



Supporting Information

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# **Palladium-Catalyzed 2-Pyridylmethyl Transfer Reactions from 2-(2-Pyridyl)ethanol Derivatives to Organic Halides Involving Chelation-Assisted Cleavage of Unstrained $sp^3C-sp^3C$ Bonds**

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## **Instrumentation and Chemicals**

$^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}$  NMR (125 MHz) spectra were taken on Varian UNITY INOVA 500 spectrometers and were recorded in  $\text{CDCl}_3$ . Chemical shifts ( $\delta$ ) are in parts per million relative to tetramethylsilane at 0.00 ppm for  $^1\text{H}$  and relative to residual  $\text{CHCl}_3$  at 77.0 ppm for  $^{13}\text{C}$  unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F<sub>254</sub>. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene and xylene were purchased from Wako Pure Chemical Co. and stored over slices of sodium. Triphenylphosphine and cesium carbonate were purchased from Wako Pure Chemical Co. Tricyclohexylphosphine was purchased from Strem. Palladium trifluoroacetate was from Aldrich Chemicals. All reactions were carried out under argon atmosphere. Preparations of pyridyl alcohols **1a** and **1d** and pyrazinyl alcohol **1b** are shown below. Alcohol **1c** was prepared by the benzylation of diisopropyl ketone with benzylmagnesium chloride.

## Experimental Procedure

### Synthesis of 2,4-dimethyl-3-(2-pyridylmethyl)-3-pentanol (**1a**)

Butyllithium (1.6 M in hexane, 13 mL, 20 mmol) was slowly added to a solution of 2-picoline (2.0 mL, 20 mmol) in tetrahydrofuran (20 mL) at  $-30\text{ }^{\circ}\text{C}$  and the reaction mixture was stirred for 30 min. Diisopropyl ketone (3.4 mL, 24 mmol) was then added, the reaction mixture was stirred for 2 h at ambient temperature. Water (30 mL) was added, and the product was extracted with ethyl acetate (20 mL  $\times$  3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. Silica gel column purification (hexane : ethyl acetate = 3 : 1) gave the pyridyl alcohol **1a** (3.5 g, 17 mmol) in 85% yield.

### Synthesis of 2,4-dimethyl-3-(2-pyrazinyl)-3-pentanol (**1b**)

Butyllithium (1.7 M in hexane, 1.8 mL, 3.1 mmol) was slowly added to a solution of diisopropylamine (0.44 mL, 3.2 mmol) in tetrahydrofuran (3.0 mL), and the mixture was stirred for an additional 10 min at  $0\text{ }^{\circ}\text{C}$ . After the mixture was cooled to  $-30\text{ }^{\circ}\text{C}$ , 2-methylpyrazine (0.28 mL, 3.0 mmol) was added and the mixture was stirred for 30 min. Diisopropyl ketone (0.51 mL, 3.6 mmol) was then added, and the reaction mixture was stirred for 2 h at ambient temperature. Water (10 mL) was added, and the product was extracted with ethyl acetate (10 mL  $\times$  3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. Silica gel column purification (hexane : ethyl acetate = 3 : 1) gave the pyrazinyl alcohol **1b** (0.40 g, 1.9 mmol) in 64% yield. Alcohol **1f** was prepared in a similar fashion.

### Typical Procedure for Palladium-catalyzed 2-Pyridylmethyl Transfer to Aryl Halides

Cesium carbonate (0.32 g, 0.97 mmol) was placed in a 30-mL two-necked reaction flask equipped with a Dimroth condenser. The cesium carbonate was dried in vacuo with heating with a hair dryer for 2 min. The flask was then filled with argon by using the standard Schlenk technique. Palladium trifluoroacetate (13.4 mg, 0.040 mmol), tricyclohexylphosphine (0.5 M in toluene, 0.16 mL, 0.080 mmol), xylene (1.6 mL), pyridyl alcohol **1a** (0.17 g, 0.81 mmol), and chlorobenzene (**2a**, 0.11 g, 0.97 mmol) were sequentially added at room temperature. The resulting mixture was heated at reflux for 6 h. After the mixture was cooled to room temperature, water (10 mL) was added. The product was extracted with ethyl acetate (10 mL  $\times$  3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. Silica gel column purification (hexane : ethyl acetate = 5 : 1) gave 2-benzylpyridine (**3a**, 0.12 g, 0.71 mmol) in 88% yield.

## Characterization Data for Compounds

**2,4-Dimethyl-3-(2-pyridylmethyl)-3-pentanol (1a):** IR (neat) 750, 1011, 1029, 1440, 1569, 1596, 2878, 2963, 3328  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.89 (d,  $J = 7.0$  Hz, 6H), 0.90 (d,  $J = 7.0$  Hz, 6H), 1.92 (sep,  $J = 7.0$  Hz, 2H), 2.91 (s, 2H), 6.37 (bs, 1H), 7.11–7.14 (m, 1H), 7.18 (d,  $J = 8.0$  Hz, 1H), 7.60 (ddd,  $J = 8.0, 8.0, 2.0$  Hz, 1H), 8.44 (d,  $J = 5.0$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.0, 18.3, 35.3, 38.1, 78.2, 121.1, 124.7, 136.9, 147.9, 161.9. Found: C, 75.55; H, 10.03; N, 6.96%. Calcd for  $\text{C}_{13}\text{H}_{21}\text{NO}$ : C, 75.32; H, 10.21; N, 6.76%.

**2,4-Dimethyl-3-pyrazinylmethyl-3-pentanol (1b):** IR (neat) 1024, 1475, 1527, 2880, 2963, 3419  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.90 (d,  $J = 7.0$  Hz, 6H), 0.92 (d,  $J = 7.0$  Hz, 6H), 1.94 (sep,  $J = 7.0$  Hz, 2H), 2.97 (s, 2H), 4.89 (bs, 1H), 8.44–8.46 (m, 2H), 8.52 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.1, 18.3, 35.3, 36.1, 78.6, 142.5, 142.7, 146.2, 157.3. Found: C, 69.37; H, 9.90; N, 13.40%. Calcd for  $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}$ : C, 69.19; H, 9.68; N, 13.45%.

**2,4-Dimethyl-3-[2-(6-methyl)pyridyl]methyl-3-pentanol (1c):** IR (neat) 792, 1010, 1033, 1460, 1579, 2962, 3329  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.87 (d,  $J = 7.0$  Hz, 6H), 0.91 (d,  $J = 7.0$  Hz, 6H), 1.91 (sep,  $J = 7.0$  Hz, 2H), 2.50 (s, 3H), 2.86 (s, 2H), 6.83 (bs, 1H), 6.96 (d,  $J = 7.5$  Hz, 1H), 6.97 (d,  $J = 7.5$  Hz, 1H), 7.48 (dd,  $J = 7.5, 7.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.2, 18.4, 24.4, 35.3, 38.1, 78.2, 120.7, 121.5, 137.2, 156.9, 161.2.

**3-[2-(6-Chloro)pyridyl]methyl-2,4-dimethyl-3-pentanol (1d):** IR (neat) 794, 1010, 1030, 1137, 1167, 1440, 1559, 1586, 2963, 3418  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.89 (d,  $J = 7.0$  Hz, 6H), 0.92 (d,  $J = 7.0$  Hz, 6H), 1.92 (sep,  $J = 7.0$  Hz, 2H), 2.91 (s, 2H), 5.10 (s, 1H), 7.13 (d,  $J = 7.5$  Hz, 1H), 7.17 (d,  $J = 7.5$  Hz, 1H), 7.57 (dd,  $J = 7.5, 7.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.1, 18.3, 35.3, 38.8, 78.3, 121.8, 123.2, 139.3, 150.1, 162.6. Found: C, 64.59; H, 8.34; N, 5.93%. Calcd for  $\text{C}_{13}\text{H}_{20}\text{ClNO}$ : C, 64.74; H, 8.34; N, 5.79%.

**3-Benzyl-2,4-dimethyl-3-pentanol (1e)<sup>1</sup>:** IR (neat) 703, 1001, 1453, 1496, 1603, 2963, 3502  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.93 (s, 6H), 1.01 (s, 6H), 1.16 (bs, 1H), 1.93 (sep,  $J = 7.0$  Hz, 2H), 2.84 (s, 2H), 7.20–7.29 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.0, 18.4, 34.6, 39.2, 77.5, 126.3, 128.3, 131.1, 138.5. Found: C, 81.41; H, 11.01%. Calcd for  $\text{C}_{14}\text{H}_{22}\text{O}$ : C, 81.50; H, 10.50%.

**2,4-Dimethyl-3-(4-pyridylmethyl)-3-pentanol (1f):** IR (neat) 997, 1025, 1313, 1378, 1456, 1602, 2971, 3336  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.93 (d,  $J = 7.0$  Hz, 6H), 0.99 (d,  $J = 7.0$  Hz, 6H), 1.93 (sep,  $J = 7.0$  Hz, 2H), 2.82 (s, 2H), 7.26 (d,  $J = 6.0$  Hz, 2H), 8.47 (d,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.0,

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<sup>1</sup> T. Imamoto, N. Takiyama, K. Nakamura, T. Hatajima, Y. Kamiya, *J. Am. Chem. Soc.* **1989**, *111*, 4392–4398.

18.2, 34.8, 39.0, 78.0, 126.5, 148.3, 149.5.

**2-Benzylpyridine (3a)**<sup>2</sup>: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.15 (s, 2H), 7.08 (dd, *J* = 5.0, 5.0 Hz, 2H), 7.19–7.22 (m, 1H), 7.24–7.30 (m, 4H), 7.54 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 8.53 (ddd, *J* = 4.5, 1.5, 1.0 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 44.8, 121.3, 123.2, 126.5, 128.7, 129.2, 136.6, 139.5, 149.4, 161.0.

**2-[(4-Trifluoromethylphenyl)methyl]pyridine (3b)**: IR (neat) 751, 1019, 1068, 1109, 1165, 1326, 1419, 1436, 1570, 1590, 1619 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.20 (s, 2H), 7.12–7.15 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.60 (dt, *J* = 7.5, 2.0 Hz, 1H), 8.55–8.58 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 44.5, 121.8, 123.3, 124.5 (q, *J* = 257 Hz), 125.6 (q, *J* = 3 Hz), 129.0 (q, *J* = 20 Hz), 129.5, 136.9, 143.7, 149.7, 160.0. Found: C, 65.63; H, 4.37; N, 6.02%. Calcd for C<sub>13</sub>H<sub>10</sub>F<sub>3</sub>N: C, 65.82; H, 4.25; N, 5.90%.

**Ethyl 4-(2-pyridyl)methylbenzoate (3c)**: IR (neat) 756, 1022, 1102, 1278, 1717, 2982 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.37 (t, *J* = 7.0 Hz, 3H), 4.21 (s, 2H), 4.35 (q, *J* = 7.0 Hz, 2H), 7.10–7.15 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.59 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 7.99 (ddd, *J* = 8.0, 1.0, 1.0 Hz, 2H), 8.55 (dd, *J* = 4.5, 1.0 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 14.4, 44.7, 60.9, 121.6, 123.3, 128.7, 129.1, 129.9, 136.8, 144.8, 149.6, 160.1, 166.6. Found: C, 74.52; H, 6.37; N, 5.82%. Calcd for C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub>: C, 74.67; H, 6.27; N, 5.81%.

**4-(2-Pyridyl)methylbenzonitrile (3d)**: IR (neat) 995, 1436, 1473, 1588, 1609, 2228, 3052 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.20 (s, 2H), 7.14–7.18 (m, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.63 (ddd, *J* = 9.5, 9.5, 2.0 Hz, 1H), 8.56 (ddd, *J* = 5.0, 1.0, 1.0 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 44.6, 110.3, 119.0, 121.9, 123.4, 129.9, 132.4, 137.0, 145.1, 149.7, 159.2. Found: C, 80.59; H, 5.39; N, 14.29%. Calcd for C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>: C, 80.39; H, 5.19; N, 14.42%.

**2-[(4-Methoxyphenyl)methyl]pyridine (3e)**: IR (neat) 1036, 1178, 1248, 1436, 1511, 1589, 1611, 2835, 2932 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.77 (s, 3H), 4.10 (s, 2H), 6.84–6.86 (m, 2H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.08–7.11 (m, 1H), 7.17–7.19 (m, 2H), 7.56 (ddd, *J* = 7.5, 2.0, 2.0 Hz, 1H), 8.53–8.55 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 43.9, 55.4, 114.1, 121.3, 123.1, 130.2, 131.7, 136.7, 149.4, 158.3, 161.5. Found: C, 78.53; H, 6.77; N, 6.76%. Calcd for C<sub>13</sub>H<sub>13</sub>NO: C, 78.36; H, 6.58; N, 7.03%.

**2-[(2-Methylphenyl)methyl]pyridine (3f)**: IR (neat) 745, 994, 1049, 1433, 1473, 1568, 1591, 2921, 3011 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.24 (s, 3H), 4.18 (s, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 7.10 (ddd, *J* = 8.0, 4.5, 0.5 Hz, 1H), 7.17–7.18 (m, 4H), 7.54 (ddd, *J* = 7.5, 7.5, 2.0 Hz, 1H), 8.55–8.56 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 19.9, 42.6, 121.3, 122.9, 126.3, 127.0, 130.4, 130.6, 136.7, 137.0, 137.7, 149.4, 160.8.

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<sup>2</sup> A. Flaherty, A. Trunkfield, W. Barton, *Org. Lett.* **2005**, 7, 4975–4978.

Found: C, 85.12; H, 7.28; N, 7.48%. Calcd for C<sub>13</sub>H<sub>13</sub>N: C, 85.21; H, 7.15; N, 7.64%.

**2-[(4-Ethenylphenyl)methyl]pyridine (3g):** IR (neat) 751, 994, 1435, 1473, 1511, 1588, 2923, 3007, 3084 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.13 (s, 2H), 5.20 (dd, *J* = 11.0, 1.0 Hz, 1H), 5.71 (dd, *J* = 17.5, 1.0 Hz, 1H), 6.69 (dd, *J* = 17.5, 11.0 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.57 (ddd, *J* = 8.5, 8.5, 2.0 Hz, 1H), 8.54–8.55 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 44.6, 113.5, 121.4, 123.2, 126.6, 129.4, 135.9, 136.7, 136.7, 139.3, 149.5, 161.0.

Found: C, 86.11; H, 6.70; N, 7.00%. Calcd for C<sub>14</sub>H<sub>13</sub>N: C, 86.12; H, 6.71; N, 7.17%.

**2-(2-Pyridylmethyl)pyridine (3h):** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.35 (s, 2H), 7.14 (dd, *J* = 8.0, 5.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.62 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 2H), 8.55–8.56 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 47.3, 121.7, 123.8, 136.8, 149.5, 159.5.

**2-(3-Methyl-2-butenyl)pyridine (3i):** IR (neat) 745, 1435, 1474, 1569, 1589, 2915, 2969 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.73 (s, 3H), 1.77 (s, 3H), 3.54 (d, *J* = 7.5 Hz, 2H), 5.41–5.44 (m, 1H), 7.09 (dd, *J* = 4.5, 2.0 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.59 (ddd, *J* = 7.5, 7.5, 2.0 Hz, 1H), 8.51–8.53 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 18.1, 26.0, 37.3, 121.1, 121.4, 122.6, 133.9, 136.6, 149.4, 161.7. Found: C, 81.62; H, 9.20%. Calcd for C<sub>10</sub>H<sub>13</sub>N: C, 81.59; H, 8.90%.

**1,3,5-Tri[(2-pyridyl)methyl]benzene (3j):** IR (neat) 749, 995, 1050, 1435, 1475, 1569, 1590, 2923, 3008 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.08 (s, 6H), 7.03 (s, 3H), 7.09–7.11 (m, 6H), 7.55 (ddd, *J* = 8.0, 2.0, 2.0 Hz, 3H), 8.52 (d, *J* = 5.0 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 44.7, 121.4, 123.4, 128.2, 136.7, 140.1, 149.4, 161.0. HRMS (DI-EI<sup>+</sup>) (*m/z*) Observed: 351.1743 ( $\Delta$  = +2.1 ppm). Calcd for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub> [M<sup>+</sup>]: 351.1735.

**Benzylpyrazine (3k):** IR (neat) 700, 748, 1018, 1057, 1403, 1496, 3030 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.18 (s, 2H), 7.23–7.34 (m, 5H), 8.41 (d, *J* = 2.5 Hz, 1H), 8.47 (s, 1H), 8.50–8.51 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 42.2, 127.0, 129.0, 129.2, 138.3, 142.6, 144.3, 145.0, 156.7. Found: C, 77.65; H, 5.95; N, 16.21%. Calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>: C, 77.62; H, 5.92; N, 16.46%.

**2-Benzyl-6-methylpyridine (3l):** IR (neat) 738, 1031, 1452, 1577, 1591, 2924, 3026 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.55 (s, 3H), 4.14 (s, 2H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 7.20–7.23 (m, 1H), 7.25–7.32 (m, 4H), 7.45 (t, *J* = 7.5 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 24.7, 44.9, 120.1, 120.9, 126.5, 128.7, 129.4, 136.9, 139.8, 158.0, 160.5.

**2-Benzyl-6-chloropyridine (3m):** IR (neat) 699, 780, 1134, 1437, 1583 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.14 (s, 2H), 6.98 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.16 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.23–7.27 (m, 3H),

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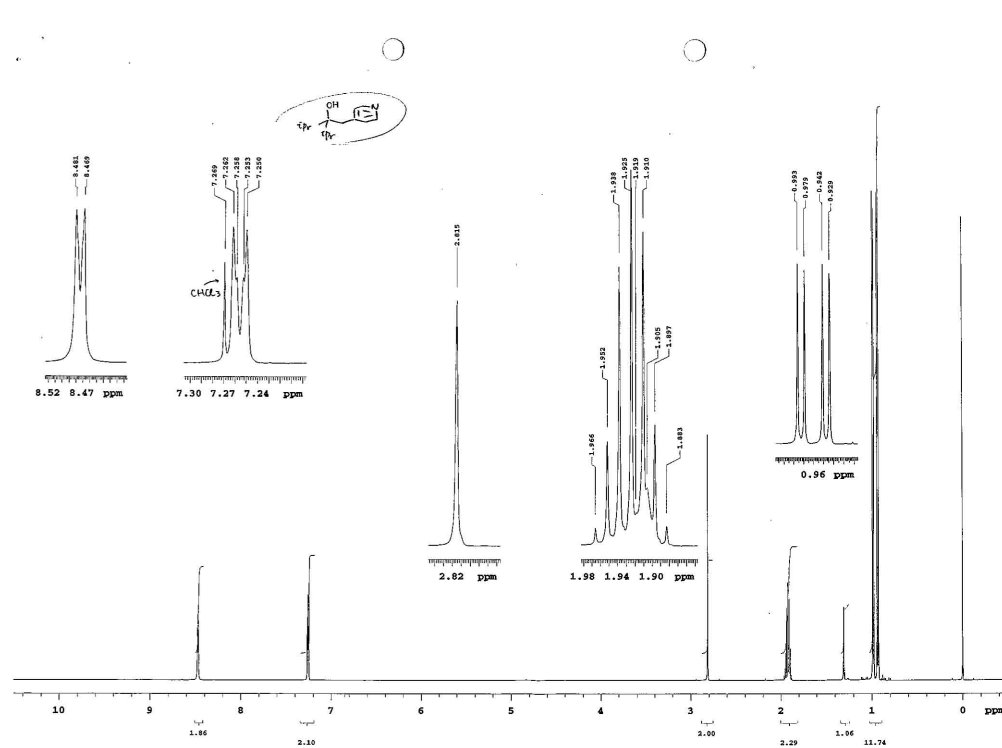
<sup>3</sup> G. Dyker, O. Muth, *Eur. J. Org. Chem.* **2004**, 4319–4322.

7.30–7.33 (m, 2H), 7.52 (t,  $J = 7.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  44.4, 109.9, 121.6, 121.9, 126.8, 128.8, 129.4, 138.8, 139.2, 162.3.

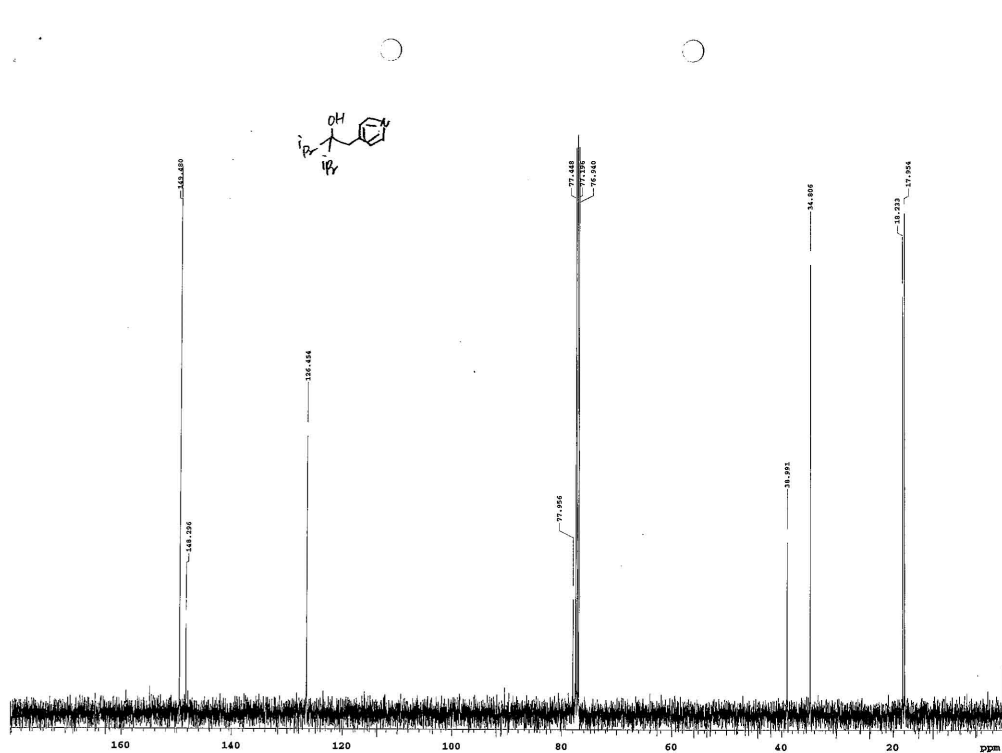
**2-Chloro-*N,N*-di[2-(2-methyl)propenyl]aniline (8):** IR (neat) 754, 898, 1040, 1120, 1442, 1480, 1588, 1652, 2821, 2971, 3073  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.72 (s, 6H), 3.57 (s, 4H), 4.84 (s, 2H), 4.93 (s, 2H), 6.93 (ddd,  $J = 7.5, 1.5$  Hz, 1H), 7.07 (dd,  $J = 7.5, 1.5$  Hz, 1H), 7.15 (ddd,  $J = 7.5, 1.5$  Hz, 1H), 7.35 (ddd,  $J = 7.5, 1.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.8, 58.8, 113.3, 123.5, 123.7, 126.9, 130.0, 130.8, 142.9, 148.1. Found: C, 71.21; H, 7.64; N, 5.98%. Calcd for  $\text{C}_{14}\text{H}_{18}\text{ClN}$ : C, 71.32; H, 7.70; N, 5.94%.

**3-Methyl-1-(2-methyl-2-propenyl)-3-[2-(2-pyridyl)ethyl]-2,3-dihydroindole (9):** IR (neat) 741, 1023, 1436, 1489, 1590, 1606, 2818, 2919  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.38 (s, 3H), 1.78 (s, 3H), 1.98 (dt,  $J = 12.5, 5.0$  Hz, 1H), 2.07 (dt,  $J = 12.5, 5.0$  Hz, 1H), 2.66 (dt,  $J = 12.5, 5.0$  Hz, 1H), 2.85 (dt,  $J = 12.5, 5.0$  Hz, 1H), 3.08 (d,  $J = 9.0$  Hz, 1H), 3.34 (d,  $J = 9.0$  Hz, 1H), 3.54 (d,  $J = 15.0$  Hz, 1H), 3.64 (d,  $J = 15.0$  Hz, 1H), 4.88 (s, 1H), 4.96 (s, 1H), 6.48 (d,  $J = 8.0$  Hz, 1H), 6.67 (ddd,  $J = 8.0, 8.0, 1.0$  Hz, 1H), 7.03–7.08 (m, 4H), 7.55 (ddd,  $J = 8.0, 8.0, 2.0$  Hz, 1H), 8.50 (dd,  $J = 5.5, 2.0$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.6, 26.3, 34.1, 41.1, 43.7, 55.6, 65.7, 106.9, 112.2, 117.5, 121.1, 122.6, 122.9, 127.8, 136.5, 137.1, 142.4, 149.4, 151.9, 162.5. Found: C, 82.19; H, 8.42; N, 9.69%. Calcd for  $\text{C}_{20}\text{H}_{24}\text{N}_2$ : C, 82.15; H, 8.27; N, 9.58%.

**Figure S1.**  $^1\text{H}$  NMR spectrum of **1f**



**Figure S2.**  $^{13}\text{C}$  NMR spectrum of **1f**





The image displays two NMR spectra for compound 3a. The top spectrum is a  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$ , showing peaks for aromatic protons (7.1-7.6 ppm) and a methine proton (8.4 ppm). The bottom spectrum is a  $^{13}\text{C}$  NMR spectrum, showing peaks for aromatic carbons (124-134 ppm) and a methine carbon (141.5 ppm).

**$^1\text{H}$  NMR Spectrum (Top):**

- Chemical structure: c1ccc2c(c1)c(c3ccccc3)nc2 (3a)
- Peak list (ppm): 8.411, 8.408, 8.397, 8.395, 8.393, 8.387, 8.385, 8.382, 8.356.
- Integration: 1H (8.4 ppm), 1H (7.5 ppm), 4H (7.3 ppm), 1H (7.2 ppm), 2H (7.1 ppm).

**$^{13}\text{C}$  NMR Spectrum (Bottom):**

- Chemical structure: c1ccc2c(c1)c(c3ccccc3)nc2 (3a)
- Peak list (ppm): 134.15, 133.95, 133.75, 133.55, 133.35, 133.15, 132.95, 132.75, 132.55, 132.35, 132.15, 131.95, 131.75, 131.55, 131.35, 131.15, 130.95, 130.75, 130.55, 130.35, 130.15, 129.95, 129.75, 129.55, 129.35, 129.15, 128.95, 128.75, 128.55, 128.35, 128.15, 127.95, 127.75, 127.55, 127.35, 127.15, 126.95, 126.75, 126.55, 126.35, 126.15, 125.95, 125.75, 125.55, 125.35, 125.15, 124.95, 124.75, 124.55, 124.35, 124.15, 123.95, 123.75, 123.55, 123.35, 123.15, 122.95, 122.75, 122.55, 122.35, 122.15, 121.95, 121.75, 121.55, 121.35, 121.15, 120.95, 120.75, 120.55, 120.35, 120.15, 119.95, 119.75, 119.55, 119.35, 119.15, 118.95, 118.75, 118.55, 118.35, 118.15, 117.95, 117.75, 117.55, 117.35, 117.15, 116.95, 116.75, 116.55, 116.35, 116.15, 115.95, 115.75, 115.55, 115.35, 115.15, 114.95, 114.75, 114.55, 114.35, 114.15, 113.95, 113.75, 113.55, 113.35, 113.15, 112.95, 112.75, 112.55, 112.35, 112.15, 111.95, 111.75, 111.55, 111.35, 111.15, 110.95, 110.75, 110.55, 110.35, 110.15, 109.95, 109.75, 109.55, 109.35, 109.15, 108.95, 108.75, 108.55, 108.35, 108.15, 107.95, 107.75, 107.55, 107.35, 107.15, 106.95, 106.75, 106.55, 106.35, 106.15, 105.95, 105.75, 105.55, 105.35, 105.15, 104.95, 104.75, 104.55, 104.35, 104.15, 103.95, 103.75, 103.55, 103.35, 103.15, 102.95, 102.75, 102.55, 102.35, 102.15, 101.95, 101.75, 101.55, 101.35, 101.15, 100.95, 100.75, 100.55, 100.35, 100.15, 99.95, 99.75, 99.55, 99.35, 99.15, 98.95, 98.75, 98.55, 98.35, 98.15, 97.95, 97.75, 97.55, 97.35, 97.15, 96.95, 96.75, 96.55, 96.35, 96.15, 95.95, 95.75, 95.55, 95.35, 95.15, 94.95, 94.75, 94.55, 94.35, 94.15, 93.95, 93.75, 93.55, 93.35, 93.15, 92.95, 92.75, 92.55, 92.35, 92.15, 91.95, 91.75, 91.55, 91.35, 91.15, 90.95, 90.75, 90.55, 90.35, 90.15, 89.95, 89.75, 89.55, 89.35, 89.15, 88.95, 88.75, 88.55, 88.35, 88.15, 87.95, 87.75, 87.55, 87.35, 87.15, 86.95, 86.75, 86.55, 86.35, 86.15, 85.95, 85.75, 85.55, 85.35, 85.15, 84.95, 84.75, 84.55, 84.35, 84.15, 83.95, 83.75, 83.55, 83.35, 83.15, 82.95, 82.75, 82.55, 82.35, 82.15, 81.95, 81.75, 81.55, 81.35, 81.15, 80.95, 80.75, 80.55, 80.35, 80.15, 79.95, 79.75, 79.55, 79.35, 79.15, 78.95, 78.75, 78.55, 78.35, 78.15, 77.95, 77.75, 77.55, 77.35, 77.15, 76.95, 76.75, 76.55, 76.35, 76.15, 75.95, 75.75, 75.55, 75.35, 75.15, 74.95, 74.75, 74.55, 74.35, 74.15, 73.95, 73.75, 73.55, 73.35, 73.15, 72.95, 72.75, 72.55, 72.35, 72.15, 71.95, 71.75, 71.55, 71.35, 71.15, 70.95, 70.75, 70.55, 70.35, 70.15, 69.95, 69.75, 69.55, 69.35, 69.15, 68.95, 68.75, 68.55, 68.35, 68.15, 67.95, 67.75, 67.55, 67.35, 67.15, 66.95, 66.75, 66.55, 66.35, 66.15, 65.95, 65.75, 65.55, 65.35, 65.15, 64.95, 64.75, 64.55, 64.35, 64.15, 63.95, 63.75, 63.55, 63.35, 63.15, 62.95, 62.75, 62.55, 62.35, 62.15, 61.95, 61.75, 61.55, 61.35, 61.15, 60.95, 60.75, 60.55, 60.35, 60.15, 59.95, 59.75, 59.55, 59.35, 59.15, 58.95, 58.75, 58.55, 58.35, 58.15, 57.95, 57.75, 57.55, 57.35, 57.15, 56.95, 56.75, 56.55, 56.35, 56.15, 55.95, 55.75, 55.55, 55.35, 55.15, 54.95, 54.75, 54.55, 54.35, 54.15, 53.95, 53.75, 53.55, 53.35, 53.15, 52.95, 52.75, 52.55, 52.35, 52.15, 51.95, 51.75, 51.55, 51.35, 51.15, 50.95, 50.75, 50.55, 50.35, 50.15, 49.95, 49.75, 49.55, 49.35, 49.15, 48.95, 48.75, 48.55, 48.35, 48.15, 47.95, 47.75, 47.55, 47.35, 47.15, 46.95, 46.75, 46.55, 46.35, 46.15, 45.95, 45.75, 45.55, 45.35, 45.15, 44.95, 44.75, 44.55, 44.35, 44.15, 43.95, 43.75, 43.55, 43.35, 43.15, 42.95, 42.75, 42.55, 42.35, 42.15, 41.95, 41.75, 41.55, 41.35, 41.15, 40.95, 40.75, 40.55, 40.35, 40.15, 39.95, 39.75, 39.55, 39.35, 39.15, 38.95, 38.75, 38.55, 38.35, 38.15, 37.95, 37.75, 37.55, 37.35, 37.15, 36.95, 36.75, 36.55, 36.35,

13C NMR spectrum of 2,2'-biphenyl. The spectrum shows peaks at 141.093, 140.292, 139.546, 136.624, 135.159, 134.463, 132.454, 131.179, 131.115, 77.426, 77.000, 76.584, and 44.771 ppm. A chemical structure of 2,2'-biphenyl is shown above the spectrum, circled and labeled '20'.

Figure S5.  $^1\text{H}$  NMR spectrum of **3h**

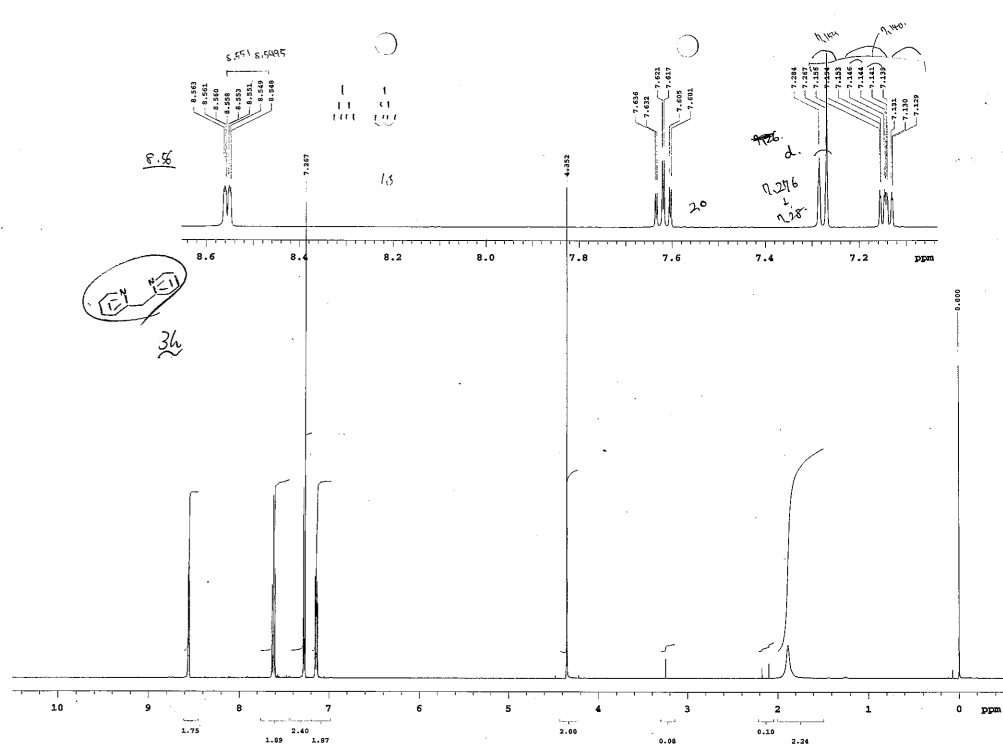


Figure S6.  $^{13}\text{C}$  NMR spectrum of **3h**

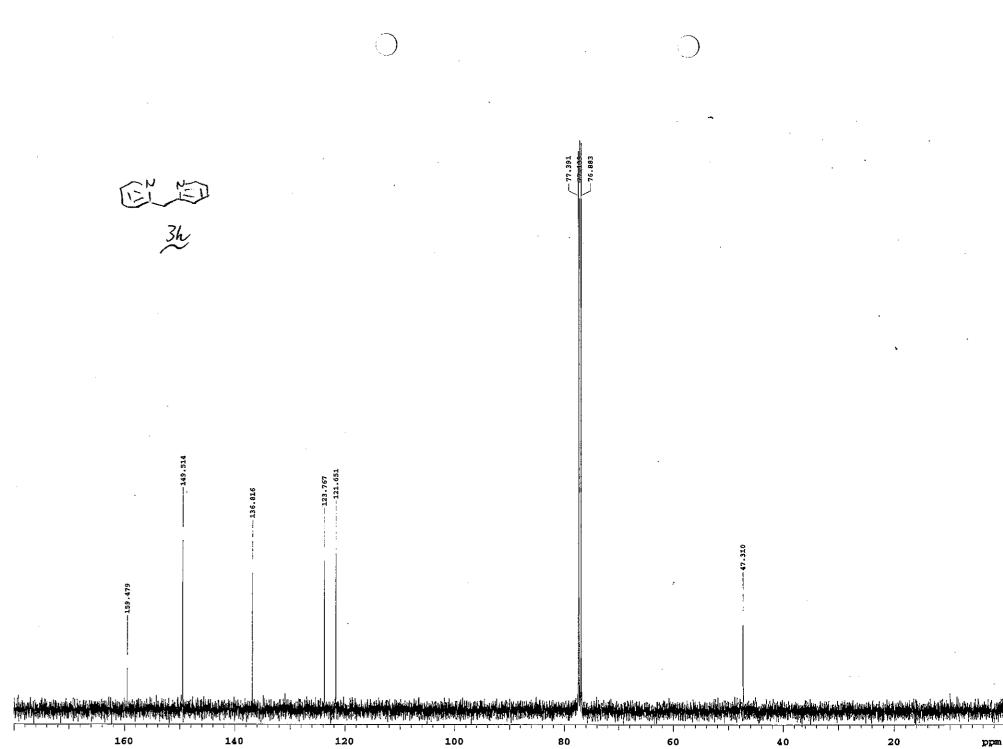


Figure S7.  $^1\text{H}$  NMR spectrum of **3j**

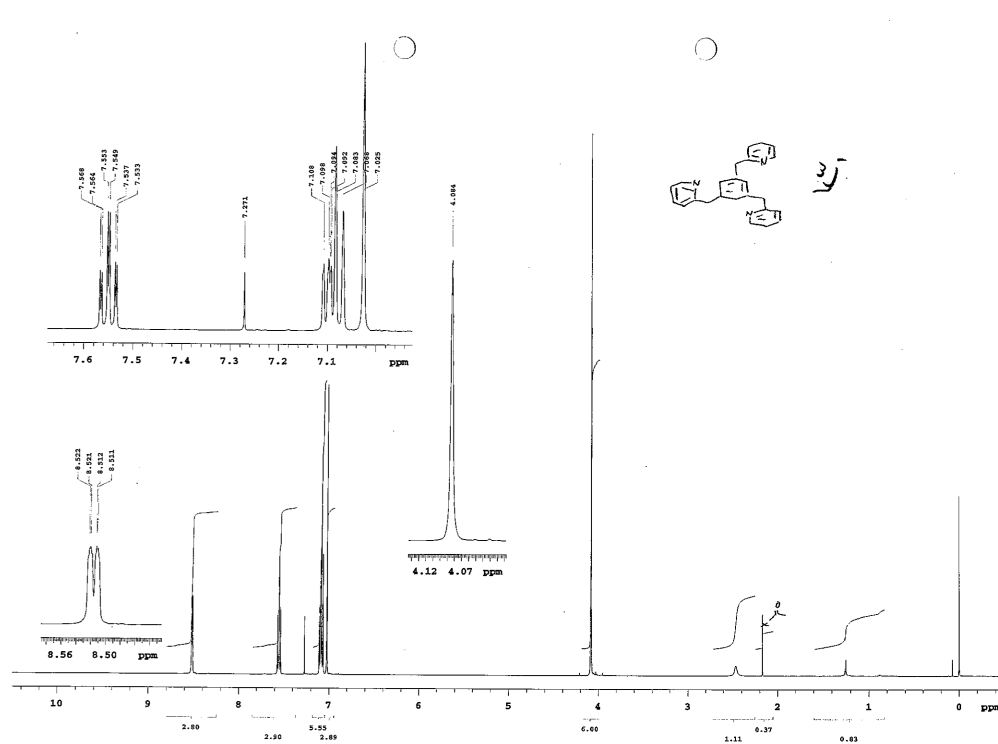


Figure S8.  $^{13}\text{C}$  NMR spectrum of **3j**

