Supporting Materials

CuBr-Catalyzed Direct Indolation of Tetrahydroisoquinolines via Cross-Dehydrogenative-Coupling between sp^3 C-H and sp^2 C-H Bonds

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Contents

- 1) Experimental details and characterization data for all new compounds;
- 2) PDF file of copies of ^1H NMR and ^{13}C NMR spectra for all new compounds.

1) Experimental details and characterization data for all new compounds

General information: ^1H NMR spectra were recorded on Varian 400 and 500 MHz spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for CDCl_3 or (2.49 ppm) the center peak of residual DMSO. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; dt, doublet of triplet; dq, doublet of quartet; ddd, doublet of doublet of doublet; dddd, doublet of doublet of doublet of doublet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). ^{13}C NMR spectra were obtained at 100 and 125 MHz and referenced to the internal solvent signals (center peak is 77.00 ppm in CDCl_3 or 40.38 ppm in DMSO-d_6). MS data were obtained by Agilent 6890N Network GC System/Agilent 5973 Mass Selective Detector or KRATOS MS25RFA Mass Spectrometer. HRMS were obtained by Kratos MS25RFA Mass Spectrometer. IR spectra were recorded by an ABB Bomem MB100 instrument. Melting points were recorded by Melting Point Apparatus, Gallenkamp. Flash column chromatography was performed over SORBENT silica gel 30-60 μm . Thin layer chromatography was performed using Sorbent Silica Gel 60 F_{254} TLC plates and visualized with ultraviolet light. All reagents were weighed and handled in air at room temperature. All reagents were purchased from Aldrich and used without further purification.

General Procedure for 2-Aryl-1,2,3,4-tetrahydro-isoquinolines^[1]: Copper(I) iodide (200 mg, 1.0 mmol) and potassium phosphate (4.25 g, 20.0 mmol) were put into a Schlenk tube. The tube was evacuated and back filled with nitrogen. 2-Propanol (10.0 mL), ethylene glycol (1.11 mL, 20.0 mmol), 1,2,3,4-tetrahydro-isoquinoline (2.0 mL, 15 mmol) and iodobenzene (1.12 mL, 10.0 mmol) were added successively by micro-syringe at room temperature. The reaction mixture was heated at 85-90 $^\circ\text{C}$ and kept for 24 h and then allowed to cool to room temperature. Diethyl ether (20 mL) and water (20 mL) were then added to the reaction mixture. The organic layer was extracted by diethyl ether (2×20 mL). The combined organic phases were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel (hexane/ethyl acetate=20:1), and the fraction with an $R_f=0.7$ was collected to give the desired product **1a** with 60-80 % isolated yields.

1,2,3,4-Tetrahydro-2-phenylisoquinoline (1a). ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.29-7.25(m, 2H), 7.17-7.12(m, 4H), 6.96(d, $J = 8.5$ Hz, 2H), 6.81(dd, $J = 7.5, 7.5$ Hz, 1H), 4.38(s, 2H), 3.53(dd,

$J = 6.0, 6.0$ Hz, 2H), 2.96(dd, $J = 6.0, 6.0$ Hz, 2H); ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 150.50, 134.82, 134.42, 129.15, 128.47, 126.49, 126.27, 125.97, 118.61, 115.09, 50.68, 46.46, 29.07; MS (EI) m/z (%) 209, 208(100), 115, 104, 91, 78, 77, 51. [^1H NMR & ^{13}C NMR spectra see S-38 & S-39]

1,2,3,4-Tetrahydro-2-(4-methoxyphenyl)isoquinoline (1b). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 7.15-7.08(m, 4H), 6.95(d, $J = 8.8$ Hz, 2H), 6.84(d, $J = 8.8$ Hz, 2H), 4.28(s, 2H), 3.75(s, 3H), 3.42(dd, $J = 6.0, 6.0$ Hz, 2H), 2.97(dd, $J = 6.0, 6.0$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 153.26, 145.11, 134.40, 134.34, 128.51, 126.34, 126.09, 125.74, 117.88, 114.41, 55.62, 52.68, 48.47, 29.18; MS (EI) m/z (%) 239(100), 238, 224, 135, 120, 104, 91, 77, 65, 51. [^1H NMR & ^{13}C NMR spectra see S-40 & S-41]

General procedure for products 3: To a mixture of 1,2,3,4-tetrahydro-2-phenylisoquinoline (20.9 mg, 0.1 mmol), CuBr (0.7 mg, 0.005 mmol), and indole (14.2 mg, 0.12 mmol), *tert*-butyl hydroperoxide (0.026 mL, 5–6M in decane) was added into the mixture under air at room temperature. Then the reaction vessel was capped. The temperature of the reaction mixture was raised to 50°C for overnight. The resulting solid was diluted with chloroform. Solvent was evaporated and the residue was purified by Thin Layer Chromatography (methylene chloride), and the fraction with an $R_f=0.9$ was collected to give the desired product **3a**.

1-(1*H*-Indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (3a). Isolated by Thin Layer Chromatography (methylene chloride, $R_f = 0.9$). Melting point is 179.0-180.0 °C. IR (KBr): $\nu_{\max}$ 3409, 3056, 3027, 2966, 2921, 1595, 1501, 1456, 1419, 1382, 1288, 1215, 1133, 1092, 1031, 937, 776, 753 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 7.86(s, 1H), 7.53(d, $J = 7.6$ Hz, 1H), 7.30-7.26(m, 2H), 7.23-7.19(m, 2H), 7.17-7.11(m, 4H), 7.03-6.99(m, 3H), 6.76(dddd, $J = 7.2, 7.2, 1.2, 1.2$ Hz, 1H), 6.60(dd, $J = 2.4, 1.2$ Hz, 1H), 6.16(s, 1H), 3.62(d, $J = 12.0$ Hz, 1H), 3.61(d, $J = 3.2$ Hz, 1H), 3.06(ddd, $J = 16.0, 7.6, 7.6$ Hz, 1H), 2.79(ddd, $J = 16.0, 4.4, 4.4$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 149.60, 137.24, 136.43, 135.41, 129.05, 128.67, 127.90, 126.52, 126.33, 125.56, 124.02, 121.98, 119.99, 119.51, 119.20, 117.99, 115.71, 110.92, 56.67, 42.37, 26.74; MS (EI) m/z (%) 325, 324(100), 323, 232, 231, 219, 218, 217, 208, 207, 206, 195, 162, 129, 118, 117, 104, 90, 89, 85, 83, 77, 57; HRMS calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2$: 324.1626; found: 324.1622.

1-[4-(2-Methoxy-propenyl)-1*H*-pyrrol-3-yl]-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (3b). Isolated by Thin Layer Chromatography (methylene chloride/diethyl ether=40:1, $R_f = 0.7$). Melting point is 172.0-174.0 °C. IR (KBr): $\nu_{\max}$ 3406, 3060, 3031, 2999, 2962, 2925, 1594, 1492, 1378, 1284, 1209, 1174, 1109, 1052, 937, 833, 807, 771, 762, 694, 668, 606 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.83(s, 1H), 7.27-7.21(m, 3H), 7.20-7.15(m, 4H), 7.02(d, $J = 8.5$ Hz, 2H), 6.87(d, $J = 2.0$ Hz, 1H), 6.78(ddd, $J = 7.0, 7.0, 1.0$ Hz, 2H), 6.57(dd, $J = 2.5$ Hz, 1H), 6.14(s, 1H), 3.65(s, 3H), 3.60(d, $J = 12.5$ Hz, 1H), 3.59(d, $J = 3.5$ Hz, 1H), 3.07(ddd, $J = 16.0, 7.5, 7.5$ Hz, 1H), 2.82(ddd, $J = 16.5, 4.0, 4.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 153.88, 149.91, 137.47, 135.49, 131.59, 129.18, 128.76, 127.99, 126.93, 126.68, 125.68, 125.01, 118.58, 118.40, 116.25, 112.24, 111.64, 101.86, 56.94, 55.66, 42.23, 26.93; MS (EI) m/z (%) 355, 354(100), 353, 263, 262, 261,

260, 250, 249, 248, 234, 218, 217, 209, 208, 207, 206, 177, 147, 132, 117, 116, 104, 91, 77; HRMS calcd for C₂₄H₂₂N₂O: 354.1732; found: 354.1725.

1-(2-Methyl-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (3c). Isolated by Thin Layer Chromatography (methylene chloride, R_f = 0.6). Melting point is 80.0-85.0 °C. IR (KBr): $\nu_{\max}$ 3407, 3064, 3027, 2917, 2852, 1596, 1492, 1460, 1423, 1374, 1305, 1215, 1129, 1019, 937, 912, 750, 741, 692, 599 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.63(s, 1H), 7.17-7.14(m, 5H), 7.08-7.03(m, 3H), 7.00(dd, *J* = 7.5, 7.5 Hz, 3H), 6.89(dd, *J* = 7.5, 7.5 Hz, 1H), 6.82(dd, *J* = 7.5, 7.5 Hz, 1H), 5.95(s, 1H), 3.67(ddd, *J* = 13.0, 8.5, 4.5 Hz, 1H), 3.60(ddd, *J* = 12.5, 5.0, 5.0 Hz, 1H), 3.07(ddd, *J* = 16.0, 8.5, 5.0 Hz, 1H), 2.98(ddd, *J* = 16.0, 5.0, 5.0 Hz, 1H), 1.99(s, 3H); ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 150.94, 138.00, 135.30, 134.88, 133.30, 128.79, 128.78, 128.65, 128.61, 128.20, 126.26, 126.04, 120.75, 120.15, 119.43, 119.15, 113.41, 109.98, 109.97, 57.08, 45.80, 27.90, 12.26; MS (EI) *m/z* (%) 338, 218, 206, 131, 130, 118, 117, 87, 86, 85, 84, 83(100), 58, 49, 47; HRMS calcd for C₂₄H₂₂N₂: 338.1783; found: 338.1778.

1-(3-Methyl-1H-indol-2-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (3d). Isolated by Thin Layer Chromatography (hexane/methylene chloride/triethyl amine=40:30:1, R_f = 0.9). IR (neat liquid): $\nu_{\max}$ 3429, 3058, 3026, 2917, 2857, 1598, 1578, 1503, 1495, 1456, 1383, 1343, 1318, 1265, 1223, 1180, 1154, 1128, 1015 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.49-7.47(m, 1H), 7.27-7.10(m, 8H), 7.07-7.04(m, 2H), 6.92(d, *J* = 8.0 Hz, 2H), 6.86-7.85(m, 1H), 6.59(s, 1H), 3.62(d, *J* =

13.6 Hz, 1H), 3.62(d, $J = 4.8$ Hz, 1H), 3.07(ddd, $J = 15.2, 8.0, 6.4$ Hz, 1H), 2.95(ddd, $J = 16.4, 4.0, 4.0$ Hz, 1H), 2.19(s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 148.74, 136.47, 135.62, 133.70, 129.07, 129.02, 128.68, 128.08, 128.03, 126.48, 124.21, 121.33, 120.78, 118.78, 118.70, 118.24, 110.42, 110.29, 70.02, 43.37, 27.57, 9.86; MS (EI) m/z (%) 339, 338, 337, 209, 208(100), 207, 206, 193, 165, 131, 130, 115, 103, 77; HRMS calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2$: 338.1783; found: 338.1777.

3-(2-Phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-1H-indole-5-carboxylic acid methyl ester (3e).

Isolated by Thin Layer Chromatography (methylene chloride, $R_f = 0.3$). Melting point is 176.0-177.0 °C. IR (KBr): ν_{max} 3407, 3027, 2954, 2921, 2888, 2860, 2835, 1700, 1685, 1654, 1617, 1597, 1560, 1497, 1435, 1311, 1289, 1251, 1222, 1113, 921, 756, 697, 669 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.25(s, 1H), 7.80(dd, $J = 8.0, 1.2$ Hz, 1H), 7.26-7.11(m, 8H), 6.96(d, $J = 8.0$ Hz, 2H), 6.76(dd, $J = 7.6, 7.6$ Hz, 1H), 6.64(d, $J = 1.6$ Hz, 1H), 6.13(s, 1H), 3.85(s, 3H), 3.58-3.54(m, 2H), 3.03(ddd, $J = 16.0, 8.4, 6.0$ Hz, 1H), 2.84(ddd, $J = 16.0, 4.8, 4.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 167.99, 149.58, 138.94, 137.03, 135.18, 128.99, 128.57, 127.68, 126.65, 125.79, 125.73, 125.21, 123.21, 122.85, 121.40, 120.24, 118.48, 116.16, 110.71, 56.77, 51.87, 42.75, 27.11; MS (EI) m/z (%) 382, 255, 223, 222, 221, 220, 208, 175, 144, 129, 118, 116, 87, 86, 85, 84, 83(100), 77, 57, 47; HRMS calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_2$: 382.1681; found: 382.1673.

1-(1-Methyl-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3f). Isolated by Thin Layer Chromatography (hexane/ethyl acetate=5:1, $R_f = 0.5$). Melting point is 113.0-114.0 °C. IR

(KBr): $\nu_{\max}$ 3423, 3056, 3019, 2925, 2848, 1596, 1500, 1370, 1329, 1284, 1218, 1199, 1109, 937, 770, 741, 692, 615 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 7.53(dd, J = 8.0, 0.8 Hz, 1H), 7.28-7.11(m, 8H), 7.04-6.99 (m, 3H), 6.75(ddd, J = 6.8, 6.8, 0.8 Hz, 1H), 6.48(s, 1H), 6.16(s, 1H), 3.67-3.57(m, 2H), 3.62(s, 3H), 3.05(ddd, J = 16.0, 9.2, 6.4 Hz, 1H), 2.80(ddd, J = 16.0, 4.8, 4.8 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 149.49, 137.38, 137.13, 135.37, 129.05, 128.64, 127.86, 126.65, 126.46, 125.53, 121.49, 120.00, 118.96, 117.77, 117.47, 115.43, 109.03, 56.56, 42.18, 32.79, 26.66; MS (EI) m/z (%) 339, 338(100), 337, 246, 245, 244, 234, 233, 232, 231, 218, 217, 211, 209, 208, 207, 206, 202, 169, 166, 77, 57; HRMS calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2$: 338.1783; found: 338.1775.

1-(6-Chloro-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (3g). Isolated by Thin Layer Chromatography (methylene chloride, R_f = 0.8). Melting point is 177.0-178.0 $^{\circ}\text{C}$. IR (KBr): $\nu_{\max}$ 3419, 3150, 3068, 3031, 2958, 2921, 2888, 2856, 1597, 1497, 1452, 1333, 1280, 1215, 1117, 1060, 937, 904, 799, 769, 739, 703, 586 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.84(s, 1H), 7.39(d, J = 8.5 Hz, 1H), 7.25-7.21(m, 4H), 7.19-7.14(m, 3H), 7.01(d, J = 8.0 Hz, 2H), 6.96(dd, J = 9.0, 1.5 Hz, 1H), 6.79(dd, J = 7.0, 7.0 Hz, 1H), 6.57(dd, J = 2.5, 1.0 Hz, 1H), 6.11(s, 1H), 3.62-3.52(m, 2H), 3.05(ddd, J = 16.0, 10.0, 6.0 Hz, 1H), 2.78(ddd, J = 16.5, 4.0, 4.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 149.79, 137.05, 136.91, 135.46, 129.23, 128.91, 128.03, 127.93, 126.79, 125.75, 125.06, 124.73, 121.03, 120.37, 119.43, 118.51, 116.18, 110.91, 56.62, 42.38, 26.63; MS (EI) m/z (%) 360, 359, 358(100), 357, 267, 266, 265, 264, 255, 254, 253, 252, 236, 218, 217, 208, 206, 162, 151, 104, 77; HRMS calcd for $\text{C}_{23}\text{H}_{19}^{37}\text{ClN}_2$: 360.1207; found: 360.1204; HRMS calcd for $\text{C}_{23}\text{H}_{19}^{35}\text{ClN}_2$: 358.1236; found: 358.1229.

1-(5-Nitro-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (3h). Isolated by filtration and washed with cold chloroform. IR (KBr): $\nu_{\max}$ 3407, 2921, 2860, 1594, 1560, 1517, 1500, 1333, 1207, 1092, 1031, 917, 839, 811, 770, 741, 700 cm^{-1} ; ^1H NMR (DMSO, 400 MHz, ppm) δ 11.62(s, 1H), 8.40(s, 1H), 7.92(d, J = 9.2 Hz, 1H), 7.47(d, J = 8.8 Hz, 1H), 7.34(d, J = 6.4 Hz, 1H), 7.18-7.15(m, 5H), 7.05-7.00(m, 3H), 6.69(dd, J = 7.8, 7.8 Hz, 1H), 6.36(s, 1H), 3.59-3.55(m, 1H), 3.52-3.46(m, 1H), 3.05-2.97(m, 1H), 2.86(ddd, J = 16.0, 4.4, 4.4 Hz, 1H); ^{13}C NMR (DMSO, 100 MHz, ppm) δ 149.77, 140.88, 140.29, 137.70, 135.51, 129.70, 129.26, 128.98, 128.46, 127.37, 126.39, 125.83, 120.91, 118.54, 117.28, 117.18, 116.02, 112.72, 55.94, 42.55, 27.20; MS (EI) m/z (%) 370, 369(100), 368, 352, 265, 264, 263, 218, 217, 216, 208, 207, 206, 162, 116, 104; HRMS calcd for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_2$: 369.1477; found: 369.1473.

1-(7-Nitro-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (3i). Isolated by Thin Layer Chromatography (hexane/ethyl acetate=5:1, R_f = 0.4). IR (neat liquid): $\nu_{\max}$ 3458, 3088, 3064, 3022, 2913, 2833, 1632, 1597, 1514, 1503, 1493, 1482, 1398, 1358, 1323, 1294, 1218, 1158, 1097, 1063 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 9.67(s, 1H), 8.08(d, J = 7.6 Hz, 1H), 7.82(d, J = 8.0 Hz, 1H), 7.27-7.14(m, 6H), 7.05(dd, J = 8.0, 8.0 Hz, 1H), 7.01(d, J = 7.6 Hz, 2H), 6.81(dd, J = 7.6, 7.6 Hz, 1H), 6.76(d, J = 1.6 Hz, 1H), 6.14(s, 1H), 3.60(ddd, J = 12.8, 4.8, 4.8 Hz, 1H), 3.54-3.47(m, 1H), 3.07(ddd, J = 16.0, 10.0, 6.0 Hz, 1H), 2.77(ddd, J = 16.4, 4.0, 4.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 149.51, 136.20, 135.25, 132.58, 130.09, 129.87, 129.16, 128.99, 128.39, 127.77,

126.90, 126.39, 125.75, 120.62, 119.24, 118.95, 116.54, 103.89, 56.51, 42.55, 26.59; MS (EI) m/z (%) 370, 369, 368, 264, 263, 217, 208, 162(100), 129, 117, 116, 115, 89, 85, 83; HRMS calcd for $C_{23}H_{19}N_3O_2$: 369.1477; found: 369.1474.

1-(1H-Indol-3-yl)-2-(4-methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinoline (3j). Isolated by Thin Layer Chromatography (methylene chloride/diethyl ether=40:1, R_f = 0.5). Melting point is 162.0-163.0 °C. IR (KBr): ν_{max} 3415, 3154, 3105, 3060, 2954, 2917, 2856, 2835, 1510, 1456, 1341, 1264, 1247, 1211, 1116, 1039, 937, 913, 823, 743 cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.86(s, 1H), 7.40(d, J = 3.0 Hz, 1H), 7.25-7.10(m, 6H), 6.98(dd, J = 8.0, 8.0 Hz, 1H), 6.93(d, J = 9.0 Hz, 2H), 6.78(d, J = 9.5 Hz, 2H), 6.50(d, J = 2.5 Hz, 1H), 5.95(s, 1H), 3.73(s, 3H), 3.52(ddd, J = 13.0, 10.0, 4.5 Hz, 1H), 3.45(ddd, J = 13.0, 4.5, 4.5 Hz, 1H), 3.02(ddd, J = 16.5, 10.5, 4.0 Hz, 1H), 2.78(ddd, J = 16.5, 4.0, 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 153.28, 144.68, 137.53, 136.41, 135.34, 128.82, 128.17, 126.78, 126.41, 125.63, 124.30, 121.92, 120.19, 119.60, 119.48, 119.06, 114.39, 110.91, 57.91, 55.56, 43.74, 26.80; MS (EI) m/z (%) 355, 354(100), 354, 353, 239, 238, 236, 232, 231, 230, 219, 218, 217, 153, 136, 123, 107, 105, 89, 85, 83, 77; HRMS calcd for $C_{24}H_{22}N_2O$: 354.1732; found: 354.1726.

1-(5-Methoxy-1H-indol-3-yl)-2-(4-methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinoline (3k). Isolated by Thin Layer Chromatography (methylene chloride/diethyl ether=40:1, R_f = 0.4). Melting point is 55.0-60.0 °C. IR (KBr): ν_{max} 3411, 2937, 2831, 1654, 1508, 1480, 1242, 1210, 1174, 1113,

1036, 917, 831, 762, 669, 616 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.82(s, 1H), 7.23-7.10(m, 5H), 6.94(d, J = 8.5 Hz, 2H), 6.79-6.75(m, 1H), 6.77(d, J = 8.5 Hz, 2H), 6.70(d, J = 2.5 Hz, 1H), 6.44(d, J = 2.5 Hz, 1H), 5.92(s, 1H), 3.73(s, 3H), 3.64(s, 3H), 3.49(ddd, J = 12.5, 10.0, 4.0 Hz, 1H), 3.41(ddd, J = 12.5, 5.5, 3.0 Hz, 1H), 3.05(ddd, J = 16.0, 10.5, 6.0 Hz, 1H), 2.80(ddd, J = 16.0, 4.0, 4.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 153.78, 153.47, 144.92, 137.70, 135.26, 131.42, 128.77, 128.15, 127.29, 126.43, 125.62, 125.22, 120.16, 118.30, 114.35, 112.15, 111.51, 101.85, 58.34, 55.60, 55.50, 43.38, 27.18; MS (EI) m/z (%) 385, 384(100), 383, 262, 261, 249, 248, 238, 237, 236, 218, 217, 192, 147, 123; HRMS calcd for $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}_2$: 384.1837; found: 384.1829.

2-(4-Methoxy-phenyl)-1-(5-nitro-1H-indol-3-yl)-1,2,3,4-tetrahydro-isoquinoline (31). Isolated by Thin Layer Chromatography (methylene chloride/diethyl ether=40:1, R_f = 0.4). Melting point is 155.0-156.0 $^{\circ}\text{C}$. IR (KBr): ν_{max} 3403, 3113, 3080, 3023, 2921, 2839, 1511, 1472, 1331, 1247, 1182, 1117, 1091, 1037, 921, 827, 762, 737, 684, 525 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 8.53(s, 1H), 8.21(d, J = 2.0 Hz, 1H), 7.99(dd, J = 8.5, 2.0 Hz, 1H), 7.26-7.12(m, 5H), 6.92(d, J = 8.5 Hz, 2H), 6.78(d, J = 9.0 Hz, 2H), 6.88(d, J = 2.5 Hz, 1H), 5.93(s, 1H), 3.73(s, 3H), 3.45-3.37(m, 2H), 3.06(ddd, J = 16.5, 9.5, 6.5 Hz, 1H), 2.89(ddd, J = 16.5, 4.0, 4.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 154.29, 144.54, 141.59, 139.29, 136.78, 135.10, 129.03, 127.95, 127.37, 126.82, 126.17, 125.84, 121.07, 117.80, 117.57, 114.46, 110.92, 58.48, 55.52, 44.22, 27.42; MS (EI) m/z (%) 400, 399, 398, 355, 354(100), 353, 263, 238, 236, 232, 231, 230, 219, 218, 217, 216, 177, 123; HRMS calcd for $\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}_3$: 399.1583; found: 399.1581.

2-(4-Methoxy-phenyl)-1-(3-methyl-1*H*-indol-2-yl)-1,2,3,4-tetrahydro-isoquinoline (3m).

Isolated by Thin Layer Chromatography (hexane/methylene chloride/triethyl amine=40:30:1, R_f = 0.8). Melting point is 112.0-113.0 °C. IR (KBr): $\nu_{\max}$ 3427, 3039, 2933, 2856, 2835, 1512, 1453, 1245, 1178, 1137, 1037, 933, 830, 740, 692, 669, 639 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.48(m, 1H), 7.28-7.22(m, 2H), 7.14-7.11(m, 1H), 7.07-7.01(m, 4H), 6.83(d, J = 9.0 Hz, 2H), 6.70(d, J = 9.0 Hz, 2H), 6.66(s, 1H), 6.56(s, 1H), 3.69(s, 3H), 3.58(ddd, J = 13.0, 9.0, 4.5 Hz, 1H), 3.44(ddd, J = 12.5, 5.0, 5.0 Hz, 1H), 3.06(ddd, J = 16.5, 9.5, 5.5 Hz, 1H), 2.99(ddd, J = 16.5, 4.0, 4.0 Hz, 1H), 2.19(s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 155.24, 143.21, 136.95, 135.77, 134.25, 128.98, 128.78, 128.09, 128.02, 126.54, 124.75, 122.24, 121.29, 118.72, 118.61, 114.33, 110.47, 110.34, 71.64, 55.42, 44.95, 27.94, 9.65; MS (EI) m/z (%) 369, 327, 315, 292, 262, 239, 238(100), 223, 191, 159.

Reference:

[1] Kwong, F. Y.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2002**, 4, 581-584.

2) PDF file of copies of ^1H NMR and ^{13}C NMR spectra for all new compounds