

Synthesis of Novel Room Temperature Chiral Ionic Liquids. Application as Reaction Media for the Heck Arylation of Aza-endocyclic Acrylates

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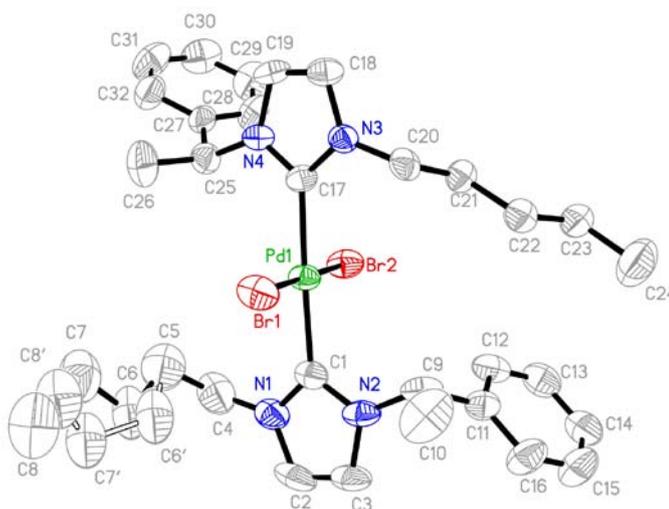
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Crystal Structure Determination

The structures of two compounds were determined. The selected crystals were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly in a stream of cold N₂. For all the structures data collection were collected at low temperature (213 K for compounds **23a** and 173 K for compounds **23b**) and using a graphite-monochromated MoK α radiation ($\lambda = 0.71073\text{\AA}$). The structure were solved by direct methods (SHELXS-97, G. M. Sheldrick, *Acta Crystallogr.* **1990**, A46, 467-473) and all non hydrogen atoms were refined anisotropically using the least-squares method on F^2 (SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen **1997**). CCDC 724261 (**23a**) and CCDC 724262 (**23b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

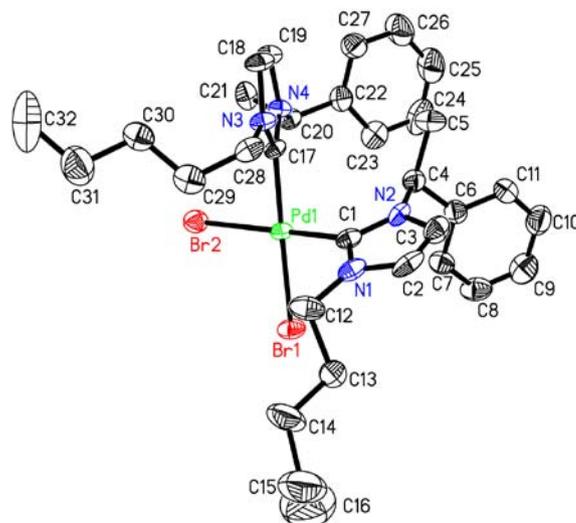
Selected crystallographic data for compound **23a**



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Selected data for *trans-anti* Pd complex **23a**: $C_{32}H_{44}Br_2N_4Pd$, $M = 750.93$, orthorhombic, space group $P2(1)2(1)2(1)$, $a = 8.7609(2) \text{ \AA}$, $b = 12.0766(3) \text{ \AA}$, $c = 31.6211(9) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 3345.57(15) \text{ \AA}^3$, $Z = 4$, crystal size $0.35 \times 0.15 \times 0.05 \text{ mm}^3$, 32050 reflections collected (6787 independent, $R_{int} = 0.0821$), 383 parameters, $R1 [I > 2\sigma(I)] = 0.0423$, $wR2 [\text{all data}] = 0.0804$, largest diff. peak and hole: 0.422 and -0.392 e\AA^{-3} .

Selected crystallographic data for compound **23b**



Selected data for *cis-syn* Pd complex **23b**: $C_{33}H_{46}Br_2C_{12}N_4Pd$, $M = 835.86$, orthorhombic, space group $P2(1)2(1)2(1)$, $a = 7.7314(8) \text{ \AA}$, $b = 17.6948(17) \text{ \AA}$, $c = 27.018(3) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 3696.3(6) \text{ \AA}^3$, $Z = 4$, crystal size $0.40 \times 0.20 \times 0.05 \text{ mm}^3$, 33902 reflections collected (9117 independent, $R_{int} = 0.0759$), 447 parameters, $R1 [I > 2\sigma(I)] = 0.0544$, $wR2 [\text{all data}] = 0.1145$, largest diff. peak and hole: 0.624 and -0.727 e\AA^{-3} .

1H NMR and ^{13}C NMR spectra for compounds **11**, **12**, **13**, **15**, **16**, **17**, **18**, **19**, **20**, **23**, **28**, **29**, **31**, **32**, **33**, **34** and **35**

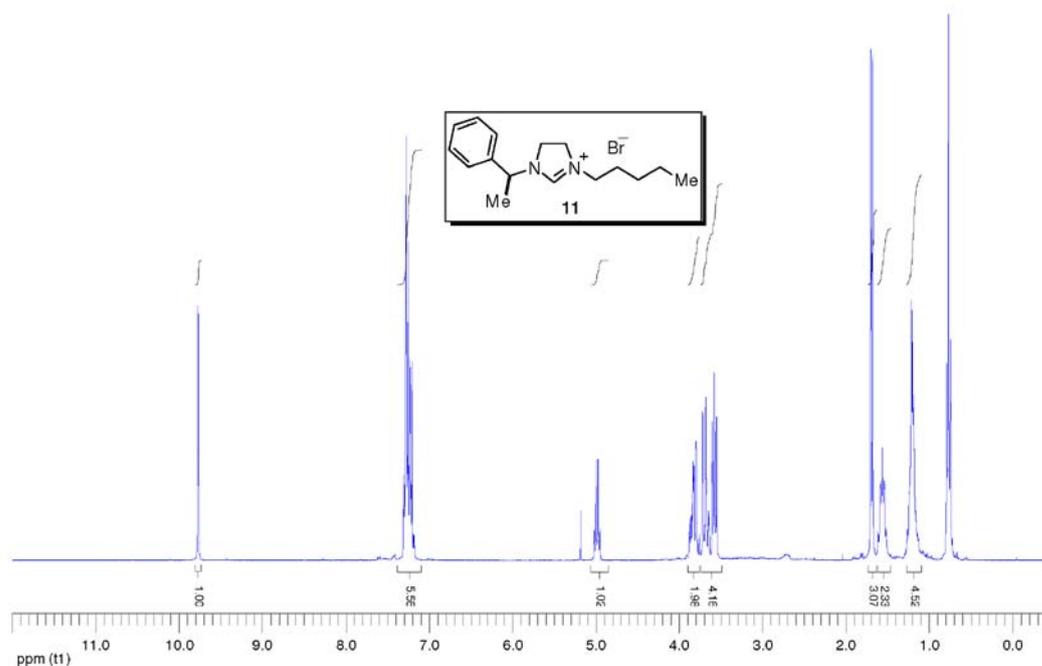


Figura S1. 1H NMR spectrum (300 MHz, $CDCl_3$) of compound **11**.

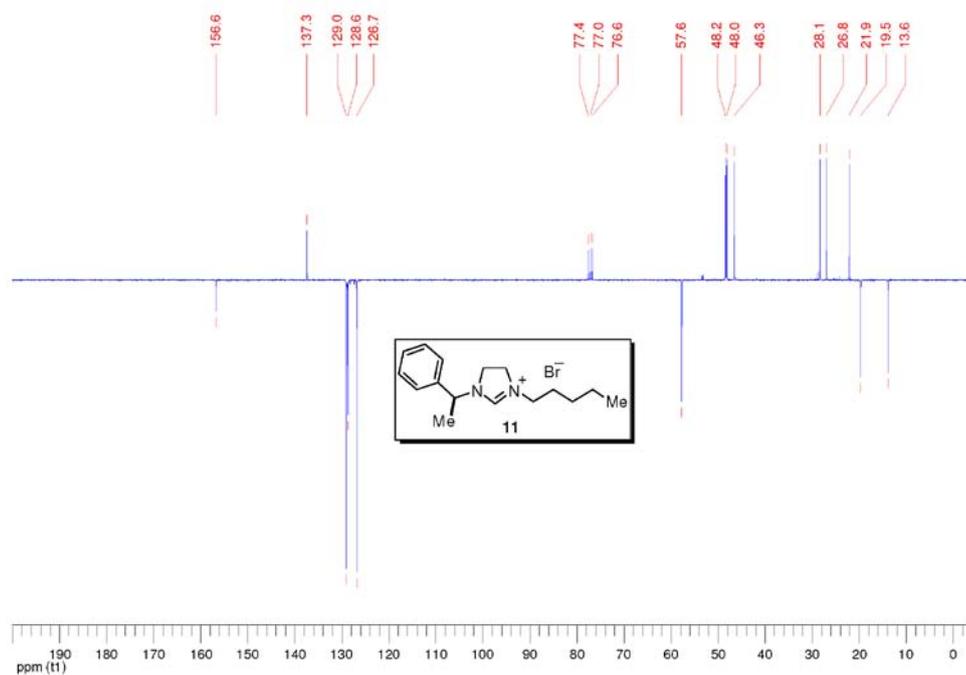


Figure S2. ^{13}C NMR spectrum (75 MHz, CDCl_3) of compound **11**.

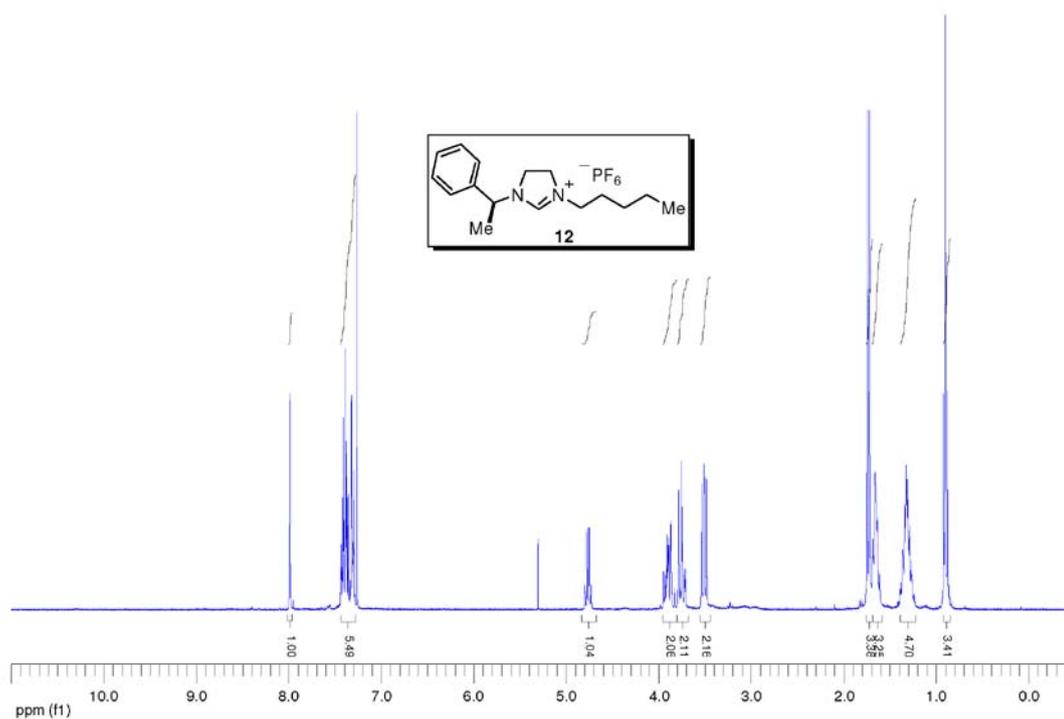


Figure S3. ^1H NMR spectrum (300 MHz, CDCl_3) of compound **12**.

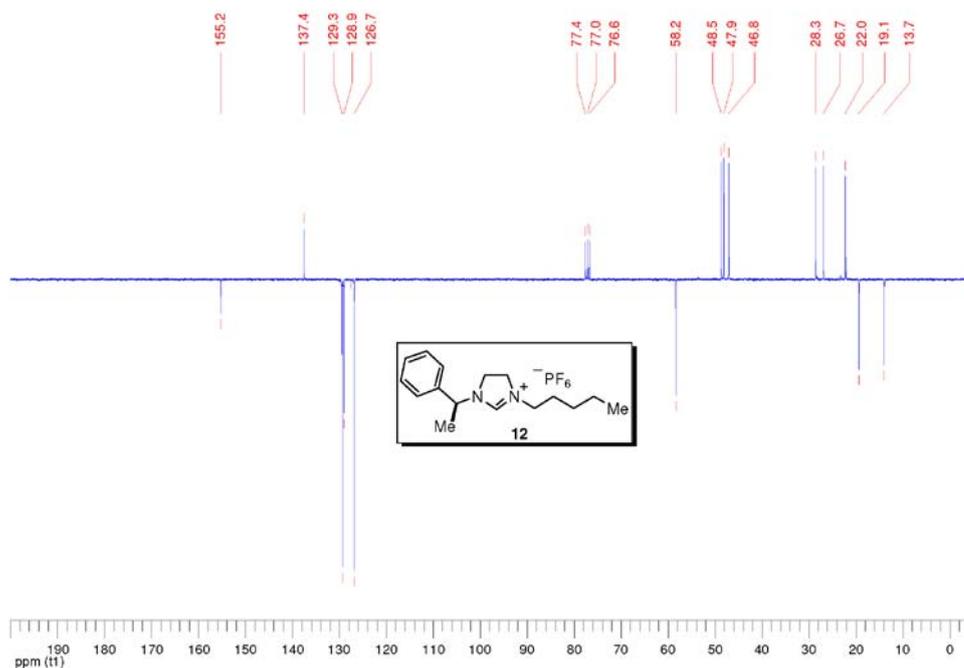


Figura S4. ¹³C NMR spectrum (75 MHz, CDCl₃) of compound 12.

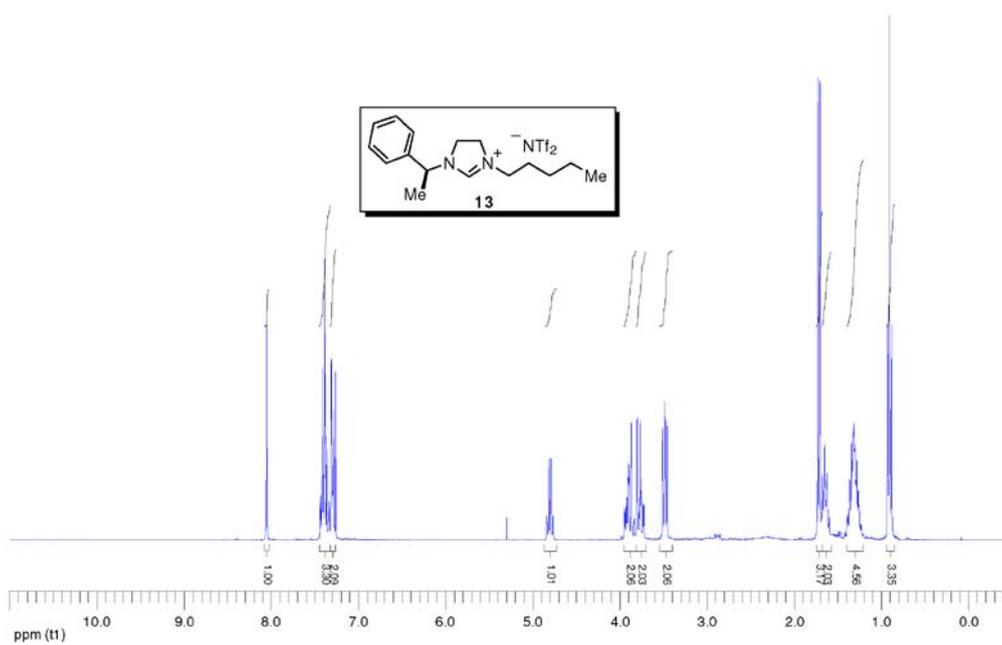


Figura S5. ¹H NMR spectrum (300 MHz, CDCl₃) of compound 13.

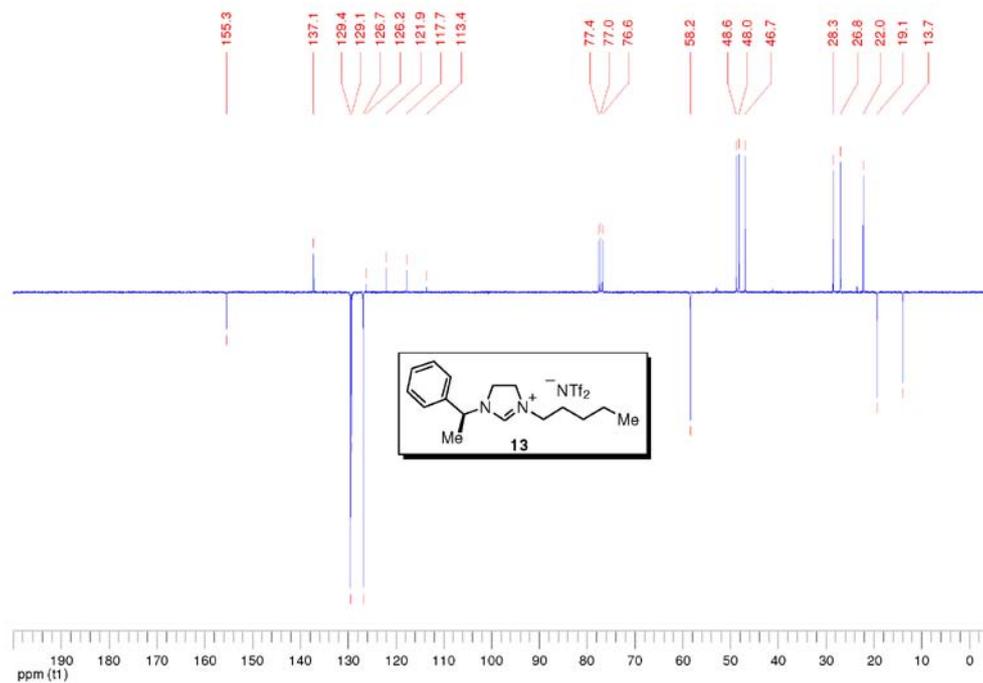


Figura S6. ¹³C NMR spectrum (75 MHz, CDCl₃) of compound 13.

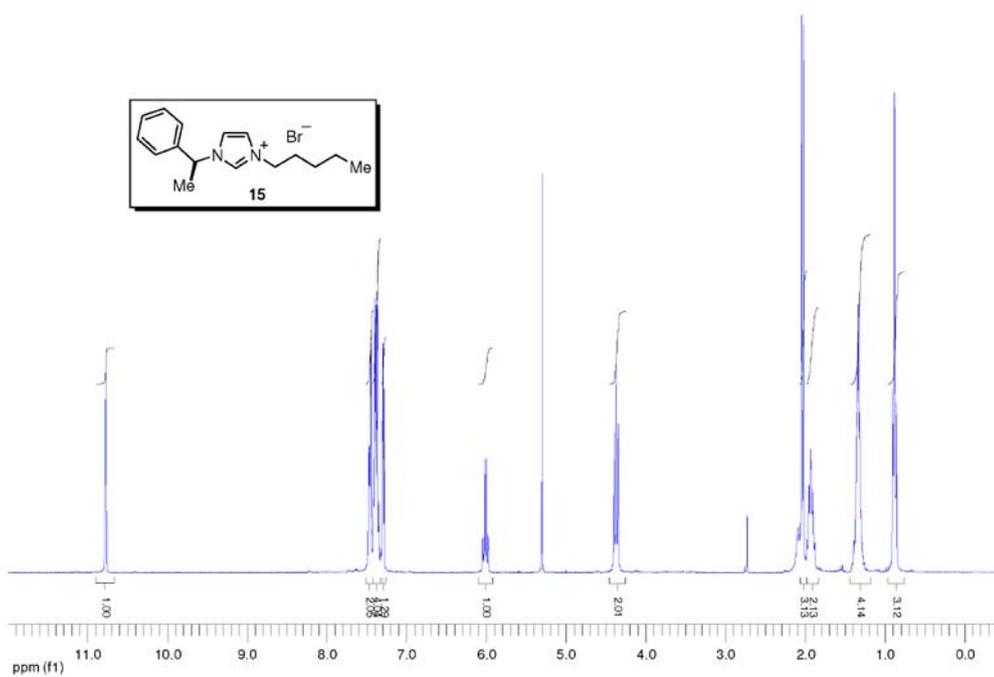


Figura S7. ¹H NMR spectrum (300 MHz, CDCl₃) of compound 15.

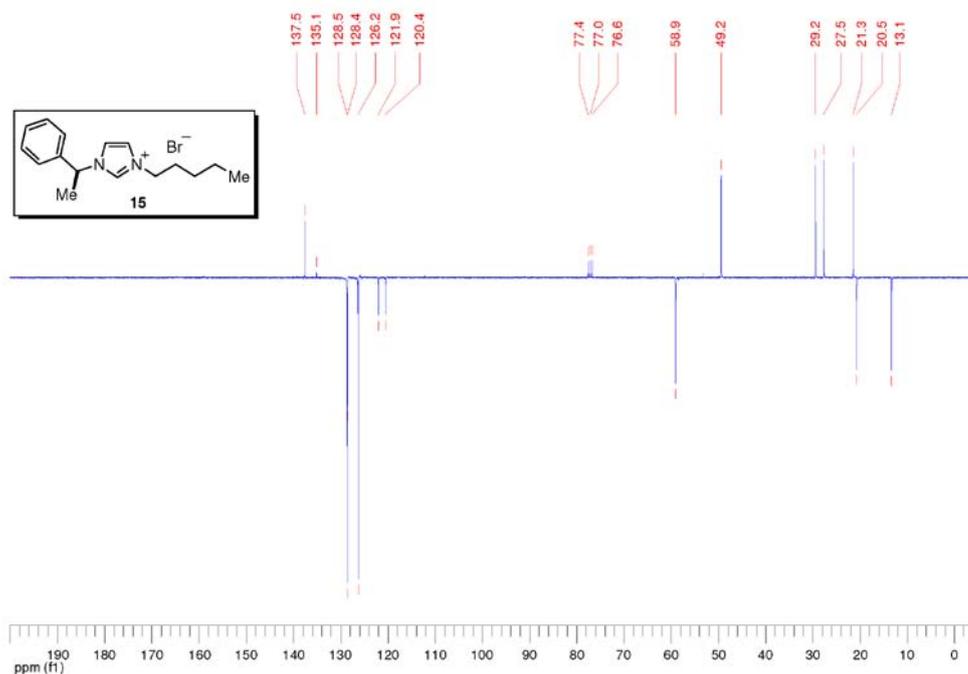


Figura S8. ¹³C NMR spectrum (75 MHz, CDCl₃) of compound 15.

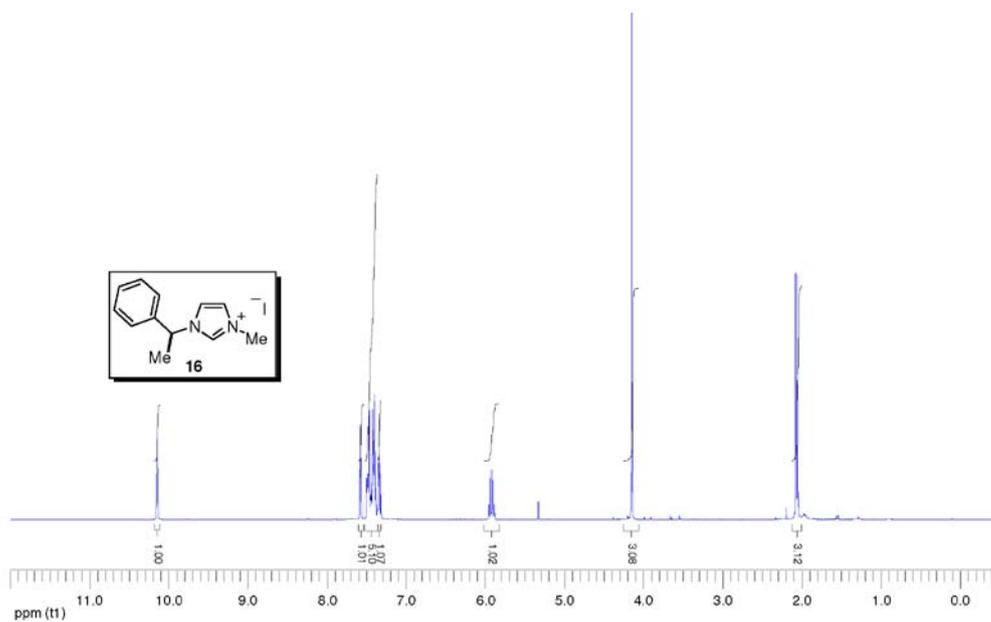


Figura S9. ¹H NMR spectrum (300 MHz, CDCl₃) of compound 16.

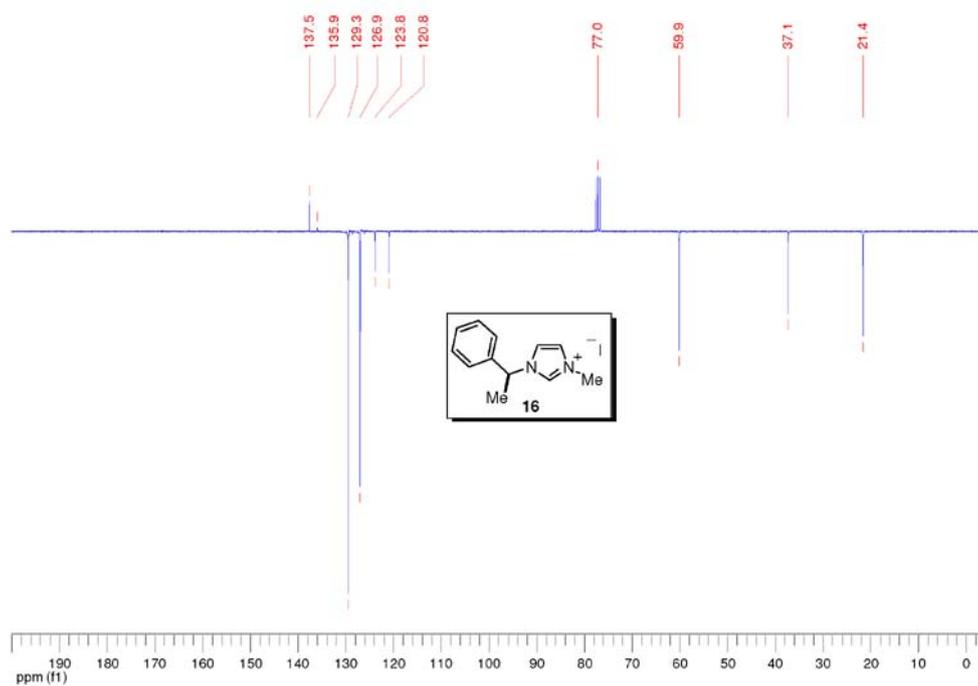


Figura S10. ^{13}C NMR spectrum (75 MHz, CDCl_3) of compound **16**.

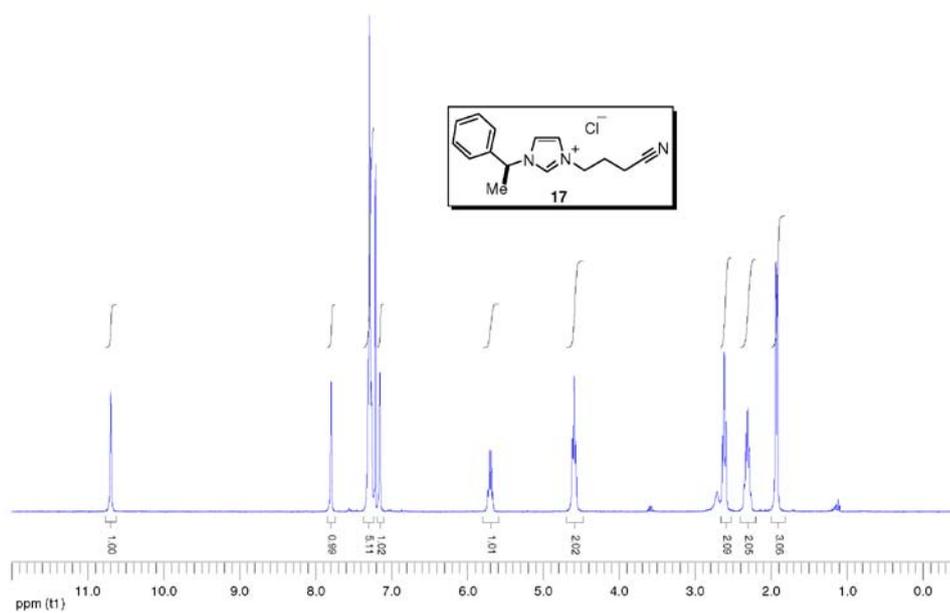


Figura S11. ^1H NMR spectrum (300 MHz, CDCl_3) of compound **17**.

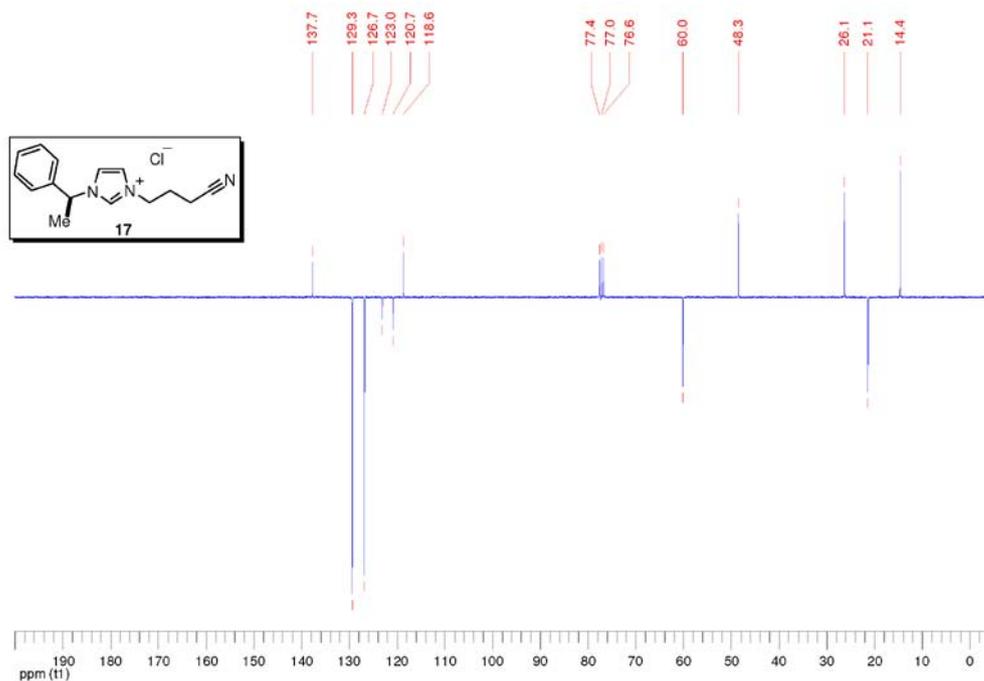


Figura S12. ¹³C NMR spectrum (75 MHz, CDCl₃) of compound 17.

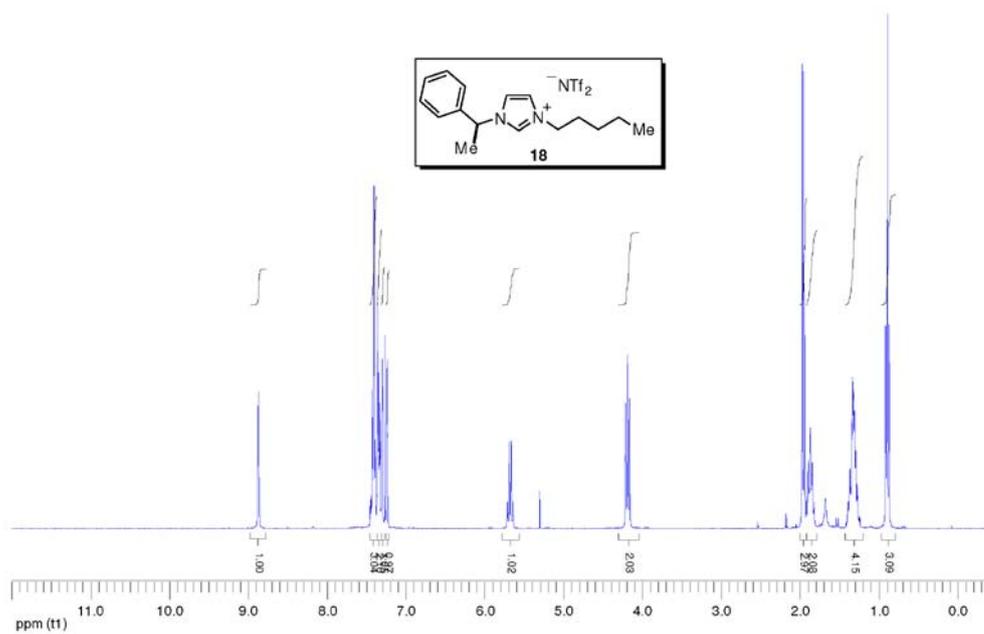


Figura S13. ¹H NMR spectrum (300 MHz, CDCl₃) of compound 18.

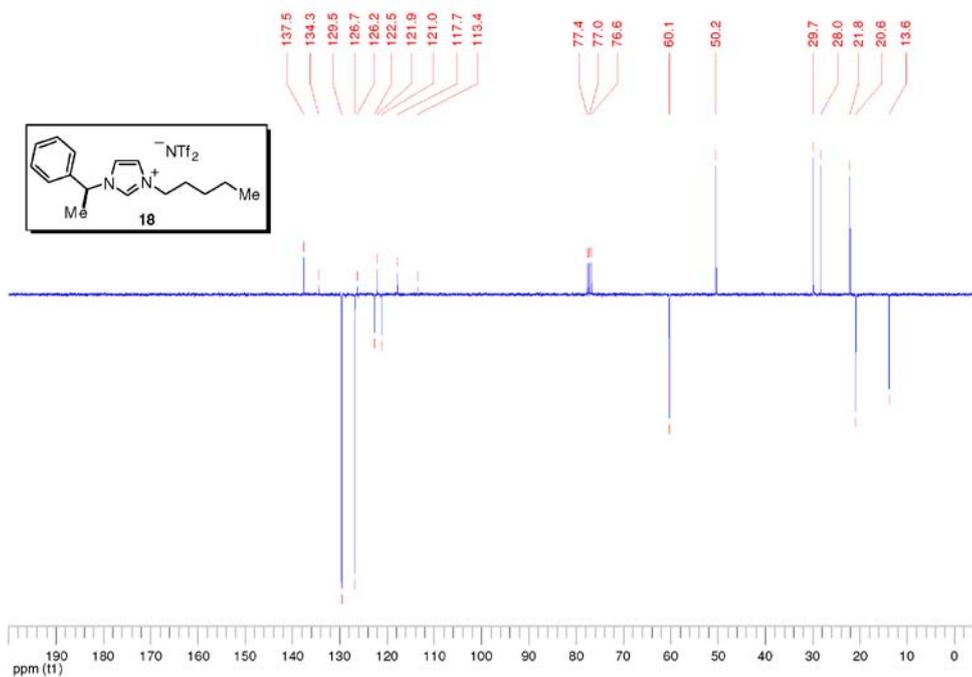


Figura S14. ^{13}C NMR spectrum (75 MHz, CDCl_3) of compound **18**.

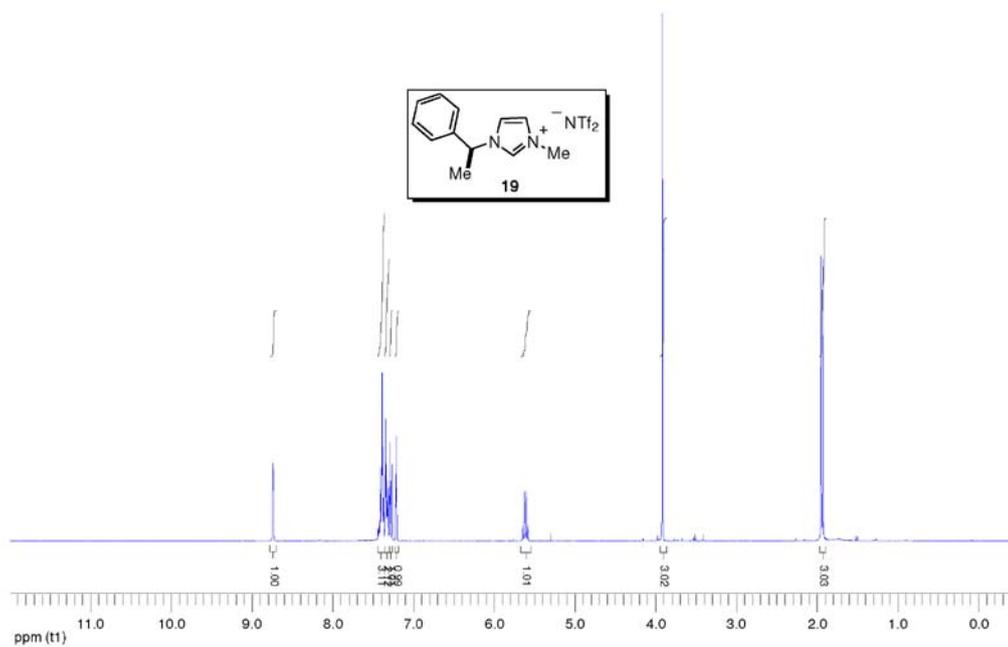


Figura S15. ^1H NMR spectrum (300 MHz, CDCl_3) of compound **19**.

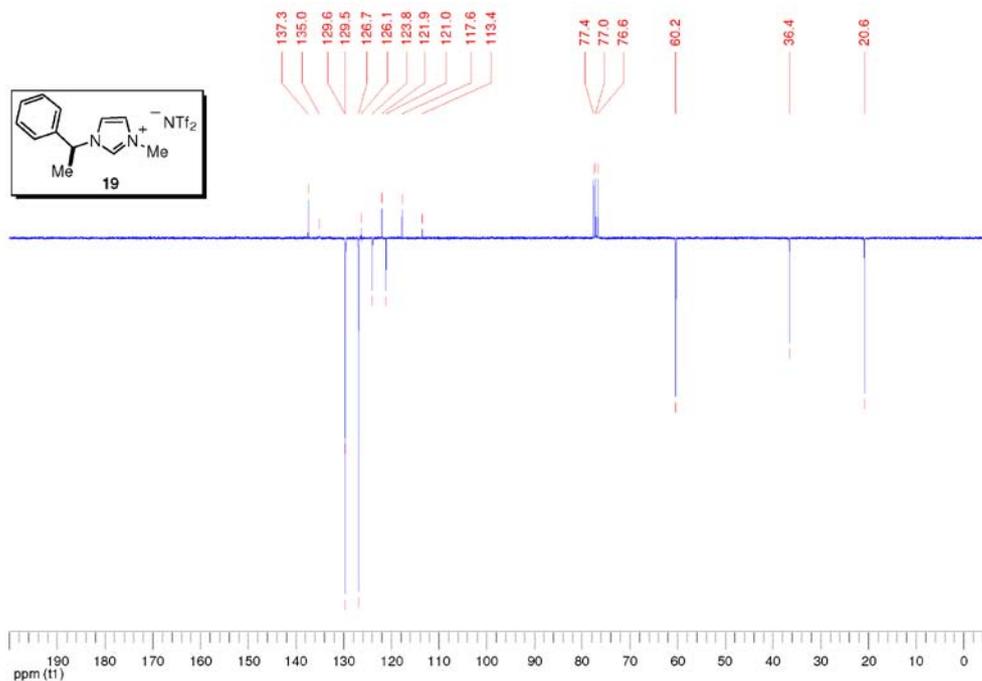


Figura S16. ¹³C NMR spectrum (75 MHz, CDCl₃) of compound 19.

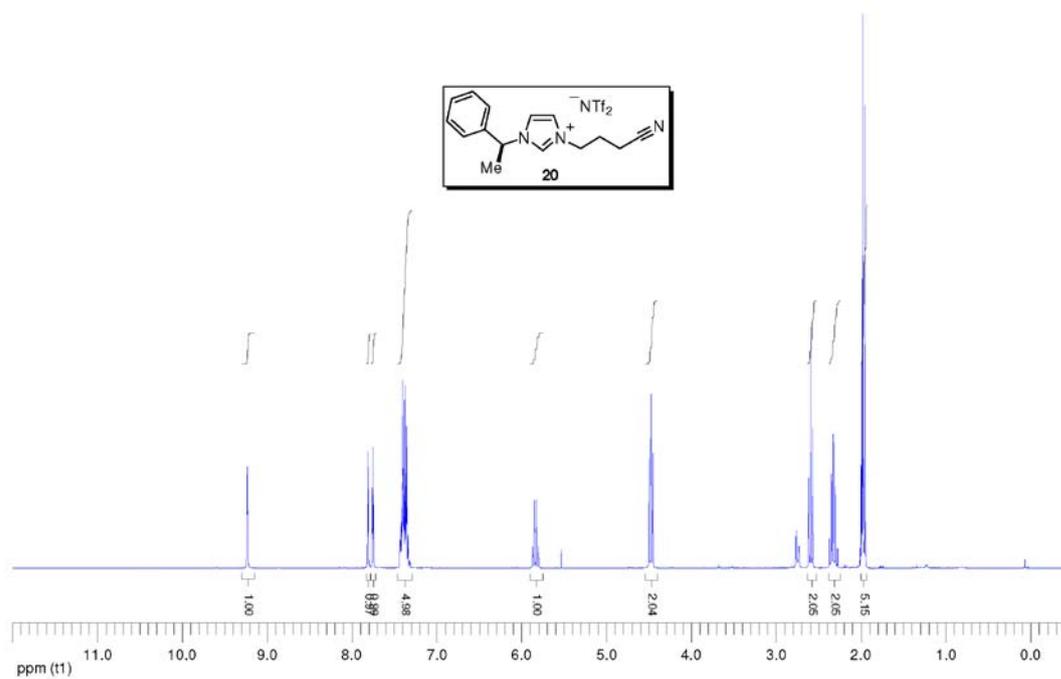


Figura S17. ¹H NMR spectrum (300 MHz, acetone-d₆) of compound 20.

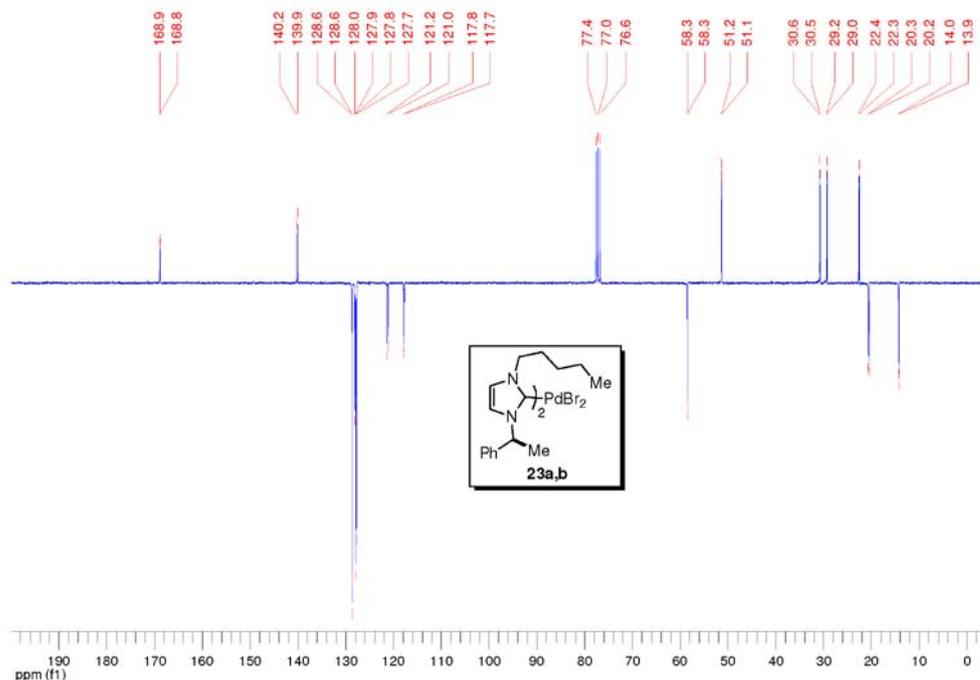


Figura S20. ^{13}C NMR spectrum (75 MHz, CDCl_3) of compound **23a,b**.

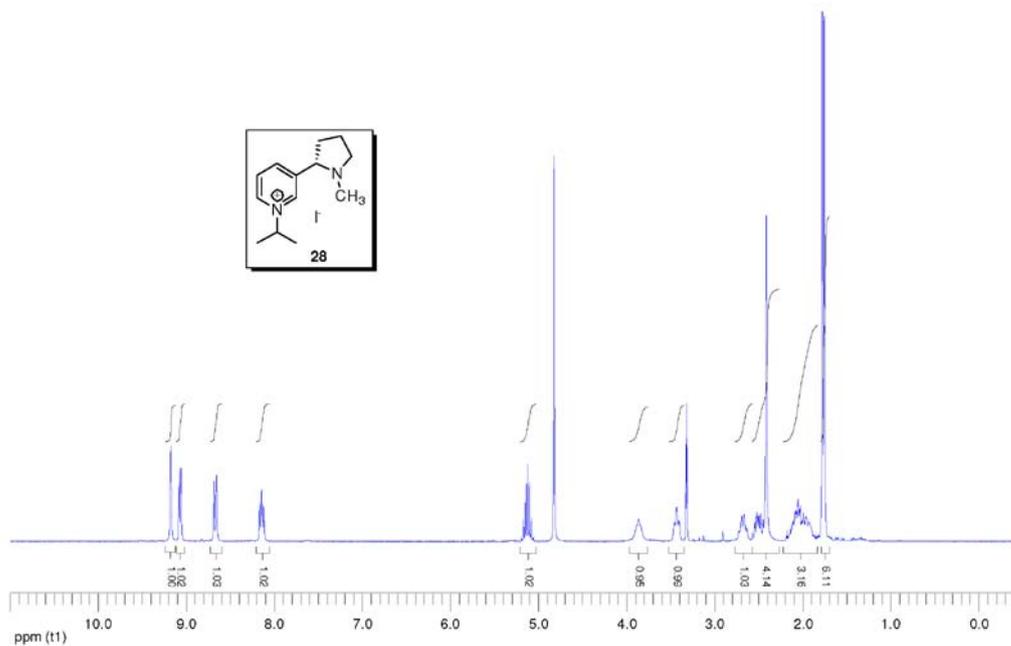


Figura S21. ^1H NMR spectrum (300 MHz, CD_3OD) of compound **28**.

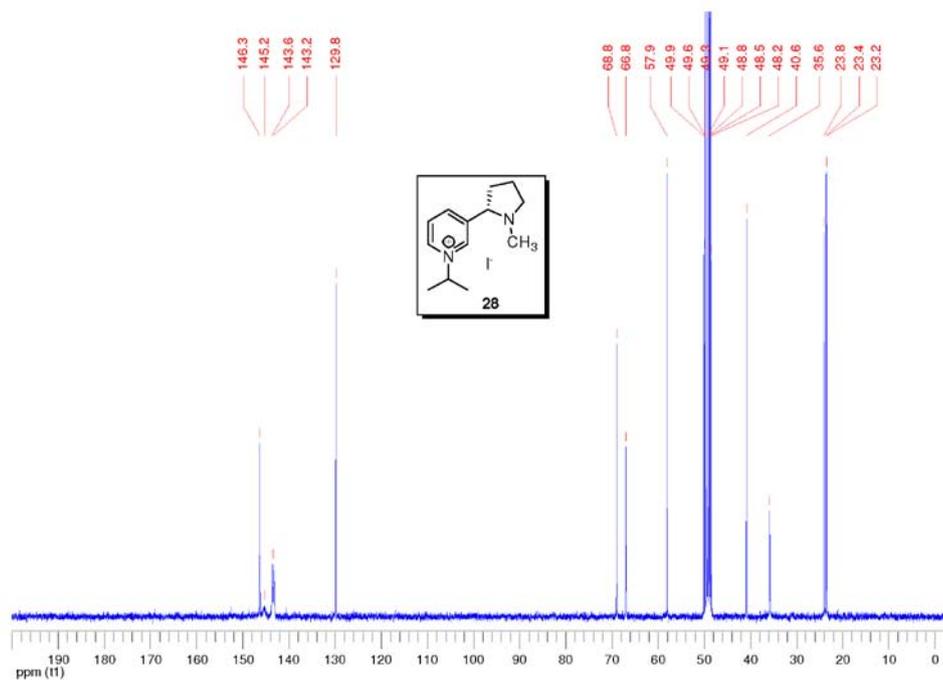


Figura S22. ¹³C NMR spectrum (75 MHz, CD₃OD) of compound 28.

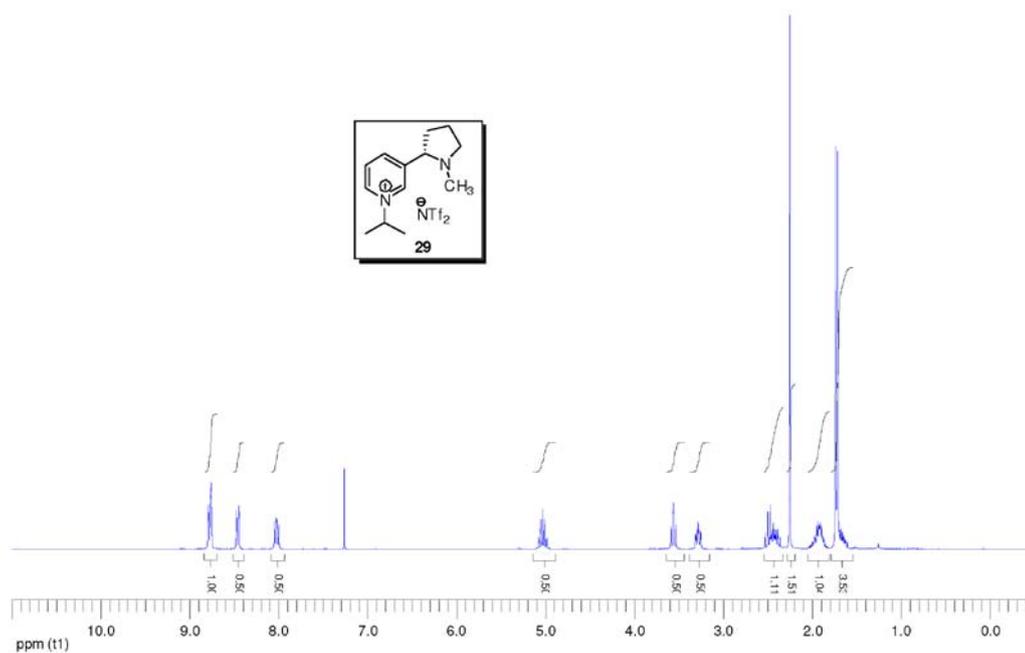


Figura S23. ¹H NMR spectrum (300 MHz, CDCl₃) of compound 29.

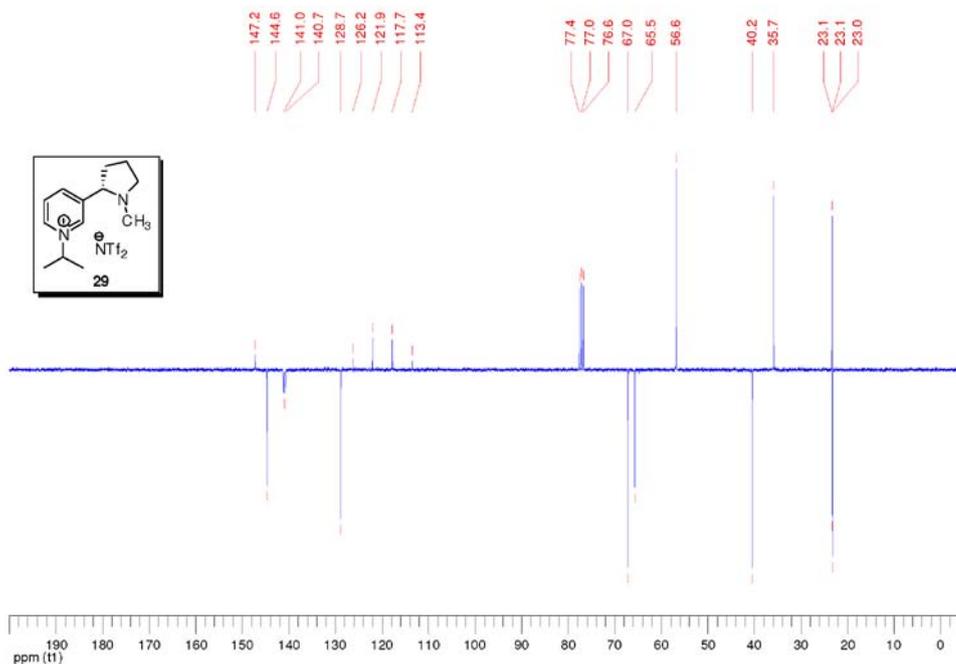


Figura S24. ¹³C NMR spectrum (75 MHz, CDCl₃) of compound 29.

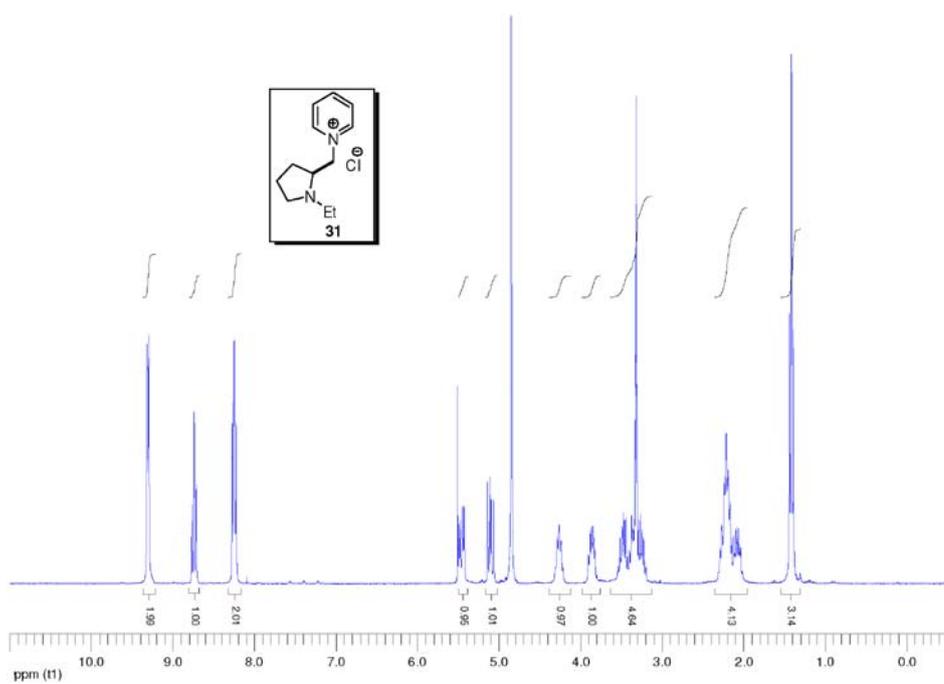


Figura S25. ¹H NMR spectrum (300 MHz, CD₃OD) of compound 31.

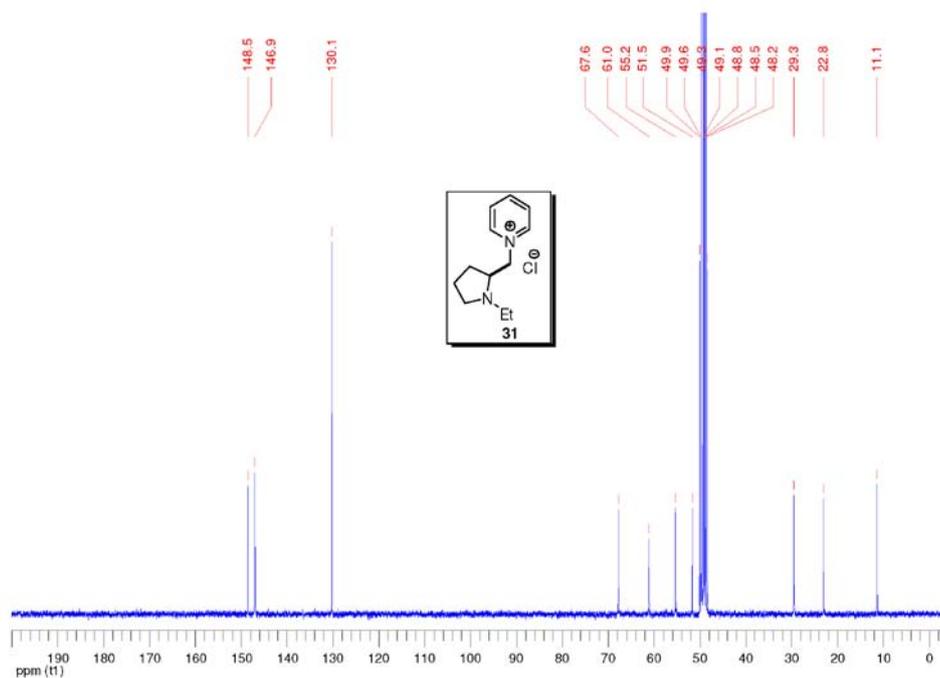


Figura S26. ^{13}C NMR spectrum (75 MHz, CD_3OD) of compound 31.

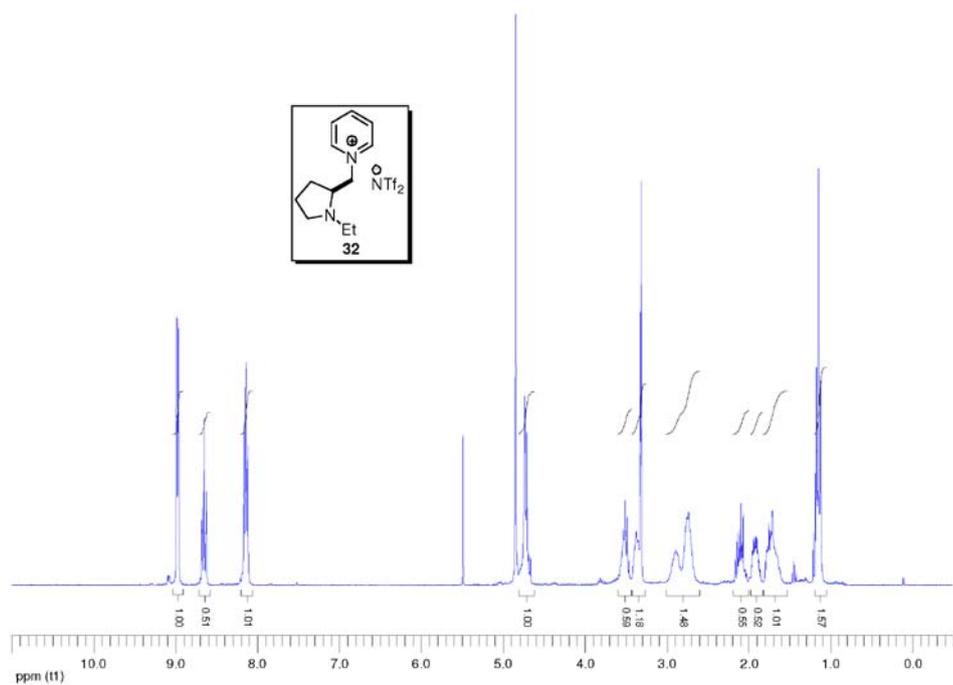


Figura S27. ^1H NMR spectrum (300 MHz, CD_3OD) of compound 32.

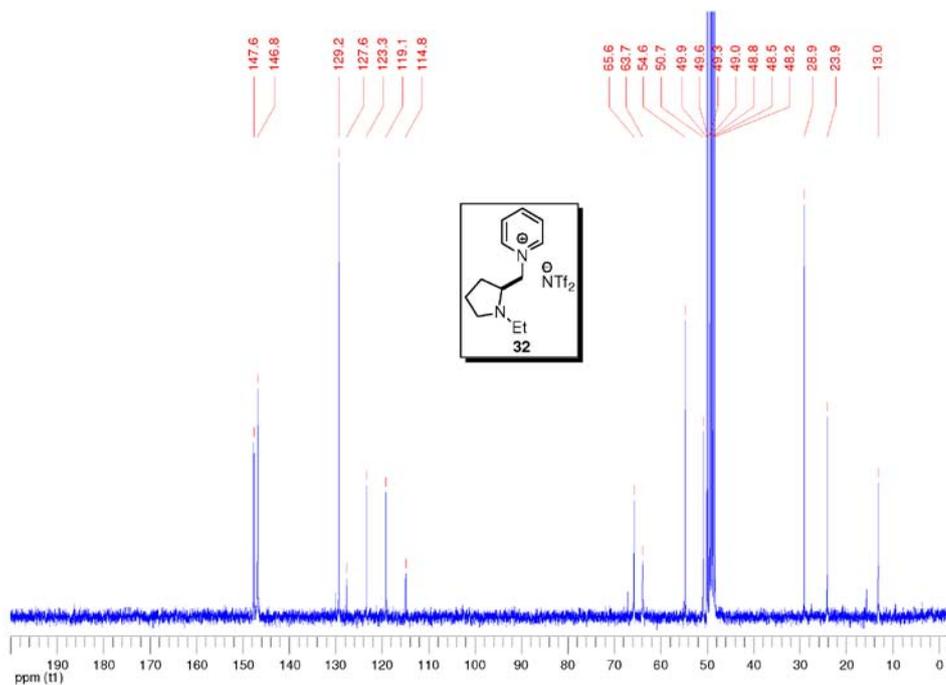


Figura S28. ¹³C NMR spectrum (75 MHz, CD₃OD) of compound 32.

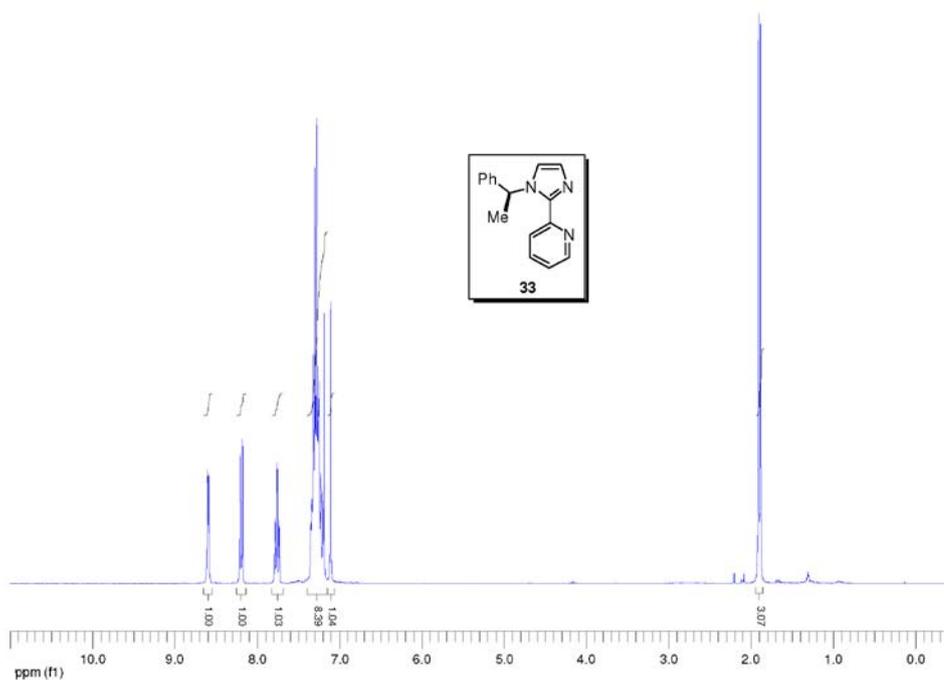


Figura S29. ¹H NMR spectrum (300 MHz, CDCl₃) of compound 33.

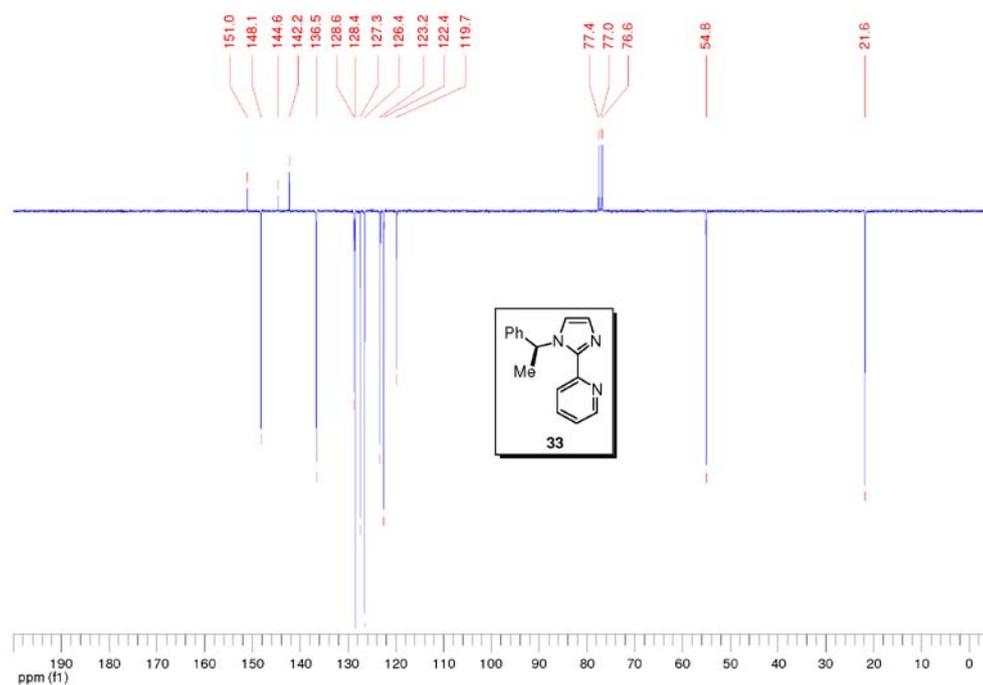


Figura S30. ¹³C NMR spectrum (75 MHz, CDCl₃) of compound 33.

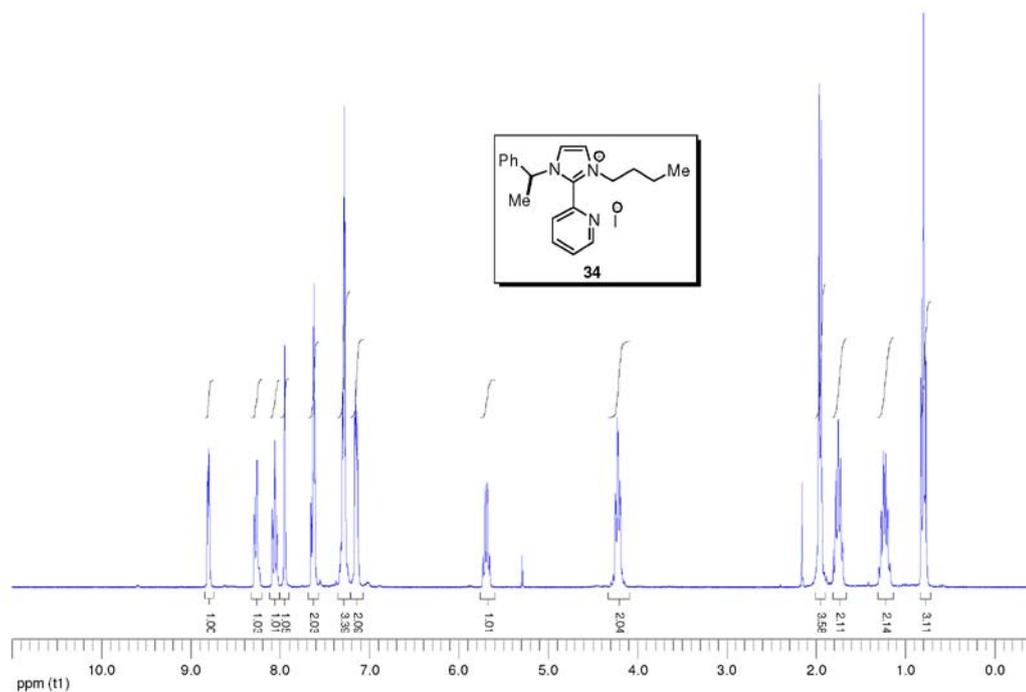


Figura S31. ¹H NMR spectrum (300 MHz, CDCl₃) of compound 34.

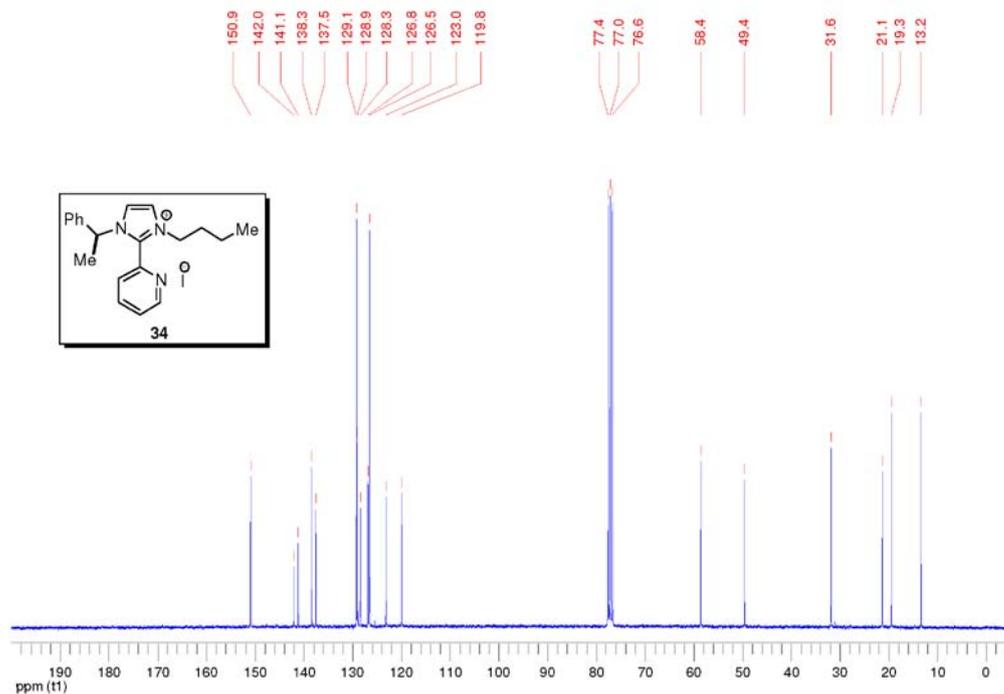


Figura S32. ¹³C NMR spectrum (75 MHz, CDCl₃) of compound 34.

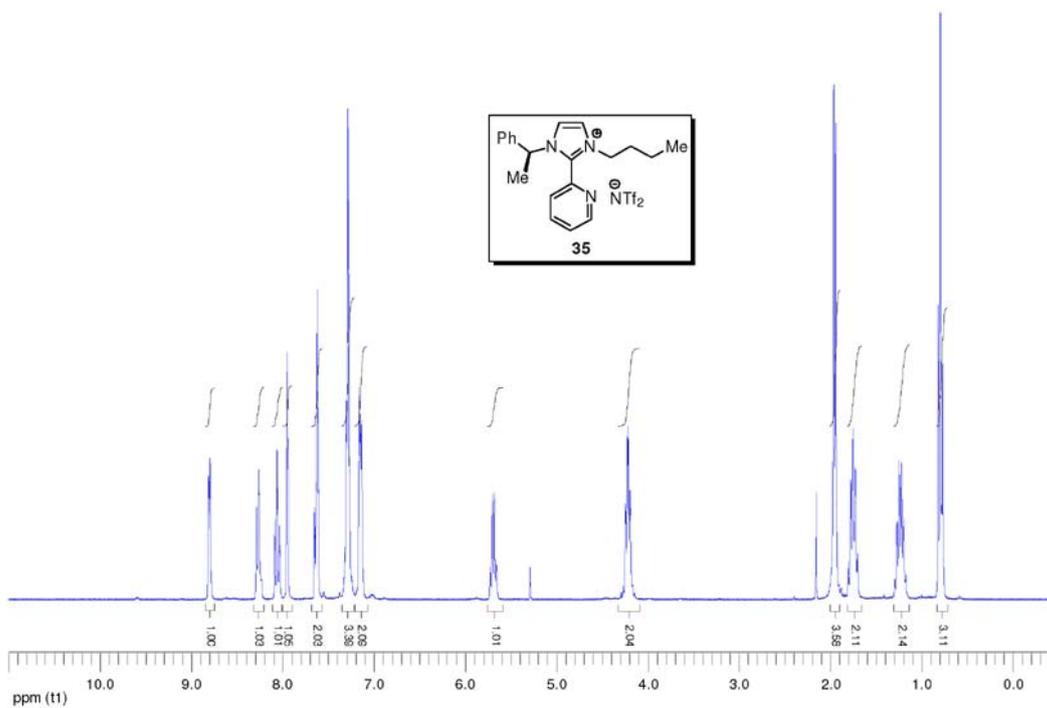


Figura S33. ¹H NMR spectrum (300 MHz, CDCl₃) of compound 35.

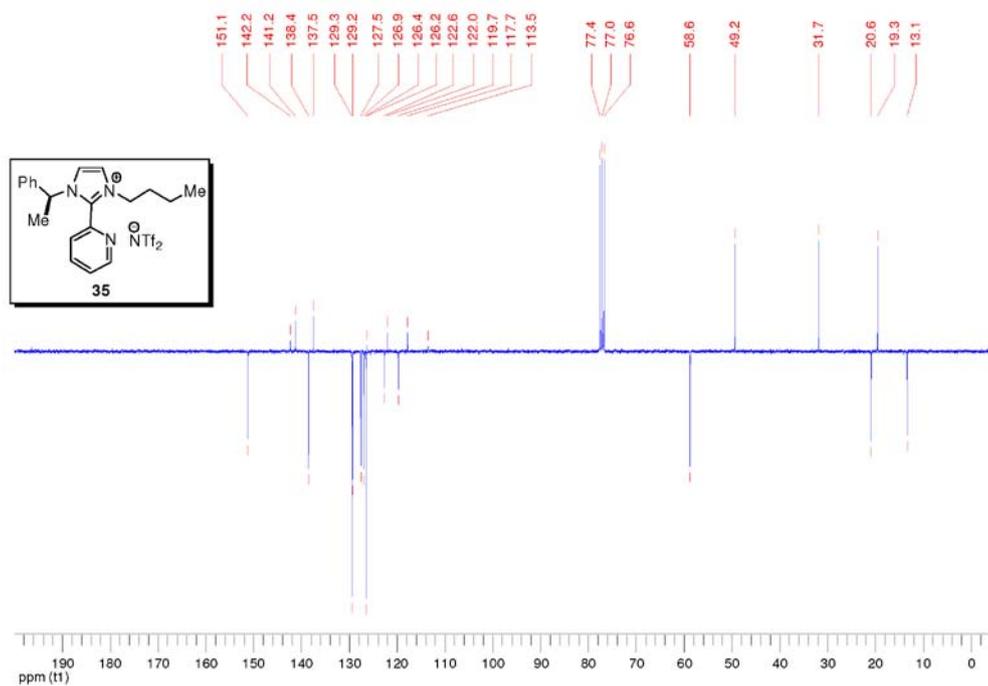


Figura S34. ^{13}C NMR spectrum (75 MHz, CDCl_3) of compound 35.