Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information for

Stepwise B-H Bond Activation of a *meta*-Carborane

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Contents

1. Experimental details

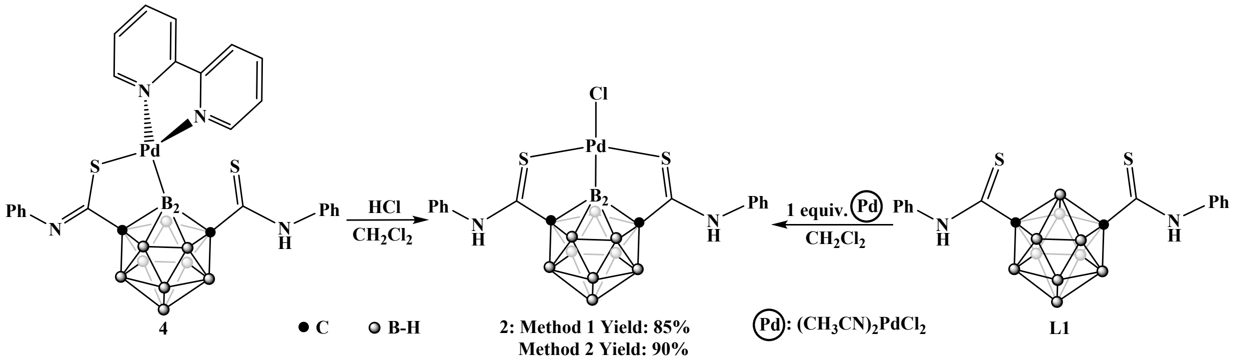
1.1 Materials:

Chemicals of Phenyl isothiocyanate, Potassium bis(trimethylsilyl)amide (KMDH), CH_3COOK and bis(acetonitrile)dichloropalladium(II) were purchased from Energy-chemical, and 1,7-Carborane were received from United Boron (Zhengzhou) Energy Materials S&T LLC. CH_2Cl_2, CH_3OH and HCl (hydrochloric acid) were purchased from Sinopharm Chemical Reagent Co., Ltd. And CH_2Cl_2 was dried over calcium hydride and freshly distilled prior to use. The starting materials (2,2′-bipyridine)dichloropalladium(II)[1] and **1**[2] were prepared by literature methods.

1.2 Methods:

^{11}B NMR spectra were recorded at 160 or 193 MHz spectrometers and externally referenced to $BF_3 \cdot OEt_2$ in C_6D_6 (δ = 0.00 ppm). The ^1H NMR spectra were recorded at 400 MHz spectrometers and ^{13}C NMR were recorded at 101 MHz spectrometers. Proton chemical shift (δH = 7.26 ($CDCl_3$), 3.31 (CD_3OD), 2.50 ((DMSO-d6)) and (δ C = 77.16 ($CDCl_3$), 49.00 (CD_3OD), 39.52 ((DMSO-d6)) are reported relative to the solvent residual peak. Coupling constants are expressed in hertz. Elemental analyses were performed on an Elementar Vario EL III analyzer. IR spectra of the solid samples (KBr tablets) in the range 400-4000 cm^{-1} were recorded on a Nicolet AVATAR-360 IR spectrometer. ESI-MS data were recorded on a Micro TOF II mass spectrometer using electrospray ionization.

1.3 Synthetic Procedures:

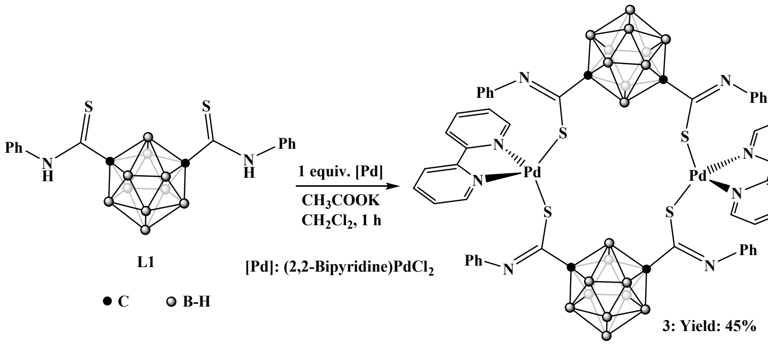


Scheme S1. Synthesis of **2**.

Synthesis of 2

Method 1: $(CH_3CN)_2PdCl_2$ (25.9 mg, 0.1 mmol) and **1** (41.4 mg, 0.1 mmol) were added in CH_2Cl_2 (10 ml) stirring for 2 h. Then the reaction mixture was concentrated and yellow solid was obtained and dried under vacuo to give the **2**: 47.2 mg 85%.^1H NMR (400 MHz; CD_3OD, 298 K): δ = 2.41-2.91 (br, 9H, B-H); 7.39 (d, J = 8 Hz, 4H, Ar-H); 7.43 (d, J = 8 Hz, 2H, Ar-H); 7.51 (t, J = 8 Hz, 4H, Ar-H) ppm. ^{11}B NMR (160 MHz; CD_3OD, 298 K): δ = -4.54; -8.25; -12.83 ppm. $^{13}C\{^1H\}$ NMR (101 MHz; DMSO-d6, 298 K): δ = 85.20 (Carborane-C); 124.61, 126.04, 127.85, 128,97 (Ar-C); 129.25 (N-C-S) ppm. IR (KBr disk, cm^{-1}): v = 494, 531, 654, 690, 745, 762, 1003, 1025, 1043, 1209, 1228, 1412, 1449, 1494, 1530, 1601, 2596, 2887, 3007, 3064, 3103, 3341, 3424 cm^{-1}. Anal. Calcd for **2** $C_{16}\ H_{21}\ B_{10}\ Pd_1\ N_2\ S_2\ Cl_1$: C, 34.60; H, 3.81; N, 5.04. Found: C, 34.76; H, 3.83; N, 5.07. ESI-MS: m/z = 519.1187 (calcd for $[M - Cl]^+$ 519.1185).

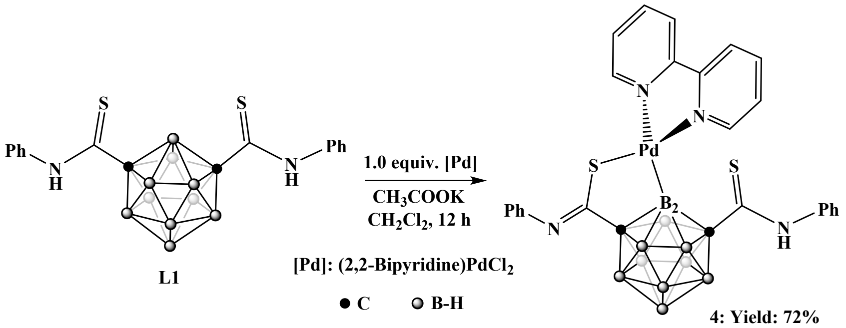
Method 2: The dilute hydrochloric acid (HCl) was added dropwise to the solution of the **4** (67.5 mg, 0.1 mmol) in CH_2Cl_2 (10 ml) at room temperature. The reaction mixture was stirred for 2 h. The solution was concentrated and yellow solid was obtained and dried under vacuo to give the **2**: 49.9 mg 90%.



Scheme S2. Synthesis of **3**.

Synthesis of 3

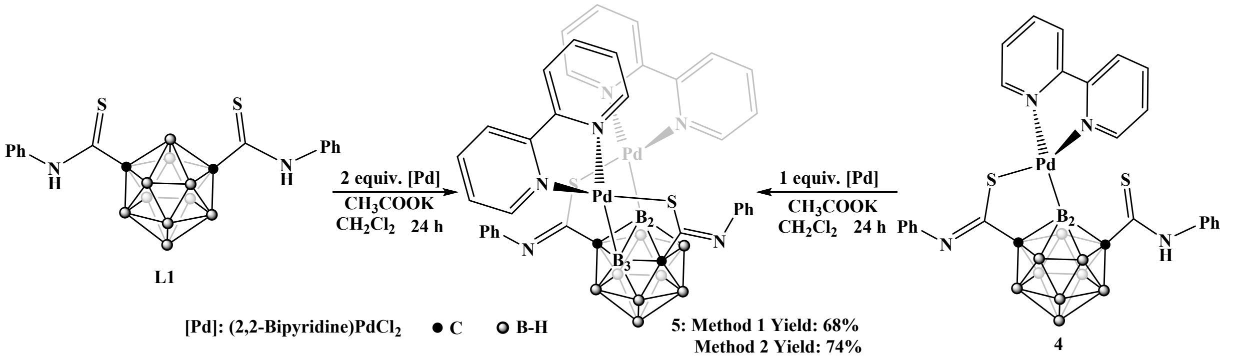
(2,2'-Bipyridine)PdCl$_2$ (33.3 mg, 0.1 mmol), **1** (41.4 mg, 0.1 mmol) and CH$_3$COOK (19.2 mg, 0.2 mmol) were added in CH$_2$Cl$_2$ (10 ml) stirring for 1 h then filtered. The filtrate was concentrated and further purified via silica gel column chromatography (CH$_2$Cl$_2$: CH$_3$OH = 50 : 1). Orange solid were obtained and dried under vacuo to give the **3**: 50.5 mg 45%. However there is no effective way to remove the acetic acid generated by the reaction completely. ^{1}H NMR (400 MHz; DMSO-d6, 298 K): 6.77 (d, J = 8 Hz, 8H, Ar-H); 6.95 (t, J = 8 Hz, 4H, Ar-H); 7.23 (t, J = 6 Hz, 8H, Ar-H); 7.45 (t, J = 8 Hz, 4H, Pyridine-H); 7.95 (t, J = 8 Hz, 4H, Pyridine-H); 8.38 (d, J = 8 Hz, 4H, Pyridine-H); 8.69 (d, J = 4 Hz, 4H, Pyridine-H) ppm. ^{11}B NMR (160 MHz; DMSO-d6, 298 K): δ = -11.12 ppm. IR (KBr disk, cm^{-1}): v = 695, 726, 764, 1068, 1154, 1356, 1446, 1583, 2583, 3440 cm^{-1}. Anal. Calcd for **3** Pd2 B20 C52 N8 S4 H56: C, 46.25; H, 4.18; N, 8.30. Found: C, 46.06; H, 4.16; N, 8.34. ESI-MS: m/z = 1351.3675 (calcd for [M + H]$^+$ 1351.3676).



Scheme S3. Synthesis of **4**.

Synthesis of 4

(2,2'-Bipyridine)PdCl$_2$ (33.3 mg, 0.1 mmol), **1** (41.4 mg, 0.1 mmol) and CH$_3$COOK (19.2 mg, 0.2 mmol) were added in CH$_2$Cl$_2$ (10 ml) stirring for 12 h. Then the reaction mixture was filtered and the precipitate was washed by CH$_2$Cl$_2$. Orange solid was obtained and dried under vacuo to give the **4**: 48.6 mg 72%. ^{1}H NMR (400 MHz; DMSO-d6, 298 K): δ = 2.86-3.98 (br, 9H, B-H); 5.96 (br, 2H, Ar-H); 6.17 (d, J = 8 Hz, 4H, Ar-H); 6.38 (br, 4H, Ar-H); 7.72 (t, J = 8 Hz, 2H, Pyridine-H); 8.22 (t, J = 8 Hz, 2H, Pyridine-H); 8.38 (d, J = 8 Hz, 4H, Pyridine-H) ppm. ^{11}B NMR (193 MHz; DMSO-d6, 298 K): δ = -9.43; -15.80 ppm. ^{13}C{^{1}H} NMR (101 MHz; DMSO-d6, 298 K): δ = 87.98 (Carborane-C); 120.50, 120.78, 124.28, 128.35 (Ar-C); 137.40, 149.35 (N-C-S); 122.59, 127.18, 151.15, 154.39, 155.27 (Pyridine-C) ppm. IR (KBr disk, cm^{-1}): v = 649, 694, 727, 761, 1154, 1342, 1409, 1445, 1469,1482, 1574, 2599, 3350 cm^{-1}. Anal. Calcd for **4** C_{26} H_{28} B_{10} Pd_1 N_4 S_2: C, 46.25; H, 4.18; N, 8.30. Found: C, 46.39; H, 4.22; N, 8.25. ESI-MS: m/z = 675.1885 (calcd for [M + H]$^+$ 675.1877).

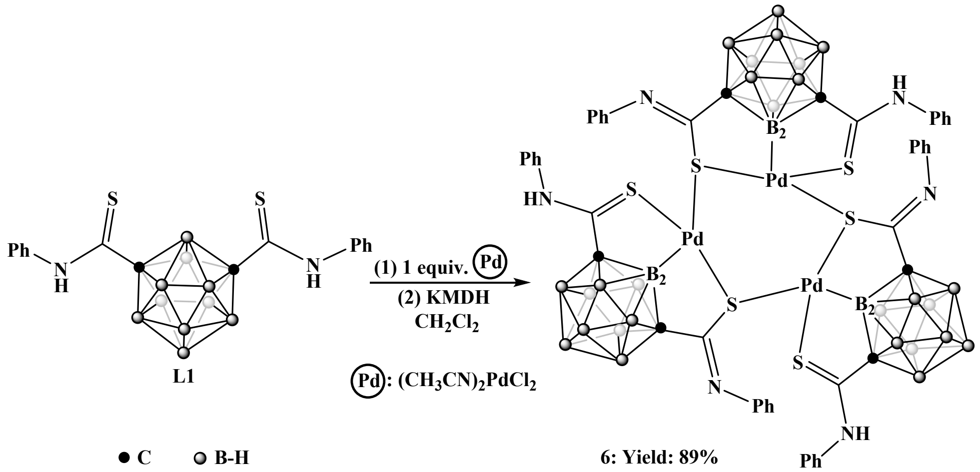


Scheme S4. Synthesis of **5**.

Synthesis of 5

Method 1: (2,2’-Bipyridine)$PdCl_2$ (33.3 mg, 0.1 mmol), **1** (20.7 mg, 0.05 mmol) and CH_3COOK (9.8 mg, 0.1 mmol) were added in CH_2Cl_2 (10 ml) stirring for 24 h. Then the reaction mixture was filtered and the precipitate was washed by CH_2Cl_2. Orange solid was obtained and dried under vacuo to give the **5**: 31.7 mg 68%. ^1H NMR (400 MHz; DMSO-d6, 298 K): δ = 6.84 (d, J = 8 Hz, 4H, Ar-H); 7.01 (d, J = 8 Hz, 2H, Ar-H); 7.30 (t, J = 4 Hz, 4H, Ar-H); 7.76 (t, J = 6 Hz, 4H, Pyridine-H); 8.14 (d, J = 4 Hz, 4H, Pyridine-H); 8.37 (q, J = 8 Hz, 4H, Pyridine-H); 8.55 (d, J = 8 Hz, 2H, Pyridine-H); 8.68 (d, 2H, Pyridine-H) ppm. ^{11}B NMR (160 MHz; DMSO-d6, 298 K): δ = -11.99 ppm. $^{13}C\{^1H\}$ NMR (101 MHz; DMSO-d6, 298 K): δ = 120.37, 120.52, 120.70, 124.13, 127.06, 128.19, 128.53, 155.19 (Ar-C and Pyridine-C); 137.25, 149.22 (N-C-S) ppm. IR (KBr disk, cm^{-1}): ν = 652, 695, 760, 1019, 1156, 1345, 1411, 1574, 2592 cm^{-1}. Anal. Calcd for **5** $C_{36}H_{32}B_{10}Pd_2N_6S_2$: C, 46.31; H, 3.45; N, 9.00. Found: C, 46.13; H, 3.48; N, 9.06. ESI-MS: m/z = 936.1437 (calcd for $[M + H]^+$ 936.1451).

Method 2: (2,2’-Bipyridine)$PdCl_2$ (33.3 mg, 0.1 mmol), the **4** (67.5 mg, 0.1 mmol) and CH_3COOK (9.8 mg, 0.1 mmol) were added in CH_2Cl_2 (10 ml) stirring for 24 h. Then the reaction mixture was filtered and the precipitate was washed by CH_2Cl_2. Orange solid was obtained and dried under vacuo to give the **5**: 69.0 mg 74%.



Scheme S5. Synthesis of **6**.

Synthesis of 6

$(CH_3CN)_2PdCl_2$ (25.9 mg, 0.1 mmol) and **1** (41.4 mg, 0.1 mmol) were added in CH_2Cl_2 (10 ml) stirring for 2 h. Then KMDH (0.2 mL) was added at room temperature. And the resulting mixture was stirred for 2 h then filtered. The filtrate was concentrated and further purified via silica gel column chromatography (CH_2Cl_2 : CH_3OH = 50 : 1). Orange red solid were obtained and dried under vacuo to give the **6**: 46.1 mg 89%. ^1H NMR

(400 MHz; $CDCl_3$, 298 K): δ = 2.01-3.19 (br, 27H, B-H); 6.88~7.24 (15H, Ar-H); 7.41~7.59 (15H, Ar-H); 8.46 (s, 3H, N-H) ppm. ^{11}B NMR (160 MHz; $CDCl_3$, 298 K): δ = -2.56; -9.66 ppm. $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3/CD_3OD$, 298 K): δ = 84.86 (Carborane-C); 121.32, 124.72, 128.26, 129.05 (Ar-C); 137.20, 149.04 (N-C-S) ppm. IR (KBr disk, cm^{-1}): v = 697, 756, 804, 895, 924, 955, 977, 1003, 1026, 1070, 1059, 1197, 1226, 1407, 1448, 1485, 1495, 1525, 1582, 1610, 2599, 1962, 3339 cm^{-1}. Anal. Calcd for **6** $C_{48}H_{60}B_{30}Pd_3N_6S_6$: C, 37.03; H, 3.88; N, 5.40. Found: C, 37.22; H, 3.90; N, 5.43. ESI-MS: m/z = 1557.3402 (calcd for $[M + H]^+$ 1557.3413).

2. NMR Spectra

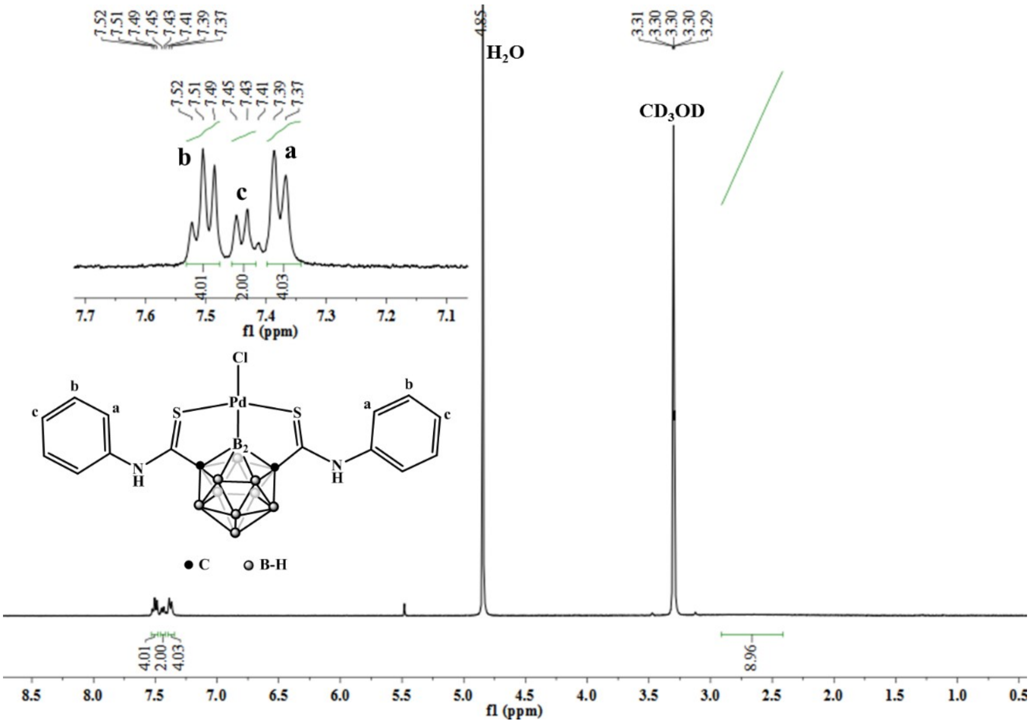


Fig. S1. ^{1}H NMR (400 MHz, CD$_3$OD, 298 K) of **2**.

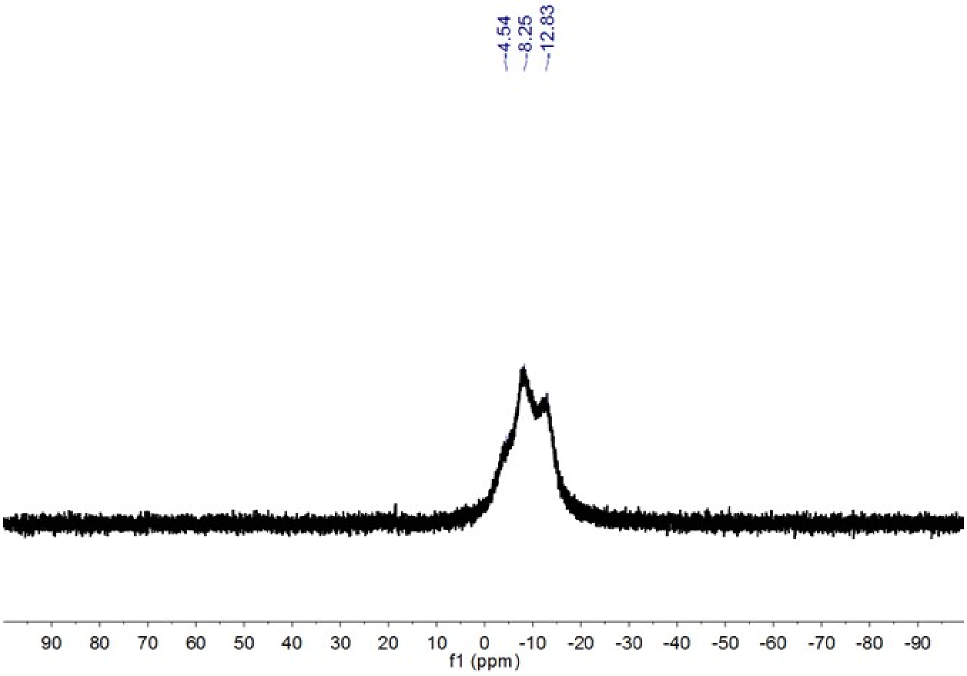


Fig. S2. ^{11}B NMR (160 MHz, CD$_3$OD, 298 K) of **2**.

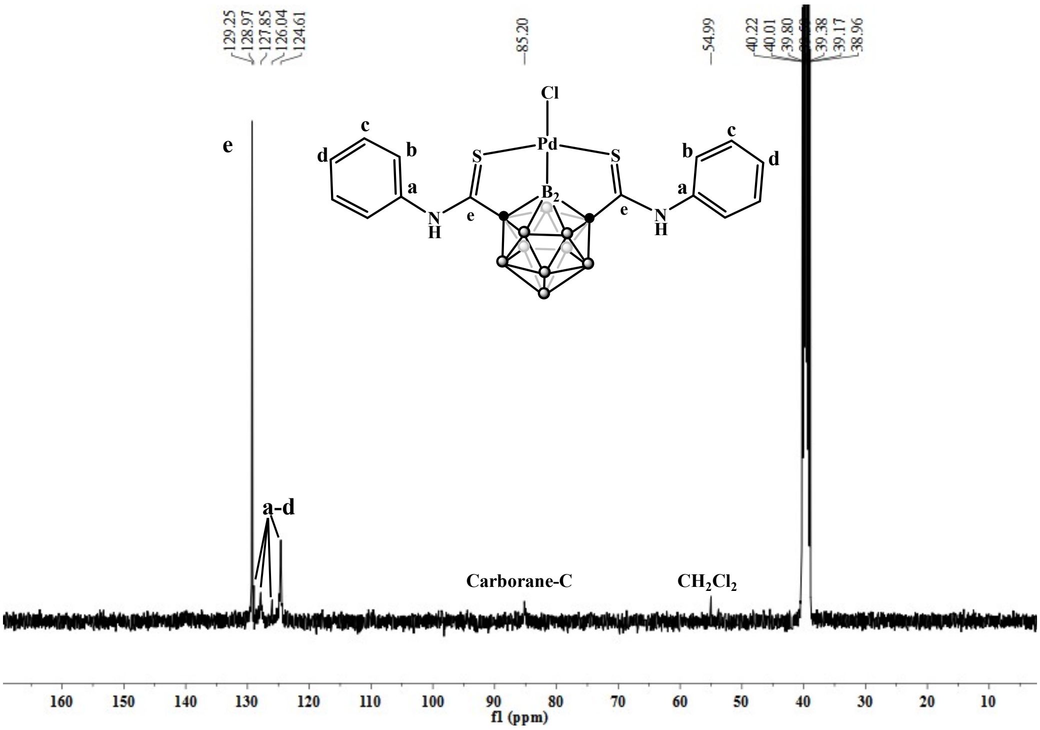


Fig. S3. $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d6, 298 K) of **2.**

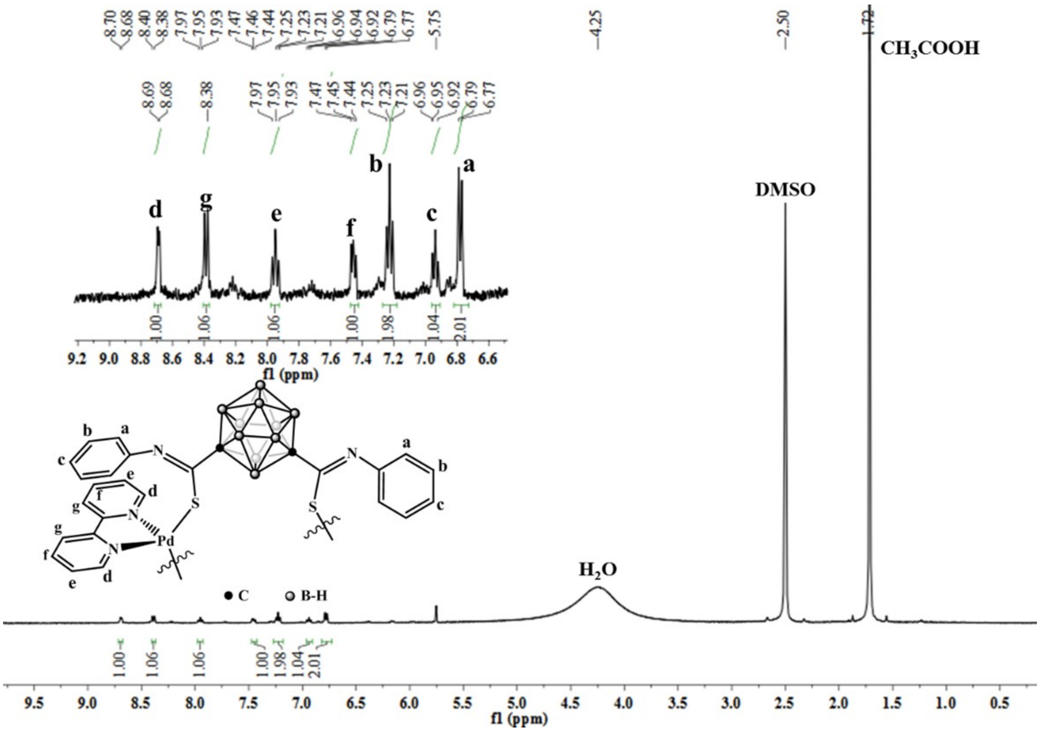


Fig. S4. ^1H NMR (400 MHz, DMSO-d6, 298 K) of **3**.

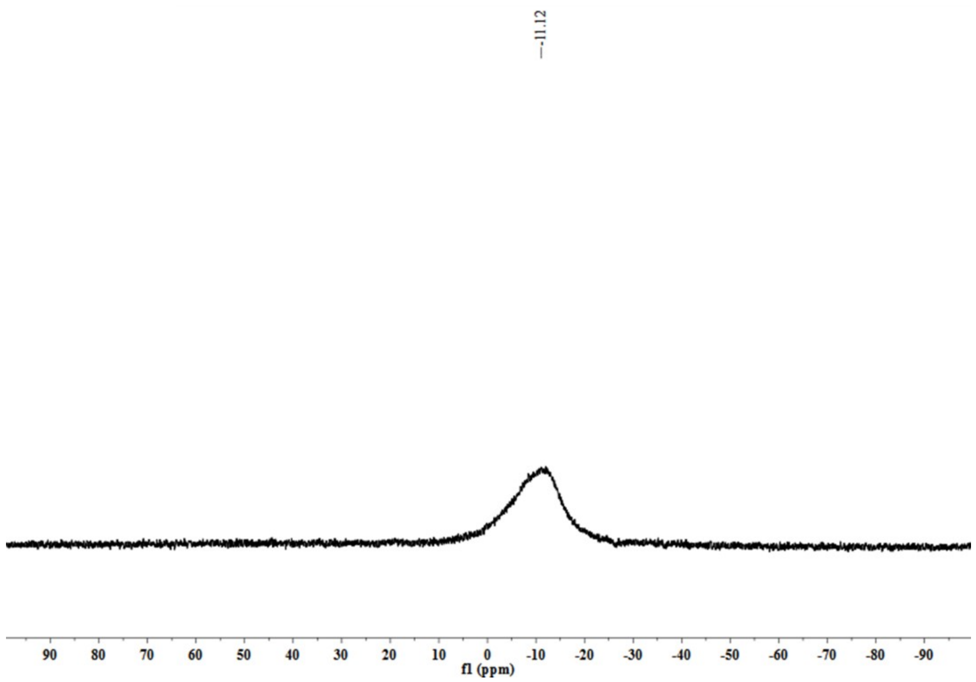


Fig. S5. ^{11}B NMR (160 MHz, DMSO-d6, 298 K) of **3**.

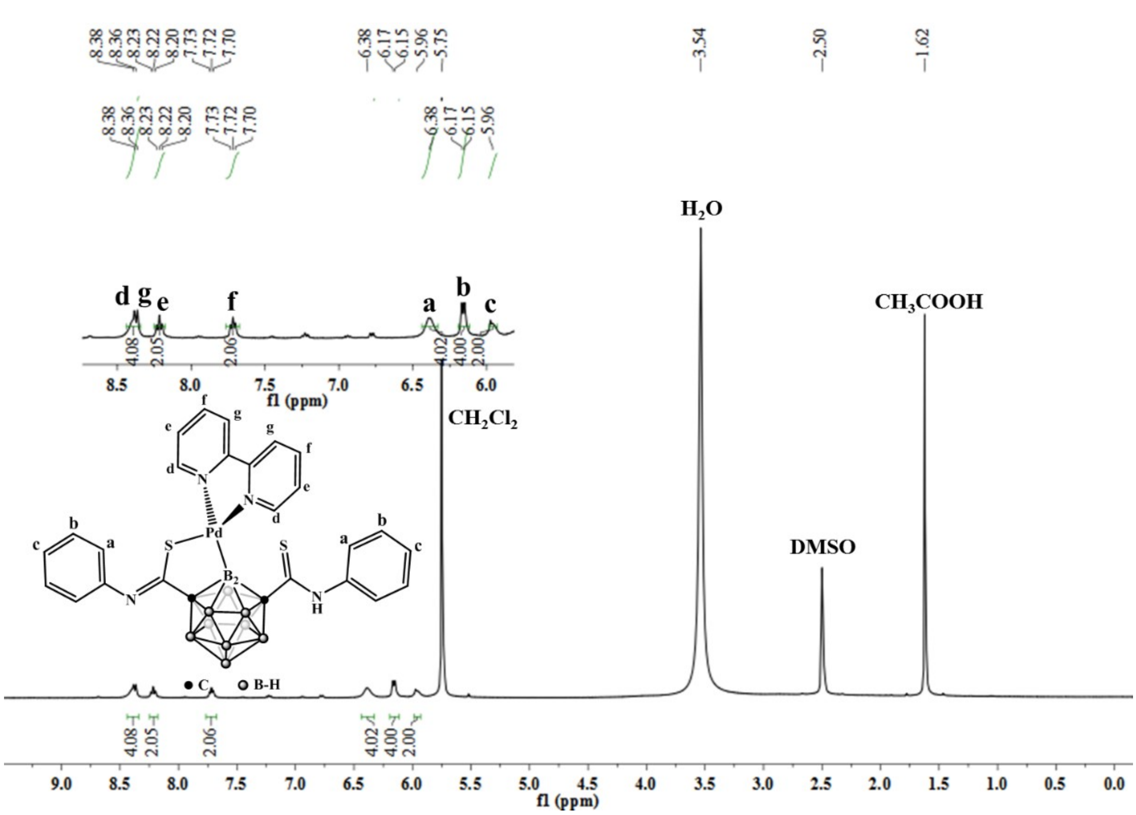


Fig. S6. ^{1}H NMR (400 MHz, DMSO-d6, 298 K) of **4**.

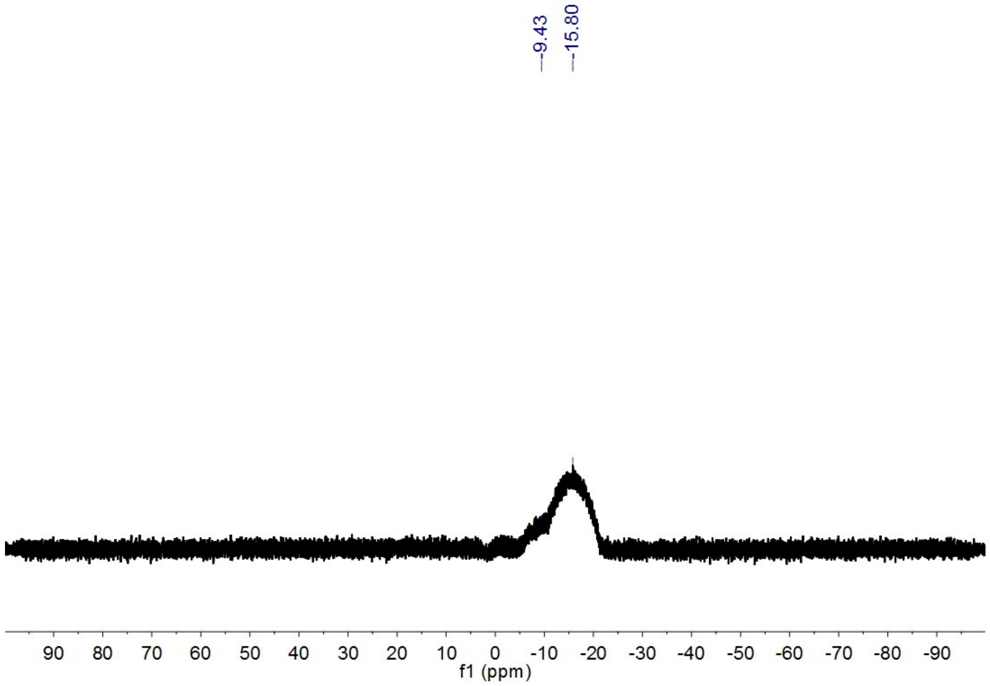


Fig. S7. ^{11}B NMR (193 MHz, DMSO-d6, 298 K) of **4**.

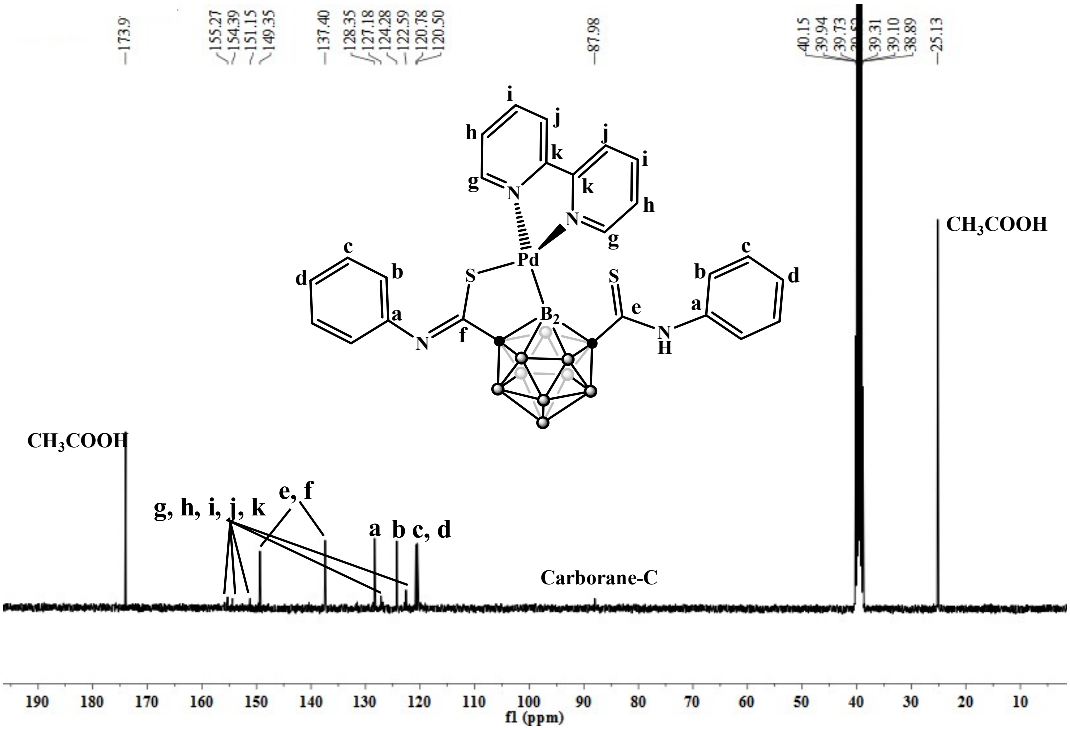


Fig. S8. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d6, 298 K) of **4**.

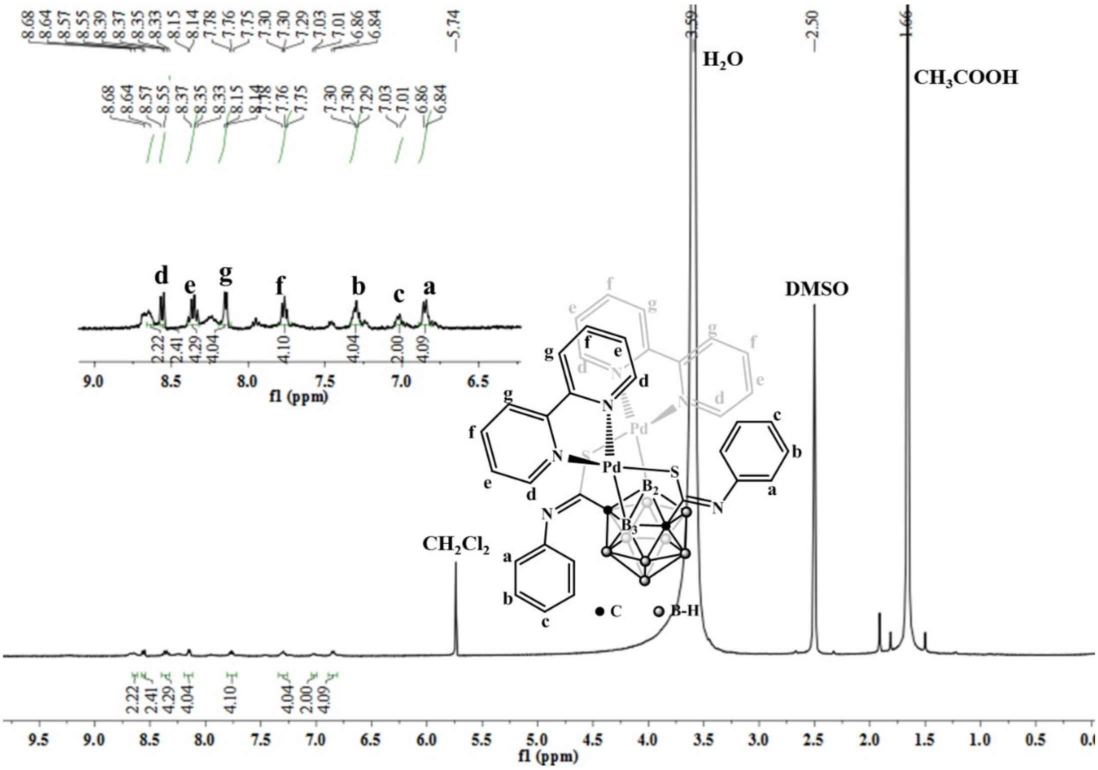


Fig. S9. ^{1}H NMR (400 MHz, DMSO-d6, 298 K) of **5**.

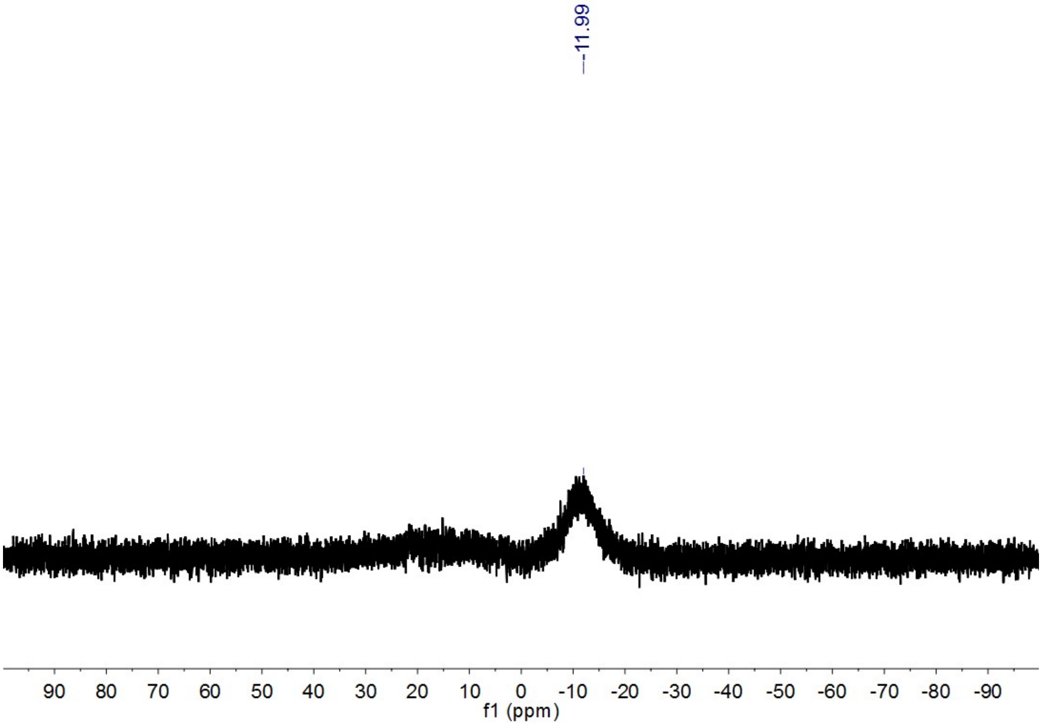


Fig. S10. ^{11}B NMR (160 MHz, DMSO-d6, 298 K) of **5**.

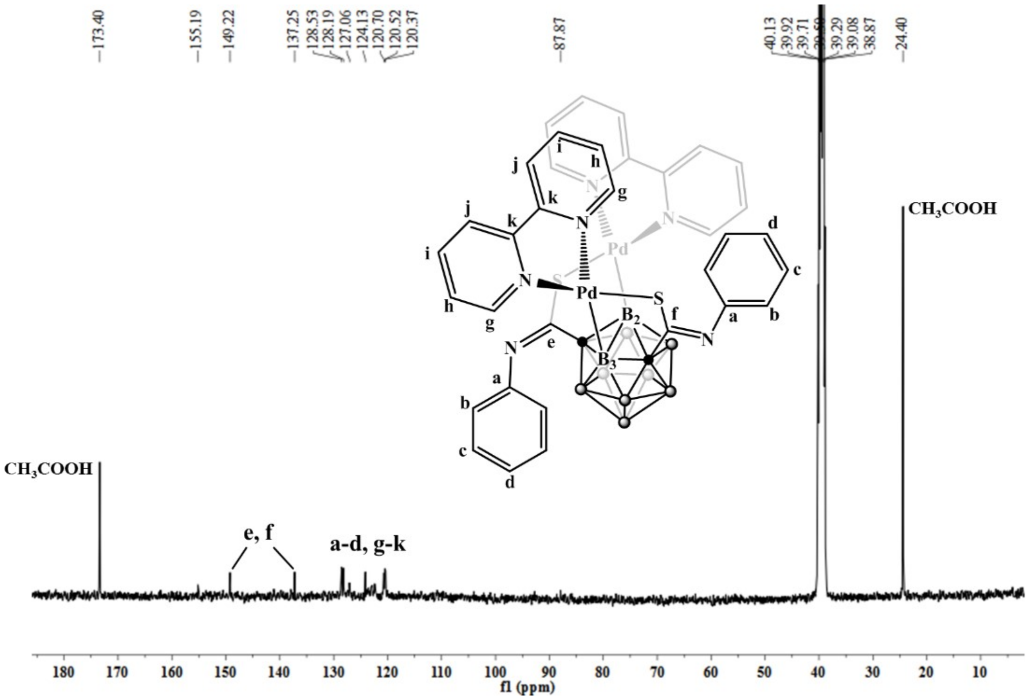


Fig. S11. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d6, 298 K) of **5**.

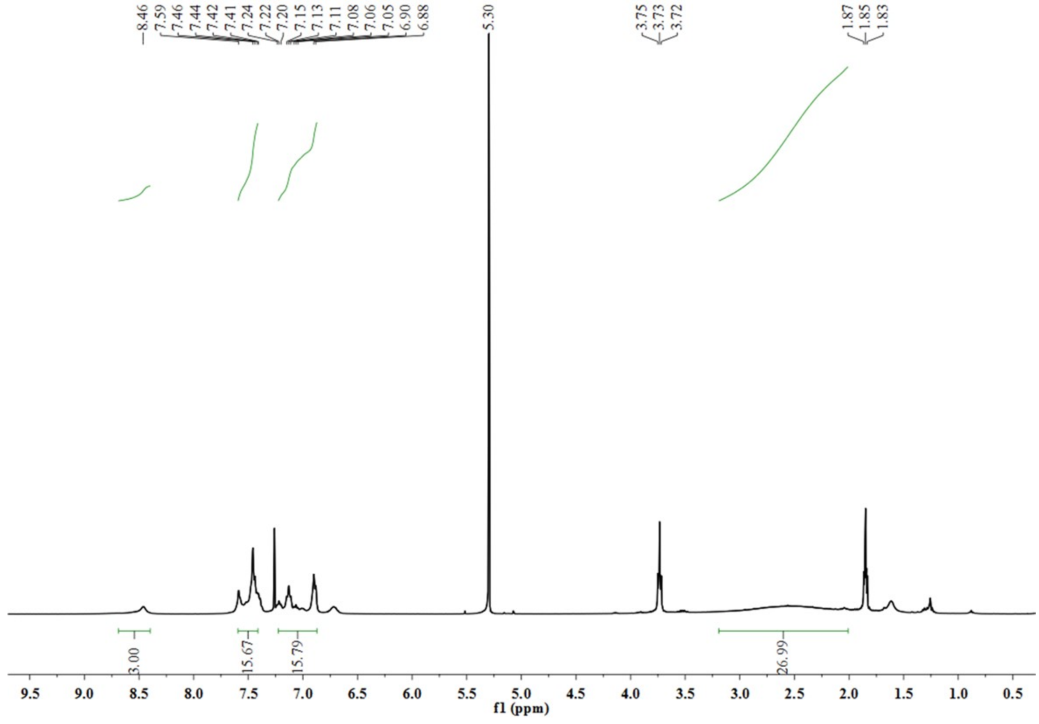


Fig. S12. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) of **6**.

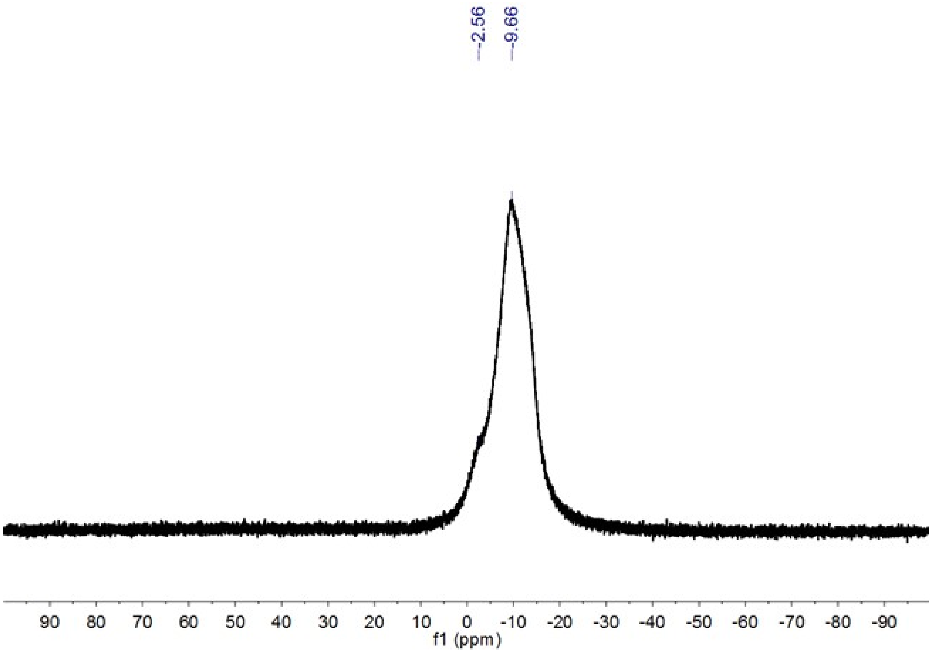


Fig. S13. ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) of **6**.

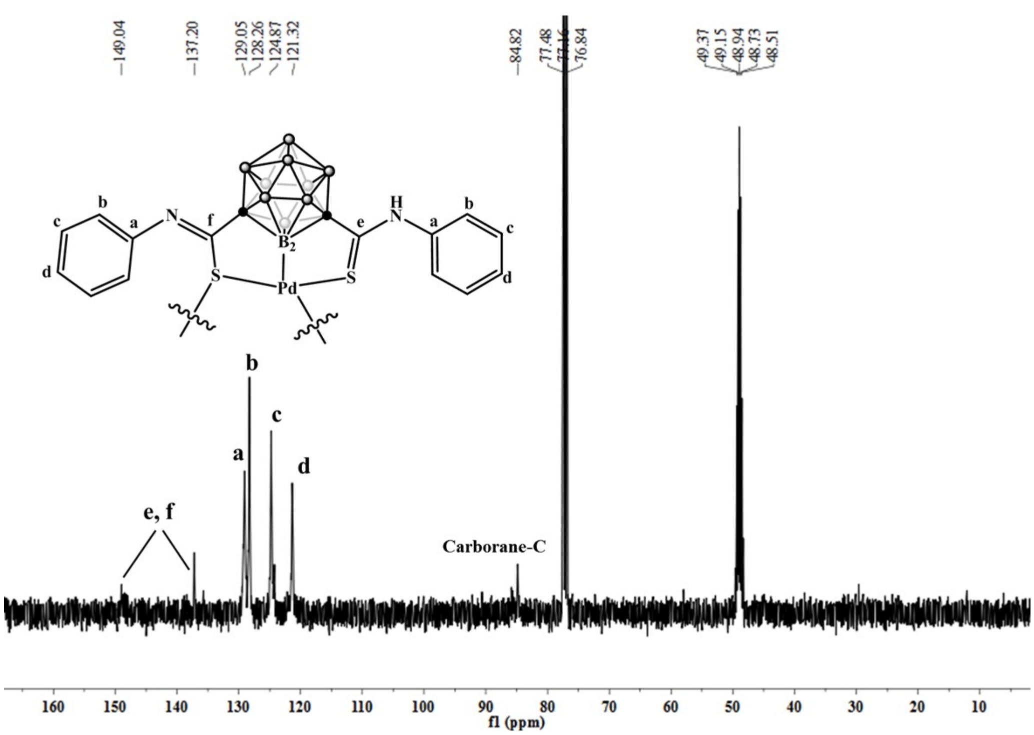


Fig. S14. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3/CD_3OD$, 298 K) of **6**.

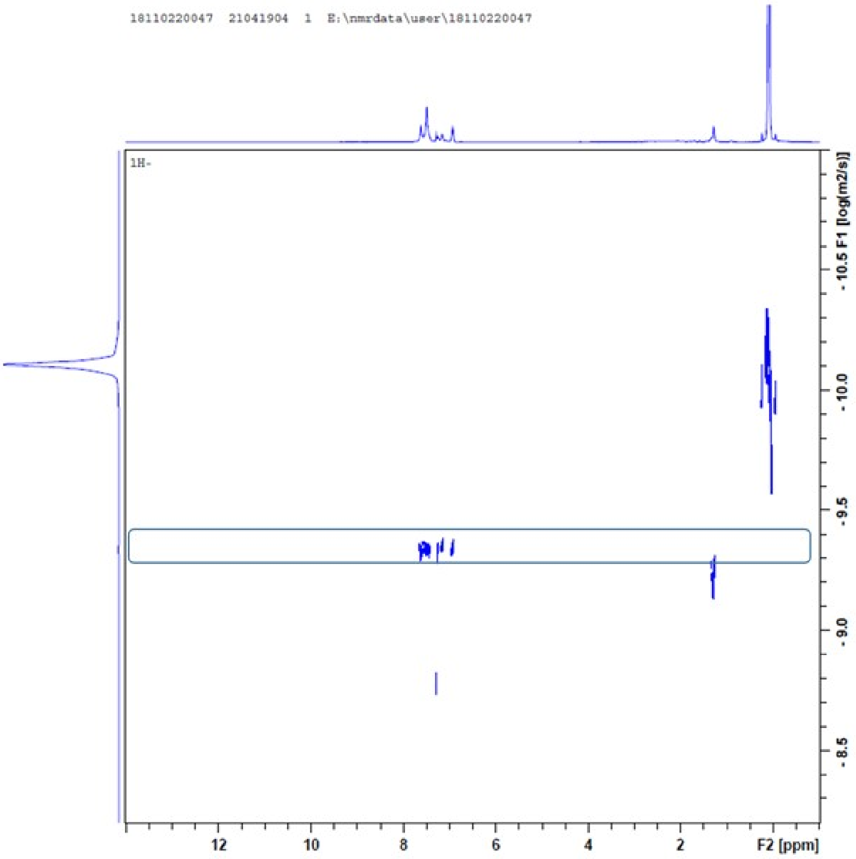


Fig. S15. ^{1}H DOSY NMR (400 MHz, $CDCl_3$, 298 K) of **6**.

3. ESI-MS data

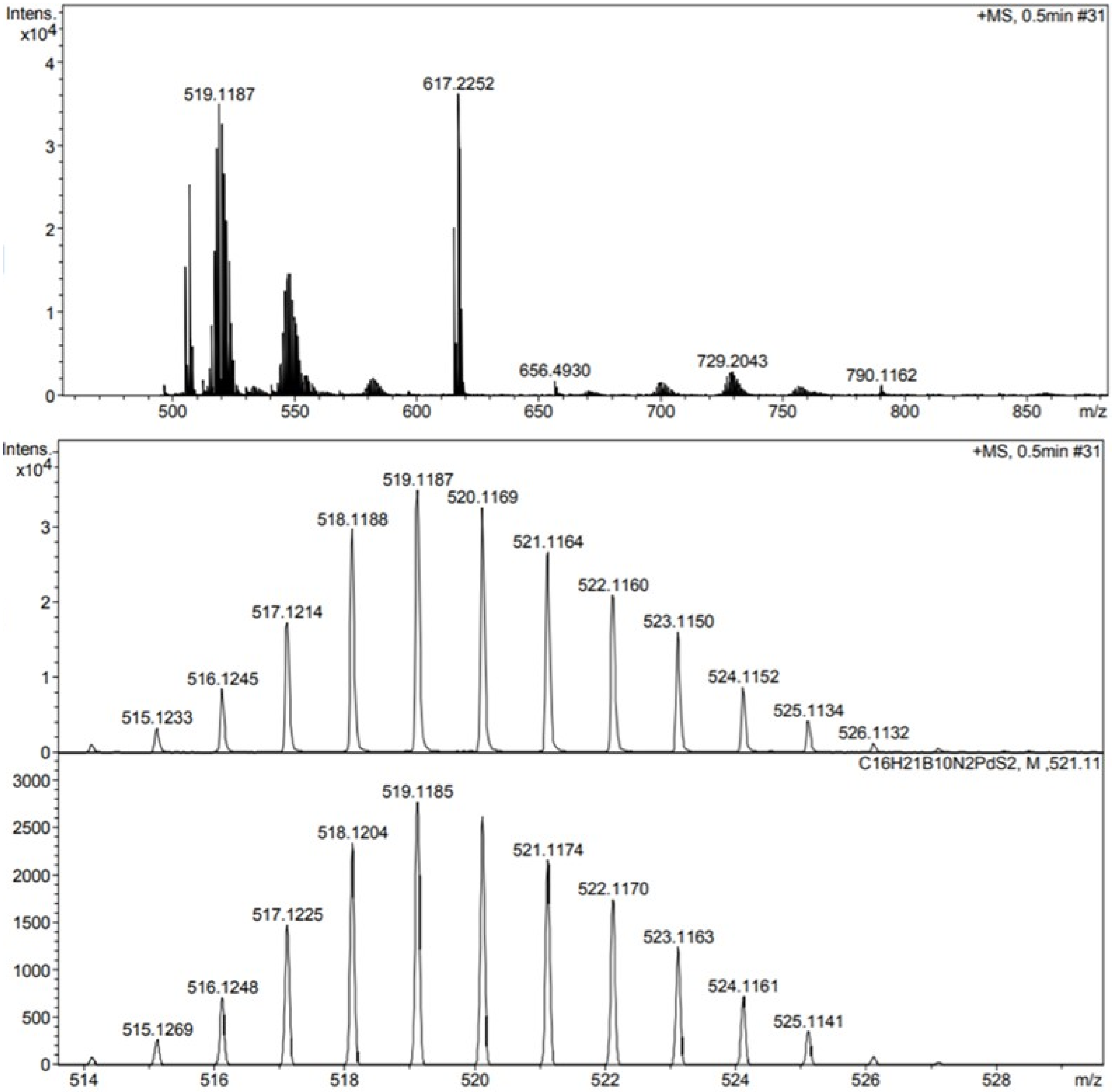


Fig. S16. Experimental (top) and theoretical (bottom) ESI-MS data of **2**.

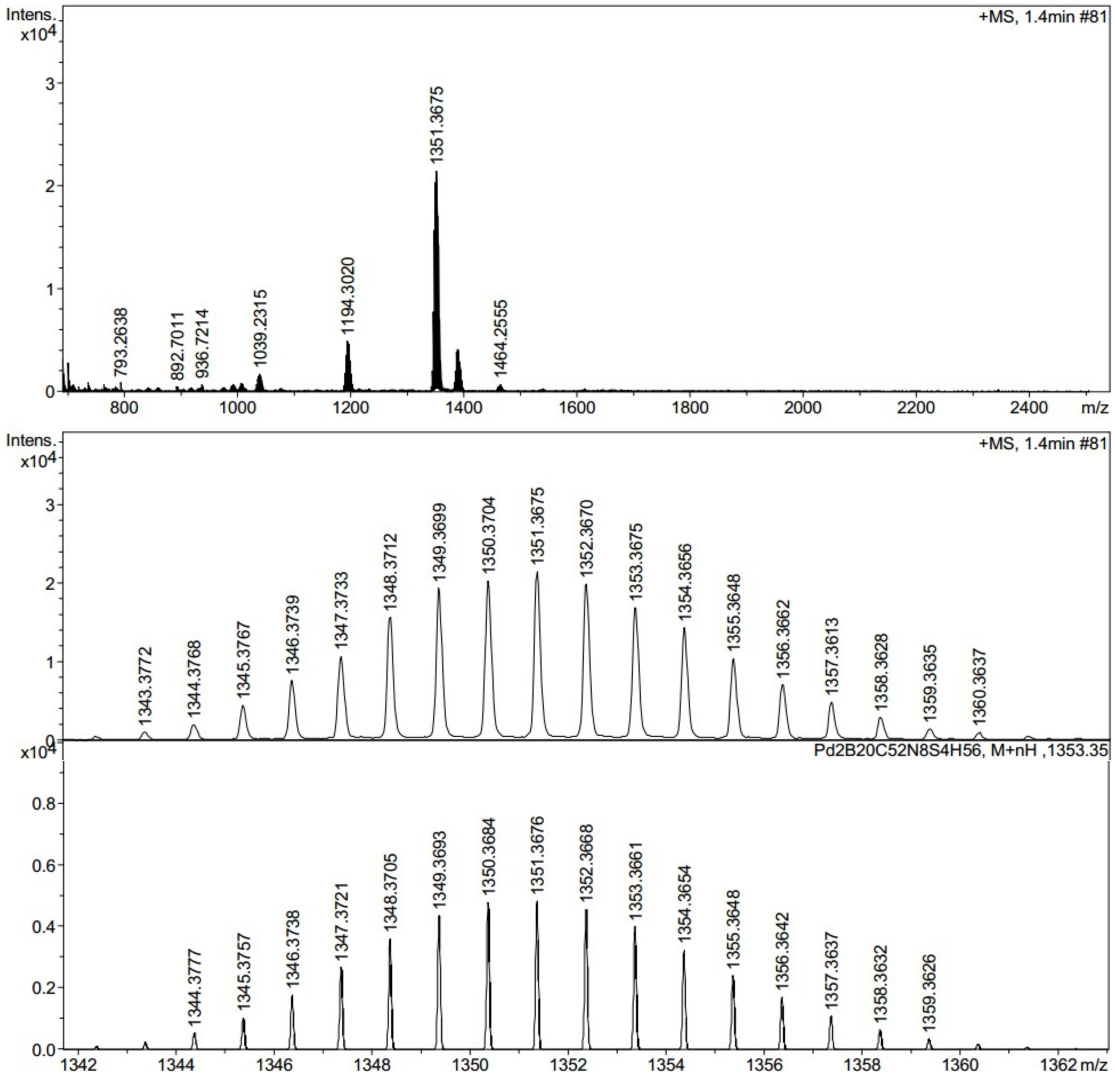


Fig. S17. Experimental (top) and theoretical (bottom) ESI-MS data of **3**.

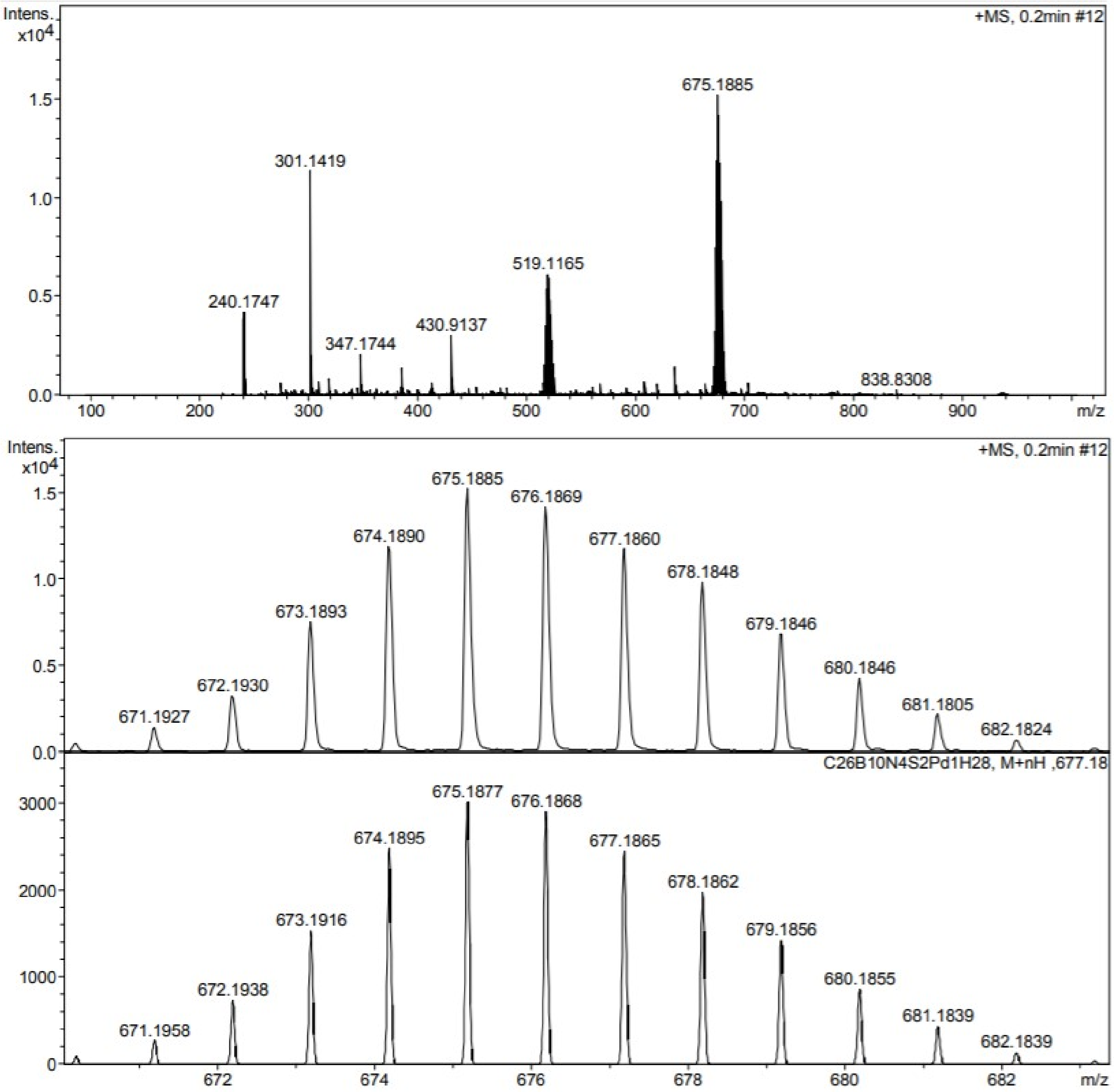


Fig. S18. Experimental (top) and theoretical (bottom) ESI-MS data of **4**.

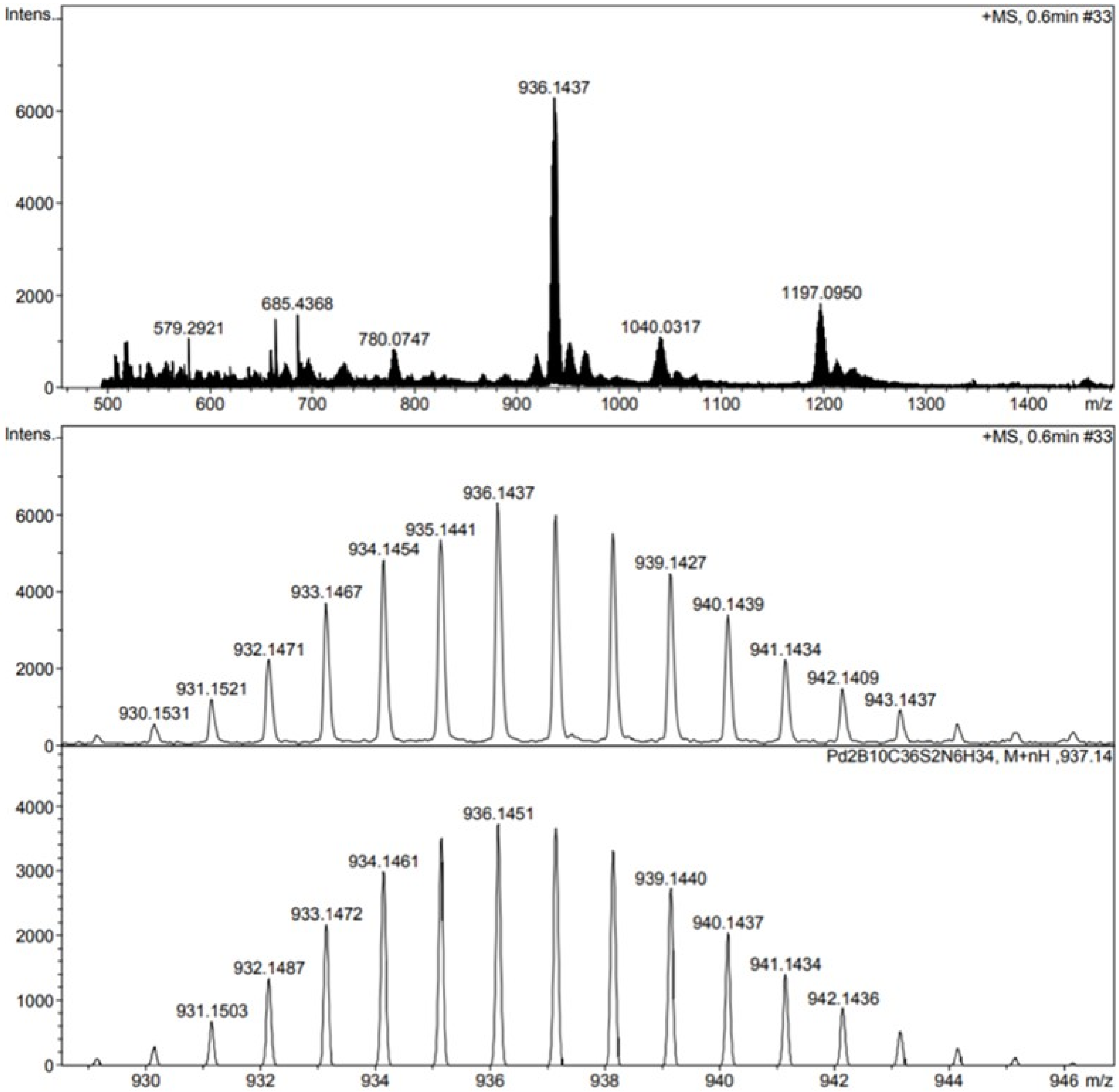


Fig. S19. Experimental (top) and theoretical (bottom) ESI-MS data of **5**.

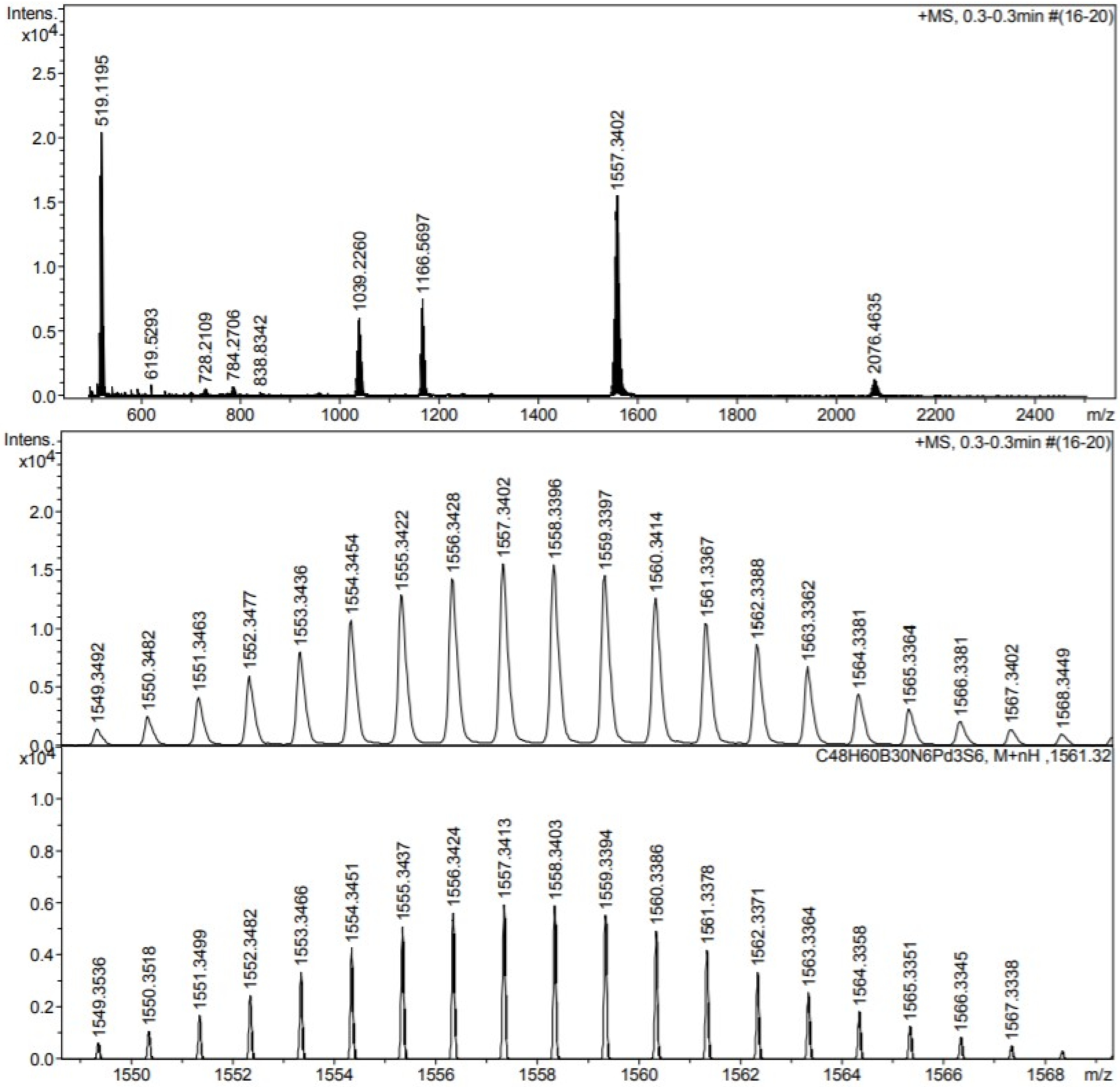


Fig. S20. Experimental (top) and theoretical (bottom) ESI-MS data of **6**.

4. X-ray crystallography details

Single crystals of **2** (CCDC: 2080792), **3** (CCDC: 2080795), **5** (CCDC: 2080794) and **6** (CCDC: 2080793) suitable for X-ray diffraction study were obtained at low temperature. X-ray intensity data of all the complexes were collected on a Bruker D8 Venture system (Cu $_{K\alpha}$, $\lambda = 1.54178$ Å).

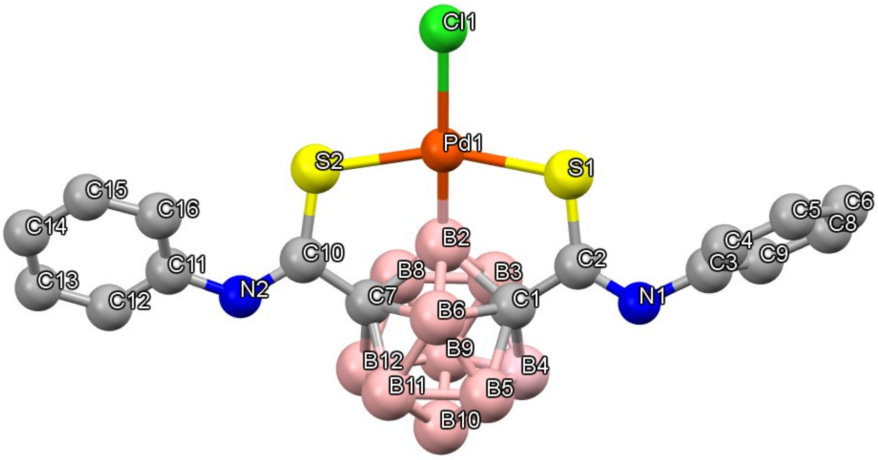


Fig. S21. Crystallographically derived molecular structures of **2** (H atoms have been omitted for clarity). The atomic number have been labeled in the structure. Color code: Pd, orange; S, yellow; N, blue; C, grey; B, pink.

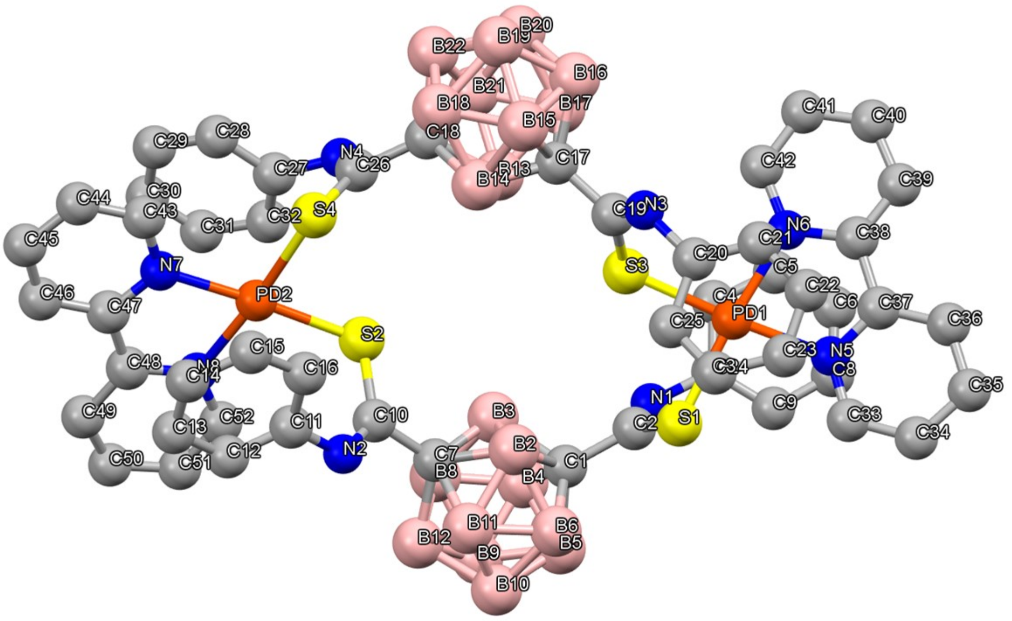


Fig. S22. Crystallographically derived molecular structures of **3** (H atoms have been omitted for clarity). The atomic number have been labeled in the structure. Color code: Pd, orange; S, yellow; N, blue; C, grey; B, pink.

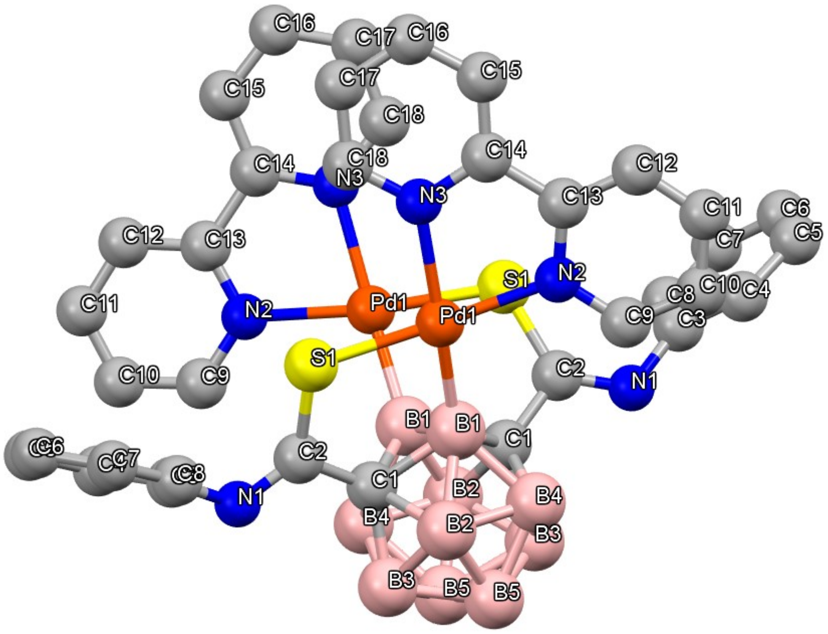


Fig. S23. Crystallographically derived molecular structures of **5** (H atoms have been omitted for clarity). The atomic number have been labeled in the structure. Color code: Pd, orange; S, yellow; N, blue; C, grey; B, pink.

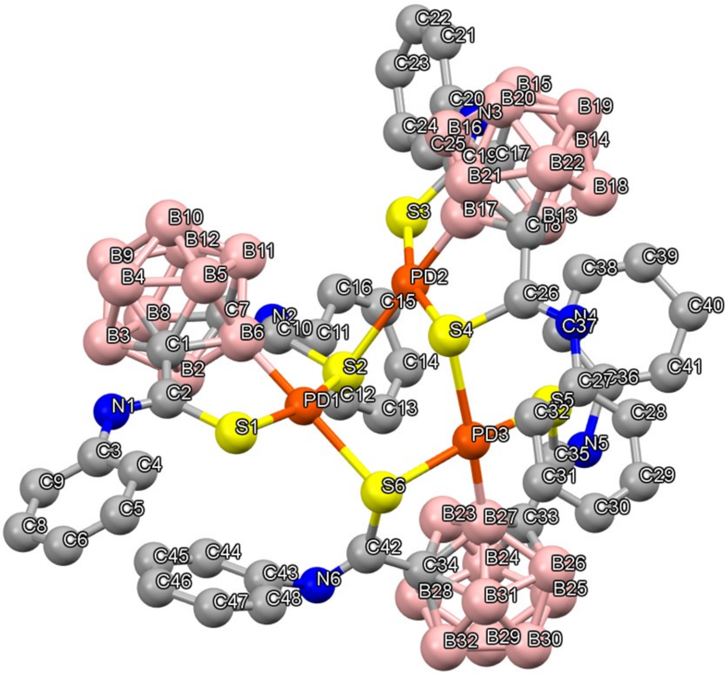


Fig. S24. Crystallographically derived molecular structures of **6** (H atoms have been omitted for clarity). The atomic number have been labeled in the structure. Color code: Pd, orange; S, yellow; N, blue; C, grey; B, pink.

Table 1. Crystal data and structure refinement for 2

Empirical formula	C16 H20 B10 Cl N2 Pd S2	
Formula weight	554.41	
Temperature	173(2) K	
Wavelength	1.34138 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.9592(4) Å	α/° = 90°.
	b = 14.7475(6) Å	β/° = 90°.
	c = 15.8848(7) Å	γ/° = 90°.
Volume	2333.05(17) Å^3	
Z	4	
Density (calculated)	1.578 Mg/m^3	
Absorption coefficient	6.193 mm^{-1}	
F(000)	1100	
Crystal size	0.230 x 0.220 x 0.210 mm^3	
Theta range for data collection	4.661 to 56.494°.	
Index ranges	-12<=h<=10, -18<=k<=18, -19<=l<=16	
Reflections collected	18940	
Independent reflections	4611 [R(int) = 0.0315]	
Completeness to theta = 53.594°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.751 and 0.518	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4611 / 2 / 296	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0190, wR2 = 0.0491	
R indices (all data)	R1 = 0.0193, wR2 = 0.0492	
Absolute structure parameter	0.016(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.338 and -0.372 e.Å^{-3}	

Table 2. Crystal data and structure refinement for 3

Empirical formula	C56 H66 B20 Cl6 N8 O Pd2 S4	
Formula weight	1637.10	
Temperature	177(2) K	
Wavelength	1.34138 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 13.2242(4) Å	$\alpha/^\circ$ = 90°.
	b = 16.7279(5) Å	$\beta/^\circ$ = 99.928(2)°.
	c = 16.6099(5) Å	$\gamma/^\circ$ = 90°.
Volume	3619.31(19) Å^3	
Z	2	
Density (calculated)	1.502 Mg/m^3	
Absorption coefficient	5.024 mm^{-1}	
F(000)	1648	
Crystal size	0.250 x 0.220 x 0.170 mm^3	
Theta range for data collection	3.742 to 55.999°.	
Index ranges	-12<=h<=16, -20<=k<=20, -20<=l<=20	
Reflections collected	29827	
Independent reflections	12922 [R(int) = 0.0777]	
Completeness to theta = 53.594°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.751 and 0.562	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12922 / 8 / 794	
Goodness-of-fit on F^2	0.978	
Final R indices [I>2sigma(I)]	R1 = 0.0624, wR2 = 0.1260	
R indices (all data)	R1 = 0.1040, wR2 = 0.1478	
Absolute structure parameter	0.036(10)	
Extinction coefficient	0.00050(9)	
Largest diff. peak and hole	0.680 and -0.866 e.Å^{-3}	

Table 3. Crystal data and structure refinement for 5

Identification code	210321b_0m_a	
Empirical formula	C38 H38 B10 Cl4 N6 Pd2 S2	
Formula weight	1105.56	
Temperature	173(2) K	
Wavelength	1.34138 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 18.177(3) Å	α/° = 90°.
	b = 16.674(2) Å	β/° = 104.882(17)°.
	c = 15.236(5) Å	γ/° = 90°.
Volume	4463.1(17) Å^3	
Z	4	
Density (calculated)	1.645 Mg/m^3	
Absorption coefficient	6.657 mm^{-1}	
F(000)	2200	
Crystal size	0.120 x 0.110 x 0.100 mm^3	
Theta range for data collection	3.741 to 56.500°.	
Index ranges	-22<=h<=17, -15<=k<=20, -17<=l<=18	
Reflections collected	18704	
Independent reflections	4483 [R(int) = 0.1012]	
Completeness to theta = 53.594°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.751 and 0.621	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4483 / 7 / 285	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0728, wR2 = 0.1997	
R indices (all data)	R1 = 0.1216, wR2 = 0.2277	
Extinction coefficient	0.00073(12)	
Largest diff. peak and hole	2.386 and -1.466 e.Å^{-3}	

Table 4. Crystal data and structure refinement for 6

Empirical formula	$C_{64}H_{104}B_{30}N_6O_6Pd_3S_6$	
Formula weight	1889.39	
Temperature	173(2) K	
Wavelength	1.34138 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.2041(10) Å	α/° = 67.421(7)°.
	b = 18.8426(15) Å	β/° = 78.754(6)°.
	c = 21.936(2) Å	γ/° = 82.420(6)°.
Volume	4559.2(7) $Å^3$	
Z	2	
Density (calculated)	1.376 Mg/m^3	
Absorption coefficient	4.298 mm^{-1}	
F(000)	1924	
Crystal size	0.048 x 0.040 x 0.010 mm^3	
Theta range for data collection	3.426 to 54.972°.	
Index ranges	-14<=h<=13, -22<=k<=22, -26<=l<=26	
Reflections collected	63300	
Independent reflections	17256 [R(int) = 0.0751]	
Completeness to theta = 53.594°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.5635	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17256 / 109 / 1008	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0542, wR2 = 0.1500	
R indices (all data)	R1 = 0.0699, wR2 = 0.1587	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.465 and -1.050 e.$Å^{-3}$	

5. References

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