Closer Insight into the Reactivity of TMP-dialkyl Zincates in Directed ortho-Zincation of Anisole: Experimental Evidence of Amido Basicity and Structural Elucidation of Key Reaction Intermediates

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Molecular structure of compound 6

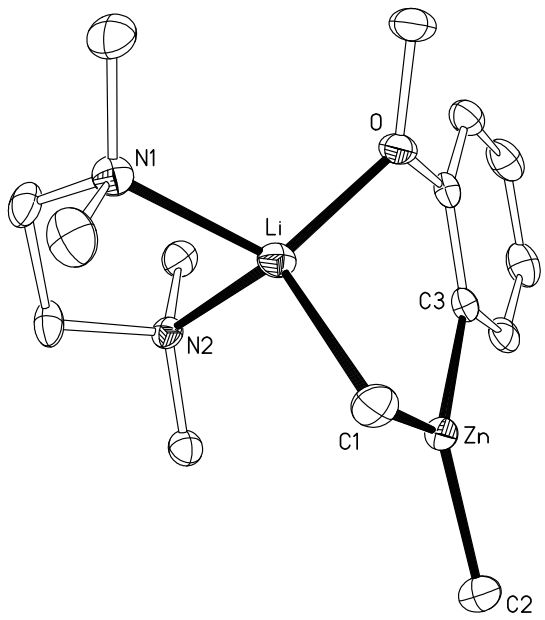


Figure 1. *Molecular structure of* **6** *with 50% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (deg): Zn–C1 2.048(3), Zn–C2 2.016(3), Zn–C3 2.045(2), Li–C1 2.290(4), Li–N1 2.144(4), Li–N2 2.108(4), Li–O 1.960(4); C1–Zn–C2 121.09(10), C1–Zn–C3 122.71(10), C2–Zn–C3 116.20(11), C1–Li–N1 113.90(18), C1–Li–N2 114.34(18), C1–Li–O 107.24(17), N1–Li–N2 86.96(14), N1–Li–O 115.07(19), N2–Li–O 118.55(19).*

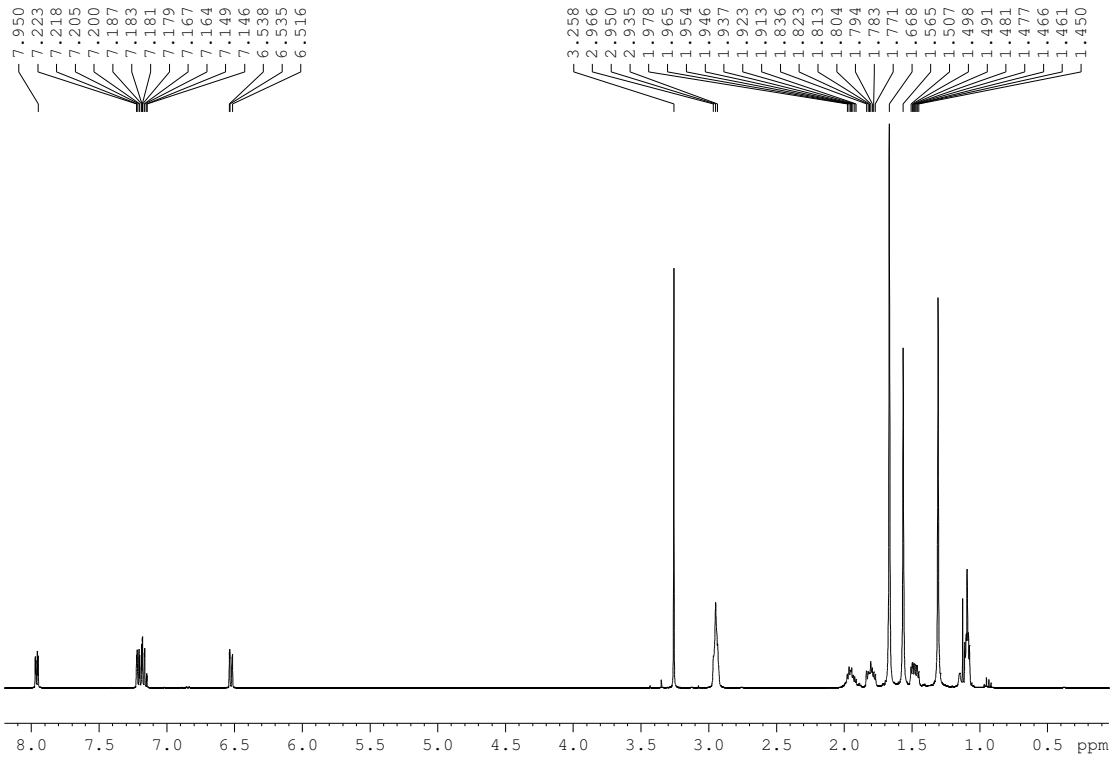
Zincate **6** constitutes the first example of a putative intermediate formed in the first step of a two-step AMMZ reaction of an aromatic molecule to be structurally defined and fully characterised. Its molecular structure can be considered a contacted ion pair and can be viewed as a six-membered [LiOCCZnC] ring system where both metals are connected through a shared methyl and an *ortho*-deprotonated anisole ligand set. The latter anion coordinates to the mixed-metal {Li(Me)Zn(Me)} fragment in an ambidentate fashion, through the carbon-zinc strong, short covalent bond [2.045(2) Å] and the oxygen-lithium dative bond [1.960(4) Å]. This two-fold coordination mode is analogous to that found in the compound [(THF)Li(C_6H_4-OMe)(TMP)Zn(^{t}Bu)] (**2**) [Zn-$C_{anisole}$ bond distance: 2.0937(16) Å; Li-$O_{anisole}$ bond distance: 1.985(3) Å],[6] the product of the direct zincation of anisole by base **1**. The bridging methyl group is strongly bound to zinc as evidenced by the short distance [2.048(3) Å] and surprisingly it also forms a medium-short Li-C bond [2.290(4) Å]. This bond is remarkably shorter (by 0.313 Å) than that found in the related dimethyl-TMP zincate [(TMEDA)Li(TMP)(Me)Zn(Me)][1] [2.603(5) Å] where the methyl group forms a secondary agostic interaction with the lithium center and it is more comparable with those found in [{LiMe(THF)}$_4$][2] [mean Li-C distance 2.240 Å]. However, it should be noted that in solution at ambient temperature this Li-C bond must cleave since both methyl groups appear equivalent in the ^{1}H and ^{13}C NMR spectra. Trigonal planar zinc completes its coordination by bonding to a terminal methyl group, at a distance [2.016(3) Å] slightly shorter than the Zn–C bridging bond length. The lithium coordination is distorted tetrahedral [average angle around Li: 109.34^o] with its terminal sites filled by the chelating diamine TMEDA. A similar structure to the one exhibited by **6** could be expected for the THF-solvated mixed-metal compound **4** where the TMEDA ligand is replaced by two THF molecules.[3] It is noteworthy that **6** is stable in hexane solution and does not undergo disproportionation. This could be due to the bidentate stabilisation provided by the TMEDA ligand which makes compound **6** more robust and therefore less prone to cleavage and rearrangement.

1 Graham, D. V.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E. *Organometallics*, **2006**, *25*, 3297.
2 Ogle, C. A.; Huckabee, B. K.; Johnson IV, H. C.; Sims, P.F.; Winslow, S. D.; Pinkerton, A. A. *Organometallics*, **1993**, *12*, 1960.
3 This is supported by the fact that both compounds displayed very similar 1H, 13C and 7Li NMR spectra.

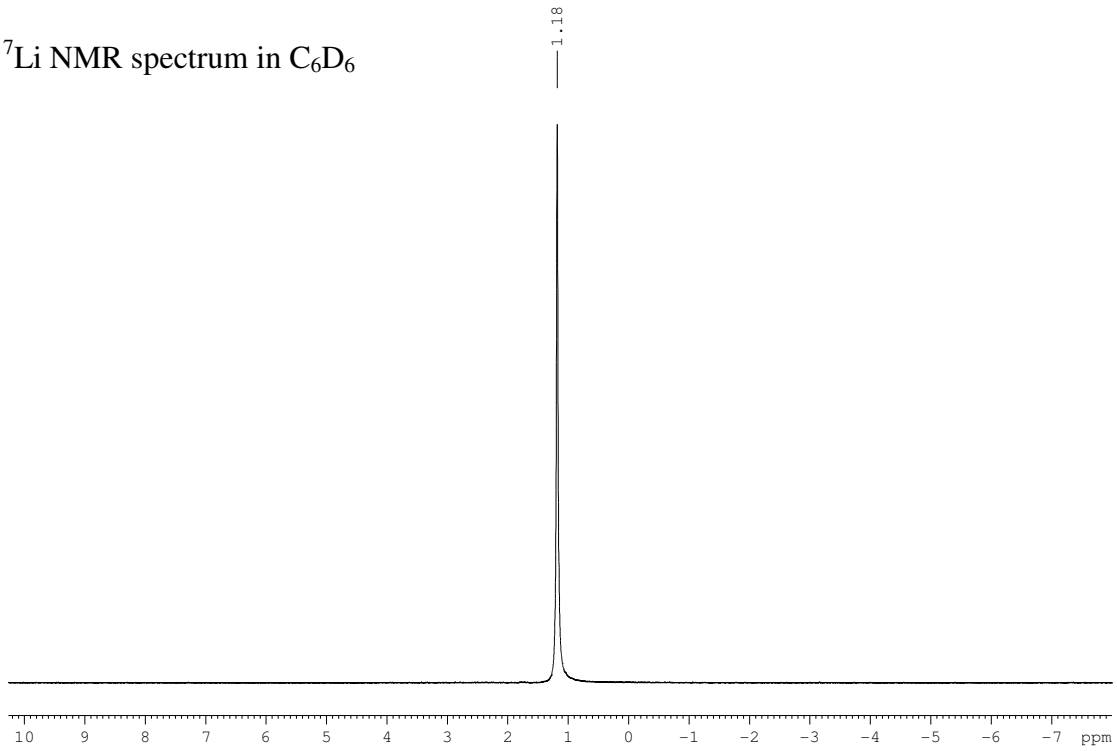
NMR spectra

Compound [(THF)Li(C_6H_4-OMe)(TMP)Zn(^{t}Bu)](2)

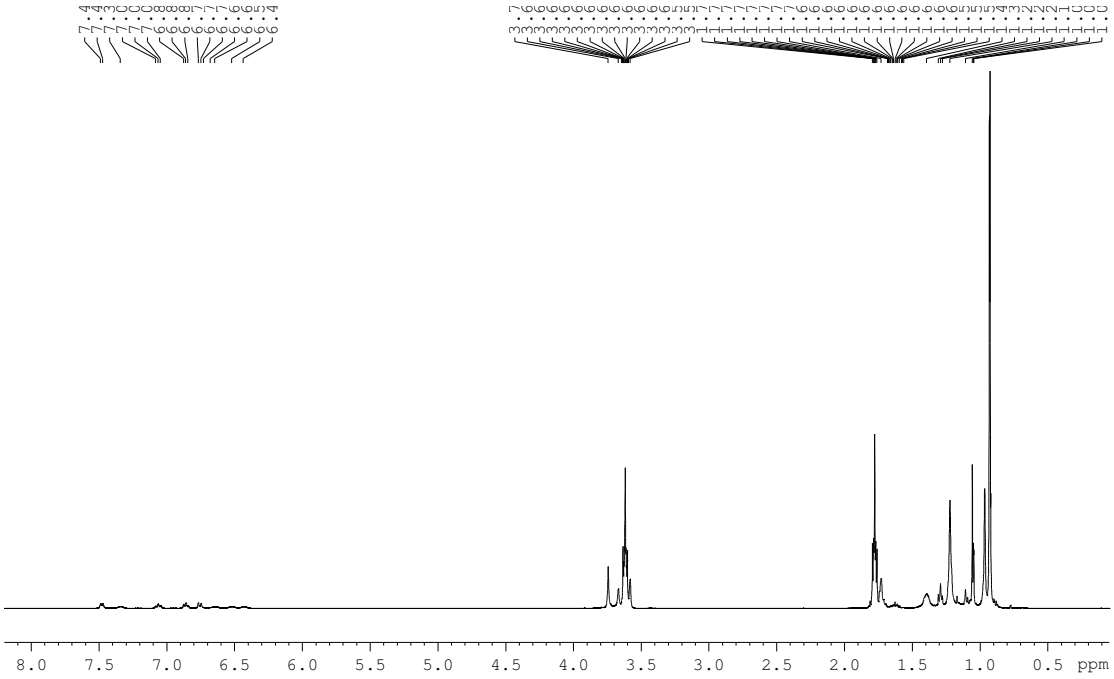
^{1}H NMR spectrum in C_6D_6



^{7}Li NMR spectrum in C_6D_6

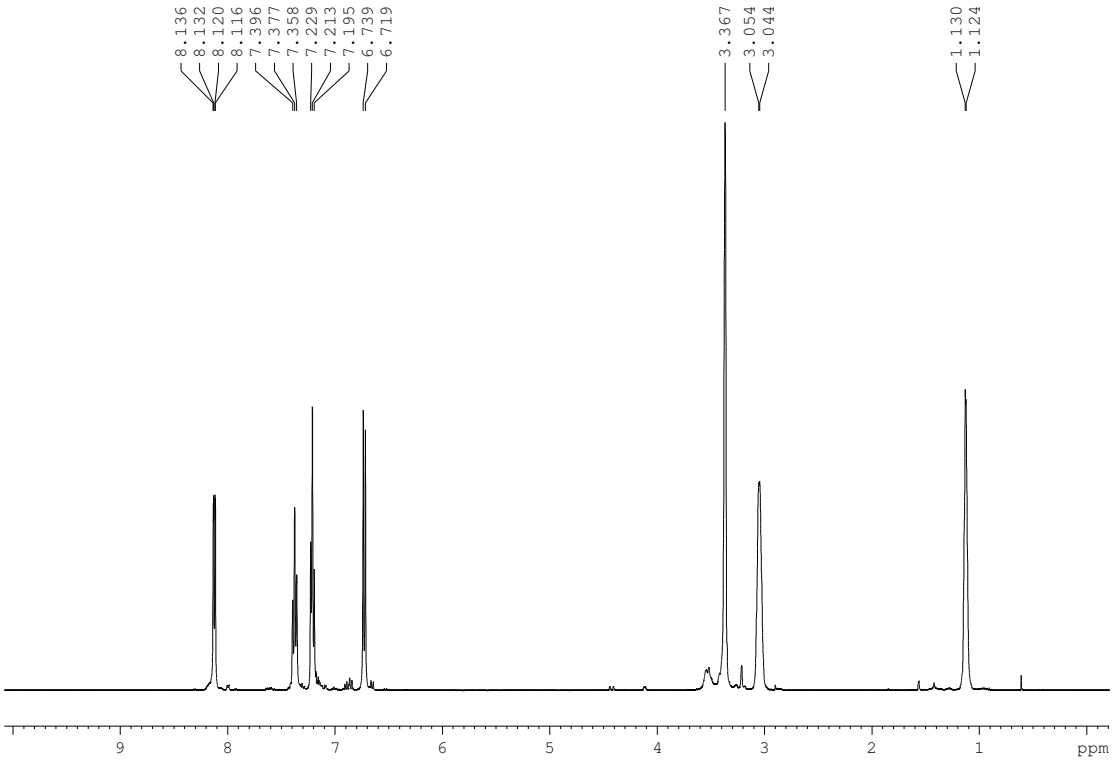


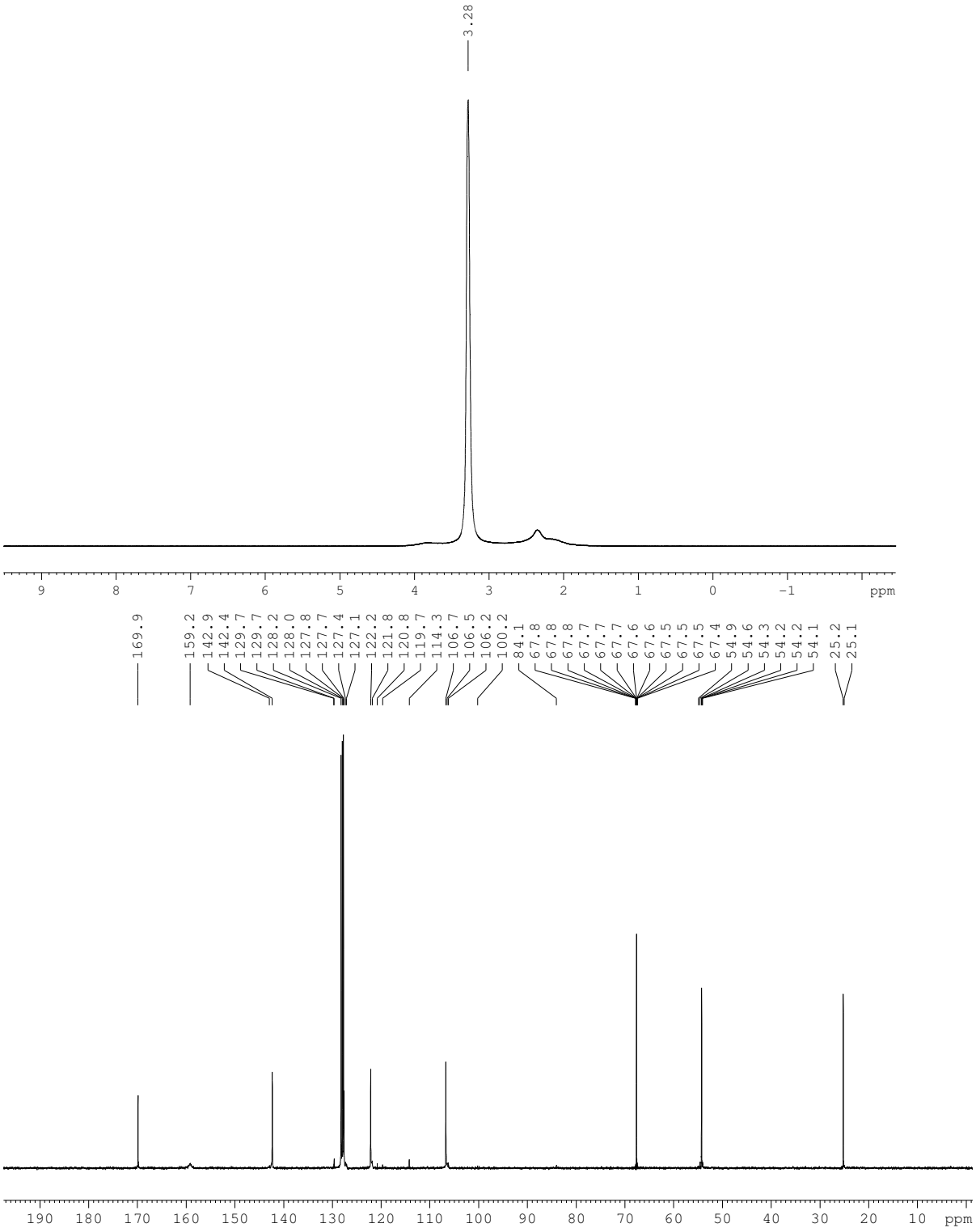
^{1}H NMR in THF



Compound [$Li_4(C_6H_4$-OMe$)_4(THF)_2$] (3)

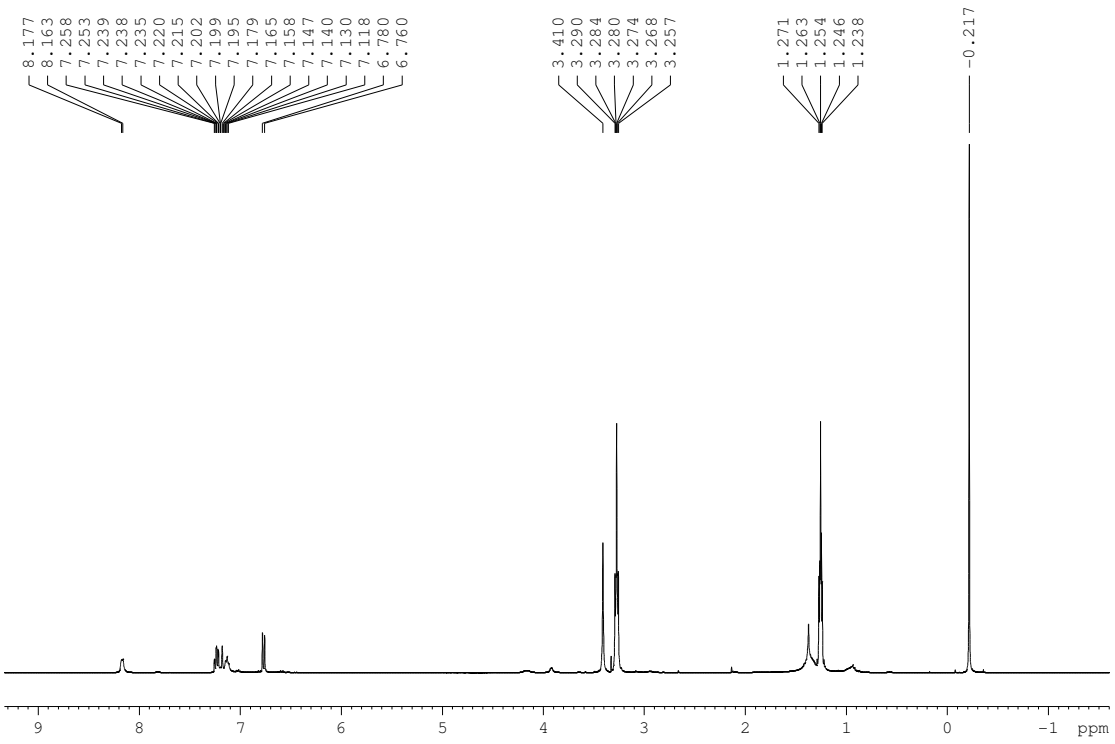
^{1}H, ^{7}Li and ^{13}C NMR spectra in C_6D_6

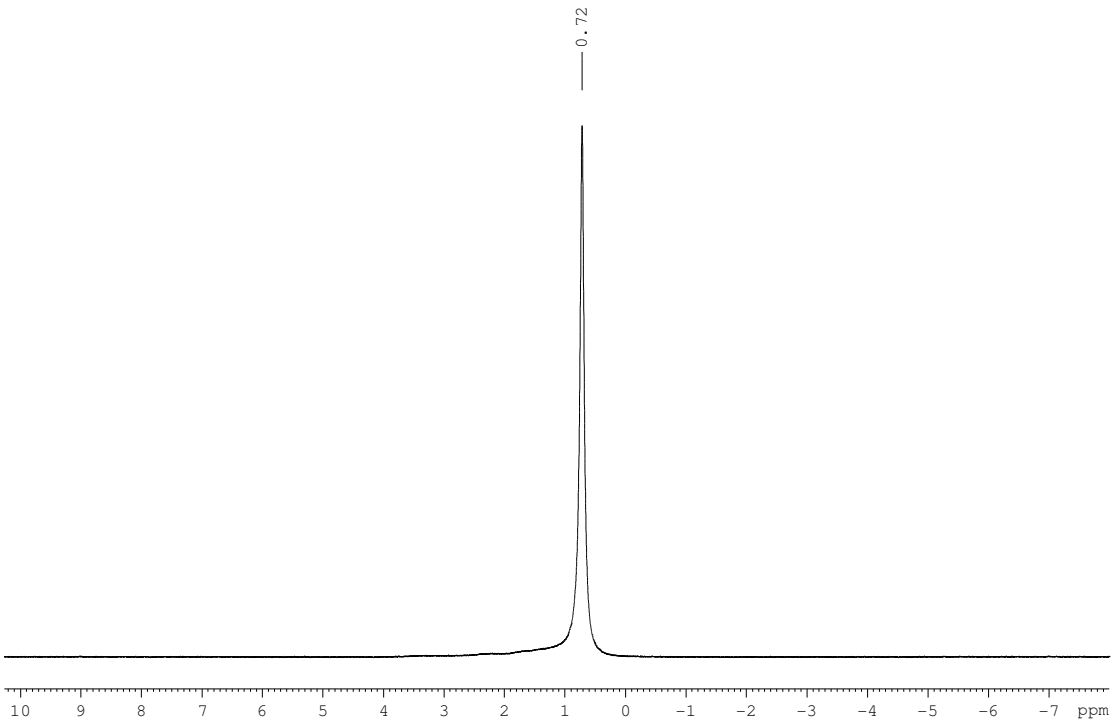


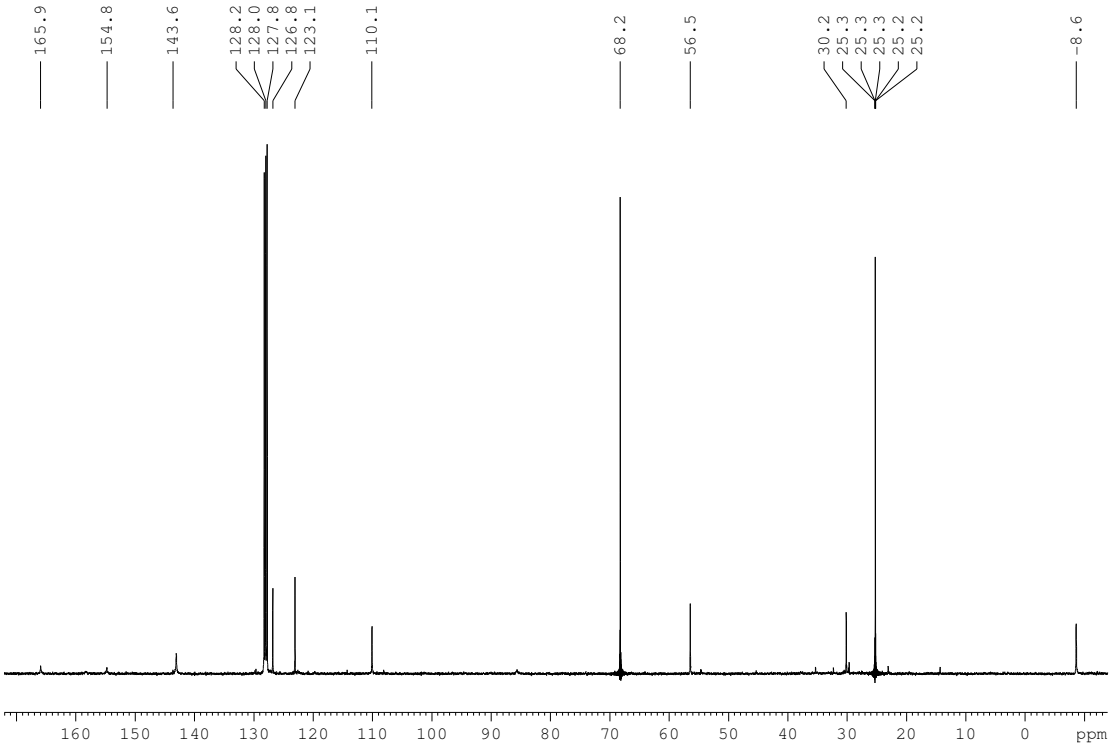

3.28
9
8
7
6
5
4
3
2
1
0
−1
ppm
169.9
159.2
142.9
142.4
129.7
129.7
128.2
128.0
127.8
127.7
127.4
127.1
122.2
121.8
120.8
119.7
114.3
106.7
106.5
106.2
100.2
84.1
67.8
67.8
67.8
67.7
67.7
67.7
67.6
67.6
67.5
67.5
67.5
67.4
54.9
54.6
54.3
54.2
54.2
54.1
25.2
25.1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound [(THF)$_2$Li(C$_6$H$_4$-OMe)(Me)Zn(Me)](4)

^{1}H, ^{7}Li and ^{13}C spectra in C$_6$D$_6$

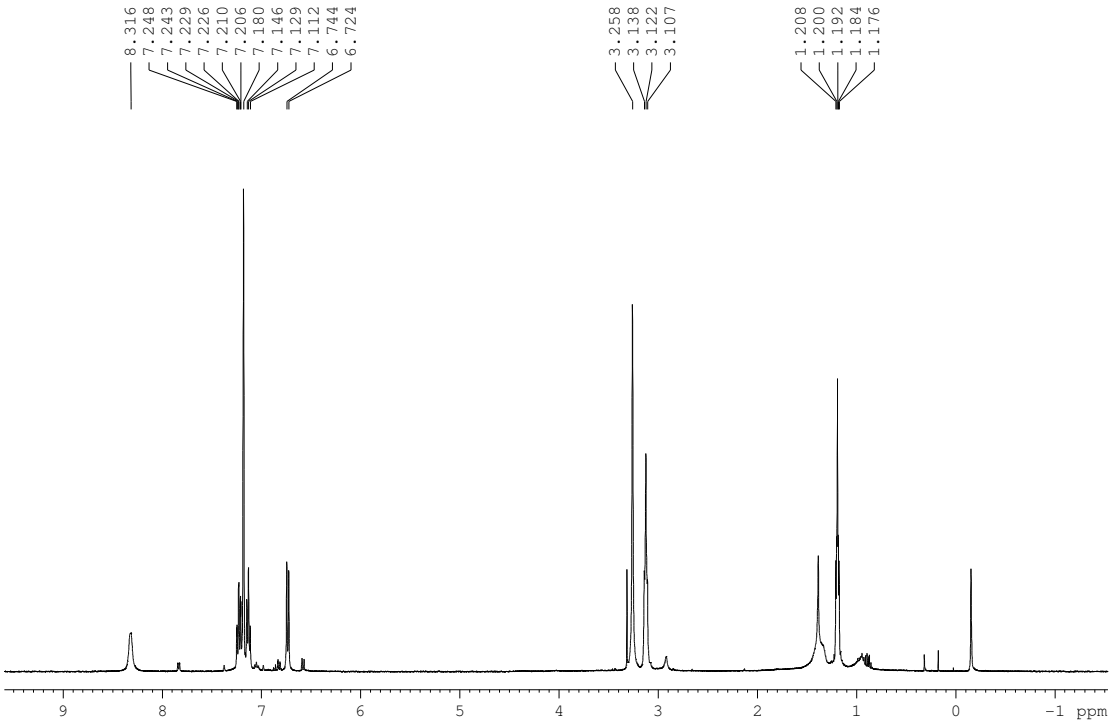


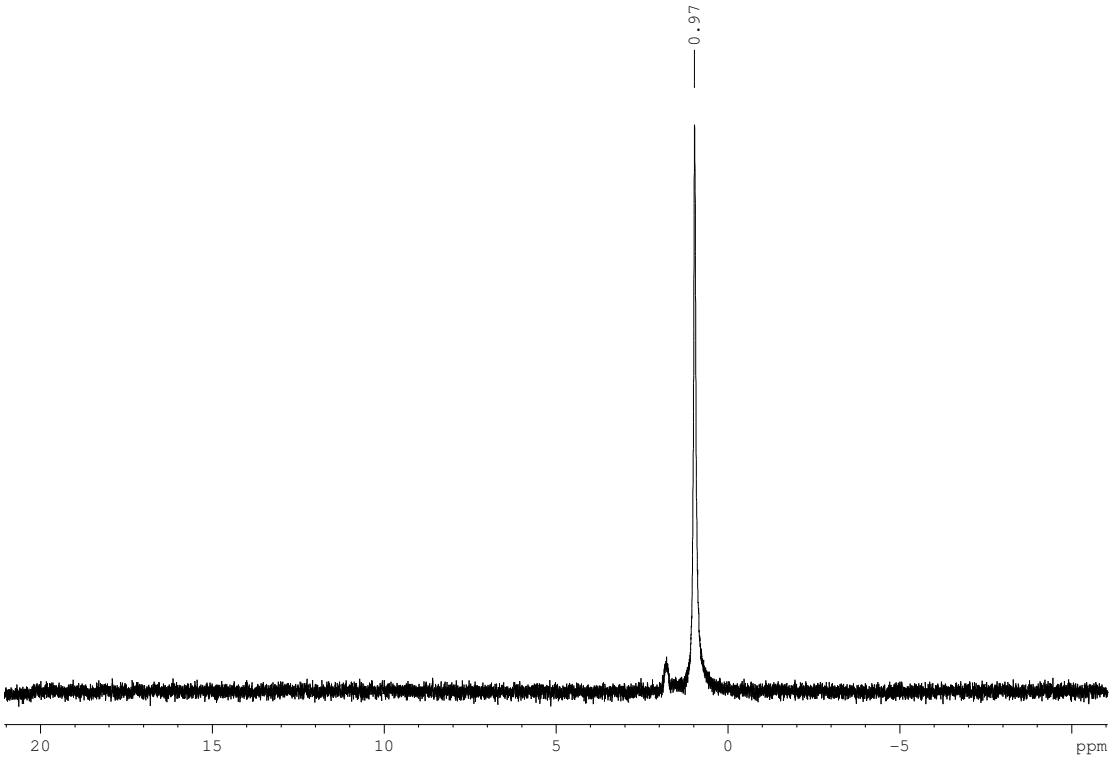




Compound $[(THF)_2Li_2Zn(C_6H_4\text{-}OMe)_4]$(5)

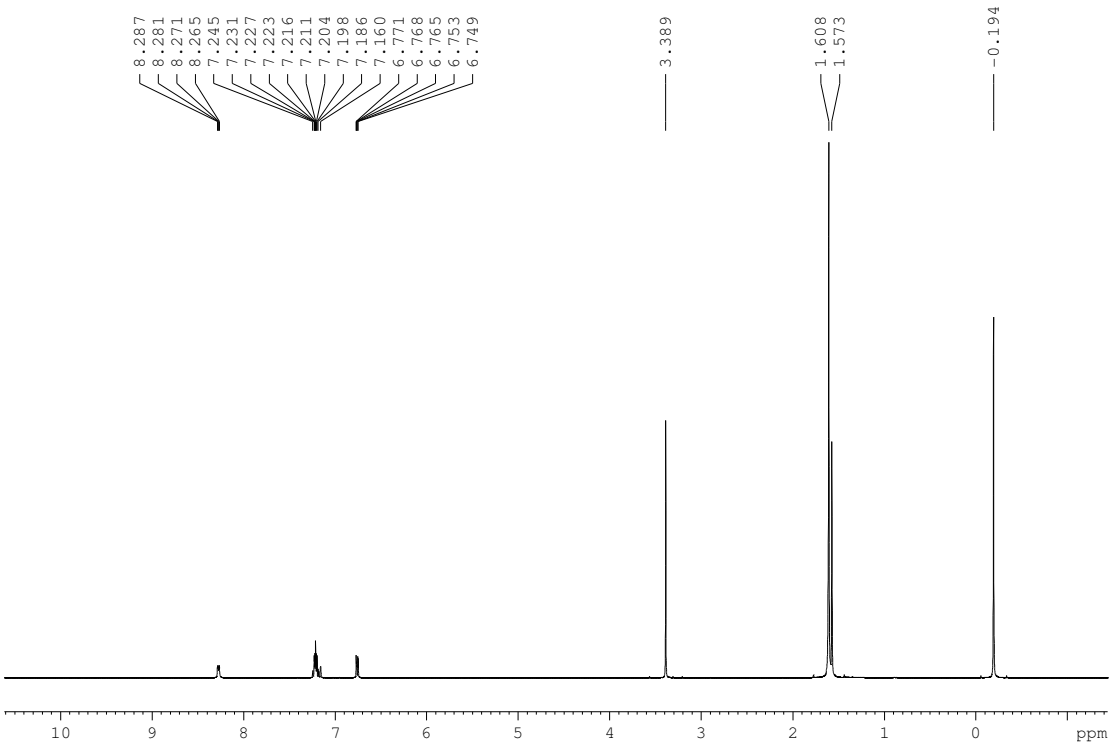
^1H, ^7Li NMR spectra in C_6D_6

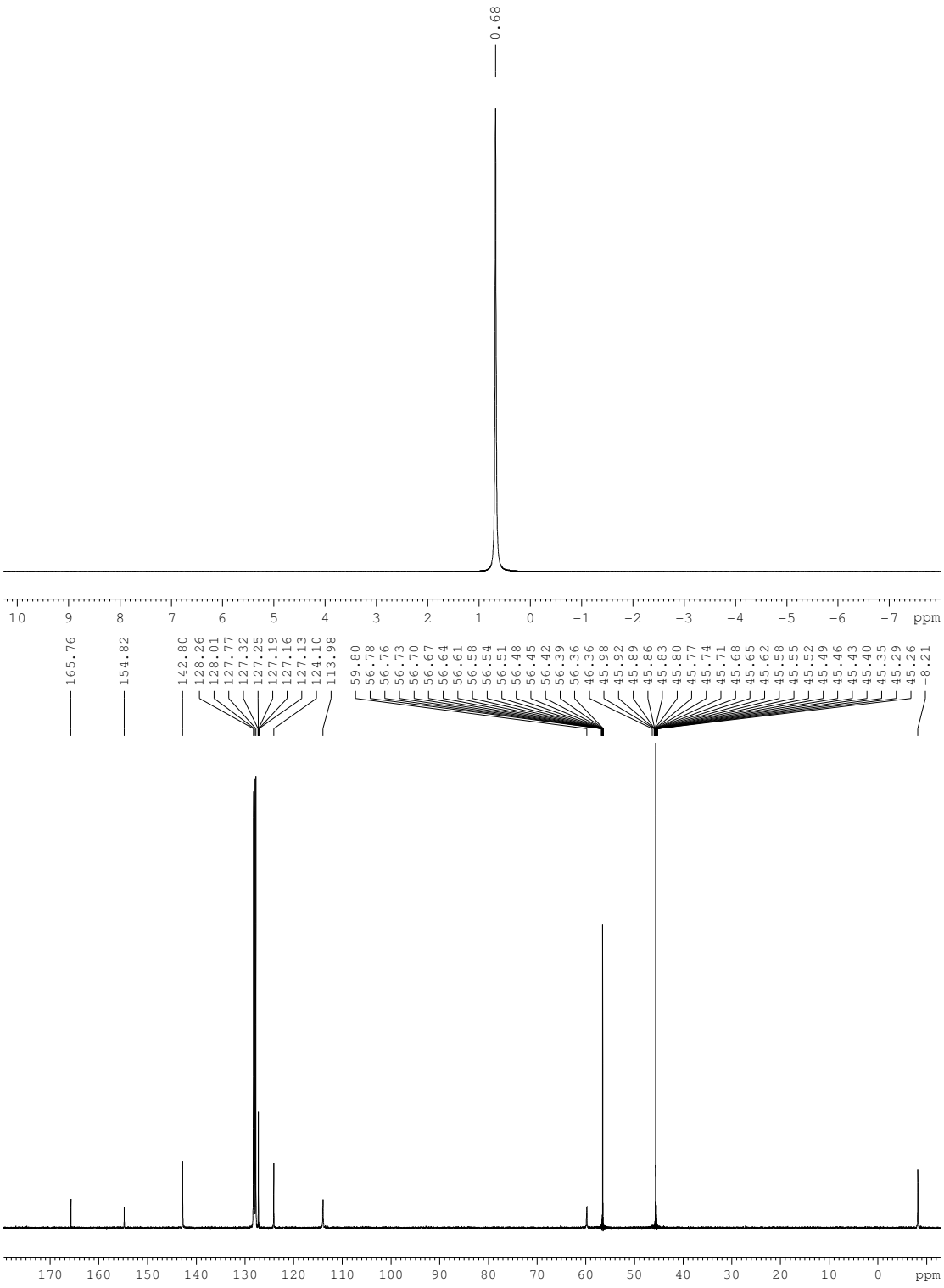




Compound [(TMEDA)Li(C_6H_4-OMe)(Me)Zn(Me)](6)

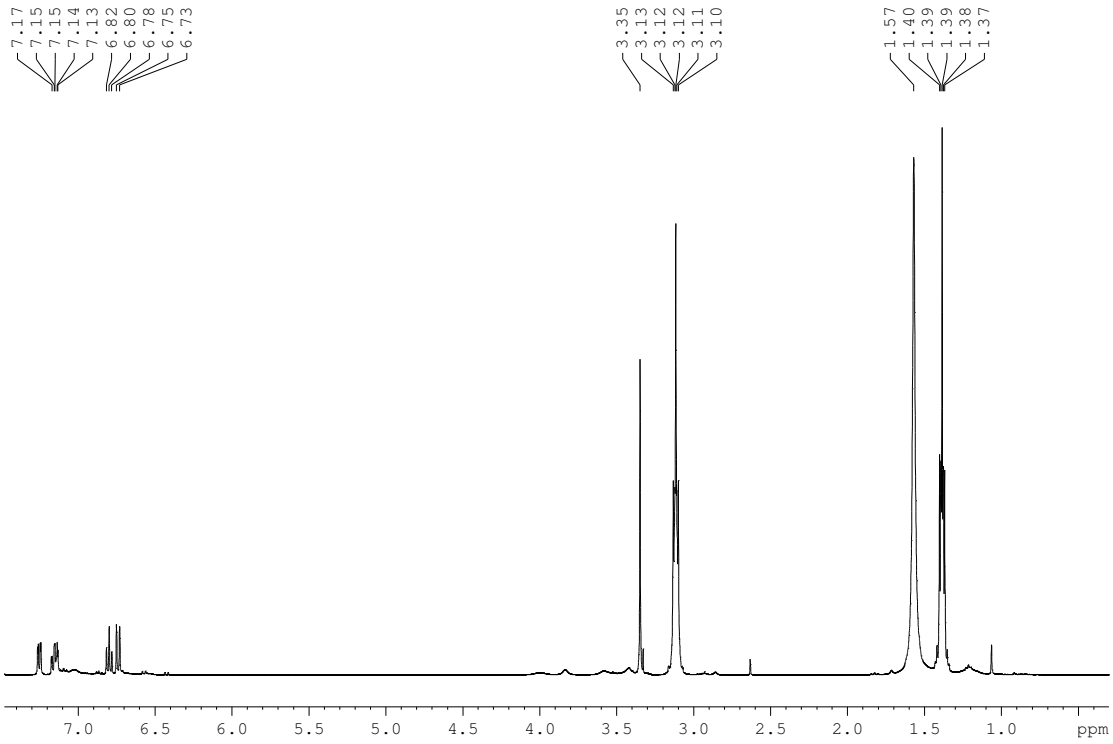
^{1}H, ^{7}Li and ^{13}C NMR spectra in C_6D_6

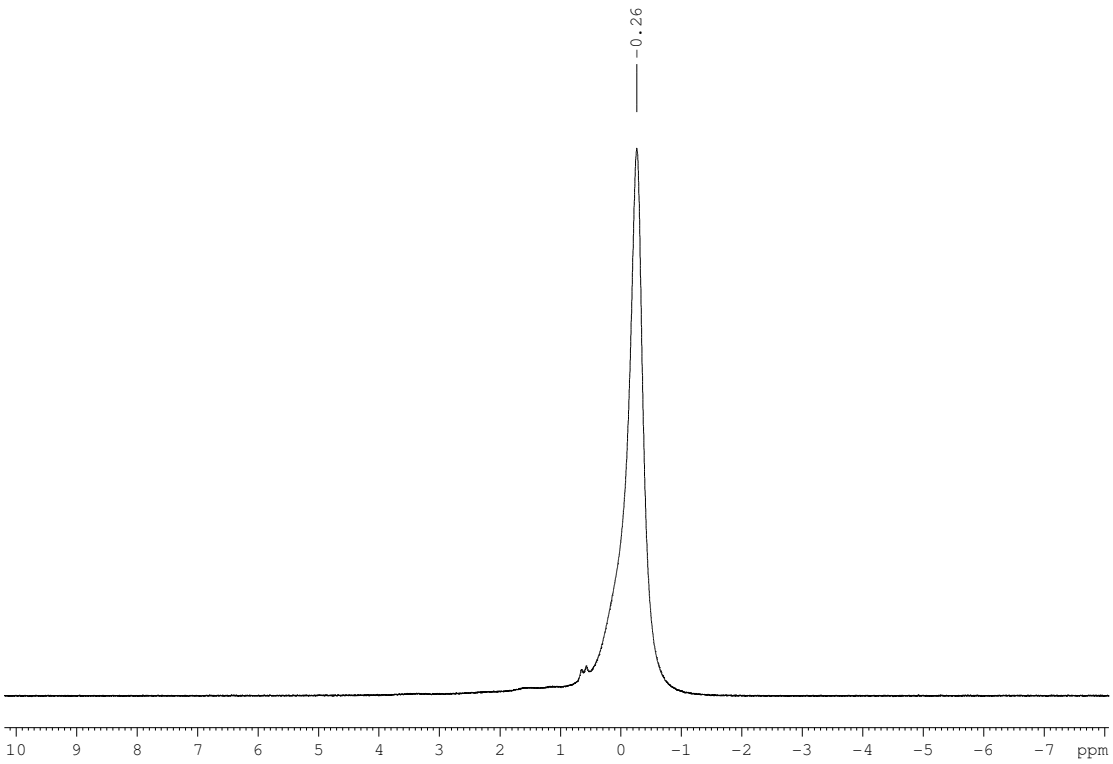


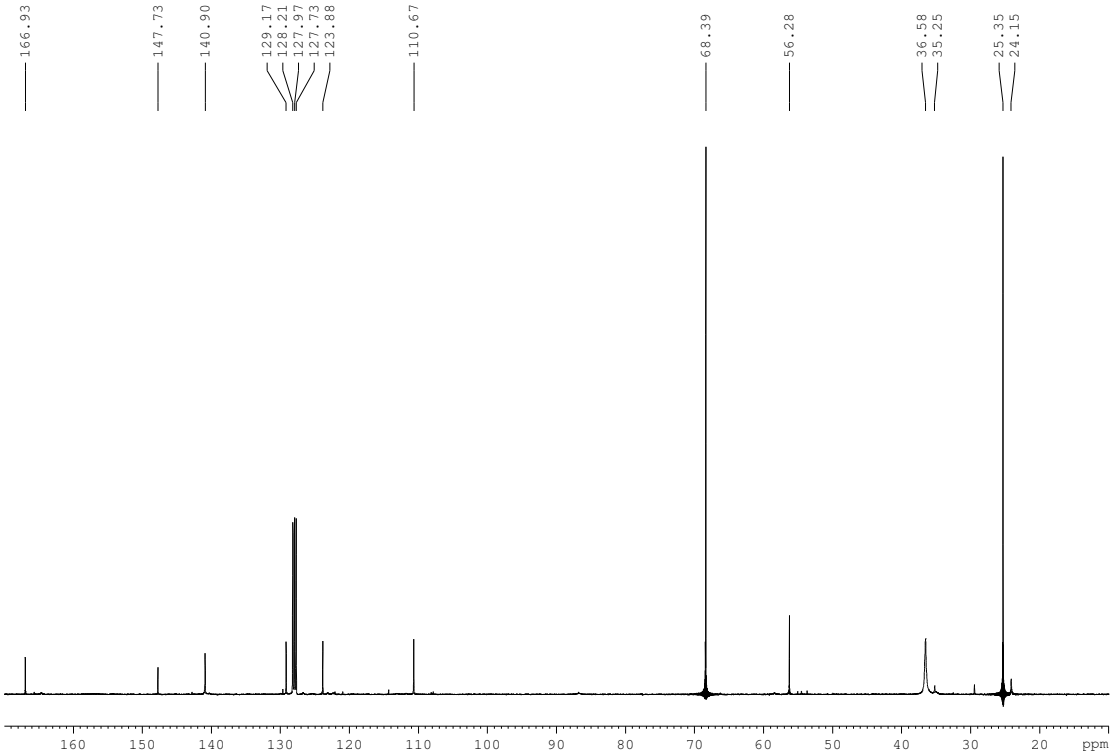

0.68
10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4 −5 −6 −7 ppm
165.76
154.82
142.80
128.26
128.01
127.77
127.32
127.25
127.19
127.16
127.13
124.10
113.98
59.80
56.78
56.76
56.73
56.70
56.67
56.64
56.61
56.58
56.54
56.51
56.48
56.45
56.42
56.39
56.36
46.36
45.98
45.92
45.89
45.86
45.83
45.80
45.77
45.74
45.71
45.68
45.65
45.62
45.58
45.55
45.52
45.49
45.46
45.43
45.40
45.35
45.29
45.26
8.21
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Compound [(THF)$_3$Li(C$_6$H$_4$-OMe)(^{t}Bu)Zn(^{t}Bu)](7)

^{1}H, ^{7}Li and ^{13}C NMR spectra in C_6D_6

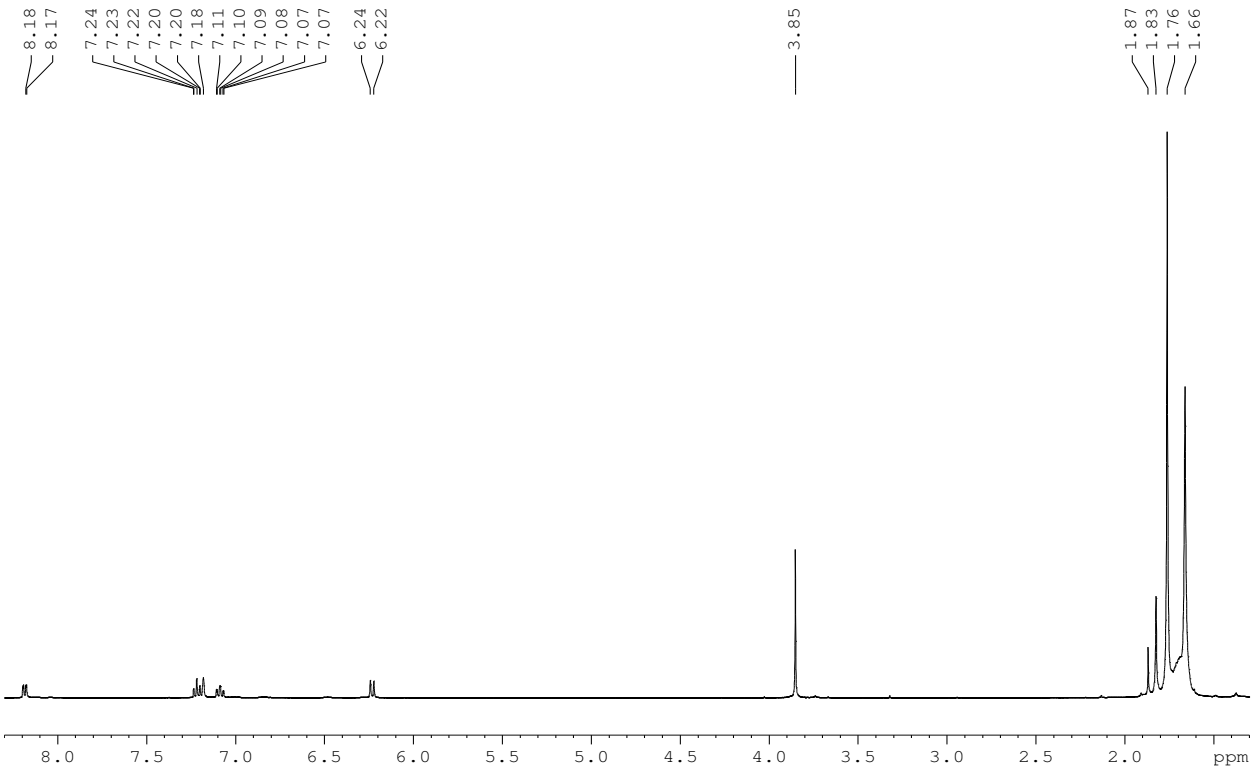


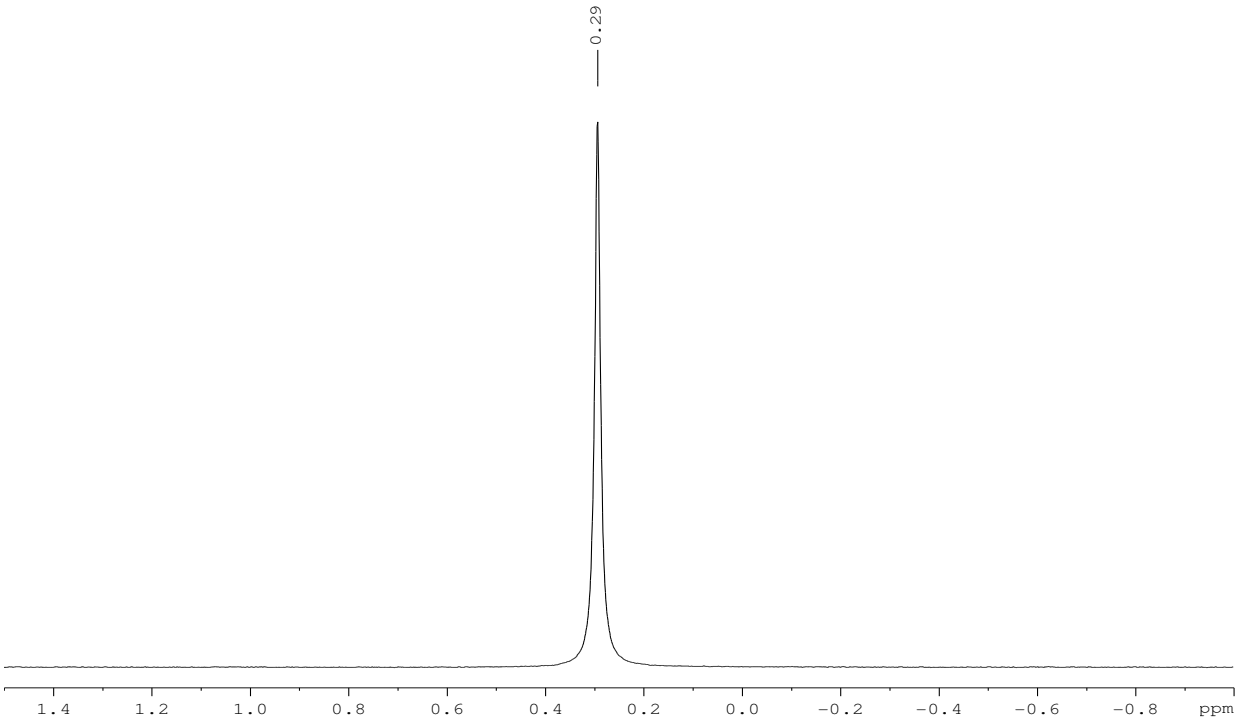


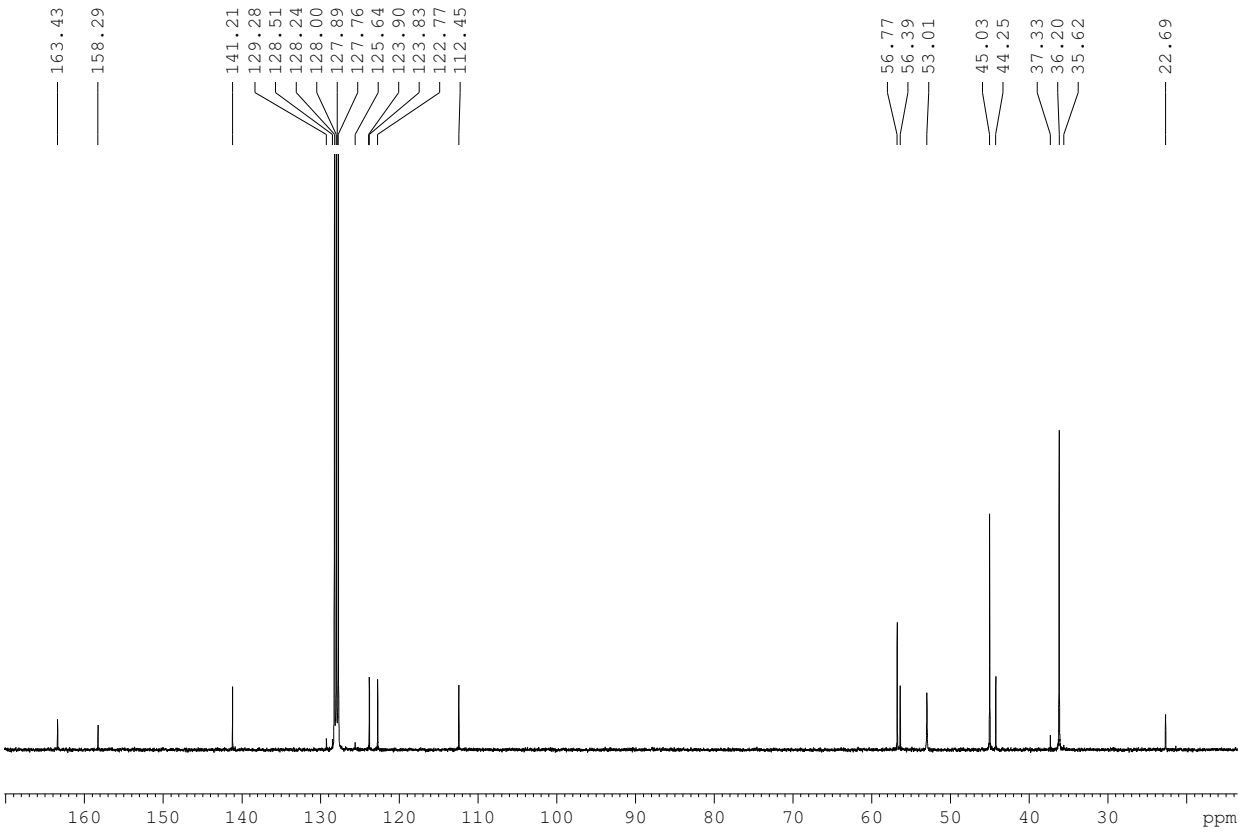


Compound [(PMDETA)Li(C_6H_4-OMe)(^{t}Bu)Zn(^{t}Bu)](8)

^{1}H, ^{7}Li and ^{13}C NMR spectra in C_6D_6

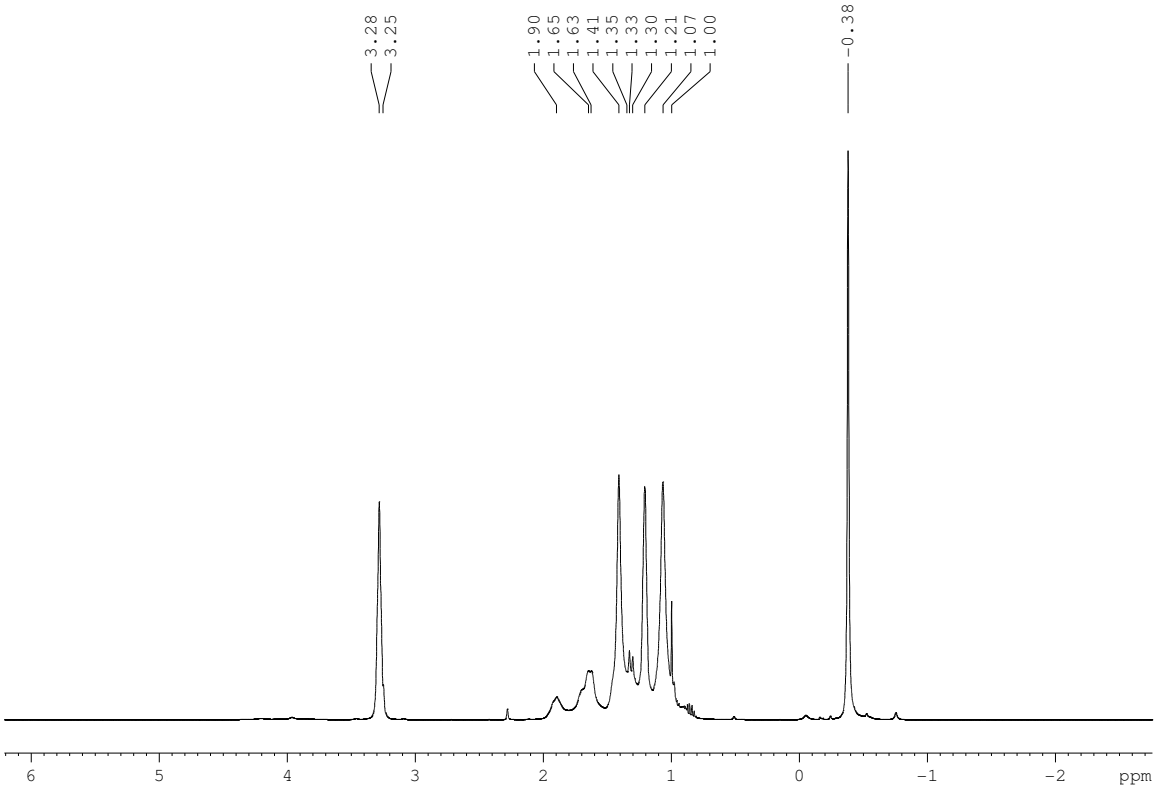


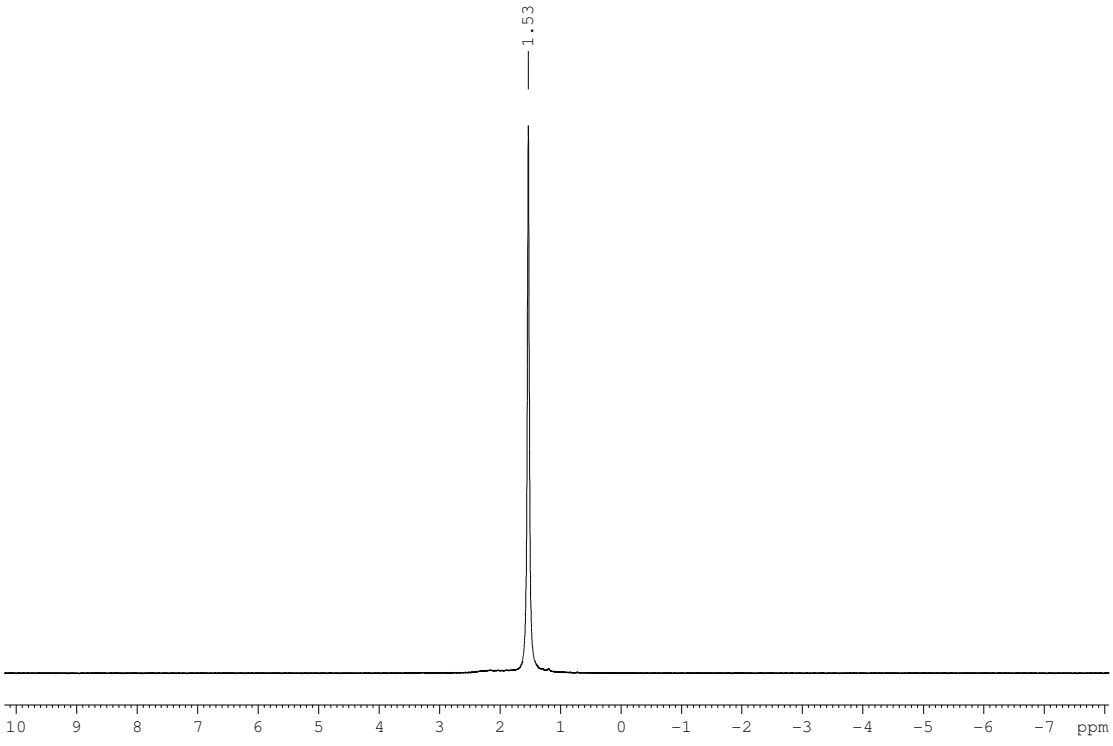


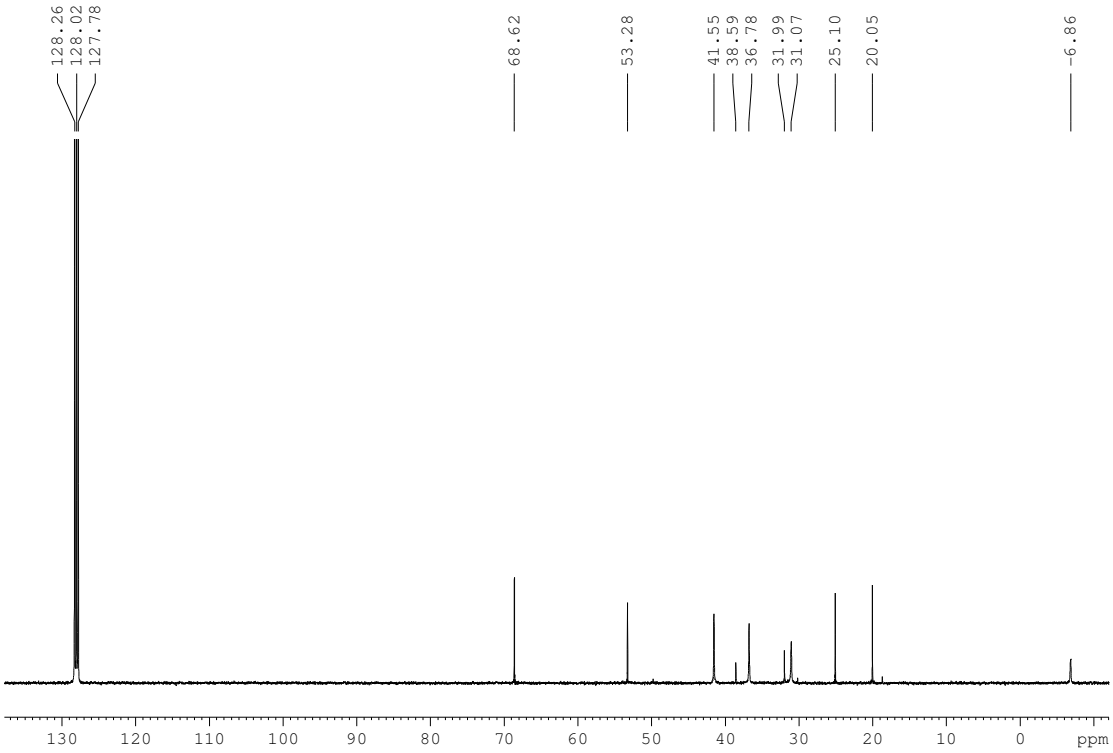


Compound [(THF)Li(TMP)(Me)Zn(Me)](9)

^{1}H, ^{7}Li and ^{13}C NMR spectra in C_6D_6



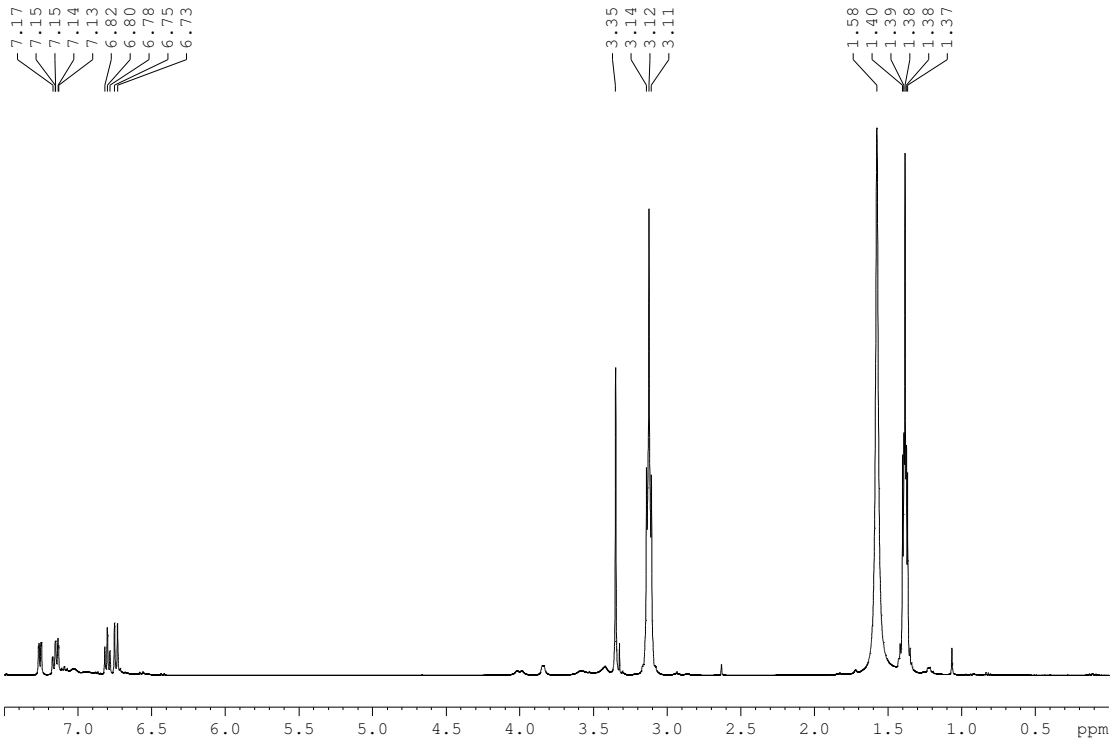




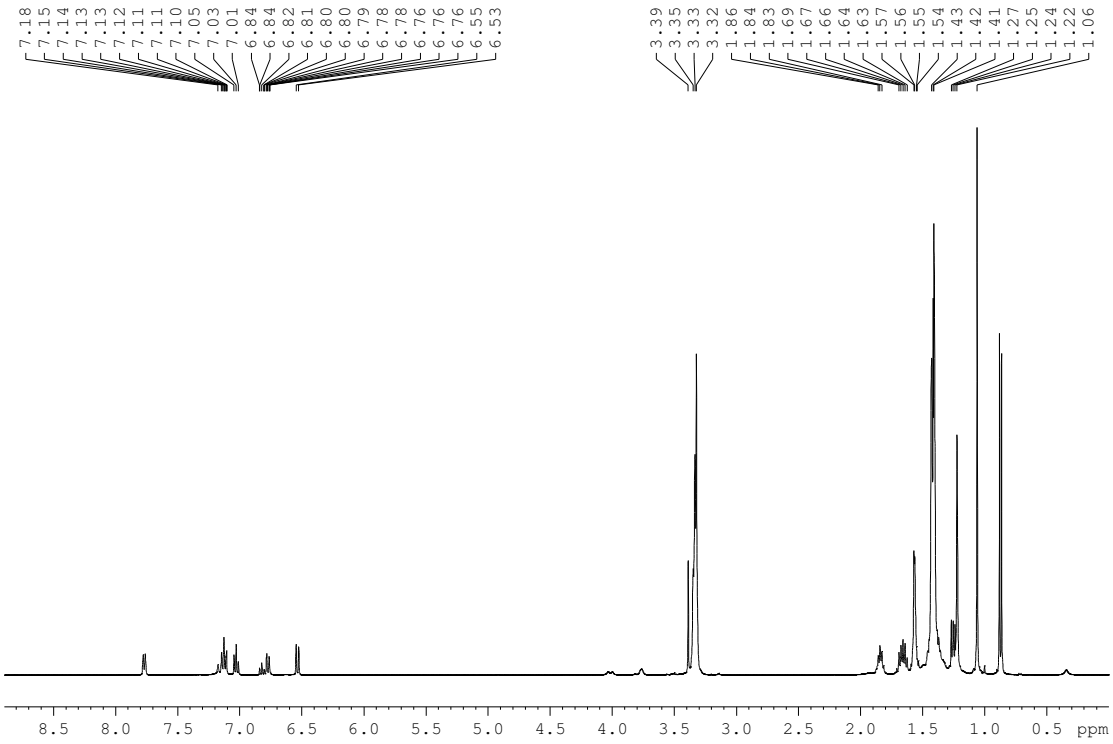
Reactions monitored by NMR

a) [(THF)$_3$Li(C$_6$H$_4$-OMe)(^{t}Bu)Zn(^{t}Bu)](7) + TMP(H) in deuterated benzene

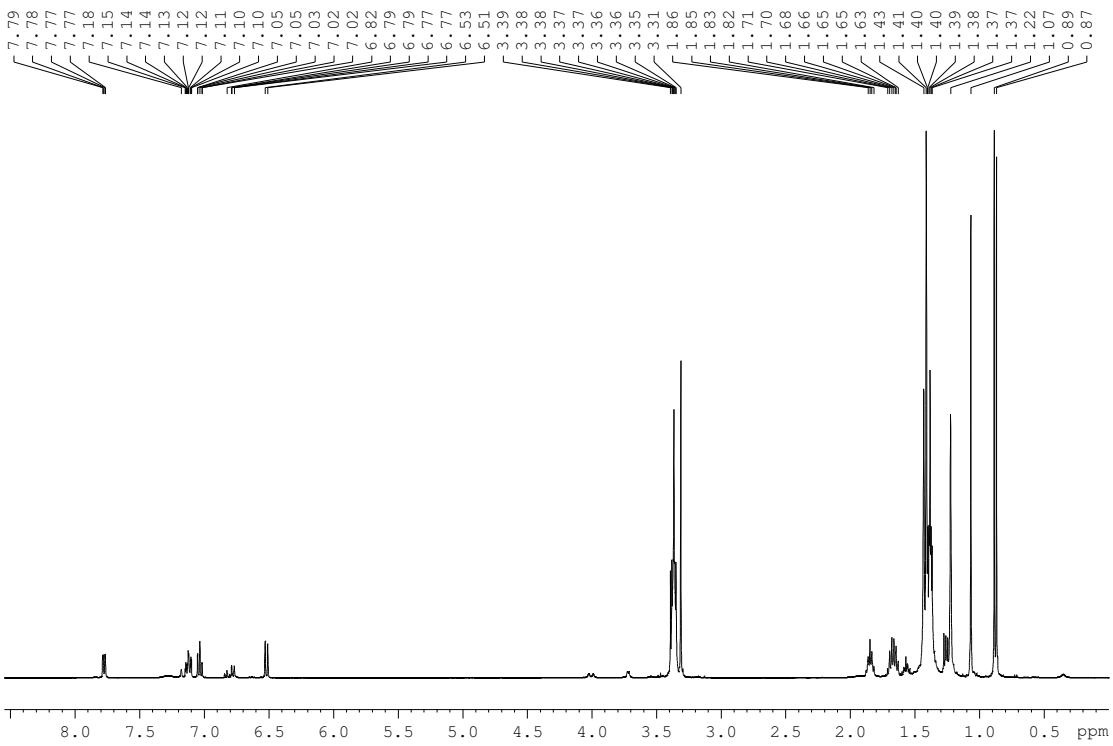
(i) ^{1}H NMR spectrum of **7** in C_6D_6:



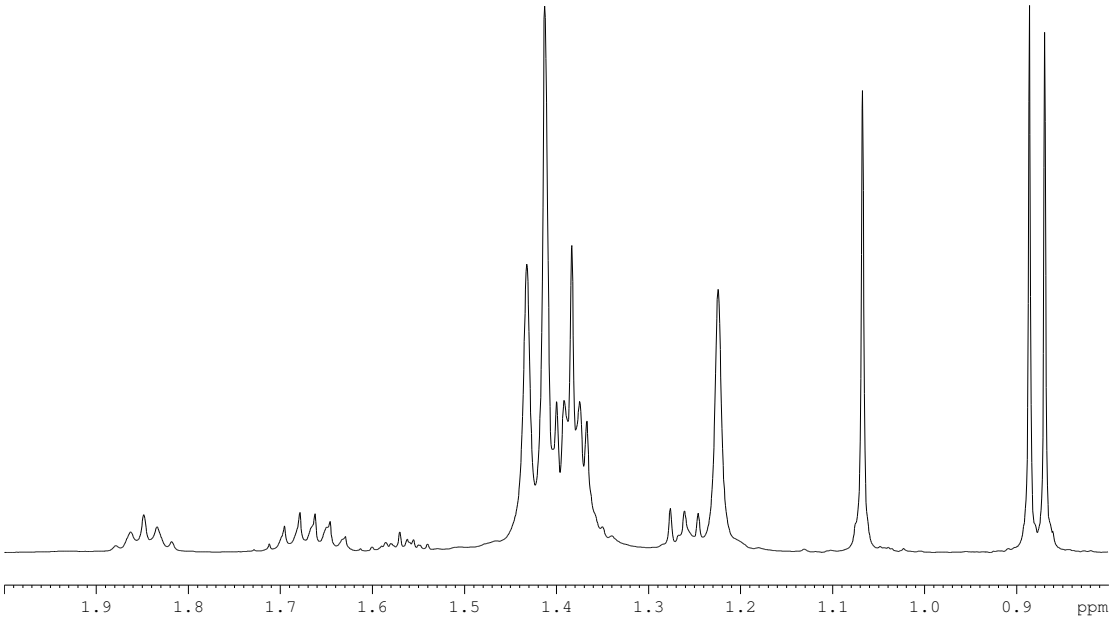
(ii) ^{1}H NMR spectrum of **7** + TMP(H) in C_6D_6 (1 hr)



(iii) ^{1}H NMR spectrum of **7** + TMP(H) in C_6D_6 (24 hrs)

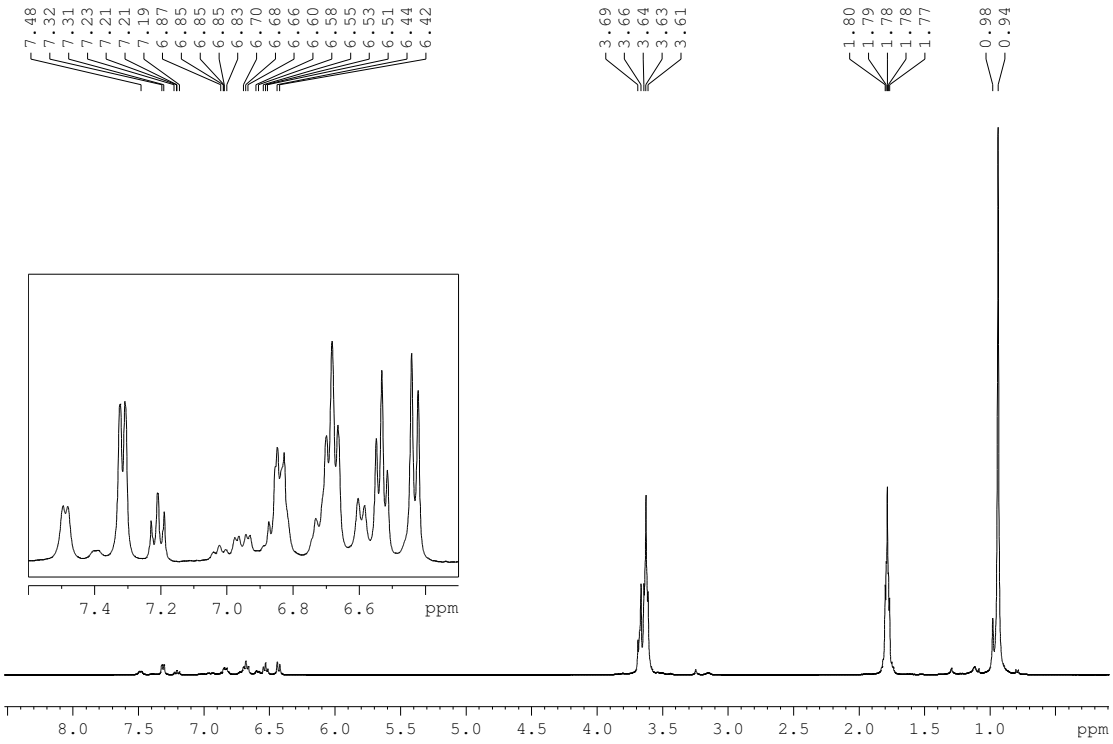


(iv) Enlarged aliphatic region of **(iii)**

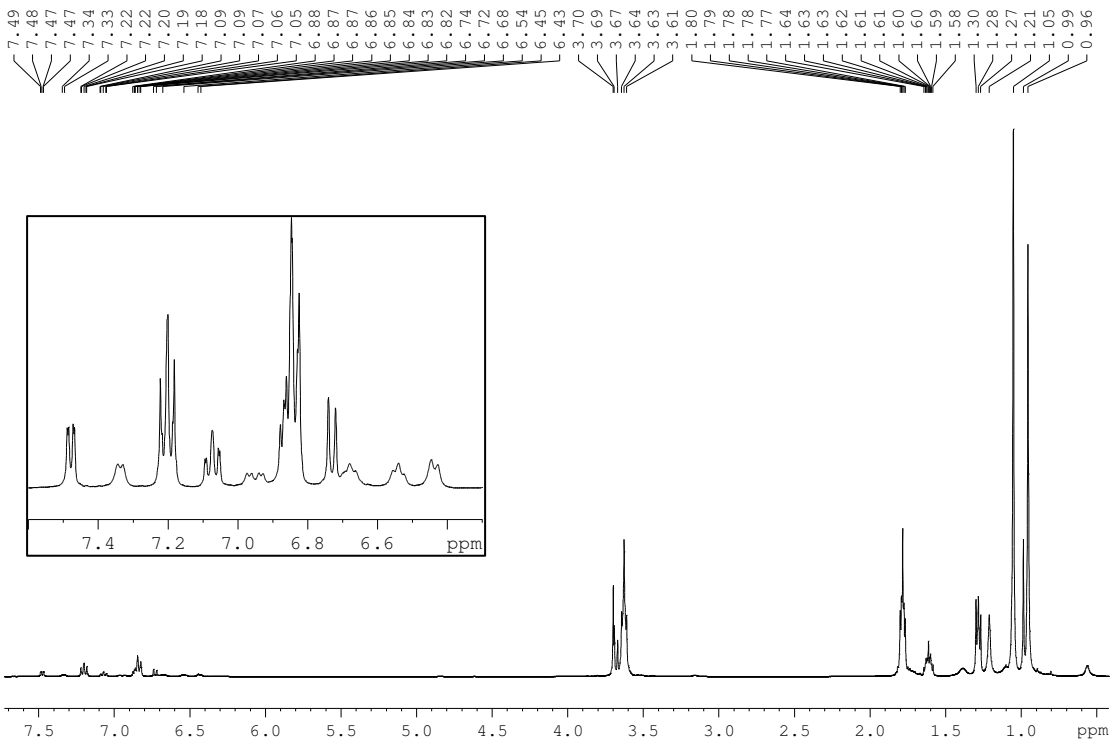


b) [(THF)$_3$Li(C$_6$H$_4$-OMe)(^{t}Bu)Zn(^{t}Bu)](7) + TMPH (2 hrs) in d^8-THF

(i) ^{1}H NMR spectrum of **7** in d^8-THF

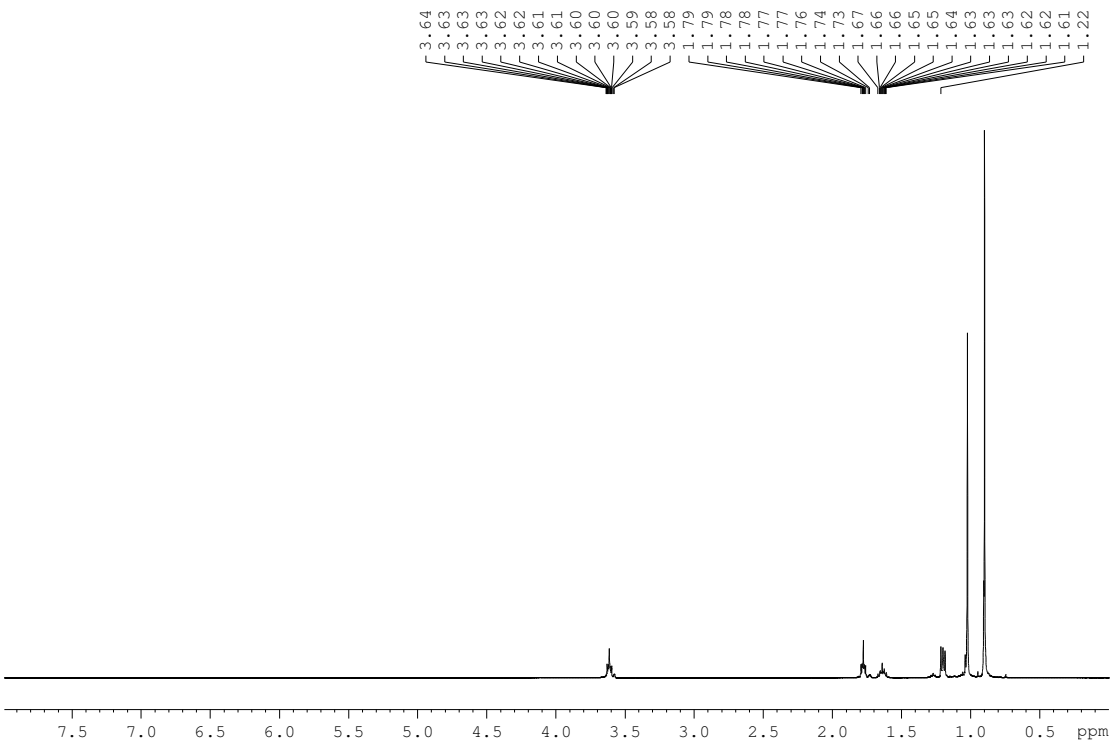


(ii) ^{1}H NMR spectrum of **7** + TMP(H) in d^8-THF (2 hrs)

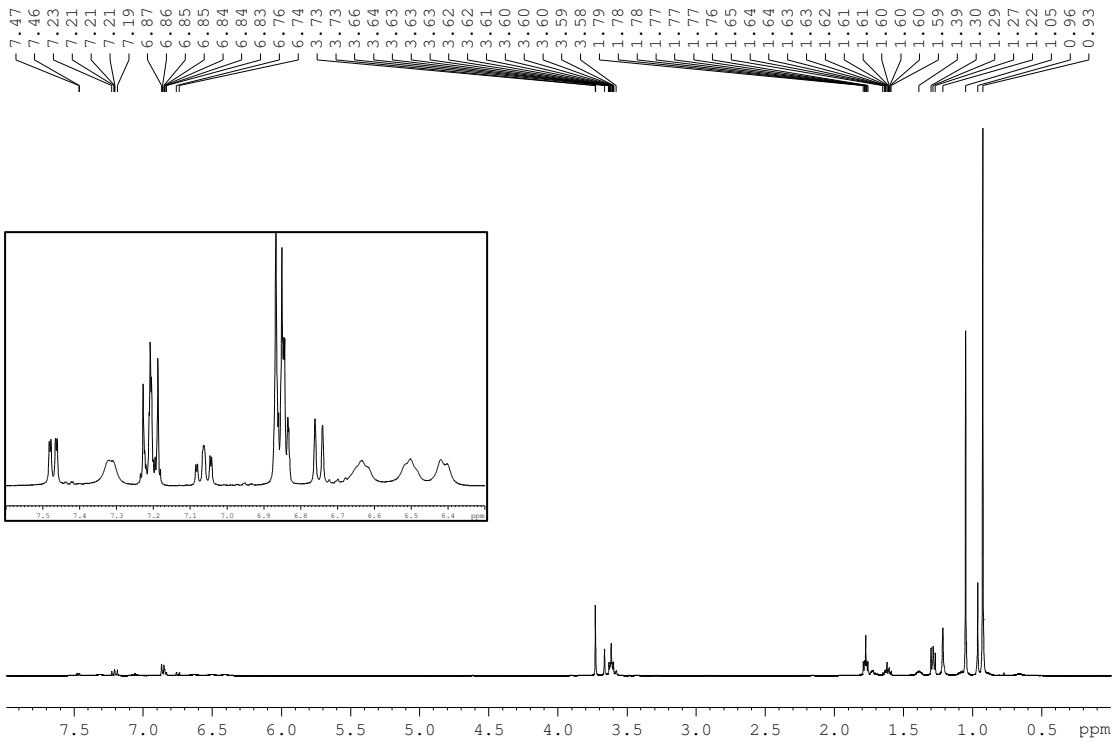


c) [(THF)Li(TMP)(tBu)Zn(tBu)](1) + anisole in d^8-THF

(i) ^{1}H NMR spectrum of **1** in d^8-THF

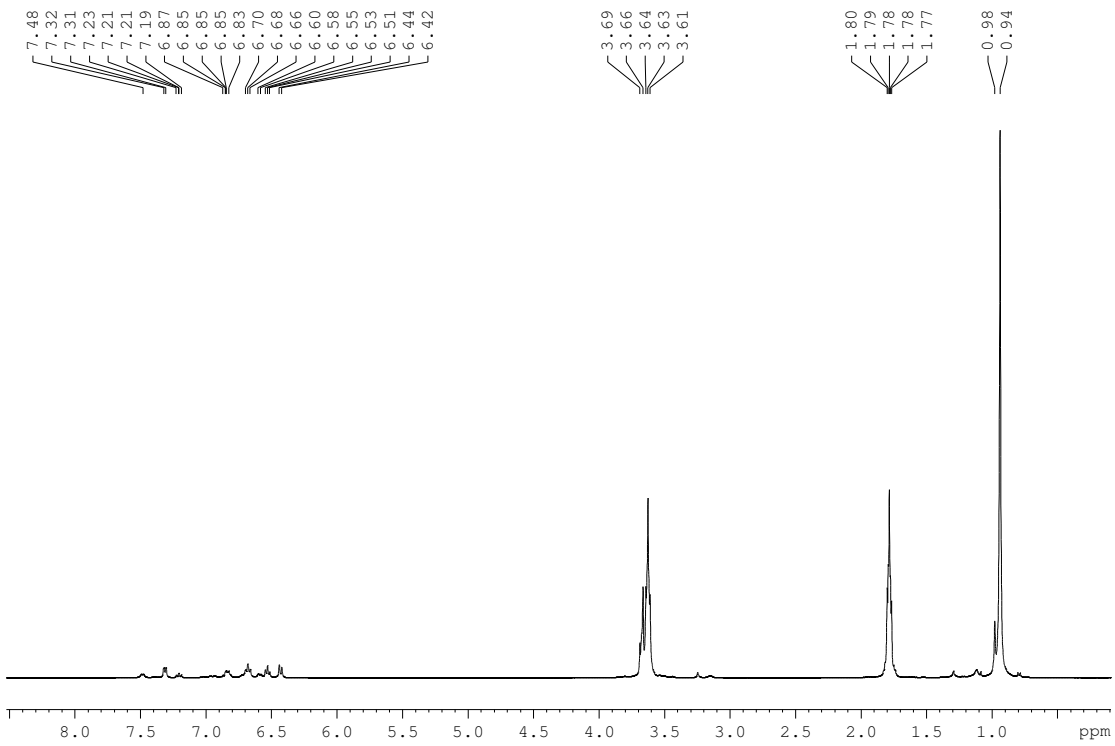


(ii) ^{1}H NMR spectrum of **1** + anisole (1 hr) in d^8-THF

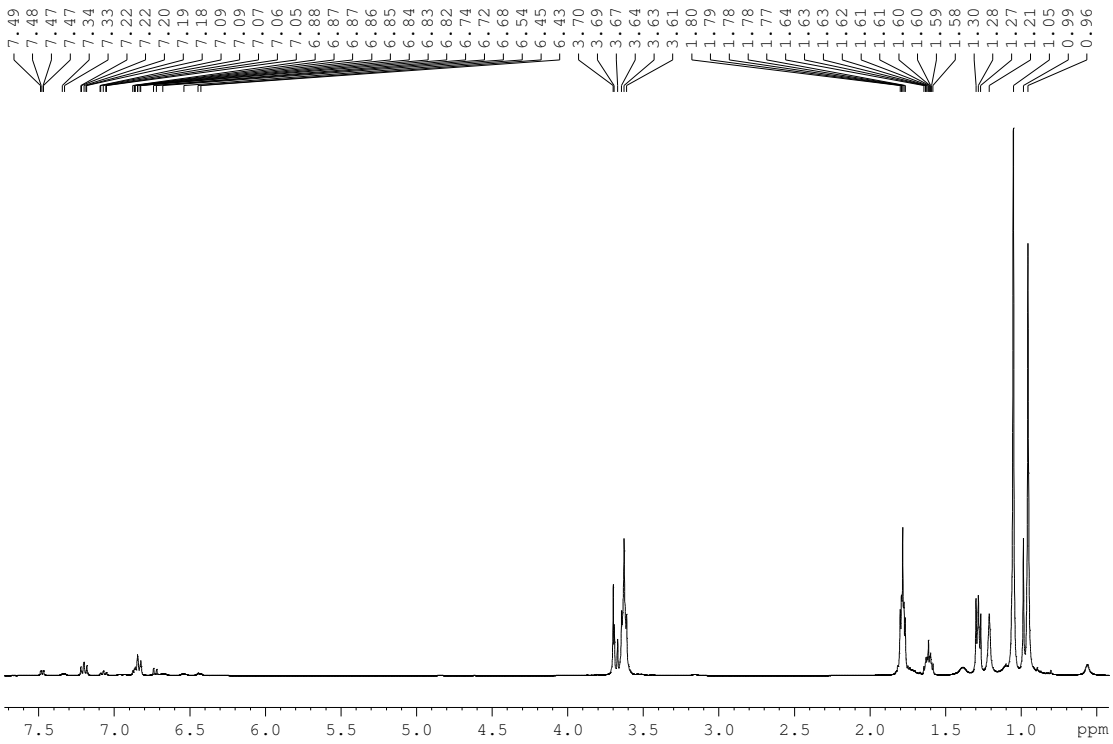


d) ^{1}H NMR spectra in d^{8}-THF of :

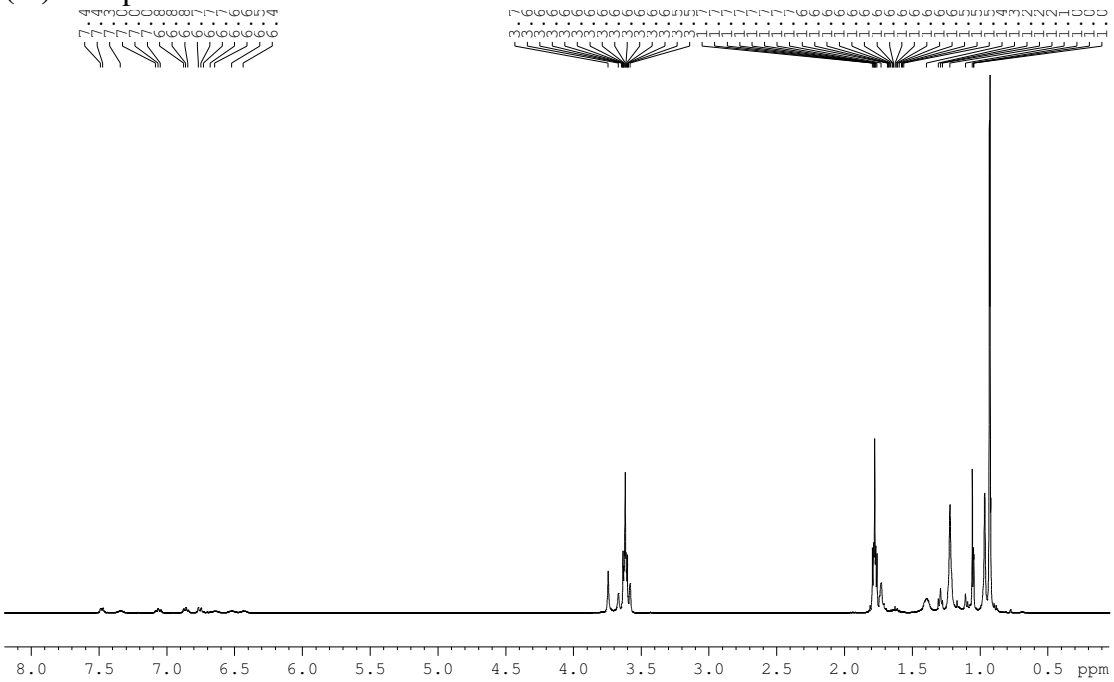
(i) Compound **7**



(ii) Compound **7** + TMPH (2 hrs)



(iii) Compound **2**



(iv) Compound **1**+anisole