Supplementary Material (ESI) for Chemical Communications

Supporting Information

Structural elaboration of the surprising *ortho*-zincation of benzylmethylether

Liam Balloch, Alan R. Kennedy, Jan Klett, Robert E. Mulvey* and Charles T. O'Hara*

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, U.K.

***** To whom correspondence should be addressed

Email: r.e.mulvey@strath.ac.uk

General Methods

Hexane was distilled from sodium-benzophenone. All synthetic work was carried out under an inert argon atmosphere using standard Schlenk techniques. Data for X-ray crystal structure determination were obtained with an Oxford Xcalibur S diffractometer using graphite monochromated Mo-Ka radiation (λ = 0.71073 Å). The ^{1}H NMR 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. Elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyser. Due to the extreme air and moisture sensitivity of **2**, ideal analyses could not be obtained.
Anal. (%): Actual C 61.99, H 10.02, N 8.03; found C 61.04, H 10.00, N 7.74.

NMR Spectroscopic Analysis of [(TMEDA)·Na(μ-TMP)(μ-$C_6H_4CH_2OMe$)Zn(^{t}Bu)] 2.

^{1}H NMR (400.13 MHz, 300 K, D_{12}-cyclohexane): δ 7.59 (d, 1H, H_{meta}), 7.01 (m, 2H, H_{para} and $H_{meta'}$), 6.90 (m, 1H, $H_{ortho'}$), 4.48 (d, 1H, PhC*H*), 4.07 (d, 1H, PhC*H*), 3.43 (s, 3H, OCH_3), 2.10 [br s, 4H, NCH_2 (TMEDA)], 1.83 [br s, 12H, NCH_3 (TMEDA)], 1.75 [m, 2H, γ-CH_2 (TMP)], 1.38 [m, 4H, β-CH_2 (TMP) (observed by COSY NMR spectroscopy)] 1.34 [s, 3H, CH_3 (TMP)], 1.29 [s, 3H, CH_3 (TMP)], 1.16 [s, 3H, CH_3 (TMP)], 1.14 [s, 3H, CH_3 (TMP)], 0.84 [s, 9H, CH_3 (^{t}Bu)].

^{13}C{^{1}H} NMR (100.62 MHz, 300 K, D_{12}-cyclohexane): δ 172.0 (C_{ortho}-Zn), 145.3 (C_{ipso}), 140.8 (C_{meta}), 129.0 (C_{para} or $C_{meta'}$), 126.8 (C_{para} or $C_{meta'}$), 125.2 ($C_{ortho'}$), 84.2 (PhCH_2), 59.1 (OCH_3), 58.3 [NCH_2 (TMEDA)], 53.4 [α-*C* (TMP)], 52.9 [α-*C* (TMP)], 46.2 [NCH_3 (TMEDA)], 41.0 [β-CH_2 (TMP)], 40.0 [β-CH_2 (TMP)], 37.4 [CH_3 (TMP)], 36.0 [CH_3 (TMP)], 35.5 [CH_3 (TMP)], 35.0 [CH_3 (TMP)], 34.6 [CCH_3 (^{t}Bu)], 20.5 [γ-CH_2 (TMP)], 20.1 [CCH_3 (^{t}Bu)].

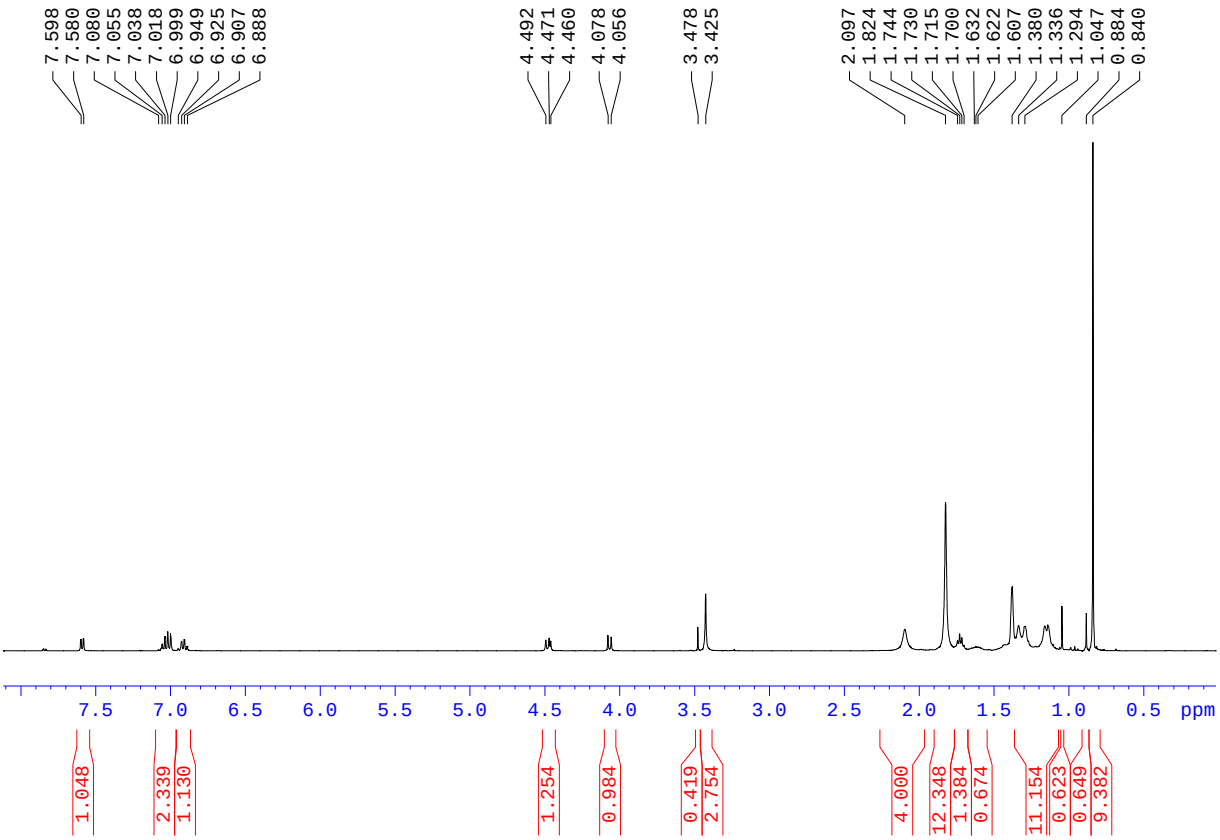

Figure S1: ^{1}H NMR (400.13 MHz, 300 K) spectrum of **2** obtained in D_{12}-cyclohexane.

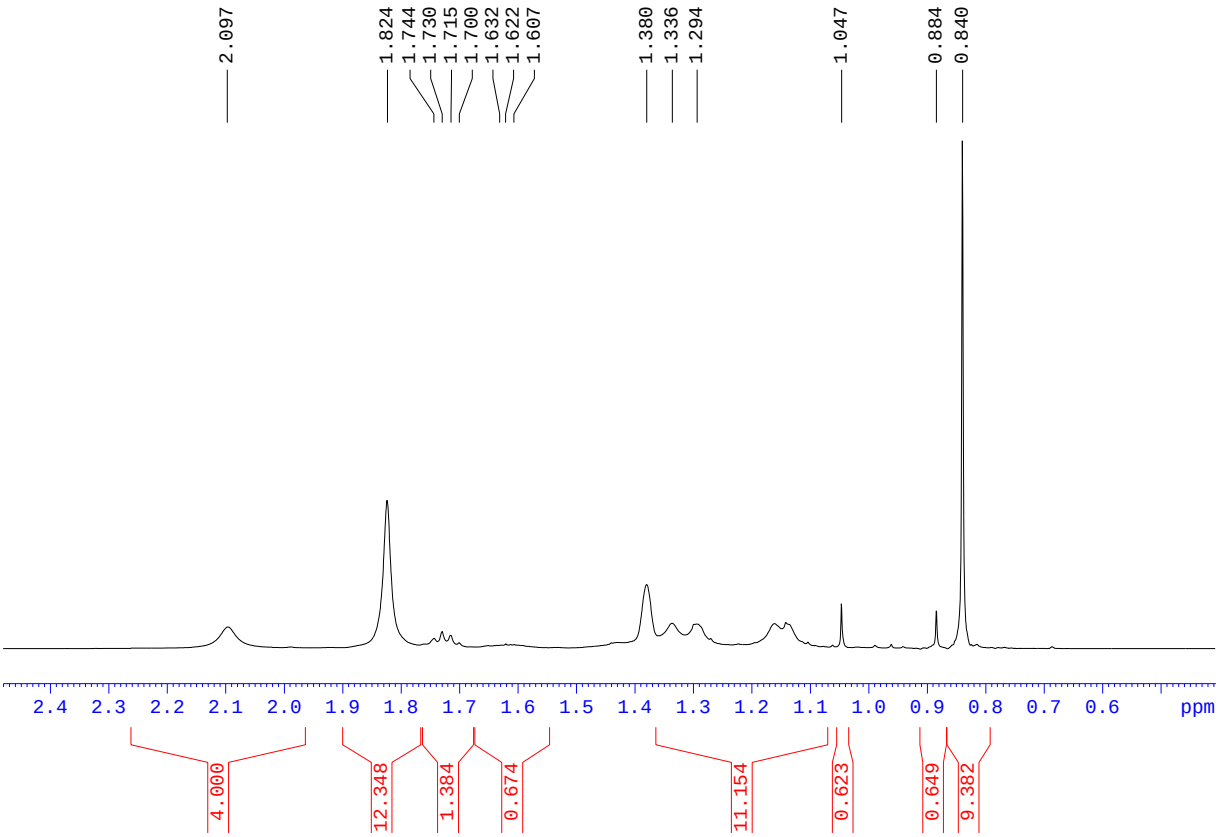

Figure S2: Aliphatic region of the ^{1}H NMR spectrum of **2** obtained in D_{12}-cyclohexane, showing all four chemically distinct TMP C*H*$_3$ groups.

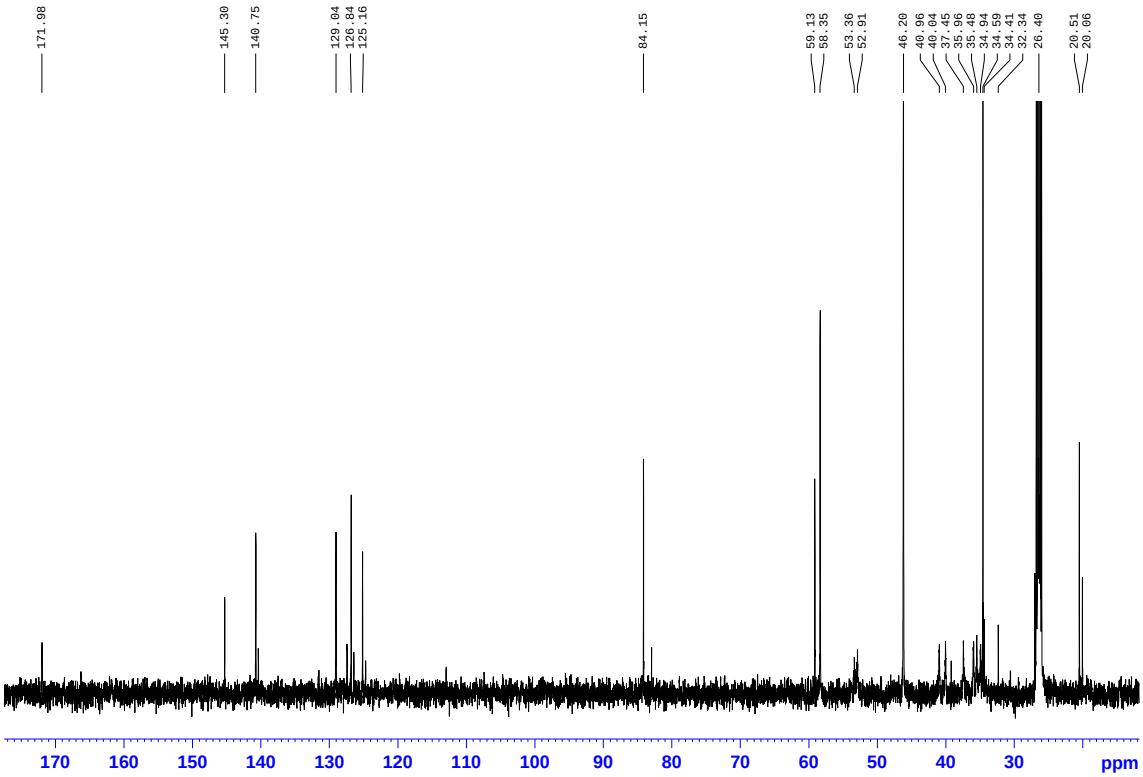

Figure S3: ^{13}C NMR (100.63 MHz, 300 K) spectrum of **2** obtained in D_{12}-cyclohexane.

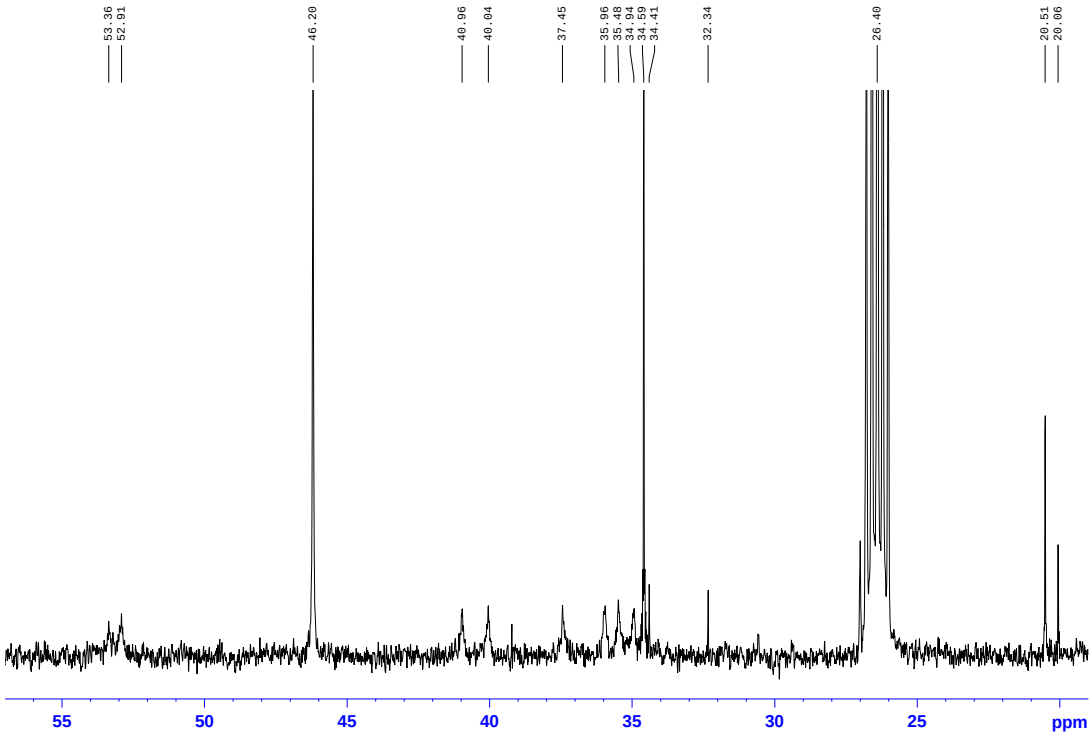

Figure S4: Aliphatic region of the ^{13}C NMR spectrum of **2** obtained in D_{12}-cyclohexane.

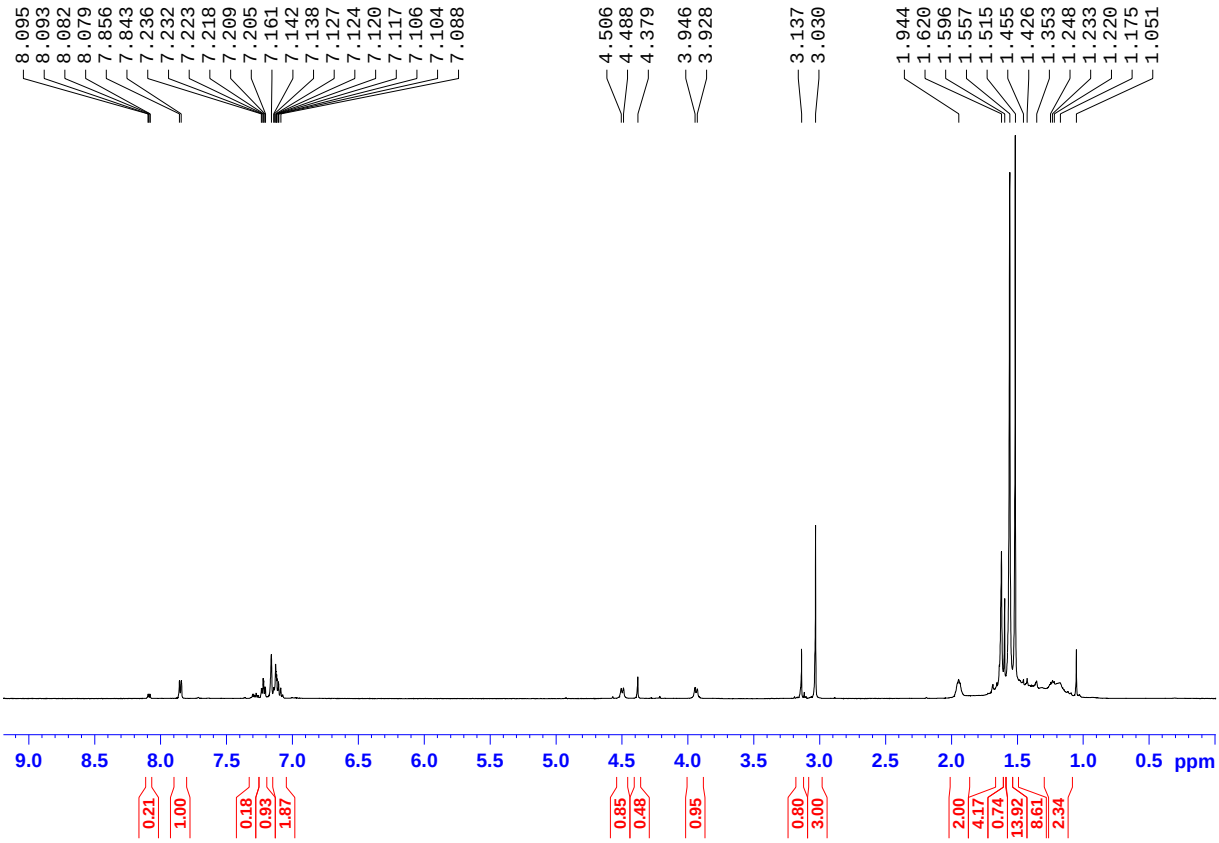

Figure S5: ^{1}H NMR (400.13 MHz, 300 K) spectrum of **2** obtained in D_6-benzene.

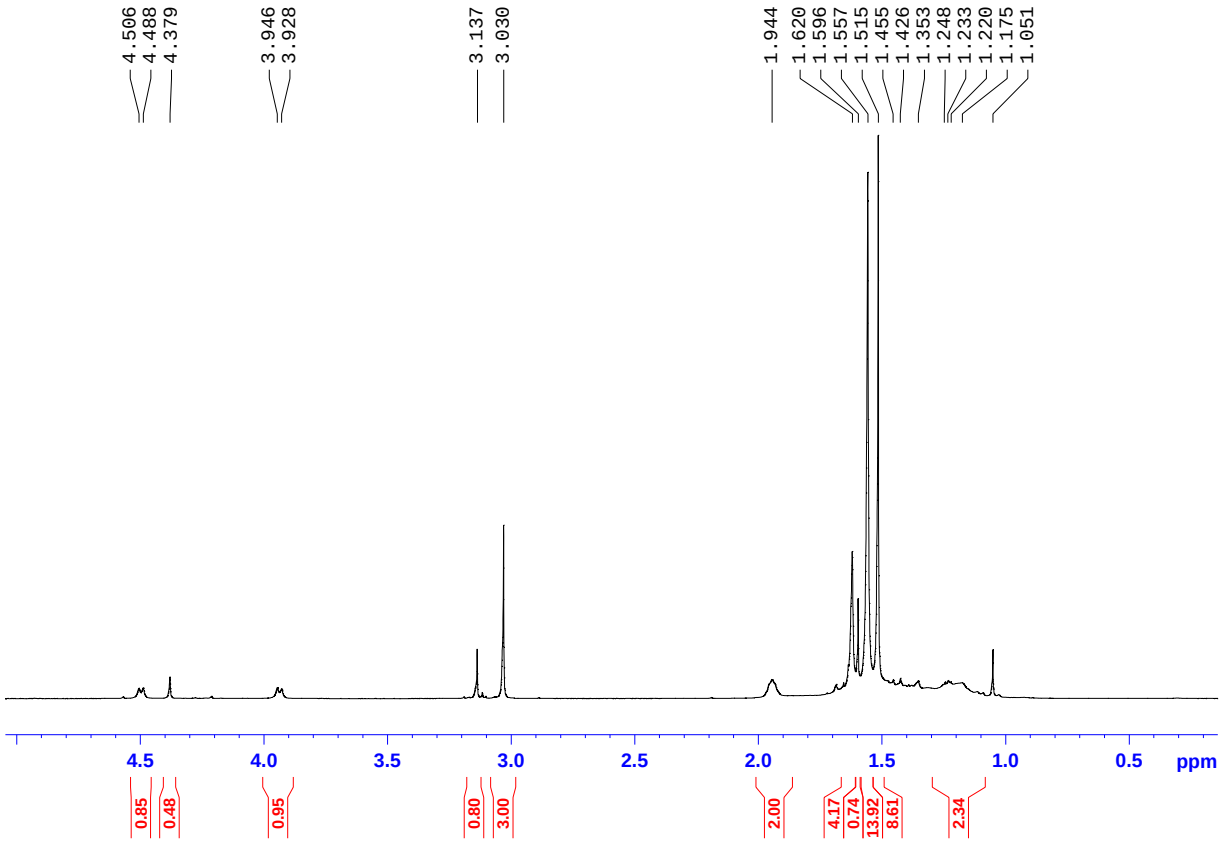

Figure S6: Aliphatic region of the ^{1}H NMR spectrum of **2** obtained in D_6-benzene.

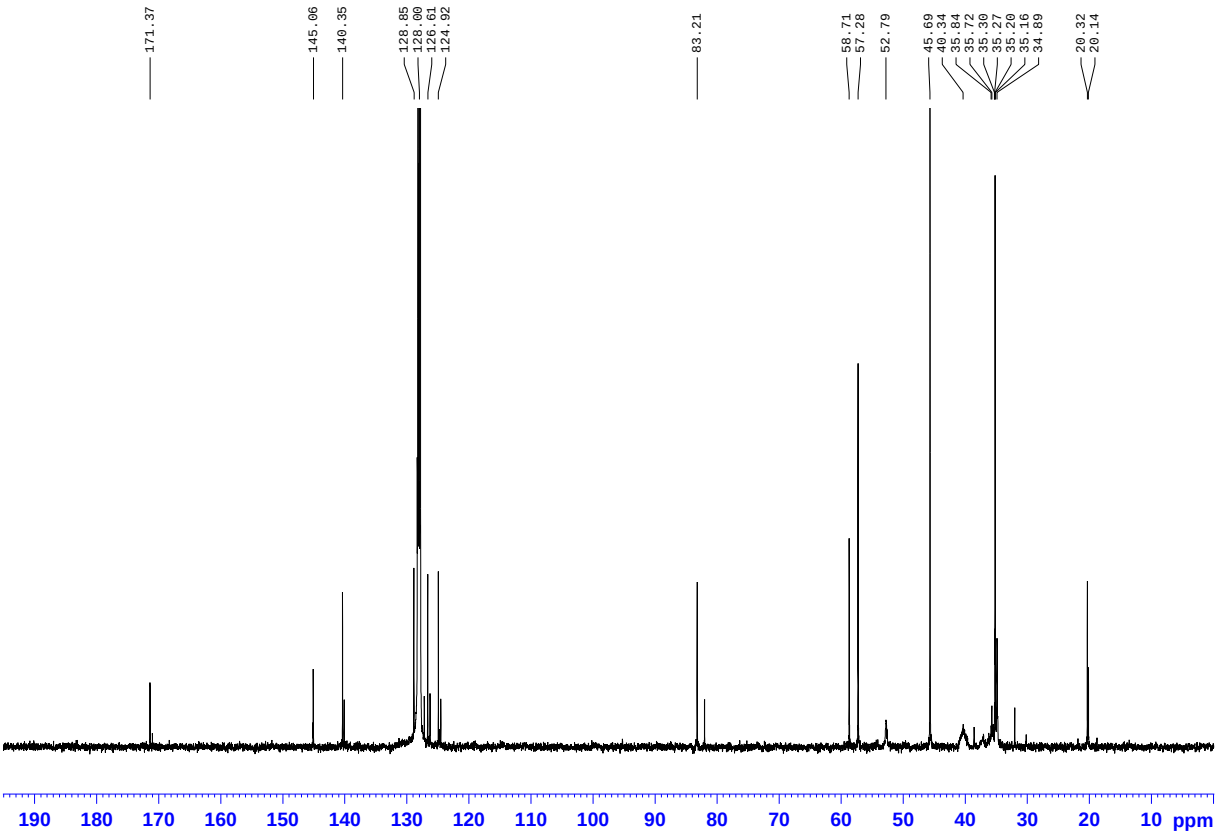

Figure S7: ^{13}C NMR (100.63 MHz, 300 K) spectrum of **2** obtained in D_6-benzene.

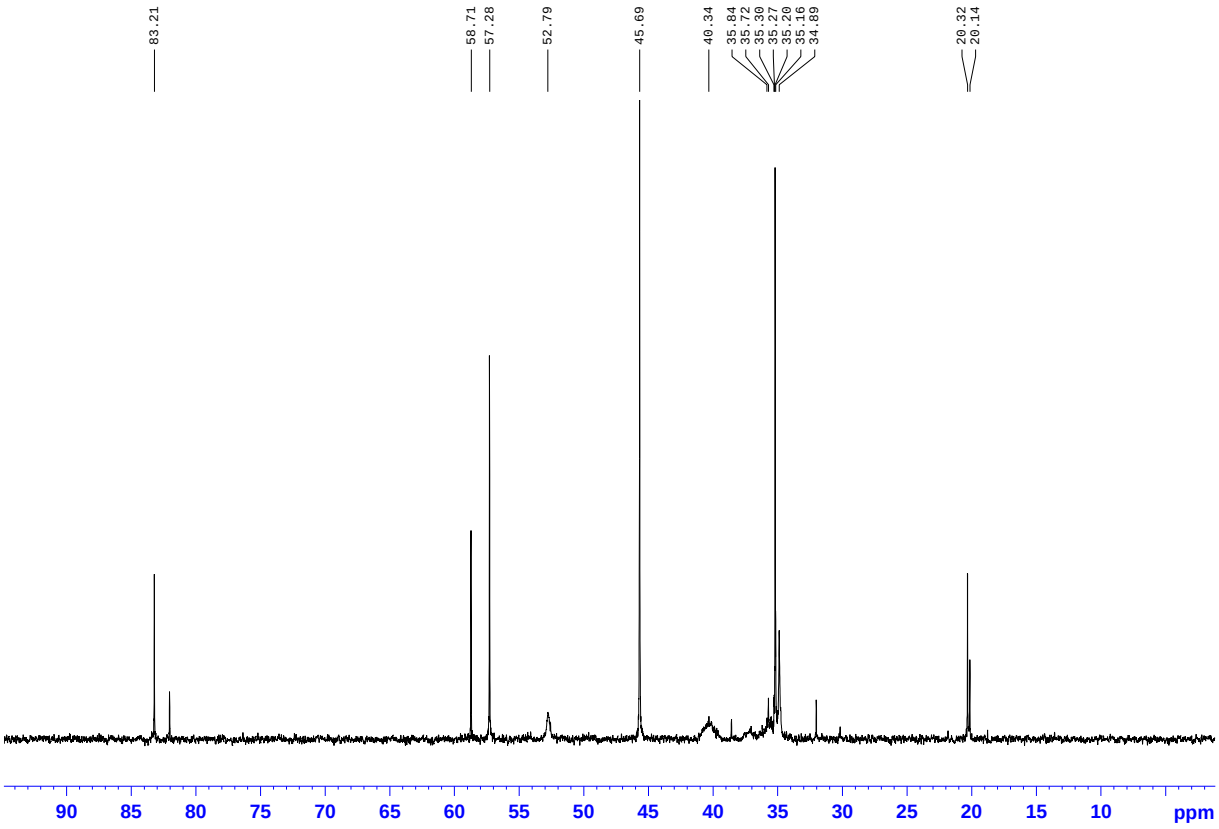

Figure S8: Aliphatic region of the ^{13}C NMR spectrum of **2** obtained in D_6-benzene.

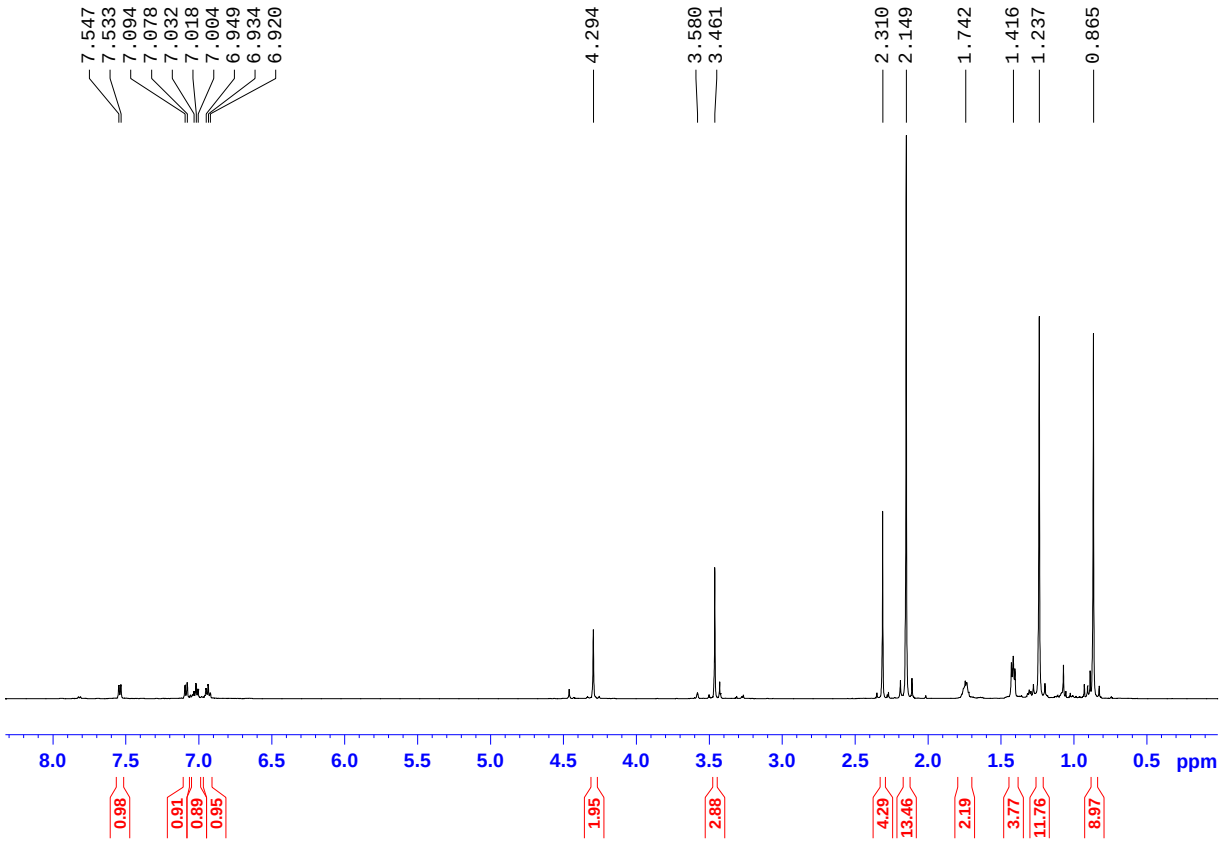

Figure S9: ^{1}H NMR (400.13 MHz, 300 K) spectrum of **2** obtained in D_8-THF.

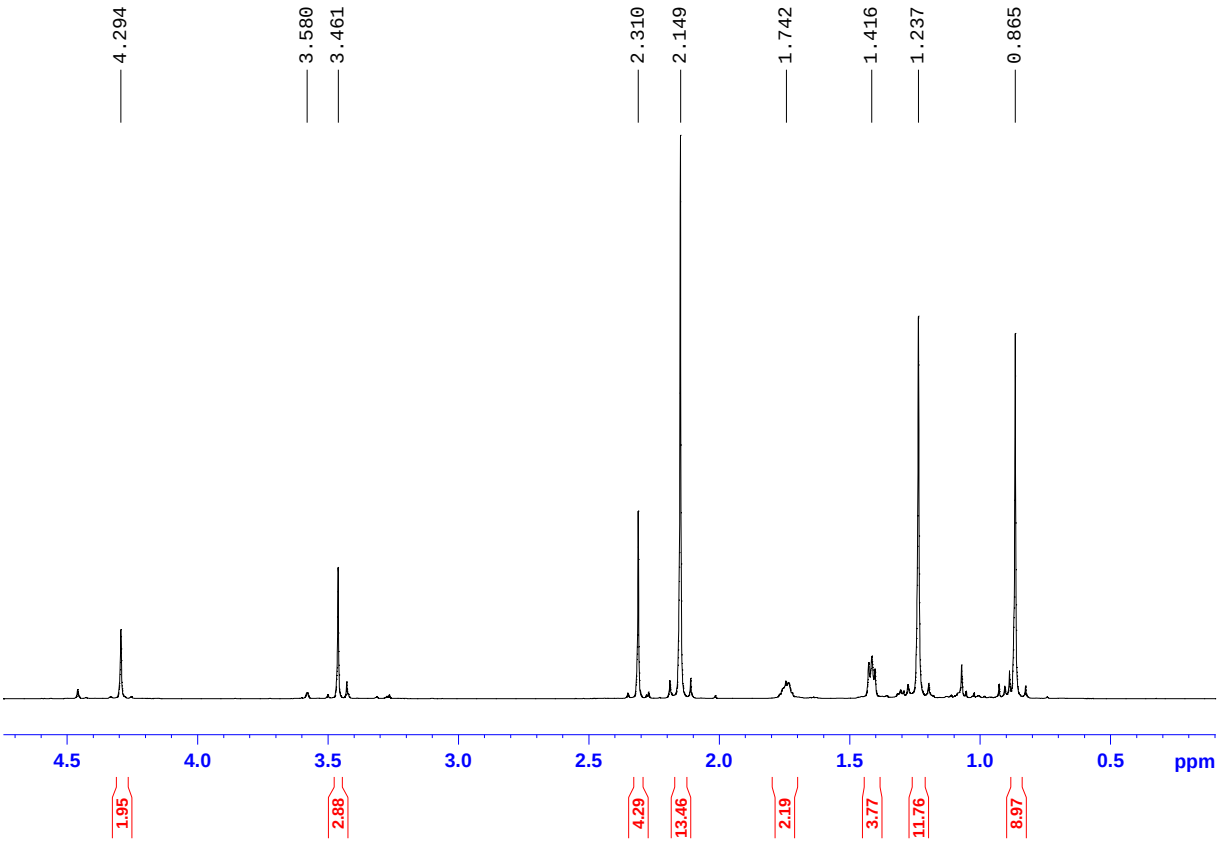

Figure S10: Aliphatic region of the ^{1}H NMR spectrum of **2** obtained in D_8-THF.

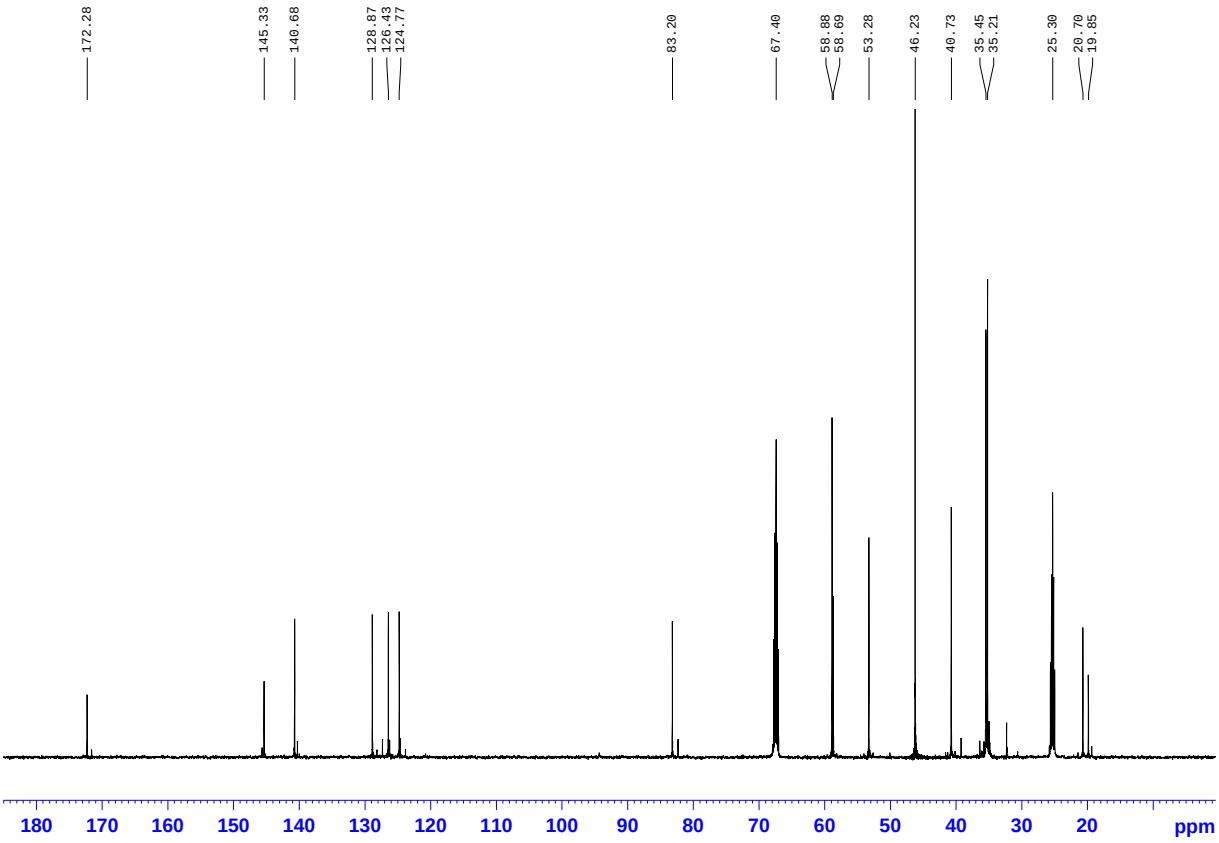

Figure S11: ^{13}C NMR (100.63 MHz, 300 K) spectrum of **2** obtained in D_8-THF.

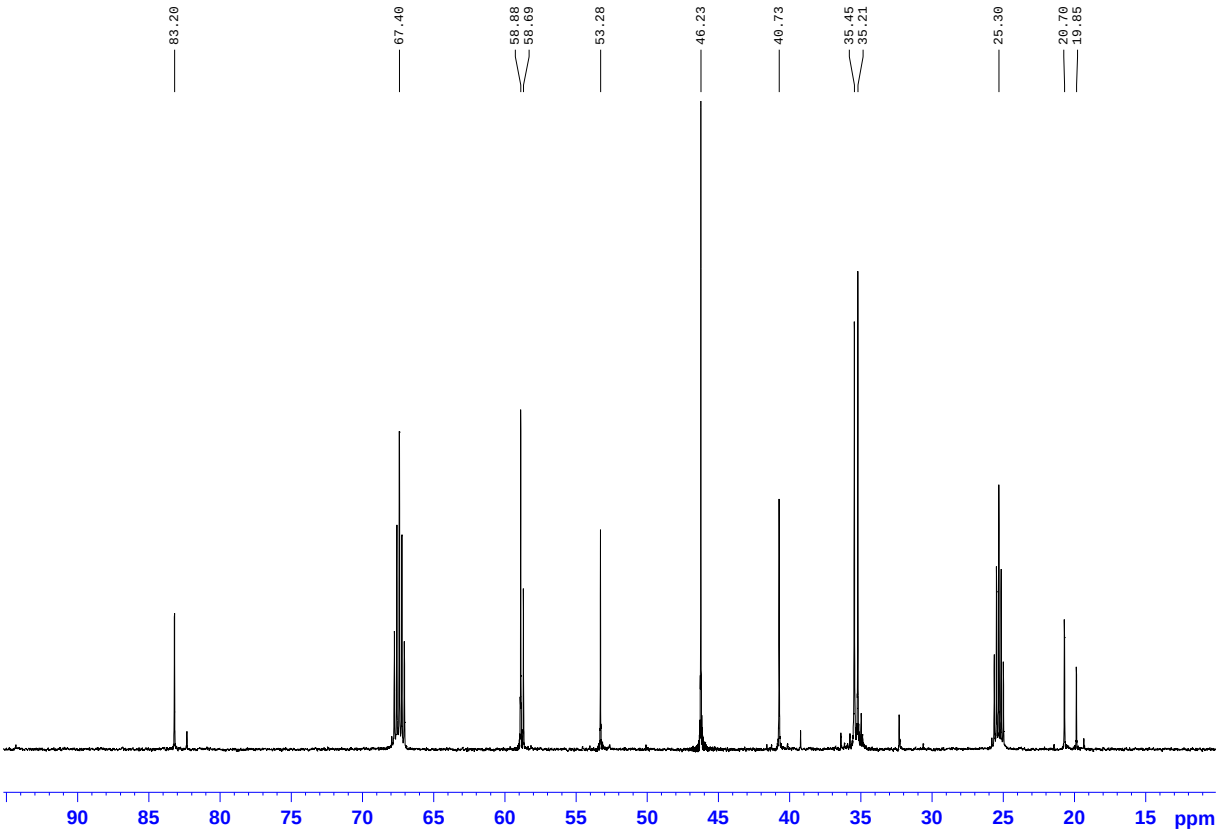

Figure S11: Aliphatic region of the ^{13}C NMR spectrum of **2** obtained in D_8-THF.

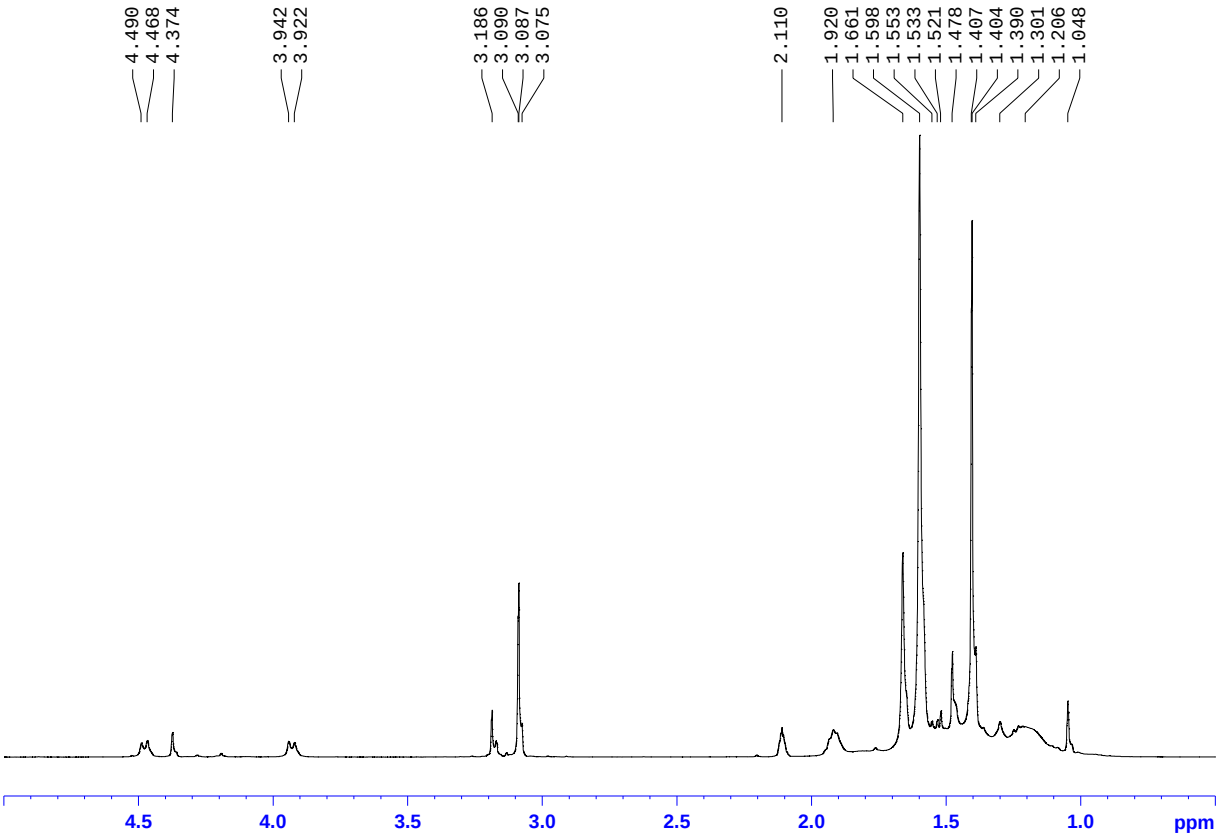

Figure S12: ^{1}H NMR (400.13 MHz, 300 K) spectrum of **2** obtained in D_8-toluene.

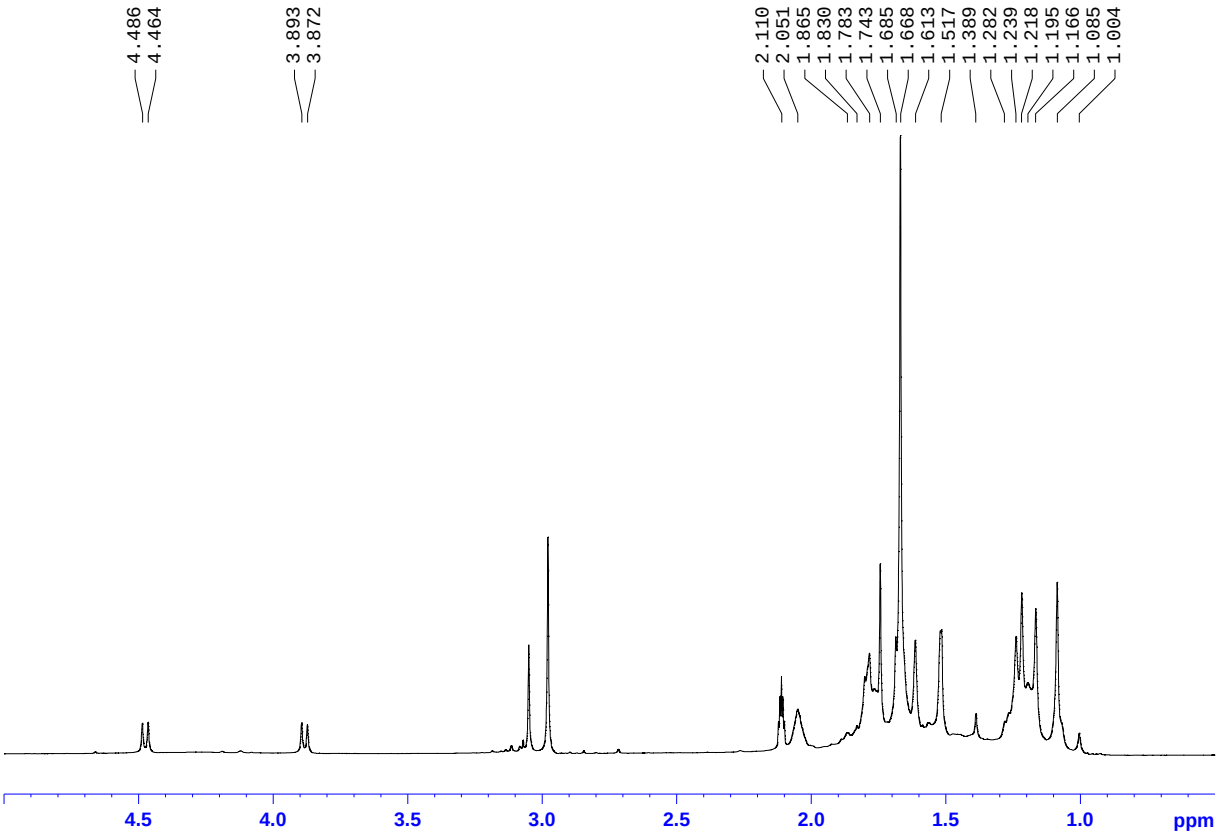

Figure S13: ^{1}H NMR (400.13 MHz, 210 K) spectrum of **2** obtained in D_8-toluene.

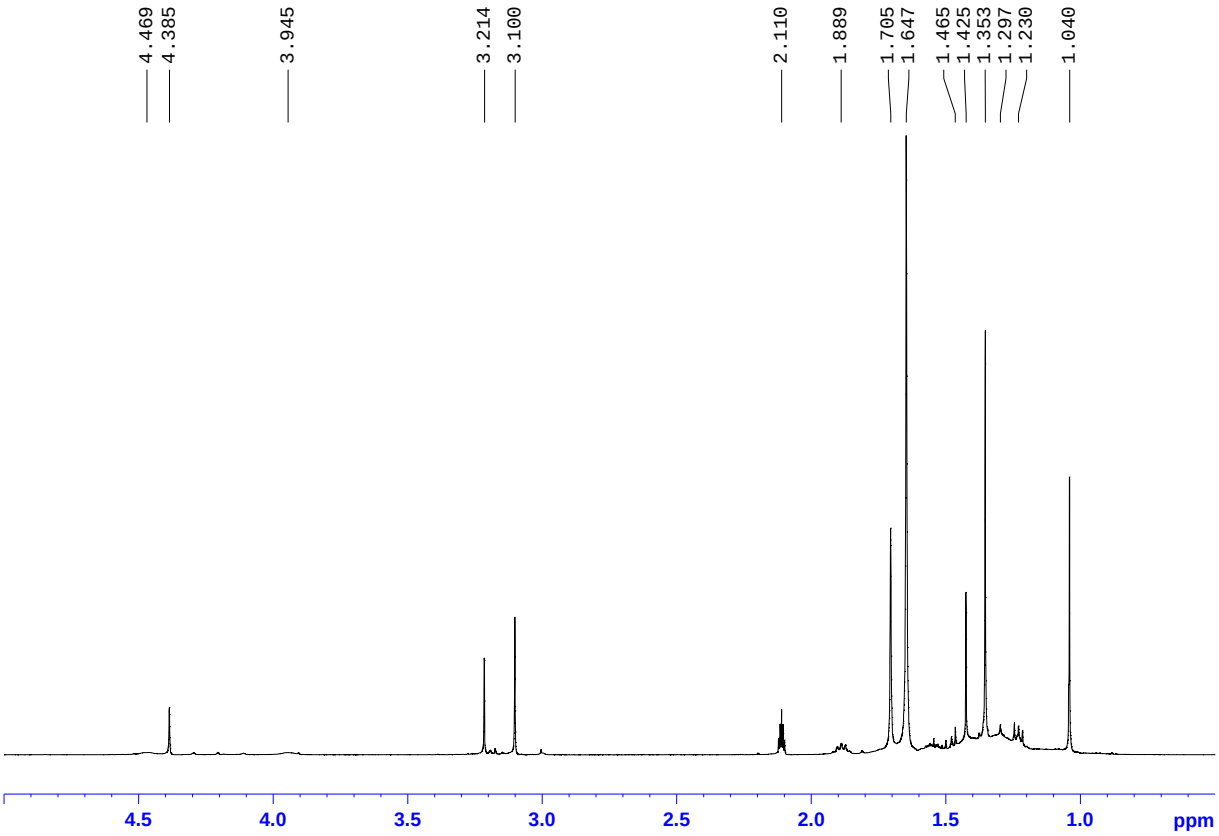

Figure S14: ^{1}H NMR (400.13 MHz, 320 K) spectrum of **2** obtained in D_8-toluene.

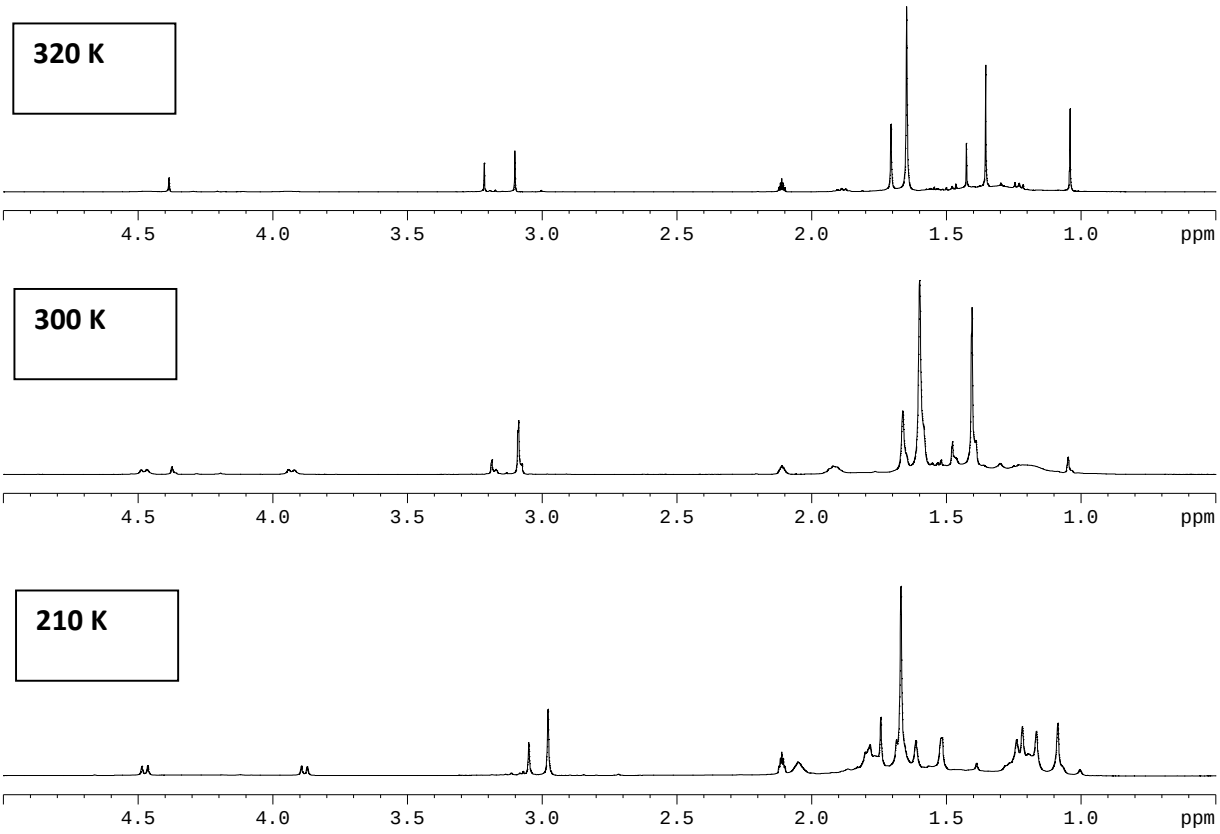

Figure S15: Collated variable temperature ^{1}H NMR (400.13 MHz) spectra plot of **2** obtained in D_8-toluene.

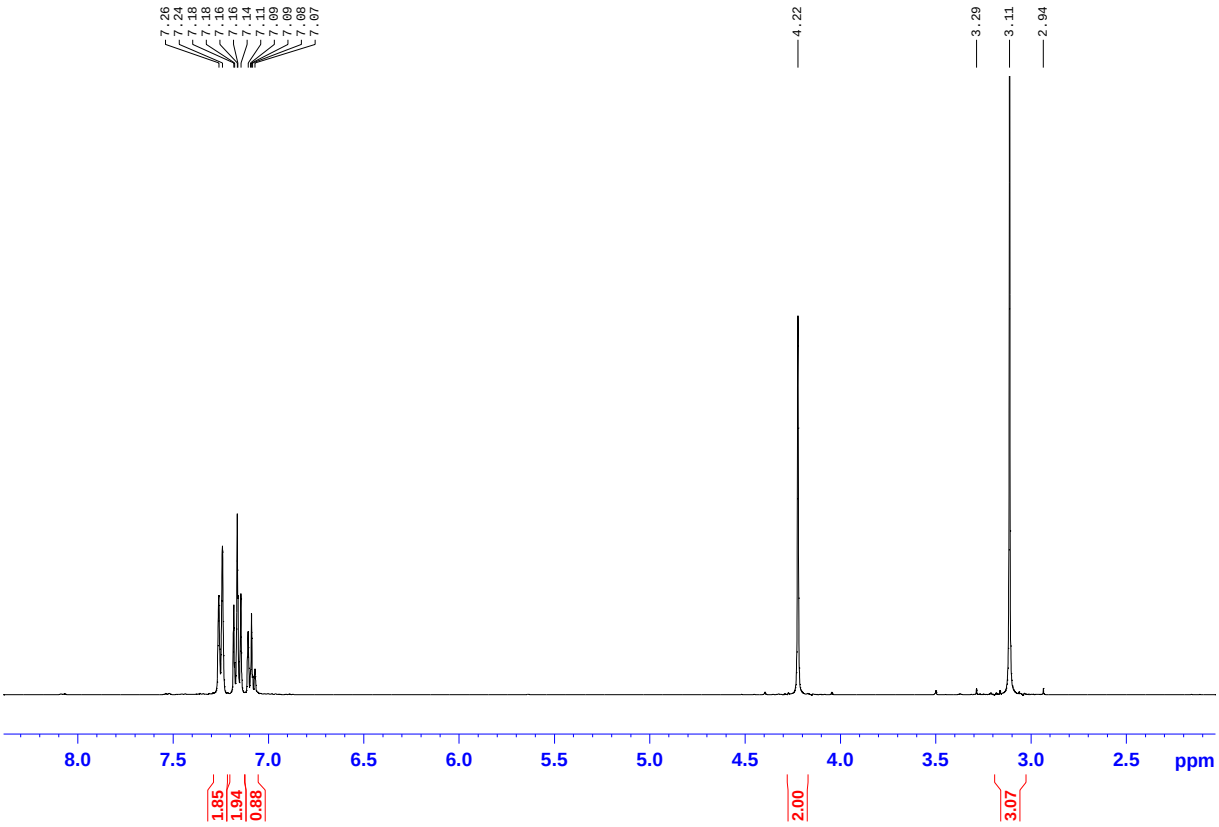

Figure S16: ^{1}H NMR (400.13 MHz, 300 K) spectrum of benzylmethylether in D_6-benzene.

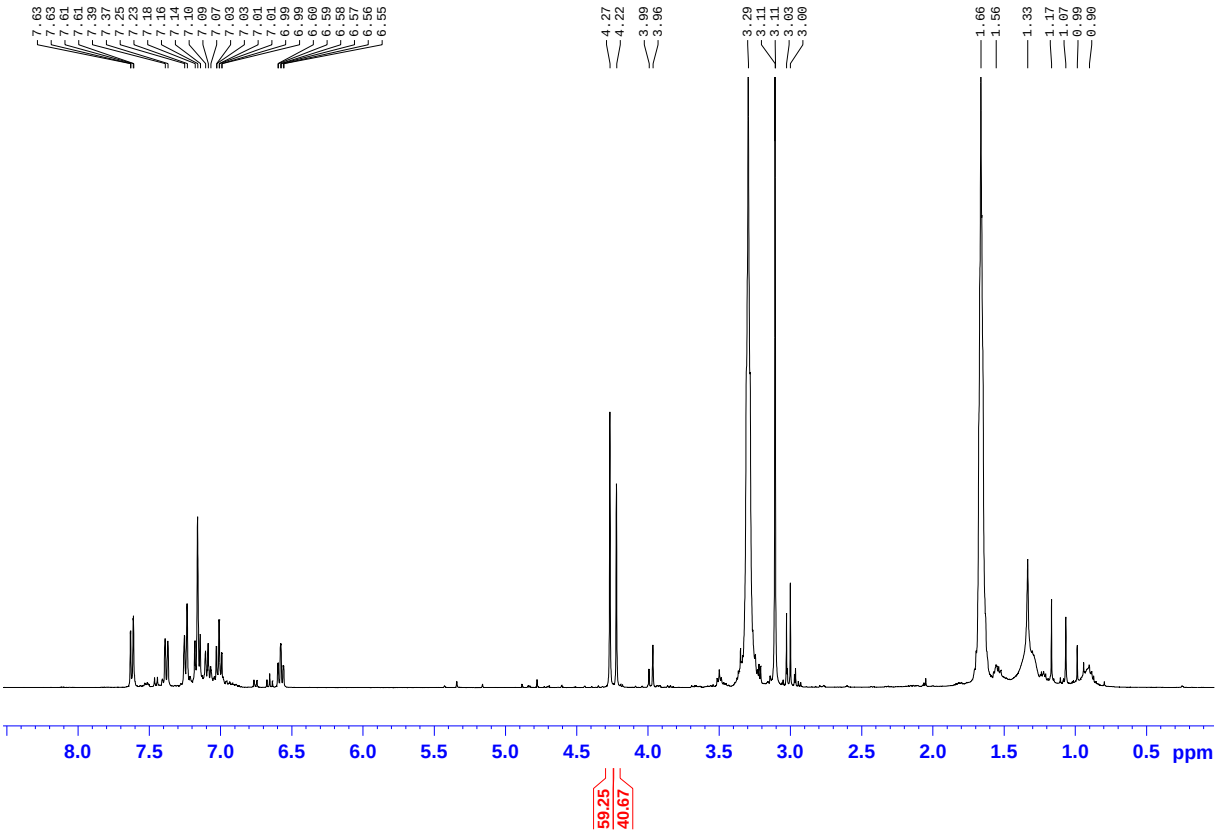

Figure S17: ^{1}H NMR (400.13 MHz, 300 K) spectrum of reaction of **2** (1:1 base to benzylmethylether) with iodine to yield **3** obtained in D_6-benzene.

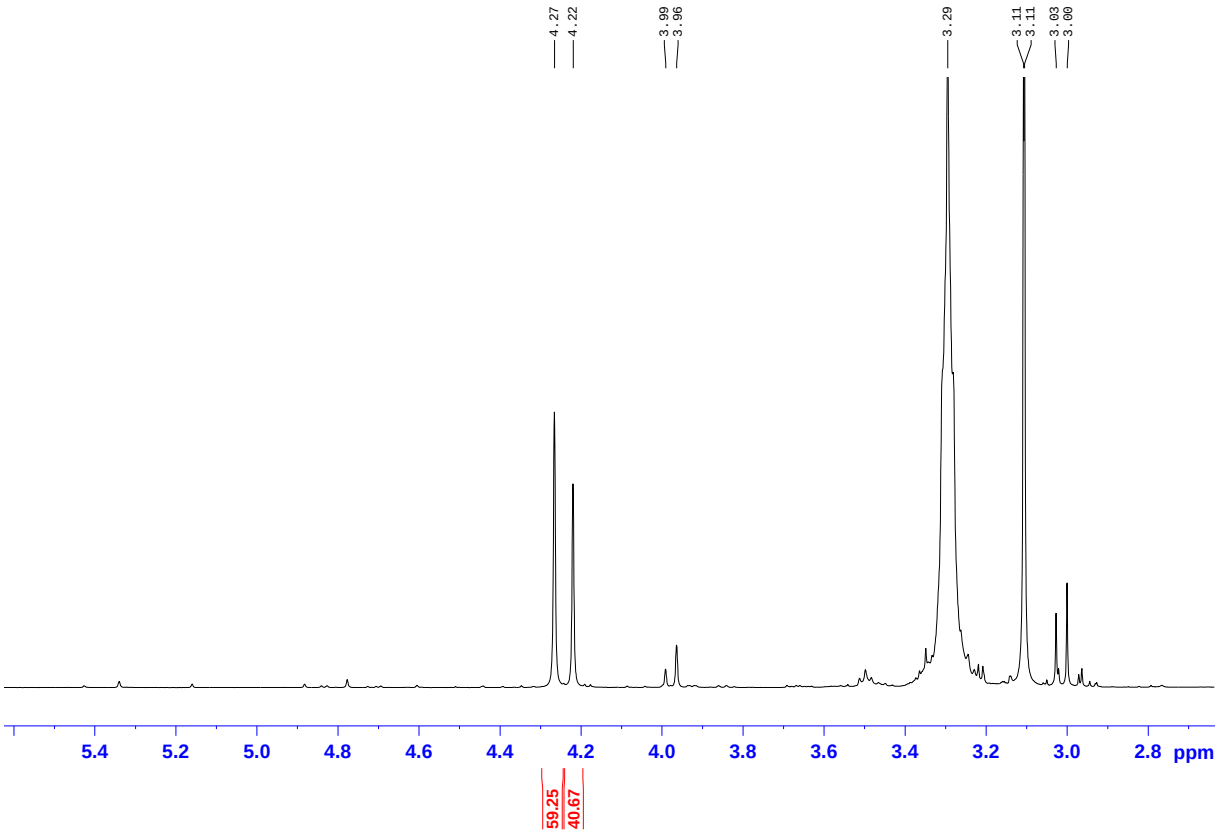

Figure S18: Aliphatic region of the ^{1}H NMR spectrum of reaction of **2** (1:1 base to benzylmethylether) with iodine to yield **3** obtained in D_6-benzene.

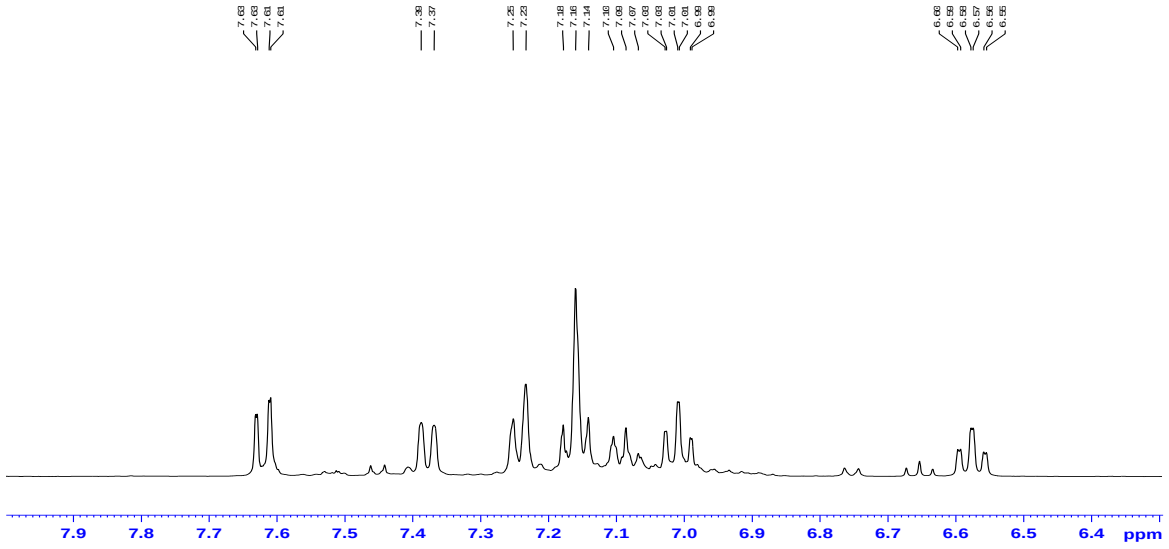

Figure S19: Aromatic region of the ^{1}H NMR spectrm of reaction of **2** (1:1 base to benzylmethylether) with iodine to yield **3** obtained in D_6-benzene.

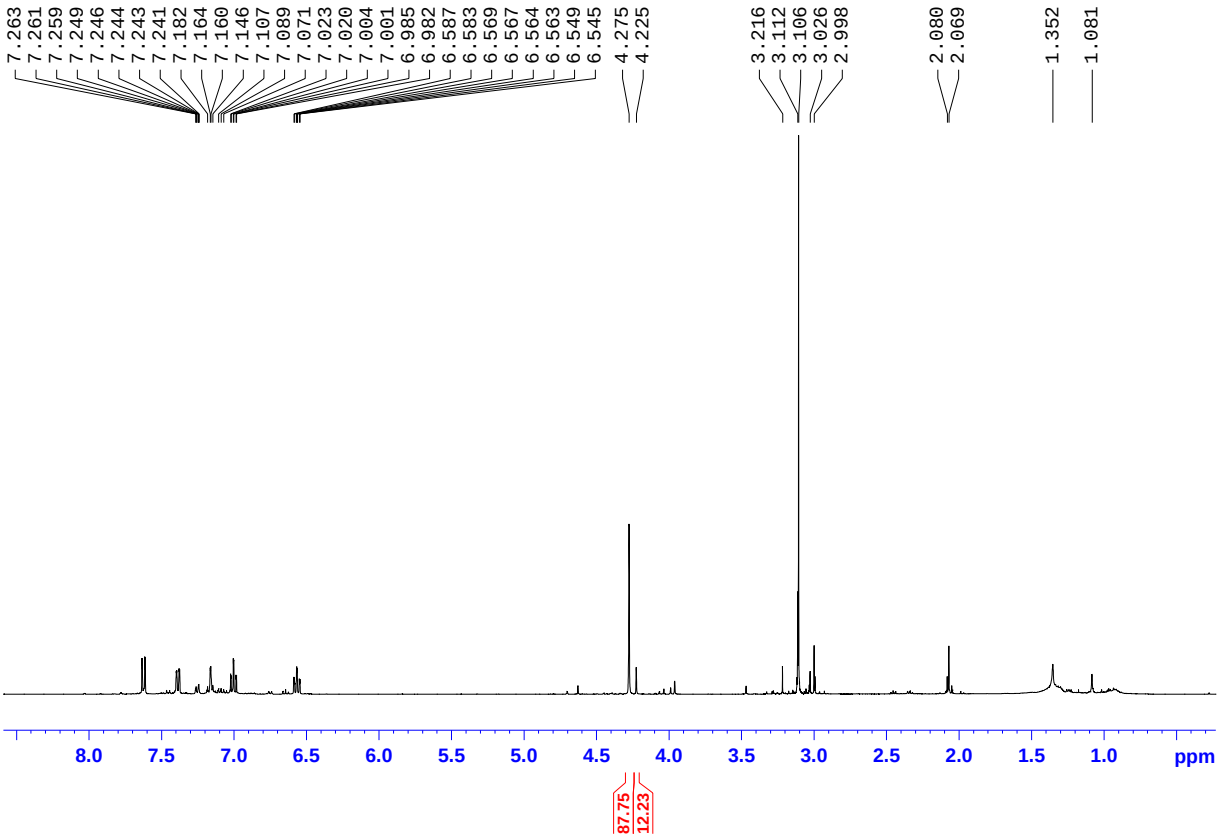

Figure S20: ^{1}H NMR (400.13 MHz, 300 K) spectrum of reaction of **2** (2:1 base to benzylmethylether) with iodine to yield **3** obtained in D_6-benzene.

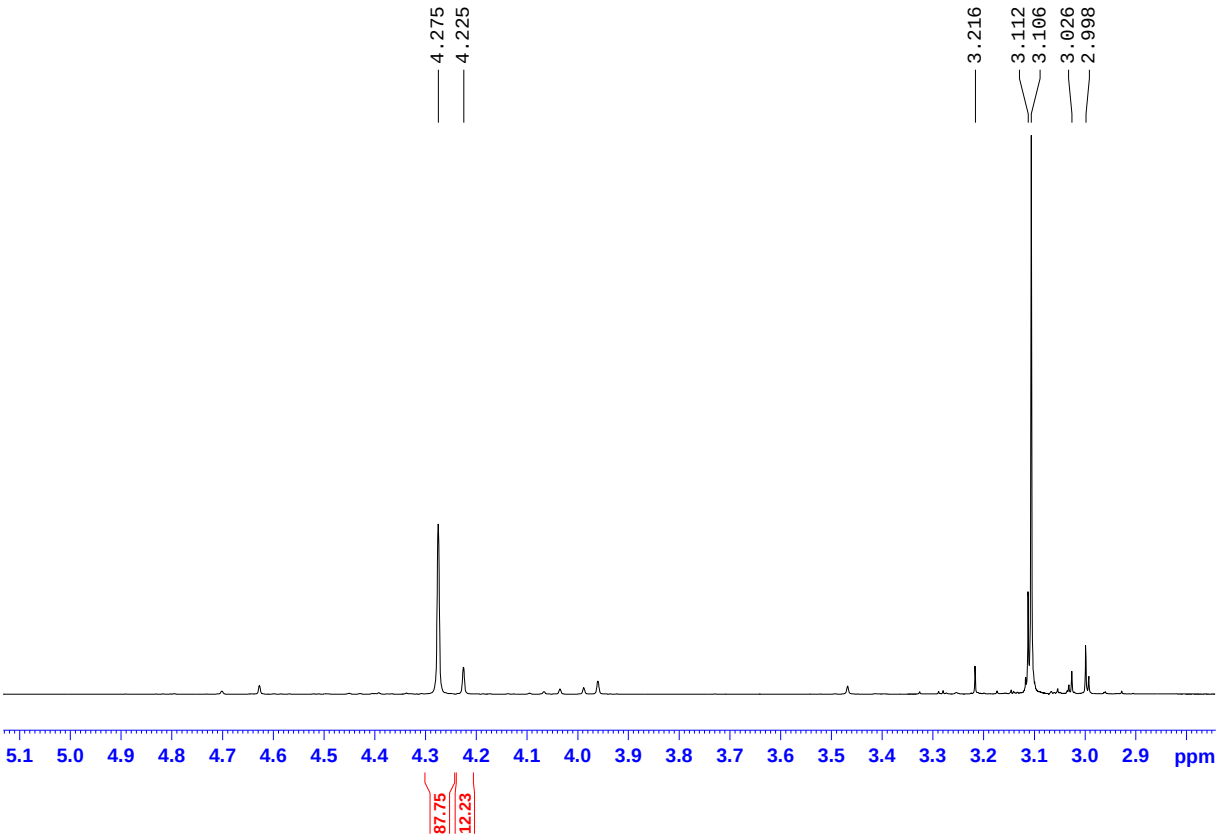

Figure S21: Aliphatic region of the ^{1}H NMR spectrum of reaction of **2** (2:1 base to benzylmethylether) with iodine to yield **3** obtained in D_6-benzene.

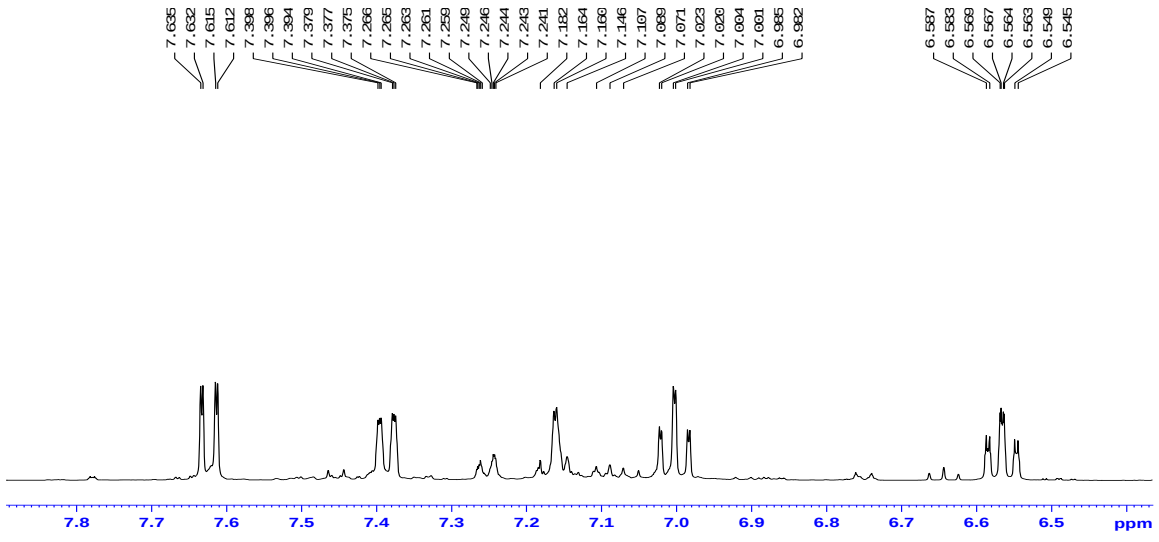

Figure S22: Aromatic region of the ^{1}H NMR spectrum of reaction of **2** (2:1 base to benzylmethylether) with iodine to yield **3** obtained in D_6-benzene.

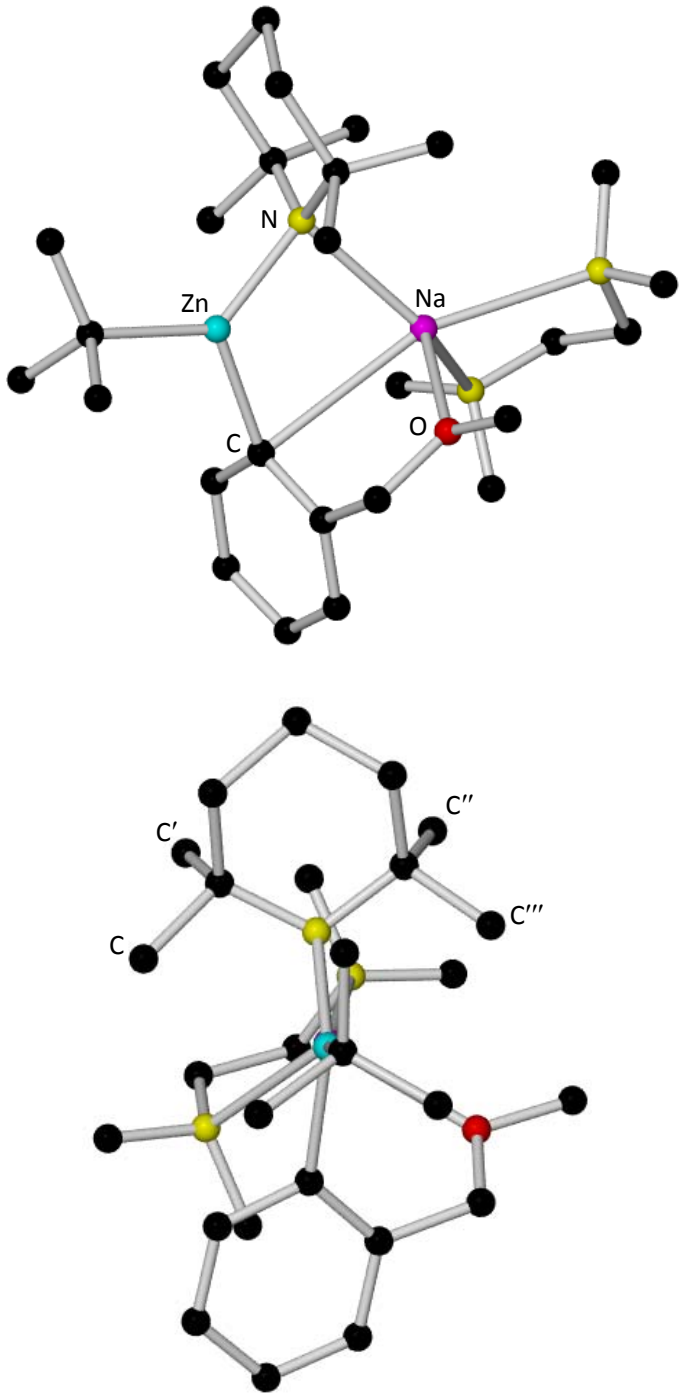

Figure S23: Alternative views of the molecular structure of **2**. Bottom view represents the view along the Zn···Na axis and emphasises the four different chemical environments of the TMP methyl groups.