Electronic Supplementary Information
for

[*closo*-$B_{10}H_8$-1,10-$(COOH)_2$]$^{2-}$: A building block for functional materials?

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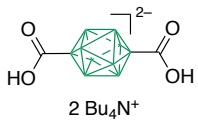
1. Synthetic details

General. Reagents and solvents were obtained commercially. Anion [*closo*-$B_{10}H_{10}$]$^{2-}$ was obtained from $B_{10}H_{14}$ according to a literature procedure.[1] Salt [*closo*-$B_{10}H_8$-1,10-$(CN)_2$]$^{2-}$ 2[Bu_4N]$^+$ (**3B[Bu$_4$N]**) was prepared according to the previously reported procedure.[2] Reactions were conducted under argon atmosphere and subsequent manipulations were carried out in air. Column chromatography was performed using 70–230 mesh silica gel (Merck). Melting points were recorded uncorrected in capillary tubes. NMR spectra were typically obtained at 500 MHz (^{1}H), 126 MHz (^{13}C) and 160 MHz (^{11}B) in acetone-d_6, CD_2Cl_2, CD_3CN or DMSO-d_6. Chemical shifts were referenced to the solvent (acetone-d_6: 2.05 ppm for ^{1}H and 29.84 ppm for ^{13}C; CD_2Cl_2: 5.32 ppm for ^{1}H and 53.84 ppm for ^{13}C; CD_3CN: 1.94 ppm for ^{1}H and 1.32 ppm for ^{13}C, DMSO-d_6: 2.50 for ^{1}H)[3] and to an external sample of neat BF_3•Et_2O in acetone-d_6, CD_2Cl_2, CD_3CN or DMSO-d_6 (^{11}B, δ = 0.0 ppm). ^{11}B NMR chemical shifts were taken from the H-decoupled spectra. IR spectra were recorded in KBr pellets or for neat samples using an ATR attachment. HR mass spectrometry was conducted with the TOF-MS ES method, most often in the negative mode.

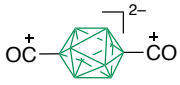
Ion exchange resin for cation exchange. Dowex-50 ion exchange resin was washed with a 6:4 H_2O/MeCN solvent mixture until the eluent was colorless, then the resin was used as the stationary phase for ion exchange chromatography.

Preparation of silica gel passivated with [Et$_4$N]$^+$[HCO$_3$]$^-$. Aqueous [Et_4N]$^+$[OH]$^-$ (2.0 mL, 35% solution in water) was stirred with a few pieces of solid CO_2 until the solution was homogenous. After concentrating the aqueous solution in vacuum, the oily residue was dissolved in MeCN (20 mL). The solution was added to silica gel to form a suspension and stirred for 15 min. The freshly prepared passivated SiO_2 was transferred into a column and washed with a few portions of appropriate eluent before using for chromatography.



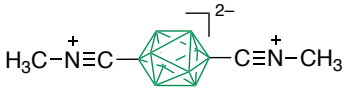
Preparation of [*closo*-B$_{10}$H$_8$-1,10-(COOH)$_2$]$^{2-}$2[Bu$_4$N]$^+$ (1B[Bu$_4$N]). To a solution of [*closo*-$B_{10}H_8$-1-(COOH)-10-(CO)]$^-$[Bu_4N]$^+$ (**5B[Bu$_4$N]**, 50.0 mg, 0.116 mmol) in MeCN (0.3 mL) 40% aq [Bu_4N]$^+$[OH]$^-$ (75.3 mg of the

solution, 0.116 mmol, 1.0 eq) was added and stirred for 10 min. The reaction mixture was evaporated to dryness to give a colorless waxy solid which was dissolved in CH_2Cl_2/Et_2O 1:1 (1 mL) and evaporated in high vacuum to give 80.0 mg (quant. yield) of pure **1B[Bu$_4$N]** as an off-white foamy solid: mp 96–100 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.71 (br q, J = 131 Hz, 8H), 0.97 (t, J = 7.3 Hz, 24H), 1.43 (sext, J = 7.4 Hz, 16H), 1.80 (quint, J = 8.0 Hz, 16H), 3.43 – 3.46 (m, 16H); ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6) δ 13.9, 20.3, 24.4, 59.2, 194.4 (q, J = 106 Hz, C=O); ^{11}B NMR (160 MHz, acetone-d_6) δ -24.9 (d, J = 126 Hz, 8B), 5.1 (s, 2B); IR v 2468 (BH), 1624 (C=O), 1482, 1270, 1119, 884, 717 cm^{-1}; HRMS (TOF ESI-) m/z calcd. for $C_2H_9B_{10}O_4$: 207.1431, found: 207.1444. Anal. Calcd. for $C_{34}H_{82}B_{10}N_2O_4$: C, 59.09; H, 11.96; N, 4.05. Found: C, 59.11; H, 11.93; N, 4.02.



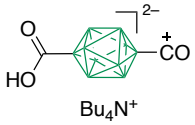
Preparation of [*closo*-B$_{10}$H$_8$-1,10-(CO)$_2$] (2B).[4] A solution of [*closo*-$B_{10}H_8$-1-(COOH)-10-(CO)]$^-$[Bu$_4$N]$^+$ (**5B[Bu$_4$N]**, 75.0 mg, 0.174 mmol) in a 6:4 H_2O/MeCN (1 mL) solvent mixture was passed through a short column filled with freshly washed ion exchange resin (~5 g, *vide supra*). The eluent was evaporated to dryness, giving 30 mg (quant. yield) of pure **2B** as a yellowish microcrystalline solid, which was used without further purification: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 1.81 (br q, J = 150 Hz, 8H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 170.1 (q, J = 103 Hz); ^{11}B NMR (160 MHz, CD_2Cl_2) δ -11.7 (d, J = 152 Hz, 8B), -5.4 (s, 2B); IR v 2549 (B-H), 2140 (CO), 1177, 693 cm^{-1}.

Notes: Soluble in but potentially reactive with acetone.



Preparation of [*closo*-B$_{10}$H$_8$-1,10-(CNMe)$_2$] (4B). To a solution of [*closo*-$B_{10}H_8$-1,10-$(CN)_2$]$^{2-}$2[Bu$_4$N]$^+$ (**3B[Bu$_4$N]**,[2] 2.00 g, 3.062 mmol) in dry CH_2Cl_2 (7 mL), MeOTf (0.84 mL, 7.67 mmol, 1.25 eq) was added dropwise at 0 °C under an argon atmosphere and stirred for 15 min at 0 °C, then at rt overnight. The formed suspension was cooled to 0 °C, stirred for 20 min. The precipitate was filtered, washed with anhydrous ethanol (1 mL) followed by cold CH_2Cl_2 (2 × 2 mL) and dried to give 330.0 mg (54% yield, range 54–67%) of the pure zwitterion product as an off-white powder: mp 233–235 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 1.08 (br q, J = 139 Hz, 8H), 4.15 (t, J = 2.7 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6)

δ 31.1 (t, J = 8.1 Hz), 126.5 (br s); ^{11}B NMR (160 MHz, acetone-d_6) δ -18.3 (d, J = 140 Hz, 8B), -2.4 (s, 2B); IR v 2512 (BH), 2288 (CN) cm^{-1}; HRMS (TOF ESI-) m/z calcd. for $C_4H_{14}B_{10}N_2$: 199.2009, found: 199.2020. Anal. Calcd. for $C_4H_{14}B_{10}N_2$: C, 24.23; H, 7.12; N, 14.13. Found: C, 23.98; H, 7.31; N, 13.89.



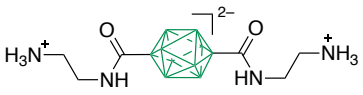
Preparation of [*closo*-$B_{10}H_8$-1-(COOH)-10-(CO)]$^-$ [Bu_4N]$^+$ (5B[Bu_4N]). One-pot procedure from 4B. To a solution of [*closo*-$B_{10}H_8$-1,10-$(CNMe)_2$] (**4B**, 198.3 mg, 1.00 mmol) in MeCN (1.0 mL), a solution of NaOH (84.0 mg, 2.10 mmol) in H_2O (2.0 mL) was added and gently heated for 10 min at 50 ºC until the solution turned homogenous. MeCN was evaporated, the remaining aqueous solution was treated with conc. HCl (0.33 mL, 3.7 mmol) and stirred for 15 min. NaOH (120.0 mg, 3.0 mmol) in H_2O (1.0 mL) was added and the reaction mixture was concentrated under vacuum at 50 ºC to ~2/3 volume (to remove $MeNH_2$). To the resulting solution, 18% aq HCl (2 mL), [Bu_4N]$^+$Cl$^-$ (334.0 mg, 1.20 mmol) and CH_2Cl_2 (3 mL) were added and stirred vigorously for 10 min. The organic layer was separated, washed with H_2O, and evaporated to dryness to give 406.0 mg (94% yield) of pure **5B[Bu_4N]**. The product was recrystallized from H_2O/acetone by slow evaporation of acetone giving 350.0 mg (81% yield) of analytically pure sample as colorless crystals: mp 138–139 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.70–1.95 (br m, 8H), 0.98 (t, J = 7.4 Hz, 12H), 1.43 (sext, J = 7.4 Hz, 8H), 1.82 (quint, J = 8.1 Hz, 8H), 3.42 – 3.46 (m, 8H), 8.84 (s, 1H); ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6) δ 13.8, 20.2, 24.3, 59.2, 173.8 (m, CO), 192.0 (q, J = 103 Hz, COOH); ^{11}B NMR (160 MHz, acetone-d_6) δ -27.8 (s, 1B), -19.4 (d, J = 138 Hz, 4B), -12.8 (d, J = 142 Hz, 4B), 33.0 (s, 1B); IR (KBr) v 2523 (B-H), 2132 (CO), 1648 (C=O), 1280, 1192 (C-O), 1103 cm^{-1}; HRMS (TOF ESI-) m/z calcd. for $C_2H_9B_{10}O_3$: 191.1482, found: 191.1506. Anal. Calcd. for $C_{18}H_{45}B_{10}NO_3$: C, 50.09; H, 10.51; N, 3.24. Found: C, 50.36; H, 10.60; N, 3.53.

Notes: 1. [*closo*-$B_{10}H_8$-1-(COOH)-10-(CO)]$^-$ [Bu_4N]$^+$ is very soluble in CH_2Cl_2 and poorly soluble in water; 2. [*closo*-$B_{10}H_8$-1,10-$(COOH)_2$]$^{2-}$2[Bu_4N]$^+$ is soluble in CH_2Cl_2 and partially soluble in water; 3. Attempts at precipitation of the product from the aqueous reaction mixture with [Bu_4N]$^+$Cl$^-$ resulted in a mixture of the product and diacid ([*closo*-$B_{10}H_8$-1,10-$(COOH)_2$]$^{2-}$2[Bu_4N]$^+$, **1B[Bu_4N]**) in the filtered solid, and lower yields of the product due to partial solubility of the diacid in water and less efficient recrystallization.

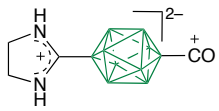
Preparation of [*closo*-$B_{10}H_8$-1,10-$(COOEt)_2$]$^{2-}$2[Et_4N]$^+$ (7B[Et_4N]). A freshly prepared solution of NaOEt, from sodium (2.4 mol eq) in dry EtOH (1 mL), was added to dicarbonyl compound **2B** (34.4 mg, 0.200 mmol) under an argon atmosphere and the reaction mixture was stirred for 15 min at r.t. Anhydrous $[Et_4N]^+Cl^-$ (79.5 mg, 0.480 mmol) was added, and after 10 min of stirring the reaction mixture was evaporated to dryness. The crude product was chromatographed using passivated silica gel (*vide supra*), with 2:1 CH_2Cl_2/MeCN eluent. If necessary, the MeCN solution of the product can be quickly passed through a thin layer of regular SiO_2 (~0.5 cm of SiO_2 in a pipette) to remove excess $[Et_4N]^+$ ion. Recrystallization from acetone/CH_2Cl_2 by slow evaporation of CH_2Cl_2 gave 64.8 mg (62% yield) of diester **7B[Et_4N]** as colorless crystals: mp 216–218 ºC; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.63 (br q, J = 122 Hz, 8H), 1.23 (t, J = 7.1 Hz, 6H), 1.33 (tt, J_1 = 7.2 Hz, J_2 = 1.8 Hz, 24H), 3.42 (q, J = 7.3 Hz, 16H), 4.08 (q, J = 7.1 Hz, 4H); ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6, major signals) δ 7.8, 15.8, 53.1, 55.8, C=O not observed; ^{11}B NMR (160 MHz, acetone-d_6) δ -25.0 (d, J = 124 Hz, 8B), 4.9 (s, 2B); IR ν 2473 (BH), 1646 (CO), 1462, 1231, 1058, 1000 cm^{-1}; HRMS (ESI-) m/z calcd. for $C_6H_{18}B_{10}O_4$: 264.2136, found: 264.1816; calcd. for $C_4H_{13}B_{10}O_3$ (M–OEt): 219.1795, found: 219.1816. Anal. Calcd. for $C_{22}H_{58}B_{10}N_2O_4$: C, 50.54; H, 11.18; N, 5.36. Found: C, 50.49; H, 11.07; N, 5.43.

The ester was hydrolytically unstable during acquisition of ^{13}C NMR spectra.

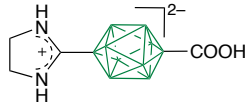
Preparation of [*closo*-$B_{10}H_8$-1,10-$(C(NHMe)_2)_2$] (9B). To a solution of [*closo*-$B_{10}H_8$-1,10-$(CNMe)_2$] (40.0 mg, 0.202 mmol) in dry MeCN (0.5 mL), a solution of 33% methylamine in EtOH (0.35 mL) was added and the reaction mixture was stirred for 15 min at rt. Solvents were evaporated and the residue was recrystallized (EtOH) giving 40.1 mg (76% yield) of pure product **9B** as colorless crystals: mp 325–326 ºC; ^{1}H NMR (400 MHz, CD_3CN) δ 0.67 (br q, J = 129 Hz, 8H), 2.97 (d, J = 5.3 Hz, 6H), 3.50 (d, J = 4.9 Hz, 6H), 6.93 (s, 2H), 7.34 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ 28.9, 33.2, 184.4 (q, J = 88 Hz); ^{11}B NMR (128 MHz, CD_3CN) δ -22.2 (d, J = 130 Hz, 8B), 7.5 (s, 2B); IR ν 3411 and 3375 (N–H), 2474 (B-H), 1603 and 1540 (N–C–N) cm^{-1}; HRMS (TOF ESI-) m/z calcd. for $C_6H_{23}B_{10}N_4$: 261.2853, found: 261.2854.



Preparation of [*closo*-$B_{10}H_8$-1,10-($CONHCH_2CH_2NH_3$)$_2$] (10B-a). To a solution of [*closo*-$B_{10}H_8$-1,10-$(CO)_2$] (**2B**, 50.0 mg, 0.290 mmol) in dry CH_2Cl_2 (1.5 mL) ethylenediamine (38.3 mg, 0.638 mmol) was added dropwise, while vigorously stirring at rt under argon. The resulting precipitate was filtered, washed with warm MeCN and dried to give pure product (quant. yield) as a colorless solid: mp >300 ºC dec; ^{1}H NMR (400 MHz, DMSO-d_6) δ -0.11 – 0.84 (br m, 8H), 2.92 (t, J = 5.3 Hz, 4H), 3.43 (q, J = 5.3 Hz, 4H), 7.71 (br s, 2H), 8.37 (br s, 6H); ^{11}B NMR (126 MHz, DMSO-d_6) δ -23.9 (8B), 7.0 (2B); IR v 3396 and 3196 (br NH), 2479 (BH) 1629 (C=O) 1489 cm^{-1}; HRMS (ESI-) m/z calcd. for $C_6H_{24}B_{10}N_4O_2$: 294.2830, found: 294.2842. Anal. Calcd. for ($C_6H_{24}B_{10}N_4O_2$ × $2H_2O$): C, 21.94; H, 8.59; N, 17.06. Found: C, 21.89; H, 8.59; N, 12.11.



Preparation of [*closo*-$B_{10}H_8$-1-(CO)-10-($C(NHCH_2)_2$)] (11B-a). A suspension of diamide **10B-a** (35.0 mg, 0.120 mmol), trimethylsilyl polyphosphate (PPSE, 146 mg, 0.96 mmol) in dry MeCN (0.2 mL) was stirred in a sealed tube at 115 ºC overnight (^{11}B NMR monitoring). The reaction mixture was quenched with a few drops of H_2O, all volatiles were evaporated and the resulting solid was extracted with CH_2Cl_2. The solvent was evaporated to give 16.0 mg (63% yield) of product **11B-a** as a colorless solid, which was sufficiently pure for the next step: mp > 300 ºC dec; ^{1}H NMR (400 MHz, CD_3CN) δ 0.5–2.1 (br m, 8H), 4.01 (s, 4H), 7.85 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ 45.8, 182.4 (q, J = 88 Hz), CO not observed; ^{11}B NMR (128 MHz, CD_3CN) δ -21.1 (s, 1B), -18.5 (d, J = 140 Hz, 4B), -12.8 (d, J = 146 Hz, 4B), 25.1 (s, 1B); IR v 3435 and 3408 (N-H), 2540 and 2519 (B-H), 2139 (CO), 1577 and 1529 (N–C–N), 1187, 1012 cm^{-1}; HRMS (ESI-) m/z calcd. for $C_4H_{15}B_{10}N_2O$: 217.2115, found: 217.2099.



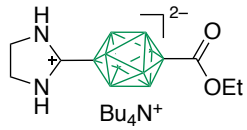
Preparation of [*closo*-$B_{10}H_8$-1-(COOH)-10-($C(NHCH_2)_2$)]$^-$[Bu_4N]$^+$ (12B-a[Bu_4N]). To a solution of [*closo*-$B_{10}H_8$-1-(CO)-10-($C(NHCH_2)_2$)] (**11B-a**, 12.0 mg, 0.056 mmol) in MeCN (0.3 mL) 40% aq [Bu_4N]$^+$OH$^-$ (38.3 mg of the solution, 0.0588 mmol, 1.05 eq) was added and stirred for 10 min. The reaction mixture was evaporated to dryness and passed through a short silica gel pad

(CH_2Cl_2/MeCN 5:2, R_f = 0.24) to give 20.0 mg (75% yield) of acid **12B-a[Bu_4N]** as a white solid: mp 200–202 ºC; ^{1}H NMR (400 MHz, CD_3CN) δ 0.51 (br q, *J* = 123.1 Hz, 8H), 0.96 (t, *J* = 7.3 Hz, 12H), 1.35 (sext, *J* = 7.4 Hz, 8H), 1.59 (quint, *J* = 8.0 Hz, 8H), 3.03–3.14 (m, 8H), 3.93 (s, 4H), 6.57 (br s, 2H); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ 13.8, 20.3, 24.3, 45.8, 59.3 (N-C-N and C=O not observed); ^{11}B NMR (126 MHz, CD_3CN) δ –23.5 (d, *J* = 125 Hz, 8B), 1.23 (s, 1B), 9.70 (s, 1B); IR *v* 3478 (NH) 3385 (br, OH), 2486 (BH) 1674 (C=O) 1655 and 1567 (N–C–N), 1051 (C–O) cm^{-1}; HRMS (ESI-) *m/z* calcd. for $C_4H_{15}B_{10}N_2O_2$: 233.2064, found: 233.2060. Anal. Calcd. for $C_{20}H_{51}B_{10}N_3O_2$: C, 50.71; H, 10.85; N, 8.87. Found: C, 50.82; H, 10.79; N, 8.76.

Preparation of [*closo*-$B_{10}H_8$-1-(COOH)-10-(C(NMeCH_2)$_2$)]$^-$[Bu_4N]$^+$ (12B-b[Bu_4N]) from [*closo*-$B_{10}H_8$-1,10-$(CO)_2$]. To a solution of [*closo*-$B_{10}H_8$-1,10-$(CO)_2$] (**2B**, 50.0 mg, 0.290 mmol) in dry CH_2Cl_2 (1.5 mL) *N,N*'-dimethylethylenediamine (0.638 mmol) was added dropwise while vigorous stirring at rt under argon. The resulting precipitate was filtered, washed with warm MeCN and dried giving crude diamide **10B-b** (100 mg) as colorless solid (mp >300 ºC dec; HRMS (ESI-) *m/z* calcd. for $C_{10}H_{32}B_{10}N_4O_2$: 350.3456, found: 350.3459; IR *v* 3423 (NH) cm^{-1}). The solid (30.0 mg) was suspended in minimum amounts of dry MeCN (0.2 mL), trimethylsilyl polyphosphate (PPSE, 146 mg, 0.960 mmol) was added and the reaction mixture was stirred in a sealed tube at 115 ºC overnight (^{11}B NMR monitoring). A few drops of H_2O were added and the reaction mixture was evaporated to dryness. The resulting solid was extracted with CH_2Cl_2 giving 12.0 mg (57% yield based on **2B**) of carbonyl derivative **11B-b** sufficiently pure product for further transformations (^{1}H NMR (400 MHz, CD_3CN) δ main signals, 0.56–1.64 (m, 8H), 3.41 (s, 6H), 3.91 (s, 4H); IR *v* 2144 (CO), 1557 (N–C–N) cm^{-1}; HRMS (ESI-) *m/z* calcd. for $C_6H_{19}B_{10}N_2O$: 245.2428, found: 245.2423). The product was dissolved in MeCN (0.5 mL) and treated with 1.0 mol equiv. of 40% aqueous [Bu_4N]$^+$OH$^-$. After removing solvents under vacuum, the final product was chromatographed on silica gel (CH_2Cl_2/MeCN 5:2, R_f = 0.26) giving 17.1 mg (69% yield) of pure acid **12B-b[Bu_4N]** as colorless crystals: mp 160–162 ºC; ^{1}H NMR (400 MHz, CD_3CN) δ 0.14–1.02 (br m, 8H), 0.96 (t, *J* = 7.3 Hz, 12H), 1.35 (sext, *J* = 7.4 Hz, 8H), 1.59 (quin, J = 8.0 Hz, 8H), 3.03 – 3.14 (m, 8H), 3.45 (s, 6H), 3.85 (s, 4H), 8.14 (br s, 1H); ^{13}C NMR (101 MHz, CD_3CN)

δ 13.8, 20.3, 24.3, 36.3, 51.2, 59.3, (N-C-N and C-O not observed); ^{11}B NMR (126 MHz, CD_3CN) δ -23.45 (d, *J* = 126.1 Hz, 8B), -0.7 (s, 1B), 11.4 (s, 1B); IR *v* 2480 (BH), 1635 (C=O), 1542 (N–C–N), 1288 (C–O) cm^{-1}; HRMS (ESI-) *m/z* calcd. for $C_6H_{19}B_{10}N_2O_2$: 261.2377, found: 261.2386. Anal. Calcd. for $C_{22}H_{55}B_{10}N_3O_2$: C, 52.66; H, 11.05; N, 8.37. Found: C, 52.08; H, 10.91; N, 7.93.

Preparation of [*closo*-$B_{10}H_8$-1-(COOEt)-10-($C(NHCH_2)_2$)]$^-$[Bu_4N]$^+$ (13B-a[Bu_4N]). A



solution of [*closo*-$B_{10}H_8$-1-(COOH)-10-($C(NMeCH_2)_2$)]$^-$[Bu_4N]$^+$ (**12B-a[Bu_4N]**, 10.0 mg, 0.021 mmol) in EtOH (0.2 mL) was stirred at 50 °C for 10 min. H_2O (0.3 mL) was added and the reaction mixture was left for slow crystallization by solvent evaporation giving 9.4 mg (89% yield) of pure ester **13B-a[Bu_4N]** as colorless crystals. The product slowly hydrolyses to starting acid in CD_3CN solutions: mp 206–208 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 0.00 – 0.94 (br m, 8H), 0.96 (t, *J* = 7.3 Hz, 12H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.34 (sext, *J* = 7.5 Hz, 8H), 1.59 (quint, *J* = 8.0 Hz, 8H), 3.04–3.09 (m, 8H), 3.93 (s, 4H), 4.13 (q, *J* = 7.1 Hz, 2H), 7.48 (s, 2H); ^{11}B NMR (126 MHz, CD_3CN) δ major signals -23.5 (d, *J* = 125 Hz, 8B), 0.4 (s, 1B), 10.6 (s, 1B); HRMS (ESI-) *m/z* calcd. for $C_6H_{19}B_{10}N_2O_2$: 261.2377, found: 261.2392.

2. NMR spectra

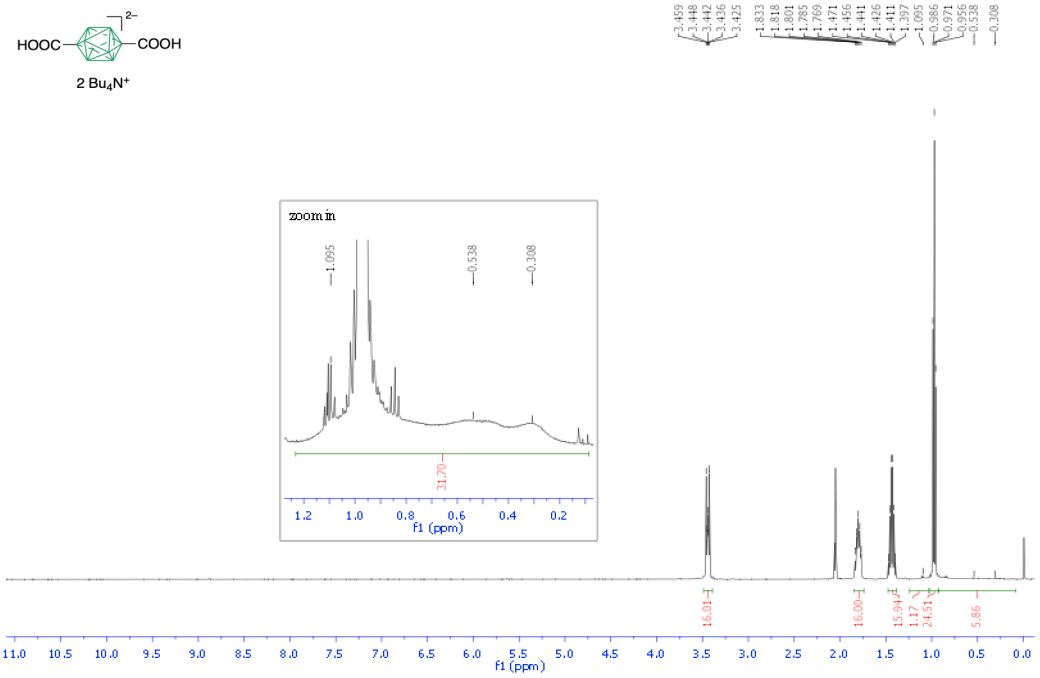


Figure S1. ^{1}H NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(COOH)_2$]$^{2-}$ 2[Bu_4N]$^{+}$ (**1B[Bu$_4$N]**) recorded in acetone-d_6 at 500 MHz.

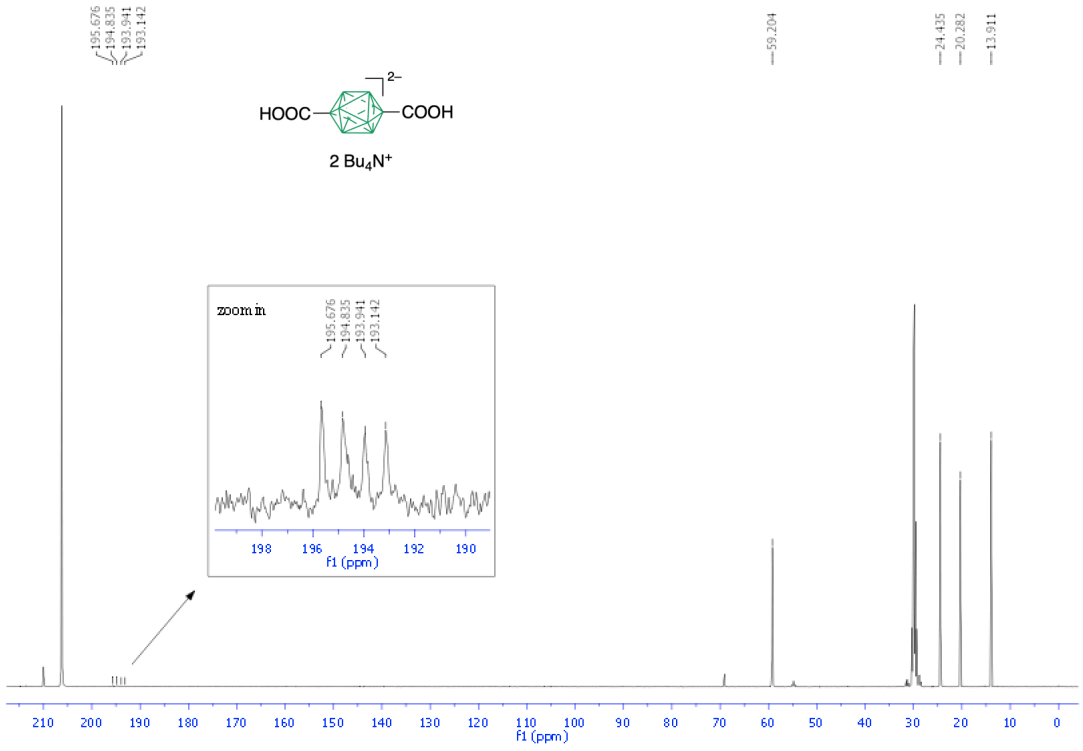


Figure S2. ^{13}C{^{1}H} NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(COOH)_2$]$^{2-}$ 2[Bu_4N]$^{+}$ (**1B[Bu$_4$N]**) recorded in acetone-d_6 at 126 MHz.

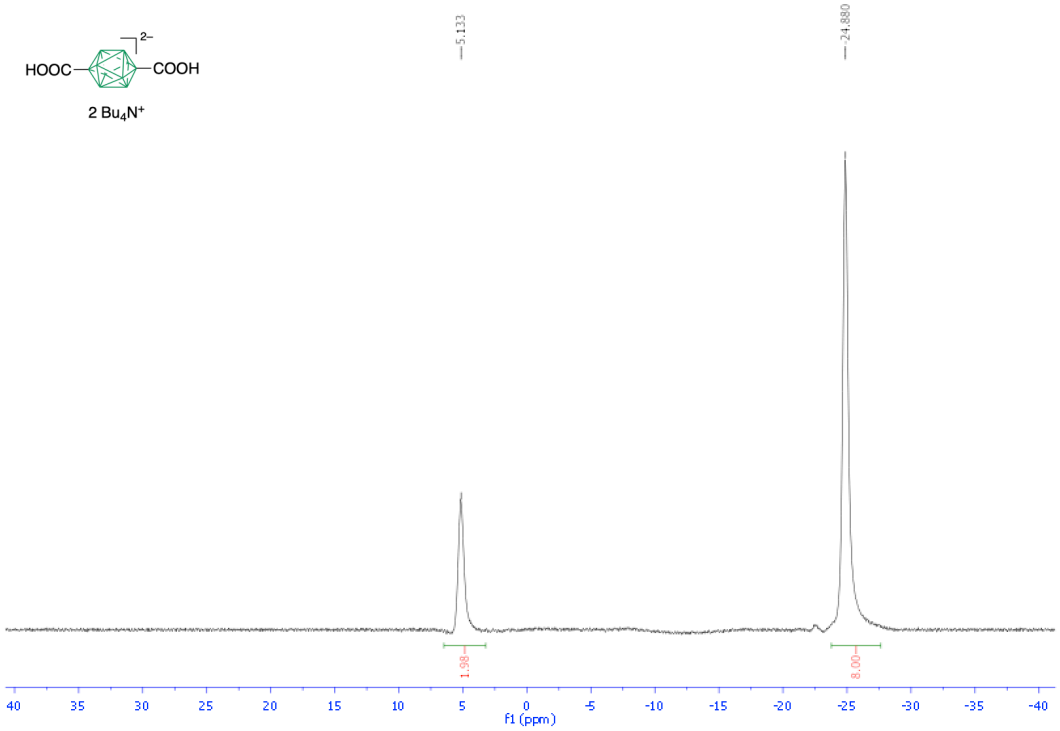


Figure S3. $^{11}B\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(COOH)_2$]$^{2-}$ 2[Bu_4N]$^{+}$ (**1B[Bu$_4$N]**) recorded in acetone-d_6 at 160 MHz.

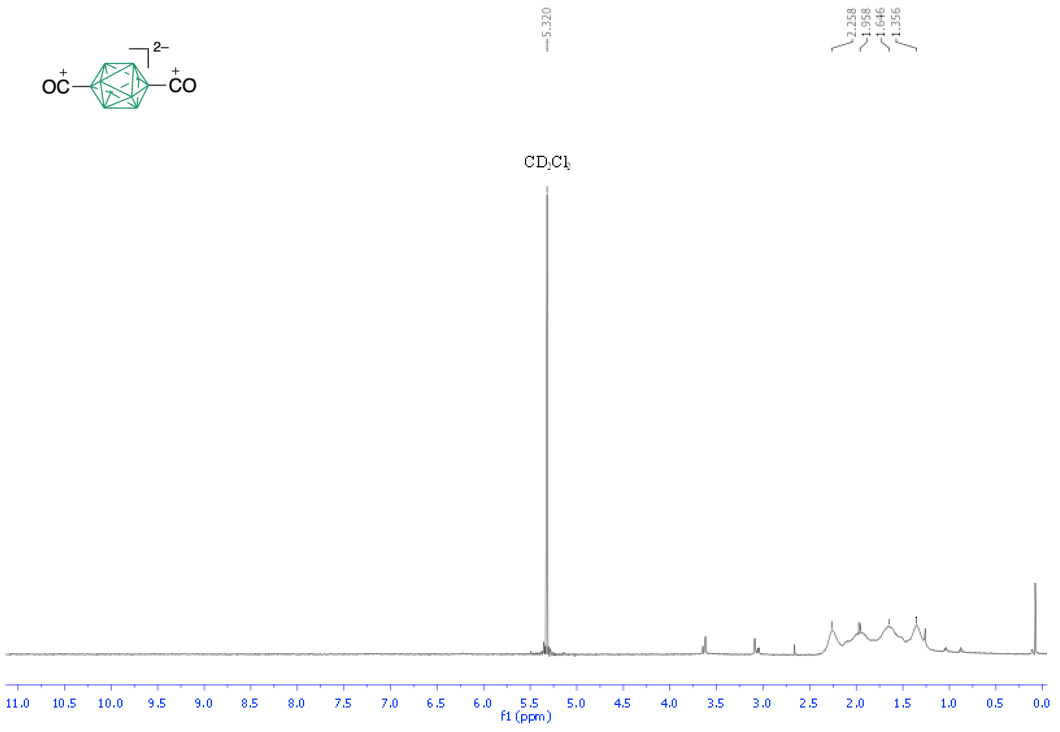


Figure S4. ^{1}H NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(CO)_2$] (**2B**) recorded in dry CD_2Cl_2 at 500 MHz.

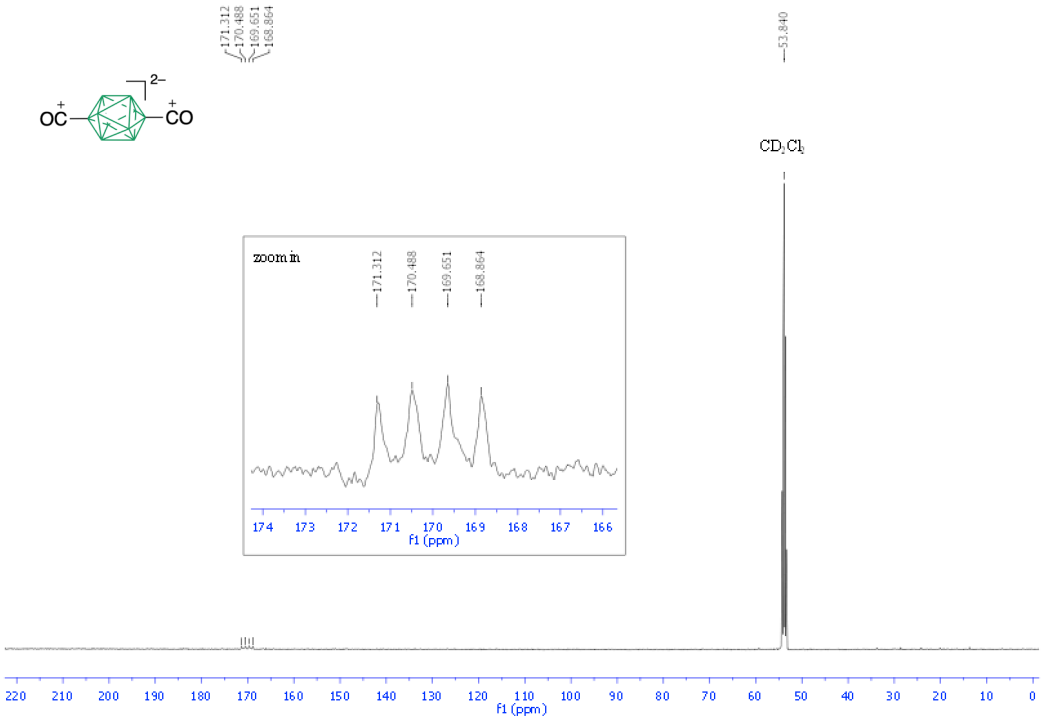


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(CO)_2$] (**2B**) recorded in dry CD_2Cl_2 at 126 MHz.

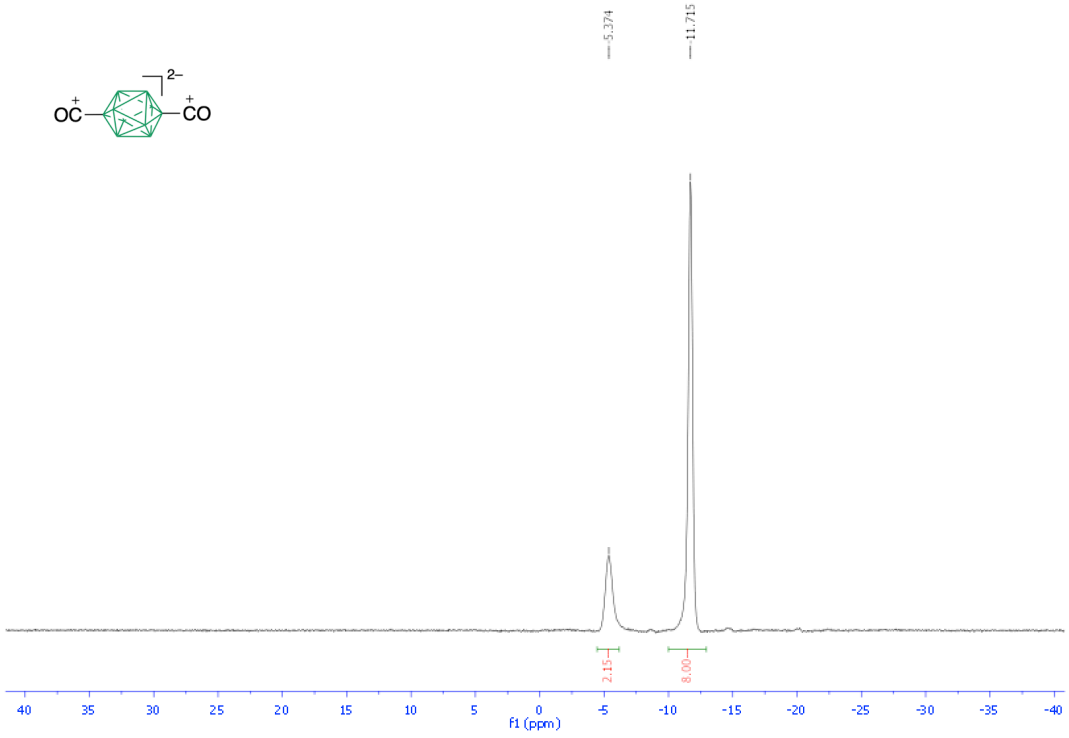


Figure S6. $^{11}B\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(CO)_2$] (**2B**) recorded in dry CD_2Cl_2 at 160 MHz.

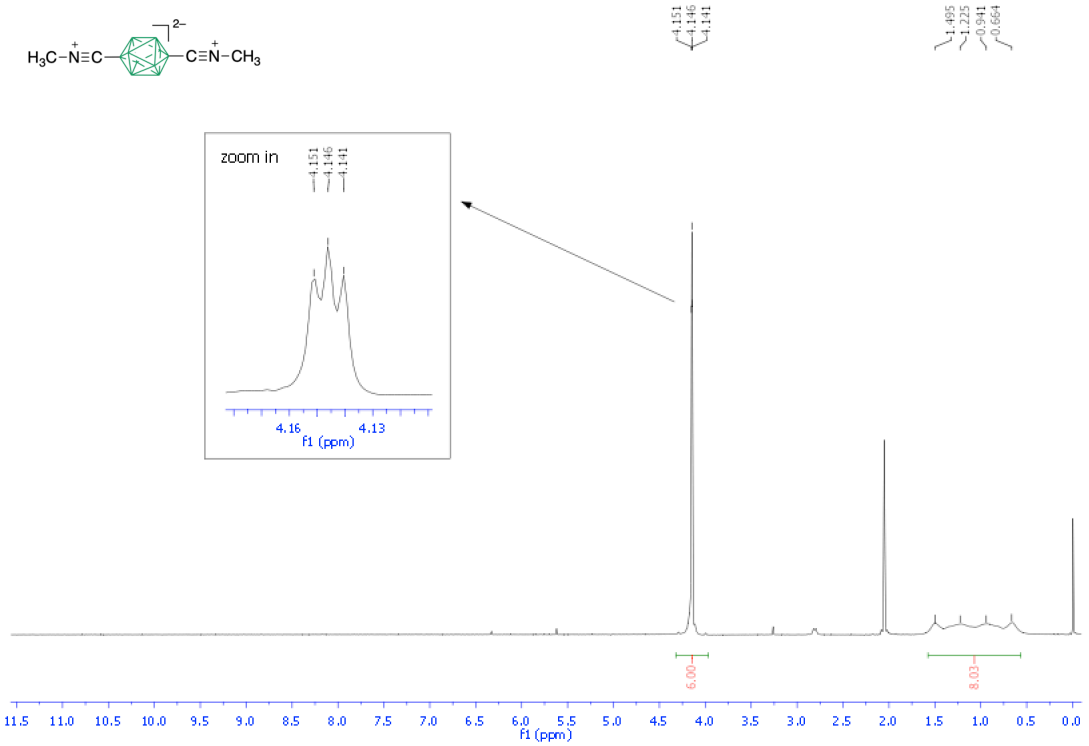


Figure S7. ^{1}H NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(CNMe)_2$] (**4B**) recorded in acetone-d_6 at 500 MHz.

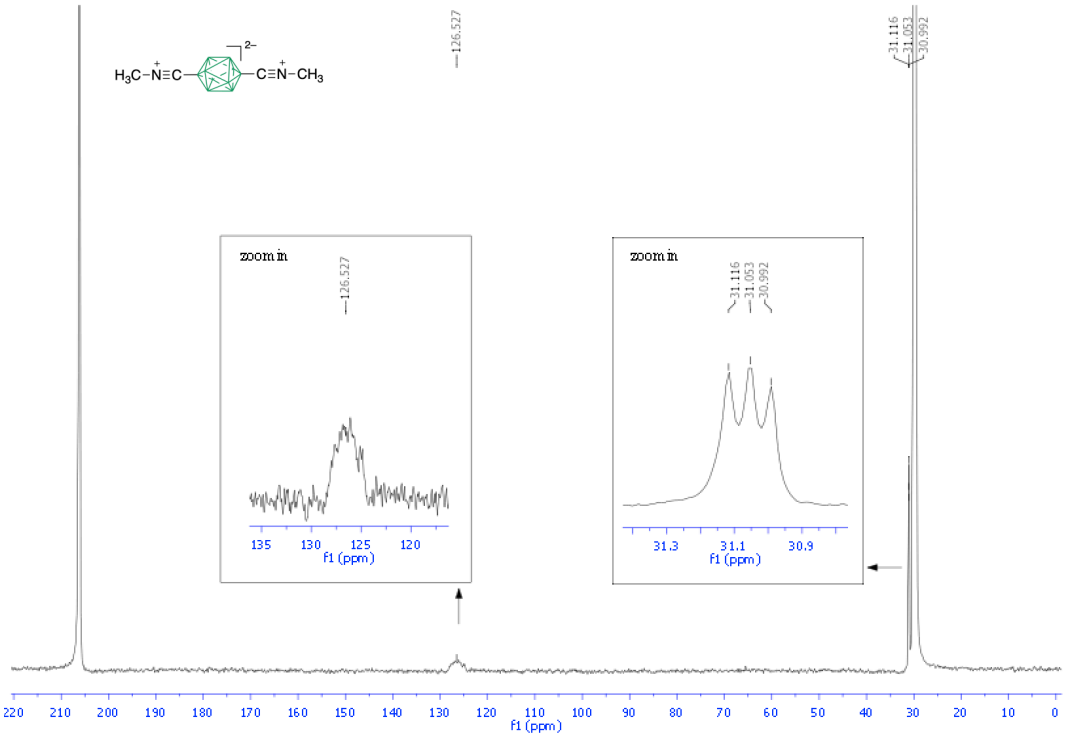


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(CNMe)_2$] (**4B**) recorded in acetone-d_6 at 126 MHz.

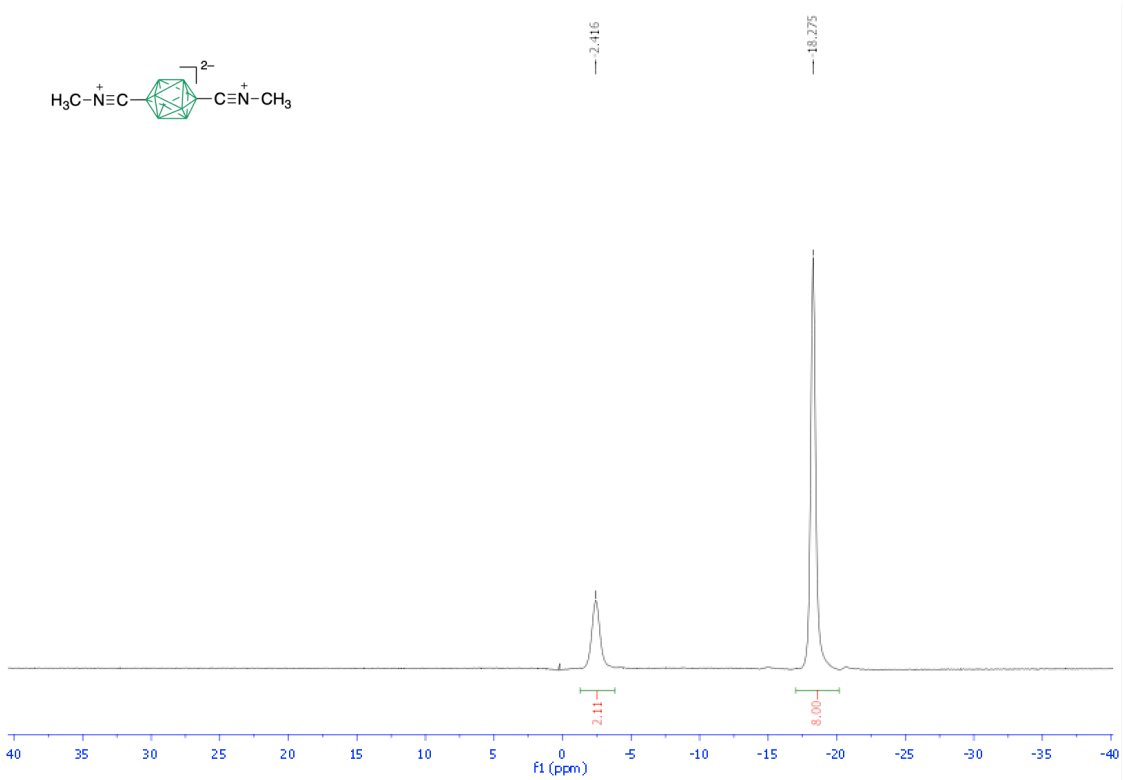


Figure S9. $^{11}B\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(CNMe)_2$] (**4B**) recorded in acetone-d_6 at 160 MHz.

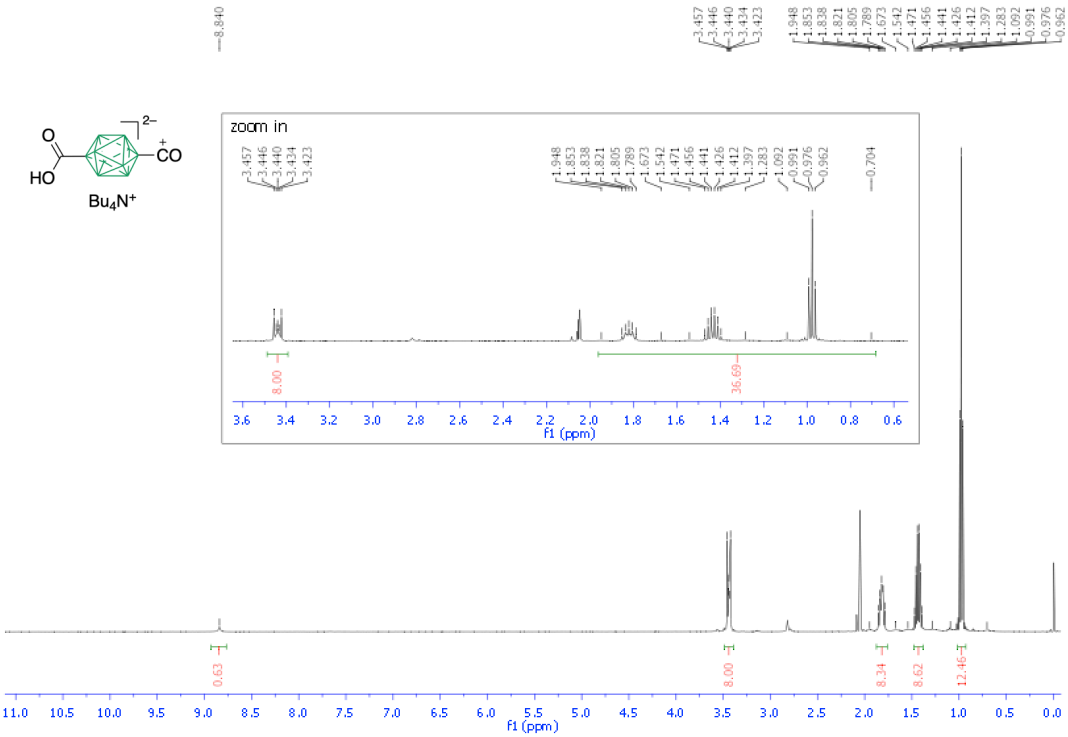


Figure S10. ^{1}H NMR spectrum for [*closo*-$B_{10}H_8$-1-(COOH)-10-(CO)]$^-$ $[Bu_4N]^+$ (**5B[Bu$_4$N]**) recorded in acetone-d_6 at 500 MHz.

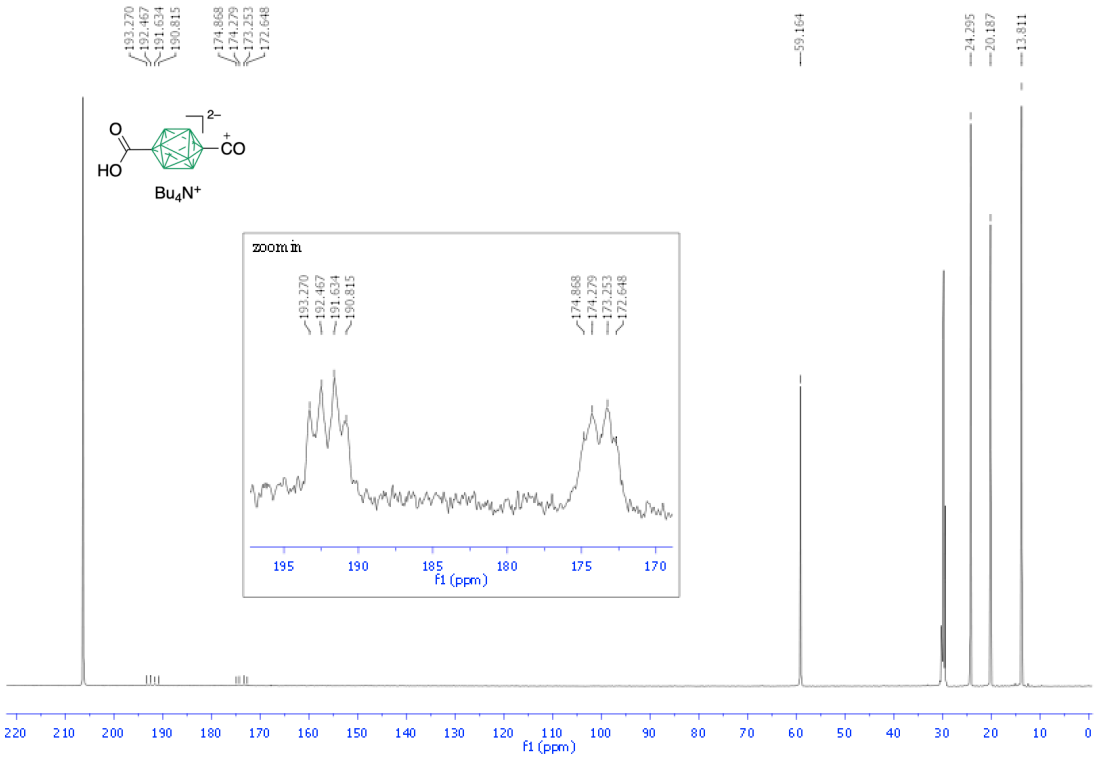


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1-(COOH)-10-(CO)]$^-$ $[Bu_4N]^+$ (**5B[Bu$_4$N]**) recorded in acetone-d_6 at 126 MHz.

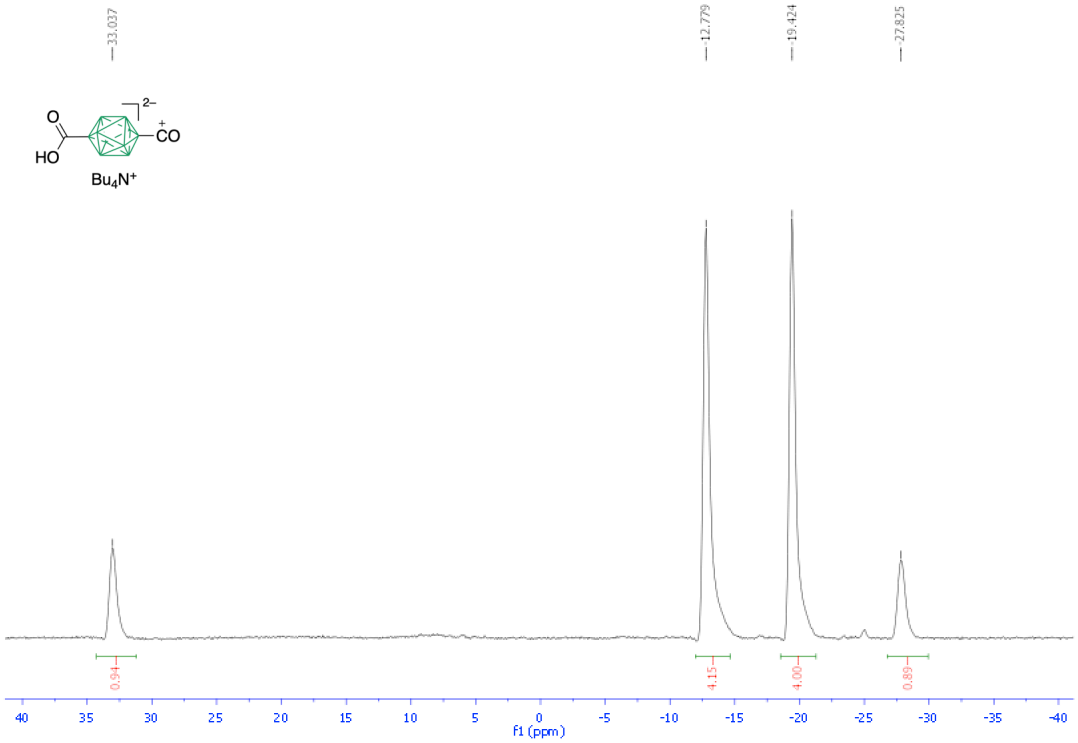


Figure S12. $^{11}B\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1-(COOH)-10-(CO)]$^-$ $[Bu_4N]^+$ (**5B[Bu$_4$N]**) recorded in acetone-d_6 at 160 MHz.

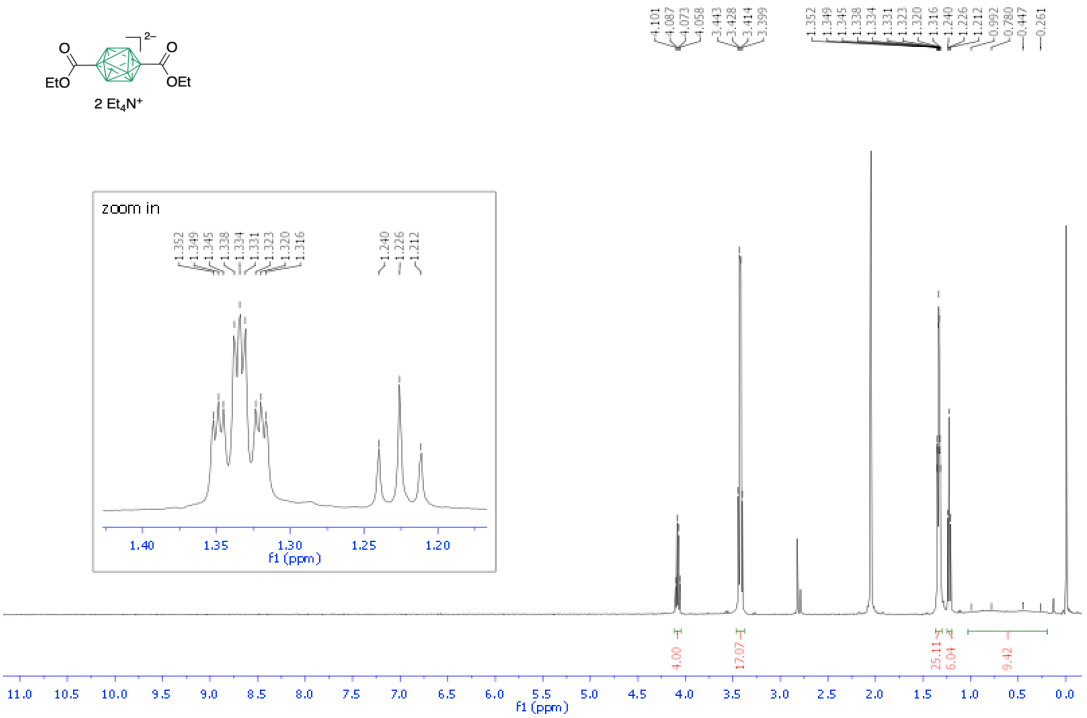


Figure S13. ^{1}H NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(COOEt)_2$]$^{2-}$ 2[Et_4N]$^{+}$ (**7B[Et$_4$N]**) recorded in acetone-d_6 at 500 MHz.

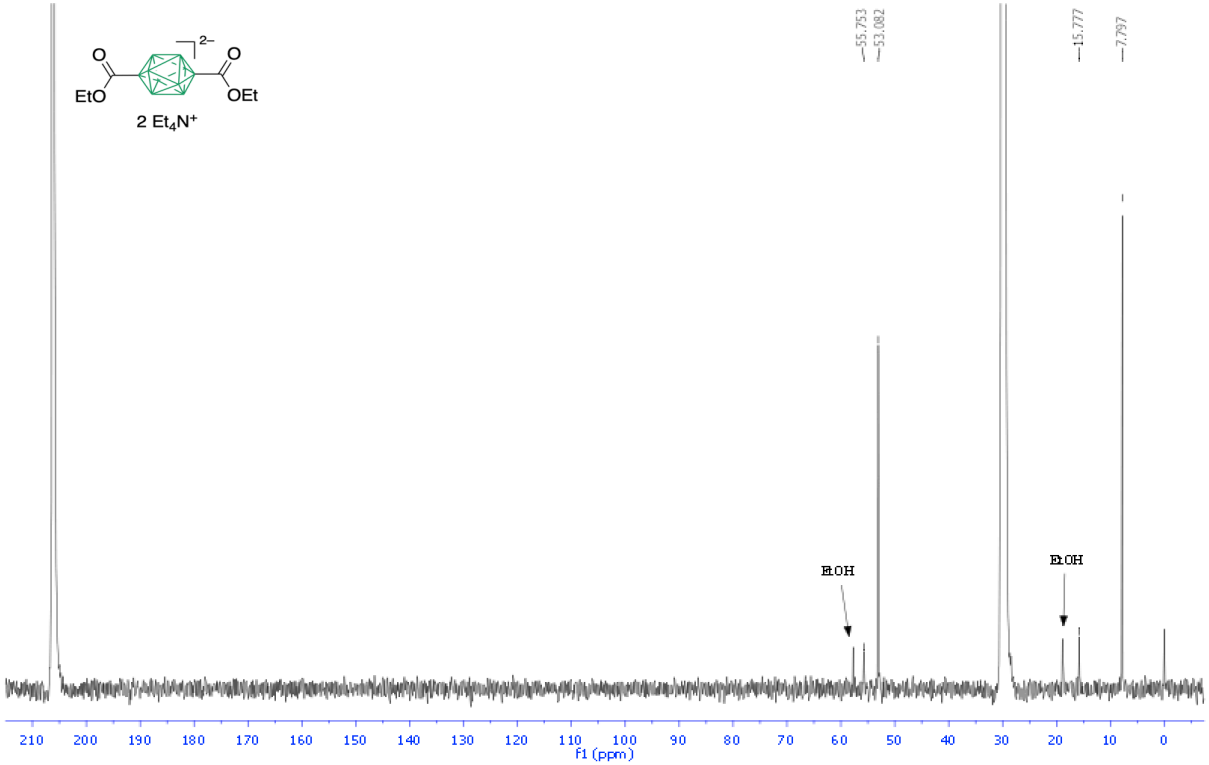


Figure S14. ^{13}C{^{1}H} NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(COOEt)_2$]$^{2-}$ 2[Et_4N]$^{+}$ (**7B[Et$_4$N]**) recorded in acetone-d_6 at 126 MHz.

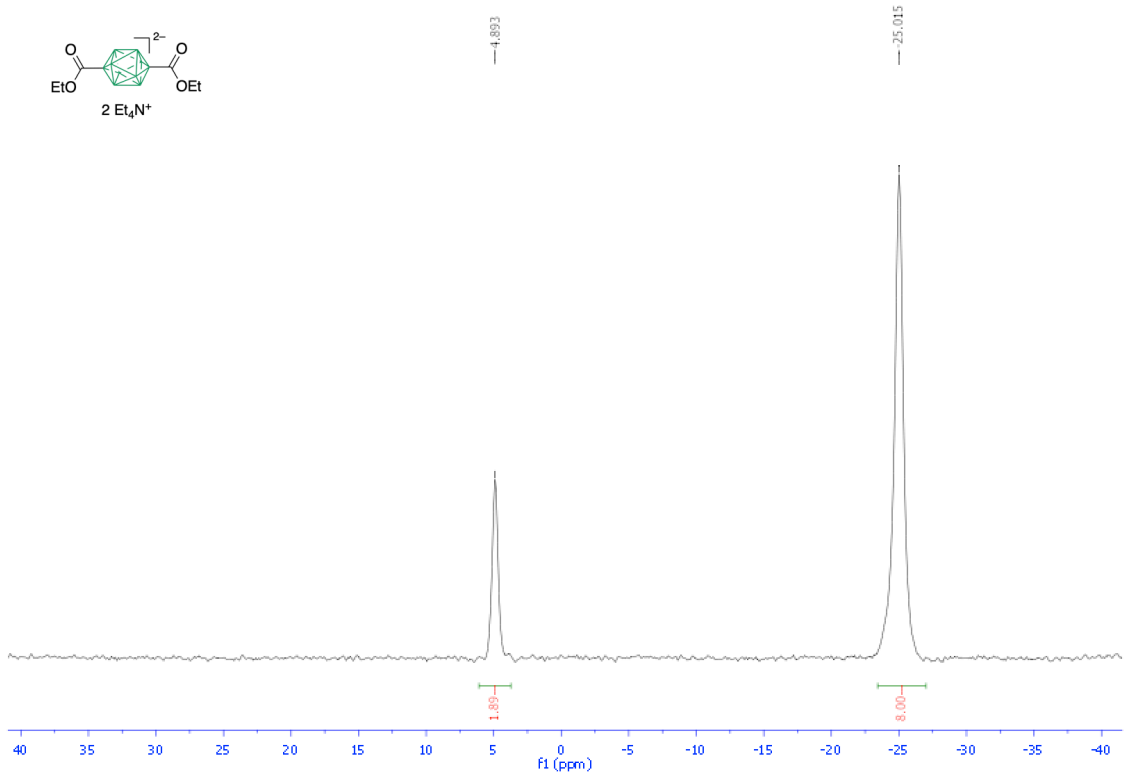


Figure S15. $^{11}B\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(COOEt)_2$]$^{2-}$ 2[Et_4N]$^+$ (**7B[Et$_4$N]**) recorded in acetone-d_6 at 160 MHz.

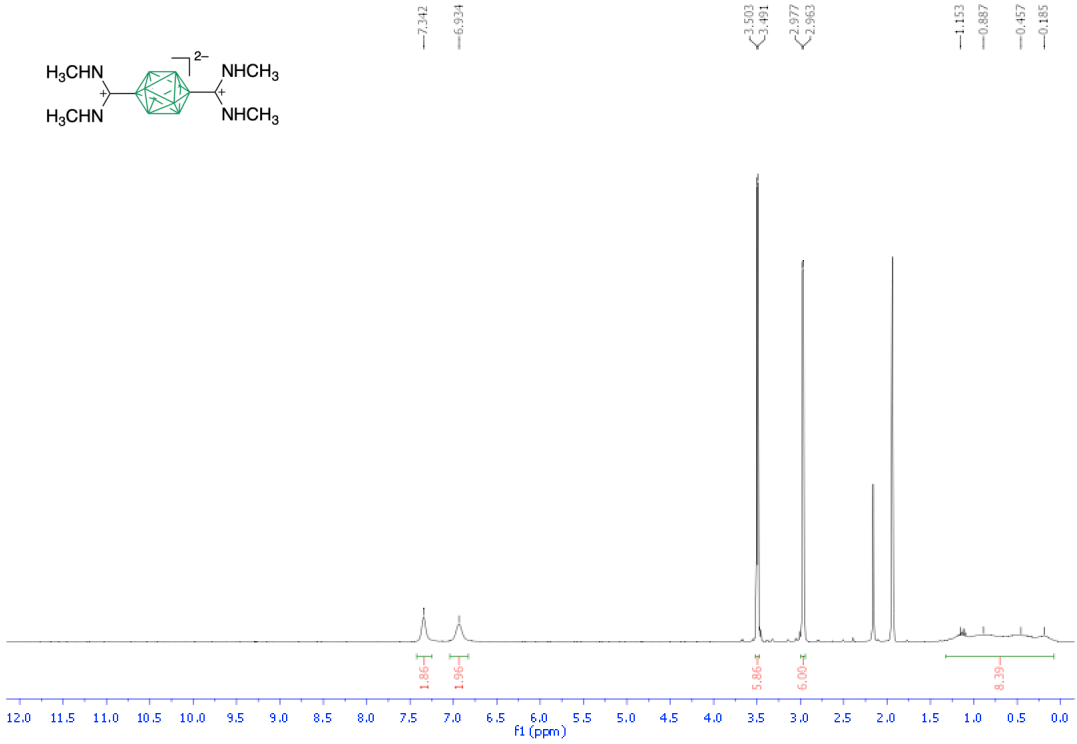


Figure S16. ^{1}H NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(C(NHMe)_2)_2$] (**9B**) recorded in CD_3CN 400 MHz.

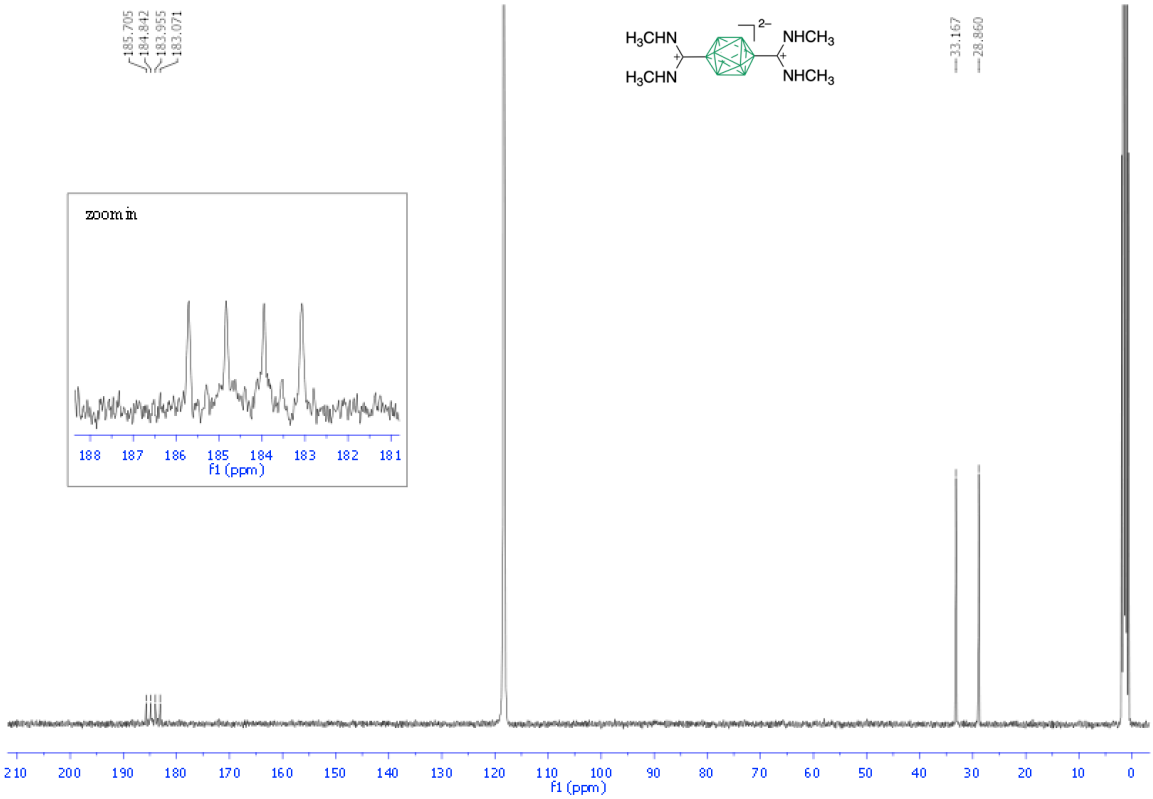


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(C(NHMe)_2)_2$] (**9B**) recorded in CD_3CN at 101 MHz.

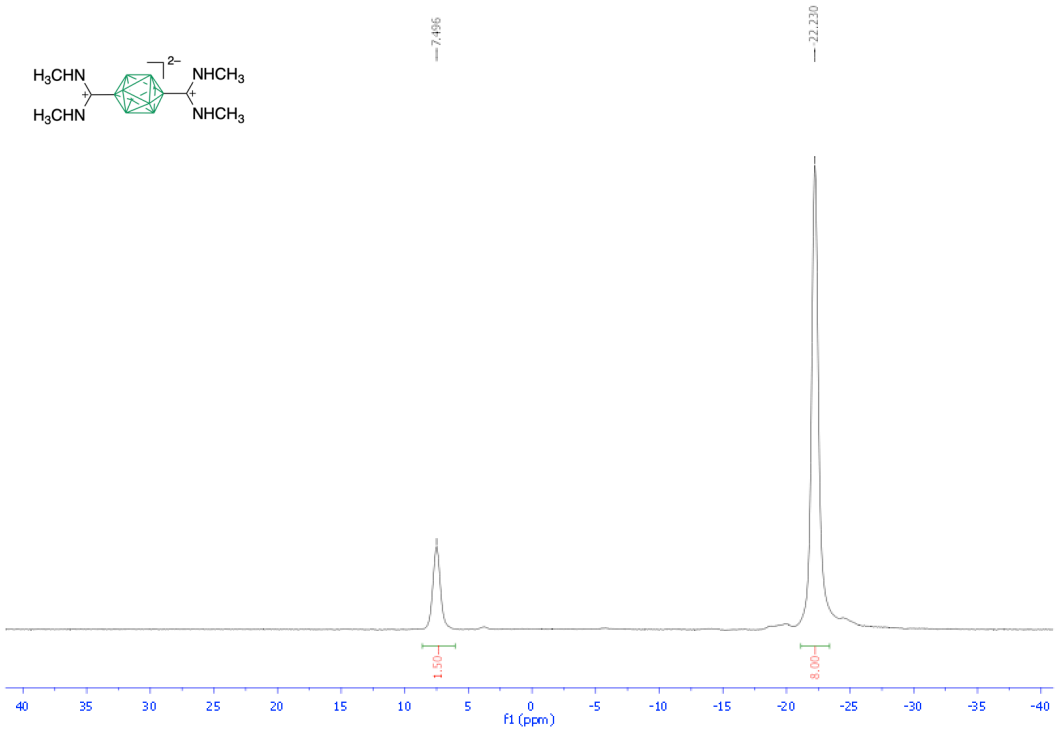


Figure S18. $^{11}B\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1,10-$(C(NHMe)_2)_2$] (**9B**) recorded in CD_3CN at 126 MHz.

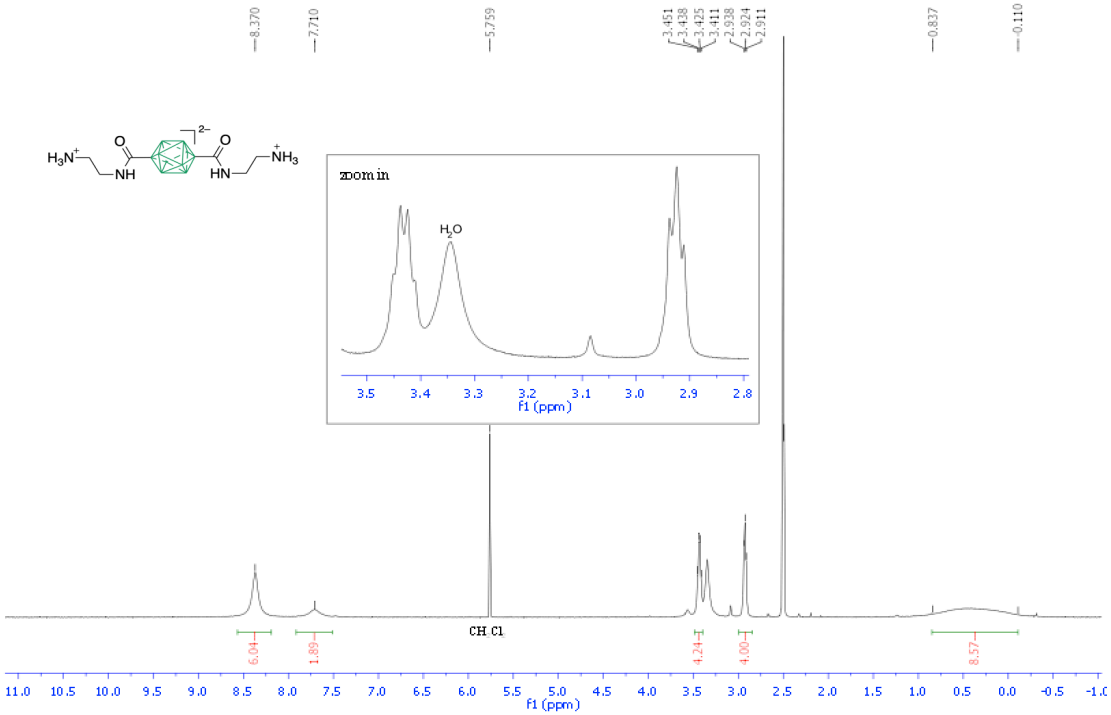


Figure S19. ^{1}H NMR spectrum for [*closo*-$B_{10}H_8$-1,10-($CONHCH_2CH_2NH_3$)] (**10B-a**) recorded in DMSO-d_6 at 400 MHz.

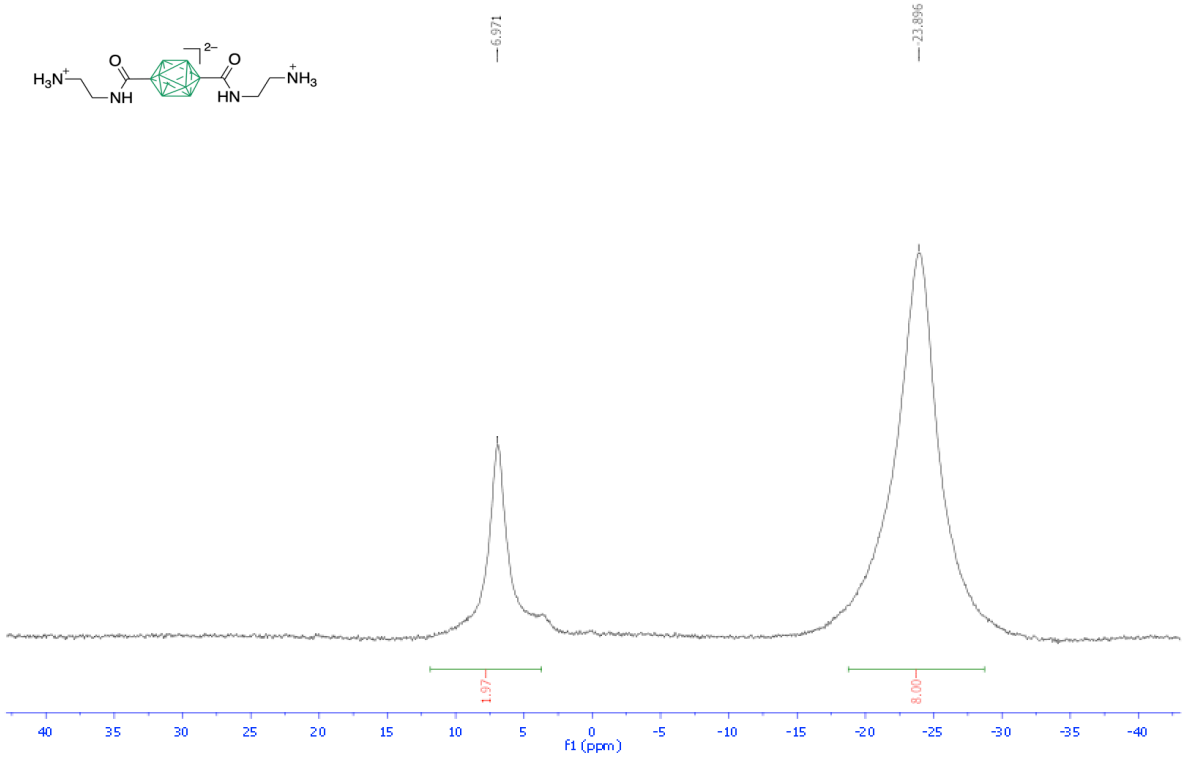


Figure S20. ^{11}B{^{1}H} NMR spectrum for [*closo*-$B_{10}H_8$-1,10-($CONHCH_2CH_2NH_3$)] (**10B-a**) recorded in DMSO-d_6 at 126 MHz.

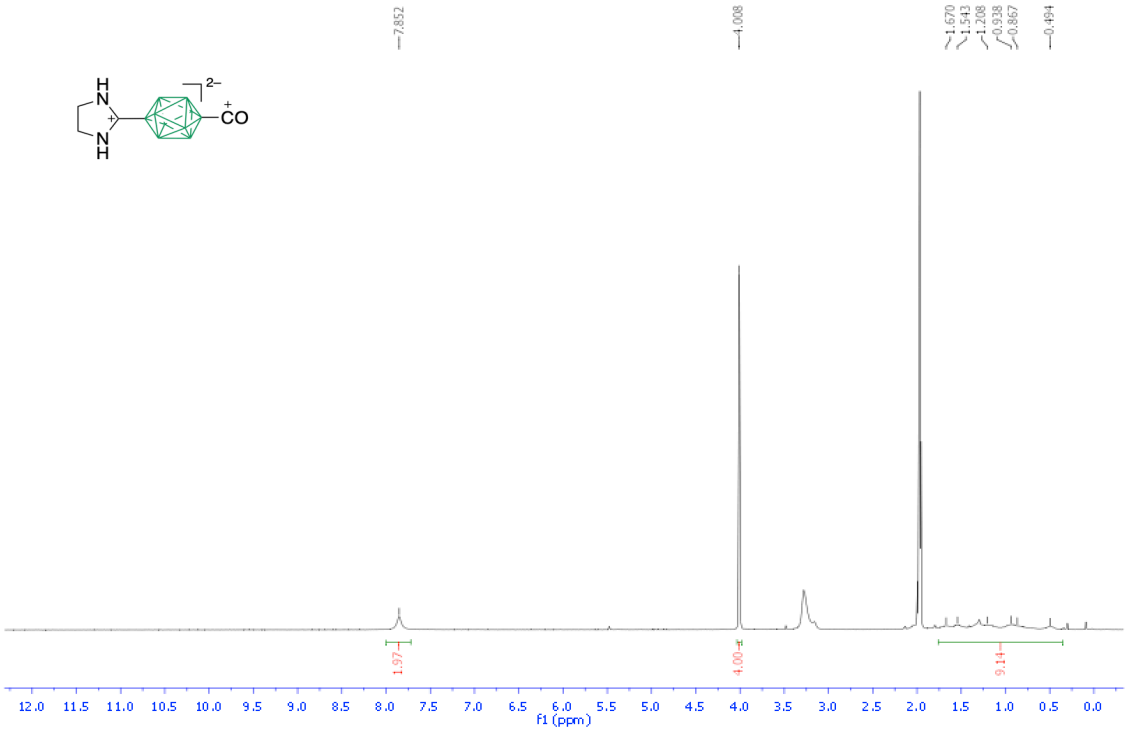


Figure S21. ^{1}H NMR spectrum for [*closo*-$B_{10}H_8$-1-(CO)-10-(($CH_2NH)_2C$)] (**11B-a**) recorded in CD_3CN at 400 MHz.

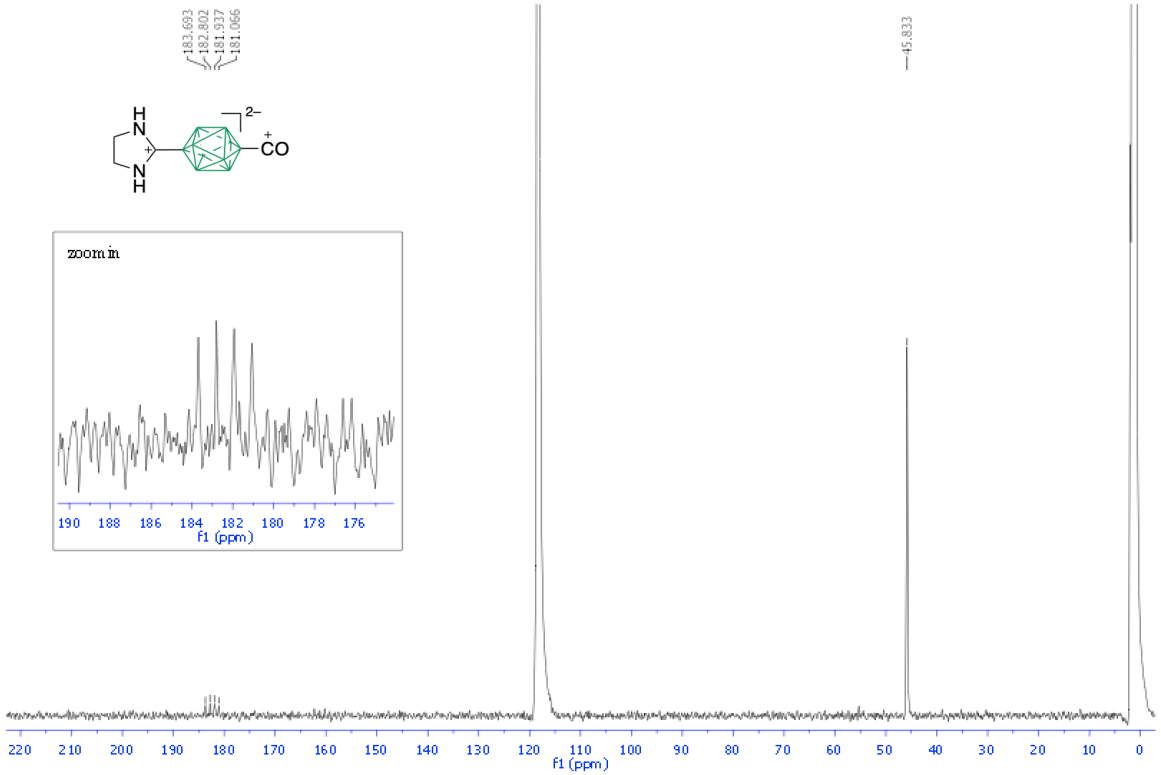


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1-(CO)-10-($C(NHCH_2)_2$)] (**11B-a**) recorded in CD_3CN at 101 MHz.

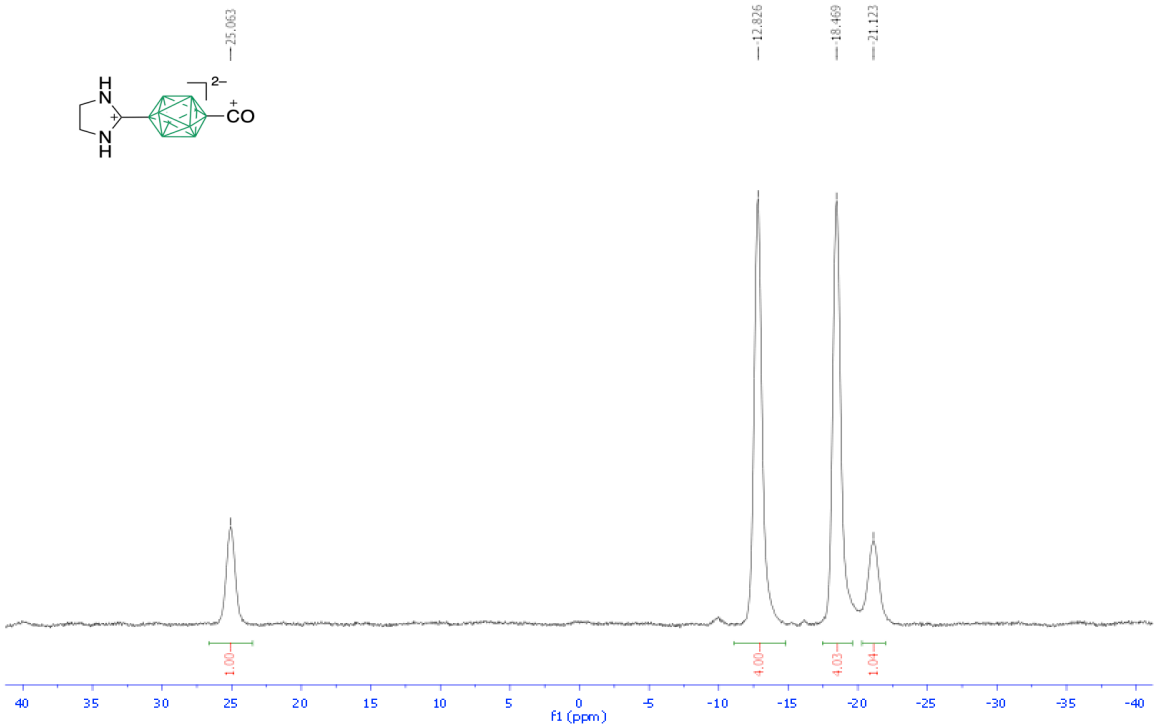


Figure S23. $^{11}B\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1-(CO)-10-($C(NHCH_2)_2$)] (**11B-a**) recorded in CD_3CN at 126 MHz.

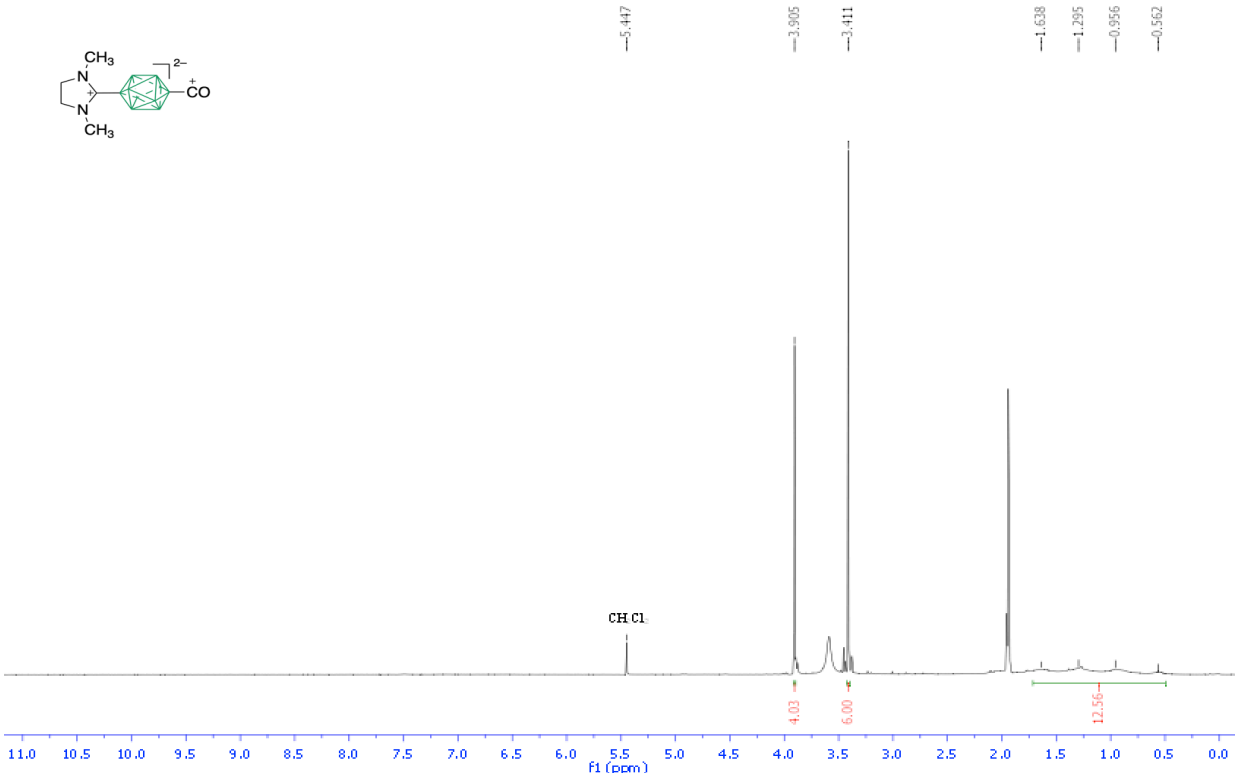


Figure S24. ^{1}H NMR spectrum for crude [*closo*-$B_{10}H_8$-1-(CO)-10-($C(NMeCH_2)_2$)] (**11B-b**) recorded in CD_3CN at 400 MHz.

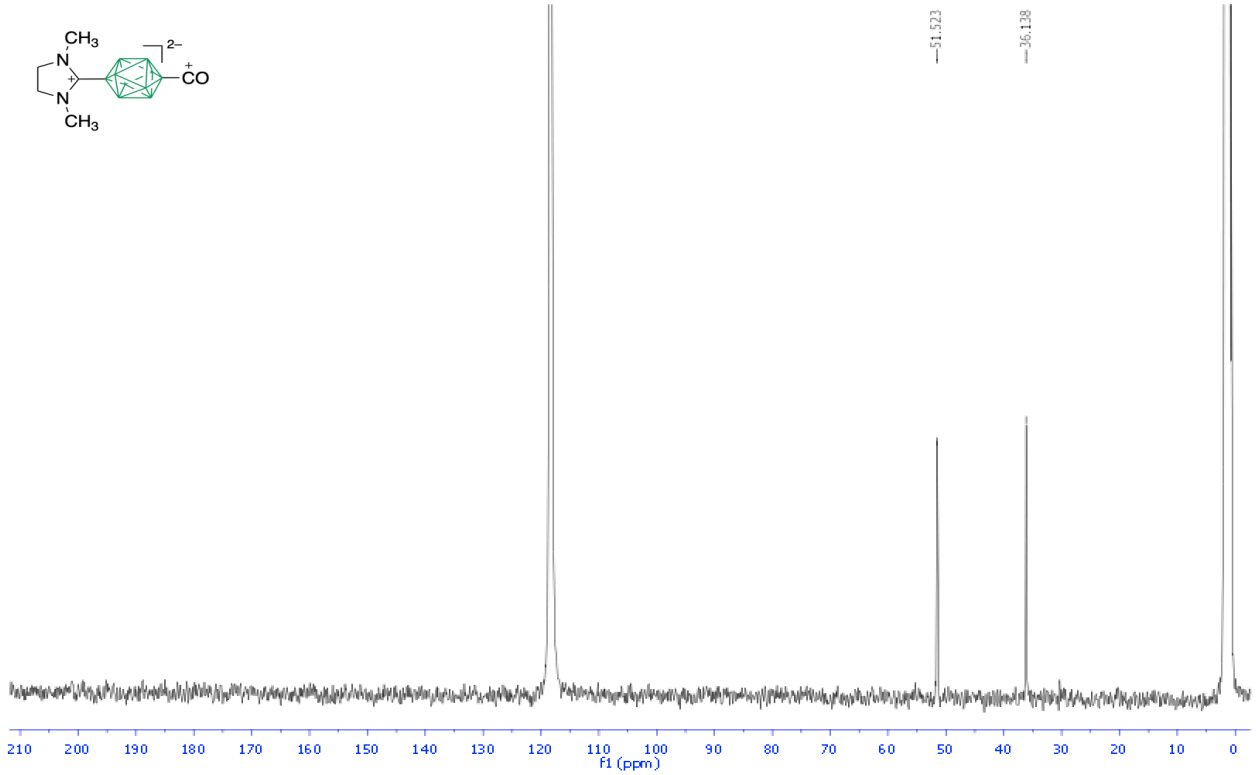


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum for crude [*closo*-$B_{10}H_8$-1-(CO)-10-($C(NMeCH_2)_2$)] (**11B-b**) recorded in CD_3CN at 101 MHz.

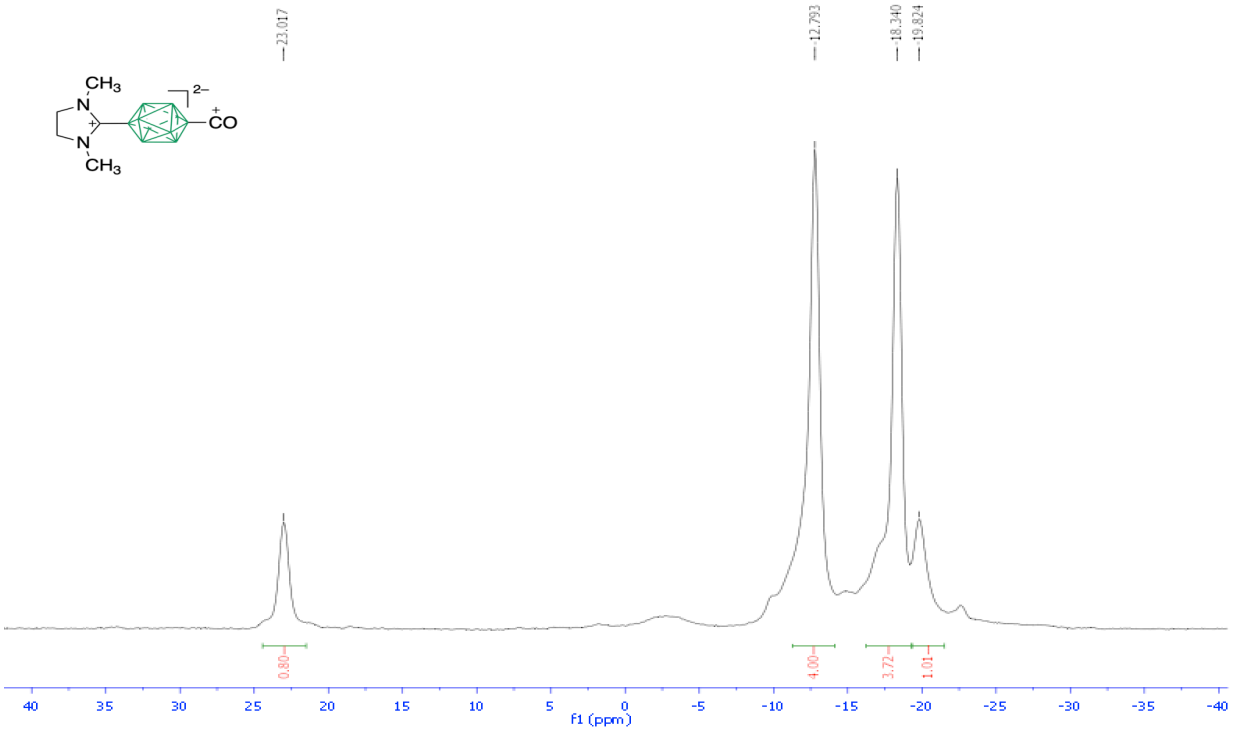


Figure S26. $^{11}B\{^{1}H\}$ NMR spectrum for crude [*closo*-$B_{10}H_8$-1-(CO)-10-($C(NMeCH_2)_2$)] (**11B-b**) recorded in CD_3CN at 126 MHz.

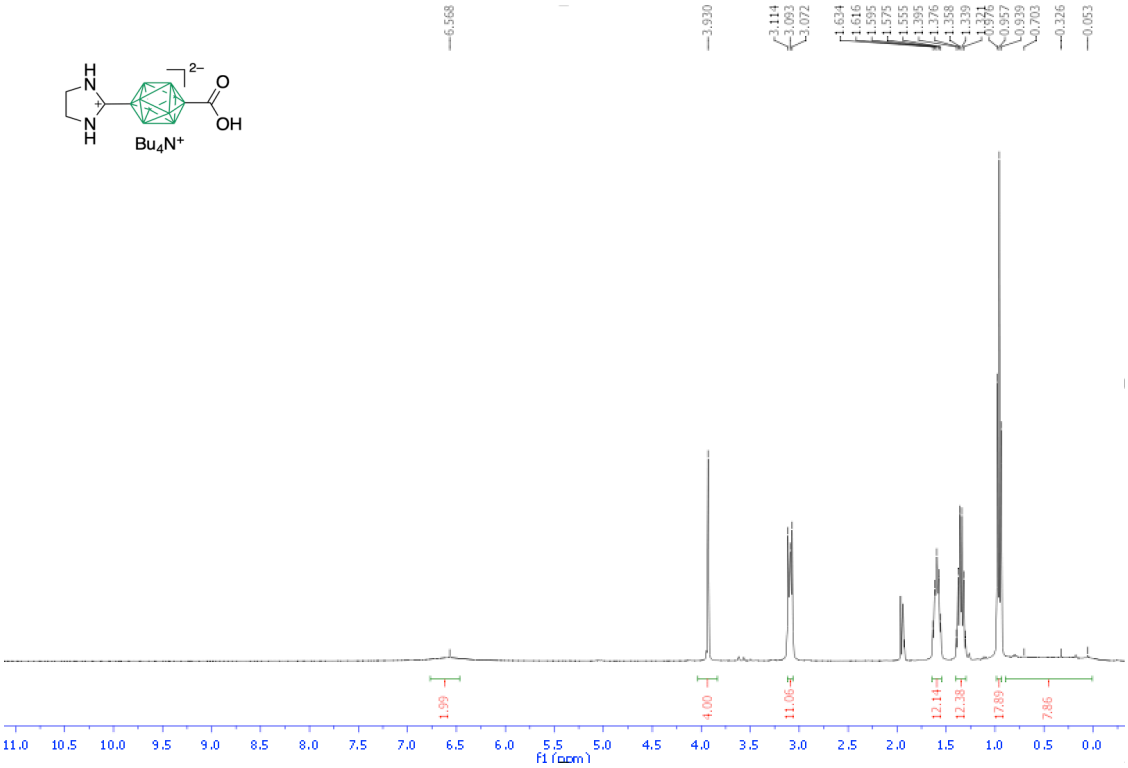


Figure S27. ^{1}H NMR spectrum [*closo*-$B_{10}H_8$-1-(COOH)-10-($C(NHCH_2)_2$)]$^-$[Bu_4N]$^+$ (**12B-a[Bu$_4$N]**) recorded in CD_3CN at 400 MHz.

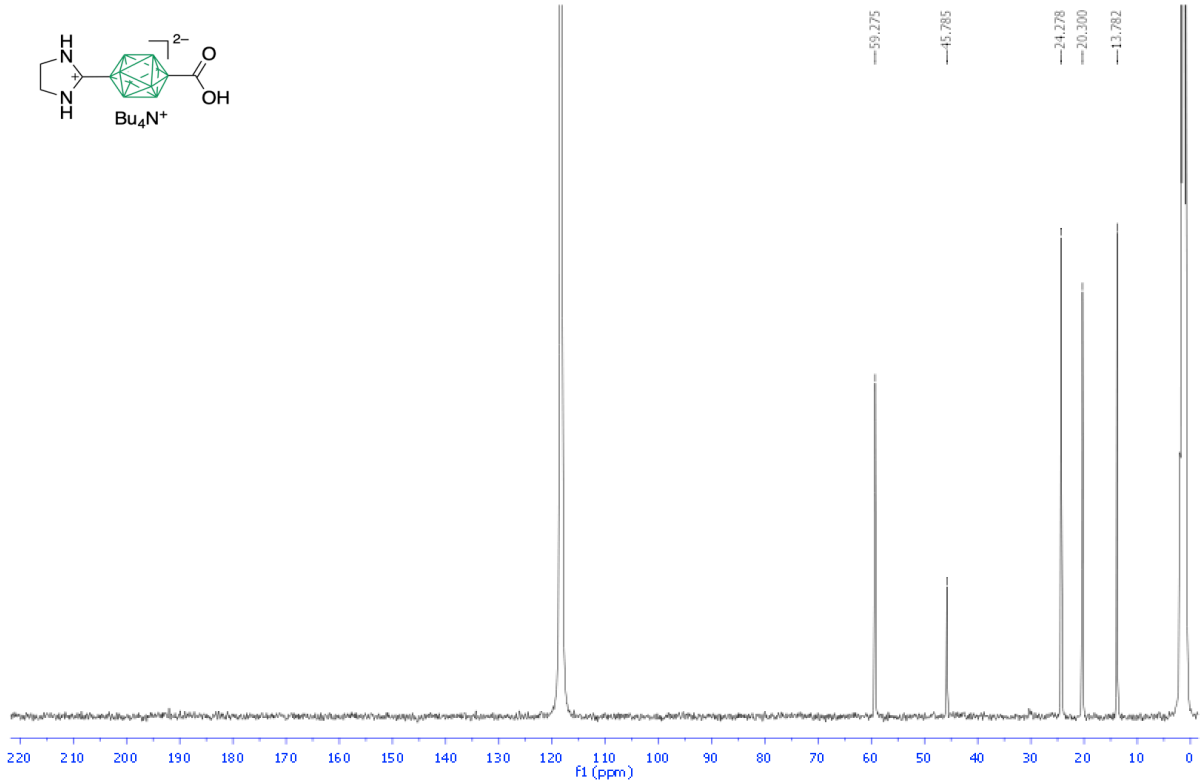


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1-(COOH)-10-($C(NHCH_2)_2$)]$^-$[Bu_4N]$^+$ (**12B-a[Bu$_4$N]**) recorded in CD_3CN at 101 MHz.

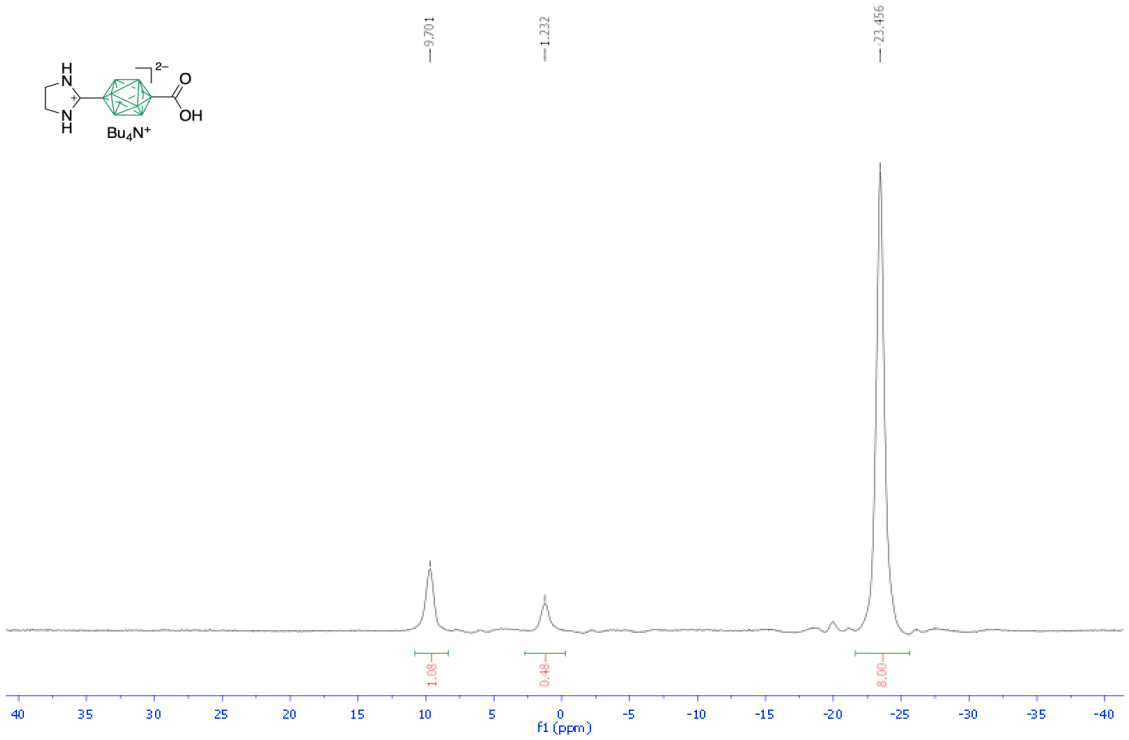


Figure S29. $^{11}B\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1-(COOH)-10-($C(NHCH_2)_2$)]$^-$[Bu_4N]$^+$ (**12B-a[Bu_4N]**) recorded in CD_3CN at 126 MHz.

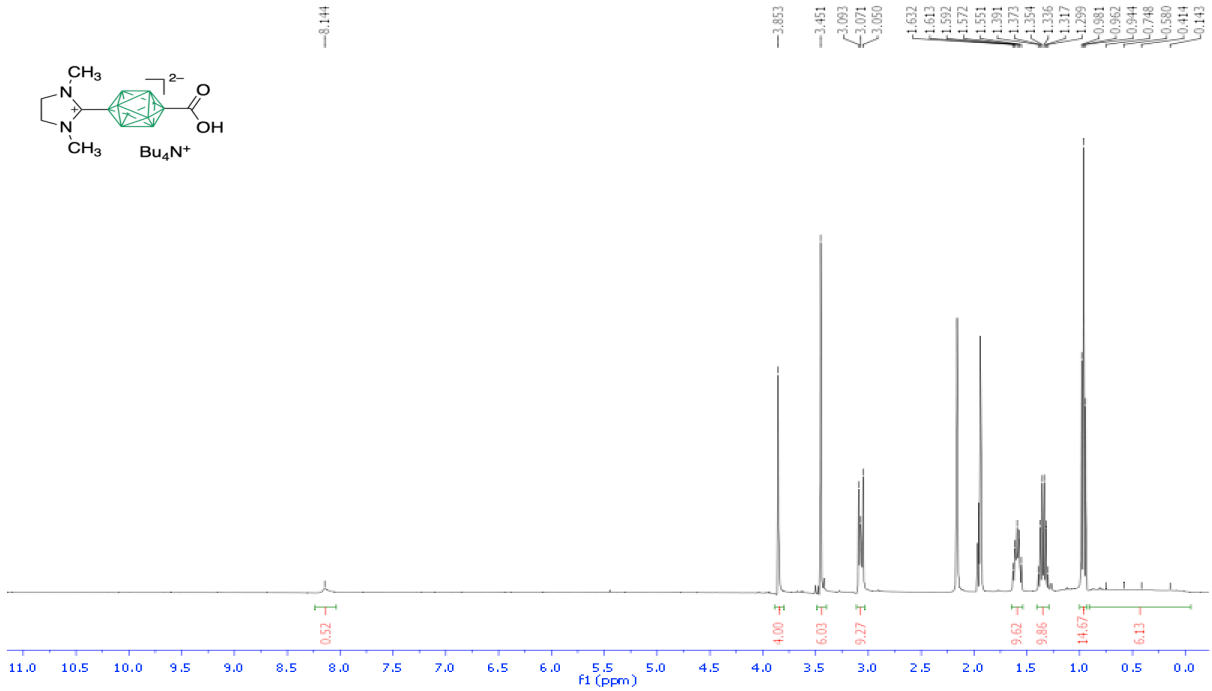


Figure S30. ^{1}H NMR spectrum for [*closo*-$B_{10}H_8$-1-(COOH)-10-($C(NMeCH_2)_2$)]$^-$[Bu_4N]$^+$ (**12B-b[Bu_4N]**) recorded in CD_3CN at 400 MHz.

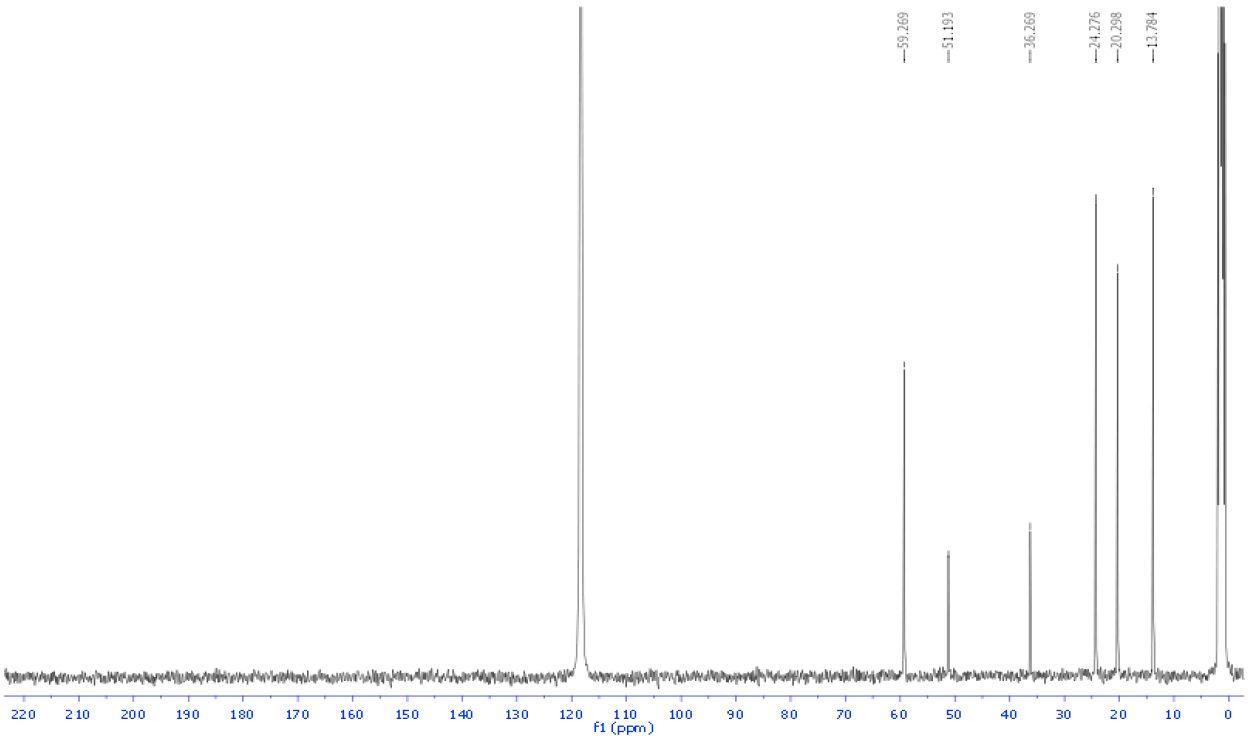


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1-(COOH)-10-($C(NMeCH_2)_2$)]$^-$ $[Bu_4N]^+$ (**12B-b[Bu_4N]**) recorded in CD_3CN at 101 MHz.

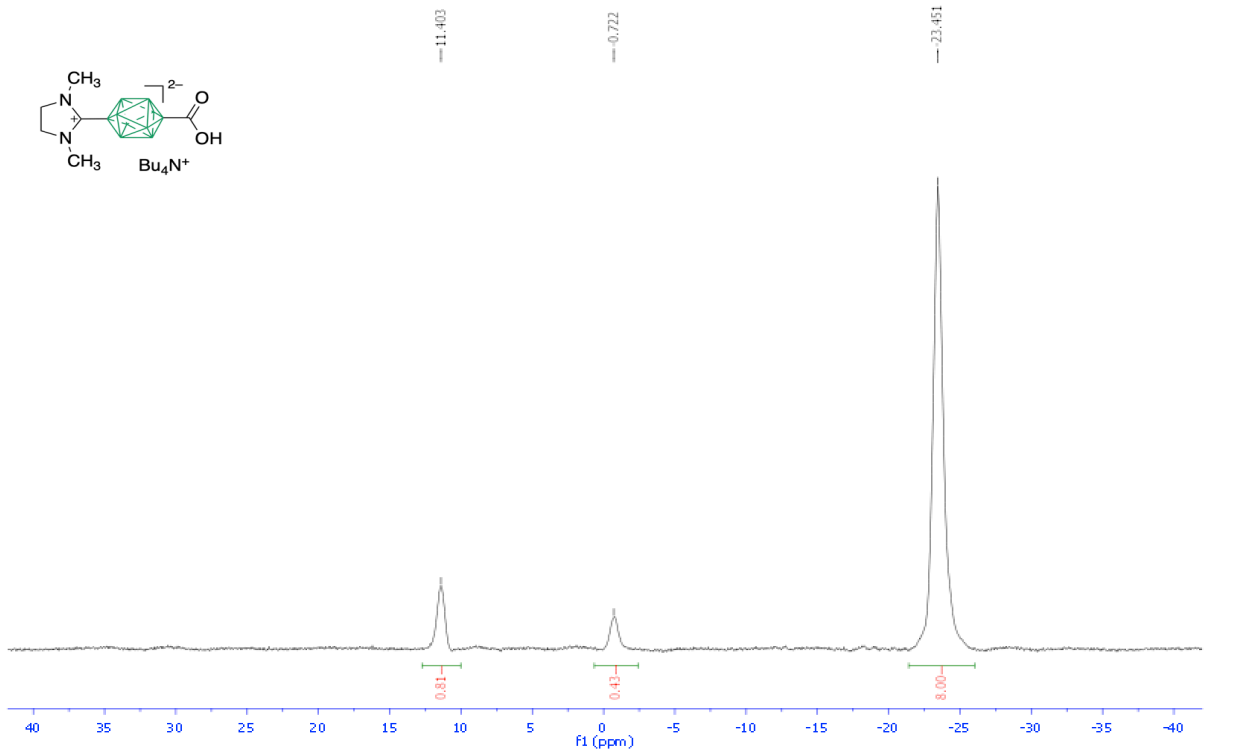


Figure S32. $^{11}B\{^{1}H\}$ NMR spectrum for [*closo*-$B_{10}H_8$-1-(COOH)-10-($C(NMeCH_2)_2$)]$^-$ $[Bu_4N]^+$ (**12B-b[Bu_4N]**) recorded in CD_3CN at 126 MHz.

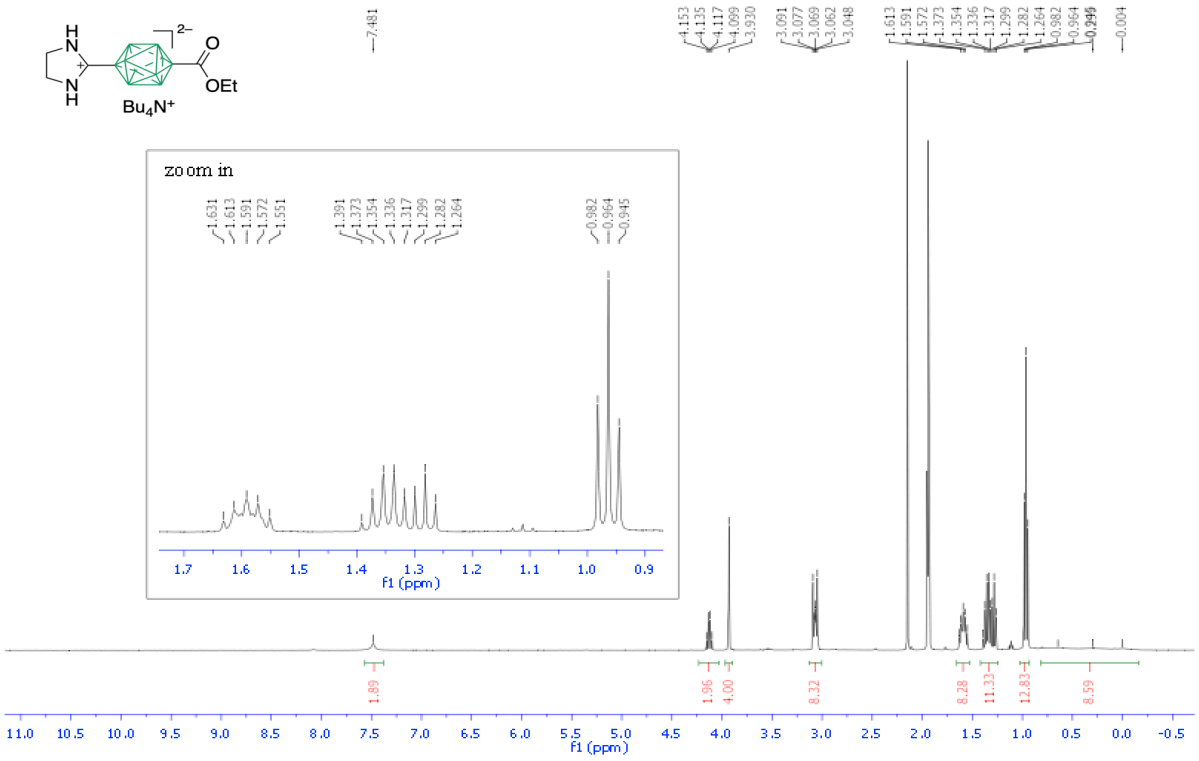


Figure S33. ^{1}H NMR spectrum for [*closo*-$B_{10}H_8$-1-(COOEt)-10-($C(NHCH_2)_2$)]$^-$[Bu_4N]$^+$ (**13B-a[Bu_4N]**) recorded in CD_3CN at 400 MHz

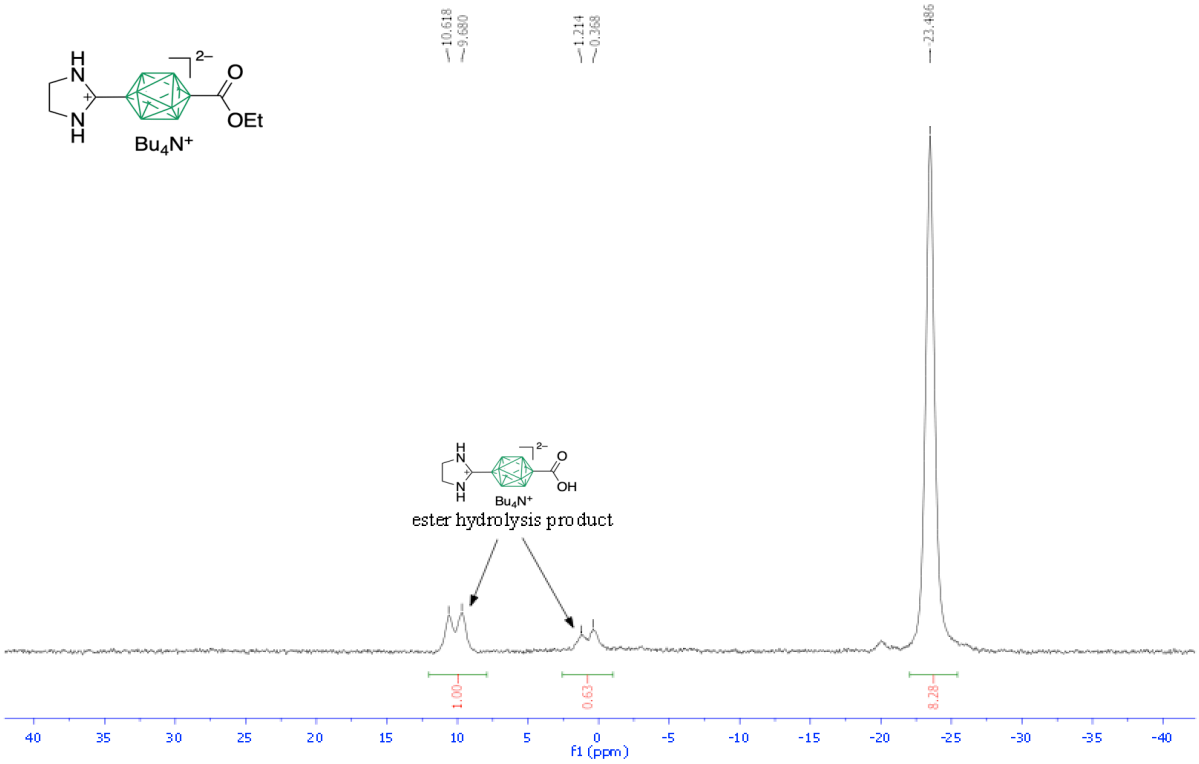


Figure S34. ^{11}B{^{1}H} NMR spectrum for [*closo*-$B_{10}H_8$-1-(COOEt)-10-($C(NHCH_2)_2$)]$^-$[Bu_4N]$^+$ (**13B-a[Bu_4N]**) recorded in CD_3CN at 126 MHz.

3. XRD data collection and refinement

Crystal data for **5B[Bu_4N]** (obtained by slow evaporation of H_2O solution containing acetone at rt) and **7B[Et_4N]** (obtained by slow evaporation of EtOH solution containing CH_2Cl_2 at rt) were collected on a dual source Rigaku SuperNova diffractometer with a Dectris Pilatus3 R 200 K-A detector, equipped with an Oxford Cryosystems Ltd. nitrogen flow apparatus (Cryostream 800 Series) at 100 K for **7B[Et_4N]** and at 297 K for **5B[Bu_4N]**. The data set for **5B[Bu_4N]** was collected at 297 K due to instability of the crystal at 100 K. Crystal data for **9B** and **13B-a[Bu_4N]** (obtained by slow evaporation of EtOH solution at rt) were collected on a Rigaku XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer. The crystals were kept at a steady T = 100.0(2) K during data collection. All crystals were measured using micro-focus X-ray Source Cu Kα radiation, λ = 1.54184 Å. The data were integrated using CrysAlisPro program.[5] Intensities for absorption were corrected using multi-scan method as in SCALE3 ABSPACK scaling algorithm implemented in CrysAlisPro program.[5] Additional crystal and refinement information are listed in Table S1.

CCDC 2072612, 2081955, 2120674 and 2126518 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Structure solution and refinement

Structures were solved with the ShelXT[6] structure solution program and refined in the ShelXL[7] by the full-matrix least-squares minimization on F^2 using OLEX2 software package.[8] All non-hydrogen atoms were refined anisotropically. Most hydrogen atoms were included in idealized positions for structure factor calculations using a riding model while N-H hydrogen atoms in **9B** and **13B-a[Bu_4N]** were refined freely. In **5B[Bu_4N]** one of the butyl groups in the tetrabutylammonium cation shows positional disorder. This was modeled by splitting four carbon atoms over two positions. The final refined occupancy ratio is 0.692(8):0.308(8). In **7B[Et_4N]** two of the ethyl groups in one of the tetraethylammonium cation show positional disorder resulting in splitting in two positions of the two carbon atoms respectively with the occupancy ratio of 0.45(2):0.55(2). The oxygen atom O1 in **7B[Et_4N]** is disordered over two positions with the occupancy ratio of 0.65(3):0.35(3). Constraints and restraints such as EADP, SADI, RIGU, and SIMU were used to aid the disorder modeling.

Table S1. Selected Structural Data.

	5B[Bu_4N] CCDC: 2072612	**7B[Et_4N]** CCDC: 2081955	**9B** CCDC:2120674	**13B-a[Bu_4N]** CCDC:2126518
Formula	$C_{18}H_{45}B_{10}NO_3$	$C_{22}H_{58}B_{10}N_2O_4$	$C_6H_{24}B_{10}N_4$	$C_{22}H_{54.97}B_{10}Cl_{0.03}N_3O_2$
Formula Weight	431.65	522.80	260.39	502.76
Crystal System	Triclinic	Monoclinic	Triclinic	Triclinic
Space Group	*P*-1	$P2_1/c$	*P*-1	*P*-1
a/Å	10.22140(10)	16.45359(6)	8.8909(4)	9.3429(2)
b/Å	11.19270(10)	10.53655(5)	9.1167(5)	10.3905(2)
c/Å	13.93660(10)	18.37001(7)	9.7494(4)	18.4914(3)
α/°	97.6090(10)	90	89.142(4)	84.664(2)
β/°	94.6980(10)	97.1637(4)	84.441(3)	82.6090(10)
γ/°	113.8440(10)	90	80.010(4)	64.955(2)
Volume/Å^3	1429.27(2)	3159.84(2)	774.60(6)	1611.32(6)
Z	2	4	2	2
θ range for data collection/°	3.236 to 76.571	2.707 to 76.570	4.557 to 74.500	4.6830 to 78.6890
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 13$, $-14 \le l \le 17$	$-20 \le h \le 20$, $-10 \le k \le 13$, $-23 \le l \le 22$	$-11 \le h \le 11$, $-11 \le k \le 11$, $-12 \le l \le 11$	$-11 \le h \le 11$, $-13 \le k \le 12$, $-22 \le l \le 22$
No. of measured, independent and observed [$I>2\sigma(I)$] reflections	30174, 5830, 5195	73357, 6577, 6407	7231, 3448, 3141	46429, 6506, 6025
*R*int	0.0179	0.0240	.	
Goodness-of-fit on F^2	1.096	1.055	1.061	1.018
Final *R* indexes [$F^2 > 2\sigma(F^2)$]	R_1=0.0591, wR_2=0.1902	R_1=0.0539 wR_2=0.1446	R_1=0.0538 wR_2=0.1523	R_1=0.0406 wR_2=0.1080
Final *R* indexes [all data]	R_1=0.0624, wR_2= 0.1945	*R_1=0.0545* *wR_2=0.1450*	R_1=0.0580 wR_2=0.1581	R_1=0.0434 wR_2=0.1103
Data/restraints/parameters	5830/130/326	6577/97/ 397	3488/0/199	6506/0/379
Largest diff. peak/hole Å^{-3}	0.285/-0.190	0.503/-0.386	0.658/-0.217	0.754/-0.242

The crystal structure of **9B** was refined as a 3-component twin with scales 0.447(5), 0.419(5) and 0.134(5). The structure **13B-a[Bu_4N]** exhibits substitutional disorder of H and Cl atoms bonded to the boron cage with 0.972(2) occupancy for H and 0.028(2) for Cl.

The crystal data and structure refinement descriptors are presented in Table S1, pertinent geometrical parameters are listed in Table S2, while molecular representations and partial packing diagrams are shown in Figures S35–S42.

Table S2. Selected interatomic distances and angles for selected derivatives.[a]

X =	**A[Q]** [b]	**5B[Bu_4N]**	**7B[Et_4N]**	**9B**	**13B-a[Bu_4N]**
X–B(1)	–	1.573(2)	1.582(2)	1.578(3)	1.558(2)
$B(1)–B(2)_{avrg}$	1.701(3)	1.689(4) [c]	1.699(1)	1.697(3)	1.692(2)
B(1)···B(2-5) [d]	1.100	1.077	1.090	1.082	1.074
$B(2)–B(3)_{avrg}$	1.835(9)	1.840(2)	1.843(10)	1.850(3)	1.849(2)
$B(2)–B(6)_{avrg}$	1.813(6)	1.798(7)	1.813(5)	1.809(3)	1.813(2)
$B(6)–B(7)_{avrg}$	1.835(9)	1.858(10)	1.841(7)	1.847(3)	1.847(2)
$B(10)–B(9)_{avrg}$	1.701(3)	1.681(8)	1.699(6)	1.697(3)	1.696(2)
B(10)···B(6-9)[d]	1.100	1.048	1.092	1.083	1.082
Y–B(10)	–	1.466(2)	1.583(2)	1.584(3)	1.577(2)
B–B(1)–X	130.3(12)	129.6(11)	130(4)	129.5(1)	129.3(2)
B–B(10)–Y	130.3(12)	129.1(14)	130.0(17)	129.5(2)	129.6(2)
B(1)···B(10)	3.717	3.619(2)	3.696(2)	3.672(3)	3.668(2)

[a] All distances are in Å and angles in degrees. Except for unique in each molecule distances B–X and the cage size B(1)···B(10), all parameters are average values and the esd refers to the distribution of individual values. [b] Q = 2,2′-bipyridinium, ref. [9]. [c] The eclipsed bonds are 1.693(2) and the staggered 1.685(2) Å. [d] The height of the square pyramid.

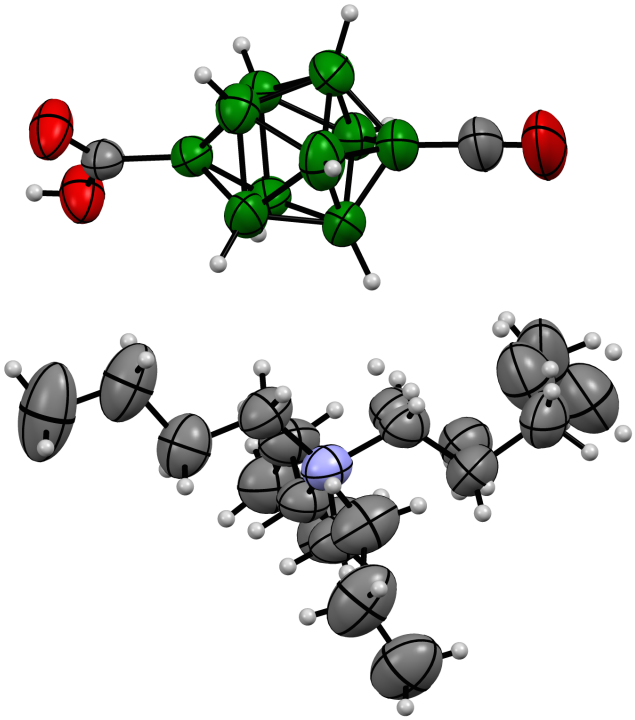


Figure S35. Atomic displacement ellipsoid representation for **5B[Bu$_4$N]**. For geometrical dimensions see Table S2.

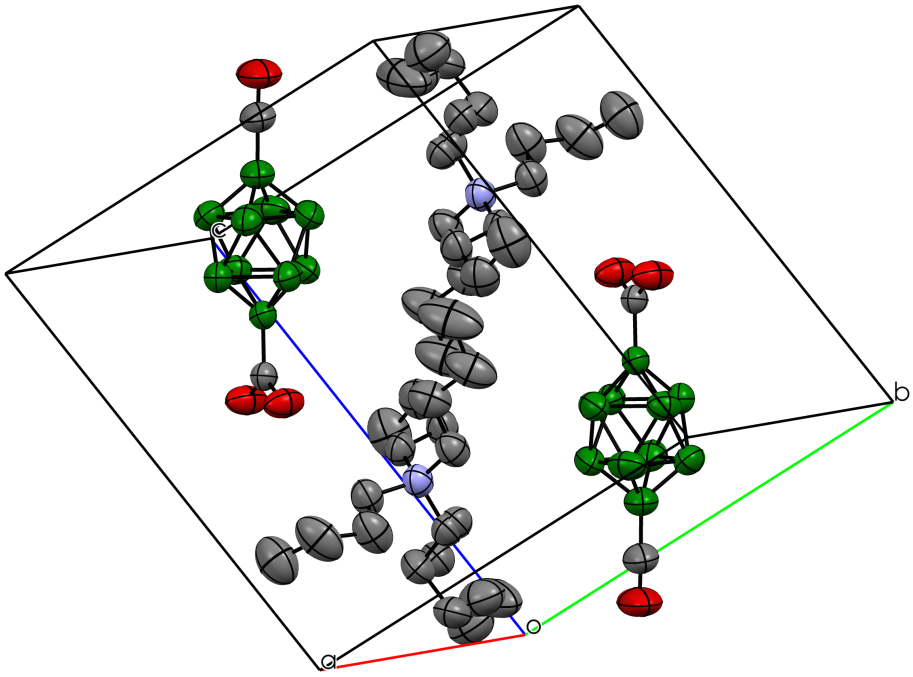


Figure S36. Unit cell packing diagram for **5B[Bu$_4$N]**. Hydrogen atoms are omitted for clarity.

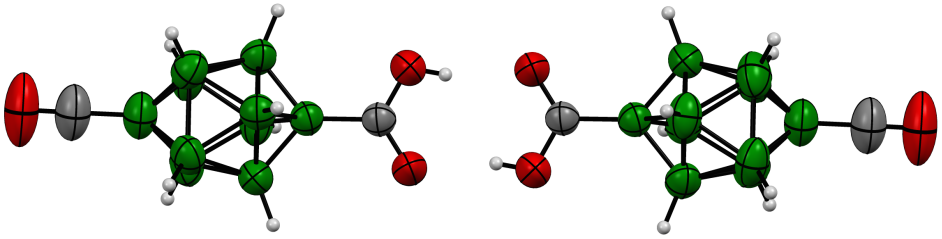


Figure S37. Two molecules of **5B** in a dimeric arrangement. The O···O separation is 2.694(1) Å. Cations are omitted for clarity.

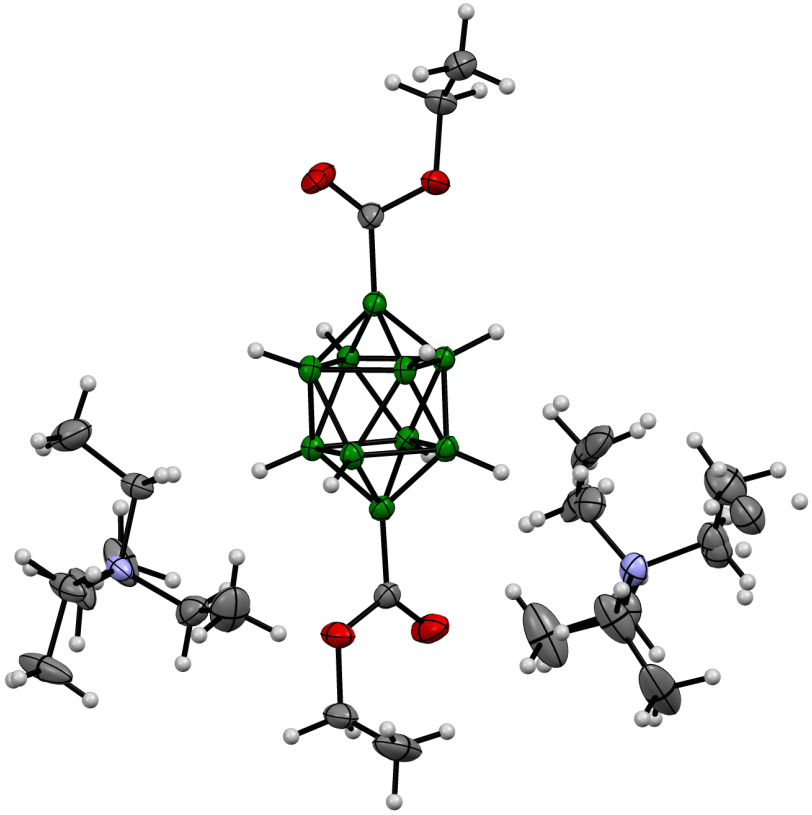


Figure S38. Atomic displacement ellipsoid representation for **7B[Et_4N]**. For geometrical dimensions see Table S2.

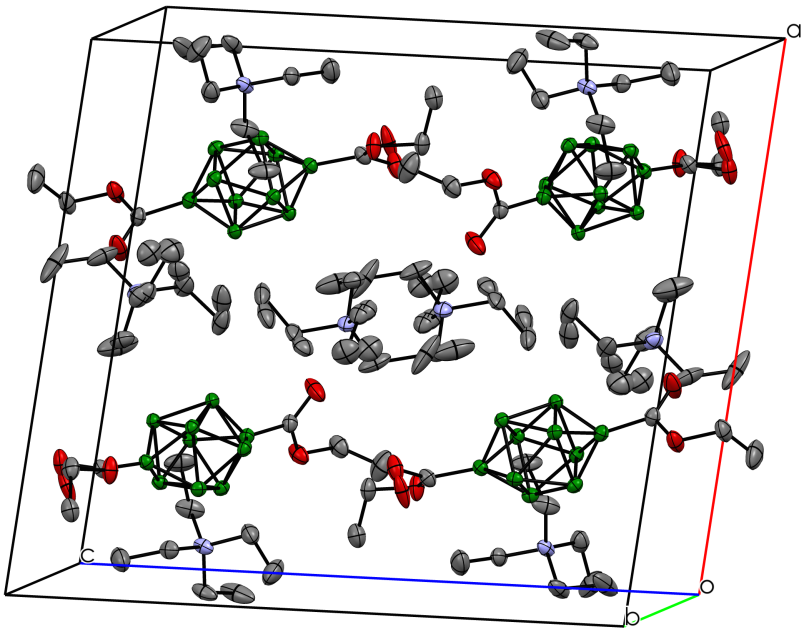


Figure S39. Unit cell packing diagram for **7B[Et_4N]**. Hydrogen atoms are omitted for clarity.

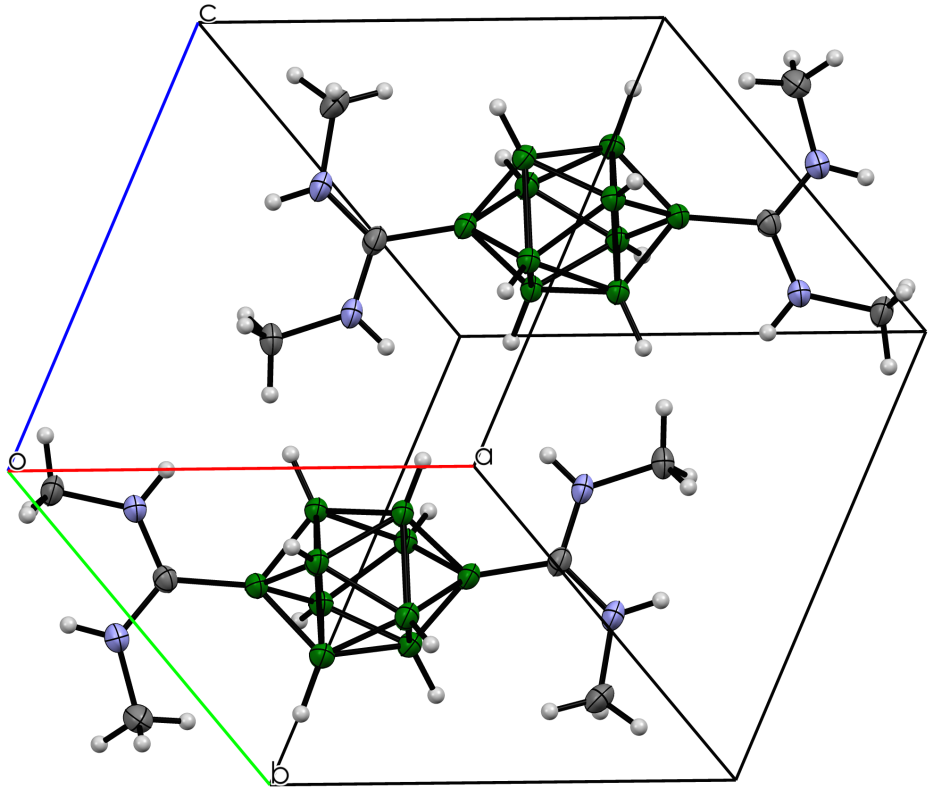


Figure S40. Unit cell packing diagram for **9B**.

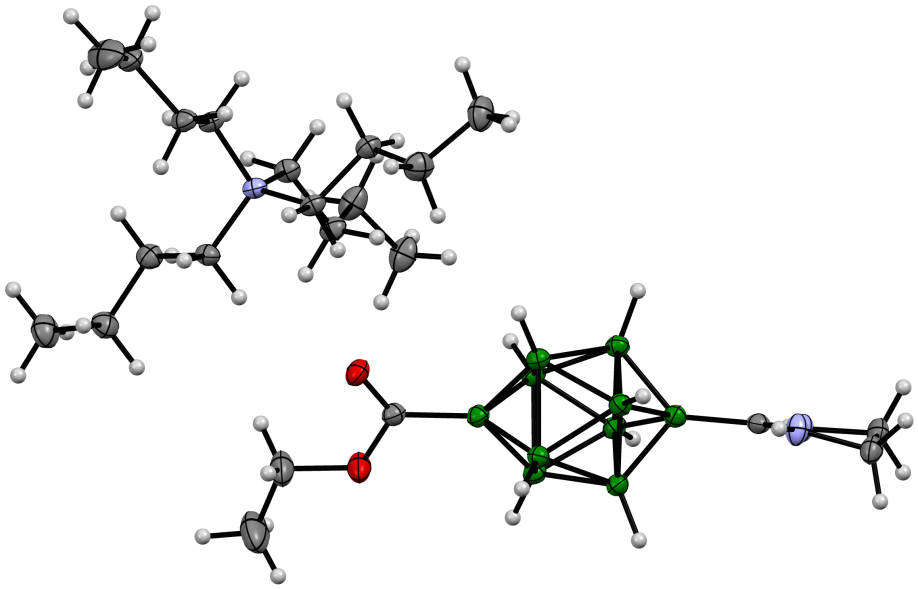


Figure S41. Atomic displacement ellipsoid representation for **13B-a[Bu$_4$N]**. For geometrical dimensions see Table S2.

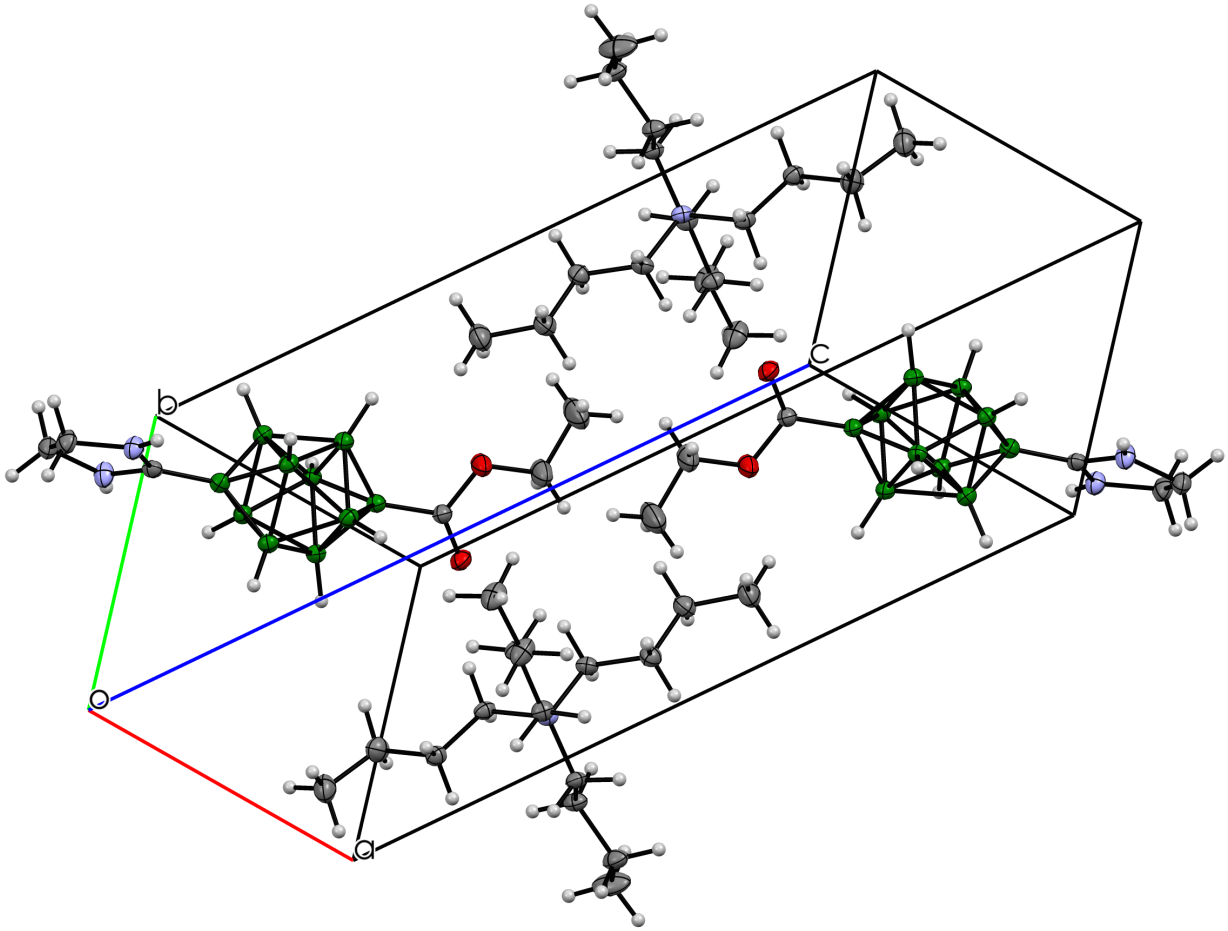


Figure S42. Unit cell packing diagram for **13B-a[Bu$_4$N]**.

4. Computational details

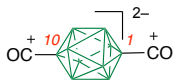
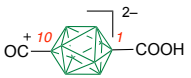
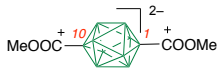
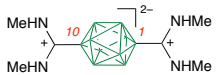
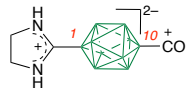
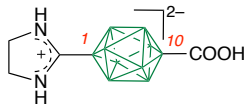
General. Quantum-mechanical calculations were carried out using Gaussian 09 suite of programs.[10] Geometry optimizations were undertaken using the B3LYP[11] functional with Karlsruhe triple-z polarization Def2TZVP basis set[12] and tight convergence limits with appropriate symmetry constraints. All calculations were performed in PhCl dielectric medium (arbitrarily chosen) with the PCM model[13] requested with SCRF(Solvent= C6H5Cl) keyword, since it was demonstrated[2] that low dielectric medium is important for obtaining accurate geometry of zwitterions, such as **2**. The ground state nature of stationary points for the obtained equilibrium geometry was confirmed with vibrational frequency calculations. Population analysis was performed with the NBO method.

Isotropic NMR shielding constants in acetone dielectric medium were obtained at the CAM-B3LYP/Def2TZVP // B3LYP/Def2TZVP level of theory using the default GIAO method (NMR keyword) supplied in the Gaussian package. The equilibrium geometry for each compound was obtained in PhCl dielectric medium (*vide supra*). The solvation model was implemented with the PCM model[13] using the SCRF(solvent=acetone) keyword.

Chemical shifts were obtained by comparison of calculated isotropic shielding constants with experimental chemical shifts for reference compounds: for [*closo*-$B_{10}H_{10}]^{2-}$ $2[Et_3NH]^+$ (**A[Et$_3$NH]**) (equatorial B atoms ^{11}B shift -27.96 ppm in acetone-d_6 vs external neat BF_3•Et_2O) and benzene (^{13}C shift 129.13 ppm in acetone-d_6).

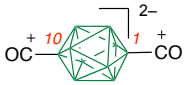
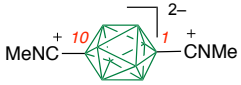
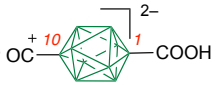
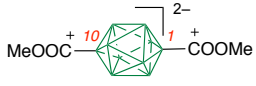
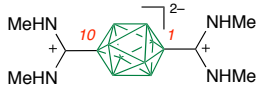
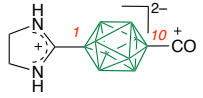
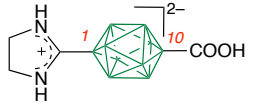
The calculated key NMR and IR signals are listed in Tables S3 and S4, respectively.

Table S3. NMR chemical shifts calculated in acetone.[a]

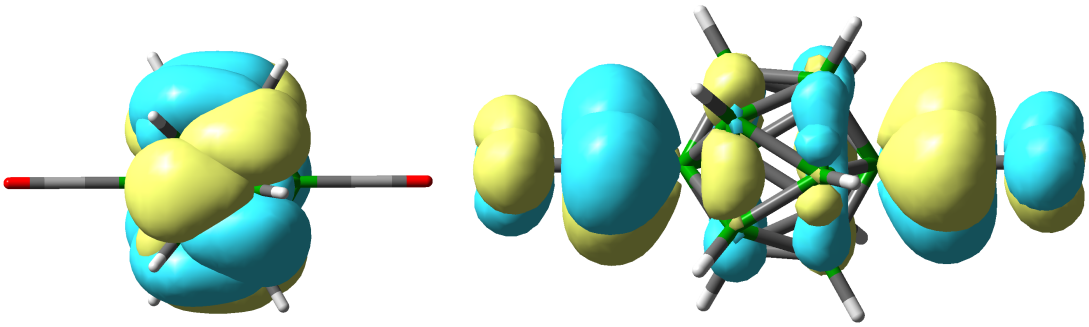
	 **2B** δ /ppm	 **4B** δ /ppm	 **5B**$^{-}$ δ /ppm	 **[7B']**$^{2-}$ δ /ppm	 **9B** δ /ppm	 **11B-a** δ /ppm	 **[12B-a]**$^{-}$ δ /ppm
B(1)	1.7	-0.7	36.4	8.0	9.1	28.6	3.1
B(2-5) [b]	-6.1	-16.2	-17.0	-24.4	-22.1	-15.8	-21.7
B(6-9) [b]	-6.1	-16.2	-9.7	-24.4	-22.1	-9.5	-22.4
B(10)	1.7	-0.7	-25.8	8.0	9.1	-20.4	14.4
C≡O	175.3	–	178.1	–	–	178.5	–
COOH	–	–	195.2	–	–	–	200.3
COOMe	–	–	–	202.2	–	–	–
CNMe	–	129.1	–	–	–	–	–
$C(NHR)_2$	–	–	–	–	189.1	187.6	195.8

[a] For computational details see the text. [b] Average value.

Table S4. Characteristic IR vibrations calculated in PhCl.[a]

 **2B** ν /cm^{-1}	 **4B** ν /cm^{-1}	 **5B**$^{-}$ ν /cm^{-1}	 **[7B']**$^{2-}$ ν /cm^{-1}	 **9B** ν /cm^{-1}	 **11B-a** ν /cm^{-1}	 **[12B-a]**$^{-}$ ν /cm^{-1}
C≡O 2193	C≡NMe 2354	C≡O 2146 COOH 1715	COOMe 1674	N–C–N 1631, 1574	C≡O 2169 N–C–N 1609, 1559	COOH 1699 N–C–N 1598, 1543

[a] For computational details see the text. [b] Average value.



HOMO, E = -8.249 eV LUMO, E = -2.978 eV

Figure S43. FMO contours and energies for [*closo*-$B_{12}H_{10}$-1,12-$(CO)_2$] (**2A**) obtained at the B3LYP/Def2TZV level of theory in PhCl dielectric medium. MO isovalue ±0.02 $(e/bohr^3)^{1/2}$.

5. Archive for DFT results

2A

```
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```

2B

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1C1O1),2SGV(H2B2),2SGD(H2B2)]\\@

5B$^-$

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SCRF(Solvent=C6H5Cl) freq(noraman, readIso)\\CO-B10-COOMe, C1 in PhCl\
\-1,1\B,-0.5091739898,1.6405598209,0.000467499\B,1.7355749161,0.240020
3644,-0.0016809418\B,0.6095666588,0.9352303439,1.3219749879\B,0.609660
1442,0.9329140686,-1.3232596917\B,-0.9652120487,0.163346267,-0.9193691
48\B,-0.9631675463,0.1665914109,0.9217380218\B,0.6112512735,-0.8178483
118,0.9201408387\B,0.6110300233,-0.8168682837,-0.9204782408\B,-0.74744
27098,-1.2418718777,0.001755964\B,1.1707354772,1.833933425,-0.00137930
87\H,-1.2174691558,2.5957471951,0.0007140849\H,2.9048918118,0.02431175
44,-0.0020732134\H,0.8401087595,1.3031929453,2.4290309668\H,0.83780130
88,1.3008197482,-2.4307940202\H,-1.8545532354,0.2221415774,-1.70963518
45\H,-1.8517773091,0.2258059917,1.7121584425\H,1.0535279178,-1.5915577
928,1.7102310332\H,1.050684178,-1.5929352923,-1.7093942645\C,-1.551347
473,-2.6043624295,0.0008785061\O,-2.9024134225,-2.4623489359,0.1544416
878\O,-1.0867915178,-3.7239531241,-0.1192387315\H,-3.2823837526,-3.357
4896733,0.1367440908\C,1.9415102371,3.0743092838,0.0007764209\O,2.5406
081645,4.0406350946,0.003634971\\Version=ES64L-G09RevD.01\State=1-A\HF
=-556.3233463\RMSD=8.658e-09\RMSF=6.836e-06\Dipole=0.4003875,1.8639304
,0.0800872\Quadrupole=3.9552576,-5.4573427,1.5020851,4.0181996,0.01312
08,-0.8759615\PG=C01 [X(C2H9B10O3)]\\@

[*closo*-$B_{12}H_{10}$-1-CO-12-C(OH)$_2$] (6A)

1\1\GINC-LOCALHOST\FOpt\RB3LYP\def2TZVP\C2H12B12O3\PIOTR\10-Jun-2021\0
\\#P B3LYP/Def2TZVP FOpt(tight) geom(noangle, nodistance) fcheck #P SC
RF(Solvent=C6H5Cl) freq(noraman, readIso)\\p-Decaborane-1-CO-12-C(OH)2
, Cs symmetry\\0,1\B,0.4333575,1.46561263,0.\B,0.41612174,0.41987346,1
.45696903\B,0.41612174,0.41987346,-1.45696903\B,0.3741119,-1.29906448,
0.89611384\B,0.3741119,-1.29906448,-0.89611384\B,-1.12874914,-1.557336
56,0.\B,-1.09599415,-0.49399272,1.46739105\B,-1.09599415,-0.49399272,-
1.46739105\B,-1.0589904,1.23502735,0.90720524\B,-1.0589904,1.23502735,
-0.90720524\B,-1.94930232,0.00806235,0.\B,1.28699369,-0.08160227,0.\H,
1.02980138,2.5032897,0.\H,0.98248478,0.73482842,2.45122002\H,0.9824847
8,0.73482842,-2.45122002\H,0.90598205,-2.15706849,1.51911471\H,0.90598
205,-2.15706849,-1.51911471\H,-1.73217502,-2.57758163,0.\H,-1.67270004
,-0.7988369,2.45703906\H,-1.67270004,-0.7988369,-2.45703906\H,-1.60571
145,2.08960122,1.51975238\H,-1.60571145,2.08960122,-1.51975238\C,-3.45
839533,0.04770117,0.\O,-4.58197933,0.07742204,0.\C,2.85724468,-0.00155
909,0.\O,3.49221554,1.12575399,0.\O,3.6047918,-1.049264,0.\H,4.5566147
7,-0.82820189,0.\H,2.84833846,1.86517991,0.\\Version=ES64L-G09RevD.01\
State=1-A'\HF=-607.7784794\RMSD=3.547e-09\RMSF=4.667e-06\Dipole=1.9840
667,0.6939297,0.\Quadrupole=26.856644,-12.0107134,-14.8459306,0.938489
2,0.,0.\PG=CS [SG(C2H4B4O3),X(H8B8)]\\

[*closo*-B10H8-1-CO-10-C(OH)$_2$] (6B)

1\1\GINC-LOCALHOST\FOpt\RB3LYP\def2TZVP\C2H10B10O3\PIOTR\10-Jun-2021\0
\\#P B3LYP/Def2TZVP FOpt(tight) geom(noangle, nodistance) fcheck #P SC
RF(Solvent=C6H5Cl) freq(noraman, readIso)\\CO-B10-C(OH)2, Cs in PhCl\\
0,1\B,1.1642172585,-0.9666931925,0.9319060368\B,1.1190410668,0.9198044
173,-0.9333967668\B,1.1642172585,-0.9666931925,-0.9319060368\B,1.11904
10668,0.9198044173,0.9333967668\B,-0.3481650713,-0.0632010194,1.315296

1601\B,-0.3088549804,-1.384035276,0.\B,-0.3481650713,-0.0632010194,-1.
3152961601\B,-0.3682605352,1.2478732412,0.\B,-1.3957767292,-0.09532377
18,0.\B,2.1870824246,0.0034713646,0.\H,1.6208968589,-1.7320214674,1.71
50430076\H,1.5335715558,1.7086194422,-1.7166853791\H,1.6208968589,-1.7
320214674,-1.7150430076\H,1.5335715558,1.7086194422,1.7166853791\H,-0.
7757840836,-0.065604978,2.4235529224\H,-0.7110511558,-2.5018417518,0.\
H,-0.7757840836,-0.065604978,-2.4235529224\H,-0.8416148921,2.345521045
5,0.\C,-2.937677494,-0.0036394461,0.\O,-3.701792003,-1.0445078768,0.\O
,-3.5729040208,1.1305339905,0.\H,-4.6488274853,-0.8065684362,0.\C,3.65
98775132,0.0402208391,0.\O,4.7904159376,0.0692364945,0.\H,-2.931520585
9,1.8667357376,0.\\Version=ES64L-G09RevD.01\State=1-A'\HF=-556.756845\
RMSD=1.697e-09\RMSF=3.762e-06\Dipole=-2.371344,0.7234637,0.\Quadrupole
=23.3887802,-10.3256238,-13.0631564,-1.5379498,0.,0.\PG=CS [SG(C2H4B4O
3),X(H6B6)]\\@

$7B^{2-}$

1\1\GINC-LOCALHOST\FOpt\RB3LYP\def2TZVP\C6H18B10O4(2-)\PIOTR\11-Jun-20
21\0\\#P B3LYP/Def2TZVP FOpt(CalcFC) geom(noangle, nodistance) fcheck
#P SCRF(Solvent=C6H5Cl) freq(noraman, readIso)\\EtOOC-B10H8-COOEt stag
gered, C2 symm, opt at Def2SVP\\-2,1\B,1.0352348018,-0.9773390911,0.68
80851239\B,-1.3287362731,-0.5114886111,-0.2930157962\B,-0.6394625883,-
0.6373894416,1.3968501614\B,0.3500303579,-0.8328515333,-1.0007697218\B
,1.3287362731,0.5114886111,-0.2930157962\B,0.6394625883,0.6373894416,1
.3968501614\B,-1.0352348018,0.9773390911,0.6880851239\B,-0.3500303579,
0.8328515333,-1.0007697218\B,0.3554401335,1.8033720833,0.1983411788\B,
-0.3554401335,-1.8033720833,0.1983411788\H,1.9702924833,-1.5872728043,
1.1217324702\H,-2.4244257856,-0.7257682378,-0.726034212\H,-1.139026698
2,-0.9657947289,2.4344400288\H,0.6870515164,-1.3222433269,-2.040785281
4\H,2.4244257856,0.7257682378,-0.726034212\H,1.1390266982,0.9657947289
,2.4344400288\H,-1.9702924833,1.5872728043,1.1217324702\H,-0.687051516
4,1.3222433269,-2.0407852814\C,-0.6983414172,-3.3445014011,0.217524159
2\O,-1.7389653366,-3.867717903,0.5875077403\O,0.3223272081,-4.14363727
58,-0.2425143786\C,-0.0891913352,5.5598613,-0.2660251902\H,0.122948981
2,5.9104980705,0.7469449953\H,0.7919598531,5.7734388602,-0.8757228622\
C,0.6983414172,3.3445014011,0.2175241592\O,1.7389653366,3.867717903,0.
5875077403\O,-0.3223272081,4.1436372758,-0.2425143786\C,0.0891913352,-
5.5598613,-0.2660251902\H,-0.1229489812,-5.9104980705,0.7469449953\H,-
0.7919598531,-5.7734388602,-0.8757228622\C,-1.3252337543,6.2281199602,
-0.830880561\H,-2.2004637827,6.0149774165,-0.214858064\H,-1.1825826251
,7.3107676794,-0.8609629504\H,-1.528054795,5.8809382808,-1.8453278404\
C,1.3252337543,-6.2281199602,-0.830880561\H,1.1825826251,-7.3107676794
,-0.8609629504\H,1.528054795,-5.8809382808,-1.8453278404\H,2.200463782
7,-6.0149774165,-0.214858064\\Version=ES64L-G09RevD.01\State=1-A\HF=-7
89.6121557\RMSD=4.156e-09\RMSF=8.970e-05\Dipole=0.,0.,-1.3108825\Quadr
upole=-2.3534725,-6.2347094,8.588182,-15.9162369,0.,0.\PG=C02 [X(C6H18
B10O4)]\\

Methyl Adamantane-1-carboxylate (8)

1\1\GINC-LOCALHOST\FOpt\RB3LYP\def2TZVP\C12H18O2\PIOTR\10-Jun-2021\0\\
#P B3LYP/Def2TZVP FOpt(tight) geom(noangle, nodistance) fcheck #P SCRF
(Solvent=C6H5Cl) freq(noraman, readIso)\\Adamantane-1-COOMe, Cs\\0,1\C
,0.0323820358,0.5890107561,1.2601009196\C,-0.381943011,-0.2154764217,0
.\C,1.5523347218,0.8180478677,1.255819569\C,2.2797145227,-0.536386975,
1.2556866602\C,0.3636394016,-1.5648904415,0.\C,1.8826238212,-1.3295501
957,0.\C,2.2797145227,-0.536386975,-1.2556866602\C,0.0323820358,0.5890
107561,-1.2601009196\C,1.9464014441,1.6129039952,0.\C,1.5523347218,0.8
180478677,-1.255819569\H,2.0204685863,-1.1025378279,2.1558259702\H,-0.
2618294629,0.0390738893,2.1593284409\H,-0.4928542521,1.5457228282,1.27

74083538\H,1.8264346756,1.3839863532,2.150680457\H,3.3626737275,-0.380
6443119,1.2757833763\H,0.0711469567,-2.1477886665,-0.8766510903\H,0.07
11469567,-2.1477886665,0.8766510903\H,2.3913972782,-2.2975488888,0.\H,
3.3626737275,-0.3806443119,-1.2757833763\H,2.0204685863,-1.1025378279,
-2.1558259702\H,-0.4928542521,1.5457228282,-1.2774083538\H,-0.26182946
29,0.0390738893,-2.1593284409\H,1.448554517,2.5877068409,0.\H,3.023847
2114,1.803856859,0.\H,1.8264346756,1.3839863532,-2.150680457\C,-1.8860
946673,-0.4471183846,0.\O,-2.4307795403,-1.5275974035,0.\O,-2.57548337
22,0.7085493936,0.\C,-4.0097025123,0.6048755804,0.\H,-4.3543560066,0.0
775902858,0.8884962459\H,-4.3761636559,1.627493592,0.\H,-4.3543560066,
0.0775902858,-0.8884962459\\Version=ES64L-G09RevD.01\State=1-A'\HF=-61
8.8328136\RMSD=6.651e-09\RMSF=8.695e-06\Dipole=0.2872133,0.9286627,0.\
Quadrupole=3.4176739,-4.102947,0.6852731,-5.6418495,0.,0.\PG=CS [SG(C6
H4O2),X(C6H14)]\\@

9B

1\1\GINC-LOCALHOST\FOpt\RB3LYP\def2TZVP\C6H24B10N4\PIOTR\31-Oct-2021\0
\\#P B3LYP/Def2TZVP FOpt(tight) geom(noangle, nodistance) fcheck #P SC
RF(Solvent=C6H5Cl) freq(noraman, readIso)\\B10H10-1,10-(C(NHMe)2)2\\0,
1\B,0.5412829091,-0.7224686139,1.192705756\B,-0.46320736,-0.7689482673
,-1.213998735\B,1.2452955859,-0.6970798096,-0.5103343796\B,-1.16538886
96,-0.8091401613,0.4796928714\B,-0.5412829091,0.7224686139,1.192705756
\B,1.1653888696,0.8091401613,0.4796928714\B,0.46320736,0.7689482673,-1
.213998735\B,-1.2452955859,0.6970798096,-0.5103343796\B,-0.0972839564,
1.8236905286,-0.0095034585\B,0.0972839564,-1.8236905286,-0.0095034585\
H,0.980229033,-1.1068844294,2.2334556375\H,-0.871488422,-1.2170535824,
-2.2439557421\H,2.298035115,-1.0534703132,-0.9471102223\H,-2.172530070
6,-1.2923209612,0.9034306863\H,-0.980229033,1.1068844294,2.2334556375\
H,2.1725300706,1.2923209612,0.9034306863\H,0.871488422,1.2170535824,-2
.2439557421\H,-2.298035115,1.0534703132,-0.9471102223\C,0.0482824203,-
3.3940882573,-0.0603334229\N,-1.0376724637,-3.9530758401,-0.5951978799
\H,-1.7303957986,-3.3056614496,-0.9328339902\C,-0.0482824203,3.3940882
573,-0.0603334229\N,1.0376724637,3.9530758401,-0.5951978799\H,1.730395
7986,3.3056614496,-0.9328339902\C,1.2937712787,5.3743287684,-0.7482088
173\H,2.2627336971,5.5003291137,-1.2229364275\H,0.5385066826,5.8498502
878,-1.3794853966\H,1.3196666415,5.8817292613,0.2197427136\C,-1.293771
2787,-5.3743287684,-0.7482088173\H,-2.2627336971,-5.5003291137,-1.2229
364275\H,-0.5385066826,-5.8498502878,-1.3794853966\H,-1.3196666415,-5.
8817292613,0.2197427136\N,-1.0005955607,4.2060054947,0.3869753211\N,1.
0005955607,-4.2060054947,0.3869753211\H,-0.8466592894,5.2020703283,0.3
318037157\H,0.8466592894,-5.2020703283,0.3318037157\C,-2.2505223536,3.
8065744295,1.0184638225\H,-2.2028127306,3.9547053614,2.0986266297\H,-3
.0618524916,4.4112052285,0.6138332957\H,-2.4457459451,2.7612472743,0.8
105821293\C,2.2505223536,-3.8065744295,1.0184638225\H,2.2028127306,-3.
9547053614,2.0986266297\H,3.0618524916,-4.4112052285,0.6138332957\H,2.
4457459451,-2.7612472743,0.8105821293\\Version=ES64L-G09RevD.01\State=
1-A\HF=-711.0483759\RMSD=1.604e-09\RMSF=2.141e-06\Dipole=0.,0.,-0.1597
519\Quadrupole=-23.0660546,57.8499621,-34.7839076,0.4711488,0.,0.\PG=C
02 [X(C6H24B10N4)]\\

11B-a

1\1\GINC-LOCALHOST\FOpt\RB3LYP\def2TZVP\C4H14B10N2O1\PIOTR\12-Nov-2021
\0\\#P B3LYP/Def2TZVP FOpt(tight) geom(noangle, nodistance) fcheck #P
SCRF(Solvent=C6H5Cl) freq(noraman, readIso)\\B10H0-1-Imidazoline-10-CO
\\0,1\B,-0.9504130337,-0.922876835,2.2788366189\B,0.9504130452,0.92287
6835,2.2788366129\B,-0.9271803942,0.9461185798,2.2782975358\B,0.927180
4058,-0.9461185798,2.27829753\B,-0.0167848493,-1.3108762359,0.78945852

73\B,-1.3105114894,0.0156604309,0.7929758217\B,0.0167848516,1.31087623
59,0.7894585272\B,1.3105114917,-0.0156604309,0.7929758135\B,-0.0000000
022,0.,-0.2722514996\B,0.000000009,0.,3.3292807571\H,-1.7403414543,-1.
6954722945,2.714146801\H,1.7403414685,1.6954722945,2.7141467902\H,-1.6
976881099,1.7382636657,2.7132803405\H,1.6976881241,-1.7382636657,2.713
2803299\H,-0.0303476453,-2.421617817,0.3627498184\H,-2.422413592,0.029
8483169,0.3629957654\H,0.0303476448,2.421617817,0.3627498182\H,2.42241
35916,-0.0298483169,0.3629957503\C,0.0000000136,0.,4.7967869998\O,0.00
00000172,0.,5.9301561205\C,-0.0000000071,0.,-1.8327086004\C,-0.7721392
365,0.0467043765,-4.0305716396\H,-1.2389696628,-0.7608065531,-4.590832
3139\H,-1.1275034785,0.9995102284,-4.4248423479\C,0.7721392087,-0.0467
043765,-4.0305716444\H,1.2389696315,0.7608065531,-4.5908323216\H,1.127
5034482,-0.9995102284,-4.4248423549\N,-1.0802865468,-0.0583384973,-2.5
989436703\N,1.080286528,0.0583384973,-2.598943677\H,2.0107115741,0.029
9451651,-2.2170449686\H,-2.0107115906,-0.0299451651,-2.2170449561\\Ver
sion=ES64L-G09RevD.01\State=1-A\HF=-594.4670922\RMSD=7.476e-09\RMSF=1.
440e-06\Dipole=0.,0.,-4.4555556\Quadrupole=-9.2602978,-16.822417,26.08
27148,-0.1561628,0.0000001,0.\PG=C02 [C2(C1B1B1C1O1),X(C2H14B8N2)]\\@

[12B-a]$^-$

1\1\GINC-LOCALHOST\FOpt\RB3LYP\def2TZVP\C4H15B10N2O2(1-)\PIOTR\14-Nov-
2021\0\\#P B3LYP/Def2TZVP FOpt(tight) geom(noangle, nodistance) fcheck
#P SCRF(Solvent=C6H5Cl) freq(noraman, readIso)\\B10H0-1-Imidazoline-1
0-COOH, C1\\-1,1\B,0.9035966219,-0.9524763377,1.4656503714\B,-0.851049
2699,0.9731999616,1.4834715867\B,-0.9394548737,-0.8648248877,1.4771732
176\B,0.9915489965,0.8855517715,1.4632952265\B,1.318353117,-0.05137648
67,-0.047394394\B,-0.0468401081,-1.2921149471,-0.0241806257\B,-1.28983
55512,0.0758077101,-0.0257523253\B,0.07580446,1.3167828799,-0.02247248
09\B,0.0055678269,0.01322596,-1.0972219798\B,0.0357854014,0.0082163969
,2.5530243476\H,1.6578421675,-1.7821239925,1.8785385686\H,-1.599205626
7,1.8033086204,1.9070153698\H,-1.7636284331,-1.6200830352,1.8983020566
\H,1.8210760961,1.6381077523,1.8789073239\H,2.4310847826,-0.104512637,
-0.4805699745\H,-0.105743998,-2.4095445554,-0.4523010135\H,-2.40959120
04,0.1291379596,-0.4408434398\H,0.1268435282,2.4352914064,-0.448146038
4\C,-0.0057758913,0.0056253524,-2.6461580771\C,-0.0783481613,-0.782239
8464,-4.8398316992\H,0.688679762,-1.2652308778,-5.4420316582\H,-1.0589
513321,-1.1191732968,-5.1830519084\C,0.0395669659,0.7576862253,-4.8529
333849\H,-0.7343421202,1.2309506544,-5.4539906347\H,1.0161819155,1.088
6271586,-5.2128757915\N,0.0948606529,-1.0775083648,-3.4148088816\N,-0.
1169714404,1.0764527647,-3.4306247167\H,-0.0726510374,2.0080337775,-3.
0532284398\H,0.0587618426,-2.0026360614,-3.0209141023\C,0.0930481053,-
0.0000226469,4.1308532081\O,1.0883941538,0.0513189029,4.8361589948\O,-
1.1307617741,-0.0780774108,4.7498197109\H,-0.9537802981,-0.0757092902,
5.7059195939\\Version=ES64L-G09RevD.01\State=1-A\HF=-670.4860911\RMSD=
5.437e-09\RMSF=5.370e-06\Dipole=-0.6796893,-0.061791,-8.2870433\Quadru
pole=-11.3739007,0.0092741,11.3646266,-0.0322491,-7.1435445,-0.4107637
\PG=C01 [X(C4H15B10N2O2)]\\@

[*closo*-$B_{10}H_8$-1-$(CH_2NH)_2$C-1O-COOEt]$^-$ ([13B-a]$^-$)

1\1\GINC-LOCALHOST\FOpt\RB3LYP\def2TZVP\C6H19B10N2O2(1-)\PIOTR\08-Dec-
2021\0\\#P B3LYP/Def2TZVP FOpt(tight) geom(noangle, nodistance) fcheck
#P SCRF(Solvent=C6H5Cl) freq(noraman, readIso)\\B10H0-1-Imidazoline-1
0-COOEt, C1\\-1,1\B,1.4496810696,0.9136905115,1.0922682933\B,1.5459067
497,-0.8728713471,-0.8006751579\B,1.5308782083,0.9646013805,-0.7488092
218\B,1.4635675053,-0.926903776,1.0403598757\B,-0.0685360444,-0.027166
6156,1.3837327554\B,-0.0082522764,1.3141794112,0.1180739371\B,0.048046
2382,0.0463065994,-1.2234983301\B,0.012114886,-1.2952562988,0.04276433

52\B,-1.0708901146,0.0023182835,0.0328681494\B,2.5792196209,0.02679997
05,0.1949581807\H,1.8259163932,1.6867386482,1.922048145\H,2.0026603602
,-1.6415317873,-1.593894523\H,1.9745668222,1.7842299088,-1.4971295911\
H,1.8516500083,-1.7397758985,1.8254332248\H,-0.5420699168,-0.062243149
6,2.480832013\H,-0.443321214,2.4306460634,0.1284671189\H,-0.3272534158
,0.0761335665,-2.3584518675\H,-0.4045379847,-2.4174784101,-0.008699984
6\C,-2.6179387131,-0.00327541,-0.0396847795\C,-4.8132842295,0.76298868
61,-0.2136242596\H,-5.4552703087,1.2457831313,0.5205408619\H,-5.113520
8375,1.0893579092,-1.2117958912\C,-4.8178227304,-0.7758718727,-0.08480
56316\H,-5.380894932,-1.260307263,-0.8801461684\H,-5.2164701492,-1.103
4660103,0.8778329101\N,-3.4006514767,1.0729785197,0.0231971671\N,-3.38
71828924,-1.0820607807,-0.17785346\H,-3.0026425281,-2.0097138029,-0.11
64815251\H,-3.0139948754,2.0015198277,-0.0002261965\C,4.1569309181,0.0
387100855,0.3036682525\O,4.823273712,0.0204791671,1.3264285675\O,4.788
3285479,0.0746820783,-0.9127526128\C,6.2258852778,0.0895190127,-0.9096
472535\C,6.6965016881,0.1269494046,-2.348126387\H,6.594920644,-0.79891
13197,-0.3925271476\H,6.5765892513,0.9612066206,-0.3527993406\H,7.7881
192474,0.1388137599,-2.3811408299\H,6.3470203245,-0.7489971508,-2.8970
576465\H,6.3291224365,1.0195246467,-2.8571146421\\Version=ES64L-G09Rev
D.01\State=1-A\HF=-749.1309787\RMSD=4.271e-09\RMSF=2.079e-06\Dipole=-6
.5793464,0.0056314,-1.5878477\Quadrupole=27.686914,-7.412282,-20.27463
2,0.4871186,-8.9963123,-0.1566658\PG=C01 [X(C6H19B10N2O2)]\\

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