Supporting Information

Synthesis of Allyl Cyanamides and *N*-Cyanoindoles via the Palladium-Catalyzed Three Component Coupling Reaction

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Experimental

General Information. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL JNM LA-300 (300 MHz) and JEOL JNM -500 (500 MHz) spectrometers. IR spectra were recorded on a SHIMADZU FTIR-8200A spectrometer. 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 toluene (WAKO), anhydrous octane (Aldrich), anhydrous THF (KANTO), dppe (1,2-bis(diphenylphosphino)ethane) (WAKO), tri(2-furyl)phosphine (TCI) and trimethylsilyl azide (TCI) was purchased and used as received. Pd₂(dba)₃·CHCl₃ was prepared according to the literature procedure.¹ Allyl methyl carbonate was prepared and distilled to use. Isocyanides are synthesized from the corresponding anilines.^{2,3} All other compounds used were commercially available.

Analytical data

Characteristic data and ¹H NMR spectra of compounds **2a-j**, **2l-m**, **2o**, **2q-s** are reported in the supporting information of ref 5 in the text.

***N*-allyl-*N*-(2-bromophenyl)cyanamide (2k).** yellow oil; ¹H NMR (300 MHz, CDCl₃) 4.07 (2H, br d, *J* = 6.5 Hz), 5.37 (1H, br d, *J* = 10.0 Hz), 5.38 (1H, br d, *J* = 17.0 Hz), 6.00 (1H, ddt, *J* = 17.0, 10.0, 6.5 Hz), 7.20 (1H, m), 7.36 (1H, td, *J* = 8.0, 1.5 Hz), 7.40 (1H, dd, *J* = 7.5, 2.0 Hz), 7.64 (1H, dd, *J* = 8.0, 1.5 Hz). ¹³C NMR (75.4 MHz, CDCl₃)

56.75, 114.54, 120.34, 121.51, 127.28, 128.61, 129.28, 130.15, 134.13, 138.76; IR (neat) 2218, 1645, 1585, 1475, 756 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{10}\text{H}_9\text{BrN}_2$ (M^+) 235.9948. Found 235.9953.

1-(*N*-allyl-*N*-cyano)-2-(trimethylsilylethynyl)aniline (2n). orange oil; ^1H NMR (500 MHz, CDCl_3) 0.27 (9H, s), 4.22 (2H, ddd, $J = 6.5, 1.0, 1.0$ Hz), 5.33 (1H, ddt, $J = 10.0, 1.0, 1.0$ Hz), 5.39 (1H, ddt, $J = 17.0, 1.0, 1.0$ Hz), 5.97 (1H, ddt, $J = 17.0, 10.0, 6.5$ Hz), 7.18 (1H, ddd, $J = 8.5, 6.5, 2.0$ Hz), 7.30 (1H, d, $J = 6.5, 1.5$ Hz), 7.32 (1H, td, $J = 8.5, 1.5$ Hz), 7.49 (1H, dd, $J = 8.5, 2.0$ Hz); ^{13}C NMR (125.6 MHz, CDCl_3) -0.27, 56.15, 100.34, 102.34, 114.53, 118.35, 120.84, 123.74, 126.53, 129.67, 130.78, 134.38, 141.91; IR (neat) 2218, 2160, 1628, 1595, 1487, 1249, 844, 987, 937, 759 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{Si}$: C, 70.57; H, 7.10; N, 10.97. Found: C, 70.39; H, 7.35; N, 10.92; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{Si}$ (M^+) 254.1239. Found 254.1243.

***N*-allyl-*N*-(naphthyl)cyanamide (2p).** yellow oil; ^1H NMR (300 MHz, CDCl_3) 4.13 (2H, br d, $J = 6.5$ Hz), 5.36 (1H, br d, $J = 10.0$ Hz), 5.38 (1H, br d, $J = 17.0$ Hz), 6.04 (1H, ddt, $J = 17.0, 10.0, 6.5$ Hz), 7.40-7.63 (4H, m), 7.80 (1H, d, $J = 8.0$ Hz), 7.87 (1H, d, $J = 8.0$ Hz), 8.12 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) 57.36, 116.00, 121.18, 122.00, 122.45, 125.30, 126.73, 127.15, 128.37, 128.60, 128.70, 130.48, 134.60, 136.76; IR (neat) 2214, 1596, 1510, 1396, 991, 937, 802, 773 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2$ (M^+) 208.1000. Found 208.1000.

4,4'-(*N*-allylcyanamidophenyl)ethane (2t). white solid; ^1H NMR (300 MHz, CDCl_3) 2.84 (4H, s), 4.17 (4H, ddd, $J = 5.5, 1.0, 1.0$ Hz), 5.37 (2H, br d, $J = 10.0$ Hz), 5.38 (1H, br d, $J = 17.0$ Hz), 5.93 (2H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.00 (2H, br d, $J = 8.5$ Hz), 7.09 (2H, br d, $J = 8.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) 36.80, 52.16, 113.66, 115.85, 119.96, 129.53, 130.11, 136.69, 137.74; IR (KBr) 2214, 1612, 1583, 1514, 991, 941, 821 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{22}\text{H}_{22}\text{N}_4$ (M^+) 342.1844. Found 342.1838.

3-allyl-5-methyl-2-(trimethylsilyl)-*N*-cyanoindole (4a). yellow oil; ^1H NMR (300 MHz, CDCl_3) 0.47 (9H, s), 4.25 (3H, s), 3.50 (2H, ddd, $J = 5.5, 2.0, 2.0$ Hz), 4.97 (1H, ddt, $J = 17.0, 2.0, 2.0$ Hz), 5.05 (1H, ddt, $J = 11.5, 2.0, 2.0$ Hz), 5.94 (1H, ddt, $J = 17.0, 11.5, 5.5$ Hz), 7.18 (1H, br dd, $J = 8.5, 1.0$ Hz), 7.29 (1H, br d, $J = 1.0$ Hz), 7.23 (1H, d, $J = 8.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) -0.17, 21.40, 29.23, 109.44, 110.77, 115.96, 119.84, 126.85, 129.21, 129.53, 133.20, 135.98, 138.16; IR (neat) 2358, 2341, 2237, 1631, 1531, 1463, 1253, 844, 798, 761 cm^{-1} ; Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{Si}$: C, 71.59; H, 7.50; N, 10.43. Found: C, 71.82; H, 7.58; N, 10.32; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{Si}$ (M^+) 268.1395. Found 268.1398.

3-allyl-5-isopropyl-2-(trimethylsilyl)-*N*-cyanoindole (4b). orange oil; ^1H NMR (300

MHz, CDCl₃) 0.47 (9H, s), 1.27 (6H, d, $J = 7.0$ Hz), 3.00 (1H, septet, $J = 7.0$ Hz), 3.57 (2H, ddd, $J = 5.5, 2.0, 2.0$ Hz), 5.50 (1H, ddt, $J = 17.0, 2.0, 2.0$ Hz), 5.05 (1H, ddt, $J = 10.0, 2.0, 2.0$ Hz), 5.94 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.27 (1H, dd, $J = 8.5, 1.5$ Hz), 7.34 (1H, d, $J = 1.5$ Hz), 7.47 (1H, d, $J = 8.5$ Hz); ¹³C NMR (75.4 MHz, CDCl₃) -0.17, 24.45, 29.28, 34.18, 109.46, 110.94, 115.97, 117.21, 124.45, 129.43, 129.46, 136.01, 138.37, 144.63; IR (neat) 2239, 2235, 1639, 1531, 1458, 1350, 1328, 1253, 993, 914, 844, 810 cm⁻¹; HRMS (EI) Calcd for C₁₈H₂₄N₂Si (M⁺) 296.1708. Found 296.1714.

3-allyl-5-methoxy-2-(trimethylsilyl)-*N*-cyanoindole (4c). yellow solid; ¹H NMR (300 MHz, CDCl₃) 0.47 (9H, s), 3.49 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 3.83 (3H, s), 4.98 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.06 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.94 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 6.94 (1H, d, $J = 2.5$ Hz), 6.98 (1H, dd, $J = 8.5, 2.5$ Hz), 7.43 (1H, d, $J = 8.5$ Hz); ¹³C NMR (75.4 MHz, CDCl₃) -0.19, 29.31, 55.83, 102.58, 109.45, 111.78, 114.42, 116.04, 129.17, 130.20, 134.46, 135.76, 136.91, 156.77; IR (KBr) 2289, 1637, 1612, 1525, 1458, 1250, 1238, 991, 904, 840, 794, 763 cm⁻¹; Anal. Calcd for C₁₆H₂₀N₂OSi: C, 67.56; H, 7.08; N, 9.84. Found: C, 67.35; H, 7.20; N, 9.68; HRMS (EI) Calcd for C₁₆H₂₀N₂OSi (M⁺) 284.1344. Found 284.1346.

3-allyl-5-(methylthio)-2-(trimethylsilyl)-*N*-cyanoindole (4d). yellow viscous oil; ¹H NMR (300 MHz, CDCl₃) 0.47 (9H, s), 2.50 (3H, s), 3.50 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 4.97 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.06 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.93 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.34 (1H, dd, $J = 8.5, 2.0$ Hz), 7.44 (1H, d, $J = 2.0$ Hz), 7.46 (1H, d, $J = 8.5$ Hz); ¹³C NMR (75.4 MHz, CDCl₃) -0.22, 17.60, 29.20, 109.0, 111.55, 116.20, 119.18, 125.84, 128.87, 130.08, 133.29, 135.69, 136.93, 138.24; IR (neat) 2237, 1637, 1600, 1527, 1450, 1328, 1253, 993, 914, 846, 800, 763 cm⁻¹; HRMS (EI) Calcd for C₁₆H₂₀N₂SSi (M⁺) 300.1116. Found 300.1112.

3-allyl-5-(phenylazo)-2-(trimethylsilyl)-*N*-cyanoindole (4e). orange solid; ¹H NMR (300 MHz, CDCl₃) 0.52 (9H, s), 3.61 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 5.03 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.10 (1H, ddt, $J = 10.5, 1.5, 1.5$ Hz), 6.00 (1H, ddt, $J = 17.0, 10.5, 5.5$ Hz), 7.45-7.55 (3H, m), 7.64 (1H, d, $J = 8.5$ Hz), 7.92 (2H, m), 8.03 (1H, dd, $J = 8.5, 2.0$ Hz), 8.13 (1H, d, $J = 2.0$ Hz); ¹³C NMR (75.4 MHz, CDCl₃) -0.23, 29.24, 108.75, 111.61, 116.36, 116.87, 119.32, 122.76, 129.06, 129.93, 130.40, 130.86, 135.67, 137.81, 141.30, 149.55, 152.53; IR (KBr) 2237, 1639, 1471, 1253, 916, 844, 765 cm⁻¹; HRMS (EI) Calcd for C₂₁H₂₂N₄Si (M⁺) 358.1613. Found 358.1619.

3-allyl-5-fluoro-2-(trimethylsilyl)-*N*-cyanoindole (4f). yellow oil; ¹H NMR (300 MHz, CDCl₃) 0.48 (9H, s), 3.48 (2H, ddd, $J = 5.5, 2.0, 2.0$ Hz), 4.97 (1H, ddt, $J = 17.0, 2.0,$

2.0 Hz), 5.08 (1H, ddt, $J = 10.0, 2.0, 2.0$ Hz), 5.91 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.09 (1H, td, $J = 8.5, 2.5$ Hz), 7.16 (1H, dd, $J = 8.5, 2.5$ Hz), 7.48 (1H, dd, $J = 8.5, 4.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) -0.26, 29.29, 105.79 (d, $^2J(\text{C}, \text{F}) = 24$ Hz), 108.02, 112.03 (d, $^3J(\text{C}, \text{F}) = 10$ Hz), 113.51 (d, $^2J(\text{C}, \text{F}) = 26$ Hz), 116.33, 129.12 (d, $^4J(\text{C}, \text{F}) = 4$ Hz), 130.37 (d, $^3J(\text{C}, \text{F}) = 10$ Hz), 135.44, 136.10, 138.21, 159.84 (d, $^1J(\text{C}, \text{F}) = 240$ Hz); IR (neat) 2239, 1639, 1595, 1461, 1253, 993, 918, 846, 802, 765 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{17}\text{FN}_2\text{Si}$ (M^+) 272.1144. Found 272.1139.

3-allyl-5-chloro-2-(trimethylsilyl)-*N*-cyanoindole (4g). brown oil; ^1H NMR (300 MHz, CDCl_3) 0.47 (9H, s), 3.47 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 4.96 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.07 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.91 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.32 (1H, dd, $J = 8.5, 2.0$ Hz), 7.46 (1H, d, $J = 8.5$ Hz), 7.48 (1H, d, $J = 2.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) -0.27, 29.15, 108.73, 112.15, 116.41, 119.83, 125.65, 128.73, 129.41, 130.62, 135.43, 137.88, 138.27; IR (neat) 2239, 1639, 1527, 1450, 1253, 993, 916, 846, 800, 763 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{ClN}_2\text{Si}$: C, 62.37; H, 5.93; N, 9.69; Cl, 12.27. Found: C, 62.21; H, 5.97; N, 9.52; Cl, 12.53; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{17}\text{ClN}_2\text{Si}$ (M^+) 288.0849. Found 288.0849.

2-allyl-5-bromo-2-(trimethylsilyl)-*N*-cyanoindole (4h). dark yellow oil; ^1H NMR (300 MHz, CDCl_3) 0.48 (9H, s), 3.48 (2H, ddd, $J = 5.5, 2.0, 2.0$ Hz), 4.96 (1H, ddt, $J = 17.0, 2.0, 2.0$ Hz), 5.08 (1H, ddt, $J = 10.0, 2.0, 2.0$ Hz), 5.92 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.42 (1H, d, $J = 8.5$ Hz), 7.47 (1H, dd, $J = 8.5, 1.5$ Hz), 7.64 (1H, d, $J = 1.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) -0.28, 29.11, 108.65, 112.53, 116.42, 116.92, 122.88, 128.27, 128.63, 131.13, 135.41, 137.74, 138.65; IR (neat) 2289, 1640, 1527, 1448, 1253, 993, 916, 844, 798, 665 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{17}\text{BrN}_2\text{Si}$ (M^+) 332.0344. Found 332.0346.

3-allyl-5-(trifluoromethyl)-2-(trimethylsilyl)-*N*-cyanoindole (4i). orange oil; ^1H NMR (300 MHz, CDCl_3) 0.50 (9H, s), 3.55 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 4.96 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.08 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.94 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.63 (2H, m), 7.79 (1H, m); ^{13}C NMR (75.4 MHz, CDCl_3) -0.30, 29.06, 108.38, 111.61, 116.52, 117.72 (q, $^3J(\text{C}, \text{F}) = 4.0$ Hz), 122.31 (q, $^3J(\text{C}, \text{F}) = 3.4$ Hz), 124.41 (q, $^1J(\text{C}, \text{F}) = 272$ Hz), 126.29 (q, $^2J(\text{C}, \text{F}) = 32$ Hz), 129.24, 129.47, 135.37, 138.43, 141.55; IR (neat) 2243, 1639, 1616, 1535, 1450, 1323, 1255, 993, 918, 856, 815, 763 cm^{-1} ; Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{N}_2\text{Si}$: C, 59.60; H, 5.31; N, 8.68. Found: C, 59.53; H, 5.33; N, 8.38; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{N}_2\text{Si}$ (M^+) 322.1112. Found 322.1111.

3-allyl-5-(methoxycarbonyl)-2-(trimethylsilyl)-*N*-cyanoindole (4j). yellow solid; ^1H

NMR (300 MHz, CDCl₃) 0.49 (9H, s), 3.56 (2H, br d, $J = 5.5$ Hz), 3.97 (3H, s), 4.96 (1H, br d, $J = 17.0$ Hz), 5.06 (1H, br d, $J = 10.5$ Hz), 5.96 (1H, ddt, $J = 17.0, 10.5, 5.5$ Hz), 7.57 (1H, d, $J = 8.5$ Hz), 8.08 (1H, dd, $J = 8.5, 1.0$ Hz), 8.24 (1H, br s); ¹³C NMR (75.4 MHz, CDCl₃) -0.32, 28.98, 52.20, 108.51, 110.96, 116.30, 122.41, 125.84, 126.70, 129.23, 129.88, 135.56, 137.71, 142.52, 166.92; IR (KBr) 2239, 1714, 1641, 1608, 1593, 1438, 1311, 1251, 970, 927, 844, 759 cm⁻¹; Anal. Calcd for C₁₇H₂₀N₂O₂Si: C, 65.35; H, 6.45; N, 8.96. Found: C, 65.56; H, 6.41; N, 8.84; HRMS (EI) Calcd for C₁₇H₂₀N₂O₂Si (M⁺) 312.1294. Found 312.1297.

3-allyl-5-nitro-2-(trimethylsilyl)-N-cyanoindole (4k). white solid; ¹H NMR (300 MHz, CDCl₃) 0.51 (9H, s), 3.57 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 4.97 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.11 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.94 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.64 (1H, d, $J = 8.5$ Hz), 8.28 (1H, dd, $J = 8.5, 2.0$ Hz), 8.44 (1H, d, $J = 2.0$ Hz); ¹³C NMR (75.4 MHz, CDCl₃) -0.38, 29.01, 107.84, 111.55, 116.66, 116.84, 120.75, 129.51, 130.01, 135.09, 140.23, 142.94, 144.73; IR (KBr) 2245, 1639, 1587, 1519, 1454, 1340, 1247, 997, 903, 846, 798, 763 cm⁻¹; Anal. Calcd for C₁₅H₁₇N₃O₂Si: C, 60.17; H, 5.72; N, 14.03. Found: C, 60.21; H, 5.56; N, 13.77; HRMS (EI) Calcd for C₁₅H₁₇N₃O₂Si (M⁺) 299.1090. Found 299.1098.

3-allyl-5-cyano-2-trimethylsilyl-N-cyanoindole (4l). white solid; ¹H NMR (300 MHz, CDCl₃) 0.50 (9H, s), 3.53 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 4.97 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.10 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.91 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.63 (2H, br s), 7.86 (1H, br s); ¹³C NMR (75.4 MHz, CDCl₃) -0.37, 29.05, 107.33, 107.89, 112.16, 116.77, 119.09, 125.27, 128.38, 129.00, 129.54, 135.07, 139.06, 141.76; IR (KBr) 2241, 2223, 1641, 1606, 1463, 1249, 997, 908, 848, 761 cm⁻¹; HRMS (EI) Calcd for C₁₆H₁₇N₃Si (M⁺) 279.1191. Found 279.1191.

3-allyl-5-acetyl-2-trimethylsilyl-N-cyanoindole (4m). white solid; ¹H NMR (300 MHz, CDCl₃) 0.49 (9H, s), 2.64 (3H, s), 3.57 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 4.96 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.07 (1H, ddt, $J = 10.5, 1.5, 1.5$ Hz), 5.96 (1H, ddt, $J = 17.0, 10.5, 5.5$ Hz), 7.59 (1H, d, $J = 8.5$ Hz), 8.01 (1H, dd, $J = 8.5, 1.5$ Hz), 8.16 (1H, d, $J = 1.5$ Hz); ¹³C NMR (75.4 MHz, CDCl₃) -0.29, 26.81, 29.04, 108.49, 111.12, 116.37, 121.12, 125.80, 129.39, 130.08, 133.29, 135.60, 138.01, 142.58, 197.34; IR (KBr) 2241, 1678, 1639, 1606, 1460, 1249, 995, 910, 850, 810, 759 cm⁻¹; HRMS (EI) Calcd for C₁₇H₂₀N₂O₂Si (M⁺) 296.1337. Found 296.1348.

3-allyl-2-(trimethylsilyl)-N-cyanoindole (4n). orange oil; ¹H NMR (500 MHz, CDCl₃) 0.50 (9H, s), 3.56 (2H, ddd, $J = 5.0, 2.0, 2.0$ Hz), 5.01 (1H, ddt, $J = 17.0, 2.0, 2.0$ Hz), 5.08 (1H, ddt, $J = 10.5, 2.0, 2.0$ Hz), 5.97 (1H, ddt, $J = 17.0, 10.5, 5.0$ Hz), 7.29 (1H,

ddt, $J = 8.0, 7.5, 1.0$ Hz), 7.39 (1H, ddt, $J = 8.0, 7.5, 1.0$ Hz), 7.55 (1H, dt, $J = 7.5, 1.0$ Hz), 7.58 (1H, dt, $J = 8.0, 1.0$ Hz); ^{13}C NMR (125.6 MHz, CDCl_3) -0.18, 29.29, 109.19 (CN), 111.13, 116.03, 120.08, 123.50, 125.43, 129.32, 129.50, 135.89 (x2), 139.93; IR (neat) 2237, 1639, 1589, 1473, 1253, 844, 993, 914, 742 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{Si}$: C, 70.57; H, 7.10; N, 10.97. Found: C, 70.67; H, 7.08; N, 11.10; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{Si}$ (M^+) 254.1239. Found 254.1250.

3-allyl-5-(trimethylsilylethynyl)-2-(trimethylsilyl)-*N*-cyanoindole (4o). orange viscous oil; ^1H NMR (300 MHz, CDCl_3) 0.24 (9H, s), 0.47 (9H, s), 3.49 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 4.94 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.06 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.93 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.47 (2H, br s), 7.63 (1H, br s); ^{13}C NMR (75.4 MHz, CDCl_3) -0.28, -0.02, 29.01, 93.35, 105.05, 108.75, 111.07, 116.26, 118.44, 123.90, 129.20, 129.33, 135.57, 137.15, 139.46; IR (neat) 2239, 2158, 1637, 1533, 1458, 1251, 993, 916, 844, 810, 759 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{Si}_2$ (M^+) 350.1634. Found 350.1638.

3-allyl-6-methyl-2-(trimethylsilyl)-*N*-cyanoindole (4p). yellow oil; ^1H NMR (300 MHz, CDCl_3) 0.47 (9H, s), 2.48 (3H, s), 3.50 (2H, ddd, $J = 5.5, 2.0, 2.0$ Hz), 4.97 (1H, ddt, $J = 17.0, 2.0, 2.0$ Hz), 5.03 (1H, ddt, $J = 10.0, 2.0, 2.0$ Hz), 5.93 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.08 (1H, br d, $J = 8.0$ Hz), 7.36 (1H, br s), 7.39 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) -0.15, 21.63, 29.33, 109.37, 111.27, 115.94, 119.69, 125.07, 127.10, 129.44, 134.99, 135.96, 35.98, 140.33; IR (neat) 2237, 1637, 1618, 1527, 1423, 1253, 995, 921, 844, 810, 765 cm^{-1} ; Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{Si}$: C, 71.59; H, 7.50; N, 10.43. Found: C, 71.30; H, 7.78; N, 10.16; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{Si}$ (M^+) 268.1395. Found 268.1401.

3-allyl-6-methoxy-2-(trimethylsilyl)-*N*-cyanoindole (4q). slightly yellow oil; ^1H NMR (300 MHz, CDCl_3) 0.46 (9H, s), 3.43 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 3.86 (3H, s), 4.97 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.03 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.92 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 6.87 (1H, dd, $J = 8.5, 2.5$ Hz), 7.02 (1H, d, $J = 2.5$ Hz), 7.38 (1H, d, $J = 8.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) -0.17, 29.31, 55.72, 94.59, 109.03, 113.29, 115.91, 120.69, 122.93, 129.49, 134.12, 135.96, 141.08, 158.90; IR (neat) 2235, 1616, 1589, 1494, 1253, 1035, 993, 927, 844, 765 cm^{-1} ; Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{OSi}$: C, 67.56; H, 7.08; N, 9.84. Found: C, 67.51; H, 7.19; N, 9.64; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{OSi}$ (M^+) 284.1344. Found 284.1346.

3-allyl-6-chloro-2-(trimethylsilyl)-*N*-cyanoindole (4r). orange oil; ^1H NMR (300 MHz, CDCl_3) 0.48 (9H, s), 3.50 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 4.95 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.06 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.91 (1H, ddt, $J = 17.0, 10.0,$

5.5 Hz), 7.23 (1H, dd, $J = 8.5, 1.5$ Hz), 7.43 (1H, d, $J = 8.5$ Hz), 7.56 (1H, d, $J = 1.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) -0.27, 29.16, 108.53, 111.41, 116.24, 120.90, 124.29, 127.92, 129.14, 131.67, 135.57, 136.85, 140.36; IR (KBr) 2239, 1639, 1604, 1467, 1253, 993, 912, 842, 812, 763 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{17}\text{ClN}_2\text{Si}$ (M^+) 288.0849. Found 288.0858.

3-allyl-6-nitro-2-(trimethylsilyl)-*N*-cyanoindole (4s). yellow solid; ^1H NMR (300 MHz, CDCl_3) 0.52 (9H, s), 3.56 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 4.94 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.10 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.93 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.62 (1H, d, $J = 8.5$ Hz), 8.16 (1H, dd, $J = 8.5, 2.0$ Hz), 8.48 (1H, d, $J = 2.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) -0.42, 29.08, 107.48, 107.68, 116.69, 118.95, 120.45, 129.09, 133.98, 135.08, 139.06, 142.88, 145.65; IR (KBr) 2239, 1643, 1606, 1533, 1469, 1255, 991, 921, 844, 756 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_2\text{Si}$ (M^+) 299.1090. Found 299.1091.

5-acetyl-3-allyl-2-(trimethylsilyl)-*N*-cyanoindole (4t). yellow oil; ^1H NMR (300 MHz, CDCl_3) 0.50 (9H, s), 2.66 (3H, s), 3.54 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 4.95 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.06 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.94 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.57 (1H, d, $J = 8.5$ Hz), 7.89 (1H, dd, $J = 8.5, 1.0$ Hz), 8.14 (1H, br s); ^{13}C NMR (75.4 MHz, CDCl_3) -0.37, 26.79, 29.10, 108.44, 111.50, 116.28, 120.04, 123.52, 129.21, 132.82, 134.36, 135.44, 139.62, 140.21, 197.07; IR (neat) 2239, 1681, 163, 1610, 1577, 1423, 1253, 993, 912, 844, 765 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{OSi}$ (M^+) 296.1344. Found 296.1349.

3-allyl-6-(trimethylsilylethynyl)-2-(trimethylsilyl)-*N*-cyanoindole (4u). yellow viscous oil; ^1H NMR (300 MHz, CDCl_3) 0.26 (9H, s), 0.47 (9H, s), 3.50 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 4.95 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.05 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.92 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 7.34 (1H, dd, $J = 8.5, 1.0$ Hz), 7.02 (1H, d, $J = 8.5$ Hz), 7.67 (1H, br s); ^{13}C NMR (75.4 MHz, CDCl_3) -0.27, -0.08, 29.15, 95.01, 104.79, 108.66, 114.64, 116.17, 119.84, 120.17, 127.36, 129.26, 129.37, 135.60, 137.53, 139.48; IR (neat) 2239, 2158, 1639, 1569, 1474, 1251, 931, 893, 844, 759 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{Si}_2$ (M^+) 350.1634. Found 350.1626.

3-allyl-4-methoxy-2-(trimethylsilyl)-*N*-cyanoindole (4v). orange oil; ^1H NMR (300 MHz, CDCl_3) 0.47 (9H, s), 3.65 (2H, ddd, $J = 5.5, 2.0, 2.0$ Hz), 3.88 (3H, s), 4.89 (1H, ddt, $J = 17.0, 2.0, 2.0$ Hz), 4.97 (1H, ddt, $J = 10.0, 2.0, 2.0$ Hz), 5.99 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 6.65 (1H, d, $J = 8.0$ Hz), 7.15 (1H, d, $J = 8.0$ Hz), 7.27 (1H, t, $J = 8.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) -0.043, 30.4, 55.37, 103.89, 104.06, 109.22, 114.67, 118.57, 126.51, 130.21, 133.86, 137.77, 141.73, 154.84; IR (neat) 2235, 1639,

1596, 1494, 1256, 1099, 995, 912, 844, 738 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{OSi}$ (M^+) 284.1344. Found 284.1345.

3-allyl-7-methoxy-2-(trimethylsilyl)-*N*-cyanoindole (4w). light yellow viscous oil; ^1H NMR (300 MHz, CDCl_3) 0.47 (9H, s), 3.49 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 3.98 (3H, s), 4.67 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.03 (1H, ddt, $J = 10.5, 1.5, 1.5$ Hz), 5.93 (1H, ddt, $J = 17.0, 10.5, 5.5$ Hz), 6.78 (1H, br d, $J = 8.0$ Hz), 7.08 (1H, dd, $J = 8.0, 1.0$ Hz), 7.16 (1H, t, $J = 8.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) -0.24, 29.19, 55.86, 103.48, 110.30, 112.17, 115.80, 124.26, 129.65, 131.30, 135.99, 137.28, 147.32; IR (neat) 2239, 1639, 1616, 1537, 1433, 1253, 1170, 1083, 993, 912, 846, 763 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{OSi}$ (M^+) 284.1344. Found 284.1344.

3-allyl-2-propyl-*N*-cyanoindole (4x). yellow oil; ^1H NMR (300 MHz, CDCl_3) 1.01 (3H, t, $J = 7.5$ Hz), 1.74 (2H, sextet, $J = 7.5$ Hz), 2.82 (2H, t, $J = 7.5$ Hz), 3.42 (2H, ddd, $J = 6.0, 1.5, 1.5$ Hz), 5.07 (1H, br d, $J = 11.5$ Hz), 5.08 (1H, br d, $J = 16.0$ Hz), 5.93 (1H, m), 7.24-7.36 (3H, m), 7.52 (2H, m); ^{13}C NMR (75.4 MHz, CDCl_3) 13.66, 22.61, 26.75, 28.42, 111.02, 115.68, 116.04, 119.72, 123.61, 123.91, 124.10, 124.22, 128.99, 135.23, 136.01; IR (KBr) 2239, 1639, 1618, 1460, 993, 916, 742 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2$ (M^+) 224.1313. Found 224.1315.

3-allyl-2-(4-methylphenyl)-*N*-cyanoindole (4y). yellow solid; ^1H NMR (300 MHz, CDCl_3) 2.44 (3H, s), 3.47 (2H, ddd, $J = 6.0, 1.5, 1.5$ Hz), 5.09 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.13 (1H, ddt, $J = 10.5, 1.5, 1.5$ Hz), 6.03 (1H, ddt, $J = 17.0, 10.5, 6.0$ Hz), 7.30-7.37 (3H, m), 7.41 (1H, td, $J = 8.0, 1.5$ Hz), 7.46 (2H, br d, $J = 8.0$ Hz), 7.59 (2H, m); ^{13}C NMR (75.4 MHz, CDCl_3) 21.32, 28.71, 107.38, 111.29, 116.20, 116.53, 120.34, 123.87, 124.92, 125.17, 129.11, 129.17, 129.53, 135.40, 135.55, 136.77, 139.59; IR (KBr) 2241, 1639, 1510, 1458, 993, 916, 823, 742 cm^{-1} ; Anal. Calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2$: C, 83.79; H, 5.92; N, 10.28. Found: C, 83.72; H, 5.95; N, 10.21; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2$ (M^+) 272.1313. Found 272.1315.

3-allyl-2-(triphenylsilyl)-*N*-cyanoindole (4z). colorless crystal; ^1H NMR (300 MHz, CDCl_3) 3.57 (2H, ddd, $J = 6.0, 1.5, 1.5$ Hz), 4.75 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 4.86 (1H, ddt, $J = 10.5, 1.5, 1.5$ Hz), 5.56 (1H, ddt, $J = 17.0, 10.5, 6.0$ Hz), 7.32 (1H, m), 7.38-7.52 (10H, m), 7.55-7.65 (2H, m), 7.67 (6H, m); ^{13}C NMR (75.4 MHz, CDCl_3) 29.72, 107.47, 111.50, 115.92, 120.73, 123.59, 125.96, 128.30, 129.31, 130.46, 130.50, 131.89, 133.56, 135.46, 136.29, 140.60; IR (KBr) 2239, 1633, 1587, 1427, 997, 906, 748, 696 cm^{-1} ; Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{Si}$: C, 81.77; H, 5.48; N, 6.35. Found: C, 81.87; H, 5.37; N, 6.37; HRMS (EI) Calcd for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{Si}$ (M^+) 440.1708. Found 440.1704.

***N*-allyl-*N'*-(4-methoxyphenyl)carbodiimide (5).**⁴ colorless oil; ^1H NMR (300 MHz,

CDCl₃) 3.78 (3H, s), 3.98 (2H, ddd, $J = 5.5, 1.5, 1.5$ Hz), 5.22 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.35 (1H, ddd, $J = 17.0, 1.5, 1.5$ Hz), 5.97 (1H, ddt, $J = 17.0, 10.0, 5.5$ Hz), 6.83 (2H, br d, $J = 9.0$ Hz), 7.03 (2H, br d, $J = 9.0$ Hz); ¹³C NMR (75.4 MHz, CDCl₃) 49.01, 55.42, 114.54, 116.79, 124.45, 128.47, 132.39, 134.03, 156.87 (N=C=N); IR (neat) 2127, 1581, 1510, 1463, 1244, 1033, 993, 923, 831 cm⁻¹; HRMS (EI) Calcd for C₁₁H₁₂N₂O (M⁺) 188.0949. Found 188.0954.

Isomerization of the carbodiimide (5) to the allyl cyanamides (2a). A toluene solution (0.5 ml) of *N*-allyl-*N'*-(4-methoxyphenyl)carbodiimide **5** (47.1 mg, 0.25 mmol), Pd₂(dba)₃·CHCl₃ (6.5 mg, 6.25 μmol), and dppe (10.0 mg, 0.025 mmol) was stirred at rt for 10 min and then at 100 °C for 1 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 5/1~1/2) to afford *N*-allyl-*N*-(4-methoxyphenyl)cyanamide **2a** in 88% yield (41.2 mg).

Isomerization of the allyl cyanamide (2n) to the *N*-cyanoindole (4n). An octane solution (0.2 ml) of 1-(*N*-allyl-*N*-cyano)-2-(trimethylsilylethynyl)aniline **2n** (25.4 mg, 0.1 mmol) and Pd(PPh₃)₄ (5.8 mg, 0.005 mmol) was stirred at rt for 10 min and then at 100 °C for 1 h under an argon atmosphere. The reaction mixture was cooled to room temperature and filtered through a short Florisil pad and concentrated. 3-Allyl-2-(trimethylsilyl)-*N*-cyanoindole **4n** was obtained in 52% NMR yield.

3-allyl-*N*-cyanoindole (6a). To a CH₃CN solution (1 ml) of the indole **4n** (127.2 mg, 0.5 mmol) was added a ether solution of HCl (1 ml, 1 mmol) and the mixture was stirred at 100 °C for 5 h. Then the reaction mixture was cooled down to room temperature and filtered through a Celite pad using ether as a eluent. The residue was purified by column chromatography (silica gel, hexane-ether 100/1~10/1) to afford 3-allyl-*N*-cyanoindole **6a** in 75% yield (68.5 mg). yellow oil; ¹H NMR (300 MHz, CDCl₃)

3.45 (2H, br dd, $J = 6.5, 1.5$ Hz), 5.15 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.17 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.99 (1H, ddt, $J = 17.0, 10.0, 6.5$ Hz), 6.99 (1H, s), 7.31 (1H, br t, $J = 8.5$ Hz), 7.40 (1H, br t, $J = 8.0$ Hz), 7.56 (1H, br d, $J = 8.0$ Hz), 7.57 (1H, br d, $J = 8.5$ Hz); ¹³C NMR (75.4 MHz, CDCl₃) 29.18, 107.70, 111.42, 117.06, 120.24, 121.55, 122.62, 123.61, 125.27, 128.03, 134.53, 137.18; IR (neat) 2243, 1641, 1612, 1571, 1456, 993, 920, 740 cm⁻¹; HRMS (EI) Calcd for C₁₂H₁₀N₂ (M⁺) 182.0843. Found 182.0844.

3-allyl-2-bromo-*N*-cyanoindole (6b). The CH₃CN solution (2 ml) of the indole **4n** (127.2 mg, 0.5 mmol) and NBS (356.0 mg, 2 mmol) was stirred at 100 °C for 3 h. Then

the reaction mixture was cooled down to room temperature and filtered through a Celite pad using ether as a eluent. The residue was purified by column chromatography (silica gel, hexane-AcOEt 100/1~20/1) to afford 3-allyl-*N*-cyanoindole **6b** in 85% yield (111.2 mg). white solid; ^1H NMR (300 MHz, CDCl_3) 3.49 (2H, br d, $J = 6.0$ Hz), 5.06 (1H, br dd, $J = 10.5, 1.5$ Hz), 5.08 (1H, br dd, $J = 16.5, 1.5$ Hz), 8.54 (1H, ddt, $J = 16.5, 10.5, 6.0$ Hz), 7.24 (1H, t, $J = 7.5$ Hz), 7.32 (1H, t, $J = 8.0$ Hz), 7.46 (1H, d, $J = 7.5$ Hz), 7.48 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) 29.43, 105.68, 109.20, 111.24, 116.83, 119.74, 120.17, 124.20, 125.32, 127.94, 133.42, 136.97; IR (KBr) 2243, 1637, 1569, 1452, 993, 916, 742 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_9\text{BrN}_2$: C, 55.19; H, 3.47; N, 10.72. Found: C, 55.32; H, 3.79; N, 10.49; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_9\text{BrN}_2$ (M^+) 259.9948. Found 259.9948.

3-allyl-2-(1-pentynyl)-*N*-cyanoindole (6c). To the Et_3N solution (1 ml) of the indole **4n** (65.3 mg, 0.25 mmol), $\text{Pd}(\text{PPh}_3)_4$ (14.5 mg, 0.0125 mmol) and CuI (4.8 mg, 0.025 mmol) was added 1-pentyne (50 μl , 0.5 mmol) and the mixture was stirred at 60 $^\circ\text{C}$ for 3 h. Then the reaction mixture was cooled down to room temperature and filtered through a Celite pad using ether as a eluent. The residue was purified by column chromatography (silica gel, hexane-ether 100/1~30/1) to afford 3-allyl-2-(1-pentynyl)-*N*-cyanoindole **6c** in 78% yield (48.4 mg). yellow oil; ^1H NMR (300 MHz, CDCl_3) 1.08 (3H, t, $J = 7.5$ Hz), 1.68 (2H, sextet, $J = 7.5$ Hz), 2.51 (2H, t, $J = 7.0$ Hz), 3.51 (2H, ddd, $J = 6.5, 1.5, 1.5$ Hz), 5.08 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.13 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.93 (1H, ddt, $J = 17.0, 10.0, 6.5$ Hz), 7.27 (1H, td, $J = 7.5, 1.0$ Hz), 7.38 (1H, td, $J = 8.0, 1.0$ Hz), 7.49 (1H, br d, $J = 8.0$ Hz), 7.53 (1H, br d, $J = 8.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) 13.41, 21.69, 21.77, 29.42, 68.51, 102.31, 106.53, 111.20, 116.42, 119.43, 120.40, 123.45, 123.93, 125.84, 127.77, 134.54, 136.12; IR (neat) 2245, 1637, 1558, 1456, 991, 916, 742 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2$ (M^+) 248.1313. Found 284.1314.

3-allylindole (6d). A THF solution of TBAF (2 ml, 2 mmol) was added to the indole **4n** (127.2 mg, 0.5 mmol) and the mixture was stirred at 50 $^\circ\text{C}$ for 1 h. Then the reaction mixture was cooled down to room temperature and filtered through a Celite pad using ether as a eluent. The residue was purified by column chromatography (silica gel, hexane-AcOEt 100/1~5/1) to afford 3-allylindole **6d** in 70% yield (55.1 mg). yellow oil; ^1H NMR (300 MHz, CDCl_3) 3.52 (2H, br d, $J = 6.5$ Hz), 5.06 (1H, br d, $J = 10.0$ Hz), 5.15 (1H, br ddt, $J = 17.0, 1.5, 1.5$ Hz), 6.06 (1H, ddt, $J = 17.0, 10.0, 6.5$ Hz), 6.98 (1H, br s), 7.10 (1H, br t, $J = 7.5$ Hz), 7.18 (1H, br t, $J = 8.0$ Hz), 7.33 (1H, br d, $J = 7.5$ Hz), 7.59 (1H, br d, $J = 8.0$ Hz), 7.91 (1H, br s: NH); ^{13}C NMR (75.4 MHz, CDCl_3)

29.76, 111.03, 114.42, 115.15, 119.04, 119.19, 120.60, 121.94, 127.36, 136.35, 137.23; IR (neat) 3417, 1638, 1618, 1456, 993, 914, 742 cm^{-1} ; Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{N}$: C, 84.03; H, 7.05; N, 8.90. Found: C, 83.91; H, 7.32; N, 8.85; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{11}\text{N}$ (M^+) 157.0891. Found 157.0893.

3-allyl-2-(trimethylsilyl)indole (6e). To a THF solution (2 ml) of the indole **4n** (127.2 mg, 0.5 mmol) at 0 °C was added MeMgBr (0.67 ml, 2 mmol: 3.0 M ether solution). The mixture was gradually warmed up to rt and stirred for 4 h. After the reaction was complete, the mixture was quenched with aqueous NH_4Cl solution and extracted with ether. The residue was purified by column chromatography (silica gel, hexane-AcOEt 50/1~15/1) to afford 3-allyl-2-(trimethylsilyl)indole **6e** in 93% yield (106.8 mg). yellow oil; ^1H NMR (300 MHz, CDCl_3) 0.37 (9H, s), 3.60 (2H, ddd, $J = 6.0, 1.5, 1.5$ Hz), 5.00 (1H, ddt, $J = 10.0, 1.5, 1.5$ Hz), 5.04 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 6.00 (1H, ddt, $J = 17.0, 10.0, 6.0$ Hz), 7.06 (1H, td, $J = 8.0, 1.0$ Hz), 7.15 (1H, td, $J = 8.0, 1.0$ Hz), 7.34 (1H, dd, $J = 8.0, 1.0$ Hz), 7.57 (1H, d, $J = 8.0$ Hz), 7.88 (1H, br s: NH); ^{13}C NMR (75.4 MHz, CDCl_3) -0.69, 30.37, 110.77, 114.67, 119.09, 119.13, 122.24, 122.42, 128.83, 133.43, 137.94, 138.19; IR (neat) 3442, 1637, 1515, 1249, 993, 914, 839, 742 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{NSi}$: C, 73.30; H, 8.34; N, 6.10. Found: C, 72.92; H, 8.54; N, 6.13; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{19}\text{NSi}$ (M^+) 229.1286. Found 229.1289.

References

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3. Suginome, M.; Fukuda, T.; Ito, Y. *Org. Lett.* **1999**, *1*, 1977-1979.
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X-ray crystallographic data

1-(*N*-allyl-*N*-cyano)-2-(triphenylsilylethynyl)aniline (2o). Detail x-ray crystallographic data for the allyl cyanamide **2o** are reported in the supporting information of ref 5 in the text.

X-ray structure of **2o**

3-allyl-2-(triphenylsilyl)-*N*-cyanoindole (4z). **Figure 1.** X-ray structure of **4z**

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	C ₃₁ H ₂₄ N ₂ Si
Formula Weight	452.63
Crystal Color, Habit	colorless, prismatic
Crystal Dimensions	0.20 X 0.30 X 0.40 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2 θ range)	24 (27.7 - 34.2°)
Omega Scan Peak Width at Half-height	0.22°
Lattice Parameters	a = 8.984(2) Å b = 15.374(3) Å c = 17.950(2) Å β = 92.62(1)° V = 2476.7(6) Å ³
Space Group	P2 ₁ (#4)
Z value	4
D _{calc}	1.214 g/cm ³
F ₀₀₀	952.00
μ (MoK α)	1.16 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku AFC5R
Radiation	MoK α (λ = 0.71069 Å) graphite monochromated
Voltage, Current	45kV, 200mA

Temperature	13.0°C
Scan Type	ω -2 θ
Scan Rate	4.0°/min (in ω) (up to 2 scans)
Scan Width	(1.00 + 0.30 tan θ)°
2 θ_{max}	55.0°
No. of Reflections Measured	Total: 6266 Unique: 5900 ($R_{int} = 0.018$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.9531 - 0.9994)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\sum w(F_o - F_c)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(F_o)} = [\sigma_e^2(F_o) + \frac{P^2}{4} F_o^2]^{-1}$
p-factor	0.0040
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 1.80\sigma(I)$)	3887
No. Variables	596
Reflection/Parameter Ratio	6.52
Residuals: R; Rw	0.055 ; 0.052
Residuals: R1	0.054
No. of Reflections to calc R1	3822
Goodness of Fit Indicator	1.27
Max Shift/Error in Final Cycle	0.38
Maximum peak in Final Diff. Map	0.24 $e^-/\text{\AA}^3$
Minimum peak in Final Diff. Map	-0.14 $e^-/\text{\AA}^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Si(1)	1.0290(1)	-0.0186(7)	0.98569(8)	3.36(3)
Si(2)	0.9667(1)	0.2925(7)	0.49551(8)	3.51(3)
N(1)	1.3040(5)	0.1249(8)	0.8753(4)	6.7(1)
N(2)	0.6924(5)	0.4272(8)	0.6134(3)	5.7(1)
C(1)	0.9415(5)	0.0652(8)	0.9206(3)	3.18(9)
C(2)	0.7962(5)	0.0870(8)	0.9025(3)	3.42(9)
C(3)	0.7955(5)	0.1672(8)	0.8621(3)	3.59(10)
C(4)	0.6797(6)	0.2194(8)	0.8304(3)	4.5(1)
C(5)	0.7172(7)	0.2959(8)	0.7956(3)	5.1(1)
C(6)	0.8654(7)	0.3215(8)	0.7915(3)	4.9(1)
C(7)	0.9804(6)	0.2712(8)	0.8203(3)	4.4(1)
C(8)	0.9420(5)	0.1941(8)	0.8549(3)	3.54(10)
C(9)	1.0322(5)	0.1307(7)	0.8907(2)	2.81(8)
C(10)	1.1791(6)	0.1266(8)	0.8835(3)	4.3(1)
C(11)	0.6544(6)	0.0399(8)	0.9206(3)	4.8(1)
C(12)	0.6004(8)	-0.0230(9)	0.8632(5)	7.3(2)
C(13)	0.670(1)	-0.0511(10)	0.8077(5)	9.3(3)
C(14)	0.8772(5)	-0.0756(8)	1.0346(3)	3.8(1)
C(15)	0.8228(7)	-0.0469(8)	1.1015(3)	5.0(1)
C(16)	0.6982(8)	-0.0865(8)	1.1299(4)	6.7(2)
C(17)	0.6296(8)	-0.1544(9)	1.0920(5)	7.3(2)
C(18)	0.6854(7)	-0.1855(8)	1.0287(4)	6.4(2)
C(19)	0.8087(7)	-0.1474(8)	0.9998(3)	5.0(1)
C(20)	1.1363(5)	-0.1014(8)	0.9342(3)	3.9(1)
C(21)	1.1469(7)	-0.1010(8)	0.8575(3)	5.3(1)
C(22)	1.2239(9)	-0.1668(9)	0.8218(4)	7.0(2)
C(23)	1.2886(8)	-0.2318(8)	0.8629(5)	7.4(2)
C(24)	1.2793(8)	-0.2345(8)	0.9392(5)	6.9(2)
C(25)	1.2031(7)	-0.1704(8)	0.9736(4)	5.4(2)
C(26)	1.1509(6)	0.0460(8)	1.0526(3)	3.8(1)
C(27)	1.0962(6)	0.1199(8)	1.0857(3)	4.6(1)
C(28)	1.1824(7)	0.1699(8)	1.1356(4)	5.5(1)
C(29)	1.3259(8)	0.1466(9)	1.1520(4)	7.5(2)
C(30)	1.3879(8)	0.0768(9)	1.1176(5)	8.8(2)
C(31)	1.3009(7)	0.0265(8)	1.0687(4)	6.2(2)
C(32)	1.0554(5)	0.3675(8)	0.5674(3)	3.38(10)
C(33)	1.2020(5)	0.3874(8)	0.5892(3)	3.39(9)
C(34)	1.2025(5)	0.4593(8)	0.6383(3)	3.39(10)
C(35)	1.3169(5)	0.5079(8)	0.6747(3)	4.2(1)
C(36)	1.2790(6)	0.5783(8)	0.7176(3)	4.6(1)
C(37)	1.1304(6)	0.6014(8)	0.7258(3)	4.7(1)
C(38)	1.0154(6)	0.5550(8)	0.6924(3)	4.2(1)
C(39)	1.0558(5)	0.4843(8)	0.6485(3)	3.37(9)
C(40)	0.8144(8)	0.4976(8)	0.3635(4)	6.1(2)
C(41)	0.8169(5)	0.4262(8)	0.6081(3)	3.9(1)
C(42)	1.3418(5)	0.3423(8)	0.5670(3)	4.3(1)
C(43)	1.3978(7)	0.2749(8)	0.6217(4)	6.1(2)
C(44)	1.3307(9)	0.2443(9)	0.6794(5)	7.7(2)

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
C(45)	1.1171(6)	0.2417(8)	0.4416(3)	4.2(1)
C(46)	1.1652(7)	0.2766(8)	0.3763(3)	5.5(2)
C(47)	1.2893(9)	0.2405(9)	0.3434(5)	7.7(2)
C(48)	1.3666(9)	0.1720(9)	0.3750(6)	8.3(2)
C(49)	1.3152(7)	0.1354(8)	0.4387(5)	6.9(2)
C(50)	1.1925(7)	0.1694(8)	0.4711(4)	5.3(1)
C(51)	0.8627(6)	0.2041(8)	0.5417(3)	3.9(1)
C(52)	0.8637(7)	0.1966(8)	0.6183(3)	5.2(1)
C(53)	0.7931(9)	0.1268(9)	0.6516(4)	6.3(2)
C(54)	0.7188(8)	0.0666(8)	0.6092(4)	6.3(2)
C(55)	0.7131(7)	0.0729(8)	0.5326(4)	5.5(1)
C(56)	0.7851(7)	0.1408(8)	0.4991(3)	5.0(1)
C(57)	0.8450(6)	0.3649(8)	0.4345(3)	4.0(1)
C(58)	0.6951(7)	0.3462(8)	0.4169(4)	5.5(1)
C(59)	0.6100(7)	0.4016(9)	0.3720(5)	7.5(2)
C(60)	0.6694(9)	0.4763(9)	0.3446(5)	7.7(2)
C(61)	0.9015(7)	0.4417(8)	0.4082(4)	5.3(1)
C(62)	0.9652(4)	0.4283(7)	0.6049(2)	2.63(8)
H(1)	0.5755	0.2015	0.8324	5.5342
H(2)	0.6393	0.3321	0.7740	6.1146
H(3)	0.8860	0.3760	0.7672	5.9246
H(4)	1.0846	0.2899	0.8179	5.3700
H(5)	0.6713	0.0084	0.9675	5.9860
H(6)	0.5766	0.0813	0.9289	5.9860
H(7)	0.5002	-0.0478	0.8668	8.5097
H(8)	0.7686	-0.0295	0.8001	10.7821
H(9)	0.6270	-0.0911	0.7721	10.7821
H(10)	0.8717	0.0007	1.1289	6.2226
H(11)	0.6623	-0.0657	1.1775	8.0623
H(12)	0.5389	-0.1788	1.1109	8.8484
H(13)	0.6366	-0.2361	1.0030	7.9298
H(14)	0.8502	-0.1700	0.9535	6.3239
H(15)	1.0977	-0.0538	0.8272	6.6392
H(16)	1.2304	-0.1661	0.7674	9.1430
H(17)	1.3441	-0.2777	0.8381	9.1643
H(18)	1.3244	-0.2830	0.9689	8.3357
H(19)	1.1955	-0.1723	1.0284	6.4420
H(20)	0.9934	0.1371	1.0728	5.4101
H(21)	1.1395	0.2206	1.1592	6.8795
H(22)	1.3871	0.1787	1.1882	9.0372
H(23)	1.4918	0.0593	1.1295	9.9665
H(24)	1.3453	-0.0235	1.0444	7.1816
H(25)	1.4200	0.4919	0.6691	5.1376
H(26)	1.3564	0.6136	0.7419	5.5654
H(27)	1.1097	0.6498	0.7573	5.7096
H(28)	0.9128	0.5714	0.6976	5.2597
H(29)	1.3236	0.3137	0.5193	5.2568
H(30)	1.4193	0.3838	0.5612	5.2568

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
H(31)	1.4943	0.2499	0.6150	6.8476
H(32)	1.3769	0.2000	0.7110	9.0290
H(33)	1.2335	0.2636	0.6903	9.0290
H(34)	1.3190	0.2644	0.2953	9.3121
H(35)	1.4560	0.1516	0.3528	9.7436
H(36)	1.3692	0.0849	0.4627	8.4822
H(37)	1.1546	0.1416	0.5156	6.6787
H(38)	0.9153	0.2398	0.6488	6.1616
H(39)	0.7997	0.1214	0.7056	7.9691
H(40)	0.6691	0.0190	0.6343	7.5145
H(41)	0.6561	0.0311	0.5015	6.7464
H(42)	0.6476	0.2932	0.4368	6.6373
H(43)	0.5074	0.3859	0.3583	8.9730
H(44)	0.6067	0.5127	0.3119	8.9704
H(45)	0.8561	0.5516	0.3451	7.7838
H(46)	1.0064	0.4562	0.4201	6.7027
H(47)	1.1116	0.3259	0.3521	7.0256
H(48)	0.7859	0.1441	0.4451	6.0160

$$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Si(1)	0.0367(7)	0.0412(8)	0.0495(8)	0.0022(6)	-0.0006(5)	-0.0022(7)
Si(2)	0.0374(7)	0.0439(8)	0.0516(8)	-0.0023(6)	-0.0028(6)	-0.0066(7)
N(1)	0.040(2)	0.080(4)	0.135(5)	-0.001(3)	0.005(3)	0.024(4)
N(2)	0.037(2)	0.069(3)	0.110(4)	0.000(2)	0.003(3)	-0.008(3)
C(1)	0.037(2)	0.038(2)	0.046(3)	0.001(2)	0.001(2)	-0.004(2)
C(2)	0.034(2)	0.047(2)	0.049(3)	0.003(2)	0.002(2)	-0.011(2)
C(3)	0.043(2)	0.050(3)	0.043(3)	0.006(2)	-0.001(2)	-0.009(2)
C(4)	0.045(3)	0.066(3)	0.059(3)	0.019(2)	-0.001(2)	-0.003(2)
C(5)	0.069(3)	0.068(3)	0.056(3)	0.028(3)	0.002(3)	0.007(3)
C(6)	0.080(3)	0.048(3)	0.059(3)	0.009(2)	0.002(3)	0.011(3)
C(7)	0.065(3)	0.055(3)	0.047(3)	-0.003(2)	0.000(2)	0.003(2)
C(8)	0.044(2)	0.047(3)	0.043(3)	0.004(2)	-0.003(2)	-0.005(2)
C(9)	0.030(2)	0.038(2)	0.038(2)	-0.004(2)	-0.003(2)	-0.001(2)
C(10)	0.039(2)	0.050(3)	0.075(4)	-0.002(2)	0.001(2)	0.006(3)
C(11)	0.030(2)	0.073(4)	0.081(4)	-0.001(2)	0.000(2)	0.013(3)
C(12)	0.083(5)	0.074(5)	0.116(6)	-0.029(4)	-0.038(4)	0.006(4)
C(13)	0.128(8)	0.114(7)	0.106(6)	-0.028(6)	-0.041(5)	-0.030(5)
C(14)	0.039(2)	0.047(3)	0.061(3)	0.002(2)	0.009(2)	0.007(2)
C(15)	0.076(4)	0.055(4)	0.059(3)	0.009(3)	0.011(3)	-0.001(3)
C(16)	0.090(5)	0.073(4)	0.095(5)	0.012(3)	0.050(4)	0.015(3)
C(17)	0.071(4)	0.079(5)	0.132(6)	-0.004(4)	0.041(4)	0.015(4)
C(18)	0.063(4)	0.058(4)	0.121(5)	-0.016(3)	0.009(3)	0.003(4)
C(19)	0.065(3)	0.054(3)	0.071(4)	-0.008(2)	0.003(3)	-0.008(3)
C(20)	0.041(3)	0.048(3)	0.061(2)	0.002(2)	0.007(2)	-0.013(2)
C(21)	0.073(4)	0.066(4)	0.062(3)	-0.011(3)	0.006(3)	-0.007(3)
C(22)	0.097(5)	0.086(5)	0.085(5)	-0.004(4)	0.022(4)	-0.039(3)
C(23)	0.079(5)	0.069(4)	0.132(5)	0.010(4)	0.018(5)	-0.051(4)
C(24)	0.077(4)	0.055(4)	0.130(5)	0.019(3)	-0.001(4)	-0.019(4)
C(25)	0.073(4)	0.057(4)	0.074(4)	0.013(3)	-0.008(3)	-0.003(3)
C(26)	0.048(2)	0.047(3)	0.050(3)	-0.006(2)	-0.008(2)	-0.002(2)
C(27)	0.052(3)	0.053(3)	0.068(4)	0.006(2)	-0.003(2)	-0.006(2)
C(28)	0.070(3)	0.065(4)	0.073(4)	-0.009(3)	0.003(3)	-0.023(3)
C(29)	0.075(4)	0.111(6)	0.095(5)	-0.001(4)	-0.026(4)	-0.036(5)
C(30)	0.061(4)	0.130(7)	0.139(7)	0.019(4)	-0.045(4)	-0.069(5)
C(31)	0.058(3)	0.082(5)	0.093(5)	0.029(3)	-0.022(3)	-0.026(4)
C(32)	0.039(2)	0.037(2)	0.052(3)	-0.002(2)	-0.002(2)	-0.004(2)
C(33)	0.039(2)	0.043(3)	0.047(3)	-0.005(2)	0.000(2)	0.002(2)
C(34)	0.040(2)	0.046(3)	0.043(3)	-0.002(2)	0.002(2)	0.001(2)
C(35)	0.042(3)	0.061(3)	0.055(3)	-0.009(2)	-0.004(2)	-0.005(2)
C(36)	0.055(2)	0.062(3)	0.059(3)	-0.021(3)	-0.001(3)	-0.015(3)
C(37)	0.062(2)	0.052(3)	0.063(4)	-0.006(3)	0.006(3)	-0.020(3)
C(38)	0.047(3)	0.055(3)	0.059(3)	0.002(2)	0.008(2)	-0.011(2)
C(39)	0.040(2)	0.042(2)	0.046(3)	-0.006(2)	-0.004(2)	0.002(2)
C(40)	0.089(4)	0.053(4)	0.090(5)	-0.001(3)	-0.011(3)	0.014(3)
C(41)	0.036(2)	0.046(3)	0.067(3)	0.000(2)	0.003(2)	-0.004(3)
C(42)	0.036(2)	0.056(3)	0.070(4)	-0.006(2)	0.002(2)	-0.018(2)
C(43)	0.052(3)	0.065(4)	0.111(5)	0.018(3)	-0.019(3)	-0.004(3)
C(44)	0.098(6)	0.085(6)	0.108(6)	0.010(5)	-0.016(4)	0.021(5)

Table 2. Anisotropic Displacement Parameters (continued)

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(45)	0.047(3)	0.055(3)	0.057(3)	0.000(2)	0.004(2)	-0.023(2)
C(46)	0.082(4)	0.067(4)	0.061(3)	-0.015(3)	0.011(3)	-0.011(3)
C(47)	0.103(6)	0.102(6)	0.092(6)	-0.010(4)	0.047(4)	-0.029(4)
C(48)	0.080(5)	0.094(6)	0.145(7)	-0.002(4)	0.042(5)	-0.045(4)
C(49)	0.056(4)	0.075(5)	0.132(6)	0.012(3)	-0.001(3)	-0.036(4)
C(50)	0.063(3)	0.056(3)	0.082(4)	0.007(3)	-0.006(3)	-0.016(3)
C(51)	0.049(3)	0.044(3)	0.054(2)	0.001(2)	0.005(2)	-0.002(2)
C(52)	0.084(4)	0.059(3)	0.054(2)	-0.006(3)	0.001(3)	-0.013(3)
C(53)	0.107(6)	0.073(4)	0.062(4)	-0.012(3)	0.022(3)	0.002(3)
C(54)	0.089(5)	0.057(4)	0.096(3)	-0.015(3)	0.033(4)	0.002(3)
C(55)	0.069(4)	0.047(3)	0.094(3)	-0.016(3)	0.010(3)	-0.017(3)
C(56)	0.069(4)	0.058(3)	0.061(4)	-0.016(3)	-0.001(3)	-0.010(2)
C(57)	0.048(2)	0.051(3)	0.052(3)	0.003(2)	-0.008(2)	-0.006(2)
C(58)	0.054(3)	0.062(4)	0.090(5)	-0.008(3)	-0.012(3)	-0.003(3)
C(59)	0.060(4)	0.087(5)	0.132(7)	0.007(3)	-0.040(4)	0.015(4)
C(60)	0.087(4)	0.082(5)	0.118(6)	0.016(4)	-0.037(4)	0.019(5)
C(61)	0.060(4)	0.055(3)	0.086(4)	-0.009(3)	-0.009(3)	0.005(3)
C(62)	0.025(2)	0.034(2)	0.040(2)	0.000(2)	-0.002(2)	0.001(2)

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table 3. Bond Lengths($\text{\AA}$)

atom	atom	distance	atom	atom	distance
Si(1)	C(1)	1.887(6)	Si(1)	C(14)	1.873(6)
Si(1)	C(20)	1.866(6)	Si(1)	C(26)	1.874(6)
Si(2)	C(32)	1.881(6)	Si(2)	C(45)	1.869(6)
Si(2)	C(51)	1.865(7)	Si(2)	C(57)	1.877(6)
N(1)	C(10)	1.139(7)	N(2)	C(41)	1.127(7)
C(1)	C(2)	1.372(7)	C(1)	C(9)	1.417(7)
C(2)	C(3)	1.429(8)	C(2)	C(11)	1.513(8)
C(3)	C(4)	1.413(8)	C(3)	C(8)	1.392(8)
C(4)	C(5)	1.380(10)	C(5)	C(6)	1.394(10)
C(6)	C(7)	1.372(9)	C(7)	C(8)	1.389(8)
C(8)	C(9)	1.404(7)	C(9)	C(10)	1.333(7)
C(11)	C(12)	1.48(1)	C(12)	C(13)	1.28(1)
C(14)	C(15)	1.389(9)	C(14)	C(19)	1.397(9)
C(15)	C(16)	1.392(10)	C(16)	C(17)	1.38(1)
C(17)	C(18)	1.35(1)	C(18)	C(19)	1.376(9)
C(20)	C(21)	1.384(9)	C(20)	C(25)	1.395(9)
C(21)	C(22)	1.40(1)	C(22)	C(23)	1.36(1)
C(23)	C(24)	1.38(1)	C(24)	C(25)	1.364(10)
C(26)	C(27)	1.382(8)	C(26)	C(31)	1.398(8)
C(27)	C(28)	1.388(9)	C(28)	C(29)	1.36(1)
C(29)	C(30)	1.37(1)	C(30)	C(31)	1.39(1)
C(32)	C(33)	1.391(7)	C(32)	C(62)	1.425(7)
C(33)	C(34)	1.414(8)	C(33)	C(42)	1.504(8)
C(34)	C(35)	1.406(7)	C(34)	C(39)	1.393(7)
C(35)	C(36)	1.381(9)	C(36)	C(37)	1.396(9)
C(37)	C(38)	1.370(8)	C(38)	C(39)	1.401(8)
C(39)	C(62)	1.399(7)	C(40)	C(60)	1.37(1)
C(40)	C(61)	1.393(10)	C(41)	C(62)	1.337(7)
C(42)	C(43)	1.497(10)	C(43)	C(44)	1.31(1)
C(45)	C(46)	1.376(9)	C(45)	C(50)	1.395(9)
C(46)	C(47)	1.40(1)	C(47)	C(48)	1.37(1)
C(48)	C(49)	1.37(1)	C(49)	C(50)	1.373(10)
C(51)	C(52)	1.380(9)	C(51)	C(56)	1.403(8)
C(52)	C(53)	1.39(1)	C(53)	C(54)	1.36(1)
C(54)	C(55)	1.38(1)	C(55)	C(56)	1.380(9)
C(57)	C(58)	1.399(8)	C(57)	C(61)	1.377(9)
C(58)	C(59)	1.379(10)	C(59)	C(60)	1.37(1)

Table 4. Bond Lengths($\text{\AA}$)

atom	atom	distance	atom	atom	distance
C(4)	H(1)	0.98	C(5)	H(2)	0.96
C(6)	H(3)	0.97	C(7)	H(4)	0.98
C(11)	H(5)	0.98	C(11)	H(6)	0.96
C(12)	H(7)	0.98	C(13)	H(8)	0.96
C(13)	H(9)	0.96	C(15)	H(10)	0.97
C(16)	H(11)	0.98	C(17)	H(12)	0.97
C(18)	H(13)	1.00	C(19)	H(14)	0.99
C(21)	H(15)	1.00	C(22)	H(16)	0.98
C(23)	H(17)	0.98	C(24)	H(18)	0.99
C(25)	H(19)	0.99	C(27)	H(20)	0.98
C(28)	H(21)	0.97	C(29)	H(22)	0.97
C(30)	H(23)	0.99	C(31)	H(24)	0.98
C(35)	H(25)	0.97	C(36)	H(26)	0.97
C(37)	H(27)	0.96	C(38)	H(28)	0.96
C(40)	H(45)	0.97	C(42)	H(29)	0.97
C(42)	H(30)	0.95	C(43)	H(31)	0.96
C(44)	H(32)	0.97	C(44)	H(33)	0.95
C(46)	H(47)	0.99	C(47)	H(34)	0.99
C(48)	H(35)	0.96	C(49)	H(36)	1.00
C(50)	H(37)	0.98	C(52)	H(38)	0.97
C(53)	H(39)	0.97	C(54)	H(40)	0.98
C(55)	H(41)	0.98	C(56)	H(48)	0.97
C(58)	H(42)	0.99	C(59)	H(43)	0.97
C(60)	H(44)	0.97	C(61)	H(46)	0.98

Table 5. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	Si(1)	C(14)	108.6(2)	C(1)	Si(1)	C(20)	111.7(3)
C(1)	Si(1)	C(26)	104.4(3)	C(14)	Si(1)	C(20)	108.5(3)
C(14)	Si(1)	C(26)	111.4(3)	C(20)	Si(1)	C(26)	112.3(3)
C(32)	Si(2)	C(45)	108.6(2)	C(32)	Si(2)	C(51)	110.3(3)
C(32)	Si(2)	C(57)	104.7(3)	C(45)	Si(2)	C(51)	108.3(3)
C(45)	Si(2)	C(57)	111.2(3)	C(51)	Si(2)	C(57)	113.7(3)
Si(1)	C(1)	C(2)	132.7(4)	Si(1)	C(1)	C(9)	119.3(4)
C(2)	C(1)	C(9)	107.1(5)	C(1)	C(2)	C(3)	108.2(5)
C(1)	C(2)	C(11)	129.3(5)	C(3)	C(2)	C(11)	122.5(5)
C(2)	C(3)	C(4)	132.8(6)	C(2)	C(3)	C(8)	108.8(5)
C(4)	C(3)	C(8)	118.4(6)	C(3)	C(4)	C(5)	118.4(6)
C(4)	C(5)	C(6)	121.2(6)	C(5)	C(6)	C(7)	121.7(6)
C(6)	C(7)	C(8)	116.8(6)	C(3)	C(8)	C(7)	123.4(6)
C(3)	C(8)	C(9)	106.2(5)	C(7)	C(8)	C(9)	130.3(6)
C(1)	C(9)	C(8)	109.7(4)	C(1)	C(9)	C(10)	126.3(5)
C(8)	C(9)	C(10)	122.8(5)	N(1)	C(10)	C(9)	177.7(8)
C(2)	C(11)	C(12)	114.6(6)	C(11)	C(12)	C(13)	127.4(8)
Si(1)	C(14)	C(15)	123.3(5)	Si(1)	C(14)	C(19)	118.3(5)
C(15)	C(14)	C(19)	118.2(6)	C(14)	C(15)	C(16)	119.9(7)
C(15)	C(16)	C(17)	120.0(7)	C(16)	C(17)	C(18)	120.6(7)
C(17)	C(18)	C(19)	120.2(7)	C(14)	C(19)	C(18)	120.9(7)
Si(1)	C(20)	C(21)	123.3(5)	Si(1)	C(20)	C(25)	119.2(5)
C(21)	C(20)	C(25)	117.4(6)	C(20)	C(21)	C(22)	120.7(7)
C(21)	C(22)	C(23)	119.5(8)	C(22)	C(23)	C(24)	121.3(7)
C(23)	C(24)	C(25)	118.8(8)	C(20)	C(25)	C(24)	122.3(7)
Si(1)	C(26)	C(27)	120.2(5)	Si(1)	C(26)	C(31)	123.2(5)
C(27)	C(26)	C(31)	116.5(6)	C(26)	C(27)	C(28)	122.2(6)
C(27)	C(28)	C(29)	119.3(7)	C(28)	C(29)	C(30)	120.8(7)
C(29)	C(30)	C(31)	119.6(7)	C(26)	C(31)	C(30)	121.5(7)
Si(2)	C(32)	C(33)	133.9(4)	Si(2)	C(32)	C(62)	119.6(4)
C(33)	C(32)	C(62)	106.0(5)	C(32)	C(33)	C(34)	108.8(5)
C(32)	C(33)	C(42)	128.0(5)	C(34)	C(33)	C(42)	123.1(5)
C(33)	C(34)	C(35)	133.3(5)	C(33)	C(34)	C(39)	108.7(5)
C(35)	C(34)	C(39)	118.0(5)	C(34)	C(35)	C(36)	118.8(5)
C(35)	C(36)	C(37)	121.3(5)	C(36)	C(37)	C(38)	121.8(6)
C(37)	C(38)	C(39)	116.1(5)	C(34)	C(39)	C(38)	124.0(5)
C(34)	C(39)	C(62)	106.7(5)	C(38)	C(39)	C(62)	129.3(5)
C(60)	C(40)	C(61)	119.8(7)	N(2)	C(41)	C(62)	176.8(7)
C(33)	C(42)	C(43)	113.9(6)	C(42)	C(43)	C(44)	127.8(7)
Si(2)	C(45)	C(46)	122.8(5)	Si(2)	C(45)	C(50)	119.1(5)
C(46)	C(45)	C(50)	117.9(6)	C(45)	C(46)	C(47)	119.5(8)
C(46)	C(47)	C(48)	121.9(9)	C(47)	C(48)	C(49)	118.4(8)
C(48)	C(49)	C(50)	120.2(9)	C(45)	C(50)	C(49)	121.9(8)
Si(2)	C(51)	C(52)	121.6(5)	Si(2)	C(51)	C(56)	120.7(5)
C(52)	C(51)	C(56)	117.7(6)	C(51)	C(52)	C(53)	120.6(6)
C(52)	C(53)	C(54)	120.4(7)	C(53)	C(54)	C(55)	120.5(7)
C(54)	C(55)	C(56)	119.5(7)	C(51)	C(56)	C(55)	121.2(6)
Si(2)	C(57)	C(58)	122.6(5)	Si(2)	C(57)	C(61)	119.7(5)

Table 5. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(58)	C(57)	C(61)	117.7(6)	C(57)	C(58)	C(59)	120.5(7)
C(58)	C(59)	C(60)	120.9(7)	C(40)	C(60)	C(59)	119.6(7)
C(40)	C(61)	C(57)	121.4(6)	C(32)	C(62)	C(39)	109.8(4)
C(32)	C(62)	C(41)	126.4(5)	C(39)	C(62)	C(41)	123.1(5)

Table 6. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(3)	C(4)	H(1)	120.9	C(5)	C(4)	H(1)	120.7
C(4)	C(5)	H(2)	119.2	C(6)	C(5)	H(2)	119.6
C(5)	C(6)	H(3)	118.1	C(7)	C(6)	H(3)	120.2
C(6)	C(7)	H(4)	121.4	C(8)	C(7)	H(4)	121.7
C(2)	C(11)	H(5)	108.8	C(2)	C(11)	H(6)	109.9
C(12)	C(11)	H(5)	108.1	C(12)	C(11)	H(6)	108.9
H(5)	C(11)	H(6)	106.2	C(11)	C(12)	H(7)	118.7
C(13)	C(12)	H(7)	113.9	C(12)	C(13)	H(8)	118.9
C(12)	C(13)	H(9)	122.6	H(8)	C(13)	H(9)	118.4
C(14)	C(15)	H(10)	120.4	C(16)	C(15)	H(10)	119.8
C(15)	C(16)	H(11)	118.6	C(17)	C(16)	H(11)	121.4
C(16)	C(17)	H(12)	118.9	C(18)	C(17)	H(12)	120.4
C(17)	C(18)	H(13)	119.6	C(19)	C(18)	H(13)	120.1
C(14)	C(19)	H(14)	118.6	C(18)	C(19)	H(14)	120.5
C(20)	C(21)	H(15)	119.8	C(22)	C(21)	H(15)	119.5
C(21)	C(22)	H(16)	120.1	C(23)	C(22)	H(16)	120.3
C(22)	C(23)	H(17)	119.7	C(24)	C(23)	H(17)	119.0
C(23)	C(24)	H(18)	121.0	C(25)	C(24)	H(18)	120.1
C(20)	C(25)	H(19)	118.6	C(24)	C(25)	H(19)	119.1
C(26)	C(27)	H(20)	118.1	C(28)	C(27)	H(20)	119.7
C(27)	C(28)	H(21)	120.2	C(29)	C(28)	H(21)	120.5
C(28)	C(29)	H(22)	121.1	C(30)	C(29)	H(22)	118.1
C(29)	C(30)	H(23)	121.3	C(31)	C(30)	H(23)	119.0
C(26)	C(31)	H(24)	119.1	C(30)	C(31)	H(24)	119.4
C(34)	C(35)	H(25)	120.0	C(36)	C(35)	H(25)	121.2
C(35)	C(36)	H(26)	120.0	C(37)	C(36)	H(26)	118.6
C(36)	C(37)	H(27)	118.2	C(38)	C(37)	H(27)	119.9
C(37)	C(38)	H(28)	121.9	C(39)	C(38)	H(28)	122.0
C(60)	C(40)	H(45)	119.7	C(61)	C(40)	H(45)	120.5
C(33)	C(42)	H(29)	109.4	C(33)	C(42)	H(30)	110.0
C(43)	C(42)	H(29)	107.7	C(43)	C(42)	H(30)	108.0
H(29)	C(42)	H(30)	107.6	C(42)	C(43)	H(31)	118.3
C(44)	C(43)	H(31)	113.9	C(43)	C(44)	H(32)	121.0
C(43)	C(44)	H(33)	120.8	H(32)	C(44)	H(33)	118.1
C(45)	C(46)	H(47)	120.5	C(47)	C(46)	H(47)	120.0
C(46)	C(47)	H(34)	118.3	C(48)	C(47)	H(34)	119.7
C(47)	C(48)	H(35)	119.7	C(49)	C(48)	H(35)	121.9
C(48)	C(49)	H(36)	120.0	C(50)	C(49)	H(36)	119.7
C(45)	C(50)	H(37)	118.4	C(49)	C(50)	H(37)	119.6
C(51)	C(52)	H(38)	119.2	C(53)	C(52)	H(38)	120.2
C(52)	C(53)	H(39)	119.0	C(54)	C(53)	H(39)	120.5
C(53)	C(54)	H(40)	118.4	C(55)	C(54)	H(40)	121.1
C(54)	C(55)	H(41)	121.1	C(56)	C(55)	H(41)	119.4
C(51)	C(56)	H(48)	118.8	C(55)	C(56)	H(48)	120.0
C(57)	C(58)	H(42)	120.8	C(59)	C(58)	H(42)	118.7
C(58)	C(59)	H(43)	119.3	C(60)	C(59)	H(43)	119.8
C(40)	C(60)	H(44)	122.0	C(59)	C(60)	H(44)	118.4
C(40)	C(61)	H(46)	119.5	C(57)	C(61)	H(46)	119.0