

Heterobimetallic metallation studies of *N,N*-dimethylphenylethylamine (DMPEA) : benzylic C-H bond cleavage/dimethylamino capture or intact DMPEA complex†‡

Supporting Information

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Synthesis of Zn(TMP)₂: TMP(H) (6.8 mL, 40 mmol) was added to hexane (40 mL) and the solution cooled to 0°C before *n*BuLi (25 mL, 1.6 M in hexanes, 40 mmol) was introduced. The resulting yellow suspension was stirred for 1 hour before all the solvent was removed *in vacuo*. ZnCl₂ (2.72 g, 20 mmol) was then added followed by diethyl ether (50 mL). The suspension was then left to stir for 2 days after which the ether was removed *in vacuo* and replaced by hexane (100 mL). The suspension was then filtered and the solid rinsed with hexane (80 mL). The solvent was then removed *in vacuo* to provide the pale yellow solid (yield: 4.0 g, 58%).

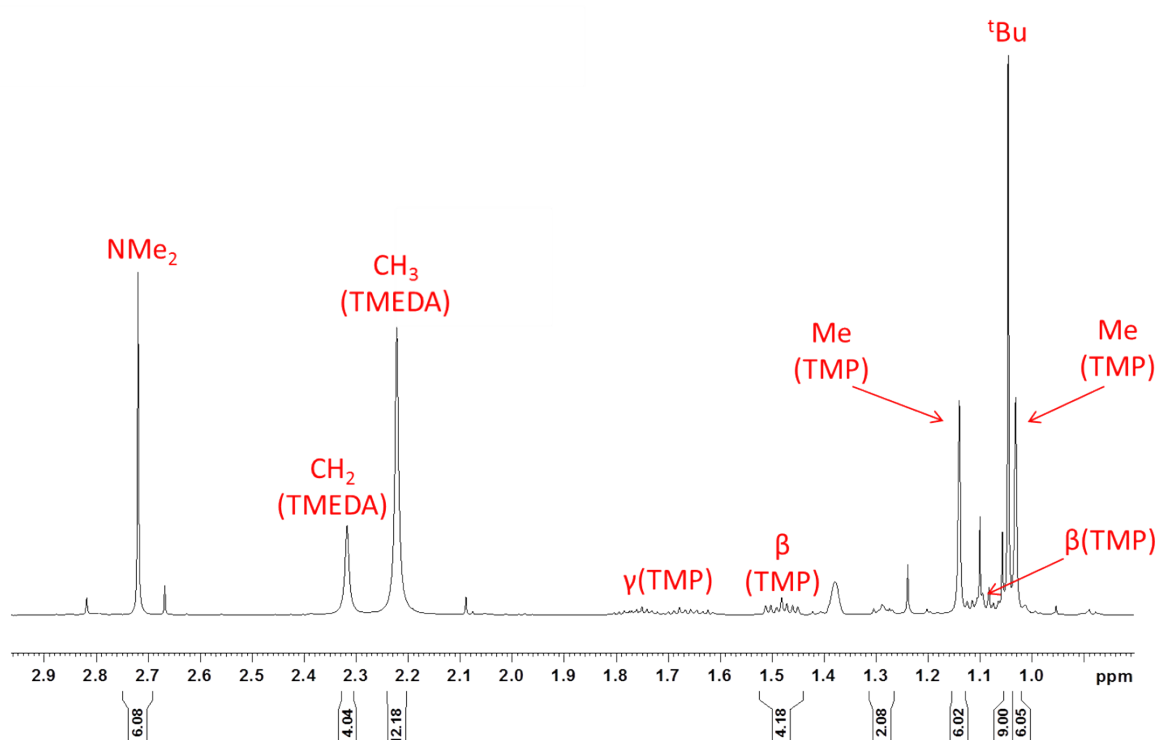


Figure S1. ¹H NMR spectrum of [(TMEDA)Na(TMP)(NMe₂)Zn(Bu^t)] **3** in C₆D₁₂ solution.

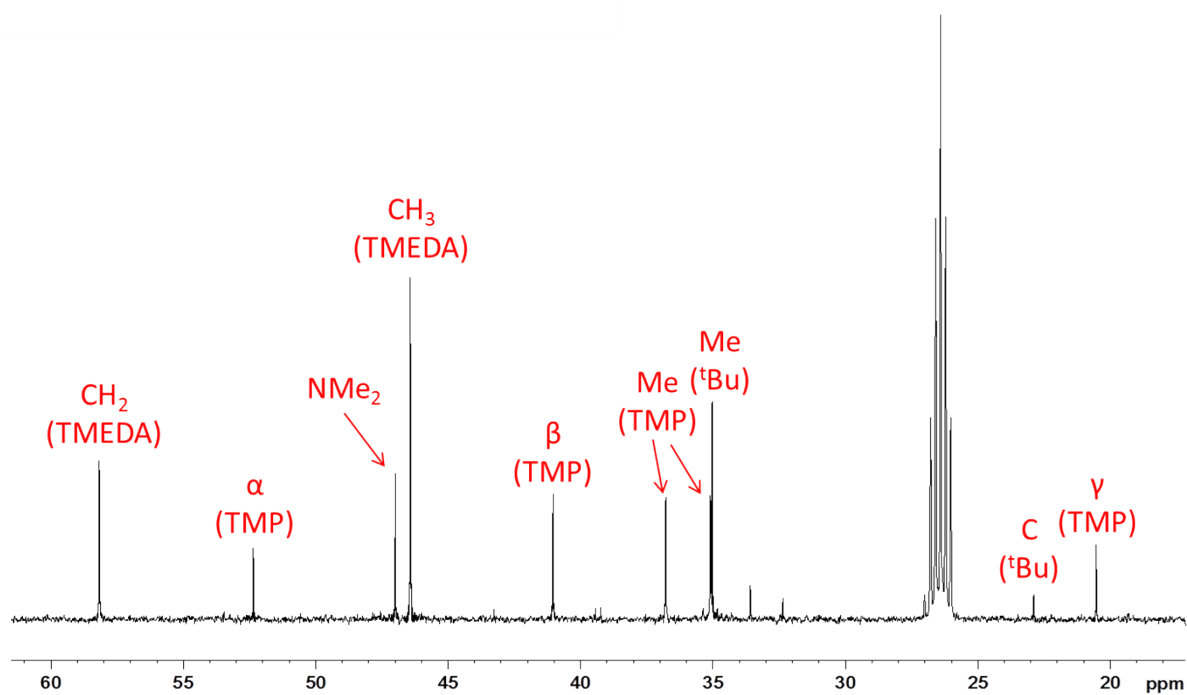


Figure S2. ^{13}C NMR spectrum of $[(\text{TMEDA})\text{Na}(\text{TMP})(\text{NMe}_2)\text{Zn}(\text{Bu}')_2]$ **3** in C_6D_{12} solution.

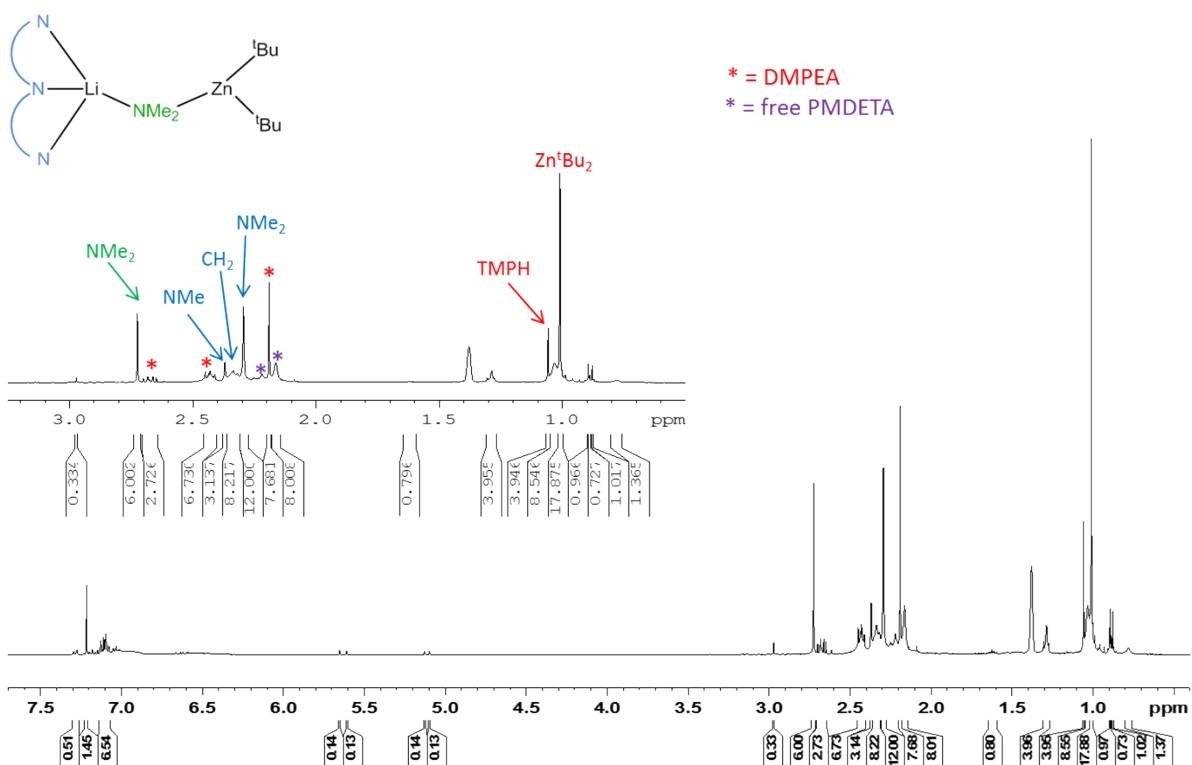


Figure S3. ^1H NMR spectrum of $[(\text{PMDETA})\text{Li}(\text{NMe}_2)\text{Zn}(\text{Bu}')_2]$ **4** in C_6D_{12} solution.

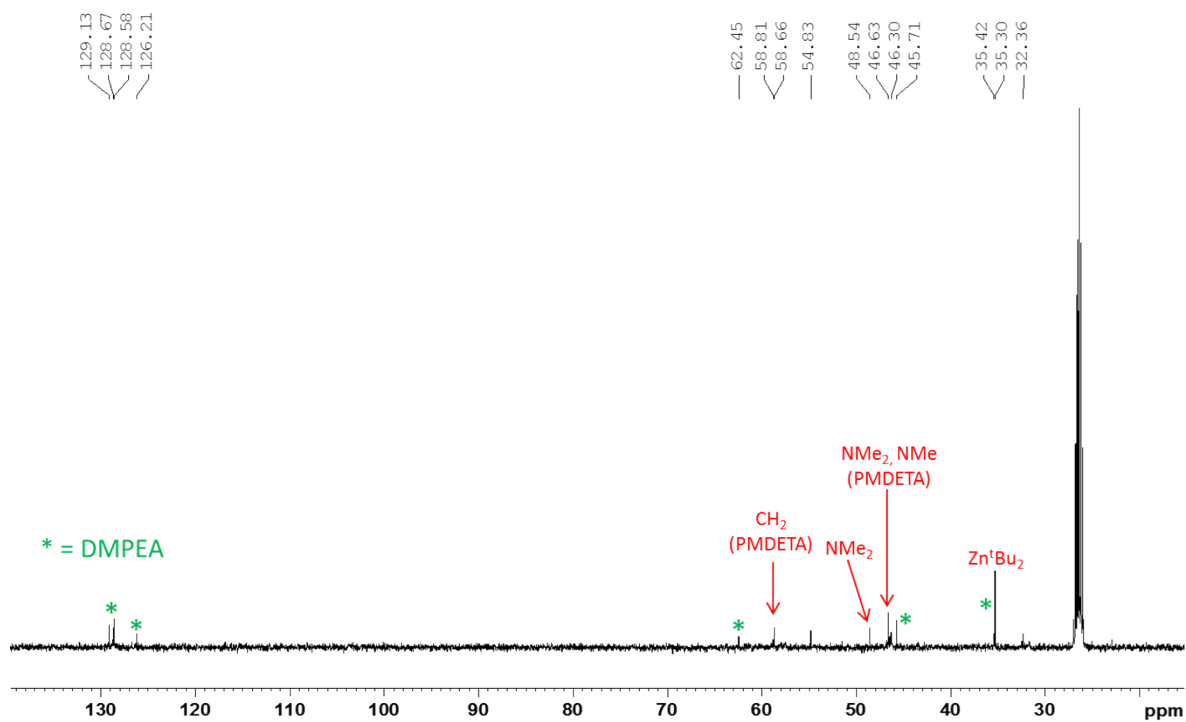


Figure S4. ^{13}C NMR spectrum of $[(\text{PMDETA})\text{Li}(\text{NMe}_2)\text{Zn}(\text{Bu}')_2]$ **4** in C_6D_{12} solution.

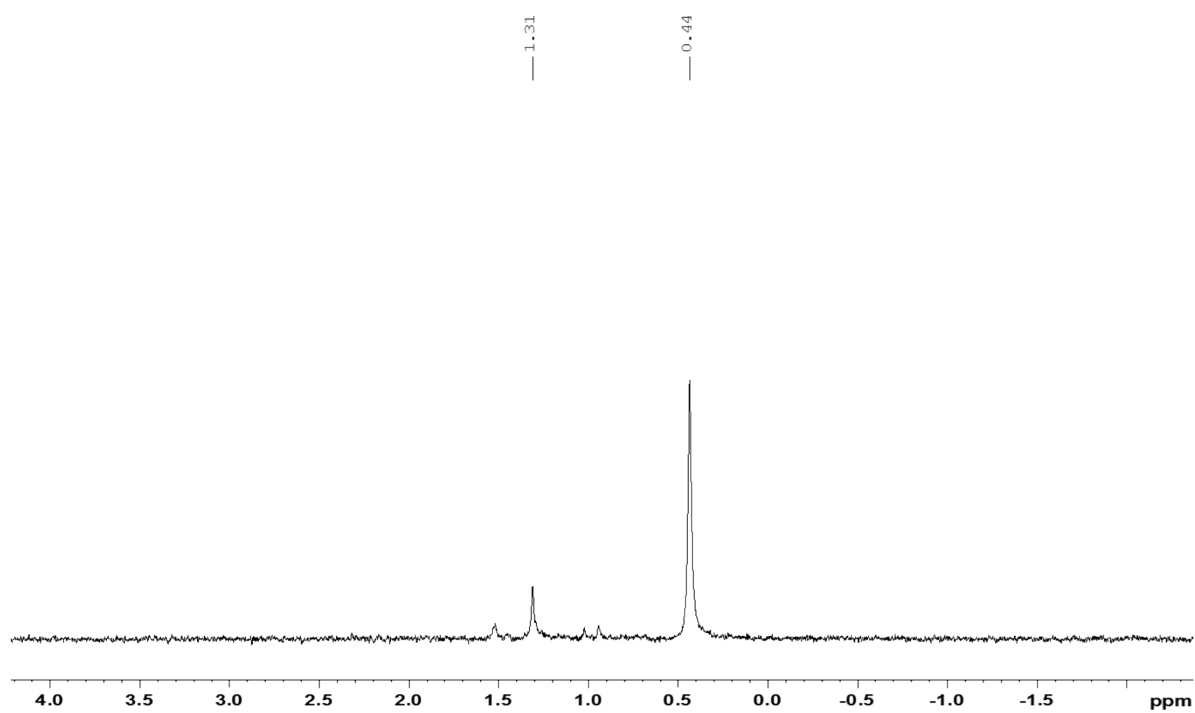


Figure S5. ^7Li spectrum of $[(\text{PMDETA})\text{Li}(\text{NMe}_2)\text{Zn}(\text{Bu}')_2]$ **4** in C_6D_{12} solution with an unidentified impurity at 1.31 ppm.

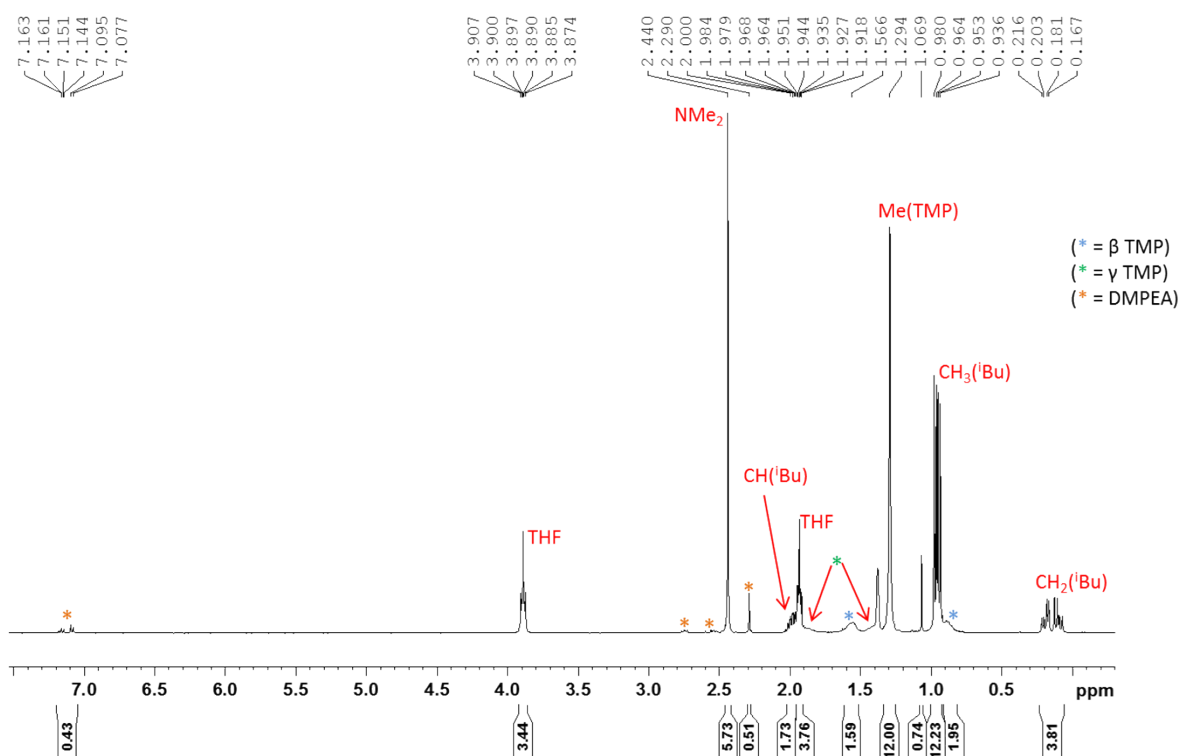


Figure S6. ^1H NMR spectrum of $[(\text{THF})\text{Li}(\text{TMP})(\text{NMe}_2)\text{Al}(\text{Bu}^i)_2]$ **5** in C_6D_{12} solution.

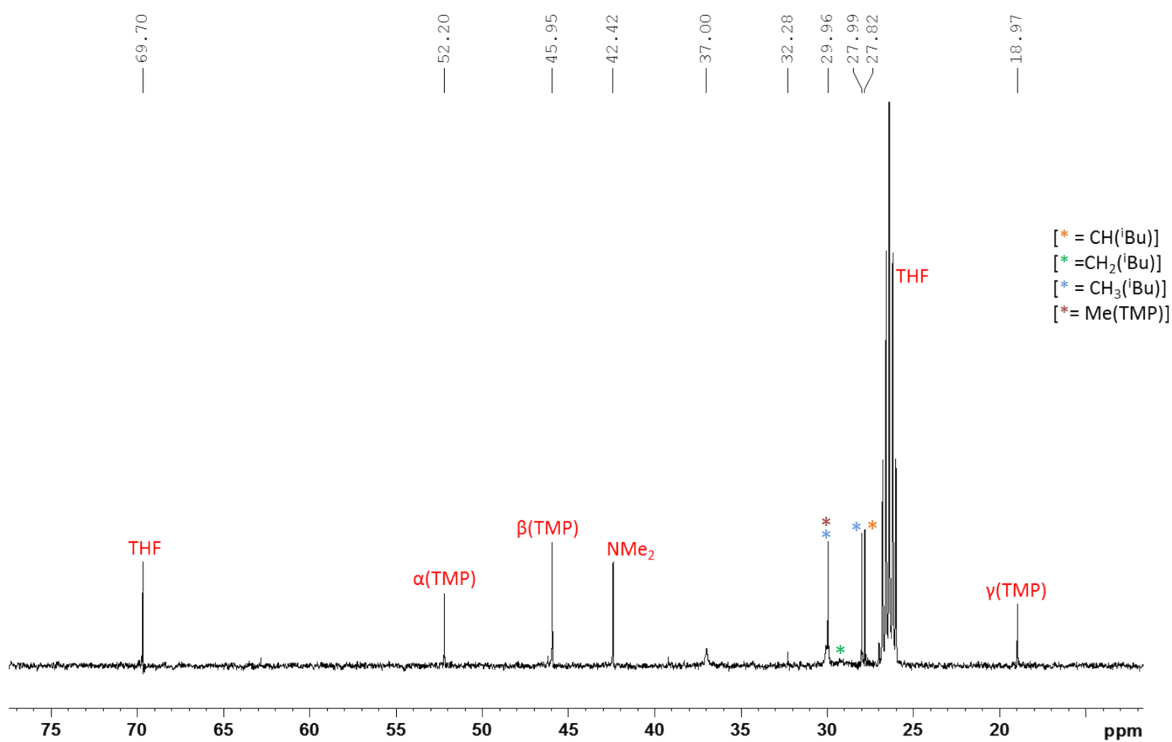


Figure S7. ^{13}C NMR spectrum of $[(\text{THF})\text{Li}(\text{TMP})(\text{NMe}_2)\text{Al}(\text{Bu}^i)_2]$ **5** in C_6D_{12} solution.

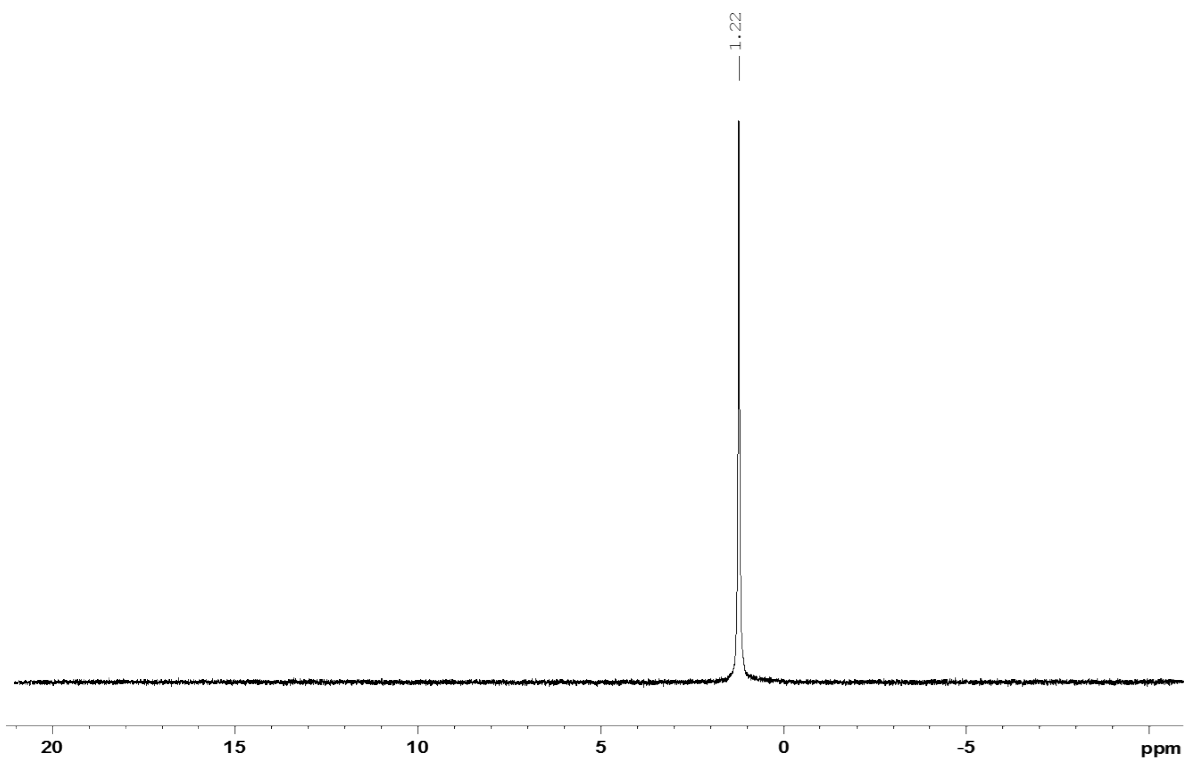


Figure S8. ^7Li spectrum of $[(\text{THF})\text{Li}(\text{TMP})(\text{NMe}_2)\text{Al}(\text{Bu}^t)_2]$ **5** in C_6D_{12} solution.

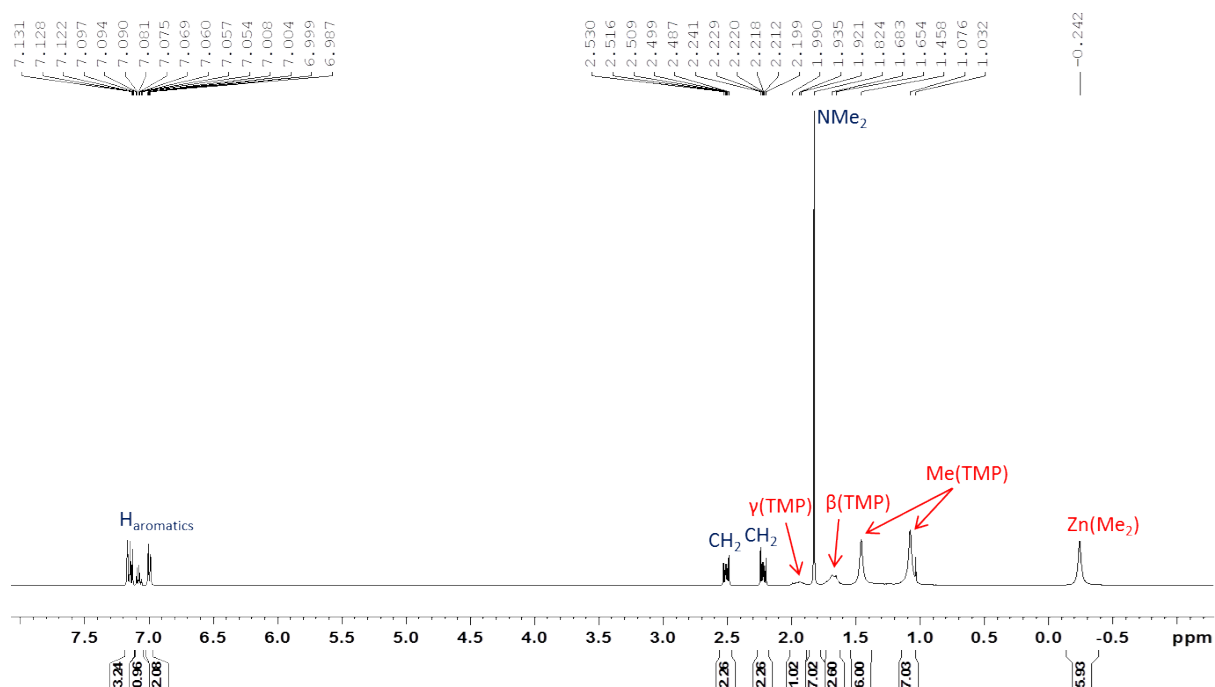


Figure S9. ^1H NMR spectrum of $[\text{DMPEA} \cdot \text{Li}(\text{TMP})\text{Zn}(\text{Me})_2]$ **6** in C_6D_6 solution.

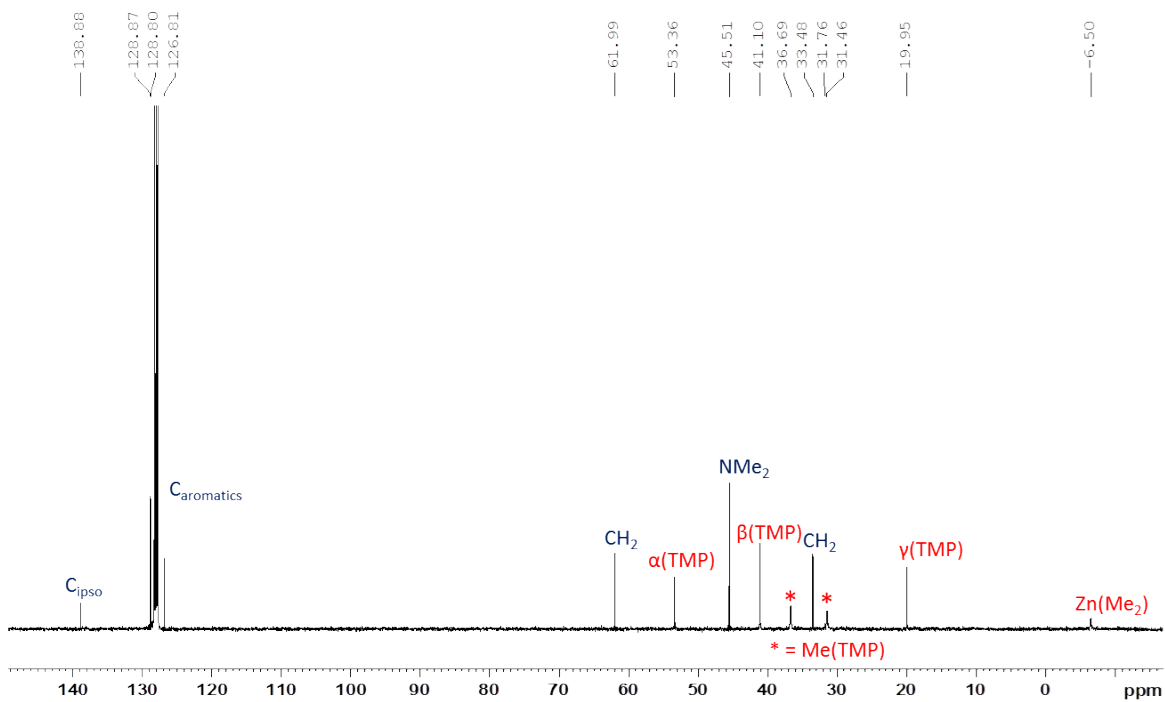


Figure S10. ^{13}C NMR spectrum of $[\text{DMPEA}\cdot\text{Li}(\text{TMP})\text{Zn}(\text{Me})_2]$ **6** in C_6D_6 solution.

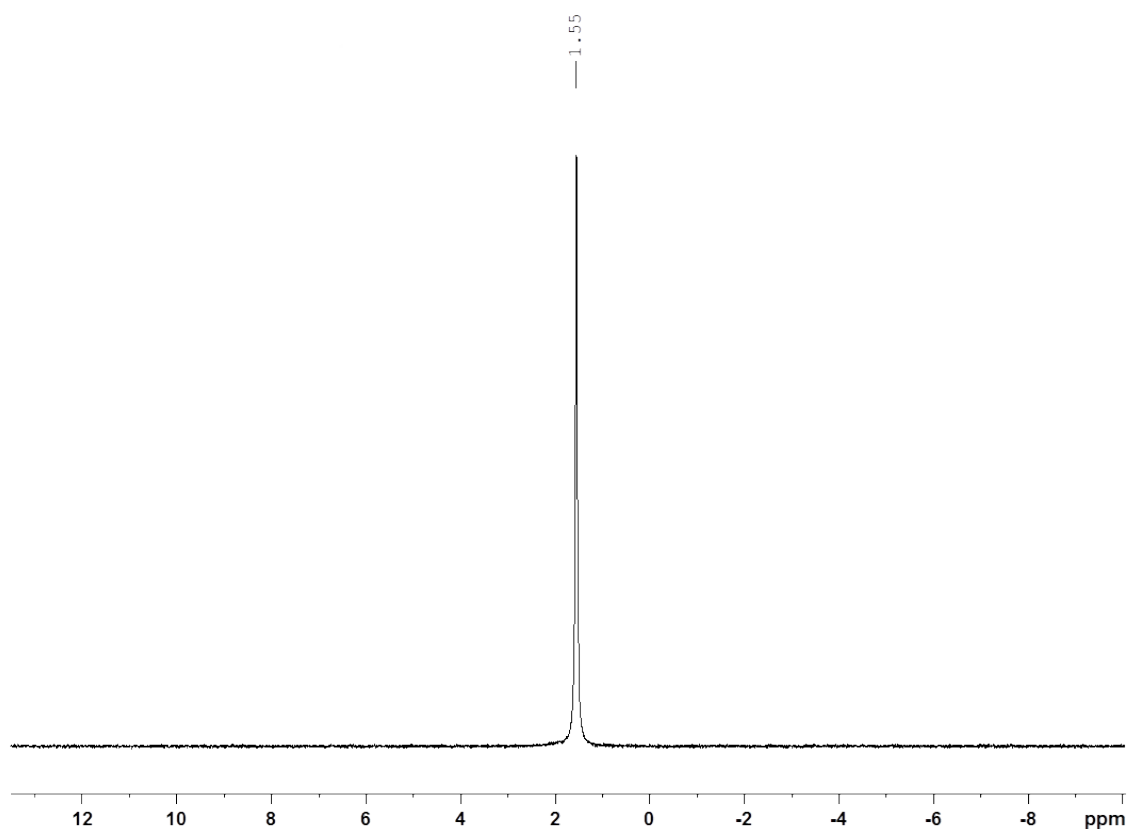


Figure S11. ^7Li NMR spectrum of $[\text{DMPEA}\cdot\text{Li}(\text{TMP})\text{Zn}(\text{Me})_2]$ **6** in C_6D_6 solution.

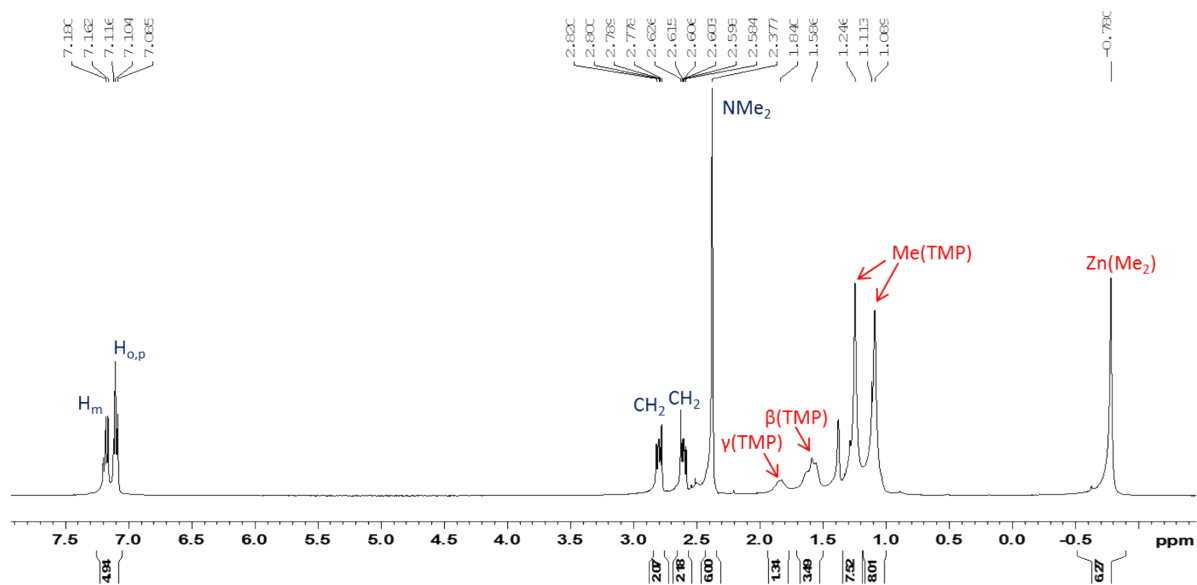


Figure S12. ^1H NMR spectrum of $[\text{DMPEA}\cdot\text{Li}(\text{TMP})\text{Zn}(\text{Me})_2]$ **6** in C_6D_{12} solution.

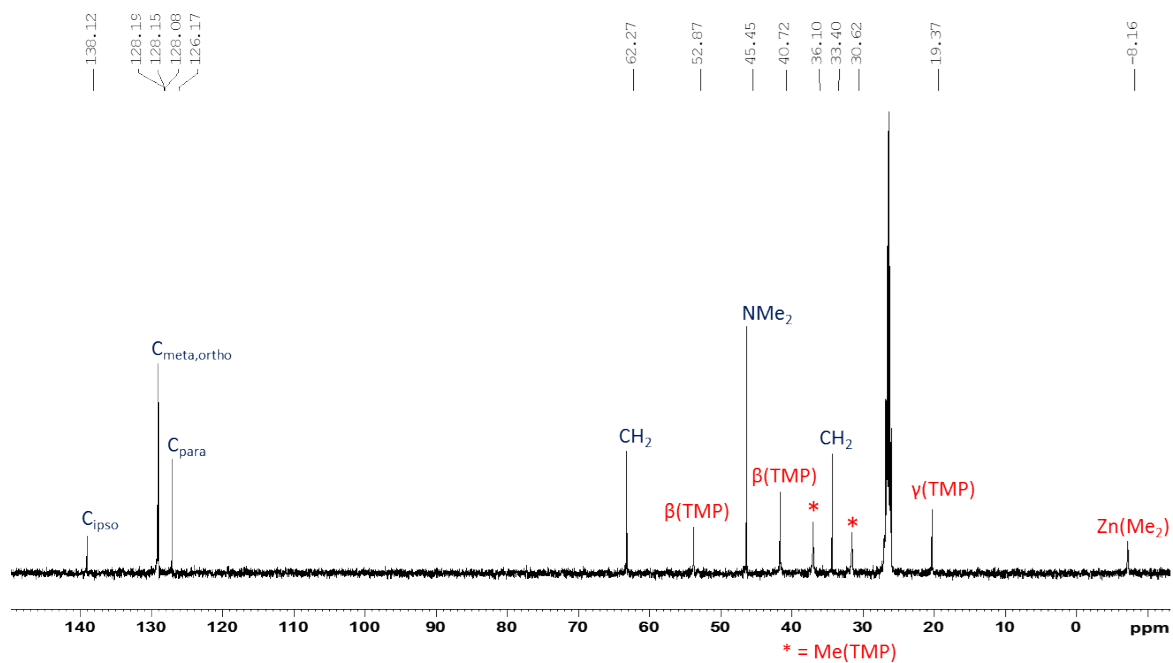


Figure S13. ^{13}C NMR spectrum of $[\text{DMPEA}\cdot\text{Li}(\text{TMP})\text{Zn}(\text{Me})_2]$ **6** in C_6D_{12} solution.

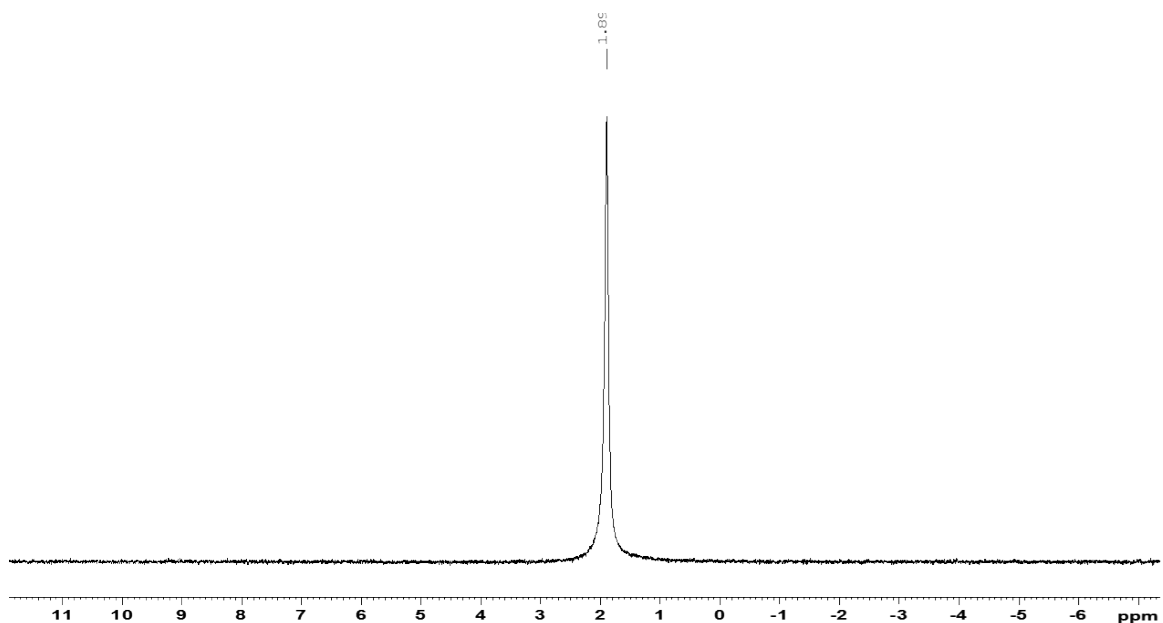


Figure S14. ^7Li NMR spectrum of $[\text{DMPEA}\cdot\text{Li}(\text{TMP})\text{Zn}(\text{Me})_2]$ **6** in C_6D_{12} solution.

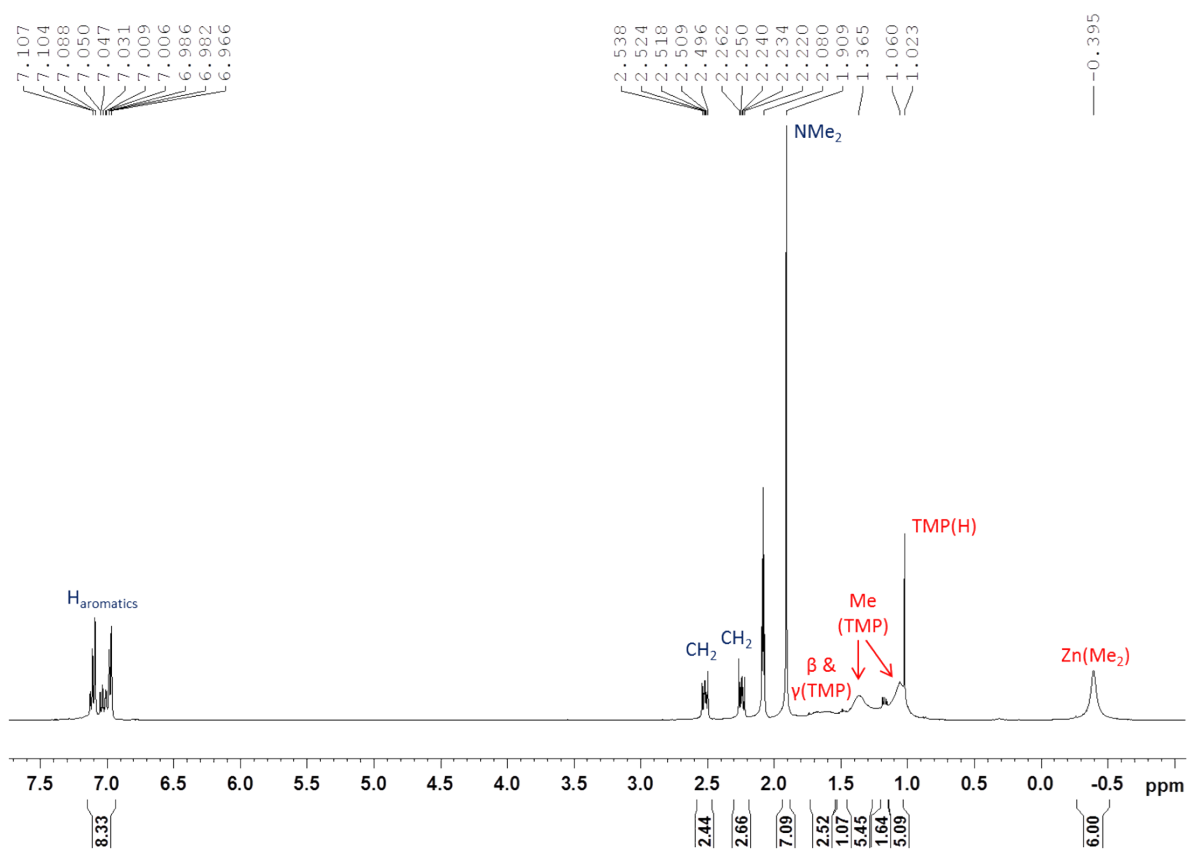


Figure S15. ^1H NMR spectrum of $[\text{DMPEA}\cdot\text{Li}(\text{TMP})\text{Zn}(\text{Me})_2]$ **6** in d_8 -toluene solution.

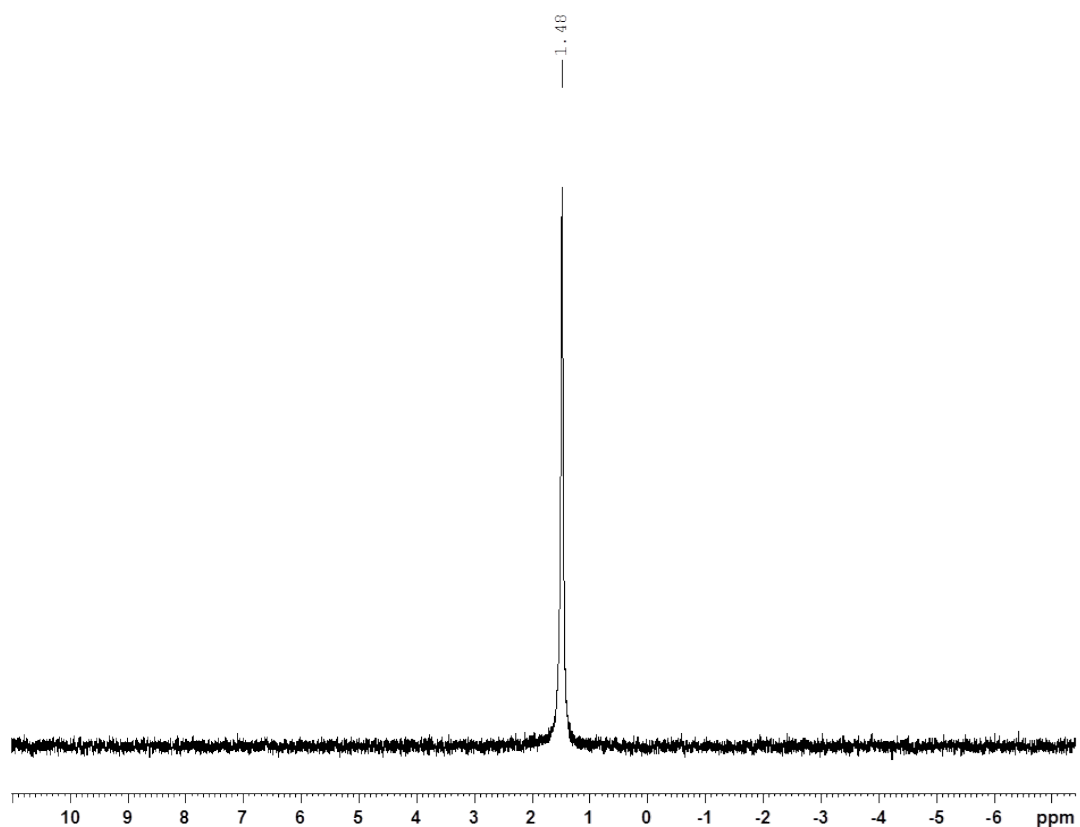


Figure S16. ^7Li NMR spectrum of $[\text{DMPEA}\cdot\text{Li}(\text{TMP})\text{Zn}(\text{Me})_2]$ **6** in d_8 -toluene solution.

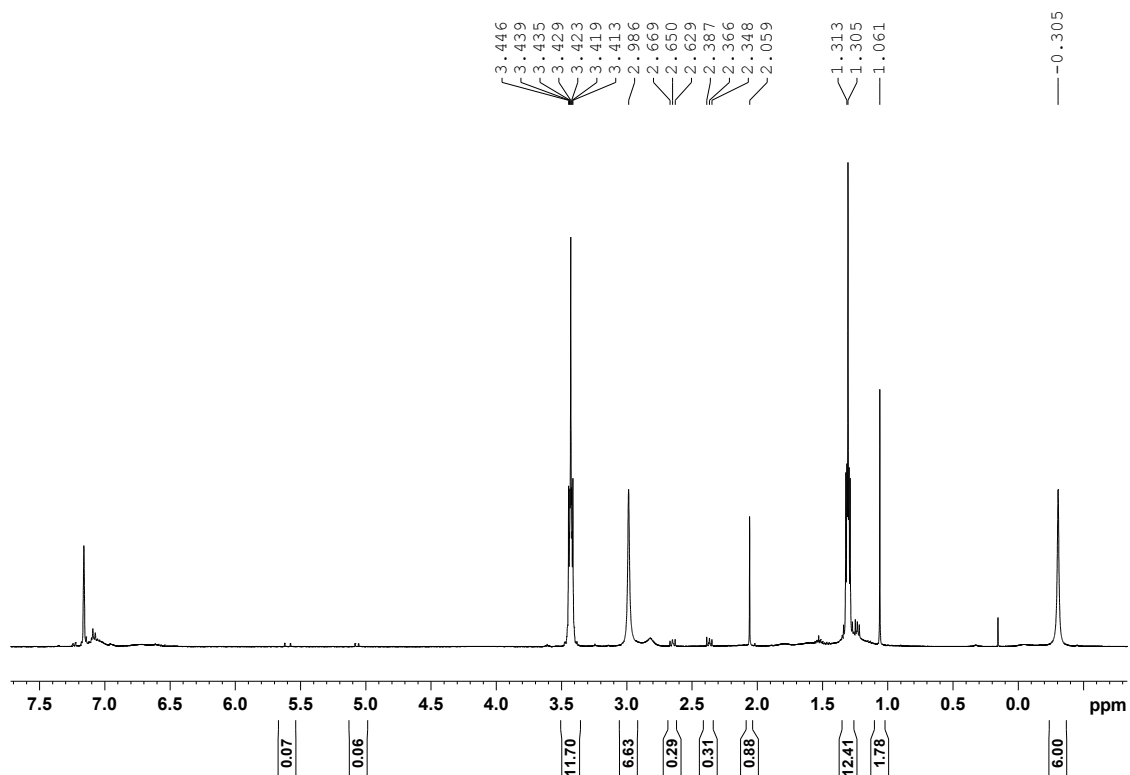


Figure S17. ^1H NMR spectrum in C_6D_6 solution of crystals of $[\text{DMPEA}\cdot\text{Li}(\text{TMP})\text{Zn}(\text{Me})_2]$ **6** dissolved in THF solution showing the emergence of a new NMe_2 resonance (at 3 ppm) resulting from the metallation and subsequent β -elimination of DMPEA.