

Cyanamide Synthesis via the Palladium-Catalyzed Cleavage of Si-N Bond

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Experimental

General Information. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM LA-300 (300 MHz). The ^1H NMR chemical shifts are reported in ppm (δ) downfield from tetramethylsilane as an internal standard; the following abbreviation for multiplicities is used (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, and br=broadened). ^{13}C NMR spectra are reported in ppm (δ) relative to the central line of triplet for CDCl_3 at 77 ppm. IR spectra were recorded on a SHIMADZU FTIR-8200A spectrometer, and absorptions are reported in cm^{-1} . High resolution mass spectra were obtained on a HITACHI M-2500S and JEOL HX110 spectrometer. Column chromatography was carried out employing Silica gel 60 N (spherical, neutral, 40~100 μm and 100~210 μm , KANTO Chemical Co. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F₂₅₄ (Merck).

Materials. Anhydrous THF (KANTO), trimethylsilyl azide (TCI), and $[\eta^3\text{-(C}_3\text{H}_5\text{)PdCl}]_2$ (TCI) were purchased and used as received. Isocyanides are synthesized from the corresponding anilines. All other compounds used were commercially available.

Representative procedure for the preparation of isocyanobenzenes 1

Synthesis of 4-methoxy-1-isocyanobenzene (1a)

To a THF solution (20 ml) of *p*-anisidine (1.3 g, 10 mmol) was added acetic formic anhydride (0.8 ml, 12 mmol) dropwise and the mixture was stirred at room temperature. After the reaction was complete, volatile materials were removed by evaporation. 4-Methoxy-1-formanilide was obtained quantitatively.

A THF solution (20 ml) of 4-methoxy-1-formanilide (10 mmol) and Et_3N (4.2 ml, 30 mmol) was cooled at 0 $^\circ\text{C}$, then phosphorous oxychloride (1.2 ml, 12 mmol) was added dropwise. After the reaction was completed, an aqueous saturated Na_2CO_3 solution was added at 0 $^\circ\text{C}$ to quench the reaction and the product was extracted with ether. The residue was purified by column

chromatography (Florisil, hexane/AcOEt = 100/1~10/1) to give 4-methoxy-1-isocyanobenzene **1a** in 78% yield.

Typical procedure for the palladium-catalyzed synthesis of cyanamides

To a THF solution (0.5 ml) of 4-methoxy-1-isocyanobenzene **1a** (66.6 mg, 0.5 mmol) and $[\eta^3\text{-(C}_3\text{H}_5\text{)PdCl}]_2$ (1.8 mg, 0.005 mmol) was added trimethylsilyl azide (80 μl , 0.6 mmol) under an argon atmosphere. The solution was stirred at room temperature for 10 minutes and then at 60 °C for 6 h. The reaction mixture was cooled to room temperature and filtered through a short Florisil pad and concentrated. The residue was purified by column chromatography (silica gel, hexane-ether 10/1~1/3) to afford (4-methoxyphenyl)cyanamide **3a** in 85% yield (63.0 mg).

Procedure for the synthesis of **4** from (2-(trimethylsilylethynyl)phenyl)cyanamide

A DMF (0.3 ml) solution of (2-(trimethylsilylethynyl)phenyl)cyanamide **3j** (64.3 mg, 0.3 mmol), CuI (5.8 mg, 0.03 mmol) and Et₃N (0.3 ml) was stirred at 80 °C for 3 h under an argon atmosphere. The reaction mixture was cooled to room temperature and filtered through a short Florisil pad and concentrated. The residue was purified by column chromatography (silica gel, hexane-ether 100/1~10/1) to afford *N*-cyano-2-(trimethylsilyl)indole **4** in 76% yield (48.6 mg).

Analytical Data

4-methoxy-1-isocyanobenzene (**1a**)

green solid; ¹H NMR (300 MHz, CDCl₃) δ 3.77 (3H, s), 6.81 (2H, br d, J = 8.5 Hz), 7.26 (2H, br d, J = 8.5 Hz); ¹³C NMR (75.4 MHz, CDCl₃) δ 55.50, 114.49, 119.43, 127.66, 159.81, 162.58 (NC); IR (neat) 2125 (NC), 1606, 1585, 1506, 1255 (C-O), 1029 (C-O), 833 cm⁻¹; HRMS (EI) Calcd for C₈H₇NO (M⁺) 133.0528. Found 133.0528.

4-isopropyl-1-isocyanobenzene (**1b**)

yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 1.24 (6H, d, J = 7.0 Hz), 2.92 (1H, septet, J = 8.5 Hz), 7.23 (2H, br d, J = 8.5 Hz), 7.29 (2H, br d, J = 8.5 Hz); ¹³C NMR (67.8 MHz, CDCl₃) δ 23.74, 34.01, 124.22, 126.19, 127.26, 150.38, 163.09 (NC); IR (neat) 2123 (NC), 1508, 837 cm⁻¹; HRMS (EI) Calcd for C₁₀H₁₁N (M⁺) 145.0891. Found 145.0886.

4-morpholino-1-isocyanobenzene (**1c**)

yellow solid; ¹H NMR (300 MHz, CDCl₃) δ 3.17 (4H, t, J = 5.0 Hz), 3.83 (4H, t, J = 5.0 Hz), 6.80 (2H, br d, J = 9.0 Hz), 7.25 (2H, br d, J = 9.0 Hz); ¹³C NMR (75.4 MHz, CDCl₃) δ 47.89, 66.28, 114.68, 117.46, 127.06, 151.03, 161.96 (NC); IR (KBr) 2121 (NC), 1604, 1512, 1240 (C-O), 1118 (C-O), 827 cm⁻¹; HRMS (EI) Calcd for C₁₁H₁₂N₂O (M⁺) 188.0949. Found 188.0956.

phenylisocyanobenzene (**1d**)

dark green oil; ¹H NMR (300 MHz, CDCl₃) δ 7.38 (5H, m).

4-(methoxycarbonyl)-1-isocyanobenzene (1e)

white solid; ^1H NMR (300 MHz, CDCl_3) δ 3.92 (3H, s), 7.42 (2H, br d, $J = 8.5$ Hz), 8.06 (2H, br d, $J = 8.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 52.27, 126.20, 129.66, 130.57, 130.67, 165.13 (C=O), 167.04 (NC); IR (KBr) 2127 (NC), 1720 (C=O), 1604, 1506, 1282 (C-O), 1105 (C-O), 835 cm^{-1} ; Anal. Calcd for $\text{C}_9\text{H}_7\text{NO}_2$: C, 67.08; H, 4.38; N, 8.69. Found: C, 67.22; H, 4.60; N, 8.58; HRMS (EI) Calcd for $\text{C}_9\text{H}_7\text{NO}_2$ (M^+) 161.0477. Found 161.0477.

4-cyano-1-isocyanobenzene (1f)

white solid; ^1H NMR (300 MHz, CDCl_3) δ 7.52 (2H, br d, $J = 8.0$ Hz), 7.74 (2H, br d, $J = 8.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 113.36, 117.12, 127.21, 129.68, 133.44, 168.86 (NC); IR (KBr) 2233 (CN), 2135 (NC), 1604, 1502, 844 cm^{-1} ; Anal. Calcd for $\text{C}_8\text{H}_4\text{N}_2$: C, 74.99; H, 3.14; N, 21.86. Found: C, 75.27; H, 3.44; N, 21.70; HRMS (EI) Calcd for $\text{C}_8\text{H}_4\text{N}_2$ (M^+) 128.0374. Found 128.0375.

4-chloro-1-isocyanobenzene (1g)

yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 7.30 (2H, br d, $J = 8.5$ Hz), 7.36 (2H, br d, $J = 8.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 125.20, 127.62, 129.73, 135.39, 165.58 (NC); IR (KBr) 2125 (NC), 1585, 1406, 829 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_7\text{H}_4\text{ClN}$ (M^+) 137.0032. Found 137.0032.

4-(trimethylsilylethynyl)-1-isocyanobenzene (1h)

yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 0.23 (9H, s), 7.28 (2H, br d, $J = 8.5$ Hz), 7.45 (2H, br d, $J = 8.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ -0.28, 97.57, 103.01, 124.48, 125.90, 126.22, 132.85, 165.68 (NC); IR (KBr) 2131 (alkyne), 2158 (NC), 1502, 1245 (SiMe_3), 862 (SiMe_3), 758 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{13}\text{NSi}$ (M^+) 199.0817. Found 199.0819.

3-(trimethylsilylethynyl)-1-isocyanobenzene (1i)

yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.18 (9H, s), 7.23-7.29 (2H, m), 7.37-7.43 (2H, m); ^{13}C NMR (75.4 MHz, CDCl_3) δ -0.32, 96.84, 102.36, 124.80, 126.07, 126.52, 129.30, 129.46, 132.59, 164.99 (NC); IR (neat) 2152 (alkyne), 2123 (NC), 1600, 1575, 1477, 1249 (SiMe_3), 844 (SiMe_3), 792, 680 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{13}\text{N}_1\text{Si}$ (M^+) 199.0817. Found 199.0820.

2-(trimethylsilylethynyl)-1-isocyanobenzene (1j)

dark greenish yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.29 (9H, s), 7.35 (3H, m), 7.52 (1H, m); ^{13}C NMR (75.4 MHz, CDCl_3) δ -0.25, 99.42, 102.92, 121.61, 126.45, 128.84, 128.98, 132.52, 167.56 (NC); IR (neat) 2165 (alkyne), 2121 (NC), 1481, 1251 (SiMe_3), 844 (SiMe_3), 759 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{13}\text{NSi}$ (M^+) 199.0817. Found 199.0816.

2,6-dimethyl-1-isocyanobenzene (1k)

white solid; ^1H NMR (300 MHz, CDCl_3) δ 2.33 (6H, s), 7.03 (2H, br d, $J = 7.5$ Hz), 7.11 (1H, m); ^{13}C NMR (75.4 MHz, CDCl_3) δ 18.36, 126.07, 127.27, 128.17, 134.21, 167.61 (NC); IR (KBr) 2121 (NC), 1471, 779, 723 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_9\text{H}_9\text{N}$ (M^+) 131.0735. Found 131.0734.

2,4-dichloro-1-isocyanobenzene (1l)

dark green solid; ^1H NMR (300 MHz, CDCl_3) δ 7.27 (1H, dd, $J = 8.5, 2.0$ Hz), 7.37 (1H, d, $J = 8.5$ Hz), 7.49 (1H, d, $J = 2.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 124.00, 128.53, 130.02, 131.70, 135.74, 170.47 (NC); IR (KBr) 2127 (NC), 1583, 1475, 817 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_7\text{H}_3\text{Cl}_2\text{N}$ (M^+) 170.9642. Found 170.9638.

2,4-dimethoxy-1-isocyanobenzene (1m)

yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 3.80 (3H, s), 3.88 (3H, s), 6.40 (1H, dd, $J = 8.5, 2.5$ Hz), 6.45 (1H, d, $J = 2.5$ Hz), 7.24 (1H, d, $J = 4.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 55.57, 55.91, 98.93, 104.46, 128.23, 156.00, 151.07, 165.82; IR (KBr) 2127 (NC), 1602, 1506, 1213 (C-O), 1026 (C-O), 804 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_9\text{H}_9\text{N}_1\text{O}_2$ (M^+) 163.0633. Found 163.0634.

3,4,5-trimethoxy-1-isocyanobenzene (1n)

white solid; ^1H NMR (300 MHz, CDCl_3) δ 3.83 (3H, s), 3.84 (6H, s), 6.58 (2H, s); ^{13}C NMR (75.4 MHz, CDCl_3) δ 56.23, 60.90, 103.95, 121.81, 139.06, 153.34, 163.05 (NC); IR (KBr) 2133 (NC), 1593, 1506, 1238 (C-O), 1128 (C-O), 840, 746 cm^{-1} ; Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_3$: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.26; H, 5.87; N, 7.22; HRMS (EI) Calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_3$ (M^+) 193.0739. Found 193.0739.

(4-methoxyphenyl)cyanamide (3a)

orange solid; ^1H NMR (300 MHz, CDCl_3) δ 3.79 (3H, s), 5.89 (1H, br s), 6.88 (2H, br d, $J = 9.0$ Hz), 6.96 (2H, br d, $J = 9.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 55.61, 111.98, 115.01, 116.84, 130.27, 156.07; IR (neat) 3182 (NH), 2223 (CN), 1596, 1508, 1240 (C-O), 1039 (C-O), 804 cm^{-1} ; Anal. Calcd for $\text{C}_8\text{H}_8\text{N}_2\text{O}$: C, 64.85; H, 5.44; N, 18.90. Found: C, 65.05; H, 5.68; N, 18.73; HRMS (EI) Calcd for $\text{C}_8\text{H}_8\text{N}_2\text{O}$ (M^+) 148.0636. Found 148.0641.

(4-isopropylphenyl)cyanamide (3b)

yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.20 (6H, d, $J = 7.0$ Hz), 2.86 (1H, septet, $J = 7.0$ Hz), 6.04 (1H, br s), 6.94 (2H, br d, $J = 8.5$ Hz), 7.17 (2H, br d, $J = 8.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 23.96, 33.36, 111.96, 115.40, 127.57, 134.85, 144.27; IR (neat) 3199 (NH), 3165 (NH), 2227 (CN), 1614, 1514, 825 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2$ (M^+) 160.1000. Found 160.1000.

(4-morpholinophenyl)cyanamide (3c)

white solid; ^1H NMR (300 MHz, CDCl_3) δ 3.08 (4H, t, $J = 5.0$ Hz), 3.85 (4H, t, $J = 5.0$ Hz), 5.74 (1H, br s), 6.88 (2H, br d, $J = 9.0$ Hz), 6.93 (2H, br d, $J = 9.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ

49.92, 66.80, 112.20, 116.54, 117.34, 130.14, 147.76; IR (KBr) 3247 (NH), 3238 (NH), 2219 (CN), 1521, 1240 (C-O), 1122 (C-O), 817 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}$ (M^+) 203.1058. Found 203.1064.

phenylcyanamide (3d)

brown oil; ^1H NMR (300 MHz, CDCl_3) δ 5.78 (1H, br s), 7.00 (2H, br d, $J = 8.5$ Hz), 7.09 (1H, br t, $J = 7.5$ Hz), 7.33 (2H, br t, $J = 7.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 111.51, 115.34, 123.55, 129.68, 137.18; IR (neat) 3174 (NH), 2229 (CN), 1600, 1502, 1434, 1249, 748 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_7\text{H}_6\text{N}_2$ (M^+) 118.0531. Found 118.0529.

(4-(methoxycarbonyl)phenyl)cyanamide (3e)

yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 3.89 (3H, s), 6.53 (1H, br s), 7.04 (2H, br d, $J = 8.5$ Hz), 8.02 (2H, br d, $J = 8.5$ Hz); ^{13}C NMR (67.8 MHz, CDCl_3) δ 52.13, 109.59, 114.79, 125.49, 131.47, 141.20, 166.07 (C=O); IR (KBr) 3220 (NH), 3174 (NH), 2235 (CN), 1728 (C=O), 1689, 1604, 1290 (C-O), 1114 (C-O), 846 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_9\text{H}_8\text{N}_2\text{O}_2$ (M^+) 176.0586. Found 176.0588.

(4-cyanophenyl)cyanamide (3f)

yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 6.64 (1H, br s), 7.09 (2H, br d, $J = 8.5$ Hz), 7.64 (2H, br d, $J = 8.5$ Hz); ^{13}C NMR (67.8 MHz, CDCl_3) δ 107.32, 108.88, 115.81, 118.14, 134.07, 141.29; IR (KBr) 3197 (NH), 3170 (NH), 2227 (CN), 1610, 1515, 829 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_8\text{H}_5\text{N}_3$ (M^+) 143.0483. Found 143.0483.

(4-chlorophenyl)cyanamide (3g)

yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 5.89 (1H, br s), 6.94 (2H, br d, $J = 8.5$ Hz), 7.30 (2H, br d, $J = 8.5$ Hz); ^{13}C NMR (67.8 MHz, CDCl_3) δ 110.98, 116.66, 128.88, 129.74, 135.82; IR (KBr) 3155 (NH), 2237 (CN), 1602, 1498, 815 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_7\text{H}_5\text{N}_2\text{Cl}$ (M^+) 152.0141. Found 152.0142.

(4-(trimethylsilylethynyl)phenyl)cyanamide (3h)

yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 0.22 (9H, s), 5.95 (1H, br s), 6.92 (2H, br d, $J = 8.5$ Hz), 7.43 (2H, br d, $J = 8.5$ Hz); ^{13}C NMR (67.8 MHz, CDCl_3) δ -0.08, 94.09, 104.14, 110.72, 115.16, 118.49, 133.49, 137.20; IR (KBr) 3130 (NH), 2248 (CN), 2154 (alkyne), 1606, 1515, 1253 (SiMe_3), 866 (SiMe_3), 840 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Si}$ (M^+) 214.0926. Found 214.0925.

(3-(trimethylsilylethynyl)phenyl)cyanamide (3i)

yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 0.23 (9H, s), 5.83 (1H, br s), 6.49 (1H, ddd, $J = 8.0, 3.5, 1.0$ Hz), 7.09 (1H, br s), 7.17 (1H, br d, $J = 8.0$ Hz), 7.27 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (67.8 MHz, CDCl_3) δ -0.16, 95.69, 103.71, 110.74, 115.48, 118.49, 124.75, 127.34, 129.63, 137.13; IR

(KBr) 3203 (NH), 3193 (NH), 2229 (CN), 2165 (alkyne), 1612, 1585, 1515, 1245 (SiMe₃), 860 (SiMe₃), 844, 763 cm⁻¹; HRMS (EI) Calcd for C₁₂H₁₄N₂Si (M⁺) 214.0926. Found 214.0927.

(2-(trimethylsilylethynyl)phenyl)cyanamide (3j)

orange oil; ¹H NMR (300 MHz, CDCl₃) δ 0.27 (9H, s), 6.39 (1H, br s), 7.01 (1H, br t, *J* = 7.5 Hz), 7.22 (1H, br d, *J* = 8.0 Hz), 7.33 (1H, br d, *J* = 8.0 Hz), 7.39 (1H, br d, *J* = 7.5 Hz); ¹³C NMR (67.8 MHz, CDCl₃) δ -0.17, 98.40, 103.15, 109.88, 110.05, 113.95, 122.98, 130.22, 132.31, 138.41; IR (neat) 3255 (NH), 2241 (CN), 2158 (alkyne), 1577, 1500, 1249 (SiMe₃), 867 (SiMe₃), 752 cm⁻¹; HRMS (EI) Calcd for C₁₂H₁₄N₂Si (M⁺) 214.0926. Found 214.0929.

(2,6-dimethylphenyl)cyanamide (3k)

white solid; ¹H NMR (300 MHz, CDCl₃) δ 2.36 (6H, s), 6.15 (1H, br s), 7.04 (3H, s); ¹³C NMR (75.4 MHz, CDCl₃) δ 18.11, 113.39, 126.38, 128.94, 131.86, 133.29; IR (KBr) 3172 (NH), 2227 (CN), 1600, 1473, 771, 692 cm⁻¹; HRMS (EI) Calcd for C₉H₁₀N₂ (M⁺) 146.0844. Found 146.0844.

(2,4-dichlorophenyl)cyanamide (3l)

yellow solid; ¹H NMR (300 MHz, CDCl₃) δ 6.22 (1H, br s), 7.23 (1H, d, *J* = 8.5 Hz), 7.29 (1H, dd, *J* = 8.5, 2.0 Hz), 7.38 (1H, d, *J* = 2.0 Hz); ¹³C NMR (67.8 MHz, CDCl₃) δ 109.14, 116.78, 120.69, 128.52, 129.05, 129.41, 132.80; IR (KBr) 3195 (NH), 2237 (CN), 1596, 1488, 810 cm⁻¹; HRMS (EI) Calcd for C₇H₄Cl₂N₂ (M⁺) 185.9751. Found 185.39751.

(2,4-dimethoxyphenyl)cyanamide (3m)

white solid; ¹H NMR (300 MHz, CDCl₃) δ 2.75 (3H, s), 3.81 (3H, s), 6.16 (1H, br s), 6.45 (2H, m), 7.03 (1H, d, *J* = 9.0 Hz); ¹³C NMR (75.4 MHz, CDCl₃) δ 55.61, 55.74, 99.38, 104.19, 111.51, 115.14, 120.07, 147.66, 156.33; IR (KBr) 3311 (NH), 3255 (NH), 2225 (CN), 1624, 1517, 1213 (C-O), 1026 (C-O), 779 cm⁻¹; Anal. Calcd for C₉H₁₀N₂O₂: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.52; H, 6.02; N, 15.58; HRMS (EI) Calcd for C₉H₁₀N₂O₂ (M⁺) 178.0742. Found 178.0745.

(3,4,5-trimethoxyphenyl)cyanamide (3n)

white solid; ¹H NMR (300 MHz, CDCl₃) δ 3.78 (3H, s), 3.83 (6H, s), 6.05 (1H, br s), 6.20 (2H, s); ¹³C NMR (75.4 MHz, CDCl₃) δ 56.13, 61.06, 92.98, 111.59, 133.48, 133.94, 153.98; IR (KBr) 3242 (NH), 2221 (CN), 1604, 1508, 1234 (C-O), 1130 (C-O), 810 cm⁻¹; HRMS (EI) Calcd for C₁₀H₁₂N₂O₃ (M⁺) 208.0848. Found 208.0851.

cyclohexylcyanamide (3o)

orange oil; ¹H NMR (300 MHz, CDCl₃) δ 1.15-1.39 (5H, m), 1.57-1.66 (1H, m), 1.77 (2H, m), 1.96 (2H, m), 3.11 (1H, m), 3.43 (1H, br s); ¹³C NMR (75.4 MHz, CDCl₃) δ 24.13, 24.99, 32.54, 54.36, 115.39; IR (neat) 3195 (NH), 2218 (CN), 1452, 1367, 1166 cm⁻¹; HRMS (EI) Calcd for C₇H₁₂N₂ (M⁺) 124.1000. Found 124.1003.

butylcyanamide (3p)

orange oil; ^1H NMR (300 MHz, CDCl_3) δ 0.92 (3H, t, $J = 7.5$ Hz), 1.36 (2H, sextet, $J = 7.5$ Hz), 1.57 (2H, quintet, $J = 7.5$ Hz), 3.06 (2H, q, $J = 7.5$ Hz), 3.60 (1H, br s); ^{13}C NMR (75.4 MHz, CDCl_3) δ 13.48, 19.36, 31.61, 45.83, 116.54; IR (neat) 3172 (NH), 2227 (CN), 1600, 1473, 771, 692 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_5\text{H}_{10}\text{N}_2$ (M^+) 98.0844. Found 98.0844.

***N*-cyano-2-(trimethylsilyl)indole (4)**

slightly yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 0.47 (9H, s), 6.77 (1H, s), 7.27 (1H, br t, $J = 7.5$ Hz), 7.37 (1H, br t, $J = 7.5$ Hz), 7.58 (1H, d, $J = 7.5$ Hz), 7.50 (1H, dd, $J = 8.0, 1.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ -1.65, 108.84, 111.17, 118.32, 121.48, 123.78, 125.27, 128.42, 140.03, 141.68; IR (KBr) 2231, 1587, 1504, 1255 (SiMe_3), 850 (SiMe_3), 767, 738 (SiMe_3) cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Si}$: C, 67.24; H, 6.58; N, 13.06. Found: C, 67.23; H, 6.44; N, 12.92; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Si}$ (M^+) 214.0926. Found 214.0929.





























