

Supporting Information

Solution and Solid-State Structures of Lithiated Phenyloxazolines

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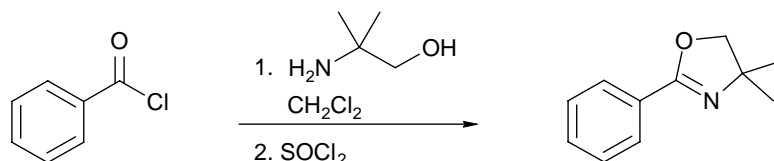
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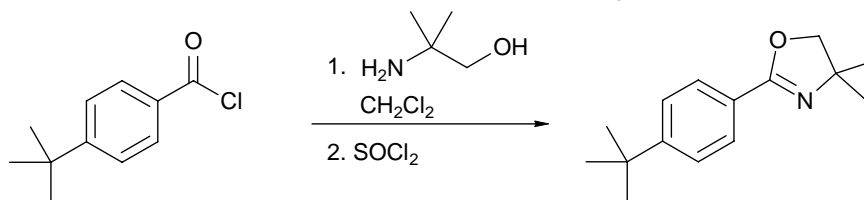
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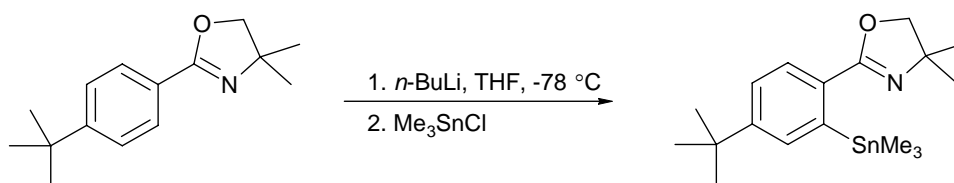
Experimental Section



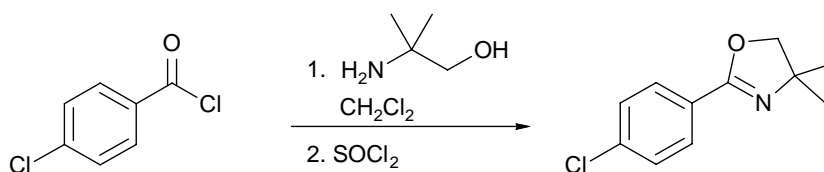
4,4-Dimethyl-2-phenyl-4,5-dihydrooxazole.^[S-1] Benzoyl chloride (4.6 mL, 40 mmol) in CH₂Cl₂ (18 mL) was added to a 0 °C solution of 2-amino-2-methyl-1-propanol (7.6 mL, 80 mmol) in CH₂Cl₂ (18 mL) over a period of 5 min during which time a white precipitate formed. The cold bath was removed and the mixture was stirred at rt for 2.5 h. The mixture was cooled to 0 °C and filtered. The mother liquor was concentrated resulting in the formation of crystals that were isolated. The combined crystals were washed with cold CH₂Cl₂ (20 mL) and allowed to dry. SOCl₂ (9.4 mL, 129 mmol) was added slowly over a period of 5 min to the white crystals of *N*-(2-hydroxy-1,1-dimethylethyl)-benzamide and stirred for 10 min. The resulting solution was carefully basified with 2M NaOH until the pH was 9-10. H₂O was added and the product extracted with Et₂O. The Et₂O was washed with brine and dried over MgSO₄. The mixture was filtered and the solvent removed *in vacuo*. The resulting oil was purified by Kugelrohr distillation (68-72 °C @ 0.4 mm Hg) resulting in white crystals of 4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (1.54 g, 8.8 mmol, 22 %). ¹H NMR (CDCl₃, 300 MHz): δ 1.37 (s, 6H), 4.08 (s, 2H), 7.33-7.48 (m, 3H), 7.90-7.98 (m, 2H). ¹³C{¹H} NMR (CDCl₃, 62.9 MHz): δ 28.3 (CH₃), 67.4 (C), 78.9 (CH₂), 127.9 (C), 128.05 (CH), 128.08 (CH), 130.98 (CH), 161.85 (C). MS (EI): M⁺ = 175.0995 (calcd for C₁₁H₁₃NO: 175.0997).



4-*t*-Butyl-4,4-dimethyl-2-phenyl-4,5-dihydrooxazole.^[S-1] 4-*t*-Butylbenzoyl chloride (7.5 mL, 40 mmol) in CH₂Cl₂ (23 mL) was added to a 0 °C solution of 2-amino-2-methyl-1-propanol (7.6 mL, 80 mmol) in CH₂Cl₂ (13 mL) over a period of 5 min during which time a white precipitate formed. The cold bath was removed and the mixture was stirred at rt for 2.5 h. The mixture was cooled to 0 °C and filtered. The mother liquor was concentrated resulting in the formation of crystals that were isolated. The combined crystals were washed with cold CH₂Cl₂ (20 mL) and allowed to dry. SOCl₂ (9.4 mL, 129 mmol) was added slowly over a period of 5 min to the white crystals of 4-*t*-butyl-*N*-(2-hydroxy-1,1-dimethyl-ethyl)-benzamide and stirred for 10 min. The resulting solution was carefully basified with 2M NaOH until the pH was 9-10. H₂O was added and the product extracted with Et₂O. The Et₂O was washed with brine and dried over MgSO₄. The mixture was filtered and the solvent removed *in vacuo*. The resulting brown crystals were purified by Kugelrohr distillation (108 °C @ 0.025 mm Hg) resulting in white crystals of 4-*t*-butyl-4,4-dimethyl-2-phenyl-4,5-dihydro-oxazole that were further purified by recrystallization from hexane (1.8 g, 7.8 mmol, 20 %). ¹H NMR (CDCl₃, 250 MHz): δ 1.32 (s, 9H), 1.37 (s, 6H), 4.08 (s, 2H), 7.37-7.45 (m, 2H), 7.84-7.93 (m, 2H). ¹³C{¹H} NMR (CDCl₃, 62.9 MHz): δ 28.36 (CH₃), 31.10 (CH₃), 34.82 (C), 67.37 (C), 78.90 (CH₂), 125.14 (CH), 127.93 (CH), 154.50 (C), 161.93 (C). MS (ESI): [MH]⁺ = 232.1707 (calcd for [C₁₅H₂₁NO+H]⁺: 232.1701).



2-(4-*t*-Butyl-2-trimethylstannylphenyl)-4,4-dimethyl-4,5-dihydrooxazole. *n*-BuLi (2.6 M, 2.3 mL, 6.0 mmol) was added slowly to a $-78\text{ }^{\circ}\text{C}$ solution of 4-*t*-butyl-4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (0.92 g, 4.0 mmol) in THF (15 mL). The solution was stored at $-78\text{ }^{\circ}\text{C}$ for 96 h then quenched with Me_3SnCl (1.8 g, 6.8 mmol) in THF (10 mL) at $-78\text{ }^{\circ}\text{C}$. The solution was stirred for 40 min then H_2O was added and the product was extracted with Et_2O . The Et_2O was washed with brine and dried over MgSO_4 . The mixture was filtered and the solvent removed *in vacuo*. The product was purified by Kugelrohr distillation ($155\text{--}180\text{ }^{\circ}\text{C}$ at 0.02 mmHg) yielding 1.3 g (3.3 mmol, 81%) of white, crystalline product. ^1H NMR (CDCl_3 , 360 MHz): δ 0.27 (s, $^2J_{\text{IH-119Sn}} = 55.3$ Hz, 9H), 1.36 (s, 6H), 1.37 (s, 9H), 4.10 (s, 2H), 7.41 (dd, $J = 8.2, 2.2$ Hz, $^5J_{\text{IH-Sn}} = 7.8$ Hz, 1H), 7.71 (d, $J = 2.2$ Hz, $^3J_{\text{IH-119Sn}} = 55.0$ Hz, 1H), 7.81 (d, $J = 8.2$ Hz, $^4J_{\text{IH-Sn}} = 24.8$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 90.56 MHz): δ -5.4 (CH_3 , $^1J_{\text{13C-119Sn}} = 379$ Hz), 28.5 (CH_3), 31.2 (CH_3), 35.0 (C), 67.2 (C), 79.5 (CH_2), 125.1 (CH, $^4J_{\text{13C-Sn}} = 9.6$ Hz), 127.5 (C), 130.6 (CH, $^3J_{\text{13C-Sn}} = 34.7$ Hz), 133.5 (CH, $^2J_{\text{13C-Sn}} = 38.5$ Hz), 144.8 (C), 153.0 (C), 163.2 (C).



2-(4-Chlorophenyl)-4,4-dimethyl-4,5-dihydrooxazole.^[S-1] 4-Chlorobenzoyl chloride (5.1 mL, 40 mmol) in CH_2Cl_2 (10 mL) was added to a $0\text{ }^{\circ}\text{C}$ solution of 2-amino-2-methyl-1-propanol (7.6 mL, 80 mmol) in CH_2Cl_2 (26 mL) over a period of 5 min during which time a white precipitate formed. The cold bath was removed and the mixture was stirred at rt overnight during which time the CH_2Cl_2 evaporated. The flask containing the white solid was cooled to $0\text{ }^{\circ}\text{C}$ and SOCl_2 (9.4 mL, 129 mmol) was added slowly over a period of 5 min via an addition funnel and then stirred for 18 h. The resulting product was carefully basified with 2M NaOH until the pH was 9-10. H_2O was added and the product extracted with 1:1 Et_2O :hexane. The organic layer was washed with brine and dried over MgSO_4 . The mixture was filtered and the solvent removed *in vacuo*. The resulting solid was purified by Kugelrohr distillation ($90\text{--}102\text{ }^{\circ}\text{C}$ @ 0.014 mmHg) resulting in white crystals of 2-(4-chlorophenyl)-4,4-dimethyl-4,5-dihydrooxazole that were further purified by recrystallization from hexane (1.8 g, 7.8 mmol, 20 %). ^1H NMR (CDCl_3 , 300 MHz): δ 1.38 (s, 6H), 4.11 (s, 2H), 7.37 (m, 2H), 7.87 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 90.56 MHz): δ 28.2 (CH_3), 67.7 (C), 79.2 (CH_2), 126.5 (C), 128.5 (CH), 129.5 (CH), 137.2 (C), 161.1 (C). MS (ESI): $[\text{MH}]^+ = 210.0676$ (calcd for $[\text{C}_{11}\text{H}_{12}\text{ClNO} + \text{H}]^+$: 210.0685).

Low temperature ^{13}C and ^6Li NMR experiment of [2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl]lithium (1**).** 4,4-Dimethyl-2-phenyl-4,5-dihydrooxazole in oil form (75 mg, 0.428 mmol) was added to a dry, N_2 -purged 10 mm NMR tube through a septum. THF (1.5 mL) was added, the solution was cooled to $-78\text{ }^\circ\text{C}$ and 2.58 M *n*-BuLi (0.166 mL, 0.428 mmol) was added slowly and the solution was shaken resulting in a yellow solution. The sample was stored at $-78\text{ }^\circ\text{C}$ for several days until a yellow precipitate formed. The solvent was removed and THF (1.5 mL) was added and the sample was shaken until the solid dissolved. A yellow precipitate formed overnight, the solvent was removed and THF (1.5 mL), Et_2O (1.0 mL) and $(\text{Me}_3\text{Si})_3\text{CH}$ (1 μL) were added. The sample was shaken until the precipitate dissolved. ^{13}C and ^6Li NMR spectra were acquired at $-114\text{ }^\circ\text{C}$. The sample was quenched with MeSSMe (50 μL , 0.44 mmol), concentrated and the quantity of the product sulfide (0.38 mmol) was determined by integration relative to pentachloroethane (30 μL , 0.25 mmol) in the ^1H NMR spectrum. See Fig. 1 for spectra.

Dilution study of [^6Li]-[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl]lithium ([^6Li]-1**).** 4,4-Dimethyl-2-phenyl-4,5-dihydrooxazole (52 mg, 0.30 mmol) was added to a dry, N_2 -purged 10 mm NMR tube in a glove box and the NMR tube was sealed with a septum. THF (1.8 mL) was added, the solution was cooled to $-78\text{ }^\circ\text{C}$ and 1.6 M [^6Li]-*n*-BuLi (0.200 mL, 0.32 mmol) was added slowly and the solution shaken. Placed in a $-50\text{ }^\circ\text{C}$ bath for several hours. Crystal formed while taking NMR spectra at $-102\text{ }^\circ\text{C}$. The solvent was removed and the crystals were rinsed with Et_2O and then THF (1.8 mL) and Et_2O (1.2 mL) were added and the solid dissolved after shaking the sample. Crystals once again formed at $-78\text{ }^\circ\text{C}$. A small portion of the solvent (ca 0.75 mL) was removed and THF (1.8 mL) and Et_2O (1.2 mL) were added and the solid dissolved after shaking the sample. ^{13}C and ^6Li NMR spectra were acquired at $-102\text{ }^\circ\text{C}$. A portion of the sample (1.0 mL) was pulled up into a syringe and added to a dry, N_2 -purged 10 mm NMR tube through a septum. The sample was diluted with THF (1.8 mL) and Et_2O (1.2 mL) and ^{13}C and ^6Li NMR spectra were acquired at $-102\text{ }^\circ\text{C}$. The relative monomer and dimer concentrations were obtained by integration of the ^6Li NMR spectra. The sample was quenched with MeSSMe (20 μL , 0.18 mmol), concentrated and the quantity of the product sulfide (0.012 mmol) was determined by integration relative to pentachloroethane (8.8 mg, 0.043 mmol) in the ^1H NMR spectrum. The concentration of the final diluted sample was therefore determined to be 0.003M. The slope of a $-\log[\text{dimer}]$ vs $-\log[\text{monomer}]$ plot was 2.3.

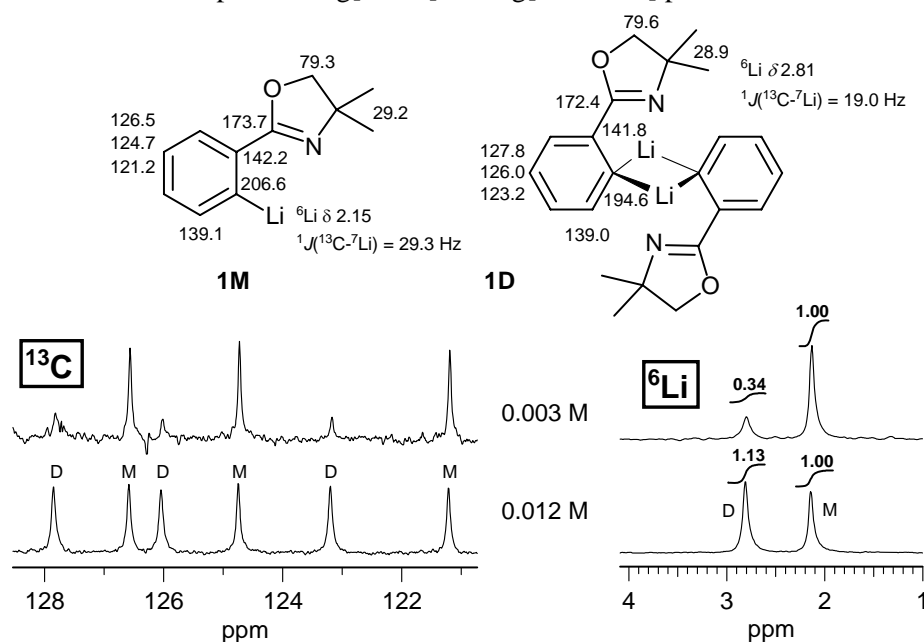


Figure S-1. ^{13}C and ^6Li NMR dilution experiment of 0.012M [^6Li]-[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl]lithium (^6Li -**1**) in 3:2 THF: Et_2O at $-102\text{ }^\circ\text{C}$.

Variable temperature ^{13}C and ^6Li NMR experiment of 5-*t*-butyl[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl]lithium (2). 4-*t*-Butyl-4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (113 mg, 0.488 mmol) was added to a dry, N_2 -purged 10 mm NMR tube in a glove box and the NMR tube was sealed with a septum. THF (1.5 mL) was added, the solution was cooled to $-78\text{ }^\circ\text{C}$ and 2.58 M *n*-BuLi (0.190 mL, 0.488 mmol) was added slowly and the solution was shaken resulting in a yellow solution. The sample was stored at $-78\text{ }^\circ\text{C}$ for several days until a yellow precipitate formed. The solvent was removed and THF (1.5 mL) was added and the sample was shaken until the solid dissolved. After several days, the yellow precipitate formed again, the solvent was removed and THF (1.5 mL), Me_2O (1.0 mL), Et_2O (0.5 mL) and $(\text{Me}_3\text{Si})_3\text{CH}$ (2 μL) were added. ^{13}C and ^6Li NMR spectra were acquired between $-136\text{ }^\circ\text{C}$ and $-23\text{ }^\circ\text{C}$. The sample was then used in a HMPA titration. See Fig. 3 for spectra.

HMPA titration of 5-*t*-butyl[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl]lithium (2). The sample used to perform the variable temperature ^{13}C and ^6Li NMR experiment was used in this HMPA titration. ^{13}C and ^6Li NMR spectra were acquired at $-118\text{ }^\circ\text{C}$. HMPA (30 μL , 0.17 mmol, 0.88 equiv) was added and ^{13}C , ^7Li and ^{31}P NMR spectra were acquired at $-139\text{ }^\circ\text{C}$. Addition quantities of HMPA (20 μL , 50 μL , 100 μL and 100 μL) were added and ^{13}C , ^7Li and ^{31}P NMR spectra were acquired at $-139\text{ }^\circ\text{C}$ after each addition. The sample was quenched with MeSSMe (54 μL , 0.47 mmol), concentrated and the quantity of the product sulfide (0.20 mmol) was determined by integration relative to pentachloroethane (15 μL , 0.125 mmol) in the ^1H NMR spectrum. See Fig. 4 for spectra. The ^7Li FIDs were processed with a Gaussian window function to provide enhanced resolution in the ^7Li spectra.

Dilution experiment of 5-*t*-butyl[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl]lithium (2). 4-*t*-Butyl-4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (95 mg, 0.41 mmol) was added to a dry, N₂-purged 10 mm NMR tube in a glove box and the NMR tube was sealed with a septum. THF (1.5 mL) was added, the solution was cooled to -78 °C and 2.58 M *n*-BuLi (0.160 mL, 0.41 mmol) was added slowly and the sample was shaken. The sample was stored at -78 °C for two days until crystals formed. The solvent was removed and THF (1.5 mL) and Et₂O (1.0 mL) were added and the sample was shaken until the solid dissolved. ¹³C and ⁶Li NMR spectra were acquired at ca -120 °C. THF (1.5 mL) and Et₂O (1.0 mL) were added and ¹³C and ⁶Li NMR spectra were acquired at ca -120 °C. The solution was diluted once more with THF (3.0 mL) and Et₂O (2.0 mL) and ¹³C and ⁶Li NMR spectra were acquired at ca -120 °C. The final molarity of the sample was not determined. A -log[dimer] vs -log[monomer] plot of variable concentration ⁶Li NMR data (assuming initial sample concentration of 0.15 M) gave a slope of 2.4.

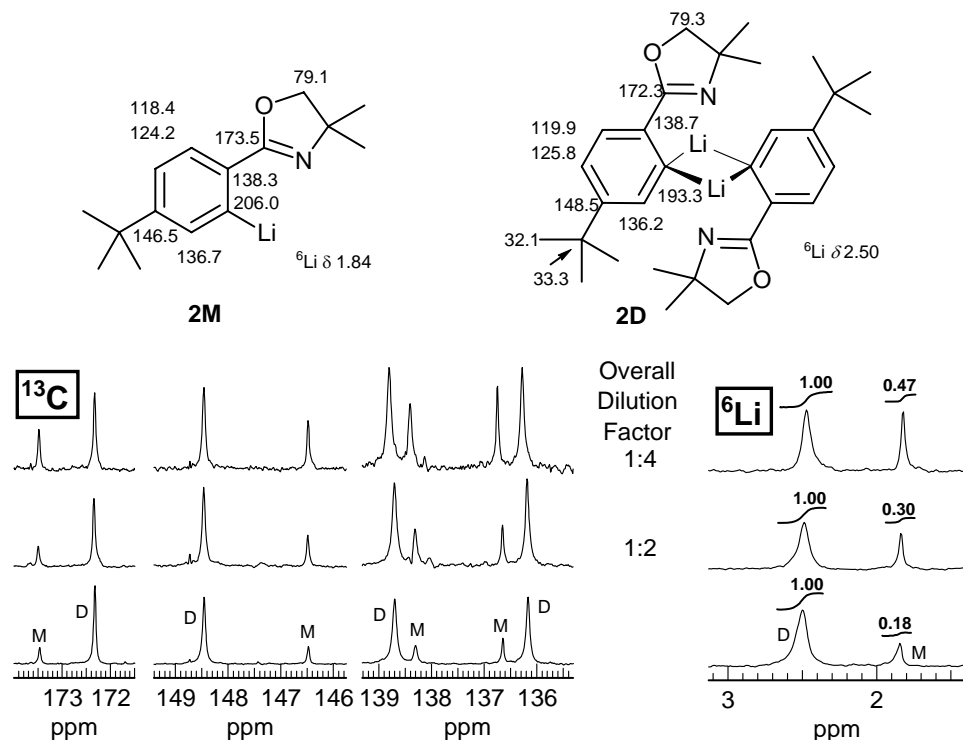


Figure S-2. ¹³C and ⁶Li NMR dilution experiment of ca. 0.12 M 5-*t*-butyl[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl]lithium ([⁶Li]-1) in 3:2 THF:Et₂O at -120 °C (sample concentration was not determined).

PMDTA titration of [⁶Li]-5-*t*-butyl[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl]lithium ([⁶Li]-2).

2-(4-*t*-Butyl-2-trimethylstannyl-phenyl)-4,4-dimethyl-4,5-dihydrooxazole (59 mg, 0.15 mmol) was added to a dry, N₂-purged 5 mm NMR tube in a glove box and the tube was sealed with a septum. THF (0.45 mL), Et₂O (0.30 mL) and (Me₃Si)₃CH (1 μL) were added, the solution was cooled to -78 °C and 1.6 M [⁶Li]-*n*-BuLi (0.098 mL, 0.16 mmol) was added slowly and the solution shaken. ¹³C and ⁶Li NMR spectra were acquired at -117 °C. PMDTA (15.5 μL, 0.074 mmol, 0.50 equiv) was added and ¹³C and ⁶Li NMR spectra were acquired at -117 °C. Addition quantities of PMDTA (15.5 μL, 31 μL and 62 μL) were added and ¹³C and ⁶Li NMR spectra were acquired at -117 °C after each addition. See Fig. 6 for spectra.

TMEDA titration of [⁶Li]-5-*t*-butyl-[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-phenyl]-lithium

([⁶Li]-2). 2-(4-*t*-Butyl-2-trimethylstannyl-phenyl)-4,4-dimethyl-4,5-dihydrooxazole (52 mg, 0.13 mmol) was added to a dry, N₂-purged 5 mm NMR tube in a glove box and the tube was sealed with a septum. THF (0.45 mL), Et₂O (0.30 mL) and (Me₃Si)₃CH (1 μL) were added, the solution was cooled to -78 °C and 1.6 M [⁶Li]-*n*-BuLi (0.084 mL, 0.13 mmol) was added slowly and the solution shaken. ¹³C and ⁶Li NMR spectra were acquired at -117 °C. TMEDA (9.4 μL, 0.062 mmol, 0.48 equiv) was added and ¹³C and ⁶Li NMR spectra were acquired at -117 °C. Addition quantities of TMEDA (9.4 μL, 9.4 μL, 9.4 μL, 37.4 μL and 37.4 μL) were added and ¹³C and ⁶Li NMR spectra were acquired at -117 °C after each addition.

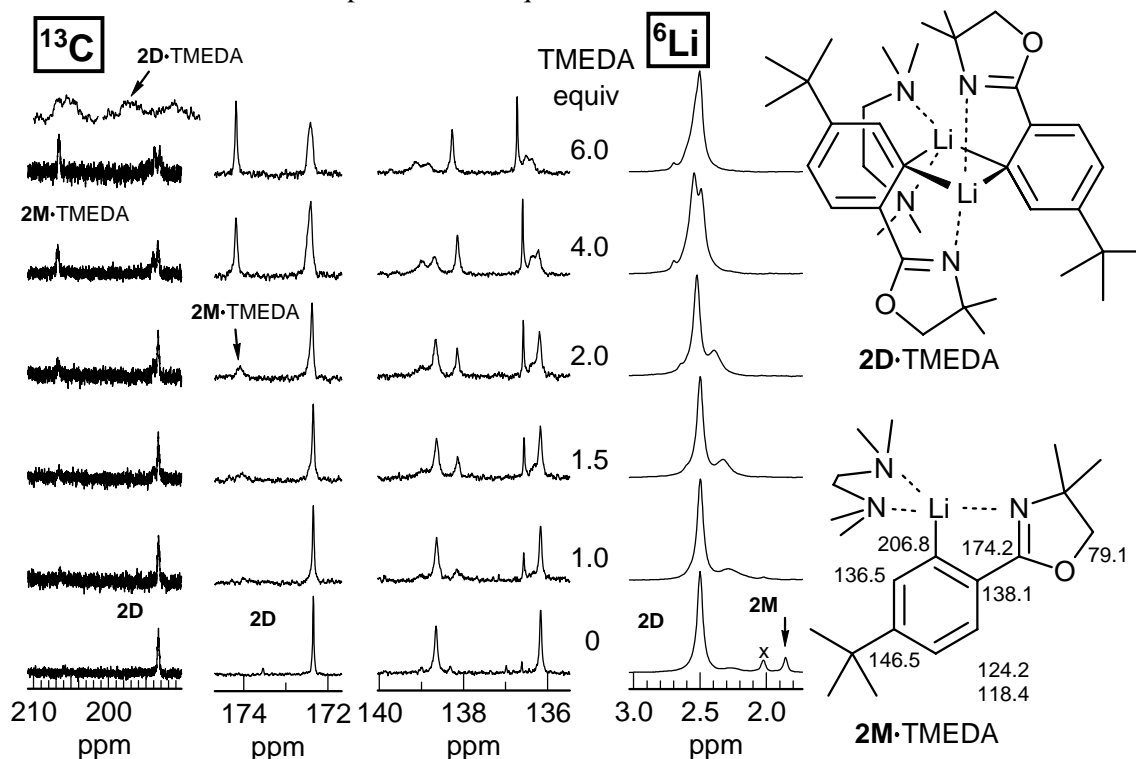
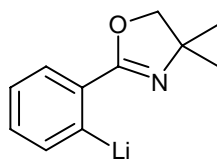


Figure S-3. TMEDA titration of 0.16 M [⁶Li]-5-*t*-butyl[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl]lithium ([⁶Li]-2) in 3:2 THF:Et₂O at -117 °C.

Low temperature ¹³C and ⁶Li NMR experiment of 5-chloro-[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl]lithium (3). 2-(4-Chloro-phenyl)-4,4-dimethyl-4,5-dihydrooxazole (0.253 g, 1.21 mmol) were added to a dry 10 mm NMR tube containing Ar. THF (1.8 mL), Et₂O (1.2 mL) and (Me₃Si)₃CH (2 μL) were added, the solution was cooled to -78 °C, and 2.6 M *n*-BuLi (0.462 mL, 1.21 mmol) was added slowly and the orange solution was shaken. Crystals formed, the solvent was removed and the crystals were redissolved in THF (1.5 mL) and Et₂O (1.0 mL). ¹³C and ⁶Li NMR spectra were acquired at -125 °C. The sample was then used in a PMDTA titration. See Fig. 5 for spectra.

PMDTA titration of 5-chloro-[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl]lithium (3). The sample used for the low temperature ¹³C and ⁶Li NMR experiment of **3** was used for this titration. PMDTA (200 μL, 0.96 mmol, 1.1 equiv) was added and ¹³C and ⁶Li NMR spectra were acquired at -125 °C. Another portion of PMDTA (200 μL, 0.96 mmol, 1.1 equiv) was added and ¹³C and ⁶Li NMR spectra were acquired at -125 °C. The sample was quenched with 3M propionic acid in Et₂O (0.50 mL, 1.5 mmol) and the quantity of 2-(4-chloro-phenyl)-4,4-dimethyl-4,5-dihydro-oxazole (0.84 mmol) was determined by integration relative to pentachloroethane (30 μL, 0.25 mmol) in the ¹H NMR spectrum. See Fig. 5 for spectra.

X-ray Crystal Structure of the THF Solvate of Dimeric 1



1

Preparation of X-ray-Quality Crystals. 4,4-Dimethyl-2-phenyl-4,5-dihydrooxazole (57 mg, 0.32 mmol) was added to a dry, N₂-purged 10 mm NMR tube through a septum. THF (1.8 mL) was added, the solution was cooled to -78 °C and 1.60 M [⁶Li]-*n*-BuLi (0.22 mL, 0.34 mmol) was added slowly and the solution was shaken resulting in a yellow solution. The sample was stored at -78 °C for several days during which time X-ray quality crystals of (1 · THF)₂ · 2THF formed.

Data Collection. A pale yellow air-sensitive solvent dependent temperature sensitive crystal with approximate dimensions 0.45 x 0.40 x 0.37 mm³ was selected under inert atmosphere of argon on a slide cooled by dry ice and attached to the tip of a glass capillary with vacuum grease. The crystal was mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with the exposure time of 10 seconds per frame. A total of 68 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 2948 strong reflections from the actual data collection.

The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of 0.80 Å. A total of 3221 data were harvested by collecting three sets of frames with 0.3° scans in ω with an exposure time 30 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.^[S-2]

Structure Solution and Refinement. The systematic absences in the diffraction data were consistent for the space groups *P*1 and *P*.^[S-3] The *E*-statistics strongly suggested the centrosymmetric space group *P* that yielded chemically reasonable and computationally stable results of refinement.

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The dinuclear complex occupies a crystallographic inversion center. There are also two solvate molecules of THF per dimer in the lattice.

The final least-squares refinement of 219 parameters against 3221 data resulted in residuals *R* (based on *F*² for *I* ≥ 2σ) and *wR* (based on *F*² for all data) of 0.0539 and 0.1419, respectively. The final difference Fourier map was featureless.

The ORTEP diagrams are drawn with 30% probability ellipsoids.

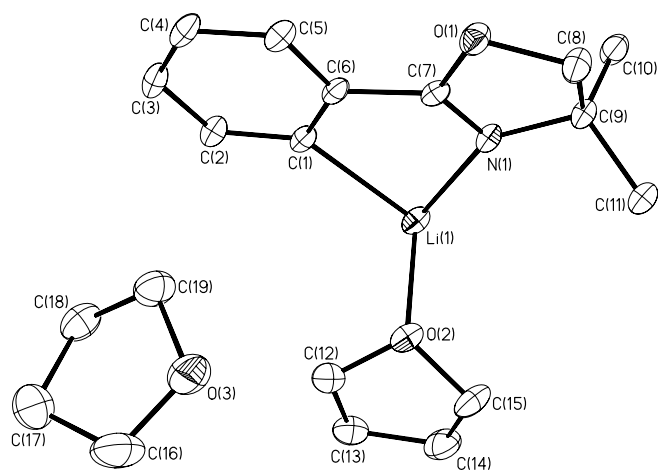


Figure S-4. The content of the asymmetric unit.

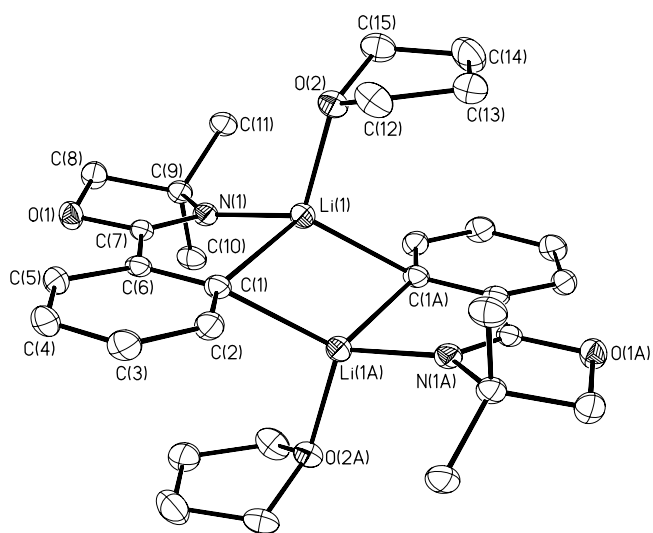


Figure S-5. The dimer structure of $(1 \cdot \text{THF})_2$.

Table S-1. Crystal data and structure refinement for $(\mathbf{1} \cdot \text{THF})_2 \cdot 2\text{THF}$.

| | | |
|-----------------------------------|---|-------------------|
| Identification code | $(\mathbf{1} \cdot \text{THF})_2 \cdot 2\text{THF}$ | |
| Empirical formula | C ₃₈ H ₅₆ Li ₂ N ₂ O ₆ | |
| Formula weight | 650.73 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | $P\bar{1}$ | |
| Unit cell dimensions | a = 9.5171(7) Å | a = 70.3860(10)°. |
| | b = 10.1009(7) Å | b = 81.2070(10)°. |
| | c = 10.3488(7) Å | g = 86.6060(10)°. |
| Volume | 926.07(11) Å ³ | |
| Z | 1 | |
| Density (calculated) | 1.167 Mg/m ³ | |
| Absorption coefficient | 0.077 mm ⁻¹ | |
| F(000) | 352 | |
| Crystal size | 0.45 x 0.40 x 0.37 mm ³ | |
| Theta range for data collection | 2.11 to 25.00°. | |
| Index ranges | -11 ≤ h ≤ 11, -10 ≤ k ≤ 12, 0 ≤ l ≤ 12 | |
| Reflections collected | 7476 | |
| Independent reflections | 3221 [R(int) = 0.0337] | |
| Completeness to theta = 25.00° | 99.1 % | |
| Max. and min. transmission | 0.9722 and 0.9663 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 3221 / 0 / 219 | |
| Goodness-of-fit on F ² | 0.995 | |
| Final R indices [I > 2σ(I)] | R1 = 0.0539, wR2 = 0.1419 | |
| R indices (all data) | R1 = 0.0693, wR2 = 0.1499 | |
| Largest diff. peak and hole | 0.324 and -0.191 e.Å ⁻³ | |

Table S-2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|-------|---------|----------|----------|-------|
| Li(1) | 3977(3) | 466(3) | -515(3) | 33(1) |
| O(1) | 790(1) | -2255(1) | 1201(1) | 35(1) |
| O(2) | 3205(1) | 2382(1) | -929(1) | 41(1) |
| O(3) | 722(2) | 3085(2) | 2728(2) | 64(1) |
| N(1) | 2515(2) | -969(2) | -376(1) | 29(1) |
| C(1) | 3901(2) | -611(2) | 1779(2) | 30(1) |
| C(2) | 4385(2) | -549(2) | 2979(2) | 34(1) |
| C(3) | 3704(2) | -1180(2) | 4324(2) | 39(1) |
| C(4) | 2452(2) | -1897(2) | 4546(2) | 39(1) |
| C(5) | 1894(2) | -1974(2) | 3413(2) | 34(1) |
| C(6) | 2616(2) | -1351(2) | 2080(2) | 28(1) |
| C(7) | 1997(2) | -1495(2) | 904(2) | 27(1) |
| C(8) | 332(2) | -2053(2) | -134(2) | 37(1) |
| C(9) | 1658(2) | -1497(2) | -1181(2) | 31(1) |
| C(10) | 2486(2) | -2680(2) | -1558(2) | 40(1) |
| C(11) | 1322(2) | -312(2) | -2468(2) | 38(1) |
| C(12) | 3851(3) | 3236(2) | -335(2) | 52(1) |
| C(13) | 4859(2) | 4198(2) | -1496(2) | 50(1) |
| C(14) | 4317(3) | 4207(3) | -2804(2) | 57(1) |
| C(15) | 3022(2) | 3283(3) | -2297(2) | 53(1) |
| C(16) | 894(3) | 4283(3) | 3085(3) | 73(1) |
| C(17) | 1899(3) | 3917(3) | 4141(3) | 61(1) |
| C(18) | 2705(2) | 2676(2) | 3893(2) | 52(1) |
| C(19) | 1604(2) | 1984(2) | 3451(3) | 52(1) |

Table S-3. Bond lengths [Å] and angles [°] for $(\mathbf{1} \cdot \text{THF})_2 \cdot 2\text{THF}$.

| | | | |
|----------------------|------------|--------------------|------------|
| Li(1)-O(2) | 1.959(3) | C(2)-C(3) | 1.393(3) |
| Li(1)-N(1) | 2.024(3) | C(2)-Li(1)#1 | 2.756(3) |
| Li(1)-C(1)#1 | 2.217(3) | C(3)-C(4) | 1.379(3) |
| Li(1)-C(1) | 2.247(3) | C(4)-C(5) | 1.385(3) |
| Li(1)-Li(1)#1 | 2.358(6) | C(5)-C(6) | 1.397(2) |
| Li(1)-C(2)#1 | 2.756(3) | C(6)-C(7) | 1.482(2) |
| O(1)-C(7) | 1.358(2) | C(8)-C(9) | 1.529(3) |
| O(1)-C(8) | 1.458(2) | C(9)-C(10) | 1.519(3) |
| O(2)-C(12) | 1.426(3) | C(9)-C(11) | 1.524(2) |
| O(2)-C(15) | 1.433(2) | C(12)-C(13) | 1.510(3) |
| O(3)-C(16) | 1.403(3) | C(13)-C(14) | 1.518(3) |
| O(3)-C(19) | 1.423(3) | C(14)-C(15) | 1.508(3) |
| N(1)-C(7) | 1.280(2) | C(16)-C(17) | 1.501(4) |
| N(1)-C(9) | 1.484(2) | C(17)-C(18) | 1.506(4) |
| C(1)-C(6) | 1.409(2) | C(18)-C(19) | 1.498(3) |
| C(1)-C(2) | 1.410(2) | | |
| C(1)-Li(1)#1 | 2.217(3) | | |
| O(2)-Li(1)-N(1) | 113.25(15) | C(6)-C(1)-Li(1) | 100.29(14) |
| O(2)-Li(1)-C(1)#1 | 107.03(14) | C(2)-C(1)-Li(1) | 144.09(16) |
| N(1)-Li(1)-C(1)#1 | 122.77(16) | Li(1)#1-C(1)-Li(1) | 63.77(14) |
| O(2)-Li(1)-C(1) | 111.23(15) | C(3)-C(2)-C(1) | 124.35(18) |
| N(1)-Li(1)-C(1) | 84.95(12) | C(3)-C(2)-Li(1)#1 | 155.90(16) |
| C(1)#1-Li(1)-C(1) | 116.23(14) | C(1)-C(2)-Li(1)#1 | 53.05(11) |
| O(2)-Li(1)-Li(1)#1 | 128.3(2) | C(4)-C(3)-C(2) | 120.04(17) |
| N(1)-Li(1)-Li(1)#1 | 115.1(2) | C(3)-C(4)-C(5) | 118.88(17) |
| C(1)#1-Li(1)-Li(1)#1 | 58.74(13) | C(4)-C(5)-C(6) | 119.64(17) |
| C(1)-Li(1)-Li(1)#1 | 57.49(13) | C(5)-C(6)-C(1) | 124.45(16) |
| O(2)-Li(1)-C(2)#1 | 102.84(13) | C(5)-C(6)-C(7) | 117.69(16) |
| N(1)-Li(1)-C(2)#1 | 100.06(13) | C(1)-C(6)-C(7) | 117.86(15) |
| C(1)#1-Li(1)-C(2)#1 | 30.55(7) | N(1)-C(7)-O(1) | 116.96(15) |
| C(1)-Li(1)-C(2)#1 | 140.32(14) | N(1)-C(7)-C(6) | 125.34(16) |
| Li(1)#1-Li(1)-C(2)#1 | 85.63(16) | O(1)-C(7)-C(6) | 117.69(14) |
| C(7)-O(1)-C(8) | 105.37(13) | O(1)-C(8)-C(9) | 103.85(14) |
| C(12)-O(2)-C(15) | 105.30(16) | N(1)-C(9)-C(10) | 108.19(14) |
| C(12)-O(2)-Li(1) | 114.38(15) | N(1)-C(9)-C(11) | 110.60(15) |
| C(15)-O(2)-Li(1) | 123.66(16) | C(10)-C(9)-C(11) | 111.47(15) |
| C(16)-O(3)-C(19) | 109.05(18) | N(1)-C(9)-C(8) | 102.26(13) |
| C(7)-N(1)-C(9) | 107.42(14) | C(10)-C(9)-C(8) | 111.14(16) |
| C(7)-N(1)-Li(1) | 107.26(14) | C(11)-C(9)-C(8) | 112.73(15) |
| C(9)-N(1)-Li(1) | 144.39(14) | O(2)-C(12)-C(13) | 106.28(17) |
| C(6)-C(1)-C(2) | 112.62(15) | C(12)-C(13)-C(14) | 104.17(18) |
| C(6)-C(1)-Li(1)#1 | 140.25(15) | C(15)-C(14)-C(13) | 104.81(18) |
| C(2)-C(1)-Li(1)#1 | 96.40(14) | O(2)-C(15)-C(14) | 105.47(17) |

| | | | |
|-------------------|------------|------------------|------------|
| O(3)-C(16)-C(17) | 108.2(2) | O(3)-C(19)-C(18) | 106.14(18) |
| C(16)-C(17)-C(18) | 102.6(2) | | |
| C(19)-C(18)-C(17) | 102.20(18) | | |

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y, -z$

Table S-4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\mathbf{1} \cdot \text{THF})_2 \cdot 2\text{THF}$. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^* 2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U ¹¹ | U ²² | U ³³ | U ²³ | U ¹³ | U ¹² |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Li(1) | 31(2) | 36(2) | 26(2) | -2(1) | -4(1) | 1(1) |
| O(1) | 35(1) | 41(1) | 26(1) | -4(1) | -4(1) | -5(1) |
| O(2) | 41(1) | 38(1) | 36(1) | -2(1) | -9(1) | 3(1) |
| O(3) | 69(1) | 57(1) | 70(1) | -16(1) | -40(1) | 14(1) |
| N(1) | 29(1) | 34(1) | 22(1) | -5(1) | -7(1) | 3(1) |
| C(1) | 31(1) | 32(1) | 22(1) | -4(1) | -4(1) | 6(1) |
| C(2) | 31(1) | 42(1) | 26(1) | -8(1) | -6(1) | 3(1) |
| C(3) | 41(1) | 51(1) | 23(1) | -10(1) | -9(1) | 7(1) |
| C(4) | 44(1) | 45(1) | 19(1) | -2(1) | -2(1) | 4(1) |
| C(5) | 33(1) | 38(1) | 25(1) | -3(1) | -3(1) | 1(1) |
| C(6) | 30(1) | 28(1) | 21(1) | -4(1) | -6(1) | 8(1) |
| C(7) | 27(1) | 26(1) | 24(1) | -3(1) | -4(1) | 5(1) |
| C(8) | 35(1) | 46(1) | 29(1) | -9(1) | -9(1) | -3(1) |
| C(9) | 32(1) | 35(1) | 24(1) | -6(1) | -9(1) | 2(1) |
| C(10) | 49(1) | 40(1) | 29(1) | -9(1) | -12(1) | 9(1) |
| C(11) | 39(1) | 41(1) | 31(1) | -6(1) | -13(1) | 5(1) |
| C(12) | 70(2) | 39(1) | 45(1) | -12(1) | -10(1) | 2(1) |
| C(13) | 47(1) | 40(1) | 59(1) | -14(1) | -7(1) | 5(1) |
| C(14) | 71(2) | 46(1) | 42(1) | 0(1) | -3(1) | 0(1) |
| C(15) | 52(1) | 53(1) | 45(1) | 4(1) | -21(1) | 8(1) |
| C(16) | 75(2) | 43(1) | 96(2) | -11(1) | -34(2) | 13(1) |
| C(17) | 56(1) | 66(2) | 65(2) | -27(1) | -9(1) | -6(1) |
| C(18) | 44(1) | 56(1) | 48(1) | -3(1) | -14(1) | 0(1) |
| C(19) | 50(1) | 45(1) | 57(1) | -10(1) | -18(1) | 9(1) |

Table S-5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\mathbf{1} \cdot \text{THF})_2 \cdot 2\text{THF}$.

| | x | y | z | U(eq) |
|--------|------|-------|-------|-------|
| H(2) | 5231 | -43 | 2862 | 41 |
| H(3) | 4102 | -1117 | 5089 | 46 |
| H(4) | 1981 | -2330 | 5459 | 46 |
| H(5) | 1024 | -2449 | 3543 | 41 |
| H(8A) | -461 | -1364 | -300 | 44 |
| H(8B) | 24 | -2951 | -184 | 44 |
| H(10A) | 3391 | -2319 | -2129 | 60 |
| H(10B) | 1930 | -3054 | -2078 | 60 |
| H(10C) | 2671 | -3429 | -710 | 60 |
| H(11A) | 845 | 459 | -2195 | 56 |
| H(11B) | 699 | -663 | -2950 | 56 |
| H(11C) | 2208 | 28 | -3087 | 56 |
| H(12A) | 4375 | 2645 | 415 | 62 |
| H(12B) | 3120 | 3791 | 54 | 62 |
| H(13A) | 5846 | 3830 | -1473 | 59 |
| H(13B) | 4832 | 5155 | -1431 | 59 |
| H(14A) | 4061 | 5173 | -3359 | 69 |
| H(14B) | 5045 | 3825 | -3379 | 69 |
| H(15A) | 2145 | 3858 | -2274 | 64 |
| H(15B) | 2960 | 2724 | -2909 | 64 |
| H(16A) | -35 | 4588 | 3473 | 87 |
| H(16B) | 1284 | 5062 | 2253 | 87 |
| H(17A) | 1377 | 3660 | 5094 | 73 |
| H(17B) | 2544 | 4707 | 3985 | 73 |
| H(18A) | 3529 | 2980 | 3156 | 62 |
| H(18B) | 3040 | 2041 | 4750 | 62 |
| H(19A) | 2060 | 1463 | 2838 | 62 |
| H(19B) | 1038 | 1317 | 4268 | 62 |

Table S-6. Torsion angles [°] for (1 · THF)₂ · 2THF .

| | | | |
|---------------------------|-------------|-------------------------|-------------|
| N(1)-Li(1)-O(2)-C(12) | 147.89(16) | C(3)-C(4)-C(5)-C(6) | 1.1(3) |
| C(1)#1-Li(1)-O(2)-C(12) | -73.73(19) | C(4)-C(5)-C(6)-C(1) | -0.8(3) |
| C(1)-Li(1)-O(2)-C(12) | 54.2(2) | C(4)-C(5)-C(6)-C(7) | 178.36(16) |
| Li(1)#1-Li(1)-O(2)-C(12) | -10.5(3) | C(2)-C(1)-C(6)-C(5) | -0.7(2) |
| C(2)#1-Li(1)-O(2)-C(12) | -105.08(16) | Li(1)#1-C(1)-C(6)-C(5) | 133.0(2) |
| N(1)-Li(1)-O(2)-C(15) | -81.6(2) | Li(1)-C(1)-C(6)-C(5) | -165.99(17) |
| C(1)#1-Li(1)-O(2)-C(15) | 56.8(2) | C(2)-C(1)-C(6)-C(7) | -179.77(15) |
| C(1)-Li(1)-O(2)-C(15) | -175.26(15) | Li(1)#1-C(1)-C(6)-C(7) | -46.2(3) |
| Li(1)#1-Li(1)-O(2)-C(15) | 120.1(3) | Li(1)-C(1)-C(6)-C(7) | 14.89(18) |
| C(2)#1-Li(1)-O(2)-C(15) | 25.5(2) | C(9)-N(1)-C(7)-O(1) | -5.6(2) |
| O(2)-Li(1)-N(1)-C(7) | -93.99(18) | Li(1)-N(1)-C(7)-O(1) | 166.19(15) |
| C(1)#1-Li(1)-N(1)-C(7) | 135.05(17) | C(9)-N(1)-C(7)-C(6) | 173.88(15) |
| C(1)-Li(1)-N(1)-C(7) | 16.96(15) | Li(1)-N(1)-C(7)-C(6) | -14.4(2) |
| Li(1)#1-Li(1)-N(1)-C(7) | 67.4(2) | C(8)-O(1)-C(7)-N(1) | -8.1(2) |
| C(2)#1-Li(1)-N(1)-C(7) | 157.23(13) | C(8)-O(1)-C(7)-C(6) | 172.40(14) |
| O(2)-Li(1)-N(1)-C(9) | 72.4(3) | C(5)-C(6)-C(7)-N(1) | 178.88(17) |
| C(1)#1-Li(1)-N(1)-C(9) | -58.5(3) | C(1)-C(6)-C(7)-N(1) | -1.9(3) |
| C(1)-Li(1)-N(1)-C(9) | -176.6(2) | C(5)-C(6)-C(7)-O(1) | -1.7(2) |
| Li(1)#1-Li(1)-N(1)-C(9) | -126.2(2) | C(1)-C(6)-C(7)-O(1) | 177.50(15) |
| C(2)#1-Li(1)-N(1)-C(9) | -36.4(3) | C(7)-O(1)-C(8)-C(9) | 17.35(18) |
| O(2)-Li(1)-C(1)-C(6) | 95.80(17) | C(7)-N(1)-C(9)-C(10) | -101.48(17) |
| N(1)-Li(1)-C(1)-C(6) | -17.20(14) | Li(1)-N(1)-C(9)-C(10) | 92.1(3) |
| C(1)#1-Li(1)-C(1)-C(6) | -141.41(17) | C(7)-N(1)-C(9)-C(11) | 136.17(16) |
| Li(1)#1-Li(1)-C(1)-C(6) | -141.41(17) | Li(1)-N(1)-C(9)-C(11) | -30.2(3) |
| C(2)#1-Li(1)-C(1)-C(6) | -116.9(2) | C(7)-N(1)-C(9)-C(8) | 15.89(18) |
| O(2)-Li(1)-C(1)-C(2) | -60.7(3) | Li(1)-N(1)-C(9)-C(8) | -150.5(2) |
| N(1)-Li(1)-C(1)-C(2) | -173.7(2) | O(1)-C(8)-C(9)-N(1) | -19.87(18) |
| C(1)#1-Li(1)-C(1)-C(2) | 62.1(3) | O(1)-C(8)-C(9)-C(10) | 95.38(17) |
| Li(1)#1-Li(1)-C(1)-C(2) | 62.1(3) | O(1)-C(8)-C(9)-C(11) | -138.65(16) |
| C(2)#1-Li(1)-C(1)-C(2) | 86.6(3) | C(15)-O(2)-C(12)-C(13) | -36.4(2) |
| O(2)-Li(1)-C(1)-Li(1)#1 | -122.8(2) | Li(1)-O(2)-C(12)-C(13) | 102.66(19) |
| N(1)-Li(1)-C(1)-Li(1)#1 | 124.2(2) | O(2)-C(12)-C(13)-C(14) | 20.9(2) |
| C(1)#1-Li(1)-C(1)-Li(1)#1 | 0.0 | C(12)-C(13)-C(14)-C(15) | 1.4(2) |
| C(2)#1-Li(1)-C(1)-Li(1)#1 | 24.52(14) | C(12)-O(2)-C(15)-C(14) | 37.0(2) |
| C(6)-C(1)-C(2)-C(3) | 1.8(3) | Li(1)-O(2)-C(15)-C(14) | -97.1(2) |
| Li(1)#1-C(1)-C(2)-C(3) | -150.40(19) | C(13)-C(14)-C(15)-O(2) | -23.0(2) |
| Li(1)-C(1)-C(2)-C(3) | 156.7(2) | C(19)-O(3)-C(16)-C(17) | -2.4(3) |
| C(6)-C(1)-C(2)-Li(1)#1 | 152.23(19) | O(3)-C(16)-C(17)-C(18) | 22.6(3) |
| Li(1)-C(1)-C(2)-Li(1)#1 | -52.9(3) | C(16)-C(17)-C(18)-C(19) | -32.7(3) |
| C(1)-C(2)-C(3)-C(4) | -1.6(3) | C(16)-O(3)-C(19)-C(18) | -19.2(3) |
| Li(1)#1-C(2)-C(3)-C(4) | -76.8(4) | C(17)-C(18)-C(19)-O(3) | 32.6(2) |
| C(2)-C(3)-C(4)-C(5) | 0.0(3) | | |

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z

X-ray Crystal Structure of THF Solvate of Dimeric 2

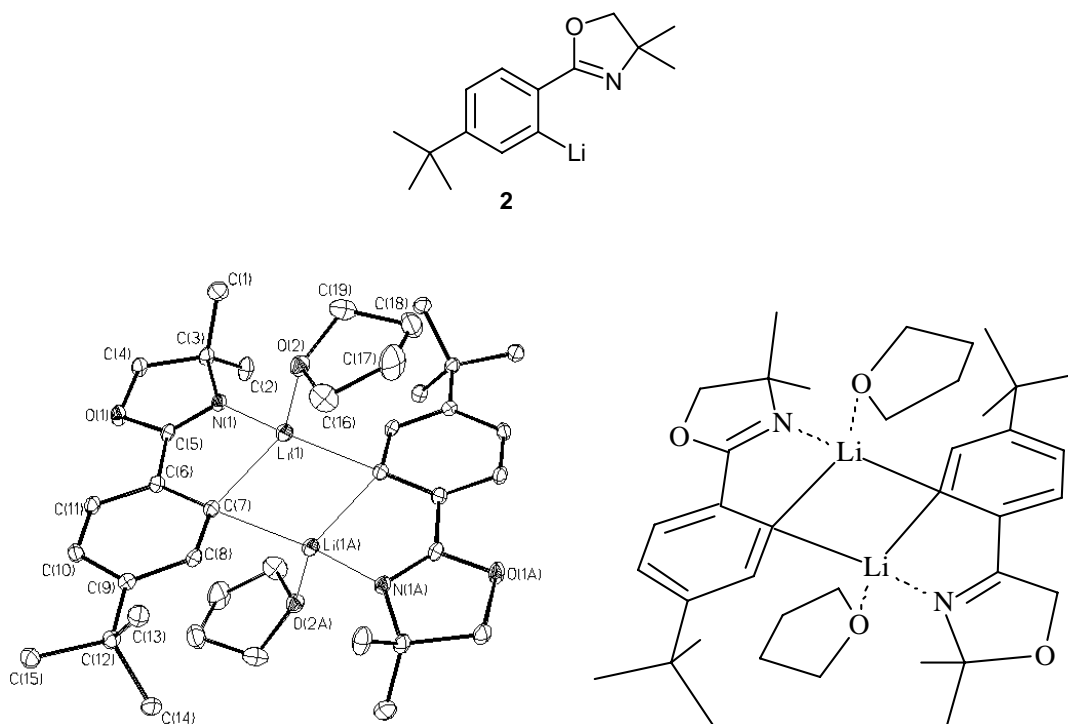


Figure S-6. X-ray crystal structure of the THF-solvated, B-type dimer of 5-*t*-butyl-[2-(4,4-dimethyl-4,5-dihydro-oxazol-2-yl)-phenyl]-lithium (**2**). Hydrogens omitted for clarity.

Preparation of X-ray Crystals of 2. 2-(4-*t*-Butyl-2-trimethylstannyl-phenyl)-4,4-dimethyl-4,5-dihydrooxazole (59 mg, 0.15 mmol) was added to a dry, N₂-purged 5 mm NMR tube in a glove box and the tube was sealed with a septum. THF (0.45 mL), Et₂O (0.30 mL) and (Me₃Si)₃CH (1 μL) were added, the solution was cooled to -78 °C and 1.6 M [⁶Li]-*n*-BuLi (0.098 mL, 0.16 mmol) was added slowly and the solution shaken. ¹³C and ⁶Li NMR spectra were acquired at -117 °C. PMDTA (15.5 μL, 0.074 mmol, 0.50 equiv) was added and ¹³C and ⁶Li NMR spectra were acquired at -117 °C. Addition quantities of PMDTA (15.5 μL, 31 μL and 62 μL) were added and ¹³C and ⁶Li NMR spectra were acquired at -117 °C after each addition. After the NMR experiment, the sample was stored at -78 °C for several days during which time X-ray quality crystals of (2·THF)₂ formed.

Data Collection. A pale-yellow air-sensitive crystal with approximate dimensions 0.4 x 0.2 x 0.1 mm³ was selected under oil under ambient conditions and attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.85 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with the exposure time of 20 seconds per frame. A total of 114 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 8436 strong reflections from the actual data collection.

The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of 0.80 Å. A total of 13893 data were harvested by collecting

three sets of frames with 0.3° scans in w with an exposure time 40 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.^[S-2]

Structure Solution and Refinement. The systematic absences in the diffraction data were consistent for the space groups P1 and P.^[S-3] The E-statistics strongly suggested the centrosymmetric space group P that yielded chemically reasonable and computationally stable results of refinement. A successful solution by the direct methods provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The dinuclear complex occupies a crystallographic inversion center. There are two independent half-dimers in the asymmetric unit. Atom C(37) is disordered over two positions in a 3:1 ratio.

The final least-squares refinement of 436 parameters against 6564 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0467 and 0.1356, respectively. The final difference Fourier map was featureless.

The ORTEP diagrams are drawn with 30% probability ellipsoids.

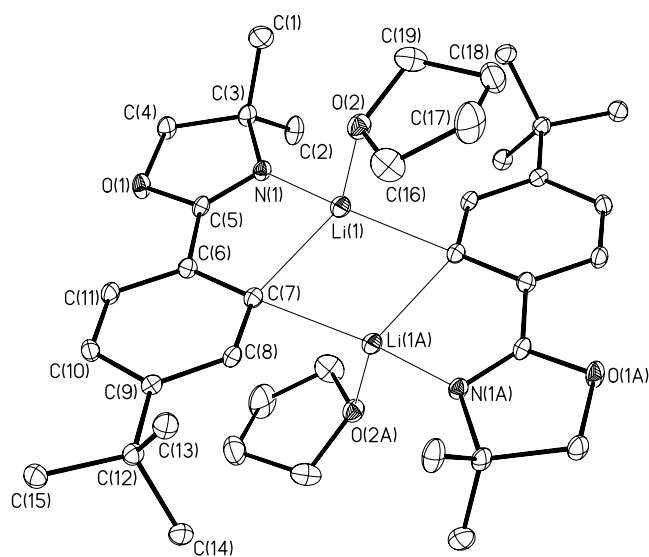


Figure S-7. The first symmetry independent dimer of $(2 \cdot \text{THF})_2$.

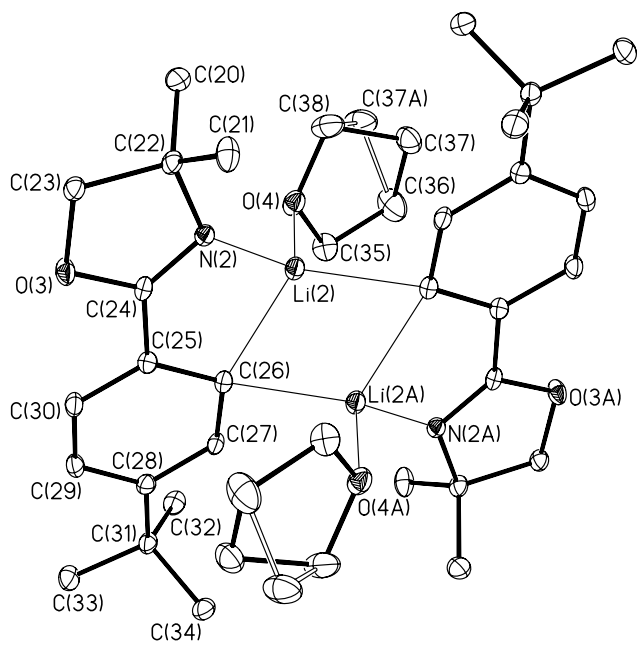


Figure S-8. The second dimer of $(2 \cdot \text{THF})_2$. Both positions of the disordered atom C(37) are shown.

Table S-7. Crystal data and structure refinement for (2·THF)₂.

| | | |
|-----------------------------------|---|--|
| Identification code | (2·THF) ₂ | |
| Empirical formula | C ₃₈ H ₅₆ Li ₂ N ₂ O ₄ | |
| Formula weight | 618.73 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | $P\bar{1}$ | |
| Unit cell dimensions | a = 11.3874(8) Å b = 12.8331(9) Å c = 15.1799(10) Å | a = 108.836(1)° b = 90.405(1)° g = 115.692(1)° |
| Volume | 1863.6(2) Å ³ | |
| Z | 2 | |
| Density (calculated) | 1.103 Mg/m ³ | |
| Absorption coefficient | 0.069 mm ⁻¹ | |
| F(000) | 672 | |
| Crystal size | 0.48 x 0.44 x 0.43 mm ³ | |
| Theta range for data collection | 2.01 to 25.00°. | |
| Index ranges | -13 ≤ h ≤ 13, -15 ≤ k ≤ 14, -18 ≤ l ≤ 17 | |
| Reflections collected | 13893 | |
| Independent reflections | 6564 [R(int) = 0.0315] | |
| Completeness to theta = 25.00° | 99.7 % | |
| Absorption correction | Empirical with SADABS | |
| Max. and min. transmission | 0.9708 and 0.9675 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 6564 / 0 / 436 | |
| Goodness-of-fit on F ² | 1.055 | |
| Final R indices [I > 2σ(I)] | R1 = 0.0467, wR2 = 0.1312 | |
| R indices (all data) | R1 = 0.0528, wR2 = 0.1356 | |
| Largest diff. peak and hole | 0.277 and -0.324 e.Å ⁻³ | |

Table S-8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\mathbf{2}\cdot\text{THF})_2$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|-------|----------|---------|---------|-------|
| O(1) | 4988(1) | 5756(1) | 2267(1) | 27(1) |
| O(2) | 5093(1) | 2778(1) | 3852(1) | 28(1) |
| O(3) | -26(1) | 5752(1) | 3136(1) | 26(1) |
| O(4) | 239(1) | 2863(1) | -38(1) | 30(1) |
| N(1) | 4085(1) | 4495(1) | 3084(1) | 20(1) |
| N(2) | -909(1) | 4514(1) | 1611(1) | 20(1) |
| Li(1) | 4656(2) | 4183(2) | 4230(2) | 23(1) |
| Li(2) | -302(2) | 4201(2) | 328(2) | 23(1) |
| C(1) | 2842(2) | 2639(1) | 1664(1) | 33(1) |
| C(2) | 1788(2) | 3953(2) | 2498(1) | 32(1) |
| C(3) | 3074(1) | 3956(1) | 2225(1) | 22(1) |
| C(4) | 3719(1) | 4842(1) | 1687(1) | 26(1) |
| C(5) | 5070(1) | 5450(1) | 3038(1) | 19(1) |
| C(6) | 6323(1) | 6224(1) | 3718(1) | 19(1) |
| C(7) | 6419(1) | 5993(1) | 4564(1) | 19(1) |
| C(8) | 7697(1) | 6708(1) | 5107(1) | 19(1) |
| C(9) | 8805(1) | 7569(1) | 4878(1) | 19(1) |
| C(10) | 8615(1) | 7756(1) | 4042(1) | 21(1) |
| C(11) | 7382(1) | 7093(1) | 3469(1) | 22(1) |
| C(12) | 10154(1) | 8258(1) | 5527(1) | 22(1) |
| C(13) | 10571(1) | 7315(1) | 5651(1) | 25(1) |
| C(14) | 10031(1) | 9050(1) | 6497(1) | 26(1) |
| C(15) | 11247(1) | 9109(1) | 5136(1) | 26(1) |
| C(16) | 6035(2) | 2926(2) | 4583(1) | 41(1) |
| C(17) | 5462(2) | 1777(2) | 4806(2) | 56(1) |
| C(18) | 4016(2) | 1133(2) | 4374(1) | 44(1) |
| C(19) | 4048(2) | 1535(2) | 3545(1) | 38(1) |
| C(20) | -2139(2) | 2625(1) | 1966(1) | 30(1) |
| C(21) | -3213(2) | 3933(2) | 1870(1) | 32(1) |
| C(22) | -1919(1) | 3941(1) | 2152(1) | 21(1) |
| C(23) | -1287(1) | 4805(1) | 3189(1) | 23(1) |
| C(24) | 68(1) | 5474(1) | 2202(1) | 19(1) |
| C(25) | 1307(1) | 6287(1) | 1972(1) | 20(1) |
| C(26) | 1423(1) | 6066(1) | 1003(1) | 20(1) |
| C(27) | 2692(1) | 6831(1) | 878(1) | 20(1) |
| C(28) | 3773(1) | 7730(1) | 1600(1) | 21(1) |
| C(29) | 3565(1) | 7907(1) | 2530(1) | 24(1) |
| C(30) | 2342(1) | 7187(1) | 2715(1) | 23(1) |
| C(31) | 5122(1) | 8457(1) | 1354(1) | 24(1) |

| | | | | |
|--------|---------|---------|----------|-------|
| C(32) | 5613(1) | 7546(2) | 775(1) | 29(1) |
| C(33) | 6178(2) | 9377(2) | 2237(1) | 32(1) |
| C(34) | 4983(2) | 9195(1) | 773(1) | 30(1) |
| C(35) | 1165(2) | 3059(2) | -688(1) | 33(1) |
| C(36) | 543(2) | 1950(2) | -1587(1) | 52(1) |
| C(37) | -850(2) | 1190(2) | -1483(2) | 38(1) |
| C(37A) | -152(9) | 939(6) | -1121(5) | 50(3) |
| C(38) | -721(2) | 1580(2) | -399(1) | 44(1) |

Table S-9. Bond lengths [Å] and angles [°] for (2·THF)₂.

| | | | |
|------------------|------------|------------------|------------|
| O(1)-C(5) | 1.3643(16) | C(7)-Li(1)#1 | 2.227(3) |
| O(1)-C(4) | 1.4437(17) | C(8)-C(9) | 1.4070(19) |
| O(2)-C(19) | 1.4298(19) | C(8)-Li(1)#1 | 2.761(3) |
| O(2)-C(16) | 1.4453(19) | C(9)-C(10) | 1.3974(19) |
| O(2)-Li(1) | 1.986(3) | C(9)-C(12) | 1.5335(19) |
| O(3)-C(24) | 1.3623(16) | C(10)-C(11) | 1.386(2) |
| O(3)-C(23) | 1.4485(17) | C(12)-C(15) | 1.5323(19) |
| O(4)-C(38) | 1.433(2) | C(12)-C(13) | 1.538(2) |
| O(4)-C(35) | 1.4470(19) | C(12)-C(14) | 1.5426(19) |
| O(4)-Li(2) | 1.985(3) | C(16)-C(17) | 1.486(3) |
| N(1)-C(5) | 1.2771(18) | C(17)-C(18) | 1.510(3) |
| N(1)-C(3) | 1.4865(17) | C(18)-C(19) | 1.502(2) |
| N(1)-Li(1) | 2.065(3) | C(20)-C(22) | 1.522(2) |
| N(2)-C(24) | 1.2824(18) | C(21)-C(22) | 1.526(2) |
| N(2)-C(22) | 1.4859(17) | C(22)-C(23) | 1.5459(19) |
| N(2)-Li(2) | 2.046(3) | C(24)-C(25) | 1.4729(19) |
| Li(1)-C(7) | 2.205(3) | C(25)-C(30) | 1.3982(19) |
| Li(1)-C(7)#1 | 2.227(3) | C(25)-C(26) | 1.4236(19) |
| Li(1)-Li(1)#1 | 2.421(4) | C(26)-C(27) | 1.4076(19) |
| Li(1)-C(5) | 2.717(3) | C(26)-Li(2)#2 | 2.229(3) |
| Li(1)-C(8)#1 | 2.761(3) | C(27)-C(28) | 1.4081(19) |
| Li(2)-C(26) | 2.225(3) | C(27)-Li(2)#2 | 2.784(3) |
| Li(2)-C(26)#2 | 2.229(3) | C(28)-C(29) | 1.395(2) |
| Li(2)-Li(2)#2 | 2.404(4) | C(28)-C(31) | 1.5358(19) |
| Li(2)-C(24) | 2.707(3) | C(29)-C(30) | 1.389(2) |
| Li(2)-C(27)#2 | 2.784(3) | C(31)-C(33) | 1.5366(19) |
| C(1)-C(3) | 1.527(2) | C(31)-C(32) | 1.537(2) |
| C(2)-C(3) | 1.523(2) | C(31)-C(34) | 1.538(2) |
| C(3)-C(4) | 1.5447(19) | C(35)-C(36) | 1.499(2) |
| C(5)-C(6) | 1.4753(19) | C(36)-C(37) | 1.502(3) |
| C(6)-C(11) | 1.3975(19) | C(36)-C(37A) | 1.587(7) |
| C(6)-C(7) | 1.4225(19) | C(37)-C(38) | 1.542(3) |
| C(7)-C(8) | 1.4052(19) | C(37A)-C(38) | 1.479(7) |
| | | | |
| C(5)-O(1)-C(4) | 106.51(10) | C(5)-N(1)-C(3) | 108.08(11) |
| C(19)-O(2)-C(16) | 108.14(12) | C(5)-N(1)-Li(1) | 106.40(11) |
| C(19)-O(2)-Li(1) | 119.47(12) | C(3)-N(1)-Li(1) | 144.64(11) |
| C(16)-O(2)-Li(1) | 111.13(12) | C(24)-N(2)-C(22) | 108.11(11) |
| C(24)-O(3)-C(23) | 106.48(10) | C(24)-N(2)-Li(2) | 106.57(11) |
| C(38)-O(4)-C(35) | 107.87(12) | C(22)-N(2)-Li(2) | 143.81(11) |
| C(38)-O(4)-Li(2) | 121.42(13) | O(2)-Li(1)-N(1) | 112.63(11) |
| C(35)-O(4)-Li(2) | 110.19(11) | O(2)-Li(1)-C(7) | 112.52(12) |

| | | | |
|-----------------------|------------|--------------------|------------|
| N(1)-Li(1)-C(7) | 86.10(10) | C(2)-C(3)-C(4) | 111.39(12) |
| O(2)-Li(1)-C(7)#1 | 105.03(11) | C(1)-C(3)-C(4) | 111.96(12) |
| N(1)-Li(1)-C(7)#1 | 125.94(12) | O(1)-C(4)-C(3) | 105.06(10) |
| C(7)-Li(1)-C(7)#1 | 113.78(10) | N(1)-C(5)-O(1) | 117.30(12) |
| O(2)-Li(1)-Li(1)#1 | 125.97(16) | N(1)-C(5)-C(6) | 126.14(12) |
| N(1)-Li(1)-Li(1)#1 | 118.54(15) | O(1)-C(5)-C(6) | 116.49(11) |
| C(7)-Li(1)-Li(1)#1 | 57.33(10) | N(1)-C(5)-Li(1) | 46.80(8) |
| C(7)#1-Li(1)-Li(1)#1 | 56.46(10) | O(1)-C(5)-Li(1) | 162.98(11) |
| O(2)-Li(1)-C(5) | 116.23(11) | C(6)-C(5)-Li(1) | 79.44(9) |
| N(1)-Li(1)-C(5) | 26.80(5) | C(11)-C(6)-C(7) | 123.34(12) |
| C(7)-Li(1)-C(5) | 59.67(7) | C(11)-C(6)-C(5) | 118.16(12) |
| C(7)#1-Li(1)-C(5) | 137.53(11) | C(7)-C(6)-C(5) | 118.36(12) |
| Li(1)#1-Li(1)-C(5) | 102.62(13) | C(8)-C(7)-C(6) | 112.75(12) |
| O(2)-Li(1)-C(8)#1 | 104.08(10) | C(8)-C(7)-Li(1) | 141.45(12) |
| N(1)-Li(1)-C(8)#1 | 101.38(10) | C(6)-C(7)-Li(1) | 101.07(11) |
| C(7)-Li(1)-C(8)#1 | 136.34(11) | C(8)-C(7)-Li(1)#1 | 96.30(10) |
| C(7)#1-Li(1)-C(8)#1 | 30.39(5) | C(6)-C(7)-Li(1)#1 | 139.74(11) |
| Li(1)#1-Li(1)-C(8)#1 | 82.27(12) | Li(1)-C(7)-Li(1)#1 | 66.22(10) |
| C(5)-Li(1)-C(8)#1 | 122.76(9) | C(7)-C(8)-C(9) | 126.28(12) |
| O(4)-Li(2)-N(2) | 114.43(11) | C(7)-C(8)-Li(1)#1 | 53.31(8) |
| O(4)-Li(2)-C(26) | 111.89(12) | C(9)-C(8)-Li(1)#1 | 157.55(11) |
| N(2)-Li(2)-C(26) | 86.05(10) | C(10)-C(9)-C(8) | 117.12(12) |
| O(4)-Li(2)-C(26)#2 | 104.53(11) | C(10)-C(9)-C(12) | 122.34(12) |
| N(2)-Li(2)-C(26)#2 | 124.55(12) | C(8)-C(9)-C(12) | 120.53(12) |
| C(26)-Li(2)-C(26)#2 | 114.66(10) | C(11)-C(10)-C(9) | 120.22(12) |
| O(4)-Li(2)-Li(2)#2 | 125.27(16) | C(10)-C(11)-C(6) | 120.24(12) |
| N(2)-Li(2)-Li(2)#2 | 117.52(15) | C(15)-C(12)-C(9) | 112.72(11) |
| C(26)-Li(2)-Li(2)#2 | 57.41(10) | C(15)-C(12)-C(13) | 107.60(11) |
| C(26)#2-Li(2)-Li(2)#2 | 57.25(10) | C(9)-C(12)-C(13) | 109.69(11) |
| O(4)-Li(2)-C(24) | 116.43(10) | C(15)-C(12)-C(14) | 108.69(11) |
| N(2)-Li(2)-C(24) | 27.01(5) | C(9)-C(12)-C(14) | 108.53(11) |
| C(26)-Li(2)-C(24) | 59.66(7) | C(13)-C(12)-C(14) | 109.58(11) |
| C(26)#2-Li(2)-C(24) | 137.77(11) | O(2)-C(16)-C(17) | 107.46(14) |
| Li(2)#2-Li(2)-C(24) | 102.65(13) | C(16)-C(17)-C(18) | 104.59(15) |
| O(4)-Li(2)-C(27)#2 | 103.73(10) | C(19)-C(18)-C(17) | 102.15(14) |
| N(2)-Li(2)-C(27)#2 | 100.52(10) | O(2)-C(19)-C(18) | 105.43(13) |
| C(26)-Li(2)-C(27)#2 | 137.15(11) | N(2)-C(22)-C(20) | 109.54(11) |
| C(26)#2-Li(2)-C(27)#2 | 30.10(5) | N(2)-C(22)-C(21) | 110.15(11) |
| Li(2)#2-Li(2)-C(27)#2 | 82.90(12) | C(20)-C(22)-C(21) | 110.41(13) |
| C(24)-Li(2)-C(27)#2 | 123.01(9) | N(2)-C(22)-C(23) | 103.07(10) |
| N(1)-C(3)-C(2) | 110.35(11) | C(20)-C(22)-C(23) | 112.14(11) |
| N(1)-C(3)-C(1) | 109.31(11) | C(21)-C(22)-C(23) | 111.29(12) |
| C(2)-C(3)-C(1) | 110.53(13) | O(3)-C(23)-C(22) | 105.05(10) |
| N(1)-C(3)-C(4) | 103.05(11) | N(2)-C(24)-O(3) | 117.28(12) |

| | | | |
|---------------------|------------|--------------------|------------|
| N(2)-C(24)-C(25) | 126.16(12) | C(30)-C(29)-C(28) | 120.17(13) |
| O(3)-C(24)-C(25) | 116.52(11) | C(29)-C(30)-C(25) | 120.38(12) |
| N(2)-C(24)-Li(2) | 46.42(8) | C(33)-C(31)-C(28) | 112.49(12) |
| O(3)-C(24)-Li(2) | 161.80(11) | C(33)-C(31)-C(32) | 107.70(12) |
| C(25)-C(24)-Li(2) | 80.05(9) | C(28)-C(31)-C(32) | 109.37(11) |
| C(30)-C(25)-C(26) | 123.18(13) | C(33)-C(31)-C(34) | 108.06(12) |
| C(30)-C(25)-C(24) | 118.29(12) | C(28)-C(31)-C(34) | 109.59(12) |
| C(26)-C(25)-C(24) | 118.41(12) | C(32)-C(31)-C(34) | 109.58(12) |
| C(27)-C(26)-C(25) | 112.82(12) | O(4)-C(35)-C(36) | 106.98(13) |
| C(27)-C(26)-Li(2) | 142.12(12) | C(35)-C(36)-C(37) | 106.62(15) |
| C(25)-C(26)-Li(2) | 100.39(11) | C(35)-C(36)-C(37A) | 97.3(3) |
| C(27)-C(26)-Li(2)#2 | 97.34(10) | C(37)-C(36)-C(37A) | 44.4(3) |
| C(25)-C(26)-Li(2)#2 | 139.28(11) | C(36)-C(37)-C(38) | 101.37(17) |
| Li(2)-C(26)-Li(2)#2 | 65.34(10) | C(38)-C(37A)-C(36) | 100.3(4) |
| C(26)-C(27)-C(28) | 126.18(12) | O(4)-C(38)-C(37A) | 106.0(3) |
| C(26)-C(27)-Li(2)#2 | 52.57(8) | O(4)-C(38)-C(37) | 104.89(14) |
| C(28)-C(27)-Li(2)#2 | 157.87(11) | C(37A)-C(38)-C(37) | 45.5(4) |
| C(29)-C(28)-C(27) | 117.24(13) | | |
| C(29)-C(28)-C(31) | 122.42(12) | | |
| C(27)-C(28)-C(31) | 120.33(12) | | |

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z

Table S-10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(2\text{-THF})_2$. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^*2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U ¹¹ | U ²² | U ³³ | U ²³ | U ¹³ | U ¹² |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| O(1) | 22(1) | 35(1) | 22(1) | 19(1) | -1(1) | 7(1) |
| O(2) | 33(1) | 31(1) | 24(1) | 13(1) | 5(1) | 17(1) |
| O(3) | 22(1) | 33(1) | 14(1) | 6(1) | 3(1) | 6(1) |
| O(4) | 41(1) | 31(1) | 21(1) | 10(1) | 8(1) | 20(1) |
| N(1) | 18(1) | 25(1) | 16(1) | 9(1) | 1(1) | 8(1) |
| N(2) | 19(1) | 22(1) | 17(1) | 8(1) | 3(1) | 8(1) |
| Li(1) | 26(1) | 24(1) | 19(1) | 9(1) | 2(1) | 11(1) |
| Li(2) | 25(1) | 26(1) | 18(1) | 9(1) | 3(1) | 11(1) |
| C(1) | 37(1) | 32(1) | 24(1) | 8(1) | -5(1) | 10(1) |
| C(2) | 24(1) | 52(1) | 31(1) | 27(1) | 6(1) | 18(1) |
| C(3) | 20(1) | 29(1) | 17(1) | 12(1) | -1(1) | 9(1) |
| C(4) | 22(1) | 33(1) | 20(1) | 13(1) | -1(1) | 7(1) |
| C(5) | 21(1) | 26(1) | 16(1) | 11(1) | 4(1) | 13(1) |
| C(6) | 19(1) | 21(1) | 19(1) | 8(1) | 3(1) | 10(1) |
| C(7) | 21(1) | 21(1) | 17(1) | 8(1) | 4(1) | 11(1) |
| C(8) | 22(1) | 24(1) | 15(1) | 9(1) | 4(1) | 11(1) |
| C(9) | 20(1) | 20(1) | 17(1) | 6(1) | 3(1) | 10(1) |
| C(10) | 20(1) | 21(1) | 22(1) | 11(1) | 5(1) | 6(1) |
| C(11) | 25(1) | 25(1) | 18(1) | 12(1) | 4(1) | 11(1) |
| C(12) | 20(1) | 24(1) | 19(1) | 8(1) | 3(1) | 8(1) |
| C(13) | 21(1) | 31(1) | 24(1) | 11(1) | 2(1) | 11(1) |
| C(14) | 23(1) | 27(1) | 21(1) | 5(1) | 1(1) | 7(1) |
| C(15) | 20(1) | 28(1) | 25(1) | 10(1) | 2(1) | 6(1) |
| C(16) | 30(1) | 45(1) | 52(1) | 18(1) | -2(1) | 20(1) |
| C(17) | 64(1) | 72(1) | 50(1) | 40(1) | 4(1) | 32(1) |
| C(18) | 53(1) | 33(1) | 52(1) | 21(1) | 25(1) | 20(1) |
| C(19) | 39(1) | 29(1) | 38(1) | 4(1) | -5(1) | 16(1) |
| C(20) | 33(1) | 26(1) | 24(1) | 10(1) | 7(1) | 7(1) |
| C(21) | 26(1) | 47(1) | 20(1) | 9(1) | 4(1) | 18(1) |
| C(22) | 21(1) | 27(1) | 16(1) | 10(1) | 6(1) | 9(1) |
| C(23) | 22(1) | 27(1) | 18(1) | 10(1) | 5(1) | 9(1) |
| C(24) | 22(1) | 25(1) | 14(1) | 8(1) | 3(1) | 14(1) |
| C(25) | 20(1) | 22(1) | 18(1) | 7(1) | 2(1) | 10(1) |
| C(26) | 21(1) | 23(1) | 17(1) | 8(1) | 1(1) | 11(1) |
| C(27) | 22(1) | 26(1) | 14(1) | 10(1) | 3(1) | 11(1) |
| C(28) | 20(1) | 22(1) | 21(1) | 10(1) | 1(1) | 9(1) |
| C(29) | 22(1) | 26(1) | 18(1) | 6(1) | -2(1) | 7(1) |
| C(30) | 24(1) | 28(1) | 14(1) | 7(1) | 2(1) | 10(1) |
| C(31) | 19(1) | 28(1) | 21(1) | 12(1) | 0(1) | 5(1) |

| | | | | | | |
|--------|-------|-------|-------|-------|-------|-------|
| C(32) | 21(1) | 38(1) | 30(1) | 17(1) | 6(1) | 11(1) |
| C(33) | 20(1) | 36(1) | 28(1) | 14(1) | -2(1) | 2(1) |
| C(34) | 26(1) | 30(1) | 31(1) | 17(1) | 1(1) | 6(1) |
| C(35) | 31(1) | 40(1) | 31(1) | 10(1) | 9(1) | 19(1) |
| C(36) | 49(1) | 54(1) | 33(1) | 2(1) | 14(1) | 16(1) |
| C(37) | 42(2) | 30(1) | 32(1) | 3(1) | 1(1) | 15(1) |
| C(37A) | 72(6) | 30(3) | 42(4) | 10(3) | 24(4) | 19(3) |
| C(38) | 61(1) | 29(1) | 44(1) | 17(1) | 22(1) | 20(1) |

Table S-11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\mathbf{2} \cdot \text{THF})_2$.

| | x | y | z | U(eq) |
|--------|-------|------|------|-------|
| H(1A) | 2191 | 2288 | 1090 | 50 |
| H(1B) | 2510 | 2125 | 2051 | 50 |
| H(1C) | 3677 | 2658 | 1491 | 50 |
| H(2A) | 1969 | 4791 | 2908 | 48 |
| H(2B) | 1401 | 3380 | 2835 | 48 |
| H(2C) | 1167 | 3686 | 1926 | 48 |
| H(4A) | 3830 | 4388 | 1055 | 31 |
| H(4B) | 3170 | 5240 | 1608 | 31 |
| H(8) | 7824 | 6601 | 5685 | 23 |
| H(10) | 9334 | 8339 | 3866 | 26 |
| H(11) | 7257 | 7229 | 2904 | 26 |
| H(13A) | 10693 | 6841 | 5040 | 38 |
| H(13B) | 9883 | 6748 | 5892 | 38 |
| H(13C) | 11404 | 7756 | 6099 | 38 |
| H(14A) | 10892 | 9513 | 6915 | 39 |
| H(14B) | 9383 | 8508 | 6777 | 39 |
| H(14C) | 9739 | 9632 | 6414 | 39 |
| H(15A) | 11319 | 8619 | 4512 | 40 |
| H(15B) | 12091 | 9505 | 5565 | 40 |
| H(15C) | 11031 | 9748 | 5080 | 40 |
| H(16A) | 6200 | 3654 | 5153 | 49 |
| H(16B) | 6885 | 3056 | 4360 | 49 |
| H(17A) | 5573 | 1977 | 5498 | 68 |
| H(17B) | 5890 | 1249 | 4524 | 68 |
| H(18A) | 3645 | 220 | 4169 | 53 |
| H(18B) | 3492 | 1411 | 4823 | 53 |
| H(19A) | 4228 | 990 | 2994 | 45 |
| H(19B) | 3194 | 1506 | 3368 | 45 |
| H(20A) | -2461 | 2130 | 1290 | 45 |
| H(20B) | -2795 | 2252 | 2330 | 45 |
| H(20C) | -1303 | 2646 | 2156 | 45 |
| H(21A) | -3038 | 4772 | 1927 | 47 |
| H(21B) | -3833 | 3655 | 2287 | 47 |
| H(21C) | -3598 | 3367 | 1214 | 47 |
| H(23A) | -1852 | 5178 | 3488 | 27 |
| H(23B) | -1160 | 4341 | 3559 | 27 |
| H(27) | 2831 | 6731 | 246 | 24 |
| H(29) | 4262 | 8521 | 3038 | 29 |
| H(30) | 2208 | 7308 | 3350 | 28 |

| | | | | |
|--------|-------|------|-------|----|
| H(32A) | 6453 | 8005 | 592 | 44 |
| H(32B) | 4955 | 6947 | 206 | 44 |
| H(32C) | 5742 | 7106 | 1157 | 44 |
| H(33A) | 7017 | 9817 | 2045 | 47 |
| H(33B) | 6297 | 8923 | 2612 | 47 |
| H(33C) | 5894 | 9975 | 2618 | 47 |
| H(34A) | 4692 | 9791 | 1150 | 45 |
| H(34B) | 4328 | 8624 | 197 | 45 |
| H(34C) | 5839 | 9641 | 603 | 45 |
| H(35A) | 2012 | 3144 | -422 | 40 |
| H(35B) | 1342 | 3823 | -808 | 40 |
| H(36A) | 1037 | 1460 | -1689 | 62 |
| H(36B) | 545 | 2213 | -2133 | 62 |
| H(37A) | -1138 | 291 | -1792 | 45 |
| H(37B) | -1476 | 1405 | -1746 | 45 |
| H(37C) | -847 | 153 | -1584 | 61 |
| H(37D) | 495 | 770 | -831 | 61 |
| H(38A) | -1580 | 1471 | -200 | 53 |
| H(38B) | -416 | 1082 | -173 | 53 |

Supporting Information References

[S-1] Meyers, A. I.; Temple, D. L.; Haidukewych, D.; Milhelich, E. D. *J. Org. Chem.* **1974**, *39*, 2787-2793. "Oxazolines. XI. Synthesis of Functionalized Aromatic and Aliphatic Acids. A Useful Protecting Group for Carboxylic Acids against Grignard and Hydride Reagents."

[S-2] Blessing, R.H. *Acta Cryst.* **1995**, *A51*, 33-38.

[S-3] All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray Systems, Madison, WI).