.40, S 21.92. Found: C 67.38, H 11.35, S 20.77.

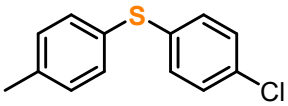
Tetrahydrothiophene (2j). According to general procedure B, the desired product (**2j**, 25.6 mg, 96%) was isolated as a colorless liquid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 2.79 (m, 4H), 1.91 (m, 4H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 32.2, 31.6. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for C_4H_9S: 89.0425. Found: 89.0264. **Elemental analysis** Calc. (%) for C_4H_8S: C 54.49, H 9.15, S 36.37. Found: C 55.47, H 9.73, S 35.98.



Bis(methylthio)methane (2k). According to general procedure B, the desired product (**2k**, 37.2 mg, 92%) was isolated as a colorless liquid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 3.63 (s, 2H), 2.14 (s, 6H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 40.6, 14.7. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_3H_9S_2$: 109.0146. Found: 109.0142. **Elemental analysis** Calc. (%) for $C_3H_8S_2$: C 33.29, H 1.01, S 59.25. Found: C 32.98, H 1.24, S 59.07.

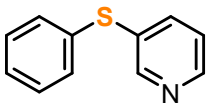


2-(phenylthio)naphthalene (2l). According to general procedure B, the desired product (**2l**, 66.3 mg, 92%) was isolated as a white solid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.88-7.75 (m, 4H), 7.54-7.27 (m, 8H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 136.3, 134.4, 133.7, 132.9, 131.6, 130.3, 129.8, 129.4, 129.2, 128.3, 127.9, 127.7, 127.2, 126.8. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_{16}H_{13}S$: 237.0738. Found: 237.0745. **Elemental analysis** Calc. (%) for $C_{16}H_{12}S$: C 82.05, H 4.94, S 13.53. Found: C 81.31, H 5.12, S 13.57.

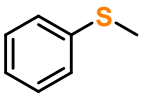


(4-chlor-phenyl)(*p*-tolyl) sulfide (2m). According to general procedure B, the desired product (**2m**, 68.7 mg, 97%) was isolated as a white solid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.33-7.17 (m, 8H), 2.36 (s, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 138.9, 136.7, 133.1, 132.8, 131.4, 131.2, 130.8, 129.7, 21.4. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_{13}H_{12}SCl$: 235.0348. Found:

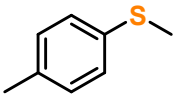
235.0341. **Elemental analysis** Calc. (%) for $C_{13}H_{11}SCl$: C 66.52, H 4.72, S 13.66. Found: C 67.11, H 4.67, S 13.61.



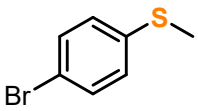
3-phenylthiopyridine (2n). According to general procedure B, the desired product (**2n**, 32.3 mg, 55%) was isolated as a yellow oil (Pentane:EtOAc = 9:1). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 8.54 (m, 1H), 8.45 (d, J = 6.0 Hz, 1H), 7.62 (d, J = 9.0 Hz, 1H), 7.41-7.30 (m, 5H), 7.25-7.20 (m, 1H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 151.72, 148.52, 138.54, 134.75, 133.91, 132.14, 130.02, 128.32, 124.44. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_{11}H_{10}SN$: 188.0534. Found: 188.0534. **Elemental analysis** Calc. (%) for $C_{11}H_9SN$: C 70.55, H 4.84, S 17.12, N 7.48. Found: C 71.42, H 4.61, S 16.99, N 7.29



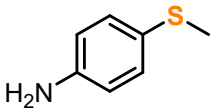
Thioanisole (2o). According to general procedure B, the desired product (**2o**, 42.1 mg, 96%) was isolated as a pale-yellow liquid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.33-7.27 (m, 4H), 7.18-7.14 (m, 1H), 2.49 (s, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 139.2, 129.4, 127.0, 125.5, 16.1. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for C_7H_9S: 125.0425. Found: 125.0442. **Elemental analysis** Calc. (%) for C_7H_8S: C 67.69, H 6.49, S 25.82. Found: C 67.31, H 6.54, S 24.79.



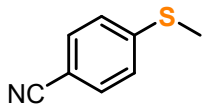
4-methylthioanisole (2p). According to general procedure B, the desired product (**2p**, 42.3 mg, 98%) was isolated as a yellow liquid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.18 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 2.46 (s, 3H), 2.32 (s, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 135.6, 135.4, 130.1, 127.6, 21.2, 16.7. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_8H_{11}S$: 139.0582. Found: 139.0581. **Elemental analysis** Calc. (%) for $C_7H_{10}S$: C 66.61, H 7.99, S 25.40. Found: C 66.39, H 7.63, S 26.01.



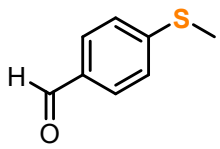
4-bromothioanisole (2q). According to general procedure B, the desired product (**2q**, 55.2 mg, 83%) was isolated as a white solid (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.41 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 2.46 (s, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 135.6, 132.3, 128.5, 118.4, 16.1. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for C_7H_8SBr: 204.9530. Found: 204.9522. **Elemental analysis** Calc. (%) for C_7H_7SBr: C 41.40, H 3.47, S 15.79. Found: C 41.85, H 3.10, S 15.51.



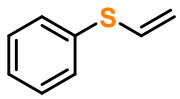
4-(methylthio)aniline (2r). According to general procedure B, the desired product (**2r**, 38.5 mg, 95%) was isolated as a brown oil (Pentane:EtOAc = 4:1). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.16 (d, J = 6.5 Hz, 2H), 6.63 (d, J = 6.5 Hz, 2H), 3.72 (brs, 2H), 2.40 (s, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 146.0, 131.4, 126.0, 116.0, 19.0 **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for $C_7H_{10}SN$: 139.0582. Found: 139.0581. **Elemental analysis** Calc. (%) for C_7H_9SN: C 60.39, H 6.52, S 23.03, N 10.06. Found: C 61.08, H 5.84, S 23.03, N 10.15.



4-cyanothioanisole (2s). According to general procedure B, the desired product (**2s**, 40.4 mg, 89%) was isolated as white solid (Pentane:EtOAc = 9:1). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.53(d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H), 2.50 (s, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 146.7, 132.6, 125.9, 119.4, 108.1, 15.0. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for C_8H_8SN: 150.0378. Found: 150.0377. **Elemental analysis** Calc. (%) for C_8H_7SN: C 64.40, H 4.73, S 21.49, N 9.39. Found: C 63.99, H 4.65, S 21.09, N 9.35.

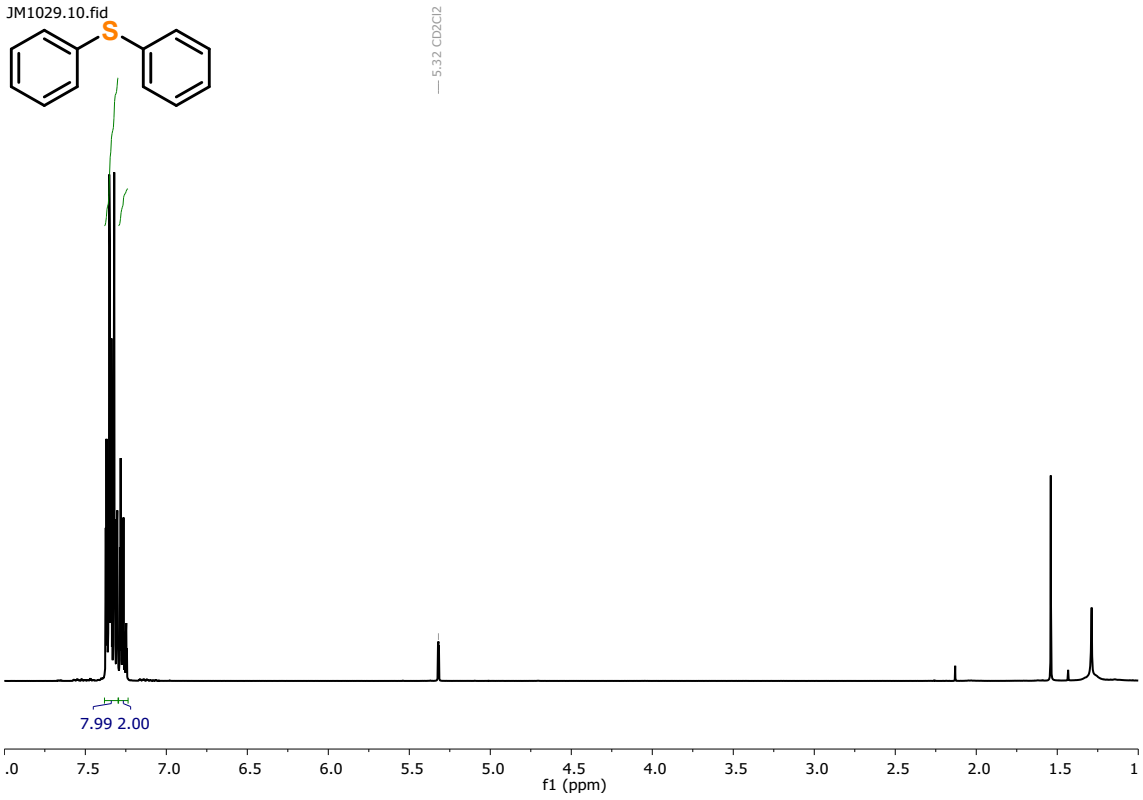


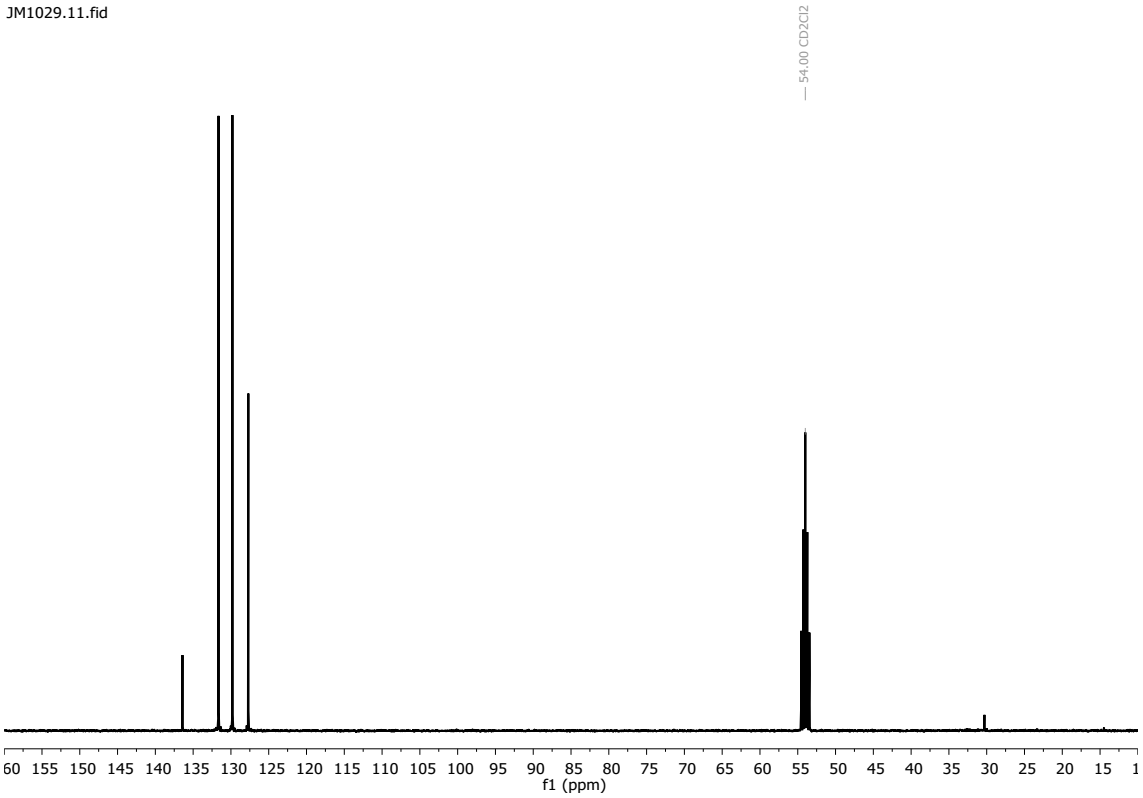
4-(methylthio)benzaldehyde (2t). According to general procedure B, the desired product (**2t**, 43.1 mg, 95%) was isolated as yellow liquid (Pentane:EtOAc = 9:1). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 9.90 (s, 1H), 7.75 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 2.53 (s, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 191.5, 148.4, 135.6, 130.3, 125.6, 15.0. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for C_8H_9SO: 153.0374. Found: 153.0374. **Elemental analysis** Calc. (%) for C_8H_8SO: C 63.13, H 5.30, S 21.07. Found: C 62.87, H 5.27, S 20.89.

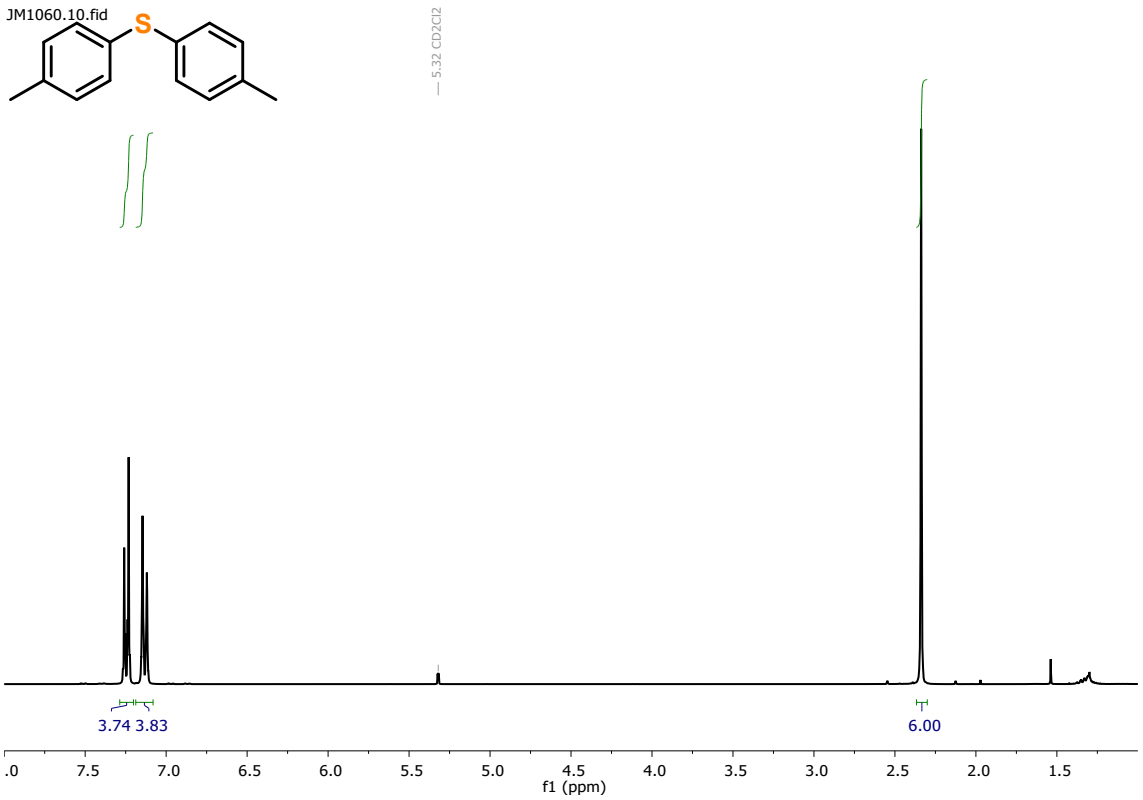


Phenyl vinyl sulfide (2w). According to general procedure B, the desired product (**2w**, 18.4 mg, 49%) was isolated as an orange oil (Pentane). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.41-7.25 (m, 5H), 6.58 (dd, J = 9.6 Hz, J = 16.6 Hz, 1H), 5.39 (d, J = 3.6 Hz, 1H), 5.34 (d, J = 10.7 Hz, 1H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): δ = 134.9, 132.4, 130.9, 129.7, 127.7, 115.9. **HRMS (ESI-TOF)** *m/z* $[M-H]^+$ Calc. for C_8H_9S: 137.0425. Found: 137.0422. **Elemental analysis** Calc. (%) for C_8H_8S: C 70.54, H 5.92, S 23.54. Found: C 71.15, H 5.22, S 23.68.

8. ^{1}H and ^{13}C NMR spectra of isolated compounds



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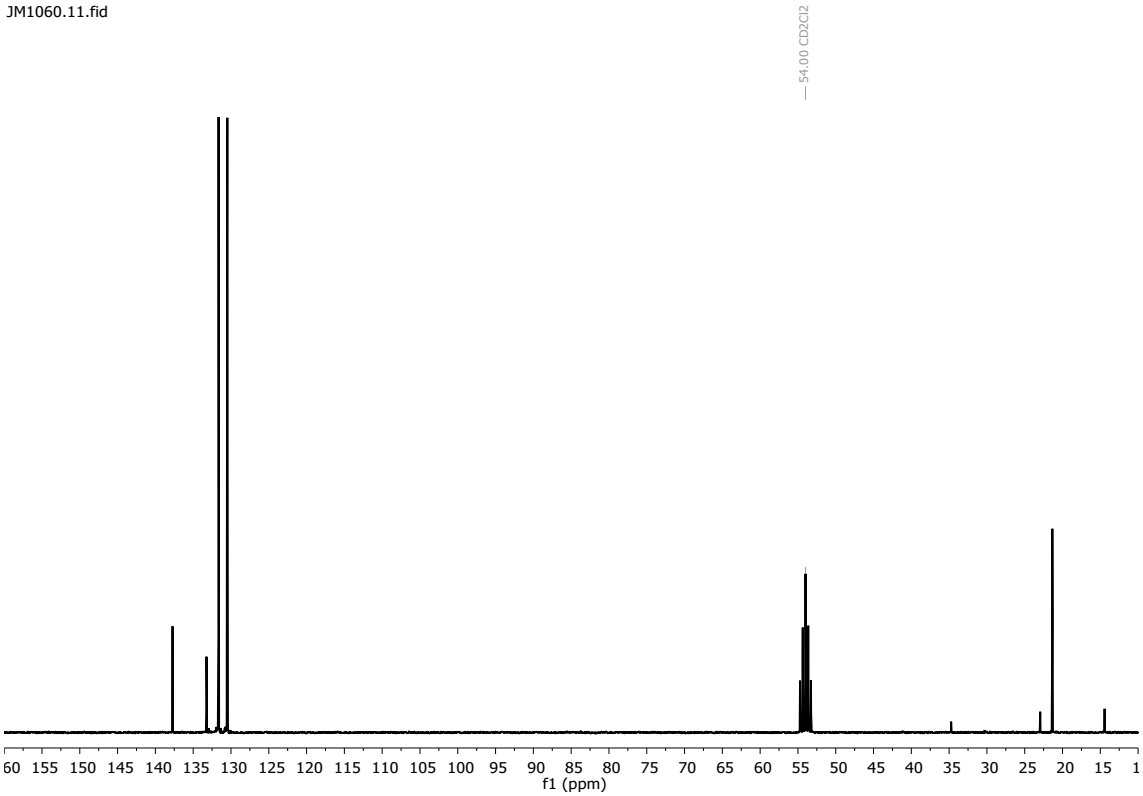
6.00
f1 (ppm)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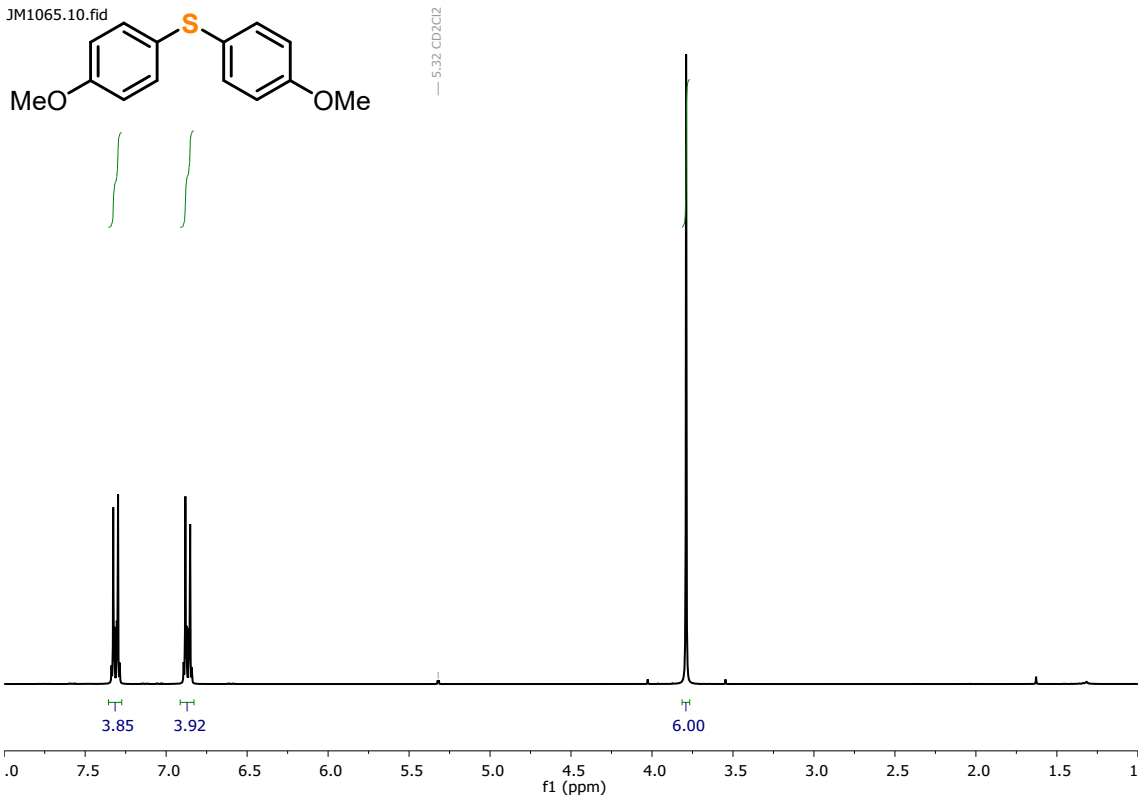
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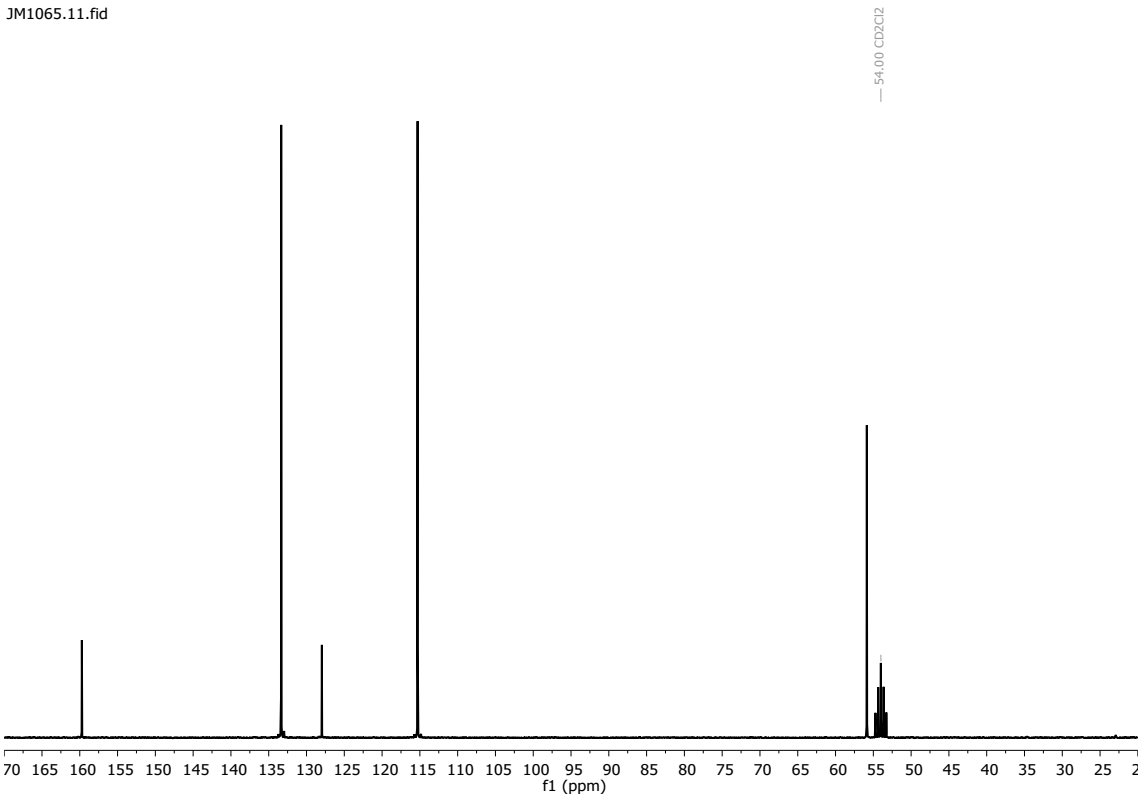
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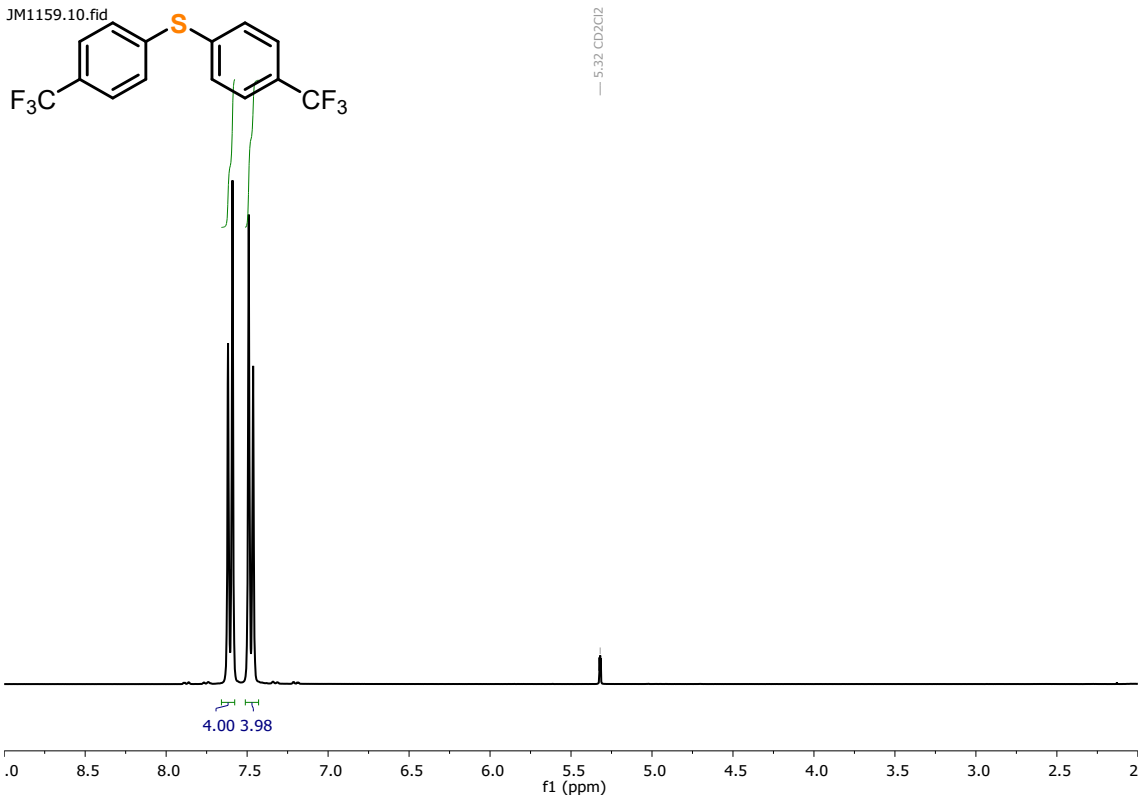
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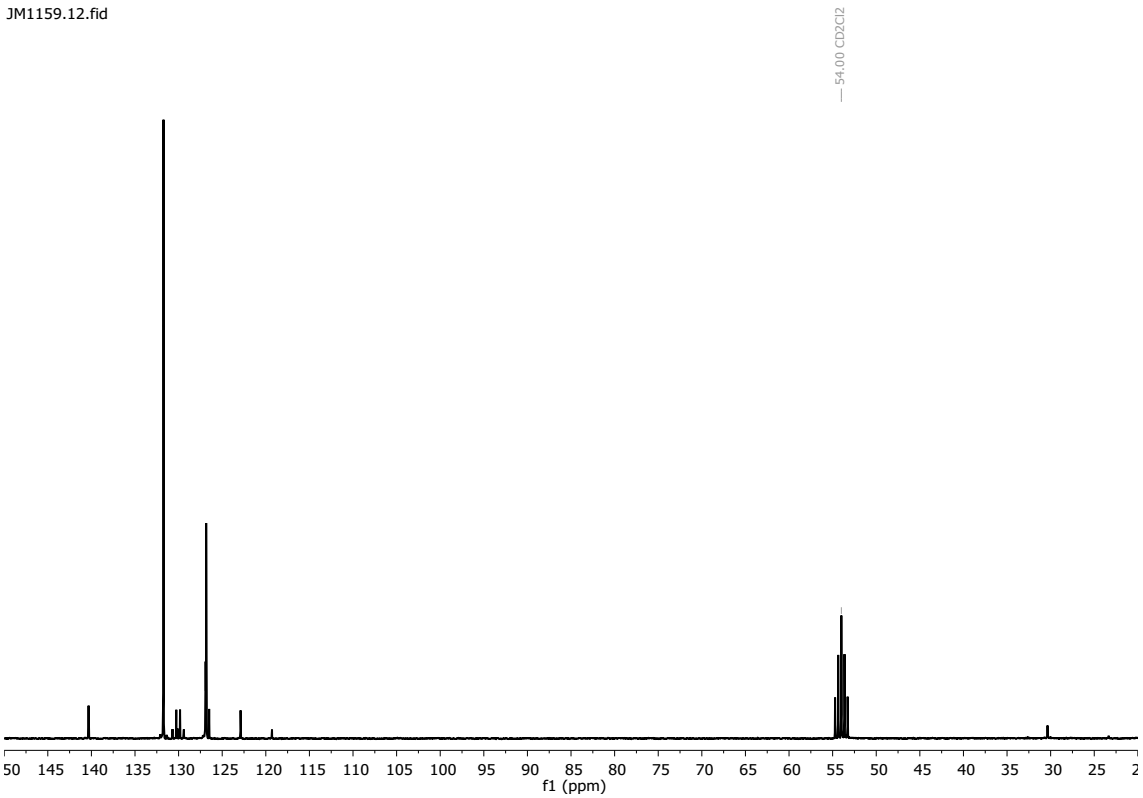
2.5
f1 (ppm)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50
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40
35
30
25
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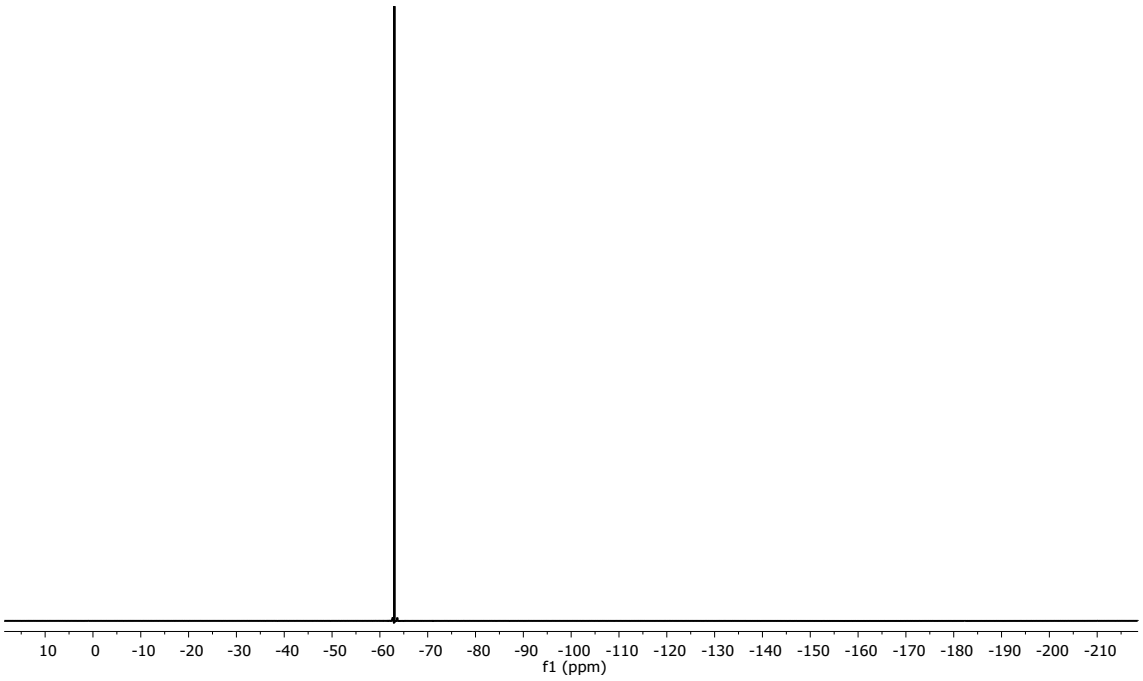

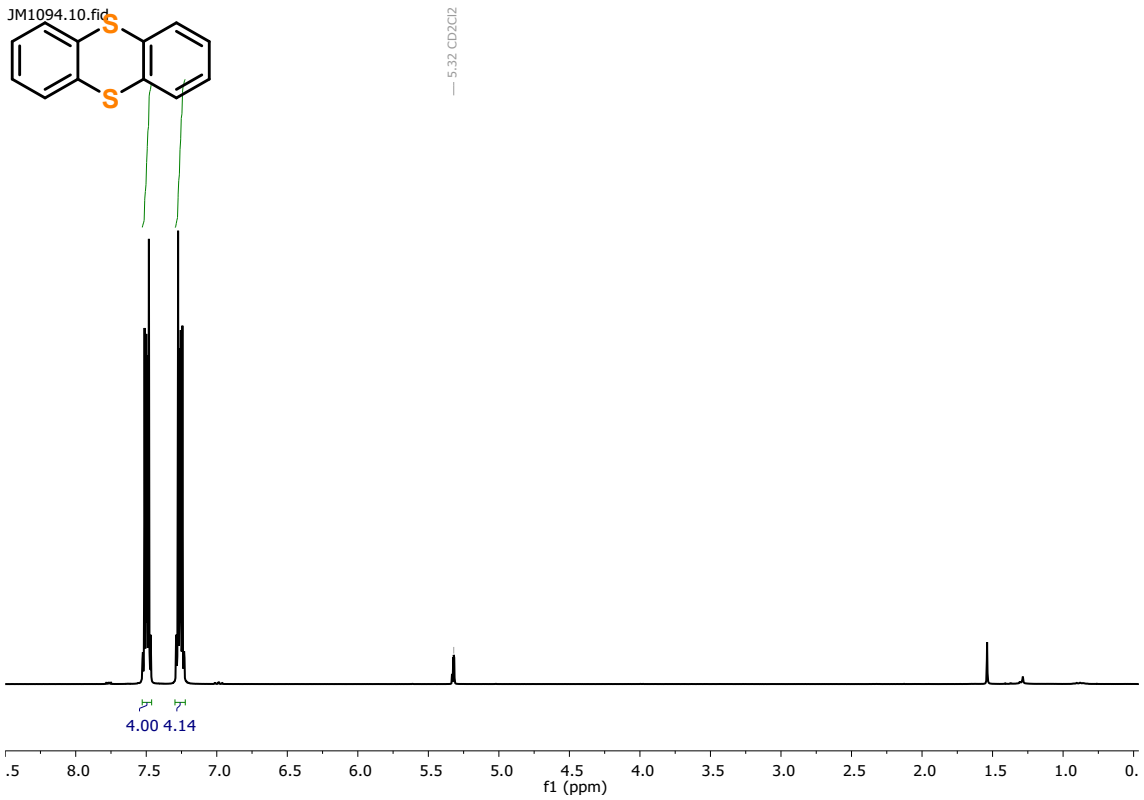
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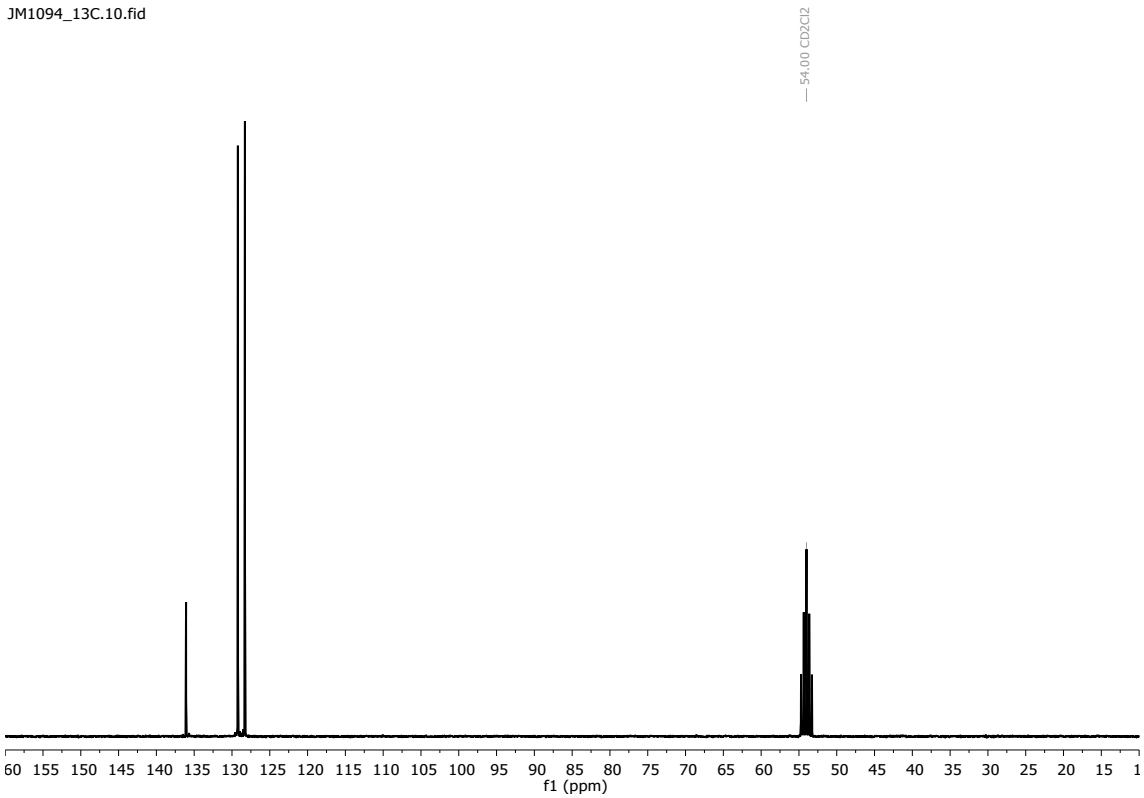
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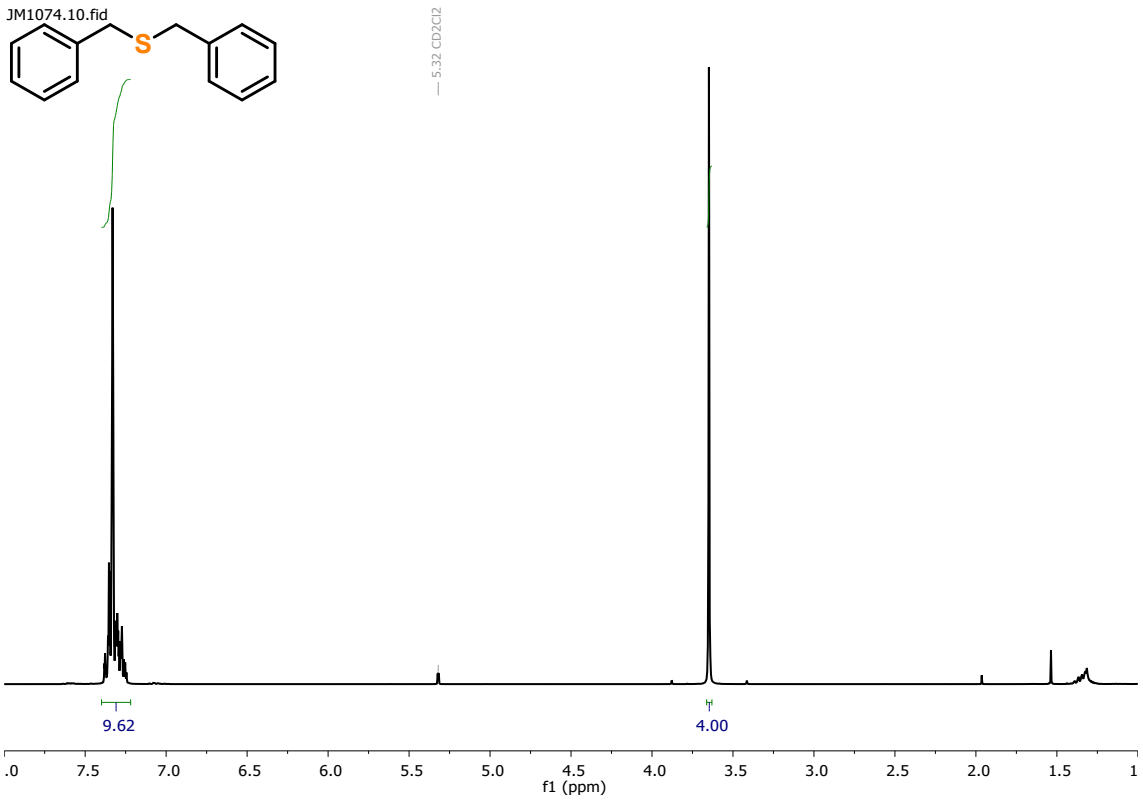
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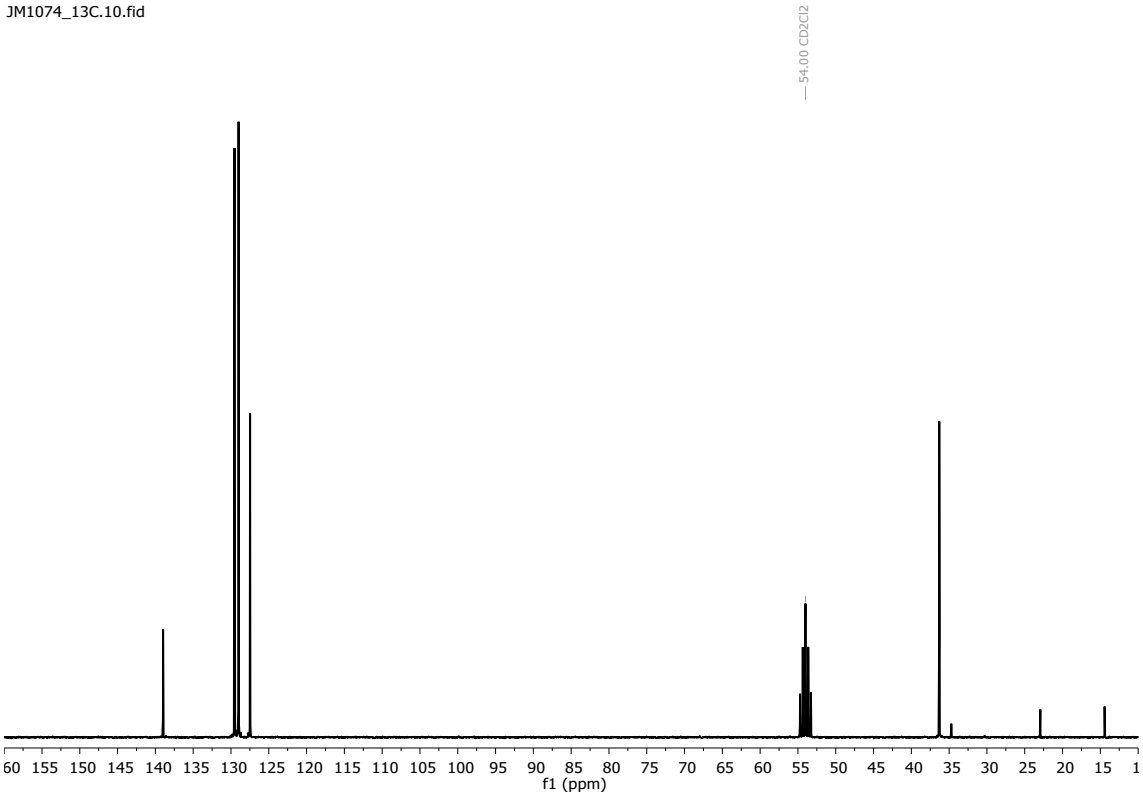
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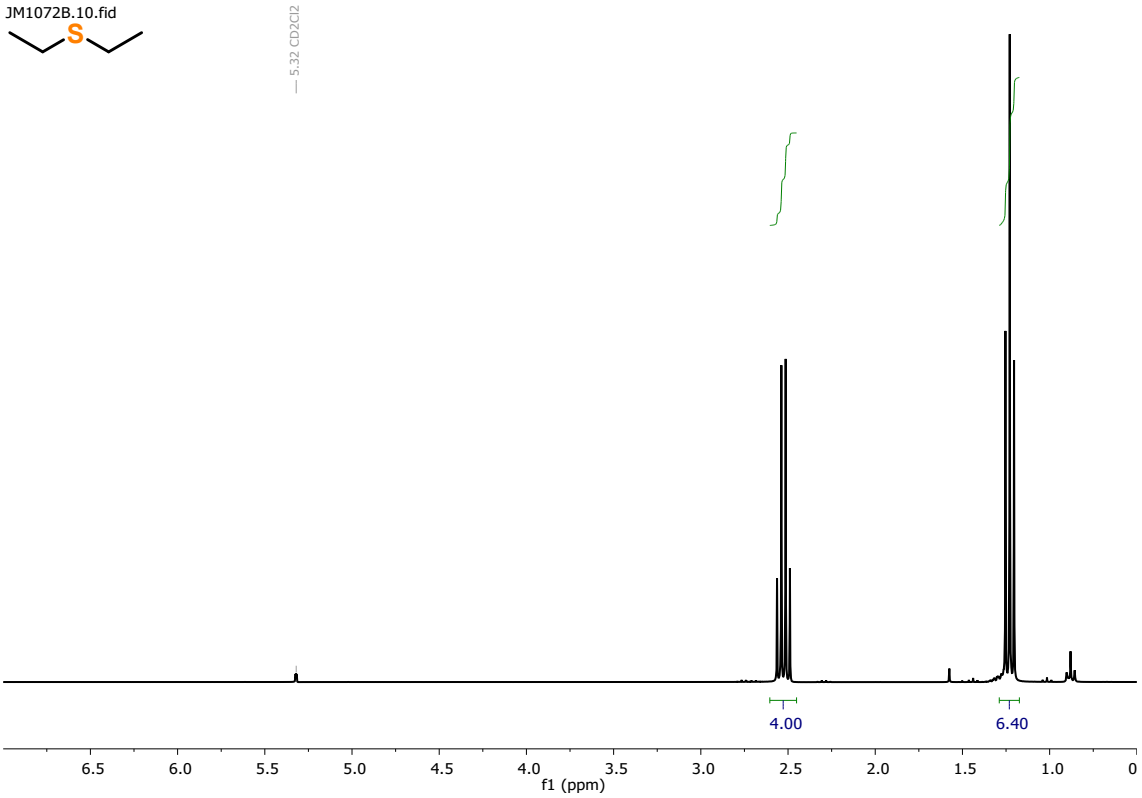

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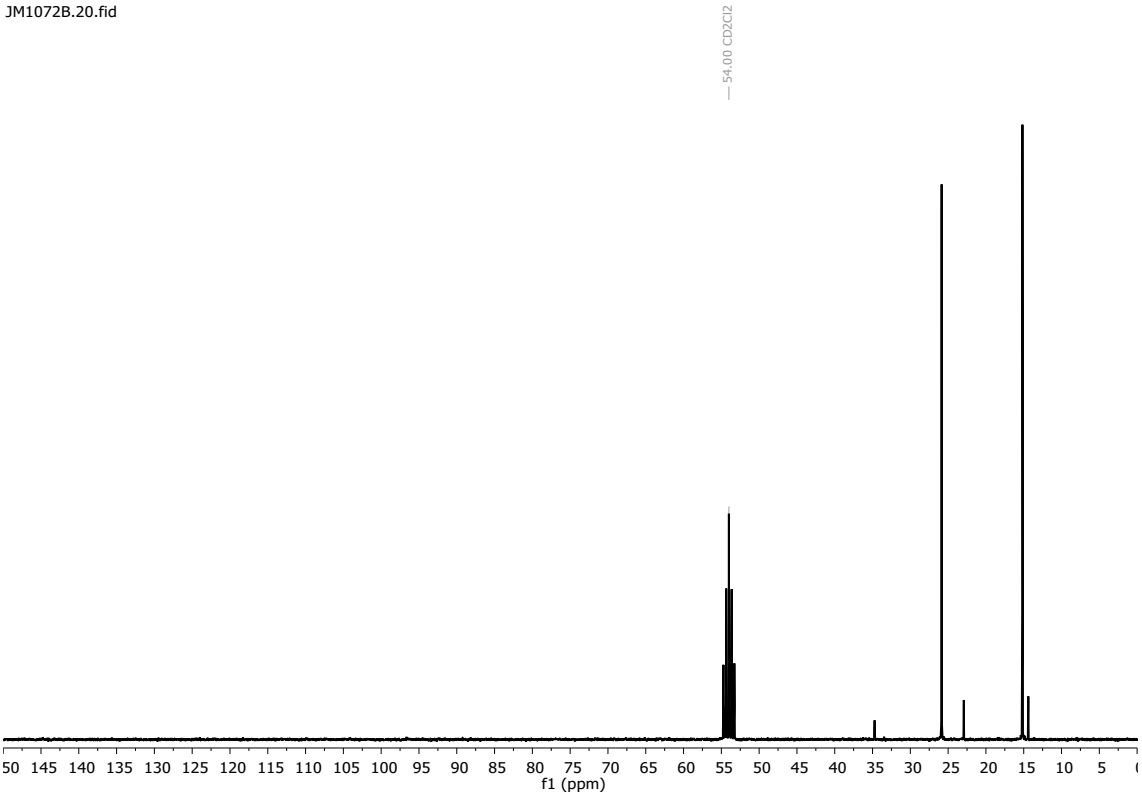

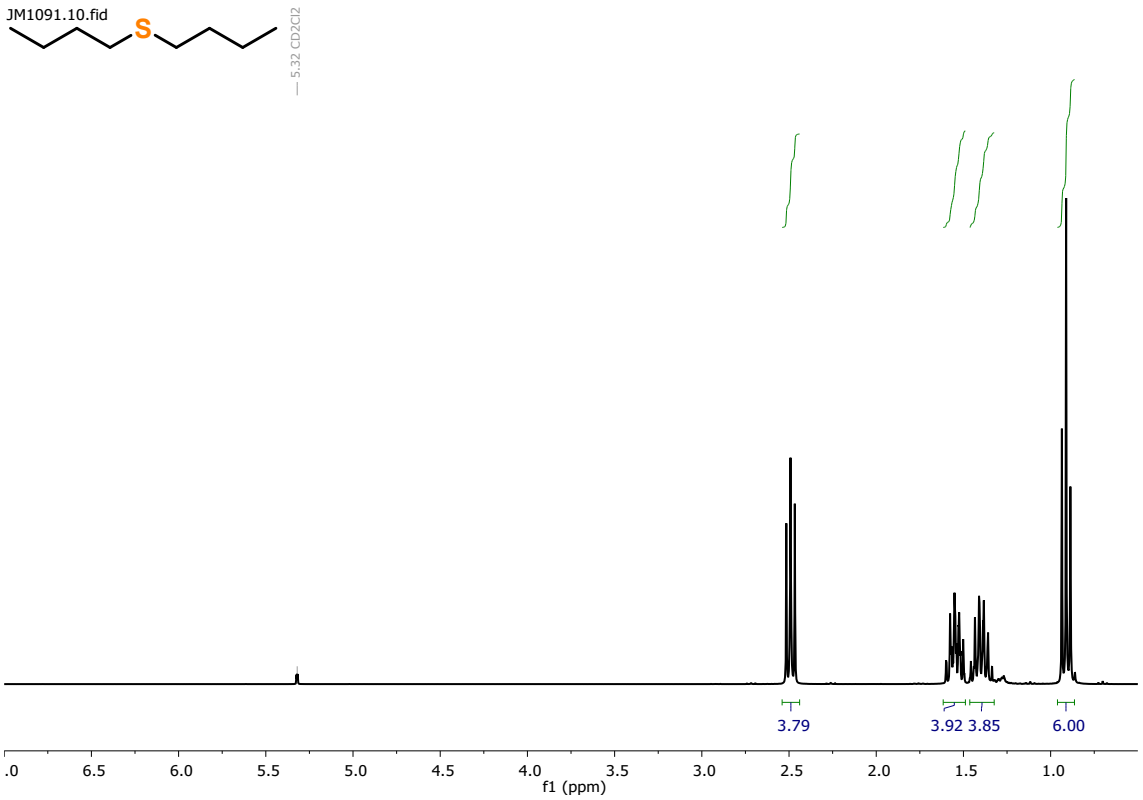
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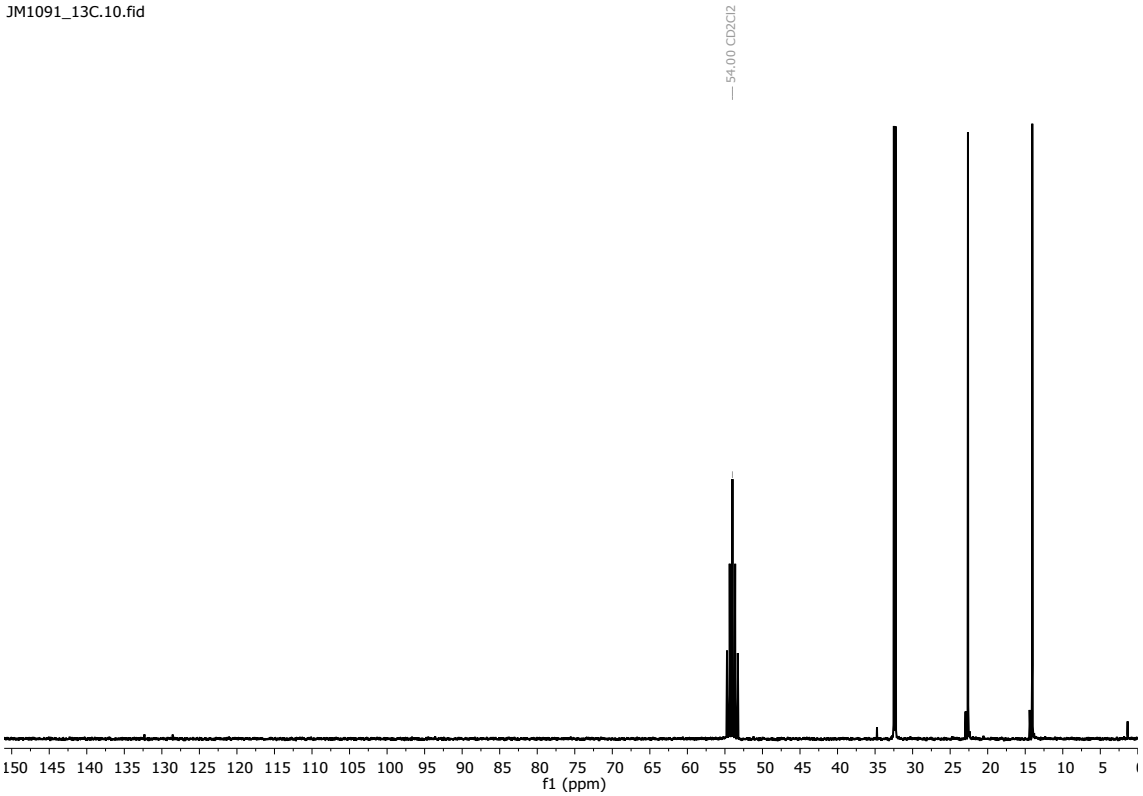
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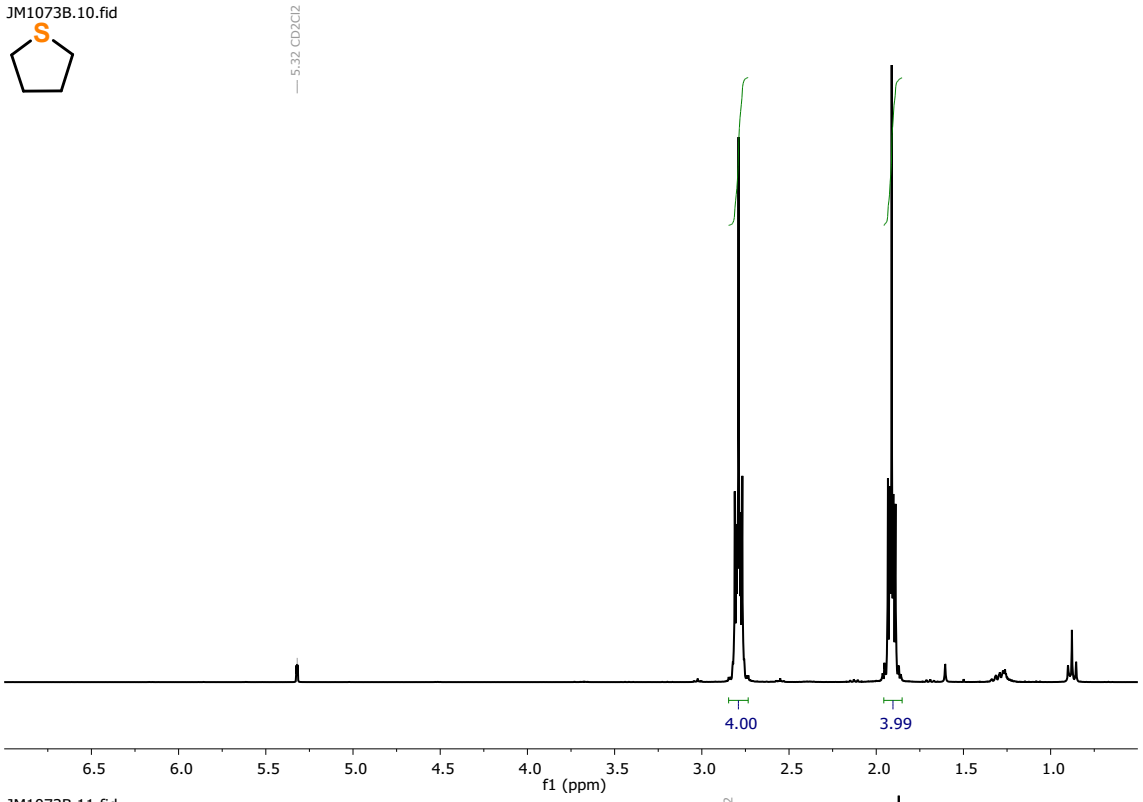
f1 (ppm)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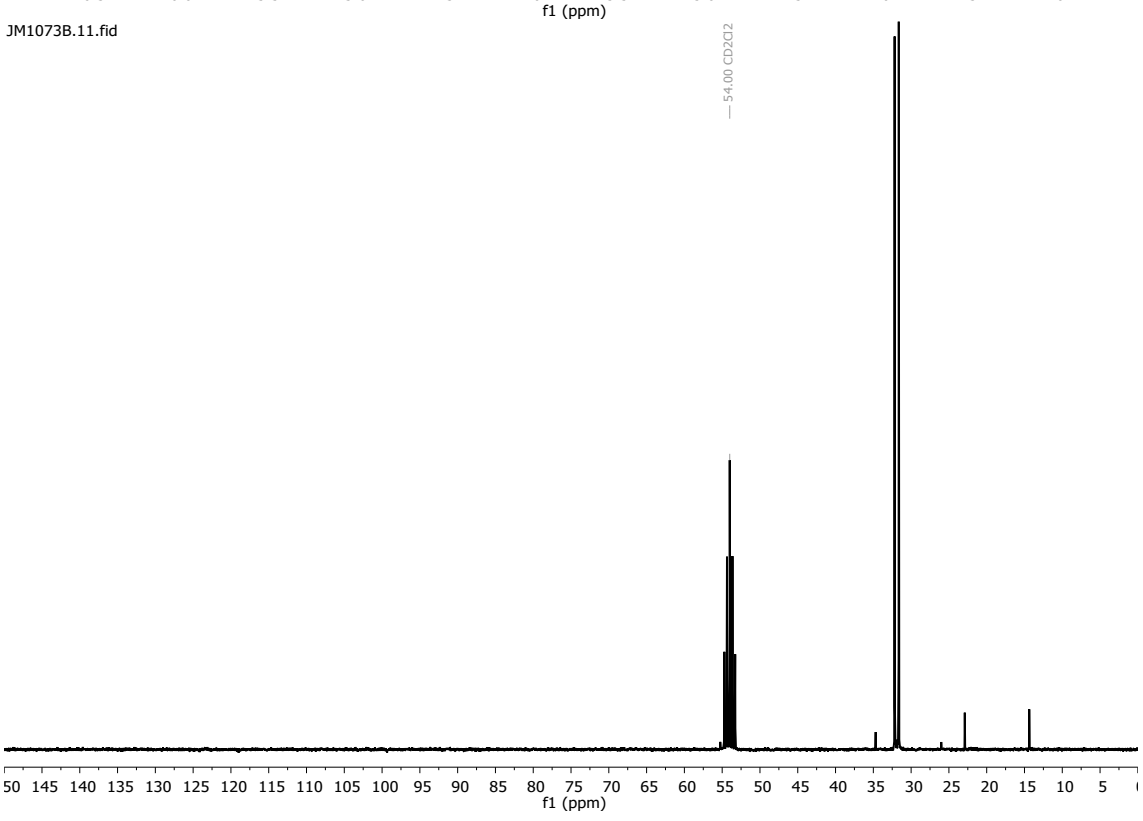
f1 (ppm)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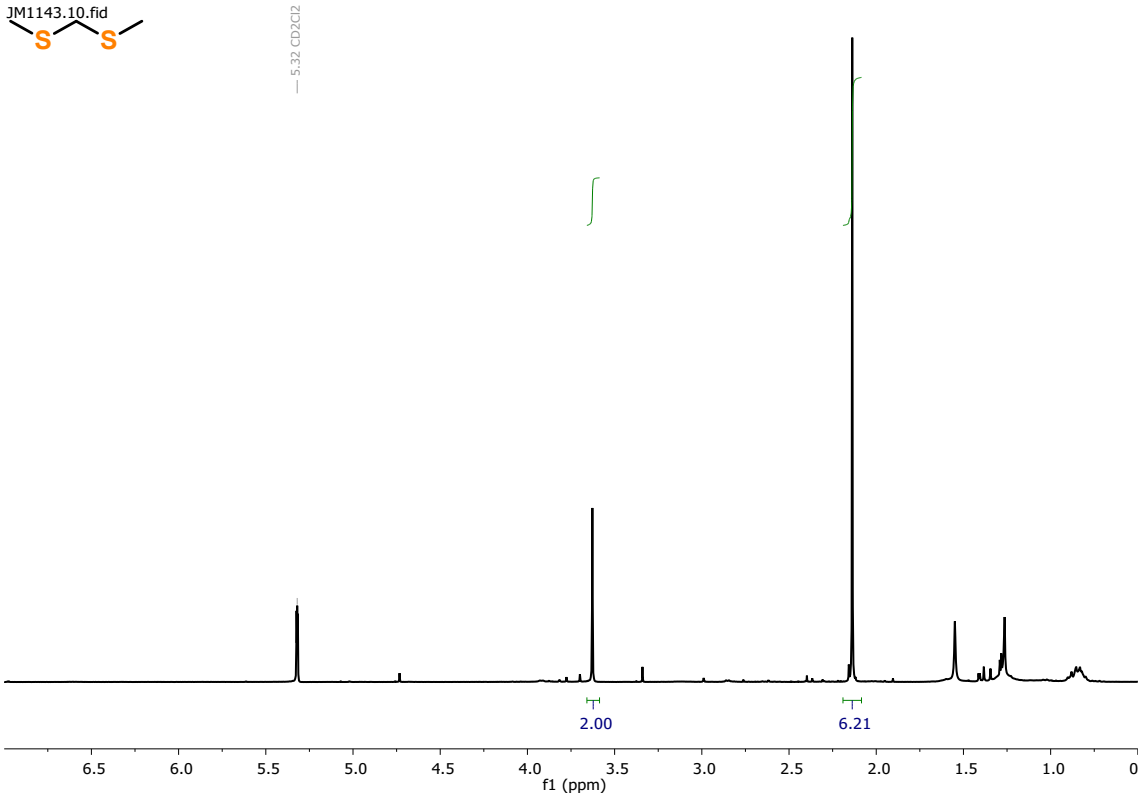
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S
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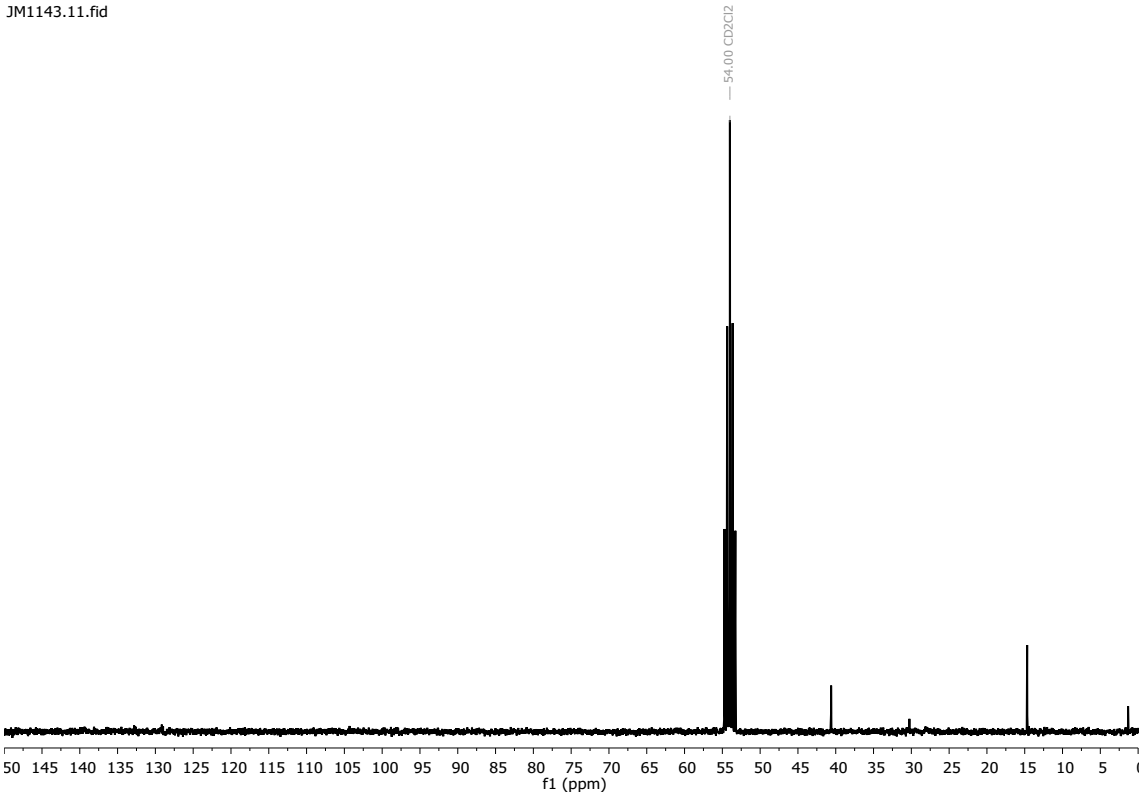
f1 (ppm)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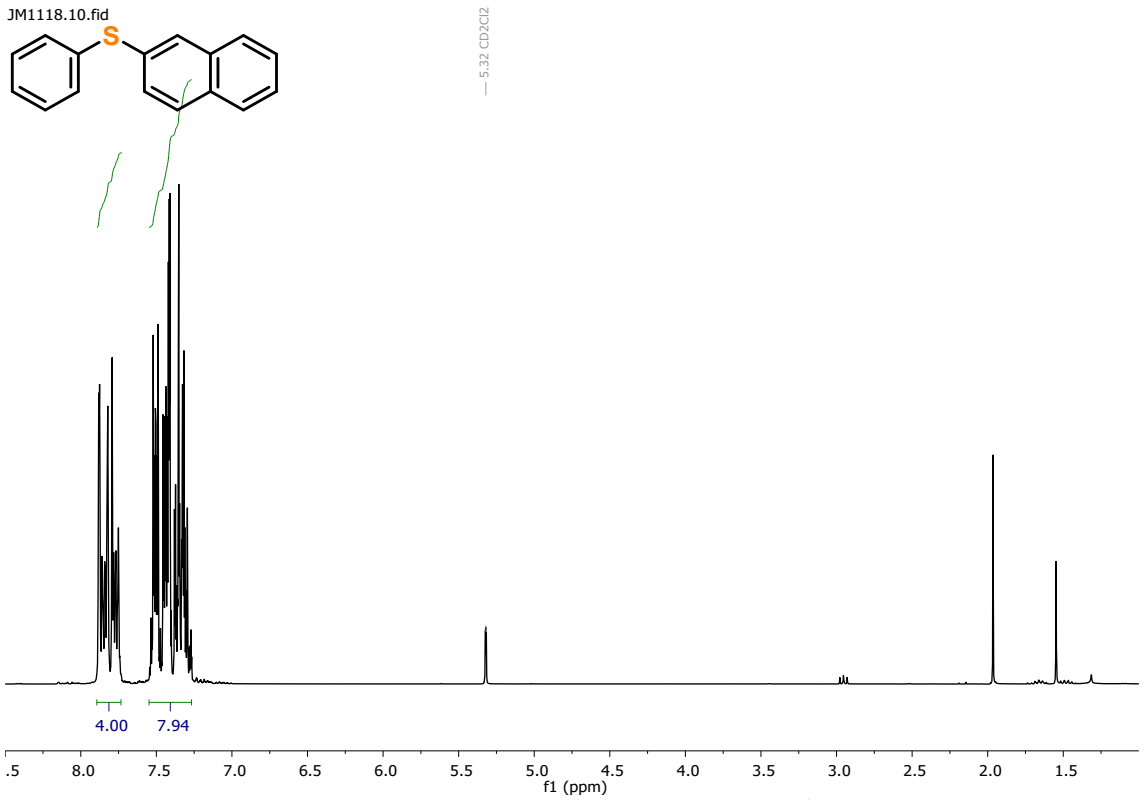
f1 (ppm)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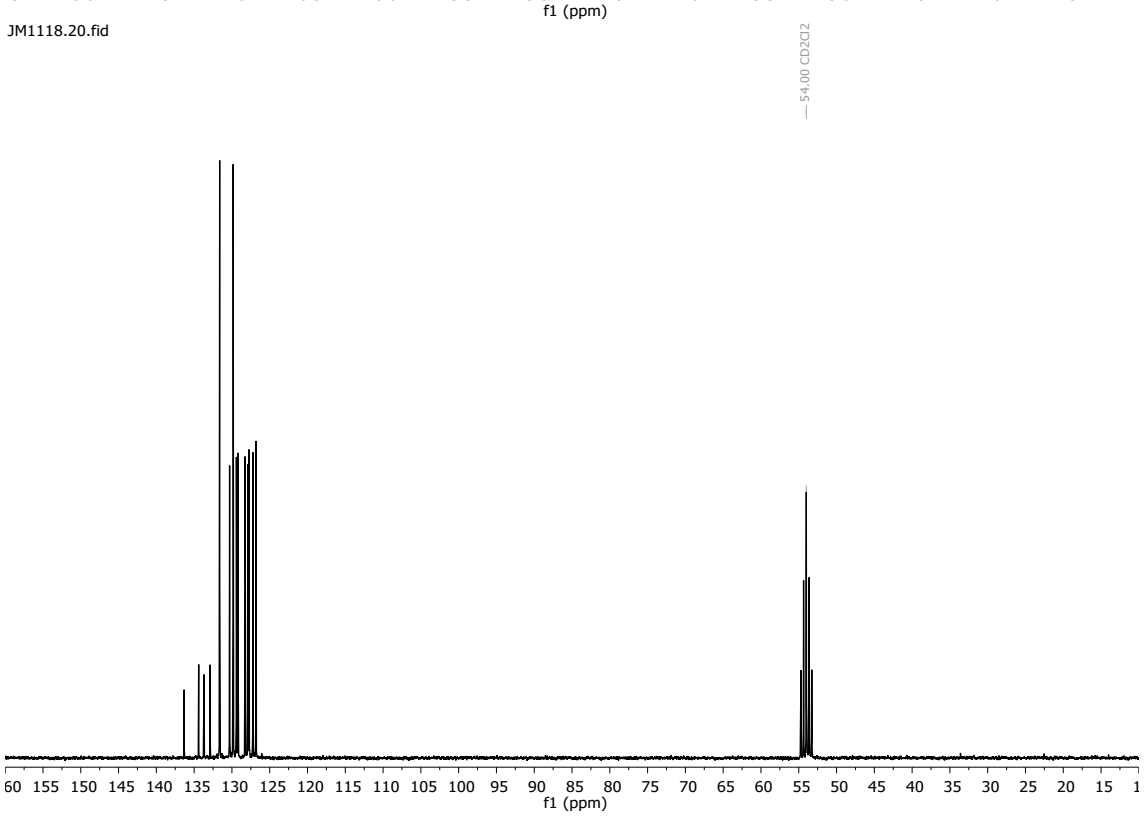
3.0
2.5
2.0
1.5
f1 (ppm)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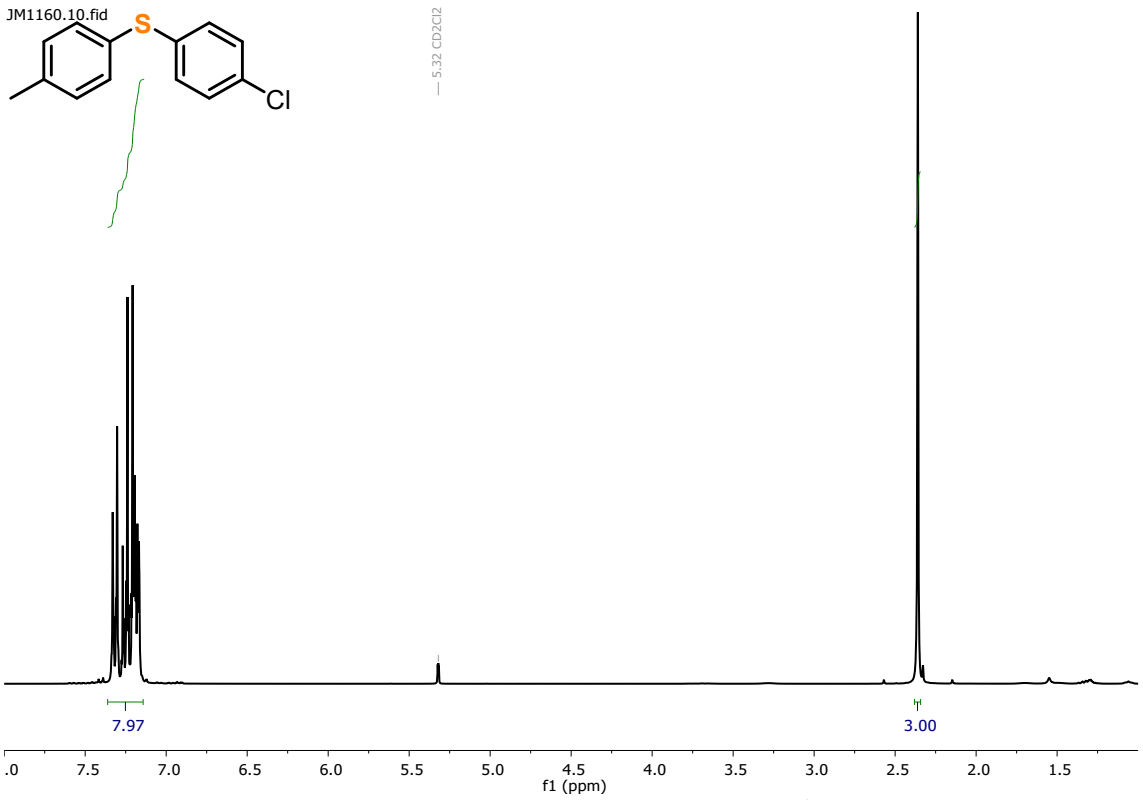
f1 (ppm)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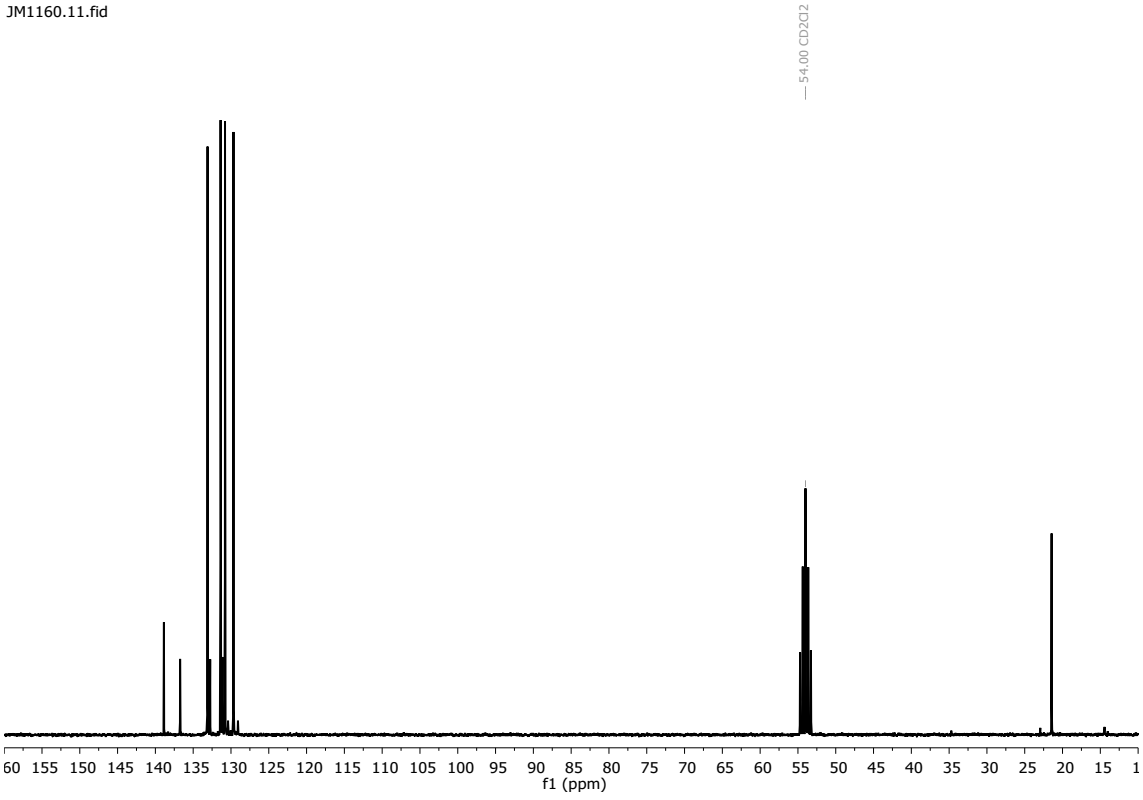
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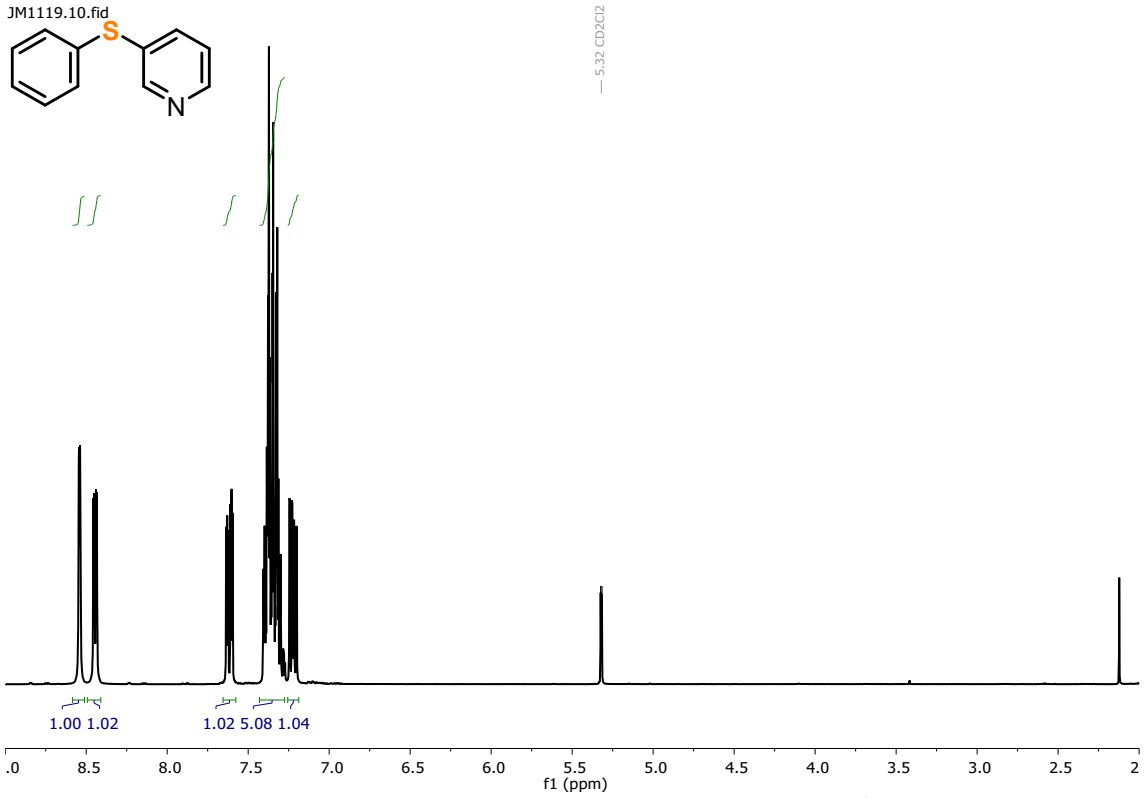
f1 (ppm)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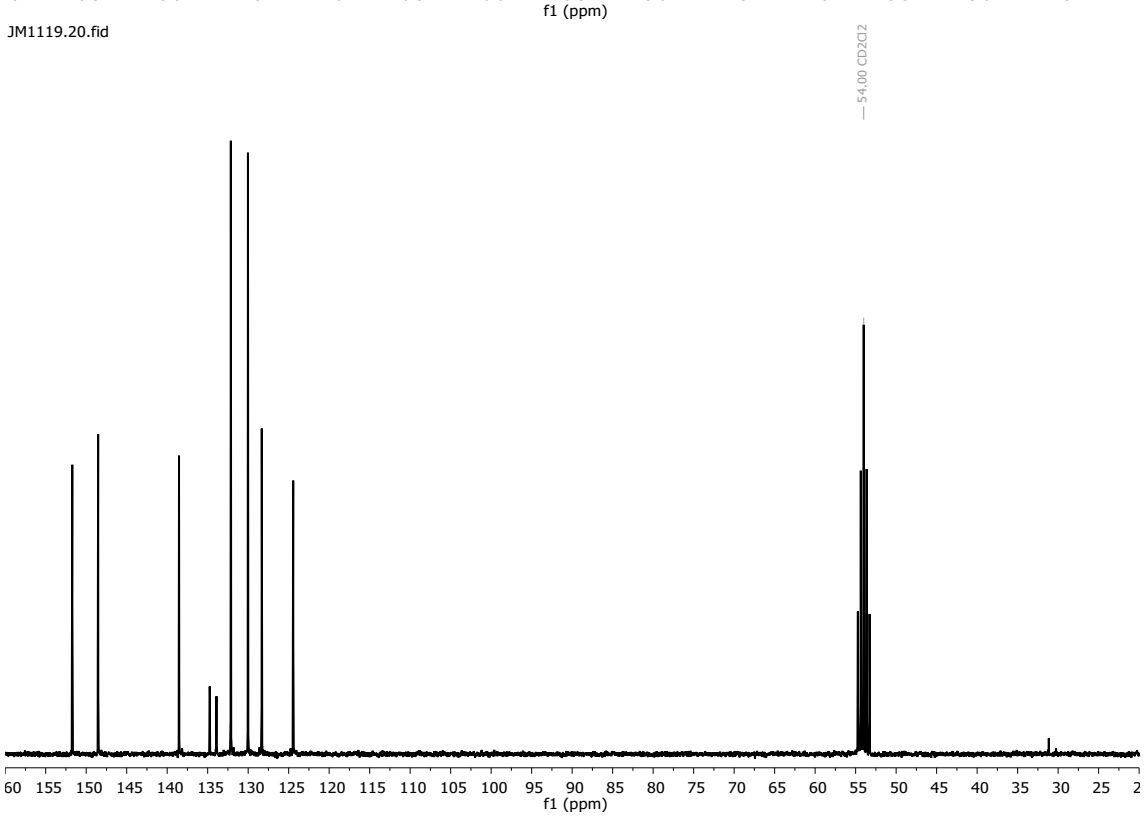
1.02 5.08 1.04
f1 (ppm)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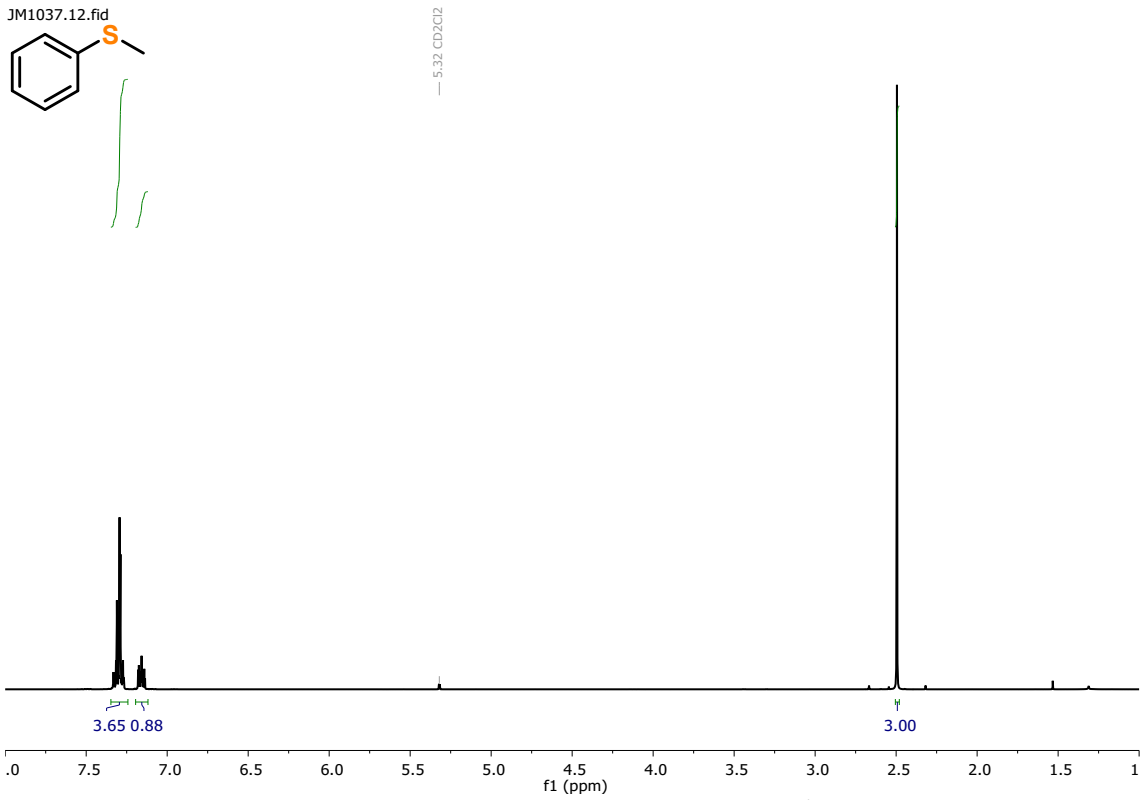
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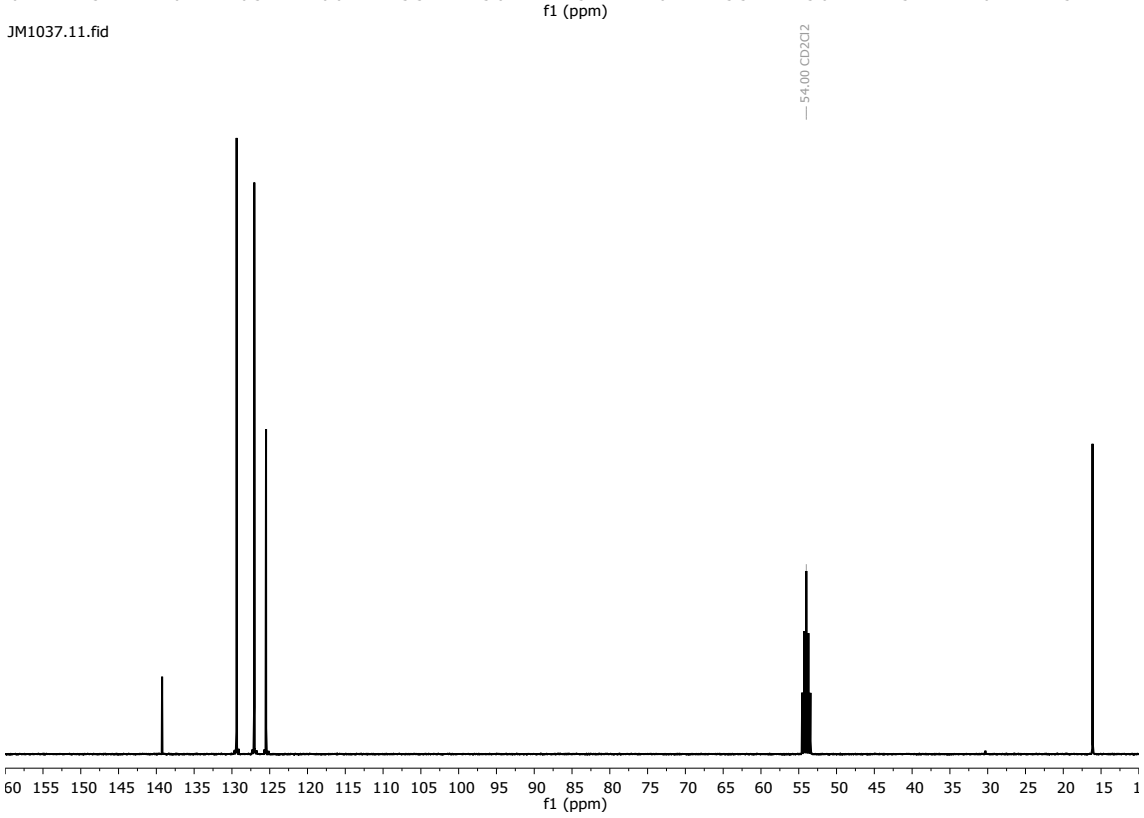
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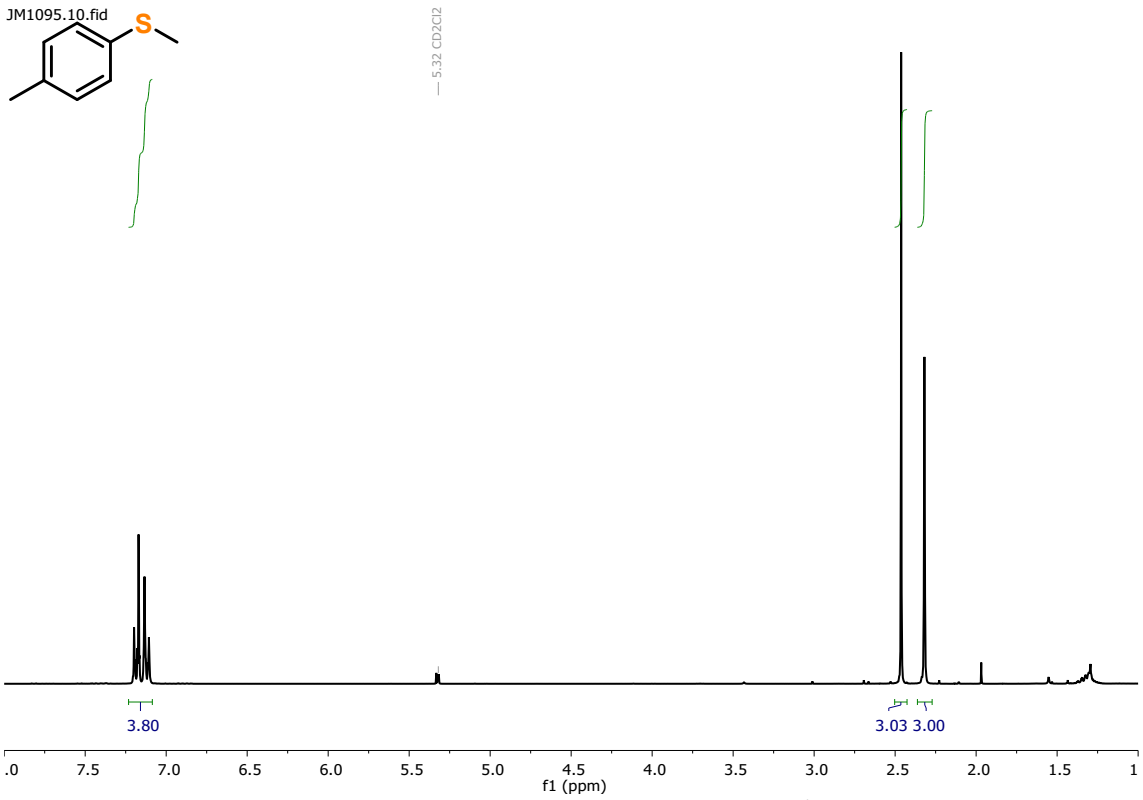
f1 (ppm)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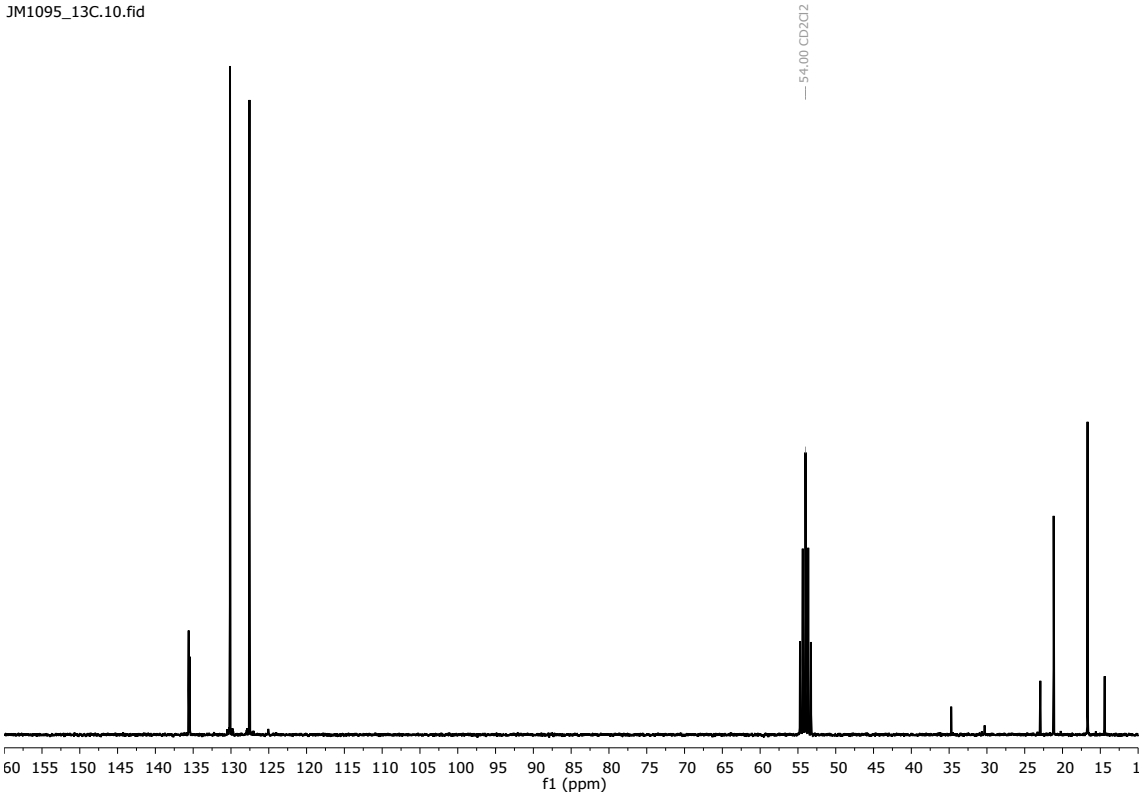
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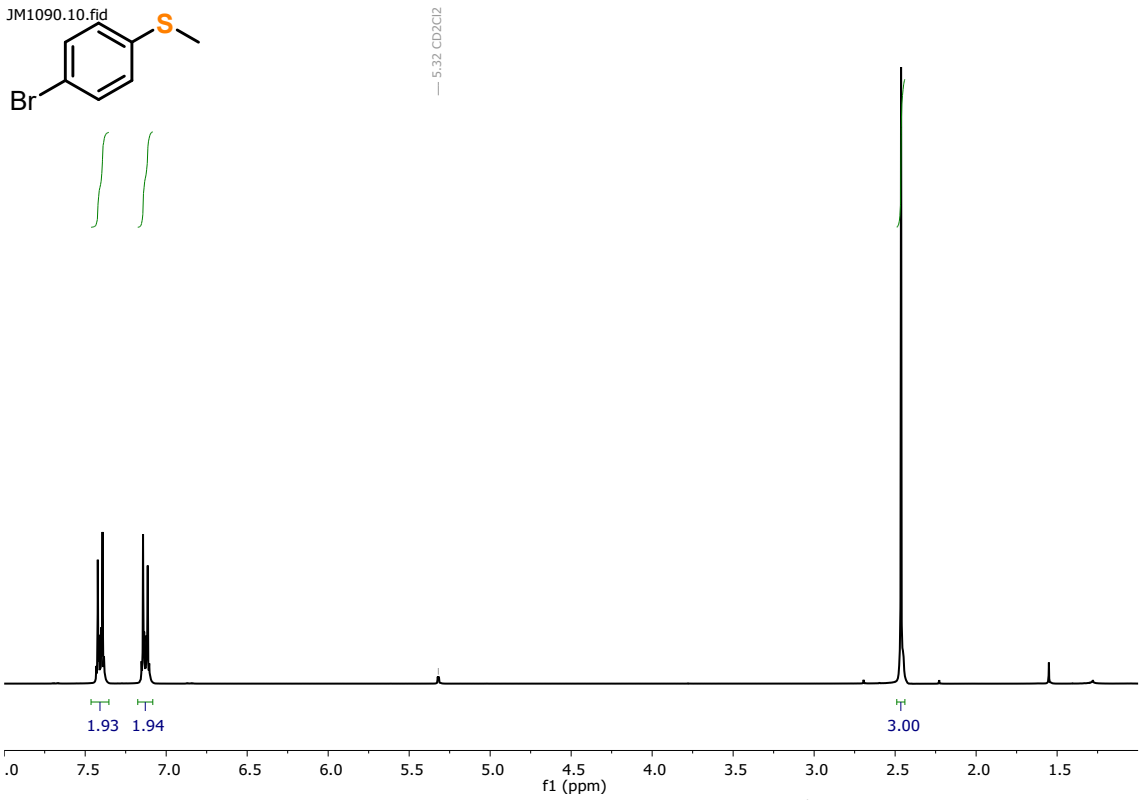
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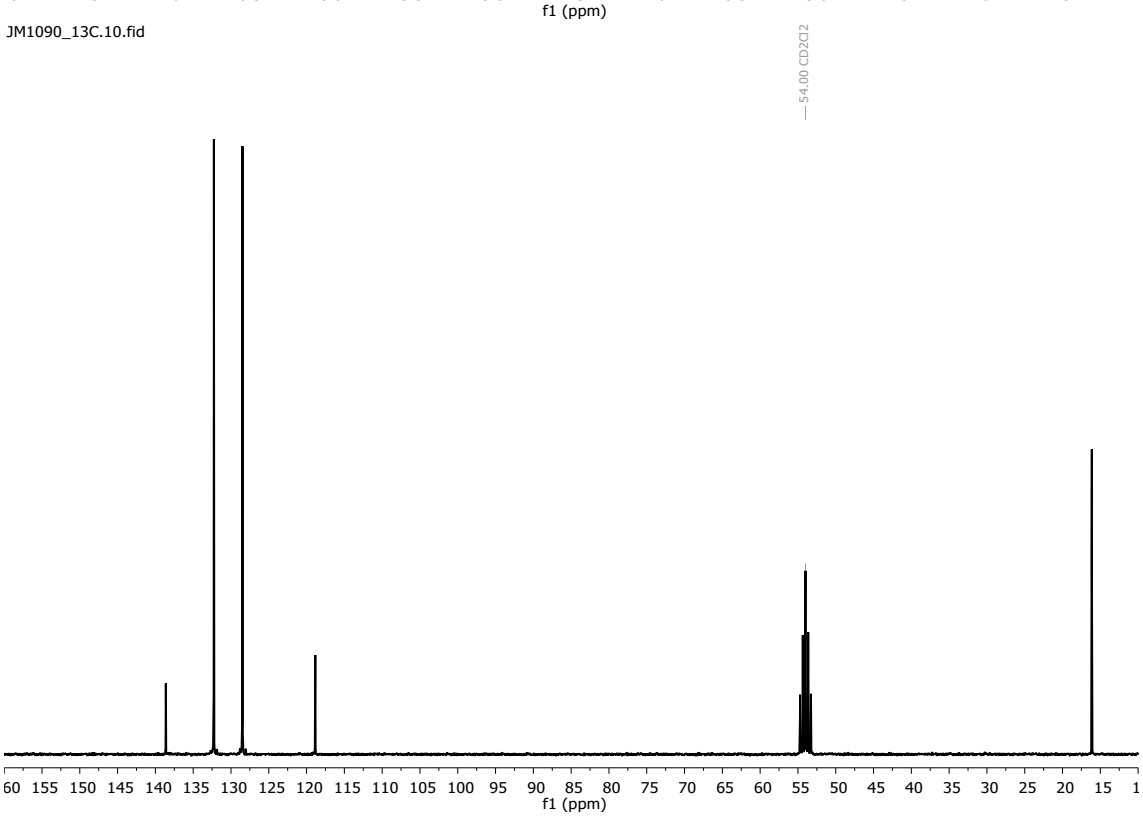
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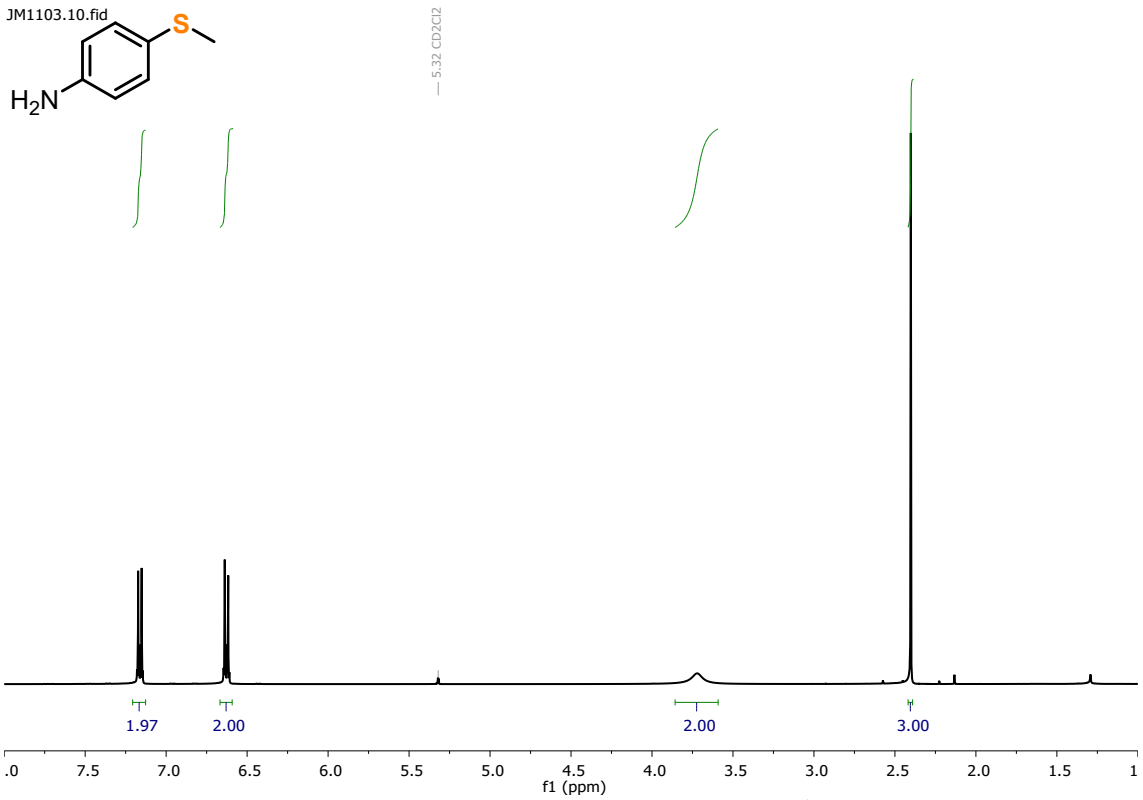
f1 (ppm)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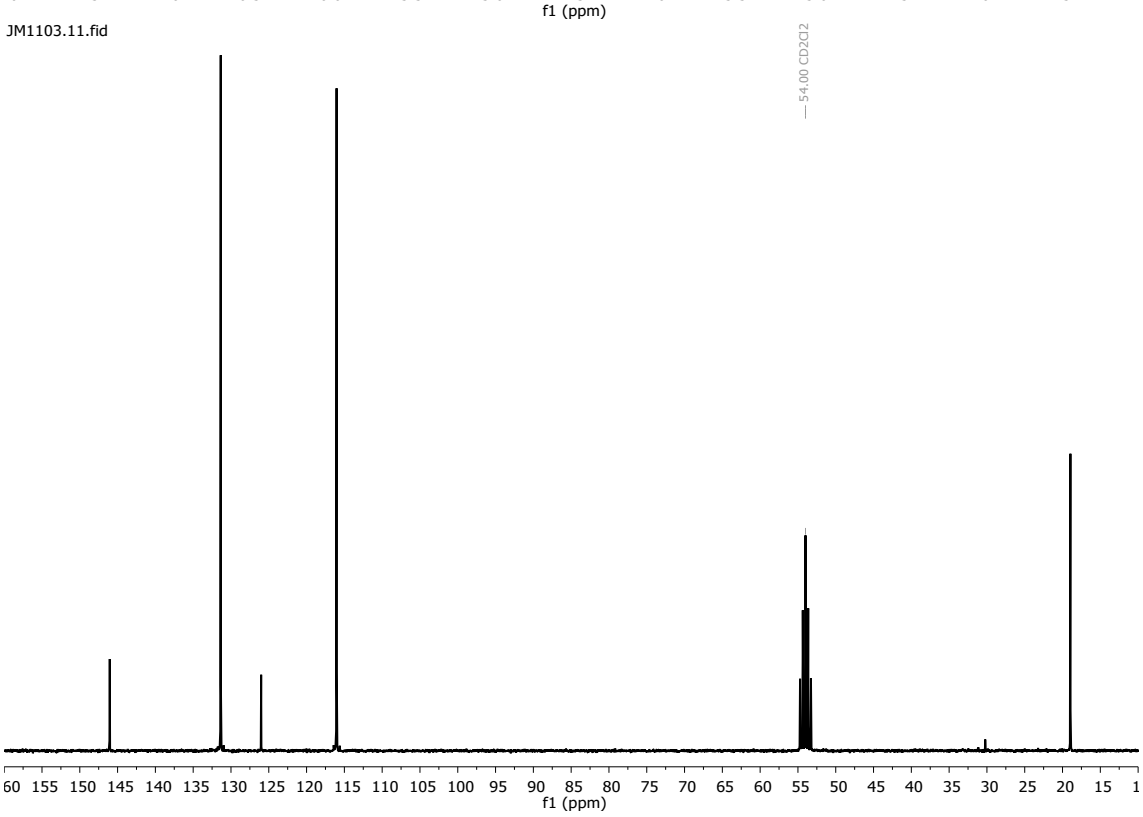
2.00
3.00
f1 (ppm)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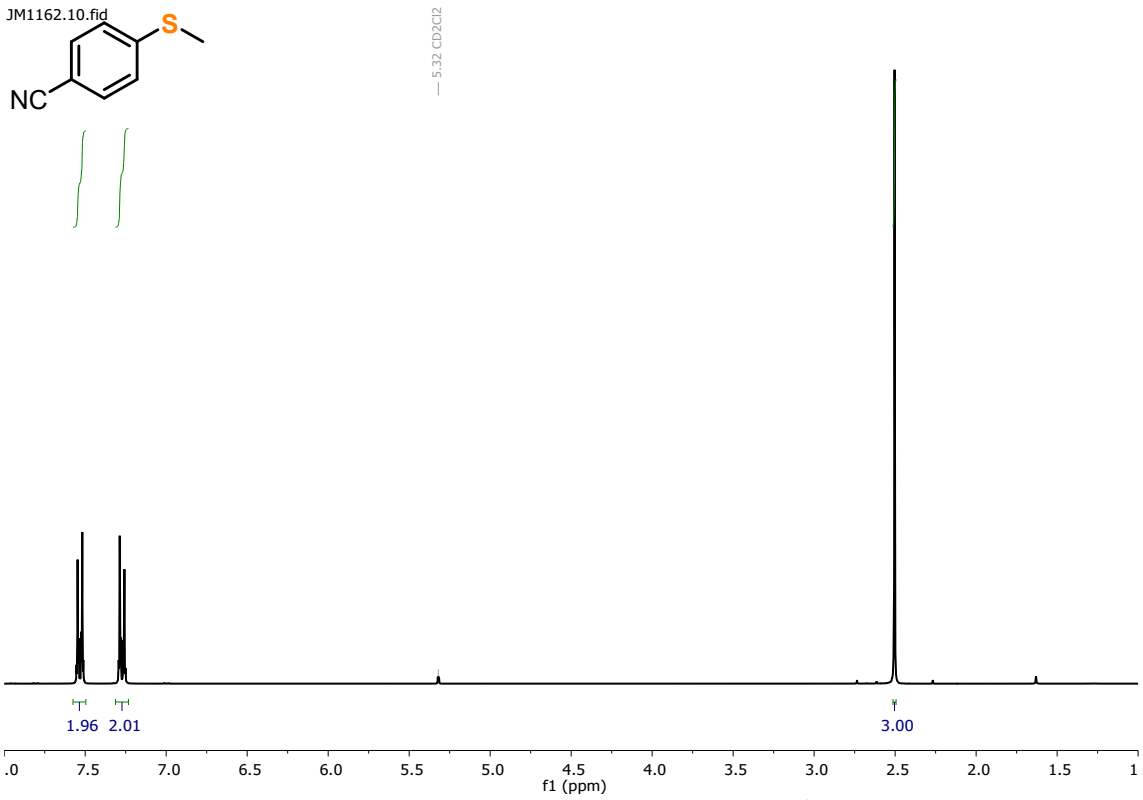
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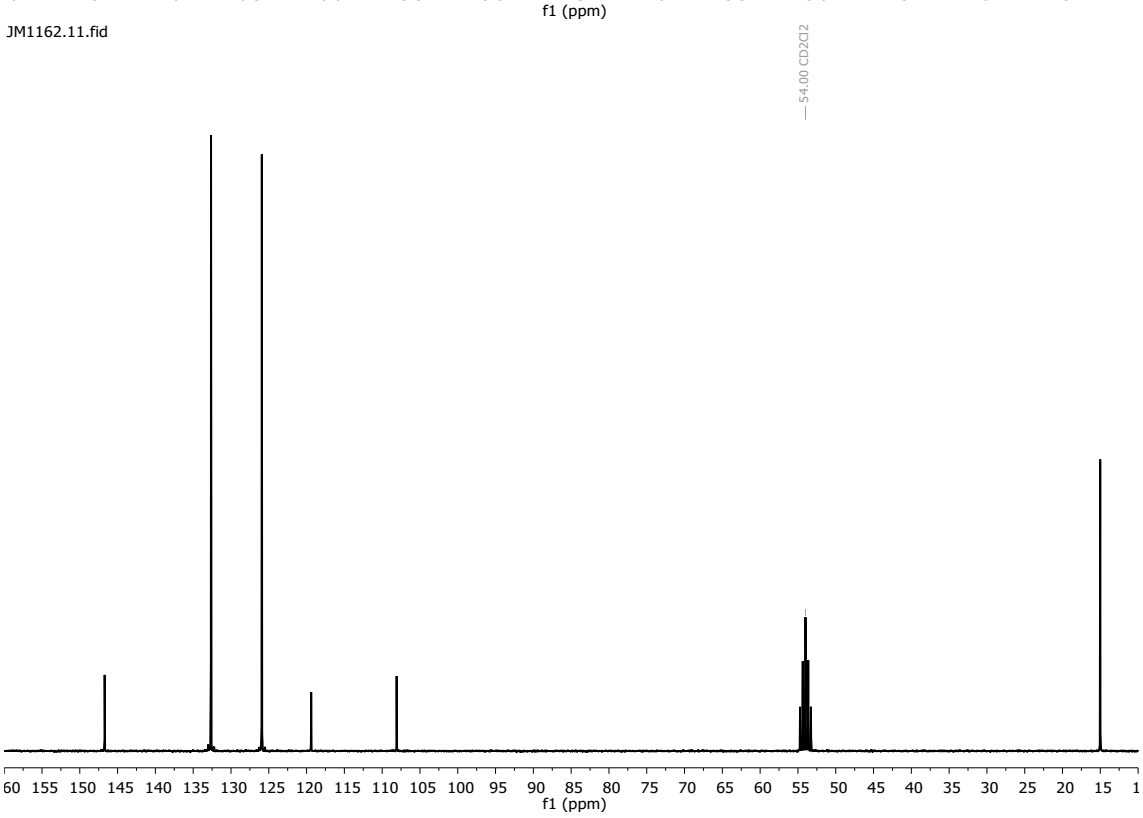
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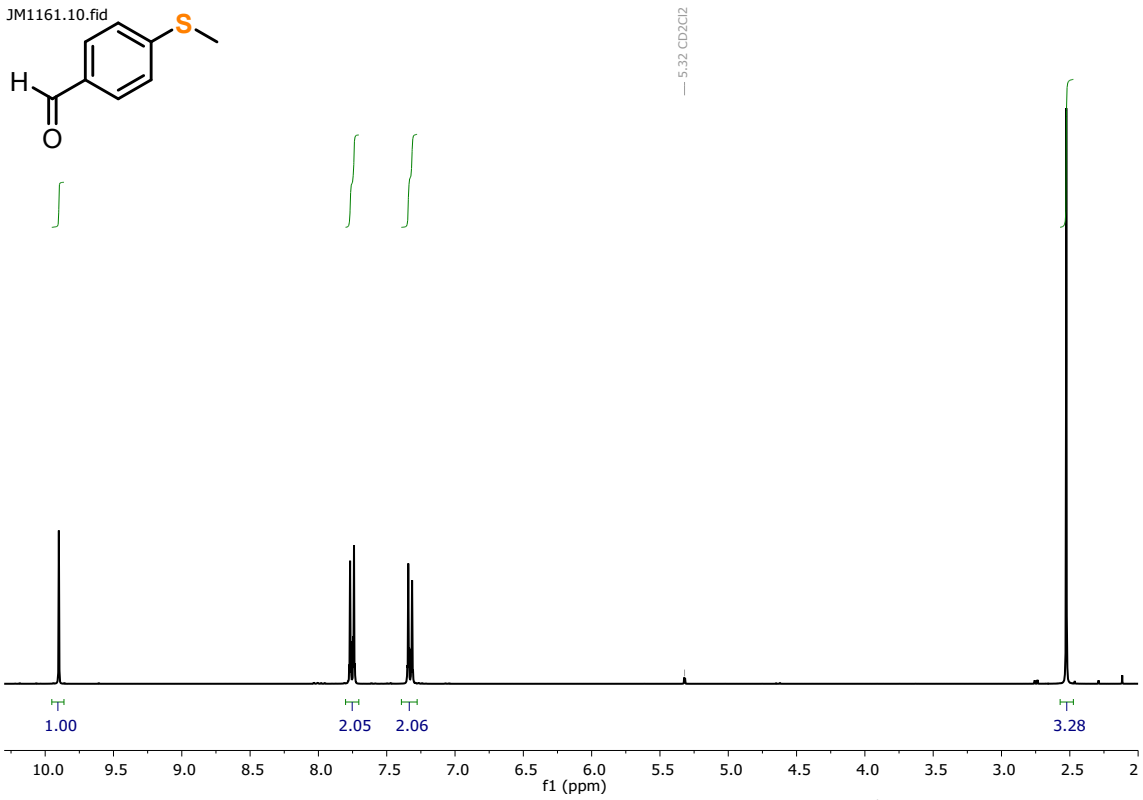
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9.0
8.5
8.0
7.5
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4.0
3.5
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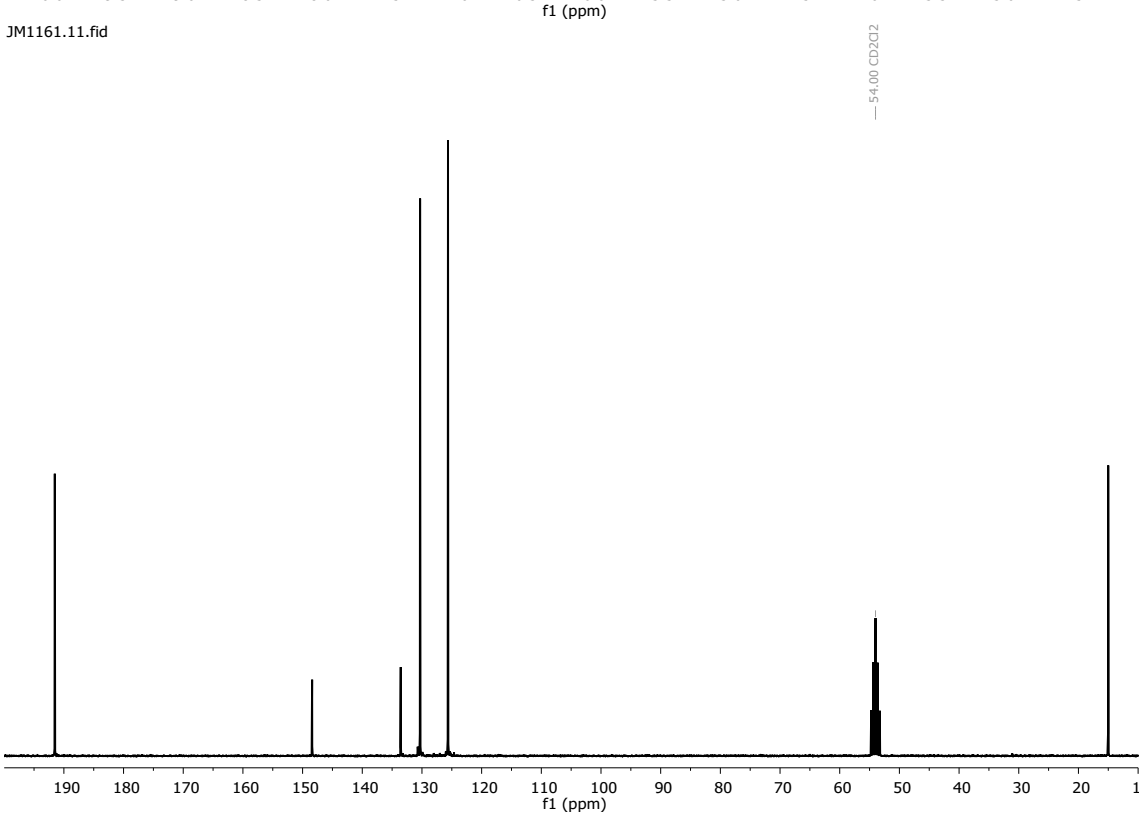
f1 (ppm)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140
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120
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100
90
80
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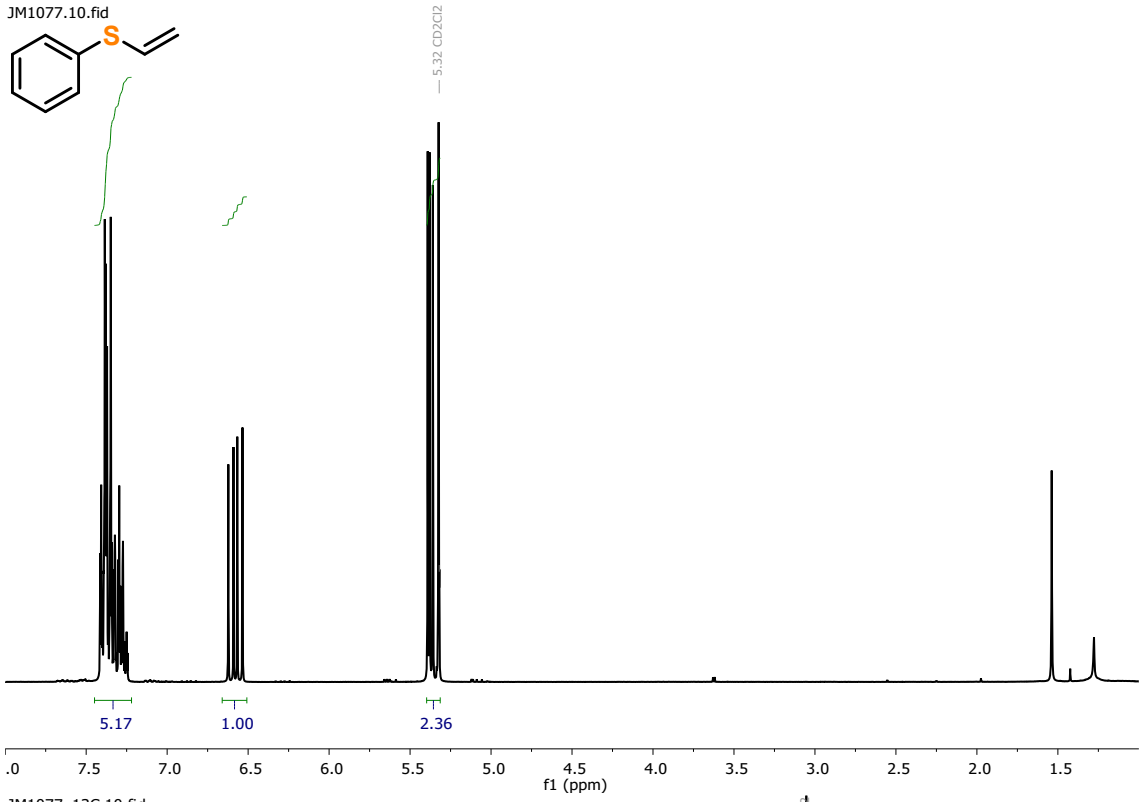
60
50
40
30
20
1
f1 (ppm)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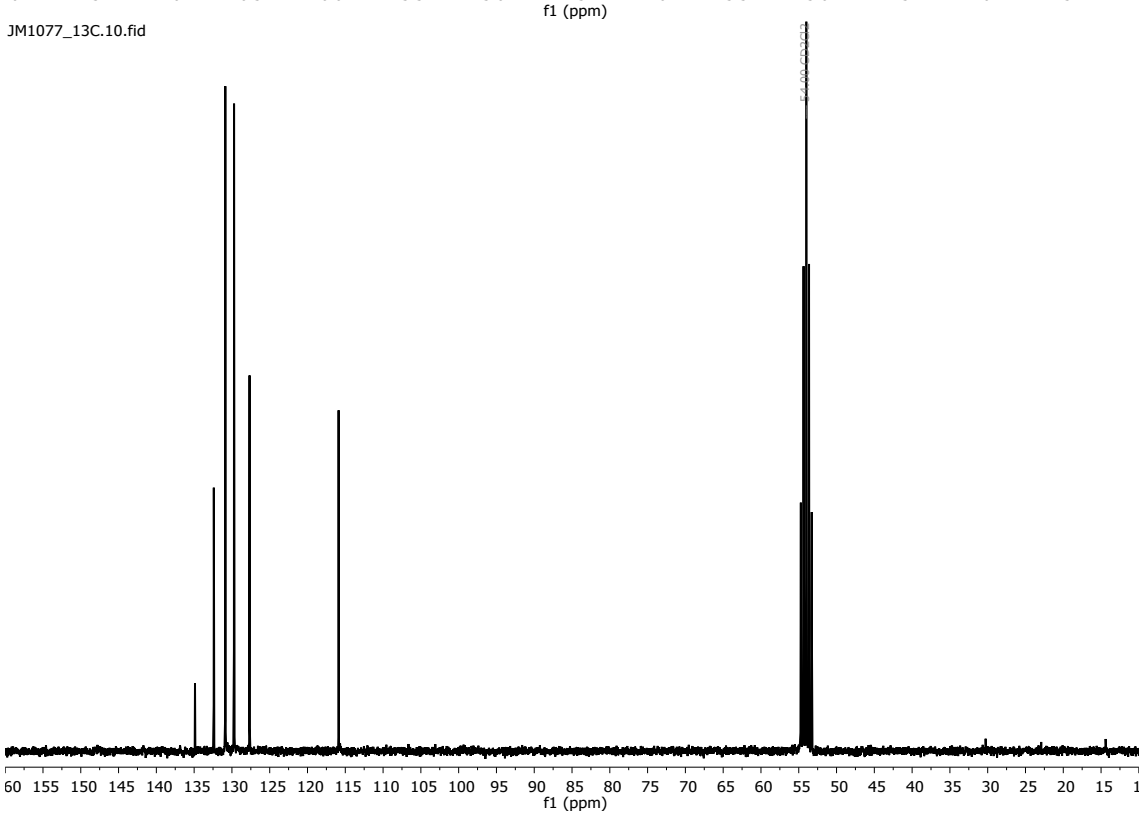
f1 (ppm)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25
20
15
f1 (ppm)

9. Mechanistic experiments

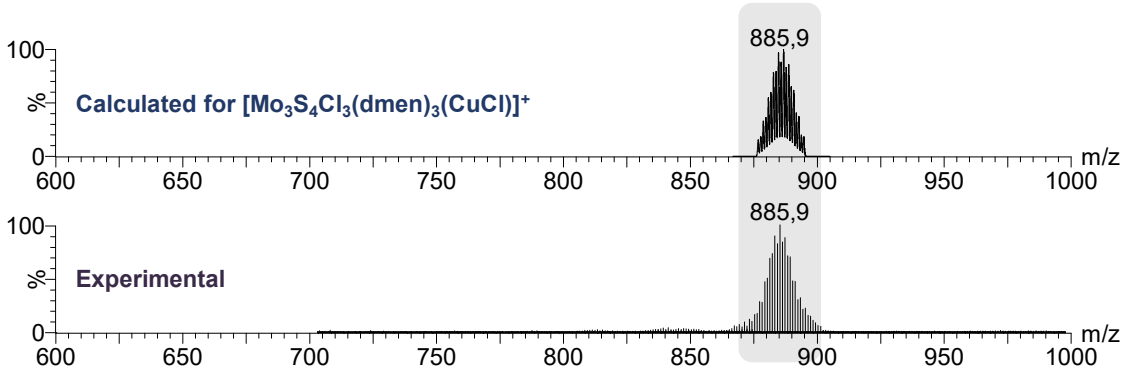

Figure S3. HRMS (ESI-TOF) spectra of catalyst $\mathbf{5}^{+}$ after diphenyl sulfoxide hydrogenation in the presence of CuCl. Spectrum registered at 20 V in CH_3CN.

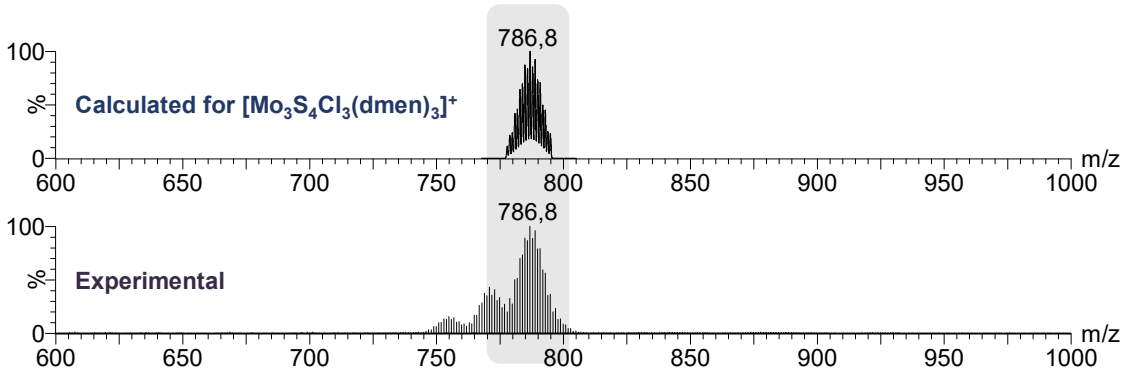

Figure S4. HRMS (ESI-TOF) spectra of catalyst $\mathbf{5}^{+}$ after diphenyl sulfoxide hydrogenation in the presence of Et_3N. Spectrum registered at 20 V in CH_3CN.

10. Computational details

Density functional theory (DFT) calculations were performed with Gaussian 09 (Revision D.01) and Gaussian 16 (Revision C.02).[5,6] Geometry optimizations were carried out at the BP86/BS1 level (using Gaussian 09),[7,8] or PBE0-D3/BS1 level (using Gaussian 16),[9] where Mo and S atoms were described using the SDD relativistic ECP and associated basis set,[10] added polarization functions for the latter ($\zeta = 0.503$),[11] and the remaining atoms were described with the 6-31G(d,p) basis set (BS1).[12,13] Solvent effects (acetonitrile, $\varepsilon = 35.688$) were included self-consistently in these optimizations through the PCM method.[14,15] All stationary points were characterized at this level of theory by analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one imaginary eigenvalue). Then, intrinsic reaction coordinate (IRC) calculations and subsequent geometry optimizations were used to confirm the minima linked by each transition state. The frequency calculations were also used to obtain the

thermochemistry corrections (zero-point, thermal, and entropic energies) at the experimental temperature (323.15 K) and at the standard 1 atm pressure, on the basis of the IGRRHO (ideal gas/rigid rotor/harmonic oscillator) approach. However, these pressures and temperatures employed do not correspond to the 1 M concentration of the standard state used for species reacting in solution. Therefore, corrections (2.1042 kcal·mol^{-1}) were applied to all Gibbs values to change the standard state to 1 M at 323.15 K. This correction has been calculated using the formula RTln(Vm) = 2.1042 kcal·mol^{-1}, where Vm = 26.5 L·mol^{-1} and corresponds to the molar volume of an ideal gas at 1 atm and 323.15 K.

In addition, single-point dispersion corrections were computed using Grimme's D3 (zero damping) parameter set when BP86/BS1 level was used.[16] Thus, the Gibbs energies in acetonitrile (G_{solv}) shown in the text were obtained adding to the potential energies in acetonitrile calculated at BP86/BS1, the Gibbs contribution at the BP86/BS1 level, the dispersion correction, and the standard state correction. When PBE0-D3/BS1 level was employed, Grimme's D3 (zero damping) dispersion corrections were implemented during the optimizations. Finally, the three-dimensional (3D) structures shown in the text were depicted using VESTA software.[17]

10.1 Absolute energy of computed species

Table S5. Electronic energies (E) computed with BP86/BS1(PCM) including solvent effects, correction to Gibbs Free energies (G corr.) at the same level of theory and Grimme's D3 dispersion correction (single-point calculations). Gibbs Free energies (G_{solv}) obtained as the sum of the three previous columns. All values are given in Hartrees.

Species	E_{solv} (PCM)	G_{corr} (PCM)	$D3_{corr}$ (0)	G_{solv} (PCM,D3)
Reagents and products				
1a	-548.6975	0.1352	-0.0242	-548.5866
2a	-473.5165	0.1356	-0.0207	-473.4015
H_2	-1.1766	-0.0029	0.0000	-1.1794
H_2O	-76.4246	0.0006	0.0000	-76.4241
Cluster species and transition states				
5^+	-2434.5020	0.4435	-0.1576	-2434.5370
TS1	-2435.6523	0.4555	-0.1631	-2435.6830
I1	-2435.6596	0.4589	-0.1641	-2435.6870
RC1	-2984.3638	0.6126	-0.2009	-2983.9521
TS2	-2984.3621	0.6116	-0.2030	-2983.9535
I2	-2984.3670	0.6141	-0.2008	-2983.9537
TS3	-2984.3662	0.6152	-0.2025	-2983.9535

Table S6. Electronic energies (E) computed with PBE0-D3/BS1(PCM) including solvent effects, correction to Gibbs Free energies (G corr.) at the same level of theory. Gibbs Free energies (G_{solv}) correspond to the sum of the two previous columns. All values are given in Hartrees.

Species	E_{solv} (PCM,D3)	G_{corr} (PCM,D3)	G_{solv} (PCM,D3)
Reagents and products			
1a	-548.0678	0.1431	-547.9247
2a	-472.9677	0.1400	-472.8276
H_2	-1.1672	-0.0026	-1.1698
H_2O	-76.3428	0.0015	-76.3413
Cluster species and transition states			
5^+	-2432.6212	0.4691	-2432.1521
TS1	-2433.76573	0.4814	-2433.2843
I1	-2433.7808	0.4852	-2433.2956
RC1	-2981.8744	0.6505	-2981.2239
TS2	-2981.8688	0.6480	-2981.2208
I2	-2981.8726	0.6526	-2981.2200
TS3	-2981.8588	0.6498	-2981.2090

Table S7. Gibs Free and potential energy values calculated with different functionals. All values are given in kcal·mol^{-1}.

	ΔG (kcal·mol^{-1})		**ΔE (kcal·mol^{-1})**	
Stationary Point	**PBE0-D3[a]**	**BP86**	**PBE0-D3**	**BP86**
TS1	21.5	20.3	14.2	16.5
I1	14.4	17.1	4.7	12.0
RC1	10.0	14.6	-11.4	7.7
TS2	12.0	13.8	-7.9	8.8
I2	12.5	13.7	-10.3	5.7
TS3	19.4	13.8	-1.7	6.2
Products	-46.7	-37.4	-47.4	-42.0

[a]Values used in the main text

10.2 Analysis of electronic properties of the system

Table S8. Energies of the **I1** and **I2** intermediates in different electronic spin states. Electronic energies (E) computed with PBE0-D3/BS1(PCM), correction to Gibbs Free energies (G corr.) at

the same level of theory. Gibbs Free energies (G_{solv}) correspond to the sum of the two previous columns. All values are given in Hartrees.

Electronic configuration	E_{solv} (PCM,D3)	G_{corr} (PCM,D3)	G_{solv} (PCM,D3)
Species: TS1			
Singlet	-2433.7657	0.4814	-2433.2843
Triplet	-2433.7353	0.4771	-2433.2582
Species: I1			
Singlet	-2433.7808	0.4852	-2433.2956
Triplet	-2433.7754	0.4831	-2433.2923
Species: I2			
Singlet	-2981.8726	0.6526	-2981.2200
Triplet	-2981.8739	0.6592	-2981.2147

10.3 Hydrogen transfer analysis

Table S9. Study of the charge distribution by an analysis of the Mulliken charges for **I1** and **I2** at the PBE0-D3/BS1(PCM) theory level. Highlighted hydrogen atoms (in red) are the corresponding to the hydrogenation process.

I1		**I2**	
Atom	**Atomic charge**	**Atom**	**Atomic charge**
Mo 1	0.01	Mo 1	-0.11
Mo 2	-0.12	Mo 2	0.01
S 3	0.15	S 3	0.10
Mo 4	-0.08	Mo 4	-0.04
Cl 5	-0.34	Cl 5	-0.40
N 6	-0.58	N 6	-0.59
C 7	-0.14	C 7	-0.14
C 8	-0.14	C 8	-0.14
N 9	-0.61	N 9	-0.59
C 10	-0.26	C 10	-0.26
C 11	-0.26	C 11	-0.25
Cl 12	-0.35	Cl 12	-0.41
S 13	-0.11	S 13	-0.11
N 14	-0.58	N 14	-0.58
C 15	-0.26	C 15	-0.26
N 16	-0.60	N 16	-0.59
C 17	-0.26	C 17	-0.26
C 18	-0.14	C 18	-0.14
C 19	-0.14	C 19	-0.14
N 20	-0.59	N 20	-0.58
C 21	-0.14	C 21	-0.14

C 22	-0.14	C 22	-0.14
N 23	-0.59	N 23	-0.59
C 24	-0.26	C 24	-0.26
Cl 25	-0.37	Cl 25	-0.38
C 26	-0.27	C 26	-0.25
H 27	0.37	H 27	0.37
H 28	0.37	H 28	0.38
H 29	0.37	H 29	0.37
H 30	0.37	H 30	0.37
H 31	0.37	H 31	0.37
H 32	0.38	H 32	0.37
H 33	0.20	H 33	0.19
H 34	0.17	H 34	0.16
H 35	0.19	H 35	0.19
H 36	0.20	H 36	0.20
H 37	0.19	H 37	0.18
H 38	0.21	H 38	0.20
H 39	0.19	H 39	0.18
H 40	0.20	H 40	0.19
H 41	0.16	H 41	0.16
H 42	0.20	H 42	0.19
H 43	0.20	H 43	0.19
H 44	0.17	H 44	0.17
H 45	0.19	H 45	0.18
H 46	0.19	H 46	0.18
H 47	0.20	H 47	0.20
H 48	0.19	H 48	0.18
H 49	0.21	H 49	0.20
H 50	0.20	H 50	0.20
H 51	0.16	H 51	0.16
H 52	0.20	H 52	0.19
H 53	0.19	H 53	0.19
H 54	0.17	H 54	0.16
H 55	0.20	H 55	0.18
H 56	0.21	H 56	0.20
H 57	0.19	H 57	0.18
H 58	0.21	H 58	0.20
H 59	0.19	H 59	0.18
H 60	0.20	H 60	0.19
H 61	0.17	H 61	0.15
H 62	0.20	H 62	0.19
S 63	-0.03	S 63	-0.35
H 64	**0.13**	S 64	-0.20
S 65	-0.04	C 65	-0.12
H 66	**0.13**	C 66	-0.09
		C 67	-0.11
		C 68	-0.13
		H 69	0.20
		C 70	-0.13

	H 71	0.20
	C 72	-0.11
	H 73	0.18
	H 74	0.18
	H 75	0.18
	C 76	-0.09
	C 77	-0.12
	C 78	-0.11
	C 79	-0.13
	H 80	0.19
	C 81	-0.14
	H 82	0.19
	C 83	-0.12
	H 84	0.18
	H 85	0.18
	H 86	0.17
	S 87	0.59
	O 88	-0.50
	H 89	**0.37**
	H 90	**0.12**

Procedure: Fragment analysis was performed by treating the organic and inorganic components of **I2** separately. The energies associated with the three possible hydrogen transfer pathways (proton transfer, hydride transfer and hydrogen atom transfer) were obtained as the sum of the energies of the organic and inorganic fragments (see Table S10). These energies were determined using single-point calculations, modifying the charge and multiplicity of the fragments according to each transfer possibility. Thus, the closest energy value to the optimized result (**I2** = 12.5 kcal·mol^{-1}) suggests which transfer pathway is involved in the process.

Table S10. Study of the character of the transferred hydrogen atom to the sulfoxide substrate in intermediate **I2**. Electronic energies (E) computed with single-point PBE0-D3/BS1(PCM) calculations on the optimized **I2** geometry of the corresponding fragment, correction to Gibbs Free energies (G corr.) at the same level of theory. Gibbs Free energies obtained as the sum of the two previous columns. All values are given in Hartrees

Fragment	**E_{solv} (PCM,D3)**	**G_{corr} (PCM,D3)**	**G_{solv} (PCM,D3)**
Proton transfer			
Inorganic	-2433.3408	0.4748	-2432.8659
Organic	-548.4956	0.1556	-548.3400
Total	-2981.8364	0.6304	-2981.2059
Hydride transfer			
Inorganic	-2432.9795	0.4755	-2432.5040
Organic	-548.6356	0.1512	-548.4845

Total	-2981.6151	0.6272	-2980.9885
Hydrogen atom transfer (HAT)			
Inorganic	-2433.1897	0.4753	-2432.7144
Organic	-548.5930	0.1531	-548.4399
Total	-2981.7827	0.6284	-2982.1543

10.4 3D views of the cluster units

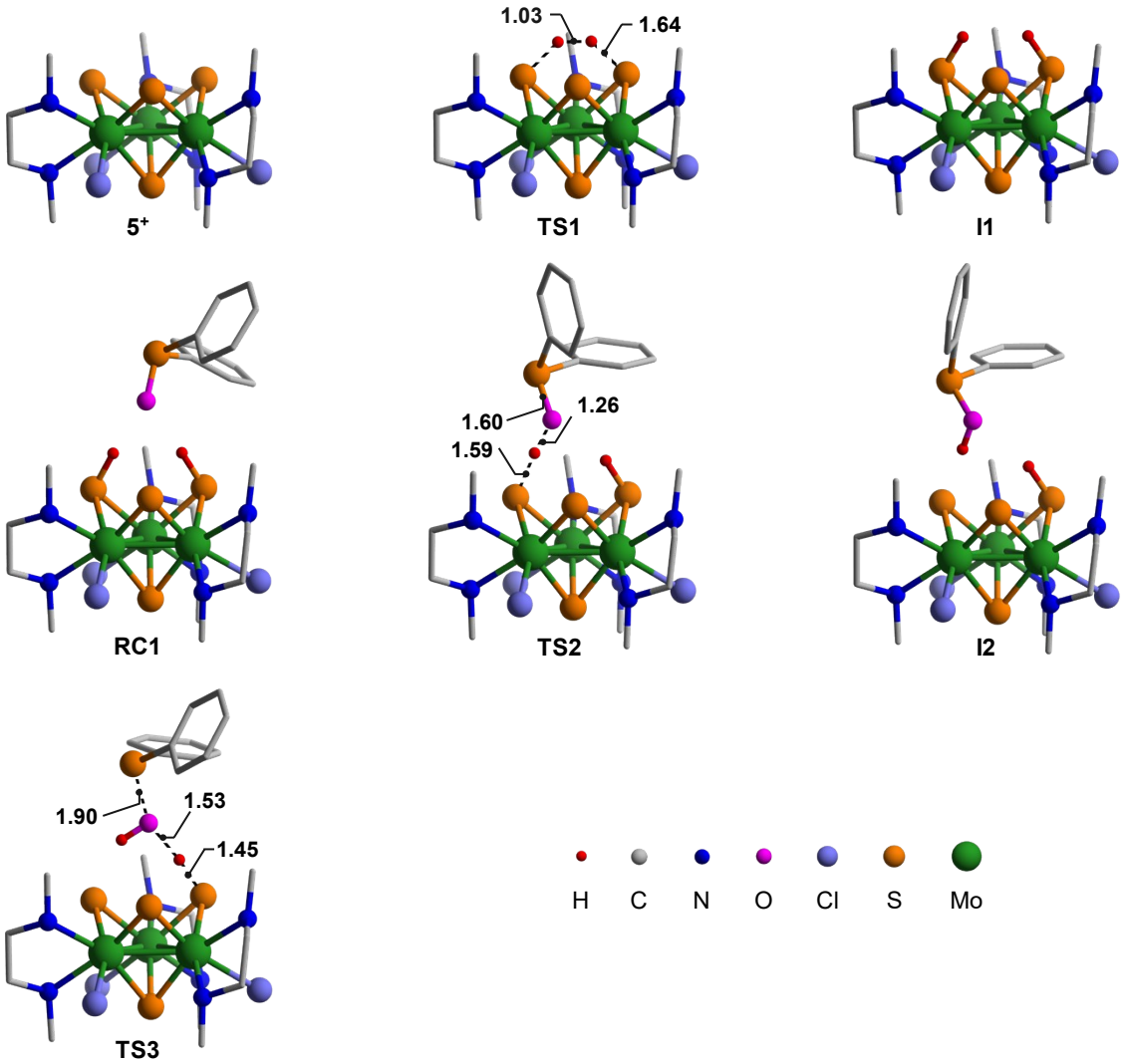

Figure S5. Optimized structures of intermediates and transition states for the Gibbs energy profile represented in Figure 5. Selected distances are given in Å.

10.5 Cartesian coordinates of the optimized structures

10.5.1 Optimized with BP86 functional

Stationary point: H_2

	x	y	z
H	0.1433	2.5505	-0.0642
H	-0.6076	2.5505	-0.0642

Stationary point: H_2O

	x	y	z
O	-1.5137	2.5201	-0.0642
H	-0.5409	2.5795	-0.0642
H	-1.7824	3.4568	-0.0642

Stationary point: Diphenyl sulfoxide (1a)

	x	y	z
C	-5.4007	1.9985	1.2796
C	-4.2912	1.7537	0.4520
C	-3.2027	2.6370	0.5105
C	-3.2028	3.7639	1.3421
C	-4.3187	3.9993	2.1615
C	-5.4132	3.1162	2.1328
H	-6.2590	1.3197	1.2494
H	-4.2822	0.8921	-0.2244
H	-2.3390	4.4370	1.3224
H	-4.3354	4.8738	2.8202
H	-6.2830	3.3048	2.7699
S	-1.7439	2.3826	-0.5978
O	-0.9693	3.7249	-0.5828
C	-0.7990	1.2479	0.5165
C	-1.0330	-0.1349	0.4706
C	0.1855	1.8085	1.3400
C	-0.2717	-0.9736	1.3028
H	-1.7902	-0.5570	-0.1991
C	0.9419	0.9593	2.1641
H	0.3469	2.8913	1.3119
C	0.7111	-0.4281	2.1478
H	-0.4414	-2.0548	1.2825
H	1.7137	1.3805	2.8166
H	1.3050	-1.0876	2.7885

Stationary point: Diphenyl sulfide (2a)

	x	y	z

C	-4.9927	1.9597	0.2844
C	-3.5955	2.0727	0.3429
C	-3.0078	3.0388	1.1861
C	-3.8229	3.8963	1.9524
C	-5.2215	3.7913	1.8664
C	-5.8099	2.8205	1.0394
H	-5.4442	1.2035	-0.3662
H	-2.9611	1.4135	-0.2569
H	-3.3639	4.6349	2.6174
H	-5.8494	4.4612	2.4628
H	-6.8995	2.7327	0.9835
S	-1.2204	3.2955	1.2474
C	-0.5518	1.6194	1.3382
C	-1.1099	0.6341	2.1790
C	0.6136	1.3362	0.5970
C	-0.5096	-0.6314	2.2603
H	-2.0099	0.8575	2.7597
C	1.2204	0.0736	0.7054
H	1.0380	2.0974	-0.0657
C	0.6589	-0.9148	1.5303
H	-0.9512	-1.3949	2.9091
H	2.1258	-0.1395	0.1278
H	1.1270	-1.9015	1.6036

Stationary point: Cluster 5^{+}

	x	y	z
S	-0.1981	-2.0645	-0.1981
Mo	-1.3812	-0.4173	0.9655
S	0.3388	1.1371	1.1042
Mo	-0.9242	1.7297	-0.7705
S	-2.9345	0.4677	-0.6011
Mo	-1.3479	-0.8348	-1.8024
Cl	-2.5618	-0.1931	-3.9256
N	0.5197	3.4924	-1.1184
C	0.2565	4.0870	-2.4657
C	-1.2413	4.2302	-2.6889
N	-1.9391	2.9200	-2.4993
C	-3.4182	3.1181	-2.5194
C	1.9843	3.3405	-0.8859
Cl	-2.0509	3.5502	0.5826
S	0.3806	0.6391	-2.3525
N	-0.4590	-2.3540	-3.2939
C	1.0156	-2.5181	-3.4383
N	-2.9476	-2.5395	-1.8593
C	-4.4043	-2.2161	-1.8705
C	-1.1208	-3.6814	-3.1008

C	-2.6236	-3.4976	-2.9621
N	-0.5015	-1.2292	2.9392
C	-0.7833	-0.2556	4.0390
C	-2.2268	0.2148	3.9568
N	-2.5246	0.7898	2.6081
C	-3.9867	1.0568	2.4750
Cl	-3.1284	-2.1355	1.5999
C	0.9073	-1.7110	3.0084
H	-0.8180	-1.9569	-4.1770
H	-2.7611	-3.0026	-0.9548
H	-1.1190	-2.0446	3.0840
H	-2.0540	1.7063	2.5266
H	0.1567	4.1529	-0.4122
H	-1.7178	2.3082	-3.3020
H	1.4648	-1.5541	-3.7133
H	1.2430	-3.2644	-4.2196
H	1.4405	-2.8530	-2.4804
H	-0.6871	-4.1411	-2.1967
H	-0.9017	-4.3454	-3.9571
H	-3.0453	-3.0753	-3.8896
H	-3.1127	-4.4712	-2.7788
H	-4.6616	-1.6894	-0.9418
H	-4.9988	-3.1444	-1.9386
H	-4.6204	-1.5735	-2.7362
H	1.0569	-2.5067	2.2660
H	1.1295	-2.1022	4.0167
H	1.5889	-0.8771	2.7838
H	-0.5948	-0.7245	5.0223
H	-0.0822	0.5883	3.9249
H	-2.4326	0.9615	4.7446
H	-2.9163	-0.6334	4.1038
H	-4.1583	1.6739	1.5829
H	-4.3564	1.5953	3.3655
H	-4.5162	0.0983	2.3743
H	2.1575	3.0145	0.1488
H	2.5020	4.3000	-1.0604
H	2.3850	2.5807	-1.5730
H	0.7106	3.4201	-3.2183
H	0.7448	5.0753	-2.5494
H	-1.6733	4.9329	-1.9566
H	-1.4410	4.6270	-3.7004
H	-3.9093	2.1395	-2.6042
H	-3.7052	3.7453	-3.3818
H	-3.7242	3.6091	-1.5845

Stationary point: TS1

	x	y	z
Mo	-1.4185	-0.4307	0.9462
Mo	-0.9366	1.6957	-0.7986
S	-2.9804	0.4810	-0.5948
Mo	-1.3630	-0.7798	-1.8072
Cl	-2.5437	-0.1344	-3.9241
N	0.5274	3.4574	-1.1502
C	0.2555	4.0452	-2.4965
C	-1.2434	4.2044	-2.6914
N	-1.9530	2.9029	-2.4781
C	-3.4285	3.1283	-2.4554
C	1.9930	3.3164	-0.9215
Cl	-1.9391	3.4968	0.6771
S	0.4740	0.5897	-2.2872
N	-0.4658	-2.3167	-3.3013
C	1.0041	-2.4664	-3.4910
N	-2.9331	-2.5098	-1.8267
C	-4.3930	-2.1997	-1.8529
C	-1.0999	-3.6483	-3.0603
C	-2.6032	-3.4869	-2.9103
N	-0.5490	-1.2362	2.9451
C	-0.8078	-0.2320	4.0206
C	-2.2486	0.2412	3.9364
N	-2.5529	0.7849	2.5768
C	-4.0221	1.0161	2.4471
Cl	-3.0915	-2.2334	1.5392
C	0.8405	-1.7648	3.0425
H	-0.8559	-1.9421	-4.1810
H	-2.7548	-2.9535	-0.9087
H	-1.1935	-2.0290	3.0995
H	-2.1064	1.7128	2.4780
H	0.1647	4.1178	-0.4434
H	-1.7633	2.2845	-3.2863
H	1.4324	-1.5043	-3.8022
H	1.2148	-3.2286	-4.2619
H	1.4658	-2.7758	-2.5414
H	-0.6485	-4.0723	-2.1470
H	-0.8779	-4.3362	-3.8970
H	-3.0391	-3.0922	-3.8440
H	-3.0753	-4.4642	-2.7032
H	-4.6627	-1.6665	-0.9318
H	-4.9801	-3.1331	-1.9182
H	-4.6064	-1.5661	-2.7263
H	0.9721	-2.5838	2.3222
H	1.0368	-2.1407	4.0620
H	1.5567	-0.9611	2.8142
H	-0.6129	-0.6755	5.0145

H	-0.1014	0.6032	3.8774
H	-2.4511	1.0034	4.7101
H	-2.9362	-0.6049	4.1061
H	-4.2130	1.6262	1.5543
H	-4.4048	1.5460	3.3377
H	-4.5288	0.0450	2.3475
H	2.1713	2.9945	0.1139
H	2.5030	4.2796	-1.0986
H	2.3984	2.5587	-1.6083
H	0.6877	3.3659	-3.2509
H	0.7536	5.0273	-2.5966
H	-1.6525	4.9163	-1.9542
H	-1.4621	4.5969	-3.7004
H	-3.9405	2.1612	-2.5443
H	-3.7265	3.7782	-3.2969
H	-3.6992	3.6056	-1.5022
S	0.4531	0.9877	1.0133
H	1.4158	0.0100	0.1669
S	-0.0367	-1.9501	-0.2021
H	1.2555	-0.9834	-0.2555

Stationary point: I1

	x	y	z
Mo	-1.4126	-0.4311	0.9571
Mo	-0.9327	1.6856	-0.7879
S	-2.9791	0.4808	-0.5757
Mo	-1.3581	-0.7716	-1.7885
Cl	-2.5210	-0.0865	-3.9016
N	0.5201	3.4602	-1.1690
C	0.2421	4.0118	-2.5281
C	-1.2576	4.1670	-2.7129
N	-1.9653	2.8713	-2.4618
C	-3.4388	3.1057	-2.4214
C	1.9866	3.3445	-0.9358
Cl	-1.9048	3.4800	0.7154
S	0.5253	0.5688	-2.2447
N	-0.4756	-2.3014	-3.3096
C	0.9905	-2.4673	-3.5112
N	-2.9383	-2.4928	-1.8293
C	-4.3962	-2.1723	-1.8421
C	-1.1249	-3.6297	-3.0942
C	-2.6250	-3.4531	-2.9327
N	-0.5596	-1.2304	2.9703
C	-0.8399	-0.2290	4.0422
C	-2.2802	0.2377	3.9321
N	-2.5620	0.7836	2.5679

C	-4.0308	1.0106	2.4221
Cl	-3.0558	-2.2653	1.5125
C	0.8301	-1.7531	3.0913
H	-0.8641	-1.9043	-4.1799
H	-2.7610	-2.9560	-0.9202
H	-1.2023	-2.0266	3.1148
H	-2.1202	1.7155	2.4812
H	0.1486	4.1323	-0.4780
H	-1.7904	2.2352	-3.2614
H	1.4311	-1.5031	-3.7978
H	1.1865	-3.2118	-4.3031
H	1.4539	-2.8103	-2.5738
H	-0.6739	-4.0794	-2.1932
H	-0.9165	-4.3020	-3.9470
H	-3.0611	-3.0356	-3.8565
H	-3.1078	-4.4286	-2.7423
H	-4.6577	-1.6530	-0.9110
H	-4.9907	-3.1001	-1.9208
H	-4.6093	-1.5222	-2.7034
H	0.9788	-2.5695	2.3714
H	1.0094	-2.1314	4.1131
H	1.5471	-0.9456	2.8797
H	-0.6607	-0.6727	5.0390
H	-0.1344	0.6093	3.9132
H	-2.5011	0.9972	4.7034
H	-2.9672	-0.6119	4.0867
H	-4.2138	1.6269	1.5321
H	-4.4257	1.5326	3.3121
H	-4.5331	0.0386	2.3096
H	2.1689	3.0664	0.1116
H	2.4859	4.3061	-1.1494
H	2.3996	2.5657	-1.5937
H	0.6670	3.3102	-3.2662
H	0.7402	4.9905	-2.6585
H	-1.6592	4.8969	-1.9892
H	-1.4875	4.5349	-3.7285
H	-3.9584	2.1414	-2.4933
H	-3.7443	3.7485	-3.2658
H	-3.6935	3.5949	-1.4697
S	0.4811	1.0428	1.0795
H	1.4820	0.3309	0.4028
S	-0.0432	-2.0403	-0.1822
H	1.2014	-1.4118	-0.3334

Stationary point: RC1

	x	y	z

Mo	-1.5123	-0.8546	0.9395
Mo	-0.9551	1.7588	0.1898
S	-3.0894	0.7232	0.1062
Mo	-1.7412	-0.1655	-1.6439
Cl	-2.8448	1.4653	-3.2543
N	0.6195	3.4654	0.3362
C	0.3095	4.4975	-0.6966
C	-1.1766	4.8068	-0.6647
N	-1.9853	3.5616	-0.8425
C	-3.4187	3.8634	-0.5538
C	2.0815	3.1877	0.3816
Cl	-1.6322	2.8983	2.3475
S	0.2606	1.2041	-1.8180
N	-1.1789	-1.0768	-3.7132
C	0.2361	-1.3048	-4.1165
N	-3.5480	-1.5040	-2.1555
C	-4.9389	-1.0237	-1.9088
C	-1.9944	-2.3091	-3.9195
C	-3.4404	-2.0221	-3.5554
N	-0.5984	-2.4910	2.3242
C	-0.6410	-2.0104	3.7378
C	-2.0004	-1.4012	4.0356
N	-2.3215	-0.3071	3.0685
C	-3.7396	0.1204	3.2477
Cl	-3.3852	-2.5346	1.0308
C	0.7112	-3.1349	2.0338
H	-1.5633	-0.3444	-4.3322
H	-3.3846	-2.2866	-1.4962
H	-1.3291	-3.2136	2.2207
H	-1.7444	0.5219	3.2957
H	0.3495	3.8545	1.2546
H	-1.9512	3.2782	-1.8380
H	0.7767	-0.3482	-4.1028
H	0.2813	-1.7346	-5.1330
H	0.7100	-1.9978	-3.4058
H	-1.5689	-3.1006	-3.2795
H	-1.9310	-2.6448	-4.9715
H	-3.8525	-1.2414	-4.2180
H	-4.0587	-2.9296	-3.6754
H	-5.0848	-0.8784	-0.8308
H	-5.6688	-1.7660	-2.2778
H	-5.0826	-0.0686	-2.4355
H	0.6833	-3.5860	1.0329
H	0.9320	-3.9135	2.7856
H	1.5041	-2.3731	2.0614
H	-0.4431	-2.8459	4.4348
H	0.1652	-1.2670	3.8605

H	-2.0313	-1.0207	5.0725
H	-2.7911	-2.1640	3.9318
H	-3.9037	1.0569	2.6991
H	-3.9583	0.2825	4.3187
H	-4.3998	-0.6644	2.8501
H	2.3007	2.5199	1.2258
H	2.6475	4.1285	0.5036
H	2.3926	2.7012	-0.5550
H	0.6176	4.0962	-1.6773
H	0.8916	5.4187	-0.5083
H	-1.4529	5.2331	0.3152
H	-1.4358	5.5491	-1.4408
H	-4.0414	3.0334	-0.9125
H	-3.7234	4.7935	-1.0665
H	-3.5468	3.9795	0.5323
S	0.5268	0.3605	1.4853
S	-0.4414	-1.9569	-0.8465
C	5.5735	0.3385	0.8886
C	5.9312	0.7829	-0.3940
C	6.1782	0.8459	2.0492
C	6.9422	1.7484	-0.5128
H	5.4149	0.3865	-1.2739
C	7.1942	1.8088	1.9139
H	5.8634	0.5030	3.0405
C	7.5751	2.2560	0.6379
H	7.2363	2.1063	-1.5045
H	7.6780	2.2146	2.8077
H	8.3627	3.0092	0.5377
C	5.1683	-2.4105	0.6083
C	6.0016	-3.0265	1.5560
C	4.9771	-2.9407	-0.6742
C	6.6816	-4.1997	1.1890
H	6.1236	-2.6053	2.5596
C	5.6625	-4.1162	-1.0254
H	4.2984	-2.4358	-1.3687
C	6.5134	-4.7420	-0.0979
H	7.3380	-4.6925	1.9129
H	5.5276	-4.5437	-2.0240
H	7.0422	-5.6591	-0.3751
S	4.2291	-0.8979	1.0844
O	3.2288	-0.6501	-0.0969
H	1.5118	-0.1748	0.6276
H	1.2450	0.3193	-1.3857

Stationary point: TS2

	x	y	z

Mo	-1.4131	-0.9925	0.5822
Mo	-0.8611	1.6077	-0.2075
S	-2.9900	0.5616	-0.2972
Mo	-1.6153	-0.3303	-2.0204
Cl	-2.7327	1.2599	-3.6757
N	0.7022	3.3220	-0.0530
C	0.4082	4.3403	-1.1033
C	-1.0797	4.6452	-1.1059
N	-1.8806	3.3963	-1.2845
C	-3.3205	3.6946	-1.0321
C	2.1634	3.0525	0.0249
Cl	-1.6007	2.7968	1.9170
S	0.3898	1.0246	-2.1882
N	-1.0283	-1.2691	-4.0736
C	0.3904	-1.4897	-4.4643
N	-3.4055	-1.7074	-2.5255
C	-4.8043	-1.2446	-2.2962
C	-1.8289	-2.5124	-4.2690
C	-3.2809	-2.2387	-3.9180
N	-0.5328	-2.6089	2.0114
C	-0.5957	-2.1064	3.4157
C	-1.9586	-1.4906	3.6829
N	-2.2653	-0.4152	2.6921
C	-3.6833	0.0183	2.8438
Cl	-3.2968	-2.6842	0.6855
C	0.7725	-3.2725	1.7552
H	-1.4165	-0.5479	-4.7032
H	-3.2349	-2.4798	-1.8571
H	-1.2714	-3.3232	1.9045
H	-1.6834	0.4142	2.9040
H	0.4103	3.7194	0.8552
H	-1.8226	3.0970	-2.2741
H	0.9238	-0.5290	-4.4557
H	0.4483	-1.9305	-5.4757
H	0.8628	-2.1715	-3.7417
H	-1.3986	-3.2903	-3.6154
H	-1.7549	-2.8619	-5.3161
H	-3.6962	-1.4699	-4.5925
H	-3.8872	-3.1550	-4.0351
H	-4.9572	-1.0753	-1.2226
H	-5.5222	-2.0062	-2.6506
H	-4.9606	-0.3045	-2.8459
H	0.7676	-3.7140	0.7496
H	0.9602	-4.0600	2.5071
H	1.5748	-2.5228	1.8137
H	-0.4102	-2.9309	4.1296
H	0.2081	-1.3603	3.5373

H	-2.0039	-1.0921	4.7128
H	-2.7483	-2.2551	3.5821
H	-3.8367	0.9458	2.2772
H	-3.9183	0.1986	3.9087
H	-4.3398	-0.7716	2.4495
H	2.3677	2.3948	0.8808
H	2.7237	3.9972	0.1459
H	2.4950	2.5546	-0.8987
H	0.7369	3.9279	-2.0728
H	0.9830	5.2666	-0.9157
H	-1.3770	5.0817	-0.1366
H	-1.3241	5.3787	-1.8954
H	-3.9298	2.8536	-1.3884
H	-3.6213	4.6137	-1.5672
H	-3.4713	3.8281	0.0492
S	0.5883	0.2370	1.1492
S	-0.3232	-2.1172	-1.1743
C	5.4685	0.2112	0.6193
C	6.1203	0.4065	-0.6121
C	5.7502	1.0034	1.7466
C	7.0835	1.4206	-0.7055
H	5.8826	-0.2224	-1.4753
C	6.7229	2.0118	1.6364
H	5.2244	0.8342	2.6917
C	7.3849	2.2184	0.4154
H	7.6032	1.5866	-1.6539
H	6.9587	2.6335	2.5051
H	8.1416	3.0047	0.3335
C	4.9481	-2.4996	0.0738
C	5.9528	-3.1572	0.8046
C	4.4915	-2.9682	-1.1652
C	6.5290	-4.3130	0.2540
H	6.2847	-2.7815	1.7780
C	5.0803	-4.1279	-1.6991
H	3.6929	-2.4339	-1.6875
C	6.0946	-4.7962	-0.9937
H	7.3150	-4.8376	0.8055
H	4.7413	-4.5068	-2.6683
H	6.5462	-5.7001	-1.4135
S	4.1576	-1.0306	0.8211
O	3.0068	-0.6424	-0.2333
H	1.8222	-0.3061	0.3817
H	1.3698	0.1413	-1.7394

Stationary point: I2

	x	y	z

Mo	-1.4056	-0.8021	0.9847
Mo	-0.9024	1.7661	0.1299
S	-3.0250	0.7028	0.0904
Mo	-1.6782	-0.1880	-1.6519
Cl	-2.8689	1.3550	-3.3171
N	0.6552	3.4909	0.2447
C	0.3442	4.4928	-0.8159
C	-1.1447	4.7966	-0.8063
N	-1.9465	3.5462	-0.9581
C	-3.3837	3.8431	-0.6938
C	2.1174	3.2288	0.3090
Cl	-1.6452	3.0090	2.2438
S	0.3172	1.1514	-1.8508
N	-1.1261	-1.1555	-3.7010
C	0.2863	-1.3571	-4.1216
N	-3.4568	-1.6194	-2.0855
C	-4.8578	-1.1835	-1.8256
C	-1.9073	-2.4166	-3.8557
C	-3.3557	-2.1666	-3.4722
N	-0.4935	-2.3752	2.4391
C	-0.5319	-1.8345	3.8291
C	-1.8988	-1.2322	4.1088
N	-2.2492	-0.1980	3.0910
C	-3.6727	0.2087	3.2557
Cl	-3.2769	-2.5394	1.1589
C	0.8051	-3.0465	2.1770
H	-1.5438	-0.4512	-4.3309
H	-3.2505	-2.3768	-1.4113
H	-1.2366	-3.0892	2.3624
H	-1.6793	0.6503	3.2568
H	0.3694	3.8971	1.1508
H	-1.8983	3.2307	-1.9427
H	0.8032	-0.3875	-4.1372
H	0.3301	-1.8113	-5.1280
H	0.7868	-2.0203	-3.4003
H	-1.4454	-3.1751	-3.2003
H	-1.8523	-2.7831	-4.8984
H	-3.8020	-1.4157	-4.1473
H	-3.9456	-3.0968	-3.5647
H	-4.9825	-0.9970	-0.7512
H	-5.5702	-1.9660	-2.1450
H	-5.0507	-0.2573	-2.3872
H	0.7892	-3.4944	1.1742
H	0.9979	-3.8295	2.9328
H	1.6099	-2.2984	2.2262
H	-0.3184	-2.6348	4.5629
H	0.2624	-1.0729	3.9100

H	-1.9272	-0.8014	5.1265
H	-2.6757	-2.0144	4.0530
H	-3.8564	1.1152	2.6647
H	-3.8942	0.4157	4.3189
H	-4.3182	-0.6063	2.8957
H	2.3329	2.5831	1.1715
H	2.6773	4.1765	0.4085
H	2.4381	2.7174	-0.6115
H	0.6612	4.0663	-1.7834
H	0.9193	5.4236	-0.6508
H	-1.4307	5.2465	0.1603
H	-1.3968	5.5205	-1.6028
H	-3.9927	2.9935	-1.0298
H	-3.6961	4.7529	-1.2387
H	-3.5217	3.9916	0.3873
S	0.5800	0.4205	1.4272
S	-0.3591	-1.9428	-0.7886
C	5.5127	0.2172	1.1921
C	6.3611	0.4457	0.0895
C	5.5869	0.9891	2.3700
C	7.3088	1.4724	0.1836
H	6.2817	-0.1641	-0.8147
C	6.5476	2.0090	2.4437
H	4.9152	0.7910	3.2109
C	7.4030	2.2489	1.3550
H	7.9777	1.6668	-0.6597
H	6.6263	2.6124	3.3525
H	8.1505	3.0454	1.4176
C	5.0033	-2.4157	0.2965
C	6.2044	-2.9236	0.8248
C	4.3439	-3.0166	-0.7865
C	6.7660	-4.0613	0.2255
H	6.6983	-2.4453	1.6756
C	4.9292	-4.1515	-1.3734
H	3.4087	-2.5984	-1.1650
C	6.1322	-4.6727	-0.8703
H	7.7031	-4.4658	0.6187
H	4.4369	-4.6247	-2.2281
H	6.5784	-5.5582	-1.3325
S	4.2228	-1.0271	1.1682
O	3.1248	-0.5200	-0.0153
H	2.2368	-0.2889	0.4761
H	1.3022	0.2700	-1.3672

Stationary point: TS3

	x	y	z

Mo	-1.5683	-0.9948	0.7198
Mo	-0.8092	1.5399	-0.0489
S	-2.9653	0.6049	-0.3715
Mo	-1.4685	-0.3750	-1.9385
Cl	-2.3464	1.2233	-3.7326
N	0.8164	3.1612	0.2990
C	0.7316	4.1774	-0.7899
C	-0.7192	4.5772	-0.9971
N	-1.5699	3.3793	-1.2708
C	-3.0088	3.7686	-1.2169
C	2.2328	2.8065	0.5782
Cl	-1.7715	2.8429	1.9292
S	0.6047	0.8612	-1.8835
N	-0.7266	-1.3834	-3.9002
C	0.7153	-1.6612	-4.1396
N	-3.2586	-1.6983	-2.5842
C	-4.6518	-1.1735	-2.5063
C	-1.5500	-2.6016	-4.1500
C	-3.0191	-2.2713	-3.9441
N	-0.9077	-2.6167	2.2532
C	-1.1017	-2.0877	3.6359
C	-2.4586	-1.4103	3.7460
N	-2.6215	-0.3513	2.7057
C	-4.0297	0.1357	2.7013
Cl	-3.5432	-2.6161	0.6585
C	0.3979	-3.3195	2.1429
H	-1.0247	-0.6615	-4.5768
H	-3.1859	-2.4550	-1.8818
H	-1.6529	-3.3104	2.0788
H	-2.0299	0.4616	2.9507
H	0.4253	3.5877	1.1553
H	-1.3997	3.0601	-2.2404
H	1.2788	-0.7185	-4.0972
H	0.8613	-2.1302	-5.1294
H	1.0878	-2.3376	-3.3559
H	-1.2126	-3.3819	-3.4466
H	-1.3901	-2.9743	-5.1794
H	-3.3404	-1.5074	-4.6734
H	-3.6430	-3.1702	-4.0998
H	-4.8986	-0.9615	-1.4578
H	-5.3655	-1.9163	-2.9068
H	-4.7136	-0.2460	-3.0947
H	0.4676	-3.8079	1.1613
H	0.4992	-4.0775	2.9407
H	1.2119	-2.5854	2.2344
H	-1.0331	-2.9074	4.3758
H	-0.2821	-1.3770	3.8382

H	-2.5939	-0.9842	4.7571
H	-3.2639	-2.1468	3.5805
H	-4.0887	1.0540	2.1027
H	-4.3652	0.3506	3.7324
H	-4.6715	-0.6401	2.2579
H	2.2763	2.1557	1.4619
H	2.8311	3.7173	0.7612
H	2.6516	2.2677	-0.2847
H	1.1583	3.7264	-1.7022
H	1.3357	5.0689	-0.5360
H	-1.1143	5.0511	-0.0819
H	-0.8048	5.3106	-1.8198
H	-3.6151	2.9560	-1.6377
H	-3.1801	4.6907	-1.8020
H	-3.2926	3.9381	-0.1676
S	0.3885	0.1174	1.4293
S	-0.4027	-2.2059	-0.9203
C	5.4318	0.2343	0.4413
C	5.8934	0.5154	-0.8629
C	5.7053	1.0953	1.5267
C	6.6540	1.6729	-1.0691
H	5.6610	-0.1568	-1.6932
C	6.4717	2.2474	1.2979
H	5.3343	0.8611	2.5291
C	6.9448	2.5355	0.0059
H	7.0211	1.9034	-2.0736
H	6.7002	2.9173	2.1318
H	7.5421	3.4358	-0.1665
C	5.0938	-2.4903	-0.2214
C	6.4842	-2.7102	-0.1729
C	4.2308	-3.3436	-0.9302
C	7.0163	-3.8015	-0.8765
H	7.1417	-2.0455	0.3942
C	4.7862	-4.4296	-1.6271
H	3.1570	-3.1456	-0.9508
C	6.1716	-4.6593	-1.6019
H	8.0958	-3.9773	-0.8538
H	4.1272	-5.0941	-2.1939
H	6.5948	-5.5074	-2.1484
S	4.3971	-1.1734	0.8075
O	2.8912	-0.8839	-0.1324
H	2.1606	-0.6947	0.5509
H	1.5228	-0.0436	-1.3039

10.5.2 Optimized with PBE0 functional

Stationary point: H_2

	x	y	z
H	0.1401	2.5505	-0.0642
H	-0.6044	2.5505	-0.0642

Stationary point: H_2O

	x	y	z
O	-1.5085	2.5274	-0.0642
H	-0.5479	2.5790	-0.0642
H	-1.7805	3.4501	-0.0642

Stationary point: Diphenyl sulfoxide (1a)

	x	y	z
C	-5.3056	1.9529	1.3084
C	-4.2272	1.7371	0.4531
C	-3.1647	2.6355	0.4796
C	-3.1597	3.7476	1.3126
C	-4.2456	3.9549	2.1594
C	-5.3136	3.0577	2.1596
H	-6.1429	1.2616	1.3036
H	-4.2187	0.8835	-0.2199
H	-2.3148	4.4293	1.2769
H	-4.2588	4.8179	2.8186
H	-6.1593	3.2239	2.8202
S	-1.7428	2.3839	-0.6199
O	-0.9746	3.7078	-0.6134
C	-0.8229	1.2746	0.4830
C	-1.0613	-0.0958	0.4399
C	0.1226	1.8322	1.3353
C	-0.3429	-0.9260	1.2977
H	-1.7918	-0.5128	-0.2484
C	0.8376	0.9914	2.1840
H	0.2855	2.9059	1.3124
C	0.6024	-0.3835	2.1676
H	-0.5165	-1.9977	1.2797
H	1.5799	1.4091	2.8579
H	1.1635	-1.0360	2.8299

Stationary point: Diphenyl sulfide (2a)

	x	y	z
C	-4.9007	1.9405	0.2708
C	-3.5197	2.0879	0.3455
C	-2.9699	3.0487	1.2004
C	-3.8067	3.8658	1.9640

C	-5.1899	3.7264	1.8643
C	-5.7400	2.7616	1.0243
H	-5.3229	1.1878	-0.3888
H	-2.8663	1.4564	-0.2489
H	-3.3773	4.6005	2.6390
H	-5.8359	4.3653	2.4595
H	-6.8178	2.6470	0.9573
S	-1.2053	3.3218	1.2905
C	-0.5619	1.6553	1.3625
C	-1.1099	0.6970	2.2214
C	0.5515	1.3389	0.5809
C	-0.5507	-0.5749	2.2823
H	-1.9738	0.9479	2.8295
C	1.1194	0.0688	0.6666
H	0.9654	2.0797	-0.0970
C	0.5679	-0.8916	1.5107
H	-0.9841	-1.3184	2.9450
H	1.9861	-0.1717	0.0577
H	1.0051	-1.8840	1.5671

Stationary point: Cluster 5^{+}

	x	y	z
S	-0.2049	-2.0358	-0.1943
Mo	-1.3703	-0.3988	0.9420
S	0.3216	1.1421	1.0899
Mo	-0.9237	1.7029	-0.7711
S	-2.9147	0.4683	-0.6003
Mo	-1.3412	-0.8217	-1.7734
Cl	-2.5569	-0.1778	-3.8730
N	0.4996	3.4471	-1.1128
C	0.2243	4.0438	-2.4367
C	-1.2640	4.1793	-2.6408
N	-1.9317	2.8714	-2.4774
C	-3.3974	3.0373	-2.5098
C	1.9508	3.2876	-0.9087
Cl	-2.0633	3.4996	0.5609
S	0.3609	0.6314	-2.3394
N	-0.4598	-2.3179	-3.2461
C	0.9991	-2.5012	-3.3520
N	-2.9252	-2.4894	-1.8310
C	-4.3633	-2.1594	-1.8141
C	-1.1361	-3.6210	-3.0750
C	-2.6246	-3.4146	-2.9433
N	-0.5013	-1.2173	2.8811
C	-0.8051	-0.2786	3.9816
C	-2.2385	0.1809	3.8846

N	-2.5044	0.7800	2.5602
C	-3.9434	1.0694	2.4100
Cl	-3.1158	-2.0947	1.5538
C	0.9031	-1.6598	2.9503
H	-0.7847	-1.9192	-4.1287
H	-2.7327	-2.9699	-0.9496
H	-1.0904	-2.0416	3.0122
H	-2.0254	1.6817	2.5108
H	0.1595	4.1022	-0.4066
H	-1.6925	2.2841	-3.2791
H	1.4707	-1.5516	-3.6040
H	1.2340	-3.2381	-4.1275
H	1.3932	-2.8497	-2.3956
H	-0.7247	-4.0961	-2.1784
H	-0.9231	-4.2754	-3.9286
H	-3.0292	-2.9666	-3.8558
H	-3.1284	-4.3749	-2.7859
H	-4.6100	-1.6851	-0.8647
H	-4.9593	-3.0724	-1.9219
H	-4.5842	-1.4782	-2.6368
H	1.0771	-2.4446	2.2144
H	1.1309	-2.0453	3.9499
H	1.5620	-0.8173	2.7322
H	-0.6309	-0.7598	4.9513
H	-0.1152	0.5676	3.8998
H	-2.4607	0.9018	4.6794
H	-2.9189	-0.6683	3.9988
H	-4.0895	1.7196	1.5480
H	-4.3196	1.5754	3.3060
H	-4.4837	0.1333	2.2636
H	2.1442	2.9679	0.1150
H	2.4669	4.2357	-1.0944
H	2.3344	2.5302	-1.5948
H	0.6656	3.3903	-3.1961
H	0.7047	5.0260	-2.5191
H	-1.6908	4.8568	-1.8950
H	-1.4749	4.5926	-3.6335
H	-3.8654	2.0611	-2.6324
H	-3.6838	3.6785	-3.3506
H	-3.7269	3.4909	-1.5742

Stationary point: TS1

	x	y	z
Mo	-1.4172	-0.4072	0.9192
Mo	-0.9475	1.6740	-0.7949
S	-2.9682	0.4805	-0.5993

Mo	-1.3667	-0.7698	-1.7850
Cl	-2.5600	-0.1393	-3.8747
N	0.5029	3.4121	-1.1331
C	0.2251	4.0054	-2.4560
C	-1.2635	4.1599	-2.6380
N	-1.9464	2.8602	-2.4641
C	-3.4092	3.0537	-2.4652
C	1.9534	3.2574	-0.9264
Cl	-1.9677	3.4557	0.6391
S	0.4359	0.5894	-2.2763
N	-0.4678	-2.2814	-3.2555
C	0.9895	-2.4390	-3.4046
N	-2.9069	-2.4770	-1.7959
C	-4.3505	-2.1700	-1.7892
C	-1.1067	-3.5943	-3.0342
C	-2.5970	-3.4193	-2.8906
N	-0.5535	-1.2304	2.8793
C	-0.8265	-0.2641	3.9613
C	-2.2551	0.2062	3.8667
N	-2.5200	0.7901	2.5365
C	-3.9622	1.0641	2.3874
Cl	-3.1052	-2.1688	1.5137
C	0.8320	-1.7239	2.9638
H	-0.8269	-1.9107	-4.1369
H	-2.7128	-2.9375	-0.9025
H	-1.1726	-2.0312	3.0196
H	-2.0501	1.6963	2.4794
H	0.1629	4.0677	-0.4273
H	-1.7303	2.2696	-3.2715
H	1.4339	-1.4902	-3.7039
H	1.2138	-3.1975	-4.1624
H	1.4233	-2.7487	-2.4517
H	-0.6726	-4.0296	-2.1279
H	-0.8872	-4.2719	-3.8679
H	-3.0193	-2.9993	-3.8091
H	-3.0788	-4.3868	-2.7095
H	-4.6092	-1.6843	-0.8494
H	-4.9327	-3.0933	-1.8856
H	-4.5771	-1.5047	-2.6238
H	0.9771	-2.5378	2.2534
H	1.0446	-2.0891	3.9742
H	1.5262	-0.9148	2.7274
H	-0.6456	-0.7246	4.9399
H	-0.1276	0.5718	3.8507
H	-2.4707	0.9364	4.6550
H	-2.9400	-0.6384	3.9933
H	-4.1157	1.7210	1.5319

H	-4.3485	1.5555	3.2875
H	-4.4903	0.1227	2.2281
H	2.1459	2.9511	0.1018
H	2.4680	4.2046	-1.1212
H	2.3405	2.4935	-1.6030
H	0.6465	3.3406	-3.2170
H	0.7173	4.9807	-2.5505
H	-1.6700	4.8417	-1.8842
H	-1.4869	4.5768	-3.6263
H	-3.8988	2.0891	-2.5931
H	-3.7003	3.7149	-3.2887
H	-3.7100	3.4970	-1.5146
S	0.4215	0.9909	1.0018
H	1.4050	-0.0053	0.1447
S	-0.0687	-1.9257	-0.1964
H	1.2490	-0.9471	-0.2501

Stationary point: I1

	x	y	z
Mo	-0.0820	-0.5818	1.4698
Mo	0.3830	1.4882	-0.2513
S	-1.6393	0.3030	-0.0373
Mo	-0.0322	-0.9355	-1.2243
Cl	-1.2145	-0.2740	-3.3075
N	1.8243	3.2390	-0.6138
C	1.5370	3.8050	-1.9452
C	0.0468	3.9512	-2.1146
N	-0.6315	2.6530	-1.9112
C	-2.0934	2.8513	-1.8952
C	3.2765	3.1114	-0.4054
Cl	-0.6067	3.2661	1.2065
S	1.8189	0.3897	-1.6928
N	0.8510	-2.4411	-2.7247
C	2.3033	-2.6187	-2.8915
N	-1.5787	-2.6382	-1.2517
C	-3.0203	-2.3228	-1.2259
C	0.1964	-3.7499	-2.5297
C	-1.2897	-3.5595	-2.3699
N	0.7685	-1.4005	3.4465
C	0.4745	-0.4384	4.5256
C	-0.9529	0.0264	4.4034
N	-1.1917	0.6177	3.0709
C	-2.6338	0.8840	2.9039
Cl	-1.7315	-2.3852	2.0290
C	2.1536	-1.8890	3.5542
H	0.4915	-2.0455	-3.5950

H	-1.3827	-3.1221	-0.3704
H	0.1505	-2.2040	3.5756
H	-0.7293	1.5292	3.0339
H	1.4752	3.9010	0.0816
H	-0.4260	2.0482	-2.7124
H	2.7636	-1.6668	-3.1544
H	2.5085	-3.3505	-3.6805
H	2.7382	-2.9774	-1.9566
H	0.6307	-4.2115	-1.6367
H	0.4004	-4.4111	-3.3805
H	-1.7147	-3.1138	-3.2750
H	-1.7824	-4.5247	-2.2065
H	-3.2685	-1.8555	-0.2742
H	-3.6095	-3.2400	-1.3374
H	-3.2489	-1.6384	-2.0445
H	2.3149	-2.7001	2.8443
H	2.3500	-2.2569	4.5671
H	2.8491	-1.0766	3.3339
H	0.6388	-0.9000	5.5067
H	1.1722	0.4004	4.4299
H	-1.1893	0.7507	5.1911
H	-1.6364	-0.8222	4.5097
H	-2.7803	1.5517	2.0557
H	-3.0378	1.3595	3.8049
H	-3.1517	-0.0595	2.7233
H	3.4745	2.8344	0.6301
H	3.7764	4.0619	-0.6222
H	3.6747	2.3381	-1.0646
H	1.9532	3.1250	-2.6957
H	2.0246	4.7802	-2.0634
H	-0.3535	4.6448	-1.3679
H	-0.1899	4.3502	-3.1071
H	-2.5891	1.8884	-2.0085
H	-2.3928	3.5068	-2.7202
H	-2.3794	3.3038	-0.9440
S	1.7806	0.8904	1.6215
H	2.8016	0.2221	0.9807
S	1.2612	-2.2059	0.3696
H	2.4952	-1.6142	0.2053

Stationary point: RC1

	x	y	z
Mo	-1.7080	-0.8445	1.1952
Mo	-0.6391	1.5604	0.5274
S	-2.7305	0.7786	-0.1681
Mo	-1.0570	-0.4048	-1.3251

Cl	-1.4306	1.1460	-3.2672
N	1.0016	3.0645	1.1061
C	1.1630	4.0392	0.0120
C	-0.1967	4.4945	-0.4479
N	-1.0133	3.3379	-0.8665
C	-2.3989	3.7802	-1.1120
C	2.3169	2.6231	1.5945
Cl	-1.8114	2.9654	2.2544
S	1.0404	0.7363	-0.9610
N	-0.0165	-1.5282	-3.0410
C	1.3856	-1.9617	-2.9497
N	-2.7520	-1.5747	-2.2861
C	-4.0767	-0.9532	-2.4697
C	-0.8778	-2.6533	-3.4493
C	-2.3042	-2.1796	-3.5579
N	-1.4581	-2.4160	2.8602
C	-1.9045	-1.8317	4.1400
C	-3.1926	-1.0762	3.9375
N	-3.0316	-0.0409	2.8968
C	-4.3414	0.5640	2.5893
Cl	-3.7043	-2.2901	0.7867
C	-0.1979	-3.1535	3.0495
H	-0.0712	-0.8174	-3.7729
H	-2.8695	-2.3187	-1.5916
H	-2.1664	-3.0911	2.5677
H	-2.4529	0.7157	3.2733
H	0.5289	3.5413	1.8761
H	-0.6584	2.9987	-1.7636
H	2.0256	-1.1002	-2.7611
H	1.7004	-2.4456	-3.8812
H	1.4897	-2.6685	-2.1265
H	-0.7814	-3.4394	-2.6931
H	-0.5461	-3.0653	-4.4103
H	-2.3884	-1.4070	-4.3291
H	-2.9640	-3.0087	-3.8371
H	-4.5162	-0.7482	-1.4947
H	-4.7365	-1.6291	-3.0249
H	-3.9568	-0.0201	-3.0232
H	0.0591	-3.6847	2.1337
H	-0.2963	-3.8720	3.8710
H	0.6045	-2.4522	3.2865
H	-2.0453	-2.6174	4.8924
H	-1.1130	-1.1643	4.4964
H	-3.5203	-0.6228	4.8801
H	-3.9814	-1.7556	3.5988
H	-4.1888	1.4765	2.0150
H	-4.8717	0.8095	3.5167

H	-4.9315	-0.1453	2.0066
H	2.1944	2.0014	2.4812
H	2.9422	3.4869	1.8452
H	2.8171	2.0436	0.8180
H	1.7114	3.5471	-0.7985
H	1.7574	4.8983	0.3465
H	-0.7262	4.9849	0.3757
H	-0.1054	5.2167	-1.2674
H	-2.9309	3.0065	-1.6643
H	-2.4043	4.7053	-1.7003
H	-2.8921	3.9521	-0.1536
S	0.1780	0.1857	2.3000
S	-0.3234	-2.2070	-0.0819
C	4.9303	0.4289	0.3974
C	4.5935	0.7825	-0.9100
C	5.5421	1.3327	1.2630
C	4.8699	2.0721	-1.3496
H	4.1284	0.0591	-1.5724
C	5.8250	2.6197	0.8069
H	5.7886	1.0392	2.2795
C	5.4835	2.9883	-0.4919
H	4.6109	2.3624	-2.3633
H	6.3039	3.3332	1.4700
H	5.6982	3.9933	-0.8421
C	5.0139	-2.2332	-0.2682
C	6.3513	-2.2341	-0.6607
C	4.0765	-3.0793	-0.8472
C	6.7454	-3.0951	-1.6801
H	7.0696	-1.5645	-0.1956
C	4.4855	-3.9352	-1.8693
H	3.0489	-3.0491	-0.4983
C	5.8147	-3.9417	-2.2850
H	7.7812	-3.1020	-2.0054
H	3.7627	-4.5966	-2.3380
H	6.1302	-4.6092	-3.0811
S	4.4590	-1.1687	1.0839
O	2.9121	-1.2440	1.0208
H	1.2518	-0.5168	1.8070
H	1.7695	-0.1788	-0.2270

Stationary point: TS2

	x	y	z
Mo	-1.4712	-1.0180	0.6931
Mo	-0.6669	1.5229	0.0815
S	-2.7946	0.6406	-0.3361
Mo	-1.2355	-0.2648	-1.8443

Cl	-2.0434	1.3855	-3.5709
N	0.9412	3.1010	0.5535
C	0.8632	4.1766	-0.4504
C	-0.5791	4.5628	-0.6519
N	-1.3784	3.3873	-1.0463
C	-2.8101	3.7382	-1.0298
C	2.3403	2.7253	0.8006
Cl	-1.6535	2.6949	2.1005
S	0.8254	0.9693	-1.7032
N	-0.3745	-1.1563	-3.7901
C	1.0559	-1.4712	-3.9333
N	-2.9613	-1.5323	-2.6457
C	-4.3459	-1.0340	-2.5745
C	-1.2005	-2.3158	-4.1725
C	-2.6605	-1.9704	-4.0238
N	-0.8768	-2.7067	2.1409
C	-1.1222	-2.2575	3.5246
C	-2.4609	-1.5693	3.6125
N	-2.5407	-0.4480	2.6567
C	-3.9126	0.0887	2.6298
Cl	-3.4422	-2.5527	0.4916
C	0.4246	-3.3871	2.0487
H	-0.5891	-0.3974	-4.4392
H	-2.9032	-2.3430	-2.0242
H	-1.5981	-3.3914	1.9088
H	-1.9370	0.3113	2.9841
H	0.5597	3.4661	1.4282
H	-1.1544	3.1483	-2.0154
H	1.6452	-0.5629	-3.8049
H	1.2591	-1.8928	-4.9245
H	1.3477	-2.1936	-3.1684
H	-0.9279	-3.1499	-3.5174
H	-0.9918	-2.6157	-5.2071
H	-2.9210	-1.1416	-4.6901
H	-3.2847	-2.8296	-4.2957
H	-4.6432	-0.9479	-1.5305
H	-5.0263	-1.7258	-3.0849
H	-4.3941	-0.0536	-3.0521
H	0.5342	-3.8363	1.0621
H	0.5031	-4.1670	2.8149
H	1.2268	-2.6618	2.1910
H	-1.0957	-3.1095	4.2154
H	-0.3133	-1.5733	3.7997
H	-2.6387	-1.2152	4.6350
H	-3.2624	-2.2698	3.3560
H	-3.9119	1.0463	2.1115
H	-4.2839	0.2347	3.6511

H	-4.5589	-0.6157	2.1032
H	2.3871	2.0285	1.6374
H	2.9432	3.6102	1.0354
H	2.7542	2.2452	-0.0883
H	1.3049	3.8015	-1.3800
H	1.4463	5.0487	-0.1292
H	-0.9997	4.9404	0.2861
H	-0.6642	5.3572	-1.4029
H	-3.3725	2.9733	-1.5640
H	-2.9715	4.7065	-1.5186
H	-3.1511	3.7879	0.0058
S	0.4717	0.0535	1.5865
S	-0.2377	-2.1473	-0.9028
C	4.8267	0.2326	-0.0168
C	4.6809	0.2942	-1.4028
C	5.4495	1.2415	0.7124
C	5.1766	1.4069	-2.0710
H	4.1849	-0.5080	-1.9415
C	5.9496	2.3470	0.0251
H	5.5331	1.1745	1.7930
C	5.8083	2.4297	-1.3577
H	5.0728	1.4771	-3.1492
H	6.4376	3.1455	0.5744
H	6.1923	3.2959	-1.8875
C	4.9170	-2.5361	0.1630
C	6.2301	-2.8018	0.5463
C	4.2266	-3.3315	-0.7452
C	6.8747	-3.8962	-0.0221
H	6.7448	-2.1714	1.2661
C	4.8893	-4.4248	-1.2997
H	3.1979	-3.0985	-1.0003
C	6.2066	-4.7040	-0.9426
H	7.8988	-4.1196	0.2596
H	4.3699	-5.0585	-2.0119
H	6.7153	-5.5581	-1.3787
S	4.0925	-1.1190	0.9000
O	2.6377	-1.2479	0.2732
H	1.7074	-0.6802	0.8975
H	1.6751	0.0291	-1.1793

Stationary point: I2

	x	y	z
Mo	-1.5416	-0.8161	0.9192
Mo	-0.7500	1.7141	0.3184
S	-2.9031	0.8614	-0.0313
Mo	-1.4163	0.0058	-1.6323

Cl	-2.2999	1.7062	-3.2871
N	0.8864	3.2652	0.7766
C	0.7890	4.3633	-0.2000
C	-0.6538	4.7766	-0.3401
N	-1.4875	3.6233	-0.7261
C	-2.9118	3.9916	-0.6453
C	2.2861	2.8699	0.9794
Cl	-1.6688	2.8606	2.4025
S	0.6676	1.1853	-1.5296
N	-0.6620	-0.8447	-3.6415
C	0.7585	-1.1539	-3.8656
N	-3.1874	-1.2490	-2.3745
C	-4.5648	-0.7497	-2.2262
C	-1.5058	-1.9974	-4.0032
C	-2.9562	-1.6555	-3.7741
N	-0.9175	-2.5394	2.3123
C	-1.1162	-2.1167	3.7113
C	-2.4503	-1.4292	3.8570
N	-2.5611	-0.2935	2.9234
C	-3.9303	0.2474	2.9525
Cl	-3.5378	-2.3584	0.7546
C	0.3681	-3.2369	2.1709
H	-0.9126	-0.0722	-4.2610
H	-3.1010	-2.0724	-1.7742
H	-1.6565	-3.2063	2.0835
H	-1.9399	0.4584	3.2345
H	0.5306	3.6127	1.6692
H	-1.3068	3.3996	-1.7078
H	1.3524	-0.2472	-3.7490
H	0.9111	-1.5558	-4.8741
H	1.0894	-1.8905	-3.1306
H	-1.2006	-2.8429	-3.3777
H	-1.3494	-2.2782	-5.0525
H	-3.2467	-0.8111	-4.4081
H	-3.5944	-2.5077	-4.0369
H	-4.8120	-0.6884	-1.1675
H	-5.2723	-1.4262	-2.7206
H	-4.6321	0.2427	-2.6762
H	0.4751	-3.6076	1.1516
H	0.4311	-4.0751	2.8747
H	1.1797	-2.5386	2.3803
H	-1.0668	-2.9805	4.3862
H	-0.2982	-1.4367	3.9706
H	-2.5923	-1.0927	4.8911
H	-3.2609	-2.1249	3.6165
H	-3.9425	1.2155	2.4543
H	-4.2685	0.3731	3.9881

H	-4.5957	-0.4437	2.4320
H	2.3452	2.1609	1.8046
H	2.9076	3.7435	1.2089
H	2.6693	2.3934	0.0745
H	1.1907	4.0024	-1.1532
H	1.3967	5.2202	0.1178
H	-1.0321	5.1421	0.6206
H	-0.7527	5.5881	-1.0711
H	-3.5044	3.2421	-1.1687
H	-3.0812	4.9703	-1.1106
H	-3.2100	4.0269	0.4041
S	0.4340	0.1936	1.6995
S	-0.3968	-1.9132	-0.7740
C	4.7505	0.3085	0.4191
C	4.7461	0.3933	-0.9742
C	5.2757	1.3100	1.2334
C	5.2885	1.5286	-1.5623
H	4.3158	-0.4011	-1.5755
C	5.8290	2.4335	0.6228
H	5.2484	1.2206	2.3151
C	5.8289	2.5422	-0.7657
H	5.2923	1.6231	-2.6433
H	6.2462	3.2260	1.2350
H	6.2509	3.4250	-1.2355
C	4.9645	-2.4696	0.6702
C	6.3327	-2.3137	0.4606
C	4.3245	-3.7029	0.5516
C	7.0760	-3.4340	0.0989
H	6.8109	-1.3450	0.5621
C	5.0865	-4.8064	0.1813
H	3.2571	-3.7954	0.7184
C	6.4561	-4.6735	-0.0425
H	8.1415	-3.3303	-0.0779
H	4.6037	-5.7716	0.0672
H	7.0424	-5.5403	-0.3302
S	3.9905	-1.0766	1.2332
O	2.6520	-1.3645	0.3418
H	1.8644	-0.8776	0.7843
H	1.5159	0.2187	-1.0393

Stationary point: TS3

	x	y	z
Mo	-1.5067	-0.9649	0.8775
Mo	-0.6010	1.4663	0.0722
S	-2.7151	0.5826	-0.4334
Mo	-1.0867	-0.4876	-1.7425

Cl	-1.7606	0.9938	-3.6718
N	1.0355	3.0103	0.5349
C	1.0783	3.9989	-0.5582
C	-0.3252	4.4155	-0.9186
N	-1.1385	3.2394	-1.2830
C	-2.5495	3.6349	-1.4419
C	2.3975	2.5998	0.9123
Cl	-1.7422	2.8879	1.8341
S	0.9535	0.7040	-1.5426
N	-0.1282	-1.5807	-3.5255
C	1.3036	-1.9202	-3.5391
N	-2.7879	-1.8092	-2.5277
C	-4.1621	-1.2828	-2.5997
C	-0.9459	-2.7661	-3.8424
C	-2.4068	-2.3924	-3.8291
N	-1.0492	-2.4971	2.5221
C	-1.4167	-1.9181	3.8289
C	-2.7573	-1.2334	3.7315
N	-2.7488	-0.2123	2.6668
C	-4.1067	0.3223	2.4666
Cl	-3.4855	-2.5203	0.6670
C	0.2572	-3.1685	2.6078
H	-0.2895	-0.8896	-4.2602
H	-2.7919	-2.5510	-1.8238
H	-1.7472	-3.2068	2.2934
H	-2.1647	0.5734	2.9639
H	0.6132	3.4655	1.3461
H	-0.8322	2.8994	-2.1976
H	1.8976	-1.0105	-3.4492
H	1.5693	-2.4326	-4.4709
H	1.5306	-2.5724	-2.6944
H	-0.7309	-3.5310	-3.0888
H	-0.6729	-3.1726	-4.8243
H	-2.6078	-1.6350	-4.5939
H	-3.0265	-3.2688	-4.0527
H	-4.5225	-1.0842	-1.5912
H	-4.8249	-2.0123	-3.0799
H	-4.1575	-0.3565	-3.1769
H	0.4658	-3.6861	1.6716
H	0.2645	-3.8901	3.4328
H	1.0361	-2.4230	2.7791
H	-1.4524	-2.6990	4.5988
H	-0.6346	-1.2045	4.1078
H	-3.0230	-0.7819	4.6947
H	-3.5348	-1.9603	3.4753
H	-4.0486	1.2270	1.8630
H	-4.5663	0.5646	3.4321

H	-4.7108	-0.4264	1.9513
H	2.3580	1.9699	1.8007
H	3.0208	3.4774	1.1187
H	2.8498	2.0307	0.0979
H	1.5804	3.5312	-1.4119
H	1.6667	4.8763	-0.2618
H	-0.8089	4.8887	-0.0578
H	-0.3099	5.1427	-1.7391
H	-3.0904	2.8324	-1.9422
H	-2.6241	4.5474	-2.0453
H	-2.9818	3.8102	-0.4554
S	0.3461	0.1394	1.7477
S	-0.2232	-2.2694	-0.5428
C	5.1874	0.1501	0.4312
C	5.2603	0.6318	-0.8812
C	5.5967	0.9285	1.5191
C	5.7688	1.9058	-1.0978
H	4.9177	0.0227	-1.7114
C	6.0971	2.2050	1.2821
H	5.5234	0.5424	2.5313
C	6.1846	2.6924	-0.0209
H	5.8338	2.2896	-2.1111
H	6.4196	2.8169	2.1182
H	6.5763	3.6887	-0.2000
C	4.8713	-2.4647	-0.5414
C	6.1901	-2.4911	-0.9997
C	3.9025	-3.3344	-1.0460
C	6.5328	-3.3945	-2.0009
H	6.9339	-1.8141	-0.5918
C	4.2678	-4.2348	-2.0428
H	2.8811	-3.2804	-0.6844
C	5.5762	-4.2646	-2.5218
H	7.5525	-3.4157	-2.3720
H	3.5203	-4.9083	-2.4508
H	5.8512	-4.9655	-3.3037
S	4.4309	-1.3936	0.8130
O	2.6981	-1.0091	0.1382
H	2.1058	-0.9012	0.9247
H	1.8172	-0.2074	-0.8211

Stationary point: ^{3}TS1

	x	y	z
Mo	-1.4007	-0.3824	0.8979
Mo	-0.9722	1.8095	-0.7099
S	-2.9609	0.5004	-0.6691
Mo	-1.4123	-0.8683	-1.8093

Cl	-2.6432	-0.2261	-3.9094
N	0.5387	3.4643	-1.1253
C	0.2371	4.0670	-2.4419
C	-1.2523	4.2580	-2.5898
N	-1.9615	2.9726	-2.4201
C	-3.4200	3.1938	-2.4072
C	1.9867	3.2275	-0.9764
Cl	-1.9139	3.5506	0.7286
S	0.2487	0.6455	-2.3191
N	-0.4917	-2.3488	-3.2620
C	0.9735	-2.4406	-3.4041
N	-2.8910	-2.6045	-1.8003
C	-4.3365	-2.2979	-1.7940
C	-1.0787	-3.6858	-3.0343
C	-2.5730	-3.5523	-2.8875
N	-0.5651	-1.2259	2.8610
C	-0.8637	-0.2806	3.9556
C	-2.2900	0.1931	3.8420
N	-2.5212	0.8060	2.5187
C	-3.9547	1.1052	2.3408
Cl	-3.1299	-2.1174	1.4949
C	0.8231	-1.7084	2.9628
H	-0.8664	-1.9961	-4.1454
H	-2.6905	-3.0539	-0.9029
H	-1.1801	-2.0334	2.9772
H	-2.0353	1.7048	2.4944
H	0.2698	4.1433	-0.4120
H	-1.7621	2.3844	-3.2309
H	1.3748	-1.4707	-3.6979
H	1.2329	-3.1852	-4.1640
H	1.4146	-2.7332	-2.4495
H	-0.6278	-4.0992	-2.1262
H	-0.8354	-4.3552	-3.8675
H	-3.0091	-3.1488	-3.8069
H	-3.0318	-4.5279	-2.6926
H	-4.5862	-1.7712	-0.8739
H	-4.9160	-3.2263	-1.8435
H	-4.5706	-1.6708	-2.6550
H	0.9876	-2.5103	2.2432
H	1.0204	-2.0860	3.9718
H	1.5128	-0.8895	2.7487
H	-0.7019	-0.7602	4.9282
H	-0.1638	0.5579	3.8746
H	-2.5192	0.9093	4.6393
H	-2.9801	-0.6509	3.9369
H	-4.0802	1.7730	1.4888
H	-4.3528	1.5944	3.2368

H	-4.4946	0.1742	2.1615
H	2.2013	2.9144	0.0451
H	2.5450	4.1429	-1.1995
H	2.3000	2.4392	-1.6631
H	0.6234	3.3932	-3.2136
H	0.7526	5.0287	-2.5464
H	-1.6267	4.9401	-1.8197
H	-1.4820	4.6963	-3.5676
H	-3.9280	2.2389	-2.5406
H	-3.7087	3.8685	-3.2207
H	-3.7094	3.6318	-1.4504
S	0.4140	1.0132	1.0486
H	1.4759	-0.0753	0.1308
S	-0.0984	-1.9572	-0.1730
H	1.3306	-0.9237	-0.2067

Stationary point: ^{3}I1

	x	y	z
Mo	-0.0904	-0.6182	1.5224
Mo	0.3864	1.5799	-0.2262
S	-1.5961	0.3076	-0.0275
Mo	-0.0138	-0.9611	-1.2295
Cl	-1.2723	-0.3142	-3.2770
N	1.8139	3.3117	-0.6361
C	1.5331	3.8403	-1.9840
C	0.0423	3.9733	-2.1599
N	-0.6238	2.6723	-1.9419
C	-2.0859	2.8649	-1.9071
C	3.2632	3.1640	-0.4212
Cl	-0.5735	3.3376	1.2870
S	1.7412	0.3986	-1.7294
N	0.8586	-2.4373	-2.7563
C	2.3121	-2.6137	-2.9157
N	-1.5540	-2.6878	-1.2581
C	-2.9956	-2.3739	-1.1992
C	0.2028	-3.7521	-2.6019
C	-1.2813	-3.5721	-2.4098
N	0.7491	-1.4333	3.4949
C	0.4636	-0.4590	4.5661
C	-0.9518	0.0374	4.4257
N	-1.1640	0.6331	3.0885
C	-2.5991	0.9322	2.9063
Cl	-1.7404	-2.3903	2.0370
C	2.1357	-1.9195	3.5953
H	0.5055	-2.0190	-3.6187
H	-1.3460	-3.2044	-0.4006

H	0.1337	-2.2360	3.6391
H	-0.6839	1.5362	3.0535
H	1.4727	3.9979	0.0397
H	-0.4237	2.0663	-2.7409
H	2.7796	-1.6531	-3.1303
H	2.5243	-3.3117	-3.7331
H	2.7350	-3.0158	-1.9930
H	0.6506	-4.2486	-1.7349
H	0.3932	-4.3796	-3.4809
H	-1.7238	-3.1005	-3.2925
H	-1.7665	-4.5447	-2.2683
H	-3.2219	-1.9029	-0.2441
H	-3.5859	-3.2923	-1.2959
H	-3.2430	-1.6916	-2.0136
H	2.2919	-2.7359	2.8903
H	2.3418	-2.2796	4.6092
H	2.8275	-1.1074	3.3635
H	0.6072	-0.9176	5.5518
H	1.1791	0.3645	4.4717
H	-1.1815	0.7692	5.2083
H	-1.6561	-0.7950	4.5254
H	-2.7217	1.5926	2.0490
H	-2.9955	1.4285	3.7992
H	-3.1389	-0.0006	2.7345
H	3.4538	2.9167	0.6233
H	3.7840	4.0956	-0.6698
H	3.6452	2.3599	-1.0529
H	1.9539	3.1403	-2.7137
H	2.0192	4.8131	-2.1279
H	-0.3616	4.6719	-1.4192
H	-0.1958	4.3639	-3.1559
H	-2.5786	1.8974	-1.9942
H	-2.4054	3.5050	-2.7376
H	-2.3600	3.3307	-0.9587
S	1.7663	0.9428	1.6818
H	2.7790	0.2254	1.1396
S	1.1635	-2.3631	0.3905
H	2.4225	-1.8973	0.2294

Stationary point: ^{3}I2

	x	y	z
Mo	-1.5335	-0.8642	1.1270
Mo	-0.7081	1.7454	0.4241
S	-2.7917	0.7568	-0.0416
Mo	-1.1948	-0.1671	-1.5148
Cl	-1.9609	1.4769	-3.2886

N	0.8519	3.3499	0.9312
C	0.7815	4.4362	-0.0630
C	-0.6612	4.7749	-0.3381
N	-1.3952	3.5754	-0.7852
C	-2.8374	3.8742	-0.8610
C	2.2510	2.9894	1.1997
Cl	-1.8375	2.9320	2.3490
S	0.7747	1.2625	-1.4398
N	-0.2926	-1.0882	-3.4134
C	1.1410	-1.4071	-3.5030
N	-2.9132	-1.4085	-2.3409
C	-4.2917	-0.8895	-2.3222
C	-1.1139	-2.2518	-3.7939
C	-2.5758	-1.8922	-3.6952
N	-0.9535	-2.5085	2.6091
C	-1.2406	-2.0376	3.9760
C	-2.5972	-1.3793	4.0045
N	-2.6564	-0.2738	3.0311
C	-4.0385	0.2207	2.9182
Cl	-3.4361	-2.5327	0.7570
C	0.3699	-3.1458	2.5471
H	-0.4859	-0.3415	-4.0830
H	-2.8919	-2.1957	-1.6869
H	-1.6516	-3.2154	2.3715
H	-2.0840	0.5005	3.3739
H	0.4480	3.7004	1.8018
H	-1.1021	3.3503	-1.7384
H	1.7267	-0.4970	-3.3699
H	1.3783	-1.8453	-4.4793
H	1.4060	-2.1158	-2.7160
H	-0.8659	-3.0729	-3.1137
H	-0.8783	-2.5754	-4.8156
H	-2.8116	-1.0825	-4.3938
H	-3.1991	-2.7550	-3.9573
H	-4.6164	-0.7787	-1.2886
H	-4.9642	-1.5859	-2.8367
H	-4.3152	0.0805	-2.8220
H	0.5134	-3.5971	1.5654
H	0.4656	-3.9172	3.3205
H	1.1401	-2.3877	2.7002
H	-1.2104	-2.8715	4.6890
H	-0.4568	-1.3242	4.2516
H	-2.8284	-1.0212	5.0153
H	-3.3694	-2.1025	3.7201
H	-4.0359	1.1677	2.3800
H	-4.4762	0.3737	3.9125
H	-4.6317	-0.5116	2.3667

H	2.2895	2.2675	2.0152
H	2.8364	3.8762	1.4698
H	2.6900	2.5408	0.3059
H	1.2811	4.0889	-0.9739
H	1.3169	5.3245	0.2951
H	-1.1454	5.1273	0.5784
H	-0.7323	5.5733	-1.0866
H	-3.3396	3.0735	-1.4018
H	-3.0029	4.8232	-1.3852
H	-3.2385	3.9398	0.1519
S	0.3712	0.3090	1.9892
S	-0.2588	-1.9713	-0.5153
C	4.7834	0.4138	0.3524
C	4.7790	0.5232	-1.0401
C	5.3240	1.3958	1.1805
C	5.3356	1.6599	-1.6111
H	4.3474	-0.2594	-1.6572
C	5.8882	2.5236	0.5878
H	5.2993	1.2878	2.2605
C	5.8878	2.6548	-0.7987
H	5.3428	1.7704	-2.6906
H	6.3176	3.3002	1.2119
H	6.3219	3.5389	-1.2550
C	4.6428	-2.3703	0.2884
C	6.0263	-2.5385	0.2939
C	3.7757	-3.2889	-0.2963
C	6.5544	-3.6653	-0.3276
H	6.6820	-1.8058	0.7551
C	4.3290	-4.4084	-0.9152
H	2.7035	-3.1234	-0.2837
C	5.7088	-4.5964	-0.9305
H	7.6295	-3.8115	-0.3420
H	3.6721	-5.1325	-1.3867
H	6.1295	-5.4717	-1.4153
S	3.9626	-0.9494	1.1471
O	2.4929	-0.9446	0.4728
H	1.7640	-0.5041	1.1153
H	1.6996	0.4327	-0.8999

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