Electronic Supporting Information

Structurally rigidified cobalt bis(dicarbollide) derivatives, chiral platform for labelling of biomolecules and new materials

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I. Materials and Methods

1. Experimental

General: Acetonitrile and dichloromethane were dried over molecular sieves (4 Å, Fluka). Other chemicals and solvents were from Aldrich, Merck, Lachner a.s. and Penta Ltd., Czech Republic, respectively, and were used without purification.

2. Instrumental Techniques

NMR spectra were measured on Jeol 600 MHz spectrometer. The spectra of all compounds were measured immediately after dissolution in particular deuterated solvent, usually acetonitrile-d_3 unless otherwise stated. ^{11}B NMR (192 MHz) chemical shifts are given in ppm to high-frequency (low field) to $F_3B.OEt_2$ as the external reference. Residual solvent ^{1}H resonances were used as internal secondary standards. The NMR data are presented in the text as follows: ^{11}B NMR: ^{11}B chemical shifts δ (ppm), multiplicity. ^{1}H NMR (600 MHz) and ^{13}C (150 MHz): chemical shifts δ are given in ppm relative to Me_4Si (0 ppm) as the external standard, coupling constants $J(H,H)$ are in Hz.

Mass spectrometry measurements were performed on a Thermo-Finnigan LCQ-Fleet Ion Trap instrument using electrospray ionization (ESI) for ionic species. Samples dissolved in acetonitrile (concentrations approximately 100 ng/ml) were introduced to the ion source by infusion of 5 µL/min, source voltage 4.5 kV, tube lens voltage -90.7 V, capillary voltage -22.0 V, capillary temperature was 270 °C, drying gas flow 7 L/min. In most cases the negative ions corresponding to the molecular ion were observed with 100% abundance for the highest peak in the isotopic distribution plot. Molecular ions $[M]^-$ were detected for all univalent anions as the base peaks in the spectra. The isotopic distribution in the boron plot of all peaks is in perfect agreement with the calculated spectral pattern. The data are presented for the most abundant mass in the boron isotopic distribution plot (100%).

Achiral HPLC All samples were analyzed on Thermo Finnigan Surveyor HPLC system equipped with Photo Diode Array detector. Chromatographic conditions: column LiCroCART RP-selected B (5 µm, 250 x 3.00 mm *I.D.*); the mobile phase was 5.0 mmol propylamine acetate (PAA) in 40% aqueous CH_3CN (pH 4.8). Samples with concentration of approximately 1 mg/mL in the mobile phase and volume of 5 µL were injected. DAD detection was carried out at fixed wavelengths 237, 285 and 290 nm.

Elemental Analysis. The samples for Elemental Analysis (EA) were prepared by precipitation from MeOH solutions by aqueous Me_4NCl or Ph_4PCl. The samples of Me_4N^+ or Ph_4P^+ salts for EA were dried in vaccum at 80 °C for 8 h. EA was performed in the following analyzer: Thermo

Scientific FlashSmart™ 2000 Elemental analyzer (United States). The combustion tube packing was supplied with the instrument and consisted of the following components: EA-2000 chromium oxidizer, high quality copper reducer, and silver cobaltous-cobaltic oxide. Analysis of the sample; portions of samples with a mass around 1 mg were weighed in tin containers together with a vanadium pentoxide (10 mg). All the determinations were done in triples.

II. Synthesis

1. Preparation of the mono-substituted derivatives of cobalt bis(dicarbollide)(1^-) ion

1.1. [8,8'-μ-O-(1',2'-$C_2B_9H_{10})_2$-3,3'-Co(III)] Cs (Cs**2**)

Dry zwitterion **1** of formula [8,8'-μ-MeO-(1',2'-$C_2B_9H_{10})_2$-3,3'-Co(III)][1] (1.6 g, 4.63 mmol) was dissolved in 25 mL of dry DME then n-butylamine (4.6 mL, 46.54 mmol) was added to the reaction mixture. The reaction was kept at 60 °C for 2 h under inert atmosphere. After cooling down, a sample from the reaction mixture was spotted on TLC (benzene-hexane mixture 1:1). The red spot of the starting zwitterion should completely disappear, and only the violet spot of the product should appear close to start, otherwise the heating was continued. The reaction was stopped, the solvents were evaporated and the residue was dried in vacuum. The residue was then treated between Et_2O (50 mL) and diluted HCl (3M, 4x 50 mL). The ether phase was separated and water layer was shaken once more with Et_2O (50 mL). Water (75 mL) was added to the combined organic extracts, and the dark violet product was precipitated with excess of aqueous CsCl. The crude product was separated by filtration and recrystallized from hot water. Dark violet crystals are collected by filtration, washed by small amount of water and dried in vacuum with increasing gradually the temperature from 50 °C to 150 °C.

Cs**2**: 1.942 g, yield 91%. ^{11}B NMR δ_B(192 MHz; CD_3CN; $Et_2O.BF_3$): 13.25 (2B, s, B8, 8'), -4.73 (2B, d, *J 142*, B10, 10'), -9.52 (3B, d, *J 146*, B4, 7, 4'), -11.09 (5B, d, *J 141*, B7', 9, 9', 12, 12'), -16.74 (4B, d, *J 150*, B5, 5', 11, 11'), -29.05 (2B, br. d, B6, 6'). ^{1}H NMR δ_H(600 MHz; CD_3CN): 3.18 (4H, s, C*H* carborane). δ_{B-H} (^{1}H-{^{11}B} NMR, 600 MHz; CD_3CN): 3.74 (4H, br s, B-H), 3.16 (4H, s, C*H* carborane), 2.55 (2H, s, B-H), 1.93 (4H, br s, B-H), 1.68 (4H, br s, B-H), 1.48 (2H, br s, B-H). ^{13}C{^{1}H} NMR δ_C (150 MHz; CD_3CN): 42.52 (4C, *C*H carborane). MS (ESI) *m/z*= 341.48 (M^-, 11%), 338.56 (100%); Calcd. for $\mathbf{2}^-$ 341.25 (11%) and 338.26 (100%) [M^-]. EA found C, 27.0; H, 8.6; N, 3.2; Calcd. for Me_3NH**2**: C, 27.2; H, 8.7; N, 3.2%.

1.2. Synthesis of [8,8'-μ-O-(1-HO$(CH_2)_3$-1,2-$C_2B_9H_9$)(1',2'-$C_2B_9H_{10}$)-3,3'-Co(III)] Me_3NH (Me_3NH**3**)

Cs**2** (3.156 g, 6.71 mmol) was dried in vacuum at 120 °C for 5 h then at 185 °C for 2.5 h. Dry DME was injected (80 mL) and the resulting solution was cooled down under stirring on a bath

of CO_2(s) and acetone. Then BuLi (2.5 M in hexane, 4 mL, 10 mmol) was added dropwise from syringe over 10 min. The bath was removed and reaction mixture was allowed to warm up under stirring to room temperature and stirred for additional 15 min. The reaction mixture was cooled down again on a bath of CO_2(s) and acetone then trimethylene oxide (1 mL, 15.38 mmol) was injected. The reaction was left to warm up slowly in the bath overnight. ESI-MS for the reaction mixture showed the presence of the starting material (50%), mono-substituted hydroxypropyl derivative (40%) and di-substituted hydroxylpropyl derivative (10%). The reaction was quenched by careful addition of MeOH and few drops of diluted HCl (3M). The solvents were removed at reduced pressure, the residue was dried in vacuum, dissolved in CH_2Cl_2-CH_3CN mixture and chromatographed on a silica gel column increasing the CH_3CN content from 10% to 50%. The first fraction contained the unreacted starting material, three subsequent fractions contained the monosubstituted product and the last 2 fractions contained rac-diastereoisomer of the disubstituted product. The fractions were evaporated. Methanol was added dropwise until dissolution of the solid material, and the compounds were precipitated by addition of an excess of aqueous Me_3N.HCl in water.

Me_3NH**3**: 0.718 g, yield 24%. ^{11}B NMR δ_B(192 MHz; CD_3CN; $Et_2O.BF_3$): 13.62 (2B, s, B8, 8'), -5.35 (1B, d, *J 150*, B10), -6.83 (2B, d, *J 133*, B4, 10'), -9.54 (1B, br d, B4'), -10.46 (1B, br d, B7), -11.42 (4B, d, *J 137*, B9, 12, 7', 9'), -13.51 (1B, d, *J 150*, B12'), -14.40 (1B, d, *J 173*, B5), -16.86 (3B, d, *J 145*, B11, 5', 11'), -25.65 (1B, d, *J 162*, B6), -30.14 (1B, d, *J 164*, B6'). ^{1}H NMR δ_H(600 MHz; CD_3CN): 3.37 (2H, td, $^3J_{HH}$ *6.05*, $^3J_{HH}$ *2.01*, CH_2-OH), 3.30 (1H, s, C*H* carborane), 3.15 (1H, s, C*H* carborane), 2.77 (9H, s, Me_3NH^+), 2.52 (1H, s, C*H* carborane), 2.42-2.33 (2*H*, m, -CH_2), 1.61-1.56 (2*H*, m, -CH_2-CH_2-OH). δ_{B-H} (^{1}H-{^{11}B} NMR, 600 MHz; CD_3CN): 4.01 (1H, br s, B-H), 3.81 (2H, br s, B-H), 3.66 (1H, br s, B-H), 3.31 (1H, s, C*H* carborane), 3.15 (1H, s, C*H* carborane), 2.53 (1H, s, C*H* carborane), 2.46 (2H, s, B-H), 1.80 (4H, br s, B-H), 1.71 (4H, br s, B-H), 1.43 (2H, br s, B-H). ^{13}C{^{1}H} NMR δ_C (150 MHz; CD_3CN): 62.02 (1C, *C* carborane), 61.43 (1C, *C*H_2-OH), 45.72 (3C, Me_3NH^+), 45.25 (1C, *C*H carborane), 43.57 (1C, *C*H carborane), 39.36 (1C, *C*H carborane), 38.18 (1C, -*C*H_2), 33.00 (1C, -*C*H_2-CH_2-OH). MS (ESI) *m/z*= 399.44 (M^-, 18%), 396.60 (100%); Calcd. for **3**$^-$ 399.30 (18%) and 396.30 (100%) [M^-]. EA found C, 27.0; H, 8.6; N, 3.2; Calcd. for Me_3NH**3**: C, 27.2; H, 8.7; N, 3.2%.

1.3. Synthesis of [8,8′-μ-O-(1-$MeSO_2$-O$(CH_2)_3$-1,2-$C_2B_9H_9$)(1',2'-$C_2B_9H_{10}$)-3,3'-Co(III)] Me_4N (Me_4N**5**)

Me_3NH**3** (260 mg, 0.57 mmol) was dried under vacuum at 70 °C for 5 h. Then dry CH_3CN (25 mL) was injected through septum, followed with solid K_2CO_3 (800 mg, 5.79 mmol) and mesyl chloride (400 μL, 5.17 mmol) from gas-tight Hamilton syringe. The reaction mixture was heated up to 45 °C and stirred for 2.5 h, when ca. 95% of the alcohol reacted (according to HPLC and MS). The solids were filtered under argon, washed with CH_3CN (3x 3 mL) and discarded. Combined organic fractions were evaporated in vacuum, then dissolved in minimal volume of

MeOH and aqueous Me_4NCl was added to precipitate a voluminous violet precipitate. This was left to settle down to walls of the flask over 10 min. (with occasional vigorous mixing). The solid was quickly, but carefully decanted, washed with water (3x 5 mL) and quickly dried in vacuum. The unreacted alcohol accumulates in mother liquors. The volume of mother liquors was reduced, and additional fraction containing ca. 10% of the alcohol was recovered, washed with water (3x 1 mL), dried and purified by fast chromatography on silica gel column 14 cm x 1.5 *I.D.* using CH_3CN-CH_2Cl_2 mixture (1:3 to 1:2). This provided additional 40 mg of the product.

Me_4N**5**: 280 mg, yield 90%. ^{11}B NMR δ_B(192 MHz; CD_3CN; $Et_2O.BF_3$): 13.76 (2B, s, B8, 8'), -5.79 (1B, d, *J 150*, B10), -7.01 (2B, d, *J 140*, B4, 10'), -9.50 (1B, br d, B4'), -10.40 (1B, br d, B7), -11.48 (4B, d, *J 133*, B9, 12, 7', 9'), -13.52 (1B, d, *J 144*, B12'), -15.07 (1B, d, *J 156*, B5), -17.10 (3B, br d, B11, 5', 11'), -25.88 (1B, d, *J 144*, B6), -30.41 (1B, d, *J 161*, B6'). ^1H NMR δ_H(600 MHz; CD_3CN): 4.16-4.08 (2H, m, C*H*$_2$-OMs), 3.26 (1H, s, C*H* carborane), 3.12 (1H, s, C*H* carborane), 3.07 (12H, s, Me_4N^+), 2.97 (3H, s, C*H*$_3$), 2.51-2.45 (1*H*, m, -C*H*$_2$), 2.40-2.35 (1*H*, m, -C*H*$_2$), 2.37 (1H, s, C*H* carborane), 1.89-1.83 (2H, m, -C*H*$_2$-CH_2-OMs). δ_{B-H} (^1H-{^{11}B} NMR, 600 MHz; CD_3CN): 3.95 (1H, br s, B-H), 3.81 (2H, br s, B-H), 3.65 (1H, br s, B-H), 3.26 (1H, s, C*H* carborane), 3.12 (1H, s, C*H* carborane), 2.72 (1H, s, C*H* carborane), 2.42 (2H, s, B-H), 1.76 (3H, br s, B-H), 1.70 (3H, br s, B-H), 1.61 (2H, br s, B-H), 1.41 (2H, br s, B-H). $^{13}C\{^1H\}$ NMR δ_C (150 MHz; CD_3CN): 70.86 (1C, *C* carborane), 56.15 (4C, Me_4N^+), 45.05 (1C, *C*H carborane), 44.53 (1C, *C*H_2-OMs), 42.82 (1C, *C*H carborane), 38.54 (1C, -*C*H_2), 37.33 (1C, *C*H_3), 29.66 (1C, -*C*H_2-CH_2-OMs). MS (ESI) *m/z*= 477.24 (*M*$^-$, 11%), 474.32 (100%); Calcd. for **5**$^-$ 477.27 (11%) and 474.28 (100%) [*M*$^-$].

1.4. Synthesis of [8,8'-μ-O-(1-$N_3(CH_2)_3$-1,2-$C_2B_9H_9$)(1',2'-$C_2B_9H_{10}$)-3,3'-Co(III)] Me_4N (Me_4N**7**)
Me_4N**5** (827mg, 1.51 mmol) was dried at room temperature together with sodium azide (1.82 g, 28.00 mmol) for 4h. Then, DMF (10 mL, anhydrous sigma aldrich) was injected and the reaction mixture was stirred at 45 °C overnight. The excess of inorganic azide was filtered off, solid washed with DMF (2x 2 mL) and the organic solvent was removed in vacuum at 45 °C. The crude products were chromatographed on a short column of silica gel (20 x 2.0 cm *I.D.*) using CH_2Cl_2:MeOH (88:12 to 88:15 b.v.). Pure fractions (MS analysis) were dissolved in MeOH and precipitated quickly by aqueous Me_4NCl.

Me_4N**7**: 487 mg, yield 65%. ^{11}B NMR δ_B(192 MHz; CD_3CN; $Et_2O.BF_3$): 13.86 (2B, s, B8, 8'), -5.81 (1B, d, *J 151*, B10), -6.86 (2B, d, *J 151*, B4, 10'), -9.11 (1B, br d, B4'), -9.59 (1B, br d, B7), -10.36 (1B, br d, B7'), -11.50 (3B, d, *J 136*, B9, 12, 9'), -13.53 (1B, d, *J 141*, B12'), -14.92 (1B, d, *J 157*, B5), -17.17 (3B, br d, B11, 5', 11'), -25.97 (1B, d, *J 130*, B6), -30.43 (1B, d, *J 178*, B6'). ^1H NMR δ_H(600 MHz; CD_3CN): 3.33-3.19 (2H, m, C*H*$_2$-N_3), 3.24 (1H, s, C*H*$_{carborane}$), 3.10 (13H, s, Me_4N^+ + C*H*$_{carborane}$), 2.45- 2.30 (2H, m, -C*H*$_2$), 2.36 (1H, s, C*H*$_{carborane}$), 1.71-1.63 (2H, m, -C*H*$_2$-CH_2-N_3). δ_{B-H} (^1H-{^{11}B} NMR, 600 MHz; CD_3CN): 3.91 (1H, br s, B-H), 3.75 (2H, br s, B-H), 3.60 (1H, br s, B-H), 3.21 (1H, s, C*H* carborane), 2.33 (2H, s, B-H), 1.73 (4H, br s, B-H), 1.56 (4H, br s, B-H), 1.37 (2H, br s, B-H). $^{13}C\{^1H\}$ NMR δ_C (150 MHz; CD_3CN): 60.10 (1C, *C*H carborane), 56.14 (4C, Me_4N^+),

51.54 (1C, *C*H_2-N_3), 44.49 (1C, *C*H carborane), 42.80 (1C, *C*H carborane), 38.52 (1C, -*C*H_2), 29.36 (1C, -*C*H_2-CH_2-N_3). MS (ESI) *m/z*= 424.50 (M^-, 10%), 421.58 (100%); Calcd. for **7**$^-$ 424.30 (10%) and 421.31 (100%) [M^-]. EA found C, 49.4; H, 5.6; N, 5.9; Calcd. for Ph_4P**7**: C, 49.0; H, 6.0; N, 5.5%.

1.5. Synthesis of [8,8´-O -[(1-(4-phenyl-1,2,3-triazolyl)-$(CH_2)_3$-1,2-$C_2B_9H_9$)(1,2-$C_2B_9H_{10}$)-3,3'-Co(III)] Me_4N (Me_4N**9**)

Me_4N**7** (75 mg, 0.152 mmol) was dried under vacuum at 80 ºC for 4 h. Dry Ethanol (30 mL) was added followed by phenylacetylene (70 μL, 0.637 mmol), CuI (7 mg, 0.037 mmol) and DIPEA (1 mL, 5.741 mmol). The reaction mixture was stirred at 37 ºC for 4 days. The solvents were evaporated and the crude product was purified on a silica column using CH_2Cl_2/CH_3CN by increasing gradually the percentage of acetonitrile. The pure fractions (MS analysis) were combined, evaporated to dryness and dissolved in minimal volume of MeOH. The click product precipitated after addition of aqueous Me_4NCl.

Me_4N**9**: 67 mg, yield 74%. ^{11}B NMR δ_B(192 MHz; CD_3CN; $Et_2O.BF_3$): 14.42 (2B, s, B8, 8'), -5.04 (1B, br d, B10), -6.23 (2B, d, *J 141*, B4, 10'), -8.91 (1B, br d, B4'), -9.61 (1B, br d, B7), -10.69 (4B, d, *J 134*, B9, 12, 7', 9'), -12.70 (1B, d, *J 141*, B12'), -14.18 (1B, d, *J 154*, B5), -16.25 (3B, br d, B11, 5', 11'), -24.97 (1B, br d, B6), -29.56 (1B, br d, B6'). ^1H NMR δ_H(600 MHz; CD_3CN): 8.01 (1H, s, C*H*$_{triazole}$), 7.80 (2H, d, $^3J_{HH}$ *7.*32, C*H*$_{phenyl}$), 7.42 (2H, t, $^3J_{HH}$ *7.*55, C*H*$_{phenyl}$), 7.32 (1H, t, $^3J_{HH}$ *7.*47, C*H*$_{phenyl}$), 4.34-4.27 (2H, m, C*H*$_2$-triazole), 3.17 (1H, s, C*H* carborane), 3.04 (12H, s, Me_4N^+), 2.96 (1H, s, C*H* carborane), 2.37-2.33 (1*H*, m, -C*H*$_2$), 2.27-2.24 (1*H*, m, -C*H*$_2$), 2.04-2.00 (2H, m, -C*H*$_2$-CH_2-triazole), 1.99 (1H, s, C*H* carborane). $^{13}C\{^1H\}$ NMR δ_C (150 MHz; CD_3CN): 129.80 (2C, *C*H$_{phenyl}$), 128.89 (1C, *C*H$_{phenyl}$), 126.38 (2C, *C*H$_{phenyl}$), 121.79 (1C, *C*H$_{triazole}$), 56.16 (4C, Me_4N^+), 50.17 (1C, *C*H_2-triazole), 44.41 (1C, *C*H carborane), 42.80 (1C, *C*H carborane), 38.50 (1C, *C*H carborane), 38.17 (1C, -*C*H_2), 30.63 (1C, -*C*H_2-CH_2-triazole). MS (ESI) *m/z*= 526.40 (M^-, 16%), 523.52 (100%); Calcd. for **9**$^-$ 526.35 (17%) and 523.36 (100%) [M^-]. EA found C, 54.8; H, 6.3; N, 4.6; Calcd. for Ph_4P**9**: C, 54.3; H, 6.0; N, 4.9%.

1.6. Synthesis of [8,8´-O -[(1-(4-trimethylsilyl-1,2,3-triazolyl)-$(CH_2)_3$-1,2-$C_2B_9H_9$)(1,2-$C_2B_9H_{10}$)-3,3'-Co(III)] Me_4N (Me_4N**10**)

Me_4N**7** (94 mg, 0.190 mmol) was dried under vacuum at 80 ºC for 4 h. Dry Ethanol (30 mL) was added followed by ethynyltrimethylsilane (90 μL, 0.650 mmol), CuI (8 mg, 0.042 mmol) and DIPEA (0.8 mL, 4.593 mmol). The reaction mixture was stirred at 37 ºC for 3 days. MS of the reaction mixture showed the presence of starting material (100%), *m/z*= 447.56 which may correspond to [8,8'-μ-O(1-$CHCN_3C_3H_6$-1,2-$C_2B_9H_9$)(1',2'-$C_2B_9H_{10}$)-3,3'-Co]$^-$ (65%) and the expected click product (20%). 40 μL of the ethynyltrimethylsilane was added to the reaction mixture and the reaction was kept heating at 37 ºC for 17 h. MS showed the same results as before. Then, CuI (6 mg, 0.031 mmol) and ethynyltrimethylsilane (100 μL, 0.702 mmol) were added. The reaction was stirred for 5 days at 37 ºC. The crude product was purified on a C18

modified silica in reverse phase mode by 55% MeOH (*v/v*). Pure fractions (MS analysis) were combined and evaporated under reduced pressure. The click product was dissolved in minimal volume of MeOH and precipitated by aqueous Me_4NCl.

Me_4N**10**: 46 mg, yield 41%. ^{11}B NMR δ_B(192 MHz; CD_3CN; $Et_2O.BF_3$): 13.87 (2B, s, B8, 8'), -5.77 (1B, d, *J 154*, B10), -6.96 (2B, d, *J 144*, B4, 10'), -9.24 (1B, br d, B4'), -9.52 (1B, br d, B7), -10.37 (1B, br d, B7'), -11.44 (3B, d, *J 144*, B9, 12, 9'), -13.45 (1B, d, *J 139*, B12'), -14.91 (1B, d, *J 157*, B5), -16.92 (3B, d, *J 138*, B11, 5', 11'), -25.82 (1B, d, *J 158*, B6), -30.38 (1B, d, *J 148*, B6'). ^1H NMR δ_H(600 MHz; CD_3CN): 7.72 (1H, s, C$H_{triazole}$), 4.34-4.26 (2H, m, CH_2-triazole), 3.19 (1H, br s, C*H* carborane), 3.09 (12H, s, Me_4N^+), 2.99 (1H, br s, C*H* carborane), 2.37-2.30 (1*H*, m, -CH_2), 2.29-2.22 (1*H*, m, -CH_2), 2.05-1.99 (2H, m, -CH_2-CH_2-triazole), 1.87 (1H, br s, C*H* carborane), 0.27 (9H, s, Me_3Si-). $^{13}C\{^1H\}$ NMR δ_C (150 MHz; CD_3CN): 130.86 (1C, *C*H$_{triazole}$), 56.17 (4C, Me_4N^+), 49.43 (1C, *C*H_2-triazole), 44.38 (1C, *C*H carborane), 42.74 (1C, *C*H carborane), 38.52 (1C, *C*H carborane), 38.35 (1C, -*C*H_2), 30.75 (1C, -*C*H_2-CH_2-triazole), -1.01 (3C, Me_3Si-). MS (ESI) *m/z*= 522.32 (M^-, 19%), 519.44 (100%); Calcd. for **10**$^-$ 522.36 (17%) and 519.37 (100%) [M^-]. EA found C, 50.4; H, 6.6; N, 5.1; Calcd. for Ph_4P**10**: C, 50.4; H, 6.5; N, 4.9%.

1.7. Synthesis of [8,8´-O -[(1-(4-aminomethyl-1,2,3-triazolyl)-$(CH_2)_3$-1,2-$C_2B_9H_9$)(1,2-$C_2B_9H_{10}$)-3,3'-Co(III)] Me_4N (Me_4N**11**)

Me_4N**7** (95 mg, 0.192 mmol) was dried under vacuum at 80 ^oC for 4 h. Dry Ethanol (30 mL) was added followed by propargylamine hydrochloride (38 mg, 0.415 mmol), CuI (9 mg, 0.047 mmol) and DIPEA (0.4 mL, 2.297 mmol). The reaction mixture was stirred at rt for 20 h. MS of the reaction mixture showed the presence of SM (100%) and click product (75%). Then the reaction mixture was heated at 37 ^oC and after 2 h, MS of the reaction mixture showed SM (95%) and click product (100%). It was kept at 37 ^oC for 3 days where MS showed only the presence of click product. The solvents were evaporated and purified on a silica column using CH_2Cl_2-CH_3CN by increasing gradually the percentage of CH_3CN from 20% to 100%. The pure fractions (MS analysis) were combined, concentrated under vacuum and dissolved in minimal volume of MeOH. The click product precipitated after addition of aqueous Me_4NCl.

Me_4N**11**: 48 mg, yield 45%. ^{11}B NMR δ_B(192 MHz; CD_3CN; $Et_2O.BF_3$): 13.80 (2B, s, B8, 8'), -5.98 (1B, d, *J 144*, B10), -7.08 (2B, d, *J 144*, B4, 10'), -9.23 (1B, br d, B4'), -9.60 (1B, br d, B7), -10.31 (1B, br d, B7'), -11.54 (3B, d, *J 115*, B9, 12, 9'), -13.51 (1B, d, *J 144*, B12'), -15.29 (1B, d, *J 162*, B5), -17.16 (3B, br d, B11, 5', 11'), -25.61 (1B, br d, B6), -30.47 (1B, br d, B6'). ^1H NMR δ_H(600 MHz; CD_3CN): 7.78 (1H, s, C$H_{triazole}$), 4.35-4.31 (1H, m, CH_2-triazole), 4.28-4.23 (1H, m, CH_2-triazole), 3.28 (2H, br s, CH_2-NH_2), 3.16 (1H, br s, C*H* carborane), 3.09 (12H, s, Me_4N^+), 3.04 (1H, s, C*H* carborane), 2.40-2.34 (1H, m, -CH_2), 2.28-2.23 (1H, m, -CH_2), 2.04-1.98 (2H, m, -CH_2-CH_2-triazole), 1.89 (1H, br s, C*H* carborane). $^{13}C\{^1H\}$ NMR δ_C (150 MHz; CD_3CN): 125.08 (1C, *C*H$_{triazole}$), 59.74 (1C, *C*H_2-NH_2), 56.10 (4C, Me_4N^+), 50.26 (1C, *C*H_2-triazole), 44.99 (1C, *C*H carborane), 42.74 (1C, *C*H carborane), 39.16 (1C, *C*H carborane), 37.91 (1C, -*C*H_2), 30.78 (1C, -*C*H_2-CH_2-

triazole). MS (ESI) *m/z*= 479.40 (M^-, 10%), 476.44 (100%); Calcd. for **11**$^-$ 479.35 (11%) and 476.35 (100%) [M^-]. EA found C, 50.0; H, 6.3; N, 7.1; Calcd. for Ph_4P**11**: C, 50.1; H, 6.2; N, 6.9%.

1.8. Synthesis of [8,8´-O -[(1-(4-(2,2´-bis-methoxycarbonyl-ethyl)-1,2,3-triazolyl)-$(CH_2)_3$-1,2-$C_2B_9H_9$)(1,2-$C_2B_9H_{10}$)-3,3'-Co(III)] Me_4N (Me_4N**12**)

Me_4N**7** (131 mg, 0.265 mmol) was dried under vacuum at 80 °C for 4 h. Dry Ethanol (30 mL) was added followed by dimethyl propargylmalonate (130 μL, 0.855 mmol), CuI (6 mg, 0.030 mmol) and DIPEA (0.5 mL, 2.871 mmol). The reaction mixture was stirred at 37 °C for 3 days. HPLC of the reaction mixture showed the presence of the starting material. Then dimethyl propargylmalonate (130 μL, 0.855 mmol), CuI (5 mg, 0.026 mmol) and DIPEA (0.5 mL, 2.871 mmol) were added and the reaction was stirred for 2 days at 37 °C. The crude product was purified on a C18 modified silica in reverse phase mode by 55% MeOH (*v/v*). Pure fractions (MS analysis) were combined and evaporated to dryness. The product was dissolved in minimal volume of MeOH and aqueous Me_4NCl was added to precipitate the click product.

Me_4N**12**.CH_3OH: 76 mg, yield= 41%. ^{11}B NMR δ_B(192 MHz; CD_3CN; $Et_2O.BF_3$): 13.74 (2B, s, B8, 8'), -5.86 (1B, d, *J 153*, B10), -7.02 (2B, d, *J 144*, B4, 10'), -9.12 (1B, br d, B4'), -9.64 (1B, br d, B7), -10.33 (1B, br d, B7'), -11.41 (3B, d, *J 130*, B9, 12, 9'), -13.46 (1B, d, *J 139*, B12'), -14.98 (1B, d, *J 155*, B5), -17.03 (3B, d, *J 125*, B11, 5', 11'), -25.75 (1B, br d, B6), -30.37 (1B, br d, B6'). ^{1}H NMR δ_H(600 MHz; CD_3CN): 7.49 (1H, s, C*H*$_{triazole}$), 4.27-4.18 (2H, m, C*H*$_2$-triazole), 3.78 (1H, t, $^3J_{HH}$ *7.64*, C*H*-CH_2-$C_{triazole}$), 3.67 (6H, s, C*H*$_3$O-), 3.19 (2H, br s, C*H*$_2$-$C_{triazole}$), 3.18 (1H, s, C*H* carborane), 3.09 (12H, s, Me_4N^+), 3.03 (1H, br s, C*H* carborane), 2.31-2.23 (1*H*, m, -C*H*$_2$), 2.21-2.17 (1*H*, m, -C*H*$_2$), 1.98-1.96 (2H, m, -C*H*$_2$-CH_2-triazole), 1.92 (1H, br s, C*H* carborane). ^{13}C{^{1}H} NMR δ_C (150 MHz; CD_3CN): 170.04 (2C, *C*=O), 144.59 (1C, *C*$_{triazole}$), 123.39 (1C, *C*H$_{triazole}$), 59.51 (1C, *C* carborane), 56.14 (4C, Me_4N^+), 53.22 (2C, *C*H_3O-), 52.31 (1C, *C*H-CH_2-$C_{triazole}$), 49.90 (1C, *C*H_2-triazole), 44.25 (1C, *C*H carborane), 42.61 (1C, *C*H carborane), 38.34 (1C, *C*H carborane), 38.11 (1C, -*C*H_2), 30.61 (1C, -*C*H_2-CH_2-triazole), 25.68 (1C, *C*H_2-$C_{triazole}$). MS (ESI) *m/z*= 594.36 (M^-, 17%), 591.48 (100%); Calcd. for **12**$^-$ 594.36 (17%) and 591.37 (100%) [M^-]. EA found C, 34.9; H, 7.2; N, 8.2; Calcd. for Me_4N**12**.CH_3OH: C, 34.5; H, 7.4; N, 8.0%.

1.9. Synthesis of [8,8´-O -[(1-(4-(2-amino-2-carboxyethyl)-1,2,3-triazolyl)-$(CH_2)_3$-1,2-$C_2B_9H_9$)(1,2-$C_2B_9H_{10}$)-3,3'-Co(III)] Me_4N (Me_4N**13**)

Me_4N**7** (129 mg, 0.261 mmol) was dried under vacuum at 80 °C for 4 h. Dry Ethanol (30 mL) was added followed by L-C-propargylglycine (74 mg, 0.652 mmol), CuI (5 mg, 0.026 mmol) and DIPEA (0.5 mL, 2.871 mmol). The reaction mixture was stirred at 37 °C and controlled by MS. After 2 days, the MS showed the presence of the starting material in reaction mixture. Then L-C-propargylglycine (70 mg, 0.619 mmol), CuI (7 mg, 0.037 mmol) and DIPEA (0.5 mL, 2.871 mmol) were added and the reaction was stirred for 2 days at 37 °C. The crude product was obtained by purification on a C18 modified silica in reverse phase mode by 45 to 55% aqueous MeOH (*v/v*). Pure fractions were combined and evaporated to dryness. The product was

dissolved in minimal volume of MeOH and precipitated by aqueous Me_4NCl. The product was crystallized twice from hot aqueous MeOH. The low isolatable yield is due to presence of a side product with *m/z*= 630 (100% abundance, formed in the reaction mixture in 15% to 20% after quenching the reaction), which was difficult to separate. This side product may possibly correspond to complexation of copper(II) hydroxide with **7**$^-$. The peaks in ^{11}B NMR spectra are broader due to aggregation in solution.

Me_4N**13**: 19 mg, yield 12%. ^{11}B NMR δ_B(192 MHz; $(CD_3)_2CO$; $Et_2O.BF_3$): 14.13 (2B, s, B8, 8'), -5.74 (1B, d, *J 149*, B10), -6.87 (2B, d, *J 155*, B4, 10'), -9.16 (3B, br d, B7, 4', 7'), -11.19 (3B, d, *J 123*, B9, 12, 9'), -13.22 (1B, d, *J 143*, B12'), -14.97 (1B, br d, B5), -16.96 (3B, br d, B11, 5', 11'), -25.79 (1B, br d, B6), -30.33 (1B, br d, B6'). ^1H NMR δ_H(600 MHz; (CD_3OD): 7.95 (4H, t, $^3J_{HH}$ *7.25*, Ph_4P^+), 7.84-7.79 (9H, m, Ph_4P^+ + C*H*$_{triazole}$), 7.77-7.71 (8H, m, Ph_4P^+), 4.38-4.31 (2H, m, C*H*$_2$-triazole), 3.99 (1H, br s, C*H*-CH_2-triazole), 3.27 (1H, s, C*H* carborane), 3.09 (1H, br s, C*H* carborane), 2.41-2.34 (1*H*, m, -C*H*$_2$), 2.33-2.27 (1*H*, m, -C*H*$_2$), 2.11-2.01 (4H, m, -C*H*$_2$-CH_2-triazole + CH-C*H*$_2$-triazole), 1.89 (1H, br s, C*H* carborane). $^{13}C\{^1H\}$ NMR δ_C (150 MHz; $(CD_3)_2CO$): 124.05 (1C, *C*H$_{triazole}$), 59.21 (1C, *C* carborane), 58.99 (1C, *C*H-CH_2-triazole), 56.03 (4C, Me_4N^+), 49.92 (1C, *C*H_2-triazole), 44.16 (1C, *C*H carborane), 42.43 (1C, *C*H carborane), 38.29 (1C, -*C*H_2), 38.20 (1C, *C*H carborane), 30.80 (1C, -*C*H_2-CH_2-triazole), 30.36 (1C, *C*H_2-C$_{triazole}$). MS (ESI) *m/z*= 537.36 (*M*$^-$, 12%), 534.40 (100%); Calcd. for **13**$^-$ 537.35 (12%) and 534.36 (100%) [*M*$^-$]. EA found C, 48.9; H, 6.4; N, 5.6; Calcd. for Ph_4P**13**.2CH_3OH: C, 48.7; H, 6.5; N, 6.0%.

1.10. Synthesis of [8,8´-O -[(1-(4-(1-pyrenyl)-1,2,3-triazolyl)-$(CH_2)_3$-1,2-$C_2B_9H_9$)(1,2-$C_2B_9H_{10}$)-3,3'-Co(III)] Me_4N (Me_4N**14**)

Me_4N**7** (34 mg, 0.069 mmol) was dried under vacuum at 80^{o}C for 4h. Dry Ethanol (10 mL) was added followed by 1-ethynylpyrene (39 mg, 0.172 mmol), CuI (3 mg, 0.016 mmol) and DIPEA (0.2 mL, 1.148 mmol). The reaction mixture was stirred at 37 ^{o}C for 3 days. HPLC of the reaction mixture showed the presence of the starting material. Then 1-ethynylpyrene (36 mg, 0.159 mmol), CuI (3 mg, 0.016 mmol) and DIPEA (0.2 mL, 1.148 mmol) were added and the reaction was stirred for 4 days at 37 ^{o}C. MS of the reaction mixture showed the presence of SM (100%) and click product (6%). The reaction mixture was heated at 50 ^{o}C. After 3 days, the MS showed increasing of abundance up to 14%. Then another portion of 1-ethynylpyrene (42 mg, 0.186 mmol) was added. The reaction mixture was heated at 60 °C for 3 days. MS showed the presence of SM (100%) and click product (36%) and temperature was increased at 70 °C. After 2 days, the abundance of the click product reached 47% and the reaction was stopped. The crude product was obtained by purification on a C18 modified silica in reverse phase mode by 60% aqueous MeOH (*v/v*). The pure fractions (MS analysis) were combined and evaporated to dryness. The product was dissolved in minimal volume of MeOH and precipitated by aqueous Me_4NCl.

Me_4N**14**: 22 mg, yield 44%. ^{11}B NMR δ_B(192 MHz; $(CD_3)_2CO$; $Et_2O.BF_3$): 14.08 (2B, s, B8, 8'), -5.85 (1B, d, *J 151*, B10), -6.94 (2B, d, *J 143*, B4, 10'), -9.04 (2B, br d, B7, 4'), -10.21 (1B, br d, B7'), -

11.29 (3B, d, *J 132*, B9, 12, 9'), -13.28 (1B, d, *J 138*, B12'), -14.88 (1B, d, *J 151*, B5), -17.00 (3B, br d, B11, 5', 11'), -25.99 (1B, br d, B6), -30.46 (1B, br d, B6'). ^{1}H NMR δ_H(600 MHz; $(CD_3)_2CO$): 8.95-8.92 (1H, m, C*H*$_{pyrenyl}$), 8.53 (1H, s, C*H*$_{triazole}$), 8.34-8.28 (4H, m, C*H*$_{pyrenyl}$), 8.22-8.20 (1H, m, C*H*$_{pyrenyl}$), 8.18-8.17 (2H, m, C*H*$_{pyrenyl}$), 8.07 (1H, td, $^{3}J_{HH}$ *7.42*, $^{3}J_{HH}$ *3.11*, C*H*$_{pyrenyl}$), 4.64-4.56 (2H, m, C*H*$_2$-triazole), 3.40 (13H, s, Me_4N^+ + C*H* carborane), 3.19 (1H, br s, C*H* carborane), 2.62-2.59 (1H, m, -C*H*$_2$), 2.54-2.48 (1H, m, -C*H*$_2$), 2.30-2.22 (3H, m, -C*H*$_2$-CH_2-triazole + C*H* carborane). ^{13}C{^{1}H} NMR δ_C (150 MHz; $(CD_3)_2CO$): 132.37 (1C, *C*$_{pyrenyl}$), 131.96 (1C, *C*$_{pyrenyl}$), 131.87 (1C, *C*$_{pyrenyl}$), 129.07 (1C, *C*$_{pyrenyl}$), 128.71 (1C, *C*H$_{pyrenyl}$), 128.53 (1C, *C*H$_{pyrenyl}$), 128.28 (1C, *C*H$_{pyrenyl}$), 128.07 (1C, *C*H$_{pyrenyl}$), 127.16 (1C, *C*H$_{pyrenyl}$), 126.94 (1C, *C*$_{pyrenyl}$), 126.26 (1C, *C*H$_{pyrenyl}$), 126.23 (1C, *C*H$_{pyrenyl}$), 125.97 (1C, *C*H$_{pyrenyl}$), 125.86 (1C, *C*H$_{pyrenyl}$), 125.81 (1C, *C*$_{pyrenyl}$), 125.45 (1C, *C*$_{pyrenyl}$), 124.75 (1C, *C*H$_{triazole}$), 55.97 (4C, Me_4N^+), 50.24 (1C, *C*H_2-triazole), 43.99 (1C, *C*H carborane), 42.39 (1C, *C*H carborane), 38.51 (1C, -*C*H_2), 38.16 (1C, *C*H carborane), 30.85 (1C, -*C*H_2-CH_2-triazole). MS (ESI) *m/z*= 650.32 (M^-, 15%), 647.44 (100%); Calcd. for **14**$^-$ 650.38 (15%) and 647.39 (100%) [M^-]. EA found C, 58.3; H, 5.6; N, 4.3; Calcd. for Ph_4P**14.**H_2O: C, 58.6; H, 5.7; N, 4.2%.

2. Preparation of the di-substituted derivatives

2.1. Synthesis of [8,8'-μ-O-(1,1'-HO-$(CH_2)_3$-1,2-$C_2B_9H_9)_2$-3,3'-Co(III)] Me_3NH (Me_3NH**4**)

The starting Cs**2** (1.0 g, 2.12 mmol) was dried in vacuum at 120 °C for 5 h then at 185 °C for 2.5 h. Dry DME was injected (30 mL) and the resulting solution was cooled down under stirring on a bath of CO_2(s) and acetone. Then BuLi (2.5 M in hexane, 2 mL, 5.0 mmol) was added dropwise from syringe over 10 min. The bath was removed and reaction mixture was allowed to warm up under stirring to room temperature and stirred for additional 15 min. The reaction mixture was cooled down again on a bath of CO_2(s) and acetone then trimethylene oxide (300 μL, 4.61 mmol) was injected. The colour changed within minutes from dark violet-black to lighter violet, nevertheless the reaction was stirred overnight in the bath, while warmed up to room temperature. HPLC and MS analysis showed the presence of rac-form of the disubstituted product as the prevailing species. The reaction was quenched by careful addition of MeOH and few drops of diluted HCl (3M). The solvents were removed at reduced pressure, the residue was dried in vacuum. The mixture was purified on a silica gel column (30 x 3.5 cm *I.D.*), increasing the CH_3CN content from initial 15% to 50%. The pure fractions were evaporated. Methanol was added dropwise until dissolution of the solid material, and the compounds were precipitated by addition of an excess of aqueous Me_3N.HCl in water.

Me_3NH**4**: 460 mg, yield 42%. ^{11}B NMR δ_B(192 MHz; CD_3CN; $Et_2O.BF_3$): 13.07 (2B, s, B8, 8'), -6.50 (2B, d, *J 140*, B10, 10'), -8.33 (2B, d, *J 161*, B4, 4'), -9.32 (2B, d, *J 162*, B7, 7'), -11.07 (2B, d, *J 137*, B9, 9'), -13.18 (2B, d, *J 134*, B12, 12'), -14.68 (2B, d, *J 135*, B5, 5'), -16.99 (2B, d, *J 128*, B11, 11'), -24.83 (2B, d, *J 128*, B6, 6'). ^{1}H NMR δ_H(600 MHz; CD_3CN): 3.51-3.48 (2*H*, m, C*H*$_2$-OH), 3.42-3.38 (2*H*, m, C*H*$_2$-OH), 2.79 (9H, s, Me_3NH^+), 2.73 (2H, s, C*H* carborane), 2.57 (2H, td, $^{3}J_{HH}$ *13.65*, $^{3}J_{HH}$

4.34, -C*H*$_2$), 2.36 (2H, td, $^3J_{HH}$ *13.42*, $^3J_{HH}$ *4.99*, -C*H*$_2$), 1.79-1.74 (2*H*, m, -C*H*$_2$-CH$_2$-OH), 1.68-1.62 (2*H*, m, -C*H*$_2$-CH$_2$-OH). $\delta_{B\text{-}H}$ (^{1}H-{^{11}B} NMR, 600 MHz; CD_3CN): 3.89 (4H, br s, B-H), 2.73 (2H, s, C*H* carborane), 2.63 (2H, s, B-H), 2.12 (8H, br s, B-H), 1.44 (2H, br s, B-H). ^{13}C{^{1}H} NMR δ_C (150 MHz; CD_3CN): 61.54 (2C, *C*H$_2$-OH), 50.50 (2C, *C* carborane), 45.73 (3C, Me_3NH^+), 38.08 (2C, -*C*H$_2$), 33.26 (2C, -*C*H$_2$-CH$_2$-OH). MS (ESI) *m/z*= 457.36 (*M*$^-$, 12%), 454.56 (100%); Calcd. for **4**$^-$ 457.34 (11%) and 454.35 (100%) [*M*$^-$]. EA found C, 30.7; H, 7.9; N, 2.8; Calcd. for Me_3NH**4**: C, 30.4; H, 8.2; N, 2.7%.

2.2. Synthesis of [8,8'-µ-O-(1,1'-$MeSO_2$-O-$(CH_2)_3$-1,2-$C_2B_9H_9)_2$-3,3'-Co(III)] Me_4N (Me_4N**6)**

The reaction was performed in analogy with Me_4N**5**. Dried Me_3NH**4** (275 mg, 0.53 mmol) was reacted in dry CH_3CN (30 ml), K_2CO_3 (1.55 g, 11.21 mmol) and mesyl chloride (500 µl, 6.46 mmol) at 45 °C for 12 h. The solids were filtered under argon, washed with CH_3CN (3x 3 mL) and discarded. Combined organic fractions were evaporated in vacuum, then dissolved in minimal volume of MeOH and aqueous Me_4NCl was added to precipitate a voluminous violet precipitate. This was left to settle down to walls of the flask over 10 min. (with occasional vigorous mixing). The solid was quickly, but carefully decanted, washed with water (3x 5 mL) and quickly dried in vacuum. The compound from mother liquors was not separated. Due to limited stability on silica gel column, the solid after precipitation was used in synthesis of azide, without additional purifications.

Me_4N**6**: 355 mg, yield 97%. ^{11}B NMR δ_B(192 MHz; $(CD_3)_2CO$; $Et_2O.BF_3$): 13.79 (2B, s, B8, 8'), -6.56 (2B, d, *J 144*, B10, 10'), -8.25 (2B, br d, B4, 4'), -9.15 (2B, br d, B7, 7'), -10.79 (2B, d, *J 139*, B9, 9'), -12.82 (2B, d, *J 135*, B12, 12'), -14.81 (2B, d, *J 139*, B5, 5'), -16.86 (2B, d, *J 147*, B11, 11'), -25.13 (2B, br d, B6, 6'). ^{1}H NMR δ_H(600 MHz; $(CD_3)_2CO$): 4.30-4.19 (4H, m, C*H*$_2$-OMs), 3.42 (12H, s, Me_4N^+), 3.07 (6H, s, CH_3), 2.77 (2H, s, C*H* carborane), 2.75-2.69 (2H, m, -C*H*$_2$), 2.53-2.48 (2H, m, -C*H*$_2$), 2.11-2.07 (2H, m, -C*H*$_2$-CH$_2$-OMs), 1.98-1.91 (2H, m, -C*H*$_2$-CH$_2$-OMs). $\delta_{B\text{-}H}$ (^{1}H-{^{11}B} NMR, 600 MHz; $(CD_3)_2CO$): 3.97 (4H, br s, B-H), 2.77 (2H, s, C*H* carborane), 2.41 (2H, s, B-H), 1.85 (2H, br s, B-H), 1.76 (4H, br s, B-H), 1.38 (4H, br s, B-H). ^{13}C{^{1}H} NMR δ_C (150 MHz; $(CD_3)_2CO$): 70.46 (2C, *C*H$_2$-OMs), 58.85 (2C, -*C*H$_2$), 55.86 (4C, Me_4N^+), 48.95 (2C, *C* carborane), 37.28 (2C, *C*H$_3$), 36.82 (2C, -*C*H$_2$-CH$_2$-OMs). MS (ESI) *m/z*= 614.20 (*M*$^-$, 15%), 610.32 (100%); Calcd. for **6**$^-$ 614.29 (15%) and 610.30 (100%) [*M*$^-$].

2.3. Synthesis of [8,8'-µ-O-(1-$N_3(CH_2)_3$-1,2-$C_2B_9H_9)_2$-3,3'-Co(III)] Me_4N (Me_4N**8**)

Me_4N**6** (325 mg, 0.48 mmol) was dried at room temperature together with sodium azide (650 mg, 10.00 mmol) for 4h. Then, DMF (10 mL, anhydrous sigma aldrich) was injected and the reaction mixture was stirred at 45 °C overnight. The excess of inorganic azide was filtered off, solid washed with DMF (2x 2 mL) and the organic solvent was removed in vacuum at 45 °C. The crude products were chromatographed on a short column of silica gel (20 x 2.0 cm *I.D.*) using CH_2Cl_2:MeOH (88:12 to 88:15 b.v.). Pure fractions were dissolved in MeOH and precipitated quickly by an excess of aqueous Me_4NCl.

Me_4N**8**: 205 mg, yield 75%. ^{11}B NMR δ_B(192 MHz; CD_3CN; $Et_2O.BF_3$): 13.77 (2B, s, B8, 8'), -6.62 (2B, d, *J 143*, B10, 10'), -8.23 (2B, d, *J 157*, B4, 4'), -9.13 (2B, d, *J 150*, B7, 7'), -10.83 (2B, d, *J 138*, B9, 9'), -12.90 (2B, d, *J 138*, B12, 12'), -14.84 (2B, d, *J 151*, B5, 5'), -16.95 (2B, d, *J 150*, B11, 11'), -25.15 (2B, br d, *J 130*, B6, 6'). ^1H NMR δ_H(600 MHz; CD_3CN): 3.35-3.26 (4H, m, C*H*$_2$-N_3), 3.08 (12H, s, Me_4N^+), 2.62 (2H, s, C*H*$_{carborane}$), 2.55-2.51 (2H, m, -C*H*$_2$), 2.40-2.34 (2H, m, -C*H*$_2$), 1.84-1.79 (2H, m, -C*H*$_2$-CH_2-N_3), 1.77-1.71 (2H, m, -C*H*$_2$-CH_2-N_3). δ_{B-H} (^1H-{^{11}B} NMR, 600 MHz; CD_3CN): 3.84 (4H, br s, B-H), 2.62 (2H, s, C*H* carborane), 2.32 (2H, s, B-H), 1.73 (4H, br s, B-H), 1.62 (2H, br s, B-H), 1.37 (4H, br s, B-H). $^{13}C\{^1H\}$ NMR δ_C (150 MHz; CD_3CN): 56.15 (4C, Me_4N^+), 51.56 (2C, *C*H_2-N_3), 49.45 (2C, *C*H carborane), 38.51 (2C, -*C*H_2), 29.62 (2C, -*C*H_2-CH_2-N_3). MS (ESI) *m/z*= 507.24 (*M*$^-$, 17%), 504.36 (100%); Calcd. for **8**$^-$ 507.35 (18%) and 504.36 (100%) [*M*$^-$]. EA found C, 22.2; H, 5.6; N, 15.6; Calcd. for K**8**: C, 22.1; H, 5.6; N, 15.5%.

2.4. Synthesis of [8,8'-O-[(1-(4-phenyl-1,2,3-triazolyl)-$(CH_2)_3$-1,2-$C_2B_9H_9)_2$-3,3'-Co(III)] Me_4N (Me_4N**15**)

Me_4N**8** (130 mg, 0.225 mmol) was dried under vacuum at 80 °C for 4 h. Dry Ethanol (30 mL) was added followed by phenylacetylene (150 µL, 1.366 mmol), CuI (10 mg, 0.052 mmol) and DIPEA (0.6 mL, 3.445 mmol). The reaction mixture was stirred at 37 °C for 36 h where MS did not show the presence of starting material or the monosubstituted product. The solvents were evaporated and the crude product was purified on a C18 modified silica in reverse phase mode by 55% MeOH (*v/v*). Reversed phase 55% MeOH (*v/v*). Pure fractions were combined and evaporated to dryness. The product was dissolved in minimal volume of MeOH and aqueous Me_4NCl was added to precipitate the click product.

Me_4N**15**: 84 mg, yield 48%. ^{11}B NMR δ_B(192 MHz; CD_3CN; $Et_2O.BF_3$): 13.29 (2B, s, B8, 8'), -6.89 (2B, d, *J 140*, B10, 10'), -8.64 (2B, br d, B4, 4'), -9.44 (2B, br d, B7, 7'), -11.14 (2B, d, *J 137*, B9, 9'), -13.12 (2B, d, *J 134*, B12, 12'), -15.03 (2B, d, *J 135*, B5, 5'), -17.08 (2B, d, *J 128*, B11, 11'), -25.16 (2B, br s, B6, 6'). ^1H NMR δ_H(600 MHz; CD_3CN): 8.01 (2H, s, C*H*$_{triazole}$), 7.83 (4H, d, $^3J_{HH}$ *7.70*, C*H*$_{phenyl}$), 7.41 (4H, t, $^3J_{HH}$ *7.66*, C*H*$_{phenyl}$), 7.31 (2H, t, $^3J_{HH}$ *7.44*, C*H*$_{phenyl}$), 4.37-4.29 (2H, m, C*H*$_2$-triazole), 4.20-4.12 (2H, m, C*H*$_2$-triazole), 3.05 (12H, s, Me_4N^+), 2.16-2.06 (4*H*, m, -C*H*$_2$), 2.02-1.94 (2*H*, m, -C*H*$_2$-CH_2-triazole), 1.89-1.84 (2H, m, -C*H*$_2$-CH_2-triazole), 1.80 (2H, s, C*H* carborane). $^{13}C\{^1H\}$ NMR δ_C (150 MHz; CD_3CN): 129.82 (4C, *C*H$_{phenyl}$), 128.97 (2C, *C*H$_{phenyl}$), 126.45 (4C, *C*H$_{phenyl}$), 121.99 (2C, *C*H$_{triazole}$), 56.13 (4C, Me_4N^+), 50.19 (2C, *C*H_2-triazole), 48.64 (2C, *C*H carborane), 38.10 (2C, -*C*H_2), 30.66 (2C, -*C*H_2-CH_2-triazole). MS (ESI) *m/z*= 711.36 (*M*$^-$, 21%), 708.48 (100%); Calcd. for **15**$^-$ 711.45 (22%) and 708.45 (100%) [*M*$^-$]. EA found C, 57.1; H, 6.2; N, 8.3; Calcd. for Ph_4P**15**: C, 57.4; H, 6.0; N, 8.0%.

2.5. Synthesis of [8,8'-O-[(1-(4-aminomethyl-1,2,3-triazolyl)-$(CH_2)_3$-1,2-$C_2B_9H_9)_2$-3,3'-Co(III)] Me_4N (Me_4N**16**)

Me_4N**8** (127 mg, 0.220 mmol) was dried under vacuum at 80 °C for 4 h. Dry Ethanol (30 mL) was added followed by propargylamine hydrochloride (107 mg, 1.169 mmol), CuI (10 mg, 0.052

mmol) and DIPEA (0.6 mL, 3.445 mmol). The reaction mixture was stirred at rt for 2 days. MS of the reaction mixture showed the presence of SM (100%), mono click product (18%) and di click product (14%). Then propargylamine hydrochloride (101 mg, 1.103 mmol), CuI (15 mg, 0.079 mmol) and DIPEA (0.6 mL, 3.445 mmol) were added and the reaction was stirred for 4 days at 37 °C where MS showed only the presence of di click product. The solvents were evaporated and purified on a silica column using CH_2Cl_2-MeOH by increasing gradually the percentage of MeOH from 20% to 100%. The pure fractions were combined, concentrated under vacuum and dissolved in minimal volume of MeOH. The click product precipitated after addition of aqueous Me_4NCl. The peaks in ^{11}B NMR spectra are broad, probably as a consequence of aggregation in solution.

Me_4N**16**: 69 mg, yield 46%. ^{11}B NMR δ_B(192 MHz; CD_3OD; $Et_2O.BF_3$): 14.34 (2B, s, B8, 8'), -5.05 (3B, br d, B10, 4, 10'), -7.53 (2B, br d, B7, 4'), -9.52 (3B, br d, B9, 7', 9'), -11.60 (2B, br d, B12, 12'), -13.83 (2B, br d, B5, 5'), -15.68 (2B, br d, B11, 11'), -23.49 (2B, br s, B6, 6'). ^1H NMR δ_H(600 MHz; CD_3OD): 8.11 (2H, s, C*H*$_{triazole}$), 7.92 (4H, t, $^3J_{HH}$ *7.14*, C*H*$_{phenyl}$), 7.78-7.75 (8H, m, C*H*$_{phenyl}$), 7.74-7.70 (8H, m, C*H*$_{phenyl}$), 4.49-4.44 (2H, m, C*H*$_2$-triazole), 4.41-4.36 (2H, m, C*H*$_2$-triazole), 4.24 (4H, s, NH_2-C*H*$_2$-triazole), 2.36-2.31 (2H, m, -C*H*$_2$), 2.28-2.23 (2H, m, -C*H*$_2$), 2.17-2.14 (2H, m, -C*H*$_2$-CH_2-triazole), 2.12 (2H, br s, C*H* carborane), 2.08-2.04 (2H, m, -C*H*$_2$-CH_2-triazole). $^{13}C\{^1H\}$ NMR δ_C (150 MHz; CD_3OD): 126.00 (2C, *C*H$_{triazole}$), 60.20 (2C, *C* carborane), 55.86 (4C, Me_4N^+), 50.83 (2C, *C*H_2-triazole), 50.37 (2C, *C*H carborane), 38.56 (2C, -*C*H_2), 35.54 (2C, NH_2-*C*H_2-triazole), 31.36 (2C, -*C*H_2-CH_2-triazole). MS (ESI) *m/z*= 617.40 (M^-, 17%), 614.48 (100%); Calcd. for **16**$^-$ 617.44 (18%) and 614.44 (100%) [M^-]. EA found C, 50.3; H, 6.2; N, 11.6; Calcd. for Ph_4P**16**: C, 50.4; H, 6.3; N, 11.8%.

2.6. Synthesis of [8,8'-O-[(1-(4-(2,2´-bis-methoxycarbonyl-ethyl)-1,2,3-triazolyl)-$(CH_2)_3$-1,2-$C_2B_9H_9)_2$-3,3'-Co(III)] Me_4N (Me_4N**17**)

Me_4N**8** (128 mg, 0.220 mmol) was dried under vacuum at 80 °C for 4 h. Dry Ethanol (30 mL) was added followed by dimethyl propargylmalonate (170 μL, 1.118 mmol), CuI (9 mg, 0.047 mmol) and DIPEA (0.6 mL, 3.445 mmol). The reaction mixture was stirred at 37 °C for 2 days. The MS of the reaction mixture did not contained peak for either the starting material or the monosubstituted. The crude product was purified on a column with C18 modified silica in reverse phase mode using 55% MeOH (*v/v*). Pure fractions were combined and evaporated to dryness. The product was dissolved in minimal volume of MeOH and aqueous Me_4NCl was added to precipitate the click product. Low isolatable reaction yield is due to presence of a side product with *m/z*= 591, which was difficult to separate. The origin of this side product could not be identified. The peaks in ^{11}B NMR spectra are broad, apparently due to an aggregation.

Me_4N**17**: 24 mg, yield 12%. ^{11}B NMR δ_B(192 MHz; CD_3CN; $Et_2O.BF_3$): 14.28 (2B, s, B8, 8'), -7.05 (4B, br d, B4, 10, 4', 10'), -10.79 (4B, d, *J 148*, B7, 9, 7', 9'), -12.49 (4B, d, *J 141*, B5, 12, 5', 12'), -16.30 (2B, br d, B11, 11'), -27.64 (2B, br d, B6, 6'). ^1H NMR δ_H(600 MHz; CD_3CN): 4.50-4.43 (2H,

m, C*H*$_2$-triazole), 4.05-4.43 (2H, m, C*H*$_2$-triazole), 3.90 (2H, t, $^3J_{HH}$ *7.42*, C*H*-CH$_2$-C$_{triazole}$), 3.69 (6H, s, C*H*$_3$O-), 3.61 (6H, s, C*H*$_3$O-), 3.16-3.12 (2H, m, C*H*$_2$-C$_{triazole}$), 3.09 (12H, s, Me_4N^+), 2.96-2.86 (2H, m, C*H*$_2$-C$_{triazole}$), 2.48-2.36 (4*H*, m, -C*H*$_2$), 1.92-1.89 (2*H*, m, -C*H*$_2$-CH$_2$-triazole), 1.84-1.77 (2H, m, -C*H*$_2$-CH$_2$-triazole), 1.79 (2H, br s, C*H* carborane). $^{13}C\{^1H\}$ NMR δ_C (150 MHz; CD_3CN): 169.78 (4C, *C*=O), 145.72 (2C, *C*$_{triazole}$), 122.40 (2C, *C*H$_{triazole}$), 59.03 (2C, *C* carborane), 56.13 (4C, Me_4N^+), 53.38 (2C, *C*H$_3$O-), 53.27 (2C, *C*H$_3$O-), 51.11 (2C, *C*H-CH$_2$-C$_{triazole}$), 49.21 (2C, *C*H$_2$-triazole), 46.33 (2C, *C*H carborane), 37.75 (2C, -*C*H$_2$), 29.37 (2C, -*C*H$_2$-CH$_2$-triazole), 25.15 (2C, *C*H$_2$-C$_{triazole}$). MS (ESI) *m/z*= 846.24 (*M*$^-$, 17%), 842.44 (100%); Calcd. for **17**$^-$ 846.47 (17%) and 842.46 (100%) [*M*$^-$]. EA found C, 50.5; H, 5.9; N, 7.5; Calcd. for Ph_4P**17**: C, 50.8; H, 6.0; N, 7.1%.

III. Crystallography

Full-sets of diffraction data for orange crystals of **3**$^-$ and **4**$^-$, were collected at 150(2)K with a Bruker D8-Venture diffractometer equipped with Cu (Cu/Kα radiation; λ =1.54178 Å) or Mo (Mo/Kα radiation; λ = 0.71073 Å) microfocus X-ray (IμS) sources, Photon CMOS detector and Oxford Cryosystems cooling device was used for data collection.

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). Obtained data were treated by XT-version 2014/5 and SHELXL-2017/4 software implemented in APEX3 v2016.5-0 (Bruker AXS) system.[2]

Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors H_{iso}(H) = 1.2 U_{eq} (pivot atom) or of 1.5U_{eq} (methyl). H atoms in methyl and methylene moieties were placed with C-H distances of 0.96, 0.97, 0.86 for N-H bonds and 1.1 Å for B-H and C-H bonds in the carborane cage. Atoms of N-H group were placed according the maxima on a difference Fourier map where appropriate and refined freely. Disorders of the solvent molecules, aliphatic chain were treated by standard methods implemented in SHELXL software package.

$R_{int} = \sum | F_o^2 - F_{o,mean}^2 | / \sum F_o^2$, GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$ for all data, $R(F) = \sum | | F_o | - | F_c | | / \sum | F_o |$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$ for all data.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 2119374-2119375 for **4**$^-$ and **3**$^-$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

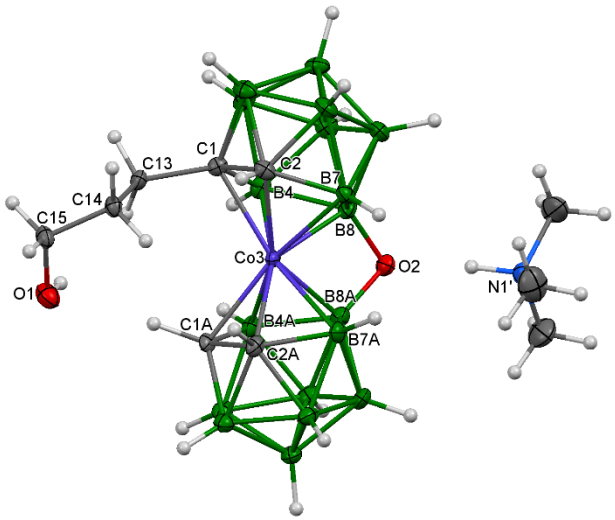


Figure S1: The molecular structure of $\mathbf{3}^-$ (ORTEP view, 40% probability level). Disordered part of hydroxypropyl chain is omitted for clarity. Selected interatomic distances [Å] and angles [°]: O2—B8 1.460(5), O2—B8A 1.462(5), B4—C1 1.696(5), B4—B9 1.762(6), C15—O1 1.460(11), B4—B5 1.763(6), B4—B8 1.841(6), B4—Co3 2.097(4), Co3—B8 2.021(4), Co3—B8A 2.021(4), Co3—B7 2.087(4), Co3—B7A 2.096(4), C13A—C1A 1.554(13), Co3—B4A 2.098(4), Co3—C2A 2.101(4), Co3—C1A 2.102(3), Co3—C2 2.103(4), Co3—C1 2.114(3), B7—C2 1.688 (6), C1—C2 1.601 (5), C2A—C1A 1.609(5), B8—O2—B8A 93.3(3), N1'—H1'···O2 2.704(4), 174.

Table S1: Experimental details for $\mathbf{3}^-$.

Crystal data	
Chemical formula	$C_7H_{26}B_{18}CoO_2 \cdot C_3H_{10}N$
M_r	455.91
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	150
a, *b*, *c* (Å)	19.2195 (12), 12.1823 (9), 20.1517 (10)
V (Å^3)	4718.3 (5)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	0.74
Crystal size (mm)	0.59 × 0.59 × 0.07
Data collection	

Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.500, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	42516, 5413, 3691
R_{int}	0.129
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.064, 0.149, 1.06
No. of reflections	5413
No. of parameters	391
No. of restraints	570
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 14.2314P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.41, −1.05

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.9-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2017*/1 (Sheldrick, 2017), Bruker *SHELXTL*.

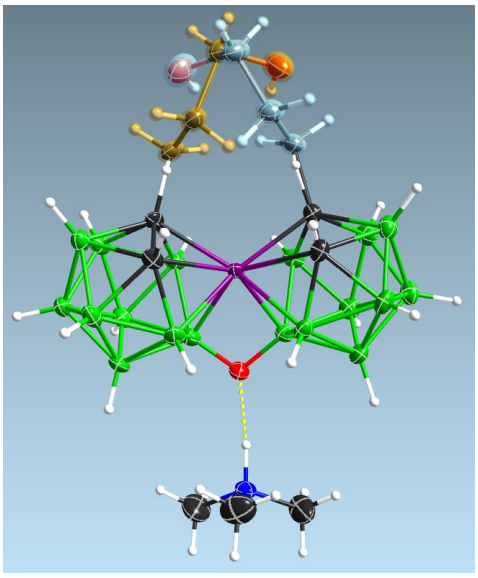


Figure S2: Schematic view of the disordered hydroxylpropyl chains (highlighted in gold and silver) with occupancy of 70:30.

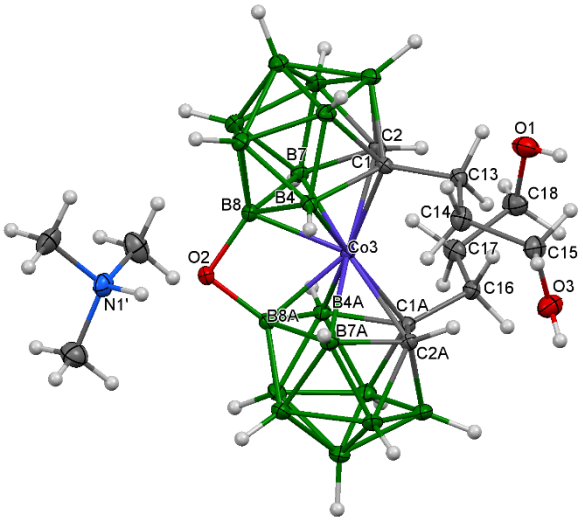


Figure S3: The molecular structure of **4**$^{-}$ (ORTEP view, 40% probability level). Selected interatomic distances [Å] and angles [°]: B5A—C1A 1.718(2), C1—C2 1.601(2), B5A—B6A 1.742(3), C1—B4 1.709(2), B5A—B10A 1.768(3), C1—B5 1.724(2), B5A—B9A 1.794(3), C1—B6 1.760(2), C1—Co3 2.1141(14), B8—B12 1.797(2), O2—B8A 1.4576(19), B7—B11 1.775(2), O2—B8 1.4630(19), C2—B7 1.691(2), Co3—B8A 2.0195(16), Co3—B8 2.0208(16), Co3—B4 2.0851(17), Co3—B4A 2.0862(17), Co3—B7 2.0893(17), Co3—B7A 2.0921(17), Co3—C1A 2.1144(15), B4A—C1A 1.708(2), C2A—C1A 1.605(2), B8A—O2—B8 93.54(11).

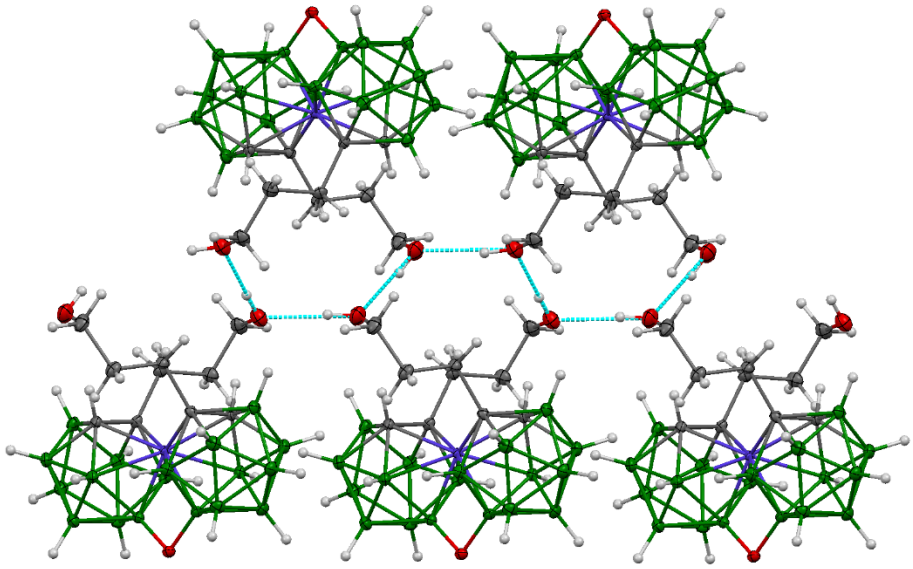


Figure S4: View of the hydrogen bonding in **4**$^{-}$ (ORTEP view, 40% probability level).

Table S2: Hydrogen-bond geometry (Å, º) for **4**$^{-}$.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1^{A}b···O3^{i}	0.81 (1)	1.85 (1)	2.660 (2)	175 (4)
N1′—H1′···O2	1.00	1.73	2.6801 (17)	158
O3—H3a···O3^{ii}	0.81 (1)	1.89 (1)	2.696 (3)	173 (4)

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*+1, −*y*+2, −*z*+1.

Table S3: Experimental details for **4**$^{-}$.

Crystal data	
Chemical formula	$C_{10}H_{32}B_{18}CoO_3 \cdot C_3H_{10}N$
M_r	513.98
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	150
a, *b*, *c* (Å)	19.5523 (7), 8.3138 (3), 33.9151 (12)
β (°)	96.284 (1)
V (Å^3)	5479.9 (3)

Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.65
Crystal size (mm)	0.59 × 0.30 × 0.09
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.636, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	61778, 6334, 5428
R_{int}	0.041
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.652
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.075, 1.07
No. of reflections	6334
No. of parameters	417
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.29, –0.39

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.9-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2017*/1 (Sheldrick, 2017), Bruker *SHELXTL*.

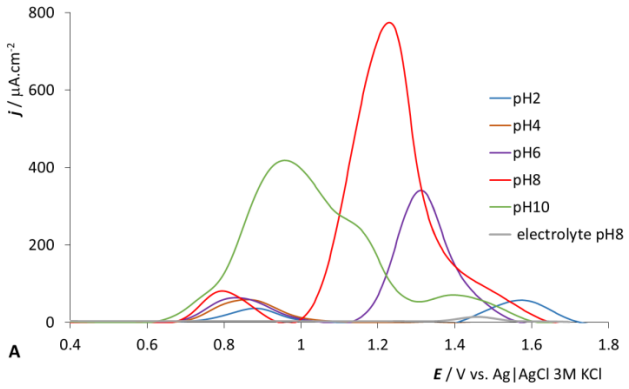
The interplanar angles of dicarbollide ligands (C1-C2-B4-B8-B7/C1A-C2A-B4A-B8A-B7A) in anionic parts of **3**$^-$ and **4**$^-$ (28.5(5) and 28.3(4)°) as well as B8-E-B8A are close to published cobalta bis(dicarbollide) compounds with sulfur or oxygen bridge between boron atoms in the structure.[3-7] The ammonium moieties are tightly connected to oxygen bridges of the anionic part in both structures. There is many structure-making weak interactions found within the unit cell, where the S-shape chain of O-H…O interacting hydroxypropyl substituents in **4**$^-$ has no further analogue in **3**$^-$. In addition, the structure of **3**$^-$ contains a minor disorder of

hydroxypropyl symmetrically localized at the second dicarbollide ligand, but in **4**$^-$, which has also the cisoid structure, the torsion angle between the pivotal atoms of the chains exhibits nearly ideal value of 59.1(8)° for substitution of C_2 symmetry.

IV. Electrochemistry

The common electrochemical cell with three-electrode system connected to an Autolab 302 potentiostat (Ecochemie, The Netherlands) was used for electrochemical measurements. An Ag|AgCl|3 M KCl reference electrode and a platinum wire (of 1 mm diameter) counter electrode were used. The measurements were performed at the room temperature. The differential pulse voltammetry (DPV) was applied with the pulse width of 50 ms, pulse amplitude of 25 mV, and scan rate of 8 mV/s. Glassy carbon electrode (GCE, 2 mm diameter, Metrohm, Switzerland) was used as the working electrode. GCE was prepared by mechanical polishing on SiC polishing papers (Struers, Denmark) and the polishing was finalized by the 1 µm diamond particles in spray on Lecloth B polishing pad (Leco, USA). GCE was sonicated for 30 s just before use to remove the rest of impurities from the mechanical polishing. The electrochemical measurements were done in phosphate buffer from NaH_2PO_4 and Na_2HPO_4 of pH = 8. Current values were normalized to the geometrical surface area of used electrodes.

The samples were dissolved in the phosphate buffer for the electrochemical measurements. The final concertation was afterwards checked by the ICP-MS (Agilent 7700, Japan) and for the anions **9**$^-$ and **11**$^-$ was estimated the saturation concentration as 50 µM.



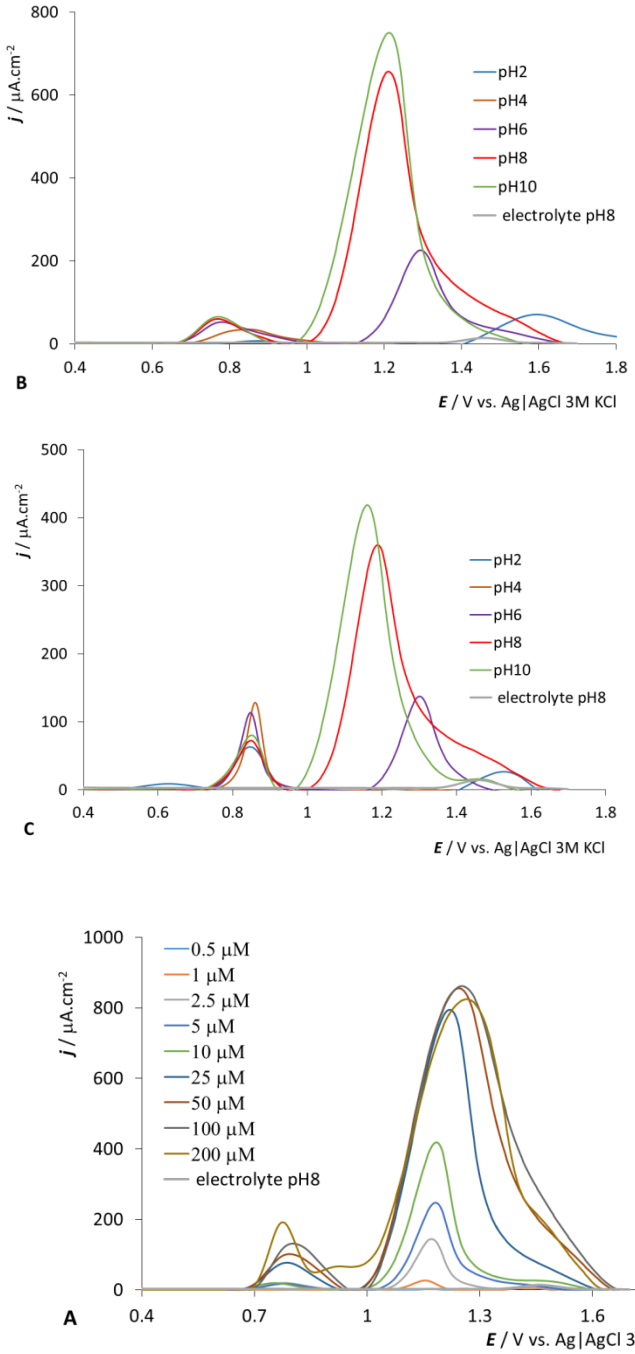


Figure S5: pH dependencies of 200 µM anions, GCE. See caption in the panel for identification of particular compounds. **A:** anion **7**$^{-}$; **B:** anion **9**$^{-}$; **C:** anion **11**$^{-}$.

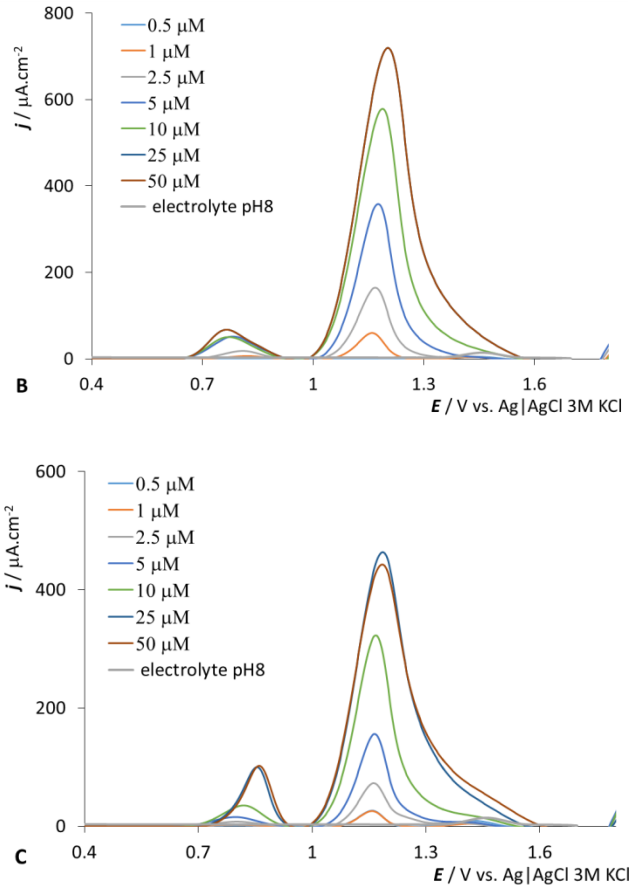


Figure S6: Concentration dependencies of selected anions at pH 8, GCE. See caption in the panel for identification of particular compound. **A**: anion **7**$^{-}$; **B**: anion **9**$^{-}$; **C**: anion **11**$^{-}$.

Electrochemistry of anions **7**$^{-}$, **9**$^{-}$ and **11**$^{-}$ indicated that the signal of the cage was not significantly affected when the oxygen bridged cluster was substituted by alkylazide or alkyltiazol group Figure S5 (only small potential shift for anion **11**$^{-}$ in the peak around E = 0.85 V could be observed and small new peak for **9**$^{-}$ at the potential around E = 1.7 V). This gives good prospects for labelling of biomolecules. The electrochemical response is shown on voltamogram in Figure S6. The concentration dependencies for **7**$^{-}$ and **11**$^{-}$ indicates strong saturation on the electrode surface or formation of aggregates in the solution (this situation is similar to the previous observed for the anion **2**$^{-}$).[8] The **9**$^{-}$ derivative has similar trend, but not so markedly pronounced. The pH dependencies for the **11**$^{-}$ and **9**$^{-}$ have similar trend – by lowering the pH, the peak signal height (at E = 1.2 V) decreases and shifts to more positive

potentials. Contrary to this, for the **7**$^-$ parent anion, the highest response for pH = 6 (with the same potential shift) can be observed.

V. Chiral HPLC separations on CPs

According to recent literature, contemporary regulations in drug design and analysis qualify chiral chromatography among tools for identification and quantification of chiral compounds and their enantiomers and determination of optical purity.[9-11] The enantiodiscrimination occurs due to interactions of the chiral selector with the chiral analyte. HPLC separations on cyclodextrin chiral stationary phases (CSPs) belong to most mature techniques in this respect and previously proved to enantiodiscriminate zwitterionic cobalt bis(dicarbollide) derivatives including semi-preparative separations and characterizations of some enantiomers using Circular Dichroism and determination of absolute configurations by XRD.[12-14] However, with few exceptions, the metallacarborane anions could not be separated by chiral HPLC, apparently due to unfavourable interactions of the solutes with silica gel backbone.[15] Here we present conditions for chiral separations of broader series of anionic compounds on several types of commercially available CD CSPs. The separations could be achieved due to presence of $NaClO_4$, which increases concentration of counterions in the mobile phase and limits interactions with solid support.

Two native β-cyclodextrin columns were used for successful enantiomer discrimination of the compounds under study: Reprosil chiral-beta-CD and CYCLOBOND I 2000 were used for the chiral separations of the analytes. The dimensions of both columns were (250 × 4.6 mm; particle size 5 µm). The chiral columns were purchased from Dr. Maisch (Ammerbuch-Entringen, Germany) and Sigma-Aldrich (Prague, Czech Republic), respectively. Chromatographic separations on these columns were performed on a Shimadzu LC20 chromatograph (Kyoto, Japan), composed of a DGU-20A3 solvent degasser, two LC-20AD binary gradient pumps, a SIL-20AC autosampler with a 100-µL sample loop, a CTO-20AC column oven, an SPD-M20A photodiode array detector (PDA) and a CBM-20A system controller. The

chromatographic data were recorded and analyzed by LabSolutions software 5.3 (Shimadzu, Kyoto, Japan). All analyses were performed in an isocratic elution mode. The mobile phase composed of methanol and aqueous solution of $NaClO_4$ (50 mmol/L) was automatically mixed by the chromatographic system according to the set ratio. The column thermostat was set at 50 °C, and mobile phase flow rates were 0.8 mL/min. The injection volume of all samples dissolved in MeOH (1 mg/mL) was 1 µL.

HPLC separations on Acetyl-ß-cyclodextrin column CYCLOBOND I 2000-Ac (250 × 4.6 mm; particle size 5 µm) were performed on Merck-Hitachi HPLC system LaChrom 7000 series equipped with a DAD 7450 detector (fixed wavelengths 260, 285, 290, and 308 nm), L7100 analytical pump and an Intelligent Injector L7250 and LaChrom software. The mobile phase composed of 70% aqueous methanol containing $NaClO_4$ (10 mmol/L) and propylammonium citrate (10 mmol/L), pH 5.6) was prepared prior the chromatography; mobile phase flow rate was adjusted to low value 0.4 mL/min., for better separation. The injection volume of all samples dissolved in MeOH (1 mg/mL) was 3 µL.

All separations were performed in isocratic mode. Retention times (R_t), capacity factors (k) and Resolution (Rs) are given in Table S4. The peak areas are also given indicating approximately equal area of the peaks corresponding to both enantiomers. Slight deviations from 50% relative area expected for enantiomers are observed for peaks that are only partly resolved (Rs< 1.0).

The dead volumes of the columns for the calculation of retention factors were determined by the baseline disturbance method. The resolution of enantiomers was calculated as follows:

$$Rs = \frac{2(Rt_2 - Rt_1)}{(W_1 + W_2)}$$

Improvements in resolution of some compounds could be further achieved on a native β-cyclodextrin CSP from another vendor. Thanks to the different manufacturing process the accessibility of the cyclodextrin cavity may be affected. It was found that monosubstituted compounds are better separated on CYCLOBOND I, whereas the disubstituted analytes are preferably separated on Reprosil chiral-beta-CD. The acetyl-β-cyclodextrin, CYCLOBOND I, 2000

Ac column proved relatively broader scope of selectivity, however only partial resolution of enantiomers could be achieved despite optimization of chromatographic conditions.

It should be noted that resolution of enantiomers could not be achieved under similar conditions on another chiral-CD columns Machery Nagel Nucleodex alpha PM (alpha-CD mimic phase), Tessek direcly bound β-cyclodextrin column effective in separations of zwitterionic metallacarboranes,[12] or on gamma-CD (Astec- Sigma Aldrich) column using similar composition of the buffer, i.e. 10 to 25 mM $NaClO_4$ in aqueous MeOH. Only a single peak for each corresponding racemic mixture was observed on these phases, as well on achiral RP column Separon RP Select B (Merck) using typical ion pair conditions for analysis of ionic cobalt bis(dicarbollide) derivatives[12] (example is shown in Fig S7). Therefore, the observed enantiodiscrimination can be attributed to the presence of chiral selector (along with a suitable linker to silica gel support).

Table S4: Chromatographic data of enantioseparated anions **3⁻, 4⁻, 7⁻** to **12⁻, 15⁻,** and **17⁻** using two native β-cyclodextin columns and acetylated β-cyclodextin column.

Reprosil chiral-beta-CD

	MeOH-$NaClO_4$ (50 mM) (80:20, *v/v*)						Area (%)	
Compound	Rt_1	Rt_2	k_1	k_2	α	Rs	A_1	A_2
3⁻	12,74	14,19	2,71	3,13	1,16	2,55	50.0	50.0
4⁻	6,88	7,76	1,00	1,26	1,26	2,75	52.2	47.8

	MeOH-$NaClO_4$ (50 mM) (50:50, *v/v*)							
Compound	Rt_1	Rt_2	k_1	k_2	α	Rs	A_1	A_2
8⁻	19,33	22,04	4,38	5,00	1,14	2,53	49.8	50.2
15⁻	35,09	45,86	7,96	10,40	1,31	4,66	50.1	49.9
17⁻	17,27	23,07	3,91	5,23	1,34	4,96	50.0	50.0

CYCLOBOND I 2000

MeOH-$NaClO_4$ (50 mM) (50:50, *v/v*)

Compound	Rt_1	Rt_2	k_1	k_2	α	Rs	A_1	A_2
7$^-$	25,73	26,95	4,93	5,22	1,06	0,98	48.9	51.1
9$^-$	32,56	33,99	6,51	6,84	1,05	0,69	45.2	54.8
10$^-$	22,88	23,80	4,28	4,49	1,05	0,81	47.1	52.9
12$^-$	20,35	21,34	3,69	3,92	1,06	1,04	49.6	50.4

MeOH-$NaClO_4$ (50 mM) (40:60, *v/v*)

Compound	Rt_1	Rt_2	k_1	k_2	α	Rs	A_1	A_2
11$^-$	53,36	55,95	11,85	12,48	1,05	0,96	47.3	52.6

CYCLOBOND I 2000-Acetyl

MeOH-$NaClO_4$ (50 mM) (50:50, *v/v*)

Compound	Rt_1	Rt_2	k_1	k_2	α	Rs	A_1	A_2
3$^-$	24.01	24.01	1.97	1.97	-	NR	-	-
4$^-$	14.91	15,56	0,84	0,93	1.09	0.80	43.5	56.5
7$^-$	22.08	22.69	1.73	1.81	1.04	0.75	48.8	51.1
8$^-$	14.76	14.76	0.82	0.82	-	NR	-	-
9$^-$	29.55	30.31	2.66	2.75	1.04	0.65	51.1	48.9
10$^-$	20.85	21.24	2.30	2.36	1.02	NR	-	-
11$^-$	37,60	39,17	3.65	3,85	1,05	0.95	49.7	50.3
12$^-$	21.56	22,20	1.67	1.75	1,05	0,70	48.6	51.4

NR=not resolved

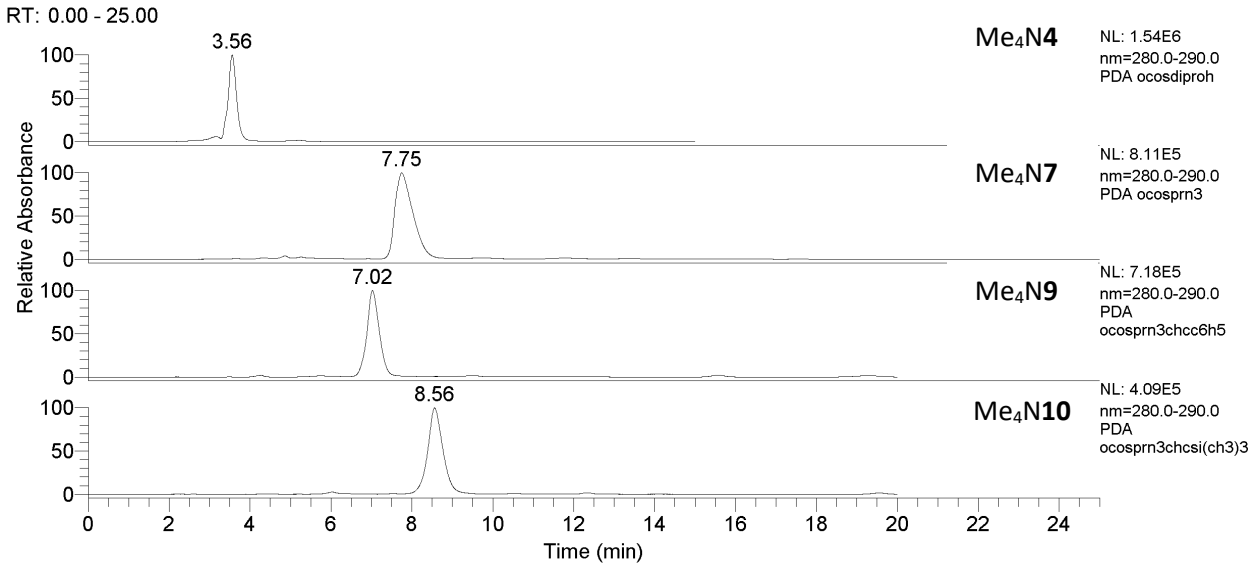


Figure S7: HPLC chromatograms with isocratic elution of four selected cobalt bis(dicarbollide) derivatives; measured with PDA detection; flow rate 0.4 ml/min; column: LiCroCART RP-selected B (5 µm, 250 x 3.00 mm *I.D.*); mobile phase: 5 mM PAA pH 4.8 with 60% ACN.

VI. NMR Spectra

VI.1. NMR spectra of **2**$^{-}$

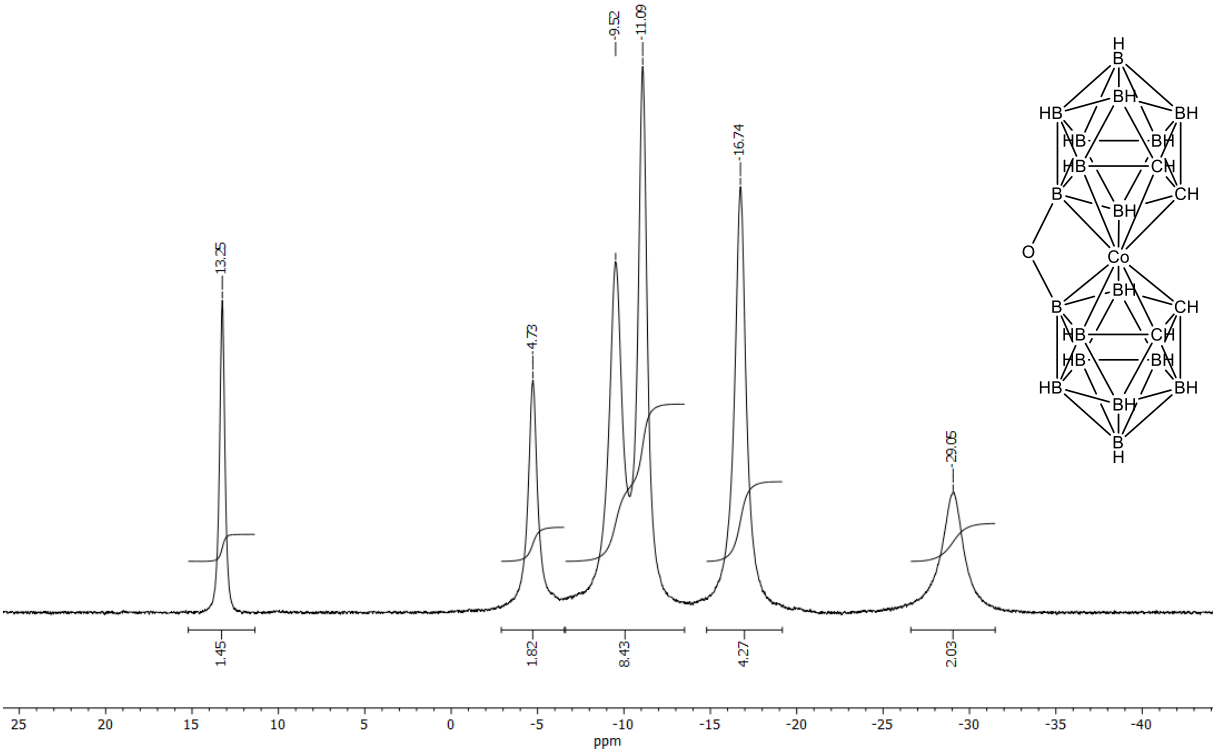


Figure S8: ^{11}B {^{1}H} NMR spectrum of Cs**2**

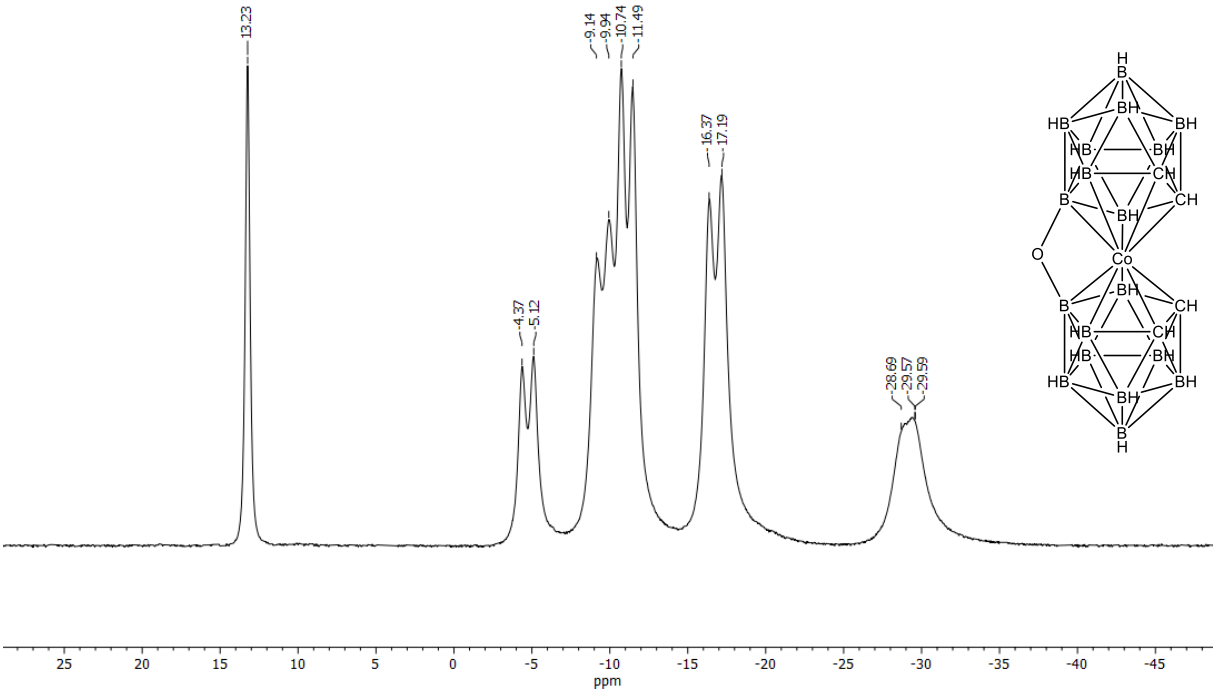


Figure S9: ^{11}B NMR spectrum of Cs**2**

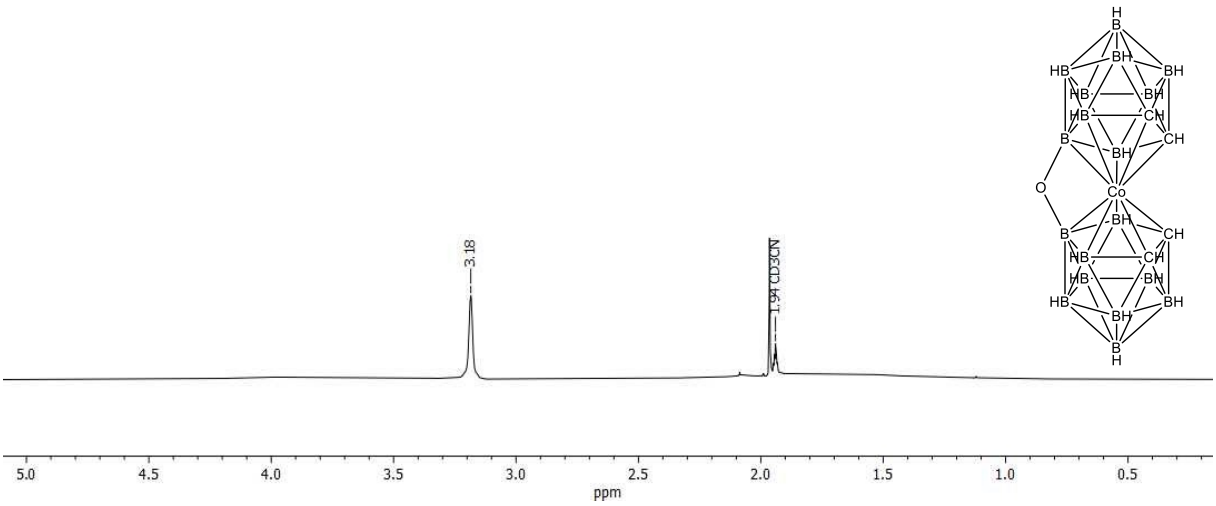


Figure S10: ^{1}H NMR spectrum of Cs**2**

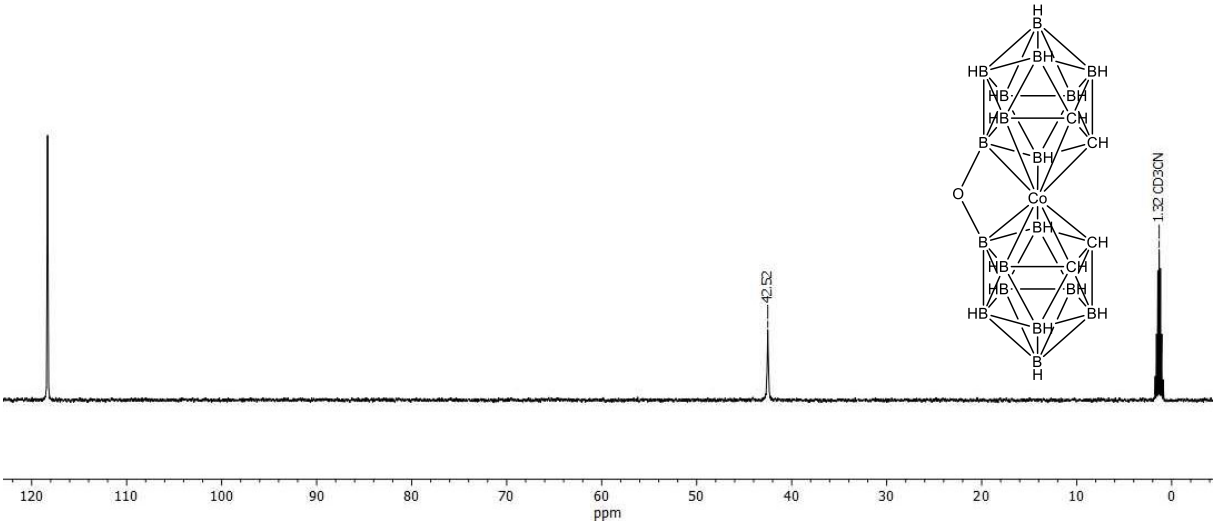


Figure S11: ^{13}C {^{1}H} NMR spectrum of Cs**2**

VI.2. NMR spectra of **3**$^{-}$

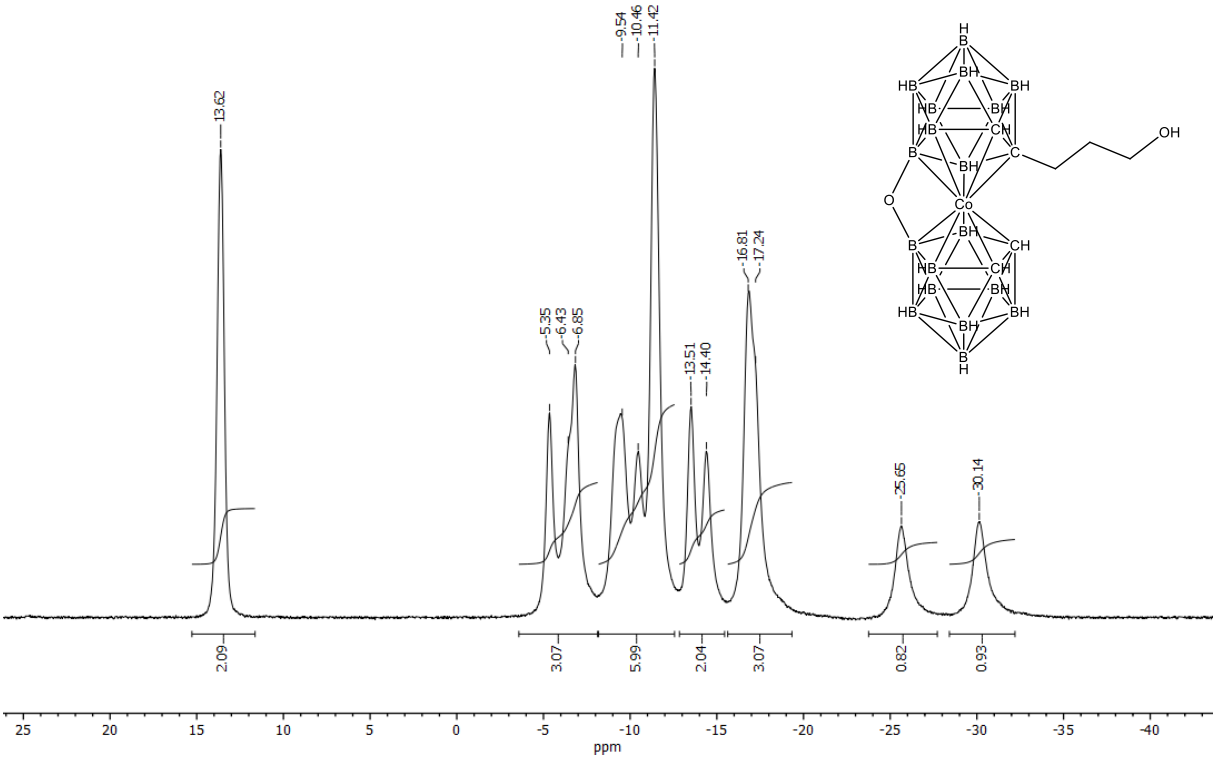


Figure S12: ^{11}B {^{1}H} NMR spectrum of Me_3NH**3**

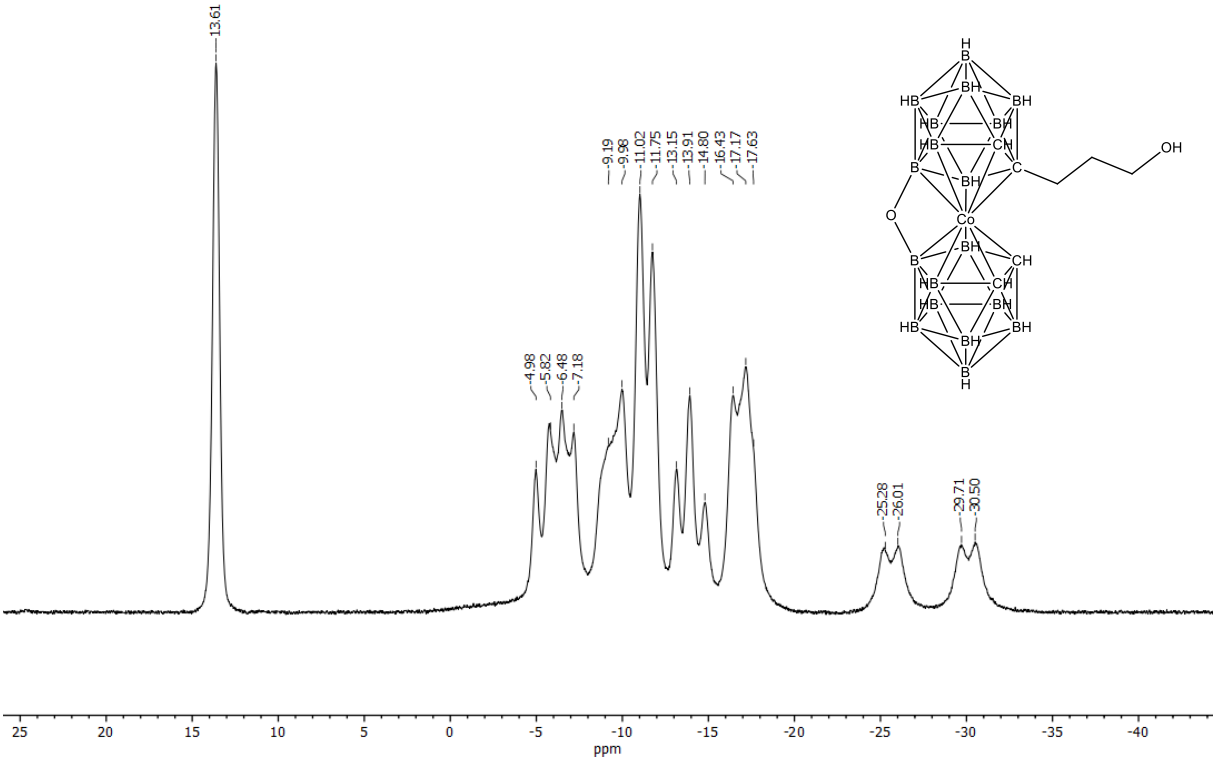


Figure S13: ^{11}B NMR spectrum of Me_3NH**3**

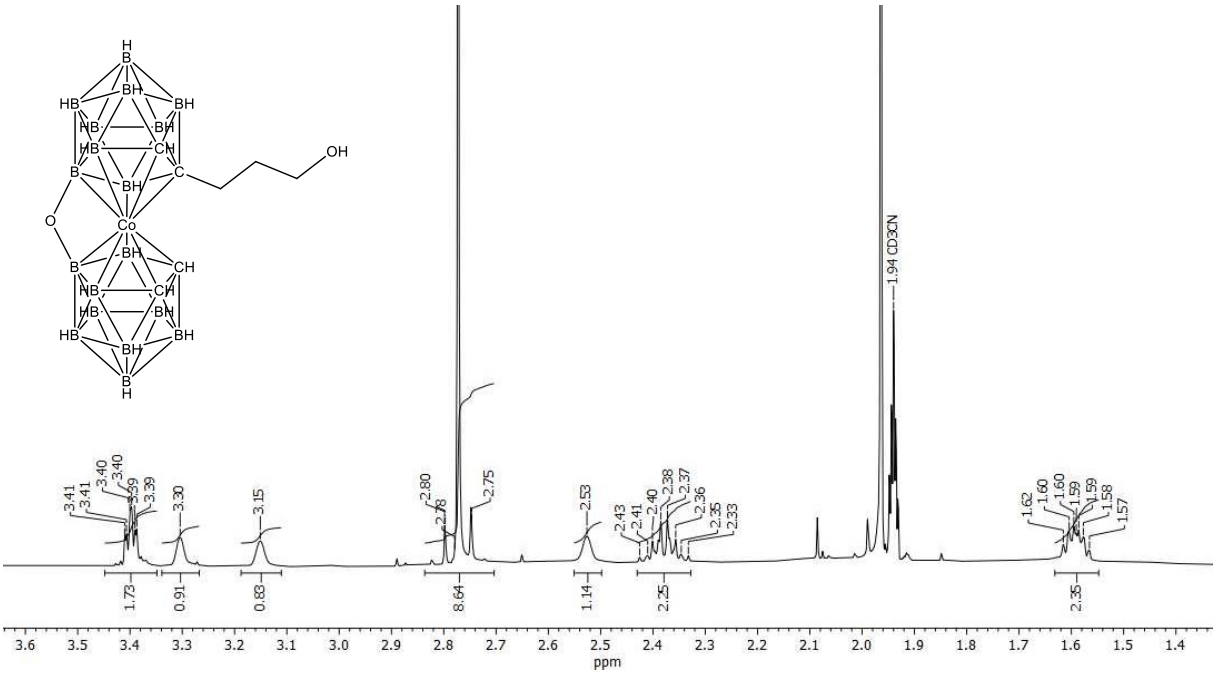


Figure S14: ^{1}H NMR spectrum of Me_3NH**3**

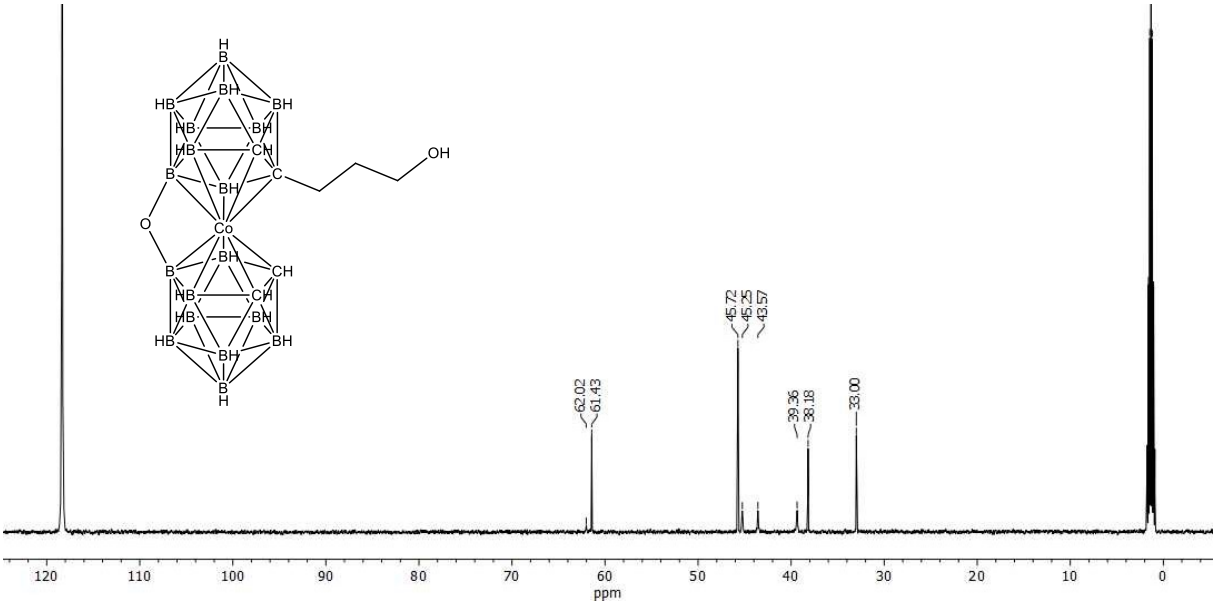


Figure S15: ^{13}C {^{1}H} NMR spectrum of Me_3NH**3**

VI.3. NMR spectra of **5**$^{-}$

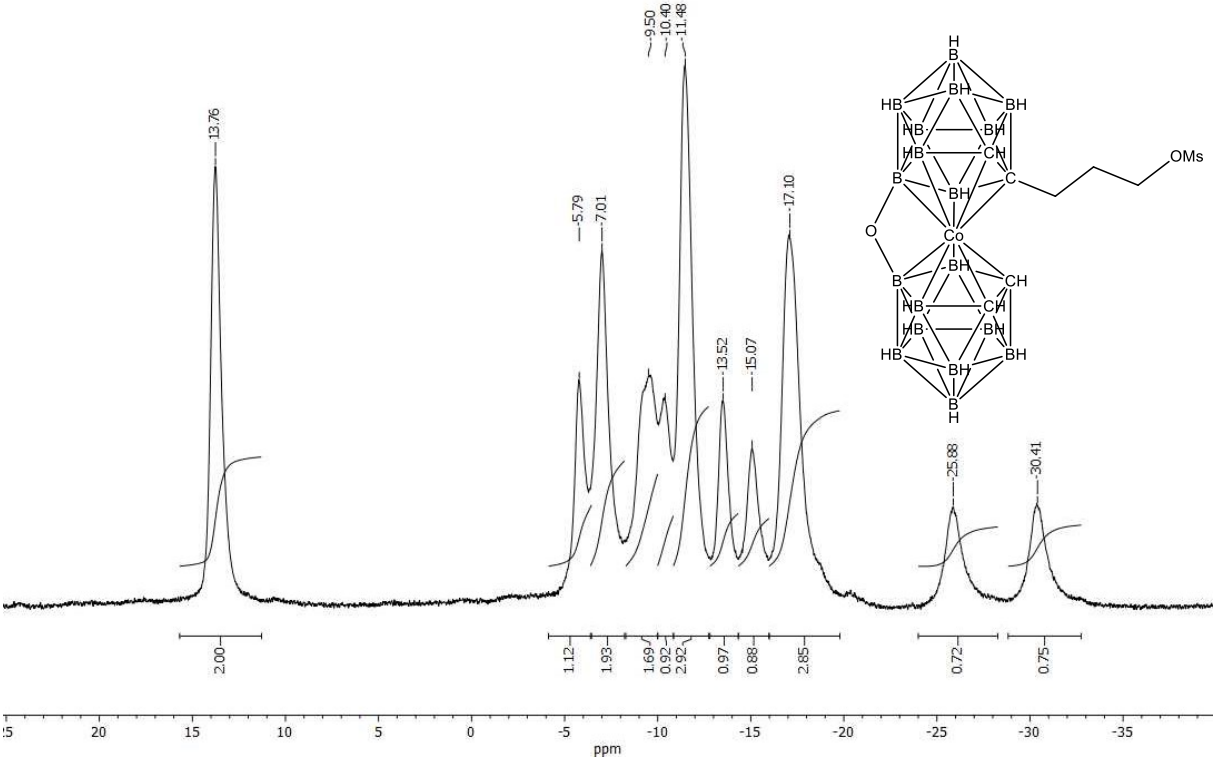


Figure S16: ^{11}B {^{1}H} NMR spectrum of Me_4N**5**

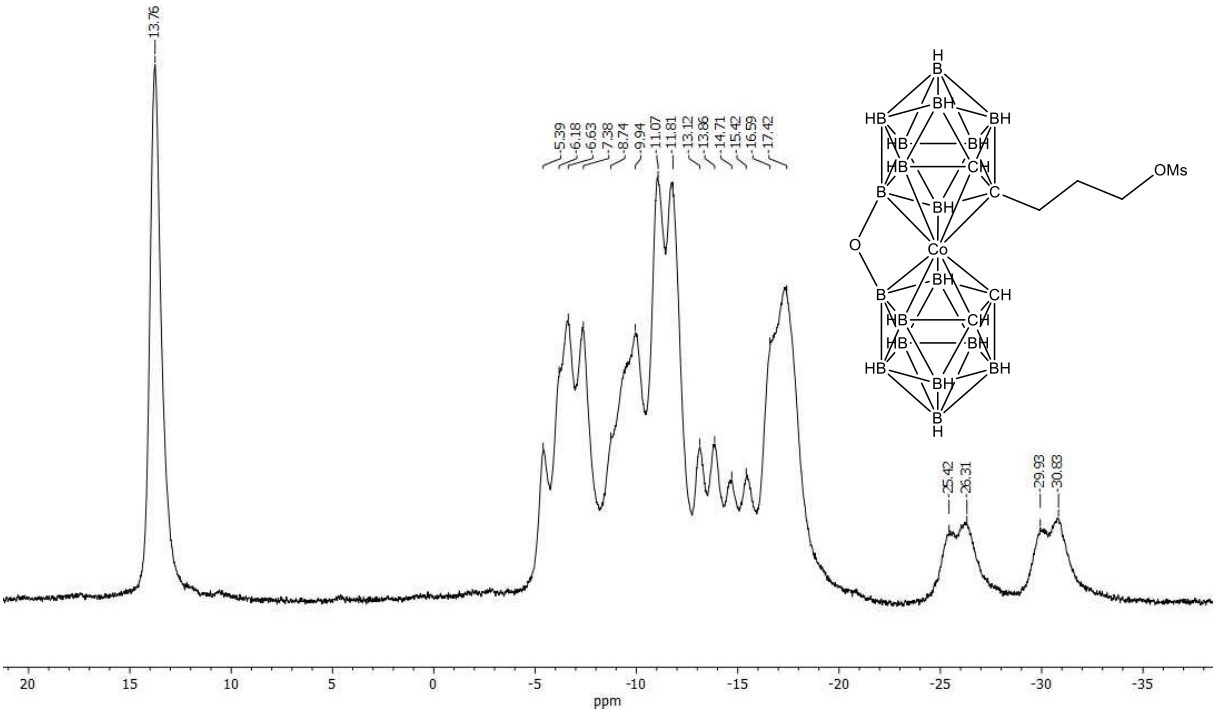


Figure S17: ^{11}B NMR spectrum of Me_4N**5**

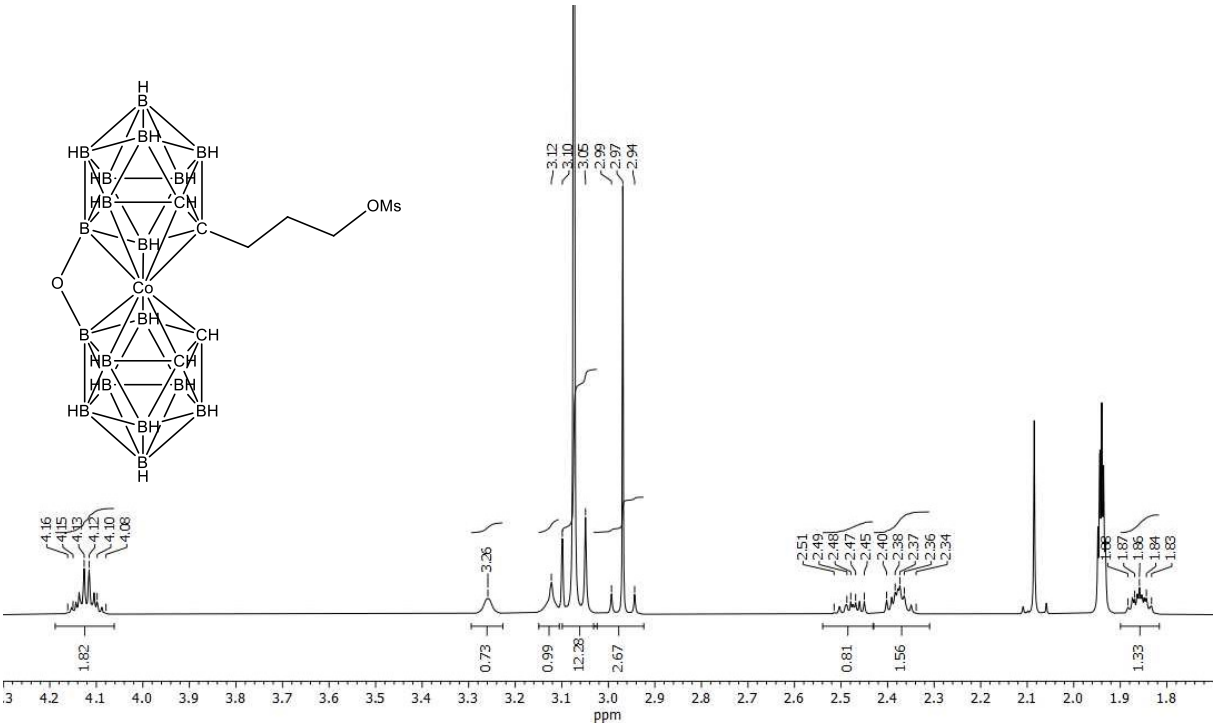


Figure S18: ^{1}H NMR spectrum of Me_4N**5**

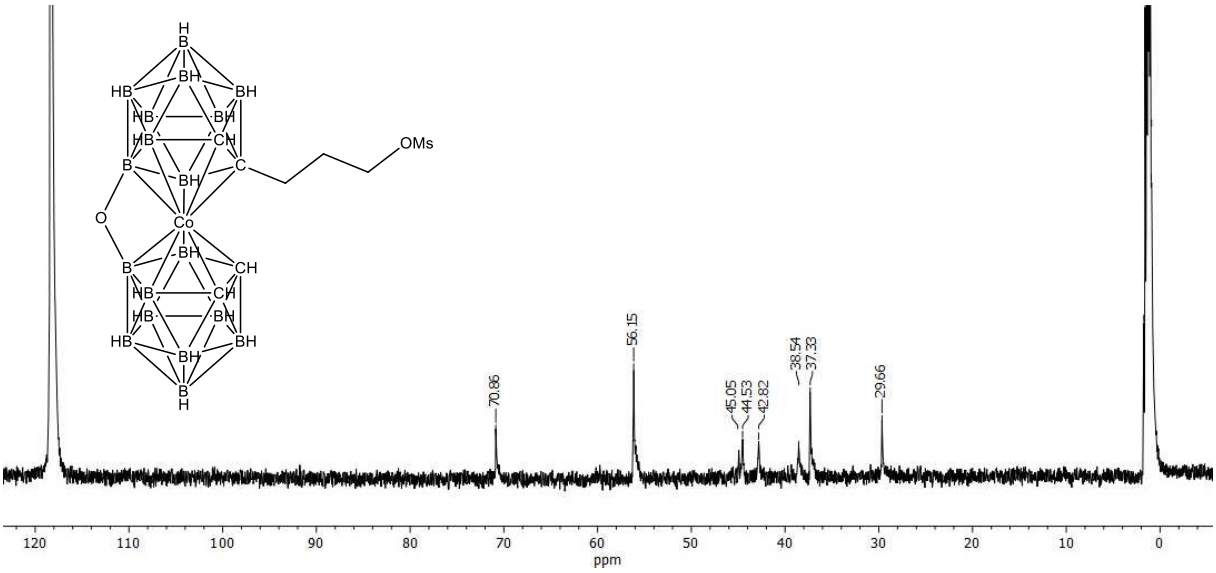


Figure S19: ^{13}C $\{^{1}H\}$ NMR spectrum of Me_4N**5**

VI.4. NMR spectra of **7**$^{-}$

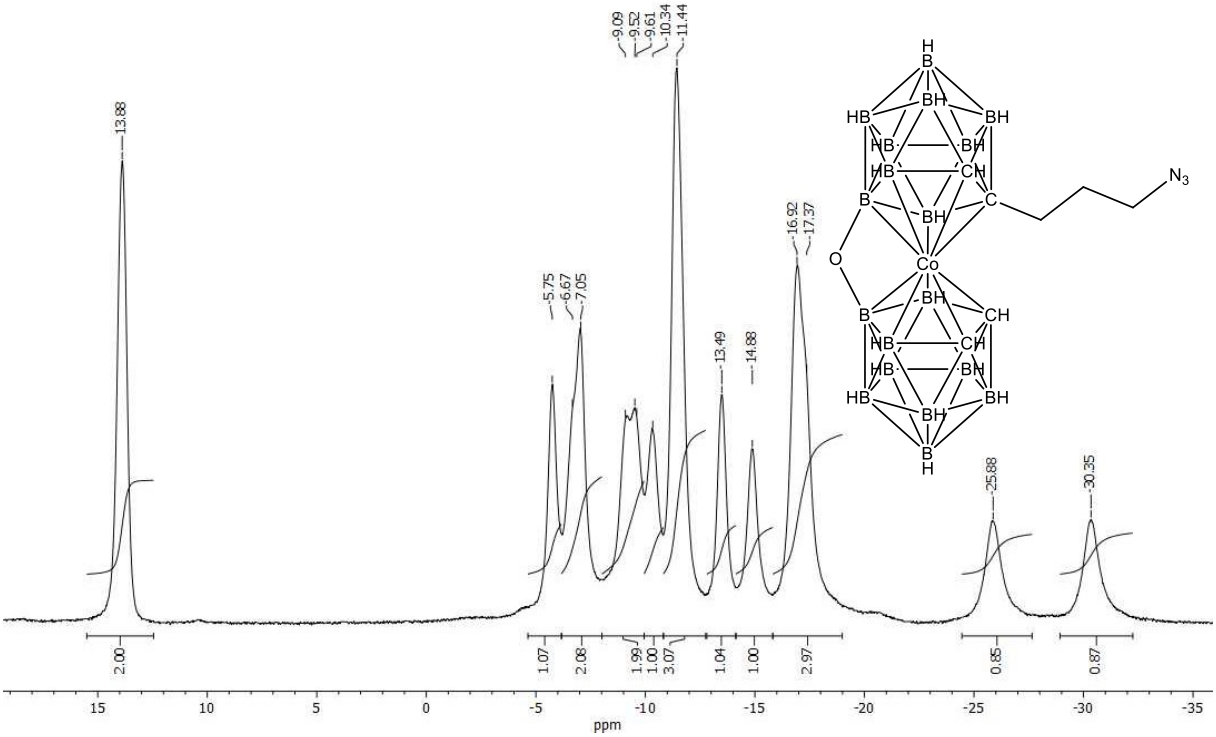


Figure S20: ^{11}B {^{1}H} NMR spectrum of Me_4N**7**

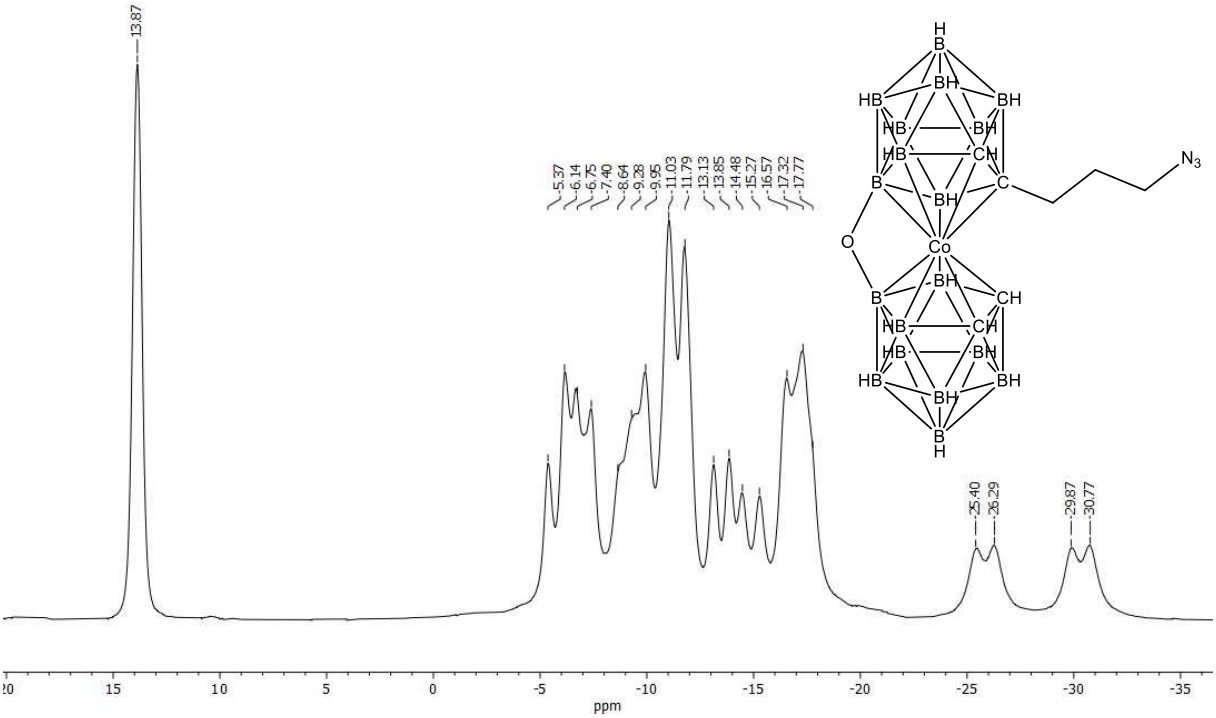


Figure S21: ^{11}B NMR spectrum of Me_4N**7**

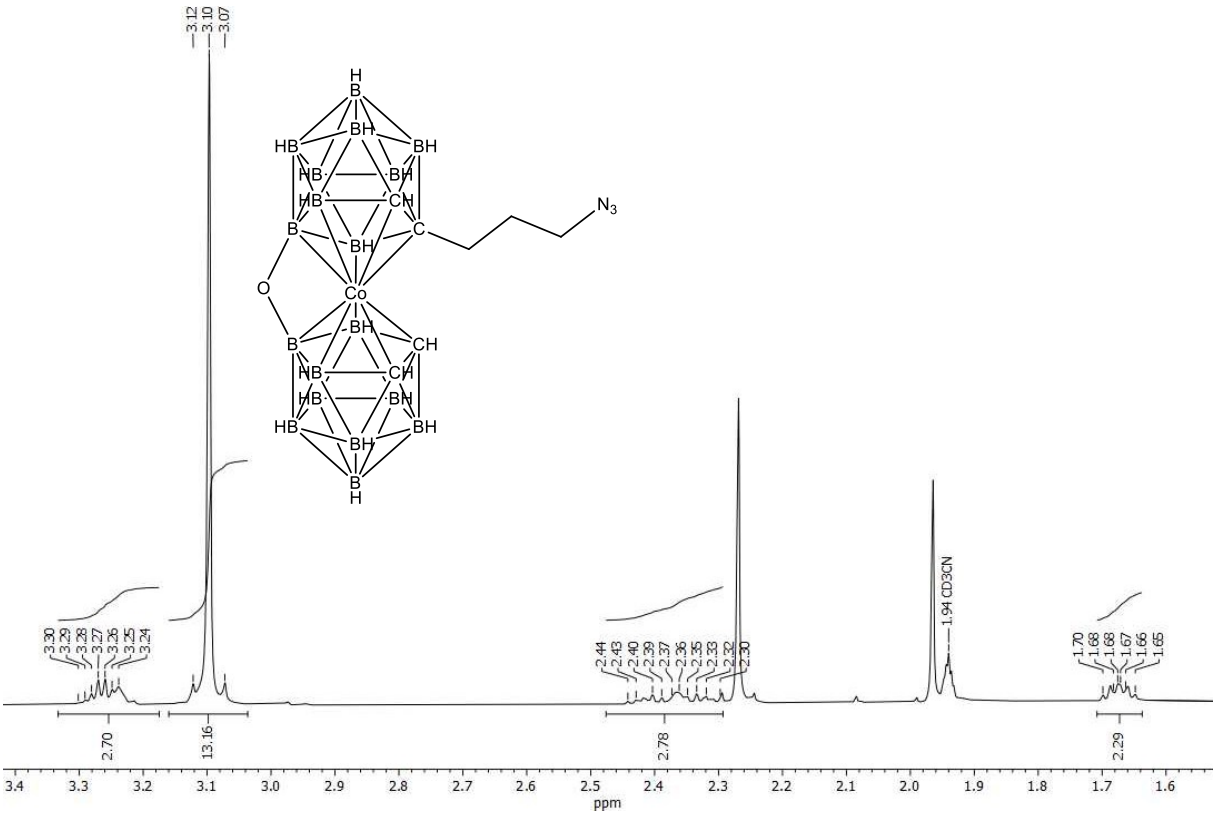


Figure S22: ^{1}H NMR spectrum of Me_4N**7**

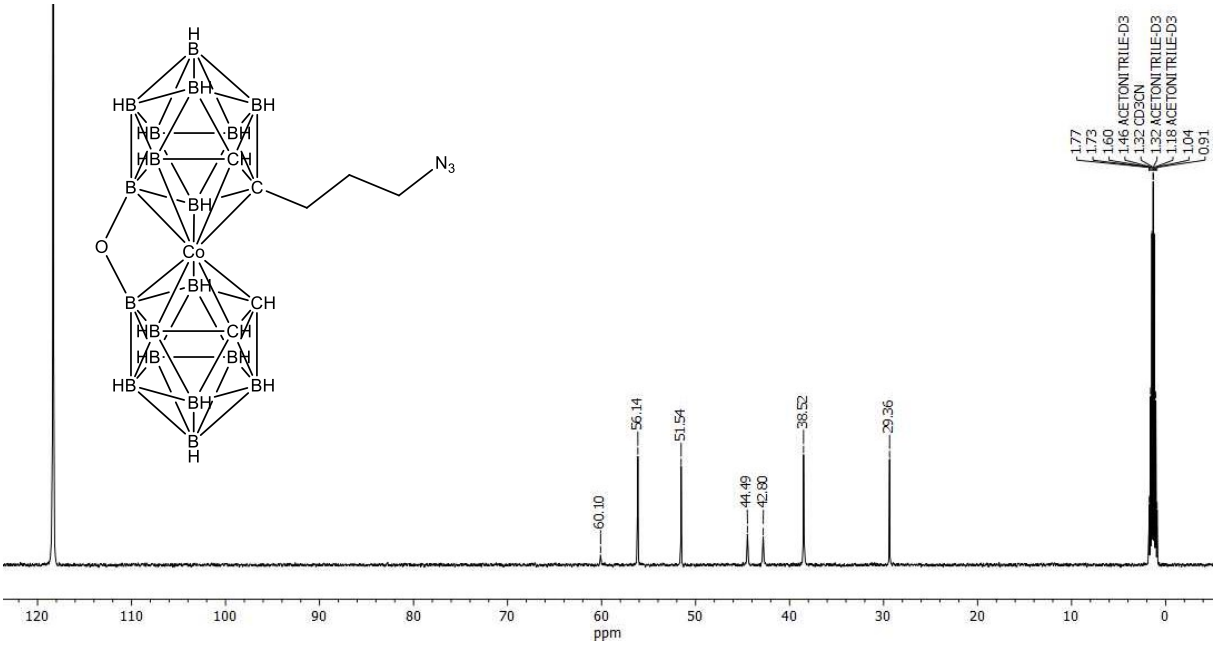


Figure S23: ^{13}C {^{1}H} NMR spectrum of Me_4N**7**

VI.5. NMR spectrum of **9**$^-$

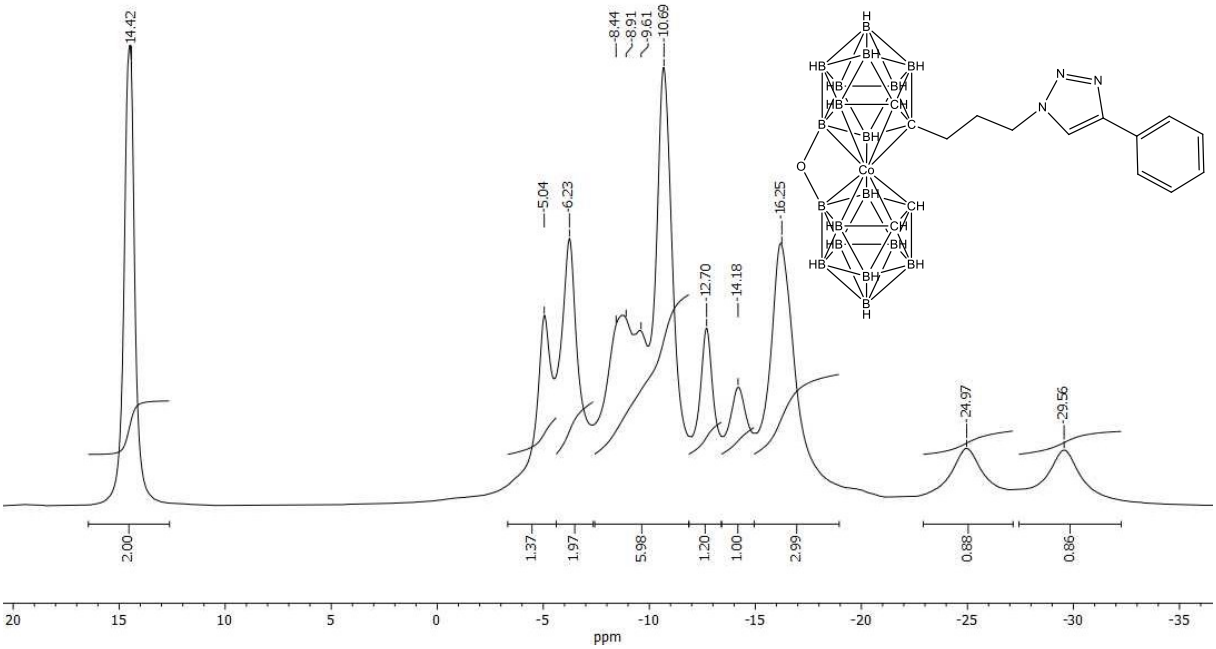


Figure S24: ^{11}B {^1H} NMR spectrum of Me_4N**9**

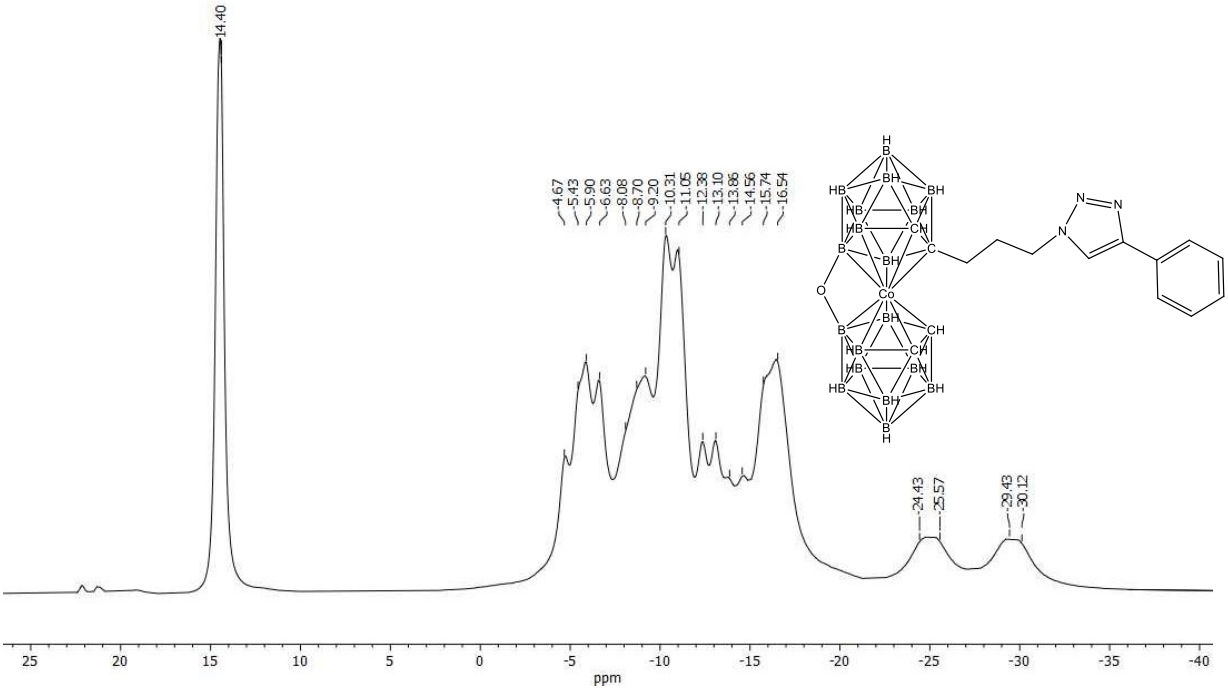


Figure S25: ^{11}B NMR spectrum of Me_4N**9**

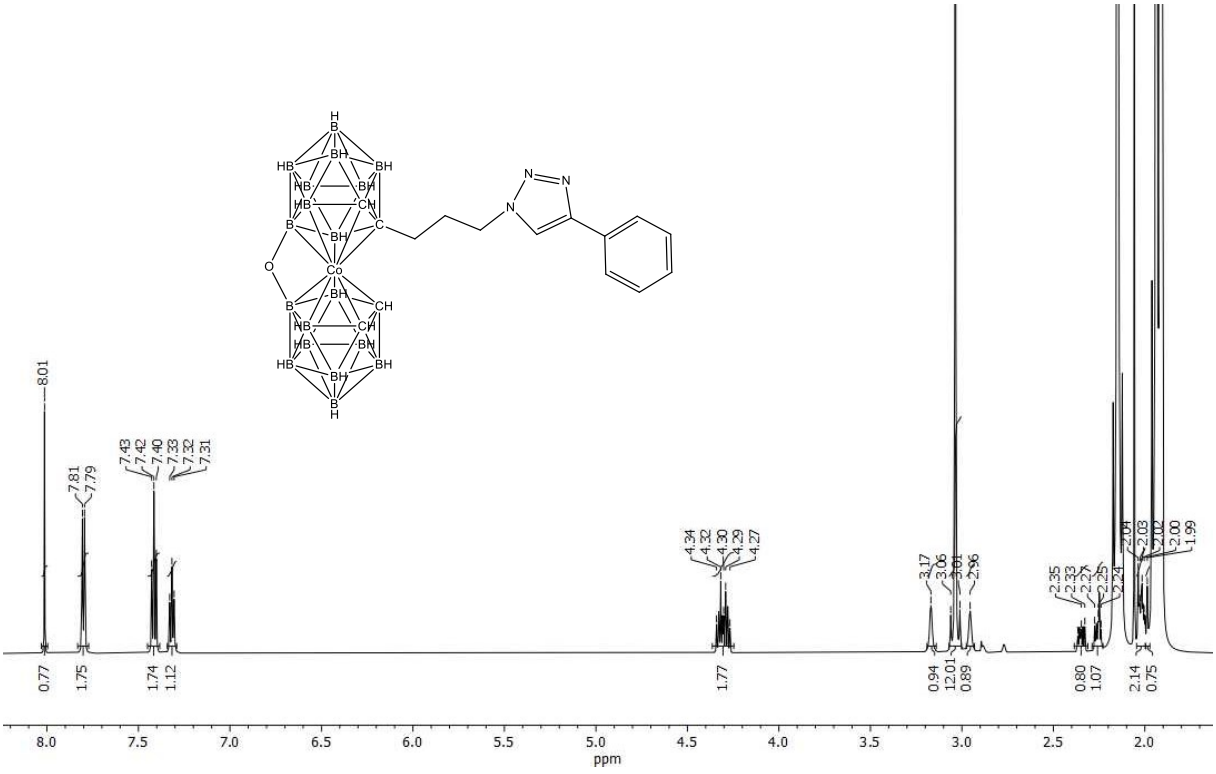


Figure S26: ^{1}H NMR spectrum of Me_4N**9**

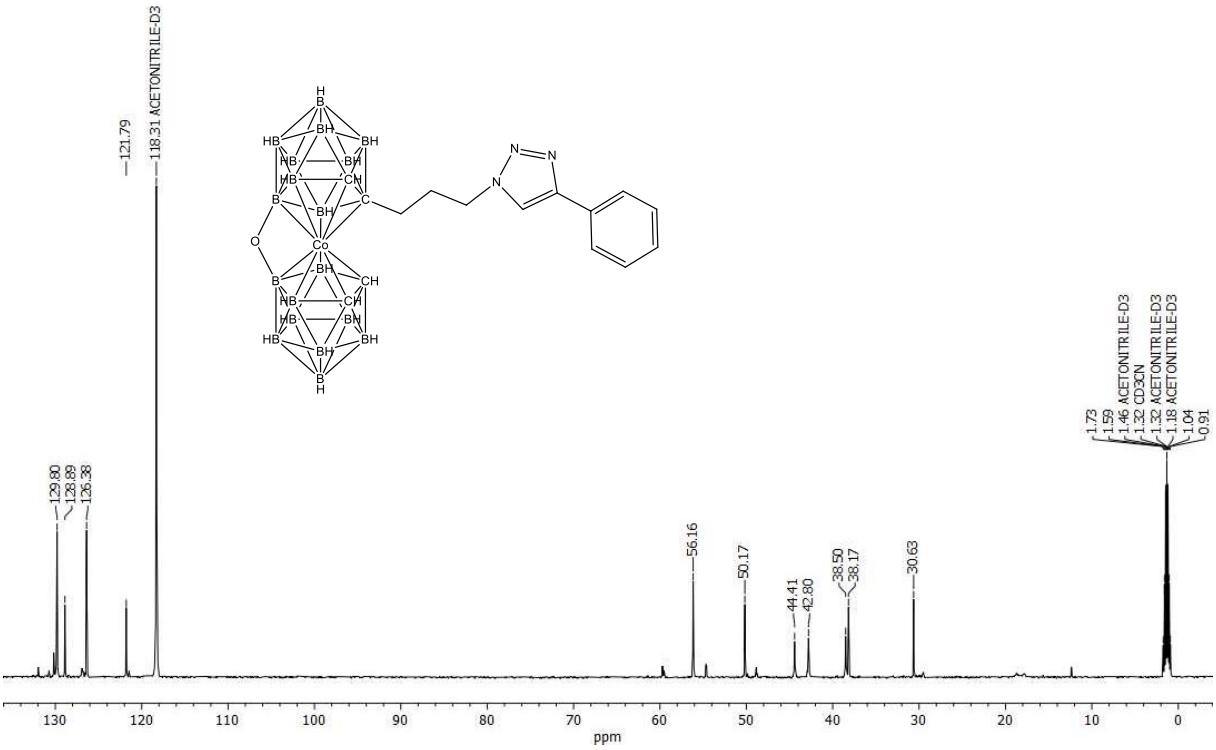


Figure S27: ^{13}C {^{1}H} NMR spectrum of Me_4N**9**

VI.6. NMR spectra of **10**$^{-}$

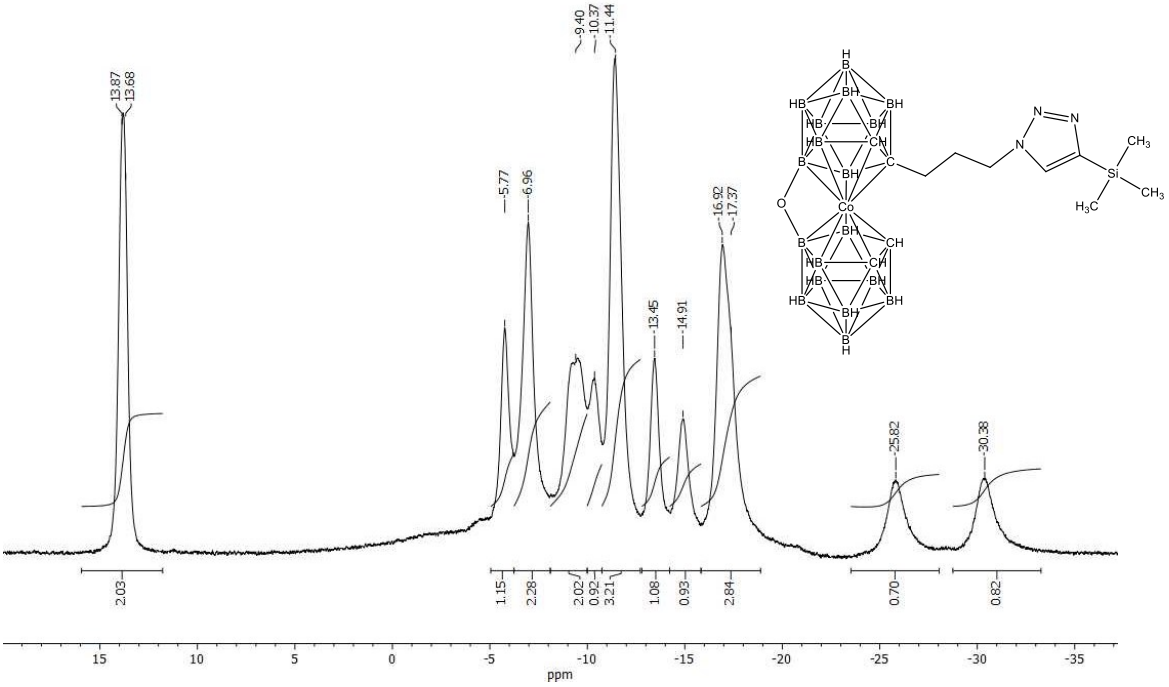


Figure S28: ^{11}B {^{1}H} NMR spectrum of Me_4N**10**

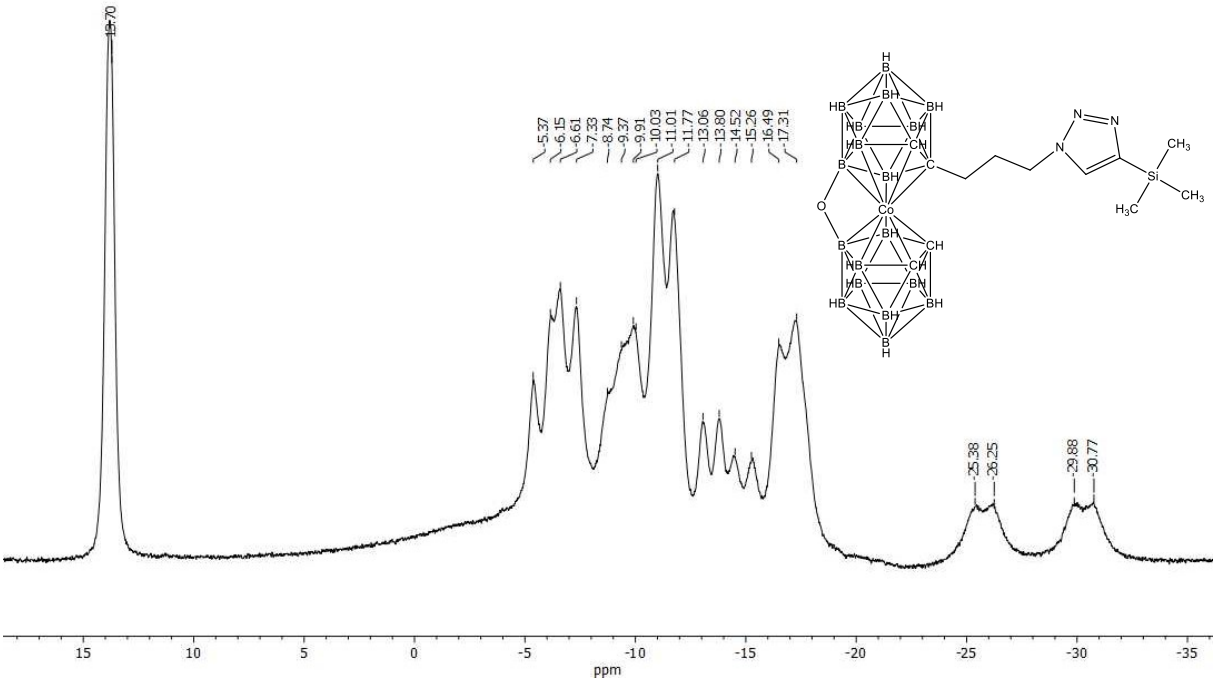


Figure S29: ^{11}B NMR spectrum of Me_4N**10**

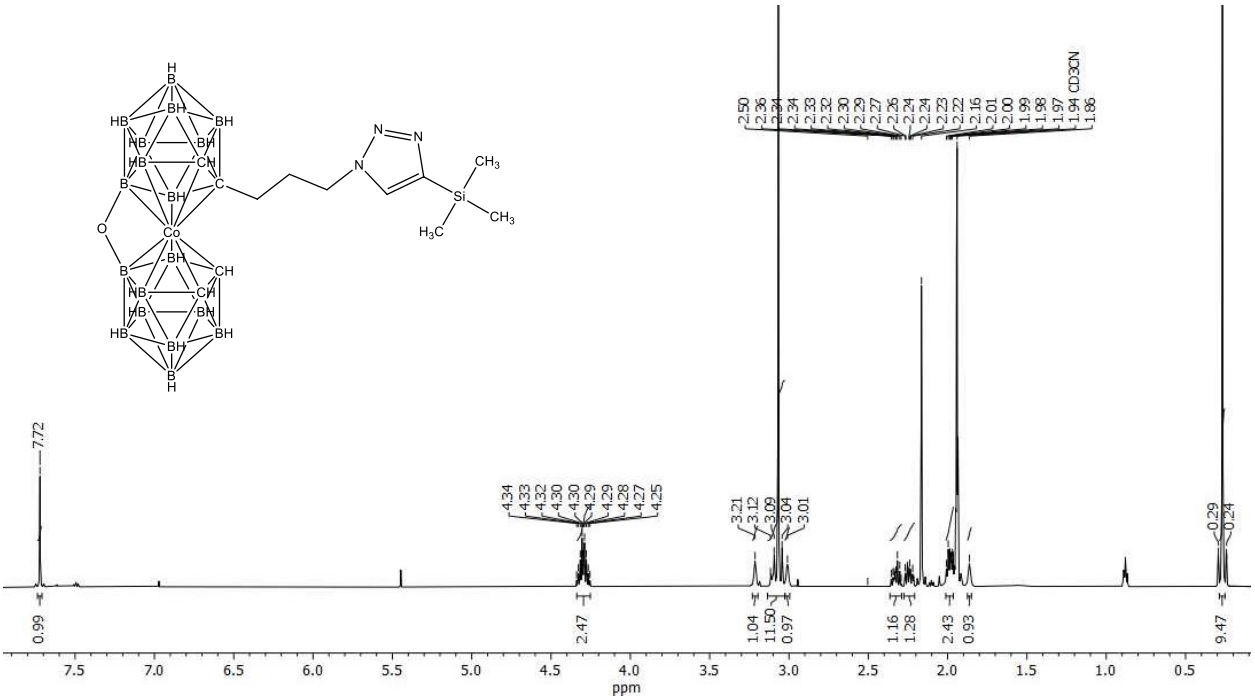


Figure S30: ^{1}H NMR spectrum of Me$_4$N**10**

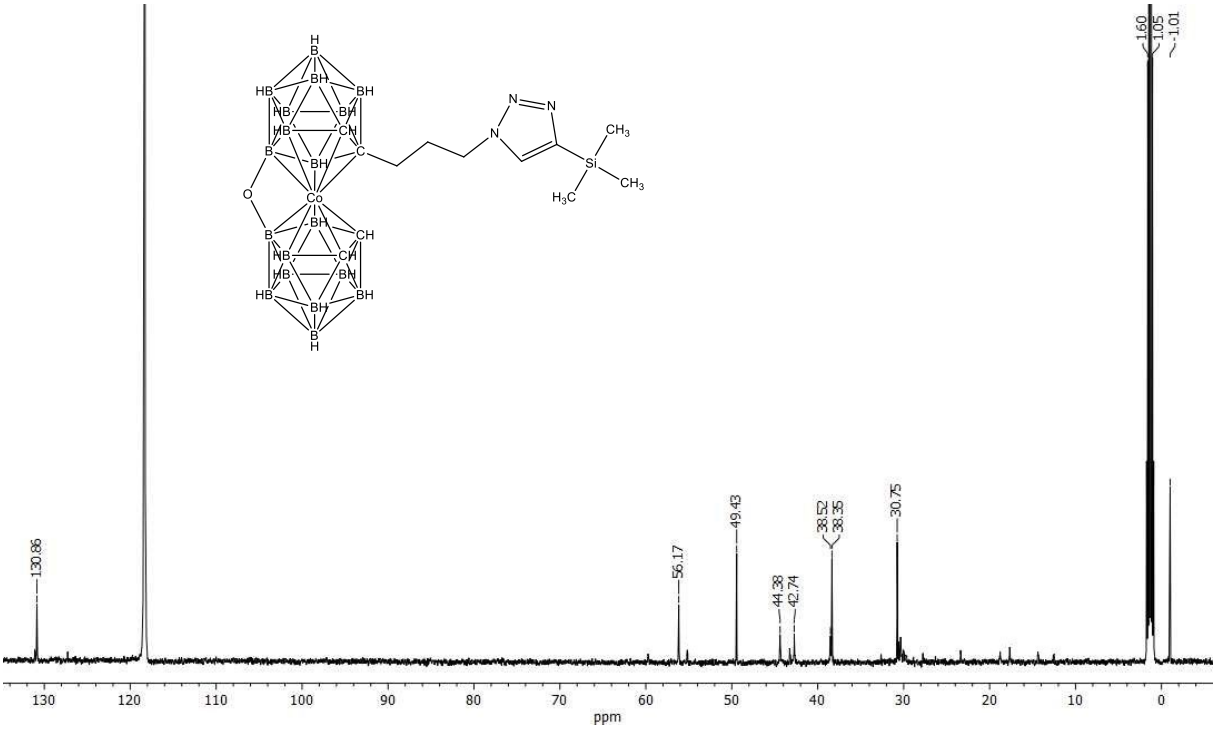


Figure S31: ^{13}C {^{1}H} NMR spectrum of Me$_4$N**10**

VI.7. NMR spectra of **11**$^-$

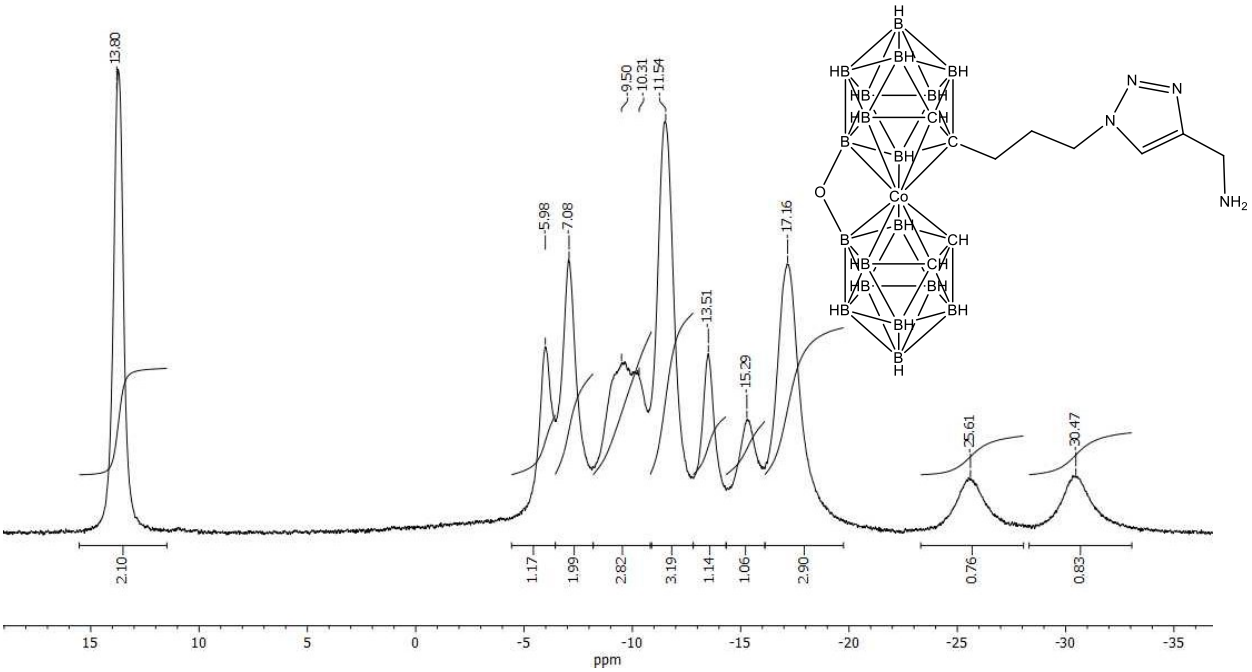


Figure S32: ^{11}B {^1H} NMR spectrum of Me_4N**11**

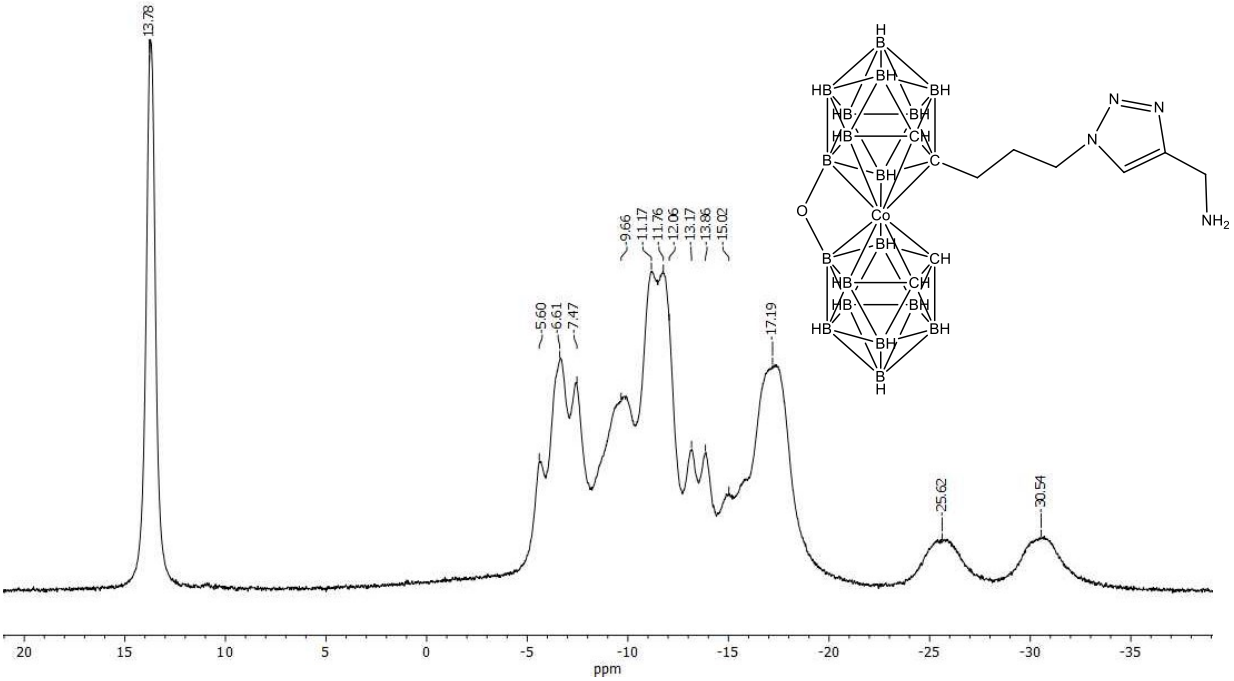


Figure S33: ^{11}B NMR spectrum of Me_4N**11**

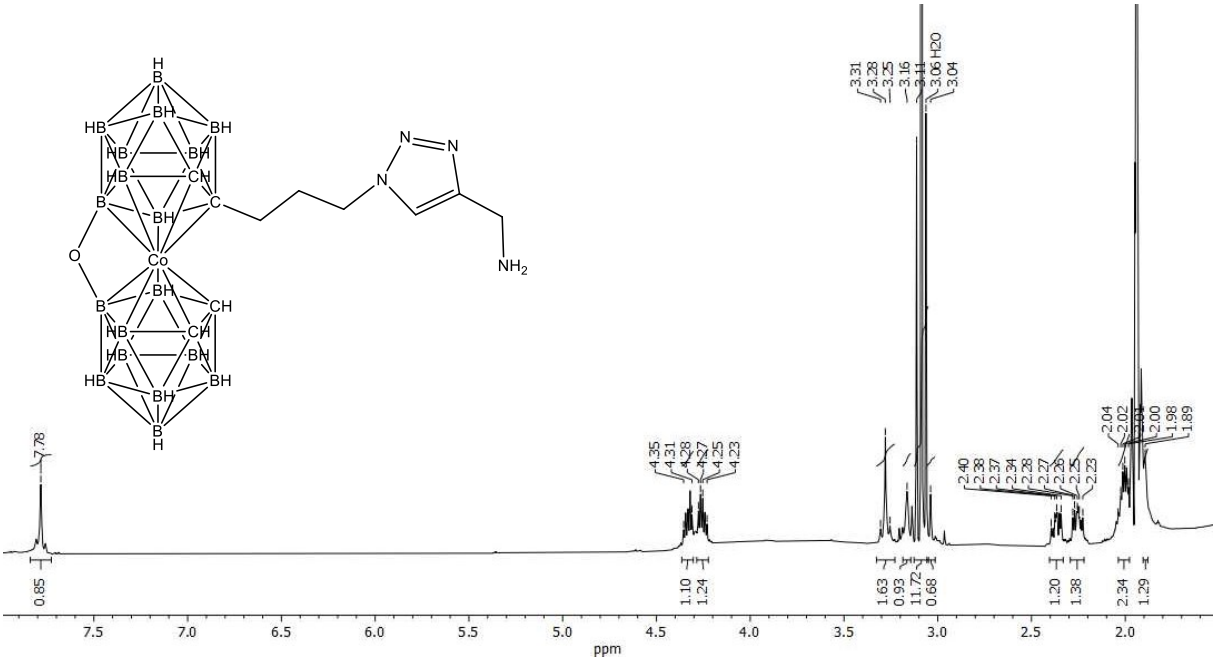


Figure S34: ^{1}H NMR spectrum of Me_4N**11**

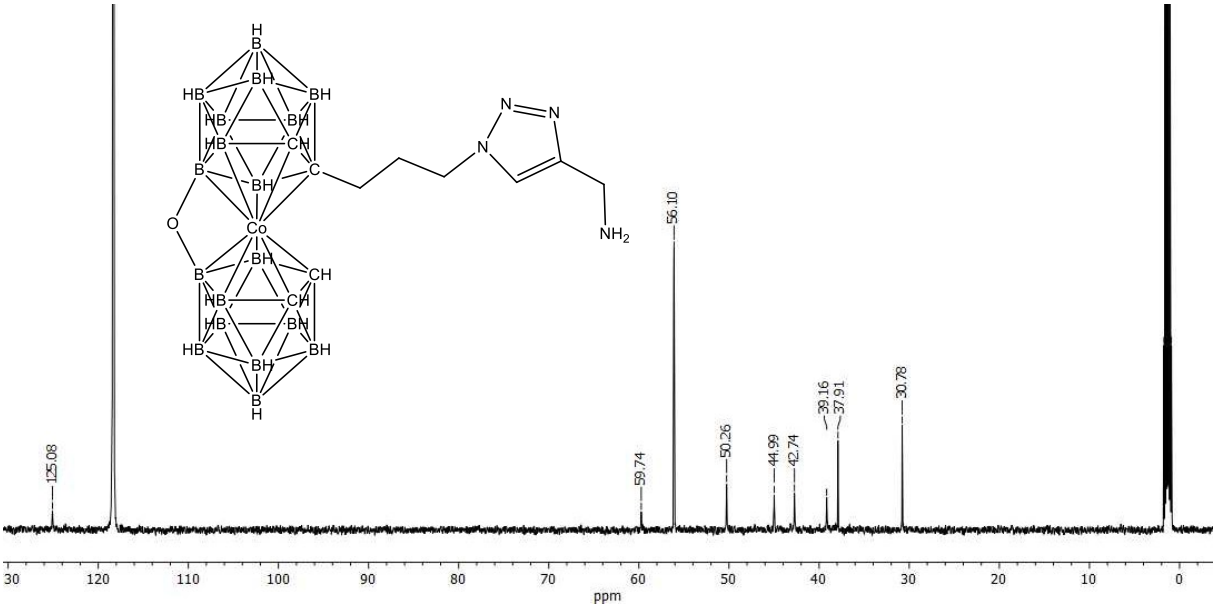


Figure S35: ^{13}C {^{1}H} NMR spectrum of Me_4N**11**

VI.8. NMR spectra of **12**$^{-}$

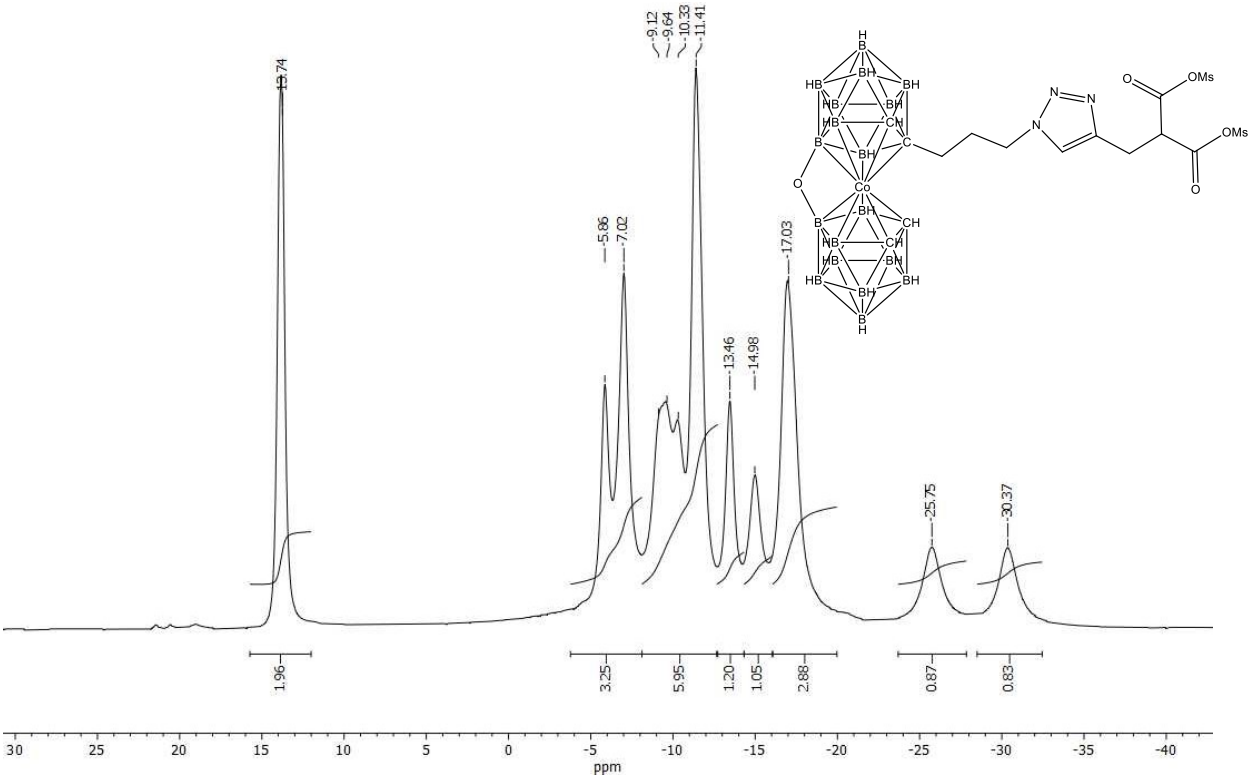


Figure S36: ^{11}B {^{1}H} NMR spectrum of Me_4N**12**

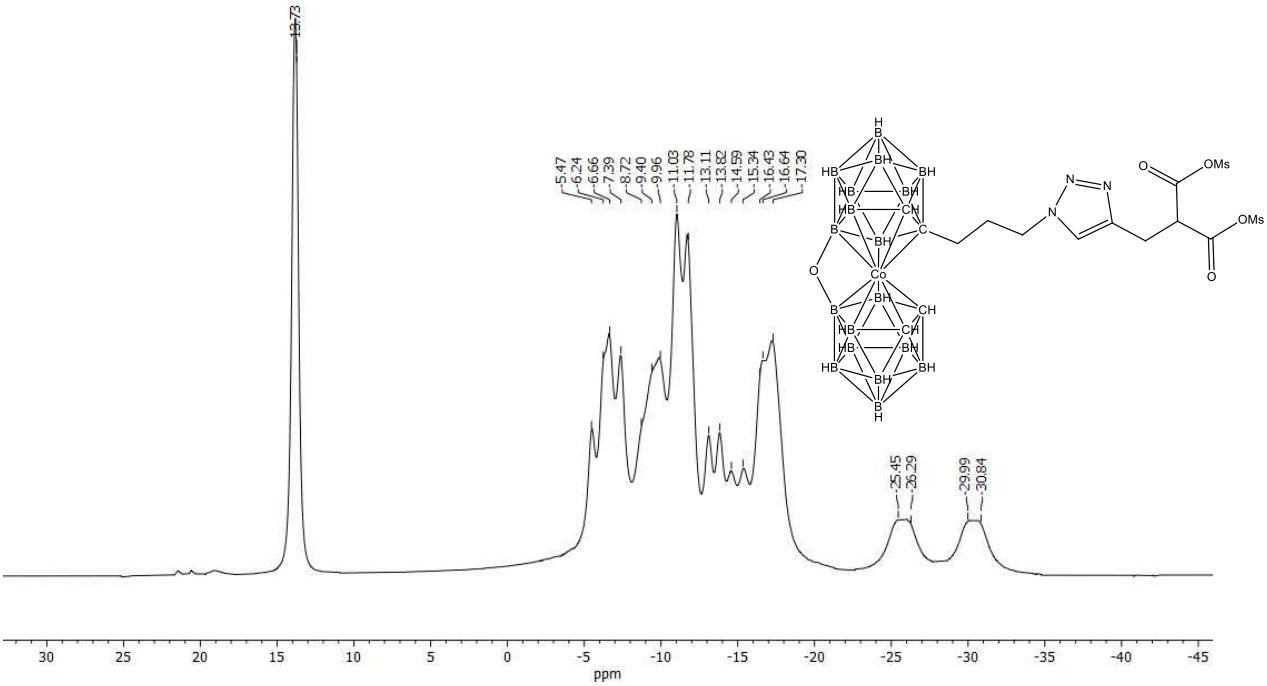


Figure S37: ^{11}B NMR spectrum of Me_4N**12**

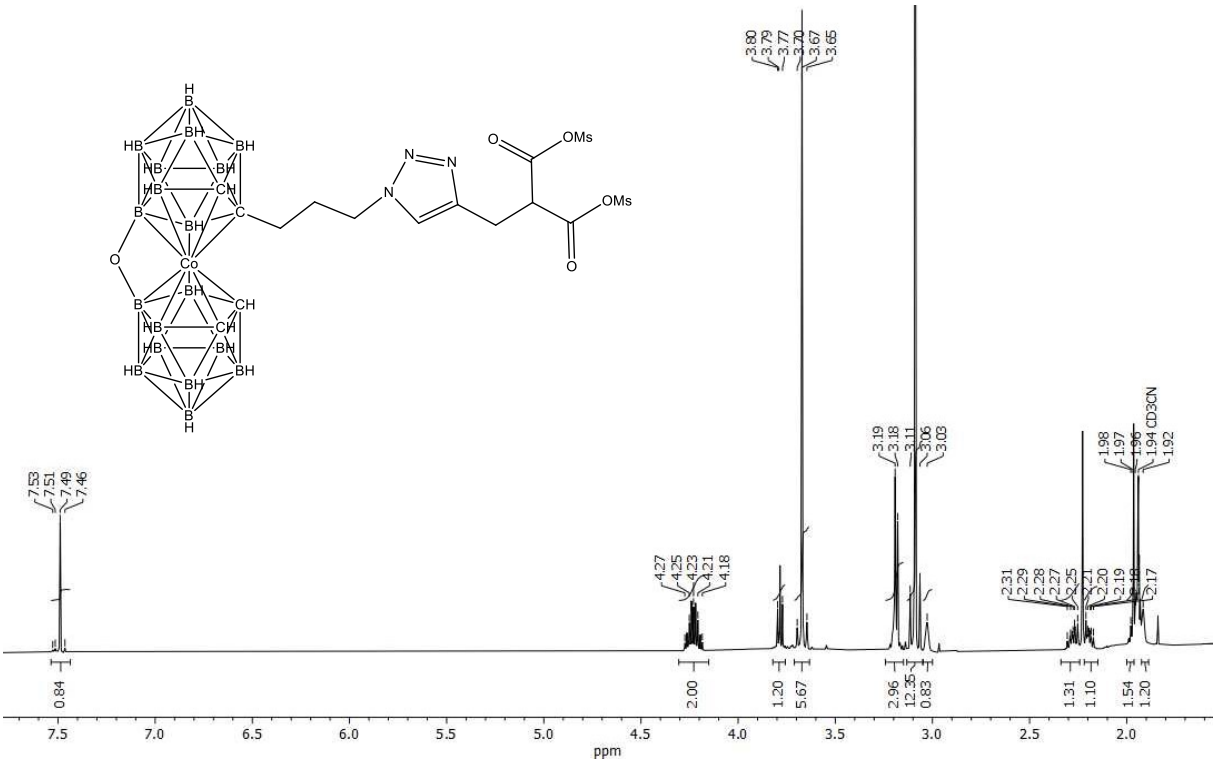


Figure S38: ^{1}H NMR spectrum of Me_4N**12**

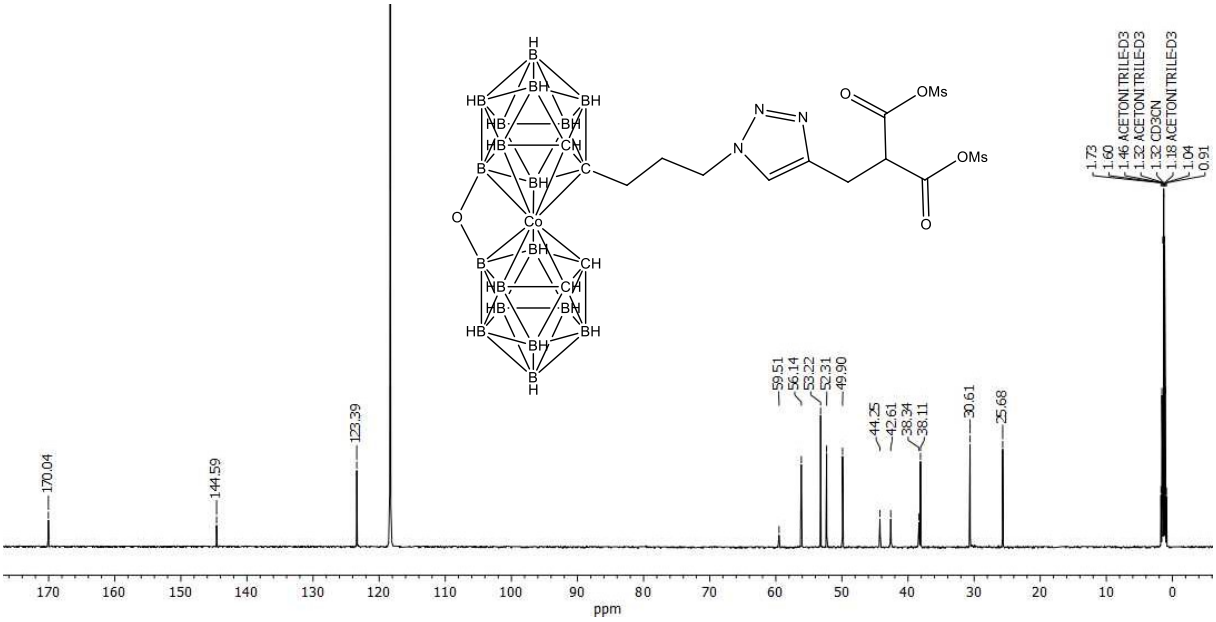


Figure S39: ^{13}C {^{1}H} NMR spectrum of Me_4N**12**

VI.9. NMR spectra of **13**$^{-}$

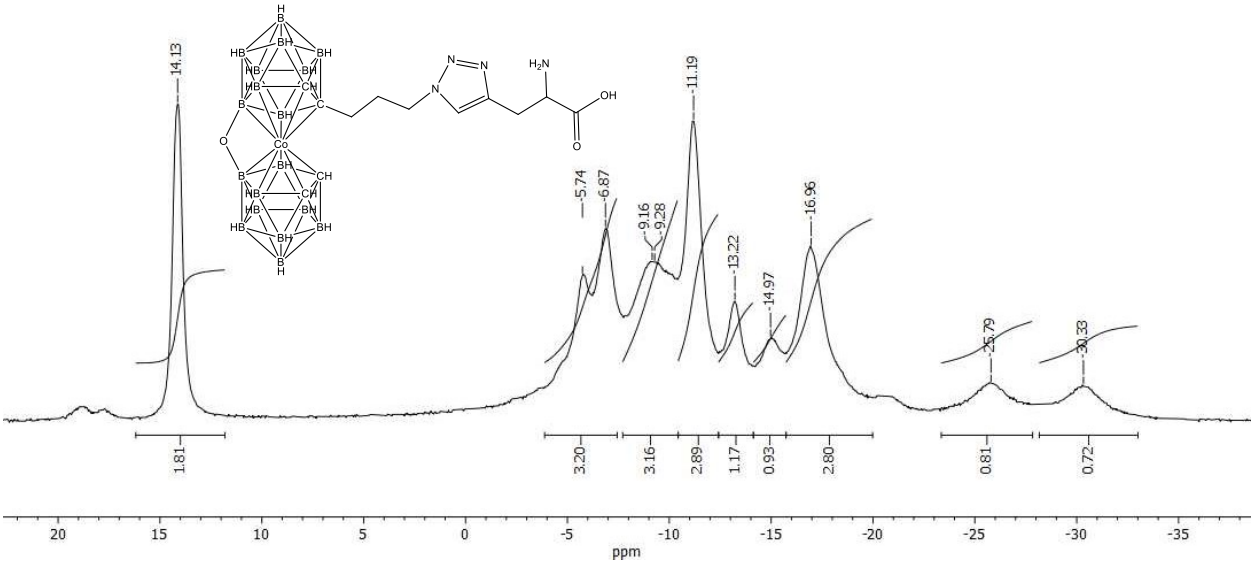


Figure S40: ^{11}B {^{1}H} NMR spectrum of Me_4N**13**

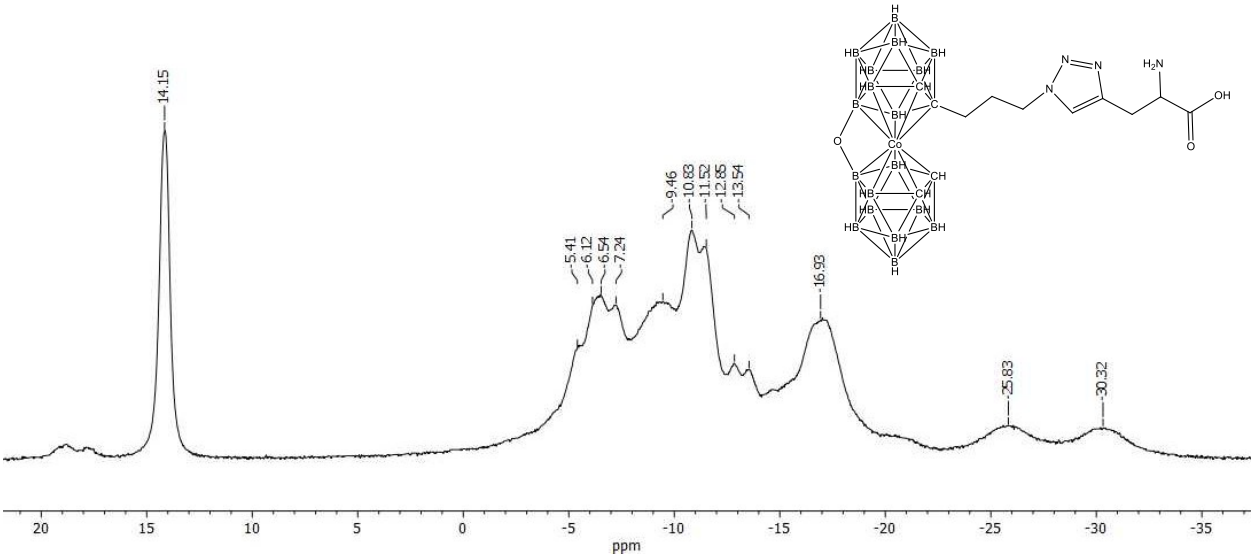


Figure S41: ^{11}B NMR spectrum of Me_4N**13**

Figure S42: ^{1}H NMR spectrum of Ph_4P**13**

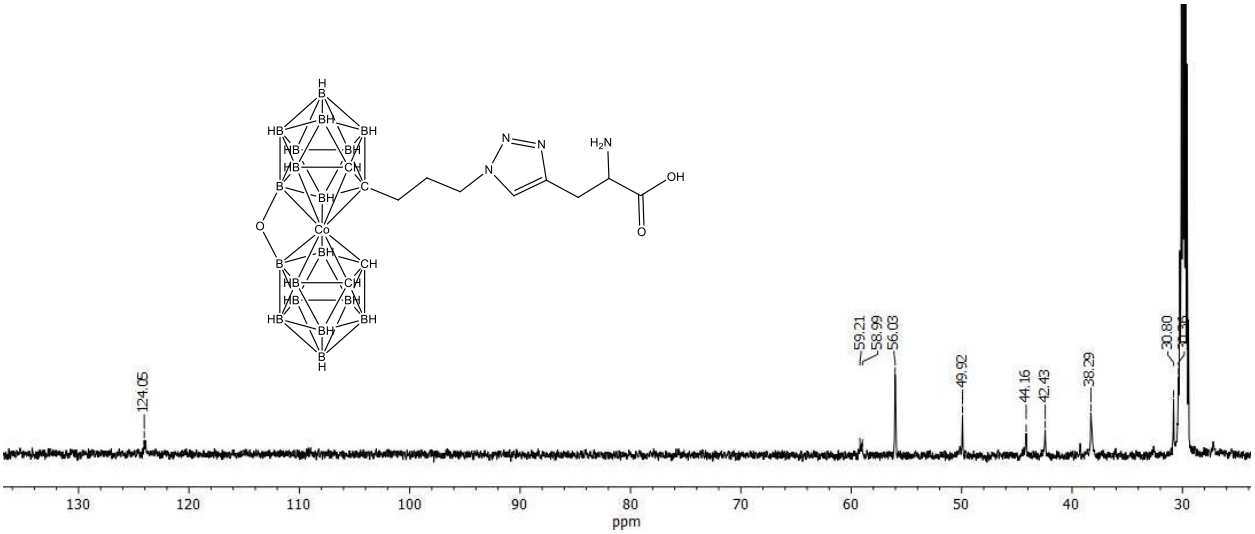


Figure S43: ^{13}C {^{1}H} NMR spectrum of Me_4N**13**

VI.10. NMR spectra of **14**$^{-}$

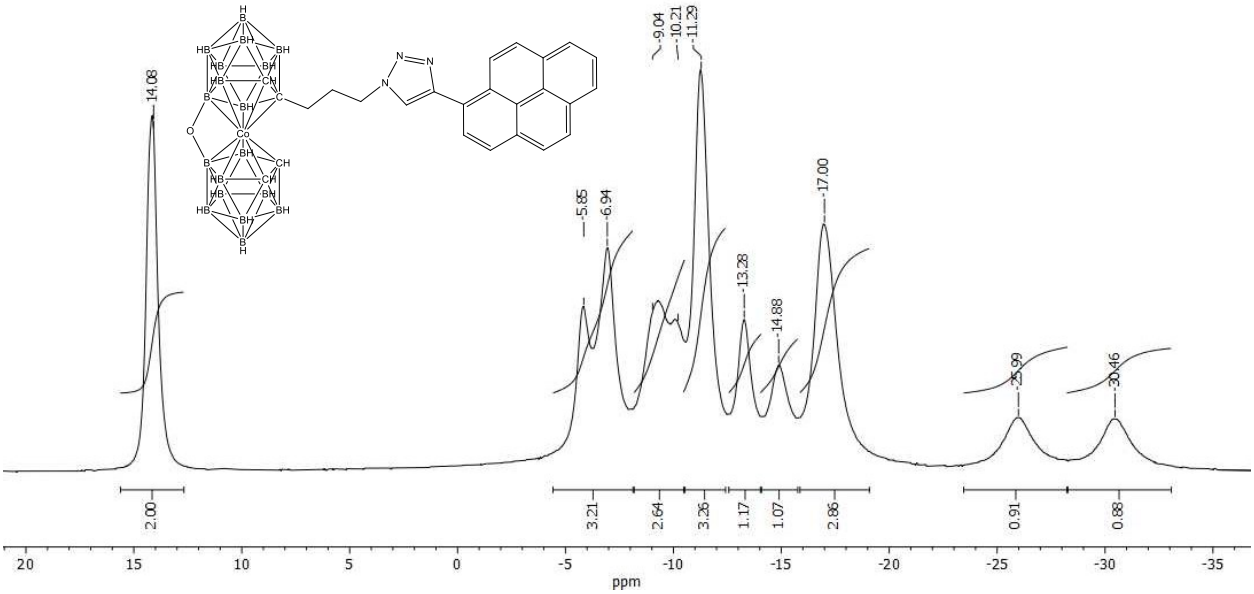


Figure S44: ^{11}B {^{1}H} NMR spectrum of Me_3NH**14**

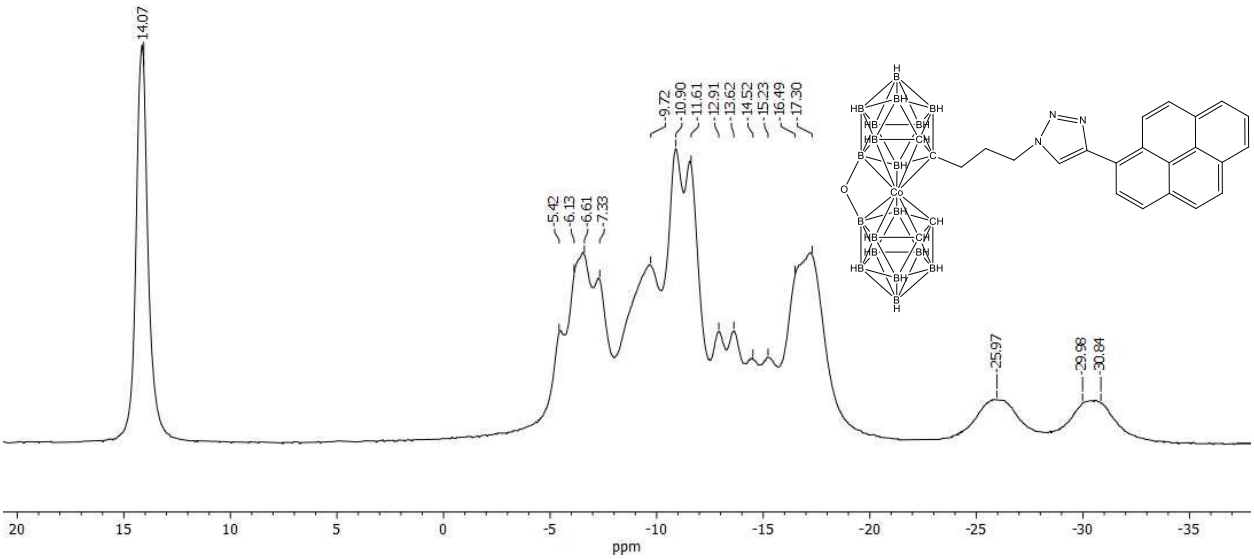


Figure S45: ^{11}B NMR spectrum of Me_3NH**14**

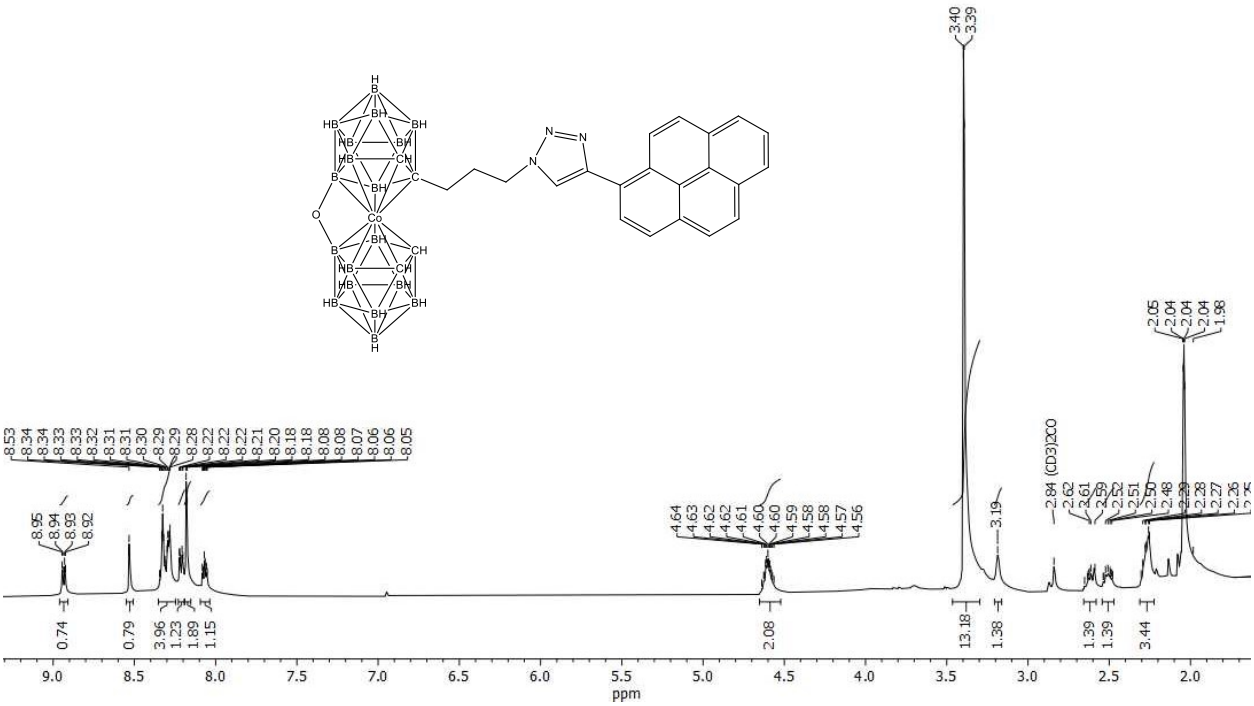


Figure S46: ^{1}H NMR spectrum of Me$_3$NH**14**

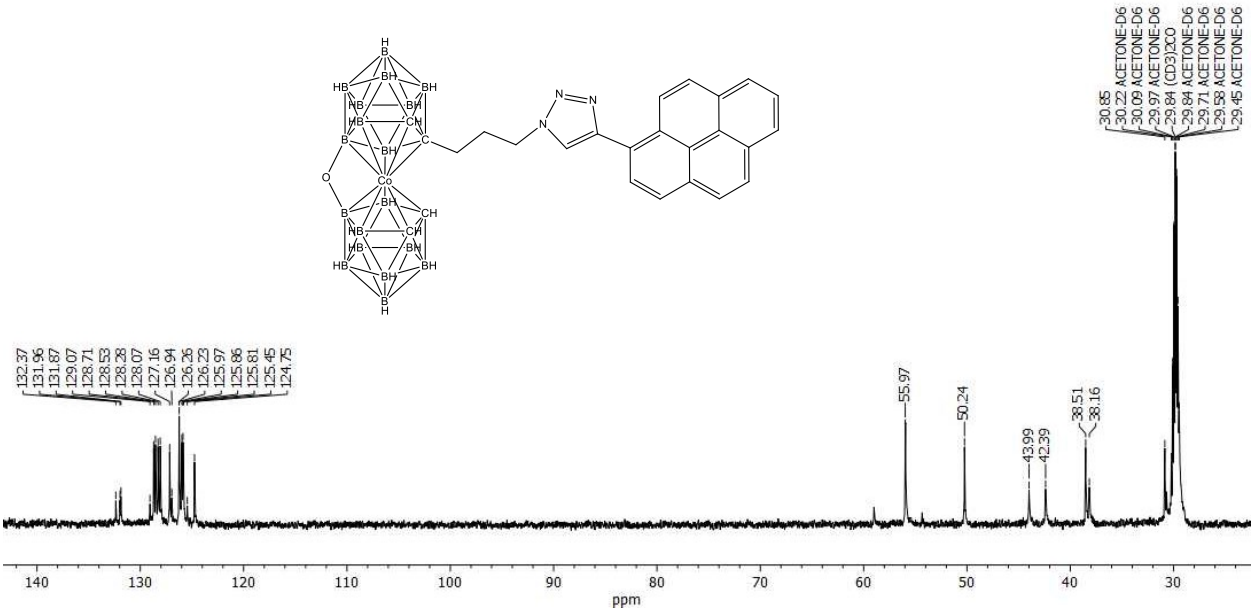


Figure S47: ^{13}C {^{1}H} NMR spectrum of Me$_3$NH**14**

VI.11. NMR spectra of **4**$^{-}$

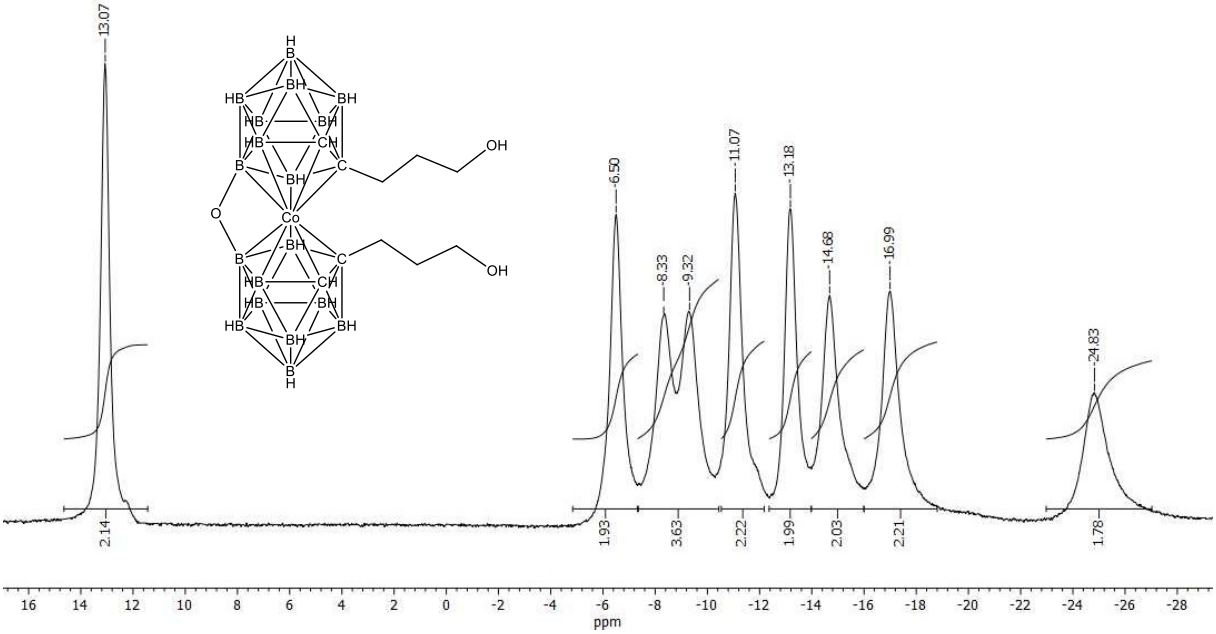


Figure S48: ^{11}B {^{1}H} NMR spectrum of Me_3NH**4**

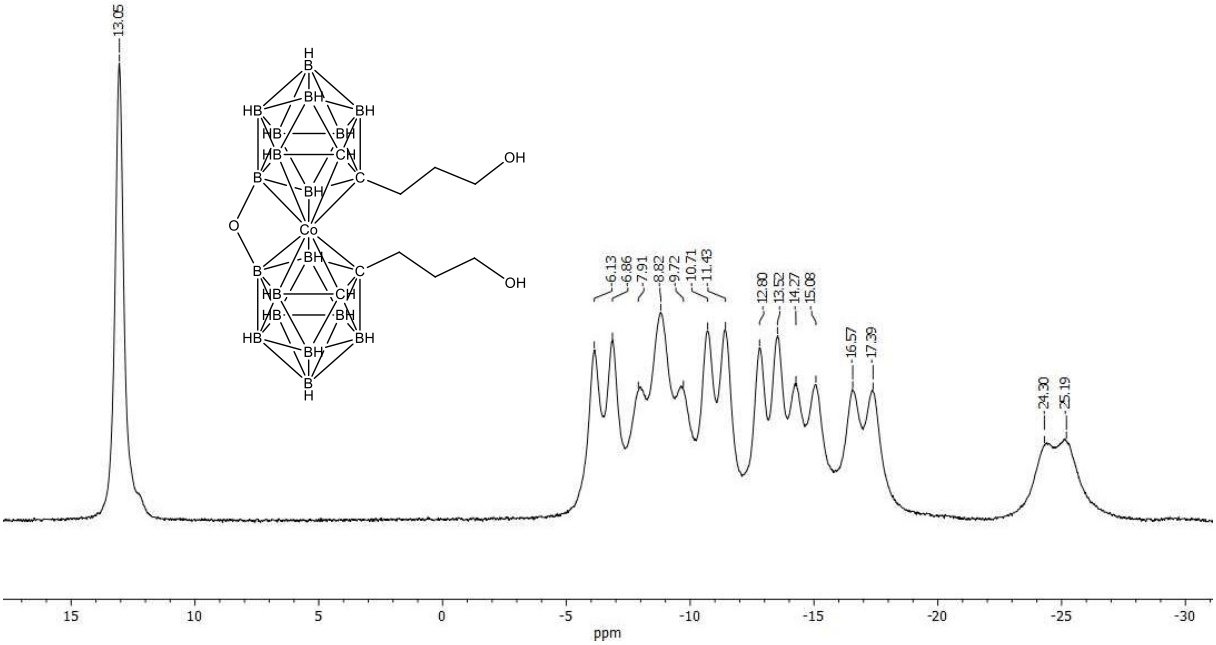


Figure S49: ^{11}B NMR spectrum of Me_3NH**4**

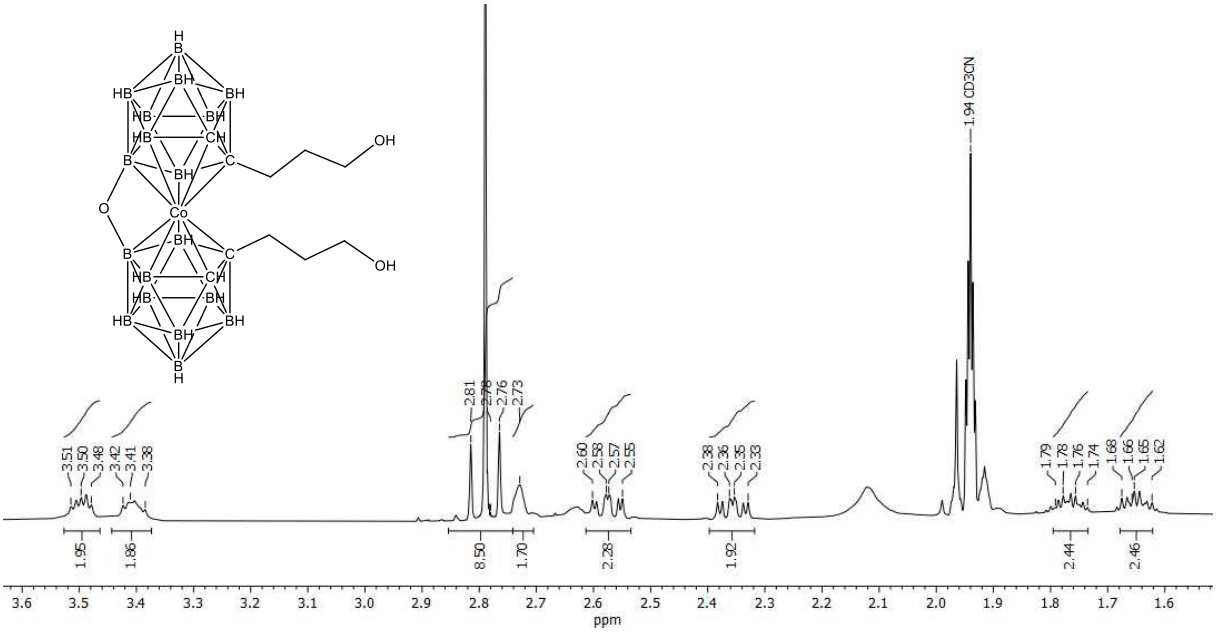


Figure S50: ^{1}H NMR spectrum of Me_3NH**4**

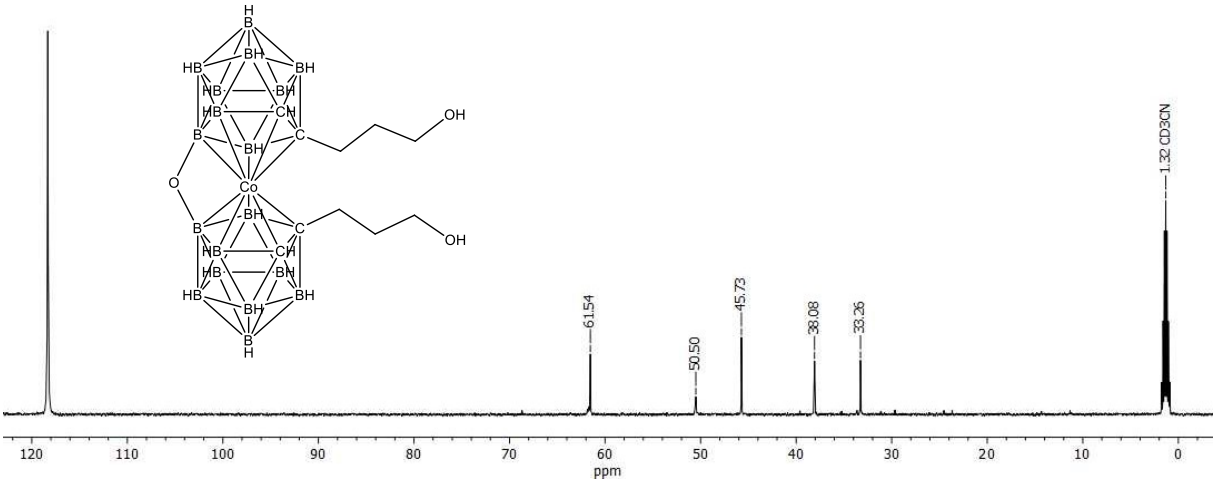


Figure S51: ^{13}C $\{^{1}H\}$ NMR spectrum of Me_3NH**4**

VI.12. NMR spectra of **6**$^{-}$

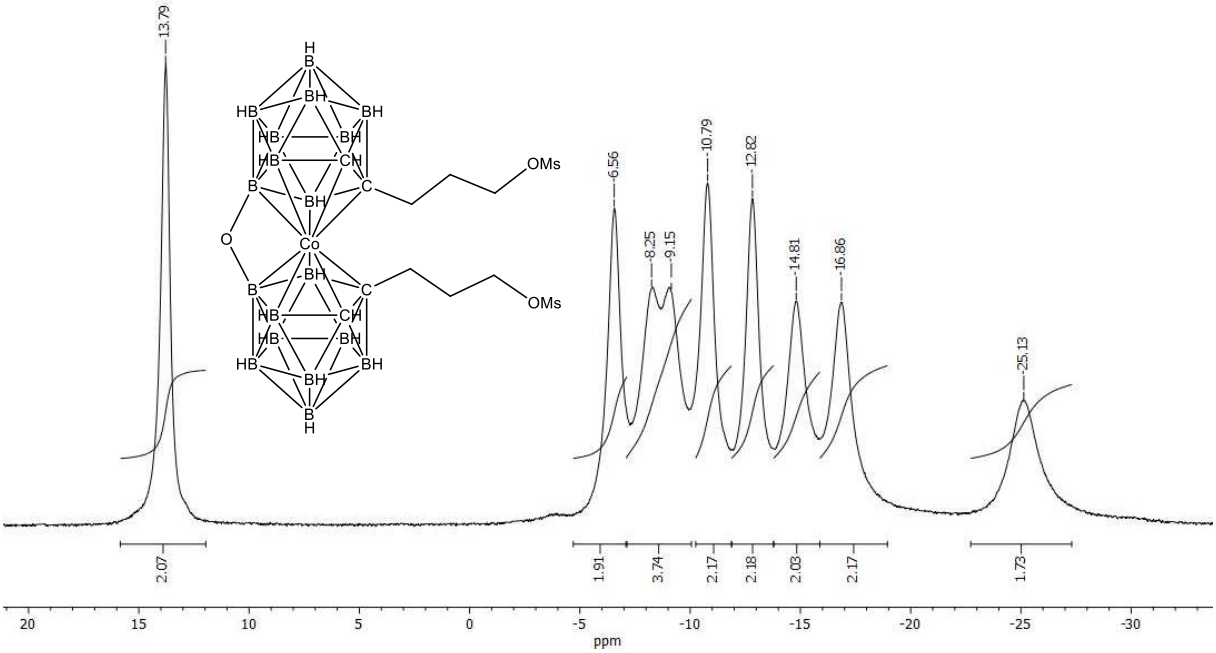


Figure S52: ^{11}B {^{1}H} NMR spectrum of Me_4N**6**

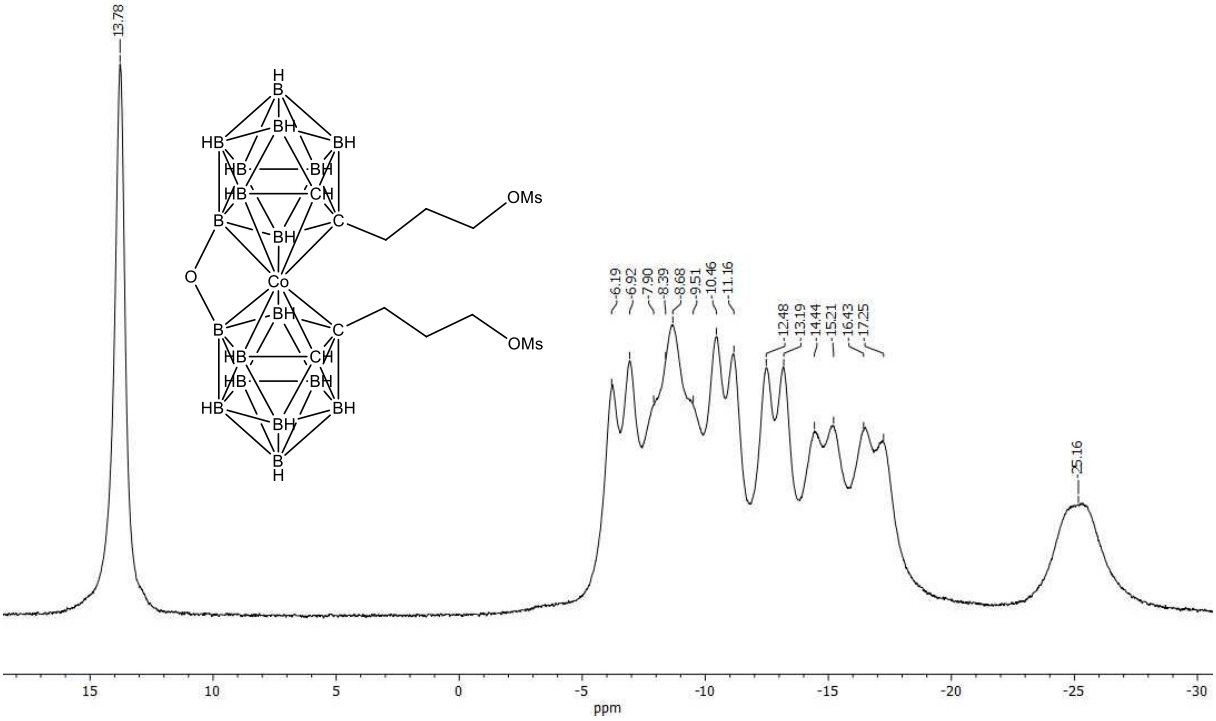


Figure S53: ^{11}B NMR spectrum of Me_4N**6**

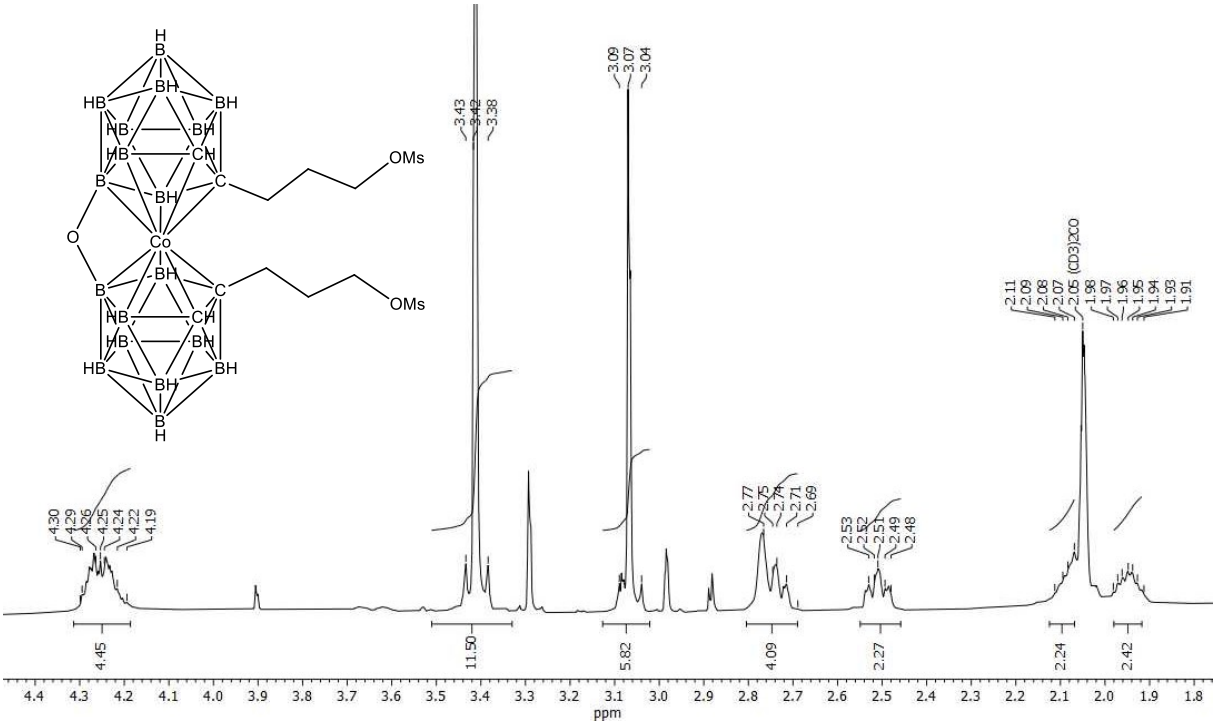


Figure S54: ^{1}H NMR spectrum of Me_4N**6**

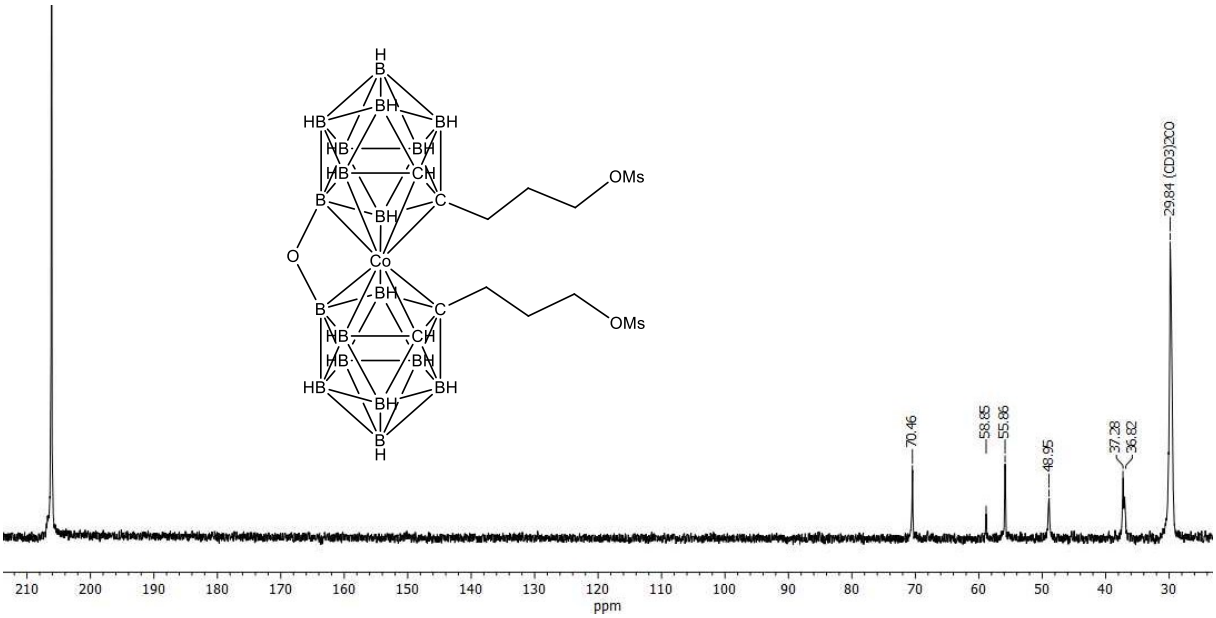


Figure S55: ^{13}C {^{1}H} NMR spectrum of Me_4N**6**

VI.13. NMR spectra of **8**$^{-}$

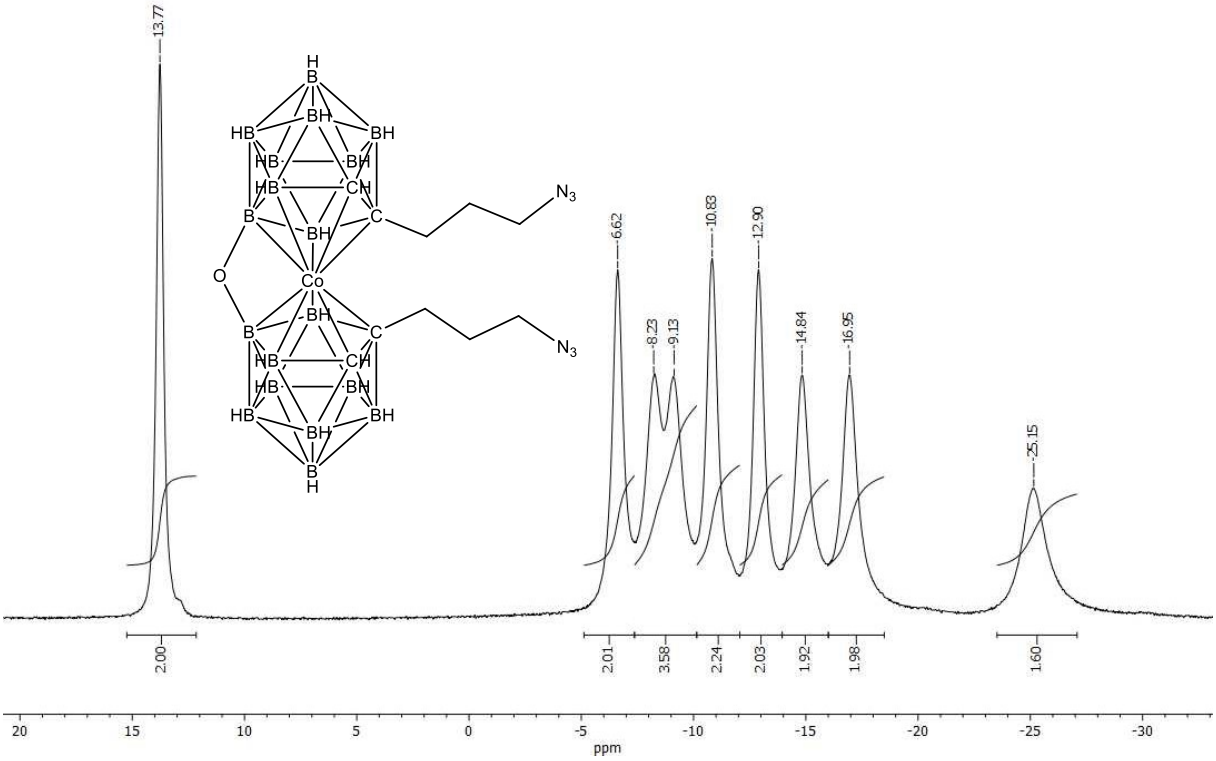


Figure S56: ^{11}B {^{1}H} NMR spectrum of Me_4N**8**

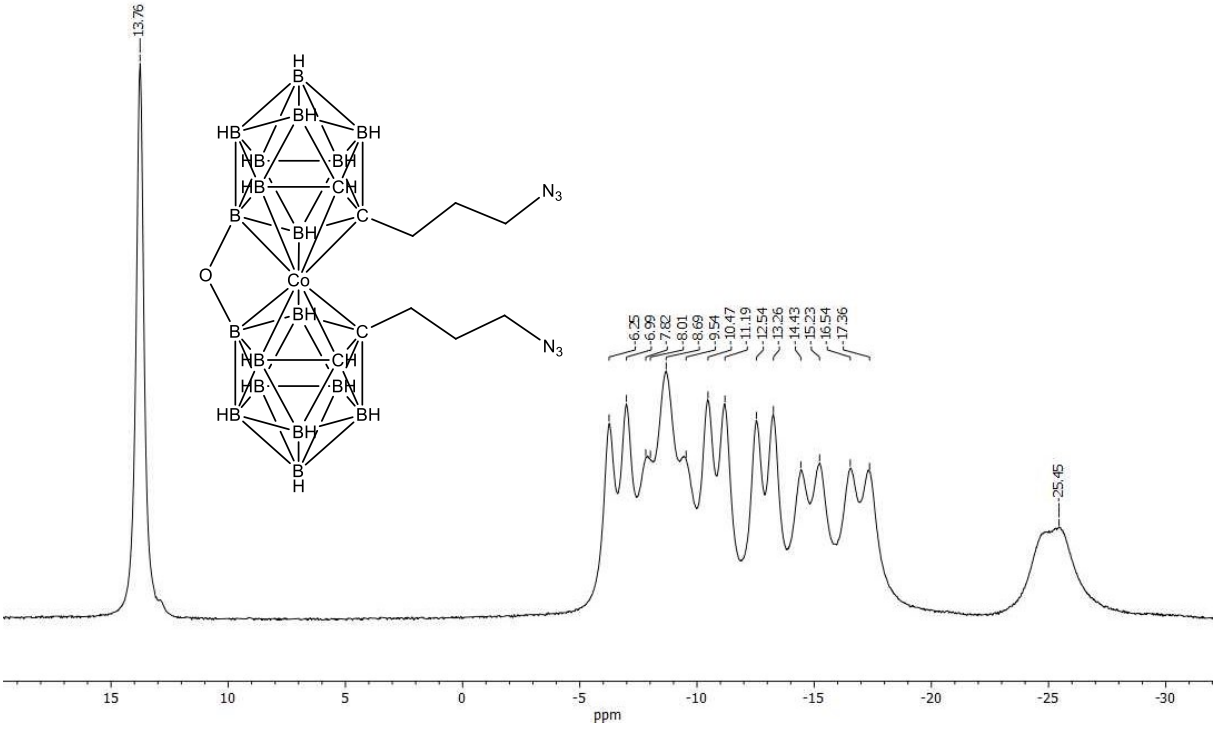


Figure S57: ^{11}B NMR spectrum of Me_4N**8**

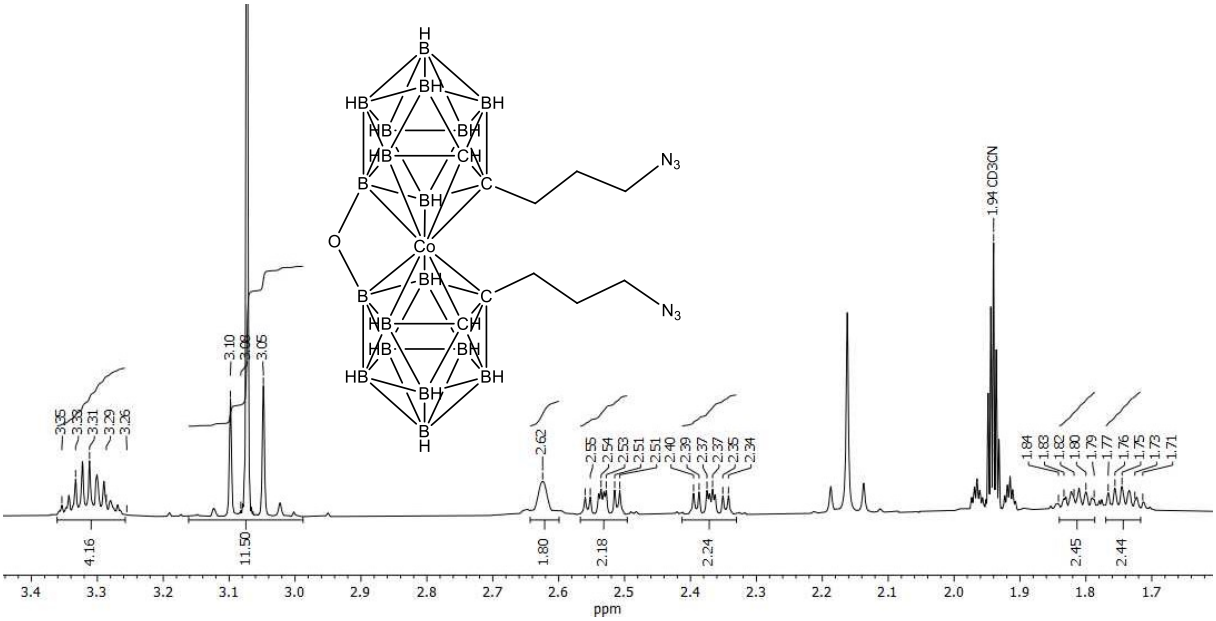


Figure S58: ^{1}H NMR spectrum of Me_4N**8**

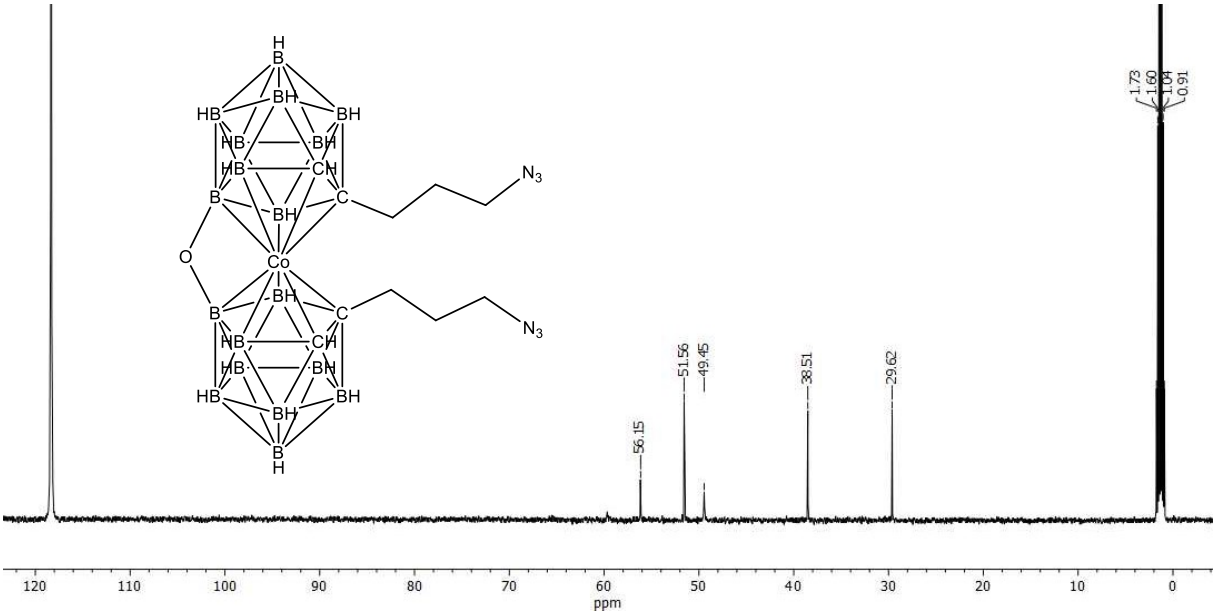


Figure S59: ^{13}C {^{1}H} NMR spectrum of Me_4N**8**

VI.14. NMR spectra of **15**$^{-}$

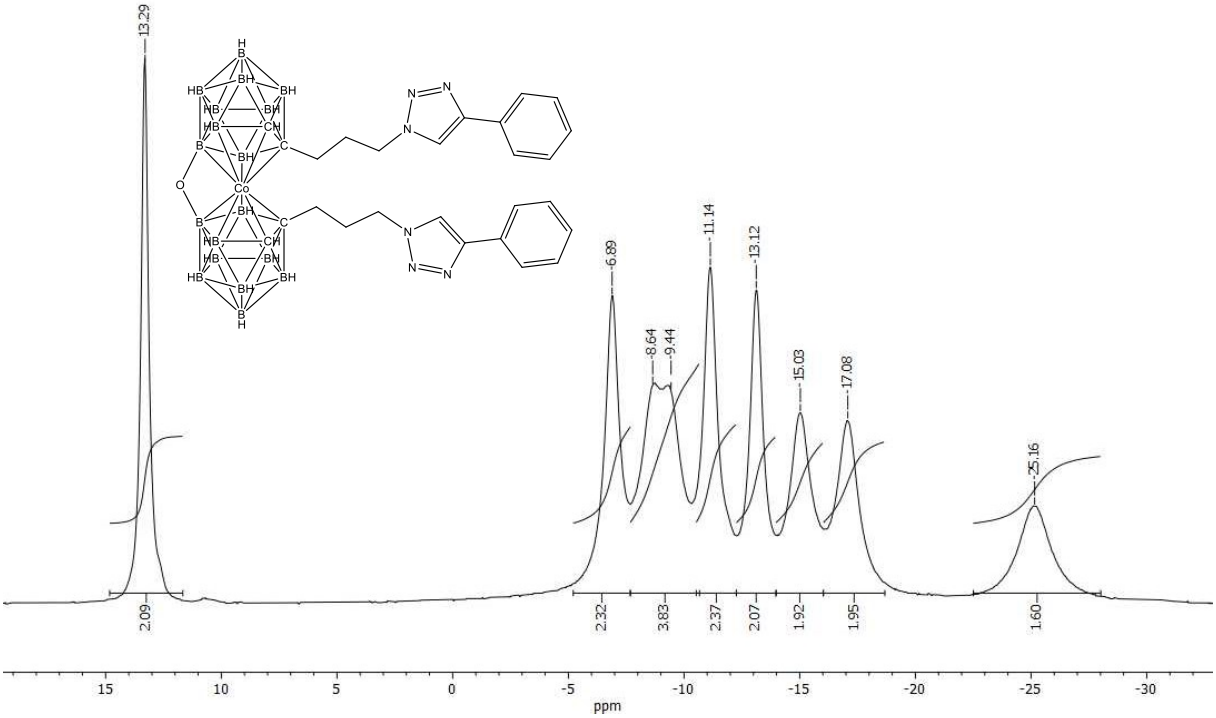


Figure S60: ^{11}B {^{1}H} NMR spectrum of Me_4N**15**

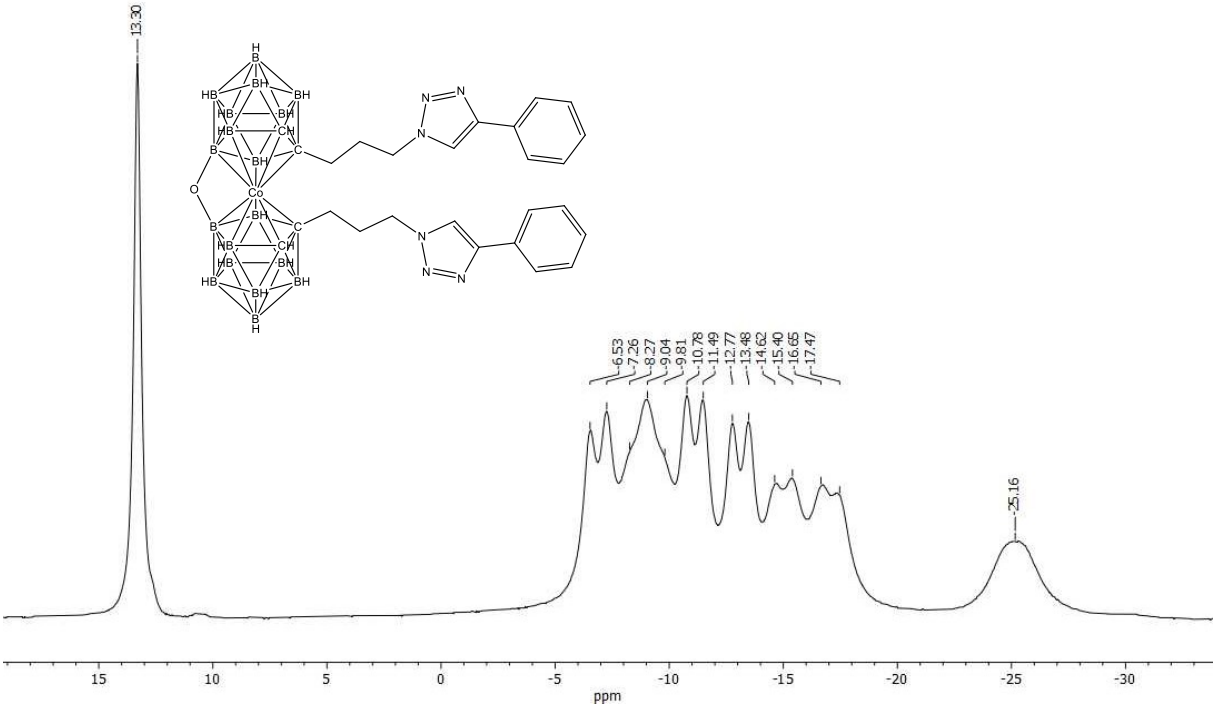


Figure S61: ^{11}B NMR spectrum of Me_4N**15**

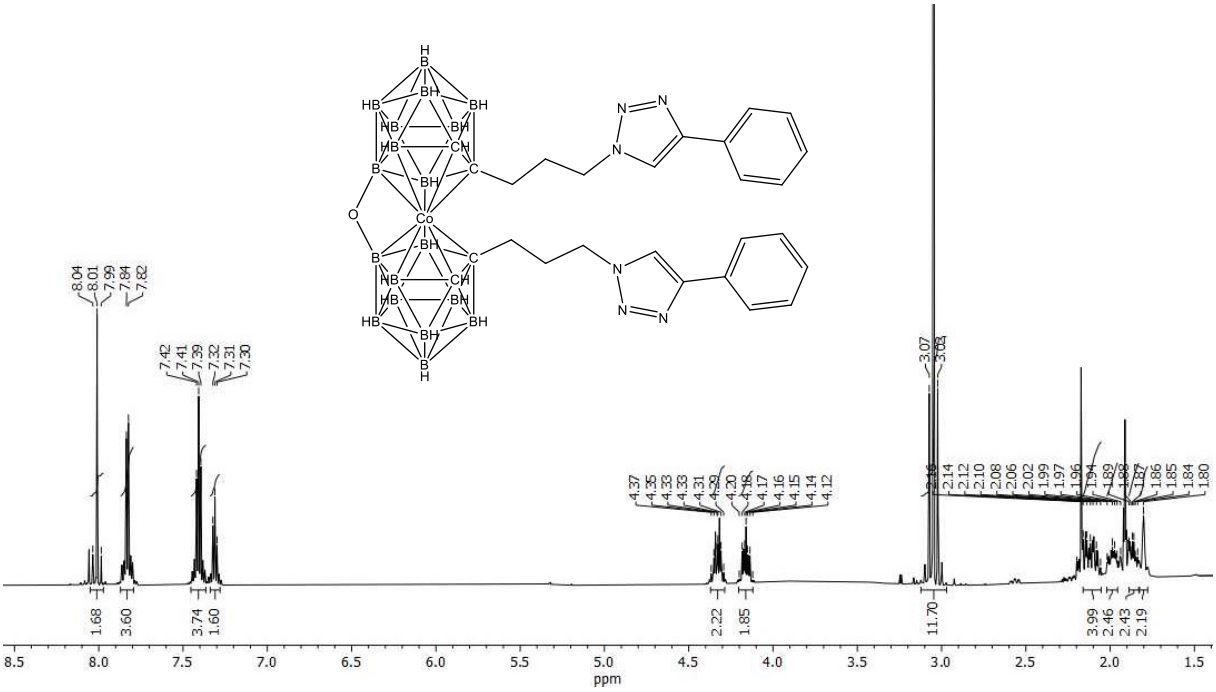


Figure S62: ^{1}H NMR spectrum of Me$_4$N**15**

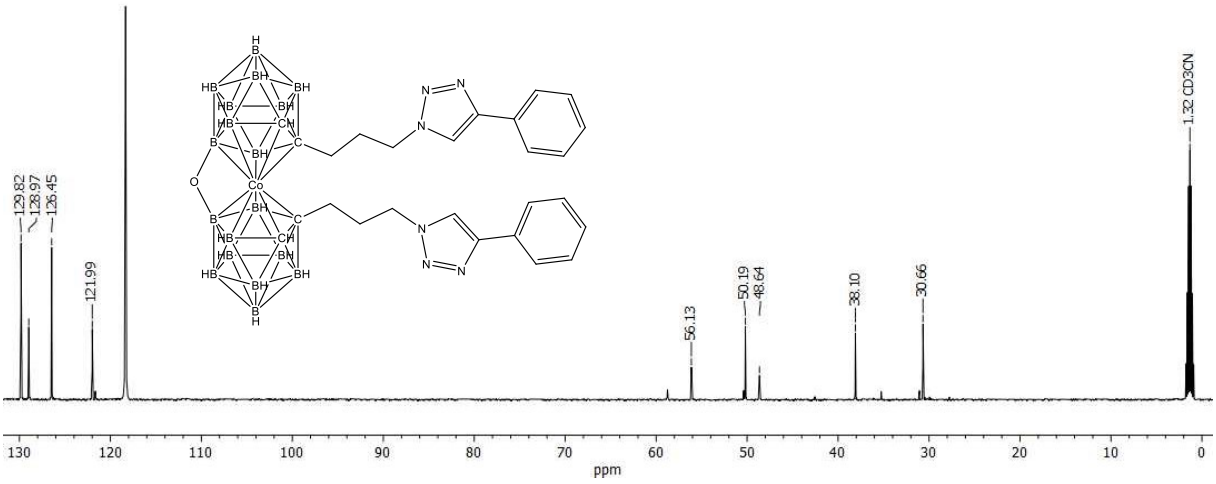


Figure S63: ^{13}C {^{1}H} NMR spectrum of Me$_4$N**15**

VI.15. NMR spectra of **16**$^{-}$

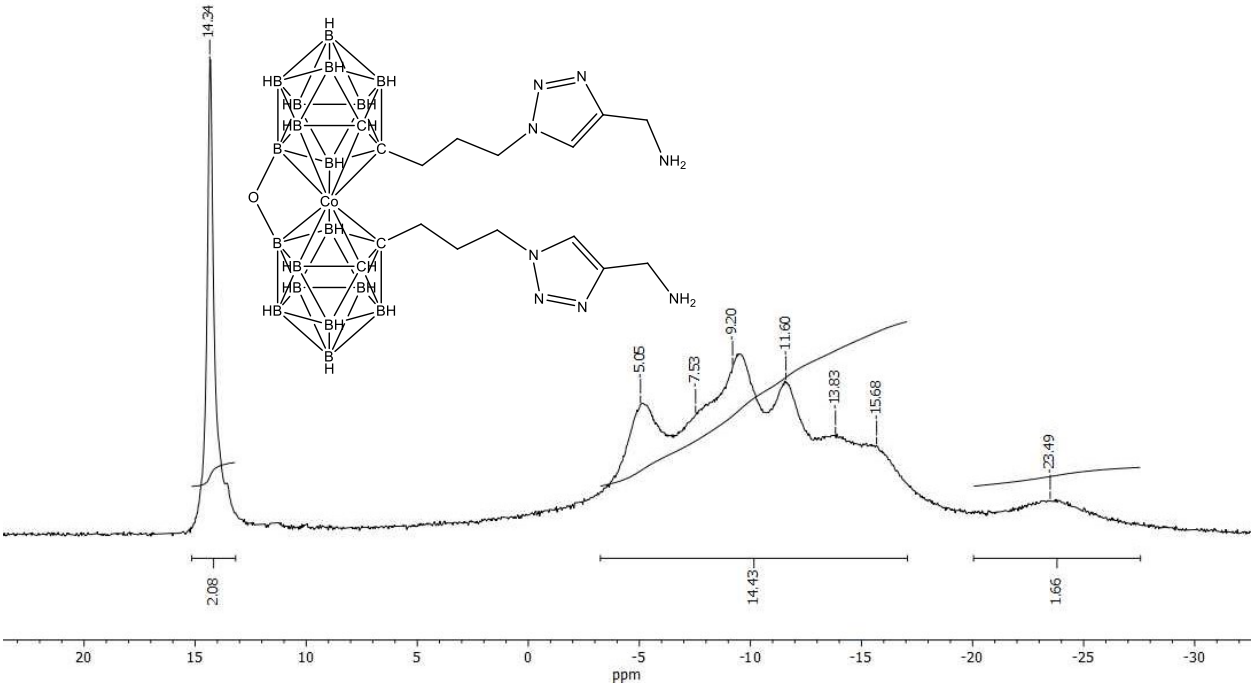


Figure S64: ^{11}B {^{1}H} NMR spectrum of Me_4N**16**

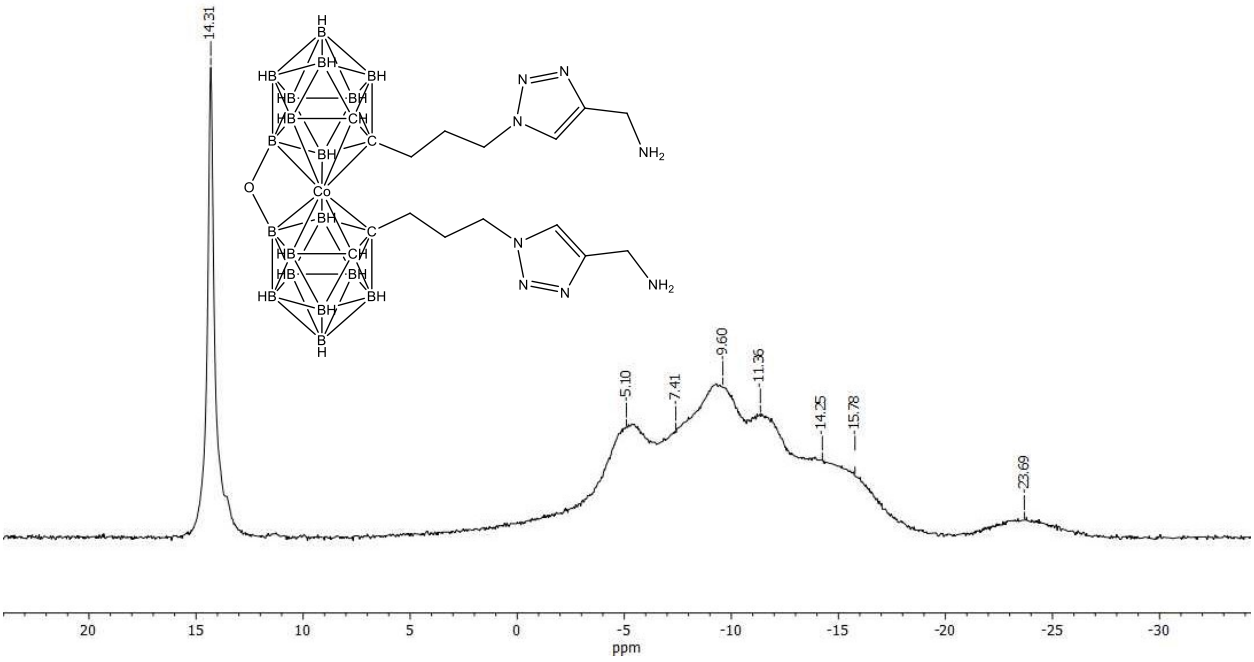


Figure S65: ^{11}B NMR spectrum of Me_4N**16**

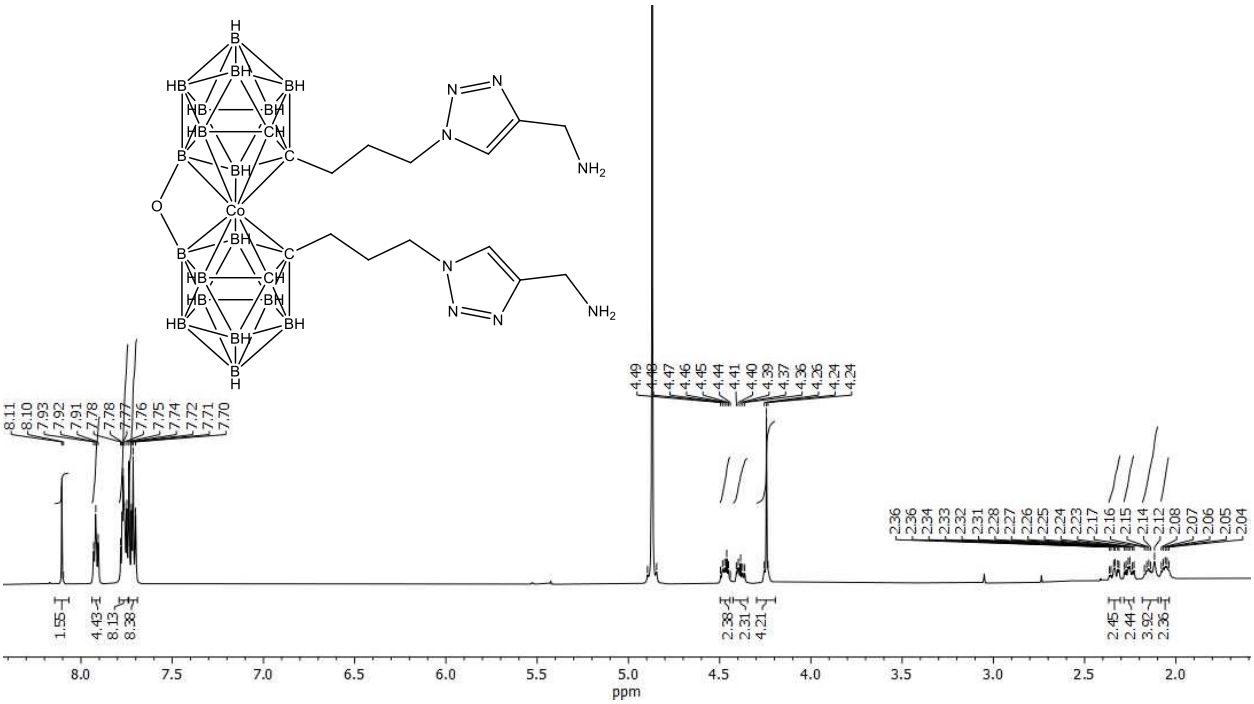


Figure S66: ^{1}H NMR spectrum of Ph_4P**16**

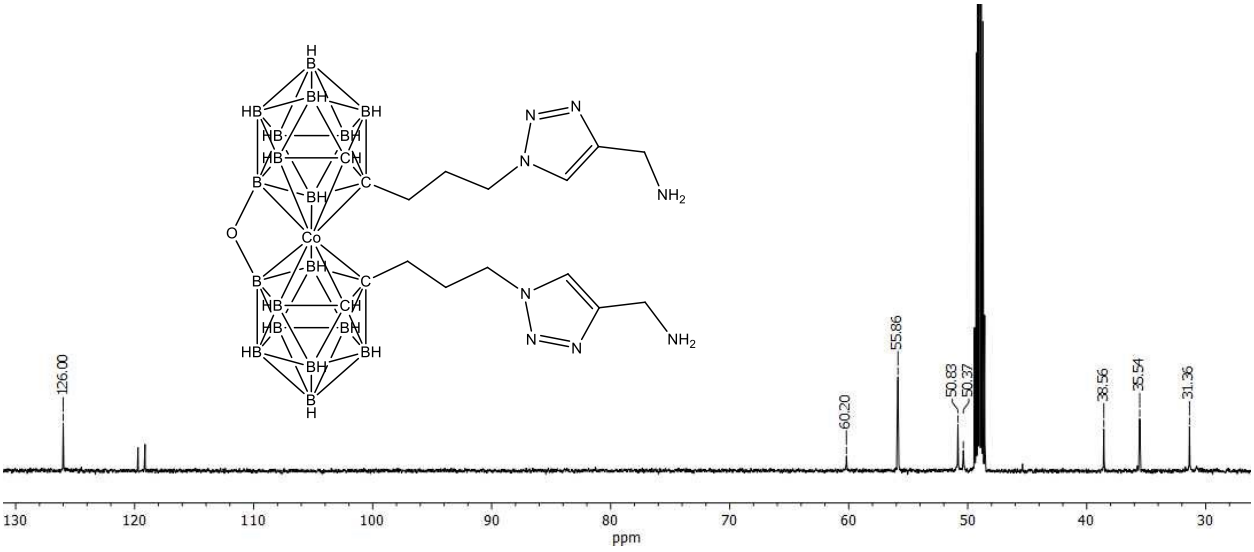


Figure S67: ^{13}C {^{1}H} NMR spectrum of Me_4N**16**

VI.16. NMR spectra of **17**$^{-}$

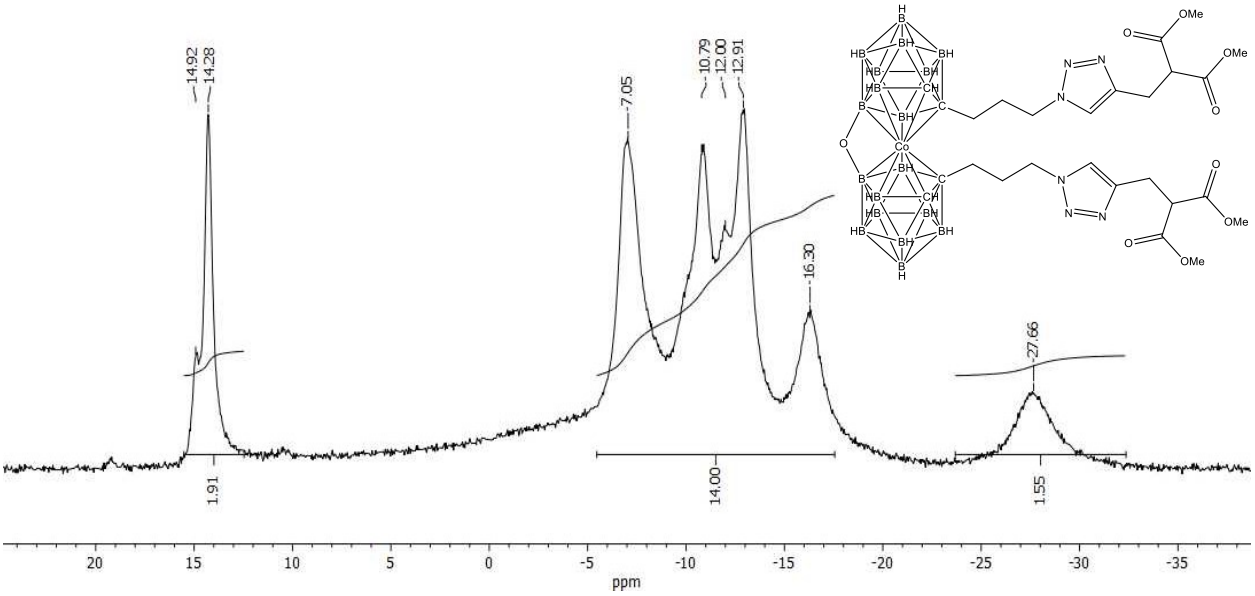


Figure S68: ^{11}B {^{1}H} NMR spectrum of Me_4N**17**

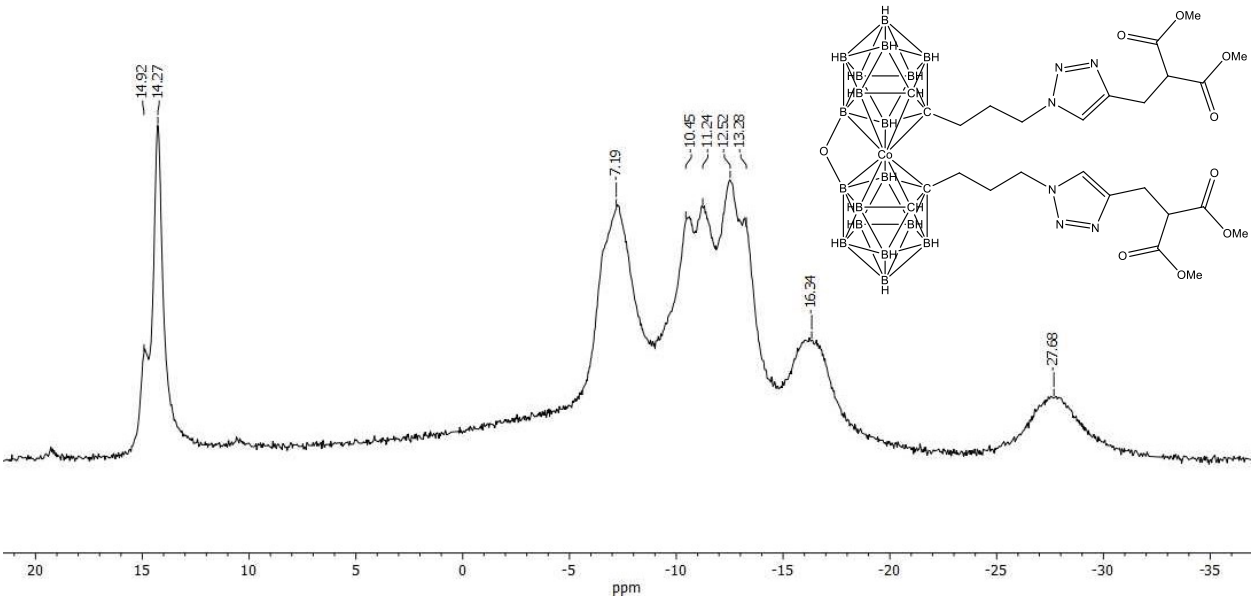


Figure S69: ^{11}B NMR spectrum of Me_4N**17**

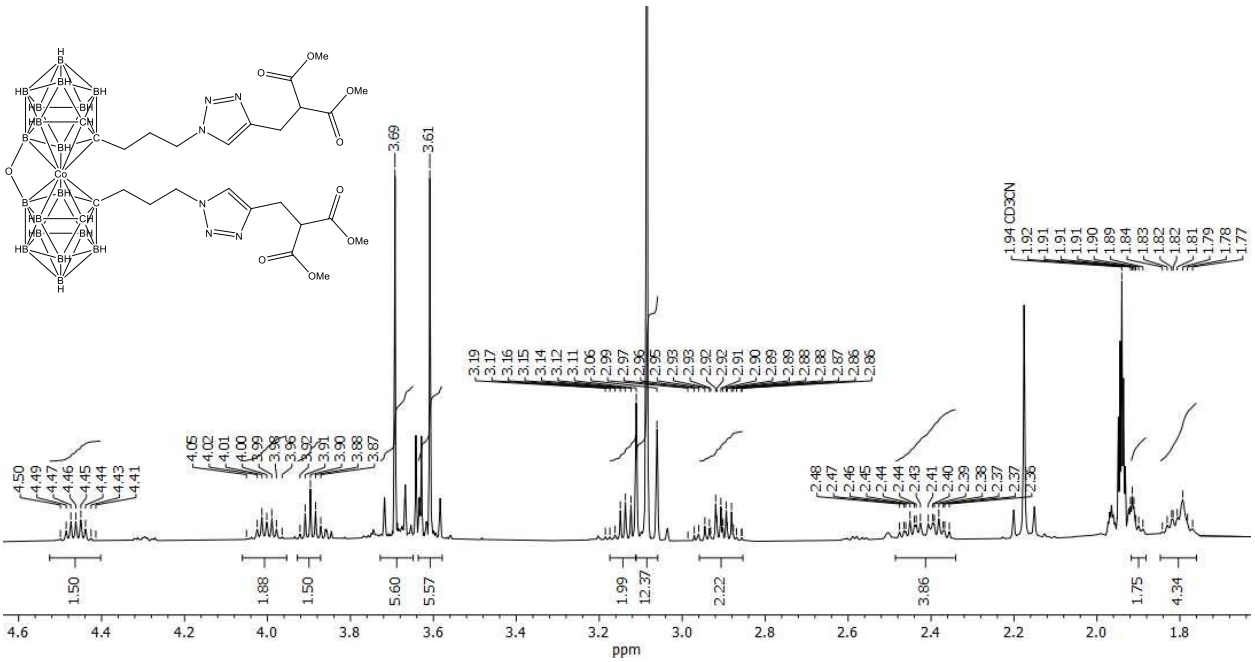


Figure S70: ^{1}H NMR spectrum of Me_4N**17**

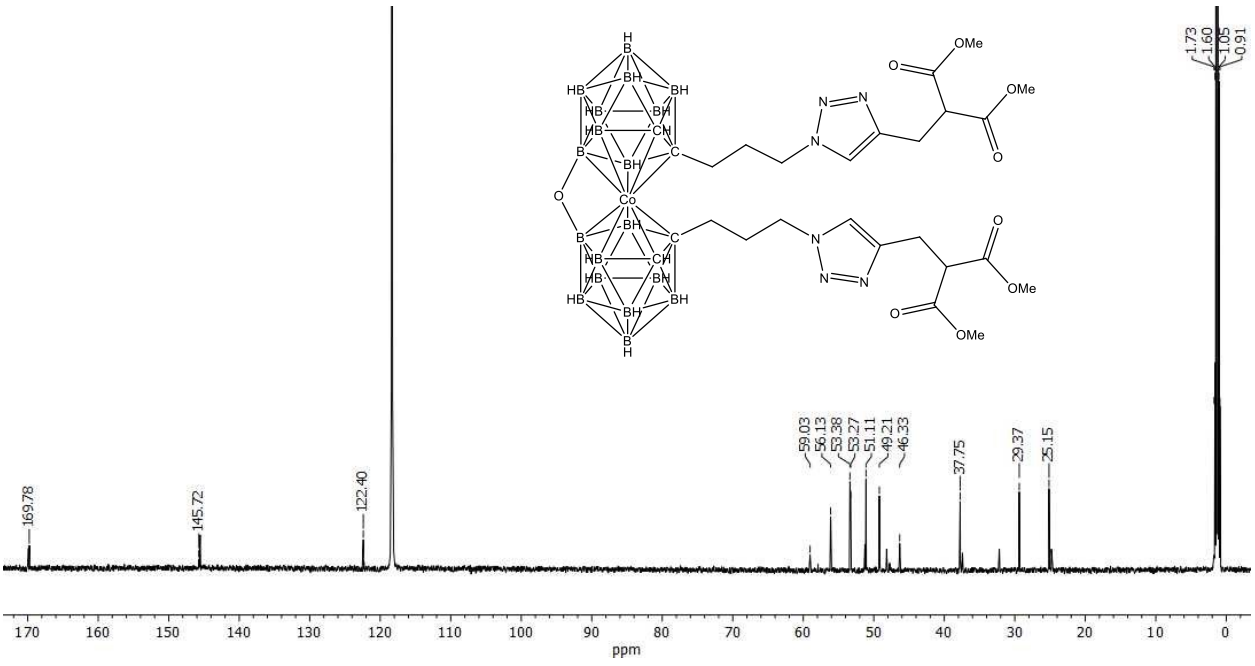


Figure S71: ^{13}C {^{1}H} NMR spectrum of Me_4N**17**

VII. ESI Mass spectra

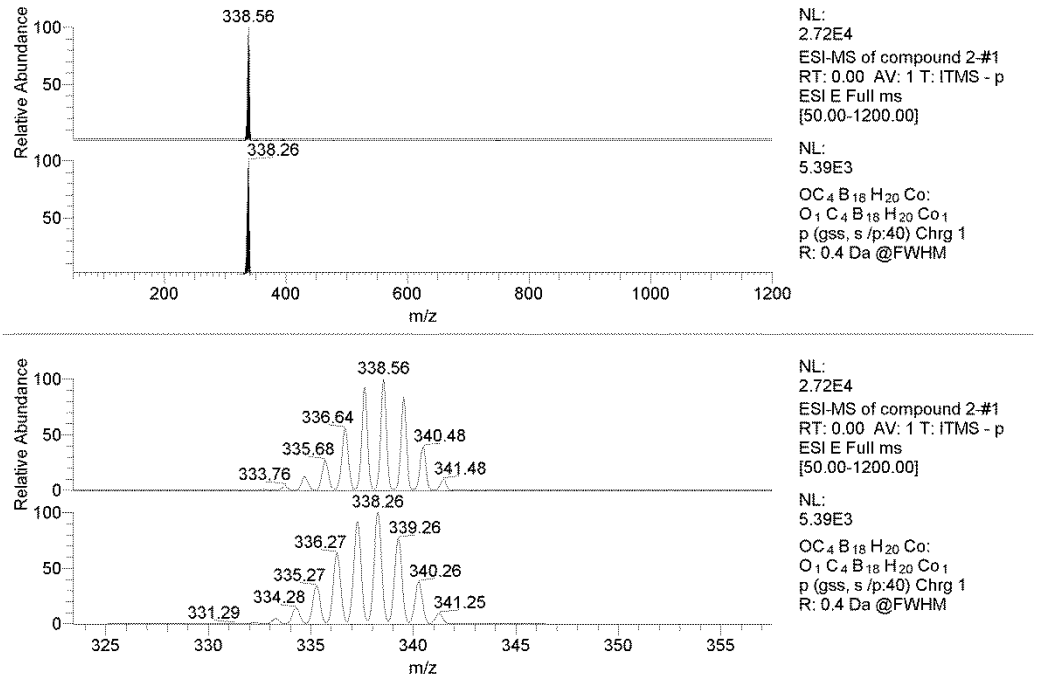


Figure S72: Spectrum of **2**$^{-}$

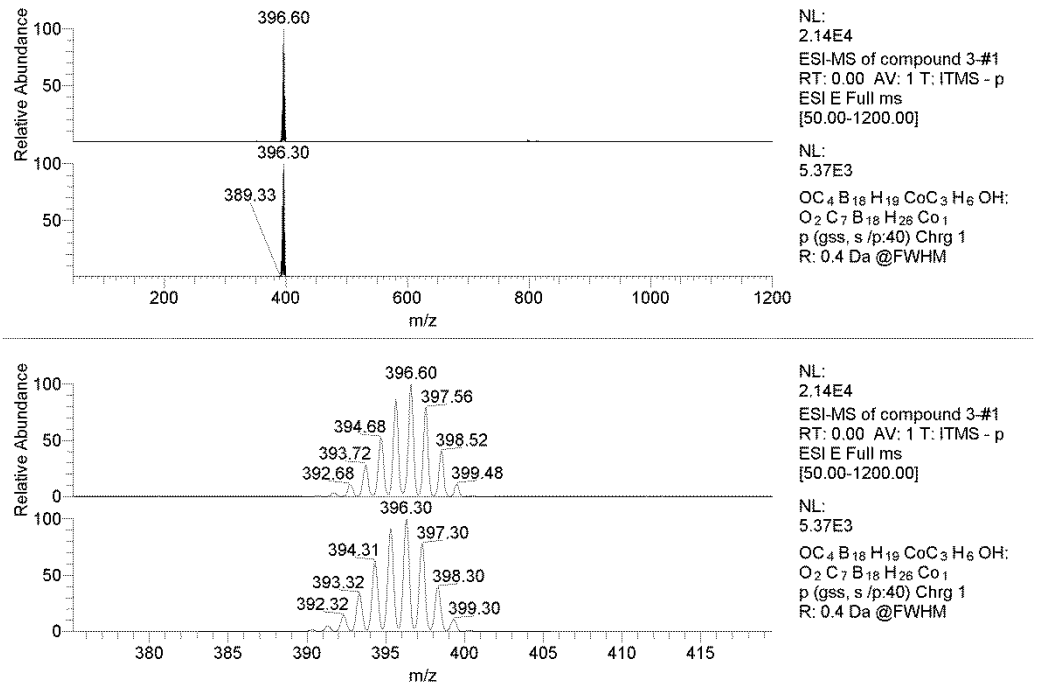


Figure S73: Spectrum of **3**$^{-}$

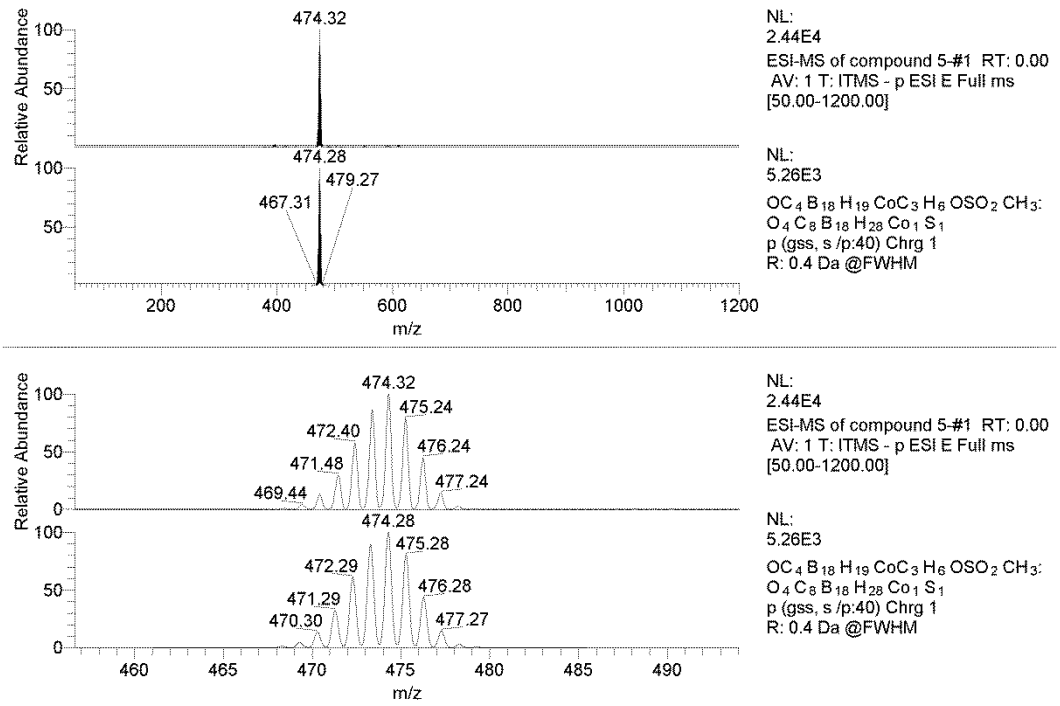


Figure S74: Spectrum of **5**$^{-}$

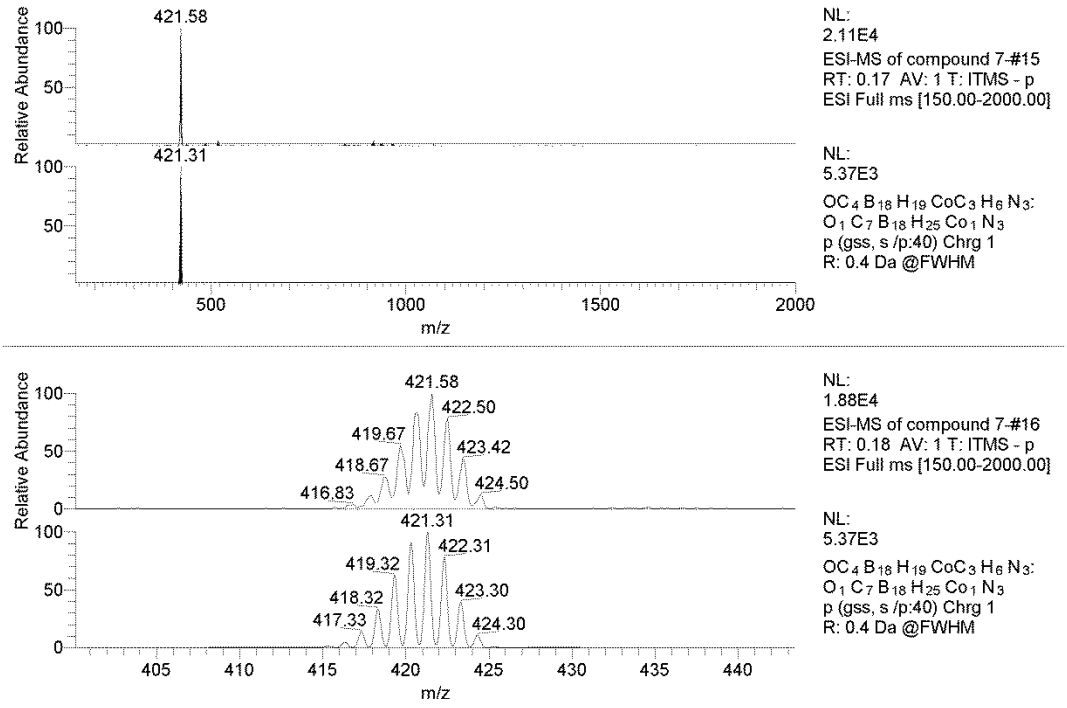


Figure S75: Spectrum of **7**$^{-}$

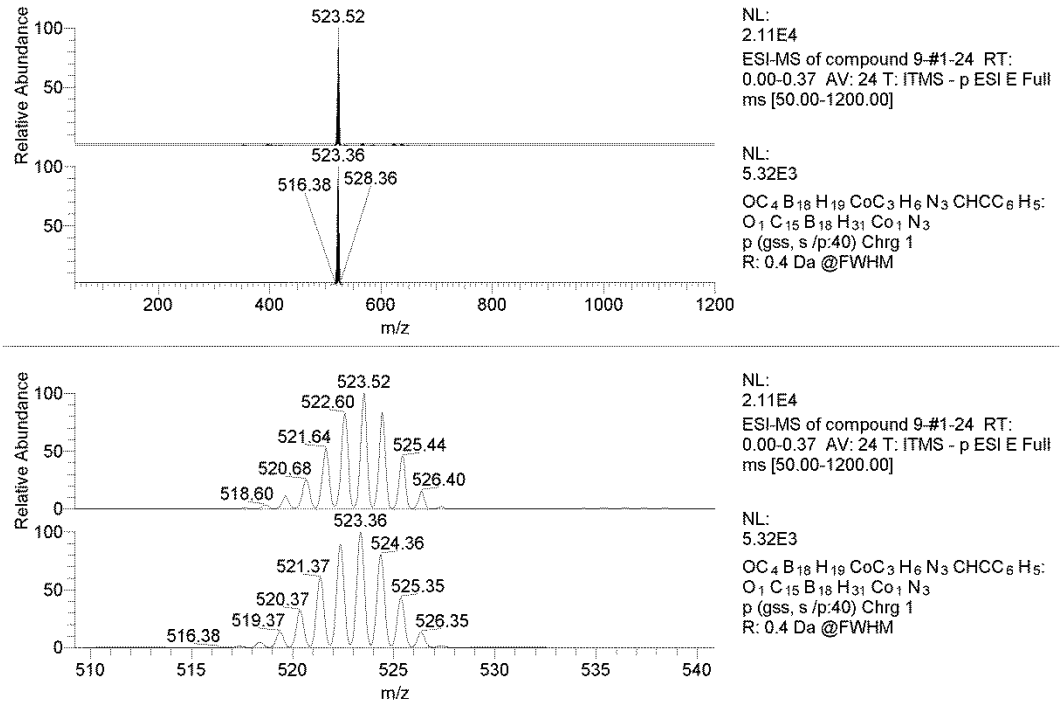


Figure S76: Spectrum of **9**$^{-}$

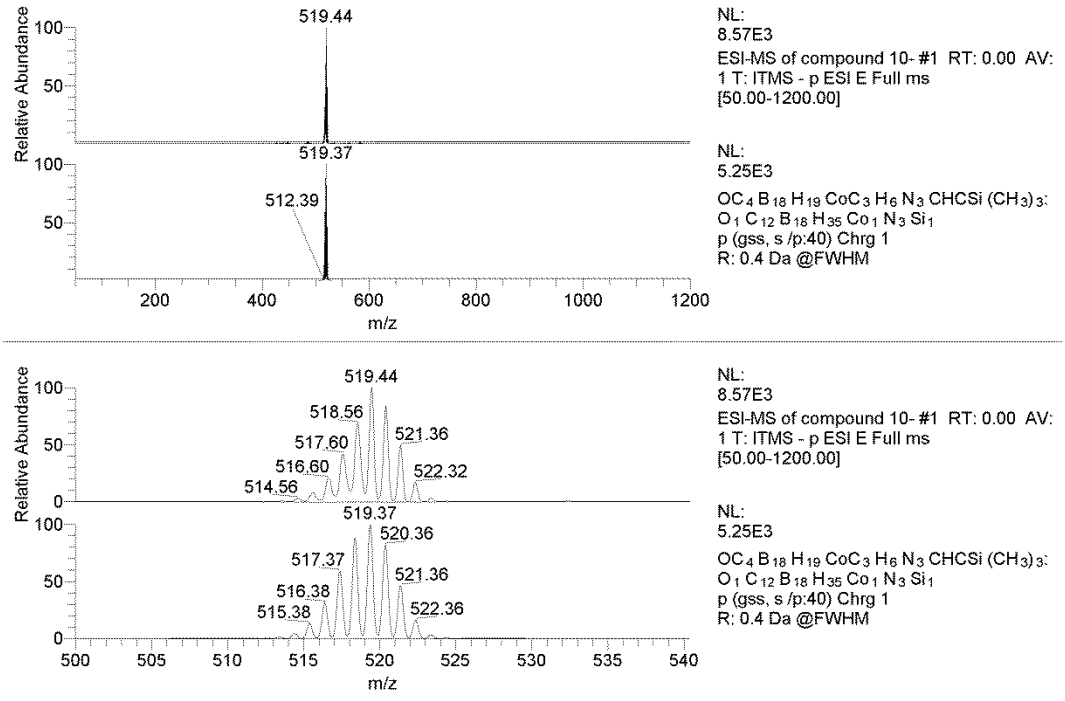


Figure S77: Spectrum of **10**$^{-}$

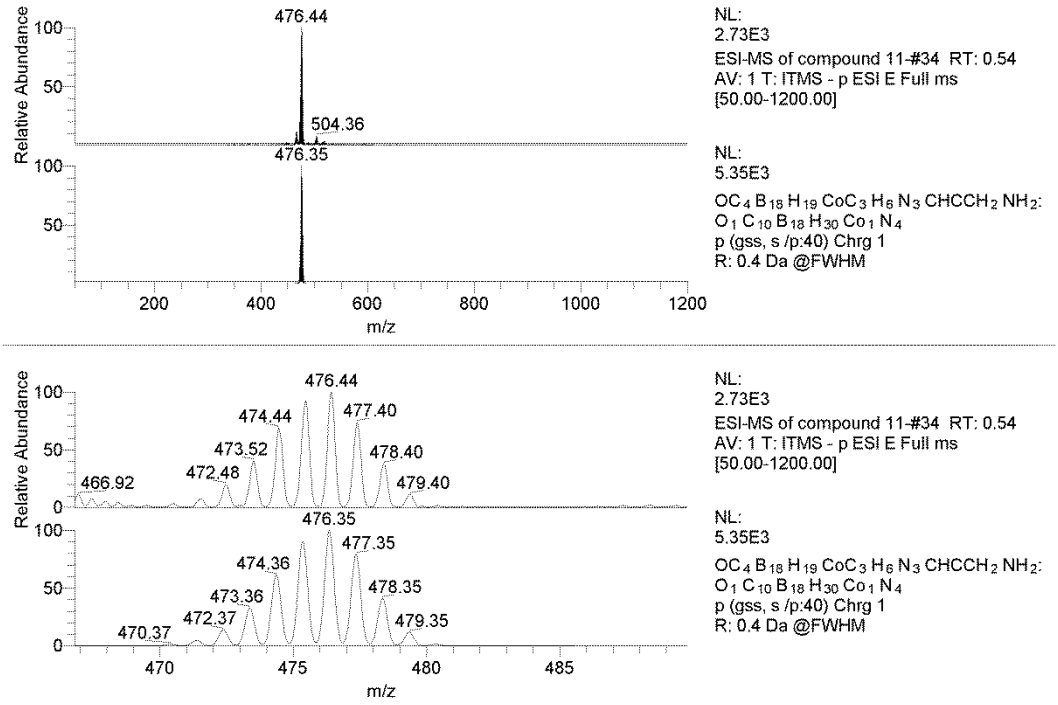


Figure S78: Spectrum of **11**$^{-}$

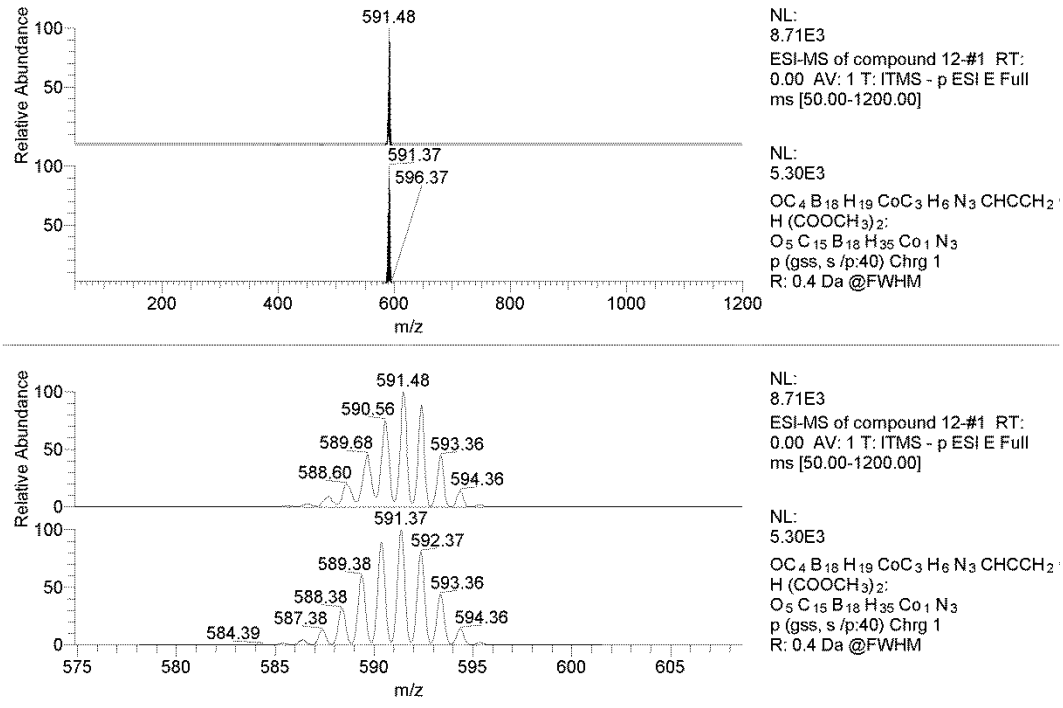


Figure S79: Spectrum of **12**$^{-}$

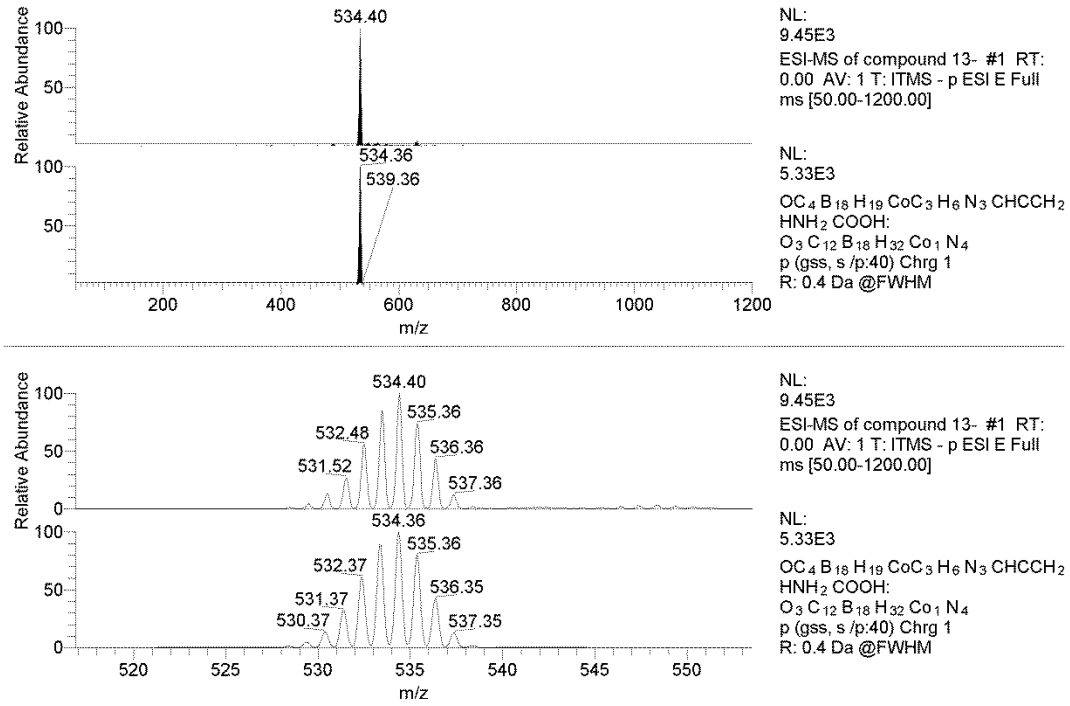


Figure S80: Spectrum of **13**$^{-}$

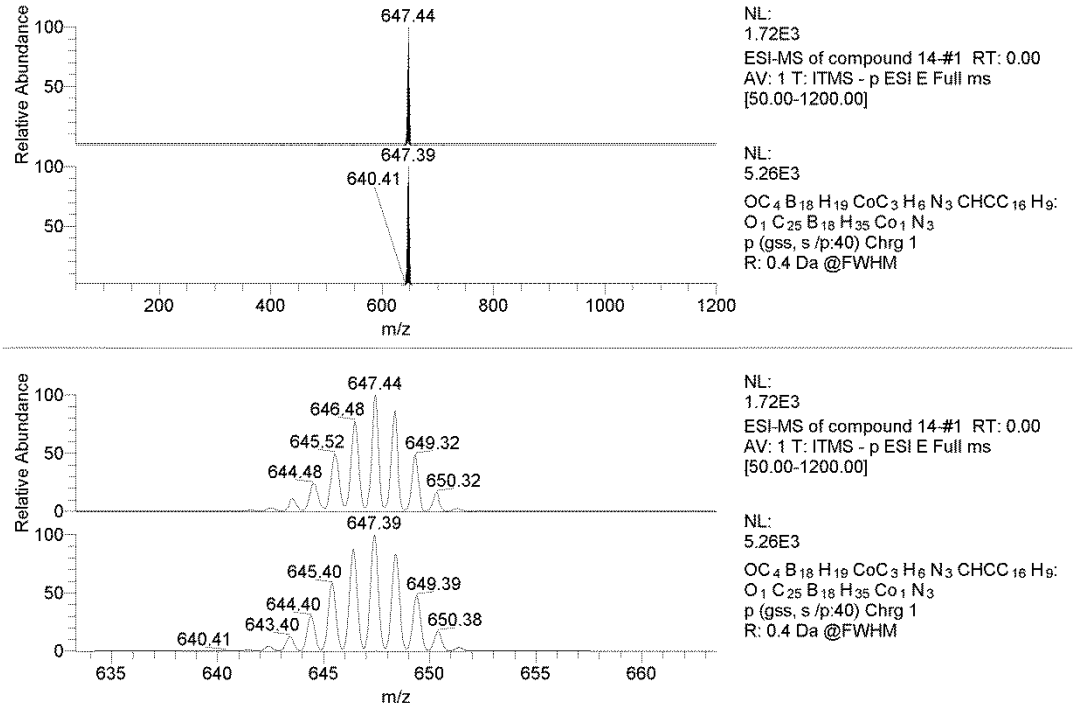


Figure S81: Spectrum of **14**$^{-}$

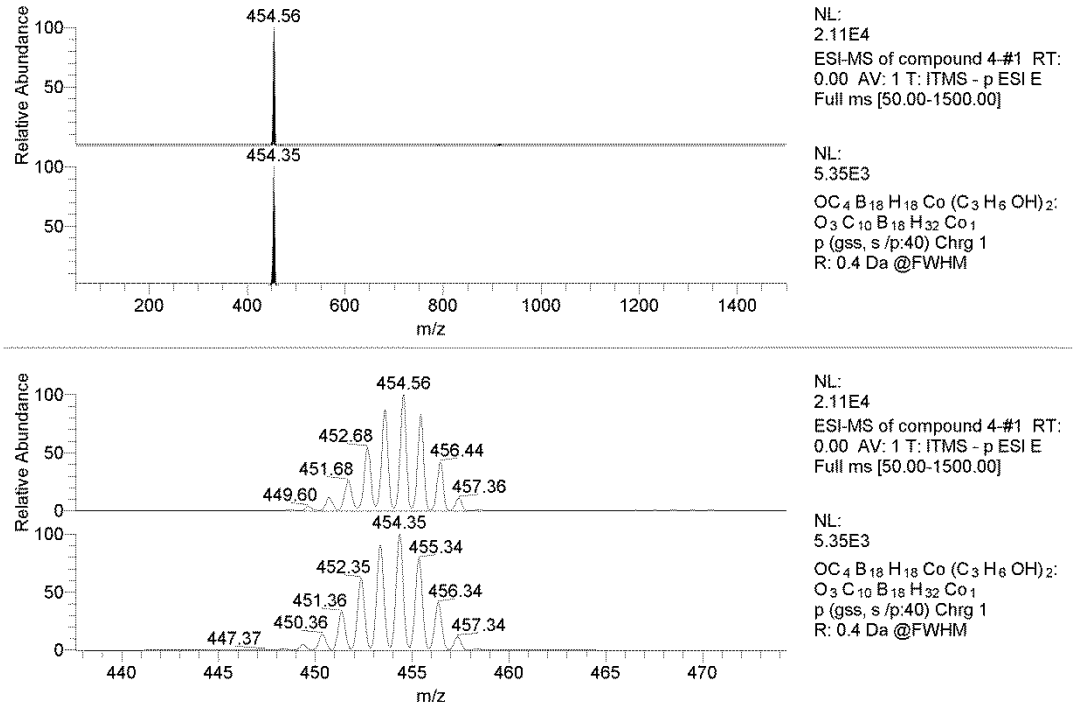


Figure S82: Spectrum of **4**$^{-}$

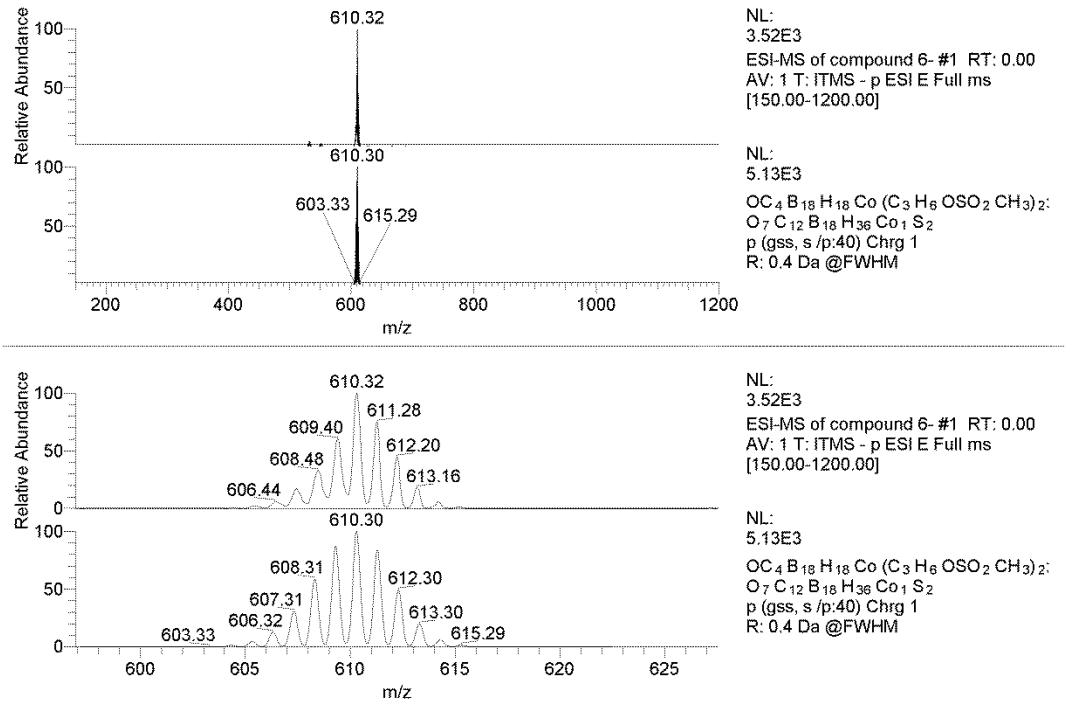


Figure S83: Spectrum of **6**$^{-}$

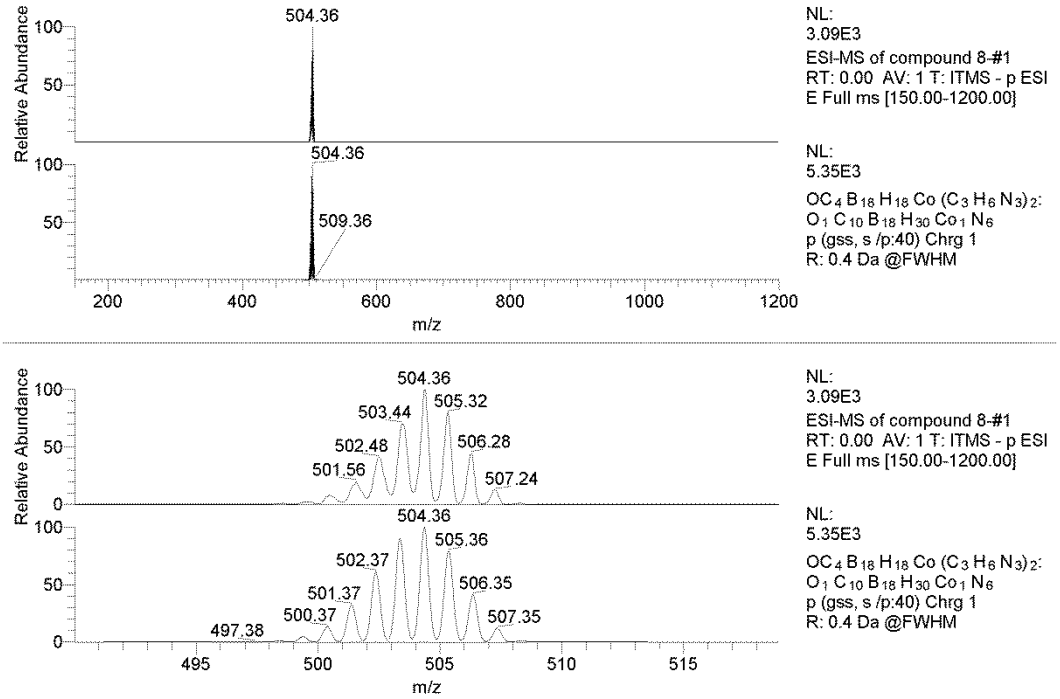


Figure S84: Spectrum of **8**$^{-}$

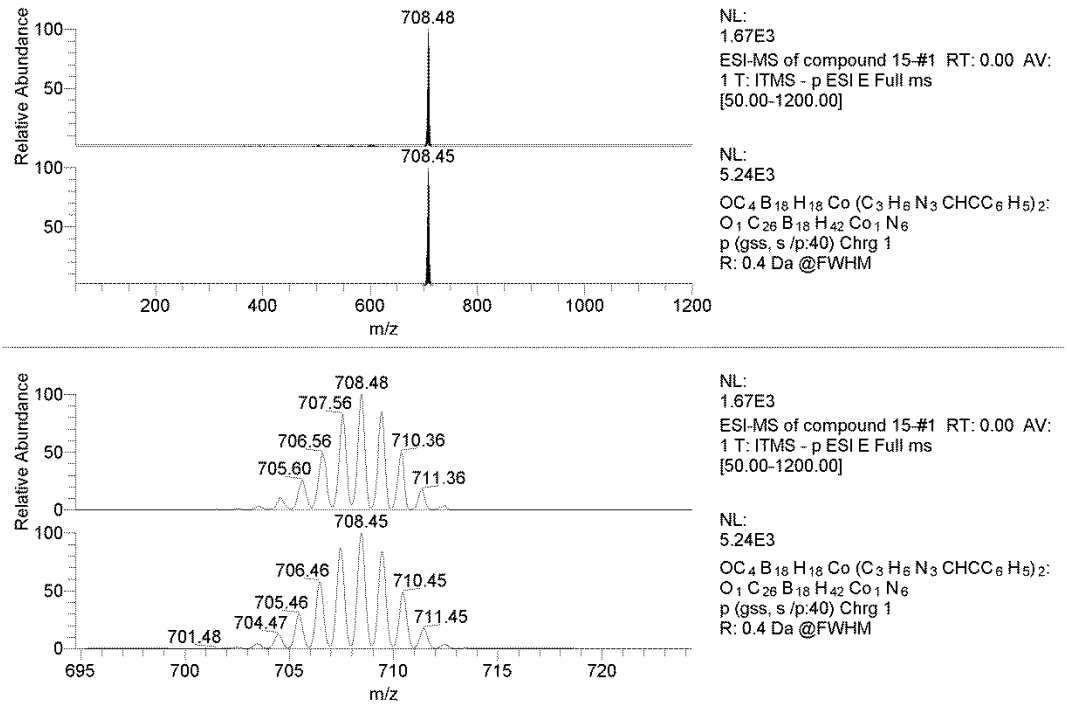


Figure S85: Spectrum of **15**$^{-}$

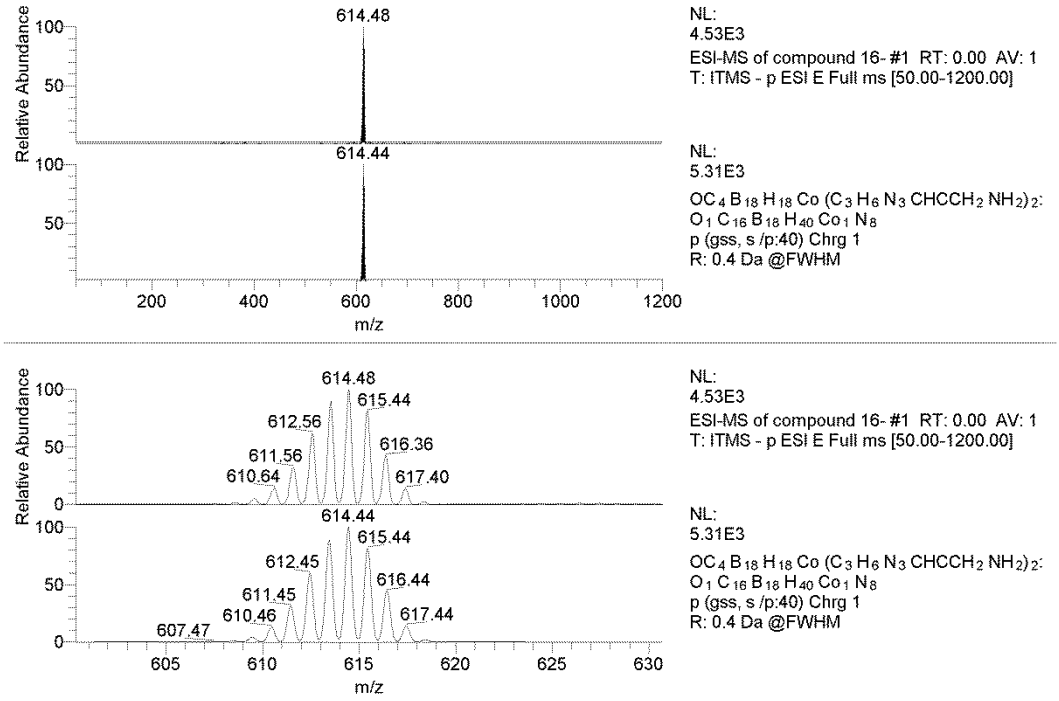


Figure S86: Spectrum of **16**$^{-}$

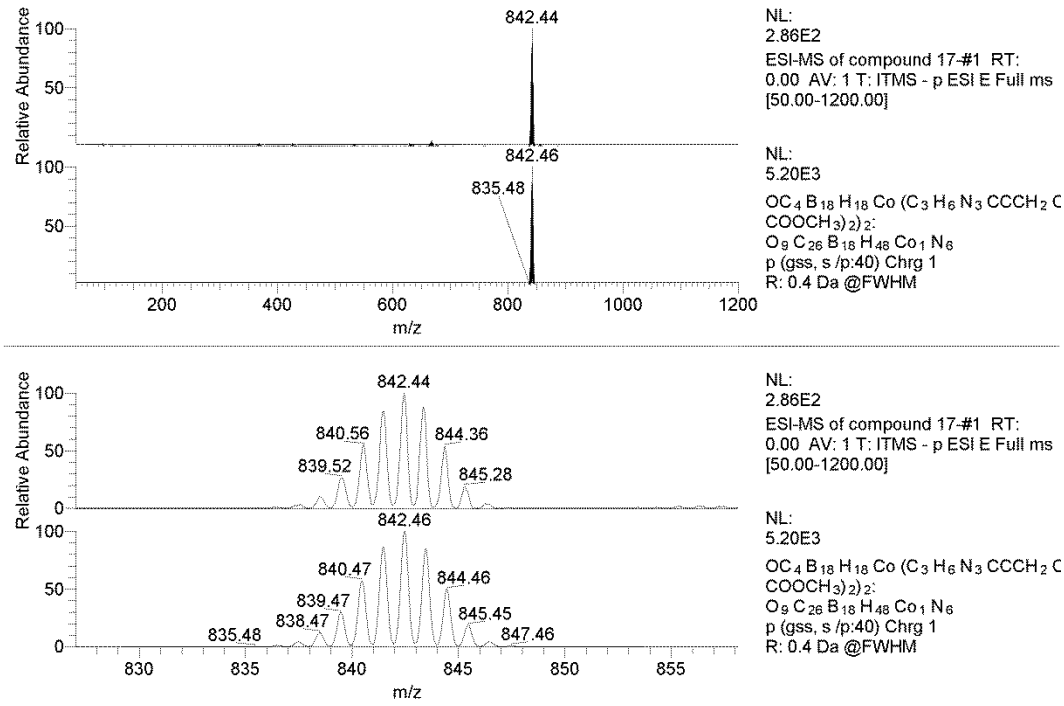


Figure S87: Spectrum of **17**$^{-}$

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