Supporting Information

Single electron transfer (SET) activity of the dialkyl-amido sodium zincate [(TMEDA)·Na(μ-TMP)(μ-^{t}Bu)Zn(^{t}Bu)] towards TEMPO and chalcone

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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 100.62 MHz. All chemical shifts are quoted relative to TMS standard at 0.00 parts per million.

Crystal data for **2**: $C_{28}H_{61}N_4NaOZn$, M_r = 558.17, monoclinic, space group C2/c, a = 17.3607(4), b= 13.0692(4), c= 28.9589(8) Å, β = 98.010(1)˚, V = 6506.4(3) Å^3, Z = 8, λ = 0.71073 Å, μ = 0.793 mm^{-1}, T = 123 K; 121087 reflections, 9475 unique, R_{int} 0.112; final refinement to convergence on F^2 gave R = 0.0382 (F, 6834 obs. data only) and R_w = 0.0809 (F^2, all data), GOF = 1.008. Butyl modeled as disordered over two sites.

Crystal data for **4**: $C_{68}H_{110}N_6Na_2O_2Zn_2$, M_r = 1220.34, triclinic, space group P $\bar{1}$, a = 11.9774(7), b= 15.1883(13), c= 20.8913(16) Å, α = 102.420(7), β = 105.102(6), γ = 91.831(6) ˚, V = 3567.7(5) Å^3, Z = 2, λ = 0.71073 Å, μ = 0.728 mm^{-1}, T = 123 K; 31018 reflections, 12537 unique, R_{int} 0.0917; final refinement to convergence on F^2 gave R = 0.0575 (F, 4451 obs. data only) and R_w = 0.1323 (F^2, all data), GOF = 0.725. One TMP and one TMEDA group were modeled as disordered. Trace solvent was removed using PLATON SQUEEZE.

Computational Details

DFT calculations were carried out using the Gaussian G03 computational package.[1] The B3LYP density functionals[2] were used along with the 6-311G(d,p) basis set.[3] After the geometry optimisation of each molecule, a frequency analysis was carried out. The resulting calculated zeropoint energy was added to the electronic energy and this is the energy value quoted below.

1. Gaussian 03, Revision B.0.5, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

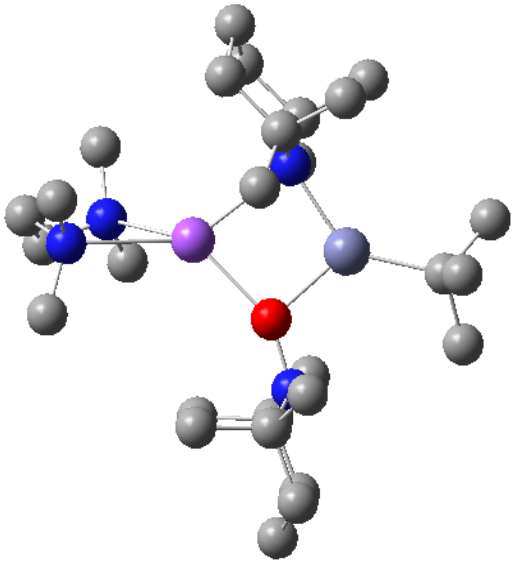
2. (a) A.D. Becke, Phys. Rev. A, **1988**, *38*, 3098. (b) C.T. Lee, W.T. Yang and R.G.Parr, Phys.Rev. B, 1998, **37**, 785.

3 (a) A. D. McLean and G. S. Chandler, J. Chem. Phys., **1980**, *72*, 5639. (b) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, J. Chem. Phys., **1980**, *72*, 650.

[(TMEDA)·Na(μ-TMP)(μ-TEMPO)Zn(^{t}Bu)] (A)

Principal Bond Lengths (Å) and Angles (°)

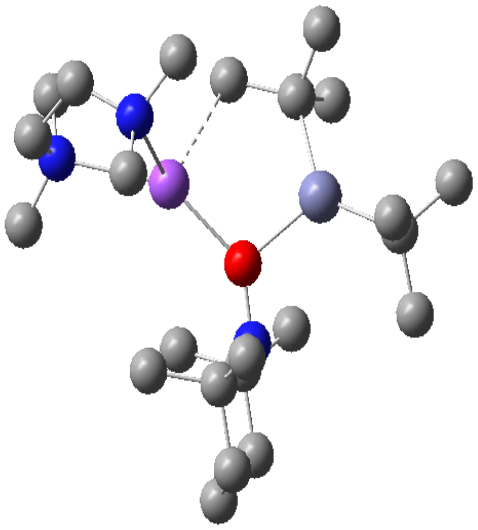
Zn-C_{ter}	2.023 Å
Zn-N	2.024 Å
N-O	1.431 Å
O-Zn	2.020 Å
O-Na	2.220 Å
Na-N_{tmeda}	2.668 Å 2.830 Å
Na-N_{tmp}	2.492 °
N-Na-N	70.2 °
N-O-Zn	114.6 °
N-O-Na	148.8 °
Zn-O-Na	95.4 °
N-Na-O	79.7 °
O-Zn-N	96.9 °
Na-N-Zn	87.4 °



[(TMEDA)·Na(μ-TEMPO)(μ-^{t}Bu)Zn(^{t}Bu)] (B)

Principal Bond Lengths (Å) and Angles (°)

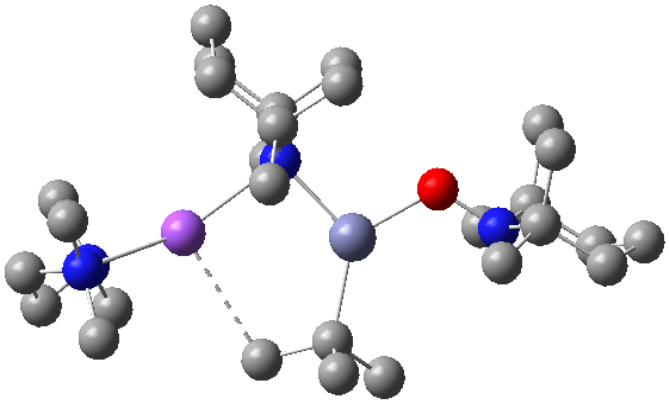
Zn-C_{ter}	2.027 Å
Zn-C_{br}	2.071 Å
N-O	1.429 Å
O-Zn	2.053 Å
O-Na	2.141 Å
Na-N	2.505 Å 2.510 Å
Na-C_{br}	2.754 °
N-O-Zn	116.8 °
N-O-Na	139.4°
Zn-O-Na	103.8°
N-Na-N	76.1°
O-Zn-C_{br}	107.7 °



[(TMEDA)·Na(μ-TMP)(μ-^{t}Bu)Zn(TEMPO)] (C)

Principal Bond Lengths (Å) and Angles (°)

Zn-O	1.923Å
Zn-C_{br}	2.037 Å
N-O	1.433 Å
N-Zn	2.051 Å
N-Na	2.374 Å
Na-N	2.569 Å 2.564 Å
Na….C_{br}	2.926 Å
N-Zn-O	105.8 °
N-O-Zn	119.2 °
N-Na-C_{br}	93.8 °
Zn-N-Na	98.3 °



N-Na-N	74.7 °
O-Zn-C_{br}	129.8 °
N-Zn-C_{br}	124.5 °

Energies/au

[(TMEDA)·Na(μ-TMP)(μ-TEMPO)Zn(^{t}Bu)] **(A)**	-3339.100295
[(TMEDA)·Na(μ-TEMPO)(μ-^{t}Bu)Zn(^{t}Bu)] **(B)**	-3088.445789
[(TMEDA)·Na(μ-TMP)(μ-^{t}Bu)Zn(TEMPO)] **(C)**	-3339.082490

Energies of the Reactions

(A) [(TMEDA)·Na(μ-TMP)(μ-^{t}Bu)Zn(^{t}Bu)] + TEMPO$^{\cdot}$ ⟶

[(TMEDA)·Na(μ-TMP)(μ-TEMPO)Zn(^{t}Bu)] + ^{t}Bu$^{\cdot}$

$\Delta E = -13.86$ kcal mol^{-1}

[(TMEDA)·Na(μ-TMP)(μ-^{t}Bu)Zn(^{t}Bu)] + 2 TEMPO$^{\cdot}$ ⟶

[(TMEDA)·Na(μ-TMP)(μ-TEMPO)Zn(^{t}Bu)] + ^{t}BuTEMPO

$\Delta E = -39.38$ kcal mol^{-1}

[(TMEDA)·Na(μ-TMP)(μ-^{t}Bu)Zn(^{t}Bu)] + TEMPO$^{\cdot}$ ⟶

[(TMEDA)·Na(μ-TMP)(μ-TEMPO)Zn(^{t}Bu)] + ½ [tBuH + $Me_2C{=}CH_2$]

$\Delta E = -40.27$ kcal mol^{-1}

(B) [(TMEDA)·Na(μ-TMP)(μ-^{t}Bu)Zn(^{t}Bu)] + TEMPO$^{\cdot}$ ⟶

[(TMEDA)·Na(μ-TEMPO)(μ-^{t}Bu)Zn(^{t}Bu)] + TMP$^{\cdot}$

$\Delta E = +1.51$ kcal mol^{-1}

$[(TMEDA)\cdot Na(\mu\text{-}TMP)(\mu\text{-}^{t}Bu)Zn(^{t}Bu)] + 2\ TEMPO^{\cdot} \longrightarrow$

$[(TMEDA)\cdot Na(\mu\text{-}TEMPO)(\mu\text{-}tBu)Zn(^{t}Bu)] + TEMPO\text{-}TMP$

$\Delta E = +14.66\ kcal\ mol^{-1}$

$[(TMEDA)\cdot Na(\mu\text{-}TMP)(\mu\text{-}^{t}Bu)Zn(^{t}Bu)] + TEMPO^{\cdot} \longrightarrow$

$[(TMEDA)\cdot Na(\mu\text{-}TEMPO)(\mu\text{-}^{t}Bu)Zn(^{t}Bu)] + TMP\text{-}TMP$

$\Delta E = +21.77\ kcal\ mol^{-1}$

(C) $[(TMEDA)\cdot Na(\mu\text{-}TMP)(\mu\text{-}^{t}Bu)Zn(^{t}Bu)] + TEMPO^{\cdot} \longrightarrow$

$[(TMEDA)\cdot Na(\mu\text{-}TMP)(\mu\text{-}^{t}Bu)Zn(TEMPO)] + {}^{t}Bu^{\cdot}$

$\Delta E = +3.31\ kcal\ mol^{-1}$

$[(TMEDA)\cdot Na(\mu\text{-}TMP)(\mu\text{-}^{t}Bu)Zn(^{t}Bu)] + 2\ TEMPO^{\cdot} \longrightarrow$

$[(TMEDA)\cdot Na(\mu\text{-}TMP)(\mu\text{-}^{t}Bu)Zn(TEMPO)] + {}^{t}BuTEMPO$

$\Delta E = -28.21\ kcal\ mol^{-1}$

$[(TMEDA)\cdot Na(\mu\text{-}TMP)(\mu\text{-}^{t}Bu)Zn(^{t}Bu)] + TEMPO^{\cdot} \longrightarrow$

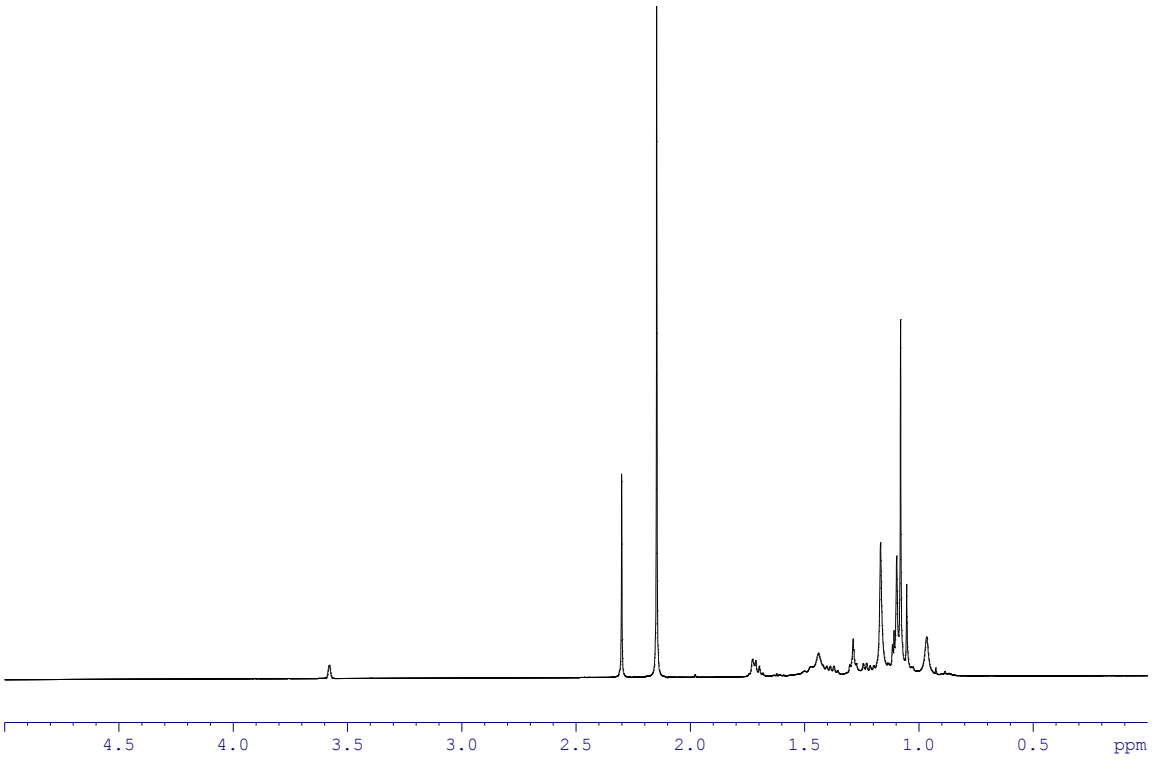
$[(TMEDA)\cdot Na(\mu\text{-}TMP)(\mu\text{-}^{t}Bu)Zn(TEMPO)] + \frac{1}{2}\,[{}^{t}BuH + Me_2C{=}CH_2]$

$\Delta E = -29.10\ kcal\ mol^{-1}$

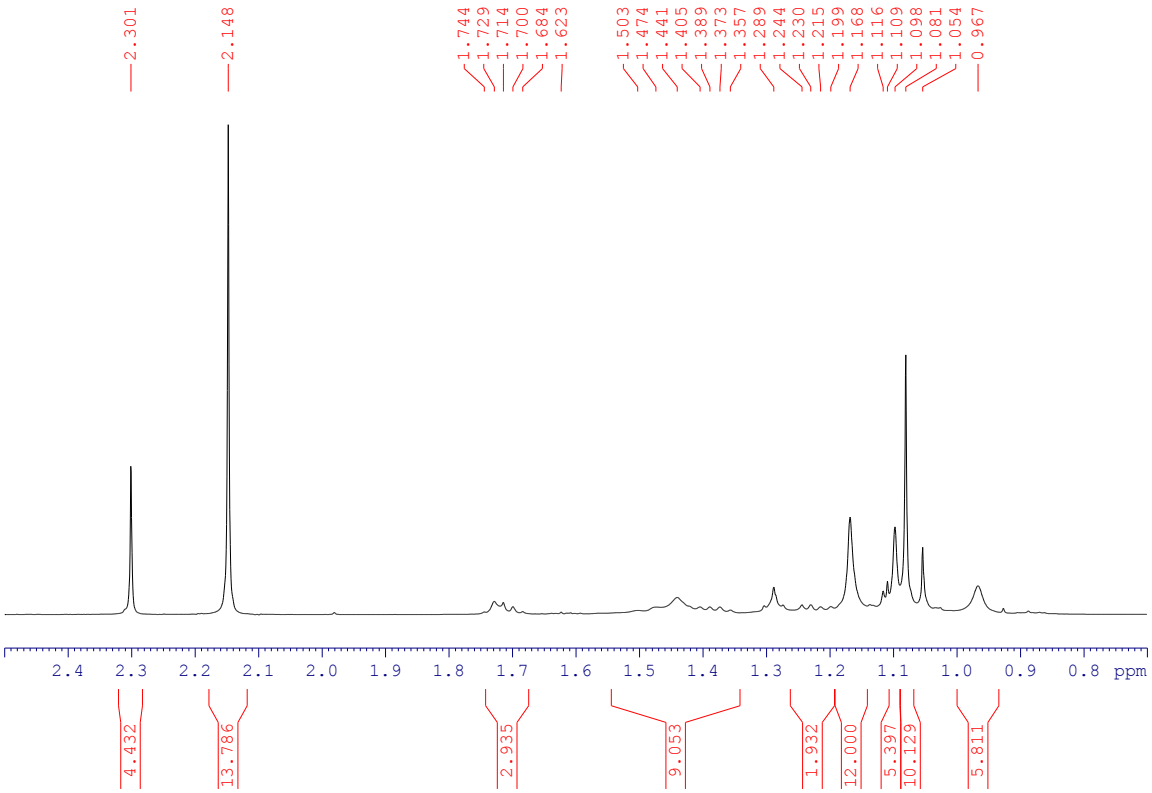
NMR Spectroscopic Analysis of [(TMEDA)·Na(μ-TMP)(μ-TEMPO)Zn(^{t}Bu)] 2.

^{1}H NMR (400.13 MHz, 300 K, d_8-THF): δ 2.30 [4H, s, CH_2-TMEDA], 2.15 [12H, s, CH_3-TMEDA], 1.71 [2H, m, γ-TMP (overlap with solvent)], 1.44 [8H, m, γ and β-TEMPO & β-TMP], 1.22 [2H, m, β-TMP], 1.16 [12H, s, CH_3-TMP & CH_3-TEMPO], 1.09 [6H, s, CH_3-TEMPO], 1.08 [9H, s, CH_3-^{t}Bu], 0.96 [6H, br, CH_3-TMP].

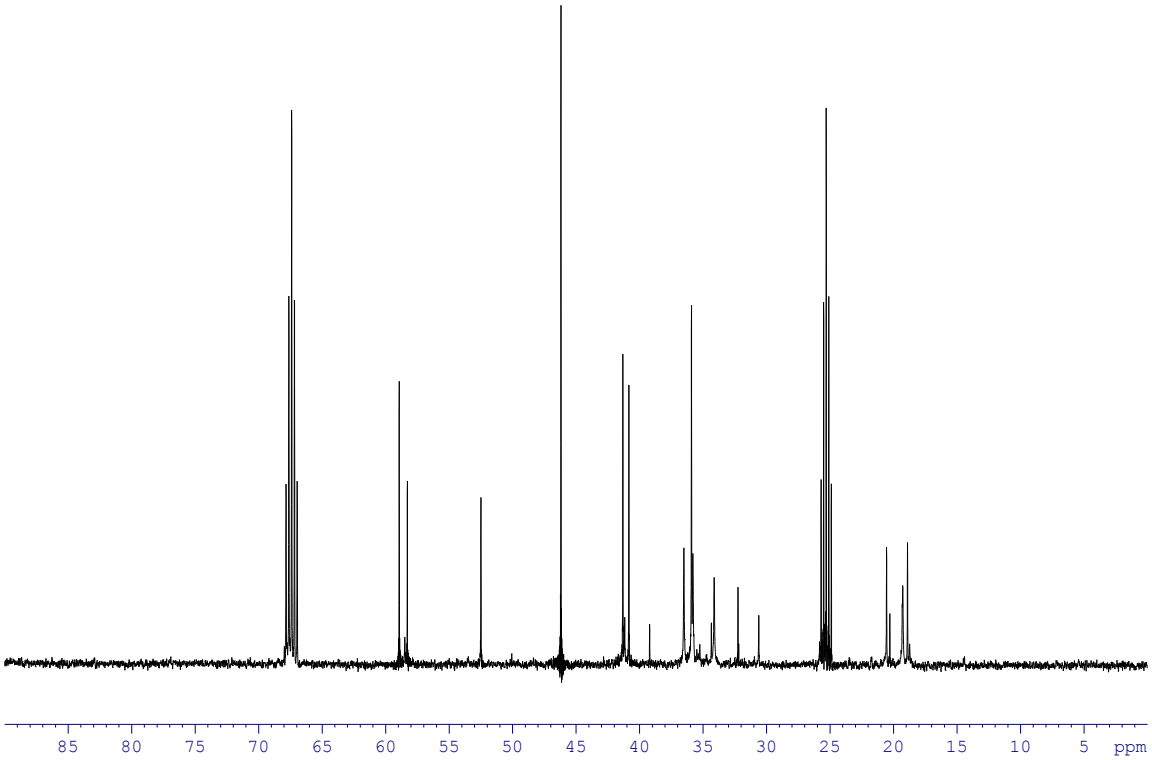
^{13}C NMR (100.62 MHz, 300 K, d_8-THF): δ 58.9 [CH_2-TMEDA], 58.3 [α-TEMPO], 52.5 [α-TMP], 46.2 [CH_3-TMEDA], 41.3 [β-TEMPO], 40.9 [β-TMP], 36.5 [CH_3-TMP/TEMPO], 35.9 [CH_3-^{t}Bu], 35.8 [CH_3-TEMPO], 34.1 [CH_3-TMP/TEMPO], 20.6 [γ-TMP], 20.3 [Cq-^{t}Bu], 19.3 [CH_3-TMP], 18.9 [γ-TEMPO].



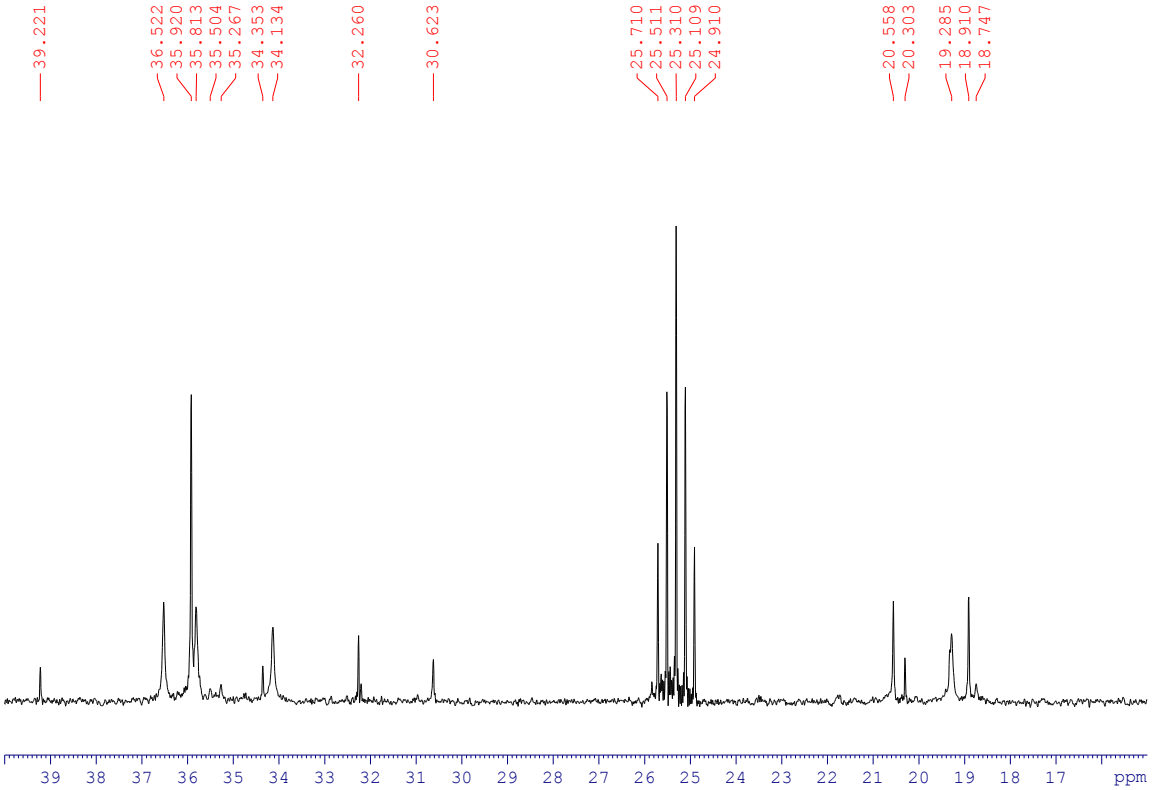
Spectrum 1. ^{1}H NMR (400.13 MHz, 300 K) spectrum of **2** in d_8-THF solution.



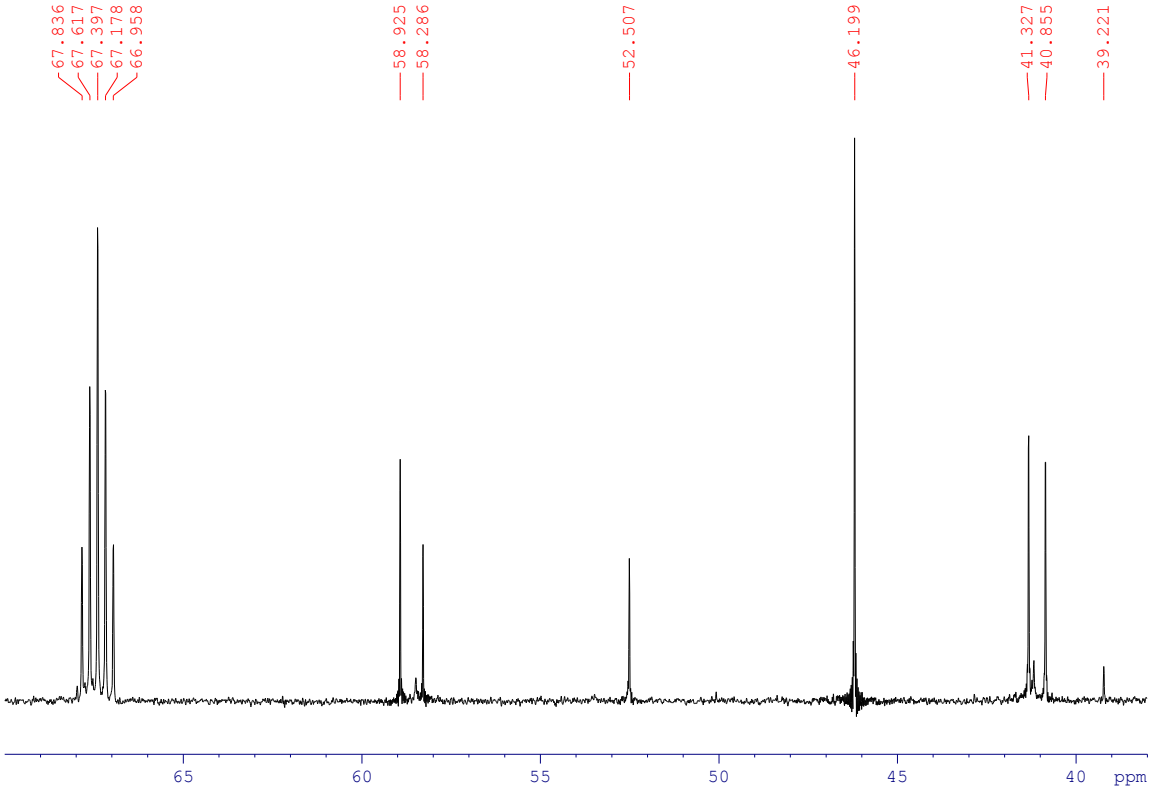
Spectrum 2. Aliphatic region of the ^{1}H NMR spectrum of **2** in d_8-THF solution, showing four chemically distinct TMP and TEMPO methyl groups.



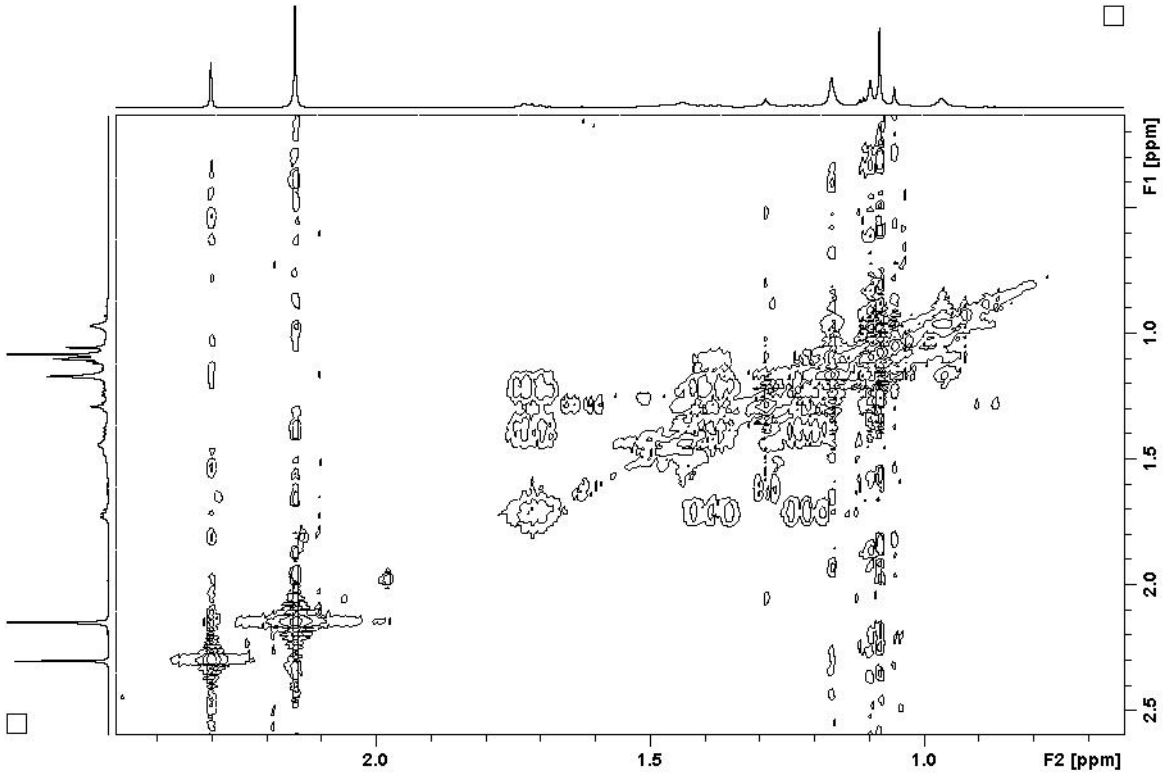
Spectrum 3. ^{13}C NMR (100.62 MHz, 300 K) spectrum of **2** in d_8-THF solution.



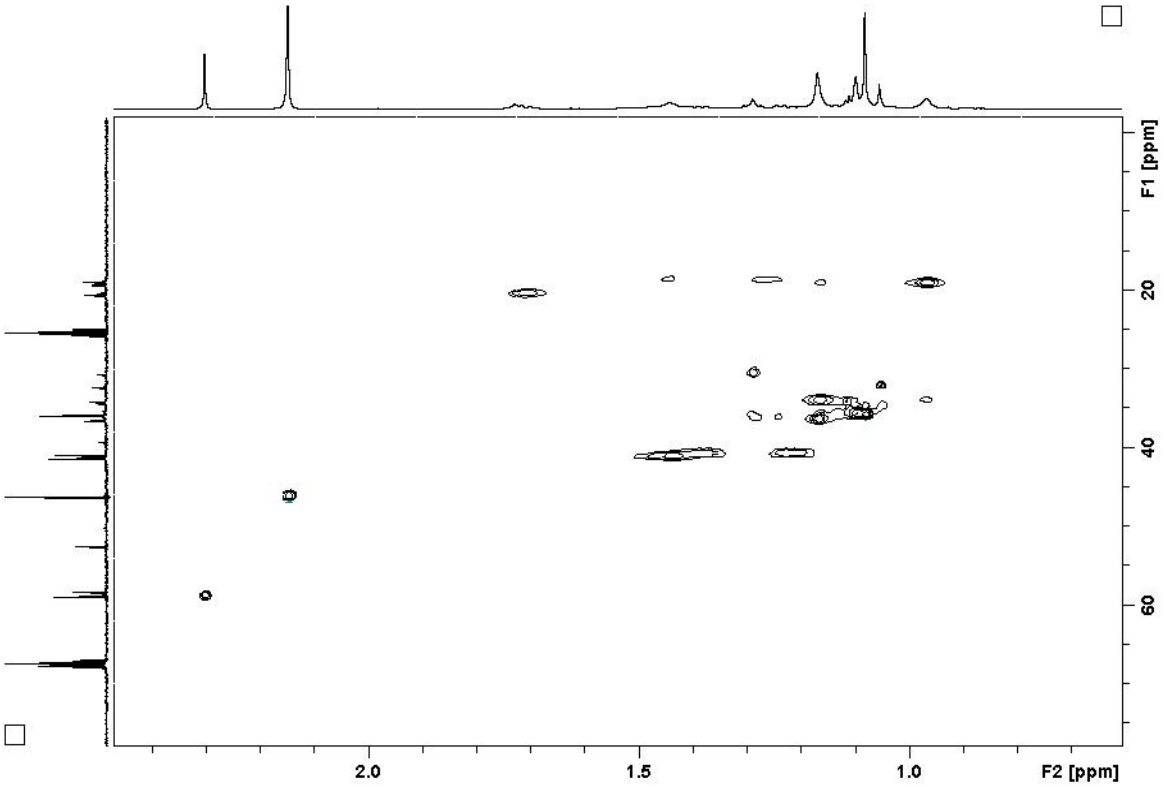
Spectrum 4. Aliphatic region (part 1) of the ^{13}C NMR spectrum of **2** in d_8-THF solution.



Spectrum 5. Aliphatic region (part 2) of the ^{13}C NMR spectrum of **2** in d_8-THF solution



Spectrum 6. Aliphatic region of the ^{1}H-^{1}H COSY spectrum of **2** in d_8-THF solution.



Spectrum 7. Aliphatic region of the ^{1}H-^{13}C HSQC spectrum of **2** in d_8-THF solution.

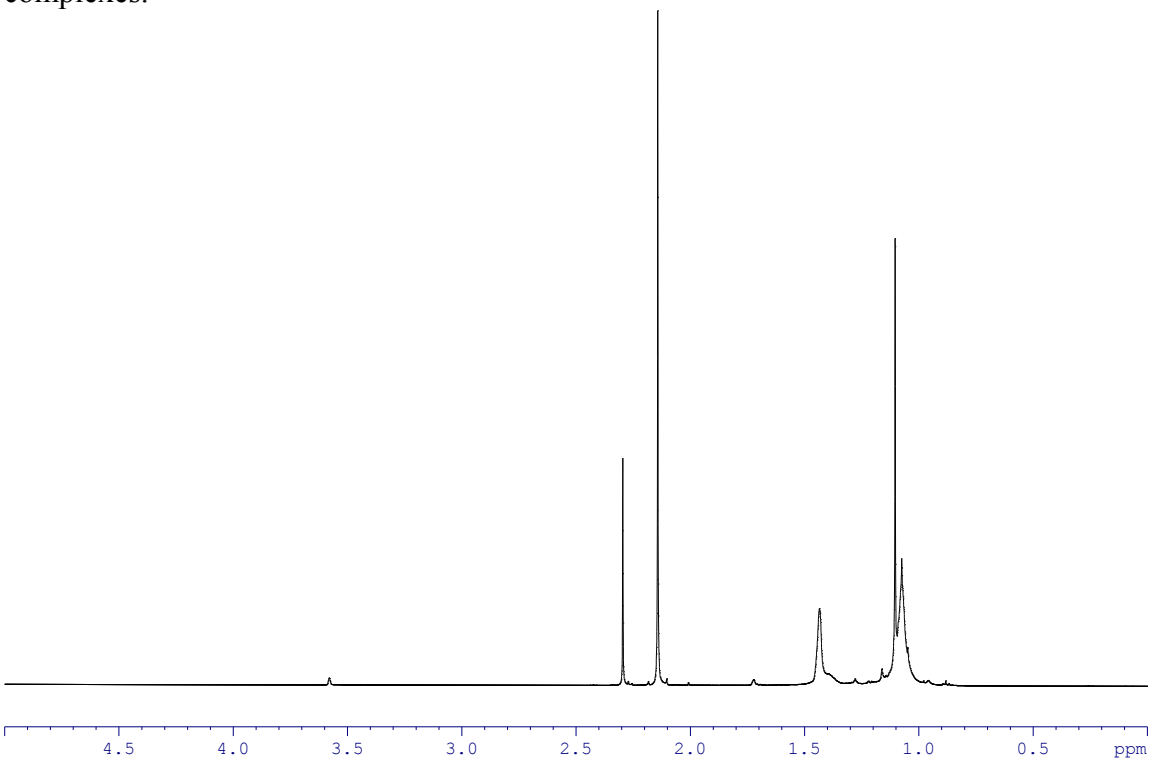
NMR Spectroscopic Analysis of [(TMEDA)·Na(μ-TEMPO)$_2$Zn(^{t}Bu)] 3.

^{1}H NMR (400.13 MHz, 300 K, d_8-THF): δ 2.30 [4H, s, CH_2-TMEDA], 2.14 [12H, s, CH_3-TMEDA], 1.44 [8H, br, β-TEMPO], 1.39 [4H, m, γ-TEMPO], 1.10 [9H, s, CH_3-^{t}Bu], 1.08 [24H, br, CH_3-TEMPO].

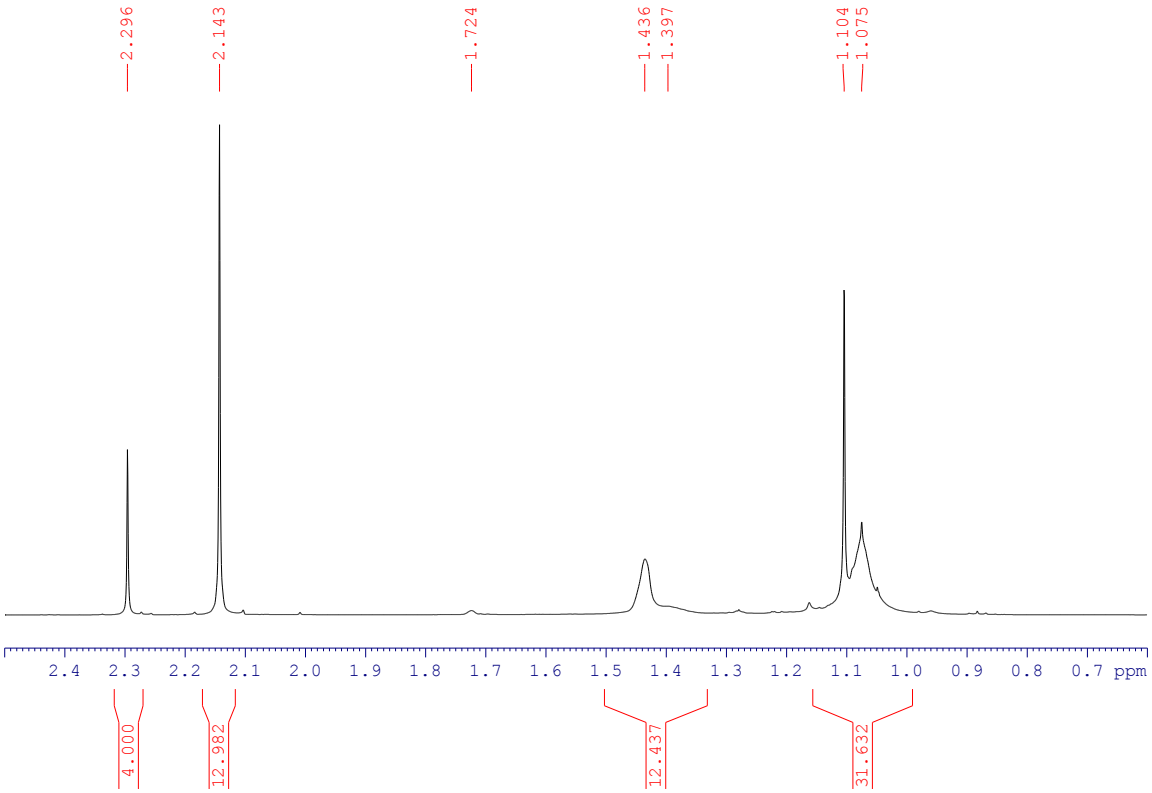
^{13}C NMR (100.62 MHz, 300 K, d_8-THF): δ 58.9 [CH_2-TMEDA], 58.5 [α-TEMPO], 46.2 [CH_3-TMEDA], 41.2 [β-TEMPO], 35.3 [CH_3-^{t}Bu], 21.7 [Cq-^{t}Bu], 18.7 [γ-TEMPO].

* No resonances could be observed for the TEMPO methyl groups. Extremely broad ^{13}C signals have previously been noted for the methyl groups of alkali-metal TEMPO

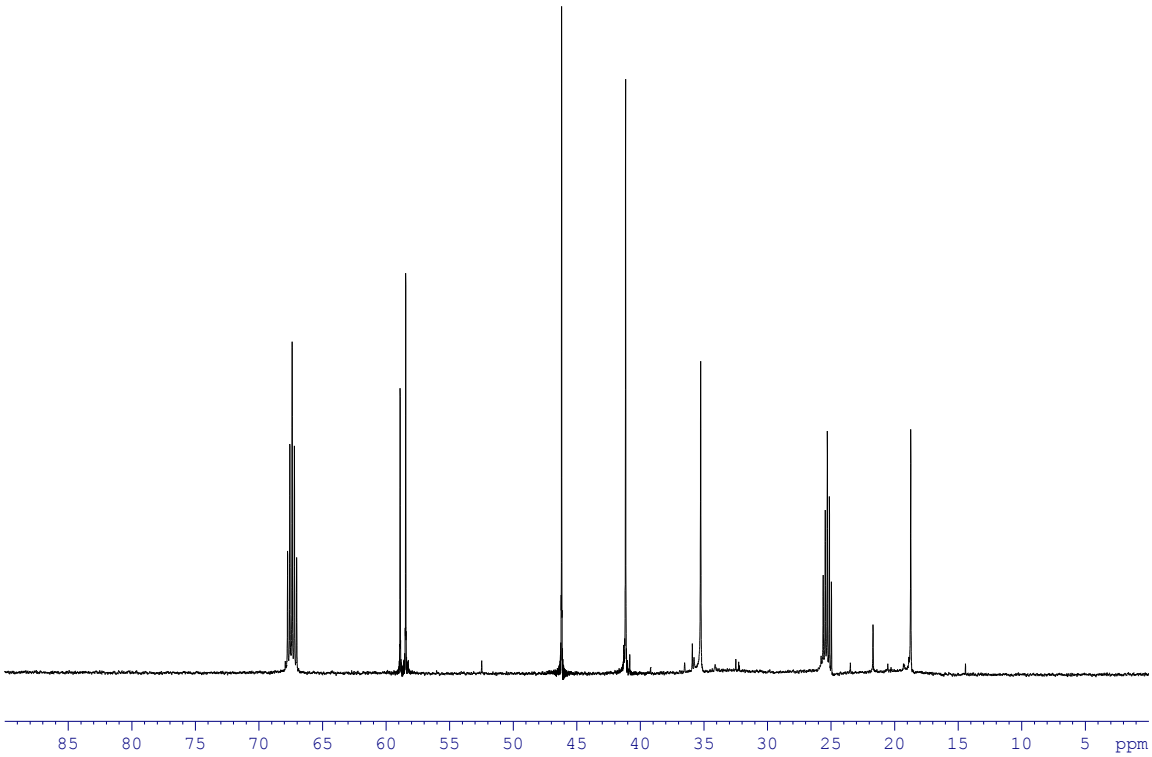
complexes.[1]



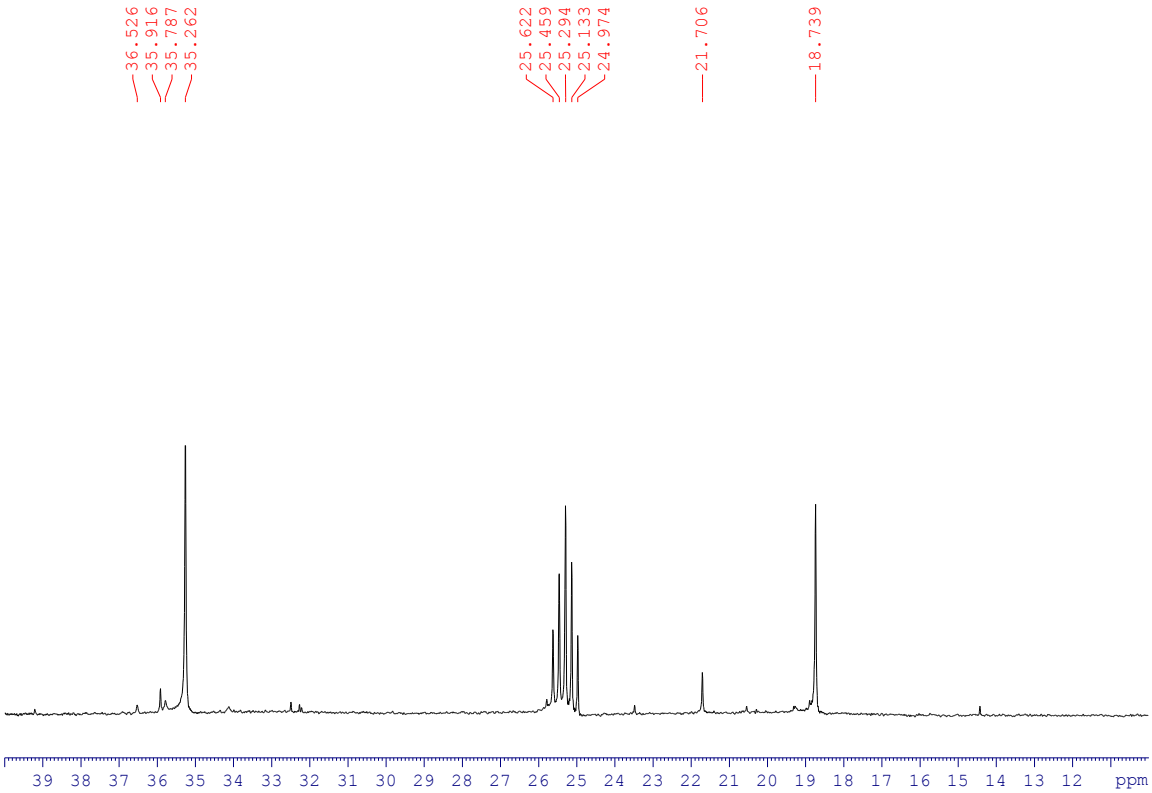
Spectrum 8. ^{1}H NMR (400.13 MHz, 300 K) spectrum of **3** in d_8-THF solution.



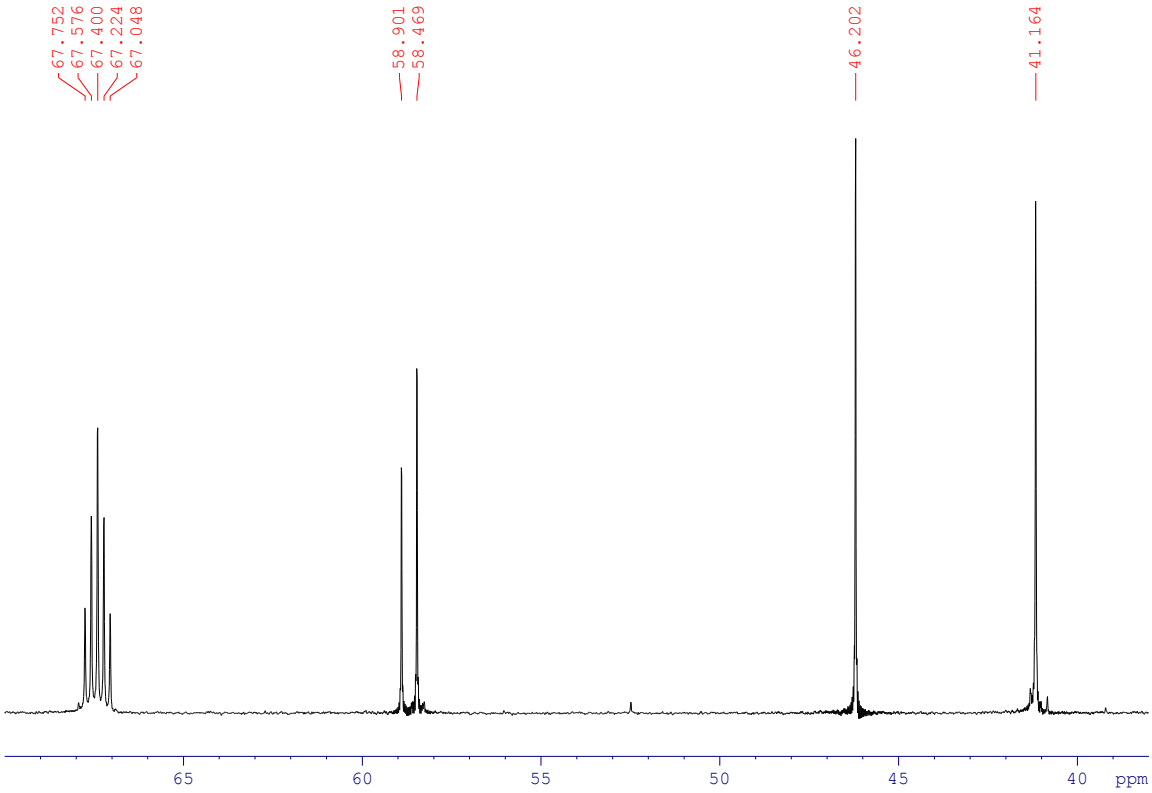
Spectrum 9. Aliphatic region of the ^{1}H NMR spectrum of **3** in d_8-THF solution.



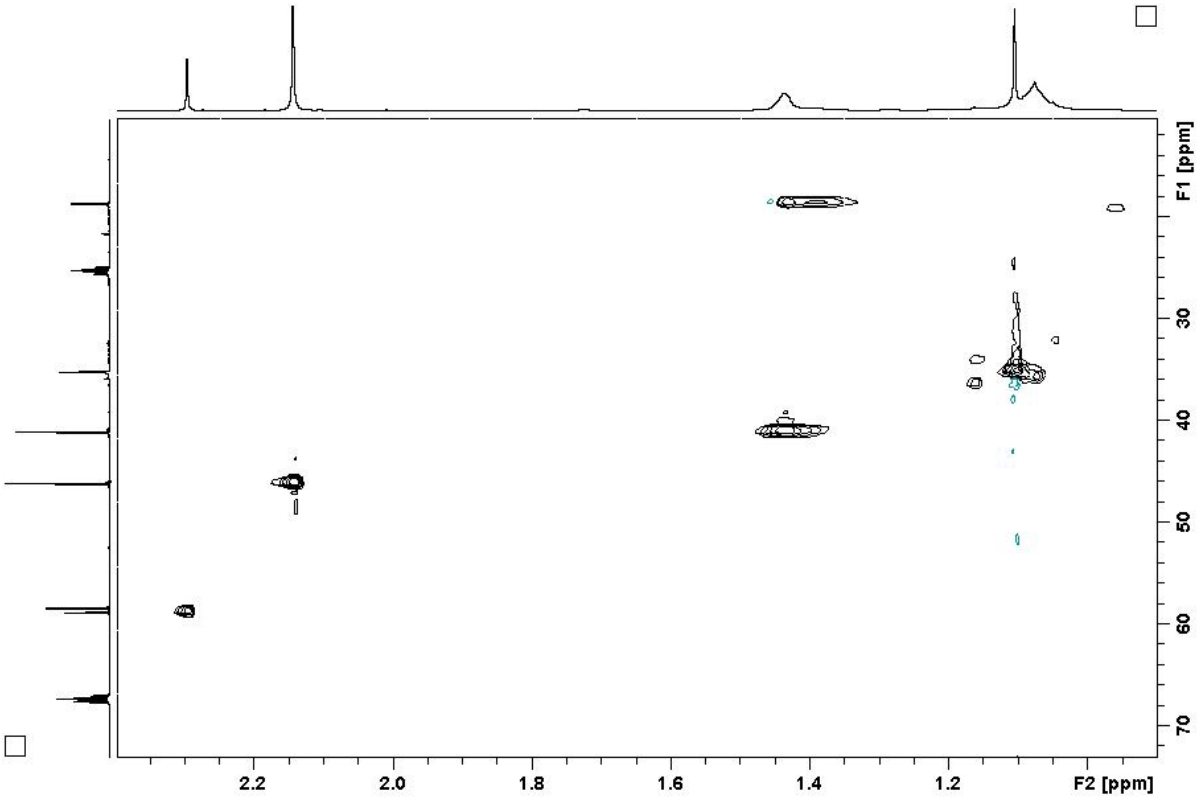
Spectrum 10. ^{13}C NMR (100.62 MHz, 300 K) spectrum of **3** in d_8-THF solution



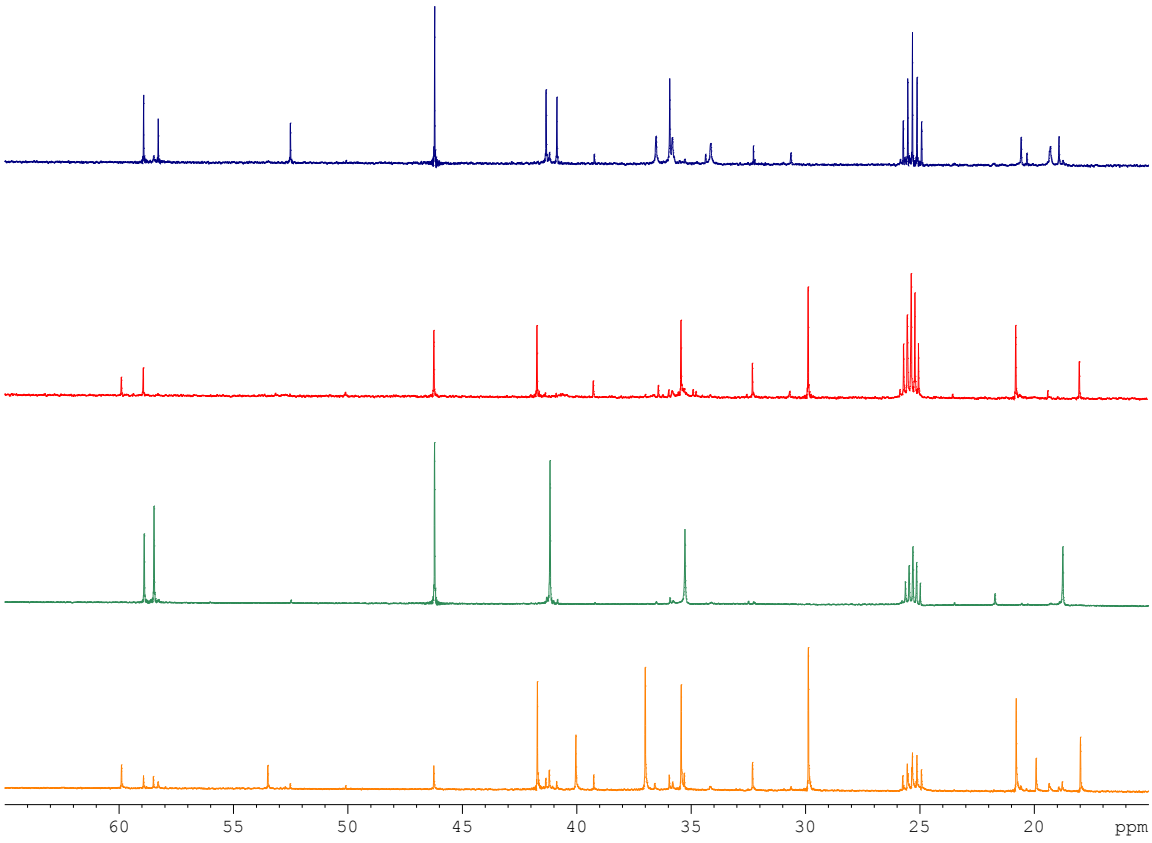
Spectrum 11. Aliphatic region (part 1) of the ^{13}C NMR spectrum of **3** in d_8-THF solution.



Spectrum 12. Aliphatic region (part 2) of the ^{13}C NMR spectrum of **3** in d_8-THF solution.

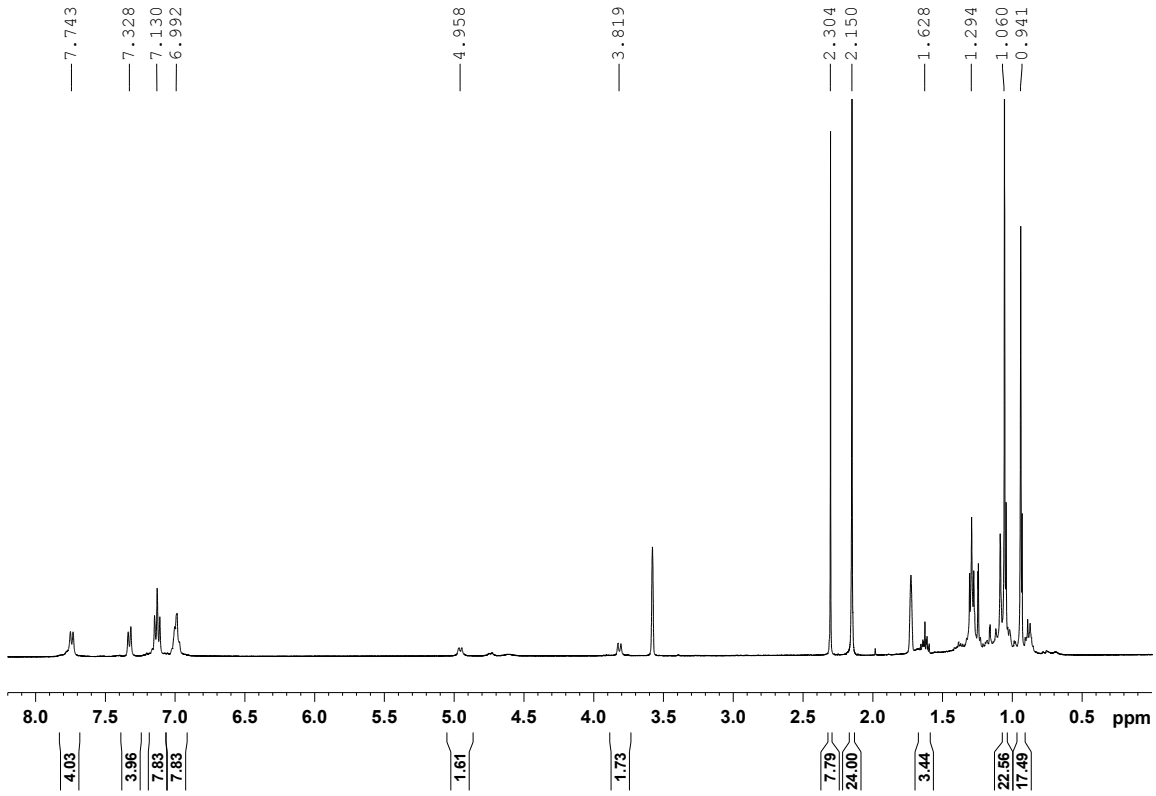


Spectrum 13. Aliphatic region of the ^{1}H-^{13}C HSQC spectrum of **3** in d_8-THF solution.



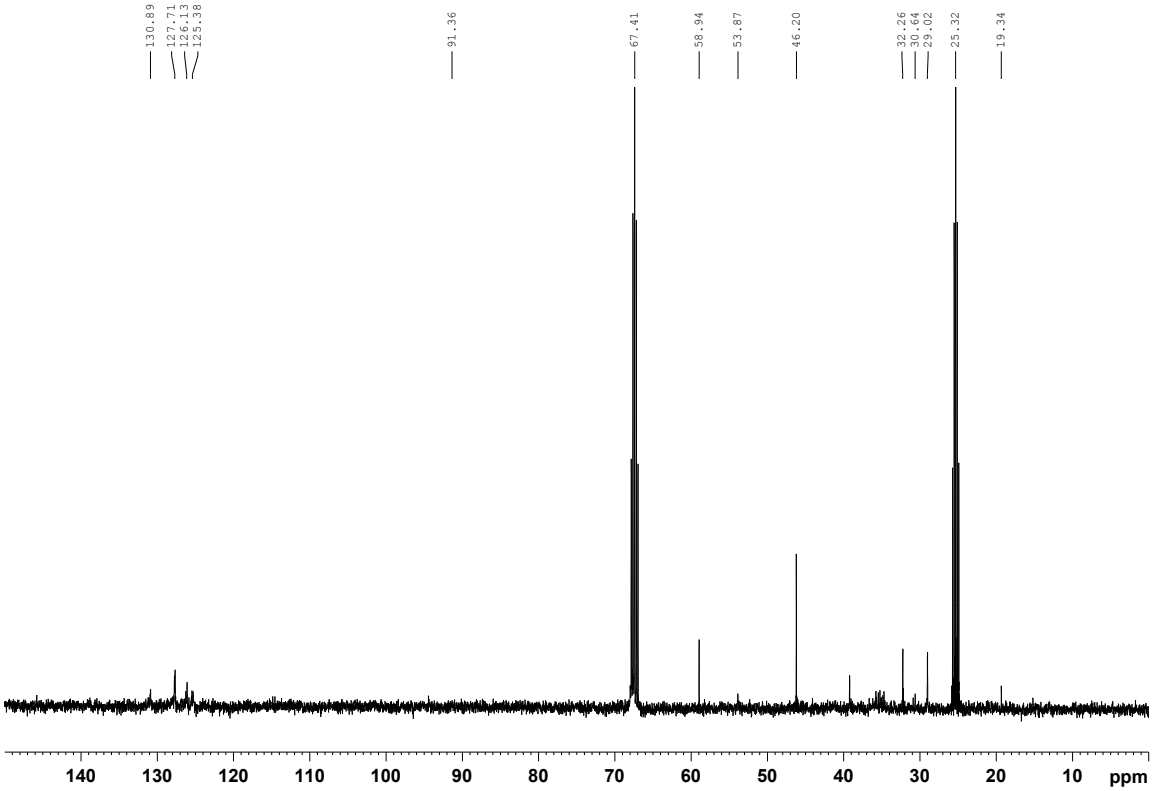
Spectrum 14. Collated ^{13}C NMR spectra of **2** (blue), the mother liquor following isolation of **2** (red), **3** (green) and the mother liquor following the isolation of **3** (orange) in d_8-THF solution, illustrating how an equimolar quantity of TEMPO is required for formation of **3**.

NMR Spectroscopic Analysis of [{ (TMEDA)· Na(μ-TMP)Zn(^{t}Bu)}$_2$(μ-OCPhCH=CHPhCHPhCH=CPh-μ-O)] 4.



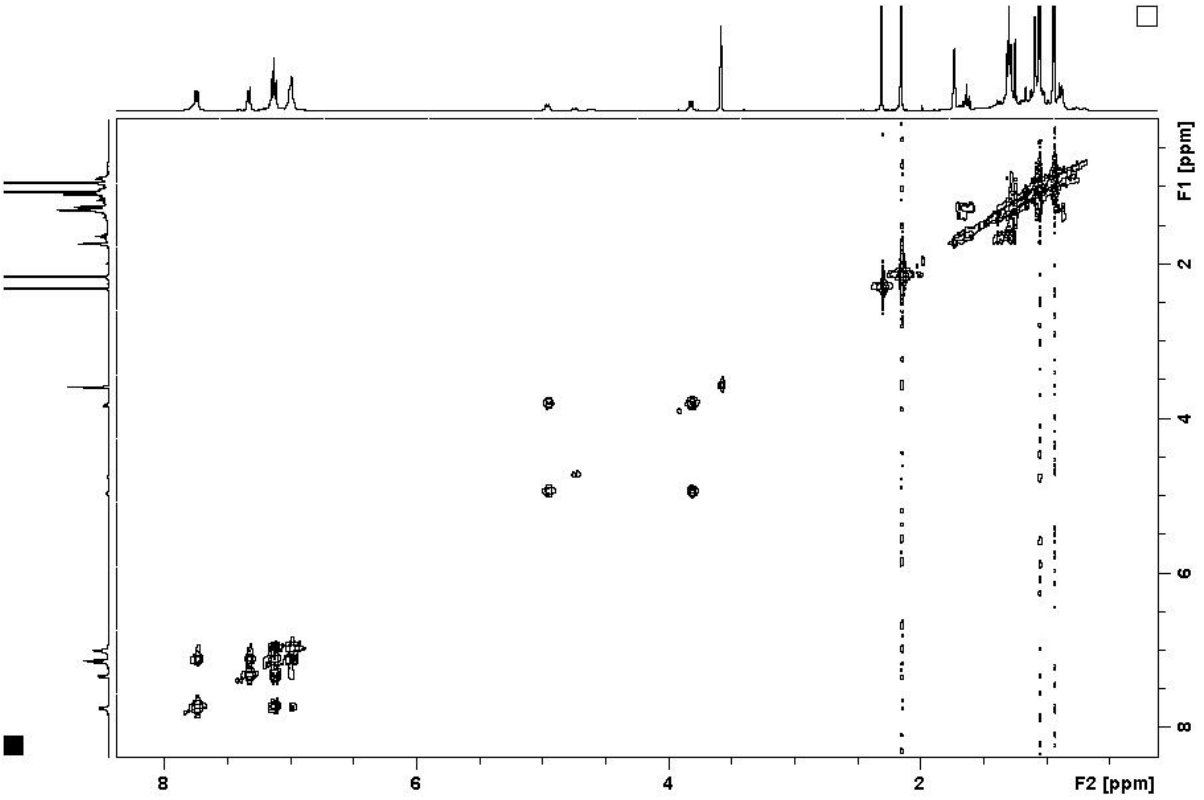
Spectrum 15. ^{1}H NMR (400.13 MHz, 300 K) spectrum of **4** in d_8-THF solution

^{1}H NMR (400.13 MHz, d_8-THF, 300K): δ (ppm) = 7.74 (d, 4H, ortho), 7.33 (d, 4H, ortho), 7.13 (t, 8H, meta), 6.99 (m, 4H, para), 4.96 (d, 2H, allylic), 3.82 (d, 2H, benzylic), 2.30 (s, 8H, TMEDA CH_2), 2.15 (s, 24H, TMEDA CH_3), 1.63 (m, 4H, TMP-γ) , 1.29 (t, 8H, TMP-β), 1.06 (s, 24H, TMP-CH_3), 0.94 (s, 18H, ^{t}Bu).

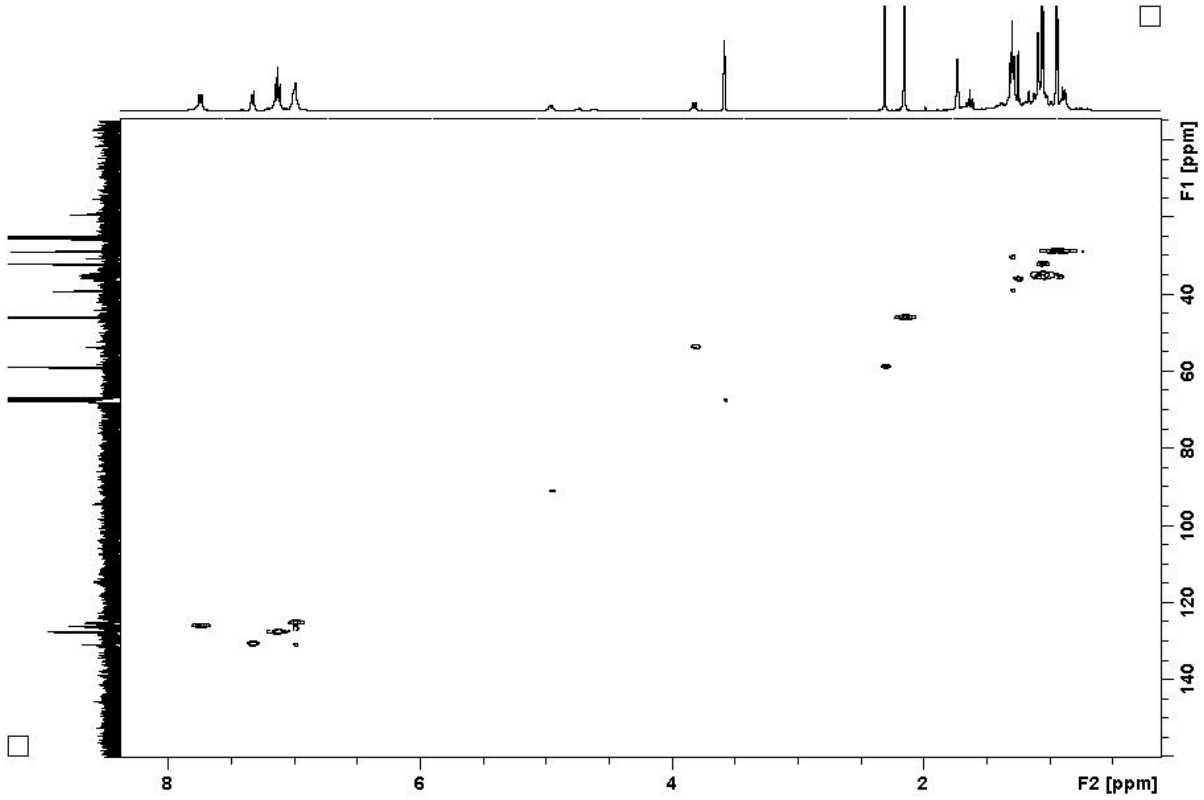


Spectrum 16. ^{13}C NMR (100.62 MHz, 300 K) spectrum of **4** in d_8-THF solution

^{13}C NMR (100.62 MHz, d_8-THF, 300K): δ (ppm) = 130.9 (CH, ortho), 127.7 (CH, meta), 126.1 (CH, ortho), 125.4 (CH, para), 91.4 (CH, allylic), 58.9 (CH_2, TMEDA), 53.9 (CH, benzylic), 46.2 (CH_3, TMEDA), 32.3 (CH_3, TMP), 30.6 (β-CH_2, TMP), 29.0 (CH_3, ^{t}Bu), 19.3 (γ-CH_2, TMP).



Spectrum 17. ^{1}H-^{1}H COSY spectrum of compound **4** in d_8-THF solution



Spectrum 18. ^{1}H-^{13}C HSQC spectrum of compound **4** in d_8-THF solution

1. L. Balloch, A. M. Drummond, P. García-Álvarez, D. V. Graham, A. R. Kennedy, J. Klett, R. E. Mulvey, C. T. O'Hara and I. D. Rushworth, *Inorg. Chem.*, 2009, **48**, 6934.