

## Task-Specific Boronium Ionic Liquids as Ashless Lubricant Additives

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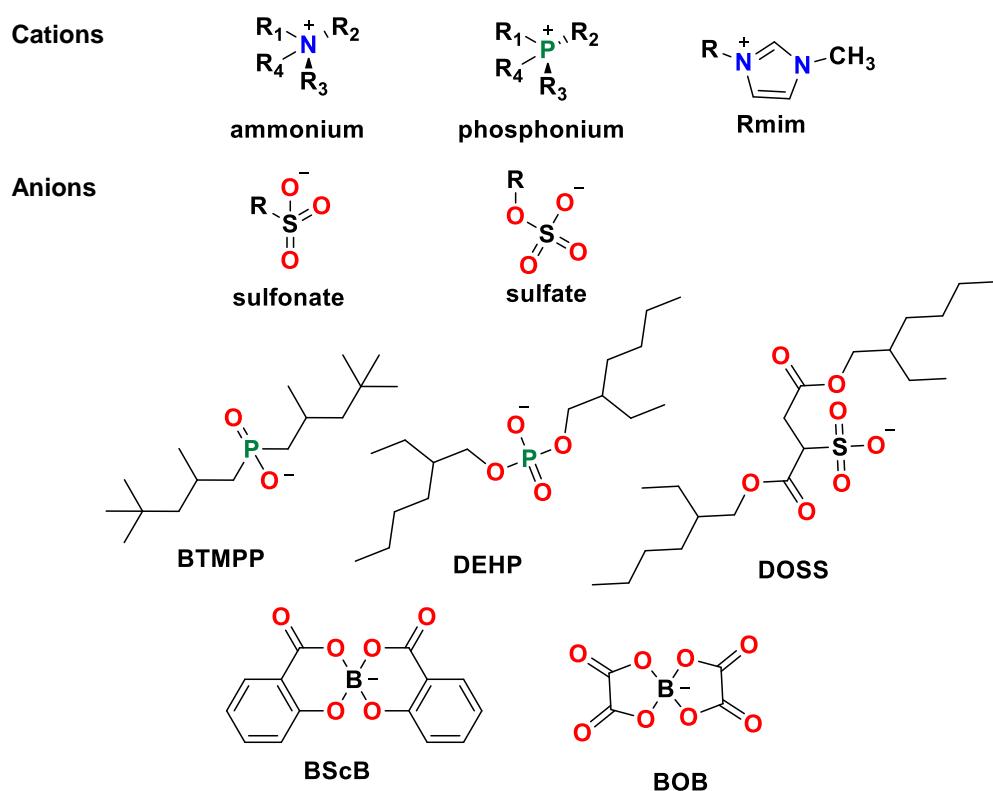
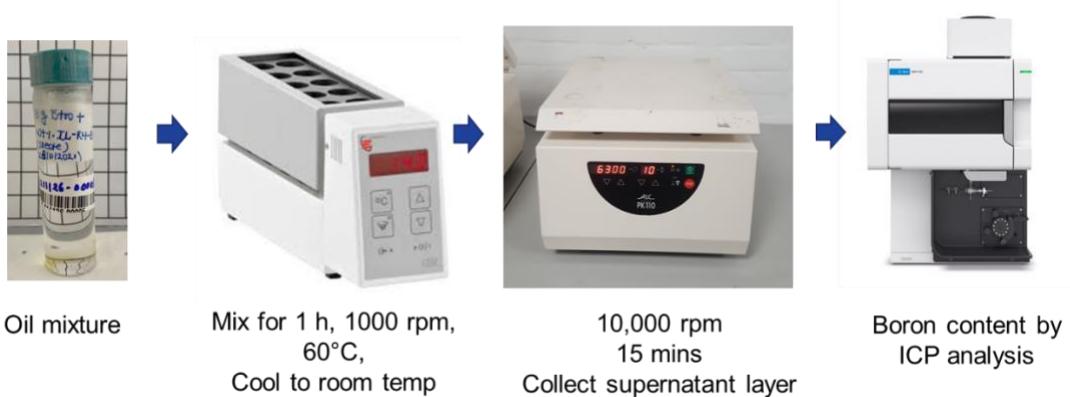
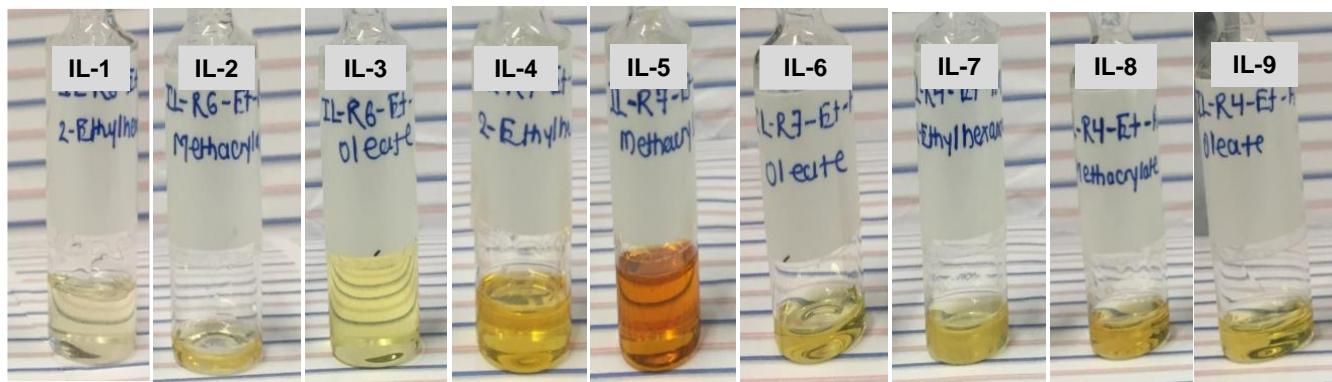


Figure S 1. Schematic representations of the commercially available cations and anions: standard ammonium, phosphonium, and dialkyl imidazolium cations and lipophilic anions, alkyl sulfonates, alkyl sulphates, or annexed from the surfactant industry, such as BTMPP, DEHP and DOSS.



**Figure S 2. Protocol of solubility measurement of boronium ILs in oil by boron content**



**Figure S 3. Photographs of nine boronium ILs.**

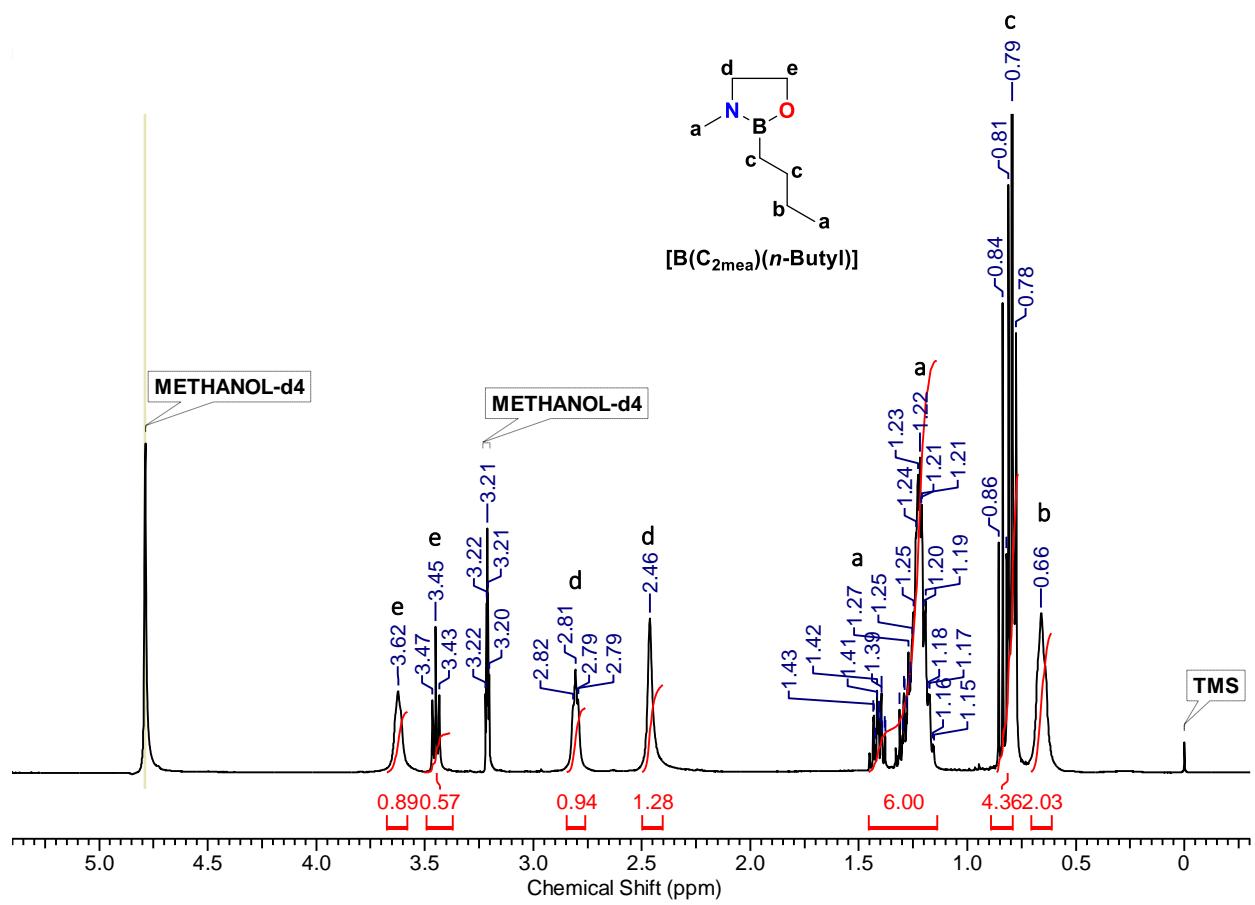
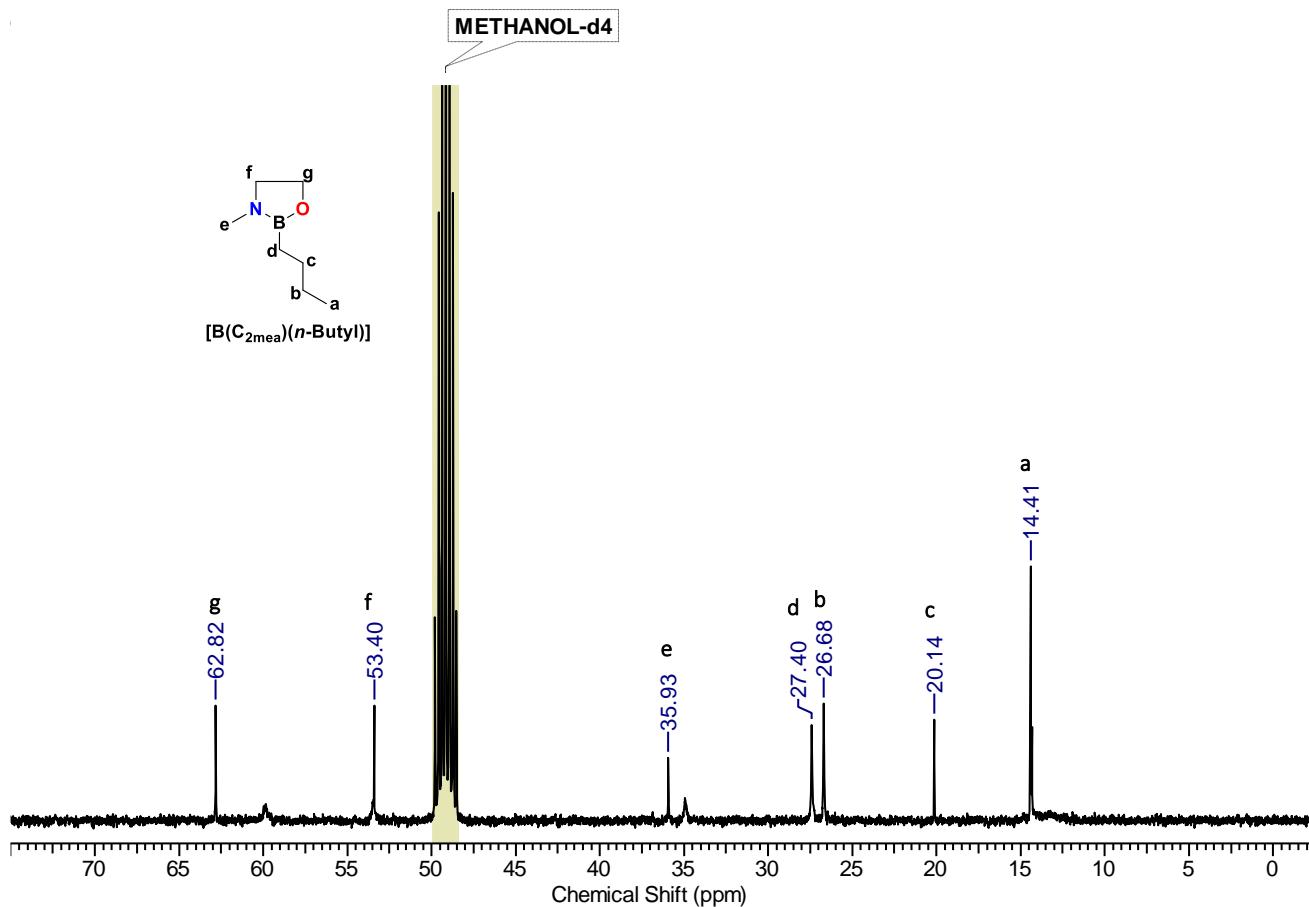
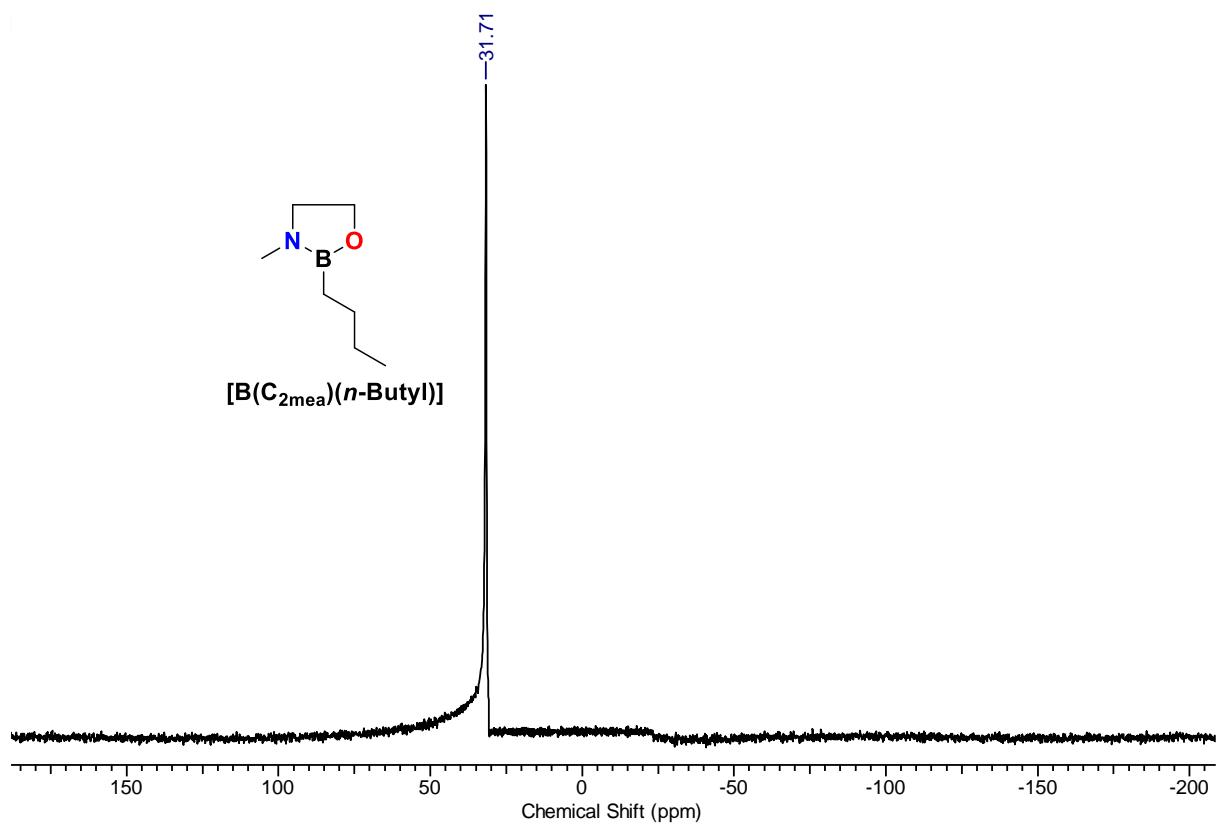


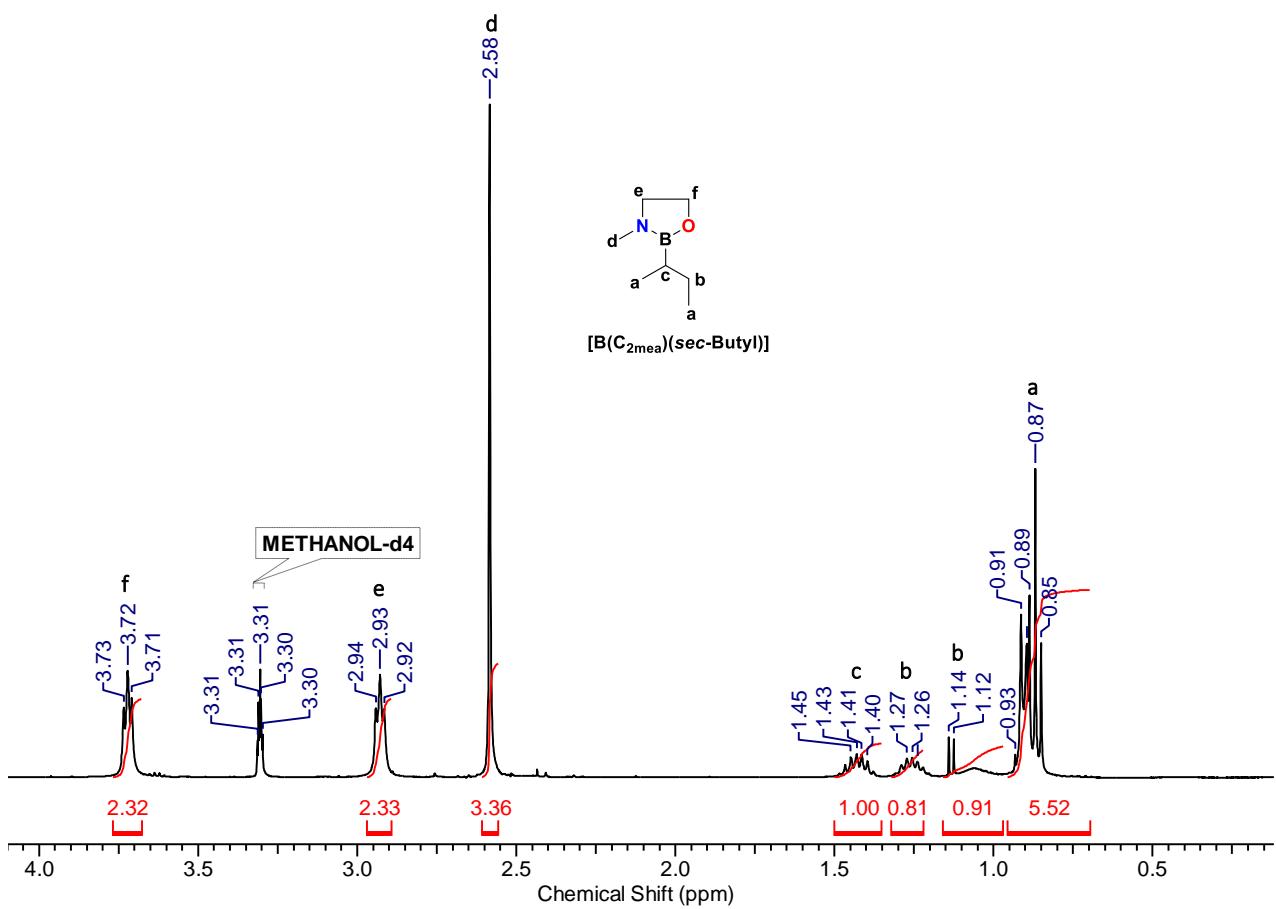
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**Figure S 5.**  $^{13}\text{C}$  NMR spectrum of  $\text{B}(\text{C}_{2\text{mea}})(n\text{-butyl})$ .

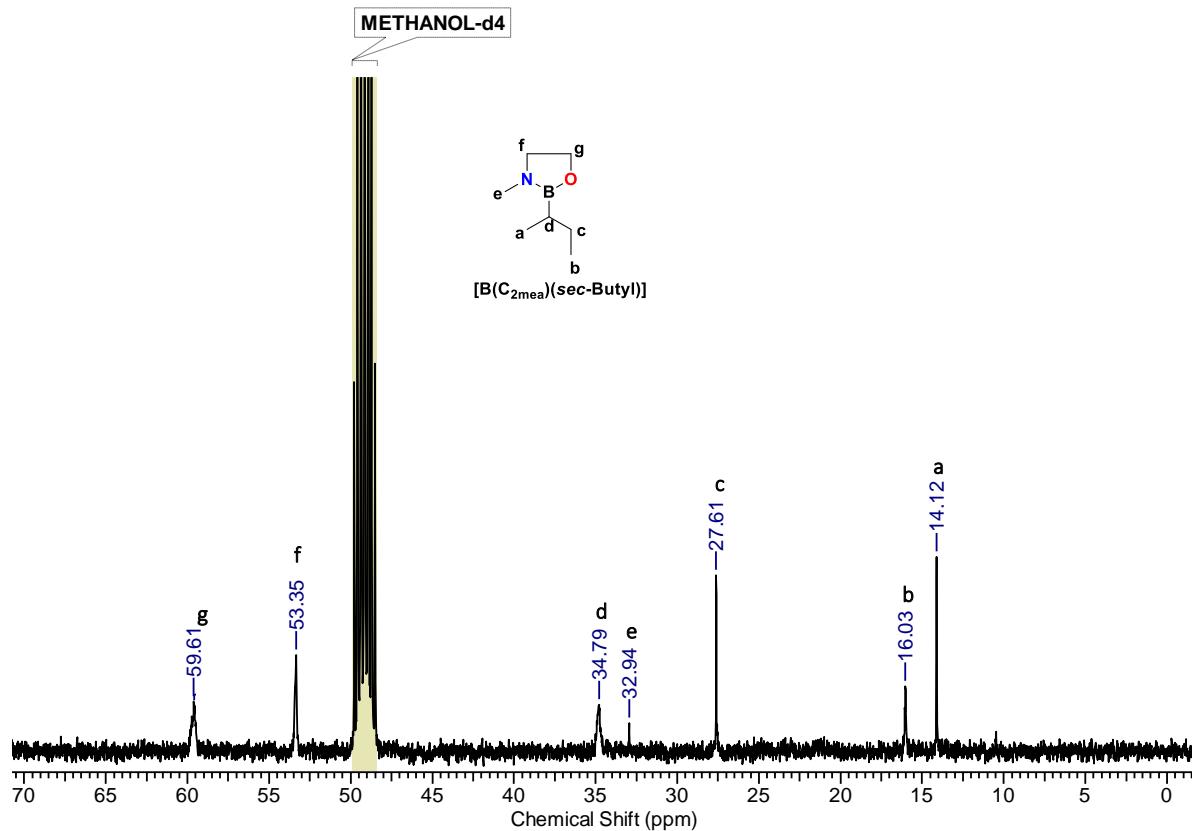


**Figure S 6.**  $^{11}\text{B}$  NMR spectrum of  $\text{B}(\text{C}_{2\text{mea}})(n\text{-butyl})$ .

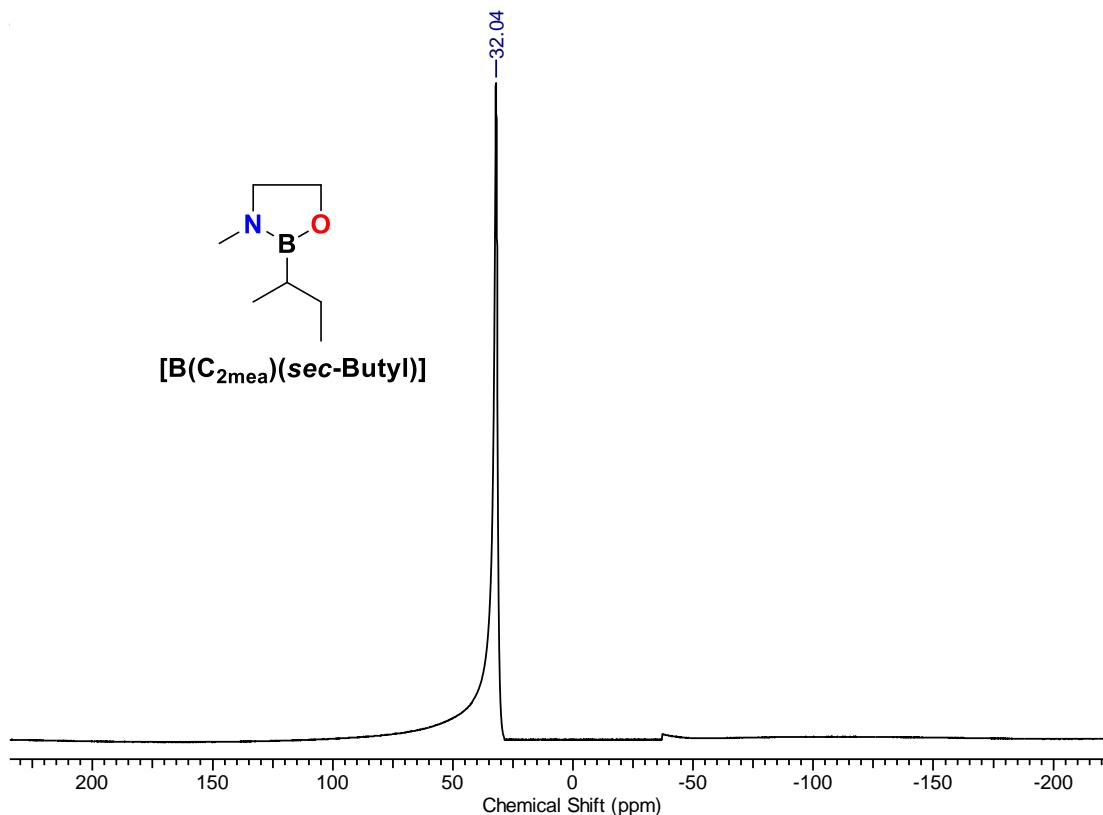


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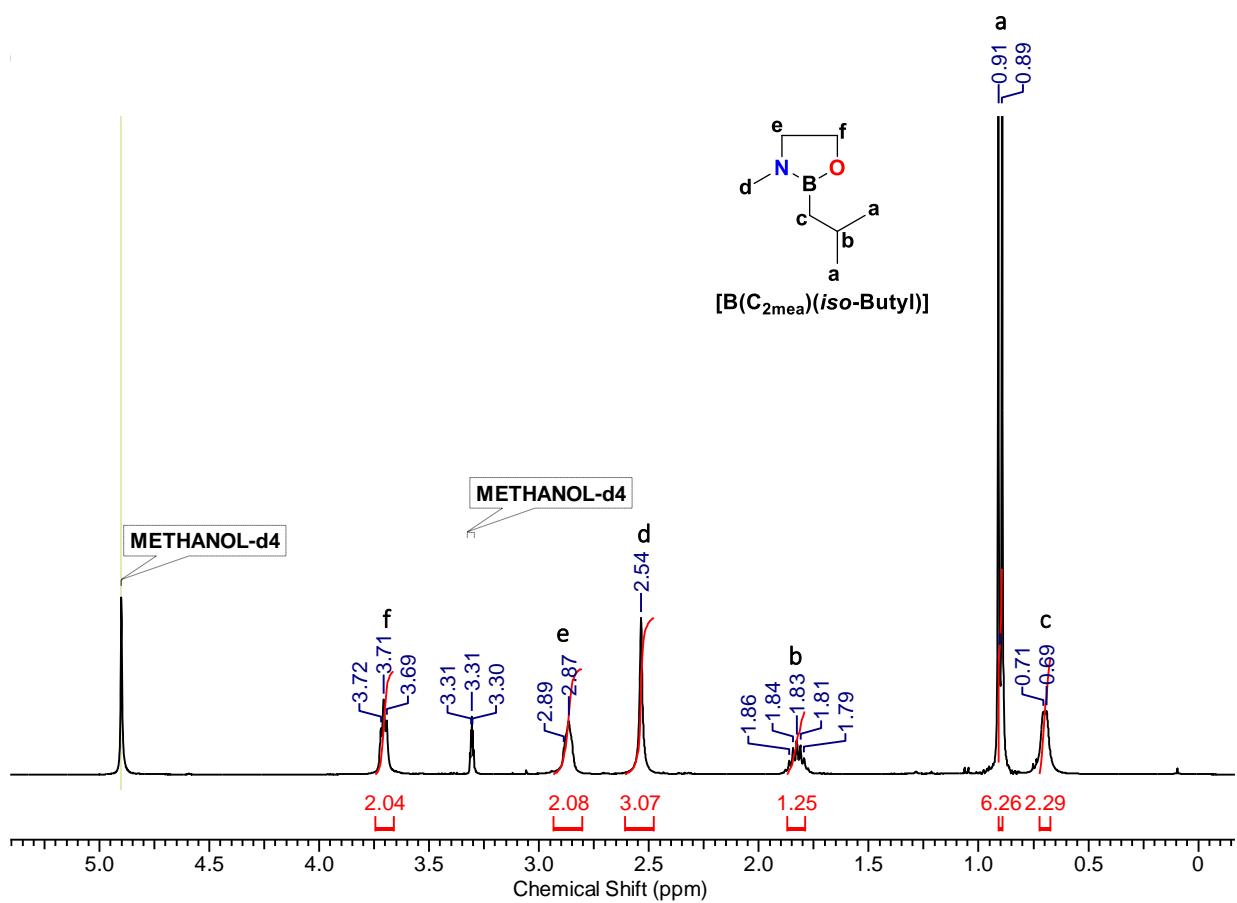
**Figure S 7.**  $^1\text{H}$  NMR spectrum of  $\text{B}(\text{C}_{2\text{mea}})(\text{sec-butyl})$ .



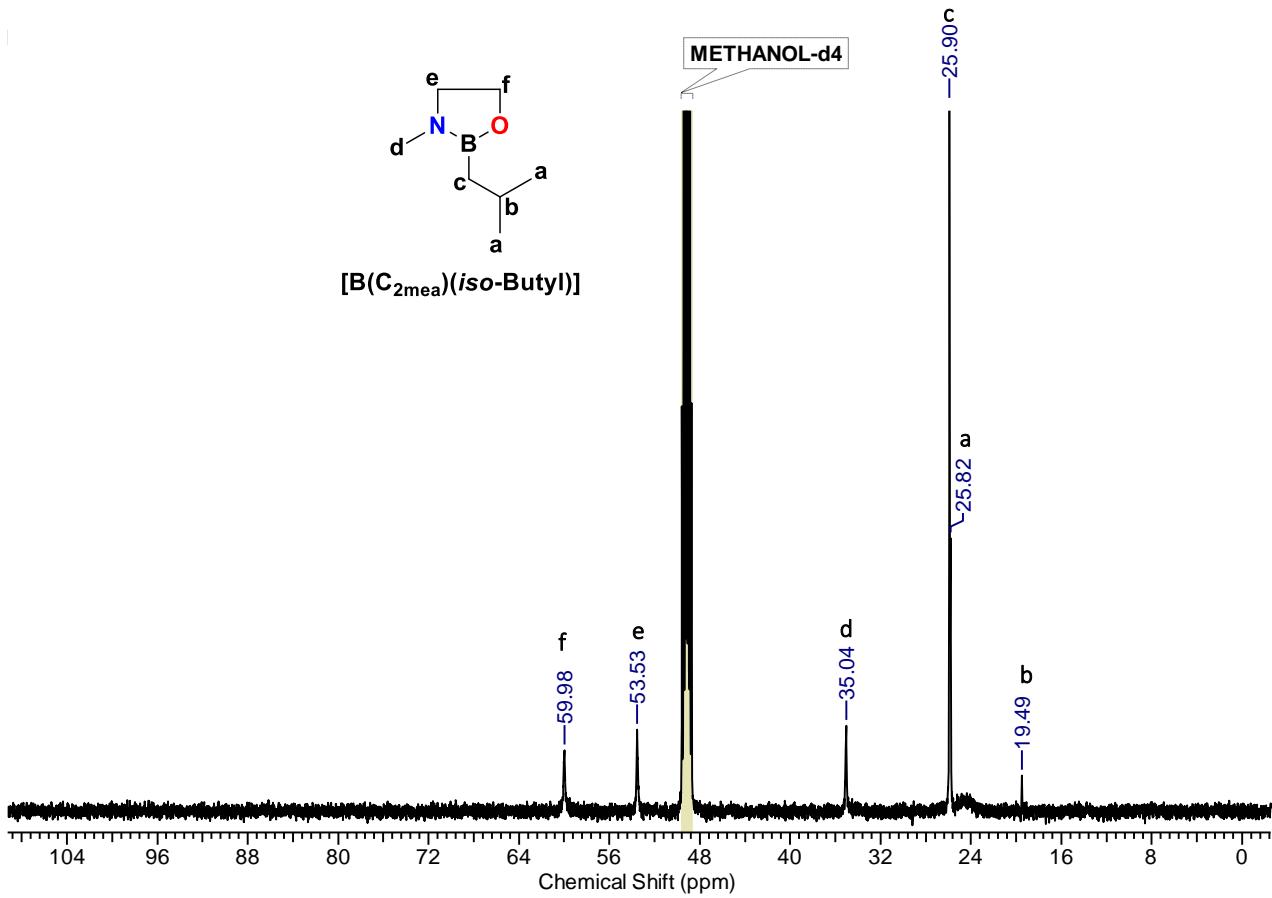
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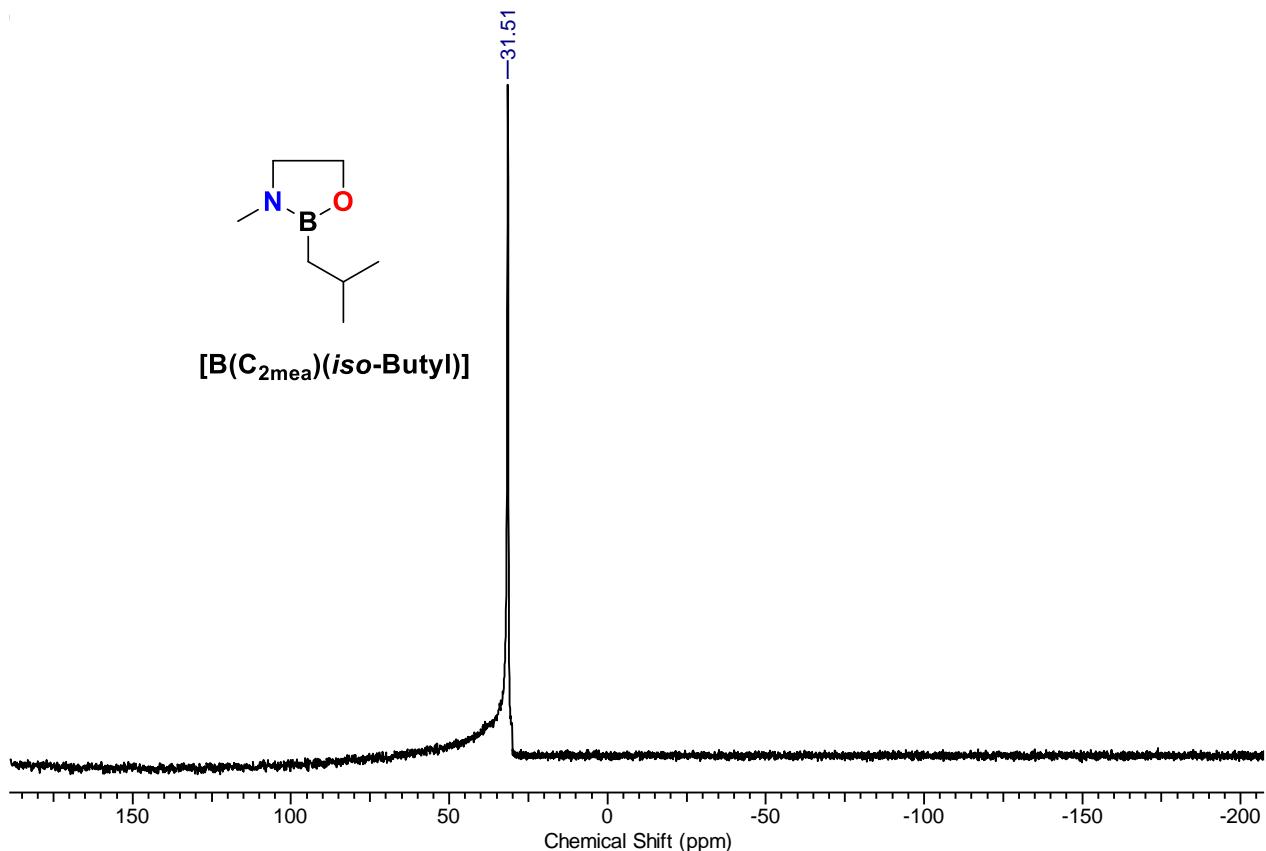
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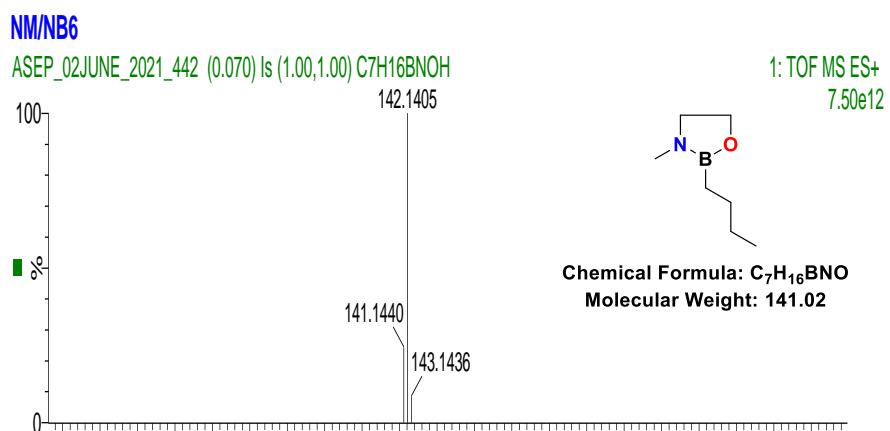
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**Figure S 11.**  $^{13}\text{C}$  NMR spectrum of  $\text{B}(\text{C}_{2\text{mea}})(\text{iso-butyl})$ .



**Figure S 12.**  $^{11}\text{B}$  NMR spectrum of  $\text{B}(\text{C}_{2\text{mea}})(\text{iso-butyl})$ .



**Figure S 13.** Mass spectrum of  $\text{B}(\text{C}_{2\text{mea}})(n\text{-butyl})$ .

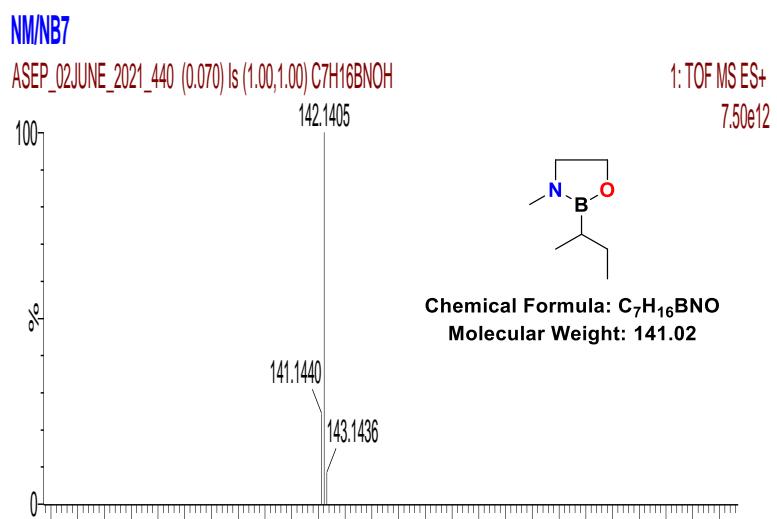


Figure S 14. Mass spectrum of B(C<sub>2</sub>mea)(sec-butyl).

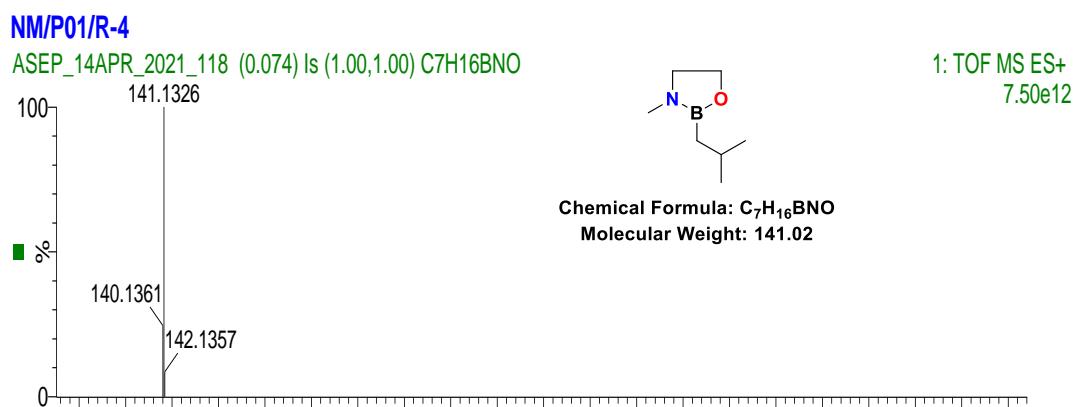


Figure S 15. Mass spectrum of B(C<sub>2</sub>mea)(iso-butyl).

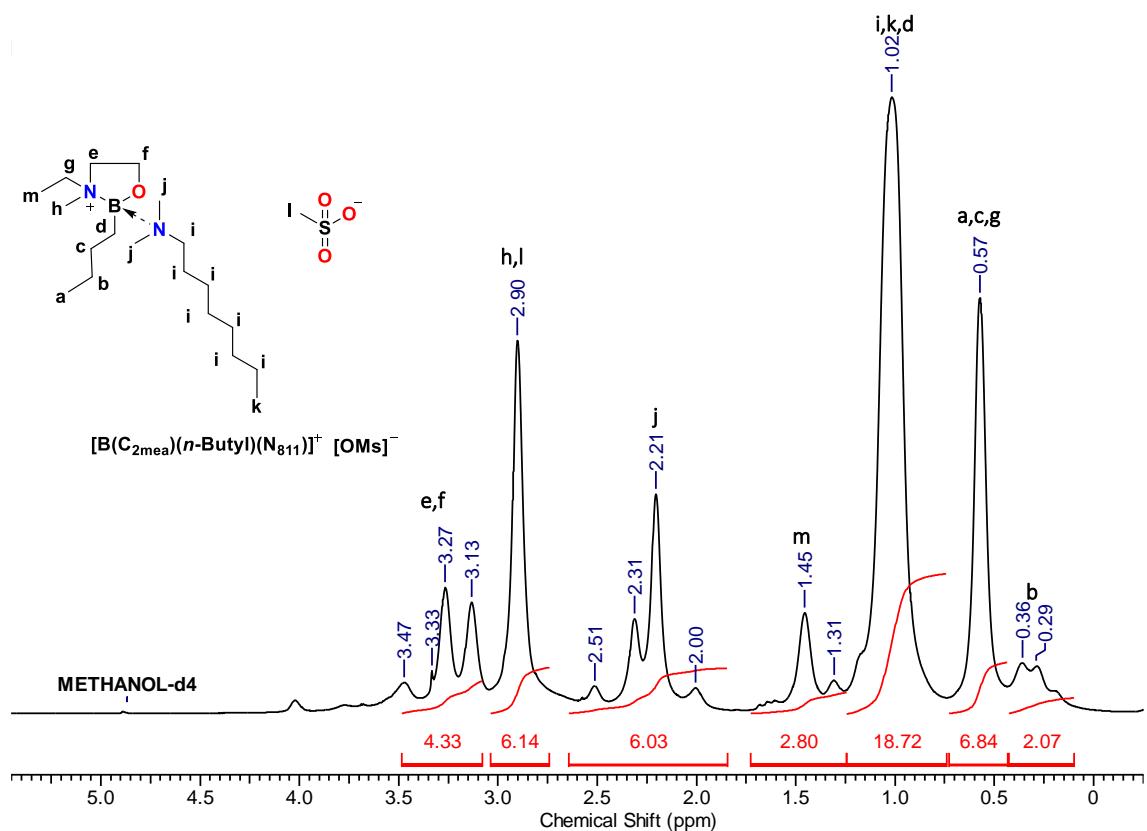


Figure S 16. <sup>1</sup>H NMR spectrum of [B(C<sub>2</sub>mea)(n-Butyl)(N<sub>8</sub>11)][OMs].

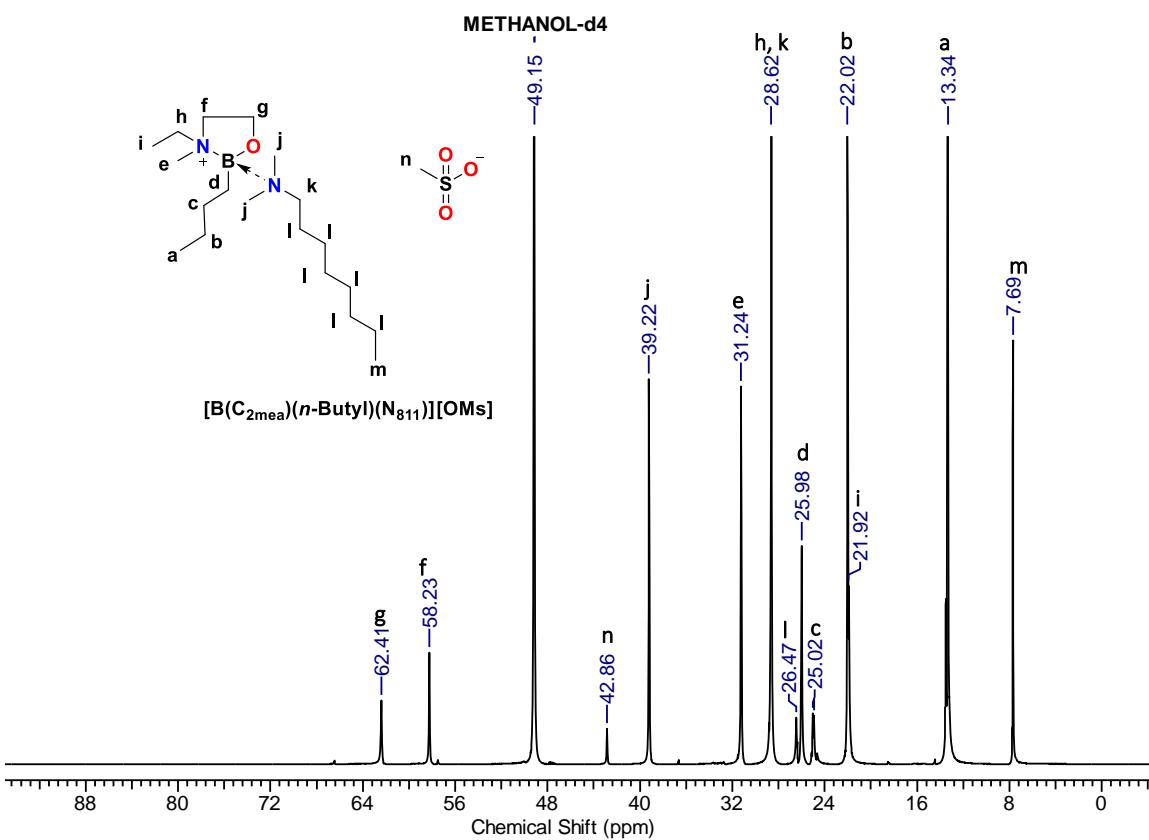
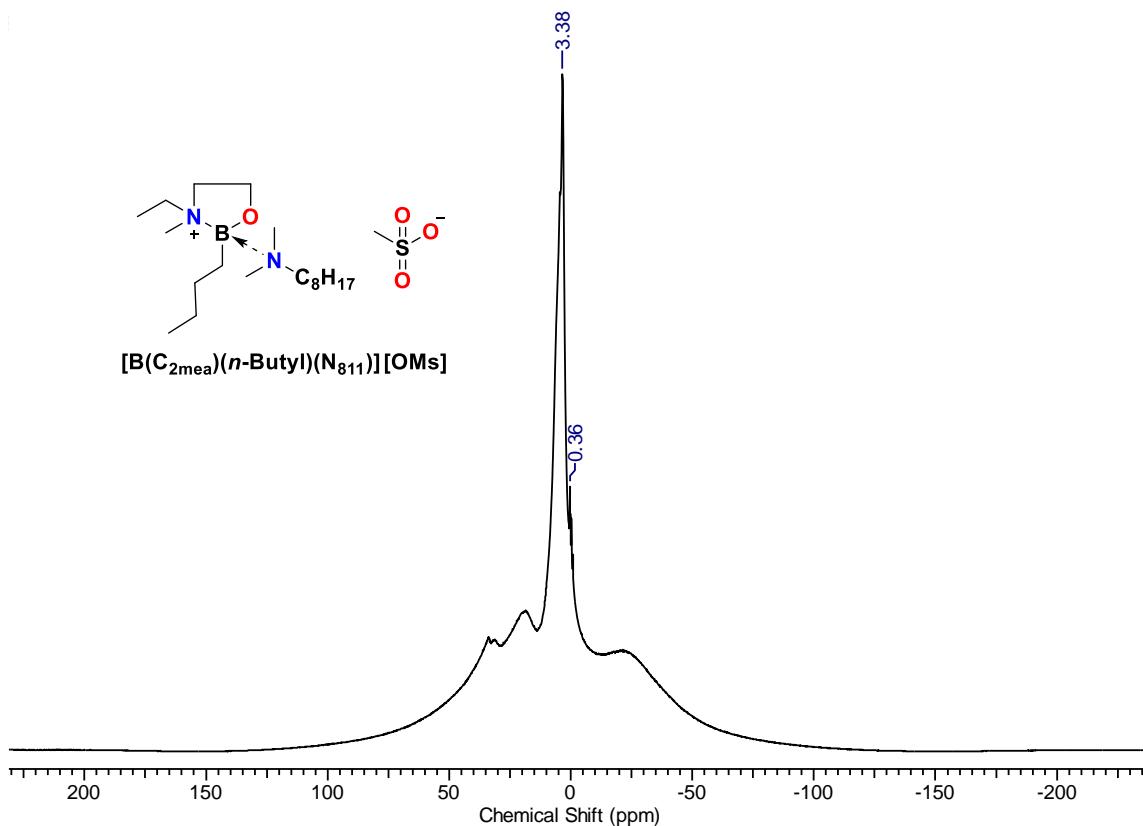
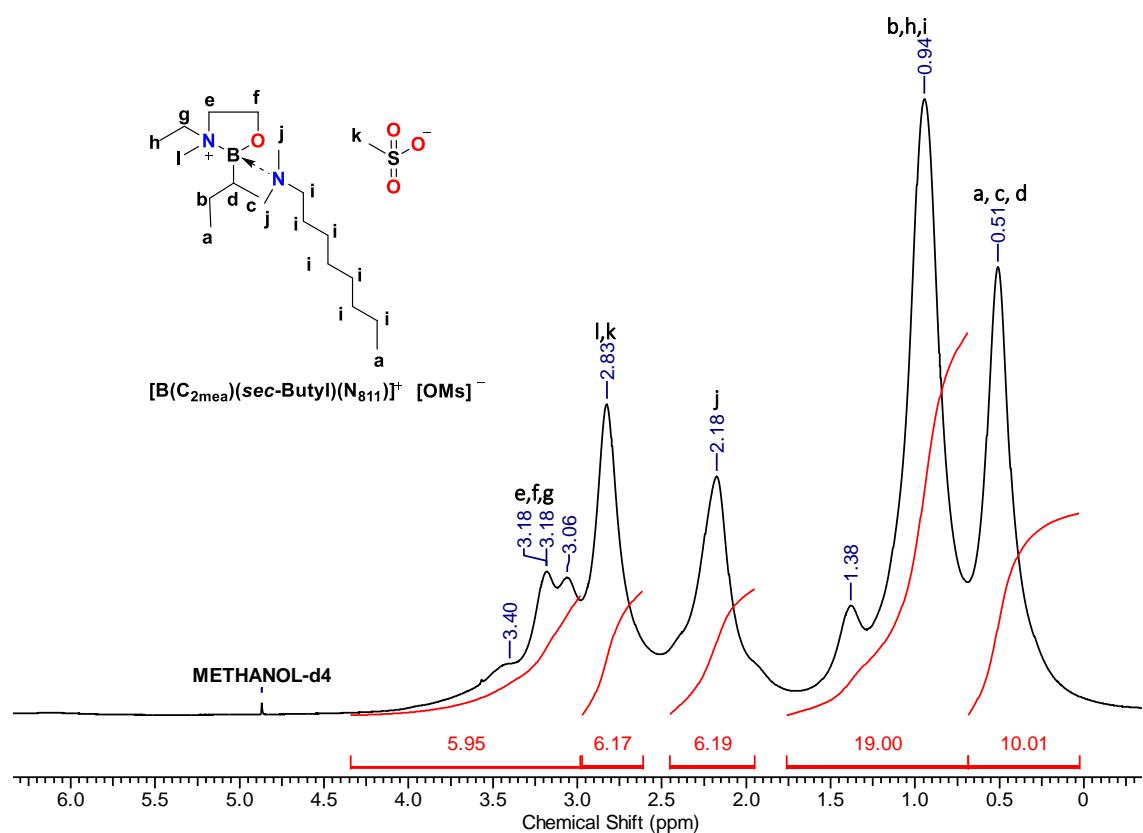


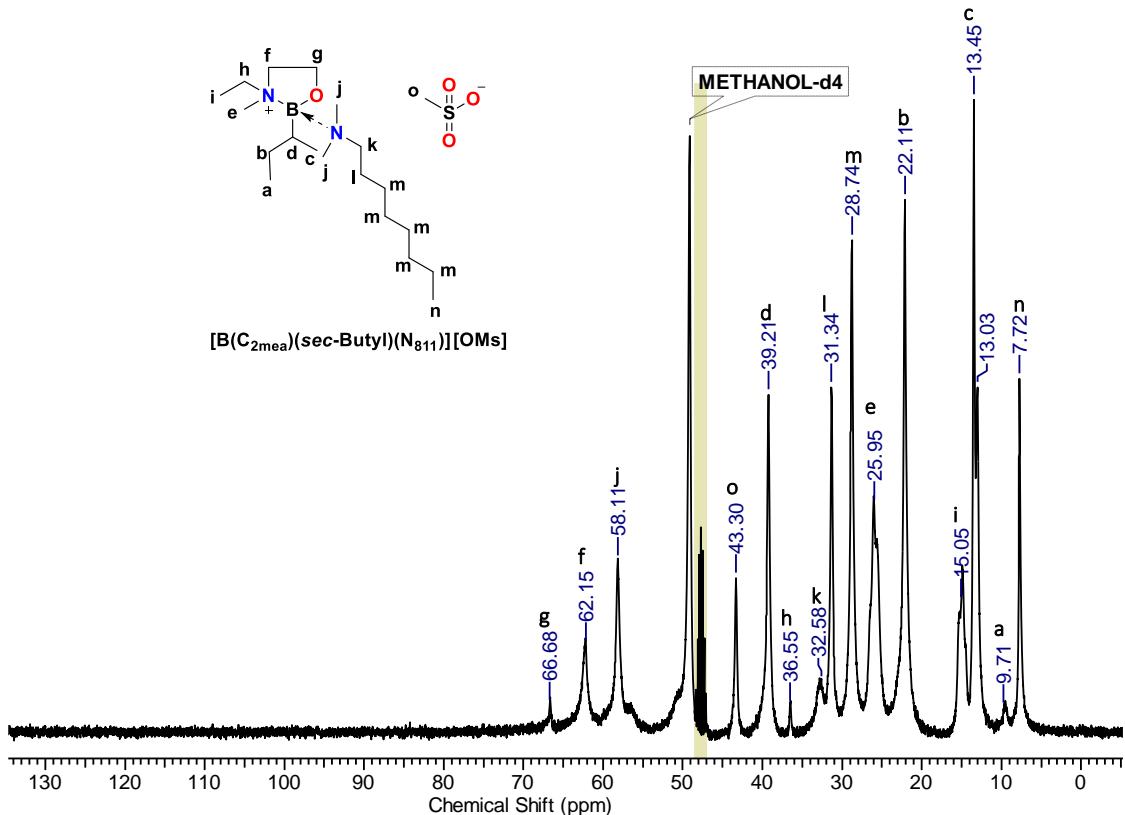
Figure S 17. <sup>13</sup>C NMR spectrum of [B(C<sub>2</sub>mea)(n-Butyl)(N<sub>8</sub>11)][OMs].



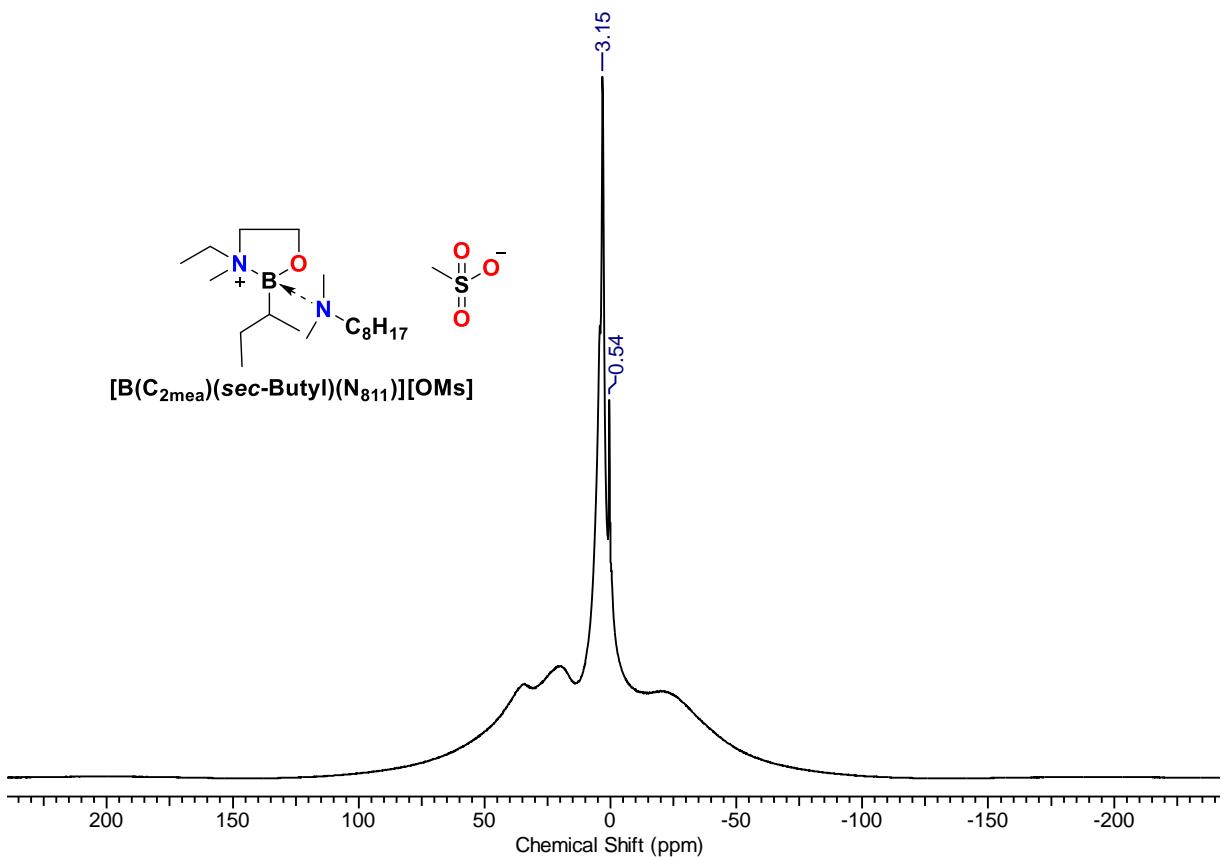
**Figure S 18.**  $^{11}\text{B}$  NMR spectrum of  $[\text{B}(\text{C}_{2\text{mea}})(n\text{-Butyl})(\text{N}_{811})][\text{OMs}]$ .



**Figure S 19.**  $^1\text{H}$  NMR spectrum of  $[\text{B}(\text{C}_{2\text{mea}})(\text{sec-Butyl})(\text{N}_{811})][\text{OMs}]$ .



**Figure S 20.**  $^{13}\text{C}$  NMR spectrum of  $[\text{B}(\text{C}_{2\text{mea}})(\text{sec-butyl})(\text{N}_{811})][\text{OMs}]$ .



**Figure S 21.**  $^{11}\text{B}$  NMR spectrum of  $[\text{B}(\text{C}_{2\text{mea}})(\text{sec-butyl})(\text{N}_{811})][\text{OMs}]$ .

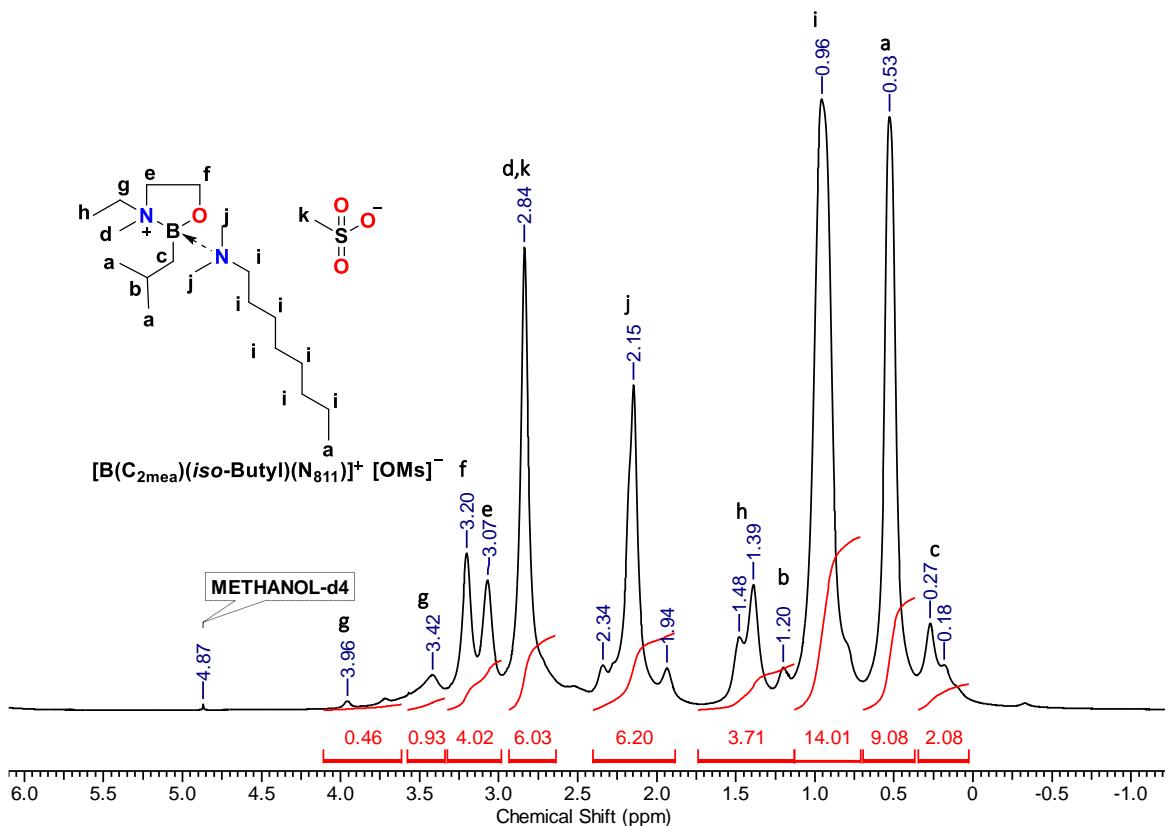


Figure S 22. <sup>1</sup>H NMR spectrum of  $[B(C_{2\text{mea}})(\text{iso-butyl})(N_{811})][\text{OMs}]$ .

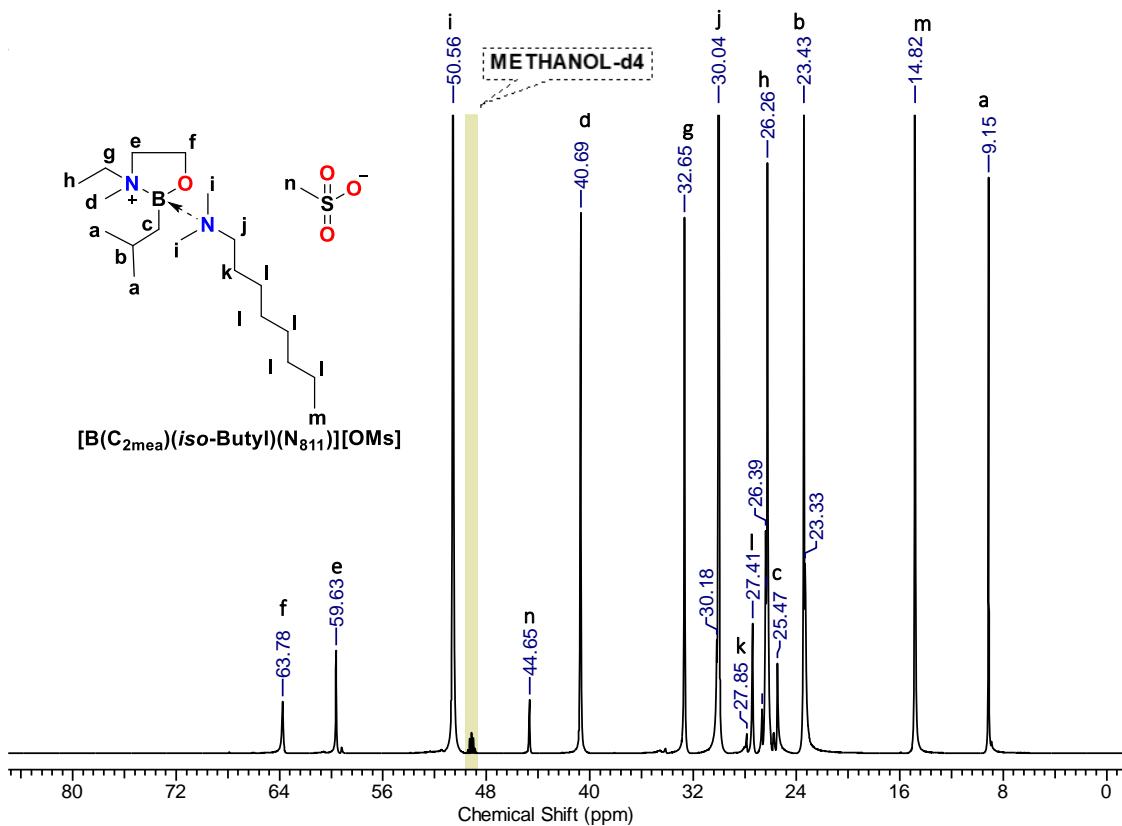
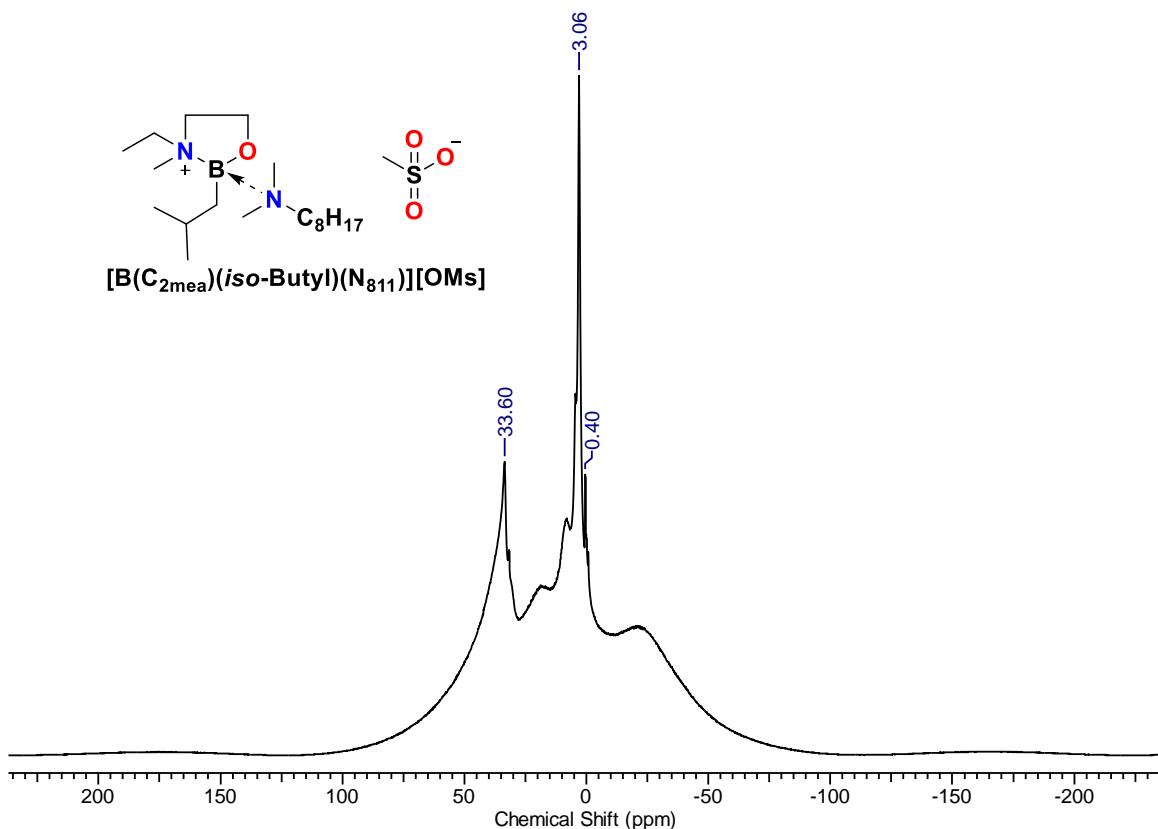
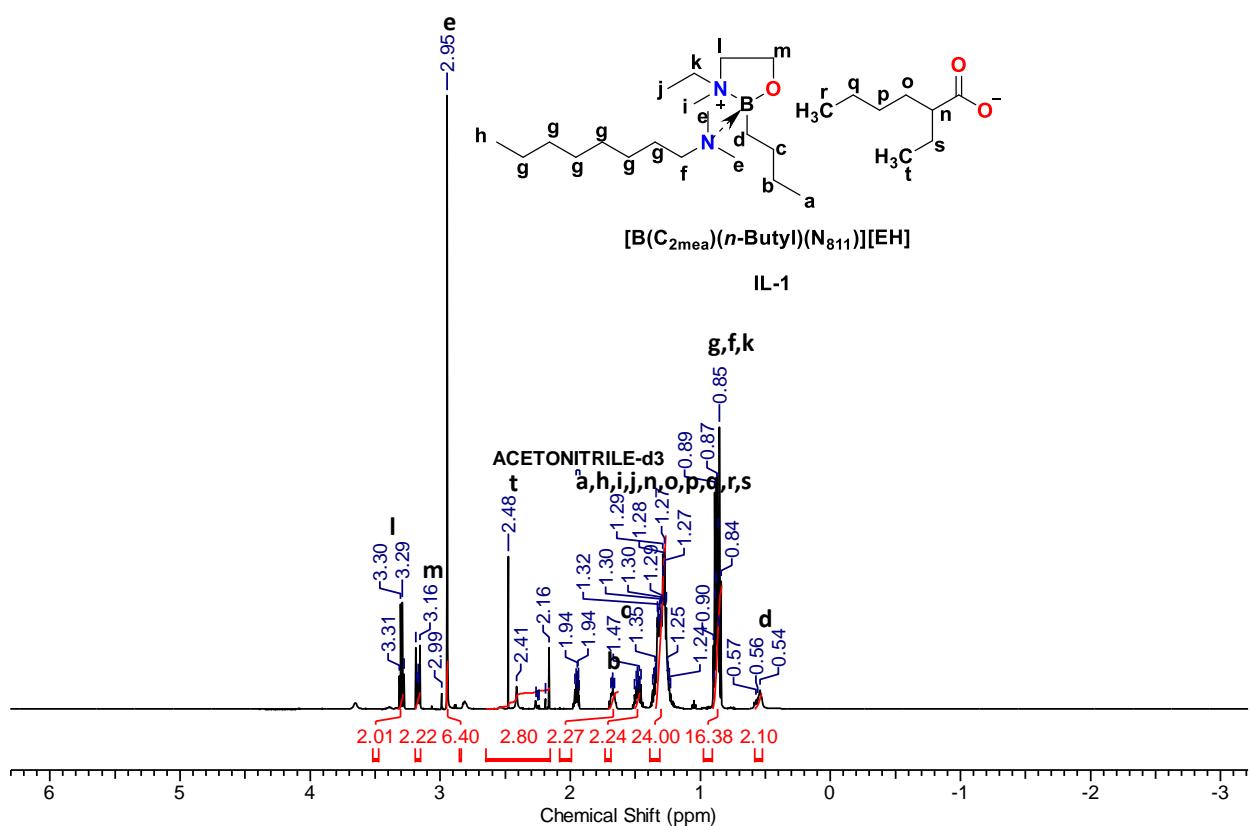


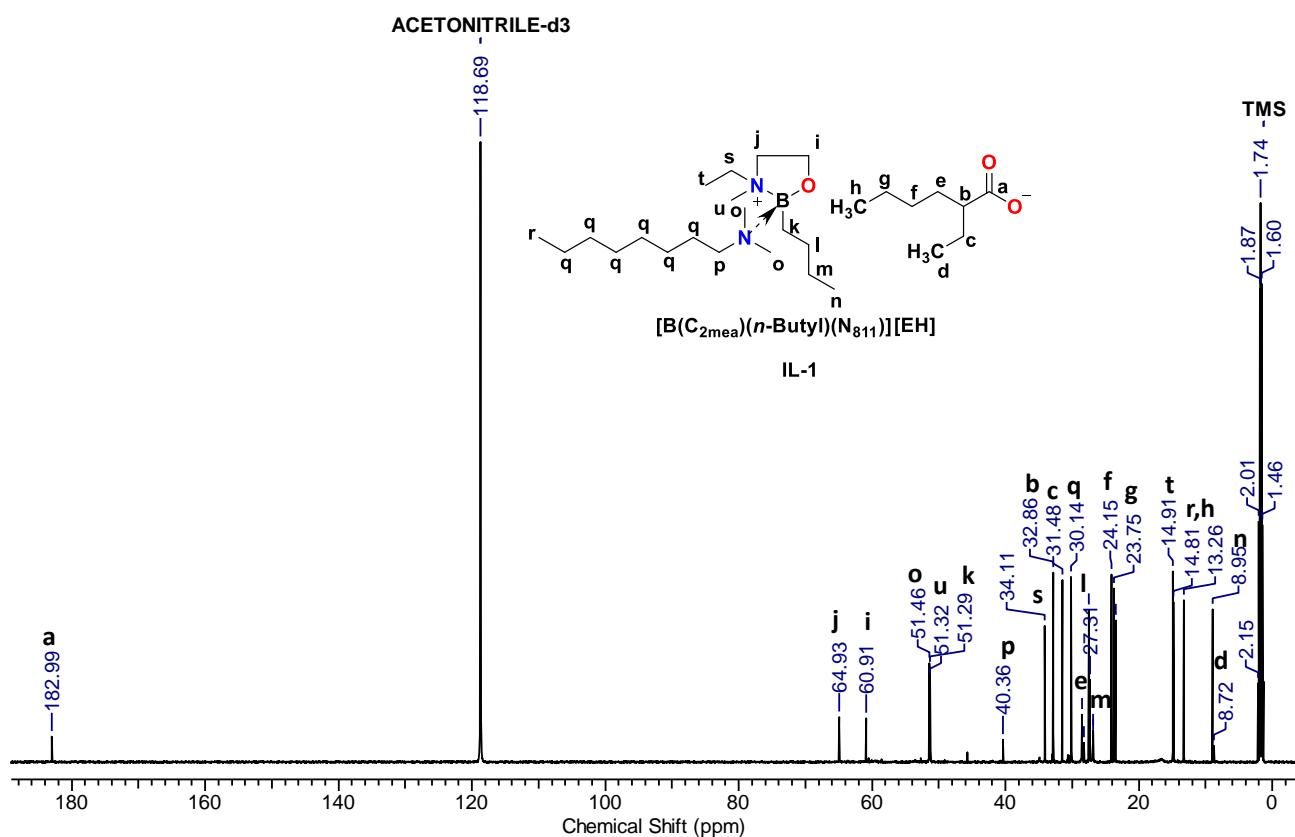
Figure S 23. <sup>13</sup>C NMR spectrum of  $[B(C_{2\text{mea}})(\text{iso-butyl})(N_{811})][\text{OMs}]$ .



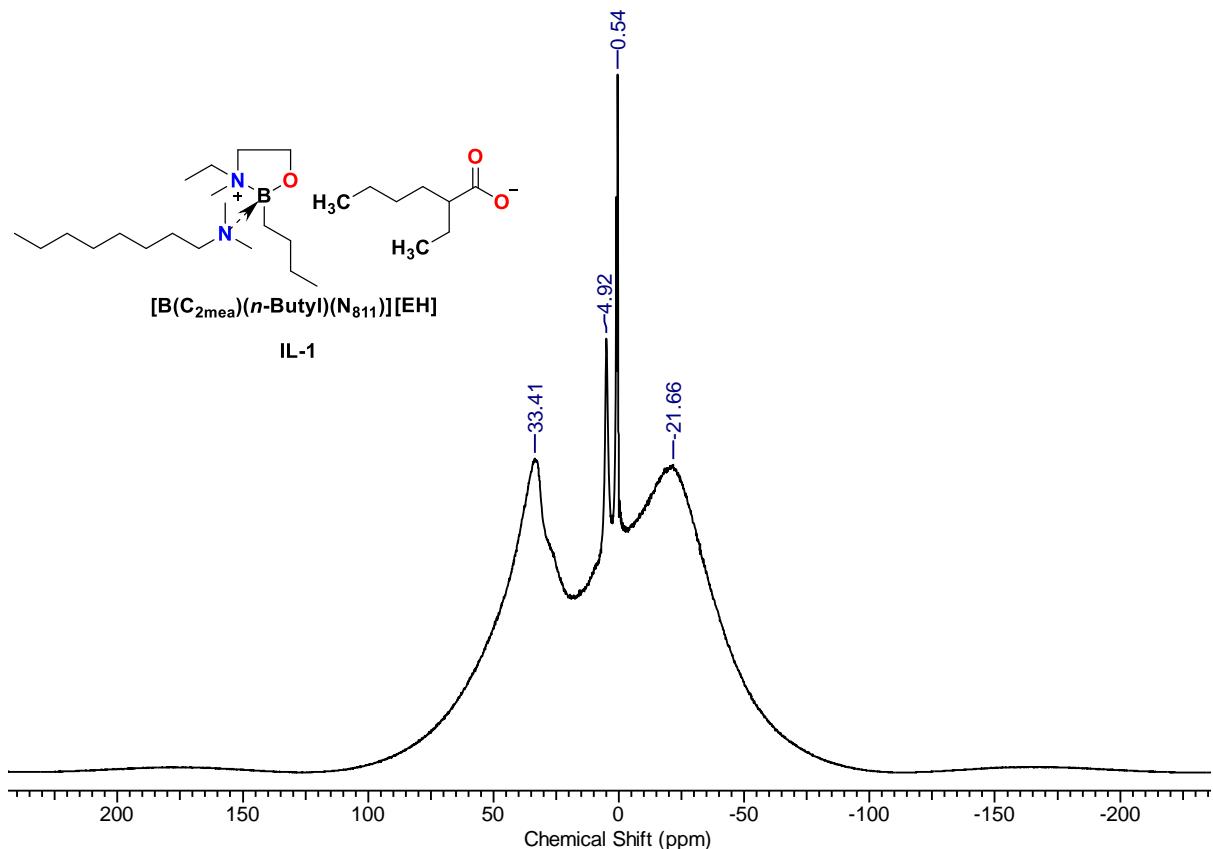
**Figure S 24.**  $^{11}\text{B}$  NMR spectrum of  $[\text{B}(\text{C}_2\text{mea})(\text{iso-Butyl})(\text{N}_{811})][\text{OMs}]$ .



**Figure S 25.**  $^1\text{H}$  NMR spectrum of IL-1  $[\text{B}(\text{C}_2\text{mea})(n\text{-Butyl})(\text{N}_{811})][\text{EH}]$ .



**Figure S 26.** <sup>13</sup>C NMR spectrum of IL-1 [B(C<sub>2</sub>mea)(n-butyl)(N<sub>811</sub>)][EH].



**Figure S 27.** <sup>11</sup>B NMR spectrum of IL-1 [B(C<sub>2</sub>mea)(n-butyl)(N<sub>811</sub>)][EH].

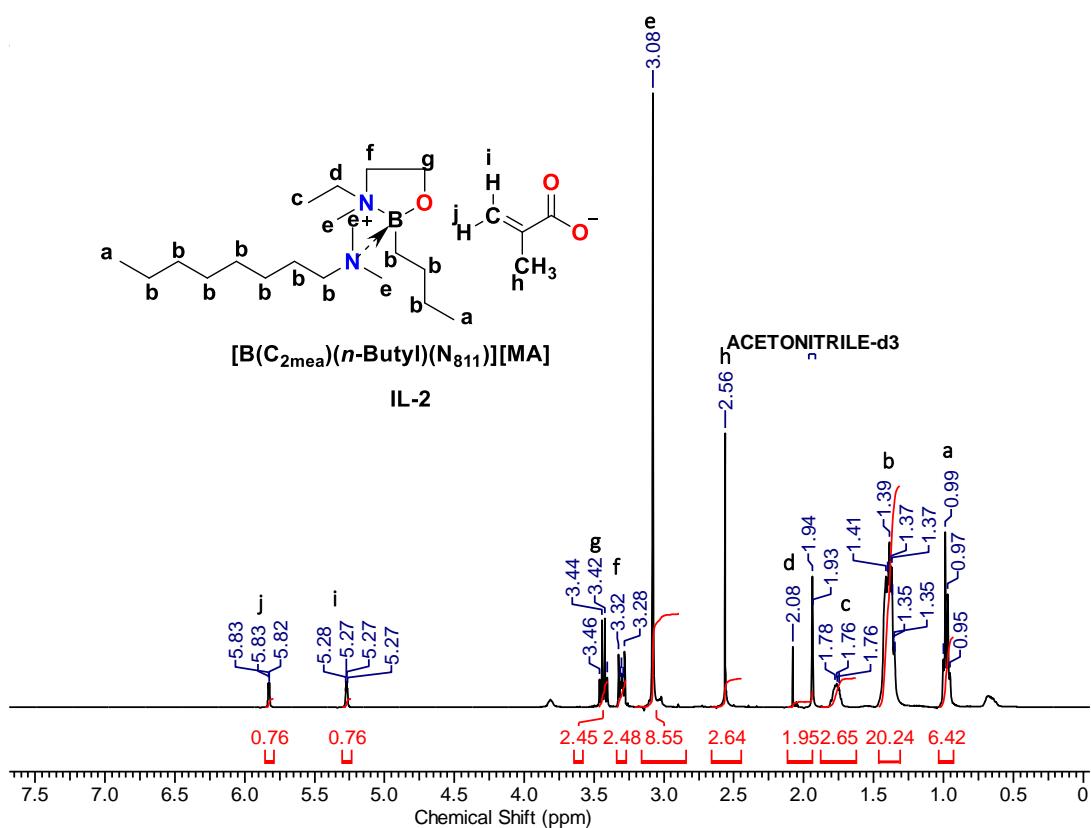


Figure S 28. <sup>1</sup>H NMR spectrum of IL-2 [B(C<sub>2</sub>mea)(n-Butyl)(N<sub>811</sub>)][MA].

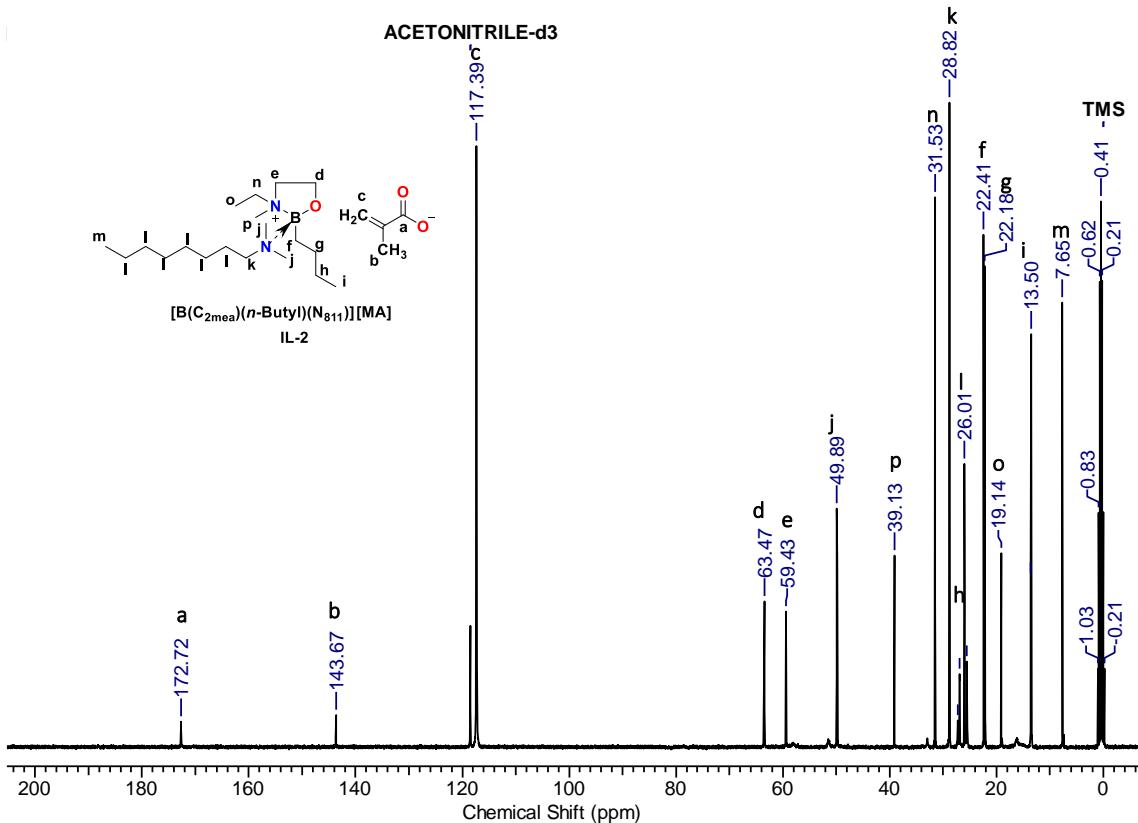
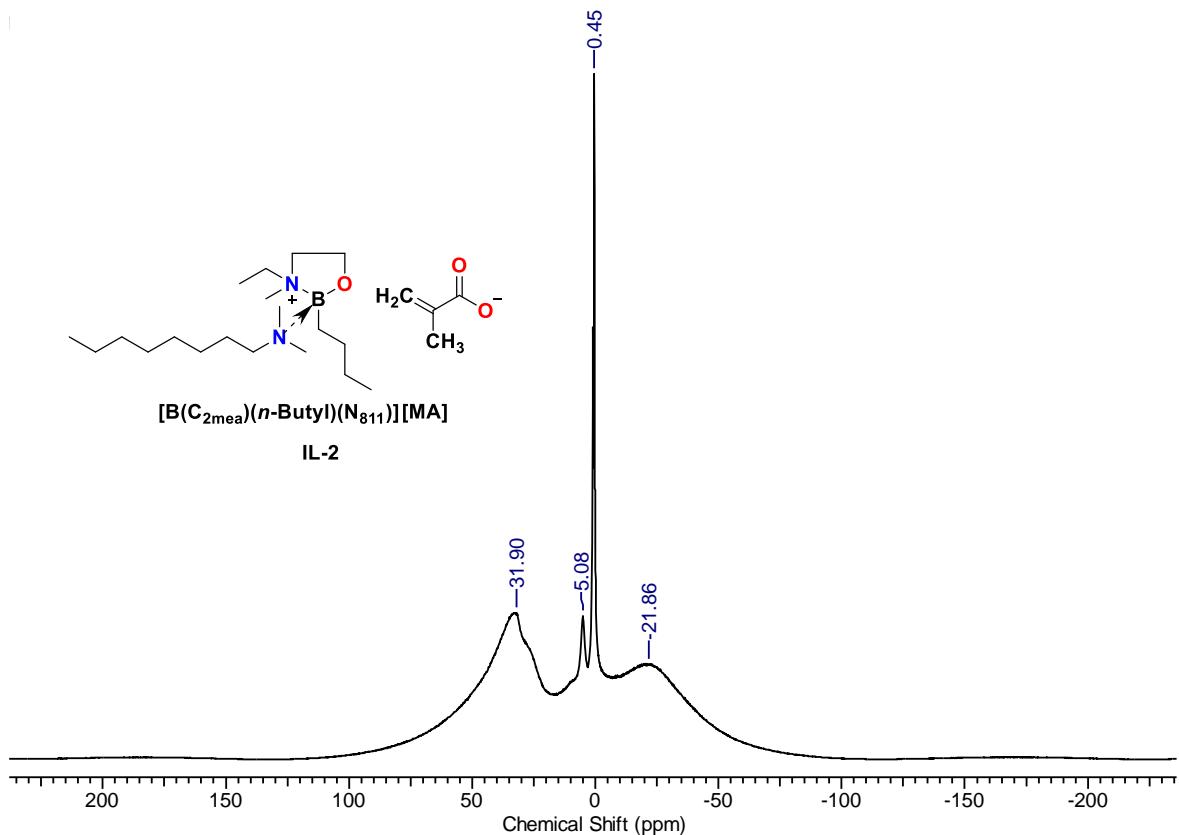
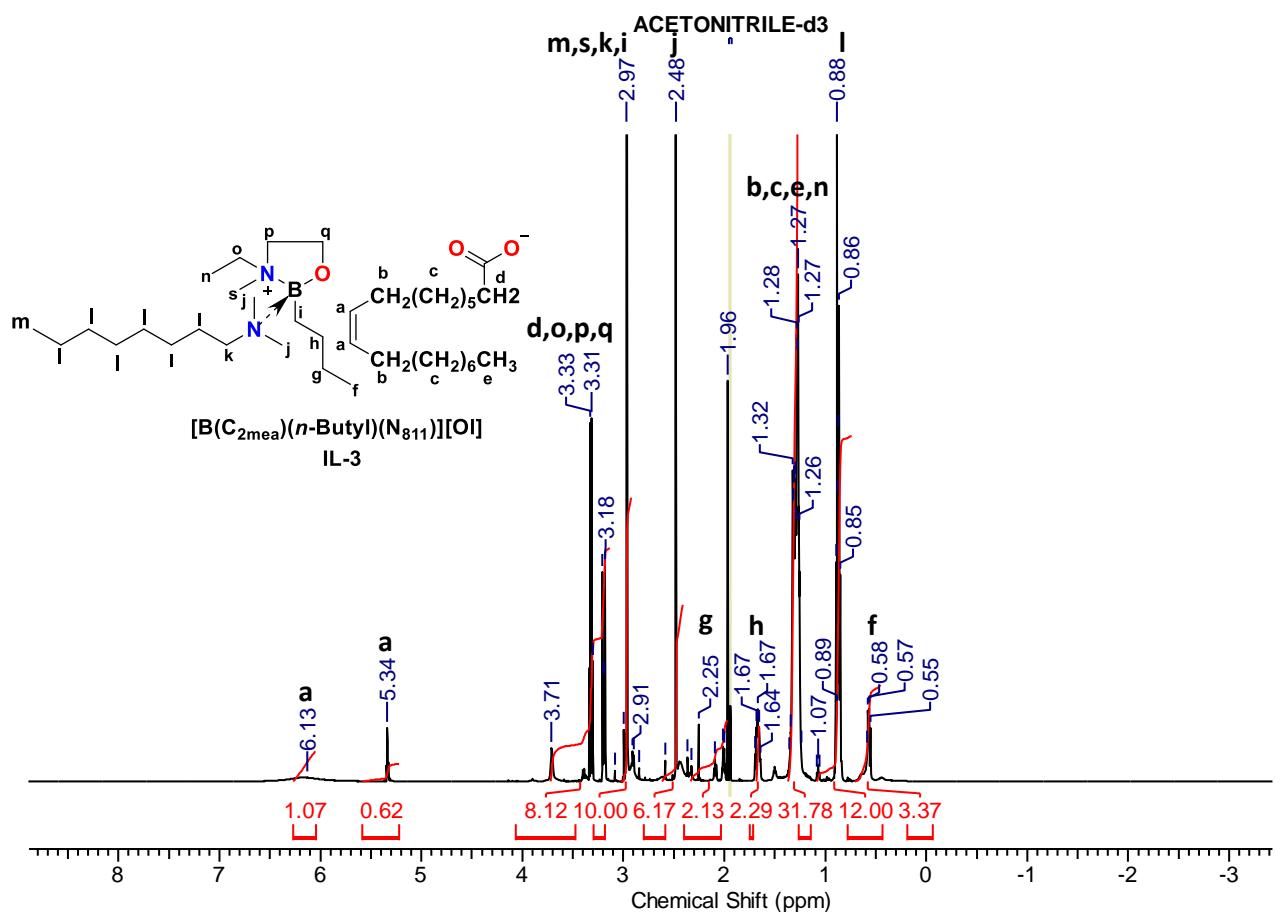


Figure S 29. <sup>13</sup>C NMR spectrum of IL-2 [B(C<sub>2</sub>mea)(n-Butyl)(N<sub>811</sub>)][MA].



**Figure S 30.**  $^{11}\text{B}$  NMR spectrum of IL-2  $[\text{B}(\text{C}_{2\text{mea}})(n\text{-Butyl})(\text{N}_{811})][\text{MA}]$ .



**Figure S 31.**  $^1\text{H}$  NMR spectrum of IL-3  $[\text{B}(\text{C}_{2\text{mea}})(n\text{-Butyl})(\text{N}_{811})][\text{OI}]$ .

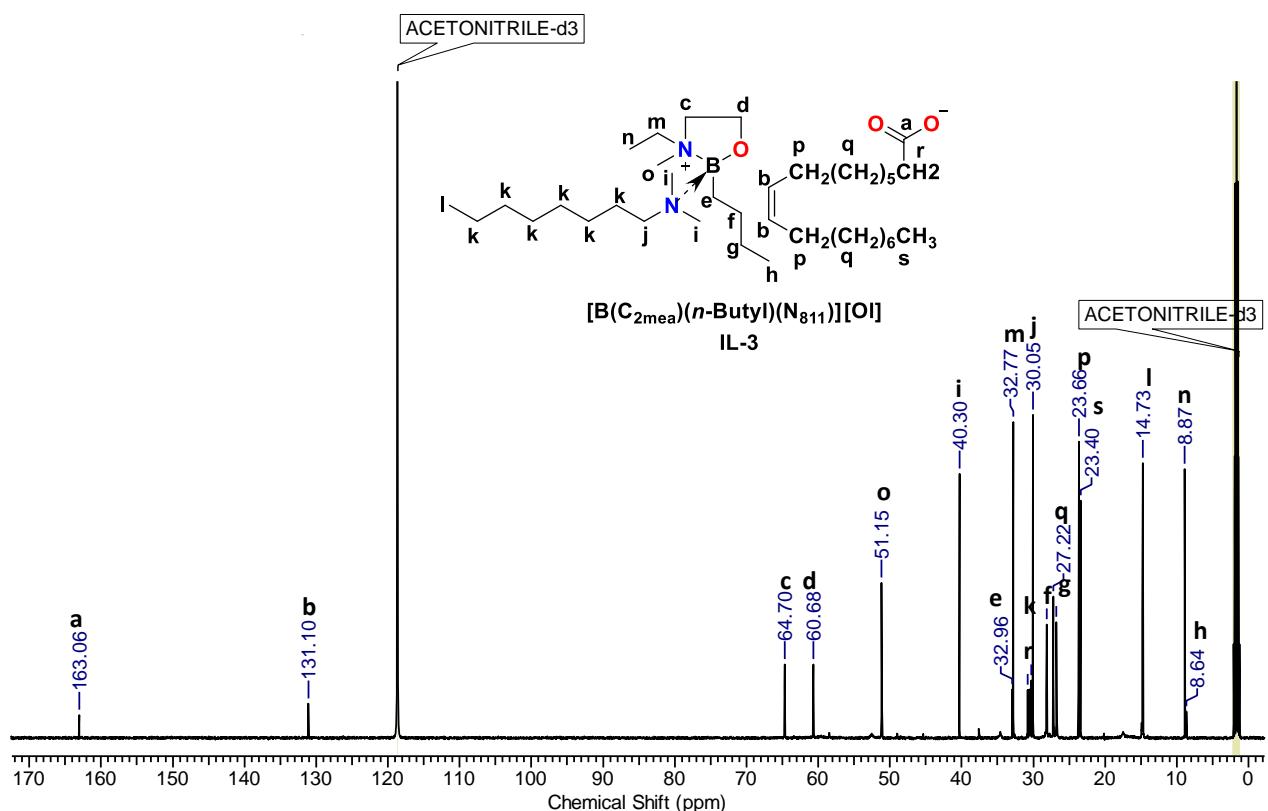


Figure S 32.  $^{13}\text{C}$  NMR spectrum of IL-3 [ $\text{B}(\text{C}_{2\text{mea}})(n\text{-Butyl})(\text{N}_{811})\text{][OI]}$ .

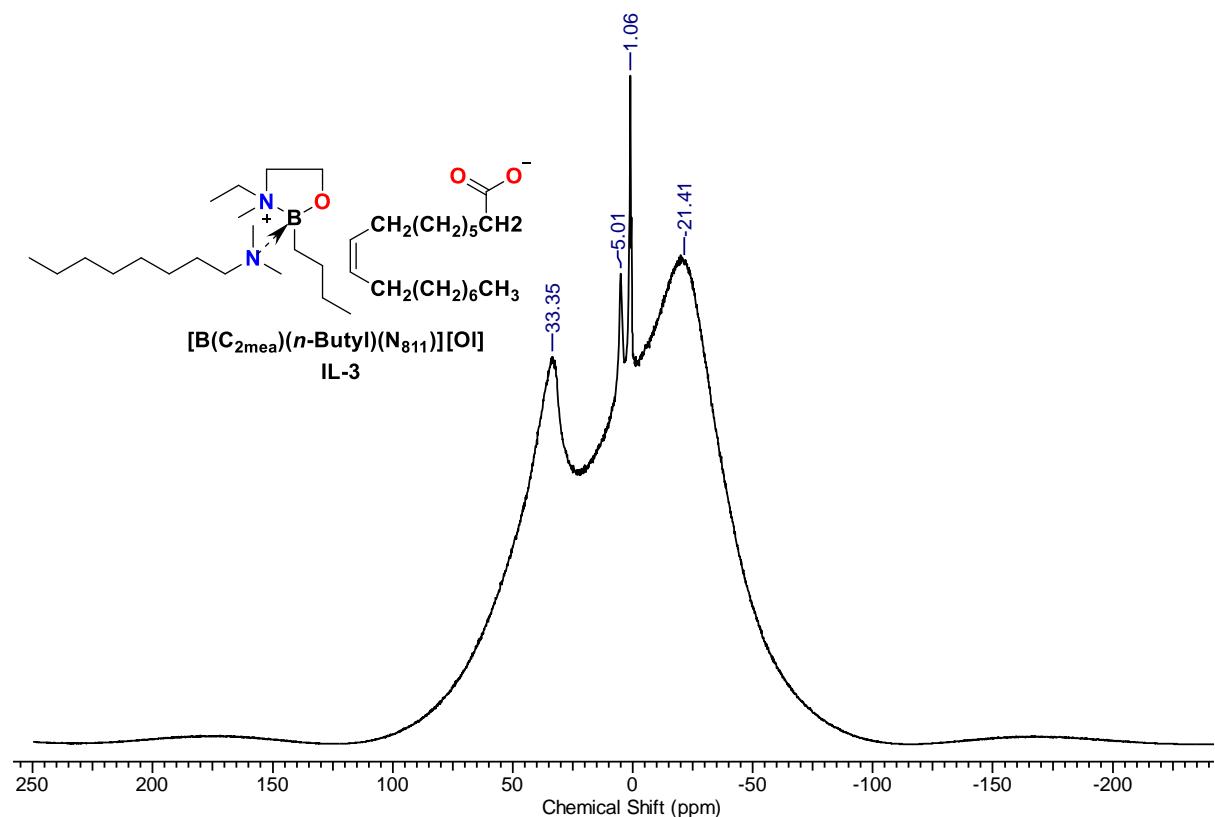


Figure S 33.  $^{11}\text{B}$  NMR spectrum of IL-3 [ $\text{B}(\text{C}_{2\text{mea}})(n\text{-Butyl})(\text{N}_{811})\text{][OI]}$ .

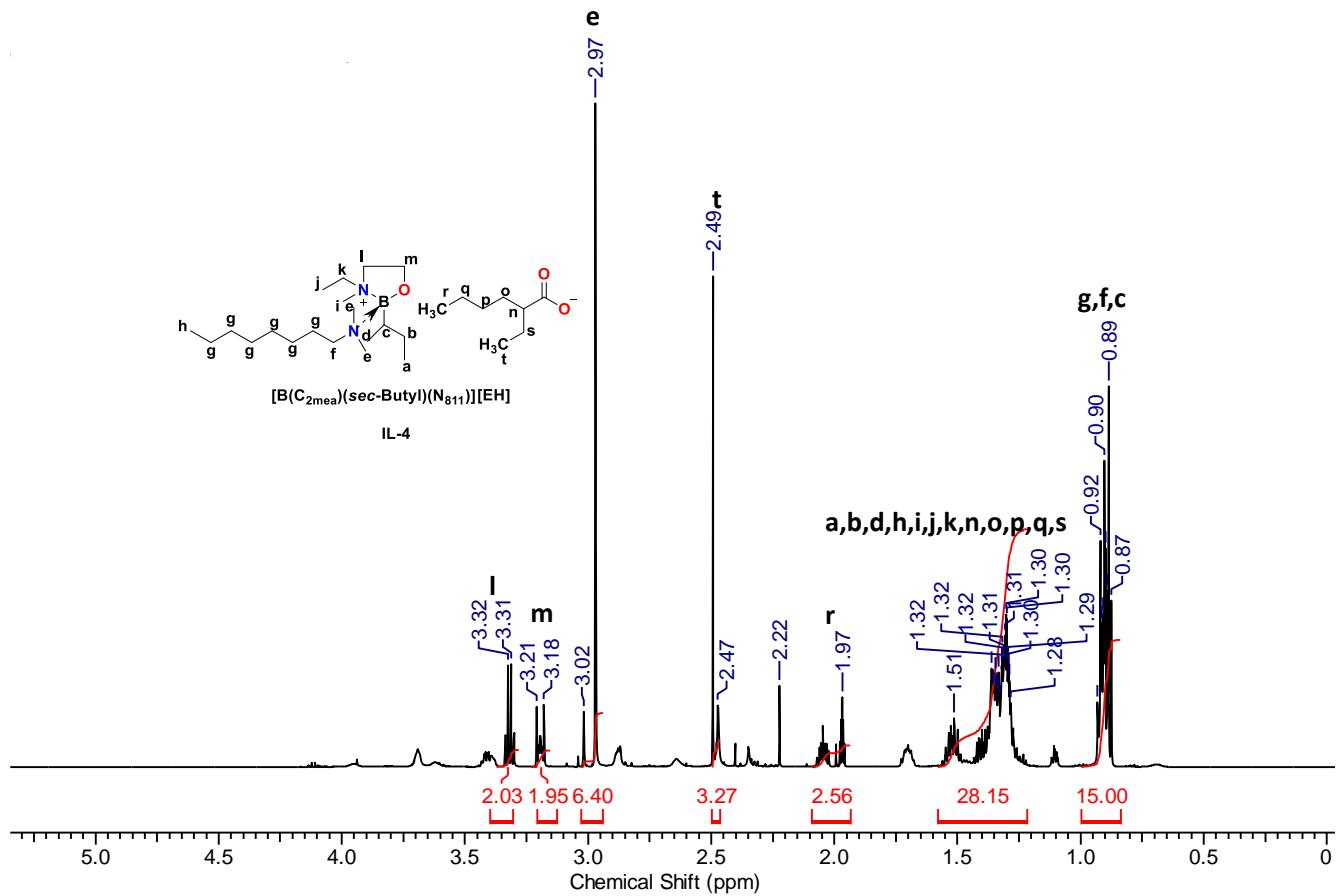
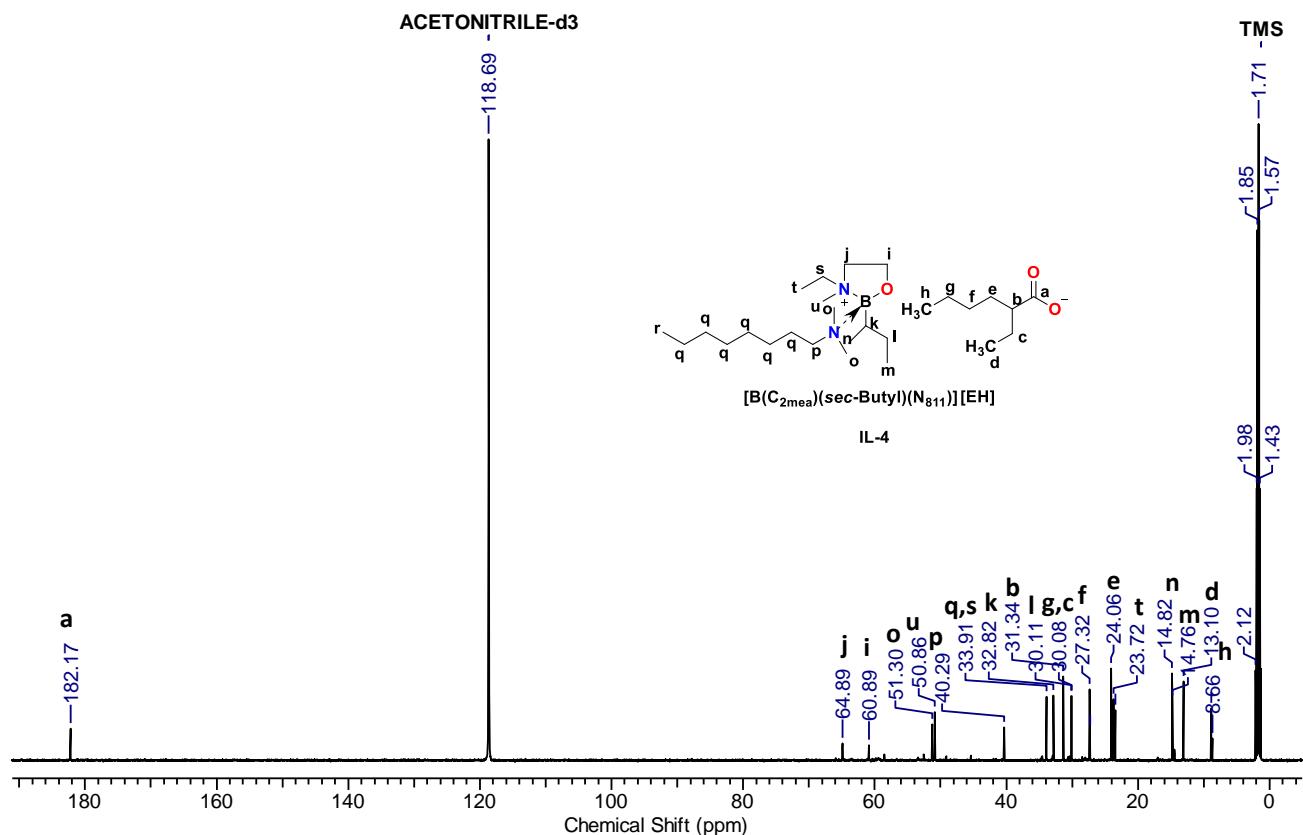
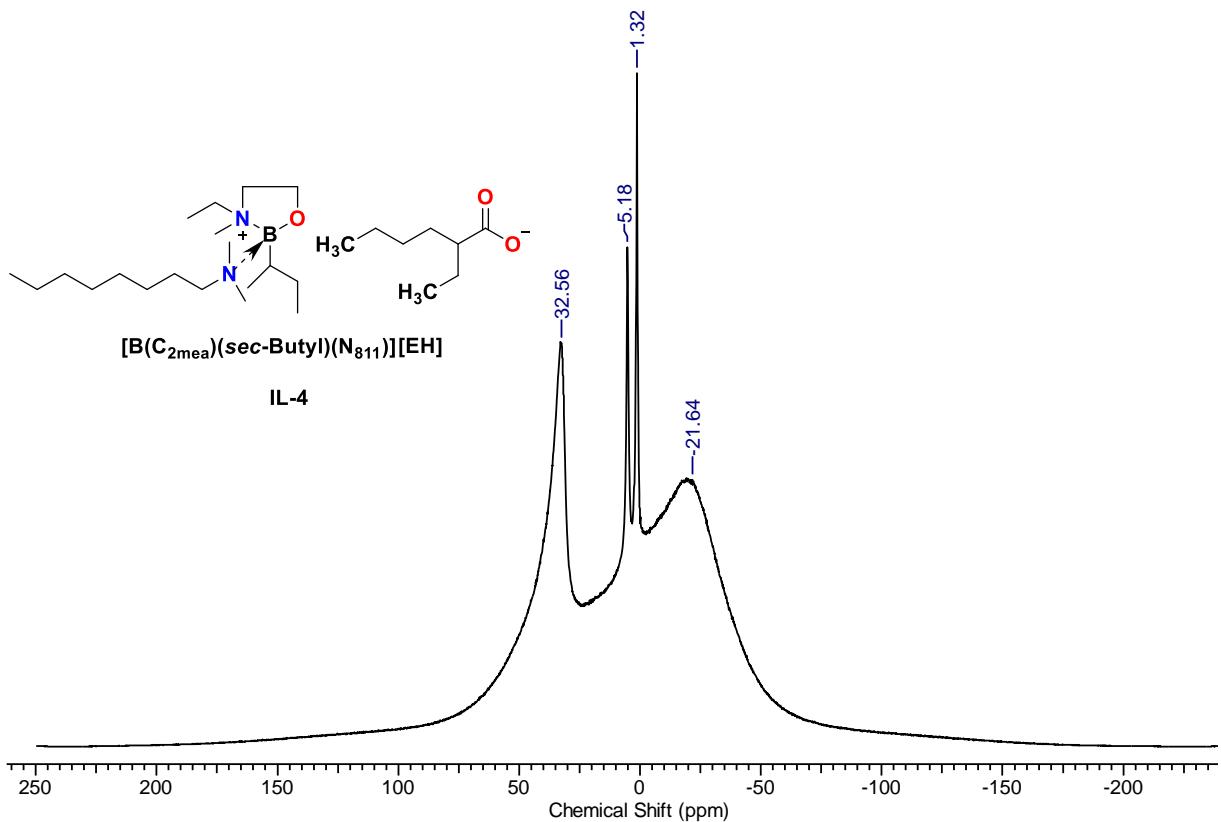


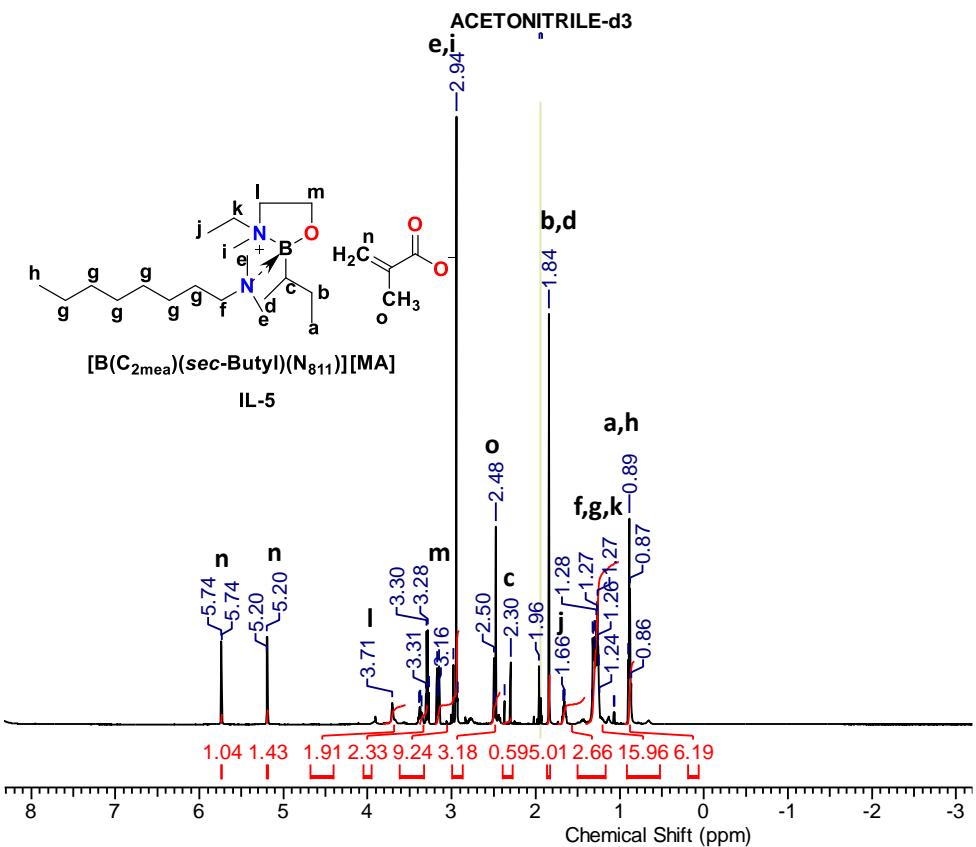
Figure S 34.  $^1\text{H}$  NMR spectrum of IL-4  $[\text{B}(\text{C}_2\text{mea})(\text{sec-butyl})(\text{N}_{811})][\text{EH}]$ .



**Figure S 35.**  $^{13}\text{C}$  NMR spectrum of IL-4 [ $\text{B}(\text{C}_{2\text{mea}})(\text{sec-butyl})(\text{N}_{811})$ ][EH].



**Figure S 36.**  $^{11}\text{B}$  NMR spectrum of IL-4 [ $\text{B}(\text{C}_{2\text{mea}})(\text{sec-butyl})(\text{N}_{811})$ ][EH].



**Figure S 37.**  $^1\text{H}$  NMR spectrum of IL-5 [B(C<sub>2</sub>mea)(sec-butyl)(N<sub>811</sub>)] [MA].

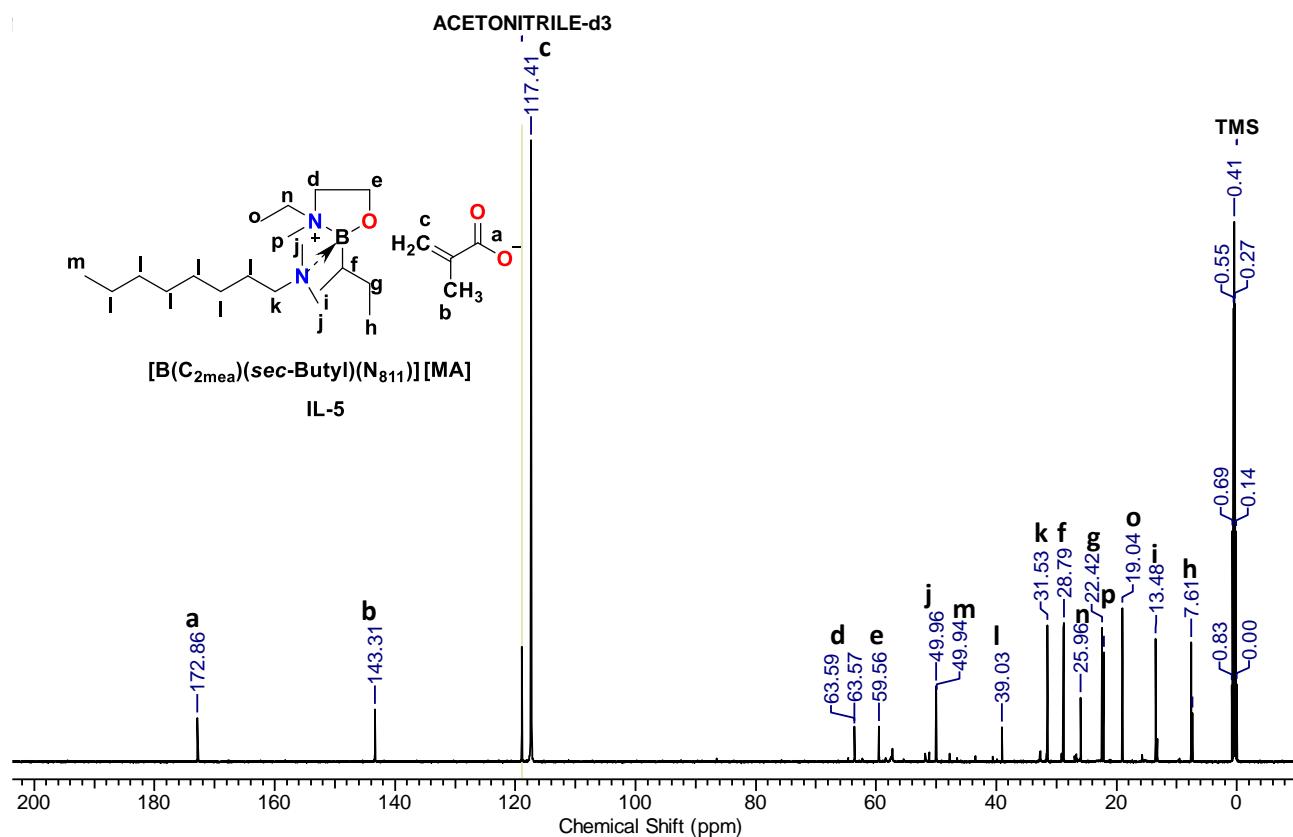


Figure S 38. <sup>13</sup>C NMR spectrum of IL-5 [B(C<sub>2</sub>mea)(sec-butyl)(N<sub>811</sub>)] [MA].

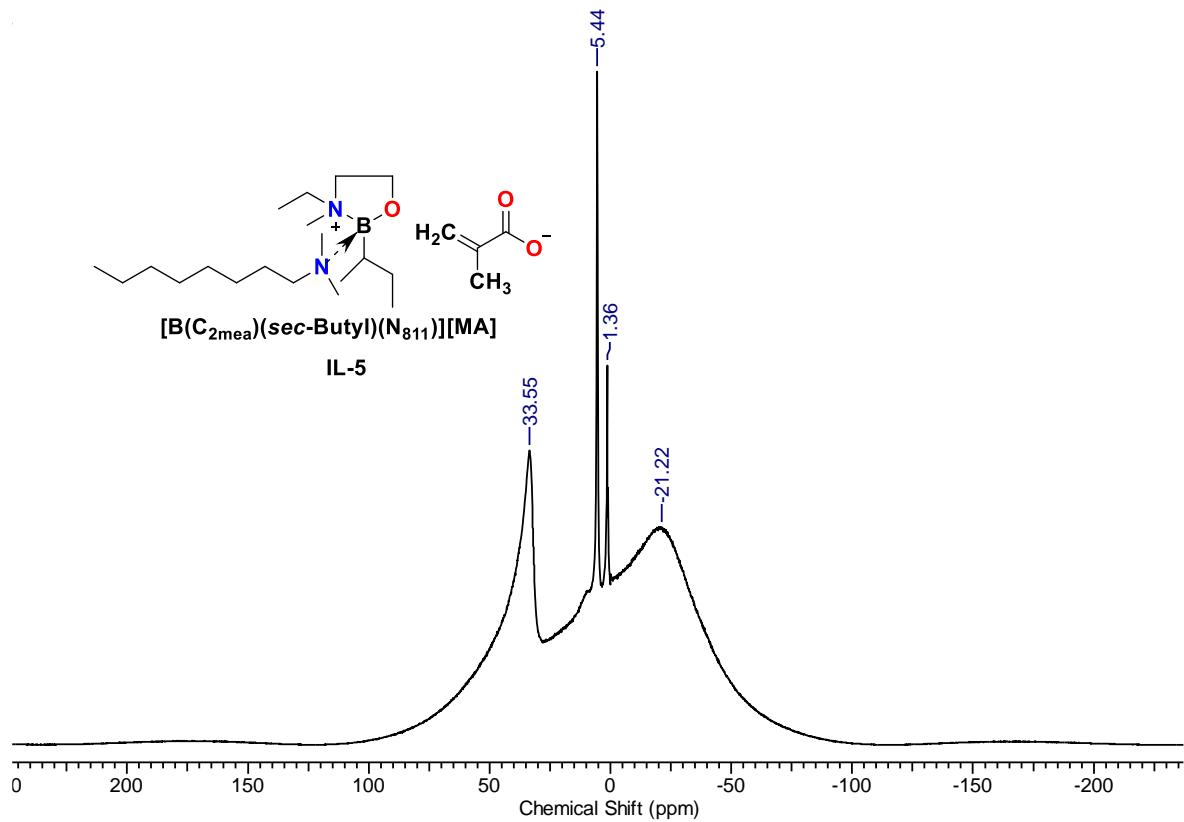


Figure S 39. <sup>11</sup>B NMR spectrum of IL-5 [B(C<sub>2</sub>mea)(sec-butyl)(N<sub>811</sub>)] [MA].

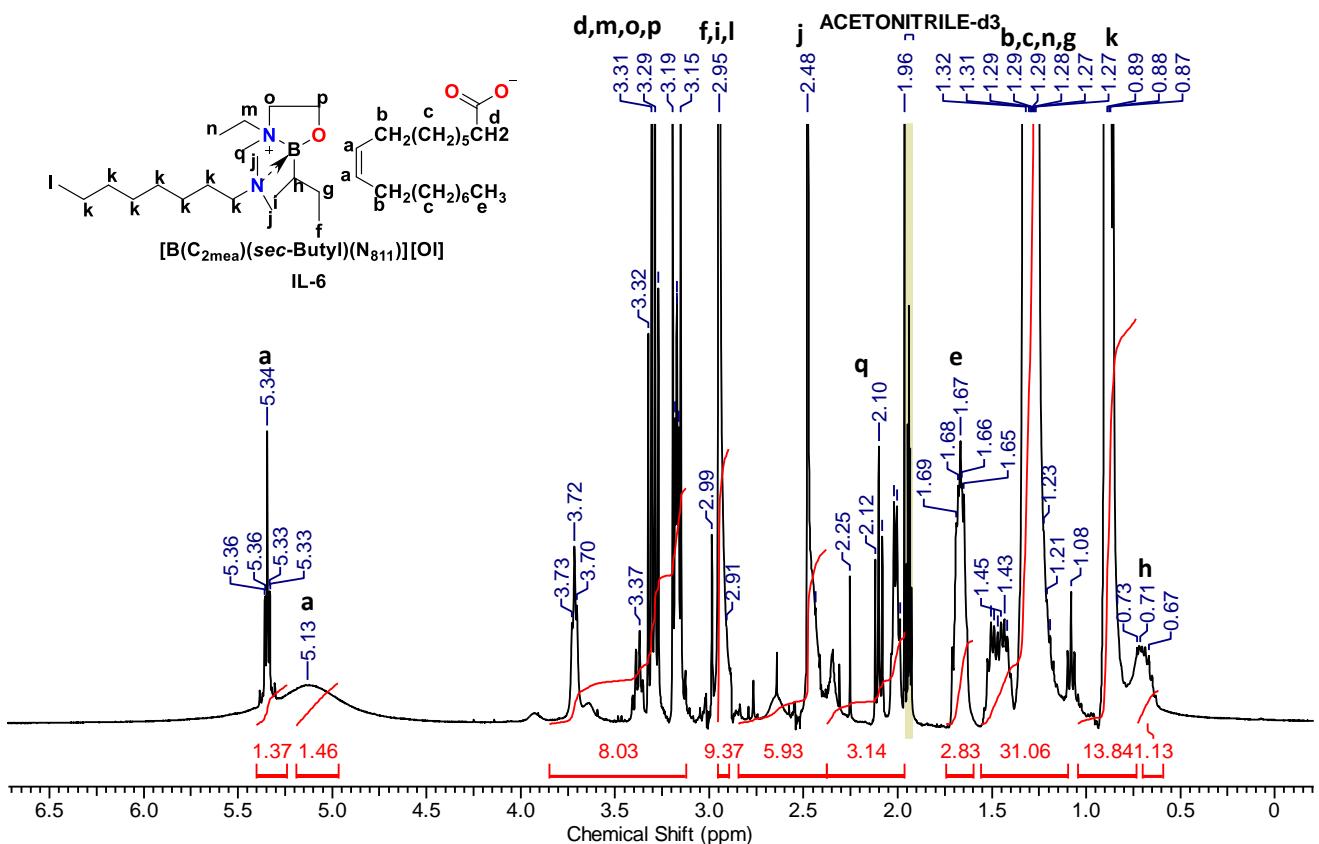


Figure S 40. <sup>1</sup>H NMR spectrum of IL-6 [B(C<sub>2</sub>mea)(sec-butyl)(N<sub>811</sub>)][OI].

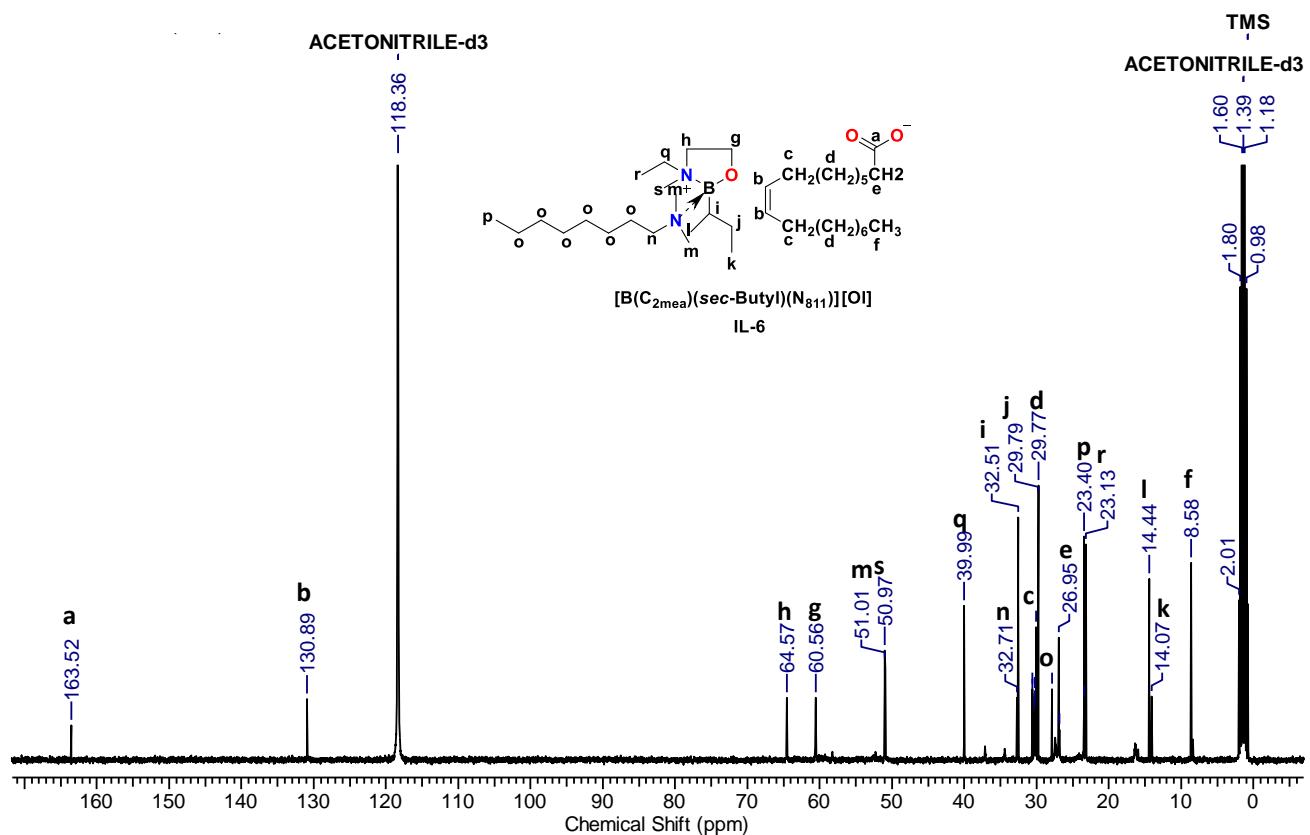
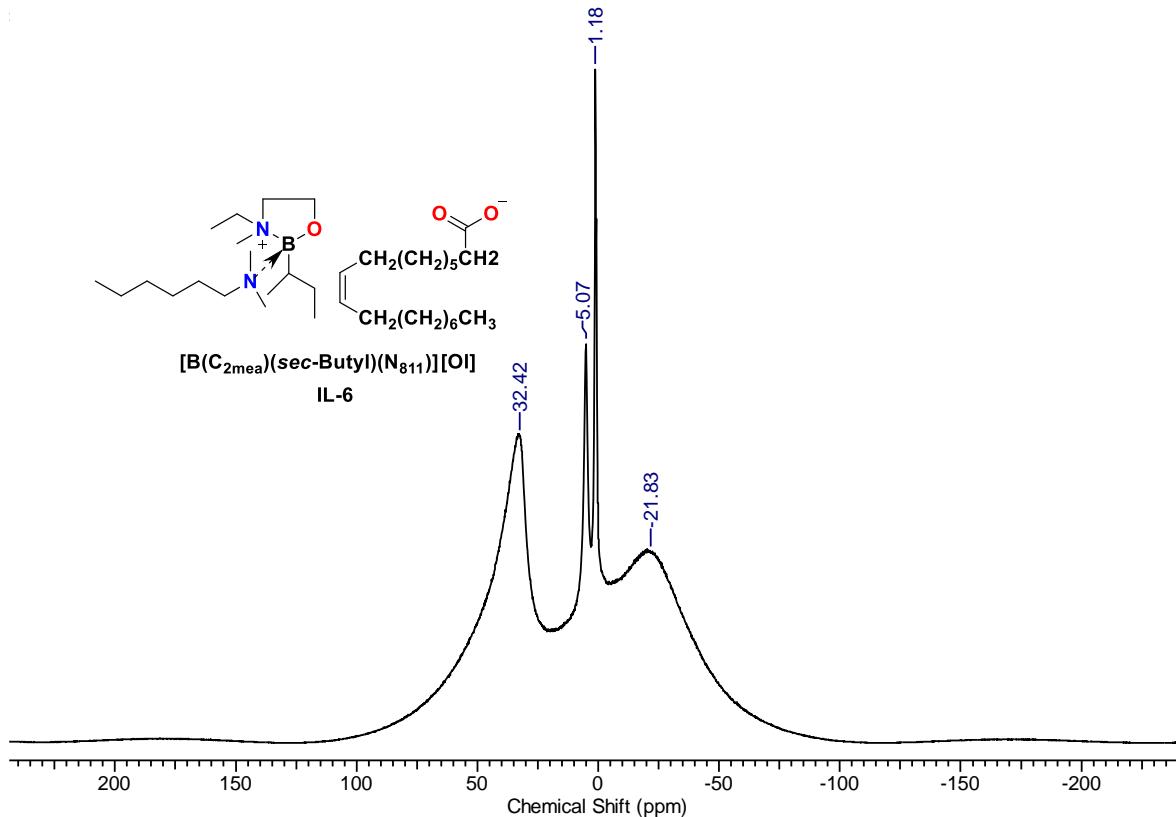
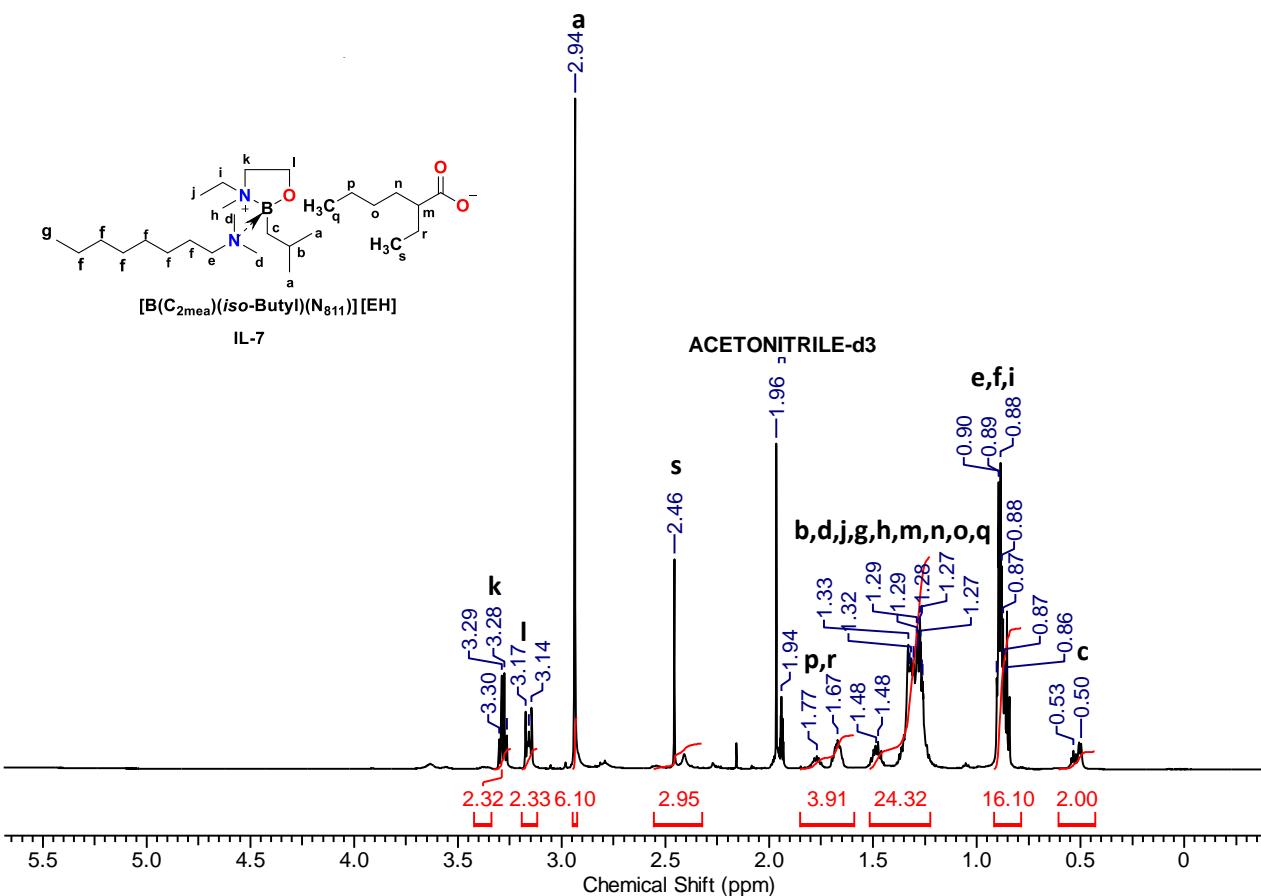


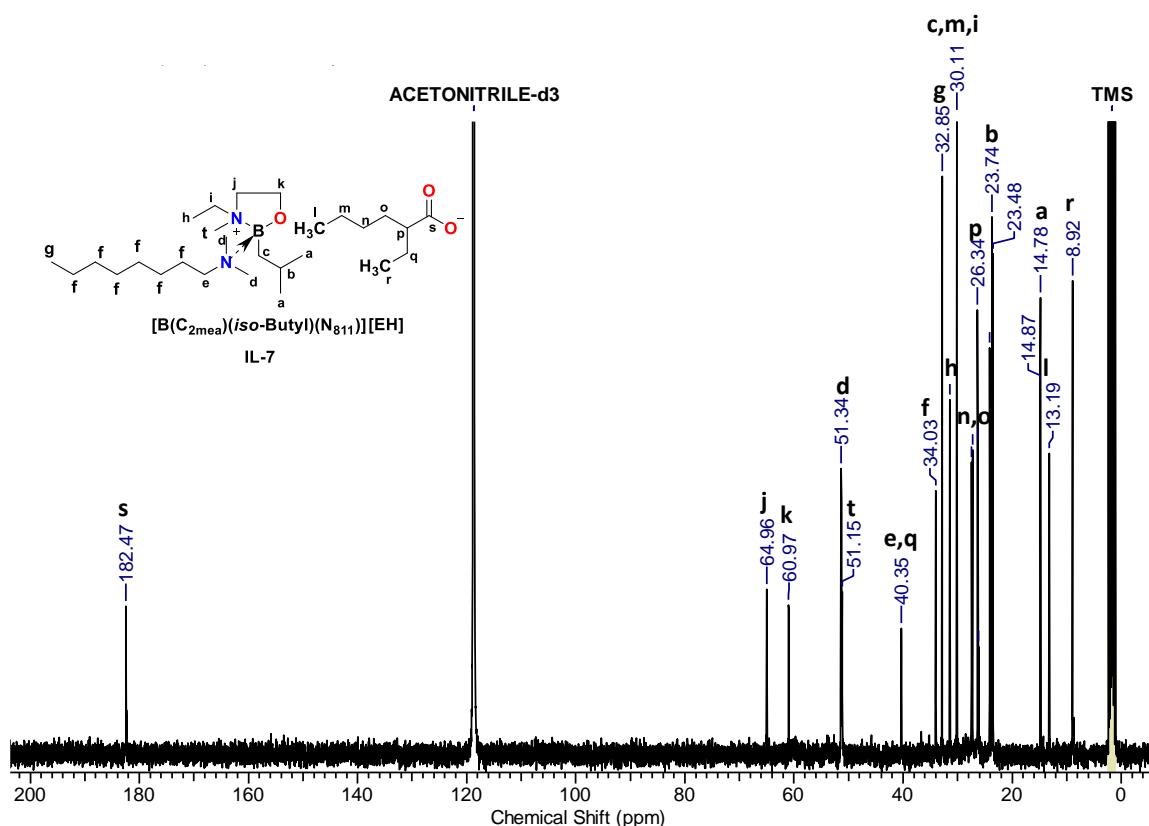
Figure S 41. <sup>13</sup>C NMR spectrum of IL-6 [B(C<sub>2</sub>mea)(sec-Butyl)(N<sub>811</sub>)][OI].



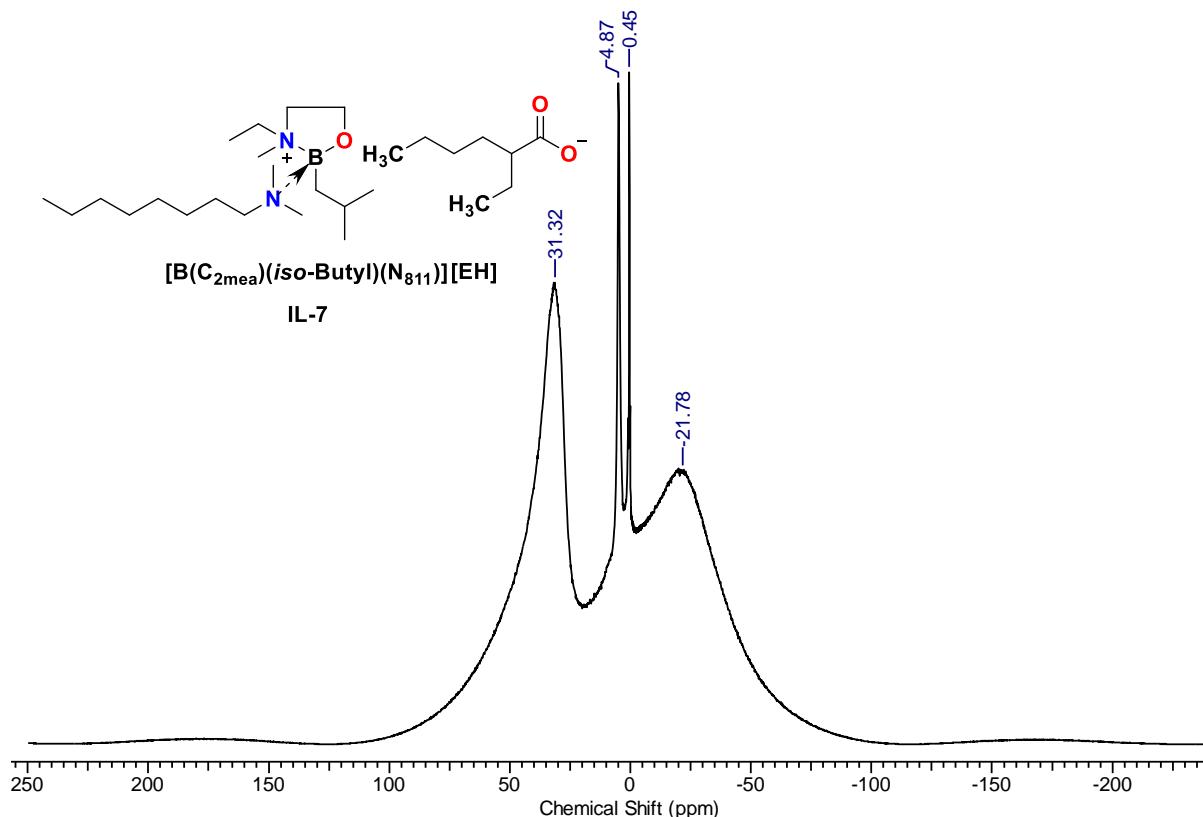
**Figure S 42.**  $^{11}\text{B}$  NMR spectrum of IL-6  $[\text{B}(\text{C}_{2\text{mea}})(\text{sec-Butyl})(\text{N}_{811})][\text{OI}]$ .



**Figure S 43.**  $^1\text{H}$  NMR spectrum of IL-7  $[\text{B}(\text{C}_{2\text{mea}})(\text{iso-Butyl})(\text{N}_{811})][\text{EH}]$ .



**Figure S 44.** <sup>13</sup>C NMR spectrum of IL-7 [B(C<sub>2</sub>mea)(iso-butyl)(N<sub>811</sub>)][EH].



**Figure S 45.** <sup>11</sup>B NMR spectrum of IL-7 [B(C<sub>2</sub>mea)(iso-butyl)(N<sub>811</sub>)][EH].

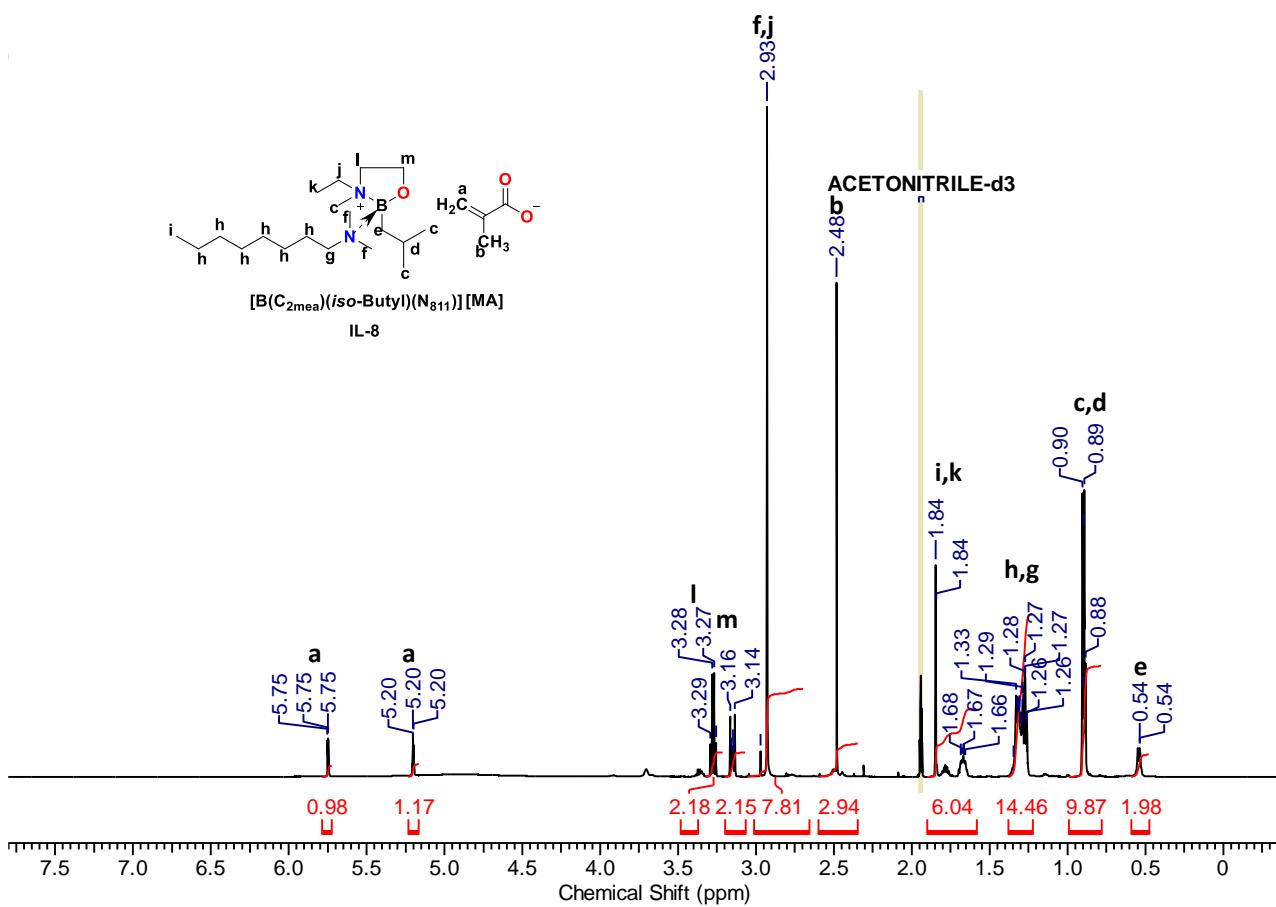


Figure S 46. <sup>1</sup>H NMR spectrum of IL-8 [B(C<sub>2</sub>mea)(iso-Butyl)(N<sub>811</sub>)][MA].

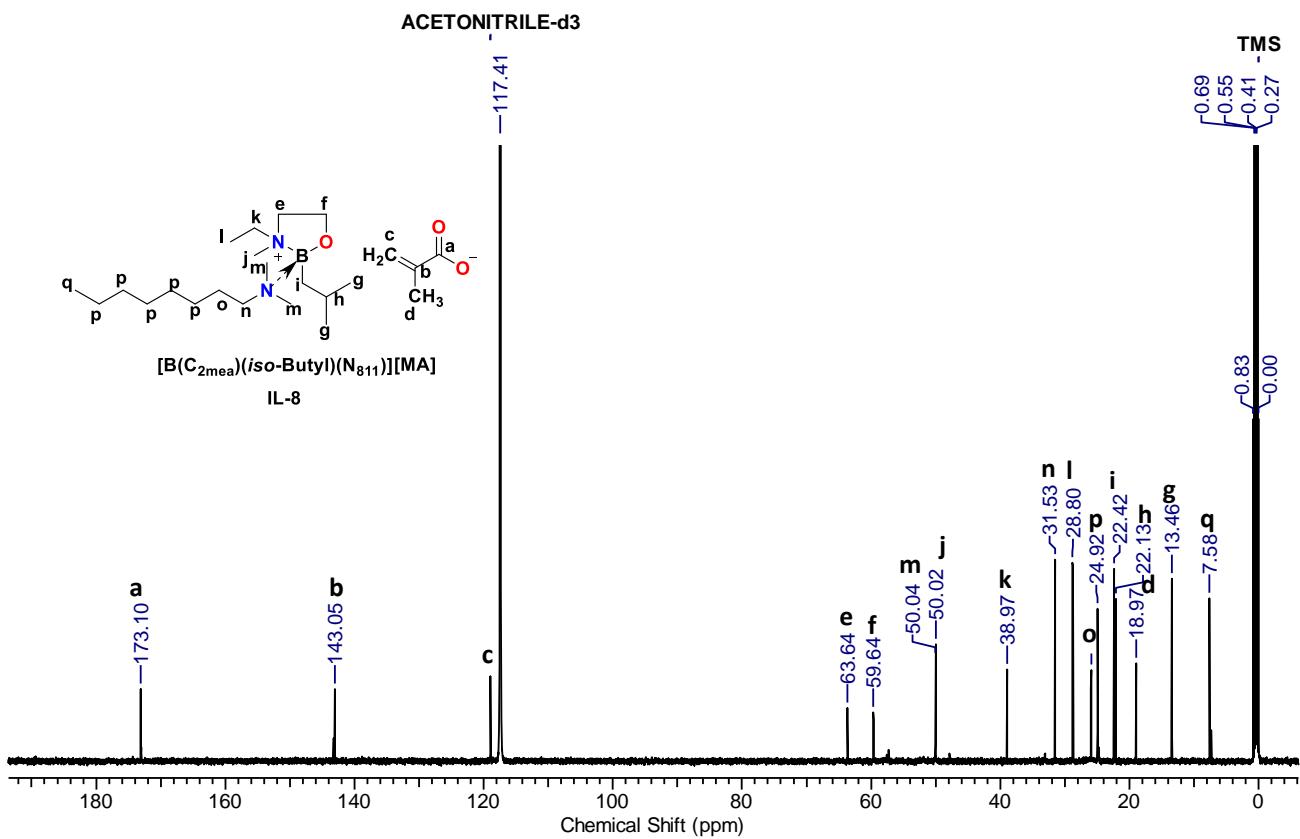
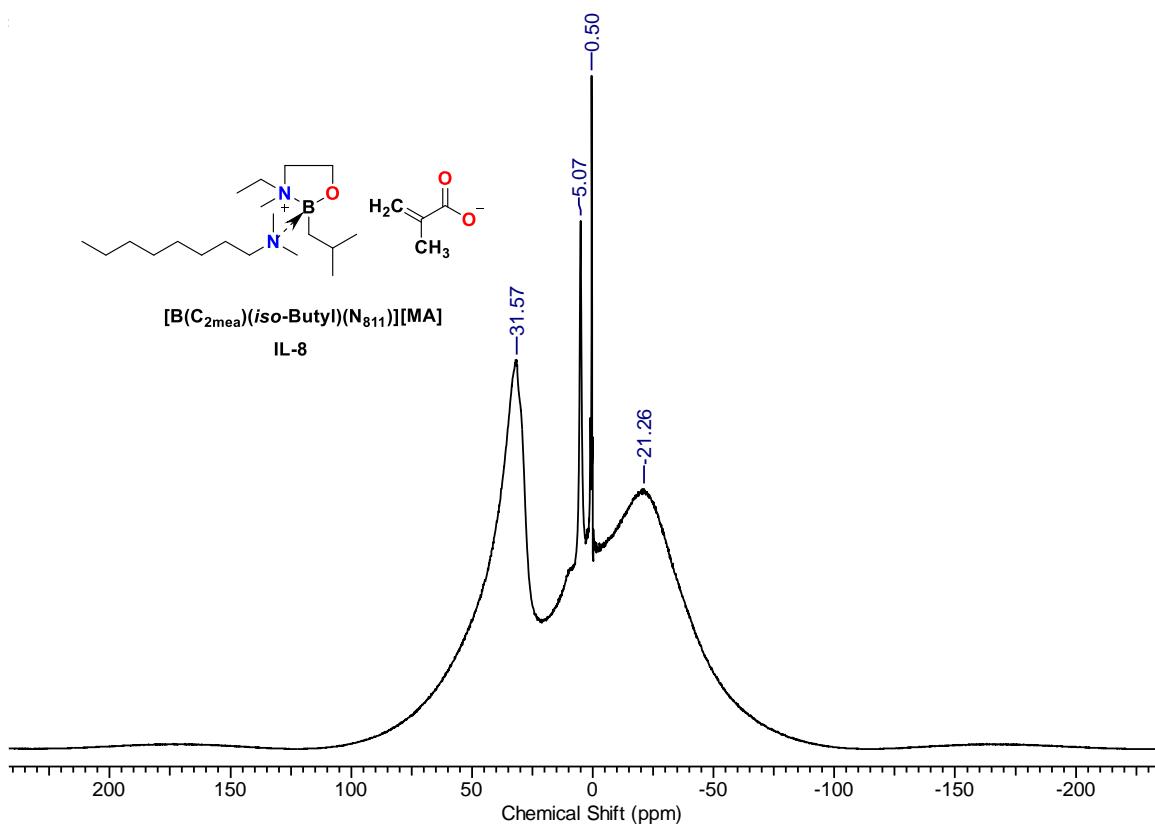
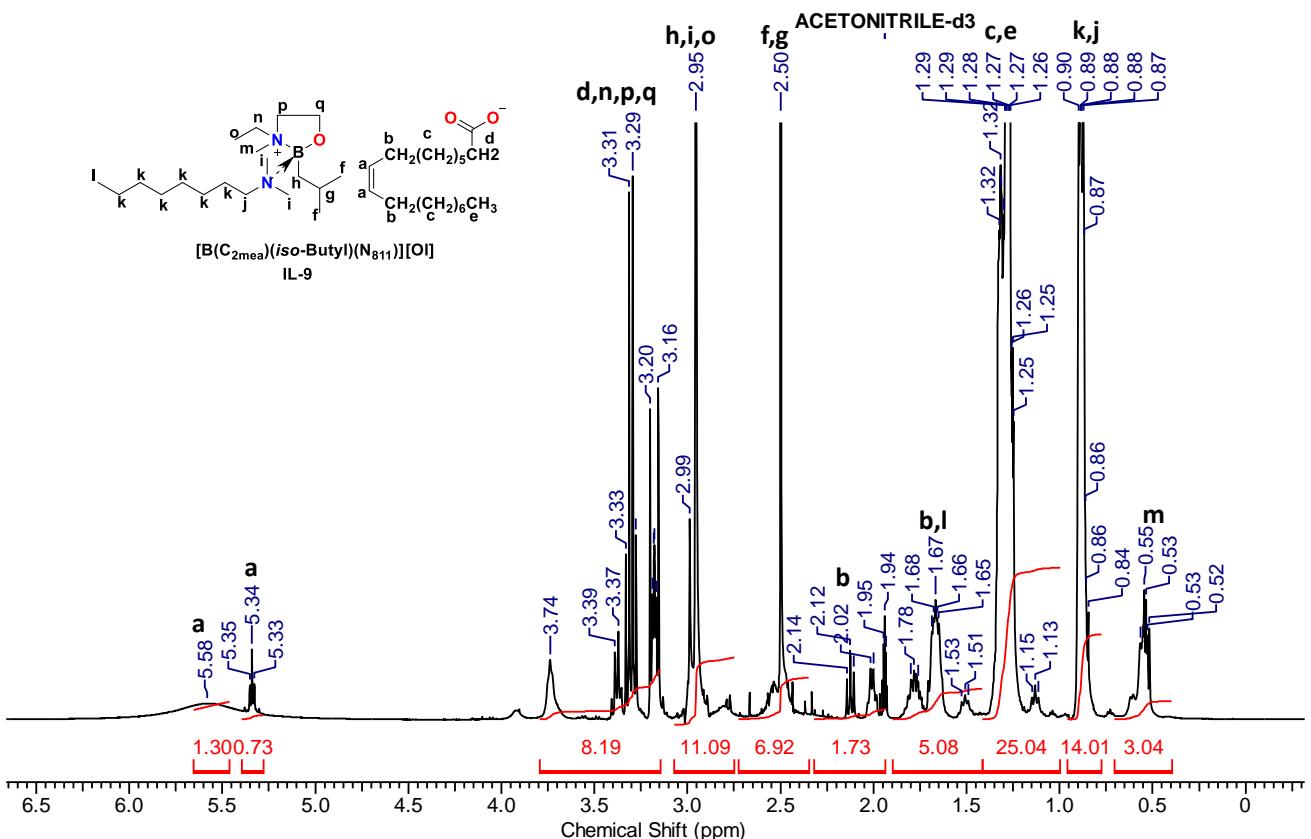


Figure S 47. <sup>13</sup>C NMR spectrum of IL-8 [B(C<sub>2</sub>mea)(iso-Butyl)(N<sub>811</sub>)][MA].



**Figure S 48.**  $^{11}\text{B}$  NMR spectrum of IL-8  $[\text{B}(\text{C}_2\text{mea})(\text{iso-Butyl})(\text{N}_{811})][\text{MA}]$ .



**Figure S 49.**  $^1\text{H}$  NMR spectrum of IL-9  $[\text{B}(\text{C}_2\text{mea})(\text{iso-butyl})(\text{N}_{811})][\text{OI}]$ .

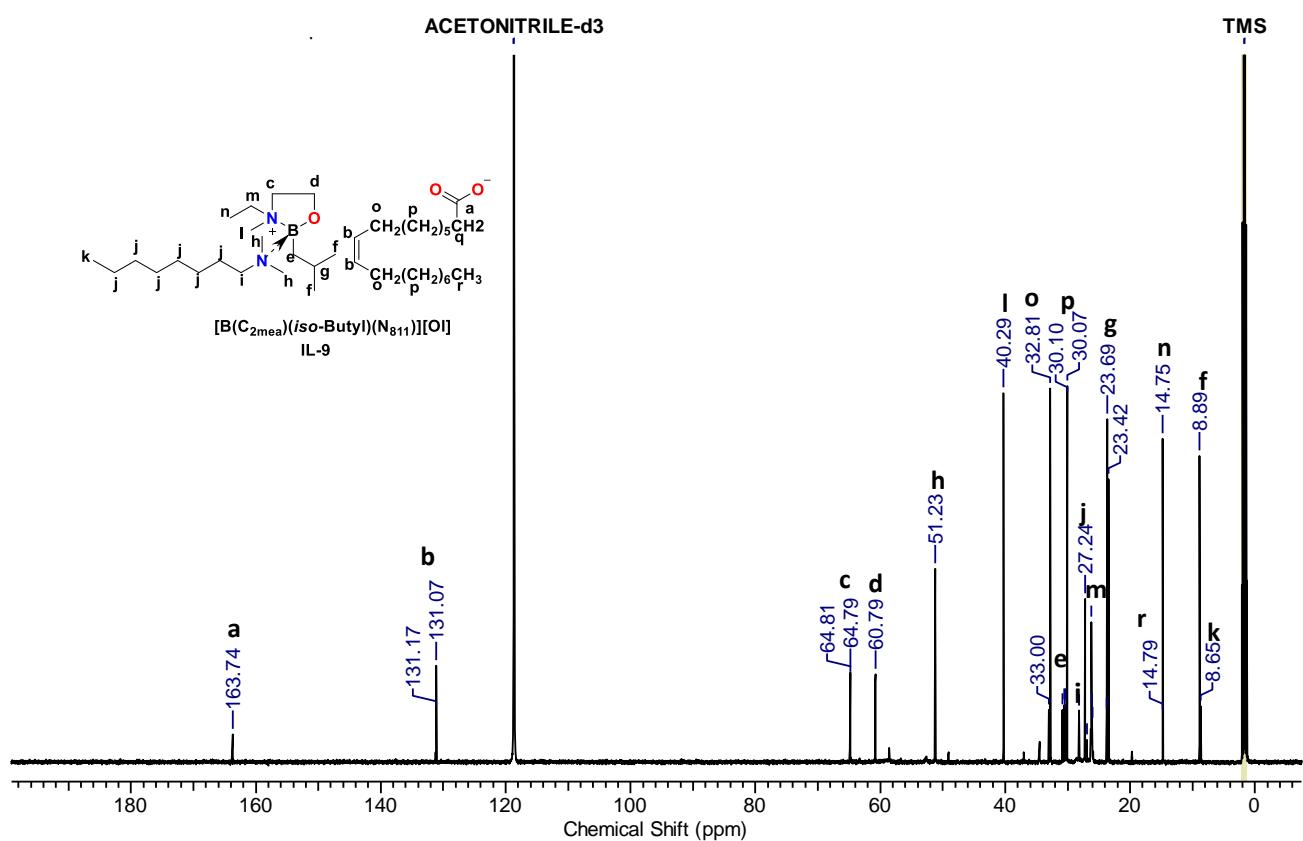


Figure S 50.  $^{13}\text{C}$  NMR spectrum of IL-9 [ $\text{B}(\text{C}_{2\text{mea}})(\text{iso-Butyl})(\text{N}_{811})\text{O}\text{I}$ ].

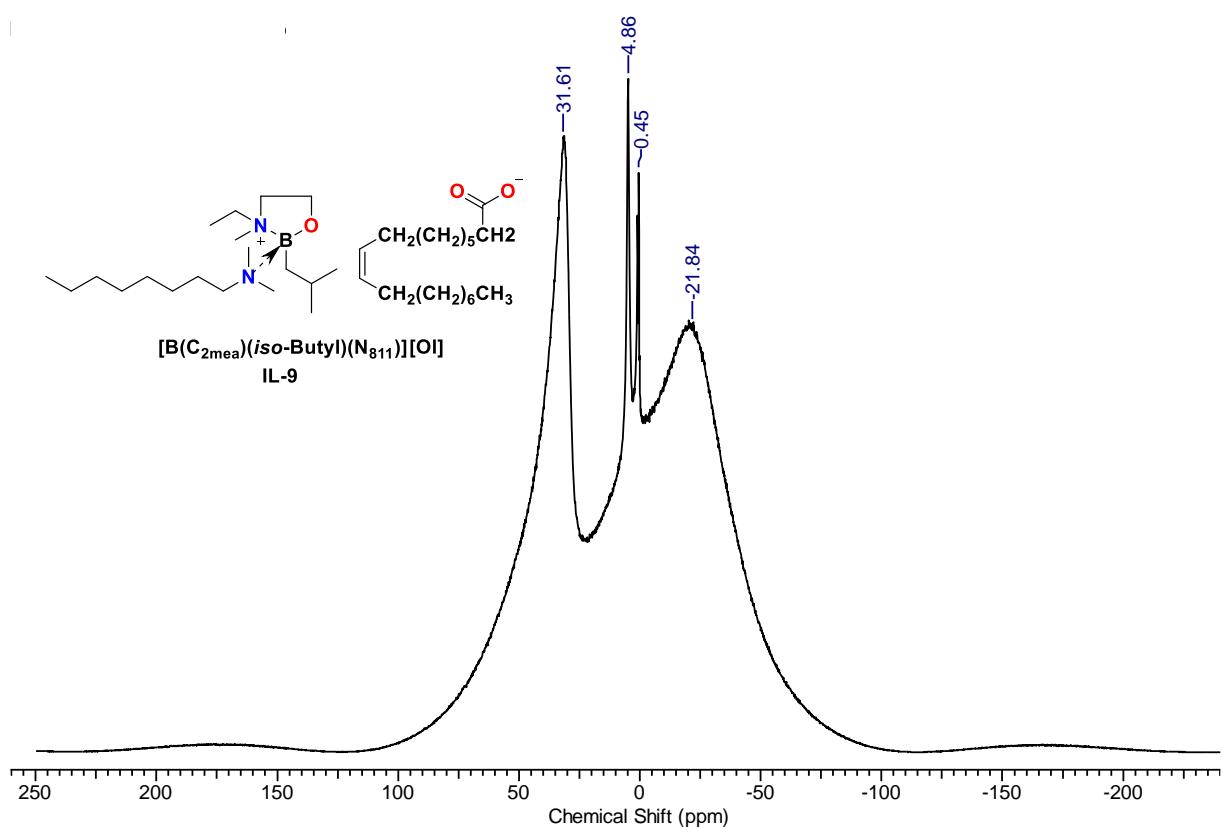


Figure S 51.  $^{11}\text{B}$  NMR spectrum of IL-9 [ $\text{B}(\text{C}_{2\text{mea}})(\text{iso-butyl})(\text{N}_{811})\text{O}\text{I}$ ].

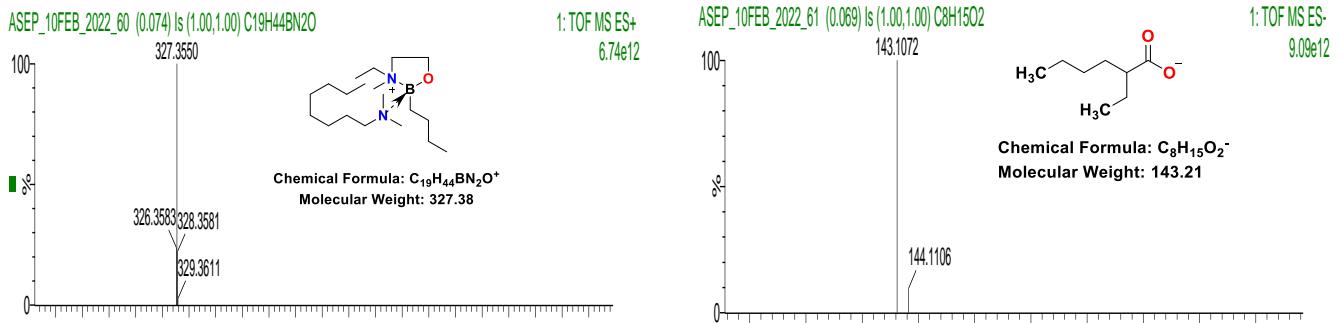


Figure S 52. Mass spectrum of IL-1 [B(C<sub>2</sub>mea)(n-butyl)(N<sub>811</sub>)] EH.

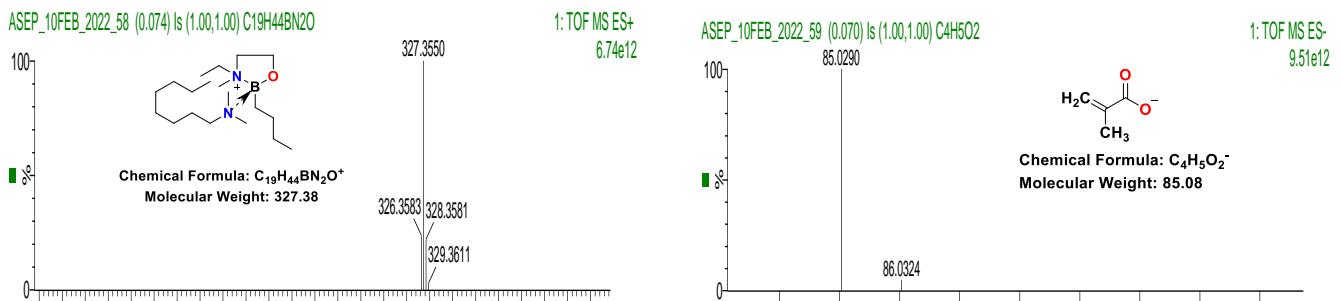


Figure S 53. Mass spectrum of IL-2 [B(C<sub>2</sub>mea)(n-butyl)(N<sub>811</sub>)][MA].

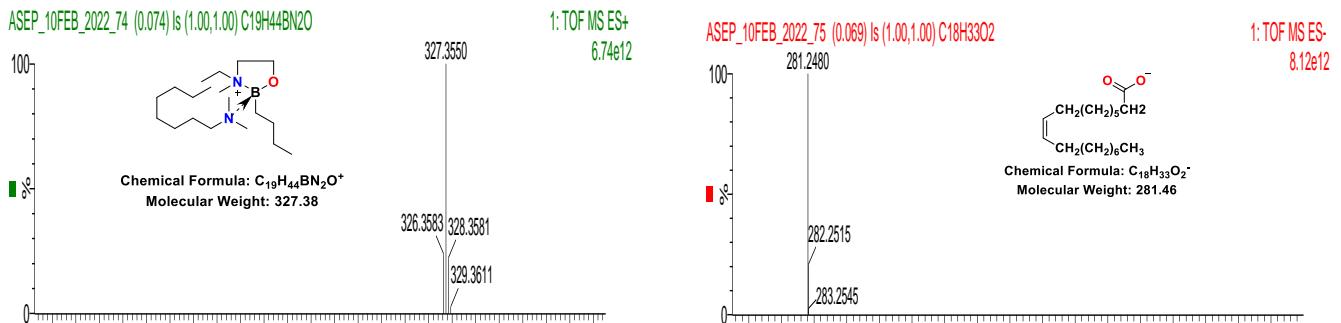


Figure S 54. Mass spectrum of IL-3 [B(C<sub>2</sub>mea)(n-butyl)(N<sub>811</sub>)][OI].

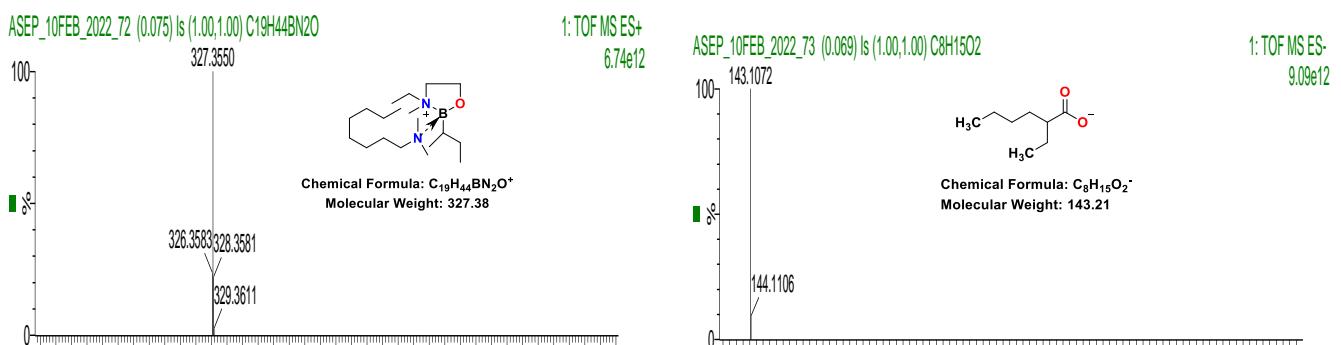


Figure S 55. Mass spectrum of IL-4 [B(C<sub>2</sub>mea)(sec-butyl)(N<sub>811</sub>)][EH].

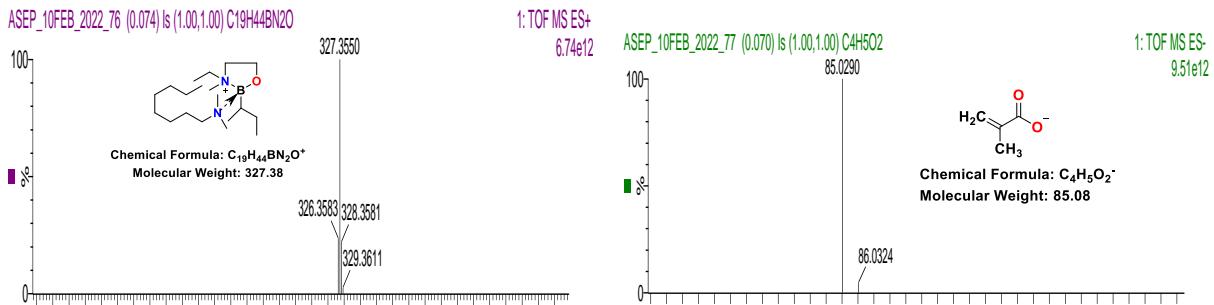


Figure S 56. Mass spectrum of IL-5 [B(C<sub>2</sub>mea)(sec-butyl)(N<sub>811</sub>)][MA].

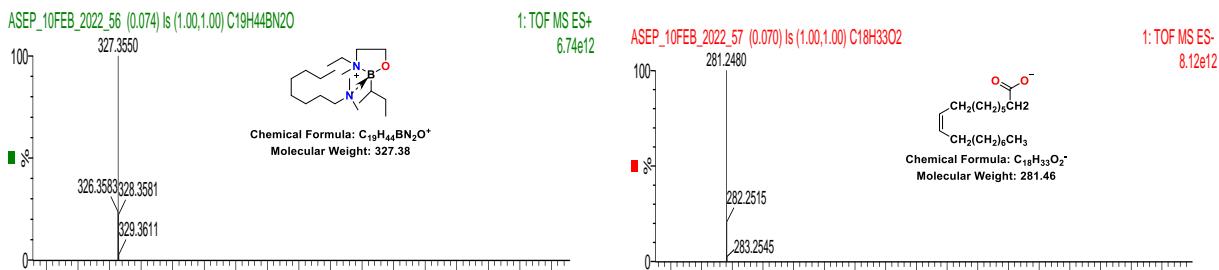


Figure S 57. Mass spectrum of IL-6 [B(C<sub>2</sub>mea)(sec-butyl)(N<sub>811</sub>)][OI].

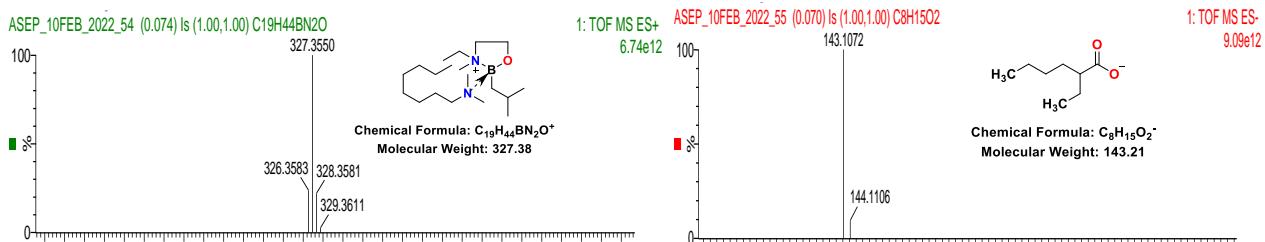


Figure S 58. Mass spectrum of IL-7 [B(C<sub>2</sub>mea)(iso-butyl)(N<sub>811</sub>)][EH].

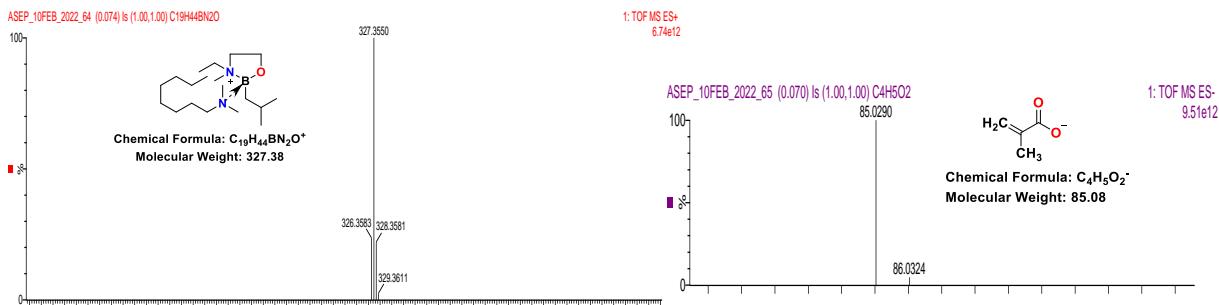
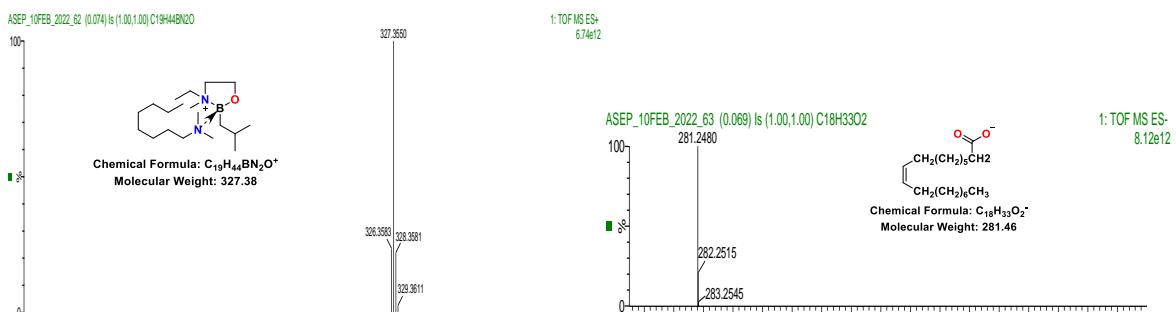
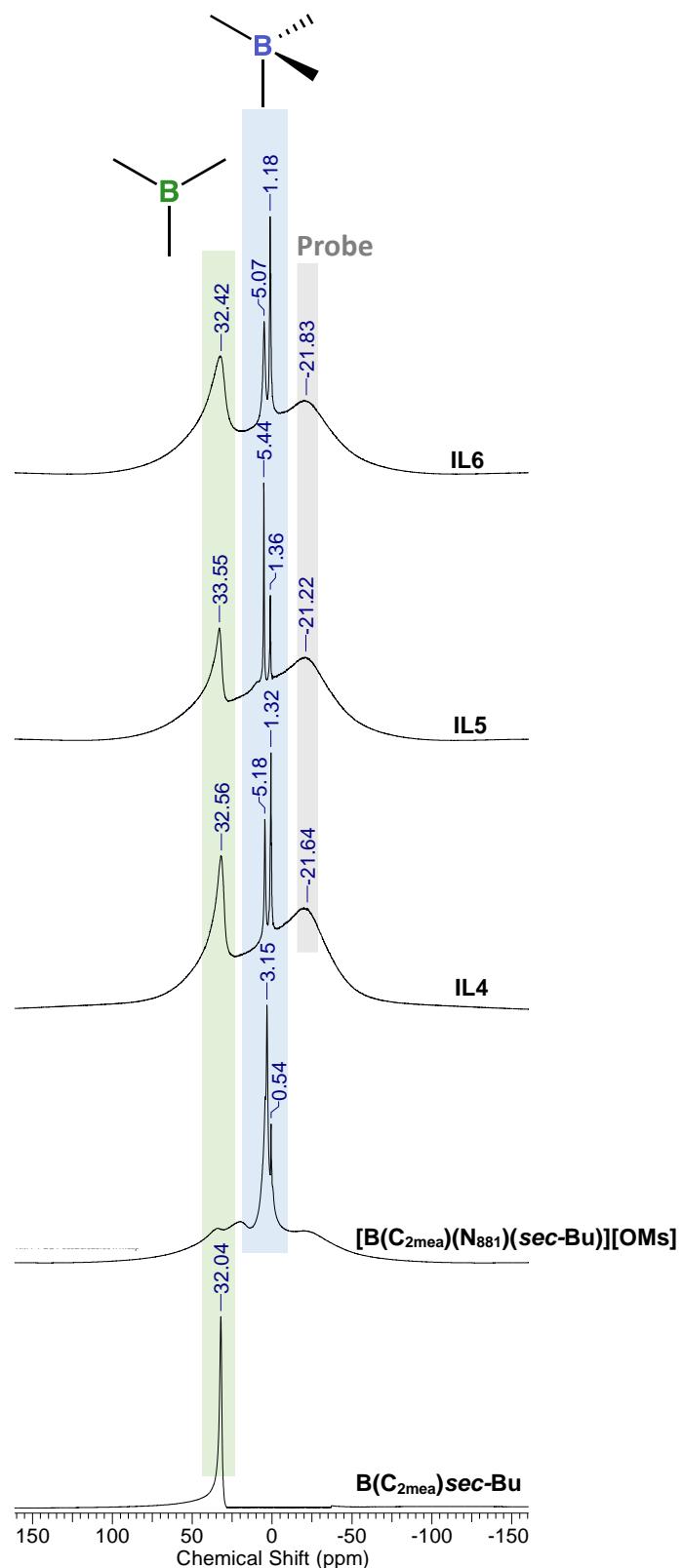


Figure S 59. Mass spectrum of IL-8 [B(C<sub>2</sub>mea)(iso-butyl)(N<sub>811</sub>)][MA].



**Figure S 60.** Mass spectrum of IL-9 [ $\text{B}(\text{C}_{2\text{mea}})(\text{iso-butyl})(\text{N}_{811})$ ][OI].



**Figure S 61.**  $^{11}\text{B}$  NMR spectra of  $\text{B}(\text{C}_{2\text{mea}})(\text{sec-Bu})$  and derived ILs: [ $\text{B}(\text{C}_{2\text{mea}})(\text{sec-Bu})(\text{N}_{811})$ ][OMs], IL-4, IL-5 and IL-6. Green-shaded area designates the chemical shift regions of tricoordinate boron compounds while blue area designates tetracoordinate species.

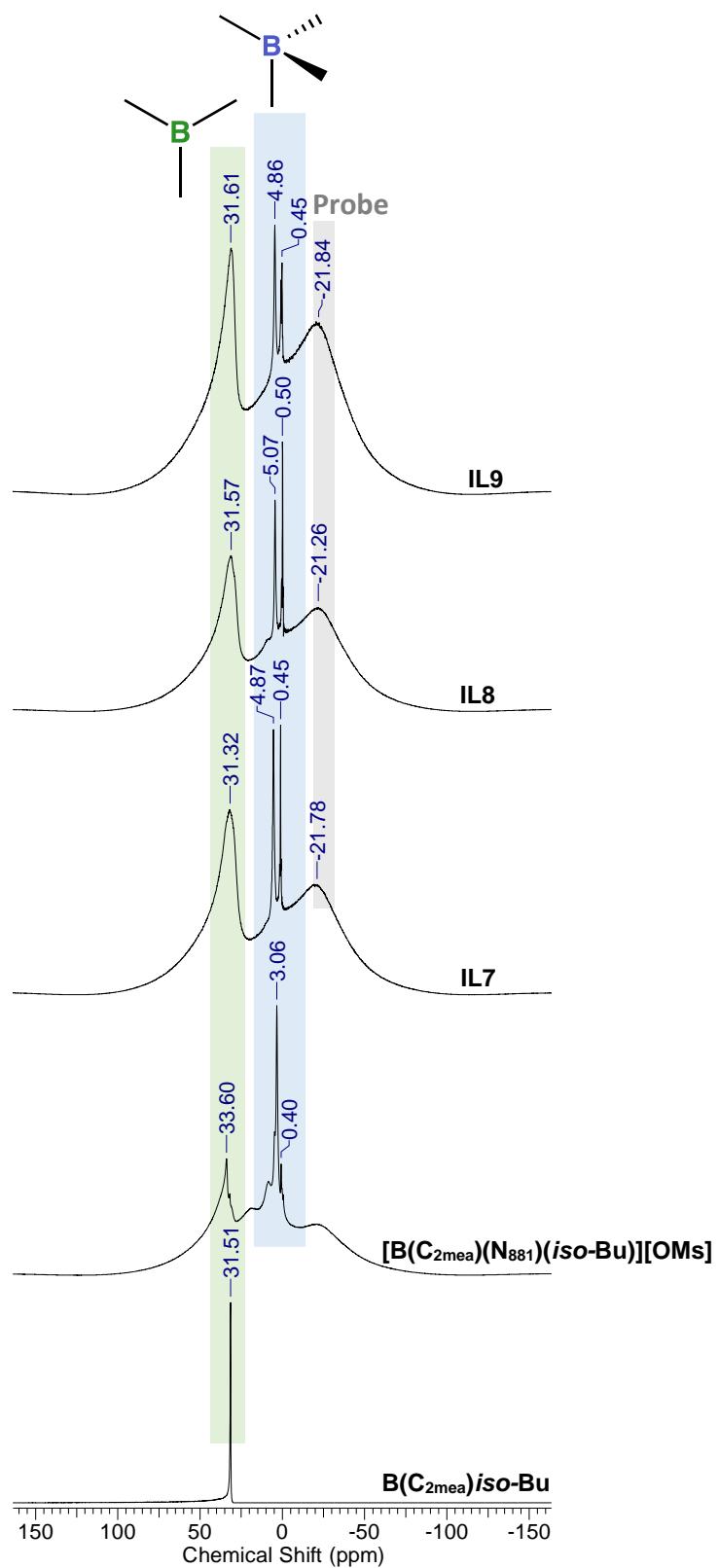


Figure S 62.  $^{11}\text{B}$  NMR spectra of  $\text{B}(\text{C}_{2\text{mea}})(\text{iso-Bu})$  and derived ILs:  $[\text{B}(\text{C}_{2\text{mea}})(\text{iso-Bu})(\text{N}_{811})][\text{OMs}]$ , IL-7, IL-8 and IL-9. Green-shaded area designates the chemical shift regions of tricoordinate boron compounds while blue area designates tetracoordinate species.

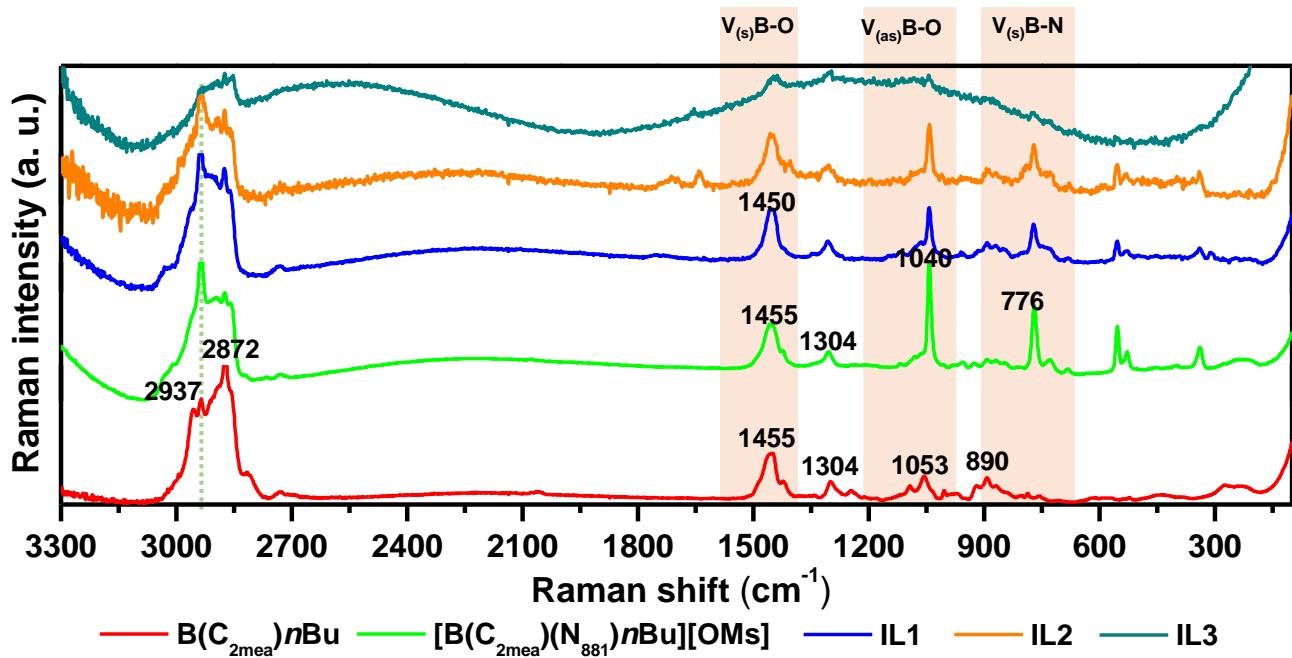


Figure S 63. Raman spectra of  $\text{B}(\text{C}_{2\text{mea}})(n\text{-Bu})$  and the derived ILs:  $[\text{B}(\text{C}_{2\text{mea}})(n\text{-Bu})(\text{N}_{881})][\text{OMs}]$ , IL-1, IL-2 and IL-3.

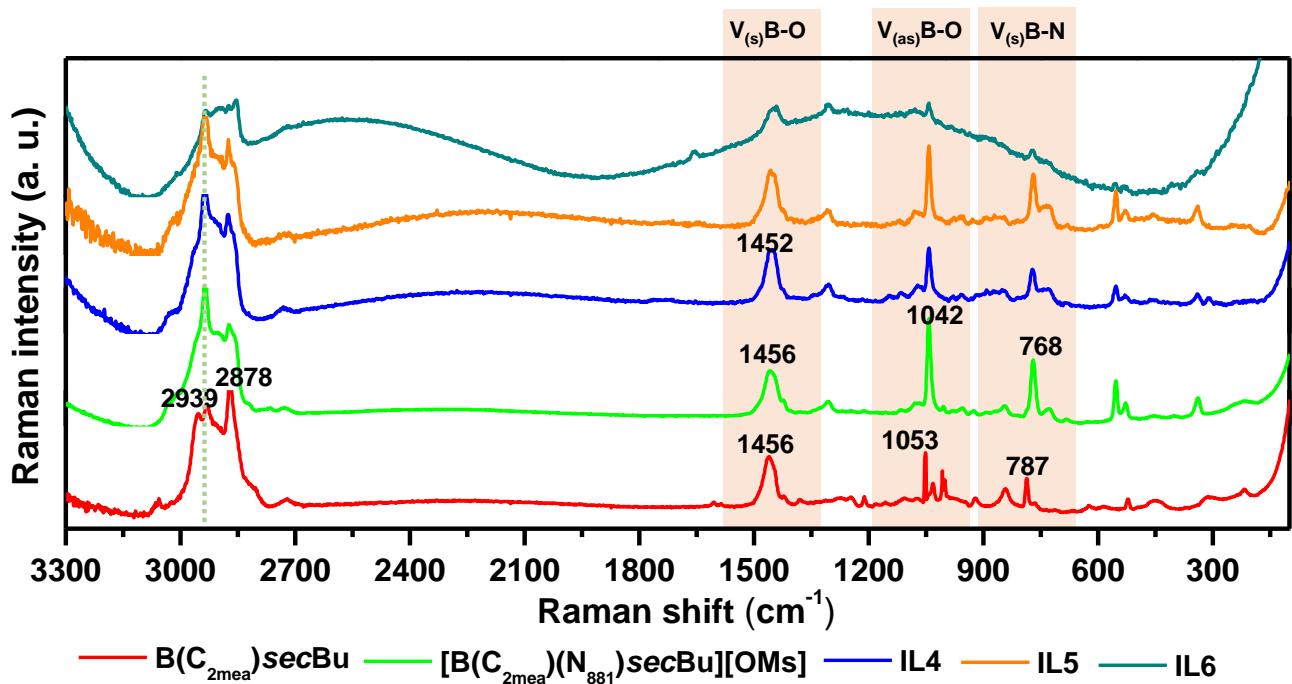


Figure S 64. Raman spectra of  $\text{B}(\text{C}_{2\text{mea}})(\text{sec-Bu})$  and the derived ILs:  $[\text{B}(\text{C}_{2\text{mea}})(\text{sec-Bu})(\text{N}_{881})][\text{OMs}]$ , IL-4, IL-5 and IL-6.

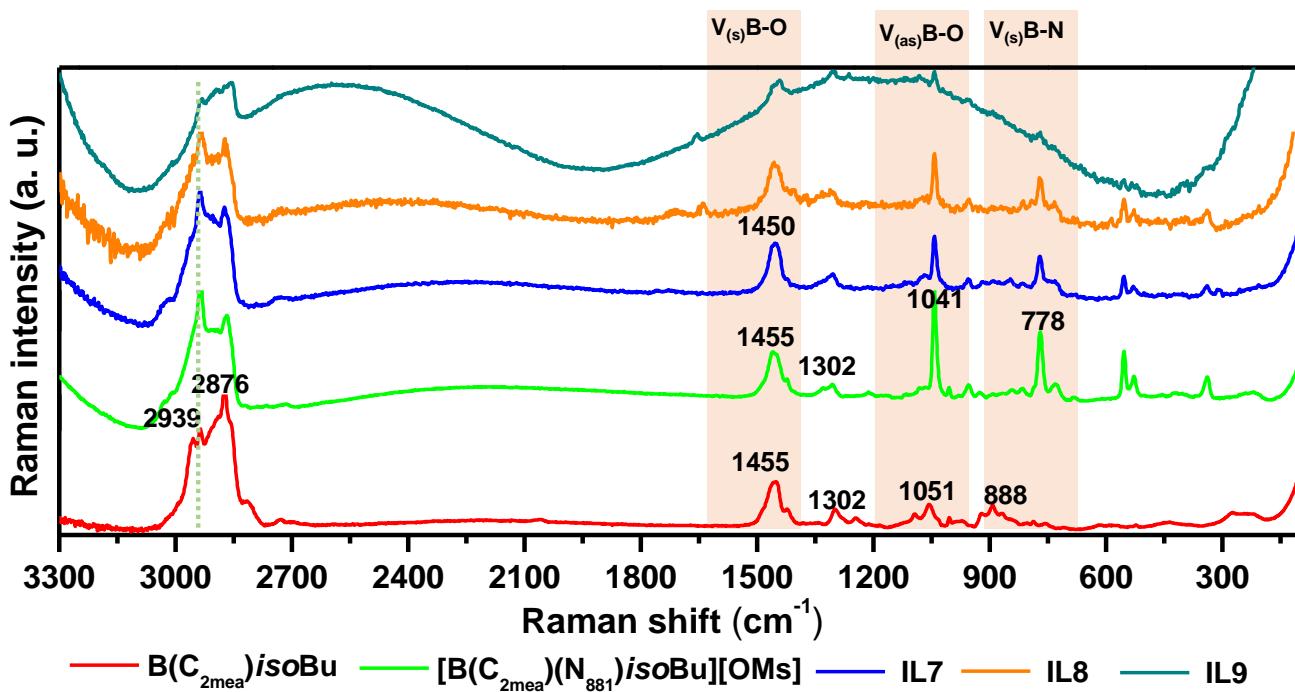


Figure S 65. Raman spectra of  $\text{B}(\text{C}_{2\text{mea}})\text{isoBu}$  and the derived ILs:  $[\text{B}(\text{C}_{2\text{mea}})(\text{iso-Bu})(\text{N}_{881})][\text{OMs}]$ , IL-7, IL-8 and IL-9.

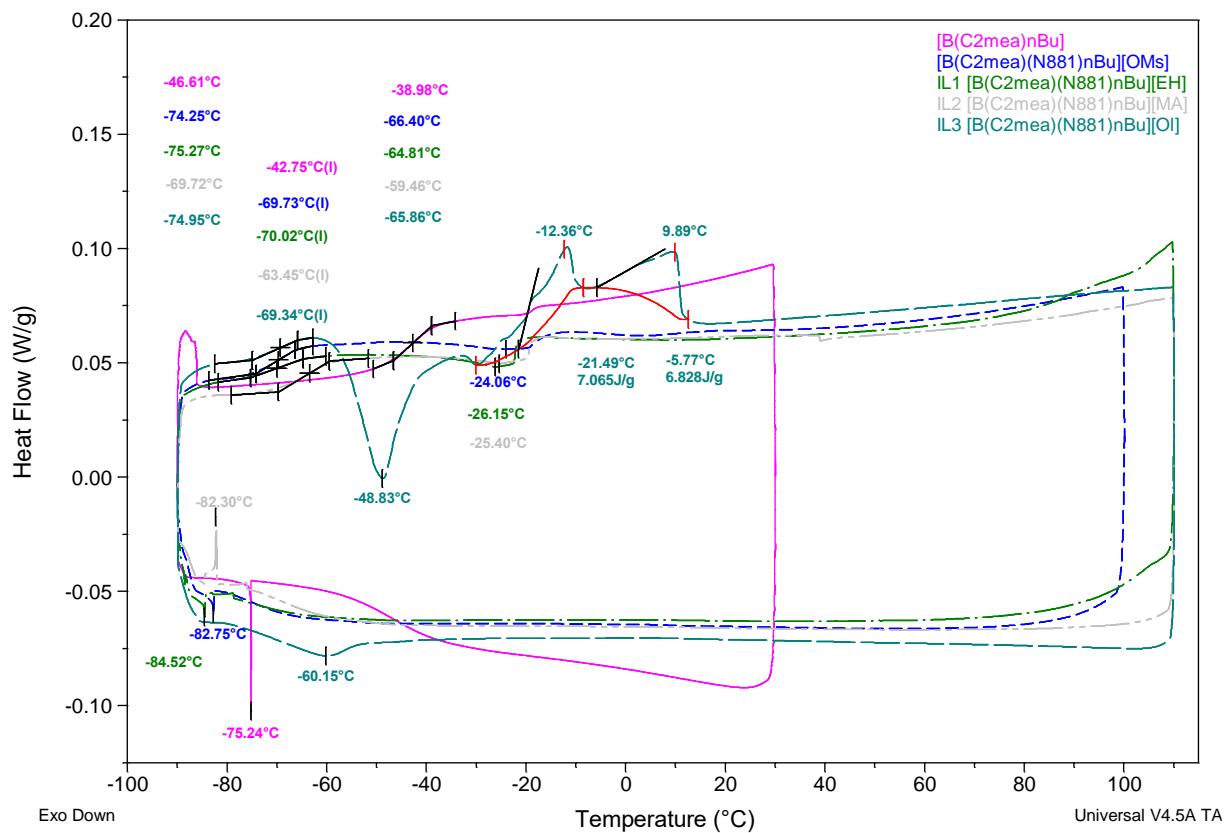
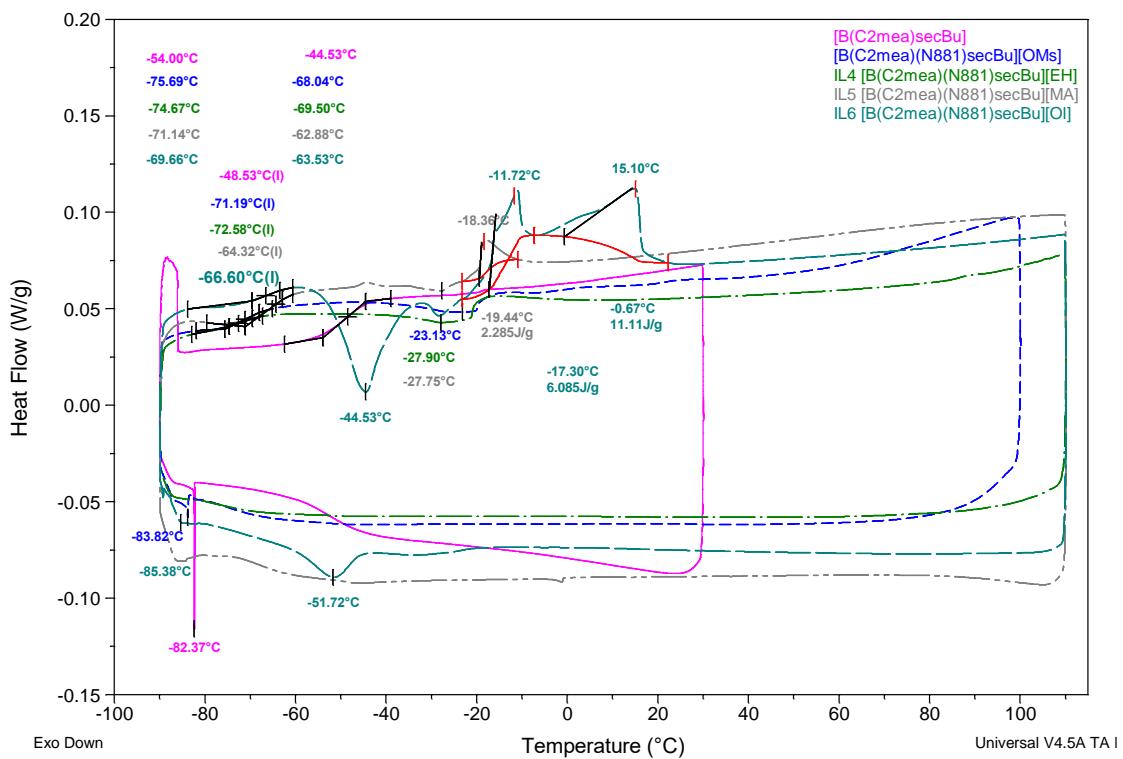
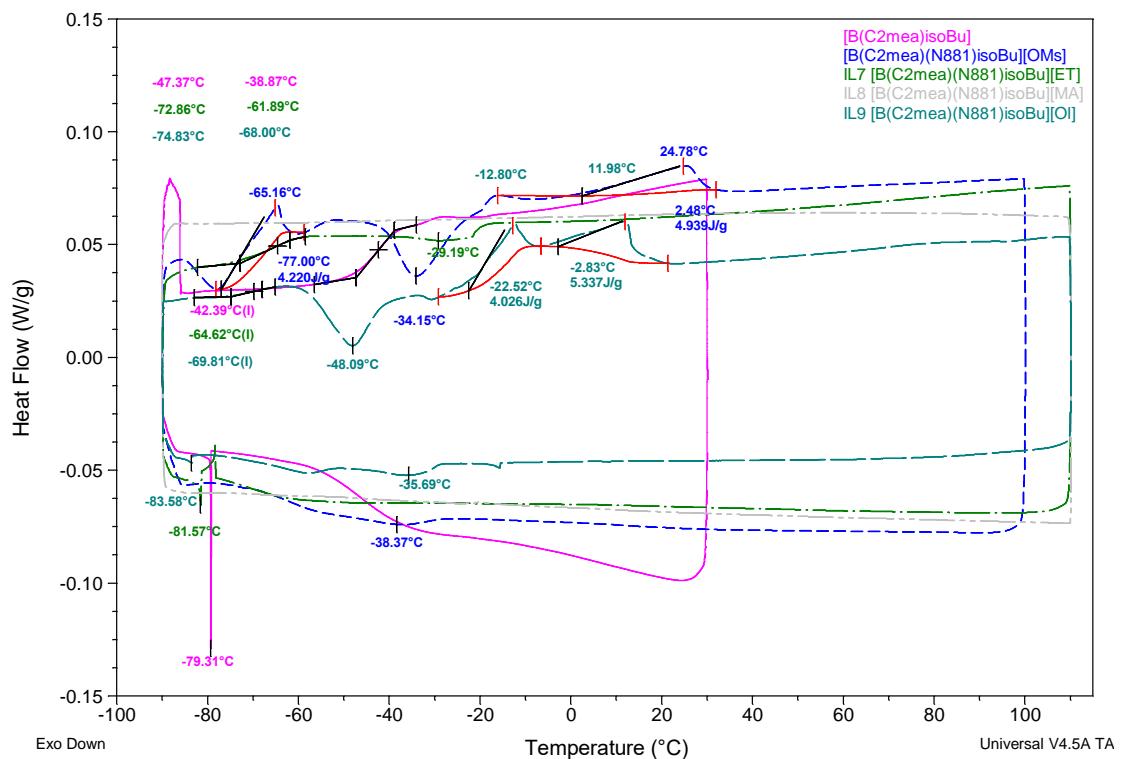


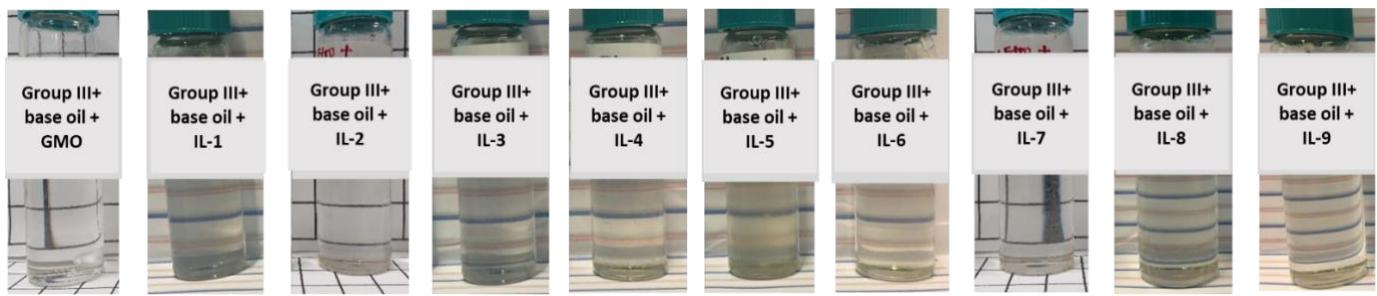
Figure S 66. DSC traces of neat of  $\text{B}(\text{C}_{2\text{mea}})\text{nBu}$ , and the derived ILs:  $[\text{B}(\text{C}_{2\text{mea}})(\text{N}_{881})\text{nBu}][\text{OMs}]$ , IL1, IL2 and IL3. Temperature scan rate:  $2 \text{ }^{\circ}\text{C min}^{-1}$ . DSC trace from the second thermal cycle.



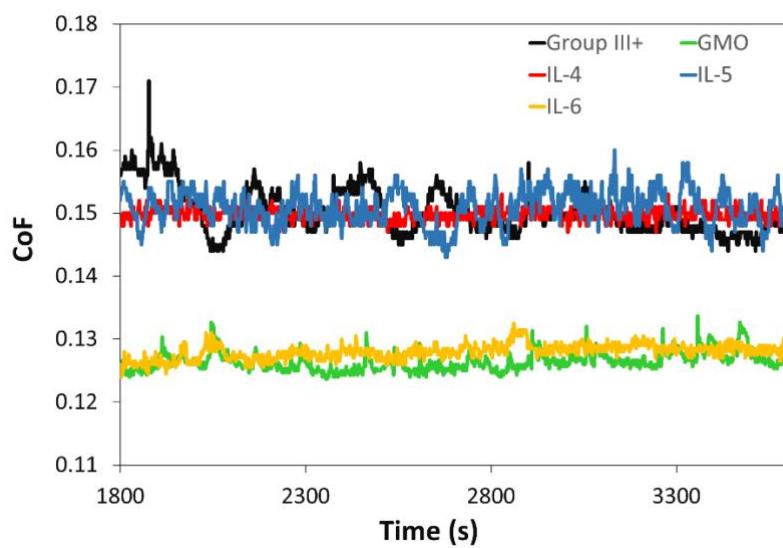
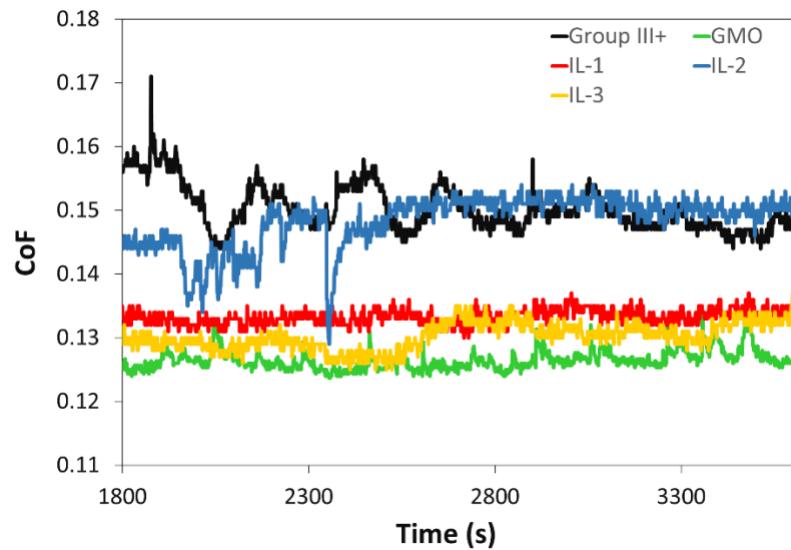
**Figure S 67.** DSC traces of neat of  $B(C_{2mea})secBu$ , and the derived ILs:  $[B(C_{2mea})(N_{881})secBu][OMs]$ , IL4, IL5 and IL6. Temperature scan rate:  $2\text{ }^{\circ}\text{C min}^{-1}$ . DSC trace from the second thermal cycle.

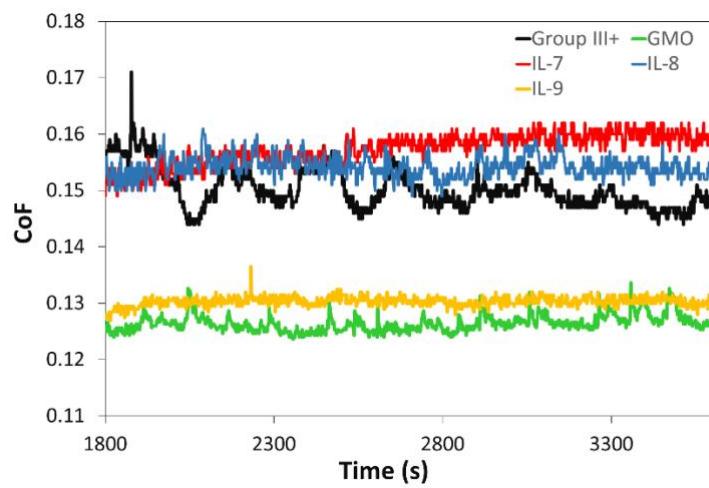


**Figure S 68.** DSC traces of neat of  $B(C_{2mea})isoBu$ , and the derived ILs:  $[B(C_{2mea})(N_{881})isoBu][OMs]$ , IL7, IL8 and IL9. Temperature scan rate:  $2\text{ }^{\circ}\text{C min}^{-1}$ . DSC trace from the second thermal cycle.

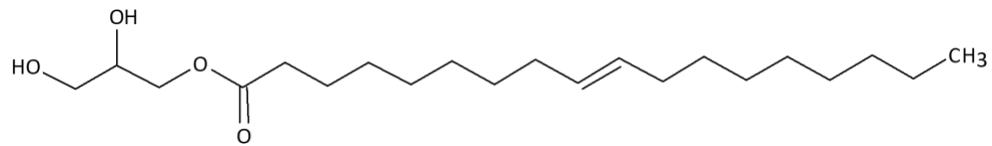


**Figure S 69. Photograph of 9 boronium ILs in Group III+ base oil.**

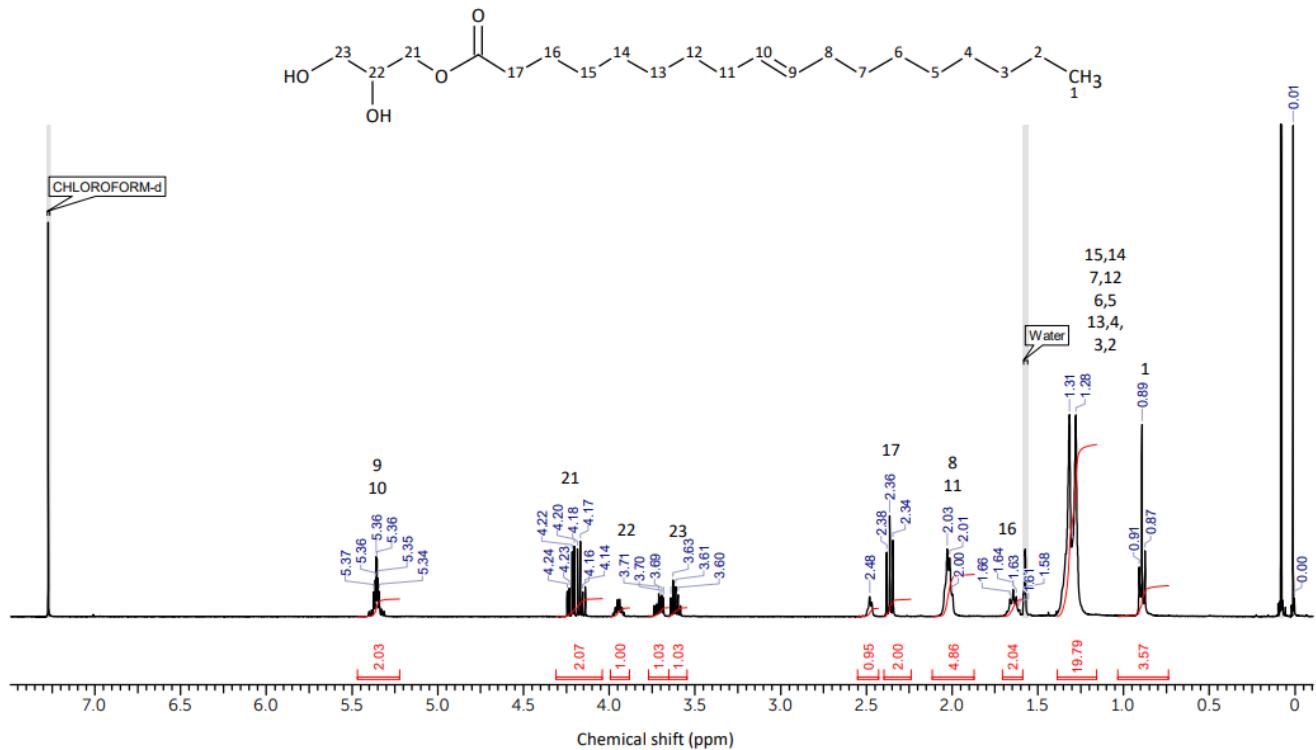




**Figure S 70. Friction coefficient profile of Group III+ base oil and mixtures containing GMO and nine new boronium ILs at 1800 s test time and above**



**Figure S 71. Chemical structure of glycerol monooleate (GMO), a common type of friction modifier.**



**Figure S 72.**  $^1\text{H}$  NMR (400 MHz) spectrum of glycerol monooleate (GMO).

