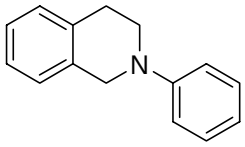
Supporting Text

General Information. ^{1}H NMR spectra were recorded on Varian 300, 400, and 500 MHz spectrometers and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for $CDCl_3$ or the center peak of residual DMSO (2.49 ppm). 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 75, 100 and 125 MHz and referenced to the internal solvent signals (central peak is 77.0 ppm in $CDCl_3$ or 40.4 ppm in DMSO-d_6). NMR spectra were obtained in $CDCl_3$ unless otherwise stated. MS data were obtained by KRATOS MS25RFA mass spectrometer. HRMS were made by McGill University. IR spectra were recorded by an ABB Bomem MB100 instrument. Melting points were recorded by Melting Point Apparatus, Gallenkamp. Thin layer chromatography was performed using Sorbent Silica Gel 60 F_{254} TLC plates and visualized with UV light. Flash column chromatography was performed over SORBENT silica gel 30-60 μm. All reagents were weighed and handled in air at room temperature. All reagents were purchased from Aldrich, Strem, and Acros and used without further purification.

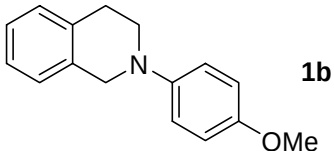
General procedure for preparing 2-aryl-1,2,3,4-tetrahydroisoquinolines:[1] Copper(I) iodide (200 mg, 1.0 mmol) and potassium phosphate (4.25 g, 20.0 mmol) were put into a Schlenk-tube. The tube was evacuated and back filled with nitrogen. 2-Propanol (10.0 ml), ethylene glycol (1.11 ml, 20.0 mmol), 1,2,3,4-tetrahydroisoquinoline (2.0 ml, 15 mmol) and iodobenzene (1.12 ml, 10.0 mmol) were added successively by microsyringe at room temperature. The reaction mixture was heated at 85-90°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 and to give the desired product **1a**.



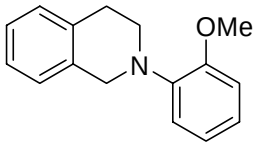
1a

1,2,3,4-Tetrahydro-2-phenylisoquinoline (1a). ^{1}H NMR (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 (125 MHz, ppm) δ 150.5, 134.8, 134.4, 129.2, 128.5, 126.5, 126.3, 126.0, 118.6, 115.1, 50.7, 46.5, 29.1; MS (EI) *m/z* (%) 209, 208(100), 115, 104, 91, 78, 77, 51.



1b

1,2,3,4-Tetrahydro-2-(4-methoxyphenyl)isoquinoline (1b). ^{1}H NMR (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 (100 MHz, ppm) δ 153.3, 145.1, 134.4, 134.3, 128.5, 126.3, 126.1, 125.7, 117.9, 114.4, 55.6, 52.7, 48.5, 29.2; MS (EI) *m/z* (%) 239(100), 238, 224, 135, 120, 104, 91, 77, 65, 51.

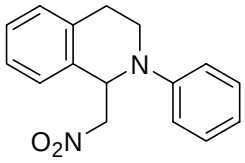


1c

1,2,3,4-Tetrahydro-2-(2-methoxyphenyl)isoquinoline (1c). ^{1}H NMR (500 MHz, ppm) δ 7.15-7.12(m, 3H), 7.10-7.07(m, 1H), 6.99(d, *J* = 8.0 Hz, 2H), 6.90(t, *J* = 8.0 Hz, 1H), 6.89(t, *J* = 8.0 Hz, 1H), 4.28(s, 2H), 3.87(s, 3H), 3.40(dd, *J* = 5.5, 5.5 Hz, 2H), 2.97(dd, *J*

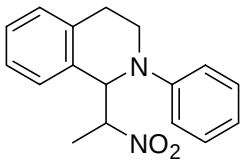
= 5.0, 5.0 Hz, 2H); ^{13}C NMR (125 MHz, ppm) δ 152.5, 141.1, 135.1, 134.5, 128.8, 126.3, 126.0, 125.6, 122.9, 120.9, 118.9, 111.3, 55.4, 53.0, 48.9, 28.8.

General procedure for Table 1 and Scheme 2: To a mixture of CuBr (1.4 mg, 0.01 mmol) and 2-phenyl-1,2,3,4-tetrahydroisoquinoline (42 mg, 0.2 mmol), CH_3NO_2 (0.022 ml, 0.4 mmol) were added. Then *tert*-butyl hydroperoxide (0.048 ml, 5.5M in decane) was added into the mixture under nitrogen at room temperature. The resulting mixture was stirred at the room temperature for overnight. The resulting suspension was diluted with diethyl ether and filtered through a short silicon gel in a pipette eluting with diethyl ether. Solvent was evaporated and the residue was purified by Thin Layer Chromatography (hexane/ethyl acetate = 5:1), and the fraction with an R_f = 0.5 was collected and concentrated to give the desired product **3a**.



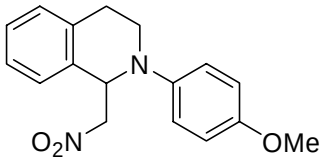
3a

1,2,3,4-Tetrahydro-1-(nitromethyl)-2-phenylisoquinoline (3a). Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.5). Melting point is 89.0-90.0°C. IR (KBr): ν_{max} 3061, 3038, 2980, 2964, 2918, 1596, 1550, 1495, 1430, 1382, 1220, 1193, 1139, 1113, 1032, 1006, 892, 775, 756, 691, 639 cm^{-1}; ^{1}H NMR (400 MHz, ppm) δ 7.25-7.20(m, 2H), 7.18(dd, *J* = 4.4, 1.6 Hz, 1H), 7.16-7.13(m, 2H), 7.08(d, *J* = 7.6 Hz, 1H), 6.94(d, *J* = 8.0 Hz, 2H), 6.81(dd, *J* = 7.4, 7.4 Hz, 1H), 5.51(dd, *J* = 7.6, 6.8 Hz, 1H), 4.81(dd, *J* = 12.0, 7.6 Hz, 1H), 4.50(dd, *J* = 12.0, 6.8 Hz, 1H), 3.64-3.53(m, 2H), 3.04(ddd, *J* = 14.0, 8.6, 5.2 Hz, 1H), 2.74(dt, *J* = 16.4, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, ppm) δ 148.2, 135.1, 132.7, 129.3, 129.0, 127.9, 126.8, 126.5, 119.2, 114.9, 78.7, 58.2, 42.0, 26.5; MS (EI) *m/z* (%) 268, 253, 209, 208(100), 193, 115, 104, 91, 77, 65, 51; HRMS calcd for $C_{16}H_{16}N_2O_2$: 268.1211; found: 268.1208.



3b

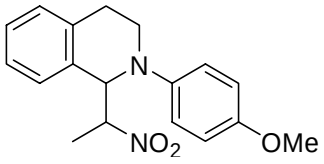
1,2,3,4-Tetrahydro-1-(1-nitroethyl)-2-phenylisoquinoline (3b). The ratio of isolated diastereoisomers is 2. Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.6). IR (neat liquid): ν_{max} 3067, 3029, 2987, 2938, 2903, 2858, 1599, 1550, 1505, 1452, 1390, 1358, 1319, 1296, 1275, 1222, 1156, 1114, 1037, 999, 950, 912 cm^{-1}; The major isomer: ^{1}H NMR (300 MHz, ppm) δ 5.21(d, *J* = 7.8 Hz, 1H), 5.03(dq, *J* = 8.4, 6.6 Hz, 1H), 3.62-3.49(m, 2H), 1.53(d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, ppm) δ 148.7, 135.5, 131.9, 129.3, 129.2, 128.2, 128.1, 126.0, 119.2, 115.3, 85.4, 62.7, 42.7, 26.4, 16.5; The minor isomer: ^{1}H NMR (300 MHz, ppm) δ 5.24(d, *J* = 7.8 Hz, 1H), 4.87(dq, *J* = 8.7, 6.9 Hz, 1H), 3.82(ddd, *J* = 13.5, 8.1, 5.7 Hz, 2H), 1.69(d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, ppm) δ 149.0, 134.6, 133.7, 129.2, 129.0, 128.6, 127.1, 126.5, 118.6, 114.3, 88.9, 61.1, 43.6, 26.8, 17.5; Other overlapped peaks: ^{1}H NMR (300 MHz, ppm) δ 7.28-7.18(m), 7.16-7.06(m), 7.00-6.95(m), 6.83-6.76(m), 3.09-2.99(m), 2.94-2.81(m); MS (EI) *m/z* (%) 282, 281, 267, 236, 208(100), 193, 165, 128, 115, 104, 91, 77, 65, 51; HRMS calcd for $C_{17}H_{18}N_2O_2$: 282.1368; found: 282.1358.



3c

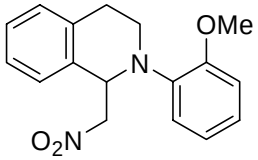
1,2,3,4-Tetrahydro-2-(4-methoxyphenyl)-1-(nitromethyl)isoquinoline (3c). Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.4). IR (neat liquid): ν_{max} 3070, 3001, 2952, 2938, 2910, 2839, 1609, 1553, 1512, 1466, 1383, 1247, 1215, 1184, 1036, 1006, 912 cm^{-1}; ^{1}H NMR (400 MHz, ppm) δ 7.24-7.17(m, 2H), 7.16-7.11(m, 2H), 6.89(d, *J* = 8.8 Hz, 2H), 6.79(d, *J* = 8.8 Hz, 2H), 5.37(dd, *J* = 8.4, 6.0 Hz, 1H), 4.80(dd, *J* = 12.0, 8.8 Hz, 1H), 4.54(dd, *J* = 12.0, 6.0 Hz, 1H), 3.73(s, 3H), 3.60-3.50(m, 2H), 3.00(ddd, *J* = 16.4, 8.8, 6.4 Hz, 1H), 2.68(dt, *J* = 16.4, 4.0 Hz, 1H); ^{13}C NMR (100

MHz, ppm) δ 153.7, 142.9, 135.2, 132.7, 129.3, 127.7, 126.8, 126.4, 118.7, 114.6, 78.9, 58.9, 55.6, 43.2, 25.9; MS (EI) *m/z* (%) 298, 267, 253, 238(100), 223, 193, 165, 115, 91, 77, 63; HRMS calcd for $C_{17}H_{18}N_2O_3$: 298.1317; found: 298.1310.



3d

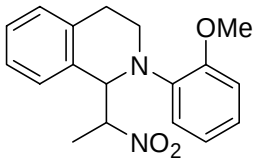
1,2,3,4-Tetrahydro-2-(4-methoxyphenyl)-1-(1-nitroethyl)isoquinoline (3d). The ratio of isolated diastereoisomers is 2. Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.4). IR (neat liquid): ν_{max} 3067, 2998, 2938, 2907, 2837, 1550, 1512, 1452, 1386, 1358, 1292, 1268, 1243, 1187, 1145, 1118, 1037, 950, 912 cm^{-1}; The major isomer: ^{1}H NMR (300 MHz, ppm) δ 3.72(s, 3H), 3.53-3.44(m, 2H), 1.52(d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, ppm) δ 153.6, 143.3, 135.7, 131.9, 129.1, 128.3, 127.9, 125.9, 118.7, 114.4, 85.7, 63.4, 55.5, 44.0, 26.0, 16.7; The minor isomer: ^{1}H NMR (300 MHz, ppm) δ 4.85(dq, *J* = 8.6, 6.6 Hz, 1H), 3.81-3.75(m, 2H), 3.74(s, 3H), 1.67(d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, ppm) δ 153.3, 143.7, 134.9, 133.5, 128.8, 127.9, 127.1, 126.4, 118.1, 114.6, 88.8, 62.1, 56.6, 45.0, 26.3, 17.2; Other overlapped peaks: ^{1}H NMR (300 MHz, ppm) δ 7.25-7.07(m), 7.01-6.98(m), 6.92-6.87(m), 6.83-6.75(m), 5.06-4.93(m), 3.02-2.92(m), 2.84-2.72(m); MS (EI) *m/z* (%) 312, 311, 281, 267, 253, 239(100), 238, 224, 191, 165, 135, 104, 91, 78, 77, 57; HRMS calcd for $C_{18}H_{20}N_2O_3$: 312.1474; found: 312.1468.



3e

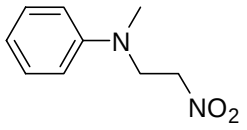
1,2,3,4-Tetrahydro-2-(2-methoxyphenyl)-1-(nitromethyl)isoquinoline (3e). Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.5). Melting point is 103.0-104.0°C. IR (KBr): ν_{max} 3075, 3007, 2957, 2919, 2839, 1596, 1553, 1501, 1381,

1250, 1220, 1178, 1140, 1117, 1030, 1003, 923, 843, 760, 650 cm^{-1}; ^1H NMR (300 MHz, ppm) δ 7.24-7.19(m, 2H), 7.17-7.11(m, 2H), 7.00(ddd, *J* = 8.1, 7.2, 1.8 Hz, 1H), 6.88-6.78(m, 3H), 5.48(dd, *J* = 8.7, 5.1 Hz, 1H), 4.80(dd, *J* = 12.0, 8.4 Hz, 1H), 4.51(dd, *J* = 12.0, 4.8 Hz, 1H), 3.81(s, 3H), 3.59(dddd, *J* = 15.0, 6.3, 2.4, 0.9 Hz, 1H), 3.46(ddd, *J* = 13.2, 11.4, 5.2 Hz, 1H), 2.97(ddd, *J* = 16.8, 11.1, 6.3 Hz, 1H), 2.70(ddd, *J* = 16.5, 3.9, 2.1 Hz, 1H); ^{13}C NMR (75 MHz, ppm) δ 152.9, 138.7, 135.2, 133.5, 129.4, 127.4, 126.7, 126.3, 124.0, 121.8, 120.9, 112.3, 79.1, 58.1, 55.8, 42.9, 26.9; MS (EI) *m/z* (%) 298, 267, 238(100), 222, 165, 128, 115, 102, 91, 77, 65, 51; HRMS calcd for $C_{17}H_{18}N_2O_3$: 298.1317; found: 298.1308.



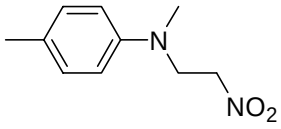
3f

1,2,3,4-Tetrahydro-2-(2-methoxyphenyl)-1-(1-nitroethyl)isoquinoline (3f). The ratio of isolated diastereoisomers is 2. Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.5). IR (neat liquid): ν_{max} 3067, 3022, 2998, 2938, 2837, 1592, 1550, 1498, 1452, 1390, 1358, 1292, 1243, 1176, 1110, 1026, 947, 915 cm^{-1}; The major isomer: ^1H NMR (300 MHz, ppm) δ 4.97(d, *J* = 7.8 Hz, 1H), 4.89(dq, *J* = 8.1, 6.6 Hz, 1H),3.76(s, 3H), 1.46(d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, ppm) δ 153.6, 139.5, 136.1, 132.8, 129.1, 128.0, 127.5, 125.8, 124.2, 123.1, 121.0, 112.9, 86.0, 63.4, 55.9, 44.5, 27.2, 16.8; The minor isomer: ^1H NMR (300 MHz, ppm) δ 5.01(d, *J* = 7.8 Hz, 1H), 4.81(dq, *J* = 7.5, 6.6 Hz, 1H), 3.82(s, 3H), 1.65(d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, ppm) δ 153.3, 139.7, 135.2, 133.9, 129.1, 127.5, 126.9, 126.2, 124.1, 123.3, 120.9, 111.8, 88.7, 62.9, 55.5, 45.0, 26.9, 16.9; Other overlapped peaks: ^1H NMR (300 MHz, ppm) δ 7.26-7.17(m), 7.14-7.09(m), 7.03-6.96(m), 6.90-6.75(m), 3.67-3.58(m), 3.52-3.36(m), 2.99-2.69(m); MS (EI) *m/z* (%) 312, 281, 266, 251, 238(100), 222, 115, 91, 77, 65, 51; HRMS calcd for $C_{18}H_{20}N_2O_3$: 312.1474; found: 312.1465.



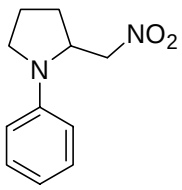
3g

***N*-Methyl-*N*-(2-nitroethyl)benzenamine (3g).** Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.4). IR (neat liquid): ν_{max} 3067, 3033, 2914, 2823, 1599, 1550, 1505, 1428, 1386, 1348, 1229, 1191, 1125, 1058, 1030, 992 cm^{-1}; ^1H NMR (300 MHz, ppm) δ 7.28-7.22(m, 2H), 6.78(dd, *J* = 7.2, 7.2 Hz, 1H), 6.72(dd, *J* = 9.0, 0.9 Hz, 2H), 4.56(t, *J* = 6.3 Hz, 2H), 4.00(td, *J* = 6.6 Hz, 2H), 2.98(s, 3H); ^{13}C NMR (75 MHz, ppm) δ 147.7, 129.4, 117.9, 112.5, 72.6, 50.6, 38.9; MS (EI) *m/z* (%) 180, 132, 120(100), 104, 91, 77, 65, 51; HRMS calcd for $C_9H_{12}N_2O_2$: 180.0899; found: 180.0901.



3h

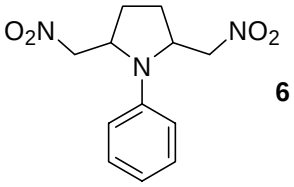
***N*,4-Dimethyl-*N*-(2-nitroethyl)benzenamine (3h).** Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.5). IR (neat liquid): ν_{max} 3019, 2921, 2865, 2820, 1616, 1554, 1522, 1452, 1432, 1348, 1323, 1229, 1128, 1055, 985, 961 cm^{-1}; ^1H NMR (300 MHz, ppm) δ 7.05(d, *J* = 8.7 Hz, 2H), 6.64(d, *J* = 8.7 Hz, 2H), 4.52(t, *J* = 6.3 Hz, 2H), 3.93(t, *J* = 6.3 Hz, 2H), 2.92(s, 3H), 2.25(s, 3H); ^{13}C NMR (75 MHz, ppm) δ 145.6, 129.9, 127.3, 113.0, 72.6, 51.0, 39.0, 20.3; MS (EI) *m/z* (%) 194, 148, 146, 134(100), 120, 118, 91, 77, 65, 51; HRMS calcd for $C_{10}H_{14}N_2O_2$: 194.1055; found: 194.1058.



5

2-(Nitromethyl)-1-phenylpyrrolidine (5). Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.6). IR (neat liquid): ν_{max} 3067, 3029, 2973, 2917,

2879, 2851, 1599, 1547, 1505, 1463, 1428, 1362, 1341, 1247, 1212, 1184, 1159, 1034, 992, 964 cm^{-1}; ^{1}H NMR (300 MHz, ppm) δ 7.29-7.22(m, 2H), 6.76(dd, *J* = 7.5, 7.5 Hz, 1H), 6.67(d, *J* = 7.8 Hz, 2H), 4.61(dd, *J* = 11.4, 3.3 Hz, 1H), 4.43-4.38(m, 1H), 4.17(dd, *J* = 11.1, 9.9 Hz, 1H), 3.51-3.44(m, 1H), 3.24-3.15(m, 1H), 2.16-2.04(m, 4H); ^{13}C NMR (75 MHz, ppm) δ 145.6, 129.5, 117.2, 111.8, 75.8, 57.4, 48.1, 29.3, 22.9; MS (EI) *m/z* (%) 206, 160, 158, 146(100), 118, 104, 91, 77, 65, 51; HRMS calcd for $C_{11}H_{14}N_2O_2$: 206.1055; found: 206.1058.

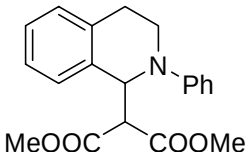


6

2,5-bis(Nitromethyl)-1-phenylpyrrolidine (6). Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.5). IR (neat liquid): ν_{max} 3067, 3036, 2970, 2924, 2879, 1599, 1547, 1498, 1456, 1428, 1379, 1351, 1309, 1222, 1177, 1037, 996, 968 cm^{-1}; *trans*-isomer: ^{1}H NMR (400 MHz, ppm) δ 6.92(ddt, *J* = 7.2, 7.2, 0.8 Hz, 1H), 6.81(d, *J* = 7.6 Hz, 2H), 4.71(dd, *J* = 11.6, 3.6 Hz, 2H), 4.60-4.56(m, 2H), 4.30(dd, *J* = 11.2, 8.8 Hz, 2H); *cis*-isomer: ^{1}H NMR (400 MHz, ppm) δ 6.87(ddt, *J* = 7.2, 7.2, 0.8 Hz, 1H), 6.79(d, *J* = 7.6 Hz, 2H), 4.64(dd, *J* = 12.0, 2.8 Hz, 2H), 4.43-4.39(m, 2H), 4.11(dd, *J* = 11.2, 8.8 Hz, 2H); overlapped peaks: ^{1}H NMR (400 MHz, ppm) δ 7.36-7.31(m, 4H), 2.35-2.05(m, 8H); ^{13}C NMR (75 MHz, ppm) δ 145.0, 141.5, 130.3, 129.1, 119.8, 119.1, 113.7, 113.1, 77.7, 74.4, 59.5, 56.3, 28.5, 26.6; MS (EI) *m/z* (%) 265, 218, 207, 205(100), 172, 158, 144, 130, 118, 104, 91, 77, 65, 51; HRMS calcd for $C_{12}H_{15}N_3O_4$: 265.1062; found: 265.1056.

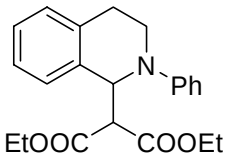
General procedure for Table 2 and 3: To a mixture of CuBr (0.7 mg, 0.005 mmol) and 2-phenyl-1,2,3,4-tetrahydroisoquinoline (209 mg, 1.0 mmol), dimethyl malonate (116 μl, 1.0 mmol) were added. Then *tert*-butyl hydroperoxide (0.20 ml, 5-6M in decane) was added into the mixture under nitrogen at room temperature. The resulting mixture was stirred at the room temperature for a certain time as mentioned in the tables. The resulting

suspension was diluted with methylene chloride. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1), and the fraction with an R_f = 0.5 was collected and concentrated to give the desired product **8a**.



8a

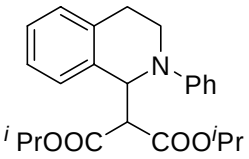
2-(2-Phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-malonic acid dimethyl ester (8a). Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.5). IR (neat liquid): ν_{max} 3065, 3022, 2959, 2911, 2843, 1765, 1754, 1740, 1596, 1577, 1504, 1476, 1450, 1436, 1386, 1344, 1307, 1273, 1232, 1199, 1162, 1136, 1111, 1019 cm^{-1}; ^{1}H NMR (300 MHz, ppm) δ 7.21-7.15(m, 3H), 7.13-7.05(m, 3H), 6.96(d, *J* = 8.1 Hz, 2H), 6.73(dd, *J* = 6.9, 6.9 Hz, 1H), 5.69(d, *J* = 9.3 Hz, 1H), 3.94(d, *J* = 9.3 Hz, 1H), 3.72-3.56(m, 2H), 3.63(s, 3H), 3.52(s, 3H), 3.05(ddd, *J* = 16.2, 8.7, 6.3 Hz, 1H), 2.85(dt, *J* = 16.2, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, ppm) δ 168.0, 167.1, 148.6, 135.5, 134.6, 128.9, 128.8, 127.5, 126.9, 125.9, 118.5, 115.0, 59.1, 58.1, 52.5, 52.4, 42.2, 26.1; MS (EI) *m/z* (%) 339, 209, 208(100), 193, 165, 128, 115, 104, 91, 77, 65, 51; HRMS calcd for $C_{20}H_{21}NO_4$: 339.1471; found: 339.1475.



8b

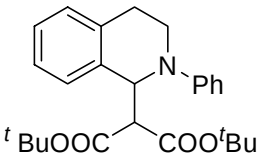
2-(2-Phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-malonic acid diethyl ester (8b). Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.5). IR (neat liquid): ν_{max} 3065, 3026, 2981, 2940, 2908, 2872, 1748, 1731, 1598, 1577, 1505, 1494, 1475, 1452, 1392, 1369, 1305, 1269, 1179, 1145, 1112, 1096, 1037, 933 cm^{-1}; ^{1}H NMR (300 MHz, ppm) δ 7.24-7.05(m, 6H), 6.96(d, *J* = 8.1 Hz, 2H), 6.72(dd, *J* = 7.2, 7.2 Hz, 1H), 5.71(d, *J* = 9.3 Hz, 1H), 4.17-3.93(m, 4H), 3.88(d, *J* = 9.0 Hz, 1H), 3.74-3.58(m,

2H), 3.06(ddd, *J* = 15.9, 8.7, 6.3 Hz, 1H), 2.87(dt, *J* = 16.5, 5.1 Hz, 1H), 1.16(t, *J* = 7.2 Hz, 3H), 1.08(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, ppm) δ 167.7, 166.9, 148.7, 135.8, 134.6, 128.9, 128.7, 127.4, 127.0, 125.9, 118.3, 114.9, 61.6, 59.5, 57.8, 42.3, 26.1, 14.0, 13.9; MS (EI) *m/z* (%) 367, 209, 208(100), 193, 165, 128, 115, 104, 91, 77, 65, 51; HRMS calcd for $C_{22}H_{25}NO_4$: 367.1784; found: 367.1789.



8c

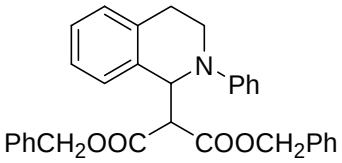
2-(2-Phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-malonic acid diisopropyl ester (8c). Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.7). IR (neat liquid): ν_{max} 3062, 3029, 2981, 2934, 2879, 2836, 1726, 1599, 1577, 1505, 1495, 1466, 1453, 1429, 1387, 1374, 1270, 1180, 1146, 1102, 1033 cm^{-1}; ^{1}H NMR (300 MHz, ppm) δ 7.28-7.05(m, 6H), 6.94(d, *J* = 8.4 Hz, 2H), 6.71(dd, *J* = 7.2, 7.2 Hz, 1H), 5.70(d, *J* = 8.7 Hz, 1H), 5.01(q, *J* = 6.3 Hz, 0.5H), 4.99(q, *J* = 6.3 Hz, 0.5H), 4.91(q, *J* = 6.3 Hz, 0.5H), 4.88(q, *J* = 6.3 Hz, 0.5H), 3.82(d, *J* = 9.0 Hz, 1H), 3.74-3.58(m, 2H), 3.04(ddd, *J* = 15.9, 8.7, 6.0 Hz, 1H), 2.85(dt, *J* = 15.9, 5.1 Hz, 1H), 1.19(d, *J* = 6.6 Hz, 3H), 1.11(d, *J* = 6.6 Hz, 3H), 1.10(d, *J* = 6.6 Hz, 3H), 1.01(d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, ppm) δ 167.4, 166.6, 148.8, 136.1, 134.7, 128.9, 128.7, 127.3, 127.1, 125.9, 118.2, 115.0, 69.2, 60.1, 57.5, 42.4, 26.2, 21.6, 21.6, 21.4; MS (EI) *m/z* (%) 395, 209, 208(100), 193, 165, 115, 104, 91, 77; HRMS calcd for $C_{24}H_{29}NO_4$: 395.2097; found: 395.2107.



8d

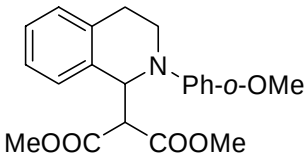
2-(2-Phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-malonic acid di-*tert*-butyl ester (8d). Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.8). Melting point is 94.0-95.0°C. IR (KBr): ν_{max} 3009, 2976, 2932, 2860, 1745, 1717, 1598, 1508, 1473, 1392, 1369, 1327, 1294, 1246, 1179, 1151, 940, 847, 760, 749, 695, 505 cm^{-1}; ^{1}H

NMR (400 MHz, ppm) δ 7.30(d, *J* = 7.6 Hz, 1H), 7.22-7.07(m, 5H), 6.95(d, *J* = 9.2 Hz, 2H), 6.70(dd, *J* = 7.2, 7.2 Hz, 1H), 5.70(d, *J* = 8.4 Hz, 1H), 3.70-3.60(m, 2H), 3.65(d, *J* = 8.4 Hz, 1H), 3.05(ddd, *J* = 16.0, 8.4, 5.6 Hz, 1H), 2.89(dt, *J* = 16.4, 5.2 Hz, 1H), 1.40(s, 9H), 1.26(s, 9H); ^{13}C NMR (100 MHz, ppm) δ 167.2, 166.2, 148.7, 136.8, 134.7, 128.9, 128.5, 127.1, 127.0, 125.8, 117.6, 114.3, 81.7, 81.6, 62.0, 56.9, 42.3, 27.9, 27.6, 26.5; MS (EI) *m/z* (%) 423, 209, 208(100), 193, 165, 115, 104, 91, 77, 57; HRMS calcd for $C_{26}H_{33}NO_4$: 423.2410; found: 423.2414.



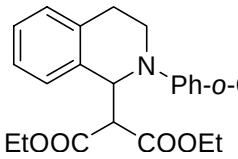
8e

2-(2-Phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-malonic acid dibenzyl ester (8e). Isolated by flash column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.5). Melting point is 113.0-114.0°C. IR (KBr): ν_{max} 3065, 3033, 2980, 2956, 2932, 2892, 1753, 1732, 1596, 1499, 1387, 1294, 1233, 1174, 1146, 996, 948, 750, 703, 693, 590, 517, 473 cm^{-1}; ^{1}H NMR (400 MHz, ppm) δ 7.31-7.06(m, 15H), 7.00(dd, *J* = 7.2, 7.2 Hz, 1H), 6.91(d, *J* = 8.0 Hz, 2H), 6.74(dd, *J* = 7.2, 7.2 Hz, 1H), 5.72(d, *J* = 9.2 Hz, 1H), 5.07(d, *J* = 12.0 Hz, 1H), 5.03(d, *J* = 12.0 Hz, 1H), 5.01(d, *J* = 12.0 Hz, 1H), 4.85(d, *J* = 12.0 Hz, 1H), 4.01(d, *J* = 9.2 Hz, 1H), 3.63-3.50(m, 2H), 3.00(ddd, *J* = 16.0, 8.8, 6.0 Hz, 1H), 2.78(dt, *J* = 16.4, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, ppm) δ 167.4, 166.6, 148.5, 135.4, 135.0, 134.8, 134.6, 129.0, 128.8, 128.4, 128.3, 128.2, 128.2, 128.0, 127.4, 127.0, 125.9, 118.5, 115.2, 67.4, 67.3, 59.4, 58.2, 42.3, 26.1; MS (EI) *m/z* (%) 491, 236, 209, 208, 207, 206(98), 193, 180, 178, 128, 107(100), 91, 79, 77, 65, 51; HRMS calcd for $C_{32}H_{29}NO_4$: 491.2096; found: 491.2085.



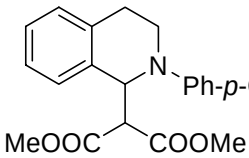
8f

2-[2-(2-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinolin-1-yl]-malonic acid dimethyl ester (8f). Isolated by flash column chromatography (hexane/ethyl acetate/triethylamine = 50:10:1, R_f = 0.4). IR (neat liquid): ν_{max} 3061, 3024, 3007, 2952, 2836, 1756, 1734, 1594, 1501, 1454, 1435, 1382, 1346, 1242, 1202, 1177, 1141, 1112, 1029 cm^{-1}; ^1H NMR (300 MHz, ppm) δ 7.23-7.06(m, 4H), 6.97-6.91(m, 1H), 6.82-6.74(m, 3H), 5.39(d, *J* = 8.7 Hz, 1H), 3.98(d, *J* = 9.0 Hz, 1H), 3.80(s, 3H), 3.63-3.47(m, 2H), 3.56(s, 3H), 3.54(s, 3H), 2.86(ddd, *J* = 17.1, 11.4, 6.9 Hz, 1H), 2.66(ddd, *J* = 16.5, 4.2, 2.4 Hz, 1H); ^{13}C NMR (75 MHz, ppm) δ 168.2, 167.4, 152.7, 139.3, 135.5, 134.9, 129.1, 127.1, 126.7, 125.7, 123.3, 121.9, 120.6, 111.5, 59.3, 58.9, 55.4, 52.3, 52.2, 43.0, 26.3; MS (EI) *m/z* (%) 369, 239, 238, 237, 236(100), 222, 220, 101, 86, 85, 84, 83, 74, 59, 47; HRMS calcd for $C_{21}H_{23}NO_5$: 369.1576; found: 369.1584.



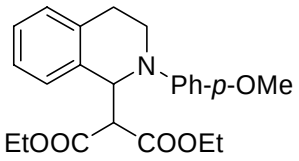
8g

2-[2-(2-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinolin-1-yl]-malonic acid diethyl ester (8g). Isolated by flash column chromatography (hexane/ethyl acetate/triethylamine = 50:10:1, R_f = 0.5). IR (neat liquid): ν_{max} 3062, 2981, 2942, 2907, 2835, 1753, 1733, 1594, 1501, 1464, 1454, 1369, 1339, 1300, 1243, 1178, 1140, 1112, 1031 cm^{-1}; ^1H NMR (300 MHz, ppm) δ = 7.25-7.05(m, 4H), 6.95-6.90(m, 1H), 6.80-6.74(m, 3H), 5.43(d, *J* = 8.4 Hz, 1H), 4.08-3.98(m, 4H), 3.92(d, *J* = 8.4 Hz, 1H), 3.79(s, 3H), 3.66-3.49(m, 2H), 2.87(ddd, *J* = 16.8, 11.1, 6.9 Hz, 1H), 2.66(ddd, *J* = 16.8, 4.2, 2.4 Hz, 1H), 1.11(t, *J* = 6.9 Hz, 3H), 1.07(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, ppm) δ 167.9, 167.3, 152.6, 149.6, 139.3, 135.6, 134.9, 129.0, 127.0, 125.6, 123.2, 121.6, 120.5, 111.3, 61.3, 61.3, 59.0, 55.3, 42.8, 26.4, 13.9; MS (EI) *m/z* (%) 397, 287, 238(100), 237, 236, 222, 220, 136, 133, 115, 88, 77, 43; HRMS calcd for $C_{23}H_{27}NO_5$: 397.1889; found: 397.1883.



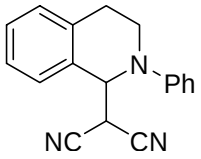
8h

2-[2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinolin-1-yl]-malonic acid dimethyl ester (8h). Isolated by flash column chromatography (hexane/ethyl acetate/triethylamine = 50:10:1, R_f = 0.3). IR (neat liquid): ν_{max} 2998, 2952, 2908, 2835, 1756, 1736, 1581, 1511, 1493, 1463, 1453, 1435, 1392, 1341, 1268, 1247, 1207, 1143, 1112, 1038, 998 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.19-7.14(m, 2H), 7.10-7.07(m, 2H), 6.98(d, *J* = 9.2 Hz, 2H), 6.75(d, *J* = 9.2 Hz, 2H), 5.47(d, *J* = 9.6 Hz, 1H), 3.95(t, *J* = 9.2 Hz, 1H), 3.71(s, 3H), 3.68-3.61(m, 1H), 3.62(s, 3H), 3.60(s, 3H), 3.54(ddd, *J* = 13.6, 5.6, 3.2 Hz, 1H), 3.00(ddd, *J* = 16.4, 10.0, 6.0 Hz, 1H), 2.74(dt, *J* = 16.8, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, ppm) δ 168.0, 167.2, 153.0, 143.2, 135.1, 134.6, 129.0, 127.3, 126.9, 125.8, 118.1, 114.2, 59.1, 55.5, 52.6, 52.6, 52.5, 52.5, 43.0, 25.5; MS (EI) *m/z* (%) 369, 239, 238(100), 237, 236, 221, 193, 136, 115, 101, 77, 59; HRMS calcd for $C_{21}H_{23}NO_5$: 369.1576; found: 369.1583.



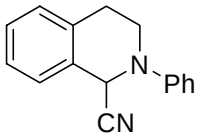
8i

2-[2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinolin-1-yl]-malonic acid diethyl ester (8i). Isolated by flash column chromatography (hexane/ethyl acetate/triethylamine = 50:10:1, R_f = 0.4). IR (neat liquid): ν_{max} 3065, 2981, 2936, 2905, 2834, 1752, 1731, 1609, 1581, 1512, 1493, 1464, 1444, 1391, 1369, 1335, 1300, 1266, 1249, 1181, 1145, 1039, 940 cm^{-1}; ^1H NMR (300 MHz, ppm) δ 7.24-7.21(m, 1H), 7.13(dd, *J* = 6.6, 1.5 Hz, 1H), 7.09-7.05(m, 2H), 6.89(d, *J* = 9.0 Hz, 2H), 6.75(d, *J* = 9.0 Hz, 2H), 5.50(d, *J* = 9.3 Hz, 1H), 4.13-3.97(m, 4H), 3.89(d, *J* = 9.0 Hz, 1H), 3.71(s, 3H), 3.69-3.62(m, 1H), 3.57-3.50(m, 1H), 2.99(ddd, *J* = 16.5, 10.2, 6.3 Hz, 1H), 2.75(dt, *J* = 16.5, 4.5 Hz, 1H), 1.14(t, *J* = 7.2 Hz, 3H), 1.12(t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, ppm) δ 167.8, 167.0, 152.9, 143.4, 135.5, 134.7, 128.9, 127.2, 127.1, 125.8, 118.0, 114.3, 61.5, 61.5, 59.5, 58.9, 55.6, 43.1, 25.7, 14.1, 14.0; MS (EI) *m/z* (%) 397, 253, 239, 238, 237, 236(100), 221, 193, 173, 160, 133, 115, 88, 87, 69, 60, 59, 55, 43; HRMS calcd for $C_{23}H_{27}NO_5$: 397.1889; found: 397.1884.



10

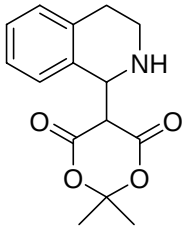
2-(2-Phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-malononitrile (10). Isolated by flash column chromatography (hexane/ethyl acetate/triethylamine = 50:10:1, R_f = 0.4). IR (neat liquid): ν_{max} 3063, 3033, 2906, 2854, 2252, 2229, 1599, 1580, 1504, 1496, 1476, 1454, 1429, 1394, 1367, 1319, 1296, 1265, 1231, 1157, 1115, 1033 cm^{-1}; ^1H NMR (300 MHz, ppm) δ 7.45(dd, *J* = 7.2, 1.8 Hz, 1H), 7.34-7.25(m, 5H), 6.98(d, *J* = 8.7 Hz, 3H), 5.34(d, *J* = 4.2 Hz, 1H), 4.18(d, *J* = 4.8 Hz, 1H), 3.80(ddd, *J* = 12.0, 7.2, 4.8 Hz, 1H), 3.50(ddd, *J* = 12.0, 6.6, 5.4 Hz, 1H), 3.16(ddd, *J* = 16.2, 6.0, 6.0 Hz, 1H), 3.03(ddd, *J* = 17.1, 6.6, 6.6 Hz, 1H); ^{13}C NMR (75 MHz, ppm) δ 147.5, 135.4, 130.5, 129.8, 129.2, 129.1, 127.3, 126.9, 121.1, 116.3, 61.6, 43.5, 29.6, 27.7; MS (EI) *m/z* (%) 274, 273, 208(100), 207, 193, 170, 154, 144, 130, 115, 106, 104, 91, 77, 65, 51; HRMS calcd for $C_{21}H_{23}NO_5$: 369.1576; found: 369.1583; HRMS calcd for $C_{18}H_{15}N_3$: 273.1266; found: 273.1273.



11

2-Phenyl-1,2,3,4-tetrahydro-isoquinoline-1-carbonitrile (11). Isolated by flash column chromatography (hexane/ethyl acetate/triethylamine = 50:10:1, R_f = 0.6). ^1H NMR (400 MHz, ppm) δ 7.37-7.21(m, 6H), 7.07(d, *J* = 8.0 Hz, 2H), 7.00(dd, *J* = 7.2, 7.2 Hz, 1H), 5.50(s, 1H), 3.77(dddd, *J* = 12.4, 6.0, 2.8, 1.2 Hz, 1H), 3.48(ddd, *J* = 12.4, 11.2, 4.0 Hz, 1H), 3.16(ddd, *J* = 16.4, 10.8, 6.0 Hz, 1H), 2.96(dt, *J* = 16.4, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, ppm) δ 148.2, 134.5, 129.4, 129.2, 128.6, 126.9, 126.7, 121.8, 117.6, 117.5, 53.3, 44.2, 28.6.

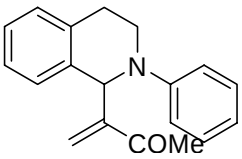
General procedure for Scheme 3: To a mixture of CuBr (3.5 mg, 0.025 mmol) and 2,2-dimethyl-[1,3]dioxane-4,6-dione (Meldrum' acid) (73.5 mg, 0.5 mmol), hexane (1 ml) and 1,2,3,4-tetrahydroisoquinoline (0.067 ml, 0.5 mmol) were added. Then *tert*-butyl hydroperoxide (0.10 ml, 5-6M in decane) was added into the mixture under nitrogen at room temperature. The resulting mixture was stirred at the room temperature for overnight. The resulting precipitate was washed with chloroform and filtered. The product **14** was obtained as white solid.



14

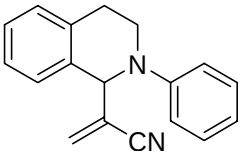
2,2-Dimethyl-5-(1,2,3,4-tetrahydro-isoquinolin-1-yl)-[1,3]dioxane-4,6-dione (14). IR (KBr): ν_{max} 3086, 2996, 2934, 1676, 1624, 1554, 1419, 1381, 1364, 1347, 1274, 1204, 1184, 1159, 1007, 889, 768, 737 cm^{-1}; ^{1}H NMR (500 MHz, DMSO, ppm) δ 9.07 (bs, 1H), 8.05(bs, 1H), 7.18-7.07(m, 4H), 5.29(s, 1H), 3.44-3.40(m, 1H), 3.28-3.22(m, 1H), 3.11(ddd, J = 17.0, 11.5, 4.5 Hz, 1H), 2.84(dd, J = 16.5, 3.0 Hz, 1H), 1.54(s, 6H); ^{13}C NMR (125 MHz, DMSO, ppm) δ 164.9, 135.8, 132.2, 128.0, 126.4, 126.0, 100.6, 72.4, 53.2, 41.4, 26.0, 25.6.

General procedure for Table 5: To a mixture of 4 Å MS (60 mg), CuBr (1.4 mg, 0.01 mmol), DABCO (2.4 mg, 0.02 mmol) and 2-phenyl-1,2,3,4-tetrahydroisoquinoline (42 mg, 0.2 mmol), methyl vinyl ketone (0.033 ml, 0.4 mmol) was added. Then *tert*-butyl hydroperoxide (0.04 ml, 5.5M in decane) was added into the mixture under nitrogen at room temperature. The temperature of reaction mixture was raised to 50°C for overnight. The resulting suspension was diluted with chloroform and filtered through a short silicon gel in a pipette eluting with chloroform. The solvent was removed by rotary evaporation and purified by Thin Layer Chromatography (hexane/ethyl acetate = 5:1), and the fraction with an R_f = 0.5 was collected and concentrated to give the desired product **16a**.



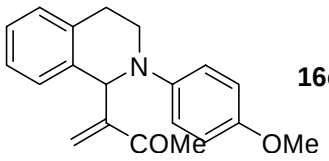
16a

3-(2-Phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-but-3-en-2-one (16a). Isolated by Thin Layer Chromatography (hexane/ethyl acetate = 5:1, R_f = 0.5). IR (neat liquid): ν_{max} 3062, 3026, 2914, 2846, 2247, 1676, 1598, 1534, 1493, 1475, 1385, 1360, 1328, 1267, 1230, 1105, 1035, 912 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.24-7.19(m, 3H), 7.16-7.10(m, 3H), 6.83(d, *J* = 8.0 Hz, 2H), 6.73(dd, *J* = 6.8, 6.8 Hz, 1H), 5.99(s, 1H), 5.93(s, 1H), 5.66(s, 1H), 3.73(ddd, *J* = 12.0, 5.6, 5.6 Hz, 1H), 3.49(ddd, *J* = 12.8, 8.0, 4.8 Hz, 1H), 3.03-2.89(m, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, ppm) δ 199.7, 150.6, 148.3, 135.6, 135.3, 129.0, 128.3, 127.8, 126.9, 126.1, 124.3, 117.6, 113.7, 58.3, 43.2, 27.7, 27.3; MS (EI) *m/z* (%) 277, 276, 262, 234, 208(100), 193, 165, 128, 115, 104, 91, 77, 65, 51; HRMS calcd for $C_{19}H_{19}NO$: 277.1467; found: 277.1458; HRMS calcd for $C_{19}H_{18}NO$: 276.1388; found: 276.1382.



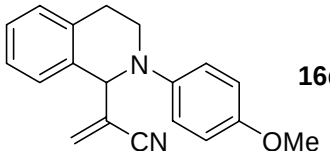
16b

2-(2-Phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-acrylonitrile (16b). Isolated by Thin Layer Chromatography (hexane/ethyl acetate = 5:1, R_f = 0.5). IR (neat liquid): ν_{max} 3061, 3026, 2914, 2848, 2221, 1598, 1503, 1475, 1387, 1324, 1300, 1229, 1158, 1114, 1036 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.29-7.23(m, 5H), 7.20-7.18(m, 1H), 6.85(d, *J* = 8.4 Hz, 2H), 6.83(dd, *J* = 7.6, 7.6 Hz, 1H), 5.97(s, 1H), 5.85(d, *J* = 1.2 Hz, 1H), 5.26(s, 1H), 3.74(ddd, *J* = 11.2, 5.2, 5.2 Hz, 1H), 3.49(ddd, *J* = 13.2, 8.4, 4.8 Hz, 1H), 3.03-2.90(m, 2H); ^{13}C NMR (100 MHz, ppm) δ 148.2, 135.7, 132.4, 130.3, 129.1, 128.1, 127.9, 127.8, 126.5, 125.0, 118.7, 117.7, 114.2, 62.5, 43.8, 28.0; MS (EI) *m/z* (%) 260, 208(100), 193, 165, 154, 140, 128, 115, 104, 91, 77, 63, 51; HRMS calcd for $C_{18}H_{16}N_2$: 260.1313; found: 260.1316.



16c

3-[2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinolin-1-yl]-but-3-en-2-one (16c). Isolated by Thin Layer Chromatography (hexane/ethyl acetate = 5:1, R_f = 0.4). IR (neat liquid): ν_{max} 2997, 2909, 2833, 2249, 1677, 1511, 1464, 1386, 1361, 1267, 1244, 1183, 1104, 1038 cm^{-1}; ^1H NMR (300 MHz, ppm) δ 7.14-7.08(m, 4H), 6.85-6.76(m, 4H), 6.00(s, 1H), 5.81(s, 1H), 5.50(d, *J* = 0.9 Hz, 1H), 3.72(s, 3H), 3.60(ddd, *J* = 12.6, 7.5, 4.8 Hz, 1H), 3.42(ddd, *J* = 12.0, 6.6, 5.8 Hz, 1H), 2.97(ddd, *J* = 15.9, 7.5, 4.8 Hz, 1H), 2.83(ddd, *J* = 16.2, 6.0, 6.0 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, ppm) δ 199.7, 152.6, 151.0, 143.1, 135.5, 135.4, 128.2, 128.1, 126.7, 126.0, 125.0, 116.8, 114.4, 58.7, 55.6, 43.6, 27.2, 27.1; MS (EI) *m/z* (%) 330(M+Na), 307, 306, 304, 292, 278, 262, 238, 236(100), 221, 193, 174, 157.

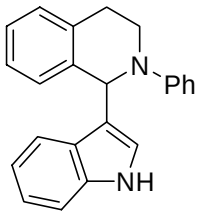


16d

2-[2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinolin-1-yl]-acrylonitrile (16d). Isolated by Thin Layer Chromatography (hexane/ethyl acetate = 5:1, R_f = 0.4). IR (neat liquid): ν_{max} 3064, 2997, 2933, 2834, 2252, 2222, 1616, 1511, 1464, 1454, 1388, 1291, 1245, 1183, 1114, 1038, 948 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.23-7.21(m, 2H), 7.18-7.15(m, 2H), 6.89-6.82(m, 4H), 5.91(s, 1H), 5.72(s, 1H), 5.12(s, 1H), 3.74(s, 3H), 3.62(ddd, *J* = 12.0, 5.2, 5.2 Hz, 1H), 3.40(ddd, *J* = 11.6, 6.4, 5.2 Hz, 1H), 2.94-2.91(m, 2H); ^{13}C NMR (100 MHz, ppm) δ 153.5, 142.9, 135.6, 132.3, 130.9, 128.5, 127.7, 127.6, 126.3, 125.5, 118.3, 117.9, 114.4, 63.8, 55.6, 44.8, 28.1; MS (EI) *m/z* (%) 291, 278, 264, 262, 238(100), 236, 221, 190, 174, 160.

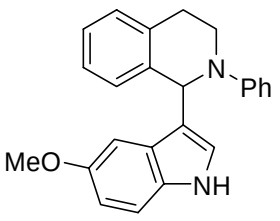
General procedure for Table 6: To a mixture of 2-phenyl-1,2,3,4-tetrahydro-isoquinoline (20.9 mg, 0.1 mmol), CuBr (0.7 mg, 0.005 mmol), and indole (14.2 mg, 0.12 mmol), *tert*-

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 and to give the desired product **18a**.



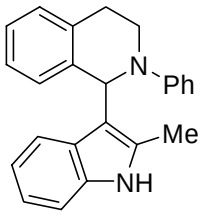
18a

1-(1*H*-Indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (18a). Isolated by Thin Layer Chromatography (methylene chloride, R_f = 0.9). Melting point is 179.0-180.0°C. IR (KBr): ν_{max} 3409, 3056, 3027, 2966, 2921, 1595, 1501, 1456, 1419, 1382, 1288, 1215, 1133, 1092, 1031, 937, 776, 753 cm^{-1}; ^{1}H NMR (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 (100 MHz, ppm) δ 149.6, 137.2, 136.4, 135.4, 129.1, 128.7, 127.9, 126.5, 126.3, 125.6, 124.0, 122.0, 120.0, 119.5, 119.2, 118.0, 115.7, 110.9, 56.7, 42.4, 26.7; 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 $C_{23}H_{20}N_2$: 324.1626; found: 324.1622.



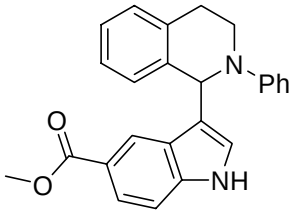
18b

1-[4-(2-Methoxy-propenyl)-1*H*-pyrrol-3-yl]-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (18b). 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): ν_{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 (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 (125 MHz, ppm) δ 153.9, 149.9, 137.5, 135.5, 131.6, 129.2, 128.8, 128.0, 126.9, 126.7, 125.7, 125.0, 118.6, 118.4, 116.3, 112.2, 111.6, 101.9, 56.9, 55.7, 42.2, 26.9; 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 $C_{24}H_{22}N_2O$: 354.1732; found: 354.1725.



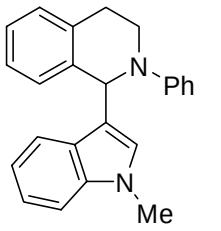
18c

1-(2-Methyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (18c). Isolated by Thin Layer Chromatography (methylene chloride, R_f = 0.6). Melting point is 80.0-85.0°C. IR (KBr): ν_{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 (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); ^{13}C NMR (125 MHz, ppm) δ 150.9, 138.0, 135.3, 134.9, 133.3, 128.8, 128.7, 128.6, 128.2, 126.3, 126.0, 120.8, 120.2, 119.4, 119.2, 113.4, 110.0, 109.9, 57.1, 45.8, 27.9, 12.3; MS (EI) *m/z* (%) 338, 218, 206, 131, 130, 118, 117, 87, 86, 85, 84, 83(100), 58, 49, 47; HRMS calcd for $C_{24}H_{22}N_2$: 338.1783; found: 338.1778.



18d

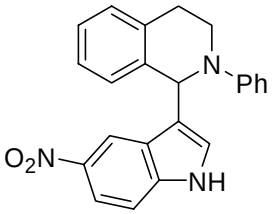
3-(2-Phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-1*H*-indole-5-carboxylic acid methyl ester (18d). Isolated by Thin Layer Chromatography (methylene chloride, R_f = 0.3). Melting point is 176.0-177.0°C. IR (KBr): ν_{max} 3407, 3027, 2954, 2921, 2888, 2860, 2835, 1700, 1685, 1654, 1617, 1597, 1560, 1497, 1435, 1311, 1289, 1251, 1222, 1113, 921, 756, 697, 669 cm^{-1}; ^1H NMR (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 (100 MHz, ppm) δ 168.0, 149.6, 138.9, 137.0, 135.2, 129.0, 128.6, 127.7, 126.7, 125.8, 125.7, 125.2, 123.2, 122.9, 121.4, 120.2, 118.5, 116.2, 110.7, 56.8, 51.9, 42.8, 27.1; MS (EI) *m/z* (%) 382, 255, 223, 222, 221, 220, 208, 175, 144, 129, 118, 116, 87, 86, 85, 84, 83(100), 77, 57; HRMS calcd for $C_{25}H_{22}N_2O_2$: 382.1681; found: 382.1673.



18e

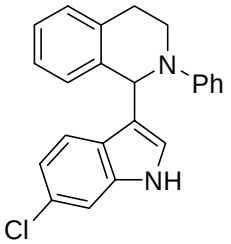
1-(1-Methyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (18e). Isolated by Thin Layer Chromatography (hexane/ethyl acetate = 5:1, R_f = 0.5). Melting point is 113.0-114.0°C. IR (KBr): ν_{max} 3423, 3056, 3019, 2925, 2848, 1596, 1500, 1370, 1329, 1284, 1218, 1199, 1109, 937, 770, 741, 692, 615 cm^{-1}; ^1H NMR (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 (100 MHz, ppm) δ 149.5, 137.4, 137.1, 135.4, 129.1, 128.6, 127.9, 126.7, 126.5, 125.5, 121.5, 120.0, 119.0, 117.8, 117.5, 115.4, 109.0, 56.6, 42.2, 32.8, 26.7; 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 $C_{24}H_{22}N_2$: 338.1783; found: 338.1775.



18f

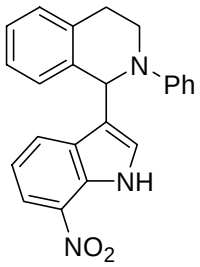
1-(5-Nitro-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (18f). Isolated by filtration and washed by cool chloroform. IR (KBr): ν_{max} 3407, 2921, 2860, 1594, 1560, 1517, 1500, 1333, 1207, 1092, 1031, 917, 839, 811, 770, 741, 700 cm^{-1}; ^{1}H NMR (DMSO, 400 MHz, ppm) δ 11.62(s, 1H), 8.40(s, 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 149.8, 140.9, 140.3, 137.7, 135.5, 129.7, 129.3, 129.0, 128.5, 127.4, 126.4, 125.8, 120.9, 118.5, 117.3, 117.2, 116.0, 112.7, 55.9, 42.6, 27.2; MS (EI) *m/z* (%) 370, 367, 366(100), 346, 320, 307, 293, 277, 231, 208, 193, 175, 165; HRMS calcd for $C_{23}H_{19}N_3O_2$: 369.1477; found: 369.1473.



18g

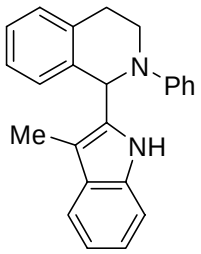
1-(6-Chloro-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (18g). Isolated by Thin Layer Chromatography (methylene chloride, R_f = 0.8). Melting point is 177.0-

178.0°C. IR (KBr): ν_{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 (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 (125 MHz, ppm) δ 149.8, 137.1, 136.9, 135.5, 129.2, 128.9, 128.0, 127.9, 126.8, 125.8, 125.1, 124.7, 121.0, 120.4, 119.4, 118.5, 116.2, 110.9, 56.6, 42.4, 26.6; 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 $C_{23}H_{19}{}^{37}ClN_2$: 360.1207; found: 360.1204; HRMS calcd for $C_{23}H_{19}{}^{35}ClN_2$: 358.1236; found: 358.1229.



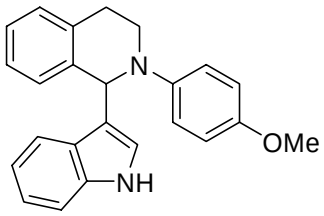
18h

1-(7-Nitro-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (18h). Isolated by Thin Layer Chromatography (hexane/ethyl acetate = 5:1, R_f = 0.4). IR (neat liquid): ν_{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 (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 (100 MHz, ppm) δ 149.5, 136.2, 135.3, 132.6, 130.1, 129.9, 129.2, 129.0, 128.4, 127.8, 126.9, 126.4, 125.8, 120.6, 119.2, 119.0, 116.5, 103.9, 56.5, 42.6, 26.6; 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.



18i

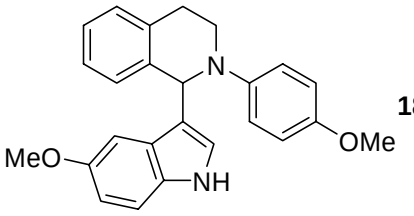
1-(3-Methyl-1*H*-indol-2-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (18i). Isolated by Thin Layer Chromatography (hexane/methylene chloride/triethyl amine = 40:30:1, R_f = 0.9). IR (neat liquid): ν_{max} 3429, 3058, 3026, 2917, 2857, 1598, 1578, 1503, 1495, 1456, 1383, 1343, 1318, 1265, 1223, 1180, 1154, 1128, 1015 cm^{-1}; ^1H NMR (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 (100 MHz, ppm) δ 148.7, 136.5, 135.6, 133.7, 129.1, 129.0, 128.7, 128.1, 128.0, 126.5, 124.2, 121.3, 120.8, 118.8, 118.7, 118.2, 110.4, 110.3, 70.0, 43.4, 27.6, 9.9; MS (EI) *m/z* (%) 339, 338, 337, 209, 208(100), 207, 206, 193, 165, 131, 130, 115; HRMS calcd for $C_{24}H_{22}N_2$: 338.1783; found: 338.1777.



18j

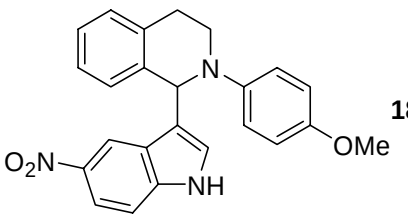
1-(1*H*-Indol-3-yl)-2-(4-methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinoline (18j). Isolated by Thin Layer Chromatography (methylene chloride/diethyl ether = 40:1, R_f = 0.5). Melting point is 162.0-163.0°C. IR (KBr): ν_{max} 3415, 3154, 3105, 3060, 2954, 2917, 2856, 2835, 1510, 1456, 1341, 1264, 1247, 1211, 1116, 1039, 937, 913, 823, 743 cm^{-1}; ^1H NMR (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), 3.52(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 (125 MHz, ppm) δ 153.3, 144.7, 137.5, 136.4, 135.3, 128.8, 128.2, 126.8, 126.4, 125.6, 124.3, 121.9, 120.2, 119.6, 119.5, 119.1, 114.4, 110.9, 57.9, 55.6, 43.7, 26.8; MS (EI) *m/z* (%) 355, 354(100), 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.



18k

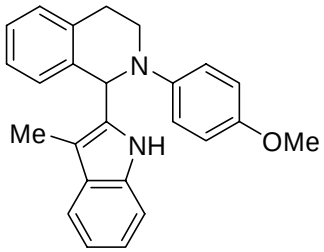
1-(5-Methoxy-1*H*-indol-3-yl)-2-(4-methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinoline (18k). Isolated by Thin Layer Chromatography (methylene chloride/diethyl ether = 40:1, R_f = 0.4). Melting point is 55.0-60.0°C. IR (KBr): ν_{max} 3411, 2937, 2831, 1654, 1508, 1480, 1242, 1210, 1174, 1113, 1036, 917, 831, 762, 669, 616 cm^{-1}; ^{1}H NMR (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 (125 MHz, ppm) δ 153.8, 153.5, 144.9, 137.7, 135.3, 131.4, 128.8, 128.2, 127.3, 126.4, 125.6, 125.2, 120.2, 118.3, 114.4, 112.2, 111.5, 101.9, 58.3, 55.6, 55.5, 43.4, 27.2; MS (EI) *m/z* (%) 385, 384(100), 383, 262, 261, 249, 248, 238, 237, 236, 218, 217, 192, 147, 123; HRMS calcd for $C_{25}H_{24}N_2O_2$: 384.1837; found: 384.1829.



18l

2-(4-Methoxy-phenyl)-1-(5-nitro-1*H*-indol-3-yl)-1,2,3,4-tetrahydro-isoquinoline (18l). Isolated by Thin Layer Chromatography (methylene chloride/diethyl ether = 40:1,

R_f = 0.4). Melting point is 155.0-156.0°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}; ^{1}H NMR (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 (125 MHz, ppm) δ 154.3, 144.5, 141.6, 139.3, 136.8, 135.1, 129.0, 128.0, 127.4, 126.8, 126.2, 125.8, 121.1, 117.8, 117.6, 114.5, 110.9, 58.5, 55.5, 44.2, 27.4; MS (EI) *m/z* (%) 400, 399, 398, 355, 354(100), 353, 263, 236, 232, 231, 230, 219, 218, 217, 216, 177, 123; HRMS calcd for $C_{24}H_{21}N_3O_3$: 399.1583; found: 399.1581.

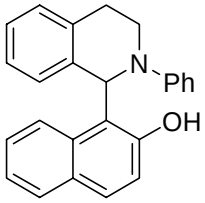


18m

2-(4-Methoxy-phenyl)-1-(3-methyl-1*H*-indol-2-yl)-1,2,3,4-tetrahydro-isoquinoline (18m). 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): ν_{max} 3427, 3039, 2933, 2856, 2835, 1512, 1453, 1245, 1178, 1137, 1037, 933, 830, 740, 692, 669, 639 cm^{-1}; ^{1}H NMR (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 (125 MHz, ppm) δ 155.2, 143.2, 137.0, 135.8, 134.3, 129.0, 128.8, 128.1, 128.0, 126.5, 124.8, 122.2, 121.3, 118.7, 118.6, 114.3, 110.5, 110.3, 71.6, 55.4, 45.0, 28.0, 9.7; MS (EI) *m/z* (%) 369, 327, 315, 292, 262, 239, 238(100), 223, 191, 159.

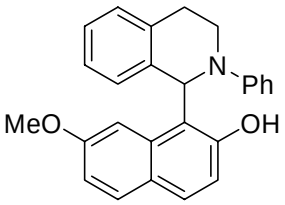
General procedure for Table 8: To a mixture of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (42 mg, 0.2 mmol), $CuBr_2$ (1.1 mg, 0.005 mmol), and 2-naphthol (14.6 mg, 0.10 mmol),

tert-butyl hydroperoxide (0.026 ml, 5.5 M in decane) was added into the mixture under nitrogen gas 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 (hexane/ethyl acetate = 5:1), and the fraction with an R_f = 0.5 was collected and to give the desired product **20a**.



20a

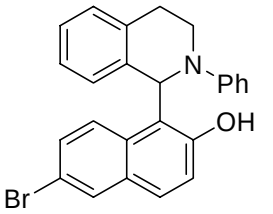
1-(2-Phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-naphthalen-2-ol (20a). Isolated by Thin Layer Chromatography (hexane/ethyl acetate = 5:1, R_f = 0.5). IR (KBr): ν_{max} 3054, 2974, 2923, 2849, 1624, 1601, 1492, 1261, 1236, 1190, 817, 770, 761, 745, 696 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 11.00(s, 1H), 8.17(d, *J* = 8.4 Hz, 1H), 7.70(d, *J* = 8.0 Hz, 1H), 7.56-7.51(m, 2H), 7.31-7.27(m, 3H), 7.17(d, *J* = 7.6 Hz, 1H), 7.10(dd, *J* = 8.0, 8.0 Hz, 3H), 6.96-6.86(m, 3H), 6.67(d, *J* = 8.0 Hz, 1H), 6.39(s, 1H), 3.68(ddd, *J* = 11.6, 5.6, 1.6 Hz, 1H), 3.62-3.54(m, 1H), 3.37(ddd, *J* = 11.6, 11.6, 3.2 Hz, 1H), 2.99(d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, ppm) δ 154.4, 149.8, 136.2, 133.4, 133.2, 129.4, 128.9, 128.8, 128.3, 128.2, 127.4, 127.0, 126.5, 126.3, 125.4, 123.0, 122.4, 120.9, 119.5, 118.3, 59.4, 55.5, 30.7; MS (EI) *m/z* (%) 351(100), 302, 258, 246, 229, 208, 167, 144, 129, 106, 77, 70; HRMS calcd for $C_{25}H_{21}NO$: 351.1623; found: 351.1619.



20b

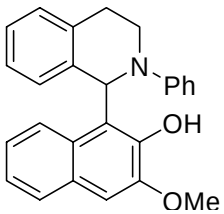
7-Methoxy-1-(2-phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-naphthalen-2-ol (20b). Isolated by Thin Layer Chromatography (hexane/ethyl acetate = 5:1, R_f = 0.5). IR (KBr):

ν_{max} 3059, 3027, 2962, 2833, 1624, 1520, 1492, 1457, 1260, 1228, 1035, 988, 827, 744, 697 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 10.95(s, 1H), 7.59(d, *J* = 8.8 Hz, 1H), 7.47-7.45(m, 2H), 7.26(d, *J* = 8.4 Hz, 2H), 7.17-7.08(m, 4H), 6.99-6.95 (m, 2H), 6.91(dd, *J* = 8.4, 8.4 Hz, 1H), 6.75(d, *J* = 7.6 Hz, 1H), 6.74(d, *J* = 8.4 Hz, 1H), 6.28(s, 1H), 3.94(s, 3H), 3.69(ddd, *J* = 11.2, 4.4, 4.4 Hz, 1H), 3.61-3.53(m, 1H), 3.38(ddd, *J* = 12.0, 12.0, 3.2 Hz, 1H), 2.99(d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, ppm) δ 158.8, 155.0, 149.8, 136.2, 134.7, 133.3, 130.4, 129.2, 128.9, 128.2, 127.3, 126.6, 126.4, 125.3, 123.7, 122.9, 117.6, 117.0, 114.0, 100.7, 59.6, 55.5, 30.7; MS (EI) *m/z* (%) 381(100), 365, 288, 259, 252, 208, 191, 174, 131, 129, 95, 57, 43; HRMS calcd for $C_{26}H_{23}NO_2$: 381.1729; found: 381.1723.



20c

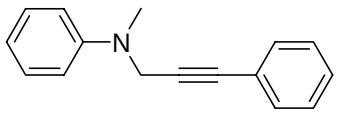
6-Bromo-1-(2-phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-naphthalen-2-ol (20c). Isolated by Thin Layer Chromatography (hexane/ethyl acetate = 5:1, R_f = 0.6). IR (KBr): ν_{max} 3062, 3024, 2962, 2835, 1590, 1508, 1492, 1450, 1388, 1357, 1321, 1262, 1233, 1160, 1120, 1075, 962, 924, 760, 745, 695 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 11.06(s, 1H), 8.02(d, *J* = 8.8 Hz, 1H), 7.83(d, *J* = 2.0 Hz, 1H), 7.57(dd, *J* = 8.8, 2.4 Hz, 1H), 7.44(d, *J* = 8.8 Hz, 1H), 7.26-7.10(m, 6H), 6.98-6.87(m, 3H), 6.61(d, *J* = 8.0 Hz, 1H), 6.31(s, 1H), 3.66(ddd, *J* = 12.0, 5.2, 1.2 Hz, 1H), 3.61-3.53(m, 1H), 3.37(ddd, *J* = 11.6, 11.6, 3.6 Hz, 1H), 2.99(d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, ppm) δ 154.8, 149.6, 135.8, 133.2, 132.0, 130.7, 130.1, 129.4, 129.0, 128.5, 128.3, 127.2, 126.7, 126.4, 125.6, 123.0, 122.7, 120.7, 118.6, 115.9, 59.6, 55.3, 30.6; MS (EI) *m/z* (%) 431(100), 429(100), 338, 336, 309, 245, 228, 208(100), 166, 149, 117, 106, 77, 66, 57, 55, 41; HRMS calcd for $C_{25}H_{20}{}^{81}BrNO$: 431.0709; found: 431.0715; HRMS calcd for $C_{25}H_{20}{}^{79}BrNO$: 429.0728; found: 429.0722.



20d

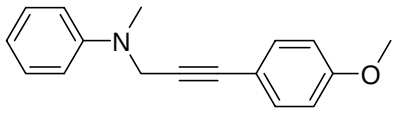
3-Methoxy-1-(2-phenyl-1,2,3,4-tetrahydro-isoquinolin-1-yl)-naphthalen-2-ol (20d). Isolated by Thin Layer Chromatography (hexane/ethyl acetate = 5:1, R_f = 0.3). IR (KBr): ν_{max} 3059, 3020, 2930, 2830, 1654, 1598, 1492, 1473, 1423, 1326, 1262, 1194, 1120, 1049, 875, 762, 745, 696 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 11.38(s, 1H), 8.12(d, *J* = 8.0 Hz, 1H), 7.63(d, *J* = 8.0 Hz, 1H), 7.45-7.28(m, 4H), 7.16-7.07 (m, 4H), 6.98-6.94(m, 2H), 6.87(dd, *J* = 7.2, 7.2 Hz, 1H), 6.69(d, *J* = 7.6 Hz, 1H), 6.42(s, 1H), 3.84(s, 3H), 3.70(dd, *J* = 11.6, 4.0 Hz, 1H), 3.63-3.55(m, 1H), 3.38(ddd, *J* = 12.0, 12.0, 3.2 Hz, 1H), 2.99(d, *J* = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, ppm) δ 149.6, 148.8, 146.5, 136.0, 133.3, 129.0, 128.5, 128.1, 127.4, 127.4, 126.5, 126.3, 125.3, 124.7, 123.0, 122.9, 120.9, 119.1, 106.4, 59.3, 55.5, 55.4, 30.8.

General procedure for Table 9 and Schemes 6, 7, and 8: To a mixture of CuBr (14.0 mg, 0.1 mmol), *N*,*N*-dimethylaniline (0.508 ml, 4.0 mmol) and phenylacetylene (0.22 ml, 2.0 mmol) was added *tert*-butyl hydroperoxide (0.4 ml, 5–6M in decane) under nitrogen over 30 seconds at room temperature. The reaction temperature was raised to 100°C over 15 min. The resulting mixture was stirred at the same temperature for 3 h. The reaction mixture was cooled to room temperature; the resulting suspension was diluted with diethyl ether and filtered through a short florisil column eluting with diethyl ether. Solvent was evaporated and the residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 95:5), and the fraction with an R_f = 0.5 was collected and concentrated to give the desired product **22a**.



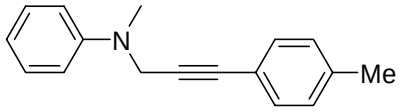
22a

***N*-Methyl-*N*-(3-phenylprop-2-ynyl)benzenamine (22a).** Isolated by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.5). ^{1}H NMR (400 MHz, ppm) δ 7.35-7.33(m, 2H), 7.28-7.20(m, 5H), 6.89-6.87(m, 2H), 6.80-6.77(m, 1H), 4.22(s, 2H), 3.00(s, 3H); ^{13}C NMR (100 MHz, ppm) δ 149.0, 131.6, 128.9, 128.0, 127.9, 122.8, 118.0, 114.2, 84.9, 84.0, 43.3, 38.7; MS (EI) *m/z* (%) 221(100), 220, 144, 116, 115, 104, 77.



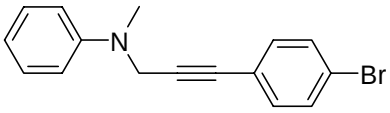
22b

***N*-(3-(4-Methoxyphenyl)prop-2-ynyl)-*N*-methylbenzenamine (22b).** Isolated by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.3). Melting point is 72.0-73.0°C. IR (KBr): ν_{max} 3065, 3006, 2969, 2818, 1604, 1508, 1251, 1030, 836, 756, 693 cm^{-1}; ^{1}H NMR (400 MHz, ppm) δ 7.29-7.23(m, 4H), 6.88(d, *J* = 8.0 Hz, 2H), 6.80-6.74(m, 3H), 4.22(s, 2H), 3.74(s, 3H), 3.00(s, 3H); ^{13}C NMR (100 MHz, ppm) δ 159.1, 149.1, 132.9, 128.9, 117.9, 114.9, 114.2, 113.6, 83.8, 83.4, 55.2, 43.3, 38.7; MS (EI) *m/z* (%) 251, 250, 146, 145(100), 102, 77; HRMS calcd for $C_{17}H_{17}NO$: 251.1310; found: 251.1317.



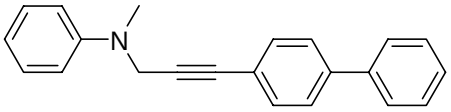
22c

***N*-Methyl-*N*-(3-*p*-tolylprop-2-ynyl)benzenamine (22c).** Isolated by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.5). IR (KBr): ν_{max} 3056, 3023, 2990, 2962, 2884, 2223, 1598, 1353, 1234, 1201, 1110, 994, 923, 819, 759, 695, 529 cm^{-1}; ^{1}H NMR (400 MHz, ppm) δ 7.26-7.22(m, 4H), 7.02(d, *J* = 8.0 Hz, 2H), 6.87(d, *J* = 8.0 Hz, 2H), 6.77(dd, *J* = 7.2, 7.2 Hz, 1H), 4.21(s, 2H), 2.99(s, 3H), 2.28(s, 3H); ^{13}C NMR (100 MHz, ppm) δ 149.1, 137.9, 131.4, 128.9, 128.7, 119.7, 117.9, 114.2, 84.2, 84.1, 43.3, 38.7, 21.5; MS (EI) *m/z* (%) 236, 235, 234, 201, 200, 199, 198, 144, 130, 129(100), 128, 119, 106, 91, 77,63, 51; HRMS calcd for $C_{17}H_{17}N$: 235.1361; found: 235.1365.



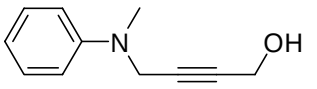
22d

***N*-(3-(4-Bromophenyl)prop-2-ynyl)-*N*-methylbenzenamine (22d).** Isolated by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.4). IR (KBr): ν_{max} 3060, 3023, 2876, 2811, 1599, 1505, 1485, 1366, 1333, 1235, 1110, 1070, 1011, 826, 752, 689, 521 cm^{-1}; ^{1}H NMR (400 MHz, ppm) δ 7.33(d, *J* = 8.4 Hz, 2H), 7.24(dd, *J* = 8.0, 6.6 Hz, 2H), 7.17(d, *J* = 8.4 Hz, 2H), 6.85(d, *J* = 8.0 Hz, 2H), 6.78(dd, *J* = 6.6, 6.6 Hz, 1H), 4.20(s, 2H), 2.98(s, 3H); ^{13}C NMR (100 MHz, ppm) δ 148.9, 133.0, 131.2, 128.9, 122.1, 121.8, 118.1, 114.1, 86.2, 83.0, 43.3, 38.7; MS (EI) *m/z* (%) 302, 301, 300, 299(100), 298, 219, 196, 195, 193, 144, 115, 114, 113, 106, 104, 77; HRMS calcd for $C_{16}H_{14}BrN$: 299.0309; found: 299.0305.



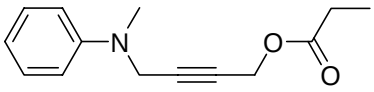
22e

***N*-Methyl-*N*-(3-biphenylprop-2-ynyl)benzenamine (22e).** Isolated by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.3). Melting point is 83.0-84.5°C. IR (KBr): ν_{max} 3060, 2815, 1596, 1505, 1485, 1370, 1109, 919, 841, 764, 750, 692, 503 cm^{-1}; ^{1}H NMR (400 MHz, ppm) δ 7.52(d, *J* = 8.0 Hz, 2H), 7.47(d, *J* = 8.0 Hz, 2H), 7.42-7.37(m, 4H), 7.31(d, *J* = 7.2 Hz, 1H), 7.26(dd, *J* = 8.0, 8.0 Hz, 2H), 6.90(d, *J* = 8.8 Hz, 2H), 6.79(dd, *J* = 7.2, 7.2 Hz, 1H), 4.25(s, 2H), 3.02(s, 3H); ^{13}C NMR (100 MHz, ppm) δ 149.1, 140.6, 140.1, 132.0, 128.9, 128.7, 127.4, 126.8, 126.7, 121.7, 118.0, 114.2, 85.6, 83.9, 43.4, 38.8; MS (EI) *m/z* (%) 298, 297, 296, 192, 191(100), 189, 129, 77; HRMS calcd for $C_{22}H_{19}N$: 297.1517; found: 297.1510.



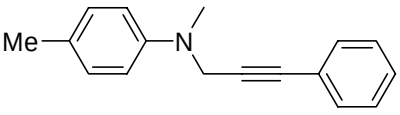
22f

4-(*N*-Methyl-*N*-phenylamino)but-2-yn-1-ol (22f). Isolated by flash column chromatography (hexane/ethyl acetate = 10:1, R_f = 0.1). IR (neat liquid): ν_{max} 3360, 3060, 2916, 2868, 1600, 1505, 1334, 1241, 1200, 1116, 1014, 924, 754, 692 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.23(dd, *J* = 8.0, 7.2 Hz, 2H), 6.81(d, *J* = 9.2 Hz, 2H), 6.77(d, *J* = 7.2 Hz, 1H), 4.14(s, 2H), 4.04(s, 2H), 2.93(s, 3H), 2.02(bs, 1H); ^{13}C NMR (100 MHz, ppm) δ 148.8, 128.9, 118.1, 114.1, 82.1, 81.1, 51.0, 42.7, 38.7; MS (EI) *m/z* (%) 176, 175(100), 174, 158, 144, 130, 115, 106, 104, 91, 77, 51, 39; HRMS calcd for $C_{11}H_{13}NO$: 175.0997; found: 175.0992.



22g

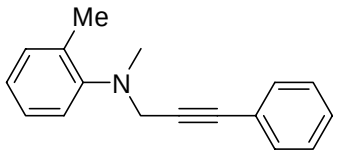
4-(*N*-Methyl-*N*-phenylamino)but-2-ynyl propiolate (22g). Isolated by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.2). IR (neat liquid): ν_{max} 3060, 3029, 2982, 2943, 2880, 1745, 1600, 1505, 1342, 1174, 1128, 1082, 995, 754, 692 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.23(dd, *J* = 9.2, 7.6 Hz, 2H), 6.80(d, *J* = 9.2 Hz, 2H), 6.76(d, *J* = 7.6 Hz, 1H), 4.62(t, *J* = 1.6 Hz, 2H), 4.05(t, *J* = 1.6 Hz, 2H), 2.93(s, 3H), 2.31(q, *J* = 7.4 Hz, 2H), 1.12(t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, ppm) δ 173.3, 148.7, 128.8, 118.0, 114.0, 82.2, 77.9, 52.2, 42.6, 38.6, 27.3, 9.0; MS (EI) *m/z* (%) 232, 231, 230, 174, 159, 158(100), 157, 156, 144, 143, 142, 120, 115, 107, 106, 105, 104, 78, 77, 57, 51, 42, 39; HRMS calcd for $C_{14}H_{17}NO_2$: 231.1259; found: 231.1253.



22h

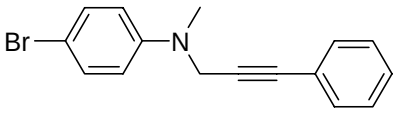
***N*,4-Dimethyl-*N*-(3-phenylprop-2-ynyl)benzenamine (20h).** Isolated by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.6). IR (neat liquid): ν_{max} 3033, 2919, 2862, 2808, 1616, 1520, 1489, 1334, 1240, 1109, 922, 807, 756, 691 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.34-7.31(m, 2H), 7.19-7.17(m, 3H), 7.04(d, *J* = 8.8 Hz, 2H), 6.79(d, *J* = 8.4 Hz, 2H), 4.15(s, 2H), 2.93(s, 3H), 2.24(s, 3H); ^{13}C NMR (100 MHz, ppm) δ 147.0, 131.5, 129.4, 127.9, 127.8, 127.4, 122.9, 114.7, 85.0, 84.1, 43.7, 38.9, 20.4; MS

(EI) *m/z* (%) 236, 235(100), 234, 220, 158, 120, 118, 115, 91; HRMS calcd for $C_{17}H_{17}N$: 235.1361; found: 253.1356.



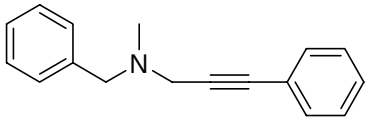
22i

***N*,2-Dimethyl-*N*-(3-phenylprop-2-ynyl)benzenamine (22i).** Isolated by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.8). IR (neat liquid): ν_{max} 3059, 3020, 2946, 2869, 2792, 1598, 1490, 1442, 1351, 1329, 1223, 1091, 919, 756, 727, 691 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.38-7.36(m, 2H), 7.23-7.12(m, 6H), 6.96(dd, *J* = 7.2, 7.2 Hz, 1H), 3.88(s, 2H), 2.84(s, 3H), 2.33(s, 3H); ^{13}C NMR (100 MHz, ppm) δ 150.2, 132.4, 131.5, 130.9, 128.0, 127.8, 126.1, 123.3, 123.0, 120.3, 85.4, 84.9, 46.2, 40.5, 18.3; MS (EI) *m/z* (%) 236, 235(100), 234, 220, 158, 120, 118, 115, 91; HRMS calcd for $C_{17}H_{17}N$: 235.1361; found: 253.1355.



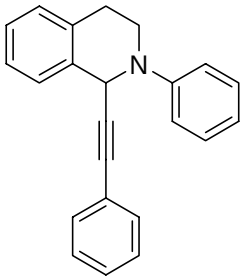
22j

4-Bromo-*N*-methyl-*N*-(3-phenylprop-2-ynyl)benzenamine (22j). Isolated by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.4). IR (KBr): ν_{max} 3072, 2957, 2897, 2815, 1597, 1503, 1367, 1241, 1203, 1116, 1076, 921, 805, 760, 693, 496 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.34-7.30(m, 4H), 7.23-7.22(m, 3H), 6.71(d, *J* = 9.2 Hz, 2H), 4.17(s, 2H), 2.96(s, 3H); ^{13}C NMR (100 MHz, ppm) δ 147.9, 131.6, 131.5, 128.0, 122.6, 115.7, 113.9, 110.0, 84.3, 84.3, 43.2, 38.8; MS (EI) *m/z* (%) 301, 300, 299, 298, 231, 220, 158, 157, 116, 115(100), 77; HRMS calcd for $C_{16}H_{14}{}^{79}BrN$: 299.0309; found: 299.0305.



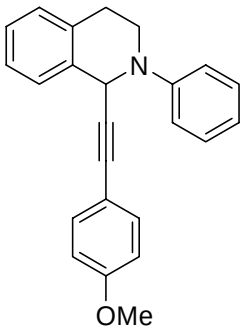
24

***N*-Benzyl-*N*-methyl-3-phenylprop-2-yn-1-amine (24).** Isolated by flash column chromatography (hexane/ethyl acetate = 10:1, R_f = 0.4). IR (neat liquid): ν_{max} 3061, 3029, 2940, 2837, 2792, 2231, 1950, 1882, 1598, 1489, 1454, 1325, 1123, 1026, 756, 691 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.45-7.43(m, 2H), 7.35-7.22(m, 8H), 3.61(s, 2H), 3.48(s, 2H), 2.38(s, 3H); ^{13}C NMR (100 MHz, ppm) δ 138.2, 131.5, 129.0, 128.1, 128.0, 127.8, 127.0, 123.1, 85.6, 84.3, 60.2, 45.7, 42.0; MS (EI) *m/z* (%) 236, 235, 234, 191, 158, 144, 132, 118, 116, 115(100), 91, 89, 65; HRMS calcd for $C_{17}H_{17}N$: 235.1361; found: 235.1366.



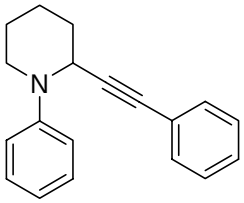
25a

2-Phenyl-1-phenylethynyl-1,2,3,4-tetrahydro-isoquinolinee (25a). Isolated by Thin Layer Chromatography (hexane/methylene chloride/diethyl ether = 100:60:1, R_f = 0.6); IR (neat liquid): ν_{max} 3061, 3024, 2920, 2832, 2210, 1950, 1598, 1503, 1489, 1451, 1442, 1377, 1287, 1201, 1069, 1029, 932 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.35-7.25(m, 5H), 7.22-7.14(m, 6H), 7.09(dd, *J* = 8.4, 0.8 Hz, 2H), 6.86(dt, *J* = 7.2, 0.8 Hz, 1H), 5.62(s, 1H), 3.75-3.61(m, 2H), 3.09(ddd, *J* = 16.8, 10.4, 6.4 Hz, 1H), 2.95(dt, *J* = 16.0, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, ppm) δ 149.3, 135.2, 134.2, 131.6, 129.0, 128.8, 127.9, 127.8, 127.3, 127.0, 126.1, 122.8, 119.5, 116.5, 88.5, 84.7, 52.3, 43.5, 29.0; MS (EI) *m/z* (%) 309, 308(100), 293, 253, 204, 203, 202, 73, 51; HRMS calcd for $C_{23}H_{19}N$: 309.1517; found: 309.1511.



25b

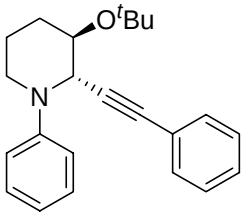
1-(4-Methoxy-phenylethynyl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (25b). Isolated by flash column chromatography (hexane/ethyl acetate = 20:1, R_f = 0.5). IR (neat liquid): ν_{max} 3061, 3025, 2932, 2836, 2206, 1600, 1499, 1374, 1246, 1172, 1106, 1033, 832, 756, 692 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.34-7.31(m, 1H), 7.30-7.26(m, 2H), 7.21-7.16(m, 4H), 7.15-7.12(m, 1H), 7.08(d, *J* = 8.0 Hz, 2H), 6.84(dd, *J* = 7.6, 7.6 Hz, 1H), 6.69(dt, *J* = 8.8, 2.4 Hz, 2H), 5.60(s, 1H), 3.73-3.60(m, 2H), 3.68(s, 3H), 3.09(ddd, *J* = 16.0, 9.6, 6.0 Hz, 1H), 2.92(dt, *J* = 16.0, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, ppm) δ 159.1, 149.3, 135.4, 134.1, 132.9, 128.9, 128.7, 127.2, 126.9, 126.0, 119.3, 116.5, 115.0, 113.5, 87.0, 84.5, 55.2, 52.3, 43.4, 29.0; MS (EI) *m/z* (%) 340, 339, 338(100), 324, 223, 220, 219, 208, 191, 189, 118, 104, 77; HRMS calcd for $C_{24}H_{20}NO$: 338.1545; found: 338.1540; $C_{24}H_{21}NO$: 339.1623; found: 339.1604.



27

1-Phenyl-2-(2-phenylethynyl)piperidine (27). Isolated by flash column chromatography (methylene chloride/hexane/diethyl ether = 50:30:1, R_f = 0.6). IR (neat liquid): ν_{max} 3063, 3032, 2937, 2856, 2821, 1598, 1501, 1489, 1442, 1377, 1346, 1304, 1245, 1165, 1118, 1023, 914, 755, 691, 525 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.33-7.31(m, 2H), 7.27-7.21(m, 5H), 7.03(d, *J* = 8.0 Hz, 2H), 6.85(dd, *J* = 7.2, 7.2 Hz, 1H), 4.72(dd, *J* = 4.0, 4.0 Hz, 1H), 3.41(d, *J* = 11.6 Hz, 1H), 3.19(ddd, *J* = 11.6, 11.6, 2.8 Hz, 1H), 1.99-1.96(m, 2H), 1.87-1.78(m, 2H), 1.73-1.65(m, 2H); ^{13}C NMR (100 MHz, ppm) δ 150.9, 131.6,

128.8, 128.0, 127.7, 123.1, 120.0, 117.7, 87.4, 85.8, 50.5, 45.8, 31.5, 26.0, 20.3; MS (EI) *m/z* (%) 262, 261(100), 260, 232, 205, 204, 106, 104, 77; HRMS calcd for $C_{19}H_{19}N$: 261.1517; found: 261.1520.



28

3-*tert*-Butoxy-1-phenyl-2-phenylethynyl-piperidine (28). Isolated by flash column chromatography (hexane/diethyl ether = 15:1, R_f = 0.4). IR (KBr): ν_{max} 3057, 2973, 2944, 1599, 1491, 1254, 1189, 1107, 1016, 915, 758, 690 cm^{-1}; ^1H NMR (400 MHz, ppm) δ 7.31-7.29(m, 2H), 7.26-7.22(m, 5H), 7.01(d, *J* = 7.6 Hz, 2H), 6.85(dd, *J* = 7.6, 7.6 Hz, 1H), 4.53(d, *J* = 2.4 Hz, 1H), 3.93(d, *J* = 2.4 Hz, 1H), 3.35(d, *J* = 11.6 Hz, 1H), 3.15(dt, *J* = 11.6, 2.4 Hz, 1H), 2.10-2.00(m, 2H), 1.66-1.60(m, 2H), 1.28(s, 9H); ^{13}C NMR (100 MHz, ppm) δ 151.4, 131.5, 128.6, 128.0, 127.9, 122.9, 120.0, 118.1, 86.6, 86.0, 74.2, 68.3, 57.7, 44.7, 28.4, 27.6, 20.7; MS (EI) *m/z* (%) 333, 277, 276(100), 263, 206, 182, 160, 115, 105, 77, 71; HRMS calcd for $C_{23}H_{27}NO$: 333.2092; found: 333.2082.

Reference

1. Kwong, F. Y., Klapars, A. & Buchwald, S. L. (2002) *Org. Lett.* **4,** 581.