

Electronic Supplementary Information

Bis(borano)hypophosphite-Based Ionic Liquids as Ultrafast-Igniting Hypergolic Fuels

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1. General information

1) Materials

Ionic liquid precursors 1-ethyl-3-methylimidazolium chloride, 1-allyl-3-methylimidazolium chloride, 1-propargyl-3-methylimidazolium bromide, were synthesized according to the reported methods.¹ 1-allyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium bromide, 1-amino-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium chloride and corresponding triaminocyclopropenium cation-based compounds were synthesized according to the reported method respectively.²⁻⁴ Sodium bis(borano)hypophosphite salt was synthesized according to the reported method.⁵ 3-Bromopropyne (99 %) was purchased from *Energy Chemical*. Perchlorocycloprop-1-ene, trichlorophosphane were purchased from *Aladdin Industrial Inc.* Dimethylamine (2.0 M in THF), diethylamine (99.5 %), 1,1,2,2,3-pentachlorocyclopropane (90 %) and dipropylamine (99.5 %) were purchased from *J&K*. Other commercial reagents were used as received.

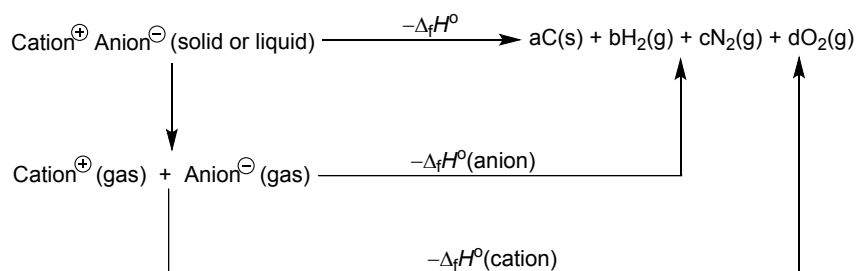
2) Product characterization

¹H and ¹³C NMR spectra were recorded on Bruker 600 AVANCE spectrometer (600 and 151 MHz, respectively) or Bruker 400 AVANCE spectrometer (400 and 101 MHz, respectively). IR spectra were performed on PerkinElmer Spectrum Two IR Spectrometers. High resolution mass spectra were performed on Shimadzu LCMS-IT-TOF mass spectrometer using electrospray ionization (ESI). Elemental analysis was performed on Flash EA-1112 elemental analyzer. Thermal property measurements were performed on TGA/DSC1 and DSC3 Mettler Toledo calorimeter equipped with auto cool accessory. Densities were measured on a Micromeritics Accupyc II 1340 gas pycnometer at 25 °C. Viscosity measurements were performed on a Brook field Rheometer DV3T at 25 °C. Ignition of ionic liquids with the oxidizer of WFNA and N₂O₄ were recorded with high speed camera Phantom v611 and Phantom v1, respectively.

3) Computational methods

Computational methods for heats of formation

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs.⁶ For all of the new ionic liquids, geometric optimization and frequency analyses were completed by using the B3LYP functional with the 6-31+G** basis set.⁷ Single energy points were calculated at the MP2/6-311 + +G** level of theory. For all of the compounds, the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. Heats of formation (HOF, $\Delta_f H^\circ$) of all of the ionic liquids were calculated based on a Born–Haber energy cycle (Scheme S1).



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

For all the ionic salts, calculation of the HOFs was simplified by using Equation (2),⁸ in which ΔH_L is the lattice energy of the ionic salts.

$$\Delta_f H^\circ (\text{ionic salts, 298K}) = \Sigma \Delta_f H^\circ (\text{cation, 298K}) + \Sigma \Delta_f H^\circ (\text{anion, 298K}) - \Delta H_L \quad (2)$$

For 1:1 salts, and considering the nonlinear nature of the cations and anion used, ΔH_L (in kJ/mol) was predicted by using Equation (3), as suggested by Jenkins et al.,⁹ in which n_M and n_X depended on the nature of ions Mp^+ and Xq^- , respectively, and had a value of 6 for nonlinear polyatomic ions.

$$\Delta H_L = U_{\text{POT}} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (3)$$

The lattice-potential energy (U_{POT}) was calculated according to Equation (4),¹⁰ in which ρ_m is the density (in $\text{g}\cdot\text{cm}^{-3}$) and M_m is the chemical formula mass of the ionic material.


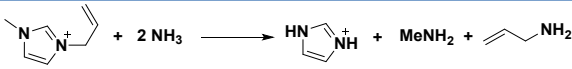

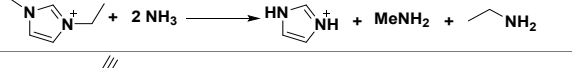

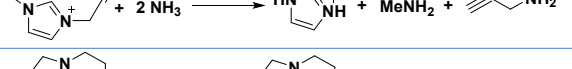
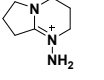
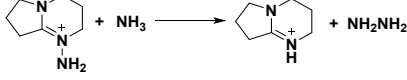

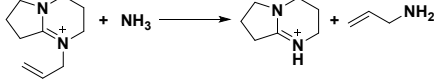

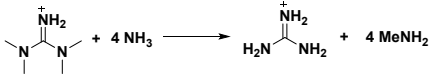

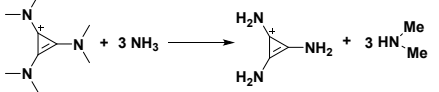
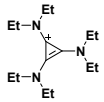
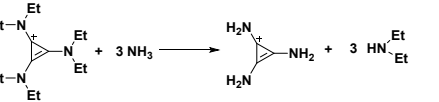
$$U_{\text{POT}} (\text{kJ/mol}) = 1981.2(\rho_m/M_m)^{1/3} + 103.8 \quad (4)$$

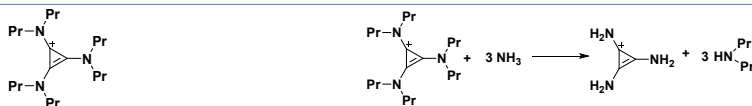
$$\Delta_f H_{(\text{g})\text{C}^{+\circ}} = \Delta_f H_{(\text{g})\text{C}^\circ} + \text{IE}_C \quad (5)$$

$$\Delta_f H_{(\text{g})\text{A}^{-\circ}} = \Delta_f H_{(\text{g})\text{A}^\circ} + \text{EA}_A \quad (6)$$

The heats of formation (HOFs) of the ionic salts were obtained by computing the component cations and anions. Specifically, the computation of HOFs for both the cations and anions was performed according to literature methods,¹¹ that is, the gas-phase HOFs of the ions were determined by using Equations (5) and (6) (IE=ionization energy; EA=electron affinity). In Equations (5) and (6), additional calculations for the corresponding neutral molecules ($\Delta_f H_{(\text{g})\text{C}^\circ}$ and $\Delta_f H_{(\text{g})\text{A}^\circ}$) were performed for the atomization reaction $\text{C}_a\text{H}_b\text{N}_c\text{O}_d\text{B}_e \rightarrow a\text{C}(\text{g}) + b\text{H}(\text{g}) + c\text{N}(\text{g}) + d\text{O}(\text{g}) + e\text{B}(\text{g})$ by using G2 theory. Based on the results from Equation (5), the HOFs of the cations were obtained by using isodesmic reactions (Table S1).

Table S1. Isodesmic reactions for the HOFs calculation of nine cations

Cation	Isodesmic reaction
	
	
	
	
	
	
	
	



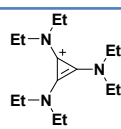
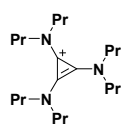
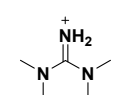
The enthalpy of reaction ($\Delta_r H^\circ_{298}$) is obtained by combining the MP2/6-311++G** energy difference for the reaction, the scaled zero-point energies, and other thermal factors. As a result the heats of formation of all new ionic liquids could be readily extracted.

Table S2. Enthalpies of the gas-phase species of cations and anions (based on G2 method)

ions	$\Delta_f H^\circ$ (kJ/mol)
	559.69
	726.96
	859.59
	526.49
	573.23
$[\text{BH}_3\text{PH}_2\text{BH}_3]^-$	-364.13

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

Cation	E(MP2) ^a	ZPE ^b	TCH ^c	ΔH_{corr}	$\Delta_f H^{\text{od}}$ (kJ/mol)
	-438.0124274	0.218346	0.228698	-437.79	647.57
	-499.1924874	0.263392	0.275958	-498.93	626.73
	-343.6051442	0.169082	0.178438	-343.43	628.55
	-380.3394968	0.149799	0.159714	-380.19	932.70
	-381.5792243	0.173896	0.184048	-381.4	747.87
	-213.5417828	0.163888	0.171482	-213.38	526.49
	-516.3251197	0.266548	0.284141	-516.05	824.27

	-751.5288101	0.437909	0.462494	-751.08	632.47
	-986.7130517	0.608357	0.641292	-986.1	479.29
	-362.015649	0.20200	0.213478	-361.81	539.78

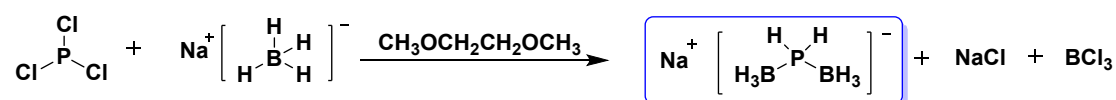
^aTotal energy calculated by B3LYP/6-31+G**//MP2/6-311++G** method (Hartree/Particle); ^bzero-point correction (Hartree/Particle); ^cthermal correction to enthalpy (Hartree/Particle); ^dheat of formation (kJ/mol).

Table S4. The calculated enthalpies of ten new ionic liquids

HILs	$\Delta_f H^\circ$ cation(kJ/mol)	$\Delta_f H^\circ$ anion(kJ/mol)	U_{pot} (kJ/mol)	ΔH_{Lat} (kJ/mol)	$\Delta_f H^\circ$ salt(kJ/mol)
1	526.4883	-364.127	479.61	484.57	-322.20
2	747.8708	-364.127	441.94	446.90	-63.15
3	628.5502	-364.127	447.89	452.85	-188.43
4	932.6973	-364.127	446.60	451.56	117.01
5	647.5729	-364.127	439.10	444.05	-160.61
6	626.7266	-364.127	426.41	431.37	-168.77
7	549.2743	-364.127	443.56	448.52	-263.37
8	824.2676	-364.127	423.50	428.45	31.69
9	632.4707	-364.127	390.53	395.49	-127.14
10	479.2898	-364.127	367.62	372.58	-257.41

2. Synthesis of hypergolic ionic liquids

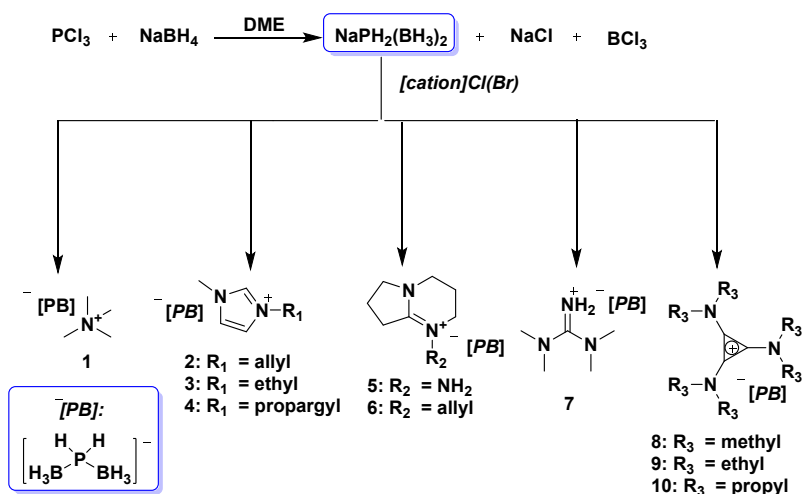
1) Synthesis of Na[BH₃PH₂BH₃].



A solution of PCl₃ (9.44 g, 68.8 mmol, 1 equiv) in dry DME (90 mL) was added via cannula to a vigorously stirred solution of NaBH₄ (10.40 g, 274.8 mmol, 4 equiv) in dry DME (120 mL) which was cooled to -60°C. Then, the solution was allowed to warm to room temperature while being stirred over 5 hours. The reaction mixture was then stirred for 12 h. After the reaction, solvent and any other volatile materials were removed on a vacuum to give a white residue. This residue was then extracted with Et₂O (3 × 100 mL portions) and filtered to obtain a clear, colorless filtrate free of precipitate. Upon evaporation of the filtrate under reduced pressure, a white solid was obtained. The white solid was heating to 45 °C at 3 Torr for 10 hours to remove the residue DME. Then the solid was dissolved into dry THF, after filtering the insoluble solid and evaporating THF, pure

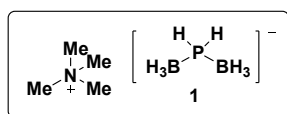
Na[BH₃PH₂BH₃] was obtained as a white solid (60 % yield). ¹H NMR (600 MHz, DMSO-*d*₆): δ 2.77 (d of septet, ¹J_{P-H} = 288 Hz, ³J_{H-H} = 7 Hz, 2H), 0.39 (m, 6H).

2) Synthesis of bis(borano)hypophosphite-based hypergolic ionic liquids.



Scheme S2. Synthesis of new bis(borano)hypophosphite-based hypergolic ionic liquids

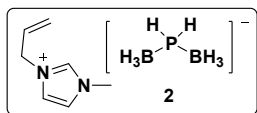
Synthesis of salt 1



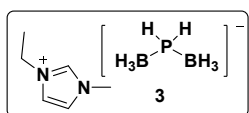
To a 100 mL flask was added 1.09 g tetramethylammonium chloride (10 mmol) and 40 mL methanol, and then 0.837 g Na[BH₃PH₂BH₃] (10 mmol) was added subsequently into the solution. The resulting solution was stirred at room temperature for 3 hours. After filtration, methanol was removed under vacuum. The salt **1** was obtained as a white solid. Yield 80 %; m.p.: 214°C(dec.); ¹H NMR (600 MHz, CD₃CN): δ ppm: -0.00-0.48 (m, 6H, BH₃), 2.42 (hept, 1H, PH), 2.86-2.91 (m, 13H, PH and CH₃); ¹³C NMR (151 MHz, CD₃CN): δ ppm: 55.85; IR (KBr): γ 2377, 2337, 2317, 2259, 1484, 1411, 1140, 1064, 947, 893, 615; ESI-HRMS: *m/z* calcd for cation C₄H₁₂N[M]⁺: 74.0964; found: 74.0968; anion calcd for B₂H₈P [M]⁻: 61.0555, found: 61.0557; elemental analysis calcd (%) for C₄H₂₀B₂NP (134.80): C 35.64, H 14.95, N 10.39; found: C 35.37, H 15.10, N 10.29.

Synthesis of HILs 2-4

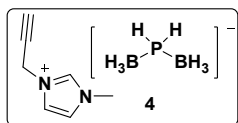
1.64 g 1-methyl-1H-imidazole (20 mmol) was dissolved in 50 mL CH₂Cl₂ at room temperature, and then 3.06 g allyl chloride (40 mmol) was slowly added into the solution. The resulting solution was stirred at room temperature for 1 day. After removing the solvent and any other volatile materials on a vacuum, the resulting residue was mixed with 50 mL CH₂Cl₂ at room temperature and then 1.69 g Na[BH₃PH₂BH₃] (20.2 mmol) was added. The reaction was stirred for 3 days, then the insoluble solid was filtrated and the solvent was evaporated, a viscous liquid was obtained. The liquid was mixed with pure water, then mixture was extracted with CH₂Cl₂ (5×30 mL). After drying the resulted solution with anhydrous Na₂SO₄ and evaporating the solvent, ionic liquid **2** was obtained as a colorless liquid in a yield of 83 %. Ionic liquid **3**, **4** can be readily synthesized via the same procedure. HILs **2-4** are viscous liquid with high yields of 80-85 %.



HIL 2 : colorless liquid, 83 % yield; ^1H NMR (600 MHz, CD_3CN): δ ppm: 0.00-0.48 (m, 6H, BH_3), 2.42 (hept, 1H, PH), 2.91 (hept, 1H, PH), 3.66 (s, 3H, CH_3), 4.57 (d, 2H, CH_2), 5.21 (dd, 2H, CH_2), 5.83 (ddt, 1H, CH), 7.16-7.19 (m, 2H, CH), 8.27 (s, 1H, CH); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 136.53, 131.23, 124.38, 122.86, 121.35, 52.01, 36.56; IR (KBr): γ 3148, 3111, 2380, 2359, 1573, 1165, 1063, 887, 751, 622; ESI-HRMS: m/z calcd for cation $\text{C}_7\text{H}_{11}\text{N}_2[\text{M}]^+$: 123.0917; found: 123.0922. anion calcd for $\text{B}_2\text{H}_8\text{P}[\text{M}]^-$: 61.0555, found: 61.0557; elemental analysis calcd (%) for $\text{C}_7\text{H}_{10}\text{B}_2\text{N}_2\text{P}$ (183.84): C 45.73, H 10.42, N 15.24; found: C 45.53, H 10.51, N 15.15.

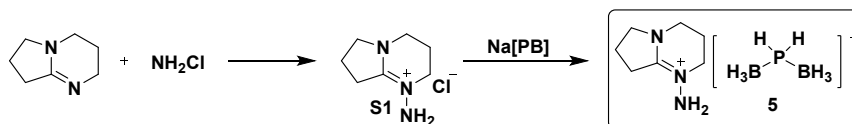


HIL 3 : colorless liquid, 85 % yield; ^1H NMR (600 MHz, CD_3CN): δ ppm: 0.21-0.69 (m, 6H, BH_3), 1.48 (t, 3H, CH_3), 2.63 (hept, 1H, PH), 3.12 (hept, 1H, PH), 3.86 (s, 3H, CH_3), 4.21 (q, 2H, CH_2), 7.37 (dd, 1H, CH), 7.43 (dd, 1H, CH), 8.50 (s, 1H, CH); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 136.11, 124.13, 122.48, 45.37, 36.43, 15.04; IR (KBr): γ 3151, 3113, 2379, 2356, 2291, 1571, 1169, 1063, 888, 621; ESI-HRMS: m/z calcd for cation $\text{C}_6\text{H}_{11}\text{N}_2[\text{M}]^+$: 111.0917; found: 111.0915; anion calcd for $\text{B}_2\text{H}_8\text{P}[\text{M}]^-$: 61.0555, found: 61.0557; elemental analysis calcd (%) for $\text{C}_6\text{H}_{10}\text{B}_2\text{N}_2\text{P}$ (171.83): C 41.94, H 11.15, N 16.30, found: C 41.73, H 11.24, N 16.19.



HIL 4 : slight yellow liquid, 80 % yield; ^1H NMR (600 MHz, CD_3CN): δ ppm: -0.01-0.47 (m, 6H, BH_3), 2.41 (hept, 1H, PH), 2.84 (t, 1H, CH), 2.90 (hept, 1H, PH), 3.66 (s, 3H, CH_3), 4.81 (d, 2H, CH_2), 7.20 (dd, 1H, CH), 7.28 (dd, 1H, CH), 8.40 (s, 1H, CH); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 136.58, 124.69, 122.63, 78.07, 74.95, 39.72, 36.74; IR (KBr): γ 3258, 3149, 3113, 2363, 1572, 1163, 1063, 888, 746, 621; ESI-HRMS: m/z calcd for cation $\text{C}_7\text{H}_9\text{N}_2[\text{M}]^+$: 121.0760; found: 121.0759; anion calcd for $\text{B}_2\text{H}_8\text{P}[\text{M}]^-$: 61.0555, found: 61.0557; elemental analysis calcd (%) for $\text{C}_7\text{H}_{17}\text{B}_2\text{N}_2\text{P}$ (181.82): C 46.24, H 9.42, N 15.41, found: C 46.01, H 9.51, N 15.31.

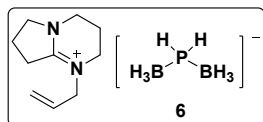
Synthesis of HIL 5



3.72 g 2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidine (30 mmol) was dissolved in 50 mL THF at 0 °C, and then NH_2Cl (1.1 eq 30 mmol) in 30 mL ether was slowly added into the solution over 1.5 hour. The resulting suspension was stirred at 0 °C for another 4 h. The mixture was filtrated and a white solid **S1** was obtained. 3.51g **S1** (20 mmol) was dissolved in CH_2Cl_2 at room temperature and then 1.69 g $\text{Na}[\text{BH}_3\text{PH}_2\text{BH}_3]$ (20.2 mmol) was added. The reaction was stirred for 3 days, then the insoluble solid was filtrated and the solvent was evaporated, a viscous liquid was obtained. The liquid was dissolved into pure water and the solution was extracted with CH_2Cl_2 (7×30mL). After drying the resulted solution with anhydrous Na_2SO_4 and evaporating the solvent, ionic liquid **5** was obtained as a colorless liquid in a yield of 75 %. ^1H NMR (600 MHz, CD_3CN): δ ppm: 0.22-0.68 (m, 6H, BH_3), 2.06-2.13 (m, 4H, CH_2), 2.63 (hept, 1H, PH), 3.03 (t,

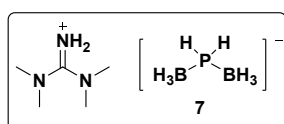
2H, CH₂), 3.12 (hept, 1H, PH), 3.31 (t, 2H, CH₂), 3.53 (t, 2H, CH₂), 3.69-3.72 (m, 2H, CH₂), 4.68 (s, 2H, NH₂); ¹³C NMR (151 MHz, CD₃CN): δ ppm: 167.72, 55.06, 50.58, 42.02, 31.02, 19.85, 18.31; IR (KBr): γ 3316, 2355, 1699, 1614, 1530, 1384, 1310, 1225, 1112, 1062, 886; ESI-HRMS: *m/z* calcd for cation C₇H₁₄N₃[M]⁺: 140.1182 ; found: 140.1183; anion calcd for B₂H₈P [M]⁻: 61.0555, found: 61.0557; elemental analysis calcd (%) for C₇H₂₂B₂N₃P (200.87): C 41.86, H 11.04, N 20.92, found: 41.65, H 11.14, N 20.76.

Synthesis of HIL 6



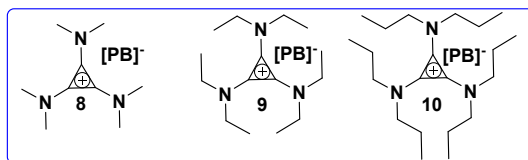
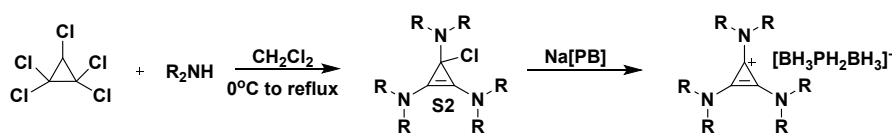
2.48 g 2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidine (20 mmol) was dissolved in 50 mL CH₂Cl₂ at 0°C, and then 4.84 g allyl bromide (40 mmol) was slowly added into the solution over 1 hour. The resulting solution was stirred at room temperature for 24 h. After the reaction, solvent and any other volatile materials were removed on a vacuum. The resulting residue was mixed with 50 mL CH₂Cl₂ at room temperature and then 1.69 g Na[BH₃PH₂BH₃] (20.2 mmol) was added. The reaction was stirred for 3 days, then the insoluble solid was filtrated and the solvent was evaporated, a viscous liquid was obtained. The liquid was dissolved into pure water and the solution was extracted with CH₂Cl₂ (6×30 mL). After drying the organic phase with anhydrous Na₂SO₄ and evaporating the solvent, ionic liquid **6** was obtained as a slight yellow liquid in a yield of 78 %. ¹H NMR (600 MHz, CD₃CN): δ ppm: -0.01-0.47 (m, 6H, BH₃), 1.83-1.87 (m, 2H, CH₂), 1.92-1.95 (m, 2H, CH₂), 2.41 (hept, 1H, PH), 2.74 (t, 2H, CH₂), 2.90 (hept, 1H, PH), 3.12-3.19 (m, 4H, CH₂), 3.47-3.50 (m, 2H, CH₂), 3.80 (dt, 2H, CH₂), 5.08-5.14 (m, 2H, CH₂), 5.65 (ddt, 1H, CH); ¹³C NMR (151 MHz, CD₃CN): δ ppm: 165.29, 131.28, 119.05, 55.38, 54.75, 44.94, 42.68, 30.67, 19.20, 18.3; IR (KBr): γ 2948, 2883, 2351, 1668, 1539, 1445, 1421, 1313, 1061, 886; ESI-HRMS: *m/z* calcd for cation C₁₀H₁₇N₂[M]⁺: 165.1386; found: 165.1383; anion calcd for B₂H₈P [M]⁻: 61.0555, found: 61.0557; elemental analysis calcd (%) for C₁₀H₂₅B₂N₂P (225.92): C 53.17, H 11.15, N 12.40, found: C 52.76, H 11.24, N 12.29.

Synthesis of HIL 7

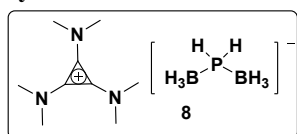


3.03 g bis(dimethylamino)methaniminium chloride (20 mmol) was dissolved in 50 mL CH₂Cl₂ at room temperature and then 1.69 g Na[BH₃PH₂BH₃] (20.2 mmol) was added. The reaction was stirred for 3 days, then the insoluble solid was filtrated and the solvent was evaporated, a viscous liquid was obtained. The liquid was dissolved into pure water and the solution was extracted with CH₂Cl₂ (6×30mL). After drying the organic phase with anhydrous Na₂SO₄ and evaporating the solvent, ionic liquid **7** was obtained as a colorless liquid in a yield of 76 %; m.p.: 25 °C; ¹H NMR (600 MHz, CD₃CN): δ ppm: -0.01-0.47 (m, 6H, BH₃), 2.41 (hept, 1H, PH), 2.72 (s, 12H, CH₃), 2.90 (hept, 1H, PH), 5.95 (s, 12H, NH₂); ¹³C NMR (151 MHz, CD₃CN): δ ppm: 161.74, 39.80; IR (KBr): γ 3335, 3234, 2367, 1641, 1614, 1560, 1411, 1063, 1040, 888; ESI-HRMS: *m/z* calcd for cation C₅H₁₄N₃[M]⁺: 116.1182; found: 116.1181. anion calcd for B₂H₈P [M]⁻: 61.0555, found: 61.0557; elemental analysis calcd (%) for C₅H₂₂B₂N₃P (176.85): C 33.96, H 12.54, N 23.76, found: C 33.82, H 12.66, N 23.58.

Synthesis of HILs 8-10

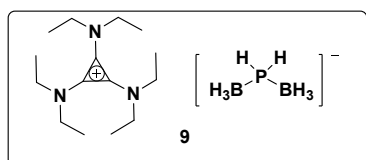


Synthesis of HIL 8



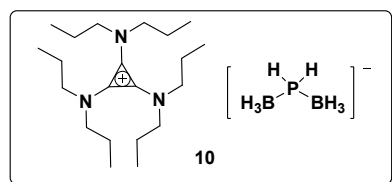
5.15 g 1,1,2,2,3-pentachlorocyclopropane (30 mmol) was dissolved in 100mL CH_2Cl_2 at 0 °C under N_2 , 12 mL dimethylamine (2 M, THF solution) was added droplet over 1 hour. The mixture was stirred at 0 °C for another 4 hours, and then the reaction was continued at room temperature for 18 hours then heat to reflux for about 5 hours. After cooling to room temperature, the mixture was poured into 200 mL acetone and white solid precipitated. After filtrating the solid and evaporating the solvent, the residue was dissolved in water, and then washed with ether ($4 \times 10\text{mL}$). The solvent was evaporated to obtain a yellow solid **S2** in 81 % yield. 4.07 g **S2** (20 mmol) was suspended in 50 mL CH_2Cl_2 at room temperature and then 1.69 g $\text{Na}[\text{BH}_3\text{PH}_2\text{BH}_3]$ (20.2 mmol) was added into the mixture. The reaction was stirred for 3 days, then the insoluble solid was filtrated and the solvent was evaporated, a yellow solid was obtained. The solid was mixed with pure water and the mixture was extracted with CH_2Cl_2 ($5 \times 30\text{mL}$). After drying the resulted solution with anhydrous Na_2SO_4 and evaporating the solvent, ionic liquid **8** was obtained as a yellow solid in a yield of 75 %; m.p.: 62 °C ^1H NMR (600 MHz, CD_3CN): δ ppm: 0.00-0.48 (m, 6H, BH_3), 2.42 (hept, 1H, PH), 2.78-3.02 (m, 19H, PH and CH_3); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 118.43, 42.35; IR (KBr): γ 2927, 2340, 1554, 1398, 1222, 1058, 1027, 885, 785; ESI-HRMS: m/z calcd for cation $\text{C}_9\text{H}_{18}\text{N}_3[\text{M}]^+$: 168.1495; found: 168.1491; anion calcd for $\text{B}_2\text{H}_8\text{P}[\text{M}]^-$: 61.0555, found: 61.0557; elemental analysis calcd (%) for $\text{C}_9\text{H}_{26}\text{B}_2\text{N}_3\text{P}$ (228.92): C 47.22, H 11.45, N 18.36, found: C 46.95, H 11.57, N 18.21.

The same procedure as that described above for the synthesis and purification of ionic liquid **8** was used for the syntheses of other HILs **9** and **10**.



HIL 9 : yellow solid, 85 % yield; m.p.: 38°C; ^1H NMR (600 MHz, CD_3CN): δ ppm: -0.01-0.47 (m, 6H, BH_3), 1.03 (t, 18H, CH_3), 2.40 (hept, 1H, PH), 2.88 (hept, 1H, PH), 3.18 (q, 12H, CH_2); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 117.02, 47.22, 14.05; IR (KBr): γ 2978, 2357, 1539, 1439, 1385, 1359, 1297, 1222, 1184, 1056, 972, 886; ESI-HRMS: m/z calcd for cation $\text{C}_{15}\text{H}_{30}\text{N}_3[\text{M}]^+$: 252.2434; found: 252.2437. anion calcd for $\text{B}_2\text{H}_8\text{P}[\text{M}]^-$: 61.0555, found: 61.0557; elemental

analysis calcd (%) for $C_{15}H_{38}B_2N_3P$ (313.08): C 57.55, H 12.23, N 13.42, found: C 57.24, H 12.36, N 13.33.



HIL 10 : pale yellow solid, 82 % yield; m.p.: 43°C; 1H NMR (600 MHz, CD_3CN): δ ppm: -0.01-0.47 (m, 6H, BH_3), 0.72 (t, 18H, CH_3), 1.41-1.49 (m, 12H, CH_2), 2.40 (hept, 1H, PH), 2.88 (hept, 1H, PH), 3.03-3.08 (m, 12H, CH_2); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 117.30, 54.56, 22.23, 10.63; IR (KBr): γ 2965, 2935, 2875, 2351, 1521, 1468, 1431, 1365, 1265, 1055, 887, 809; ESI-HRMS: m/z calcd for cation $C_{21}H_{42}N_3[M]^+$: 336.3373; found: 336.3369; anion calcd for $B_2H_8P[M]^-$: 61.0555, found: 61.0557; elemental analysis calcd (%) for $C_{21}H_{50}B_2N_3P$ (397.25): C 63.49, H 12.69, N 10.58, found: C 63.14, H 12.80, N 10.51.

3. Crystal structure data of salt 1

Table S5. Crystallographic data for ionic salt **1**

CCDC	1430389
Formula	$C_4H_{20}NPB_2$
<i>Mr</i>	134.80
crystal system	Monoclinic
space group	$P2_1/m$
<i>a</i> [Å]	6.1712(3) ^a
<i>b</i> [Å]	8.0425(5) ^a
<i>c</i> [Å]	10.4934(4) ^a
α [Å]	90.00
β [Å]	98.806(4) ^a
γ [Å]	90.00
<i>V</i> [Å ³]	514.67(4) ^a
<i>Z</i>	2
<i>T</i> [K]	293
ρ_{calcd} [Mg·m ⁻³]	0.870
<i>M</i> [mm ⁻¹]	1.752
<i>F</i> (000)	152.0
θ [°]	13.934 to 134.124
index range	$-7 \leq h \leq 4$ $-8 \leq k \leq 9$ $-12 \leq l \leq 12$
reflections collected	3019
independent reflections	997 [$R_{\text{int}} = 0.0307$, $R_{\text{sigma}} = 0.0267$]

data/restraints/parameters	997/0/67
GOF on F ²	1.094
R ₁ [I>2σ(I)]	0.0609
wR ₂ [I>2σ(I)]	0.1716
R ₁ (all data)	0.0668
wR ₂ (all data)	0.1810
largest diff. peak and hole [e Å ⁻³]	0.42/-0.17

^a The values in the parenthesis represent the estimated standard deviation of the data in term of accuracy on the last significant figure.

4. The standard deviation of ID times

Table S6. The standard deviation of ID time with WFNA^a

Test (ms) IL	1	2	3	4	5	6	Average value (SD) ^b
2	1.29	1	1.29	0.86	1.14	1.14	1.1 (0.2)
3	1.71	2.14	2	2	2.14	2.14	2.0 (0.2)
4	1	0.86	1	1.14	1.29	1	1.0 (0.1)
5	6.29	2	7.43	6	5.71	7.57	5.8 (2.0)
6	2.86	2.71	3.14	3.29	3.57	3.14	3.1 (0.3)
7	2	1.71	2.29	2	2.86	1.71	2.1 (0.4)
8	14.57	10.43	9.43	10.43	7	10	10.3 (2.4)
9	13.43	10.29	14.57	15	13.14	13	13.2 (1.7)
10	8	9.43	9.57	8.29	9	10.14	9.1 (0.8)

^a HILs 2-10: The standard deviation of ID time with WFNA was estimated. Each sample was recorded on average of six measurements. ^b The values into parenthesis represent standard deviation.

Table S7. The standard deviation of ID time with N₂O₄

Test (ms) IL	1	2	3	4	5	6	Average value (SD) ^b
2	15.57	20	16.43	10.43	13.86	12.86	14.9 (3.3)
3	18.57	26.43	17.43	16.86	19.29	18.57	19.5 (3.5)
4	400.29	371.29	454.57	385.43	535.29	379.57	421.1 (63.4)
5	345.14	448	294	261.14	396.57	315.14	343.3 (69.0)
6	403	303.14	319.14	397.14	354.43	334.57	351.9 (41.0)
7	283.43	385.57	413.71	409.71	394	353.57	373.3 (49.0)

^aHILs 2-7: The standard deviation of ID times with N₂O₄ was estimated. Each sample was recorded on average of six measurements. ^b The values into parenthesis represent standard deviation.

5. Hydrolysis study of hypergolic ionic liquids

Possible hydrolysis of the $\{BH_3\}$ moiety contained in the [PB] anion is particularly studied as the model reaction. The details can be concluded as below.

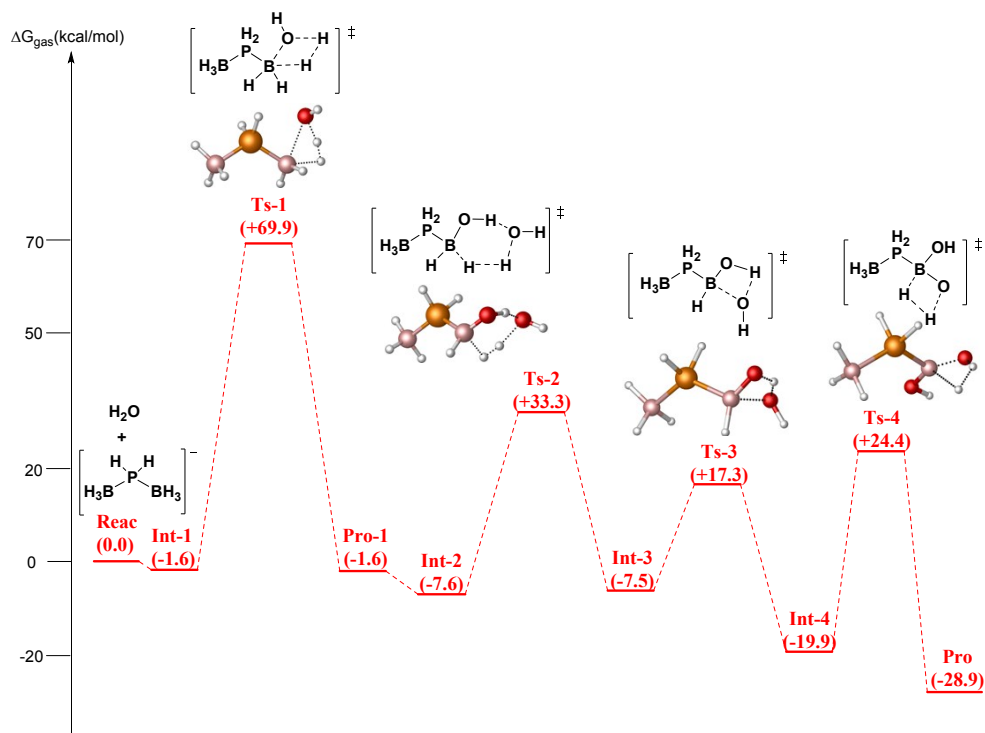


Figure S1. The energy barriers of four transition states for a reasonable hydrolysis mechanism.

When HIL **3** was dissolved and stored in deuterium oxide at room temperature for one month, no obviously chemical degradation could be observed from the ^1H NMR analysis except that the proton of C2 position on the imidazolium cation was exchanged by deuterium. The ^1H NMR spectral was given as below.

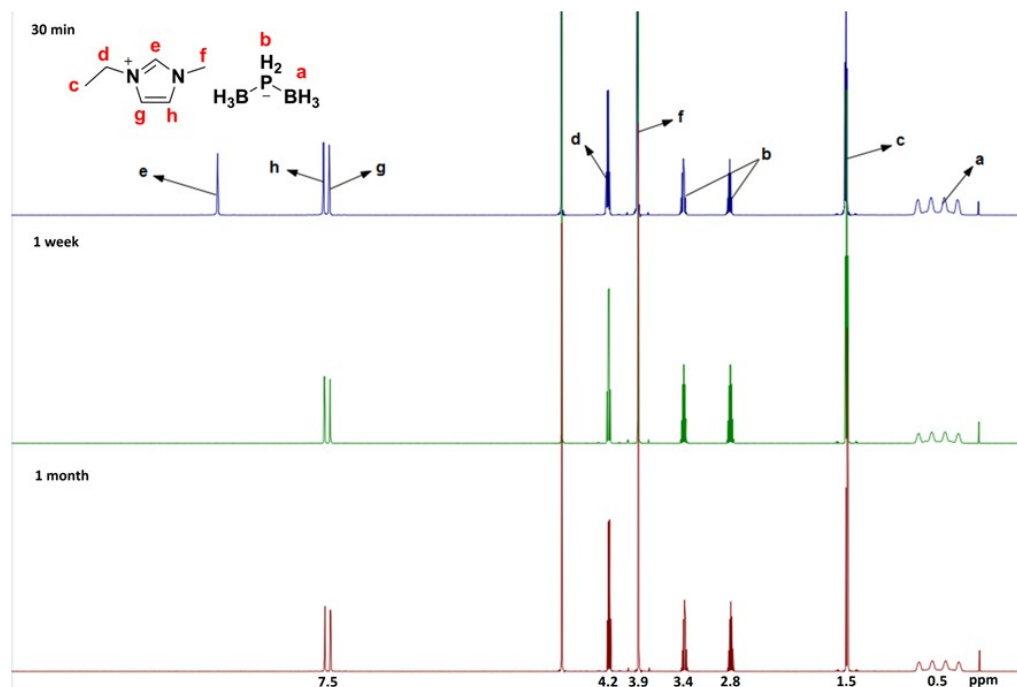
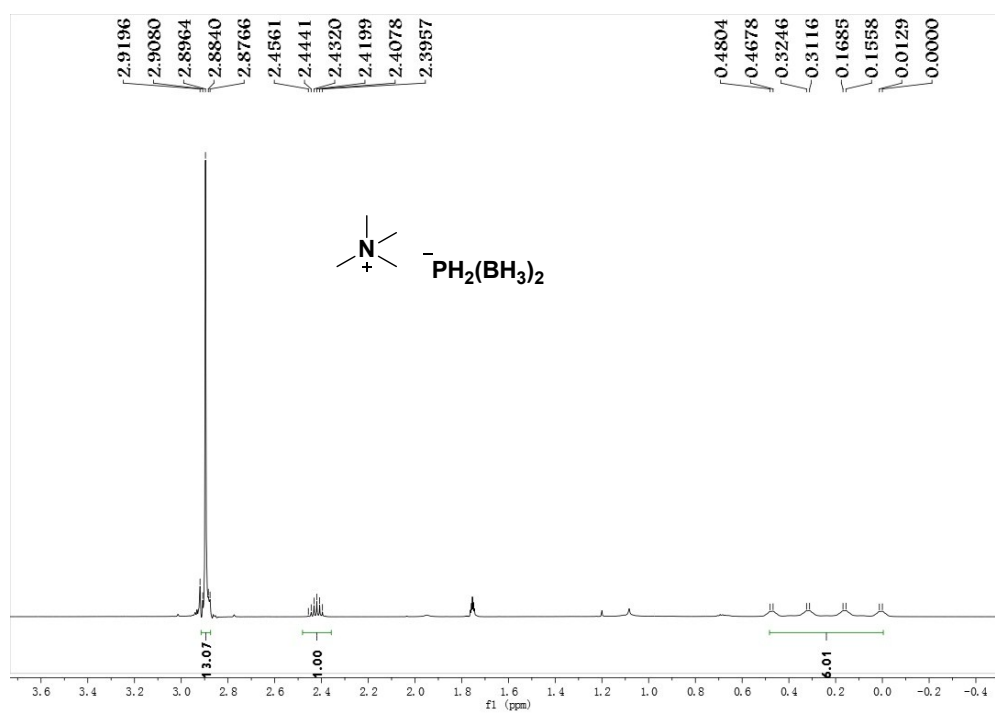


Figure S2. Water stability experiment of HIL **3** by ^1H NMR.

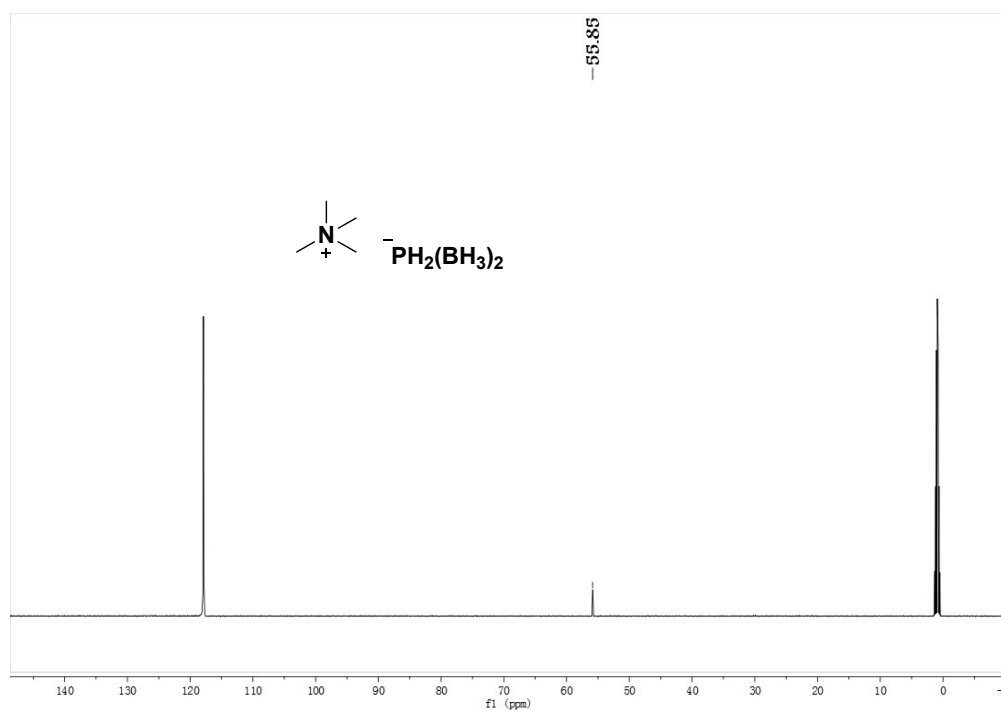
6. References

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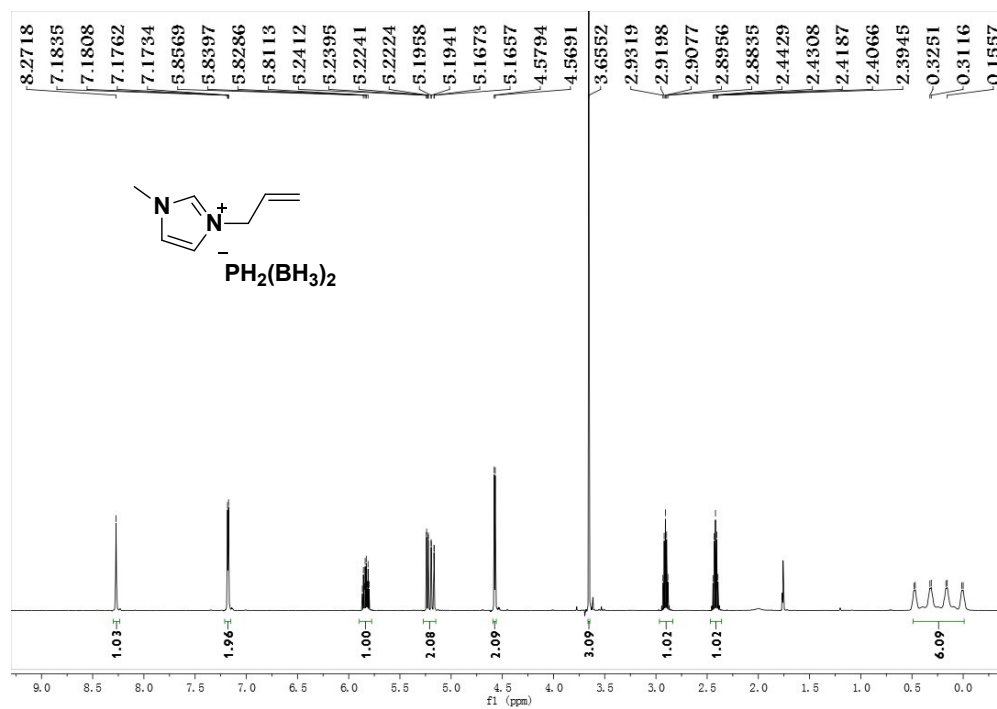
7. NMR Spectra



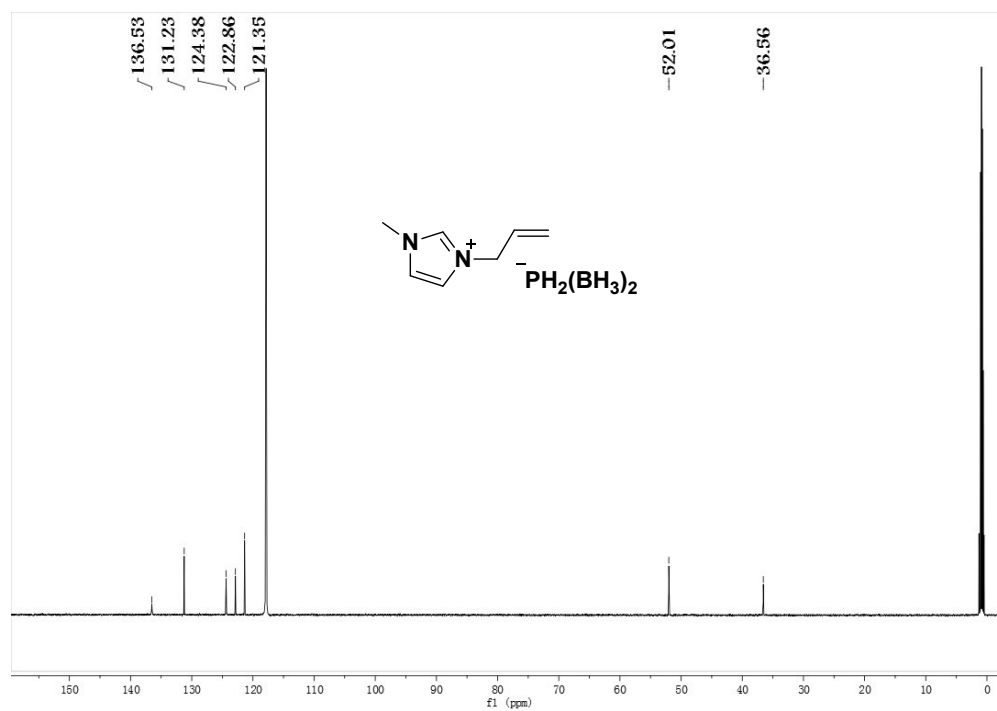
$^1\text{H-NMR}$ spectrum of salt **1**



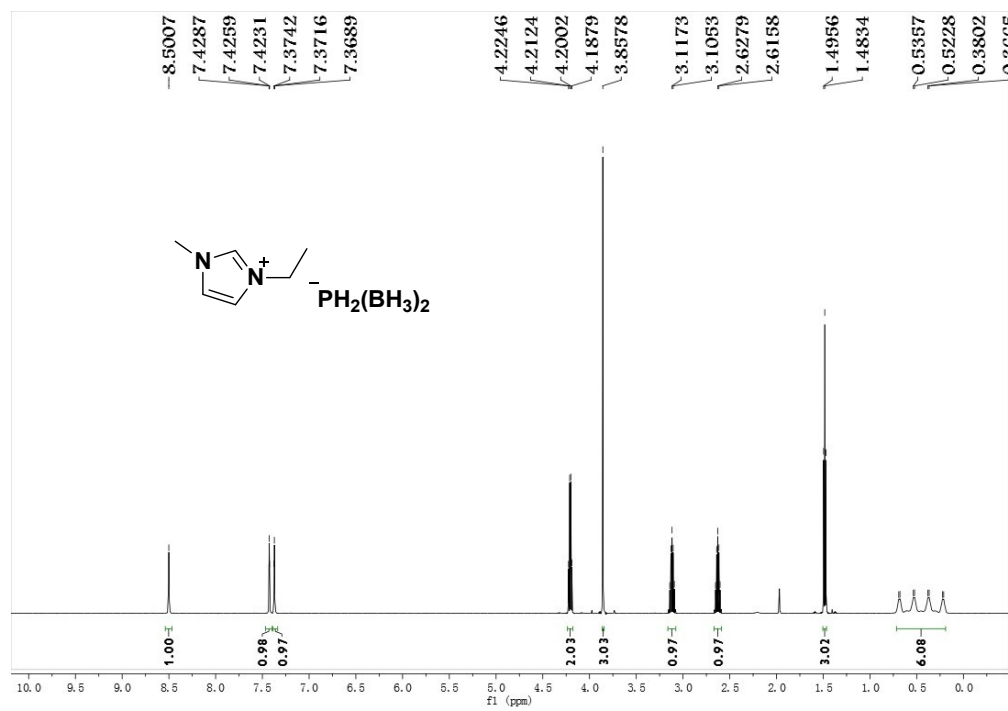
$^{13}\text{C-NMR}$ spectrum of salt **1**



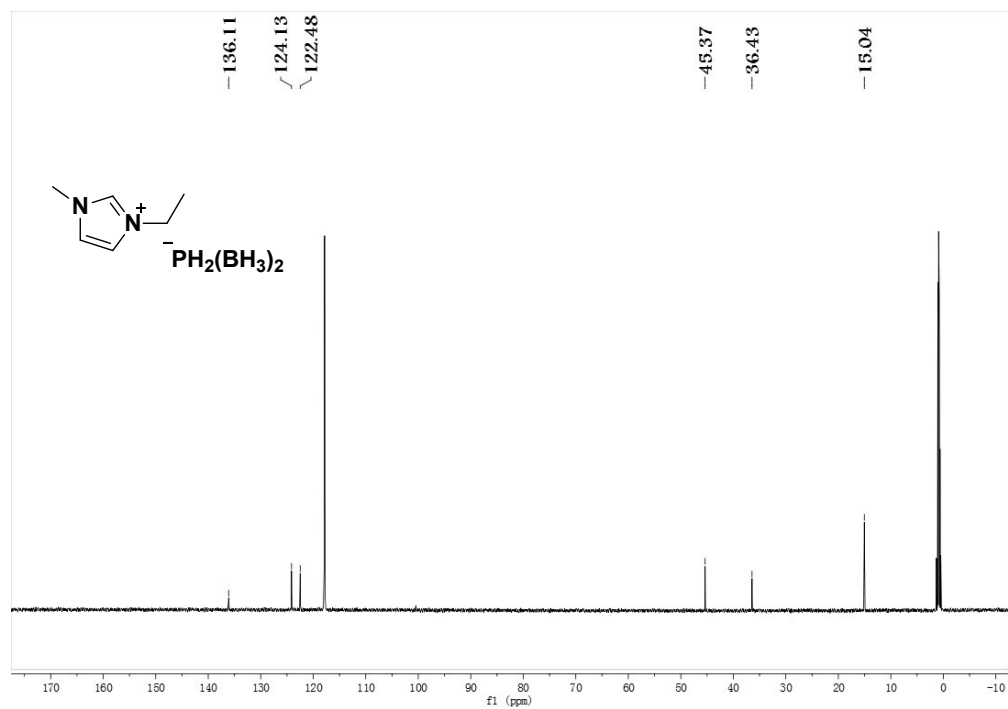
¹H-NMR spectrum of ionic liquid 2



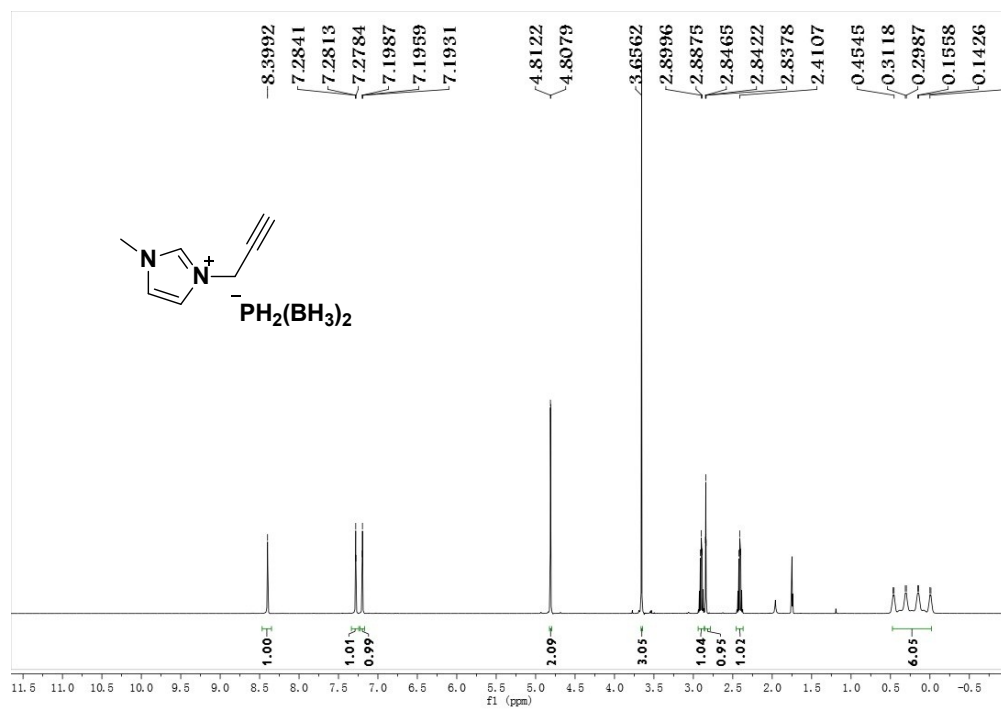
¹³C-NMR spectrum of ionic liquid 2



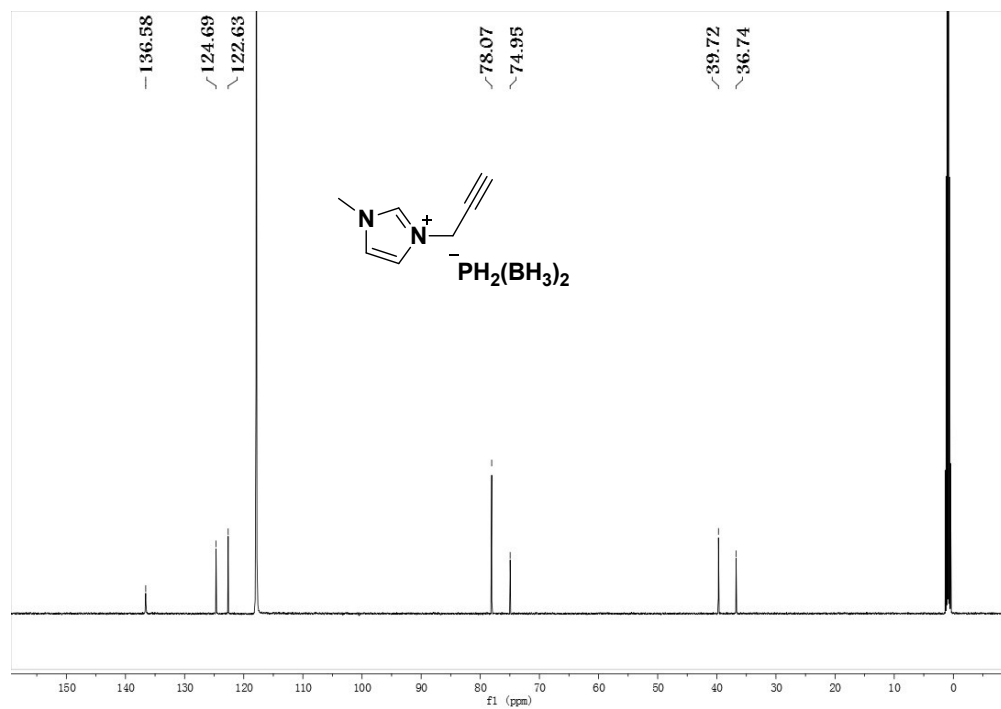
¹H-NMR spectrum of ionic liquid 3



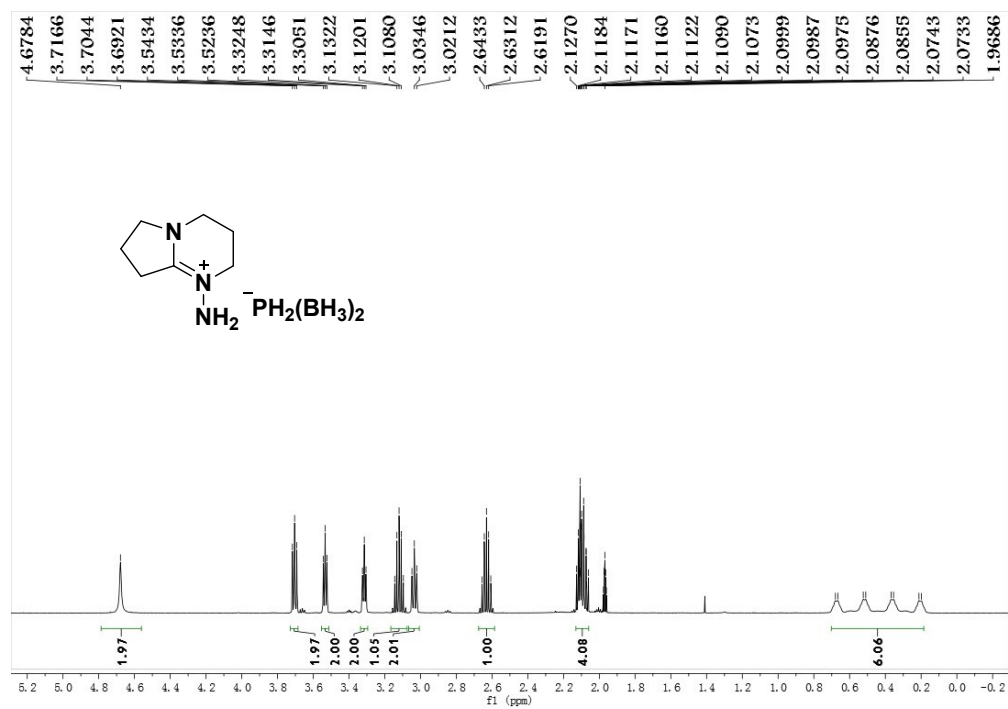
¹³C-NMR spectrum of ionic liquid 3



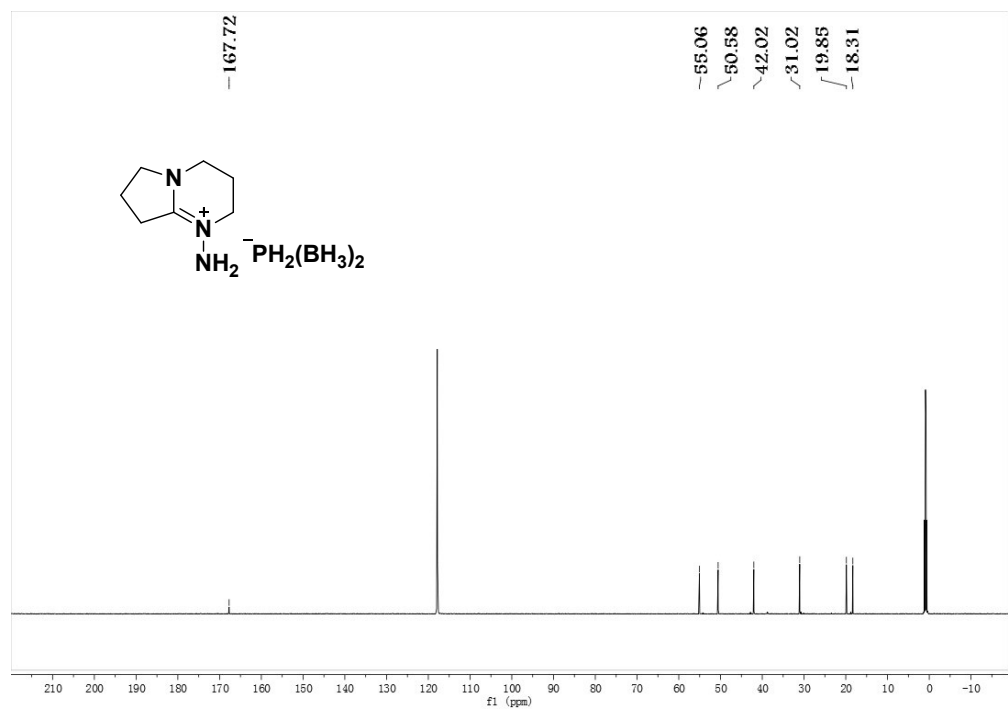
$^1\text{H-NMR}$ spectrum of ionic liquid **4**



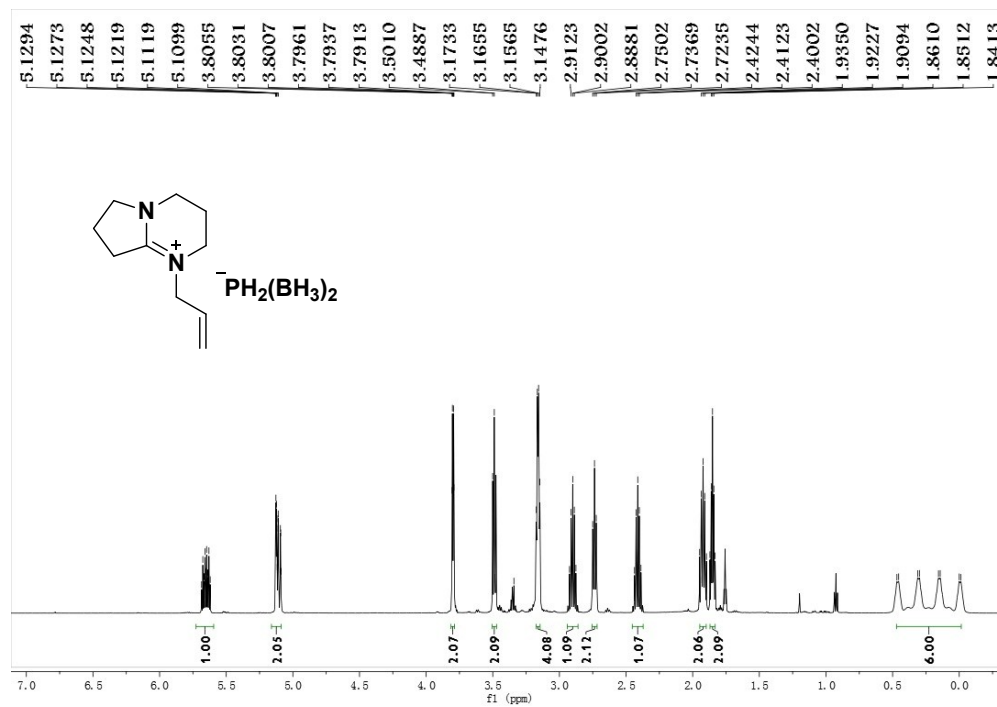
$^{13}\text{C-NMR}$ spectrum of ionic liquid **4**



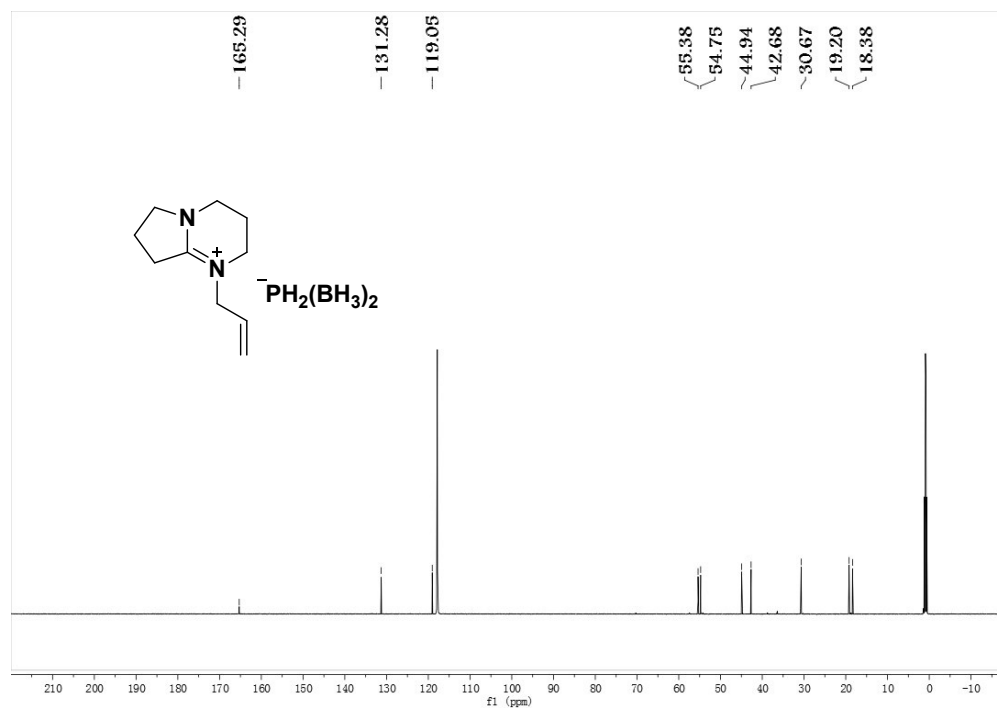
¹H-NMR spectrum of ionic liquid 5



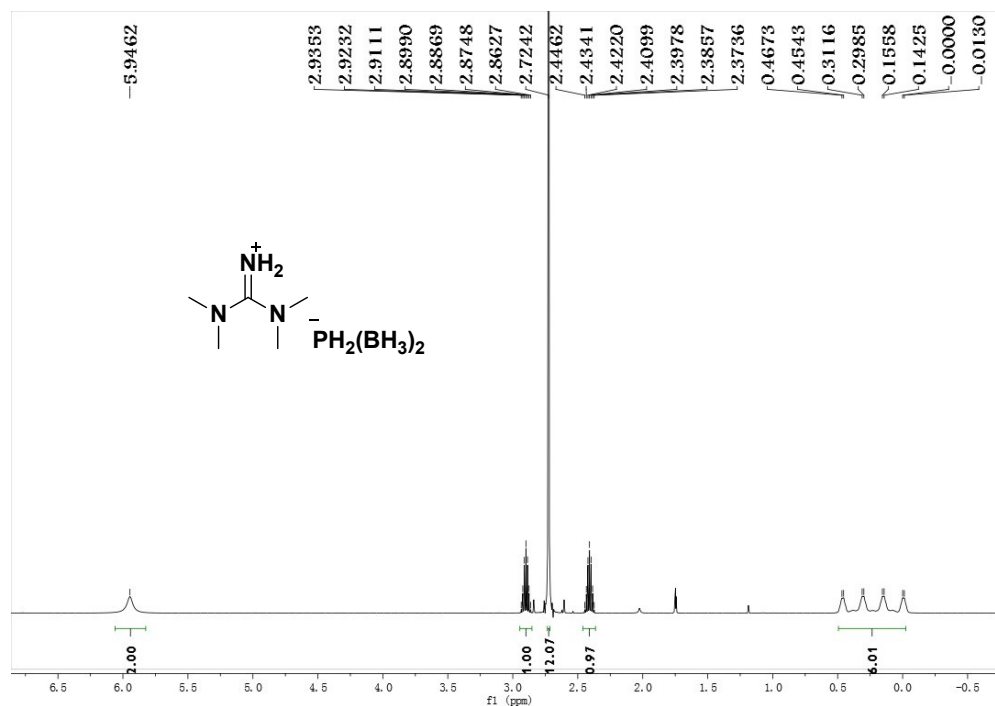
¹³C-NMR spectrum of ionic liquid 5



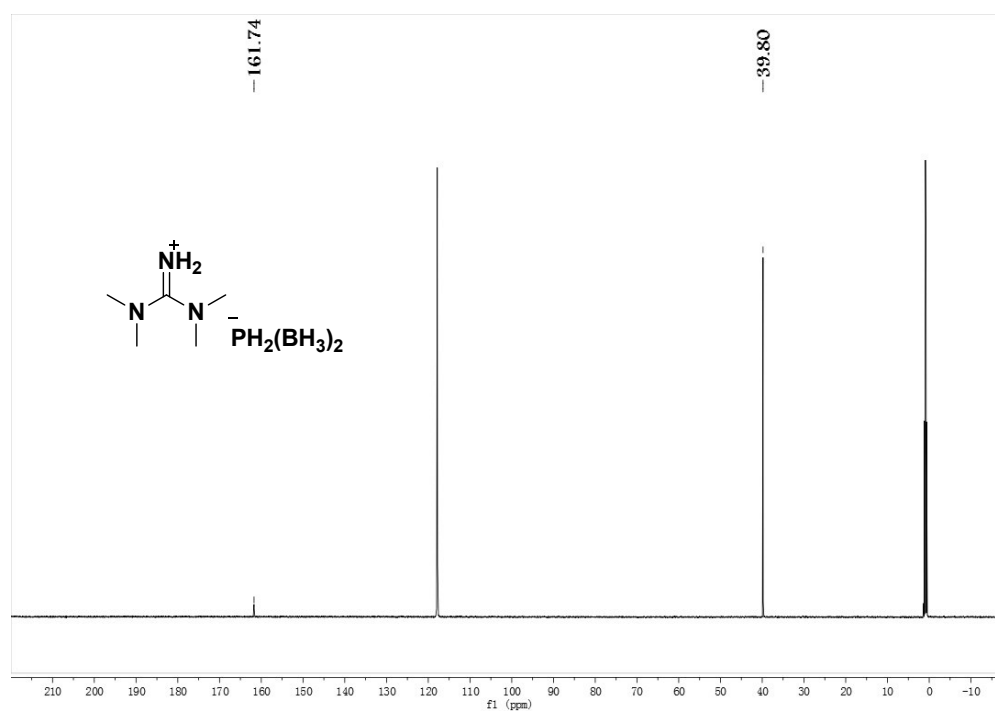
$^1\text{H-NMR}$ spectrum of ionic liquid 6



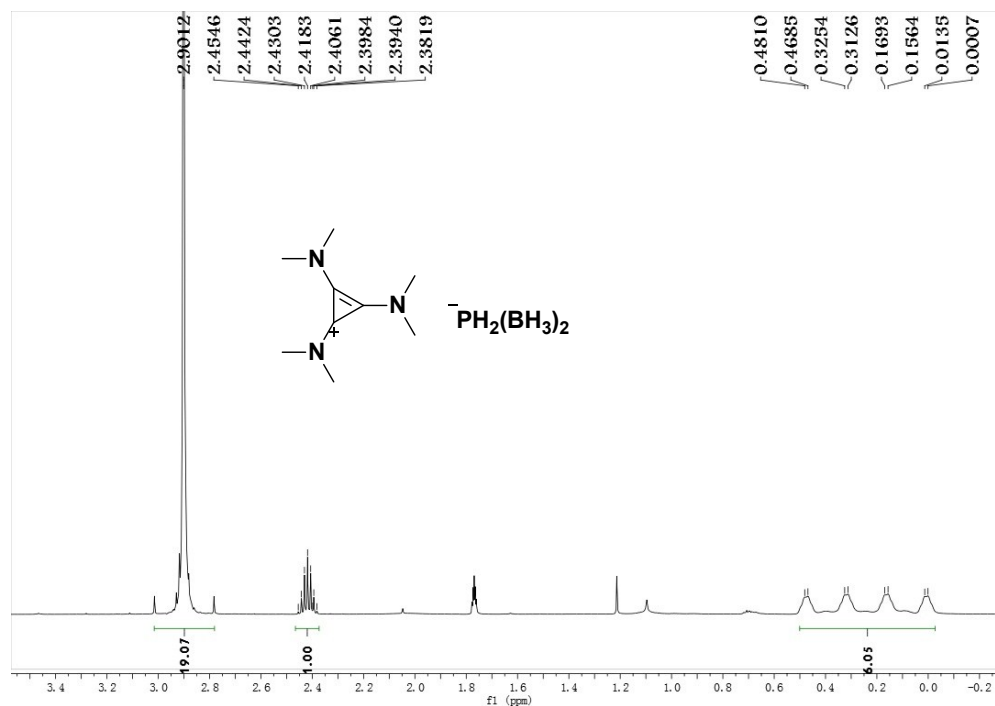
$^{13}\text{C-NMR}$ spectrum of ionic liquid 6



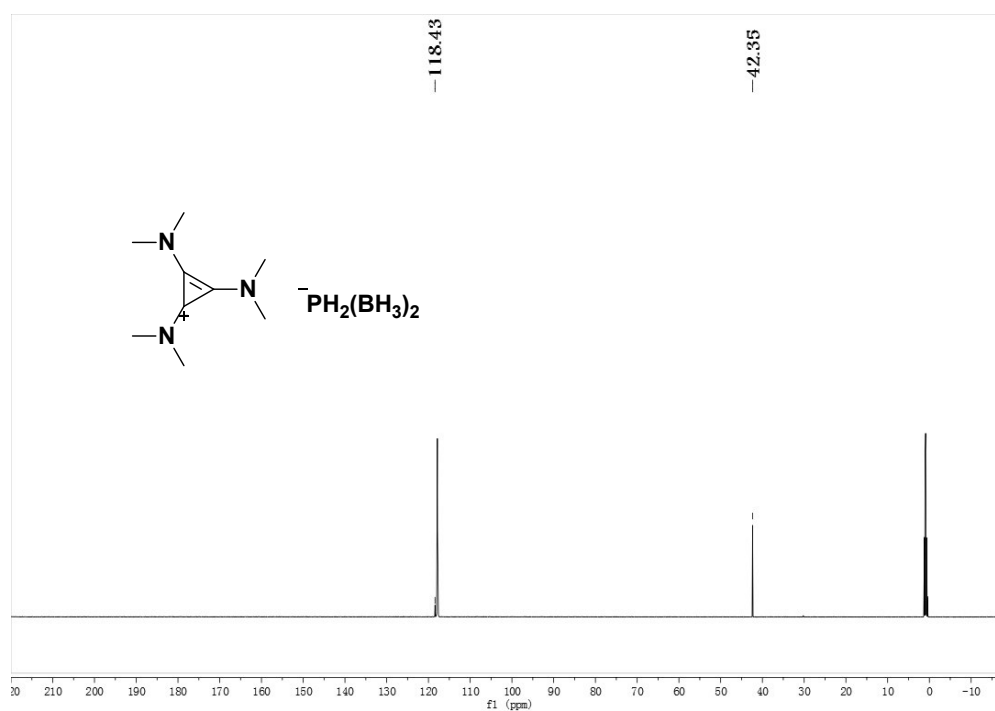
$^1\text{H-NMR}$ spectrum of ionic liquid 7



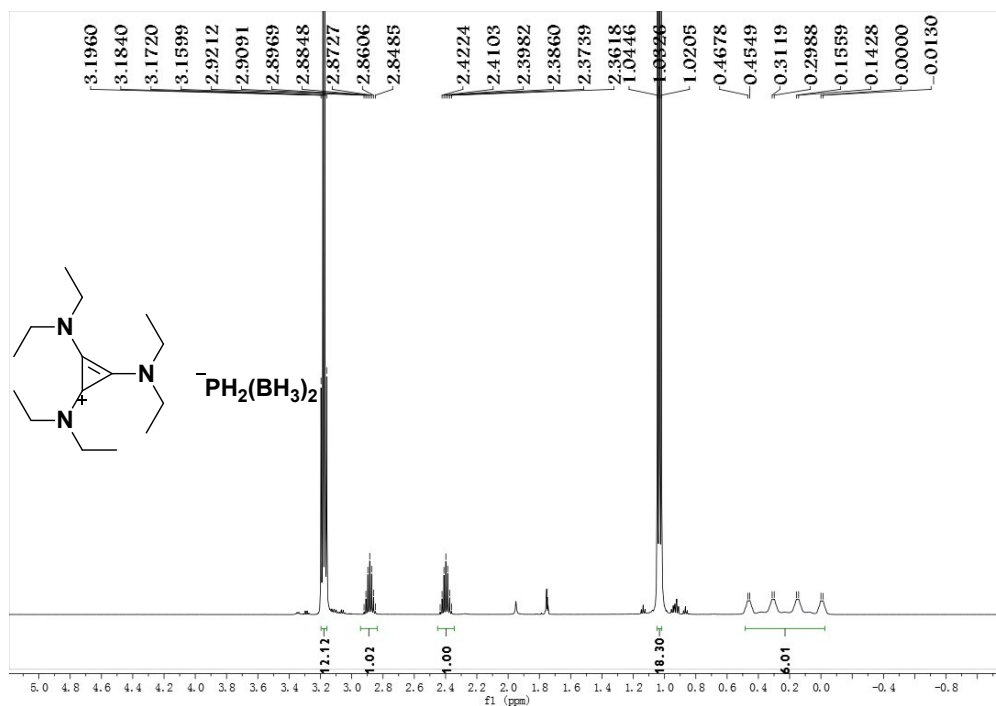
$^{13}\text{C-NMR}$ spectrum of ionic liquid 7



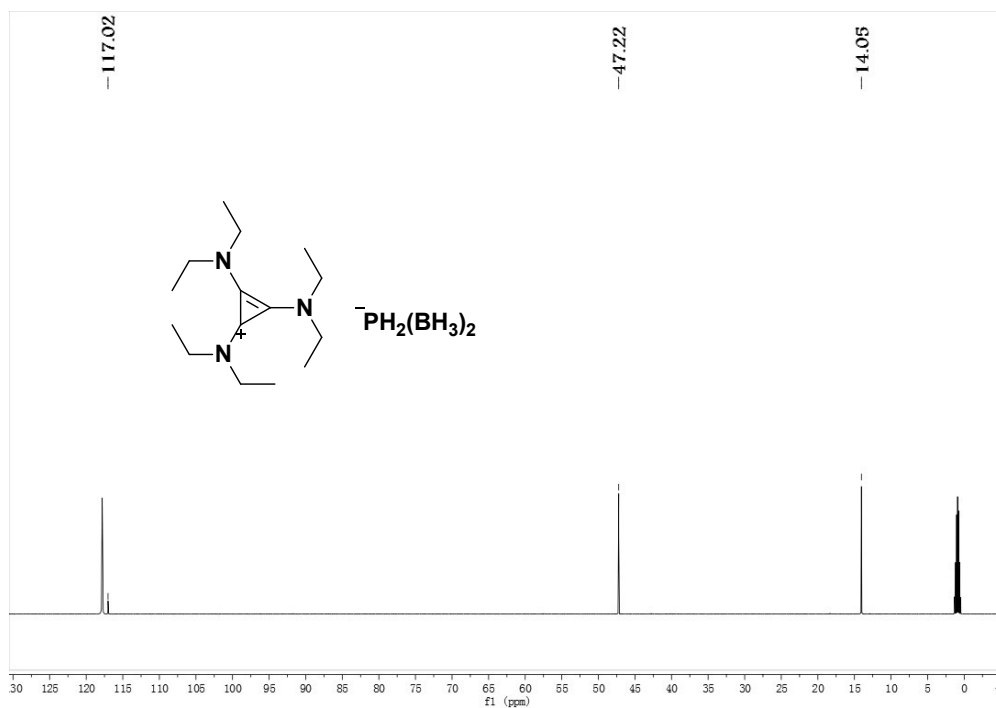
$^1\text{H-NMR}$ spectrum of ionic liquid **8**



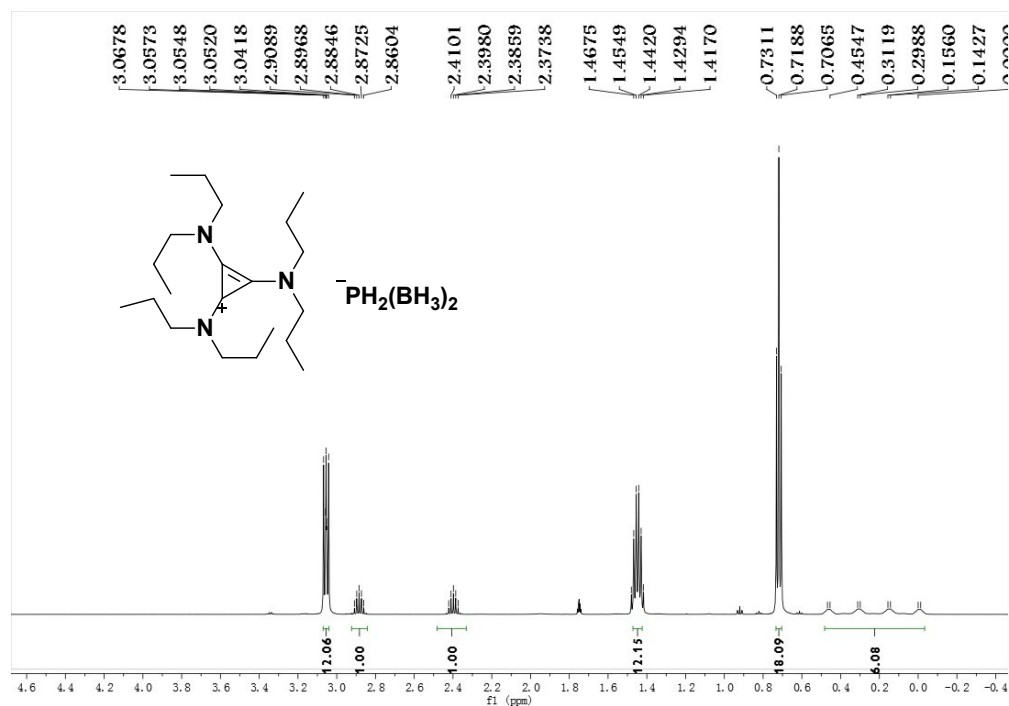
$^{13}\text{C-NMR}$ spectrum of ionic liquid **8**



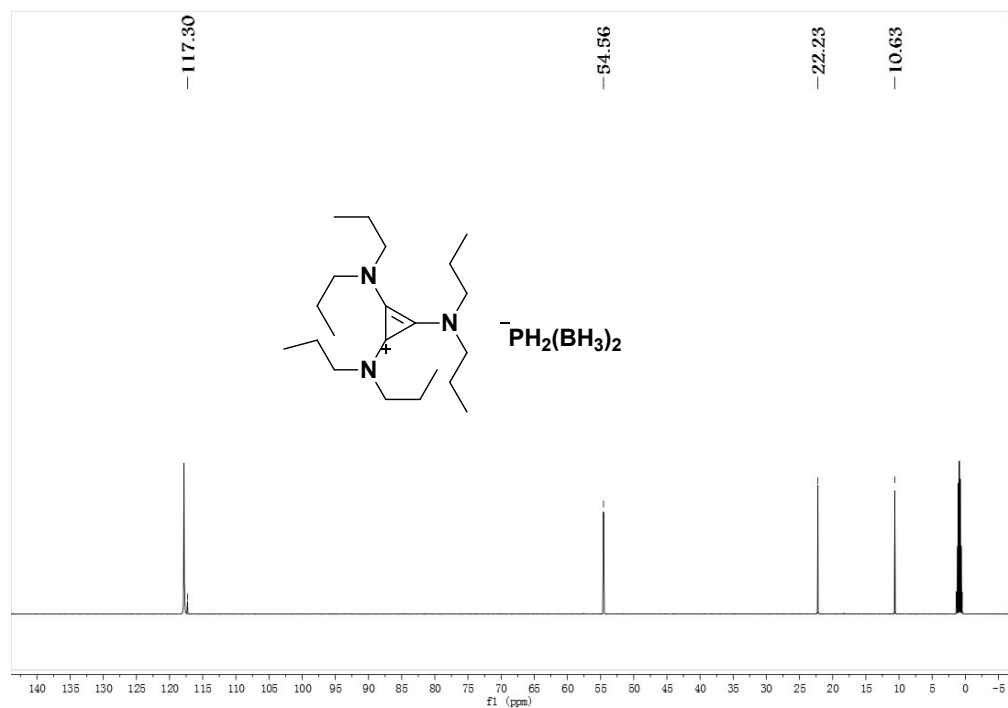
^1H -NMR spectrum of ionic liquid **9**



^{13}C -NMR spectrum of ionic liquid **9**



$^1\text{H-NMR}$ spectrum of ionic liquid 10



$^{13}\text{C-NMR}$ spectrum of ionic liquid 10