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Electronic Supplementary Information

Hypergolic fuels based on water-stable borohydride cluster anions with ultralow ignition delay times

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General methods: ¹H, ¹³C, and ¹¹B NMR spectra were collected on a Bruker AVANCE 600 spectrometer operating at 600 MHz, 151 MHz and 193 MHz, respectively. All ¹H and ¹³C chemical shifts were measured relative to internal residual protons or carbons in the lock solvents and are referenced to Me₄Si (0.0 ppm). Unless otherwise specified, ¹¹B chemical shifts were referenced to external $BF_3 \cdot O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. The melting points and decomposition points were recorded using a Mettler-Toleto DSC1 calorimeter from 0 to 400 °C at a scan rate of 10 °C min-1 in closed aluminum containers. Infrared (IR) spectra were recorded by using KBr pellets on a Thermo Nicolet 380 FTIR spectrometer. Densities were measured at 25 °C using a Micromeritics Accupyc 1340 gas pycnometer. Elemental analyses were obtained by using a Vario EL cube elemental analyzer. Specific impulse data were calculated by Explo5 (version 6.02) software. For solid salts at room temperature, hypergolicity was assessed by droplet tests with WFNA and/or N₂O₄, (about 40 uL) dropped onto excess powdered samples (10 mg). For liquid salts at room temperature, hypergolicity was assessed by droplet tests with ionic liquid samples (15-20 mg) dropped into excess WFNA or N₂O₄. The ignition process was recorded at 1000 frames per second with a high-speed camera.

Reactants: All the organic solvents used in the study were of analytical grade without further purification unless otherwise noted. Sodium borohydride (98%, Aladdin), iodine (99.8%, Aladdin) N-methylimidazole (99%, Energy Chemical), iodoethane (98%, Aladdin), 1-iodopropane (98%, Aladdin), 1-iodobutane (99%, Aladdin), allyl bromide (98%, Aladdin), propargyl bromide (98%, Aladdin), decaborane (98%, J&K), boron trifluoride ether complex $BF_3 \cdot OEt_2$ (98%, SCRC), diglyme (98%, SCRC).

Calculation Methods

The heats of formation of $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$ were referenced to a previous work.¹ The heat of formation of $[B_6H_7]^-$ was computed by G2 method, using the Gaussian 09 suite of programs.² The other structures were optimized by DFT method at the B3LYP/6-31+G(d, p) level. Single energy points were calculated at the MP2/6-311++G(d, p) level. All of the optimized structures were characterized to be true local-energy minima on the potential-energy surface without imaginary frequencies. Heats of formation of all salts were calculated based on Born-Haber energy cycle (Scheme S1), simplified by equation (1).³



Scheme S1 Boron-Haber cycle for the formation of ionic liquids; The number of moles of the respective products are given by *a*-*d*.

$$\Delta H_{\rm f} (\text{ionic salts}, 298\text{K}) = \Sigma \Delta H_{\rm f} (\text{cation}, 298\text{K}) + \Sigma \Delta H_{\rm f} (\text{anion}, 298\text{K}) - \Delta H_{\rm L}$$
(1)

in which $\Delta H_{\rm L}$ is the lattice energy of the ionic salts, which could be predicted by equation (2) proposed by Jenkins et al..⁴

$$\Delta H_{\rm L} = U_{\rm POT} + [p(n_{\rm M}/2 - 2) + q(n_{\rm X}/2 - 2)]RT$$
(2)

for M_pX_q salts, $n_M = n_X = 6$ for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} has the form shown in equation (3).

$$U_{\rm POT}(\rm kJ\ mol^{-1}) = \gamma (\rho_m/M_m)^{1/3} + \delta$$
 (3)

for M₂X (2:1) salts, where $\gamma = 8375.6$ kJ mol⁻¹ cm and $\delta = -178.8$ kJ mol⁻¹; for MX (1:1) salts, where $\gamma = 1981.2$ kJ mol⁻¹ cm and $\delta = 103.8$ kJ mol⁻¹. ρ_m is density (g cm⁻³) and M_m is the chemical formula mass of the ionic material.

The heats of formation ($\Delta H_{\rm f}$) of the cations were computed by using the method of isodesmic reations.⁵⁻⁷ The isodesmic reactions for cations are shown in Scheme S2. The enthalpy of isodesmic reactions ($\Delta_{\rm r}H_{298}$) is obtained by combining the MP2/6-311+G(d,p) energy difference for the reaction, the scaled zero-point energy, and other thermal factors.



Scheme S2 Isodesmic reactions for calculating the heats of formation of cations.

<mark>∆H</mark> Salts	$\Delta H_{\rm f}^{\rm a}$ (cation)	<mark>ΔH_f ^a (anion)</mark>	$\Delta H_{\rm L}{}^{\rm b}$
	[kJ/mol]	[kJ/mol]	[kJ/mol]
<mark>1a</mark>	<mark>630.1</mark>	<mark>-361.2</mark>	<mark>1030.3</mark>
<mark>1b</mark>	<mark>611.2</mark>	<mark>-361.2</mark>	<mark>994.7</mark>
<mark>1c</mark>	<mark>588.3</mark>	<mark>-361.2</mark>	<mark>971.7</mark>
<mark>1d</mark>	<mark>740.1</mark>	<mark>-361.2</mark>	1012.9
<mark>1e</mark>	<mark>933.8</mark>	<mark>-361.2</mark>	1044.5
<mark>1f</mark>	<mark>864.4</mark>	<mark>-361.2</mark>	1035.9
<mark>2a</mark>	<mark>630.1</mark>	<mark>-52.3</mark>	1049.7
<mark>2b</mark>	<mark>611.2</mark>	<mark>-52.3</mark>	<u>1013.3</u>
<mark>2c</mark>	<mark>588.3</mark>	<mark>-52.3</mark>	<mark>970.3</mark>
<mark>2d</mark>	<mark>740.1</mark>	<mark>-52.3</mark>	<mark>1032.8</mark>
<mark>2e</mark>	<mark>933.8</mark>	<mark>-52.3</mark>	<mark>1067.8</mark>
<mark>2f</mark>	<mark>864.4</mark>	<mark>-52.3</mark>	<mark>1048.8</mark>
<mark>3a</mark>	<mark>630.1</mark>	<mark>-8.12</mark>	<mark>448.4</mark>
<mark>3b</mark>	<mark>611.2</mark>	<mark>-8.12</mark>	<mark>440.9</mark>
<mark>3c</mark>	<mark>588.3</mark>	<mark>-8.12</mark>	<mark>432.7</mark>
<mark>3d</mark>	<mark>740.1</mark>	<mark>-8.12</mark>	<mark>450.7</mark>
<mark>3e</mark>	<mark>933.8</mark>	<mark>-8.12</mark>	<mark>456.9</mark>
<mark>3f</mark>	<mark>864.4</mark>	<mark>-8.12</mark>	<mark>457.4</mark>

Table S1 Enthalpies of the gas-phase species of cations and anions and lattice energies

^a Heat of formation. ^b Lattice energy.

NBO analysis



Fig. S1 NBO charge distribution of borohydride cluster anions.

Atom	No	Natural Charge	Atom	No	Natural Charge
В	1	-0.17640	В	13	-0.17641
Н	2	0.00859	Н	14	0.00859
В	3	-0.17336	В	15	-0.17337
Н	4	0.00823	Н	16	0.00823
В	5	-0.17732	В	17	-0.17732
Н	6	0.00870	Н	18	0.00869
В	7	-0.17313	В	19	-0.17314
Н	8	0.00822	Н	20	0.00822
В	9	-0.17705	В	21	-0.17705
Н	10	0.00868	Н	22	0.00868
В	11	-0.17339	В	23	-0.17340
Н	12	0.00824	Н	24	0.00824

Table S2 NBO analysis of $[B_{12}H_{12}]^{2-}$ at B3LYP/6-311+G(d, p) level

Table S3. NBO analysis of $[B_{10}H_{10}]^{2-}$ at B3LYP/6-311+G(d, p) level

Atom	No	Natural Charge	Atom	No	Natural Charge
В	1	-0.16852	В	11	-0.16875
Н	2	-0.00671	Н	12	-0.00670
В	3	-0.16844	В	13	-0.16882
Н	4	-0.00673	Н	14	-0.00668
В	5	-0.16846	В	15	-0.16853
Н	6	-0.00674	Н	16	-0.00673
В	7	-0.16879	В	17	-0.16861
Н	8	-0.00669	Н	18	-0.00671
В	9	-0.28705	В	19	-0.28678
Н	10	-0.01176	Н	20	-0.01179

Atom	No	Natural Charge
В	1	-0.14664
Н	2	-0.00332
В	3	-0.23668
Н	4	-0.00349
В	5	-0.23719
Н	6	-0.00351
В	7	-0.14534
Н	8	-0.00357
В	9	-0.14636
Н	10	-0.00345
В	11	-0.23673
Н	12	-0.00351
Н	13	0.16982

Table S4 NBO analysis of $[B_6H_7]^-$ at B3LYP/6-311+G(d, p) level

<mark>Drop Test</mark>

T = -10 ms	T = 0 ms	T = 1 ms	T = 2 ms 🕴	T = 17 ms •	T = 30 ms

Fig. S2 A series of high-speed camera photos of a droplet of WFNA contacting with 2f.

Specific Impulse Curves



Fig. S3 Specific impulse curves of hypergolic fuels reacted with N_2O_4 : a) $[B_{10}H_{10}]^{2-}$ ILs / N_2O_4 ; b) $[B_6H_7]^-$ ILs / N_2O_4 .

Crystal Structure Analysis

empirical formula	$C_{14}H_{38}B_{12}N_4$
Mr	392.20
crystal size [mm ³]	$0.50 \times 0.34 \times 0.23$
crystal system	Monoclinic
space group	P2(1)/n
a [Å]	9.600(3)
b [Å]	10.708(3)
c [Å]	11.824(3)
α [°]	90
β [°]	98.996(3)
γ [°]	90
V [Å ³]	1200.6(5)
Z	2
T [K]	153(2)
λ (MoK α)	0.71073
$\rho_{calc} \left[mg \ mm^{-3} \right]$	1.085
μ[mm ⁻¹]	0.057

Table S5 Crystallographic data for [1-methyl-3-propylimidazolium]₂B₁₂H₁₂ (1b)

F(000)	420
Θ range [°]	2.97 to 31.50
	$-14 \le h \le 10$,
index ranges	$-15 \le k \le 14,$
	$-17 \le 1 \le 17$
reflns collected	11724
independent reflns	3973[R(int) = 0.0278]
GOF	1.001
Final R indexes [I> 2σ (I)]	$R_1 = 0.0476, wR_2 = 0.1056$
Final R indexes [all data]	$R_1 = 0.0565, wR_2 = 0.1112$
largest differential peak and hole	0.249/-0.184

Table S6 Crystallographic data for [1-methyl-3-propylimidazolium]₂B₁₀H₁₀ (2b)

empirical formula	$C_{14}H_{36}B_{10}N_4$
Mr	368.57
crystal size [mm ³]	$0.52 \times 0.23 \times 0.20$
crystal system	Orthorhombic
space group	Pbca
a [Å]	14.185(2)
b [Å]	10.6148(16)
c [Å]	30.936(5)
α [°]	90
β [°]	90
γ [°]	90
V [Å ³]	4658.1(12)
Z	8
T [K]	153(2)
λ (MoK α)	0.71073
$\rho_{calc} \ [mg \ mm^{-3}]$	1.051
μ [mm ⁻¹]	0.056

F(000)	1584
Theta range [°]	2.49 to 28.70
index ranges	$-19 \le h \le 18$,
	$-14 \le k \le 14,$
	$-41 \le l \le 41$
reflns collected	37153
independent reflns	5980[R(int) = 0.0389]
GOF	1.003
Final R indexes [I> 2σ (I)]	$R_1 = 0.0594, wR_2 = 0.1602$
Final R indexes [all data]	$R_1 = 0.0648, wR_2 = 0.1653$
largest differential peak and hole	0.258/-0.263

Table S7 Crystallographic data for $[{}^{n}Bu_{4}N]B_{6}H_{7}$

empirical formula	$C_{16}H_{43}B_6N$
Mr	314.37
Crystal size [mm ³]	$0.26 \times 0.24 \times 0.23$
Crystal system	Monoclinic
Space group	P2(1)/n
a [Å]	8.6160(17)
b [Å]	17.164(3)
c [Å]	15.238(3)
α [°]	90
β [°]	99.15(3)
γ [°]	90
V [Å ³]	2224.7(8)
Z	4
T [K]	153(2)
λ (MoK α)	0.71073
$\rho_{\rm calc} [{ m mg} { m mm}^{-3}]$	0.939
r 17	0.040

F(000)	704
Theta range [°]	2.37 to 27.49
Index ranges	$-8 \le h \le 11$,
	$-22 \le k \le 21$,
	$-19 \le l \le 17$
Reflns collected	15025
Independent reflns	5073[R(int) = 0.0327]
GOF	1.218
Final R indexes [I> 2σ (I)]	$R_1 = 0.0766, wR_2 = 0.1758$
Final R indexes [all data]	$R_1 = 0.0878, wR_2 = 0.1911$
Largest differential peak and hole	0.224/-0.208

$$R1 = \sum ||F0 - |Fc|| + \sum |F0|; \ wR2 = \left[\sum w(F02 - Fc2)2 + \sum w(F02)2\right] \frac{1}{2}$$

CCDC 1523664-1523666 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Syntheses

The preparation of ionic liquid precursors:⁸⁻¹⁰ 1-ethyl-3-methylimidazolium iodide, 1-propyl-3-methylimidazolium iodide, 1-butyl-3-methylimidazolium iodide, 1-allyl-3-methylimidazolium bromide,¹¹ 1-propargyl-3-methylimidazolium bromide,¹² and 3-cyanomethyl-1-methylimidazolium chloride¹³ were prepared by quarternization of 1-methylimidazole with iodoethane, 1-iodopropane, 1-iodobutane, allyl bromide, propargyl bromide and chloroacetonitrile, respectively.

 $[Et_3NH]_2B_{12}H_{12}$.¹⁴ A solution of iodine (102.8 g, 0.405 mol) in 180 mL of diglyme was added dropwise over a period of 6 h to a suspension of Na[BH₄] (48.95 g, 1.294 mol) in anhydrous diglyme (200 mL) at 100 °C. During the addition of iodine the amount of insoluble Na[BH₄] decreased and at the end a yellow color of the reaction mixture was observed. The reaction mixture was stirred over night at 100 °C to complete the formation of $[B_3H_8]^-$ followed by an additional 24 h reflux to completely disproportionate $[B_3H_8]^-$ to $[B_{12}H_{12}]^{2-}$ and $[BH_4]^-$ (at this stage the yellow color disappeared and a white precipitate started to form). The solvent was distilled off under reduced pressure giving a large amount of white solid. The white solid was dissolved in water (300 mL) and concentrated hydrochloric acid (140 mL) was added carefully to the reaction mixture (caution: hydrogen evolution). The acidified clear solution was stored at 6 °C overnight. Colorless crystals of boric acid precipitated and were removed by filtration. The filtrate was treated with Et₃N (200 mL) (pH = 9 - 10) and a white precipitate readily formed (the white precipitate contained the product $[Et_3NH]_2[B_{12}H_{12}]$ and remaining boric acid), which was collected by filtration. The solid was resuspended in water (150 mL, 50 °C), stirred for two hours, and then filtered to remove the more soluble boric acid impurity. The product $[Et_3NH]_2[B_{12}H_{12}]$ (11.8 g, 0.082 mol, 42%) remained as a white solid.

 $Na_2B_{12}H_{12}$: Solid [Et₃NH]₂[B₁₂H₁₂] (3.0 g, 8.68 mmol) was added to a solution of 2.5 equivalents of NaOH (0.868 g, 21.7 mmol) dissolved in water in a polyethylene beaker. The suspension was heated on an oil bath until it became a clear solution. Then the solution was evaporated to dryness. The white solid remaining in the beaker was redissolved in THF (40 mL). The undissolved impurities were removed by filtration. The solvent was distilled off under reduced pressure giving a large amount of white solid, namely $Na_2B_{12}H_{12}$ (yield >90%).

[Et₃NH]₂B₁₀H_{10:}¹⁵ Decaborane (5 g, 41 mmol) is dissolved in xylene (50 mL) in a three-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. The flask is flushed with nitrogen and trimethylamine (15 mL) is added in small portions over a period of 2 minutes. At this stage, a yellow-white amine borane adduct precipitates. The temperature of the xylene solution is raised to 100 ± 5 °C and the reaction mixture is stirred for 3 hours under nitrogen. During this stage, hydrogen gas is evolved and [Et₃NH]₂B₁₀H₁₀ is formed, together with covalent [Et₃NH]₂B₁₀H₁₂. The temperature for another 5 hours. The covalent [Et₃NH]₂B₁₀H₁₂ is converted to the ionic [Et₃NH]₂B₁₀H₁₀ during the reflux period. The solution is cooled to 0 °C and filtered. A pale yellow solid is obtained, which is washed isopropyl alcohol (5 x 10 mL) to remove the major portion of the yellow color and any covalent impurities. After a final washing with diethyl ether and drying in vacuum for 12 hours, 12.1 g of product is obtained (white solid, 92%).

 $Na_2B_{10}H_{10}$: Solid [Et₃NH]₂[B₁₀H₁₀] (3.0 g, 9.3 mmol) was added to a solution of 2.5 equivalents of NaOH (0.932g, 23.3 mmol) dissolved in water in a polyethylene beaker. The suspension was heated on an oil bath until it became a clear solution. Then the solution was evaporated to dryness. The white solid remaining in the beaker was redissolved by THF (40 mL). The undissolved impurities were removed by filtration. The solvent was distilled off under reduced pressure giving a large amount of white solid, namely $Na_2B_{10}H_{10}$ (yield: >90%).

Synthesis of $B_{12}H_{12}^{2-}$ salts (1a – 1f): Na₂B₁₂H₁₂ (0.563 g, 3 mmol) was dissolved in water (25 mL) and an aqueous solution (25 mL) of imidazolium-based ionic liquids (6 mmol) was added dropwise. After stirring at room temperature for 1 hour, solids were removed by filtration, and the solvent was removed under reduced pressure.

Synthesis of $B_{10}H_{10}^{2-}$ salts (2a – 2f): Na₂B₁₀H₁₀ (0.164 g, 1 mmol) was dissolved in solvent (10 mL, 2a – 2c using ethanol and 2d – 2f using methanol) and a corresponding solution (20 mL) of imidazolium-based ionic liquids (2 mmol) was added. After stirring at -10 °C for 1 hour solids were removed by filtration, and the solvent was removed under reduced pressure.

Synthesis of B_6H_7 ionic liquids (3a – 3f): In a 500 mL, three-necked flask, 15 g (0.4 mol) of powdered sodium borohydride was added to 250 cm³ of anhydrous diglyme. The flask was equipped with a magnetic stirrer, a 150 cm³ pressure equalizing funnel, a condenser connected to an oil bubbler and a nitrogen inlet. The flask was placed in a silicone oil bath, flushed with nitrogen and the bath heated to 55-60 °C. The effluent gas was bubbled through acetone solution to destroy any diborane which may have formed. The dropping funnel was filled with diglyme (80 mL) and distilled $BF_3 \cdot O(C_2H_5)_2$ (25 mL; 0.19 mol). With the flow of nitrogen stopped and the nitrogen inlet closed, addition of BF $_3 \cdot O(C_2H_5)_2$ was started and continued over a period of 90 min. The temperature of the oil bath was raised to 100 °C and kept at this temperature for 1 h. The temperature of the oil bath was raised to 165-180 °C and the solution was refluxed for 36 h. A gentle stream of nitrogen was allowed to flow, heating was stopped and the solution which contained a white precipitate was cooled to 50 °C. The diglyme solution was filtered, and the white precipitate was collected and added to the solid remaining in the round-bottomed flask. The reaction flask was placed in an ice bath and cold water (50 mL) was added to the solid. A vigorous reaction occurred and the mixture was stirred until effervescence subsided. The aqueous solution was filtered and the solid borates were washed with cold water (10 mL). A hydrochloric acid solution (1 M) was added dropwise into the solution above, adjusting the pH value ~ 7.0. The ionic liquid precursor (30 mmol) was dissolved in water (20 mL) and added to the aqueous filtrate. The mixture was stirred until the system becomes an emulsion. The mixture was poured into a separatory funnel, standing for several hours until stratification (in this process, heating could accelerate two-phase separation). After the aqueous layer was removed (another small portion of hydrochloric acid solution was dropped into the aqueous solution to test the completion of precipitation), the upper layer was dissolved in acetonitrile (15 mL), and poured into a round-bottom flask after drying over anhydrous sodium sulfate. The solvent was removed by

evaporation leaving behind an ionic liquid. After further drying under dynamic vacuum at ambient temperature, a pure ionic liquid was obtained.

[Et₃NH]₂B₁₂H₁₂: white solid (11.810 g, 42%). ¹¹B NMR (193 MHz, CD₃CN, 298 K) δ = -14.85 ppm (d, *J* = 126.0 Hz); ¹H NMR (600 MHz, CD₃CN, 298 K) δ = 3.16 (q, *J* = 7.3 Hz, 12H; CH₂), 1.44 - 0.55 ppm (m, *J* = 7.3 Hz, 30H, B-H overlapped by -CH₃). ¹³C NMR (151 MHz, CD₃CN, 298 K) δ = 48.12, 9.13 ppm. IR (KBr): σ = 3127, 3020, 2977, 2960, 2482, 1471, 1403, 1392, 1160, 1065, 1030, 843, 717. Elemental analysis calcd (%) for C₁₂H₄₄B₁₂N₂ (346.22): C 41.63, H 12.81, N 8.09; found: C 41.66, H 12.86, N 8.12.

[3-Ethyl-1-methylimidazolium]₂**B**₁₂**H**₁₂ (1a): white solid (0.880 g, 81%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -14.95 ppm (d, *J* = 124.6 Hz). ¹H NMR (600 MHz, DMSO-d₆, 298 K) δ = 9.09 (s, 2H; CH), 7.78 (t, *J* = 1.6 Hz, 2H, CH), 7.69 (t, *J* = 1.6 Hz, 2H, CH), 4.19 (q, *J* = 7.3 Hz, 4H; CH₂), 3.84 (s, 6H; CH₃), 1.41 (t, *J* = 7.3 Hz, 6H; CH₃), 1.35 – 0.35 ppm (m, 12H, B-H). ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 137.03, 124.16, 122.80, 50.81, 36.31, 23.40, 10.98 ppm. IR (KBr): σ = 3154, 3116, 2984, 2954, 2483, 2454, 1622, 1566, 1167, 1061, 832, 757, 644, 619 cm⁻¹. Elemental analysis: calcd (%) for C₁₂H₃₄B₁₂N₄ (364.16): C 39.58, H 9.41, N 15.39; found: C 39.61, H 9.36, N 15.26.

1-Methyl-3-propylimidazolium]₂**B**₁₂**H**₁₂ (**1b**): white solid (0.985 g, 84%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -14.96 ppm (d, *J* = 125.2 Hz); ¹H NMR (600 MHz, DMSO-d₆, 298 K) δ = 9.08 (s, 2H; CH), 7.78 (t, *J* = 1.5 Hz, 2H; CH), 7.69 (t, *J* = 1.4 Hz, 2H; CH), 4.12 (t, *J* = 7.1 Hz, 4H, CH₂), 3.85 (s, 6H, CH₃), 1.80 (dd, *J* = 14.5, 7.3 Hz, 4H; CH₂), 1.32 – 0.37 (m, 18H, B-H overlapped by CH₃), 0.85 ppm (t, *J* = 7.4 Hz, 6H; CH₃); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 136.75, 124.10, 122.50, 44.68, 36.26, 15.67 ppm. IR (KBr): σ = 3149, 3118, 3093, 2966, 2466, 1618, 1570, 1167, 1060, 841, 621 cm⁻¹. Elemental analysis: calcd (%) for C₁₄H₃₈B₁₂N₄ (392.21): C 42.87, H 9.77, N 14.28; found: C 42.86, H 9.58, N 14.18.

[3-Butyl-1-methylimidazolium]₂**B**₁₂**H**₁₂ (**1c**): white solid (1.02 g, 81%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -14.99 ppm (d, *J* = 124.5 Hz); ¹H NMR (600 MHz, DMSO-d₆, 298 K) δ = 9.09 (s, 2H; CH), 7.77 (t, *J* = 1.5 Hz, 2H; CH), 7.70 (t, *J* = 1.4 Hz, 2H; CH), 4.16 (t, *J* = 7.2 Hz, 4H; CH₂), 3.84 (s, 6H; CH₃), 1.81 – 1.71 (m, 4H; CH₂), 1.25 (dq, *J* = 14.7, 7.3 Hz, 4H; CH₂), 0.90 (m, 6H; CH₃), 1.33 – 0.37 ppm (m, 18H; B-H overlapped by CH₃); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 137.02, 124.15, 122.80, 49.04, 36.30, 31.90, 19.32, 13.83 ppm. IR (KBr): σ = 3140, 3115, 3088, 2963, 2873, 2467, 1610, 1570, 1461, 1168, 1058, 842, 756 cm⁻¹. Elemental analysis: calcd (%) for C₁₆H₄₂B₁₂N₄ (420.26): C 45.73, H 10.07, N 13.33; found: C 45.72, H 10.13, N 13.25.

[3-Allyl-1-methylimidazolium]₂**B**₁₂**H**₁₂ (**1d**): white solid (0.73 g, 63%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -14.95 ppm (d, *J* = 124.5 Hz); ¹H NMR (600 MHz, DMSO-d₆, 298 K) δ = 9.10 (s, 2H; CH), 7.73 (t, *J* = 1.5 Hz, 2H; CH), 7.71 (t, *J* = 1.6 Hz, 2H; CH), 6.04 (m, *J* = 16.3, 10.3, 5.9 Hz, 2H; CH), 5.36 (dd, *J* = 10.3, 1.0 Hz, 2H; CH), 5.30 (dd, *J* = 17.1, 1.1 Hz, 2H; CH), 4.84 (d, *J* = 5.9 Hz, 4H; CH₂), 3.87 (s, 6H; CH₃), 1.32 – 0.38 ppm (m, 12H; B-H); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 137.15, 132.31, 124.32, 122.87, 120.72, 51.34, 36.38 ppm. IR (KBr): σ = 3151, 3118, 3096, 2956, 2495, 2465, 1624, 1573, 1562, 1446, 1423, 1173, 1061, 926, 837, 763, 621 cm⁻¹. Elemental analysis: calcd (%) for C₁₄H₃₄B₁₂N₄ (388.18): C 43.32, H 8.83, N 14.43; found: C 43.36, H 8.57, N 14.50.

[1-Methyl-3-(prop-2-yn-1-yl)-imidazolium]₂**B**₁₂**H**₁₂ (1e): yellow solid (0.73 g, 63%). ¹¹B NMR (193 MHz, DMSO-d₆) δ -14.93 ppm (d, J = 125.7 Hz); ¹H NMR (600 MHz, DMSO-d₆, 298 K) δ = 9.20 (s, 2H; CH), 7.79 (s, 2H; CH), 7.75 (s, 2H; CH), 5.20 (d, J = 2.5 Hz, 4H; CH₂), 3.88 (s, 6H; CH₃), 1.34 - 0.35 ppm (m, 12H; B-H); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 137.12, 124.59, 122.68, 79.49, 76.68, 39.03, 36.53 ppm. IR (KBr): $\sigma = 3272$, 3136, 3085, 2969, 2467, 1573, 1557, 1359, 1163, 1061, 839, 755, 684, 619 cm⁻¹. Elemental analysis: calcd (%) for C₁₄H₃₀B₁₂N₄ (384.15): C 43.77, H 7.87, N 14.58; found: C 43.05, H 7.94, N 14.15.

[3-(Cyanomethyl)-1-methylimidazolium]₂**B**₁₂**H**₁₂ (**1f**): white solid (0.54 g, 47%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -14.95 ppm (d, *J* = 125.7 Hz); ¹H NMR (600 MHz, DMSO-d₆, 298 K) δ = 9.23 (s, 2H; CH), 7.89 (t, *J* = 1.8 Hz, 2H; CH), 7.79 (t, *J* = 1.7 Hz, 2H; CH), 5.57 (s, 4H; CH₂), 3.89 (s, 6H, CH₃), 1.34 - 0.37 ppm (m, 12H; B-H); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 138.25, 124.92, 123.10, 115.33, 37.36, 36.72 ppm. IR (KBr): σ = 3137, 3151, 3085, 2977, 2942, 2483, 2465, 1626, 1579, 1556, 1167, 1064, 839, 756, 621 cm⁻¹. Elemental analysis: calcd (%) for C₁₂H₂₈B₁₂N₆ (386.12): C 37.33, H 7.31, N 21.77; found: C 37.35, H 7.35, N 21.53.

Note! Considering that the ¹¹B chemical shift of $[B_{10}H_{10}]^{2-}$ is partly overlapped by that of BF₃·OEt₂, we gave up using it as external reference. But there is no large deviation in the chemical shift, and the shape of the NMR peak is consistent with the previous report.¹⁶

[Et₃NH]₂B₁₀H₁₀: white solid (12.1 g, 92%). ¹¹B NMR (193 MHz, CD₃CN, 298 K) δ = -1.81 (d, J = 139.8 Hz), -29.80 ppm (d, J = 125.2 Hz); ¹H NMR (600 MHz, CD₃CN, 298 K) δ = 3.22 (q, J = 7.3 Hz, 12H; CH₂), 3.58 – 2.75 (m, 14H; B-H overlapped by CH₂), 1.31 (t, J = 7.3 Hz, 18H), 0.04 ppm (m, J = 251.5, 116.3 Hz, 8H, B-H); ¹³C NMR (151 MHz, CD₃CN, 298 K) δ = 48.05, 9.10 ppm. IR (KBr): σ = 3063, 2981, 2944, 2464, 1448, 1403, 1161, 1033, 1011, 842, 789 cm⁻¹. Elemental analysis: calcd

(%) for $C_{12}H_{42}B_{10}N_2$ (322.58): C 44.68, H 13.12, N 8.68; found: C 44.50, H 13.38, N, 8.67.

[3-Ethyl-1-methylimidazolium]₂**B**₁₀**H**₁₀ (**2a**): white solid (0.317 g, 94%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -1.70 (d, *J* = 138.4 Hz), -29.59 ppm (d, *J* = 122.4 Hz); ¹H NMR (600 MHz, DMSO-d₆, 298 K) δ = 9.12 (s, 2H; CH), 7.78 (t, *J* = 1.6 Hz, 2H; CH), 7.69 (t, *J* = 1.6 Hz, 2H; CH), 4.20 (q, *J* = 7.3 Hz, 4H; CH₂), 3.85 (s, 6H; CH₃), 3.35 - 2.54 (m, 2H; B-H), 1.41 (t, *J* = 7.3 Hz, 6H; CH₃), 0.28 - -0.63 ppm (m, 8H; B-H); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 136.78, 124.08, 122.46, 44.66, 36.27, 15.76 ppm. IR (KBr): σ = 3148, 3105, 2986, 2949, 1454, 1625, 1573, 1467, 1430, 1347, 1012, 821, 759, 644, 616 cm⁻¹. Elemental analysis: calcd (%) for C₁₂H₃₂B₁₀N₄ (340.52): C 42.33, H 9.47, N 16.45; found: C 42.27, H 9.35, N, 16.35.

[1-Methyl-3-propylimidazolium]₂**B**₁₀**H**₁₀ (**2b**): white solid (0.318 g, 86%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -1.71 (d, *J* = 140.3 Hz), -29.61 ppm (d, *J* = 124.0 Hz); ¹H NMR (600 MHz, DMSO-d₆, 298 K) δ = 9.11 (s, 2H; CH), 7.77 (t, *J* = 1.5 Hz, 2H; CH), 7.71 (t, *J* = 1.4 Hz, 2H; CH), 4.13 (t, *J* = 7.1 Hz, 4H; CH₂), 3.85 (s, 6H; CH₃), 3.33 – 2.54 (m, 2H; B-H), 1.80 (h, *J* = 7.3 Hz, 4H; CH₂), 0.85 (t, *J* = 7.4 Hz, 6H; CH₃), 0.28 – -0.67 ppm (m, 8H; B-H); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 137.07, 124.15, 122.78, 50.78, 36.31, 23.43, 10.98 ppm. IR (KBr): σ = 3144, 3104, 2967, 1487, 2446, 1630, 1575, 1172, 1012, 765, 622 cm⁻¹. Elemental analysis: calcd (%) for C₁₄H₃₆B₁₀N₄ (368.57): C 45.62, H 9.84, N 15.20; found: C 45.54, H 9.78, N, 15.06.

[3-Butyl-1-methylimidazolium]₂**B**₁₀**H**₁₀ (**2c**): white solid (0.381 g, 96%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -1.70 (d, *J* = 138.4 Hz), -29.59 ppm (d, *J* = 122.4 Hz); ¹H NMR (600 MHz, DMSO-d₆, 298 K) δ = 9.12 (s, 2H; CH), 7.77 (t, *J* = 1.6 Hz, 2H; CH), 7.70 (t, *J* = 1.6 Hz, 2H; CH), 4.17 (t, *J* = 7.2 Hz, 4H; CH₂), 3.85 (s, 6H; CH₃), 3.33 – 2.54 (m, 2H; B-H), 1.79 – 1.72 (m, 4H; CH₂), 1.30 – 1.20 (m, 4H; CH₂), 0.90 (t, *J* = 7.4 Hz, 6H; CH₃), 0.33 – -0.66 ppm (m, 8H; B-H); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 137.05, 124.12, 122.77, 49.03, 36.31, 31.96, 19.34, 13.86 ppm. IR (KBr): σ = 3140, 3102, 3070, 2958, 2929, 2871, 2477, 2457, 1570, 1562, 1461, 1166, 1013, 849, 776, 751, 625 cm⁻¹. Elemental analysis: calcd (%) for C₁₆H₄₀B₁₀N₄ (396.62): C 48.45, H 10.17, N 14.13; found: C 48.26, H 10.22, N, 14.01.

[3-Allyl-1-methylimidazolium]₂**B**₁₀**H**₁₀ (**2d**): white solid (0.245 g, 67%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -1.66 (d, *J* = 140.5 Hz), -29.59 ppm (d, *J* = 125.4 Hz); ¹H NMR (600 MHz, DMSO-d₆, 298 K) δ = 9.11 (s, 2H; CH), 7.73 (t, *J* = 1.7 Hz, 2H; CH), 7.70 (t, *J* = 1.8 Hz, 2H; CH), 6.04 (ddt, *J* = 16.5, 10.4, 6.0 Hz, 2H; CH), 5.36 (q, *J* = 1.2 Hz, 1H; CH), 5.35 (q, *J* = 1.2 Hz, 1H; CH), 5.32 – 5.30 (dd, 1H; CH), 5.28 (dd, *J* = 2.3, 1.3 Hz, 1H; CH), 4.84 (d, *J* = 5.9 Hz, 4H; CH₂), 3.86 (s, 6H; CH₃), 3.32 – 2.54 (m, 2H; B-H), 0.24 – -0.63 ppm (m, 8H; B-H); ¹³C NMR (151 MHz,

DMSO-d₆, 298 K) δ = 137.18, 132.37, 124.30, 122.85, 120.66, 51.32, 36.37 ppm. IR (KBr): σ = 3144, 3105, 3022, 2969, 2948, 2499, 2454, 2417, 1617, 1570, 1447, 1419, 1324, 1164, 1011, 991, 944, 841, 757, 621 cm⁻¹. Elemental analysis: calcd (%) for C₁₄H₃₂B₁₀N₄ (364.54): C 46.13, H 8.85, N 15.37; found: C 45.98, H 8.86, N, 15.33.

[1-Methyl-3-(prop-2-yn-1-yl)-imidazolium]₂**B**₁₀**H**₁₀ (2e): white solid (0.185 g, 52%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -1.71 (d, *J* = 141.5 Hz), -29.60 ppm (d, *J* = 125.1 Hz); ¹H NMR (600 MHz, DMSO-d₆, 298 K) δ = 9.20 (s, 2H; CH), 7.79 (t, *J* = 1.8 Hz, 2H; CH), 7.75 (t, 2H; CH), 5.20 (d, *J* = 2.4 Hz, 4H; CH₂), 3.87 (s, 6H; CH₃), 3.32 - 2.54 (m, 2H; B-H), 0.27 - -0.63 ppm (m, 8H; B-H); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 137.15, 124.57, 122.65, 79.45, 76.74, 39.03, 36.52 ppm. IR (KBr): σ = 3137, 3101, 3069, 2950, 2456, 1610, 1575, 1545, 1426, 1167, 1012, 831, 745, 620 cm⁻¹. Elemental analysis: calcd (%) for C₁₄H₂₈B₁₀N₄ (360.51): C 46.64, H 7.83, N 15.54; found: C 46.61, H 7.61, N, 15.33.

[3-(Cyanomethyl)-1-methylimidazolium]₂**B**₁₀**H**₁₀ (**2f**): white solid (0.341 g, 94%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -1.71 (d, *J* = 138.4 Hz), -29.57 ppm (d, *J* = 121.7 Hz); ¹H NMR (600 MHz, DMSO-d₆, 298 K) δ = 9.24 (s, 2H; CH), 7.89 (s, 2H; CH), 7.79 (s, 2H; CH), 5.59 (d, *J* = 2.7 Hz, 4H; CH₂), 3.88 (s, 6H; CH₃), 3.34 – 2.55 (m, 2H; B-H), 0.26 – -0.63 ppm (m, 8H; B-H); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 138.27, 124.90, 123.07, 115.32, 37.36, 36.72 ppm. IR (KBr): σ = 3156, 3113, 3086, 2970, 3953, 2934, 2500, 2458, 1626, 1581, 1561, 1350, 1172, 1017, 921, 832, 761, 668, 620 cm⁻¹. Elemental analysis: calcd (%) for C₁₂H₂₆B₁₀N₆ (362.48): C 39.76, H 7.23, N 23.18; found: C 39.80, H 7.28, N, 23.10.

[3-Ethyl-1-methylimidazolium]B₆**H**₇ (**3a**): colorless liquid (2.710 g, 17%). ¹¹B NMR (193 MHz, DMSO-d₆) δ -13.12 ppm (d, J = 146.2 Hz); ¹H NMR (600 MHz, CD₃CN, 298 K) δ 8.43 (s, 1H; CH), 7.37 (d, J = 1.5 Hz, 1H; CH), 7.32 (d, J = 1.3 Hz, 1H; CH), 4.15 (q, J = 7.3 Hz, J = 1.3 Hz, 2H; CH), 3.80 (s, 3H; CH₃), 1.44 (t, J = 7.3 Hz, 3H; CH₃), 1.57 – 0.37 (m, 9H; B-H overlapped by CH₃), -5.61 ppm (s, 1H; B-H^{fac}); ¹³C NMR (151 MHz, DMSO-d₆) δ 136.17, 123.53, 121.93, 44.11, 35.70, 15.07 ppm. IR(KBr): $\sigma = 3149$, 3115, 2985, 2956, 2531, 1571, 1465, 1388, 1336, 1168, 830, 745, 700, 645, 619 cm⁻¹. Elemental analysis: calcd (%) for C₆H₁₈B₆N₂ (183.09): C 39.36, H 9.91, N 15.30; found: C 39.68, H 9.87, N 15.74.

[1-Methyl-3-propylimidazolium]B₆**H**₇ (**3b**): colorless liquid (3.012 g, 23%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -13.13 ppm (d, *J* = 146.4 Hz); ¹H NMR (600 MHz, CD₃CN, 298 K) δ = 8.46 (s, 1H; CH), 7.35 (d, *J* = 1.5 Hz, 1H; CH), 7.33 (d, *J* = 1.5 Hz, 1H; CH), 4.08 (t, *J* = 7.2 Hz, 2H; CH₂), 3.81 (s, 3H; CH₃), 1.89 – 1.76 (m, 2H; CH₂), 1.51 – 0.52 (m, 9H; B-H overlapped by CH₃), 0.95 (t, 4H; CH₂), -5.61 ppm (s, 1H; B-H^{fac}); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 136.39, 123.54, 122.17, 50.28, 35.79, 22.79, 10.38 ppm. IR (KBr): σ = 3145, 3112, 2966, 2877, 2527, 1569,

1456, 1168, 1053, 831, 748, 620 cm⁻¹. Elemental analysis: calcd (%) for $C_7H_{20}B_6N_2$ (197.11): C 42.65, H 10.23, N 14.21; found: C 42.77, H 10.06, N 14.60.

[3-Butyl-1-methylimidazolium]B₆**H**₇ (**3c**): colorless liquid (2.861 g, 21%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -13.12 ppm (d, *J* = 145.5 Hz); ¹H NMR (600 MHz, CD₃CN, 298 K) δ = 8.43 (s, 1H; CH), 7.35 (d, *J* = 1.6 Hz, 1H; CH), 7.32 (d, *J* = 1.3 Hz, 1H; CH), 4.10 (t, *J* = 7.3 Hz, 2H; CH₂), 3.80 (s, 3H; CH₃), 1.83 – 1.74 (m, 2H; CH₂), 1.30 (dq, *J* = 14.9, 7.4 Hz, 3H; CH₃), 1.57 – 0.41 (m, 11H; B-H overlapped by CH₂ and CH₃), 0.91 (t, *J* = 7.4 Hz, 3H; CH₃), -5.61 ppm (s, 1H; B-H^{fac}); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 136.42, 123.55, 122.20, 48.50, 35.75, 31.29, 18.73, 13.22 ppm. IR (KBr): σ = 3147, 3113, 2960, 2934, 2874, 2529, 1571, 1463, 1167, 1056, 833, 748, 619 cm⁻¹. Elemental analysis: calcd (%) for C₈H₂₂B₆N₂ (211.14): C 45.51, H 10.50, N 13.27; found: C 45.38, H 10.19, N 13.31.

[3-Allyl-1-methylimidazolium]B₆**H**₇ (**3d**): colorless liquid (1.890 g, 15%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -13.13 ppm (d, *J* = 146.8 Hz); ¹H NMR (600 MHz, CD₃CN, 298 K) δ 8.42 (s, 1H; CH), 7.33 (d, *J* = 4.4 Hz, 2H; CH), 5.99 (dq, *J* = 10.7, 6.1 Hz, 1H; CH), 5.40 (d, *J* = 10.2 Hz, 1H; CH), 5.34 (d, *J* = 17.1 Hz, 1H; CH), 4.73 (d, *J* = 6.0 Hz, 2H; CH₂), 3.81 (s, 3H; CH₃), 1.71 – 0.43 (m, 6H; B-H), -5.61 ppm (s, 1H; B-H^{fac}); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 136.49, 131.52, 123.71, 122.26, 120.21, 50.79, 35.86 ppm. IR (KBr): σ = 3146, 3113, 3088, 2955, 2531, 1572, 1446, 1422, 1164, 991, 944, 830, 746, 619 cm⁻¹. Elemental analysis: calcd (%) for C₇H₁₈B₆N₂ (195.1): C 43.09, H 9.30, N 14.36; found: C 42.94, H 9.53, N 14.74.

[1-Methyl-3-(prop-2-yn-1-yl)-imidazolium]B₆**H**₇ (**3e**): white solid (2.661 g, 21%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -13.15 ppm (d, *J* = 147.0 Hz); ¹H NMR (600 MHz, CD₃CN, 298 K) δ = 8.43 (s, 1H; CH), 7.37 (d, 1H; CH), 7.32 (d, 1H; CH), 4.15 (d, *J* = 7.3 Hz, 2H; CH₂), 3.80 (s, 3H; CH₃), 3.01 (t, 1H; CH), 1.57 – 0.37 (m, 6H; B-H), -5.61 ppm (s, 1H; B-H^{fac}); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 136.58, 124.05, 122.14, 78.94, 76.11, 38.49, 35.98 ppm. IR (KBr): σ = 3258, 3139, 3083, 2957, 2522, 2501, 2135, 1595, 1573, 1552, 1440, 1413, 1348, 1261, 1161, 828, 743, 730, 707, 678, 60, 610 cm⁻¹. Elemental analysis: calcd (%) for C₇H₁₆B₆N₂ (193.08): C 43.54, H 8.35, N 14.51; found: C 43.36, H 8.23, N 14.66.

[3-(Cyanomethyl)-1-methylimidazolium]B₆**H**₇ (**3f**): white solid (2.271 g, 18%). ¹¹B NMR (193 MHz, DMSO-d₆, 298 K) δ = -13.14 ppm (d, *J* = 144.8 Hz); ¹H NMR (600 MHz, CD₃CN, 298 K) δ = 8.59 (s, 1H; CH), 7.51 (d, *J* = 1.6 Hz, 1H; CH), 7.41 (d, *J* = 1.5 Hz, 1H; CH), 5.20 (s, 2H; CH₂), 3.84 (s, 3H; CH₃), 1.62 – 0.39 (m, 6H; B-H), -5.61 ppm (s, 1H; B-H^{fac}); ¹³C NMR (151 MHz, DMSO-d₆, 298 K) δ = 137.72, 124.38, 122.58, 114.76, 36.83, 36.18 ppm. IR (KBr): σ = 3155, 3122, 3096, 2967, 2927, 2535, 2513, 1605, 1582, 1563, 1428, 1329, 1285, 1177, 1084, 925, 847, 744, 620, 608 cm⁻¹. Elemental analysis: calcd (%) for $C_6H_{15}B_6N_3$ (194.07): C 37.13, H 7.79, N 21.65; found: C 37.42, H 7.74, N 21.08.

NMR Spectra



~14.53

 $[Et_3NH]_2B_{12}H_{12}$

50 45 20 15 10 -10 -15 -20 -50 40 35 30 25 0 f1 (ppm) -5 -25 -30 -35 -40 -45 5



3.19 3.15 3.15 3.15



¹¹B NMR









¹¹B NMR

<14.67









90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 f1 (ppm)







 $\begin{bmatrix} & & & \\ &$





90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 f1 (ppm)





~29.47

~-1.38

 $[Et_3NH]_2B_{10}H_{10}$

¹¹B NMR



[Et₃NH]₂B₁₀H₁₀











¹H NMR











~29.91

¹¹B NMR















¹¹B NMR



(3a)





¹¹B NMR

 $\begin{bmatrix} \sqrt{1} + 1 \\ H_3 C^{-N} \sqrt{N} \\ CH_2 CH_2 CH_2 CH_3 \end{bmatrix} B_6 H_7$ (3b)







¹³C NMR





(**3d**)







(**3e**)





<12.77 <13.52

¹¹B NMR







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