

Supplementary Information

Synthesis and X-ray characterization of 15- and 16-vertex *closo*-carboranes

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Supplementary Method

General Procedure

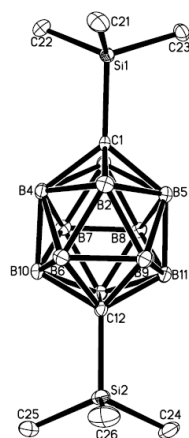
Unless otherwise noted, all experiments were performed under an atmosphere of dry argon with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were refluxed over sodium benzophenone ketyl for several days and freshly distilled prior to use. CH₂Cl₂ was refluxed over CaH₂ for several days and distilled immediately before use. All other chemicals were purchased from either Aldrich or Acros Chemical Company and used as received unless otherwise noted. The ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 and 100 MHz, respectively. The ¹¹B NMR spectra were recorded on a Bruker DPX 300 spectrometer at 96 MHz or a Bruker DPX 400 spectrometer at 128 MHz, respectively. All chemical shifts were reported in δ units with references to the residual protons or carbons of the deuterated solvents for proton or carbon chemical shifts, and to external BF₃·OEt₂ (0.0 ppm) for boron chemical shifts. Mass spectra were recorded on a Thermo Finnigan MAT 95 XL spectrometry.

Experimental Section

Preparation of 1,2-TMS₂-1,2-C₂B₁₀H₁₀ (1a). To a THF (20 mL) solution of *o*-carborane (4.61 g, 32.0 mmol) was slowly added ⁿBuLi (40.0 mL of 1.6 M in *n*-hexane, 64.0 mmol) at 0 °C, and the reaction mixture was stirred at this temperature for 1 h, and then at room temperature for another 1 h. To the resultant solution was slowly added chlorotrimethylsilane (8.5 mL, 66.7 mmol) at 0 °C, the mixture was stirred at this temperature for 1 h, and then at room temperature overnight. After hydrolysis with water (20 mL) and extraction with diethyl ether (3 x 20 mL), the organic solutions were combined, dried with MgSO₄ and concentrated to dryness in vacuo. The residue was recrystallized from acetone to afford **1a** (7.57 g, 82%) as colorless crystals. ¹H NMR (CDCl₃): δ 0.32 (s, 18H, Si(CH₃)₃). ¹³C{¹H} NMR (CDCl₃): δ 1.6 (Si(CH₃)₃), 74.7 (cage C). ¹¹B{¹H} NMR (CDCl₃): δ 1.7 (2B), -5.9 (2B), -9.0 (4B), -11.2 (2B). HRMS: *m/z* calcd for C₈H₂₈B₁₀Si₂ [M]⁺: 288.2743. Found: 288.2743. This is a known compound.¹

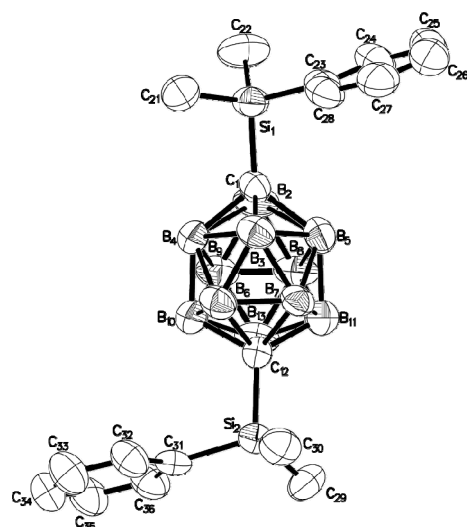
Preparation of 1,2-DMPS₂-1,2-C₂B₁₀H₁₀ (1b). To a THF (20 mL) solution of *o*-carborane (4.61 g, 32.0 mmol) was slowly added ⁿBuLi (40.0 mL of 1.6 M in *n*-hexane, 64.0 mmol) at 0°C, the mixture was stirred at this temperature for 1 h, and then at room temperature overnight. Chlorodimethylphenylsilane (11.2 mL, 66.7 mmol) was then slowly added to the above suspension at 0°C, the mixture was stirred at this temperature for 1 h, and then at room temperature overnight. After hydrolysis with water (20 mL) and extraction with diethyl ether (3 x 20 mL), the solutions were combined, dried with MgSO₄ and concentrated to dryness in vacuo. The residue was recrystallized from diethyl ether to afford **1b** (11.2 g, 85%) as colorless crystals. M.P.: 154-156°C. ¹H NMR (CDCl₃): δ 0.33 (s, 12H, Si(CH₃)₂), 7.45 (m, 4H, SiC₆H₅), 7.50 (m, 2H, SiC₆H₅), 7.54 (m, 4H, SiC₆H₅). ¹³C{¹H} NMR (CDCl₃): δ 0.1 (Si(CH₃)₂), 74.8 (cage C), 127.9, 130.7, 134.0, 135.4 (SiC₆H₅). ¹¹B{¹H} NMR (CDCl₃): δ 1.4 (2B), -6.9 (2B), -9.6 (4B), -11.5 (2B). HRMS: *m/z* calcd for C₁₇H₂₉B₁₀Si₂ [M-CH₃]⁺: 398.2786. Found: 398.2784.

Preparation of 1,12-TMS₂-1,12-C₂B₁₁H₁₁ (2a). To a THF (30 mL) solution of **1a** (2.89 g, 10.0 mmol) was added finely cut Na metal (0.69 g, 30.0 mmol), and the mixture was stirred at room temperature for 1 day. Removal of excess Na metal and THF afforded a pale yellow solid. DME (20 mL) was then added, giving a yellow solution. HBBBr₂·SMe₂ (20.0 mL of 1.0 M in dichloromethane, 20.0 mmol) was slowly added to the solution at -78°C, the mixture was stirred at this temperature for 1 h, and then at room temperature overnight. After removal of the solvent, the residue was subjected to chromatographic separation (SiO₂, 300 ~ 400 mesh, *n*-hexane as eluent), affording **1a** (0.35 g, 12%) and **2a** (0.60 g, 20%) both as white solid. X-ray-quality crystals of **2a** were obtained by recrystallization from *n*-hexane. M.P.: 40-41°C. ¹H NMR (CDCl₃): δ 0.32 (s, 9H, Si(CH₃)₃), 0.20 (s, 9H, Si(CH₃)₃). ¹³C{¹H} NMR (CDCl₃): δ 120.5 (cage C), 98.4 (cage C), -1.0, -1.2 (Si(CH₃)₃). ¹¹B{¹H} NMR (CDCl₃): δ 15.2 (1B), 8.5 (2B), 0.0 (1B), -2.6 (3B), -7.5 (4B). HRMS: *m/z* calcd for C₈H₂₇B₁₁Si₂ [M - 2H]⁺: 298.2750. Found: 298.2747.



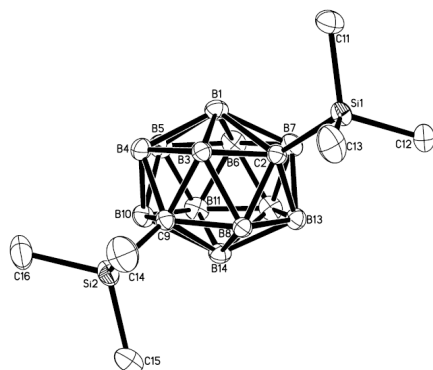
Supplementary Figure 1. Molecular structure of **2a** (hydrogen atoms are omitted for clarity).

Preparation of 1,12-DMPS₂-1,12-C₂B₁₁H₁₁ (2b**).** To a THF (40 mL) solution of **1b** (8.23 g, 20.0 mmol) was added finely cut Na metal (0.93 g, 40.6 mmol), and the mixture was stirred at room temperature for 1 day. Removal of excess Na metal and THF afforded a yellow solid. DME (30 mL) was then added, giving a yellow solution. HBBBr₂·SMe₂ (40.0 mL of 1.0 M in dichloromethane, 40.0 mmol) was slowly added to the solution at -78°C, and the mixture was stirred at this temperature for 1 h, and then at room temperature overnight. After removal of the solvent, the residue was subjected to chromatographic separation (SiO₂, 300 ~ 400 mesh) using *n*-hexane/CH₂Cl₂ (4/1 in v/v) as eluent to give **1b** (0.36 g, 4%) and **2b** (2.48 g, 29%) both as white solid. X-ray-quality crystals of **2b** were obtained by recrystallization from *n*-hexane. M.P.: 89-90°C. ¹H NMR (CDCl₃): δ 0.52 (s, 12H, Si(CH₃)₂), 7.38 (m, 5H, SiC₆H₅), 7.47 (m, 5H, SiC₆H₅). ¹³C{¹H} NMR (CDCl₃): δ -2.9 (Si(CH₃)₂), 97.6 (cage C), 119.6 (cage C), 127.9, 128.0, 130.1, 130.2, 134.4, 134.5 (SiC₆H₅). ¹¹B{¹H} NMR (CDCl₃): δ 14.7 (1B), 8.1 (2B), -0.7 (1B), -2.8 (3B), -8.1 (3B), -16.8 (1B). HRMS: *m/z* calcd for C₁₈H₃₃B₁₁Si₂ [M]⁺: 423.3146. Found: 423.3144.



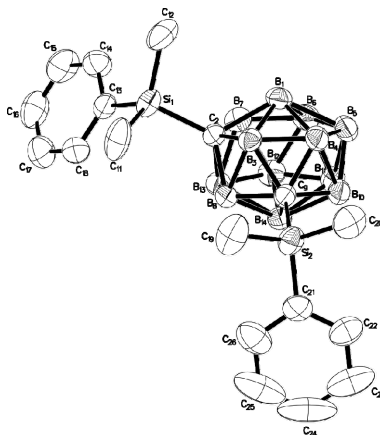
Supplementary Figure 2. Molecular structure of **2b** (hydrogen atoms are omitted for clarity).

Preparation of 2,9-TMS₂-2,9-C₂B₁₂H₁₂ (3a**).** To a THF (30 mL) solution of **2a** (3.00 g, 10.0 mmol) was added finely cut Na metal (0.69 g, 30.0 mmol), and the mixture was stirred at room temperature overnight. Removal of excess Na metal and THF afforded a pale yellow solid. CH₂Cl₂ (20 mL) was then added, giving a yellow solution. HBBBr₂·SMe₂ (30.0 mL of 1.0 M in dichloromethane, 30.0 mmol) was slowly added to the solution at -78°C, the mixture was stirred at this temperature for 1 h, and then at room temperature overnight. After removal of the solvent, the residue was subjected to chromatographic separation (SiO₂, 300 ~ 400 mesh, *n*-hexane as eluent), affording **2a** (0.06 g, 2%) and **3a** (0.62 g, 20%) both as white solid. X-ray-quality crystals of **3a** were obtained by recrystallization from *n*-hexane. M.P.: 50-51°C. ¹H NMR (CDCl₃): δ 0.27 (s, 18H, Si(CH₃)₃). ¹³C{¹H} NMR (CDCl₃): δ 82.5 (cage C), -1.6 (Si(CH₃)₃). ¹¹B{¹H} NMR (CDCl₃): δ 9.9 (2B), -3.6 (4B), -10.0 (4B), -20.6 (2B). HRMS: *m/z* calcd for C₈H₃₀B₁₂Si₂ [M]⁺: 312.3078. Found: 312.3066.



Supplementary Figure 3. Molecular structure of **3a** (hydrogen atoms are omitted for clarity).

Preparation of 2,9-DMPS₂-2,9-C₂B₁₂H₁₂ (3b). To a THF (20 mL) solution of **2b** (3.20 g, 7.59 mmol) was added finely cut Na metal (0.89 g, 38.6 mmol), and the mixture was stirred at room temperature overnight. Removal of excess Na metal and THF afforded a pale yellow solid. CH₂Cl₂ (25 mL) was then added, giving a yellow solution. HBBBr₂·SMe₂ (25.0 mL of 1.0 M in dichloromethane, 25.0 mmol) was slowly added to the solution at -78°C, the mixture was stirred at this temperature for 1 h, and then at room temperature overnight. After removal of the solvent, the residue was subjected to chromatographic separation (SiO₂, 300 ~ 400 mesh) using *n*-hexane/CH₂Cl₂ (4/1 in v/v) as eluent to give **2b** (0.10 g, 3%) and **3b** (0.49 g, 15%) both as white solid. X-ray-quality crystals of **3b** were obtained by recrystallization from *n*-hexane. M.P.: 123-125°C. ¹H NMR (CDCl₃): δ 0.39 (s, 6H, Si(CH₃)₂), 0.47 (s, 6H, Si(CH₃)₂), 7.37 (m, 4H, SiC₆H₅), 7.43 (m, 2H, SiC₆H₅), 7.49 (m, 4H, SiC₆H₅). ¹³C{¹H} NMR (CDCl₃): δ -3.5 (Si(CH₃)₂), 82.0 (cage C), 127.9, 130.4, 133.7, 134.8 (SiC₆H₅). ¹¹B{¹H} NMR (CDCl₃): δ 9.6 (2B), -3.9 (4B), -10.2 (4B), -20.5 (2B). HRMS: *m/z* calcd for C₁₈H₃₄B₁₂Si₂ [M]⁺: 436.3397. Found: 436.3399.

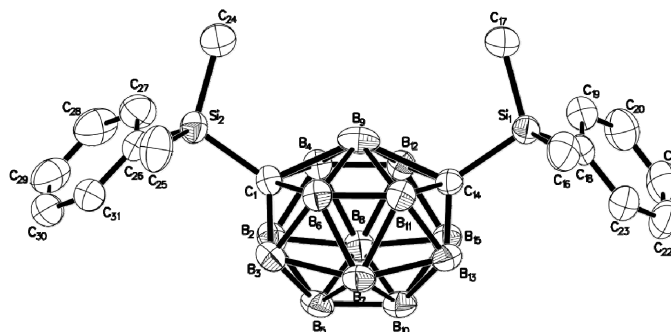


Supplementary Figure 4. Molecular structure of **3b** (hydrogen atoms are omitted for clarity).

Preparation of 1,14-TMS₂-1,14-C₂B₁₃H₁₃ (4a). To a THF (30 mL) solution of **3a** (3.12 g, 10.0 mmol) was added finely cut Na metal (0.69 g, 30.0 mmol), and the mixture was stirred at room temperature overnight. Removal of excess Na metal and THF afforded a pale yellow solid. CH₂Cl₂ (20 mL) was then added, giving a yellow solution. HBBBr₂·SMe₂ (30.0 mL of 1.0 M in dichloromethane, 30.0 mmol) was slowly added to the solution at -78°C, the mixture was stirred at this temperature for 1 h, and then at room temperature overnight. After removal of the solvent, the residue was subjected to chromatographic separation (SiO₂, 300 ~ 400 mesh, *n*-hexane as eluent), affording **3a** (0.16 g, 5%) and **4a** (0.26 g, 8%) both as white solid. ¹H NMR (CDCl₃): δ 0.42 (s, 18H, Si(CH₃)₃). ¹³C{¹H} NMR (CDCl₃): δ -0.3 (Si(CH₃)₃), the

cage *C* atoms were not observed. $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): δ 16.3 (2B), -1.0 (4B), -4.5 (4B), -6.1 (1B), -20.5 (2B). HRMS: m/z calcd for $\text{C}_8\text{H}_3\text{B}_{13}\text{Si}_2$ $[\text{M}]^+$: 324.3251. Found: 324.3244.

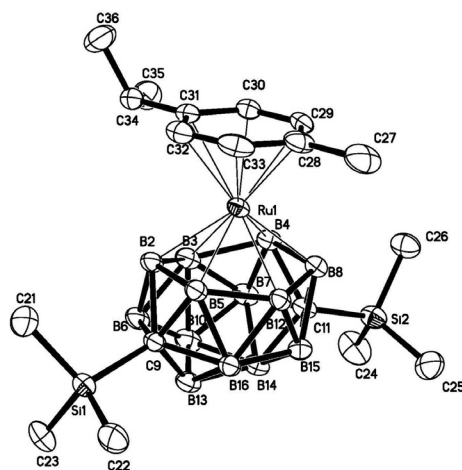
Preparation of 1,14-DMPS₂-1,14-C₂B₁₃H₁₃ (4b). To a THF (15 mL) solution of **3b** (640 mg, 1.47 mmol) was added finely cut Na metal (98 mg, 4.26 mmol), and the mixture was stirred at room temperature overnight. Removal of excess Na metal and THF afforded a pale yellow solid. CH_2Cl_2 (4.5 mL) was then added, giving a pale yellow solution. $\text{HBBBr}_2\cdot\text{SMe}_2$ (4.50 mL of 1.0 M in dichloromethane, 4.50 mmol) was slowly added to the solution at -78°C , the mixture was stirred at this temperature for 1 h, and then at room temperature overnight. After removal of the solvent, the residue was subjected to chromatographic separation (SiO_2 , 300 ~ 400 mesh) using *n*-hexane/ CH_2Cl_2 (4/1 in v/v) as eluent to give **3b** (36 mg, 6%) and **4b** (23 mg, 3%) both as white solid. X-ray-quality crystals of **4b** were obtained by recrystallization from *n*-hexane. M.P.: $133\text{--}134^\circ\text{C}$. ^1H NMR (CDCl_3): δ 0.70 (s, 12H, $\text{Si}(\text{CH}_3)_2$), 7.41 (m, 6H, SiC_6H_5), 7.63 (m, 4H, SiC_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -2.1 ($\text{Si}(\text{CH}_3)_2$), 57.7 (cage *C*), 127.9, 130.2, 134.5, 135.0 (SiC_6H_5). $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): δ 15.0 (2B), -1.8 (4B), -5.7 (4B), -10.8 (1B), -21.3 (2B). HRMS: m/z calcd for $\text{C}_{18}\text{H}_{35}\text{B}_{13}\text{Si}_2$ $[\text{M}]^+$: 448.3554. Found: 448.3558.



Supplementary Figure 5. Molecular structure of **4b** (hydrogen atoms are omitted for clarity).

Preparation of 9,11-TMS₂-1-(*p*-cymene)-1,9,11-RuC₂B₁₃H₁₃ (5Ru). To a THF (10 mL) solution of **4a** (324 mg, 1.0 mmol) was added finely cut Na metal (69 mg, 3.0 mmol), and the mixture was stirred at room temperature for one day. Removal of excess Na metal gave a clear yellow solution. The above solution was slowly added to a THF (10 mL) suspension of $[(p\text{-cymene})\text{RuCl}_2]_2$ (306 mg, 0.50 mmol) at -30°C , the mixture was then stirred at room temperature overnight to give a deep brown solution. Removal of the precipitate and solvent gave a deep brownish sticky solid. Chromatographic separation (SiO_2 , 300-400 mesh, using *n*-hexane/ CH_2Cl_2 (4:1 in V/V as eluent) gave **4a** (81 mg, 25%) as a white solid and **5Ru** as a

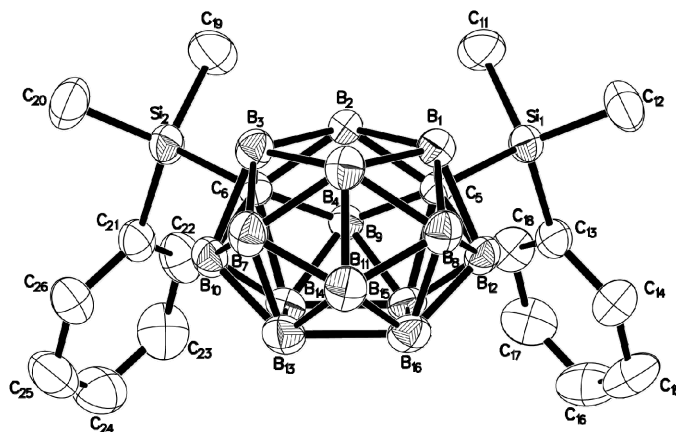
yellow solid (213 mg, 38%). X-ray-quality crystals of **5Ru** were obtained by recrystallization from toluene. M.P.: 130-131°C. ^1H NMR (CD_2Cl_2): δ 5.65 (d, J = 6.3 Hz, 2H, C_6H_4), 5.56 (d, J = 6.3 Hz, 2H, C_6H_4), 2.81 (m, 1H, $\text{C}_6\text{H}_4\text{CH}$), 2.15 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 1.23 (d, J = 6.9 Hz, 6H, CHCH_3), 0.25 (s, 18H, SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 118.9, 109.2, 97.3, 94.4 (C_6H_4), 55.5 (cage C), 29.9 ($\text{C}_6\text{H}_4\text{CH}_3$), 22.7 (CHCH_3), 18.0 ($\text{C}_6\text{H}_4\text{CH}$), 0.2 ($\text{Si}(\text{CH}_3)_3$). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 0.1 (2B), -10.3 (2B), -13.0 (2B), -16.8 (1B), -21.3 (4B), -28.2 (2B). HRMS: m/z calcd for $\text{C}_{18}\text{H}_{45}\text{B}_{13}\text{RuSi}_2$ $[\text{M}]^+$: 559.3411; Found: 559.3420.



Supplementary Figure 6. Molecular structure of **5Ru** (hydrogen atoms are omitted for clarity).

Preparation of 5,6-(DMPS)₂-5,6-C₂B₁₄H₁₄ (5b**).** To a THF (5 mL) solution of **4b** (53 mg, 0.1 mmol) was added finely cut Na metal (7 mg, 0.3 mmol), and the mixture was stirred at room temperature for 3 days. Removal of excess Na metal and THF afforded a colorless solid. CH_2Cl_2 (0.4 mL) was then added, giving a yellow solution. $\text{HBBBr}_2 \cdot \text{SMe}_2$ (0.4 mL of 1.0 M in dichloromethane, 0.4 mmol) was slowly added to the solution at -78°C , the mixture was stirred at this temperature for 1 h, and then at room temperature overnight. After hydrolysis with water and extraction with dichloromethane (5 mL x 3), the solutions were combined, dried with MgSO_4 and concentrated to dryness in vacuo. Chromatographic separation (SiO_2 , 300 ~ 400 mesh, n -hexane/ CH_2Cl_2 (4/1 in v/v) as eluent) afforded **5b** (14 mg, 26%) as a white solid. X-ray-quality crystals of **5b** were obtained by recrystallization from n -hexane. M.P.: 148-149°C. ^1H NMR (400 MHz, CDCl_3): δ 0.46 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 0.59 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 7.48, (m, 6H, SiC_6H_5), 7.64 (d, 4H, SiC_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ -2.7

(Si(CH₃)₂), 59.4 (cage C), 128.1, 130.8, 134.1, 135.2 (SiC₆H₅). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ 14.3 (1B), -0.9 (4B), -13.0 (4B), -16.5 (3B), -18.3 (2B). HRMS: *m/z* calcd for C₁₈H₃₆B₁₄Si₂ [M]⁺: 460.3742. Found: 460.3749.



Supplementary Figure 7. Molecular structure of **5b** (hydrogen atoms are omitted for clarity).

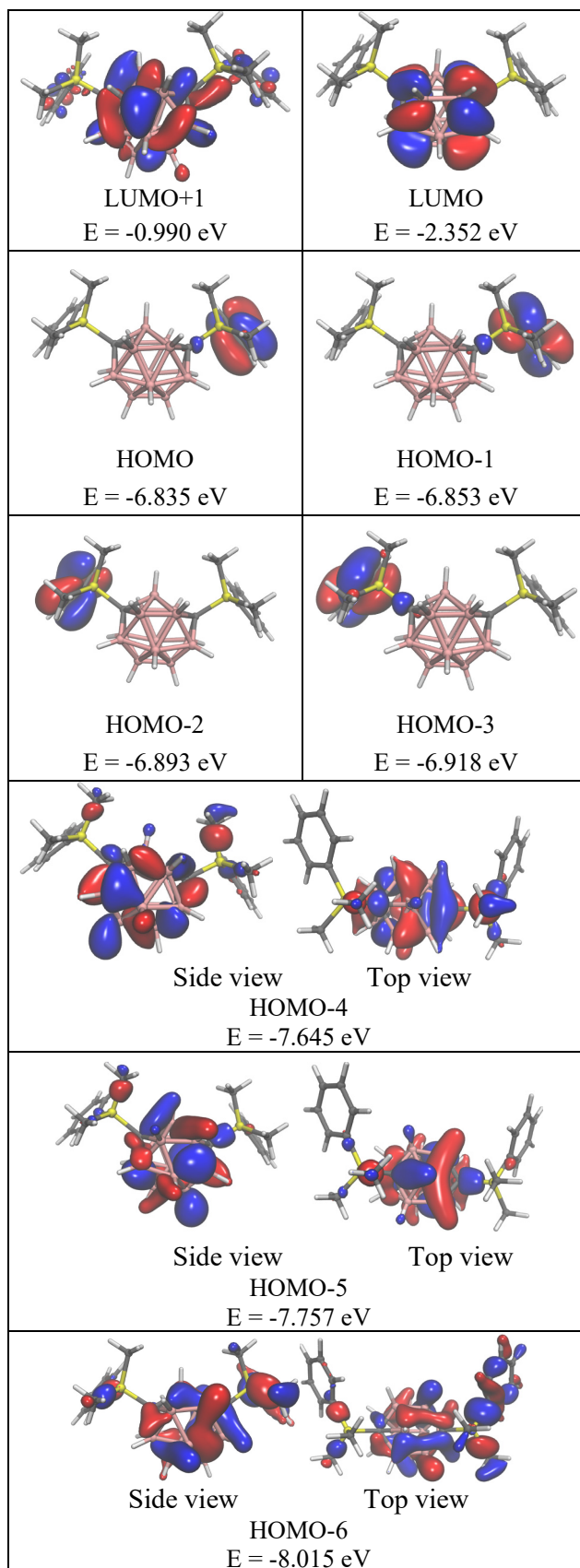
X-ray Structure Determination. All data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo-K α radiation. An empirical absorption correction was applied using the SADABS program.² All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.³ All hydrogen atoms were geometrically fixed using the riding model.

Details of the crystal structures were deposited in the Cambridge Crystallographic Data Centre with CCDC 1997899-1997905 for **2a**, **2b**, **3a**, **3b**, **4b**, **5b**, and **5Ru**, respectively.

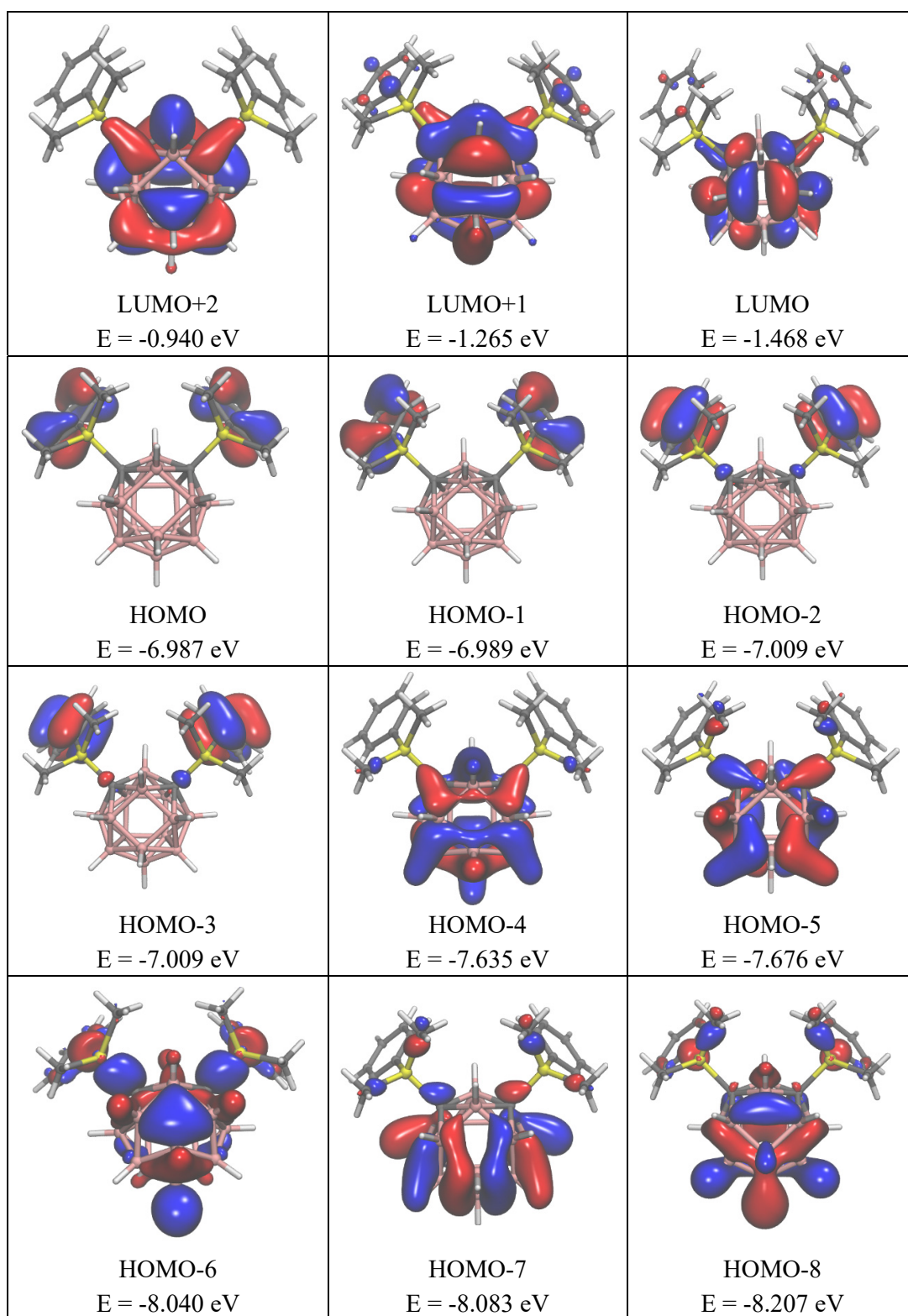
Computational detail

All of these calculations were carried out with the Gaussian 09 program.⁴ Optimization of compounds **4b** and **5b** were performed at B3LYP-D3/6-31G(d,p) level of theory.⁵ Frequency calculations were made to determine the characteristics of all stationary points as energy minima. The orbital energies were calculated at the same level. The graphics of molecular orbitals were produced by using the visualizing software VMD.⁶

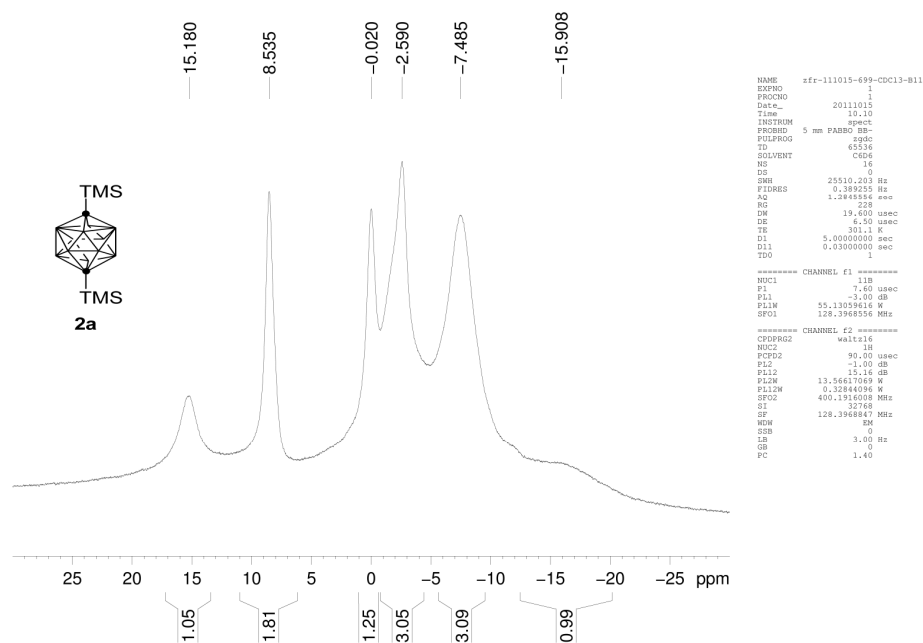
For Cartesian coordinates in .txt format for the optimized structures of **4b** and **5b**, see: Supplementary Data 1 and Supplementary Data 2.



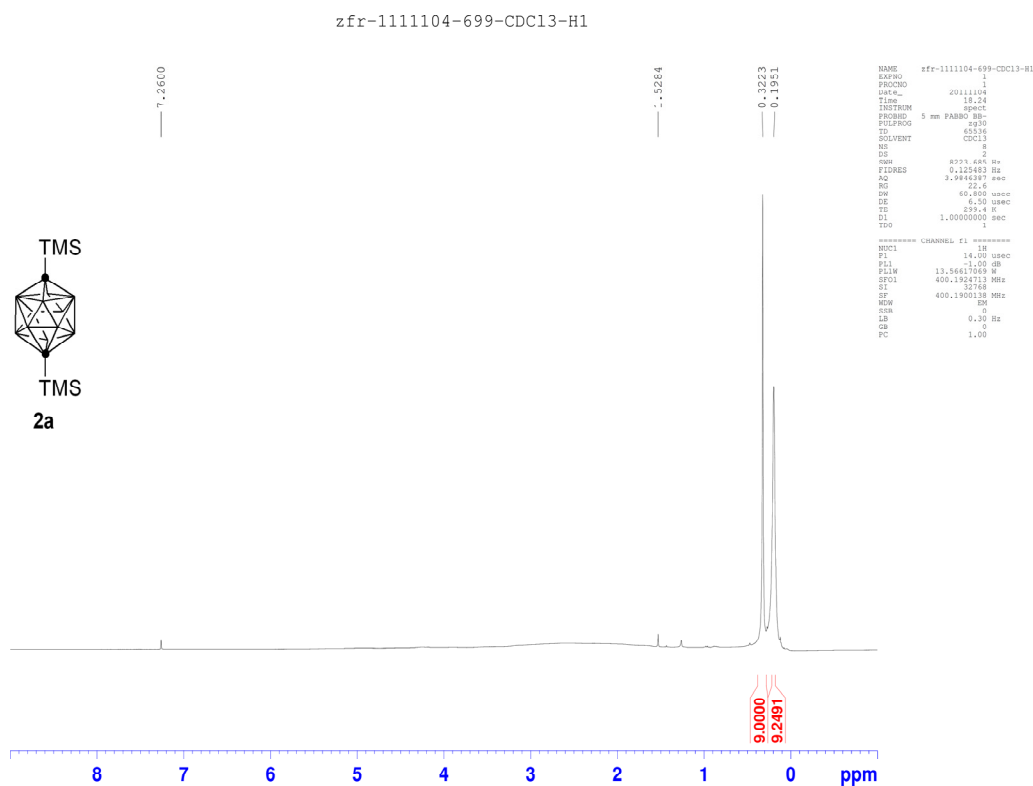
Supplementary Figure 8. Selected calculated molecular orbitals of 4b



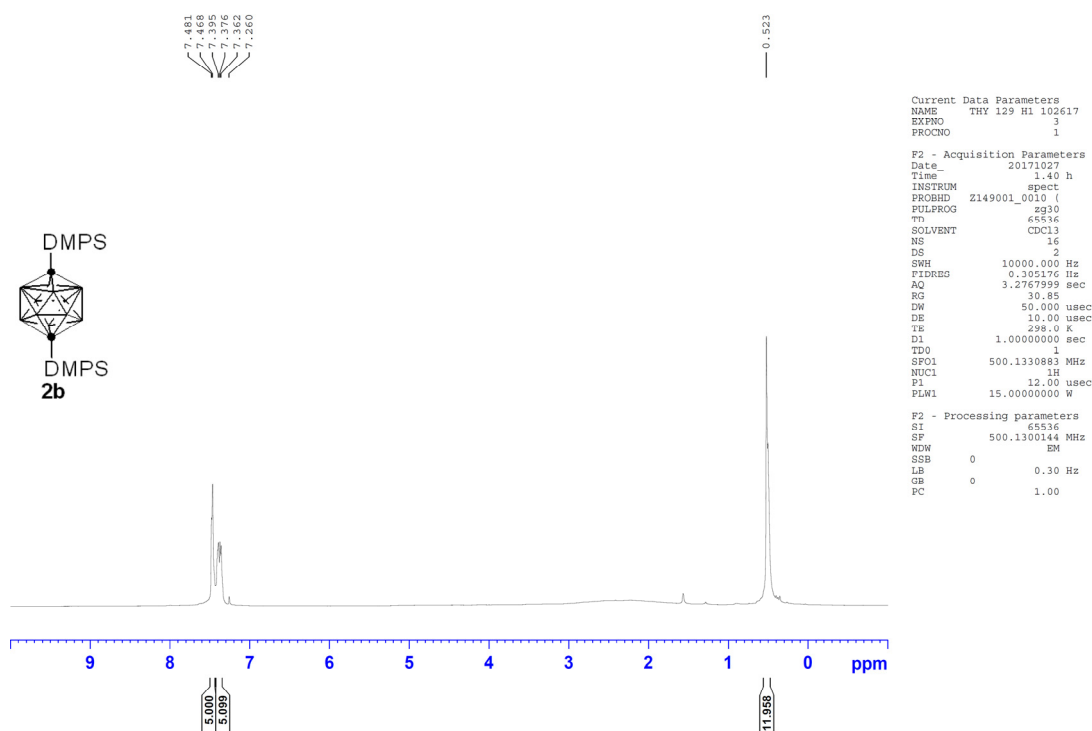
Supplementary Figure 9. Selected calculated molecular orbitals of 5b



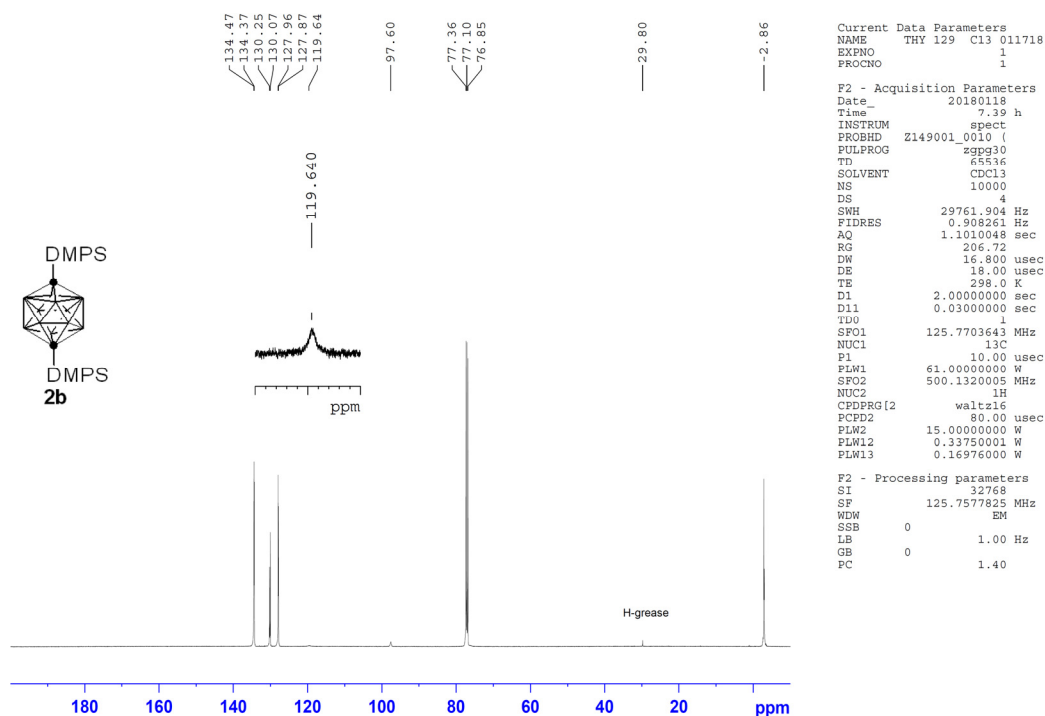
Supplementary Figure 10. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **2a** in CDCl_3 .



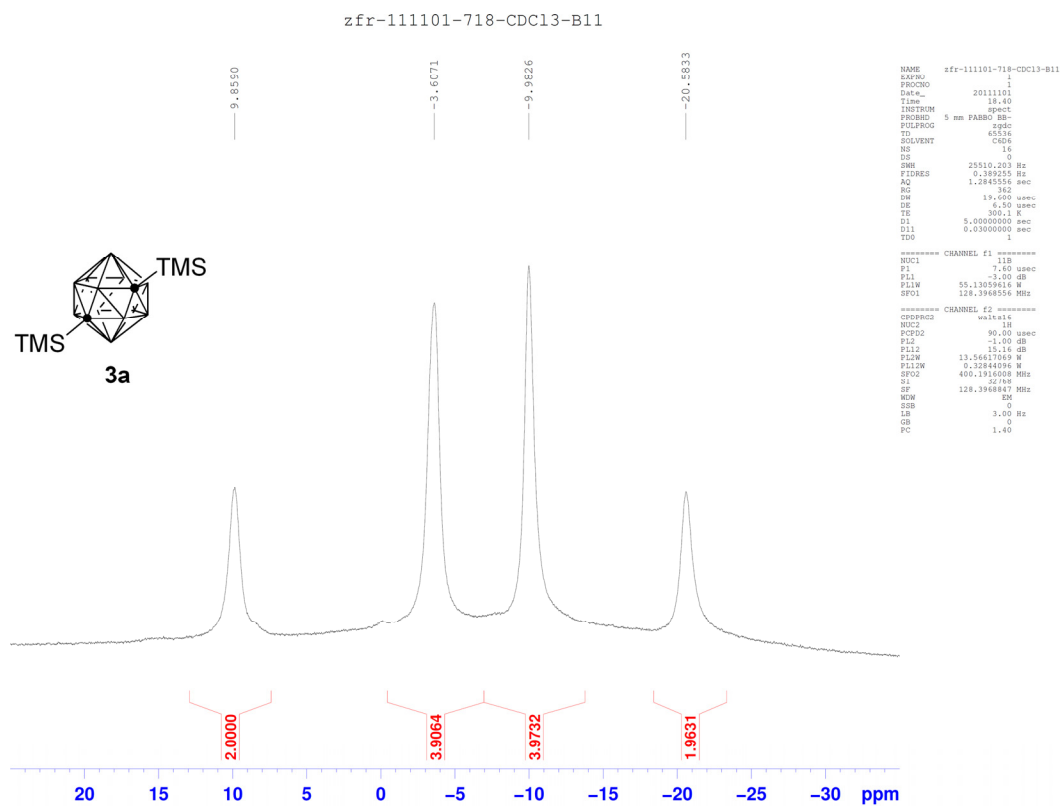
Supplementary Figure 11. ^1H NMR spectrum of **2a** in CDCl_3 .



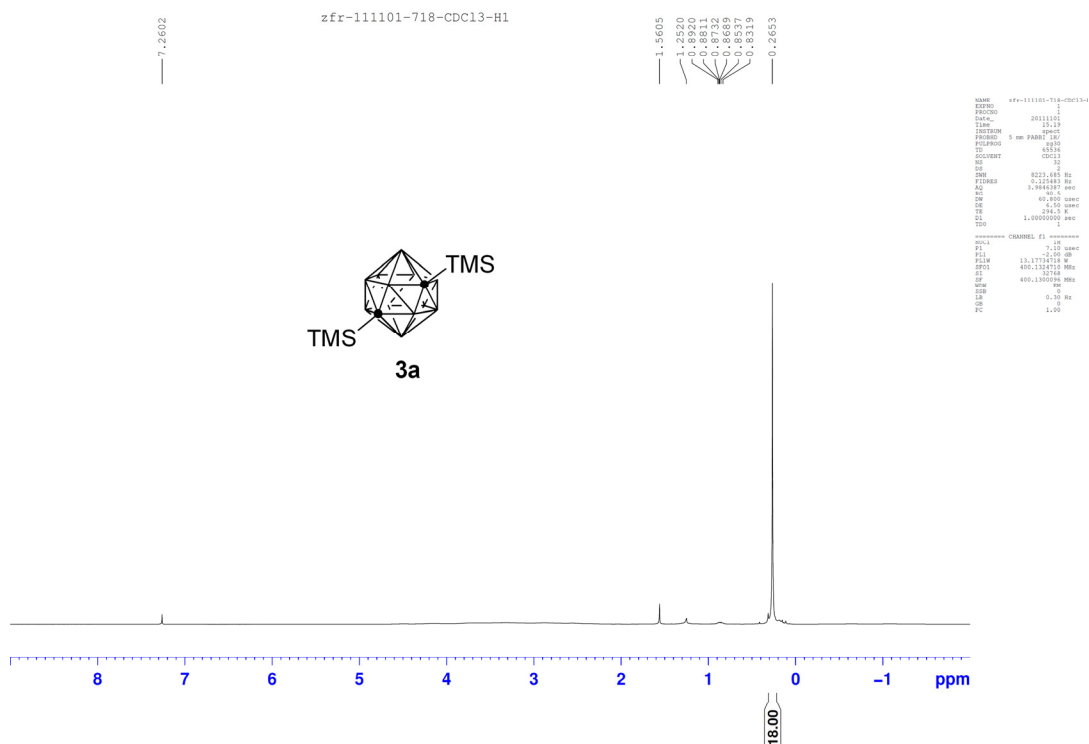
Supplementary Figure 14. ^1H NMR spectrum of **2b** in CDCl_3 .



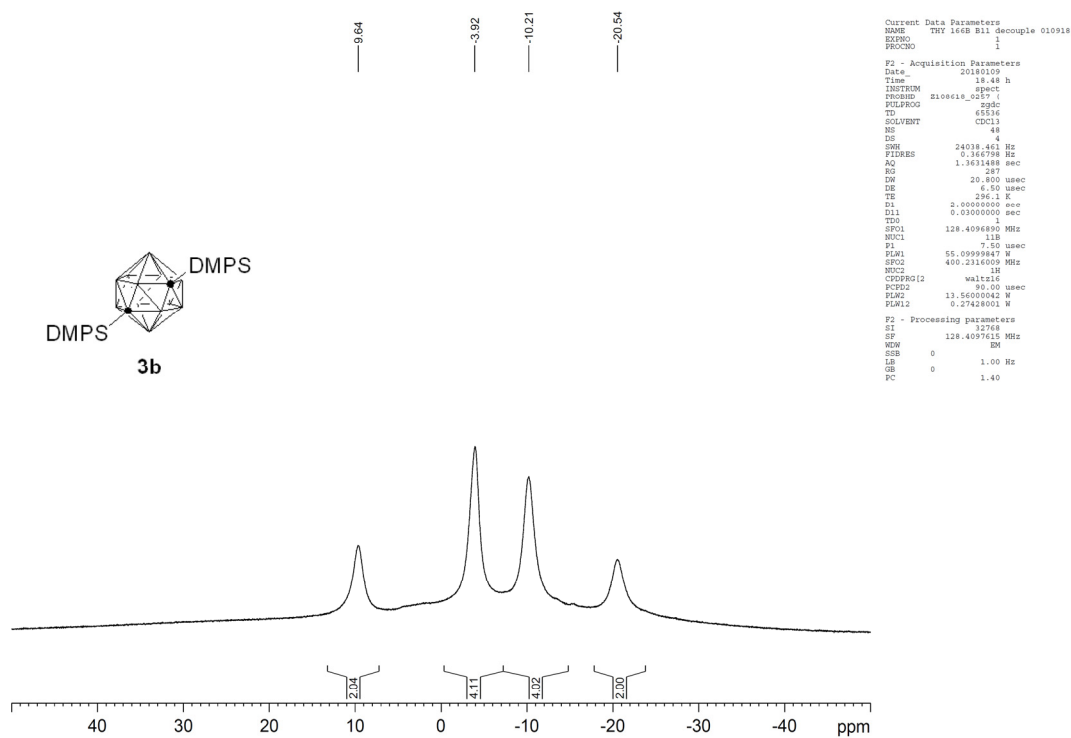
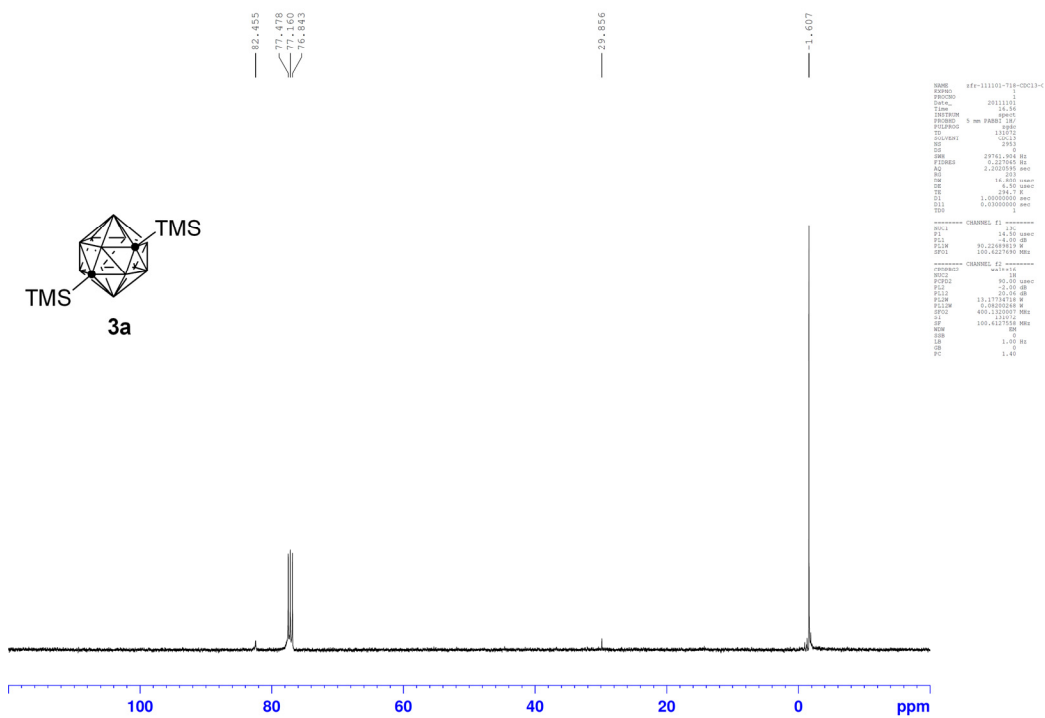
Supplementary Figure 15. ^{13}C NMR spectrum of **2b** in CDCl_3 .

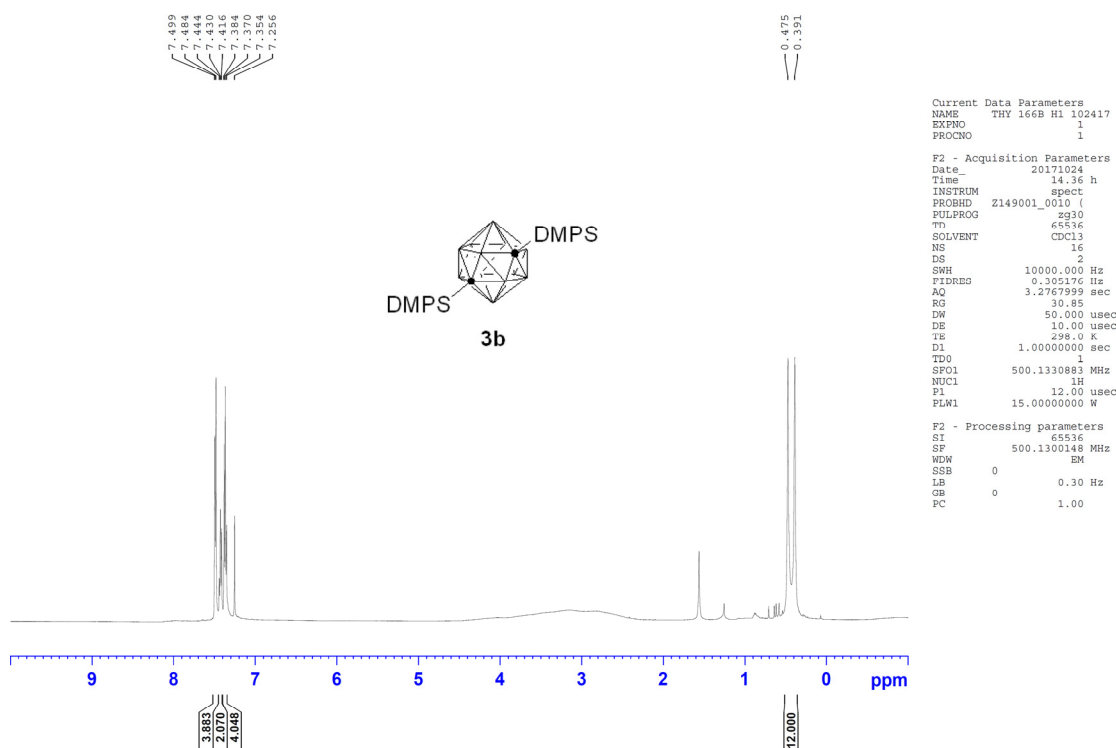


Supplementary Figure 16. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3a** in CDCl_3 .

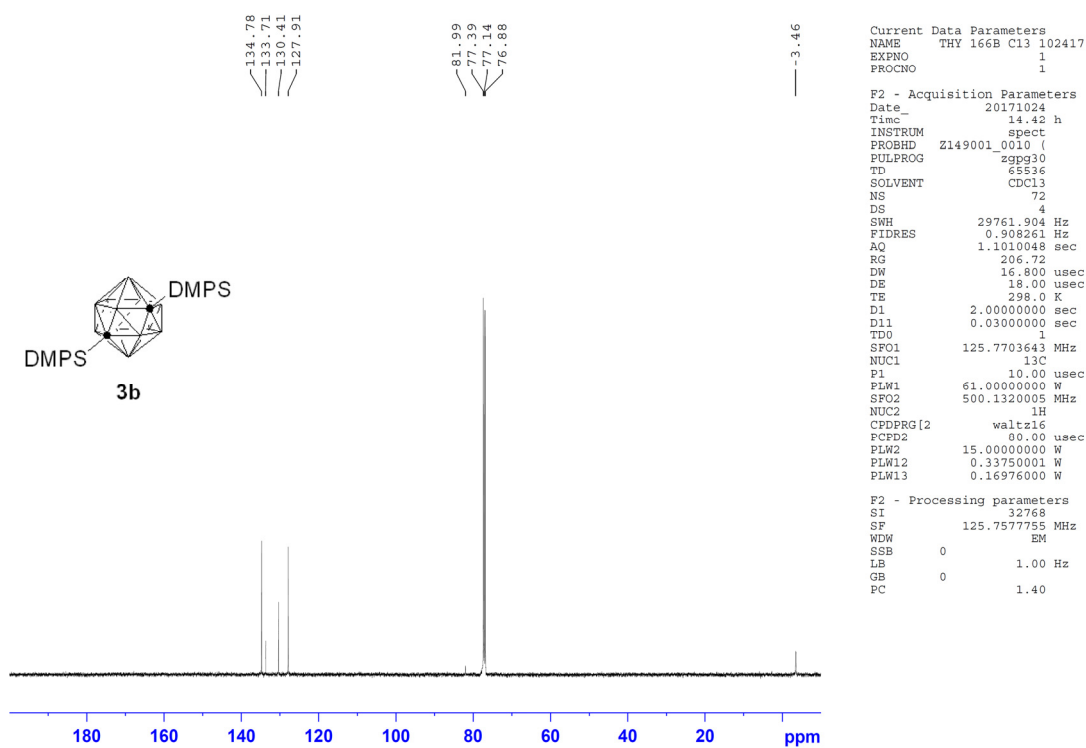


Supplementary Figure 17. ^1H NMR spectrum of **3a** in CDCl_3 .

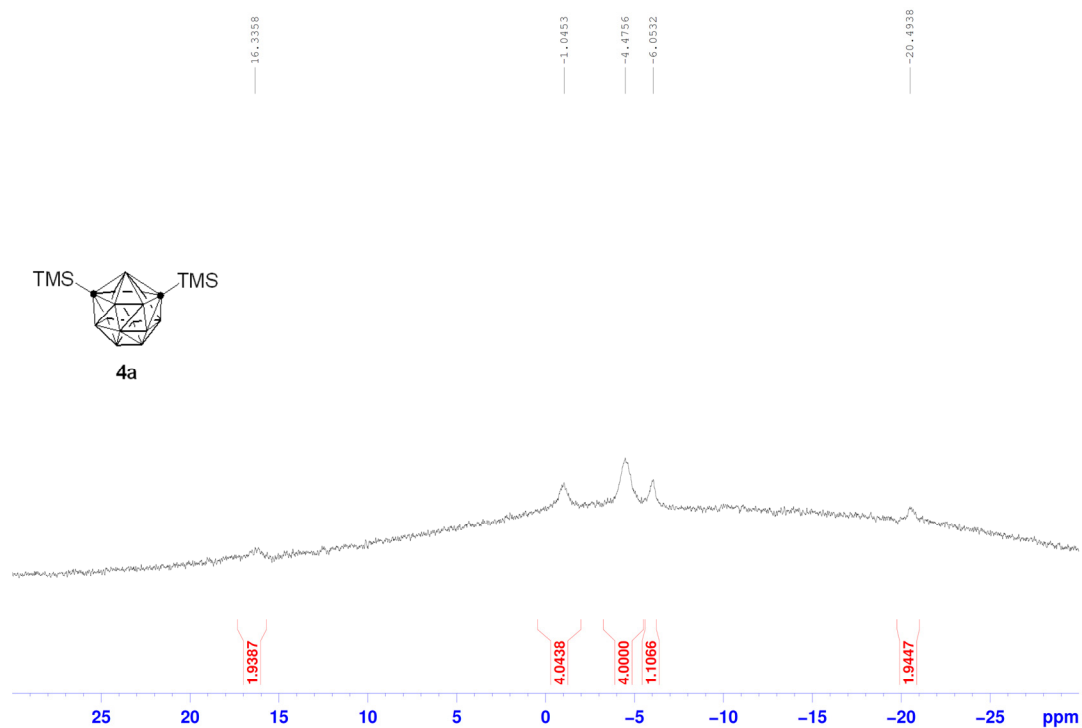




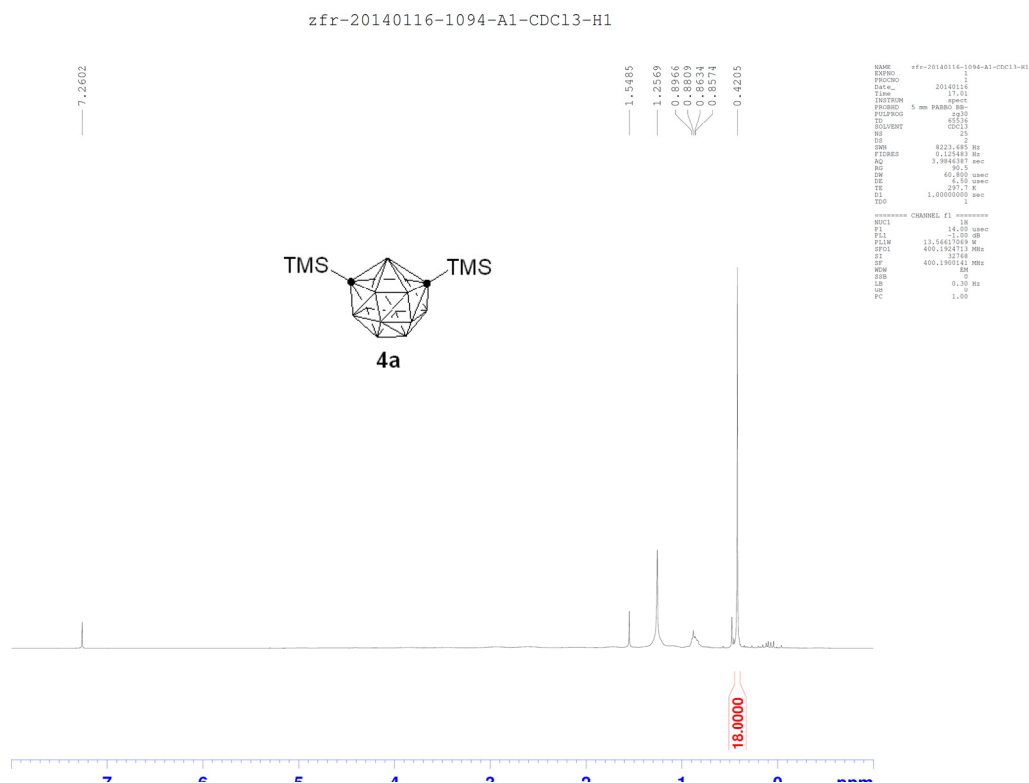
Supplementary Figure 20. ^1H NMR spectrum of **3b** in CDCl_3 .



Supplementary Figure 21. ^{13}C NMR spectrum of **3b** in CDCl_3 .

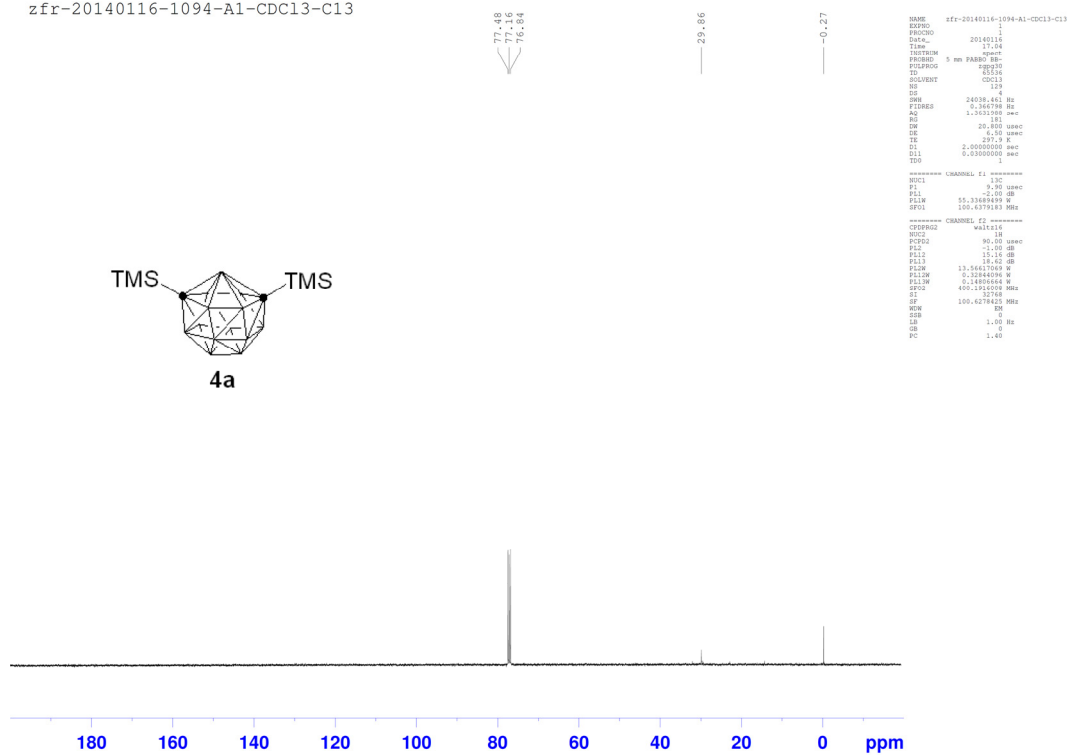


Supplementary Figure 22. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4a** in CDCl_3 .

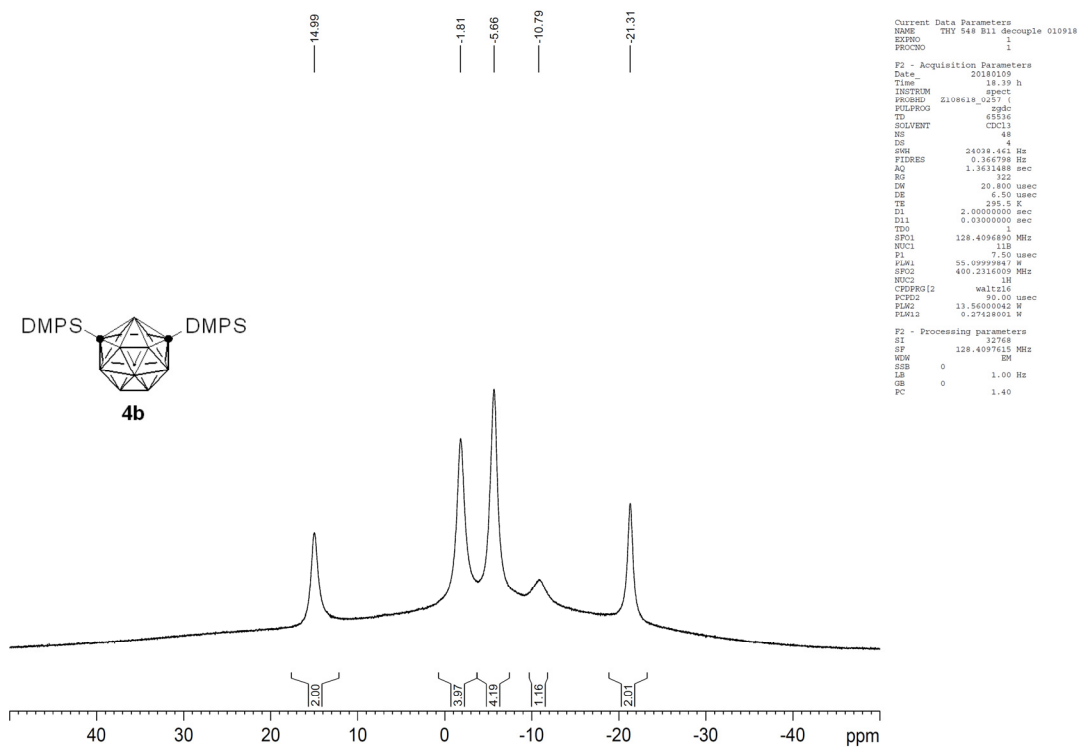


Supplementary Figure 23. ^1H NMR spectrum of **4a** in CDCl_3 .

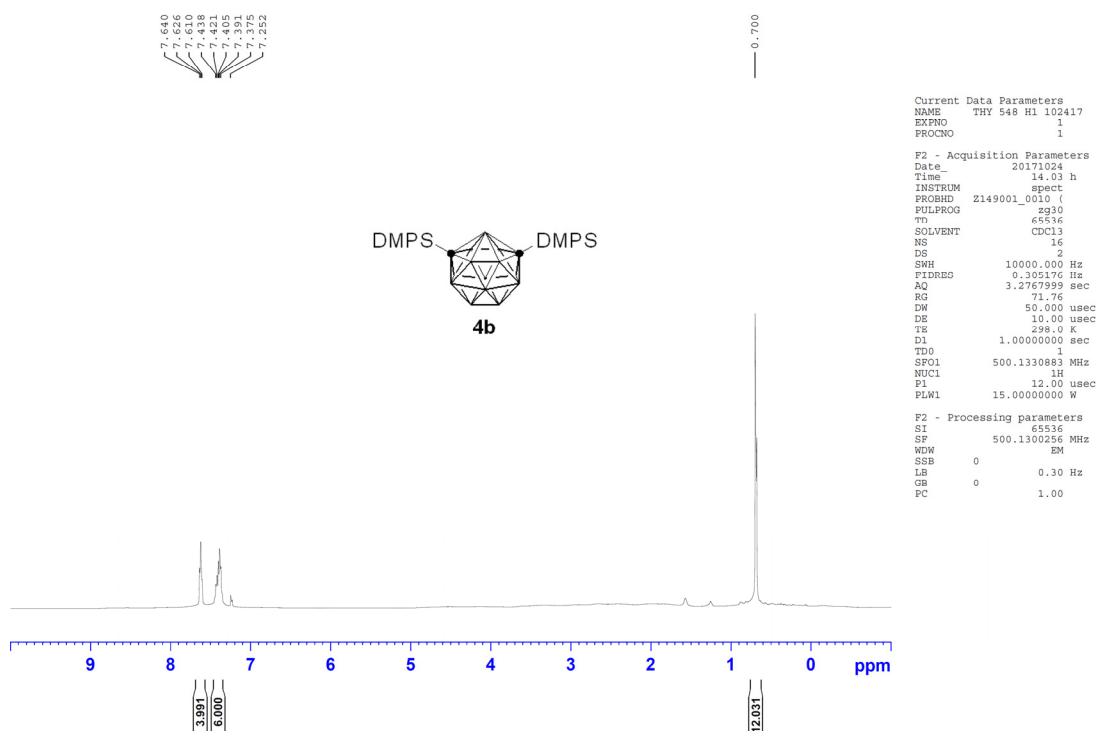
zfr-20140116-1094-A1-CDC13-C13



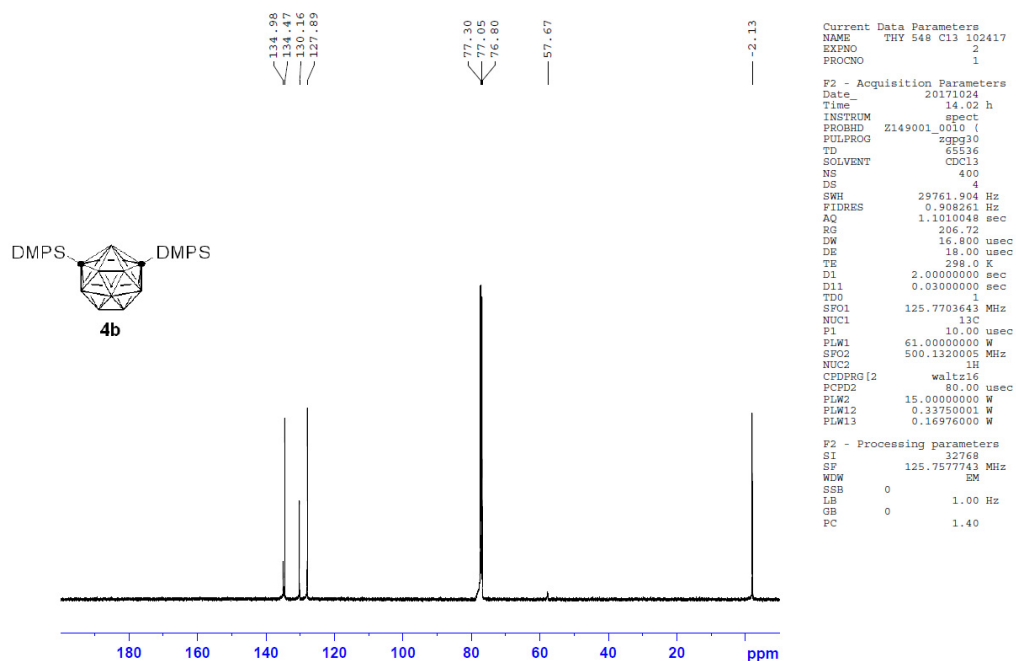
Supplementary Figure 24. ¹³C NMR spectrum of **4a** in CDCl₃.



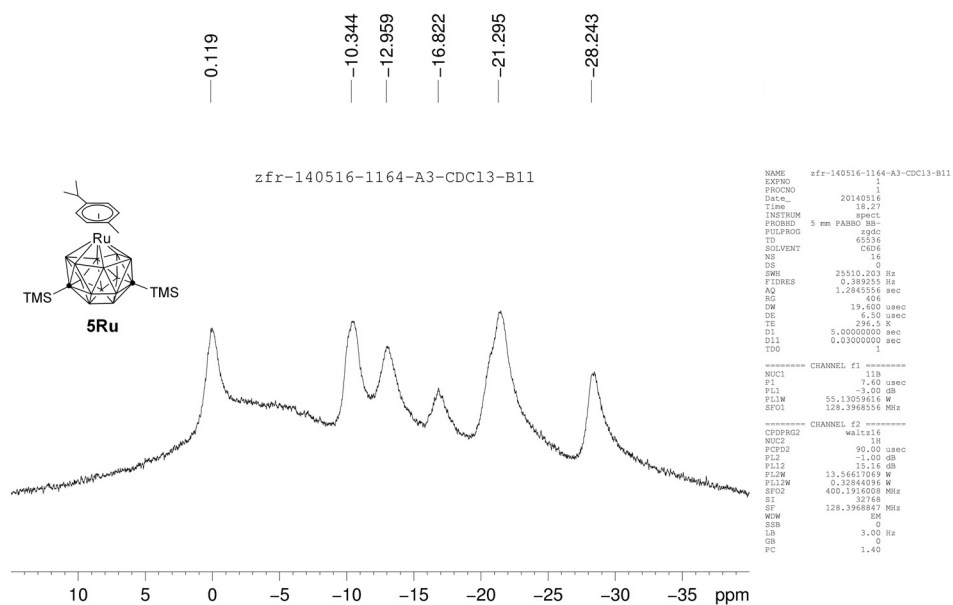
Supplementary Figure 25. ¹¹B{¹H} NMR spectrum of **4b** in CDCl₃.



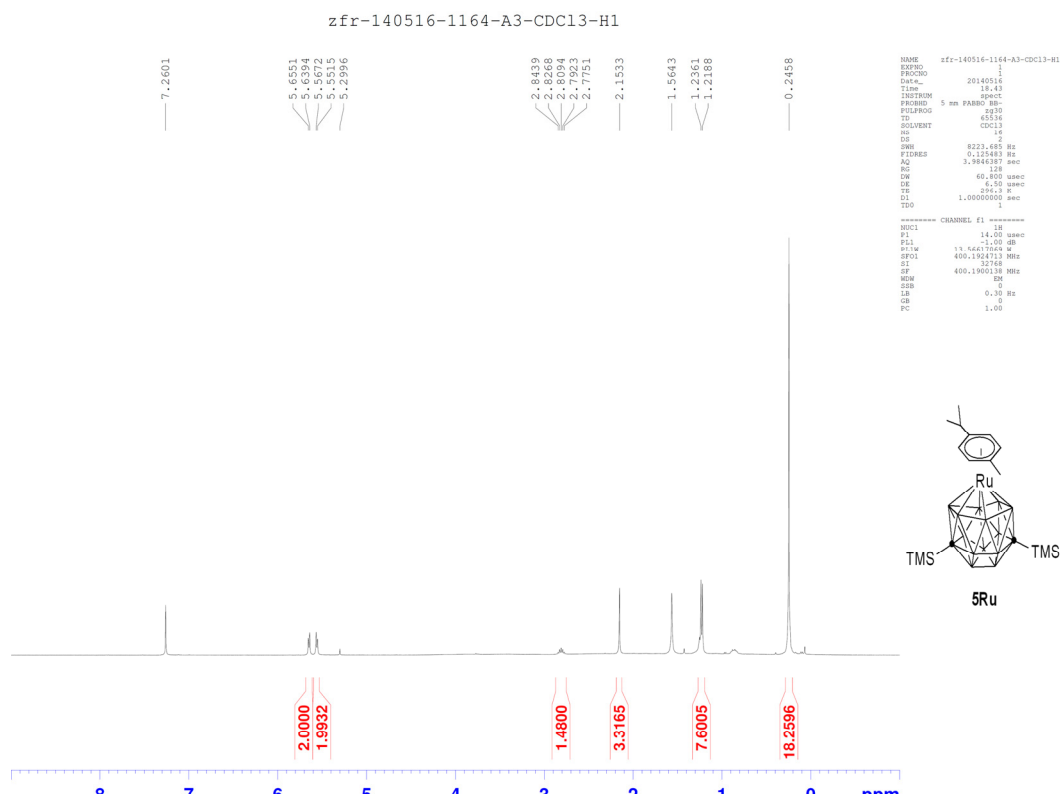
Supplementary Figure 26. ^1H NMR spectrum of **4b** in CDCl_3 .



Supplementary Figure 27. ^{13}C NMR spectrum of **4b** in CDCl_3 .

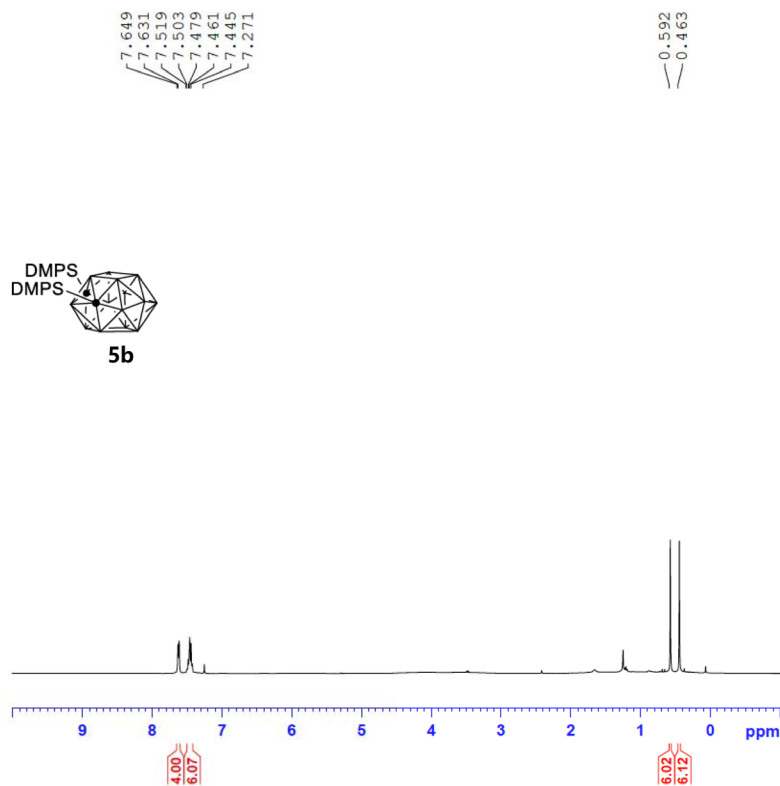


Supplementary Figure 28. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **5Ru** in CDCl_3 .

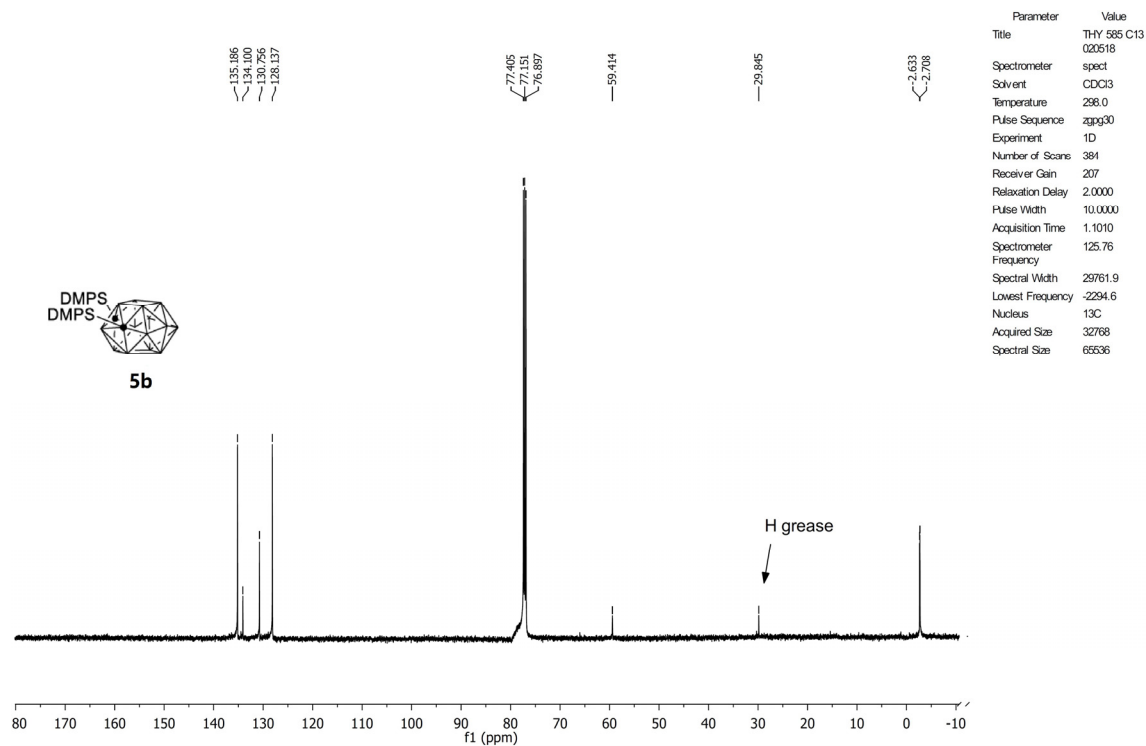


Supplementary Figure 29. ^1H NMR spectrum of **5Ru** in CDCl_3 .





Supplementary Figure 32. ^1H NMR spectrum of **5b** in CDCl_3 .



Supplementary Figure 33. ^{13}C NMR spectrum of **5b** in CDCl_3 .

Supplementary Reference

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