Experimental Details

General Comments. Chemicals were purchased and used without further purification unless otherwise specified. All reactions using anhydrous solvents were carried out under an atmosphere of industrial argon in flame-dried glassware with magnetic stirring. Anhydrous solvent was dispensed from a solvent purification system that passes solvent through two columns of dry neutral alumina. Reactions were monitored by thin layer chromatography (TLC, Merck), and detected by examination under UV light (254 nm and 365 nm). Flash column chromatography was performed using silica gel [230−400 mesh (40−63 μm)]. Extracts were concentrated *in vacuo* using both a rotary evaporator (bath temperatures up to 40 °C) at a pressure of either 15 mmHg (diaphragm pump) or 0.1 mmHg (oil pump), as appropriate. High vacuum procedures were carried out at room temperature. ^{1}H and proton-decoupled ^{13}C spectra were measured in $CDCl_3$ at 400, or 600 MHz, and 101 or 151 MHz respectively unless otherwise noted. All spectra in $CDCl_3$ were referenced at TMS = 0 ppm. High-resolution mass spectrometry was performed on positive mode and ESI ionization techniques were used, unless otherwise noted. Melting points were taken on an EZ-melting apparatus and were uncorrected. Infrared spectra were taken on a Bruker Tensor 27 spectrometer. All microwave experiments were run in a biotage initiator EXP EU 400W microwave synthesizer 2.0 serial number 11031.

General Procedure A (nucleophilic aromatic substitution). To an oven-dried 20 mL microwave vial was added K_2CO_3 (3 equiv). The vial was evacuated under vacuum and backfilled with argon. To the vial was added DMF or CH_3CN (1.0 M), the respective amine (1.2 equiv), and 2-fluorobenzophenone (1 equiv). The mixture was heated to 180 °C in a microwave reactor for 2-4 hours. Upon completion by TLC, the crude mixture was poured into water (50 mL) and extracted with CH_2Cl_2 (3 x 75 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography or recrystallization to yield the desired ketone.

General Procedure B (alkylation of 2-mercaptobenzophenone). To a flame-dried 50 mL round bottom flask was added 2-mercaptobenzophenone (1.0 equiv). The flask was evacuated under high vacuum and backfilled with argon. To the flask was added acetonitrile (0.1 M), the respective bromide (1.3-1.5 equiv), and K_2CO_3 or Cs_2CO_3 (3 equiv). The mixture was then heated to 65 °C for 18 hours and then cooled to room temperature. The reaction was gravity filtered through fluted filter paper to remove K_2CO_3 or Cs_2CO_3. The filtrate was concentrated *in vacuo* and the crude mixture was purified by flash column chromatography.

General Procedure C (alkylation of 2-mercaptobenzophenone). To a flame-dried 50 mL round bottom flask was added 2-mercaptobenzophenone (1.0 equiv). The flask was evacuated under high vacuum and backfilled with argon. To the flask was added acetonitrile (0.1 M), the respective bromide (1.3-1.5 equiv), and K_2CO_3 or Cs_2CO_3 (3 equiv). The mixture was then stirred at room temperature for 18 hours. Upon completion by TLC, the reaction was gravity filtered through fluted filter paper to remove K_2CO_3 or Cs_2CO_3. The filtrate was concentrated *in vacuo* and the crude mixture was purified by flash column chromatography.

General Procedure D (microwave hydrazone formation). To an oven-dried 5-25 mL argon backfilled microwave vial was added a solution of the respective ketone (1 equiv) in anhydrous EtOH (0.1 M). To the vial was added AcOH (2 equiv) and anhydrous hydrazine (10 equiv). The vial was heated in a microwave reactor at 170 °C for 2-5 hours. The reaction mixture was then concentrated *in vacuo,* dissolved in diethyl ether (50 mL), and washed with H_2O (3 x 30 mL). The organic layer was dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by flash column chromatography to yield the desired hydrazone.

General Procedure E (hydrazone formation). Following literature precedent,[1] to the desired alkylated benzophenone (1 equiv) in anhydrous EtOH (0.06 M) was added anhydrous hydrazine (12-20 equiv.) and glacial acetic acid (1.2 equiv). The reaction was heated to 80 °C for 18-120 h with additional hydrazine and AcOH added as needed if poor conversion was observed by TLC. The reaction was allowed to cool and EtOH was removed *in vacuo*. The residue was taken up in diethyl ether (30 mL) and H_2O (20 mL). The layers were separated, and the organic layer was washed with H_2O (2 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo.*

General Procedure F (reduction after hydrazone). Argon was bubbled through a solution of the crude hydrazone from general procedure E (1 equiv) in CH_3OH (0.3 M) for 15 minutes. 10% Palladium on carbon (0.05-0.1 equiv) was added and argon was bubbled through the mixture for an additional 5 minutes. The reaction was sparged with H_2 (g) for 5 minutes and then stirred for 18-28 h at room temperature under 1 atm of H_2 (g). The crude product was filtered through Celite with CH_2Cl_2 and concentrated *in vacuo*. In some cases, the ^{1}H NMR of the crude reaction mixture showed incomplete conversion and the crude material was resubmitted under the same reaction conditions for an additional 18 h. The crude product was purified by flash column chromatography using 2-40 % EtOAc:hexanes as the eluent on neutral alumina.

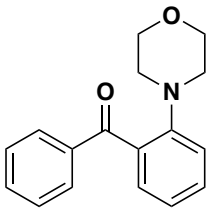
General Procedure G (sequential one-pot insertion). To a flame-dried 7 mL scintillation vial under argon atmosphere was added the desired hydrazone (1 equiv) followed by anhydrous CH_2Cl_2 or CH_3CN (0.01 M). To the vial was added MnO_2 (8 equiv). The resulting dark suspension was stirred until full conversion of the starting material was observed by TLC. Upon pausing stirring, a color change from clear to magenta was observed from formation of the diazo. The vial was then cooled to 0 °C and the desired rhodium catalyst was added (0.01 equiv). The reaction mixture was warmed to room temperature and allowed to react from 10 min to 12 h. The crude reaction mixture was filtered over Celite to remove MnO_2, concentrated *in vacuo*, and purified by flash column chromatography to yield the desired insertion product.

General Procedure H (two-pot insertion). To a flame-dried scintillation vial under argon atmosphere was added the desired hydrazone (1 equiv) followed by anhydrous CH_2Cl_2 or CH_3CN (0.01 M). To the vial was added MnO_2 (8 equiv). The resulting dark suspension was stirred until full conversion of the starting material was observed by TLC. The reaction mixture was filtered over Celite into a new flame-dried, argon backfilled 20 mL scintillation vial using the same solvent. The magenta solution was cooled to 0 °C and the desired rhodium catalyst was added (0.01 equiv). The reaction mixture was warmed to room temperature and allowed to stir from 10 min to 12 h. The crude reaction mixture was concentrated *in vacuo* and purified by flash column chromatography to yield the desired insertion product.

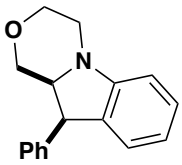
General Procedure I (one-pot insertion). To a flame-dried scintillation vial under argon atmosphere was added the desired hydrazone (1 equiv) followed by anhydrous CH_2Cl_2 or CH_3CN (0.01 M). The vial was cooled to 0 °C and MnO_2 (8 equiv) and the desired rhodium catalyst (0.01 equiv) were added. The resulting dark suspension was warmed to room temperature and allowed to stir from 10 min to 12 h. The crude reaction mixture was filtered over Celite, concentrated *in vacuo*, and purified by flash column chromatography to yield the desired insertion product.

Note: *Hydrazones were often isolated as a mixture of E/Z isomers or used without further purification. As such ^{1}H NMR peaks have been reported only for selected examples.*

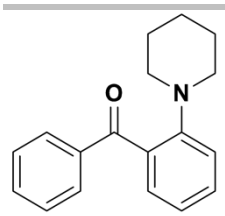
INDOLINES



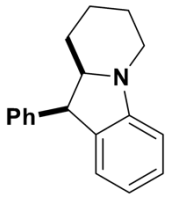
(2-morpholinophenyl)(phenyl)methanone (**1**) was synthesized according to general procedure A using 2-fluorobenzophenone (2.0 mL, 12 mmol), morpholine (1.2 mL, 14 mmol), K_2CO_3 (4.90 g, 35.5 mmol) and CH_3CN (2.4 mL). The crude product was purified by flash column chromatography (10:90, EtOAc:hexanes) affording **1** as a yellow solid (286 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.51 – 7.37 (m, 4H), 7.16 (td, *J* = 7.5, 1.1 Hz, 1H), 7.07 (dd, *J* = 8.1, 1.0 Hz, 1H), 3.31 – 3.26 (m, 4H), 3.04 – 2.84 (m, 4H). Proton NMR data of the crude material was consistent with the reported literature values.[2]



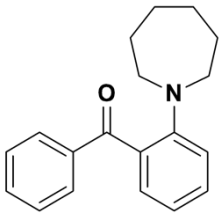
10-phenyl-3,4,10,10a-tetrahydro-1*H*-[1,4]oxazino[4,3-*a*]indole (**2c**) was synthesized according to general procedure H using hydrazone **1c** (23 mg, 0.083 mmol), MnO_2 (58 mg, 0.66 mmol), and Rh_2(*R*-PTAD)$_4$ (1 mg, 0.0006 mmol) in CH_2Cl_2 (0.01 M). The crude product was purified by flash column chromatography (7:93, EtOAc:hexanes) affording **2c** as a white solid (16 mg, 78%, 100:0 er, 93:7 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, , 3H), 7.18 (td, *J* = 7.7, 1.3 Hz, 1H), 7.07 (m, 3H), 6.74 (td, *J* = 7.4, 1.0 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 4.43 (d, *J* = 8.4 Hz, 1H), 3.82 (dd, *J* = 10.4, 3.4 Hz, 1H), 3.70 (ddd, *J* = 10.7, 8.3, 3.2 Hz, 1H), 3.62 – 3.38 (m, 3H), 3.18 – 3.02 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 138.4, 132.1, 128.6, 128.3, 128.2, 126.9, 125.5, 118.7, 106.7, 68.5, 65.7, 65.3, 48.8, 45. AMM (ESI) *m/z* calcd for $C_{17}H_{18}NO^+$ $[M+H]^+$ 252.1383, found 252.1381. $[\alpha]_D^{23}$ = -0.189 (c = 33.75, $CHCl_3$).



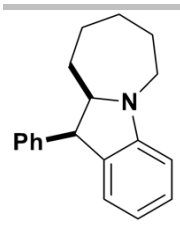
phenyl(2-(piperidin-1-yl)phenyl)methanone (**2**) was synthesized according to general procedure A using 2-fluorobenzophenone (1.71 mL, 9.90mmol), cyclohexyl amine (1.13 mL, 11.0 mmol), K_2CO_3 (4.17 g, 39.8 mmol) and DMF (10 mL). The crude product was recrystallized (35:65 H_2O:CH_3OH) affording **2** as an off-white solid (922 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.78 – 7.74 (m, 2H), 7.59 – 7.49 (m, 1H), 7.48 – 7.34 (m, 4H), 7.15 – 6.98 (m, 2H), 2.84 (dd, *J* = 6.0, 4.6 Hz, 4H), 1.27 (td, *J* = 7.3, 6.4, 4.1 Hz, 2H), 1.21 – 1.06 (m, 4H). Proton NMR data of the crude material was consistent with the reported literature values.[2]



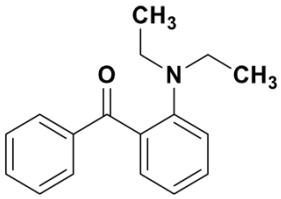
10-phenyl-6,7,8,9,9a,10-hexahydropyrido[1,2-*a*]indole (**2a**) was synthesized according to general procedure G using hydrazone **1a** (26 mg, 0.09 mmol), MnO_2 (87 mg, 0.73 mmol), and Rh_2(*R*-PTAD)$_4$ (1 mg, 0.0006 μmol) in CH_3CN (0.01 M). The crude product was purified by flash column chromatography (6:94, EtOAc:hexanes) affording **2a** as a yellow oil (16 mg, 70%, 96:4 er, >95:5 dr). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 – 7.22 (m, 2H), 7.23 – 7.18 (m, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 3H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 4.27 (d, *J* = 8.2 Hz, 1H), 3.68 (d, *J* 3.6 Hz, 1H), 3.40 (s, 1H), 2.63 (td, *J* = 12.0, 3.0 Hz, 1H), 1.81 – 1.72 (m, 1H), 1.66 (d, *J* = 13.3 Hz, 1H), 1.52 – 1.40 (m, 2H), 1.34 (qt, *J* = 13.2, 3.8 Hz, 1H), 0.93 (qd, *J* = 12.5, 3.8 Hz, 1H);^{3}C NMR (101 MHz, $CDCl_3$) δ 151.8, 141.3, 132.3, 129.0, 128.4, 127.6, 126.8, 124.5, 118.1, 106.0, 74.6, 54.6, 45.6, 29.3, 25.0, 24.3. ν_{max} 2929, 2821, 1485, 748 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{18}H_{20}N$+ $[M+H]^+$ 250.1590, found 250.1585. $[\alpha]_D^{23}$ = -0.0325 (c = 83.8, $CHCl_3$).



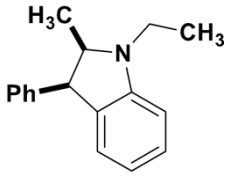
(2-(azepan-1-yl)phenyl)(phenyl)methanone (**3**) was synthesized according to general procedure A using 2-fluorobenzophenone (1.70 mL, 9.90 mmol), cycloheptyl amine (1.12 mL, 11.4 mmol), K_2CO_3 (3.00 g, 24.8 mmol) and DMF (8.00 mL). The crude product was purified by flash column chromatography (4:96 EtOAc:hexanes) affording **3** as a yellow oil (1.25 g, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.61 – 7.47 (m, 1H), 7.46 – 7.39 (m, 2H), 7.36 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 1H), 7.29 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.04 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.84 (td, *J* = 7.4, 1.0 Hz, 1H), 3.70 – 2.39 (m, 4H), 1.63 – 1.53 (m, 4H), 1.46 – 1.38 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 151.9, 138.0, 132.5, 131.2, 130.7, 130.0, 128.5, 128.1, 118.0, 117.4, 53.6, 28.5, 27.7; IR (neat): ν_{max} 2923, 2851, 1651, 1592, 704 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{19}H_{22}NO$+ $[M+H]^+$ 280.1696, found 280.1693.



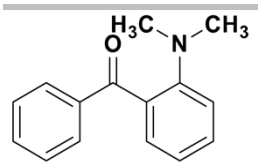
1-phenyl-7,8,9,10,10a,11-hexahydro-6*H*-azepino[1,2-*a*]indole (**2d**) was synthesized by general procedure G using hydrazone **1d** (25 mg, 0.084 mol), MnO_2 (58 mg, 0.67 mmol), and Rh_2(*R*-PTAD)$_4$ (1 mg, 0.0006mmol) in CH_2Cl_2. The crude product was purified by flash column chromatography (2:98, EtOAc:hexanes) affording **2d** as a yellow oil (16 mg, 97%, 100:0 er, >95:5 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 2H), 7.23 – 7.17 (m, 1H), 7.14 – 7.07 (m, 3H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 7.9 Hz, 1H), 4.49 (d, *J* = 9.4 Hz, 1H), 3.93 (td, *J* = 9.7, 2.3 Hz, 1H), 3.51 – 3.41 (m, 1H), 3.22 – 3.10 (m, 1H), 1.95 – 1.84 (m, 1H), 1.84 – 1.73 (m, 1H), 1.74 – 1.65 (m, 1H), 1.66 – 1.59 (m, 1H), 1.50 – 1.41 (m, 1H), 1.43 – 1.34 (m, 1H), 1.35 – 1.23 (m, 1H), 1.21 – 1.08 (m, 1H);^{13}C NMR (151 MHz, $CDCl_3$) δ 153.1, 140.9, 132.5, 129.6, 128.0, 127.9, 126.5, 124.9, 117.1, 106.5, 69.4, 52.2, 48.7, 31.6, 28.2, 26.9, 26.7; v_{max} 3049, 2921, 1493, 769 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{19}H_{22}N^+$ 264.1747, found 264.1744. $[\alpha]_D^{23}$ = -0.007 (c = 72.9, $CHCl_3$).



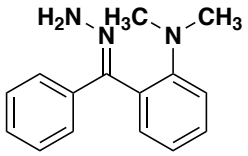
(2-(diethylamino)phenyl)(phenyl)methanone (**4**) was synthesized according to general procedure A using 2-fluorobenzophenone (1.70 mL, 9.97 mmol), diethylamine (1.9 mL, 11 mmol), K_2CO_3 (4.46 g, 32.3 mmol) and DMF (10 mL). The crude product was purified by flash column chromatography (50:50 toluene:hexanes) affording **4** as a yellow oil (626 mg, 27%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.54 – 7.46 (t, *J* = 7.5, 4.8, 1H), 7.44 – 7.32 (m, 4H), 7.11 – 6.97 (m, 2H), 2.95 (q, *J* = 7.1 Hz, 4H), 0.81 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 149.8, 137.8, 134.3, 132.5, 130.7, 129.7, 129.7, 127.9, 121.3, 120.5, 46.7, 11.7; IR (neat): v_{max} 2971, 2930, 1655, 1484, 1314, cm^{-1}; AMM (ESI) *m/z* calcd for $C_{17}H_{20}NO$+ $[M+H]^+$254.1539, found 254.1537.



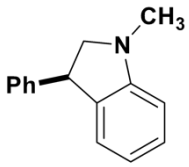
1-ethyl-2-methyl-3-phenylindoline (**2f**) was synthesized according to general procedure g using hydrazone **1f** (24 mg, 0.90 mmol), MnO_2 (63 mg, 0.72 mmol), and Rh_2(*R*-PTAD)$_4$ (1 mg, 0.0006 mmol) in CH_2Cl_2. The crude product was purified by flash column chromatography (4:96, EtOAc:hexanes) affording indoline **2f** as a yellow oil (18 mg, 86%, 100:0 er, >95:5 dr). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 – 7.22 (m, 2H), 7.21 – 7.16 (m, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 4.33 (d, *J* = 8.8 Hz, 1H), 4.08 – 3.84 (m, 1H), 3.49 – 3.32 (m, 1H), 3.20 – 3.04 (m, 1H), 1.11 (td, *J* = 7.2, 1.1 Hz, 3H), 0.84 (d, *J* = 6.6, 1.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.0, 140.5, 133.1, 129.3, 128.0, 127.9, 126.5, 125.2, 117.5, 106.9, 61.5, 51.6, 38.7, 14.5, 10.5.; v_{max} 3025, 2868, 1483, 2929, 1605 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{17}H_{20}N$+ $[M+H]^+$ 238.1590, found 238.1586. $[\alpha]_D^{23}$ = 0.002 (c = 86.02, $CHCl_3$).



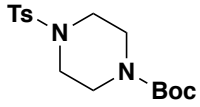
(2-(dimethylamino)phenyl)(phenyl)methanone (**5**) was isolated as a byproduct from general procedure A using 2-fluorobenzophenone (1.70 mL, 9.97 mmol), 4-methyl cyclohexylamine (1.42 mL, 10.7 mmol), K_2CO_3 (1.66 g, 12.0 mmol) and DMF (8.0 mL). The crude product was purified by flash column chromatography (3.5:96.5, EtOAc:hexanes) affording ketone **5** as a yellow oil (700 mg, 30%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.60 – 7.50 (m, 1H), 7.48 – 7.36 (m, 3H), 7.32 (s, 1H), 7.03 – 6.98 (m, 1H), 6.94 – 6.86 (m, 1H), 2.70 (s, 6H). Proton NMR data of the crude material was consistent with the reported literature values.[2]



(***E***)**-2-(hydrazineylidene(phenyl)methyl)-*N*,*N*-dimethylaniline** (**1e**) was synthesized according to general procedure D using ketone **5** (188 mg, 0.834 mmol), hydrazine (0.262 mL, 8.58 mmol), acetic acid (0.091 mL, 1.55 mmol), and anhydrous ethanol (2.8 mL). The crude product was purified by flash column chromatography (66:34, EtOAc:hexanes) affording hydrazone **1c** as a white solid (269 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.34 (ddd, J = 8.3, 7.2, 1.7 Hz, 1H), 7.32 – 7.25 (m, 3H), 7.06 – 7.00 (m, 2H), 6.98 – 6.91 (m, 1H), 5.85 (s, 2H), 2.75 (s, 6H).

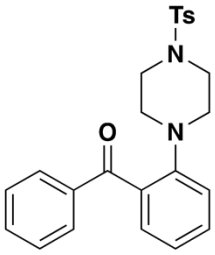


1-methyl-3-phenylindoline (**2e**) was synthesized by general procedure G using hydrazone **1e** (25 mg, 0.11 mol), MnO_2 (75 mg, 0.86 mmol), and Rh_2(*R*-PTAD)$_4$ (1 mg, 0.0006 mmol) in CH_2Cl_2 (4.0 mL) over 4 hours. The crude product was purified by flash column chromatography (5:95, EtOAc:hexanes) affording indoline **2e** as a brown oil (18 mg, 99%, 82:18 er). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 4H), 7.28 – 7.21 (m, 1H), 7.18 – 7.12 (m, 1H), 6.93 – 6.87 (m, 1H), 6.74 – 6.66 (m, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 4.41 (t, *J* = 8.8 Hz, 1H), 3.74 (td, *J* = 8.8, 0.7 Hz, 1H), 3.22 (td, *J* = 8.8, 0.8 Hz, 1H), 2.81 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.4, 143.1, 133.2, 128.5, 128.2, 127.86, 126.7, 124.6, 118.2, 107.5, 65.1, 47.4, 36.2; v_{max} 2805, 1724, 1606, 1490, 747 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{15}H_{15}N$+ $[M+H]^+$ 210.1283, found 210.1271. $[\alpha]_D^{23}$ = -0.136(c = 88.3, $CHCl_3$).

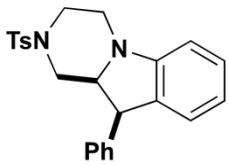


***tert*-butyl 4-tosylpiperazine-1-carboxylate** (**6**). To a solution of *N*-boc-piperazine (3.0g, 16 mmol) in dry CH_2Cl_2 (80 mL) was added triethylamine (6.6 g, 55 mmol) followed by tosyl chloride (2.2 g, 35 mmol). The mixture was cooled to room temperature then diluted in CH_2Cl_2 (50 mL). The reaction mixture was washed with 1 M HCl (3 x 25 mL) and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The solid was purified by flash chromatography (20:80 EtOAc/hexanes) to yield the product as white solid (0.790

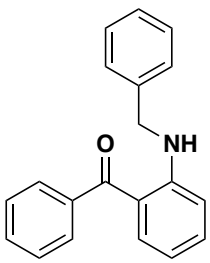
g, 14%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 3.52 – 3.45 (m, 4H), 2.96 – 2.89 (m, 4H), 2.42 (s, 3H), 1.39 (s, 9H). Proton NMR data was consistent with the reported literature values.[3]



phenyl(2-(4-tosylpiperazin-1-yl)phenyl)methanone (**7**)**.** Piperazine (**6**) (822 mg, 2.31 mmol) was stirred with 4 M HCl in dioxane (10.0 mL, 40 mmol) for 12 hours and the crude product was isolated by concentration *in vacuo*. The crude deprotected material was used to synthesize ketone **7** according to general procedure A using 2-fluorobenzophenone (0.26 mL, 2.3 mmol), piperazine **6** (650 mg, 2.7 mmol), K_2CO_3 (1.10 g, 30 mmol) and CH_3CN (10 mL). The crude product was purified by flash column chromatography (30:70 EtOAc:hexanes) affording the desired ketone as a yellow crystalline solid (139 mg, 14% over two steps). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.52 – 7.38 (m, 4H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.22 – 7.08 (m, 4H), 7.04 (d, *J* = 8.1 Hz, 1H), 2.94 (t, *J* = 4.9 Hz, 4H), 2.52 (s, 7H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.3, 150.4, 143.5, 137.5, 133.6, 132.2, 132.0, 131.9, 130.2, 129.5, 129.3, 127.8, 127.6, 123.4, 119.3, 51.3, 45.6, 21.6; IR (neat): 2955, 2916, 1648, 1449, 1165, cm^{-1}; AMM (ESI) *m/z* calcd for $C_{17}H_{20}NO+$ $[M+H]^+$ 421.1586, found 421.1576; m.p. 171.1-172.9 °C.

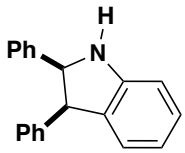


10-phenyl-2-tosyl-1,2,3,4,10,10a-hexahydropyrazino[1,2-*a*]indole (**2b**) was synthesized by general procedure G using hydrazone **1b** (2 mg, 0.05 mmol), MnO_2 (32 mg, 0.37 mmol), and Rh_2(*R*-PTAD)$_4$ (1 mg, 0.0006 mmol) in CH_2Cl_2. The crude product was purified by flash column chromatography (60:40, CH_2Cl_2:hexanes) affording indoline **2b** as a white solid (13.1. mg, 68%, 100:0 er, >95:5 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.19 (m, 5H), 7.16-7.12 (m, 1H), 7.06 – 6.97 (m, 3H), 6.75-6.71 (m,1H), 6.52 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 8.4 Hz, 1H), 3.75 – 3.66 (m, 2H), 3.63-3.59 (m, 1H), 3.43-3.39 (m, 1H), 3.07-3.01 (m, 1H), 2.38 (s, 3H), 2.37-2.31 (m, 1H), 1.87 (t, *J* = 11.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.5, 143.6, 137.8, 133.0, 131.9, 129.6, 128.7, 128.4, 128.2, 127.4, 127.1, 125.6, 119.1, 107.0, 65.4, 49.3, 47.4, 44.4, 44.0, 21.5; ; v_{max} 2920, 1450, 1482, 1166 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{24}H_{25}N_2O_2S+$ $[M+H]^+$ 405.1631, found 405.1627. $[\alpha]_D^{23}$ = 0.076 (c = 42, $CHCl_3$); m.p. 180.9-182.1 °C.

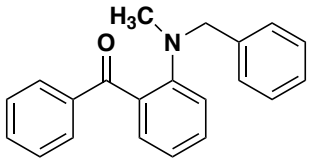


(2-(benzylamino)phenyl)(phenyl)methanone (**8**) To a flame-dried round-bottom flask under Ar was added dry CH_2Cl_2 (35.5 mL, 0.1M) followed by 2-aminobenzophenone (700 mg, 3.54 mmol), benzaldehyde (0.43 mL, 4.3 mmol) and two drops of acetic acid. The mixture

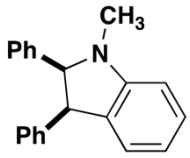
stirred at room temperature for 15 min. To the flask was added $Na(AcO)_3BH$ (1.5 g, 7.1 mmol) by quickly removing and replacing the rubber septa. The reaction was stirred for 5 min at which point full conversion was observed by TLC. The reaction was concentrated by rotary evaporation and isolated by silica column chromatography (8:92 EtOAc:hexanes)to yield **8** as a yellow oil (785 mg, 77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.04 (t, *J* = 5.5 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.56 – 7.51 (m, 2H), 7.50 – 7.44 (m, 2H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.57 (t, *J* = 7.5 Hz, 1H), 4.53 (d, *J* = 5.6 Hz, 2H).Proton NMR data was consistent with reported literature values.[4]



(2*S*,3*R*)-2,3-diphenylindoline (**2g**) was synthesized by general procedure H using hydrazone **1g** (25 mg, 0.083 mmol), MnO_2 (32 mg, 0.66 mmol), and Rh_2(*R*-PTAD)$_4$ (1 mg, 0.0006 mmol) in CH_3CN. The crude product was purified by flash column chromatography (4:95.5:0.5, $EtOAc_2$:hexanes:Et_3N) affording indoline **2g** as a yellow amorphous solid (21.6. mg, 97%, >99.05:0.5 er, >95:5 dr). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.17 (t, *J* = 7.6 Hz, 1H), 7.07 – 6.95 (m, 9H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.75 – 6.69 (m, 2H), 5.24 (d, *J* = 9.1 Hz, 1H), 4.73 (d, *J* = 9.0 Hz, 1H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.7, 140.0, 139.3, 131.2, 129.3, 128.1, 127.6, 127.5, 127.2, 126.9, 126.2, 125.8, 119.3, 109.1, 68.9, 54.1; AMM (ESI) *m/z* calcd for $C_{20}H_{18}N^+$ $[M+H]^+$ 272.1434, found 272.1431. $[\alpha]_D^{23}$ = -0.039 (c = 15.3, $CHCl_3$).



(2-(benzyl(methyl)amino)phenyl)(phenyl)methanone (**9**) was synthesized according to general procedure A using 2-fluorobenzophenone (0.35 mL, 2.0 mmol), *N*-benzylmethylamine (260 mg, 1.74 mmol), K_2CO_3 (829 mg, 5.99 mmol) and CH_3CN (10 mL). The crude product was purified by flash column chromatography (5:95 EtOAc:hexanes) affording **9** as a yellow oil (368.1 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 2H), 7.68 – 7.55 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 3H), 7.44 – 7.36 (m, 1H), 7.25 – 7.16 (m, 3H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.00 – 6.84 (m, 2H), 4.16 (s, 2H), 2.58 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.6, 151.5, 137.9, 137.8, 132.7, 131.5, 131.3, 130.1, 129.8, 128.3, 128.2, 127.8, 126.9, 120.6, 118.6, 59.9, 41.1 AMM (ESI) *m/z* calcd for $C_{17}H_{20}NO^+$ $[M+H]^+$302.1539, found 302.1540.

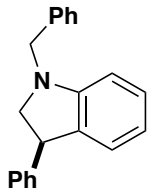


1-methyl-2,3-diphenylindoline (**7a**) was synthesized by general procedure G using hydrazone **5a** (25 mg, 0.08 mmol), MnO_2 (55 mg, 0.63 mmol), and $Rh_2(OAc)_4$ (1 mg, 0.002 mmol) in CH_2Cl_2. The crude product was purified by flash column chromatography (20:80 CH_2Cl_2:hexanes) affording indoline **7a** as a white amorphous solid (17 mg, 76%, >95:5 dr). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.21 (td, *J* = 7.7, 1.3 Hz, 1H), 7.10 – 7.01 (m, 5H), 7.01 – 6.91 (m, 4H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.74 (td, *J* = 7.4, 1.0 Hz, 1H), 6.71 – 6.64 (m, 2H), 4.73 (d, *J* = 8.9 Hz, 1H), 4.63 (d, *J* = 8.9 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.0, 140.0, 137.7, 132.2, 129.3,

128.3, 128.1, 127.6, 127.4, 126.9, 126.0, 125.4, 118.9, 107.9, 76.6, 53.4, 34.4; IR 3035, 2799, 1599, 1481, 700; AMM (ESI) *m/z* calcd for $C_{21}H_{20}N^{+}[M+H]^{+}$ 286.1590, found 286.1586.

1-methyl-2,3-diphenylindoline (**7a)** was synthesized by general procedure G using hydrazone **5a** (25 mg, 0.079 mmol), MnO_2 (55 mg, 0.63 mmol), and $Rh_2(Mes)_4$ (1 mg, 0.00094 mmol) in CH_2Cl_2. The crude product was purified by flash column chromatography (20:80 CH_3Cl_2/Hexanes) affording indoline **7a** as a white amorphous solid (12.5 mg, 56% >95:5dr). Proton NMR data was consistent with characterization described above.

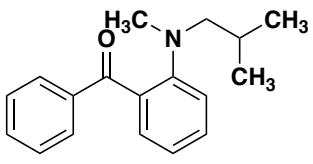
1-methyl-2,3-diphenylindoline (**7a)** was synthesized by general procedure G using hydrazone **5a** (25 mg, 0.079 mmol), MnO_2 (55 mg, 0.63 mmol), and Rh_2(*R*-PTAD)$_4$ (1 mg, 0.00079 mmol) in CH_2Cl_2. The crude product was purified by flash column chromatography (20:80 CH_3Cl_2/Hexanes) affording indoline **7a** as a white amorphous solid (8.9 mg, 39% >95:5 dr). Proton NMR data was consistent with characterization described above.



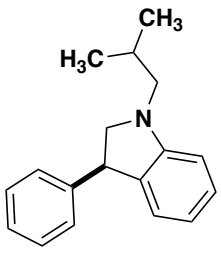
1-benzyl-3-phenylindoline (6a) was synthesized by general procedure G using hydrazone **5a** (25 mg, 0.079 mmol), MnO_2 (55 mg, 0.63 mmol), and $Rh_2(OAc)_4$ (1 mg, 0.002 mmol) in CH_2Cl_2. The crude product was purified by flash column chromatography (20:80 CH_2Cl_2:hexanes) affording indoline **6a** as a yellow oil (1 mg, 4%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.27 (m, 10H), 7.14 (t, *J* = 7.5, 1.0 Hz, 1H), 6.92 (d, *J* = 7.4, 1.3 Hz, 1H), 6.71 (d, *J* = 7.4, 1.0 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 4.51 – 4.39 (m, 2H), 4.21 (d, *J* = 14.7 Hz, 1H), 3.76 (t, *J* = 9.1 Hz, 1H), 3.26 (t, *J* = 8.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5, 143.4, 138.2, 133.1, 128.51, 128.50, 128.2, 128.0, 127.8, 127.2, 126.7, 124.9, 118.1, 107.4, 62.6, 53.6, 47.3; IR 3033, 2819, 1598, 1234, 738: $v_{max:}$ 1598 cm^1; AMM (ESI) *m/z* calcd for $C_{21}H_{20}N^{+}[M+H]^{+}$ 286.1590, found 286.1586.

1-benzyl-3-phenylindoline (6a) was synthesized by general procedure G using hydrazone **5a** (25 mg, 0.079 mmol), MnO_2 (40 mg, 0.48 mmol), and $Rh_2(Mes)_4$ (1 mg , 0.0009 mmol) in CH_2Cl_2. The crude product was purified by flash column chromatography affording indoline **6a** as a yellow oil (4 mg, 19 %). Proton NMR data was consistent with characterization described above.

1-benzyl-3-phenylindoline (**6a)** (9 mg, 39%) was synthesized by general procedure G using hydrazone **5a** (25 mg, 0.079 mmol), MnO_2 (55 mg, 0.63 mmol), and Rh_2(R-PTAD)$_4$ (1 mg , 0.0008 mmol) in CH_2Cl_2. The crude product was purified by flash column chromatography affording indoline **6a** as a yellow oil. Proton NMR data was consistent with characterization described above.

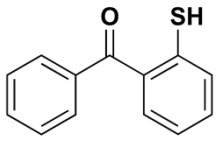


(2-(isobutyl(methyl)amino)phenyl)(phenyl)methanone (**10**) was synthesized according to general procedure A using 2-fluorobenzophenone (1.20 mL, 7.01 mmol), *N*-methylisobutylamine (1.00 mL, 8.37 mmol), K_2CO_3 (2.30g, 16.6 mmol) and DMF (8.00 mL). The crude product was purified by flash column chromatography (10:90, DCM:hexanes) affording ketone **10** as a yellow oil (828 mg, 44%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H), 7.54 – 7.48 (m, 1H), 7.46 – 7.34 (m, 3H), 7.29 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.92 (td, *J* = 7.4, 0.9 Hz, 1H), 2.73 (d, *J* = 7.3 Hz, 2H), 2.64 (s, 3H), 1.87 – 1.71 (m, 1H), 0.66 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.6, 152.0, 138.0, 132.6, 131.1, 130.7, 130.2, 129.8, 128.1, 119.4, 118.0, 63.1, 41.9, 26.7, 20.2.; IR 2954, 1655, 1594, 1448, 698: v_{max}1594 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{18}H_{22}NO^+$ 268.1696, found 268.1696.

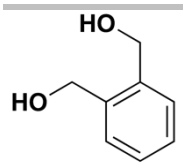


1-isobutyl-3-phenylindoline (**6b)** was synthesized by general procedure G using hydrazone **5b** (15 mg, 0.055 mmol), MnO_2 (38 mg, 0.44 mmol), and $Rh_2(Mes)_4$ (1 mg , 0.0009 mmol) in CH_2Cl_2. The crude product was purified by flash column chromatography (20:80 CH_2Cl_2:hexanes) affording indoline **6b** as a yellow oil (10 mg, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.15 (m, 5H), 7.14 – 7.05 (m, 1H), 6.85 (dt, *J* = 7.3, 1.3 Hz, 1H), 6.61 (td, *J* = 7.4, 1.0 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 4.41 (t, *J* = 8.9 Hz, 1H), 3.81 (t, *J* = 9.2 Hz, 1H), 3.28 (t, *J* = 8.7 Hz, 1H), 2.95 (dd, *J* = 13.2, 7.6 Hz, 1H), 2.82 (dd, *J* = 13.0, 7.1 Hz, 1H), 1.97 – 1.90 (m, 1H), 0.98 (t, *J* = 6.6 Hz, 6H). Regioisomers of this compound proved difficult to isolate by a myriad of chromatography techniques. As such we have included a proton NMR of a mixture of 95:5, 6b:7b.

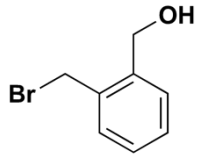
BENZODIHYDROTHIOPHENES



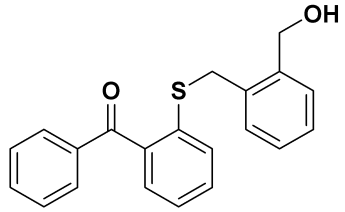
(2-mercaptophenyl)(phenyl)methanone (**11**). Thiosalicylic acid (2.22 g, 14.2 mmol, 1.0 equiv) and sodium hydride (60% in mineral oil, 1.43 g, 36.9. mmol, 2.6 equiv) were added to a 250-mL oven-dried round-bottom flask under argon. Anhydrous THF (17.2 mL) was added at 0 °C, and the resulting slurry was stirred under reflux for 1 h. The mixture was cooled down to 0 °C and phenyllithium (1.8 M in dibutyl ether, 18.0 mL, 33 mmol, 2.3 equiv) was added by syringe dropwise for 10 min, and the resulting dark mixture was stirred at room temperature for 20 h. Water (60.0 ml) was carefully added, followed by addition of ethyl acetate (150 mL) and 1M aqueous HCl solution (60.0 mL) The mixture was extracted, the layers were separated, and the aqueous layer was extracted with ethyl acetate (2 x 150 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude oil obtained was purified by flash chromatography (5:95 EtOAc:hexanes) to afford the desired product as light yellow crystals (2.19 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.81 (m, 2H), 7.56-7.63 (m, 1H), 7.40-7.51 (m, 4H), 7.35 (dt, *J* = 15.9, 1.5 Hz, 1H), 7.19 (dt, *J* = 7.5, 1.3 Hz, 1H), 4.21 (s, 1H). Proton NMR data of the crude material was consistent with the reported literature values.[5]



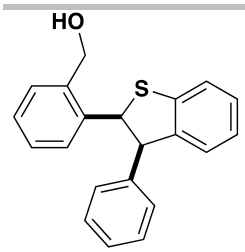
1,2-phenylenedimethanol (**12**) was synthesized by reduction of phthalic acid (1.66 g, 10.0 mmol) with lithium aluminum hydride (1.13 g, 30.0 mmol) in THF (100 mL) at 0 °C. The solution was allowed to warm to room temperature and left stirring for 20 hours. The solution was then cooled to 0 °C and quenched with 0.54 mL H_2O, followed by 0.54 mL NaOH (aqueous 15%), then 1.64 mL H_2O and left stirring for 30 minutes. Na_2SO_4 was added and allowed to stir an additional 30 minutes, when the suspension was filtered. The filter cake was washed with EtOAc (3 x 50 mL) and the crude material (1.16 g, 84%) was taken to the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 4H), 4.78 (s, 4H), 2.79 (s, 2H). Proton NMR data of the crude material was consistent with the reported literature values.[6]



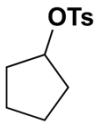
(2-(bromomethyl)phenyl)methanol (**13**) was synthesized by bromination of 1,2-phenylenedimethanol (1.06 g, 7.71 mmol) in toluene (15.4 mL) at 60 °C using HBr (48% wt, 0.97 mL). The reaction was continued to heat for 20 minutes and allowed to cool to room temperature before it was further cooled to 0 °C and quenched with saturated Na_2CO_3 (5mL) and extracted with diethyl ether (3 x 10 mL). The organic phase was dried over Na_2SO_4 and concentrated. The resulting oil was purified by flash column chromatography (20:80, EtOAc:hexanes) to afford a white solid (0.71 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.29 (m, 4H), 4.88 (d, *J* = 5.2 Hz, 2H), 4.67 (s, 2H), 1.79 (br t, *J* = 5.6 Hz, 1H). Proton NMR data of purified compound was consistent with the reported literature values.[7]



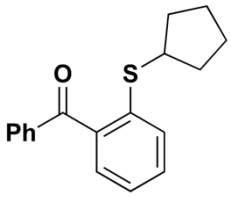
(2-((2-(hydroxymethyl)benzyl)thio)phenyl)(phenyl)methanone (**14**) was synthesized according to general procedure C using **11** (202 mg, 0.942 mmol), K_2CO_3 (392 mg, 2.83 mmol) and **13** (249 mg, 1.23 mmol) in CH_3CN (9.5 mL). The crude material was purified by flash column chromatography (10:90, EtOAc:hexanes) affording an amorphous yellow solid (276 mg, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.60 – 7.53 (m, 1H), 7.47 – 7.37 (m, 4H), 7.37 – 7.28 (m, 3H), 7.22 (td, *J* = 7.5, 1.5 Hz, 1H), 7.14 (td, *J* = 7.5, 1.4 Hz, 1H), 7.10 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.65 (s, 2H), 4.14 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) 196.9, 141.7, 139.2, 137.2, 134.5, 134.2, 133.3, 132.6, 130.6, 130.4, 130.1, 129.1, 128.7, 128.5, 128.0, 127.9, 126.8, 62.9, 37.6. AMM (ESI) m/z calcd for $C_{21}H_{18}O_2SNa^+$ $[M+Na]^+$ 357.0920, found 357.0936; m.p. 88.2-91.8 °C.



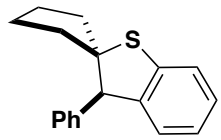
(2-((2*S*, 3*R*)-3-phenyl-2,3-dihydrobenzo[*b*]thiophen-2-yl)phenyl)methanol (**4c**) was synthesized according to general procedure H using hydrazone **3c** (24 mg, 0.06 mmol), MnO_2 (52 mg, 0.60 mmol) and Rh_2(*R*-PTAD)$_4$ (1 mg, 0.0006 mmol), and CH_3CN. The crude product was purified by flash column chromatography (33:67, EtOAc:hexanes) affording **4c** as an amorphous white solid (16.1 mg, 85%, 97:3 er, >95:5 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.8 Hz, 1H), 7.21 – 7.15 (m, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.05 – 7.00 (m, 2H), 6.98 (q, *J* = 8.0 Hz, 3H), 6.92 – 6.88 (m, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.4 Hz, 2H), 5.67 (d, *J* = 7.9 Hz, 1H), 4.92 (d, *J* = 7.9 Hz, 1H), 4.46 (d, *J* = 12.5 Hz, 1H), 4.41 (d, *J* = 12.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.2, 141.8, 138.2, 138.0, 136.3, 129.7, 129.5, 128.3, 128.0, 127.8, 127.7, 127.6, 127.0, 126.1, 124.9, 122.0, 63.4, 59.4, 54.3; AMM (ESI) m/z calcd for $C_{21}H_{18}OSNa^+$ $[M+Na]^+$ 341.0971, found 341.0992; $[\alpha]_D^{22}$ = -42.0 (c = 0.02, $CHCl_3$).



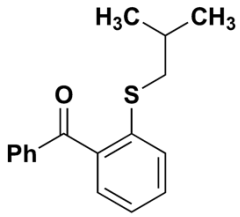
Cyclopentyl 4-methylbenzenesulfonate (**15**) was synthesized from cyclopentanol (0.90 mL, 9.9 mmol) in CH_2Cl_2 cooled to 0 °C (19.8 mL). To the solution of cyclopentanol was added p-toluenesulfonylchloride (2.26 g, 11.8 mmol), triethylamine (1.4 ml, 9.9 mmol) and 4-dimethylaminopyridine (364 mg, 4.91 mmol). The solution was left stirring overnight, then diluted with H_2O (20 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash column chromatography (10:90 EtOAc:hexanes) affording a clear oil (1.00 g, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 5.07 – 4.91 (m, 1H), 2.47 (s, 3H), 1.91 – 1.67 (m, 6H), 1.59 – 1.49 (m, 2H). Proton NMR data of purified compound was consistent with the reported literature values.[8]



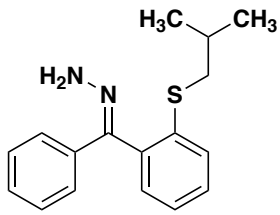
(2-(cyclopentylthio)phenyl)(phenyl)methanone (**16**) was synthesized according to general procedure B using **11** (255 mg, 1.19 mmol), K_2CO_3 (493 mg, 3.57 mmol) and cyclopentyl tosylate (588 mg, 2.60 mmol) in CH_3CN (11.9 mL). The mixture was heated to 60 °C for 16 hours. The crude product was purified by flash column chromatography (10:90 EtOAc:hexanes) affording **16** as a yellow oil (253 mg, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.59 – 7.55 (m, 1H), 7.53 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.33 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.27 – 7.24 (m, 1H), 3.55 (d, *J* = 6.1 Hz, 1H), 2.07 – 1.90 (m, 2H), 1.73 – 1.62 (m, 2H), 1.56 – 1.49 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.0, 140.2, 137.5, 136.9, 133.1, 130.8, 130.4, 130.1, 128.9, 128.4, 125.3, 46.3, 33.4, 24.7; AMM (ESI) m/z calcd for $C_{18}H_{19}OS^+$ $[M+H]^+$ 283.1151, found 283.1146.



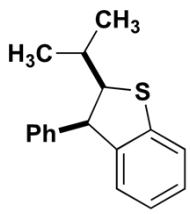
(*R*)-3-phenyl-3*H*-spiro[benzo[*b*]thiophene-2,1'-cyclopentane] (**4d**) was synthesized according to general procedure G using hydrazone **3d** (36 mg, 0.12 mmol), MnO_2 (83 mg, 0.90 mmol), Rh_2(*R*-PTAD)$_4$ (2 mg, 0.0012 mmol), and CH_2Cl_2. The crude product was purified by flash column chromatography (0:100, EtOAc:hexanes) affording **4d** as a white solid (23 mg, 84%, 89:11 er). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.29 – 7.25 (m, 1H), 7.25 – 7.20 (m, 3H), 7.20 – 7.10 (m, 1H), 7.05 – 6.92 (m, 2H), 4.43 (s, 1H), 2.29 – 2.08 (m, 1H), 2.01 – 1.89 (m, 1H), 1.88 – 1.78 (m, 1H), 1.80 – 1.65 (m, 2H), 1.66 – 1.57 (m, 2H), 1.53 – 1.44 (m, 1H);^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 141.4, 139.5, 129.6, 128.2, 127.6, 127.1, 125.8, 124.3, 122.3, 72.6, 62.3, 40.7, 35.2, 23.2, 22.9. AMM (ESI) m/z calcd for $C_{18}H_{18}S$ $[M]^+$ 266.1129, found 266.1129; m.p. 64.1-65.8 °C; $[\alpha]_D^{26}$ = -6.3 (c = 0.03, $CHCl_3$).



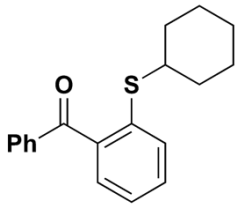
(2-(isobutylthio)phenyl)(phenyl)methanone (**17**) was synthesized according to the general procedure B using thiol **11** (255 mg, 1.19 mmol), K_2CO_3 (493 mg, 3.56 mmol) and 1-bromo-2-methylbutane (0.30 mL, 2.7 mmol) in CH_3CN (11.9 mL). The crude material was purified by flash column chromatography (10:90 EtOAc:hexanes) affording **17** as yellow oil (307 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.51 – 7.39 (m, 4H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.20 (m, 1H), 2.72 (d, *J* = 6.9Hz, 2H), 1.83 – 1.72 (m, 1H), 0.93 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.9, 140.1, 137.4, 136.8, 133.1, 130.5, 130.1, 129.9, 128.9, 128.4, 125.3, 43.5, 28.1, 22.0; AMM (ESI) m/z calcd for $C_{17}H_{19}OS^+$ $[M+H]^+$ 271.1151, found 271.1144.



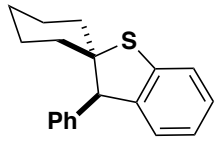
(*E*)-((2-(isobutylthio)phenyl)(phenyl)methylene)hydrazine (3e) was synthesized according to general procedure using ketone **17** (226 mg, 0.835 mmol), N_2H_4 (0.26 mL, 8.4 mmol), AcOH (0.10 mL, 1.7 mmol) and anhydrous EtOH (2.7 mL). Following purification by flash column chromatography (10:90, EtOAc:hexanes), hydrazone **3e** was obtained as a light-yellow oil (200 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 3H), 7.43 (td, *J* = 7.6, 1.5 Hz, 1H), 7.37 – 7.29 (m, 4H), 7.16 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.42 (s, 2H), 2.75 (d, *J* = 6.9 Hz, 2H), 1.88 – 1.74 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H).



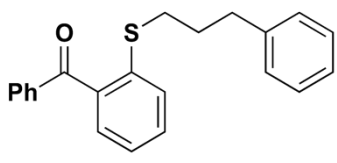
(2*R*,3*R*)-2-isopropyl-3-phenyl-2,3-dihydrobenzo[*b*]thiophene (**4e**) was synthesized according to general procedure G using hydrazone **3e** (22 mg 0.080 mmol) MnO_2 (56 mg 0.65 mmol), Rh_2(*R*-PTAD)$_4$ (1 mg, 0.0006 mmol), and CH_3CN. The crude product was purified by flash column chromatography (0:100 EtOAc:hexanes) affording **4e** as a white solid (13 mg, 63%, 99:1 er, >95:5 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.28 – 7.25 (m, 2H), 7.25 – 7.19 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 4.48 (d, *J* = 7.4 Hz, 1H), 4.13 (dd, *J* = 10.0, 7.4 Hz, 1H), 1.74 – 1.63 (m, 1H), 0.96 (t, *J* = 7.2 Hz, 6H);^{13}C NMR (151 MHz, $CDCl_3$) δ 143.4, 139.0, 137.9, 127.0, 126.3, 125.8, 125.2, 123.6, 122.6, 120.6, 62.3, 54.0, 27.1, 20.8, 19.6; AMM (ESI) m/z calcd for $C_{17}H_{18}S^+$ $[M]^+$ 254.1129, found 254.1138; $[\alpha]_D^{24}$ = -118.8 (c = 0.02, $CHCl_3$); m.p. 146.1-147.2 °C.



(2-(cyclohexylthio)phenyl)(phenyl)methanone (**18**) was synthesized according to general procedure B using **11**(250 mg, 1.17 mmol), K_2CO_3 (485 mg, 3.51 mmol) and bromocyclohexane (0.22 mL, 1.8 mmol) in CH_3CN (11.7 mL). The crude product was purified by flash column chromatography (10:90, EtOAc:hexanes) affording **18** as a yellow oil (268 mg, 77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.59 – 7.52 (m, 2H), 7.46 – 7.39 (m, 3H), 7.35 – 7.28 (m, 2H), 3.11 – 3.00 (m, 1H), 1.91 – 1.81 (m, 2H), 1.74 – 1.65 (m, 2H), 1.60 – 1.51 (m, 1H), 1.33 – 1.11 (m, 5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.2, 142.5, 137.5, 133.8, 133.2, 132.9, 130.0, 130.0, 128.4, 128.3, 126.4, 47.4, 33.1, 25.9, 25.7; AMM (ESI) m/z calcd for $C_{19}H_{21}OS^+$ $[M+H]^+$ 297.1308, found 297.1307.

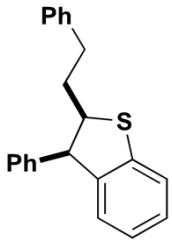


(*R*)-3-phenyl-3*H*-spiro[benzo[*b*]thiophene-2,1'-cyclohexane] (**4f**) was synthesized according to general procedure G using hydrazone **3f** (26 mg 0.08 mmol), MnO_2 (58 mg 0.7 mmol), Rh_2(*R*-PTAD)$_4$ (1 mg, 0.0006 mmol), and CH_2Cl_2. The crude product was purified by flash column chromatography (0:100, EtOAc:hexanes) affording **4f** as a white solid (21 mg, 88%, 99:1 er). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 3H), 7.26 – 7.22 (m, 1H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.00 – 6.94 (m, 2H), 4.29 (s, 1H), 2.17 (d, *J* = 11.3 Hz, 1H), 1.74 – 1.68 (m, 1H), 1.68 – 1.59 (m, 3H), 1.59 – 1.47 (m, 3H), 1.19 – 1.10 (m, 1H), 1.10 – 0.99 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.9, 140.8, 138.3, 130.0, 128.0, 127.4, 127.1, 126.0, 124.0, 122.2, 67.3, 65.7, 38.9, 33.9, 25.4, 24.6, 23.8; AMM (ESI) m/z calcd for $C_{19}H_{20}S^+$ $[M]^+$ 280.1280, found 280.1297. $[\alpha]_D^{24}$ = 40.9 (c = 0.02, $CHCl_3$); m.p. 97.0-100.5 °C.

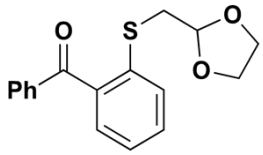


phenyl(2-((3-phenylpropyl)thio)phenyl)methanone (**19**) was synthesized according to general procedure B using **11** (273 mg, 1.27 mmol), K_2CO_3 (531 mg, 3.89 mmol) and 3-phenylpropyl bromide (0.29 mL, 1.9 mmol) in CH_3CN (12.8 mL). The crude product was purified by flash column chromatography (66:37 hexanes:petroleum ether, then 10:90 EtOAc:hexanes) affording **19** as a yellow oil (378 mg, 89%). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.80 – 7.71 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.60 – 7.47 (m, 4H), 7.36 (d, *J* = 4.3 Hz, 2H),

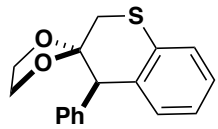
7.25 (t, *J* = 7.5 Hz, 2H), 7.20 – 7.08 (m, 3H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.83 (p, *J* = 7.4 Hz, 2H);^{13}C NMR (151 MHz, $CDCl_3$) δ 196.9, 141.2, 140.1, 137.4, 136.1, 133.1, 130.5, 130.1, 129.9, 129.1, 128.5, 128.4, 128.4, 125.9, 125.4, 34.6, 33.6, 30.3; AMM (ESI) m/z calcd for $C_{22}H_{20}OSNa^+$ $[M+Na]^+$ 355.1127, found 355.1115.



2-phenethyl-3-phenyl-2,3-dihydrobenzo[*b*]thiophene (**4g)** was synthesized according to the general procedure G using hydrazone **3g** (34 mg 0.1 mmol) MnO_2 (70.mg, 0.8 mmol), Rh_2(*R*-PTAD)$_4$ (2 mg, 0.0012 mmol), and CH_3CN. The crude product was purified by flash column chromatography (0:100, EtOAc:hexanes) affording **4g** as a white solid (24 mg, 77%, 75:25 er, 80:20 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 3H), 7.27 – 7.26 (m, 1H), 7.23 – 7.19 (m, 4H), 7.19 – 7.12 (m, 2H), 7.09 – 7.05 (m, 2H), 7.03 – 6.96 (m, 2H), 4.58 (d, *J* = 7.6 Hz, 1H), 4.18 – 4.10 (m, 1H), 2.73 (ddd, *J* = 14.0, 9.0, 5.0 Hz, 1H), 2.58 – 2.50 (m, 1H), 1.78 – 1.69 (m, 1H), 1.64 – 1.55 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 141.2, 141.2, 138.8, 129.4, 128.5, 128.3, 128.3, 127.8, 127.2, 125.9, 125.8, 124.5, 122.5, 57.5, 55.2, 34.7, 33.1; AMM (ESI) m/z calcd for $C_{22}H_{20}S^+$ $[M]^+$ 316.1280, found 316.1290; $[\alpha]_D^{25}$ = 30.9 (c = 0.03, $CHCl_3$); m.p. 94.1-99.6 °C.

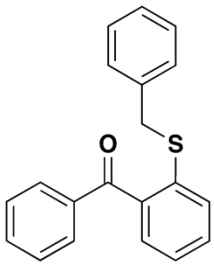


(2-(((1,3-dioxolan-2-yl)methyl)thio)phenyl)(phenyl)methanone (**21**) was synthesized according to general procedure B using **11** (419 mg, 1.96 mmol), Cs_2CO_3 (1.9 g, 5.7 mmol) and 2-bromo-methyl-1,3 dioxalane (0.30 mL, 2.9 mmol) in CH_3CN (19 mL). The crude product was purified by flash column chromatography (20:80, EtOAc:hexanes) affording **21** as a yellow oil (496 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 2H), 7.67 – 7.61 (m, 1H), 7.60 – 7.54 (m, 1H), 7.51 – 7.42 (m, 3H), 7.35 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.32 – 7.25 (m, 1H), 5.12 – 4.98 (m, 1H), 4.05 – 3.91 (m, 2H), 3.91 – 3.78 (m, 2H), 3.10 (d, *J* = 4.1 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.7, 140.5, 137.3, 135.8, 133.1, 130.9, 130.6, 130.1, 129.0, 128.4, 125.9, 102.7, 65.3, 38.6; AMM (ESI) m/z calcd for $C_{17}H_{16}O_3SNa^+$ $[M+Na]^+$ 323.0712, found 323.0732.

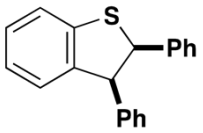


(*R*)-4-phenylspiro[thiochromane-3,2'-[1,3]dioxolane] (**4h**) was synthesized according to general procedure G using hydrazone **3h** (31 mg 0.10 mmol), MnO_2 (69 mg, 0.79 mmol), Rh_2(*R*-PTAD)$_4$ (2 mg, 0.001 mmol), and CH_2Cl_2. The crude product was purified by flash column chromatography (0:100, EtOAc:hexanes) affording **4h** as a white solid (26 mg, 97%, 97:3 er). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.4 Hz, 3H), 7.26 – 7.18 (m, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 4.17 (d, *J* = 1.6 Hz, 1H), 4.11 – 3.91 (m, 4H), 3.11 (d, *J* = 12.5 Hz, 1H), 2.81 (dd, *J* = 12.4, 1.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.6, 135.7,

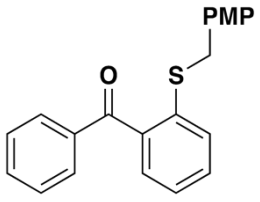
131.9, 131.6, 130.1, 128.0, 127.1, 127.0, 125.4, 124.4, 106.5, 65.4, 65.3, 53.7, 30.2; AMM (ESI) m/z calcd for $C_{17}H_{16}O_2S^+$ $[M]^+$ 284.0866, found 284.0869; m.p. 93.5-97.8 °C; $[\alpha]_D^{25}$ = 277.8 (c = 0.02, $CHCl_3$).



(2-(Benzylthio)phenyl)(phenyl)methanone (**22**)**.** A solution of thiol **11** (0.300 g, 1.40 mmol, 1.0 equiv) in anhydrous THF (2.9 mL) was added to a 50-mL round bottom flask containing a suspension of sodium hydride (60% in mineral oil, 0.056 g, 1.41 mmol, 1.0 equiv) in anhydrous THF (2.9 mL) under Ar. The resulting mixture was stirred for 15 min and benzyl bromide (0.244 g, 1.4 mmol, 1.0 equiv) was added dropwise at 0 °C, and the mixture was stirred for 1 h at room temperature. Saturated aqueous NH_4Cl (25 ml) was added and the mixture was extracted with diethyl ether (2 x 60 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude material was purified by flash chromatography (5:95,EtOAc:hexanes) to afford the desired product as a light yellow solid (0.334 g, 79%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72-7.75 (m, 2H), 7.54-7.58 (m, 1H), 7.39-7.44 (m, 3H), 7.35-7.38 (m, 1H), 7.34 (dd, J = 6.4, 1.3 Hz, 1H), 7.26 (dt, J = 10.5, 6.1, 1.0 Hz, 1H), 7.17-7.23 (m, 5H), 4.04 (s, 2H). Proton NMR data was consistent with the reported literature values.[9]

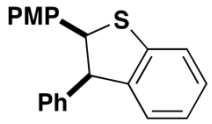


2,3-diphenyl-2,3-dihydrobenzo[b]thiophene (**4a**). was synthesized according to a modified general procedure I using hydrazone **3a** (28 mg 0.090 mmol), MnO_2 (69 mg, 0.68 mmol), Rh_2(R-PTAD)$_4$ (1 mg, 0.0006 mmol), and CH_2Cl_2. The solvent was removed *in vacuo*, and the resulting black solid was redispersed (10:90, EtOAc:hexanes), the suspension was filtered through a pad of silica gel to remove the catalyst and manganese oxide, rinsed with the same solvent mixture, the solvent was removed *in vacuo* to afford the desired product as an off white amorphous solid (25.6 mg, 100% 97:3 er, >95:5 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.11 – 7.02 (m, 7H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.95 – 6.91 (m, 2H), 6.78 – 6.67 (m, 2H), 5.27 (d, *J* = 7.9 Hz, 1H), 4.89 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.3, 141.9, 138.2, 137.8, 129.9, 128.9, 128.2, 127.9, 127.6, 127.5, 127.1, 126.2, 125.1, 122.4, 60.3, 59.8; AMM (ESI) *m/z* calcd for $C_{20}H_{16}S$ $[M+H]^+$ 289.1006, found 289.1047.



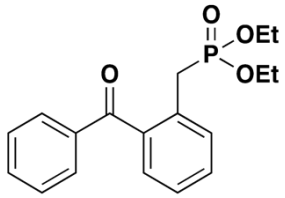
(2-((4-methoxybenzyl)thio)phenyl)(phenyl)methanone (**23**)**.** A solution of **11** (0.500 g, 2.3 mmol, 1.0 equiv) in anhydrous THF (4.80 mL) was added to a 50-mL round bottom flask containing a suspension of sodium hydride (60% in mineral oil, 0.093 g, 2.3 mmol, 1.0 equiv) in anhydrous THF (4.90 mL) under Ar. The resulting mixture was stirred for 15 min and p-methoxybenzyl bromide (0.372 g, 2.33 mmol, 1.0 equiv) was added dropwise at 0 °C, and the mixture was stirred for 1h at room temperature. Saturated aqueous NH_4Cl (25

mL) was added and the mixture extracted with diethyl ether (2 x 60 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude material was purified by flash chromatography (95:5 EtOAc:hexanes) to afford the desired product as a white amorphous solid (0.659 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.69 (m, 2H), 7.62 – 7.50 (m, 1H), 7.48 – 7.31 (m, 5H), 7.31 – 7.22 (m, 1 H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 8.2 Hz, 2H), 4.00 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 158.8, 140.9, 137.40, 135.5, 133.0, 131.4, 130.4, 130.1, 128.9, 128.9, 128.4, 126.0, 113.9, 55.2, 39.2; AMM (ESI) *m/z* calcd for $C_{21}H_{19}S^+$ $[M+H]^+$ 335.1061, found 335.1098.



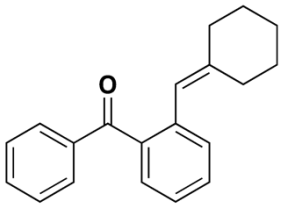
(2*S*,3*R*)-2-(4-methoxyphenyl)-3-phenyl-2,3-dihydrobenzo[*b*]thiophene (**4b**) was synthesized according to a modified general procedure I using hydrazone **3b** (22 mg, 0.065 mmol), MnO_2 (54 mg 0.94 mmol) and Rh_2(*R*-PTAD)$_4$ (1 mg, 0.0006 mmol), and CH_2Cl_2. The solvent was removed *in vacuo*, and the resulting black solid was redispersed (10:90, EtOAc:hexanes), the suspension was filtered through a pad of silica gel to remove the catalyst and manganese oxide, rinsed with the same solvent mixture, and the solvent was removed *in vacuo* to afford the desired product as a white amorphous solid (18.9 mg, 77 %, 97:3 er, >95:5dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.7 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.14 – 7.01 (m, 4H), 7.02 – 6.96 (m, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.77 – 6.72 (m, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 5.23 (d, *J* = 7.8 Hz, 1H), 4.82 (d, *J* = 7.8 Hz, 1H), 3.70 (s, 3H);^{13}C NMR (151 MHz, $CDCl_3$) δ 157.8, 141.3, 140.7, 137.1, 128.7, 128.6, 126.9, 126.7, 125.8, 125.0, 123.8, 121.1, 112.0, 59.0, 58.1, 54.1, 28.7; AMM (ESI) *m/z* calcd for $C_{20}H_{16}S$ $[M+H]^+$ 289.1006, found 289.1047.

INDANES

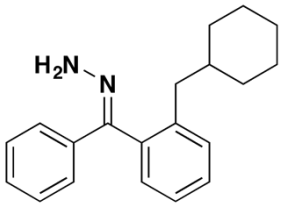


Diethyl 2-benzoylphenylmethylphosphonate (30). Following a modified literature procedure,[10] to a solution of 2-methylbenzophenone (2.0 mL, 11 mmol) and *N*-bromosuccinimide (2.2 g, 12 mmol) in CCl_4 (100 mL) under argon was added 2,2′-azobis(2-methylpropionitrile) (AIBN, 0.091 g, 0.55 mmol). The reaction mixture was stirred at reflux for 3 h and then more AIBN (0.091 g, 0.55 mmol) was added. The reaction mixture was refluxed for another 2 h and then allowed to cool to room temperature. The solution was added to H_2O (200 mL), extracted with CH_2Cl_2 (2 x 50 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford the desired crude bromo-compound as a red oil. The crude material was dissolved in triethyl phosphite (4.2 mL, 24 mmol) and the reaction mixture was stirred at reflux for 18 h and then allowed to cool to room temperature. The solution was added to H_2O (20 mL), extracted with CH_2Cl_2 (2 x 20 mL), dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by flash column chromatography (60:40, EtOAc:hexanes) to afford the desired phosphonate ester **30** as a yellow oil (1.05 g, 29%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (dd, *J* =

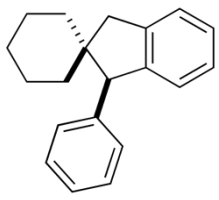
8.3, 1.4 Hz, 2H), 7.58 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.52-7.49 (m, 1H), 7.48-7.44 (m, 3H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.33-7.28 (m, 1H), 3.98-3.84 (m, 4H), 3.53 (d, $^{1}J_{H\text{-}P}$ = 22.3 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 6H). ^{1}H NMR is consistent with published data.[11]



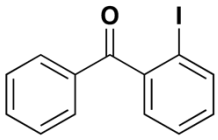
2-(Cyclohexylidenemethyl)benzophenone (31). Following a literature procedure,[12] to a solution of phosphonate **30** (0.522 g, 1.57 mmol) and cyclohexanone (0.16 mL, 1.6 mmol) in anhydrous THF (6.0 mL) was added NaH (60% in mineral oil, 0.075 g, 1.9 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. The reaction mixture was quenched with H_2O (20 mL), extracted with CH_2Cl_2 (2 x 20 mL), dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by flash column chromatography (5:95, EtOAc:hexanes) to afford the desired benzophenone **31** as a clear oil (0.310 g, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45-7.37 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 6.04 (s, 1H), 2.13 (t, *J* = 6.1 Hz, 2H), 1.97 (t, *J* = 6.1 Hz, 2H), 1.50-1.34 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.9, 144.6, 139.2, 138.1, 137.2, 132.9, 130.3, 130.0, 129.9, 128.3, 128.2, 126.1, 120.5, 37.1, 29.7, 28.3, 27.5, 26.6.; AMM (ESI) *m/z* calcd for $C_{20}H_{21}O^{+}$ $[M+H]^{+}$ 277.1587 found 277.1597; IR (neat): 1666, 2854, 2925, 1599 cm^{-1}.



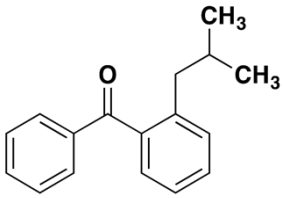
(2-Cyclohexylmethyl)benzophenone hydrazone (**8a**) was synthesized according to general procedure E, benzophenone **31** (0.329 g, 1.19 mmol), N_2H_4 (0.60 mL, 18 mmol), AcOH (0.080 mL, 1.4 mmol) and anhydrous EtOH (18.0 mL) were used. The crude reaction mixture was taken into general procedure F, 10% palladium on carbon (0.064 g, 0.060 mmol) and CH_3OH (4.0 mL) were used. Following purification by flash column chromatography on neutral alumina (97:3, hexanes:EtOAc), hydrazone **8a** was obtained as a yellow oil (0.164 g, 47%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.40 – 7.30 (m, 3H), 7.30 – 7.23 (m, 3H), 7.13 (d, *J* = 7.2 Hz, 1H), 5.33 (s, 2H), 2.35 – 2.27 (m, 2H), 1.63 – 1.58 (m, 1H), 1.57 – 1.52 (m, 3H), 1.52 – 1.47 (m, 1H), 1.47 – 1.40 (m, 1H), 1.10 – 0.97 (m, 3H), 0.82 (qd, *J* = 12.1, 3.6 Hz, 1H), 0.73 (qd, *J* = 12.1, 3.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.2, 140.3, 138.3, 132.6, 130.7, 129.0, 128.8, 128.1, 128.0, 126.7, 126.0, 41.1, 38.1, 33.3, 33.3, 26.4, 26.2, 26.2; AMM (ESI) *m/z* calcd for $C_{20}H_{25}N_2^{+}$ $[M+H]^{+}$ 293.2012 found 293.2012.



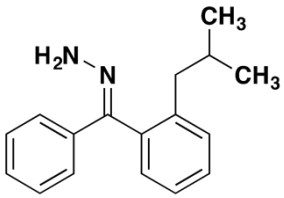
1-Phenylspiro(cyclohexane-1,2'-indane) (**9a**) was synthesized by general procedure H using hydrazone **8a** (42 mg, 0.14 mmol), MnO_2 (100 mg, 1.14 mmol), and Rh_2(*R*-PTAD)$_4$ (2 mg, 0.001 mmol) in CH_2Cl_2 (9 mL). The crude product was purified by flash column chromatography (4:96, EtOAc:hexanes) affording indane **9a** as a white solid (34 mg, 89%, 99:1 er). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 4H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 6.9 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 4.01 (s, 1H), 3.04 (d, *J* = 15.7 Hz, 1H), 2.79 (d, *J* = 15.6 Hz, 1H), 1.69 (d, *J* = 11.8 Hz, 1H), 1.66 – 1.59 (m, 1H), 1.59 – 1.53 (m, 1H), 1.53 – 1.48 (m, 1H), 1.48 – 1.40 (m, 2H), 1.38 – 1.29 (m, 1H), 1.14 (d, *J* = 13.5 Hz, 1H), 1.11 – 1.02 (m, 1H), 0.79 (td, *J* = 12.7, 4.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.0, 143.3, 141.0, 123.0, 127.9, 126.6, 126.4, 126.4, 125.6, 124.9, 63.3, 48.8, 42.0, 38.0, 32.6, 26.2, 23.9, 23.1; IR (neat) 3024, 2927, 1451, 720 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{20}H_{26}N^+$ $[M+NH_4]^+$ 280.2060 found 280.2074; m.p. 94 °C; $[\alpha]_D^{24}$ = 31.8(c = 0.30, $CHCl_3$).



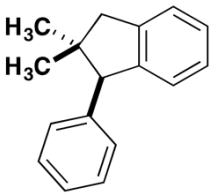
2-Iodobenzophenone (28). A solution of 2-aminobenzophenone (6.00 g, 30.4 mmol) and concentrated H_2SO_4 (35.8 mL, 645 mmol) in H_2O (17.9 mL) was stirred vigorously at room temperature for 45 minutes. The solution was cooled to 0 °C and a solution of $NaNO_2$ (2.73 g, 39.6 mmol) in H_2O (6.10 mL) was added dropwise. The solution was stirred at 0 °C for 2.5 h at which time a solution of KI (25.2 g, 152 mmol) in H_2O (28.7 mL) was slowly added. The reaction mixture was allowed to warm to room temperature and stirred for 27 h. EtOAc (80 mL) was added and the organic layer was washed with brine (50 mL), saturated $Na_2S_2O_3$ (2 x 50 mL), and then H_2O (50 mL). The organic layer was dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by flash column chromatography (95:5, hexanes:EtOAc) to afford the desired benzophenone **28** as a yellow oil (6.49 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.64 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.33 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.21 (td, *J* = 7.7, 1.7 Hz, 1H). ^{1}H NMR is consistent with published data.[13]



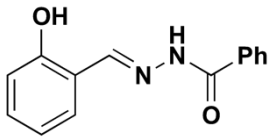
(2-Methylpropyl)benzophenone (29). Following a modified literature procedure,[14] a solution of **28** (0.250 g, 0.811 mmol), isobutylboronic acid (0.165 g, 1.57 mmol), K_2CO_3 (0.335 g, 2.42 mmol) and Ag_2O (0.470 g, 2.03 mmol) in anhydrous toluene (2.5 mL) was heated at 120 °C for 18 h and then allowed to cool to room temperature. The reaction mixture was filtered through Celite with diethyl ether (25 mL), concentrated *in vacuo*, and purified by flash column chromatography (4:96, EtOAc:hexanes) to afford the desired benzophenone **29** as a clear oil (0.088 g, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.58 – 7.52 (m, 1H), 7.46 – 7.36 (m, 3H), 7.30 – 7.20 (m, 3H), 2.57 (d, *J* = 7.3 Hz, 2H), 1.87 – 1.72 (m, 1H), 0.80 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 140.7, 138.9, 138.0, 133.2, 131.0, 130.2, 123.0, 128.6, 128.5, 125.2, 42.4, 30.3, 22.5; AMM (ESI) *m/z* calcd for $C_{17}H_{19}O^+$ $[M+H]^+$ 239.1430 found 239.1431; IR (neat): 1666, 1599, 2925, 2869, 2955 cm^{-1}.



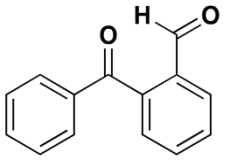
(2-Methylpropyl)benzophenone hydrazone (8b) was synthesized according to general procedure E, benzophenone **29** (0.400 g, 1.68 mmol), N_2H_4 (1.6 mL, 50 mmol), AcOH (0.17 mL, 3.0 mmol) and anhydrous EtOH (28.0 mL) were used. Following purification by flash column chromatography (10:90, EtOAc:hexanes), hydrazone **8b** was obtained as a light-yellow solid (0.279 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.41 – 7.30 (m, 3H), 7.30 – 7.24 (m, 3H), 7.13 (d, *J* = 7.4 Hz, 1H), 5.33 (br s, 2H), 2.30 (dd, *J* = 7.4, 1.8 Hz, 2H), 1.84 – 1.74 (m, 1H), 0.81 (d, *J* = 6.6 Hz, 3H), 0.74 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 140.7, 138.3, 132.5, 130.6, 129.0, 128.9, 128.1, 128.0, 126.8, 126.0, 42.5, 28.7, 22.7, 22.6; AMM (ESI) m/z calcd for $C_{17}H_{21}N_2^+$ $[M+H]^+$ 253.1699 found 253.1699.



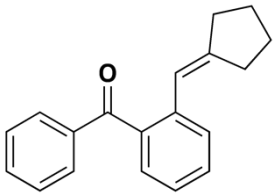
2,2-Dimethyl-1-phenylindane (9b) was synthesized according to general procedure I using hydrazone **8b** (37 mg, 0.15 mmol), MnO_2 (102 mg, 1.17 mmol), and Rh_2(*R*-PTAD)$_4$ (2 mg, 0.001 mmol) in CH_2Cl_2 (9.0 mL). The crude product was purified by flash column chromatography (4:96, EtOAc:hexanes) affording indane **9b** as a white solid (24 mg, 73%, 92:8 er). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.26-7.22 (m, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.1 Hz, 2H), 7.05 (d, *J* = 7.4 Hz, 1H), 4.04 (s, 1H), 2.85 (d, *J* = 15.3 Hz, 1 H), 2.80 (d, *J* = 15.3 Hz, 1 H), 1.24 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 143.6, 140.7, 129.7, 128.0, 126.7, 126.5, 126.3, 125.6, 124.8, 62.3, 47.4, 45.5, 28.6, 24.5; AMM (ESI) *m/z* calcd for $C_{17}H_{22}N^+[M+NH_4]^+$ 240.1747 found 240.1757; m.p. 64 °C; $[\alpha]_D^{24}$ = 80.8(c = 0.70, $CHCl_3$).



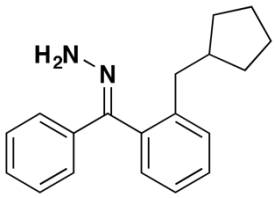
(*E*)-*N*'-(2-hydroxybenzylidene)benzohydrazide (34). To a solution of benzhydrazide (2.70 g, 19.8 mmol) in ethanol (10.0 mL) was added salicylaldehyde (2.10 mL, 19.8mmol) in ethanol (20.0 mL). The reaction mixture was stirred at room temperature for 12 hours before it was filtered and washed with additional ethanol and concentrated to afford hydrazone **34** as a white solid (3.54 g, 84%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.11 (s, 1H), 11.29 (s, 1H), 8.65 (s, 1H), 7.94 (d, *J* = 7.9, 2H), 7.64-7.53 (m, 4H), 7.31 (t, *J* = 7.9 Hz, 1H), 6.93 (t, *J* = 8.1 Hz, 2H). Proton NMR data of the crude material was consistent with the reported literature values.[15]



2-Benzoylbenzaldehyde (**35**). Following a literature procedure,[16] lead (IV) acetate (1.86 g, 4.20 mmol) was added slowly to a solution of **34** (1.00 g, 4.21 mmol) in THF (25.0 mL) in a flame-dried flask. Upon addition of lead (IV) acetate the mixture bubbled and turned yellow. After stirring for two hours the reaction was concentrated *in vacuo* and purified by flash column chromatography (5:95 to 20:80, EtOAc:hexanes) to afford **35** as an off-white solid (0.749 g, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.06 – 8.01 (m, 1H), 7.80 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.73 – 7.66 (m, 2H), 7.63 – 7.58 (m, 1H), 7.53 – 7.49 (m, 1H), 7.49 – 7.45 (m, 2H). ^{1}H NMR is consistent with published data.[17]

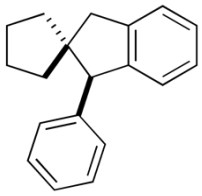


2-(Cycloheptylidenemethyl)benzophenone (36) Following a literature procedure,[18] to a solution of cyclopentyl triphenylphosphonium bromide (0.616 g, 1.49 mmol) in THF (2.25 mL) was added 1 M KO*t*-Bu in THF (1.60 mL, 1.60 mmol). The reaction mixture was stirred for 1 h at room temperature and then a solution of benzaldehyde **35 (**0.300 g, 1.42mmol) in THF (2.3 mL) was added. The reaction mixture was stirred at room temperature for an additional 2 h, concentrated *in vacuo*, and flushed through a plug of silica (5:95, EtOAc:hexanes) to afford the desired benzophenone **36** as a light-yellow oil (0.328 g, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.43 – 7.39 (m, 2H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.27 – 7.23 (m, 1H), 6.27 – 6.24 (m, 1H), 2.40 (t, *J* = 7.2 Hz, 2H), 2.23 (t, *J* = 7.2 Hz, 2H), 1.67 (p, *J* = 7.0 Hz, 2H), 1.56 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.9, 149.0, 138.2, 137.9, 137.7, 133.0, 130.1, 129.9, 128.6, 128.3, 128.2, 125.4, 118.5, 35.1, 31.1, 26.8, 25.4; AMM (ESI) *m/z* calcd for $C_{19}H_{19}O^+$ $[M+H]^+$ 263.1430 found 263.1428; IR (neat): ν_{max} 2951, 2869, 1599, 1663 cm^{-1}.

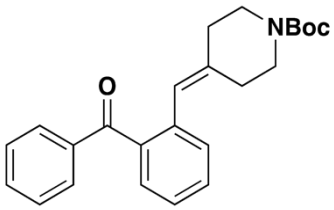


(2-Cyclopentylmethyl)benzophenone hydrazone (8c) was synthesized according to general procedure E, benzophenone **36** (0.325 g, 1.24 mmol), N_2H_4 (1.0 mL, 32 mmol), AcOH (0.14 mL, 2.4 mmol) and anhydrous EtOH (21 mL) were used. The crude reaction material was taken into general procedure F, 10% palladium on carbon (0.067 g, 0.063 mmol) and CH_3OH (4.2 mL) were used. Following purification by flash column chromatography on neutral alumina (5:95, EtOAc:hexanes), hydrazone **8c** was obtained as a yellow solid (0.257 g, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.42 – 7.36 (m, 2H), 7.33 (tt, *J* = 7.1, 1.9 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.12 (d, *J* = 7.4 Hz, 1H), 5.33 (s, 2H), 2.49 – 2.40 (m, 2H), 2.08 – 1.99 (m, 1H), 1.68 – 1.60 (m, 1H), 1.59 – 1.46 (m, 3H), 1.46 – 1.35 (m, 2H), 1.12 – 1.04 (m, 1H), 1.04 – 0.96 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.2, 141.3, 138.3, 132.3, 130.2,

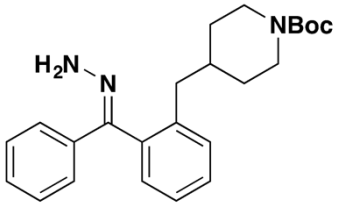
128.9, 128.9, 128.1, 128.0, 126.7, 126.0, 40.3, 39.0, 32.7, 32.6, 24.8, 24.8; AMM (ESI) m/z calcd for $C_{19}H_{23}N_2^+$ $[M+H]^+$ 279.1856 found 279.1857.



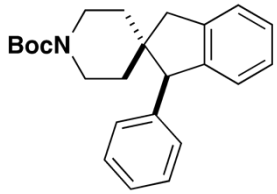
1-Phenylspiro(cyclopentane-1,2'-indane) (9c) was synthesized according to general procedure I using hydrazone **8c** (51 mg, 0.18 mmol), MnO_2 (126 mg, 1.48 mmol), and Rh_2(*R*-PTAD)$_4$ (2 mg, 0.001 mmol) in CH_2Cl_2 (9.0 mL). The crude product was purified by flash column chromatography (4:96, EtOAc:hexanes) affording indane **9c** as a clear oil (39 mg, 86 %, 93:7 er). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 3H), 7.23 – 7.16 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.07 – 7.00 (m, 3H), 4.16 (s, 1H), 2.99 (d, *J* = 15.4 Hz, 1H), 2.78 (d, *J* = 15.5 Hz, 1H), 1.74 – 1.61 (m, 4H), 1.62 – 1.54 (m, 1H), 1.52 – 1.44 (m, 1H), 1.23 – 1.16 (m, 1H), 1.15 – 1.08 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 143.6, 142.1, 129.5, 128.1, 126.7, 126.4, 126.4, 125.4, 124.7, 60.1, 57.2, 44.9, 39.3, 33.8, 23.5, 23.4; IR (neat) 3024, 2952, 2871, 745, 703 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{19}H_{24}N^+$ $[M+NH_4]^+$ 266.1903 found 266.1915; $[\alpha]_D^{26}$ = -1.32 (c = 0.79, $CHCl_3$).



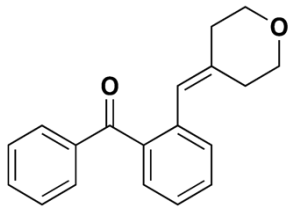
***tert*-butyl 4-(2-benzoylbenzylidene)piperidine-1-carboxylate (32).** Following a literature procedure,[12] to a solution of phosphonate **30** (0.162 g, 0.517 mmol) and 1-boc-4-piperidone (0.099 g, 0.497 mmol) in anhydrous THF (2 mL) was added NaH (60% in mineral oil, 0.021 g, 0.525 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. The reaction mixture was quenched with H_2O (10 mL), extracted with CH_2Cl_2 (2 x 10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by flash column chromatography (15:85, EtOAc:hexanes) to afford the desired benzophenone **32** as an off-white amorphous solid (0.142 g, 77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.55 (td, *J* = 7.4, 1.3 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.45 – 7.38 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.20 (s, 1H), 3.26 (dt, *J* = 15.3, 5.9 Hz, 4H), 2.20 (bs, 2H), 2.08 – 2.03 (m, 2H), 1.44 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.6, 154.7, 139.8, 139.0, 138.0, 136.2, 133.0, 130.1, 130.1, 129.9, 128.4, 126.6, 123.0, 79.56, 45.6, 44.8, 44.0, 35.8, 29.4, 28.5; AMM (ESI) *m/z* calcd for $C_{24}H_{28}NO_3^+$ $[M+H]^+$ 378.2064 found 378.2071; IR (neat): 2936, 2869, 1693, 1666, 1599 cm^{-1}. Note: This compound forms rotamers due to the Boc protecting group. The final indane structure was proved by crystal structure.



***tert*-butyl (*E*)-4-(2-(hydrazineylidene(phenyl)methyl)benzylidene)piperidine-1-carboxylate** (**8d**) was synthesized according to general procedure E, benzophenone **32** (0.207 g, 0.548 mmol), N_2H_4 (0.20 mL, 7.0 mmol), AcOH (0.040 mL, 0.70 mmol) and anhydrous EtOH (8.3 mL) were used. The crude reaction mixture was taken into general procedure F, 10% palladium on carbon (0.030 g, 0.028 mmol) and CH_3OH (1.9 mL) were used. Purification by flash column chromatography on neutral alumina (12:88, EtOAc:hexanes), hydrazone **8d** was obtained as a white solid (0.162 g, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 6.8 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.15 (d, *J* = 7.3 Hz, 1H), 5.35 (s, 2H), 3.95 (br s, 2H), 2.56 – 2.27 (m, 4H), 1.61 – 1.44 (m, 3H), 1.41 (s, 9H), 1.06 – 0.89 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.8, 148.8, 139.4, 138.2, 132.6, 130.9, 129.2, 128.9, 128.2, 128.1, 127.1, 125.9, 79.1, 44.1, 43.5, 40.3, 36.4, 32.1, 28.4; AMM (ESI) m/z calcd for $C_{24}H_{32}N_3O_2^+$ $[M+H]^+$ 394.2489 found 394.2505. Note: This compound forms rotamers due to the Boc protecting group. The final indane structure was proved by crystal structure.

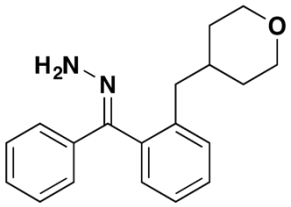


1-Phenylspiro((*tert*-butyl 4-methylidenepiperidine-1-corboxylate)-1,2'-indane) (9d) was synthesized according to general procedure H using hydrazone **8d** (32 mg, 0.081 mmol), MnO_2 (56 mg, 0.64 mmol), and Rh_2(*R*-PTAD)$_4$ (2 mg, 0.001 mmol) in CH_2Cl_2 (5.4 mL). The crude product was purified by flash column chromatography (10:90, EtOAc:hexanes) affording indane **9d** as a white solid (30 mg, 91 %, 96:4er). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 3H), 7.26 – 7.19 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 7.04 – 6.98 (m, 2H), 4.06 (s, 1H), 3.92 (br s, 1H), 3.73 (br s, 1H), 3.07 (d, *J* = 15.7 Hz, 1H), 3.02 (t, *J* = 11.8 Hz, 1H), 2.95 – 2.88 (m, 1H), 2.86 (d, *J* = 15.6 Hz, 1H), 1.75 – 1.63 (m, 2H), 1.41 (s, 9H), 1.14 – 1.01 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 145.4, 142.2, 140.2, 129.8, 128.2, 127.0, 126.8, 125.7, 125.0, 79.4, 62.4, 46.9, 40.8, 37.0, 32.2, 28.6; IR (neat) 3023.8, 2930.9, 1694.0, 1423.4, 748.4 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{24}H_{29}NO_2Na^+$ $[M+Na]^+$ 386.2091, found 386.2095 m.p. 96.3 ºC; $[\alpha]_D^{25}$ = -12.1 (c = 0.45, $CHCl_3$). Note: This compound forms rotamers due to the Boc protecting group. The final structure was proved by crystal structure.

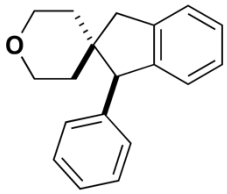


2-(4-Benzylidenetetrahydro-2*H*-pyran)benzophenone (33) Following a literature procedure,[12] to a solution of phosphonate **30** (0.560 g, 1.69 mmol) and tetrahydro-4H-pyran-4-one (0.160 mL, 1.73 mmol) in anhydrous THF (7 mL) was added NaH (60% in mineral oil, 0.0740 g, 1.85 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. The reaction mixture was quenched with H_2O (20 mL), extracted with CH_2Cl_2 (2 x 20 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by flash column chromatography (15:85, EtOAc:hexanes) to afford the desired benzophenone **33** as a light-yellow oil (0.142 g, 77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.56 (td, *J* = 7.6, 1.2 Hz, 1H), 7.49 – 7.40 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 6.17 (s, 1H), 3.53 (q, *J* = 5.7 Hz, 4H), 2.28 (t, *J* = 5.5 Hz, 2H), 2.13 (t, *J* = 5.4 Hz, 2H);

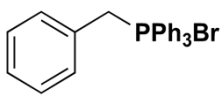
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.7, 139.1, 138.0, 136.2, 133.1, 130.2, 130.1, 130.0, 128.5, 128.5, 126.6, 122.3, 110.1, 69.2, 68.4, 36.8, 30.9; AMM (ESI) *m/z* calcd for $C_{19}H_{19}O_2^+$ $[M+H]^+$ 279.1380 found 279.1393; IR (neat): ν_{max} 2907, 2847, 1663, 1599 cm^{-1}.



2-((Tetrahydro-2H-pyran-4-yl)methyl)benzophenone hydrazone (**8e**) was synthesized according to general procedure E, benzophenone **33** (0.293 g, 1.05mmol), N_2H_4 (0.40 mL, 13 mmol), AcOH (0.070 mL, 1.2 mmol) and anhydrous EtOH (17.0 mL) were used. The crude reaction mixture was taken into general procedure F, 10% palladium on carbon (0.057 g, 0.054 mmol) and CH_3OH (3.6 mL) were used. Following purification by flash column chromatography on neutral alumina (88:12 to 60:40, hexanes:EtOAc), hydrazone **8e** was obtained as a yellow oil (0.222 g, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.42 – 7.32 (m, 3H), 7.30 – 7.24 (m, 3H), 7.16 (dd, *J* = 7.3, 1.6 Hz, 1H), 5.35 (s, 2H), 3.84 (dd, *J* = 11.1, 3.1 Hz, 1H), 3.79 (dd, *J* = 10.9, 3.2 Hz, 1H), 3.17 (td, *J* = 11.8, 2.3 Hz, 1H), 3.13 (td, *J* = 11.7, 2.3 Hz, 1H), 2.42 – 2.33 (m, 2H), 1.69 – 1.60 (m, 1H), 1.45 – 1.40 (m, 1H), 1.38 – 1.33 (m, 1H), 1.25 – 1.18 (m, 1H), 1.16 – 1.08 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.8, 139.2, 138.2, 132.6, 130.9, 129.1, 128.9, 128.2, 128.1, 127.1, 125.9, 67.9, 67.8, 40.6, 35.4, 33.1, 33.0; AMM (ESI) m/z calcd for $C_{19}H_{22}N_2O^+$ $[M+H]^+$ 295.1805 found 295.1806.

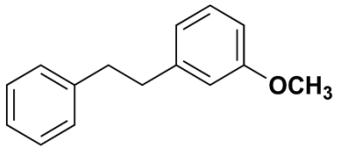


1-Phenylspiro((tetrahydro-2H-pyran-4-yl)-1,2'-indane) (**9e**) was synthesized according to general procedure I using hydrazone **8e** (38 mg, 0.13 mmol), MnO_2 (89 mg, 1.0 mmol), and Rh_2(*R*-PTAD)$_4$ (2 mg, 0.001 mmol) in CH_2Cl_2 (8 mL). The crude product was purified by flash column chromatography (10:90, EtOAc:hexanes) affording indane **9e** as a white solid (30 mg, 89 %, 94:6 er). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 3H), 7.25 – 7.19 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 2H), 4.06 (s, 1H), 3.87 (dt, *J* = 11.7, 3.9 Hz, 1H), 3.69 (dt, *J* = 11.7, 4.0 Hz, 1H), 3.64 (td, *J* = 11.5, 2.6 Hz, 1H), 3.52 (td, *J* = 11.4, 2.5 Hz, 1H), 3.13 (d, *J* = 15.6 Hz, 1H), 2.92 (d, *J* = 15.6 Hz, 1H), 1.87 (ddd, *J* = 13.4, 11.2, 4.5 Hz, 1H), 1.61 (dq, *J* = 13.8, 2.9 Hz, 1H), 1.25 (ddd, *J* = 13.6, 11.2, 4.6 Hz, 1H), 1.05 (dq, *J* = 13.6, 2.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.4, 142.3, 140.2, 129.8, 128.2, 127.0, 126.8, 126.78, 125.8, 125.0, 65.4, 65.1, 62.8, 46.1, 41.6, 37.8, 33.1; IR (neat): 3020, 2918, 2845, 1453, 1102 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{19}H_{24}NO^+$ $[M+NH_4]^+$ 282.1852 found 282.2846; m.p. 126.5 °C; $[\alpha]_D^{26}$ = 7.70 (c = 0.50, $CHCl_3$).

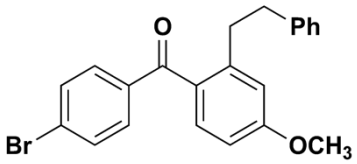


Benzyltriphenylphosphonium bromide (24). Following a modified literature procedure,[19] triphenylphosphine (1.69 g, 6.44 mmol) was added to a solution of benzyl bromide (0.69 mL, 5.9 mmol) in anhydrous toluene (10 mL). The reaction mixture was refluxed open to air overnight. The white precipitate formed was collected by vacuum filtration and the filter cake was rinsed with toluene and hexanes

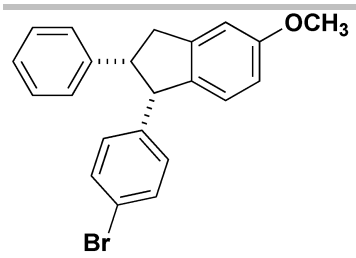
and then dried by pulling air through the cake for 2 h to give the phosphonium salt as a white powder (2.47 g, 97%) which was used without further purification.



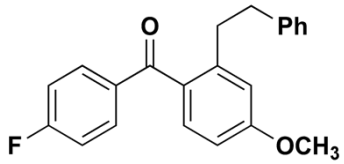
1-Methoxy-3-phenethylbenzene (25). Following a modified literature procedure,[20] sodium hydride (60% in mineral oil, 0.112 g, 3.05 mmol) was added to a solution of Wittig salt **24** (1.00 g, 2.31 mmol) and anhydrous THF (23 mL) in a flame-dried flask at 0 ºC. A solution of m-anisaldehyde (0.28 mL, 2.3 mmol) in THF (23 mL) was added to the sodium hydride mixture dropwise and allowed to warm to room temperature. After 23 hours, the reaction was quenched by the addition of H_2O (40 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with H_2O (1 x 30 mL), brine (1 x 30 mL), dried over Na_2SO_4, filtered, concentrated *in vacuo* and purified by flash column chromatography (1:99 to 5:95, EtOAc:hexanes) to afford the alkene product as mixture of isomers (0.483 g, 98%). Hydrogenation: A solution of the alkene isomers in EtOAc (23.0 mL) was added to a flask with palladium on carbon (10% Pd/C, 0.0759 g) under argon. The solution was sparged with hydrogen gas while stirring for five minutes and the reaction was left to stir overnight under an atmosphere of hydrogen. The flask was flushed with argon gas prior to filtering through Celite and concentrating *in vacuo* to afford the product **25** as a clear oil (0.473 g, 97%) with no purification necessary. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.23 – 7.16 (m, 4H), 6.79 (d, *J* = 7.4 Hz, 1H), 6.77 – 6.71 (m, 2H), 3.78 (s, 3H), 2.96 – 2.87 (m, 4H). ^{1}H NMR is consistent with published data.[20]



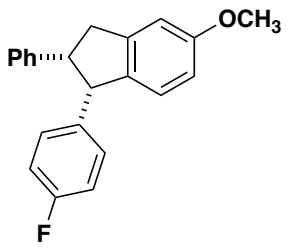
(4-Bromophenyl)(4-methoxy-2-phenethylphenyl)methanone (26). Following a modified literature procedure,[21] tin (IV) chloride in CH_2Cl_2 (1.0 M, 3.5 mL, 3.5 mmol) was added to a solution of **25** (0.455 g, 2.14 mmol) in CH_2Cl_2 (6.3 mL) in a flame-dried flask at 0 °C. A solution of 4-bromobenzoyl chloride (0.713 g, 3.25 mmol) in CH_2Cl_2 (6.3 mL) was slowly added to the tin (IV) chloride mixture. After addition was complete, the reaction was warmed to room temperature and stirred for 24 hours. The reaction was quenched by pouring into H_2O (40 mL) and extracted with Et_2O (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by flash column chromatography (5:95 to 65:35, CH_2Cl_2) to yield ketone **26** as a white amorphous solid (0.476 g, 56%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.12 (d, *J* = 7.4 Hz, 3H), 6.79 (s, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 3.78 (s, 3H), 3.10 – 3.02 (m, 2H), 2.94 – 2.86 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.4, 161.5, 144.7, 141.5, 137.6, 132.2, 131.6, 131.6, 129.9, 128.6, 128.3, 127.7, 126.0, 116.4, 110.5, 55.4, 38.2, 35.8; AMM (ESI) *m/z* calcd $C_{22}H_{20}BrO_2Na^+$ $[M+Na]^+$ 417.0459 found 417.0466.



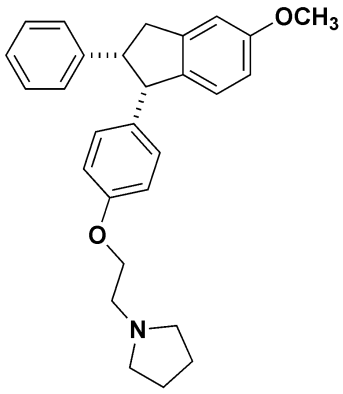
(1*S*,2*R*)-1-(4-bromophenyl)-5-methoxy-2-phenyl-2,3-dihydro-1*H*-indene (**9f)** was synthesized according to general procedure H using hydrazone **8f** (25 mg, 0.061mmol), MnO_2 (42 mg, 0.49 mmol), and Rh_2(*S*-PTAD)$_4$ (1.0 mg, 0.0006 mmol) in CH_2Cl_2. The crude product was purified by flash column chromatography (60:40, CH_2Cl_2:hexanes) affording indane **9f** as a clear oil (15 mg, 65%, 97:3 er, >95:5 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.08 (m, 2H), 7.08 – 7.02 (m, 3H), 7.00 – 6.91 (m, 2H), 6.81 – 6.78 (m, 2H), 6.76 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.47 – 6.40 (m, 2H), 4.55 (d, *J* = 8.0 Hz, 1H), 4.05 – 3.98 (m, 1H), 3.85 (s, 3H), 3.32 (dd, *J* = 15.8, 8.5 Hz, 1H), 3.21 (dd, *J* = 15.8, 7.5 Hz, 1H);^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 145.4, 140.8, 140.3, 136.9, 130.7, 130.6, 128.3, 127.8, 126.2,125.9, 119.8, 112.8, 109.8, 55.5, 55.4, 52.1, 37.0; AMM (ESI) *m/z* calcd for $C_{22}H_{19}BrONa^+$ $[M+Na]^+$ 401.0511, found 401.0533; $[\alpha]_D^{23}$ = 0.147 (c = 70, $CHCl_3$).



(4-fluorophenyl)(4-methoxy-2-phenethylphenyl)methanone (27) Following a modified literature procedure,[21] tin (IV) chloride in CH_2Cl_2 (1.0 M, 4.1 mL, 4.1 mmol) was added to a solution of **25** (0.531 g, 2.50 mmol) in CH_2Cl_2 (7.5 mL) in a flame-dried flask at 0 °C. A solution of 4-fluorobenzoyl chloride (0.531 g, 3.34 mmol) in CH_2Cl_2 (7.5 mL) was slowly added to the tin (IV) chloride mixture. After addition was complete the reaction was warmed to room temperature and stirred for 24 hours. The reaction was quenched by pouring into H_2O (40 mL) and extracted with Et_2O (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by flash column chromatography (0:100 to 10:90, EtOAc:hexanes) to yield ketone **27** as a white amorphous solid (0.296 g, 36%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.17 – 7.00 (m, 5H), 6.79 (d, *J* = 2.6 Hz, 1H), 6.74 (dd, *J* = 8.4, 2.6 Hz, 1H), 3.80 (s, 3H), 3.09 – 3.01 (m, 2H), 2.94 – 2.86 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.2, 165.5 (d, *J* = 254.3 Hz), 161.4, 144.5, 141.6, 135.2 (d, *J* = 2.9 Hz), 132.8 (d, *J* = 9.2 Hz), 132.0, 130.4, 128.6, 128.4, 126.0, 116.3, 115.4 (d, *J* = 21.9 Hz), 110.6, 55.4, 38.2, 35.9; AMM (ESI) *m/z* calcd $C_{22}H_{20}FO_2^+$ $[M+H]^+$ 335.1442 found 335.1443.



(1*S*,2*R*)-1-(4-fluorophenyl)-5-methoxy-2-phenyl-2,3-dihydro-1*H*-indene (**9g)** was synthesized according to general procedure H using hydrazone **8g** (25mg, 0.072 mmol), MnO_2 (50 mg, 0.58 mmol), and Rh_2(*S*-PTAD)$_4$ (1.0 mg, 0.0006 mmol) in CH_2Cl_2. The crude product was purified by flash column chromatography (2:98, EtOAc:hexanes) affording indane **9g** as a clear oil (14.5 mg, 93%, 92:8 er, >95:5 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 – 7.01 (m, 3H), 7.00 – 6.93 (m, 2H), 6.81 – 6.74 (m, 3H), 6.72 – 6.65 (m, 2H), 6.54 – 6.47 (m, 2H), 4.58 (d, *J* = 8.0 Hz, 1H), 4.04 – 3.95 (m, 1H), 3.85 (s, 3H), 3.32 (dd, *J* = 15.7, 8.5 Hz, 1H), 3.21 (dd, *J* = 15.8, 7.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.27 (d, *J* = 243.9 Hz), 159.2, 145.4, 141.0, 137.3, 136.9, (d, *J* = 3.0 Hz), 130.3 (d, *J* = 7.6 Hz), 128.36, 127.7, 126.1, 126.0, 114.3 (d, *J* = 21.2 Hz), 112.8, 109.7, 55.4, 55.3, 52.2, 37.0; AMM (ESI) *m/z* calcd for $C_{22}H_{20}FO^+$ $[M]^+$ 318.1420 found 318.1408; $[\alpha]_D^{23}$ = -0.143 (c = 71.5, $CHCl_3$).



1-(2-(4-((1*S*,2*R*)-5-methoxy-2-phenyl-2,3-dihydro-1*H*-inden-1-yl)phenoxy)ethyl)pyrrolidine (**11a)** was synthesized following a modified literature procedure.[22] To a flame-dried 5 mL μW vial was added $Cu(OAc)_2$ (1 mg, 0.006 mmol) and **9f** (50 mg, 0.13 mmol). The vial was capped and backfilled with argon. To a separate 20 mL flame-dried scintillation vial was added lithium *tert*-butoxide (32 mg, 0.40 mmol). The vial was sealed with a septum and backfilled with argon and amine **28** (2.00 mL, 0.07 M) added by syringe. The vial was heated in a microwave reactor for 20 min at 130 °C. The vial was removed from the reactor and $Cu(OAc)_2$ (1 mg, 0.006 mmol) was added by quickly removing the microwave cap and replacing it. This process was repeated by adding $Cu(OAc)_2$ (1 mg, 0.006 mmol) every 20 min for 2 h. The crude product was dissolved in H_2O (25 mL) and extracted with CH_2Cl_2. (3 x 10 mL). The organic layers were combined and washed with H_2O (3 x 25 mL) and brine (1 x 25 mL). The organic layer was concentrated *in vacuo* and purified by flash column chromatography (5:95, CH_3OH:CH_3Cl) affording **11a** as a brown oil (25.9 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 – 7.03 (m, 3H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.95 (s, 1H), 6.82 – 6.78 (m, 2H), 6.77 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.56 (d, *J* = 8.3 Hz, 2H), 6.47 (d, *J* = 8.3 Hz, 2H), 4.55 (d, *J* = 7.9 Hz, 1H), 4.03 – 3.93 (m, 3H), 3.85 (s, 3H), 3.32 (dd, *J* = 15.7, 8.6 Hz, 1H), 3.19 (dd, *J* = 15.7, 7.5 Hz, 1H), 2.85 (t, *J* = 6.0 Hz, 2H), 2.62 (s, 4H), 1.88 – 1.73 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 156.9, 145.4, 141.4, 137.8, 133.6, 129.9, 128.5, 127.56, 126.0, 125.95, 113.7, 112.7, 109.7, 66.4, 55.4, 55.2, 54.9, 54.6, 52.4, 37.1, 23.4; AMM (ESI) *m/z* calcd for $C_{28}H_{32}NO_2^+$ $[M+H]^+$ 414.2428, found 414.2428; $[\alpha]_D^{23}$ = -0.033 (c = 16.5, $CHCl_3$).

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