Supporting Information

A Bimetallic Catalyst and Dual Role Catalyst: Synthesis of *N*-(Alkoxycarbonyl)indoles from 2-(Alkynyl)phenylisocyanates

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1. Preparation of the substrates.

Isocyanates **1a-g** were synthesized from the corresponding anilines or methyl benzoates.¹ Allyl carbonates **2a-f** were synthesized from allyl chloroformate and the corresponding alcohols.

2. Analytical data

Analytical data for the isocyanates **1a-f**, allylindoles **3a-j**, allylanilines **4a** and **4c** have been reported.¹

2-(ethynyl)phenyl-1-isocyanate (1g); slightly yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 3.50 (1H, s), 7.05 (1H, br d, *J* = 8.0 Hz), 7.14 (1H, br t, *J* = 7.5 Hz), 7.30 (1H, td, *J* = 8.0, 1.0 Hz), 7.47 (1H, dd, *J* = 7.5, 1.0 Hz); ¹³C NMR (75.4 MHz, CDCl₃) δ 79.0, 85.2, 119.4, 122.9, 123.9, 125.4, 130.0, 133.0; IR (neat) 3292, 2275, 2262, 1598, 1506, 758 cm⁻¹; HRMS (EI) Calcd for C₉H₅NO (M⁺) 143.0371. Found 143.0370.

N-(methoxycarbonyl)-3-(3-phenyl-2-propenyl)-2-propylindole (3k); yellow oil; ¹H NMR (270 MHz, CDCl₃) δ 0.98 (3H, t, *J* = 7.0 Hz), 1.64 (2H, sextet, *J* = 7.0 Hz), 3.01 (2H, t, *J* = 7.0 Hz), 3.60 (2H, dd, *J* = 5.5, 1.0 Hz), 4.05 (3H, s), 6.31 (1H, dt, *J* = 14.5, 5.5 Hz), 6.43 (1H, br d, *J* = 14.5 Hz), 7.17-7.32 (7H, m), 7.49 (1H, m), 8.08 (1H, m); ¹³C NMR (75.4 MHz, CDCl₃) δ 14.1, 23.3, 27.5, 25.6, 53.3, 115.6, 116.6, 118.4, 122.7, 123.6, 125.9, 126.9, 128.0, 128.4, 130.0, 130.4, 135.6, 137.3, 138.0, 152.3; IR (neat) 1732, 1651, 1598, 1456, 1359, 1228, 1137, 1120, 966, 765, 746 cm⁻¹; HRMS (EI) Calcd for C₂₂H₂₃NO₂ (M⁺) 333.1728. Found 333.1723.

N-(propoxycarbonyl)-2-propylindole (6a); colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 1.02 (3H, t, *J* = 7.0 Hz), 1.07 (3H, t, *J* = 7.5 Hz), 1.72 (2H, sextet, *J* = 7.5 Hz), 1.87 (2H, sextet, *J* = 7.0 Hz), 2.97 (2H, t, *J* = 7.5 Hz), 4.39 (2H, t, *J* = 7.0 Hz), 6.35 (1H, s), 7.17 (1H, td, *J* = 7.0, 1.5 Hz), 7.22 (1H, td, *J* = 7.5, 1.5 Hz), 7.48 (1H, br dd, *J* = 7.0, 1.5 Hz), 8.18 (1H, br d, *J* = 7.5 Hz); ¹³C NMR (75.4 MHz, CDCl₃) δ 10.6, 14.0, 22.0, 22.0, 32.0, 68.6, 107.5, 115.6, 119.7, 122.8, 123.3, 129.5, 136.5, 142.3, 152.1; IR (neat) 1737, 1593, 1569, 1456, 1325, 1080, 746 cm⁻¹; Anal. Calcd for C₁₅H₁₉NO₂: C, 73.44; H, 7.80; N, 5.70. Found: C, 73.44; H, 8.13; N, 5.63; HRMS (EI) Calcd for C₁₅H₁₉NO₂ (M⁺) 245.1415. Found 245.1416.

N-(propoxycarbonyl)-2-(cyclopentyl)indole (6b); colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 1.06 (3H, t, *J* = 7.5 Hz), 1.58-1.82 (6H, m), 1.87 (2H, sextet, *J* = 7.5 Hz), 2.13 (2H, m), 3.74 (1H, br quintet, *J* = 7.5 Hz), 4.39 (2H, t, *J* = 7.0 Hz), 6.42 (1H, s), 7.17

(1H, td, $J = 7.0, 1.5$ Hz), 7.21 (1H, td, $J = 7.0, 1.5$ Hz), 7.43 (1H, br dd, $J = 7.0, 1.5$ Hz), 8.05 (1H, br d, $J = 7.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 10.5, 22.0, 24.9, 32.9, 39.3, 68.6, 105.2, 115.6, 119.8, 122.7, 123.3, 129.4, 136.7, 146.6, 152.1; IR (neat) 1737, 1593, 1566, 1456, 1323, 1087, 742 cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2$: C, 75.24; H, 7.79; N, 5.16. Found: C, 75.33; H, 7.98; N, 5.38; HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2$ (M^+) 271.1572. Found 271.1566.

***N*-(propoxycarbonyl)-2-(*tert*-butyl)indole (6c)**; colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 1.07 (3H, t, $J = 7.5$ Hz), 1.49 (9H, s), 1.90 (2H, sextet, $J = 7.5$ Hz), 4.42 (2H, t, $J = 7.5$ Hz), 6.49 (1H, s), 7.16 (1H, td, $J = 7.5, 1.5$ Hz), 7.21 (1H, td, $J = 7.0, 1.5$ Hz), 7.44 (1H, br d, $J = 7.0$ Hz), 7.90 (1H, br d, $J = 7.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 10.5, 22.0, 30.4, 34.0, 69.0, 107.0, 115.2, 120.0, 122.5, 123.4, 128.7, 137.3, 150.5, 152.5; IR (neat) 1747, 1552, 1456, 1321, 1068, 740 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_2$ (M^+) 259.1572. Found 259.1569.

***N*-(propoxycarbonyl)-2-phenylindole (6d)**; yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.72 (3H, t, $J = 7.5$ Hz), 1.45 (2H, sextet, $J = 7.5$ Hz), 4.14 (2H, t, $J = 7.0$ Hz), 6.57 (1H, s), 7.25 (1H, td, $J = 7.5, 1.0$ Hz), 7.29-7.44 (6H, m), 7.54 (1H, br d, $J = 7.5$ Hz), 8.19 (1H, br d, $J = 8.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 10.2, 21.6, 68.6, 110.6, 115.4, 120.5, 123.1, 124.4, 127.7, 127.7, 128.7, 129.4, 134.4, 137.2, 140.5, 151.8; IR (neat) 1733, 1558, 1454, 1321, 1218, 761, 748, 698 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2$ (M^+) 279.1259. Found 279.1261.

***N*-(propoxycarbonyl)-2-(4-methoxyphenyl)indole (6e)**; slightly yellow solid; mp 85.0°C; ^1H NMR (300 MHz, CDCl_3) δ 0.78 (3H, t, $J = 7.5$ Hz), 1.53 (2H, sextet, $J = 7.5$ Hz), 3.84 (3H, s), 4.17 (2H, t, $J = 7.0$ Hz), 6.53 (1H, d, $J = 1.0$ Hz), 6.92 (2H, br d, $J = 8.5$ Hz), 7.22-7.33 (2H, m), 7.34 (2H, br d, $J = 8.5$ Hz), 7.53 (1H, br d, $J = 7.5$ Hz), 8.17 (1H, br d, $J = 8.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 10.2, 21.7, 55.3, 68.6, 110.1, 113.1, 115.4, 120.3, 123.1, 124.2, 126.8, 129.4, 130.0, 137.0, 140.4, 151.9, 159.3; IR (KBr) 1720, 1616, 1589, 1506, 1454, 1325, 1037, 808, 752 cm^{-1} ; Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3$: C, 73.70; H, 6.19; N, 4.52. Found: C, 73.79; H, 6.26; N, 4.55; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3$ (M^+) 309.1365. Found 309.1368.

***N*-(propoxycarbonyl)-2-(4-trifluoromethylphenyl)indole (6f)**; yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.70 (3H, t, $J = 7.5$ Hz), 1.46 (2H, sextet, $J = 7.0$ Hz), 4.14 (2H, t, $J = 6.5$ Hz), 6.60 (1H, s), 7.23 (1H, br t, $J = 7.5$ Hz), 7.33 (1H, td, $J = 8.0, 1.0$ Hz), 7.51 (2H, br d, $J = 8.5$ Hz), 7.53 (1H, d, $J = 7.5$ Hz), 7.61 (1H, br d, $J = 8.5$ Hz), 8.17 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 10.2, 21.6, 68.9, 111.7, 115.6, 120.8, 123.42, 124.1 ($^1J(\text{C}, \text{F}) = 271$ Hz: CF_3), 124.7 ($^3J(\text{C}, \text{F}) = 3.6$ Hz), 125.1, 129.0, 129.1, 129.7 ($^2J(\text{C}, \text{F}) = 33$ Hz), 137.3, 138.0 ($^4J(\text{C}, \text{F}) = 1.5$ Hz), 138.8, 151.6; IR (neat) 1735,

1618, 1452, 1323, 1164, 1124, 1068, 817, 748 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{16}\text{F}_3\text{NO}_2$ (M^+) 347.1133. Found 347.1115.

***N*-(propoxycarbonyl)indole (6g)**; colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 1.06 (3H, t, $J = 7.5$ Hz), 1.85 (2H, sextet, $J = 7.0$ Hz), 4.38 (2H, t, $J = 7.0$ Hz), 6.58 (1H, d, $J = 4.5$ Hz), 7.26 (1H, td, $J = 7.5, 1.0$ Hz), 7.32 (1H, br td, $J = 8.0, 1.0$ Hz), 7.56 (1H, br d, $J = 7.5$ Hz), 7.62 (1H, d, $J = 4.5$ Hz), 8.16 (1H, br d, $J = 8.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 10.4, 22.1, 68.7, 107.9, 115.1, 120.9, 122.9, 124.4, 125.5, 130.5, 135.2, 151.15; IR (neat) 1739, 1608, 1585, 1533, 1454, 1328, 1060, 765, 746 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2$: C, 70.66; H, 6.29; N, 6.89. Found: C, 70.91; H, 6.44; N, 6.89; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2$ (M^+) 203.0946. Found 203.0948.

***N*-(methoxycarbonyl)-2-propylindole (6h)**; white solid; mp 66.0°C; ^1H NMR (300 MHz, CDCl_3) δ 1.05 (3H, t, $J = 7.5$ Hz), 1.75 (2H, sextet, $J = 7.5$ Hz), 3.00 (2H, t, $J = 7.5$ Hz), 4.06 (3H, s), 6.39 (1H, s), 7.22 (1H, td, $J = 7.0, 1.5$ Hz), 7.26 (1H, td, $J = 7.0, 1.5$ Hz), 7.47 (1H, br dd, $J = 7.0, 1.5$ Hz), 8.09 (1H, br d, $J = 7.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 14.0, 22.0, 31.9, 53.4, 107.6, 115.5, 119.7, 122.9, 123.4, 129.5, 136.4, 142.3, 152.6; IR (KBr) 1733, 1591, 1566, 1458, 1338, 1082, 754 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$: C, 71.86; H, 6.95; N, 6.44. Found: C, 71.85; H, 7.19; N, 6.44; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ (M^+) 217.1102. Found 217.1102.

***N*-(isopropoxycarbonyl)-2-propylindole (6i)**; colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 1.01 (3H, t, $J = 7.5$ Hz), 1.46 (6H, d, $J = 6.0$ Hz), 1.72 (2H, sextet, $J = 7.5$ Hz), 2.96 (2H, t, $J = 7.5$ Hz), 5.27 (2H, septet, $J = 6.0$ Hz), 6.34 (1H, s), 7.17 (1H, td, $J = 7.0, 1.5$ Hz), 7.19 (1H, td, $J = 7.5, 1.5$ Hz), 7.43 (1H, br dd, $J = 7.0, 1.5$ Hz), 8.09 (1H, br d, $J = 7.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 14.0, 22.0, 22.2, 32.1, 71.1, 107.4, 115.6, 119.6, 122.7, 123.2, 129.5, 136.6, 142.3, 151.5; IR (neat) 1735, 1593, 1569, 1456, 1317, 1078, 746 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2$: C, 73.44; H, 7.80; N, 5.70. Found: C, 73.62; H, 8.04; N, 5.67; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ (M^+) 245.1415. Found 245.1415.

***N*-(tert-butoxycarbonyl)-2-propylindole (6j)**; yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.01 (3H, t, $J = 7.5$ Hz), 1.67 (9H, s), 1.71 (2H, sextet, $J = 7.5$ Hz), 2.96 (2H, t, $J = 7.5$ Hz), 6.33 (1H, s), 7.16 (1H, td, $J = 7.5, 1.5$ Hz), 7.20 (1H, td, $J = 7.0, 1.5$ Hz), 7.43 (1H, br dd, $J = 7.0, 1.5$ Hz), 8.07 (1H, br d, $J = 7.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 13.9, 22.1, 28.2, 32.2, 83.5, 107.1, 115.5, 119.6, 122.5, 123.1, 129.4, 136.6, 142.2, 150.6; IR (neat) 1732, 1593, 1568, 1454, 1328, 1164, 1080, 746 cm^{-1} ; Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_2$: C, 74.09; H, 8.16; N, 5.40. Found: C, 74.20; H, 8.39; N, 5.38; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_2$ (M^+) 259.1572. Found 259.1574.

***N*-(benzyloxycarbonyl)-2-propylindole (6k)**; colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 0.99 (3H, t, $J = 7.5$ Hz), 1.67 (2H, sextet, $J = 7.5$ Hz), 2.94 (2H, t, $J = 7.5$ Hz), 5.44 (2H, s), 6.34 (1H, s), 7.14-7.23 (2H, m), 7.33-7.50 (6H, m), 8.07 (1H, m); ^{13}C NMR (75.4 MHz, CDCl_3) δ 13.9, 22.0, 32.0, 68.6, 107.7, 115.7, 119.7, 122.9, 123.4, 128.6, 128.7, 128.7, 129.5, 135.0, 136.5, 142.3, 151.8; IR (neat) 1732, 1593, 1569, 1456, 1325, 1074, 746, 698 cm^{-1} ; Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_2$: C, 77.79; H, 6.52; N, 4.77. Found: C, 78.00; H, 6.83; N, 4.71; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_2$ (M^+) 293.1415. Found 293.1413.

***N*-(allyloxycarbonyl)-2-propylindole (6l)**; slightly yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.00 (3H, t, $J = 7.5$ Hz), 1.71 (2H, sextet, $J = 7.5$ Hz), 2.97 (2H, t, $J = 7.5$ Hz), 4.92 (2H, ddd, $J = 6.0, 1.5, 1.5$ Hz), 5.36 (1H, ddt, $J = 10.5, 1.5, 1.5$ Hz), 5.47 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 6.08 (1H, ddt, $J = 17.0, 10.5, 6.0$ Hz), 6.36 (1H, s), 7.15-7.25 (2H, m), 7.44 (1H, m), 8.03 (1H, br d, $J = 7.5$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 13.9, 22.0, 31.9, 67.4, 107.7, 115.6, 119.5, 119.7, 122.8, 123.3, 129.5, 131.5, 136.4, 142.2, 151.7; IR (neat) 1735, 1593, 1569, 1456, 1323, 1076, 991, 935, 765, 746 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2$: C, 74.04; H, 7.04; N, 5.75. Found: C, 74.32; H, 7.23; N, 5.70; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2$ (M^+) 243.1259. Found 243.1263.

***N*-(propoxycarbonyl)-2-(1-pentynyl)aniline (7a)**; slightly yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.99 (3H, t, $J = 7.5$ Hz), 1.09 (3H, t, $J = 7.5$ Hz), 1.68 (2H, sextet, $J = 7.0$ Hz), 1.72 (2H, sextet, $J = 7.0$ Hz), 2.48 (2H, t, $J = 7.0$ Hz), 4.14 (2H, t, $J = 7.0$ Hz), 6.95 (1H, td, $J = 7.5, 1.0$ Hz), 7.24-7.37 (2H, m), 7.42 (1H, br s; NH), 8.11 (1H, br d, $J = 8.0$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) δ 10.3, 13.4, 21.5, 22.1, 22.2, 66.8, 75.9, 97.4, 112.0, 117.3, 122.1, 128.8, 131.4, 139.0, 153.3; IR (neat) 3398 (N-H), 1739, 1581, 1521, 1452, 1230, 1209, 1070, 756 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2$: C, 73.44; H, 7.80; N, 5.70. Found: C, 73.53; H, 8.03; N, 5.68; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ (M^+) 245.1415. Found 245.1415.

3. Reference

(1) Kamijo, S.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 3230-3233.

4. NMR spectra