

Supporting information for the paper titled:
*Binding, Release, and Functionalization of CO₂ at a Nucleophilic
Oxo Anion Complex of Titanium*

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S1. Experimental Details

A. General Considerations.

All manipulations were carried out either in a Vacuum Atmospheres model MO-40M glovebox under an atmosphere of N₂ or using standard Schlenk techniques. All solvents were degassed and dried using a solvent-purification system provided by Glass Contour. After purification, all solvents were stored under an atmosphere of N₂ over 4 Å molecular sieves. Deuterated benzene (Cambridge Isotope Labs) was dried by stirring over CaH₂ for 24 h and was subsequently vacuum-transferred onto 4 Å molecular sieves. Deuterated tetrahydrofuran (Cambridge Isotopes Labs) was dried by stirring over sodium metal with a catalytic amount of benzophenone and subsequently vacuum-transferred onto 4 Å molecular sieves. The formate complex HC(O)OTi(N[^tBu]Ar)₃ and complex [(Et₂O)₂Li][OTi(N[^tBu]Ar)₃] ([Li][1]) were prepared according to literature procedures.¹ All other reagents were used as supplied by the vendor without further purification. Celite 435 (EMD Chemicals), alumina (Aldrich) and 4 Å molecular sieves (Aldrich) were dried prior to use by heating at 200 °C for 48 h under dynamic vacuum. All glassware was oven dried at 220 °C prior to use. NMR spectra were obtained on either a Varian 500 Inova spectrometer equipped with a Oxford Instruments Ltd. superconducting magnet, a Bruker 400-AVANCE spectrometer equipped with a Magnex Scientific superconducting magnet, or a Varian Mercury 300 spectrometer equipped with an Oxford Instruments Ltd. superconducting magnet. Proton NMR spectra were referenced to residual C₆D₅H (7.16 ppm) or residual C₄H₇D₇O (3.58 ppm).² ¹³C NMR spectra were referenced internally to naturally abundant ¹³C benzene (128.06 ppm), pyridine (150.35 ppm), or THF (67.21 ppm).² IR spectra were collected on a Perkin-Elmer 2000 FT-IR spectrophotometer. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.

B. Crystallographic Structure Determination.

Low-temperature data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo/Kα radiation (λ = 0.71073 Å), performing ω- and φ-scans, or on a Bruker X8 four circle diffractometer coupled to a Bruker Apex II CCD detector with graphite monochromated Cu/Kα radiation (λ = 1.54178 Å). All structures were solved either by direct or Patterson methods using SHELXS and refined against F² on all data by full-matrix least squares with SHELXL-97.³ A semi-empirical absorption correction (SADABS) was applied to the diffraction data for all structures.⁴ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

C. Computational Studies.

All calculations were carried out using ADF 2008.01 from [Scientific Computing and Modeling](#) on a 32-processor Quantum Cube workstation from [Parallel Quantum Solutions](#).^{5, 6} The calculations were performed using the OLYP functionals, which are a combination of the OPTX exchange functional of Handy and Cohen used with Lee, Yang, and Parr's nonlocal correlation function (LYP).⁷⁻⁹ In addition, all calculations were carried out using the zero-order regular approximation (ZORA) for relativistic effects.¹⁰⁻¹² The basis sets used were triple-ζ with a polarization function (TZP) for all non-hydrogen atoms and double-ζ with a polarization function (DZP) for all other calculations, as supplied with ADF. The starting geometry for the calculations was derived from the solid-state structure of the complex Me₃SiOC(O)OTi(N[^tBu]Ar)₃; the Me₃Si group was removed and the lithium counter cation was placed with the carbonate bond in a κ²-fashion. The geometry was then optimized. Chemical shielding tensors were calculated for the ¹³C nuclei in the optimized structures by the GIAO method using the ADF package.¹³⁻¹⁶ Frequency calculations were computed using optimized structures as described above.

D. Synthesis of ([Li][O₂COTi(N[^tBu]Ar)₃])₆ ([Li][2]).

A solution of [Li][1] (3.12 g, 4.17 mmol) in diethyl ether (100 mL) was prepared in a 250 mL Schlenk flask fitted with a rubber septum. The flask was removed from the glove box and attached to the Schlenk manifold. The reaction vessel was cooled to 0 °C using an ice bath. The flask was placed under a slight static vacuum by evacuating the hose connected to the Schlenk flask, closing the valve to the vacuum manifold, opening the sidearm valve of the flask, and then closing the sidearm valve of the flask. CO₂ (107 mL, 4.39 mmol, 1.05 equiv) was then introduced to the flask via a syringe and the reaction mixture was vigorously stirred using a magnetic stir bar. The color of the solution changed from yellow to orange as the reaction proceeded. After stirring for 1 h, the reaction mixture was dried under reduced pressure while being kept at 0 °C. The flask was returned to the glove box, and the resulting orange residue was triturated with *n*-hexane (40 mL) and then dried under reduced pressure. The resulting yellow powder was suspended in *n*-pentane (20 mL) and collected on a sintered glass frit via vacuum filtration. The powder was dried under reduced pressure. Yield: 1.85 g (2.88 mmol, 69%) Crystals of [Li][2] suitable for single-crystal X-ray diffraction studies were grown by slow evaporation of solutions of [Li][2] in benzene at

room temperature. ^1H NMR (C_6D_6 , 20 °C, 400 MHz, δ): 6.75 (s, 3 H, *p*-H), 6.30 (br, 6 H, *o*-H), 2.24 (s, 18 H, Ar- CH_3), 1.75 (s, 27 H, $\text{NC}(\text{CH}_3)_3$). ^{13}C NMR (C_6D_6 , 20 °C, 100 MHz, δ): 162.9 (s, O_2CO), 153.3 (s, *ipso*-Ar), 136.6 (s, *o*-Ar), 126.6 (s, *p*-Ar), 62.2 (s, $\text{NC}(\text{CH}_3)_3$), 31.4 (s, $\text{NC}(\text{CH}_3)_3$), 21.8 ppm (s, Ar- CH_3). IR (KBr, thin film): 2963, 2915, 2863, 1598 (vs), 1588 cm^{-1} . Elemental analysis: Calculated for $\text{C}_{37}\text{H}_{54}\text{LiN}_3\text{O}_3\text{Ti}$: C, 69.04; H, 8.46; N, 6.53%. Found: C, 68.84; H, 8.39; N, 6.28%.

E. Synthesis of $\text{Me}_3\text{SiOC}(\text{O})\text{OTi}(\text{N}[\text{tBu}]\text{Ar})_3$ (**3**).

A suspension of $[\text{Li}][\mathbf{2}]$ (0.679 g, 1.05 mmol) in diethyl ether (15 mL) was prepared and cooled in the liquid nitrogen bathed cold well of the glove box. A solution of $\text{Me}_3\text{SiOS}(\text{O})_2\text{CF}_3$ (0.235 g, 1.05 mmol) in diethyl ether (3 mL) was prepared and cooled in the cold well. Both mixtures were frozen, subsequently allowed to partially thaw, and then combined. The reaction mixture was allowed to warm to room temperature while stirring. As the reaction progressed, the originally yellow suspension became a homogeneous orange mixture. After stirring for 2 h, the reaction mixture was taken to dryness under reduced pressure, triturated with *n*-hexane, and dried again. The resulting orange residue was extracted into diethyl ether (~10 mL) and filtered through a pad of Celite on a sintered glass frit. The filtrate solution was concentrated under reduced pressure and then stored at -35 °C. After standing for 24 h, yellow crystals had formed. The crystals were collected on a sintered glass frit via vacuum filtration and then dried under reduced pressure. Yield: 0.469 g (0.66 mmol, 63%) ^1H NMR (C_6D_6 , 20 °C, 400 MHz, δ): 6.73 (s, 3 H, *p*-H), 6.13 (br, 6 H, *o*-H), 2.19 (s, 18 H, Ar- CH_3), 1.39 (s, 27 H, $\text{NC}(\text{CH}_3)_3$). ^{13}C NMR (C_6D_6 , 20 °C, 100 MHz, δ): 153.2 (s, $\text{Me}_3\text{SiOC}(\text{O})\text{O}$), 152.9 (s, *ipso*-Ar), 137.0 (s, *o*-Ar), 127.8 (s, *m*-Ar), 127.07 (s, *p*-Ar), 62.8 (s, $\text{NC}(\text{CH}_3)_3$), 30.9 (s, $\text{NC}(\text{CH}_3)_3$), 22.0 (s, Ar- CH_3), 0.12 ppm (s, $(\text{H}_3\text{C})_3\text{Si}$). IR (KBr, thin film): 1691 (vs), 1598 (s), 1588 (s) cm^{-1} . Elemental analysis: Calculated for $\text{C}_{40}\text{H}_{63}\text{N}_3\text{O}_3\text{SiTi}$: C, 67.67; H, 8.94; N, 5.92%. Found: C, 67.53; H, 8.84; N, 5.82%.

F. Thermal stability study of **3**.

A solution of **3** in C_6D_6 was prepared. The solution was transferred into an NMR tube, which was degassed and then flame-sealed. The ^1H NMR spectrum was collected. The NMR tube was then heated at 80 °C for 12 h. The ^1H NMR spectrum was then recollected. There was complete consumption of the starting material after the heating period. ^1H NMR (C_6D_6 , 20 °C, 400 MHz, δ): 6.75 (s, 3 H, *p*-H), 6.09 (v br, 6 H, *o*-H), 2.23 (s, 18 H, Ar- CH_3), 1.32 (s, 27 H, $\text{NC}(\text{CH}_3)_3$) (Figure S 7). For comparison, a treatment of $[\text{Li}][\mathbf{1}]$ with Me_3SiCl was performed. A solution of the two reagents in THF (2 mL each) were prepared separately and then cooled in the freezer to -35 °C. After cooling, the solution of Me_3SiCl was added dropwise to the stirring solution of $[\text{Li}][\mathbf{1}]$. The reaction mixture was stirred and allowed to warm to room temperature. After stirring for 1 h, the reaction mixture was taken to dryness under reduced pressure to give a bright yellow powder. A sample of the powder was dissolved in C_6D_6 and the ^1H NMR spectrum was collected. The product of the reaction had resonances that were identical to the product obtained from heating complex **3** (Figure S 8).

G. Reaction of $\text{tBuC}(\text{O})\text{Cl}$ with $[\text{Li}][\mathbf{2}]$ to form $\text{tBuC}(\text{O})\text{OTi}(\text{N}[\text{tBu}]\text{Ar})_3$ (**4**).

A suspension of $[\text{Li}][\mathbf{2}]$ (0.187 g, 0.29 mmol) in diethyl ether (10 mL) was prepared and cooled to -173 °C. A solution of pivaloyl chloride (0.035 g, 0.29 mmol) in diethyl ether (2 mL) was prepared and cooled to -173 °C. The two mixtures were allowed to thaw and were subsequently combined. The yellow mixture was stirred and allowed to warm to room temperature. The mixture changed from yellow to orange over the course of 1 h and gas evolution was observed when the cap of the vessel was removed. The reaction mixture was then dried under reduced pressure. The orange residue was extracted into toluene (5 mL). The solution was filtered through a pad of Celite on a glass fiber filter. The filtrate solution was dried under reduced pressure. The orange residue was dissolved in a minimum volume of diethyl ether (~3 mL) and the solution was stored at -35 °C. After standing for 6 h, orange crystals had deposited on the bottom of the vial. The mother liquor was decanted away from the crystals, and these were washed with *n*-pentane (1 mL). The crystals of **4** were dried under reduced pressure. Yield: 0.106 g. A second crop of the material was obtained by concentrating the mother liquor under reduced pressure and storing the solution at -35 °C. 2nd crop: 0.047 g. Total yield: 0.153 g (0.23 mmol, 78%) ^1H NMR (CDCl_3 , 20 °C, 400 MHz, δ): 6.76 (s, 3 H, *p*-H), 6.24 (br, 6 H, *o*-H), 2.25 (s, 18 H, Ar- CH_3), 1.22 (s, 9 H, $(\text{O})\text{CC}(\text{CH}_3)_3$), 1.13 (s, 27 H, $\text{NC}(\text{CH}_3)_3$). ^{13}C NMR (CDCl_3 , 20 °C, 100 MHz, δ): 180.2 (s, $\text{OC}(\text{O})$), 151.2 (s, *ipso*-Ar), 136.3 (s, *o*-Ar), 127.3 (s, *m*-Ar), 126.4 (s, *p*-Ar), 62.4 (s, $\text{NC}(\text{CH}_3)_3$), 39.9 (s, $(\text{O})\text{CC}(\text{CH}_3)_3$), 30.2 (s, $\text{NC}(\text{CH}_3)_3$), 27.8 (s, $(\text{O})\text{CC}(\text{CH}_3)_3$), 21.6 ppm (s, Ar- CH_3). IR (KBr, thin film): 1680 (vs), 1598, 1588 cm^{-1} . Elemental analysis: Calculated for $\text{C}_{41}\text{H}_{63}\text{N}_3\text{O}_2\text{Ti}$: C, 72.65; H, 9.37; N, 6.20%. Found: C, 72.57; H, 9.39; N, 6.26%.

H. Synthesis of $[(12\text{-crown-4})\text{Li}][\mathbf{1}]$

A solution of $[\text{Li}][\mathbf{1}]$ (0.256 g, 0.351 mmol) in THF (5 mL) was prepared. A solution of 12-crown-4 (0.062 g, 0.351) mmol in THF (7 mL) was added to the stirring solution of oxo anion complex at 23 °C. The mixture was stirred for 45 min and then

dried under reduced pressure. The yellow residue was dried further by adding *n*-hexane (5 mL) and then taking the mixture to dryness under reduced pressure. The bright yellow solids were suspended in *n*-hexane, collected on a sintered glass frit via vacuum filtration, and dried under reduced pressure. Yield: 0.220 g (81%). This material displays spectroscopic signals consistent with the closely related parent oxo complex [(Et₂O)₂Li][OTi(N^tBu)Ar₃].¹ ¹H NMR (C₆D₆, 20 °C, 400 MHz, δ): 6.81 (s, 3 H, *p*-H), 6.35 (br, 6 H, *o*-H), 2.55 (m, 8H, 12-crown-4), 2.25 (m, 8H, 12-crown-4), 2.39 (s, 18 H, Ar-CH₃), 1.78 (s, 27 H, NC(CH₃)₃). ¹³C NMR (C₆D₆, 20 °C, 125 MHz, δ): 156.0 (s, *ipso*-Ar), 135.6 (s, *o*-Ar), 130.9 (s, *m*-Ar), 124.2 (s, *p*-Ar), 66.3 (s, 12-crown-4), 56.8 (s, NC(CH₃)₃), 33.5 (s, NC(CH₃)₃), 22.1 (s, Ar-CH₃). Elemental analysis: Calculated for C₄₄H₇₀LiN₃O₅Ti: C, 68.11; H, 9.09; N, 5.41%. Found: C, 66.71; H, 9.15; N, 5.13%.

S2. Crystallographic Details

A. Complex [Li][2] • (C₆H₆)_{1.33}

Complex [Li][2] • 1.33 (C₆H₆) crystallizes in the space group $R\bar{3}$ and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. Four molecules of interstitial benzene are each disordered over three positions that are related by a crystallographic three-fold axis. Each benzene molecule was constrained to a third occupancy in each possible position. Similarity restraints on the 1,2 and 1,3 distances and rigid bond restraints were applied to the disordered benzene molecules.

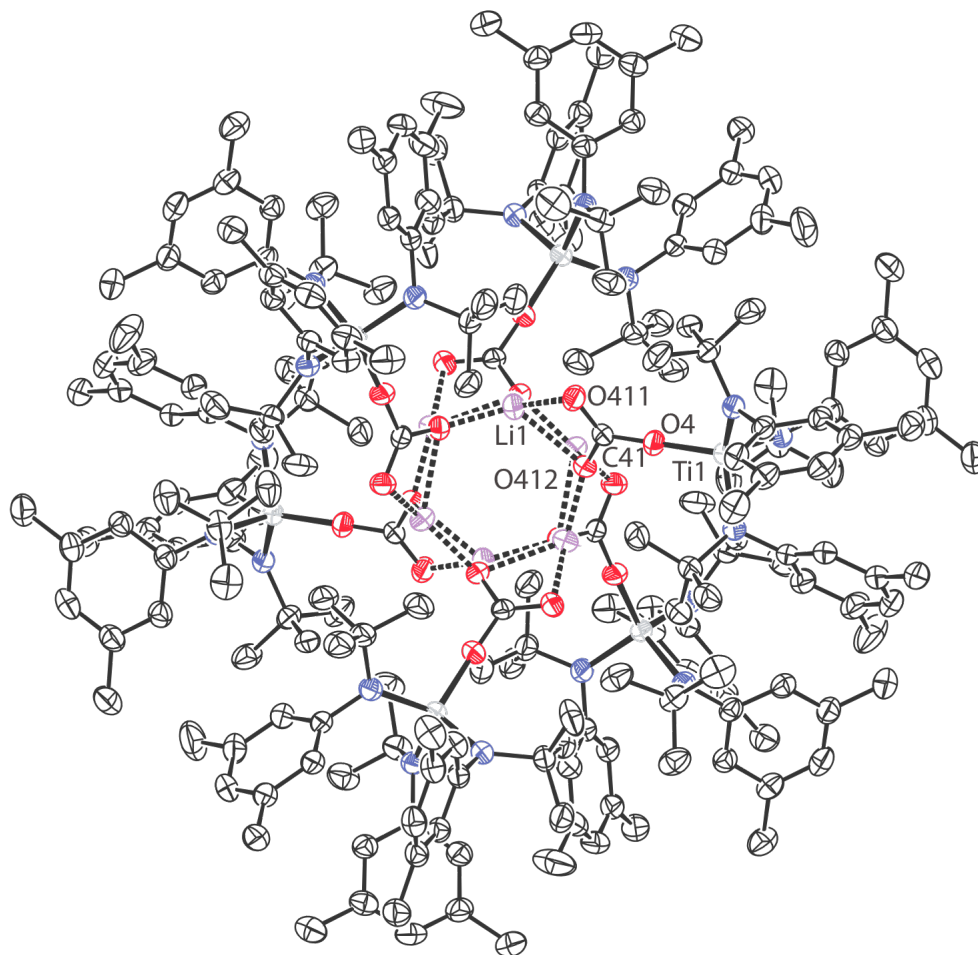


Figure S 1. Hexameric structure of [Li][2] with thermal ellipsoids at 50% probability.

B. Complex 3

Complex **3** crystallizes in the space group *Pbca* and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. No restraints were used in the refinement.

Table S 1. Crystal data and structure refinement statistics for [Li][**2**] and **3**.

| | [Li][2] | 3 |
|--|---|---|
| Reciprocal Net # /CCDC # | X8_10044/819846 | 10068/819847 |
| Empirical formula | C ₄₅ H ₆₂ LiN ₃ O ₃ Ti | C ₄₀ H ₆₃ N ₃ O ₃ SiTi |
| Formula weight | 560.86 | 709.92 |
| Temperature | 100(2) K | 100(2) K |
| Wavelength | 1.54178 Å | 0.71073 Å |
| Crystal system | Trigonal | Orthorhombic |
| Space group | <i>R</i> $\bar{3}$ | <i>Pbca</i> |
| Unit cell dimensions | <i>a</i> = 28.8490(6) Å, α = 90° <i>b</i> = 28.8490(6) Å, β = 90° <i>c</i> = 23.5478(6) Å, γ = 120° | <i>a</i> = 19.9166(18) Å, α = 90° <i>b</i> = 19.1716(18) Å, β = 90° <i>c</i> = 21.779(2) Å, γ = 90° |
| Volume | 19307.2(7) Å ³ | 8316.1(13) Å ³ |
| <i>Z</i> | 18 | 8 |
| Density (calculated) | 1.152 g/cm ³ | 1.134 g/cm ³ |
| Absorption coefficient | 1.987 mm ⁻¹ | 0.272 mm ⁻¹ |
| <i>F</i> (000) | 7236 | 3072 |
| Crystal size | 0.10 × 0.10 × 0.03 mm ³ | 0.50 × 0.50 × 0.25 mm ³ |
| Theta range for collection | 3.80 to 68.22°. | 1.75 to 25.35°. |
| Index ranges | -36 ≤ <i>h</i> ≤ 35, -30 ≤ <i>k</i> ≤ 35, -28 ≤ <i>l</i> ≤ 26 | -23 ≤ <i>h</i> ≤ 23, -23 ≤ <i>k</i> ≤ 23, -26 ≤ <i>l</i> ≤ 26 |
| Reflections collected | 46114 | 105056 |
| Independent reflections | 7754 [<i>R</i> (int) = 0.0556] | 7611 [<i>R</i> (int) = 0.0814] |
| Completeness to θ_{\max} | 97.9 % | 100% |
| Absorption correction | Multi-scan (SADABS) | Multi-scan (SADABS) |
| Max. and min. transmission | 0.9428 and 0.8260 | 0.9352 and 0.8761 |
| Refinement method | Full-matrix least-squares on <i>F</i> ² | Full-matrix least-squares on <i>F</i> ² |
| Data / restraints / parameters | 7754 / 470 / 603 | 7611 / 0 / 451 |
| Goodness-of-fit on <i>F</i> ² | 1.061 | 1.023 |
| Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> ₁ = 0.0560, <i>wR</i> ₂ = 0.1485 | <i>R</i> ₁ = 0.0427, <i>wR</i> ₂ = 0.0987 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.0749, <i>wR</i> ₂ = 0.1605 | <i>R</i> ₁ = 0.0620, <i>wR</i> ₂ = 0.1113 |
| Largest diff. peak and hole | 0.443 and -0.412 e Å ⁻³ | 0.328 and -0.323 e Å ⁻³ |

S2. 1D NMR Spectra

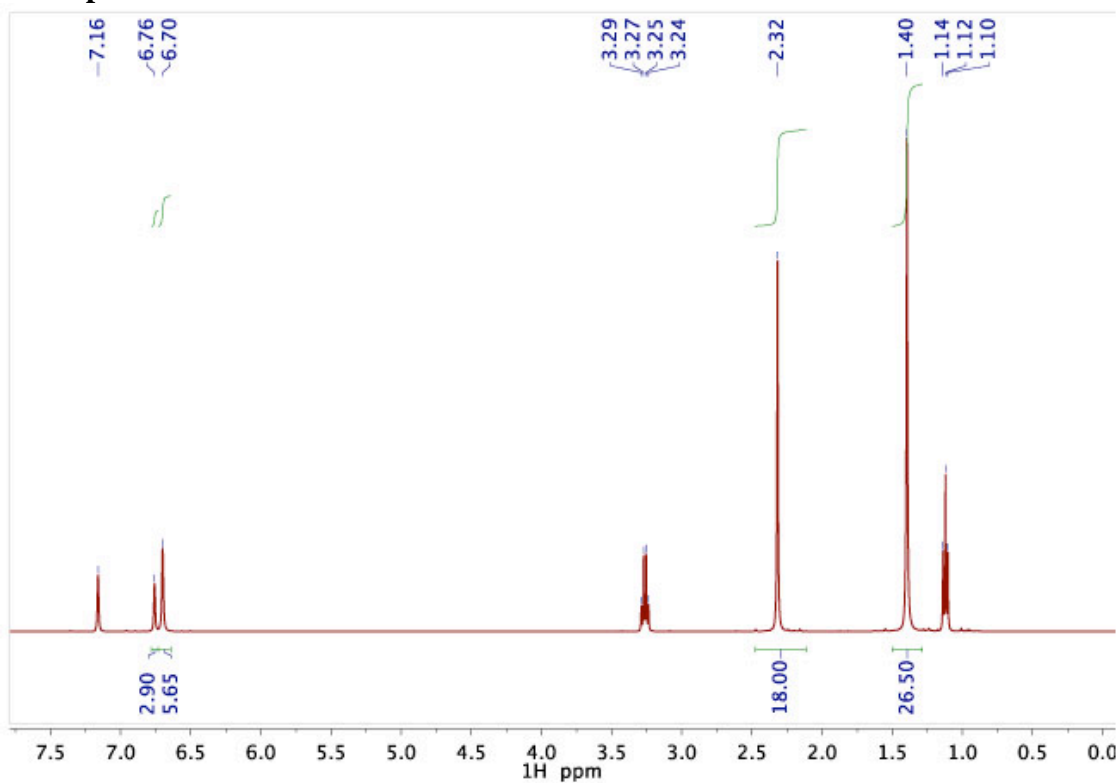


Figure S 2. Proton NMR spectrum of [Li][1] in C₆D₆ 400 MHz, 20 °C.

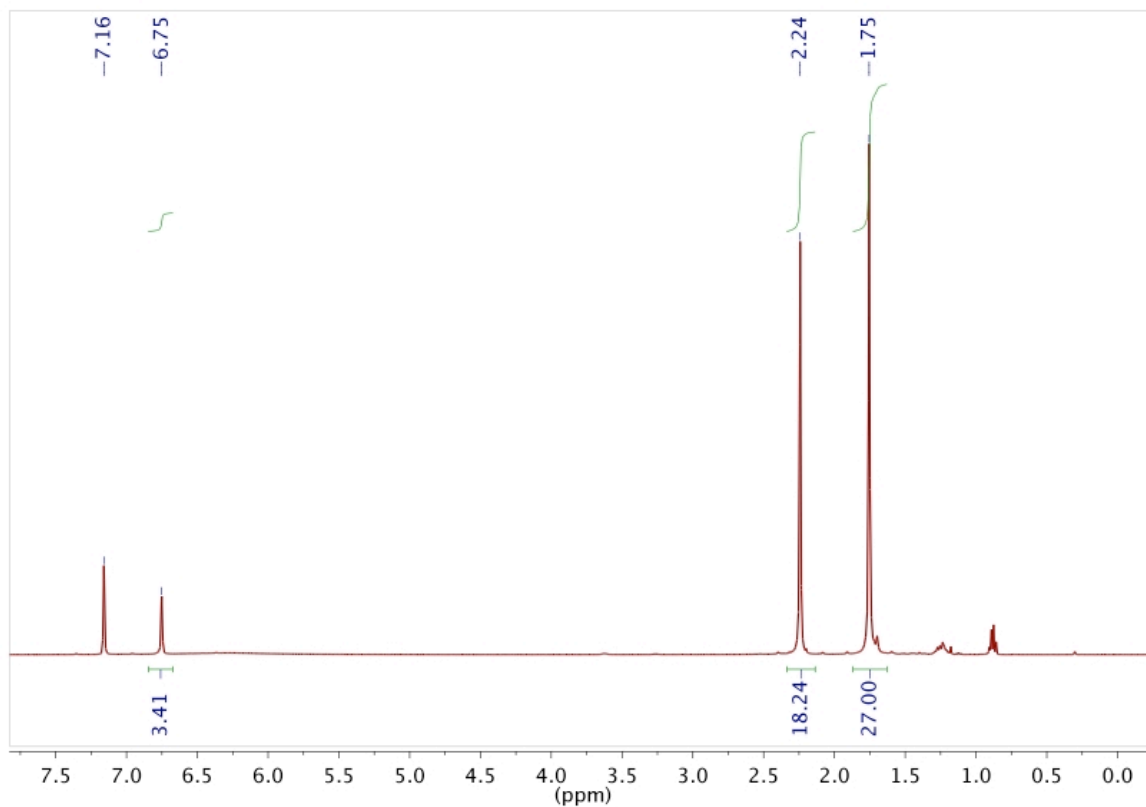


Figure S 3. Proton NMR spectrum of [Li][2] in C_6D_6 , 400 MHz, 20 °C, residual *n*-hexane present.

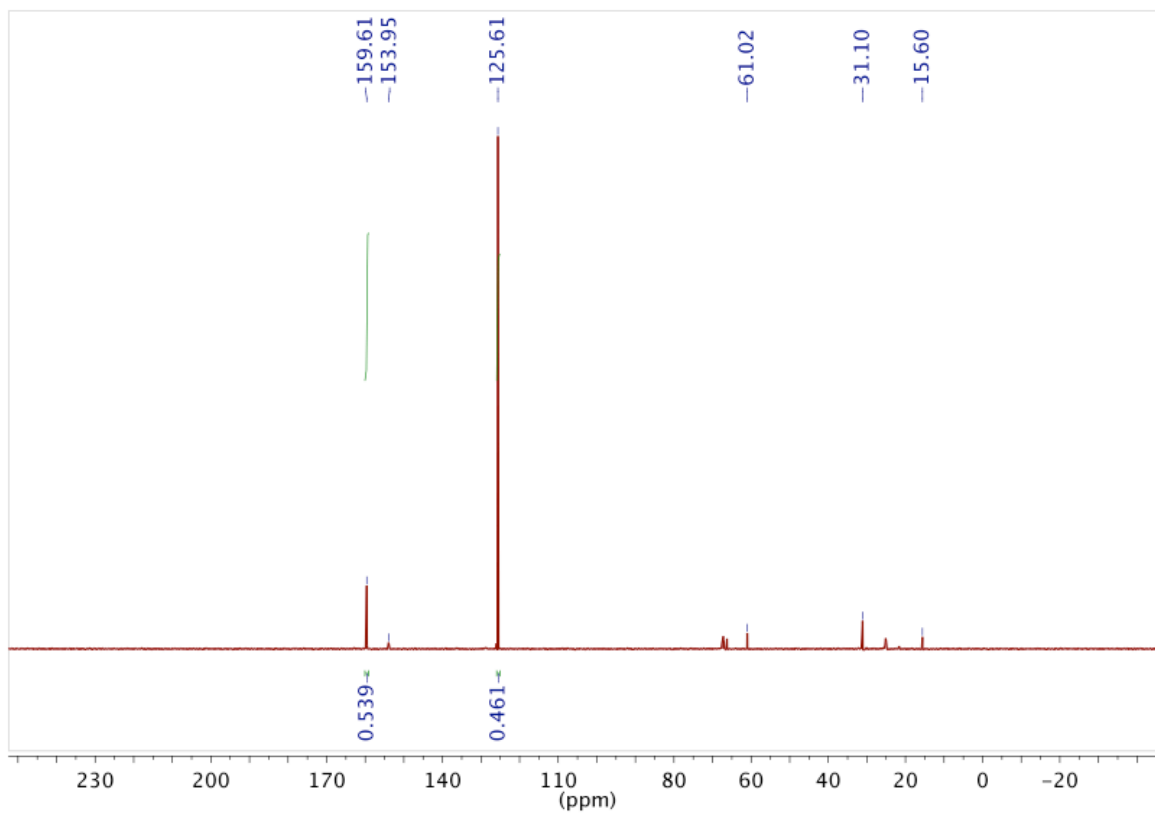


Figure S 4. ^{13}C NMR spectrum of [Li][2] in $THF-d_8$, 125 MHz, -20 °C. Excess $^{13}CO_2$ is present

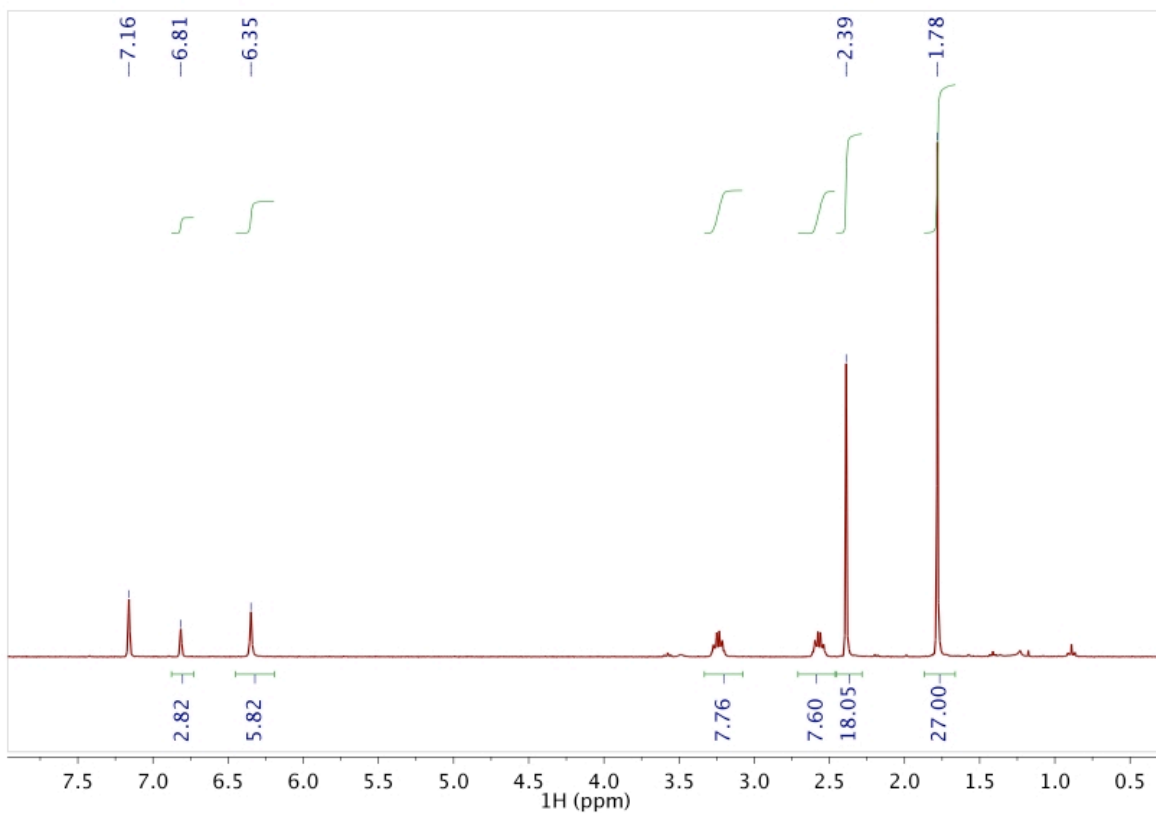


Figure S 5. Proton NMR spectrum of [(12-crown-4)Li][1] in C₆D₆ 400 MHz, 20 °C.

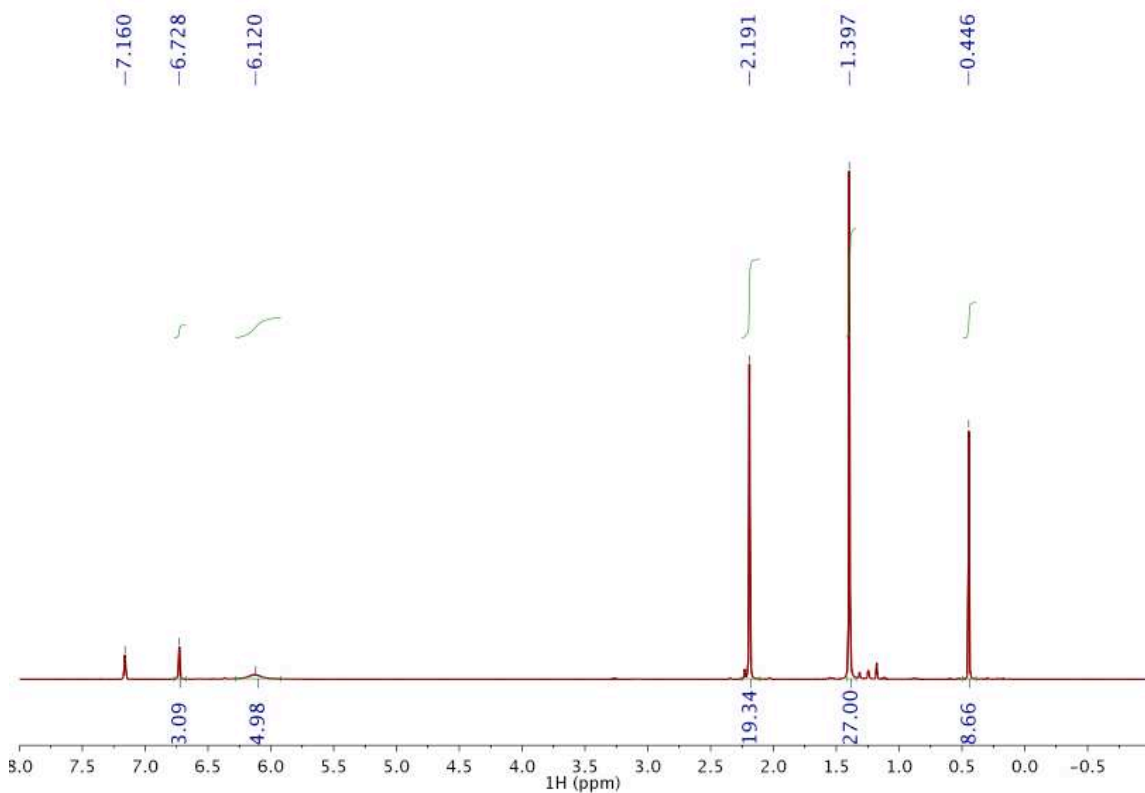


Figure S 6. Proton NMR spectrum of 3 in C₆D₆ 400 MHz, 20 °C.

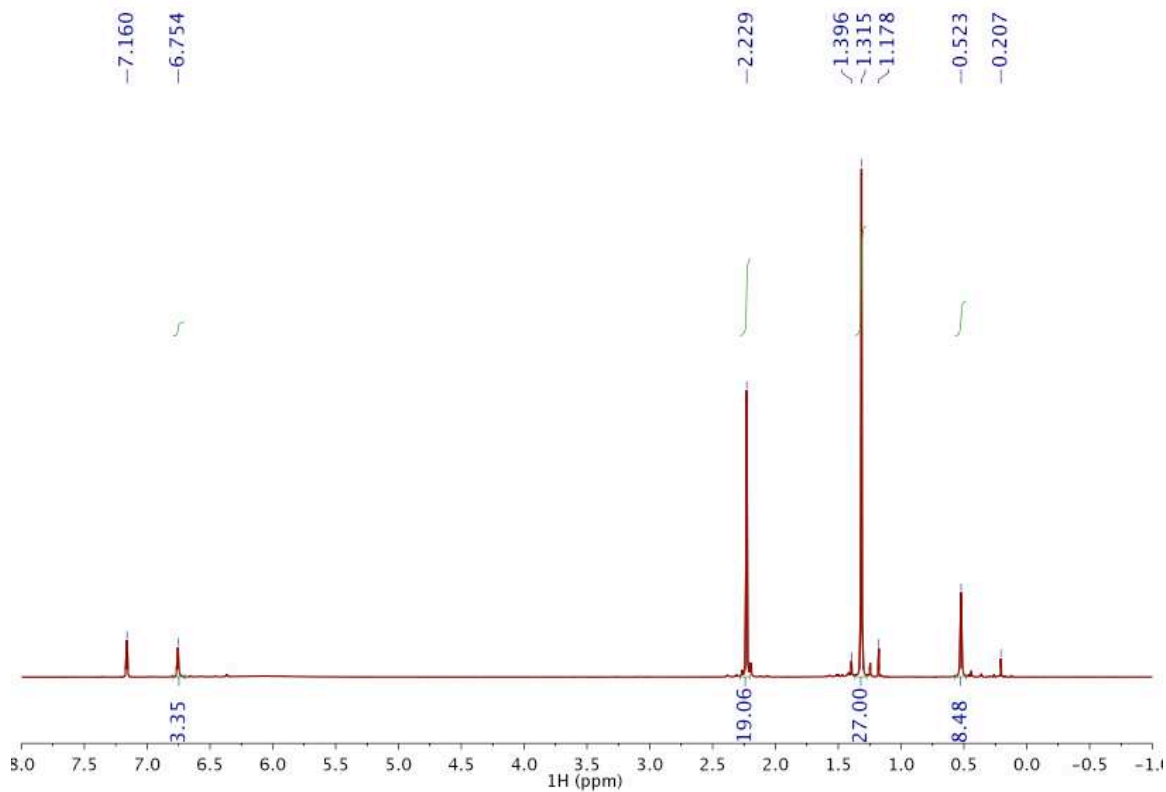


Figure S 7. Proton NMR spectrum of product from thermolysis of **3** in C_6D_6 400 MHz, 20 °C.

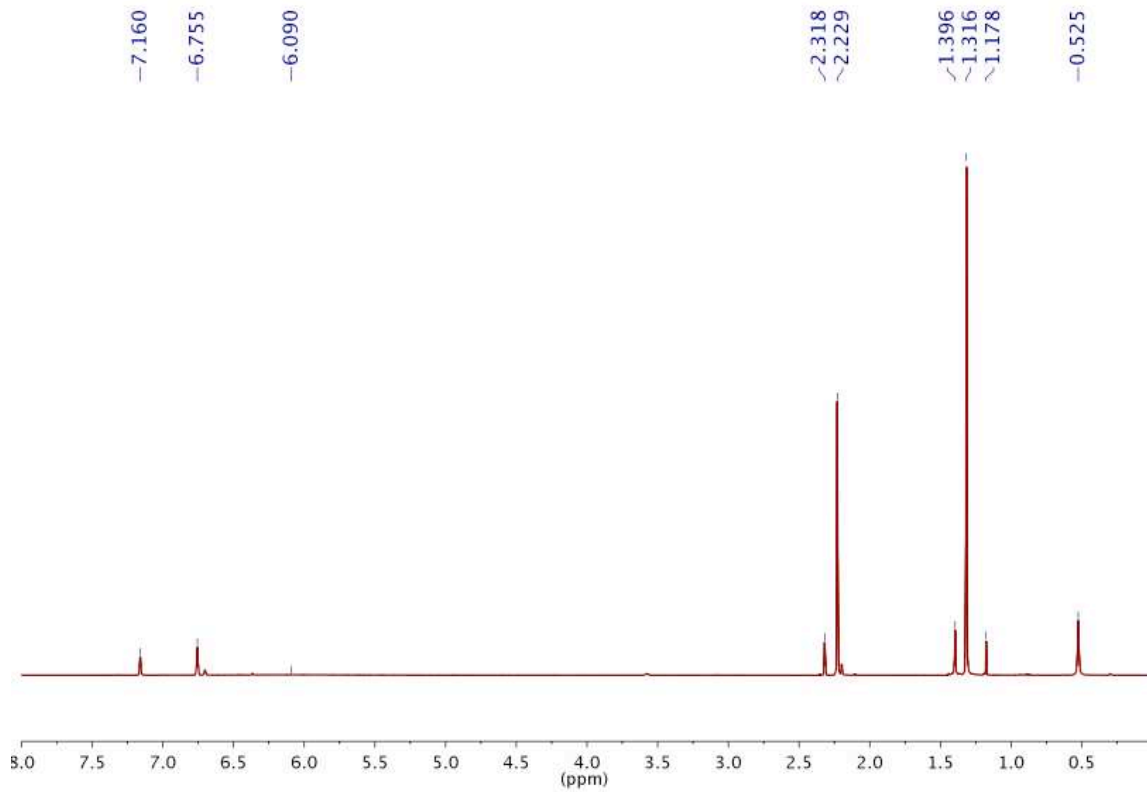


Figure S 8. Proton NMR spectrum of product from the reaction of Me_3SiCl and $[Li][\mathbf{1}]$ in C_6D_6 500 MHz, 20 °C.

S3. DOSY Spectra

DOSY Spectra were collected using a Bruker 400-AVANCE spectrometer equipped with a Magnex Scientific superconducting magnet. Data collection was performed using a stimulated echo experiment (stegp1s1d). A gradient length of 3200 μs and a Stejskal-Tanner diffusion delay of 0.1 s were used in the data collection. The gradient ratio was varied from 2% to 95% in 16 steps. The diffusion coefficient was calculated using the Bayesian DOSY Transform as implemented by Mnova NMR.

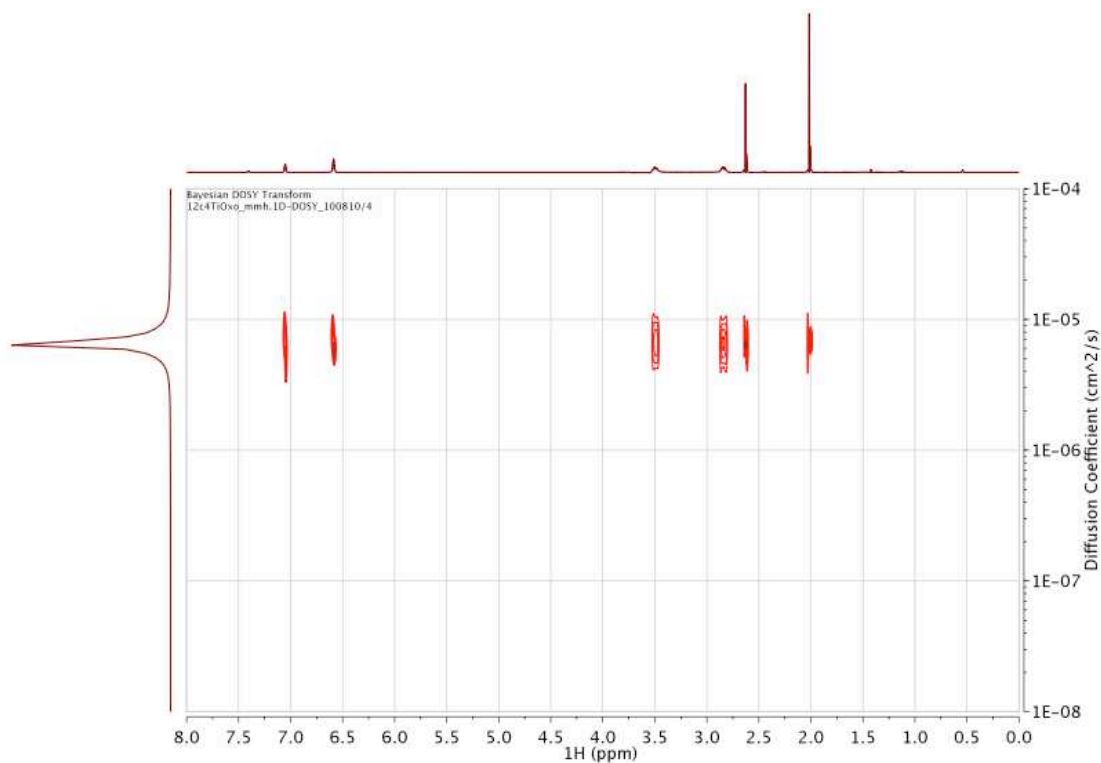


Figure S 9. 2D-DOSY of [(12-crown-4)Li][1] in C₆D₆, 25 °C, 400 MHz.

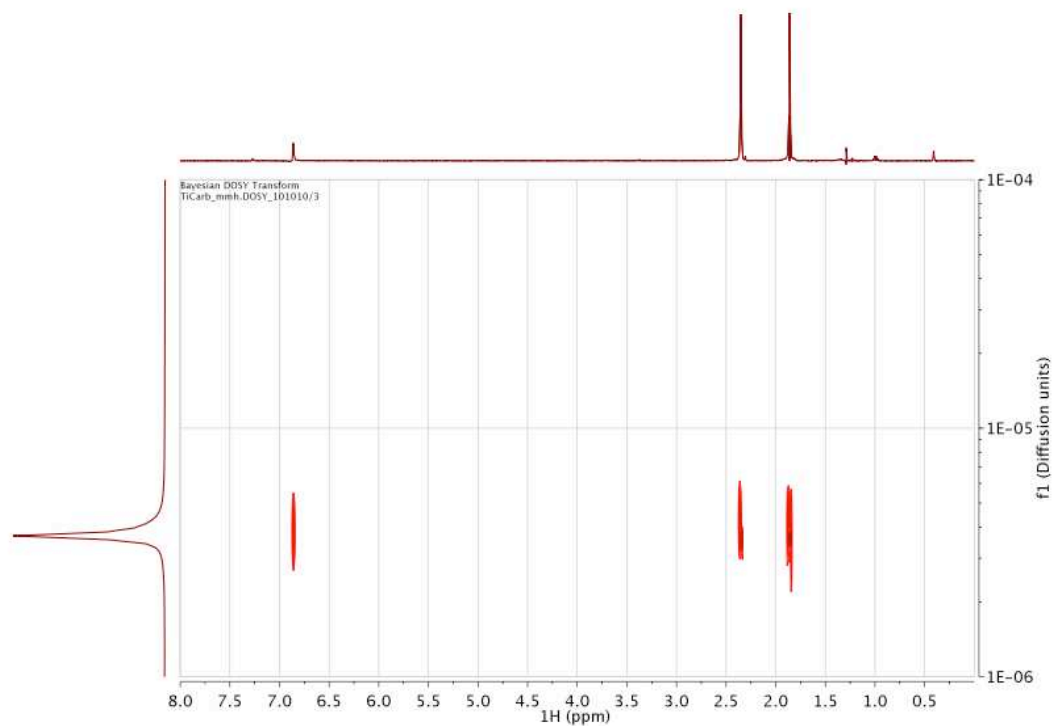


Figure S 10. 2D-DOSY of [Li][2] in C₆D₆, 25 °C, 400 MHz.

S4. Computational Details

Table S 2. Optimized atomic coordinates for [Li][2]

| Atom | x | y | z |
|------|----------|-----------|----------|
| C | 1.98852 | 16.356423 | 5.175173 |
| C | 1.363884 | 15.309387 | 5.873802 |
| C | 0.695128 | 15.528118 | 7.082931 |
| C | 0.628824 | 16.831631 | 7.589083 |
| C | 1.2138 | 17.904828 | 6.909346 |
| C | 1.893154 | 17.65011 | 5.713248 |
| C | 0.058342 | 14.38591 | 7.840536 |
| C | 1.092097 | 19.31446 | 7.441057 |
| N | 2.734242 | 16.07597 | 3.975864 |
| C | 4.234186 | 15.904733 | 4.213299 |
| C | 4.515612 | 15.163551 | 5.539294 |
| Ti | 1.833267 | 16.179386 | 2.231722 |
| N | 1.237109 | 14.41718 | 1.613064 |
| C | 1.056659 | 13.352391 | 2.565991 |
| C | 2.091073 | 12.459883 | 2.889654 |

| | | | |
|---|-----------|-----------|-----------|
| C | 1.904329 | 11.407995 | 3.792483 |
| C | 0.64434 | 11.242519 | 4.376527 |
| C | -0.414243 | 12.108811 | 4.078354 |
| C | -0.190281 | 13.162261 | 3.185383 |
| C | 3.031113 | 10.448432 | 4.101195 |
| C | -1.772132 | 11.89253 | 4.705505 |
| O | 3.103337 | 16.789886 | 1.02332 |
| C | 3.918111 | 17.21525 | 0.067033 |
| O | 3.518039 | 18.131744 | -0.725853 |
| N | 0.31833 | 17.434365 | 2.296976 |
| C | -1.015535 | 16.920863 | 2.488284 |
| C | -1.502752 | 16.692247 | 3.785759 |
| C | -2.814767 | 16.259143 | 4.015904 |
| C | -3.651565 | 16.037747 | 2.917692 |
| C | -3.199081 | 16.234823 | 1.608502 |
| C | -1.885747 | 16.67171 | 1.412161 |
| C | -3.320961 | 16.027866 | 5.421127 |
| C | -4.123542 | 16.025607 | 0.43094 |
| O | 5.08006 | 16.698636 | -0.031164 |
| C | 0.365468 | 18.938917 | 2.066231 |
| C | -0.487934 | 19.684636 | 3.116129 |
| C | 1.809469 | 19.459906 | 2.183755 |
| C | -0.144787 | 19.308546 | 0.653852 |
| C | 1.067025 | 13.980203 | 0.163782 |
| C | 0.939225 | 15.199507 | -0.767101 |
| C | 2.282842 | 13.148431 | -0.306008 |
| C | -0.215708 | 13.137562 | -0.014719 |
| C | 4.934644 | 17.282069 | 4.258319 |
| C | 4.874658 | 15.068277 | 3.091762 |
| H | 5.939442 | 14.932858 | 3.316445 |
| H | 6.018482 | 17.147919 | 4.374313 |
| H | 4.812184 | 15.541345 | 2.114134 |
| H | 4.764039 | 17.842161 | 3.334458 |
| H | 4.587906 | 17.883035 | 5.104273 |
| H | 5.600452 | 15.037609 | 5.647622 |
| H | 4.154167 | 15.710724 | 6.414802 |
| H | 3.063648 | 12.590445 | 2.428392 |
| H | 4.009438 | 10.892344 | 3.887788 |
| H | 3.023349 | 10.141557 | 5.153894 |

| | | | |
|---|-----------|-----------|-----------|
| H | 0.483536 | 10.420742 | 5.076549 |
| H | 0.336018 | 14.409698 | 8.901743 |
| H | 0.360523 | 13.416831 | 7.434419 |
| H | 1.429413 | 14.30519 | 5.467281 |
| H | 1.077539 | 19.332535 | 8.536877 |
| H | 1.921115 | 19.946878 | 7.104553 |
| H | 0.162019 | 19.788355 | 7.096431 |
| H | -0.843373 | 16.878096 | 4.626989 |
| H | -0.190368 | 12.214232 | 0.571057 |
| H | -0.996749 | 13.848957 | 2.949062 |
| H | 0.114296 | 17.014057 | 8.533971 |
| H | -1.72962 | 11.984577 | 5.798801 |
| H | -1.037944 | 14.438262 | 7.7948 |
| H | -2.152979 | 10.886861 | 4.484566 |
| H | -2.504914 | 12.615115 | 4.336859 |
| H | -3.051783 | 15.02624 | 5.7813 |
| H | -2.893577 | 16.748051 | 6.12636 |
| H | -4.412472 | 16.110712 | 5.469669 |
| H | -4.677655 | 15.707549 | 3.084896 |
| H | -4.915824 | 15.304884 | 0.662843 |
| H | -4.614187 | 16.966025 | 0.142167 |
| H | -3.58261 | 15.659546 | -0.449177 |
| H | -1.543924 | 19.402974 | 3.068279 |
| H | -1.535472 | 16.829366 | 0.398129 |
| H | -0.421519 | 20.764608 | 2.931492 |
| H | -0.126887 | 19.490081 | 4.130483 |
| H | -1.105335 | 13.705169 | 0.276491 |
| H | -1.210293 | 19.093485 | 0.535157 |
| H | -0.00831 | 20.384842 | 0.482634 |
| H | 0.418777 | 18.774448 | -0.117985 |
| H | 0.725725 | 14.84806 | -1.782792 |
| H | 1.792218 | 20.555739 | 2.190734 |
| H | 2.422759 | 19.149222 | 1.33966 |
| H | 1.849641 | 15.794228 | -0.814854 |
| H | 2.282879 | 19.132847 | 3.110902 |
| H | 3.21713 | 13.703202 | -0.170354 |
| H | 2.356434 | 12.199688 | 0.232978 |
| H | 2.357534 | 18.477929 | 5.188822 |
| H | 2.181052 | 12.910604 | -1.373532 |

| | | | |
|----|-----------|-----------|-----------|
| H | 2.948741 | 9.533598 | 3.49739 |
| H | 0.119094 | 15.849726 | -0.464398 |
| H | -0.319094 | 12.859878 | -1.071691 |
| H | 4.420935 | 14.077936 | 3.042266 |
| H | 4.060012 | 14.167561 | 5.543527 |
| Li | 5.185835 | 17.886275 | -1.415847 |

Table S 3. Calculated Chemical Shielding Constant and Corrected Chemical Shift for CO₂ and [Li][2].

| | Calculated Isotropic Chemical Shielding Constant (σ) | Calculated δ_{iso} (¹³ C) ^a | Observed δ |
|-----------------|---|---|-------------------|
| CO ₂ | -56.23 ppm | 125.69 ppm | 126 ppm |
| [Li][2] | -19.771 ppm | 162.15 ppm | 160 ppm |

^a) Referenced vs. CO₂ in THF-*d*₈ at 125.69 ppm

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