Electronic Supplementary Information (ESI)

[$Cu_{30}I_{16}(mtpmt)_{12}(\mu_{10}\text{-}S_4)$]: An Unusual 30-Membered Copper(I) Cluster Derived from the C-S Bond Cleavage and its Use in Heterogeneous Catalysis

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Experimental Section

General: 3-(Dimethylamino)-2-methyl-1-(p-tolyl)prop-2-en-1-one was prepared according to the published procedures.[S1] All chemicals were obtained from commercial sources and used as received. ^1H and ^{13}C NMR spectra were recorded at ambient temperature on a Varian UNITYplus-300 or 400 spectrometer. ^1H NMR chemical shifts were referenced to the solvent signal in $CDCl_3$ or DMSO-d_6. The IR spectra were recorded on an FTRI-1000 spectrophotometer as KBr disk (4000-400cm^{-1}). The elemental analyses for C, H, N and S were performed on a Carlo-Erba EA1110 CHNO-S micro-analyzer. The uncorrected melting points were determined in argon-sealed capillary tubes on a Mel-Temo II apparatus.

Preparation of 5-methyl-4-(p-tolyl)pyrimidine-2-thiol (mtpmtH)

A mixture containing 3-(dimethylamino)-2-methyl-1-(p-tolyl)prop-2-en-1-one (2.03 g, 0.01 mol), KOH (0.672 g, 0.012 mol) and thiourea (0.76 g, 0.01mol) in EtOH (30 mL) was heated under refluxing for 5 hours and then was cooled to ambient temperature. The mixture was treated with an aqueous solution of HCl to pH = 5~6. After filtration, the yellow residue was recrystallized from $CHCl_3$ and DMF to give yellow crystals of mtpmtH, which were collected by filtration and dried *in vacuo*. Yield: 1.68 g (78 %). m.p. 175-177 °C. ^1H NMR (DMSO-d_6, 400 MHz): δ: 13.732 (s, 1H), 8.018 (s, 1H), 7.544-7.524 (d, 2H, J = 8.0), 7.334-7.314 (d, 2H, J = 8.0), 2.381 (s, 3H), 2.114 (s, 3H). ^{13}C NMR (DMSO-d_6, 400 MHz): δ: 180.4, 171.3, 167.0, 166.6, 162.1, 148.1, 127.2, 118.3, 22.9, 17.9. Anal. Calcd for $C_{12}H_{12}N_2S$: C 66.63, H 5.59, N 12.95, S 14.82 %; found C 66.78, H 5.43, N 13.32, S 14.66 %. HRMS calcd for $C_{12}H_{12}N_2S$ 216.0721, found 216.0716. IR (KBr, disk): 1606(m), 1573(m), 1566(m), 1369(w), 1281(s), 1209(w), 1144(s), 1048(w), 1009(w), 824(w), 763(m), 725 (w), 420(w) cm^{-1}.

Preparation of $[Cu_{30}I_{16}(mtpmt)_{12}(\mu_{10}\text{-}S_4)]$ (1), $[(bmtpms)Cu(\mu\text{-}I)]_n$ (2) and bmtpms

To a Pyrex glass tube (15 cm in length, 7 mm in inner diameter) were added CuI (9.5 mg, 0.05 mmol), Hmtpmt (10 mg, 0.05 mmol), and 2 mL of MeCN. The tube was sealed and heated in an oven at 120 °C for 2000 mins and then cooled to 60 °C at a rate of 5 °C/60 min to form red crystals of **1**·3MeCN (*ca.* 1% yield) with coupled with a small amount of black solid Cu_2S, which were separated by filtration, washed with MeCN, and dried *in vacuo*. Anal. Calcd for $C_{144}H_{132}Cu_{30}I_{16}N_{24}S_{16}$ (**1**): C 26.01, H 2.00, N 5.06, S 7.72%; found: C 25.82, H 2.33, N 4.90, S 7.90%. IR (KBr, disk): 1612(w), 1561(m), 1506(w), 1439(w), 1397(s), 1224(w), 1144(m), 1002(w), 885(w), 824(m), 773(m), 678(w), 551(w), 471(w) cm^{-1}.

When the filtrate were further cooled to 25 ºC, a yellow crystalline solid of bmtpms was formed in several minutes, which was collected by filtration, with Et_2O and dried *in vacuo*. Yield: 4.2 mg (42%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 8.866 (s, 2H), 7.532-7.512 (d, J = 8 Hz, 2H), 7.306-7.286 (d, J = 8Hz, 2H), 2.423 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ: 166.8, 163.8, 158.4, 141.3, 133.4, 129.5, 129.1, 126.5, 21.6, 17.3. Anal. Calcd for $C_{24}H_{22}N_4S$: C 58.38, H 4.49, N 11.35, S 6.49%; found: C 58.25, H 4.67, N 11.76, S 6.87%. HRMS calcd for $C_{24}H_{22}N_4S$ 398.1565, found 398.1561. IR (KBr, disk): 1610(w), 1564(s), 1524(w), 1507(w), 1443(w), 1398(s), 1385(s), 1346(m), 1233(w), 1135(m), 1006(w), 934(w), 879(w), 827(m), 775(m), 665(w), 547(w) cm^{-1}.

The filtrate was kept at 0 ºC for two days to form several red needles of **2**·0.5MeCN coupled with some yellow powder of bmtpms, which were separated by hands under microscope. Anal. Calcd for $C_{24}H_{22}CuIN_4S$ (**2**): C 48.94, H 3.76, N 9.51, S 5.44%; found: C 48.67, H 3.37, N 9.44, S 5.89%. IR (KBr, disk): 1608(w), 1566(s), 1524(w), 1507(w), 1441(w), 1397(s), 1386(s), 1345(m), 1236(w), 1133(m), 1006(w), 934(w), 877(w), 829(m), 776(m), 666(w), 544(w) cm^{-1}.

Preparation of $[Cu_{30}I_{16}(mtpmt)_{12}(\mu_{10}\text{-}S_4)]$ (1), $[(bmptmds)\{Cu(\mu\text{-}I)\}_2]_2$ (3), bmtpms and bmptmds

To a Pyrex glass tube (15 cm in length, 7 mm in inner diameter) were added CuI (9.5 mg, 0.05 mmol), Hmtpmt (5 mg, 0.025 mmol), and 1.6 mL of MeCN and 0.4 ml of DMF. The tube was sealed and heated in an oven at 120 °C for 2000 mins and then cooled to room temperature at a rate of 5 °C/60 min to form red crystals of **1**·3MeCN, which were collected by filtration, washed with MeCN, and dried *in vacuo*. Yield: 7 mg (53% based on Cu).

Diethyl ether (15 mL) was carefully layered onto the above MeCN solution, forming yellow plates of **3**·MeCN, which were isolated by filtration, washed with Et_2O, and dried *in vacuo*. Yield: 1.8 mg (9% based on Cu). Anal. Calcd for $C_{48}H_{44}Cu_4I_4N_8S_4$ (**3**): C35.53, H 2.69, N 6.91, S 7.93%; found: C 35.78, H 2.47, N 6.68, S 8.02%. IR (KBr, disk): 1610(w), 1563(s), 1523(m), 1502(m), 1442(w), 1395(s), 1365(m), 1277(w), 1227(w), 1191(w), 1135(m), 1006(m), 882(w), 829(m), 772(s), 664(w), 577(w), 514(w), 476(w), 439(w) cm^{-1}.

The filtrate was further concentrated to dryness *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane : ethyl acetate = 10 : 1) to afford bmtpms (*ca*. 5%) and bmptmds (*ca*. 5%) ligands. For bmptmds: m.p. 171.7-172.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ:

8.431 (s, 2H), 7.502-7.482 (d, J = 8 Hz, 2H), 7.240-7.220 (d, J = 8Hz, 2H), 2.396 (s, 3H), 2.347 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ: 167.1, 165.7, 160.0, 140.1, 143.7, 129.3, 129.2, 124.7, 21.6, 17.2. Anal. Calcd for $C_{24}H_{22}N_4S_2$: C 66.94, H 5.15, N 13.01, S 14.89 %; found C 66.65, H 5.36, N 13.41, S 14.52 %. HRMS calcd for $C_{24}H_{22}N_4S_2$ 430.1286, found 430.1286. IR (KBr, disk): 1612(w), 1556(s), 1508(m), 1397(s), 1356(w), 1339(m), 1240(m), 1135(s), 1001(m), 865(w), 826(m), 776(m), 700(w), 655(w), 574(w), 524(w) cm^{-1}.

Preparation of [(bmtpms)Cu(μ-I)]$_n$ (2)

To the CuI (19 mg, 0.1 mmol) solution in MeCN (3 mL) was added the solution of bmtpms (39 mg, 0.1 mmol) in $CHCl_3$ (3 mL). The mixture was stirred at room temperature for 3h and then filtered. Et_2O (30 mL) was layered onto the filtrate to produce red crystals of **2**·0.5MeCN in several days, which were collected by filtration, washed with Et_2O and dried in air. Yield: 44 mg (75%).

Preparation of [(bmptmds){Cu(μ-I)}$_2$]$_2$ (3)

Compound **3**·MeCN was prepared as yellow crystals in the above manner to that described for **2**, using CuI (19 mg, 0.1 mmol) and bmptmds (43 mg, 0.1 mmol) starting materials in $CHCl_3$ and MeCN. Yield: 39 mg, 96 % (based on Cu).

Preparation of [Cu$_6$(mtpmt)$_6$] (4)

To a Pyrex glass tube (15 cm in length, 7 mm in inner diameter) were added CuI (9.5 mg, 0.05 mmol), Hmtpmt (10 mg, 0.05 mmol), and 2 mL of MeCN and 0.1 ml of DMF under Ar. The tube was sealed and heated in an oven at 120 °C for 2000 mins and then cooled to temperature at a rate of 5 °C/60 min to form yellow crystals of **4**, which were collected by filtration, washed with MeCN, and dried in air. Yield: 10 mg (67% based on Cu). Anal. Calcd for $C_{72}H_{66}Cu_6N_{12}S_6$: C 51.69, H 3.98, N 10.05, S 11.50%; found: C 51.52 H 4.11, N 10.23, S 11.35%. IR (KBr, disk): 1611(w), 1561(s), 1502(w), 1394(s), 1362(m), 1226(w), 1190(w), 1135(m), 1007(m), 879(w), 830(m), 772(m), 663(w), 534(w), 439(w) cm^{-1}.

General catalytic procedure for the N-arylation of nitrogen-containing heterocycles with boronic acids

To a solution of nitrogen-containing heterocycle (1.0 mmol), boronic acid (1.2 mmol) in MeOH (5 mL) was **1** (11 mg). The mixture was refluxing for 5 h. After cooling to ambient temperature, the mixture was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 10mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated to dryness *in vacuo*. The residue was purified by flash chromatography on silica gel.

1-Phenyl-1H-imidazole[S2] (Table 1, entry 1) ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.20 (br, 1H), 7.27 (br, 1H), 7.32-7.48 (m, 5H), 7.85 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 118.2, 121.4, 127.4, 129.8, 130.3, 135.5, 137.3.

1-p-Tolyl-1H-imidazole[S2] (Table 1, entry 2) ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 2.40 (s, 3H), 7.19 (s, 1H), 7.24-7.26 (d, 5H), 7.82 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 21.1, 118.5, 121.6, 130.3, 130.5, 135.1, 135.7, 137.6.

1-m-Tolyl-1H-imidazole[S3] (Table 1, entry 3) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.40 (s, 3H), 7.14-7.19 (m, 4H), 7.25 (s, 1H), 7.32 (t, J = 7.6Hz, 1H), 7.83 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 21.3, 118.1, 118.4, 121.9, 128.1, 129.5, 130.2, 135.5, 137.2, 139.9.

1-o-Tolyl-1H-imidazole[S4] (Table 1, entry 4) ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 2.17 (s, 3H), 7.04 (s, 1H), 7.18-7.20 (m, 2H), 7.26-7.30 (m, 1H), 7.33-7.36 (m, 2H), 7.57 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 17.4, 120.4, 126.3, 126.7, 128.7, 129.1, 131.1, 133.6, 136.4, 137.3.

1-(3,5-dimethylphenyl)-1H-imidazole[S5] (Table 1, entry 5) ^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ 2.36 (s, 6H), 6.97 (s, 3H), 7.17 (s, 1H), 7.23 (s, 1H), 7.81 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 21.2, 118.1, 119.1, 128.9, 130.1, 135.5, 137.2, 139.6.

1-(4-Methoxy-pheny)-1H-imidazole[S6] (Table 1, entry 6) ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 3.85 (s, 3H), 6.96-7.00 (m, 2H), 7.19 (d, J = 8.4Hz, 2H), 7.23-7.32 (m, 2H), 7.76 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 55.7, 115.0, 118.9, 123.3, 130.2, 130.8, 136.0, 159.0.

1-(4-fluorophenyl)-1H-imidazole[S7] (Table 1, entry 7) ^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ 7.15-7.24 (m, 4H), 7.35 (s, 2H), 7.80 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 116.7 (d, J = 22Hz), 118.5, 123.3 (d, J = 8Hz), 130.4, 133.5, 135.6, 161.5 (d, J = 246Hz).

1-(naphthalen-2-yl)-1H-imidazole[S8] (Table 1, entry 8) ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.26 (s, 1H), 7.38 (s, 1H), 7.48-7.57 (m, 3H). 7.78 (s, 1H), 7.84-7.97(m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 118.5, 119.1, 120.3, 126.6, 127.5, 127.9, 128.0, 130.2, 130.7, 132.3, 133.6, 134.8, 136.0.

1-(naphthalen-1-yl)-1H-imidazole[S8] (Table 1, entry 9) ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.29 (d, J = 6.8Hz, 2H), 7.44 (d, J = 7.2Hz, 1H), 7.80 (s, 1H). 7.49-7.61 (m, 4H), 7.79 (s, 1H), 7.94 (d, J = 8.0Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 121.3, 123.6, 125.2, 127.0, 127.6, 128.3, 129.2, 129.4, 134.0, 134.4.

1-p-Tolyl-1H-pyrazole[S9] (Table 1, entry 10) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.36 (s, 3H), 6.42 (s, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.0Hz, 2H), 7.69 (s, 1H), 7.85 (d, J = 1.6Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 21.0, 107.4, 119.3, 126.818, 130.0, 136.3, 138.1, 140.9.

1-p-Tolyl-1H-benzoimidazole[S10] (Table 1, entry 11) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.44 (s, 3H), 7.28-7.38 (m, 6H), 7.49-7.51 (t, 1H), 7.86-7.88 (t, 1H), 8.80 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 21.2, 110.6, 120.6, 122.8, 123.7, 124.1, 130.7, 133.8, 133.9, 138.2, 142.5, 144.0.

X-ray diffraction crystallography

Single crystals of **1**·3MeCN, **2**·0.5MeCN, **3**·MeCN and **4** suitable for X-ray diffraction were obtained directly from the above preparations. Diffraction intensities of **1**·3MeCN, **2**·0.5MeCN, **3**·MeCN and **4** were collected on a Rigaku Mercury CCD X-ray diffractometer (Mo-Kα, λ = 0.71073 Å). A red prism of **1** with dimensions 0.50 mm × 0.40 mm × 0.20 mm, a red needle of **2** with dimensions 0.39 mm × 0.12 mm × 0.10 mm, or a yellow plate of **3** with dimensions 0.25 mm × 0.20 mm × 0.10 mm, or a yellow block of **4** with dimensions 0.70 mm × 0.30 mm × 0.20 mm was mounted at the top of a glass fiber with grease at 193K (**1**) or 223K (**4**) in a stream of gaseous nitrogen or at 298K (**2** and **3**). The collected data were reduced by using the program *CrystalClear* (Rigaku and MSC, Ver. 1.3, 2001). The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of **1**·3MeCN, **2**·0.5MeCN, **3**·MeCN and **4** were solved by direct methods and refined by full matrix least-squares on F^2.[S11] For **1**·3MeCN and **2**·0.5MeCN, the site occupation factor for the MeCN solvent molecules were fixed to be 0.5 to give reasonable temperature factors. All non-H atoms except those of the MeCN molecules in **1**·3MeCN and **2**·0.5MeCN were refined anisotropically. For **1**·3MeCN and **2**·0.5MeCN, the hydrogen atoms for MeCN were not located. Other hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. The final refinement was based on 16417 (**1**·3MeCN), 4687 (**2**·0.5MeCN), 3880 (**3**·MeCN) and 6222 (**4**) reflections with $I > 2.00\sigma(I)$ and 1092 (**1**·3MeCN), 267 (**2**·0.5MeCN), 333 (**3**·MeCN) or 434 (**4**) variable parameters. All the calculations were performed on a Dell workstation using the *CrystalStructure* crystallographic software package (Rigaku and MSC, Ver.3.60, 2004). A summary of the important crystallographic information for **1**·3MeCN, **2**·0.5MeCN, **3**·MeCN and **4** are tabulated in Table S1.

Table S1 Summary of crystallographic data for **1**·3MeCN, **2**·0.5MeCN, **3**·MeCN and **4**

	1·3MeCN	**2**·0.5MeCN	**3**·MeCN	**4**
Empirical formula	$C_{150}H_{141}Cu_{30}I_{16}N_{27}S_{16}$	$C_{50}H_{47}Cu_2I_2N_9S_2$	$C_{50}H_{47}Cu_4I_4N_9S_4$	$C_{72}H_{66}Cu_6N_{12}S_6$
Formula weight	6771.46	1218.97	1663.97	1673.09
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$C2/c$	$P2_1/c$	$P\bar{1}$	$C2/c$
a/Å	31.206(6)	13.591(3)	9.2606(19)	27.694(4)
b/Å	32.079(6)	26.495(5)	11.579(2)	13.3920(18)
c/Å	20.393(4)	7.4948(15)	14.140(3)	18.751(3)
α/°			83.58(3)	
β/°	106.70(3)	96.05(3)	80.89(3)	90.182(2)
γ/°			78.86(3)	
V/Å^3	19554(7)	2683.8(10)	1463.7(5)	6954.3(16)
Z	4	2	1	4
D_c/(g·cm^3)	2.300	1.508	1.888	1.598
F(000)	12816	1212	802	3408
μ/mm^{-1}	5.931	2.062	3.727	2.035
Total reflections	49699	15400	13952	16294
Unique reflections	22097	6051	5294	7893
R_{int}	0.0691	0.0409	0.0393	0.0286
No. observations [$I > 2.00\sigma(I)$]	16417	4687	3880	6222
No. variables	1092	267	333	434
R_1[a]	0.0930	0.0596	0.0598	0.0373
wR_2[b]	0.2289	0.1356	0.1416	0.0775
GOF[c]	1.171	1.112	1.075	0.996
Residual peaks (e·Å^{-3})	2.290, -1.322	1.291, -0.769	0.901, -0.939	0.453, -0.507

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] $wR_2 = \{\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. [c] GOF $= \{\sum w[(F_o^2-F_c^2)^2/(n-p)]\}^{1/2}$, where n is the number of reflections and p is the number of parameters.

Table S2 Selected bond lengths (Å) and angles (°) of **1**[a]

Cu(1)-N(1)	1.997(10)	Cu(1)-N(3)	2.002(9)
Cu(1)-I(1)	2.5726(18)	Cu(1)···Cu(2)	2.594(2)
Cu(1)···Cu(3)	2.904(2)	Cu(2)-N(5)	2.001(9)
Cu(2)-S(2)	2.237(3)	Cu(2)-I(1)	2.573(2)
Cu(2)···Cu(3)	2.788(2)	Cu(3)-S(3)	2.299(3)
Cu(3)-S(2)	2.323(4)	Cu(3)-S(1)	2.431(4)
Cu(3)-S(7)	2.457(4)	Cu(4)-N(7)	2.003(10)
Cu(4)-S(6)	2.251(4)	Cu(4)···Cu(5)	2.545(2)
Cu(4)-I(2)	2.583(2)	Cu(4)···Cu(6)	2.763(3)
Cu(5)-N(9)	1.995(10)	Cu(5)-N(11)	2.009(10)
Cu(5)-I(2)	2.569(2)	Cu(5)···Cu(6)	2.918(3)
Cu(6)-S(4)	2.289(3)	Cu(6)-S(6)	2.327(4)
Cu(6)-S(5)	2.365(3)	Cu(6)-S(7)	2.542(4)
Cu(7)-S(5A)	2.268(4)	Cu(7)-I(3)	2.540(2)
Cu(7)-I(5)	2.564(2)	Cu(7)···Cu(8)	2.831(3)
Cu(7)···Cu(9)	2.912(2)	Cu(8)-N(6)	2.001(11)
Cu(8)-N(10A)	2.023(11)	Cu(8)-I(3)	2.5480(18)
Cu(8)···Cu(9)	2.795(2)	Cu(9)-S(3)	2.302(4)
Cu(9)-S(5A)	2.320(4)	Cu(9)-S(8A)	2.386(3)
Cu(9)-S(8AA)	2.386(15)	Cu(9)-I(6)	2.6646(19)
Cu(10)-S(1A)	2.297(3)	Cu(10)-I(5)	2.564(2)
Cu(10)-I(4)	2.578(2)	Cu(10)···Cu(11)	2.709(3)
Cu(10)···Cu(12)	2.811(2)	Cu(11)-N(8)	1.969(11)
Cu(11)-N(2A)	2.003(10)	Cu(11)-I(4)	2.5467(17)
Cu(11)···Cu(12)	2.789(2)	Cu(12)-S(4)	2.313(4)
Cu(12)-S(8)	2.346(4)	Cu(12)-S(1A)	2.360(4)
Cu(12)-S(8A)	2.478(17)	Cu(12)-I(6)	2.6618(17)
Cu(13)-S(7)	2.226(4)	Cu(13)-I(7)	2.488(2)
Cu(13)-I(6)	2.676(2)	Cu(14)-S(2)	2.369(4)
Cu(14)-S(6)	2.370(3)	Cu(14)···Cu(15)	2.582(2)
Cu(14)-I(7)	2.6311(17)	Cu(14)-I(8)	2.682(2)
Cu(15)-N(4)	2.000(10)	Cu(15)-N(12)	2.015(11)
Cu(15)-I(8)	2.523(2)		
N(1)-Cu(1)-N(3)	120.2(4)	N(1)-Cu(1)-I(1)	117.5(3)

N(3)-Cu(1)-I(1)	118.2(3)	N(5)-Cu(2)-S(2)	120.4(3)
N(5)-Cu(2)-I(1)	111.8(3)	S(2)-Cu(2)-I(1)	127.71(11)
S(3)-Cu(3)-S(2)	123.80(13)	S(3)-Cu(3)-S(1)	108.31(14)
S(2)-Cu(3)-S(1)	119.10(13)	S(3)-Cu(3)-S(7)	106.34(12)
S(2)-Cu(3)-S(7)	100.49(13)	S(1)-Cu(3)-S(7)	92.16(12)
N(7)-Cu(4)-S(6)	119.3(3)	N(7)-Cu(4)-I(2)	109.0(3)
S(6)-Cu(4)-I(2)	131.59(10)	N(9)-Cu(5)-N(11)	120.6(4)
N(9)-Cu(5)-I(2)	113.4(3)	N(11)-Cu(5)-I(2)	122.1(3)
S(4)-Cu(6)-S(6)	125.07(14)	S(4)-Cu(6)-S(5)	106.85(12)
S(6)-Cu(6)-S(5)	119.79(12)	S(4)-Cu(6)-S(7)	110.34(13)
S(6)-Cu(6)-S(7)	93.30(13)	S(5)-Cu(6)-S(7)	95.41(13)
S(5A)-Cu(7)-I(3)	122.71(11)	S(5A)-Cu(7)-I(5)	112.66(11)
I(3)-Cu(7)-I(5)	116.73(7)	N(6)-Cu(8)-N(10A)	123.8(4)
N(6)-Cu(8)-I(3)	119.1(3)	N(10A)-Cu(8)-I(3)	113.6(3)
S(3)-Cu(9)-S(5A)	119.19(13)	S(3)-Cu(9)-S(8A)	93.25(12)
S(5A)-Cu(9)-S(8A)	107.43(14)	S(3)-Cu(9)-S(8AA)	114.2(4)
S(5A)-Cu(9)-S(8AA)	84.3(4)	S(8A)-Cu(9)-S(8AA)	25.4(4)
S(3)-Cu(9)-I(6)	116.02(11)	S(5A)-Cu(9)-I(6)	115.91(10)
S(8A)-Cu(9)-I(6)	99.21(11)	S(8AA)-Cu(9)-I(6)	100.9(4)
S(1A)-Cu(10)-I(5)	108.05(12)	S(1A)-Cu(10)-I(4)	126.02(12)
I(5)-Cu(10)-I(4)	118.21(7)	N(8A)-Cu(11)-N(2)	123.0(4)
N(8)-Cu(11)-I(4)	113.3(3)	N(2)A-Cu(11)-I(4)	119.9(3)
S(4)-Cu(12)-S(8)	107.16(13)	S(4)-Cu(12)-S(1A)	119.07(13)
S(8)-Cu(12)-S(1A)	91.25(13)	S(4) Cu(12)-S(8A)	86.8(4)
S(8)-Cu(12)-S(8A)	24.9(4)	S(1A)-Cu(12)-S(8A)	114.1(4)
S(4)-Cu(12)-I(6)	110.74(10)	S(8)-Cu(12)-I(6)	102.48(10)
S(1A)-Cu(12)-I(6)	121.20(10)	S(8A)-Cu(12)-I(6)	97.1(4)
S(7)-Cu(13)-I(7)	127.66(12)	S(7)-Cu(13)-I(6)	117.73(12)
I(7)-Cu(13)-I(6)	114.34(7)	S(2)-Cu(14)-S(6)	121.73(14)
S(2)-Cu(14)-I(7)	101.07(9)	S(6)-Cu(14)-I(7)	101.76(10)
S(2)-Cu(14)-I(8)	104.41(10)	S(6)-Cu(14)-I(8)	107.42(11)
I(7)-Cu(14)-I(8)	121.71(7)	N(4)-Cu(15)-N(12)	109.5(4)
N(4)-Cu(15)-I(8)	125.6(3)	N(12)-Cu(15)-I(8)	124.9(3)

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[a] Symmetry code: A: *x*, 1 - *y*, 5/2 + *z*.

Table S3 Selected bond lengths (Å) and angles (°) of **2**[a]

I(1A)-Cu(1)	2.5619(9)	I(1)-Cu(1)	2.5856(11)
Cu(1)-N(1)	2.057(4)	Cu(1)-N(3)	2.067(4)
S(1)-C(1)	1.770(6)	S(1)-C(13)	1.779(5)
I(1)-Cu(1)-I(1B)	115.27(3)	N(1)-Cu(1)-N(3)	93.95(18)
N(1)-Cu(1)-I(1B)	116.30(13)	I(1)-Cu(1)-I(1B)	115.27(3)
N(1)-Cu(1)-I(1)	106.27(12)	N(3)-Cu(1)-I(1)	112.12(13)
Cu(1A)-I(1)-Cu(1)	98.61(3)		

[a] Symmetry codes: A: x, $1/2 - y$, $1/2 + z$; B: x, $1/2- y$, $1/2 + z$.

Table S4 Selected bond lengths (Å) and angles (°) of **3**[a]

I(1)-Cu(1)	2.5593(16)	I(1A)-Cu(2)	2.7046(17)
I(1)-Cu(2)	2.7177(17)	I(2)-Cu(1)	2.5837(17)
I(2A)-Cu(2)	2.6919(15)	Cu(1)-N(1)	2.045(7)
Cu(1)-S(2)	2.402(3)	Cu(2)-N(3)	2.085(7)
Cu(2A)···Cu(2)	2.910(3)	Cu(1A)···Cu(2)	2.6866(18)
S(1)-C(1)	1.789(9)	S(1)-S(2)	2.037(3)
S(2)-C(13)	1.795(8)	Cu(1)-I(1)-Cu(2A)	61.31(5)
Cu(1)-I(1)-Cu(2)	80.24(5)	Cu(2A)-I(1)-Cu(2)	64.92(5)
Cu(1)-I(2)-Cu(2A)	61.19(4)	N(1)-Cu(1)-S(2)	87.6(2)
N(1)-Cu(1)-I(1)	120.4(2)	S(2)-Cu(1)-I(1)	114.59(7)
N(1)-Cu(1)-I(2)	110.7(2)	S(2)-Cu(1)-I(2)	102.00(8)
I(1)-Cu(1)-I(2)	116.56(5)	N(3)-Cu(2)-I(2A)	104.9(2)
N(3)-Cu(2)-I(1A)	114.3(2)	I(2A)-Cu(2)-I(1A)	108.32(5)
N(3)-Cu(2)-I(1)	107.2(2)	I(2A)-Cu(2)-I(1)	106.28(5)
I(1A)-Cu(2)-I(1)	115.08(5)		

[a] Symmetry code: A: $1 + x$, $1 - y$, $1 - z$.

Table S5 Selected bond lengths (Å) and angles (°) of **4**[a]

Cu(1)-N(1)	2.015(2)	Cu(1)-S(2)	2.2630(8)
Cu(1)-S(3A)	2.2635(8)	Cu(1)···Cu(2)	2.7802(5)
Cu(2)-N(3)	2.024(2)	Cu(2)-S(1)	2.2389(8)
Cu(2)-S(3)	2.2607(8)	Cu(3)-N(5)	2.033(2)
Cu(3)-S(1A)	2.2356(8)	Cu(3)-S(2)	2.2592(8)
Cu(2)···Cu(3)	3.0128(6)	Cu(3)···Cu(1A)	2.8085(6)
N(1)-Cu(1)-S(2)	126.27(7)	N(1)-Cu(1)-S(3A)	125.19(7)
S(2)-Cu(1)-S(3A)	104.45(3)	N(3)-Cu(2)-S(1)	128.99(7)
N(3)- Cu(2)-S(3)	117.66(7)	S(1)-Cu(2)-S(3)	109.86(3)
N(5)-Cu(3)-S(1A)	127.33(7)	N(5)-Cu(3)-S(2)	119.63(7)
S(1A)-Cu(3)-S(2)	109.52(3)		

[a] Symmetry code: x, 1 -y, z-1/2

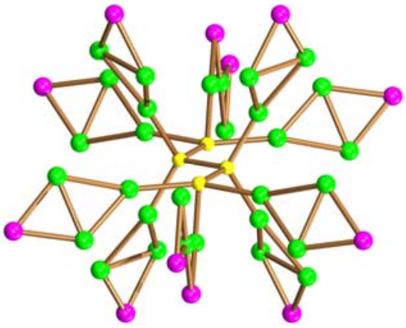


Fig. S1 View of the μ_{10}-S_4^{2-} ion connecting the eight [Cu_3I] and two [Cu_3I_2] fragments in **1**. Only one set of the disordered S_4^{2-} ion was depicted.

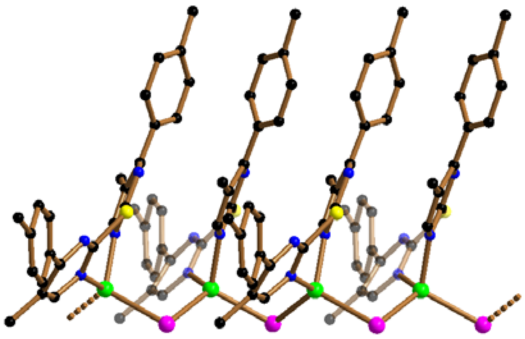


Fig. S2 View of a section of the 1D chain of **2** extending along the c axis. All hydrogen atoms are omitted for clarity.

Fig. S3 View of the molecular structure of **3**. All hydrogen atoms are omitted for clarity.

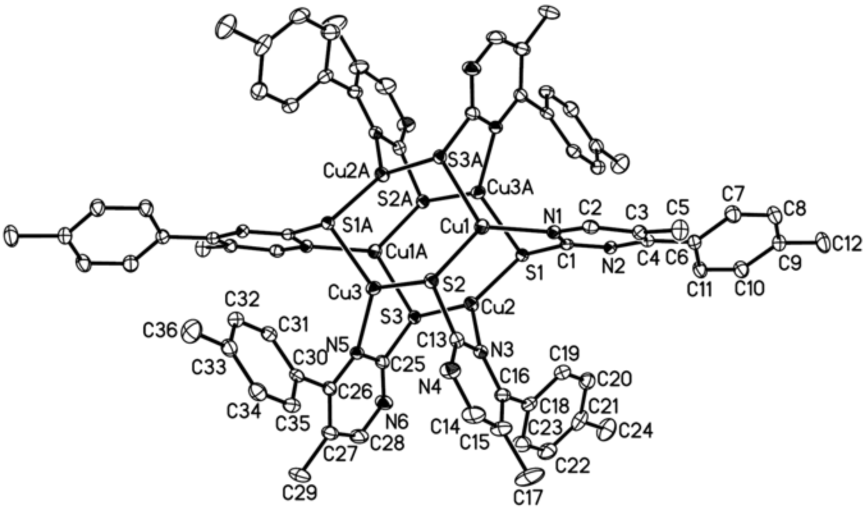
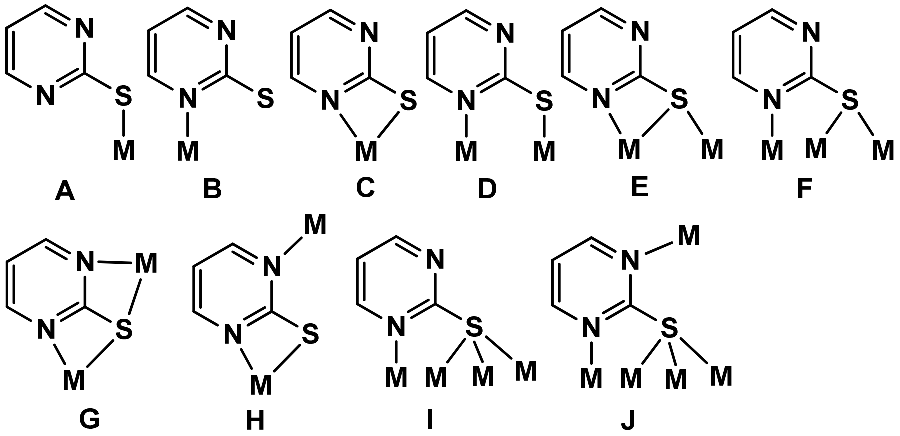


Fig. S4 Molecular structure of **4** with 30 % probability. All hydrogen atoms are omitted for clarity.



Scheme S1 Coordination modes of the pyrimidine-2-thiolate ligand

Fig. S5. The ^{1}H NMR Spectra of·mtpmtH

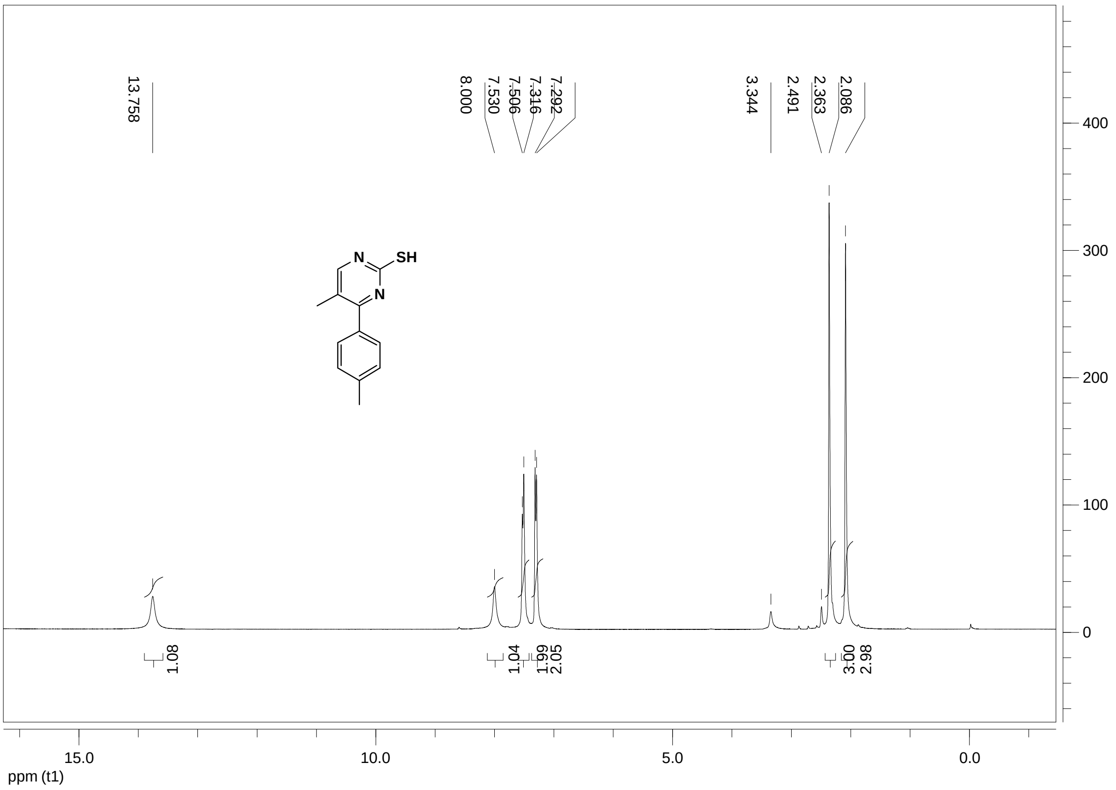


Fig. S6. The ^{13}C NMR Spectra of·mtpmtH

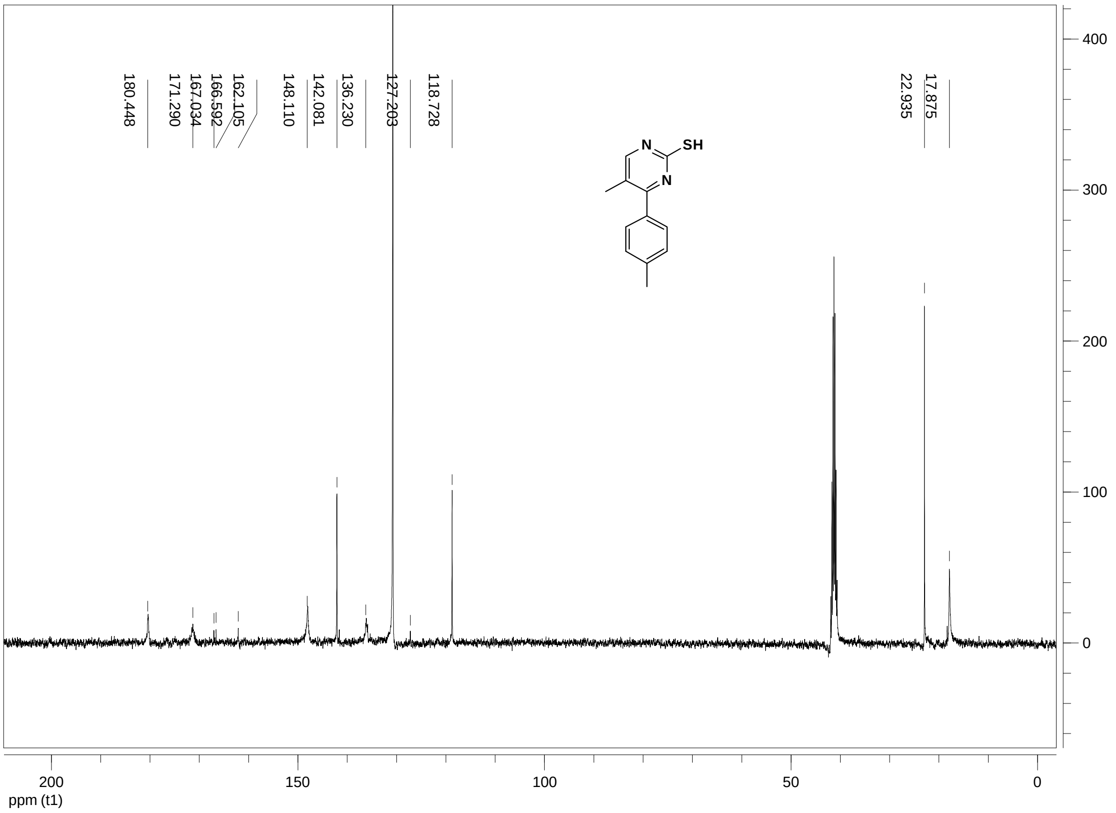


Fig. S7. The ^{1}H NMR Spectra of·bmptmds

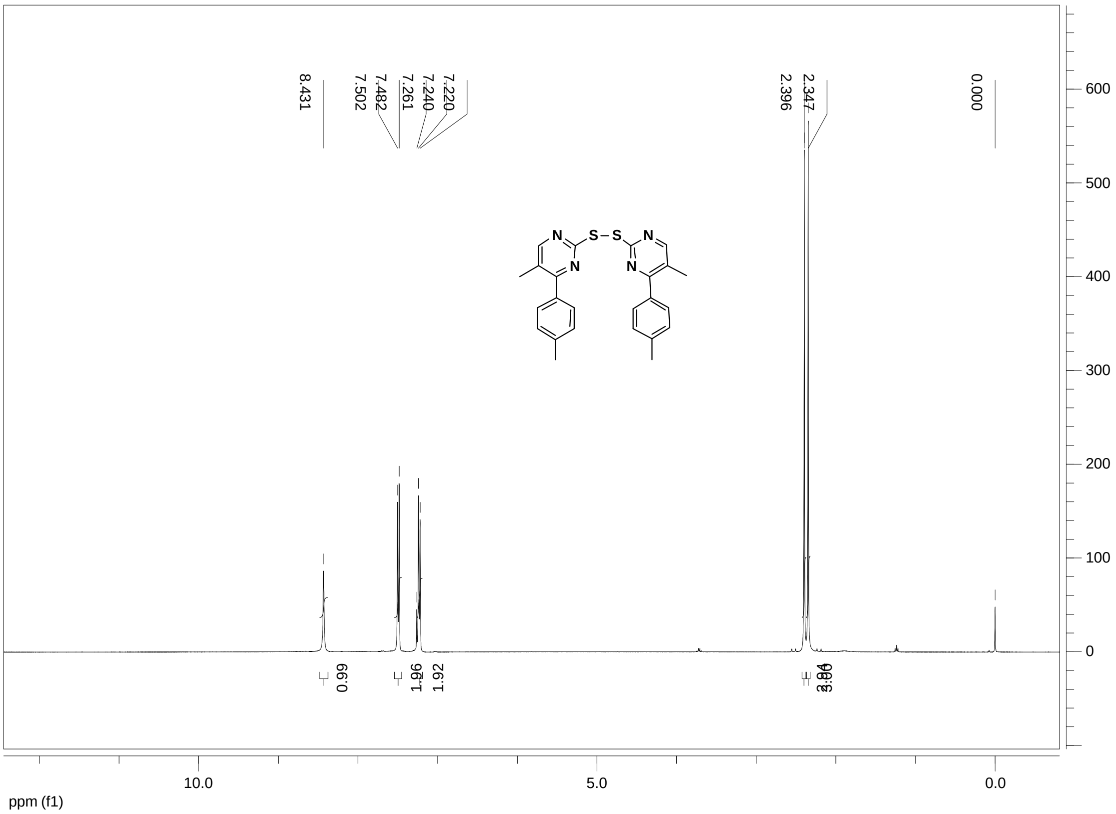


Fig. S8. The ^{13}C NMR Spectra of·bmptmds

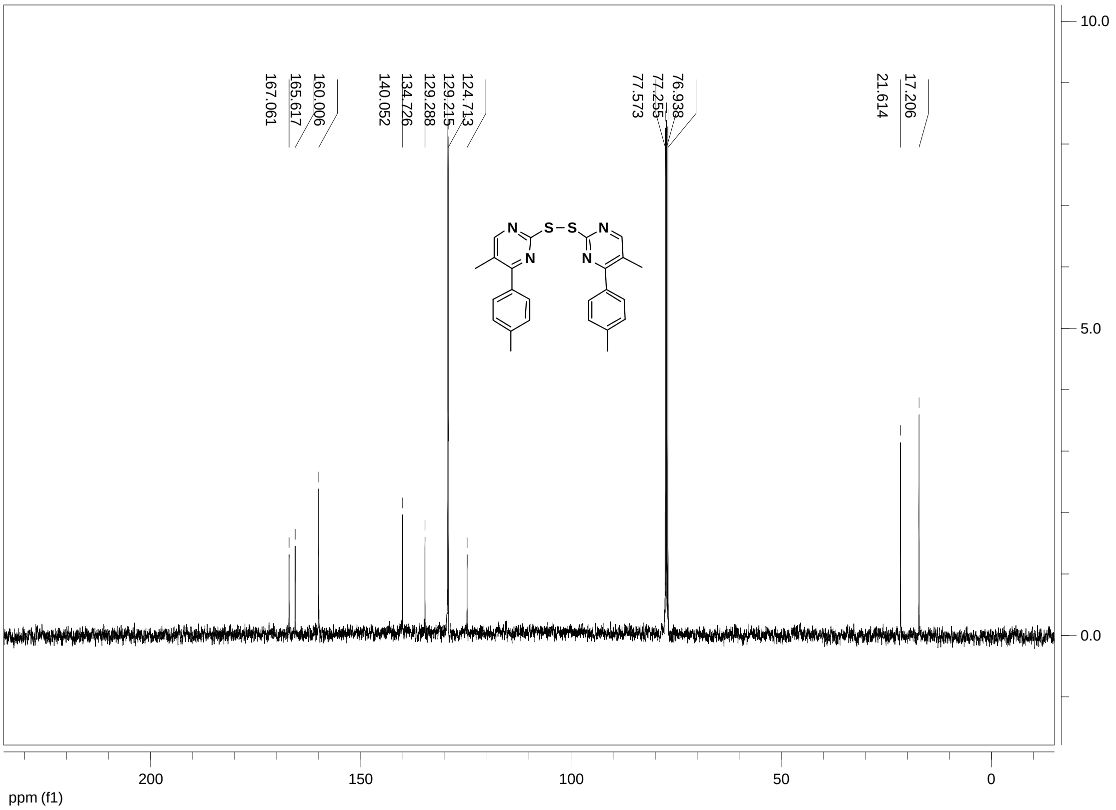


Fig. S9. The ^{1}H NMR Spectra of·bmptpms

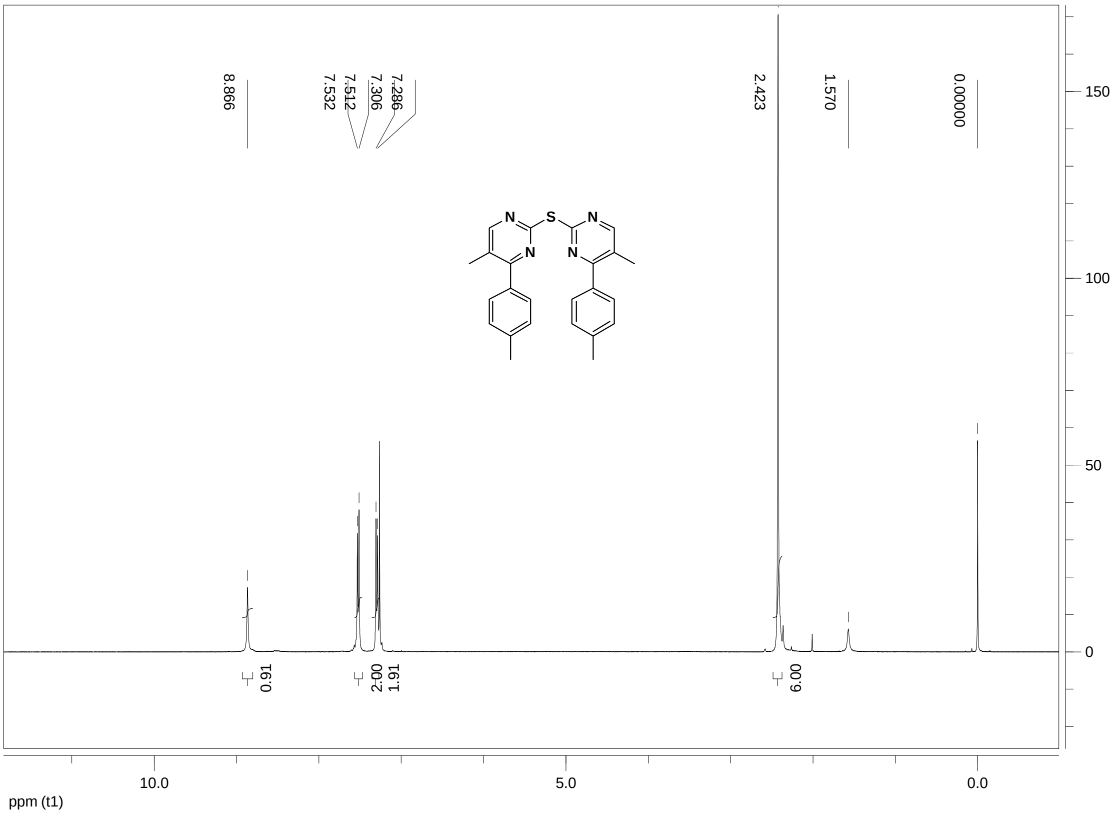


Fig. S10. The ^{13}C NMR Spectra of·bmptpms

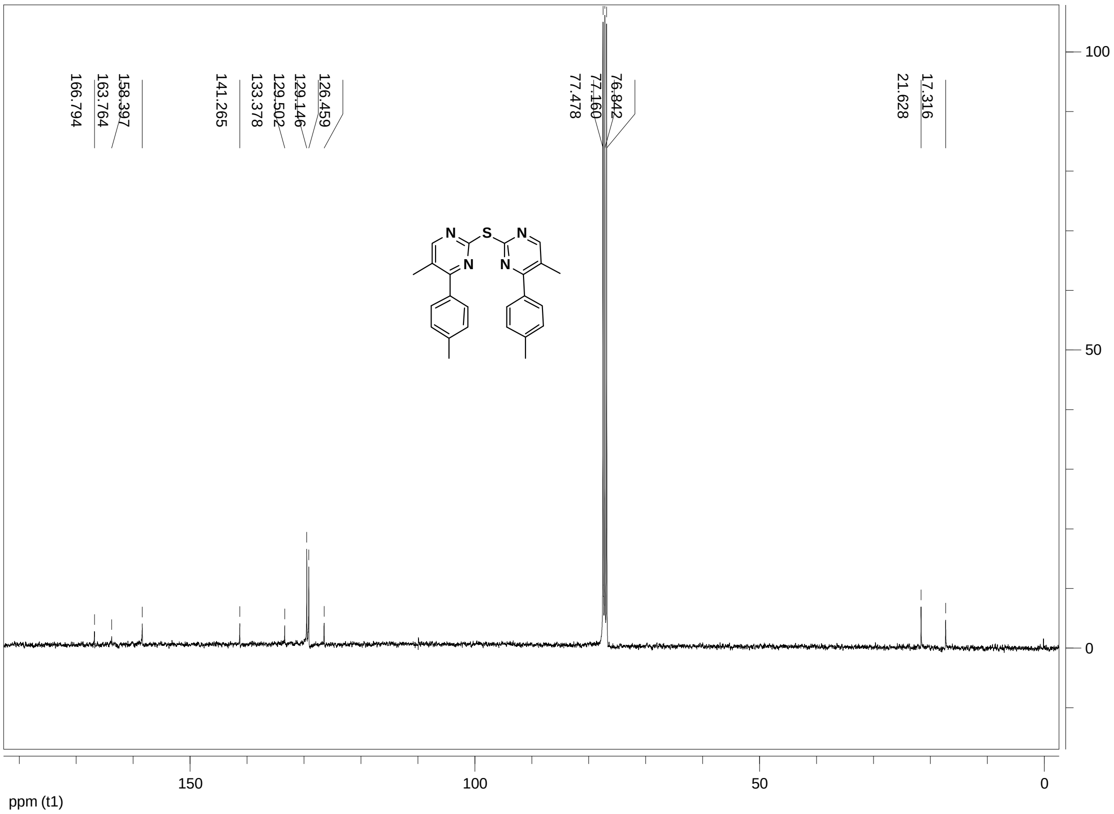
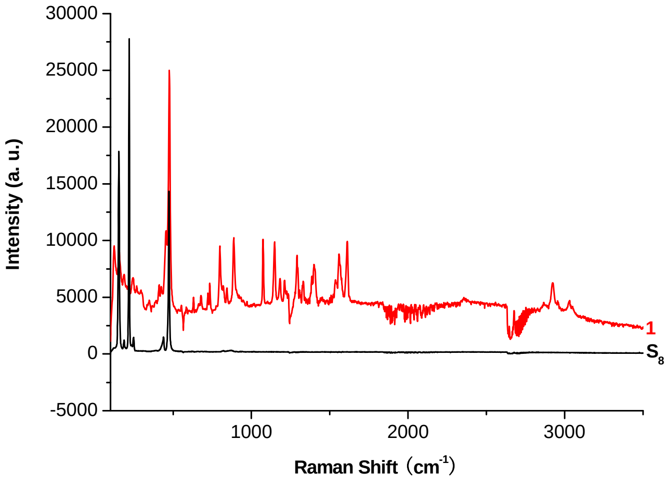


Fig. S11. The resonance Raman spectra of **1** and S_8



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