Chiral Brønsted Base-Promoted Nitroalkane Alkylation: Enantioselective Synthesis of *sec*-Alkyl-3-Substituted Indoles

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Experimental Section

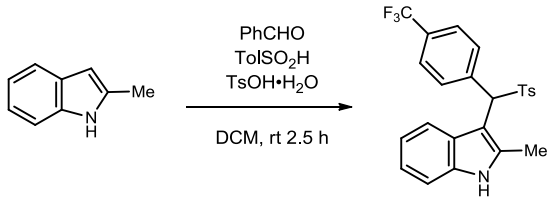
All reagents and solvents were commercial grade and purified prior to use when necessary. Phenylnitromethane, *para*-methoxy-phenylnitromethane and *para*-nitro-phenylnitromethane were prepared using the Kornblum procedure.[1] Arylsulfonylalkyl indoles were prepared as reported in the literature.[2] Catalysts

[1] Kornblum, N.; Larson, H. O.; Blackwood, R. K.; Mooberry, D. D.; Oliveto, E. P.; Graham, G. E. *J. Am. Chem. Soc*. **1956**, *78*, 1497-1501.
[2] Adapted from: Palmieri, A.; Petrini, M. *J. Org. Chem*. **2007**, *72*, 1863-1866.

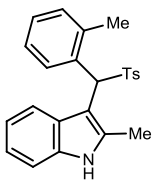
were synthesized according to their respective literature preparations: **4a**,[3] **4b**[4,5] and **4c**.[5] Toluene was dried by passage through a column of activated alumina as described by Grubbs.[6] Thin layer chromatography (TLC) was performed using glass-backed silica gel (250 μm) plates and flash chromatography utilized 230–400 mesh silica gel from Sorbent Technologies. UV light, and/or the use of potassium iodoplatinate and potassium permanganate solutions were used to visualize products.

Nuclear magnetic resonance spectra (NMR) were acquired on a Bruker DRX-500 (500 MHz), Bruker AV-400 (400 MHz) or Bruker AV II-600 (600 MHz) instrument. Chemical shifts are measured relative to residual solvent peaks as an internal standard set to δ 7.26 and δ 77.0 ($CDCl_3$). IR spectra were recorded on a Thermo Nicolet IR100 spectrophotometer and are reported in wavenumbers (cm^{-1}). Compounds were analyzed as neat films on a NaCl plate (transmission). Mass spectra were recorded on a Waters LCT spectrometer by use of the ionization method noted.

General Procedure for Arylsulfonylalkyl Indoles: 2-Methylindole (420 mg, 3.2 mmol), toluenesulfinic acid (560 mg, 3.6 mmol) and toluenesulfonic acid monohydrate (290 mg, 1.5 mmol) were combined in a round-bottomed flask and suspended in ethyl acetate or CH_2Cl_2 (10 mL). The aldehyde (3.0 mmol) was added and the pot stirred for 2.5 h. The reaction was quenched with satd aq $NaHCO_3$ (7 mL), extracted with solvent, dried (Na_2SO_4) and passed through a plug of decolorizing carbon and Celite. Concentration provided crude material that could be purified by flash column chromatography.



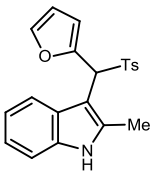
2-Methyl-3-(tosyl(4-(trifluoromethyl)phenyl)methyl)-1*H*-indole (5d). 2-Me-indole (420 mg, 3.20 mmol) and *para*-(trifluoromethyl)benzaldehyde (522 mg, 3.00 mmol) were combined in CH_2Cl_2 according to the general procedure. Precipitation from CH_2Cl_2 with hexanes yielded a yellow solid (1.2 g, 95%). IR (film) 3372, 2918, 1618 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (br s, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.15-7.09 (m, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 5.66 (s, 1H), 2.33 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 144.4, 137.2, 135.6, 135.5, 135.0, 130.3, 129.1, 128.6, 126.9, 125.3, 125.3, 121.8, 120.9, 120.3, 110.4, 103.7, 69.0, 21.5, 11.9; HRMS (ESI): Exact mass calcd for $C_{24}H_{21}F_3NO_2S$ $[M+H]^+$ 444.1245, found 444.1256.



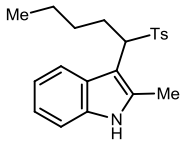
2-Methyl-3-(*o*-tolyl(tosyl)methyl)-1*H*-indole (5e). 2-Me-indole (420 mg, 3.20 mmol) and *ortho*-tolualdehyde (360 mg, 3.00 mmol) were combined in ethyl acetate and refluxed for 2.5 h according to the general procedure. Flash column chromatography (SiO_2, 10-33% ethyl acetate in hexanes) yielded a tan solid (790 mg, 68%). R_f = 0.2 (20% EtOAc/hexanes); IR (film) 3341, 3055, 1460 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.7 Hz, 1H), 7.85 (br s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.35-7.29 (m, 1H), 7.21-7.17 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.09-7.04 (m, 2H), 7.00-6.99 (m, 1H), 5.67 (s, 1H), 2.35 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H); ^{13}C

[3] Nugent, B. M.; Yoder, R. A.; Johnston, J. N. *J. Am. Chem. Soc.* **2004**, *126*, 3418-3419. Hess, A. S.; Yoder, R. A.; Johnston, J. N. *Synlett* **2006**, 147-149.
[4] Singh, A.; Johnston, J. N. *J. Am. Chem. Soc.* **2008**, *130*, 5866-5867.
[5] Davis, T. A.; Wilt, J. C.; Johnston, J. N. *J. Am. Chem. Soc.* **2010**, *132*, 2880-2882.
[6] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

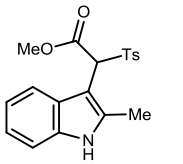
NMR (100 MHz, $CDCl_3$) ppm 144.2, 136.8, 136.1, 135.5, 134.8, 132.2, 130.9, 129.2, 129.2, 128.9, 127.9, 127.7, 125.9, 121.3, 120.0, 119.8, 110.2, 103.4, 65.9, 21.5, 19.7, 12.1; HRMS (ESI): Exact mass calcd for $C_{24}H_{23}NNaO_2S$ $[M+Na]^+$ 412.1347, found 412.1356.



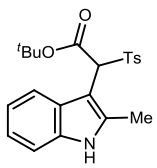
3-(Furan-2-yl(tosyl)methyl)-2-methyl-1*H*-indole (5f). 2-Me-indole (420 mg, 3.20 mmol) and 2-furaldehyde (288 mg, 3.00 mmol) were combined in CH_2Cl_2 according to the general procedure. The tan solid was used without further purification (930 mg, 85%). IR (film) 3366, 1595 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.44-7.43 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.12-7.10 (m, 3H), 7.05 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.67 (d, *J* = 3.4 Hz, 1H), 6.38 (dd, *J* = 3.2, 1.8, 1H), 5.67 (s, 1H), 2.35 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 146.1, 144.3, 143.0, 135.8, 135.3, 135.0, 129.1, 128.9, 127.1, 121.6, 121.0, 120.0, 111.9, 110.8, 110.2, 102.0, 64.5, 21.6, 11.9; HRMS (CI): Exact mass calcd for $C_{21}H_{18}NO_3S$ $[M-H]^-$ 366.1002, found 366.1019.



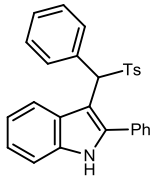
2-Methyl-3-(1-tosylpentyl)-1*H*-indole (5g). 2-Me-indole (420 mg, 3.20 mmol) and valeraldehyde (258 mg, 3.00 mmol) were combined in ethyl acetate and refluxed according to the general procedure. Flash column chromatography (SiO_2, 10-30% ethyl acetate in hexanes) yielded a tan solid (700 mg, 62%). R_f = 0.3 (20% EtOAc/hexanes); IR (film) 3352, 2958, 1461 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (br s, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.10-7.03 (m, 4H), 4.20 (d, *J* = 8.0 Hz, 1H), 2.56-2.45 (m, 2H), 2.38 (s, 3H), 1.87 (s, 3H), 1.34-1.17 (m, 4H), 0.80 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 143.9, 135.8, 135.1, 129.1, 128.9, 121.3, 120.7, 119.9, 110.3, 103.0, 65.6, 29.3, 25.4, 22.3, 21.5, 13.8, 11.2; HRMS (CI): Exact mass calcd for $C_{21}H_{25}NNaO_2S$ $[M+Na]^+$ 378.1504, found 378.1516.



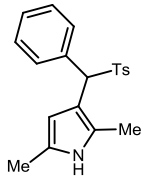
Methyl 2-(2-methyl-1*H*-indol-3-yl)-2-tosylacetate (5h). 2-Me-indole (420 mg, 3.20 mmol) and methyl 2-hydroxy-2-methoxyacetate (360 mg, 3.00 mmol) were combined in CH_2Cl_2 according to the general procedure. Flash column chromatography (SiO_2, 10-50% ethyl acetate in hexanes) yielded an off-white solid (850 mg, 80%). R_f = 0.3 (50% EtOAc/hexanes); IR (film) 3385, 2953, 1743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (br s, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.08-7.05 (m, 1H), 6.97-6.93 (m, 1H), 5.30 (s, 1H), 3.74 (s, 3H), 2.36 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 165.9, 144.9, 136.9, 134.8, 134.4, 129.7, 129.2, 126.9, 121.6, 120.2, 119.6, 110.4, 99.0, 68.6, 52.9, 21.6, 11.7; HRMS (ESI): Exact mass calcd for $C_{19}H_{19}KNO_4S$ $[M+K]^+$ 396.0672, found 396.0678.



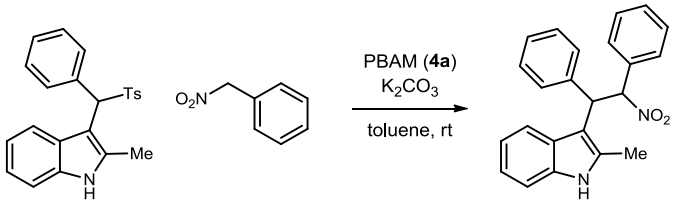
***tert*-Butyl 2-(2-methyl-1*H*-indol-3-yl)-2-tosylacetate (5i).** 2-Me-indole (420 mg, 3.20 mmol) and *tert*-butyl 2-oxoacetate (390 mg, 3.00 mmol) were combined in CH_2Cl_2 according to the general procedure. Flash column chromatography (SiO_2, 20% ethyl acetate in hexanes) yielded a colorless solid (390 mg, 33%). R_f = 0.2 (33% EtOAc/hexanes); IR (film) 3379, 2978, 1734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (br s, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.09-7.06 (m, 1H), 6.98-6.94 (m, 1H), 5.20 (s, 1H), 2.36 (s, 3H), 2.21 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 164.3, 144.6, 136.9, 134.9, 134.9, 129.5, 129.1, 121.3, 120.0, 119.8, 110.4, 99.1, 83.6, 69.9, 27.8, 21.5, 11.7; HRMS (ESI): Exact mass calcd for $C_{22}H_{26}NO_4S$ $[M+H]^+$ 400.1583, found 400.1574.



2-Phenyl-3-(phenyl(tosyl)methyl)-1*H*-indole (5k). 2-Phenyl-indole (618 mg, 3.20 mmol) and benzaldehyde (318 mg, 3.00 mmol) were combined in ethyl acetate according to the general procedure. The solid that precipitated before workup was washed with ethyl acetate to provide the desired product as a brown solid (690 mg, 53%). IR (film) 3338, 3058, 1494 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27-8.26 (m, 1H), 8.10 (s, 1H), 7.80 (dd, *J* = 7.3, 1.8, 2H), 7.40-7.30 (m, 7H), 7.25-7.22 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.00-6.98 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.79 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 143.7, 139.4, 135.9, 133.0, 131.3, 130.2, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 126.9, 123.6, 122.7, 120.7, 110.8, 105.2, 70.0, 21.5; HRMS (CI): Exact mass calcd for $C_{28}H_{24}NO_2S$ $[M+H]^+$ 438.1522, found 438.1501.



2,5-Dimethyl-3-(phenyl(tosyl)methyl)-1*H*-pyrrole (5l). 2,5-Dimethylpyrrole (304 mg, 3.20 mmol) and benzaldehyde (318 mg, 3.00 mmol) were combined in CH_2Cl_2 according to the general procedure. Flash column chromatography (SiO_2, 20-33% ethyl acetate in hexanes) yielded a tan solid (300 mg, 30%). R_f = 0.2 (20% EtOAc/hexanes); IR (film) 3368, 2923, 1597 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (br s, 1H), 7.56-7.53 (m, 2H), 7.48 (d, *J* = 8.2, 2H), 7.31-7.27 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.26 (d, *J* = 2.0 Hz, 1H), 5.10 (s, 1H), 2.37 (s, 3H), 2.20 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 143.8, 135.6, 134.1, 130.0, 129.0, 128.9, 128.4, 128.1, 126.0, 125.9, 110.2, 106.6, 69.7, 21.5, 12.9, 10.6; HRMS (ESI): Exact mass calcd for $C_{20}H_{21}KNO_2S$ $[M+K]^+$ 378.0930, found 378.0937.

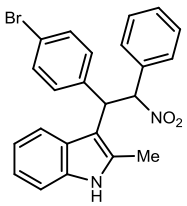


2-Methyl-3-(2-nitro-1,2-diphenylethyl)-1*H*-indole (6a). General Procedure: To a flame dried vial equipped with a stir bar was added the sulfone (38 mg, 0.10 mmol), PBAM (5.1 mg, 0.010 mmol) and potassium carbonate (96 mg, 0.70 mmol). The solid was suspended in toluene (1 mL) with stirring and phenylnitromethane (14 mg, 0.10 mmol) was added immediately. The mixture was stirred for 22 hours before dilution with water and extraction with ethyl acetate. The organic layer was filtered through silica gel, concentrated and determined to be 1.2:1 dr by NMR. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded a yellow-pink solid (28 mg, 78%). The major diastereomer was determined to be 81% ee and the minor diastereomer was determined to be 81% ee by chiral HPLC analysis (see HPLC data below).

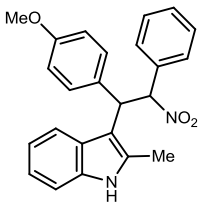
Method A: To a vial equipped with a stir bar was added the sulfone (38 mg, 0.10 mmol), PBAM (5.1 mg, 0.010 mmol) and potassium carbonate (96 mg, 0.70 mmol). The solid was suspended in toluene (1 mL) and water (500 µL) with stirring and phenylnitromethane (14 mg, 0.10 mmol) was added immediately. The mixture was stirred for 22 hours before dilution with water and extraction with ethyl acetate. The organic layer was filtered through silica gel, concentrated and determined to be 1.4:1 dr by NMR. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded a yellow-pink solid (34 mg, 95%). The major diastereomer was determined to be 86% ee and the minor diastereomer was determined to be 86% ee by chiral HPLC analysis (see HPLC data below).

Method B: To a flame dried vial equipped with a stir bar was added the sulfone (36 mg, 0.10 mmol), PBAM (5 mg, 0.01 mmol) and potassium carbonate (96 mg, 0.70 mmol). The solid was suspended in toluene (1 mL) and stirred for 3 days. Phenylnitromethane (14 mg, 0.10 mmol) was added and stirred for 16 hours before dilution with water and extraction with ethyl acetate. The organic layer was filtered through silica gel, concentrated and determined to be 1.25:1 dr by NMR. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded a yellow-pink solid (33 mg, 93%). The major diastereomer was determined to be 88% ee and the minor diastereomer was determined to be 89% ee by chiral HPLC analysis (see HPLC data below).

Chiral HPLC analysis (Chiralcel IA, 8% EtOH/hexanes, 1 mL/min, $t_r(d_2e_1$, minor) = 9.3 min, $t_r(d_2e_2$, minor) = 10.7 min, $t_r(d_1e_1$, major) = 13.0 min, $t_r(d_1e_2$, major) = 14.8 min); R_f = 0.3 (25% EtOAc/hexanes); IR (film) 3411, 2922, 1552 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{23}H_{21}N_2O_2$ $[M+H]^+$ 357.1603, found 357.1607. ***d₁*, major**: (85% ee) $[\alpha]_D^{20}$ -31 (*c* 0.20, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 6.1, 1.9 Hz, 1H), 7.59 (s, 1H), 7.52 (d, *J* = 7.4, 2H), 7.39 (d, *J* = 7.1 Hz, 2H), 7.30 (dd, *J* = 7.9, 7.6 Hz, 2H), 7.21-7.15 (m, 4H), 7.12-7.11 (m, 1H), 7.06-7.02 (m, 2H), 6.68 (d, *J* = 12.2 Hz, 1H), 5.34 (d, *J* = 12.2 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 140.2, 135.2, 133.8, 131.8, 129.5, 128.8, 128.4, 127.6, 127.3, 127.1, 121.1, 119.6, 118.7, 110.5, 109.3, 93.1, 46.8, 29.7, 12.2; ***d₂*, minor**: (recrystallized, 94% ee) $[\alpha]_D^{20}$ -66 (*c* 0.10, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.77 (dd, *J* = 5.9, 3.1 Hz, 1H), 7.61 (dd, *J* = 7.0, 3.5 Hz, 2H), 7.34-7.33 (m, 3H), 7.24-7.23 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.11-7.07 (m, 4H), 7.02 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.68 (d, *J* = 12.2 Hz, 1H), 5.38 (d, *J* = 12.2 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 138.9, 135.4, 133.6, 132.4, 129.8, 128.9, 128.5, 128.4, 128.3, 126.7, 126.5, 121.2, 119.8, 118.8, 110.7, 110.0, 93.5, 46.4, 12.3.



3-(1-(4-Bromophenyl)-2-nitro-2-phenylethyl)-2-methyl-1*H*-indole (6b). Sulfone (45 mg, 0.10 mmol) and phenylnitromethane (14 mg, 0.10 mmol) were combined and stirred for 22 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (32 mg, 74%). R_f = 0.3 (20% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 10% IPA/hexanes, 1 mL/min, $t_r(d_1e_1$, major) = 14.0 min, $t_r(d_1e_2$, major) = 18.2 min, $t_r(d_2e_1$, minor) = 16.1 min, $t_r(d_2e_2$, minor) = 32.1 min); IR (film) 3408, 3059, 2924, 1552 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$)[7] ***d₁*, major** δ 7.85-7.05 (14H), 6.61 (d, *J* = 12.2 Hz, 1H), 5.34 (d, *J* = 12.2 Hz, 1H), 2.55 (s, 3H); **d_2, minor** δ 7.85-7.05 (14H), 6.62 (d, *J* = 12.1 Hz, 1H), 5.29 (d, *J* = 12.1 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$)[8] ppm 139.3, 138.0, 135.4, 135.2, 133.5, 133.3, 132.6, 131.9, 131.4, 130.2, 130.0, 129.6, 129.1, 129.0, 128.5, 128.4, 127.5, 126.5, 121.4, 121.3, 121.0, 120.4, 119.9, 119.8, 118.5, 118.4, 110.8, 110.6, 109.3, 108.7, 93.2, 92.9, 46.4, 45.8, 12.2, 12.1; HRMS (ESI): Exact mass calcd for $C_{23}H_{20}BrN_2O_2$ $[M+H]^+$ 435.0708, found 435.0687.

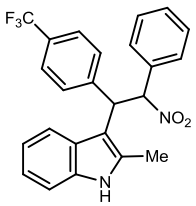


3-(1-(4-Methoxyphenyl)-2-nitro-2-phenylethyl)-2-methyl-1*H*-indole (6c). Sulfone (39 mg, 0.10 mmol) and phenylnitromethane (14 mg, 0.10 mmol) were combined and stirred for 22 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (26 mg, 68%). R_f = 0.3 (20% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 10% EtOH/hexanes, 1 mL/min, $t_r(d_1e_1$, major) = 10.5 min, $t_r(d_1e_2$, major) = 11.9 min, $t_r(d_2e_1$, minor) = 13.6 min, $t_r(d_2e_2$, minor) = 18.6 min); IR (film) 3410, 3032, 2932, 1610 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) ***d₁*, major** δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.58 (br s, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 7.0 Hz, 2H), 7.22-7.02

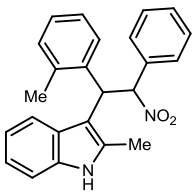
[7] Due to isolation as a mixture of diastereomers, overlapping peaks in the aromatic region are not listed individually, but are listed as a number of hydrogens over a range (ppm). Peaks that could be assigned to their respective diastereomer with confidence are listed with proper integration and splitting. Please see spectra in Supporting Information II.

[8] Due to isolation as a mixture of diastereomers, all carbons are listed and are not assigned to one specific diastereomer. Please see spectra in Supporting Information II.

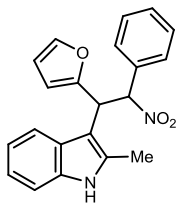
(6H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 7.1 Hz, 1H), 5.29 (d, *J* = 12.0 Hz, 1H), 3.74 (s, 3H), 2.27 (s, 3H); **d_2, minor** δ 7.81 (br s, 1H), 7.77-7.76 (m, 1H), 7.62-7.60 (m, 2H), 7.35-7.34 (m, 3H), 7.22-7.02 (5H), 6.63-6.61 (m, 3H) 5.32 (d, *J* = 12.6 Hz, 1H), 3.64 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 158.4, 157.9, 135.4, 135.2, 133.8, 133.7, 132.4, 132.3, 131.7, 131.0, 129.8, 129.5, 128.9, 128.4, 128.4, 127.6, 126.7, 121.1, 1121.0, 119.7, 119.6, 118.8, 118.7, 114.2, 113.7, 110.7, 110.5, 110.1, 109.5, 93.8, 93.6, 55.2, 55.0, 46.1, 45.7, 12.2, 12.1; HRMS (ESI): Exact mass calcd for $C_{24}H_{23}N_2O_3$ $[M+H]^+$ 387.1709, found 387.1693.



2-Methyl-3-(2-nitro-2-phenyl-1-(4-(trifluoromethyl)phenyl)ethyl)-1*H*-indole (6d). Sulfone (42 mg, 0.10 mmol) and phenylnitromethane (14 mg, 0.10 mmol) were combined and stirred for 22 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (30 mg, 71%). R_f = 0.3 (20% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 8% EtOH/hexanes, 1 mL/min, t_r(d_2e_1, minor) = 8.2 min, t_r(d_2e_2, minor) = 9.6 min, t_r(d_1e_1, major) = 10.4 min, t_r(d_1e_2, major) = 13.3 min); IR (film) 3408, 1619 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) ***d_1*, major** δ 7.64-7.04 (14H), 6.69 (d, *J* = 12.0 Hz, 1H), 5.39 (d, *J* = 12.0 Hz, 1H), 2.29 (s, 3H); **d_2, minor** δ 7.90 (br s, 1H), 7.72-7.71 (m, 1H), 7.64-7.04 (12H), 6.68 (d, *J* = 12.0 Hz, 1H), 5.45 (d, *J* = 12.0 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 144.3, 143.0, 135.4, 135.2, 133.4, 133.1, 132.8, 132.1, 130.2, 129.7, 129.4, 129.2, 129.1, 128.8, 128.5, 128.3, 127.6, 127.5, 126.4, 125.8, 125.8, 125.3, 125.3, 121.5, 121.4, 120.0, 119.9, 118.4, 118.3, 110.9, 110.7, 109.0, 108.3, 93.1, 92.6, 46.7, 46.1, 12.2, 12.1; HRMS (ESI): Exact mass calcd for $C_{24}H_{20}F_3N_2O_2$ $[M+H]^+$ 425.1477, found 425.1485.

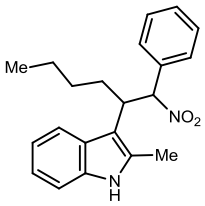


2-Methyl-3-(2-nitro-2-phenyl-1-(*o*-tolyl)ethyl)-1*H*-indole (6e). Sulfone (37 mg, 0.10 mmol) and phenylnitromethane (14 mg, 0.10 mmol) were combined and stirred for 72 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (28 mg, 76%). R_f = 0.4 (20% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 10% EtOH/hexanes, 1 mL/min, t_r(d_1e_1, major) = 11.2 min, t_r(d_2e_1, minor) = 13.0 min, t_r(d_2e_2, minor) = 14.0 min, t_r(d_1e_2, major) = 16.6 min; IR (film) 3409, 2922, 1552 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) ***d_1*, major** δ 7.86-7.01 (14H), 6.64 (d, *J* = 12.0 Hz, 1H), 5.26 (d, *J* = 12.0 Hz, 1H), 2.30 (s, 3H), 2.03 (s, 3H); **d_2, minor** δ 7.86-7.01 (14H), 6.72 (d, *J* = 12.1 Hz, 1H), 5.52 (d, *J* = 12.1 Hz, 1H), 2.52 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 137.6, 136.7, 136.2, 135.4, 135.1, 134.1, 133.3, 132.9, 132.7, 131.4, 131.0, 129.7, 129.3, 128.9, 128.4, 128.3, 128.0, 127.2, 126.9, 126.8, 126.4, 125.9, 125.3, 124.8, 121.1, 120.9, 119.5, 119.4, 118.8, 110.5, 110.3, 107.6, 106.3, 94.2, 92.0, 44.0, 41.5, 20.0, 19.8, 12.4, 12.1; HRMS (ESI): Exact mass calcd for $C_{24}H_{21}N_2O_2$ $[M-H]^-$ 369.1603, found 369.1596.

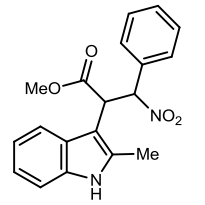


3-(1-(Furan-2-yl)-2-nitro-2-phenylethyl)-2-methyl-1*H*-indole (6f). Sulfone (35 mg, 0.10 mmol) and phenylnitromethane (14 mg, 0.10 mmol) were combined and stirred for 22 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (24 mg, 69%). R_f = 0.2 (25% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 5% EtOH/hexanes, 1 mL/min, t_r(d_1e_1, major) = 11.8 min, t_r(d_1e_2, major) = 13.5 min, t_r(d_2e_1, minor) = 15.5 min, t_r(d_2e_2, minor) = 16.5 min); IR (film) 3408, 2923, 1553 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) ***d_1*, major** δ 7.86 (br s, 1H), 7.84-7.82 (m, 1H), 7.64-7.05 (9H), 6.52 (d, *J* = 11.8 Hz, 1H), 6.07 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.90 (d, *J* = 3.2 Hz, 1H), 5.40 (d, *J* = 11.8, 1H), 2.54 (s, 3H); **d_2, minor** δ 7.64-7.05 (10H), 7.60 (br s, 1H), 6.46 (d, *J* = 11.8 Hz, 1H), 6.29 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.25 (d, *J* = 3.2 Hz, 1H), 5.39 (d, *J* = 11.7, 1H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 153.0, 151.6, 141.8, 141.6, 135.3, 135.1, 133.4, 133.3, 133.0, 132.5, 129.9, 129.5, 128.8, 128.5, 128.3, 128.1, 127.4, 126.8, 126.7, 121.3, 121.2, 119.8, 119.6, 118.9, 118.8, 110.6, 110.4,

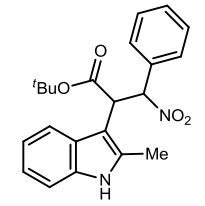
110.4, 110.1, 107.7, 107.3, 106.8, 106.5, 92.5, 92.0, 40.9, 29.7, 12.0, 11.9; HRMS (ESI): Exact mass calcd for $C_{21}H_{19}N_2O_3$ $[M+H]^+$ 347.1396, found 347.1401.



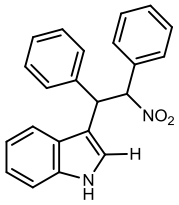
2-Methyl-3-(1-nitro-1-phenylhexan-2-yl)-1*H*-indole (6g). Sulfone (36 mg, 0.10 mmol) and phenylnitromethane (14 mg, 0.10 mmol) were combined and stirred for 22 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (17 mg, 51%). R_f = 0.5 (20% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 2% IPA/hexanes, 1 mL/min, $t_r(d_1e_1$, major) = 17.3 min, $t_r(d_1e_2$, major) = 19.2 min, $t_r(d_2e_1$, minor) = 24.1 min, $t_r(d_2e_2$, minor) = 29.2 min); IR (film) 3407, 2955, 1549 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) ***d*₁, major** δ 7.55 (br s, 1H), 7.48-7.08 (9H), 6.03 (d, *J* = 9.9 Hz, 1H), 3.86 (br s, 1H), 2.17 (br s, 1H) 2.09 (s, 3H), 1.76-0.99 (5H), 0.79 (t, *J* = 7.2 Hz, 3H); ***d*₂, minor** δ 7.82 (br s, 1H), 7.69 (dd, *J* = 7.6, 2.3 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.48-7.08 (5H), 6.03 (d, *J* = 9.9 Hz, 1H), 3.86 (br s, 1H), 2.45 (s, 3H) 1.85 (br s, 1H), 1.76-0.99 (5H), 0.67 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 135.4, 134.3, 134.0, 129.9, 129.1, 129.1, 128.3, 128.1, 127.5, 121.0, 120.9, 119.3, 118.5, 110.8, 110.6, 95.3, 95.2, 42.7, 41.5, 30.8, 29.6, 29.2, 22.4, 22.2, 13.9, 13.8, 11.7; HRMS (ESI): Exact mass calcd for $C_{21}H_{25}N_2O_2$ $[M+H]^+$ 337.1916, found 337.1917.



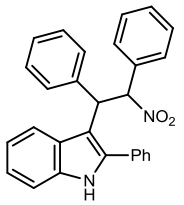
Methyl 2-(2-methyl-1*H*-indol-3-yl)-3-nitro-3-phenylpropanoate (6h). Sulfone (36 mg, 0.10 mmol) and phenylnitromethane (14 mg, 0.10 mmol) were combined and stirred for 22 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (16 mg, 47%). R_f = 0.2 (20% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 5% IPA/hexanes, 1 mL/min, $t_r(d_2e_1$, minor) = 19.0 min, $t_r(d_1e_1$, major) = 20.2 min, $t_r(d_2e_2$, minor) = 22.0 min, $t_r(d_1e_2$, major) = 25.2 min); IR (film) 3399, 2952, 2922, 1735, 1554 cm^{-1}; ***d*₁, major**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (br s, 1H), 7.88-7.85 (m, 1H), 7.75-7.73 (m, 2H), 7.47-7.44 (m, 3H), 7.28-7.24 (m, 1H), 7.18-7.13 (m, 2H), 6.48 (d, *J* = 11.8 Hz, 1H), 5.02 (d, *J* = 11.8 Hz, 1H), 3.46 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 169.7, 135.2, 134.6, 133.1, 130.2, 129.1, 128.2, 126.4, 121.6, 120.2, 118.8, 110.6, 103.4, 90.7, 52.2, 47.1, 11.8; HRMS (ESI): Exact mass calcd for $C_{19}H_{17}N_2O_4$ $[M-H]^-$ 337.1188, found 337.1180.



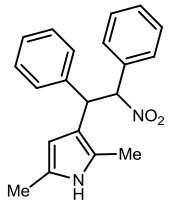
***tert*-Butyl 2-(2-methyl-1*H*-indol-3-yl)-3-nitro-3-phenylpropanoate (6i).** Sulfone (38 mg, 0.10 mmol) and phenylnitromethane (14 mg, 0.10 mmol) were combined and stirred for 72 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (21 mg, 55%). R_f = 0.4 (20% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 2% IPA/hexanes, 1 mL/min, $t_r(d_2e_1$, minor) = 26.5 min, $t_r(d_2e_2$, minor) = 30.4 min, $t_r(d_1e_1$, major) = 46.0 min, $t_r(d_1e_2$, major) = 57.7 min); IR (film) 3403, 2979, 1722, 1556 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) ***d*₁, major,** δ 7.92 (br s, 1H), 7.91-7.89 (m, 1H), 7.75-7.73 (m, 2H), 7.47-7.08 (6H), 6.39 (d, *J* = 11.8 Hz, 1H), 4.93 (d, *J* = 11.8 Hz, 1H), 2.55 (s, 3H), 1.13 (s, 9H); ***d*₂, minor,** δ 7.66 (br s, 1H), 7.47-7.08 (9H), 6.30 (d, *J* = 11.8 Hz, 1H), 4.71 (br s, 1H), 2.02 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 168.1, 133.6, 130.1, 128.9, 128.5, 128.4, 121.4, 121.3, 119.9, 119.1, 110.5, 103.9, 90.7, 82.2, 48.6, 27.8, 27.6; HRMS (ESI): Exact mass calcd for $C_{22}H_{24}N_2NaO_4$ $[M+Na]^+$ 403.1634, found 403.1623.



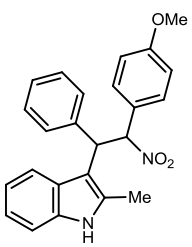
3-(2-Nitro-1,2-diphenylethyl)-1*H*-indole (6j). Sulfone (34 mg, 0.10 mmol) and phenylnitromethane (14 mg, 0.10 mmol) were combined and stirred for 22 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (22 mg, 65%). R_f = 0.2 (20% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 15% EtOH/hexanes, 1 mL/min, $t_r(d_2e_1$, minor) = 9.9 min, $t_r(d_1e_1$, major) = 12.4 min, $t_r(d_2e_2$, minor) = 14.4 min, $t_r(d_1e_2$, major) = 16.2 min); IR (film) 3419, 1549 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) ***d*$_1$, major** δ 8.13 (br s, 1H), 7.59-6.99 (15H), 6.18 (d, *J* = 12.0 Hz, 1H), 5.39 (d, *J* = 11.9 Hz, 1H); ***d*$_2$, minor** δ 7.90 (br s, 1H), 7.59-6.99 (14H), 6.84 (d, *J* = 1.5 Hz, 1H), 6.30 (d, *J* = 12.1 Hz, 1H), 5.42 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 139.9, 138.4, 136.2, 133.2, 129.8, 129.7, 128.8, 128.8, 128.7, 128.6, 128.3, 128.2, 128.1, 127.9, 127.5, 126.9, 126.5, 122.6, 122.4, 121.7, 120.2, 119.8, 119.7, 119.0, 118.9, 115.6, 111.2, 111.0, 95.6, 95.0, 47.3, 46.1; HRMS (ESI): Exact mass calcd for $C_{22}H_{18}N_2NaO_2$ $[M+Na]^+$ 365.1266, found 365.1273.



3-(2-Nitro-1,2-diphenylethyl)-2-phenyl-1*H*-indole (6k). Sulfone (44 mg, 0.10 mmol) and phenylnitromethane (14 mg, 0.10 mmol) were combined and stirred for 72 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (20 mg, 49%). R_f = 0.5 (20% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 10% EtOH/hexanes, 1 mL/min, $t_r(d_2e_1$, minor) = 8.4 min, $t_r(d_2e_2$, minor) = 11.5 min, $t_r(d_1e_1$, major) = 13.6 min, $t_r(d_1e_2$, major) = 26.4 min; IR (film) 3409, 3062, 1552 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) ***d*$_1$, major** δ 8.13-7.01 (20H), 6.74 (d, *J* = 12.0 Hz, 1H), 5.43 (d, *J* = 12.0 Hz, 1H); ***d*$_2$, minor** δ 8.13-7.01 (20H), 6.63 (d, *J* = 12.0 Hz, 1H), 5.42 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 140.4, 139.2, 136.9, 136.9, 136.0, 135.8, 133.6, 133.3, 132.6, 132.2, 129.7, 129.3, 129.1, 129.1, 128.9, 128.8, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 127.8, 127.7, 127.2, 126.7, 126.7, 122.3, 122.1, 120.3, 120.3, 120.2, 120.1, 111.4, 111.2, 110.5, 109.8, 93.9, 93.9, 47.4, 46.6; HRMS (ESI): Exact mass calcd for $C_{28}H_{23}N_2O_2$ $[M+H]^+$ 419.1760, found 419.1750.

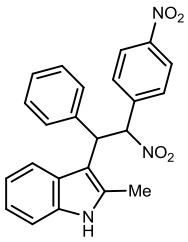


2,5-Dimethyl-3-(2-nitro-1,2-diphenylethyl)-1*H*-pyrrole (6l). Sulfonyl pyrrole (34 mg, 0.10 mmol) and phenylnitromethane (14 mg, 0.10 mmol) were combined and stirred for 22 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (22 mg, 69%). R_f = 0.4 (20% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 5% EtOH/hexanes, 1 mL/min, $t_r(d_2e_1$, minor) = 9.9 min, $t_r(d_2e_2$, minor) = 11.1 min, $t_r(d_1e_1$, major) = 12.1 min, $t_r(d_1e_2$, major) = 18.1 min); IR (film) 3428, 1652, 1646 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) ***d*$_1$, major** δ 7.51-7.00 (m, 11H), 6.11 (d, *J* = 11.9 Hz, 1H), 5.66 (d, *J* = 2.2 Hz, 1H), 4.83 (d, *J* = 11.9 Hz, 1H), 2.04 (s, 3H), 1.90 (s, 3H); ***d*$_2$, minor** δ 7.51-7.00 (m, 11H), 6.08 (d, *J* = 11.9 Hz, 1H), 5.98 (d, *J* = 1.1 Hz, 1H), 4.88 (d, *J* = 11.9 Hz, 1H), 2.21 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 141.1, 139.9, 133.9, 133.5, 129.4, 129.4, 128.8, 128.6, 128.4, 128.3, 128.1, 127.3, 127.0, 126.4, 125.8, 125.7, 122.8, 122.5, 117.4, 116.0, 104.2, 103.6, 95.7, 95.5, 47.2, 47.1, 13.1, 13.0, 10.9, 10.8; HRMS (ESI): Exact mass calcd for $C_{20}H_{21}N_2O_2$ $[M+H]^+$ 321.1603, found 321.1604.

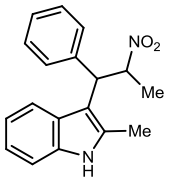


3-(2-(4-Methoxyphenyl)-2-nitro-1-phenylethyl)-2-methyl-1*H*-indole (6m). Sulfone (38 mg, 0.10 mmol) and arylnitromethane (17 mg, 0.10 mmol) were combined and stirred for 22 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (20 mg, 52%). R_f = 0.3 (25% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 8% EtOH/hexanes, 1 mL/min, $t_r(d_2e_1$, minor) = 13.4 min, $t_r(d_2e_2$, minor) = 15.0 min, $t_r(d_1e_1$, major) = 19.7 min, $t_r(d_1e_2$, major) = 27.3 min); IR (film) 3409, 2925, 1609, 1549 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) ***d*$_1$, major** δ

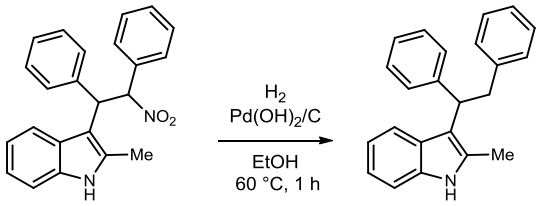
7.68 (d, *J* = 7.5 Hz, 1H), 7.61 (br s, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.28 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.20-7.17 (m, 1H), 7.12-7.09 (m, 1H), 7.08-7.01 (m, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 6.66-6.63 (m, 1H), 5.32 (d, *J* = 12 Hz, 1 H), 3.68 (s, 3H), 2.33 (s, 3H), ^{1}H NMR (600 MHz, $CDCl_3$); ***d*$_2$, minor** δ 7.81 (br s, 1H), 7.75 (dd, *J* = 4.8, 3.0 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.21 (dd, *J* = 6.1, 3.0 Hz, 1H), 7.20-7.17 (m, 2H), 7.12-7.09 (m, 4H), 7.08-7.01 (m, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.66-6.63 (m, 1H), 5.35 (d, *J* = 12 Hz, 1H), 3.77 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 160.6, 160.3, 140.4, 139.1, 135.4, 135.2, 132.4, 131.8, 129.8, 129.0, 128.8, 128.5, 128.3, 127.3, 127.0, 126.7, 126.4, 126.0, 125.8, 121.2, 121.0, 119.7, 119.6, 118.7, 118.7. 114.2, 113.8, 110.6, 110.5, 110.0, 109.5, 93.0, 92.9, 55.3, 55.1, 46.8, 46.1, 12.3, 12.2; HRMS (ESI): Exact mass calcd for $C_{24}H_{23}N_2O_3$ $[M+H]^+$ 387.1709, found 387.1690.



2-Methyl-3-(2-nitro-2-(4-nitrophenyl)-1-phenylethyl)-1*H*-indole (6n). Sulfone (38 mg, 0.10 mmol) and arylnitromethane (18 mg, 0.10 mmol) were combined and stirred for 22 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (25 mg, 52%). R_f = 0.4 (25% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 15% IPA/hexanes, 1 mL/min, t_r(*d*$_1$*e*$_1$, major) = 9.1 min, t_r(*d*$_1$*e*$_2$, major) = 9.6 min, t_r(*d*$_2$*e*$_1$, minor) = 22.5 min, t_r(*d*$_2$*e*$_2$, minor) = 39.5 min); IR (film) 3409, 1557 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) ***d*$_1$, major** δ 8.20-7.04 (13H), 7.69 (br s, 1H), 6.79 (d, *J* = 12.1 Hz, 1H), 5.31 (d, *J* = 12.6 Hz, 1H), 2.30 (s, 3H); ***d*$_2$, minor** δ 8.20-7.04 (13H), 7.92 (br s, 1H), 6.79 (d, *J* = 12.1 Hz, 1H), 5.33 (d, *J* = 12.0 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 148.5, 148.3, 140.2, 140.0, 139.3, 137.9, 135.3, 132.6, 131.9, 129.5, 129.0, 128.7, 128.6, 128.3, 127.4, 127.1, 127.0, 126.3, 126.2, 124.0, 123.5, 121.5, 121.4, 120.0, 119.9, 118.5, 118.3, 110.8, 109.0, 108.3, 92.4, 92.1, 47.3, 47.2, 12.3, 12.1; HRMS (ESI): Exact mass calcd for $C_{23}H_{20}N_3O_4$ $[M+H]^+$ 402.1454, found 402.1437.

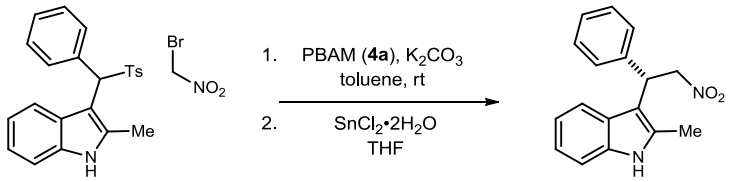


2-Methyl-3-(2-nitro-1-phenylpropyl)-1*H*-indole (6o). Sulfone (38 mg, 0.10 mmol) and nitroethane (11 mg, 0.15 mmol) were combined and stirred for 72 hours according to the general procedure. Flash column chromatography (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound (19 mg, 65%). R_f = 0.3 (20% EtOAc/hexanes); chiral HPLC analysis (Chiralcel IA, 3% IPA/hexanes, 1 mL/min, t_r(*d*$_1$*e*$_1$, major) = 30.2, t_r(*d*$_2$*e*$_1$, minor) = 35.2 min, t_r(*d*$_2$*e*$_2$, minor) = 45.7 min, t_r(*d*$_1$*e*$_2$, major) = 48.8 min); IR (film) 3408, 2924, 1549 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) ***d*$_1$, major** δ 7.91 (br s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.76-7.09 (8H), 5.83-5.76 (m, 1H), 4.75 (d, *J* = 11.4 Hz, 1H), 2.47 (s, 3H), 1.51 (d, *J* = 6.6 Hz, 3H); ***d*$_2$, minor** δ 7.76-7.09 (10H), 5.83-5.76 (m, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 2.43 (s, 3H), 1.63 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 140.3, 139.7, 135.3, 135.2, 132.5, 132.2, 128.8, 128.6, 128.2, 127.3, 127.0, 127.0, 126.6, 126.6, 121.4, 121.0, 119.9, 119.6, 118.8, 118.7, 110.7, 110.6, 110.0, 109.6, 86.1, 85.6, 48.4, 47.6, 19.7, 19.4, 12.3, 12.2; HRMS (ESI): Exact mass calcd for $C_{18}H_{19}N_2O_2$ $[M+H]^+$ 295.1447, found 295.1458.



3-(1,2-Diphenylethyl)-2-methyl-1*H*-indole (9). To a flame dried vial equipped with a stir bar was added **6a** (17 mg, 50 µmol, 84% ee), $Pd(OH)_2$/C (20 wt %, 37 mg) and EtOH (1mL). The reaction was purged twice with hydrogen gas and then placed under 1 bar of hydrogen gas at 60 °C for 1 hour. The reaction was filtered through Celite and concentrated. Flash column chromatography (SiO_2, 9% ethyl acetate in hexanes) yielded a yellow oil

(13 mg, 84%). R_f = 0.5 (20% EtOAc/hexanes); $[\alpha]_D^{20}$ -42 (*c* 0.80, $CHCl_3$); IR (film) 3414, 3059, 2922 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (br s, 1H), 7.46-7.42 (m, 3H), 7.30-7.27 (m, 2H), 7.25-7.18 (m, 2H), 7.16-7.06 (m, 4H), 7.01-6.97 (m, 1H), 6.94-6.91 (m, 2H), 4.42 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.62 (dd, *J* = 13.0, 5.6 Hz, 1H), 3.49 (dd, *J* = 12.9, 10.1 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 144.7, 141.3, 135.4, 131.8, 129.0, 128.1, 127.8, 127.6, 125.8, 125.6, 120.6, 119.6, 119.0, 113.3, 110.2, 44.2, 40.2, 11.7; HRMS (CI): Exact mass calcd for $C_{23}H_{22}N$ $[M+H]^+$ 312.1705, found 312.1752.



***(S)*-2-Methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (10).** To a flame dried vial equipped with a stir bar, was added sulfone **5a** (38 mg, 0.10 mmol), PBAM (5.1 mg, 0.010 mmol) and potassium carbonate (96 mg, 0.70 mmol). The solid was suspended in toluene (1 mL) and stirred, immediately followed by addition of bromonitromethane (21 mg, 0.15 mmol). The reaction was stirred at room temperature for 72 hours, diluted with water and extracted with ethyl acetate. The organic layer was filtered through silica gel and resuspended in THF (1 mL). $SnCl_2$•$2H_2O$ (36 mg, 0.15 mmol) was added to the solution and the reaction was stirred for 5 min. The crude reaction mixture was diluted with H_2O and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered and concentrated. Flash column chromatography of the residue (SiO_2, 10-20% ethyl acetate in hexanes) yielded the title compound as a yellow oil (11 mg, 40%) and sulfone **5a** (10 mg, 25%). R_f = 0.3 (20% EtOAc/hexanes); $[\alpha]_D^{20}$ -13.5 (*c* 0.37, $CHCl_3$). Stereochemistry determined to be (*S*) by correlation to the literature value.[9]

[9] Herrera, R. P.; Sgarzani, V.; Bernardi, L.; Ricci, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 6576-6579.