Supplementary Material

Novel Asymmetric Boronium-Cation-Based Ionic Liquids Synthesized for Hypergolic Fuels

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Contents

1.Synthesis procedure

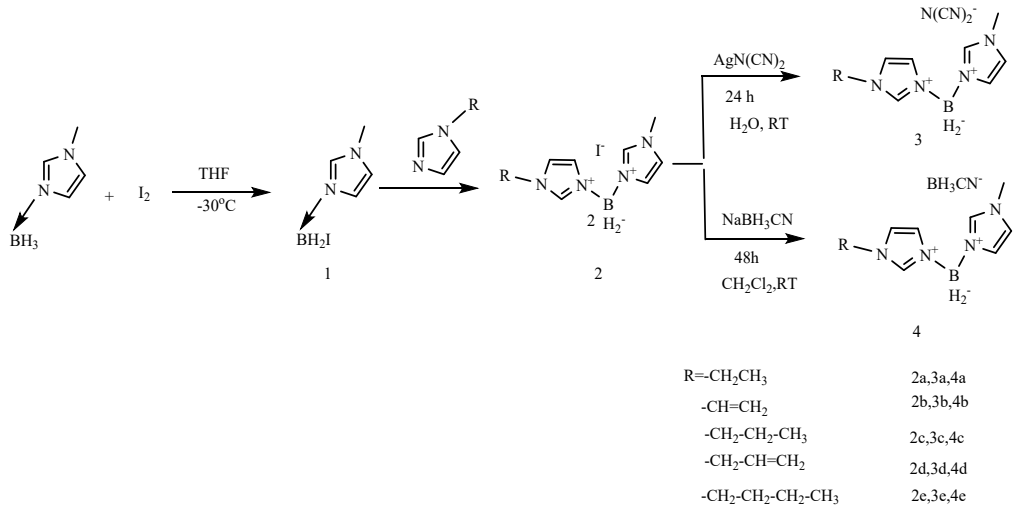


Figure S1 The synthetic route for the asymmetric boronium-cation-based ionic liquids

Synthesis of 1-methylimidazole borane complex

The product was a colorless liquid; yield, 92 %. ^{1}H NMR(DMSO-d_6, 400 MHz): δ= 1.77 – 2.47 (m, 3H, BH_3), 3.67 – 3.72 (s, 3H, CH_3), 6.96 – 7.03 (s, 1H, N-CH=CH-N), 7.24 – 7.36 (s, 1H, N-CH=CH-N), 7.92 – 8.40 ppm (s, 1H, N-CH=N); ^{13}C NMR (101 MHz, Deuterium Oxide) δ = 34.24, 122.07, 126.31, 137.78 ppm; IR (KBr): $\tilde{\nu}$= 3137, 2358, 2309, 2262, 1549, 1301, 1174, 831, 748 cm^{-1}

Synthesis of (1-ethyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium iodide (2a)

The product 2a was a viscous transparent liquid; yield, 42 %. ^{1}H NMR(DMSO-d_6, 400 MHz): δ= 1.32 – 1.45 (s, 3H, CH_3), 3.79 – 3.84 (s, 3H, CH_3), 4.07 – 4.25 (s, 2H, CH_2), 7.37 – 7.43 (d, 2H, N-CH=CH-N), 7.53 – 7.59 (s, 1H, N-CH=CH-N), 7.66 – 7.70 (s, 1H, N-CH=CH-N), 8.73 – 8.80 (s, 1H,N-CH=N), 8.80 – 8.90 ppm (s, 1H, N-CH=N); ^{13}C NMR (101 MHz, DMSO-d6) δ = 15.34 , 34.97 , 43.19 , 121.92 , 123.39 , 124.76 , 124.85 , 137.80 , 138.74 ppm; IR (KBr): $\tilde{\nu}$= 3445, 3113, 3068, 2959, 2876, 2427, 1544, 1162, 1128 cm^{-1}.

Synthesis of (1-methyl-1H-imidazol-3-ium-1-yl)(1-vinyl-1H-imidazol-3-ium-1-yl) dihydroboronium iodide (2b)

The product 2b was a viscous transparent liquid; yield, 40 %. ^{1}H NMR(DMSO-d_6, 400 MHz): δ= 3.60 – 3.87 (s, 3H, CH_3), 5.24 – 5.35 (dt, 1H, CH2=CH), 5.83 – 5.93 (dd, 1H, CH=CH), 7.17 – 7.28 (dd, 1H, CH2=CH), 7.36 – 7.42 (t, 1H, N-CH=CH-N), 7.49 – 7.56 (m, 2H, N-CH=CH-N), 8.01 – 8.06 (s, 1H, N-CH=CH-N), 8.65 – 8.70 (s, 1H, N-CH=N), 9.01 – 9.06 ppm (s, 1H, N-CH=N);^{13}C NMR (101 MHz, DMSO-d_6) δ = 35.45, 107.59, 119.60, 124.03, 125.38, 126.27, 129.41, 138.01, 139.48 ppm; IR：$\tilde{\nu}$= 3433, 3124, 2972, 2928, 2892, 2433, 1537, 1161, 1130 cm^{-1}.

Synthesis of (1-methyl-1H-imidazol-3-ium-1-yl)(1-propyl-1H-imidazol-3-ium-1-yl) dihydroboronium iodide (2c)

The product 2c was a viscous transparent liquid; yield, 44% . ^{1}H NMR(DMSO-d_6, 400 MHz): δ= 0.74 – 0.85 (td, 3H, CH_3), 1.68 – 1.86 (m, 2H, CH_2), 3.76 – 3.85 (s, 3H, CH_3), 4.02 – 4.12 (q, 2H,CH_2), 7.34 – 7.38 (d, 1H, N-CH=CH-N), 7.38 – 7.42 (d, 1H, N-CH=CH-N), 7.52 – 7.58 (d, 1H, N-CH=CH-N), 7.61 – 7.68 (d, 1H, N-CH=CH-N), 8.66 – 8.75 (s, 1H, N-CH=N), 8.75 – 8.86 ppm (s, 1H, N-CH=N) ^{13}C NMR (101 MHz, DMSO-d_6) δ = 10.48, 22.99, 34.95, 49.42, 122.32, 123.51, 124.79, 124.95, 138.18, 138.82 ppm; IR (KBr): $\tilde{\nu}$= 3445, 3113, 3068, 2965, 2876, 2427, 1544, 1161, 1129 cm^{-1}.

Synthesis of (1-allyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium iodide (2d)

The product 2d was a viscous transparent liquid; yield, 42%. ^{1}H NMR (400 MHz, DMSO-d6) :δ= 3.75 – 3.83 (s, 3H, CH_3), 4.74 – 4.83 (dt, 2H, CH_2), 5.18 – 5.34 (m, 2H, CH_2), 5.92 – 6.10 (m, 1H, CH), 7.35 – 7.40 (s, 1H, N-CH=CH-N), 7.40 – 7.44 (s, 1H, N-CH=CH-N), 7.53 – 7.56 (s, 1H, N-CH=CH-N), 7.56 – 7.60 (s, 1H, N-CH=CH-N), 8.69 – 8.75 (s, 1H, N-CH=N), 8.75 – 8.81 ppm (s, 1H, N-CH=N); ^{13}C NMR (101 MHz, DMSO-d_6) δ = 34.95, 50.05, 119.58, 122.34, 123.49, 124.83, 125.10, 132.31, 138.19, 138.85 ppm; IR：$\tilde{\nu}$= 3478, 3110, 2941, 2426, 1542, 1423, 1160, 1124 cm^{-1}.

Synthesis of (1-butyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium iodide (2e)

The product 2e was a viscous transparent liquid; yield, 42 %. ^{1}H NMR(DMSO-d_6, 400 MHz): δ= 0.76 – 0.91 (t, 3H, CH_3), 1.14 – 1.26 (dt, 2H, CH_2), 1.68 – 1.80 (p, 2H,

CH_2), 3.78 – 3.80 (s, 3H, CH_3), 4.05 – 4.15 (t, 2H, CH_2), 7.36 – 7.38 (m, 1H, N-CH=CH-N), 7.38 – 7.41 (t, 1H, N-CH=CH-N), 7.54 – 7.56 (s, 1H, N-CH=CH-N), 7.58 – 7.69 (s, 1H, N-CH=CH-N), 8.71 – 8.73 (s, 1H, N-CH=N), 8.76 – 8.88 ppm (s, 1H, N-CH=N); ^{13}C NMR (101 MHz, DMSO-d_6) δ = 13.77, 19.37, 32.0 , 35.48, 48.16, 122.81, 124.00, 125.30, 125.45, 138.64, 139.32 ppm; IR (KBr): $\tilde{\nu}$= 3112, 3068, 2959, 2933, 2870, 2427, 1543, 1161, 1128 cm^{-1}.

Synthesis of (1-ethyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (3a)

The aqueous solution of **2a**(20 mmol) in 40 ml H_2O was added dropwise into the suspension of silver dicyanamide (4.18 g, 24 mmol) in 60 ml H_2O.In the absence of light ,the mixture should be with vigorously stirring for 24h. After filtration,the water could be removed by rotary evaporation to get a viscous transparent liquid **3a**. 85% Yield. ^{1}H NMR (400 MHz, DMSO-d6) :δ = 1.35 – 1.46 (td, 3H, CH_3), 3.77 – 3.82 (s, 3H, CH_3), 4.09 – 4.19 (s, 2H, CH_2), 7.33 – 7.43 (m, 2H, N-CH=CH-N), 7.50 – 7.59 (s, 1H, N-CH=CH-N), 7.60 – 7.72 (s, 1H, N-CH=CH-N), 8.65 – 8.71 (s, 1H, N-CH=N), 8.72 – 8.80 ppm (s, 1H, N-CH=N); ^{13}C NMR (101 MHz, DMSO-d_6) δ = 15.77, 35.31, 43.72, 119.56, 122.45, 123.96 , 125.41 (d, *J*=9.8), 138.35, 139.30 ppm; ^{11}B NMR (193 MHz, DMSO-d_6) δ = -9.20 ppm; IR (KBr): $\tilde{\nu}$= 3487, 3135, 3079, 2987, 2429, 2239, 2130, 1546, 1161, 1129 cm^{-1}; HRMS (ESI) m/z: $[M]^+$ calcd for $C_9H_{18}BN_4^+$: 191.14625, found: 191.14568. $[M]^-$ calcd for $C_2N_3^-$:66.00867,found: 66.00907.

Synthesis of (1-methyl-1H-imidazol-3-ium-1-yl)(1-vinyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (3b)

The following compound was all synthesized like **3a.** The product **3b** was a viscous transparent liquid; yield, 90%. ^{1}H NMR (400 MHz, DMSO-d6) :δ=3.74 – 3.84 (s, 3H, CH_3), 5.24 – 5.35 (dt, 1H, CH), 5.83 – 5.93 (dd, 1H, CH), 7.17 – 7.28 (dd, 1H, CH), 7.36 – 7.42 (t, 1H, N-CH=CH-N), 7.49 – 7.56 (m, 2H, N-CH=CH-N), 8.01 – 8.06 (s, 1H, N-CH=CH-N), 8.65 – 8.70 (s, 1H, , N-CH=N), 9.01 – 9.06 (s, 1H, N-CH=N). ^{13}C NMR (101 MHz, DMSO-d_6) δ = 34.89, 107.07, 119.10, 123.54, 124.94, 125.80, 128.96, 137.57, 139.02 ppm; ^{11}B NMR (193 MHz, DMSO-d_6) δ = -8.42 ppm; IR (KBr): $\tilde{\nu}$= 3483, 3135, 3077, 2957, 2872, 2432, 2237, 2136, 1538, 1161, 1130 cm^{-1};

HRMS (ESI) m/z: $[M]^+$ calcd for $C_9H_{16}BN_4^+$: 189.13060, found: 189.13036. $[M]^-$ calcd for $C_2N_3^-$:66.00867,found: 66.00966.

Synthesis of (1-methyl-1H-imidazol-3-ium-1-yl)(1-propyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (3c)

The product **3c** was a viscous transparent liquid; yield,87%. ^{1}H NMR (400 MHz, DMSO-d6) :δ = 0.79 – 0.85 (td, 3H, CH_3), 1.74 – 1.83 (q, 2H, CH_2), 3.75 – 3.82 (s, 3H, CH_3), 4.02 – 4.10 (m, 2H, CH_2), 7.33 – 7.37 (s, 1H, N-CH=CH-N), 7.37 – 7.42 (s, 1H, N-CH=CH-N), 7.49 – 7.55 (s, 1H, N-CH=CH-N), 7.59 – 7.65 (s, 1H, N-CH=CH-N), 8.64 – 8.71 (s, 1H, N-CH=N), 8.72 – 8.79 ppm (s, 1H, N-CH=N); ^{13}C NMR (101 MHz, DMSO-d_6) δ = 10.98, 23.47, 35.33, 49.96, 119.57, 122.79, 124.00, 125.40 (d, *J*=16.3), 138.70, 139.33 ppm; ^{11}B NMR (193 MHz, DMSO-d_6) δ = -9.53 ppm; IR (KBr): $\tilde{\nu}$= 3488, 3131, 3077, 2968, 2879, 2429, 2239, 2130, 1546, 1161, 1129 cm^{-1}; HRMS (ESI) m/z: $[M]^+$ calcd for $C_{10}H_{18}BN_4^+$: 205.16190, found: 205.16201. $[M]^-$ calcd for $C_2N_3^-$:66.00867,, found66.00884.

Synthesis of (1-allyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (3d)

The product **3d** was a viscous transparent liquid; yield, 85%.^{1}H NMR (400 MHz, DMSO-d6) :δ= 3.73 – 3.80 (s, 3H, CH_3), 4.72 – 4.79 (d, 2H, CH_2), 5.16 – 5.25 (dd, 1H,CH), 5.25 – 5.33 (dd ,1H,CH), 5.95 – 6.10 (1H, ddt), 7.34 – 7.43 (dt, 2H, N-CH=CH-N), 7.50 – 7.58 (dt, 2H,N-CH=CH-N), 8.67 – 8.72 (s,1H,N-CH=N), 8.73 – 8.78 ppm (s, 1H, N-CH=N); ^{13}C NMR (101 MHz, DMSO-d_6) δ = 35.35, 50.57, 119.54, 120.04, 122.87, 124.01, 125.36, 125.63, 132.86, 138.76, 139.40 ppm; ^{11}B NMR (193 MHz, DMSO-d_6) δ = -8.68 ppm; IR (KBr): $\tilde{\nu}$= 3426, 3129, 2429, 2229, 2136, 1543, 1160, 1126 cm^{-1}; HRMS (ESI) m/z: $[M]^+$ calcd for $C_{10}H_{16}BN_4^+$: 203.14625, found: 203.14596. $[M]^-$ calcd for $C_2N_3^-$:66.00867, found 66.00940.

Synthesis of (1-butyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (3e)

The product **3e** was a viscous transparent liquid; yield, 86%. ^{1}H NMR (400 MHz, DMSO-d6) :δ= 0.85 – 0.94 (t, 3H, CH_3), 1.19 – 1.30 (q, 2H,CH_2), 1.70 – 1.83 (p, 2H, CH_2), 3.74 – 3.83 (s, 3H,CH_3), 4.06 – 4.14 (t, 2H, CH_2), 7.35 – 7.42 (d, 2H, N-

CH=CH-N), 7.51 – 7.56 (s, 1H, N-CH=CH-N), 7.60 – 7.65 (s, 1H, N-CH=CH-N), 8.65 – 8.70 (s, 1H, N-CH=N), 8.73 – 8.78 ppm (s, 1H, N-CH=N);.^{13}C NMR (101 MHz, DMSO-d_6) δ = 13.75, 19.40, 32.02, 35.33, 48.18, 119.56, 122.79, 124.00, 125.33, 125.48, 138.66, 139.33 ppm; ^{11}B NMR (193 MHz, DMSO-d_6) δ = -9.59 ppm; IR (KBr): $\tilde{\nu}$= 3487, 3132, 3078, 2961, 2872, 2429, 2232, 2133, 1546, 1162, 1129cm^{-1}; HRMS (ESI) m/z: $[M]^+$ calcd for $C_{11}H_{20}BN_4^+$: 219.17755, found: 219.17756. $[M]^-$ calcd for $C_2N_3^-$: 66.00867, found66.00926.

Synthesis of (1-ethyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) cyanoborohydride (4a)

The product 4a was a viscous transparent liquid; yield 80%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.03 – 0.50 (dd, 3H, BH_3), 1.26 – 1.49 (m, 3H, CH_3), 3.77 – 3.80 (s, 3H, CH_3), 4.06 – 4.18 (d, 2H, CH_2), 7.31 – 7.39 (d, 2H, N-CH=CH-N), 7.49 – 7.52 (s, 1H), 7.58 – 7.63 (s, 1H), 8.63 – 8.65 (s, 1H, N-CH=N), 8.70 – 8.73 (s, 1H, N-CH=N). ^{13}C NMR (101 MHz, DMSO-d_6) δ =15.79, 43.74, 122.48, 123.99, 125.39, 125.49, 139.31.IR (KBr): $\tilde{\nu}$= 3428, 3138, 3082, 2982, 2948, 2428, 2322, 2221, 2171, 1609, 1549, 1450, 1262, 1128, 1066 cm^{-1}. HRMS (ESI) m/z: $[M]^+$ calcd for $C_9H_{18}BN_4^+$: 191.14625, found: 191.14601.

Synthesis of (1-methyl-1H-imidazol-3-ium-1-yl)(1-vinyl-1H-imidazol-3-ium-1-yl) cyanoborohydride (4b)

The product 4b was a viscous transparent liquid; yield 72%.^{1}H NMR (400 MHz, DMSO-d_6): δ = -0.41 – 0.81 (dd, 3H, BH_3), 3.79 – 3.81 (s, 3H, CH_3), 5.24 – 5.37 (d, 1H.CH=CH_2), 5.83 – 5.97 (d, 1H,CH=CH_2), 7.20 – 7.29 (dd, 1H, CH=CH_2), 7.36 – 7.42 (s, 1H, N-CH=CH-N), 7.50 – 7.52 (s, 1H, N-CH=CH-N), 7.52 – 7.55 (s, 1H, N-CH=CH-N), 7.92 – 8.12 (s, 1H, N-CH=CH-N), 8.66 – 8.70 (s, 1H, N-CH=N), 9.01 – 9.06 (s, 1H, N-CH=N). ^{13}C NMR (101 MHz, DMSO-d_6) δ= 35.43, 107.60, 119.58, 124.01, 125.40, 126.27, 129.38, 137.97, 139.46.IR (KBr): $\tilde{\nu}$= 3425, 3134, 2432, 2322, 2223, 2167, 1651, 1537, 1423, 1263, 1129, 1006 cm^{-1}. HRMS (ESI) m/z: $[M]^+$ calcd for $C_9H_{16}BN_4^+$: 189.13060, found: 189.13016.

Synthesis of (1-methyl-1H-imidazol-3-ium-1-yl)(1-propyl-1H-imidazol-3-ium-1-yl) cyanoborohydride (4c)

The product 4c was a viscous transparent liquid; yield 79%.^{1}H NMR (400 MHz, DMSO-d_6): δ = -0.19 – 0.57 (m, 3H, BH_3), 0.81 – 0.85 (td, 3H, CH_3), 1.76 – 1.82 (q, 2H, CH_2), 3.78 – 3.80 (m, 3H, CH_3), 4.05 – 4.08 (m, 2H, CH_2), 7.36 – 7.37 (s, 1H, N-CH=CH-N), 7.38 – 7.40 (s, 1H, N-CH=CH-N), 7.52 – 7.54 (s, 1H, N-CH=CH-N), 7.59 – 7.65 (s, 1H, N-CH=CH-N), 8.66 – 8.68 (s, 1H, N-CH=N), 8.71 – 8.77 (s, 1H, N-CH=N). ^{13}C NMR (101 MHz, DMSO-d_6) δ= 10.98, 23.47, 35.38, 49.96, 122.82, 124.03, 125.34, 125.50, 138.70, 139.34.IR (KBr): $\tilde{\nu}$= 3410, 3133, 3082, 2967, 2878, 2428, 2331, 2222, 2173, 1611, 1546, 1458, 1263, 1127, 1047 cm^{-1}. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{10}H_{18}BN_4^+$: 205.16190, found: 205.16164.

Synthesis of (1-allyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) cyanoborohydride (4d)

The product 4d was a viscous transparent liquid; yield 76%.^{1}H NMR (400 MHz, DMSO-d_6): δ= -0.12 – 1.00 (m, 3H, BH_3), 3.87 (s, 3H, CH_3), 4.85 (d, 2H, CH_2), 5.12 – 5.48 (m, 2H, CH_2=CH-CH_2), 6.10 (dtt, 1H, CH_2=CH-CH2), 7.34 – 7.70 (m, 4H, N-CH=CH-N), 8.66 – 8.89 (m, 2H, N-CH=N).^{13}C NMR (101 MHz, DMSO-d_6) δ 35.38, 35.40, 50.60, 120.13, 122.87, 124.01, 125.39, 125.67, 132.80, 138.72, 139.38.IR (KBr): $\tilde{\nu}$= 3424, 3136, 2428, 2362, 2172, 1642, 1546, 1424, 1261, 1128, 995 cm^{-1} HRMS (ESI) m/z: $[M]^+$ calcd for $C_{10}H_{16}BN_4^+$: 203.14625, found: 203.14606.

Synthesis of (1-butyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) cyanoborohydride (4e)

The product 4e was a viscous transparent liquid; yield 80%.^{1}H NMR (400 MHz, DMSO-d_6): δ= 0.01 – 0.51 (m, 3H, BH_3), 0.88 (td, 3H, CH_3), 1.23 (q, 2H, CH_2), 1.76 (p, 2H,CH_2), 3.80 (s, 3H,CH_3), 4.10 (dt, 2H, CH_2), 7.37 (d, 2H, N-CH=CH-N), 7.52 (s, 1H, N-CH=CH-N), 7.61 (s, 1H, N-CH=CH-N), 8.65 (s, 1H, N-CH=N), 8.73 (s, 1H, N-CH=N).^{13}C NMR (101 MHz, DMSO-d_6) δ 13.73, 19.39, 32.03, 35.36, 40.54, 48.21, 122.80, 124.01, 125.35, 125.49, 138.65, 139.33. IR (KBr): $\tilde{\nu}$= 3415, 3133, 3078, 2967, 2878, 2429, 2330, 2172, 1612, 1546, 1458, 1263, 1161, 1128, 1048 cm^{-1}. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{11}H_{20}BN_4^+$: 219.17755, found: 219.17731.

2 .NMR and HRMS-ESI Spectra

^{1}HNMR ^{13}CNMR ^{11}BNMR spectra and HRMS of the ionic liquids

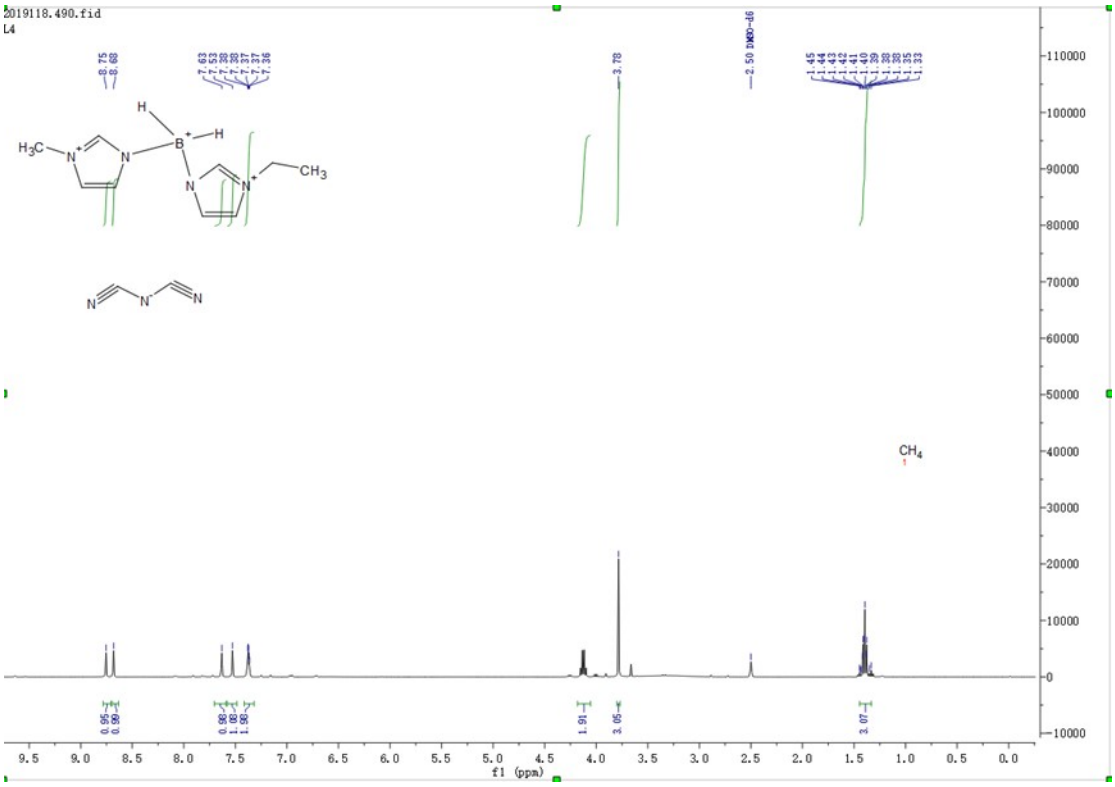


Figure S2 ^{1}HNMR (400 MHz) of (1-ethyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

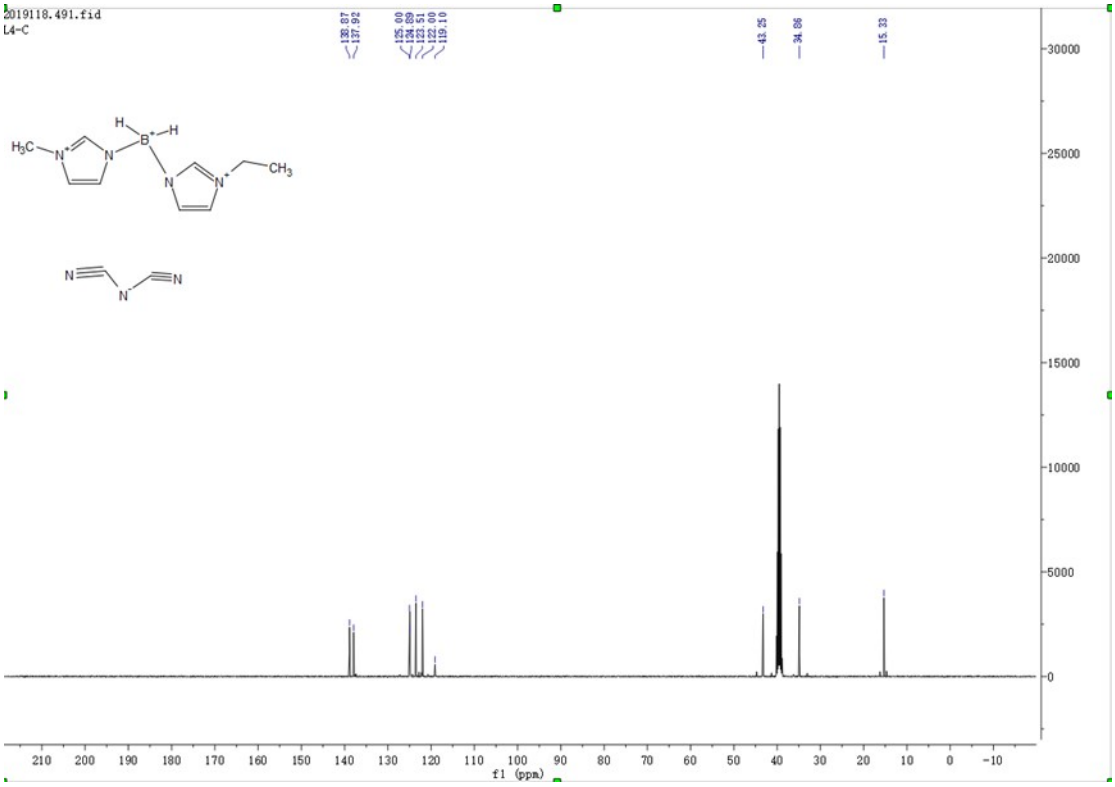


Figure S3 ^{13}CNMR (101 MHz) of (1-ethyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

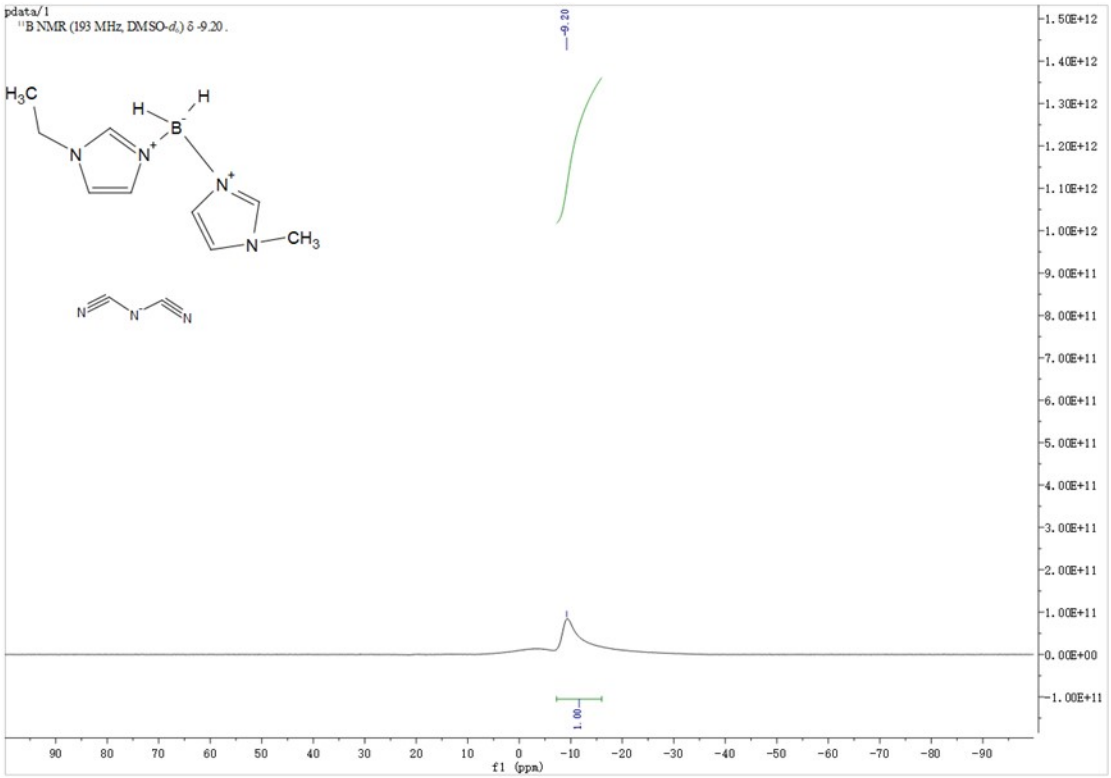


Figure S4 ^{11}BNMR (193 MHz) of (1-ethyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

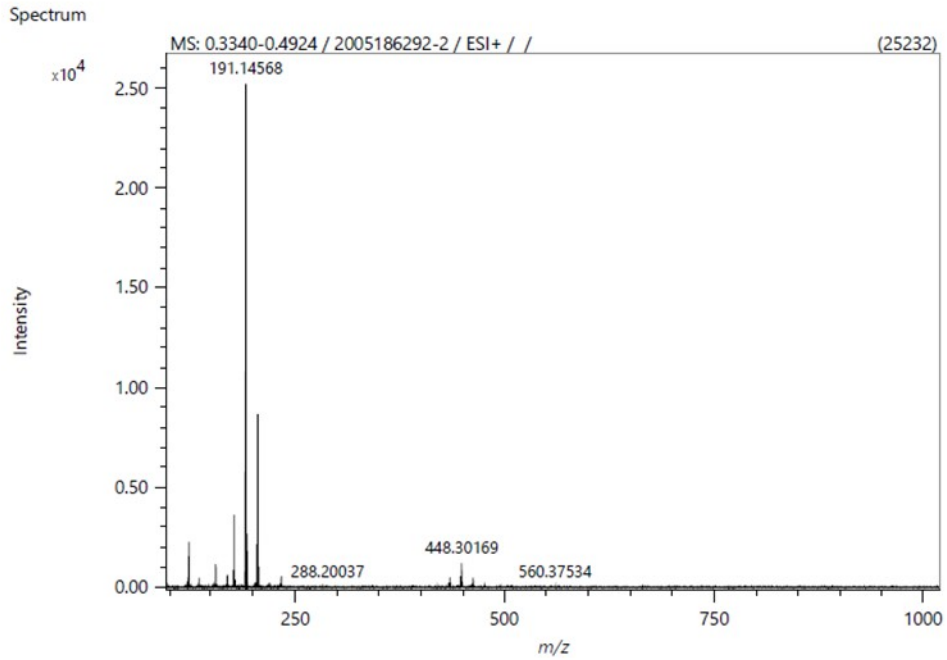


Figure S5 HRMS-ESI spectrum of (1-ethyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (positive) solvent (CH_2Cl_2) .

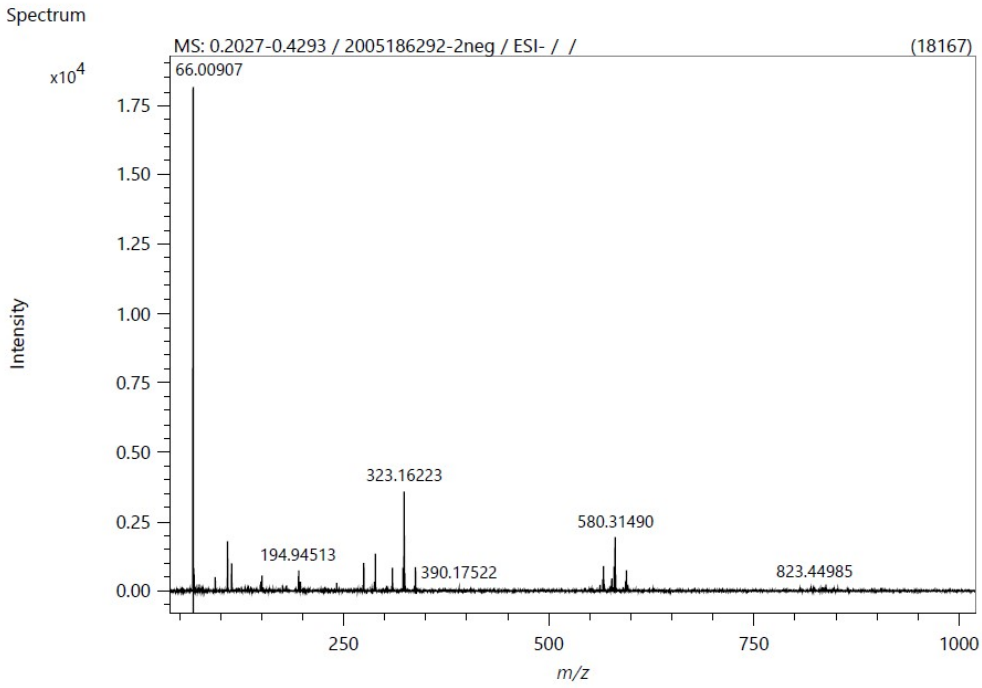


Figure S6 HRMS-ESI spectrum of (1-ethyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (negative) solvent (CH_2Cl_2).

Figure S7 ^{1}HNMR (400 MHz) of (1-propyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

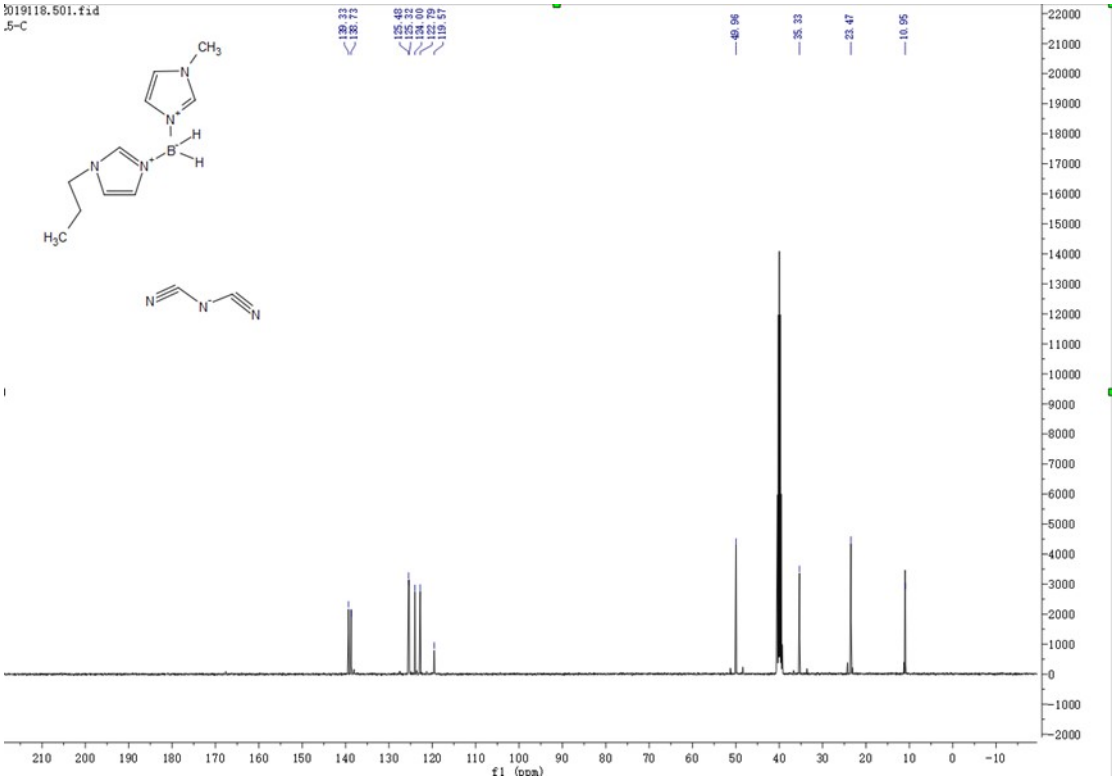


Figure S8 ^{13}CNMR (101 MHz) of (1-propyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

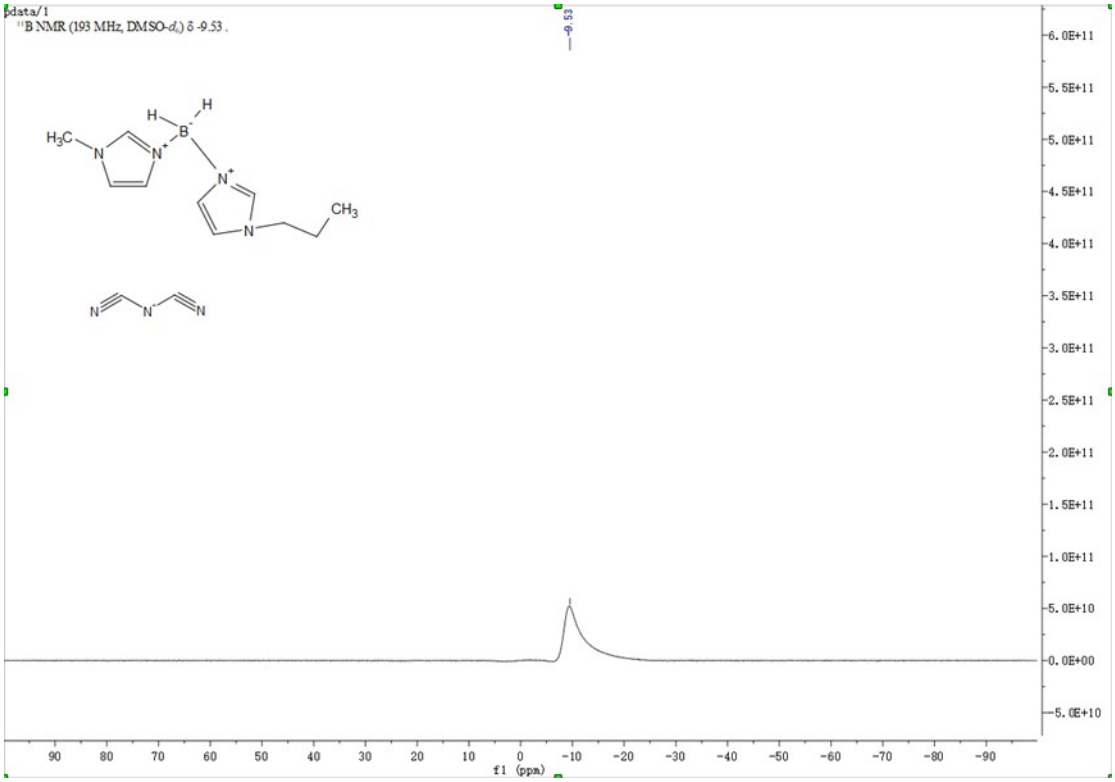


Figure S9 ^{11}BNMR (193 MHz) of (1-propyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

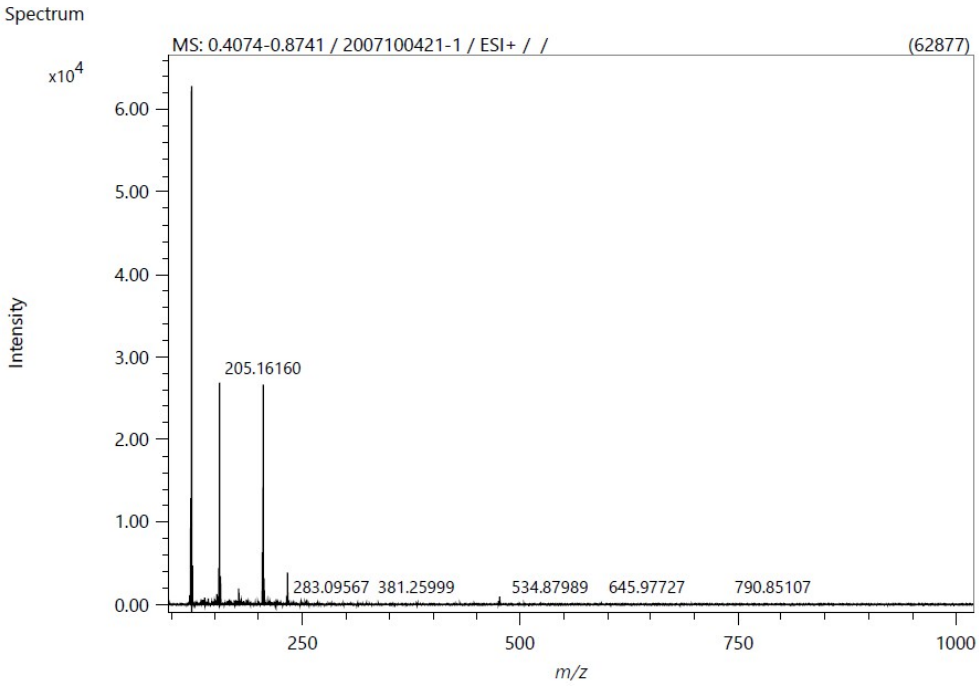


Figure S10 HRMS-ESI spectrum of (1-propyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (positive) solvent (CH_2Cl_2).

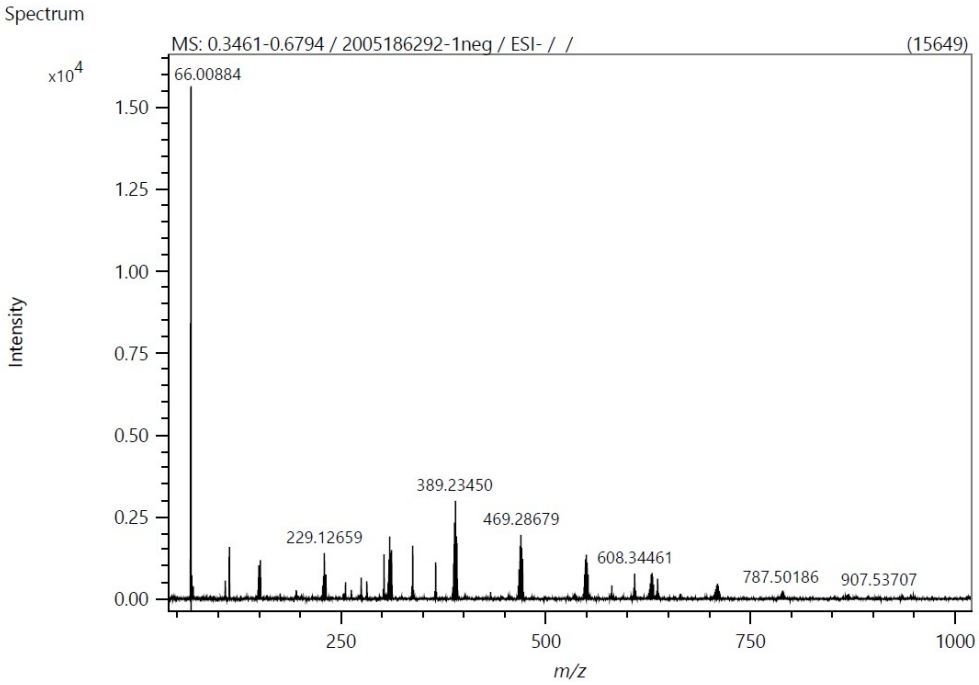


Figure S11 HRMS-ESI spectrum of (1-propyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (negative) solvent (CH_2Cl_2).

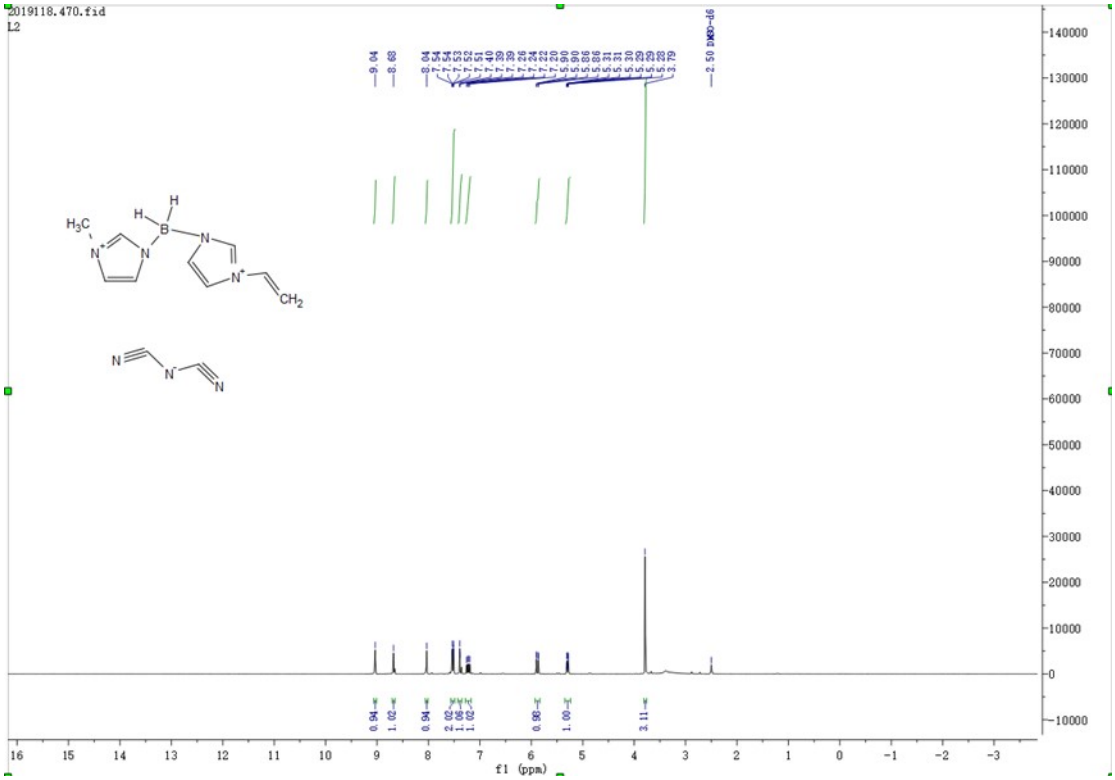


Figure S12 ^{1}HNMR (400 MHz) of (1-vinyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

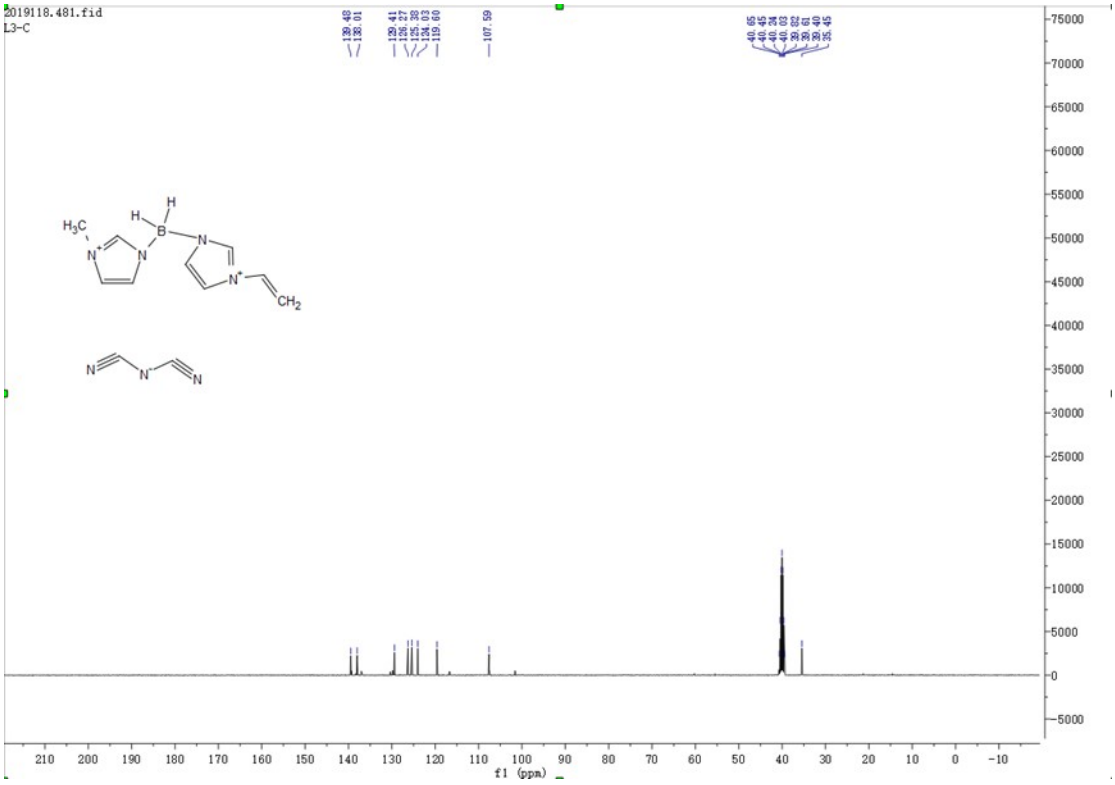


Figure S13 ^{13}CNMR (101 MHz) of (1-vinyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

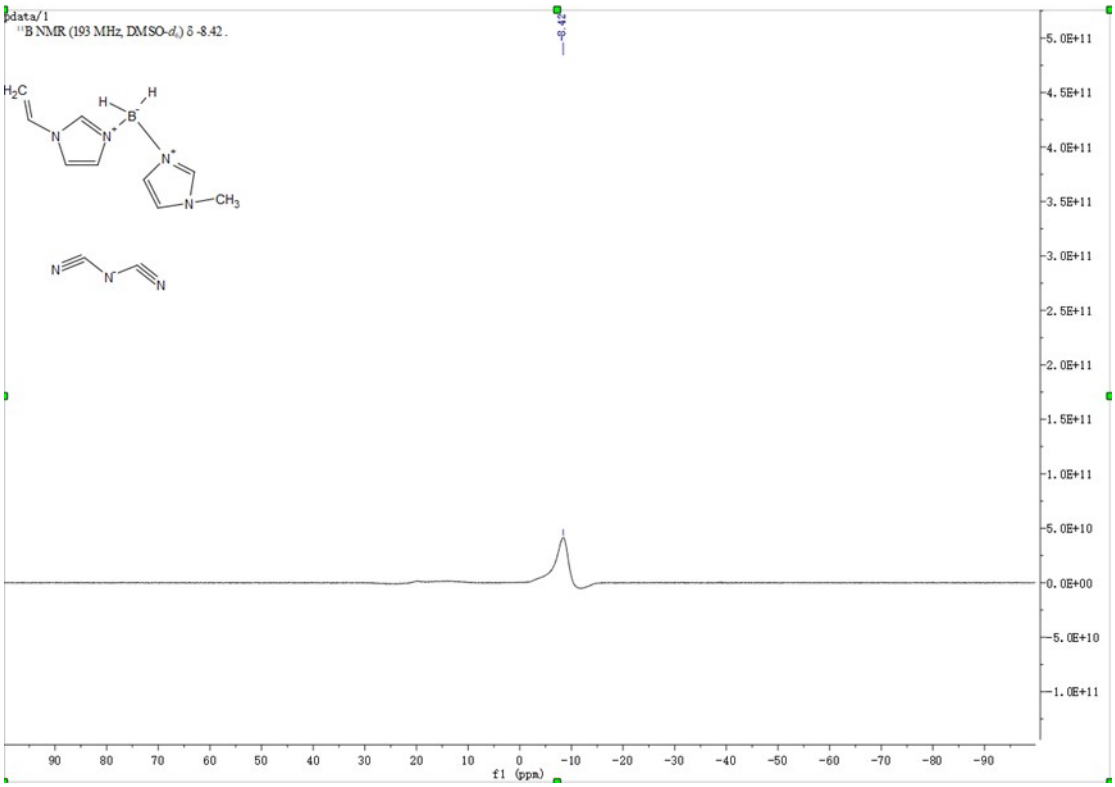


Figure S14 ^{11}BNMR (193 MHz) of (1-vinyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

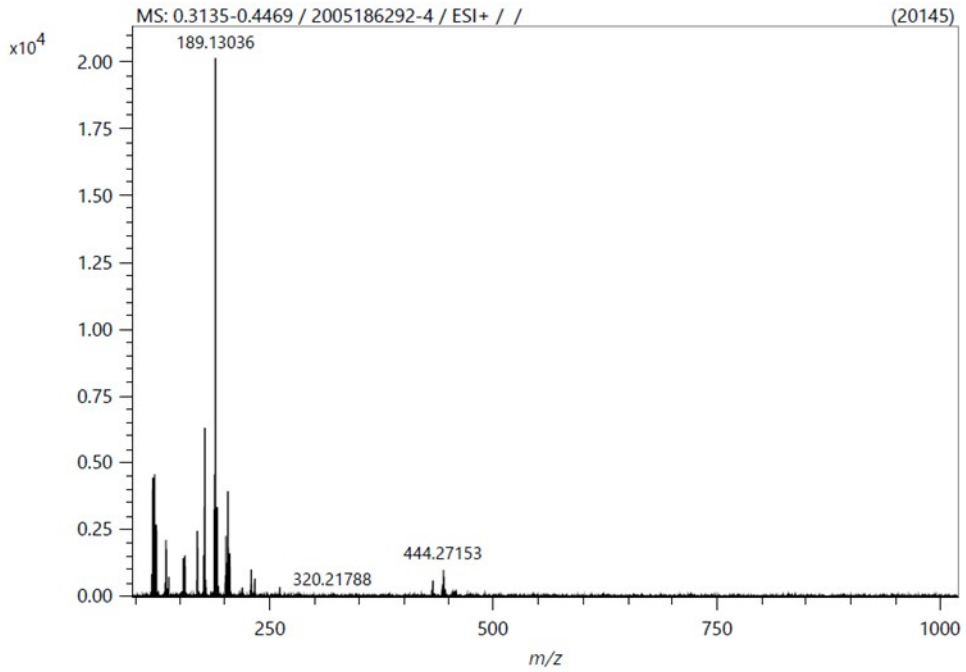


Figure S15 HRMS-ESI SPECTRUMof (1-vinyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (positive) solvent (CH_2Cl_2).

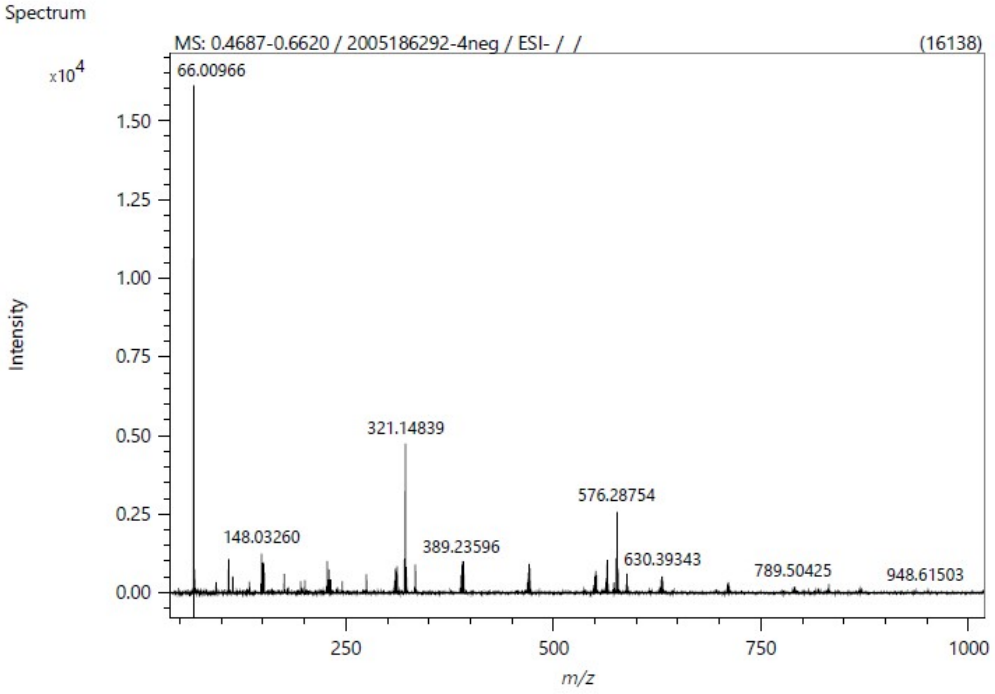


Figure S16 HRMS-ESI SPECTRUM of (1-vinyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (negative) solvent (CH_2Cl_2).

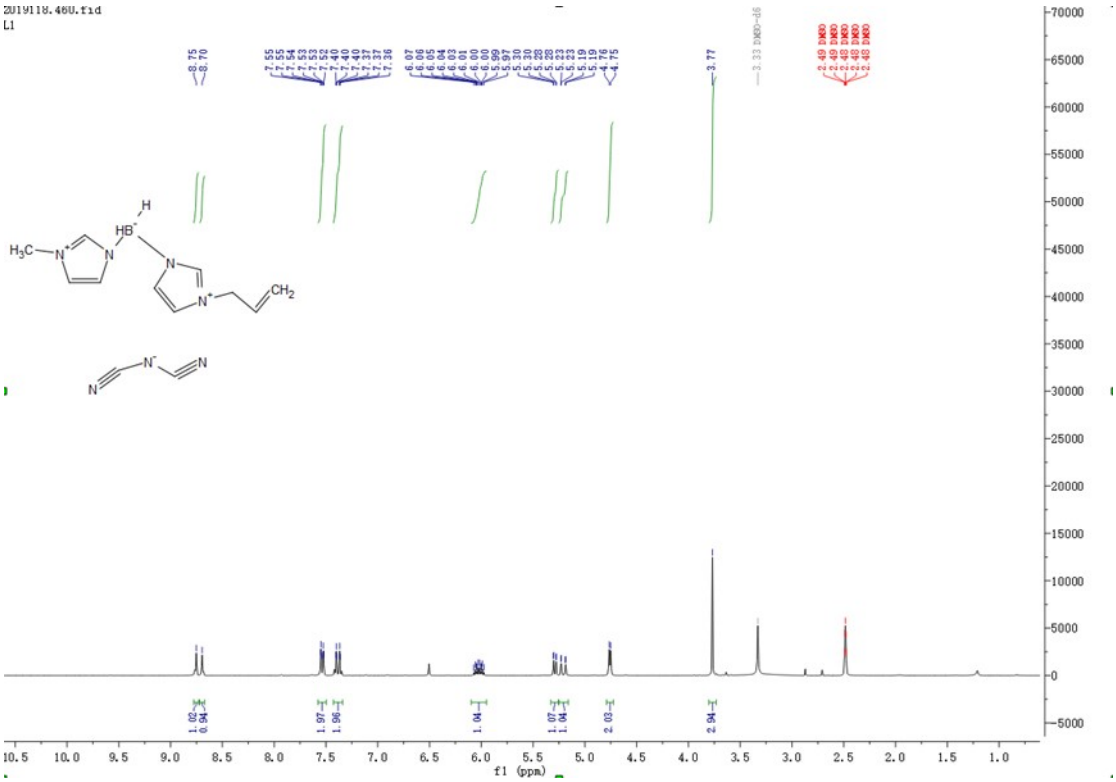


Figure S17 ^{1}HNMR (400 MHz) of (1-allyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

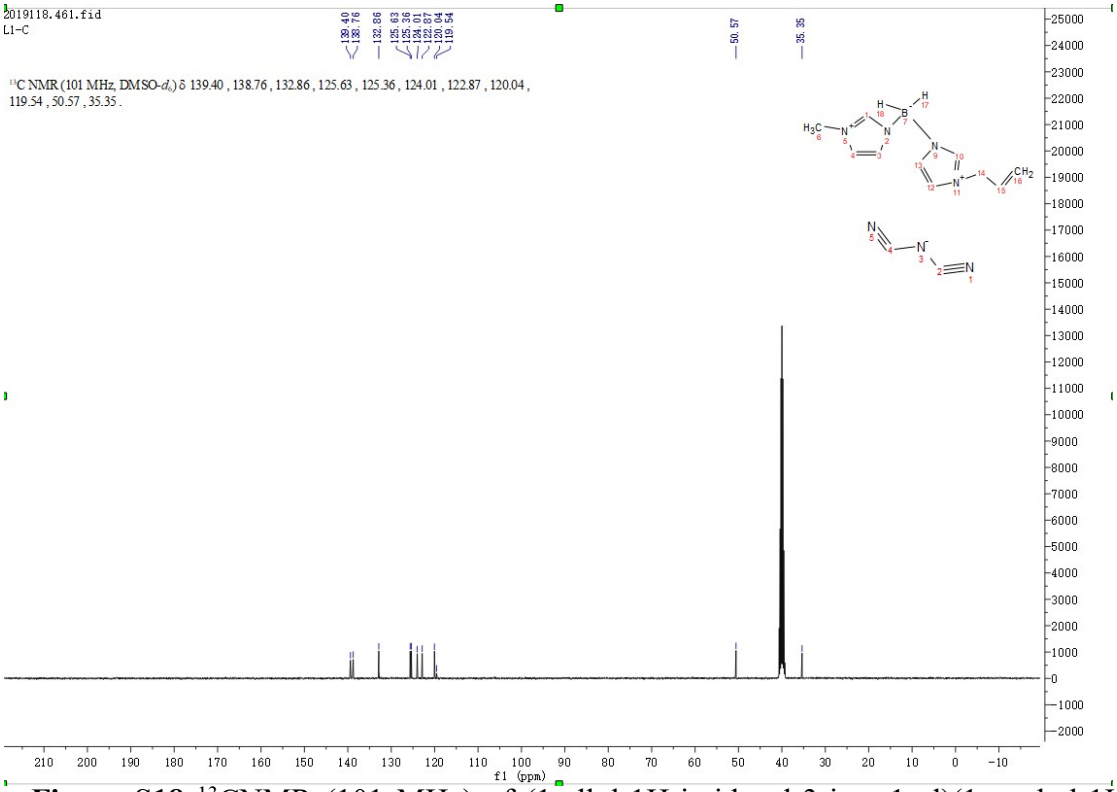


Figure S18 ^{13}CNMR (101 MHz) of (1-allyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

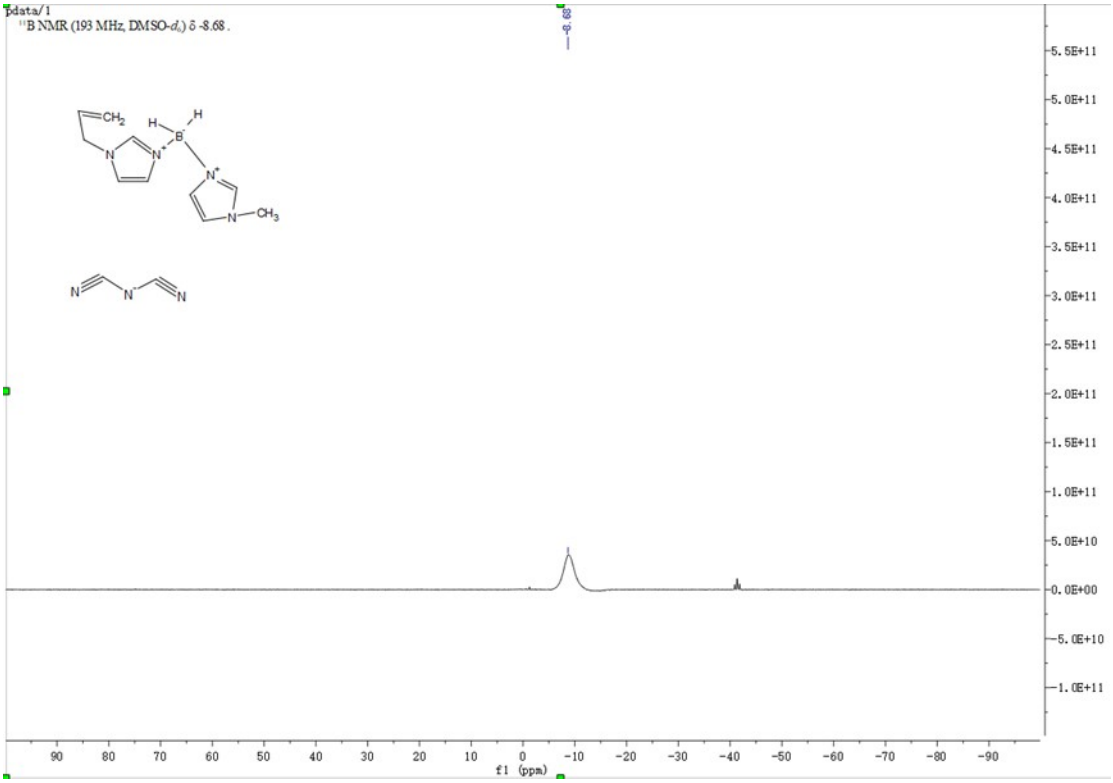


Figure S19 ^{11}BNMR (193 MHz) of (1-allyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

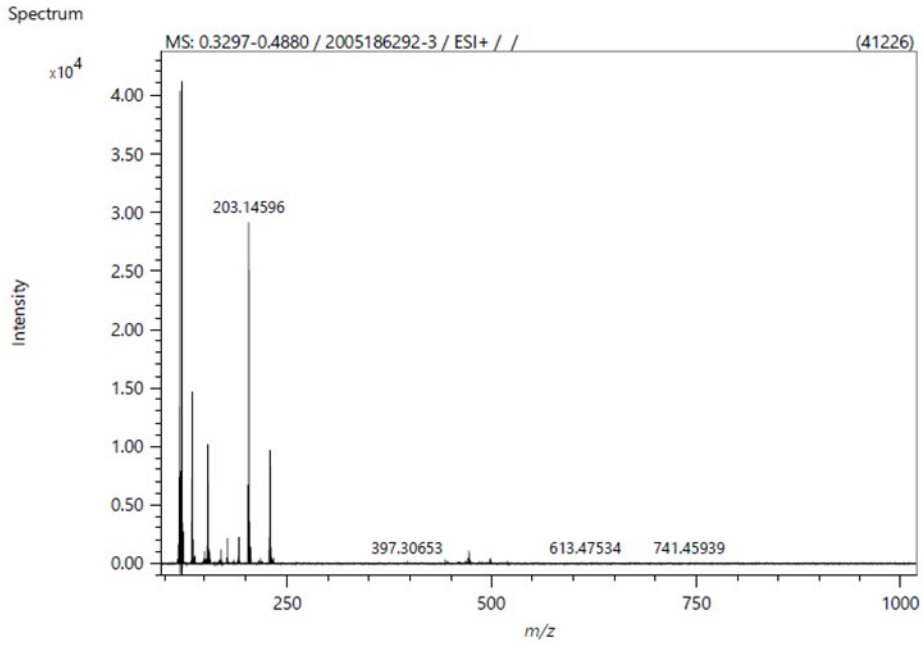


Figure S20 HRMS-ESI SPECTRUM of (1-allyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (positive) solvent (CH_2Cl_2).

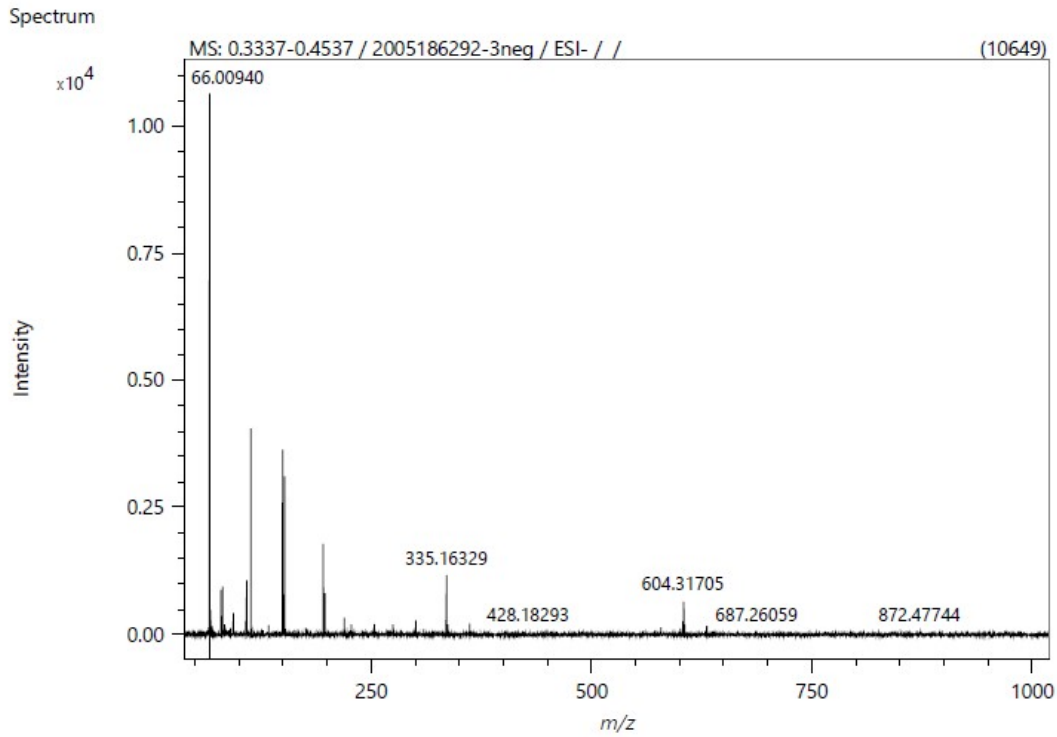


Figure S21 HRMS-ESI SPECTRUMof (1-allyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (negative) solvent (CH_2Cl_2).

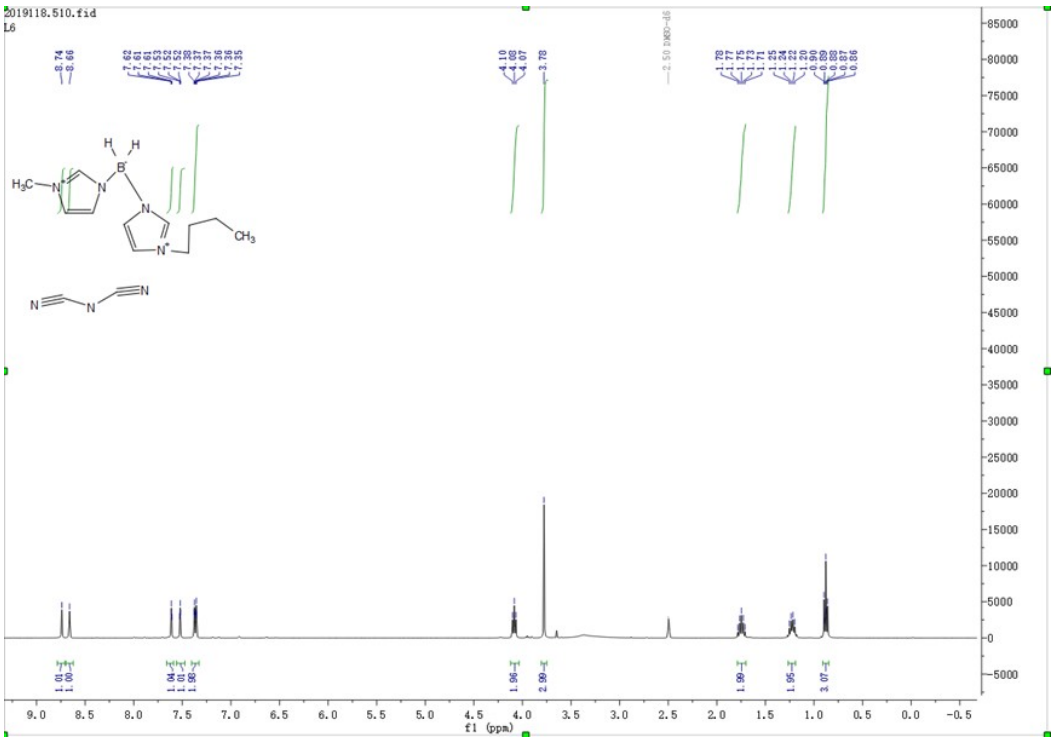


Figure S22 ^{1}HNMR (400 MHz) of (1-butyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

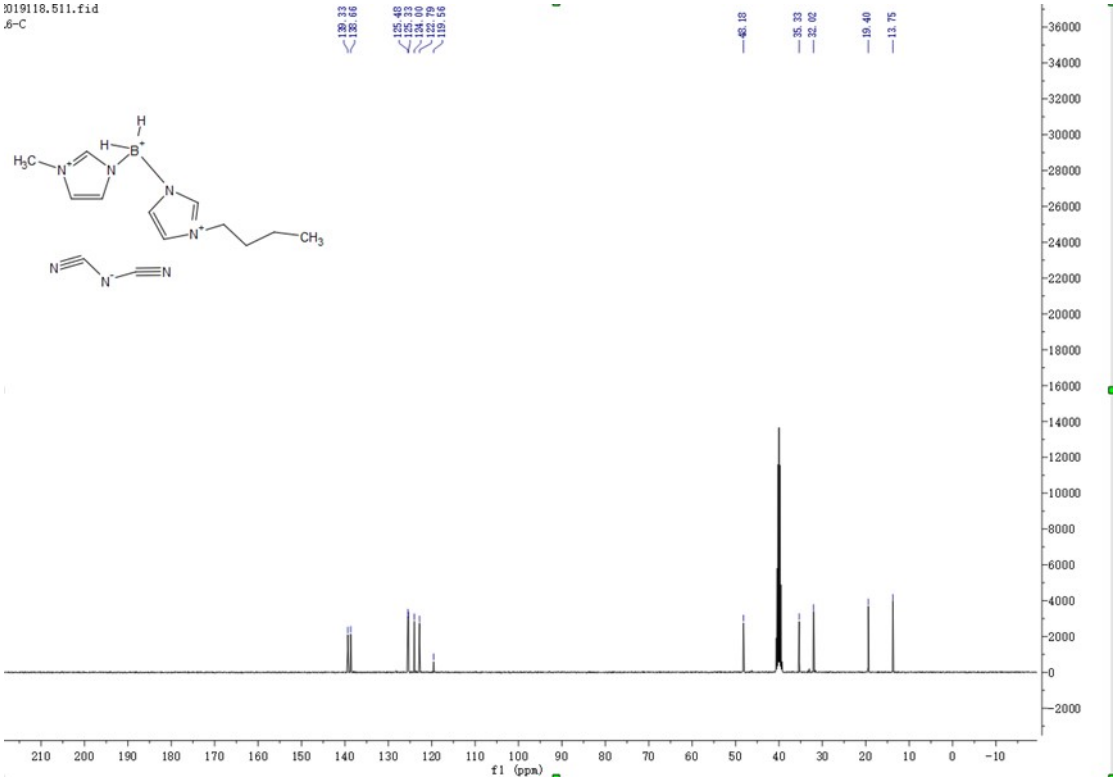


Figure S23 ^{13}CNMR (101 MHz) of (1-butyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

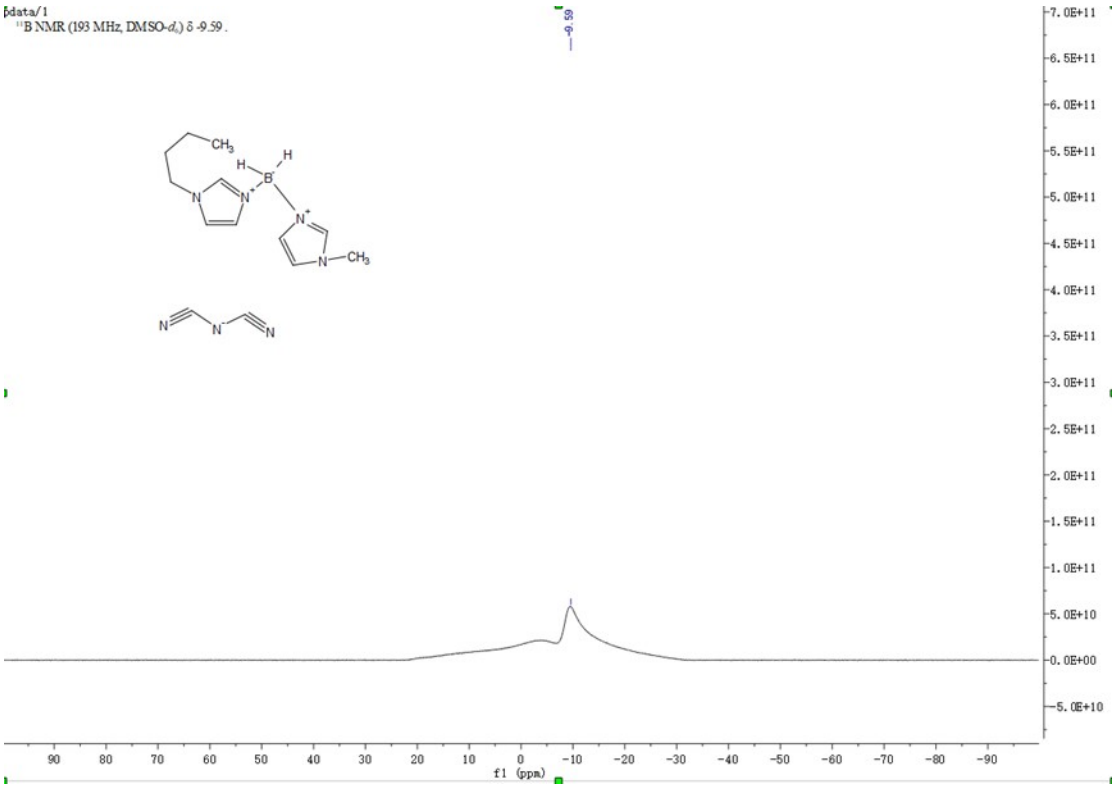


Figure S24 ^{11}BNMR (193 MHz) of (1-butyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide in DMSO-D_6.

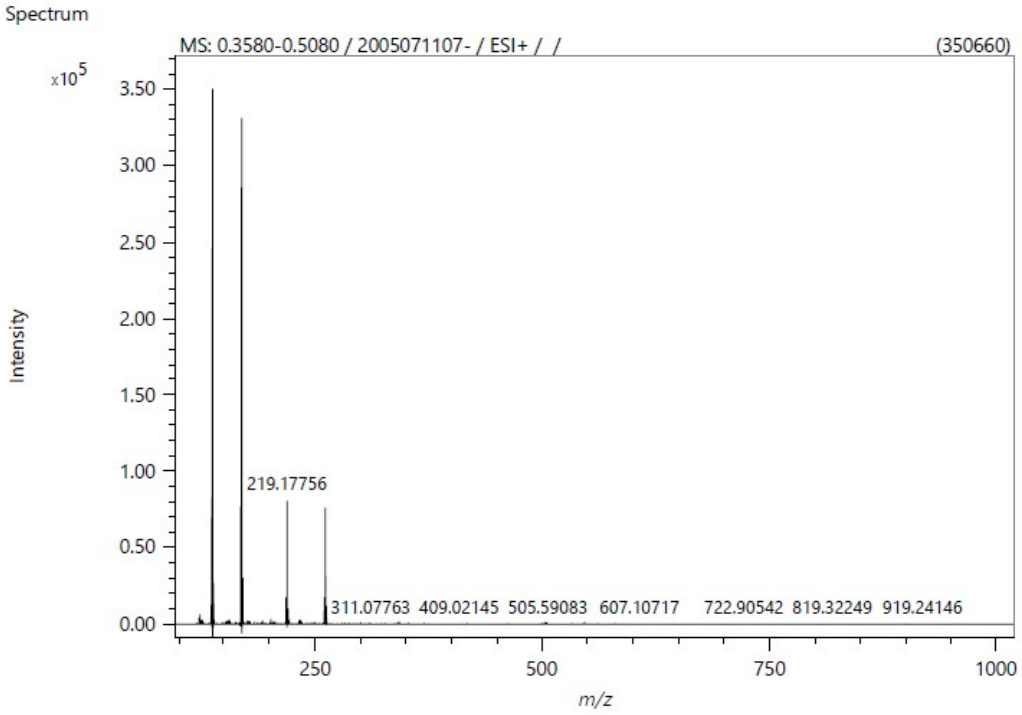


Figure S25 HRMS-ESI SPECTRUMof (1-butyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (positive) solvent (CH_2Cl_2).

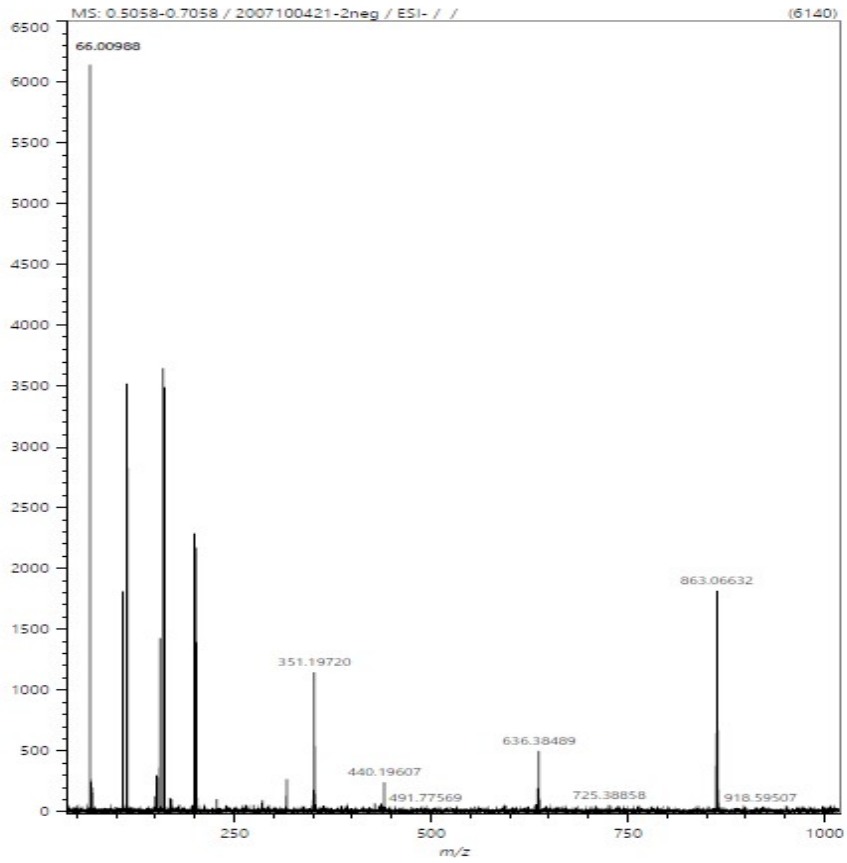


Figure S26 HRMS-ESI SPECTRUM of (1-butyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium dicyandiamide (negative) solvent (CH_2Cl_2).

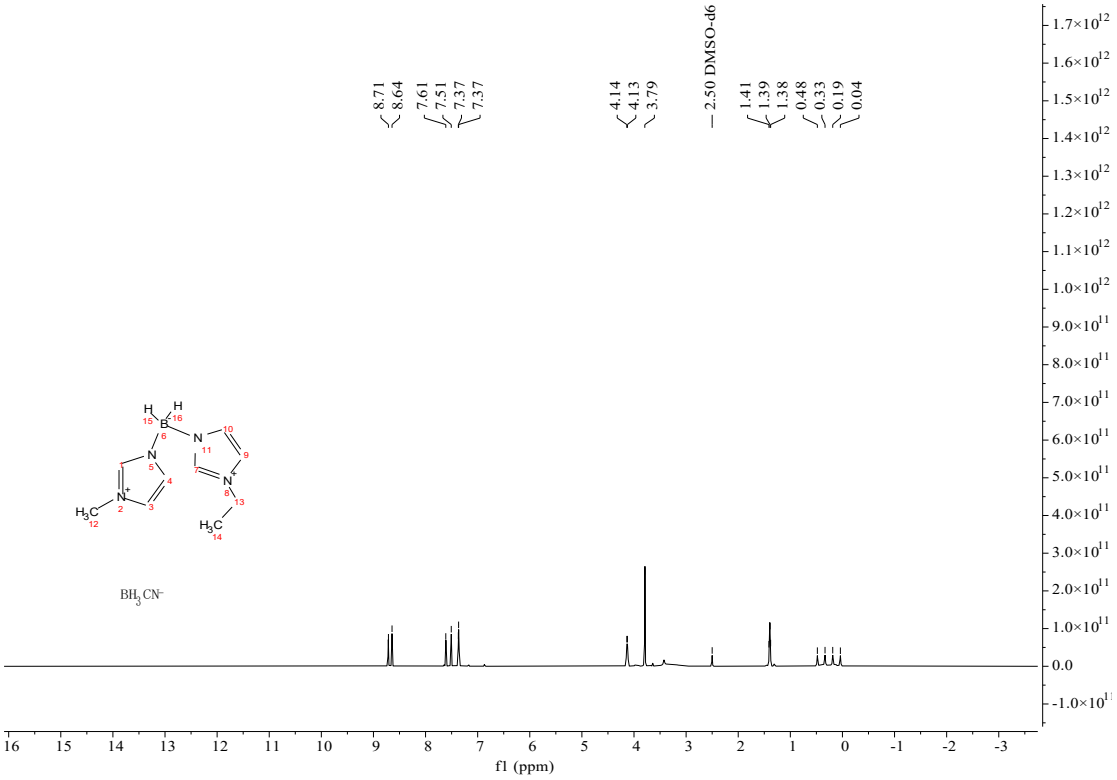


Figure S27 ^{1}HNMR (400 MHz) of (1-ethyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride in DMSO-D_6.

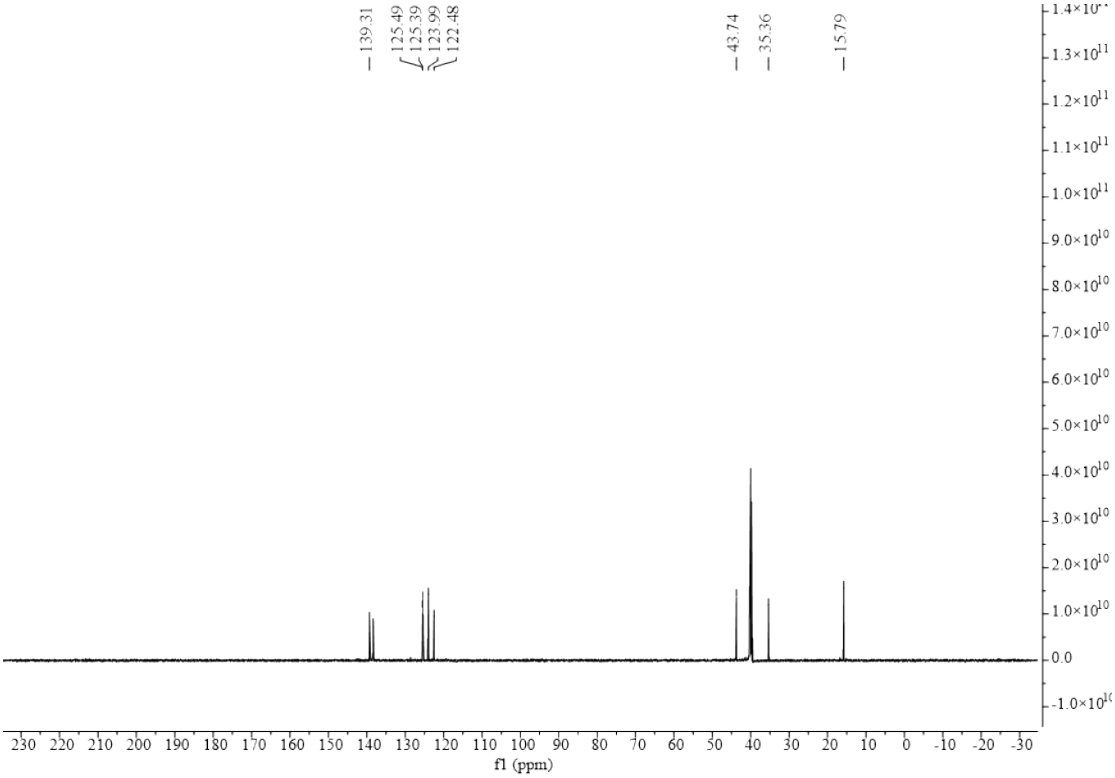


Figure S28 ^{13}CNMR (101 MHz) of (1-ethyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride in DMSO-D_6.

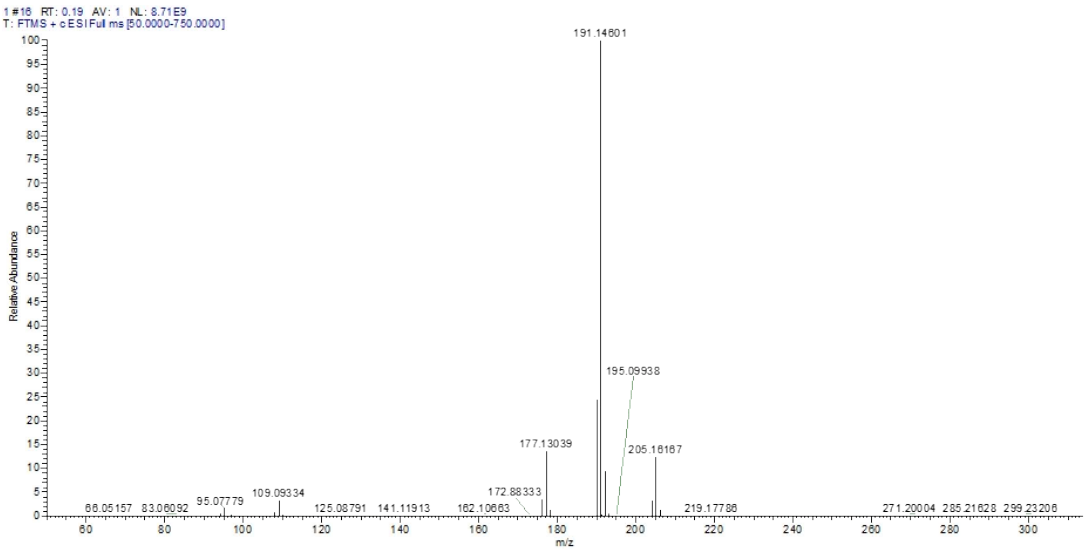


Figure S29 HRMS-ESI spectrum of (1-ethyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride (positive) solvent (H_2O).

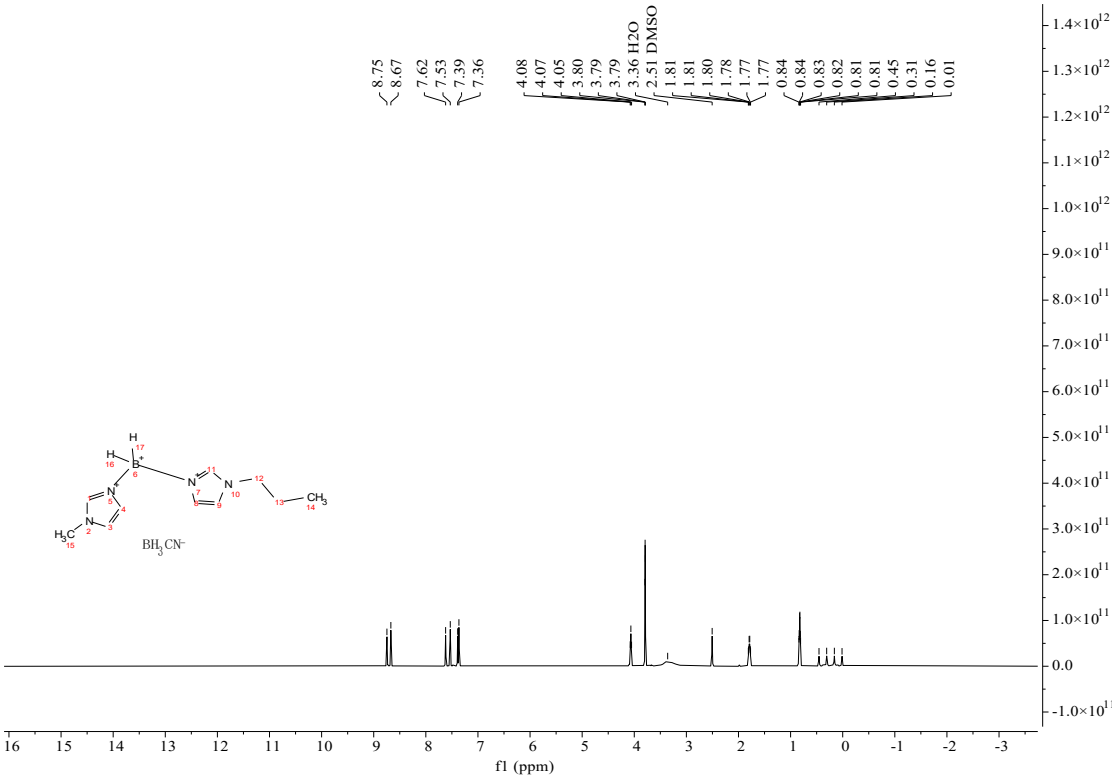


Figure S30 ^{1}HNMR (400 MHz) of (1-propyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride in DMSO-D_6.

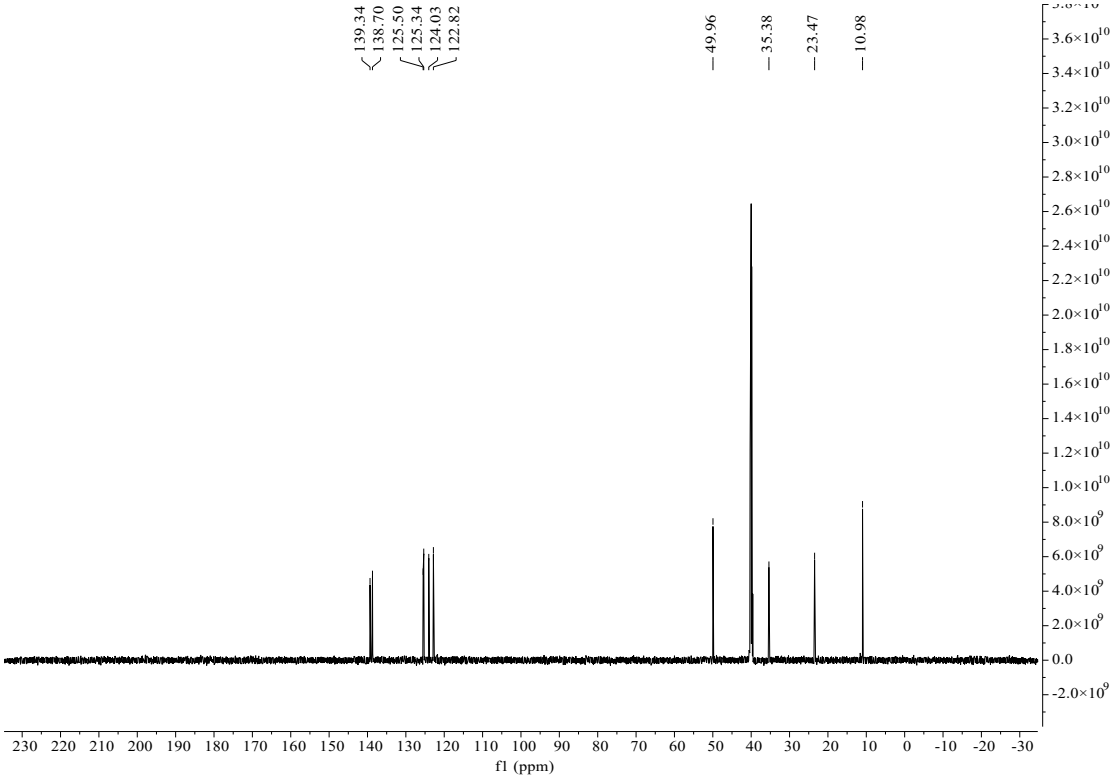


Figure S31 ^{13}CNMR (101 MHz) of (1-propyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride in DMSO-D_6.

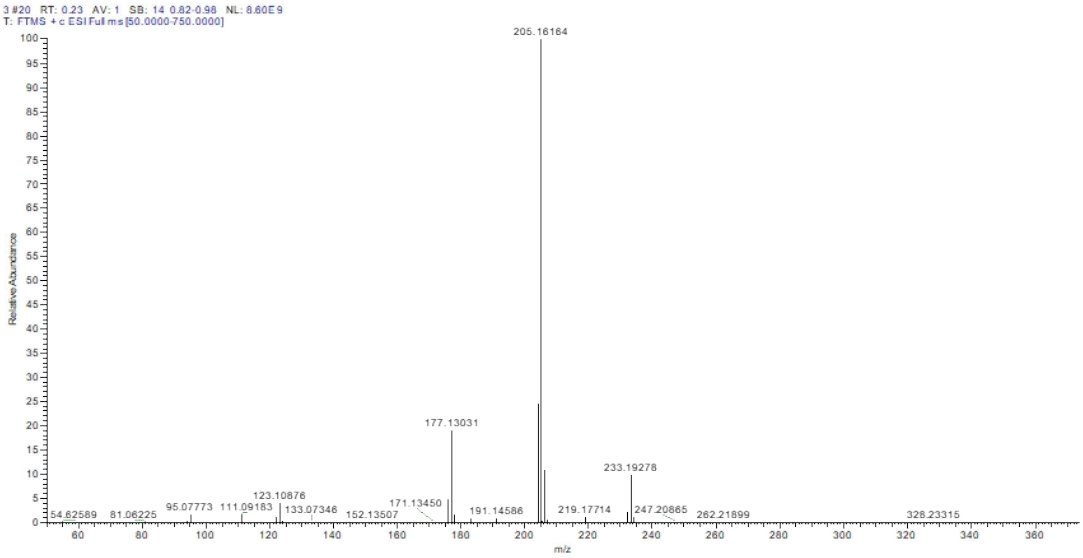


Figure S32 HRMS-ESI spectrum of (1-propyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride (positive) solvent (H_2O).

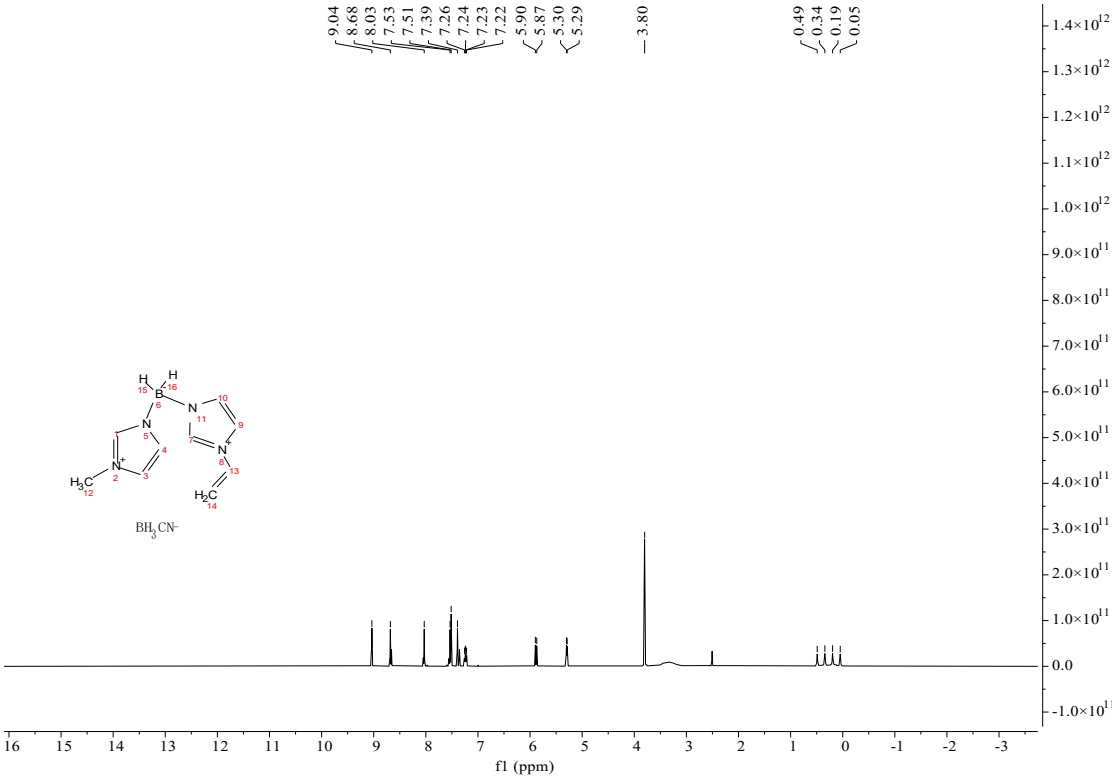


Figure S33 ^{1}HNMR (400 MHz) of (1-vinyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride in DMSO-D_6.

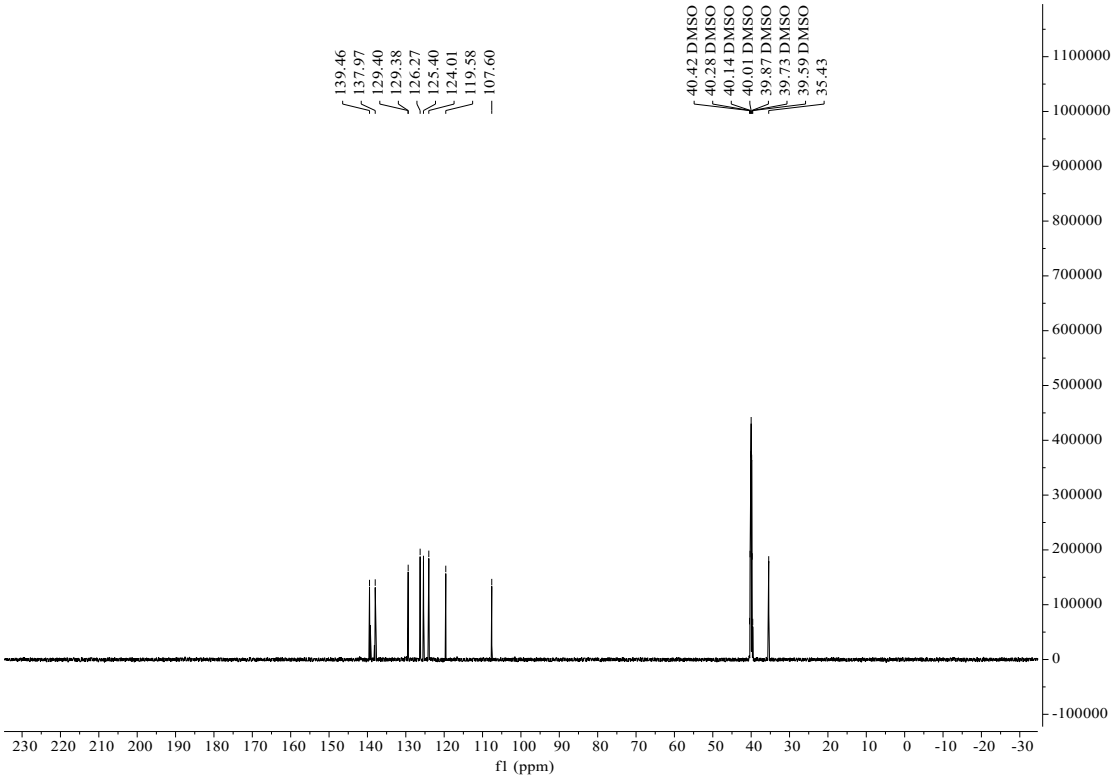


Figure S34 ^{13}CNMR (101 MHz) of (1-vinyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride in DMSO-D_6.

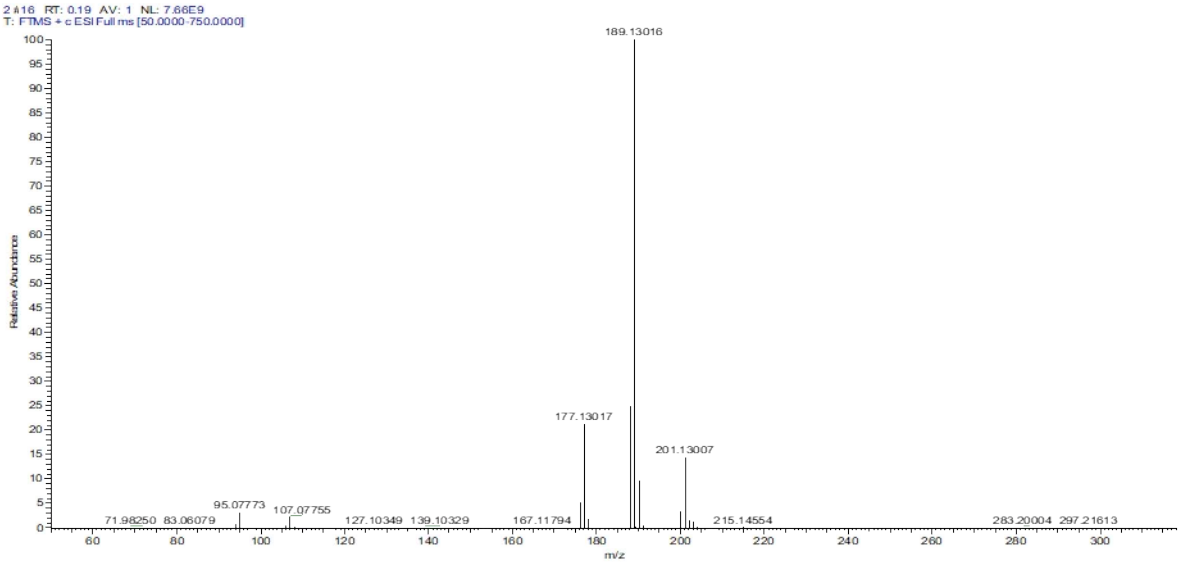


Figure S35 HRMS-ESI SPECTRUMof (1-vinyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride (positive) solvent (H_2O).

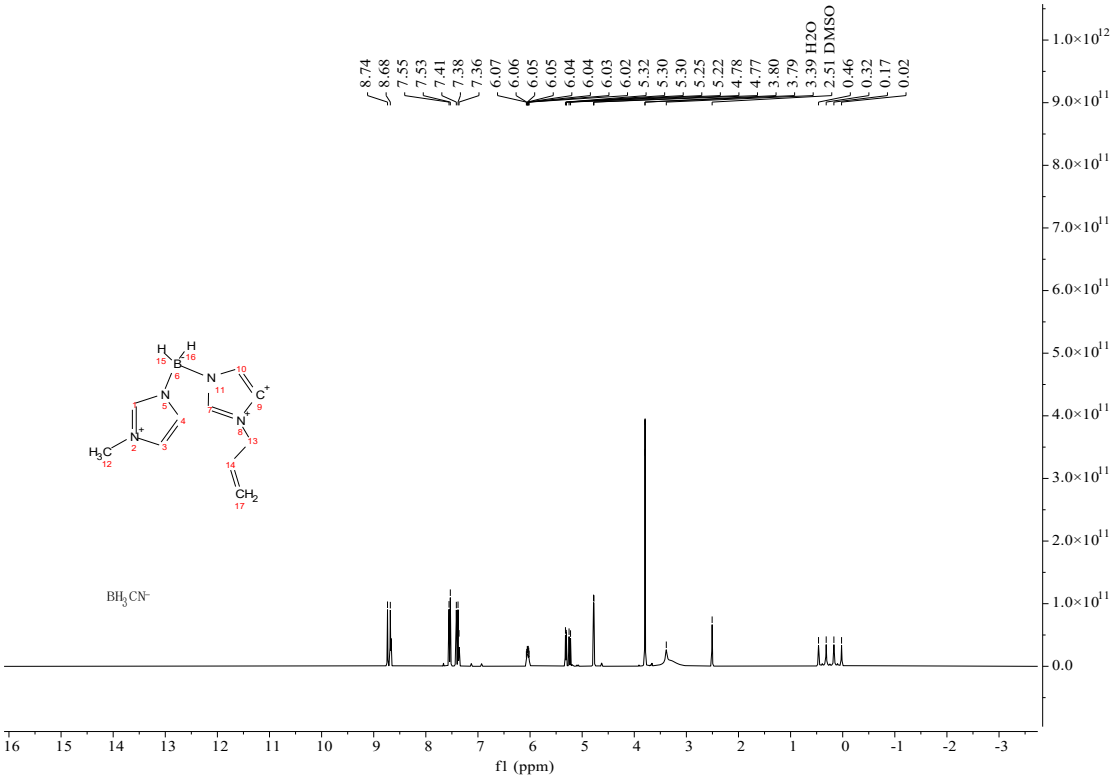


Figure S36 ^{1}HNMR (400 MHz) of (1-allyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride in DMSO-D_6.

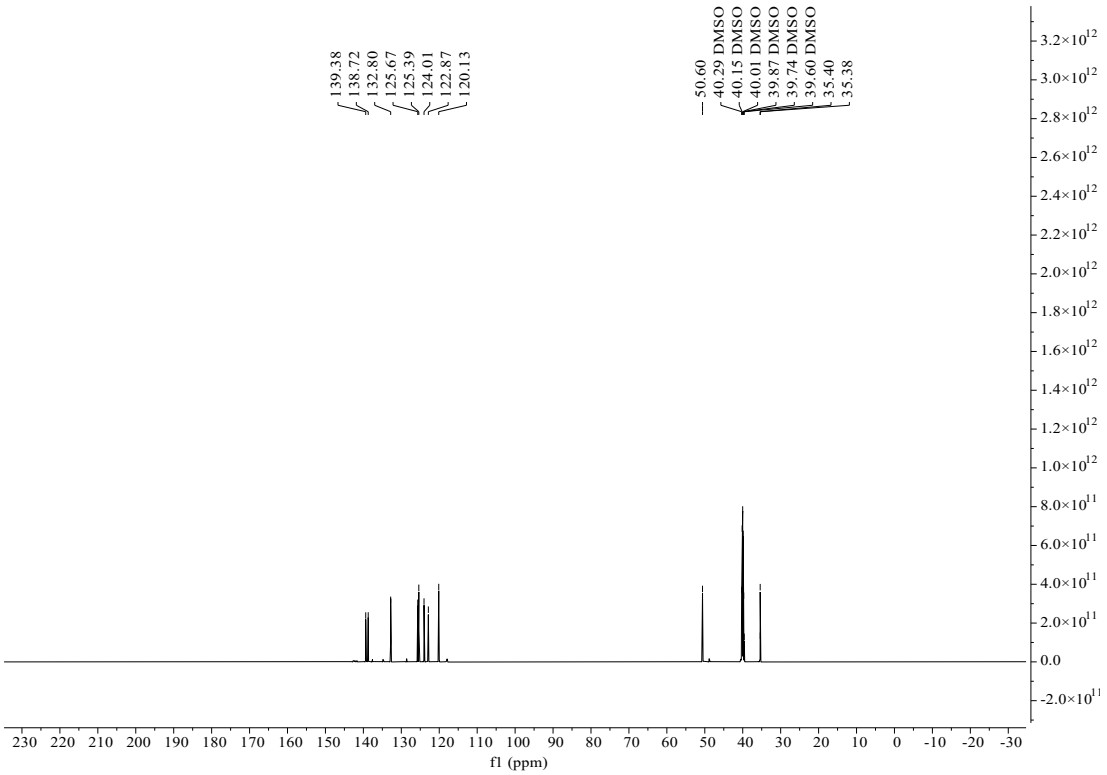


Figure S37 ^{13}CNMR (101 MHz) of (1-allyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride in DMSO-D_6.

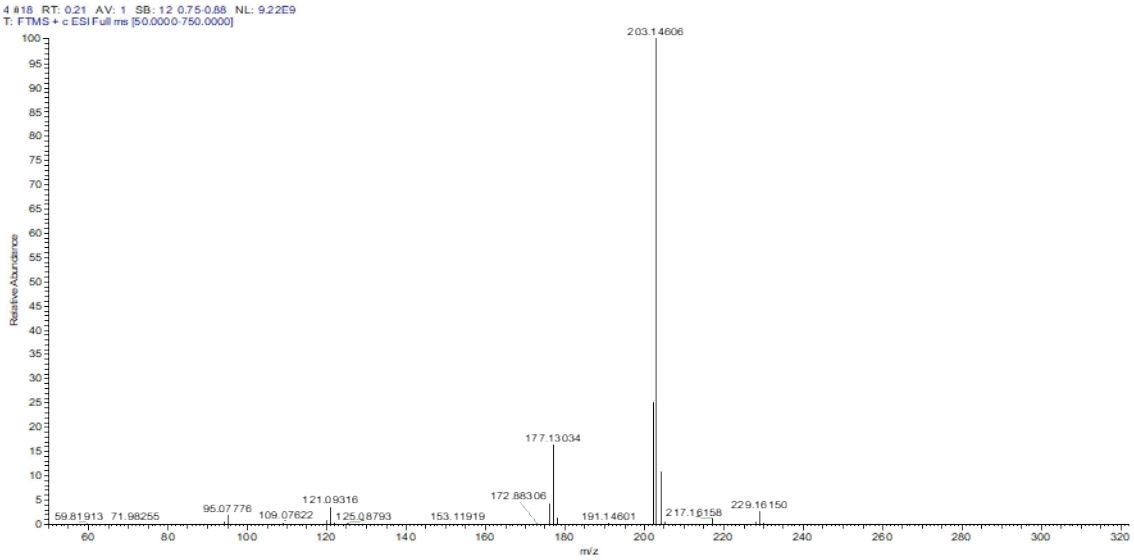


Figure S38 HRMS-ESI SPECTRUMof (1-allyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride (positive) solvent (H_2O).

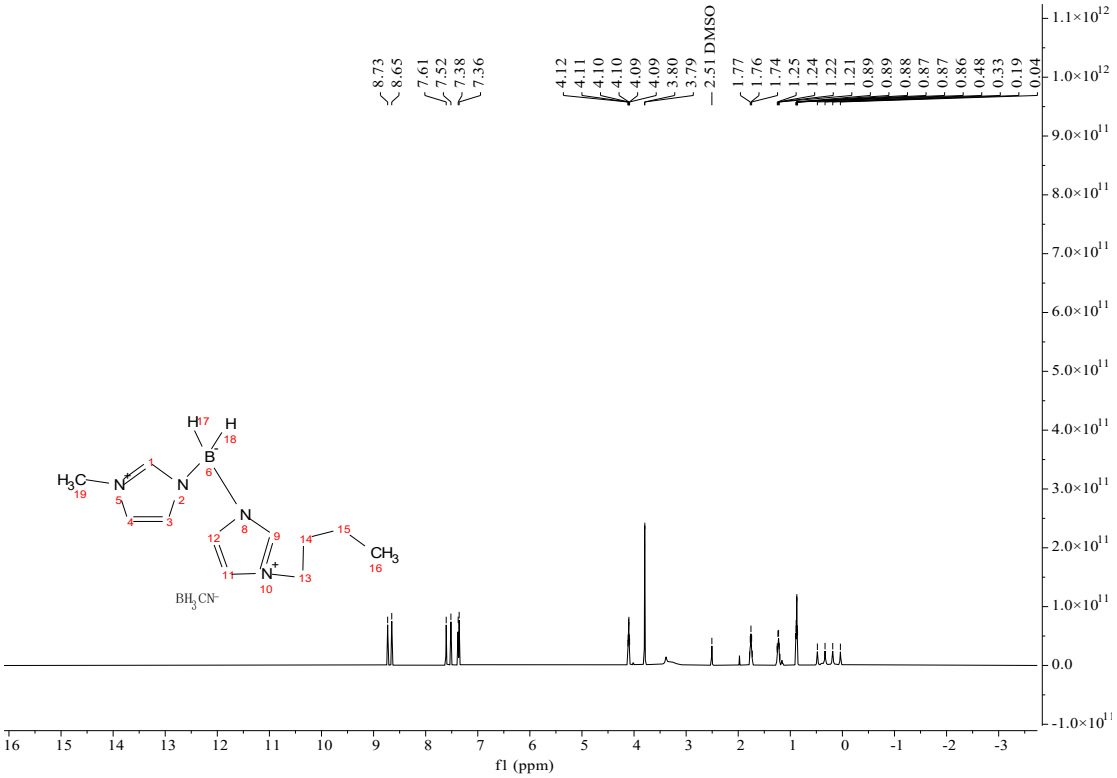


Figure S39 ^{1}HNMR (400 MHz) of (1-butyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride in DMSO-D_6.

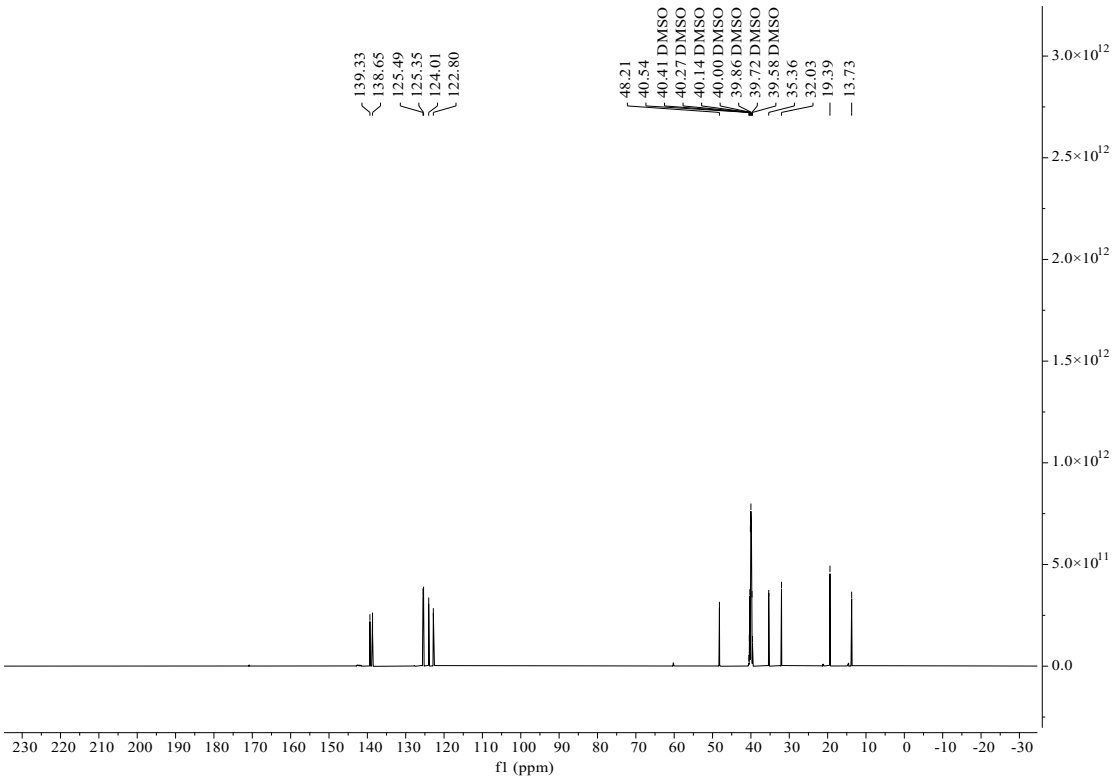


Figure S40 ^{13}CNMR (101 MHz) of (1-butyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride in DMSO-D_6.

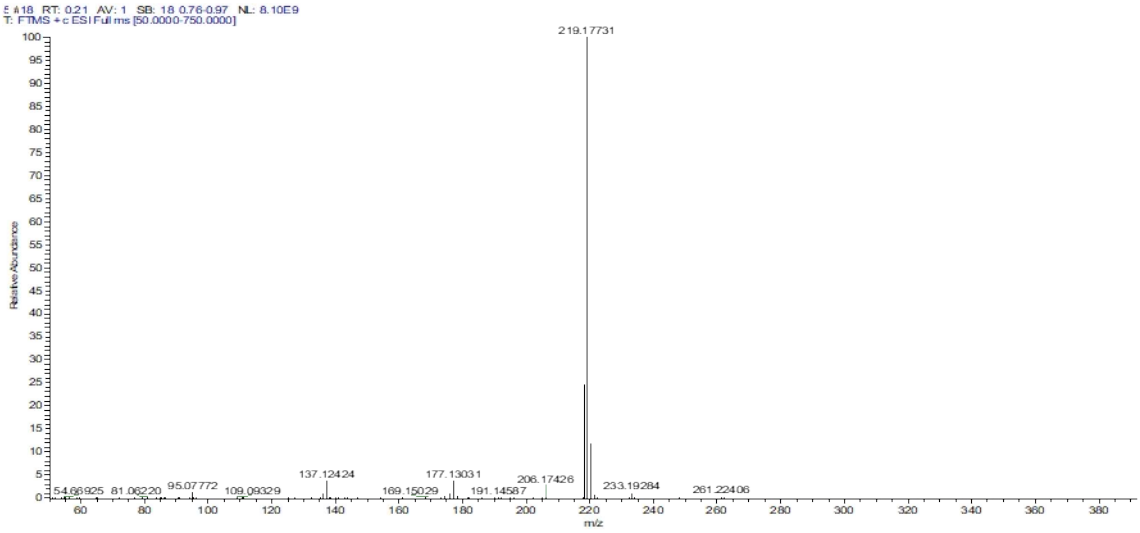


Figure S41 HRMS-ESI SPECTRUMof (1-butyl-1H-imidazol-3-ium-1-yl)(1-methyl-1H-imidazol-3-ium-1-yl) dihydroboronium cyanoborohydride (positive) solvent (H_2O).

3.Computational details

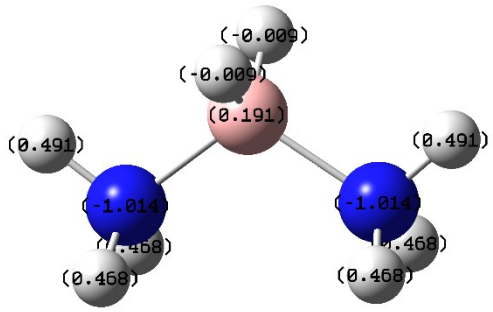
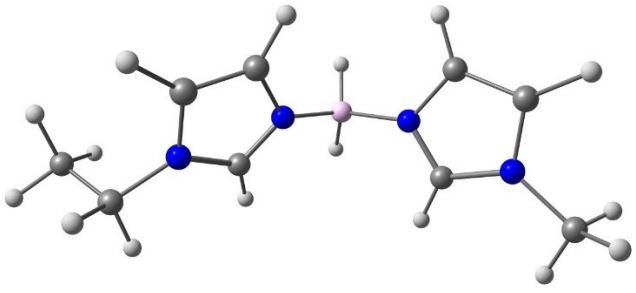
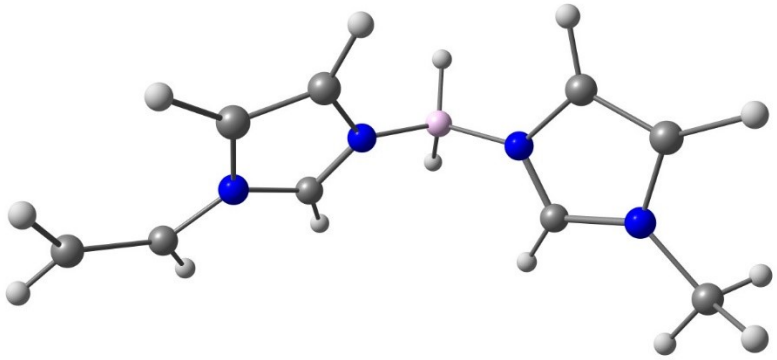


Figure. S42. NPA charge of the $BH_2(NH_3)_2^+$.

3.1 Geometry optimizated coordinate for the cations



H	0.353929000	0.217453000	2.274392000
H	0.448350000	-1.765986000	1.868779000
N	-0.822200000	-0.486725000	0.486418000
C	-1.244643000	-1.341313000	-0.514614000
C	-1.738504000	0.478514000	0.589134000
C	-2.424954000	-0.867583000	-1.013917000
H	-0.686210000	-2.222696000	-0.786145000
H	-1.705560000	1.289577000	1.300044000
H	-3.067946000	-1.244464000	-1.793767000
N	1.762961000	-0.421474000	0.618249000
C	2.419163000	0.733229000	0.487746000
C	2.506443000	-1.387299000	-0.033576000
H	2.109960000	1.676139000	0.911391000
C	3.615105000	-0.791366000	-0.565010000
H	2.204405000	-2.422451000	-0.043740000
H	4.438988000	-1.195686000	-1.131987000
N	3.543705000	0.547922000	-0.225352000
N	-2.723026000	0.282291000	-0.305223000
C	4.537446000	1.573402000	-0.558013000
H	5.504169000	1.302622000	-0.128866000
H	4.626034000	1.663992000	-1.642425000
H	4.214926000	2.527860000	-0.141856000
C	-3.939692000	1.106593000	-0.452621000
H	-4.079230000	1.287880000	-1.521782000
H	-3.727246000	2.069430000	0.018311000
C	-5.171819000	0.448437000	0.166799000
H	-6.036563000	1.104630000	0.033171000
H	-5.398670000	-0.508784000	-0.311206000
H	-5.033640000	0.277780000	1.238269000
B	0.430588000	-0.645415000	1.440640000



H	0.396146000	-0.256448000	2.373047000
H	0.499298000	-2.125075000	1.594674000
N	-0.887937000	-0.650760000	0.563699000
C	-1.356661000	-1.311036000	-0.559336000
C	-1.816085000	0.237418000	0.910149000
C	-2.577245000	-0.799357000	-0.887002000
H	-0.798896000	-2.106528000	-1.026823000
H	-1.759345000	0.895978000	1.762914000
H	-3.259471000	-1.057387000	-1.679362000
N	1.695785000	-0.528829000	0.535108000
C	2.303486000	0.659551000	0.561246000
C	2.421438000	-1.337734000	-0.319333000
H	1.995645000	1.503356000	1.159127000
C	3.468697000	-0.612202000	-0.812735000
H	2.153186000	-2.368847000	-0.485911000
H	4.262408000	-0.878579000	-1.493034000
N	3.378334000	0.646504000	-0.245546000
N	-2.860426000	0.182043000	0.053560000
C	4.313615000	1.755513000	-0.459942000
H	5.310460000	1.468868000	-0.118957000
H	4.344246000	2.011529000	-1.520742000
H	3.973811000	2.620623000	0.109489000
B	0.433440000	-0.945341000	1.388955000
C	-4.020457000	1.002317000	0.157179000
H	-4.019269000	1.615418000	1.051263000

C	-5.012724000	1.030109000	-0.729039000
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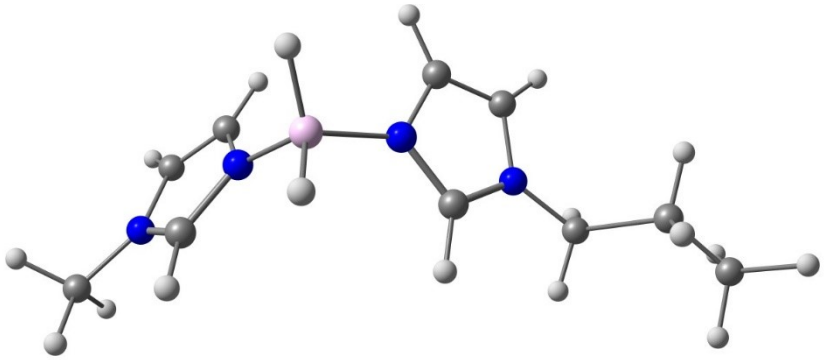

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C	2.100334000	1.479990000	-0.583961000
H	0.464632000	2.863111000	0.000452000
H	0.996730000	-1.233993000	0.808484000
H	2.844905000	2.022141000	-1.145093000
N	-2.209361000	0.371685000	0.484187000
C	-3.013079000	-0.667304000	0.715635000
C	-2.712301000	1.036520000	-0.618468000
H	-2.897933000	-1.370137000	1.526002000
C	-3.827300000	0.374598000	-1.048439000
H	-2.252509000	1.931925000	-1.004592000
H	-4.501535000	0.572338000	-1.867175000
N	-4.005255000	-0.697166000	-0.192275000
N	2.233209000	0.133650000	-0.295028000
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H	-6.053559000	-1.170081000	-0.152956000

H	-5.055592000	-2.213221000	-1.205625000
H	-4.975275000	-2.389153000	0.563495000
B	-1.005698000	0.798951000	1.423767000
C	3.387993000	-0.718724000	-0.638594000
H	3.055121000	-1.756925000	-0.552868000
H	3.624841000	-0.536181000	-1.691123000
C	4.606536000	-0.458680000	0.255187000
H	4.897257000	0.595639000	0.174300000
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C	5.786531000	-1.357400000	-0.131312000
H	6.106676000	-1.178532000	-1.163656000
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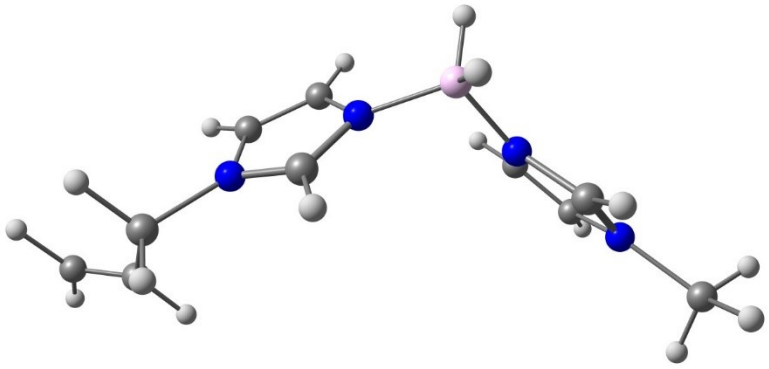

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C	-2.393348000	0.493551000	1.209451000
N	-2.088066000	0.620218000	-0.132762000
C	-4.897966000	-1.645322000	-0.314679000
B	-1.023665000	1.580022000	-0.810045000
C	1.218565000	0.276231000	-1.010555000
N	2.412265000	0.199411000	-0.397065000
C	2.395329000	1.070582000	0.677535000
C	1.162721000	1.660167000	0.680274000

N	0.432696000	1.150511000	-0.377749000
C	3.570044000	-0.610616000	-0.842625000
C	4.140500000	-1.444576000	0.271194000
C	5.413038000	-1.365705000	0.666003000
H	-2.989446000	-0.235961000	-1.879349000
H	-3.988013000	-0.712132000	2.199029000
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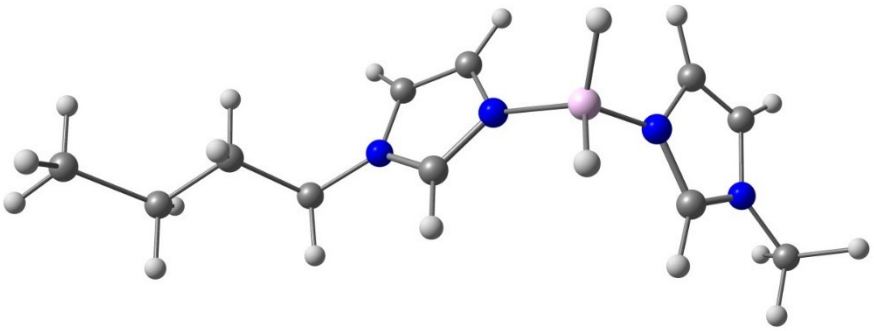
H	-5.846006000	-1.219745000	0.020343000
H	-4.919305000	-1.758864000	-1.398597000
H	-1.128914000	1.437747000	-1.999289000
H	-1.207968000	2.697943000	-0.415236000
H	0.949611000	-0.271894000	-1.900292000
H	3.246424000	1.190279000	1.328530000
H	0.757112000	2.417460000	1.332173000
H	3.204935000	-1.239773000	-1.660696000
H	4.324639000	0.068453000	-1.250871000
H	3.461565000	-2.158245000	0.735521000
H	5.801906000	-2.009580000	1.448316000
H	6.113654000	-0.668393000	0.212299000



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C	4.628257000	0.621322000	-0.520363000
C	3.551903000	1.288309000	-0.007201000
N	2.740535000	0.374623000	0.638619000
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B	1.412391000	0.682888000	1.442139000
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C	-5.494597000	-0.876695000	-0.204199000
C	-6.715033000	-0.236625000	0.466925000
H	2.951727000	-1.738664000	0.946896000
H	5.483334000	0.970177000	-1.077911000
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H	1.257274000	-0.190624000	2.253798000
H	1.507152000	1.788996000	1.896976000
H	-0.811200000	-1.137687000	1.141119000
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H	-4.011271000	0.000998000	1.116147000
H	-4.323388000	0.942274000	-0.339195000
H	-5.672447000	-0.961051000	-1.284619000
H	-5.366688000	-1.901674000	0.169031000
H	-7.618089000	-0.823118000	0.274697000
H	-6.584307000	-0.173024000	1.552829000
H	-6.889998000	0.777097000	0.089983000

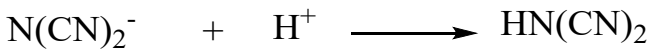


Figure S41 protonation reaction of dicyandiamide anion

Table S1 Heat of formation of the compound

Compounds	Heat of the formation
1-methylimidazole	127.1[a]
1-ethylimidazole	97.91[b]
1-propylimidazole	76.2[b]
1-butylimidazole	55.4[b]
1-vinylimidazole	223.7[b]
1-allylimidazole	212.8[b]
NH_3	-45.9[a]
$BH_2(NH_3)^{2+}$	418.46[b]

[a] The data was got from the NIST [b]Heat of formation was calculated based on G2

Table S2 Enthalpies of the gas-phase species of cations and anions (based on isodesmic reactions).

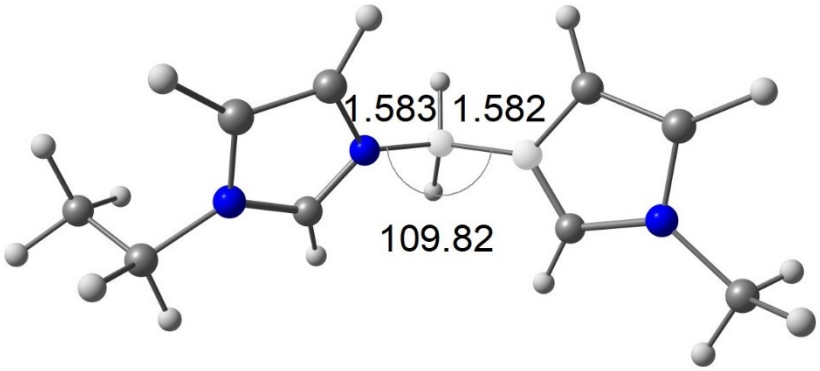
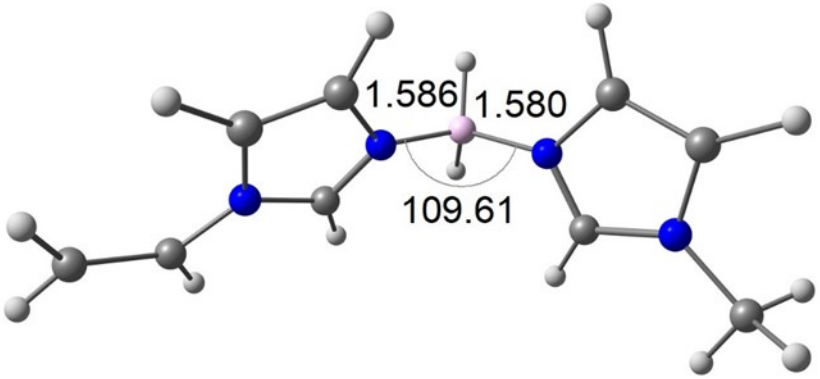
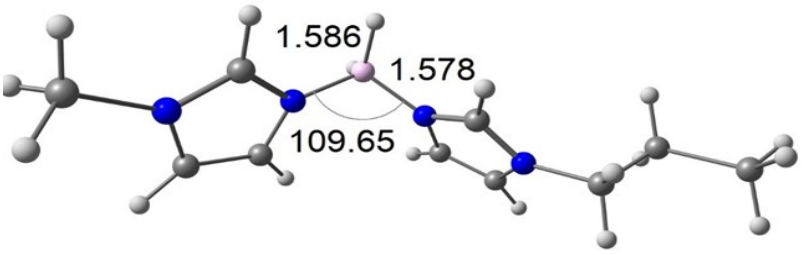
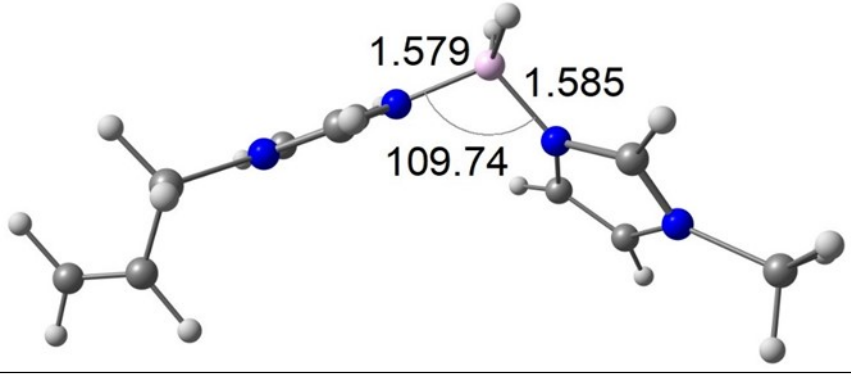
Compound	E_0(a.u.)	ZPE(a.u.)	T_C(a.u.)	H_T KJ/mol
1-methylimidazole	-264.8298954	0.098967	0.105307	15.9798432
1-vinylimidazole	-302.80676	0.103732	0.110759	17.71141296
2-buthylimidazole	-382.4209903	0.184402	0.194616	25.74418272
1-propylimidazole	-343.2252806	0.155963	0.164841	22.37682144
1-allylimidazole	-342.0020938	0.132327	0.140673	21.03592608
1-ethylimidazole	-304.0292598	0.12753	0.135051	18.95653008
CH_4	-40.3796279	0.044816	0.048629	9.61059024
NH_3	-56.4154632	0.034373	0.038191	9.62319264
$BH_2(NH_3)_2^+$	-138.6134981	0.104521	0.110416	14.8582296

Table S3 Enthalpies of the gas-phase species of cations (based on isodesmic reactions)

Compound	E_0(a.u.)	ZPE(a.u.)	T_C(a.u.)	H_T KJ/mol
2a	-594.7005807	0.2562	0.271208	37.82736384
2b	-593.474067	0.232351	0.24681	36.44362032
2c	-633.8972456	0.284599	0.301002	41.34343344

2d	-632.6742095	0.261018	0.276829	39.85130928
2e	-673.0934798	0.312987	0.330777	44.8393392

Table S4 Optimized structures of cations of the ionic liquid

Ionic liquids	Cations
3a	
3b	
3c	
3d	

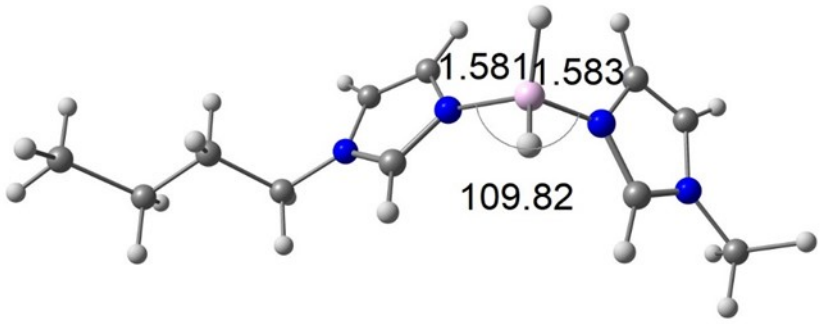
3e	

Table S7 The lattice energy with heat of formation of cation and anion of ionic salts

Compound	ΔH_L [kJ mol^{-1}]	$\Delta H_f^{[}$ (cation) [kJ mol^{-1}]	ΔH_f (anion) [kJ mol^{-1}]
3a	430.07	572.51	118.6
3b	430.33	708.55	118.6
3c	419.00	549.99	118.6
3d	421.89	685.29	118.6
3e	413.56	526.93	118.6
4a	433.04	572.51	-80.6
4b	422.95	708.55	-80.6
4c	436.47	549.99	-80.6
4d	429.36	685.29	-80.6
4e	414.84	526.93	-80.6