Supporting Information

Indium-Mediated One-Pot Three-Component Reaction of Aromatic Amines, Enol Ethers and Allylic Bromides

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General Methods

All reactions were performed under argon atmosphere. ¹H and ¹³C NMR spectra were measured on Bruker Avance 300 spectrometer. Chemical shift values were recorded in parts per million using the residual undeuterated solvent as an internal reference and coupling constants in hertz. Infrared spectra (IR) were recorded on a Perkin Elmer 16F PC FT-IR spectrophotometer and frequencies are given in reciprocal centimeters. Electron-impact mass spectra (EIMS) were recorded in the form of *m/z* on a Agilent GC-MSD (6850-5973) system. High-resolution mass spectral analyses were carried out at the Korea Basic Science Institute, Seoul, Korea. Analytical thin layer chromatographies were carried out by precoated silica gel (Merck Kiese 60F₂₅₄ layer thickness 0.25 mm). Flash column chromatography was performed on silica gel grade 230-400 mesh (Merck Kieselgel 60 Art 9385). All commercial reagent were used without any further purification. Anhydrous THF was purchased from Aldrich Chem. Co.

Typical Experimental Procedure

A mixture of indium (2 mmol) and allylic bromide (3 mmol) in THF (2 mL) was stirred for 1 h at room temperature under argon. Aromatic amine (1 mmol) and enol ether (2 mmol) were added to the reaction mixture. After stirring for 2 h, the reaction was quenched with saturated aqueous ammonium chloride (5 mL). The whole mixture was extracted with EtOAc (3×20 mL). The combined organic layer was washed with water (20mL), dried over MgSO₄, and evaporated. A pure product was obtained by flash column chromatography on silica gel (*n*-hexane/EtOAc, 20:1).

***N*-(1-Methyl-3-butenyl)aniline** (Table 1, entry 1): 91%; IR (neat) ν 3404, 3052, 2972, 2926, 1640, 1602, 1508, 1452, 1430, 1376, 1318, 1180, 1256, 1154, 994, 916, 748, 692 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.19-7.13 (m, 2H), 6.70-6.64 (m, 1H), 6.59-6.56 (m, 2H), 5.89-5.75 (m, 1H), 5.13-5.06 (m, 2H), 3.54 (sxt, 1H, $J = 6.0$ Hz), 2.39-2.29 (m, 1H), 2.26-2.16 (m, 1H), 1.19 (d, 3H, $J = 6.0$ Hz); ^{13}C NMR (CDCl_3) δ 147.3, 134.9, 129.2, 117.5, 117.0, 113.2, 47.9, 40.8, 20.3. MS (EI, 70 eV): m/z (%) 161 (M^+ , 7.8), 120 (100), 104 (4.3), 91 (3.4), 77 (12.0); HRMS (EI): calcd for $\text{C}_{11}\text{H}_{15}\text{N}$ (M^+) 161.1204, found 161.1204.

4-Fluoro-*N*-(1-methyl-3-butenyl)aniline (Table 2, entry 1): 88%; IR (neat) ν 3406, 3076, 2970, 2926, 1640, 1612, 1510, 1456, 1402, 1376, 1314, 1220, 1156, 1098, 994, 916, 820, 770 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.91-6.83 (m, 2H), 6.55-6.48 (m, 2H), 5.89-5.75 (m, 1H), 5.11-5.05 (m, 2H), 3.47 (sxt, 1H, $J = 6.0$ Hz), 2.37-2.28 (m, 1H), 2.25-2.16 (m, 1H), 1.18 (d, 3H, $J = 6.0$ Hz); ^{13}C NMR (CDCl_3) δ 157.1, 154.0, 143.7, 134.8, 117.7, 115.8, 115.5, 114.3, 114.2, 48.6, 40.7, 20.2; MS (EI, 70 eV): m/z (%) 179 (M^+ , 7.8), 138 (100), 122 (6.2), 109 (5.8), 95 (10.4), 83 (7.9), 75 (6.2); HRMS (EI) calcd for $\text{C}_{11}\text{H}_{14}\text{FN}$ (M^+) 179.1110, found 179.1103.

4-Chloro-*N*-(1-methyl-3-butenyl)aniline (Table 2, entry 2): 82%; IR (neat) ν 3412, 3076, 2972, 2926, 1640, 1600, 1500, 1450, 1400, 1376, 1316, 1294, 1252, 1178, 1158, 1092, 994, 918, 814 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.12-7.07 (m, 2H), 6.52-6.48 (m, 2H), 5.87-5.74 (m, 1H), 5.12-5.06 (m, 2H), 3.49 (sxt, 1H, $J = 6.3$ Hz), 2.36-2.16 (m, 2H), 1.18 (d, 3H, $J = 6.3$ Hz); ^{13}C NMR (CDCl_3) δ 145.9, 134.6, 129.0, 121.4, 117.7, 114.3, 48.1, 40.6, 20.1; MS (EI, 70 eV) m/z (%) 197 ($\text{M}^+ + 2$, 4.8), 195 (M^+ , 15.0), 153 (100), 138 (6.2), 119 (34.3), 111 (13.4), 99 (7.7), 91 (10.0), 75 (13.1); HRMS (EI) calcd for $\text{C}_{11}\text{H}_{14}\text{ClN}$ (M^+) 195.0815, found 195.0813.

2-Methoxy-*N*-(1-methyl-3-butenyl)aniline (Table 2, entry 3): 81%; IR (neat) ν 3418, 3072, 2962, 2930, 2832, 1640, 1602, 1514, 1456, 1428, 1376, 1348, 1302, 1250, 1220, 1178, 1162, 1112, 1052, 1030, 994, 914, 734 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.88-6.83 (m, 1H), 6.77-6.74 (m, 1H), 6.66-6.59 (m, 2H), 5.91-5.77 (m, 1H), 5.13-5.06 (m, 2H), 3.82 (s, 3H), 3.54 (sxt, 1H, $J = 6.6$ Hz), 2.44-2.35 (m, 1H), 2.26-2.16 (m, 1H), 1.21 (d, 3H, $J = 6.6$ Hz); ^{13}C NMR (CDCl_3) δ 146.8, 137.2, 135.1, 121.2, 117.2, 116.0, 110.2, 109.5, 55.3, 47.7, 40.9, 20.3; MS (EI, 70 eV) m/z (%) 191 (M^+ , 12.6), 150 (100), 134 (7.3), 120 (53.8), 106 (2.6), 93 (5.2), 77 (6.3); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{17}\text{NO}$ (M^+) 191.1310, found 191.1318.

3-Methoxy-*N*-(1-methyl-3-butenyl)aniline (Table 2, entry 4): 85%;

IR (neat) ν 3394, 3074, 2962, 2920, 2834, 1638, 1614, 1510, 1494, 1460, 1342, 1302, 1260, 1210, 1162, 1052, 994, 914, 828, 754, 688 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.06 (t, 1H, $J = 8.4$ Hz), 6.26-6.13 (m, 3H), 5.89-5.75 (m, 1H), 5.12-5.07 (m, 2H), 3.75 (s, 3H), 3.52 (sxt, 1H, $J = 6.6$ Hz), 2.38-2.29 (m, 1H), 2.25-2.16 (m, 1H), 1.18 (d, 3H, $J = 6.6$ Hz); ^{13}C NMR (CDCl_3) δ 160.8, 148.7, 134.9, 129.9, 117.5, 106.4, 102.0, 99.2, 55.0, 47.9, 40.8, 20.3; MS (EI, 70 eV) m/z (%) 191 (M^+ , 10.1), 150 (100), 135 (12.9), 118 (3.9), 107 (10.2), 92 (7.3), 77 (7.4); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{17}\text{NO}$ (M^+) 191.1310, found 191.1312.

4-Methoxy-*N*-(1-methyl-3-butenyl)aniline (Table 2, entry 5): 94%;

IR (neat) ν 3386, 2926, 2830, 1640, 1512, 1464, 1236, 1180, 1158, 1040, 994, 914, 818, 756 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.80-6.74 (m, 2H), 6.59-6.54 (m, 2H), 5.89-5.75 (m, 1H), 5.11-5.05 (m, 2H), 3.73 (s, 3H), 3.46 (sxt, 1H, $J = 6.0$ Hz), 2.37-2.28 (m, 1H), 2.24-2.14 (m, 1H), 1.17 (d, 3H, $J = 5.7$ Hz); ^{13}C NMR (CDCl_3) δ 152.9, 141.5, 135.0, 117.5, 114.9, 114.8, 55.7, 48.9, 40.8, 20.3; MS (EI, 70 eV) m/z (%) 191 (M^+ , 18.8), 150 (100), 135 (17.0), 122 (7.8), 108 (9.5), 99 (7.7), 92 (4.5), 80 (6.2), 77 (6.0); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{17}\text{NO}$ (M^+) 191.1310, found 191.1304.

4-(1-Methyl-3-butenylamino)benzonitrile (Table 2, entry 6): 5%; IR

(neat) ν 3356, 3076, 2970, 2924, 2210, 1640, 1606, 1522, 1450, 1376, 1340, 1274, 1172, 994, 918, 822 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.43-7.39 (m, 2H), 6.55-6.51 (m, 2H), 5.87-5.73 (m, 1H), 5.15-5.06 (m, 2H), 3.61 (qui, 1H, $J = 6.6$ Hz), 2.39-2.22 (m, 2H), 1.23 (d, 3H, $J = 6.6$ Hz); ^{13}C NMR (CDCl_3) δ 150.4, 134.0, 133.8, 120.5, 118.3, 112.5, 98.3, 47.5, 40.5, 20.0; MS (EI, 70 eV) m/z (%) 186 (M^+ , 3.6), 145 (100), 128 (5.8), 117 (5.1), 102 (12.7), 90 (6.8), 76 (4.8); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2$ (M^+) 186.1157, found 186.1151.

***N*-(1-Methyl-3-butenyl)-4-aminobiphenyl** (Table 2, entry 7):

94%; IR (neat) ν 3404, 3024, 2960, 2924, 1640, 1612, 1522, 1490, 1442, 1406, 1376, 1322, 1298, 1274, 1252, 1190, 1158, 994, 914, 824, 762, 718, 696 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.63 (d, 2H, $J = 8.4$ Hz), 7.53-7.44 (m, 4H), 7.36-7.30 (m, 1H), 6.74 (d, 2H, $J = 8.4$ Hz), 6.00-5.86 (m, 1H), 5.23-5.18 (m, 2H), 3.68 (sxt, 1H, $J = 6.6$ Hz), 2.50-2.41 (m, 1H), 2.36-2.28 (m, 1H), 1.31 (d, 3H, $J = 6.6$ Hz); ^{13}C NMR (CDCl_3) δ 146.8, 141.2, 134.8, 129.9, 128.6, 127.9, 126.2, 125.9, 117.6, 113.4, 47.9, 40.8, 20.3; MS (EI, 70 eV) m/z (%) 237 (M^+ , 11.1), 196 (100), 180 (8.4), 168 (4.6), 152 (20.2), 141 (5.7), 127 (2.4), 115 (7.0), 98 (3.6), 77 (2.7); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{19}\text{N}$ (M^+) 237.1517, found 237.1513.

***N*-(1-Methyl-3-butenyl)-5-aminoindan** (Table 2, entry 8): 92%; IR (neat) ν 3402, 3074, 2956, 2842, 1638, 1618, 1584, 1500, 1438, 1424, 1374, 1328, 1292, 1250, 1212, 1164, 1088, 994, 912, 842, 804 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.01 (d, 1H, $J = 8.4$ Hz), 6.51 (d, 1H, $J = 1.5$ Hz), 6.40 (dd, 1H, $J = 8.4, 2.1$ Hz), 5.90-5.76 (m, 1H), 5.13-5.06 (m, 2H), 3.51 (sxt, 1H, $J = 6.6$ Hz), 2.80 (q, 4H, $J = 7.8$ Hz), 2.38-2.29 (m, 1H), 2.25-2.15 (m, 1H), 2.02 (qui, 2H, $J = 7.8$ Hz), 1.18 (d, 6.6 Hz); ^{13}C NMR (CDCl_3) δ 146.1, 145.4, 135.1, 132.8, 124.7, 117.3, 111.8, 109.5, 48.3, 40.9, 33.1, 31.9, 20.4; MS (EI, 70 eV) m/z (%) 201 (M^+ , 14.5), 160 (100), 144 (5.7), 132 (13.0), 115 (22.8), 105 (4.7), 91 (12.3), 77 (6.4); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{19}\text{N}$ (M^+) 201.1517, found 201.1514.

***N*-(1-Methyl-3-butenyl)-1,4-benzodioxin-6-amine** (Table 2, entry 9): 88%; IR (neat) ν 3392, 2972, 2926, 1624, 1594, 1508, 1456, 1328, 1294, 1278, 1242, 1210, 1176, 1070, 914, 884, 830, 796 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.68 (d, 1H, $J = 8.4$ Hz), 6.55-6.48 (m, 2H), 5.89-5.75 (m, 1H), 5.11-5.05 (m, 2H), 4.23-4.15 (m, 4H), 3.42 (sxt, 1H, $J = 6.0$ Hz), 2.37-2.27 (m, 1H), 2.23-2.14 (m, 1H), 1.16 (d, 3H, $J = 6.0$ Hz); ^{13}C NMR (CDCl_3) δ 144.0, 142.3, 135.4, 134.9, 117.6, 117.4, 107.4, 102.1, 64.7, 64.1, 48.7, 40.8, 20.3; MS (EI, 70 eV) m/z (%) 219 (M^+ , 10.4), 178 (100), 150 (3.8), 136 (4.9), 122 (8.6), 107 (3.1), 93 (2.4), 79 (9.4), 77 (2.2); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$ (M^+) 219.1259, found 219.1262.

4-(Phenylamino)-6-hepten-1-ol (Table 3, entry 1): 72%; IR (neat) ν 3354, 3052, 2930, 1640, 1602, 1504, 1432, 1320, 1256, 1180, 1056, 914, 748, 692 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.24-7.12 (m, 2H), 6.71-6.66 (m, 1H), 6.61-6.57 (m, 2H), 5.87-5.73 (m, 1H), 5.10-5.04 (m, 2H), 3.61 (t, 2H, $J = 6.0$ Hz), 3.48-3.40 (m, 1H), 2.29 (t, 2H, $J = 6.6$ Hz), 1.72-1.45 (m, 4H); ^{13}C NMR (CDCl_3) δ 147.4, 134.6, 129.3, 117.7, 117.3, 113.5, 62.7, 52.5, 38.6, 30.8, 29.3; MS (EI, 70 eV) m/z (%) 205 (M^+ , 6.1), 164 (100), 146 (40.2), 130 (22.7), 118 (25.5), 104 (38.7), 91 (12.9), 77 (39.1); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{19}\text{NO}$ (M^+) 205.1467, found 205.1475.

***N*-(1-Ethyl-3-butenyl)aniline** (Table 3, entry 2): 17%; IR (neat) ν 3408, 2964, 2930, 1640, 1602, 1506, 1460, 1430, 1320, 1278, 1180, 1154, 994, 914, 748, 692 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.18-7.12 (m, 2H), 6.68-6.63 (m, 1H), 6.59-6.55 (m, 2H), 5.89-5.75 (m, 1H), 5.12-5.06 (m, 2H), 3.36 (qui, 1H, $J = 6.0$ Hz), 2.32-2.26 (m, 2H), 1.65-1.47 (m, 2H), 0.95 (t, 3H, $J = 7.8$ Hz); ^{13}C NMR (CDCl_3) δ 147.8, 135.0, 129.2, 117.4, 116.8, 113.2, 53.7, 38.1, 26.9, 10.2; MS (EI, 70 eV) m/z (%) 175 (M^+ , 7.4), 146 (3.7), 134 (100), 118 (10.4), 104 (7.9), 92 (4.2), 77 (11.2); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{17}\text{N}$ (M^+) 175.1361, found 175.1369.

***N*-(1,1-Dimethyl-3-butenyl)aniline** (Table 3, entry 3): 52%; IR (neat) ν 3406, 3054, 2974, 2928, 1638, 1600, 1508, 1490, 1430, 1382, 1364, 1322, 1252, 1208, 1180, 996, 914, 746, 694 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.17-7.11 (m, 2H), 6.76-6.72 (m, 3H), 5.91-5.77 (m, 1H), 5.12-5.04 (m, 2H), 2.37 (d, 2H, $J = 7.8$ Hz), 1.30 (s, 6H); ^{13}C NMR (CDCl_3): δ 146.6, 134.4, 128.9, 118.3, 118.2, 117.3, 53.4, 46.4, 27.9; MS (EI, 70 eV) m/z (%) 175 (M^+ , 3.0), 134 (100), 118 (8.2), 93 (6.5), 77 (10.8); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{17}\text{N}$ (M^+) 175.1361, found 175.1360.

***N*-(1-Allylcyclohexyl)aniline** (Table 3, entry 4): 34%; IR (neat) ν 3418, 3054, 3014, 2930, 2854, 1638, 1600, 1508, 1496, 1450, 1322, 1256, 1170, 998, 912, 744, 692 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.15-7.09 (m, 2H), 6.73-6.67 (m, 3H), 5.87-5.73 (m, 1H), 5.05-4.95 (m, 2H), 2.44 (dd, 2H, $J = 0.9, 7.2$ Hz), 1.89-1.84 (m, 2H), 1.58-1.40 (m, 7H), 1.36-1.24 (m, 1H); ^{13}C NMR (CDCl_3) δ 146.6, 134.3, 128.9, 117.5, 117.5, 116.5, 55.4, 42.9, 36.1, 25.8, 21.7; MS (EI, 70 eV) m/z (%) 215 (M^+ , 2.6), 174 (100), 144 (3.0), 132 (7.6), 117 (4.2), 106 (8.8), 93 (10.2), 77 (11.2); HRMS (EI) calcd for $\text{C}_{15}\text{H}_{21}\text{N}$ (M^+) 215.1674, found 215.1681.

Methyl-3-(Phenylamino)-5-hexenoate (Table 3, entry 5): 52%; IR (neat) ν 3390, 2952, 1732, 1640, 1602, 1436, 1370, 1312, 1172, 994, 918, 750, 694 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.24-7.14 (m, 2H), 6.73-6.68 (m, 1H), 6.64-6.61 (m, 2H), 5.88-5.74 (m, 1H), 5.12 (d, 1H, $J = 12.3$ Hz), 3.91 (qui, 1H, $J = 6.3$ Hz), 3.66 (s, 3H), 2.59 (A part of ABX system, 1H, $J_{\text{AB}} = 15.2$ Hz, $J_{\text{AX}} = 5.7$ Hz), 2.51 (B part of ABX system, 1H, $J_{\text{AB}} = 15.2$ Hz, $J_{\text{BX}} = 6.3$ Hz), 2.44-2.29 (m, 2H); ^{13}C NMR (CDCl_3) δ 172.2, 146.7, 134.0, 129.3, 118.3, 117.7, 113.6, 51.6, 49.7, 38.5, 38.3; MS (EI, 70 eV) m/z (%) 219 (M^+ , 10.1), 178 (100), 146 (38.1), 118 (22.2), 104 (87.7), 91 (9.7), 77 (23.3); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$ (M^+) 219.1259, found 219.1262.

***N*-(1-Ethyl-3-butenyl)-4-methoxyaniline** (Table 3, entry 6): 20%; IR (neat) ν 3390, 2960, 2930, 2830, 640, 1512, 1464, 1440, 1236, 1180, 1152, 1040, 912, 818 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.79-6.74 (m, 2H), 6.58-6.52 (m, 2H), 5.89-5.74 (m, 1H), 5.10-5.04 (m, 2H), 3.74 (s, 3H), 3.26 (qui, 1H, $J = 6.0$ Hz), 2.30-2.25 (m, 2H), 1.60-1.48 (m, 2H), 0.95 (t, 3H, $J = 7.8$ Hz); ^{13}C NMR (CDCl_3) δ 151.8, 142.0, 135.1, 117.3, 114.9, 114.7, 55.8, 54.7, 38.0, 26.8, 10.2; MS (EI, 70 eV) m/z (%) 205 (M^+ , 10.1), 176 (3.2), 164 (100), 149 (9.7), 134 (18.9), 122 (22.9), 107 (7.6), 95 (4.3), 77 (6.3); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{19}\text{NO}$ (M^+) 205.1467, found 205.1467.

***N*-(1,2-Dimethyl-3-butenyl)-4-methoxyaniline** (Table 4, entry 1): 51%; dr = 62:38; IR (neat) ν 3394, 2964, 2830, 1618, 1512, 1464, 1378,

1232, 1180, 1040, 914, 818 cm^{-1} ; ^1H NMR (CDCl_3) major isomer: δ 7.78-7.75 (m, 2H), 6.56-6.52 (m, 2H), 5.80-5.68 (m, 1H), 5.13-4.99 (m, 2H), 3.74 (s, 3H), 3.35 (qui, 1H, $J = 6.6$ Hz), 2.50-2.39 (m, 1H), 1.07 (d, 6H, $J = 6.6$ Hz); minor isomer: δ 7.78-7.75 (m, 2H), 6.56-6.52 (m, 2H), 5.89-5.79 (m, 1H), 5.13-4.99 (m, 2H), 3.74 (s, 3H), 3.36 (qui, 1H, $J = 6.6$ Hz), 2.50-2.39 (m, 1H), 1.11 (d, 3H, $J = 6.6$ Hz), 1.07 (d, 3H, $J = 6.6$ Hz); ^{13}C NMR (CDCl_3) major isomer: δ 152.3, 142.1, 140.3, 116.3, 115.5, 115.4, 56.2, 53.9, 42.3, 17.6, 16.6; minor isomer: δ 152.3, 142.2, 141.7, 115.5, 115.4, 115.2, 56.2, 53.8, 42.19, 17.7, 15.1; MS (EI, 70 eV) m/z (%) 205 (M^+ , 7.4), 150 (100), 135 (7.2), 119 (3.1), 108 (4.1), 92 (1.9), 77 (2.6); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{19}\text{NO}$ (M^+) 205.1467, found 205.1472.

***N*-(1,3-Dimethyl-3-butenyl)-4-methoxyaniline** (Table 4, entry 2):

60%; IR (neat) ν 3384, 2964, 2928, 1648, 1512, 1456, 1374, 1234, 1040, 888, 818 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.80-6.75 (m, 2H), 6.60-6.55 (m, 2H), 4.79 (d, 2H, $J = 18.6$ Hz), 3.74 (s, 3H), 3.52 (sxt, 1H, $J = 6.0$ Hz), 2.33 (dd, 1H, $J = 6.6, 13.8$ Hz), 2.09 (dd, 1H, $J = 7.2, 13.8$ Hz), 1.74 (s, 3H), 1.17 (d, 3H, $J = 6.0$ Hz); ^{13}C NMR (CDCl_3): δ 151.9, 143.0, 141.7, 114.9, 114.7, 112.8, 55.7, 47.3, 45.6, 22.3, 20.8; MS (EI, 70 eV) m/z (%) 205 (M^+ , 8.5), 150 (100), 135 (10.5), 122 (4.9), 107 (7.3), 92 (3.9), 80 (5.4), 77 (5.1); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{19}\text{NO}$ (M^+) 205.1467, found 205.1469.

Methyl-2-[1-(4-Methoxyphenylamino)ethyl]-3-butenolate (Table

4, entry 3): 64%; dr = 80:20; IR (neat) ν 3366, 2952, 2832, 1732, 1638, 1512, 1438, 1238, 1196, 1168, 1038, 926, 822 cm^{-1} ; ^1H NMR (CDCl_3) major isomer: δ 6.80-6.75 (m, 2H), 6.63-6.58 (m, 2H), 6.03-5.88 (m, 1H), 5.25-5.03 (m, 2H), 3.86 (qui, 1H, $J = 6.6$ Hz), 3.74 (s, 3H), 3.69 (s, 3H), 3.25 (dd, 1H, $J = 5.7, 9.6$ Hz), 1.13 (d, 3H, $J = 6.6$ Hz); minor isomer: δ 6.80-6.75 (m, 2H), 6.63-6.58 (m, 2H), 6.03-5.88 (m, 1H), 5.25-5.03 (m, 2H), 3.74 (s, 3H), 3.72 (qui, 1H, $J = 6.6$ Hz), 3.69 (s, 3H), 3.28 (dd, 1H, $J = 5.4, 9.9$ Hz), 1.19 (d, 3H, $J = 6.6$ Hz); ^{13}C NMR (CDCl_3) major isomer: δ 173.7, 152.8, 141.0, 132.5, 120.2, 116.0, 115.3, 56.08, 54.7, 52.3, 51.8, 18.0; minor isomer: δ 173.2, 152.8, 141.3, 134.0, 119.4, 116.0, 115.3, 56.1, 55.2, 53.1, 52.3, 18.6; MS (EI, 70 eV) m/z (%) 249 (M^+ , 5.6), 150 (100), 134 (7.6), 122 (3.2), 108 (3.9), 92 (2.2), 77 (3.5); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3$ (M^+) 249.1365, found 249.1373.

4-Methoxy-*N*-(1-methyl-2-phenyl-3-butenyl)aniline (Table 4, entry

4): 54%; dr = 70:30; IR (neat) ν 3386, 3028, 2966, 2830, 1678, 1600, 1510, 1464, 1452, 1292, 1240, 1180, 1154, 1038, 920, 820, 754, 702 cm^{-1} ; ^1H NMR (CDCl_3) major isomer: δ 7.35-7.16 (m, 5H), 6.81-6.75 (m, 2H), 6.61-6.56 (m, 2H), 6.23-6.02 (m, 1H), 5.23-5.08 (m, 2H), 3.77-3.68 (m, 1H), 3.73 (s, 3H), 3.60 (dd, 1H, $J = 5.0, 9.4$ Hz), 1.11 (d, 3H, $J = 6.5$ Hz); minor isomer: δ

7.35-7.16 (m, 5H), 6.81-6.75 (m, 2H), 6.61-6.56 (m, 2H), 6.23-6.02 (m, 1H), 5.23-5.08 (m, 2H), 3.77-3.68 (m, 1H), 3.75 (s, 3H), 3.47 (t, 1H, $J = 7.0$ Hz), 1.02 (d, 3H, $J = 6.4$ Hz); ^{13}C NMR (CDCl_3) major isomer: δ 152.6, 142.2, 141.7, 137.2, 129.0, 128.4, 126.9, 118.4, 115.9, 115.3, 56.2, 54.7, 54.1, 17.5; minor isomer: δ 152.5, 141.9, 141.3, 139.8, 129.1, 128.8, 127.0, 117.0, 115.4, 115.4, 56.2, 55.2, 53.8, 18.6; MS (EI, 70 eV) m/z (%) 267 (M^+ , 1.3), 150 (100), 135 (5.3), 115 (3.9), 108 (3.0), 91 (3.1), 77 (2.6); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{21}\text{NO}$ (M^+) 267.1623, found 267.1615.

***N*-[1-(Methyl-*d*)-3-butenyl]aniline-*d*₅** (Scheme 3): 76%; IR (neat) ν 3402, 3076, 2924, 2270, 1640, 1574, 1476, 1434, 1400, 1354, 1292, 1258, 1212, 1142, 994, 914, 824, 748 cm^{-1} ; ^1H NMR (CDCl_3): δ 5.90-5.76 (m, 1H), 5.12-5.07 (m, 2H), 3.53 (qui, 1H, $J = 6.0$ Hz), 2.39-2.30 (m, 1H), 2.26-2.17 (m, 1H), 1.18 (dt, 2H, $J = 6.0, 5.3$ Hz); ^{13}C NMR (CDCl_3) δ 147.7, 135.4, 129.2 (t), 118.0, 117.0 (t), 113.3 (t), 48.3, 41.3, 20.5 (t); MS (EI, 70 eV) m/z (%) 167 (M^+ , 7.5), 126 (100), 109 (4.9), 96 (2.3), 82 (10.7); HRMS (EI) calcd for $\text{C}_{11}\text{H}_9\text{D}_6\text{N}$ (M^+) 167.1581, found 167.1583.

^1H NMR spectrum of *N*-(1-Methyl-3-butenyl)aniline (Table 1, entry 1).

¹³C NMR spectrum of *N*-(1-Methyl-3-butenyl)aniline (Table 1, entry 1).

^1H NMR spectrum of **4-Fluoro-N-(1-methyl-3-butenyl)aniline** (Table 2, entry 1).

¹³C NMR spectrum of **4-Fluoro-N-(1-methyl-3-butenyl)aniline** (Table 2, entry 1).

^1H NMR spectrum of **4-Chloro-*N*-(1-methyl-3-butenyl)aniline** (Table 2, entry 2).

¹³C NMR spectrum of 4-Chloro-N-(1-methyl-3-butenyl)aniline (Table 2, entry 2).

^1H NMR spectrum of **2-Methoxy-*N*-(1-methyl-3-butenyl)aniline** (Table 2, entry 3).

¹³C NMR spectrum of **2-Methoxy-N-(1-methyl-3-butenyl)aniline** (Table 2, entry 3).

^1H NMR spectrum of **3-Methoxy-N-(1-methyl-3-butenyl)aniline** (Table 2, entry 4).

¹³C NMR spectrum of 3-Methoxy-N-(1-methyl-3-butenyl)aniline (Table 2, entry 4).

^1H NMR spectrum of **4-Methoxy-N-(1-methyl-3-butenyl)aniline** (Table 2, entry 5).

¹³C NMR spectrum of **4-Methoxy-N-(1-methyl-3-butenyl)aniline** (Table 2, entry 5).

^1H NMR spectrum of **4-(1-Methyl-3-butenylamino)benzonitrile** (Table 2, entry 6).

¹³C NMR spectrum of **4-(1-Methyl-3-butenylamino)benzonitrile** (Table 2, entry 6).

¹H NMR spectrum of *N*-(1-Methyl-3-butenyl)-4-aminobiphenyl (Table 2, entry 7).

¹³C NMR spectrum of *N*-(1-Methyl-3-butenyl)-4-aminobiphenyl (Table 2, entry 7).

^1H NMR spectrum of *N*-(1-Methyl-3-butenyl)-5-aminoindan (Table 2, entry 8).

¹³C NMR spectrum of *N*-(1-Methyl-3-butenyl)-5-aminoindan (Table 2, entry 8).

^1H NMR spectrum of *N*-(1-Methyl-3-butenyl)-1,4-benzodioxin-6-amine (Table 2, entry 9).

¹³C NMR spectrum of *N*-(1-Methyl-3-butenyl)-1,4-benzodioxin-6-amine (Table 2, entry 9).

¹H NMR spectrum of **4-(Phenylamino)-6-hepten-1-ol** (Table 3, entry 1).

¹³C NMR spectrum of **4-(Phenylamino)-6-hepten-1-ol** (Table 3, entry 1).

¹H NMR spectrum of *N*-(1-Ethyl-3-butenyl)aniline (Table 3, entry 2).

¹³C NMR spectrum of *N*-(1-Ethyl-3-butenyl)aniline (Table 3, entry 2).

^1H NMR spectrum of *N*-(1,1-Dimethyl-3-butenyl)aniline (Table 3, entry 3).

¹³C NMR spectrum of *N*-(1,1-Dimethyl-3-butenyl)aniline (Table 3, entry 3).

^1H NMR spectrum of *N*-(1-Allylcyclohexyl)aniline (Table 3, entry 4).

¹³C NMR spectrum of *N*-(1-Allylcyclohexyl)aniline (Table 3, entry 4).

¹H NMR spectrum of **Methyl-3-(Phenylamino)-5-hexenoate** (Table 3, entry 5).

¹³C NMR spectrum of **Methyl-3-(Phenylamino)-5-hexenoate** (Table 3, entry 5).

^1H NMR spectrum of *N*-(1-Ethyl-3-butenyl)-4-methoxyaniline (Table 3, entry 6).

¹³C NMR spectrum of *N*-(1-Ethyl-3-butenyl)-4-methoxyaniline (Table 3, entry 6).

^1H NMR spectrum of *N*-(1,2-Dimethyl-3-butenyl)-4-methoxyaniline (Table 4, entry 1).

¹³C NMR spectrum of *N*-(1,2-Dimethyl-3-butenyl)-4-methoxyaniline (Table 4, entry 1).

^1H NMR spectrum of *N*-(1,3-Dimethyl-3-butenyl)-4-methoxyaniline (Table 4, entry 2).

¹³C NMR spectrum of *N*-(1,3-Dimethyl-3-butenyl)-4-methoxyaniline (Table 4, entry 2).

^1H NMR spectrum of **Methyl-2-[1-(4-Methoxyphenylamino)ethyl]-3-butenolate** (Table 4, entry 3).

¹³C NMR spectrum of **Methyl-2-[1-(4-Methoxyphenylamino)ethyl]-3-butenolate** (Table 4, entry 3).

^1H NMR spectrum of **4-Methoxy-*N*-(1-methyl-2-phenyl-3-butenyl)aniline** (Table 4, entry 4).

¹³C NMR spectrum of 4-Methoxy-N-(1-methyl-2-phenyl-3-butenyl)aniline (Table 4, entry 4).

^1H NMR spectrum of *N*-[1-(Methyl-*d*)-3-butenyl]aniline-*ring-d*₅ (Scheme 3).

¹³C NMR spectrum of *N*-[1-(Methyl-*d*³)-3-butenyl]aniline-*ring-d*₅ (Scheme 3).