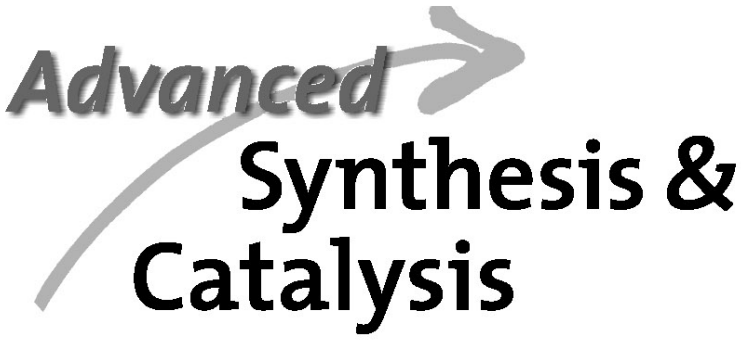

Supporting Information

Supporting Information for

Gold-Catalysed Direct Couplings of Indoles and Pyrroles with 1,3-Dicarbonyl Compounds

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General Remarks: Temperatures are reported as bath temperature. Solvents used in extraction and purification were distilled prior to use. Compounds were visualised on analytical thin-layer chromatograms (TLC) by UV light (254 nm). The products, after usual work-up, were purified by flash chromatography on silica gel (230-400 mesh) eluting with *n*-hexane/ethyl acetate mixtures. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Varian Mercury-300 FT NMR and a Bruker AC 200 E spectrometer. EI (70eV) mass spectra were recorded with a Varian Saturn 2100 T GC/MS instrument and ESI accurate mass measurements were recorded with a Mass spectrometer Finnigan TSQ Quantum Ultra with accurate mass options instrument. I R were recorded with a Perkin-Elmer 683 spectrometer. Only the most significant IR absorptions are given. All starting materials, catalysts, and solvents if not otherwise stated, are commercially available and were used as purchased, without further purification. The products **3a**,[1] **3b**,[2] **3c**,[3] **3f**[4] **and 3g**[5] are known and were determined using comparison of their physical and spectral data with those reported in literature.

3-(1*H*-Indol-3-yl)-5-methyl-cyclohex-2-enone (3c): IR (KBr): ν = 3220, 1630, 740 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 200 MHz) δ = 1.10 (d, *J* = 5.7 Hz, 3H), 2.12-2.51 (m, 4H), 3.00 (d, *J* = 17.3 Hz 1H), 6.47 (s, 1H), 7.15-7.22 (m, 2H), 7.46-7.50 (m, 1H), 7.84-7.88 (m, 1H), 8.02 (d, *J* = 2.7 Hz, 1H), 11.87 (s, 1H), ^{13}C NMR ([D$_6$]DMSO, 50.3 MHz) δ = 21.0, 29.6, 36.0, 45.1, 112.5, 114.1, 119.4, 120.3, 121.0, 122.3, 124.4, 129.1, 137.6, 155.1, 198.4. MS (70 EV, EI, relative intensity): 226 [(M + 1)$^{+}$, 100)], 225 (M*, 28), 183 (38), 154 (29). ESI-HRMS calculated for $C_{15}H_{16}NO$: 226.1226. Found: 226.1229.

3-(1*H*-Indol-3-yl)-5-phenyl-cyclohex-2-enone (3d): IR (KBr): ν = 3160, 1630, 1580, 730 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 300 MHz) δ = 2.49-2.53 (m, 1H), 2.72-2.81 (m, 1H), 2.93-3.03

(m, 1H), 3.15-3.22 (m, 1H), 3.34-3.45 (m, 1H), 6.56 (s, 1H), 7.14-7.49 (m, 8 H), 7.86-7.88 (m, 1H), 8.06 (s, 1H), 11.90 (s, 1H). ^{13}C NMR ([D_6]DMSO, 75.45 MHz) δ = 36.2, 40.7, 44.6, 113.2, 114.6, 120.0, 121.0, 121.7, 123.0, 127.2, 127.8, 129.1, 130.2, 138.3, 144.8, 155.6, 198.3. ESI-HRMS calculated for $C_{20}H_{18}NO$: 288.1383. Found: 288.1389.

5-Methyl-3-(1-methyl-1*H*-indol-3-yl)-cyclohex-2-enone (3e): IR (KBr): ν = 1640, 1590, 740 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 1.07 (d, *J* = 5.7 Hz, 3H), 2.02-2.79 (m, 5H), 3.68 (s, 3H), 6.59 (s, 1H), 7.16-7.31 (m, 4H), 7.92 (d, *J* = 7.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ = 21.3, 29.8, 33.1, 36.6, 45.4, 110.0, 114.3, 120.5, 121.1, 121.3, 122.7, 125.3, 131.0, 138.0, 154.5, 199.9. MS (70 EV, EI, relative intensity): 239 (M^*, 100), 198 (72), 169 (40). ESI-HRMS calculated for $C_{16}H_{18}NO$: 240.1383. Found: 240.1387.

3-(2-Phenyl-1*H*-indol-3-yl)-cyclohex-2-enone (3h): IR (KBr): ν = 3230, 1630, 730 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 2.00-2.05 (m, 2H), 2.48-251 (m, 4H), 6.45 (s, 1H), 7.20-7.23 (m, 1H), 7.26-7.29 (m, 1H), 7.41-7.43 (m, 2H), 7.46-7.48 (m, 2H), 7.54-7.55 (m, 2H), 7.73-7.75 (m, 1H), 8.59 (bs, 1H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ = 23.3, 30.6, 37.5, 111.1, 114.1, 119.9, 121.1, 123.1, 127.2, 128.1, 128.3, 128.9, 132.7, 136.0, 136.9, 157.8, 199.5. MS (70 EV, EI, relative intensity): 287 (M^*, 100), 270 (78), 258 (66), 230 (64). ESI-HRMS calculated for $C_{20}H_{18}NO$: 288.1383. Found: 288.1385.

4-(2-Phenyl-1*H*-indol-3-yl)-pent-3-en-2-one (3i): IR (KBr): ν = 3300, 1650, 1600, 740 cm^{-1}. ^{1}H NMR ([D_6]acetone, 200 MHz) δ = 2.21 (s, 3H), 2.34 (s, 3H), 6.56 (s, 1H), 7.07- 7.21 (m, 3H), 7.40-7.54 (m, 3H), 7.63-7.63 (m, 3H), 11.50 (bs, 1H). ^{13}C NMR ([D_6]acetone, 50.3 MHz) δ = 21.6, 32.1, 112.4, 116.8, 119.9, 120.8, 122.8, 126.8, 127.3, 127.9, 128.7, 128.8, 129.3, 133.6, 137.4, 150.3, 197.9. MS (70 EV, EI, relative intensity): 275 (M^+, 100), 260 (65), 217 (82); MS (70 EV, EI, relative intensity): 295 (M^+, 57), 281 (100), 253 (21). ESI-HRMS calculated for $C_{19}H_{18}NO$: 276.1383. Found: 276.1380.

3-(5-Bromo-1*H*-indol-3-yl)-5,5-dimethyl-cyclohex-2-enone (3j): IR (KBr): ν = 3210, 1640, 1590, 790 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 1.15 (s, 6H), 2.40 (s, 2H), 2.68 (s, 2H), 6.60 (s, 1H), 7.26-7.34 (m, 3H), 7.52-7.54 (m, 1H), 8.10 (s, 1H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ = 27.9, 28.0, 32.8, 41.6, 50.5, 113.5, 114.1, 114.3, 119.0, 122.4, 124.8, 126.2, 129.9, 136.3, 152.8, 198.1. MS (70 EV, EI, relative intensity): 320 [$(M+1)^+$, 65], 318 [$(M+1)^+$, 58], 264 (47), 262 (42), 155 (100). ESI-HRMS calculated for $C_{16}H_{17}BrNO$: 320.0468. Found: 320.0471.

3-(2-Butyl-1*H*-indol-3-yl)-5,5-dimethyl-cyclohex-2-enone (3k): IR (KBr): ν = 3220, 1640, 740 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 0.88 (t, *J* = 6.6 Hz, 3H), 1.17 (s, 6H), 1.25-1.43 (m, 2H), 1.64-1.72 (m, 2H), 2.40 (s, 2H), 2.78 (s, 2H), 2.85 (t, *J* = 8.6 Hz, 2H), 6.21 (s, 1H),

7.12-7.17 (m, 2H), 7.30-7.35 (m, 1H), 7.62-7.66 (m, 1H), 8.80 (bs, 1H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ = 13.8, 22.5, 27.2, 28.3, 31.8, 34.3, 44.8, 51.2, 110.9, 119.7, 120.5, 121.9, 124.8, 126.7, 135.4, 139.1, 156.6, 200.0. MS (70 EV, EI, relative intensity): 295 (M^+, 57), 281 (100), 253 (21). ESI-HRMS calculated for $C_{20}H_{26}NO$: 296.2009. Found: 296.2010.

3-(1*H*-Pyrrol-2-yl)-cyclohex-2-enone (6a): IR (KBr): ν = 3320, 1650, 1600, 740 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 2.00-2.16 (m, 2H); 2.42-2.49 (m, 2H), 2.69-2.75 (m, 2H), 6.27-6.31 (m, 1H), 6.55 (s, 1H), 6.66 (s, 1H), 7.08 (s, 1H), 10.70 (bs, 1H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ = 22.4, 26.5, 37.3, 110.6, 113.5, 116.9, 124.4, 130.1, 152.1, 200.8. MS (70 EV, EI, relative intensity): 161 (M^+, 100), 133 (81), 105 (84). ESI-HRMS calculated for $C_{10}H_{12}NO$: 162.0913. Found: 162.0918.

5,5-Dimethyl-3-(1*H*-pyrrol-2-yl)-cyclohex-2-enone (6b): IR (KBr): ν = 3280, 1640, 1600, 720 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 1.09 (s, 6H); 2.31 (s, 2H), 2.57 (s, 2H), 6.26-6.30 (m, 1H), 6.58 (s, 1H), 6.65-6.67 (m, 1H), 7.07-7.08 (m, 1H), 10.70 (bs, 1H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ = 28.3, 29.0, 33.2, 40.3, 50.9, 110.6, 113.4, 115.8, 124.3, 130.4, 149.9, 200.7. MS (70 EV, EI, relative intensity): 189 (M^+, 100), 133 (92), 105 (95). ESI-HRMS calculated for $C_{12}H_{16}NO$: 190.1226. Found: 190.1220.

3-(5-Ethyl-1*H*-pyrrol-2-yl)-5,5-dimethyl-cyclohex-2-enone (6c): IR (KBr): ν = 3290, 1650, 1600, 780 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 1.09 (s, 6H); 1.28 (t, *J* = 7.5 Hz, 3H), 2.28 (s, 2H), 2.55 (s, 2H), 2.75 (q, *J* = 7.5 Hz, 2H), 6.02 (s, 1H), 6.56-6.59 (m, 2H), 10.40 (bs, 1H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ = 13.5, 21.1, 28.3, 28.4, 33.2, 40.1, 51.1, 107.6, 114.2, 114.6, 129.1, 142.3, 149.5, 200.2. MS (70 EV, EI, relative intensity): 218 [$(M+1)^+$, 55], 217 (M^+, 8), 203 (17), 147 (100), 119 (16). ESI-HRMS calculated for $C_{14}H_{20}NO$: 218.1539. Found: 218.1535.

5,5-Dimethyl-3-(4,5,6,7-tetrahydro-1*H*-indol-2-yl)-cyclohex-2-enone (6d): IR (KBr): ν = 3300, 1640, 1600, 800 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 1.08 (s, 6H); 1.69-1.79 (m, 4H), 2.17-2.27 (m, 2H), 2.52-2.54 (m, 4H), 2.65-2.71 (m, 2H), 6.35 (s, 1H), 6.44 (s, 1H), 9.70 (bs, 1H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ = 22.7, 22.9, 23.5, 26.9, 28.4, 29.6, 33.3, 40.2, 51.0, 112.8, 114.3, 120.3, 128.5, 135.3, 149.4, 199.8. MS (70 EV, EI, relative intensity): 244 [$(M+1)^+$, 87], 243 (M^+, 12), 203 (17), 147 (100), 119 (16). ESI-HRMS calculated for $C_{16}H_{22}NO$: 244.1696. Found: 244.1693.

3-(2,5-Dimethyl-1*H*-pyrrol-3-yl)-5,5-dimethyl-cyclohex-2-enone (6e): IR (KBr): ν = 3240, 1630, 1580 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 1.09 (s, 6H), 2.20 (s, 3H), 2.28 (s, 2H), 2.39 (s, 3H), 2.58 (s, 2H), 6.01 (s, 1H), 6.16 (s, 1H), 9.61 (bs, 1H). ^{13}C NMR ($CDCl_3$,

50.3 MHz) δ = 12.3, 14.7, 28.2, 28.3, 33.1, 43.0, 50.5, 105.5, 118.7, 126.6, 128.5, 156.9, 200.4. MS (70 EV, EI, relative intensity): 218 [$(M+1)^+$, 50], 217 (M^+, 38), 203 (50), 161 (53), 133 (100). ESI-HRMS calculated for $C_{14}H_{20}NO$: 218.1539. Found: 218.1540.

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