

Pd-Catalyzed Selective Addition of Heteroaromatic C-H Bonds to C-C Triple Bonds Under Mild Conditions

Supporting Information

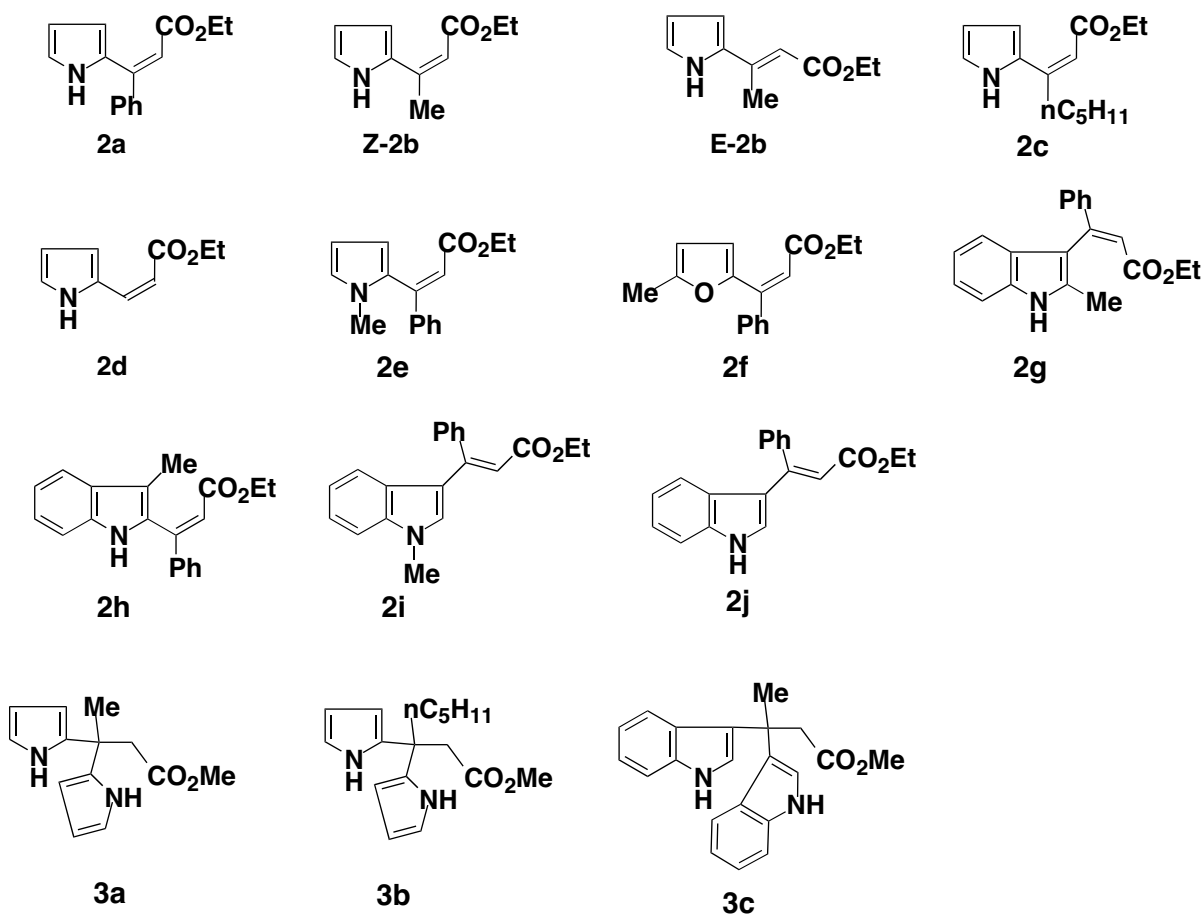
Spectroscopic data of compounds **2a-j** and **3a-c**

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Spectroscopic data of compounds 2a-j and 3a-c



(2Z) Ethyl 3-(2-pyrrolyl)-3-phenyl-2-propenoate (2a). Light yellow oil, ^1H NMR (CDCl_3 , 300 MHz) δ 1.21 (t, $J = 7.2$ Hz, 3H, CH_3), 4.12 (q, $J = 7.2$ Hz, 2H, CH_2), 5.48 (s, 1H, vinyl), 5.99 (m, 1H, aryl), 6.10 (m, 1H, aryl), 6.95 (m, 1H, aryl), 7.24-7.32 (m, 5H, aryl), 12.75 (br s, 1H, NH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 14.17, 60.53, 109.63, 109.70, 118.97, 122.77, 127.73, 128.11, 128.81, 130.25, 142.46, 149.15, 168.82. IR (neat, cm^{-1}) 3192 (N-H), 1675 (C=O). Anal. calcd for $\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}$: C 74.67, H 6.27, N 5.80; found: C 74.66, H 6.39, N 5.62.

(2Z) Ethyl 3-(2-pyrrolyl)-2-butenate (Z-2b). Light yellow oil, ^1H NMR (CDCl_3 , 300 MHz) δ 1.30 (t, $J = 7.2$ Hz, 3H, CH_3), 2.27 (d, $J = 0.9$ Hz, 3H, CH_3), 4.18 (q, $J = 7.2$ Hz, 2H, CH_2), 5.57 (d, $J = 0.9$ Hz, 1H, vinyl), 6.25 (m, 1H, aryl), 6.62 (m, 1H, aryl), 6.99 (m, 1H, aryl), 12.91 (br s, 1H, NH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 14.21, 24.48, 60.30, 108.66, 109.41, 114.36, 121.88, 130.22, 144.36, 168.82. IR (neat, cm^{-1}) 3380 (N-H), 1716 (C=O). Anal. calcd for $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$: C 67.02, H 7.31, N 7.82; found: C 66.87, H 7.31, N 7.67.

(2E) Ethyl 3-(2-pyrrolyl)-2-butenolate (E-2b). Light yellow oil, ^1H NMR (CDCl_3 , 300 MHz) δ 1.30 (t, $J = 7.2$ Hz, 3H, CH_3), 2.53 (d, $J = 0.9$ Hz, 3H, CH_3), 4.19 (q, $J = 7.2$ Hz, 2H, CH_2), 5.94 (d, $J = 0.9$ Hz, 1H, vinyl), 6.28 (m, 1H, aryl), 6.59 (m, 1H, aryl), 6.87 (m, 1H, aryl), 8.70 (br s, 1H, NH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 14.35, 15.84, 59.63, 108.62, 110.47, 111.38, 121.38, 132.66, 145.65, 167.36.

(2Z) Methyl 3-(2-pyrrolyl)-2-octenoate (2c). Light yellow oil, ^1H NMR (CDCl_3 , 300 MHz) δ 0.90 (t, $J = 7.5$ Hz, 3H, CH_3), 1.35 (m, 4H, CH_2), 1.65 (m, 2H, CH_2), 2.54 (t, $J = 7.5$ Hz, 2H, CH_2), 3.74 (s, 3H, CH_3), 5.57 (s, 1H, vinyl), 6.27 (m, 1H, aryl), 6.63 (m, 1H, aryl), 6.99 (m, 1H, aryl), 12.95 (br s, 1H, NH); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 13.98, 22.44, 31.10, 31.79, 38.45, 51.56, 107.46, 109.54, 114.34, 122.02, 129.78, 149.82, 169.55. IR (neat, cm^{-1}) 3396 (N-H), 1733 (C=O). Anal. calcd for $\text{C}_{13}\text{H}_{19}\text{O}_2\text{N}$: C 70.56, H 8.65, N 6.33; found: C 70.66, H 8.69, N 6.28.

(2Z) Ethyl 3-(2-pyrrolyl)-2-propenoate (2d). Light yellow oil, ^1H NMR (CDCl_3 , 300 MHz) δ 1.31 (t, $J = 6.9$ Hz, 3H, CH_3), 4.20 (q, $J = 6.9$ Hz, 2H, CH_2), 5.52 (d, $J = 12.3$ Hz, 1H, vinyl), 6.25 (m, 1H, aryl), 6.49 (m, 1H, aryl), 6.75 (d, $J = 12.3$ Hz, 1H, vinyl), 6.98 (m, 1H, aryl), 12.25 (br s, 1H, NH); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 14.20, 60.36, 107.63, 110.07, 118.52, 122.85, 129.05, 134.63, 169.15. IR (neat, cm^{-1}) 3274 (N-H), 1687 (C=O). Anal. calcd for $\text{C}_9\text{H}_{11}\text{O}_2\text{N}$: C 65.44, H 6.71, N 8.48; found: C 65.58, H 6.79, N 8.33.

(2Z) Ethyl 3-(1-methyl-2-pyrrolyl)-3-phenyl-2-propenoate (2e). Light yellow oil, ^1H NMR (CDCl_3 , 300 MHz) δ 1.20 (t, $J = 7.2$ Hz, 3H, CH_3), 3.32 (s, 3H, CH_3), 4.12 (q, $J = 7.2$ Hz, 2H, CH_2), 6.12 (m, 1H, aryl), 6.20 (m, 1H, aryl), 6.37 (s, 1H, vinyl), 6.73 (m, 1H, aryl), 7.34 (m, 5H, aryl); ^{13}C NMR (CDCl_3 , 75 MHz) δ 13.94, 34.14, 59.84, 107.59, 111.48, 118.61, 123.56, 127.80, 128.26, 129.36, 129.66, 140.17, 146.85, 165.75. IR (neat, cm^{-1}) 1722 (C=O).

(2Z) Ethyl 3-(2-methyl-5-furyl)-3-phenyl-2-propenoate (2f). Light yellow oil, ^1H NMR (CDCl_3 , 300 MHz) δ 1.21 (t, $J = 7.2$ Hz, 3H, CH_3), 2.22 (s, 3H, CH_3), 4.14 (q, $J = 7.2$ Hz, 2H, CH_2), 5.80 (1H, s, vinyl), 5.99 (d, $J = 3.3$ Hz, 1H, aryl), 6.45 (d, $J = 3.3$ Hz, 1H, aryl), 7.25-7.48 (m, 5H, aryl); ^{13}C NMR (CDCl_3 , 75 MHz) δ 13.68, 14.11, 60.24, 107.90, 115.98, 125.82, 128.09, 128.72,

128.97, 139.60, 141.94, 149.25, 153.81, 166.55. IR (neat, cm^{-1}) 1716 (C=O). Anal. calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3$: C 74.98, H 6.29; found: C 74.43, H 6.28.

(2Z) Ethyl 3-(2-methyl-3-indole)-3-phenyl-2-propenoate (2g). Yellow crystals, m.p. 138.4-139.2 °C, ^1H NMR (CDCl_3 , 300 MHz) δ 1.14 (t, $J = 6.9$ Hz, 3H, CH_3), 1.86 (s, 3H, CH_3), 4.09 (q, $J = 6.9$ Hz, 2H, CH_2), 6.41 (s, 1H, vinyl), 6.97-7.05 (m, 4H, aryl), 7.21-7.35 (5H, m, aryl), 8.65 (s, 1H, NH). ^{13}C NMR (CDCl_3 , 75 MHz) δ 12.53, 14.07, 59.82, 110.57, 116.66, 119.02, 119.37, 120.75, 128.05, 128.14, 128.23, 129.08, 129.19, 135.29, 135.98, 141.42, 150.95, 166.47. IR (CDCl_3 , cm^{-1}) 3347 (N-H), 1699 (C=O). Anal. calcd for $\text{C}_{20}\text{H}_{19}\text{O}_2\text{N}$: C 78.66, H 6.27, N 4.59; found: C 78.27, H 6.32, N 4.48.

(2Z) Ethyl 3-(3-methyl-2-indole)-3-phenyl-2-propenoate (2h). White crystals, m.p. 116.7-117.8 °C, ^1H NMR (CDCl_3 , 300 MHz) δ 1.23 (t, $J = 6.9$ Hz, 3H, CH_3), 1.80 (s, 3H, CH_3), 4.14 (q, $J = 6.9$ Hz, 2H, CH_2), 6.13 (s, 1H, vinyl), 7.30-7.36 (m, 9H, aryl), 10.15 (s, 1H, NH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 10.23, 14.06, 60.53, 111.22, 115.84, 117.73, 119.21, 123.57, 125.74, 128.35, 128.65, 128.80, 128.98, 130.30, 136.11, 141.23, 148.19, 166.86. IR (CDCl_3 , cm^{-1}) 3367 (N-H), 1672 (C=O). Anal. calcd for $\text{C}_{20}\text{H}_{19}\text{O}_2\text{N}$: C 78.66, H 6.27, N 4.59; found: C 78.50, H 6.34, N 4.91

(2E) Ethyl 3-(1-methyl-3-indole)-3-phenyl-2-propenoate (2i): White crystals, mp 112.7-113.5 °C, ^1H NMR (CDCl_3 , 300 MHz) δ 1.11 (t, $J = 7.2$ Hz, 3H, CH_3), 3.69 (s, 3H, CH_3), 4.03 (q, $J = 7.2$ Hz, 2H, CH_2), 6.53 (s, 1H, vinyl), 6.71 (s, 1H, aryl), 7.22-7.84 (m, 8H, aryl), 7.83 (d, $J = 7.8$ Hz, 1H, aryl). ^{13}C NMR (CDCl_3 , 75 MHz) δ 14.08, 33.09, 59.50, 109.88, 111.70, 117.14, 121.04, 121.13, 122.69, 125.60, 127.66, 128.11, 128.72, 133.60, 138.02, 140.40, 152.19, 166.92. IR (CDCl_3 , cm^{-1}) 1714 (C=O). Anal. calcd for $\text{C}_{20}\text{H}_{19}\text{O}_2\text{N}$: C 78.66, H 6.27, N 4.59; found: C 78.27, H 6.27, N 4.54.

(2Z) Ethyl 3-(3-indole)-3-phenyl-2-propenoate (2j). White crystals, mp 135.4-136.5 °C, ^1H NMR (CDCl_3 , 300 MHz) δ 1.13 (t, $J = 6.9$ Hz, 3H, CH_3), 4.05 (q, $J = 6.9$ Hz, 2H, CH_2), 6.56 (s, 1H, vinyl), 6.83 (d, $J = 2.7$ Hz, 1H, aryl), 7.18-7.32 (m, 3H, aryl), 7.39 (m, 5H, aryl), 7.81 (d, $J = 7.5$ Hz, 1H, aryl), 8.48 (br s, 1H, NH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 14.08, 59.64, 111.74, 112.32, 118.67, 120.83, 121.28, 122.98, 124.98, 127.67, 127.73, 128.75, 129.19, 137.05, 140.21, 152.36, 167.02. IR

(CDCl₃, cm⁻¹) 3345 (N-H), 1689 (C=O). Anal. calcd for C₁₉H₁₇O₂N: C 78.33, H 5.88, N 4.81; found: C 77.86, H 5.89, N 4.71.

Ethyl 3-bis(2-Pyrryl)propanoate (3a). Light yellow oil, ¹H NMR (CDCl₃, 300 MHz) δ 1.05 (t, *J* = 6.9 Hz, 3H, CH₃), 1.64 (s, 3H, CH₃), 2.90 (s, 2H, CH₂), 3.93 (q, *J* = 6.9 Hz, 2H, CH₂), 5.93 (m, 2H, aryl), 6.01 (m, 2H, aryl), 6.50 (m, 2H, aryl), 8.44 (s, 2H, NH); ¹³C NMR (CDCl₃, 75 MHz) δ 13.88, 28.78, 37.70, 46.27, 60.55, 104.43, 107.58, 117.01, 136.34, 172.35. IR (CDCl₃, cm⁻¹) 3382 (N-H), 1720 (C=O).

Methyl 3-bis(2-pyrryl)octanoate (3b). Light yellow oil, ¹H NMR (CDCl₃, 300 MHz) δ 0.84 (t, *J* = 7.2 Hz, 3H, CH₃), 1.23 (m, 8H, 4CH₂), 3.00 (s, 2H, CH₂), 3.55 (s, 3H, CH₃), 6.00 (m, 2H, aryl), 6.11 (m, 2H, aryl), 6.61 (m, 2H, aryl), 8.44 (br s, 2H, NH); ¹³C NMR (CDCl₃, 75 MHz) δ 13.98, 22.43, 23.99, 32.04, 40.51, 41.64, 43.12, 51.71, 105.25, 107.58, 116.99, 135.32, 173.02. IR (CDCl₃, cm⁻¹) 3372 (N-H), 1716 (C=O).

Ethyl 3-bis(3-indole)butanoate (3c). Yellow crystals, mp 179.5-180.1°C, ¹H NMR (CDCl₃, 300 MHz) δ 0.78 (t, *J* = 7.2 Hz, 3H, CH₃), 2.01 (s, 3H, CH₃), 3.30 (s, 2H, CH₂), 3.76 (q, *J* = 7.2 Hz, 2H, CH₂), 6.87 (t, *J* = 7.5 Hz, 2H, aryl), 7.07-7.10 (m, 4H, aryl), 7.30 (d, *J* = 7.8 Hz, 2H, aryl), 7.35 (d, *J* = 8.4 Hz, 2H, aryl), 7.88 (s, 2H, NH); ¹³C NMR (CDCl₃, 75 MHz) δ 13.73, 27.44, 37.84, 45.76, 59.73, 111.05, 118.83, 121.02, 121.32, 122.95, 126.11, 136.97, 171.73. IR (CDCl₃, cm⁻¹) 3403 (N-H), 1712 (C=O).