

Supplementary Material

Direct Synthesis of *C*-substituted [RC(O)CH₂-CB₁₁H₁₁]⁻ Carborate Anions

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S1. Numbering Scheme for the $[\text{RC}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$ Anions

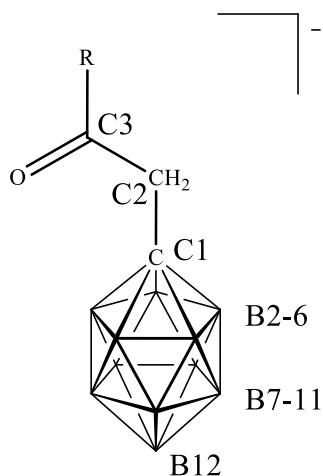


Figure S1. Numbering scheme for the $[\text{RC}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$ anions.

S2. Experimental Details and Spectroscopic Data

General remarks: All compounds are stable to air and moisture. The reactions were carried out under atmospheric air and pressure.

Starting materials: NaBH_4 (98 %, Abcr), NH_3 (aq) (≥ 25 %, Roth), dichloromethane (VWR), diethyl ether (≥ 99.5 %, Roth), CuCl (Roth), sodium ascorbate (Alfa Aesar), NEt_3 (99.5 %, Acros), NH_4Cl (98 %, Aldrich), Na_2SO_4 (technical) and KOH (85 %, Grüssing) were used without further work up. HCCCO_2Et (99 %, Alfa Aesar) was freshly distilled. HCCCO_2Me (99 %, Thermo Scientific), $\text{HCCCO}_2\text{NH}_2$ (96%, Thermo Scientific), and HCCCOMe (98%, Thermo Scientific) were used as received. $\text{K}_2[\text{B}_{11}\text{H}_{11}]$ was synthesised by oxidation of $[\text{B}_{11}\text{H}_{14}]^-$ with PbO_2 as described.[1-3] $[\text{Me}_3\text{NH}][\text{B}_{11}\text{H}_{14}]$ was synthesised according to literature.[4,5]

NMR spectroscopy: Nuclear magnetic resonance measurements were performed on either a BRUKER Avance 400 spectrometer with following probe heads: 5 mm broadband BBFO probe with automatic frequency tuning, 5 mm QNP probe (^1H / ^{13}C), and 5 mm broadband inverse probe or on a BRUKER Avance III 600 spectrometer with the probe heads 5 mm broadband inverse with automatic frequency tuning and a 3 mm QXI quadrupole resonance inverse probe head (^1H / ^{13}C). Acetonitrile- d_3 and water- d_2 (Deutero) were used as solvents.

Table S1. Resonance frequencies and standards of measured nuclei.

Nuclei	Resonance frequencies [MHz]		Standard
	BRUKER Avance 400	BRUKER Avance III 600	
^1H	400.13	600.27	$(\text{CH}_3)_4\text{Si}$
^{11}B	128.38	192.59	$\text{BF}_3 \cdot \text{OEt}_2$
^{13}C	100.63	150.95	$(\text{CH}_3)_4\text{Si}$
^{14}N	28.91	-	CH_3NO_2

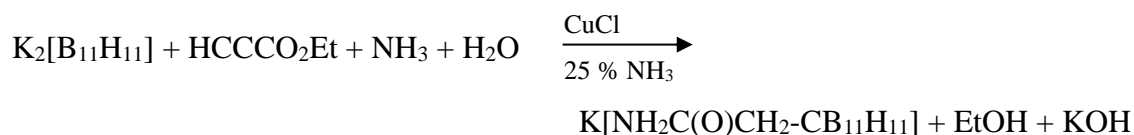
Vibrational spectroscopy: Vibrational spectroscopic measurements were performed on a Bruker VERTEX 70 spectrometer with a diamond ATR unit. The samples were investigated in a frequency range from 4000 cm^{-1} to 400 cm^{-1} .

Mass spectroscopy: Mass spectra were analysed on a Bruker Daltonics micrOTOF mass spectrometer with Agilent 1100 Series liquid chromatograph (LC) in negative mode by electrospray ionisation (ESI).

Thermal analysis: The use of a Netzsch STA 449 F5 Jupiter provided thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. The sample was heated in a $40\text{ }\mu\text{L}$ aluminium crucible with an aluminium lid in a nitrogen atmosphere with a heating rate of 5 K/min with a constant nitrogen flow of 25 mL/min during the measurement.

Crystal structure determinations: The data collection was performed using an Oxford Diffraction Gemini E Ultra diffractometer with a $2\text{K} \times 2\text{K}$ EOS CCD camera, a four-circle goniometer with κ geometry, a sealed-tube Mo radiation source, and an Oxford Instruments Cryojet cooling unit. Processing of the raw data, scaling of diffraction data, and the application of an empirical absorption correction were performed with the *CrysAlisPro* program.^[6] The structures were solved by direct methods and refined against F^2 .^[7-9] The graphics were prepared with the program *Diamond*.^[10]

S2.1. Synthesis of K[NH₂C(O)CH₂-CB₁₁H₁₁] with K₂[B₁₁H₁₁] and Ethyl Propiolate



Reaction 2.1.1

Equimolar amounts of CuCl / work up method 1:

In a 250 mL beaker 1 mL (9.867 mmol, 2.32 eq.) of HCCCO₂Et was placed and mixed with 20 mL of a 25% aqueous NH₃ solution. While stirring the solution CuCl (0.421 g, 4.253 mmol, 1.00 eq.) was added and the colour of the solution changed from blue to green. After stirring for 15 minutes at room temperature, ca. 100 mg of sodium ascorbate were added. This turned the green solution brown and produced a yellow solid. After stirring 10 minutes, K₂B₁₁H₁₁ (1.004 g, 4.822 mmol, 1.13 eq.) was added. After stirring for another 2 hours, the suspension was filtered off and triethylamine and [NH₄]Cl were added to the mixture. Following extraction three times each with 70 mL dichloromethane and drying of the organic phase with sodium sulphate. After removal of the solvent under reduced pressure, 1.238 g (4.096 mmol, 85 %) [Et₃NH][NH₂C(O)CH₂-CB₁₁H₁₁] was obtained as an orange solid.

To synthesized the potassium salt, [Et₃NH][NH₂C(O)CH₂-CB₁₁H₁₁] was mixed with KOH (1.422 g, 21.543 mmol, 5.26 eq.) dissolved in 3 mL deionised water and extracted three times each with 50 mL diethyl ether. The solvent was removed under reduced pressure and 0.514 g (2.149 mmol, 45 %) K[NH₂C(O)CH₂-CB₁₁H₁₁] was obtained (total yield based on the amount of K₂[B₁₁H₁₁] used: 38 %). This compound was crystallised from water and gave colourless needles which could be examined by x-ray.

NMR data for [Et₃NH][NH₂C(O)CH₂-CB₁₁H₁₁]:

¹H{¹¹B} NMR (400.13 MHz, CD₃CN, 300 K): δ = 1.27 (t, ³J_{HH} = 7.3 Hz, 9H, [HN(CH₂CH₃)₃]⁺), 1.50 (s, 6H, [NH₂C(O)CH₂-CB₁₁H₁₁]⁻), 1.78 (s, 5H, [NH₂C(O)CH₂-CB₁₁H₁₁]⁻), 2.61 (s, 2H, [NH₂C(O)CH₂-CB₁₁H₁₁]⁻), 3.12 (t, ³J_{HH} = 7.3 Hz, 6H, [HN(CH₂CH₃)₃]⁺), 4.68 (s, 1H, [HN(CH₂CH₃)₃]⁺), 5.53 (s, 1H, [NH₂C(O)CH₂-CB₁₁H₁₁]⁻), 5.89 (s, 1H, [NH₂C(O)CH₂-CB₁₁H₁₁]⁻).

^{11}B NMR (128.38 MHz, CD_3CN , 300 K): $\delta = -13.2$ (d, $^1J_{\text{BH}} = 144$ Hz, 10B, $B(2-11)\text{-H}$), -9.6 (d, $^1J_{\text{BH}} = 138$ Hz, 1B, $B12\text{-H}$).

^{14}N NMR (28.91 MHz, CD_3CN , 300 K): $\delta = -135.6$ (s, $[\text{Et}_3\text{NH}][\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$).

NMR data for $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$:

$^1\text{H}\{^{11}\text{B}\}$ NMR (400.13 MHz, D_2O , 300 K): $\delta = 2.06$ (s, 6H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 2.40 (s, 5H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 3.31 (s, 2H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 7.06 (s, 1H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 7.26 (s, 1H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$).

^{11}B NMR (128.38 MHz, D_2O , 300 K): $\delta = -12.7$ (d, $^1J_{\text{BH}} = 136$ Hz, 10B, $B(2-11)\text{-H}$), -9.5 (d, $^1J_{\text{BH}} = 130$ Hz, 1B, $B12\text{-H}$).

^{13}C NMR (100.62 MHz, D_2O , 300 K): $\delta = 176.9$ (t, $^2J_{\text{CH}} = 6$ Hz, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 67.4 (s, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 48.0 (t, $^1J_{\text{CH}} = 133$ Hz, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$).

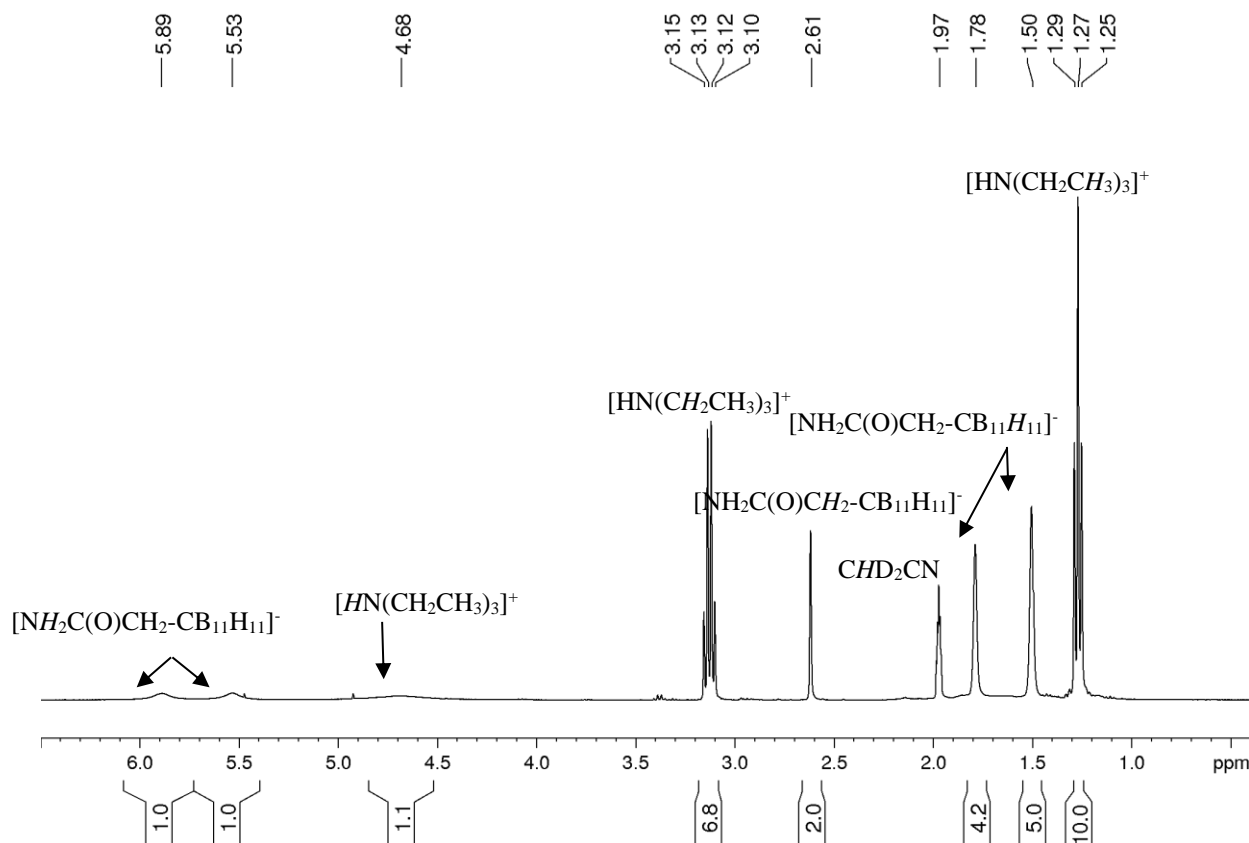


Figure S2. $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum (400.13 MHz, CD_3CN , 300 K) of $[\text{Et}_3\text{NH}][\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$. Note that the integrals of the resonances of $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$ are underdetermined by about 20%. This is caused by the $^1\text{H}\{^{11}\text{B}\}$ decoupling process which does not include $^1\text{H}\{^{10}\text{B}\}$ couplings. The natural ratio of ^{11}B to ^{10}B is approximately 80 to 20.

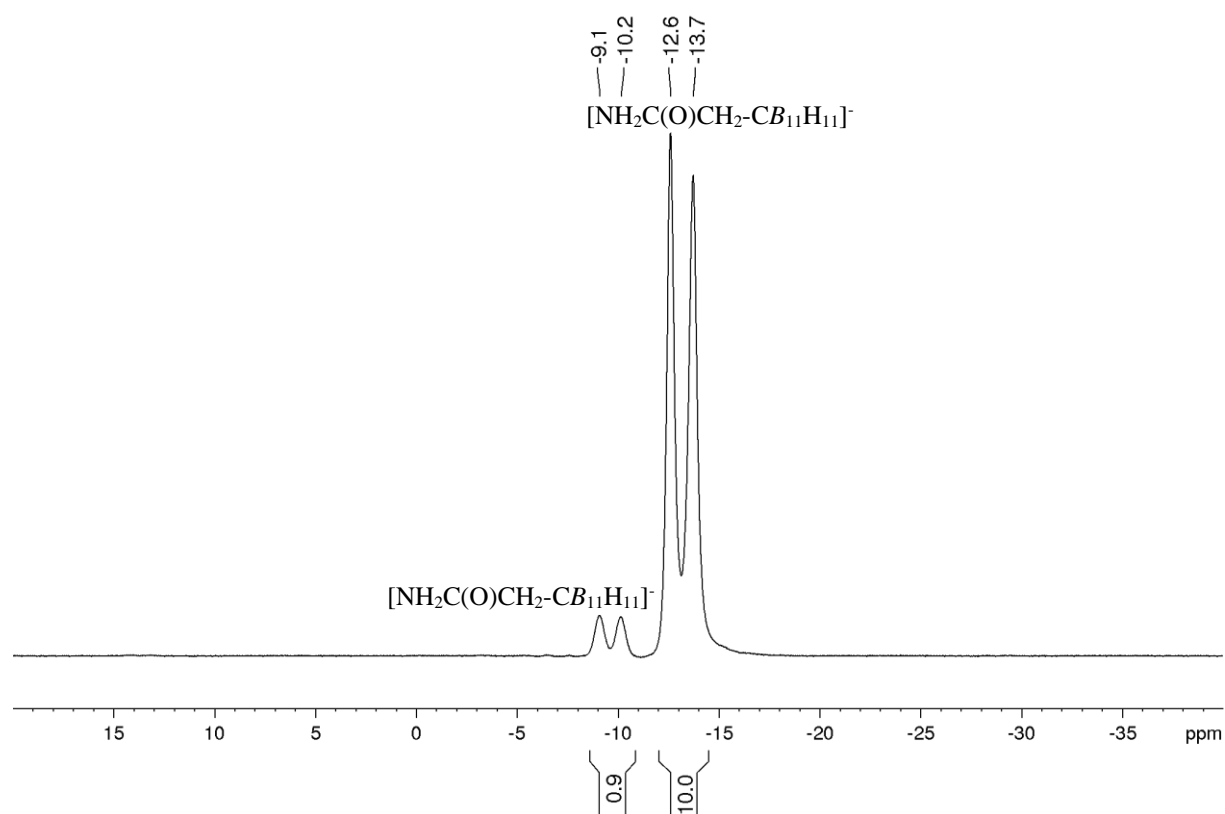


Figure S3. ^{11}B NMR spectrum (128.38 MHz, CD_3CN , 300 K) of $[\text{Et}_3\text{NH}][\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

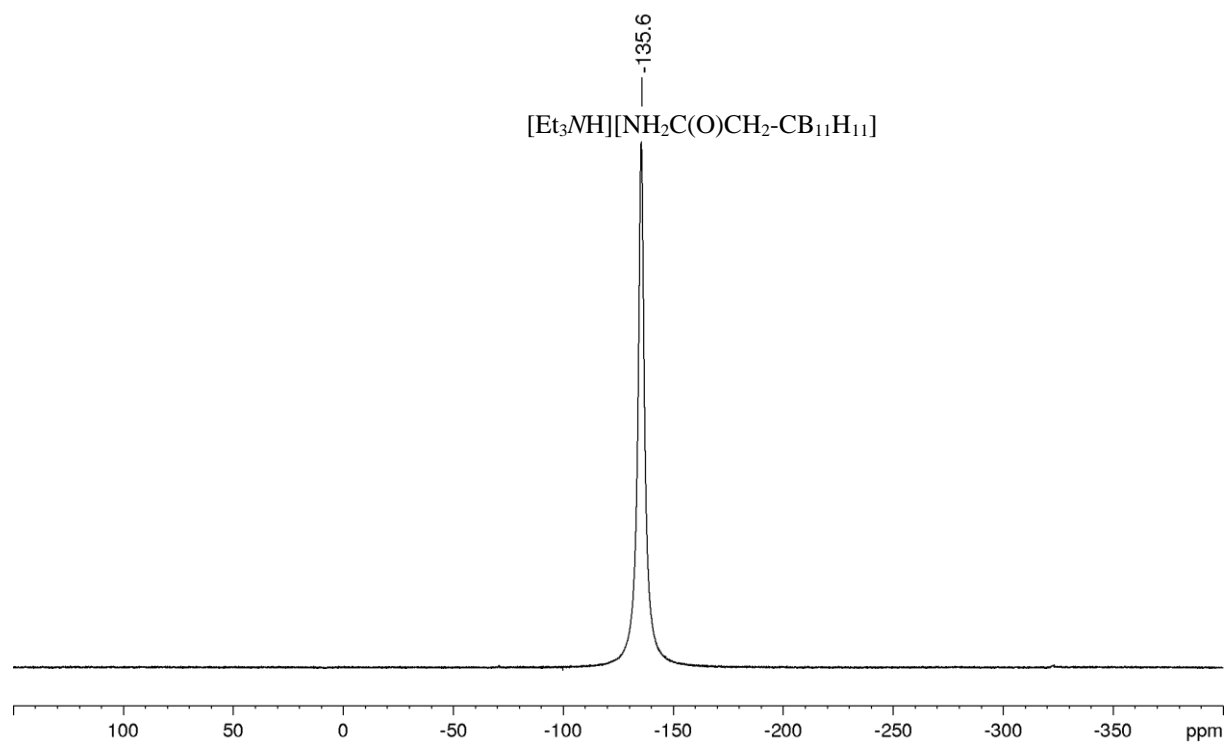


Figure S4. ^{14}N NMR spectrum (28.91 MHz, CD_3CN , 300 K) of $[\text{Et}_3\text{NH}][\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

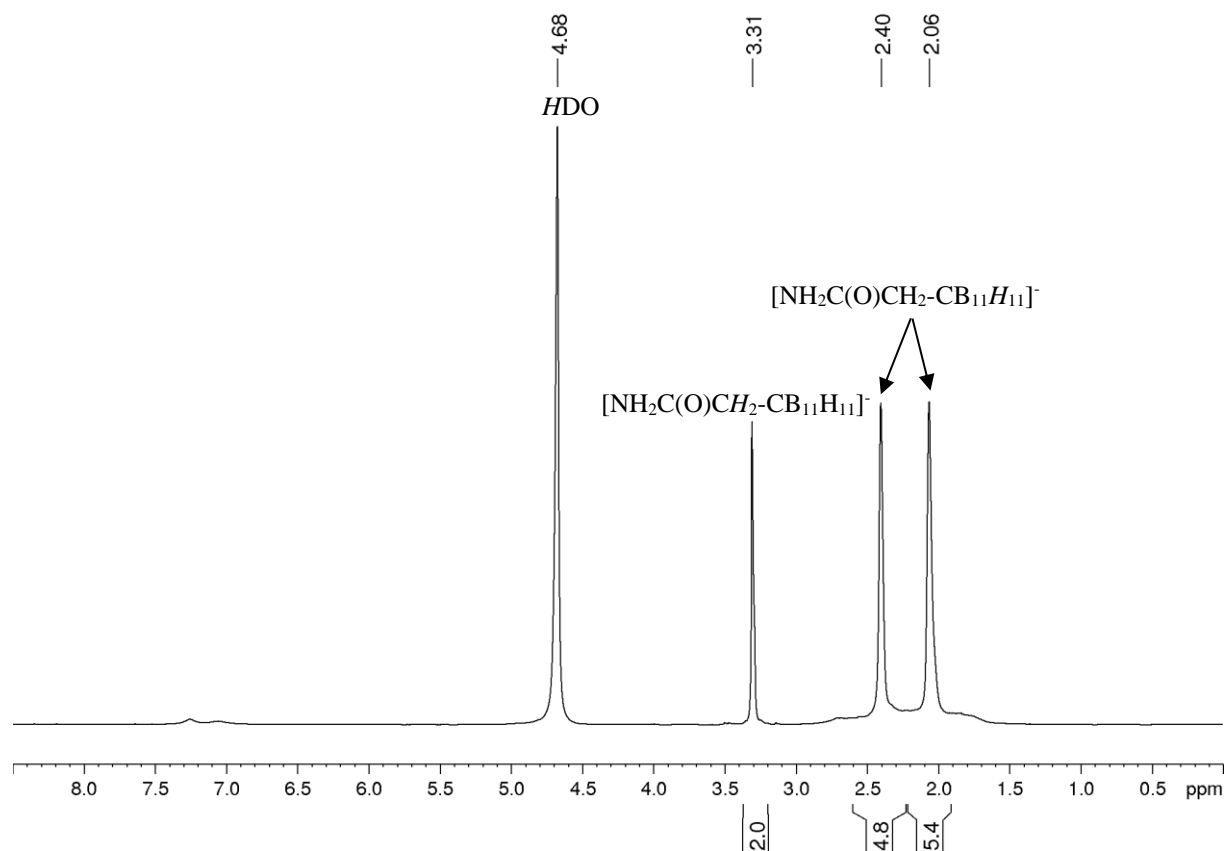


Figure S5. $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum (400.13 MHz, D_2O , 300 K) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

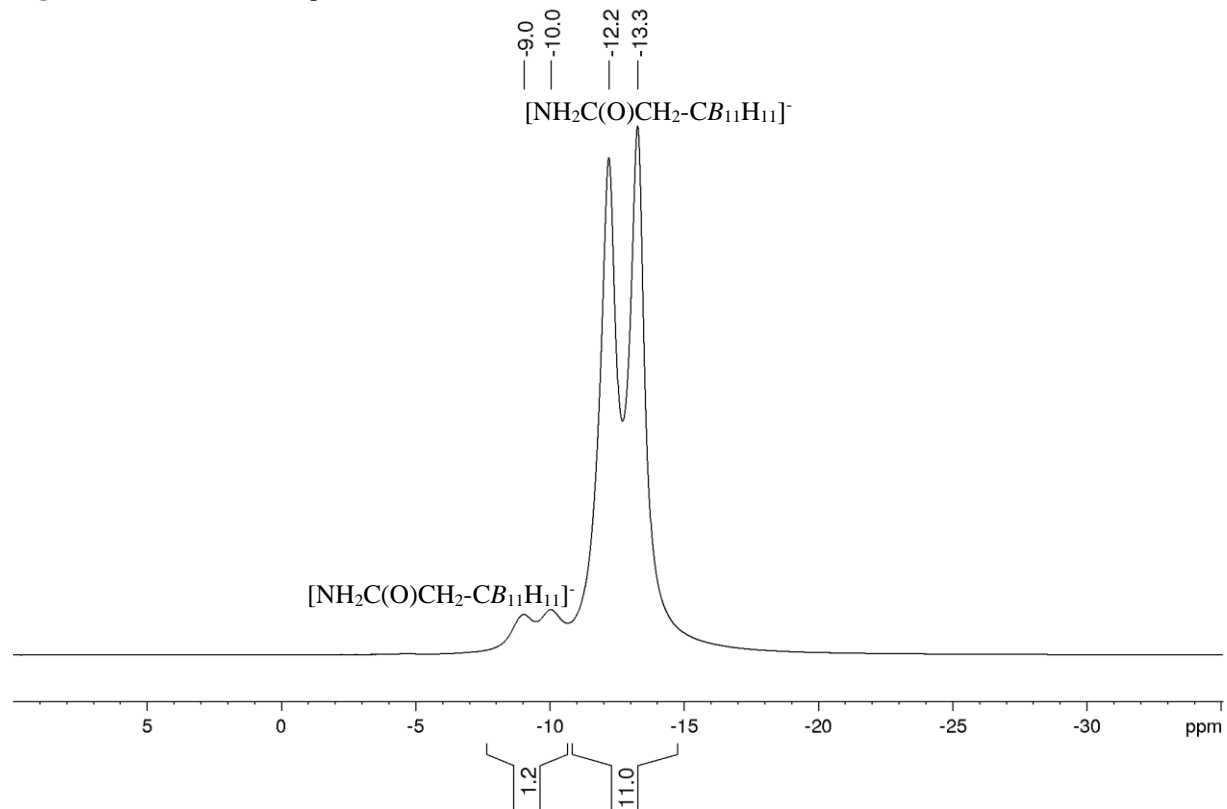


Figure S6. ^{11}B NMR spectrum (128.38 MHz, D_2O , 300 K) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

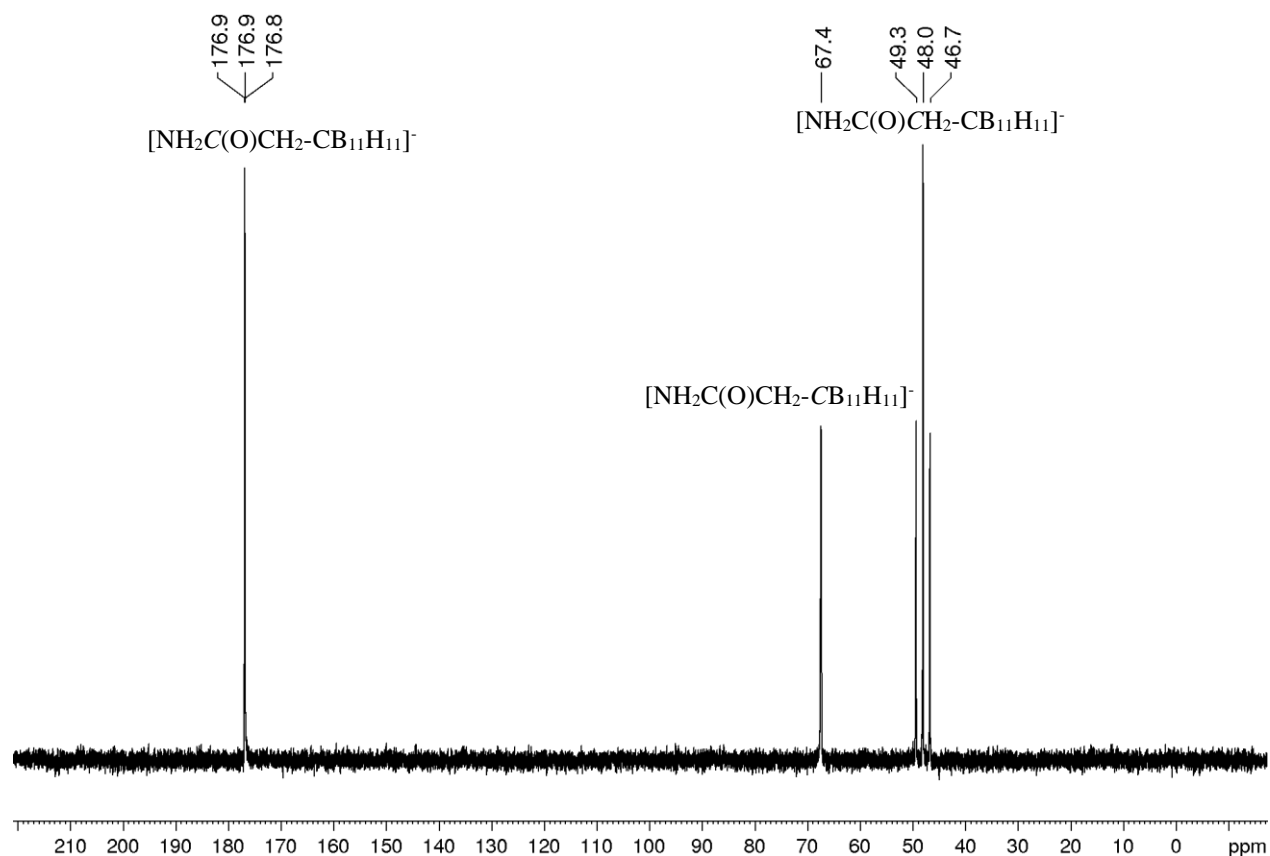


Figure S7. ^{13}C NMR spectrum (100.62 MHz, D_2O , 300 K) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

Reaction 2.1.2

Equimolar amounts of CuCl / work up method 2:

In a 50 mL beaker 0.5 mL (4.934 mmol, 2.06 eq.) of HCCCO_2Et was placed and mixed with 10 mL of a 25% aqueous NH_3 solution. While stirring the solution CuCl (0.237 g, 2.394 mmol, 1.00 eq.) was added and the colour of the solution changed from blue to green. After stirring for 15 minutes at room temperature, ca. 100 mg of sodium ascorbate were added. This turned the green solution brown and produced a yellow solid. After stirring 10 minutes, $\text{K}_2[\text{B}_{11}\text{H}_{11}]$ (0.497 g, 2.387 mmol, 1.00 eq.) was added. After stirring for another 3 hours, carefully 14 mL of concentrated hydrochloric acid and 0.7 mL of triethylamine were added to the mixture. Following extraction three times each with 50 mL dichloromethane and drying of the organic phase with sodium sulphate. After removal of the solvent under reduced pressure, 0.367 g (1.214 mmol, 51 %) of $[\text{Et}_3\text{NH}][\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$ was obtained as an orange solid.

To synthesized the potassium salt, $[\text{Et}_3\text{NH}][\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$ (0.357 g, 1.181 mmol, 1.00 eq.) was mixed with KOH (0.485 g, 8.644 mmol, 7.32 eq.) dissolved deionised water and stirred for 10 minutes at room temperature. The aqueous solution was reduced and extracted three times each with 50 mL diethyl ether. The organic solvent was dried with potassium carbonate and removed under reduced pressure. A white solid was obtained, which was dried high vacuum (0.215 g, 0.899 mmol, 76 %). The total yield based on the amount of $\text{K}_2[\text{B}_{11}\text{H}_{11}]$ used: 39 %.

Analytical data for $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$:

$^1\text{H}\{^{11}\text{B}\}$ NMR (400.13 MHz, CD_3CN , 300 K): δ = 1.50 (s, 6H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 1.78 (s, 5H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 2.61 (s, 2H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 5.50 (s, 1H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 5.86 (s, 1H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$).

^{11}B NMR (128.38 MHz, CD_3CN , 300 K): δ = -13.2 (d, $^1J_{\text{BH}}$ = 144 Hz, 10B, *B*(2-11)-H), -9.6 (d, $^1J_{\text{BH}}$ = 138 Hz, 1B, *B*12-H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CD_3CN , 300 K): δ = 172.0 (s, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 65.3 (s, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 47.3 (s, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$).

ESI-MS [*m/z*]: found = 200.22 (calc. = 200.23, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$).

IR (diamond ATR): ν [cm^{-1}] = 3619 (m), 3474 (m), 3380 (m), 3292 (w), 3229 (m), 3205 (m), 2941 (w), 2563 (s), 2525 (s), 2495 (s), 2361 (w), 2341 (w), 1995 (w), 1665 (s), 1609 (s), 1443 (m), 1394 (m), 1305 (w), 1215 (m), 1176 (w), 1112 (m), 1045 (m), 966 (m), 946 (m), 818 (w), 720 (m), 683 (w), 649 (w), 584 (m), 526 (m), 456 (m), 434 (m).

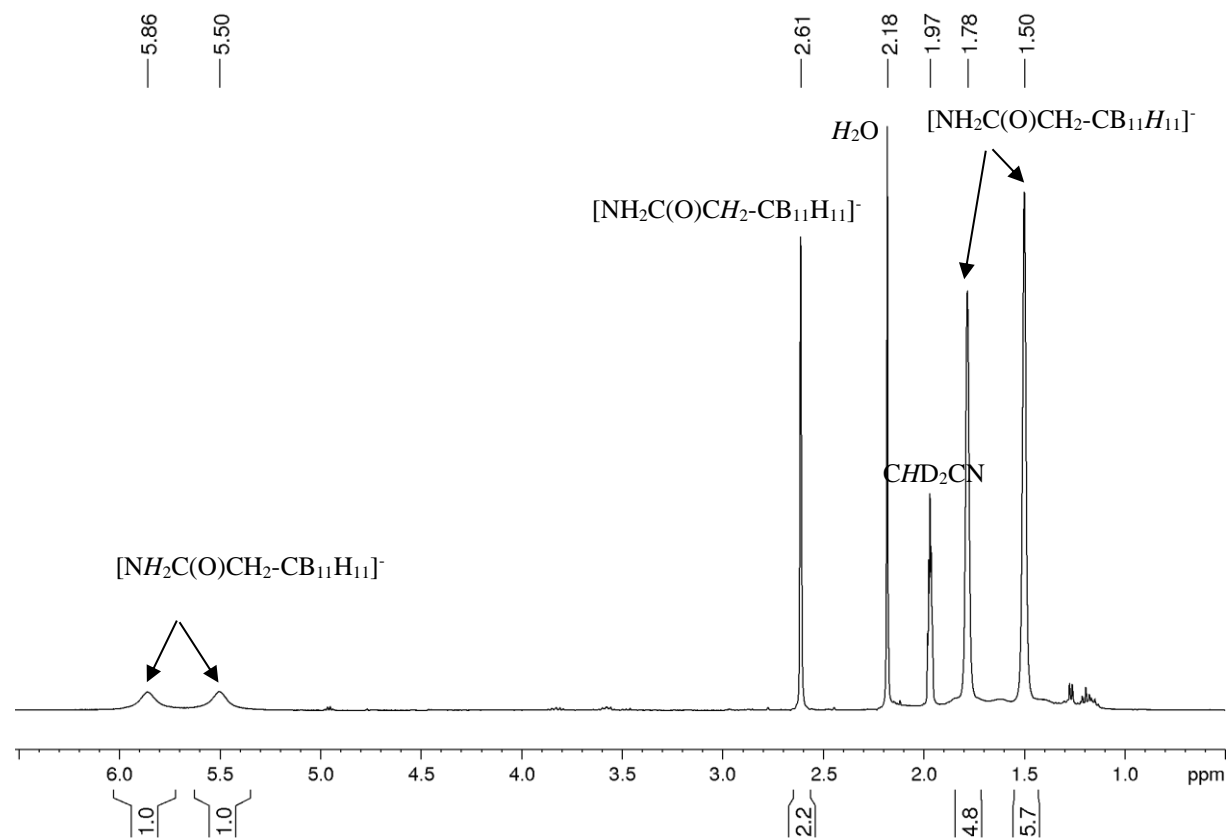


Figure S8. $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum (400.13 MHz, CD_3CN , 300 K) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

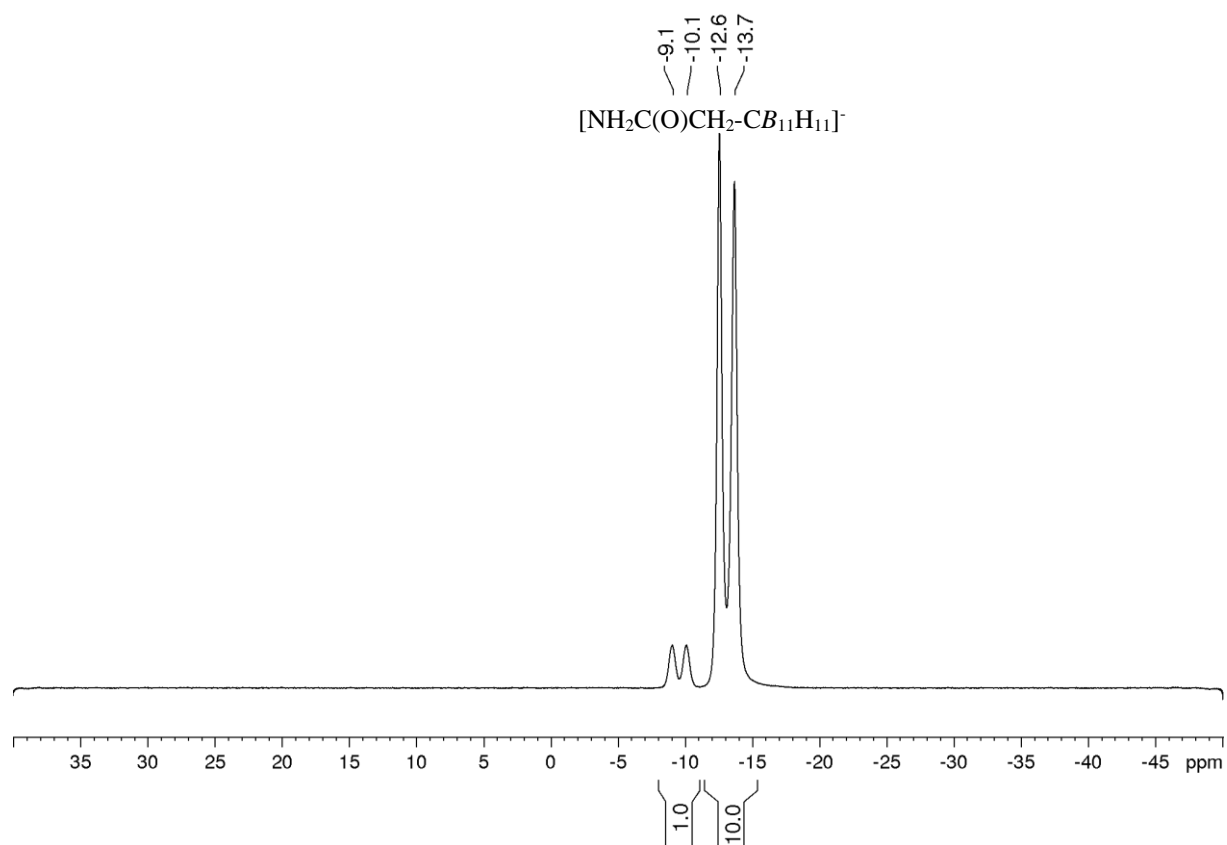


Figure S9. ^{11}B NMR spectrum (128.38 MHz, CD_3CN , 300 K) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

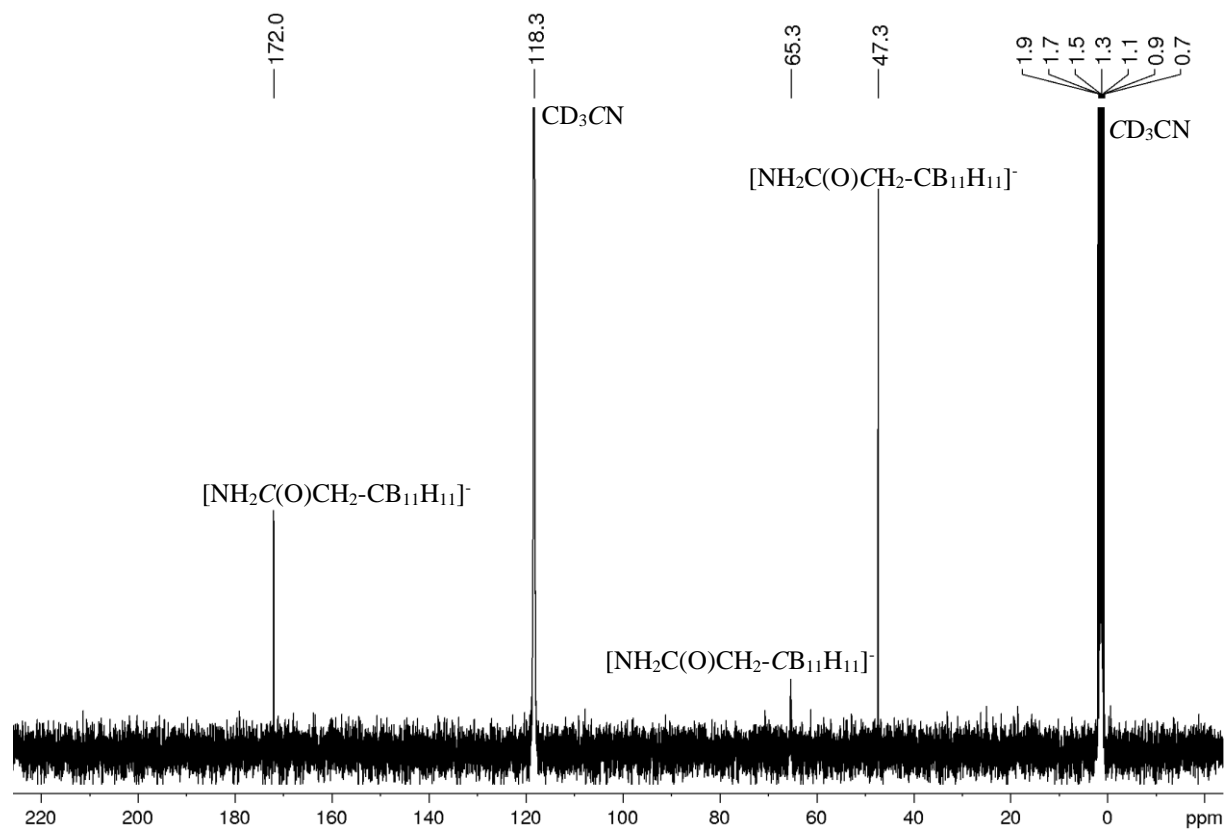


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.62 MHz, CD_3CN , 300 K) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

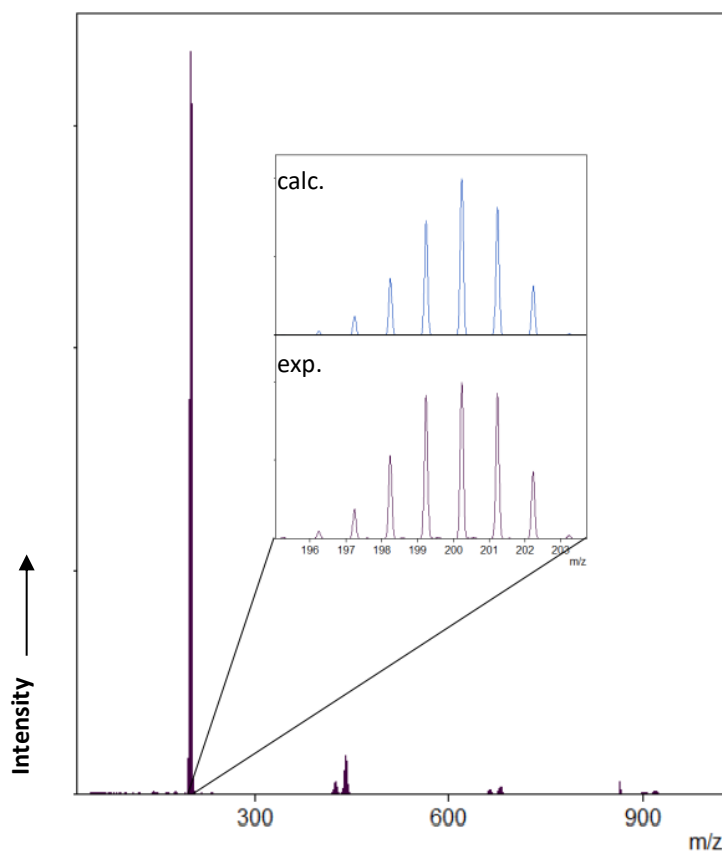


Figure S11. ESI-mass spectrum (negative mode) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$. The simulated mass spectrum is shown above.

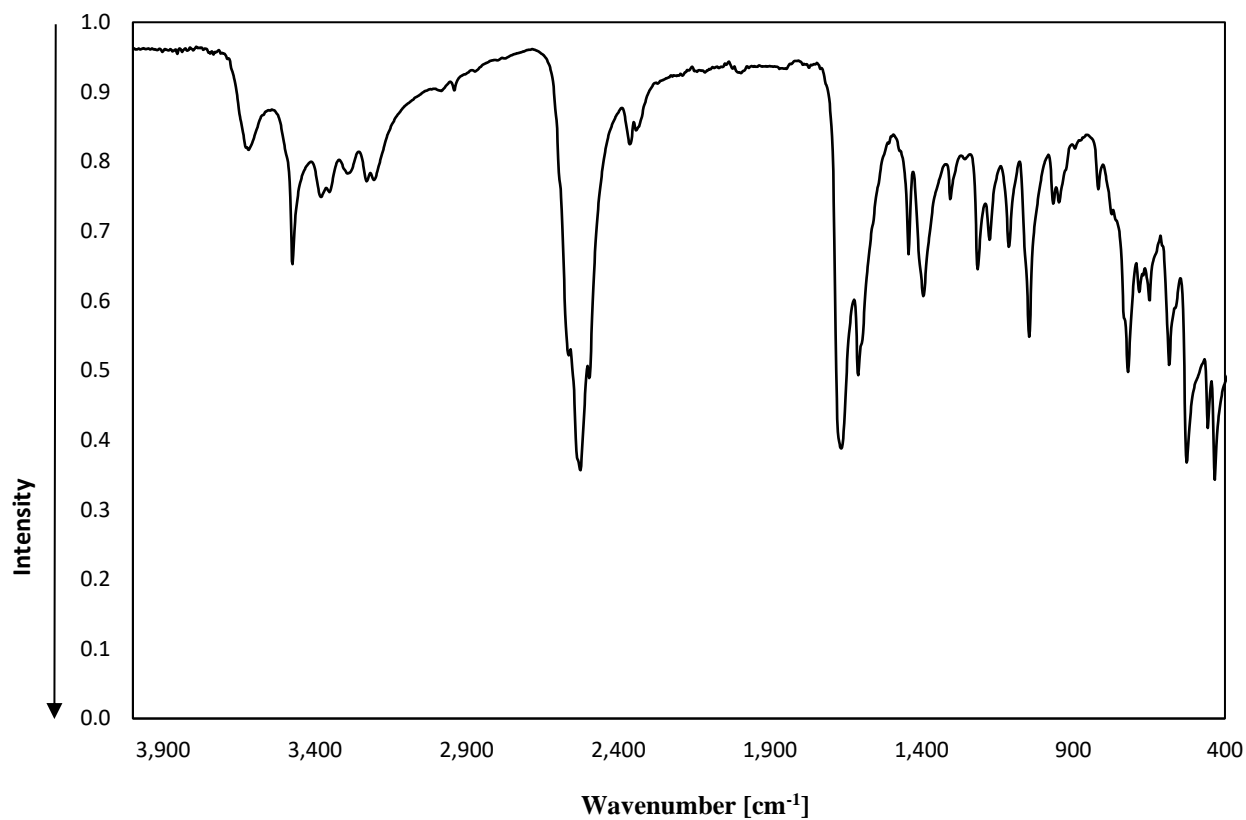


Figure S12. IR spectrum (diamond-ATR) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

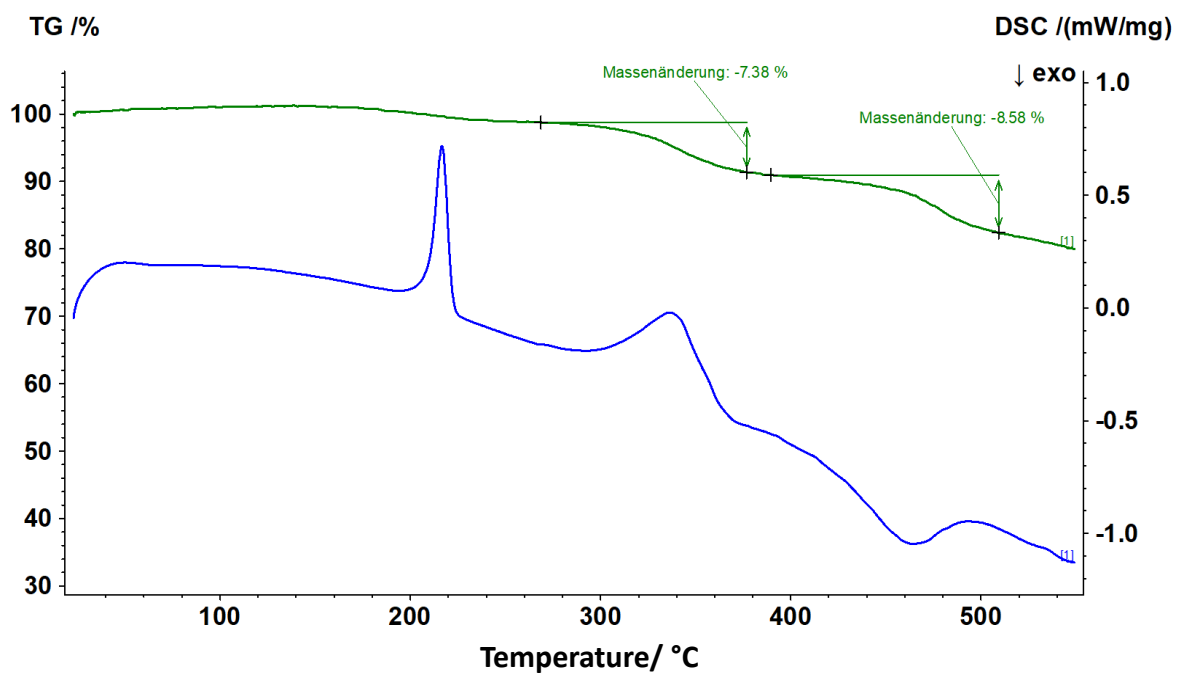


Figure S13. DSC/TGA of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$ until 550 °C.

Reaction 2.1.3

With catalytic amounts of CuCl:

In a 100 mL beaker CuCl (0.040 g, 0.404 mmol, 0.34 eq.) and sodium ascorbate (ca. 100 mg) was mixed with 20 mL of a 25% aqueous NH₃ solution. Ethyl propiolate (0.35 mL, 3.454 mmol, 2.90 eq.) was added to the blue solution. After stirring for 10 minutes, K₂[B₁₁H₁₁] (0.248 mg, 1.191 mmol, 1.00 eq.) was added. For one hour the reaction suspension was mixed at room temperature and then potassium carbonate was added until the solution was saturated. The precipitate formed was filtered off and the solution extracted three times with each 40 mL ethyl acetate. The combined organic phase was dried with sodium sulphate and removed under reduced pressure. The obtained light yellow solid was dried at high vacuum (0.239 mg, 0.999 mmol, 84 %). The solid consists of 38 % K[NH₂C(O)CH₂-CB₁₁H₁₁], 6 % K[CH₃CH₂OC(O)CH₂-CB₁₁H₁₁] and 57 % HCCC(O)NH₂ as well as solvent residues.

¹H{¹¹B} NMR (600.27 MHz, CD₃CN, 300 K): δ = 1.23 (t, ³J_{HH} = 7.1 Hz, 3H, [CH₃CH₂OC(O)CH₂-CB₁₁H₁₁]⁻/EtOAc), 1.50 (s, 6H, [NH₂C(O)CH₂-CB₁₁H₁₁]⁻/ [CH₃CH₂OC(O)CH₂-CB₁₁H₁₁]⁻), 1.75 (s, 1H, [CH₃CH₂OC(O)CH₂-CB₁₁H₁₁]⁻), 1.78 (s, 4H, [NH₂C(O)CH₂-CB₁₁H₁₁]⁻), 2.62 (s, 2H, [NH₂C(O)CH₂-CB₁₁H₁₁]⁻), 2.72 (s, 0.3H, [CH₃CH₂OC(O)CH₂-CB₁₁H₁₁]⁻), 3.24 (s, 1.4H, HCCC(O)NH₂), 4.09 (q, ³J_{HH} = 7.1 Hz, 1.3H, [CH₃CH₂OC(O)CH₂-CB₁₁H₁₁]⁻), 5.75 (s, 1H, [NH₂C(O)CH₂-CB₁₁H₁₁]⁻), 6.02 (s, 1H, [NH₂C(O)CH₂-CB₁₁H₁₁]⁻), 6.35 (s, 1.5H, HCCC(O)NH₂), 6.77 (s, 1.5H, HCCC(O)NH₂).

¹¹B NMR (192.59 MHz, CD₃CN, 300 K): δ = -13.2 (d, ¹J_{BH} = 142 Hz, 10B, B(2-11)-H), -9.6 (d, ¹J_{BH} = 135 Hz, 1B, B12-H).

¹³C{¹H} NMR (150.95 MHz, CD₃CN, 300 K): δ = 154.3 (HCCC(O)NH₂), 78.9 (HCCC(O)NH₂), 74.9 (HCCC(O)NH₂), 47.2 (s, [NH₂C(O)CH₂-CB₁₁H₁₁]⁻), 45.7 (s, [CH₃CH₂OC(O)CH₂-CB₁₁H₁₁]⁻).

ESI-MS [m/z]: found = 202.23 (calc. = 202.24, [ND₂C(O)CH₂-CB₁₁H₁₁]⁻), 229.23 (calc. = 229.24, [B₁₁H₁₁CCH₂C(O)OCH₂CH₃]⁻). The sample had been prior dissolved in deuterated solvent which caused an H/D exchange.

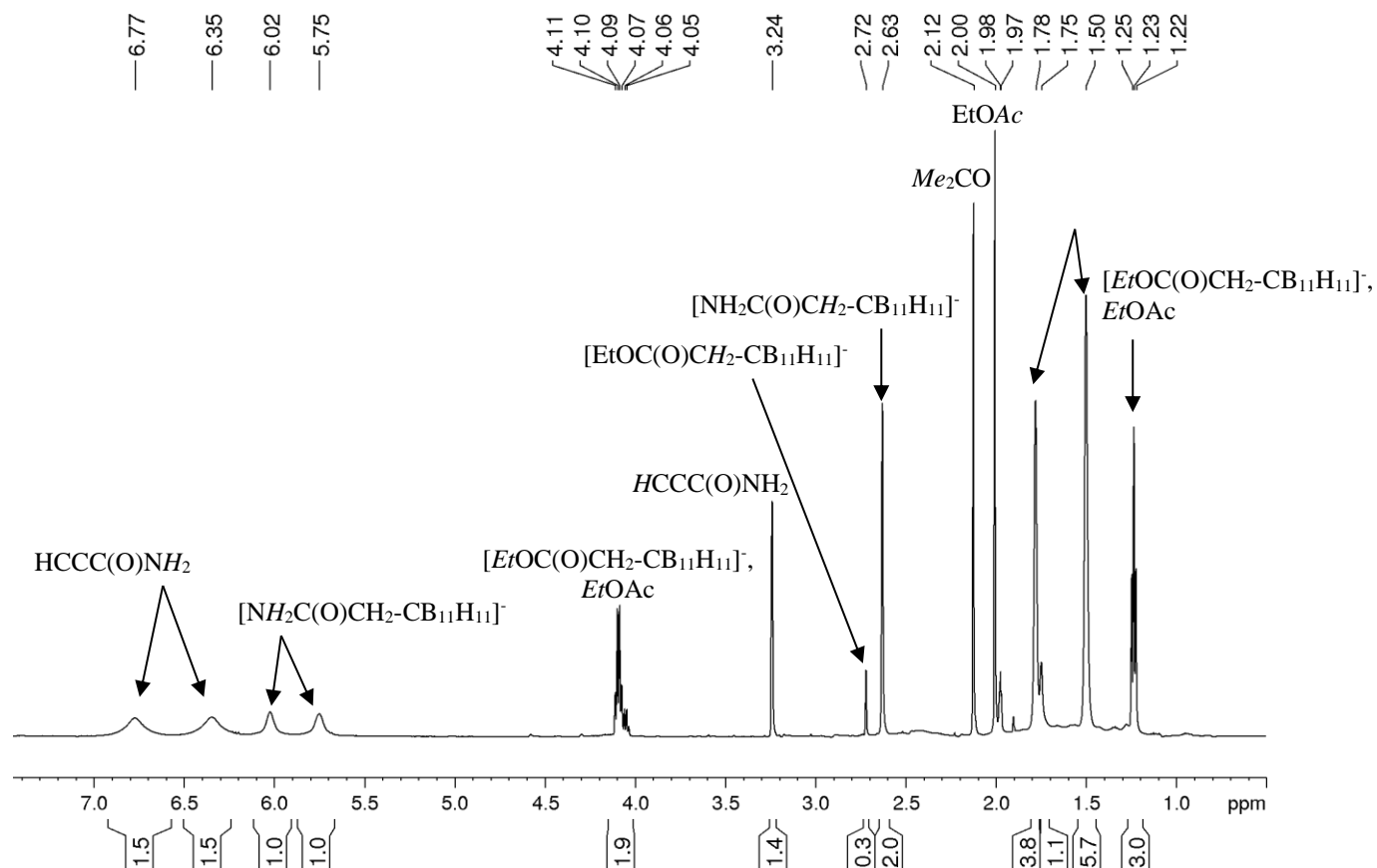


Figure S14. $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum (600.27 MHz, CD_3CN , 300 K) of reaction 2.1.3. The spectrum shows a mixture of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$ (38%), $\text{K}[\text{EtOC}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$ (6%) and $\text{HCCC}(\text{O})\text{NH}_2$ (57%).

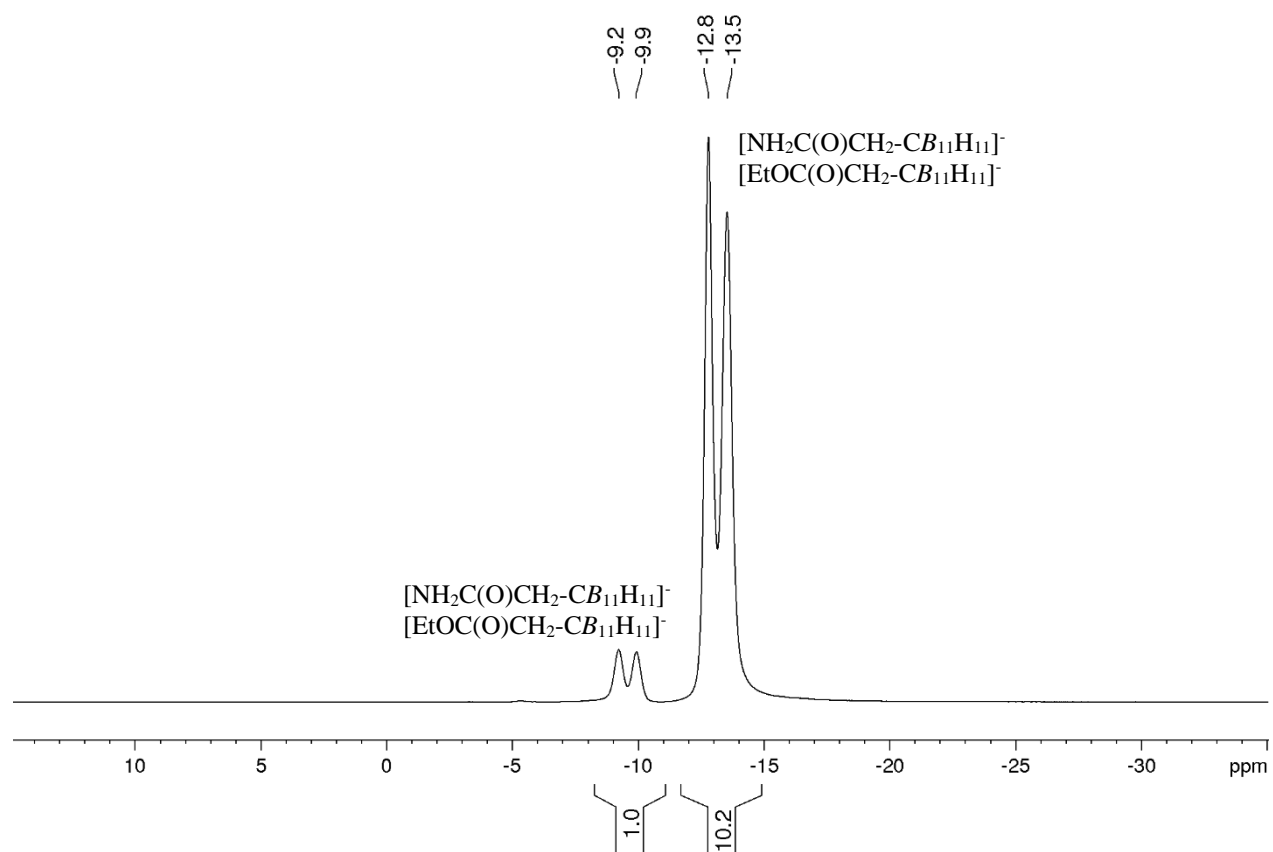


Figure S15. ^{11}B NMR spectrum (192.59 MHz, CD_3CN , 300 K) of reaction 2.1.3. The sample consists of a mixture of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$ (38%), $\text{K}[\text{EtOC}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$ (6%) and $\text{HCCC}(\text{O})\text{NH}_2$ (57%).

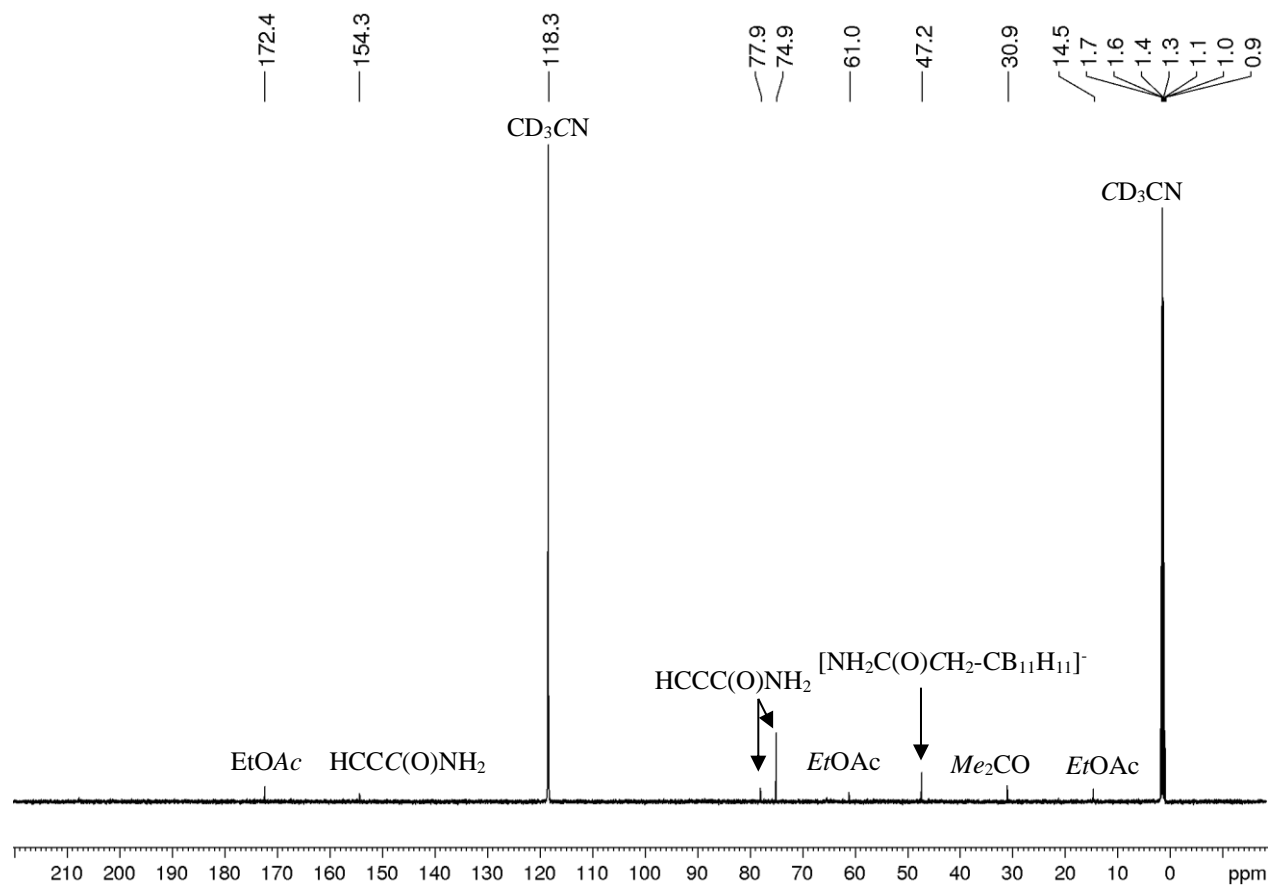


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (150.95 MHz, CD_3CN , 300 K) of reaction 2.1.3. The sample consists of a mixture of $\text{K}[\text{NH}_2\text{C(O)CH}_2\text{-CB}_{11}\text{H}_{11}]$ (38%), $\text{K}[\text{EtOC(O)CH}_2\text{-CB}_{11}\text{H}_{11}]$ (6%) and HCCC(O)NH_2 (57%). The small amount (6%) of $\text{K}[\text{EtOC(O)CH}_2\text{-CB}_{11}\text{H}_{11}]$ was not detected.

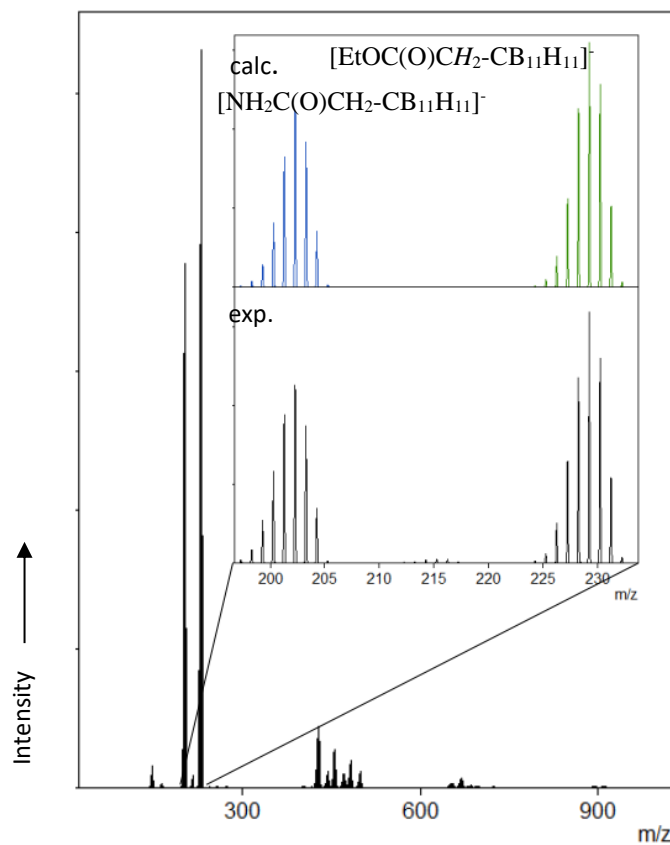


Figure S17. ESI-mass spectrum (negative mode) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$ and $\text{K}[\text{CH}_3\text{CH}_2\text{OC}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$. The simulated mass spectrum is shown above.

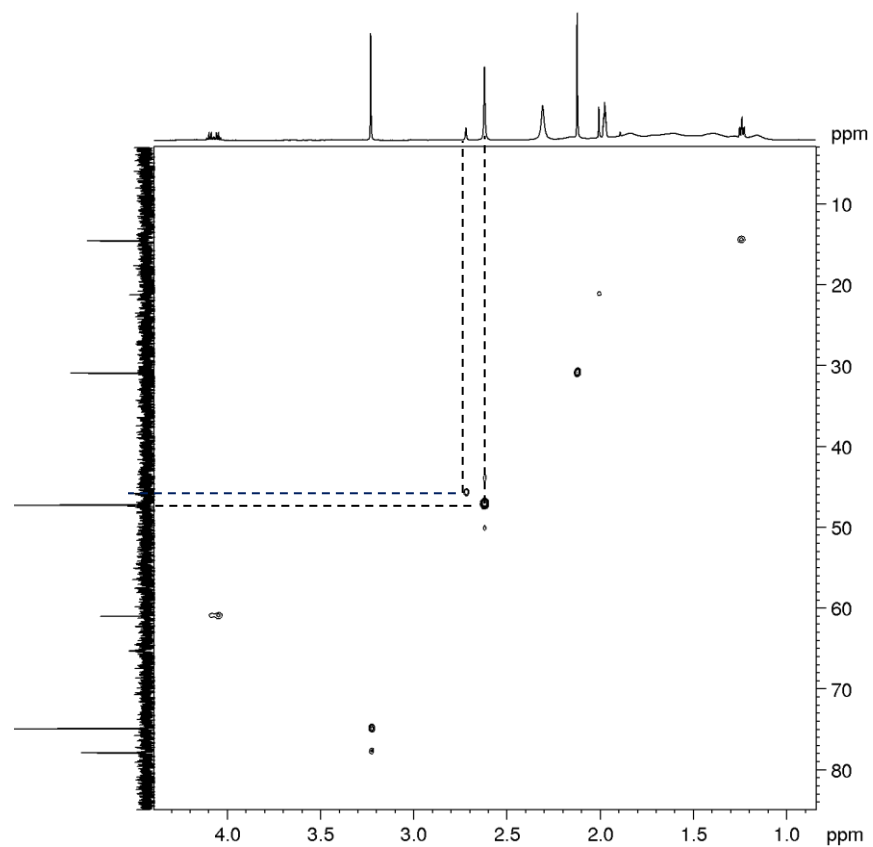


Figure S18. ^1H - ^{13}C HSQC NMR spectrum (600.27 MHz, 150.95 MHz, CD_3CN , 300 K) of reaction 2.1.3.

S2.2. Pyrolysis of K[NH₂C(O)CH₂-CB₁₁H₁₁]

In a thermogravimetric DSC/TGA experiment K[NH₂C(O)CH₂-CB₁₁H₁₁] was heated up to 350 °C in an aluminium crucible with a lid in a nitrogen atmosphere and hold at this temperature for 60 minutes. The obtained pyrolysis product was examined by NMR spectroscopy.

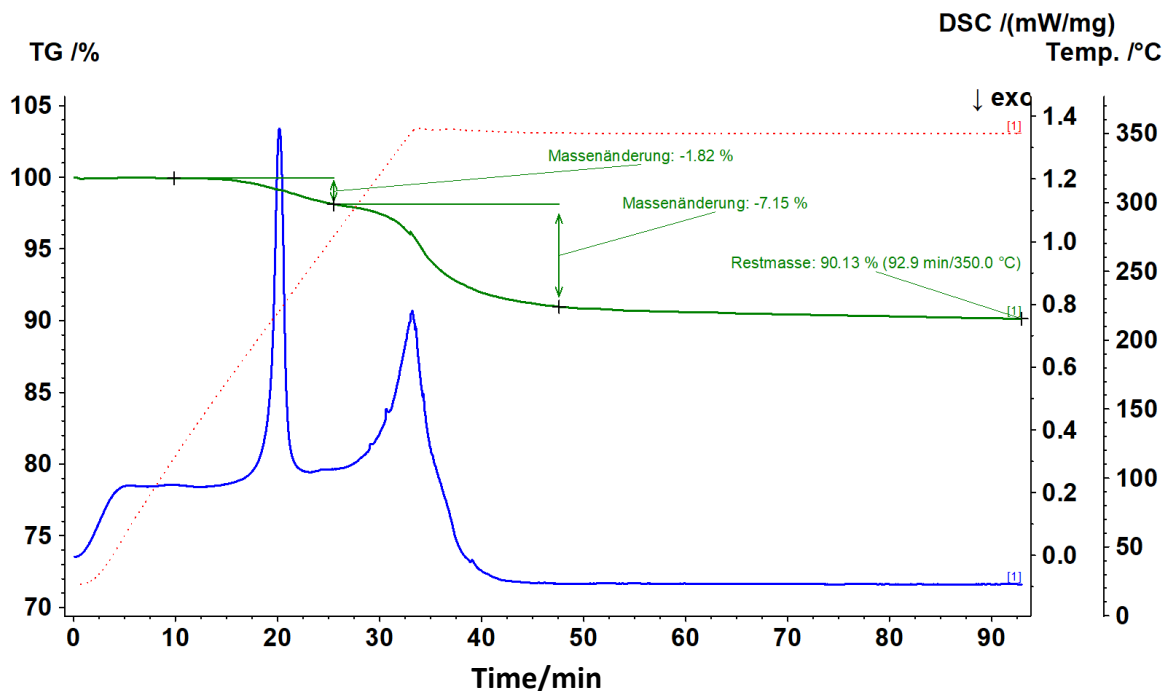


Figure S19. DSC/TGA of K[NH₂C(O)CH₂-CB₁₁H₁₁]. The solid was heated from room temperature to 350 °C with a heat rate of 5 K/min and hold at this temperature for 60 minutes.

¹H{¹¹B} NMR (400.13 MHz, CD₃CN, 300 K): δ = 1.54 (s, 6H, [NCCH₂-CB₁₁H₁₁]⁻), 1.79 (s, 5H, [NCCH₂-CB₁₁H₁₁]⁻), 2.96 (s, 2H, [NCCH₂-CB₁₁H₁₁]⁻).

¹¹B NMR (128.38 MHz, CD₃CN, 300 K): δ = -13.4 (d, ¹J_{BH} = 126 Hz d, 5B, B(2-11)-H), -12.7 (d, ¹J_{BH} = 102 Hz, 10B, B(2-11)-H), -9.5 (d, ¹J_{BH} = 136 Hz, 1B, B12-H).

¹³C{¹H} NMR (150.95 MHz, CD₃CN, 300 K): δ = 118.6 ([NCCH₂-CB₁₁H₁₁]⁻), 61.4 ([NCCH₂-CB₁₁H₁₁]⁻), 29.1 ([NCCH₂-CB₁₁H₁₁]⁻).

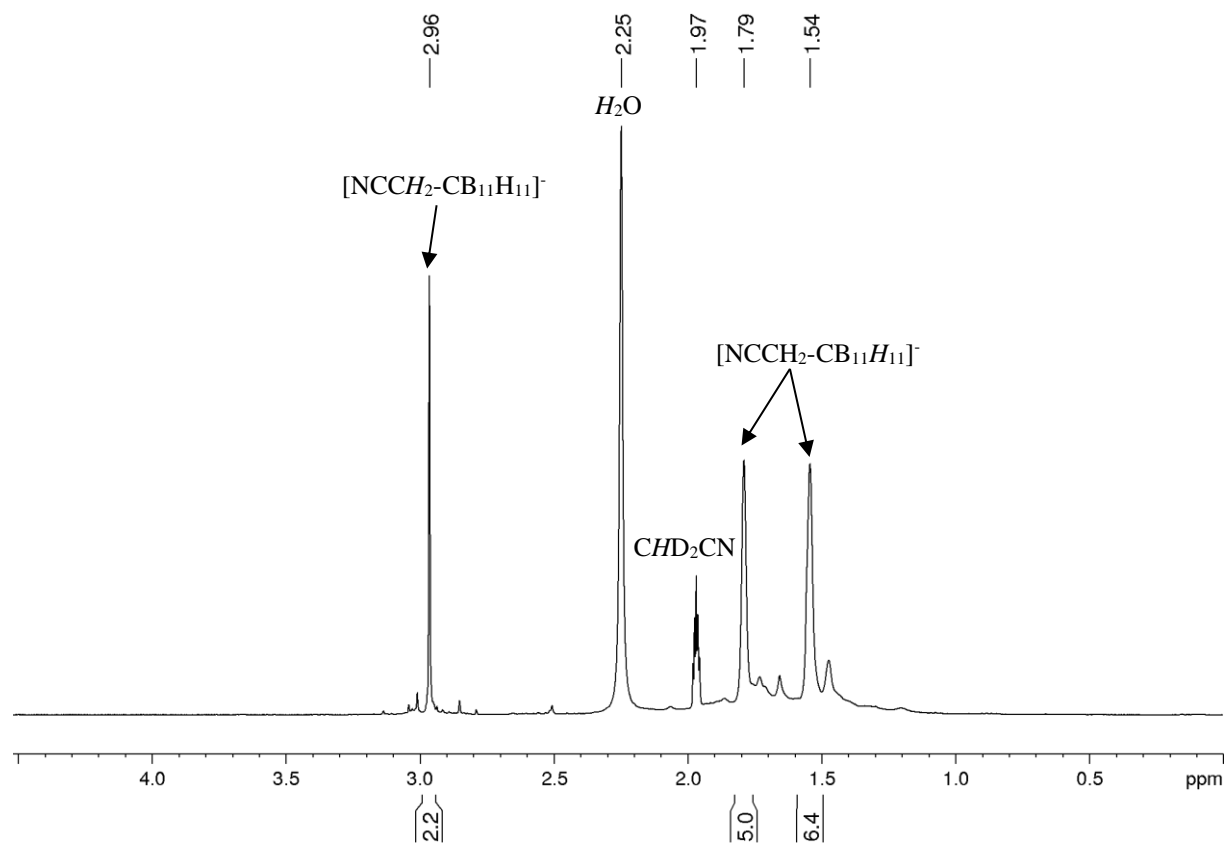


Figure S20. $^1H\{^{11}B\}$ NMR spectrum (400.13 MHz, CD_3CN , 300 K) of $K[NCCH_2-CB_{11}H_{11}]$.

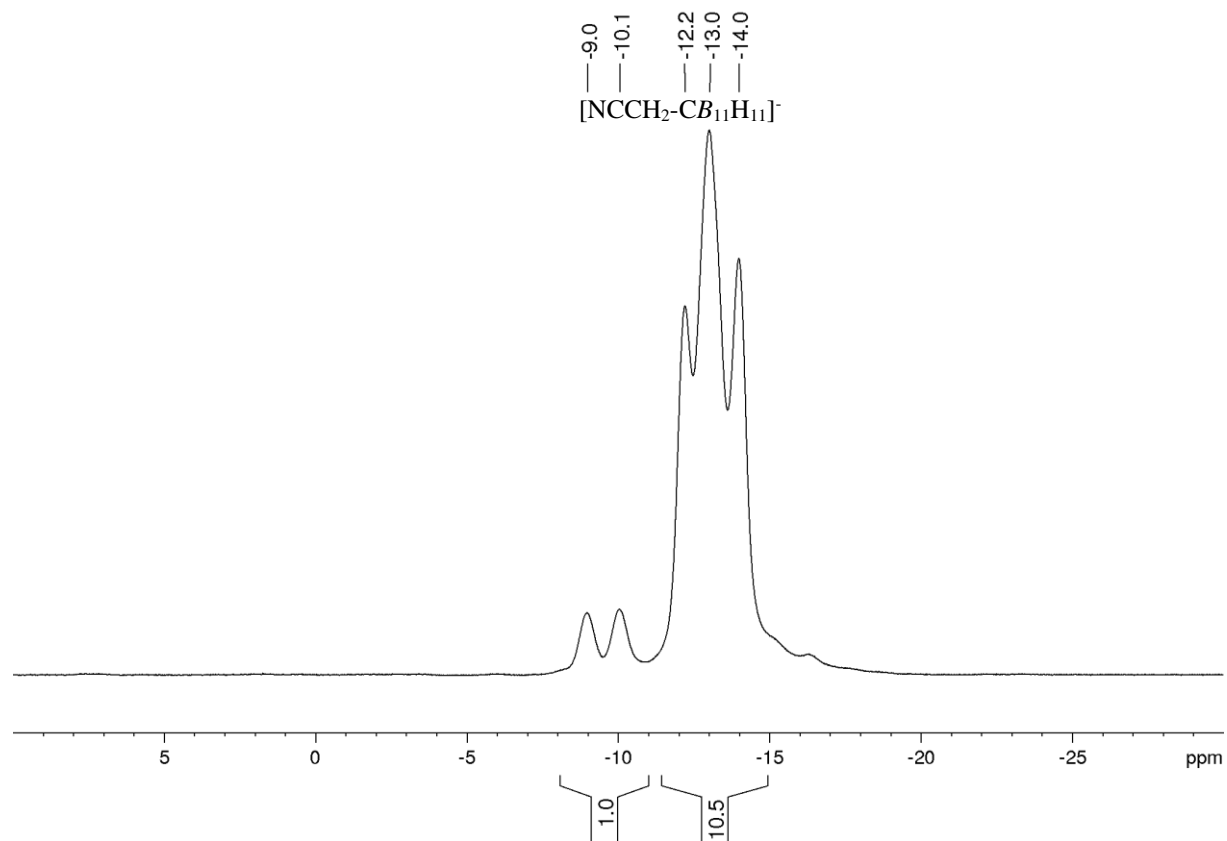


Figure S21. ^{11}B NMR spectrum (128.38 MHz, CD_3CN , 300 K) of $\text{K}[\text{NCCH}_2\text{-CB}_{11}\text{H}_{11}]$.

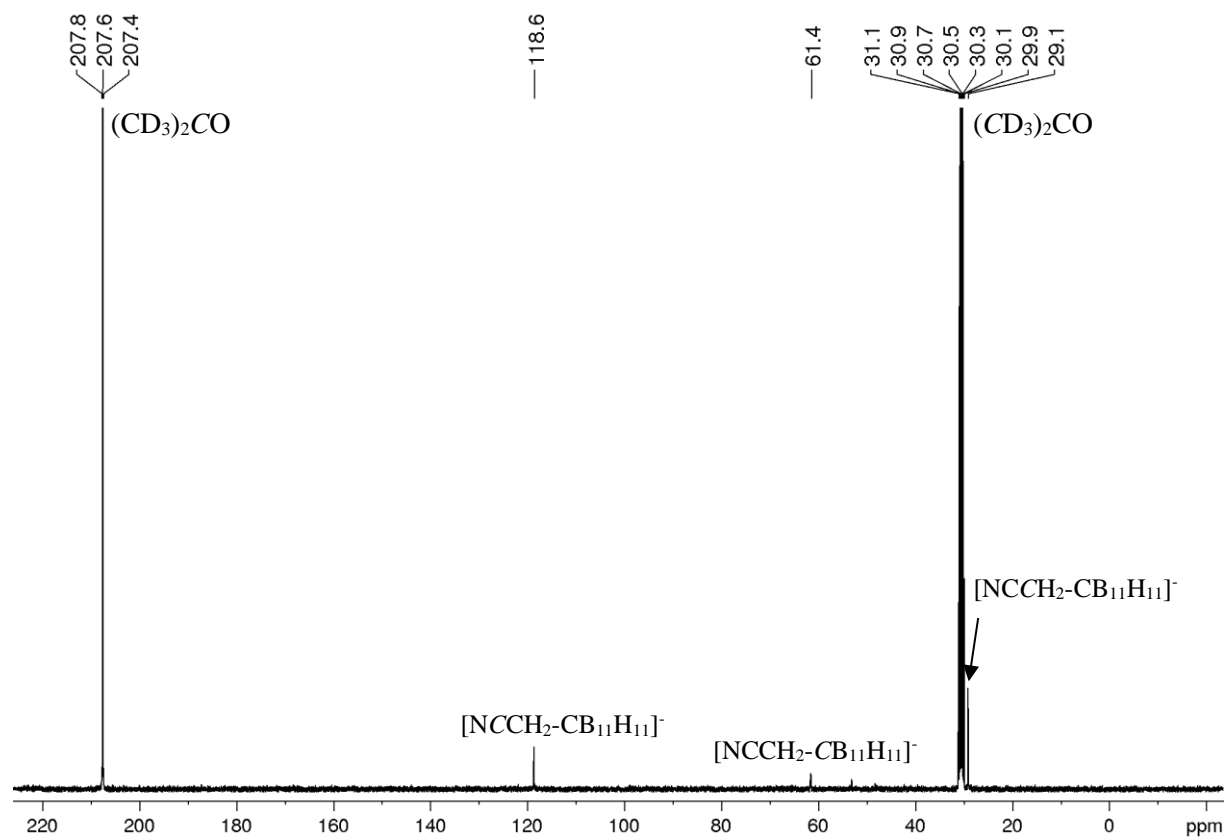


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.62 MHz, $(\text{CD}_3)_2\text{CO}$, 300 K) of $\text{K}[\text{NCCH}_2\text{-CB}_{11}\text{H}_{11}]$.

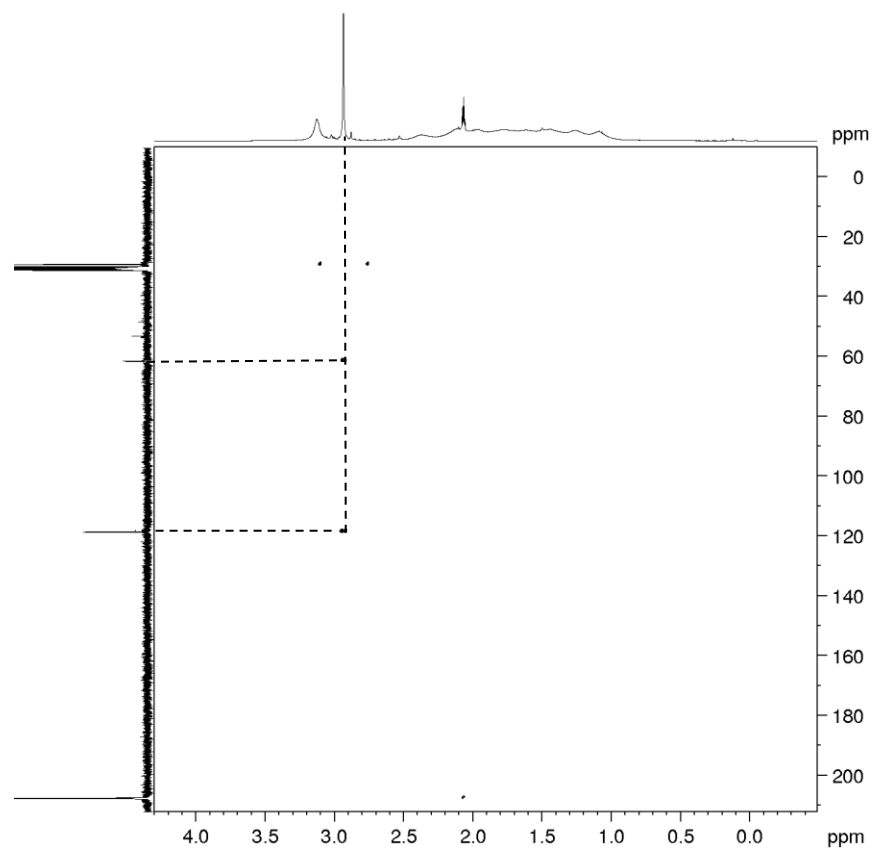


Figure S23. ^1H - ^{13}C HSQC NMR spectrum (400.13 MHz, 100.62 MHz, $(\text{CD}_3)_2\text{CO}$, 300 K) of $\text{K}[\text{NCCH}_2\text{-CB}_{11}\text{H}_{11}]$.

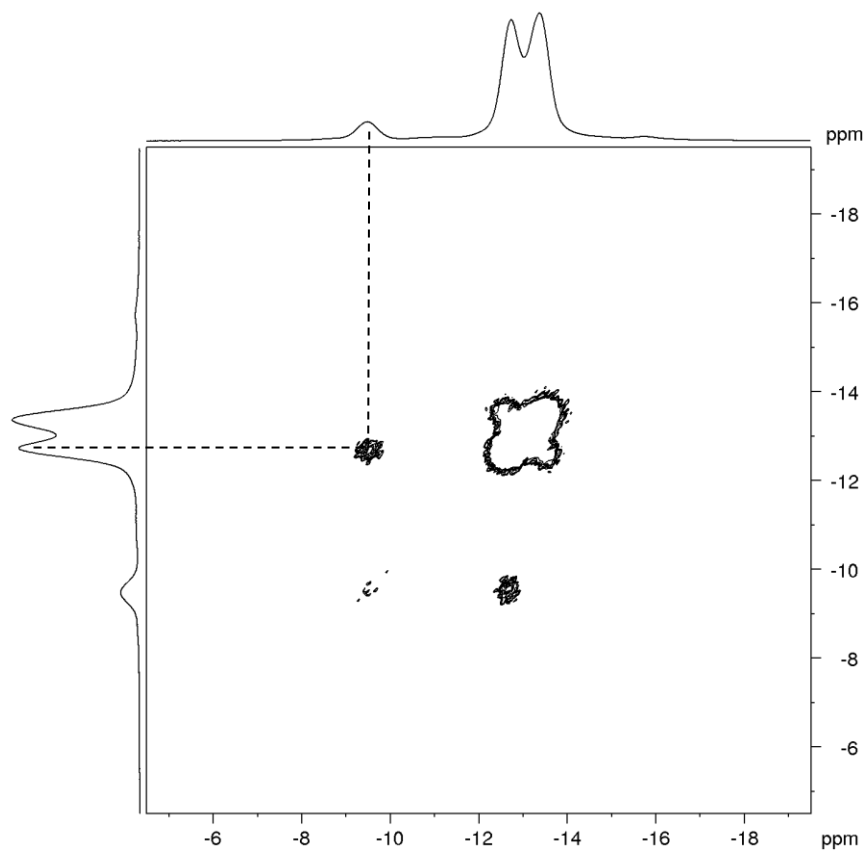


Figure S24. ^{11}B - ^{11}B COSY NMR spectrum (128.38 MHz, CD_3CN , 300 K) of $\text{K}[\text{NCCH}_2\text{-CB}_{11}\text{H}_{11}]$.

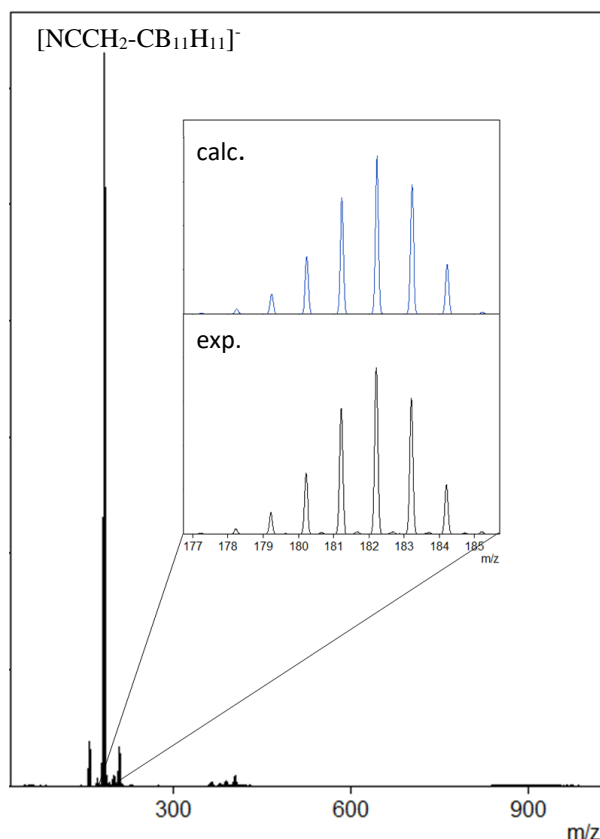
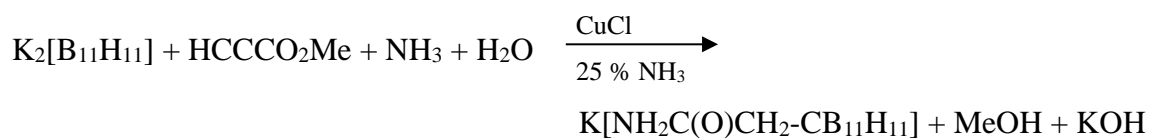


Figure S25. ESI-mass spectrum (negative mode) of $\text{K}[\text{NCCH}_2\text{-CB}_{11}\text{H}_{11}]$. The simulated mass spectrum is shown above.

S2.3. Synthesis of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$ with $\text{K}_2[\text{B}_{11}\text{H}_{11}]$ and Methyl Propiolate



Reaction 2.3.1

In a 100 mL beaker CuCl (0.050 g, 0.505 mmol, 0.30 eq.) and sodium ascorbate (ca. 200 mg) were solved in 15 mL of a 25% aqueous NH_3 solution. First methyl propiolate (0.33 mL, 3.729 mmol, 2.22 eq.) and after 5 minutes stirring, $\text{K}_2[\text{B}_{11}\text{H}_{11}]$ (0.350 g, 1.681 mmol, 1.00 eq.) were added. The reaction suspension was stirred for 1 hour at room temperature and then potassium carbonate was added until the solution was saturated. The precipitate formed was filtered off and the solution extracted three times with each 50 mL ethyl acetate. The combined organic phase was dried with

sodium sulphate and removed under reduced pressure. The obtained light-yellow solid was dried at high vacuum and the yield was 0.305 g (1.275 mmol, 76 %) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600.27 MHz, CD_3CN , 300 K): $\delta = 1.47$ (s, 6H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 1.75 (s, 5H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 2.61 (s, 2H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 3.81 (m).

^{11}B NMR (192.59 MHz, CD_3CN , 300 K): $\delta = -13.2$ (d, $^1J_{\text{BH}} = 142$ Hz, 10B, $B(2-11)\text{-H}$), -9.6 (d, $^1J_{\text{BH}} = 136$ Hz, 1B, $B12\text{-H}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CD_3CN , 300 K): $\delta = 173.4$ (s, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 65.1 (s, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 46.7 (s, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$).

ESI-MS (negativ-mode): $m/z = 202.24$ (calc. = 202.24, $[\text{ND}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$). The sample had been prior dissolved in deuterated solvent which caused an H/D exchange.

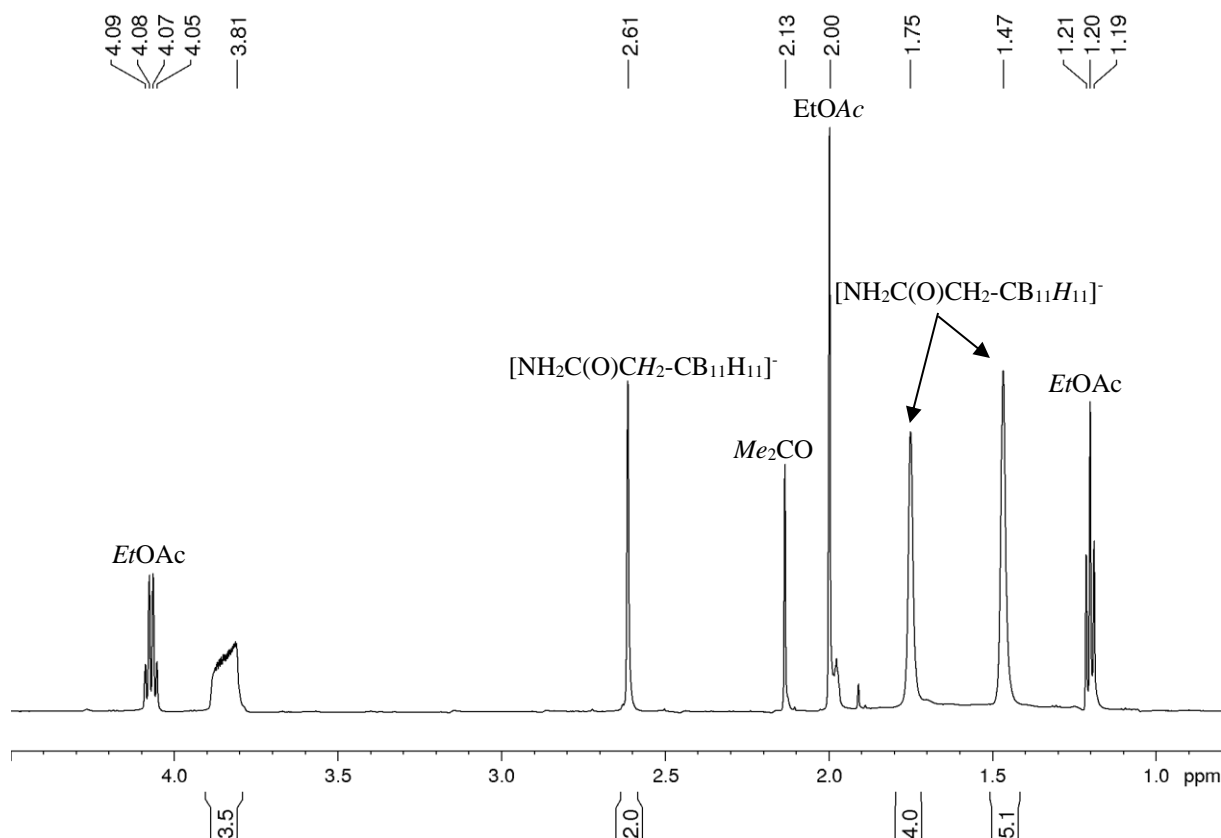


Figure S26. $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum (600.27 MHz, CD_3CN , 300 K) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

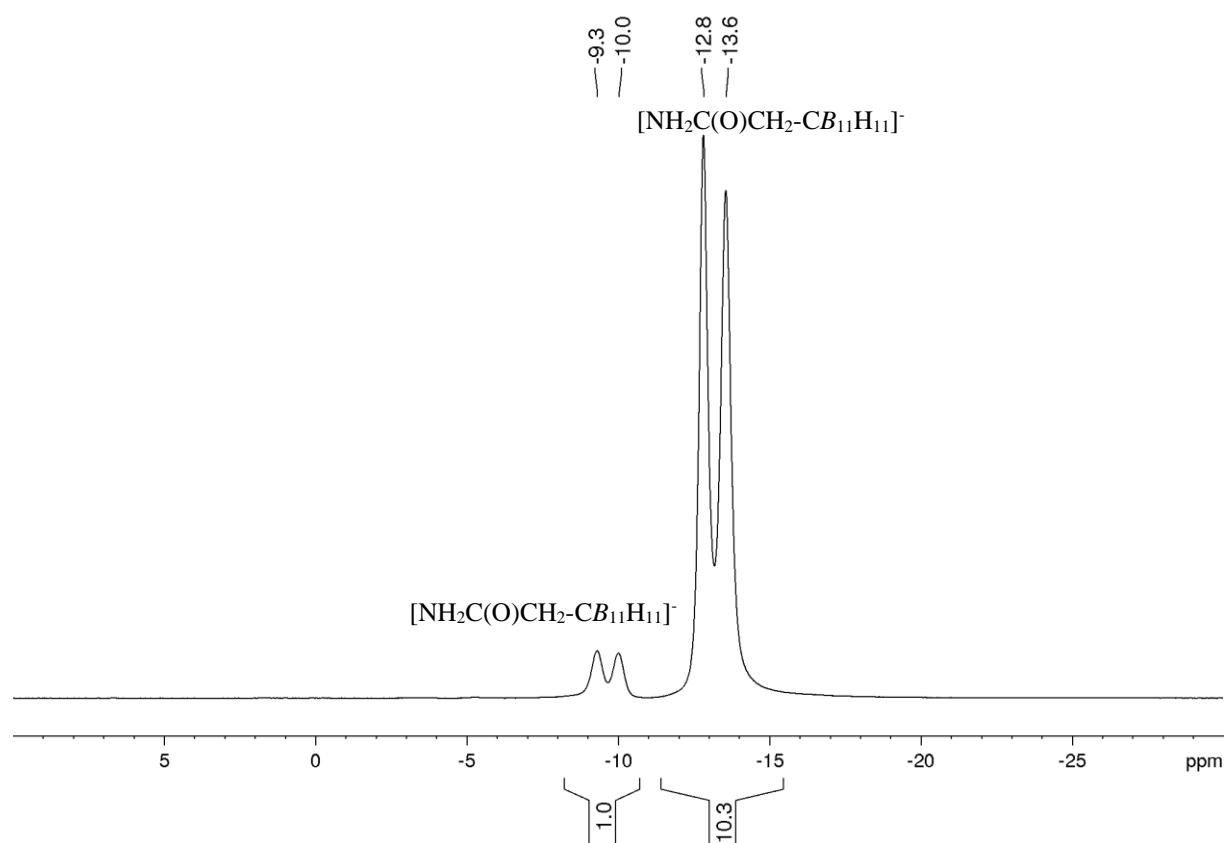


Figure S27. ^{11}B NMR spectrum (192.59 MHz, CD_3CN , 300 K) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

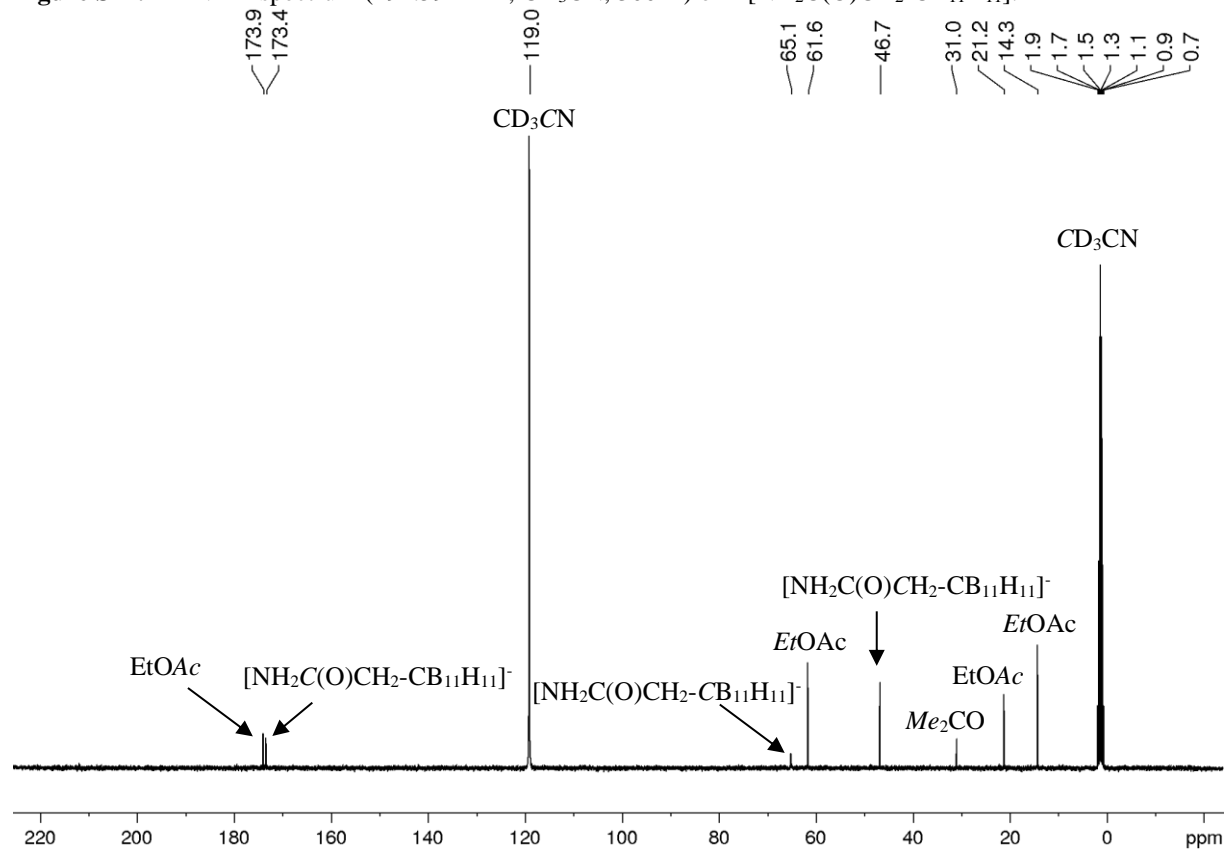


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (150.95 MHz, CD_3CN , 300 K) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

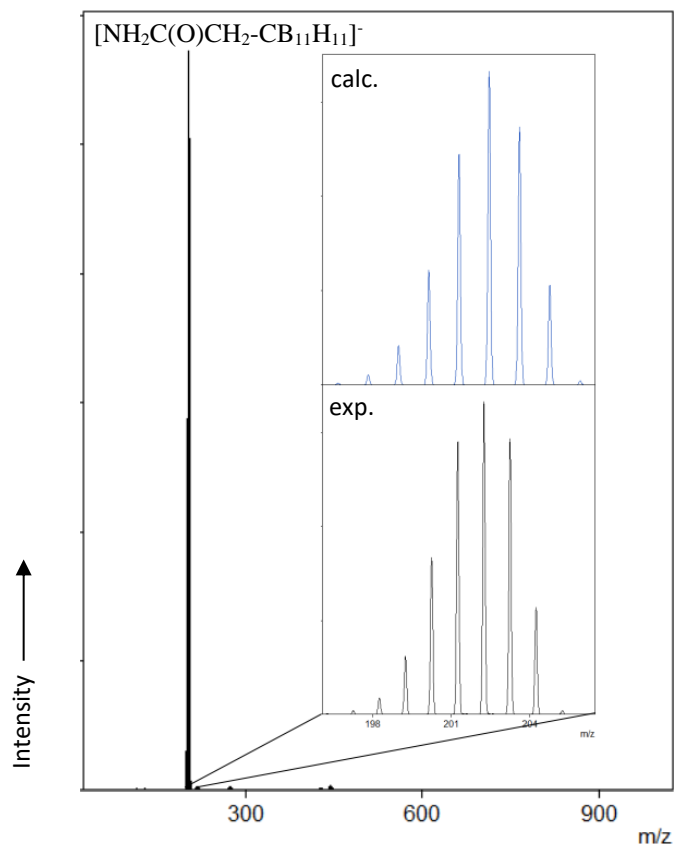
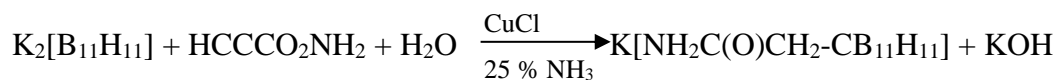


Figure S29. ESI-mass spectrum (negative mode) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$. The simulated mass spectrum is shown above.

S2.4. Synthesis of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$ with $\text{K}_2[\text{B}_{11}\text{H}_{11}]$ and Propiolamide



In a 100 mL beaker CuCl (0.051 g, 0.515 mmol, 0.21 eq.) and sodium ascorbate (ca. 100 mg) were solved in 25 mL of a 25% aqueous NH_3 solution. After stirring for 15 minutes propiolamide (0.270 g, 3.910 mmol, 1.62 eq.) was added. After stirring for 5 minutes $\text{K}_2[\text{B}_{11}\text{H}_{11}]$ (0.502 g, 2.411 mmol, 1.00 eq.) was added. The reaction suspension was stirred for 2 hours at room temperature and then potassium carbonate was added until the solution was saturated. The precipitate formed was filtered off and the solution extracted three times with each 70 mL ethyl acetate. The combined organic phase was dried with sodium sulphate and removed under reduced

pressure. The obtained light yellow solid was dried at high vacuum (0.374 g, 1.564 mmol, 65 %). The solid consists of 65 % $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$ and 35 % propiolamide.

$^1\text{H}\{^{11}\text{B}\}$ NMR (400.13 MHz, CD_3CN , 300 K): δ = 1.48 (s, 6H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 1.76 (s, 5H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 2.61 (s, 2H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 3.25 (s, 0.5H, $\text{HCCC}(\text{O})\text{NH}_2$), 5.80 (s, 1H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 6.06 (s, 1H, $[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 6.42 (s, 0.5H, $\text{HCCC}(\text{O})\text{NH}_2$), 6.83 (s, 0.5H, $\text{HCCC}(\text{O})\text{NH}_2$).

^{11}B NMR (128.39 MHz, CD_3CN , 300 K): δ = 13.2 (d, $^1J_{\text{BH}}$ = 142 Hz, 10B, $\text{B}(2\text{-}11)\text{-H}$), -9.6 (d, $^1J_{\text{BH}}$ = 134 Hz, 1B, $\text{B}12\text{-H}$).

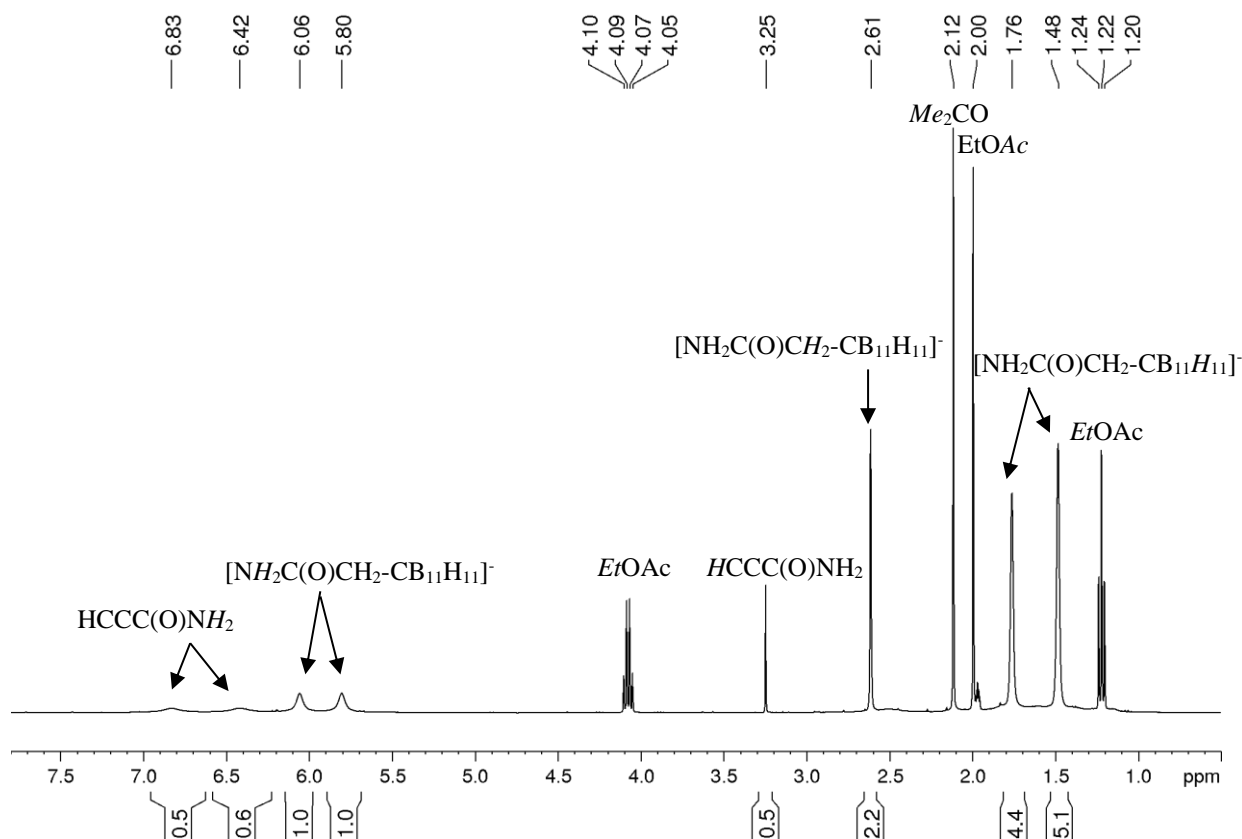


Figure S30. $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum (400.13 MHz, CD_3CN , 300 K) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

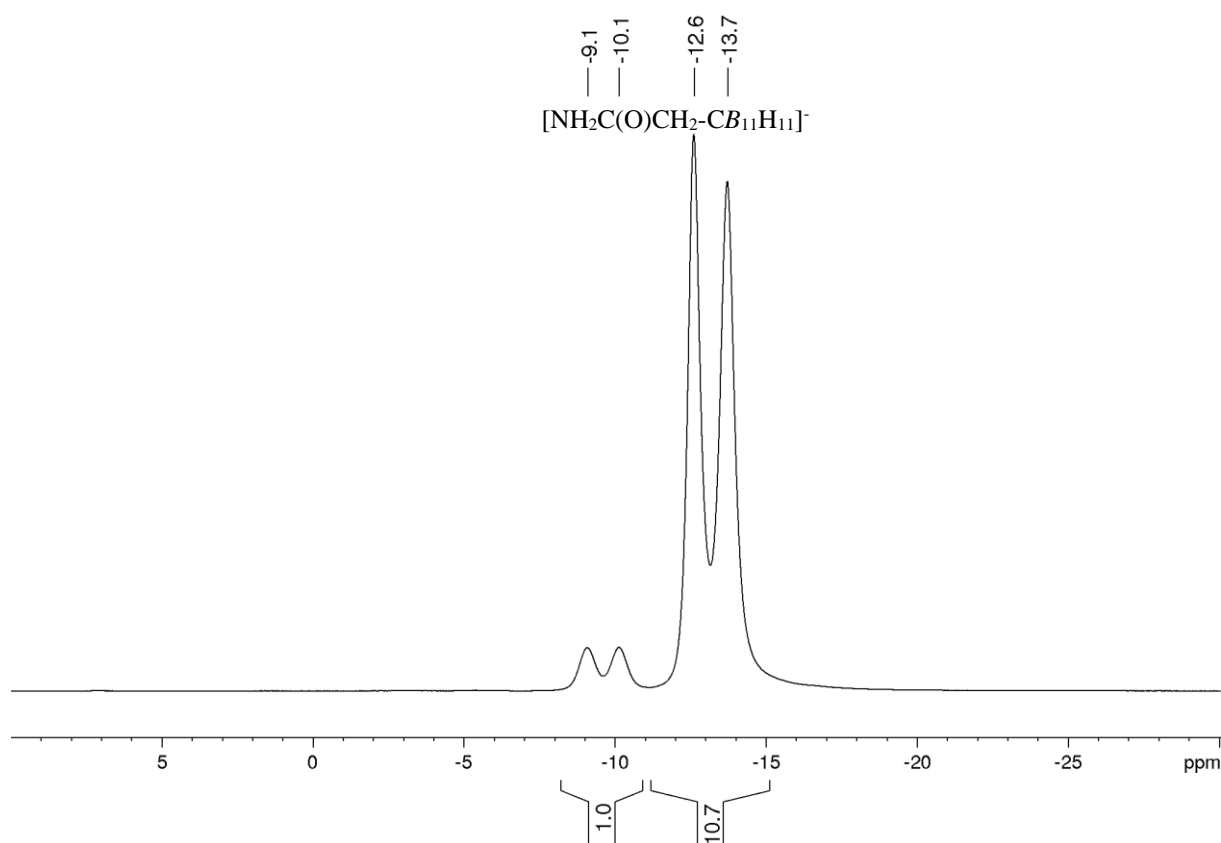
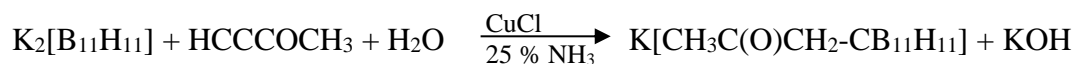


Figure S31. ^{11}B NMR spectrum (128.38 MHz, CD_3CN , 300 K) of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

S2.5. Synthesis of $\text{K}[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$ with $\text{K}_2[\text{B}_{11}\text{H}_{11}]$ and 3-Butyn-2-one



In a 100 mL beaker CuCl (0.078 g, 0.788 mmol, 0.23 eq) and sodium ascorbate (ca. 200 mg) were solved in 12 mL of a 25% aqueous NH_3 solution. The components were completely dissolved and 3-butyne-2-one (0.6 mL, 7.668 mmol, 2.28 eq.) was added. After stirring for 30 minutes, $\text{K}_2[\text{B}_{11}\text{H}_{11}]$ (0.699 mg, 3.357 mmol, 1.00 eq.) was added. The reaction suspension was stirred for 1 hour at room temperature and then potassium carbonate was added until the solution was saturated. The precipitate formed was filtered off and the solution extracted three times with each 80 mL ethyl acetate. The combined organic phase was dried with sodium sulphate and removed under reduced pressure. The obtained light-yellow solid was dried at high vacuum (38 %, 0.305 g, 1.280 mmol).

$^1\text{H}\{^{11}\text{B}\}$ NMR (400.13 MHz, CD_3CN , 300 K): δ = 1.50 (s, 6H, $[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 1.74 (s, 5H, $[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 2.11 (s, 3H, $[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 2.79 (s, 2H, $[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$).

^{11}B NMR (128.38 MHz, CD_3CN , 300 K): δ = 13.2 (d, $^1J_{\text{BH}}$ = 145 Hz, 10B, $B(2-11)\text{-H}$), -9.3 (d, $^1J_{\text{BH}}$ = 136 Hz, 1B, $B12\text{-H}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150.95 MHz, CD_3CN , 300 K): δ = 172.7 (s, $[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 64.3 (s, $[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 52.8 (s, $[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$), 31.8 (s, $[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$).

ESI-MS (negativ-mode): m/z = 199.23 (calc. = 199.23, $[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]^-$).

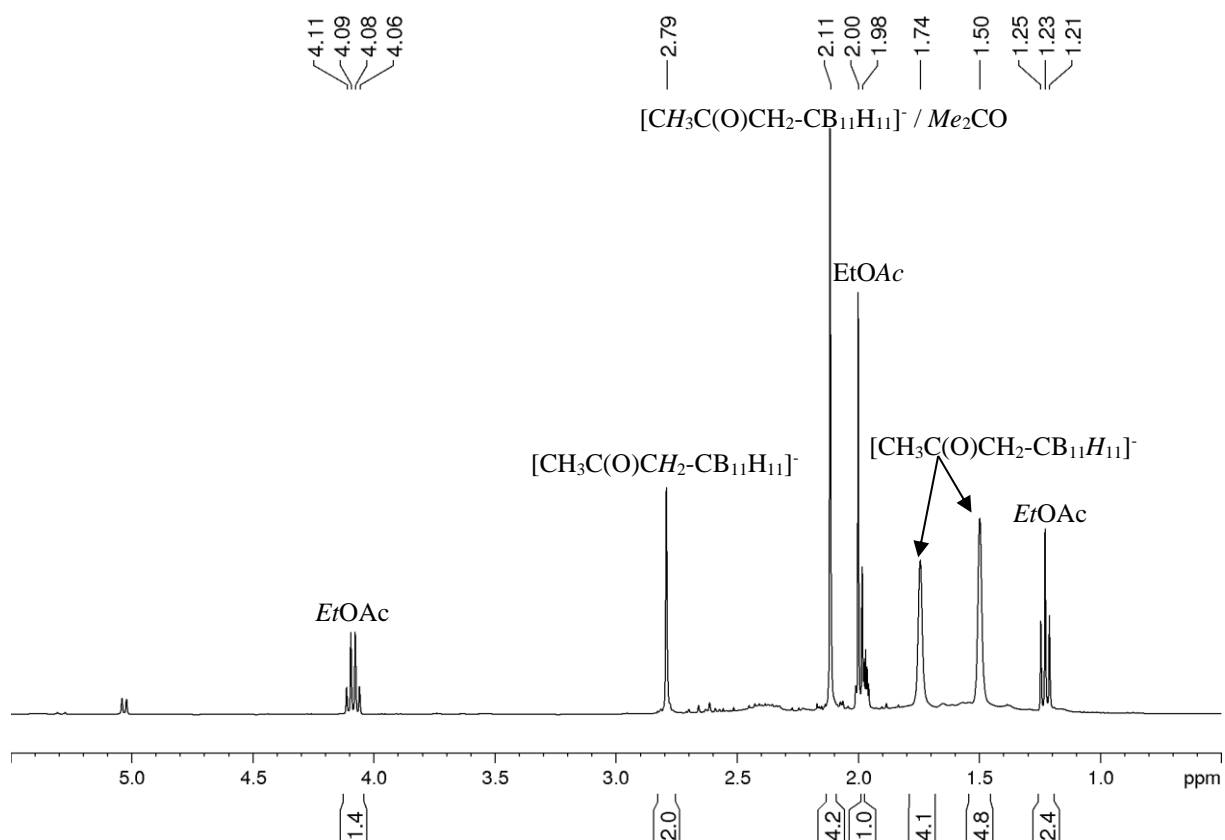


Figure S32. $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum (400.13 MHz, CD_3CN , 300 K) of $\text{K}[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

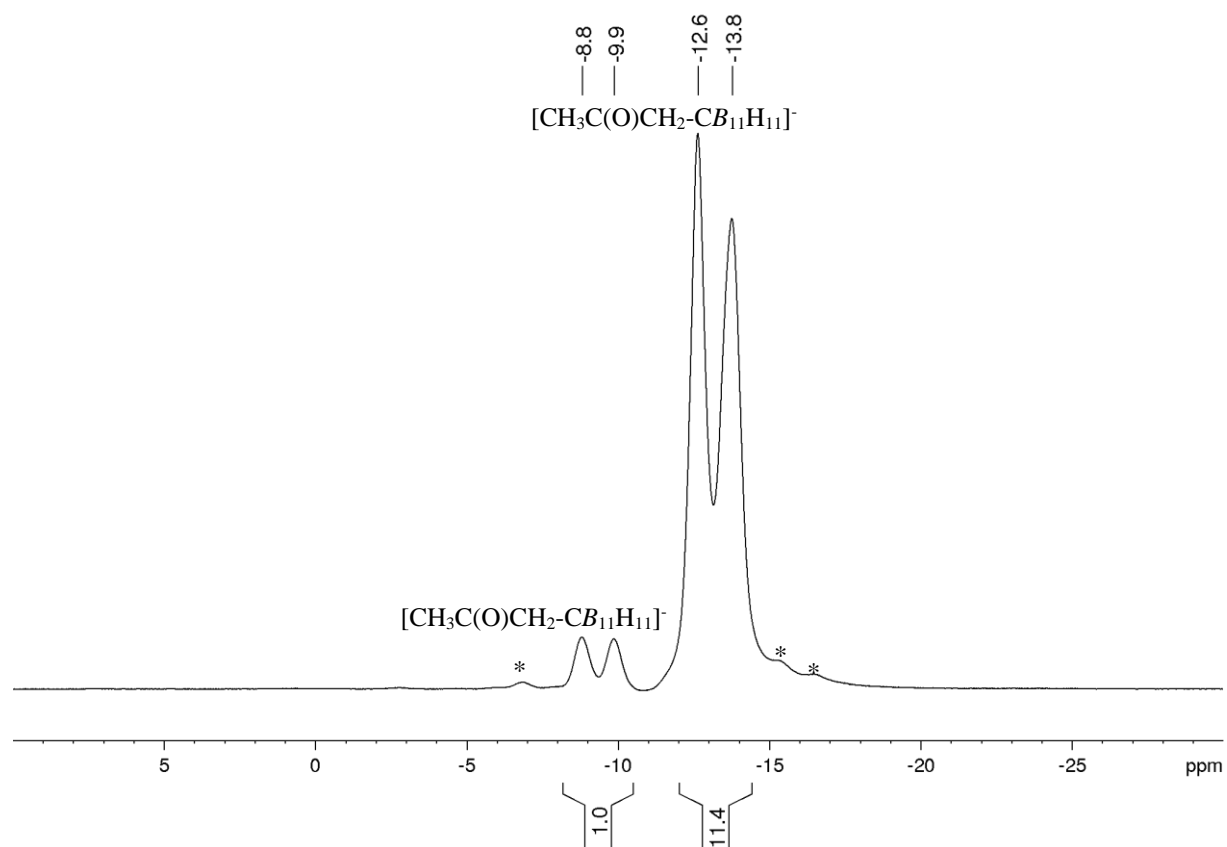


Figure S33. ^{11}B NMR spectrum (128.38 MHz, CD_3CN , 300 K) of $\text{K}[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$. Impurities marked with * originate from an impurity in the $[\text{B}_{11}\text{H}_{11}]^{2-}$ starting material.

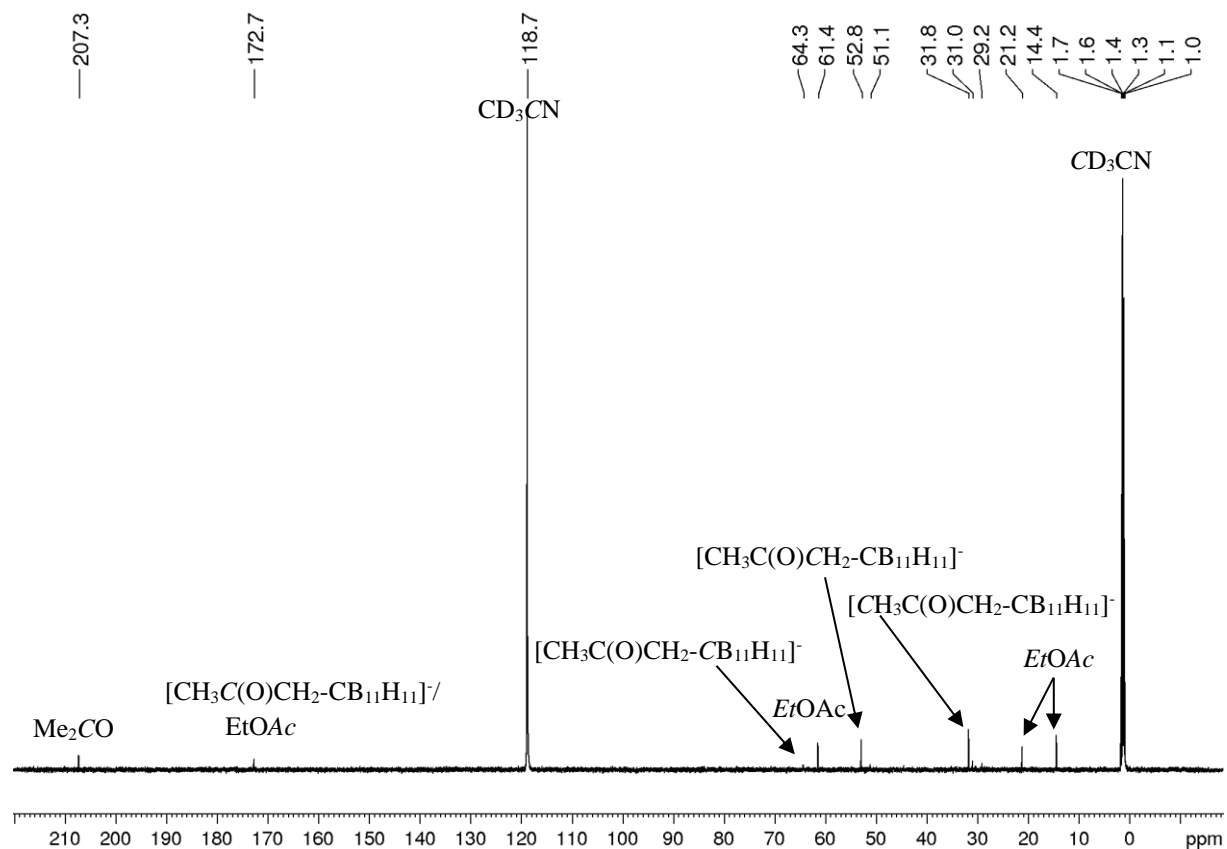


Figure S34. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (150.95 MHz, CD_3CN , 300 K) of $\text{K}[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

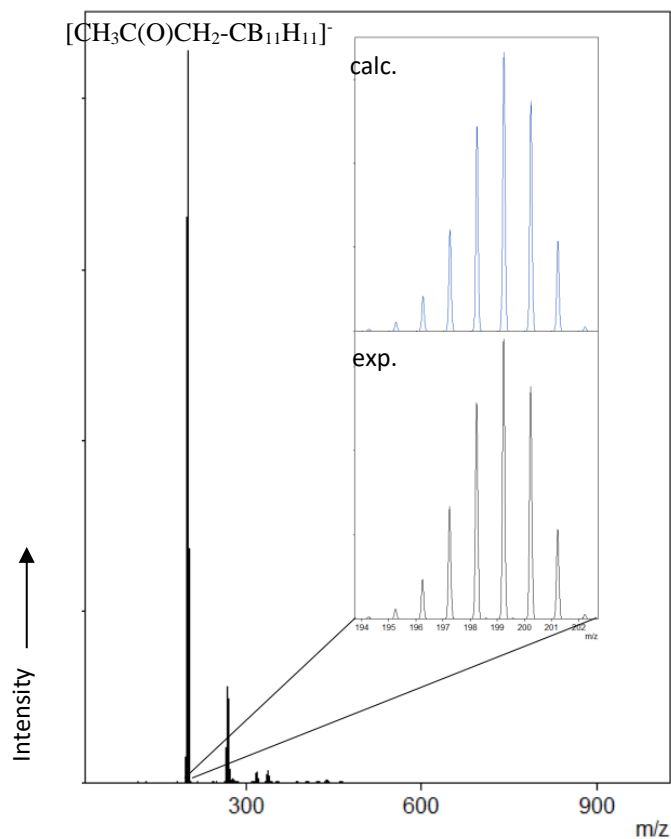


Figure S35. ESI-mass spectrum (negative mode) of $\text{K}[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$. The simulated mass spectrum is shown above.

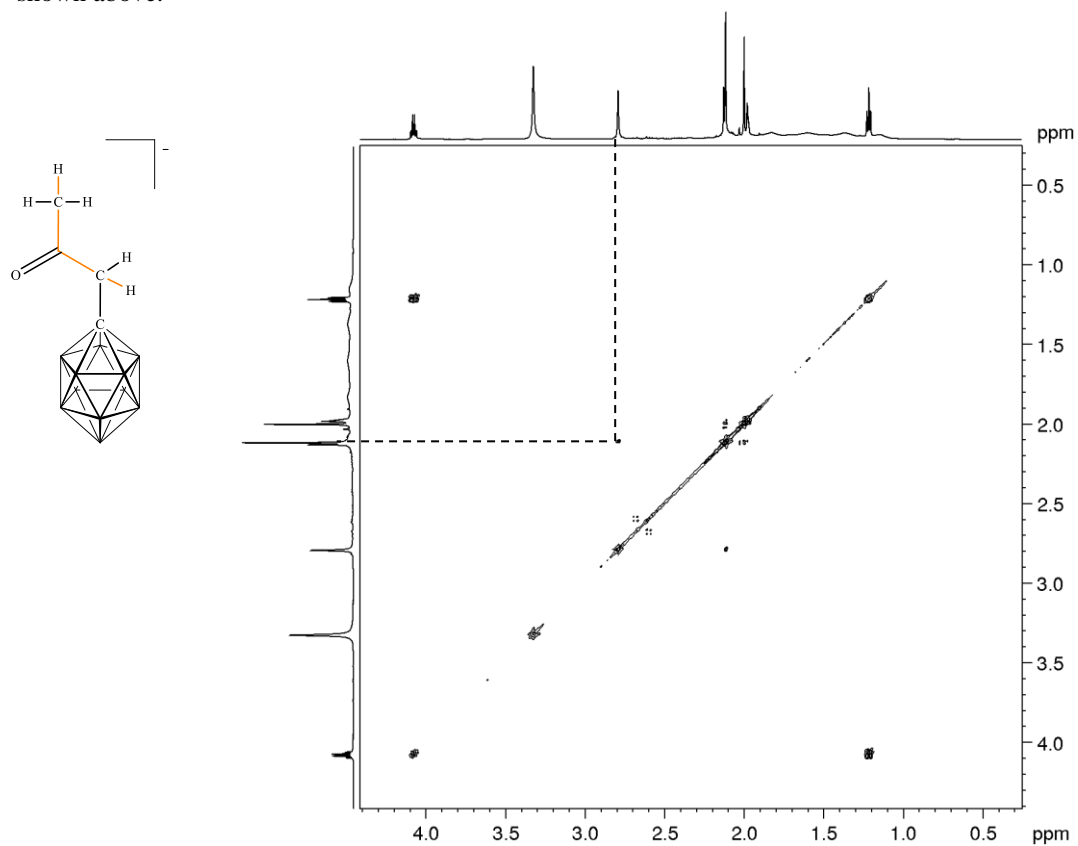


Figure S36. ^1H - ^1H COSY NMR spectrum (600.27 MHz, CD_3CN , 300 K) of $\text{K}[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

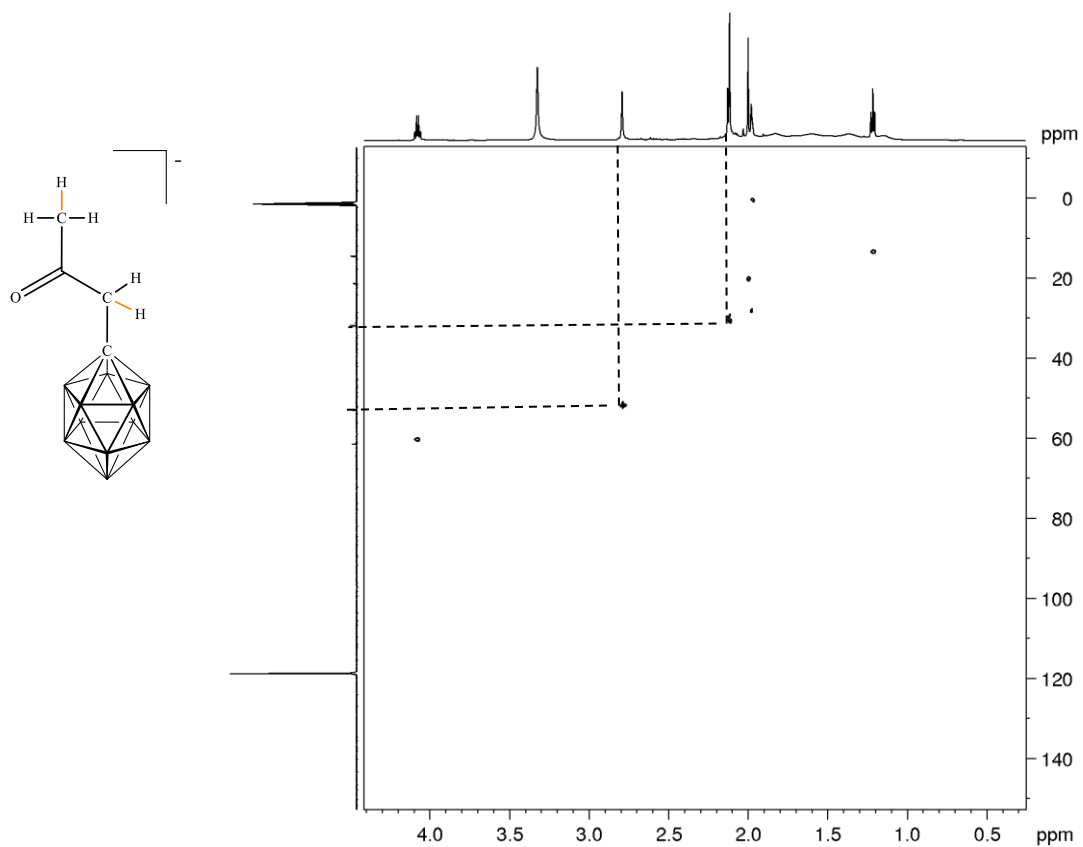


Figure S37. ¹H-¹³C HSQC NMR spectrum (600.27 MHz, 150.95 MHz, CD₃CN, 300 K) of K[CH₃C(O)CH₂-CB₁₁H₁₁].

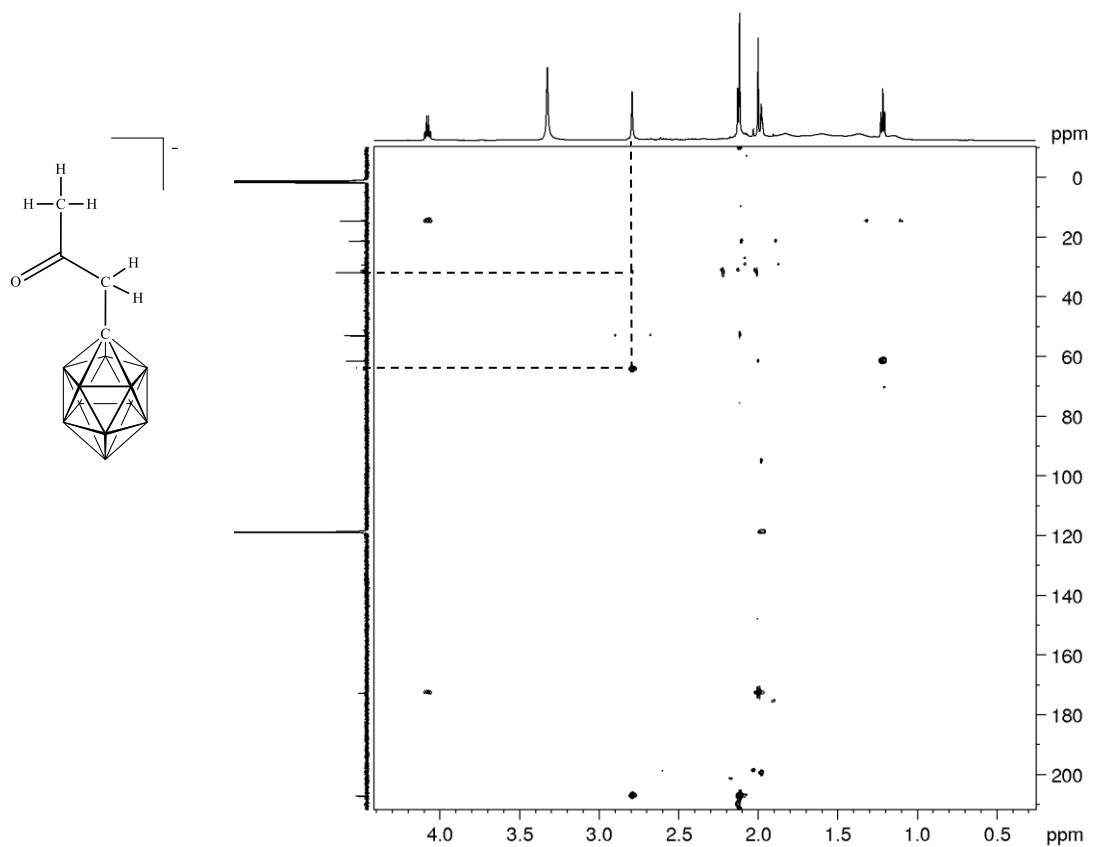


Figure S38. ^1H - ^{13}C HMBC NMR spectrum (600.27 MHz, 150.95 MHz, CD_3CN , 300 K) of $\text{K}[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

S3. NMR Data for $[\text{Cu}(\text{B}_{11}\text{H}_{11})_2]^{3-}$

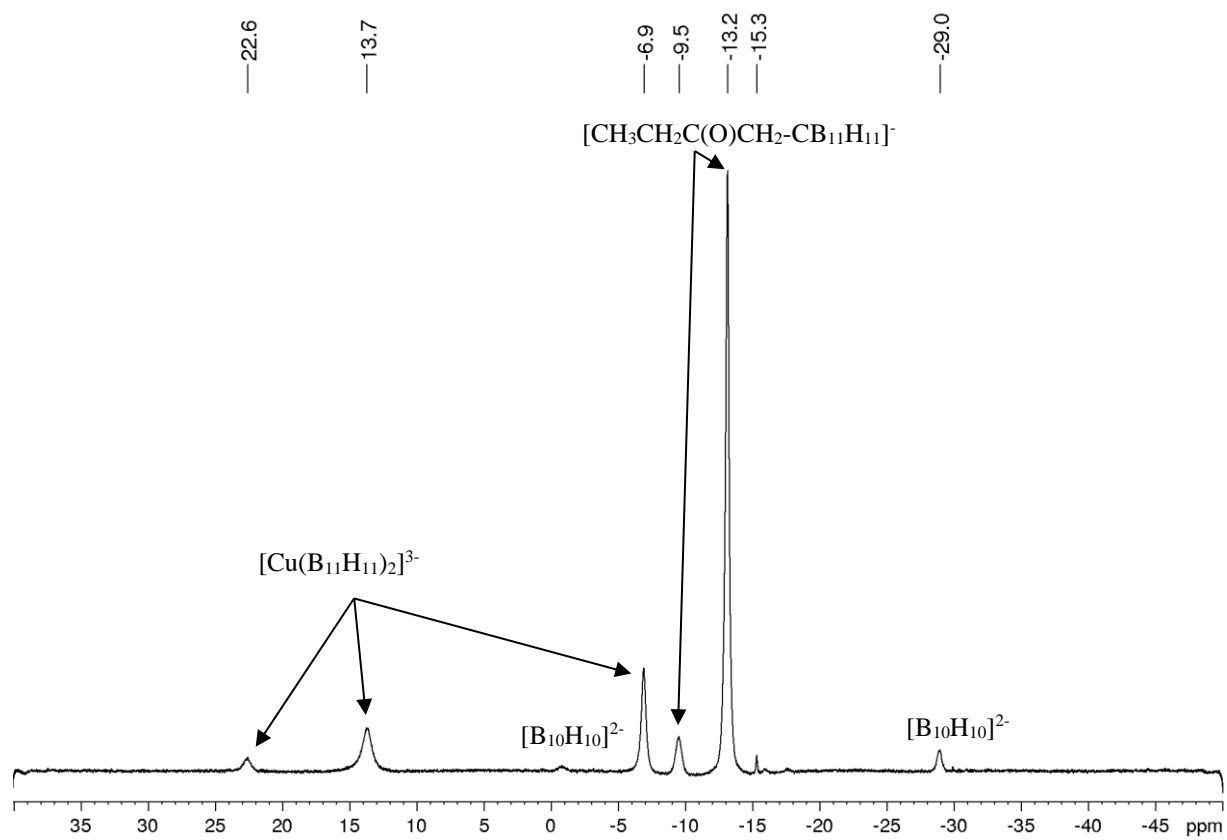


Figure S39. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (128.38 MHz, CD_3CN , 300 K) of the reaction between $\text{K}_2[\text{B}_{11}\text{H}_{11}]$, Cu, CuO and ethyl propiolate in dry acetonitrile.

S4. Crystal Structure Data

S4.1. $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$

Suitable single crystals of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$ were obtained by evaporation from aqueous solution.

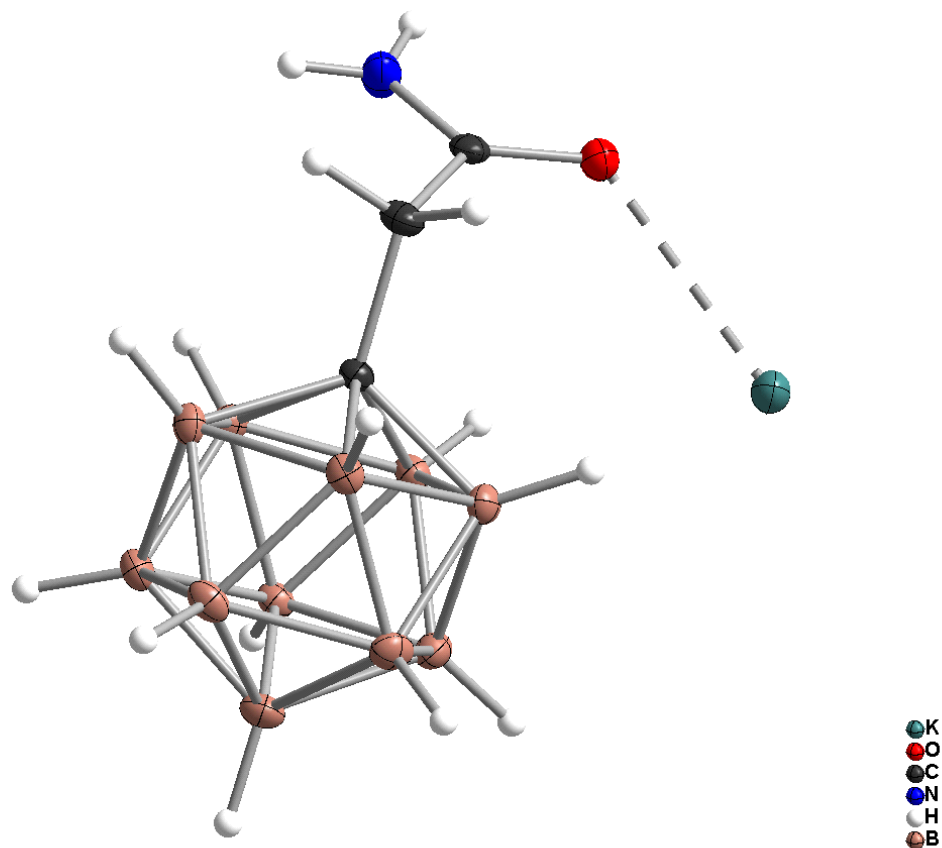


Figure S40. Part of the crystal structure of $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii.

Table S2. Crystal data and structure refinement for $\text{K}[\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$.

Empirical formula	$\text{C}_3\text{H}_{15}\text{B}_{11}\text{NOK}$
Formula weight	239.32
Temperature [K]	150(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	12.2160(2)
b [Å]	9.27158(15)
c [Å]	10.7602(2)

α [°]	90
β [°]	98.2749(17)
γ [°]	90
Volume [Å ³]	1206.03(4)
<i>Z</i>	4
ρ_{calc} [cm ³]	1.3172
μ [mm ⁻¹]	0.404
<i>F</i> (000)	488.9
Radiation	Mo K α (λ = 0.71073)
2 Θ range for data collection [°]	5.54 to 62.08
Index ranges	$-17 \leq h \leq 16$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$
Reflections collected	22392
Independent reflections	3569 [$R_{\text{int}} = 0.0285$, $R_{\text{sigma}} = 0.0190$]
Data/restraints/parameters	3569/0/214
Goodness-of-fit on F^2	1.109
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0278$, $wR_2 = 0.0724$
Final R indexes [all data]	$R_1 = 0.0324$, $wR_2 = 0.0755$
Largest diff. peak/hole [e Å ⁻³]	0.46/-0.23

S4.2. [NEt₃CH₂Cl][NH₂C(O)CH₂-CB₁₁H₁₁]

Single crystals of [NEt₃CH₂Cl][NH₂C(O)CH₂-CB₁₁H₁₁] were formed in very small amounts (<1%) during the synthesis of [NEt₃H][NH₂C(O)CH₂-CB₁₁H₁₁] from a reaction containing Et₃N and CH₂Cl₂ (see reactions 2.1.1 and 2.1.2 in the supplementary material). The reaction of Et₃N with CH₂Cl₂ to form the [NEt₂CH₂Cl]⁺ cation is well known.[11-13] Subsequent reaction with KOH produces K[NH₂C(O)CH₂-CB₁₁H₁₁] with small amounts (<1%) of [NEt₃CH₂Cl][NH₂C(O)CH₂-CB₁₁H₁₁]. Due to the different solubility of K[NH₂C(O)CH₂-CB₁₁H₁₁] and [NEt₃CH₂Cl][NH₂C(O)CH₂-CB₁₁H₁₁] in dichloromethane, [NEt₃CH₂Cl][NH₂C(O)CH₂-CB₁₁H₁₁] can be easily separated. After concentrating the dichloromethane solution, a few milligrams (< 5 mg) of [NEt₃CH₂Cl][NH₂C(O)CH₂-CB₁₁H₁₁] were isolated.

Table S3. Crystal data and structure refinement for [NEt₃CH₂Cl][NH₂C(O)CH₂-CB₁₁H₁₁]

Empirical formula	C ₁₀ H ₃₂ B ₁₁ N ₂ OCl
Formula weight	350.73
Temperature [K]	150(2)
Crystal system	orthorhombic
Space group	<i>Pmc</i> 2 ₁
<i>a</i> [Å]	16.942(3)
<i>b</i> [Å]	11.9220(15)
<i>c</i> [Å]	9.9542(16)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å ³]	2010.6(5)
<i>Z</i>	4
ρ_{calc} [cm ³]	1.159
μ [mm ⁻¹]	0.190
<i>F</i> (000)	744.0

Radiation	Mo K α ($\lambda = 0.71073$)
2 Θ range for data collection [°]	4.808 to 52.74
Index ranges	$-21 \leq h \leq 19, -14 \leq k \leq 13, -12 \leq l \leq 12$
Reflections collected	7441
Independent reflections	3563 [$R_{\text{int}} = 0.1528, R_{\text{sigma}} = 0.2728$]
Data/restraints/parameters	3563/293/262
Goodness-of-fit on F^2	0.987
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0966, wR_2 = 0.1273$
Final R indexes [all data]	$R_1 = 0.2255, wR_2 = 0.1764$
Largest diff. peak/hole [$e \text{ \AA}^{-3}$]	0.28/-0.27

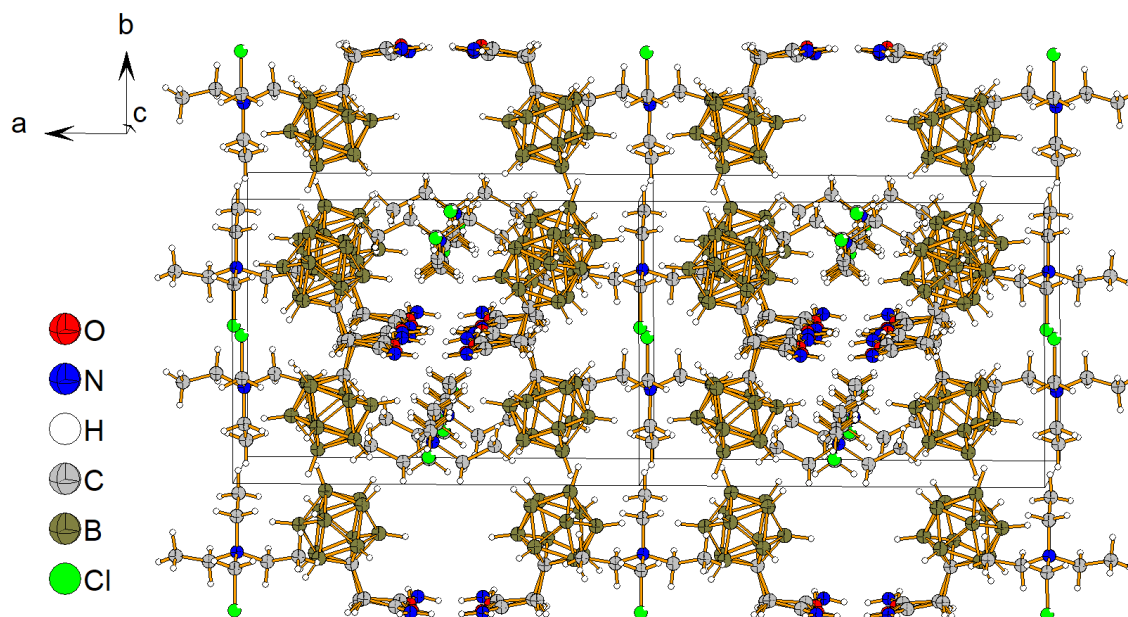


Figure S41. Packing of the ions in the crystal structure of $[\text{NEt}_3\text{CH}_2\text{Cl}][\text{NH}_2\text{C}(\text{O})\text{CH}_2\text{-CB}_{11}\text{H}_{11}]$. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii.

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