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Supplementary Information

Amino Functionalized $[B_{12}H_{12}]^{2-}$ Salts as Hypergolic Fuels

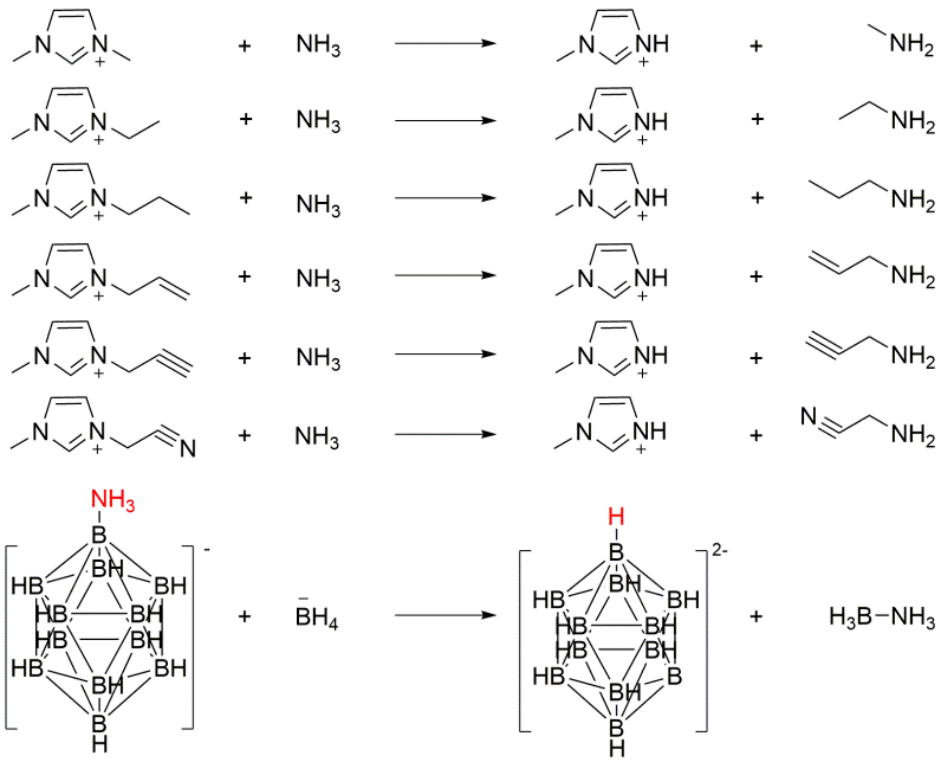
Hao Li,[a,b] Yanqiang Zhang,[a*] Long Liu,[a] Nianming Jiao,[a,c] Xianghai Meng,[b] and Suojiang Zhang[a*]

[a] *Division of Ionic Liquids and Green Engineering，Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China. E-mail: yqzhang@ipe.ac.cn, sjzhang@ipe.ac.cn; FAX: +86-10-82544875*

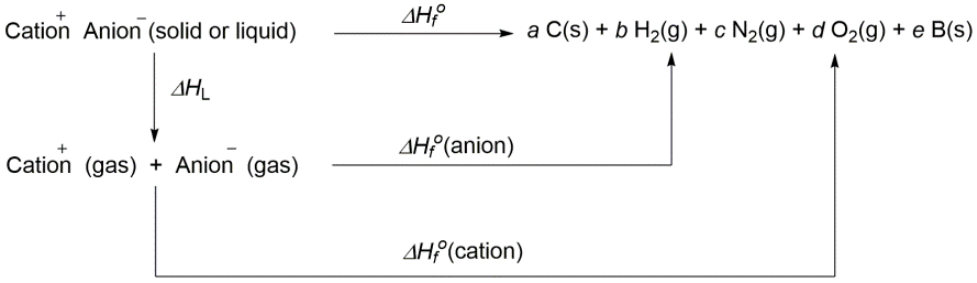
[b] *School of Chemistry Engineering, China University of Petroleum (Beijing), Beijing 102249, China*

[c] *School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China*

Contents S1



Scheme S1. Isodesmic reactions of seven ions



Scheme S2. Born-Haber cycle for the formation of salts

Table S1. Enthalpies of the gas-phase species for part cations (C+) and anions (A-) (G2 method)

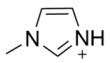
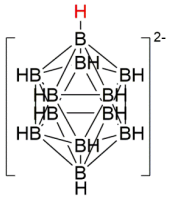
Ions	ΔH_f^o/kJ mol^{-1}
	693.69
	-361.24

Table S2. Enthalpies of the gas-phase species of seven ions based on isodesmic reactions

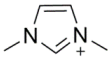
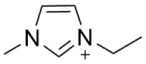
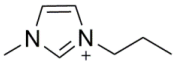
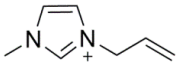
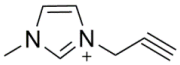
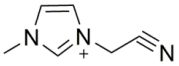
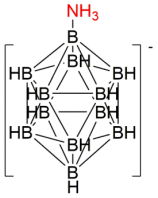
Ions	E(MP2) /kJ mol^{-1}	ZPE	TCH	ΔH_{corr} /kJ mol^{-1}	ΔH_f^o /kJ mol^{-1}
	-304.4035356	0.139957	0.148121	-304.26	666.89
	-343.6051443	0.169084	0.178439	-343.43	625.70
	-382.8006934	0.197643	0.208394	-382.60	614.42
	-381.5792991	0.173998	0.184101	-381.40	744.48
	-380.3396735	0.149819	0.159697	-380.19	937.05
	-396.4154208	0.139197	0.148821	-396.27	867.60
	-360.5424935	0.198397	0.208640	-360.34	-207.57

Table S3. Calculated enthalpies of salts

Compounds	ΔH_{cation} /kJ mol^{-1}	ΔH_{anion} /kJ mol^{-1}	Upot /kJ mol^{-1}	ΔH_L /kJ mol^{-1}	ΔH_{salt} /kJ mol^{-1}	ΔH_{salt} /J g^{-1}
1	666.89	-207.57	429.71	434.67	24.66	96.71
2	625.70	-207.57	416.74	421.70	-3.56	-13.23
3	614.42	-207.57	413.23	418.18	-11.33	-40.05
4	744.48	-207.57	422.88	427.84	109.08	388.13
5	937.05	-207.57	425.16	430.11	299.37	1072.98
6	867.60	-207.57	421.19	426.14	233.89	835.33
1′	666.89	-361.24	1063.22	1070.657	-98.1111	-291.91

Table S4. Selected bond lengths [Å] for **1**

Atom-Atom	Length/Å	Atom-Atom	Length/Å
N3-B9	1.564(8)	B12-B2	1.783(11)
B5-B9	1.772(9)	B12-B1	1.793(10)
B5-B3	1.794(9)	B3-B10	1.773(11)
B5-B4	1.782(9)	B3-B6	1.783(9)
B5-B5	1.796(9)	B3-B2	1.807(10)
B5-B6	1.797(9)	B3-B1	1.764(10)
B8-B9	1.765(9)	B7-B6	1.784(9)
B8-B7	1.781(9)	B11-B10	1.787(9)
B8-B11	1.812(10)	B11-B1	1.803(12)
B8-B10	1.775(10)	B10-B11	1.763(9)
B8-B6	1.773(9)	B10-B6	1.817(11)
B9-B12	1.766(10)	B2-B1	1.768(11)
B9-B7	1.759(8)	N1-C3	1.318(8)
B9-B11	1.769(9)	N1-C1	1.352(9)
B4-B3	1.791(10)	N1-C4	1.472(10)
B4-B7	1.781(9)	N2-C3	1.325(8)
B4-B6	1.793(9)	N2-C2	1.385(8)
B4-B2	1.807(9)	N2-C5	1.446(8)
B12-B11	1.764(10)	C1-C2	1.322(10)

Table S5. Selected bond angles [°] for **1**

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
N3-B9-B5	120.3(5)	B5-B4-B2	59.9(4)
B7-B9-B5	61.1(3)	B3-B4-B5	107.9(5)
B7-B9-B8	60.7(4)	B3-B4-B6	59.7(4)
B7-B9-B12	109.7(5)	B3-B4-B2	60.3(4)
B7-B9-B11	110.1(5)	B7-B4-B5	60.3(3)
B5-B12-B2	60.6(4)	B7-B4-B3	107.6(5)
B5-B12-B1	108.2(5)	B7-B4-B6	59.9(4)
B9-B12-B5	59.9(4)	B7-B4-B2	108.2(5)
B9-B12-B2	107.9(5)	B6-B4-B5	108.2(4)
B9-B12-B1	108.0(5)	B6-B4-B2	108.2(5)
B11-B12-B5	109.0(5)	B1-B3-B4	108.2(5)
B11-B12-B9	60.1(4)	B1-B3-B10	61.8(4)
B11-B12-B2	108.7(5)	B1-B3-B6	109.4(5)
B11-B12-B1	60.9(4)	B1-B3-B2	59.3(4)
B2-B12-B1	59.3(4)		

Table S6. Selected Torsion angles [°] for **1**

A-B-C-D	Angle/°	A-B-C-D	Angle/°	A-B-C-D	Angle/°
N3-B9-B12-B5	-109.3(6)	B5-B9-B11-B12	36.3(4)	B12-B2-B1-B10	98.4(6)
N3-B9-B12-B11	110.6(6)	B5-B9-B11-B10	-66.2(6)	B1-B3-B10-B8	101.5(5)
N3-B9-B12-B2	-147.6(5)	B5-B9-B11-B1	-2.4(6)	B1-B3-B10-B11	36.8(5)
N3-B9-B12-B1	149.7(5)	B5-B12-B11-B8	-0.2(7)	B1-B3-B10-B6	138.9(5)
B9-B5-B4-B3	-62.8(5)	B5-B12-B11-B9	-36.0(4)	B1-B3-B6-B8	-0.5(7)
B9-B5-B4-B7	37.6(4)	B5-B12-B11-B10	62.3(6)	B1-B3-B6-B4	100.4(5)
B9-B5-B4-B6	0.2(6)	B5-B12-B11-B1	100.7(5)	B1-B3-B6-B7	63.1(6)
B9-B5-B4-B2	-100.7(5)	B5-B12-B2-B4	-38.0(4)	B1-B3-B6-B10	-37.9(5)
B9-B5-B12-B11	36.1(5)	B5-B12-B2-B3	-100.3(5)	B1-B3-B2-B5	-101.8(6)
B9-B5-B12-B2	137.3(5)	B5-B12-B2-B1	-138.8(5)	B1-B3-B2-B4	-139.2(5)
B9-B5-B12-B1	100.7(6)	B5-B12-B1-B3	-2.7(7)	B1-B3-B2-B12	-39.1(5)
B9-B5-B7-B8	-36.0(4)	B5-B12-B1-B11	-102.1(5)	B3-B4-B7-B5	101.0(5)
B9-B5-B7-B4	-136.9(5)	B5-B12-B1-B10	-65.1(7)	B3-B4-B7-B8	-0.4(6)
B9-B5-B7-B6	-99.2(5)	B5-B12-B1-B2	37.2(5)	B3-B4-B7-B9	62.8(5)
B9-B5-B2-B4	99.3(5)	B1-B12-B11-B8	-100.9(5)	B3-B4-B7-B6	-37.2(4)
B9-B5-B2-B12	-37.7(4)	B1-B12-B11-B9	-136.7(5)	B3-B4-B6-B8	101.1(5)
B9-B5-B2-B3	62.0(6)	B1-B12-B11-B10	-38.4(5)	B3-B4-B6-B7	138.1(5)
B9-B5-B2-B1	-0.4(6)	B1-B12-B2-B5	138.8(5)	B3-B4-B6-B10	37.3(4)
B5-B9-B12-B11	-140.1(5)	B1-B12-B2-B4	100.8(5)	B3-B4-B2-B5	-137.8(5)
B5-B9-B12-B2	-38.3(5)	B1-B12-B2-B3	38.4(5)	B3-B4-B2-B12	-99.8(6)
B5-B9-B12-B1	-101.0(5)	B12-B2-B1-B3	136.1(5)	B3-B4-B2-B1	-36.0(5)
B5-B9-B11-B8	-103.3(5)	B12-B2-B1-B11	35.8(4)		

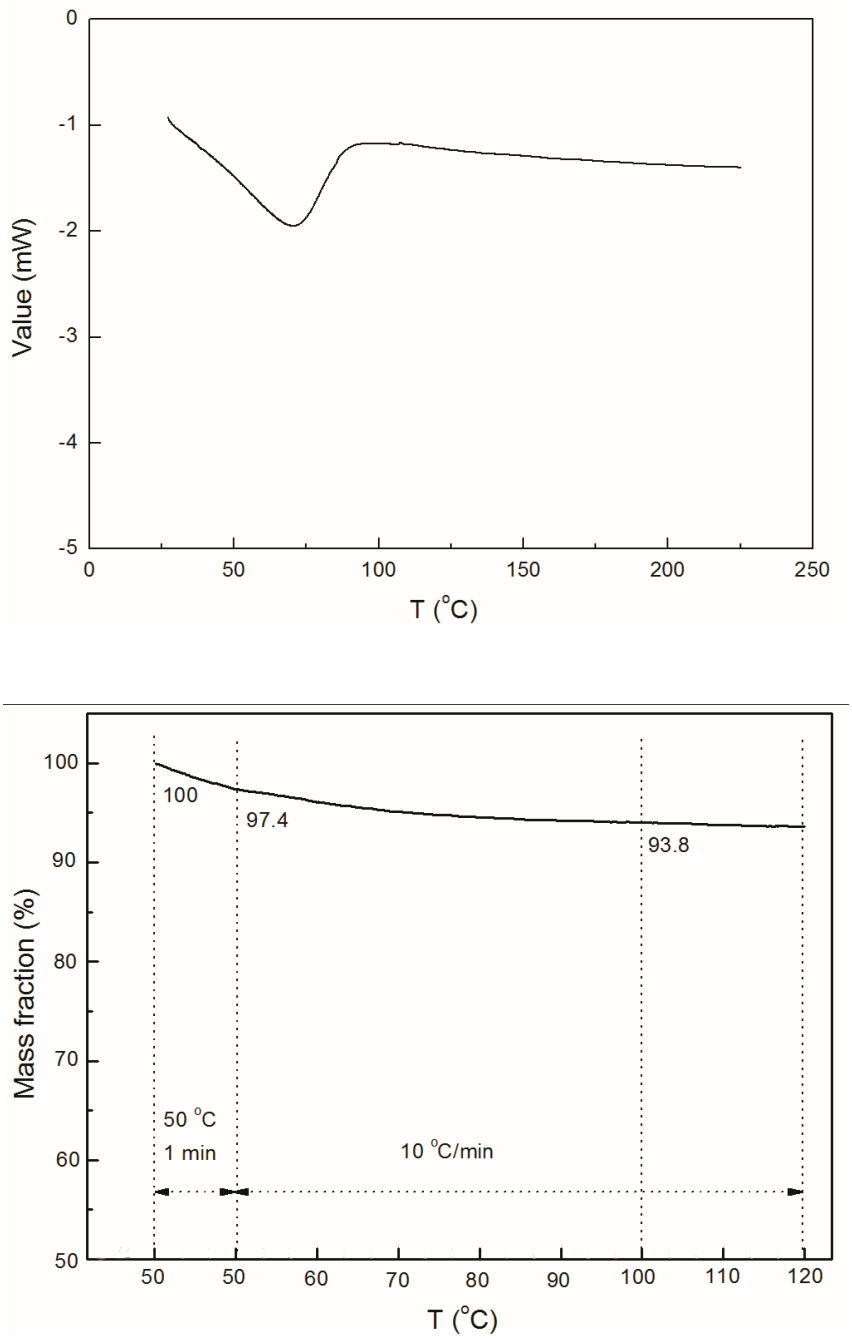


Figure S1. DSC and TG curve of **1.**

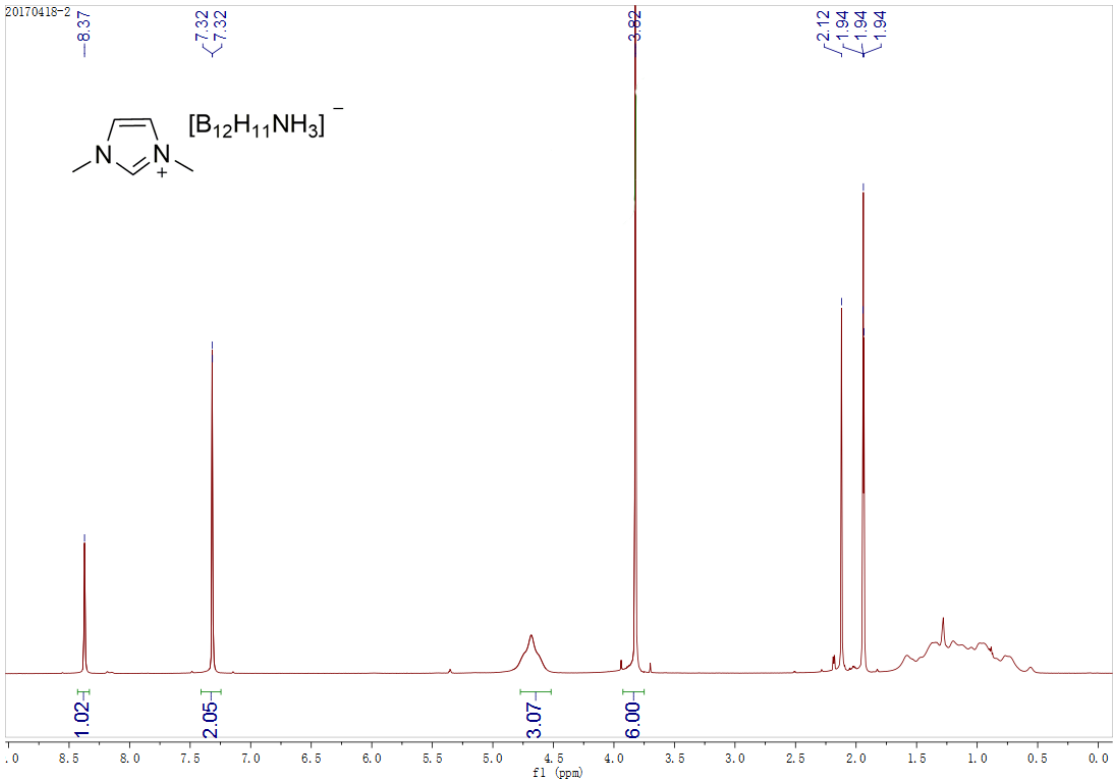


Figure S2. ^{1}H NMR of 1, 3-dimethylimidazolium 1-ammonio-closo-dodecaborate (**1**)

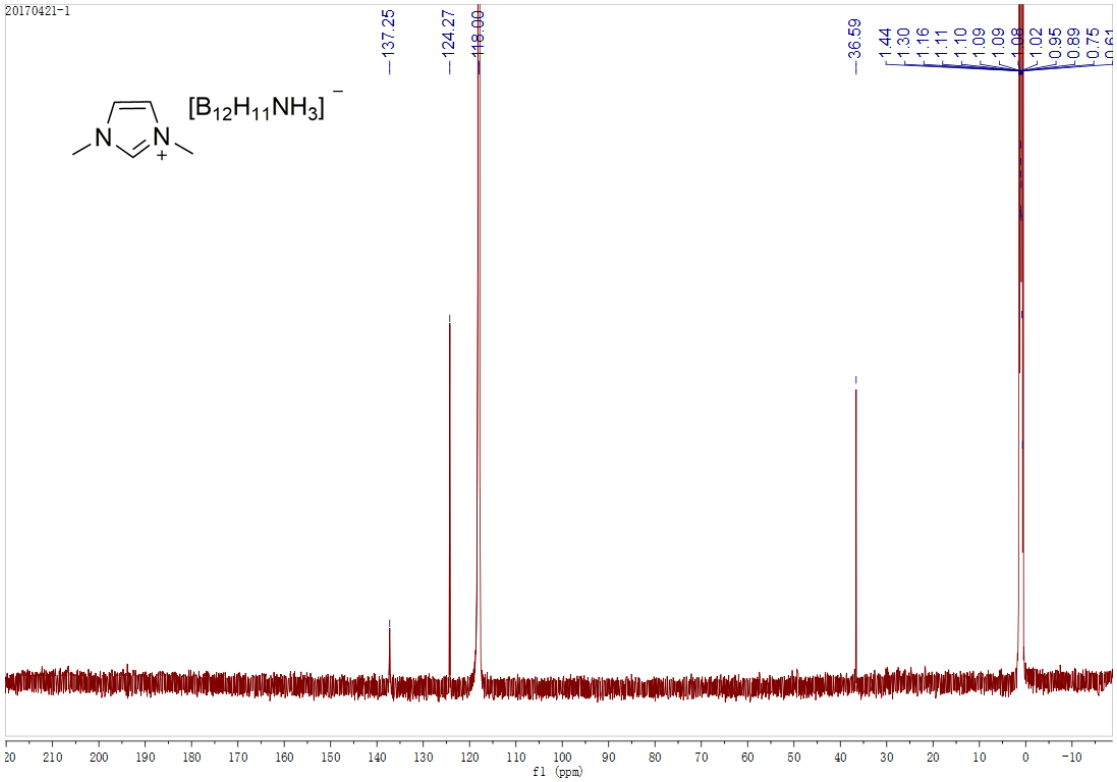


Figure S3. ^{13}C NMR of 1, 3-dimethylimidazolium 1-ammonio-closo-dodecaborate (**1**)

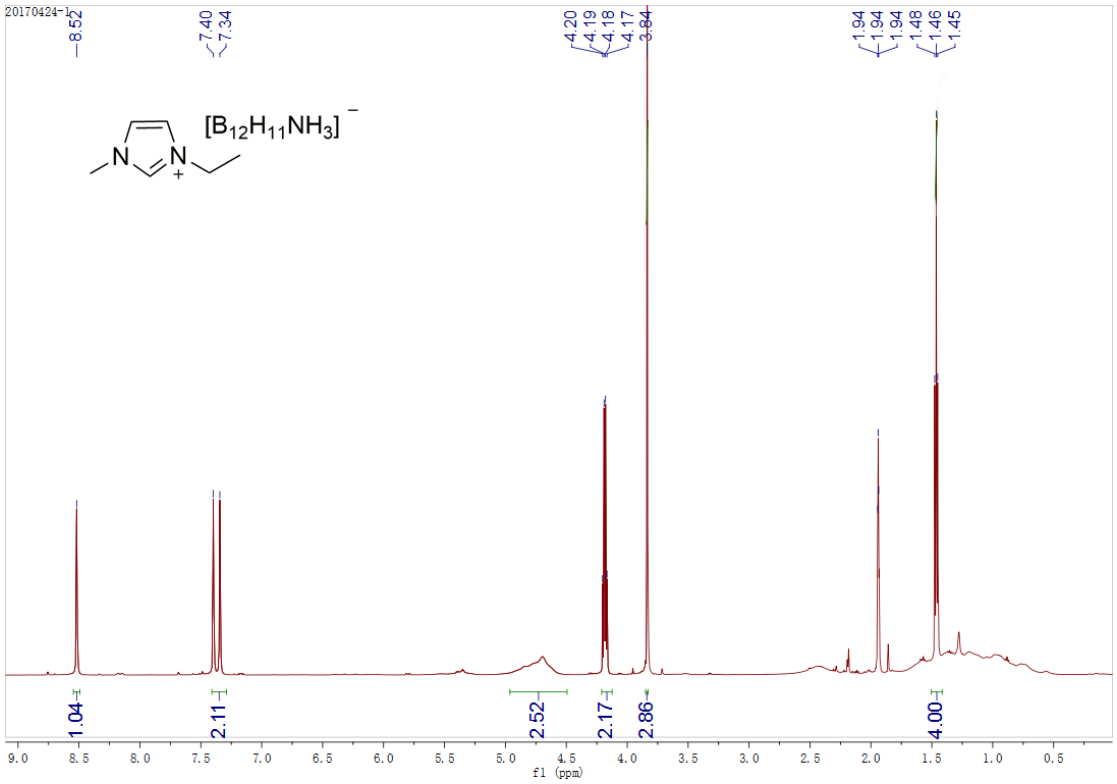


Figure S4. ^{1}H NMR of 1-ethyl-3-methylimidazolium 1-ammonio-closo-dodecaborate (**2**)

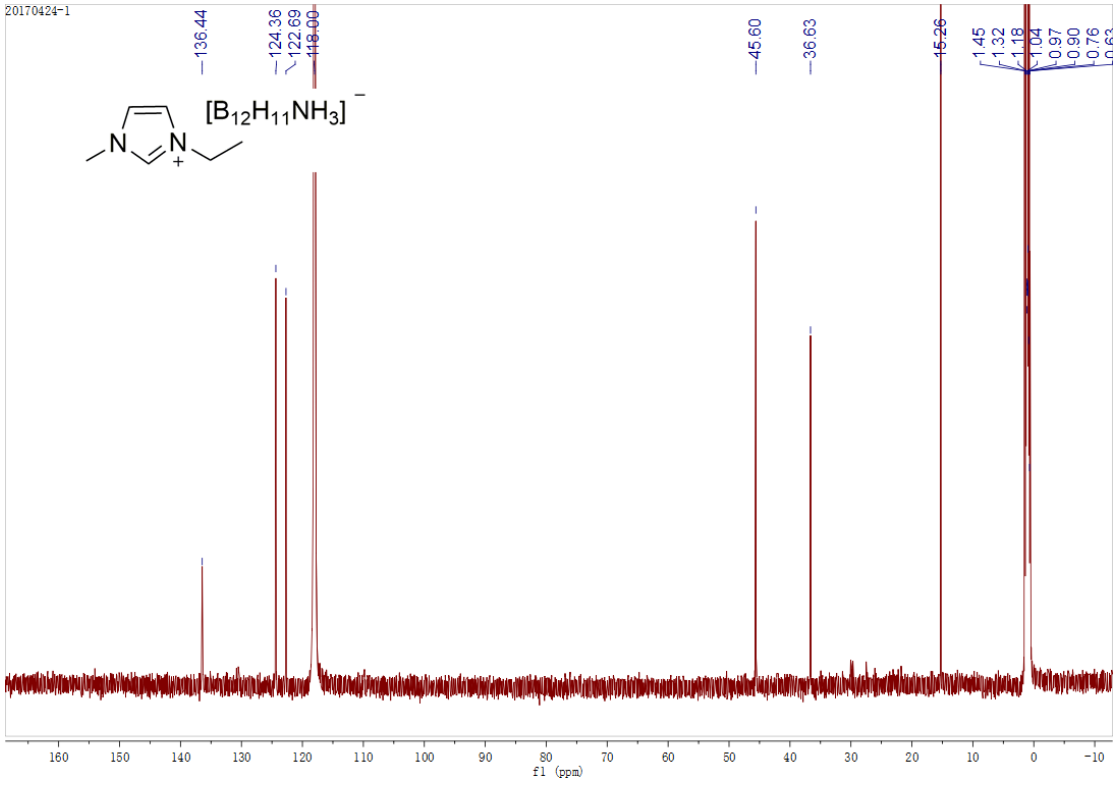


Figure S5. ^{13}C NMR of 1-ethyl-3-methylimidazolium 1-ammonio-closo-dodecaborate (**2**)

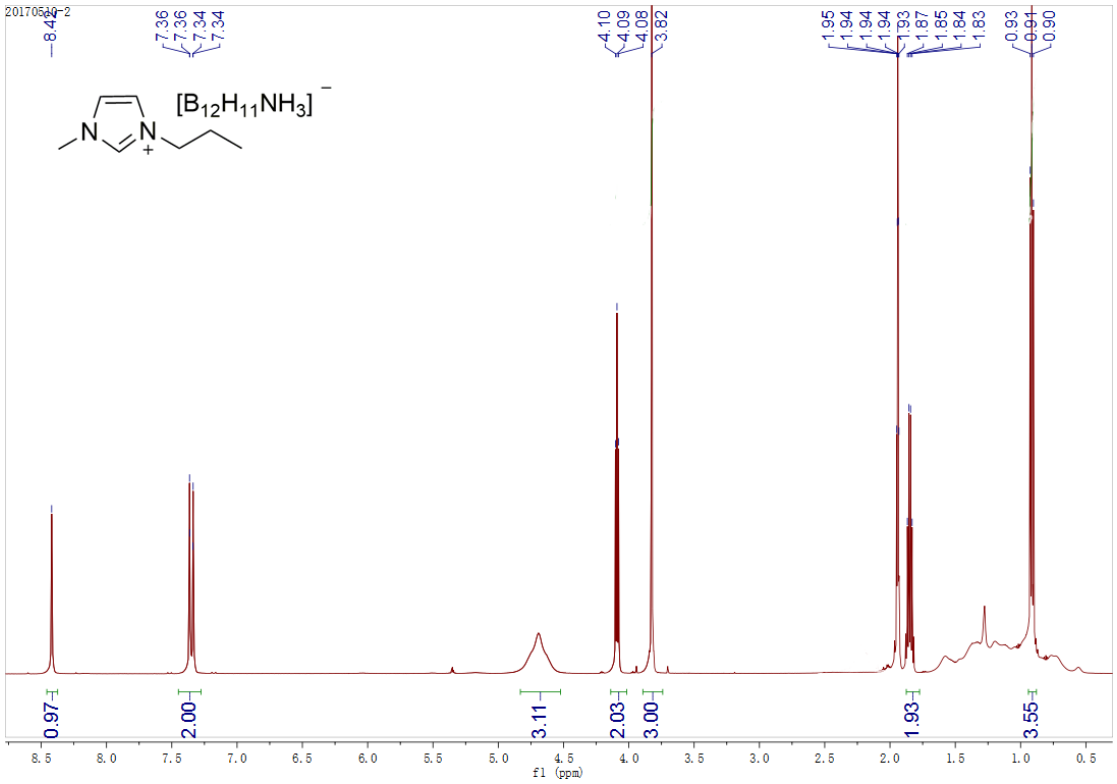


Figure S6. ^{1}H NMR of 1-propyl-3-methylimidazolium 1-ammonio-closo-dodecaborate (**3**)

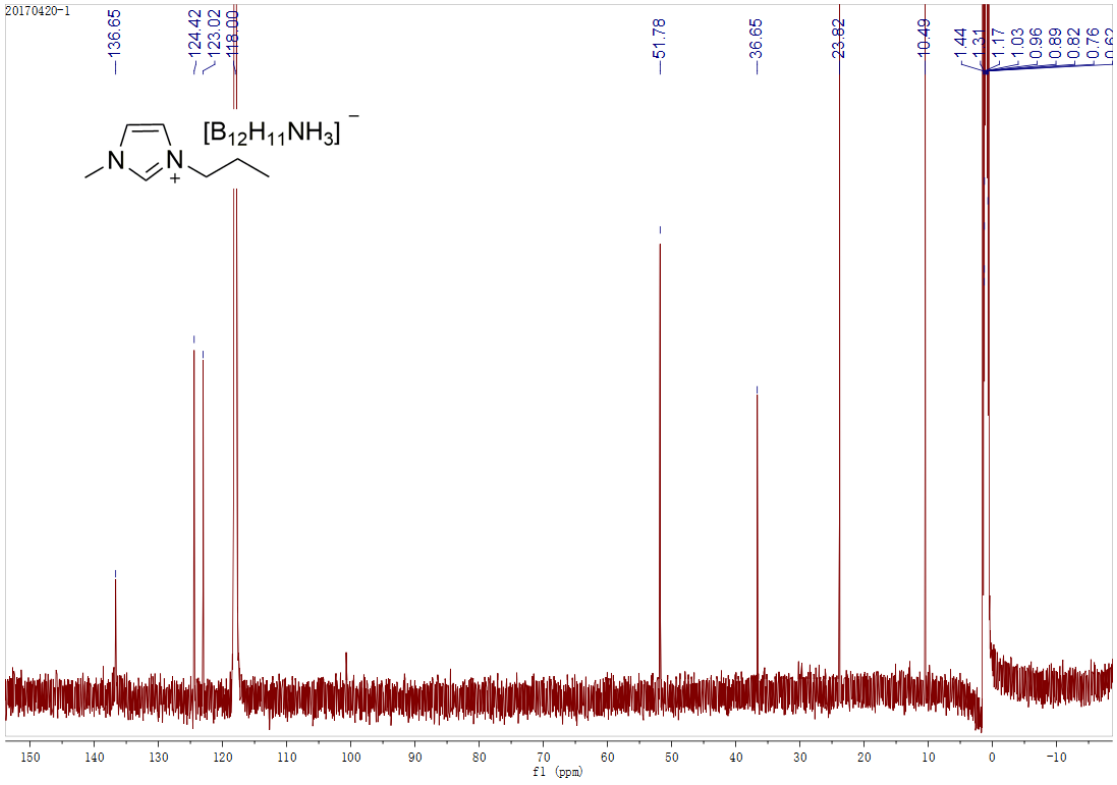


Figure S7. ^{13}C NMR of 1-propyl-3-methylimidazolium 1-ammonio-closo-dodecaborate (**3**)

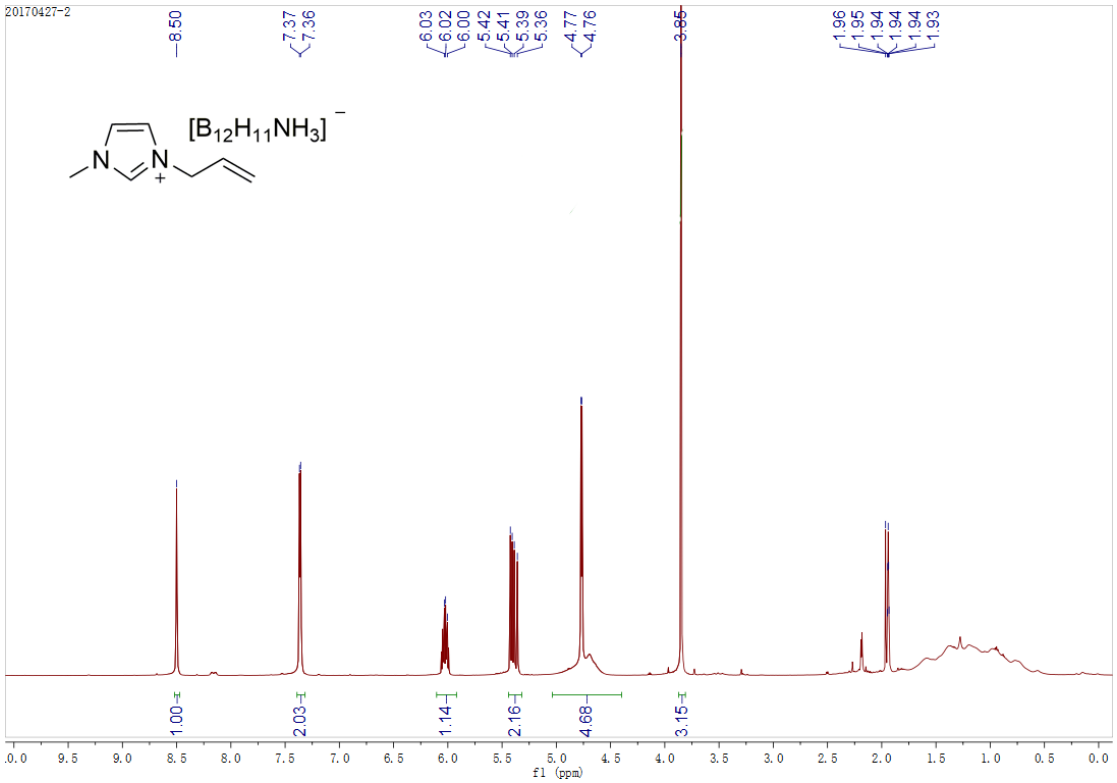


Figure S8. ^{1}H NMR of 1-allyl-3-methylimidazolium 1-ammonio-closo-dodecaborate (**4**)

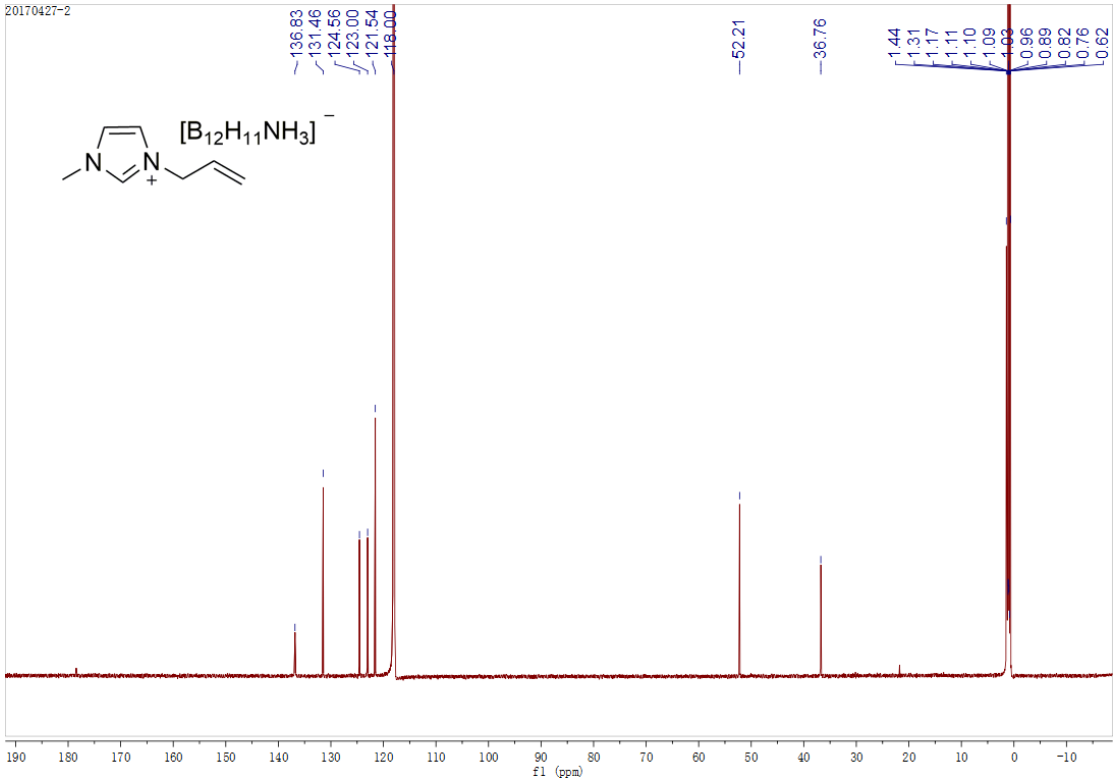


Figure S9. ^{13}C NMR of 1-allyl-3-methylimidazolium 1-ammonio-closo-dodecaborate (**4**)

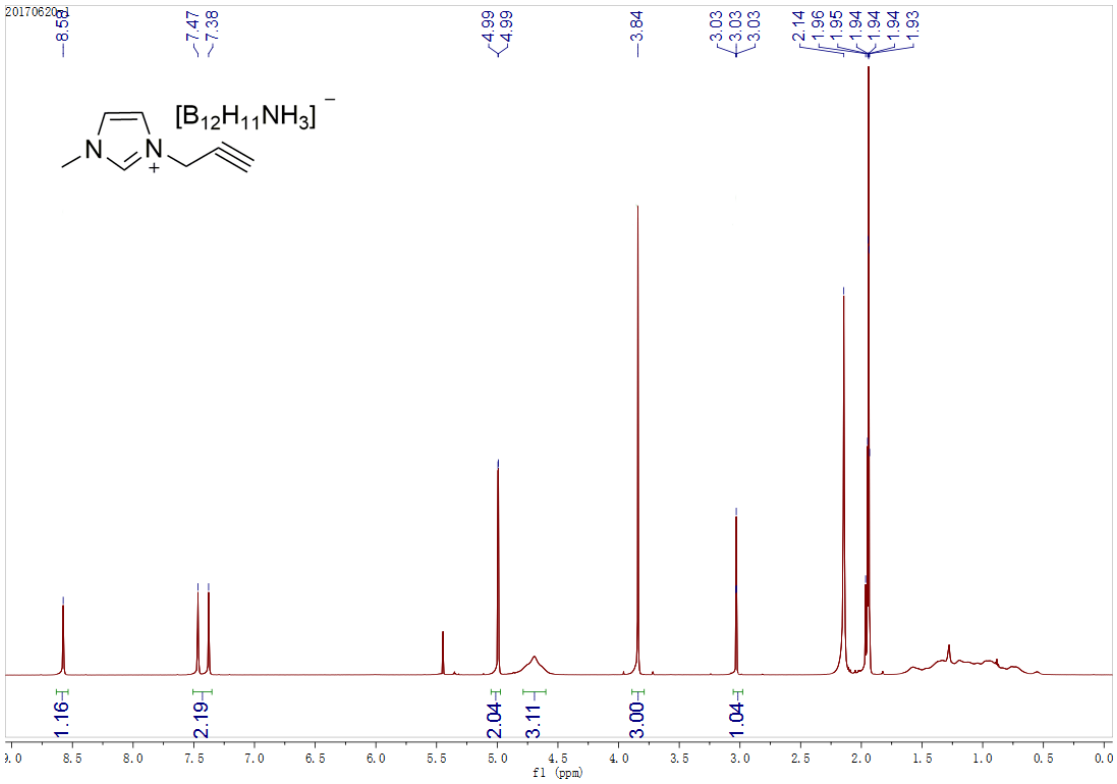


Figure S10. ^{1}H NMR of 1-propargyl-3-methylimidazolium 1-ammonio-closo-dodecaborate (**5**)

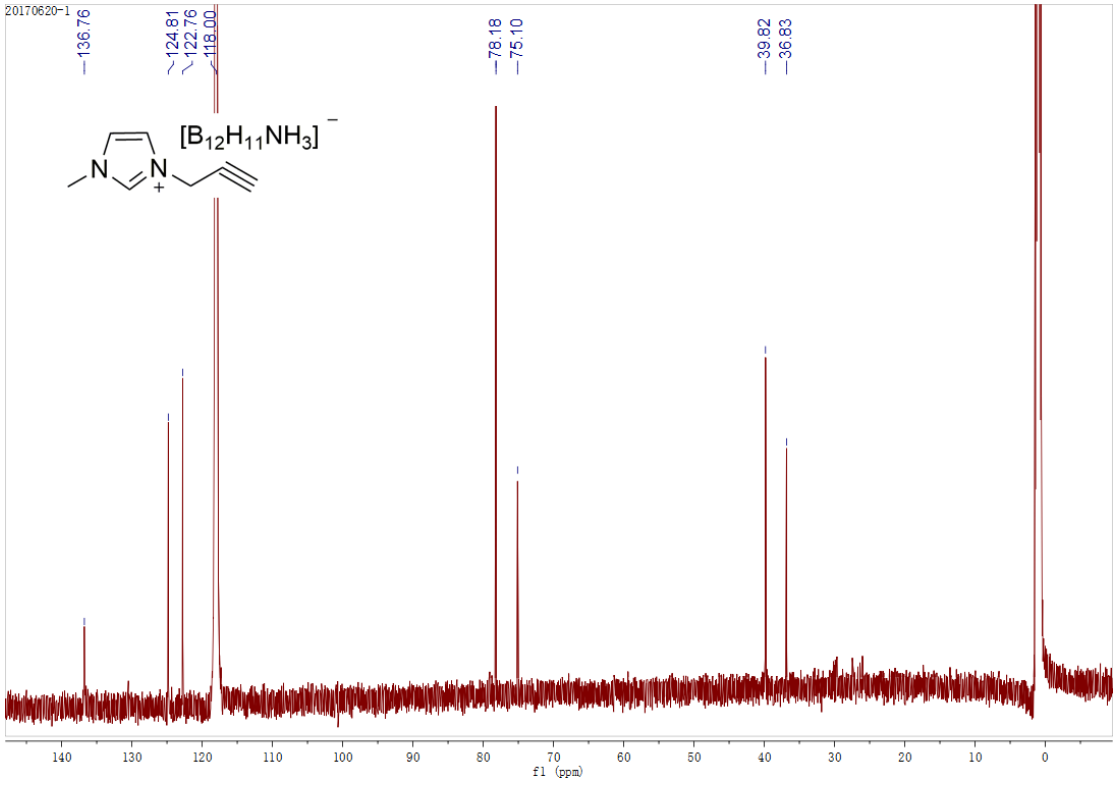


Figure S11. ^{13}C NMR of 1-propargyl-3-methylimidazolium 1-ammonio-closo-dodecaborate (**5**)

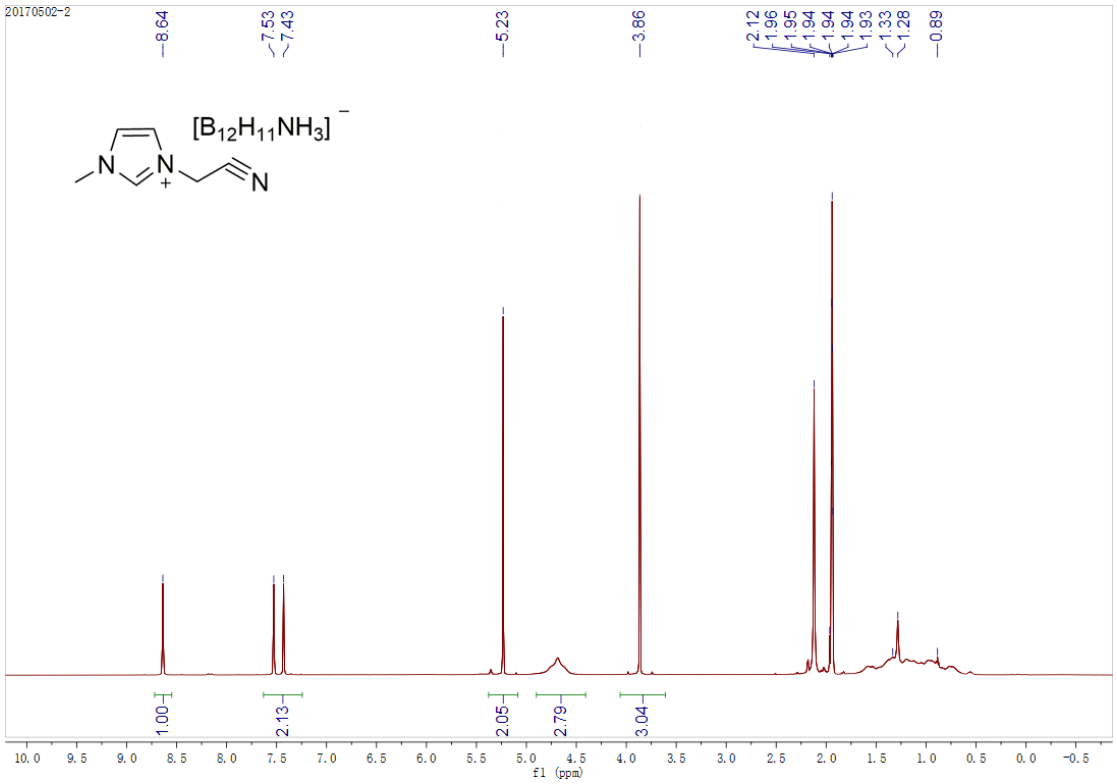


Figure S12. ^{1}H NMR of 1-cyanomethyl-3-methylimidazolium 1-ammonio-closo-dodecaborate (**6**)

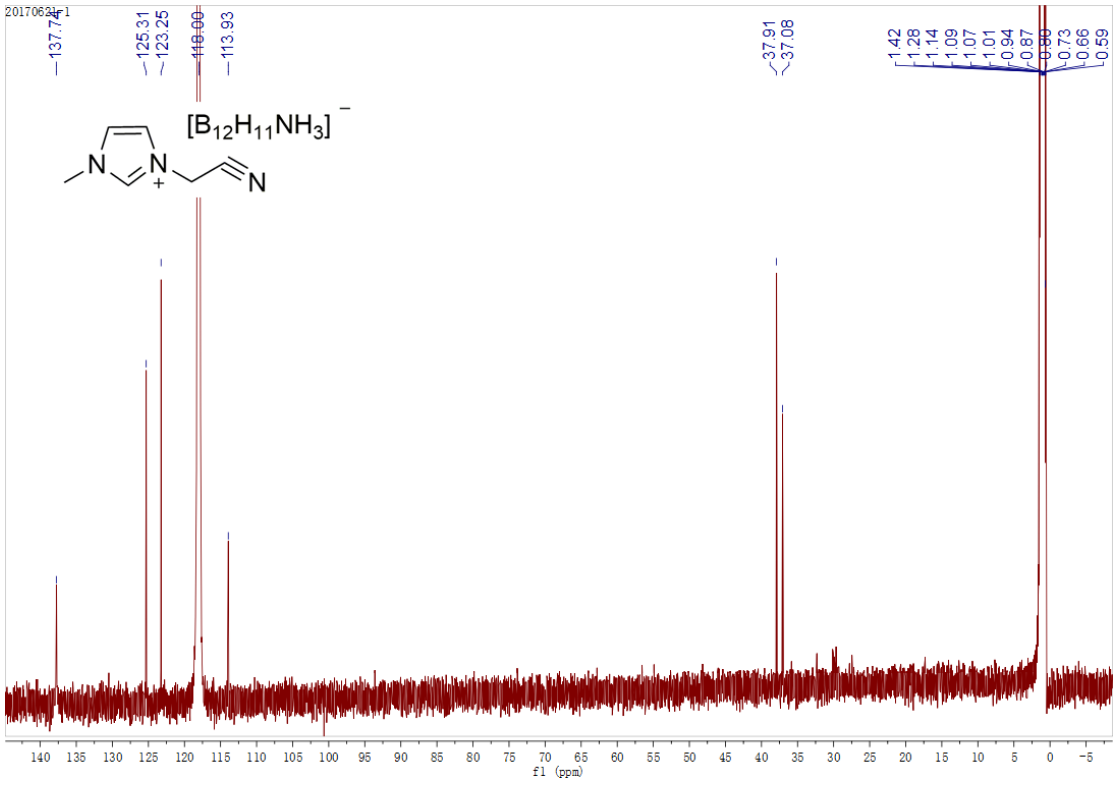


Figure S13. ^{13}C NMR of 1-cyanomethyl-3-methylimidazolium 1-ammonio-closo-dodecaborate (**6**)

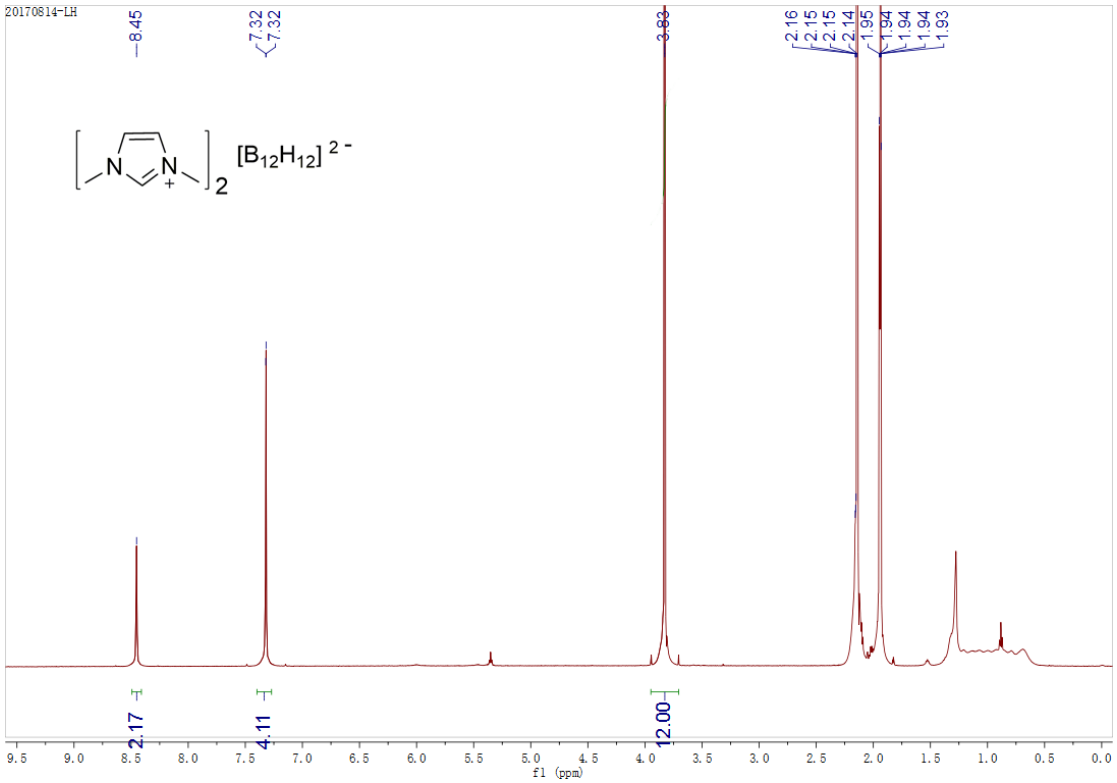


Figure S14. ^{1}H NMR of 1, 3-dimethylimidazolium dodecaborate (**1'**)

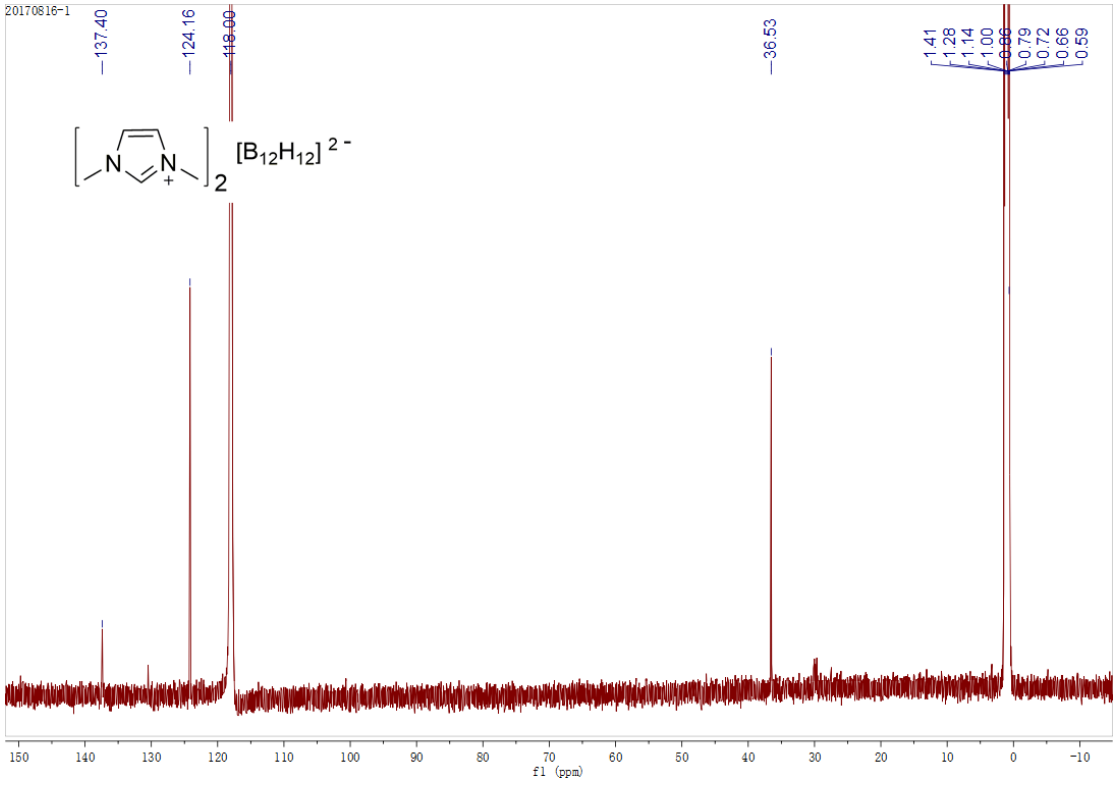


Figure S15. ^{13}C NMR of 1, 3-dimethylimidazolium dodecaborate (**1'**)