

# Clean and Efficient Synthesis of *O*-Silylcarbamates and Ureas in Supercritical Carbon Dioxide

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### General remarks

**Caution! All high pressure scCO<sub>2</sub> reactions should be carried out with adequate containment and with extreme caution.**

<sup>1</sup>H NMR spectra were recorded on a Bruker DPX-400 (400 MHz) and DRX-500 (500 MHz) at ambient temperature, using the chemical shift of a residual protic solvent (CHCl<sub>3</sub> at δ 7.28 ppm or DMSO at δ 2.50 ppm) as an internal reference. All shifts are quoted in parts per million (ppm) relative to CHCl<sub>3</sub> or DMSO. The multiplicity of the signal is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), dq (doublet of quartets), quint. (quintet), sext. (sextet), sept. (septet) and br (broad). <sup>13</sup>C NMR spectra were recorded on a Bruker DPX-400 (101 MHz), Bruker DRX-500 (126 MHz) with cryoprobe and Bruker Avance 700 (176 MHz) spectrometer using the central resonance of the triplet of CDCl<sub>3</sub> at δ 77.0 ppm as an internal reference.

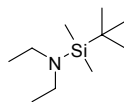
Infrared spectra were recorded on a Nicolet 510 series FT-IR or PerkinElmer Spectrum One series FT-IR spectrometer using KBr pellet, thin film on NaCl window or neat sample on top of a diamond sampling tip. Melting points were determined using an Electrothermal IA 9010 or Büchi 510 melting point apparatus. Microanalyses were carried out by the Department of Chemistry (University of Cambridge, UK) or Chemical & Micro Analytical Services Pty. Ltd. (Australia). Mass spectra were recorded by the EPSRC Swansea Mass Spectrometry Service (UK), the School of Chemistry (University of Melbourne, Australia) or CSIRO (Australia).

Flash column chromatography was carried out using Merck Kieselgel 60 (230-400 mesh) silica. Analytical and preparative thin layer chromatography (TLC) was done on pre-coated 0.2 mm thick Merck Kieselgel 60 F<sub>254</sub> silica gel plates and visualized by absorption of UV light and cerium (IV) sulfate or permanganate dip.

Reactions in supercritical carbon dioxide were conducted in a 10 mL stainless steel cell. Carbon dioxide (Messer 99.9995% - further purified over an Oxisorb<sup>®</sup> catalyst) was delivered to the reaction using a NWA Pickel PM101 air driven pump at the desired pressure. Heating of the cell was achieved by the use of a heating tape. The system pressure was measured by a pressure transducer (A105, RDP Electronics) and displayed on a digital display (E308, RDP Electronics). The internal temperature was monitored by an Industrial Mineral Insulated thermocouple (Type K, RS Electronics) and displayed on a temperature indicator (T200, RS Electronics).

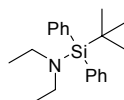
**Synthesis of *N*-silylamines:**

**(*tert*-Butyldimethylsilyl)diethylamine (2).<sup>1</sup> Representative Procedure A**



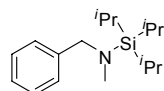
*n*-BuLi (1.59 M in THF; 16.8 mL, 26.6 mmol,) was added drop wise to a stirred solution of diethylamine (1.77 g, 24.2 mmol) in dry THF (35 mL) at -78 °C. The reaction mixture was stirred at -78 °C for 2 h then *tert*-butyl-chlorodimethylsilane (3.64 g, 24.2 mmol) in dry THF (15 mL) was added. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. The THF was removed under nitrogen *via* distillation, dry pentane was added and the mixture stirred for 1 h to ensure complete precipitation of the lithium salts. The liquid part was separated *via* cannula and the pentane removed under nitrogen *via* distillation. The residue was purified *via* vacuum distillation to yield the title compound **2** (2.19 g, 48%) as a colourless oil: bp 46 °C, 5 mmHg; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.05 (s, 6H), 0.88 (s, 9H), 1.00 (t, *J* = 7.0 Hz, 6H), 2.86 (q, *J* = 7.0 Hz, 4H).

**(*tert*-Butyldiphenylsilyl)diethylamine (3).<sup>2</sup>**



Representative procedure A using *n*-BuLi (1.59 M in THF; 16.8 mL, 26.6 mmol), diethylamine (1.77 g, 24.2 mmol) and *tert*-butyl-chlorodiphenylsilane (6.65 g, 24.2 mmol) gave the title compound **3** (5.16 g, 68%) as a pale yellow oil: b.p. 164 °C, 4 mmHg; IR (thin film) 3072, 3053, 2968, 2932, 2901, 2860, 1602 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.07 (dt, *J* = 7.0, 1.5 Hz, 6H), 1.17 (s, 9H), 3.05 (dq, *J* = 7.0, 1.5 Hz, 4H), 7.36-7.71 (m, 10H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 14.8, 19.7, 28.9, 40.8, 127.5, 128.9, 136.0, 136.7; MS (CI) *m/z* 312 (M+H)<sup>+</sup>; HRMS (ES) *m/z* 312.2143 (312.2142 calcd. for C<sub>20</sub>H<sub>30</sub>NSi).

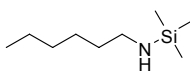
***N*-Benzyl-*N*-methyl-(triisopropylsilyl)amine (4)**



Representative procedure A using *N*-methyl-*N*-benzylamine (3.0 mL, 23 mmol), *n*-BuLi (1.59 M in hexanes; 16.0 mL, 25 mmol) and triisopropylsilyl chloride (4.96 mL, 23 mmol) gave the title compound **4** (4.76 g, 74%) as a colourless oil: b.p. 151-152 °C, 5 mmHg; IR (thin film) 3026, 2944, 2890, 2865, 2797, 1604, 1494, 1464, 1382, 1356, 1322, 1203, 1136, 1006 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz,

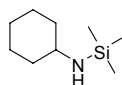
$\text{CDCl}_3$ )  $\delta$  1.13 (d,  $J = 7.0$  Hz, 18H), 1.25 (sept.,  $J = 7.0$  Hz, 3H), 2.42 (s, 3H), 4.04 (s, 2H), 7.24-7.26 (m, 1H), 7.31-7.33 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.5, 18.7, 36.1, 55.3, 126.3, 127.4, 128.2, 141.3; MS (CI)  $m/z$  278; HRMS (EI)  $m/z$  278.2297 (278.2297 calcd. for  $\text{C}_{17}\text{H}_{32}\text{NSi}$  278.2297); Anal. Calcd. for  $\text{C}_{17}\text{H}_{31}\text{NSi}$ : C, 73.6; H, 11.3; N, 5.1. Found: C, 73.6; H, 11.2; N, 5.3.

### Hexyl-trimethylsilylamine (5).<sup>3</sup>



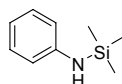
Representative procedure A using *n*-BuLi (1.59 M in THF; 11.9 mL, 19.0 mmol), hexylamine (1.97 g, 19.4 mmol) and chlorotrimethylsilane (2.11 g, 19.4 mmol) gave the title compound **5** (1.60 g, 49%) as a colourless oil: b.p. 122 °C, 150 mmHg; IR (thin film) 2956, 2926, 2856, 1247, 1056, 896, 832, 746  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.05 (s, 9H), 0.38 (br s, 1H), 0.91 (t,  $J = 7.0$  Hz, 3H), 1.27-1.37 (m, 6H), 1.37-1.41 (m, 2H), 2.70 (dt,  $J = 7.5, 7.0$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  -0.1, 14.1, 22.7, 26.6, 31.7, 34.7, 41.9; Anal. Calcd. for  $\text{C}_9\text{H}_{23}\text{NSi}$ : C, 62.3; H, 13.4; N, 8.1. Found: C, 62.3; H, 13.3; N, 8.0.

### *N*-Trimethylsilylcyclohexylamine (18).<sup>4</sup>



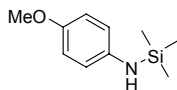
Representative procedure A using cyclohexylamine (1.7 mL, 1.49 g, 15 mmol), *n*-BuLi (1.6 M in hexane; 9.8 mL, 14.7 mmol) and chlorotrimethylsilane (2.3 mL, 1.96 g, 18 mmol) gave the title compound **18** (2.16 g, 84%) as a colourless oil: b.p. 60 °C, 9 mmHg;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.02 (s, 9H), 0.94-1.28 (m, 6H), 1.52-1.57 (m, 1H), 1.65-1.80 (m, 4H), 2.55 (m, 1H).

### *N*-Trimethylsilylaniline (20).<sup>5</sup>



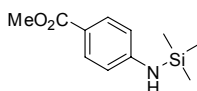
Representative procedure A using aniline (1.9 mL, 1.86 g, 20 mmol), *n*-BuLi (1.6 M in hexane; 12.0 mL, 19 mmol) and chlorotrimethylsilane (2.54 mL, 2.39 g, 22 mmol) gave the title compound **20** (2.53 g, 76%) as a yellow oil: b.p. 106 °C, 25 mmHg;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.30 (s, 9H), 3.45 (br s, 1H), 6.68 (d,  $J = 8.5$  Hz, 2H), 6.73 (t,  $J = 7.5$  Hz, 1H), 7.17 (dd,  $J = 8.5, 7.5$  Hz, 2H).

***N*-Trimethylsilyl-*p*-anisidine (**21**).**<sup>6</sup>



Representative procedure A using *p*-anisidine (1.85 g, 15 mmol), *n*-BuLi (1.5 M in hexane; 10 mL, 15 mmol) and TMSCl (2.3 mL, 1.96 g, 18 mmol) gave title compound **21** (2.11 g, 72%, purity 90% by <sup>1</sup>H NMR) as a colourless oil: b.p. 115 °C, 9 mmHg; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.25 (s, 9H), 3.21 (br s, 1H), 3.74 (s, 3H), 6.60 (d, *J* = 9.0 Hz, 2H), 6.74 (d, *J* = 9.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 0.08, 55.8, 114.9, 116.8, 141.0, 151.9.

**Methyl 4-(trimethylsilylamino)benzoate (**22**).**



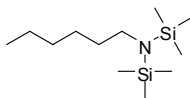
Representative procedure A using methyl 4-aminobenzoate (2.27 g, 15 mmol), *n*-BuLi (1.5 M in hexane; 10 mL, 15 mmol) and TMSCl (2.3 mL, 1.96 g, 18 mmol) gave title compound **22** (0.69 g, 21%, purity 60% by <sup>1</sup>H NMR) as a colourless oil: b.p. 109 °C, 0.5 mmHg; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.30 (s, 9H), 3.82 (br s, 1H), 3.85 (s, 3H), 6.62 (d, *J* = 9.0 Hz, 2H), 7.85 (d, *J* = 9.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ -0.1, 51.5, 115.3, 119.0, 131.4, 152.2, 167.2. Full characterisation was not possible as the title compound **22** was inseparable by distillation from methyl 4-aminobenzoate.

**2-Ethyl-1,1,1,3,3,3-hexamethyldisilazane (**34**).**<sup>7</sup>



Sodium bis(trimethylsilyl)amide (3.67 g, 20 mmol) was dissolved in hexamethyldisilazane (10 mL) and iodoethane (1.6 mL, 20 mmol) was added. The mixture was heated at 80 °C overnight. Stirring was stopped and the precipitated salts allowed to settle. The clear solution was separated from the salts *via* cannula and the product purified *via* distillation to give 2-ethyl-1,1,1,3,3,3-hexamethyldisilazane (**34**) (1.64 g, 43%) as a colourless oil: b.p. 60-62 °C, 20 mmHg; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.08 (s, 18H), 0.98 (t, *J* = 7.0 Hz, 3H), 2.84 (q, *J* = 7.0 Hz, 2H).

***N,N*-Bis(trimethylsilyl)hexylamine (37).**



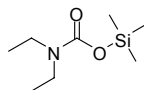
Representative procedure A using hexylamine (2.0 mL, 1.52 g, 15 mmol), *n*-BuLi (1.6 M in hexane; 20.6 mL, 33 mmol) and chlorotrimethylsilane (4.6 mL, 36 mmol) gave the title compound **37** (2.65 g, 72%) as a colourless oil: b.p. 132 °C, 37 mmHg; IR (thin film) 2956, 2931, 2862, 1249, 1072, 928, 872, 834, 819, 753, 679 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.08 (s, 18H), 0.89 (t, *J* = 7.0 Hz, 3H), 1.16-1.37 (m, 8H), 2.72 (dd, *J* = 9.0, 7.5 Hz, 2H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ 2.1, 14.1, 22.8, 26.9, 31.8, 35.5, 45.7; MS (EI) *m/z* 245 (M<sup>+</sup>); HRMS (EI) *m/z* 245.1990 (245.1990 calcd. for C<sub>12</sub>H<sub>31</sub>NSi<sub>2</sub>); Anal. Calcd. for C<sub>12</sub>H<sub>31</sub>NSi<sub>2</sub>: C, 58.7; H, 12.7; N, 5.7; Si, 22.9. Found: C, 58.6; H, 12.8; N, 5.7; Si, 22.8.

***Synthesis of silylcarbamates:***

**Synthesis of silyl carbamates in scCO<sub>2</sub>. Representative procedure B**

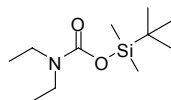
A 10 mL high pressure stainless steel cell was sealed and evacuated and refilled with nitrogen (three cycles). The silylamine was injected through the inlet port and the cell connected to the CO<sub>2</sub> line and charged with CO<sub>2</sub> (99.9995% - further purified over an Oxisorb<sup>®</sup> catalyst) to approximately 760 psi (volume *ca.* 1 mL liquid carbon dioxide). The cell was heated to the specified temperature and the pressure adjusted to *ca.* 1800 psi by the addition of further CO<sub>2</sub>. The reagents were maintained at this temperature and pressure for 17 h before the cell was allowed to cool to room temperature. The contents of the cell were vented into dry diethyl ether (50 mL), and once atmospheric pressure had been reached, the cell was opened and washed with further aliquots of dry diethyl ether (3 × 10 mL). The combined organic fractions were concentrated *in vacuo* to furnish the crude material which was analysed crude by <sup>1</sup>H NMR spectroscopy.

***N,N*-Diethyl trimethylsilylcarbamate (6).<sup>8</sup>**



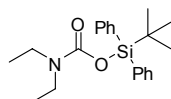
*N,N*-Diethyl trimethylsilylamine (**1**) (0.77 g, 5.3 mmol) was treated with scCO<sub>2</sub> according to representative procedure B at 40 °C to afford the title compound **6** (0.80 g, 81%) as a colourless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.26 (s, 9H), 1.08 (*app* q, *J* = 7.0 Hz, 3H), 1.09 (*app* q, *J* = 7.0 Hz, 3H), 3.20 (t, *J* = 7.0 Hz, 2H), 3.26 (q, *J* = 7.0 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ -0.16, 13.2, 13.8, 41.1, 41.5, 154.7; The highly sensitive nature of compound **6** precluded further characterization.

**(tert-Butyldimethylsilyl)-N,N-diethyl carbamate (7).**



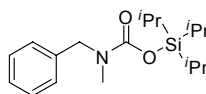
(*tert*-Butyldimethylsilyl)diethylamine (**2**) (0.84 g, 4.5 mmol) was treated with  $scCO_2$  according to representative procedure B at 60 °C to afford (*tert*-butyldimethylsilyl)-N,N-diethyl carbamate (**7**) (0.86 g, 83%) as a colourless oil; IR ( $CHCl_3$ ) 3073, 2964, 2933, 2892, 2860, 1670  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  0.27 (s, 6H), 0.93 (s, 9H), 1.11 (br t,  $J = 7.0$  Hz, 6H), 3.23 (q,  $J = 7.0$  Hz, 2H), 3.27 (q,  $J = 7.0$  Hz, 2H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  -4.62, 13.4, 14.1, 17.6, 25.7, 41.4, 41.8, 154.8; MS (CI)  $m/z$  232 (M+H) $^+$ ; HRMS (ES)  $m/z$  232.1724 (232.1727 calcd. for  $C_{11}H_{26}NO_2Si$ ).

**(tert-Butyldiphenylsilyl)-N,N-diethyl carbamate (8).**



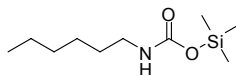
(*tert*-Butyldiphenylsilyl)diethylamine (**3**) (1.03 g, 3.3 mmol) was treated with  $scCO_2$  according to representative procedure B at 100 °C to afford (*tert*-butyldiphenylsilyl)-N,N-diethyl carbamate (**8**) (1.11 g, 95%) as a pale yellow oil; IR ( $CHCl_3$ ) 3075, 3054, 3018, 2964, 2934, 2896, 2861, 1678, 1591  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.12 (s, 9H), 1.24 (t,  $J = 7.0$  Hz, 6H), 3.30 (q,  $J = 7.0$  Hz, 2H), 3.43 (q,  $J = 7.0$  Hz, 2H), 7.30-7.80 (m, 10H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  13.4, 14.4, 19.2, 27.1, 41.7, 42.2, 127.6, 129.7, 132.8, 135.3, 153.8; MS (CI)  $m/z$  356 (M+H) $^+$ ; HRMS (ES)  $m/z$  356.2041 (356.2040 calcd. for  $C_{21}H_{30}NO_2Si$ ).

**N-Benzyl-N-methyl triisopropylsilylcarbamate (9).**



N-Benzyl-N-methyl triisopropylsilylamine (**4**) (449 mg, 1.6 mmol) was treated with  $scCO_2$  according to representative procedure B at 100 °C to afford N-benzyl-N-methyl triisopropylsilylcarbamate (**9**) (494 mg, 95%) as a colourless oil;  $R_f$  0.61 (hexane : EtOAc, 2 : 1); IR ( $CHCl_3$ ) 2945, 2893, 2868, 1683, 1465, 1397, 1224, 1159  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.10 (d,  $J = 7.5$  Hz, 9H), 1.14 (d,  $J = 7.5$  Hz, 9H), 1.35 (sept.,  $J = 7.5$  Hz, 3H), 2.89 (2 x s, 3H), 4.52 (2 x s, 2H), 7.24-7.30 (m, 3H), 7.33-7.37 (m, 2H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  12.1, 17.9, 34.3, 52.3, 53.2, 127.1, 127.3, 127.8, 128.6, 137.8, 137.8, 155.2, 155.5; MS (CI)  $m/z$  356 (M $^+$ ); HRMS (EI)  $m/z$  322.2202 (322.2197 calcd. for  $C_{18}H_{32}NO_2Si$ ); Anal. Calcd. for  $C_{18}H_{32}NO_2Si$ : C, 67.2; H, 9.7; N, 4.4. Found: C, 67.2; H, 9.8; N, 4.4.

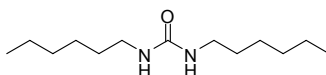
***N*-Hexyltrimethylsilyl carbamate (10).**



Hexyl trimethylsilylamine **5** (0.74 g, 4.3 mmol) was treated with  $\text{scCO}_2$  according to representative procedure B at 40 °C to afford *N*-hexyltrimethylsilyl carbamate (**10**) (0.76 g, 82%) as a colourless oil; IR ( $\text{CHCl}_3$ ) 2959, 2930, 2872, 2858, 1694  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.29 (s, 9H), 0.90 (t,  $J$  = 6.5 Hz, 3H), 1.27-1.35 (m, 6H), 1.46-1.51 (m, 2H), 3.15 (dt,  $J$  = 6.5, 6.0 Hz, 2H), 4.68 (br s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  -0.07, 14.0, 22.5, 26.4, 29.8, 31.4, 41.0, 155.2; Anal. Calcd. for  $\text{C}_{10}\text{H}_{23}\text{N}_2\text{OSi}$ : C, 55.3; H, 10.7; N, 6.4. Found: C, 55.4; H, 10.7; N, 6.4.

***Synthesis of symmetrical ureas:***

**1,3-Dihexylurea (17).<sup>9</sup>**

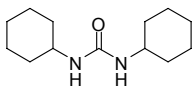


A 10 mL stainless steel cell containing a stirrer bar was sealed and the cell evacuated and refilled with nitrogen (3 cycles). Hexyl trimethylsilylamine (**5**) (271 mg, 1.56 mmol) was added and the cell connected to the  $\text{CO}_2$  line and charged with  $\text{CO}_2$  (99.9995% - further purified over an Oxisorb<sup>®</sup> catalyst) to approximately 1200 psi. The cell was heated to 40 °C and the pressure adjusted to *ca.* 1800 psi by the addition of further  $\text{CO}_2$ . The mixture was stirred at 40 °C for 17 h. The cell was allowed to cool to room temperature before being carefully vented over a period of one hour.

The contents of the cell was left untouched and the cell heated to 120 °C and the reaction mixture stirred overnight. The reaction vessel was cooled to room temperature and the cell charged to *ca.* 1200 psi by the addition of  $\text{CO}_2$ . The cell was vented and the process repeated a further two times. The cell was disassembled and the majority of the white/grey solid removed by spatula. The cell was washed further with EtOAc ( $3 \times 10$  mL) and the washing solution concentrated *in vacuo*. The solids were combined and placed under high vacuum for 1 h to remove any remaining hexamethyldisiloxane. 1,3-Dihexylurea (**17**) was obtained as a white crystalline solid (128 mg, 72%): m.p. 73-74 °C (hexane);  $R_f$  0.27 (hexane : EtOAc, 1 : 1); IR (thin film) 3325, 2956, 2928, 2855, 1612, 1574, 1478, 1461, 1249, 1220  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86 (t,  $J$  = 7.0 Hz, 6H), 1.27 (m, 8H), 1.44 (tt,  $J$  = 7.0, 7.0 Hz, 4H), 3.12 (dt,  $J$  = 7.0, 5.0 Hz, 4H), 4.67 (br t,  $J$  = 5.0 Hz, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  15.6, 24.2, 28.2, 31.9, 33.2, 42.2, 160.2; MS (CI)  $m/z$  229 ( $\text{M}+\text{H}$ )<sup>+</sup>; HRMS (ES)  $m/z$  229.2276 (229.2274 calcd. for  $\text{C}_{13}\text{H}_{29}\text{N}_2\text{O}$ ); Anal. Calcd. for  $\text{C}_{13}\text{H}_{28}\text{N}_2\text{O}$ : C, 68.4; H, 12.4; N, 12.3. Found: C, 68.4; H, 12.1; N, 12.2.

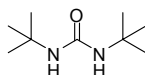


**1,3-Bis(cyclohexyl)urea (23).**<sup>10</sup> Representative procedure C.



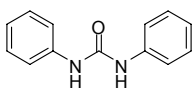
A 10 cm<sup>3</sup> stainless steel vessel was sealed and then evacuated and refilled with N<sub>2</sub> (3 cycles). *N*-trimethylsilylcyclohexylamine (**18**) (217 mg, 1.0 mmol) was injected through the inlet port. The vessel was filled with liquid CO<sub>2</sub> to approximately one-third capacity and heated to 120 °C, at which time the pressure was adjusted to 2000 psi (13.8 MPa). After 17 h, the vessel was allowed to cool to room temperature and the CO<sub>2</sub> vapour was vented into MeOH (20 cm<sup>3</sup>). The vessel was rinsed with another portion of MeOH (40 cm<sup>3</sup>) and the combined fractions were then concentrated under reduced pressure. Purification by flash column chromatography (EtOAc : petroleum ether 1 : 1) gave the title compound **23** (58 mg, 52%) as a white crystalline solid: m.p. 220 °C; *R*<sub>f</sub> 0.27 (EtOAc : hexane, 1 : 1); IR (thin film) 3298, 2929, 2854, 1631, 1562, 1450, 1319, 1254, 1093, 891 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.13-1.36 (m, 12H), 1.59 (m, 2H), 1.71 (m, 4H), 1.94 (m, 4H), 3.47 (m, 2H).

**1,3-Di-*tert*-butylurea (24).**<sup>11</sup>



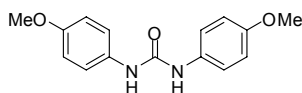
Representative procedure C using methyl *N*-trimethylsilyl-*tert*-butylamine (**19**) (382 μL, 291 mg, 2.0 mmol) gave the title compound **24** (22 mg, 13%) as a white crystalline solid: m.p. 210 °C; *R*<sub>f</sub> 0.22 (EtOAc : hexane, 1 : 1); IR (thin film) 3349, 2965, 1637, 1560, 1448, 1390, 1361, 1293, 1232, 1210 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.32 (s, 18H), 3.92 (br s, 2H).

**1,3-Diphenylurea (25).**<sup>11</sup>



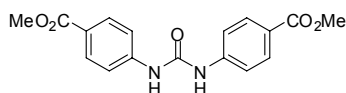
Representative procedure C using *N*-trimethylsilylaniline (**20**) (178 μL, 165 mg, 1.0 mmol) gave the title compound **25** (91 mg, 85%) as a white crystalline solid: m.p. 245 °C (hexane); *R*<sub>f</sub> 0.35 (EtOAc : hexane, 3 : 7); IR (thin film) 3278, 1646, 1593, 1547, 1497, 1447, 1440, 1314, 1294, 1231 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 6.96 (t, *J* = 7.5 Hz, 2H), 7.28 (dd, *J* = 8.5, 7.5 Hz, 4H), 7.45 (d, *J* = 8.5 Hz, 4H), 8.66 (s, 2H).

**1,3-Bis(4-methoxyphenyl)urea (26).**<sup>11</sup>



Representative procedure C using *N*-trimethylsilyl-*p*-anisidine (**21**) (90 % in *N,N*-bis(trimethylsilyl)-*p*-anisidine; 195 mg, 1.0 mmol) gave the title compound **26** (94 mg, 69%) as a white crystalline solid: m.p. 233 °C;  $R_f$  0.20 (EtOAc : hexane, 2 : 3); IR (thin film) 3298, 1633, 1606, 1557, 1509, 1244, 1169, 1027, 826  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  3.70 (s, 6H), 6.85 (d,  $J = 9.0$  Hz, 4H), 7.32 (d,  $J = 9.0$  Hz, 4H), 8.37 (br s, 2H).

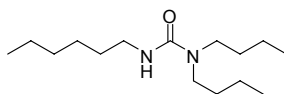
**1,3-Bis(4-carbomethoxyphenyl)urea (27).**<sup>12</sup>



Representative procedure C using methyl 4-(trimethylsilylamino)benzoate (**22**) (60% in methyl 4-aminobenzoate; 223 mg, 1.0 mmol) gave the title compound **27** (66 mg, 40%) as a white crystalline solid: m.p. 257-258 °C;  $R_f$  0.20 (EtOAc : hexane, 2 : 3); IR (thin film) 3438, 3331, 3269, 1717, 1692, 1661, 1596, 1539, 1510, 1428, 1407, 1274, 1172, 1113, 850, 764  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  3.82 (s, 6H), 7.60 (d,  $J = 9.0$  Hz, 4H), 7.90 (d,  $J = 9.0$  Hz, 4H), 9.22 (br s, 2H).

**Synthesis of unsymmetrical ureas:**

**1,1-Dibutyl-3-hexylurea (28). Representative procedure D.**

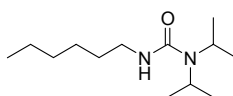


Hexyl trimethylsilylamine (**7**) (200 mg, 1.16 mmol) was added to a 10 mL stainless steel cell containing a stirrer bar was sealed and the cell evacuated and refilled with nitrogen (3 cycles). The cell was connected to the CO<sub>2</sub> line and charged with CO<sub>2</sub> (99.9995% - further purified over an Oxisorb<sup>®</sup> catalyst) to approximately 1200 psi. The cell was heated to 40 °C and the pressure adjusted to *ca.* 1800 psi by the addition of further CO<sub>2</sub>. The mixture was stirred at 40 °C for 18 h. The cell was allowed to cool to room temperature before being carefully vented over a period of one hour.

The cell was evacuated and refilled with nitrogen (3 cycles). *N,O*-bistrimethylsilylacetamide (129  $\mu\text{L}$ , 1.16 mmol) was added and the mixture stirred for 10 mins. Dibutylamine (295  $\mu\text{L}$ , 1.74 mmol) was added, the cell was sealed and heated to 120 °C and the reaction mixture stirred overnight. The reaction vessel was cooled to room temperature and disassembled. The product was removed by

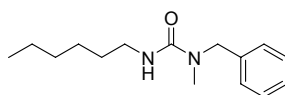
washing with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL) and the washing solution concentrated *in vacuo*. Purification by flash column chromatography (EtOAc : hexane, 1 : 1) gave the title compound **28** (217 mg, 73%) as a clear oil; *R<sub>f</sub>* 0.40 (EtOAc : hexane, 3 : 7); IR (thin film) 3340, 2957, 2928, 2860, 1622, 1532, 1306, 1292, 1235, 750, 730 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.88 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 6H), 1.25-1.34 (m, 10H), 1.46-1.54 (m, 6H), 3.15 (t, *J* = 7.0 Hz, 4H), 3.21 (t, *J* = 7.0 Hz, 2H), 4.39 (br s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 13.9, 14.0, 20.2, 22.6, 26.6, 30.3, 30.6, 31.5, 40.9, 47.4, 157.4; MS (EI) *m/z* 256 (M<sup>+</sup>); HRMS (EI) *m/z* 256.2505 (256.2509 calcd. for C<sub>15</sub>H<sub>32</sub>N<sub>2</sub>O); Anal. Calcd. for C<sub>15</sub>H<sub>32</sub>N<sub>2</sub>O: C, 70.3; H, 12.6; N, 10.9; O, 6.2. Found: C, 70.1; H, 12.4; N, 10.9; O, 6.3.

### 1,1-Diisopropyl-3-hexylurea (29).



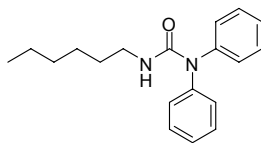
Representative procedure D using hexyl trimethylsilylamine (**7**) (200 mg, 1.16 mmol), *N,O*-bistrimethylsilylacetamide (129 μL, 1.16 mmol) and diisopropylamine (243 μL, 1.74 mmol) gave the title compound **29** (185 mg, 70%) as a clear oil; *R<sub>f</sub>* 0.63 (EtOAc : hexane, 1 : 1); IR (thin film) 3355, 2960, 2926, 2858, 1619, 1524, 1324, 1216, 1161, 1132, 1050, 767 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.20 (d, *J* = 7.0 Hz, 12H), 1.28 (m, 6H), 1.48 (m, 2H), 3.21 (qd, *J* = 7.0, 1.5 Hz, 2H), 3.99 (sept., *J* = 7.0 Hz, 2H), 4.15 (br s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.0, 21.4, 22.5, 26.7, 30.3, 31.5, 40.7, 44.9, 157.3; MS (EI) *m/z* 228 (M<sup>+</sup>); HRMS (EI) *m/z* 228.2198 (228.2202 calcd. for C<sub>13</sub>H<sub>28</sub>N<sub>2</sub>O).

### 1-Methyl-1-benzyl-3-hexylurea (30).



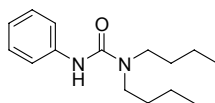
Representative procedure D using hexyl trimethylsilylamine (**7**) (200 mg, 1.16 mmol), *N,O*-bistrimethylsilylacetamide (129 μL, 1.16 mmol) and *N*-methylbenzylamine (225 μL, 1.74 mmol) gave the title compound **30** (164 mg, 57%, 90% purity by <sup>1</sup>H NMR) as a white solid: m.p. 55-55 °C (petroleum ether); *R<sub>f</sub>* 0.44 (EtOAc : hexane, 1 : 1); IR (thin film) 3330, 2957, 2926, 2858, 1621, 1533, 1368, 1240, 1027, 728, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.26 (m, 6H), 1.46 (m, 2H), 2.87 (s, 3H), 3.23 (q, *J* = 7.0 Hz, 2H), 4.41 (br s, 1H), 4.48 (s, 2H), 7.24 (m, 3H), 7.32 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 13.4, 22.6, 26.6, 30.3, 31.6, 34.4, 41.0, 52.2, 127.1, 127.2, 128.6, 138.0, 158.4; MS (EI) *m/z* 248 (M<sup>+</sup>); HRMS (EI) *m/z* 248.1882 (248.1889 calcd. for C<sub>15</sub>H<sub>24</sub>N<sub>2</sub>O). The title compound **30** was inseparable for traces of symmetrical urea **17** by flash chromatography.

**1,1-diphenyl-3-hexylurea (31).**



Representative procedure D using hexyl trimethylsilylamine (**7**) (200 mg, 1.16 mmol), *N,O*-bistrimethylsilylacetamide (129  $\mu$ L, 1.16 mmol) and diphenylamine (294 mg, 1.74 mmol) gave the title compound **31** (21 mg, 6%) as a white solid: mp 47-49 °C;  $R_f$  0.41 (EtOAc : hexane, 1 : 4); IR (thin film) 2956, 2926, 2857, 1667, 1591, 1489, 1297, 1252, 1073, 753, 692  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J = 7.0$  Hz, 3H), 1.27-1.31 (m, 6H), 1.46 (m, 2H), 3.24 (dt,  $J = 7.0, 4.5$  Hz, 2H), 4.55 (br t,  $J = 4.5$  Hz, 1H), 7.21 (t,  $J = 7.5$  Hz, 2H), 7.26 (d,  $J = 7.5$  Hz, 4H), 7.35 (dd,  $J = 7.5, 7.5$  Hz, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 22.5, 26.4, 29.9, 31.4, 40.8, 125.9, 127.3, 129.3, 142.9, 156.1; MS (EI)  $m/z$  296 ( $\text{M}^+$ ); HRMS (EI)  $m/z$  296.1870 (296.1883 calcd. for  $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}$ ); Anal. Calcd. for  $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}$ : C, 77.0; H, 8.2; N, 9.5; O, 5.4. Found: C, 76.9; H, 8.2; N, 9.5; O, 5.4.

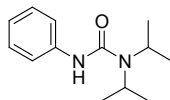
**1,1-Dibutyl-3-phenylurea (32).<sup>13</sup> Representative procedure E**



Trimethylsilylaniline (**20**) (150 mg, 0.907 mmol) was added to a 10 mL stainless steel cell containing a stirrer bar was sealed and the cell evacuated and refilled with nitrogen (3 cycles). The cell was connected to the  $\text{CO}_2$  line and charged with  $\text{CO}_2$  (99.9995% - further purified over an Oxisorb<sup>®</sup> catalyst) to approximately 1200 psi. The cell was heated to 100 °C and the pressure adjusted to *ca.* 2000 psi by the addition of further  $\text{CO}_2$ . The mixture was stirred at 100 °C for 18 h. The cell was allowed to cool to room temperature before being carefully vented over a period of one hour.

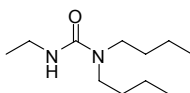
The cell was evacuated and refilled with nitrogen (3 cycles). *N,O*-bistrimethylsilylacetamide (222  $\mu$ L, 0.907 mmol) was added and the mixture stirred for 10 mins. Dibutylamine (231  $\mu$ L, 1.36 mmol) was added, the cell was sealed and heated to 120 °C and the reaction mixture stirred overnight. The reaction vessel was cooled to room temperature and disassembled. The product was removed by washing with  $\text{CH}_2\text{Cl}_2$  (3 x 20 mL) and the washing solution concentrated *in vacuo*. Purification by flash column chromatography (EtOAc : hexane, 3 : 7) gave the title compound **32** (92 mg, 42%) as a white solid: m.p. 81-82 °C (petroleum ether);  $R_f$  0.71 (EtOAc : hexane, 3 : 7); IR (thin film) 3294, 2957, 2928, 2870, 1634, 1596, 1500, 1444, 1317, 1241, 1220, 752  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.96 (t,  $J = 7.5$  Hz, 6H), 1.36 (sext.,  $J = 7.5$  Hz, 4H), 1.60 (m, 4H), 3.29 (m, 4H), 6.31 (br s, 1H), 7.00 (tt,  $J = 7.0, 1.0$  Hz, 1H), 7.27 (m, 2H), 7.38 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 20.2, 30.8, 47.5, 119.7, 122.7, 128.8, 139.3, 154.9; MS (EI)  $m/z$  248 ( $\text{M}^+$ ); HRMS (EI)  $m/z$  248.1878 (248.1889 calcd. for  $\text{C}_{15}\text{H}_{24}\text{N}_2\text{O}$ ).

**1,1-Diisopropyl-3-phenylurea (33).**<sup>14</sup>



Representative procedure E using trimethylsilylaniline (**20**) (150 mg, 0.907 mmol), *N,O*-bistrimethylsilylacetamide (222  $\mu$ L, 0.907 mmol) and diisopropylamine (190  $\mu$ L, 1.36 mmol) gave the title compound **33** (18 mg, 9%) as a white solid: m.p. 114-116 °C (petroleum ether);  $R_f$  0.68 (EtOAc : hexane, 3 : 7); IR (thin film) 3286, 2970, 2930, 1632, 1521, 1445, 1332, 1247, 1147, 1055, 756, 743  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.32 (d,  $J = 7.0$  Hz, 12H), 3.99 (sept.,  $J = 7.0$  Hz, 2H), 6.19 (br s, 1H), 7.00 (tt,  $J = 7.0, 1.0$  Hz, 1H), 7.28 (m, 2H), 7.36 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.5, 45.4, 119.6, 122.6, 128.8, 139.3, 154.2; MS (EI)  $m/z$  220 ( $\text{M}^+$ ); HRMS (EI)  $m/z$  220.1569 (220.1576 calcd. for  $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}$ ).

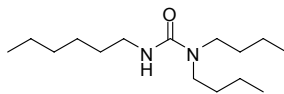
**1,1-Dibutyl-3-ethylurea (36).**<sup>15</sup>



A 10 mL stainless steel cell containing a stirrer bar was sealed and the cell evacuated and refilled with nitrogen (3 cycles). 2-Ethyl-1,1,1,3,3,3-hexamethyldisilazane (**34**) (107 mg, 0.56 mmol) was added and the cell connected to the  $\text{CO}_2$  line and charged with  $\text{CO}_2$  (99.9995% - further purified over an Oxisorb<sup>®</sup> catalyst) to approximately 800 psi. The cell was heated to 120 °C and the pressure adjusted to *ca.* 3000 psi by the addition of further  $\text{CO}_2$ . The mixture was stirred at 100 °C for 52 h. The cell was allowed to cool to room temperature before being carefully vented over a period of one hour.

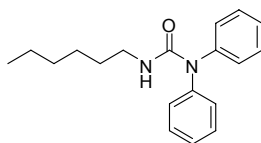
Dibutylamine (143  $\mu$ L, 0.84 mmol) was added to the cell *via* the inlet port and the cell was resealed and heated to 120 °C overnight with stirring. The reaction vessel was cooled to room temperature and the cell charged to *ca.* 1200 psi by the addition of  $\text{CO}_2$ . The cell was vented and the process repeated a further two times. The cell was opened and washed with EtOAc (3  $\times$  10 mL). The combined organic fractions were concentrated *in vacuo* and purified by flash column chromatography (EtOAc; 1%  $\text{NEt}_3$ ) to furnish 1,1-dibutyl-3-ethylurea **36** (39 mg, 34%) as a colourless oil;  $R_f$  0.18 (hexane : EtOAc, 1 : 1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.91 (t,  $J = 7.5$  Hz, 6H), 1.11 (t,  $J = 7.0$  Hz, 3H), 1.29 (quint.,  $J = 7.5$  Hz, 4H), 1.49 (m, 4H), 3.14 (t,  $J = 7.5$  Hz, 4H), 3.24 (ddd,  $J = 14.5, 7.0, 5.5$  Hz, 2H), 4.17 (br s, 1H).

**1,1-Dibutyl-3-hexylurea (28). Representative procedure F.**



To a 10 cm<sup>3</sup> stainless steel vessel was added dibutylamine (84  $\mu$ L, 65 mg, 0.5 mmol). The vessel was sealed and then evacuated and refilled with N<sub>2</sub> (3 cycles). *N,N*-Bis(trimethylsilyl)hexylamine (**37**) (152  $\mu$ L, 123 mg, 0.5 mmol) was then injected through the inlet port. The vessel was filled with liquid CO<sub>2</sub> to approximately one-quarter capacity and heated to 150 °C, at which time the pressure was adjusted to 2000 psi (13.8 MPa). After 17 h, the vessel was allowed to cool to room temperature and the CO<sub>2</sub> vapour was vented into EtOAc (20 cm<sup>3</sup>). The vessel was rinsed with another portion of EtOAc (40 cm<sup>3</sup>) and the combined fractions were then concentrated under reduced pressure. Purification by flash column chromatography (EtOAc : hexane, 1 : 4) gave the title compound **28** (33 mg, 26%) as a pale yellow oil: Spectral data as above.

**3-Hexyl-1,1-diphenylurea (31).**

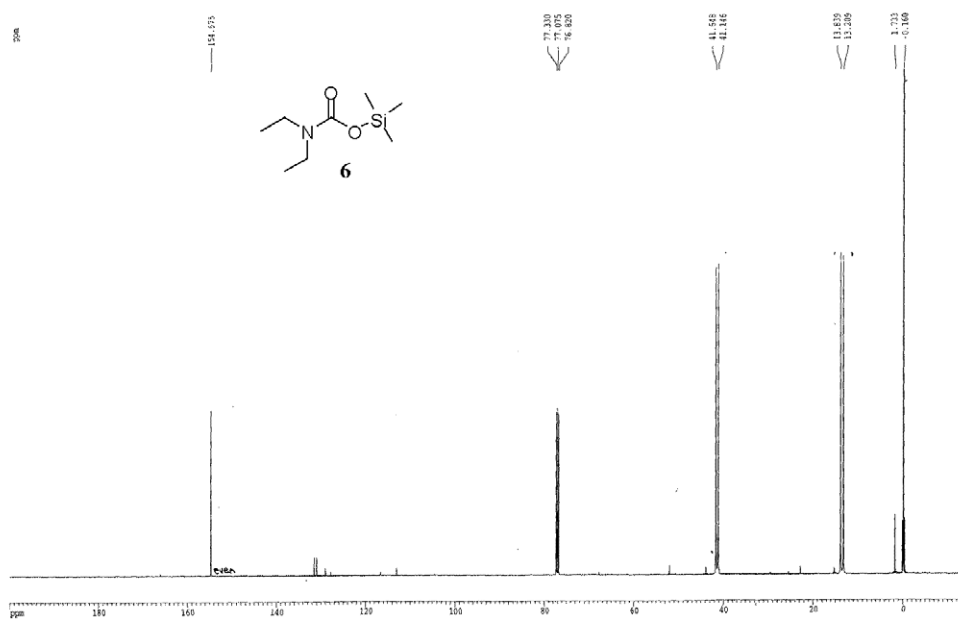
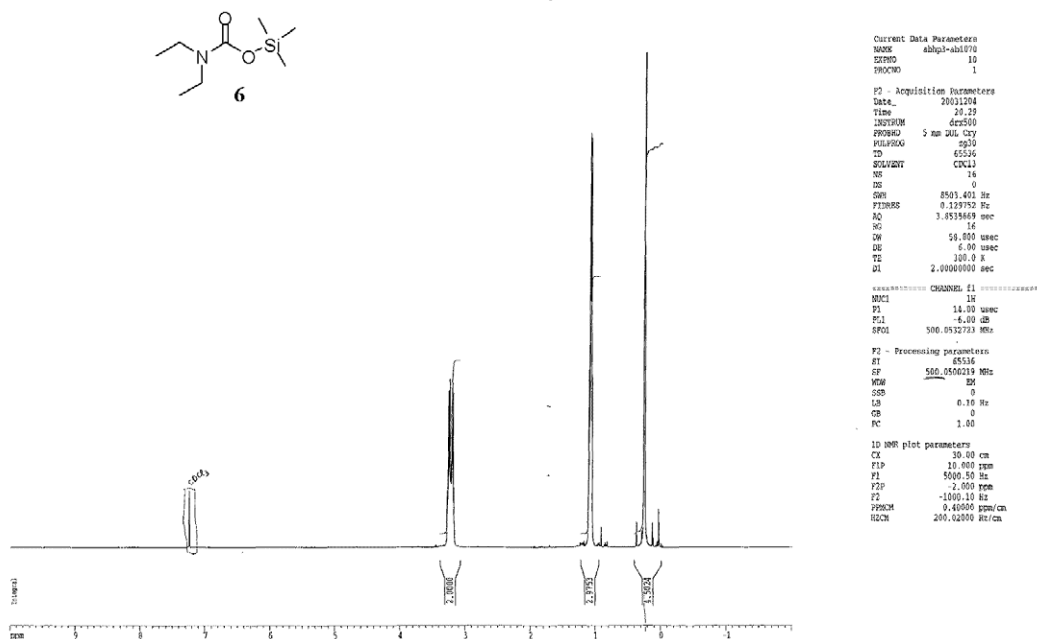


Representative procedure F using diphenylamine (85 mg, 0.5 mmol) and *N,N*-Bis(trimethylsilyl)hexylamine (**27**) (152  $\mu$ L, 123 mg, 0.5 mmol) gave the title compound **31** (59 mg, 40%) as a white crystalline solid: Spectral data as above.

**References**

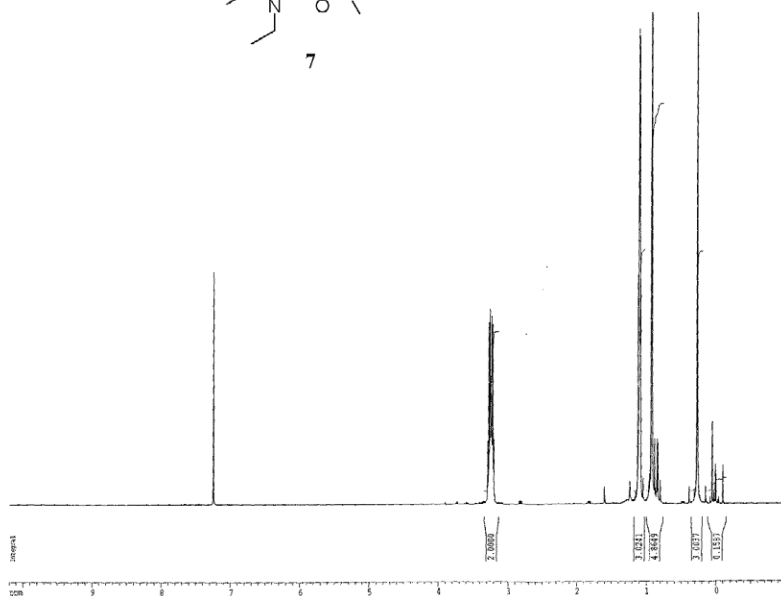
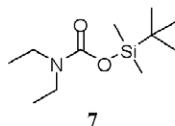
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Avance 500 1H Cryo  
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Current Data Parameters
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F2 - Acquisition Parameters
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PULPROG  zg30
TD        65536
SOLVENT  cpd13
NS        16
DS        4
SFO      500.1401 Hz
FIDRES   0.129752 Hz
AQ        3.852669 sec
RG        16
DM        58.800 usec
DE        6.00 usec
TE        300.0 K
D1        2.0000000 sec

***** CHANNEL f1 *****
NUC1      1H
P1        14.00 usec
PL1       -6.00 dB
SFO1     500.052723 MHz

F2 - Processing parameters
SI        65536
SF        500.050218 MHz
WDW       EM
SSB       0
LB        0.10 Hz
GB        0
PC        1.00

ID NMR plot parameters
CX        30.00 cm
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F1        5100.51 Hz
F2P       -1.000 ppm
P2        -500.05 Hz
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Avance 500 13C Cryo  
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