Electronic Supporting Information

Direct observation of arene···sulphur dioxide interaction: Role of metal ions in electronic modulation for binding and activation

Sandhya Singh,[a] Shruthi Dinesh,[a] Archana Yadav,[a] Sakthi Raje,[a] Ray J. Butcher,[b] Mahesh Sundararajan*[c] and Raja Angamuthu*[ad]

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EXPERIMENTAL SECTION

Materials.

2-Aminobenzenethiol (SDFCL), 9-Anthracenecarboxaldehyde (Sigma-Aldrich), $Zn(OAc)_2 \cdot 2H_2O$ (Rankem), $Cd(OAc)_2 \cdot 2H_2O$(Merck),and SO_2cylinder (6 Sigma gases) were used as received from commercial sources. Solvents were distilled under dry nitrogen atmosphere using conventional methods.

Methods.

Elemental analyses were carried out on a PerkinElmer CHNS/O analyzer. NMR spectra were recorded on JEOL 500 MHz and JEOL 400 MHz spectrometers. The temperature was kept constant using a variable-temperature unit within the error limit of ±1 K. The software MestReNova was used for the processing of the NMR spectra. Tetramethylsilane (TMS) or the deuterated solvent residual peaks were used for calibration. Mass spectrometry measurements were performed on Agilent 6546 LC/Q-TOF system equipped with an electrospray interface. Spectra were collected by constant infusion of the sample dissolved in methanol or acetonitrile with 0.1% formic acid.

Computational Details.

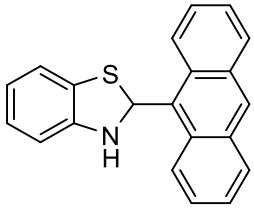
Both geometry optimizations and harmonic vibrational frequency calculations are carried out with TURBOMOLE 7.2 electronic structure program (TURBOMOLE V7.2, **2017**, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH,, 1989-2015, TURBOMOLE GmBH, since 2007, available from http://www.turbomole.com.). We have used B3LYP functional (Becke, A. D.; Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, **1993**, 98, 5648-5652, Lee, C.; Yang, W.; Parr, R. G.; Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B*. **1988**, 37, 785-789) in conjunction with def2-TZVP basis set (Schaefer, A.; Huber, C.; Ahlrichs, R., Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr, *J. Chem. Phys.* **1994**, 100, 5829-5835) for all atoms. Throughout the calculations, we have used D3 correction (Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu, *J. Chem. Phys.* **2010**, *132*, 154104) with Becke-Johnson damping factor (D3-BJ) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of Damping Function in Dispersion Corrected Density Functional Theory, *J.*

Comput. Chem. **2011**, *32 (11)*, 1456-1465. We have used this computational strategy to understand the electronic structure for several systems (*Phys. Chem. Chem. Phys.*, 2007, 9, 2498-2506, Inorg. Chem. 2019, 58, 6184, Inorg. Chem. 2019, 58, 6257).

X-ray crystallography

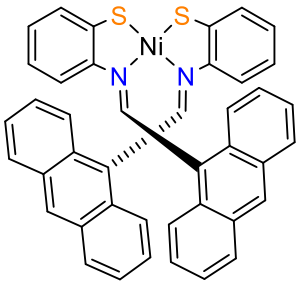
Single-crystal X-ray data were collected on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The linear absorption coefficients, the scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. Data integration and reduction were conducted with SAINT. An empirical absorption correction was applied to the collected reflections with SADABS during data processing with the SAINT routine in Apex2. The lattice parameters and structural data are provided as tables at the end of this Supporting Information.

Synthesis of 2-(anthracenyl)benzothiazoline (H-L)



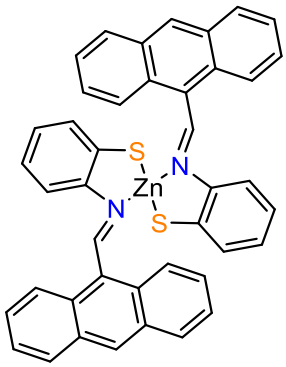
In a 100 mL Schlenk flask 9-Anthracenecarboxaldehyde (206 mg, 1 mmol) was dissolved in dry ethanol (3 mL) under N_2 atmosphere. In this ethanolic solution, 2-aminothiophenol (125 mg, 1 mmol) was slowly injected with vigorous stirring. The homogeneous solution was stirred at room temperature for 6 h under N_2 atmosphere. The yellow colour precipitate was formed and it was filtered. Yield: 190 mg (60.6%).^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ_H= 8.78 (d, *J* = 8.6 Hz, 2H), 8.51 (s, 1H), 8.16 (d, *J* = 3.9 Hz, 1H), 8.06 – 8.03 (m, 2H), 7.53 – 7.46 (m, 4H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 8.1 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 1H), 4.47 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) δ_C= 146.61, 131.68, 130.70, 130.06, 129.52, 127.98, 127.90, 126.21, 125.82, 125.12, 124.41, 122.13, 121.05, 110.50, 65.63. ESI-MS: *m/z* = 314.1005 (calcd.314.1003) = $[C_{21}H_{16}NS]^+$. Anal.Calcd (%) for ($C_{21}H_{15}NS$): C 80.48, H 4.82, N 4.47, S 10.23; found: C 79.56, H 4.93, N 4.38, S 10.11.

Synthesis of [NiL_2]



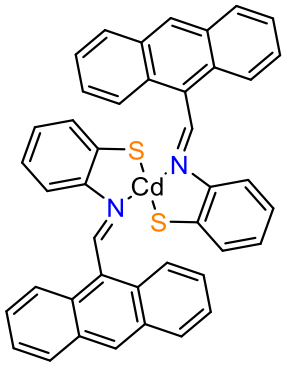
In a 100 mL Schlenk flask 9-Anthracenecarboxaldehyde (206 mg, 1 mmol) was dissolved in dry ethanol (3 mL) under N_2 atmosphere. In this ethanolic solution, 2-aminothiophenol (125 mg, 1 mmol) was slowly injected with vigorous stirring. The yellow colour solution was refluxed at 80 °C for 30 mins. Then nickel(II) acetate tetrahydrate (124 mg, 0.5 mmol) in ethanol (20 mL) was added to this solution under nitrogen atmosphere. The reaction mixture was refluxed at 80 °C for 2 h under nitrogen atmosphere. The dark reddish brown precipitate was formed and it was filtered. Then the precipitate was washed by cold ethanol (10 mL) and dried under vacuum. Yield: 240 mg (70%). X-ray quality needle-like brown colour crystals were obtained in $CHCl_3$ layering with methanol at -22 °C in 4 days.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H = 11.70 (d, *J* = 7.2 Hz, 2H), 8.54 (s, 2H), 8.22 (s, 2H), 8.00 (d, *J* = 16.1 Hz, 4H), 7.73 – 7.68 (m, 3H), 7.39 – 7.32 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 7.3 Hz, 2H), 6.79 – 6.72 (m, 2H), 6.53 (t, *J* = 8.0 Hz, 2H), 6.17 (d, *J* = 7.6 Hz, 2H), 5.67 (d, *J* = 7.8 Hz, 2H). Anal.Calcd (%) for ($C_{42}H_{28}N_2NiS_2$): C 73.80, H 4.13, N 4.10; found: C 72.78, H 3.83, N 4.10.

Synthesis of [ZnL_2]



In a 100 mL Schlenk flask 9-Anthracenecarboxaldehyde (412 mg, 2mmol) was dissolved in dry ethanol (3 mL) under N_2 atmosphere. In this ethanolic solution, 2-aminothiophenol (250 mg, 1 mmol) was slowly injected with vigorous stirring. The yellow colour solution was refluxed at 80 °C for 30 mins. Then zinc(II) acetate dihydrate (219 mg, 1mmol) in ethanol (20 mL) was added to this solution under nitrogen atmosphere. The reaction mixture was refluxed at 80 °C for 2 h under nitrogen atmosphere. Dark orange colour precipitate was formed and it was filtered and dried under vacuum. Yield: 600 mg (87%). X-ray quality needle-like redcolour crystals were obtained in $CHCl_3$ diffused by diethylether at 5 °Cin 2 days.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):δ_H= 9.51 (s, 3H), 8.46 (s, 3H), 7.52 – 7.43 (m, 8H), 6.89 – 6.61 (m, 14H).Anal.Calcd (%) for ($C_{42}H_{28}N_2ZnS_2$·0.5$CH_3CH_2OCH_2CH_3$): C 72.67, H 4.57, N 3.85; found: C 71.99, H 3.69, N 3.97.

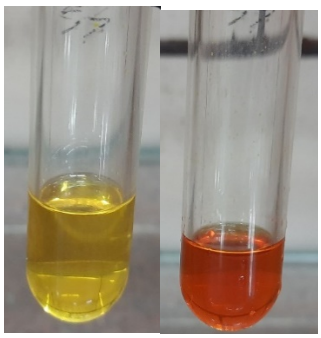
Synthesis of [CdL_2]



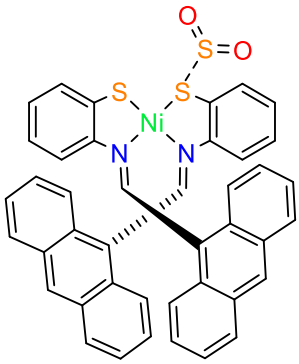
In a 100 mL Schlenk flask 9-Anthracenecarboxaldehyde (206 mg, 1mmol) was dissolved in dry ethanol (3 mL) under N_2 atmosphere. In this ethanolic solution, 2-aminothiophenol (125 mg, 1 mmol) was slowly injected with vigorous stirring. The yellow colour solution was refluxed at 80 °C for 30 mins. Then cadmium(II) acetate dihydrate (133 mg, 0.5mmol) in ethanol (20 mL) was added to this solution under nitrogen atmosphere. The reaction mixture was refluxed at 80 °C for 2 h under nitrogen atmosphere. Yellow colour precipitate was formed and it was filtered and dried under vacuum. Yield: 200 mg (54.2%). X-ray quality needle-like red colour crystals were obtained in $CHCl_3$ diffused by diethylether at 5 °C in 2 days.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):δ_H = 9.38 (s, 2H), 8.41 (s, 2H), 8.13 (d, *J* = 8.6 Hz, 4H), 7.93 (d, *J* = 8.3 Hz, 4H), 7.54 – 7.44 (m, 4H), 7.41 – 7.34 (m, 4H), 7.03 – 6.69 (m, 8H).Anal.Calcd (%) for ($C_{42}H_{28}N_2CdS_2$): C 68.43, H 3.83, N3.80; found: C 67.64, H 3.54, N 4.25.

Interaction of 2-(anthracenyl)benzothiazoline with SO_2

Pale yellow powder of 2-(anthracenyl)benzothiazoline (100 mg, 0.3 mmol) was dissolved in dry dichloromethane (7 mL) and purged SO_2 for 20 min at room temperature. While purging SO_2, color of solution changed from yellow to red. The solution was kept standing at -20 °C and the precipitate formed overnight was filtered and dried. Yield: 65 mg (52%)^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H = 11.55 (s, 1H), 8.64 (s, 1H), 8.08 (d, J = 8.4 Hz, 3H), 7.82 (d, J = 8.5 Hz, 2H), 7.66 – 7.60 (m, 1H), 7.58 – 7.43 (m, 6H). ESI-MS: *m/z* (cation mode) = 312.0848 (calcd. 312.0847) = 2-(anthracenyl)benzothiazoliumcation ; *m/z* (anion mode) = 96.9597 (calcd. 96.9596) = $[HSO_4]$



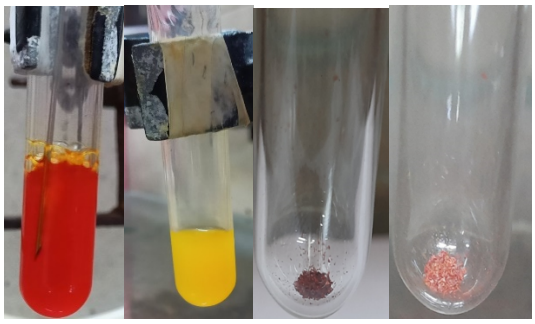
Interaction of $[NiL_2]$ with SO_2



In a 15 mL Schlenk tube reddish brown powder of $[NiL_2]$ (57 mg, 0.08mmol) was dissolved in dry dichloromethane (5 mL). Then sulphur dioxide is purged in this reddish brown solution for 5 min at room temperature. Then the solution was kept at -20 °C. Red colour crystals were formed in 7 days. Yield: 13 mg (20%).

Interaction of [ZnL_2] with SO_2

Red color crystals of [$Zn(Anbt)_2$] (30 mg, 0.043 mmol) were dissolved in dry dichloromethane (8 mL) and purged SO_2 for 20 min at room temperature. While purging SO_2, color of solution changed from red to yellow. ESI-MS: *m/z* (cation mode) = 312.0841 (calcd. 312.0847) = 2-(anthracenyl)benzothiazoliumcation.*m/z* (anion mode) = 96.9599 (calcd. 96.9596) = [HSO_4]



Interaction of [CdL_2] with SO_2

Red color crystals of [CdL_2] (30 mg, 0.040 mmol) were dissolved in dry dichloromethane (8 mL) and purged SO_2 for 20 min at room temperature. While purging SO_2, color of solution changed from red to yellow. ESI-MS: *m/z* (cation mode) = 312.0840 (calcd. 312.0847) = 2-(anthracenyl)benzothiazoliumcation. m/z (anion mode) = 96.9597 (calcd. 96.9596) = [HSO_4]

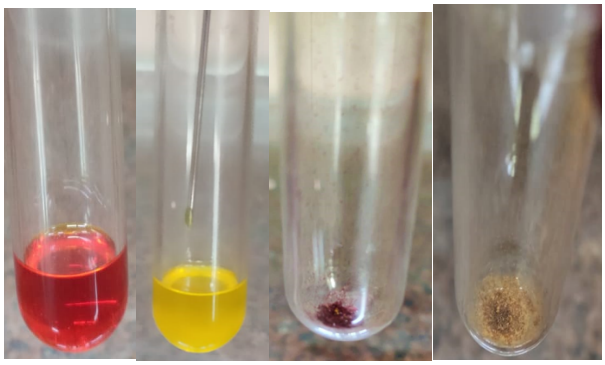


Figure S 1.^{1}H NMR of 2-(anthracenyl)benzothiazoline (HL) in $CDCl_3$.

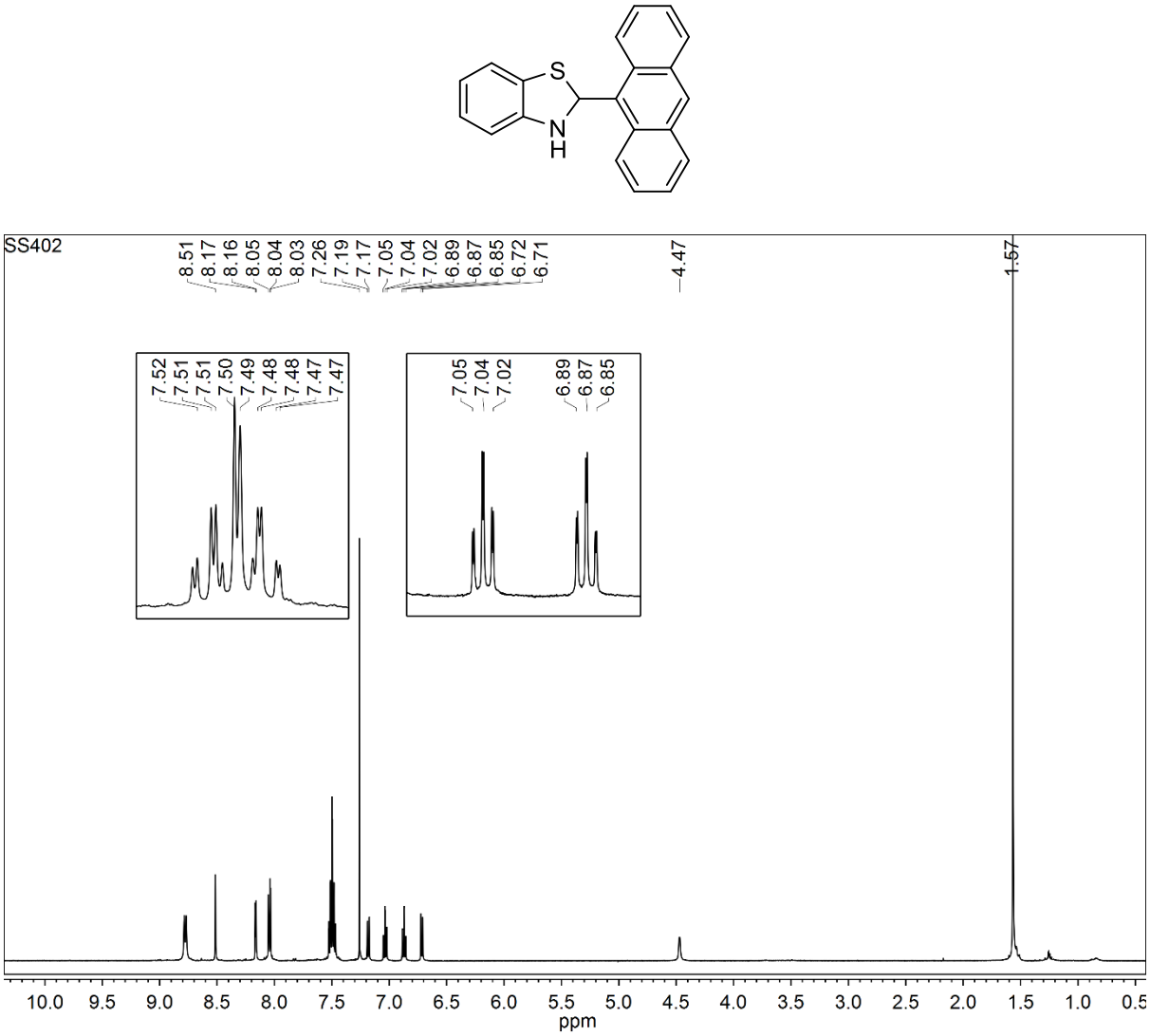
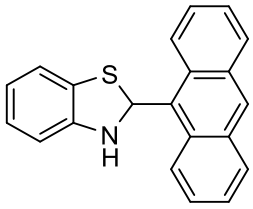


Figure S 2. ^{13}C NMR of 2-(anthracenyl)benzothiazoline (HL) in $CDCl_3$.



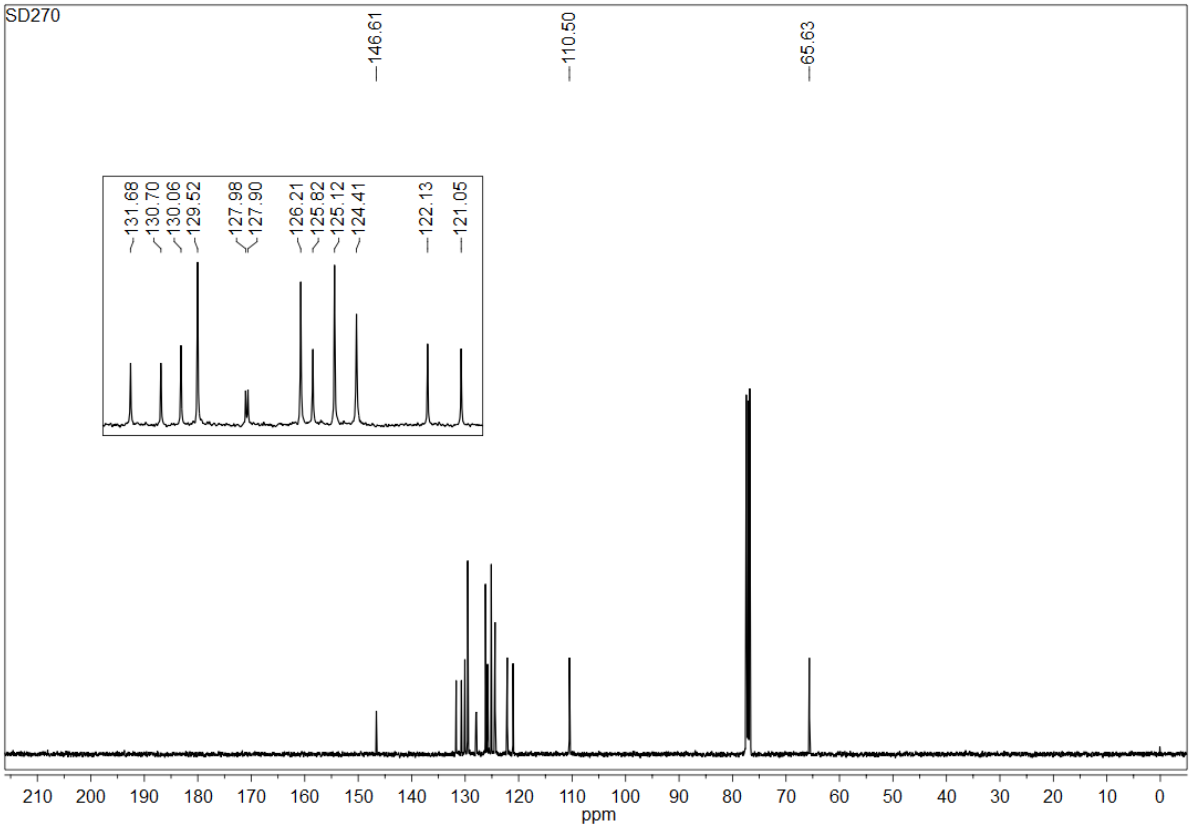
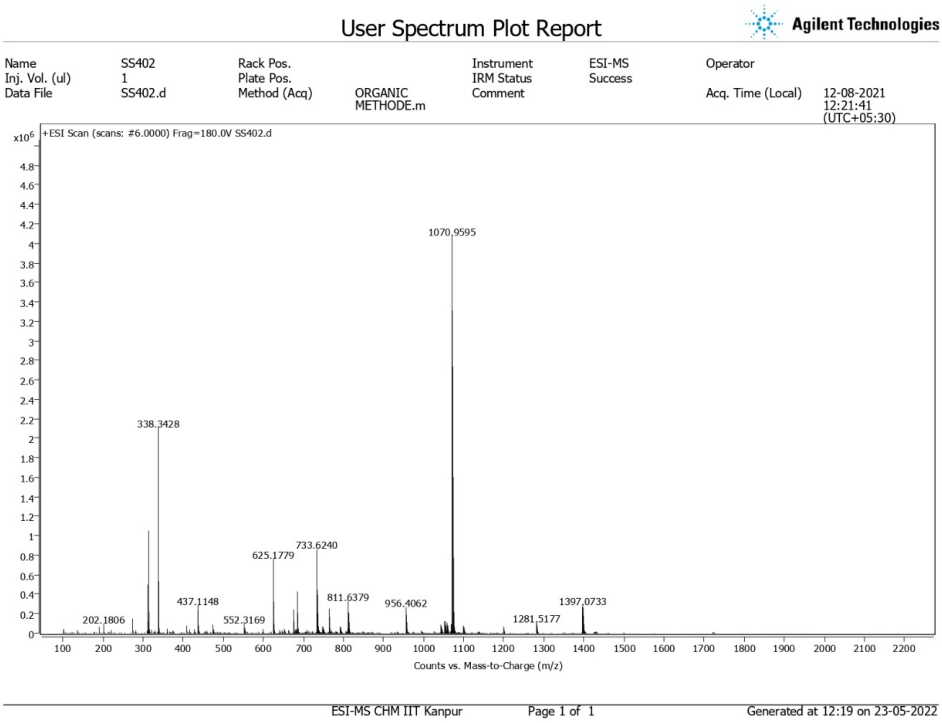


Figure S 3. ESI-MS of 2-(anthracenyl)benzothiazoline.



Calculated *m/z* for $[L+H]^+ = [C_{21}H_{16}NS]^+$ = 314.1003; observed *m/z* = 314.1005

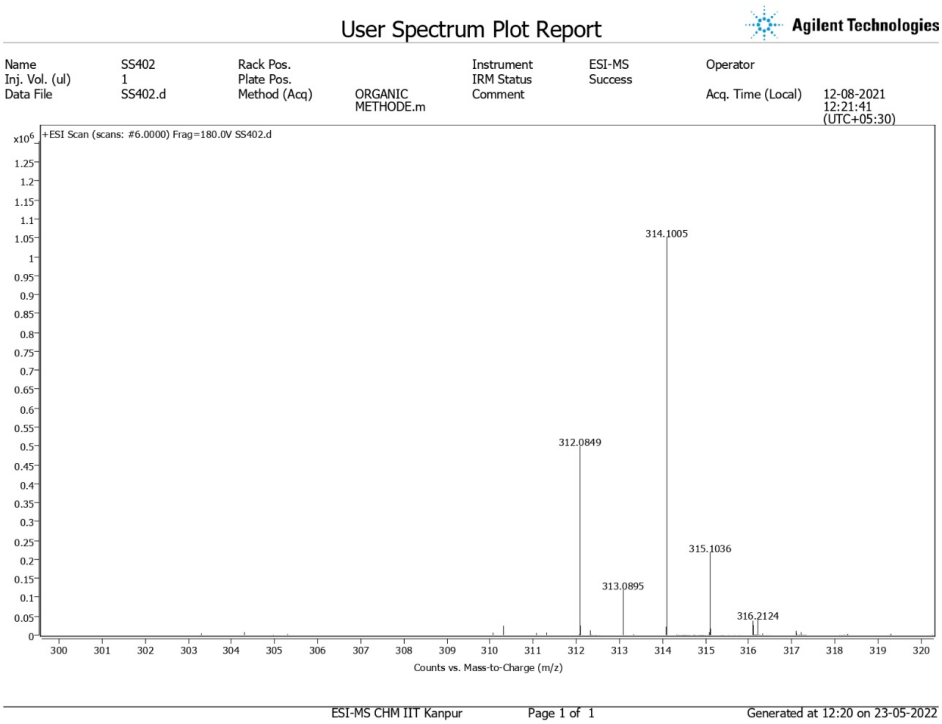


Figure S 4. Simulated for $[C_{21}H_{16}NS]^+$

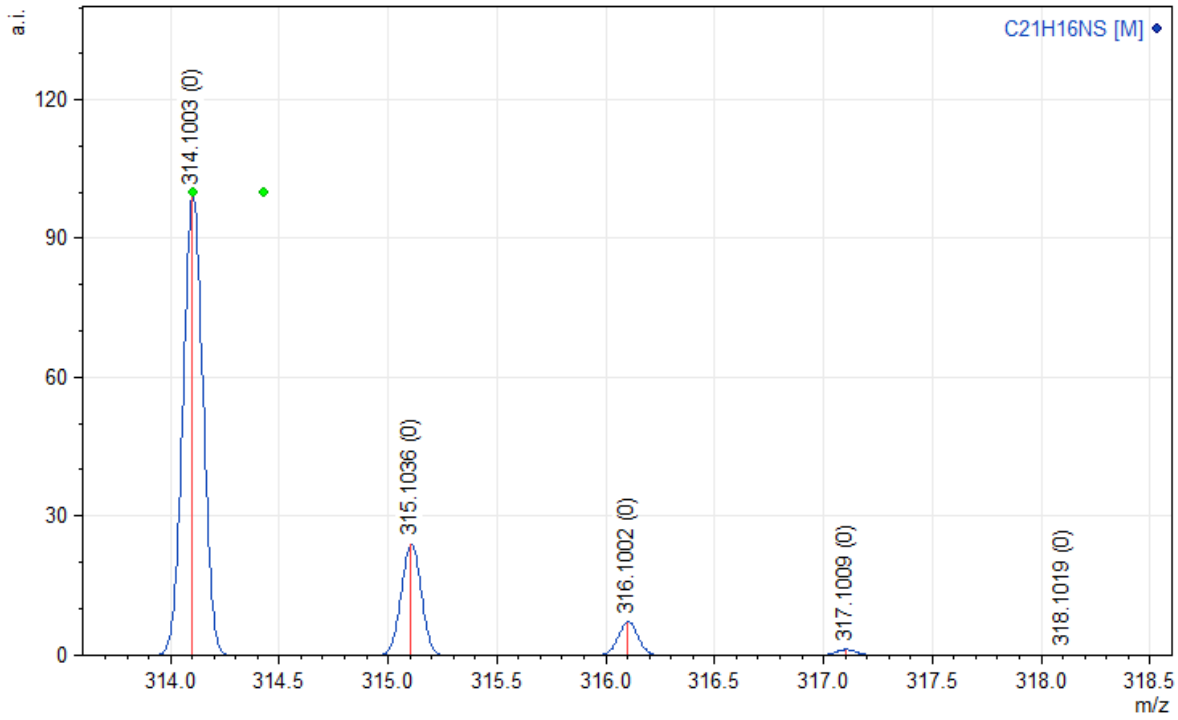


Figure S 5.^{1}H NMR of 2-(anthracenyl)benzothiazolium bisulfate in $CDCl_3$

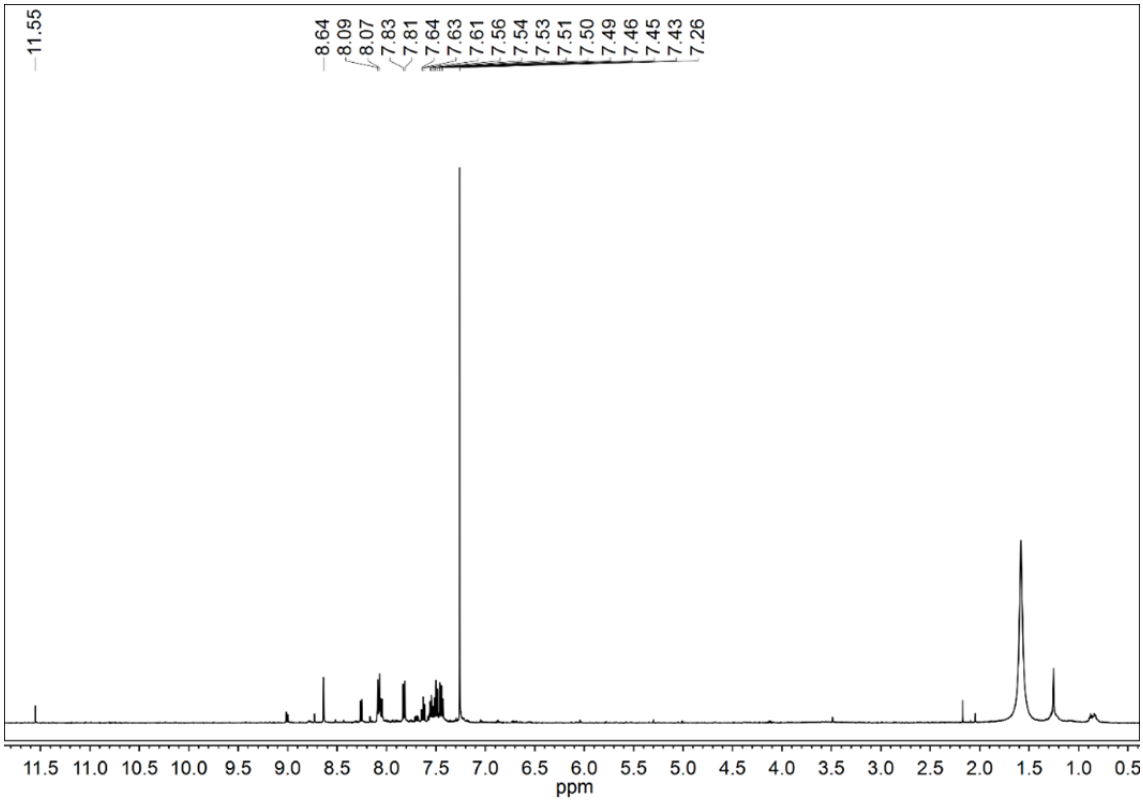
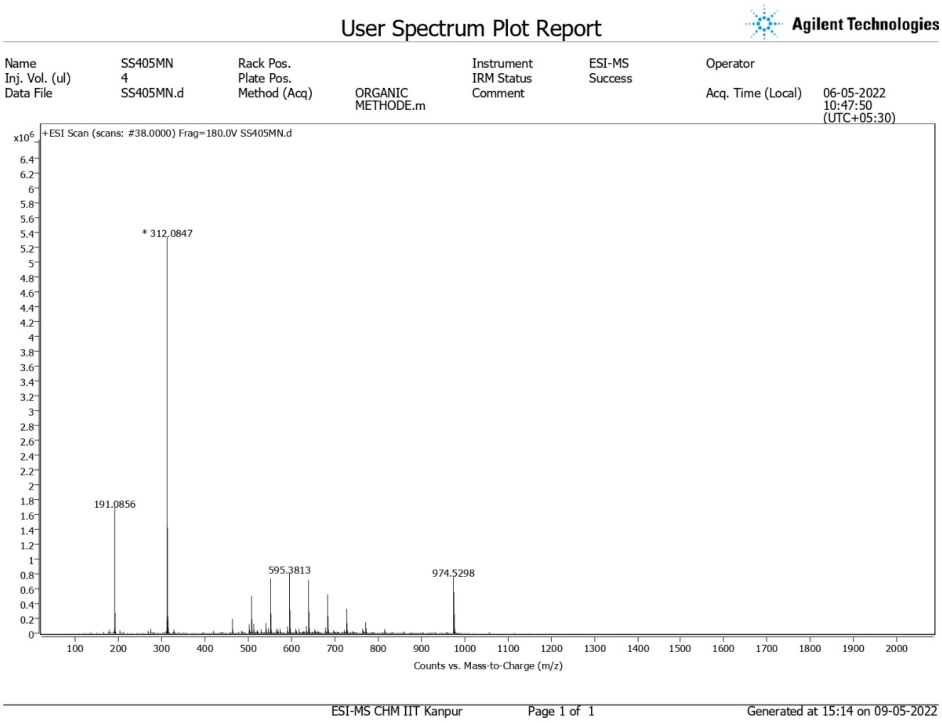


Figure S 6. ESI-MS (in positive mode) after reacting HL with SO_2



Calculated *m/z* for $[L+H]^+ = [C_{21}H_{14}NS]^+$ = 312.0848; observed *m/z* = 312.0847.

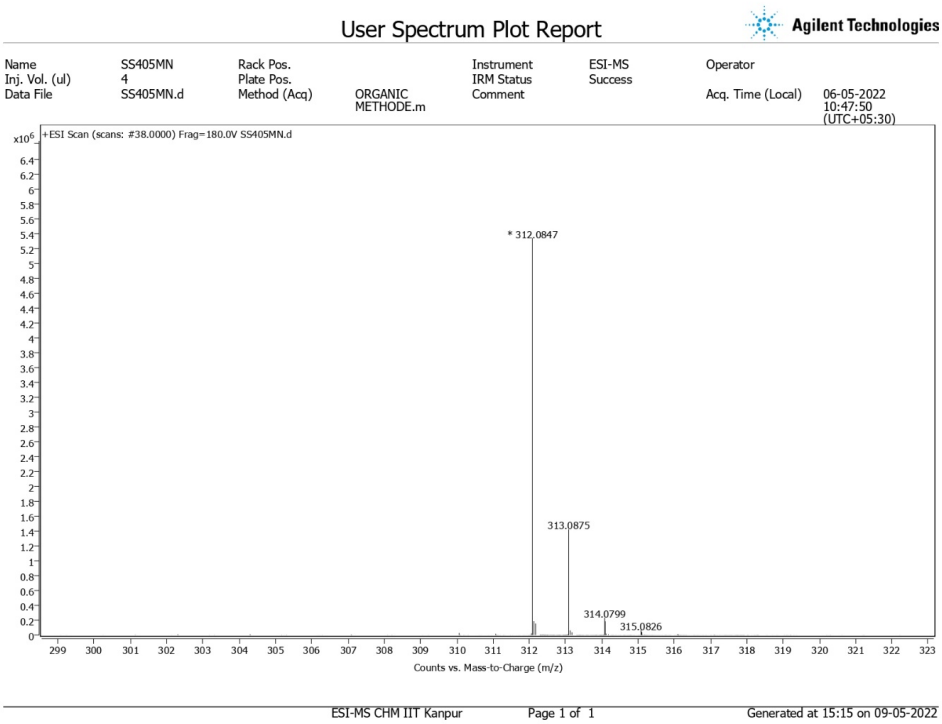


Figure S 7. Simulated for $[C_{21}H_{14}NS]^+$

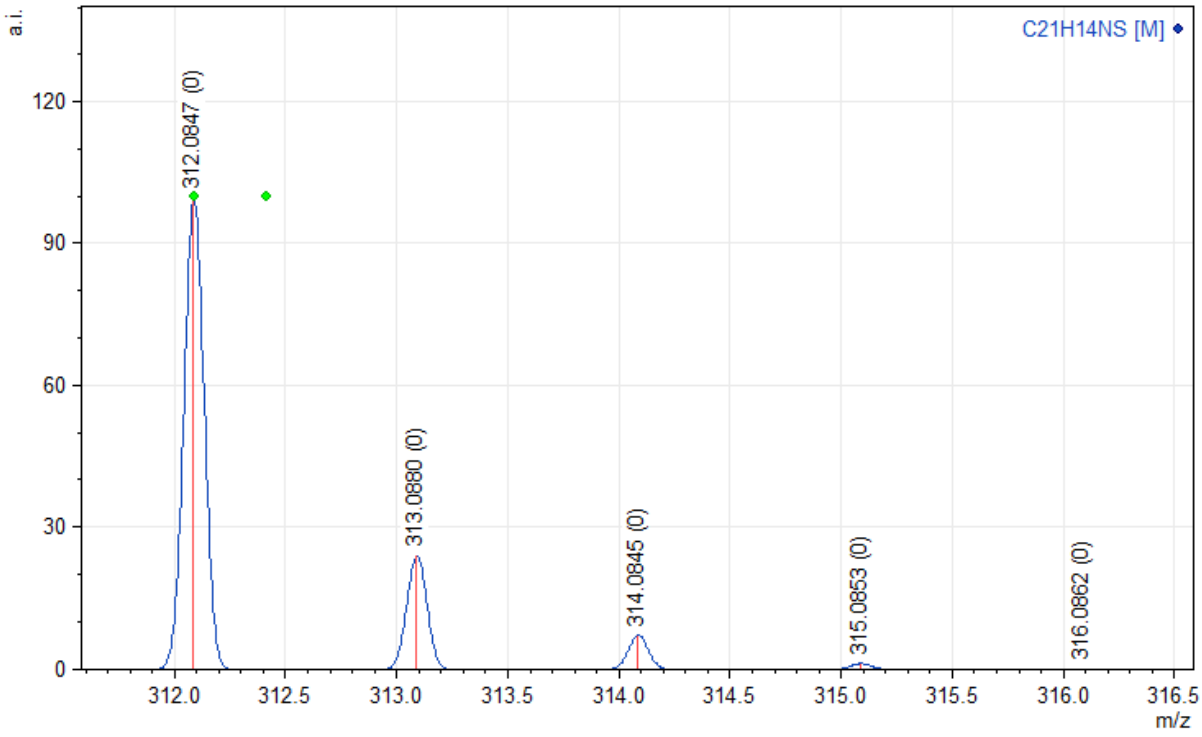
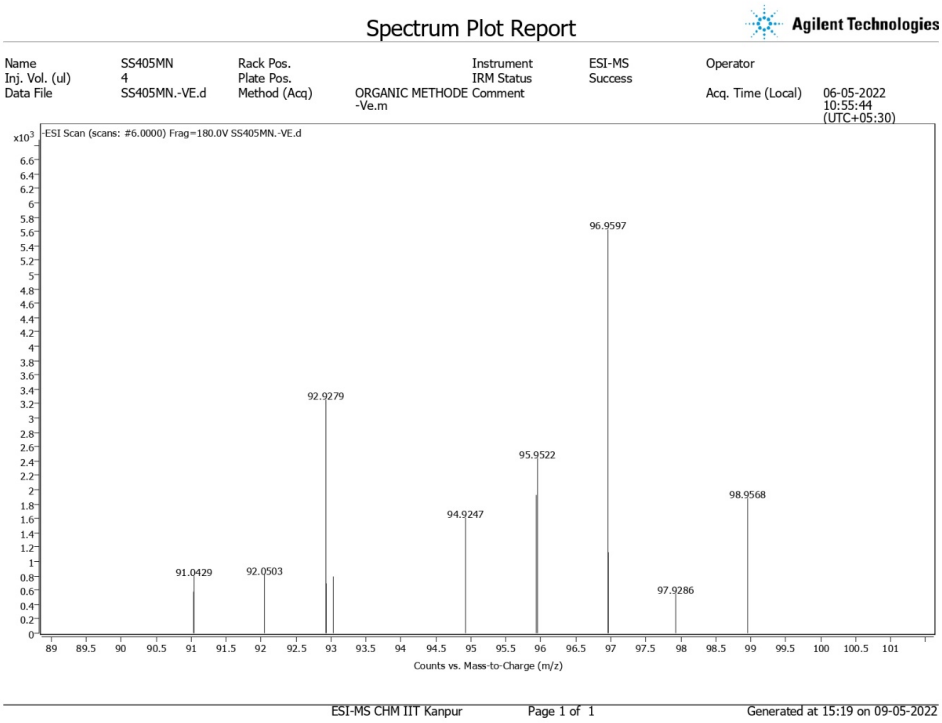


Figure S 8. ESI-MS (in negative mode)after reacting HL with SO_2



Calculated *m/z* for $[HSO_4]^-$ = 96.9596; observed *m/z* = 96.9597.

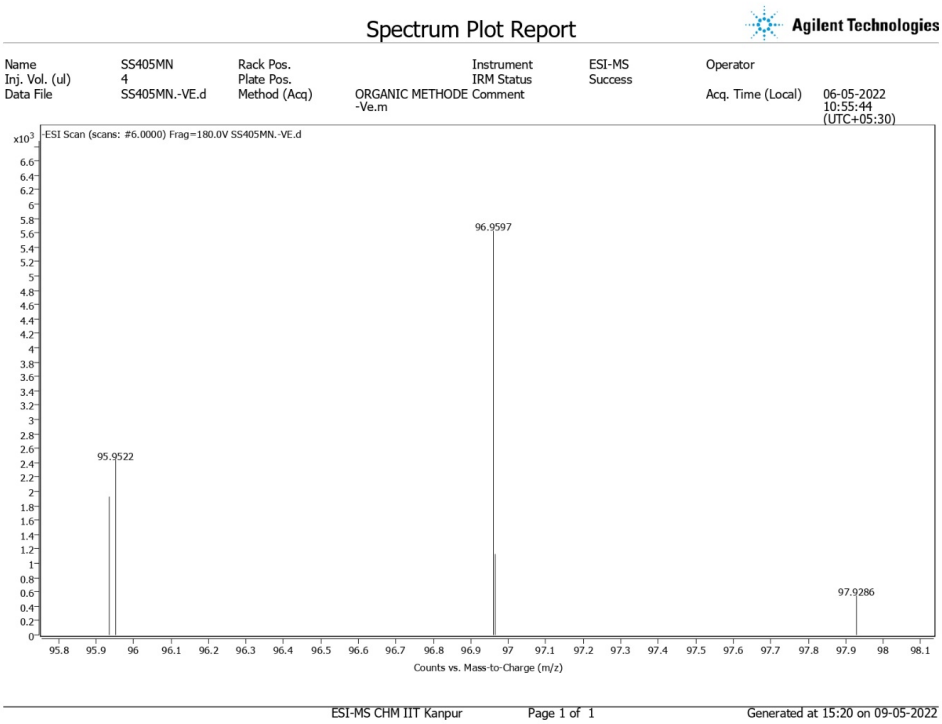


Figure S 9. Simulated for [HSO_4]

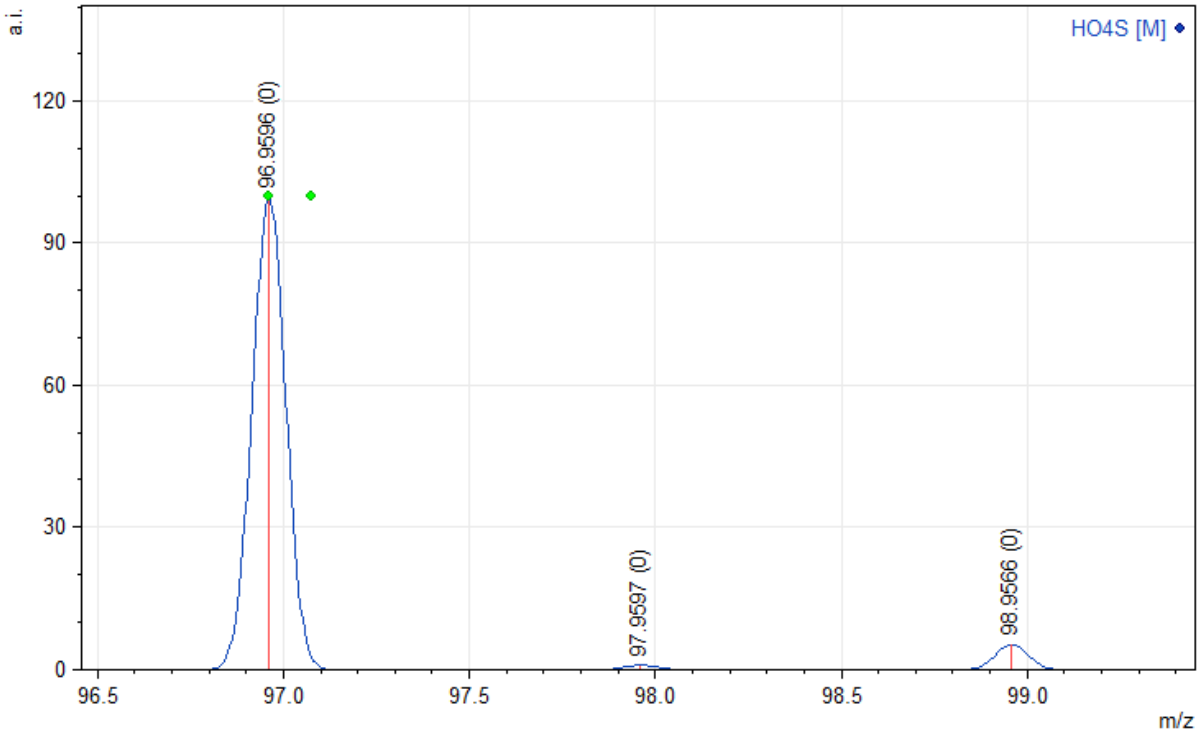


Figure S 10. ^{1}HNMR of [NiL_2] in $CDCl_3$.

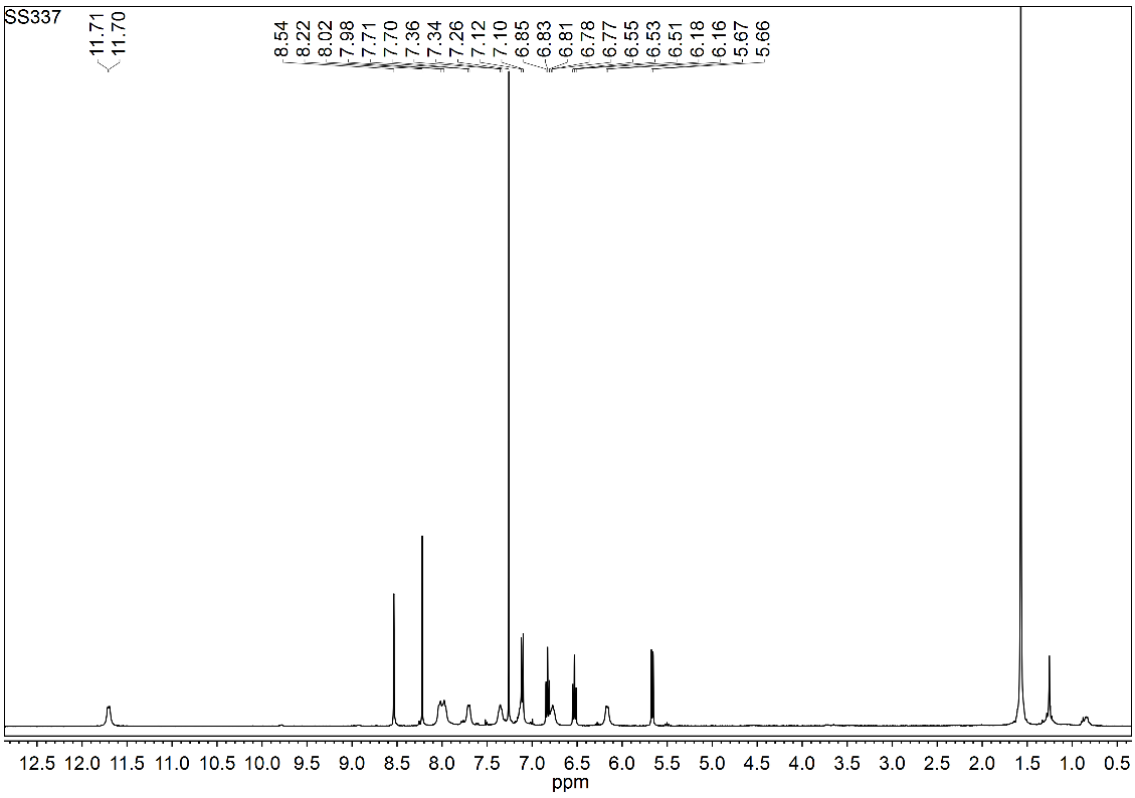


Figure S 11. Stacked ^{1}H NMR of $[NiL_2]\cdot 2SO_2$ (top) and $[NiL_2]$ (bottom)

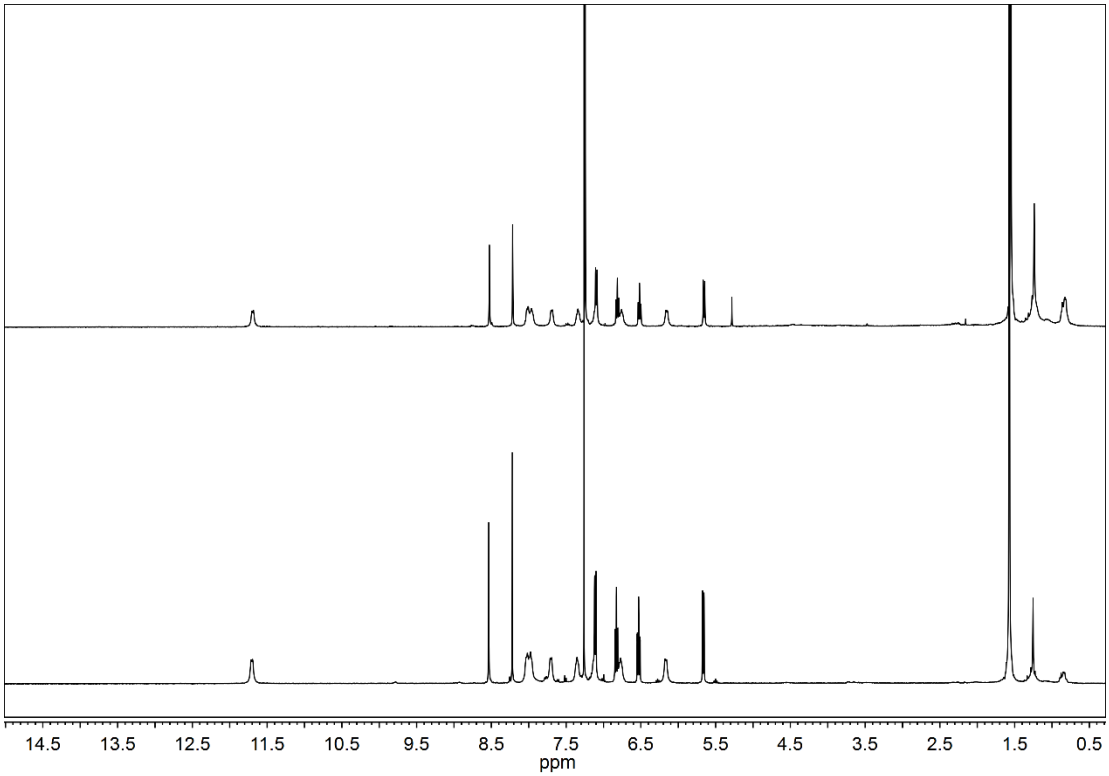


Figure S 12. ^{1}HNMR of [ZnL_2] in $CDCl_3$

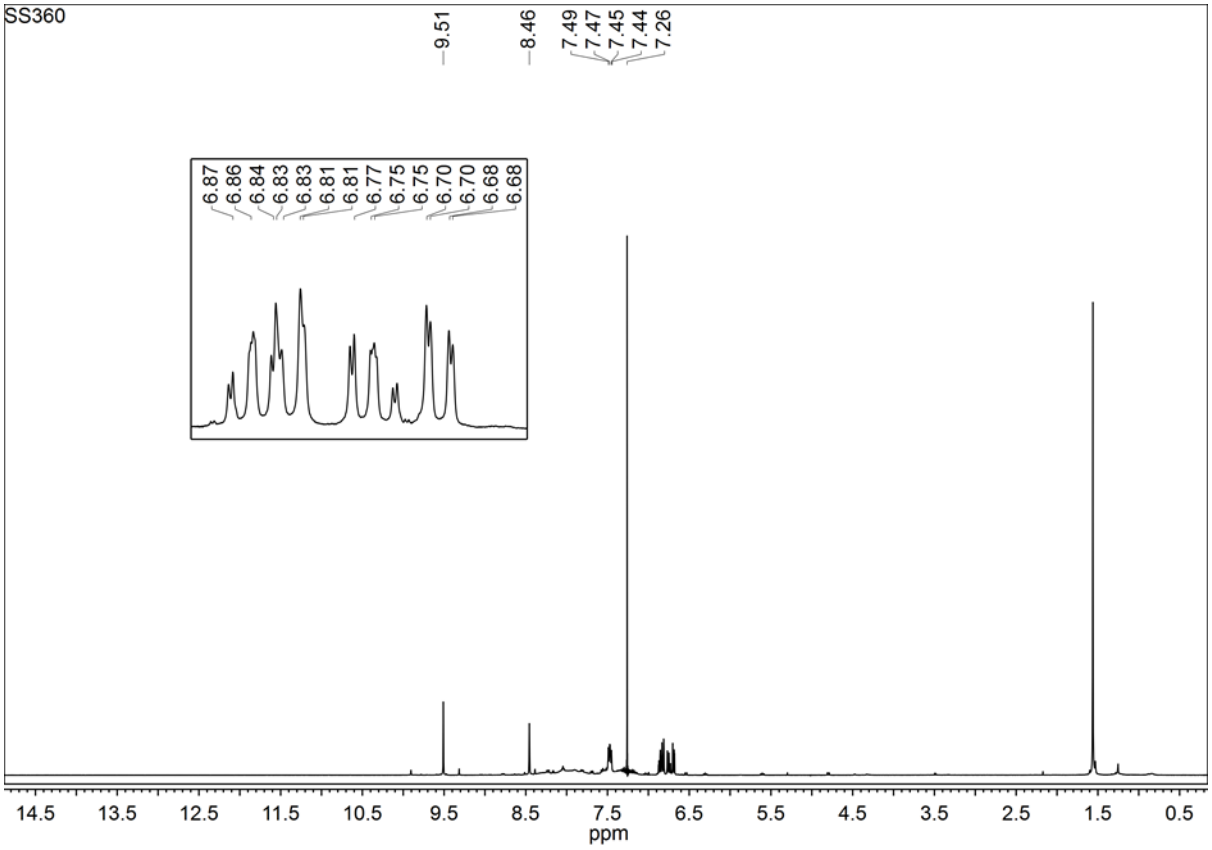
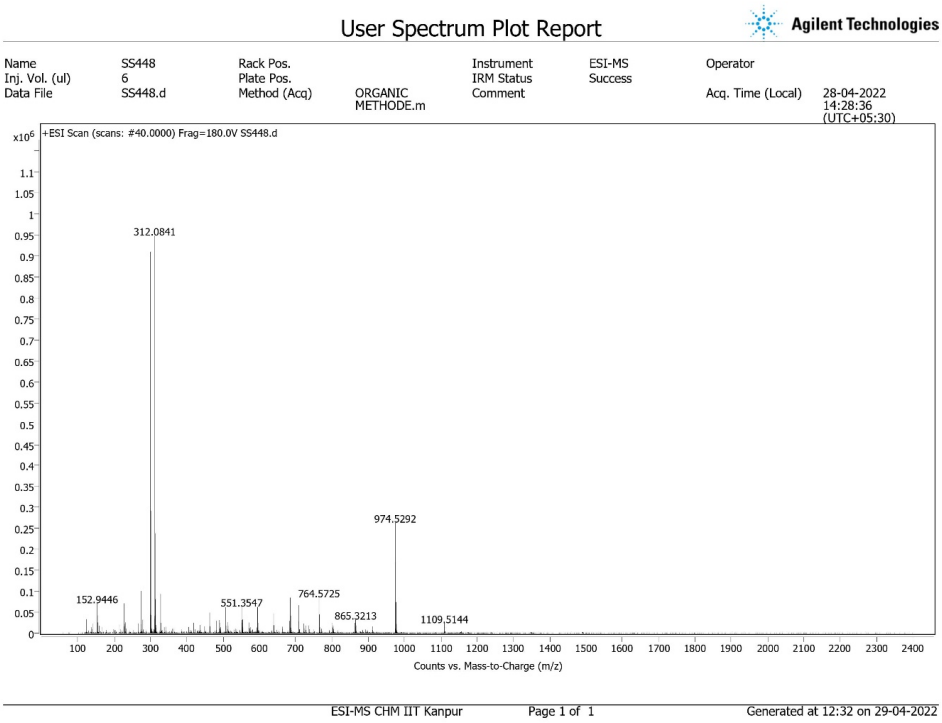


Figure S 13. ESI-MS (in positive mode) after reacting [ZnL_2] with SO_2



Calculated *m/z* for $[L+H]^+ = [C_{21}H_{14}NS]^+$ = 312.0847; observed *m/z* = 312.0841.

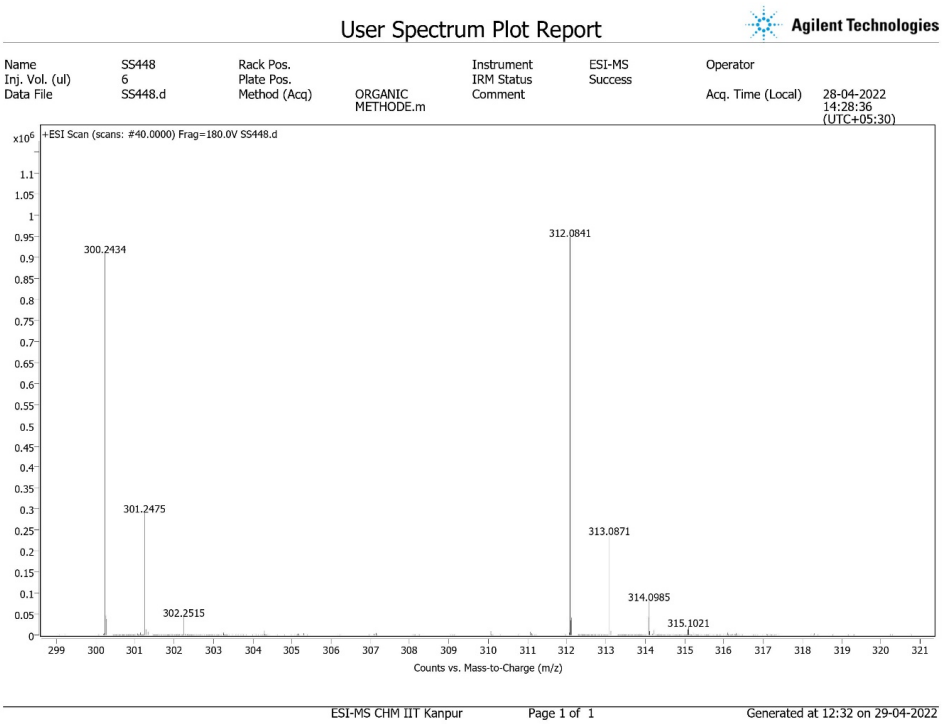


Figure S 14. Simulated for $[C_{21}H_{14}NS]^+$

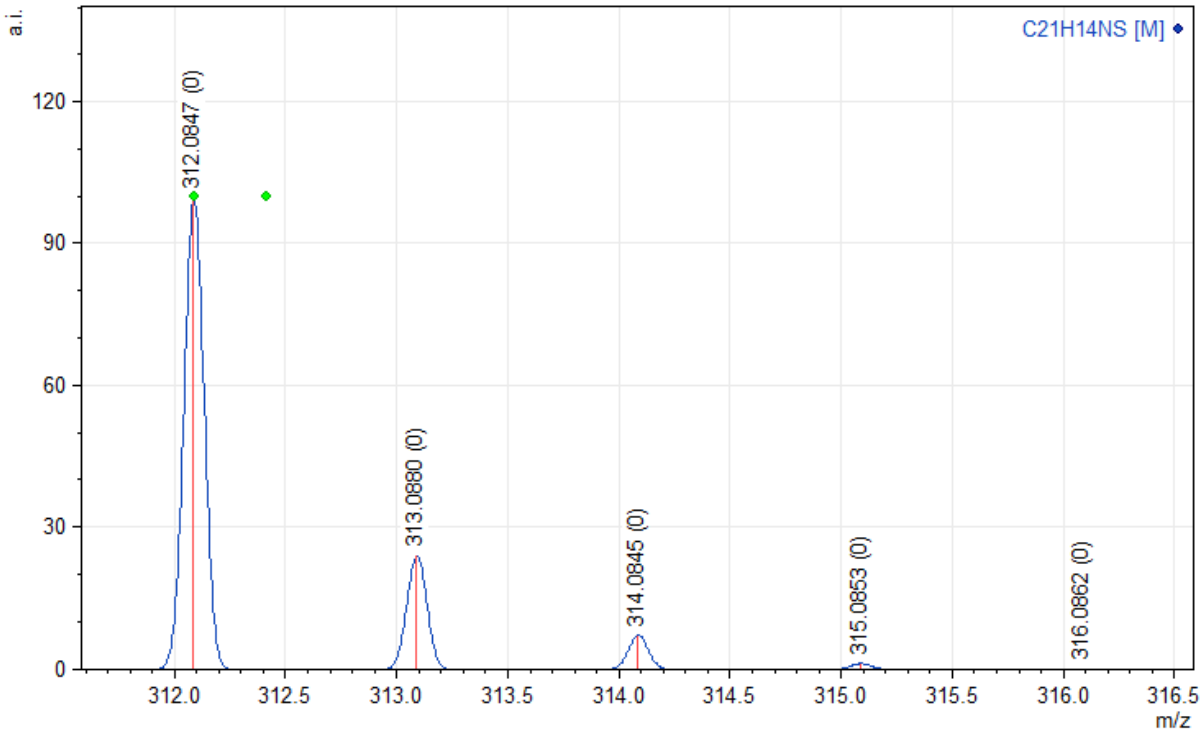
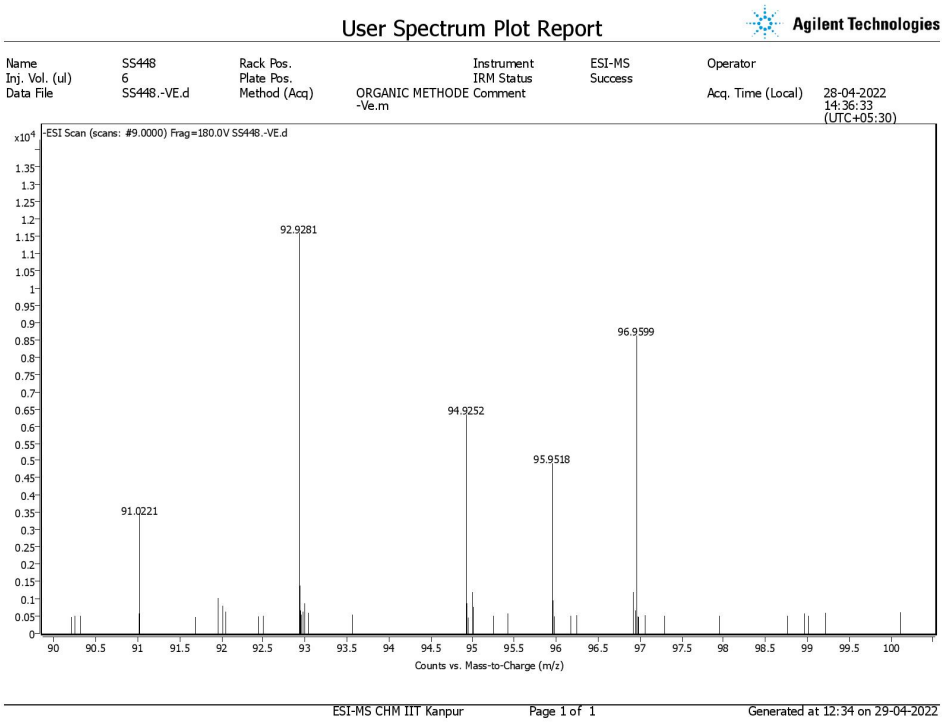


Figure S 15. ESI-MS (in negative mode) after reacting [ZnL_2] with SO_2.



Calculated *m/z* for $[HSO_4]^-$= 96.9596; observed *m/z* = 96.9599.

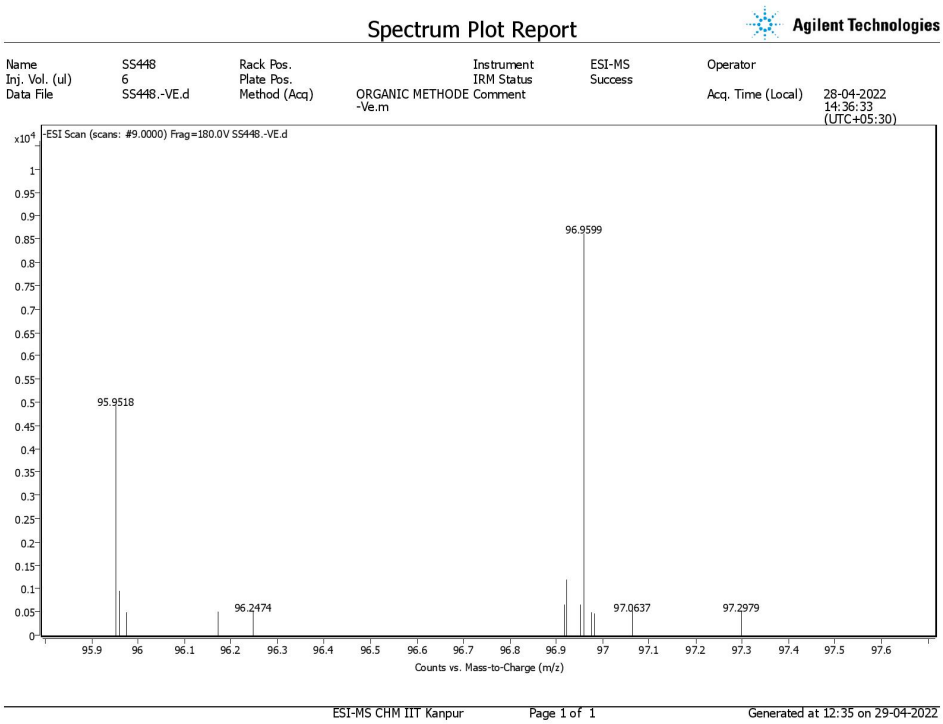


Figure S 16. Simulated for [HSO_4]

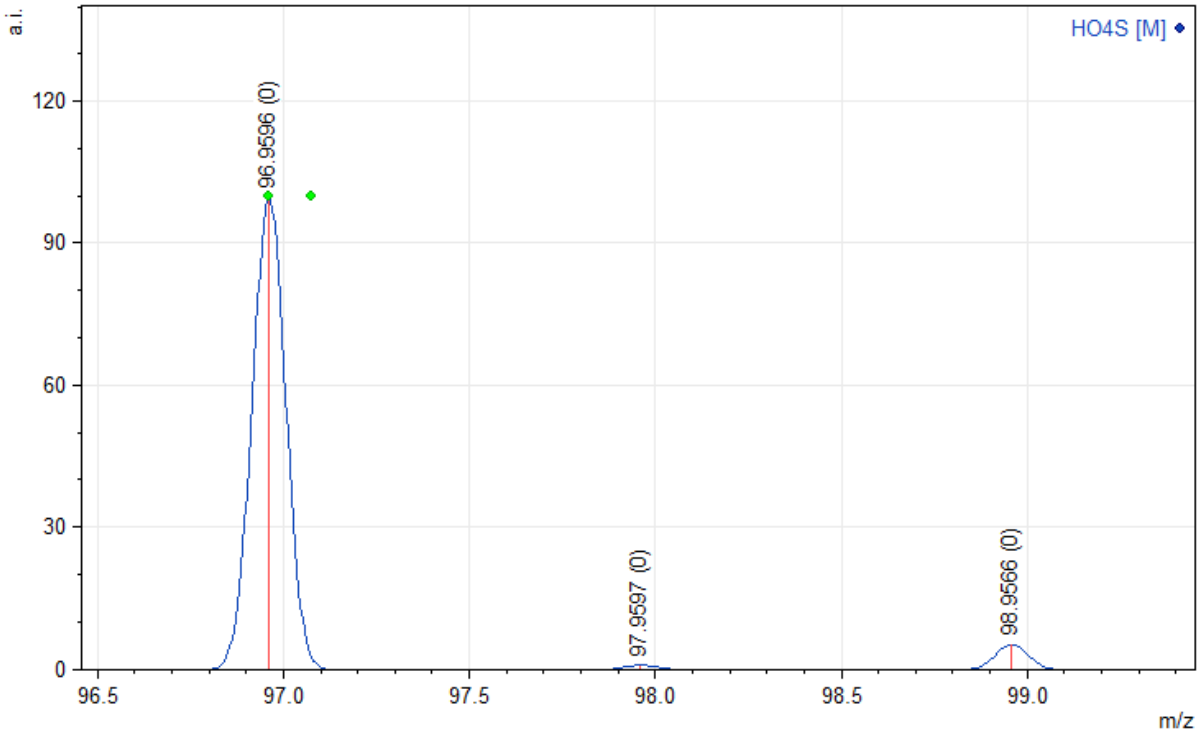


Figure S 17. ^{1}HNMR of [CdL_2)] in $CDCl_3$

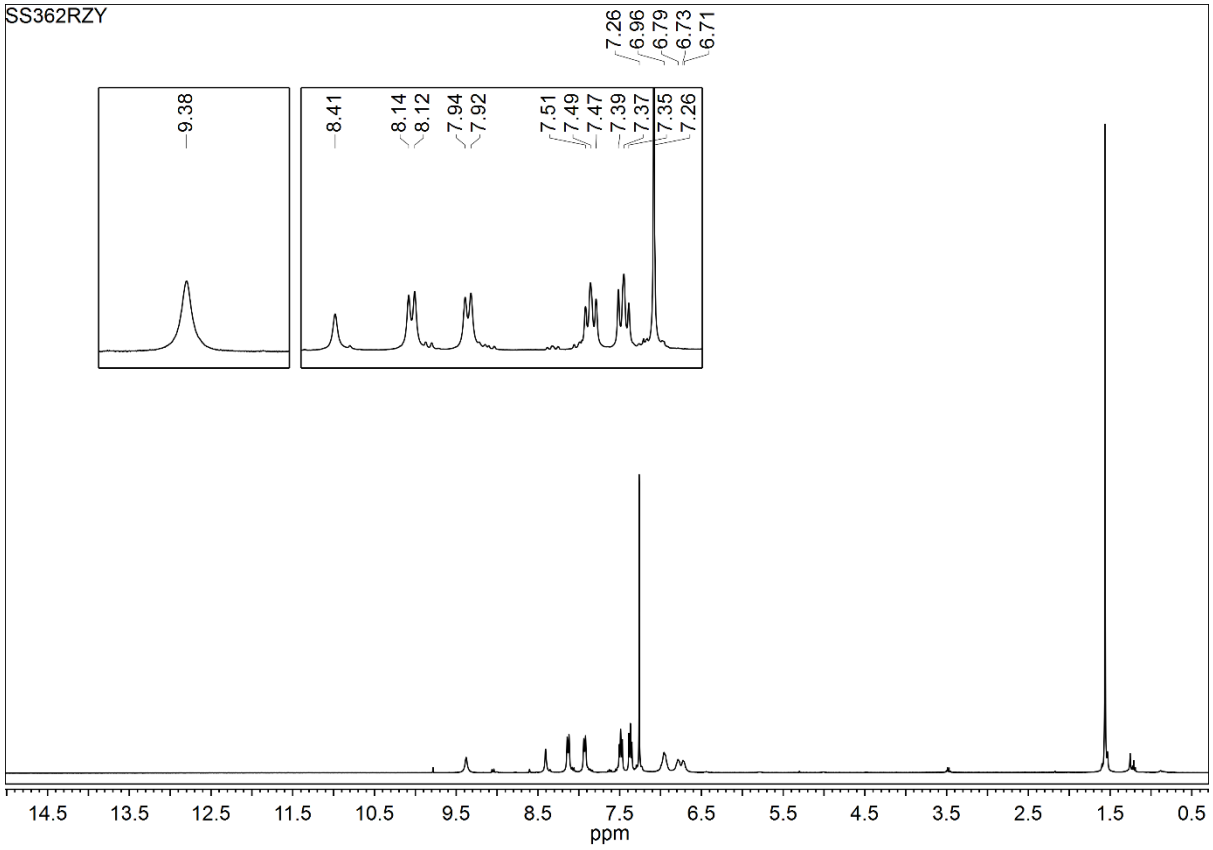
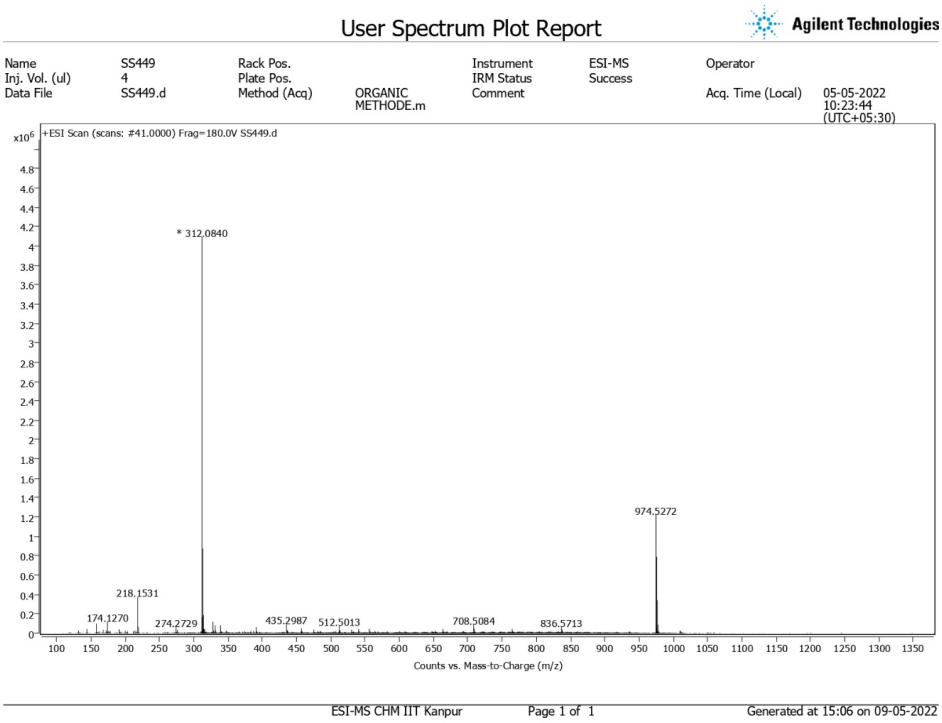


Figure S 18. ESI-MS (in positive mode) after reacting [CdL_2] with SO_2.



Calculated *m/z* for $[L+H]^+ = [C_{21}H_{14}NS]^+$ = 312.0847; observed *m/z* = 312.0840.

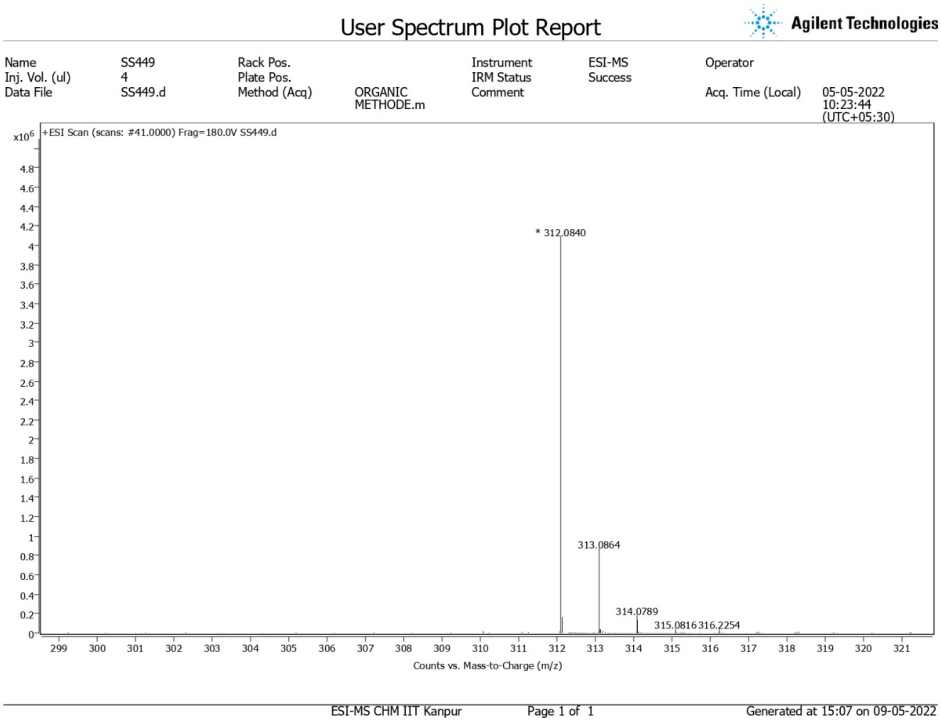


Figure S 19. Simulated for $[C_{21}H_{14}NS]^+$

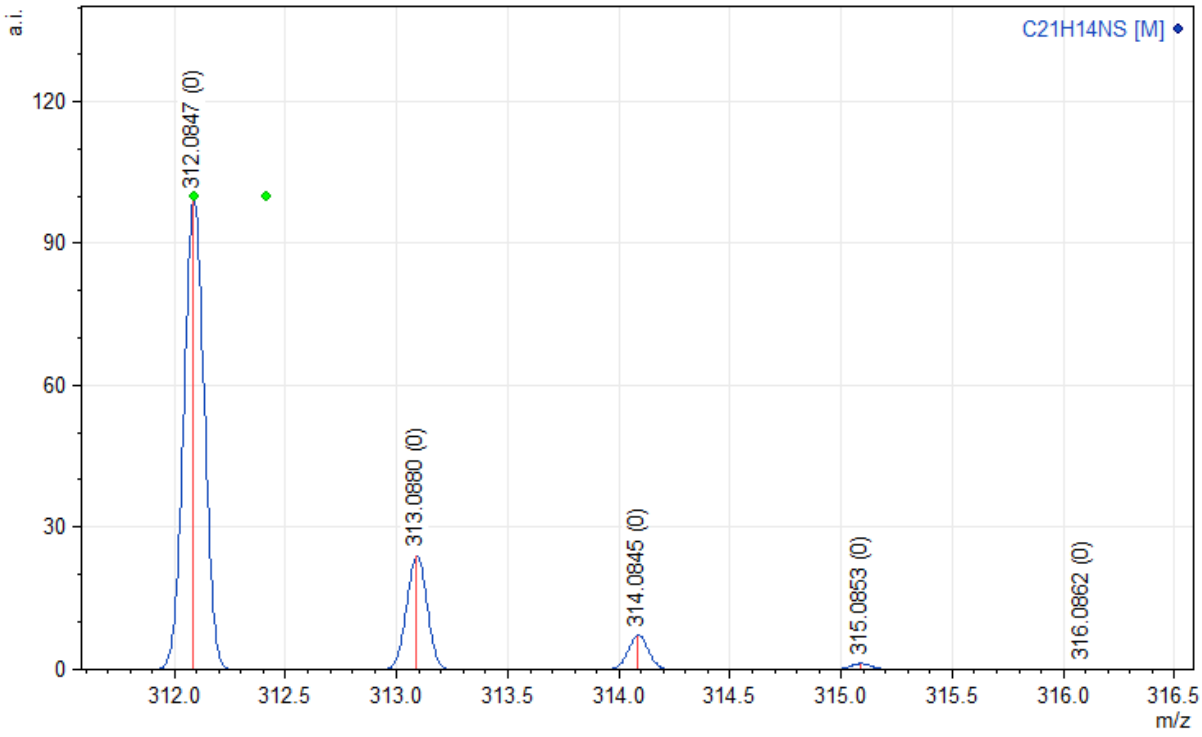
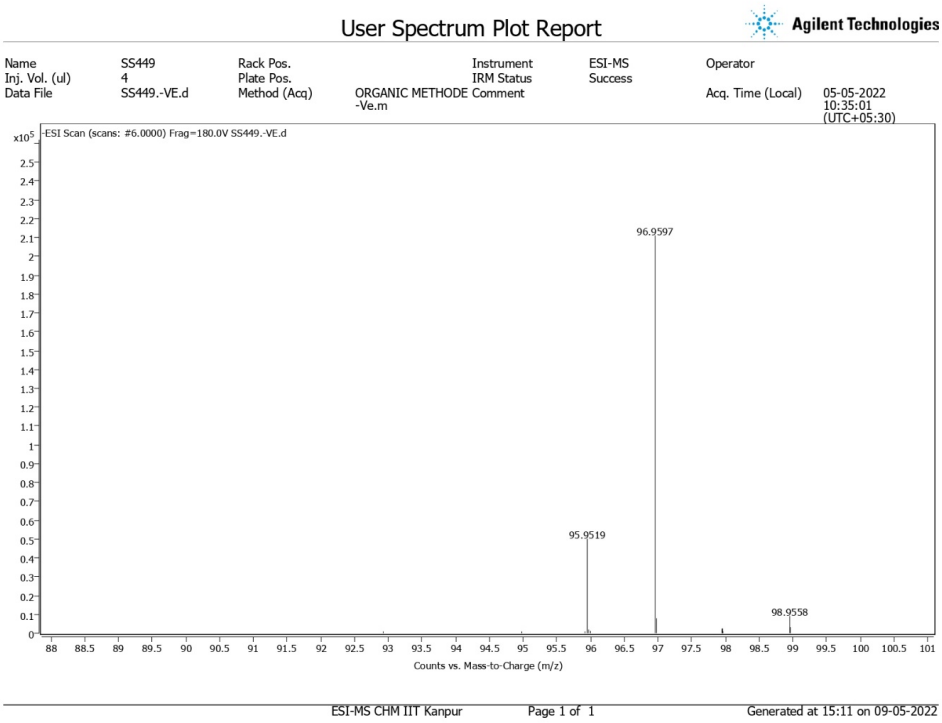


Figure S 20. ESI-MS (in negative mode) after reacting [CdL_2] with SO_2.



Calculated *m/z* for $[HSO_4]^-$ = 96.9596; observed *m/z* = 96.9597.

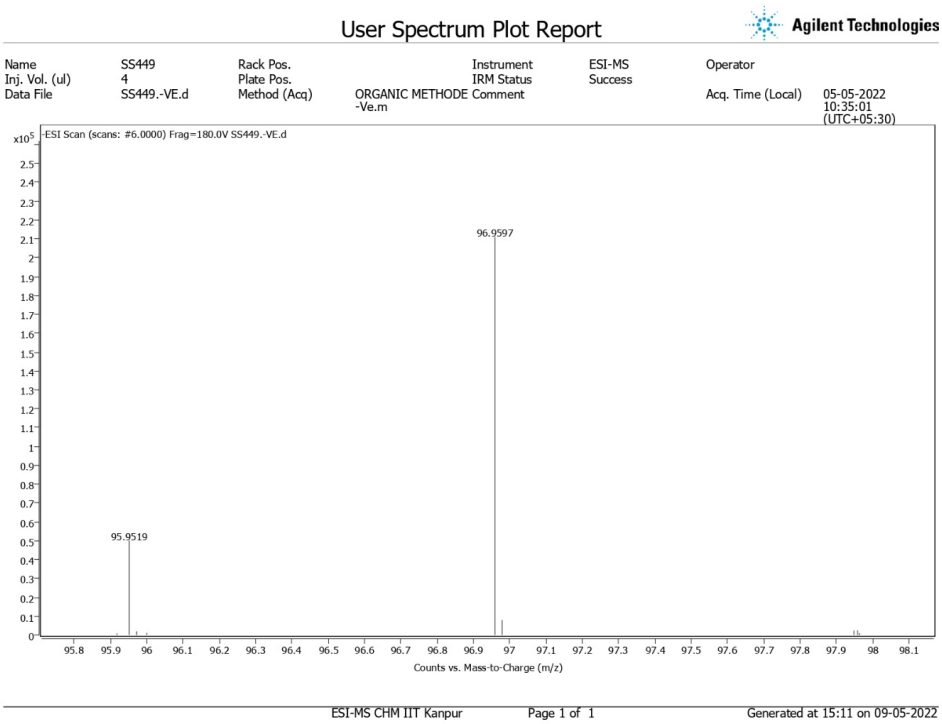


Figure S 21. Simulated for [HSO_4]

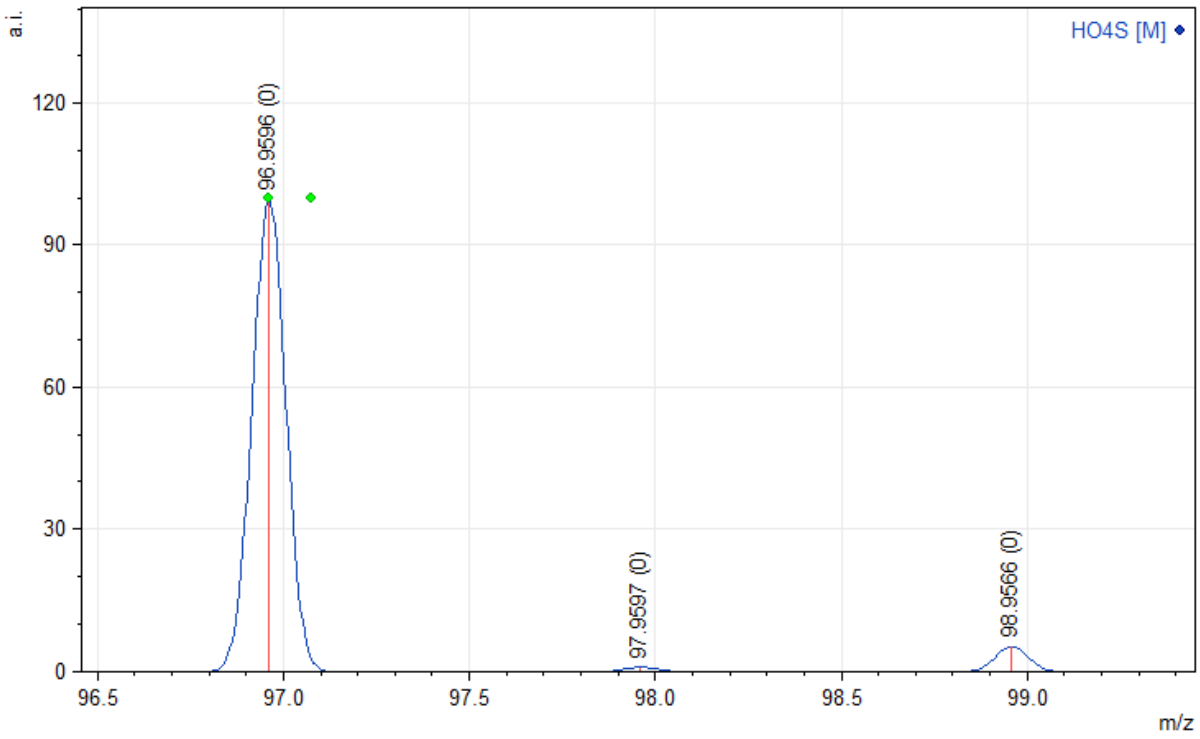
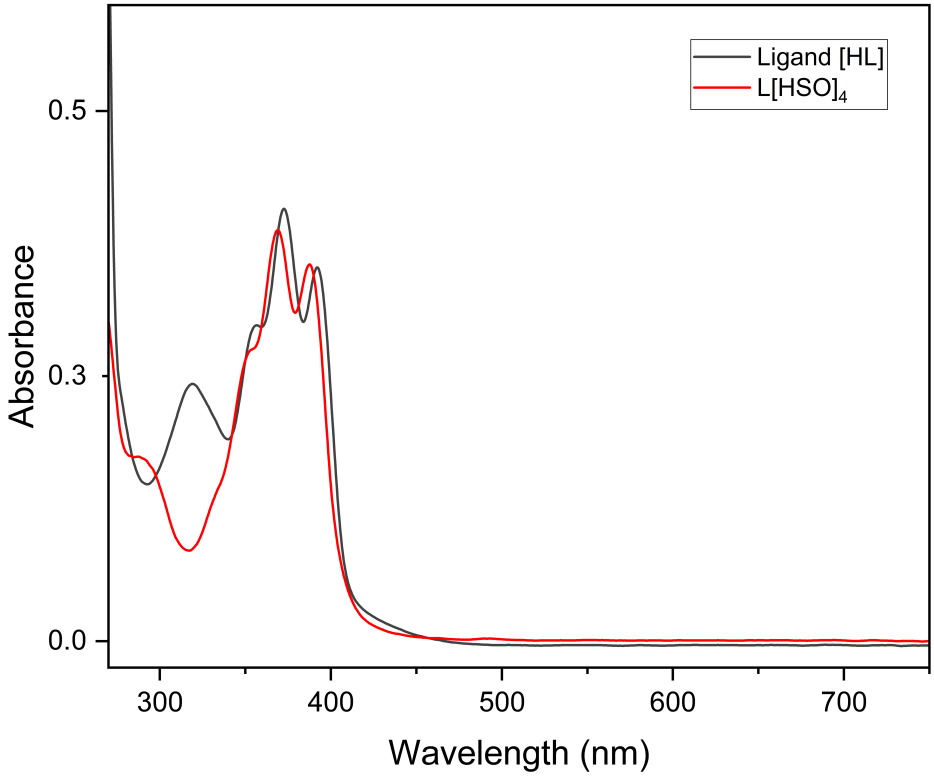


Figure S 22. UV-vis spectrum of 0.01mM [HL] and 0.01mM [$LHSO_4$] in DCM at RT



Compounds [HL] (left) and [$LHSO_4$] (right)

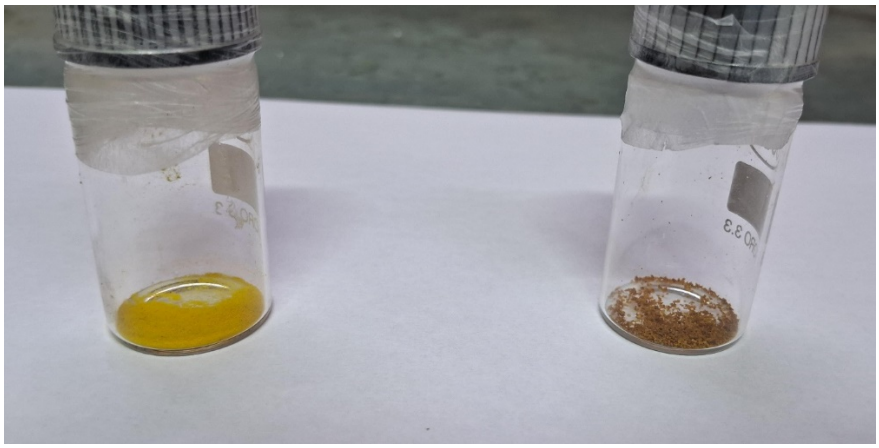


Figure S 23. UV-Vis spectrum of [NiL_2] (0.00735 mM in DCM)

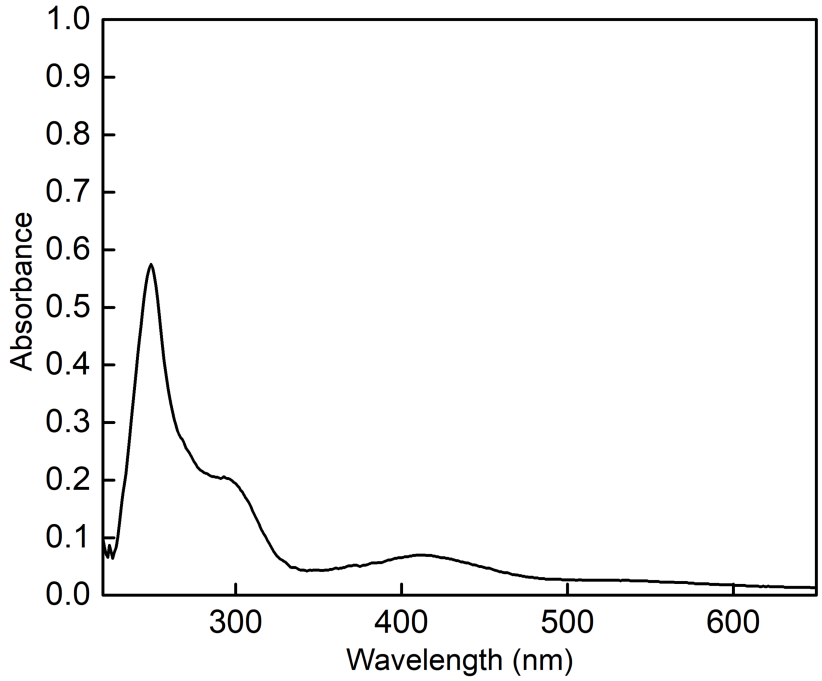


Figure S 24. UV-Vis spectrum of [ZnL_2] (0.00735 mM in DCM)

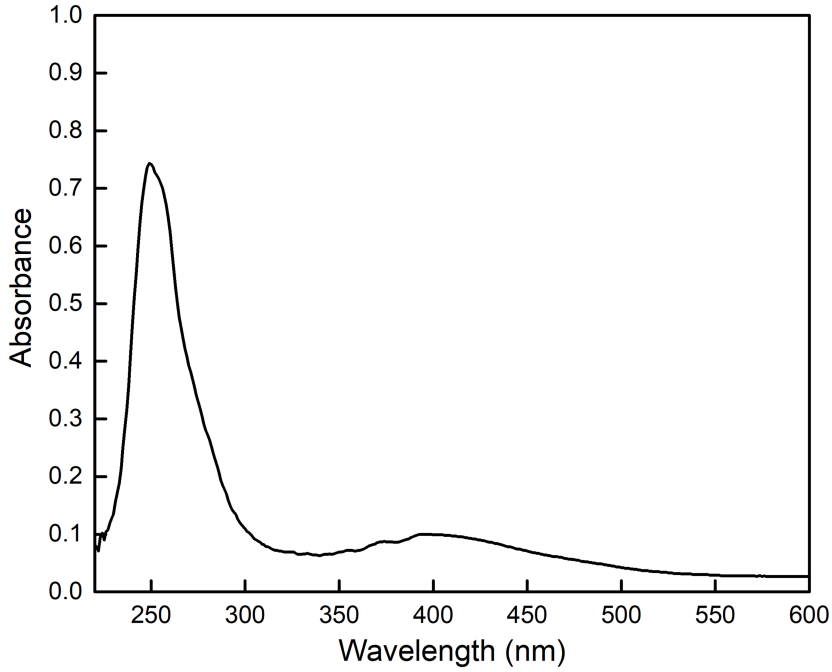


Figure S 25. UV-Vis spectrum of [CdL_2] (0.00735 mM in DCM)

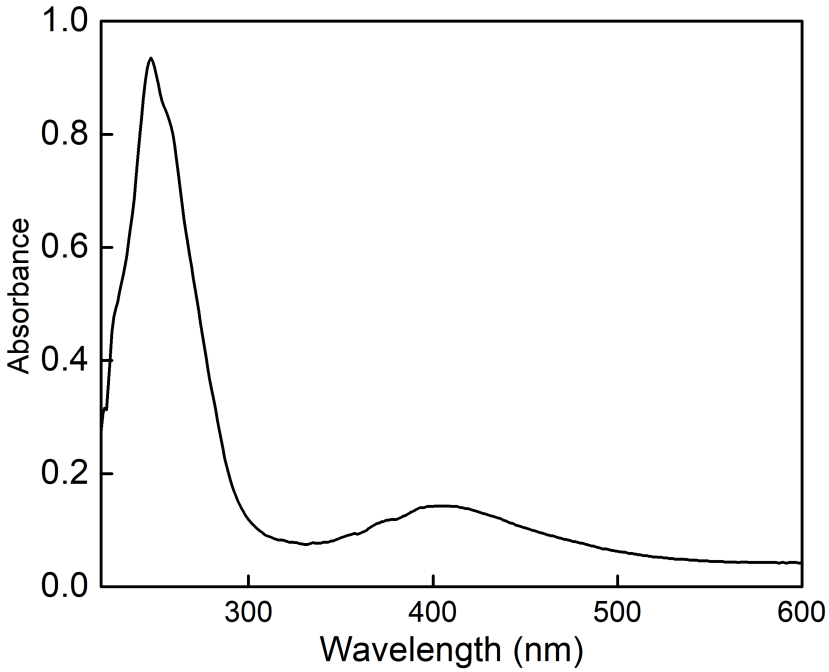
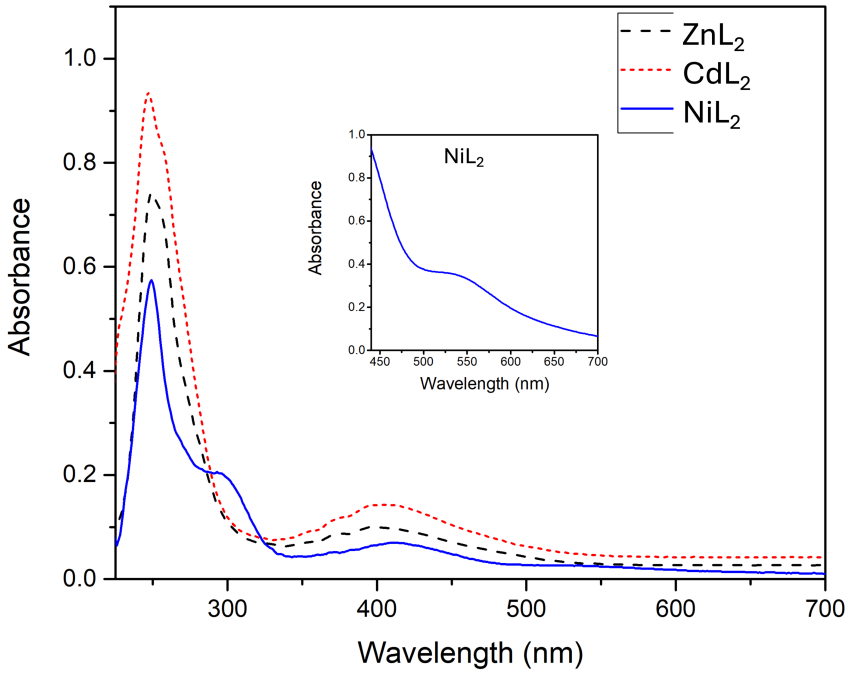
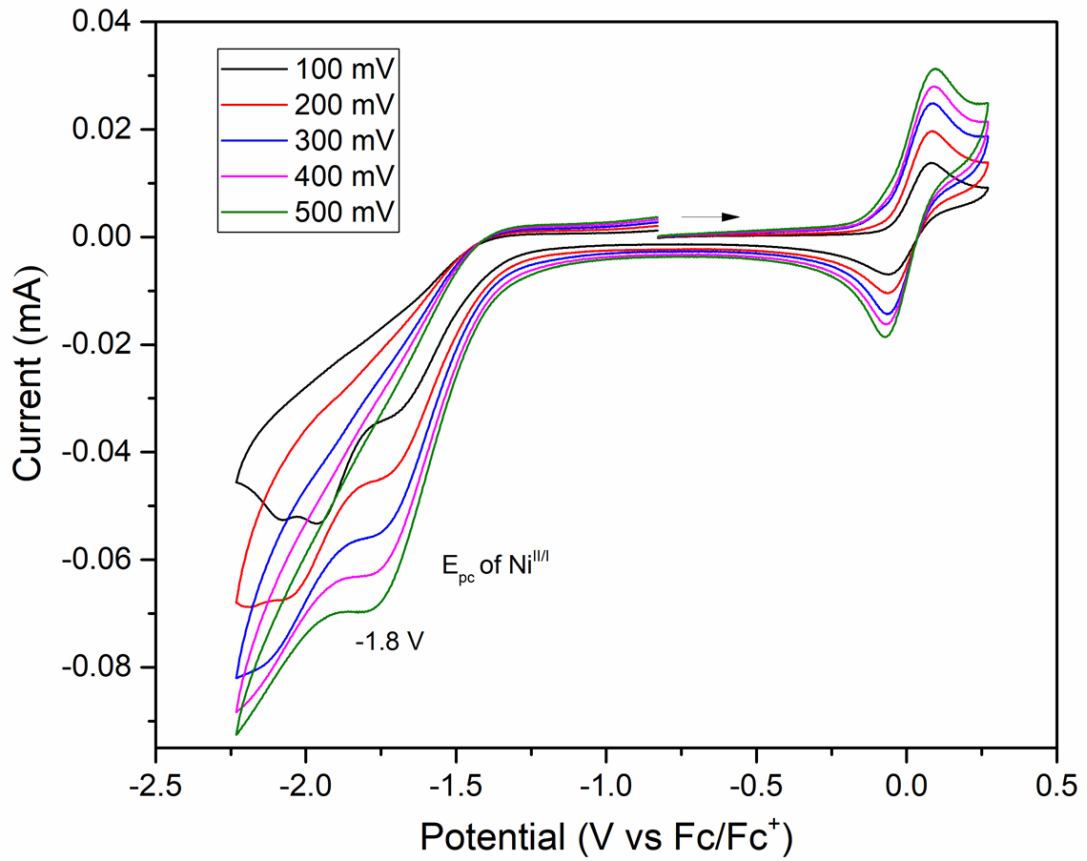


Figure S 26. UV-Vis spectrum of [NiL_2], [CdL_2] and [NiL_2].



UV-Vis spectrum of [NiL_2], [CdL_2] and [NiL_2] (0.00735 mM in DCM) and [NiL_2](0.1 mM) (inset)

Figure S 27. Cyclic Voltammetry (CV) of [NiL_2].



Cyclic voltammogram of the [NiL_2] in CH_2Cl_2 at different scan rates. The reversible event centred around 0.0 V is of ferrocene (internal standard). GC working electrode; Pt counter electrode; Ag/AgCl reference electrode was used at 25 °C with the solution concentration of 1 mM and 0.1 M NBu_4PF_6.

Figure S 28. Thermogravimetric analysis of $[NiL_2]\cdot 2SO_2$

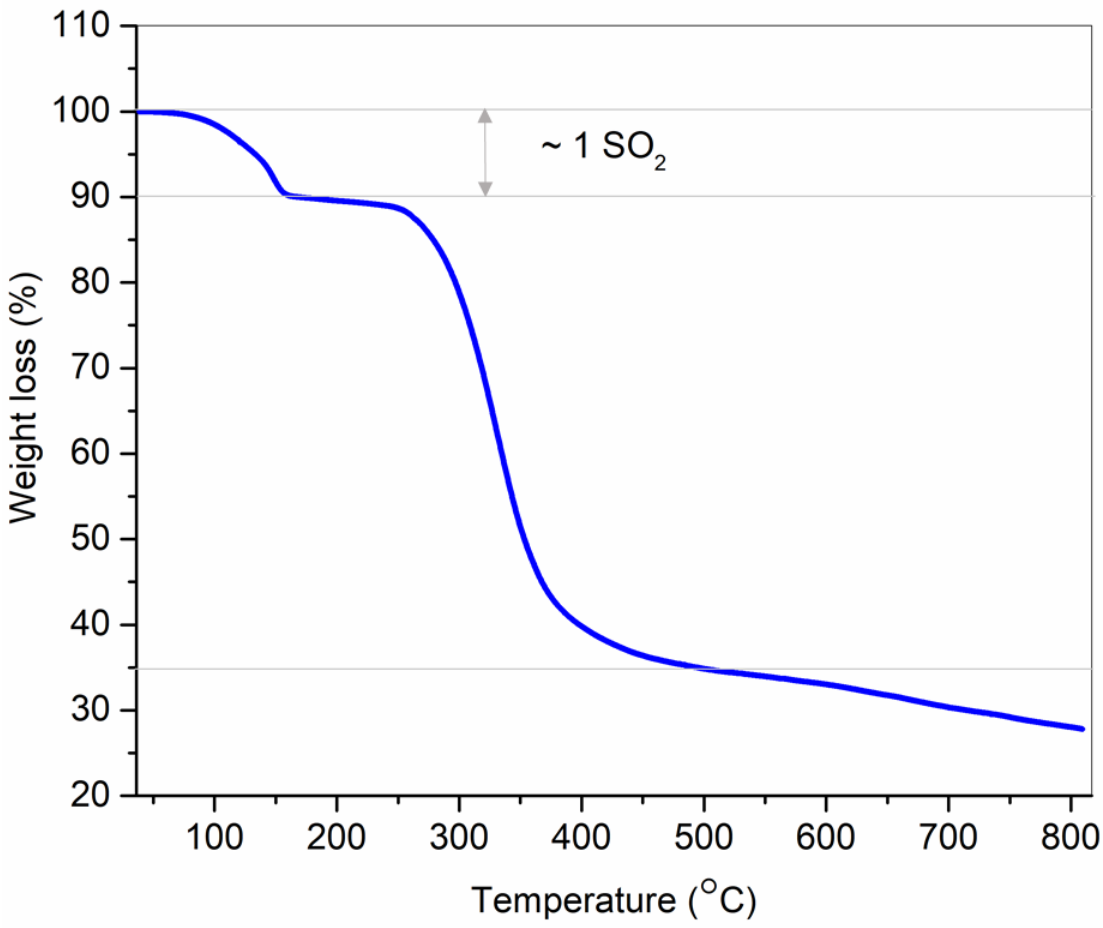


Figure S 29. FT-IR for [NiL_2] and [NiL_2]·$2SO_2$

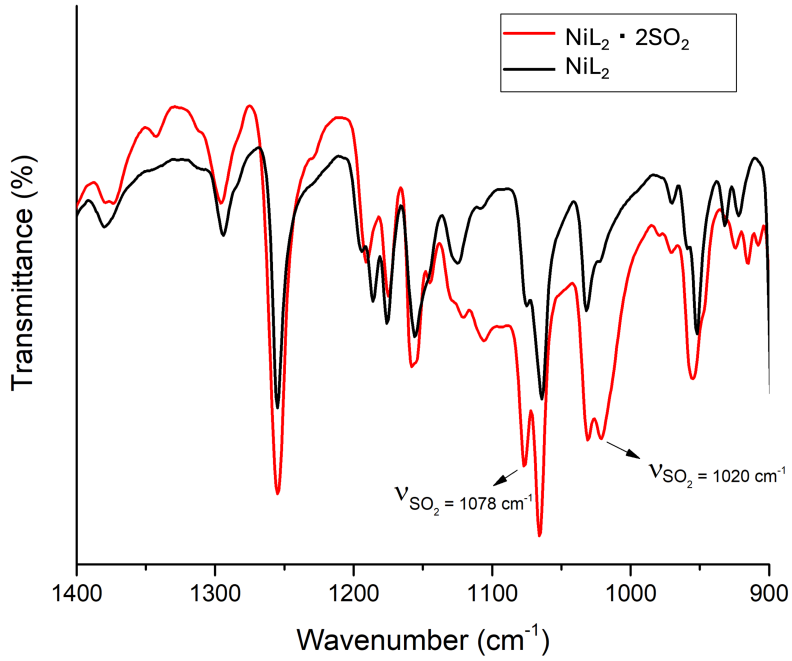
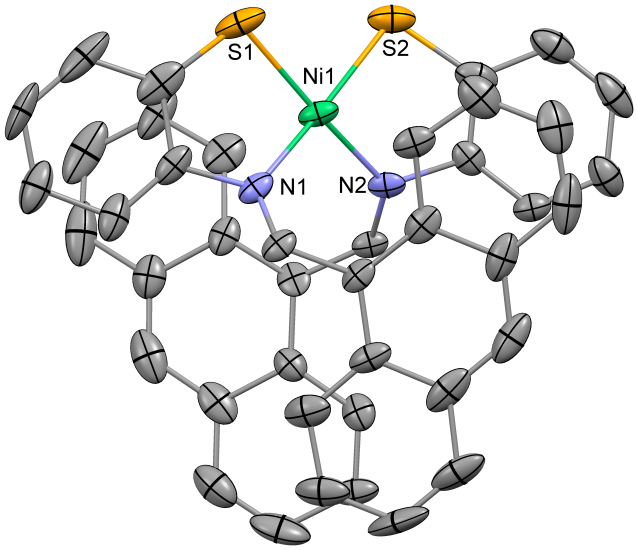
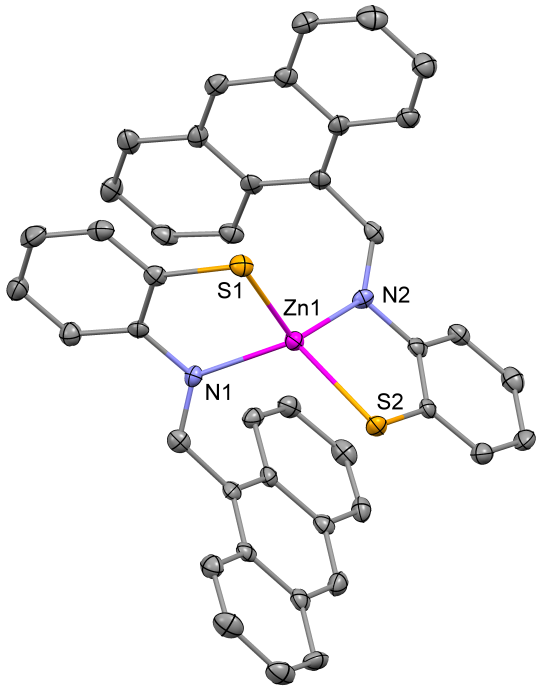


Figure S 30. ORTEP of [NiL_2] drawn at 50% probability



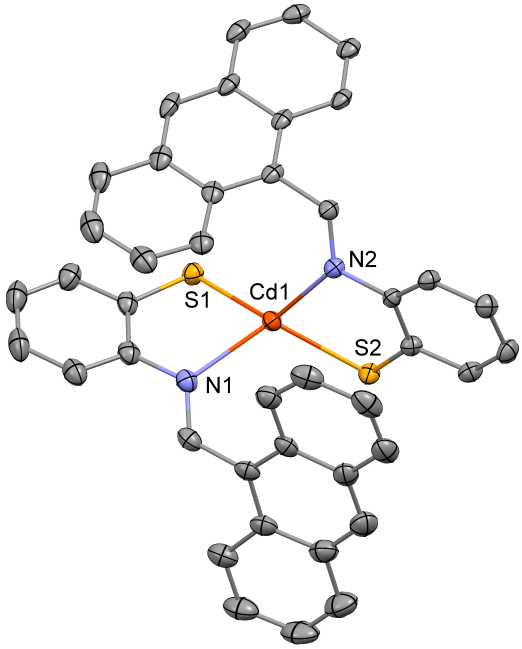
Hydrogen atoms and solvent molecules are omitted for clarity. Selected distances [Å] and angles [°]: Ni(1)-S(1), 2.187(2); Ni(1)-S(2), 2.186(2); Ni(1)-N(2), 1.930(5); Ni(1)-N(1), 1.914(6); S(2)-Ni(1)-S(1), 87.19(8); N(2)-Ni(1)-S(1), 171.70(16); N(2)-Ni(1)-S(2), 86.54(17); N(1)-Ni(1)-S(1), 87.24(17); N(1)-Ni(1)-S(2), 170.51(17); N(1)-Ni(1)-N(2), 99.9(2).

Figure S 31. ORTEP of [ZnL_2] drawn at 50% probability



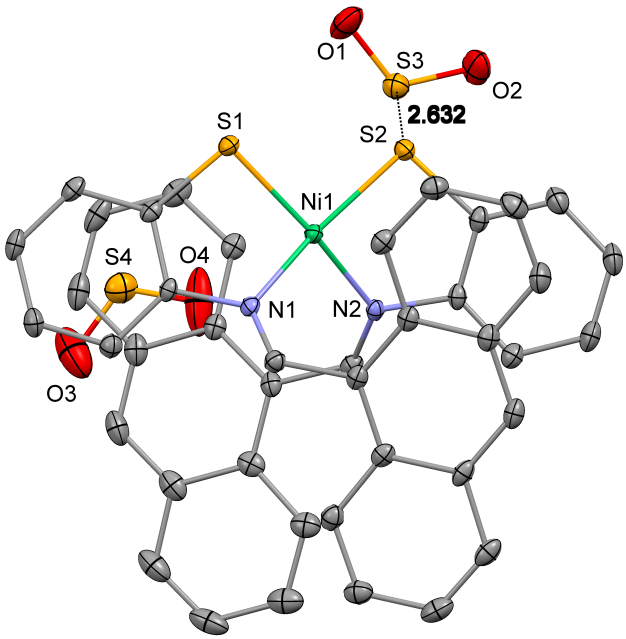
Hydrogen atoms and solvent molecules are omitted for clarity. Selected distances [Å] and angles [°]: Zn(1)-S(1), 2.2764(11); Zn(1)-S(2), 2.2751(10); Zn(1)-N(2), 2.080(3); Zn(1)-N(1), 2.087(3); S(2)-Zn(1)-S(1), 129.04(4); N(2)-Zn(1)-S(2), 88.01(9); N(2)-Zn(1)-S(1), 118.32(9); N(1)-Zn(1)-S(2), 116.19(9); N(1)-Zn(1)-S(1), 87.34(9); N(1)-Zn(1)-N(2), 121.93(12).

Figure S 32**.** ORTEP of [CdL_2] drawn at 50% probability



Hydrogen atoms and solvent molecules are omitted for clarity. Selected distances [Å] and angles [°]: Cd(1)-S(1), 2.4432(7); Cd(1)-S(2), 2.4403(7); Cd(1)-N(2), 2.306(2); Cd(1)-N(1), 2.336(2); S(2)-Cd(1)-S(1), 132.66(2); N(2)-Cd(1)-S(2), 81.77(5); N(2)-Cd(1)-S(1), 125.17(5); N(1)-Cd(1)-S(2), 118.32(6); N(1)-Cd(1)-S(1), 81.08(6); N(2)-Cd(1)-N(1), 123.66(7).

Figure S 33. ORTEP of $[NiL_2]\cdot 2SO_2$ drawn at 50% probability



Hydrogen atoms and solvent molecules are omitted for clarity. Selected distances [Å] and angles [°]: Ni(1)-S(1), 2.1791(5); Ni(1)-S(2), 2.1840(6); Ni(1)-N(2), 1.9231(16); Ni(1)-N(1), 1.9037(16); S(3)-O(2), 1.4371(18); S(3)-O(1), 1.4358(18); S(4)-O(4), 1.396(2); S(4)-O(3), 1.408(2) S(1)-Ni(1)-S(2), 94.05(2); N(1)-Ni(1)-S(1), 87.28(5); N(1)-Ni(1)-S(2), 162.03(6); N(1)-Ni(1)-N(2), 95.90(7); N(2)-Ni(1)-S(1), 164.93(5); N(2)-Ni(1)-S(2), 87.46(5); O(1)-S(3)-O(2), 115.86(12); O(4)-S(4)-O(3), 117.23(17).

Table S 1. Crystallographic data for $[NiL_2]\cdot 2CHCl_3$

Identification code	22octa	2348655
Empirical formula	C44 H30 Cl6 N2 Ni S2	
Molecular weight	922.21	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	Cc	
Unit cell dimensions	a = 22.540(3) Å	α = 90°
	b = 7.2448(8) Å	β = 95.286(5)°
	C = 24.023(3) Å	γ = 90°
Volume	3906.3(8) $Å^3$	
Z	2	
Density (calculated)	1.162 mg/m^3	
Absorption coefficient	0.632 mm^{-1}	
F(000)	1416.0	
Crystal size	0.26 x 0.24 x 0.22 mm^3	
Theta range for data collection	5.91 to 50.098°	
Index ranges	-26<=h<=26,-8<=k<=8,-28<=1<=28	
Reflections collected	21812	
Independent reflections	6914 [R_{int} = 0.0516, R_{sigma} = 0.0664]	
Completeness to theta = 25.049°	100%	
Absorption correction	Semi-empirical from equivalents	
Max. and min transmission	0.746 and 0.674	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	6916/2/424	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2 sigma(I)]	R1 = 0.0478, wR2 = 0.1123	
R indices (all data)	R1= 0.0611, wR2 = 0.1198	
Largest diff. peak and hole	0.32 and -0.27 e.$Å^{-3}$	
Flack parameter	0.11(2)	

Table S 2. Crystallographic data for $[ZnL_2]\cdot 2CHCl_3$

Identification code	17decd_0m_a	2348657
Empirical formula	C44 H30 Cl6 N2 S2 Zn	
Molecular weight	928.89	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.5194(8) Å	α = 90°
	b = 14.7126(9) Å	β = 96.677(2)°
	C = 24.0486(15) Å	γ = 90°
Volume	4048.1(5)$Å^3$	
Z	4	
Density (calculated)	1.524 mg/m^3	
Absorption coefficient	1.142 mm^{-1}	
F(000)	1888.0	
Crystal size	0.29 x 0.23x 0.13 mm^3	
Theta range for data collection	4.392 to 50.1°	
Index ranges	-13<=h<=13,-17<=k<=17,-28<=1<=28	
Reflections collected	19051	
Independent reflections	9921 [R_{int} = 0.0868, R_{sigma} = 0.1112]	
Completeness to theta = 28.321°	98.4%	
Absorption correction	Semi-empirical from equivalents	
Max. and min transmission	0.746 and 0.674	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	9921/0/496	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2 sigma(I)]	R1 = 0.0634, wR2 = 0.1249	
R indices (all data)	R1= 0.1136 R2 = 0.1432	
Largest diff. peak and hole	0.70 and -0.91 e.$Å^{-3}$	

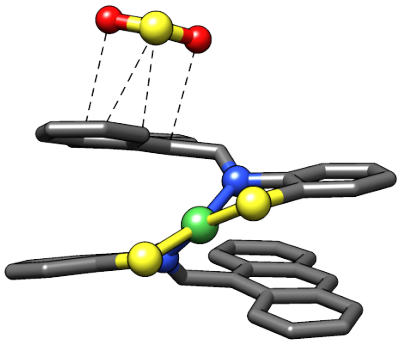
Table S 3. Crystallographic data for $[CdL_2]_3 \cdot 2(C_2H_5)_2O$

Identification code	24decd_a	2348658
Empirical formula	C134 H104 Cd3 N6 O2 S6	
Molecular weight	2359.79	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 31.979(3) Å	α = 90°
	b = 7.7793(6)Å	β = 91.219(4)°
	C = 42.007(3) Å	γ = 90°
Volume	10448.0(14)$Å^3$	
Z	12	
Density (calculated)	1.406 mg/m^3	
Absorption coefficient	0.779 mm^{-1}	
F(000)	4488.0	
Crystal size	0.26 x 0.24 x 0.22 mm^3	
Theta range for data collection	4.596 to 56.74°	
Index ranges	-42<=h<=42,-10<=k<=10,-56<=1<=55	
Reflections collected	82669	
Independent reflections	13058 [R_{int} = 0.0587, R_{sigma} = 0.0393]	
Completeness to theta = 28.370°	99.8%	
Absorption correction	Semi-empirical from equivalents	
Max. and min transmission	0.746 and 0.673	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	13058/0/636	
Goodness-of-fit on F^2	1.158	
Final R indices [I>2 sigma(I)]	R1 = 0.0386, wR2 = 0.1090	
R indices (all data)	R1= 0.0549 R2 = 0.1209	
Largest diff. peak and hole	0.62 and -0.66 e.$Å^{-3}$	

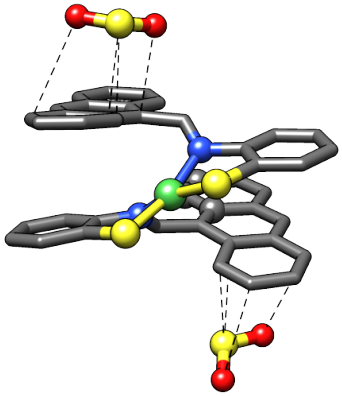
Table S 4. Crystallographic data for $[NiL_2]\cdot 2SO_2$

Identification code	2dece_0m_a	2348656
Empirical formula	$C_{42}H_{28}N_2NiO_4S_4$	
Molecular weight	811.61	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.0523(3) Å	α = 90°
	b = 19.6399(6)Å	β = 100.2670(10)°
	C = 16.1066(5) Å	γ = 90°
Volume	3440.22(18)$Å^3$	
Z	4	
Density (calculated)	1.567 mg/m^3	
Absorption coefficient	0.857 mm^{-1}	
F(000)	1672.0	
Crystal size	0.26 x 0.24 x 0.22 mm^3	
Theta range for data collection	4.596 to 56.74°	
Index ranges	-14<=h<=14,-26<=k<=26,-21<=1<=21	
Reflections collected	54743	
Independent reflections	8565 [R_{int} = 0.0527, R_{sigma} = 0.0356]	
Completeness to theta = 28.323°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min transmission	0.746 and 0.693	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	8571/0/478	
Goodness-of-fit on F^2	1.193	
Final R indices [I>2 sigma(I)]	R1 = 0.0365, wR2 = 0.0729	
R indices (all data)	R1= 0.0529 R2 = 0.0829	
Largest diff. peak and hole	0.69 and -0.52 e.$Å^{-3}$	

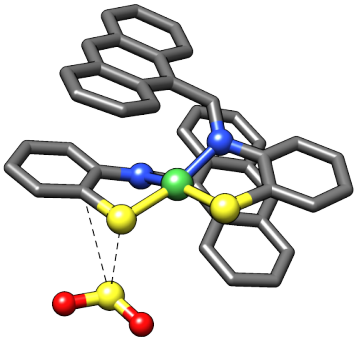
Figure S 34. Optimized structures and computed SO_2 free energies.



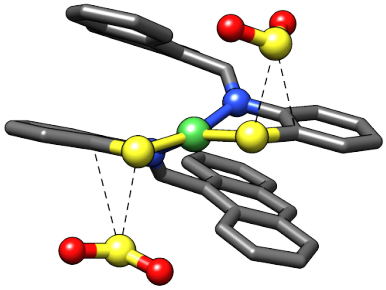
ΔG_{SO2} = +1.40 kcal/mol



ΔG_{SO2} = +0.62 kcal/mol



ΔG_{SO2} = –4.18 kcal/mol



ΔG_{SO2} = –7.15 kcal/mol

Optimized structures (in Å) and computed SO_2 free energies (in kcal/mol)bound to [NiL_2] species in different orientations and stoichiometry.

Figure S 35. Superposition of Zn- and Cd-optimized structures on the [NiL_2] complex

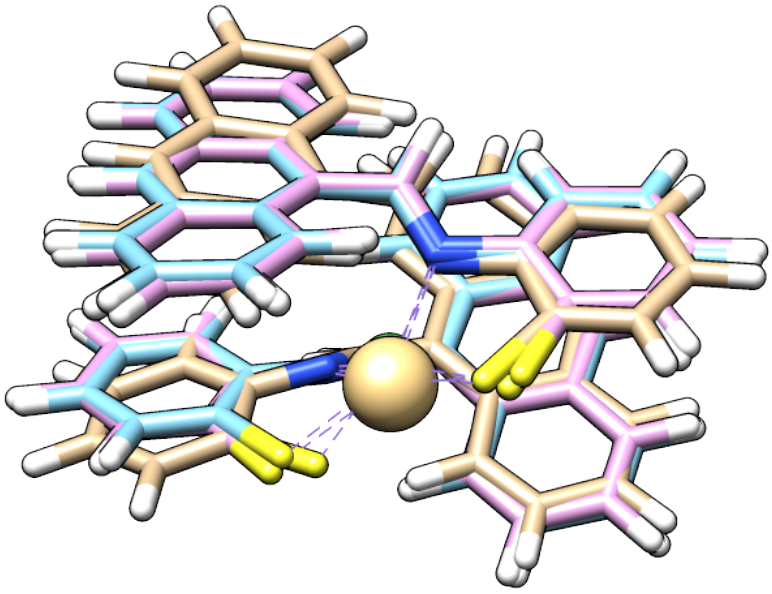


Figure S 36. Optimized structures of Ni-complex in singlet (S=0) and triplet (S=1).

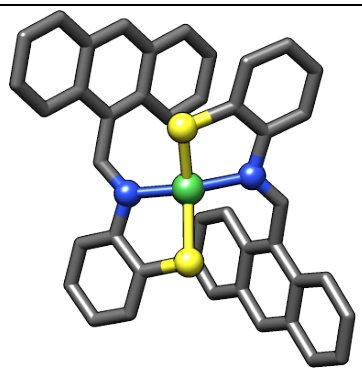
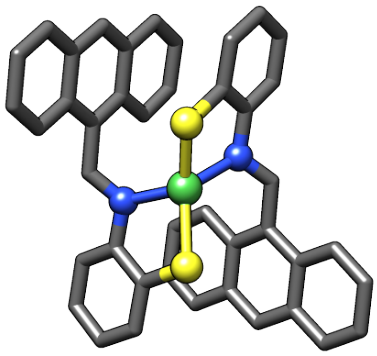
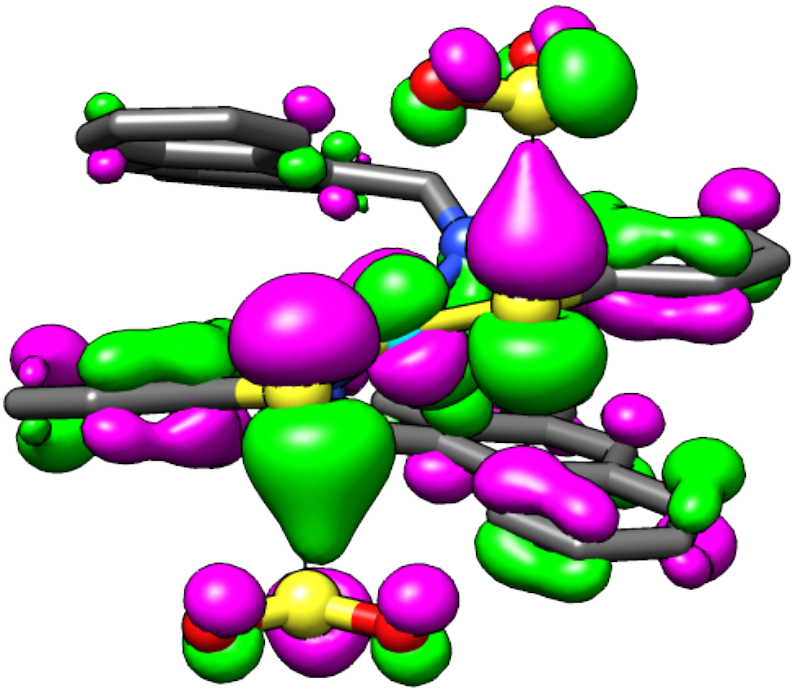
	
ΔE = +23.46 kcal/mol	ΔE = + 5.12 kcal/mol
Optimized structures of Ni-complex in singlet (S=0) and triplet (S=1) using [ZnL_2] X-ray structure.	

Figure S 37. Highest Occupied Molecular Orbital (HOMO) of SO_2.



Highest Occupied Molecular orbital (HOMO) of SO_2 indicating the favorable interaction of SO_2 with the thiolate of $[NiL_2]$ molecule (contour value: 0.03 a.u)

Table S 5. Optimized coordinates (in Å) of Ni, Zn and Cd complexes.

[NiL_2]

Ni	8.320232000	6.396149000	11.381054000
S	8.800166000	6.070426000	9.256977000
S	6.313375000	7.098108000	10.812918000
N	7.889035000	7.119050000	13.230191000
N	10.025678000	5.364409000	11.771827000
C	10.522087000	5.857688000	9.484012000
C	11.011700000	5.541127000	10.760758000
C	6.499808000	7.060157000	13.533912000
C	7.356092000	3.859649000	12.368551000
H	7.957850000	3.908742000	11.474346000
C	5.997148000	6.990176000	14.830316000
H	6.674044000	6.893551000	15.669091000
C	12.379152000	5.421011000	10.992142000
H	12.745643000	5.261838000	11.997806000
C	9.955747000	4.041472000	15.098794000
C	10.492617000	9.184827000	10.393324000
H	9.871023000	9.493960000	9.564048000
C	7.977935000	3.954161000	13.645536000
C	11.899795000	9.149105000	10.242577000
H	12.343712000	9.415738000	9.292620000
C	5.182828000	3.598974000	13.398991000
H	4.111371000	3.504032000	13.283299000

C	6.006036000	3.696698000	12.251805000
H	5.560911000	3.659897000	11.266741000
C	13.276605000	5.571348000	9.946572000
H	14.340232000	5.504162000	10.132787000
C	4.258108000	7.089950000	12.661634000
H	3.583660000	7.113833000	11.815481000
C	8.682049000	7.716581000	14.046894000
H	8.248218000	8.119664000	14.959106000
C	10.118331000	7.903802000	13.883015000
C	3.761613000	7.048664000	13.954656000
H	2.690492000	7.041860000	14.115090000
C	5.744675000	3.603713000	14.639072000
H	5.132901000	3.497395000	15.526040000
C	9.362026000	4.183203000	13.821085000
C	7.151098000	3.750859000	14.804167000
C	11.439937000	5.987817000	8.436273000
H	11.073245000	6.223577000	7.445726000
C	9.119784000	3.775255000	16.235916000
C	5.637371000	7.080013000	12.426851000
C	12.686441000	8.800286000	11.297515000
H	13.765472000	8.797084000	11.207866000
C	11.894161000	3.972495000	16.566202000
H	12.963236000	4.063688000	16.705122000
C	11.356827000	4.165227000	15.327509000

H	12.015299000	4.427153000	14.512774000
C	7.740572000	3.681241000	16.062028000
H	7.110695000	3.517915000	16.929376000
C	10.938574000	7.667548000	15.011425000
C	9.903204000	8.812344000	11.566134000
H	8.829394000	8.868783000	11.654586000
C	10.244808000	4.511533000	12.709212000
H	11.196086000	3.985825000	12.687686000
C	12.798584000	5.839707000	8.664981000
H	13.494195000	5.960473000	7.843708000
C	4.627745000	6.983173000	15.044955000
H	4.238262000	6.904474000	16.051213000
C	12.909700000	8.127786000	13.645485000
H	13.987660000	8.185459000	13.543864000
C	10.421708000	7.289776000	16.284341000
H	9.361648000	7.123172000	16.406624000
C	12.112415000	8.423783000	12.544774000
C	9.716530000	3.611270000	17.517912000
H	9.067886000	3.408135000	18.361692000
C	12.363366000	7.792845000	14.882970000
C	10.681299000	8.360373000	12.669249000
C	11.241823000	7.118314000	17.360447000
H	10.818728000	6.840635000	18.316484000
C	12.645176000	7.262384000	17.233634000

H	13.280246000	7.110205000	18.096850000
C	11.067213000	3.689169000	17.680473000
H	11.511883000	3.549871000	18.657461000
C	13.187693000	7.573435000	16.022817000
H	14.260139000	7.673796000	15.905629000

[ZnL_2]

Zn	7.453425000	10.980623000	12.012455000
S	8.275825000	11.780204000	10.030112000
S	8.456569000	10.136256000	13.891746000
N	6.260100000	9.645956000	10.832698000
N	6.510066000	12.405054000	13.305448000
C	6.084861000	8.418748000	11.169947000
H	5.973704000	7.669149000	10.384637000
C	5.279806000	8.588540000	13.529592000
C	7.057477000	15.046506000	11.068298000
C	6.366842000	13.634385000	12.962401000
H	6.416113000	14.405982000	13.732915000
C	6.939758000	6.894615000	12.901592000
C	6.185377000	14.064442000	11.579275000
C	7.033292000	6.488603000	14.274662000
C	4.323846000	9.595722000	13.217954000
H	4.199663000	9.900018000	12.191359000
C	5.186135000	13.490081000	10.766932000
C	8.621012000	5.236428000	12.333767000
H	9.248411000	4.754929000	11.594700000
C	6.973611000	11.389076000	7.659682000
H	7.651468000	12.147234000	7.289065000
C	6.083779000	7.960791000	12.555283000
C	4.226347000	12.559141000	11.254708000

H	4.254661000	12.272971000	12.293690000
C	3.571166000	10.179983000	14.194006000
H	2.850454000	10.944081000	13.930223000
C	5.233033000	9.464509000	8.621403000
H	4.522443000	8.749546000	9.018422000
C	5.871874000	12.339883000	16.960378000
H	5.244668000	12.835926000	17.689400000
C	7.780268000	6.243343000	11.955624000
H	7.771355000	6.561571000	10.922257000
C	6.584126000	12.047987000	14.668207000
C	3.723169000	9.806907000	15.552212000
H	3.136240000	10.302312000	16.314074000
C	7.062804000	11.028576000	9.011523000
C	3.281531000	12.023346000	10.430400000
H	2.562862000	11.316167000	10.826111000
C	6.950896000	15.430463000	9.690271000
C	8.105274000	15.619539000	11.841655000
H	8.244348000	15.308165000	12.868014000
C	6.272107000	7.149706000	15.234453000
H	6.366110000	6.856378000	16.274079000
C	5.393710000	8.175098000	14.899975000
C	6.179342000	10.031281000	9.477458000
C	4.606714000	8.827962000	15.889927000
H	4.730365000	8.527459000	16.922609000

C	7.507556000	10.661404000	16.401060000
H	8.172571000	9.861773000	16.700868000
C	5.983233000	14.831453000	8.888844000
H	5.922176000	15.106825000	7.842008000
C	7.863578000	16.386176000	9.163700000
H	7.771029000	16.664412000	8.120825000
C	5.098308000	13.882097000	9.388449000
C	8.696840000	4.824667000	13.687663000
H	9.376559000	4.030262000	13.968120000
C	7.927404000	5.440049000	14.629416000
H	7.988712000	5.147359000	15.670613000
C	8.963102000	16.533138000	11.300236000
H	9.754917000	16.952943000	11.907436000
C	7.446739000	10.994115000	15.040279000
C	6.051450000	10.802163000	6.811008000
H	6.008879000	11.110076000	5.773408000
C	5.795037000	12.691379000	15.623429000
H	5.089427000	13.448277000	15.302838000
C	8.841564000	16.926710000	9.944012000
H	9.536497000	17.646778000	9.531445000
C	6.744782000	11.325267000	17.346048000
H	6.814080000	11.035842000	18.387542000
C	4.109577000	13.283220000	8.557968000
H	4.078153000	13.566373000	7.513355000

C	3.228841000	12.374461000	9.058523000
H	2.487757000	11.917953000	8.415880000
C	5.165709000	9.839468000	7.290548000
H	4.419512000	9.402715000	6.639875000

[CdL_2]

Cd	7.992640000	0.918109000	25.994454000
S	5.575652000	1.250820000	26.216268000
S	9.864302000	-0.623688000	26.345841000
N	7.974341000	3.029358000	27.133023000
N	8.925228000	0.892239000	23.784394000
C	10.676649000	2.205045000	29.280315000
C	10.191081000	2.746091000	28.068925000
C	9.891900000	2.141216000	30.467537000
H	8.872345000	2.499428000	30.456180000
C	11.010490000	2.776705000	26.917093000
C	10.396552000	1.615681000	31.622211000
H	9.780719000	1.586300000	32.512002000
C	11.999822000	1.649763000	29.324915000
C	12.325632000	2.199981000	26.977143000
C	6.600481000	5.004297000	27.493455000
H	7.496615000	5.555113000	27.751733000
C	5.375632000	5.648065000	27.485219000
H	5.308355000	6.692305000	27.761312000
C	11.712205000	1.091015000	31.667589000
H	12.091159000	0.673414000	32.591382000
C	10.737975000	-0.341553000	24.846585000
C	6.851005000	1.575883000	22.756892000
C	10.212458000	0.331735000	23.719334000

C	4.349023000	3.618638000	26.700565000
H	3.469142000	3.075166000	26.381331000
C	5.577302000	2.940596000	26.698439000
C	12.777467000	1.647376000	28.170492000
H	13.768276000	1.208728000	28.204841000
C	12.484977000	1.100484000	30.545077000
H	13.485950000	0.686611000	30.559237000
C	8.146574000	0.896844000	22.765872000
H	8.439623000	0.351802000	21.865224000
C	4.241947000	4.940462000	27.094776000
H	3.274476000	5.427048000	27.077266000
C	6.717057000	3.659351000	27.127439000
C	5.721431000	0.858718000	22.309017000
C	10.621553000	3.399084000	25.698117000
H	9.650875000	3.860672000	25.633342000
C	6.726862000	2.913972000	23.192084000
C	8.831495000	3.279879000	28.054106000
H	8.533379000	3.904750000	28.898672000
C	5.792034000	-0.492928000	21.866381000
H	6.741860000	-1.009237000	21.872640000
C	12.038022000	-0.857630000	24.741341000
H	12.447462000	-1.379877000	25.596231000
C	7.840150000	3.722337000	23.555908000
H	8.829433000	3.299779000	23.506284000

C	5.424718000	3.519771000	23.232127000
C	10.996272000	0.498059000	22.572836000
H	10.599602000	1.076676000	21.747635000
C	11.450555000	3.411144000	24.614588000
H	11.126800000	3.890017000	23.698928000
C	13.149900000	2.216491000	25.816528000
H	14.125219000	1.750000000	25.875196000
C	7.673556000	5.011384000	23.969582000
H	8.539434000	5.602199000	24.241908000
C	12.793049000	-0.711508000	23.591080000
H	13.795703000	-1.119257000	23.554292000
C	6.383270000	5.589416000	24.055073000
H	6.271044000	6.604421000	24.411513000
C	5.293114000	4.861202000	23.689612000
H	4.299716000	5.287956000	23.743855000
C	4.429979000	1.484169000	22.346834000
C	4.675474000	-1.159783000	21.450950000
H	4.756761000	-2.185166000	21.113511000
C	4.316727000	2.787137000	22.822340000
H	3.335864000	3.246653000	22.870443000
C	12.727189000	2.801256000	24.662656000
H	13.355327000	2.798774000	23.782595000
C	12.278187000	-0.018583000	22.498738000
H	12.874279000	0.131431000	21.608052000

C	3.404955000	-0.532041000	21.472555000
H	2.530790000	-1.081068000	21.147124000
C	3.288913000	0.751146000	21.916555000
H	2.321994000	1.238157000	21.954410000

[NiL_2] without SO_2

Ni	5.332932000	12.378611000	3.709384000
S	5.507709000	12.000649000	1.544214000
S	7.476281000	12.845760000	3.929161000
N	3.414781000	12.431779000	3.429603000
N	5.273560000	12.278406000	5.650441000
C	1.900020000	15.700463000	8.218352000
H	2.210622000	16.473668000	8.910625000
C	4.464127000	16.204224000	5.549693000
C	1.344170000	10.150330000	1.323753000
H	0.370434000	9.679127000	1.307315000
C	5.800315000	16.042557000	3.098123000
H	6.310083000	15.992039000	2.145382000
C	2.643869000	15.535500000	7.016976000
C	3.749914000	16.332898000	6.735093000
H	4.061396000	17.077758000	7.458454000
C	3.522177000	10.485149000	0.330260000
H	4.233480000	10.287722000	-0.461239000
C	4.068147000	15.212475000	4.585396000
C	3.778620000	10.348540000	5.871069000
C	2.254722000	9.925515000	0.291698000
H	1.979142000	9.287480000	-0.538940000
C	2.966592000	11.544239000	2.414348000
C	0.997471000	10.545224000	8.361380000

H	0.723642000	11.117710000	9.238087000
C	3.910863000	11.290963000	1.405395000
C	6.143544000	13.212098000	6.274084000
C	2.157527000	10.837139000	7.704191000
H	2.762769000	11.658022000	8.059296000
C	1.681526000	9.072764000	6.082095000
C	2.607674000	13.269936000	3.976618000
H	1.553348000	13.209009000	3.711485000
C	2.565910000	10.099652000	6.558611000
C	2.257282000	14.511638000	6.085230000
C	1.142797000	13.695823000	6.426232000
H	0.855974000	12.882569000	5.774507000
C	5.908269000	13.770675000	7.524801000
H	4.988890000	13.551553000	8.052505000
C	5.579040000	17.043876000	5.271113000
H	5.886205000	17.752529000	6.029680000
C	7.281822000	13.548668000	5.523186000
C	7.975870000	14.980512000	7.345142000
H	8.691653000	15.680469000	7.758466000
C	4.747414000	15.206767000	3.334289000
H	4.434788000	14.533583000	2.553703000
C	6.242524000	16.954915000	4.085308000
H	7.098142000	17.587828000	3.887201000
C	6.822234000	14.665340000	8.061471000

H	6.627486000	15.127419000	9.020452000
C	5.457290000	9.561977000	4.196183000
H	6.216152000	10.211522000	4.602320000
C	8.204554000	14.431212000	6.092550000
H	9.090275000	14.698186000	5.530807000
C	4.634377000	11.419000000	6.364894000
H	4.747255000	11.488628000	7.444575000
C	4.165364000	9.520872000	4.789528000
C	0.467923000	8.816629000	6.778643000
H	-0.183548000	8.036637000	6.402716000
C	0.819889000	14.913259000	8.492051000
H	0.255909000	15.053739000	9.405001000
C	3.003258000	14.332945000	4.899075000
C	1.700221000	10.971359000	2.383672000
H	1.013101000	11.129449000	3.205362000
C	0.439407000	13.900343000	7.578156000
H	-0.406071000	13.264686000	7.805531000
C	3.238465000	8.540119000	4.292160000
C	0.136850000	9.521377000	7.897634000
H	-0.781382000	9.307891000	8.429832000
C	2.025734000	8.350271000	4.942569000
H	1.336337000	7.604585000	4.562691000
C	4.811425000	7.893109000	2.568589000
H	5.065643000	7.307895000	1.694561000

C	3.588898000	7.762514000	3.153717000
H	2.858416000	7.062856000	2.767301000
C	5.765715000	8.779940000	3.121330000
H	6.749786000	8.854432000	2.678863000

[NiL_2] with one SO_2 bound at the Thiolate site

Ni	5.313857000	12.423044000	3.663707000
S	5.447629000	12.054295000	1.500531000
S	7.437746000	12.984427000	3.823292000
N	3.390044000	12.450800000	3.425558000
N	5.303874000	12.309002000	5.606228000
C	1.903254000	15.680871000	8.250862000
H	2.224688000	16.443849000	8.949635000
C	4.443161000	16.205449000	5.562635000
C	1.315131000	10.130676000	1.366058000
H	0.349309000	9.643217000	1.369938000
C	5.717707000	16.102691000	3.074983000
H	6.198605000	16.081465000	2.106105000
C	2.639564000	15.520896000	7.043651000
C	3.748112000	16.314946000	6.761645000
H	4.070828000	17.048334000	7.491697000
C	3.469783000	10.495302000	0.331802000
H	4.170746000	10.304975000	-0.470268000
C	4.030836000	15.229354000	4.589561000
C	3.825080000	10.367269000	5.825463000
C	2.211170000	9.914218000	0.319695000
H	1.932025000	9.266118000	-0.501799000
C	2.933451000	11.554962000	2.420662000

C	1.037595000	10.550714000	8.310165000
H	0.763424000	11.114543000	9.192367000
C	3.861665000	11.313405000	1.395438000
C	6.181900000	13.240977000	6.225071000
C	2.203037000	10.842066000	7.662185000
H	2.811197000	11.655586000	8.029671000
C	1.727735000	9.092421000	6.023163000
C	2.581395000	13.277290000	3.988158000
H	1.524516000	13.198954000	3.739690000
C	2.612359000	10.113995000	6.510864000
C	2.238475000	14.510334000	6.103406000
C	1.115763000	13.703821000	6.440235000
H	0.814365000	12.902585000	5.780861000
C	5.989496000	13.759072000	7.500825000
H	5.096677000	13.512507000	8.060640000
C	5.548546000	17.054755000	5.274883000
H	5.870392000	17.750462000	6.039422000
C	7.284509000	13.629172000	5.451935000
C	8.044809000	14.992096000	7.288984000
H	8.775799000	15.673366000	7.705632000
C	4.679051000	15.252155000	3.322045000
H	4.347867000	14.593436000	2.536324000
C	6.181227000	16.995760000	4.070367000
H	7.026547000	17.639025000	3.862838000

C	6.918392000	14.643049000	8.029891000
H	6.758420000	15.065873000	9.013173000
C	5.507830000	9.588742000	4.155444000
H	6.256952000	10.237228000	4.576158000
C	8.227871000	14.490960000	6.008708000
H	9.095748000	14.768267000	5.425940000
C	4.678443000	11.438595000	6.320996000
H	4.803156000	11.498351000	7.399865000
C	4.215438000	9.543150000	4.742254000
C	0.506861000	8.840227000	6.708437000
H	-0.147028000	8.067684000	6.321820000
C	0.814287000	14.904990000	8.519054000
H	0.253698000	15.043173000	9.434620000
C	2.975777000	14.340716000	4.909925000
C	1.675692000	10.963051000	2.415417000
H	1.000972000	11.111786000	3.248885000
C	0.417624000	13.907106000	7.595615000
H	-0.438071000	13.283243000	7.817561000
C	3.295885000	8.557213000	4.242591000
C	0.171814000	9.538798000	7.830357000
H	-0.752194000	9.328579000	8.353507000
C	2.078450000	8.370012000	4.884975000
H	1.390273000	7.625027000	4.501561000
C	4.890766000	7.903720000	2.539873000

H	5.157854000	7.307702000	1.676833000
C	3.661686000	7.773584000	3.112840000
H	2.939013000	7.066073000	2.725885000
C	5.837222000	8.799912000	3.091701000
H	6.832179000	8.873371000	2.673601000
S	8.868958000	10.753895000	4.719065000
O	10.019533000	11.437887000	5.275247000
O	9.059550000	10.047378000	3.466390000

[NiL_2] with two SO_2 bound at thiolate sites

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symmetry c1

Ni	5.337712000	12.412868000	3.623169000
S	5.491105000	11.839431000	1.502991000
S	7.462164000	12.951726000	3.768170000
N	3.413243000	12.454493000	3.378581000
N	5.334385000	12.322130000	5.564986000
C	1.847907000	15.597336000	8.222288000
H	2.171291000	16.323859000	8.958136000
C	4.467163000	16.162476000	5.619084000
C	1.288204000	10.101310000	1.409076000
H	0.294462000	9.673169000	1.413860000
C	5.775308000	16.135102000	3.143466000
H	6.244639000	16.153288000	2.169922000
C	2.613421000	15.460616000	7.030130000
C	3.745618000	16.240586000	6.804647000
H	4.061559000	16.943130000	7.567451000
C	3.488072000	10.261527000	0.434357000
H	4.207673000	9.971218000	-0.319508000
C	4.064884000	15.223920000	4.606051000
C	3.847597000	10.387303000	5.792516000
C	2.200298000	9.746631000	0.418712000

H	1.912968000	9.048293000	-0.356810000
C	2.942814000	11.525636000	2.410514000
C	1.027227000	10.631374000	8.232707000
H	0.749681000	11.203228000	9.108540000
C	3.876957000	11.145295000	1.438582000
C	6.228420000	13.245717000	6.175162000
C	2.204915000	10.903466000	7.598804000
H	2.820011000	11.710206000	7.970096000
C	1.728680000	9.146890000	5.966397000
C	2.609207000	13.300516000	3.920138000
H	1.557696000	13.237675000	3.650509000
C	2.619566000	10.161259000	6.458704000
C	2.212638000	14.494606000	6.042795000
C	1.052947000	13.716356000	6.315510000
H	0.742224000	12.951905000	5.617913000
C	6.057135000	13.764193000	7.453638000
H	5.169961000	13.525514000	8.025374000
C	5.584571000	17.009959000	5.377022000
H	5.898636000	17.680384000	6.167026000
C	7.325059000	13.621568000	5.389691000
C	8.115139000	14.987190000	7.209532000
H	8.852428000	15.669417000	7.612908000
C	4.730226000	15.281532000	3.351734000
H	4.368157000	14.684197000	2.532389000

C	6.231529000	16.986791000	4.178170000
H	7.080208000	17.635073000	4.002073000
C	6.998476000	14.643494000	7.967373000
H	6.854238000	15.069581000	8.951585000
C	5.567696000	9.534423000	4.198361000
H	6.311162000	10.191163000	4.616631000
C	8.280203000	14.480876000	5.928889000
H	9.141563000	14.752417000	5.334214000
C	4.707377000	11.456955000	6.283759000
H	4.837616000	11.519053000	7.362002000
C	4.255440000	9.530516000	4.741494000
C	0.491049000	8.922219000	6.631082000
H	-0.169556000	8.158136000	6.239155000
C	0.726820000	14.848546000	8.429197000
H	0.143906000	14.970706000	9.332929000
C	2.987971000	14.343768000	4.869161000
C	1.658341000	10.994255000	2.404164000
H	0.961122000	11.241948000	3.193606000
C	0.324590000	13.902710000	7.455025000
H	-0.560482000	13.304031000	7.625446000
C	3.335096000	8.545286000	4.242295000
C	0.151431000	9.632354000	7.744217000
H	-0.783829000	9.440868000	8.254320000
C	2.094594000	8.397774000	4.851036000

H	1.404197000	7.655882000	4.465512000
C	4.981984000	7.791474000	2.632492000
H	5.272277000	7.151752000	1.808959000
C	3.727239000	7.712386000	3.157173000
H	3.005689000	7.003774000	2.770048000
C	5.922800000	8.693983000	3.183220000
H	6.935802000	8.729979000	2.806571000
S	8.915830000	10.779236000	4.803181000
O	10.103498000	11.515905000	5.182698000
O	9.021387000	9.899237000	3.654513000
S	4.673941000	13.912121000	-0.174427000
O	3.359293000	14.115916000	0.414260000
O	5.664933000	14.936178000	0.099337000

[NiL_2] with SO_2 on the arene site

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symmetry c1

Ni	5.309741444	12.365689407	3.646192332
S	5.442095712	11.964729065	1.484747311
S	7.462777887	12.796349527	3.808846983
N	3.384542557	12.432269928	3.405633911
N	5.304826705	12.243022168	5.590572667
C	1.874926535	15.596946276	8.271838782
H	2.192047225	16.345719473	8.987710357
C	4.465143656	16.135050925	5.633158968
C	1.253538875	10.166538184	1.343218713
H	0.272452712	9.710424014	1.345189353
C	5.784950975	16.048410988	3.168233747
H	6.286208938	16.030564263	2.209826152
C	2.631129783	15.446745923	7.075412277
C	3.751402411	16.234536618	6.822217373
H	4.067936879	16.955766796	7.566889246
C	3.424009353	10.456389011	0.320961718
H	4.123684083	10.239397414	-0.475719552
C	4.062133413	15.174636886	4.640461682
C	3.792731382	10.334360419	5.787914431
C	2.149436926	9.912306024	0.304855230
H	1.856351588	9.265041951	-0.512488173

C	2.908969175	11.551353271	2.397731966
C	1.016707867	10.514536473	8.280783264
H	0.759694373	11.056837582	9.181467178
C	3.835377671	11.273461681	1.379104434
C	6.215763683	13.144988612	6.203817591
C	2.190150056	10.791461589	7.641147408
H	2.826178680	11.570677459	8.034012286
C	1.667248569	9.101008265	5.955097151
C	2.586402880	13.257411239	3.985631528
H	1.528023580	13.195654550	3.740114637
C	2.576287271	10.088161667	6.467381554
C	2.235022525	14.455420085	6.113453257
C	1.099579374	13.654560633	6.419866115
H	0.804436685	12.863270732	5.745886126
C	6.038548461	13.680090233	7.473740281
H	5.139916495	13.459567717	8.035506857
C	5.580002463	16.980998226	5.373934047
H	5.892315482	17.666746185	6.151303295
C	7.332068275	13.477389624	5.419513798
C	8.113265692	14.869038003	7.235417824
H	8.852608844	15.553656762	7.632828546
C	4.735832308	15.203244467	3.387005539
H	4.415589170	14.554439599	2.588330186
C	6.233139831	16.930986187	4.179878828

H	7.084826489	17.572434438	3.993710451
C	6.984203212	14.554212212	7.989603663
H	6.833932072	14.998667109	8.964635499
C	5.472302033	9.542311848	4.122780327
H	6.221863091	10.213823859	4.508772235
C	8.287954050	14.337668241	5.966657885
H	9.155143595	14.601838895	5.375406599
C	4.674575438	11.376220828	6.302391120
H	4.821775308	11.400984069	7.378651167
C	4.167995539	9.523200654	4.693756626
C	0.436490764	8.867674637	6.629369160
H	-0.237910667	8.123933768	6.222277585
C	0.772332380	14.829961661	8.509005071
H	0.196606451	14.961480787	9.416113769
C	2.989070275	14.296309154	4.928602319
C	1.633699075	10.997053687	2.386820617
H	0.957463246	11.172652955	3.213677955
C	0.382513224	13.848765926	7.565013148
H	-0.482010485	13.229181983	7.763349432
C	3.242224035	8.546641094	4.192219834
C	0.120653455	9.545225392	7.769461218
H	-0.810256809	9.347948473	8.285596539
C	2.011127049	8.382295108	4.813684595
H	1.314854701	7.650784446	4.420007308

C	4.855406374	7.828363043	2.528174624
H	5.126121776	7.207073207	1.684746767
C	3.614753335	7.735280230	3.084983900
H	2.887144360	7.031252277	2.701273275
C	5.799673078	8.725095479	3.072690938
H	6.795048392	8.782197753	2.653150150
S	6.346686796	7.692040046	6.249005089
O	5.357811313	6.662104314	6.042046841
O	6.087401089	8.679727600	7.271882142

[NiL_2] with two SO_2 on the arene site

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symmetry c1

Ni	5.372656613	12.358651625	3.679694634
S	5.520119712	11.986940698	1.516112213
S	7.524123114	12.787254510	3.861002518
N	3.449140314	12.444366883	3.425028348
N	5.351305269	12.222123122	5.621549274
C	1.950514817	15.666860264	8.273875945
H	2.275664496	16.418889753	8.982502766
C	4.564766951	16.128391293	5.649412102
C	1.318224962	10.228108629	1.309391269
H	0.333354552	9.780553388	1.294236019
C	5.880913358	16.027344008	3.183054451
H	6.370293330	16.007554774	2.218812767
C	2.713532661	15.486244443	7.086430578
C	3.848375338	16.252321228	6.833037270
H	4.167450444	16.982648899	7.567194179
C	3.500758734	10.514862753	0.312269103
H	4.205982184	10.305578326	-0.481543803
C	4.156790316	15.160826910	4.668898133
C	3.813258257	10.332695813	5.797025149
C	2.221761025	9.982853204	0.275402160

H	1.930542191	9.352642212	-0.555747307
C	2.975184442	11.580429815	2.402120846
C	1.015237040	10.575375176	8.258361463
H	0.758953086	11.125948739	9.154173089
C	3.908684500	11.310609273	1.387514489
C	6.257694889	13.119195979	6.247664403
C	2.202593442	10.823909484	7.633339657
H	2.851917777	11.588566058	8.033073616
C	1.662088519	9.143497054	5.942126074
C	2.654835664	13.268677587	4.012702808
H	1.595721643	13.214178950	3.769274023
C	2.586382481	10.110642154	6.464775059
C	2.306213560	14.492157554	6.132168388
C	1.152730064	13.718763692	6.436826838
H	0.846791312	12.926556510	5.768970007
C	6.065327391	13.650607218	7.516897172
H	5.160700874	13.426486439	8.067481694
C	5.675591242	16.974558398	5.377283279
H	5.982070426	17.674106797	6.144109326
C	7.379929929	13.457600548	5.475168962
C	8.138461694	14.846407923	7.302967559
H	8.871259522	15.532616510	7.709156744
C	4.824399043	15.185689493	3.410013531
H	4.507432888	14.530525645	2.615586746

C	6.329814144	16.917297695	4.182688949
H	7.174506924	17.564328628	3.987254012
C	7.003007245	14.525695818	8.045202343
H	6.841454326	14.967538855	9.019533548
C	5.485977815	9.521860751	4.134589442
H	6.249281066	10.168139829	4.537108095
C	8.327774193	14.319021601	6.034575112
H	9.200038865	14.588061188	5.453236301
C	4.708943547	11.356160967	6.323320266
H	4.850062038	11.372683198	7.400861302
C	4.178930717	9.522582585	4.699803714
C	0.420098805	8.936135118	6.604179244
H	-0.265017041	8.205811876	6.190841958
C	0.830695074	14.924920105	8.509619144
H	0.249110746	15.079346695	9.409351889
C	3.067422756	14.303803088	4.954682354
C	1.694981680	11.038266392	2.369891136
H	1.011784132	11.206940375	3.192492613
C	0.430007300	13.940826109	7.573892245
H	-0.449255334	13.341819477	7.771194342
C	3.235819964	8.570522397	4.183459696
C	0.105179524	9.623617694	7.738432687
H	-0.835880884	9.447884883	8.243647886
C	1.999665874	8.423522054	4.799656879

H	1.291440603	7.709185865	4.396214345
C	4.835239582	7.852058420	2.506904709
H	5.093834539	7.243112003	1.650832353
C	3.593998120	7.769640529	3.064284354
H	2.854140993	7.084857345	2.669615960
C	5.797487380	8.718040605	3.069322428
H	6.793796549	8.763061962	2.650474429
S	2.950668602	17.389554130	2.537817720
O	3.034201548	18.221802297	3.713381878
O	3.499420535	17.897122749	1.304807768
S	6.180464189	7.523649919	6.242046911
O	5.202447889	6.508783895	5.933297562
O	5.877252875	8.450481941	7.308919268