**Palladium-Catalyzed Functionalization of Indoles with 2-Acetoxyethyl Substituted
Electron-deficient Alkenes**

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1. Pd₂(dba)₃·CHCl₃/bpy-Catalyzed coupling of indoles with 2-acetoxymethyl substituted electron-deficient alkenes.

(1) 3-(2'-methoxycarbonyl-2'-propenyl)indole (3aa).

Typical Procedure: A dried reaction tube equipped with a magnetic stirring bar was charged with indole **1a** (59 mg, 0.5 mmol), methyl 2-acetoxymethylacrylate (96 mg, 0.6 mmol), Pd₂(dba)₃·CHCl₃ (12.9 mg, 2.5 mol%), bipyridine (7.8 mg, 10 mol%), and toluene (1 mL). Then the reaction was heated at 80 °C with stirring for 12 hours as monitored by TLC. Filtration of the reaction mixture through a small pad of silica gel (Et₂O), concentration, and purification of the dark oil by flash chromatography on silica gel (eluent: ethyl acetate: petroleum ether = 1:5) afforded **3aa** as a yellow solid (90 mg, 84%). m.p. 69-71 °C (Hexane); ¹H NMR (CDCl₃, 300 MHz): δ 8.04 (bs, 1 H), 7.53 (d, *J* = 7.5 Hz, 1 H), 7.36 (d, *J* = 8.1 Hz, 1 H), 7.19 (t, *J* = 8.4 Hz, 1 H), 7.10 (t, *J* = 8.1 Hz, 1 H), 7.03 (d, *J* = 2.4 Hz, 1 H), 6.20 (s, 1 H), 5.49 (s, 1 H), 3.78 (s, 2 H), 3.76 (s, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 167.8, 139.3, 136.2, 127.2, 125.6, 122.8, 121.9, 119.2, 119.0, 112.6, 111.1, 51.9, 27.5 ppm; MS (70 eV): *m/z* (%) 215 (M⁺, 100); IR (neat): ν 3378, 1697, 1628, 1433, 1424, 1310, 1287, 1141, 745 cm⁻¹; HRMS calcd for C₁₃H₁₃NO₂ 215.09462; Found: 215.09223.

(2) 3-(2'-Methoxycarbonyl-2'-propenyl)-4-benzyloxyindole (3ba)

The reaction of indole **1b** (112 mg, 0.5 mmol) with methyl 2-acetoxymethyl acrylate **2a** (96 mg, 0.6 mmol) in the presence of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (13 mg, 2.5 mol%) and bipyridine (7.8 mg, 10 mol%) in 1 mL of toluene for 12 h afforded 121 mg (76%) of **3ba**: oil; ^1H NMR (CDCl_3 , 300 MHz): δ 8.19 (bs, 1 H), 7.60-7.32 (m, 5 H), 7.12 (t, $J = 7.8$ Hz, 1 H), 6.99 (d, $J = 8.1$ Hz, 1 H), 6.88 (s, 1 H), 6.59 (d, $J = 7.5$ Hz, 1 H), 6.21 (s, 1 H), 5.37 (s, 1 H), 5.17 (s, 2 H), 3.98 (s, 2 H), 3.74 (s, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 168.0, 153.7, 140.8, 138.1, 137.3, 128.3, 127.5, 127.3, 125.4, 122.6, 121.7, 117.3, 112.8, 104.7, 100.4, 69.6, 51.6, 28.8 ppm; MS (70 eV) m/z (%) 230 (100), 321 (M^+ , 93.94); IR (neat): ν 3408, 1712, 1631 cm^{-1} ; HRMS m/z (MALDI) calcd for $\text{C}_{20}\text{H}_{20}\text{NO}_3^+(\text{M}^+ + \text{H})$ 322.1438; Found: 322.1439.

(3) 3-(2'-Methoxycarbonyl-2'-propenyl)-5-benzyloxyindole (3ca):

The reaction of indole **1c** (112 mg, 0.5 mmol) with methyl 2-acetoxymethyl acrylate **2a** (96 mg, 0.6 mmol) in the presence of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (13 mg, 2.5 mol%) and bipyridine (7.8 mg, 10 mol%) in 1 mL of toluene for 12 h afforded 115 mg (72%) of **3ca**: oil; ^1H NMR (CDCl_3 , 300 MHz): δ 7.98 (bs, 1 H), 7.48 (d, $J = 7.8$ Hz, 2 H), 7.40-7.19 (m, 3 H), 7.27 (d, $J = 7.8$ Hz, 1 H), 7.06-6.90 (m, 3 H), 6.18 (s, 1 H), 5.46 (s, 1 H), 5.08 (s, 2 H), 3.77 (s, 3 H),

3.73 (s, 2 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 167.8, 152.9, 139.1, 137.5, 131.6, 128.4, 127.7, 127.6, 127.5, 125.6, 123.7, 112.6, 112.1, 111.8, 102.5, 70.9, 51.8, 27.5 ppm; MS (70 eV) m/z (%) 321 (M^+ , 100); IR (neat): ν 3414, 1715, 1628 cm^{-1} ; HRMS m/z (MALDI) calcd for $\text{C}_{20}\text{H}_{20}\text{NO}_3^+(\text{M}^++\text{H})$ 322.1438; Found: 322.1441.

(4) 3-(2'-Methoxycarbonyl-2'-propenyl)-6-benzyloxyindole (3da):

The reaction of indole **1d** (112 mg, 0.5 mmol) with methyl 2-acetoxymethyl acrylate **2a** (96 mg, 0.6 mmol) in the presence of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (13 mg, 2.5 mol%) and bipyridine (7.8 mg, 10 mol%) in 1 mL of toluene for 12 h afforded 119 mg (74%) of **3da**: oil; ^1H NMR (CDCl_3 , 300 MHz): δ 7.98 (bs, 1 H), 7.50-7.28 (m, 6 H), 6.95-6.82 (m, 3 H), 6.23 (s, 1 H), 5.52 (s, 1 H), 5.09 (s, 2 H), 3.78 (s, 3 H), 3.77 (s, 2 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 167.9, 155.5, 139.4, 137.3, 136.9, 128.5, 127.8, 127.4, 125.5, 121.9, 121.7, 119.6, 112.6, 110.0, 96.0, 70.5, 51.8, 27.6 ppm; MS (70 eV) m/z (%) 230 (100), 321 (M^+ , 27.6); IR (neat): ν 3411, 1716, 1629 cm^{-1} ; HRMS m/z (MALDI) calcd for $\text{C}_{20}\text{H}_{20}\text{NO}_3^+(\text{M}^++\text{H})$ 322.1438; Found: 322.1440.

(5) 3-(2'-Methoxycarbonyl-2'-propenyl)-4-bromoindole (3ea):

The reaction of indole **1e** (98 mg, 0.5 mmol) with methyl 2-acetoxymethyl acrylate (96 mg, 0.6 mmol) in the presence of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (13 mg, 2.5 mol%) and bipyridine (7.8 mg, 10 mol%) in 1 mL of toluene for 10 h afforded 105 mg (72%) of **3ea**: solid, m.p. 110-111°C; ^1H NMR (CDCl_3 , 300 MHz): δ 8.23 (bs, 1 H), 7.24-7.15 (m, 2 H), 6.95-6.87 (m, 2 H), 6.18 (s, 1 H), 5.24 (s, 1 H), 3.93 (s, 2 H), 3.71 (s, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 167.9, 140.8, 137.6, 126.2, 125.4, 124.6, 124.0, 122.9, 114.3, 113.7, 110.5, 51.9, 28.1 ppm; MS (70 eV): m/z (%): 43 (100), 293 (M^+ (^{79}Br), 61.56), 295 (M^+ (^{81}Br), 59.46); IR (neat): ν 3363, 1705, 1631, 1436, 1142, 736 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_9\text{BrNO}_2$ ($\text{M}^+ - \text{CH}_3$) 277.98167; Found: 277.98377.

(6) 3-(2'-Methoxycarbonyl-2'-propenyl)-5-bromoindole (3fa):

The reaction of indole **1f** (98 mg, 0.5 mmol) with methyl 2-acetoxymethyl acrylate **2a** (96 mg, 0.6 mmol) in the presence of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (13 mg, 2.5 mol%) and bipyridine (7.8 mg, 10 mol%) in 1 mL of toluene for 10 h afforded 101 mg (69%) of **3fa**: oil; ^1H NMR (CDCl_3 , 300 MHz): δ 8.30 (bs, 1 H), 7.66 (s, 1 H), 7.25 (d, $J = 8.7$ Hz, 1 H), 7.18 (d, $J = 8.7$ Hz, 1 H), 6.99 (s, 1 H), 6.23 (s, 1 H), 5.50 (s, 1 H), 3.78 (s, 3 H), 3.73 (s, 2 H); ^{13}C NMR (CDCl_3 , 75.4

MHz): δ 167.7, 139.0, 134.9, 128.9, 125.9, 124.7, 124.1, 121.5, 112.6, 112.5, 112.2, 51.9, 27.4 ppm; MS (70 eV) m/z (%) 154 (100), 293 (M^+ (^{79}Br), 98.56), 295 (M^+ (^{81}Br), 95.05); IR (neat): ν 3418, 1707, 1631 cm^{-1} ; HRMS m/z (MALDI) calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_2^{79}\text{Br}^+(\text{M}^++\text{H})$ 294.0124; Found: 294.0133.

(7) 3-(2'-Methoxycarbonyl-2'-propenyl)-6-bromoindole (3ga):

The reaction of indole **1g** (98 mg, 0.5 mmol) with methyl 2-acetoxymethyl acrylate (96 mg, 0.6 mmol) in the presence of $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (13 mg, 2.5 mol%) and bipyridine (7.8 mg, 10 mol%) in 1 mL of toluene for 10 h afforded 100 mg (68%) of **3ga**: oil; ^1H NMR (CDCl_3 , 300 MHz): δ 8.23 (bs, 1 H), 7.47 (s, 1 H), 7.39 (d, $J = 8.4$ Hz, 1 H), 7.19 (dd, $J = 1.8, 8.4$ Hz, 1 H), 6.97 (s, 1 H), 6.22 (s, 1 H), 5.49 (s, 1 H), 3.77 (s, 3 H), 3.76 (s, 2 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 167.7, 139.2, 137.0, 126.1, 125.7, 123.4, 122.6, 120.3, 115.5, 114.0, 113.0, 51.9, 27.5 ppm; MS (70 eV) m/z (%) 156 (100), 293 (M^+ (^{79}Br), 7.89), 295 (M^+ (^{81}Br), 7.43); IR (neat): ν 3420, 1709, 1630, 1454, 1144 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_9\text{BrNO}_2$ ($M^+-\text{CH}_3$) 277.98167; Found: 277.98203.

(8) 3-(2'-Methoxycarbonyl-2'-propenyl)-5-methylindole (3ha):

The reaction of indole **1h** (66 mg, 0.5 mmol) with methyl 2-acetoxymethyl acrylate (96 mg, 0.6 mmol) in the presence of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (13 mg, 2.5 mol%) and bipyridine (7.8 mg, 10 mol%) in 1 mL of toluene for 12 h afforded 84 mg (73%) of **3ha**: oil; ^1H NMR (CDCl_3 , 300 MHz): δ 7.96 (bs, 1 H), 7.31 (s, 1 H), 7.25 (d, J = 8.1 Hz, 1 H), 7.06-6.92 (m, 2 H), 6.20 (s, 1 H), 5.49 (s, 1 H), 3.78 (s, 3 H), 3.76 (s, 2 H), 2.46 (s, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 167.9, 139.4, 134.6, 128.6, 127.5, 125.6, 123.6, 123.0, 118.7, 112.2, 110.8, 51.9, 27.5, 21.5 ppm; MS (70 eV): m/z (%) 156 (100), 229 (M^+ , 19.69); IR (neat): ν 3412, 1713, 1630, 1437, 1139, 794 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2$ 229.11028; Found: 229.11186.

(9) 3-(2'-Methoxycarbonyl-2'-propenyl)-5-methoxyindole (3ia):

The reaction of indole **1i** (74 mg, 0.5 mmol) with methyl 2-acetoxymethyl acrylate (96 mg, 0.6 mmol) in the presence of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (13 mg, 2.5 mol%) and bipyridine (7.8 mg, 10 mol%) in 1 mL of toluene for 10 h afforded 93 mg (76%) of **3ia**: oil; ^1H NMR (CDCl_3 , 300 MHz): δ 7.99 (bs, 1 H), 7.25 (d, J = 8.4 Hz, 1 H), 7.00 (d, J = 2.4 Hz, 1 H), 6.95 (d, J = 2.1 Hz, 1 H), 6.85 (dd, J = 2.4, 8.4 Hz, 1 H), 6.21 (s, 1 H), 5.48 (s, 1 H), 3.84 (s, 3 H), 3.78 (s, 3 H), 3.75 (s, 2 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 167.9, 153.9, 139.3, 131.4, 127.7, 125.6, 123.6, 112.4, 112.1, 111.8, 100.8, 55.9, 51.9, 27.6 ppm; MS (70 eV) m/z (%) 59 (100), 245 (M^+ , 33); IR (neat): ν 3411, 1717, 1629, 1487, 1140 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_3$ 245.10519; Found: 245.10475.

(10) 3-(2'-Methoxycarbonyl-2'-propenyl)-2-methylindole (3ja):

The reaction of indole **1j** (66 mg, 0.5 mmol) with methyl 2-acetoxymethyl acrylate **2a** (96 mg, 0.6 mmol) in the presence of Pd(dba)₂ (14.4 mg, 5 mol%) and bipyridine (7.8 mg, 10 mol%) in 1 mL of toluene for 23 h afforded 77 mg (67%) of **3ja**: oil; ¹H NMR (CDCl₃, 300 MHz): δ 7.96 (bs, 1 H), 7.45 (d, *J* = 7.5 Hz, 1 H), 7.27 (d, *J* = 7.5 Hz, 1 H), 7.18-7.05 (m, 2 H), 6.20 (s, 1 H), 5.39-5.36 (m, 1 H), 3.81 (s, 3 H), 3.74 (s, 2 H), 2.35 (s, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 167.9, 138.9, 135.2, 132.3, 128.5, 125.2, 120.8, 119.1, 118.1, 110.2, 107.5, 51.8, 26.3, 11.5 ppm; MS (70 eV) *m/z* (%) 144 (100), 229 (*M*⁺, 58.24); IR (neat): ν 3400, 1720, 1630 cm⁻¹; HRMS *m/z* (MALDI) calcd for C₁₄H₁₅NO₂Na⁺(*M*⁺+Na) 252.0995; Found: 252.1016.

(11) 3-(2'-Phenylsulfonyl-2'-propenyl)-1H-indole (3ac):

The reaction of indole **1a** (59 mg, 0.5 mmol) with 2-phenylsulfonyl-2-propenyl acetate **2c** (144 mg, 0.6 mmol) in the presence of Pd₂(dba)₃·CHCl₃ (12.9 mg, 2.5 mol%) and bipyridine (7.8 mg, 10 mol%) in 1 mL of toluene for 15 h afforded 111 mg (75%) of **3ac**: white solid, m.p. 146-147°C (ethyl acetate/hexane); ¹H NMR (CDCl₃, 300 MHz): δ 8.02 (bs, 1 H), 7.95-7.90 (m, 2 H), 7.67-7.62 (m, 1 H), 7.58-7.51 (m, 2 H), 7.32 (d, *J* = 8.4 Hz, 1 H), 7.16 (t,

$J = 8.4$ Hz, 1 H), 7.09-6.95 (m, 3 H), 6.39 (s, 1 H), 5.55-5.51 (m, 1 H), 3.72 (s, 2 H); ^{13}C NMR (DMSO, 75.4 MHz): δ 149.7, 138.5, 136.3, 133.8, 129.5, 127.8, 126.2, 124.8, 124.6, 121.1, 118.5, 117.7, 111.5, 108.2, 25.2 ppm; MS (70 eV) m/z (%) 155 (100), 297 (M^+ , 11.54); IR (neat): ν 3332, 1747 cm^{-1} ; HRMS m/z (MALDI) calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{SNa}^+(\text{M}^+ + \text{Na})$ 320.0716; Found: 320.0735.

2. $\text{Pd}(\text{acac})_2/\text{PPh}_3$ -Catalyzed coupling of *N*-protected indoles with 2-acetoxymethyl substituted electron-deficient alkenes.

(1) 3-(2'-methoxycarbonyl-2'-propenyl)-1-methylindole (3ka):

Typical Procedure: A dried reaction tube equipped with a magnetic stirring bar was charged with indole **1k** (131 mg, 1.0 mmol), methyl 2-acetoxymethyl acrylate **2a** (160 mg, 1.0 mmol), $\text{Pd}(\text{acac})_2$ (15 mg, 5 mol%), PPh_3 (26 mg, 10 mol%), and HOAc (0.5 mL). Then the reaction was heated at 80 $^\circ\text{C}$ with stirring for 23 hours as monitored by TLC. Filtration of the reaction mixture through a small pad of silica gel (Et_2O), concentration, and purification of the dark oil by flash chromatography on silica gel (eluent: ethyl acetate: petroleum ether = 1:5) afforded 192 mg (84%) of **3ka**: oil; ^1H NMR (300 MHz, CDCl_3): δ 7.51 (d, $J = 7.8$ Hz, 1 H), 7.28 (d, $J = 7.8$ Hz, 1 H), 7.21 (t, $J = 7.8$ Hz, 1 H), 7.09 (t, $J = 7.8$ Hz, 1 H), 6.87 (s, 1 H), 6.18 (s, 1

H), 5.51-5.46 (m, 1 H), 3.75 (s, 5 H), 3.73 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.6, 139.5, 136.9, 127.5, 127.4, 125.3, 121.3, 119.0, 118.6, 110.9, 109.0, 51.6, 32.3, 27.4; IR(neat): 1720, 1631 cm^{-1} ; MS m/z (%) 229 (M^+ , 100); HRMS m/z (MALDI) calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2\text{Na}^+(\text{M}^++\text{Na})$ 252.0995; Found: 252.1000.

(2) 3-(2'-Methoxycarbonyl-2'-propenyl)-1-buthylindole (3la)

The reaction of 1-buthylindole **11** (161 mg, 1.0 mmol) with 2-acetoxymethyl acrylate **2a** (192 mg, 1.2 mmol) in the presence of $\text{Pd}(\text{acac})_2$ (15 mg, 5 mol%) and PPh_3 (26 mg, 10 mol%) in 2 mL of HOAc for 9 h afforded 219 mg (81%) of **3la**: yellow oil; ^1H NMR (300 MHz, CDCl_3): δ 7.52 (d, $J = 7.8$ Hz, 1 H), 7.32 (d, $J = 7.5$ Hz, 1 H), 7.20 (t, $J = 6.9$ Hz, 1 H), 7.08 (t, $J = 8.1$ Hz, 1 H), 6.94 (s, 1 H), 6.19 (s, 1 H), 5.50-5.46 (m, 1 H), 4.08 (t, $J = 7.2$ Hz, 2 H), 3.78 (s, 3 H), 3.77 (s, 2 H), 1.85-1.73 (m, 2 H), 1.40-1.25 (m, 2 H), 0.94 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.8, 139.6, 136.3, 127.7, 126.6, 125.4, 121.2, 119.2, 118.6, 111.0, 109.3, 51.8, 45.8, 32.3, 27.5, 20.1, 13.7; IR(neat): 1721, 1631 cm^{-1} ; MS m/z (%) 271 (M^+ , 100); HRMS m/z (MALDI) calcd for $\text{C}_{17}\text{H}_{22}\text{NO}_2^+(\text{M}^++\text{H})$ 272.1645; Found: 272.1638.

(3) 3-(2'-Methoxycarbonyl-2'-propenyl)-1-allylindole (3ma)

The reaction of 1-allylindole **1m** (157 mg, 1.0 mmol) with 2-acetoxymethyl acrylate **2a** (192 mg, 1.2 mmol) in the presence of Pd(acac)₂ (15 mg, 5 mol%) and PPh₃ (26 mg, 10 mol%) in 2 mL of HOAc for 18 h afforded 189 mg (74%) of **3ma**: yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 7.51 (d, *J* = 7.8 Hz, 1 H), 7.29 (d, *J* = 7.8 Hz, 1 H), 7.19 (t, *J* = 7.8 Hz, 1 H), 7.08 (t, *J* = 7.8 Hz, 1 H), 6.94 (s, 1 H), 6.19 (s, 1 H), 6.03-5.90 (m, 1 H), 5.51-5.48 (m, 1 H), 5.18 (d, *J* = 10.2 Hz, 1 H), 5.05 (d, *J* = 17.7 Hz, 1 H), 4.71-4.68 (m, 2 H), 3.77 (s, 5 H); ¹³C NMR (75 MHz, CDCl₃): δ 167.8, 139.5, 136.4, 133.5, 127.8, 126.5, 125.5, 121.5, 119.2, 118.9, 117.1, 111.6, 109.6, 51.8, 48.6, 27.5; IR(neat): 1720, 1631 cm⁻¹; MS *m/z* (%) 170 (100), 255 (M⁺, 99.57); HRMS *m/z* (MALDI) calcd for C₁₆H₁₈NO₂⁺(M⁺+H) 256.1332; Found: 256.1347.

(4) 3-(2'-Methoxycarbonyl-2'-propenyl)-1-benzylindole (3na)

The reaction of 1-benzylindole **1n** (100 mg, 0.5 mmol) with 2-acetoxymethyl acrylate **2a** (96 mg, 0.6 mmol) in the presence of Pd(acac)₂ (7.5 mg, 5 mol%) and PPh₃ (13 mg, 10 mol%) in 1 mL of HOAc for 15 h afforded 125 mg (82%) of **3na**: yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 7.61 (d, *J* = 7.5 Hz, 1 H), 7.38-7.10 (m, 8 H), 7.02 (s, 1 H), 6.26 (s, 1 H), 5.56 (s, 1 H), 5.31 (s, 2 H), 3.85 (s, 2 H), 3.81 (s, 3 H), ¹³C NMR (75 MHz, CDCl₃): δ 167.7, 139.5, 137.6, 136.7, 128.6, 127.9, 127.4, 126.9, 126.6, 125.5, 121.7, 119.2, 119.0, 111.9, 109.7, 51.8,

49.8, 27.5; IR(neat): 1719, 1630 cm^{-1} ; MS m/z (%) 91 (100), 305 (M^+ , 25.63); HRMS m/z (MALDI) calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_2\text{Na}^+(\text{M}^++\text{Na})$ 328.1308; Found: 328.1316.

(5) 3-(2'-methoxycarbonyl-2'-propenyl)-1,2-dimethylindole (3oa)

The reaction of 1,2-dimethylindole **1o** (73 mg, 0.5 mmol) with 2-acetoxymethyl acrylate **2a** (96 mg, 0.6 mmol) in the presence of $\text{Pd}(\text{acac})_2$ (7.5 mg, 5 mol%) and bipyridine (13 mg, 10 mol%) in 1 mL of HOAc for 10 h afforded 87 mg (72%) of **3oa**: yellow oil; ^1H NMR (300 MHz, CDCl_3): δ 7.50 (d, $J = 7.8$ Hz, 1 H), 7.31 (d, $J = 8.1$ Hz, 1 H), 7.21 (t, $J = 7.8$ Hz, 1 H), 7.12 (t, $J = 7.8$ Hz, 1 H), 6.25-6.20 (m, 1 H), 5.42-5.38 (m, 1 H), 3.84 (s, 3 H), 3.80 (s, 2 H), 3.69 (s, 3 H), 2.39 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.8, 139.1, 136.5, 134.1, 127.6, 125.1, 120.4, 118.7, 118.1, 108.4, 106.8, 51.7, 29.4, 26.5, 10.1; IR(neat): 1720, 1630 cm^{-1} ; MS m/z (%) 158 (100), 243 (M^+ , 49.93); HRMS m/z (MALDI) calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2\text{Na}^+(\text{M}^++\text{Na})$ 266.1152; Found: 266.1158.

(6) 6-benzyloxy 3-(2'-methoxycarbonyl-2'-propenyl)-1-methylindole (3pa)

The reaction of 6-benzyloxy-1-allylindole **1p** (119 mg, 0.5 mmol) with 2-acetoxymethyl

acrylate **2a** (96 mg, 0.6 mmol) in the presence of Pd(acac)₂ (7.5 mg, 5 mol%) and PPh₃ (13 mg, 10 mol%) in 1 mL of HOAc for 11 h afforded 125 mg (75%) of **3pa**: yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 7.53 (d, *J* = 7.2 Hz, 2 H), 7.48-7.32 (m, 4 H), 6.93-6.89 (m, 2 H), 6.82 (s, 1 H), 6.25 (s, 1 H), 5.57 (s, 1 H), 5.17 (s, 2 H), 3.81 (s, 3 H), 3.78 (s, 2 H), 3.69 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 167.7, 155.4, 139.6, 137.6, 137.4, 128.4, 127.7, 127.4, 126.4, 125.4, 122.3, 119.7, 111.2, 109.2, 94.2, 70.5, 51.7, 32.5, 27.5; IR(neat): 1719, 1625 cm⁻¹; MS *m/z* (%) 244 (100), 335 (M⁺, 18.24); HRMS *m/z* (MALDI) calcd for C₂₁H₂₁NO₃Na⁺(M⁺+Na) 358.1414; Found: 358.1419.

(7) 3-(2'-acetyl-2'-propenyl)-1-methylindole (3kb)

The reaction of 1-methylindole **1k** (131 mg, 1.0 mmol) with 3-acetoxymethyl-3-buten-2-one **2b** (170 mg, 1.2 mmol) in the presence of Pd(acac)₂ (15 mg, 5 mol%) and PPh₃ (26 mg, 10 mol%) in 1 mL of HOAc for 22.5 h afforded 168 mg (79%) of **3kb**: oil; ¹H NMR (300 MHz, CDCl₃): δ 7.49 (d, *J* = 6.9 Hz, 1 H), 7.29 (d, *J* = 7.8 Hz, 1 H), 7.21 (t, *J* = 6.9 Hz, 1 H), 7.08 (t, *J* = 7.8 Hz, 1 H), 6.87 (s, 1 H), 6.04 (s, 1 H), 5.70 (s, 1 H), 3.74 (s, 3 H), 3.72 (s, 2 H), 2.36 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 199.6, 147.8, 136.9, 127.5, 125.7, 121.3, 118.92, 118.89, 118.6, 111.2, 109.0, 32.3, 26.0, 25.9; IR(neat): 1675, 1626 cm⁻¹; MS *m/z* (%) 213 (M⁺, 100); HRMS *m/z* (MALDI) calcd for C₁₄H₁₅NONa⁺(M⁺+Na) 236.1046; Found: 236.1052.

(8) 3-(2-phenylsulfonyl-2-propenyl)-1-methylindole (3kc)

The reaction of 1-methylindole **1k** (132 mg, 1.0 mmol) with 2-phenylsulfonyl-2-propenyl acetate **2c** (288 mg, 1.2 mmol) in the presence of Pd(acac)₂ (15 mg, 5 mol%) and PPh₃ (26 mg, 10 mol%) in 2 mL of HOAc for 11 h afforded 236 mg (76%) of **3kc**: white solid, m.p. 128-129°C; ¹H NMR (300 MHz, CDCl₃): δ 7.90 (d, *J* = 8.1 Hz, 2 H), 7.62 (t, *J* = 6.6 Hz, 1 H), 7.51 (t, *J* = 7.8 Hz, 2 H), 7.25 (d, *J* = 8.1 Hz, 1 H), 7.20 (t, *J* = 7.2 Hz, 1 H), 7.10 (d, *J* = 7.8 Hz, 1 H), 7.00 (t, *J* = 7.2 Hz, 1 H), 6.79 (s, 1 H), 6.40 (s, 1 H), 5.57 (s, 1 H), 3.76 (s, 2 H), 3.73 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 149.7, 138.9, 136.9, 133.3, 129.0, 128.09, 128.08, 128.05, 127.0, 124.7, 121.7, 119.0, 118.6, 109.2, 108.2, 32.6, 25.6; IR(neat): 1615, 1303 cm⁻¹; MS *m/z* (%) 169 (100), 311 (M⁺, 8.46); HRMS *m/z* (MALDI) calcd for C₁₈H₁₈NO₂S⁺(M⁺+H) 312.1053; Found: 312.1044.

(9) 3-(2'-cyano-2'-propenyl)-1-methylindole (3kd)

The reaction of 1-methylindole **1k** (127 mg, 1.0 mmol) with 2-acetoxymethyl acrylonitrile **2d** (150 mg, 1.2 mmol) in the presence of Pd(acac)₂ (15 mg, 5 mol%) and PPh₃

(25 mg, 10 mol%) in 2 mL of HOAc for 16 h afforded 143 mg (75%) of **3kd**: white solid, m.p. 51-52°C (ethyl acetate/Hexane); ¹H NMR (300 MHz, CDCl₃): δ 7.46 (d, *J* = 7.8 Hz, 1 H), 7.31-7.16 (m, 2 H), 7.10 (t, *J* = 8.1 Hz, 1 H), 6.92 (s, 1 H), 5.84 (s, 1H), 5.70 (s, 1 H), 3.70 (s, 3 H), 3.65 (s, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 137.0, 130.3, 127.6, 127.1, 122.3, 121.8, 119.1, 118.9, 118.5, 109.4, 108.1, 32.6, 30.5; IR(neat): 2221, 1617, 1474, 742 cm⁻¹; MS *m/z* (%) 144 (100), 196 (M⁺, 20.29); Anal. Calcd. for C₁₃H₁₂N₂: (%) C 79.56, H 6.16, N 14.27; Found: C 79.60, H 6.21, N 14.37.

(10) 3-(2'-methoxycarbonyl-1'-buten-3'-yl)-1-methylindole (3ke).

The reaction of **1k** (67 mg, 0.5 mmol) with **2e** (113 mg, 0.6 mmol) in the presence of Pd(acac)₂ (8 mg, 5 mol%) and PPh₃ (13 mg, 10 mol%) in 2 mL of HOAc for 3 h afforded 80 mg (66%) of **3ke**. Compound **2e** (7 mg, 6%) was recovered. The reaction of **1k** (66 mg, 0.5 mmol) with **2g** (277 mg, 1.5 mmol) in the presence of Pd(acac)₂ (14 mg, 10 mol%) and PPh₃ (26 mg, 20 mol%) in 2 mL of HOAc for 3.25 h afforded 62 mg (51%) of **3ke**. Compound **2g** (25 mg, 9%) was recovered. **3ke**: oil; ¹H NMR (300 MHz, CDCl₃): δ 7.59 (d, *J* = 7.8 Hz, 1 H), 7.33 (d, *J* = 7.8 Hz, 1 H), 7.26 (t, *J* = 7.8 Hz, 1 H), 7.13 (t, *J* = 7.8 Hz, 1 H), 6.92 (s, 1 H), 6.26 (s, 1 H), 5.58 (s, 1 H), 4.40 (q, *J* = 6.9 Hz, 1 H), 3.80 (s, 3 H), 3.77 (s, 3 H), 1.59 (d, *J* = 6.9 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 167.8, 144.9, 137.2, 126.8, 126.2, 123.8, 121.4, 119.5, 118.6, 117.6, 109.1, 51.7, 32.6, 32.0, 20.3; IR(neat): 1721, 1625, 1465, 1147 cm⁻¹; MS

m/z (%) 243 (M^+ , 100); HRMS m/z (ESI) calcd for $C_{15}H_{17}NO_2Na^+(M^+ + Na)$ 266.1151; Found: 266.1154.

(11) 3-(2'-methoxycarbonyl-1'-hexen-3'-yl)-1-methylindole (3kf).

The reaction of **1k** (66 mg, 0.5 mmol) with **2f** (323 mg, 1.5 mmol) in the presence of Pd(acac)₂ (14 mg, 10 mol%) and PPh₃ (27 mg, 20 mol%) in 2 mL of HOAc for 12 h afforded 61 mg (45%) of **3kf**: oil; ¹H NMR (300 MHz, CDCl₃): δ 7.59 (d, J = 7.8 Hz, 1 H), 7.28 (d, J = 7.8 Hz, 1 H), 7.21 (t, J = 7.8 Hz, 1 H), 7.08 (t, J = 7.8 Hz, 1 H), 6.89 (s, 1 H), 6.22 (s, 1 H), 5.62 (s, 1 H), 4.20 (t, J = 7.5 Hz, 1 H), 3.75 (s, 3 H), 3.73 (s, 3 H), 1.95-1.87 (m, 2 H), 1.45-1.32 (m, 2 H), 0.94 (t, J = 7.2 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 167.9, 144.1, 137.1, 127.3, 126.6, 123.7, 121.4, 119.5, 118.6, 116.3, 109.1, 51.8, 37.4, 36.8, 32.7, 21.2, 14.1; IR(neat): 1719, 1626, 1469, 1149 cm⁻¹; MS m/z (%) 228 (100), 271 (M^+ , 41.59); HRMS m/z (EI) calcd for $C_{17}H_{21}NO_2^+(M^+)$ 271.1572; Found: 271.1585.

Pulse Sequence: s2pu1