Facile and Atom Efficient Amidolithium Catalyzed C-C and C-N Formation for the Construction of Substituted Guanidines and Propiolamidines

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	<u>Pages</u>
Experimental details	2-8
Figure S1	9
Figure S2	10

General Considerations. All manipulations were carried out in either a nitrogen filled drybox or under nitrogen using Schlenk-line techniques. Toluene, hexane, and ether were purified by passage through a column of activated alumina using an apparatus purchased from Anhydrous Engineering. Pentane and THF were distilled under nitrogen from Na/K alloy. Deuterated benzene and toluene were dried by vacuum transfer from Na/K alloy. Diisopropylcarbodiimide, pentafluoroaniline, 2,6-dimethylaniline, p-anisidine, o-anisidine, p-aminobenzylcyanide, p-chloroaniline, 1,4-diaminobenzene, and BuLi (1.6 M in hexane) were purchased from Aldrich Chemical Company and used without further purification. ^1H and ^{13}C NMR spectra were run on a Varian Gemini-200, a Bruker 300 MHz, or a Bruker 500MHz spectrometer using the residual protons of the deuterated solvent for reference. Guanidines **1-5**, **7** and **9** were prepared and reported previously in Ong, T.-G.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.*, **2003**, *125*, 8100-8101.

General procedure for the guanylation of aromatic amines with diisopropylcarbodiimide to yield compounds 1-9 using $\text{LiN}(\text{SiMe}_3)_2$. A vial was loaded with 0.1 equiv $\text{LiN}(\text{SiMe}_3)_2$, 40 equiv carbodiimide, 40 equiv arylamine, 10 equiv 1,3-dimethoxybenzene or $(\text{Me}_3\text{Si})_2\text{O}$ as an internal standard, and approximately 0.5 mL C_6D_6 . The solution was subsequently transferred to a sealed-NMR tube and a single pulse ^1H NMR spectrum was obtained. The tube was left at room temperature until all of the aniline was consumed. The conversion and yield were determined by comparison of the integration of the internal standard and a well-resolved signal for the product guanidine. The identity of the guanidine product was further confirmed by GC-MS.

Preparation of N-2,6-dimethylphenyl-N',N''-diisopropylguanidine (1). Yield: 98%; Isolated yield 90%. This compound has been reported previously.¹

N-phenyl-N',N''-diisopropylguanidine (2). Yield: 96%. This compound has been reported previously.¹

N-pentafluorophenyl-N',N''-diisopropylguanidine (3). Yield: 96%. This compound has been reported previously.¹

N-*p*-methoxyphenyl-N',N''-diisopropylguanidine (4). Yield: 98%. This compound has been reported previously.¹

N-*o*-methoxyphenyl-N',N''-diisopropylguanidine (5). Yield: 58% (25 °C); Isolated yield: 96% (100°C). This compound has been reported previously.¹

N-*o*-chlorophenyl-N',N''-diisopropylguanidine (6). A solution of 2-chloroaniline (1.184 g, 9.281 mmol), diisopropylcarbodiimide (1.169 g, 9.281 mmol) and LiN(SiMe₃)₂ (78 mg, 0.464 mmol) in 40 mL of toluene was allowed to stir at room temperature for a period of 18 hours. The volatiles were removed *in vacuo* to afford a white solid, which was further purified by washing with 10 mL of ether. Yield: 1.818 g (72.3%). ¹H NMR (CDCl₃): 1.17 (d, 12H, CH₃), 3.56 (br, 2H, NH), 3.76 (sept, 2H, CH), 6.89 (d, 2H, C₆H₄), 7.12 (t, 1H, C₆H₄), 7.32(d, 1H, C₆H₄). ¹³C NMR (CDCl₃): 23.3 (CH₃), 43.4 (CH), 122.6, 125.2, 127.5, 129.9, 128.3, 137.0 (C₆H₄), 150.0 (CN₃). HRMS ESI (*m/z*): calcd for C₁₃H₂₀N₃Cl 253.1346; found 253.1326. Anal. calcd. for C₁₃H₂₀N₃Cl: C, 61.53; H, 7.94; N, 16.56, Found: C, 61.18; H, 7.64; N, 16.86.

N-*p*-cyanomethylphenyl-N',N''-diisopropylguanidine (7). Yield: 83.3%. This compound has been reported previously.¹

N-*p*-aminomethylphenyl-N',N''-diisopropylguanidine (8). Yield: 96%; Isolated yield: 90%. ¹H NMR (CDCl₃): 1.12 (d, 12H, CH₃), 1.34 (br, 2H, CH₂), 3.55 (br, 2H, CH), 3.70 (br, 2H, NH), 3.75(br, 2H, NH), 6.78 (d, 2H, C₆H₄), 7.09 (d, 2H, C₆H₄). ¹³C NMR (CDCl₃): 23.3 (CH₃), 43.2 (CH), 46.1 (CH₂), 123.5, 128.8, 136.1, 148.8 (C₆H₄), 150.2 (CN₃). HRMS ESI (*m/z*): calcd for C₁₄H₂₄N₄ 248.2001; found 248.2023. Anal. calcd. for C₁₄H₂₄N₄: C, 67.70; H, 9.74; N, 22.56, Found: C, 67.66; H, 9.64; N, 23.00.

N-*o*-bromophenyl-N',N''-diisopropylguanidine (9). Isolated yield: 71.2% (100°C). This compound has been reported previously.¹

N-*t*-butyl-N'-*p*-methoxyphenyl-N''-phenylguanidine (10). A solution of *p*-anisidine (0.042 g, 0.344 mmol), 1,3-*t*-butyl-phenylcarbodiimide (0.050 g, 0.287 mmol), LiN(SiMe₃)₂ (~2 mg, 0.014

mmol) and TMEDA (~7 mg, 0.057 mmol) in 0.5 mL of C₆D₆ was loaded into an NMR tube at room temperature and allowed to react for 18 hours. The yield of the reaction was determined to be 95% by comparison of the integration of the internal standard and a well-resolved signal for the product guanidine. The product was further purified by removing the solvent *in vacuo* to afford a white solid. The solid was redissolved in 2 mL of ether and hexane (50:50 by volume) and was cooled to –30°C to afford a white solid, which was isolated by filtration (isolated yield: 90%). ¹H NMR (CDCl₃): 1.42 (s, 9H, *t*-Bu), 3.77 (s, 3H, OCH₃), 3.97 (br, 1H, NH), 5.50 (br, 1H, NH), 6.85 (br, 3H), 6.95 (br, 4H), 7.25 (br, 2H). ¹³C NMR (CDCl₃): 29.4 (CH₃), 51.0 (CMe₃), 55.4 (OCH₃), 114.6, 121.4, 121.8, 123.1, 123.6, 125.6, 129.3, 147.3 (aromatic carbon), 150.2 (CN₃). HRMS ESI (*m/z*): calcd for C₁₈H₂₃N₃O, 297.1841; found 297.1857. Anal. calcd. for C₁₈H₂₃N₃O: C, 72.70; H, 7.80; N, 14.13, Found: C, 72.75; H, 7.88; N, 14.30.

Preparation of N,N'-diphenyl-N''-*t*-butylguanidine (11). A solution of aniline (0.055 g, 0.597 mmol), 1,3-*t*-butyl-phenylcarbodiimide (0.096 g, 0.551 mmol), LiN(SiMe₃)₂ (~5 mg, 0.0300 mmol) and TMEDA (0.010 g, 0.0862 mmol) in 0.5 mL of C₆D₆ was loaded into an NMR tube at room temperature and allowed to react for 18 hours. The yield of the reaction was determined to be 70.0 % by comparison of the integration of the internal standard and a well-resolved signal for the product guanidine. The product was further purified by removing the solvent *in vacuo* to afford a white solid. The solid was redissolved in 2 mL of ether and hexane (50:50 by volume) and was cooled to –30 °C to afford a white solid, which was isolated by filtration (isolated yield 62%). ¹H NMR (CDCl₃): 1.46 (s, 9H, *t*-Bu), 3.98 (br, 1H, NH), 3.59 (br, 1H, NH), 6.90-7.40 (m, 10H, C₆H₅). ¹³C NMR (CDCl₃): 29.4 (CH₃), 51.1 (CMe₃), 121.6, 122.9, 123.4, 129.3 (C₆H₅), 146 (CN₃). HRMS ESI (*m/z*): calcd for C₁₇H₂₁N₃ 267.1735; found 267.1853. Anal. calcd. for C₁₇H₂₁N₃: C, 76.37; H, 7.92; N, 15.72, Found: C, 76.62; H, 7.72; N, 15.57.

N-*p*-methoxyphenyl-N',N''-dicyclohexylguanidine (12). A solution of *p*-anisidine (0.370 g, 2.99 mmol), dicyclohexylcarbodiimide (0.615 g, 2.99 mmol) and LiN(SiMe₃)₂ (~25 mg, 0.15 mmol) in 15 mL of toluene was allowed to stir at room temperature. A white cloudy solution was observed after 18 hour of reaction time. The reaction mixture was dried *in vacuo* to afford a white solid, which was washed with 10 mL ether. Yield: 0.934g (95%). ¹H NMR (CDCl₃): 0.95-1.45 (m, 10H, CH₂ of cyclohexyl), 1.60 (m, 6H, CH₂ of cyclohexyl), 1.97 (m, 4H, CH₂ of cyclohexyl), 3.37 (br,

2H, CH of cyclohexyl), 3.59 (br, 2H, NH), 3.73 (s, 3H, OCH₃), 6.75 (d, 4H, C₆H₄). ¹³C NMR (CDCl₃): 24.9 (CH₂), 25.6 (CH₂), 33.8 (CH₂), 50.1 (CH), 114.5, 124.3, 143.2, 150.5 (C₆H₄), 154.4 (CN₃). HRMS ESI (*m/z*): calcd for C₂₀H₃₁N₃O 329.2467; found, 329.2484. Anal. calcd. for C₂₀H₃₁N₃O: C, 72.91; H, 9.48; N, 12.75, Found: C, 72.88; H, 9.63; N, 12.59.

N-*o*-bromophenyl-N,N''-diphenylguanidine (13). A solution of 2-bromoaniline (0.886 g, 5.149 mmol), 1,3-diphenylcarbodiimide (1.000 g, 5.149 mmol) and LiN(SiMe₃)₂ (0.062 g, 0.257 mmol) in 40 mL of toluene was heated in a thick-walled glass vessel with a Teflon stopcock at 100 °C for 18 hours. The resulting brown cloudy solution was dried *in vacuo* to afford a brown oil. The brown oil was triturated with 20 mL of hexane and was stirred for 2 days. The volatiles were removed *in vacuo* and the residue was dissolved in 10 mL of ether. The saturated solution was cooled to -30 °C to afford a white solid, which was isolated by filtration. Yield: 1.240 g (65.7%). ¹H NMR (CDCl₃): 6.0 (br, 2H, NH), 6.85 (m, 1H, aromatic), 7.05 (m, 2H, aromatic), 7.31 (m, 10H, aromatic), 7.56 (m, 1H, aromatic). ¹³C NMR (CDCl₃): 121.4, 122.2, 123.0, 123.7, 128.3, 129.3, 129.5, 132.7, 132.8, 144.8 (aromatic carbon), 158.0 (CN₃). HRMS ESI (*m/z*): calcd for C₁₉H₁₆BrN₃ 365.0528; found, 365.0536. Anal. calcd. for C₁₉H₁₆BrN₃: C, 62.31; H, 4.40; N, 11.47, Found: C, 62.55; H, 4.23; N, 11.56.

Preparation of guanidine 14 from 2,3-dimethylindole. A solution of 2,3-dimethylindole (0.050 g, 0.34 mmol), diisopropylcarbodiimide (0.036 g, 0.29 mmol), LiN(SiMe₃)₂ (~2 mg, 0.01 mmol) and TMEDA (~10 mg, 0.02 mmol) in 0.5 mL of C₆D₆ was loaded into an NMR tube at room temperature and allowed to react for 18 hours. Yield of the reaction was determined to be 92.7 % by comparison of the integration of the internal standard and a well-resolved signal for the product guanidine. The product was further purified by removing the solvent *in vacuo* to afford a white solid. The solid was redissolved in 2 mL of ether and hexane (50:50 by volume) and was cooled to -30 °C to afford a white solid, which was isolated by filtration (Isolated yield: 70%). ¹H NMR (CDCl₃): 0.85 (d, 3H, CH₃), 0.95 (d, 3H, CH₃), 1.05 (d, 3H, CH₃), 1.15 (d, 3H, CH₃), 2.12 (s, 3H, CH₃), 2.20 (s, 3H, CH₃), 3.08 (br, 2H, CH), (4.10, 1H, NH), 7.19 (d, 1H, C₆H₄), 7.21 (d, 1H, C₆H₄), 7.33 (m, 1H, C₆H₄), 7.56 (m, 1H, C₆H₄). ¹³C NMR (CDCl₃): 8.6 (CH₃), 10.1 (CH₃), 23.7 (CH₃, br), 24.4 (CH₃, br), 45.1 (CH, br), 47.6 (CH, br), 107.8, 109.6, 118.0, 120.0, 121.5, 128.4, 130.7, 135.1 (C of indole ring), 141.4(CN₃). HRMS ESI (*m/z*): calcd for C₁₇H₂₅N₃ 271.2048; found,

271.2083. Anal. calcd. for $C_{17}H_{25}N_3$: C, 75.23; H, 9.28; N, 15.48, Found: C, 75.54; H, 9.32; N, 15.65.

Preparation of 15 from acetamide and diisopropylcarbodiimide. A solution of acetamide (0.500 g, 9.08 mmol), diisopropylcarbodiimide (1.430 g, 11.35 mmol), $LiN(SiMe_3)_2$ (~76 mg, 0.454 mmol) and TMEDA (0.263 g, 2.270 mmol) in 45 mL of toluene was loaded into a sealed Schlenk flask and heated at 80°C for 18 hours. The product was further purified by removing the solvent *in vacuo* to afford a white solid. The solid was redissolved in 10 mL of ether and was cooled to -30°C to afford a white solid, which was isolated by filtration. The yield of the reaction was determined to be 53.0% (0.850g). 1H NMR ($CDCl_3$): 1.14 (d, 12H, CH_3), 1.99 (s, 3H, $COCH_3$), 3.80 (br, 2H, CH). ^{13}C NMR ($CDCl_3$): 21.9 (CH_3), 27.3 ($COCH_3$), 41.5 (CH), 156.7 (CN_3), 183.1 ($COCH_3$). HRMS ESI (m/z): calcd for $C_9H_{19}N_3O$ 185.1528; found 185.1522. Anal. calcd. for $C_9H_{19}N_3O$: C, 58.35; H, 10.34; N, 22.68, Found C, 58.53; H, 10.29; N, 22.44.

General procedure for the catalytic addition of terminal alkyne to carbodiimide to yield compounds 16-19 using $LiN(SiMe_3)_2$. A vial was loaded with 1 equiv $LiN(SiMe_3)_2$ (5 mg, 0.030 mmol) 20 equiv 1,3-diisopropylcarbodiimide (75 mg, 0.598 mmol), 20 equiv alkyne, 10 equiv 1,3-dimethoxybenzene or toluene as a internal standard, and approximately 0.5 mL C_6D_6 . The solution was subsequently transferred to a sealed-NMR tube and single pulse 1H NMR spectrum was obtained. The tube was left at 80°C until all of the substrates were consumed. The conversion and yield were determined by comparison of the integration of the internal standard and a well-resolved signal for the product propiolamidines. The identity of the propiolamidines **16-19** were further confirmed by GC-MS. Compounds **16-19** have been reported previously.²

Preparation of $[Li(^iPr)NC(HN^iPr)N(C_6H_5)(THF)]_2$ (I). In a round bottom flask in the drybox containing 40 mL of toluene, aniline (200 mg, 2.15 mmol) and lithium bis(trimethylsilyl)amide (359 mg, 2.15 mmol) were added. A white precipitate formed immediately. Upon addition of 1,3-diisopropylcarbodiimide (271 mg, 2.15 mmol) and excess THF (1.0 mL), the solution became clear. The mixture was allowed to stir for 18 hrs. All volatiles were removed to give compound **I**. Yield: 430 mg (67 %). 1H NMR (500 MHz, C_6D_6): δ 0.95 (d, J = 6.1 Hz, 6H, CH_3), 1.18 (br, 6H, CH_3), 1.25 (m, 4H, THF), 3.23 (m, 1H, CH), 3.46 (t, 4H, THF), 3.67 (br d, 1H, NH), 3.80 (m, 1H,

CH), 6.68 (m, 1H, aromatic), 6.96 (m, 2H, aromatic), 7.26 (m, 2H, aromatic). ^{13}C (500 MHz, C_6D_6): δ 24.5 (CH_3), 25.2 (CH_3), 25.3 (THF), 43.8 (*CH*), 45.8 (*CH*), 68.3 (THF), 113.5 (br, aromatic carbon), 117.4 (br, aromatic carbon), 129.0 (aromatic carbon), 157.3 (br, aromatic carbon), 162.2 (br, CN_3). Anal. calcd. for $\text{C}_{17}\text{H}_{28}\text{LiN}_3\text{O}$: C, 68.66; H, 9.49; N, 14.13; Found: C, 68.36; H, 9.84; N, 14.31.

Preparation of $[\text{Li}(\text{PrNC}(\text{HN}^i\text{Pr})\text{N}(\text{C}_6\text{H}_4\text{OMe}))_2]$ (II). In a round bottom flask in the drybox containing 40 mL of toluene, 2-methoxyaniline (200 mg, 1.62 mmol) and lithium bis(trimethylsilyl)amide (272 mg, 1.62 mmol) were added. The solution became cloudy. Addition of 1,3-diisopropylcarbodiimide (204 mg, 1.620 mmol) did not produce any observable change. The mixture was allowed to stir for 18 hrs. All volatiles were removed to give compound **II**. Yield: 280 mg (68 %). ^1H NMR (500 MHz, C_6D_6): δ 0.85 (d, $J = 5.6$ Hz, 3H, CH_3), 1.00 (d, $J = 4.1$ Hz, 3H, CH_3), 1.17 (d, $J = 4.9$ Hz, 3H, CH_3), 1.22 (d, $J = 4.9$ Hz, 3H, CH_3), 3.11 (s, 3H, OCH_3), 3.27 (m, 1H, *CH*), 3.68 (m, 1H, *CH*), 3.71 (br, 1H, NH), 6.37 (m, 1H, aromatic), 6.50 (m, 1H, aromatic), 7.00 (m, 1H, aromatic), 7.13 (m, 1H, aromatic),. ^{13}C (500 MHz, C_6D_6): δ 22.8 (CH_3), 25.0 (CH_3), 25.2 (CH_3), 25.6 (CH_3), 44.1 (*CH*), 45.5 (*CH*), 55.0 (OCH_3), 109.8 (aromatic carbon), 113.0 (aromatic carbon), 114.7 (aromatic carbon), 122.9 (aromatic carbon), 146.4 (aromatic carbon), 148.9 (aromatic carbon), 162.7 (CN_3). Anal. calcd. for $\text{C}_{14}\text{H}_{22}\text{LiN}_3\text{O}$: C, 65.87; H, 8.69; N, 16.46, Found C, 65.64; H, 8.75; N, 16.57.

Structural determinations for I and II: Single crystals were mounted on thin glass fibers using viscous oil and then cooled to the data collection temperature. Crystal data and details of the measurements are summarized in Table 1. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω -scans at 0° , 90° , and 180° in ϕ . Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied. The structures were solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.1 program library.

Table 1. Crystal data and structure refinement summary for **I** and **II**.

Compound	I	II
Empirical formula	C ₁₇ H ₂₈ LiN ₃ O	C ₅₆ H ₈₈ Li ₄ N ₁₂ O ₄
Formula weight	297.36	1021.14
Temperature (K)	198(2)	203(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	P2 ₁ 2 ₁ 2	C2/c
a (Å)	10.3998(14)	38.889(6)
b (Å)	19.173(3)	10.2786(13)
c (Å)	9.2415(12)	35.177(4)
β (deg)		116.908(4)
Volume (Å ³)	1842.7(4)	12539(3)
Z	4	8
Calculated density (Mg/m ³)	1.072	1.082
Absorption coefficient (mm ⁻¹)	0.067	0.068
F(000)	648	4416
Theta range for data collection	2.23 to 21.96 deg.	1.30 to 20.81 deg.
Reflections collected / unique	10673 / 2194 [R(int) = 0.0638]	26740 / 6257 [R(int) = 0.0485]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9987 and 0.9934	0.9864 and 0.9797
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	2194 / 0 / 199	6257 / 0 / 685
Goodness-of-fit on F ²	1.030	1.018
Final R indices [I>2σ(I)]	R1 = 0.0475, wR2 = 0.1006	R1 = 0.0622, wR2 = 0.1566
R indices (all data)	R1 = 0.0736, wR2 = 0.1115	R1 = 0.0958, wR2 = 0.1804

References:

¹Ong, T.-G.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2003**, *125*, 8100-8101.

² Zhang, W.-X.; Nishiura, M.; Hou, Z. *J. Am. Chem. Soc.* **2005**, *127*, 16788.

Figure S1. Molecular structure and atom numbering scheme (selected atoms) for

$[\text{Li}(\text{}^i\text{PrNC}(\text{HN}^i\text{Pr})\text{N}(\text{C}_6\text{H}_5)(\text{THF})_2)]_2$ (**I**). Thermal ellipsoids are shown at 30% probability and hydrogen atoms have been omitted for clarity. Only the asymmetric unit is labeled and the other half of the molecule is generated by a C_2 -axis oriented perpendicular to the Li_2N_2 plane. Selected bond distances ($\text{\AA}$): Li(1)-O(1) 1.919(6), Li(1)-N(1) 2.016(6), Li(1)-N(2A), 2.031(6), Li(1)-N(2) 2.204(6), N(1)-C(1), 1.307(4), N(2)-C(1) 1.388(4), N(3)-C(1) 1.369(4). Selected bond angles (deg): O(1)-Li(1)-N(1) 111.7(3), O(1)-Li(1)-N(2A) 116.8(3), N(1)-Li(1)-N(2A) 127.4(3), O(1)-Li(1)-N(2) 121.8(3), N(1)-Li(1)-N(2) 65.39(19), C(1)-N(1)-C(2) 120.6(3), C(1)-N(1)-Li(1) 94.2(3), C(2)-N(1)-Li(1) 145.1(3), C(1)-N(2)-C(5) 119.5(3), C(1)-N(2)-Li(1A) 111.3(3), C(5)-N(2)-Li(1A) 127.8(3), C(1)-N(2)-Li(1) 84.1(2), C(5)-N(2)-Li(1) 119.3(2), N(1)-C(1)-N(3) 124.6(3), N(1)-C(1)-N(2) 115.9(3), N(3)-C(1)-N(2) 119.5(3).

Fig. S2. Molecular structure and atom numbering scheme (selected atoms) for

$[\text{Li}^i\text{PrNC}(\text{HN}^i\text{Pr})\text{N}(\text{C}_6\text{H}_4\text{OMe})]_2$ (**II**). Thermal ellipsoids are shown at 30% probability and hydrogen atoms have been omitted for clarity. Only one molecule of the asymmetric unit is presented. Selected bond distances (Å): Li(1)-O(2) 1.952(7), Li(1)-N(1) 1.982(8), Li(1)-N(6) 1.993(8), Li(1)-N(2) 2.189(8), Li(2)-O(1) 1.928(8), Li(2)-N(4) 1.947(8), Li(2)-N(2) 1.974(8), Li(2)-N(6) 2.159(8), N(1)-C(4) 1.298(5), N(2)-C(4) 1.374(5), N(3)-C(4) 1.390(5), N(4)-C(18) 1.299(5), N(5)-C(18) 1.379(5), N(6)-C(18) 1.390(5). Selected bond angles (deg): O(2)-Li(1)-N(1) 137.6(4), O(2)-Li(1)-N(6) 83.3(3), N(1)-Li(1)-N(6) 137.1(4), O(2)-Li(1)-N(2) 124.9(4), N(1)-Li(1)-N(2) 65.9(2), N(6)-Li(1)-N(2) 104.9(3), C(4)-N(1)-C(1) 120.6(4), C(4)-N(1)-Li(1) 94.0(3), C(1)-N(1)-Li(1) 143.6(4), C(4)-N(2)-C(5) 121.3(3), C(4)-N(2)-Li(2) 125.5(4), C(5)-N(2)-Li(2) 109.9(3), C(4)-N(2)-Li(1) 83.2(3), C(5)-N(2)-Li(1) 133.7(3), Li(2)-N(2)-Li(1) 73.8(3), N(1)-C(4)-N(2) 116.9(4), N(1)-C(4)-N(3) 123.4(4), N(2)-C(4)-N(3) 119.7(4).