Supporting Information

Synthesis and structural elucidation of homometallic anthracenolates *via* deprotonative metallation of anthrone

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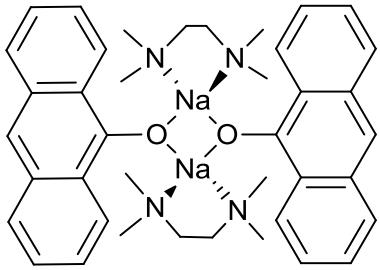
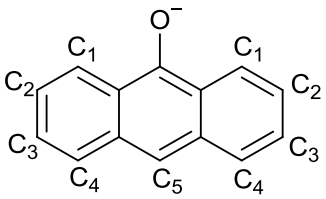
General Methods

Hexane, purchased from Sigma Aldrich was distilled from sodium-benzophenone. All synthetic work was carried out under a protective inert argon atmosphere using standard Schlenk techniques. Data for X-ray crystal structure determination were obtained with an Oxford Diffraction Gemini S Diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 123(2) K. The ^{1}H NMR spectroscopic experiments were performed on a Bruker DPX400 spectrometer with an operating frequency of 400.13 MHz. The ^{13}C NMR spectra were recorded on the same instrument at an operating frequency of 100.63 MHz. All chemical shifts are quoted relative to TMS standard at 0.00 parts per million.

NMR spectroscopic analysis of [2(TMEDA)·$Na_2(C_{14}H_9O)_2$] (2)

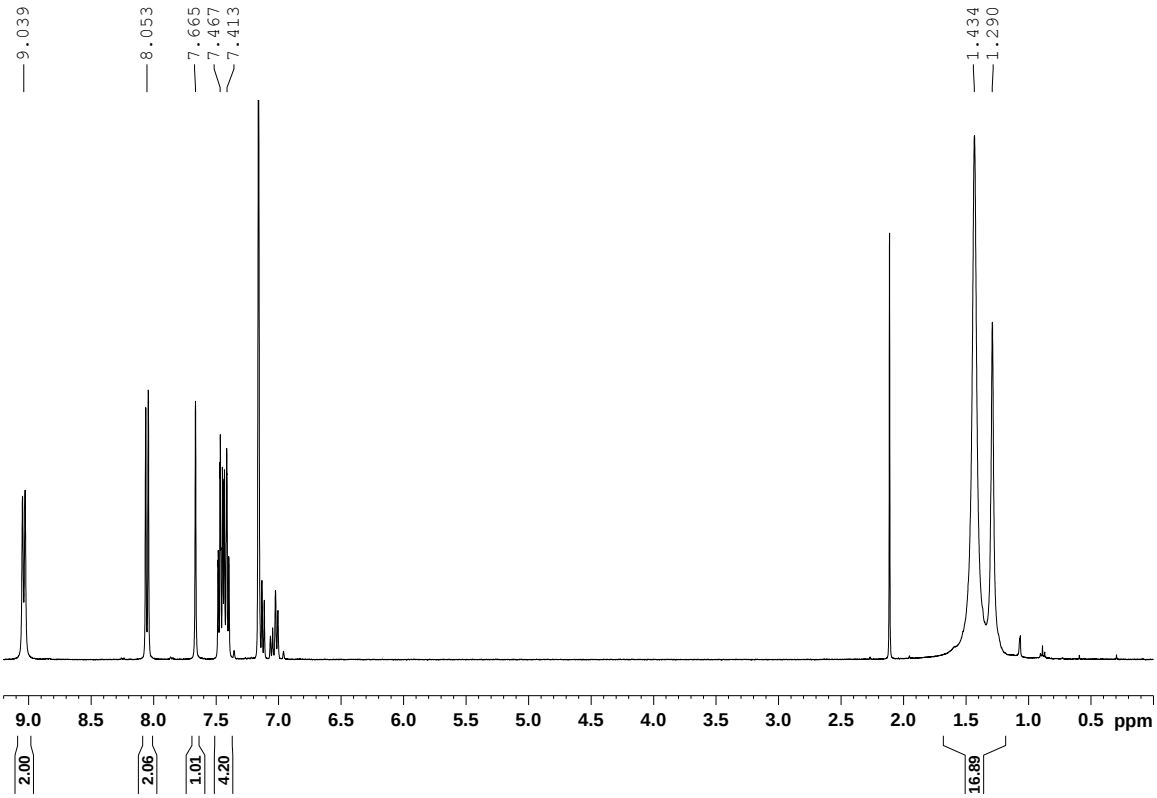




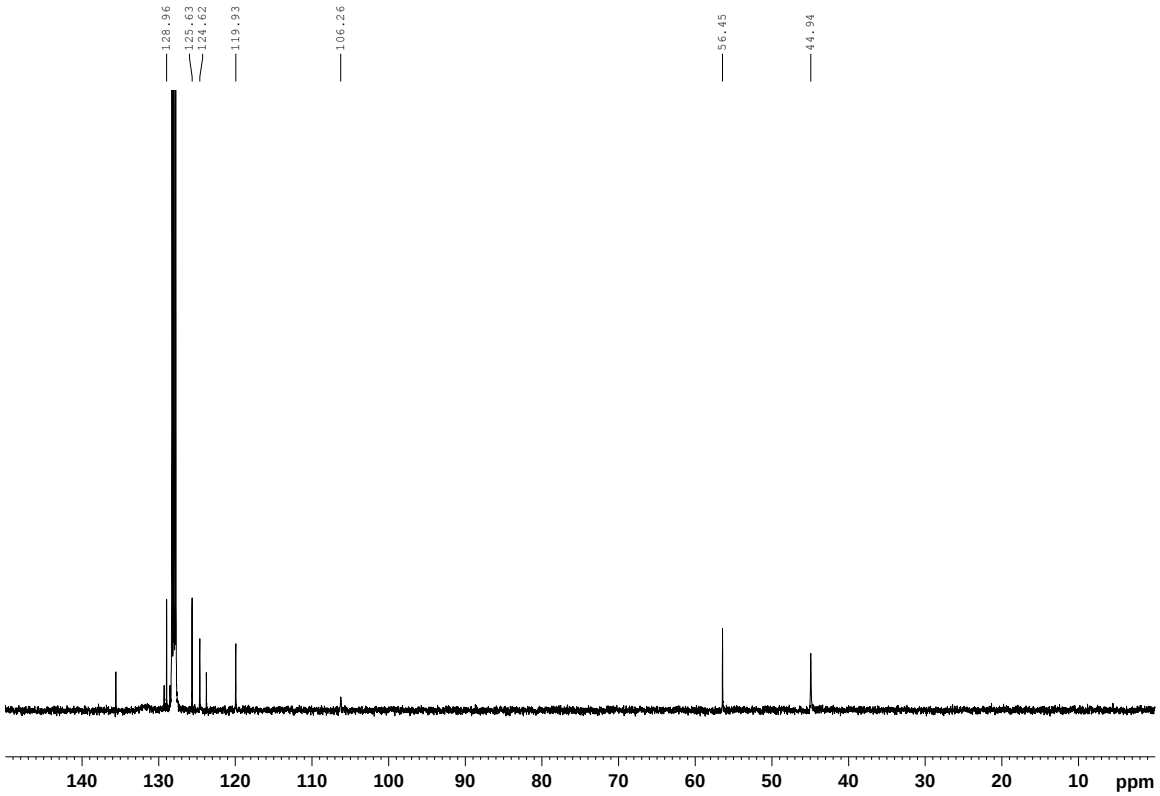
(2)

^{1}H NMR (400.13 MHz, 298K, C_6D_6):- δ 9.04 (2H, d, C_1), 8.05 (2H, d, C_4), 7.67 (1H, s, C_5), 7.47 (2H, t, C_3), 7.42 (2H, t, C_2), 1.43 (12H, s, TMEDA-CH_3), 1.29 (4H, s, TMEDA-CH_2).

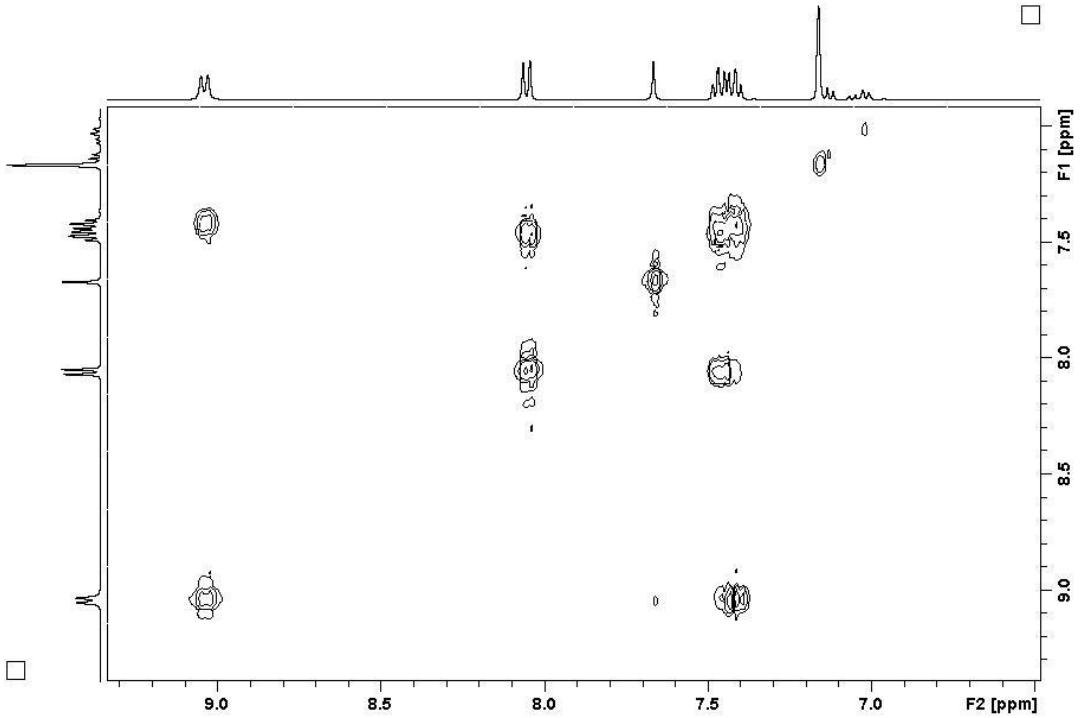
^{13}C NMR (400.13 MHz, 298K, C_6D_6):- δ 129.0 (C_4), 125.6 (C_3), 124.6 (C_1), 120.0 (C_2), 106.3 (C_5), 56.5 (TMEDA-*C*H_2), 44.9 (TMEDA-*C*H_3)



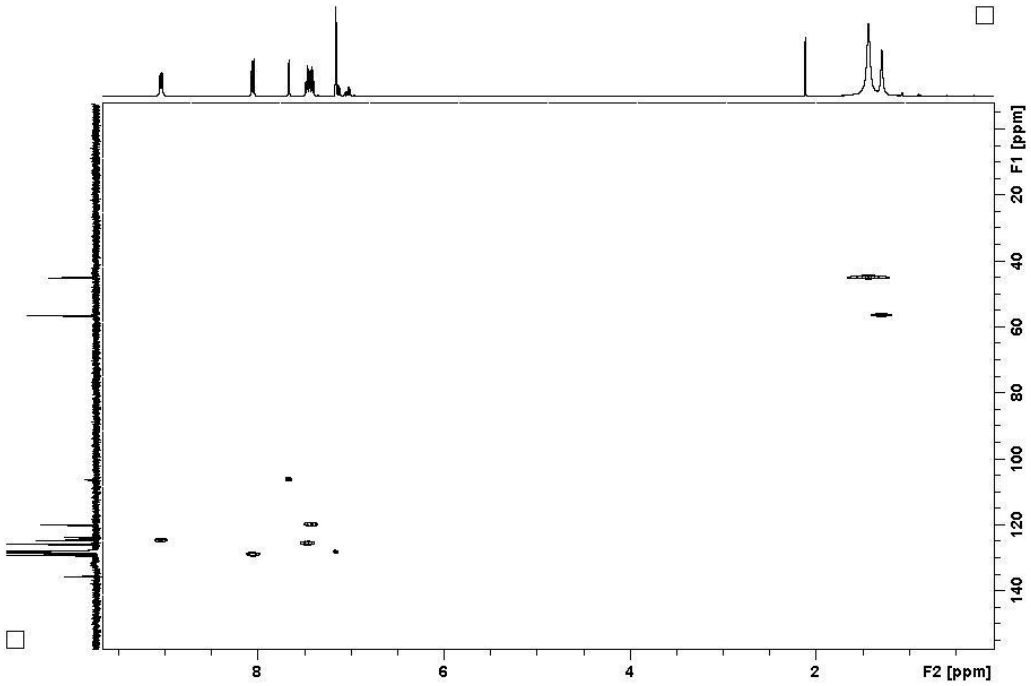
Spectrum 1. ^{1}H NMR (400.13 MHz, 300 K) spectrum of **2** in C_6D_6 solution.



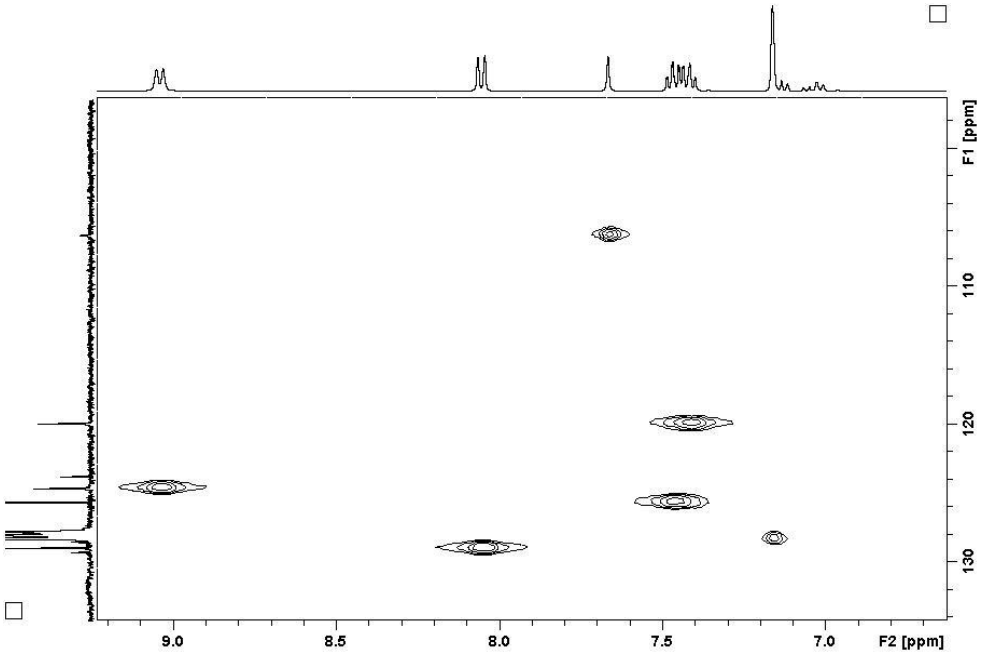
Spectrum 2. ^{13}C NMR (100.63 MHz, 300 K) spectrum of **2** in C_6D_6 solution.



Spectrum 3. COSY (^1H, ^1H) spectrum of **2** in C_6D_6 solution (expanded aromatic region).

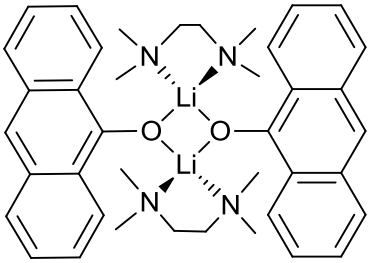


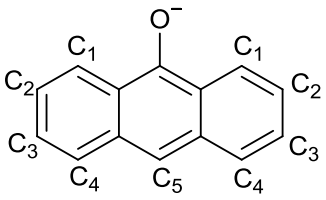
Spectrum 4. HSQC (^{1}H, ^{13}C) spectrum of **2** in C_6D_6 solution.



Spectrum 5. HSQC (^{1}H, ^{13}C) spectrum of **2** in C_6D_6 solution (Expanded aromatic region).

NMR spectroscopic analysis of [2(TMEDA)·$Li_2(C_{14}H_9O)_2$] (3)

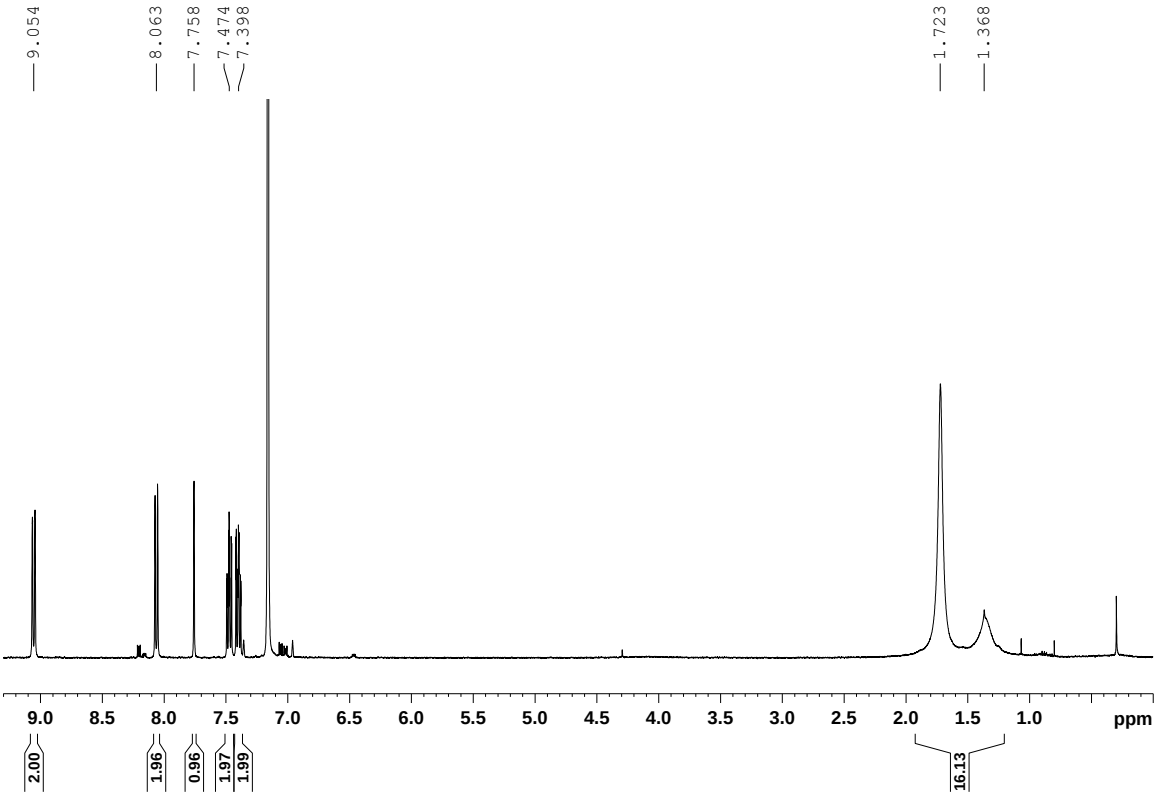




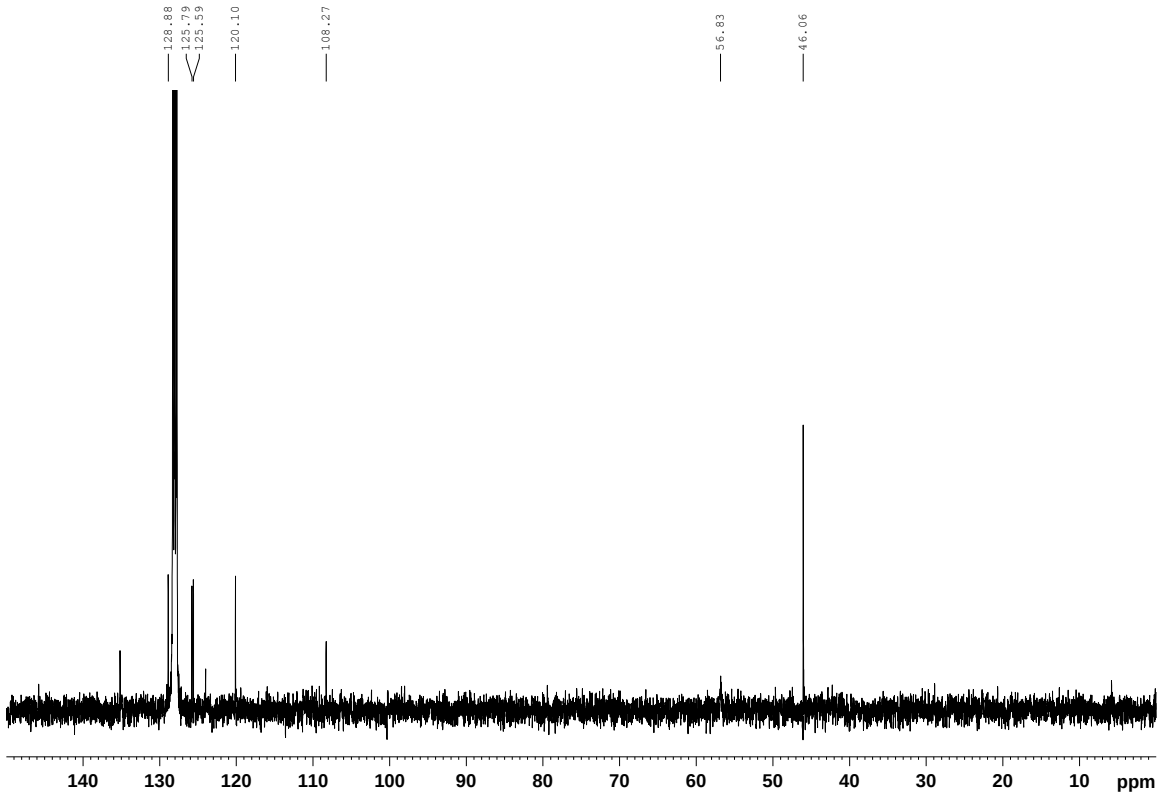
(3)

^{1}H NMR (400.13 MHz, 298K, C_6D_6):- δ 9.06 (2H, d, C_1), 8.06 (2H, d, C_4), 7.76 (1H, s, C_5), 7.47 (2H, t, C_2), 7.40 (2H, t, C_3), 1.72 (12H, s, TMEDA-CH_3), 1.37 (4H, s, TMEDA-CH_2).

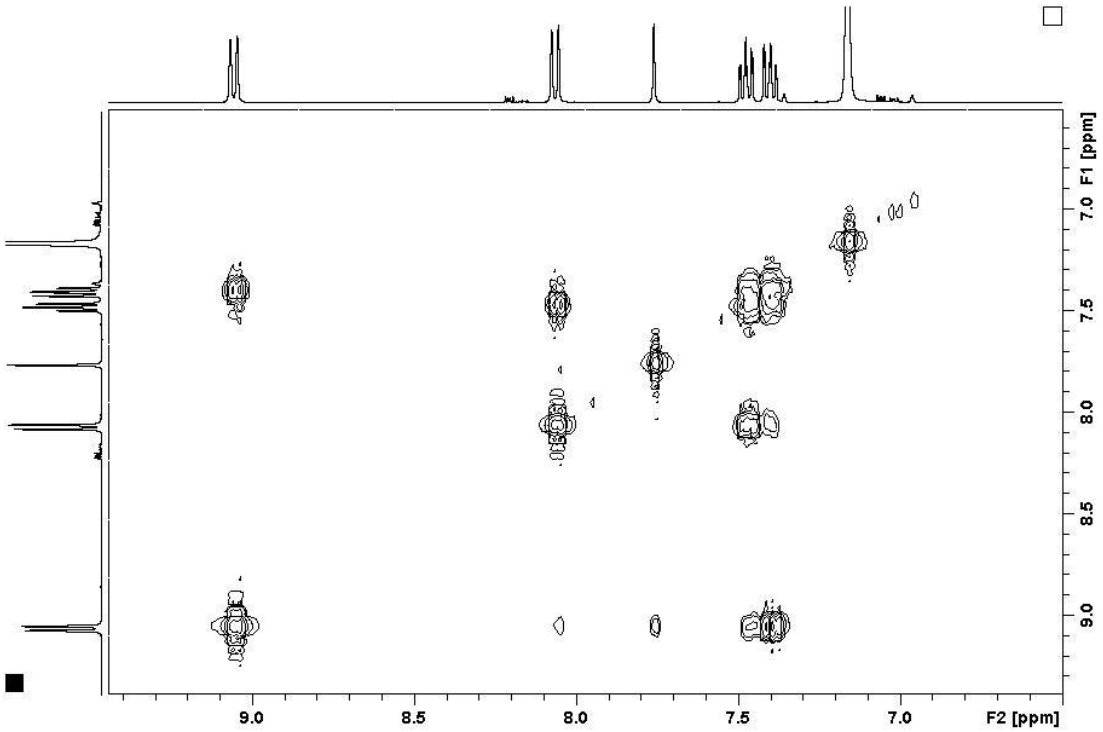
^{13}C NMR (400.13 MHz, 298K, C_6D_6):- δ 128.9 (C_4), 125.8 (C_1), 125.6 (C_2), 120.1 (C_3), 108.3 (C_5), 59.8 (TMEDA-*C*H_2), 46.1 (TMEDA-*C*H_3).



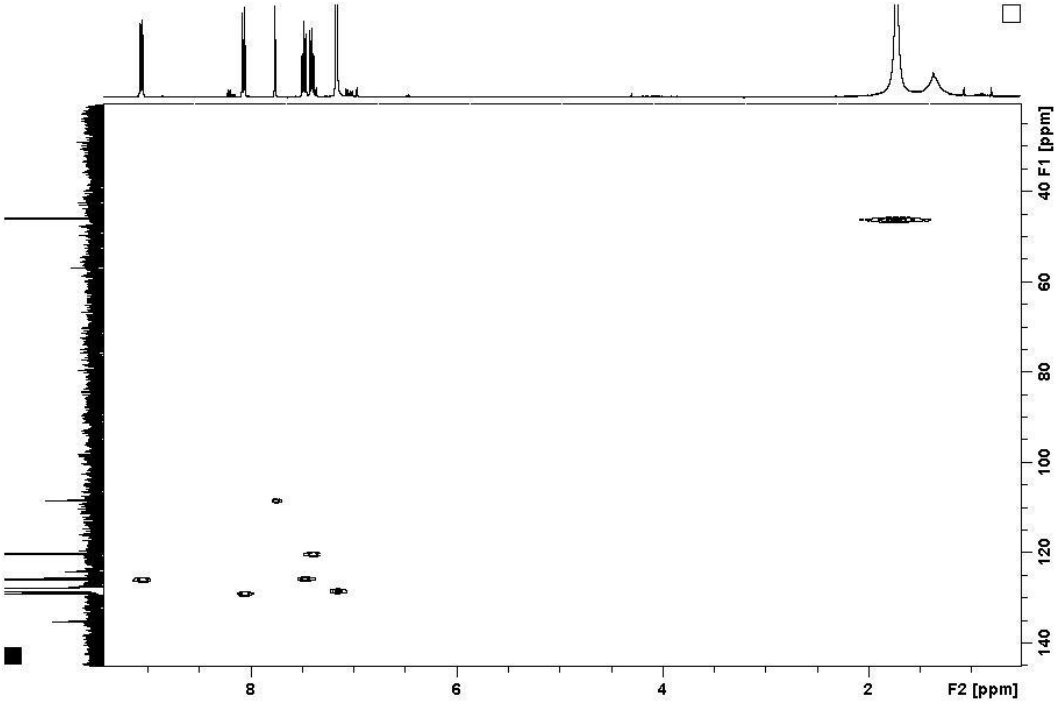
Spectrum 6. ^{1}H NMR (400.13 MHz, 300 K) spectrum of **3** in C_6D_6 solution.



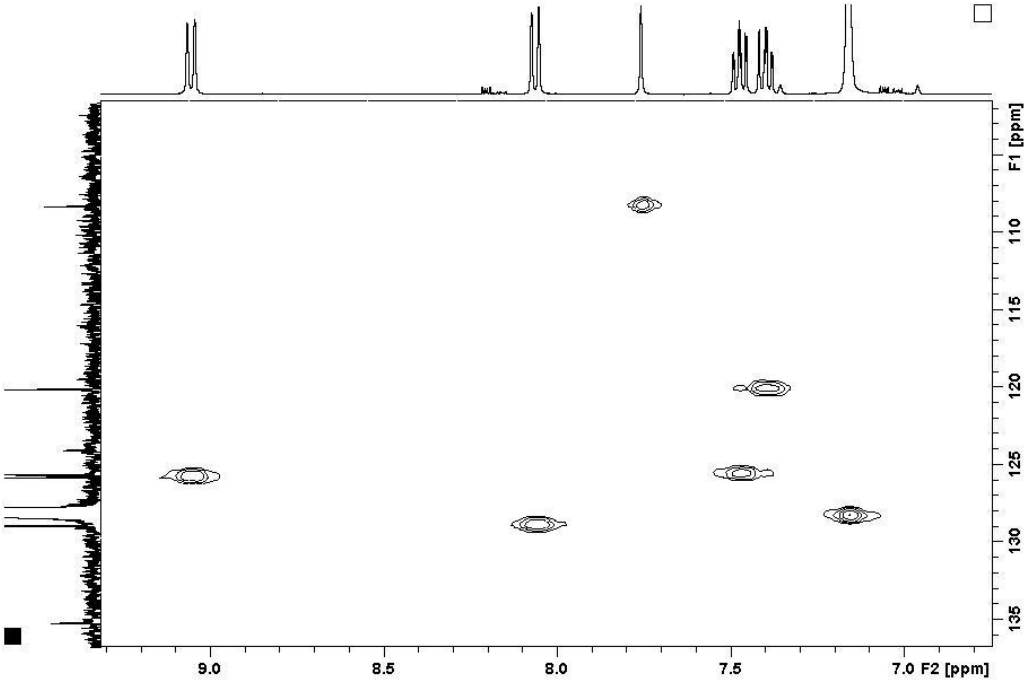
Spectrum 7. ^{13}C NMR (100.63 MHz, 300 K) spectrum of **3** in C_6D_6 solution.



Spectrum 8. COSY (^1H, ^1H) spectrum of **3** in C_6D_6 solution (expanded aromatic region).

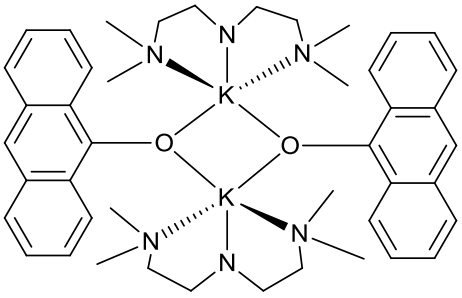


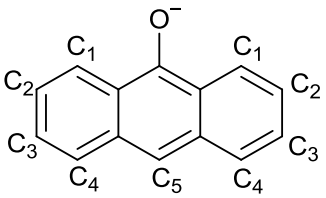
Spectrum 9. HSQC (^{1}H, ^{13}C) spectrum of **3** in C_6D_6 solution.



Spectrum 10. HSQC (^{1}H, ^{13}C) spectrum of **3** in C_6D_6 solution (Expanded aromatic region).

NMR spectroscopic analysis of [2(PMDETA)·$K_2(C_{14}H_9O)_2$] (4)





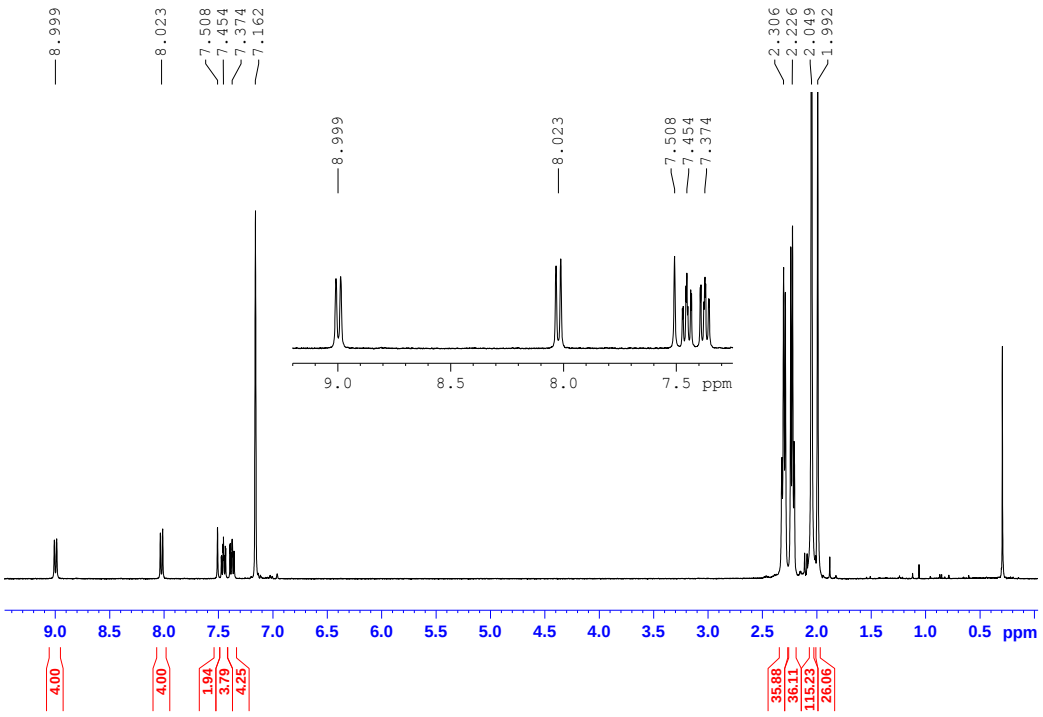
(4)

^{1}H NMR (400.13 MHz, 298K, C_6D_6):- δ 8.99 (2H, d, C_1), 8.03 (2H, d, C_4), 7.51 (1H, s, C_5), 7.51 (2H, t, C_2), 7.45 (2H, t, C_3), 2.31 (4H, t, CH_2-PMDETA), 2.23 (4H, t, CH_2-PMDETA), 2.05 (12H, s, CH_3-PMDETA(outer)), 1.99 (3H, s, CH_3-PMDETA(central)).

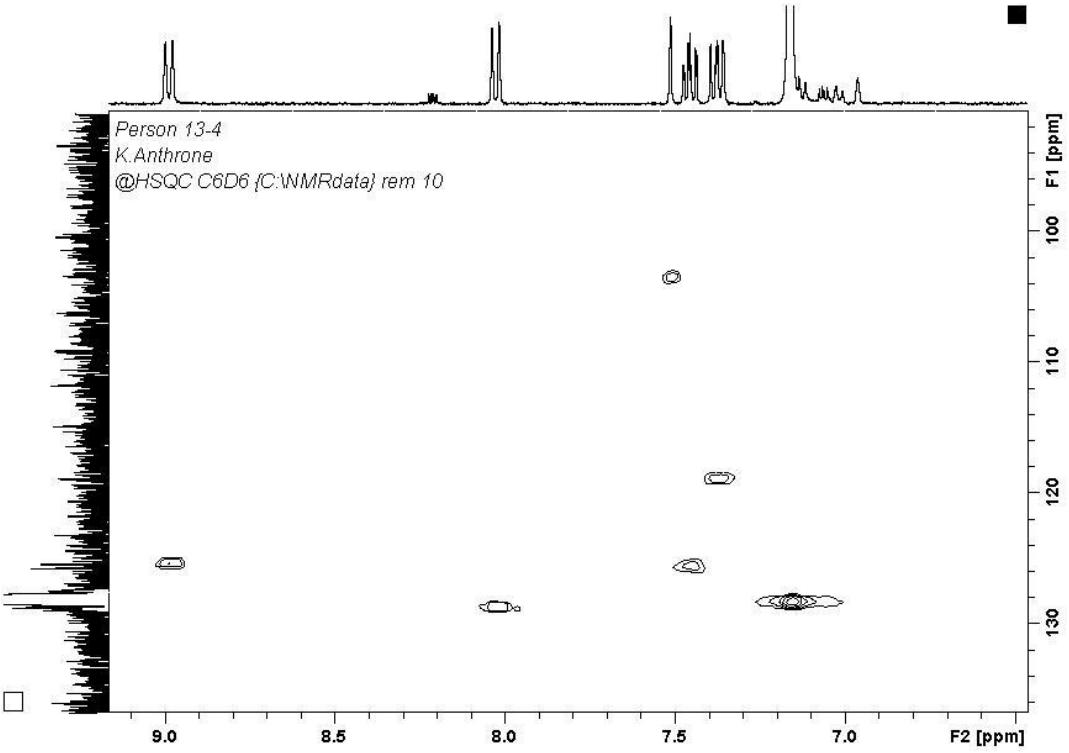
^{13}C NMR (400.13 MHz, 298K, C_6D_6):- δ 128.5 (C_4), 125.7 (C_3), 125.4 (C_1), 118.8 (C_5), 103.3 (C_2), 58.0 (PMDETA Et_1), 56.7 (PMDETA Et_2), 45.8 (PMDETA Me (outer)), 42.7 (PMDETA Me (central))

^{1}H NMR (400.13 MHz, 298K, d^8-THF):- δ 8.66 (2H, d, C_1), 7.58 (2H, d, C_4), 7.13 (1H, s, C_3), 6.94 (2H, t, C_2), 6.91 (2H, t, C_5), 2.42 (4H, t, CH_2-PMDETA), 2.30 (4H, t, CH_2-PMDETA), 2.15 (12H, s, CH_3-PMDETA(outer)), 2.19 (3H, s, CH_3-PMDETA(central)).

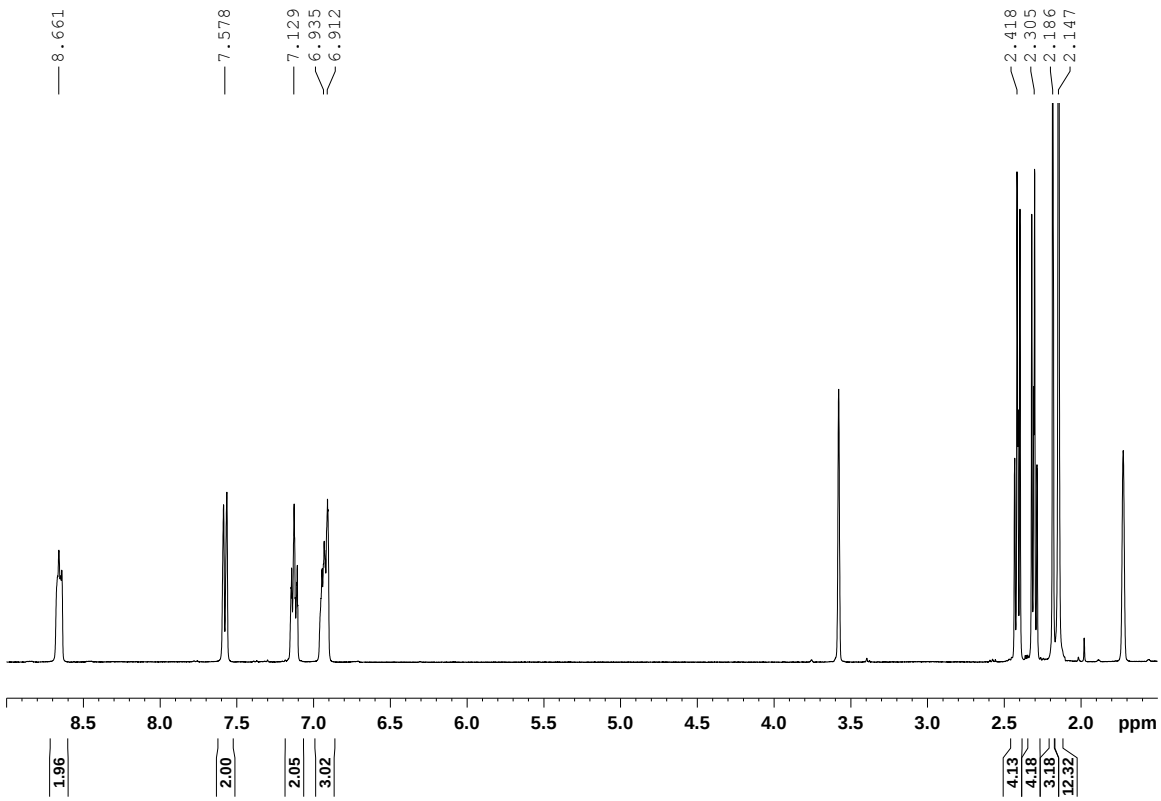
^{13}C NMR (400.13 MHz, 298K, d^8-THF):- δ 128.0 (C_4), 126.5 (C_1), 125.5 (C_3), 117.9 (C_2), 101.7 (C_5), 59.0 (PMDETA Et_1), 57.4 (PMDETA Et_2), 46.2 (PMDETA Me (outer)), 43.3 (PMDETA Me (central))



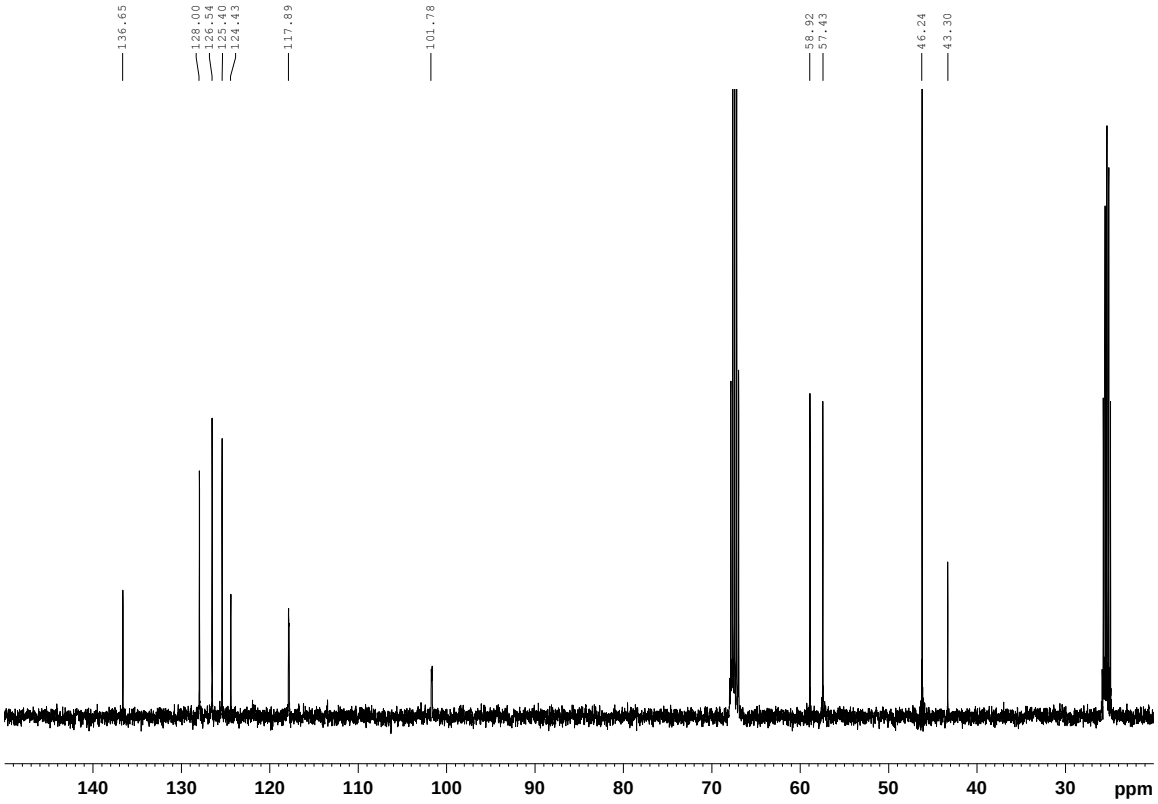
Spectrum 11. ^{1}H NMR (400.13 MHz, 300 K) spectrum of **4** in C_6D_6 solution.



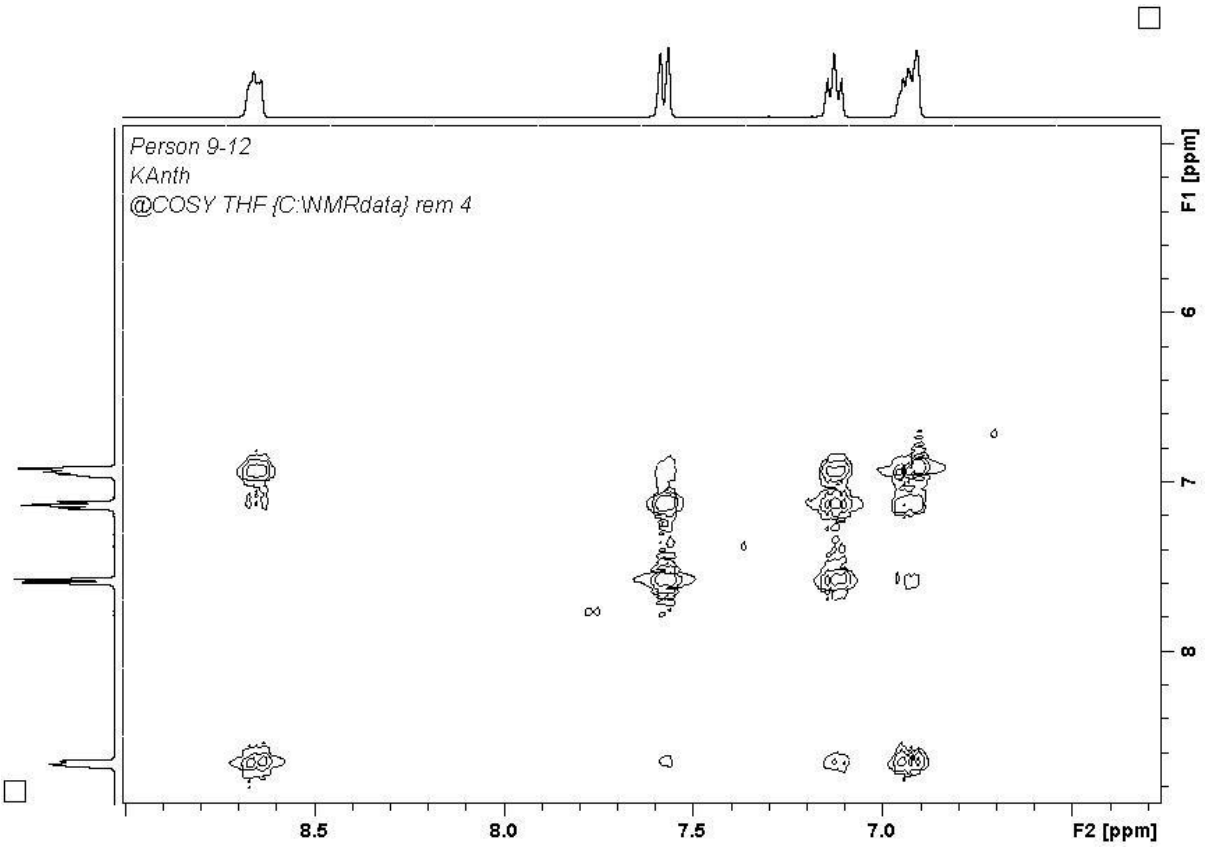
Spectrum 12. HSQC (^{1}H, ^{13}C) spectrum of **4** in C_6D_6 solution (Expanded aromatic region).



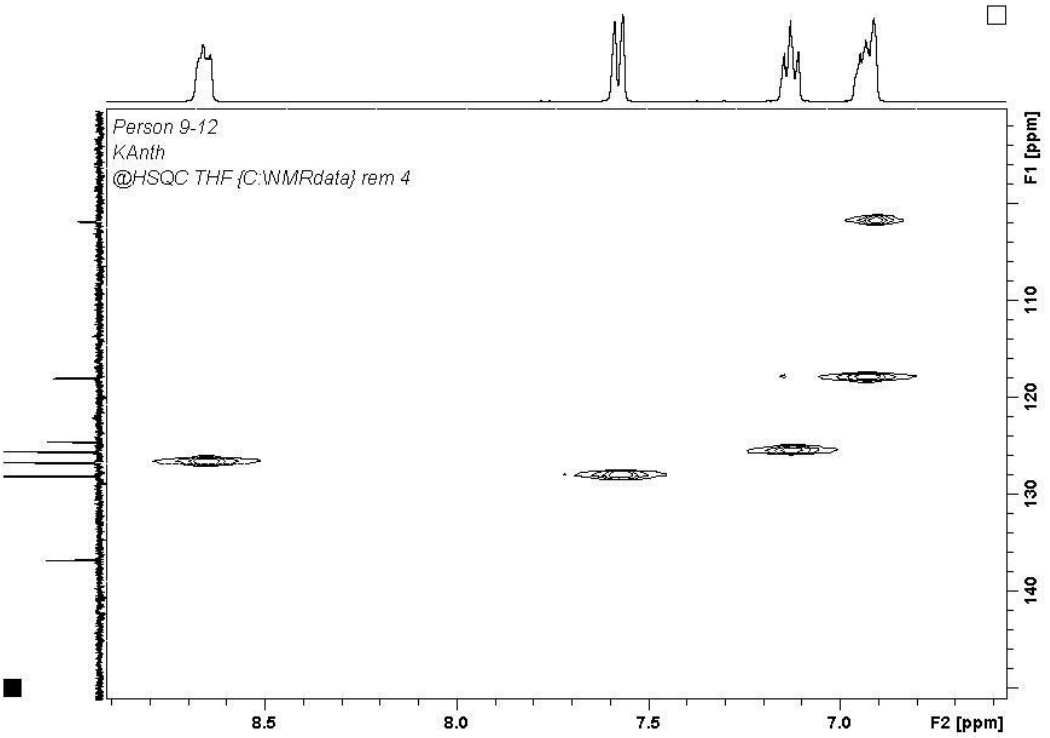
Spectrum 13. ^{1}H NMR (400.13 MHz, 300 K) spectrum of **4** in d^{8}-THF solution.



Spectrum 14. ^{13}C NMR (100.63 MHz, 300 K) spectrum of **4** in d^{8}-THF solution.

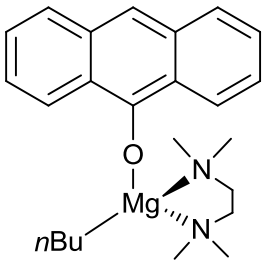


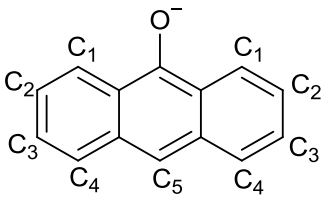
Spectrum 15. COSY (^{1}H, ^{1}H) spectrum of **4** in d^{8}-THF solution (expanded aromatic region).



Spectrum 16. HSQC (^{1}H, ^{13}C) spectrum of **4** in d^{8}-THF solution (Expanded aromatic region).

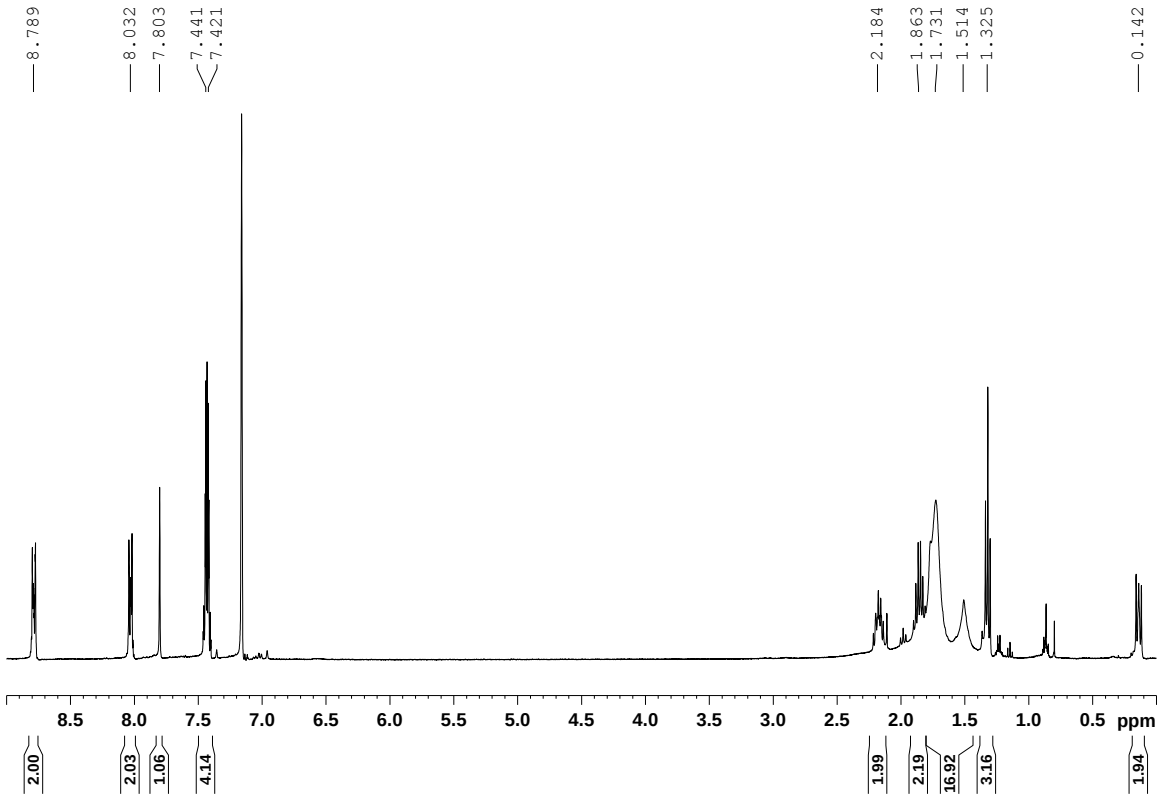
NMR spectroscopic analysis of [(TMEDA)·Mg(*n*Bu)(C$_{14}$H$_{9}$O)] (5)



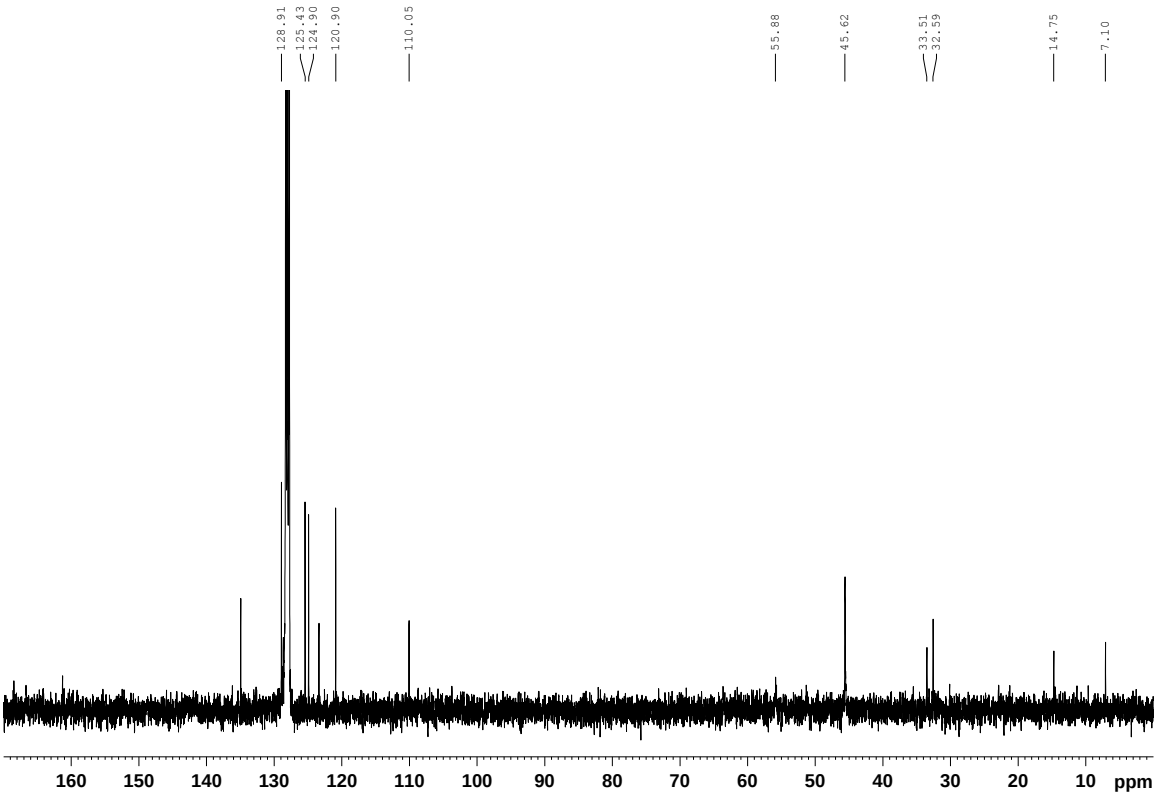


^{1}H NMR (400.13 MHz, 298K, C_6D_6):- δ 8.79 (2H, d, C_1), 8.03 (2H, d, C_4), 7.80 (1H, s, C_5), 7.44 (2H, t, C_2), 7.42 (2H, t, C_3), 2.18 (2H, m, CH_2 *n*Bu), 1.86 (2H, m, CH_2 *n*Bu), 1.73 (12H, bs, TMEDA-CH_3), 1.51 (4H, bs, TMEDA-CH_2), 1.33 (3H, m, CH_3 *n*Bu), 0.14 (2H, t, CH_2-Mg).

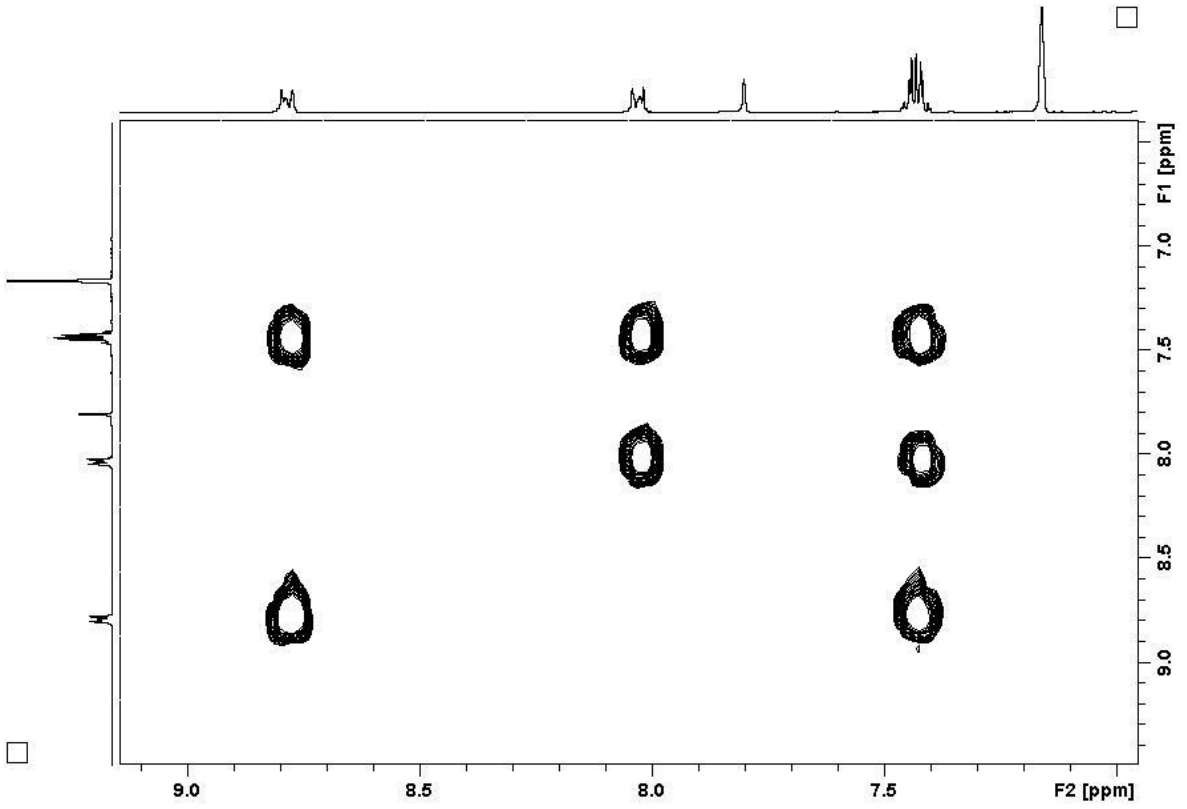
^{13}C NMR (400.13 MHz, 298K, C_6D_6):- δ 128.9 (C_4), 125.4 (C_2), 124.9 (C_1), 120.9 (C_3), 110.1 (C_5), 55.9 (TMEDA-CH_2), 45.6 (TMEDA-CH_3), 33.5 (β-CH_2 *n*Bu), 32.6 (γ-CH_2 *n*Bu), 14.7 (CH_3 *n*Bu), 7.1 (α-CH_2 *n*Bu).



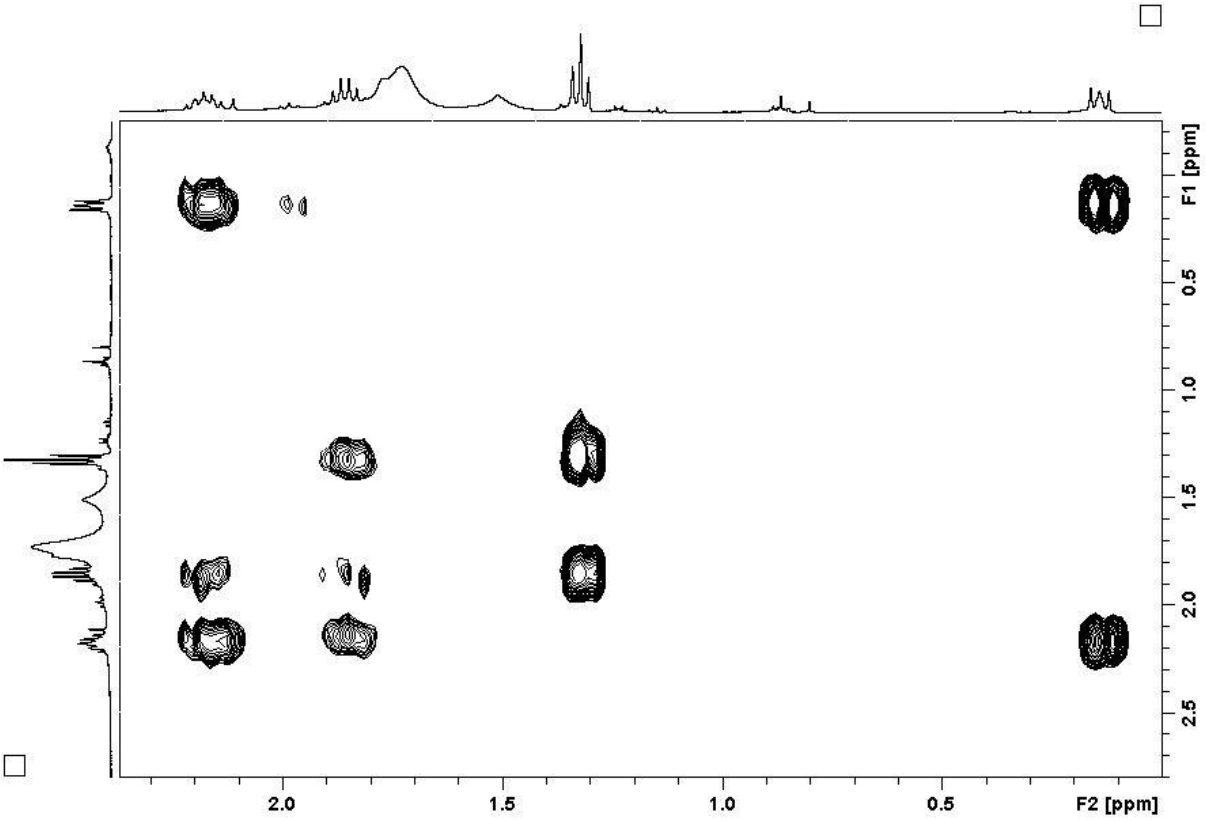
Spectrum 17. ^{1}H NMR (400.13 MHz, 300 K) spectrum of **5** in C_6D_6 solution.



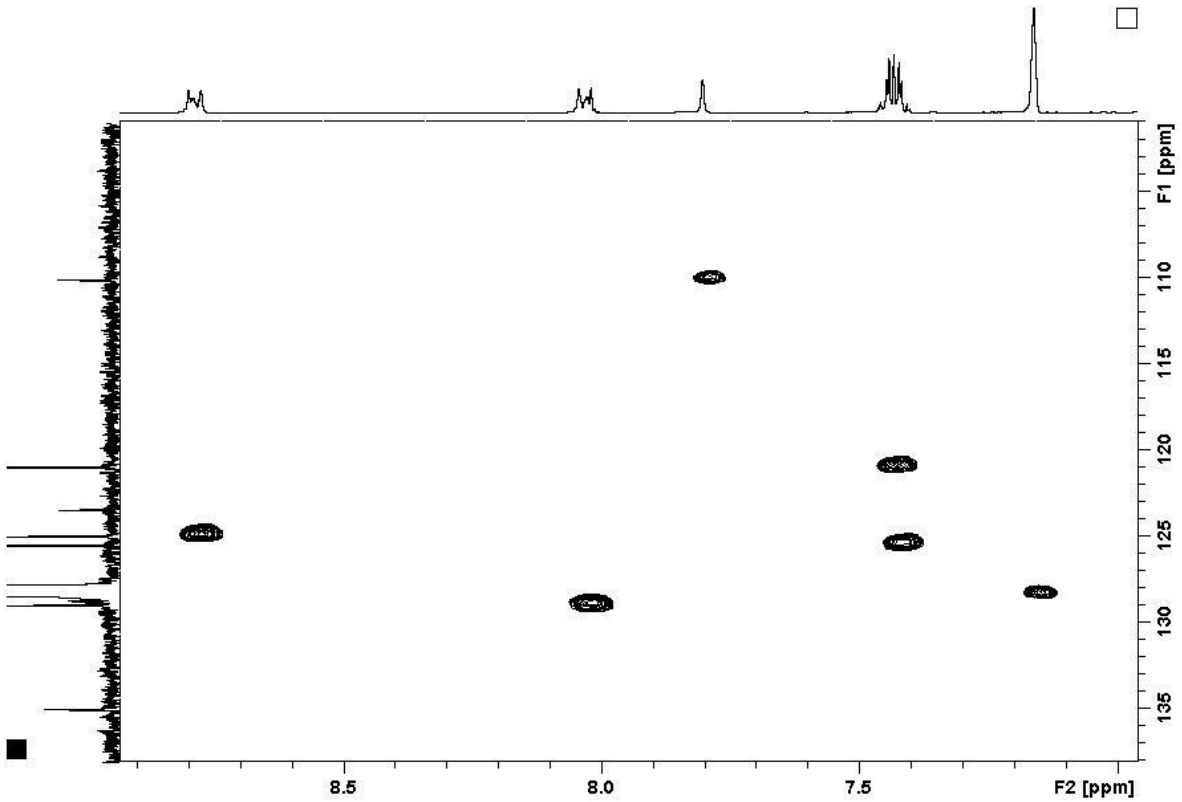
Spectrum 18. ^{13}C NMR (100.63 MHz, 300 K) spectrum of **5** in C_6D_6 solution.



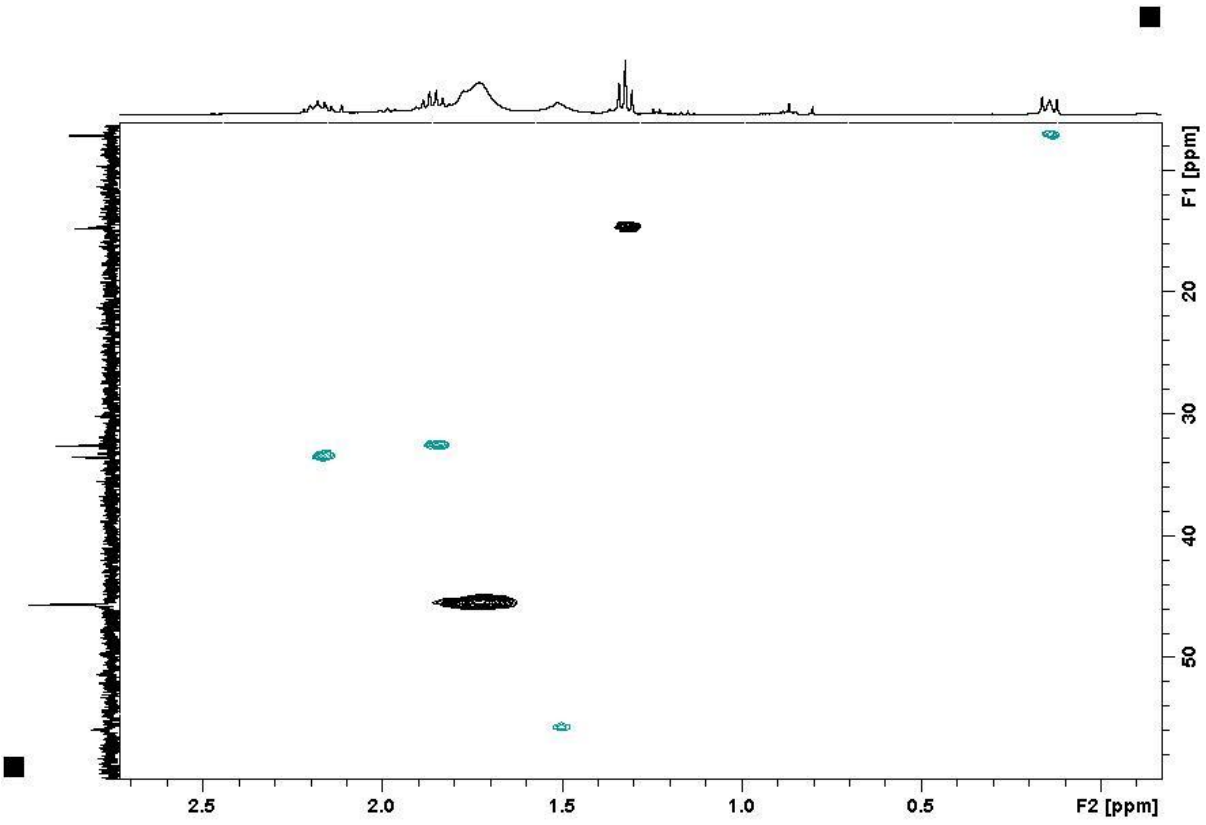
Spectrum 19. COSY (^1H, ^1H) spectrum of **5** in C_6D_6 solution (expanded aromatic region).



Spectrum 20. COSY (^{1}H, ^{1}H) spectrum of **5** in C_6D_6 solution (expanded aliphatic region).

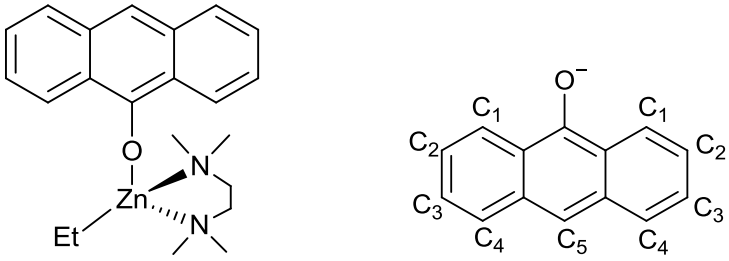


Spectrum 21. HSQC (^{1}H, ^{13}C) spectrum of **5** in C_6D_6 solution (Expanded aromatic region).



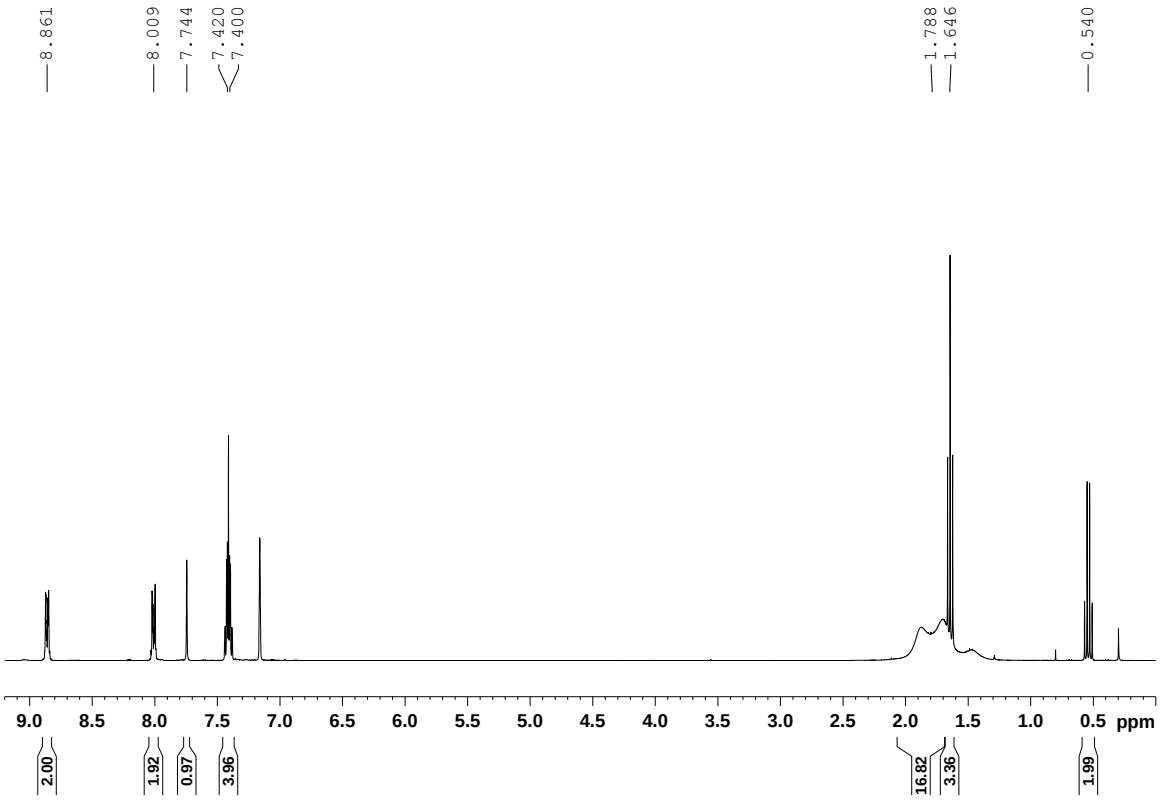
Spectrum 22. HSQC (^{1}H, ^{13}C) spectrum of **5** in C_6D_6 solution (Expanded aliphatic region).

NMR spectroscopic analysis of [(TMEDA)·Zn(Et)($C_{14}H_9O$)] (6)

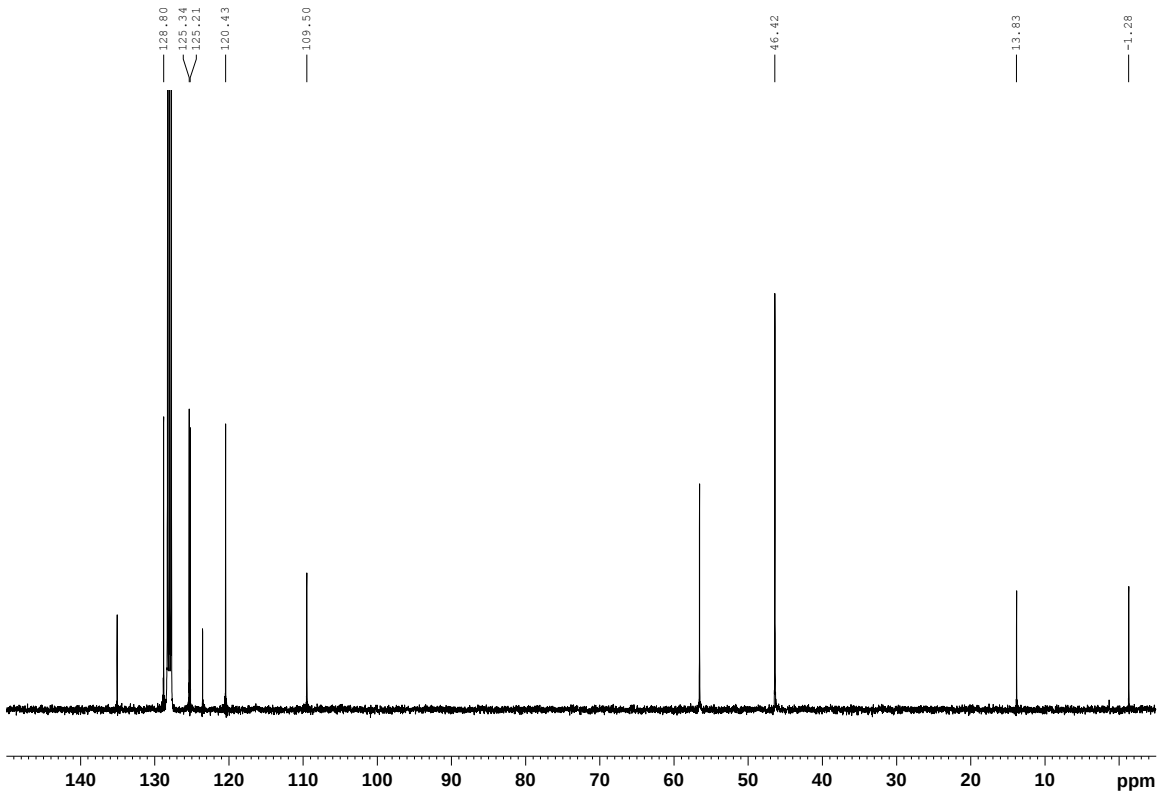


^{1}H NMR (400.13 MHz, 298K, C_6D_6):- δ 8.86 (2H, d, C_1), 8.01 (2H, d, C_4), 7.74 (1H, s, C_5), 7.42 (2H, t, C_2), 7.40 (2H, t, C_3), 1.78 (16H, bs, TMEDA), 1.65 (3H, t, Et-CH_3), 0.54 (2H, q, Et-CH_2).

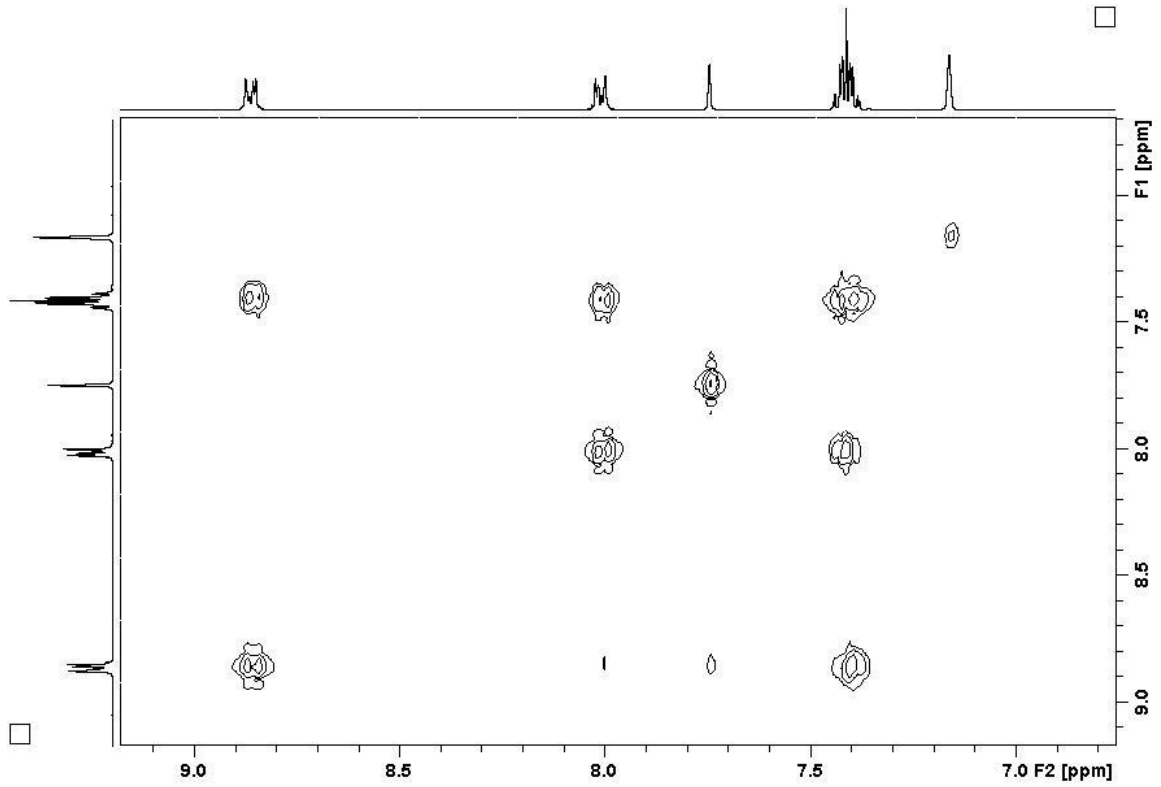
^{13}C NMR (400.13 MHz, 298K, C_6D_6):- δ 128.8 (C_4), 125.3 (C_2), 125.2 (C_1), 120.4 (C_3), 109.5 (C_5), 46.4 (TMEDA(r. t.)), 13.8 (Et-*C*H_3), -1.3 (Et-*C*H_2).



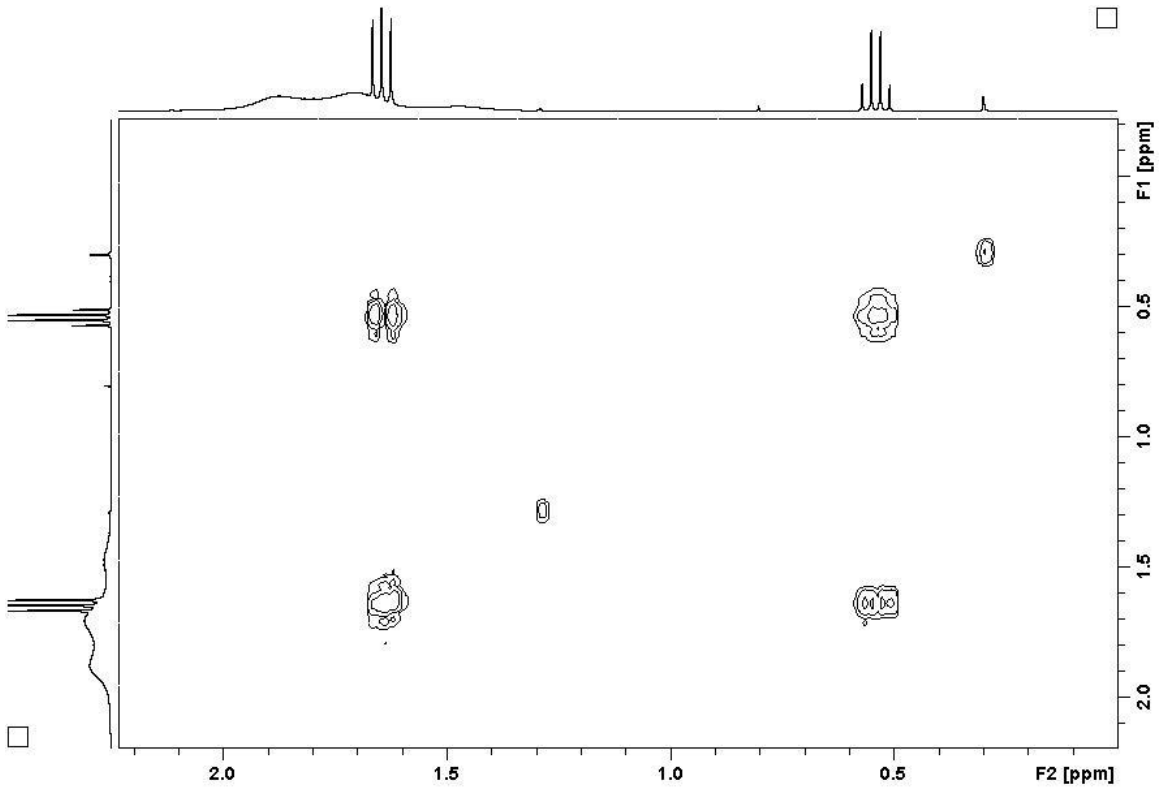
Spectrum 23. ^{1}H NMR (400.13 MHz, 300 K) spectrum of **6** in C_6D_6 solution.



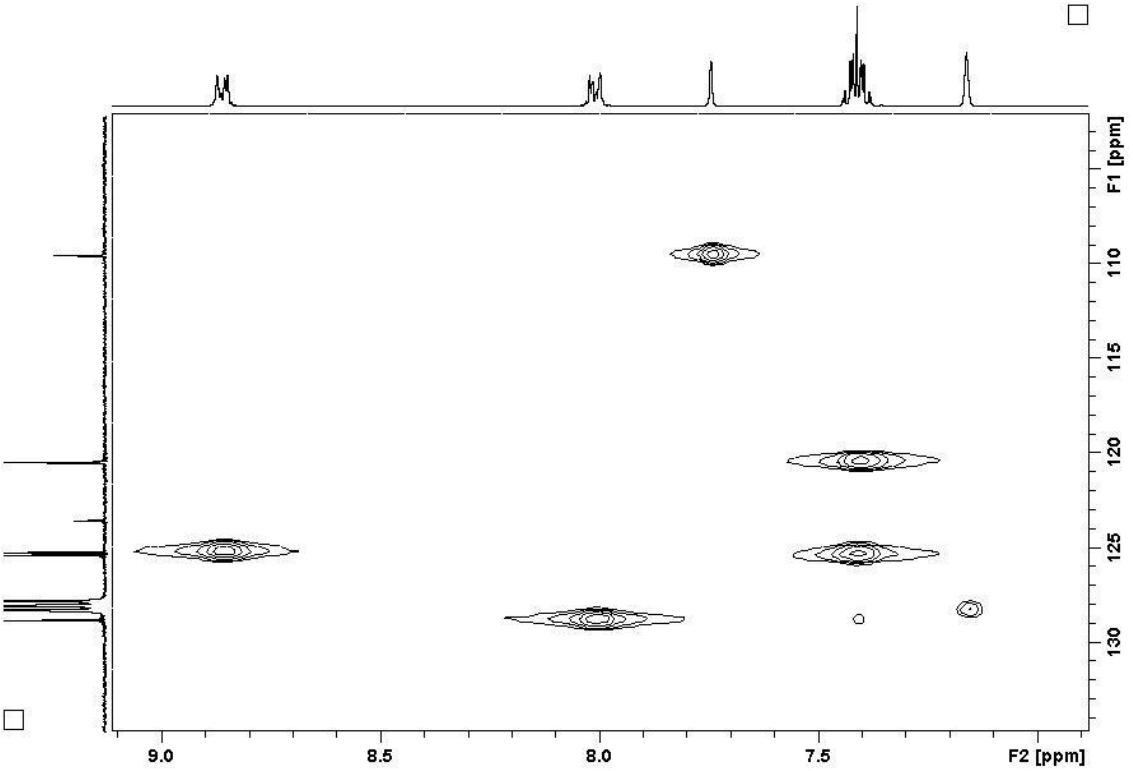
Spectrum 24. ^{13}C NMR (100.63 MHz, 300 K) spectrum of **6** in C_6D_6 solution.



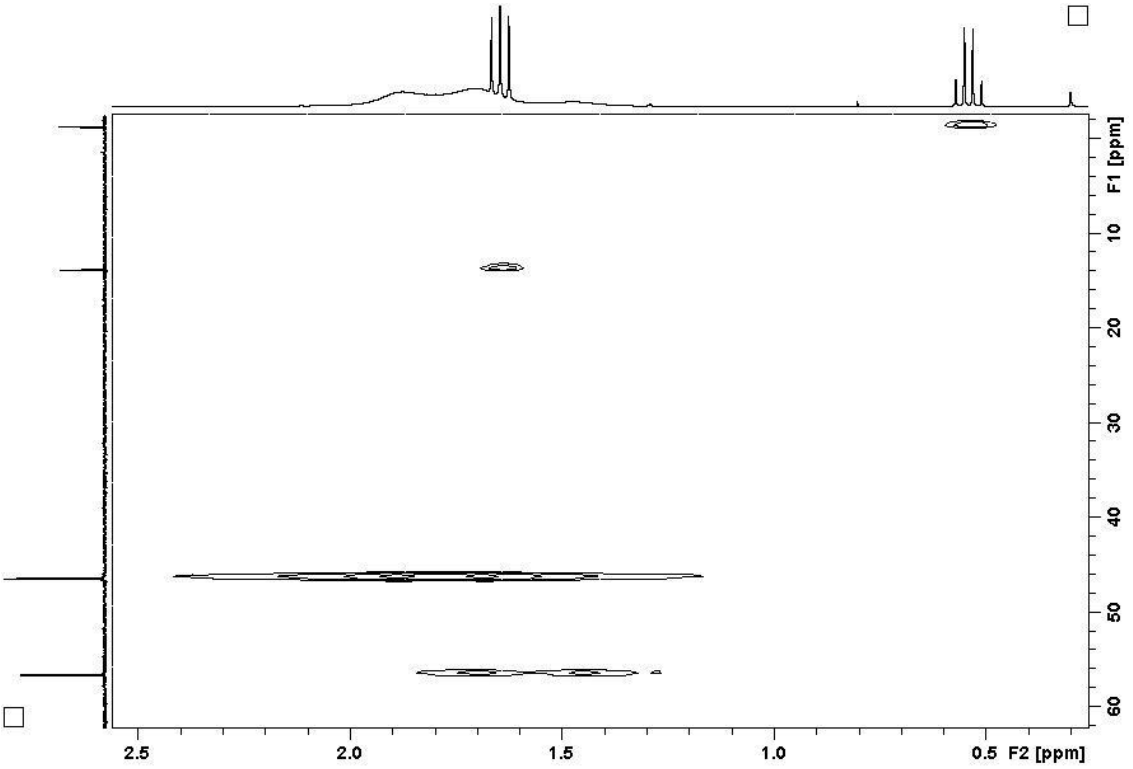
Spectrum 25. COSY (^{1}H, ^{1}H) spectrum of **6** in C_6D_6 solution (expanded aromatic region).



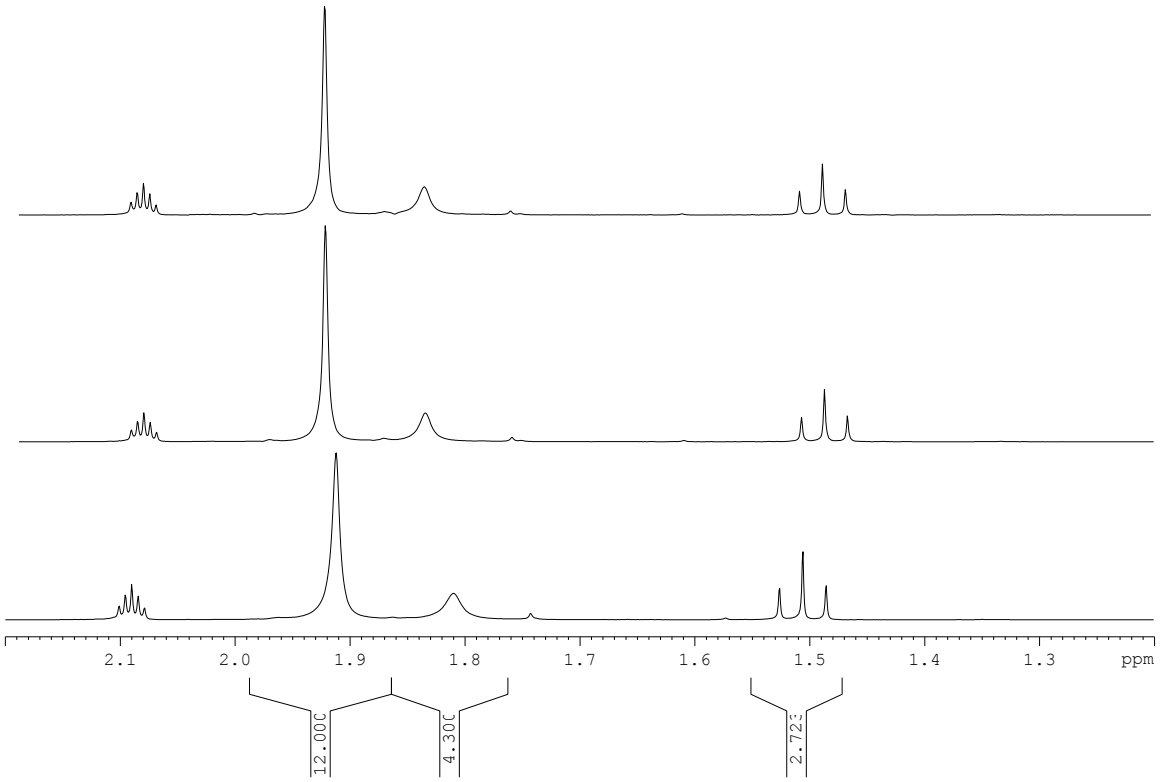
Spectrum 26. COSY (^{1}H, ^{1}H) spectrum of **6** in C_6D_6 solution (expanded aliphatic region).



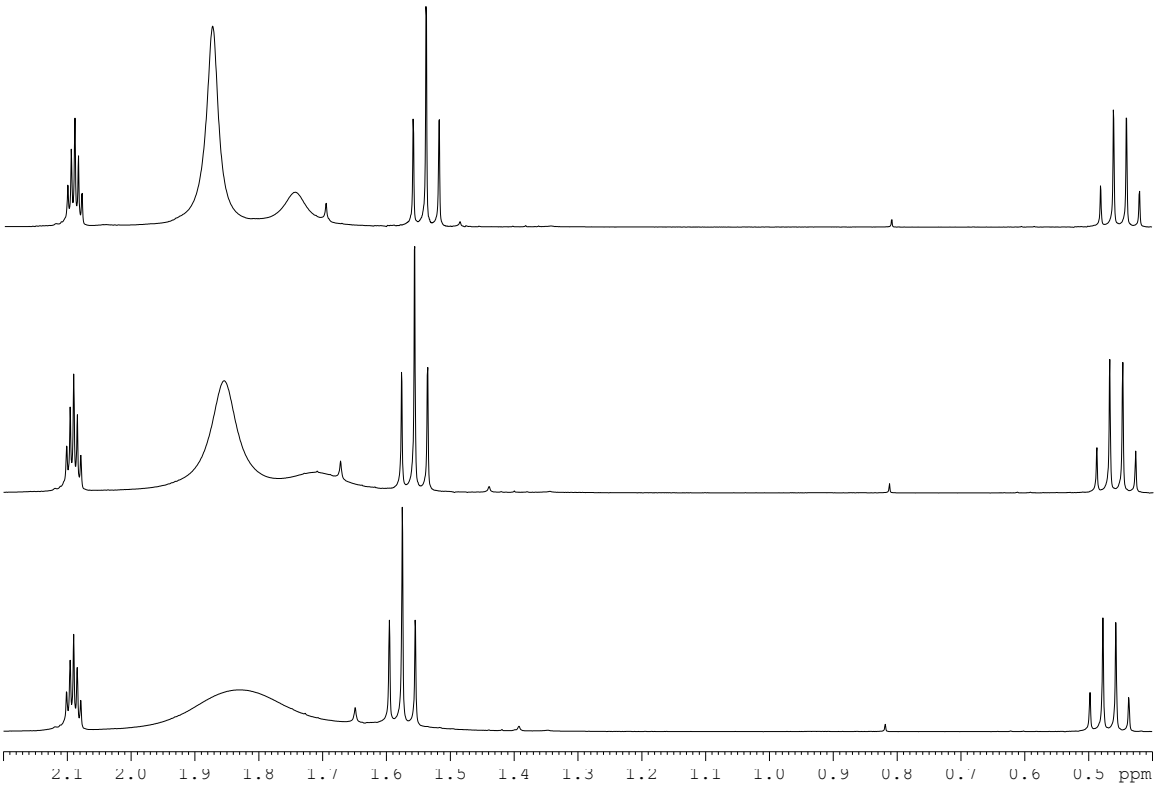
Spectrum 27. HSQC (^{1}H, ^{13}C) spectrum of **5** in C_6D_6 solution (Expanded aromatic region).



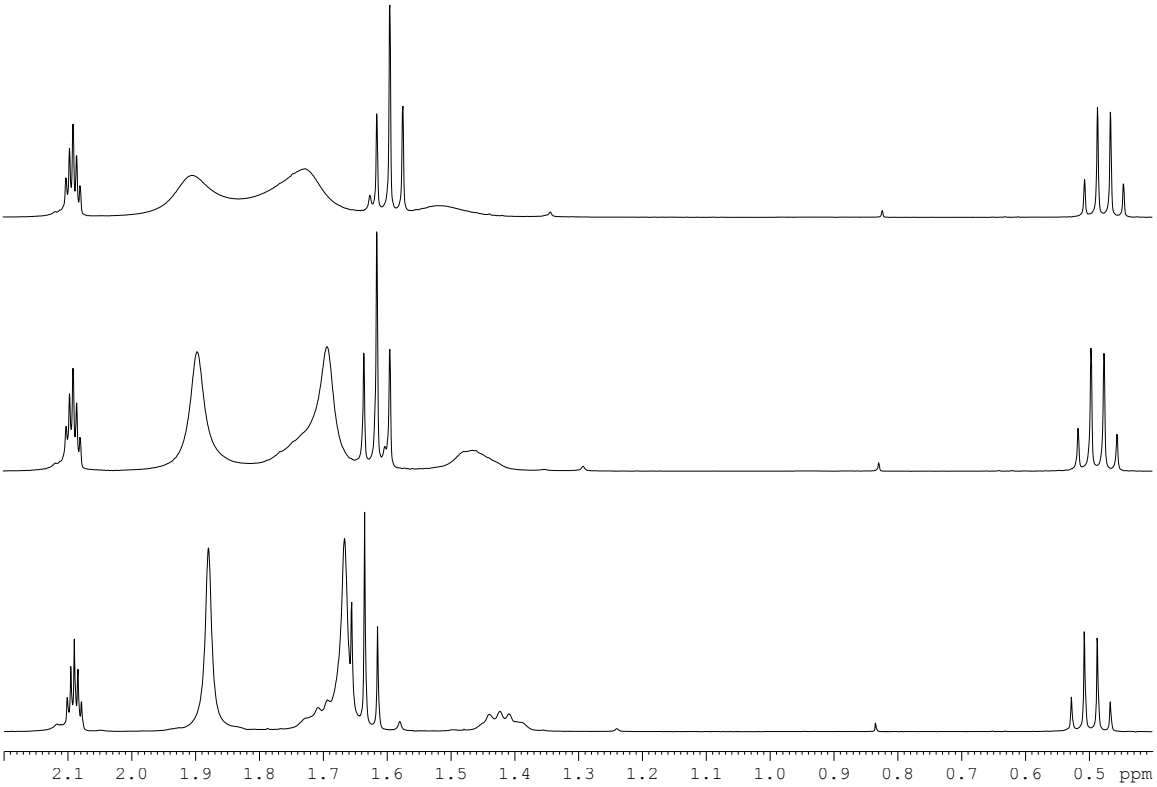
Spectrum 28. HSQC (^{1}H, ^{13}C) spectrum of **6** in C_6D_6 solution (Expanded aliphatic region).



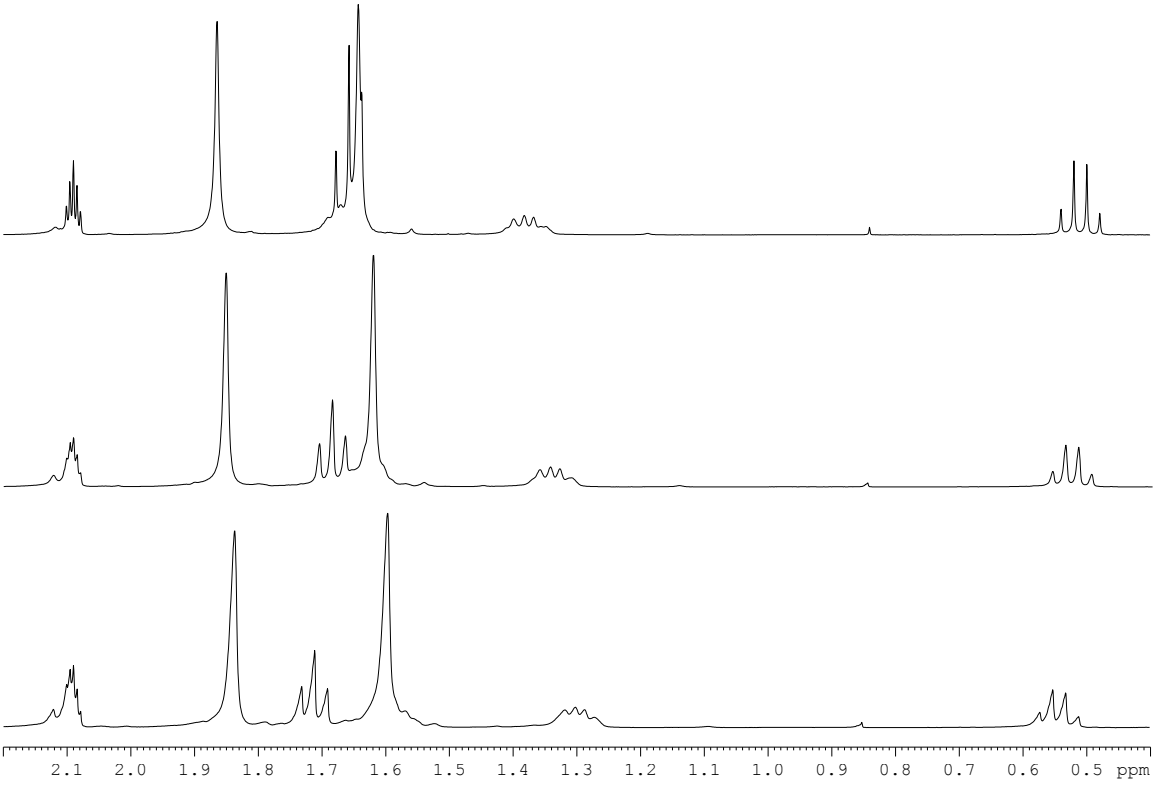
Spectrum 29. ^{1}H NMR (400.13 MHz, 353-333 K (top to bottom)) spectrum of **6** in d^{8}-tol. solution.



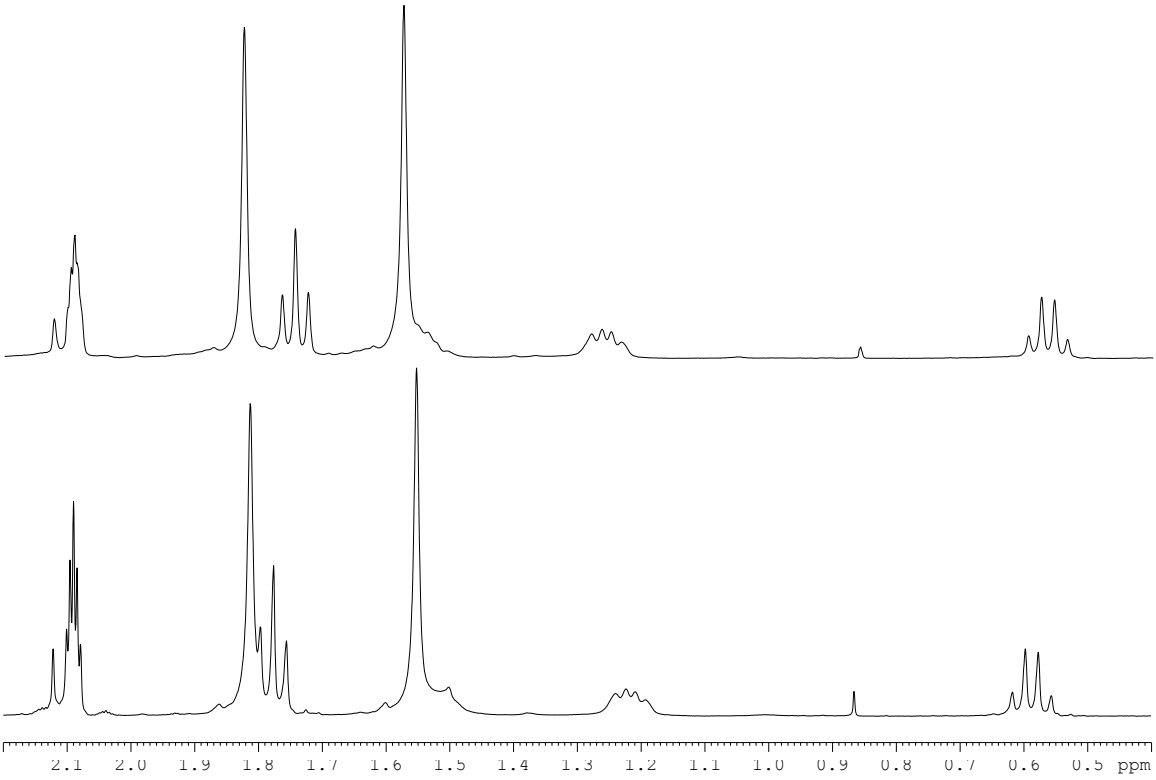
Spectrum 30. ^{1}H NMR (400.13 MHz, 323-300 K (top to bottom)) spectrum of **6** in d^{8}-tol. solution.



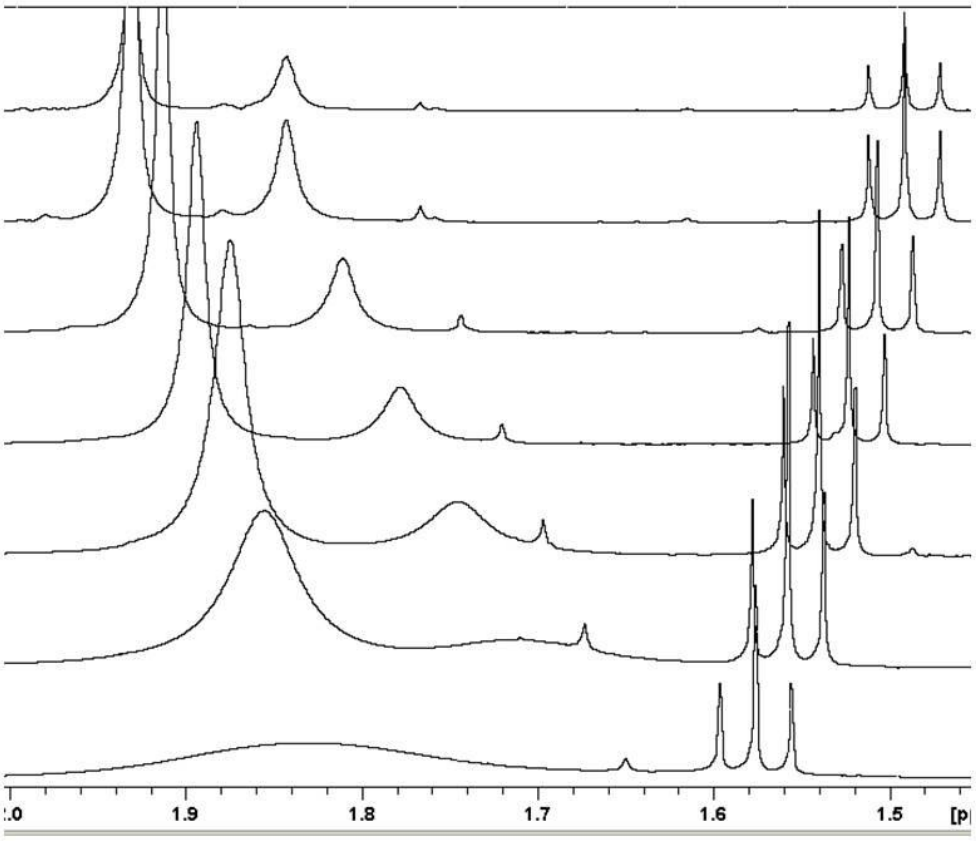
Spectrum 31. ^{1}H NMR (400.13 MHz, 293-273 K (top to bottom)) spectrum of **6** in d^{8}-tol solution.



Spectrum 32. ^{1}H NMR (400.13 MHz, 263-243 K (top to bottom)) spectrum of **6** in d^{8}-tol solution.

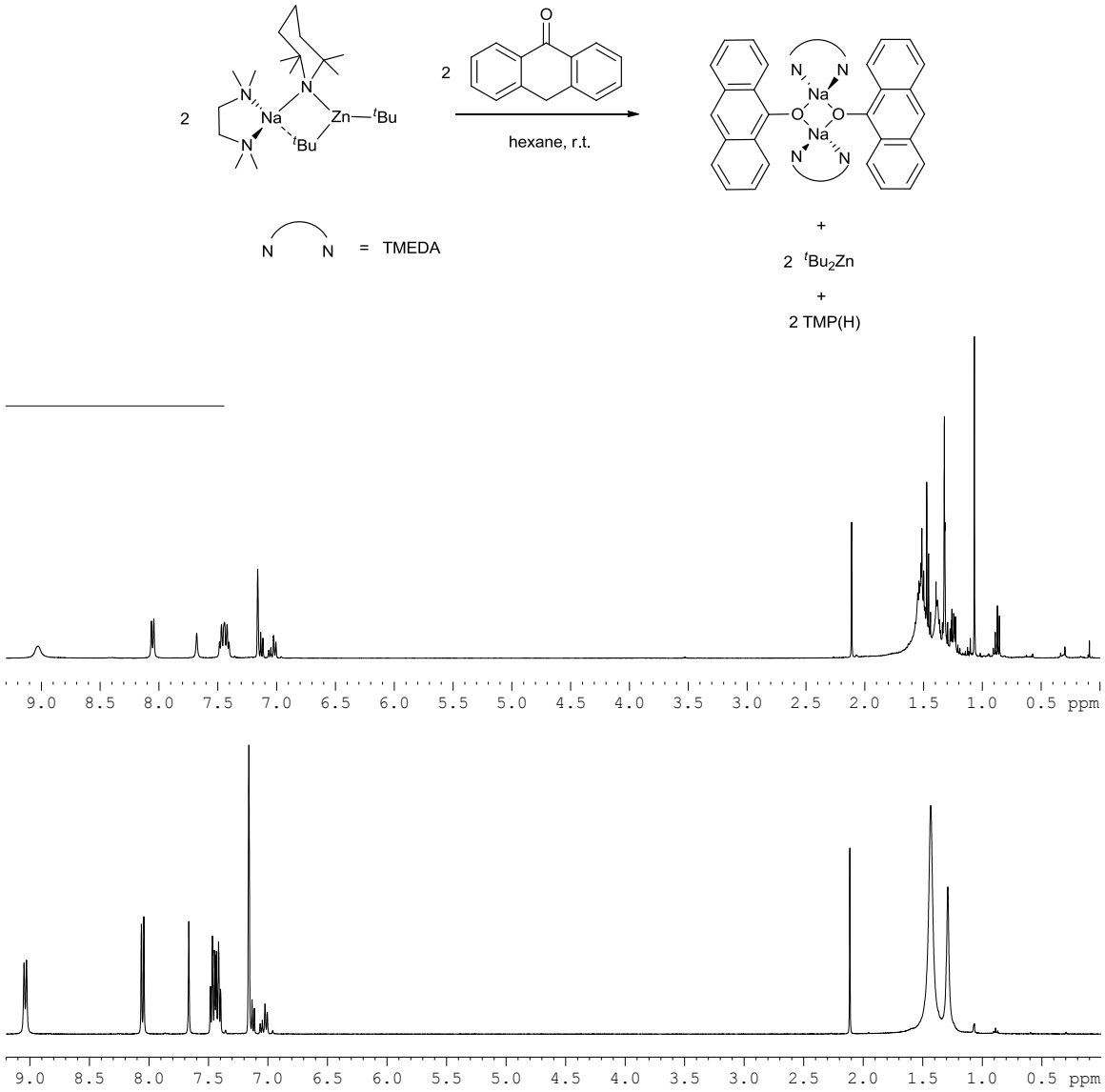


Spectrum 33. ^{1}H NMR (400.13 MHz, 233-223 K (top to bottom)) spectrum of **6** in d^{8}-tol solution.

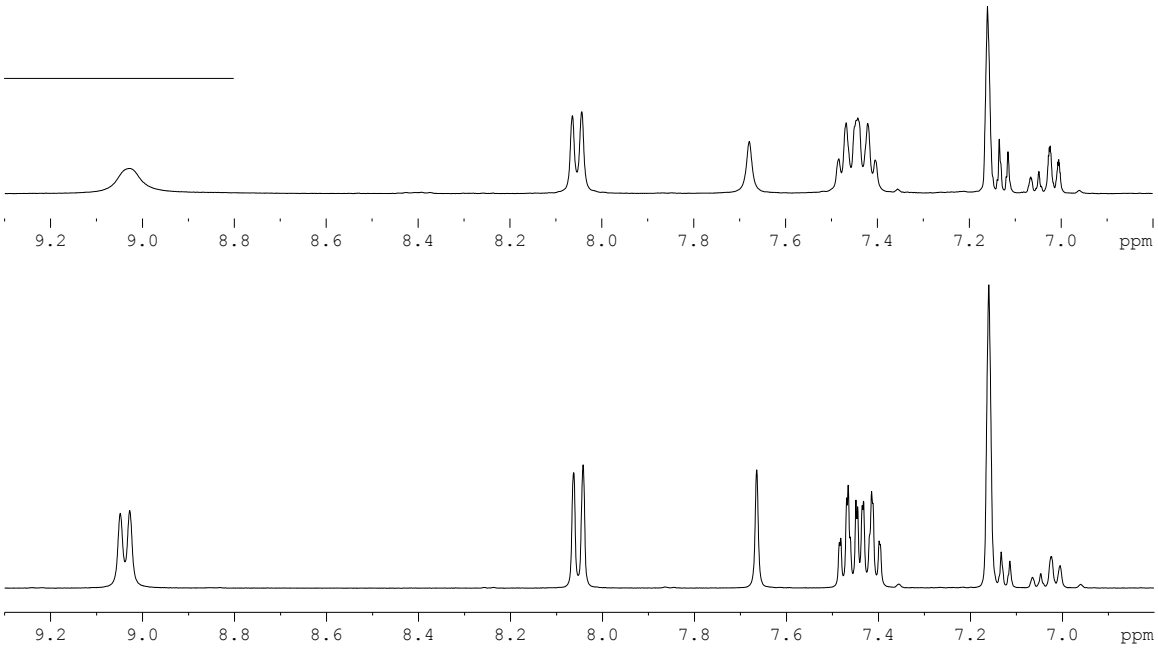


Spectrum 34. ^{1}H NMR (400.13 MHz, 363-303 K (top to bottom)) spectrum of **6** in d^{8}-tol solution.

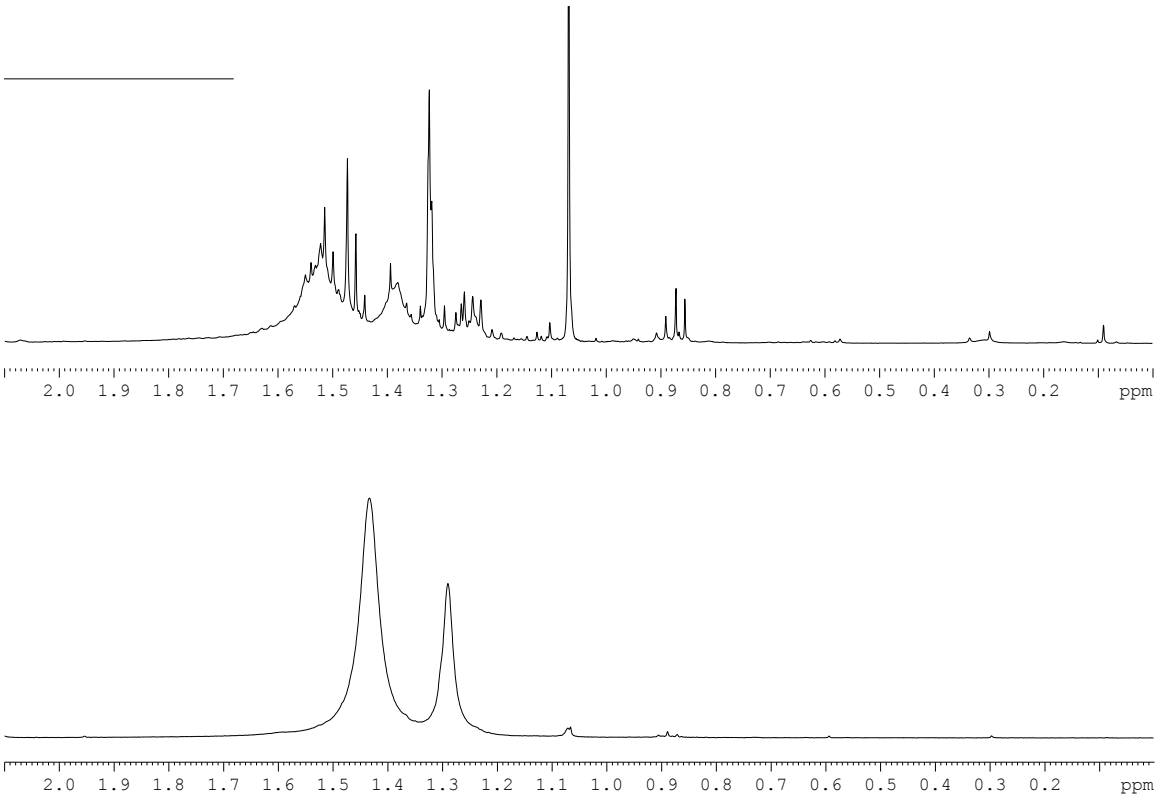
† Spectroscopic evidence of disproportionation and amide basicity in the reaction:



Spectrum 35(a).^{1}H NMR (400.13 MHz, 300 K) spectrum, comparing an aliquot of the reaction solution (top) with crystalline **2** (bottom). TMP(H) evident at 1.06 ppm in top spectrum.



Spectrum 35(b).^{1}H NMR (400.13 MHz, 300 K) spectrum, comparing an aliquot of the reaction solution (top) with crystalline **2** (bottom) (expanded aromatic region).



Spectrum 35(c).^{1}H NMR (400.13 MHz, 300 K) spectrum, comparing an aliquot of the reaction solution (top) with crystalline **2** (bottom) (expanded aliphatic region). TMP(H) evident at 1.06 ppm in top spectrum.

Electronic Supplementary Material (ESI) for Dalton Transactions