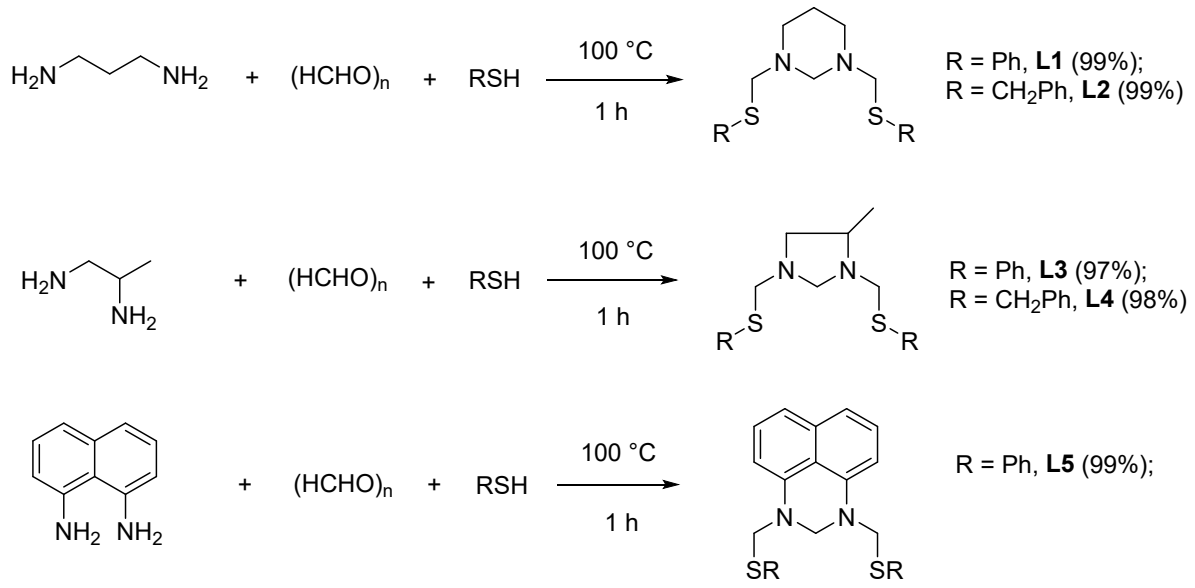
Electronic Supplementary Information

Contents

General experimental section

All reactions were carried out in the open atmosphere. Solvents were distilled under nitrogen atmosphere according to the standard procedures. Other chemicals were obtained from commercial sources and used as received. All ^{1}H NMR (400 MHz or 500 MHz), ^{13}C (125.75 MHz) spectra were recorded at 25 ºC. ^{1}H NMR chemical shifts are referenced with respect to the chemical shift of the residual proton present in the deuterated solvent. $^{13}C\{^{1}H\}$ NMR spectra were referenced with respect to the chemical shift of the carbon atom of $CDCl_3$. Chemical shifts are in parts per million (ppm) and coupling constants are in Hz. ATR-FTIR spectra were recorded using Perkin-Elmer Spectrum Rx. High resolution mass spectra (ESI+/–) were obtained using Agilent AdvanceBio 6545XT LC/Q-TOF system. Electronic absorption spectra (800-200 nm) were recorded on a Shimadzu (Model UV-2450) spectrophotometer at room temperature. Elemental analyses were carried out using EuroEA Elemental Analyser.

Results and discussion



Scheme S1. Synthesis of a series of new bis(thioether) ligands **L1-L5**.

To expand the scope of the reaction between primary diamines, secondary phosphine and paraformaldehyde giving the procarbene bis(phosphine) ligand,[1,2] the reaction between 1,3-diaminopropane, thiophenol and paraformaldehyde in a 1:2:3 molar ratio under heating conditions was carried out to give compound **L1** as a colorless solid in an excellent yield (99%) after removing all volatiles of the reaction mixture followed by cooling at 0 °C (Scheme S1). The analogous reaction using benzyl mercaptan gave yet another new compound **L2** in 99% yield as a colorless viscous oily compound. 1,2-Diaminopropane undergoes similar reactions

with thiophenol and benzyl mercaptan to give the imidazolidine-based bis(thioether) compounds **L3** and **L4** in excellent yields (97 and 98%), respectively. In addition, 1,8-diaminonaphthalene reacts with thiophenol and paraformaldehyde under similar reaction conditions to yield the dihydroperimidine-based compound **L5** as a light pink colored air-stable solid in an excellent yield (99%). Compounds **L1**-**L4** are air-stable and well soluble in common organic solvents such as CH_2Cl_2, chloroform, diethyl ether, THF, acetonitrile, methanol and ethanol, but are sparingly soluble in n-hexane or pentane. **L5** is well soluble in CH_2Cl_2, chloroform, and acetonitrile and not soluble in hexane. All were characterized by ^1H, ^{13}C NMR, ATR-FTIR, UV-vis and HRMS(ESI+) methods. In contrast to the ^1H NMR spectra of **L1**, **L2** and **L4**, the spectrum of **L3** features well resolved peaks owing to its rigid structure. For example, the diastereotopic NCH_2N protons appear at δ = 3.67 ppm as a doublet of doublet with J(H-H) = 24.0, 4.0Hz.

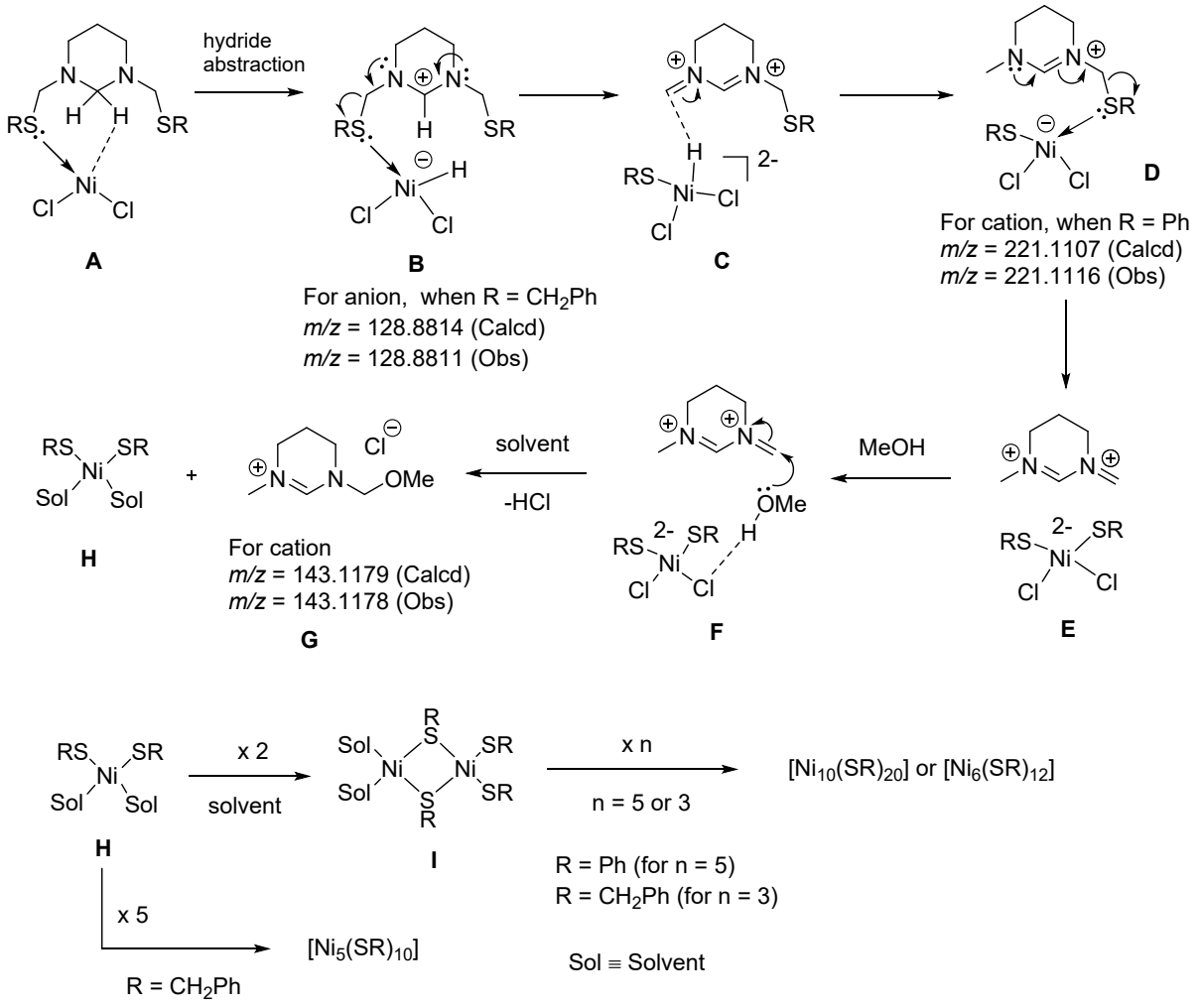


Figure S1. Proposed mechanism for the formation of $[Ni_{10}(SPh)_{20}]$, $[N_{i6}(SCH_2Ph)_{12}]$ and $[Ni_5(SCH_2Ph)_{10}]$with by-products.

A plausible mechanism for the formation of toroidal nickel thiolates is given in Figure S1, which is based on the isolated and detected by-products formed in their synthesis (See Fig. S38-40, 50-52 for HRMS spectra). The coordination of the sulfur atom of the thioether molecule to the nickel(II) may lead to the formation of the pyrimidinium ion-linked nickel hydride complex **B** via the abstraction of hydride from the "NCH_2N" moiety. This type of abstraction has been proposed and supported by DFT calculation for the formation of bis(phosphine)-NHC coordinated nickel complex.[3] **B** undergoes the C-S bond cleavage and transfers its hydrogen to the methylene carbon to give **D**. The cation in **D** was detected by HRMS(ESI+) spectrum of the reaction mixture displaying a major peak at *m/z* = 221.1116 (calc. 221.1107). The coordination of the thioether sulfur atom in **D** promotes the cleavage of the remaining C-S bond to give the dicationic species **E**, which undergoes a nucleophilic attack by the methanol to give the pyrimidinium ion with chloride as the counter anion **G** and the dithiolate bound nickel(II) species **H** in the presence of solvent. **G** was detected by HRMS (ESI+) method displaying a peak at *m/z* = 143.1178 (calc. 143.1179). **H** dimerizes to **I**, which then undergoes oligomerization based on the steric hindrance of the R group attached to the sulfur atoms to yield the cyclic Ni_{10}, Ni_6 and Ni_5 toroidal systems.

X-ray structures and refinement data

The solvents used for and the method of crystallization of **1**, **5** and **8** are given in their respective experimental sections. Data collections were performed using a Bruker APEX-II or D8 Venture APEX3 CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The space group for every structure was obtained by XPREP program. The structures were solved by SHELXT[4] which successfully located most of the nonhydrogen atoms. Subsequently, least-squares refinements were carried out on F^2 using SHELXL Version 2018/3[5] to locate the remaining nonhydrogen atoms. Nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were fixed in calculated positions. The crystal structures were plotted using ORTEP and Mercury programs. The refinement data for all the structures are summarized in Table S1. Crystallographic data were deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. These data can be obtained free of charge upon quoting the depository numbers CCDC 2370249-2370251 from web interface (at http://www.ccdc.cam.ac.uk).

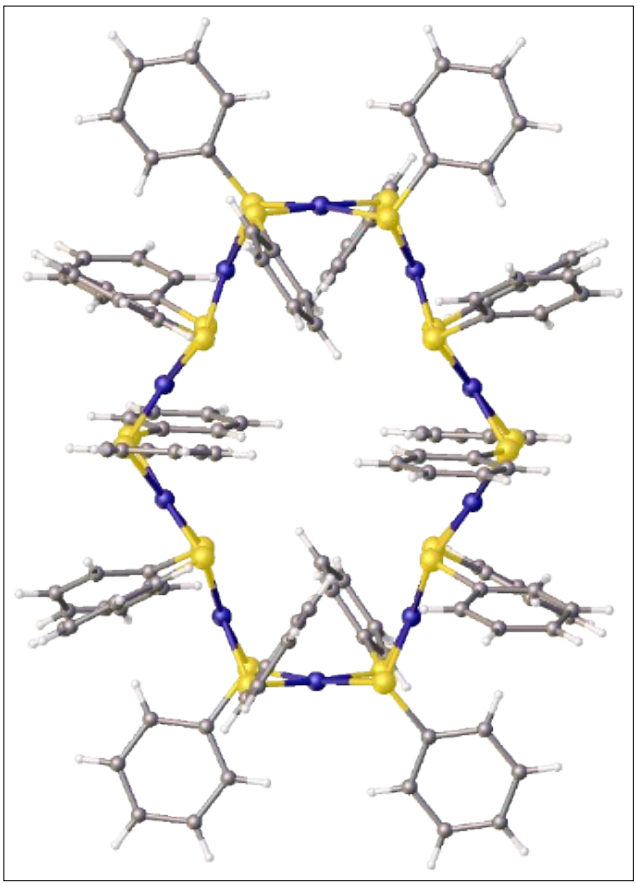
Computational methods

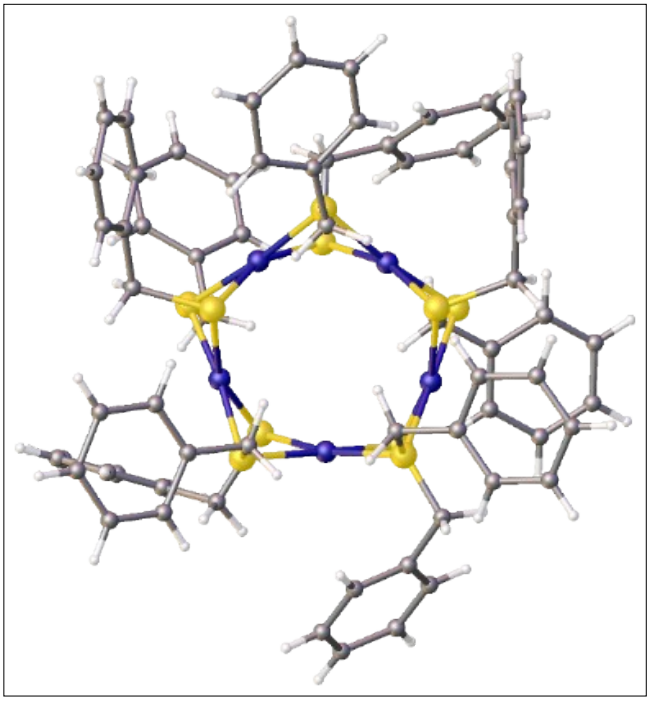
The Gaussian 16[6] software for both ground and excited states calculations was utilized. For the ground state, the crystal structure coordinates as the starting geometry were used and all three structures (**1**, **5** and **8**) were optimized at the BP86[7] level of theory. The def2SVPP[8] basis set was applied for Ni, while the 6-311g(d,p)[9] basis set was used for other main group elements of the compounds. To account for the relativistic effects of Ni, the SDD[10] pseudopotential basis set was employed. After optimization, a Hessian matrix calculation at the same level of theory was performed, which finds no imaginary frequencies, confirming that the structures are at their minima on the potential energy surface.

For the excited state calculations, the ground state optimized structures as the starting point were used. These calculations were performed at the B3LYP[11,12,13] level of theory with the def2SVPP basis set for Ni and the 6-311g(d,p) basis set for the other main group elements. In addition to the relativistic SDD[5] pseudopotential, the CPCM solvent model with tetrahydrofuran as a solvent was utilized with Grimme's dispersion D3 correction[14,15].

Up to 100 excited states were calculated for $[Ni_5(SCH_2Ph)_{10}]$ and $[Ni_6(SCH_2Ph)_{12}]$, while for $[Ni_{10}(SPh)_{20}]\in CH_2Cl_2$, more than 180 states were examined. Owing to the rapid increase in computational cost with the number of states, it was not calculated beyond 180 states for $[Ni_{10}(SPh)_{20}]\in CH_2Cl_2$. To address this issue, all phenyl groups in Ni_{10} (**1**) were replaced by methyl groups and extended the excited state calculations up to 300 states, achieving convergence within the experimental wavelength region. In the excited state analysis, various pairs of HOMO-x and LUMO+y orbitals were thoroughly investigated with significant percentage, as presented in Table S10. This table provides details of the transitions from the respective excited states, highlighting reasonable oscillator strengths and percentages of configuration interaction expansion coefficients. To gain a deeper understanding of these transitions, we calculated the percentages of holes and electrons responsible for specific HOMO-LUMO transitions, also shown in Table S11-17.

For the non-covalent interaction (NCI) analysis[16], the Bader's quantum theory of atoms in molecules (QTAIM)[17] method with Multiwfn[18] software was used.





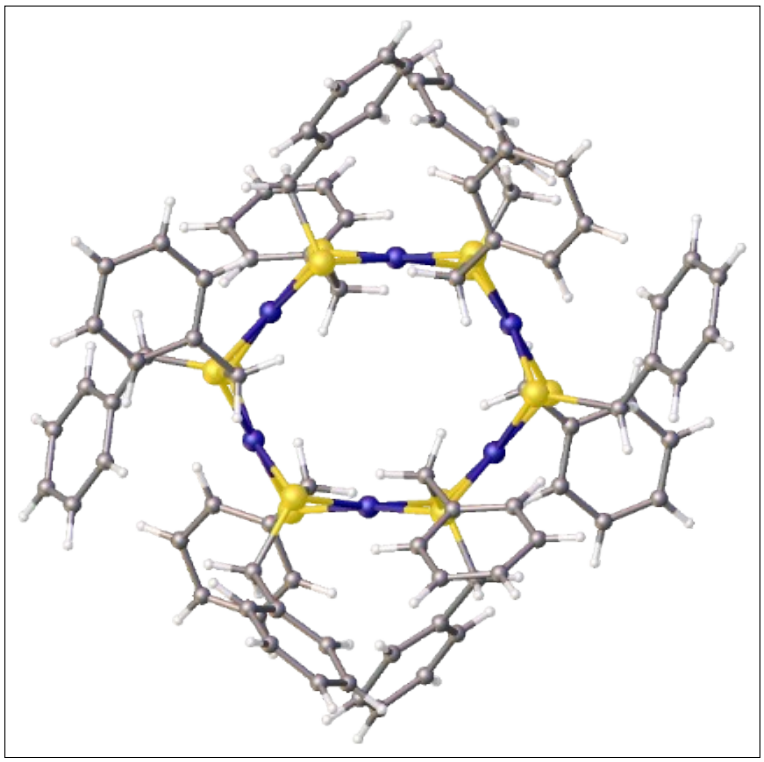
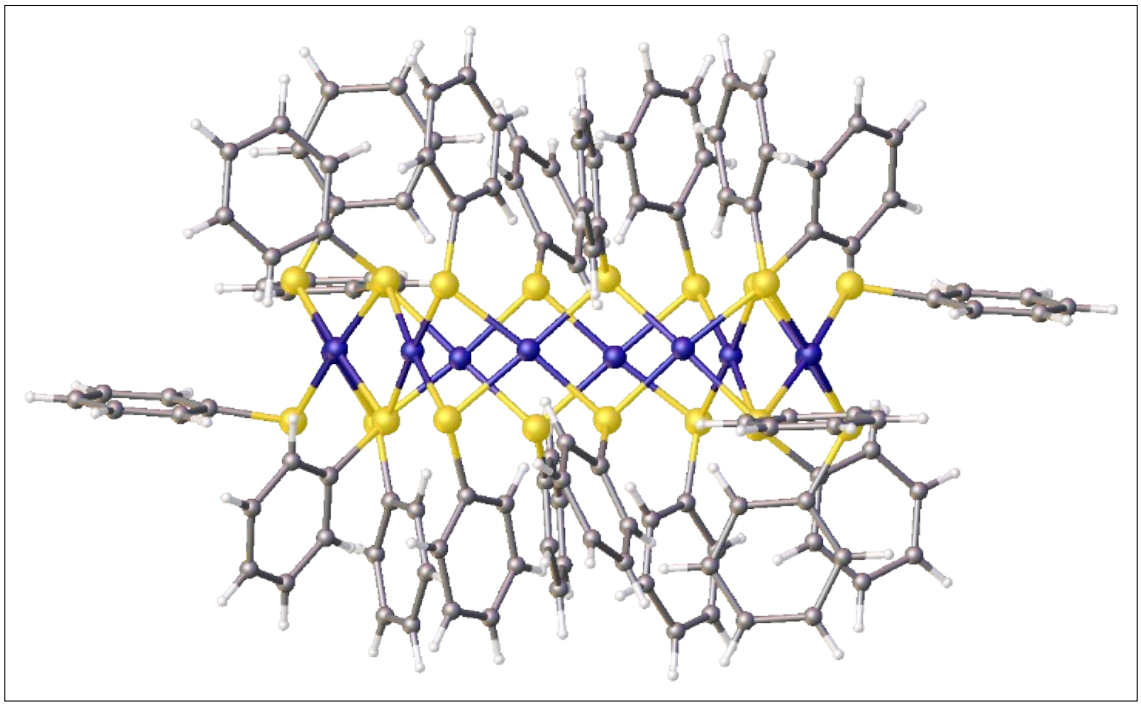


Figure S2. Top views of the X-ray structures of $[Ni_{10}(SPh)_{20}]$ (**1**), $[Ni_5(SCH_2Ph)_{10}]$ (**5**), and $[Ni_6(SCH_2Ph)_{12}]$ (**8**). The solvent molecule in **1** is omitted for clarity.



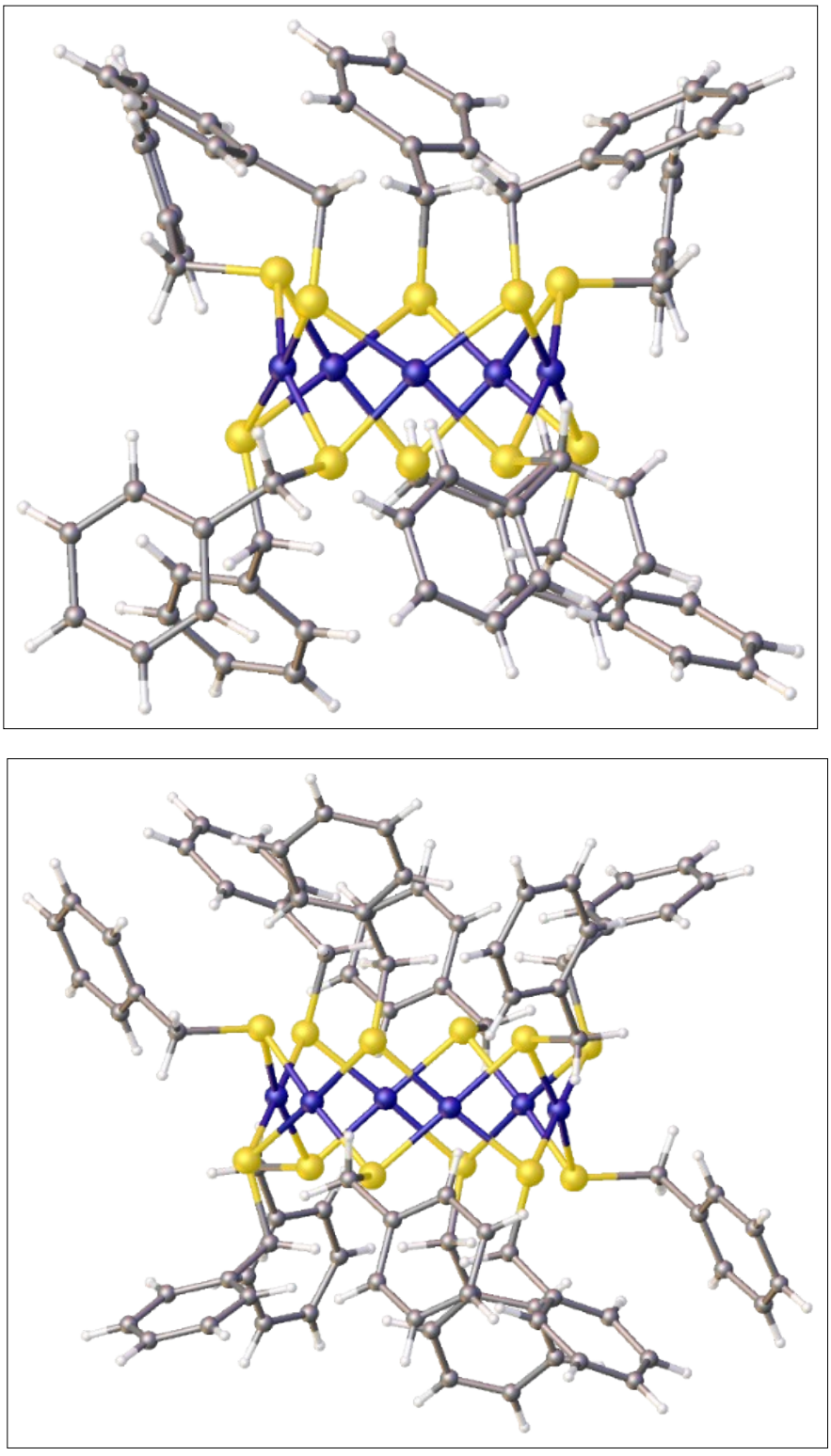


Figure S3. Side views of the X-ray structures of $[Ni_{10}(SPh)_{20}]$ (**1**), $[Ni_5(SCH_2Ph)_{10}]$ (**5**), and $[Ni_6(SCH_2Ph)_{12}]$ (**8**). The solvent molecule in **1** is omitted for clarity.

Table S1. Crystallographic data for complexes **1**, **5** and **8**.

	1·3CH_2Cl_2	**5**	**8**
Empirical formula	$C_{123}H_{106}Cl_6Ni_{10}S_{20}$	$C_{70}H_{70}Ni_5S_{10}$	$C_{84}H_{84}Ni_6S_{12}$
Formula weight	3025.07	1525.41	1830.49
Wavelength (Å)	0.71073	0.71073	0.71073
Temperature (K)	100(2)	120(2)	120(2)
Crystal system	Triclinic	Monoclinic	Tetragonal
Space group	*P*-1	$P2_1/c$	$P\text{-}42_1c$
a/Å	14.5800(10)	17.0792(6)	18.8191(8)
b/Å	15.8532(10)	12.2511(5)	18.8191(8)
c/Å	15.9538(10)	33.0819(12)	23.116(3)
α/degree	64.536(2)	90	90
β/degree	81.865(2)	93.3490(10)	90
γ/degree	70.873(2)	90	90
Volume ($Å^3$)	3145.5(4)	6910.2(4)	8186.7(13)
Z	1	4	4
D_{calcd}, g cm^{-3}	1.597	1.466	1.485
μ/mm^{-1}	1.968	1.680	1.701
F(000)	1546	3160	3792
θ range (degree)	2.045 to 25.00	2.047 to 27.105	2.068 to 25.329
Limiting indices	-17<=h<=17, -18<=k<=18, -18<=k<=18	-21<=h<=21, -15<=k<=15, -42<=k<=42	-22<=h<=22, -22<=k<=22, -27<=k<=27
Total / unique no. of reflns.	53676 / 11057	256724 / 15238	216649 / 7478
R_{int}	0.0349	0.0772	0.1124
Data / restr./ params.	11057 / 25 / 730	15238 / 0 / 766	7478 / 0 / 462
GOF (F^2)	1.045	1.017	1.089
R1, *wR2*	0.0408, 0.1093	0.0270, 0.0566	0.0225, 0.0516
R indices (all data) *R1*, *wR2*	0.0484, 0.1160	0.0391, 0.0609	0.0270, 0.0521
Largest different peak and hole (e $Å^{-3}$)	1.278 and -1.071	1.088 and -0.501	0.334 and -0.301

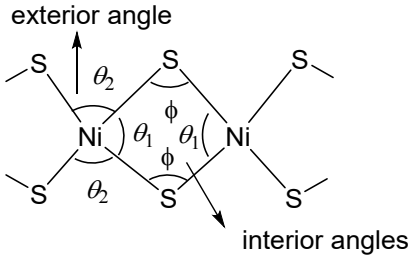
For $[Ni_{10}(SPh)_{20}]\cdot 3CH_2Cl_2$

Table S2. Angle between nickel square planes and dihedral angles in **1**·$3CH_2Cl_2$.

Ni square planes	Angles between Ni square planes	Ni-S-S-Ni dihedral angles (δ)[a]	δ (°)
S1 S2 Ni1 S3 S4 and S3 S4 Ni2 S5 S6	13.58 (0.03)	Ni(1)-S(3)-S(4)-Ni(2) (concave)	199.20 (360-160.80(5))
S3 S4 Ni2 S5 S6 and S5 S6 Ni3 S7 S8	68.40 (0.03)	Ni(2)-S(6)-S(5)-Ni(3) (convex)	118.54(5)
S5 S6 Ni3 S7 S8 and S7 S8 Ni4 S9 S10	69.71 (0.03)	Ni(3)-S(8)-S(7)-Ni(4) (convex)	117.57(4)
S7 S8 Ni4 S9 S10 and S9 S10 Ni5 $S2^i$ $S1^i$	14.11(0.05)	Ni(4)-S(9)-S(10)-Ni(5) (concave)	198.78 (360-161.22(5))
S9 S10 Ni5 $S2^i$ $S1^i$ and $S2^i$ $S1^i$ $Ni1^i$ $S4^i$ $S3^i$	69.51(0.02)	Ni(5)-$S(1)^i$ -$S(2)^i$ -$Ni(1)^i$ (convex)	113.67(4)

[a] Dihedral angle between the adjacent NiS_4 square plane is given as the inner-ring angle between the planes of Ni-S-S and S-S-Ni in which S-S refers to the non-bonded S atoms through which adjacent nickel square planes are fused.

Table S3. Interior and exterior angles (°), nickel atom displacement from square plane and Ni-S bond distances (Å) in **1**·3CH_2Cl_2.



Interior (θ_1)	**Average: 82.05°**	**Interior (φ)**	**Average** at convex: **80.52(4)**; at concave: **94.75(4)**
S(1)-Ni(1)-S(2)	78.64(4)	Ni(1)-S(3)-Ni(2)	94.64(4) (concave)
S(4)-Ni(1)-S(3)	83.46(4)	Ni(1)-S(4)-Ni(2)	95.05(4) (concave)
S(4)-Ni(2)-S(3)	83.28(4)	Ni(2)-S(5)-Ni(3)	79.95(4) (convex)
S(6)-Ni(2)-S(5)	82.82(4)	Ni(2)-S(6)-Ni(3)	80.67(4) (convex)
S(6)-Ni(3)-S(5)	82.76(4)	Ni(4)-S(7)-Ni(3)	80.63(3) (convex)
S(7)-Ni(3)-S(8)	81.86(4)	Ni(3)-S(8)-Ni(4)	80.27(4) (convex)
S(7)-Ni(4)-S(8)	82.00(4)	Ni(4)-S(9)-Ni(5)	94.66(4) (concave)
S(9)-Ni(4)-S(10)	83.45(4)	Ni(5)-S(10)-Ni(4)	94.66(4) (concave)
S(10)-Ni(5)-S(9)	83.83(4)	Ni(1)-S(1)-Ni(5)^{i}	80.71(3) (convex)
S(2)^{i} -Ni(5)-S(1)^{i}	78.42(4)	Ni(5)^{i} -S(2)-Ni(1)	80.90(4) (convex)
Exterior (θ_2): **Average**: **97.79(4)**			
S(3)-Ni(1)-S(1)	98.72(4)	S(9)-Ni(4)-S(7)	100.78(4)
S(4)-Ni(1)-S(2)	98.98(4)	S(10)-Ni(4)-S(8)	93.25(4)
S(3)-Ni(2)-S(5)	94.89(4)	S(9)-Ni(5)-S(2)^{i}	100.10(4)
S(4)-Ni(2)-S(6)	98.60(4)	S(10)-Ni(5)-S(1)^{i}	97.66(4)
S(7)-Ni(3)-S(5)	98.18(4)		
S(6)-Ni(3)-S(8)	96.75(4)		
Ni atoms	**Displacement** **(Average**: **0.08)**		
Ni3	0.105	Ni5	0.028

Ni1	0.067	Ni4	0.107
Ni2	0.095		
	Average: **3.01**		
Ni(1)-Ni(5)	2.8587(7)		
Ni(2)-Ni(3)	2.8531(7)	Average at convex: **2.856(7)**	
Ni(3)-Ni(4)	2.8554(7)		
Ni1-Ni2	3.2339(5)	Average at concave: **3.235(6)**	
Ni4-Ni5	3.2369(7)		
	Average: **2.2062(2)**		
S(2)-Ni(1)	2.2071(10)		
S(1)-Ni(1)	2.1984(10)		
S(3)-Ni(1)	2.1982(10)		
S(4)-Ni(1)	2.1895(10)		
S(3)-Ni(2)	2.2006(11)		
S(4)-Ni(2)	2.1949(10)		
S(5)-Ni(2)	2.2196(10)		
S(6)-Ni(2)	2.2035(10)		
S(5)-Ni(3)	2.2215(10)		
S(6)-Ni(3)	2.2045(10)		
S(7)-Ni(3)	2.2117(10)		
S(8)-Ni(3)	2.2129(10)		
S(7)-Ni(4)	2.2017(10)		
S(8)-Ni(4)	2.2168(10)		
S(9)-Ni(4)	2.2007(11)		
S(10)-Ni(4)	2.2100(10)		
S(10)-Ni(5)	2.1924(11)		
S(9)-Ni(5)	2.2017(10)		
S(1)-Ni(5)^{i}	2.2166(10)		
S(2)-Ni(5)^{i}	2.1992(10)		

Table S4. Sum of the three angles (°) around sulfur atoms in **1**·3CH_2Cl_2.

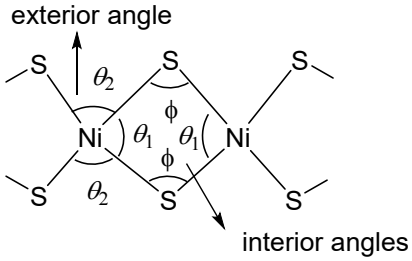
			Sum
S1	C(7)-S(1)-Ni(1)	112.15(14)	
	C(7)-S(1)-Ni(5)^{i}	114.53(14)	307.39
	Ni(1)-S(1)-Ni(5)^{i}	80.71(3)	
S2	C(1)-S(2)-Ni(1)	114.64(14)	
	C(1)-S(2)-Ni(5)^{i}	117.22(14)	312.76
	Ni(5)^{i} -S(2)-Ni(1)	80.90(4)	
S3	C(13)-S(3)-Ni(1)	108.06(14)	
	Ni(1)-S(3)-Ni(2)	94.64(4)	313.13
	C(13)-S(3)-Ni(2)	110.43(14)	
S4	C(19)-S(4)-Ni(2)	105.34(14)	
	C(19)-S(4)-Ni(1)	107.48(14)	307.87
	Ni(1)-S(4)-Ni(2)	95.05(4)	
S5	C(25)-S(5)-Ni(2)	103.40(13)	
	C(25)-S(5)-Ni(3)	109.48(14)	292.83
	Ni(2)-S(5)-Ni(3)	79.95(4)	
S6	C(31)-S(6)-Ni(2)	111.68(14)	
	C(31)-S(6)-Ni(3)	114.54(13)	306.89
	Ni(2)-S(6)-Ni(3)	80.67(4)	
S7	C(37)-S(7)-Ni(4)	112.11(13)	
	C(37)-S(7)-Ni(3)	114.75(13)	307.49
	Ni(4)-S(7)-Ni(3)	80.63(3)	
S8	C(43)-S(8)-Ni(3)	110.21(13)	
	C(43)-S(8)-Ni(4)	107.66(13)	298.14
	Ni(3)-S(8)-Ni(4)	80.27(4)	
S9	C(49)-S(9)-Ni(4)	107.76(14)	
	C(49)-S(9)-Ni(5)	107.45(14)	309.87
	Ni(4)-S(9)-Ni(5)	94.66(4)	
S10	C(55)-S(10)-Ni(5)	105.84(14)	
	C(55)-S(10)-Ni(4)	104.83(13)	305.33
	Ni(5)-S(10)-Ni(4)	94.66(4)	

Symmetry transformations are used to generate equivalent atoms: –x+1, –y+1, –z

For $[Ni_5(SCH_2Ph)_{10}]$ 5

Table S5. Dihedral, interior, and exterior angles (°), nickel atom displacement from square plane and Ni-S bond distances (Å) in $[Ni_5(SCH_2Ph)_{10}]$ **5**.

Ni-S-S-Ni dihedral angles (δ)	
Ni(1)-S(2)-S(1)-Ni(2)	118.79(2)
Ni(2)-S(4)-S(3)-Ni(3)	114.04(2)
Ni(3)-S(6)-S(5)-Ni(4)	114.92(2)
Ni(5)-S(10)-S(9)-Ni(1)	112.73(2)



Average values

θ_1 : 81.5° ; θ_2 : 98.8°; φ : 79.8 °

Ni-S = 2.20 Å; Ni-Ni 2.82 Å

Interior (θ_1)	**Average: 81.55(2)°**	**Interior (φ)**	**Average 79.79(2) °**
S(1)-Ni(1)-S(2)	82.19(2)	Ni(1)-S(1)-Ni(2)	81.287(18)
S(1)-Ni(2)-S(2)	81.50(2)	Ni(1)-S(2)-Ni(2)	80.980(19)
S(4)-Ni(2)-S(3)	80.812(19)	Ni(3)-S(3)-Ni(2)	79.112(17)
S(3)-Ni(3)-S(4)	81.684(19)	Ni(3)-S(4)-Ni(2)	79.078(18)
S(5)-Ni(3)-S(6)	80.874(19)	Ni(4)-S(5)-Ni(3)	79.975(18)
S(5)-Ni(4)-S(6)	81.13(2)	Ni(4)-S(6)-Ni(3)	79.502(18)
S(7)-Ni(4)-S(8)	82.37(2)	Ni(4)-S(7)-Ni(5)	81.387(19)
S(7)-Ni(5)-S(8)	82.27(2)	Ni(4)-S(8)-Ni(5)	81.225(19)
S(9)-Ni(5)-S(10)	82.22(2)	Ni(5)-S(9)-Ni(1)	77.874(19)
S(9)-Ni(1)-S(10)	82.26(2)	Ni(1)-S(10)-Ni(5)	77.499(18)
Exterior (θ_2): **Average**: **98.82(6)**			
S(1)-Ni(1)-S(9)	97.21(2)	S(5)-Ni(4)-S(7)	98.97(2)
S(2)-Ni(1)-S(10)	100.48(2)	S(8)-Ni(4)-S(6)	99.24(2)

S(1)-Ni(2)-S(3)	89.03(2)	S(9)-Ni(5)-S(7)	97.87(2)
S(2)-Ni(2)-S(4)	108.82(2)	S(8)-Ni(5)-S(10)	99.44(2)
S(3)-Ni(3)-S(5)	97.85(2)		
S(4)-Ni(3)-S(6)	99.28(2)		
Atoms	**Ni displacement Average: 0.1258 Å**		**Average angle: 107.981(5)°**
Ni1	0.150	Ni(1)-Ni(5)-Ni(4)	107.284(11)
Ni2	0.065	Ni(3)-Ni(4)-Ni(5)	110.864(11)
Ni3	0.163	Ni(2)-Ni(3)-Ni(4)	103.477(11)
Ni4	0.105	Ni(3)-Ni(2)-Ni(1)	111.892(11)
Ni5	0.146	Ni(5)-Ni(1)-Ni(2)	106.388(11)
	Average Ni-S: 2.1991(2) Å		**Average Ni…Ni: 2.8196(2) Å**
S(1)-Ni(1)	2.1793(5)	Ni(1)-Ni(5)	2.7592(4)
S(1)-Ni(2)	2.2004(5)	Ni(1)-Ni(2)	2.8528(4)
S(2)-Ni(1)	2.1920(6)	Ni(2)-Ni(3)	2.8051(4)
S(2)-Ni(2)	2.2015(5)	Ni(3)-Ni(4)	2.8174(4)
S(3)-Ni(3)	2.1894(5)	Ni(4)-Ni(5)	2.8634(4)
S(3)-Ni(2)	2.2153(5)		
S(4)-Ni(3)	2.1966(5)		
S(4)-Ni(2)	2.2098(5)		
S(5)-Ni(4)	2.1869(5)		
S(5)-Ni(3)	2.1974(5)		
S(6)-Ni(4)	2.2025(5)		
S(6)-Ni(3)	2.2035(5)		
S(7)-Ni(4)	2.1953(5)		
S(7)-Ni(5)	2.1963(5)		
S(8)-Ni(4)	2.1977(5)		
S(8)-Ni(5)	2.2012(6)		
S(9)-Ni(5)	2.1935(6)		
S(9)-Ni(1)	2.1968(6)		
S(10)-Ni(1)	2.2017(5)		

S(10)-Ni(5)	2.2065(6)		

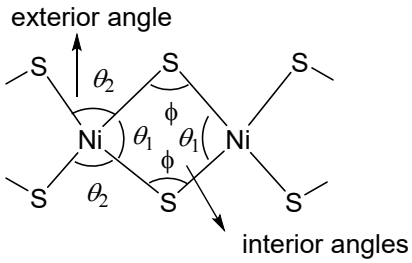
Table S6. Sum of the three angles (°) around sulfur atoms in $[Ni_5(SCH_2Ph)_{10}]$ **5**.

			Sum
S1	C(1)-S(1)-Ni(1)	111.30(8)	
	C(1)-S(1)-Ni(2)	108.83(7)	
	Ni(1)-S(1)-Ni(2)	81.287(18)	301.42(11)
S2	C(8)-S(2)-Ni(1)	116.33(7)	
	C(8)-S(2)-Ni(2)	117.51(7)	
	Ni(1)-S(2)-Ni(2)	80.980(19)	314.82(10)
S3	C(15)-S(3)-Ni(3)	111.25(7)	
	C(15)-S(3)-Ni(2)	106.94(7)	
	Ni(3)-S(3)-Ni(2)	79.112(17)	297.30(10)
S4	C(22)-S(4)-Ni(3)	113.17(7)	
	C(22)-S(4)-Ni(2)	121.05(7)	
	Ni(3)-S(4)-Ni(2)	79.078(18)	313.30(10)
S5	C(29)-S(5)-Ni(4)	116.15(7)	
	C(29)-S(5)-Ni(3)	115.41(7)	
	Ni(4)-S(5)-Ni(3)	79.975(18)	311.54(10)
S6	C(36)-S(6)-Ni(4)	109.14(7)	
	C(36)-S(6)-Ni(3)	109.23(7)	
	Ni(4)-S(6)-Ni(3)	79.502(18)	297.87(10)
S7	C(50)-S(7)-Ni(4)	107.23(7)	
	C(50)-S(7)-Ni(5)	110.11(7)	
	Ni(4)-S(7)-Ni(5)	81.387(19)	298.73(10)
S8	C(43)-S(8)-Ni(4)	114.77(7)	
	C(43)-S(8)-Ni(5)	116.90(8)	
	Ni(4)-S(8)-Ni(5)	81.225(19)	312.90(11)
S9	C(64)-S(9)-Ni(5)	115.12(8)	
	C(64)-S(9)-Ni(1)	114.29(7)	
	Ni(5)-S(9)-Ni(1)	77.874(19)	307.28(11)
S10	C(57)-S(10)-Ni(1)	106.97(7)	

	C(57)-S(10)-Ni(5)	110.52(8)	
	Ni(1)-S(10)-Ni(5)	77.499(18)	294.99(11)
			Average angle: **305.015**

For $[Ni_6(SCH_2Ph)_{12}]$ 8

Table S7. Dihedral, interior, and exterior angles (°), nickel atom displacement from square plane and Ni-S bond distances (Å) in $[Ni_6(SCH_2Ph)_{12}]$ **8**.



Interior (θ_1)	**Average: 82.01(3)°**	**Interior (φ)**	**Average 83.08(3)°**
S(1)-Ni(1)-S(2)	82.11(3)	Ni(1)-S(1)-Ni(2)	82.23(3)
S(1)-Ni(2)-S(2)	82.25(4)	Ni(1)-S(2)-Ni(2)	80.93(3)
S(4)-Ni(2)-S(3)	81.59(3)	Ni(3)-S(3)-Ni(2)	86.40(3)
S(3)-Ni(3)-S(4)	81.58(3)	Ni(3)-S(4)-Ni(2)	86.77(3)
S(5)-Ni(3)-S(6)	82.44(3)	Ni(4)-S(5)-Ni(3)	81.38(3)
S(5)-Ni(4)-S(6)	82.12(3)	Ni(4)-S(6)-Ni(3)	80.80(3)
Exterior (θ_2): Average: **98.42(3)°**			
S(1)-Ni(2)-S(3)	97.80(4)	$S(6)^i$-Ni(4)-S(5)	98.66(3)
S(4)-Ni(2)-S(2)	99.22(3)	S(6)-Ni(4)-$S(5)^i$	98.66(3)
S(5)-Ni(3)-S(3)	97.92(3)		
S(4)-Ni(3)-S(6)	99.40(3)		
$S(1)-Ni(1)-S(2)^i$	97.84(3)		
$S(1)^i$ -Ni(1)-S(2)	97.84(3)		
atoms	**Ni displacement Average**: **0.054**		**Average**: **119.17**
Ni1	0.088	Ni(1)-Ni(2)-Ni(3)	124.09
Ni2	0.018	Ni(2)-Ni(3)-Ni(4)	118.24

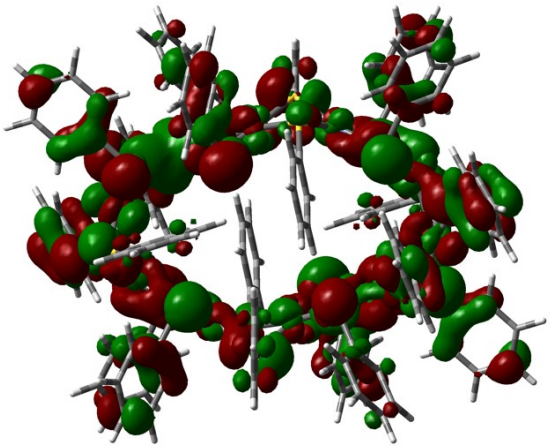
Ni3	0.099	Ni(3)-Ni(4)-Ni3	120.91
Ni4	0.011	Ni(4)-Ni(3)-Ni(2)	118.24
		Ni(2)-Ni(1)-Ni(2)	114.35
	Average: **2.1963(9)**		**Average**: **2.9122(6)**
Ni(1)-S(1)	2.1832(9)	Ni(1)-Ni(2)	2.8746(6)
Ni(1)-S(2)	2.2205(9)	Ni2-Ni3	3.0079(8)
Ni(2)-S(1)	2.1885(9)	Ni(3)-Ni(4)	2.8543(5)
Ni(2)-S(2)	2.2090(9)		
Ni(2)-S(3)	2.1930(9)		
Ni(2)-S(4)	2.1934(9)		
Ni(3)-S(3)	2.2014(9)		
Ni(3)-S(4)	2.1855(9)		
Ni(3)-S(5)	2.1784(9)		
Ni(3)-S(6)	2.2054(9)		
Ni(4)-S(5)	2.1993(8)		
Ni(4)-S(6)	2.1987(8)		

Symmetry transformations used to generate equivalent atoms: i = –x+1, –y, z

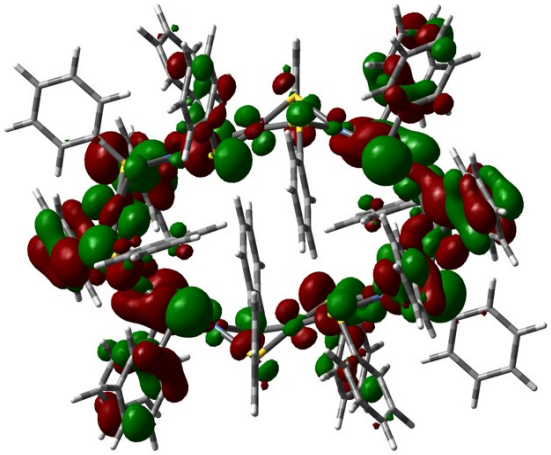
Table S8. Sum of the three angles (°) around sulfur atoms in $[Ni_6(SCH_2Ph)_{12}]$ **8**.

			Sum
S1	C(1)-S(1)-Ni(1)	114.27(12)	310.3
	C(1)-S(1)-Ni(2)	113.78(12)	
	Ni(1)-S(1)-Ni(2)	82.23(3)	
S2	C(8)-S(2)-Ni(2)	105.24(13)	293.2
	C(8)-S(2)-Ni(1)	107.08(12)	
	Ni(2)-S(2)-Ni(1)	80.93(3)	
S3	C(15)-S(3)-Ni(2)	104.10(12)	298.4
	C(15)-S(3)-Ni(3)	107.86(12)	
	Ni(2)-S(3)-Ni(3)	86.40(3)	
S4	C(22)-S(4)-Ni(3)	115.88(11)	317.7
	C(22)-S(4)-Ni(2)	115.01(12)	
	Ni(3)-S(4)-Ni(2)	86.77(3)	
S5	C(29)-S(5)-Ni(3)	114.63(11)	312.9
	C(29)-S(5)-Ni(4)	116.90(12)	
	Ni(3)-S(5)-Ni(4)	81.38(3)	
S6	C(36)-S(6)-Ni(4)	101.34(11)	294.4
	C(36)-S(6)-Ni(3)	112.28(12)	
	Ni(4)-S(6)-Ni(3)	80.80(3)	
			Average: 304.5

DFT calculations



HOMO-4



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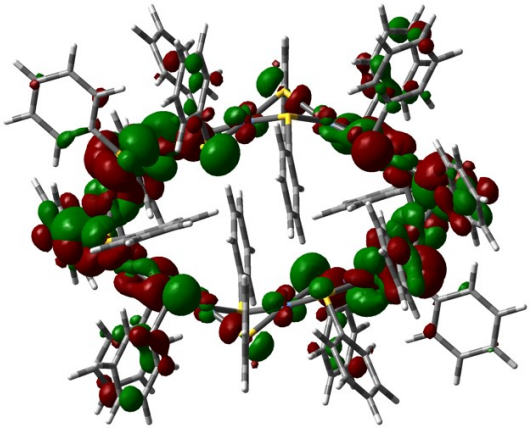

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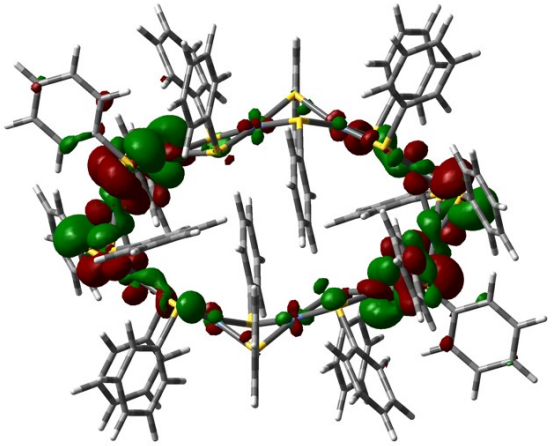

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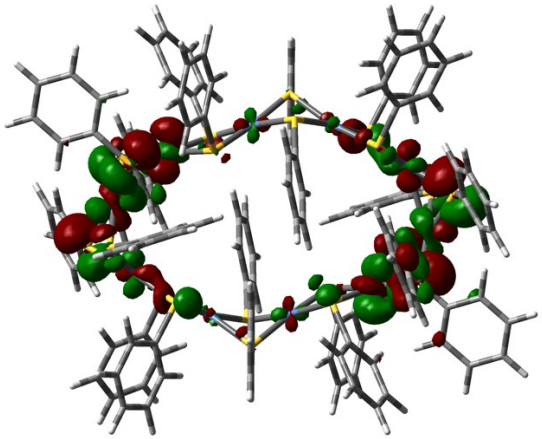

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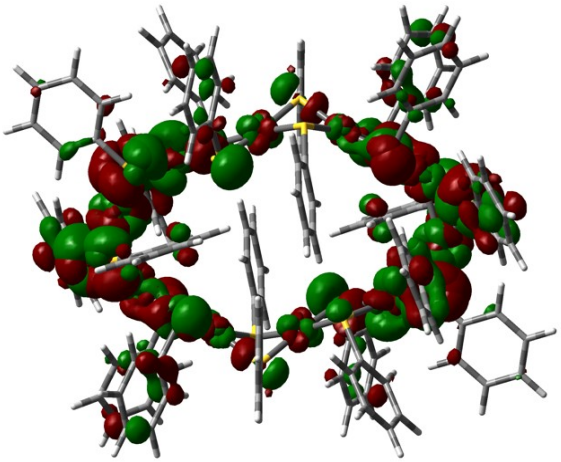
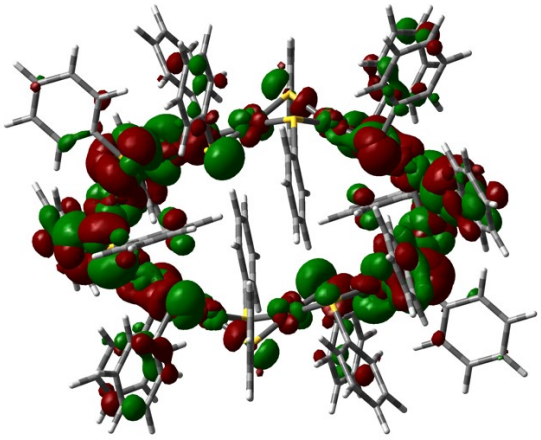
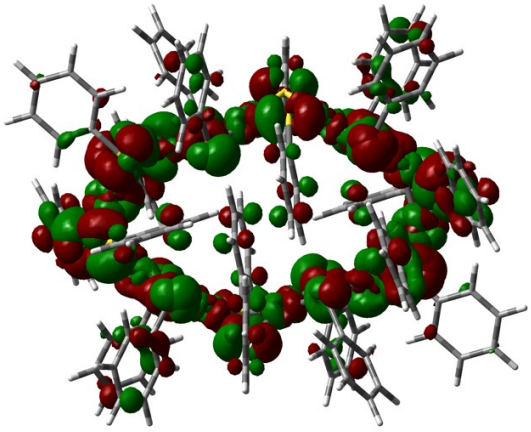


LUMO

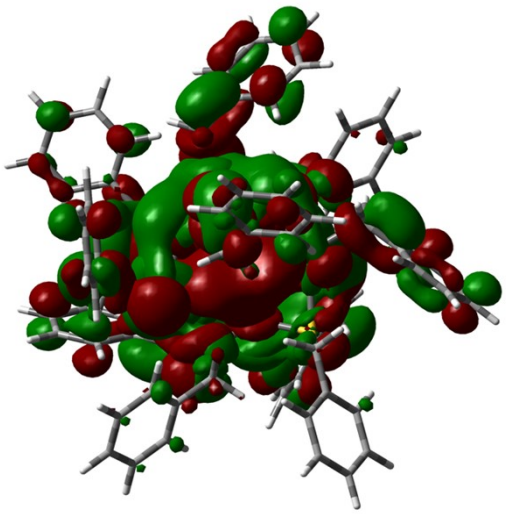


LUMO+1



LUMO+2

Figure S4. Molecular orbitals of $[Ni_{10}(SPh)_{20}]$ **1** as determined by DFT calculations. Colour codes: Ni, sky blue; S, yellow; C, grey; and H, white.



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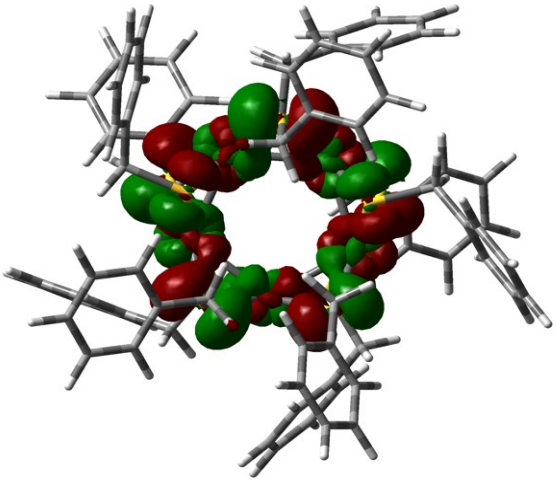
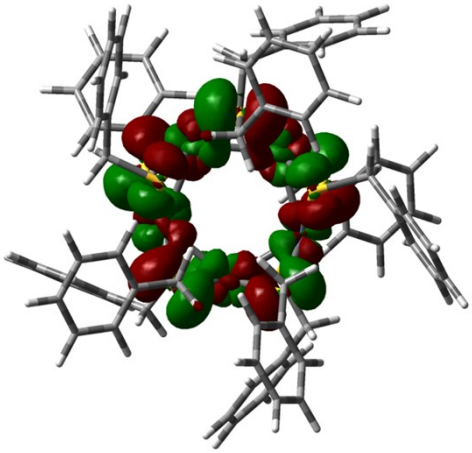
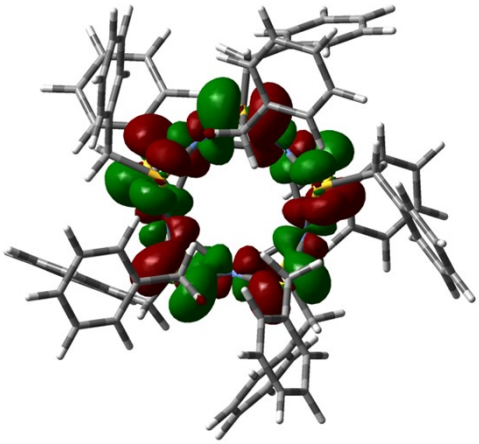


HOMO-2



HOMO-1



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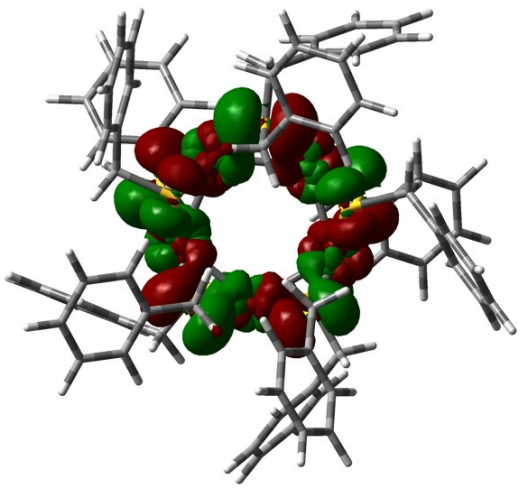
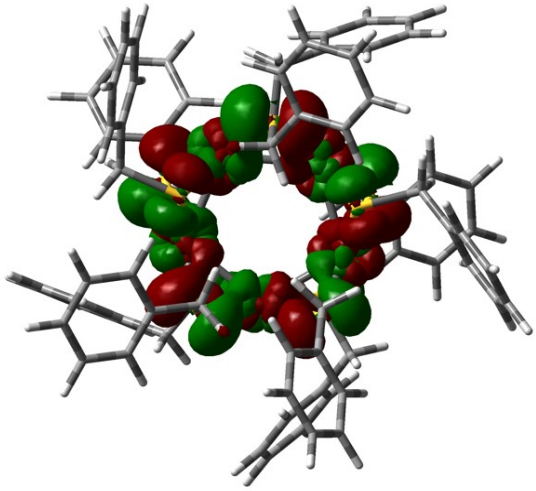
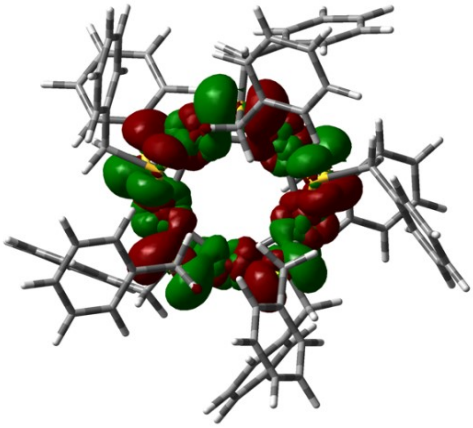


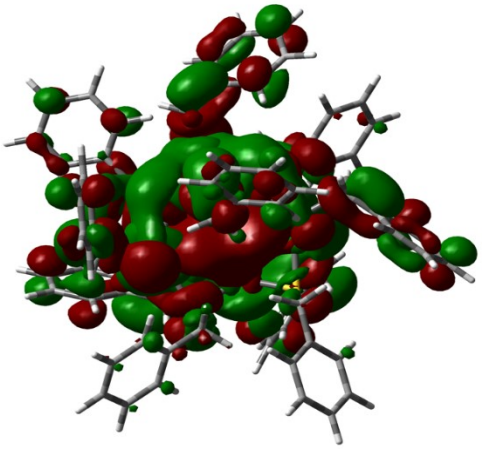
LUMO



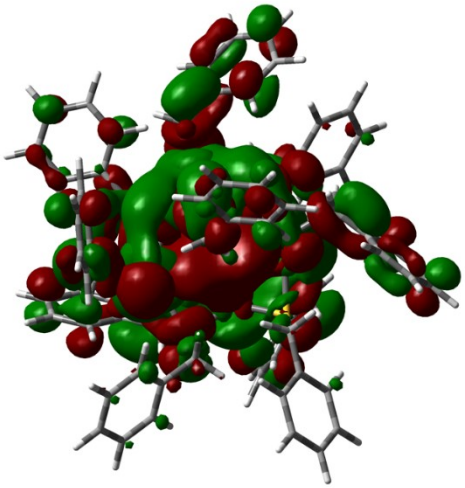
LUMO+1



LUMO+2

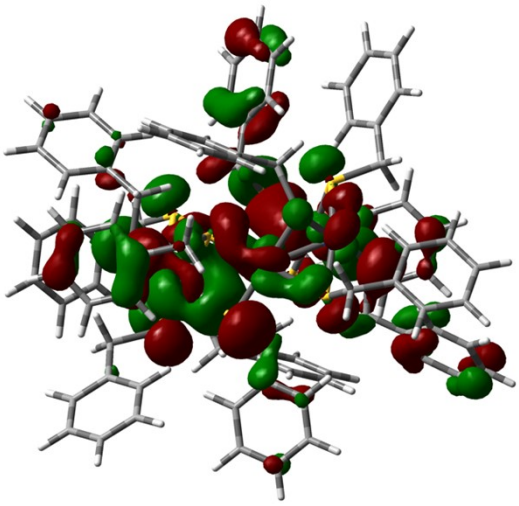


LUMO+4

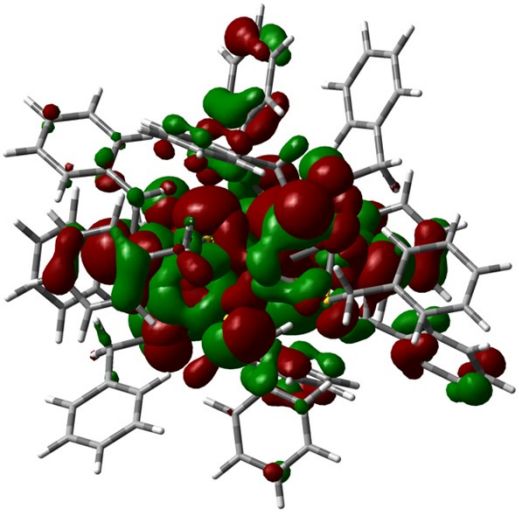


LUMO+5

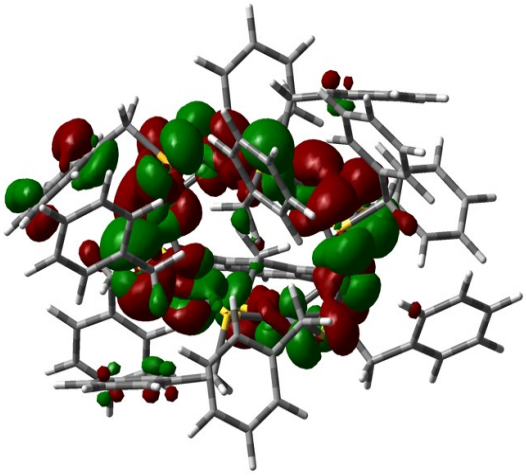
Figure S5. Molecular orbitals of $[Ni_5(SCH_2Ph)_{10}]$ **5** as determined by DFT calculations. Colour codes: Ni, sky blue; S, yellow; C, grey; and H, white.



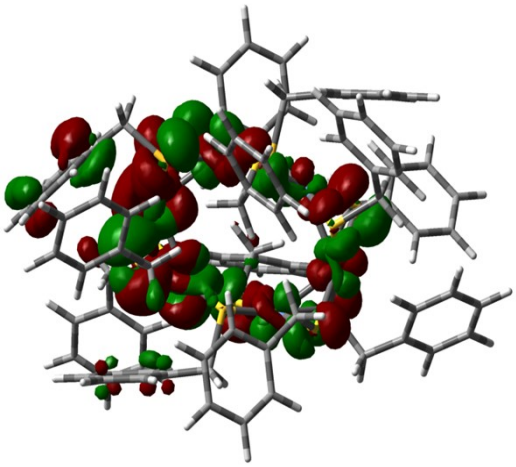
HOMO-7



HOMO-4



HOMO-2



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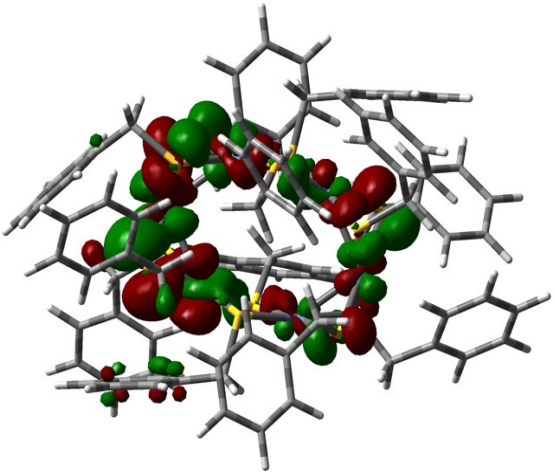
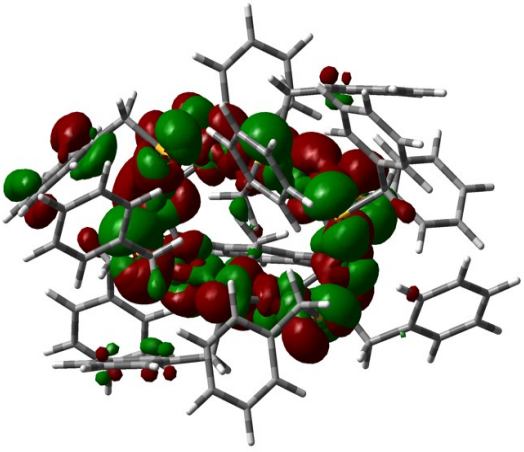
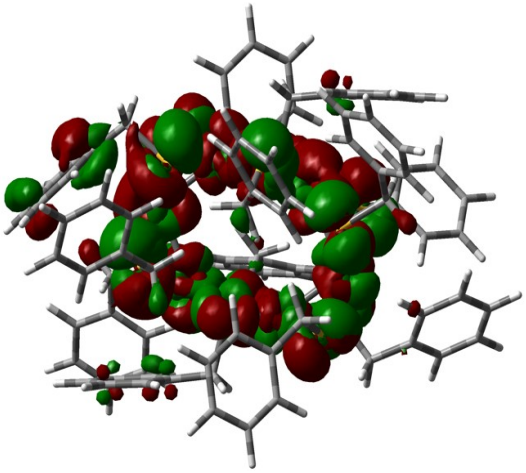


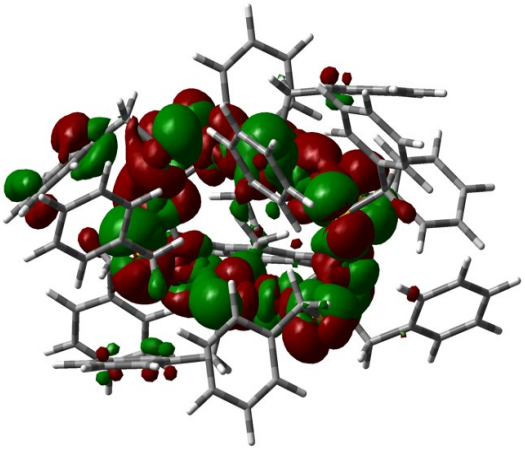
HOMO



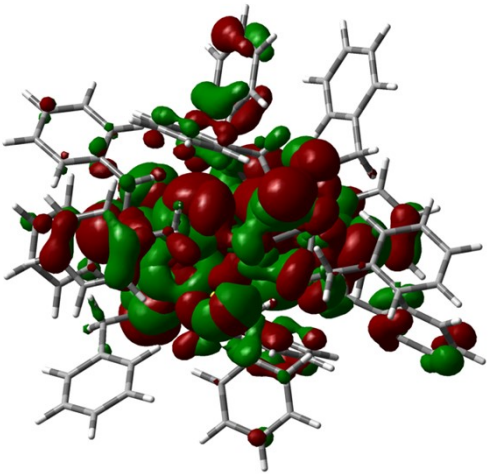
LUMO



LUMO+1



LUMO+2



LUMO+3

Figure S6. Molecular orbitals of $[Ni_6(SCH_2Ph)_{12}]$ **8** as determined by DFT calculations. Colour codes: Ni, sky blue; S, yellow; C, grey; and H, white.

Table S9: The calculated HOMO-LUMO energy gap (in eV) and corresponding wavelength, λ (nm) of $[Ni(\mu_2\text{-}SR)_2]_n$ (n = 5, 6, 10; R = CH_2Ph, Ph) systems at TD-B3LYP level of theory.

Nanoclusters	HOMO-LUMO gap (eV)	λ (nm)
$[Ni_5(SCH_2Ph)_{10}]$	3.012	322.80
$[Ni_6(SCH_2Ph)_{12}]$	3.169	348.40
$[Ni_{10}(SPh)_{20}]$	3.212	349.98

Table S10. Characteristic vertical transition wavelengths (energies), oscillator strengths (f), configuration interactions (CI), expansion coefficients and percentage CI coefficients of $[Ni_5(SCH_2Ph)_{10}]$ **5**, $[Ni_6(SCH_2Ph)_{12}]$ **8**, and $[Ni_{10}(SMe)_{20}]$ **1** determined by theoretical calculations.

Molecule	Excited state	Wavelength/nm(ev)	f	Dominant configuration	CI expansion coefficient
$[Ni_5(SCH_2Ph)_{10}]$	S53	347.42 (3.5688)	0.0354	H-12 → L	0.24697 (12.199%)
				H-9 → L+2	0.23025 (10.603%)
	S71	324.64 (3.8192)	0.1170	H-2 → L+5	0.23227 (10.789%)
				H-3 → L+5	-0.21635 (9.3615%)
	S74	**322.47 (3.8448)**	**0.1574**	**H-17 → L**	**0.23049 (10.625%)**
				H-2 → L+5	**0.25565 (13.071%)**
	S77	320.06 (3.8738)	0.1242	H-17 → L+2	-0.22051 (9.7249%)
				H-6 →L+2	0.23168 (10.735%)
	S29	**415.76 (2.9821)**	**0.0024**	**H-4 → L+1**	**0.36169 (26.164%)**
	S32	397.08 (3.1224)	0.0044	H-2 → L+1	0.32754 (21.456%)
$[Ni_6(SCH_2Ph)_{12}]$	S65	351.03 (3.5320)	0.0395	H-12 → L+1	0.21485 (9.2321%)
	S71	**343.39 (3.6106)**	**0.0758**	**H-11 →L+1**	**0.21335 (9.1036%)**

				H-7 →L+3	**0.27968 (15.644%)**
	S31	423.95 (2.9245)	0.0169	H-4 → L	0.42221 (35.652%)
				H-5 → L	0.24951 (12.451%)
	S32	420.93 (2.9455)	0.0154	H-4 → L+1	0.47621 (45.355%)
	S33	418.01 (2.9661)	0.0136	H-5 → L+1	0.36521 (26.676%)
	S34	417.09 (2.9726)	0.0106	H-5 → L+1	0.34099 (23.255%)
	S35	**411.38 (3.0139)**	**0.0229**	**H-1 → L+2**	**0.26223 (13.753%)**
$[Ni_{10}(SMe)_{20}]$	**S60**	**449.51 (2.7582)**	**0.012**	**H-16 → L**	**0.27004 (14.584%)**
				H-8 → L	**0.24103 (11.619%)**
	S179	**349.98 (3.5426)**	**0.0903**	**H-26 → L**	**0.25535 (13.041%)**
				H-10 → L+7	**-0.17092 (5.8427)**
	S34	**609.26 (2.0350)**	**0.0035**	**H → L+1**	**0.29832 (17.799%)**
				H → L+4	**0.28467 (16.207%)**

Table S11. Analysis of the excited state S74 and hole electron transition orbitals of $[Ni_5(SCH_2Ph)_{10}]$ at TD-B3LYP level of theory. Occ. stands for electron occupancy.

MO	Occu.	Hole (%)	Electron (%)
HOMO-17	2	10.625	0
HOMO-14	2	6.366	0
HOMO-10	2	2.329	0
HOMO-5	2	8.944	0
HOMO-4	2	2.516	0
HOMO-2	2	13.071	0
HOMO-1	2	9.323	0
LUMO	0	0	13.101
LUMO+1	0	0	2.329
LUMO+2	0	0	3.89
LUMO+3	0	0	8.944
LUMO+5	0	0	24.911

Table S12. Analysis of the excited state S29 and hole electron transition orbitals of $[Ni_5(SCH_2Ph)_{10}]$ at TD-B3LYP level of theory. Occ. stands for electron occupancy.

MO	Occu.	Hole(%)	Electron(%)
HOMO-4	2	37.823	0
HOMO-3	2	3.427	0
HOMO-2	2	22.988	0
HOMO-1	2	3.405	0
HOMO	2	7.909	0
LUMO	0	0	10.488
LUMO+1	0	0	29.267
LUMO+2	0	0	23.517
LUMO+3	0	0	12.279

Table S13. Analysis of the excited state S71 and hole electron transition orbitals of $[Ni_6(SCH_2Ph)_{12}]$ at TD-B3LYP level of theory. Occ. stands for electron occupancy.

MO	Occu.	Hole(%)	Electron(%)
HOMO-19	2	4.649	0
HOMO-18	2	4.66	0
HOMO-17	2	3.552	0
HOMO-15	2	4.452	0
HOMO-13	2	2.115	0
HOMO-12	2	5.142	0
HOMO-11	2	11.984	0
HOMO-7	2	18.989	0
HOMO-4	2	6.89	0
HOMO-3	2	2.934	0
LUMO	0	0	14.976
LUMO+1	0	0	18.697
LUMO+2	0	0	6.226
LUMO+3	0	0	15.644

LUMO+4	0	0	2.986
LUMO+5	0	0	6.838

Table S14. Analysis of the excited state S35 and hole electron transition orbitals of $[Ni_6(SCH_2Ph)_{12}]$ at TD-B3LYP level of theory. Occ. stands for electron occupancy.

MO	**Occu.**	**Hole(%)**	**Electron(%)**
HOMO-5	2	10.853	0
HOMO-3	2	5.568	0
HOMO-2	2	9.141	0
HOMO-1	2	35.582	0
HOMO	2	17.257	0
LUMO	0	0	2.137
LUMO+1	0	0	16.721
LUMO+2	0	0	34.742
LUMO+3	0	0	3.083
LUMO+4	0	0	13.932
LUMO+5	0	0	7.786

Table S15. Analysis of the excited state S60 and hole electron transition orbitals of $[Ni_{10}(SMe)_{20}]$ at TD-B3LYP level of theory. Occ. stands for electron occupancy.

MO	Occu.	Hole(%)	Electron(%)
HOMO-22	2	3.262	0
HOMO-19	2	2.423	0
HOMO-16	2	14.584	0
HOMO-15	2	2.406	0
HOMO-14	2	2.24	0
HOMO-11	2	2.036	0
HOMO-10	2	5.564	0
HOMO-8	2	11.619	0
HOMO-7	2	3.37	0
HOMO-4	2	7.861	0
HOMO-2	2	4.01	0
LUMO	0	0	41.728
LUMO+2	0	0	13.637
LUMO+4	0	0	4.01

Table S16. Analysis of the excited state S179 and hole electron transition orbitals of $[Ni_{10}(SMe)_{20}]$ at TD-B3LYP level of theory. Occ. stands for electron occupancy.

MO	Occu.	Hole(%)	Electron(%)
HOMO-30	2	2.285	0
HOMO-26	2	13.041	0
HOMO-25	2	4.794	0
HOMO-19	2	2.761	0
HOMO-13	2	6.045	0
HOMO-10	2	8.448	0
HOMO-5	2	4.614	0
LUMO	0	0	20.12
LUMO+2	0	0	2.761
LUMO+3	0	0	3.283
LUMO+7	0	0	13.219
LUMO+8	0	0	2.605

Table S17. Analysis of the excited state S34 and hole electron transition orbitals of $[Ni_{10}(SMe)_{20}]$ at TD-B3LYP level of theory. Occ. stands for electron occupancy.

MO	Occu.	Hole	Electron
HOMO-38	2	5.969	0
HOMO-11	2	2.152	0
HOMO-10	2	3.327	0
HOMO	2	55.602	0
LUMO	0	0	13.396
LUMO+1	0	0	17.799
LUMO+2	0	0	7.424
LUMO+3	0	0	10.049
LUMO+4	0	0	18.381

Table S18. Topological parameters of $[Ni_{10}(SPh)_{20}]\in CH_2Cl_2$ at Bond Critical Points (BCP).

Interactions	ρ(r) (a.u.)	Δρ(r) (a.u.)	Distance (Å)	G(r) (a.u.)	V(r) (a.u.)	Eint (KJ/mol)	Sign(λ_2)ρ
S···Cl	0.0070	0.022	3.58	0.00451	-0.00332	-8.71666	-0.0070
S···Cl	0.0065	0.020	3.64	0.00409	-0.00300	-7.8765	-0.0065
S···Cl	0.0046	0.014	3.84	0.00274	-0.00196	-5.14598	-0.0046
S···Cl	0.0072	0.024	3.53	0.00487	-0.00354	-9.29427	-0.0072
S···Cl	0.0055	0.017	3.73	0.00340	-0.00246	-6.45873	-0.0055
S···Cl	0.0048	0.015	3.79	0.00297	-0.00209	-5.487295	-0.0048

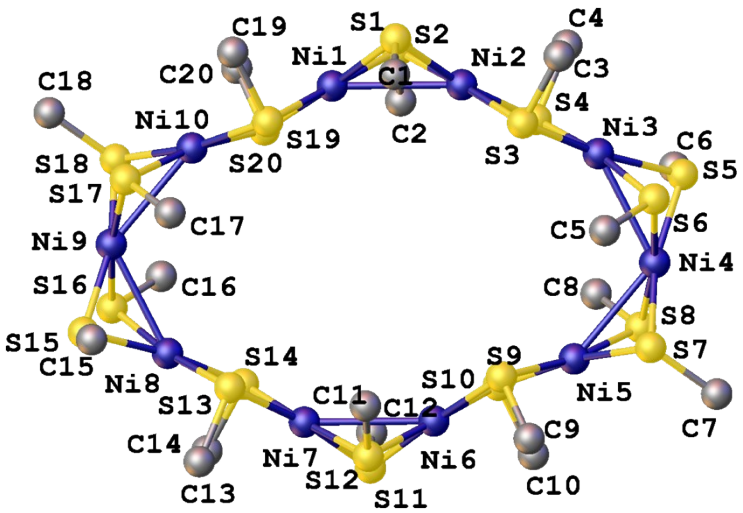


Figure S7. Top view of the optimized geometry of $[Ni_{10}(SMe)_{20}]$. H atoms are excluded for clarity.

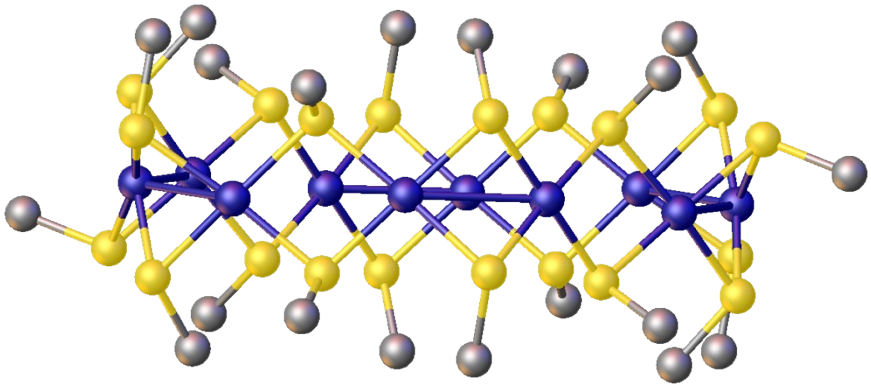


Figure S8. Side view of the optimized geometry of $[Ni_{10}(SMe)_{20}]$. H atoms are excluded for clarity.

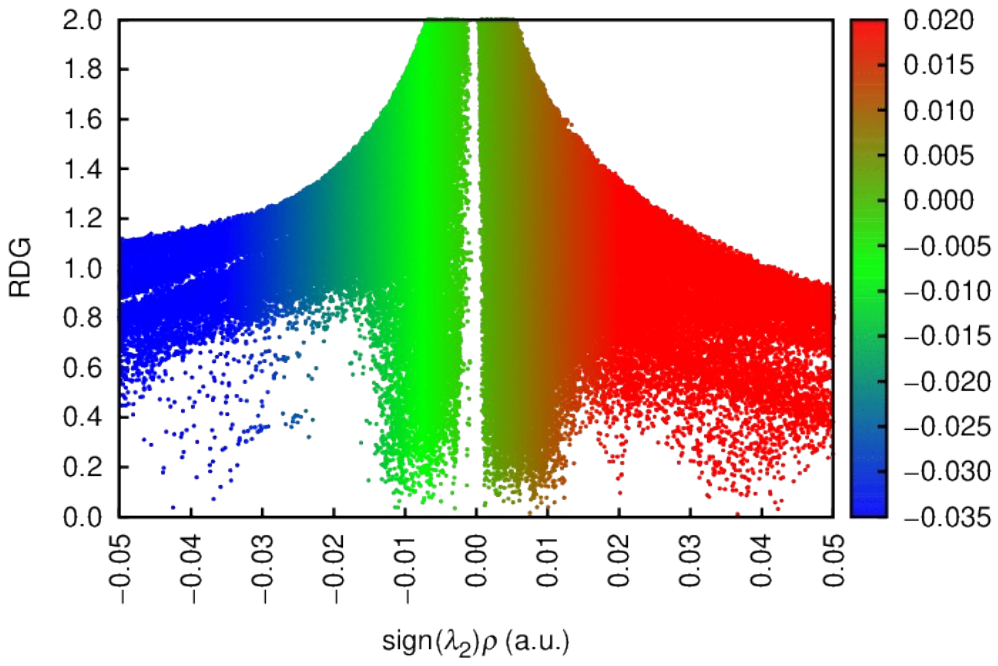
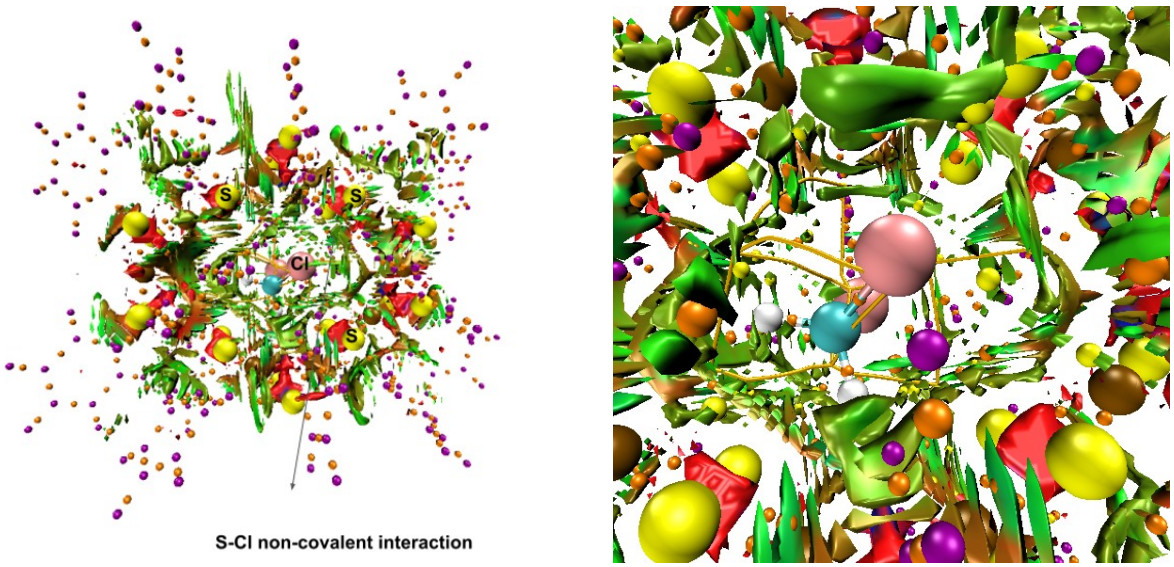


Figure S9. Reduced Density Gradient (RDG) vs. Sign(λ_2)ρ plot for non-covalent interaction analysis.



(A) (B)

Figure S10. The molecular graphs of $[Ni_{10}(SPh)_{20}]\in CH_2Cl_2$ **1** obtained from QTAIM and Non-Covalent Interaction methods (A). (B) is an expanded view of the graph. The bond and ring critical points are shown in orange and yellow colors, respectively. The green isosurface between sulfur and chlorine indicates the non-covalent interaction. C, S, Cl, H and Ni are shown in cyan, yellow, pink, white and ochre, respectively.

NMR, ATR-FTIR, HRMS, UV-Vis, Elemental analysis data

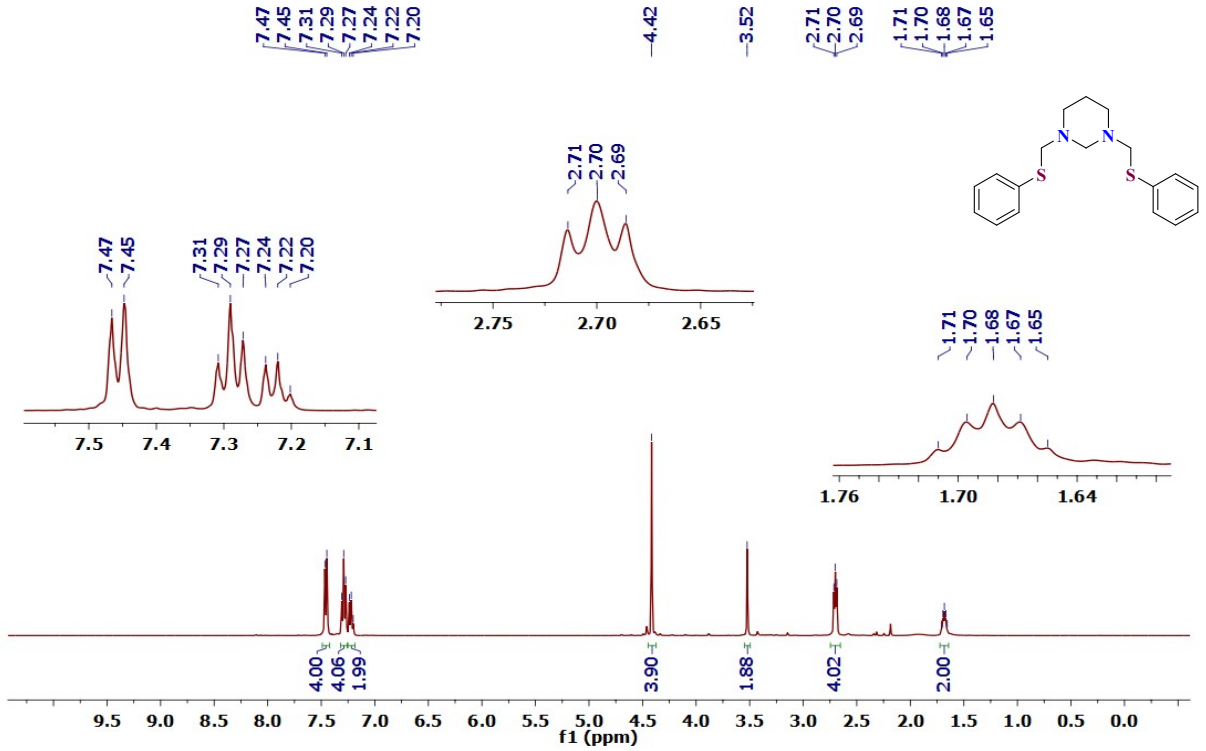


Figure S11. ^{1}H NMR (400 MHz, 25 ºC) spectrum of 1,3-bis((phenylthio)methyl)hexahydropyrimidine **L1** in $CDCl_3$.

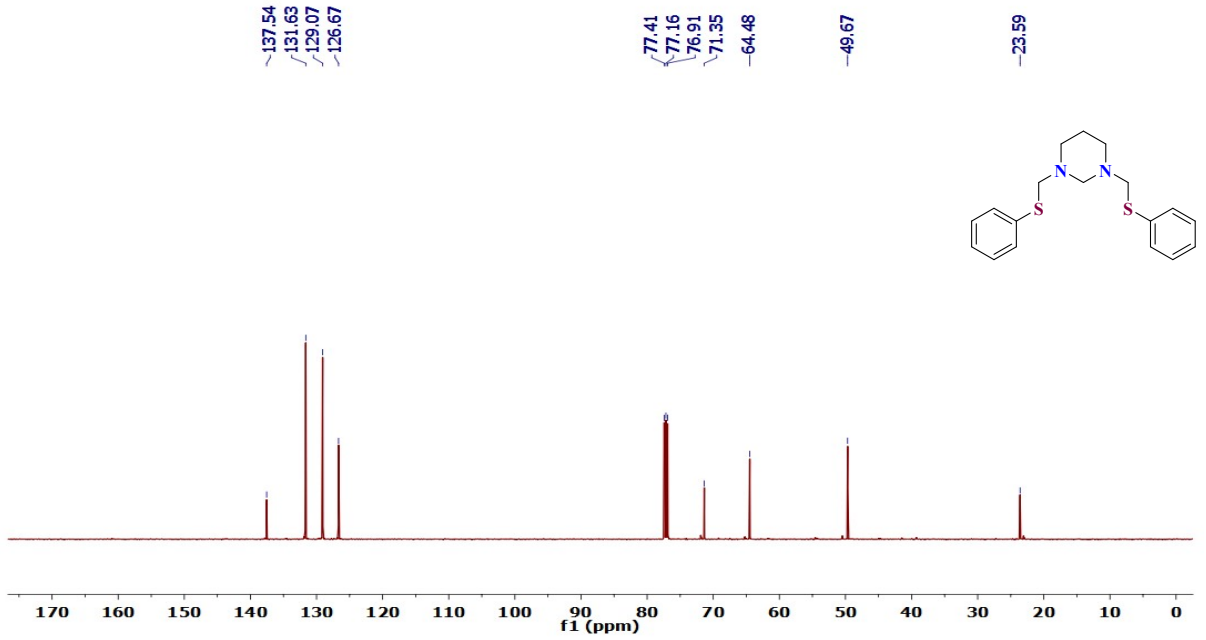


Figure S12. $^{13}C\{^{1}H\}$ NMR (125.75 MHz, 25 ºC) spectrum of 1,3-bis((phenylthio)methyl)hexahydropyrimidine **L1** in $CDCl_3$.

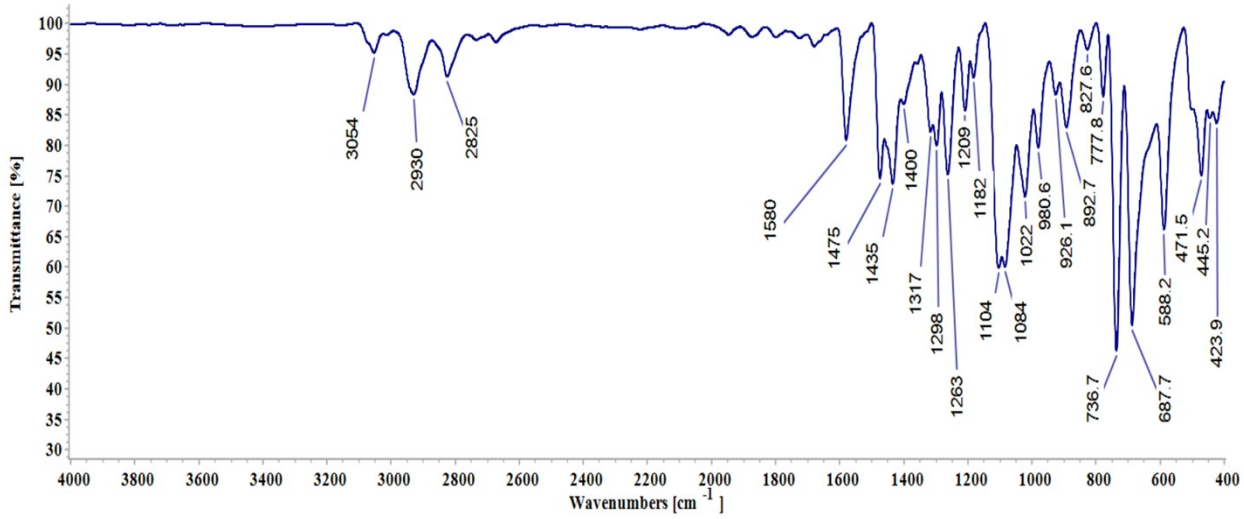
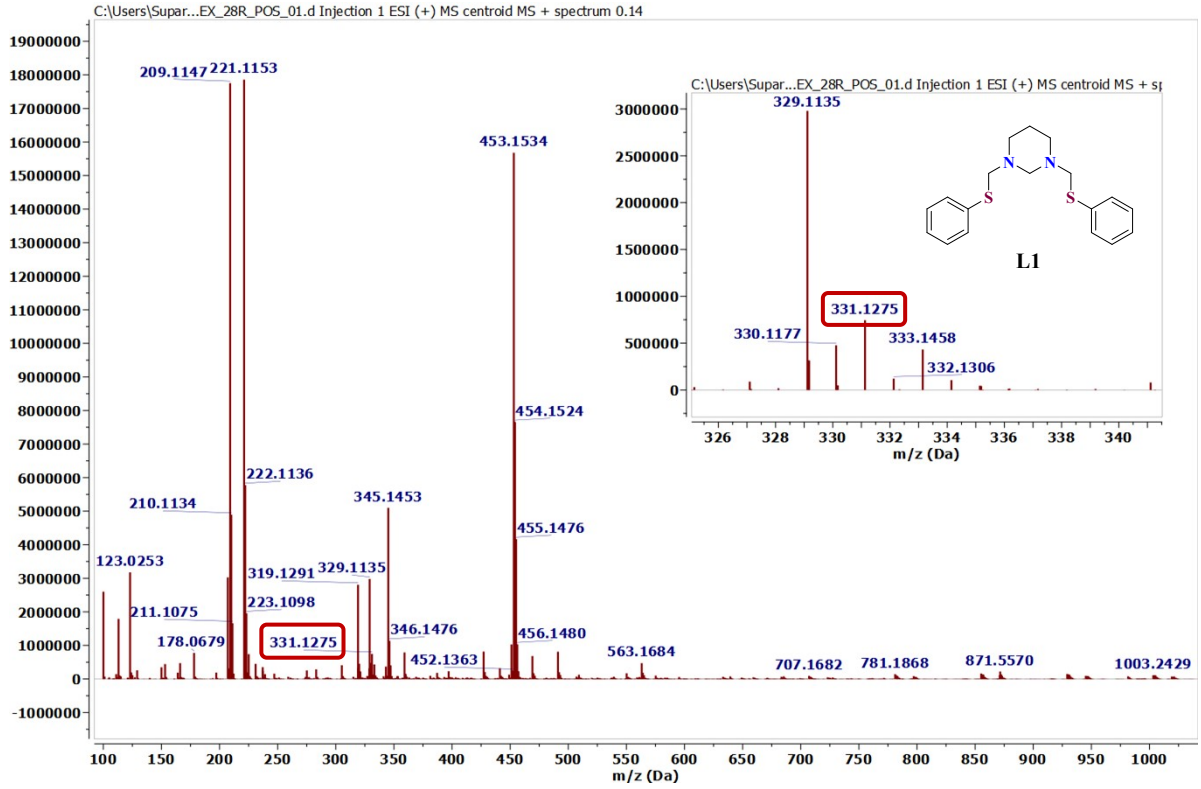


Figure S13. ATR-FTIR spectrum of 1,3-bis((phenylthio)methyl)hexahydropyrimidine **L1**.



Compound name	Calcd *m/z* for $[M+H]^+$	Observed *m/z* for $[M+H^+]$
1,3-bis((phenylthio)methyl)hexahydropyrimidine	331.1297	331.1275

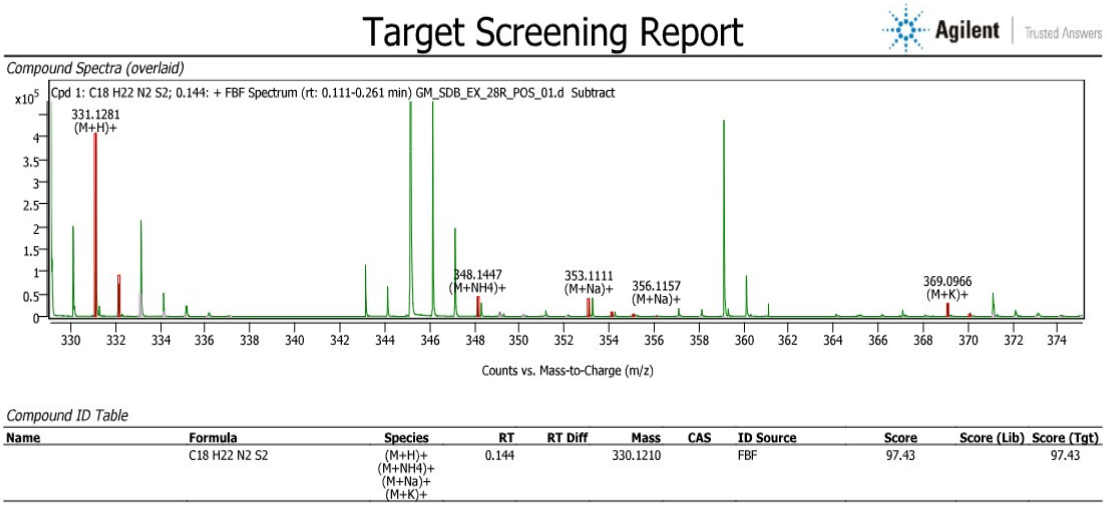


Figure S14. HRMS (+ESI) spectrum of 1,3-bis((phenylthio)methyl)hexahydropyrimidine **L1**.

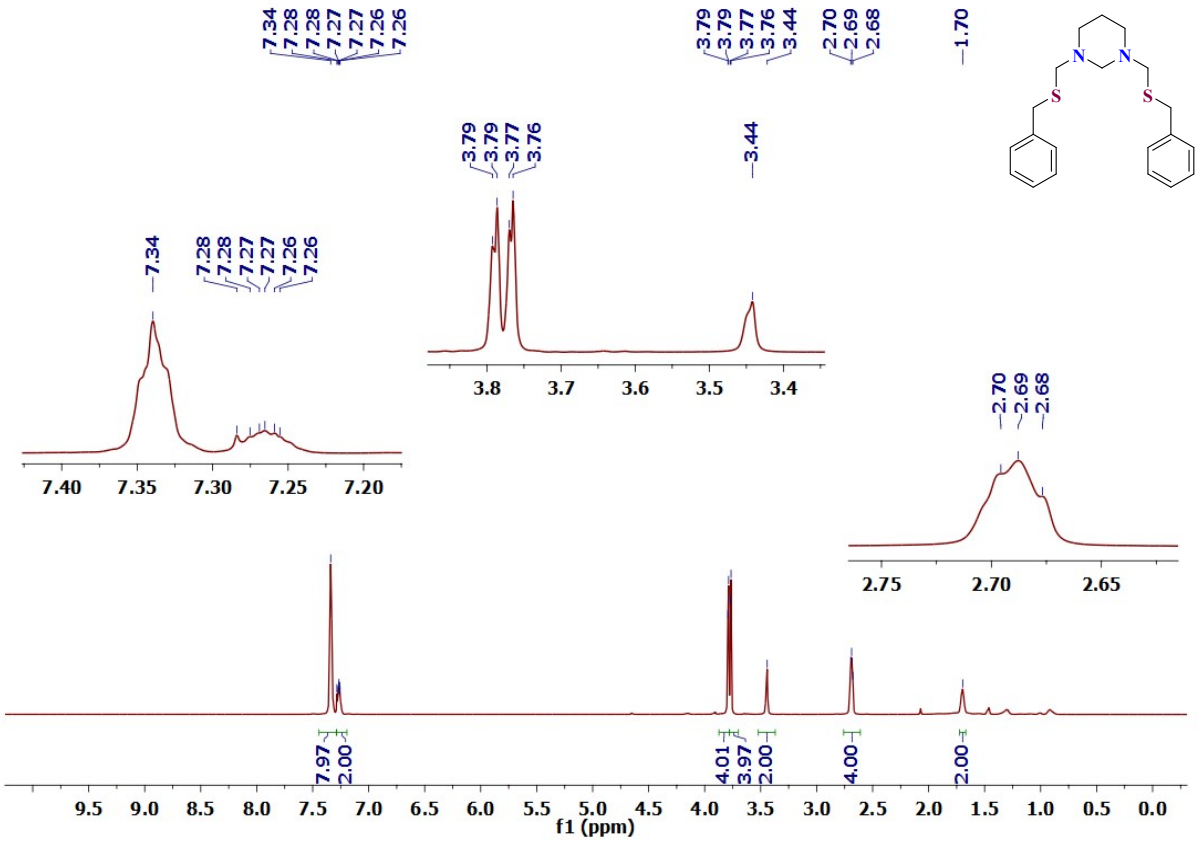


Figure S15. ^{1}H NMR (500 MHz, 25 ^{o}C) spectrum of 1,3-bis((benzylthio)methyl)hexahydropyridine **L2** in $CDCl_3$.

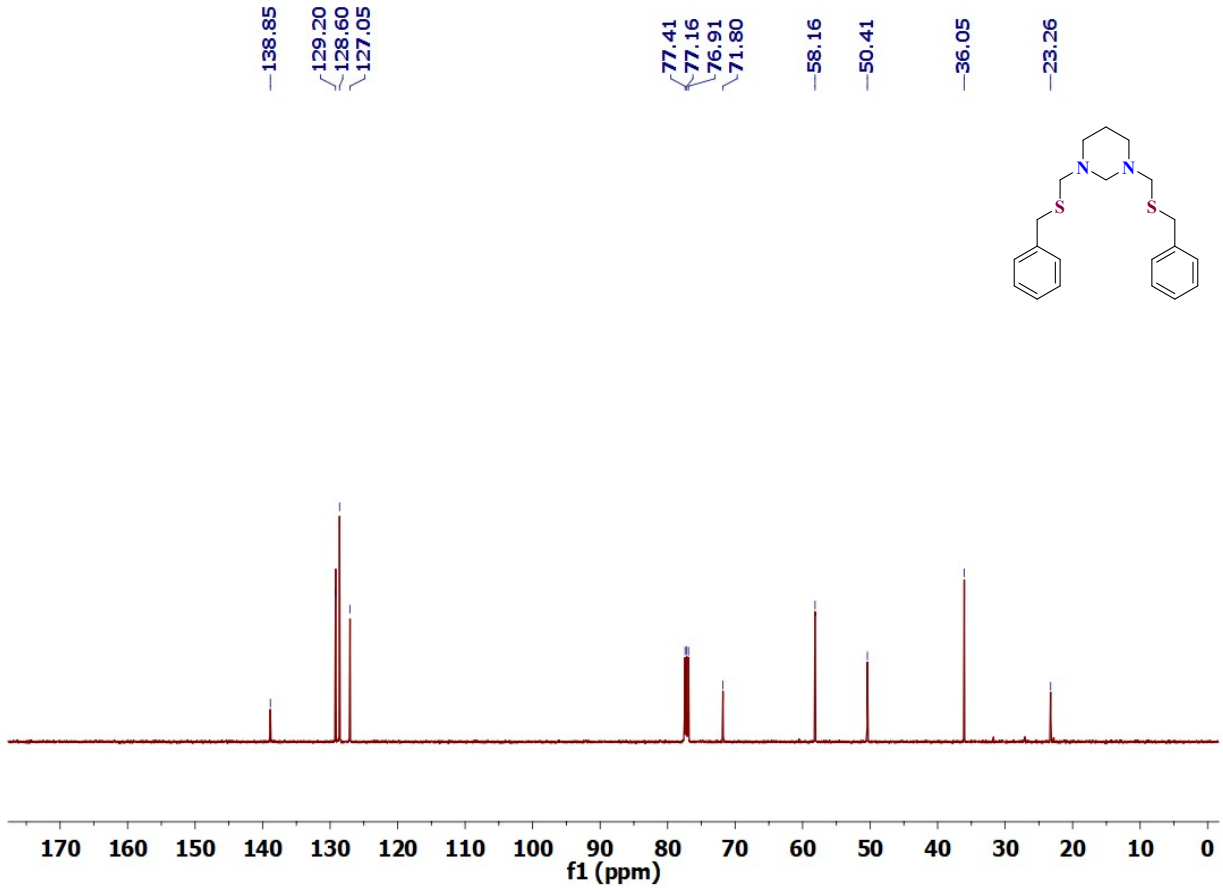


Figure S16. $^{13}C\{^{1}H\}$ NMR (125.75 MHz, 25 ºC) spectrum of 1,3-bis((benzylthio)methyl)hexahydropyrimidine **L2** in $CDCl_3$.

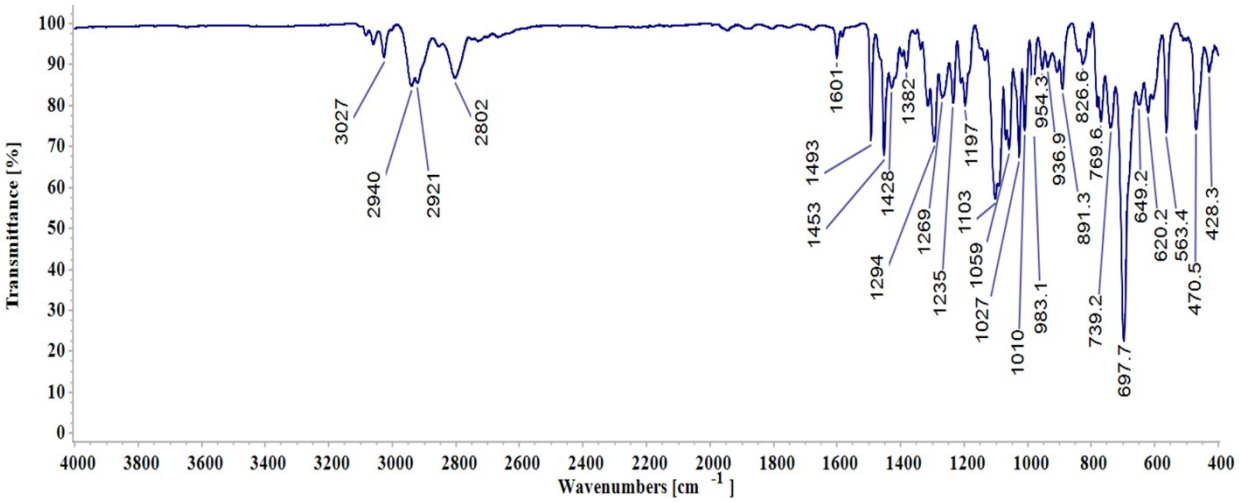
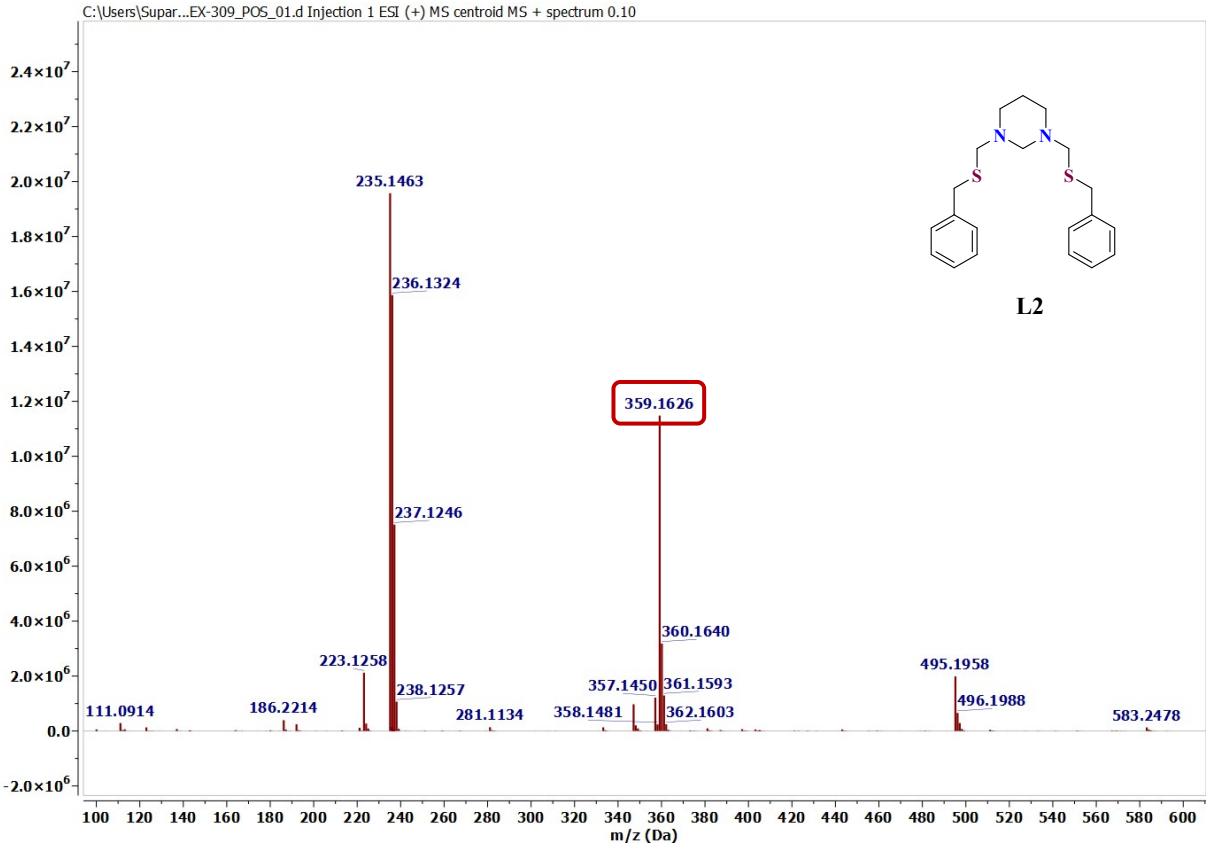


Figure S17. ATR-FTIR spectrum of 1,3-bis((benzylthio)methyl)hexahydropyrimidine **L2**.



Compound name	Calcd *m/z* for $[M+H]^+$	Observed *m/z* for $[M+H^+]$
1,3-bis((benzylthio)methyl)hexahydropyrimidine	359.1610	359.1626

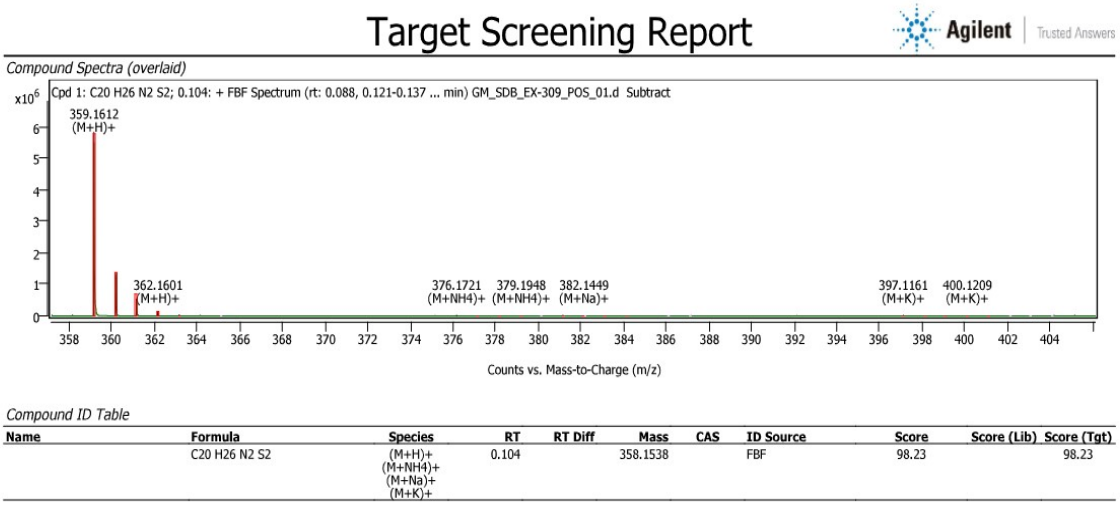


Figure S18. HRMS (+ESI) spectrum of 1,3-bis((benzylthio)methyl)hexahydropyrimidine **L2**.

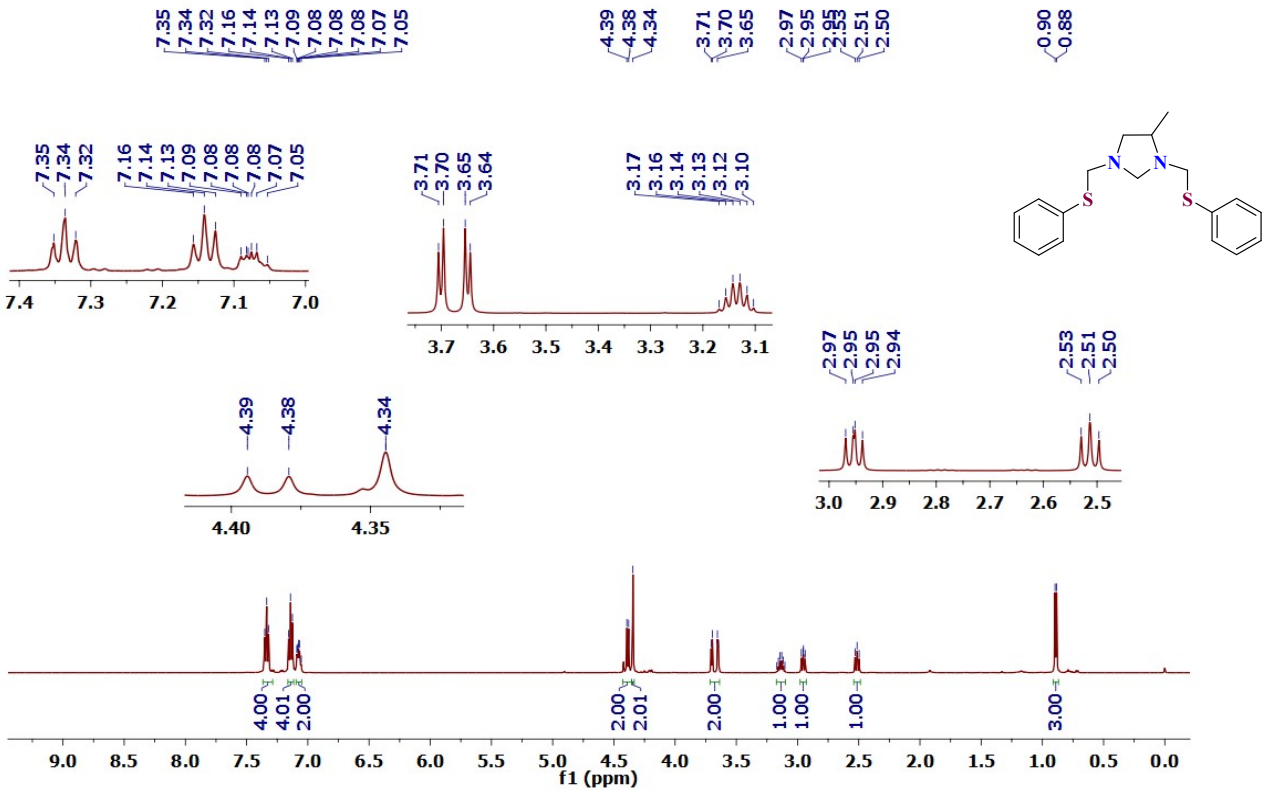


Figure S19. ^{1}H NMR (400 MHz, 25 ºC) spectrum of 4-methyl-1,3-bis((phenylthio)methyl)imidazolidine **L3** in $CDCl_3$

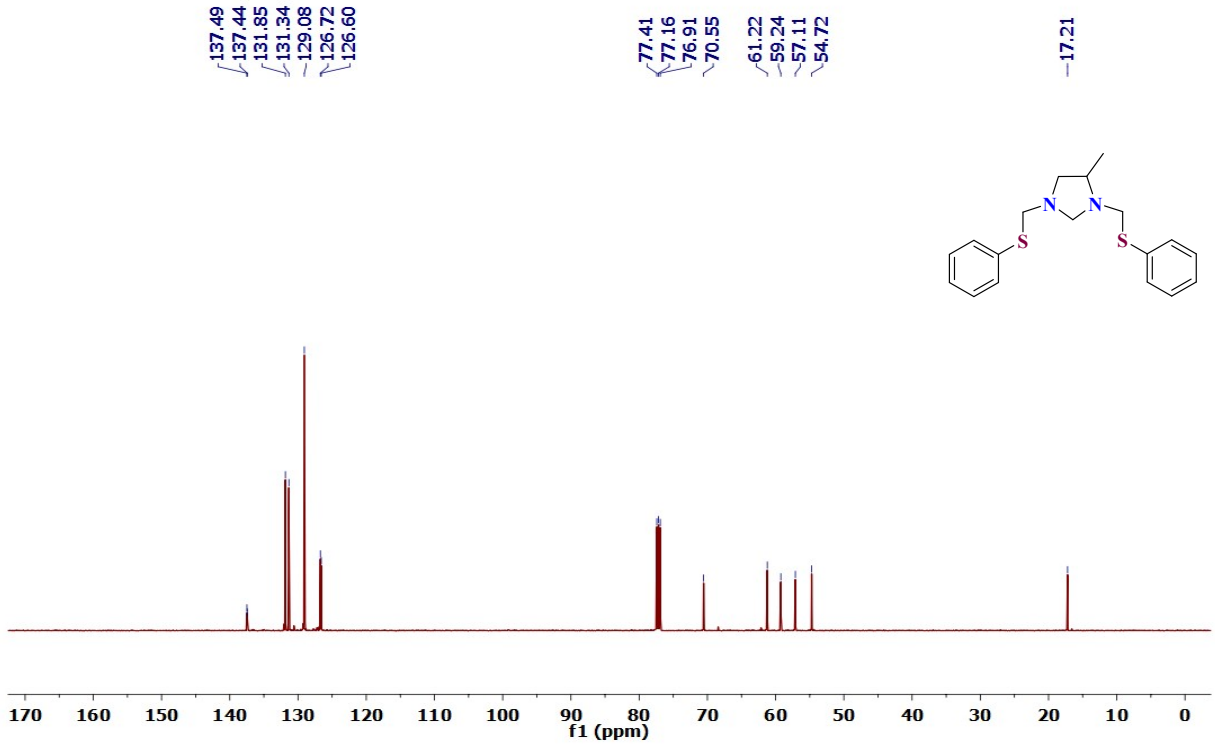


Figure S20. $^{13}C\{^{1}H\}$ NMR (125.75 MHz, 25 ºC) spectrum of 4-methyl-1,3-bis((phenylthiol)methyl)imidazolidine **L3** in $CDCl_3$.

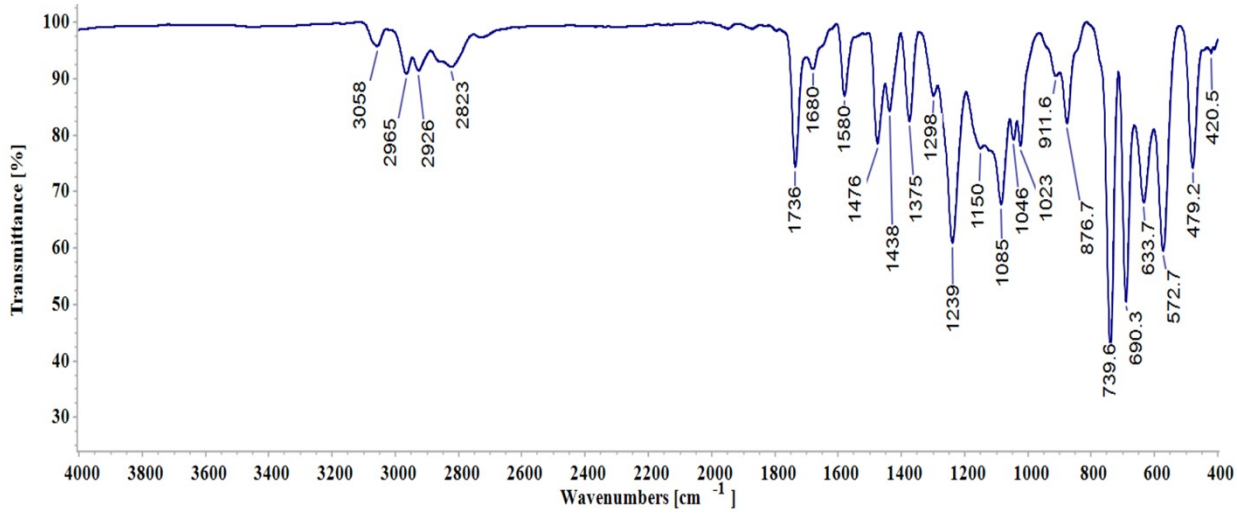
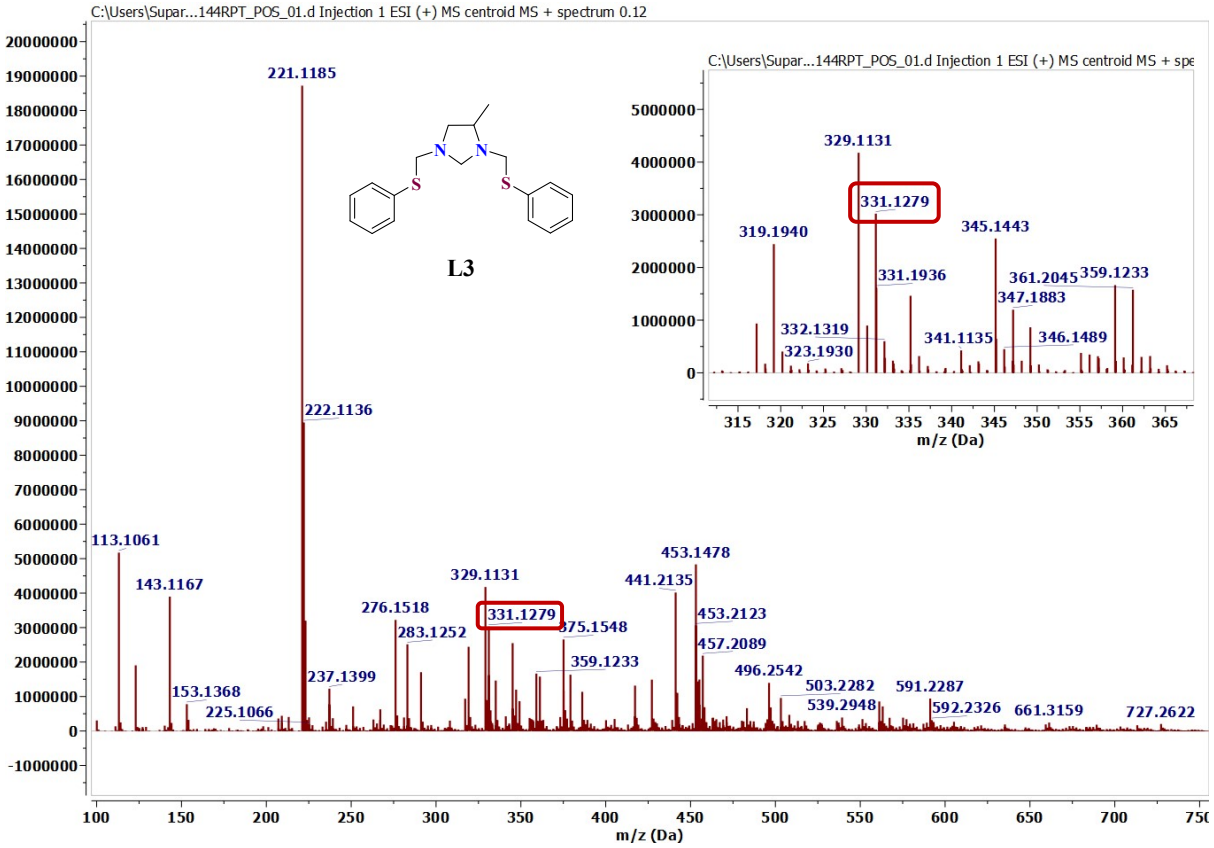


Figure S21. ATR-FTIR spectrum of 4-methyl-1,3-bis((phenylthiol)methyl)imidazolidine **L3**.



Compound name	Calcd *m/z* for [M+H$^+$]	Observed *m/z* for [M+H$^+$]
4-methyl-1,3-bis((phenylthiol)methyl)imidazolidine	331.1297	331.1279

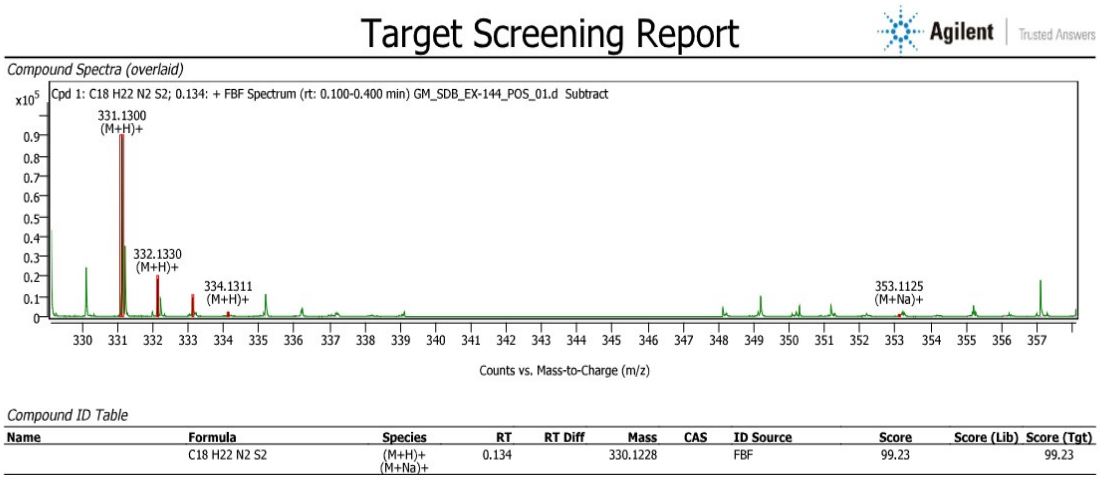


Figure S22. HRMS (+ESI) spectrum of 4-methyl-1,3-bis((phenylthiol)methyl)imidazolidine **L3**.

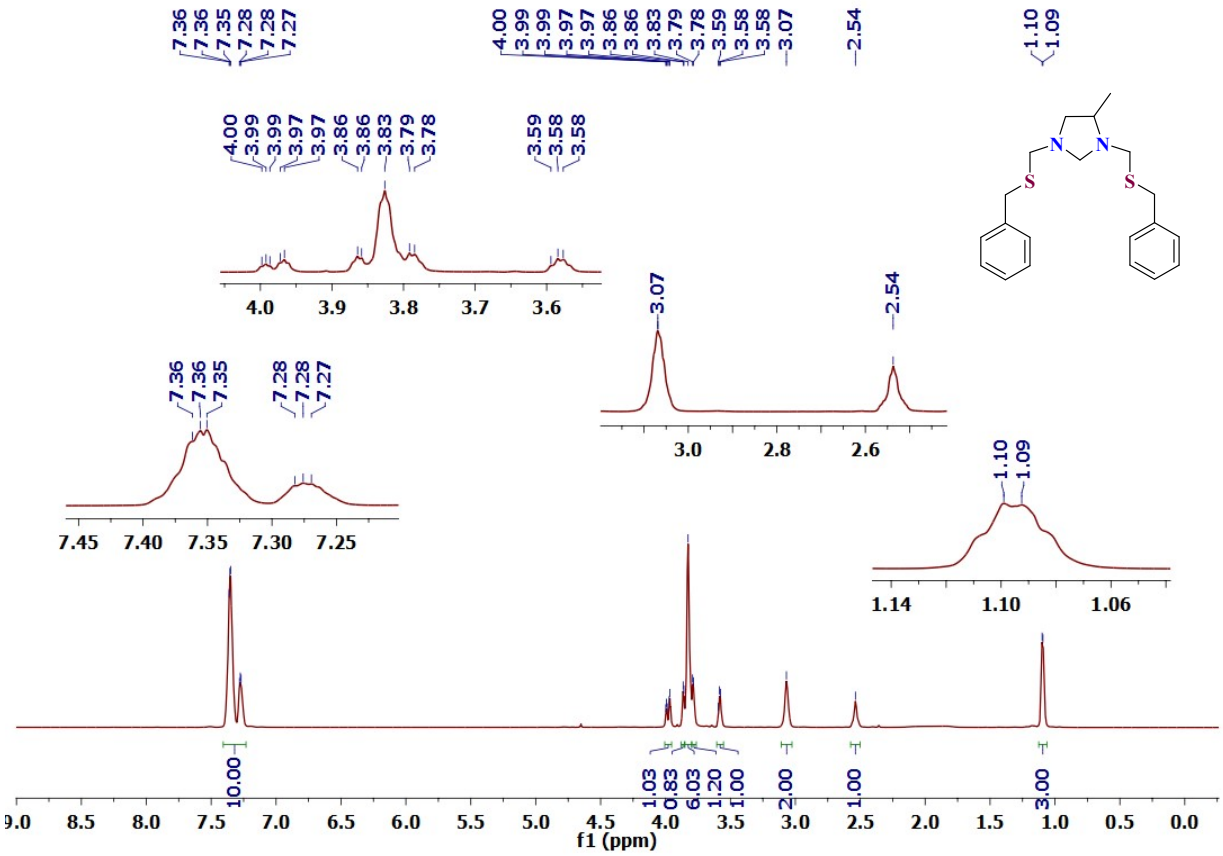


Figure S23. ^{1}H NMR (500 MHz, 25 ^{o}C) spectrum of 4-methyl-1,3-bis((benzylthio)methyl)imidazolidine **L4** in $CDCl_3$

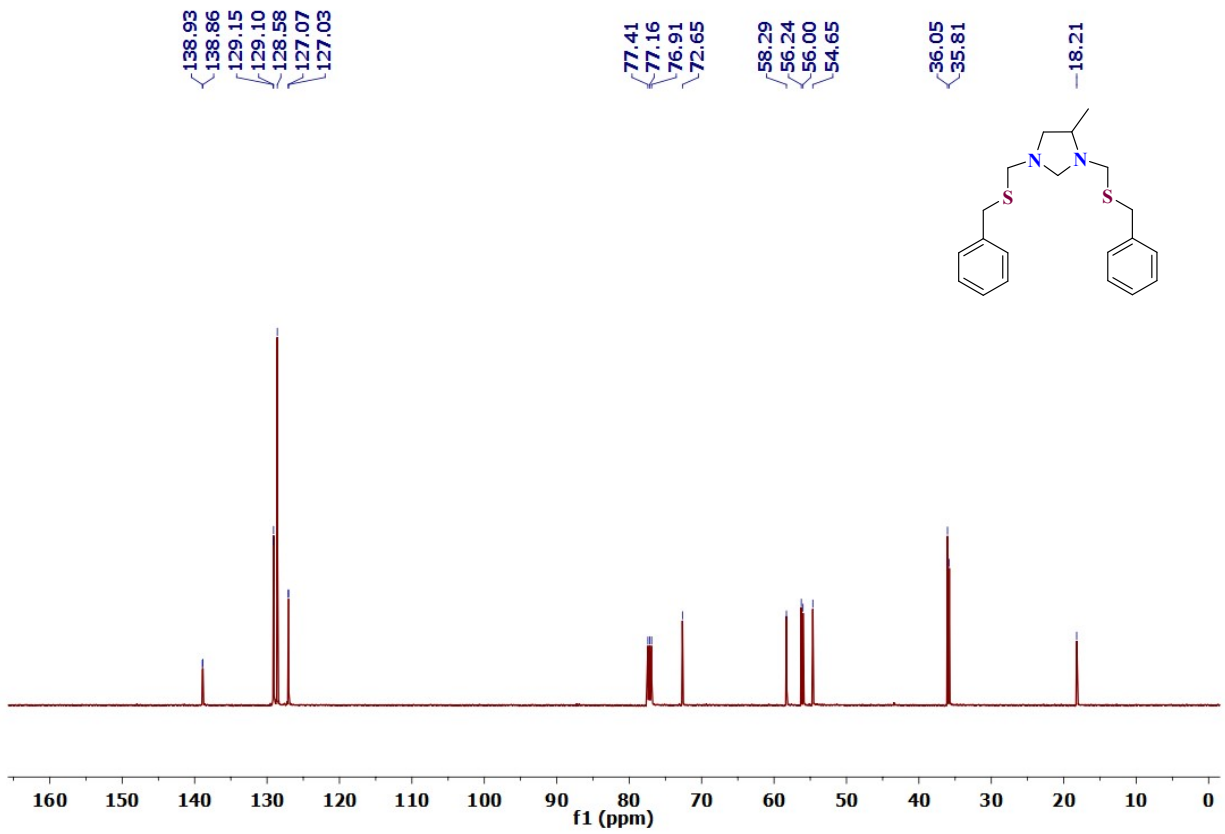


Figure S24. $^{13}C\{^{1}H\}$ NMR (125.75 MHz, 25 ºC) spectrum of 4-methyl-1,3-bis((benzylthio)methyl)imidazolidine **L4** in $CDCl_3$.

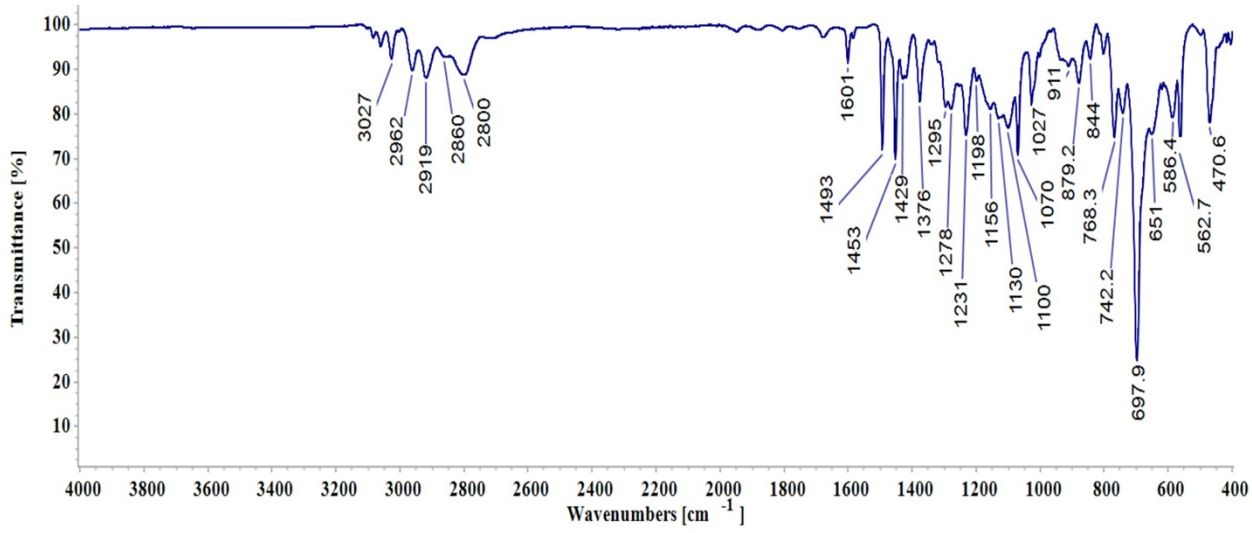
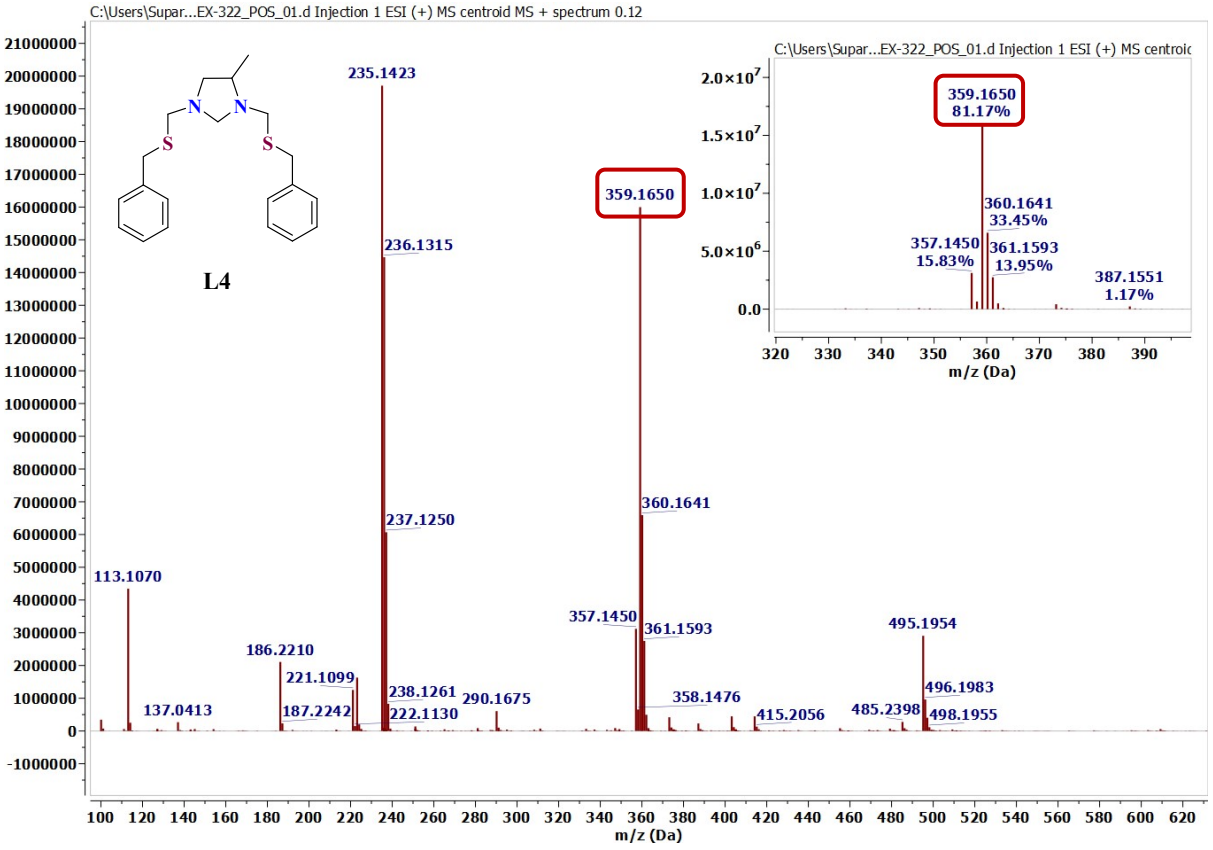


Figure S25. ATR-FTIR spectrum of 4-methyl-1,3-bis((benzylthio)methyl)imidazolidine **L4**.



Compound name	Calcd *m/z* for [M+H$^+$]	Observed *m/z* for [M+H$^+$]
4-methyl-1,3-bis((benzylthio)methyl)imidazolidine	359.1610	359.1650

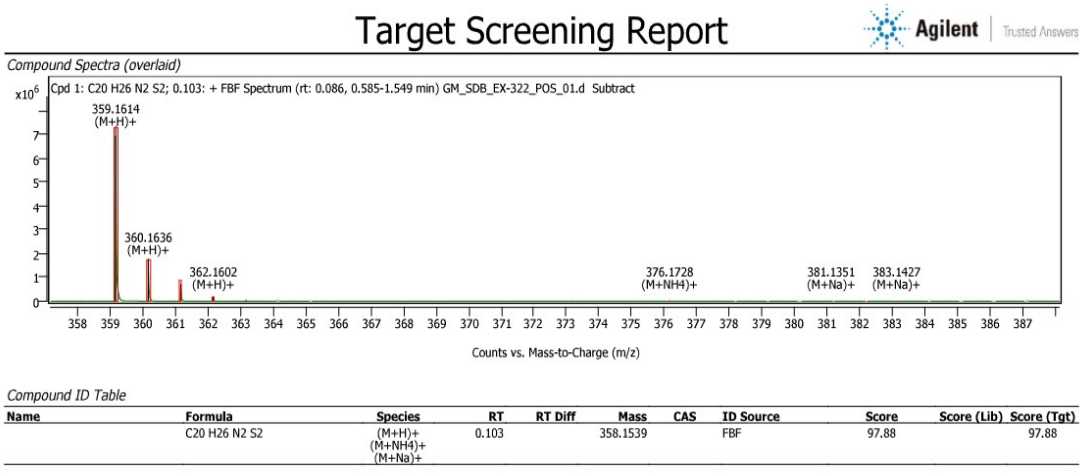


Figure S26. HRMS (+ESI) spectrum of 4-methyl-1,3-bis((benzylthio)methyl)imidazolidine **L4**.

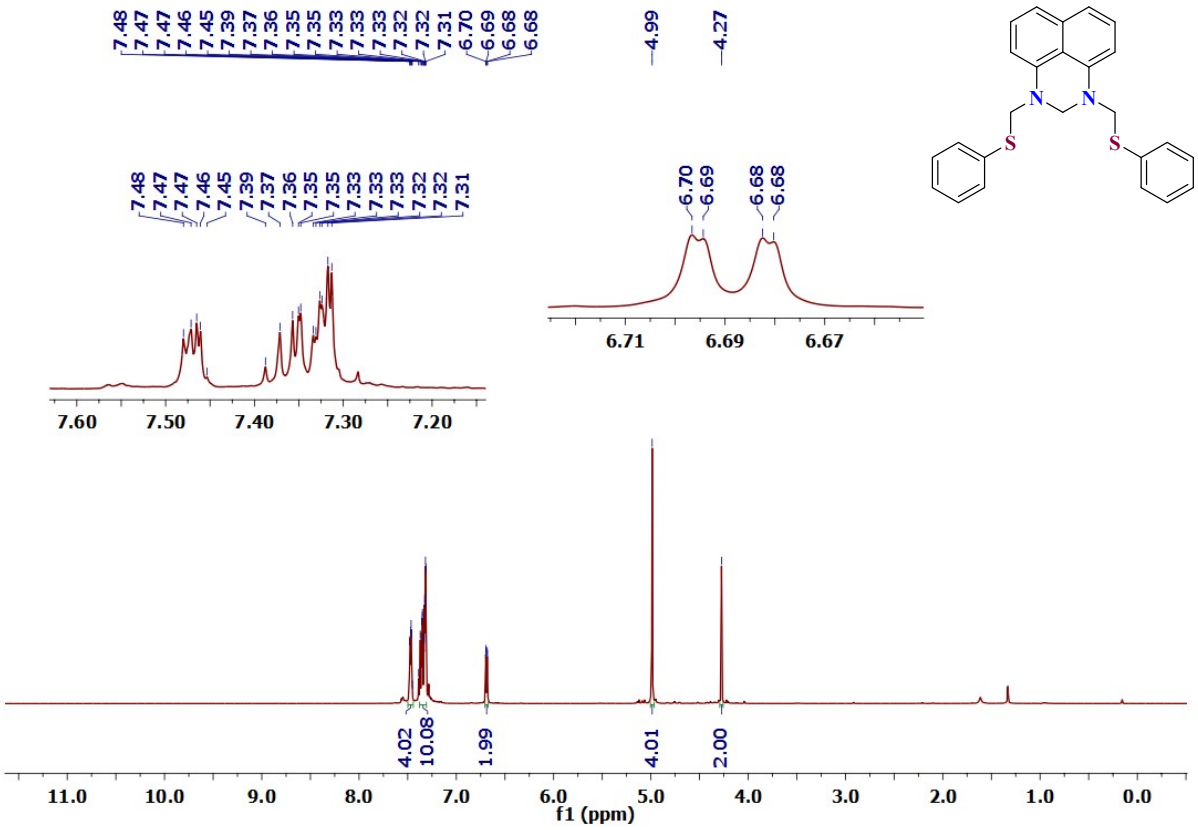


Figure S27. ^{1}H NMR (500 MHz, 25 ºC) spectrum of 1,3-bis((phenylthio)methyl)-2,3-dihydro-1H-perimidine **L5**.

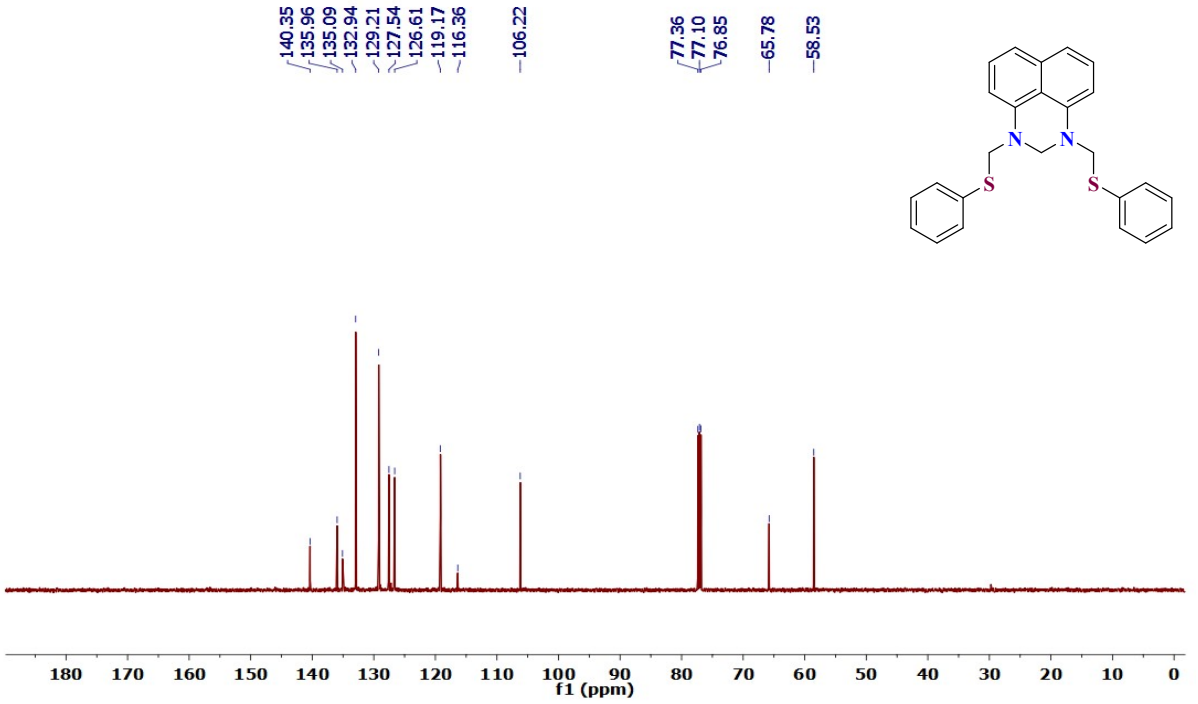


Figure S28. ^{13}C NMR (125.75 MHz, 25 ºC) spectrum of 1,3-bis((phenylthio)methyl)-2,3-dihydro-1H-perimidine **L5**.

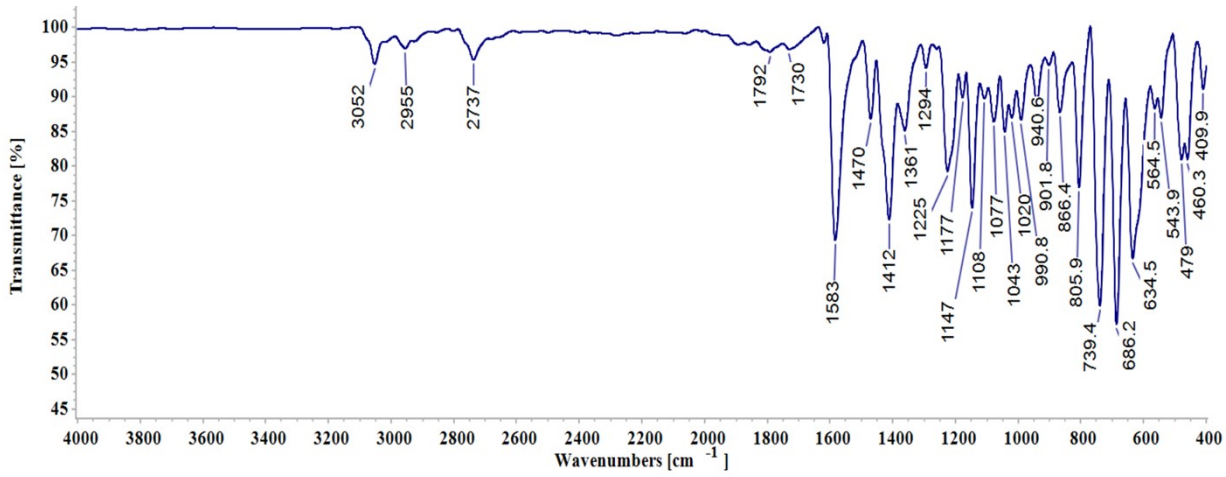
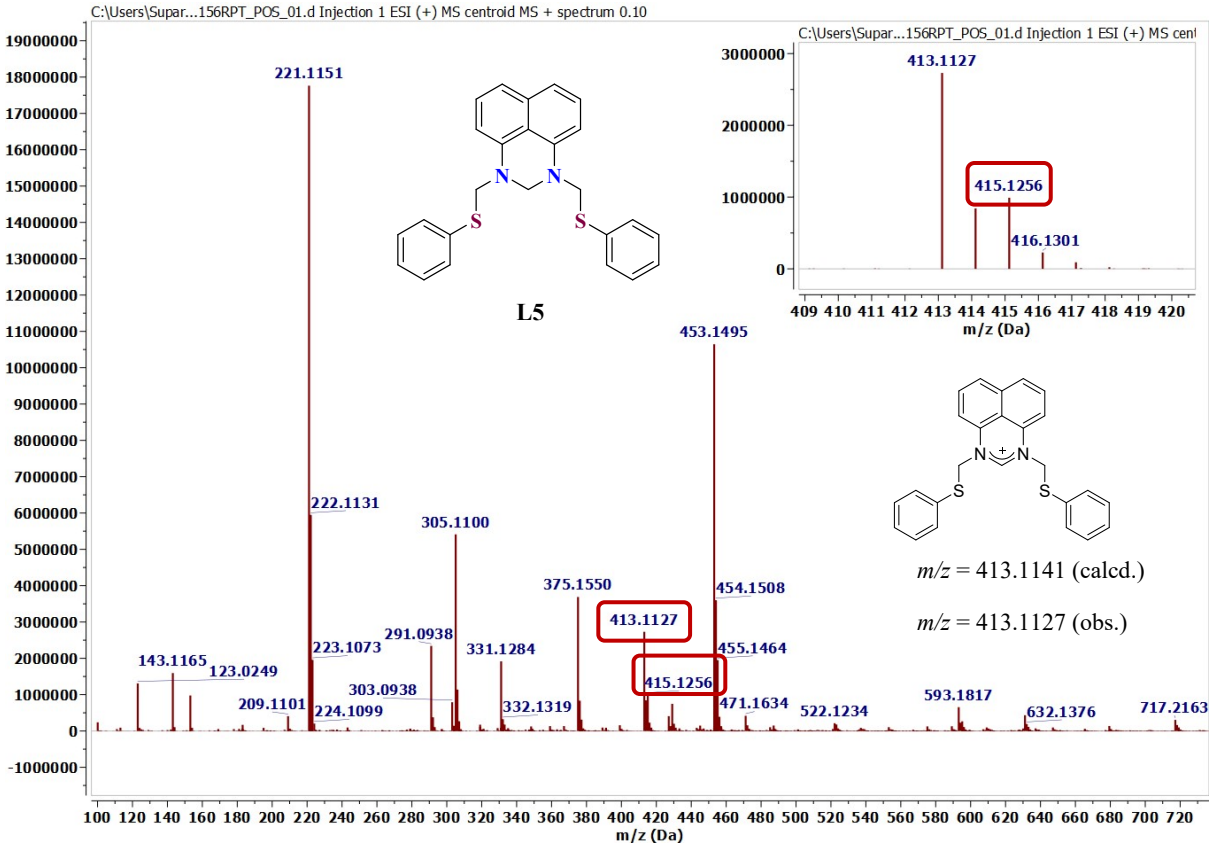


Figure S29. ATR-FTIR spectrum of 1,3-bis((phenylthio)methyl)-2,3-dihydro-1H-perimidine **L5**.



Compound name	Calcd *m/z* for $[M+H]^+$	Observed *m/z* for $[M+H^+]$
1,3-bis((phenylthiol)methyl)-2,3-dihydro-1H-perimidine	415.1297	415.1256

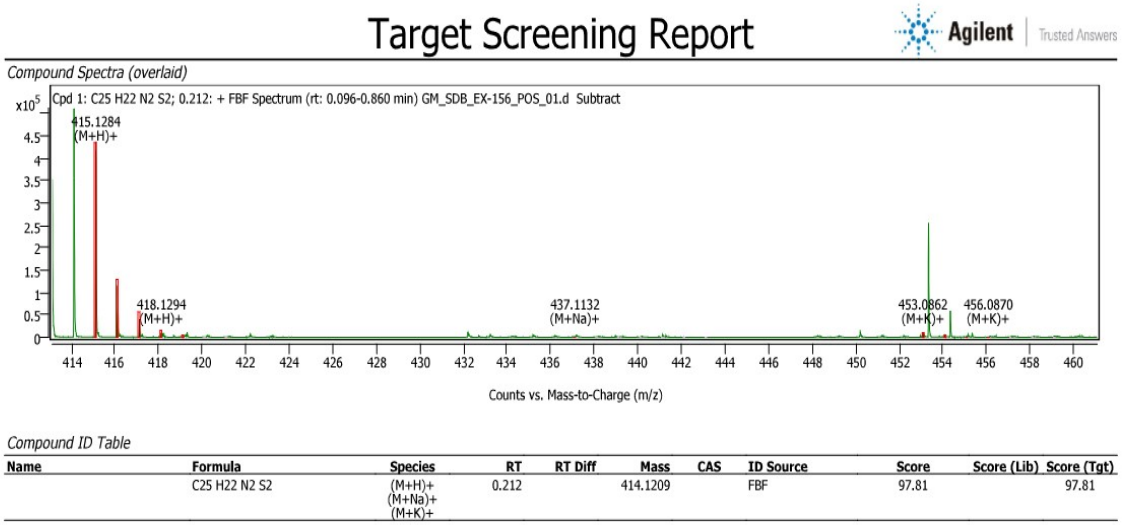


Figure S30. HRMS (+ESI) spectrum of 1,3-bis((phenylthio)methyl)-2,3-dihydro-1H-perimidine **L5**.

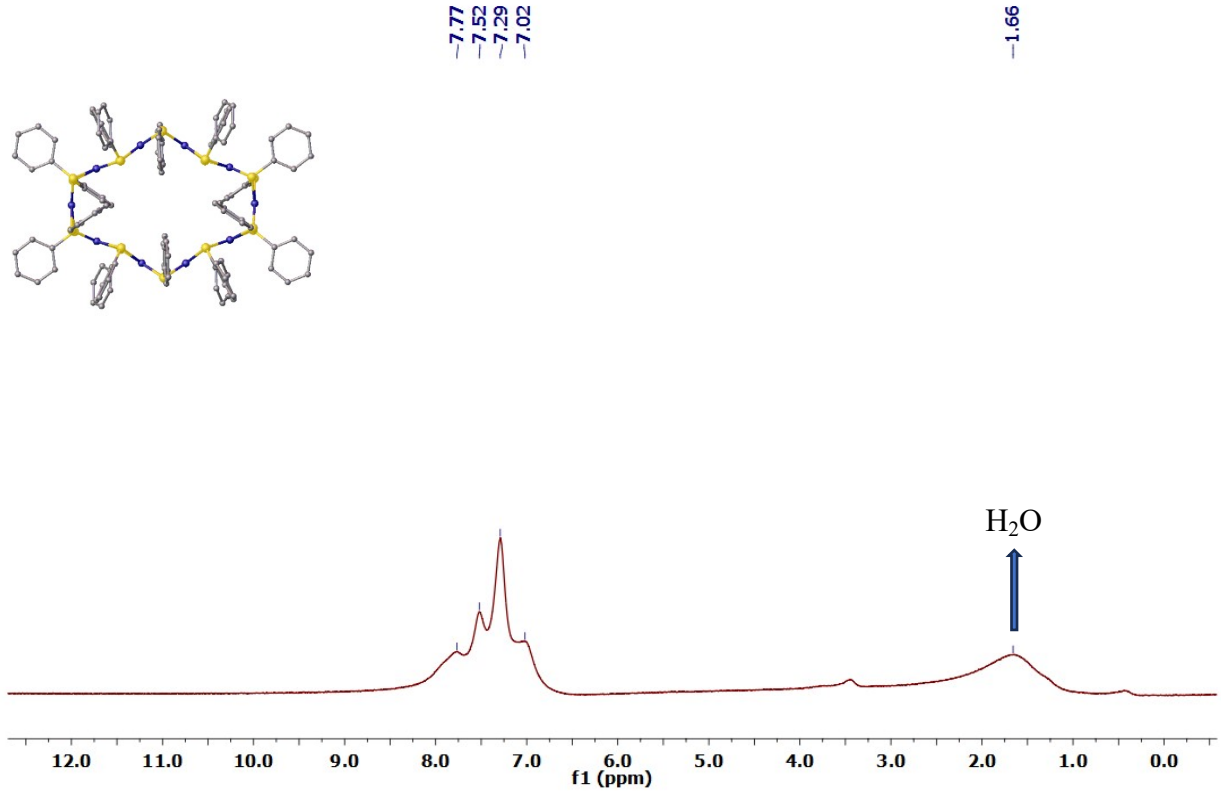


Figure S31. ^{1}H NMR (500 MHz, 25 ºC) spectrum of cyclic $[Ni(\mu_2\text{-}SPh)_2]_{10}$ **1** in $CDCl_3$.

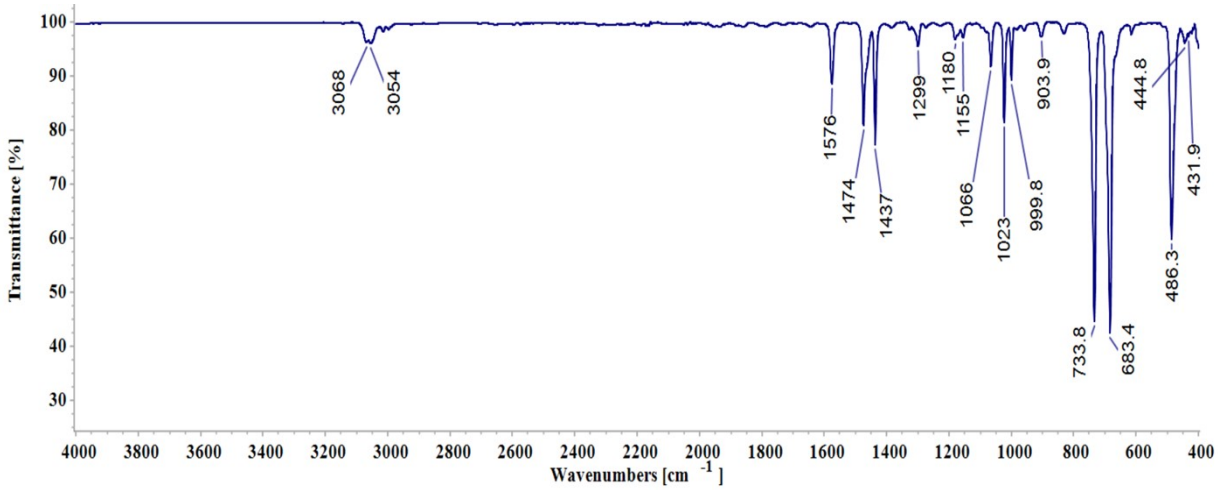


Figure S32. ATR-FTIR spectrum of cyclic $[Ni_{10}(SPh)_{20}]$ **1**.

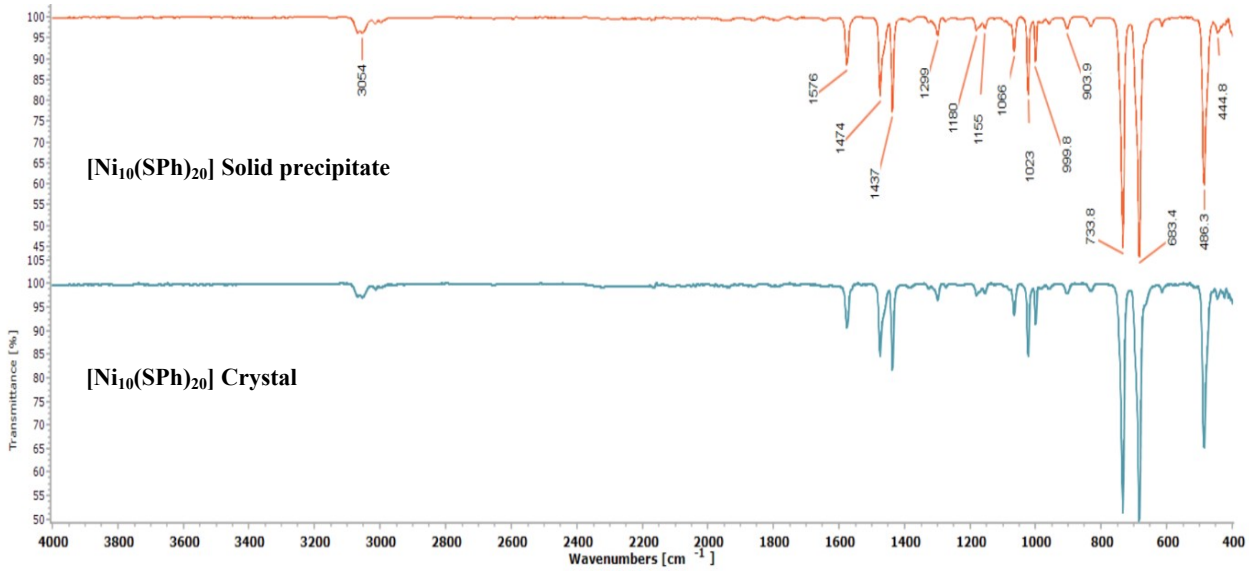
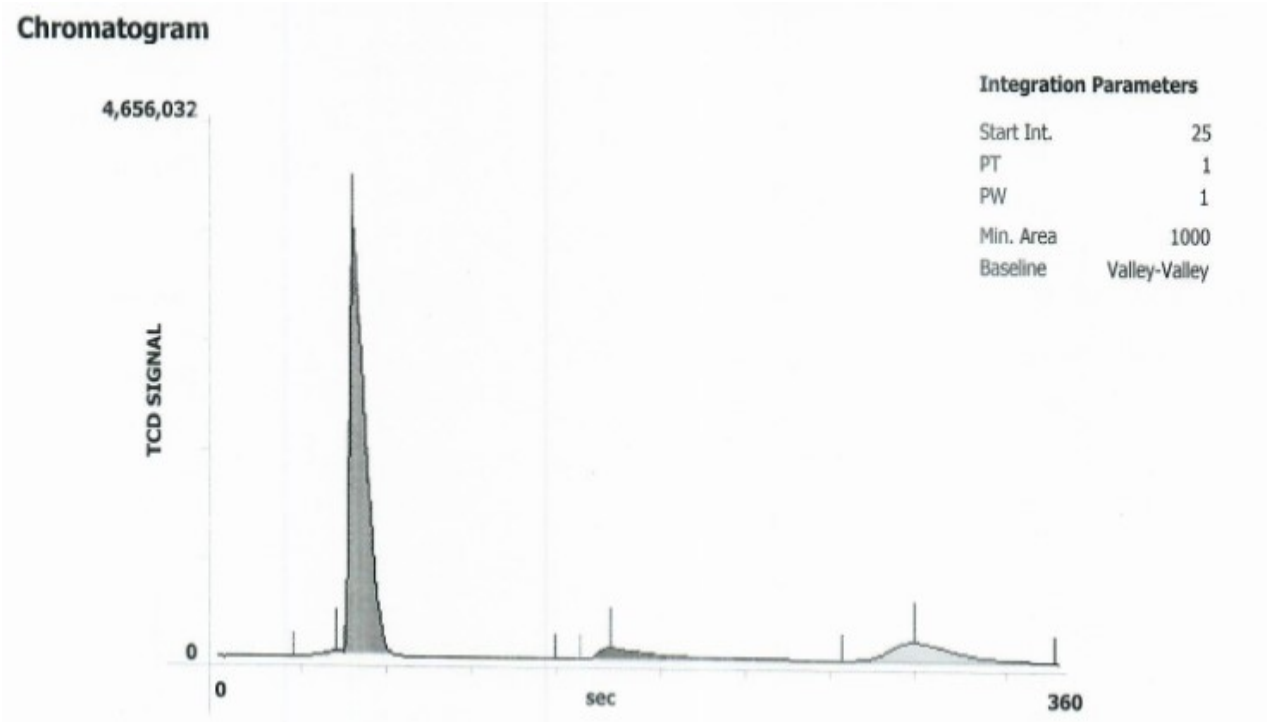


Figure S33. Comparison of ATR-FTIR spectra of the precipitate of $[Ni_{10}(SPh)_{20}]$ (top) and crystals of $[Ni_{10}(SPh)_{20}]$ (bottom) **1**.



Results

R

Element	RT (s)	Start (s)	End (s)	Area	Area %	Element %
Nitrogen	-	-	-	-	-	-
Carbon	57	54	144	3,434,509	77.432	50.802
Hydrogen	167	154	266	390,722	8.809	3.358
Sulphur	297	266	357	610,299	13.759	22.169
Oxygen	-	-	-	-	-	-

		Intercept	Slope		Correlation
Nitrogen		0.053	4.702310 E-07		0.999300
Carbon		0.062	1.850636 E-07		0.999961
Hydrogen		0.003	1.102979 E-07		0.998615
Sulphur		0.009	4.846958 E-07		0.999400
Oxygen		-	-		-

Figure S34. Chromatogram of elemental analysis for $[Ni_{10}(SPh)_{20}]$ **1**.

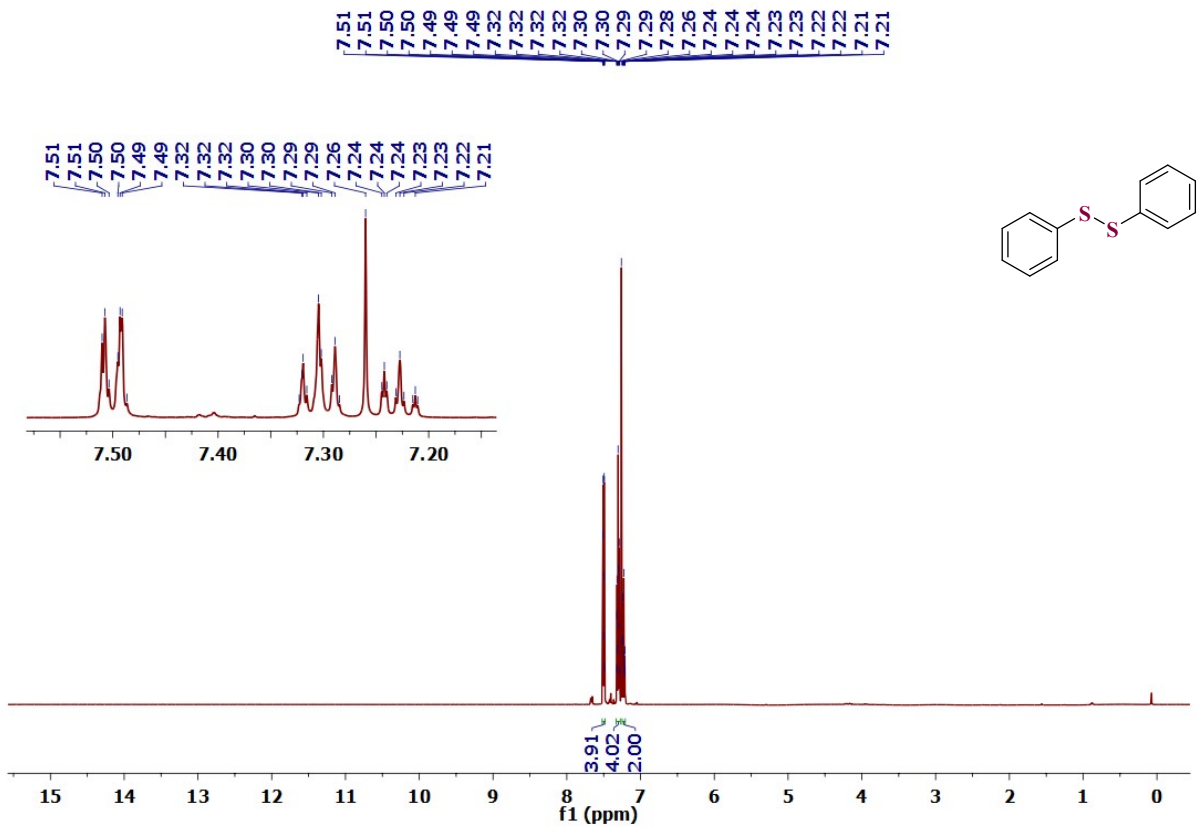


Figure S35. ^{1}H NMR (500 MHz, 25 ºC) spectrum of 1,2-diphenyldisulfane **2** in $CDCl_3$

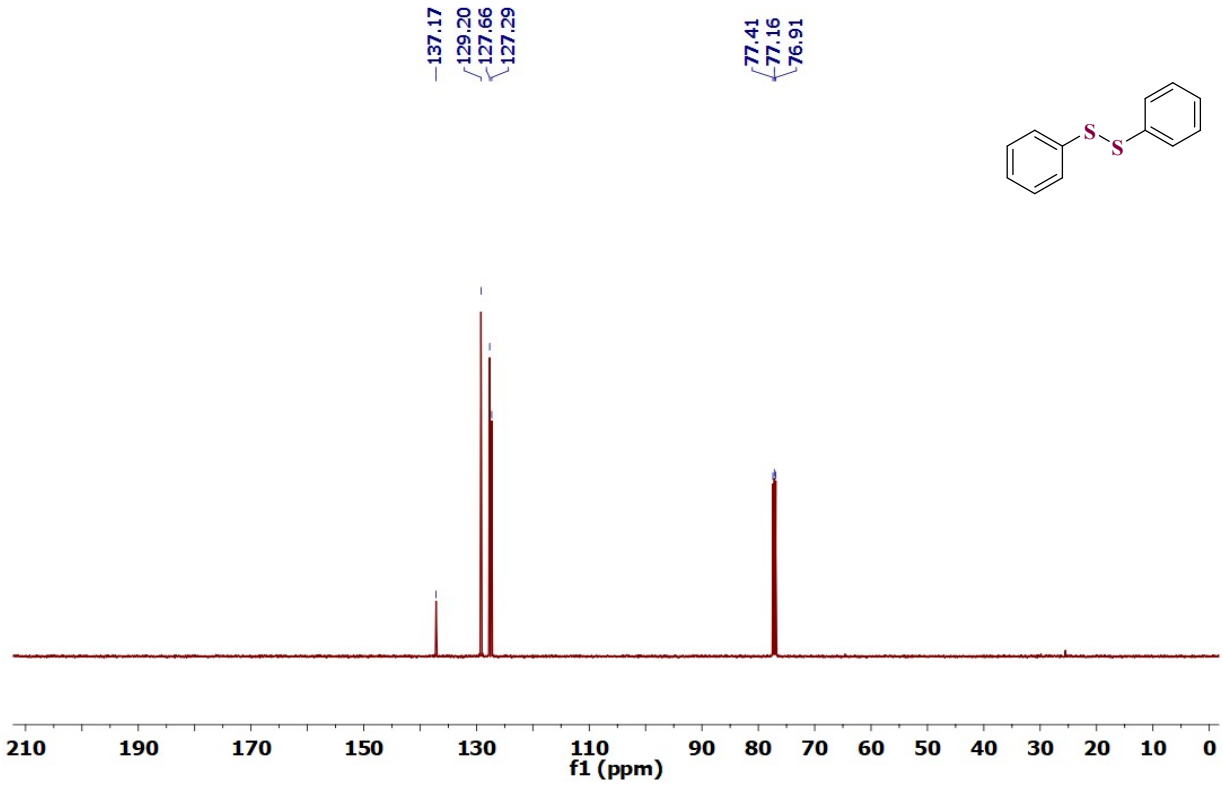


Figure S36. ^{13}C NMR (125.75 MHz, 25 ºC) spectrum of 1,2-diphenyldisulfane **2** in $CDCl_3$

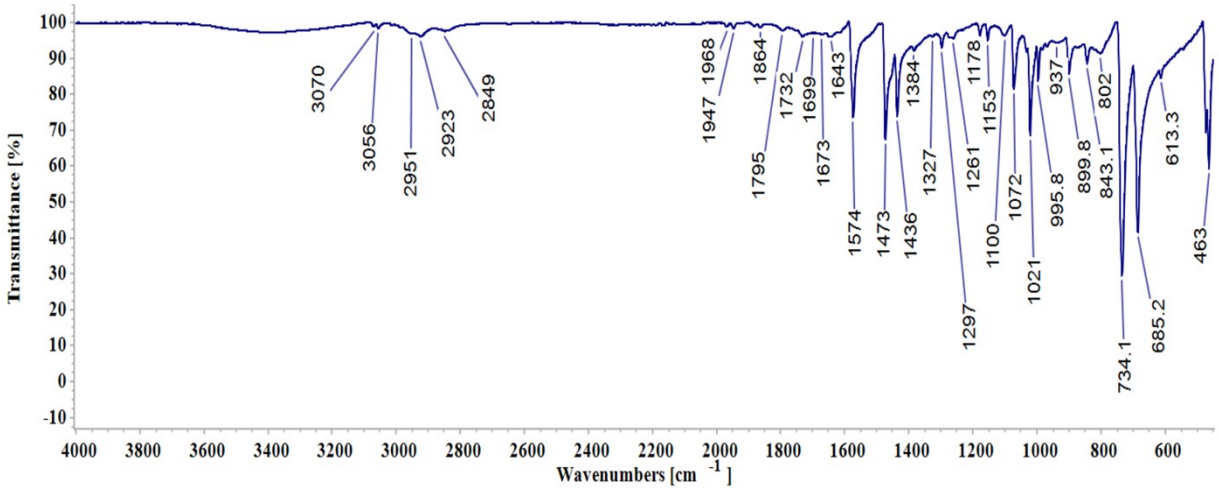


Figure S37. ATR-FTIR spectrum of 1,2-diphenyldisulfane **2**.

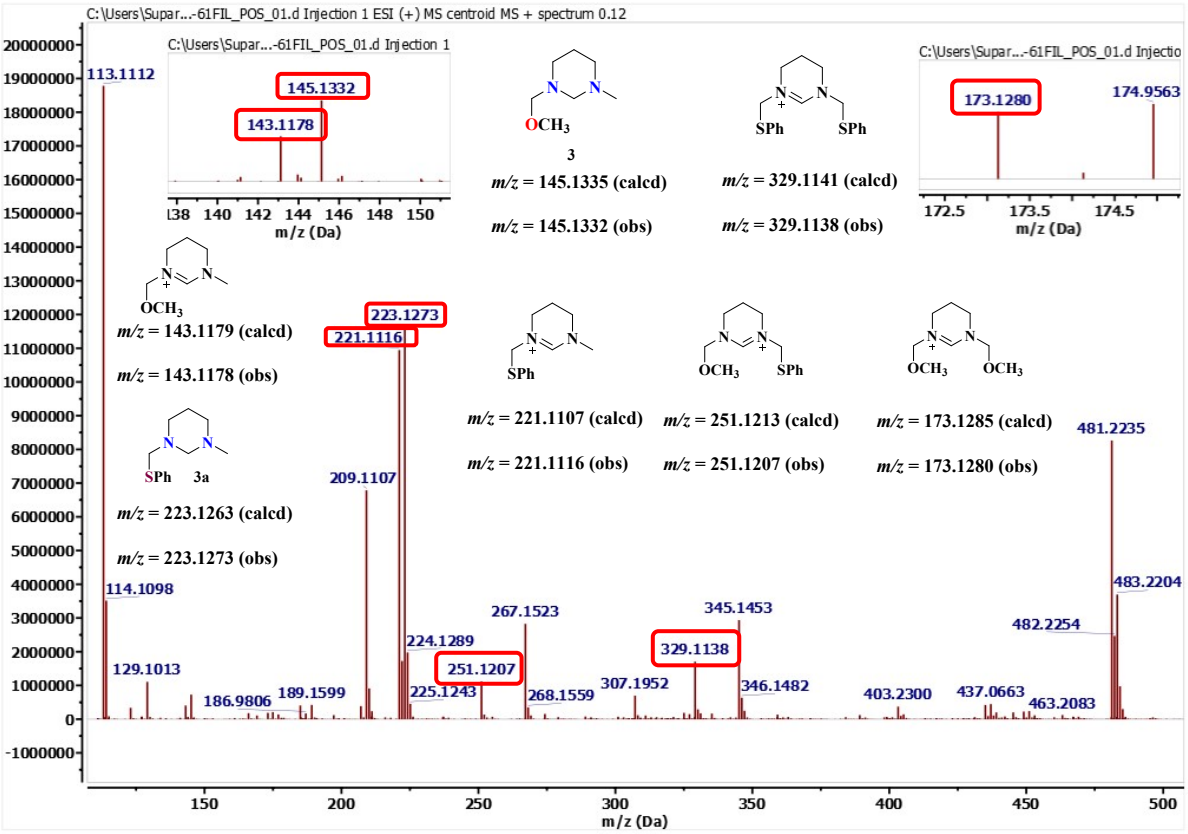


Figure S38. HRMS (+ESI) spectrum of the reaction mixture obtained using **L1** and $NiCl_2$•$6H_2O$ which gave $[Ni_{10}(SPh)_{20}]$. Both the room temperature and refluxing conditions show similar spectra.

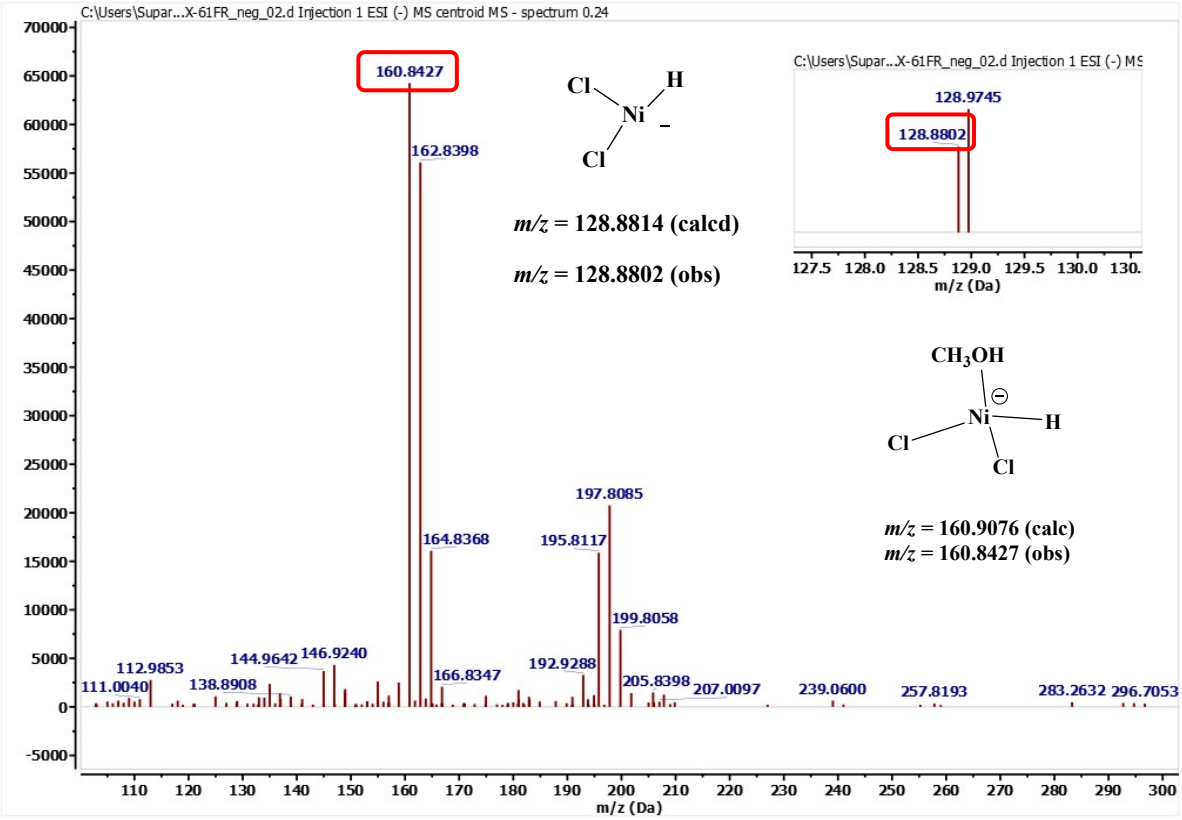
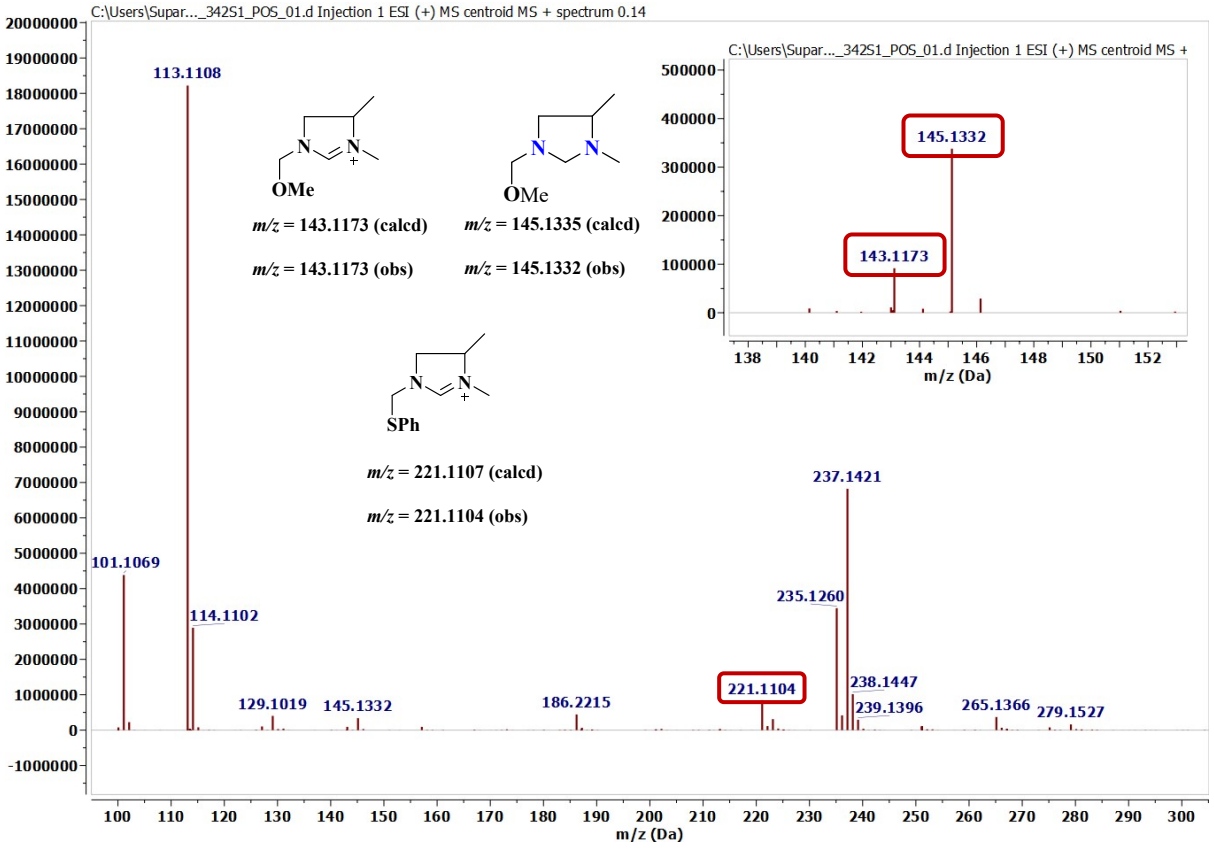


Figure 39. HRMS (-ESI) spectrum of the reaction mixture obtained using **L1** and $NiCl_2$•$6H_2O$ which gave $[Ni_{10}(SPh)_{20}]$ under both room temperature and refluxing conditions.



Compound name	Calcd *m/z* for $[M+H]^+$	Observed *m/z* for $[M+H^+]$
1-(methoxymethyl)-3-methylhexahydropyrimidine	145.1335	145.1332

Figure S40. HRMS (+ESI) spectrum of the reaction mixture obtained using **L3** and $NiCl_2 \cdot 6H_2O$.

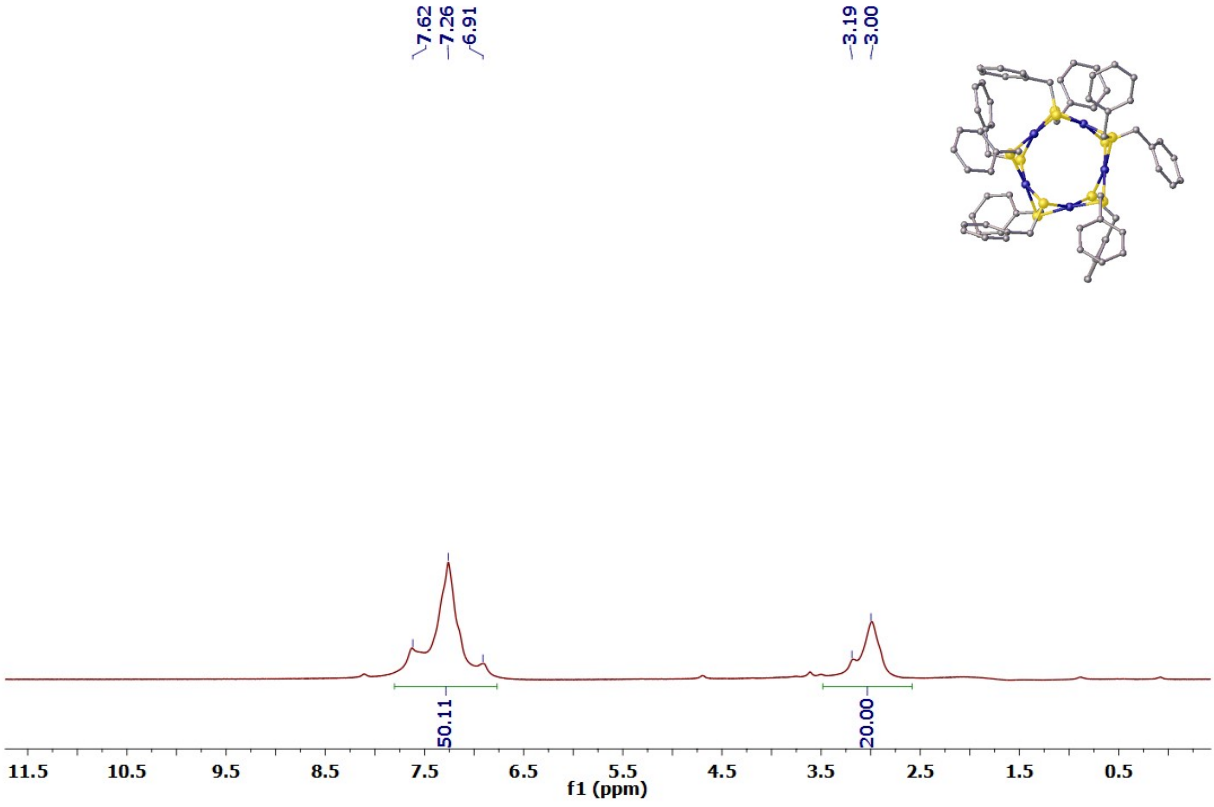


Figure S41. ^1H NMR (500 MHz, 25 ºC) spectrum of $[Ni_5(SCH_2Ph)_{10}]$ **5** in $CDCl_3$

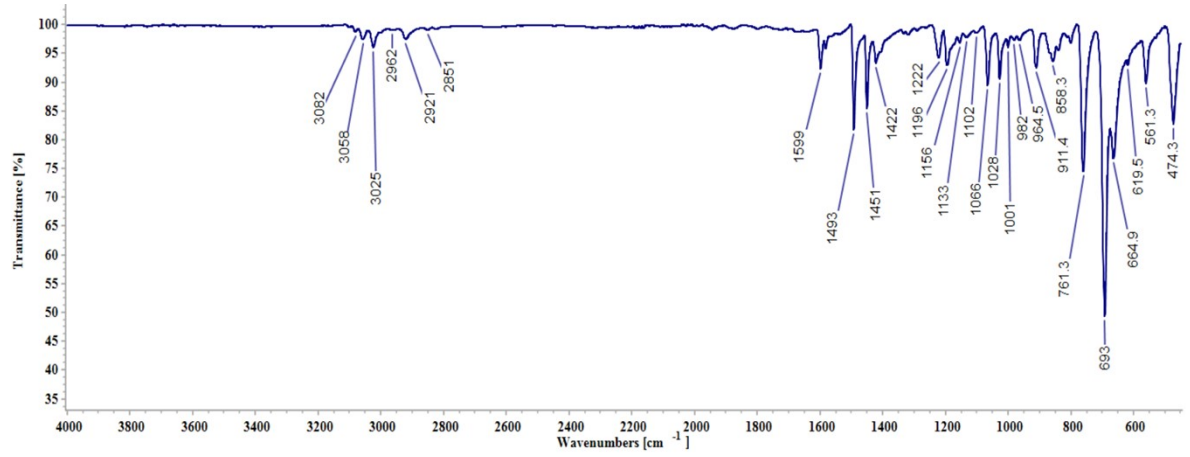


Figure S42. ATR-FTIR spectrum of $[Ni_5(SCH_2Ph)_{10}]$ **5.**

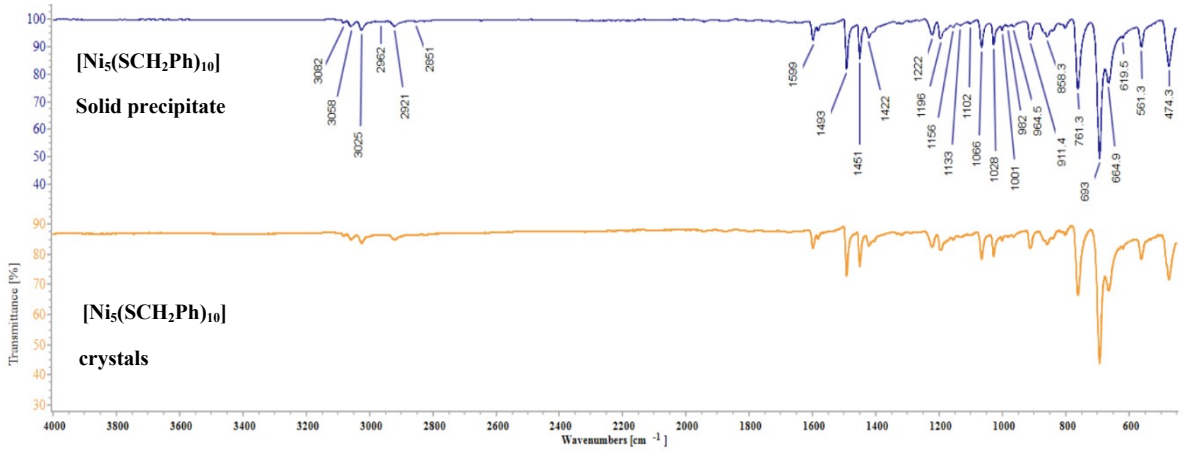
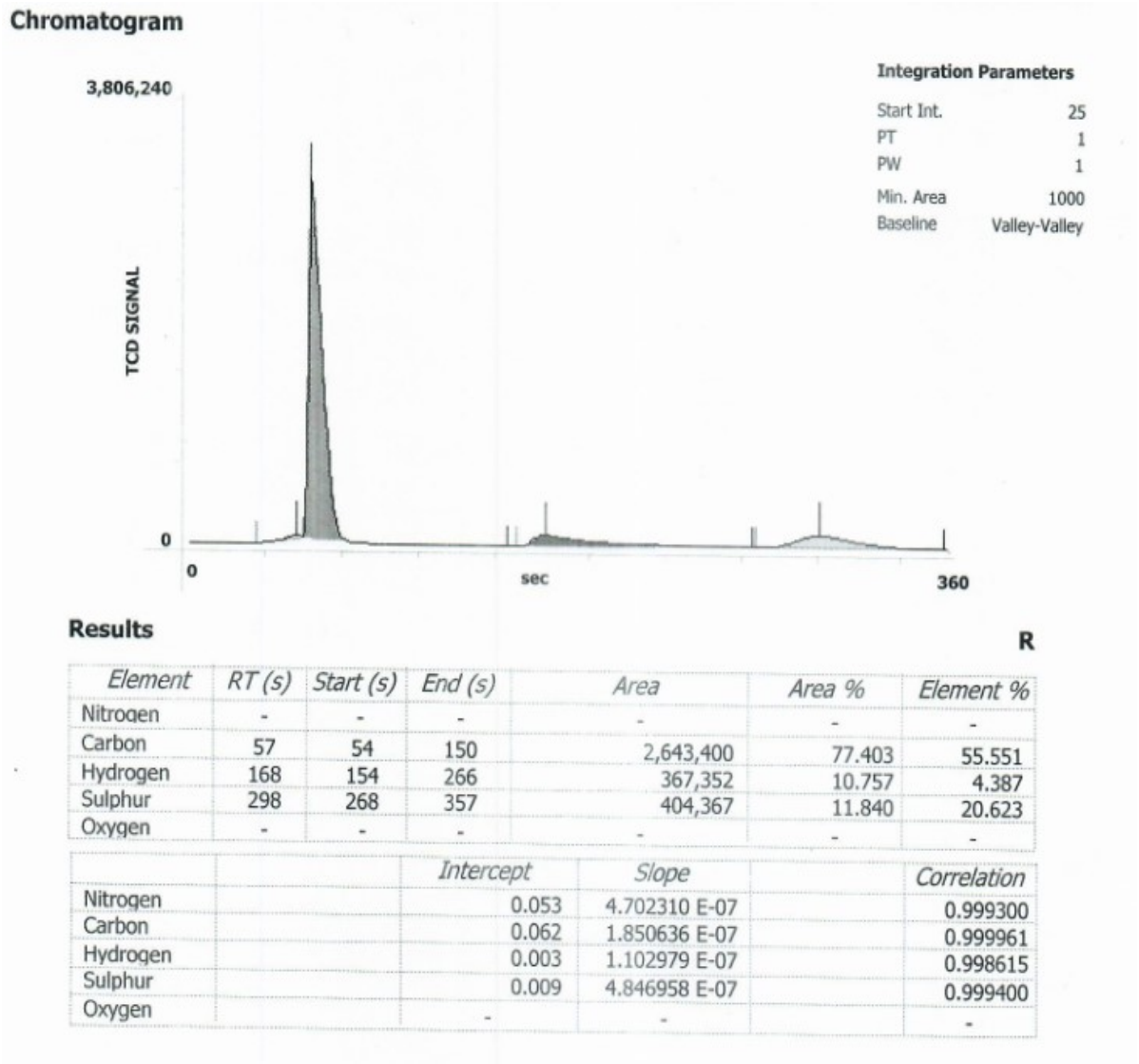


Figure S43. Comparison of ATR-FTIR spectra of the precipitate of $[Ni_5(SCH_2Ph)_{10}]$ (top) and crystals of $[Ni_5(SCH_2Ph)_{10}]$ (bottom) **5**.



Results

R

Element	RT (s)	Start (s)	End (s)	Area	Area %	Element %
Nitrogen	-	-	-	-	-	-
Carbon	57	54	150	2,643,400	77.403	55.551
Hydrogen	168	154	266	367,352	10.757	4.387
Sulphur	298	268	357	404,367	11.840	20.623
Oxygen	-	-	-	-	-	-

		Intercept	Slope		Correlation
Nitrogen		0.053	4.702310 E-07		0.999300
Carbon		0.062	1.850636 E-07		0.999961
Hydrogen		0.003	1.102979 E-07		0.998615
Sulphur		0.009	4.846958 E-07		0.999400
Oxygen		-	-		-

Figure S44. Chromatogram of elemental analysis for $[Ni_5(SCH_2Ph)_{10}]$ **5**.

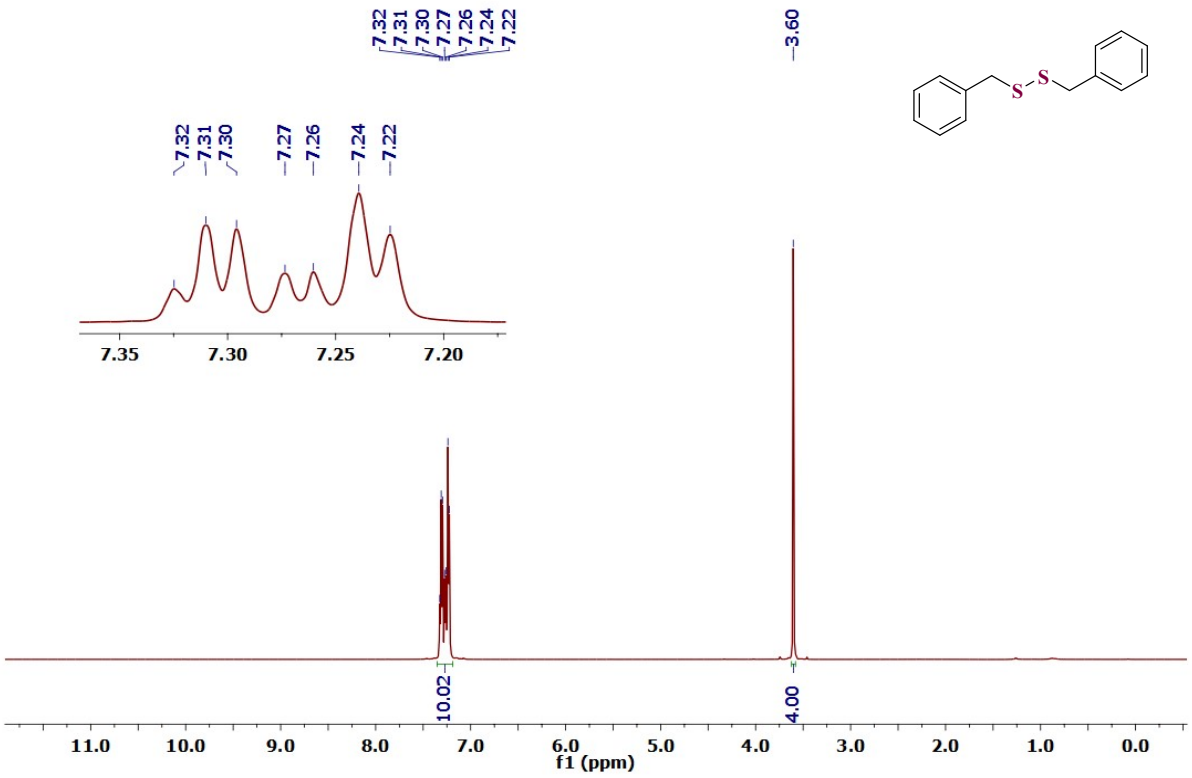


Figure S45. ^{1}H NMR (500 MHz, 25 ºC) spectrum of 1,2-dibenzyldisulfane **6** in $CDCl_3$.

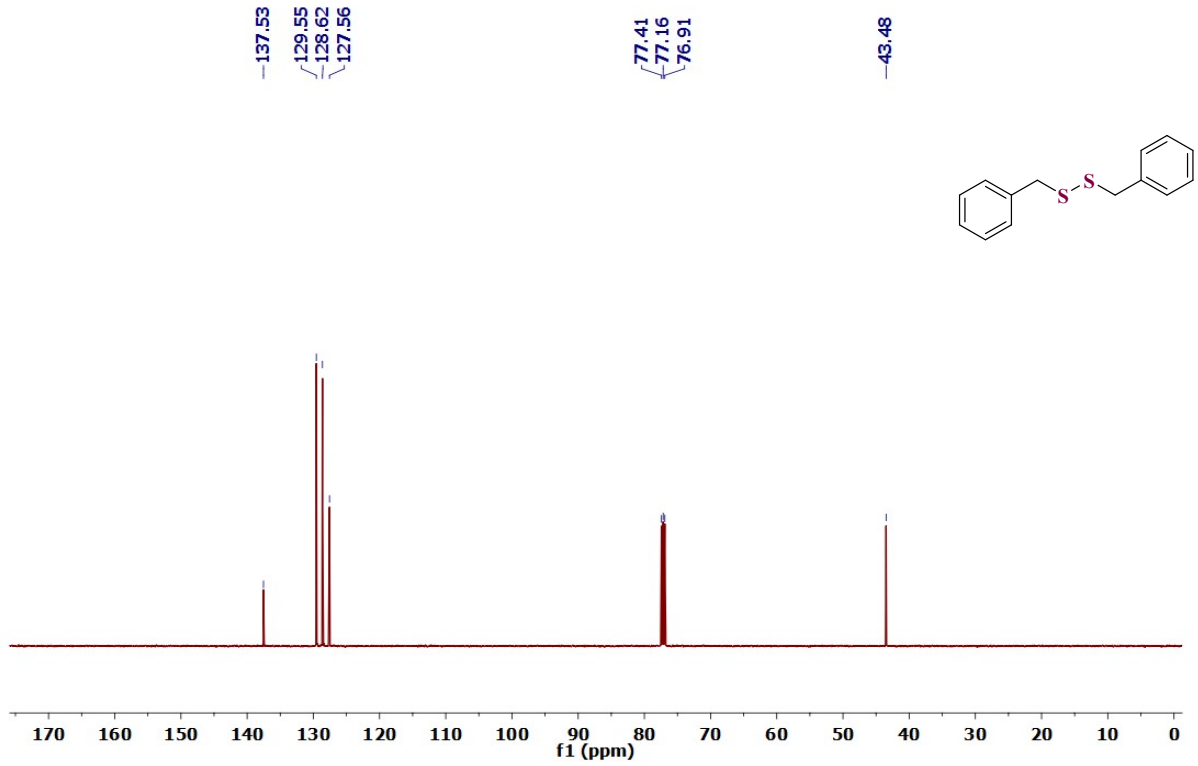


Figure S46. ^{13}C NMR (125.75 MHz, 25 ºC) spectrum of 1,2-dibenzyldisulfane **6** in $CDCl_3$.

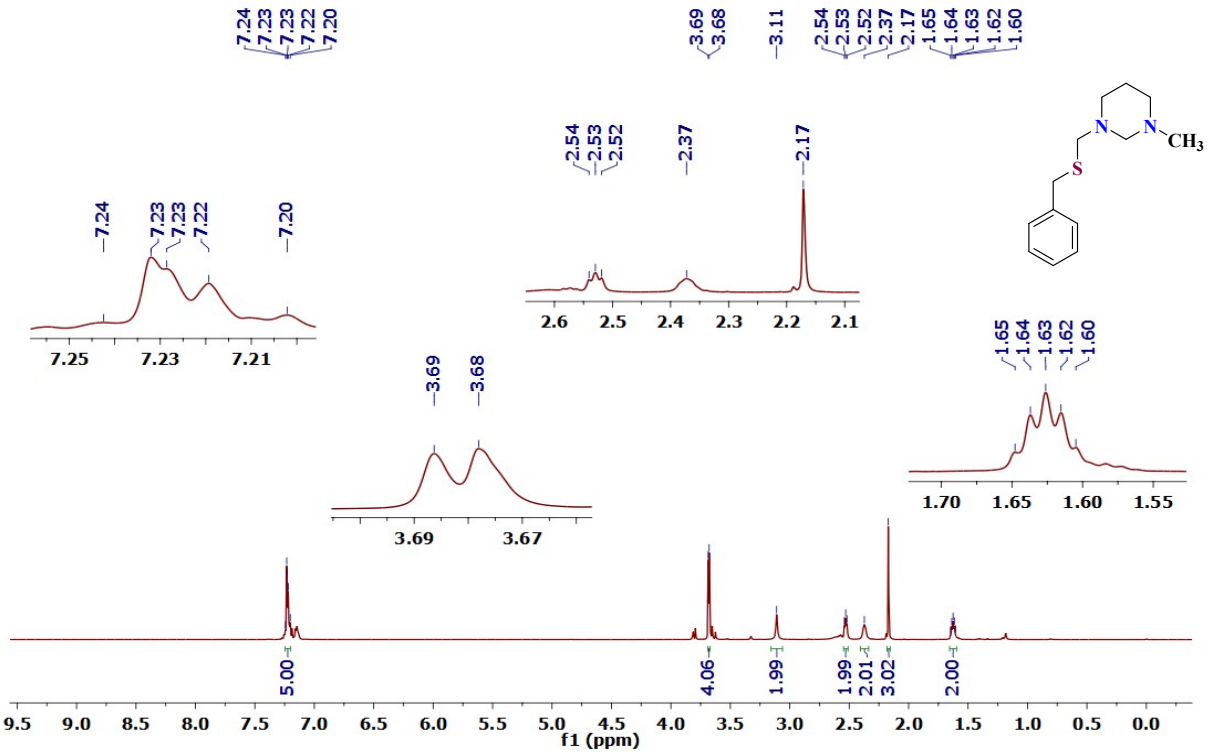


Figure S47. ^{1}H NMR (500 MHz, 25 ºC) spectrum of 1-((benzylthio)methyl)-3-methyl)hexahydropyrimidine **7** in $CDCl_3$.

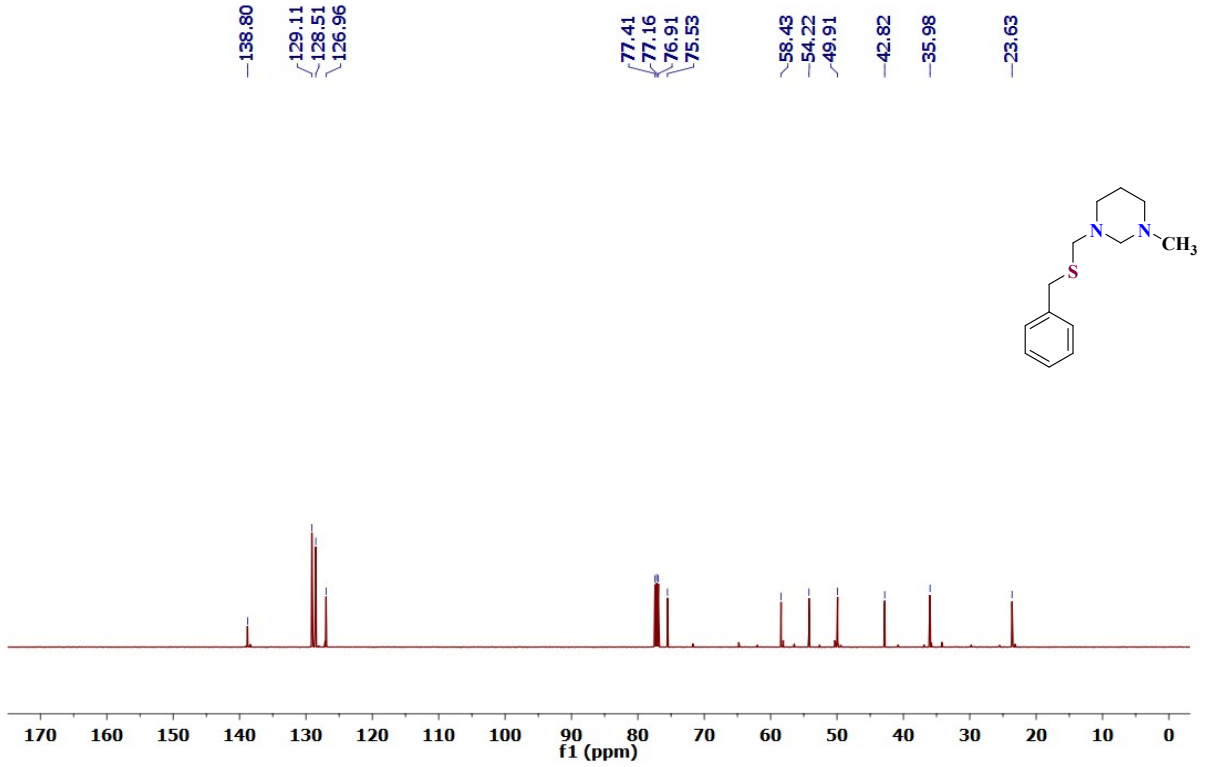


Figure S48. ^{13}C NMR (125.75 MHz, 25 ºC) spectrum of 1-((benzylthio)methyl)-3-methyl)hexahydropyrimidine **7** in $CDCl_3$.

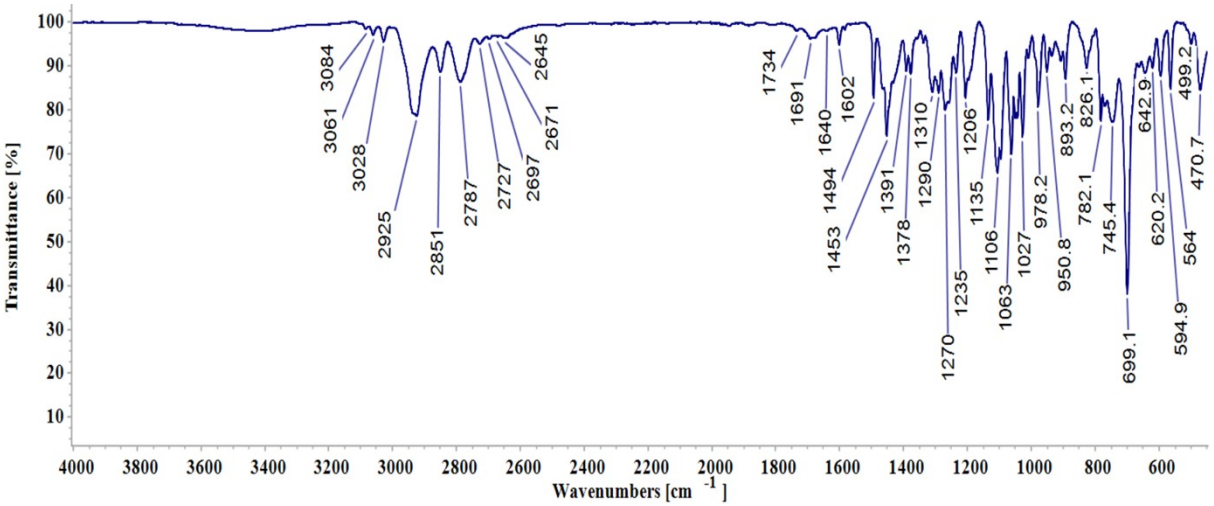
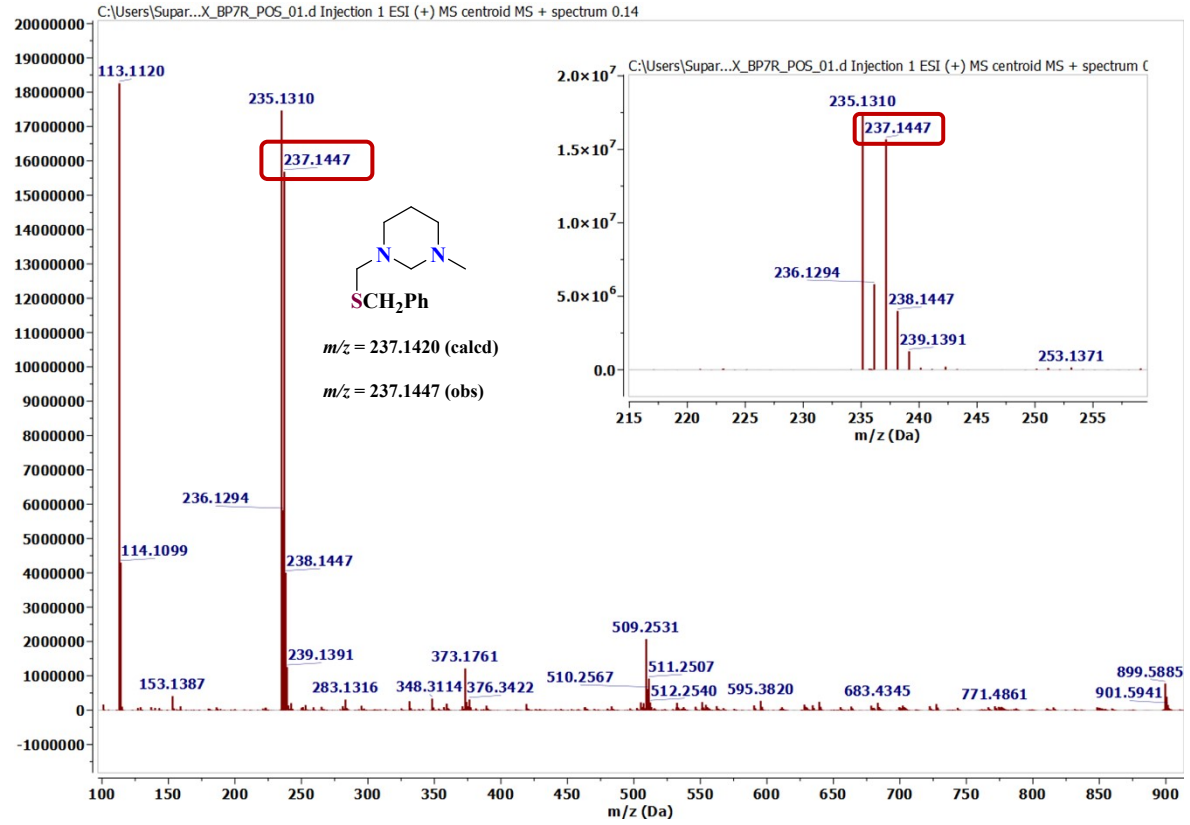


Figure S49. ATR-FTIR spectrum of 1-((benzylthio)methyl)-3-methyl)hexahydropyrimidine **7**.



Compound name	Calcd *m/z* for $[M+H]^+$	Observed *m/z* for $[M+H^+]$
1-((benzylthio)methyl)-3-methyl)hexahydropyrimidine	237.1420	237.1447

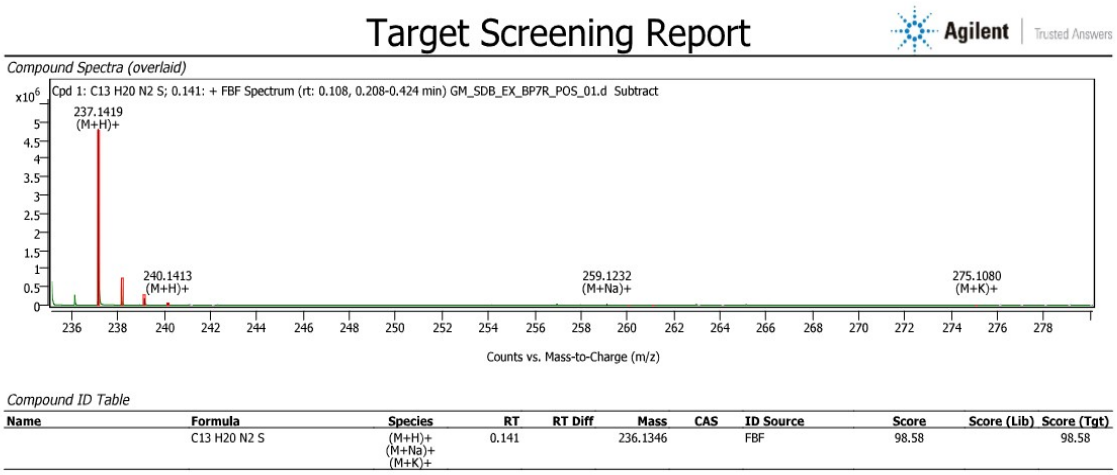


Figure S50. HRMS (+ESI) spectrum of 1-((benzylthio)methyl)-3-methyl)hexahydropyrimidine **7**.

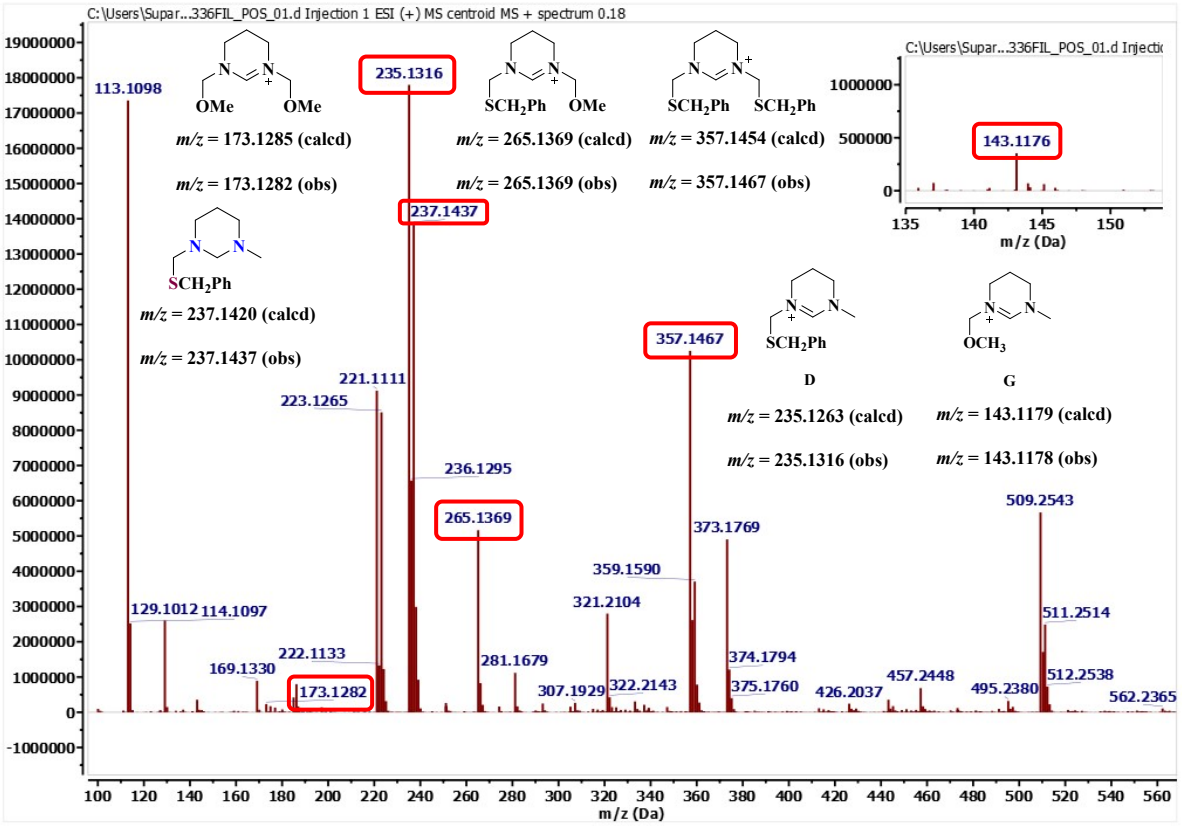


Figure S51. HRMS (+ESI) spectrum of the reaction mixture obtained using **L2** and $NiCl_2$•$6H_2O$ which gave $[Ni_5(SCH_2Ph)_{10}]$ under refluxing conditions.

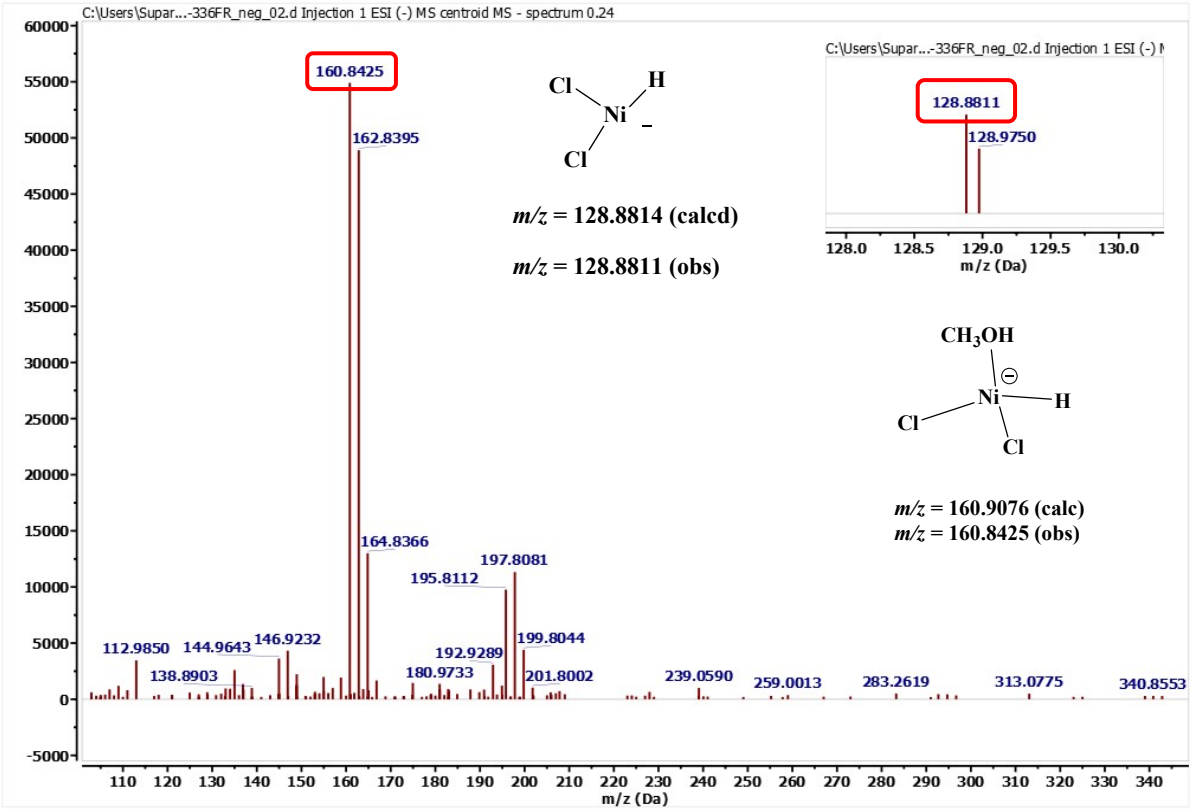


Figure 52. HRMS (-ESI) spectrum of the reaction mixture obtained using **L2** and $NiCl_2$•$6H_2O$ which gave $[Ni_5(SCH_2Ph)_{10}]$ under refluxing conditions.

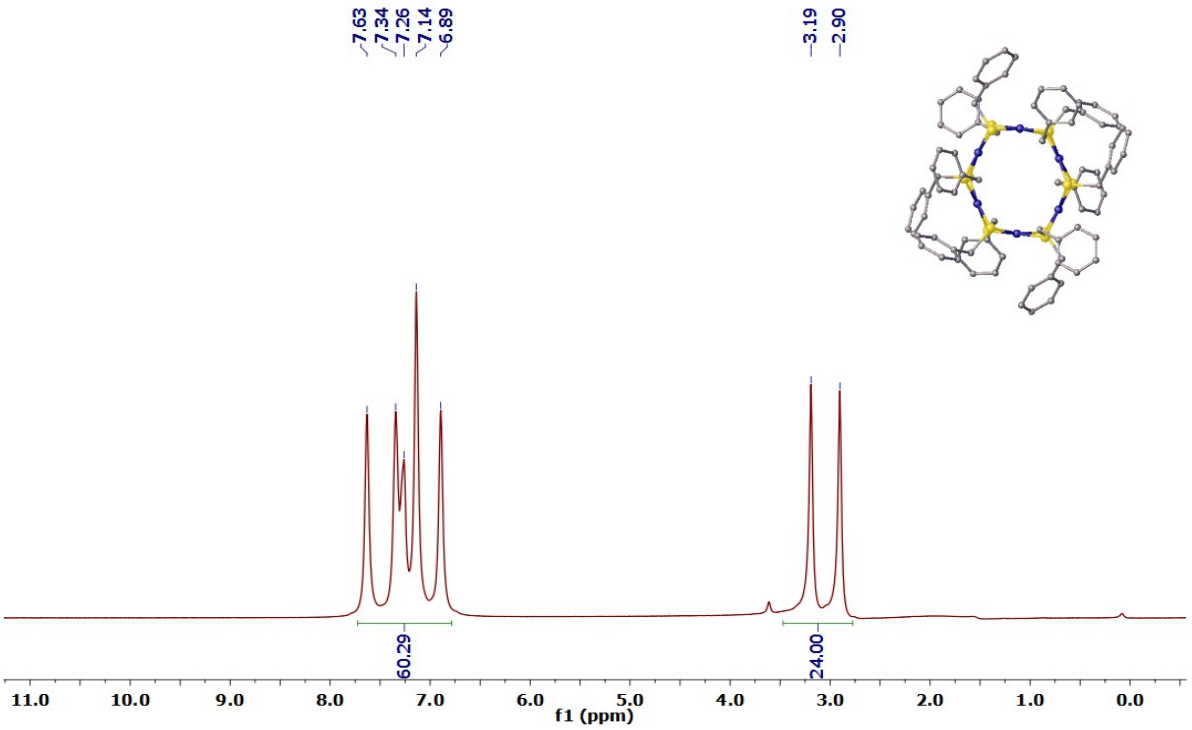


Figure S53. ^{1}H NMR (500 MHz, 25 ºC) spectrum of cyclic $[Ni_6(SCH_2Ph)_{12}]$ **8** in $CDCl_3$.

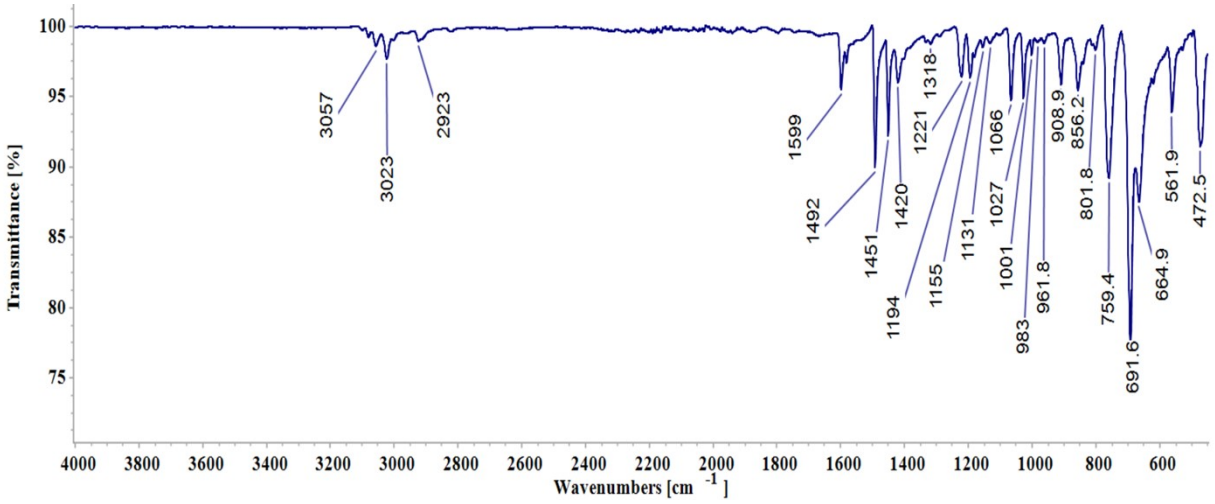


Figure S54. ATR-FTIR spectrum of cyclic $[Ni_6(SCH_2Ph)_{12}]$ **8**.

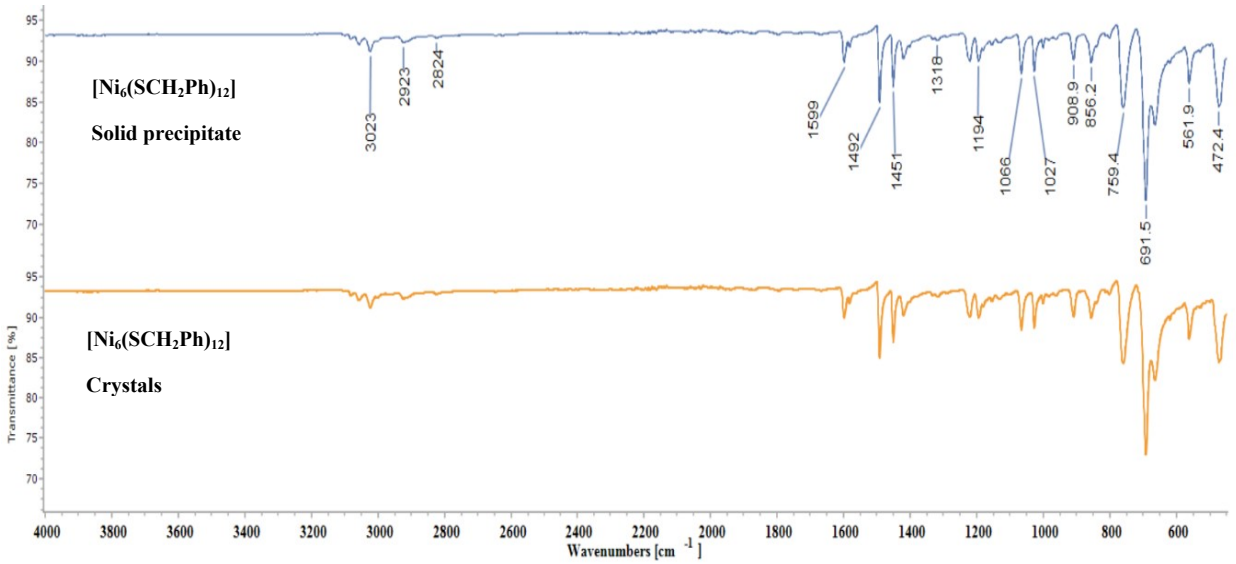


Figure S55. Comparison of ATR-FTIR spectra of the precipitate of $[Ni_6(SCH_2Ph)_{12}]$ (top) and crystals of $[Ni_6(SCH_2Ph)_{12}]$ (bottom) **8**.

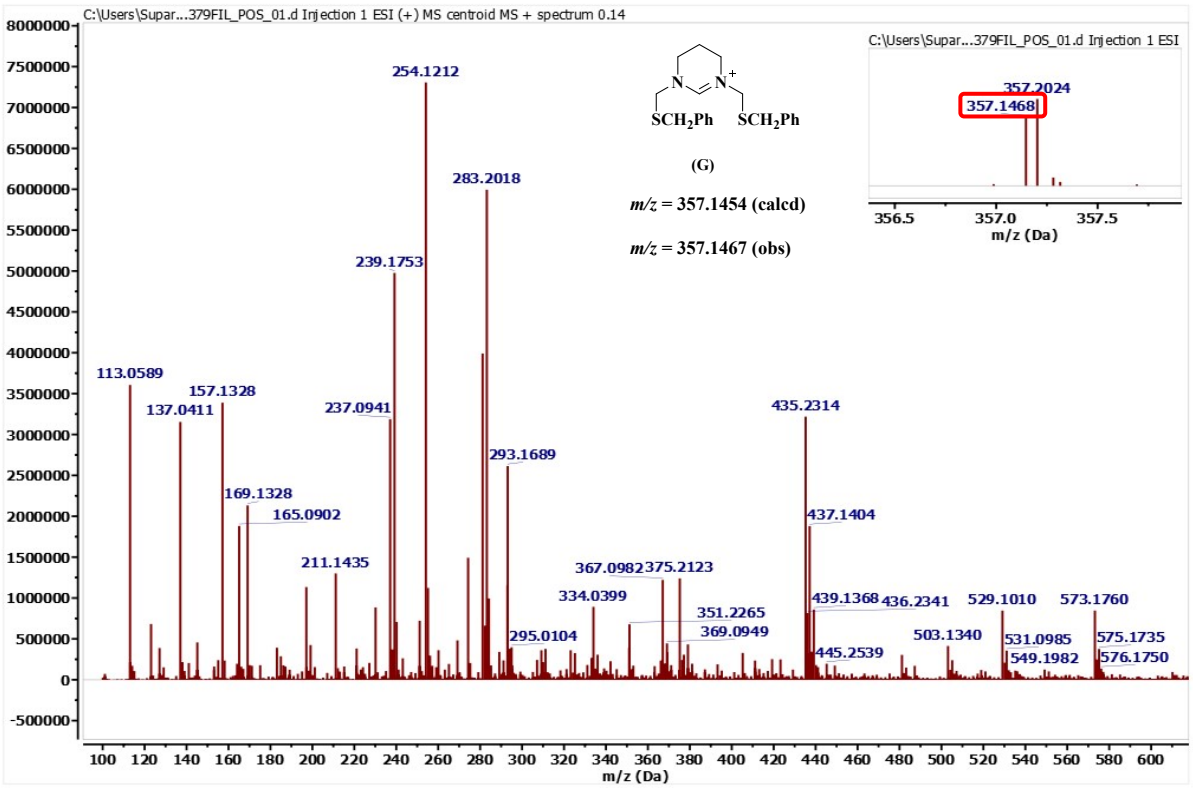


Figure S56. HRMS (+ESI) spectrum of the reaction mixture obtained using **L4** and $Ni(acac)_2$ in acetonitrile at room temperature which gave $[Ni_6(SCH_2Ph)_{10}]$.

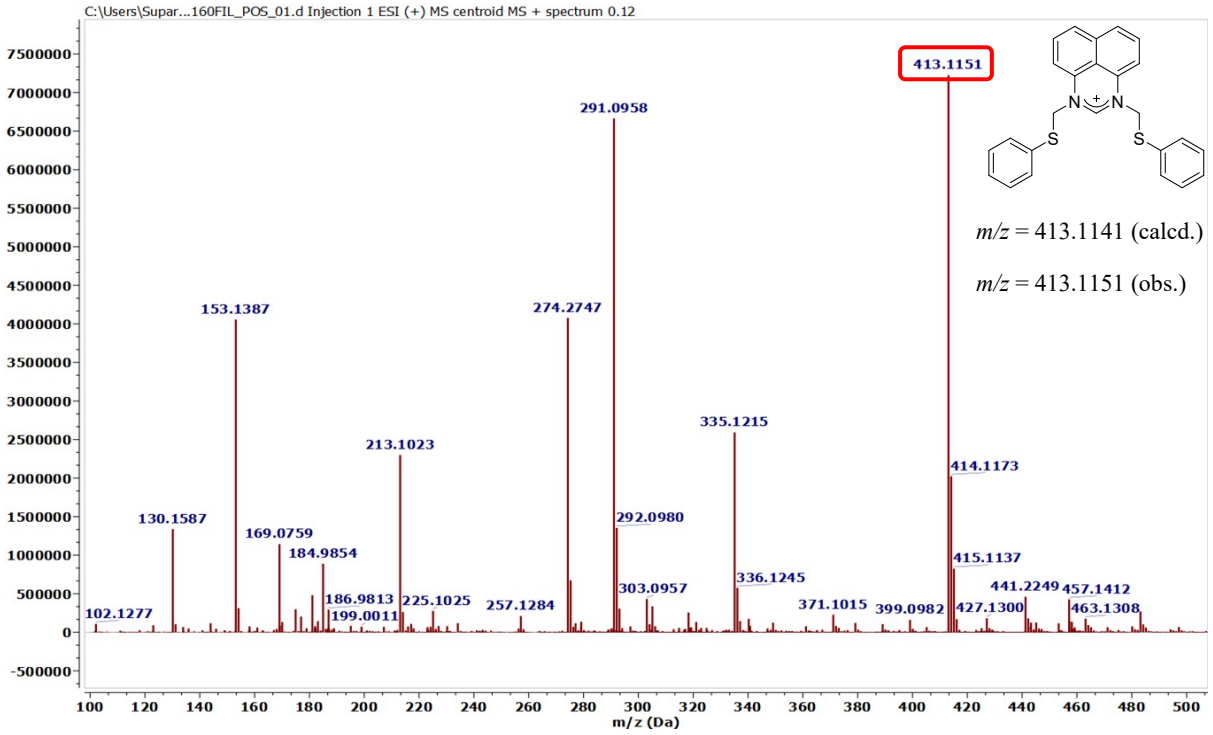


Figure S57. HRMS (+ESI) spectrum of the filtrate part of the reaction mixture of ligand **L5** and $NiCl_2 \cdot 6H_2O$ in acetonitrile at room temperature.

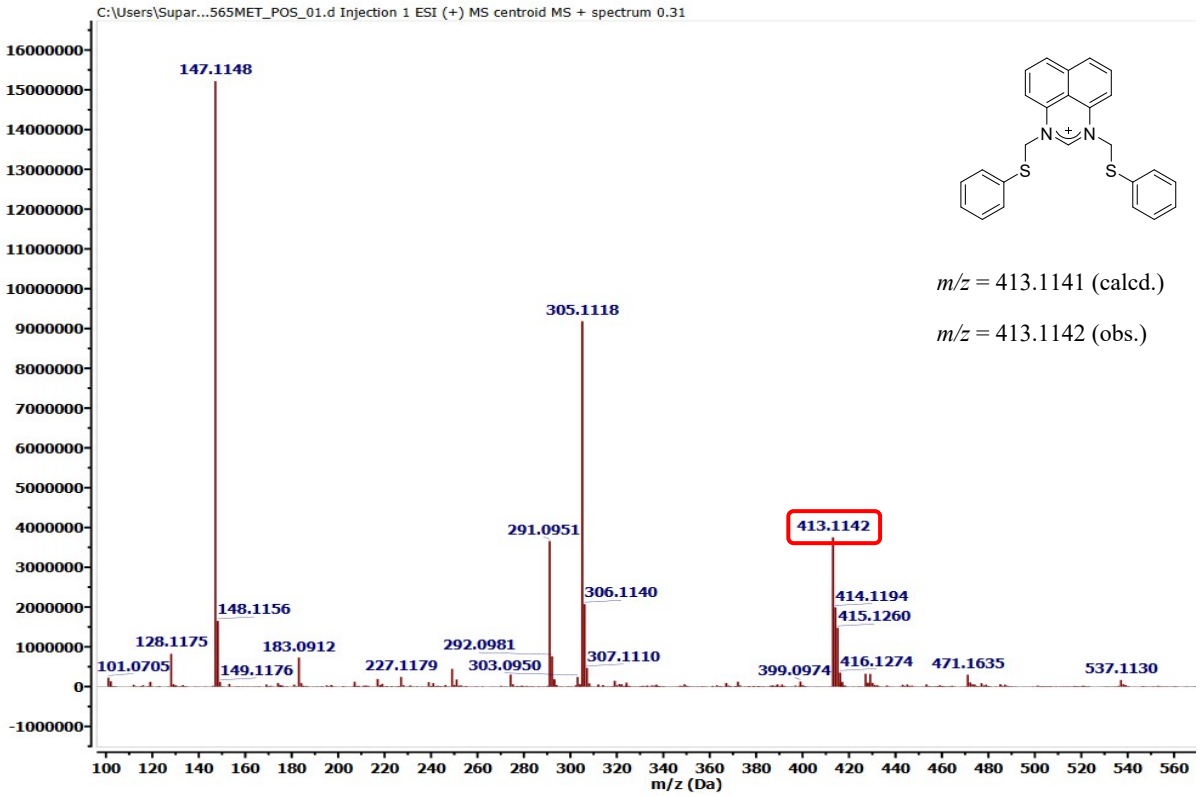


Figure S58. HRMS (+ESI) spectrum of the reaction mixture of ligand **L5** and $NiCl_2$•DME in presence of 4 equivalents of KOBu^t in DMF.

Table S19. Cartesian coordinates of $[Ni_{10}(SMe)_{10}]$ at BP86 level of theory with mixed basis set.

Ni	-1.008167	3.667614	-0.080100
Ni	-5.910297	0.359064	-0.070127
Ni	-4.099505	2.404847	0.085934
Ni	1.812648	3.617413	-0.030667
Ni	4.749287	2.045005	0.230012
S	-5.771779	2.190462	-1.378949
S	3.413694	2.812232	-1.388073
S	0.442276	4.382395	-1.625162
S	-6.570678	-1.529224	0.958116
S	-2.506884	2.739533	-1.463464
S	3.116086	2.765469	1.557341
S	-5.566213	1.771248	1.627735
S	5.932233	1.036697	1.820529

S	0.397960	4.663616	1.346150
S	-2.434678	2.944676	1.467942
Ni	1.008276	-3.667537	0.080119
Ni	5.910420	-0.358955	0.070061
Ni	4.099301	-2.404372	-0.086267
Ni	-1.812565	-3.617779	0.030841
Ni	-4.749163	-2.045242	-0.229779
S	5.771957	-2.190726	1.378336
S	-3.413538	-2.812521	1.388276
S	-0.441987	-4.382436	1.625270
S	6.571131	1.529545	-0.957680
S	2.506897	-2.739113	1.463321
S	-3.116422	-2.766548	-1.557246
S	5.565716	-1.770430	-1.628256
S	-5.932072	-1.036957	-1.820268
S	-0.397794	-4.663991	-1.345923
S	2.434264	-2.943987	-1.468115
C	7.184687	-3.245092	0.825075
H	8.110974	-2.838635	1.259105
H	7.019854	-4.266726	1.201354
H	7.272289	-3.269039	-0.272135
C	-4.125827	-4.397226	2.010556
H	-3.364307	-4.895669	2.630072
H	-5.021057	-4.182380	2.613753
H	-4.401750	-5.066080	1.181974
C	-7.184965	3.244607	-0.826461
H	-8.111031	2.837659	-1.260504
H	-7.272806	3.269017	0.270720
H	-7.020379	4.266122	-1.203172
C	-3.155310	4.476053	2.207226
H	-2.389823	4.967432	2.827471
H	-3.488371	5.177921	1.428694

H	-4.021548	4.193204	2.826067
C	-3.072193	4.088346	-2.583519
H	-3.328765	4.996264	-2.018486
H	-2.262048	4.322504	-3.290663
H	-3.960550	3.730301	-3.125219
C	4.125934	4.396951	-2.010378
H	5.021247	4.182135	-2.613460
H	3.364436	4.895293	-2.630000
H	4.401708	5.065862	-1.181795
C	0.475257	3.279375	-3.103582
H	-0.290058	2.492820	-3.011795
H	0.274150	3.896491	-3.993198
H	1.470337	2.814472	-3.190292
C	4.840610	0.391868	3.156303
H	4.571873	1.229716	3.817457
H	3.926047	-0.064098	2.750601
H	5.414296	-0.359799	3.718391
C	4.617250	-1.029759	-3.022047
H	3.903025	-1.778221	-3.396598
H	4.054169	-0.144469	-2.692509
H	5.319916	-0.760101	-3.823964
C	-0.351228	-3.912615	-3.028870
H	-0.360218	-4.732494	-3.763720
H	-1.228586	-3.262113	-3.177045
H	0.561227	-3.306121	-3.148904
C	3.072359	-4.087822	2.583444
H	2.262289	-4.321920	3.290692
H	3.328872	-4.995779	2.018448
H	3.960772	-3.729727	3.125014
C	-0.475052	-3.279445	3.103702
H	0.289749	-2.492424	3.011644
H	-1.470377	-2.815135	3.190762

H	-0.273263	-3.896444	3.993245
C	-4.618220	1.031414	3.022281
H	-4.054513	0.146310	2.693328
H	-3.904601	1.780335	3.397070
H	-5.321239	0.761644	3.823850
C	0.351073	3.912013	3.028995
H	1.227258	3.259782	3.176497
H	0.362099	4.731749	3.763977
H	-0.562490	3.307290	3.149492
C	-4.840391	-0.392561	-3.156212
H	-3.926440	0.064684	-2.750563
H	-4.570519	-1.230891	-3.816287
H	-5.414488	0.357960	-3.719407
C	-3.949830	-4.206947	-2.356032
H	-3.204953	-4.776116	-2.933841
H	-4.408658	-4.872944	-1.610338
H	-4.737954	-3.825904	-3.024302
C	3.949159	4.205251	2.357586
H	4.407994	4.871997	1.612567
H	3.204136	4.773779	2.935832
H	4.737242	3.823685	3.025602
C	3.154957	-4.474873	-2.208368
H	3.488394	-5.177043	-1.430276
H	2.389354	-4.966064	-2.828612
H	4.020937	-4.191538	-2.827346
C	6.397132	1.679834	-2.780017
H	6.897854	2.615551	-3.075194
H	6.912537	0.835808	-3.261966
H	5.343111	1.711767	-3.094878
C	-6.396345	-1.679441	2.780425
H	-6.912065	-0.835648	3.262446
H	-6.896626	-2.615372	3.075668

H	-5.342270	-1.710934	3.095148

Table S20. Cartesian coordinates of $[Ni_{10}(SPh)_{10}]\bullet CH_2Cl_2$ at BP86 level of theory with mixed basis set

Ni	1.078967	-3.922627	0.111897
Ni	5.589438	-0.166112	0.075380
Ni	3.894325	-2.214276	0.110238
Ni	-1.467267	-3.932595	0.025374
Ni	-4.152954	-2.033079	-0.019571
S	5.562345	-1.901406	-1.362485
S	-2.656079	-2.820979	-1.474049
S	-0.156177	-5.125267	-1.341545
S	5.781795	1.578023	1.491434
S	2.346049	-2.864529	-1.356661
S	-2.691221	-2.795447	1.456705
S	5.380239	-1.684637	1.697245
S	-5.583310	-1.334158	1.561332
S	-0.234847	-5.014287	1.562645
S	2.338314	-2.832207	1.568689
C	7.052288	2.686865	0.863269
C	0.034850	-4.559989	-3.029186
C	-0.210456	-2.860159	3.375117
H	-0.165516	-2.193771	2.517310
C	7.849819	-2.780052	0.005363
H	8.002204	-1.728173	0.267388
C	8.153184	2.199558	0.130959
H	8.226451	1.125421	-0.067526
C	3.458094	-0.084825	2.933031
H	3.317078	0.350859	1.941114
C	-3.512080	-4.035675	-2.469305
C	3.222012	-4.170362	2.385461
C	-4.574770	-0.780911	2.933399

C	6.934385	4.068762	1.120276
H	6.085299	4.446110	1.694528
C	-3.704156	-3.993494	2.329936
C	6.734339	-3.134969	-0.779645
C	-0.273647	-4.256022	3.179816
C	-0.067529	-3.208942	-3.414872
H	-0.307998	-2.454602	-2.665783
C	-4.144396	-3.616791	-3.656649
H	-4.085493	-2.568377	-3.961742
C	9.116584	3.092289	-0.360252
H	9.963356	2.707816	-0.938453
C	4.441155	-1.077574	3.095681
C	-3.592197	-5.379605	-2.054231
H	-3.093803	-5.680486	-1.127950
C	3.167828	-5.484642	-1.879448
H	2.728507	-5.734249	-0.909576
C	8.992818	4.470666	-0.120428
H	9.744093	5.165583	-0.509595
C	-3.407963	-0.026342	2.706723
H	-3.195830	0.303093	1.685505
C	-4.695625	-4.726271	1.643758
H	-4.823381	-4.596233	0.563898
C	-2.573641	0.330127	3.768089
H	-1.688465	0.935325	3.559277
C	-4.896105	-1.196031	4.238785
H	-5.785250	-1.809684	4.411069
C	3.122905	-4.151231	-2.333730
C	0.387613	-5.535096	-3.983988
H	0.497509	-6.578505	-3.674205
C	2.689127	0.335130	4.022748
H	1.961053	1.139464	3.880136
C	4.628100	-1.681867	4.353352

H	5.366819	-2.480525	4.469053
C	7.903094	4.952892	0.625335
H	7.799738	6.025092	0.824128
C	7.404587	-5.470707	-0.666643
H	7.226713	-6.517226	-0.936840
C	8.727107	-3.773450	0.463013
H	9.585052	-3.491419	1.082288
C	6.521900	-4.484641	-1.129574
H	5.666485	-4.757001	-1.751374
C	2.974092	-4.420957	3.747080
H	2.246248	-3.812886	4.289411
C	-4.941433	-5.893585	-4.013424
H	-5.503426	-6.615581	-4.614412
C	-4.303970	-6.305393	-2.830404
H	-4.364860	-7.348689	-2.503777
C	-4.857205	-4.551160	-4.422285
H	-5.353262	-4.225118	-5.342162
C	4.199381	-4.916523	1.691945
H	4.412401	-4.695085	0.640970
C	3.692222	-3.805150	-3.573587
H	3.665164	-2.765910	-3.911527
C	-0.338957	-5.114933	4.295531
H	-0.391404	-6.196836	4.142039
C	8.504302	-5.121408	0.136599
H	9.188550	-5.895058	0.499991
C	3.759526	-6.473338	-2.677699
H	3.787340	-7.508222	-2.320955
C	3.833155	-1.277394	5.439102
H	3.968901	-1.758967	6.413073
C	2.869299	-0.267210	5.280602
H	2.260691	0.050918	6.133700
C	0.155646	-2.846379	-4.751115

H	0.062930	-1.794446	-5.044960
C	-3.548725	-4.130028	3.720595
H	-2.801338	-3.531510	4.247213
C	-2.893114	-0.079961	5.074237
H	-2.239912	0.195150	5.909071
C	-0.192071	-2.332018	4.672405
H	-0.124637	-1.248325	4.800636
C	-4.051784	-0.841073	5.304843
H	-4.299920	-1.169700	6.319409
C	-4.385918	-5.014621	4.420537
H	-4.265996	-5.120217	5.503870
C	4.668947	-6.174469	3.718654
H	5.236442	-6.951082	4.242003
C	3.696252	-5.430183	4.405065
H	3.501829	-5.621983	5.465608
C	4.318912	-6.135548	-3.922148
H	4.783291	-6.907754	-4.543916
C	-5.376547	-5.743854	3.744277
H	-6.033872	-6.421262	4.299298
C	-0.330462	-4.578588	5.592373
H	-0.380838	-5.251668	6.454532
C	-0.252069	-3.187719	5.785362
H	-0.237059	-2.773958	6.798860
C	-5.531580	-5.594689	2.353575
H	-6.317933	-6.135781	1.817415
C	0.510772	-3.815569	-5.702872
H	0.699033	-3.524954	-6.741371
C	4.921946	-5.910754	2.360035
H	5.697653	-6.460349	1.816777
C	4.286058	-4.801424	-4.362301
H	4.724540	-4.530724	-5.328259
C	0.630092	-5.159722	-5.312779

H	0.919970	-5.921490	-6.043399
Ni	-1.099159	3.963713	-0.080316
Ni	-5.593690	0.179619	-0.075425
Ni	-3.885434	2.218287	-0.095391
Ni	1.435672	3.928749	0.002610
Ni	4.134317	2.040140	0.028122
S	-5.573596	1.912388	1.363791
S	2.661047	2.854882	1.498337
S	0.149587	5.144021	1.383157
S	-5.762936	-1.544754	-1.511885
S	-2.343957	2.867281	1.377617
S	2.615296	2.741980	-1.422742
S	-5.361727	1.692547	-1.693725
S	5.557103	1.346614	-1.557297
S	0.217627	5.065401	-1.522319
S	-2.320865	2.845353	-1.538676
C	-7.024298	-2.676957	-0.906492
C	-0.042840	4.552095	3.062243
C	0.186816	2.945290	-3.366728
H	0.140504	2.281996	-2.507292
C	-7.833269	2.815600	-0.034968
H	-7.994000	1.765683	-0.299692
C	-8.123152	-2.216827	-0.153476
H	-8.206452	-1.147875	0.067422
C	-3.381384	0.139940	-2.899629
H	-3.202871	-0.248734	-1.893907
C	3.546259	4.100309	2.429868
C	-3.225900	4.146964	-2.392281
C	4.579119	0.789533	-2.948579
C	-6.898693	-4.051226	-1.199301
H	-6.053605	-4.406999	-1.792689
C	3.618591	3.952572	-2.299160

C	-6.725288	3.157727	0.766117
C	0.239041	4.338303	-3.154901
C	0.057072	3.193865	3.423047
H	0.290248	2.459168	2.652896
C	4.218379	3.712085	3.606516
H	4.173245	2.670706	3.937525
C	-9.072168	-3.129825	0.328218
H	-9.916641	-2.766433	0.923066
C	-4.425301	1.065196	-3.084046
C	3.608375	5.435800	1.984316
H	3.077949	5.717110	1.069704
C	-3.180464	5.461920	1.977137
H	-2.735127	5.740351	1.017675
C	-8.937833	-4.501327	0.056624
H	-9.678038	-5.212000	0.438393
C	3.418523	0.016882	-2.755043
H	3.155678	-0.292625	-1.739683
C	4.587921	4.711531	-1.608681
H	4.705784	4.591844	-0.526741
C	2.635893	-0.367529	-3.847704
H	1.764845	-1.004263	-3.672283
C	4.936108	1.206368	-4.244998
H	5.819843	1.835066	-4.388765
C	-3.135100	4.115815	2.392518
C	-0.390362	5.509258	4.036657
H	-0.497140	6.558889	3.747343
C	-2.613184	-0.286930	-3.986755
H	-1.829584	-1.030291	-3.819888
C	-4.677179	1.592812	-4.364739
H	-5.463918	2.341042	-4.499071
C	-7.853394	-4.955810	-0.713917
H	-7.742937	-6.021935	-0.939589

C	-7.368413	5.500445	0.646835
H	-7.183121	6.544644	0.920865
C	-8.692306	3.819144	-0.504835
H	-9.544136	3.547255	-1.136934
C	-6.503511	4.504302	1.121478
H	-5.654058	4.766481	1.755695
C	-3.009790	4.340537	-3.768070
H	-2.288230	3.716109	-4.300343
C	5.022510	5.996964	3.884688
H	5.603108	6.733334	4.449529
C	4.344766	6.379897	2.714581
H	4.392082	7.415564	2.362231
C	4.953788	4.664249	4.327249
H	5.480649	4.359977	5.237464
C	-4.186305	4.922391	-1.706797
H	-4.367997	4.753312	-0.640264
C	-3.708249	3.732590	3.619452
H	-3.679070	2.684361	3.927908
C	0.299947	5.209940	-4.260334
H	0.343413	6.290734	-4.095993
C	-8.459386	5.164211	-0.173629
H	-9.129380	5.945773	-0.546479
C	-3.778279	6.425685	2.800948
H	-3.805971	7.470623	2.474819
C	-3.888940	1.177841	-5.450855
H	-4.077961	1.598150	-6.444085
C	-2.861551	0.236400	-5.267641
H	-2.255023	-0.088298	-6.119681
C	-0.162920	2.805480	4.752521
H	-0.071363	1.747941	5.026086
C	3.478656	4.078697	-3.692158
H	2.749286	3.464114	-4.225207

C	2.989327	0.044161	-5.144242
H	2.373420	-0.252508	-5.999961
C	0.187345	2.428042	-4.668985
H	0.140770	1.344357	-4.810945
C	4.135979	0.833807	-5.337974
H	4.410839	1.166431	-6.344349
C	4.305914	4.975313	-4.389111
H	4.195125	5.070849	-5.474390
C	-4.712251	6.086930	-3.775071
H	-5.296029	6.837865	-4.317658
C	-3.751967	5.318383	-4.451294
H	-3.581518	5.466426	-5.522875
C	-4.343521	6.050353	4.031814
H	-4.812898	6.802959	4.673551
C	5.273407	5.729453	-3.707520
H	5.923040	6.416893	-4.259353
C	0.303760	4.686491	-5.562644
H	0.351335	5.369257	-6.417385
C	0.245865	3.296827	-5.772193
H	0.246694	2.894791	-6.790556
C	5.414456	5.592131	-2.314073
H	6.183199	6.152669	-1.772359
C	-0.512495	3.757591	5.723477
H	-0.698101	3.448129	6.757032
C	-4.930063	5.882993	-2.399971
H	-5.694009	6.454386	-1.862632
C	-4.308924	4.704191	4.433373
H	-4.750982	4.404700	5.389182
C	-0.630093	5.109080	5.358910
H	-0.915628	5.857483	6.104948
Cl	0.045380	-0.043138	-1.561197
Cl	0.379895	0.158805	1.383144

C	-0.548783	-0.585963	0.039653
H	-1.608935	-0.296909	0.134197
H	-0.411603	-1.685843	0.094963

Table S21. Cartesian coordinates of $[Ni_5(SCH_2Ph)_{10}]$ at BP86 level of theory with mixed basis set

C	-1.970530	2.653081	3.442611
S	-3.240448	-0.747780	0.706620
S	-2.360257	0.782138	-1.692665
C	1.734142	-2.857505	2.333635
S	2.404371	2.243249	0.220507
S	1.809381	0.517109	2.554038
C	-1.129190	-4.495628	-0.864695
C	-3.027713	-1.627668	2.337896
S	-0.776997	-2.936156	0.116870
C	-0.187925	-0.498556	-3.902926
C	2.516364	2.796172	-1.550742
C	4.033082	-1.460242	-1.994226
C	-0.789621	3.767043	-1.365490
Ni	-1.734885	-1.201331	-0.889010
S	2.415509	-2.187317	0.730521
S	2.447693	-0.497801	-1.710515
S	-1.255493	1.163871	2.555053
Ni	-2.034291	1.109658	0.482904
C	-4.197726	0.699508	-2.057711
S	-0.490453	-1.825390	-2.626254
Ni	2.328778	0.026919	0.455791
Ni	0.479506	1.837528	1.302716
Ni	0.910715	-1.880612	-0.881828
S	-1.072073	3.117442	0.352349
C	3.146155	1.600425	3.300592
H	-1.173515	-0.045999	-4.095315

H	0.476227	0.263282	-3.466994
H	-4.688560	0.193615	-1.209944
H	-4.533027	1.749142	-2.090959
H	0.134026	4.364909	-1.303358
H	-0.634279	2.922161	-2.053973
H	-1.261885	2.867106	4.259385
H	-1.974544	3.502529	2.740334
H	-3.195545	-0.858173	3.108426
H	-1.990190	-1.984559	2.418195
H	3.881119	-1.986292	-2.951346
H	4.124765	-2.207298	-1.188870
H	1.103231	-2.087622	2.803382
H	1.099477	-3.709748	2.043051
H	3.943925	0.902774	3.604864
H	3.532832	2.257320	2.504479
H	3.316830	2.166249	-1.976907
H	1.592255	2.544804	-2.092095
H	-2.154199	-4.787888	-0.582574
H	-1.114272	-4.234003	-1.935553
C	-1.955718	4.615810	-1.814766
C	-2.271533	5.817772	-1.145387
C	-2.737228	4.235151	-2.924621
C	-3.339622	6.617460	-1.575606
H	-1.671836	6.122362	-0.280360
C	-3.804236	5.038197	-3.359944
H	-2.497410	3.303332	-3.449297
C	-4.110536	6.230437	-2.685168
H	-3.569156	7.548473	-1.046316
H	-4.395333	4.734133	-4.230848
H	-4.942744	6.856840	-3.023069
C	2.614241	2.386984	4.470438
C	2.695893	1.880435	5.783248

C	2.001173	3.641963	4.265106
C	2.181888	2.608503	6.867564
H	3.172824	0.908361	5.954623
C	1.488200	4.372065	5.347614
H	1.937998	4.048207	3.248635
C	1.574851	3.856200	6.652622
H	2.258282	2.201789	7.881614
H	1.025438	5.349382	5.173405
H	1.175557	4.427042	7.497542
C	-0.128142	-5.572100	-0.533985
C	-0.375346	-6.498816	0.499891
C	1.091775	-5.652867	-1.239081
C	0.570031	-7.485094	0.821764
H	-1.322677	-6.449343	1.049460
C	2.036721	-6.639148	-0.921016
H	1.291548	-4.940621	-2.048129
C	1.780164	-7.557082	0.112423
H	0.359528	-8.200243	1.624066
H	2.974757	-6.694288	-1.483528
H	2.517092	-8.328817	0.358607
C	-4.452137	-0.010387	-3.362302
C	-4.549387	-1.417891	-3.403170
C	-4.573513	0.711711	-4.567593
C	-4.768533	-2.083782	-4.617837
H	-4.461224	-1.988786	-2.471483
C	-4.790239	0.047347	-5.784917
H	-4.507529	1.805797	-4.544892
C	-4.887206	-1.353507	-5.813487
H	-4.851227	-3.175730	-4.631309
H	-4.888114	0.624235	-6.710742
H	-5.061755	-1.873757	-6.761188
C	2.863337	-3.282669	3.237587

C	3.247050	-2.487788	4.337179
C	3.556840	-4.488384	2.996591
C	4.294651	-2.890256	5.180234
H	2.707284	-1.553178	4.528098
C	4.605737	-4.889166	3.836388
H	3.262911	-5.114495	2.146248
C	4.978825	-4.090987	4.931188
H	4.576039	-2.267056	6.036196
H	5.131277	-5.829838	3.639447
H	5.795981	-4.405818	5.588869
C	0.403862	-1.104817	-5.149693
C	-0.416078	-1.796661	-6.067080
C	1.783225	-0.996416	-5.421504
C	0.130848	-2.362476	-7.227689
H	-1.490085	-1.883441	-5.865846
C	2.330959	-1.559791	-6.584486
H	2.420757	-0.455931	-4.712179
C	1.506490	-2.246641	-7.490308
H	-0.518878	-2.892225	-7.932696
H	3.403098	-1.460390	-6.786514
H	1.932597	-2.686278	-8.398315
C	-3.350618	2.339416	3.958430
C	-3.531755	1.758001	5.231099
C	-4.486648	2.596527	3.161558
C	-4.817466	1.448095	5.700456
H	-2.655244	1.552376	5.856326
C	-5.772477	2.288990	3.630329
H	-4.355788	3.047672	2.171069
C	-5.941861	1.712545	4.900993
H	-4.941665	1.002067	6.692999
H	-6.644836	2.502852	3.003610
H	-6.945853	1.474521	5.267921

C	-4.019274	-2.757969	2.450481
C	-3.604567	-4.099325	2.321046
C	-5.384170	-2.491219	2.692582
C	-4.529020	-5.149646	2.435398
H	-2.544415	-4.310382	2.139567
C	-6.309072	-3.539186	2.802829
H	-5.714718	-1.451810	2.799925
C	-5.884806	-4.872713	2.673677
H	-4.190212	-6.187399	2.342678
H	-7.364031	-3.315802	2.995085
H	-6.606730	-5.691334	2.763111
C	5.226305	-0.541638	-2.042142
C	5.933455	-0.230623	-0.860926
C	5.647877	0.038782	-3.256443
C	7.037589	0.633400	-0.896159
H	5.617316	-0.681335	0.087086
C	6.750672	0.906289	-3.292852
H	5.110437	-0.200964	-4.181539
C	7.448376	1.206424	-2.111750
H	7.581211	0.857933	0.027704
H	7.067452	1.344873	-4.245077
H	8.310183	1.881411	-2.138656
C	2.861063	4.264591	-1.694824
C	3.822760	4.884122	-0.868595
C	2.266237	5.028062	-2.721697
C	4.173976	6.227863	-1.061331
H	4.291454	4.302993	-0.067773
C	2.619422	6.372970	-2.917924
H	1.526080	4.560109	-3.381081
C	3.573347	6.978585	-2.085874
H	4.921396	6.691123	-0.408242
H	2.143948	6.946642	-3.720530

H	3.847437	8.028367	-2.233951

Table S22. Cartesian coordinates of $[Ni_6(SCH_2Ph)_{12}]$ at BP86 level of theory with mixed basis set

Ni	2.262045	-0.935088	-0.910009
Ni	-2.803988	0.550895	-1.639731
Ni	-0.556823	-0.331706	-2.519626
S	0.580512	-2.097537	-1.784439
S	1.373971	0.670657	-2.157203
S	-3.965761	-0.176904	0.116995
S	-2.519764	-1.423776	-2.647891
S	-1.638273	1.372146	-3.423874
S	-2.722185	2.451284	-0.540046
C	-0.563229	-4.246008	-0.399240
C	-0.377456	-2.755752	-0.327401
C	-3.904045	-2.011988	0.348861
C	-3.398439	-1.175880	-4.279079
C	-0.881601	3.027045	-3.057347
C	2.182653	0.337935	-3.828830
C	-4.409940	3.068165	-0.053110
C	0.503796	-5.114419	-0.078899
C	-1.794948	-4.804659	-0.799270
C	-0.904819	-7.052562	-0.508885
C	-1.967377	-6.197386	-0.846820
C	0.333969	-6.505149	-0.130323
H	-2.621621	-4.145593	-1.081863
H	-2.933370	-6.613661	-1.151054
H	-1.039148	-8.138539	-0.545884
H	1.171680	-7.162808	0.124255
H	1.471178	-4.684445	0.201288
H	0.184821	-2.431393	0.560457
H	-1.327459	-2.206297	-0.304684

H	-3.262328	-2.395987	-0.457306
H	-3.406838	-2.211535	1.311671
H	-2.909184	-0.328014	-4.788087
H	-3.224396	-2.088707	-4.870112
H	-1.684273	3.753179	-3.275460
H	-0.694995	3.073593	-1.977595
H	1.635353	-0.504575	-4.279685
H	1.999091	1.242706	-4.427549
H	-4.990638	3.204048	-0.979353
H	-4.895220	2.284799	0.554253
Ni	-2.146965	0.848510	0.895334
Ni	2.907375	-0.611821	1.584970
Ni	0.638281	0.205785	2.512383
S	-0.545559	1.978602	1.893832
S	-1.329496	-0.780203	2.184426
S	4.010933	0.208756	-0.152392
S	2.560724	1.354174	2.572871
S	1.755720	-1.467235	3.379053
S	2.974520	-2.529640	0.499985
C	0.183557	4.487377	0.919597
C	0.410285	3.020516	0.685665
C	3.768112	2.011149	-0.524469
C	3.737794	1.049240	3.999883
C	1.051521	-3.166024	3.104123
C	-2.123032	-0.423898	3.850718
C	4.702783	-2.956318	0.014113
C	-0.572519	5.282871	0.037744
C	0.734819	5.083253	2.075674
C	-0.209512	7.234649	1.446919
C	0.541353	6.446991	2.338468
C	-0.762731	6.648957	0.297062
H	1.312218	4.459072	2.769095

H	0.975728	6.896155	3.237753
H	-0.368423	8.297975	1.653233
H	-1.364309	7.251542	-0.390761
H	-1.035347	4.824162	-0.839650
H	0.162863	2.674396	-0.327711
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H	2.747396	2.291982	-0.244685
H	3.826502	2.054800	-1.624344
H	3.228942	0.404261	4.733036
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H	0.909623	-3.328305	2.028781
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C	5.174898	-0.992717	3.542956
C	7.101669	0.568678	2.240607
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C	7.264166	-0.824613	2.305593
H	7.839889	1.188316	1.723083
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H	8.135706	-1.301081	1.844820
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C	-6.647561	0.484747	-3.133875
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H	-8.677797	-0.246957	-3.400587
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C	-4.838958	6.718281	1.029616
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C	-3.221885	5.661416	2.502239
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C	-3.957673	6.796692	2.120731
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H	-2.502484	5.719796	3.324734
H	-3.833196	7.740808	2.660925
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C	4.415868	3.920050	1.006495
C	7.127329	3.597992	0.358455
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H	7.493656	5.247525	1.726122
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H	7.019585	-6.467963	-2.042396
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C	2.688160	4.151433	-3.794635
H	1.457144	3.921246	-2.026473
C	2.760918	4.010219	-5.192555
H	1.692471	3.426192	-6.991110
H	3.554784	4.510197	-3.229441
H	3.685115	4.260321	-5.723167

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