Electronic Supplementary Material (ESI) for Dalton Transactions.


# Electronic supporting information

## Solid state and solution studies of *n*-butyllithium magnesiates stabilised by Lewis donors.

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# INDEX

**Table 1.** Crystal data and structure refinement details.

| **Lithium magnesiate** | **1** | **2** | **3** | **5** | **6** |
|---|---|---|---|---|---|
| Formula | $C_{38}H_{90}Li_2Mg_2N_4$ | $C_{42}H_{100}Li_2Mg_2N_6$ | $C_{44}H_{98}Li_2Mg_2N_4$ | $C_{36}H_{86}Li_2Mg_2N_4O_2$ | $C_{19}H_{38}LiMgO_2$ |
| Formula weight | 665.64 | 751.78 | 745.76 | 669.59 | 329.74 |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | P bca | P $2_1$/n | P $2_1$ | P $2_1$/c | C 2/c |
| *a* [Å] | 13.8489(4) | 12.0911(7) | 9.9060(12) | 10.0718(2) | 10.5458(8) |
| *b*[Å] | 17.5351(6) | 15.5710(7) | 14.5510(13) | 13.5833(2) | 22.265(2) |
| *c*[Å] | 19.0192(7) | 13.7974(7) | 17.7804(17) | 16.9469(3) | 18.0116(12) |
| $\beta$ [°] | 90 | 101.390(6) | 96.405(11) | 95.751(2) | 93.437(7) |
| *V* [Å$^3$] | 4618.7(3) | 2546.5(2) | 2546.9(5) | 2306.81(7) | 4221.6(6) |
| Z | 4 | 2 | 2 | 2 | 8 |
| $\rho_{calcd.}$[g cm$^{-3}$] | 0.957 | 0.980 | 0.972 | 0.964 | 1.038 |
| Absorption coefficient [mm$^{-1}$] | 0.641 | 0.078 | 0.077 | 0.678 | 0.090 |
| *T* [K] | 123(2) | 123(2) | 123(2) | 123(2) | 123(2) |
| Radiation type, wavelength [Å] | CuKα, 1.54180 | MoKα, 0.71073 | MoKα, 0.71073 | CuKα, 1.54180 | MoKα, 0.71073 |
| θ range for data collection [°] | 6.39 to 73.34 | 3.42 to 26.00 | 2.92 to 26.00 | 6.18 to 73.59 | 3.03 to 26.00 |
| Reflections collected | 14556 | 13451 | see experimental | 17305 | 11951 |
| Reflections unique | 4547 | 4986 | 7794 | 4601 | 4082 |
| Data/restraints/parameters | 3327 | 3167 | 4128 | 4029 | 2704 |
| Goodness-of-fit on F$^2$ | 253 | 275 | 484 | 231 | 228 |
| Final *R* indexes [I>2σ (I)] | 1.023 | 1.035 | 0.940 | 1.042 | 1.103 |
| Final *R* indexes (all data) | $R_1$= 0.0501<br>$wR_2$= 0.1387 | $R_1$= 0.0706<br>$wR_2$= 0.1839 | $R_1$= 0.0714<br>$wR_2$= 0.1625 | $R_1$= 0.0508<br>$wR_2$= 0.1450 | $R_1$ = 0.0924<br>$wR_2$ = 0.2420 |
| Largest diff. peak/hole [e.Å$^{-3}$] | $R_1$= 0.0709<br>$wR_2$= 0.1596 | $R_1$= 0.1148<br>$wR_2$= 0.2114 | $R_1$= 0.1355<br>$wR_2$= 0.1895 | $R_1$= 0.0565<br>$wR_2$= 0.1521 | $R_1$ = 0.1318<br>$wR_2$ = 0.2721 |

**NMR spectra of 1, [TMPDA·Li(μ-$^n$Bu)$_2$Mg($^n$Bu)]$_2$**

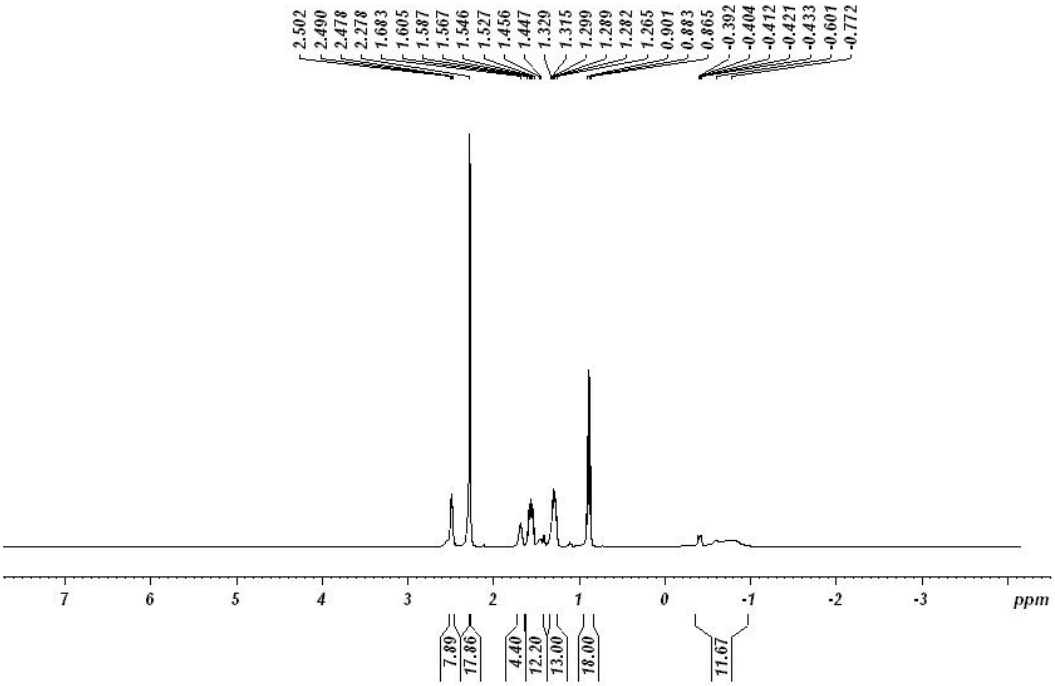


**Fig. S1**. $^1$H NMR Spectrum of **1** in *cyc*-$C_6D_{12}$ solution.

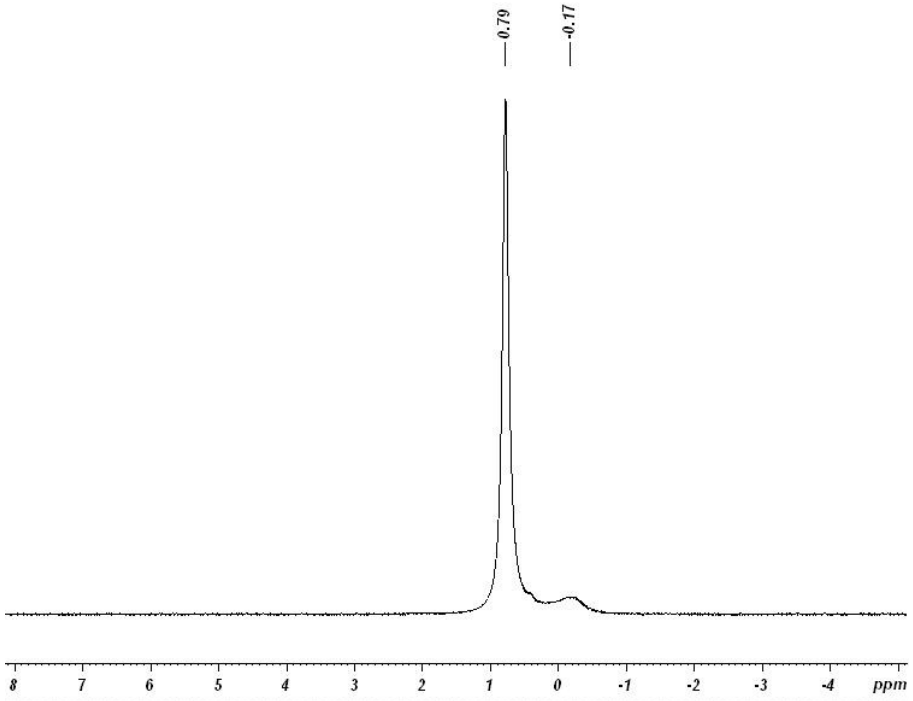


**Fig. S2**. $^7$Li NMR Spectrum of **1** in *cyc*-$C_6D_{12}$ solution.

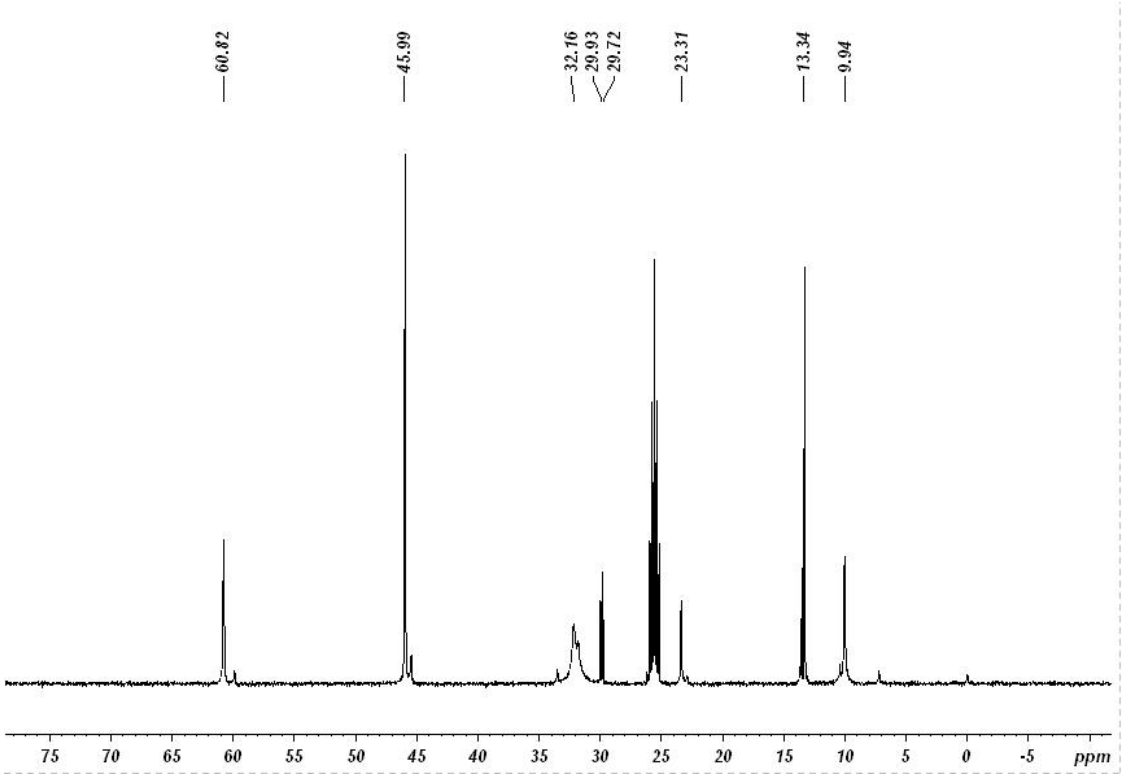


**Fig. S3.** $^{13}C$ NMR Spectrum of **1** in *cyc*-$C_6D_{12}$ solution.

**NMR spectra of 2, [(PMDETA)Li(μ-$^n$Bu)Mg(μ-$^n$Bu)($^n$Bu)]$_2$**

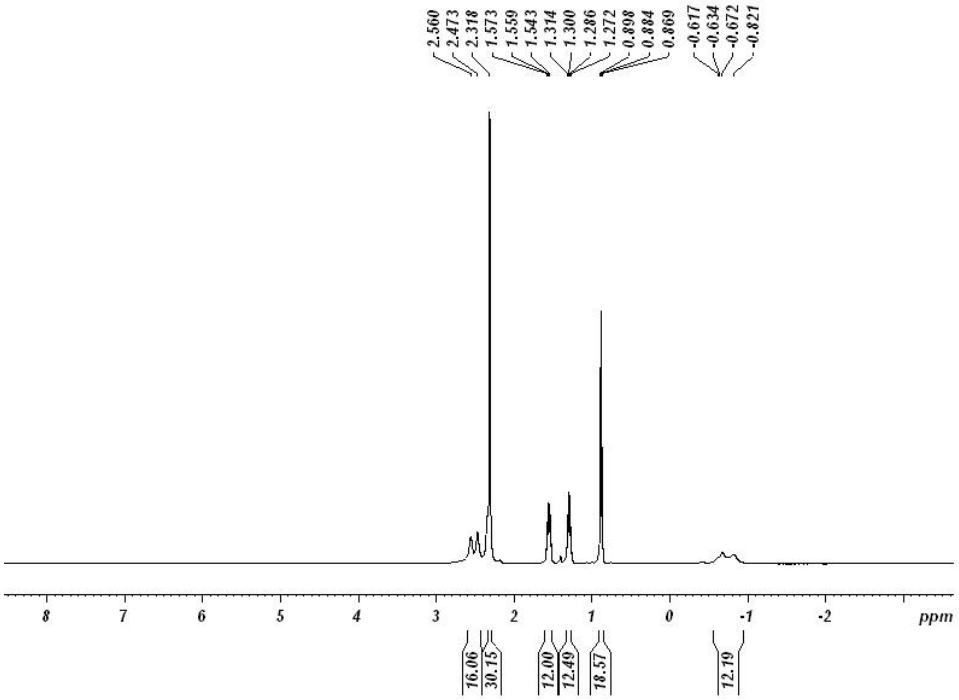


**Fig S4.** $^1H$ NMR Spectrum of **2** in *cyc*-$C_6D_{12}$ solution.

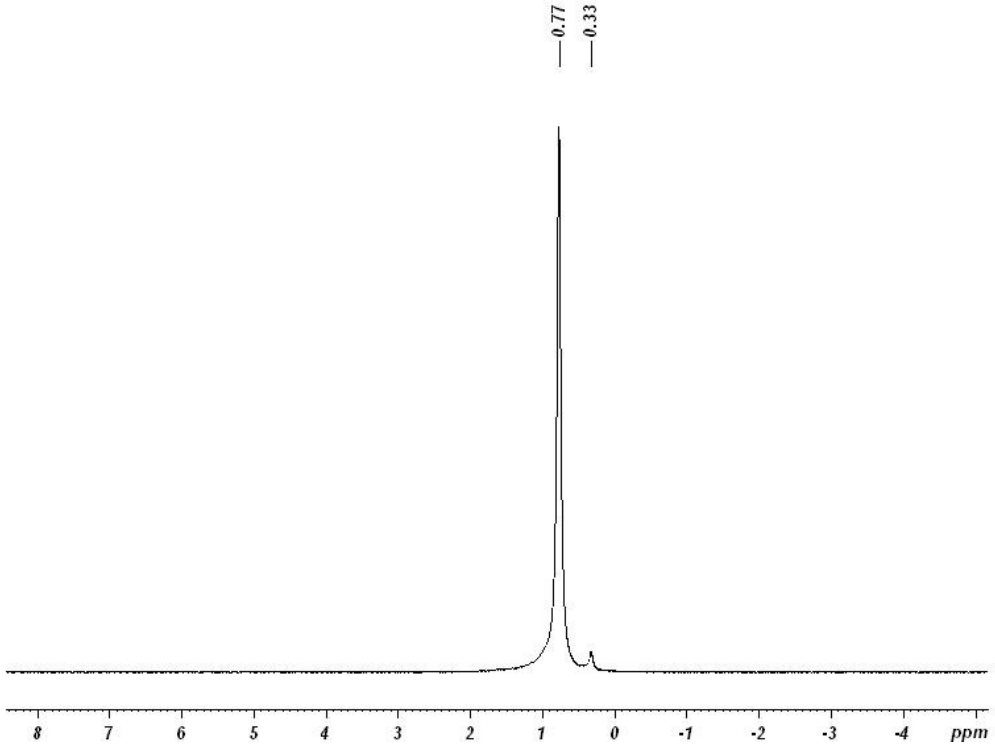


**Fig. S5.** $^{7}$Li NMR Spectrum of **2** in *cyc*-$C_6D_{12}$ solution.

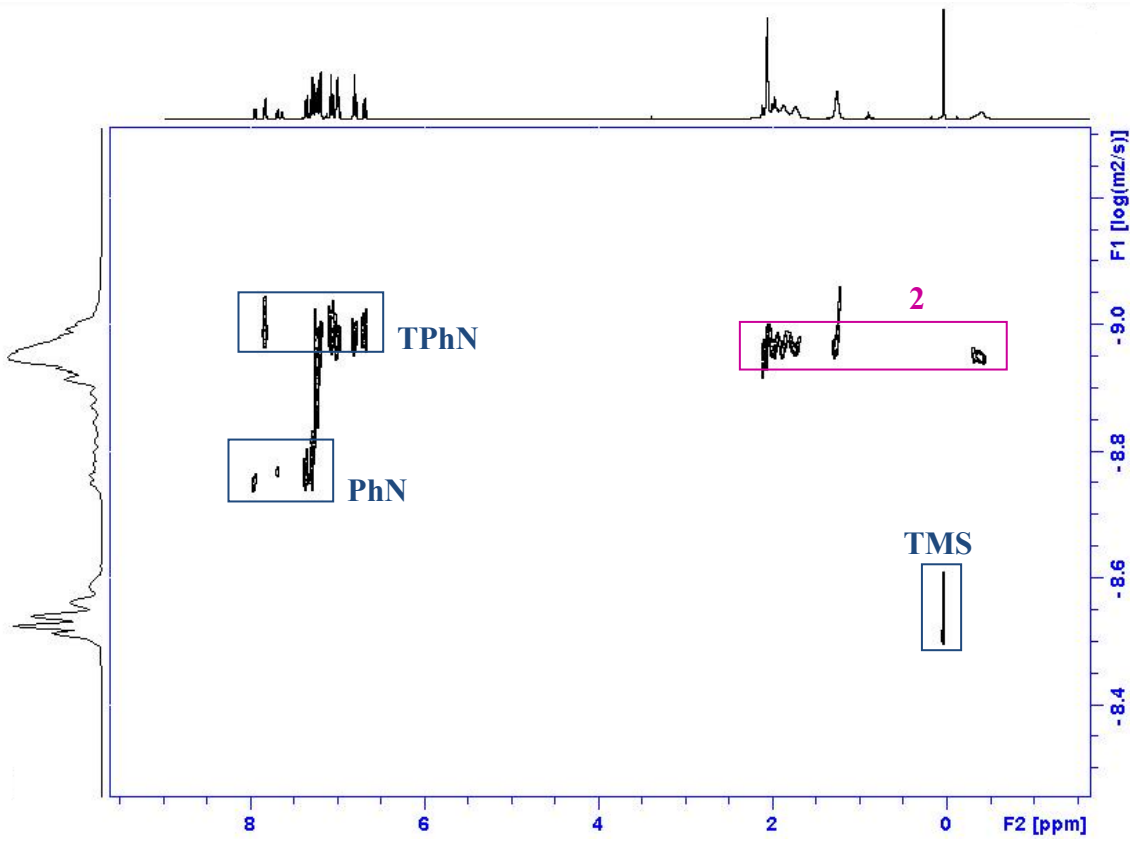


**Fig. S6.** $^{1}$H-DOSY spectrum of **2** in D$^{8}$-toluene solution.

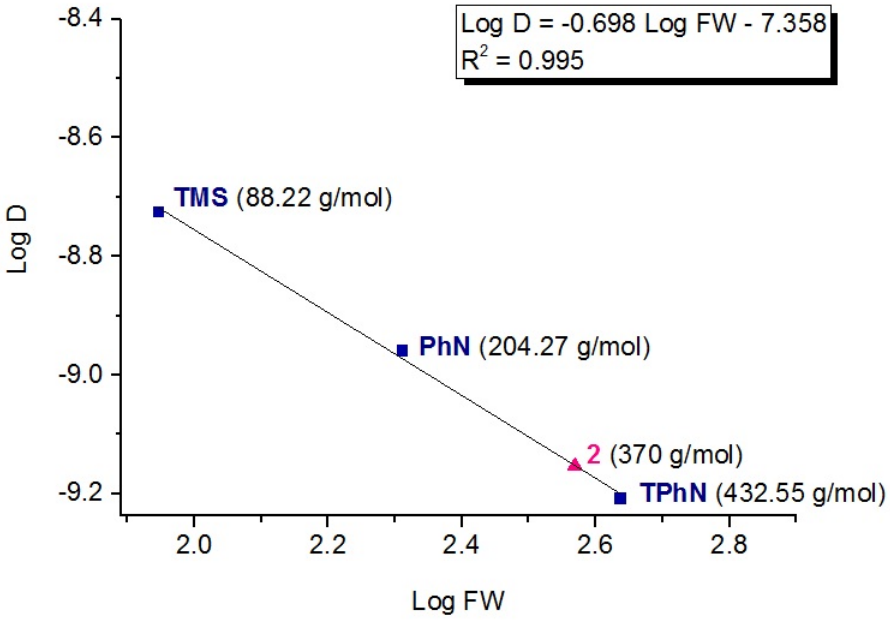


**Fig. S7.** log *D* – log FW representation from the $^{1}$H-DOSY data obtained for the mixture of **2,** TPhN, PhN and TMS in D$^{8}$-toluene

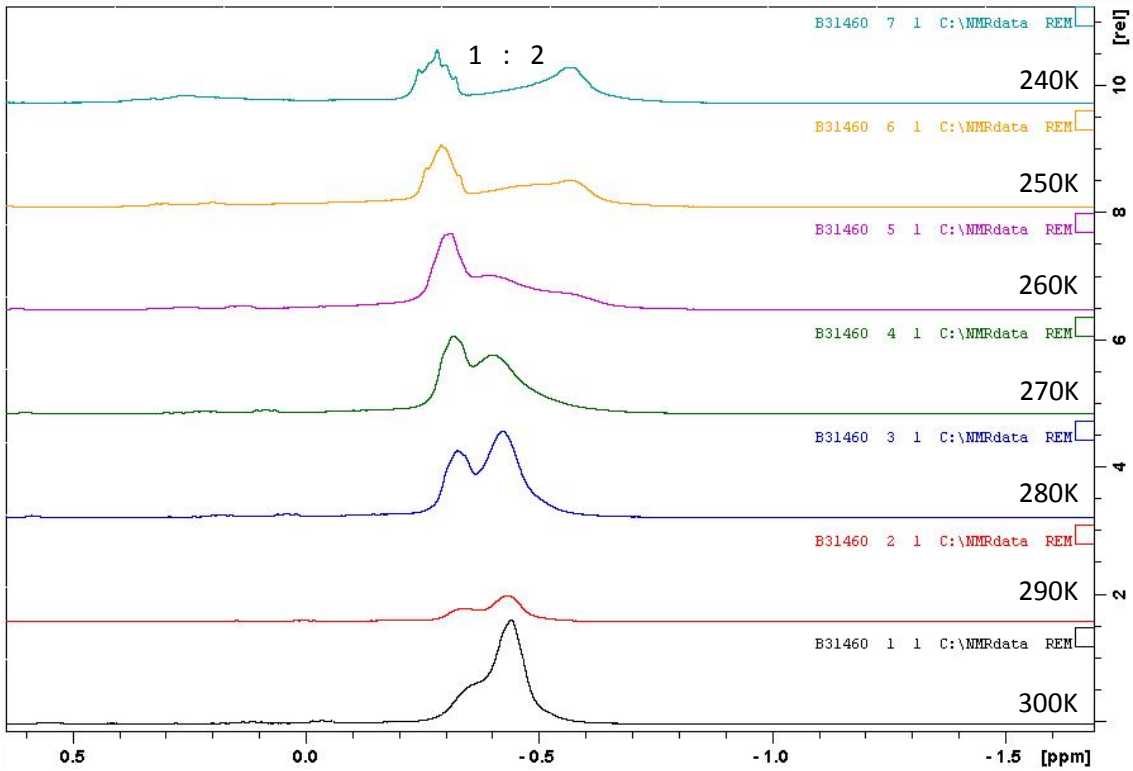


**Fig. S8.** Variable temperature experiments of **2** in D$^{8}$-toluene.

**NMR spectra of 3, [(*R*,*R*)-TMCDA·Li(μ-Bu)$_2$Mg(Bu)]$_2$**

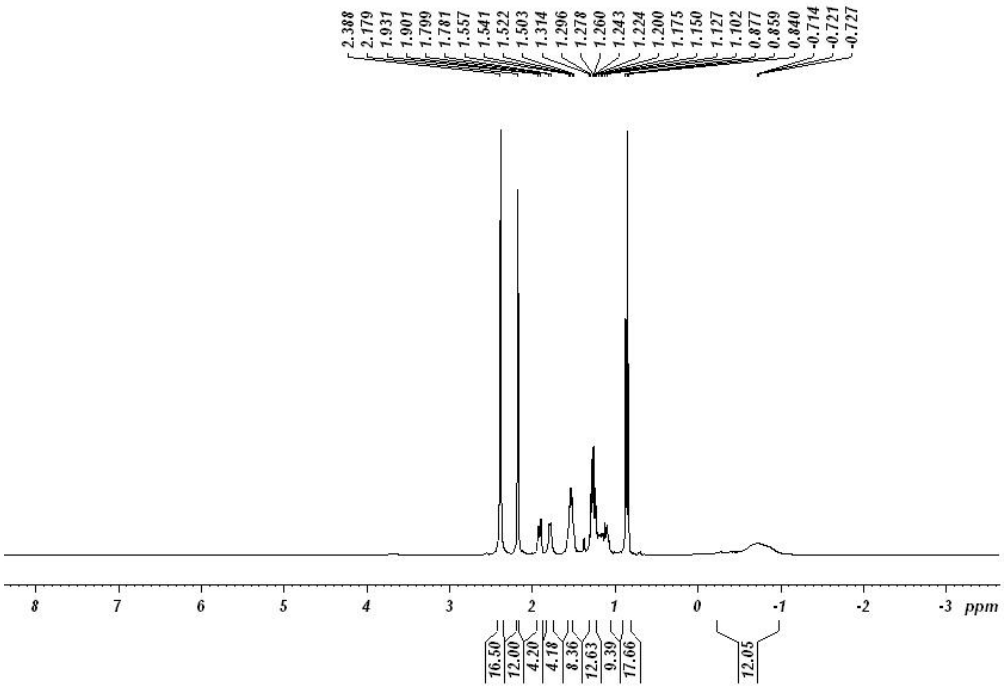


**Fig. S9.** $^{1}$H NMR Spectrum of **3** in *cyc*-$C_6D_{12}$ solution.

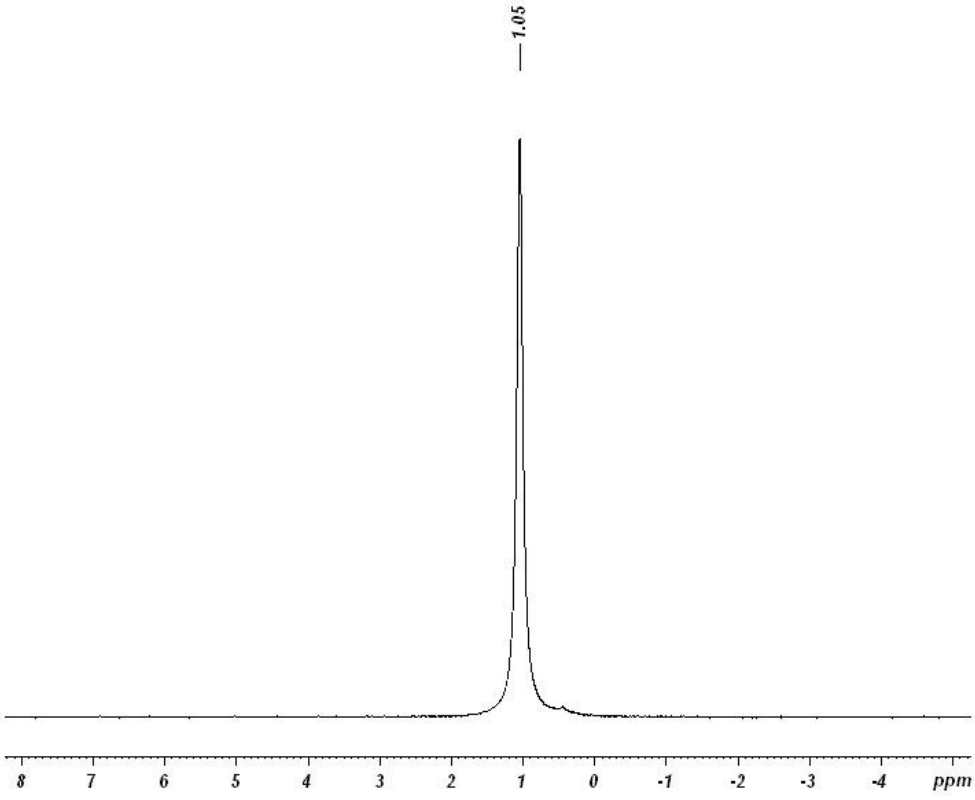


**Fig. S10.** $^{7}$Li NMR Spectrum of **3** in *cyc*-$C_6D_{12}$ solution.

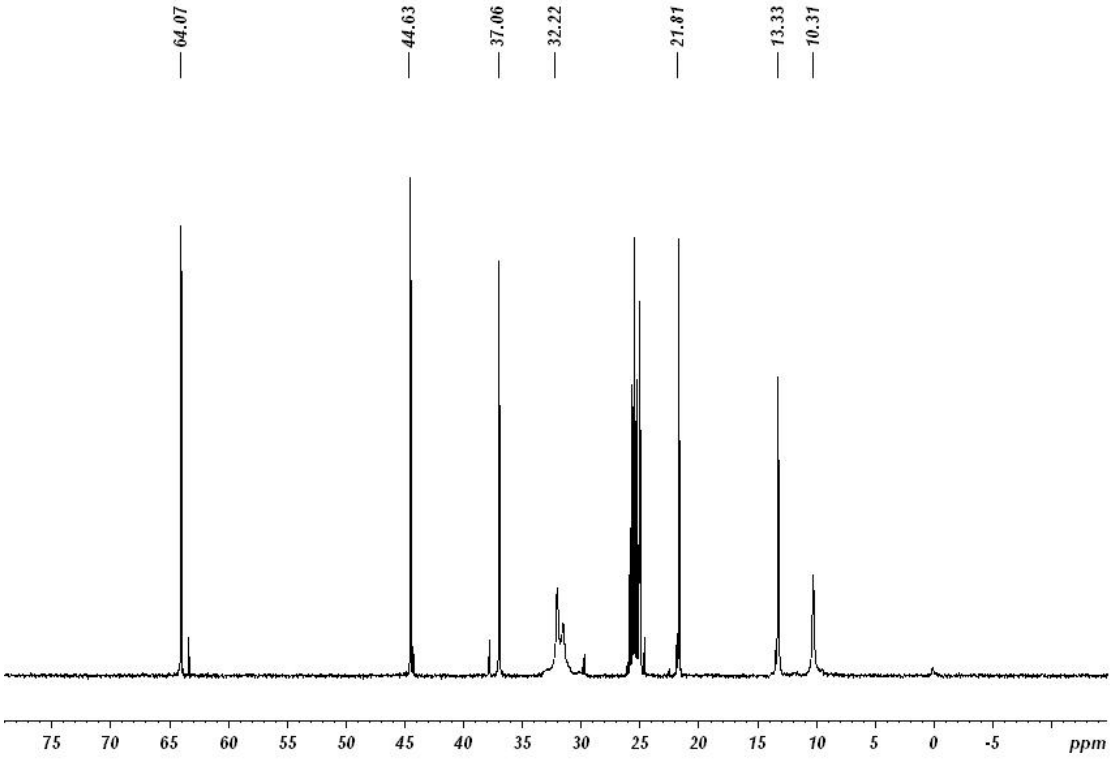


**Fig. S11.** $^{13}C$ NMR Spectrum of **3** in *cyc*-$C_6D_{12}$ solution.

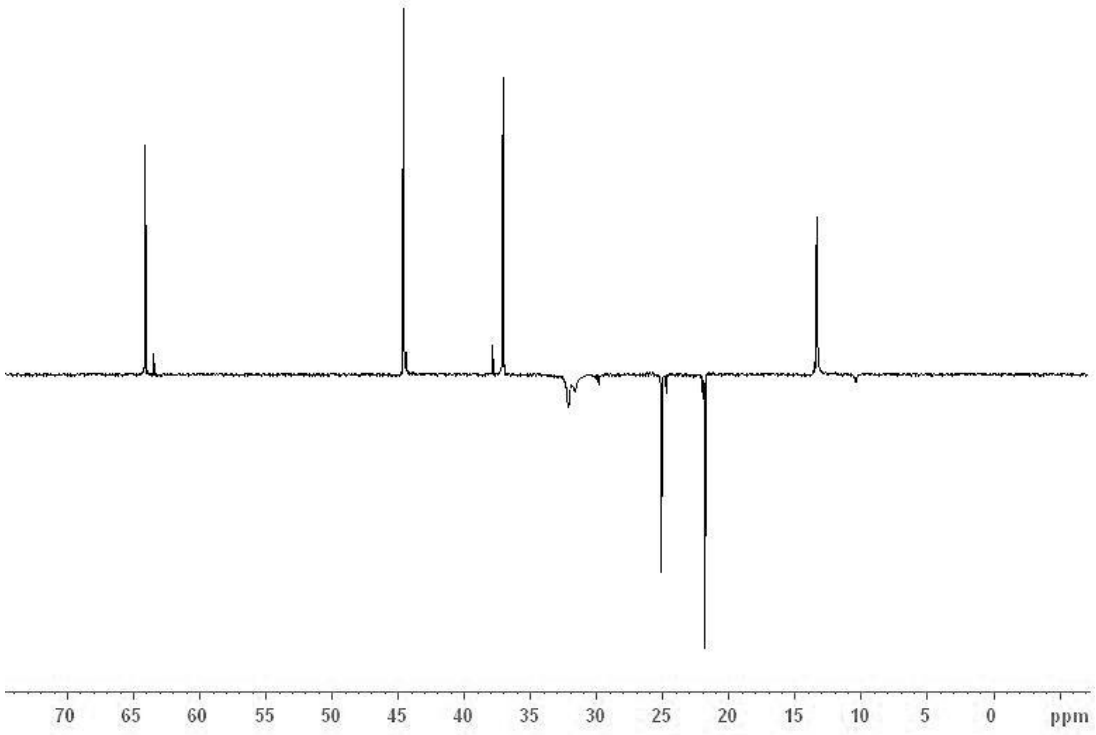


**Fig. S12.** $^{13}C$ DEPT spectrum of **3** in *cyc*-$C_6D_{12}$ solution.

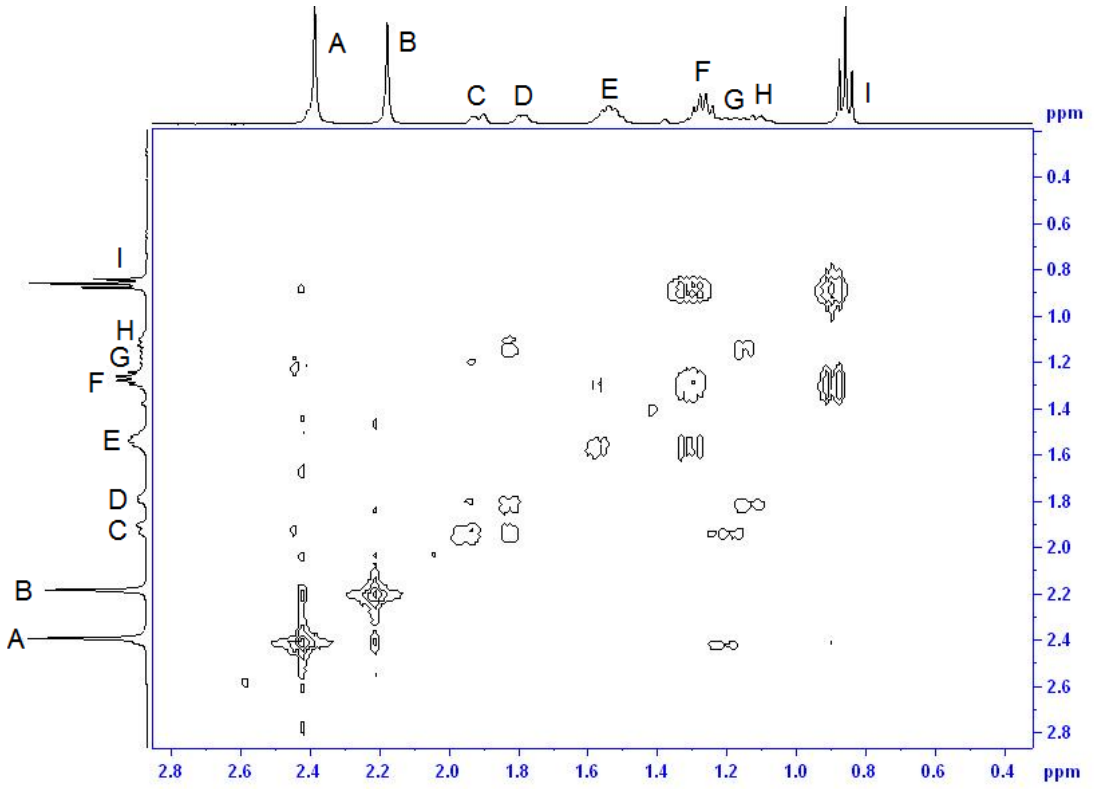


**Fig. S13.** COSY spectrum of **3** in *cyc*-$C_6D_{12}$ solution.

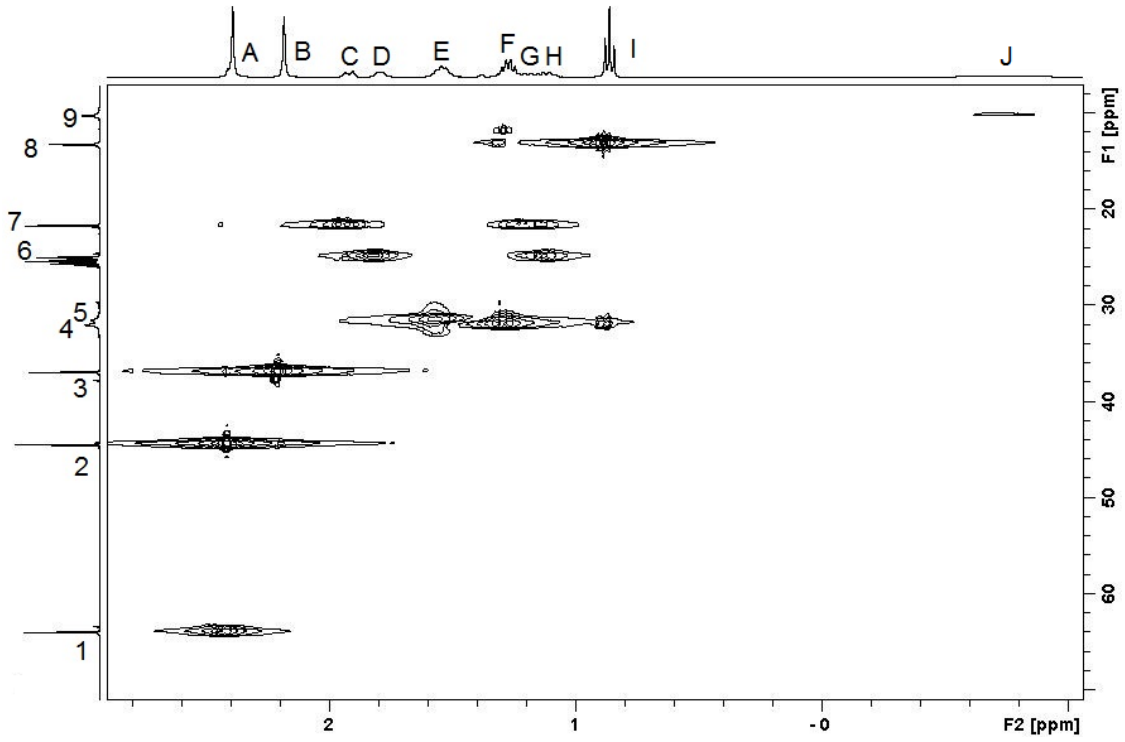


**Fig. S12.** HSQC spectrum of **3** in *cyc*-$C_6D_{12}$ solution.

**NMR spectra of 4, [(TMEDA)·LiMg$^{n}$Bu$_3$]x**

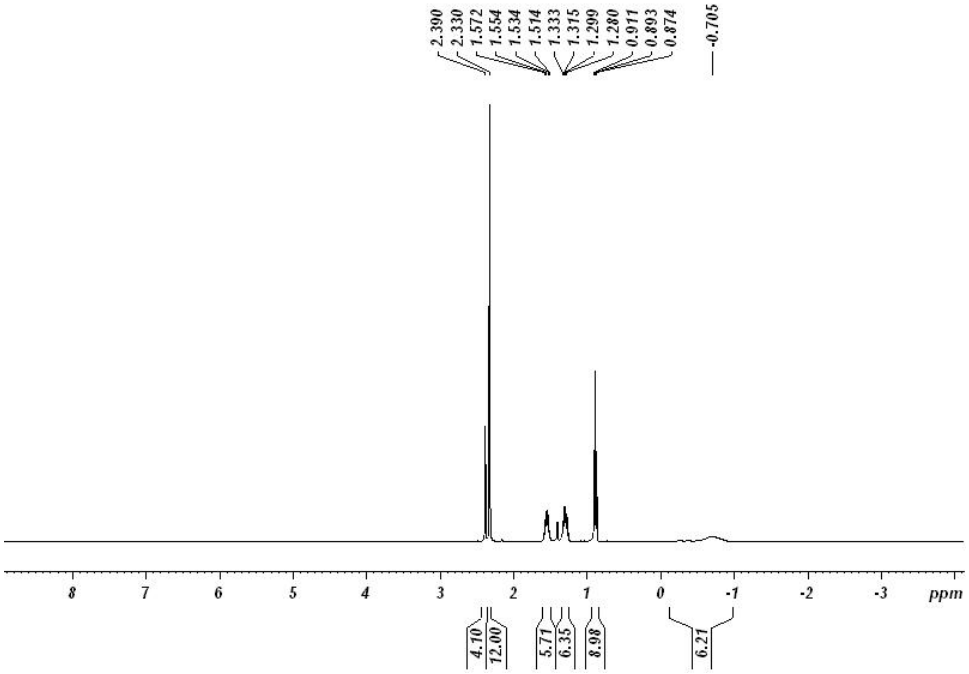


**Fig. S12.** $^{1}$H NMR Spectrum of **4** in *cyc*-$C_6D_{12}$ solution.

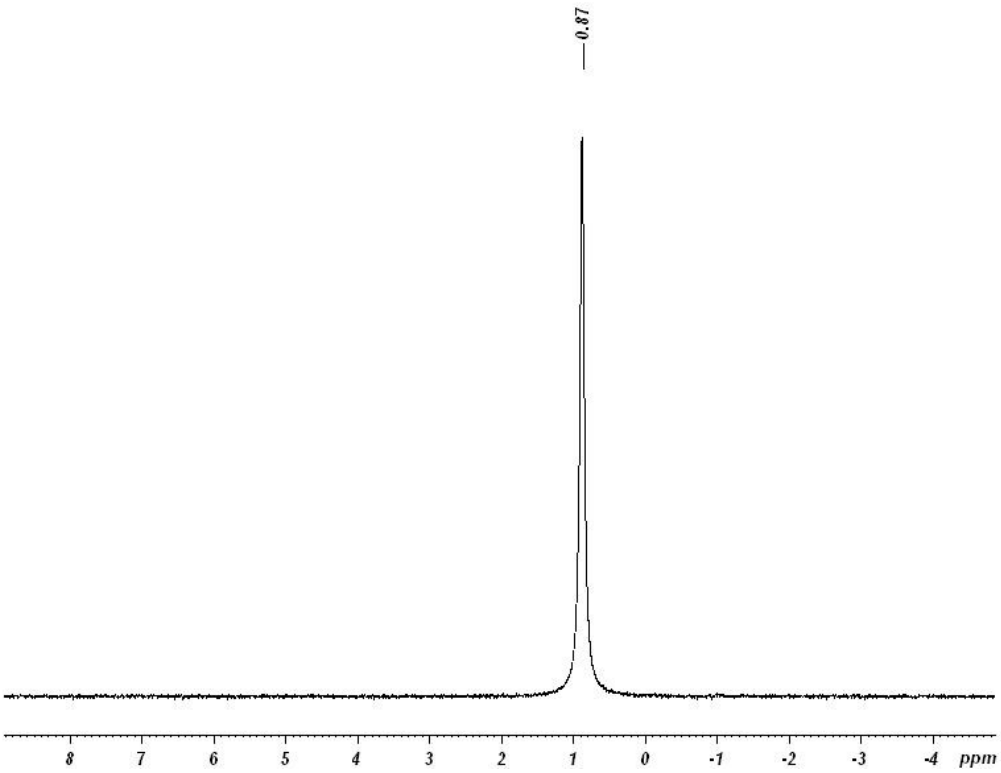


**Fig. S13.** $^{7}$Li NMR Spectrum of **4** in *cyc*-$C_6D_{12}$ solution.

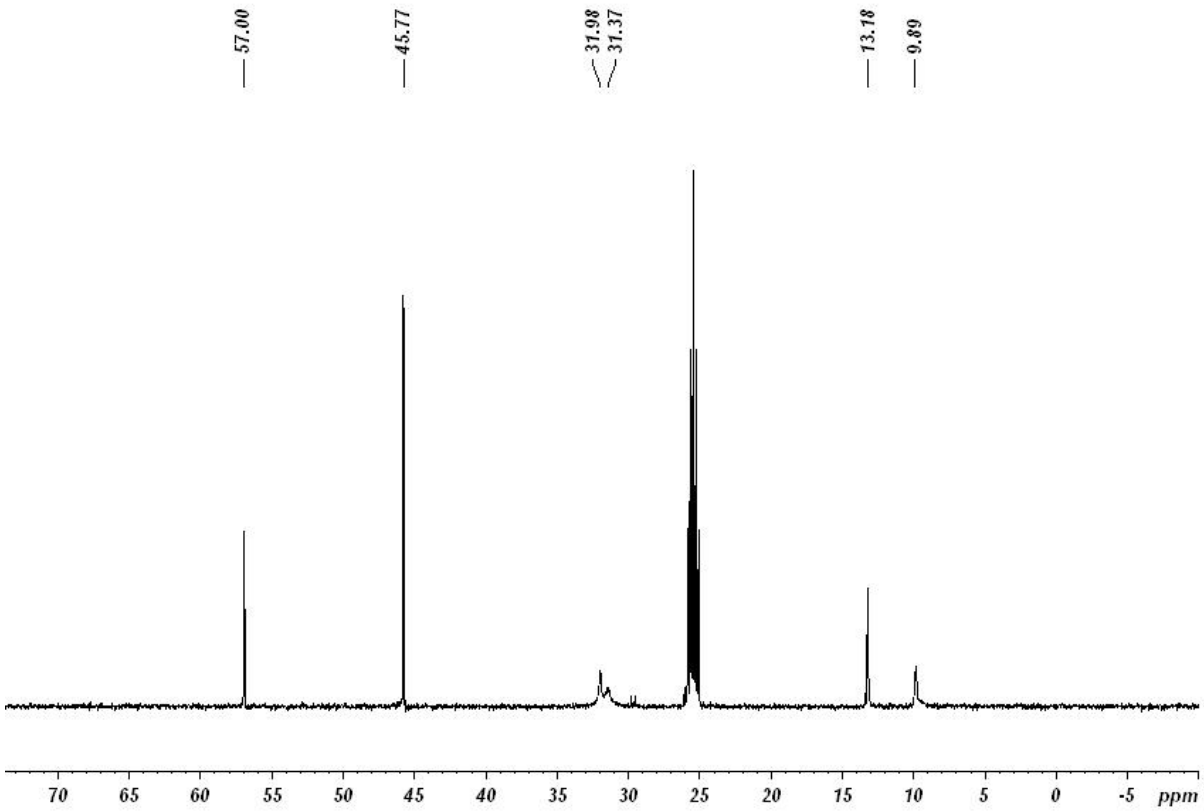


**Fig. S14.** $^{13}C$ NMR Spectrum of **4** in *cyc*-$C_6D_{12}$ solution.

**NMR spectra of 5, [TMEDA·Li(μ-$^n$Bu)(μ-O$^n$Bu)Mg($^n$Bu)]$_2$**

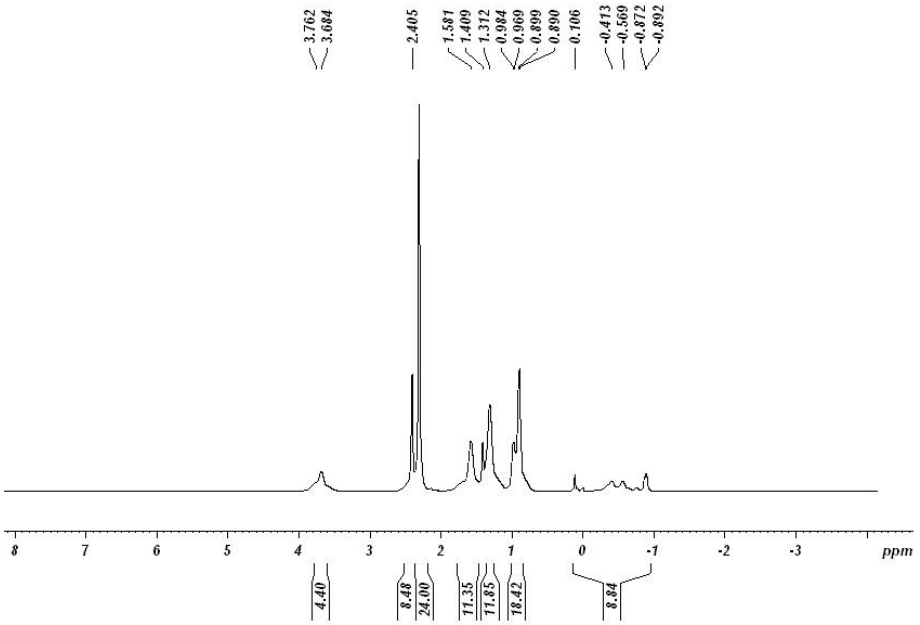


**Fig. S15.** $^1H$ NMR Spectrum of compound **5** in *cyc*-$C_6D_{12}$ solution.

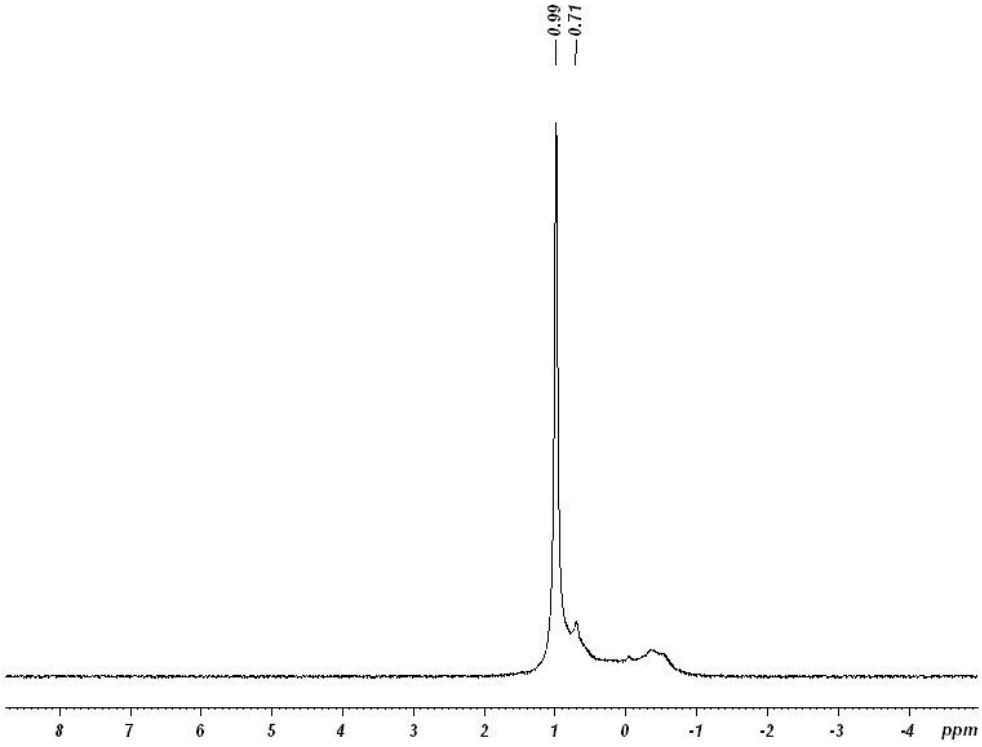


**Fig. S16.** $^{7}$Li NMR Spectrum of compound **5** in *cyc*-$C_6D_{12}$ solution.

**NMR spectra of 6, [(dioxane)·Li(μ-$^{n}$Bu)$_2$Mg($^{n}$Bu)]$_\infty$**

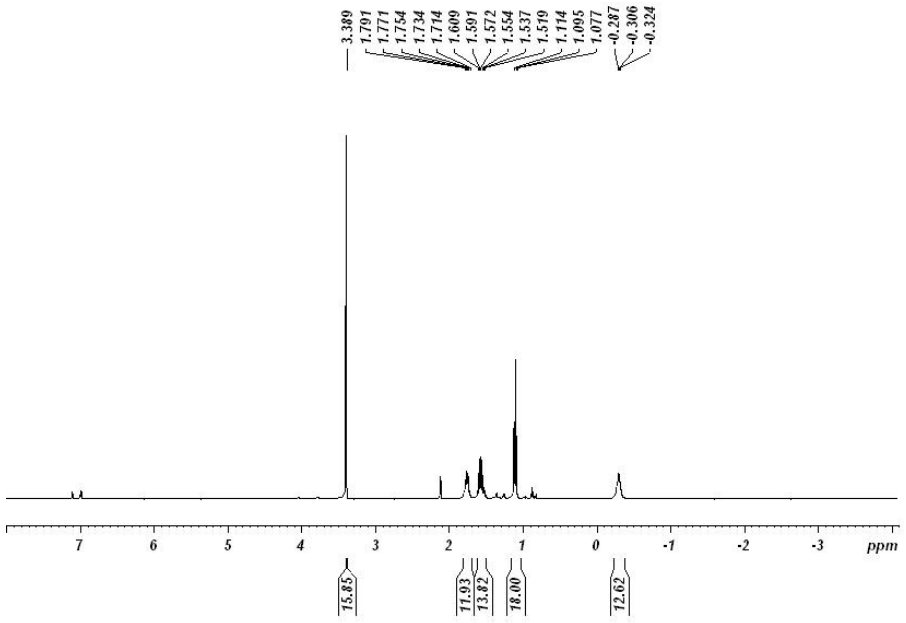


**Fig. S17.** $^{1}$H NMR Spectrum of **6** in D$^{8}$-tol solution at 343K.

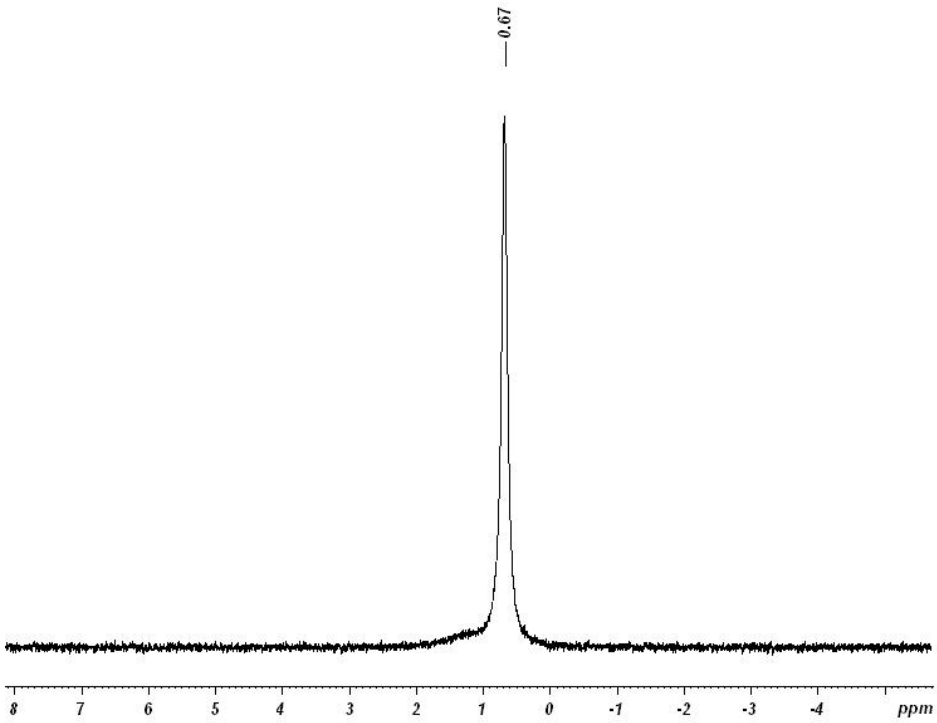


**Fig. S18.** $^{7}$Li NMR Spectrum of compound **6** in D$^{8}$-toluene solution at 343K.

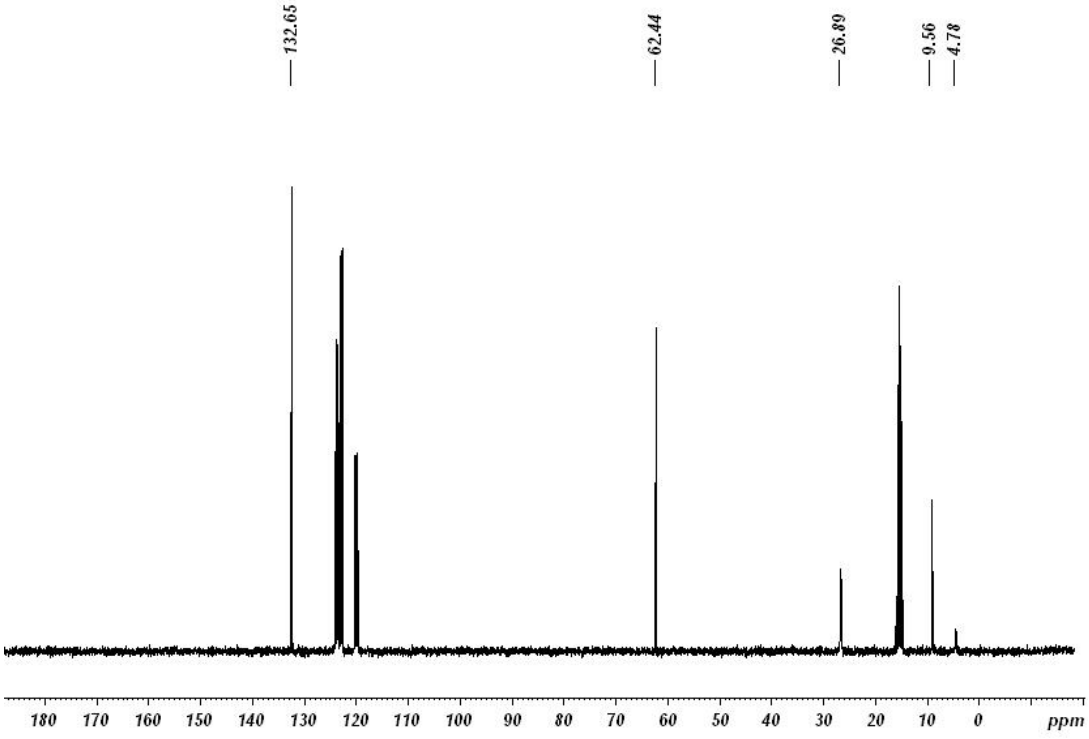


**Fig. S19.** $^{13}$C NMR Spectrum of compound **6** in D$^{8}$-toluene solution at 343K.

**NMR spectra of free Lewis bases**

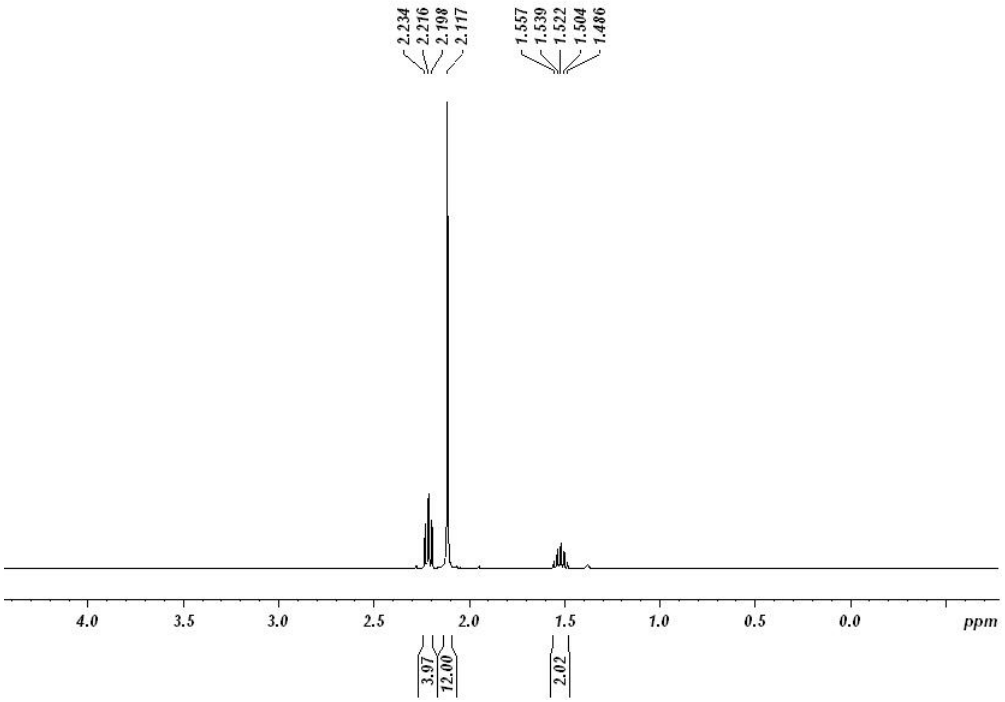


**Fig. S20.** $^{1}$H NMR Spectrum of TMPDA in *cyc*-$C_6D_{12}$ solution.

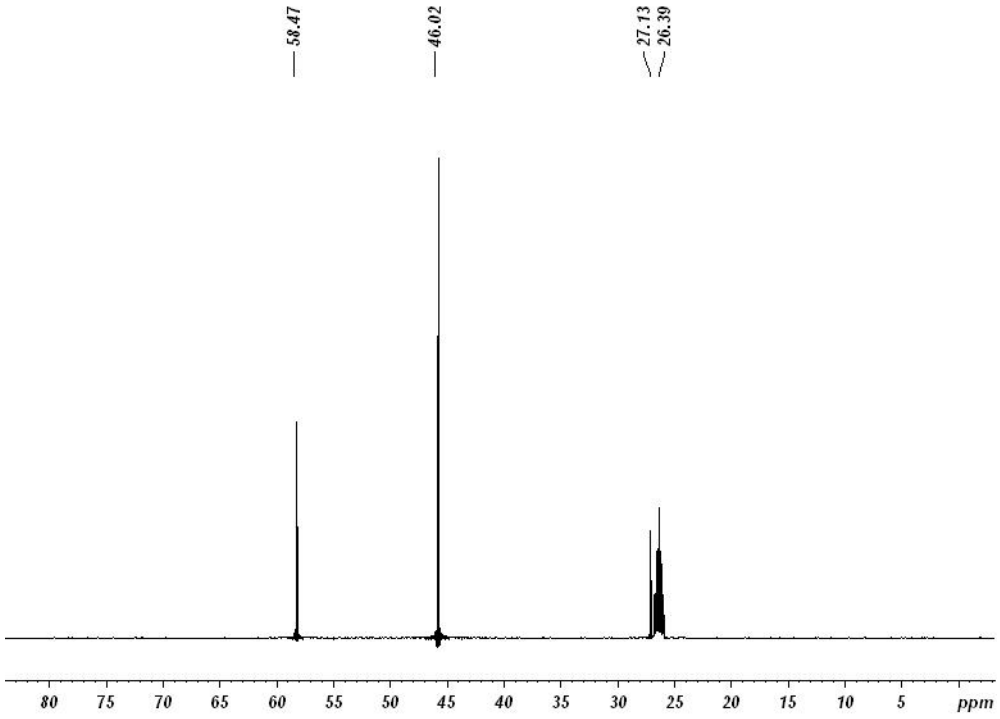


**Fig. S21.** $^{13}$C NMR Spectrum of TMPDA in *cyc*-$C_6D_{12}$ solution.

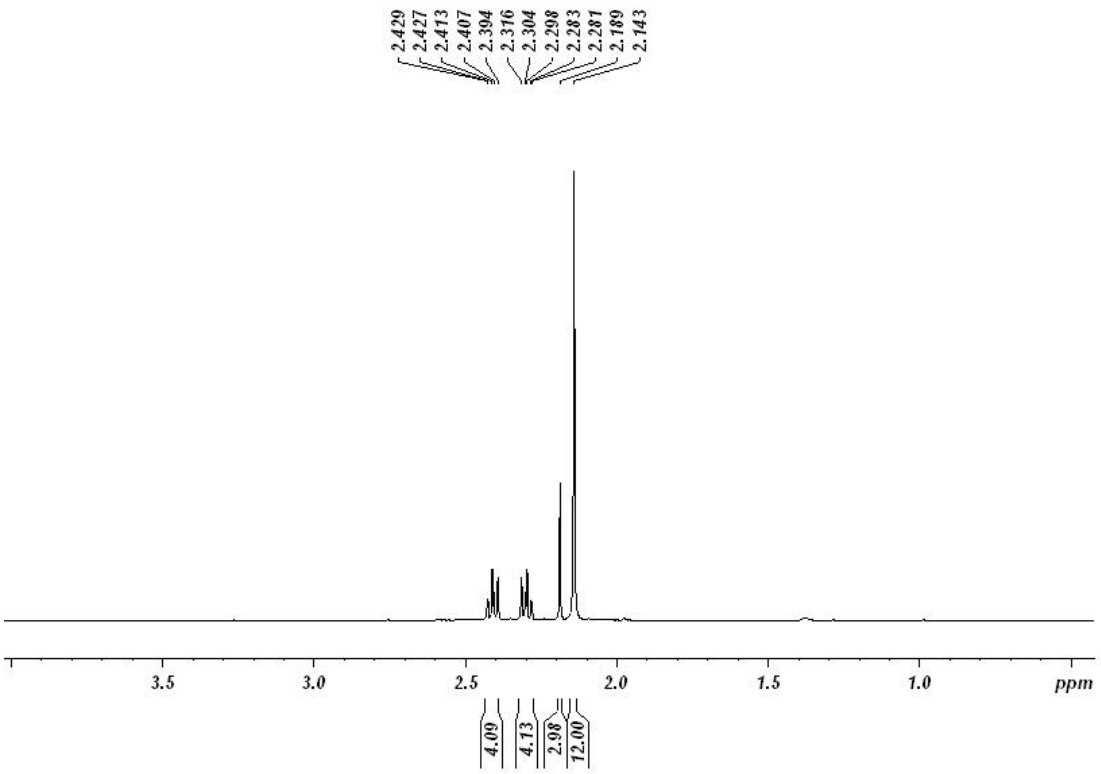


**Fig. S22.** $^{1}$H NMR Spectrum of PMDETA in *cyc*-$C_6D_{12}$ solution.

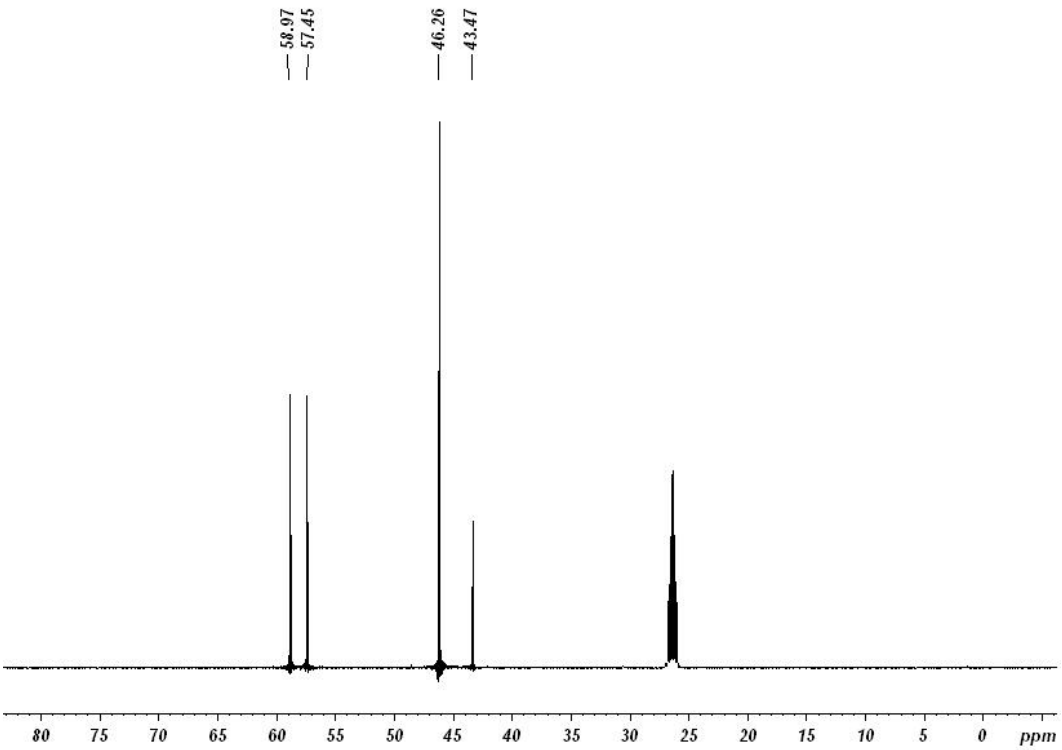


**Fig. S23.** $^{13}$C NMR Spectrum of PMDETA in *cyc*-$C_6D_{12}$ solution.

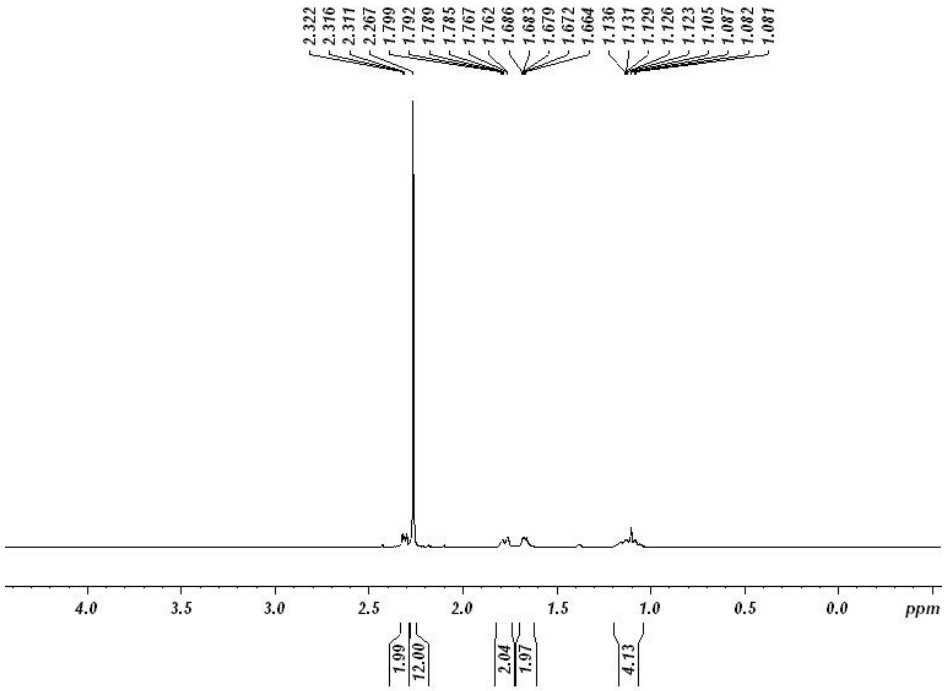


**Fig. S24.** $^{1}$H NMR Spectrum of (*R,R*)-TMCDA in *cyc*-$C_6D_{12}$ solution.

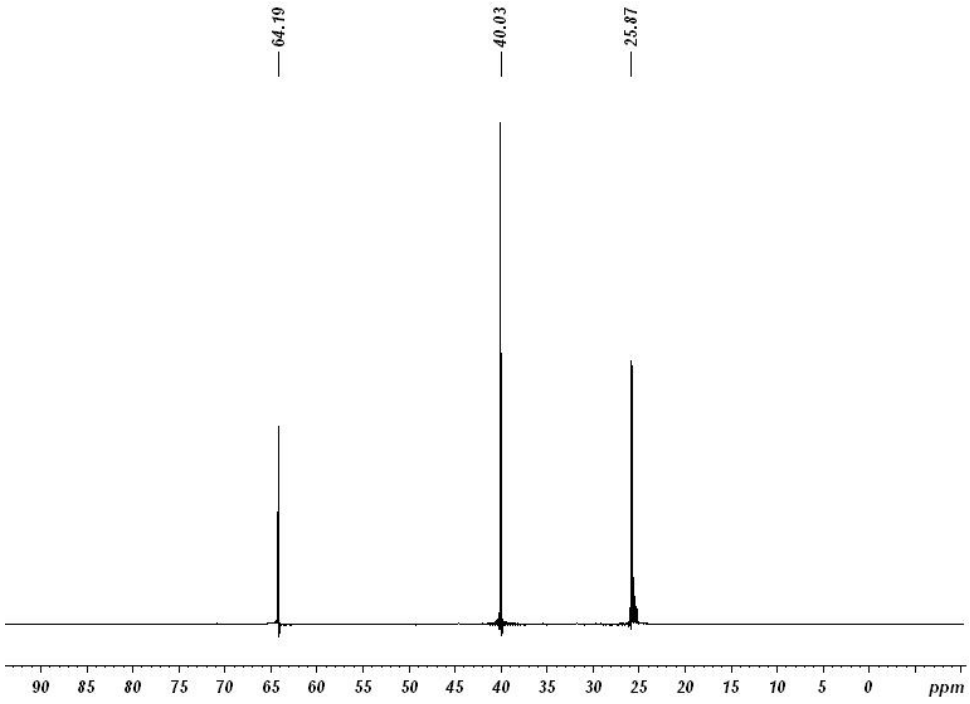


**Fig. S25.** $^{13}$C NMR Spectrum of (*R,R*)-TMCDA in *cyc*-$C_6D_{12}$ solution.

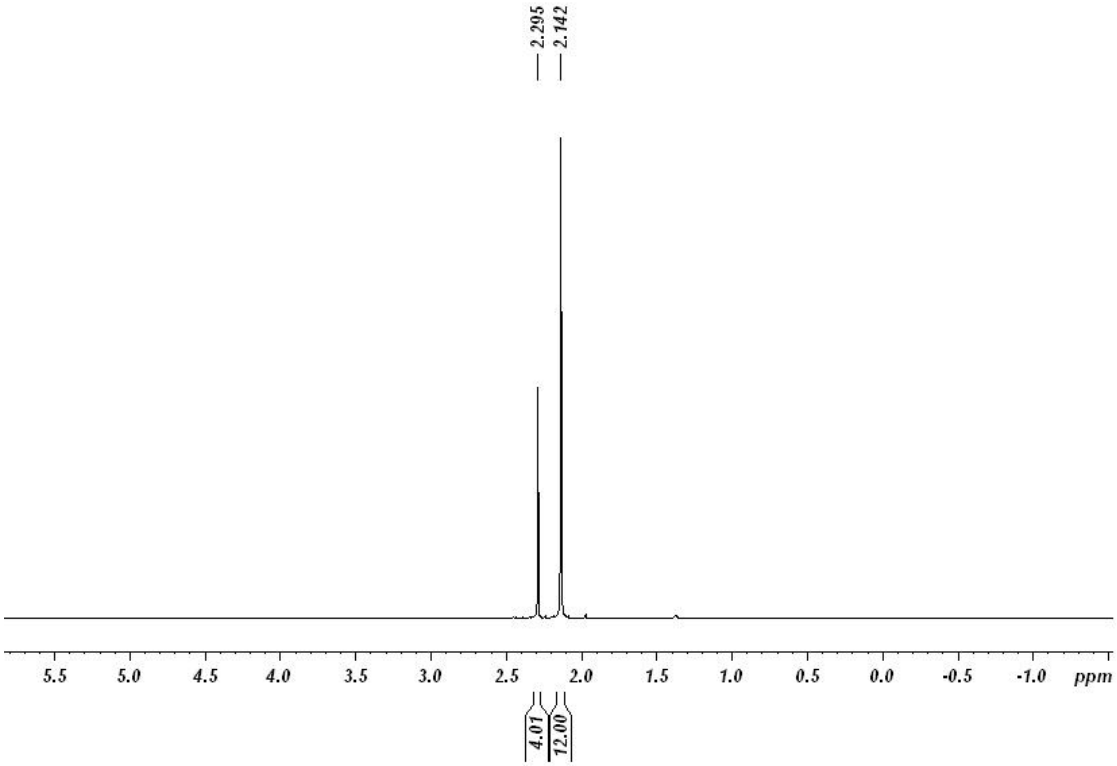


**Fig. S26.** $^{1}$H NMR Spectrum of TMEDA in *cyc*-$C_6D_{12}$ solution.

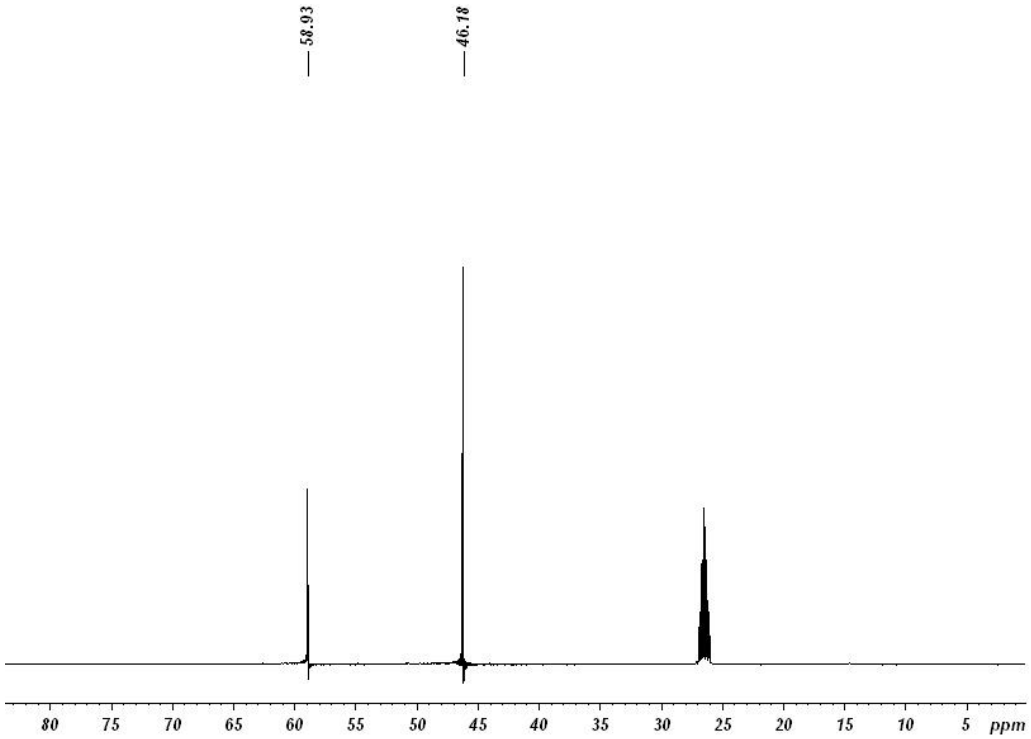


**Fig. S27.** $^{13}$C NMR Spectrum of TMEDA in *cyc*-$C_6D_{12}$ solution.