

Electronic supporting information

Synthetic and Reactivity Studies of Hetero-tri-anionic Sodium Zincates Javier Francos, Alan R. Kennedy and Charles T. O'Hara*

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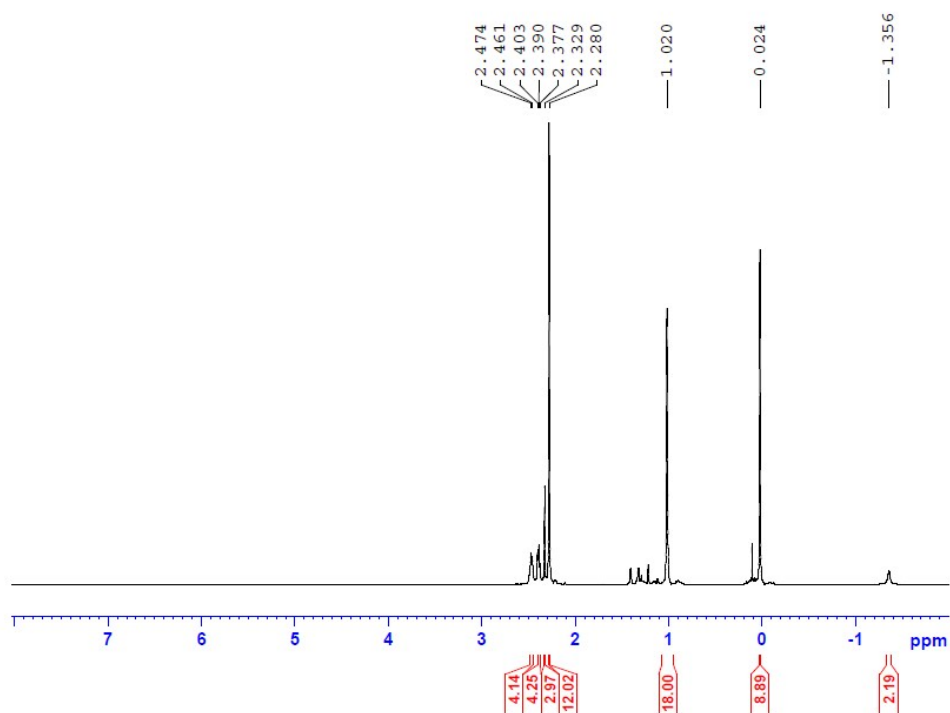


Figure S1. ¹H NMR of [(PMEDTA)Na(μ-CH₂SiMe₃)Zn'Bu₂] (2) in cyc-C₆D₁₂.

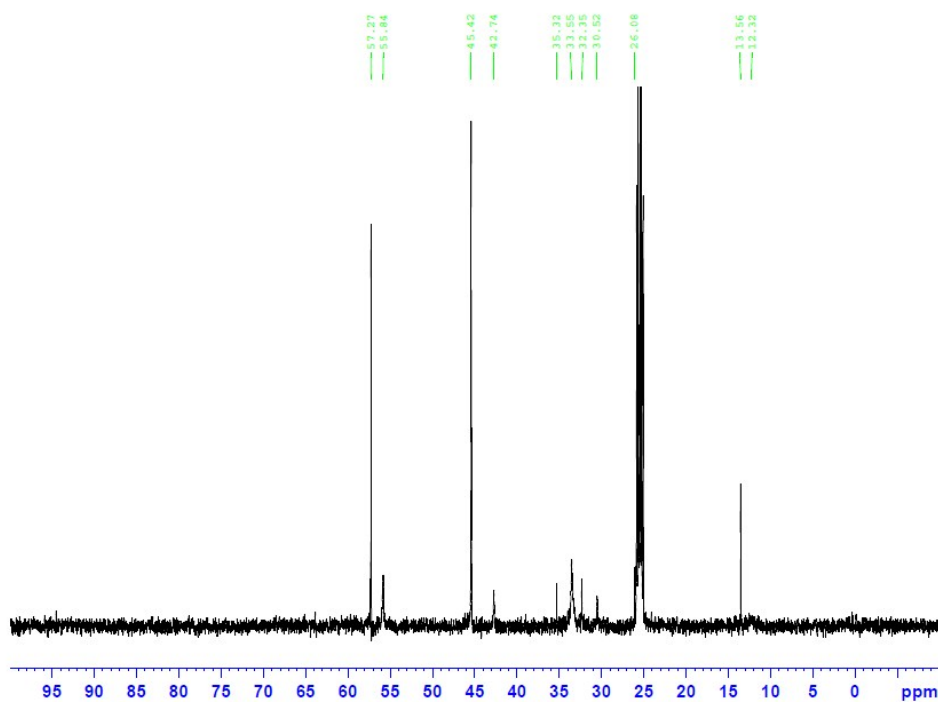


Figure S2. ¹³C NMR of [(PMEDTA)Na(μ-CH₂SiMe₃)Zn'Bu₂] (2) in cyc-C₆D₁₂.

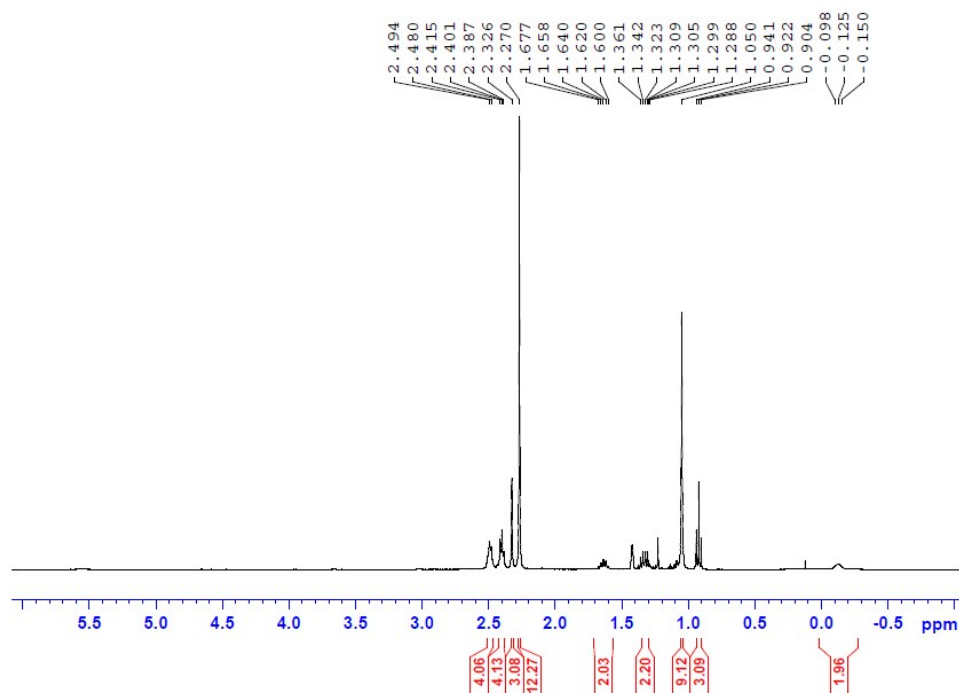


Figure S3. ¹H NMR of [(PMEDTA)Na(μ-*n*Bu)Zn'*n*Bu₂] (3) in cyc-C₆D₁₂.

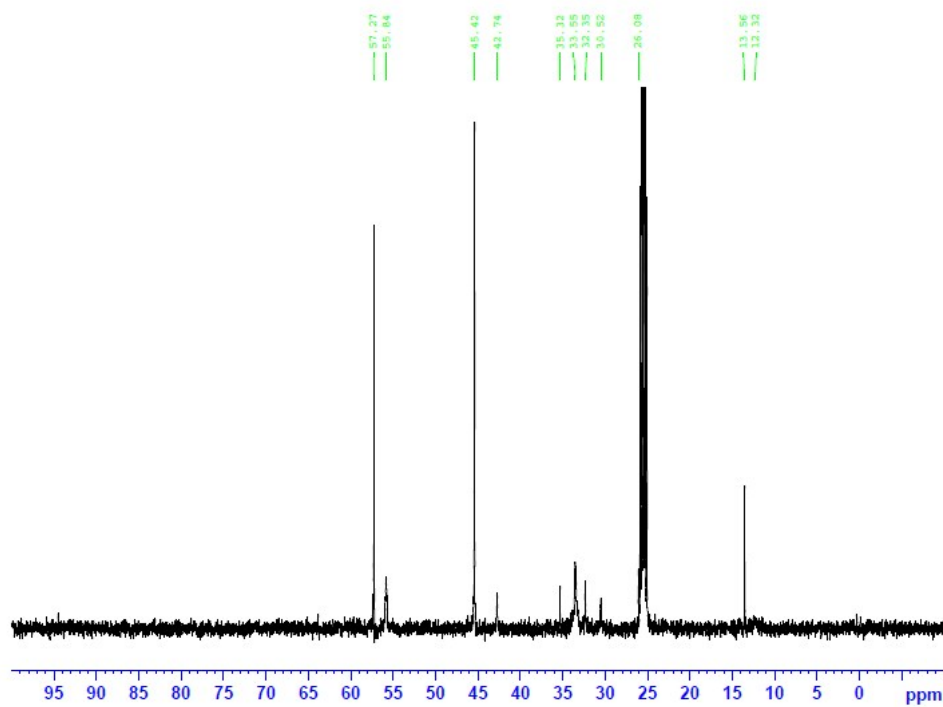


Figure S4. ¹³C NMR of [(PMEDTA)Na(μ-*n*Bu)Zn'*n*Bu₂] (3) in cyc-C₆D₁₂.

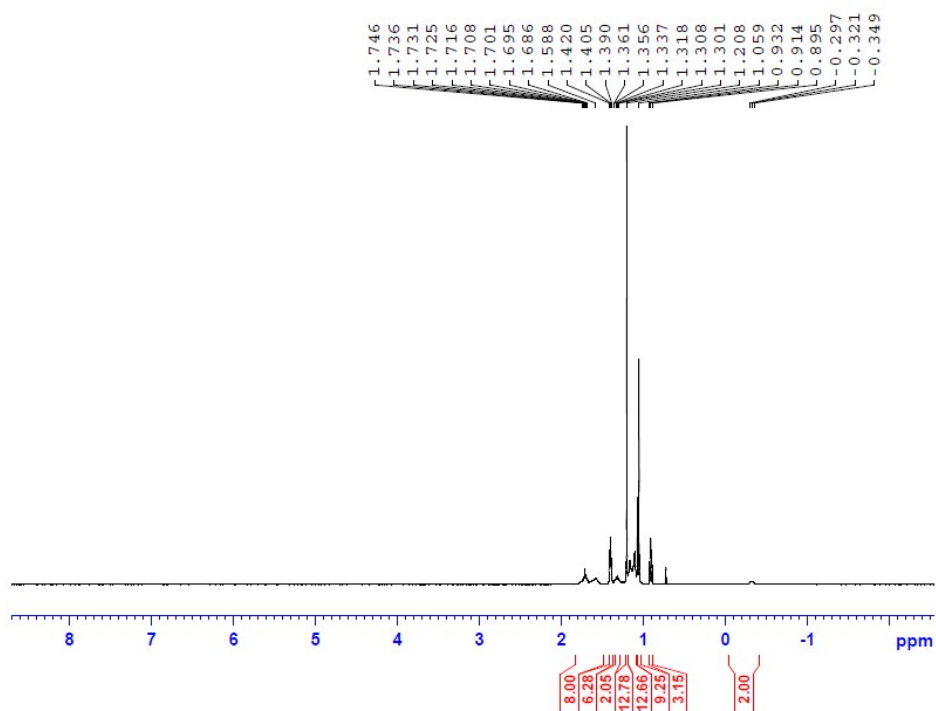


Figure S5. ¹H NMR of [(TMPH)Na(μ-TMP)(μ-*n*Bu)Zn'*n*Bu] (**4**) in *cyc*-C₆D₁₂.

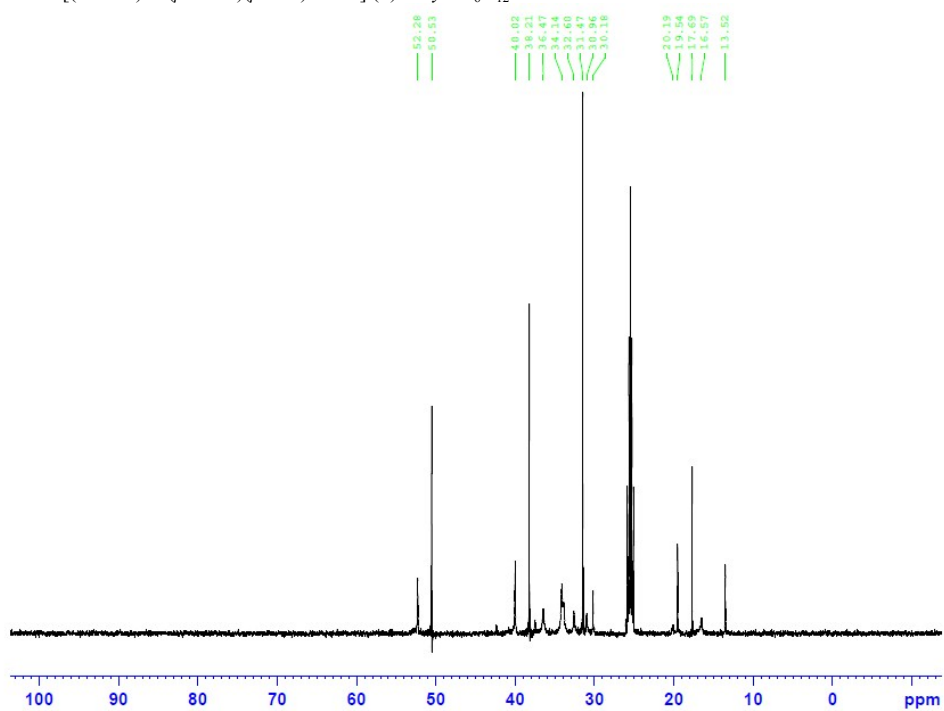


Figure S6. ¹³C NMR of [(TMPH)Na(μ-TMP)(μ-*n*Bu)Zn'*n*Bu] (**4**) in *cyc*-C₆D₁₂.

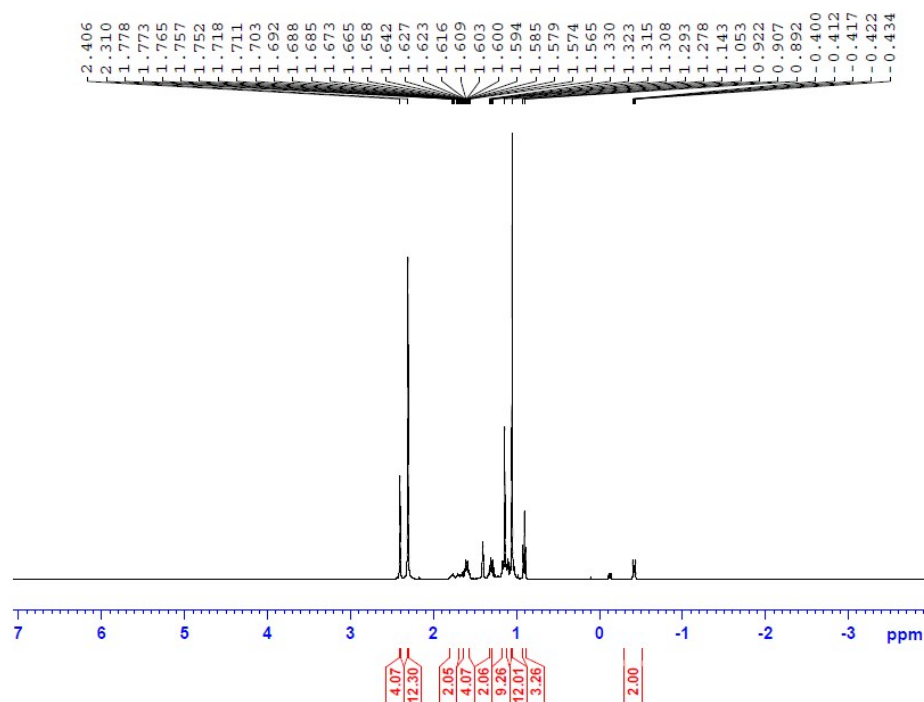


Figure S7. ¹H NMR of [(TMEDA)Na(μ-TMP)(μ-*n*Bu)Zn'*n*Bu] (**5**) in *cyc*-C₆D₁₂.

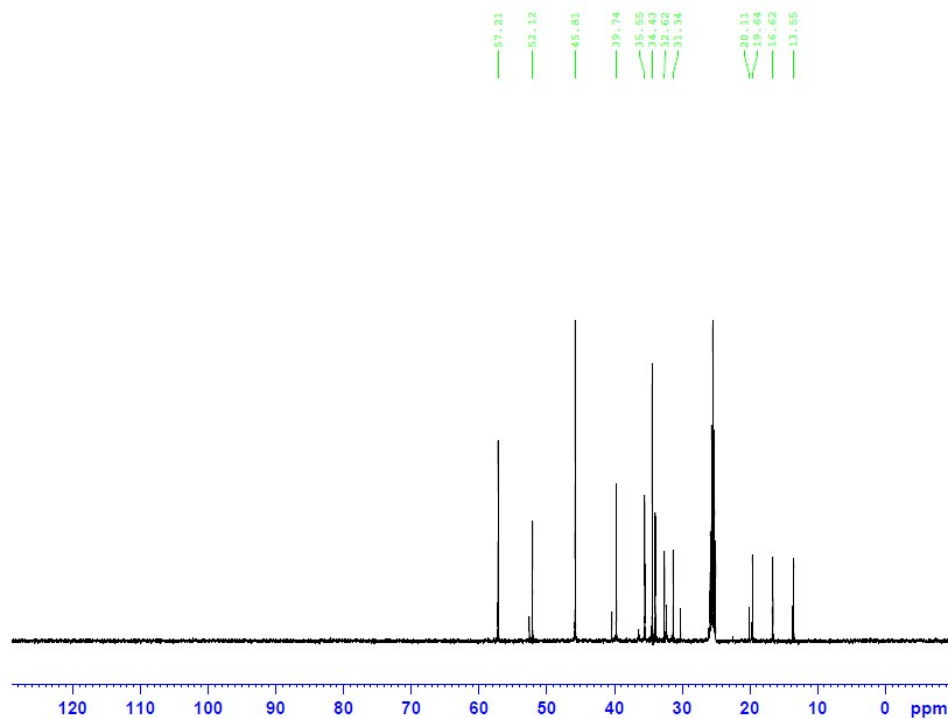


Figure S8. ¹³C NMR of [(TMEDA)Na(μ-TMP)(μ-*n*Bu)Zn'*n*Bu] (**5**) in *cyc*-C₆D₁₂.

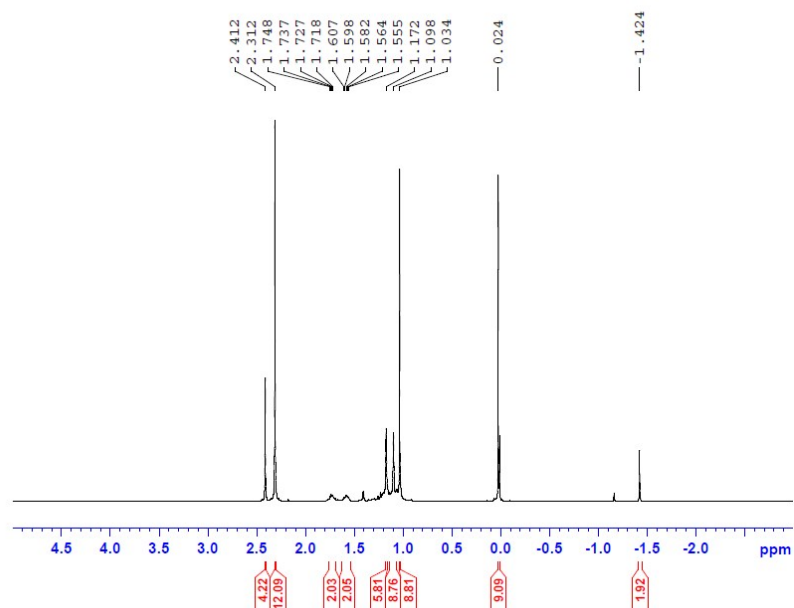


Figure S9. ¹H NMR of [(TMEDA)Na(μ-TMP)(μ-CH₂SiMe₃)Zn'Bu] (6) in cyc-C₆D₁₂.

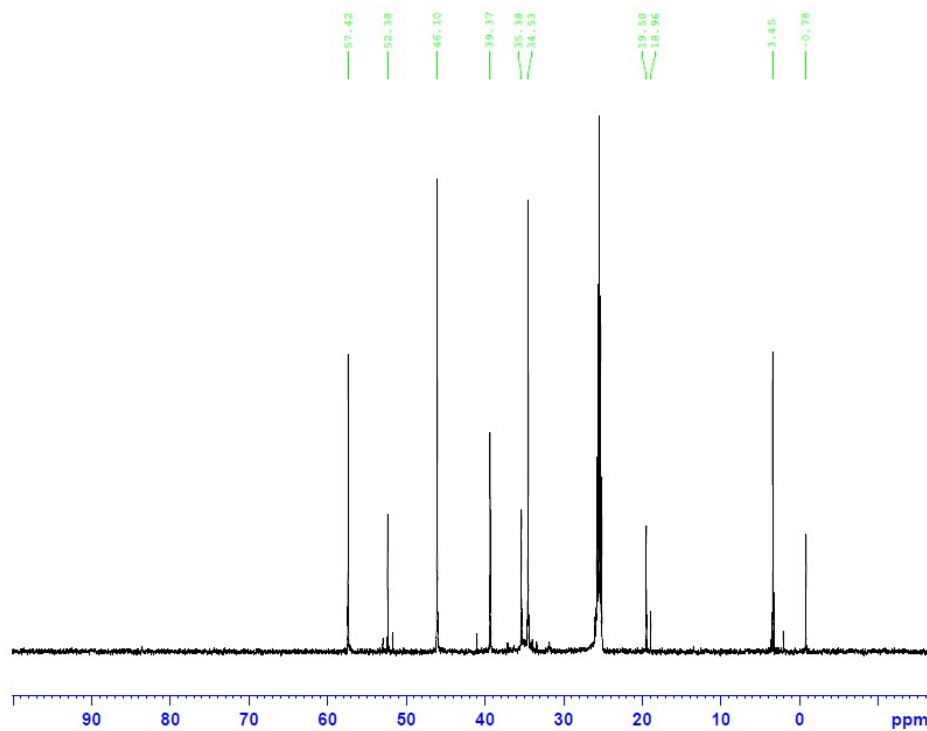


Figure S10. ¹³C NMR of [(TMEDA)Na(μ-TMP)(μ-CH₂SiMe₃)Zn'Bu] (6) in cyc-C₆D₁₂.

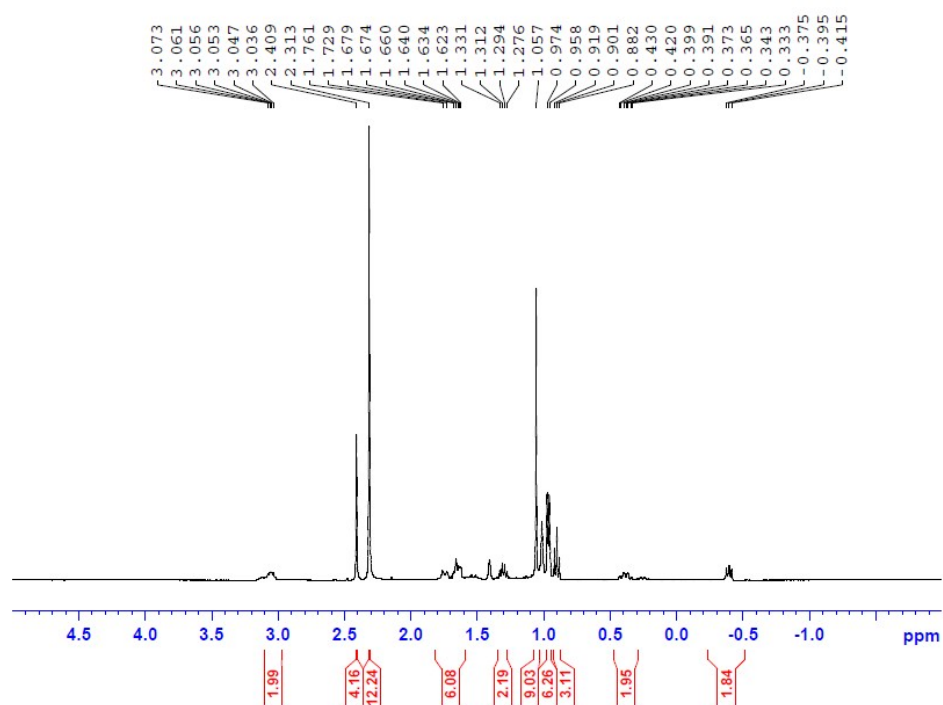


Figure S11. ¹H NMR of [(TMEDA)Na(μ-cis-DMP)(μ-nBu)ZnBu] (7) in cyc-C₆D₁₂.

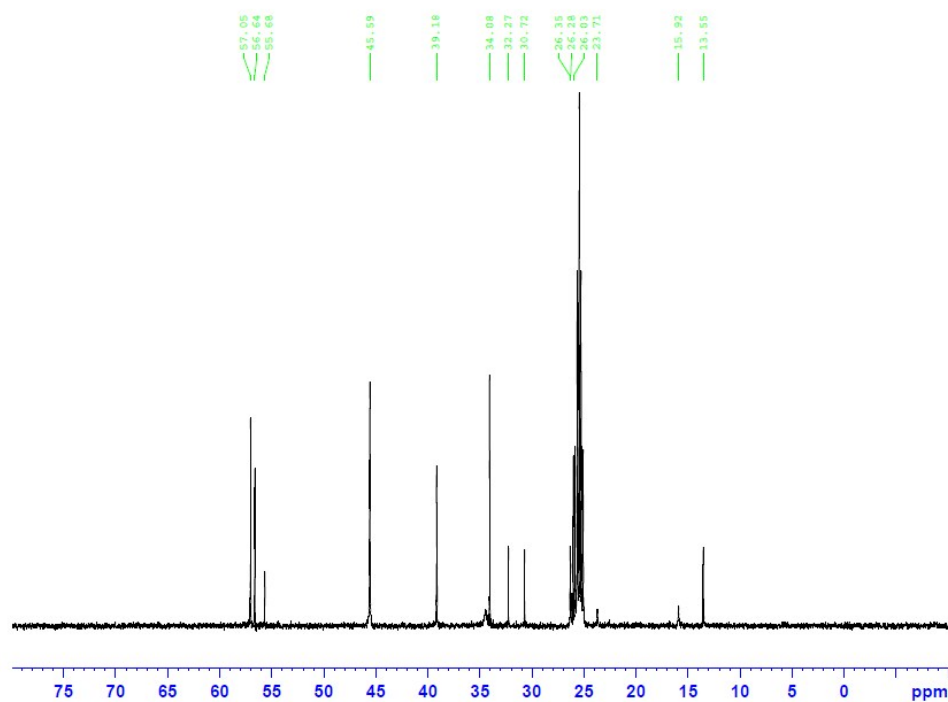


Figure S12. ¹³C NMR of [(TMEDA)Na(μ-cis-DMP)(μ-nBu)ZnBu] (7) in cyc-C₆D₁₂.

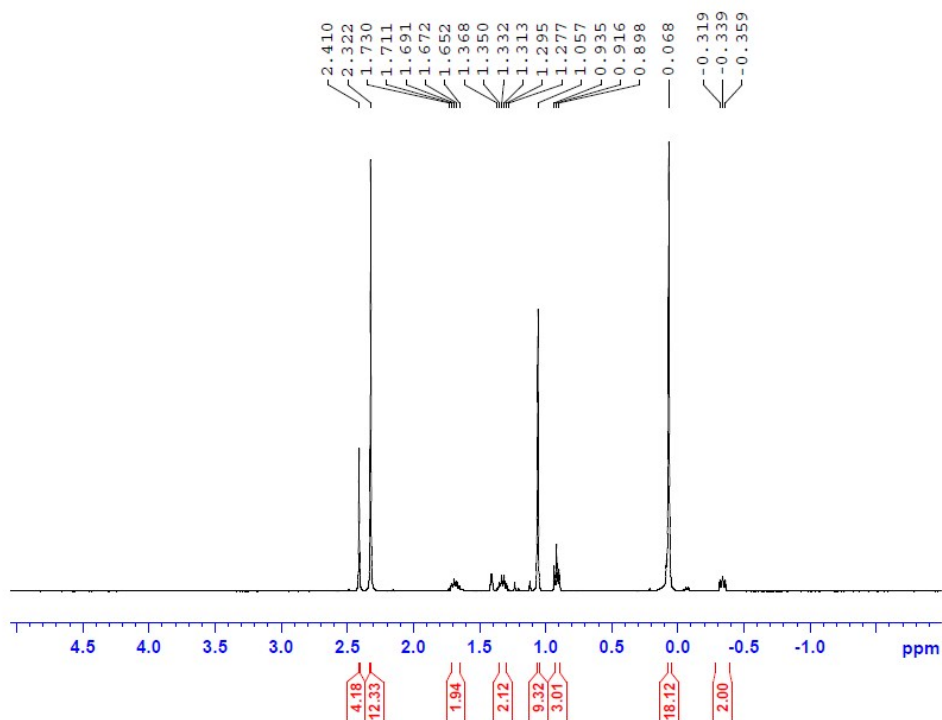


Figure S13. ¹H NMR of [(TMEDA)Na(μ-HMDS)(μ-*n*Bu)Zn^{*n*}Bu] (**8**) in cyc-C₆D₁₂.

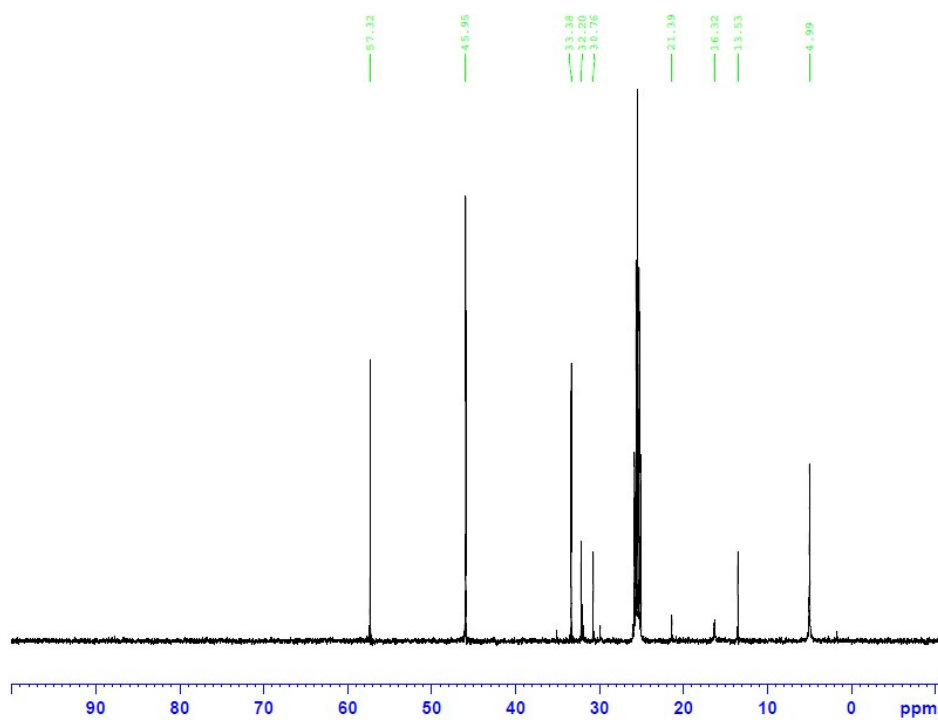


Figure S14. ¹³C NMR of [(TMEDA)Na(μ-HMDS)(μ-*n*Bu)Zn^{*n*}Bu] (**8**) in cyc-C₆D₁₂.

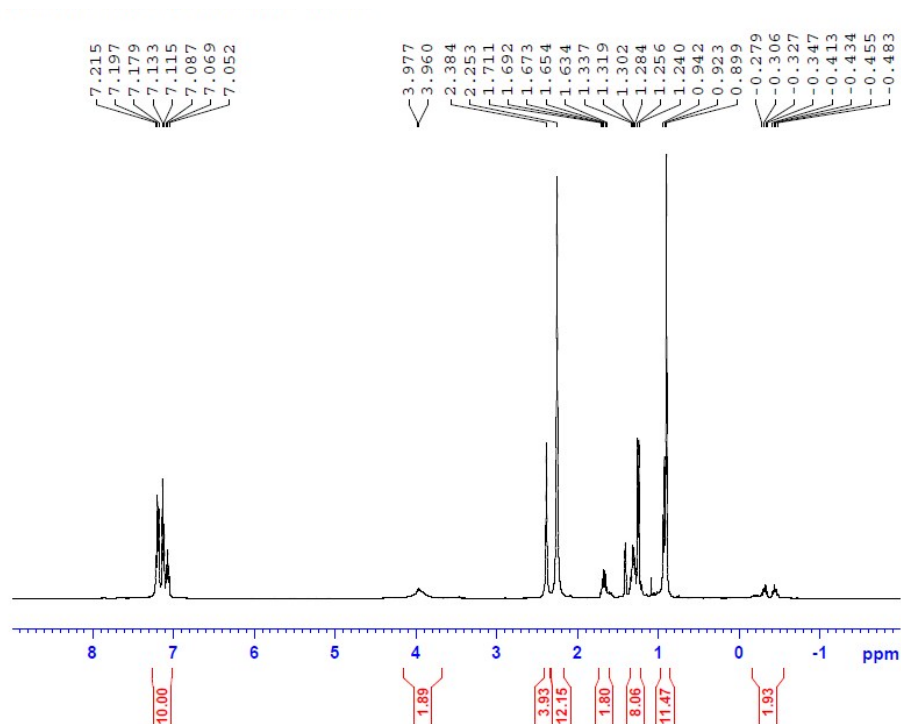


Figure S15. ¹H NMR of [(TMEDA)Na(μ-PEA)(μ-*n*Bu)Zn'*n*Bu] (9) in *cyc*-C₆D₁₂.

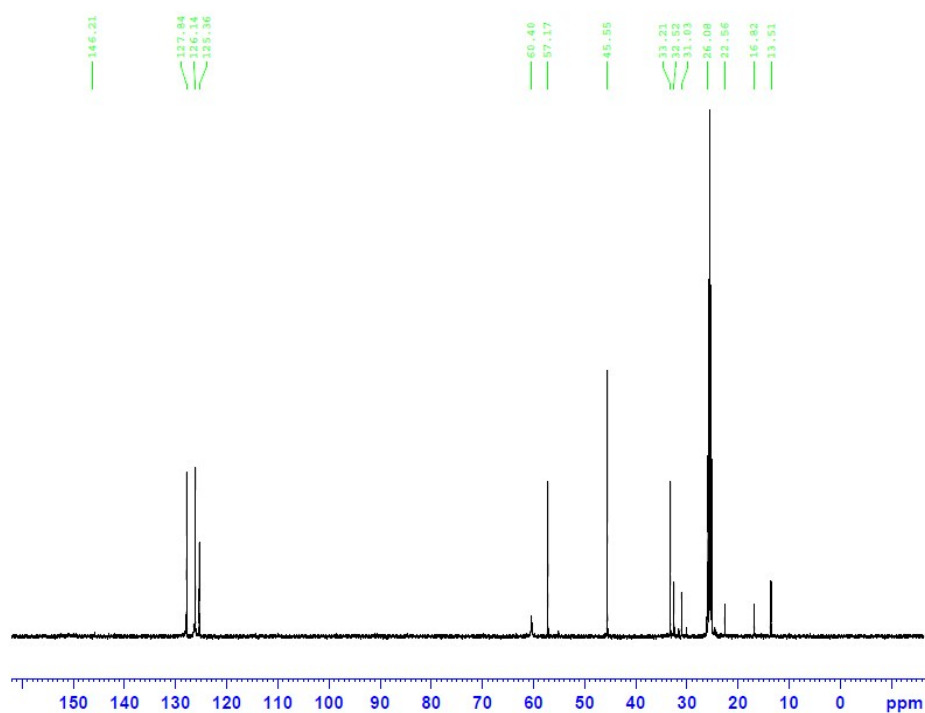


Figure S16. ¹³C NMR of [(TMEDA)Na(μ-PEA)(μ-*n*Bu)Zn'*n*Bu] (9) in *cyc*-C₆D₁₂.

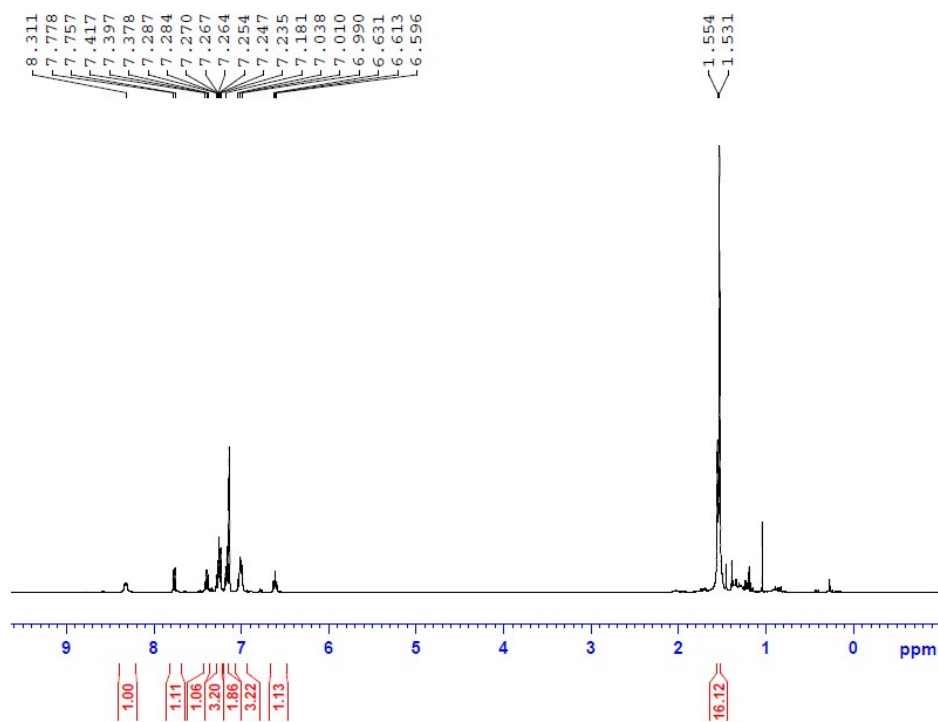


Figure S17. ¹H NMR of [(TMEDA)NaN(Ph)(1-Naphthyl)]₂ (**10**) in C₆D₆.

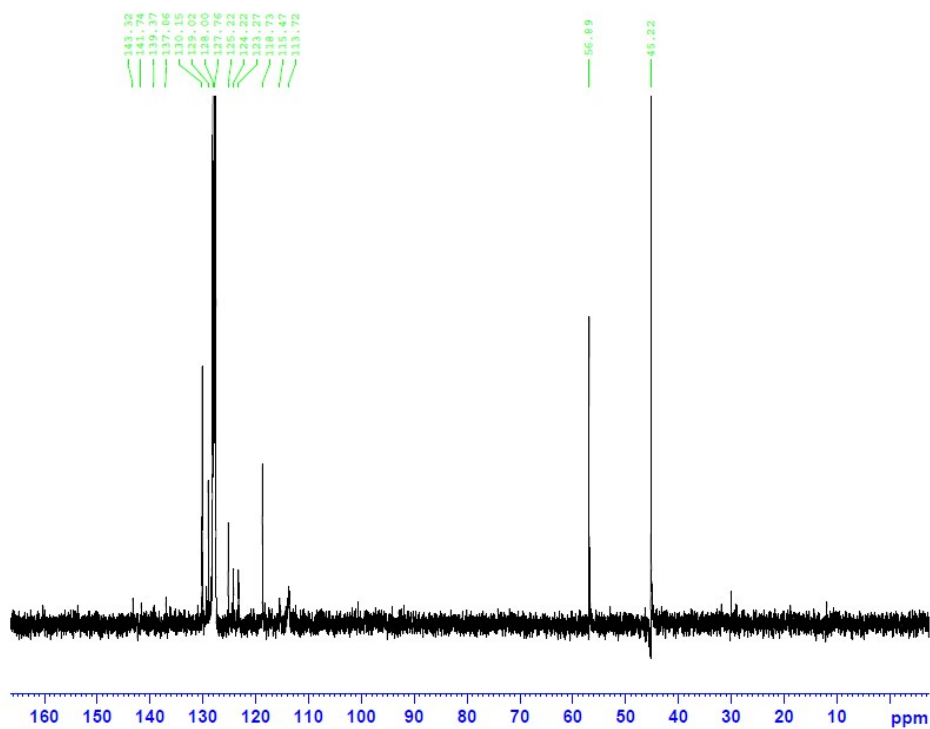


Figure S18. ¹³C NMR of [(TMEDA)NaN(Ph)(1-Naphthyl)]₂ (**10**) in C₆D₆.

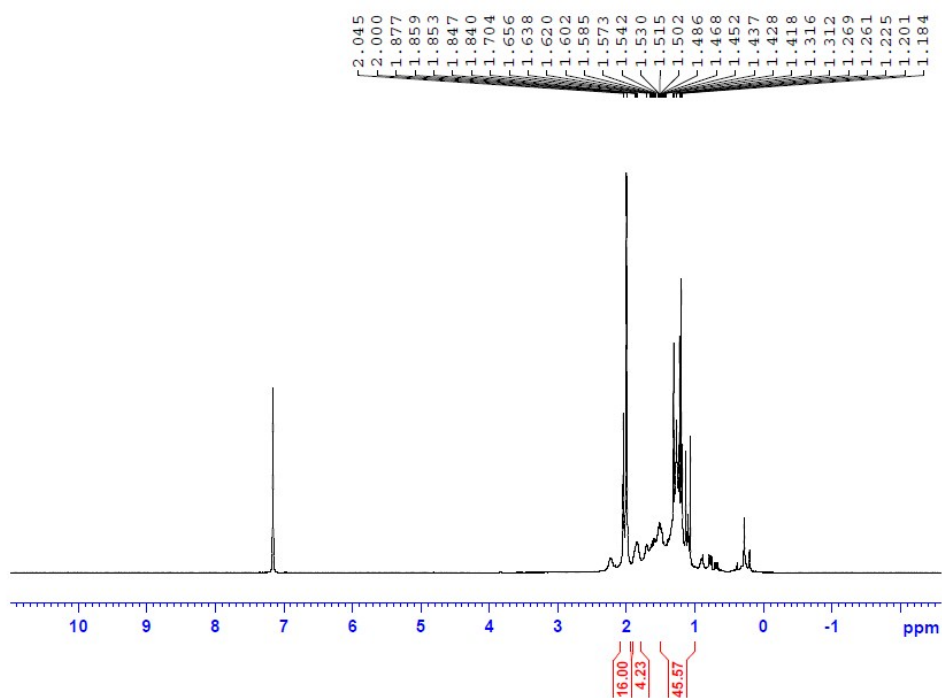


Figure S19. ¹H NMR of [(TMEDA)Na(μ-TMP)(μ-TEMPO)Zn'Bu] (12) in C₆D₆.

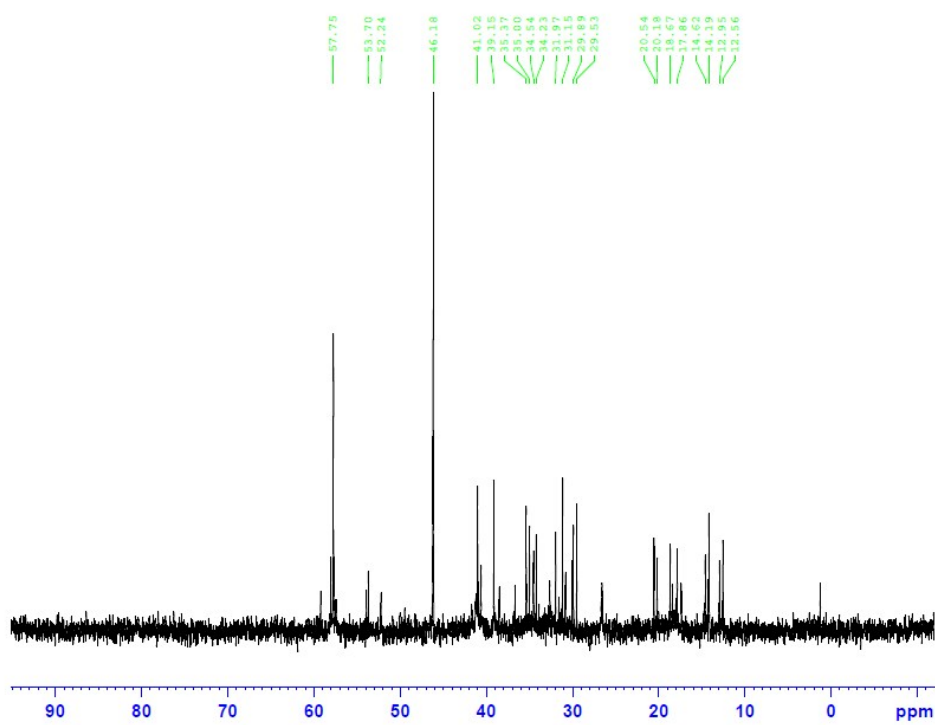


Figure S20. ¹³C NMR of [(TMEDA)Na(μ-TMP)(μ-TEMPO)Zn'Bu] (12) in C₆D₆.

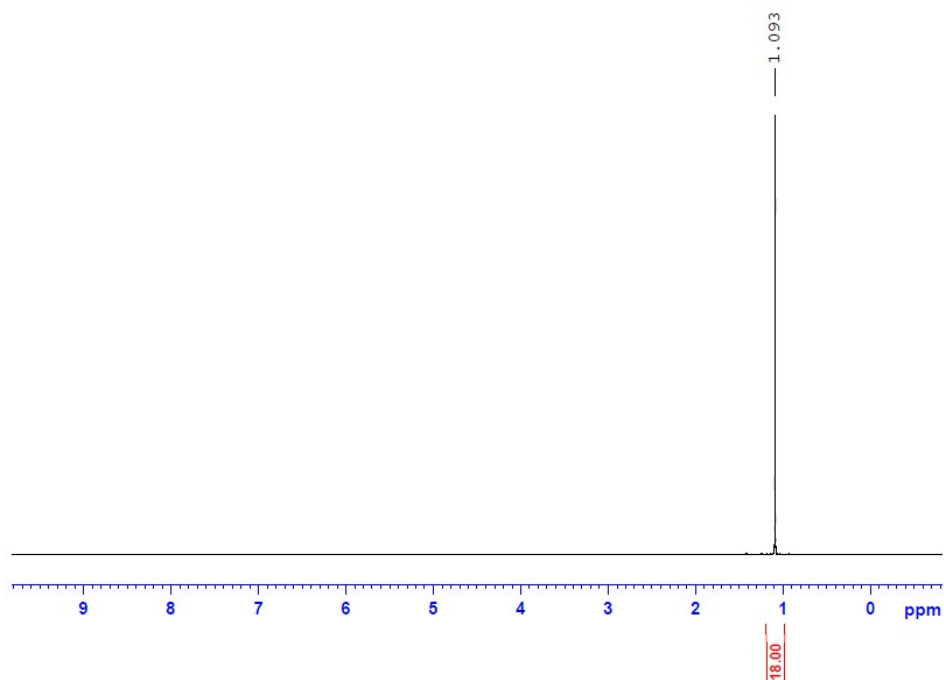


Figure S21. ^1H NMR of Bu_2Zn in $\text{cyc-C}_6\text{D}_{12}$.

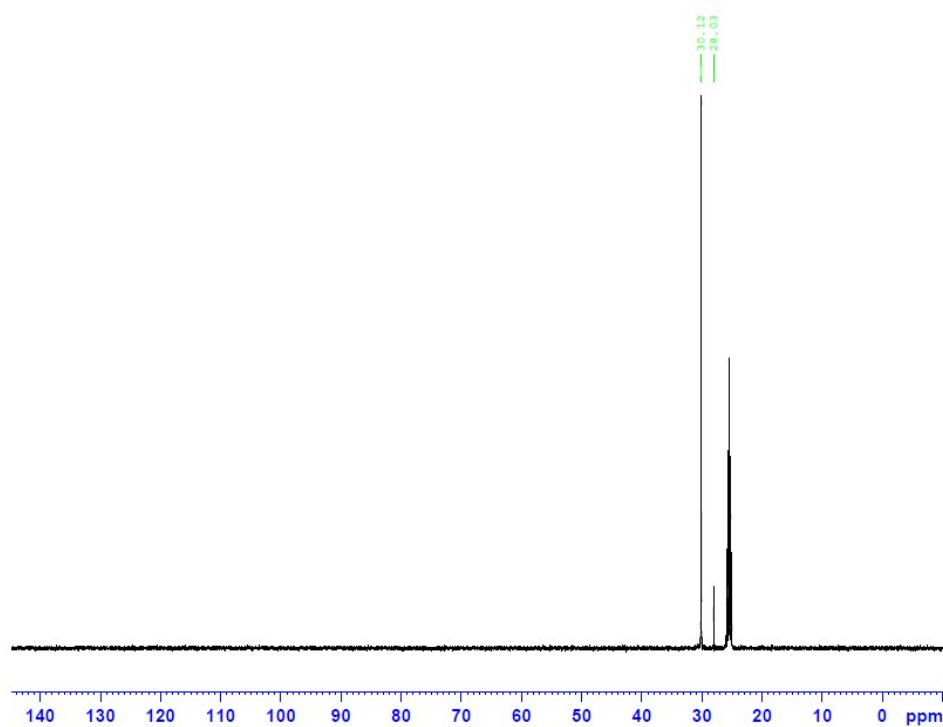


Figure S22. ^{13}C NMR of Bu_2Zn in $\text{cyc-C}_6\text{D}_{12}$.

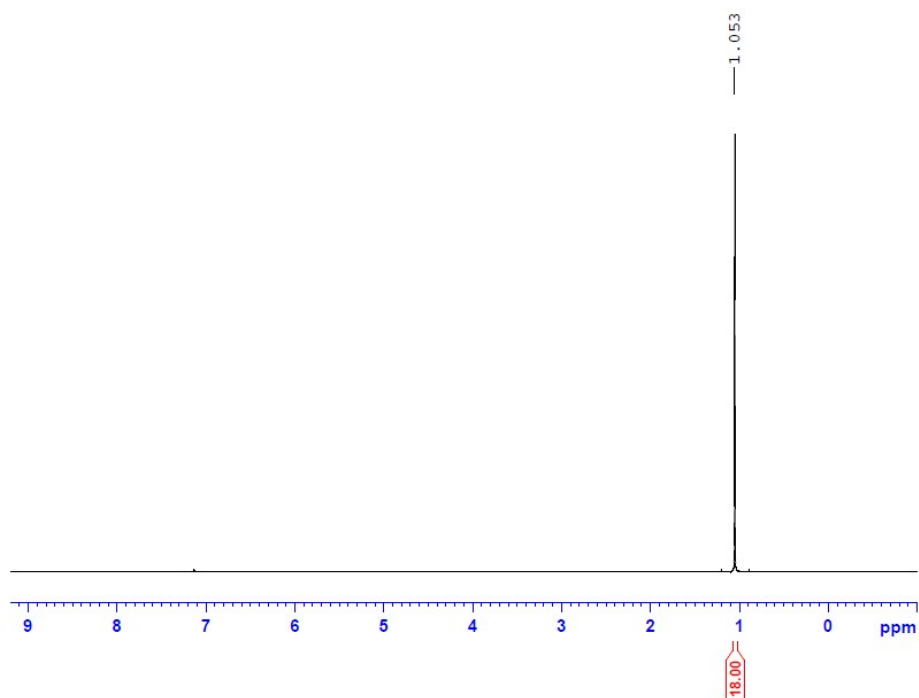


Figure S23. ^1H NMR of $t\text{Bu}_2\text{Zn}$ in C_6D_6 .

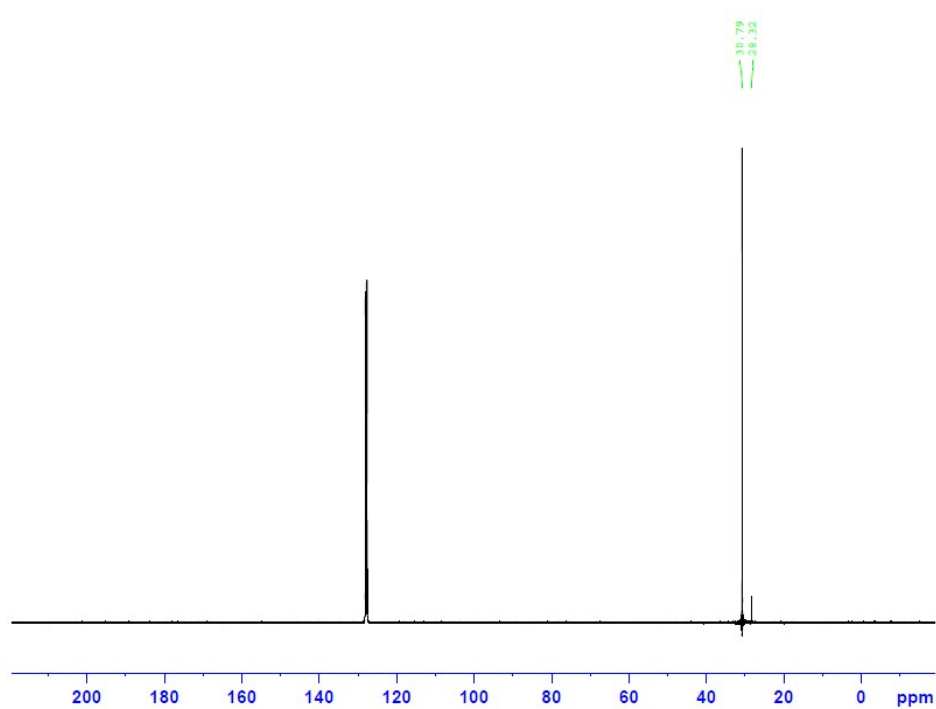


Figure S24. ^{13}C NMR of $t\text{Bu}_2\text{Zn}$ in C_6D_6 .

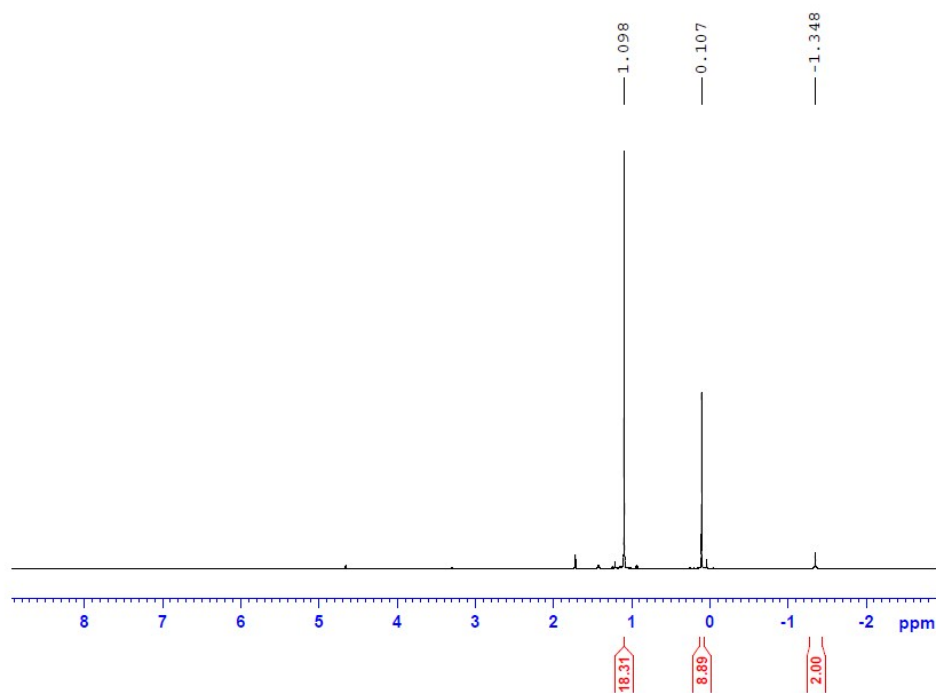


Figure S25. ^1H NMR of a mixture $(\text{CH}_2\text{SiMe}_3)\text{Na} + t\text{Bu}_2\text{Zn}$ in $\text{cyc-C}_6\text{D}_{12}$.

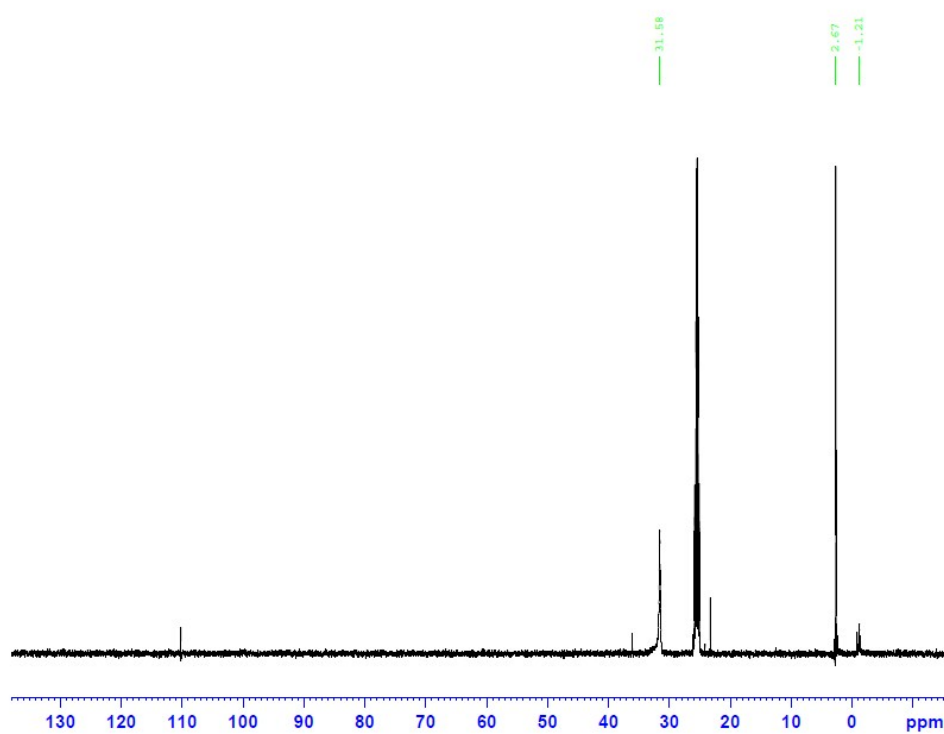


Figure S26. ^{13}C NMR of a mixture $(\text{CH}_2\text{SiMe}_3)\text{Na} + t\text{Bu}_2\text{Zn}$ in $\text{cyc-C}_6\text{D}_{12}$.

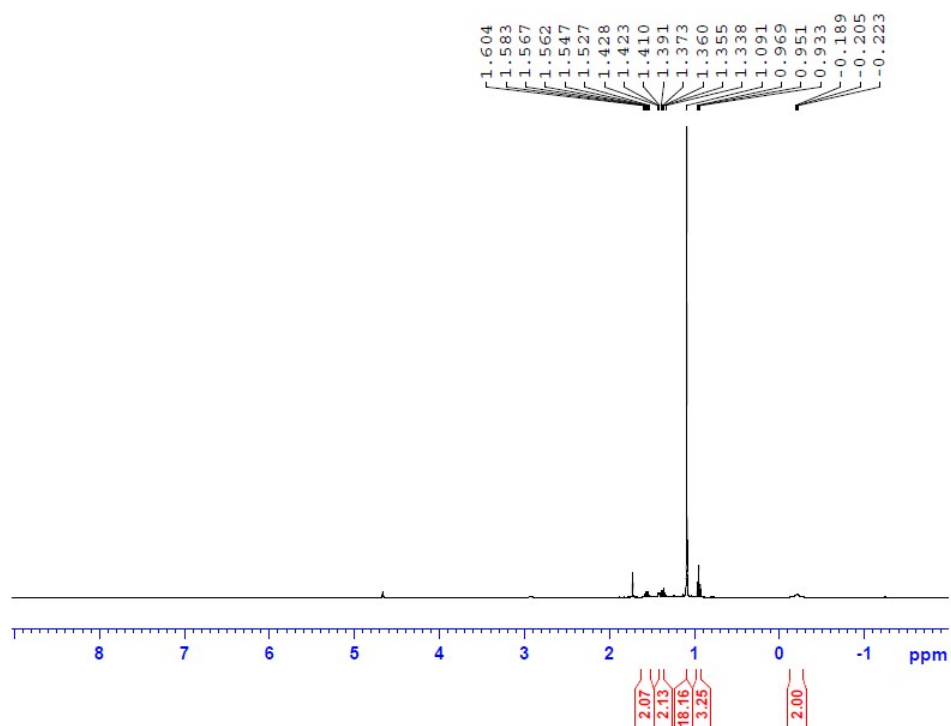


Figure S27. ¹H NMR of a mixture *n*BuNa + *t*Bu₂Zn in cyc-C₆D₁₂.

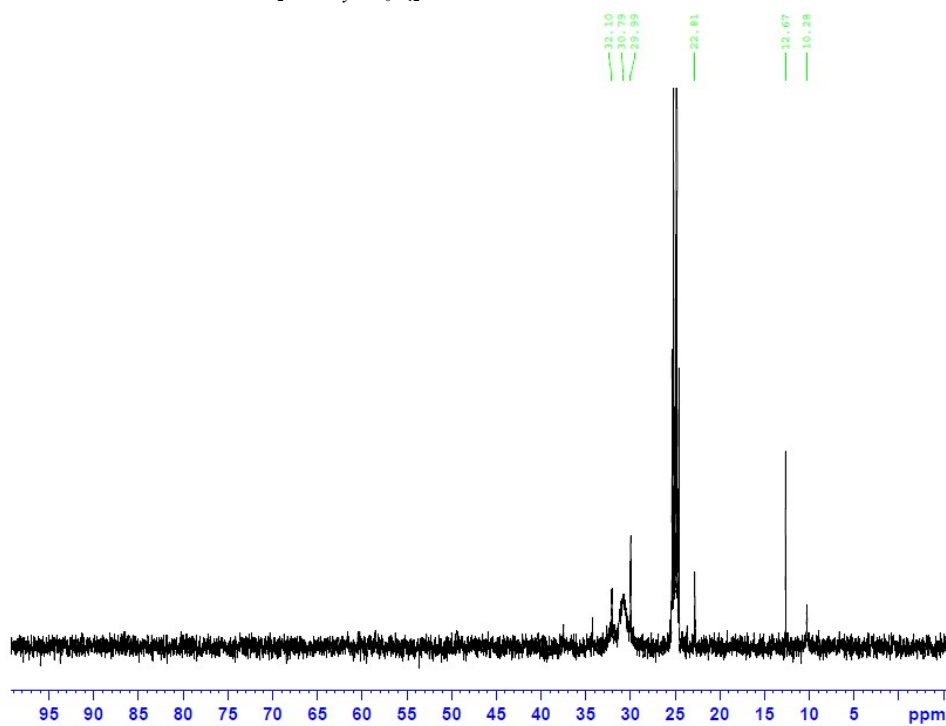


Figure S28. ¹³C NMR of a mixture *n*BuNa + *t*Bu₂Zn in cyc-C₆D₁₂.

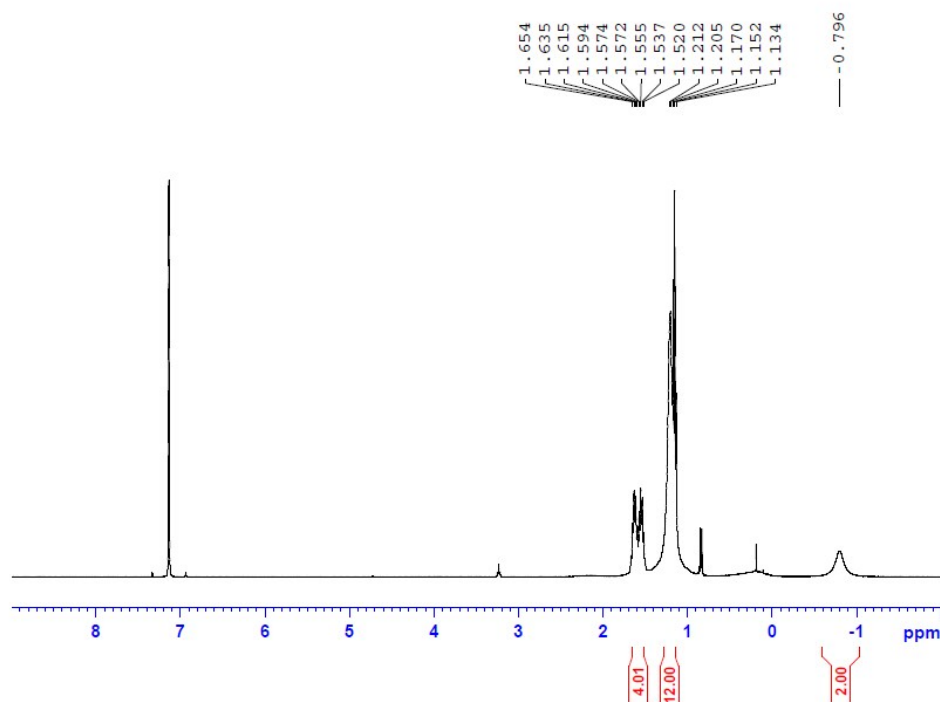


Figure S29. ^1H NMR of a mixture $n\text{BuNa} + t\text{Bu}_2\text{Zn}$ in C_6D_6 .

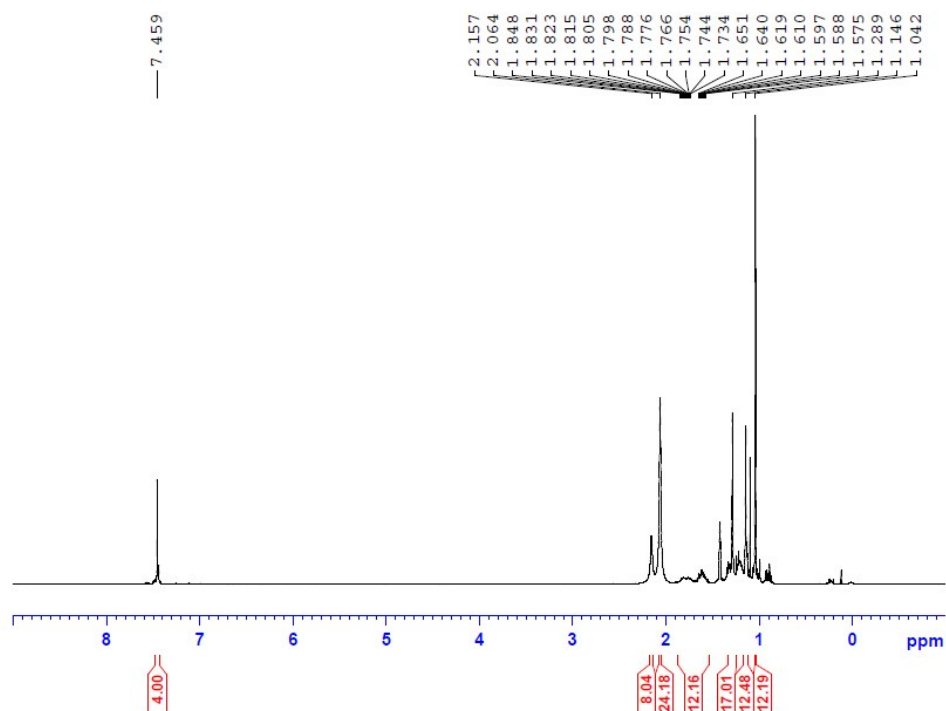


Figure S30. ^1H NMR of $\{(\text{TMEDA})\text{Na}(\mu\text{-TMP})\text{Zn}(t\text{Bu})_2\text{C}_6\text{H}_4\}$ in $\text{cyc-C}_6\text{D}_{12}$.

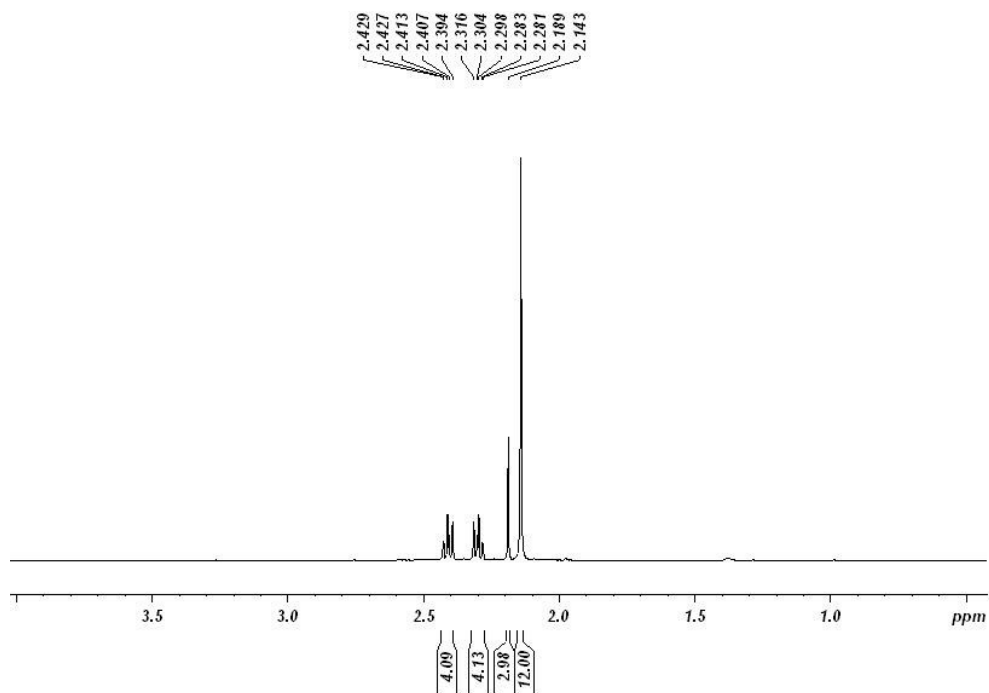


Figure S31. ¹H NMR of PMEDTA in *cyc*-C₆D₁₂.

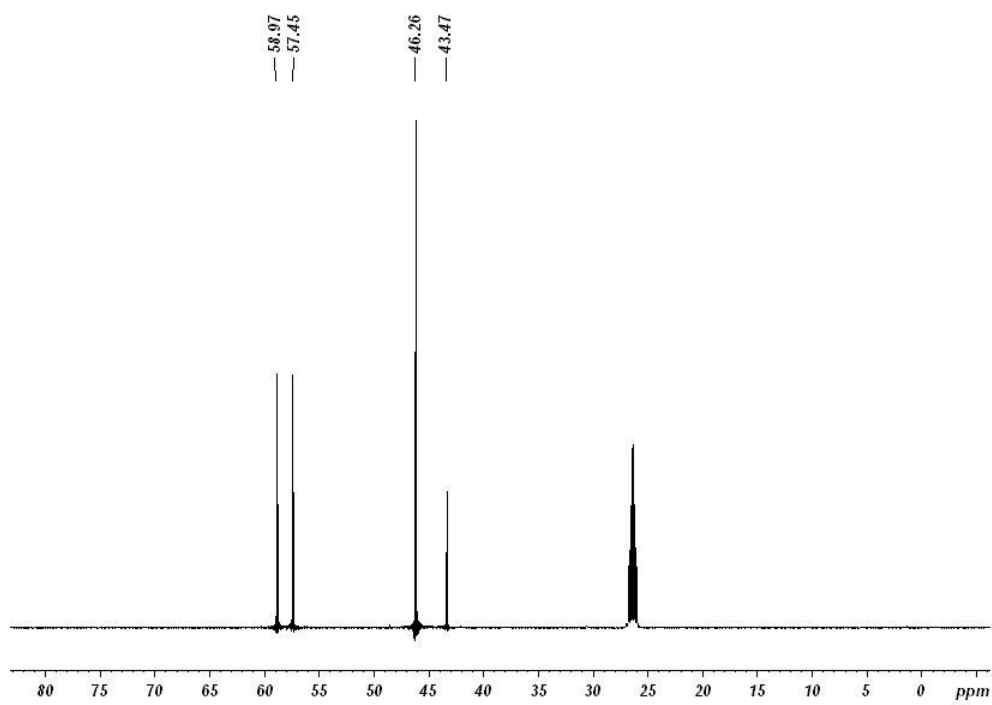


Figure S32. ¹³C NMR of PMEDTA in *cyc*-C₆D₁₂.

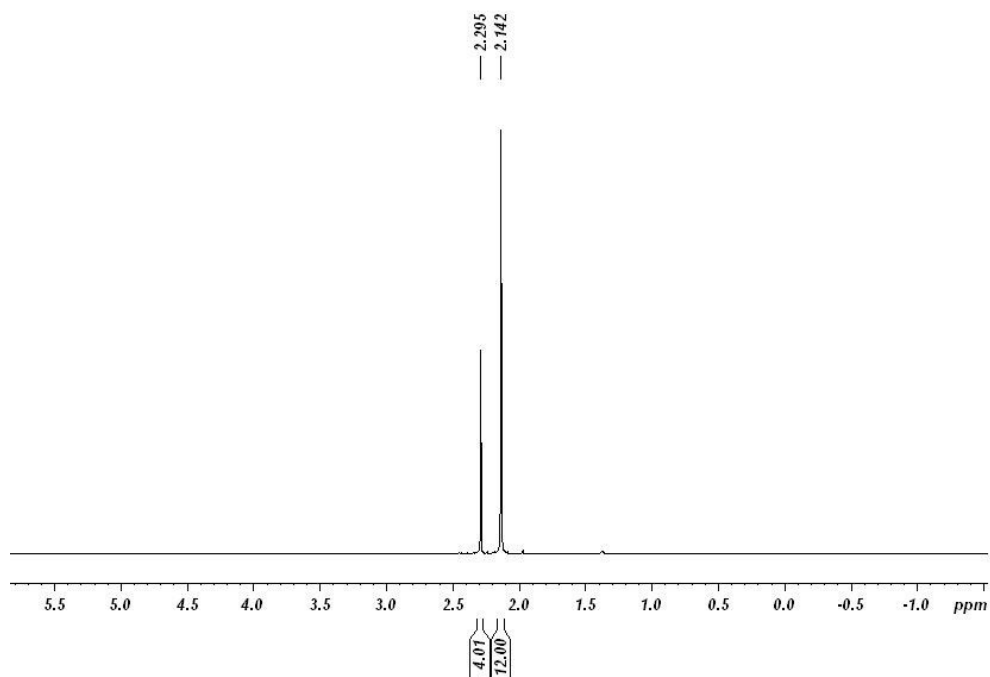


Figure S33. ¹H NMR of TMEDA in *cyc*-C₆D₁₂.

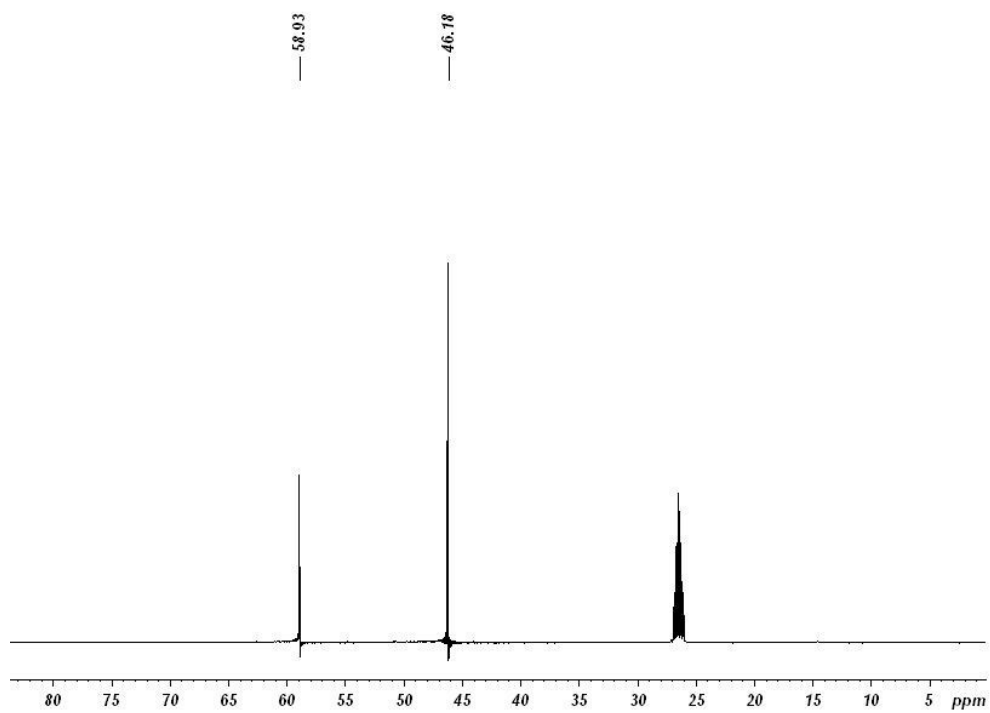


Figure S34. ¹³C NMR of TMEDA in *cyc*-C₆D₁₂.

Table S1. Crystal data and structure refinement parameters.

	2	3	4	5	6	8	9	10	12
Formula	C ₂₁ H _{52.3} N ₃ NaSi _{1.16} Zn	C ₂₁ H ₅₀ N ₃ NaZn	C ₂₆ H ₅₅ N ₂ NaZn	C ₂₃ H ₅₂ N ₃ NaZn	C ₂₃ H ₅₄ N ₃ NaSiZn	C ₂₀ H ₅₂ N ₃ NaSi ₂ Zn	C ₃₀ H ₅₂ N ₃ NaZn	C ₄₄ H ₅₆ N ₆ Na ₂	C ₂₈ H ₆₁ N ₄ NaOZn
Formula weight	467.86	433.00	484.08	459.04	489.14	479.19	543.11	714.93	558.17
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> <i>n</i> <i>m</i> <i>a</i>	<i>P</i> -1	<i>P</i> <i>n</i> <i>m</i> <i>a</i>	<i>P</i> 2 ₁	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	9.3481(8)	8.9544(4)	16.6824(6)	20.3535(4)	10.7214(6)	20.6820(8)	11.3918(2)	9.6350(6)	10.5426(9)
<i>b</i> [Å]	15.2611(9)	17.3198(6)	10.3773(3)	12.3267(3)	11.3849(5)	13.2093(5)	12.8158(3)	10.5208(6)	10.6529(9)
<i>c</i> [Å]	20.2444(15)	17.1909(6)	16.9440(5)	10.8623(2)	14.4618(10)	10.5957(5)	21.9314(4)	20.1793(7)	15.3375(13)
α [°]					67.460(5)			93.485(4)	86.581(7)
β [°]	98.331(7)	93.431(4)	102.622(3)		73.938(5)		95.897(2)	97.698(4)	73.239(8)
γ [°]					64.719(5)			99.085(5)	76.553(7)
<i>V</i> [Å ³]	2857.6(4)	2661.33(18)	2862.43(16)	2725.26(10)	1460.69(14)	2894.7(2)	3184.93(11)	1994.72(18)	1604.1(2)
<i>Z</i>	4	4	4	4	2	4	4	2	2
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.087	1.081	1.123	1.119	1.112	1.100	1.133	1.190	1.156
Absorption coefficient [mm ⁻¹]	0.910	0.948	0.887	0.929	0.910	2.172	1.341	0.089	0.804
<i>T</i> [K]	123	123	123	123	123	123	123	123	123
Radiation type, wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	1.54184	1.54184	0.71073	0.71073
2 θ max [°]	52	58	54.00	60.62	54	146.32	145.72	58.17	54.00
Reflections collected	36410	14151	19545	15899	29718	10564	40601	53408	17293
Reflections unique	6216	6541	6244	4022	6281	2978	11813	9799	7011
Reflections obs	4659	4264	5089	3277	5259	2505	10481	7405	5790
Goodness-of-fit on F ²	1.074	1.009	1.031	1.033	1.038	1.113	1.037	1.020	1.025
Final <i>R</i> indexes [I>2 σ (I)]	R1 = 0.0897 wR2 = 0.2359	R1 = 0.0493 wR2 = 0.0927	R1 = 0.0313 wR2 = 0.0676	R1 = 0.0275 wR2 = 0.0600	R1 = 0.0440 wR2 = 0.1041	R1 = 0.0408 wR2 = 0.0897	R1 = 0.0388 wR2 = 0.0904	R1 = 0.0550 wR2 = 0.1334	R1 = 0.0456 wR2 = 0.0993
Final <i>R</i> indexes (all data)	R1 = 0.1130 wR2 = 0.2548	R1 = 0.0957 wR2 = 0.1095	R1 = 0.0448 wR2 = 0.0738	R1 = 0.0417 wR2 = 0.0631	R1 = 0.0579 wR2 = 0.1122	R1 = 0.0518 wR2 = 0.0949	R1 = 0.0470 wR2 = 0.0965	R1 = 0.0765 wR2 = 0.1491	R1 = 0.0605 wR2 = 0.1075
Largest diff. peak/hole [e.Å ⁻³]	1.604/-1.182	0.935/-0.662	0.396/-0.236	0.935/-0.662	0.622/-0.514	0.348/-0.298	0.317/-0.438	0.802/-0.349	1.264/-0.421

¹ G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122.