Electronic Supplementary Material (ESI) for ChemComm.


# SUPPORTING INFORMATION of SYNTHESES, STRUCTURES, AND COMPUTATIONS

## Lewis base-complexed magnesium dithiolenes

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## SUPPORTING INFORMATIONS of SYNTHESES

### Materials and Methods

**General.**

The syntheses of air-sensitive compounds were performed under purified argon using Schlenk techniques and an inert atmosphere drybox (M-Braun LabMaster SP). Chemicals were purchased from Aldrich and Strem and used as received. Toluene and THF were dried and distilled under argon from Na or Na/benzophenone prior to use. The anhydrous acetonitrile (from Aldrich) was dried and distilled from $CaH_2$, which was then stored over 3A molecular sieves. $^1H$ NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer. X-ray intensity data for **2**-**4** were collected at room temperature on a Bruker D8 Quest PHOTON 100 CMOS X-ray diffractometer system with Incoatec Microfocus Source (IμS) monochromated Mo Kα radiation (λ = 0.71073 Å, sealed tube) using phi and omega-scan technique.

Compound **2**: 100 ml of THF was added to a 250 mL Schlenk flask containing both [:C{[N(2,6-$Pr^i_2C_6H_3$)]$_2$CHCLi}] (4.000 g, 10.14 mmol) and elemental sulfur (1.318 g, 41.11 mmol) in an ice bath, giving a dark purple solution immediately. The resulting solution was allowed to be gradually warmed to room temperature and then stirred one more hour. Addition of 11 mL of mesityl magnesium bromide (1.0 M in THF) in the Schlenk flask immediately resulted in a brown color mixture, which was then stirred for 30 mins. After the volatile materials were removed in vacuo, the residue was extracted using 100 mL of toluene. After subsequently removing toluene from the filtrate in vacuo, the residue was rinsed using 100 mL of hexane, then dried in vacuo, and finally recrystallized in THF, giving colorless crystals of **2** (3.875 g, 48.1% yield). Mp: gradually decomposed (>110 °C) and melt (> 270 °C). $^1H$ NMR (400.14 MHz, THF-$d_8$): $\delta$ 1.24 [d, 24H, CH(C*H*$_3$)$_2$], 1.77 (THF), 2.94 [m, 4H, C*H*(CH$_3$)$_2$], 3.62 (THF), 7.08 [d, 4H, Ar-*H*], 7.19 [t, 2H, Ar-*H*]. $^{13}C\{^1H\}$ NMR (100.63 MHz, THF-$d_8$): $\delta$ 24.63, 24.74 [CH(*C*H$_3$)$_2$], 26.55 (THF), 29.85 [*C*H(CH$_3$)$_2$], 68.39 (THF), 123.34 [N*CC*N], 127.1, 128.4, 137.8, 148.3 [Ar-*C*], 160.7 [N*C*(=S)N]. Crystal data for **2**: $C_{43}H_{66}MgN_2O_4S_3$, fw = 795.46, orthorhombic, $P2_12_12$, $a$ = 13.3056(6) Å, $b$ = 13.8070(7) Å, $c$ = 12.8135(6) Å, $V$ = 2353.97(19) Å$^3$, $Z$ = 2, R1 = 0.0519 for 4111 data ($I > 2\sigma(I)$), w$R_2$ = 0.1372 (all data).

Compound **3**: In the glovebox, 8 mL of toluene was added to a Schlenk tube containing **2** (0.400 g, 0.50 mmol) and [:C{N($Pr^i$)CMe}$_2$] (0.182 g, 1.01 mmol) at room temperature. The resulting mixture was stirred under ambient temperature over 2h, giving a slurry containing colorless crystalline solid. The slurry was heated to get a clear solution and then kept stationary under ambient temperature over two days, giving

X-ray quality colorless crystals of **3**. The $^{1}$H NMR reaction shows that **3** is synthesized in a quantitative yield. Mp: gradually decomposed (>255 °C) and melt at 293 °C. $^{1}$H NMR (400.14 MHz, $C_6D_6$): $\delta$ 1.21 [d, 24H, CH(C$H_3$)$_2$, NHC], 1.56 (s, 12H, C$H_3$CCC$H_3$), 1.58 [d, 12H, CH(C$H_3$)$_2$, dithiolene], 1.68 [d, 12H, CH(C$H_3$)$_2$, dithiolene], 3.48 [m, 4H, C$H$(CH$_3$)$_2$, dithiolene], 4.90 [m, 4H, C$H$(CH$_3$)$_2$, NHC], 7.26-7.36 [m, 6H, Ar-$H$]. $^{13}$C{$^{1}$H} NMR (100.63 MHz, $C_6D_6$): $\delta$ 10.2 ($C$H$_3$CC$C$H$_3$) 23.0 [CH($C$H$_3$)$_2$, NHC], 25.05, 25.14 [CH($C$H$_3$)$_2$, dithiolene], 29.8 [$C$H(CH$_3$)$_2$, dithiolene], 52.9 [$C$H(CH$_3$)$_2$, NHC], 123.8 (CH$_3$$CC$CH$_3$), 125.3, [S(N)$CC$(N)S], 126.0, 137.3, 148.3 [Ar-$C$], 162.0 [N$C$(=S)N], 179.8 [NCN]. Crystal data for **3·toluene**: $C_{56}H_{82}MgN_6S_3$, fw = 959.76, monoclinic, $P2_1/n$, $a$ = 15.5287(7) Å, $b$ = 20.6762(10) Å, $c$ = 18.7622(9) Å, $\beta$ =93.047(2)°, $V$ = 6015.5(5) Å$^3$, $Z$ = 4, R1 = 0.0628 for 6903 data ($I > 2\sigma(I)$), wR$_2$ = 0.1597 (all data).

Compound **4**: 6 mL of the mixed solvent [THF (3 mL)/MeCN (3 mL)] was added to a Schlenk tube containing **3** (0.400 g, 0.50 mmol) at room temperature, which was then stirred overnight. After removing the volatiles in vacuo, the residue was dissolved in $CH_3CN$ to make a saturate solution. This solution was then kept stationary at 18 °C over three days, giving **4** as yellow crystals. Mp: gradually decomposed (>108 °C) and gradually melt (> 240 °C). $^{1}$H NMR (400.14 MHz, $CD_3CN$): $\delta$ 1.20 [d, 24H, CH(C$H_3$)$_2$, dithiolene], 1.22 [d, 24H, CH(C$H_3$)$_2$, dithiolene], 1.47 [d, 24H, CH(C$H_3$)$_2$, imidazolium], 1.81 (m, THF), 2.21 (s, 12H, C$H_3$CCC$H_3$, imidazolium) 2.78 [m, 8H, C$H$(CH$_3$)$_2$, dithiolene], 3.65 (m, THF), 4.46 [m, 4H, C$H$(CH$_3$)$_2$, imidazolium], 7.20 [d, 8H, Ar-$H$], 7.34 [t, 4H, Ar-$H$], 8.36 [s, 2H, NC($H$)N]. $^{13}$C{$^{1}$H} NMR (100.63 MHz, $CD_3CN$): $\delta$ 9.01 ($C$H$_3$CC$C$H$_3$) 23.14, 24.55, 24.67 [CH($C$H$_3$)$_2$], 26.61 (THF), 30.09 [$C$H(CH$_3$)$_2$, dithiolene], 51.58 [$C$H(CH$_3$)$_2$, imidazolium], 68.66 (THF), 124.49, [S(N)$CC$(N)S], 128.0 (CH$_3$$CC$CH$_3$), 130.6 [NC(H)N], 127.4, 129.7, 137.4, 148.8 [Ar-$C$], 160.4 [N$C$(=S)N]. Crystal data for **4**: $C_{80}H_{118}MgN_8OS_6$, fw =1424.49, monoclinic, $P2_1/n$, $a$ = 14.5228(12) Å, $b$ = 16.6577(13) Å, $c$ = 18.4634(14) Å, $\beta$ = 92.673(2)°, $V$ = 4461.7(6) Å$^3$, $Z$ = 2, R1 = 0.0828 for 5798 data ($I > 2\sigma(I)$), wR$_2$ = 0.2429 (all data).

Dimesityl disulphide: $^{1}$H NMR (400.14 MHz, $C_6D_6$): $\delta$ 2.00 [s, 6H, $CH_3$], 2.31 [s, 12H, $CH_3$], 6.65 [s, 4H, Ar-H]. The cell constants of the single-crystal of dimesityl disulphide (*i.e.*, a = 6.4974(8) Å, b = 17.579(2) Å, c = 14.930(2) Å, β = 97.228(3)°, volume = 1691.6(4) Å$^3$) match those for Mes-S-S-Mes with the CCDC number of 859846 (private communication, by A. L. Rheingold).

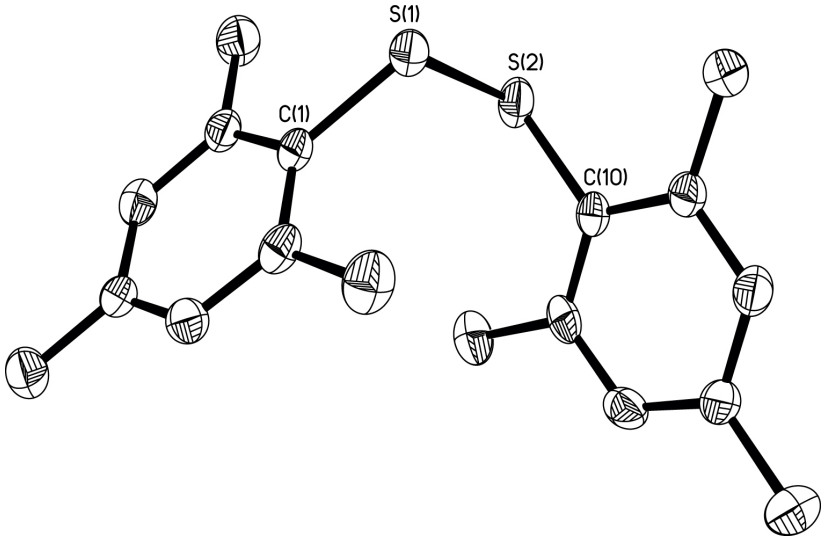


Figure S1. Molecular structure of Dimesityl disulphide. (thermal ellipsoids represent 30% probability; hydrogen atoms on carbons are omitted for clarity). Selected bond distances (Å) and angles (deg): S(1)–S(2) 2.052(2), S(1)–C(1) 1.769(6); C(1)–S(1)–S(2) 103.7(2).

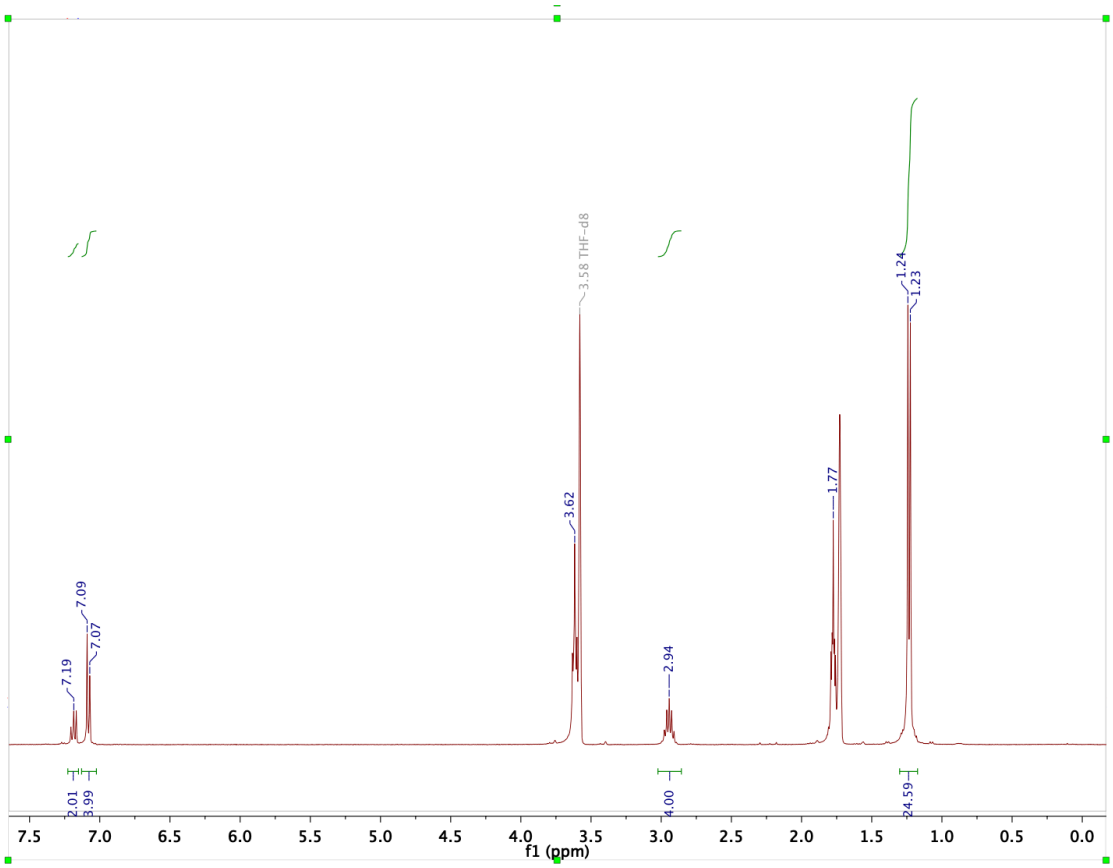


Figure S2. The $^{1}H$ NMR spectrum of compound **2** in THF-$d_8$

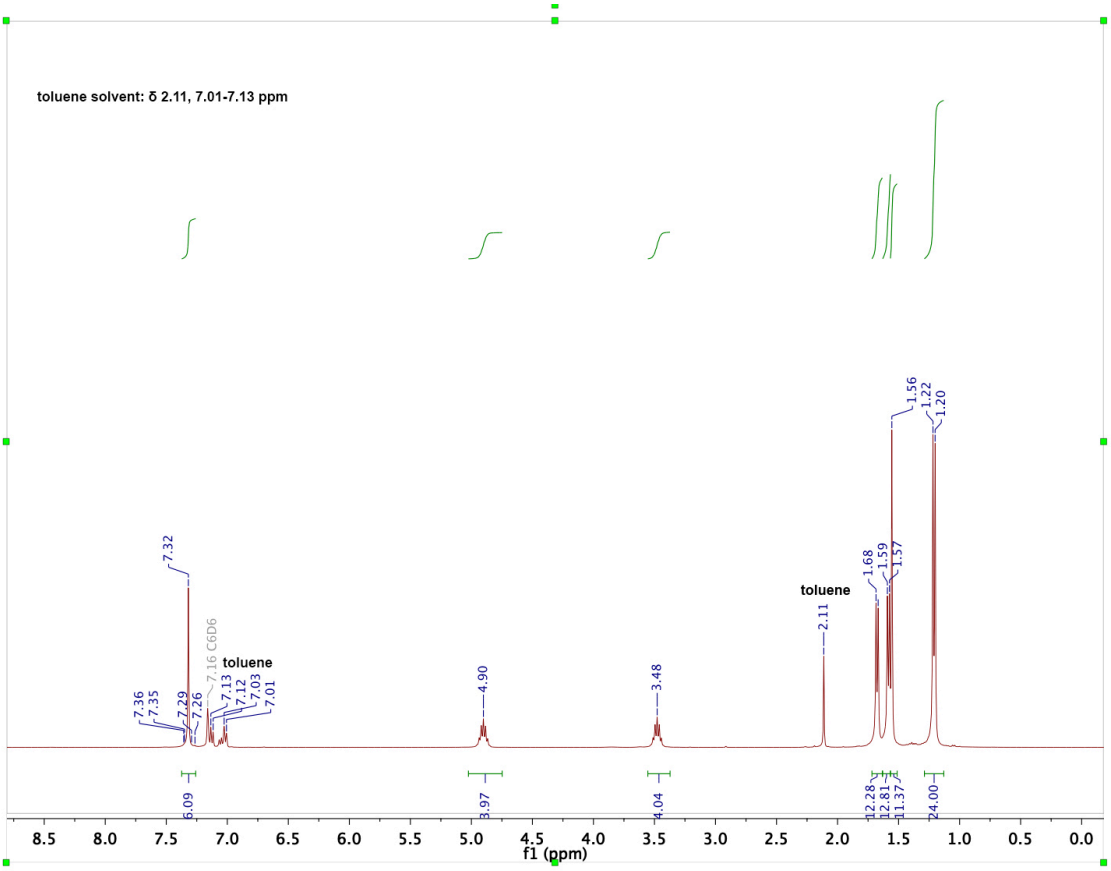


Figure S3. The $^{1}H$ NMR spectrum of compound **3** in $C_6D_6$.

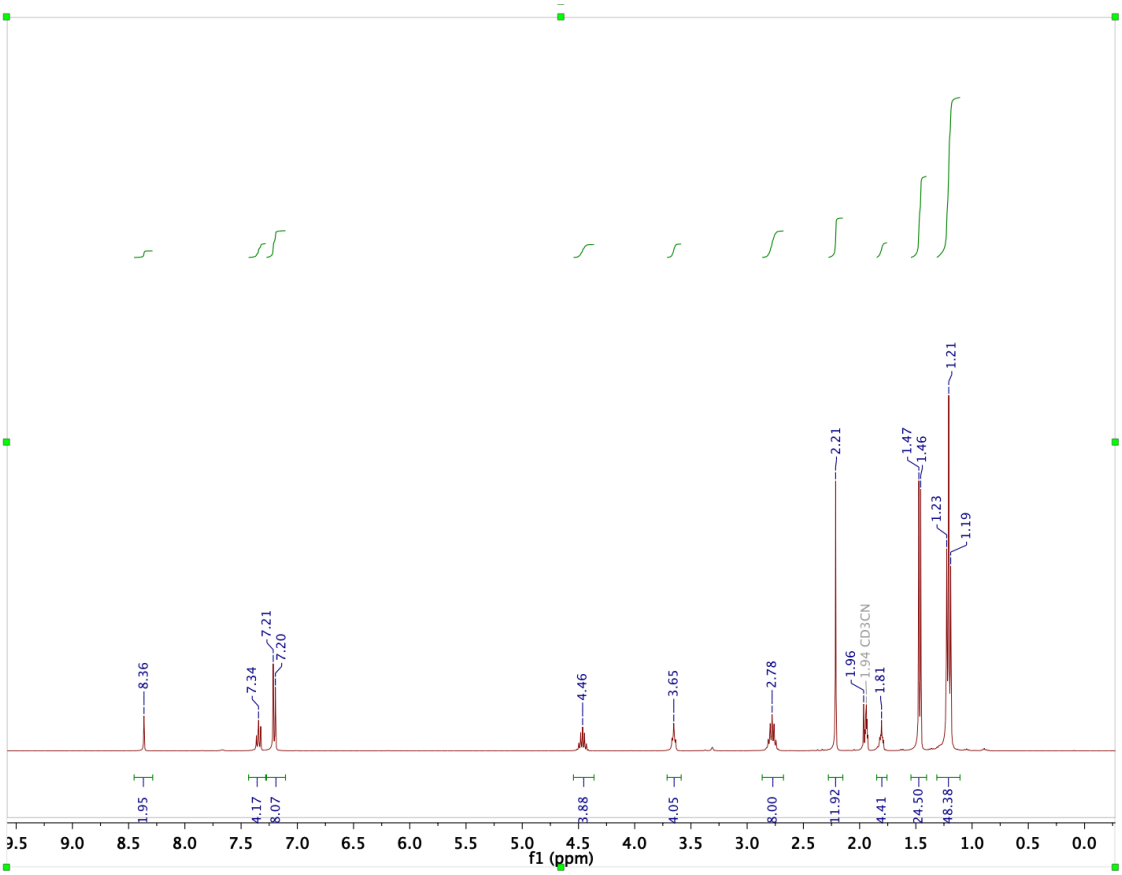


Figure S4. The $^{1}H$ NMR spectrum of compound **4** in $CD_3CN$.

## SUPPORTING INFORMATIONS of COMPUTATIONS

All computations employed the Gaussian09 programs:
For Gaussian 09: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09*, revision D.01; Gaussian, Inc., Wallingford CT, 2013.

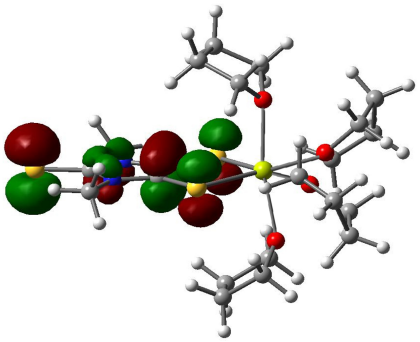


**Fig. S5** HOMO of the simplified **2-Me** model.

**Table S1.** Coordinates of the B3LYP/6-311G** optimized geometry of **2-Me**.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 12 | 0 | 0.911182 | -0.007145 | -0.008040 |
| 2 | 16 | 0 | -6.040421 | -0.013429 | 0.014800 |
| 3 | 16 | 0 | -0.806881 | -1.160786 | 1.402850 |
| 4 | 7 | 0 | -3.501293 | -0.701783 | 0.863602 |
| 5 | 6 | 0 | -4.341603 | -0.041871 | 0.006123 |
| 6 | 6 | 0 | -2.160737 | -0.471521 | 0.514195 |
| 7 | 6 | 0 | -3.943123 | -1.531000 | 1.967802 |
| 8 | 8 | 0 | 2.552680 | 1.033919 | -1.076278 |
| 9 | 6 | 0 | 2.495873 | 1.387366 | -2.494257 |
| 10 | 1 | 0 | 1.518579 | 1.834162 | -2.681794 |
| 11 | 1 | 0 | 2.587884 | 0.472264 | -3.079718 |
| 12 | 6 | 0 | 3.647356 | 2.368675 | -2.731970 |
| 13 | 1 | 0 | 4.540181 | 1.840805 | -3.078407 |
| 14 | 1 | 0 | 3.390876 | 3.121358 | -3.478585 |
| 15 | 6 | 0 | 3.890063 | 2.960475 | -1.336051 |
| 16 | 1 | 0 | 3.168681 | 3.752565 | -1.120527 |
| 17 | 1 | 0 | 4.894798 | 3.368360 | -1.212181 |
| 18 | 6 | 0 | 3.640795 | 1.754441 | -0.440437 |
| 19 | 1 | 0 | 4.522821 | 1.105910 | -0.404321 |
| 20 | 1 | 0 | 3.325113 | 1.991751 | 0.573115 |
| 21 | 8 | 0 | 0.995793 | 1.818920 | 1.367654 |
| 22 | 6 | 0 | 0.729457 | 3.144885 | 0.845156 |
| 23 | 1 | 0 | 0.699048 | 3.064411 | -0.238714 |
| 24 | 1 | 0 | 1.547500 | 3.806397 | 1.158161 |
| 25 | 6 | 0 | -0.614332 | 3.578732 | 1.450226 |
| 26 | 1 | 0 | -0.582154 | 4.625518 | 1.759110 |
| 27 | 1 | 0 | -1.412394 | 3.461286 | 0.717742 |
| 28 | 6 | 0 | -0.822448 | 2.616794 | 2.648545 |
| 29 | 1 | 0 | -1.032069 | 3.142643 | 3.581847 |
| 30 | 1 | 0 | -1.644761 | 1.930220 | 2.448057 |
| 31 | 6 | 0 | 0.487918 | 1.832994 | 2.725170 |
| 32 | 1 | 0 | 1.229414 | 2.330506 | 3.364359 |
| 33 | 1 | 0 | 0.346447 | 0.799621 | 3.031645 |
| 34 | 16 | 0 | -0.825762 | 1.017851 | -1.499929 |
| 35 | 7 | 0 | -3.523714 | 0.604208 | -0.878389 |
| 36 | 6 | 0 | -2.171631 | 0.350998 | -0.581506 |
| 37 | 6 | 0 | -4.023852 | 1.424005 | -1.966657 |
| 38 | 8 | 0 | 2.578055 | -0.920492 | 1.134706 |
| 39 | 6 | 0 | 2.501920 | -1.220940 | 2.564212 |
| 40 | 1 | 0 | 1.534007 | -1.688258 | 2.748179 |
| 41 | 1 | 0 | 2.553952 | -0.281544 | 3.115721 |
| 42 | 6 | 0 | 3.677998 | -2.156506 | 2.864864 |
| 43 | 1 | 0 | 4.538257 | -1.590575 | 3.232716 |
| 44 | 1 | 0 | 3.420034 | -2.902372 | 3.617723 |
| 45 | 6 | 0 | 3.995240 | -2.769150 | 1.492757 |
| 46 | 1 | 0 | 3.315944 | -3.595860 | 1.270552 |
| 47 | 1 | 0 | 5.020084 | -3.136276 | 1.414341 |
| 48 | 6 | 0 | 3.727120 | -1.595506 | 0.560855 |
| 49 | 1 | 0 | 4.577428 | -0.904610 | 0.548715 |
| 50 | 1 | 0 | 3.467818 | -1.866690 | -0.459989 |
| 51 | 8 | 0 | 1.197817 | -1.814899 | -1.381208 |
| 52 | 6 | 0 | 0.978587 | -3.157023 | -0.879428 |
| 53 | 1 | 0 | 0.897876 | -3.089055 | 0.202806 |
| 54 | 1 | 0 | 1.842164 | -3.773210 | -1.161664 |
| 55 | 6 | 0 | -0.313300 | -3.650032 | -1.545564 |
| 56 | 1 | 0 | -0.230488 | -4.701111 | -1.829270 |

| | | | | | |
|---|---|---|---|---|---|
| 57 | 1 | 0 | -1.151078 | -3.543733 | -0.857139 |
| 58 | 6 | 0 | -0.490537 | -2.717421 | -2.772133 |
| 59 | 1 | 0 | -0.593134 | -3.267056 | -3.709683 |
| 60 | 1 | 0 | -1.368302 | -2.083606 | -2.646889 |
| 61 | 6 | 0 | 0.769640 | -1.850081 | -2.765407 |
| 62 | 1 | 0 | 1.577758 | -2.291355 | -3.363550 |
| 63 | 1 | 0 | 0.577525 | -0.825833 | -3.074558 |
| 64 | 1 | 0 | -4.648023 | 0.824861 | -2.632996 |
| 65 | 1 | 0 | -4.635749 | 2.238278 | -1.573117 |
| 66 | 1 | 0 | -3.169100 | 1.822702 | -2.509406 |
| 67 | 1 | 0 | -3.600957 | -2.559650 | 1.832175 |
| 68 | 1 | 0 | -3.542190 | -1.152635 | 2.910719 |
| 69 | 1 | 0 | -5.031106 | -1.499049 | 1.983303 |

**Table S2.** Coordinates of the B3LYP/6-311G** optimized geometry of **3-Me**.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 12 | 0 | 0.030033 | -0.000005 | 0.000000 |
| 2 | 16 | 0 | -6.828597 | -0.000038 | -0.000004 |
| 3 | 16 | 0 | -1.601369 | -0.584956 | 1.723887 |
| 4 | 16 | 0 | -1.601373 | 0.584916 | -1.723894 |
| 5 | 7 | 0 | -4.294631 | -0.348941 | 1.030961 |
| 6 | 7 | 0 | -4.294632 | 0.348884 | -1.030968 |
| 7 | 6 | 0 | -5.126876 | -0.000032 | -0.000004 |
| 8 | 6 | 0 | -2.951111 | -0.218920 | 0.649031 |
| 9 | 6 | 0 | -2.951113 | 0.218872 | -0.649036 |
| 10 | 7 | 0 | 2.275264 | -2.131691 | 0.929329 |
| 11 | 7 | 0 | 1.275181 | -3.035403 | -0.746152 |
| 12 | 6 | 0 | 1.360885 | -1.871022 | -0.049903 |
| 13 | 6 | 0 | 2.741625 | -3.448807 | 0.860686 |
| 14 | 6 | 0 | 2.106194 | -4.016645 | -0.203283 |
| 15 | 6 | 0 | 0.363461 | -3.301295 | -1.891280 |
| 16 | 1 | 0 | 0.668588 | -4.281176 | -2.259430 |
| 17 | 6 | 0 | -1.092922 | -3.402165 | -1.428758 |
| 18 | 1 | 0 | -1.198502 | -4.142423 | -0.632247 |
| 19 | 1 | 0 | -1.469138 | -2.447408 | -1.060753 |
| 20 | 1 | 0 | -1.721742 | -3.707565 | -2.268907 |
| 21 | 6 | 0 | 0.571497 | -2.301714 | -3.029527 |
| 22 | 1 | 0 | 1.628953 | -2.230668 | -3.298472 |
| 23 | 1 | 0 | 0.017594 | -2.639921 | -3.908877 |
| 24 | 1 | 0 | 0.185310 | -1.315364 | -2.770192 |
| 25 | 6 | 0 | 2.224601 | -5.402174 | -0.749409 |
| 26 | 1 | 0 | 2.916793 | -5.986089 | -0.142971 |
| 27 | 1 | 0 | 2.605417 | -5.409294 | -1.775485 |
| 28 | 1 | 0 | 1.264563 | -5.926367 | -0.746852 |
| 29 | 6 | 0 | 3.758233 | -4.065388 | 1.767594 |
| 30 | 1 | 0 | 3.800213 | -5.140689 | 1.593230 |
| 31 | 1 | 0 | 3.518250 | -3.920501 | 2.822440 |
| 32 | 1 | 0 | 4.762597 | -3.667868 | 1.595860 |
| 33 | 6 | 0 | 2.582065 | -1.134629 | 1.981812 |
| 34 | 1 | 0 | 2.117504 | -0.218699 | 1.613603 |
| 35 | 6 | 0 | 4.080777 | -0.842033 | 2.111928 |
| 36 | 1 | 0 | 4.215393 | 0.058300 | 2.716309 |
| 37 | 1 | 0 | 4.626016 | -1.648687 | 2.603228 |
| 38 | 1 | 0 | 4.531813 | -0.662690 | 1.133313 |
| 39 | 6 | 0 | 1.918799 | -1.497222 | 3.315224 |
| 40 | 1 | 0 | 2.041117 | -0.671374 | 4.020322 |
| 41 | 1 | 0 | 0.850436 | -1.674961 | 3.180273 |
| 42 | 1 | 0 | 2.363723 | -2.386185 | 3.767360 |
| 43 | 7 | 0 | 2.275230 | 2.131726 | -0.929320 |
| 44 | 7 | 0 | 1.275113 | 3.035421 | 0.746149 |
| 45 | 6 | 0 | 1.360850 | 1.871039 | 0.049906 |
| 46 | 6 | 0 | 2.741560 | 3.448854 | -0.860679 |
| 47 | 6 | 0 | 2.106106 | 4.016680 | 0.203283 |
| 48 | 6 | 0 | 0.363380 | 3.301296 | 1.891271 |
| 49 | 1 | 0 | 0.668481 | 4.281185 | 2.259419 |

| | | | | | |
|---|---|---|---|---|---|
| 50 | 6 | 0 | -1.093003 | 3.402130 | 1.428740 |
| 51 | 1 | 0 | -1.721833 | 3.707530 | 2.268882 |
| 52 | 1 | 0 | -1.198594 | 4.142374 | 0.632217 |
| 53 | 1 | 0 | -1.469199 | 2.447361 | 1.060748 |
| 54 | 6 | 0 | 0.571432 | 2.301723 | 3.029523 |
| 55 | 1 | 0 | 0.017537 | 2.639936 | 3.908877 |
| 56 | 1 | 0 | 0.185246 | 1.315370 | 2.770199 |
| 57 | 1 | 0 | 1.628891 | 2.230683 | 3.298458 |
| 58 | 6 | 0 | 2.224472 | 5.402217 | 0.749399 |
| 59 | 1 | 0 | 2.605289 | 5.409357 | 1.775474 |
| 60 | 1 | 0 | 1.264418 | 5.926380 | 0.746839 |
| 61 | 1 | 0 | 2.916645 | 5.986148 | 0.142955 |
| 62 | 6 | 0 | 3.758165 | 4.065450 | -1.767578 |
| 63 | 1 | 0 | 3.800128 | 5.140752 | -1.593214 |
| 64 | 1 | 0 | 3.518195 | 3.920559 | -2.822426 |
| 65 | 1 | 0 | 4.762534 | 3.667945 | -1.595833 |
| 66 | 6 | 0 | 2.582062 | 1.134668 | -1.981796 |
| 67 | 1 | 0 | 2.117514 | 0.218730 | -1.613591 |
| 68 | 6 | 0 | 1.918804 | 1.497242 | -3.315218 |
| 69 | 1 | 0 | 2.041132 | 0.671386 | -4.020305 |
| 70 | 1 | 0 | 0.850439 | 1.674976 | -3.180277 |
| 71 | 1 | 0 | 2.363727 | 2.386202 | -3.767362 |
| 72 | 6 | 0 | 4.080782 | 0.842102 | -2.111897 |
| 73 | 1 | 0 | 4.215422 | -0.058238 | -2.716262 |
| 74 | 1 | 0 | 4.626007 | 1.648761 | -2.603205 |
| 75 | 1 | 0 | 4.531815 | 0.662784 | -1.133276 |
| 76 | 6 | 0 | -4.744139 | 0.796593 | -2.335319 |
| 77 | 1 | 0 | -4.367822 | 1.801286 | -2.540236 |
| 78 | 1 | 0 | -4.381376 | 0.121164 | -3.113403 |
| 79 | 1 | 0 | -5.832321 | 0.799958 | -2.321183 |
| 80 | 6 | 0 | -4.744136 | -0.796658 | 2.335310 |
| 81 | 1 | 0 | -4.367808 | -1.801347 | 2.540225 |
| 82 | 1 | 0 | -4.381384 | -0.121226 | 3.113397 |
| 83 | 1 | 0 | -5.832317 | -0.800035 | 2.321172 |

**Table S3.** Coordinates of the B3LYP/6-311G** optimized geometry of $[\mathbf{4}]^{2-}$ (in $C_2$ symmetry).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 16 | 0 | 7.065427 | 0.054637 | -0.589304 |
| 2 | 16 | 0 | 1.882151 | -1.787368 | 0.219572 |
| 3 | 16 | 0 | 1.805359 | 1.762030 | -0.033638 |
| 4 | 16 | 0 | -7.065426 | -0.054634 | -0.589305 |
| 5 | 16 | 0 | -1.805360 | -1.762032 | -0.033640 |
| 6 | 16 | 0 | -1.882150 | 1.787365 | 0.219575 |
| 7 | 7 | 0 | 4.571090 | -1.062966 | -0.170870 |
| 8 | 7 | 0 | 4.522571 | 1.106209 | -0.321181 |
| 9 | 7 | 0 | -4.522571 | -1.106208 | -0.321182 |
| 10 | 7 | 0 | -4.571088 | 1.062967 | -0.170868 |
| 11 | 6 | 0 | 5.372961 | 0.032295 | -0.360817 |
| 12 | 6 | 0 | 3.210775 | -0.679474 | -0.011167 |
| 13 | 6 | 0 | 3.180956 | 0.688164 | -0.105679 |
| 14 | 6 | 0 | 4.934543 | 2.468844 | -0.492073 |
| 15 | 6 | 0 | 4.936823 | 3.026268 | -1.782227 |
| 16 | 6 | 0 | 5.331512 | 4.359449 | -1.921849 |
| 17 | 1 | 0 | 5.339467 | 4.809949 | -2.908755 |
| 18 | 6 | 0 | 5.706970 | 5.116876 | -0.819918 |
| 19 | 1 | 0 | 6.008051 | 6.152316 | -0.948341 |
| 20 | 6 | 0 | 5.688596 | 4.549385 | 0.447745 |
| 21 | 1 | 0 | 5.975542 | 5.147609 | 1.306346 |
| 22 | 6 | 0 | 5.300633 | 3.220684 | 0.637301 |
| 23 | 6 | 0 | 5.278256 | 2.631426 | 2.041254 |
| 24 | 1 | 0 | 4.943529 | 1.597303 | 1.955497 |
| 25 | 6 | 0 | 4.265134 | 3.363346 | 2.940271 |
| 26 | 1 | 0 | 3.269052 | 3.336670 | 2.493215 |
| 27 | 1 | 0 | 4.217284 | 2.885398 | 3.925089 |
| 28 | 1 | 0 | 4.547129 | 4.410944 | 3.092718 |
| 29 | 6 | 0 | 6.684993 | 2.607480 | 2.666119 |
| 30 | 1 | 0 | 7.375352 | 2.050686 | 2.029069 |
| 31 | 1 | 0 | 7.079107 | 3.620563 | 2.803980 |
| 32 | 1 | 0 | 6.655863 | 2.124823 | 3.649220 |
| 33 | 6 | 0 | 4.525995 | 2.225892 | -3.010901 |
| 34 | 1 | 0 | 4.245527 | 1.227884 | -2.673471 |
| 35 | 6 | 0 | 3.288542 | 2.834616 | -3.694900 |
| 36 | 1 | 0 | 2.979099 | 2.209840 | -4.539317 |
| 37 | 1 | 0 | 2.454589 | 2.896838 | -2.993123 |
| 38 | 1 | 0 | 3.496098 | 3.838895 | -4.080994 |
| 39 | 6 | 0 | 5.701676 | 2.065050 | -3.992334 |
| 40 | 1 | 0 | 5.405768 | 1.433294 | -4.836667 |
| 41 | 1 | 0 | 6.020989 | 3.032518 | -4.395999 |
| 42 | 1 | 0 | 6.555042 | 1.598879 | -3.495141 |
| 43 | 6 | 0 | 5.043579 | -2.416589 | -0.161985 |
| 44 | 6 | 0 | 5.069880 | -3.139367 | -1.367174 |
| 45 | 6 | 0 | 5.524893 | -4.460094 | -1.332297 |
| 46 | 1 | 0 | 5.551832 | -5.036481 | -2.251003 |
| 47 | 6 | 0 | 5.937184 | -5.047037 | -0.143018 |
| 48 | 1 | 0 | 6.285963 | -6.075437 | -0.135885 |
| 49 | 6 | 0 | 5.895058 | -4.317991 | 1.038502 |
| 50 | 1 | 0 | 6.212012 | -4.783112 | 1.966178 |
| 51 | 6 | 0 | 5.445718 | -2.995178 | 1.053808 |
| 52 | 6 | 0 | 5.400948 | -2.226340 | 2.367424 |
| 53 | 1 | 0 | 5.001625 | -1.234955 | 2.150853 |
| 54 | 6 | 0 | 4.446469 | -2.891431 | 3.375920 |

| | | | | | |
|---|---|---|---|---|---|
| 55 | 1 | 0 | 4.374976 | -2.286673 | 4.286717 |
| 56 | 1 | 0 | 3.446971 | -2.992668 | 2.947426 |
| 57 | 1 | 0 | 4.798898 | -3.887337 | 3.665905 |
| 58 | 6 | 0 | 6.810389 | -2.034748 | 2.956490 |
| 59 | 1 | 0 | 6.762543 | -1.429238 | 3.868311 |
| 60 | 1 | 0 | 7.267790 | -2.995644 | 3.217660 |
| 61 | 1 | 0 | 7.457172 | -1.526581 | 2.238294 |
| 62 | 6 | 0 | 4.620841 | -2.528502 | -2.687865 |
| 63 | 1 | 0 | 4.306352 | -1.504515 | -2.485519 |
| 64 | 6 | 0 | 3.401187 | -3.268444 | -3.266391 |
| 65 | 1 | 0 | 3.062472 | -2.776988 | -4.184454 |
| 66 | 1 | 0 | 3.642510 | -4.308425 | -3.513463 |
| 67 | 1 | 0 | 2.575788 | -3.262340 | -2.551884 |
| 68 | 6 | 0 | 5.781851 | -2.460695 | -3.697114 |
| 69 | 1 | 0 | 5.455872 | -1.959994 | -4.615013 |
| 70 | 1 | 0 | 6.621696 | -1.901531 | -3.279009 |
| 71 | 1 | 0 | 6.133382 | -3.461830 | -3.970969 |
| 72 | 6 | 0 | -5.372960 | -0.032293 | -0.360818 |
| 73 | 6 | 0 | -3.180956 | -0.688164 | -0.105680 |
| 74 | 6 | 0 | -3.210775 | 0.679474 | -0.011166 |
| 75 | 6 | 0 | -5.043576 | 2.416590 | -0.161980 |
| 76 | 6 | 0 | -5.069876 | 3.139370 | -1.367168 |
| 77 | 6 | 0 | -5.524889 | 4.460097 | -1.332288 |
| 78 | 1 | 0 | -5.551827 | 5.036486 | -2.250994 |
| 79 | 6 | 0 | -5.937181 | 5.047039 | -0.143009 |
| 80 | 1 | 0 | -6.285961 | 6.075438 | -0.135873 |
| 81 | 6 | 0 | -5.895056 | 4.317989 | 1.038509 |
| 82 | 1 | 0 | -6.212012 | 4.783108 | 1.966186 |
| 83 | 6 | 0 | -5.445717 | 2.995176 | 1.053813 |
| 84 | 6 | 0 | -5.400949 | 2.226336 | 2.367427 |
| 85 | 1 | 0 | -5.001626 | 1.234951 | 2.150856 |
| 86 | 6 | 0 | -6.810392 | 2.034741 | 2.956490 |
| 87 | 1 | 0 | -6.762547 | 1.429230 | 3.868310 |
| 88 | 1 | 0 | -7.267793 | 2.995637 | 3.217661 |
| 89 | 1 | 0 | -7.457173 | 1.526576 | 2.238292 |
| 90 | 6 | 0 | -4.446473 | 2.891424 | 3.375927 |
| 91 | 1 | 0 | -3.446974 | 2.992664 | 2.947435 |
| 92 | 1 | 0 | -4.798903 | 3.887329 | 3.665914 |
| 93 | 1 | 0 | -4.374981 | 2.286665 | 4.286723 |
| 94 | 6 | 0 | -4.620836 | 2.528509 | -2.687860 |
| 95 | 1 | 0 | -4.306345 | 1.504522 | -2.485517 |
| 96 | 6 | 0 | -3.401184 | 3.268454 | -3.266386 |
| 97 | 1 | 0 | -3.062468 | 2.776999 | -4.184448 |
| 98 | 1 | 0 | -3.642509 | 4.308435 | -3.513457 |
| 99 | 1 | 0 | -2.575785 | 3.262352 | -2.551878 |
| 100 | 6 | 0 | -5.781847 | 2.460702 | -3.697109 |
| 101 | 1 | 0 | -5.455867 | 1.960004 | -4.615009 |
| 102 | 1 | 0 | -6.621690 | 1.901535 | -3.279004 |
| 103 | 1 | 0 | -6.133381 | 3.461836 | -3.970961 |
| 104 | 6 | 0 | -4.934545 | -2.468842 | -0.492077 |
| 105 | 6 | 0 | -4.936827 | -3.026263 | -1.782233 |
| 106 | 6 | 0 | -5.331517 | -4.359444 | -1.921856 |
| 107 | 1 | 0 | -5.339474 | -4.809942 | -2.908764 |
| 108 | 6 | 0 | -5.706974 | -5.116873 | -0.819927 |
| 109 | 1 | 0 | -6.008055 | -6.152313 | -0.948351 |
| 110 | 6 | 0 | -5.688597 | -4.549386 | 0.447737 |
| 111 | 1 | 0 | -5.975542 | -5.147611 | 1.306337 |
| 112 | 6 | 0 | -5.300633 | -3.220685 | 0.637296 |
| 113 | 6 | 0 | -5.278254 | -2.631430 | 2.041250 |
| 114 | 1 | 0 | -4.943524 | -1.597307 | 1.955495 |
| 115 | 6 | 0 | -4.265132 | -3.363354 | 2.940265 |
| 116 | 1 | 0 | -4.217280 | -2.885407 | 3.925083 |
| 117 | 1 | 0 | -4.547128 | -4.410951 | 3.092710 |

| | | | | | |
|---|---|---|---|---|---|
| 118 | 1 | 0 | -3.269051 | -3.336678 | 2.493207 |
| 119 | 6 | 0 | -6.684989 | -2.607482 | 2.666117 |
| 120 | 1 | 0 | -7.375348 | -2.050685 | 2.029068 |
| 121 | 1 | 0 | -7.079106 | -3.620564 | 2.803976 |
| 122 | 1 | 0 | -6.655858 | -2.124827 | 3.649219 |
| 123 | 6 | 0 | -4.526001 | -2.225885 | -3.010905 |
| 124 | 1 | 0 | -4.245535 | -1.227876 | -2.673473 |
| 125 | 6 | 0 | -3.288544 | -2.834605 | -3.694903 |
| 126 | 1 | 0 | -2.979101 | -2.209827 | -4.539318 |
| 127 | 1 | 0 | -2.454593 | -2.896825 | -2.993124 |
| 128 | 1 | 0 | -3.496097 | -3.838884 | -4.080997 |
| 129 | 6 | 0 | -5.701680 | -2.065045 | -3.992340 |
| 130 | 1 | 0 | -5.405773 | -1.433286 | -4.836671 |
| 131 | 1 | 0 | -6.020989 | -3.032513 | -4.396007 |
| 132 | 1 | 0 | -6.555048 | -1.598877 | -3.495147 |
| 133 | 12 | 0 | 0.000000 | -0.000002 | 0.399641 |
| 134 | 8 | 0 | -0.000001 | -0.000004 | 2.543673 |
| 135 | 6 | 0 | 1.191601 | 0.080165 | 3.361461 |
| 136 | 1 | 0 | 1.585495 | 1.098138 | 3.290096 |
| 137 | 1 | 0 | 1.919907 | -0.616145 | 2.945867 |
| 138 | 6 | 0 | 0.722436 | -0.261912 | 4.775198 |
| 139 | 1 | 0 | 0.733318 | -1.345497 | 4.927958 |
| 140 | 1 | 0 | 1.350841 | 0.198535 | 5.541634 |
| 141 | 6 | 0 | -0.722438 | 0.261893 | 4.775199 |
| 142 | 1 | 0 | -1.350844 | -0.198559 | 5.541632 |
| 143 | 1 | 0 | -0.733321 | 1.345477 | 4.927966 |
| 144 | 6 | 0 | -1.191602 | -0.080175 | 3.361460 |
| 145 | 1 | 0 | -1.585497 | -1.098148 | 3.290089 |
| 146 | 1 | 0 | -1.919907 | 0.616138 | 2.945869 |

## SUPPORTING INFORMATIONS of X-RAY

### Compound 2

**Table S4.** Sample and crystal data for **2**.

| | | |
|---|---|---|
| **Identification code** | **2** | |
| **Chemical formula** | $C_{43}H_{66}MgN_2O_4S_3$ | |
| **Formula weight** | 795.46 g/mol | |
| **Temperature** | 296(2) K | |
| **Wavelength** | 0.71073 Å | |
| **Crystal size** | 0.100 x 0.180 x 0.320 mm | |
| **Crystal system** | orthorhombic | |
| **Space group** | $P2_12_12$ (No. 18) | |
| **Unit cell dimensions** | a = 13.3056(6) Å | α = 90° |
| | b = 13.8070(7) Å | β = 90° |
| | c = 12.8135(6) Å | γ = 90° |
| **Volume** | 2353.97(19) $Å^3$ | |
| **Z** | 2 | |
| **Density (calculated)** | 1.122 $g/cm^3$ | |
| **Absorption coefficient** | 0.210 $mm^{-1}$ | |
| **F(000)** | 860 | |

**Table S5.** Data collection and structure refinement for **2**.

| | | |
|---|---|---|
| **Theta range for data collection** | 2.21 to 27.88° | |
| **Index ranges** | -17<=h<=17, -18<=k<=18, -16<=l<=16 | |
| **Reflections collected** | 38275 | |
| **Independent reflections** | 5611 [R(int) = 0.0396] | |
| **Max. and min. transmission** | 0.7457 and 0.6384 | |
| **Structure solution technique** | direct methods | |
| **Structure solution program** | SHELXS-97 (Sheldrick 2008) | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | |
| **Refinement program** | SHELXL-2014/7 (Sheldrick, 2014) | |
| **Function minimized** | $\Sigma\, w(F_o^2 - F_c^2)^2$ | |
| **Data / restraints / parameters** | 5611 / 500 / 371 | |
| **Goodness-of-fit on $F^2$** | 1.048 | |
| **$\Delta/\sigma_{max}$** | 0.002 | |
| **Final R indices** | 4111 data; $I>2\sigma(I)$ | R1 = 0.0519, wR2 = 0.1236 |
| | all data | R1 = 0.0788, wR2 = 0.1372 |
| **Weighting scheme** | $w=1/[\sigma^2(F_o^2)+(0.0719P)^2+0.2954P]$ where $P=(F_o^2+2F_c^2)/3$ | |
| **Absolute structure parameter** | 0.364(19) | |
| **Largest diff. peak and hole** | 0.288 and -0.284 eÅ$^{-3}$ | |
| **R.M.S. deviation from mean** | 0.037 eÅ$^{-3}$ | |

**Table S6.** Bond lengths (Å) for **2**.

| | | | |
|---|---|---|---|
| Mg1-O2' | 2.093(13) | Mg1-O2' | 2.093(13) |
| Mg1-O1' | 2.139(10) | Mg1-O1' | 2.139(10) |
| Mg1-O2 | 2.187(9) | Mg1-O2 | 2.187(9) |
| Mg1-O1 | 2.143(9) | Mg1-O1 | 2.143(9) |
| Mg1-S2 | 2.5339(12) | Mg1-S2 | 2.5339(12) |
| S1-C1 | 1.721(7) | S1'-C1 | 1.671(11) |
| S2-C2 | 1.724(3) | N1-C1 | 1.378(4) |
| N1-C2 | 1.404(4) | N1-C3 | 1.425(4) |
| C1-N1 | 1.378(4) | C1-S1' | 1.671(11) |
| C2-C2 | 1.360(6) | C3-C8 | 1.390(7) |
| C3-C4 | 1.387(6) | C4-C5 | 1.394(6) |
| C4-C12' | 1.514(16) | C4-C12 | 1.528(13) |
| C5-C6 | 1.363(8) | C6-C7 | 1.343(7) |
| C7-C8 | 1.413(6) | C8-C9 | 1.489(7) |
| C9-C10 | 1.499(9) | C9-C11 | 1.524(8) |
| C12-C13 | 1.509(15) | C12-C14 | 1.512(15) |
| C12'-C13' | 1.48(2) | C12'-C14' | 1.509(18) |
| O1-C18 | 1.453(14) | O1-C15 | 1.410(15) |
| C15-C16 | 1.464(14) | C16-C17 | 1.529(14) |
| C17-C18 | 1.450(13) | O1'-C18' | 1.45(2) |
| O1'-C15' | 1.377(19) | C15'-C16' | 1.446(16) |
| C16'-C17' | 1.522(17) | C17'-C18' | 1.385(16) |
| O2-C22 | 1.445(15) | O2-C19 | 1.479(15) |
| C19-C20 | 1.510(16) | C20-C21 | 1.557(18) |
| C21-C22 | 1.460(17) | O2'-C19' | 1.43(2) |
| O2'-C22' | 1.41(2) | C19'-C20' | 1.50(2) |
| C20'-C21' | 1.55(2) | C21'-C22' | 1.40(2) |

**Table S7.** Bond angles (°) for **2**.

| | | | |
|---|---|---|---|
| O2'-Mg1-O2' | 178.5(13) | O2'-Mg1-O1' | 89.4(9) |
| O2'-Mg1-O1' | 89.5(11) | O2'-Mg1-O1' | 89.5(11) |
| O2'-Mg1-O1' | 89.3(9) | O1'-Mg1-O1' | 85.9(8) |
| O2-Mg1-O2 | 164.5(8) | O2-Mg1-O1 | 87.6(7) |
| O2-Mg1-O1 | 81.8(8) | O2-Mg1-O1 | 81.8(8) |
| O2-Mg1-O1 | 87.6(7) | O1-Mg1-O1 | 93.3(7) |
| O2'-Mg1-S2 | 88.6(9) | O2'-Mg1-S2 | 92.5(6) |
| O1'-Mg1-S2 | 92.2(4) | O1'-Mg1-S2 | 177.3(6) |
| O2-Mg1-S2 | 97.2(3) | O2-Mg1-S2 | 93.8(5) |
| O1-Mg1-S2 | 175.0(6) | O1-Mg1-S2 | 88.6(4) |
| O2'-Mg1-S2 | 92.5(6) | O2'-Mg1-S2 | 88.6(9) |
| O1'-Mg1-S2 | 177.3(6) | O1'-Mg1-S2 | 92.2(4) |
| O2-Mg1-S2 | 93.8(5) | O2-Mg1-S2 | 97.2(3) |
| O1-Mg1-S2 | 88.6(4) | O1-Mg1-S2 | 175.1(6) |
| S2-Mg1-S2 | 89.82(5) | C2-S2-Mg1 | 95.03(11) |
| C1-N1-C2 | 110.9(3) | C1-N1-C3 | 122.9(3) |
| C2-N1-C3 | 126.1(3) | N1-C1-N1 | 104.4(4) |
| N1-C1-S1 | 127.82(19) | N1-C1-S1 | 127.82(19) |
| N1-C1-S1' | 124.9(4) | N1-C1-S1' | 125.3(4) |
| N1-C1-S1' | 125.3(4) | N1-C1-S1' | 124.9(4) |
| C2-C2-N1 | 106.91(17) | C2-C2-S2 | 130.06(10) |
| N1-C2-S2 | 123.0(2) | C8-C3-C4 | 122.7(3) |
| C8-C3-N1 | 118.5(4) | C4-C3-N1 | 118.8(4) |
| C3-C4-C5 | 117.0(5) | C3-C4-C12' | 112.9(12) |
| C5-C4-C12' | 129.9(12) | C3-C4-C12 | 129.5(10) |
| C5-C4-C12 | 113.5(10) | C4-C5-C6 | 121.7(5) |
| C7-C6-C5 | 120.4(4) | C6-C7-C8 | 121.5(5) |
| C3-C8-C7 | 116.7(4) | C3-C8-C9 | 124.4(4) |
| C7-C8-C9 | 118.9(5) | C10-C9-C8 | 112.9(4) |
| C10-C9-C11 | 113.1(7) | C8-C9-C11 | 110.5(5) |
| C13-C12-C14 | 111.3(15) | C13-C12-C4 | 116.2(17) |

| | | | |
|---|---|---|---|
| C14-C12-C4 | 116.4(17) | C13'-C12'-C14' | 113.6(19) |
| C13'-C12'-C4 | 104(2) | C14'-C12'-C4 | 106.3(18) |
| C18-O1-C15 | 105.4(8) | C18-O1-Mg1 | 128.5(10) |
| C15-O1-Mg1 | 126.0(10) | O1-C15-C16 | 104.9(10) |
| C17-C16-C15 | 100.7(11) | C16-C17-C18 | 96.6(10) |
| O1-C18-C17 | 108.6(10) | C18'-O1'-C15' | 104.8(10) |
| C18'-O1'-Mg1 | 129.3(14) | C15'-O1'-Mg1 | 123.8(11) |
| O1'-C15'-C16' | 109.1(12) | C17'-C16'-C15' | 104.0(11) |
| C18'-C17'-C16' | 100.9(10) | O1'-C18'-C17' | 112.6(12) |
| C22-O2-C19 | 107.5(8) | C22-O2-Mg1 | 124.2(9) |
| C19-O2-Mg1 | 125.4(10) | O2-C19-C20 | 106.0(10) |
| C21-C20-C19 | 103.0(11) | C22-C21-C20 | 105.0(13) |
| O2-C22-C21 | 102.7(12) | C19'-O2'-C22' | 109.9(11) |
| C19'-O2'-Mg1 | 128.8(15) | C22'-O2'-Mg1 | 120.5(13) |
| O2'-C19'-C20' | 102.7(14) | C19'-C20'-C21' | 106.1(14) |
| C22'-C21'-C20' | 104.2(14) | O2'-C22'-C21' | 109.8(14) |

## Compound 3·toluene

**Table S8.** Sample and crystal data for **3·toluene**.

| | |
|---|---|
| **Identification code** | **3·toluene** |
| **Chemical formula** | $C_{56}H_{82}MgN_6S_3$ |
| **Formula weight** | 959.76 g/mol |
| **Temperature** | 297(2) K |
| **Wavelength** | 0.71073 Å |
| **Crystal size** | 0.120 x 0.210 x 0.280 mm |
| **Crystal system** | monoclinic |
| **Space group** | $P2_1/n$ (No. 14) |
| **Unit cell dimensions** | a = 15.5287(7) Å α = 90° |
| | b = 20.6762(10) Å β = 93.047(2)° |
| | c = 18.7622(9) Å γ = 90° |
| **Volume** | 6015.5(5) $Å^3$ |
| **Z** | 4 |
| **Density (calculated)** | 1.060 $g/cm^3$ |
| **Absorption coefficient** | 0.171 $mm^{-1}$ |
| **F(000)** | 2080 |

**Table S9.** Data collection and structure refinement for **3·toluene**.

| | | |
|---|---|---|
| **Theta range for data collection** | 2.25 to 26.00° | |
| **Index ranges** | -19<=h<=19, -25<=k<=25, -23<=l<=23 | |
| **Reflections collected** | 175989 | |
| **Independent reflections** | 11797 [R(int) = 0.0900] | |
| **Max. and min. transmission** | 0.7457 and 0.6223 | |
| **Structure solution technique** | direct methods | |
| **Structure solution program** | SHELXS-97 (Sheldrick 2008) | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | |
| **Refinement program** | SHELXL-2014/7 (Sheldrick, 2014) | |
| **Function minimized** | $\Sigma\, w(F_o^2 - F_c^2)^2$ | |
| **Data / restraints / parameters** | 11797 / 355 / 669 | |
| **Goodness-of-fit on $F^2$** | 1.039 | |
| **Final R indices** | 6903 data; I>2σ(I) | R1 = 0.0628, wR2 = 0.1318 |
| | all data | R1 = 0.1244, wR2 = 0.1597 |
| **Weighting scheme** | $w=1/[\sigma^2(F_o^2)+(0.0592P)^2+2.5708P]$ where $P=(F_o^2+2F_c^2)/3$ | |
| **Largest diff. peak and hole** | 0.286 and -0.181 eÅ$^{-3}$ | |
| **R.M.S. deviation from mean** | 0.036 eÅ$^{-3}$ | |

**Table S10.** Bond lengths (Å) for **3·toluene**.

| | | | |
|---|---|---|---|
| Mg1-C39 | 2.226(3) | Mg1-C28 | 2.229(3) |
| Mg1-S2 | 2.4507(12) | Mg1-S3 | 2.4495(12) |
| S1-C1 | 1.677(3) | S2-C2 | 1.739(2) |
| S3-C3 | 1.735(2) | N1-C1 | 1.355(3) |
| N1-C2 | 1.408(3) | N1-C16 | 1.432(3) |
| N2-C1 | 1.356(3) | N2-C3 | 1.403(3) |
| N2-C4 | 1.436(3) | C2-C3 | 1.346(3) |
| C4-C9 | 1.385(4) | C4-C5 | 1.388(4) |
| C5-C6 | 1.396(4) | C5-C13 | 1.511(4) |
| C6-C7 | 1.368(5) | C7-C8 | 1.348(5) |
| C8-C9 | 1.389(4) | C9-C10' | 1.494(14) |
| C9-C10 | 1.501(9) | C10-C12 | 1.525(9) |
| C10-C11 | 1.537(10) | C10'-C12' | 1.525(16) |
| C10'-C11' | 1.535(12) | C13-C15 | 1.516(5) |
| C13-C14 | 1.514(5) | C16-C17 | 1.377(4) |
| C16-C21 | 1.387(4) | C17-C18 | 1.389(4) |
| C17-C25 | 1.507(4) | C18-C19 | 1.358(5) |
| C19-C20 | 1.366(5) | C20-C21 | 1.394(4) |
| C21-C22 | 1.511(4) | C22-C23 | 1.523(5) |
| C22-C24 | 1.519(5) | C25-C26 | 1.519(5) |
| C25-C27 | 1.520(5) | N3-C28 | 1.358(4) |
| N3-C29 | 1.391(4) | N3-C36 | 1.467(4) |
| N4-C28 | 1.343(4) | N4-C30 | 1.385(4) |
| N4-C31 | 1.507(5) | C29-C30 | 1.339(4) |
| C29-C35 | 1.499(4) | C30-C34 | 1.500(5) |
| C31-C33 | 1.448(6) | C31-C32 | 1.466(6) |
| C36-C38 | 1.496(5) | C36-C37 | 1.514(5) |
| N5-C39 | 1.357(3) | N5-C40 | 1.391(4) |
| N5-C47 | 1.466(4) | N6-C39 | 1.349(4) |
| N6-C41 | 1.382(4) | N6-C42 | 1.482(4) |
| C40-C41 | 1.339(4) | C40-C46 | 1.491(4) |
| C41-C45 | 1.493(5) | C42-C44 | 1.478(5) |

| | | | |
|---|---|---|---|
| C42-C43 | 1.513(5) | C47-C49 | 1.523(5) |
| C47-C48 | 1.528(5) | C50-C51 | 1.39 |
| C50-C55 | 1.39 | C50-C56 | 1.457(7) |
| C51-C52 | 1.39 | C52-C53 | 1.39 |
| C53-C54 | 1.39 | C54-C55 | 1.39 |
| C50'-C51' | 1.39 | C50'-C55' | 1.39 |
| C50'-C56' | 1.472(12) | C51'-C52' | 1.39 |
| C52'-C53' | 1.39 | C53'-C54' | 1.39 |
| C54'-C55' | 1.39 | | |

**Table S11.** Bond angles (°) for **3·toluene**.

| | | | |
|---|---|---|---|
| C39-Mg1-C28 | 111.95(12) | C39-Mg1-S2 | 127.12(9) |
| C28-Mg1-S2 | 102.28(9) | C39-Mg1-S3 | 96.82(8) |
| C28-Mg1-S3 | 125.76(11) | S2-Mg1-S3 | 94.23(4) |
| C2-S2-Mg1 | 92.49(9) | C3-S3-Mg1 | 92.78(9) |
| C1-N1-C2 | 110.46(19) | C1-N1-C16 | 124.9(2) |
| C2-N1-C16 | 124.6(2) | C1-N2-C3 | 110.91(19) |
| C1-N2-C4 | 123.7(2) | C3-N2-C4 | 125.39(19) |
| N1-C1-N2 | 105.3(2) | N1-C1-S1 | 127.35(18) |
| N2-C1-S1 | 127.40(19) | C3-C2-N1 | 106.9(2) |
| C3-C2-S2 | 130.46(19) | N1-C2-S2 | 122.63(17) |
| C2-C3-N2 | 106.5(2) | C2-C3-S3 | 130.00(19) |
| N2-C3-S3 | 123.51(17) | C9-C4-C5 | 123.1(2) |
| C9-C4-N2 | 118.5(2) | C5-C4-N2 | 118.5(2) |
| C4-C5-C6 | 116.9(3) | C4-C5-C13 | 121.7(2) |
| C6-C5-C13 | 121.4(3) | C7-C6-C5 | 120.9(3) |
| C8-C7-C6 | 120.5(3) | C7-C8-C9 | 121.8(3) |
| C4-C9-C8 | 116.8(3) | C4-C9-C10' | 127.1(14) |
| C8-C9-C10' | 116.1(15) | C4-C9-C10 | 119.9(9) |
| C8-C9-C10 | 123.3(9) | C9-C10-C12 | 109.9(16) |
| C9-C10-C11 | 106.8(14) | C12-C10-C11 | 111.8(11) |
| C9-C10'-C12' | 121(3) | C9-C10'-C11' | 117(2) |
| C12'-C10'-C11' | 108.0(16) | C5-C13-C15 | 110.8(3) |
| C5-C13-C14 | 112.9(3) | C15-C13-C14 | 111.6(3) |
| C17-C16-C21 | 123.3(2) | C17-C16-N1 | 118.7(2) |
| C21-C16-N1 | 118.0(2) | C16-C17-C18 | 117.2(3) |
| C16-C17-C25 | 122.4(3) | C18-C17-C25 | 120.3(3) |
| C19-C18-C17 | 121.0(3) | C20-C19-C18 | 120.8(3) |
| C19-C20-C21 | 120.8(3) | C16-C21-C20 | 116.8(3) |
| C16-C21-C22 | 122.8(2) | C20-C21-C22 | 120.4(3) |
| C21-C22-C23 | 112.5(3) | C21-C22-C24 | 111.1(3) |
| C23-C22-C24 | 110.9(3) | C17-C25-C26 | 112.2(3) |
| C17-C25-C27 | 111.8(3) | C26-C25-C27 | 110.4(3) |
| C28-N3-C29 | 111.2(3) | C28-N3-C36 | 121.3(3) |

| | | | |
|---|---|---|---|
| C29-N3-C36 | 127.5(3) | C28-N4-C30 | 111.7(3) |
| C28-N4-C31 | 125.2(3) | C30-N4-C31 | 123.0(3) |
| N4-C28-N3 | 104.0(3) | N4-C28-Mg1 | 129.1(2) |
| N3-C28-Mg1 | 124.8(3) | C30-C29-N3 | 106.3(3) |
| C30-C29-C35 | 128.5(3) | N3-C29-C35 | 125.2(3) |
| C29-C30-N4 | 106.8(3) | C29-C30-C34 | 129.6(3) |
| N4-C30-C34 | 123.6(3) | C33-C31-C32 | 127.1(4) |
| C33-C31-N4 | 115.0(4) | C32-C31-N4 | 110.4(4) |
| N3-C36-C38 | 112.4(3) | N3-C36-C37 | 112.2(3) |
| C38-C36-C37 | 114.8(4) | C39-N5-C40 | 111.4(3) |
| C39-N5-C47 | 121.1(3) | C40-N5-C47 | 127.4(3) |
| C39-N6-C41 | 111.9(3) | C39-N6-C42 | 125.5(3) |
| C41-N6-C42 | 122.6(3) | N6-C39-N5 | 103.6(2) |
| N6-C39-Mg1 | 129.8(2) | N5-C39-Mg1 | 122.0(2) |
| C41-C40-N5 | 106.4(3) | C41-C40-C46 | 127.8(3) |
| N5-C40-C46 | 125.8(3) | C40-C41-N6 | 106.6(3) |
| C40-C41-C45 | 129.5(3) | N6-C41-C45 | 123.8(3) |
| N6-C42-C44 | 112.8(3) | N6-C42-C43 | 109.4(3) |
| C44-C42-C43 | 116.2(4) | N5-C47-C49 | 111.9(3) |
| N5-C47-C48 | 111.6(3) | C49-C47-C48 | 114.3(3) |
| C51-C50-C55 | 120.0 | C51-C50-C56 | 122.2(7) |
| C55-C50-C56 | 117.8(7) | C50-C51-C52 | 120.0 |
| C53-C52-C51 | 120.0 | C54-C53-C52 | 120.0 |
| C55-C54-C53 | 120.0 | C54-C55-C50 | 120.0 |
| C51'-C50'-C55' | 120.0 | C51'-C50'-C56' | 133.5(19) |
| C55'-C50'-C56' | 106.4(19) | C52'-C51'-C50' | 120.0 |
| C53'-C52'-C51' | 120.0 | C52'-C53'-C54' | 120.0 |
| C55'-C54'-C53' | 120.0 | C54'-C55'-C50' | 120.0 |

## Compound 4

**Table S12.** Sample and crystal data for **4**.

| | |
|---|---|
| **Identification code** | **4** |
| **Chemical formula** | $C_{80}H_{118}MgN_8OS_6$ |
| **Formula weight** | 1424.49 g/mol |
| **Temperature** | 297(2) K |
| **Wavelength** | 0.71073 Å |
| **Crystal size** | 0.100 x 0.190 x 0.280 mm |
| **Crystal system** | monoclinic |
| **Space group** | $P2_1/n$ (No. 14) |
| **Unit cell dimensions** | a = 14.5228(12) Å α = 90° |
| | b = 16.6577(13) Å β = 92.673(2)° |
| | c = 18.4634(14) Å γ = 90° |
| **Volume** | 4461.7(6) $Å^3$ |
| **Z** | 2 |
| **Density (calculated)** | 1.060 $g/cm^3$ |
| **Absorption coefficient** | 0.204 $mm^{-1}$ |
| **F(000)** | 1540 |

**Table S13.** Data collection and structure refinement for **4**.

| | | |
|---|---|---|
| **Theta range for data collection** | 2.52 to 25.25° | |
| **Index ranges** | -17<=h<=17, -19<=k<=19, -1<=l<=22 | |
| **Reflections collected** | 8053 | |
| **Max. and min. transmission** | 0.7457 and 0.6389 | |
| **Structure solution technique** | direct methods | |
| **Structure solution program** | SHELXS-97 (Sheldrick 2008) | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | |
| **Refinement program** | SHELXL-2014/7 (Sheldrick, 2014) | |
| **Function minimized** | $\Sigma\, w(F_o^2 - F_c^2)^2$ | |
| **Data / restraints / parameters** | 8053 / 344 / 569 | |
| **Goodness-of-fit on $F^2$** | 1.090 | |
| **Final R indices** | 5798 data; $I>2\sigma(I)$ | R1 = 0.0828, wR2 = 0.2230 |
| | all data | R1 = 0.1107, wR2 = 0.2429 |
| **Weighting scheme** | $w=1/[\sigma^2(F_o^2)+(0.0912P)^2+5.9344P]$ where $P=(F_o^2+2F_c^2)/3$ | |
| **Largest diff. peak and hole** | 0.643 and -0.332 eÅ$^{-3}$ | |
| **R.M.S. deviation from mean** | 0.065 eÅ$^{-3}$ | |

**Table S14.** Bond lengths (Å) for **4**.

| | | | |
|---|---|---|---|
| S1-C1 | 1.690(4) | S2-C2 | 1.723(4) |
| S2-Mg1 | 2.513(3) | S2-Mg1 | 2.545(3) |
| S3-C3 | 1.727(4) | S3-Mg1 | 2.550(3) |
| S3-Mg1 | 2.563(3) | Mg1-O1 | 2.123(13) |
| Mg1-O1' | 2.149(12) | Mg1-S2 | 2.545(3) |
| Mg1-S3 | 2.563(3) | N1-C1 | 1.352(5) |
| N1-C2 | 1.406(5) | N1-C16 | 1.445(5) |
| N2-C1 | 1.348(5) | N2-C3 | 1.406(5) |
| N2-C4 | 1.433(5) | C2-C3 | 1.341(5) |
| C4-C9 | 1.382(7) | C4-C5 | 1.400(7) |
| C5-C6 | 1.408(8) | C5-C13' | 1.496(10) |
| C5-C13 | 1.493(18) | C6-C7 | 1.360(11) |
| C7-C8 | 1.349(11) | C8-C9 | 1.389(8) |
| C9-C10 | 1.470(13) | C9-C10' | 1.477(13) |
| C10-C11 | 1.529(14) | C10-C12 | 1.518(15) |
| C10'-C11' | 1.535(15) | C10'-C12' | 1.528(17) |
| C13-C15 | 1.551(14) | C13-C14 | 1.51(2) |
| C13'-C14' | 1.512(13) | C13'-C15' | 1.574(14) |
| C16-C21 | 1.391(7) | C16-C17 | 1.389(7) |
| C17-C25 | 1.501(9) | C17-C18 | 1.381(9) |
| C18-C19 | 1.353(13) | C19-C20 | 1.345(12) |
| C20-C21 | 1.399(8) | C21-C22 | 1.498(9) |
| C22-C23 | 1.512(10) | C22-C24 | 1.521(9) |
| C25-C26 | 1.531(9) | C25-C27 | 1.522(9) |
| O1-C31 | 1.347(14) | O1-C28 | 1.372(16) |
| C28-C29 | 1.477(16) | C29-C30 | 1.423(16) |
| C30-C31 | 1.460(16) | O1'-C28' | 1.34(2) |
| O1'-C31' | 1.311(18) | C28'-C29' | 1.46(2) |
| C29'-C30' | 1.40(2) | C30'-C31' | 1.44(2) |
| N3-C32 | 1.321(6) | N3-C33 | 1.384(7) |
| N3-C40 | 1.447(8) | N4-C32 | 1.320(6) |
| N4-C34 | 1.380(6) | N4-C35 | 1.467(7) |
| C32-H32 | 0.95(2) | C33-C34 | 1.360(9) |
| C33-C39 | 1.523(8) | C34-C38 | 1.459(9) |
| C35-C37 | 1.472(9) | C35-C36 | 1.476(7) |
| C40-C41 | 1.505(10) | C40-C42 | 1.501(10) |

**Table S15.** Bond angles (°) for **4**.

| | | | |
|---|---|---|---|
| C2-S2-Mg1 | 96.24(15) | C2-S2-Mg1 | 96.19(15) |
| C3-S3-Mg1 | 95.13(15) | C3-S3-Mg1 | 95.48(15) |
| O1-Mg1-S2 | 109.2(8) | O1'-Mg1-S2 | 101.4(7) |
| O1-Mg1-S3 | 101.7(9) | O1'-Mg1-S3 | 107.4(7) |
| S2-Mg1-S3 | 87.57(9) | O1-Mg1-S2 | 99.0(8) |
| O1'-Mg1-S2 | 106.7(7) | S2-Mg1-S2 | 151.77(13) |
| S3-Mg1-S2 | 85.96(9) | O1-Mg1-S3 | 106.0(9) |
| O1'-Mg1-S3 | 100.6(7) | S2-Mg1-S3 | 86.37(9) |
| S3-Mg1-S3 | 152.07(13) | S2-Mg1-S3 | 86.61(9) |
| C1-N1-C2 | 111.2(3) | C1-N1-C16 | 126.2(3) |
| C2-N1-C16 | 122.6(3) | C1-N2-C3 | 110.9(3) |
| C1-N2-C4 | 126.3(3) | C3-N2-C4 | 122.8(3) |
| N2-C1-N1 | 104.9(3) | N2-C1-S1 | 127.6(3) |
| N1-C1-S1 | 127.4(3) | C3-C2-N1 | 106.2(3) |
| C3-C2-S2 | 128.6(3) | N1-C2-S2 | 125.2(3) |
| C2-C3-N2 | 106.9(3) | C2-C3-S3 | 129.0(3) |
| N2-C3-S3 | 124.1(3) | C9-C4-N2 | 117.9(4) |
| C9-C4-C5 | 124.2(4) | N2-C4-C5 | 117.8(4) |
| C4-C5-C6 | 115.8(6) | C4-C5-C13' | 123.1(8) |
| C6-C5-C13' | 121.1(9) | C4-C5-C13 | 121(2) |
| C6-C5-C13 | 123(2) | C7-C6-C5 | 119.5(7) |
| C6-C7-C8 | 123.6(6) | C7-C8-C9 | 119.8(7) |
| C4-C9-C8 | 117.1(6) | C4-C9-C10 | 122.4(11) |
| C8-C9-C10 | 120.3(12) | C4-C9-C10' | 121.7(10) |
| C8-C9-C10' | 121.2(11) | C9-C10-C11 | 115.0(19) |
| C9-C10-C12 | 108.9(14) | C11-C10-C12 | 108.6(15) |
| C9-C10'-C11' | 111.9(15) | C9-C10'-C12' | 113.5(18) |
| C11'-C10'-C12' | 109.4(14) | C5-C13-C15 | 115(2) |
| C5-C13-C14 | 113(4) | C15-C13-C14 | 110(2) |
| C5-C13'-C14' | 112.2(13) | C5-C13'-C15' | 110.3(12) |

| | | | |
|---|---|---|---|
| C14'-C13'-C15' | 110.7(11) | C21-C16-C17 | 123.2(5) |
| C21-C16-N1 | 118.7(4) | C17-C16-N1 | 118.0(4) |
| C16-C17-C25 | 122.6(5) | C16-C17-C18 | 116.3(7) |
| C25-C17-C18 | 121.1(6) | C19-C18-C17 | 122.2(8) |
| C20-C19-C18 | 120.6(7) | C19-C20-C21 | 121.4(8) |
| C16-C21-C20 | 116.4(6) | C16-C21-C22 | 121.3(4) |
| C20-C21-C22 | 122.3(6) | C21-C22-C23 | 111.8(6) |
| C21-C22-C24 | 113.7(7) | C23-C22-C24 | 109.5(7) |
| C17-C25-C26 | 111.8(5) | C17-C25-C27 | 113.0(7) |
| C26-C25-C27 | 111.2(7) | C31-O1-C28 | 100.2(15) |
| C31-O1-Mg1 | 131.6(17) | C28-O1-Mg1 | 122.7(18) |
| O1-C28-C29 | 107.8(16) | C28-C29-C30 | 102.3(13) |
| C29-C30-C31 | 103.8(13) | O1-C31-C30 | 109.1(15) |
| C28'-O1'-C31' | 103.6(14) | C28'-O1'-Mg1 | 129.7(18) |
| C31'-O1'-Mg1 | 123.0(15) | O1'-C28'-C29' | 112.6(18) |
| C30'-C29'-C28' | 97.3(16) | C29'-C30'-C31' | 107.2(17) |
| O1'-C31'-C30' | 110.8(16) | C32-N3-C33 | 107.4(5) |
| C32-N3-C40 | 126.3(5) | C33-N3-C40 | 126.2(5) |
| C32-N4-C34 | 110.2(5) | C32-N4-C35 | 125.6(4) |
| C34-N4-C35 | 124.2(5) | H32-C32-N3 | 130(4) |
| H32-C32-N4 | 120(4) | N3-C32-N4 | 109.1(5) |
| C34-C33-N3 | 108.6(5) | C34-C33-C39 | 129.0(7) |
| N3-C33-C39 | 122.4(7) | C33-C34-N4 | 104.6(5) |
| C33-C34-C38 | 131.0(6) | N4-C34-C38 | 124.4(6) |
| C37-C35-N4 | 109.8(5) | C37-C35-C36 | 112.6(6) |
| N4-C35-C36 | 111.3(5) | N3-C40-C41 | 112.2(5) |
| N3-C40-C42 | 110.3(6) | C41-C40-C42 | 111.7(8) |