

## Electronic Supplementary Information

# Ionic Liquid Solubilized Boranes as Hypergolic Fluids

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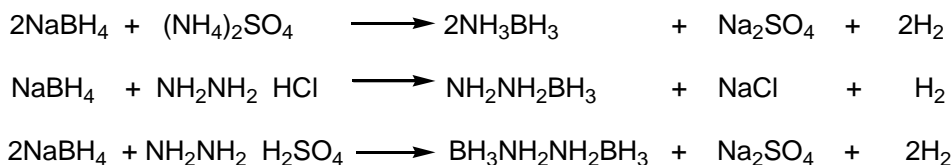
10-62733830; Tel: + 86 10-62731991; E-mail: hxgao@cau.edu.cn;

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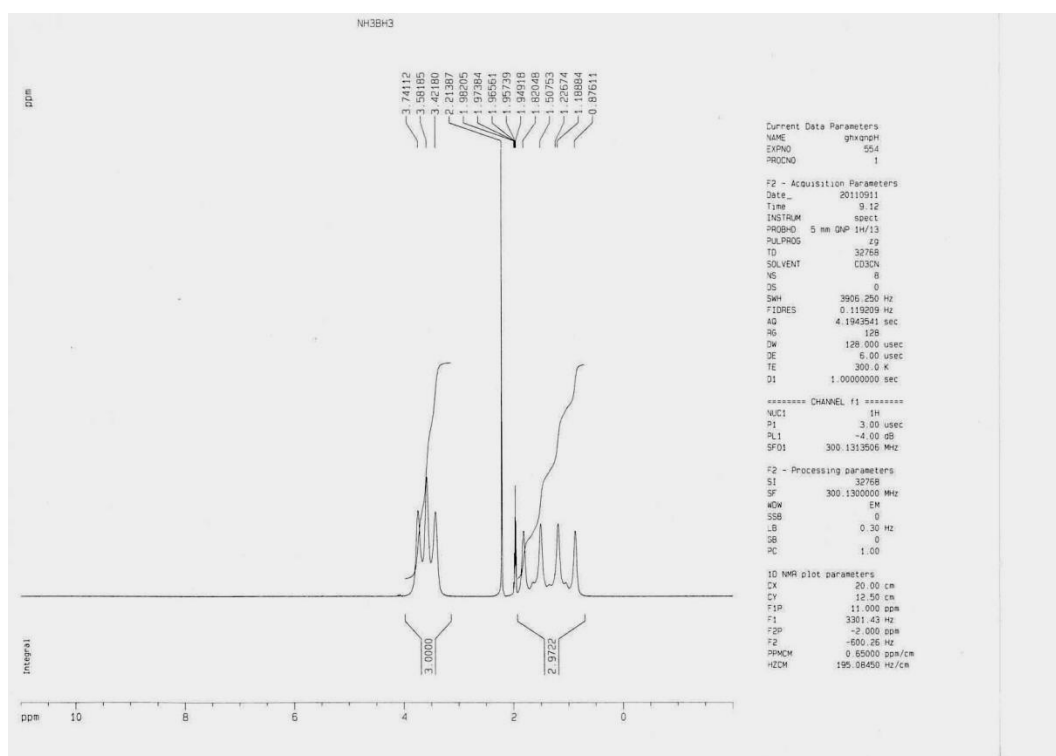
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**General.** Starting materials  $\text{NH}_3\text{BH}_3$ <sup>1</sup>,  $\text{NH}_2\text{NH}_2\text{BH}_3$ <sup>2</sup> and  $\text{BH}_3\text{NH}_2\text{NH}_2\text{BH}_3$ <sup>2</sup> 1-butyl-3-methylimidazolium tetrafluoroborate ( $\text{bmimBF}_4$ )<sup>3</sup>, 1-butyl-3-methylimidazolium dicyanamide ( $\text{bmimDCA}$ )<sup>4</sup>, N-Butyl-N-methylpyrrolidinium dicyanamide ( $\text{Pyrr}_{14}\text{DCA}$ )<sup>5,6</sup> were prepared according to a literature procedure (Scheme S1). WFNA was distilled from the mixture of  $\text{NaNO}_3$  and  $\text{H}_2\text{SO}_4$  (1:1.2). The <sup>1</sup>H and <sup>13</sup>C spectra were recorded on a Bruker 300 MHz spectrometer operating at 300 and 75 MHz, respectively. The <sup>1</sup>H and <sup>13</sup>C spectra were referenced to external/internal samples of TMS. <sup>11</sup>B spectra were recorded on 500 MHz (Bruker AVANCE 500) NMR spectrometer operating at 160.5 MHz (referenced to 17%  $[\text{BF}_3(\text{OEt}_2)]$  in  $\text{CDCl}_3$ ). All other chemicals were obtained commercially as analytical grade materials and were used as received. IR spectra were recorded by using KBr pellets on a Biorad Model 3000 FTS spectrometer. Computations were performed by using the Gaussian 09 (Revision A.02) suites of programs,<sup>7</sup> and Cheetah 4.0 or 6.0.<sup>8</sup> The geometric optimization and the frequency analyses were carried out using B3LYP functional analyses with the 6-311+G\*\* basis set.<sup>9</sup> Single energy points were

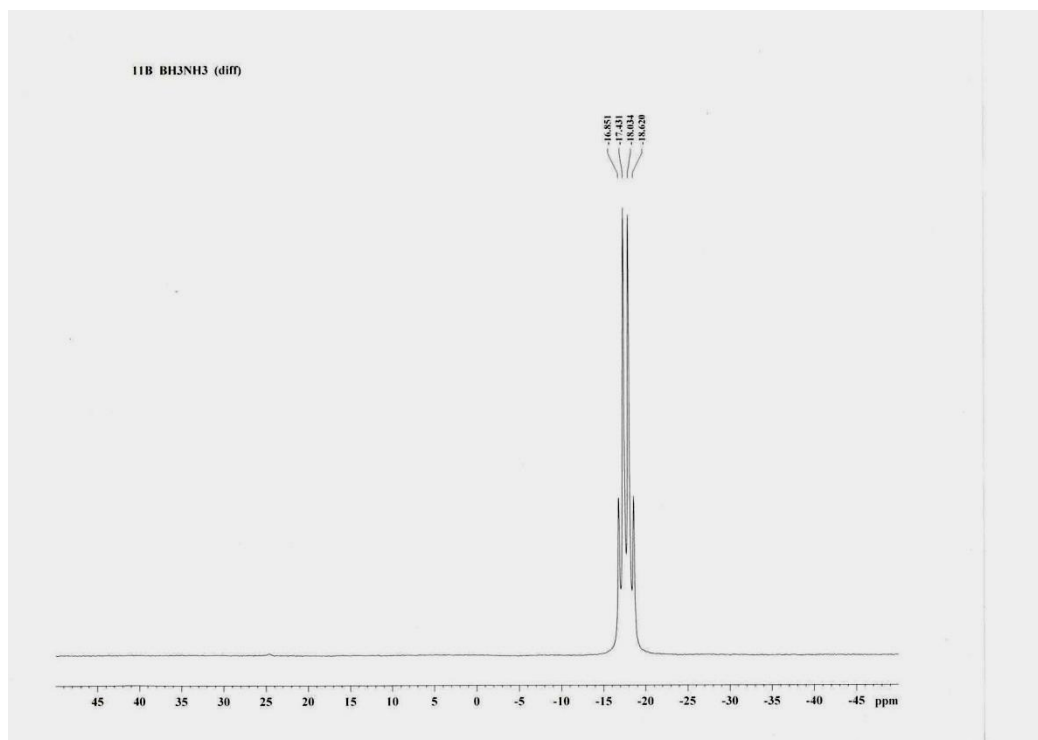
calculated at the MP2/6-311++G\*\* level.<sup>10</sup> All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.



Scheme S1. Synthesis of ammonia borane (AB), hydrazine borane (HB), and hydrazine bis-borane (HBB).



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Figure 1S. <sup>1</sup>H NMR (300 MHz) of synthesized AB in *d*-MeCN.



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Figure 2S. <sup>11</sup>B NMR (160.5 MHz) of synthesized AB in *d*-MeCN.

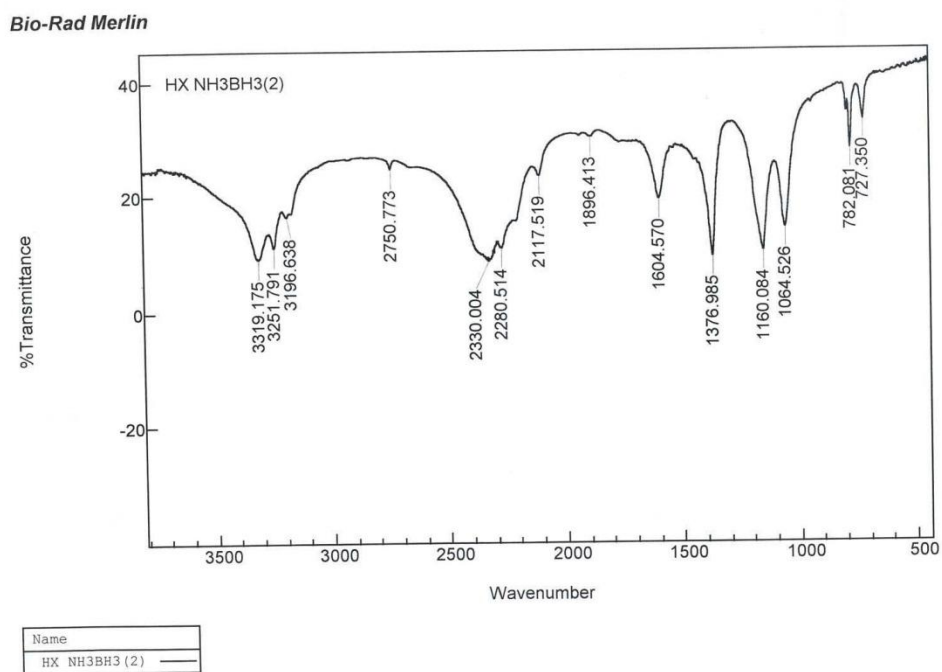
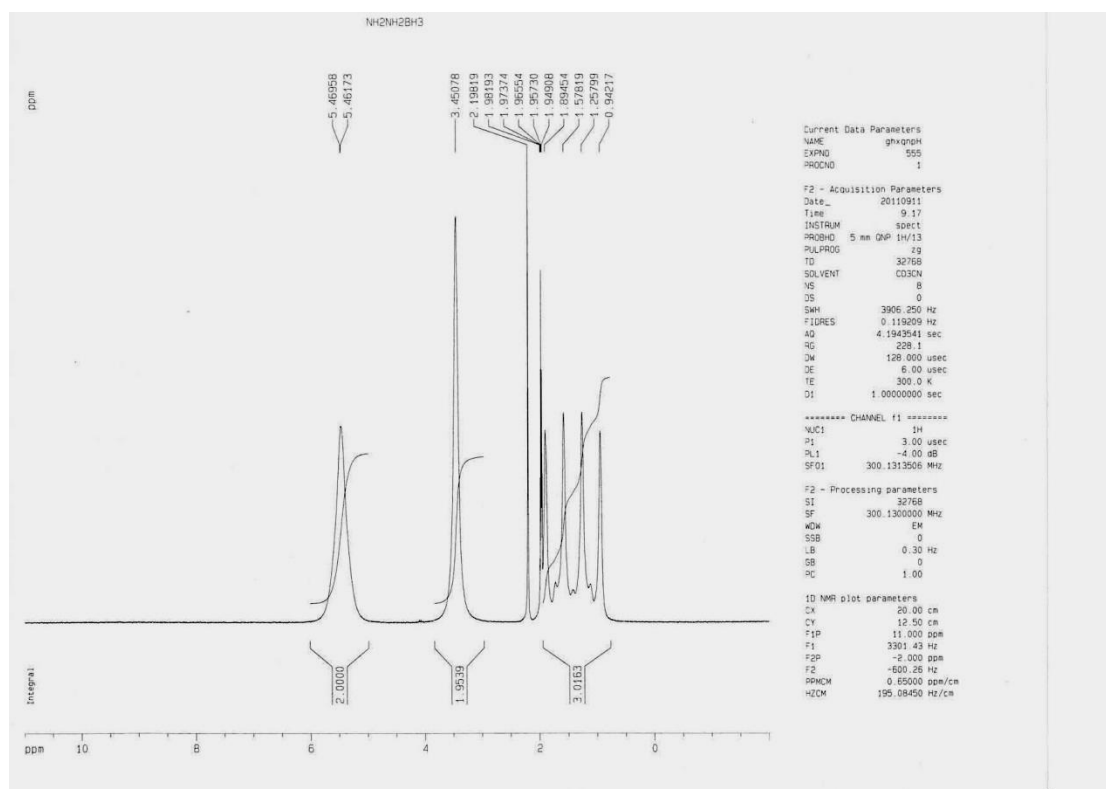
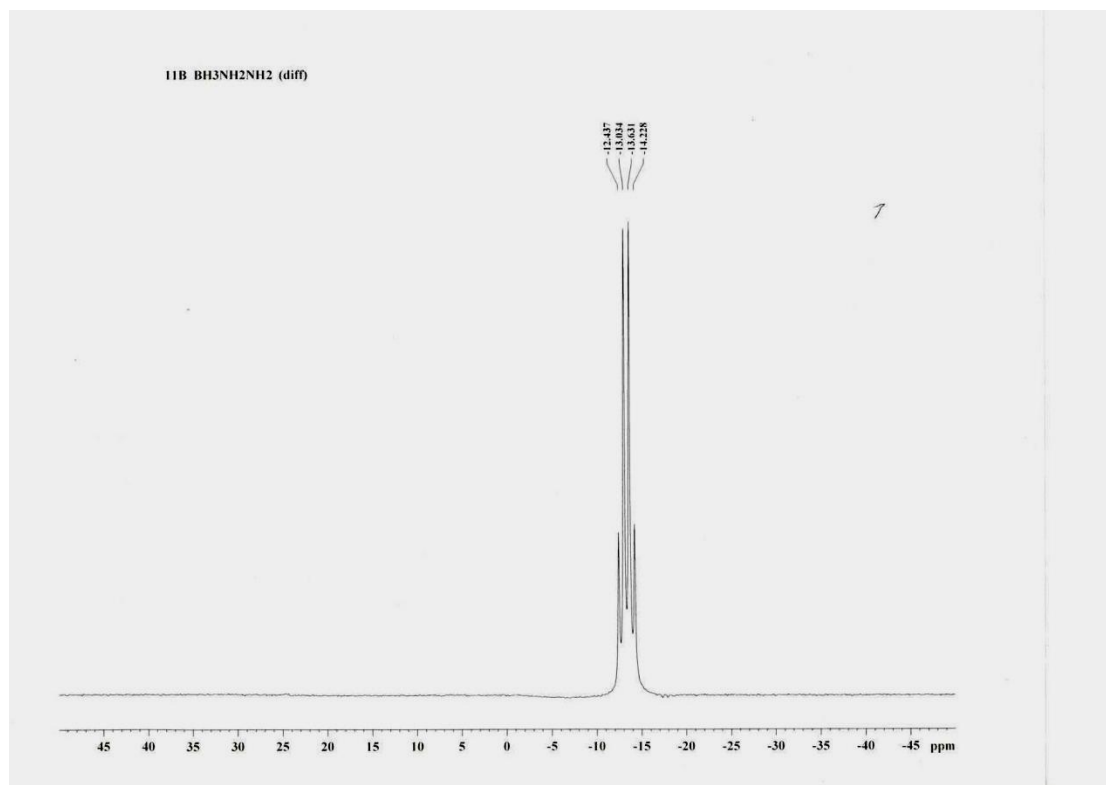


Figure 3S. IR of synthesized AB.

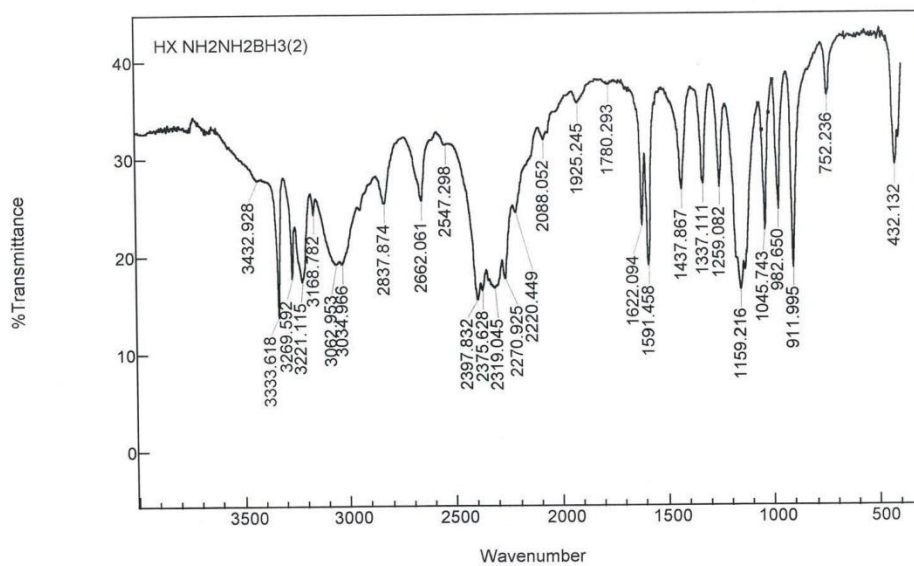


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Figure 4S.  $^1\text{H}$  NMR (300 MHz) of synthesized HB in *d*-MeCN.



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Figure 5S.  $^{11}\text{B}$  NMR (160.5 MHz) of synthesized HB in *THF*.

Bio-Rad Merlin



Name
HX NH <sub>2</sub> NH <sub>2</sub> BH <sub>3</sub> (2)

Figure 6S. IR of synthesized HB.

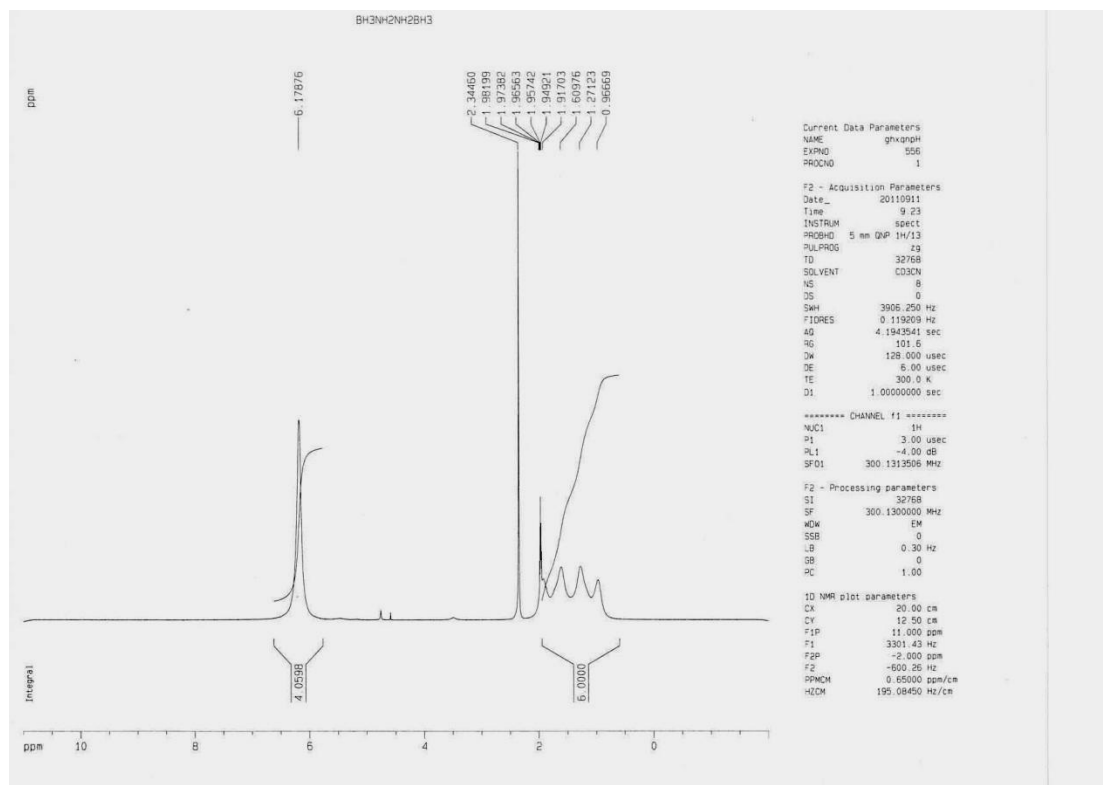
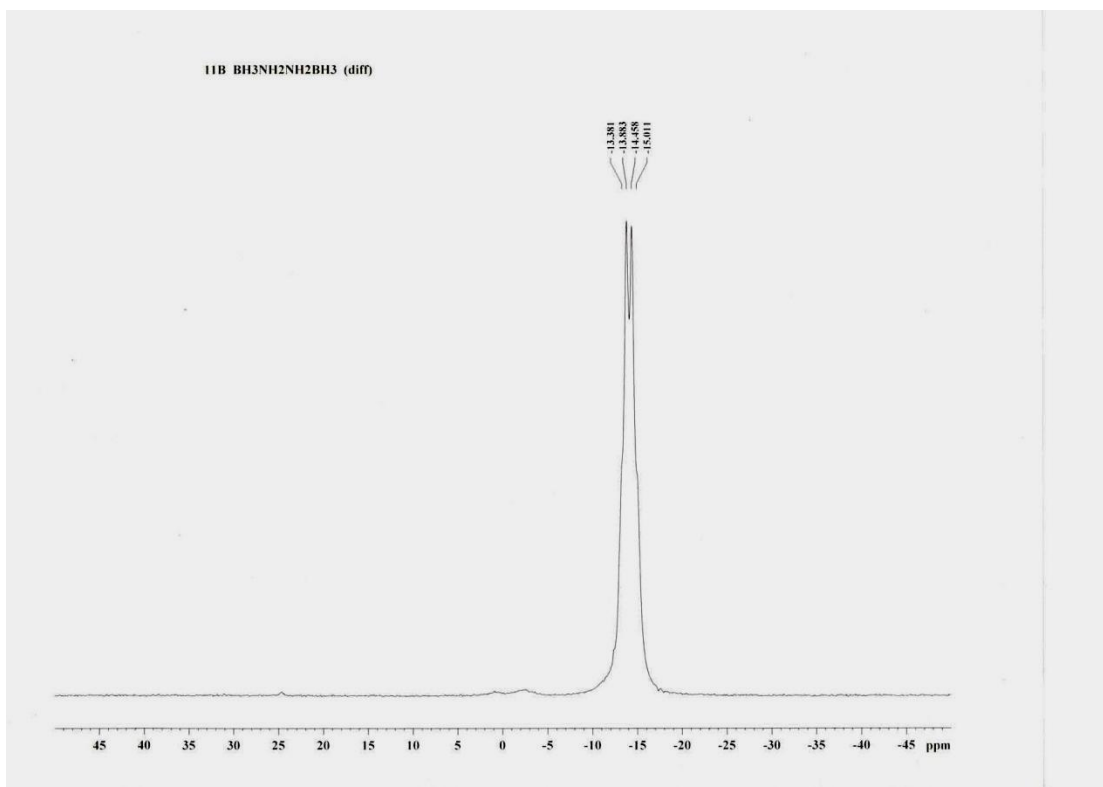


Figure 7S. <sup>1</sup>H NMR (300 MHz) of synthesized BHB in *d*-MeCN.



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Figure 8S. <sup>11</sup>B NMR (160.5 MHz) of synthesized BHB in THF.

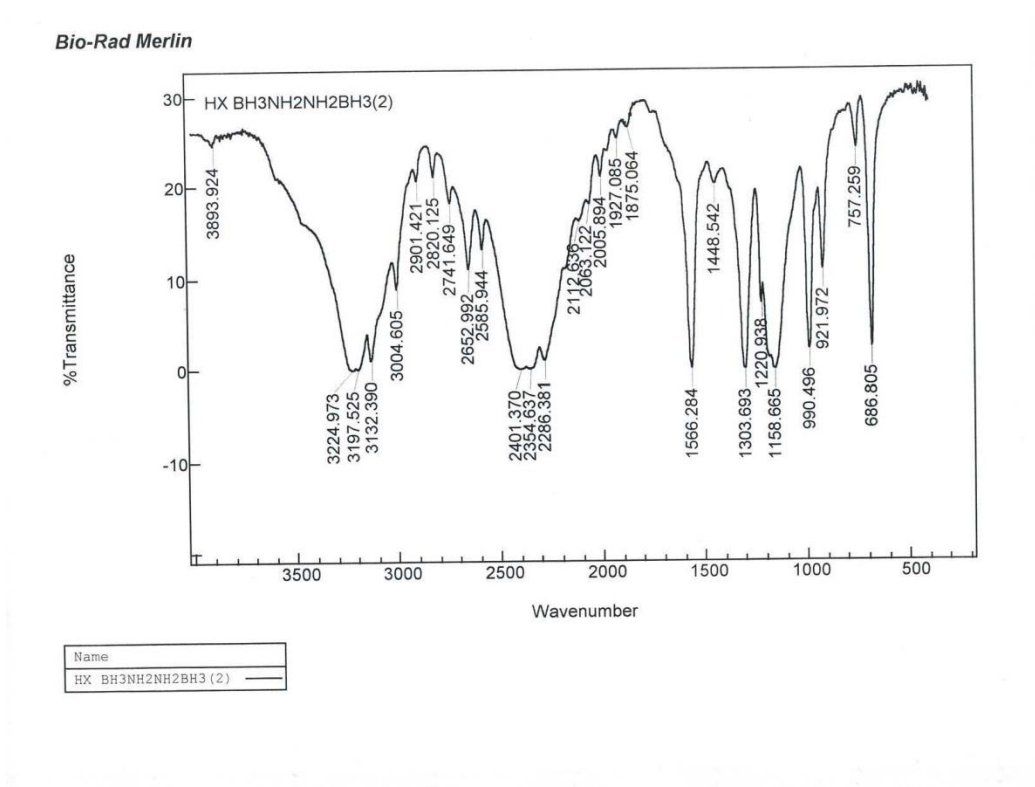
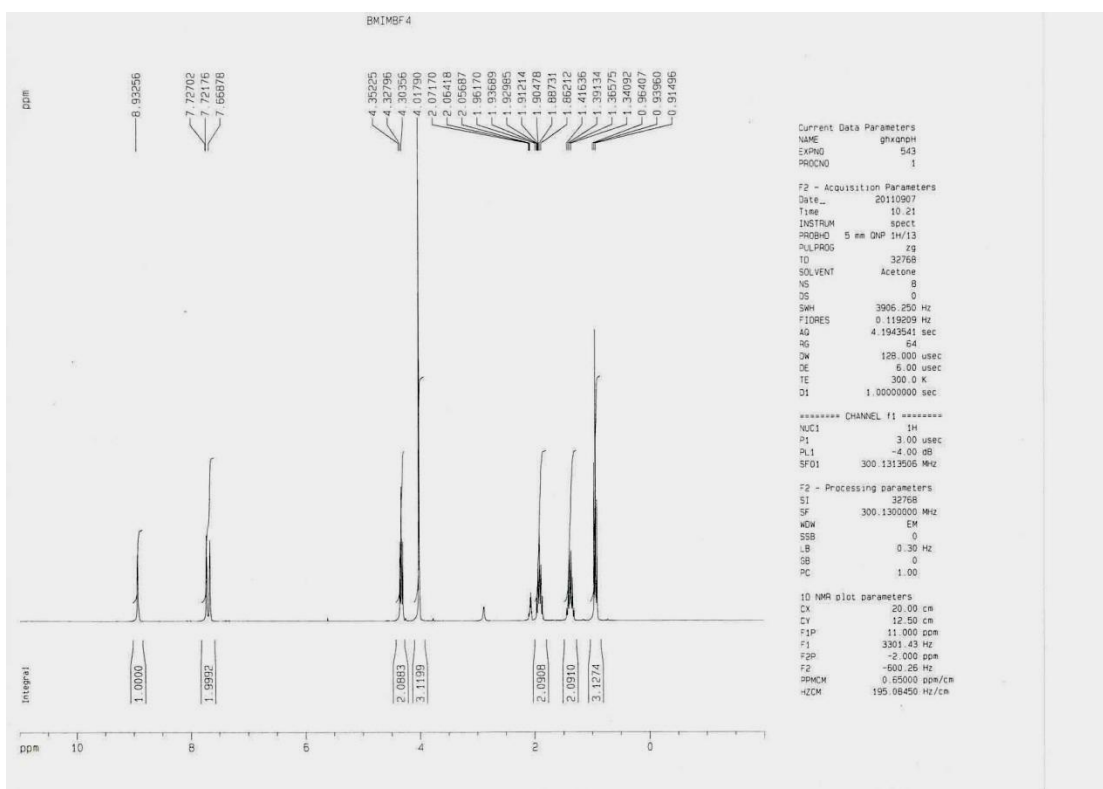
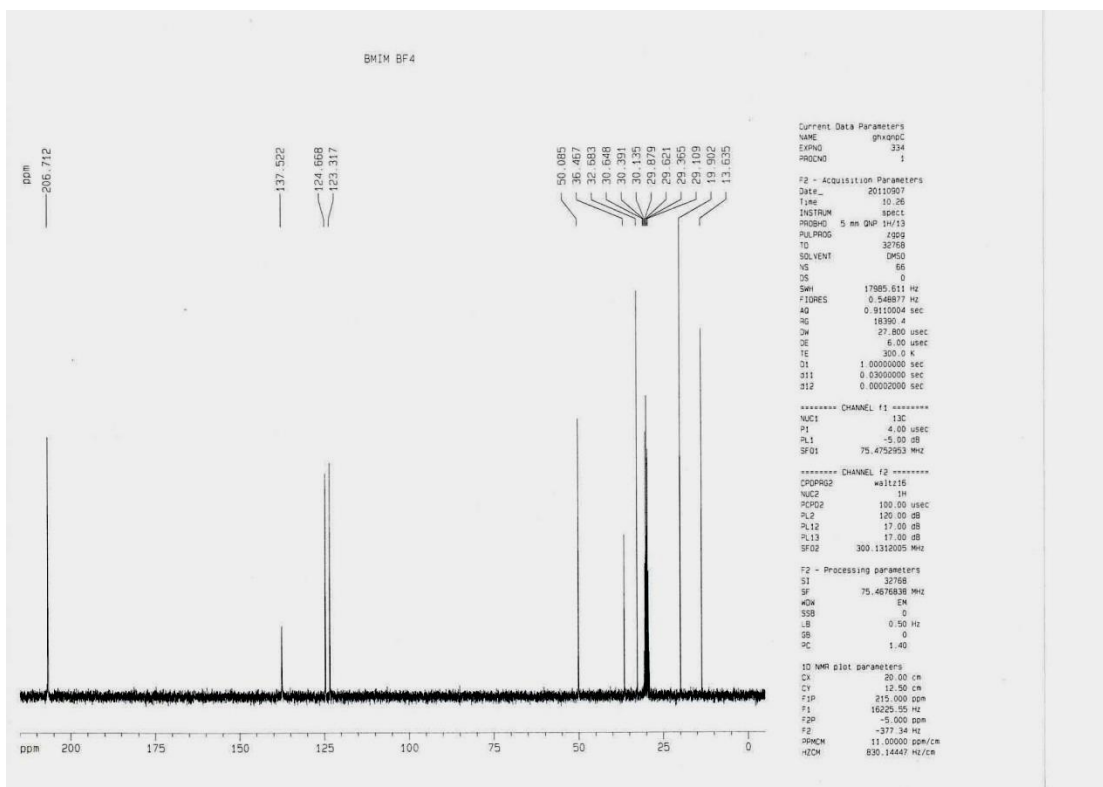


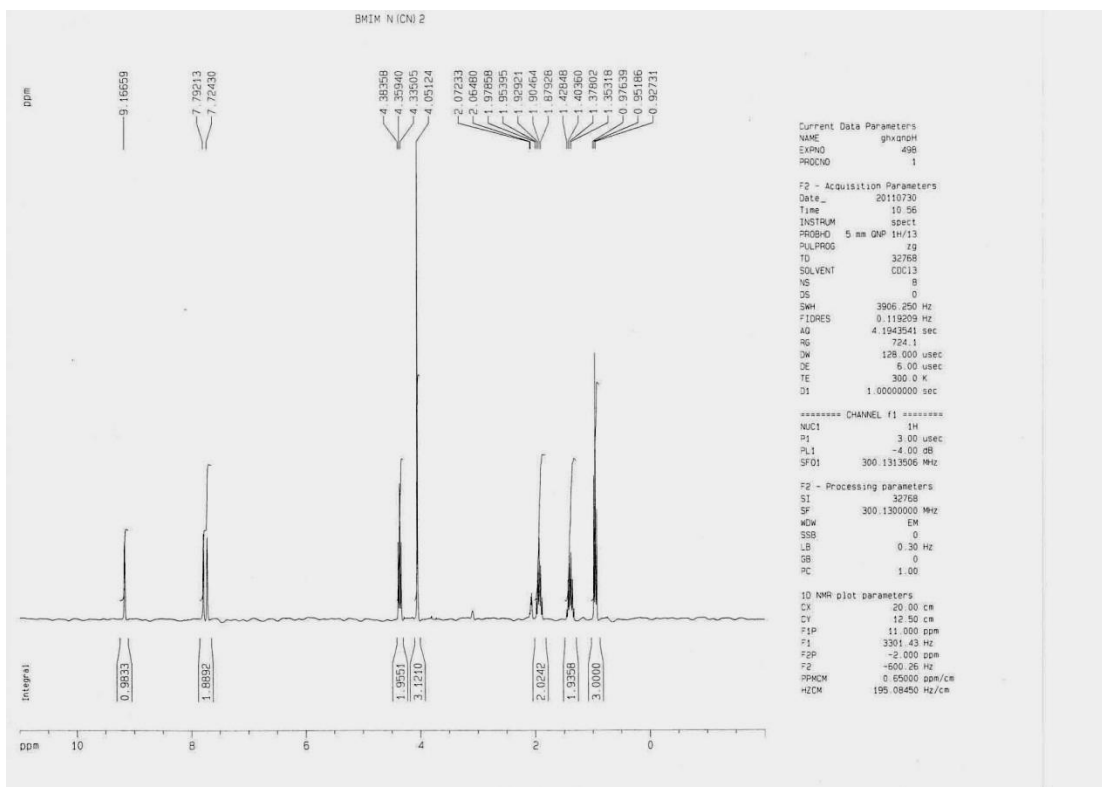
Figure 9S. IR of synthesized BHB.



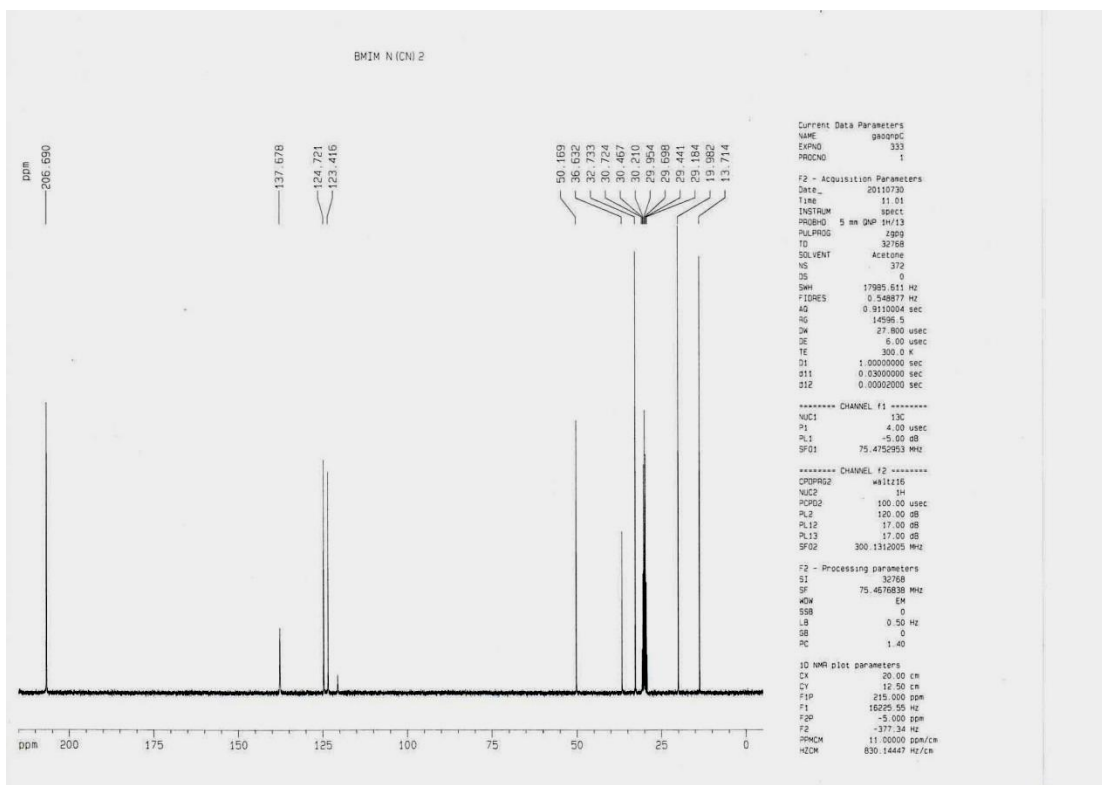
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 Figure 10S.  $^1\text{H}$  NMR (300 MHz) of synthesized  $\text{bmimBF}_4$  in  $d_6$ -acetone.



13  
 Figure 11S.  $^{13}\text{C}$  NMR (160.5 MHz) of synthesized  $\text{bmimBF}_4$  in  $d_6$ -acetone. Ref. to MeCN, 1.94 ppm.  $J_{\text{B-H}} = 94$  Hz,  $J_{\text{N-H}} = 45$  Hz.

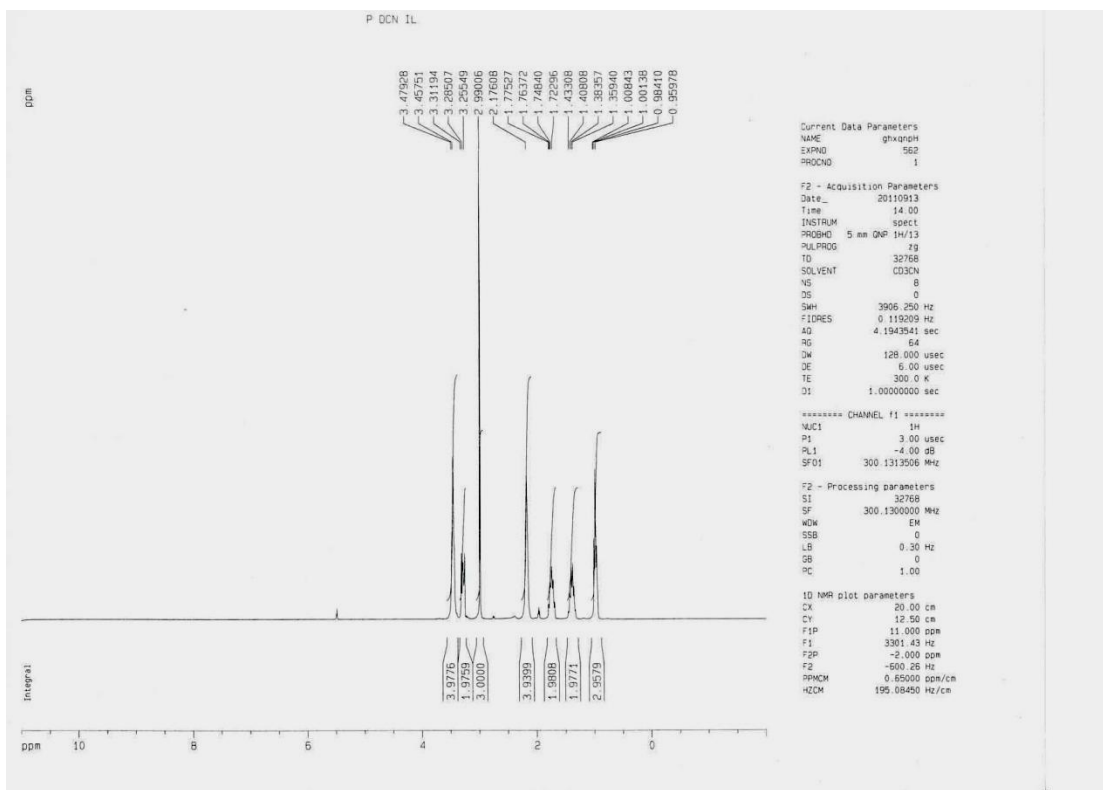


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 Figure 12S. <sup>1</sup>H NMR (300 MHz) of synthesized bmimDCA in *d*-MeCN.

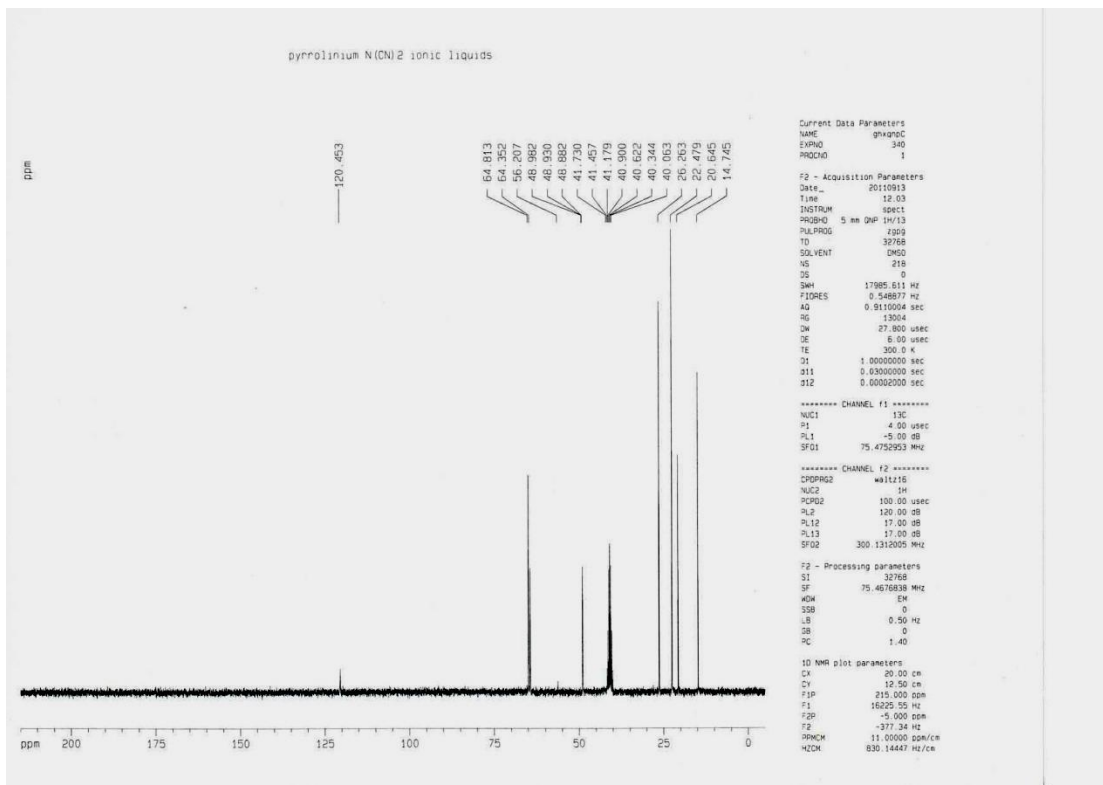


13  
 Figure 13S. <sup>13</sup>C NMR (160.5 MHz) of synthesized bmimDCA in *d*-MeCN.

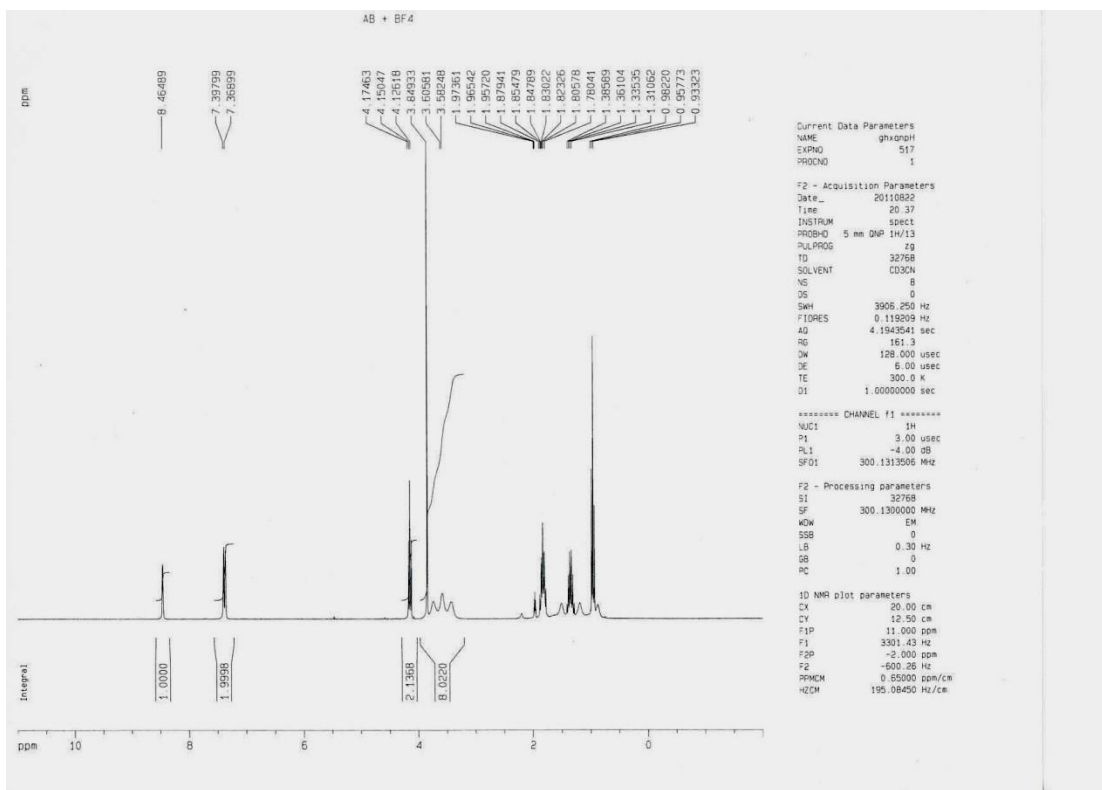




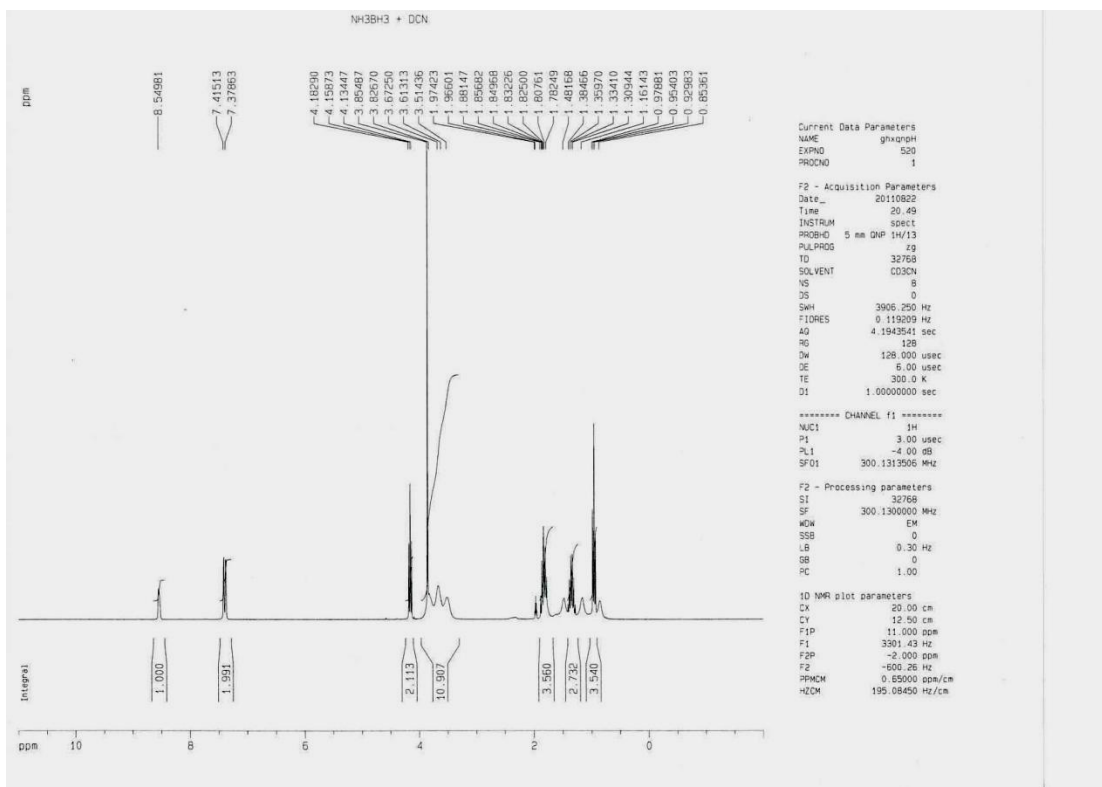
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 Figure 14S.  $^1\text{H}$  NMR (300 MHz) of synthesized Pyr<sub>14</sub>DCA in *d*-MeCN.



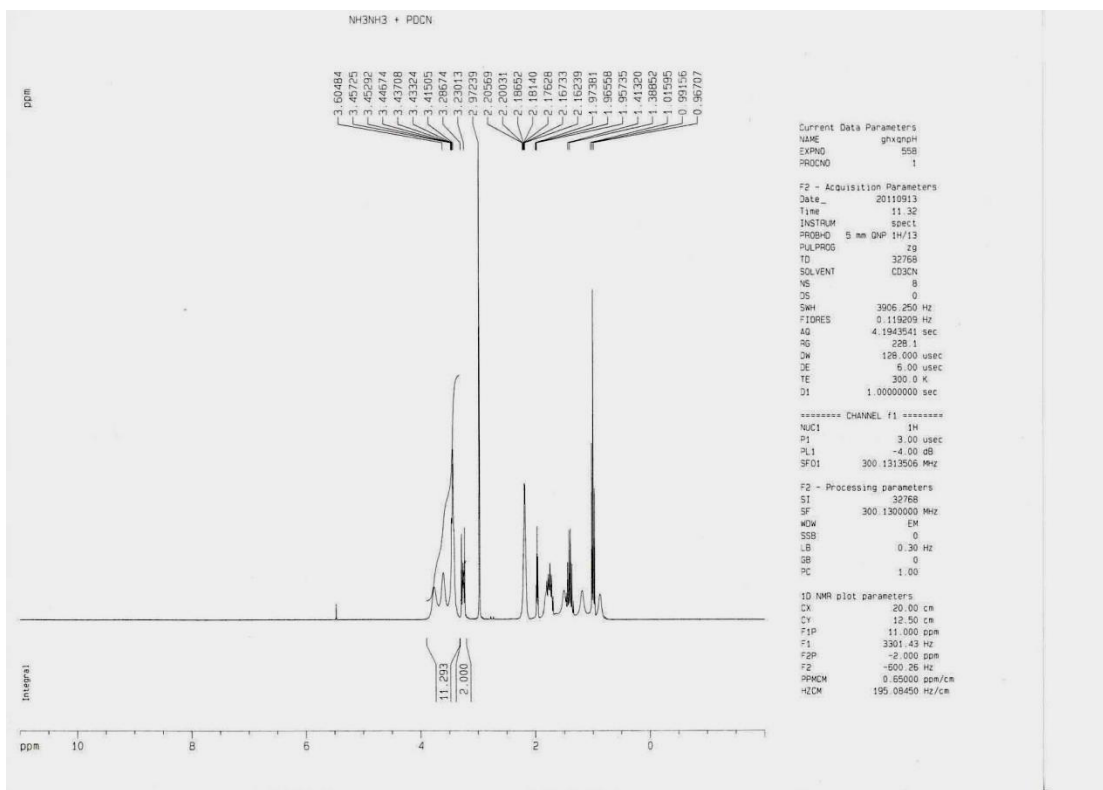
13  
 Figure 15S.  $^{13}\text{C}$  NMR (160.5 MHz) of synthesized Pyr<sub>14</sub>DCA in *d*-MeCN.



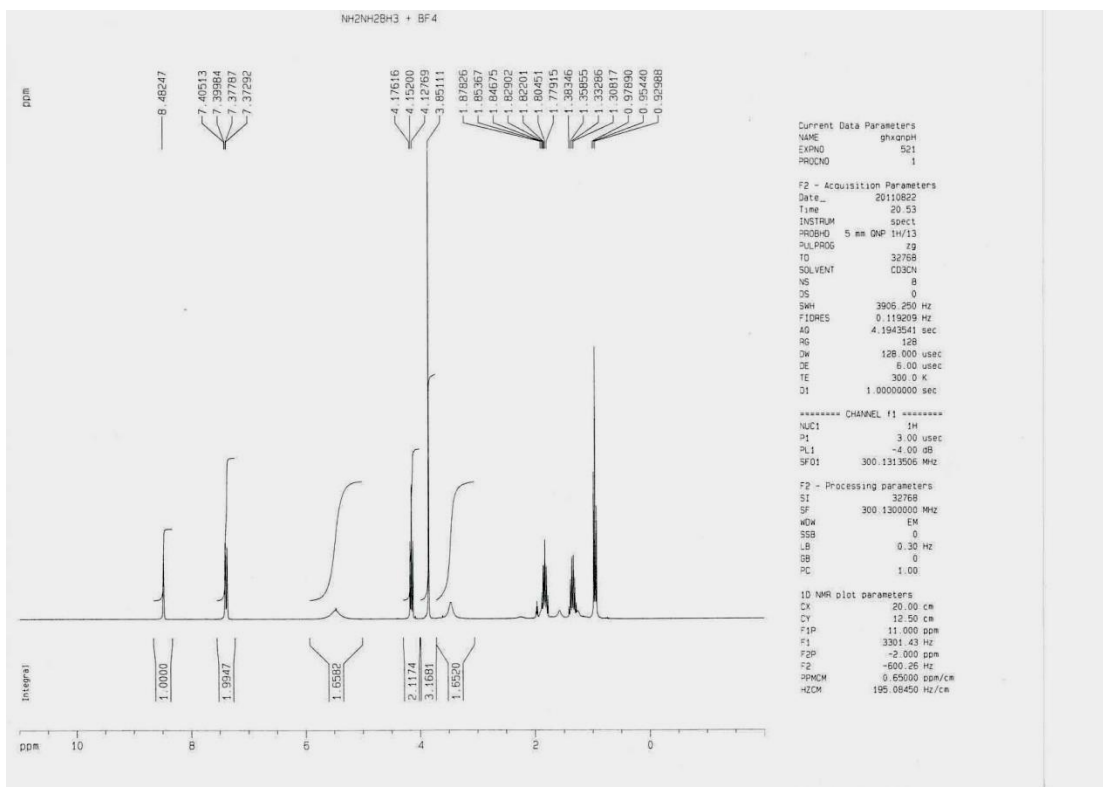
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 Figure 16S. <sup>1</sup>H NMR (300 MHz) of AB/bmimBF<sub>4</sub> solution in *d*-MeCN.



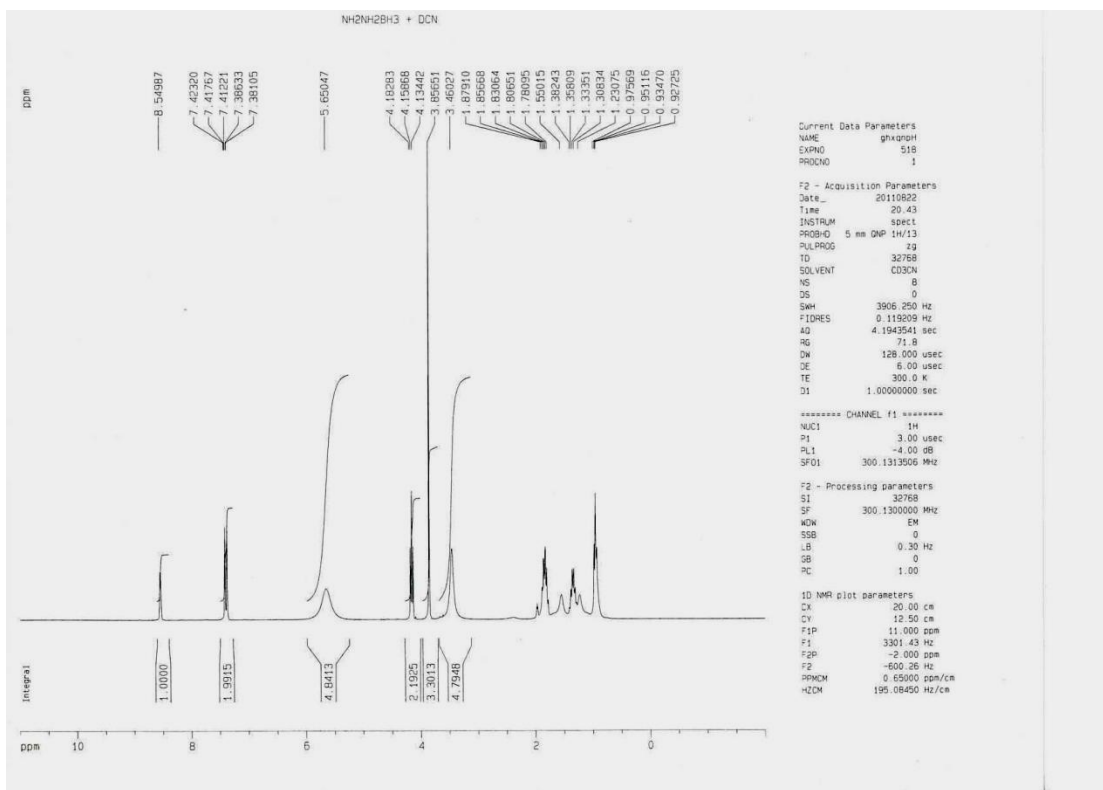
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 Figure 17S. <sup>1</sup>H NMR (300 MHz) of AB/bmimDCA solution in *d*-MeCN.



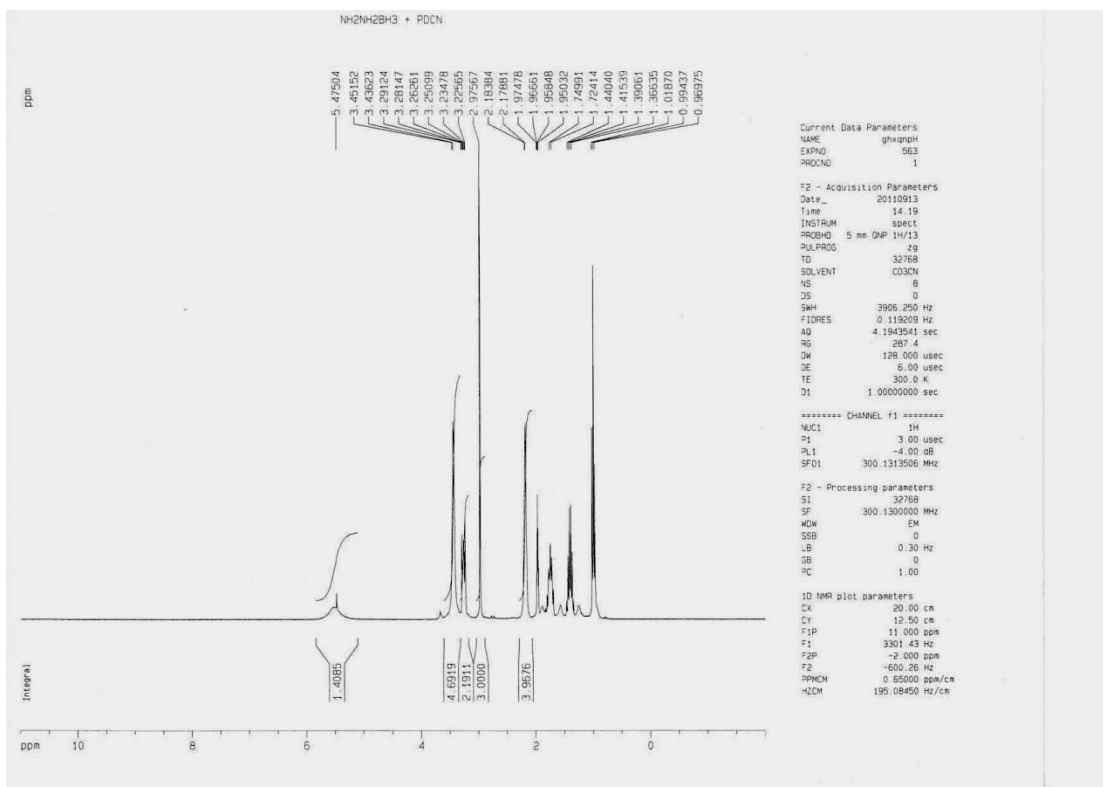
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 Figure 18S.  $^1\text{H}$  NMR (300 MHz) of AB/Pyrr<sub>14</sub>DCA solution in *d*-MeCN.



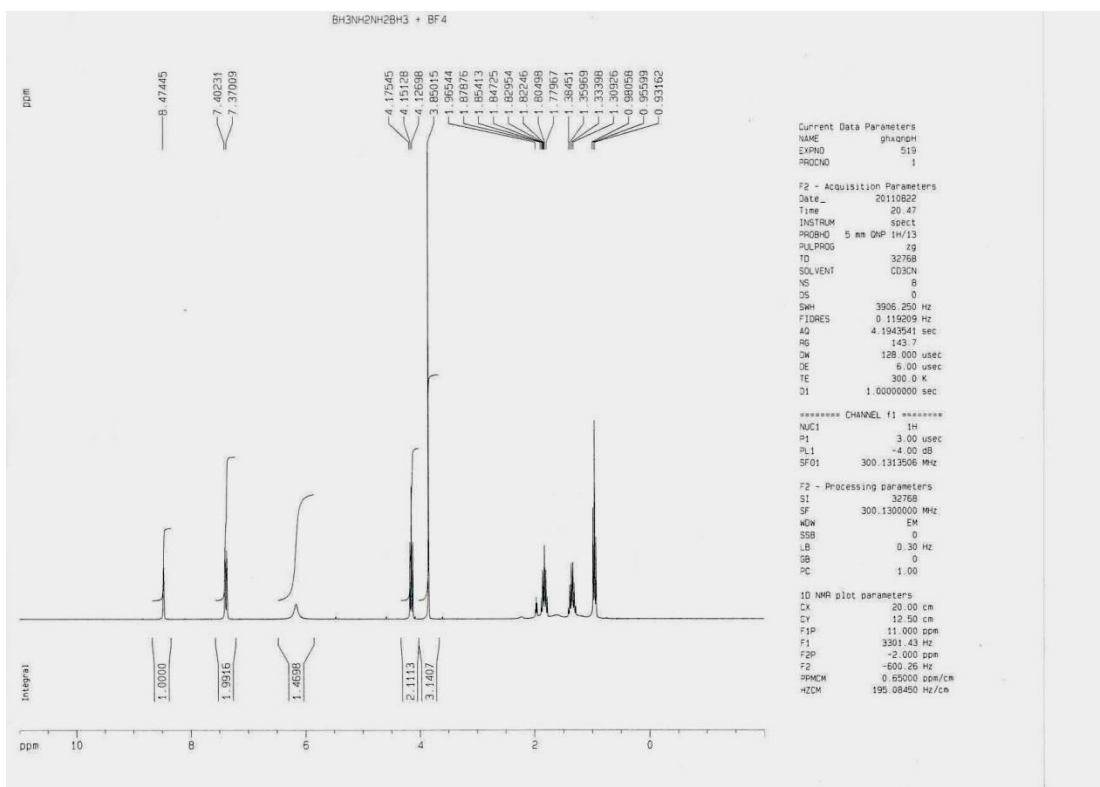
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 Figure 19S.  $^1\text{H}$  NMR (300 MHz) of HB/ bmimBF<sub>4</sub> solution in *d*-MeCN.



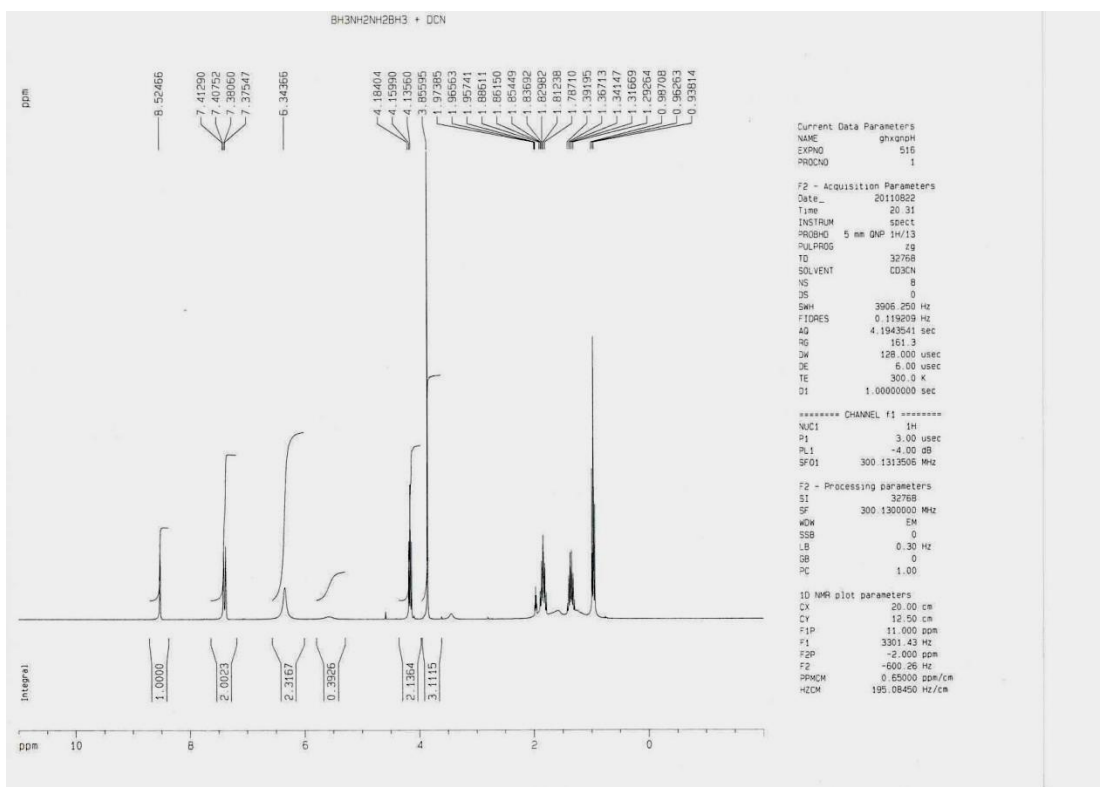
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 Figure 20S. <sup>1</sup>H NMR (300 MHz) of HB/bmimDCA solution in *d*-MeCN.



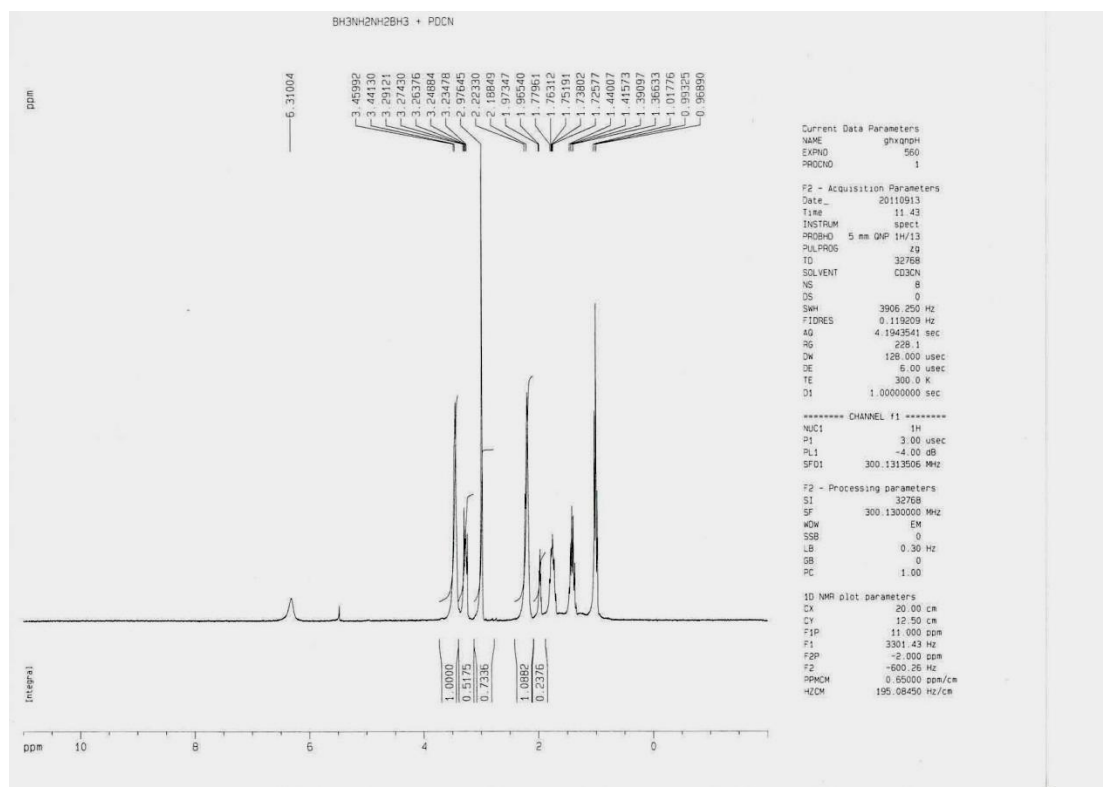
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 Figure 21S. <sup>1</sup>H NMR (300 MHz) of HB/Pyrr<sub>14</sub>DCA solution in *d*-MeCN.



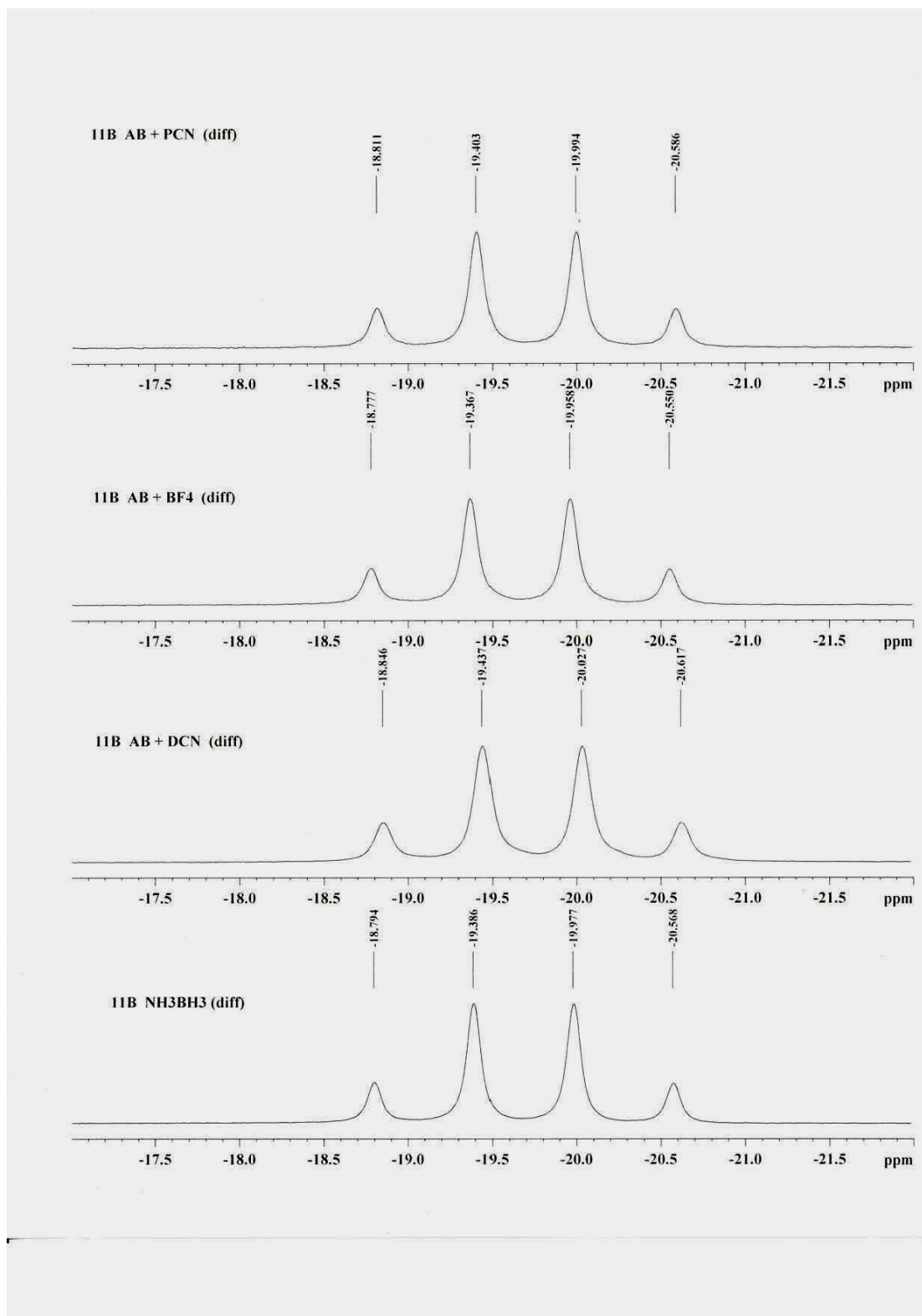
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 Figure 22S. <sup>1</sup>H NMR (300 MHz) of BHB / bmimBF<sub>4</sub> solution in *d*-MeCN.



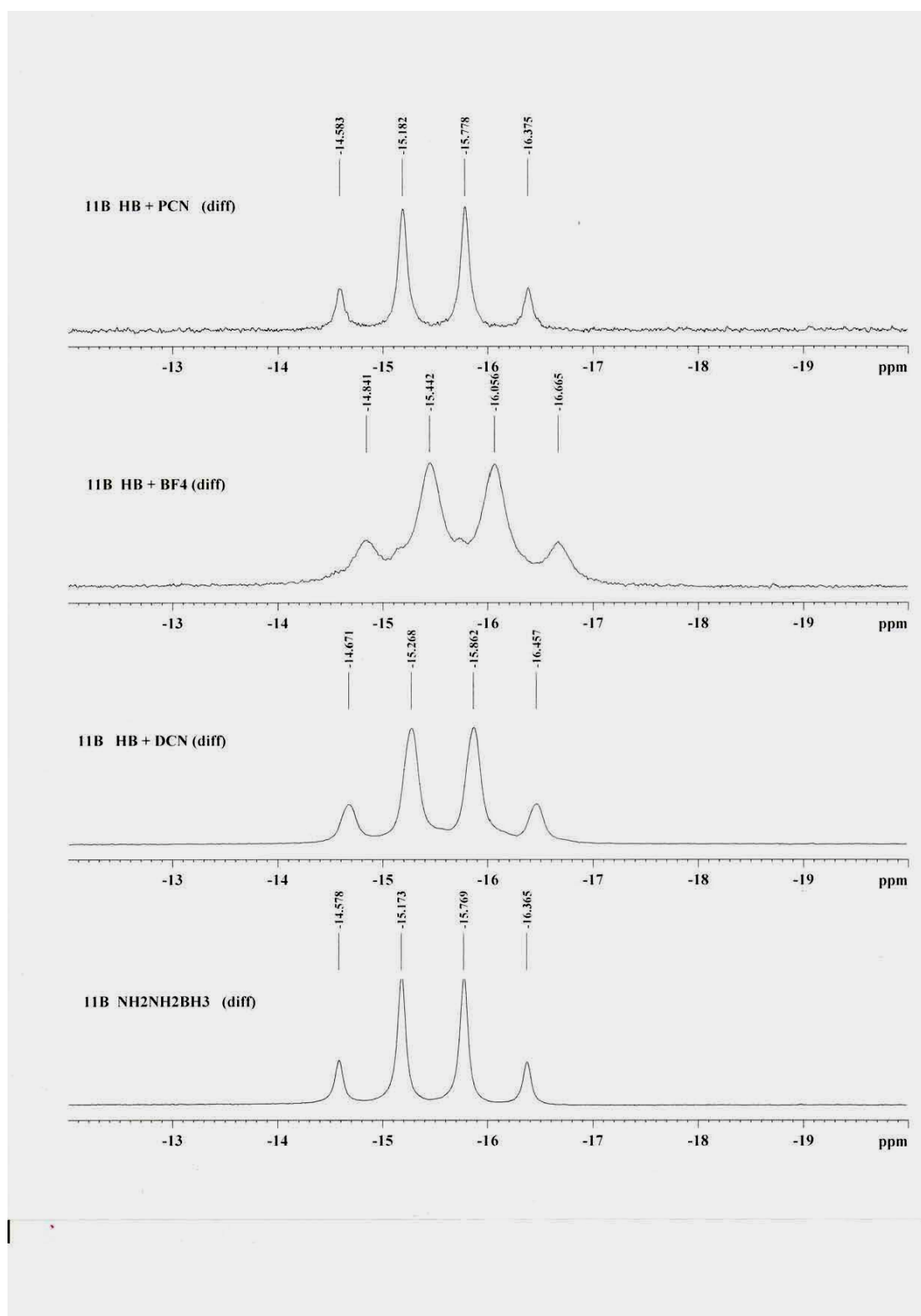
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 Figure 23S. <sup>1</sup>H NMR (300 MHz) of BHB / bmimDCA solution in *d*-MeCN.



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Figure 24S.  $^1\text{H}$  NMR (300 MHz) of BHB /Pyrr<sub>14</sub>DCA solution in *d*-MeCN.



<sup>11</sup>  
Figure 25S.  $^{11}\text{B}$  NMR (300 MHz) of solution of AB, AB/bmimBF<sub>4</sub>, AB/bmimDCA and AB/Pyrr14DCA solution in *d*-MeCN.



<sup>11</sup>  
Figure 26S.  $^{11}\text{B}$  NMR (300 MHz) of solution of HB, HB/bmimBF<sub>4</sub>, HB/bmimDCA and HB/Pyrr<sub>14</sub>DCA solution in *d*-MeCN.



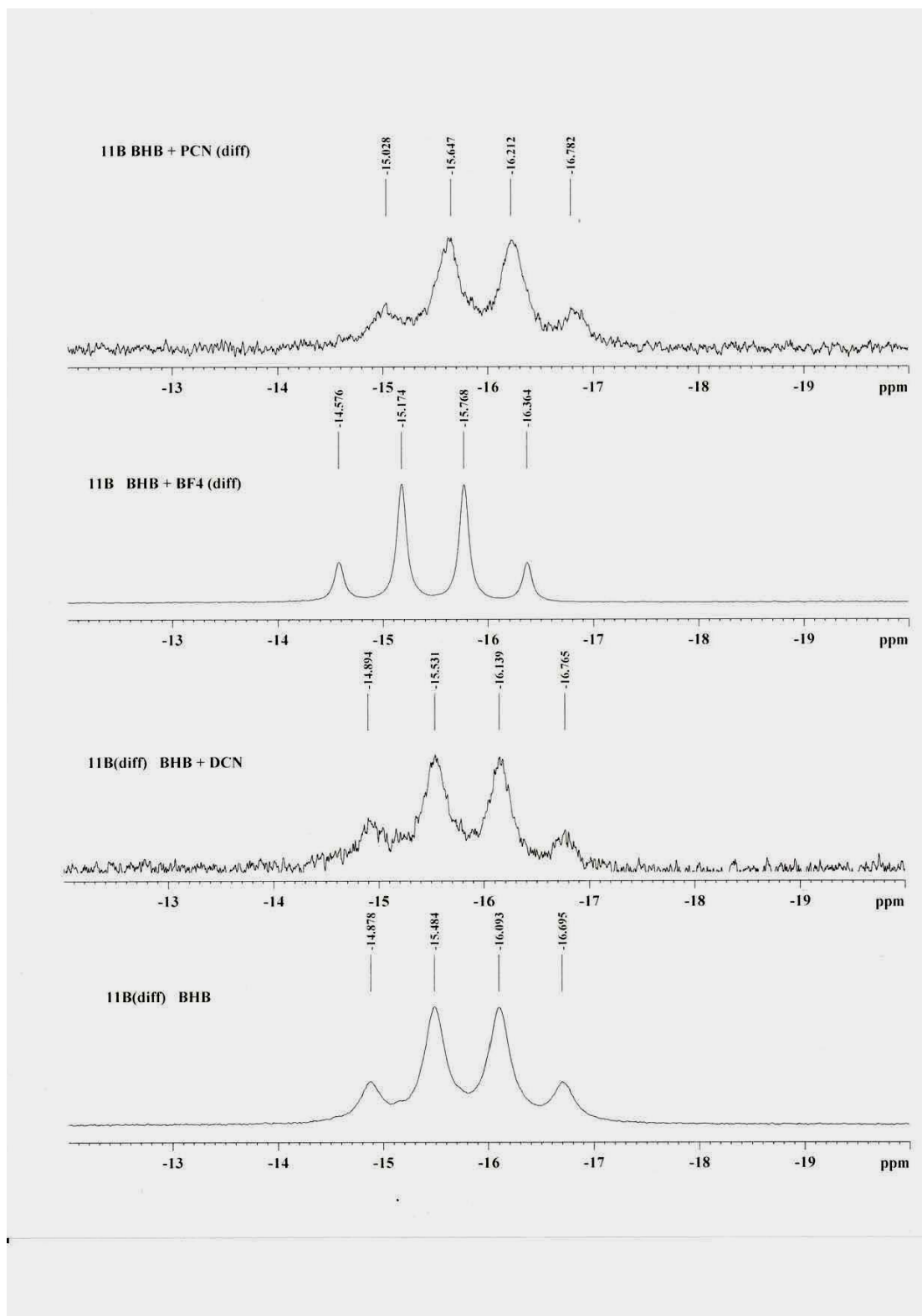


Figure 27S.  $^{11}\text{B}$  NMR (300 MHz) of solution of BHB, BHB/bmimBF<sub>4</sub>, BHB/bmimDCA and BHB/Pyrr<sub>14</sub>DCA solution in *d*-MeCN.

Oxidizer WFNA (3mL used) was placed in a vial (40mL) and the fuel was loaded into pipette(liquid) or spatulas(solid). High speed movies were recorded with OLYMPUS® i-Speed 3 high speed Digital camera at 500 or 1000 frames/s. Ignition delay times were determined by counting the frames between the droplet first hitting the surface and the sign of the first visible flame.

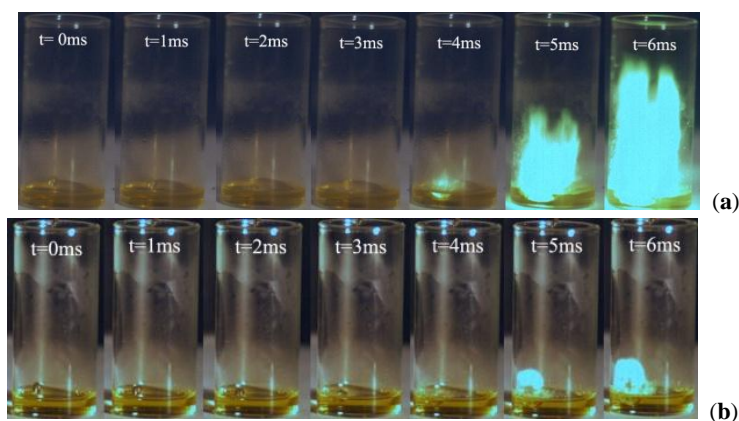


Figure 28s. The reproducible ignition delay tests recorded with a series of high speed camera photos of hypergolic fuels contacting WFNA—(a) AB in bmimDCA solution; (b) AB in Pyr<sub>14</sub>DCA solution;

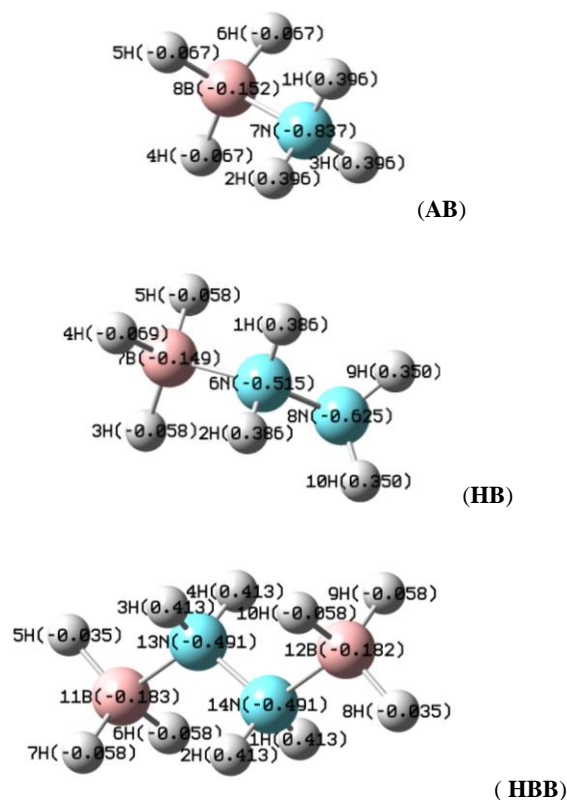


Figure 29S. NBO analysis of AB, HB and HBB.

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