Enantioselective Organo-SOMO Cascade Cycloadditions: A Rapid Approach to Molecular Complexity from Simple Aldehydes and Olefins.

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Supporting Information

Contents

1. General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] All aldehydes were purified by distillation or silica gel chromatography prior to use. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel 63 according to the method of Still.[3] Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by fluorescence quenching or by staining using CAM, $KMnO_4$, or *p*-anisaldehyde stains.

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 (400 MHz), Inova 500 (500 MHz), or Bruker 500 (500 MHz), and are internally referenced to residual protio solvent signals. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration, and assignment. Data for ^{13}C NMR are reported in terms of chemical shift and multiplicity when applicable. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were obtained from the Princeton University Mass Spectral facility by electrospray ionization, electron ionization, chemical ionization, or fast atom/ion bombardment techniques as indicated. Supercritical fluid chromatography (SFC) was performed on a Berger Minigram equipped with a diode array UV detector (λ = 214–300 nm) using a chiral column (25 cm) and guard column (5 cm) as noted for each compound. High Pressure Liquid chromatography (HPLC) was performed on a Hewlett-Packard 1100 Series chromatograph using a chiral column (25 cm) and guard column (5 cm) as noted for each compound. Optical rotations were measured on a Jasco P-1010 polarimeter with $[a]_D$ values reported in 10^{-1} dg cm^2 g^{-1}; concentration (c) is in g/100 mL. **Specific Notes Regarding SOMO Formal Cycloaddition Reactions**: Glassware was

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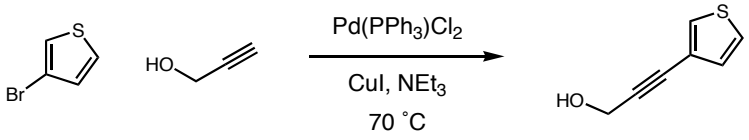
[1] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed., Pergamon Press, Oxford, **1988**.
[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics,* **1996**, *15*, 1518.
[3] Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

dried overnight in an oven at 120 °C prior to use. Due to the heterogeneous nature of the reactions, stirring was found to be important for maximum reaction efficiency. Qualitative analysis of reaction progress was monitored by TLC but also conveniently approximated by the color of the mixture resulting from oxidant consumption. The mixture, initially deep blue in color (arising from the oxidizing iron(III) salts), changes to bright red with reaction progress.

2. Substrate Preparation

Commercially available styrenes or dienes were purified by aqueous base wash to remove stabilizers followed by drying and distillation prior to use.[4] 3-(3-Methoxyphenyl)propanal[5], 3-(benzo[1,3]dioxol-5-yl)propanal[6], and 1-methyleneindane[7] were prepared as previously reported.



3-(Thiophen-3-yl)prop-2-yn-1-ol. To a dry flask containing 3-bromothiophene (3.0 mL, 32.0 mmol, 1.0 equiv), $Pd(PPh_3)Cl_2$ (672 mg, 0.96 mmol, 0.03 equiv), and CuI (364.8 mg, 1.92 mmol, 0.06 equiv) was added freshly distilled NEt_3 (32.0 mL). The resulting mixture was sparged with argon, treated with freshly distilled propargyl alcohol (3.72 mL, 64.0 mmol, 2.0 equiv), and heated to 70 °C. After 12 h, the mixture was cooled to room temperature, treated with Et_2O (100 mL), filtered through Celite, and concentrated to give a brown oil. Purification by silica gel column chromatography (20-30% EtOAc/hexanes) gave the title compound as an amber oil (3.90 g, 88%). R_f 0.44 (30% EtOAc/hexanes); IR (film) 3340, 3107, 1359, 1026; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 3.2 Hz, 1H, Ar**H**), 7.27 (dd, *J* = 5.2, 3.2 Hz, 1H, Ar**H**), 7.15 (d, *J* = 5.2 Hz, 1H, Ar**H**), 4.48 (d, *J* = 6.0 Hz, 2H, C**H**$_2$OH), 1.70-1.66 (m, 1H, O**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 129.8, 129.2, 125.5, 121.5, 86.8, 81.0, 51.7; HRMS (ESI-TOF) m/z calculated

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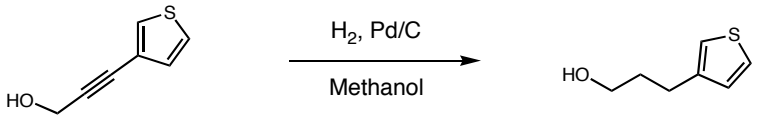
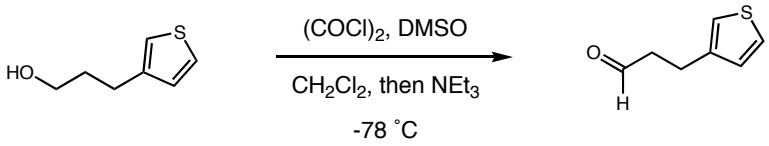
[4]East, G. C.; LaFlair, R. T. *Polymer Letters*. **1965**, *3*, 891-892.
[5] Browder, C. C.; Marmsater, F. P.; West, F. G. *Can. J. Chem*. **2004**, *82*, 375-385.
[6] Datta, S.; Odedra, A.; Liu, R.-S. *J. Am. Chem. Soc.* **2005**, *127*, 11606-11607.
[7] Palmer, A. M.; Munch, G.; Brehm, C.; Zimmermann, P. J.; Buhr, W.; Senn-Bilfinger, J.; Feth, M. P.; Simon, W. A. *Bioorg. Med. Chem*. **2009**, *17*, 368-384.

for C_7H_7OS ($[M+H]^+$) 139.0212, found 139.0214.

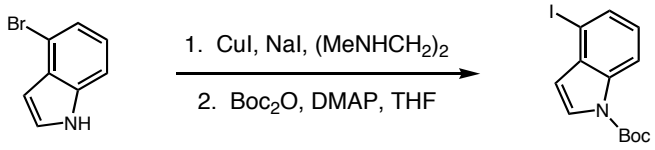


3-(Thiophen-3-yl)propan-1-ol. A mixture of 3-(thiophen-3-yl)prop-2-yn-1-ol (3.90 g, 28.2 mmol), palladium on carbon ((10 wt%, dry), 390 mg), and MeOH (100 mL) was aged under a balloon of hydrogen for 8 h. The mixture was passed through Celite and concentrated to afford a pale yellow oil. Purification by silica gel chromatography (30% EtOAc/hexanes) afforded the title compound as a pale yellow oil (3.20 g, 80%). R_f 0.31 (30% EtOAc/hexanes); IR (film) 3324, 2940, 1050; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.25 (m, 1H, Ar**H**), 6.98-6.95 (m, 2H, Ar**H**), 3.69 (t, *J* = 6.1 Hz, 2H, C**H**$_2$OH), 2.74 (t, *J* = 7.3 Hz, 2H, ArC**H**$_2$), 1.95-1.87 (m, 2H, CH_2C**H**$_2$$CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1, 128.3, 125.5, 120.2, 62.3, 33.3, 26.5; HRMS (ESI-TOF) m/z calculated for $C_7H_{11}OS$ ($[M+H]^+$) 243.0525, found 243.0526.



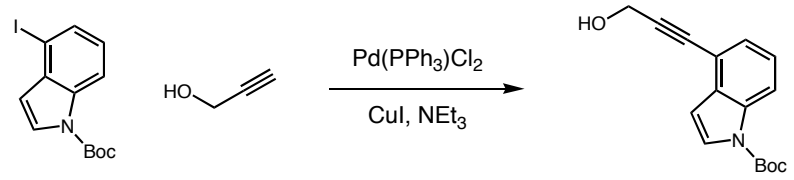
3-(Thiophen-3-yl)propanal. To a solution of oxalyl chloride (736 μL, 8.4 mmol, 1.2 equiv) in CH_2Cl_2 (40 mL) at -78 °C was added a solution of DMSO (596 μL, 8.4 mmol, 1.2 equiv) in CH_2Cl_2 (5 mL) over 10 min. After an additional 20 min, 3-(thiophen-3-yl)propan-1-ol (1.0 g, 7.0 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added dropwise and the resulting solution allowed to stir for 1 h at -78 °C. NEt_3 (2.4 mL, 17.5 mmol, 2.5 equiv) was added and the reaction was allowed to warm to room temperature. Saturated NH_4Cl (100 mL) was added, the layers separated, organics washed with brine, dried over Na_2SO_4, filtered, and concentrated to yield a yellow oil. Purification by silica gel chromatography (10-15% EtOAc/hexanes) afforded the title compound as a clear colorless oil (862 mg, 88%). R_f 0.43 (15% EtOAc/hexanes); IR (film) 2824, 1723, 1409; ^{1}HNMR (500 MHz, $CDCl_3$) δ 9.82 (t, *J* = 1.5 Hz, 1H, C**H**O), 7.22 (dd, *J* = 4.9, 3.1 Hz, 1H, Ar**H**), 6.99-6.97 (m, 1H, Ar**H**), 6.95 (d, *J* = 4.9 Hz, 1H, Ar**H**), 2.99 (t, *J* = 7.3 Hz, 2H, ArC**H**$_2$), 2.79 (dt, *J* = 7.3, 1.5 Hz, 2H, C**H**$_2$CHO); ^{13}C NMR (125 MHz, $CDCl_3$) δ

201.7, 140.6, 128.0, 125.9, 120.7, 44.5, 22.7; HRMS (EI) m/z calculated for C_7H_8OS ($[M]^+$) 140.0296, found 140.0297.

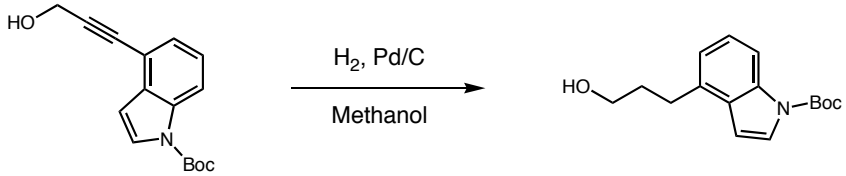


***Tert*-butyl 4-iodo-1*H*-indole-1-carboxylate**. According to the previously outlined procedure[8], NaI (3.0 g, 20.0 mmol, 2.0 equiv) and CuI (170.0 mg, 1.0 mmol, 0.1 equiv) were added to a dry schlenk flask. The flask was evacuated/backfilled with argon (three times) and 4-bromoindole (1.27 mL, 10.0 mmol, 1.0 equiv) was added followed by *N*,*N'*-dimethylethylenediamine (214 μL, 2.0 mmol, 0.2 equiv) and dioxane (10 mL). The flask was sealed and heated to 110 °C. After 24 h, the mixture was cooled to room temperature, poured onto 30% NH_4OH (10 mL), extracted with CH_2Cl_2, the combined organics dried over Na_2SO_4, filtered, and concentrated to furnish crude 4-iodoindole as a clear colorless oil. The crude product was dissolved in THF (30 mL) and treated with DMAP (1.83 g, 15.0 mmol, 1.5 equiv) followed by Boc anhydride (4.36 g, 20.0 mmol, 2.0 equiv) at room temperature. After 1 h, the reaction was diluted with EtOAc (50 mL) and washed with 1 M aqueous citric acid (2 times, 50 mL), H_2O (50 mL), and brine (50 mL). The organics were dried over Na_2SO_4, filtered, and concentrated to furnish the crude product. Purification by silica gel column chromatography (5% Et_2O/hexanes) afforded the title compound as a clear colorless oil (3.40 g, 99%). R_f 0.35 (10% Et_2O/hexanes); IR (film) 2978, 1734, 1416, 1342, 1140, 1023; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.9 Hz, 1H, Ar**H**), 7.65 (d, *J* = 3.9 Hz, 1H, Ar**H**), 7.61 (d, *J* = 7.6 Hz, 1H, Ar**H**), 7.04 (t, *J* = 7.9 Hz, 1H, Ar**H**), 6.52 (d, *J* = 3.9 Hz, 1H, Ar**H**), 1.68 (s, 9H, $C(C\mathbf{H}_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 134.8, 134.5, 132.0, 126.3, 125.5, 115.0, 110.4, 87.4, 84.3, 28.2; HRMS (ESI-TOF) m/z calculated for $C_{13}H_{14}INO_2$ ($[M+H]^+$) 344.0142, found 344.0140.

[8] Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14844-14845.

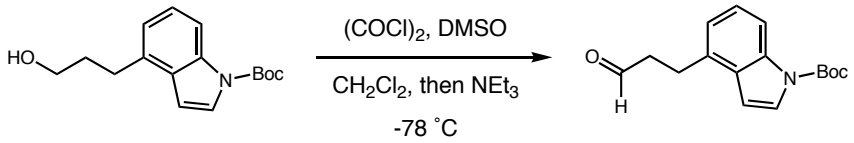


***Tert*-butyl 4-(3-hydroxyprop-1-ynyl)-1H-indole-1-carboxylate**. To a dry flask containing *tert*-butyl 4-iodo-1*H*-indole-1-carboxylate (1.0 g, 2.9 mmol, 1.00 equiv), $Pd(PPh_3)Cl_2$ (41.0 mg, 0.058 mmol, 0.02 equiv), and CuI (22.0 mg, 0.12 mmol, 0.04 equiv) was added freshly distilled NEt_3 (5.8 mL). The resulting mixture was sparged with argon, treated with freshly distilled propargyl alcohol (0.42 mL, 7.28 mmol, 2.5 equiv), and stirred at room temperature. After 12 h, the mixture was filtered through a plug of silica gel and concentrated to give a brown oil. Purification by silica gel column chromatography (20% EtOAc/hexanes) afforded the title compound as a white solid (735.0 mg, 93%). R_f 0.65 (50% Ethyl acetates/hexanes); IR (film) 3414, 2979, 1735, 1422, 1348, 1327, 1286, 1158, 1132, 1024 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H, Ar**H**CN), 7.63 (d, *J* = 2.9 Hz, 1H, Ar**H**N), 7.33 (d, *J* = 7.3 Hz, 1H, Ar**H**CHCC), 7.25 (t, *J* = 8.0 Hz, 1H, Ar**H**CHC), 6.73 (d, *J* = 3.7 Hz, 1H, Ar**H**CHN), 4.59 (d, *J* = 6.2 Hz, 2H, C**H**$_2$OH), 1.77 (t, *J* = 6.2 Hz, 1H, O**H**), 1.67 (s, 9H, (C**H**$_3$)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 134.8, 132.1, 126.5, 126.4, 124.0, 115.8, 114.5, 106.5, 89.9, 84.0, 83.7, 51.8, 28.1; HRMS (ESI-TOF) m/z calculated for $C_{16}H_{17}NO_3Na$ ($[M+Na]^+$) 294.1101, found 294.1099.

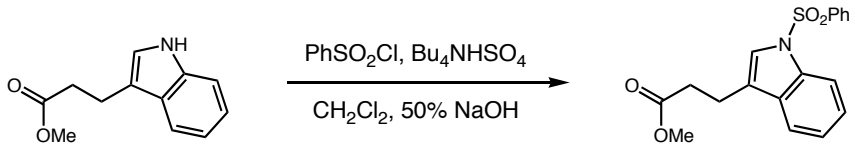


***Tert*-butyl 4-(3-hydroxypropyl)-1*H*-indole-1-carboxylate**. A mixture of *tert*-butyl 4-(3-hydroxyprop-1-ynyl)-1H-indole-1-carboxylate (1.5 g, 5.5 mmol), palladium on carbon ((10 wt%, dry), 150 mg), and MeOH (13.5 mL) was aged under a balloon of hydrogen for 36 h. The mixture was passed through Celite and concentrated to afford a pale yellow oil. Purification by silica gel chromatography (20% EtOAc/hexanes) afforded the title compound as a white solid (1.34 g, 88%). R_f 0.56 (50% Ethyl acetates/hexanes); IR (film) 3378, 2978, 2938, 1731, 1428, 1346, 1282, 1155, 1127 cm^{-1}; ^1H NMR (500 MHz,

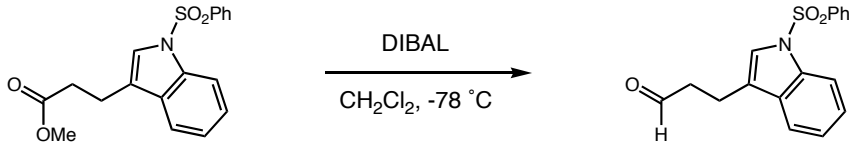
$CDCl_3$) δ 8.01 (d, *J* = 6.0 Hz, 1H, Ar**H**CN), 7.61 (d, *J* = 3.1 Hz, 1H, Ar**H**N), 7.25 (t, *J* = 8.0 Hz, 1H, Ar**H**CHCN), 7.07 (d, *J* = 7.3 Hz, 1H, Ar**H**CCH_2), 6.65 (d, *J* = 3.7 Hz, 1H, Ar**H**CHN), 3.70 (dd, *J* = 11.0, 6.1 Hz, 2H, C**H**$_2$OH), 2.96 (t, *J* = 7.5 Hz, 2H, CH_2C**H**$_2$C), 1.97 (dddd, *J* = 6.4, 6.4, 6.4, 6.4 Hz, 2H, CH_2C**H**$_2CH_2$), 1.67 (s, 9H, (C**H**$_3)_3$), 1.34 (t, *J* = 4.6 Hz, 1H, O**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 135.1, 134.2, 129.7, 125.5, 124.3, 122.2, 113.0, 105.4, 83.6, 62.3, 33.5, 29.1, 28.2; HRMS (ESI-TOF) m/z calculated for $C_{16}H_{21}NO_3Na$ ([M+Na]$^+$) 298.1414, found 298.1416.



***Tert*-butyl 4-(3-oxopropyl)-1*H*-indole-1-carboxylate**. To a solution of oxalyl chloride (490 μL, 5.6 mmol, 1.2 equiv) in CH_2Cl_2 (37 mL) at -78 °C was added a solution of DMSO (400 μL, 5.6 mmol, 1.2 equiv) in CH_2Cl_2 (5 mL) over 10 min. After an additional 20 min, *tert*-butyl 4-(3-hydroxypropyl)-1*H*-indole-1-carboxylate (1.30 g, 4.7 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added dropwise and the resulting solution allowed to stir for 1 h at -78 °C. NEt_3 (2.0 mL, 14.1 mmol, 3.0 equiv) was added and the reaction was allowed to warm to room temperature. Saturated NH_4Cl (100 mL) was added, the layers separated, organics washed with brine, dried over Na_2SO_4, filtered, and concentrated to yield a white solid. Recrystalization from (5% EtOAc/hexanes) afforded the title compound as a white solid (911 mg, 71%). R_f 0.44 (20% Ethyl acetates/hexanes); IR (film): 2980, 1726, 1429, 1346, 1325, 1283, 1155, 1127 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.86 (s, 1H, C**H**O), 8.03 (d, *J* = 7.0 Hz, 1H, Ar**H**CN), 7.62 (d, *J* = 3.2 Hz, 1H, Ar**H**N), 7.25 (t, *J* = 6.8 Hz, 1H, Ar**H**CHCN), 7.06 (d, *J* = 7.3 Hz, 1H, Ar**H**CCH_2), 6.61 (d, *J* = 3.8 Hz, 1H, Ar**H**CHN), 3.20 (t, *J* = 7.6 Hz, 2H, CH_2C**H**$_2$C), 2.86 (ddd, *J* = 7.9, 7.9, 1.1 Hz, 2H, C**H**$_2$CHO), 1.67 (s, 9H, (C**H**$_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.7, 149.7, 135.2, 132.5, 129.4, 125.8, 124.4, 122.0, 113.5, 105.0, 83.8, 44.6, 28.3, 25.2; HRMS (ESI-TOF) m/z calculated for $C_{16}H_{20}NO_3$ ([M+H$^+$) 274.1438, found 274.1440.

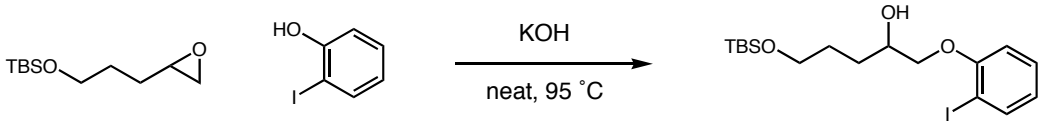


Methyl 3-(1-(phenylsulfonyl)-1*H*-indol-3-yl)propanoate. To a solution of methyl 3-(1*H*-indol-3-yl)propanoate (1.0 g, 4.9 mmol, 1.0 equiv), Bu_4NHSO_4 (0.17 g, 0.5 mmol, 0.1 equiv), benzene sulfonyl chloride (1.1 mL, 8.6 mmol, 1.75 equiv), and CH_2Cl_2 (25.0 mL) was added 50% NaOH (2.5 mL). The reaction was stirred for 18 h at room temperature, quenched with H_2O (25 mL), extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated to afford a white solid. Purification by silica gel column chromatography (20% Ethyl acetate/hexanes) afforded the title compound as a white solid (1.5 g, 89%). R_f 0.63 (50% Ethyl acetates/hexanes); IR (film) 2951, 1733, 1447, 1365, 1278, 1172, 1120, 1098, 978 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 1H, Ar**H**), 7.85 (d, *J* = 7.8 Hz, 2H, Ar**H**), 7.54-7.48 (m, 2H, Ar**H**), 7.43 (t, *J* = 7.9 Hz, 2H, Ar**H**), 7.35 (s, 1H, Ar**H**), 7.34 (t, *J* = 7.5 Hz, 1H, Ar**H**), 7.25 (t, *J* = 6.5 Hz, 1H, Ar**H**), 3.67 (s, 2H, $CO_2C\mathbf{H_3}$), 3.00 (t, *J* = 7.5 Hz, 2H, $C\mathbf{H_2}$Ar), 2.70 (t, *J* = 7.9 Hz, 2H, $C\mathbf{H_2}CO_2Me$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 138.1, 135.2, 133.7, 130.6, 129.2 (2C), 126.7 (2C), 124.9, 123.2, 122.8, 121.7, 119.3, 113.7, 51.8, 33.4, 20.2; HRMS (ESI-TOF) m/z calculated for $C_{18}H_{18}NO_4S$ ($[M+H]^+$) 344.0951, found 344.0951.



3-(1-(Phenylsulfonyl)-1*H*-indol-3-yl)propanal. To a solution of methyl 3-(1-(phenylsulfonyl)-1*H*-indol-3-yl)propanoate (1.6 g, 4.6 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (23 mL), at -78 °C was added diisobutylaluminum hydride (0.83 mL, 4.6 mmol, 1.0 equiv) dropwise. After an additional 15 min, the reaction mixture was transferred via cannula to flask at 0 °C containing a saturated aqueous solution of potassium sodium tartrate. The resulting mixture was stirred at room temperature for 4 h, the layers separated, extracted with CH_2Cl_2, the combined organics dried over Na_2SO_4, and concentrated to yield a white solid. Purification by silica gel column chromatography (10% Hexanes/CH_2Cl_2) afforded the title compound as a white solid (950 mg, 66% yield).

R_f 0.51 (50% Ethyl acetates/hexanes); IR (film): 3111, 2834, 2735, 1720, 1447, 1360, 1176, 1119, 1098, 1087, 975 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.85 (s, 1H, C**H**O), 8.00 (d, *J* = 7.7 Hz, 1H, Ar**H**), 7.87 (d, *J* = 6.2 Hz, 2H, Ar**H**), 7.54-7.44 (m, 4H, Ar**H**), 7.36-7.27 (m, 3H, Ar**H**), 3.00 (t, *J* = 5.8 Hz, 2H, C**H**$_2$Ar), 2.86 (t, *J* = 6.0 Hz, 2H, C**H**$_2$CHO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.1, 138.0, 135.2, 133.8, 130.5, 129.2 (2C), 126.7 (2C), 125.0, 123.2, 122.8, 121.5, 119.2, 113.8, 42.8, 17.3; HRMS (ESI-TOF) m/z calculated for $C_{17}H_{16}NO_3S$ ($[M+H]^+$) 314.0845, found 314.0842.



5-(*Tert*-butyldimethylsilyloxy)-1-(2-iodophenoxy)pentan-2-ol. To a Schlenk flask containing 2-iodophenol (3.30 g, 15.0 mmol, 1.0 equiv) and *tert*-butyldimethy(2-(oxiran-2-yl)ethoxy)silane[9] (3.24 g, 15.0 mmol, 1.0 equiv) was added finely ground NaOH (30.0 mg, 0.75 mmol, 0.05 equiv). The resulting mixture was heated to 95 °C and aged for 48 h with stirring. The resulting black oil was passed through a plug of silica gel (30% EtOAc/hexanes eluent) and concentrated to a pale yellow oil which was dissolved in EtOAc (50 mL), extracted (1M NaOH), the organic layer washed with brine, dried over Na_2SO_4, filtered, and concentrated to an oil. Purification by silica gel column chromatography (10-15% EtOAc/hexanes) afforded the title compound as a pale yellow syrup (4.31 g, 66%). R_f 0.27 (20% EtOAc/hexanes); IR (film) 3413, 2928, 2856, 1247, 1094, 1051, 1018; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 1H, Ar**H**), 7.29 (t, *J* = 7.3 Hz, 1H, Ar**H**), 6.83 (d, *J* = 8.2 Hz, 1H, Ar**H**), 6.73 (t, *J* = 7.6 Hz, 1H, Ar**H**), 4.10-4.04 (m, 1H, ArOCH$_2$C**H**OH), 4.02 (dd, *J* = 8.9, 4.3 Hz, 1H, ArOC**H**$_2$), 3.93 (dd, *J* = 8.9, 6.4 Hz, 1H, ArOC**H**$_2$), 3.71 (t, *J* = 5.2 Hz, 1H, C**H**$_2$OTBS), 3.14 (d, *J* = 4.0 Hz, 1H, O**H**), 1.87-1.62 (m, 5H, C**H**$_2$CH$_2$OTBS, C**H**$_2$CH$_2$CH$_2$OTBS), 0.91 (s, 9H, SiC(C**H**$_3$)$_3$, 0.09 (s, 6H, Si(C**H**$_3$)$_2$; ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 139.2, 129.6, 122.9, 112.4, 86.8, 73.2, 69.8, 62.8, 30.4, 28.8, 26.0, 18.4, -5.3; HRMS (ESI-TOF) m/z calculated for $C_{17}H_{30}IO_3Si$ ($[M+H]^+$) 437.1003, found 437.1005.

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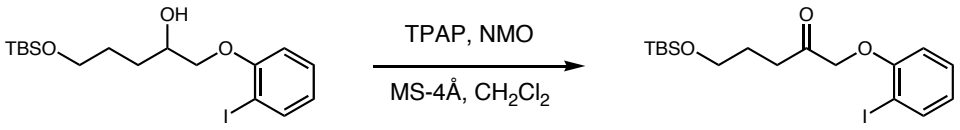
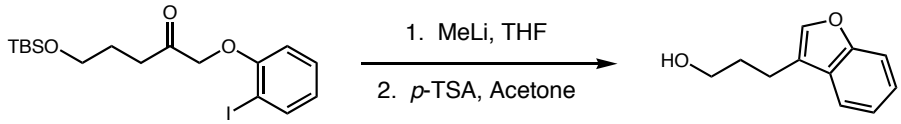
[9] Xie, C.; Nowak, P.; Kishi, Y. *Org. Lett.* **2002**, *4*, 4427-4429.

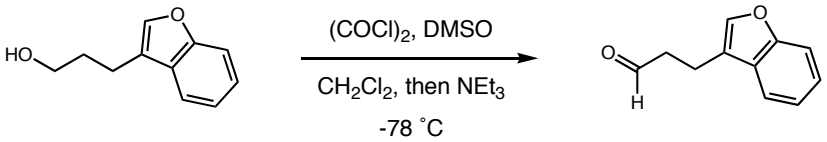


5-(*Tert*-butyldimethylsilyloxy)-1-(2-iodophenoxy)pentan-2-one. To a mixture of 5-(*tert*-butyldimethylsilyloxy)-1-(2-iodophenoxy)pentan-2-ol (4.31 g, 9.9 mmol, 1.0 equiv), *N*-methylmorpholine *N*-oxide (1.76 g, 15.0 mmol, 1.5 equiv), 4Å molecular sieves (5.0 g), MeCN (2.0 mL), and CH_2Cl_2 (20.0 mL) at 0 °C was added tetrapropylammonium perruthenate (140 mg, 0.4 mmol, 0.04 equiv). The mixture was warmed to room temperature and allowed to stir for 3 h. Filtration through a plug of silica gel (CH_2Cl_2 eluent) followed by concentration afforded the crude product as a pale yellow oil. Purification by silica gel column chromatography (10% EtOAc/hexanes) afforded the title compound as a clear colorless oil (2.71 g, 63%). R_f 0.32 (10% EtOAc/hexanes); IR(film) 2928, 2856, 1720, 1100, 1018; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 1H, Ar**H**), 7.29 (t, *J* = 6.7 Hz, 1H, Ar**H**), 6.77 (t, *J* = 8.9 Hz, 1H, Ar**H**), 6.69 (d, *J* = 8.2 Hz, 1H, Ar**H**), 4.56 (s, 2H, ArOC**H**$_2$), 3.66 (t, *J* = 6.1 Hz, 2H, C**H**$_2$OTBS), 2.84 (t, *J* = 7.0 Hz, 2H, COC**H**$_2$CH$_2$), 1.92-1.83 (m, 2H, C**H**$_2$CH$_2$OH), 0.88 (s, 9H, SiC(C**H**$_3$)$_3$), 0.04 (s, 6H, Si(C**H**$_3$)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.6, 156.4, 139.8, 129.6, 123.5, 111.9, 86.2, 76.8, 62.1, 36.2, 26.2, 26.0, 18.4, -5.3; HRMS (ESI-TOF) m/z calculated for $C_{17}H_{28}IOSi$ ([M+H]$^+$) 435.0847, found 435.0846.

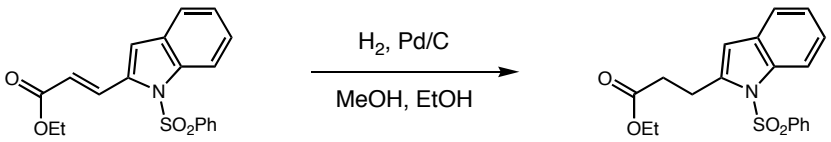


3-(Benzofuran-3-yl)propan-1-ol. To a solution of methyl lithium (1.6 M in Et_2O, 13.4 mL, 21.5 mmol, 5.0 equiv) in THF (25 mL) was slowly added a solution of 5-(*tert*-butyldimethylsilyloxy)-1-(2-iodophenoxy)pentan-2-one in THF (15 mL) at -78 °C. After stirring for 15 min at -78 °C, the solution was allowed to slowly reach room temperature and stir for an additional 3 h. The solution was cooled to 0 °C, quenched with saturated aqueous NH_4Cl (40 mL), organics were extracted three times (EtOAc), dried over Na_2SO_4, and concentrated to a yellow oil. The crude product was dissolved in acetone (10 mL) and treated with H_2O (5 mL) and *p*-toluenesulfonic acid hydrate (500.0 mg, 2.6 mmol, 0.6 equiv). After stirring at room temperature for 3 h, the mixture was

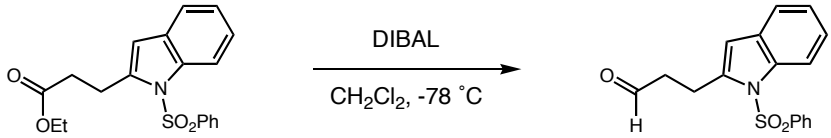
concentrated via rotary evaporation and the residue extracted (EtOAc), dried over Na_2SO_4, and concentrated to a yellow oil. Purification by silica gel chromatography (20-30% EtOAc/hexanes) afforded the title compound as a pale yellow oil (533.2 mg, 70% yield). R_f 0.27 (30% EtOAc/hexanes); IR (film) 3326, 2940, 1452, 1091, 1057; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.2 Hz, 1H, Ar**H**), 7.47 (d, *J* = 8.0 Hz, 1H, Ar**H**), 7.44 (s, 1H, Ar**H**), 7.30 (t, *J* = 7.2 Hz, 1H, Ar**H**), 7.24 (t, *J* = 7.5 Hz, 1H, Ar**H**), 3.75 (t, *J* = 6.0 Hz, 2H, C**H**$_2$OH), 2.56 (t, *J* = 7.6 Hz, 2H, ArC**H**$_2$), 2.05-1.95 (m, 2H, C**H**$_2$CH$_2$OH), 1.47 (bs, 1H, O**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4, 141.2, 128.2, 124.2, 122.3, 119.8, 119.6, 111.5, 62.3, 31.9, 19.8; HRMS (ESI-TOF) m/z calculated for $C_{11}H_{13}O_2$ ($[M+H]^+$) 177.0910, found 177.0910.



3-(Benzofuran-3-yl)propanal. To a solution of oxalyl chloride (318.3 μL, 3.63 mmol, 1.2 equiv) in CH_2Cl_2 (25 mL) at -78 °C was added a solution of DMSO (257.4 μL, 3.63 mmol, 1.2 equiv) in CH_2Cl_2 (5 mL) over 10 min. After an additional 20 min, 3-(benzofuran-3-yl)propan-1-ol (533.2 mg, 3.02 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added dropwise and the resulting solution allowed to stir for 1 h at -78 °C. NEt_3 (1.04 mL, 7.55 mmol, 2.5 equiv) was added and the reaction was allowed to warm to room temperature. Saturated NH_4Cl (100 mL) was added, the layers separated, organics washed with brine, dried over Na_2SO_4, filtered, and concentrated to yield a colorless oil. Purification by silica gel chromatography (10% EtOAc/hexanes) afforded the title compound as a clear colorless oil which solidified upon standing (450 mg, 86%). R_f 0.27 (10% EtOAc/hexanes); IR (solid) 2827, 1721, 1452, 1091; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (t, *J* = 1.2 Hz, 1H, C**H**O), 7.55 (d, *J* = 7.6 Hz, 1H, Ar**H**), 7.48 (d, *J* = 8.2 Hz, 1H, Ar**H**), 7.44 (s, 1H, Ar**H**), 7.31 (t, *J* = 7.3 Hz, 1H, Ar**H**), 7.25 (t, *J* = 7.3 Hz, 1H, Ar**H**), 3.03 (t, *J* = 7.3 Hz, 2H, ArC**H**$_2$), 2.88 (t, *J* = 7.3 Hz, 2H, Ar**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.4, 155.4, 141.5, 127.7, 124.5, 122.5, 119.3, 118.8, 111.6, 43.0, 16.1; HRMS (EI) m/z calculated for $C_{11}H_{10}O_2$ ($[M]^+$) 174.0681, found 174.0682.



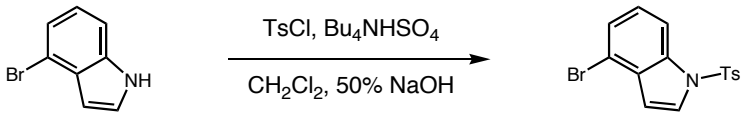
Ethyl 3-(1-(phenylsulfonyl)-1*H*-indol-2-yl)propanoate. A mixture of ethyl 3-(1-(phenylsulfonyl)-1*H*-indol-2-yl)acrylate[10] (2.4 g, 6.7 mmol), methanol (84.0 mL), ethanol (50.0 mL), and palladium on carbon (10 wt%, dry), 240 mg was aged under a balloon of hydrogen for 3 h. The mixture was passed through Celite and concentrated to afford a pale yellow oil. Purification by silica gel column chromatography (20% EtOAc/hexanes) afforded the title compound as a white solid (1.10 g, 46%) R_f 0.27 (20% Ethyl acetates/hexanes); IR (film) 2984, 1732, 1448, 1369, 1177, 1147, 1092 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.3 Hz, 1H, Ar**H**), 7.78-7.76 (m, 2H, Ar**H**), 7.53 (t, *J* = 7.5 Hz, 1H, Ar**H**), 7.43-7.40 (m, 2H, Ar**H**), 7.30-7.27 (m, 1H, Ar**H**), 7.22 (t, *J* = 7.7 Hz, 1H, Ar**H**), 6.42 (d, *J* = 0.5 Hz, 2H, Ar**H**CN), 5.14 (q, *J* = 7.1 Hz, 2H, C**H**$_2$CH$_3$), 3.35 (t, *J* = 7.5 Hz, 2H, C**H**$_2$Ar), 2.81 (t, *J* = 7.6 Hz, 2H, C**H**$_2$CO$_2$Et), 1.22 (t, *J* = 7.1 Hz, 3H, CH$_2$C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 140.1, 138.7, 137.1, 133.7, 129.6, 129.3 (2C), 126.3 (2C), 124.2, 123.7, 120.3, 114.7, 109.5, 60.6, 33.7, 24.6, 14.2; HRMS (ESI-TOF) m/z calculated for $C_{19}H_{20}NO_4S$ ($[M+H]^+$) 358.1108, found 358.1107.



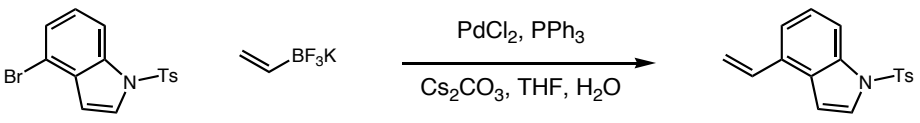
3-(1-(Phenylsulfonyl)-1*H*-indol-2-yl)propanal. To a solution of ethyl-3-(1-(phenylsulfonyl)-1*H*-indol-2-yl)propanoate (1.10 g, 3.1 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (15.0 mL) at -78 °C was added diisobutylaluminum hydride (0.54 mL, 3.1 mmol, 1.0 equiv) dropwise. After an additional 15 min, the reaction mixture was transferred via cannula to flask at 0 °C containing a saturated aqueous solution of potassium sodium tartrate. The resulting mixture was stirred at room temperature for 12 h, the layers separated, extracted with CH_2Cl_2, the combined organics dried over Na_2SO_4, and concentrated to yield a white solid. Purification by recrystalization (5% EtOAc/hexanes) afforded the title compound as a white solid (700.0 mg, 73% yield). R_f 0.24 (20%

[10] Lee, V.; Cheung, M.-K.; Wong, W.-T.; Cheng, K-F. *Tetrahderon* **1996**, *52*, 9455-9468.

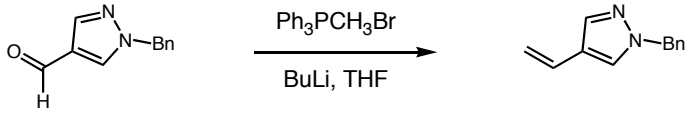
Ethylacetates/ hexanes); IR (film) 3069, 2829, 2728, 1722, 1593, 1568, 1448, 1365, 1175, 1146, 1091, 1052, 1021, 911 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.83 (s, 1H, C**H**O), 8.17 (d, *J* = 8.4 Hz, 1H, Ar**H**), 7.74 (dd, *J* = 8.7, 1.3 Hz, 2H, Ar**H**), 7.53 (t, *J* = 7.5 Hz, 1H, Ar**H**), 7.43-7.40 (m, 3H, Ar**H**), 7.29 (ddd, *J* = 7.4, 7.4, 1.2 Hz, 1H, Ar**H**), 7.23 (ddd, *J* = 8.0, 8.0, 0.8 Hz, 1H, Ar**H**), 6.40 (s, 1H, Ar**H**CN), 3.34 (t, *J* = 7.3 Hz, 2H, C$\mathbf{H_2}$Ar), 2.98 (t, *J* = 6.9 Hz, 2H, C$\mathbf{H_2}$CHO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.8, 139.8, 138.6, 137.2, 133.8, 129.5, 129.3 (2C), 126.2 (2C), 124.4, 123.8, 120.4, 114.8, 110.1, 43.3, 21.8; HRMS (ESI-TOF) m/z calculated for $C_{17}H_{16}NO_3S$ ($[M+H]^+$) 314.0845, found 314.0842.



1-Tosyl-4-bromo-1*H*-indole. To a solution of methyl 4-bromoindole (3.92 g, 20.0 mmol, 1.0 equiv), Bu_4NHSO_4 (0.679 g, 2.0 mmol, 0.1 equiv), *p*-toluenesulfonyl chloride (4.00 g, 21.0 mmol, 1.05 equiv), and CH_2Cl_2 (100 mL) was added 50% NaOH (10 mL). The reaction was stirred for 45 min at room temperature, quenched with H_2O (25 mL), extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated 15 mL. The material was passed through a plug of silica gel (30% EtOAc/hexanes eluent) and concentrated to furnish a white solid which was used without further purification (6.61 g, 98%). R_f 0.39 (10% EtOAc/hexanes); IR (film) 1416, 1373, 1355, 1193, 1168, 1000; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 1H, Ar**H**), 7.71 (d, *J* = 8.4 Hz, 2H, Ar**H**), 7.58 (d, *J* = 3.6 Hz, 1H, Ar**H**), 7.35 (d, *J* = 7.6 Hz, 1H, Ar**H**), 7.20 (d, *J* = 8.4 Hz, 2H, Ar**H**), 7.13 (t, *J* = 8.0 Hz, 1H, Ar**H**), 6.69 (d, *J* = 3.6 Hz, 1H, Ar**H**), 2.32 (s, 3H, ArC$\mathbf{H_3}$); ^{13}C NMR (500 MHz, $CDCl_3$) δ 145.4, 135.0, 134.9, 131.4, 130.1, 126.9, 126.2, 125.6, 115.0, 112.6, 108.8, 21.7; HRMS (ESI-TOF) m/z calculated for $C_{15}H_{13}BrNO_2S$ ($[M+H]^+$) 349.9845, found 349.9848.



1-Tosyl-4-vinyl-1*H*-indole. According to a previously outlined procedure[11], 1-tosyl-4-bromoindole (1.751 g, 5.0 mmol, 1 equiv), was added to a pressure flask containing Cs_2CO_3 (4.9 g, 15.0 mmol, 3.0 equiv), $PdCl_2$ (17.7 mg, 0.10 mmol, 0.02 equiv), PPh_3 (78.7 mg, 0.3 mmol, 0.06 equiv), potassium vinyltrifluoroborate (669.8 mg, 5.0 mmol, 1.0 equiv), and THF/H_2O (9:1, 10 mL). The resulting mixture was sparged with argon, sealed, and heated to 85 °C. After stirring for 22 h, the mixture was cooled to room temperature, diluted with H_2O, extracted with CH_2Cl_2, dried over Na_2SO_4, filtered, and concentrated to furnish the crude product as an oil. Purification by silica gel chromatography (5-7.5% EtOAc/hexanes) afforded the title compound as a clear colorless syrup (787.2 mg, 53%). R_f 0.28 (10% EtOAc/hexanes); IR (film) 1596, 1480, 1372, 1361, 1180, 1129, 1090; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 1H, Ar**H**), 7.79 (d, *J* = 8.3 Hz, 2H, Ar**H**), 7.63 (d, *J* = 3.7 Hz, 1H, Ar**H**), 7.40 (d, *J* = 7.5 Hz, 1H, Ar**H**), 7.31 (t, *J* = 8.0 Hz, 1H, Ar**H**), 7.24 (d, *J* = 8.3 Hz, 2H, Ar**H**), 7.02 (dd, *J* = 17.6, 11.1 Hz, 1H, ArC**H**CH_2), 6.86 (d, *J* = 3.7 Hz, 1H, Ar**H**), 5.83 (d, *J* = 17.6 Hz, 1H, ArCHC**H**$_2$), 5.83 (d, *J* = 11.1 Hz, 1H, ArCHC**H**$_2$), 2.38 (s, 3H, ArC**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 135.1 (2C), 133.7, 130.8, 129.9, 129.0, 126.9, 126.5, 124.7, 119.9, 116.0, 112.8, 107.2, 21.6; HRMS (ESI-TOF) m/z calculated for $C_{17}H_{15}NO_2S$ ($[M+H]^+$) 298.0896, found 298.0899.



1-Benzyl-4-vinyl-1*H*-pyrazole. To a stirred suspension of methyltriphenylphosphonium bromide (2.90 g, 8.13 mmol, 1.30 equiv) in anhydrous THF (62.5 mL) at -78 °C was slowly added *n*-butyllithium (2.5 M in hexanes, 3.25 mL, 8.13 mmol, 1.30 equiv) and the reaction allowed to warm to 0 °C. After 1 h, 1-benzyl-4-formylpyrazole[12] (1.17 g, 6.25 mmol, 1.0 equiv) was added and the reaction allowed to stir at room temperature for 12 h. The crude reaction mixture was concentrated onto silica gel and the solid residue purified by silica gel column chromatography (10-20% EtOAc/hexanes) to afford the title

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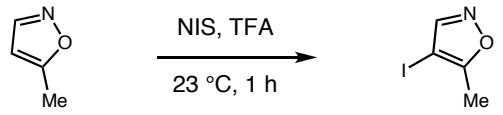
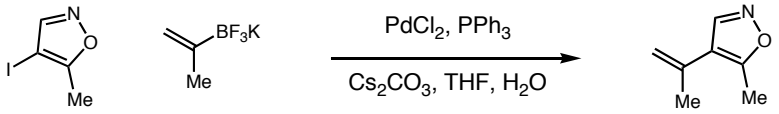
[11] Molander, G. A.; Brown, A. R. *J. Org. Chem.* **2006**, *71*, 9681-9686.
[12] Werner, A.; Sanchez-Migallon, A.; Fruchier, A.; Eleguero, J.; Fernandez-Castano, C.; Foces-Foces, C. *Tetrahedron* **1995**, *51*, 4779-4800.

compound as a clear colorless oil (1.119 g, 97%). R_f 0.33 (20% EtOAc/hexanes); IR (film) 1638, 1455, 1151, 991, 896; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 1H, Ar**H**), 7.38-7.29 (m, 4H, Ar**H**), 7.22 (d, *J* = 6.7 Hz, 2H, Ar**H**), 6.51 (dd, *J* = 17.7, 11.0 Hz, 1H, ArC**H**CH_2), 5.45 (dd, *J* = 17.7, 1.2 Hz, 1H, ArCCHC**H**$_2$), 5.27 (s, 2H, ArC**H**$_2$Ar), 5.06 (dd, *J* = 11.0, 1.2 Hz, 1H, ArCHC**H**$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 136.4, 128.9, 128.1, 127.7, 127.0, 126.7, 121.5, 112.1, 56.1; HRMS (ESI-TOF) m/z calculated for $C_{12}H_{13}N_2$ ($[M+H]^+$) 185.1073, found 185.1073.



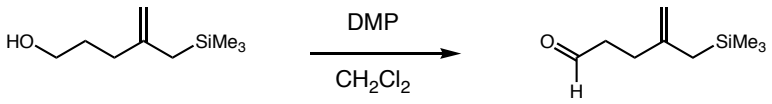
4-Iodo-5-methylisoxazole. According to the previously reported procedure[13], 5-methylisoxazole (820.6 μL, 10.0 mmol, 1.0 equiv) was slowly added to a solution of *N*-iodosuccinimide (2.25 g, 10 mmol, 1.0 equiv) in trifluoroacetic acid (10 mL). After stirring at room temperature for 1 h, the reaction was carefully quenched by addition of H_2O (50 mL). Hexanes (50 mL) was added followed by solid $NaHSO_3$ (to reduce residual iodine, as indicated by color). The layers were separated, organics washed with H_2O then brine, dried, and concentrated to afford a clear colorless oil (1.68 g, 80%) which was used without further purification. R_f 0.38 (10% EtOAc/hexanes); IR (film) 1588, 1466, 1060 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H, Ar**H**), 2.48 (s, 3H, C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 154.8, 54.9, 11.9; HRMS (ESI-TOF) m/z calculated for C_4H_5INO ($[M+H]^+$) 209.9410, found 209.9410.



5-Methyl-4-(prop-1-en-2-yl)isoxazole. According to a previously outlined procedure[14], 4-iodo-5-methylisoxazole (1.05 g, 5.0 mmol, 1.0 equiv), was added to a pressure flask containing Cs_2CO_3 (4.9 g, 15.0 mmol, 3.0 equiv), $PdCl_2$ (17.7 mg, 0.10 mmol, 0.02

[13] Zhou, J.; Oh, L. M.; Ma, P. (Bristol-Myers Squibb Pharma Co.). U.S. Patent 6,562,965, 2003.
[14] See reference 10.

equiv), PPh_3 (78.7 mg, 0.3 mmol, 0.06 equiv), potassium isopropenyltrifluoroborate[15] (819.3 mg, 5.0 mmol, 1.0 equiv), and THF/H_2O (9:1, 10 mL). The resulting mixture was sparged with argon, sealed, and heated to 85 °C. After stirring for 24 h, the mixture was cooled to room temperature, diluted with H_2O, extracted with CH_2Cl_2, dried over Na_2SO_4, filtered, and concentrated to furnish the crude product as an oil. Purification by silica gel chromatography (5-10% Et_2O/petroleum ether) afforded the title compound as a clear colorless oil (445.0 mg, 73%). R_f 0.5 (10% Et_2O/petroleum ether); IR (film) 2978, 1642, 1475, 1228, 882; ^1H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H, ArH), 5.10 (s, 1H, ArC(CH_3)C**H**$_2$), 5.07 (s, 1H, ArC(CH_3)C**H**$_2$), 2.50 (s, 3H, ArC**H**$_3$), 2.05 (s, 3H, ArC(C**H**$_3$)CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 149.6, 133.3, 117.0, 113.8, 22.8, 12.5; HRMS (ESI-TOF) m/z calculated for $C_7H_{10}NO$ ($[M+H]^+$) 124.0757, found 124.0758.



4-((Trimethylsilyl)methyl)pent-4-enal. To a mixture of 2-trimethylsilyl-methyl-pent-1ene-ol[16] (1.0 g, 5.8 mmol, 1.0 equiv), $NaHCO_3$ (974 mg, 11.6 mmol, 2.0 equiv), and CH_2Cl_2 (50 mL) at 0 °C was added Dess-Martin periodinane (2.97 g, 7.0 mmol, 1.21 equiv). The resulting mixture was allowed to warm to room temperature and stir for 1 h before saturated solutions of $NaHCO_3$ (25 mL) and $Na_2S_2O_8$ (25 mL) were added and the biphasic mixture was allowed to stir for 3 h. The crude product was extracted with CH_2Cl_2, the combined organics dried over Na_sSO_4, filtered, and concentrated to furnish a clear colorless oil. Purification by silica gel column chromatography (4% Et_2O/hexanes) afforded the title compound as a clear colorless oil (503.2 mg, 51%). R_f 0.50 (10% EtOAc/hexanes); IR (film) 2954, 1726, 1634, 1415, 1248, 839 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.75 (t, 1H, *J* = 1.6 Hz, C**H**O), 4.54 (m, 2H, C=C**H**2), 2.55 (t, 2H, *J* = 7.5 Hz, C**H**$_2$CHO), 2.26 (t, 2H, *J* = 7.5 Hz, C**H**$_2$$CH_2$CHO), 1.50 (s, 2H, C**H**$_2$Si(CH_3)$_3$), 0.0 (s, 9H,

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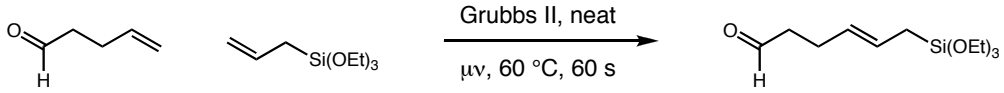
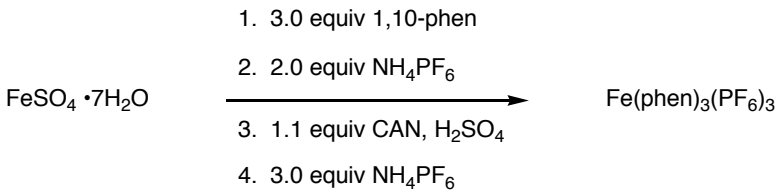
[15] Molander, G. A.; Ribagorda, M. *J. Am. Chem. Soc.* **2003**, *125*, 11148-11149.
[16] Lee, T. V.; Channon, J. A.; Cregg, C.; Porter, J. R.; Roden, F. S.; Yeoh, H. T. L. *Tetrahedron*, **1989**, *45*, 5877.

Si(C**H**$_3$)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.8, 145.0, 108.9, 43.3, 31.6, 28.5, 0.05; HRMS (EI$^+$) m/z calculated for $C_8H_{15}OSi$ ([M-CH_3]$^+$) 155.0892, found 155.0887.



6-(Triethoxysilyl)hex-4-enal. According to the previously outlined procedure[17], a mixture of 4-pentenal (1.1 mL, 11.15 mmol, 1.0 equiv), allyltriethoxysilane (5.0 mL, 22.3 mmol, 2.0 equiv), and Grubbs second generation catalyst (141.0 mg, 0.16 mmol, 0.015 equiv) under argon was aged at 60 °C with stirring in a CEM microwave reactor for 60 s. Direct purification of the crude mixture by silica gel column chromatography (5 to 10% EtOAc/hexanes) afforded the title compound as a clear colorless oil as an inseparable 1.9 : 1 mixture of olefin isomers favoring the *E*-isomer (667.8 mg, 23%). For the mixture of isomers: R_f 0.37 (15% EtOAc/hexanes); IR (film) 2974, 2886, 1726, 1390, 1167, 1100, 1078, 957, 798 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82-9.78 (m, 1H, C**H**O), 5.58-5.31 (m, 2H, C**H**C=C**H**C), 3.88-3.82 (m, 6H, OC**H**$_2$CH$_3$), 2.57-2.47 (m, 2H, C**H**$_2$CHO), 2.43-2.34 (m, 2H, C**H**$_2$CH$_2$CHO), 1.67-1.58 (m, 2H, C**H**$_2$Si), 1.27-1.22 (m, 9H, OCH$_2$C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.6, 128.1, 126.6, 125.4, 124.6, 58.7, 43.6, 25.4, 19.9, 18.3, 16.4, 12.4; HRMS (EI$^+$) m/z calculated for $C_{12}H_{25}OSi$ ([M+H]$^+$) 261.1517, found 261.1515.

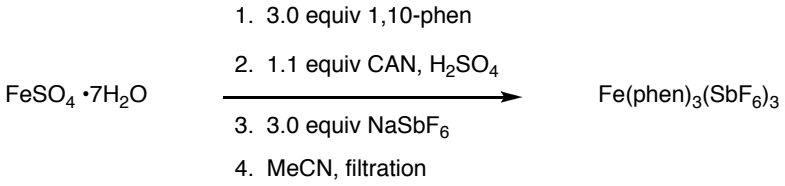
3. Oxidant Preparation



Iron trisphenanthroline trishexafluorophosphate. According to the previously

[17] Michaut, A.; Boddaert, T.; Coquerel, Y.; Rodriguez, J. *Synthesis* **2007**, *18*, 2867.

outlined procedure[18], a solution of iron sulfate heptahydrate (12.5 g, 45.0 mmol, 1.0 equiv) in distilled H_2O (200 mL) was added 1,10-phenanthroline (24.3 g, 135.0 mmol, 3.0 equiv). After stirring for 2 h, ammonium hexafluorophosphate (14.7 g, 90.0 mmol, 2.0 equiv) was added portionwise. After stirring for 1 h, the thick red suspension was filtered and the resulting solid washed with H_2O (500 mL), taken up in 1 M H_2SO_4 (800 mL), and slowly treated with solid CAN (27.4 g, 50.0 mmol, 1.1 equiv). The resulting deep blue solution was allowed to stir for 15 min and treated with ammonium hexafluorophosphate (22.0 g, 135.0 mmol, 3.0 equiv). A blue solid immediately fell precipitated out under a yellow liquor which was filtered off, washed with H_2O (500 mL) then Et_2O, and dried under vacuum (0.10 torr) at 95 °C for 8 h to afford the title compound as a deep blue solid which was used without further manipulation (42.2 g, 94%). Anal. calculated for $C_{36}H_{24}F_{18}FeN_6P_3$: C, 41.92; H, 2.35; F, 33.16; Fe, 5.41; N, 8.15; P, 9.01. Found: C, 42.27; H, 2.46; F, 32.64; Fe, 5.81; N, 7.91; P, 7.98.



Iron trisphenanthroline trishexafluoroantimonate. To a solution of iron sulfate heptahydrate (13.90 g, 50.0 mmol, 1.0 equiv) in distilled H_2O (400 mL) was added 1,10-phenanthroline (27.0 g, 135.0 mmol, 3.0 equiv). After stirring for 2 h, concentrated sulfuric acid (28 mL) in H_2O (100 mL) was added followed by CAN (30.14 g, 55.0 mmol, 1.1 equiv). The resulting deep blue solution was allowed to stir for 15 min and treated with sodium hexafluoroantimonate (38.8 g, 150.0 mmol, 3.0 equiv). A blue solid immediately fell precipitated out under a yellow liquor which was filtered off, washed with H_2O (500 mL) then Et_2O, and dried under vacuum (0.10 torr) at 95 °C for 8 h to afford the crude title compound as a deep blue solid. Purification of the title compound was achieved as follows: the solid was dissolved in MeCN (500 mL), filtered through a medium fritted glass funnel, concentrated, and dried under vacuum (0.10 torr) at 95 °C for 8 h. The resulting blue solid was pulverized using a mortar and pestle to afford the

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[18] Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593-5603.

title compound as a blue powder (48.4 g, 75%). Anal. calculated for $C_{36}H_{24}F_{18}FeN_6P_3$: C, 33.17; H, 1.86; F, 26.23; Fe, 4.28; N, 6.45; Sb, 28.02. Found: C, 34.45; H, 2.09; F, 22.86; Fe, 4.37; N, 7.24; Sb, 26.90.

4. General procedure

To an oven-dried 10 mL round-bottom flask containing oven-dried Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv), catalyst **1** ((2*R*,5*R*)-2-*tert*-butyl-3,5-dimethylimidazolidin-4-one trifluoroacetic acid salt,[19] 22.7 mg, 0.08 mmol, 0.2 equiv), the styrene (1.20 mmol, 3.0 equiv, if solid), the aldehyde (0.4 mmol, 1.0 equiv, if solid), and $Fe(phen)_3(SbF_6)_3$ (1.30 g, 1.0 mmol, 2.5 equiv.) under argon at -78 °C was added THF (5.3 mL). The mixture was degassed three times by applying vacuum and backfilling with argon while stirring vigorously. The styrene (1.20 mmol, 3.0 equiv., if liquid) was added followed by the aldehyde (0.4 mmol, 1.0 equiv, if liquid) and the reaction allowed to stir at the indicated temperature for 12 h under inert atmosphere. The reaction mixture was diluted with Et_2O, passed through a plug of silica gel (eluted with Et_2O), and concentrated. Diastereomeric ratios were determined by ^1H NMR analysis of the crude reaction mixtures thus obtained (500 MHz, $CDCl_3$, d1=10 s). Purification by silica gel column chromatography yielded the title compounds. Enantiomeric excess was determined by chiral HPLC or SFC analysis of the corresponding alcohols. To that end, a fraction of the purified title compound was dissolved in 4:1 (CH_2Cl_2:EtOH) and treated with $NaBH_4$ (2.0 equiv). Upon complete consumption of the aldehyde as indicated by TLC analysis, the reaction was quenched with saturated aqueous NH_4Cl, the product extracted (CH_2Cl_2), dried over Na_2SO_4, filtered, and concentrated. Purification by silica gel column chromatography afforded the corresponding alcohol.

5. Experimental Data for Cyclized Products

Table 1, entry 3:

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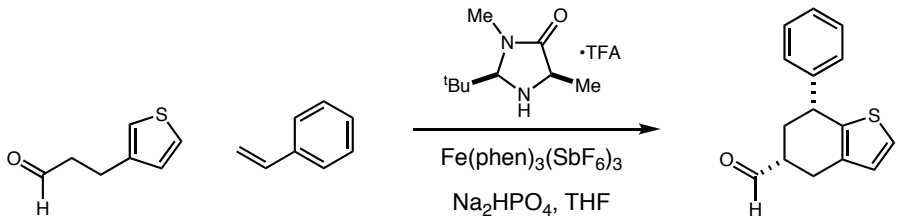
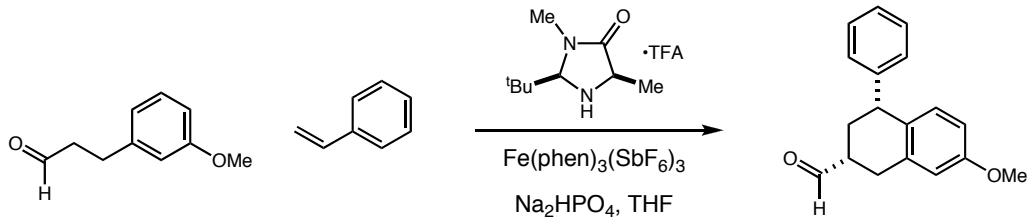
[19] The imidazolidinone catalyst was prepared as previously reported: Graham, T. H.; Jones, C. M.; Jui, N. T.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2008**, *130*, 16494-16495.



(5*R*,7*R*)-4,5,6,7-tetrahydro-7-phenylbenzo[*b*]thiophene-5-carbaldehyde. According to the general procedure, 3-(thiophen-3-yl)propanal (51.0 μL, 0.40 mmol, 1.0 equiv), styrene (137.4 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (1.30 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -10 °C for 12 h to afford a clear colorless oil after workup. Analysis by ^{1}H NMR using 3,5-bis-trifluoromethylbromobenzene (34.5 μL, 0.2 mmol, 0.5 equiv) as an internal standard indicated 84% conversion with a diastereomeric ratio of 10.7:1. Purification by silica gel column chromatography (10% EtOAc/hexanes) afforded the (5*R*)-4,5,6,7-tetrahydro-7-phenylbenzo[*b*]thiophene-5-carbaldehydes as a white solid as a 10.8:1 mixture of diastereomers (80.1 mg, 83% yield). An analytically pure sample of the major diastereomer was obtained by column chromatography under the conditions outlined above omitting the leading fractions. **(5*R*,7*R*)-4,5,6,7-tetrahydro-7-phenylbenzo[*b*]thiophene-5-carbaldehyde**: R_f 0.39 (15% EtOAc/hexanes); IR (solid) 2921, 2850, 1720, 1493, 1446, 964, 763 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (s, 1H, C**H**O), 7.36-7.24 (m, 5H, Ar**H**), 7.14 (d, *J* = 5.2 Hz, 1H, Ar**H**), 6.85 (d, *J* = 5.2 Hz, 1H, Ar**H**), 4.19 (dd, *J* = 11.3, 5.5 Hz, 1H, ArC**H**Ar), 3.06-2.97 (m, 1H, CHC**H**$_2$Ar), 2.96-2.84 (m, 2H, CHC**H**$_2$Ar, C**H**CHO), 2.58-2.52 (m, 1H, CHC**H**$_2$CH), 1.86 (dd, *J* = 24.7, 11.6 Hz, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.9, 144.8, 140.0, 134.2, 128.7, 128.0, 127.3, 127.2, 124.2, 48.1, 43.7, 34.1, 25.2; HRMS (ESI-TOF) m/z calculated for $C_{15}H_{15}O_S$ ($[M+H]^+$) 243.0838, found 243.0838; $[\alpha]_D$ +109.2 (*c* = 2.29, CH_2Cl_2, 23 °C); Chiral HPLC analysis of the corresponding alcohol (ADH, 3% EtOH/hexanes, 0.8 mL/min, 214 nm) indicated 90% ee, t_R (minor) = 20.2 min, t_R (major) = 21.5 min. **(5*R*,7*S*)-4,5,6,7-tetrahydro-7-phenylbenzo[*b*]thiophene-5-carbaldehyde (minor diastereomer, characteristic signals)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.72 (s, 1H, C**H**O), 7.25 (d, *J* = 5.2 Hz, 1H, Ar**H**), 6.88 (d, *J* = 5.2 Hz, 1H, Ar**H**), 4.39 (t, *J* = 5.6 Hz, 1H, ArC**H**Ar).

Table 2, entry 1:

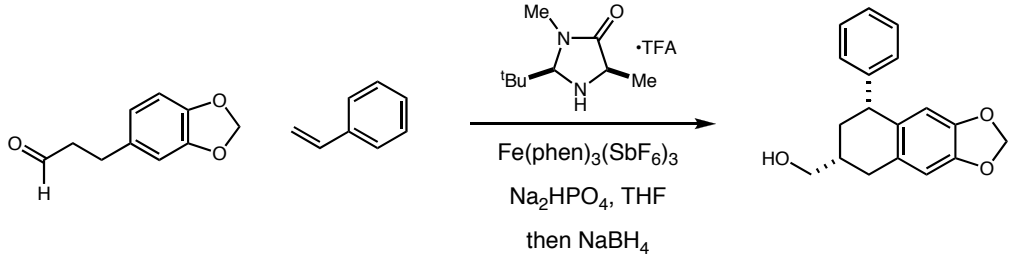


(2*R*,4*R*)-1,2,3,4-tetrahydro-7-methoxy-4-phenylnaphthalene-2-carbaldehyde.

According to the general procedure, 3-(3-methoxyphenyl)propanal (62.0 μL, 0.40 mmol, 1.0 equiv), styrene (137.4 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (1.30 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -10 °C for 12 h to afford a pale yellow oil after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of >20:1 with a regioisomeric ratio of 10.8:1 favoring the *para*-coupled product. Purification by silica gel column chromatography (10% EtOAc/hexanes) afforded (2*R*,4*R*)-1,2,3,4-tetrahydro-7-methoxy-4-phenylnaphthalene-2-carbaldehyde (73.9 mg, 69%) and (2*R*,4*R*)-1,2,3,4-tetrahydro-5-methoxy-4-phenylnaphthalene-2-carbaldehyde (7.5 mg, 7%). **(2*R*,4*R*)-1,2,3,4-tetrahydro-7-methoxy-4-phenylnaphthalene-2-carbaldehyde**: R_f 0.41 (20% EtOAc/hexanes); IR (solid) 2931, 2836, 1722, 1609, 1500, 1263, 1240, 1044, 774 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (d, *J* = 1.2 Hz, 1H, C**H**O), 7.15-7.35 (m, 5H, Ar**H**), 6.72 (s, 1H, Ar**H**), 6.71 (d, *J* = 11.9 Hz, 1H, Ar**H**), 6.6 (d, *J* = 11.9 Hz, 1H, Ar**H**), 4.1 (dd, *J* = 5.5, 11.6 Hz, 1H, ArC**H**Ar), 3.78 (s, 3H, OC**H**$_3$), 3.16-3.0 (m, 2H, ArC**H**$_2$), 2.87 (m, 1H, CHOC**H**), 2.48 (dq, *J* = 2.7, 13.1 Hz, 1H, C**H**$_2$CHAr), 1.78 (dd, *J* = 24.7, 11.9 Hz, 1H, C**H**$_2$CHAr); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.1, 257.9, 146.3, 136.0, 131.5, 130.7, 128.7, 126.3, 112.9, 112.6, 55.3, 47.6, 45.7, 42.7, 33.8, 29.6; HRMS (EI$^+$) m/z calculated for $C_{18}H_{18}O_2$ ([M]$^+$) 266.1304, found 266.1307; $[\alpha]_D$ +40.3 (c = 1.0, $CHCl_3$, 22 °C); Chiral SFC analysis of the corresponding alcohol (ASH, 5-25% MeOH/CO_2, 4.0 mL/min, 220 nm) indicated 94% ee, t_R (minor) = 5.69 min, t_R (major) = 6.02 min. **(2*R*,4*R*)-1,2,3,4-tetrahydro-5-methoxy-4-phenylnaphthalene-2-carbaldehyde (minor regioisomer)**: R_f 0.5 (20% EtoAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (s, 1H, C**H**O), 7.23-7.12 (m, 3H, Ar**H**), 7.13 (t, *J* = 7.6 Hz, 1H, Ar**H**), 6.99 (d, *J* = 7.3 Hz, 2H, Ar**H**), 6.86 (d, *J* = 7.6 Hz, 1H, Ar**H**), 6.67 (d, *J* = 7.9 Hz, 1H, Ar**H**), 4.36 (t, *J* = 7.6 Hz, 1H, ArC**H**Ar),

3.45 (s, 3H, OC**H**$_3$), 3.12 (dd, *J* = 16.5, 4.9 Hz, 1H, ArC**H**$_2$), 2.97 (dd, *J* = 16.5, 4.9 Hz, 1H, ArC**H**$_2$), 2.66 (dddd, *J* = 14.7, 9.5, 4.9, 4.9 Hz, 1H CHOC**H**), 2.58-2.55 (m, 1H, CHC**H**$_2$CH), 1.95 (ddd, *J* = 19.7, 9.8, 8.2 Hz, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.3, 157.8, 147.0, 137.3, 128.2, 127.3 (2C), 127.2, 125.7, 121.5, 108.9, 55.3, 46.7, 40.0, 33.9, 29.0.

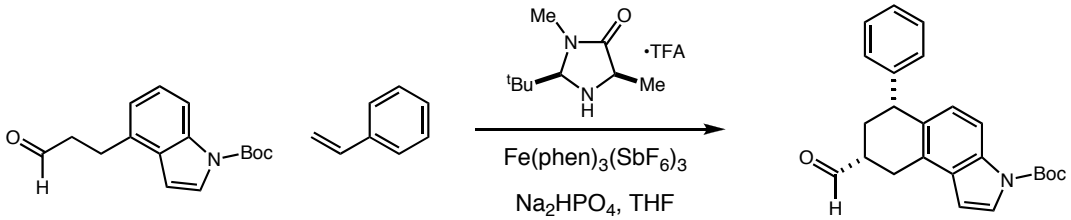
Table 2, entry 2:



((5*R*,7*R*)-5,6,7,8-tetrahydro-5-phenylnaphtho[2,3-*d*][1,3]dioxol-7-yl)methanol.
According to the general procedure, 3-(benzo[*d*][1,3]dioxol-6-yl)propanal (60.4 μL, 0.40 mmol, 1.0 equiv), styrene (137.4 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (1.304 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -10 °C for 12 h to afford the crude title compound as a white solid after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 7.7:1. The crude product was dissolved in 4:1 (CH_2Cl_2:EtOH, 10 ml) and treated with $NaBH_4$ (30.4 mg, 0.8 mmol, 2.0 equiv). Upon complete consumption of the aldehydes as indicated by TLC analysis (R_f 0.37 (15% EtOAc/hexanes)), the reaction was quenched with saturated aqueous NH_4Cl, the product extracted (CH_2Cl_2), dried over Na_2SO_4, filtered, and concentrated to afford a white solid. Purification by silica gel column chromatography (30% EtOAc/hexanes) afforded the ((7*R*)-5,6,7,8-tetrahydro-5-phenylnaphtho[2,3-*d*][1,3]dioxol-7-yl)methanols as an 8.1:1 mixture of diastereomers as a white solid. An analytically pure sample of the major diastereomer was obtained by column chromatography under the conditions outlined above omitting the leading fractions. **((5*R*,7*R*)-5,6,7,8-tetrahydro-5-phenylnaphtho[2,3-*d*][1,3]dioxol-7-yl)methanol**: R_f 0.24 (30% EtOAc/hexanes); IR (solid) 3338, 2915, 1501, 1482, 1376, 1230, 1037, 932, 839 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.3 Hz, 2H, Ar**H**), 7.22 (t, *J* = 7.3 Hz, 1H, Ar**H**), 7.16 (d, *J* = 8.2

Hz, 2H, Ar**H**), 6.60 (s, 1H, Ar**H**), 6.23 (s, 1H, Ar**H**), 5.84 (s, 2H, OC**H**$_2$O), 3.99 (dd, *J* = 11.9, 5.2 Hz, 1H, ArC**H**Ar), 3.67-3.58 (m, 2H, C**H**$_2$OH), 2.85 (dd, *J* = 16.5, 4.9 Hz, 1H, ArC**H**$_2$), 2.60 (dd, *J* = 16.5, 12.5 Hz, 1H, ArC**H**$_2$), 2.24-2.17 (m, 1H, CHC**H**$_2$CH), 2.15-2.05 (m, 1H, C**H**CH$_2$OH), 1.57 (bs, 1H, CH$_2$O**H**), 1.50 (dd app. q, *J* = 12.4 Hz, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 145.8, 145.7, 132.9, 129.5, 128.8, 128.6, 126.4, 109.3, 108.4, 100.7, 67.8, 46.8, 37.7, 37.4, 3.4; HRMS (ESI-TOF) m/z calculated for $C_{18}H_{19}O_3$ ([M+H]$^+$) 283.1329, found *m/z* 283.1328; $[\alpha]_D$ +34.0 (c = 2.43, CH_2Cl_2, 23 °C); Chiral SFC analysis (ASH, 5-25% MeOH/CO_2, 4.0 mL/min, 300 nm) indicated 94% ee, t_R (major) = 7.57 min, t_R (minor) = 7.90 min. **((5*S*,7*R*)-5,6,7,8-tetrahydro-5-phenylnaphtho[2,3-*d*][1,3]dioxol-7-yl)methanol (minor diastereomer, characteristic signals)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.40 (s, 1H, Ar**H**), 6.40 (s, 1H, Ar**H**), 5.88 (dd, *J* = 6.4, 1.2 Hz, 2H, OC**H**$_2$O), 4.18 (t, *J* = 5.2 Hz, 1H, ArC**H**), 3.57-3.52 (m, 2H, C**H**$_2$OH), 2.92 (dd, *J* = 16.2, 5.2 Hz, 1H, ArC**H**$_2$), 2.51 (dd, *J* = 16.2, 10.4 Hz, 1H, ArC**H**$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 43.9, 34.6, 32.7, 31.8.

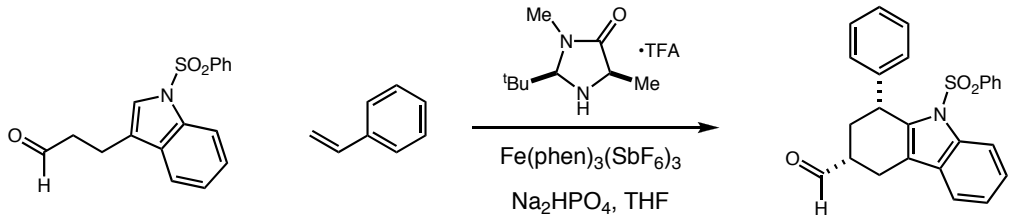
Table 2, entry 3:



(6*R*,8*R*)-*tert*-butyl-8-formyl-6-phenyl-6,7,8,9-tetrahydro-3*H*-benzo[*e*]indole-3-carboxylate. According to the general procedure, *tert*-butyl 4-(3-oxopropyl)-1*H*-indole-1-carboxylate (109.3 mg, 0.40 mmol, 1.0 equiv), styrene (137.4 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (1.30 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -10 °C for 12 h to afford a clear colorless oil after workup. Analysis by ^{1}H NMR using 3,5-bis-trifluoromethylbromobenzene (34.5 μL, 0.2 mmol, 0.5 equiv) indicated 84% conversion with a diastereomeric ratio of >20:1. Purification by silica gel column chromatography (10% EtOAc/hexanes) afforded the title compound as a white solid as a single diastereomer (125.0 mg, 83% yield). R_f 0.39 (20% Ethyl acetate/hexanes); IR (film) 2978, 2930, 1727, 1476, 1427, 1385, 1370, 1344, 1324, 1300,

1288, 1154, 1120, 766, 732, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.83 (d, *J* = 0.9 Hz, 1H, C**H**O), 7.81 (d, *J* = 6.8 Hz, 1H, Ar**H**CN), 7.63 (d, *J* = 2.9 Hz, 1H, Ar**H**N), 7.34-7.31 (m, 2H, Ar**H**), 7.27-7.25 (m, 1H, Ar**H**), 7.19-7.17 (m, 2H, Ar**H**), 6.76 (d, *J* = 8.7 Hz, 1H, Ar**H**), 6.65 (d, *J* = 3.7 Hz, 1H, Ar**H**CHN), 4.28 (dd, *J* = 11.4, 5.3 Hz, 1H, ArC**H**Ar), 3.31 (dd, *J* = 16.5, 4.4 Hz, 1H, ArC$\mathbf{H}_2$), 3.20 (dd, *J* = 16.6, 11.2 Hz, 1H, ArC$\mathbf{H}_2$), 2.98-2.94 (m, 1H, C**H**CHO), 2.59-2.55 (m, 1H, C$\mathbf{H}_2$CHAr$_2$), 1.84 (dd, *J* = 24.7, 12.4 Hz, 1H, C$\mathbf{H}_2$CHAr$_2$), 1.64 (s, 9H, (C$\mathbf{H}_3$)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.1, 149.7, 146.4, 133.1, 133.0, 129.5, 128.7 (2C), 128.6 (2C), 126.9, 126.6, 126.0, 125.9, 113.2, 105.1, 83.7, 47.3, 46.1, 33.9, 28.1 (3C), 26.0; HRMS (ESI-TOF) m/z calculated for $C_{24}H_{26}NO_3$ ([M+H^+) 376.1907, found 376.1908; $[\alpha]_D$ +63.5 (*c* =1.00, CH_2Cl_2, 24 °C); Chiral HPLC analysis of the corresponding alcohol (OD-H, 10% EtOH/hexanes, 1.0mL/min, 254 nm) indicated 94% ee, t_R(major) = 10.5 min, t_R(minor) = 12.7 min.

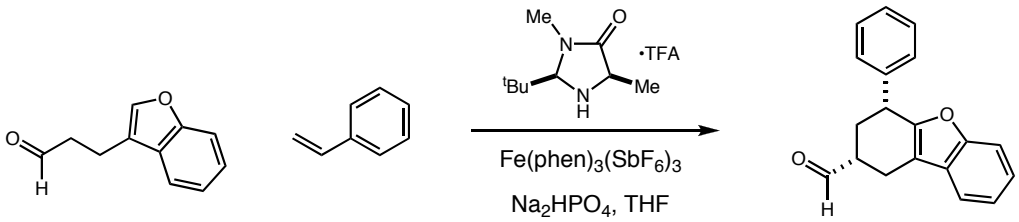
Table 2, entry 4:



(1*R*,3*R*)-1-phenyl-9-(phenylsulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazole-3-carbaldehyde. According to the general procedure, 3-(1-(phenylsulfonyl)-1*H*-indol-3-yl)propanal (125.4 mg, 0.40 mmol, 1.0 equiv), styrene (137.4 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (1.304 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -20 °C for 12 h to afford a clear colorless oil after workup. Analysis by ^1H NMR indicated a diastereomeric ratio of 10.0:1. Purification by silica gel column chromatography (14% EtOAc/hexanes) afforded the title compound as a white solid as a an 8.0:1 mixture of diastereomers (117.0 mg, 70% yield). An analytically pure sample of the major diastereomer was obtained by column chromatography under the conditions outlined above omitting the leading fractions. **(1*R*,3*R*)-1-phenyl-9-(phenylsulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazole-3-carbaldehyde**: R_f 0.49 (50% Ethyl acetates/hexanes); IR (film) 3063, 3028, 2926, 2848, 2721, 1722, 1449, 1368, 1172,

1136, 1090, 969, 910, 750, 726, 686 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.29 (s, 1H, C**H**O), 8.14 (d, *J* = 8.2 Hz, 1H, Ar**H**), 7.52 (d, *J* = 7.4 Hz, 1H, Ar**H**), 7.40-7.35 (m, 4H, Ar**H**), 7.32 (t, *J* = 7.6 Hz, 1H, Ar**H**), 7.19 (t, *J* = 7.6 Hz, 2H, Ar**H**), 7.14-7.08 (m, 3H, Ar**H**), 6.88 (d, *J* = 6.3 Hz, 2H, Ar**H**), 4.90 (t, *J* = 6.0 Hz, 1H, ArC**H**Ar), 3.24 (dd, *J* = 16.7, 5.5 Hz, 1H, ArC$\mathbf{H}_2$), 2.88 (dd, *J* = 16.5, 6.0 Hz, 1H, ArC$\mathbf{H}_2$), 2.77-2.68 (m, 2H, C**H**CHO, C$\mathbf{H}_2$CHAr$_2$), 2.21 (ddd, *J* = 13.1, 6.5, 6.5 Hz, 1H, C$\mathbf{H}_2$CHAr$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.5, 143.3, 138.7, 137.1, 135.8, 133.0, 129.5, 128.8 (2C), 128.4 (2C), 128.2 (2C), 126.7, 126.2 (2C), 124.9, 123.5, 119.4, 118.6, 115.0, 45.2, 39.8, 34.6, 19.7; HRMS (ESI-TOF) m/z calculated for $C_{25}H_{22}NO_3SNa$ ($[M+Na]^+$) 438.1134, found 438.1131; $[\alpha]_D$ -20.5 (*c* = 0.62, CH_2Cl_2, 26 °C); Chiral HPLC analysis of the corresponding alcohol (AS-H, 20% EtOH/hexanes, 1.0mL/min, 254 nm) indicated 92% ee, t_R(major) = 8.6 min, t_R(minor) = 13.7 min.

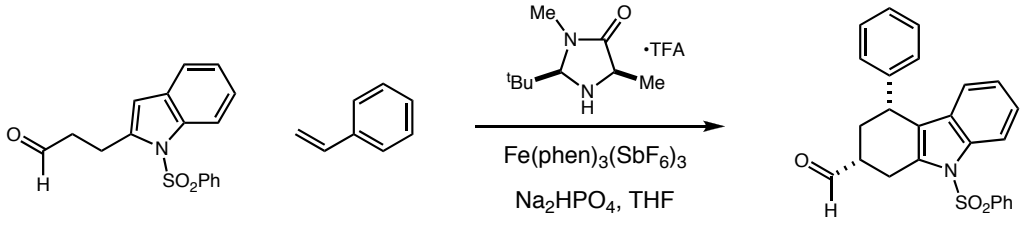
Table 2, entry 5:



(2*R*,7*R*)-4-phenyl-1,2,3,4,4a,9b-hexahydrodibenzo[b,d]furan-2-carbaldehyde:
According to the general procedure, 3-(benzofuran-3-yl)propanal (69.7 mg, 0.40 mmol, 1.0 equiv), styrene (137.4 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (1.30 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -10 °C for 12 h to afford a colorless wax after workup. Analysis by ^1H NMR indicated a diastereomeric ratio of 7.5:1. Purification by silica gel column chromatography (10% EtOAc/hexanes) afforded the (2R)-4-phenyl-1,2,3,4,4a,9b-hexahydrodibenzo[b,d]furan-2-carbaldehydes as a 7.8:1 mixture of diastereomers as a white solid (93.6 mg, 85% yield). An analytically pure sample of the major diastereomer was obtained by column chromatography under the conditions outlined above omitting the leading fractions. **(2*R*,4*R*)-4-phenyl-1,2,3,4,4a,9b-hexahydrodibenzo[b,d]furan-2-carbaldehyde**: R_f 0.22 (10% EtOAc/hexanes); IR (solid) 3029, 2920, 2853, 1723, 1451, 1255, 1177, 1009, 746 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (s, 1H, C**H**O), 7.50-7.46 (m, 1H, Ar**H**), 7.36-7.14 (m, 8H, Ar**H**), 4.25 (dd, *J* = 9.6, 6.0 Hz, 1H, ArC**H**Ar), 3.05-2.85 (m, 3H, ArC**H**$_2$, C**H**CHO), 2.67 (dd, *J* = 13.9, 6.0 Hz, 1H, CHC**H**$_2$CH), 1.86 (dd (app q), *J* = 11.2 Hz, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.4, 155.0, 154.0, 141.4, 128.9, 128.1, 128.0, 127.4, 124.0, 122.6, 118.8, 133.3, 111.4, 47.6, 41.7, 34.3, 20.6; HRMS (ESI-TOF) exact mass calculated for $[M+H]^+$ ($C_{19}H_{17}O_2$) requires *m/z* 277.1223, found *m/z* 277.1222; $[\alpha]_D$ +25.0 (c = 1.85, CH_2Cl_2, 24 °C); Chiral SFC analysis of the corresponding alcohol (ASH, 5-25% MeOH/CO_2, 4.0 mL/min, 254 nm) indicated 93% ee, t_R (minor) = 6.72 min, t_R (major) = 7.28 min. **(2*R*,4*S*)-4-phenyl-1,2,3,4,4a,9b-hexahydrodibenzo[b,d]furan-2-carbaldehyde (minor diastereomer, characteristic signals)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73 (s, 1H, C**H**O), 4.35 (t, *J* = 5.6 Hz, 1H, ArC**H**Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.2, 153.3, 141.9, 127.2, 118.9, 113.5, 43.3, 38.8, 32.6, 20.5.

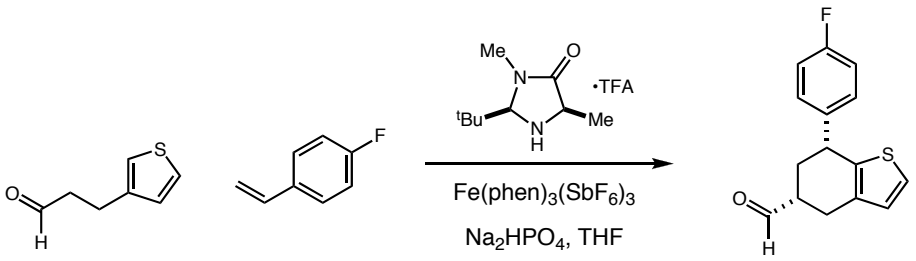
Table 2, entry 6:



(2*R*,4*R*)-4-phenyl-9-(phenylsulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carbaldehyde. According to the general procedure, 3-(1-(phenylsulfonyl)-1*H*-indol-2-yl)propanal (125.4 mg, 0.40 mmol, 1.0 equiv), styrene (137.4 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (1.304 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -20 °C for 12 h to afford a clear colorless oil after workup. Analysis by ^{1}H NMR indicated a diastereomeric ratio of 6.0:1. Purification by silica gel column chromatography (66% CH_2Cl_2/hexanes) afforded the title compound as a white solid as a 6.0:1 mixture of diastereomers (128.0 mg, 77% yield). An analytically pure sample of the major diastereomer was obtained by column chromatography under the conditions outlined above omitting the leading fractions. **(2*R*,4*R*)-4-phenyl-9-(phenylsulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carbaldehyde**: R_f 0.20 (20% ethyl acetates/

hexanes); IR (film) 2927, 1723, 1605, 1448, 1372, 1174, 1148, 1090, 750, 725, 702, 686 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.72 (s, 1H, C**H**O), 8.16 (d, *J* = 8.4 Hz, 1H, Ar**H**), 7.84 (d, *J* = 7.5 Hz, 2H, Ar**H**), 7.59 (t, *J* = 7.5 Hz, 1H, Ar**H**), 7.48 (t, *J* = 8.0 Hz, 2H, Ar**H**), 7.24-7.20 (m, 4H, Ar**H**), 7.00-6.95 (m, 3H, Ar**H**), 6.56 (d, *J* = 7.8 Hz, 1H, Ar**H**), 4.14-4.12 (m, 1H, ArC**H**Ar), 3.47 (dd, *J* = 17.9, 5.4 Hz, 1H, ArC$\mathbf{H}_2$), 3.26 (ddd, *J* = 17.8, 10.2, 2.8 Hz, 1H, ArC$\mathbf{H}_2$), 2.89-2.84 (m, 1H, C**H**CHO), 2.58-2.55 (m, 1H, C$\mathbf{H}_2$CHAr$_2$), 1.73 (ddd, *J* = 13.2, 11.7, 10.2 Hz, 1H, C$\mathbf{H}_2$CHAr$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.9, 143.0, 138.6, 136.9, 134.5, 133.8, 129.3 (2C), 129.0, 128.7 (2C), 127.8 (2C), 126.9, 126.4 (2C), 124.3, 123.3, 120.9, 120.1, 114.5, 47.6, 40.3, 33.9, 24.3; HRMS (ESI-TOF) m/z calculated for $C_{25}H_{22}NO_3S$ ($[M+H]^+$) 416.1315, found 416.1305; $[\alpha]_D$ -46.7 (*c* = 0.3, CH_2Cl_2, 25 °C); Chiral HPLC analysis of the corresponding alcohol (OD-H, 10% EtOH/ hexanes, 1.0mL/ min, 254 nm) indicated 92% ee, t_R(minor) = 22.4 min, t_R(major) = 26.9 min. **(2*R*,4*S*)-4-phenyl-9-(phenylsulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carbaldehyde (minor diastereomer)**: R_f 0.20 (20% Ethyl acetates/hexanes); IR (film) 2922, 1724, 1603, 1491, 1448, 1371, 1174, 1148, 1090, 964, 909, 749, 727, 702, 687 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.71 (s, 1H, C**H**O), 8.18 (d, *J* = 8.4 Hz, 1H, Ar**H**), 7.86 (d, *J* = 7.4 Hz, 2H, Ar**H**), 7.59 (t, *J* = 7.5 Hz, 1H, Ar**H**), 7.48 (t, *J* = 8.0 Hz, 2H, Ar**H**), 7.27-7.22 (m, 4H, Ar**H**), 7.06-7.01 (m, 3H, Ar**H**), 6.83 (d, *J* = 7.7 Hz, 1H, Ar**H**), 4.24 (t, *J* = 5.1 Hz, 1H, ArC**H**Ar), 3.47 (dd, *J* = 18.1, 5.6 Hz, 1H, ArC$\mathbf{H}_2$), 3.29 (dd, *J* = 16.9, 7.1 Hz, 1H, ArC$\mathbf{H}_2$), 2.84-2.82 (m, 1H, C$\mathbf{H}_2$CHO), 2.25-2.19 (m, 2H, C$\mathbf{H}_2$CHAr$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.5, 142.9, 138.7, 136.8, 134.5, 133.8, 129.3 (2C), 129.0, 128.6 (2C), 128.0 (2C), 126.8, 126.4 (2C), 124.4, 123.5, 119.8, 119.4, 114.5, 43.5, 37.1, 32.0, 24.1; HRMS (ESI-TOF) m/z calculated for $C_{25}H_{22}NO_3S$ ($[M+H]^+$) 416.1315, found 416.1306; $[\alpha]_D$ +8.6 (*c* = 0.29, CH_2Cl_2, 25 °C); Chiral HPLC analysis of the corresponding alcohol (OD-H, 10% IPA/ hexanes, 1.0mL/ min, 230 nm) indicated 29% ee, t_R(major) = 20.0 min, t_R(minor) = 24.9 min.

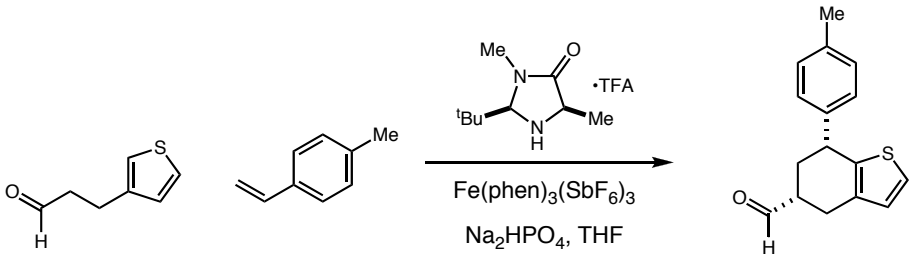
Table 3, entry 1:



(5*R*,7*R*)-7-(4-fluorophenyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carbaldehyde. According to the general procedure, 3-(thiophen-3-yl)propanal (51.0 μL, 0.40 mmol, 1.0 equiv), 4-fluorostyrene (143.7 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (1.304 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -10 °C for 12 h to afford a colorless oil after workup. Analysis by ^{1}H NMR indicated a diastereomeric ratio of 11.0:1. Purification by silica gel column chromatography (5-10% EtOAc/hexanes) afforded the (5*R*)-7-(4-fluorophenyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carbaldehydes as a 12.5:1 mixture of diastereomers as a white solid (82.1 mg, 79% yield). An analytically pure sample of the major diastereomer was obtained by column chromatography under the conditions outlined above omitting the leading fractions. **(5*R*,7*R*)-7-(4-fluorophenyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carbaldehyde**: R_f 0.24 (10% EtOAc/hexanes); IR (film) 2925, 1723, 1605, 1509, 1447, 1223, 1158, 1095, 832, 784, 717 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (d, *J* = 0.92 Hz, 1H, C**H**O), 7.22-7.21 (m, 2H, Ar**H**CN), 7.14 (dd, *J* = 5.2, 1.2 Hz, 1H, Ar**H**), 7.03-6.99 (m, 2H, Ar**H**), 6.84 (d, *J* = 5.2 Hz, 1H, Ar**H**), 4.18 (dd, *J* = 11.6, 5.2 Hz, 1H, ArC**H**Ar), 3.03-3.00 (m, 1H, C**H$_2$**Ar), 2.92-2.83 (m, 2H, C**H$_2$**Ar, C**H**CHO), 2.55-2.51 (m, 1H, C**H**$_2$CHAr$_2$), 1.78 (dd, *J* = 24.4, 11.6 Hz, 1H, C**H**$_2$CHAr$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.6, 161.0, 140.4, 139.7, 134.2, 129.5, 129.4, 127.2, 124.3, 115.5, 115.4, 47.9, 42.9, 34.1, 25.2; HRMS (ESI-TOF) m/z calculated for $C_{15}H_{14}FOS$ ($[M+H]^+$) 261.0744, found 261.0742; $[\alpha]_D$ +59.1 (*c* = 2.26, CH_2Cl_2, 24 °C); Chiral SFC analysis of the corresponding alcohol (IC, 5-10% MeOH/CO_2, 4.0 mL/min, 254 nm) indicated 93% ee, t_R(minor) = 8.41 min, t_R(major) = 8.76 min. **(5*R*,7*S*)-7-(4-fluorophenyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carbaldehyde (minor diastereomer, characteristic signals)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73 (s, 1H, C**H**O), 6.87 (d, *J* = 4.9 Hz, 1H, Ar**H**), 4.34 (t, *J* = 5.5 Hz, 1H, ArC**H**Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.6, 162.7,

140.9, 134.6, 48.0, 43.3, 34.2, 25.0.

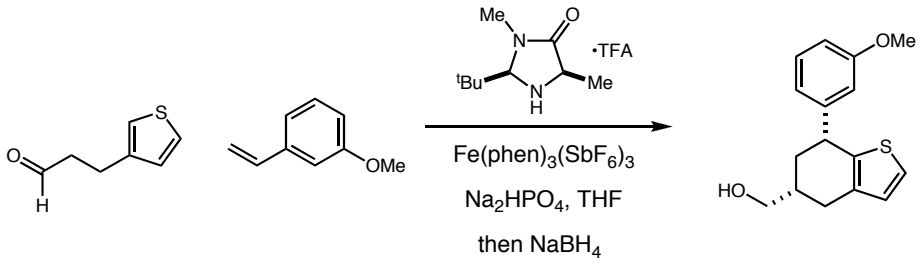
Table 3, entry 2:



(5*R*,7*R*)-4,5,6,7-tetrahydro-7-*p*-tolylbenzo[*b*]thiophene-5-carbaldehyde. According to the general procedure, 3-(thiophen-3-yl)propanal (51.0 μL, 0.40 mmol, 1.0 equiv), 4-methylstyrene (158.3 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (1.30 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -10 °C for 12 h to afford a colorless syrup after workup. Analysis by ^{1}H NMR indicated a diastereomeric ratio of 14.8:1. Purification by silica gel column chromatography (5-10% EtOAc/hexanes) afforded the (5*R*)-4,5,6,7-tetrahydro-7-*p*-tolylbenzo[*b*]thiophene-5-carbaldehydes as a 14.3:1 mixture of diastereomers as a white solid (83.8 mg, 82% yield). An analytically pure sample of the major diastereomer was obtained by column chromatography under the conditions outlined above omitting the leading fractions. **(5*R*,7*R*)-4,5,6,7-tetrahydro-7-*p*-tolylbenzo[*b*]thiophene-5-carbaldehyde**: R_f 0.26 (10% EtOAc/hexanes); IR (film) 2920, 2851, 2719, 1721, 1513, 1446, 964, 814, 716 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (s, 1H, C**H**O), 7.16-7.12 (m, 5H, Ar**H**), 6.84 (d, *J* = 5.2 Hz, 1H, Ar**H**), 4.15 (dd, *J* = 11.0, 4.9 Hz, 1H, ArC**H**Ar), 3.01-2.99 (m, 1H, C**H**$_2$Ar), 2.89-2.86 (m, 2H, C**H**$_2$Ar, C**H**CHO), 2.35 (s, 3H, C**H**$_3$Ar), 2.35-2.33 (m, 1H, C**H**$_2$CHAr$_2$), 1.81 (dd, *J* = 24.4, 11.6 Hz, 1H, C**H**$_2$CHAr$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.9, 141.8, 140.3, 137.0, 134.1, 129.4, 127.9, 127.2, 124.1, 48.1, 43.3, 34.1, 25.3, 21.2; HRMS (ESI-TOF) m/z calculated for $C_{16}H_{17}OS$ ($[M+H]^+$) 257.0995, found 257.0994; $[\alpha]_D$ +65.1 (*c* = 2.02, CH_2Cl_2, 24 °C); Chiral SFC analysis of the corresponding alcohol (AS-H, 5-10% MeOH/CO_2, 4.0 mL/min, 254 nm) indicated 91% ee, t_R(major) = 11.1 min, t_R(minor) = 12.1 min. **(5*R*,7*S*)-4,5,6,7-tetrahydro-7-*p*-tolylbenzo[*b*]thiophene-5-carbaldehyde (minor diastereomer, characteristic signals)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.72 (s,

1H, C**H**O), 6.87 (d, *J* = 5.0 Hz, 1H, Ar**H**), 4.33 (t, *J* = 5.5 Hz, 1H, ArC**H**Ar).

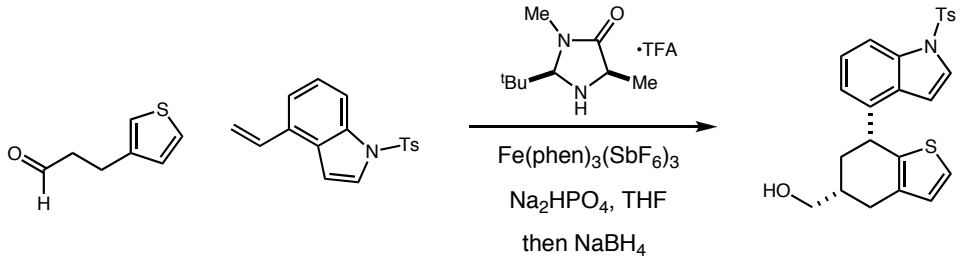
Table 3, entry 3:



((5*R*,7*R*)-4,5,6,7-tetrahydro-7-(3-methoxyphenyl)benzo[*b*]thiophen-5-yl)methanol. According to the general procedure, 3-(thiophen-3-yl)propanal (51.0 μL, 0.40 mmol, 1.0 equiv), 3-methoxystyrene (203.8 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (1.30 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -20 °C for 12 h to afford a colorless solid after workup. Analysis by ^{1}H NMR indicated a diastereomeric ratio of 19.0:1. The crude product was dissolved in 4:1 (CH_2Cl_2:EtOH, 10 ml) and treated with $NaBH_4$ (30.4 mg, 0.8 mmol, 2.0 equiv). Upon complete consumption of the aldehydes as indicated by TLC analysis (R_f 0.30 (15% EtOAc/hexanes)), the reaction was quenched with saturated aqueous NH_4Cl, the product extracted (CH_2Cl_2), dried over Na_2SO_4, filtered, and concentrated to afford a white solid. Purification by silica gel column chromatography (20-30% EtOAc/hexanes) afforded the title compound as a single diastereomer as a white solid (99.2 mg, 90% yield). R_f 0.21 (20% EtOAc/hexanes); IR (film) 3356, 2914, 2835, 1599, 1584, 1486, 1451, 1435, 1261, 1152, 1080, 1039, 781, 764, 723 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 8.4 Hz, 1H, Ar**H**), 7.10 (d, *J* = 5.2 Hz, 1H, Ar**H**), 6.86 (d, *J* = 7.6 Hz, 1H, Ar**H**), 6.81-6.79 (m, 3H, Ar**H**), 4.11 (d, *J* = 11.3 Hz, 1H, ArC**H**Ar), 3.79 (s, 3H, OC**H$_3$**), 3.70-3.63 (m, 2H, C**H$_2$**OH), 2.88 (dd, *J* = 15.9, 4.9 Hz, 1H, C**H$_2$**Ar), 2.46-2.40 (m, 1H, C**H$_2$**Ar), 2.30-2.27 (m, 1H, C**H$_2$**CHAr$_2$), 2.18-2.15 (m, 1H, C**H**CH$_2$OH), 1.60 (q, *J* = 12.3 Hz, 1H, C**H$_2$**CHAr$_2$), 1.46 (bs, 1H, O**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 147.3, 140.1, 135.6, 129.4, 127.1, 123.6, 120.4, 113.7, 112.1, 67.6, 55.2, 44.0, 38.0, 37.6, 28.8; HRMS (ESI-TOF) m/z calculated for $C_{16}H_{18}OS$ ([M+H]$^+$) 275.1100, found 275.1099; $[\alpha]_D$ +58.0 (*c* = 1.87, CH_2Cl_2, 24 °C); Chiral SFC analysis (AS-H, 5-20% iPrOH/CO_2, 4.0 mL/min, 254 nm) indicated 94% ee,

t_R(major) = 6.04 min, t_R(minor) = 6.31 min.

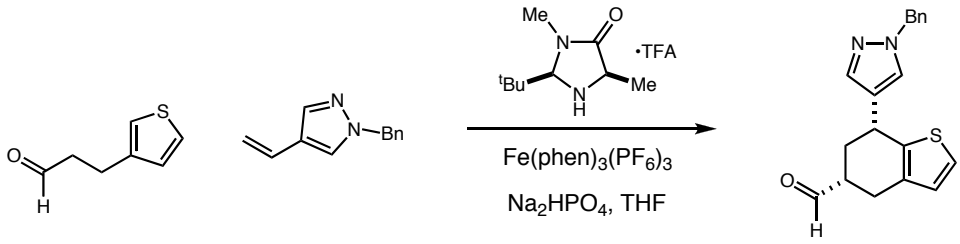
Table 3, entry 4:



((5*R*,7*R*)-4,5,6,7-tetrahydro-7-(1-tosyl-1*H*-indol-4-yl)benzo[*b*]thiophen-5-yl)methanol. According to the general procedure, 3-(thiophen-3-yl)propanal (51.0 μL, 0.40 mmol, 1.0 equiv), 1-tosyl-4-vinyl-1*H*-indole (356.9 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (1.30 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -20 °C for 12 h to afford a colorless solid after workup. Analysis by ^{1}H NMR indicated a diastereomeric ratio of >20:1. The crude product was dissolved in 4:1 (CH_2Cl_2:EtOH, 10 ml) and treated with $NaBH_4$ (30.4 mg, 0.8 mmol, 2.0 equiv). Upon complete consumption of the aldehydes as indicated by TLC analysis (R_f 0.30 (15% EtOAc/hexanes)), the reaction was quenched with saturated aqueous NH_4Cl, the product extracted (CH_2Cl_2), dried over Na_2SO_4, filtered, and concentrated to afford a white solid. Purification by silica gel column chromatography (20-30% EtOAc/hexanes) afforded the title compound as a single diastereomer as a white solid (151.1 mg, 87% yield). R_f 0.12 (15% EtOAc/hexanes); IR (film) 3361, 2921, 2873, 1597, 1423, 1372, 1179, 1165, 1130, 760, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 1H, Ar**H**), 7.77 (d, *J* = 8.2 Hz, 1H, Ar**H**), 7.51 (d, *J* = 3.3 Hz, 1H, Ar**H**), 7.28-7.22 (m, 4H, Ar**H**), 7.12 (d, *J* = 7.3 Hz, 1H, Ar**H**), 7.08 (d, *J* = 4.9 Hz, 1H, Ar**H**), 6.81 (d, *J* = 4.9 Hz, 1H, Ar**H**), 6.42 (bs, 1H, O**H**), 4.47-4.43 (m, 1H, ArC**H**Ar), 3.69 (dd, *J* = 10.7, 6.1 Hz, 1H, C**H**$_2$OH), 3.63 (dd, *J* = 10.7, 6.1 Hz, 1H, C**H**$_2$OH), 2.92 (dd, *J* = 15.9, 4.9 Hz, 1H, ArC**H**$_2$), 2.47 (dd, *J* = 15.3, 11.3 Hz, 1H, ArC**H**$_2$CH), 2.36 (s, 3H, ArC**H**$_3$), 2.30-2.25 (m, 1H, ArC**H**$_2$CH), 2.24-2.16 (m, 1H, C**H**CH$_2$OH), 1.68 (q, *J* = 12.2 Hz, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 139.6, 138.4, 135.7, 135.3, 135.1, 130.0, 127.2, 127.0, 125.9, 124.7, 123.8, 122.5, 112.2, 107.1, 67.6, 38.1, 36.5, 28.9, 21.7; HRMS (ESI-TOF) m/z calculated

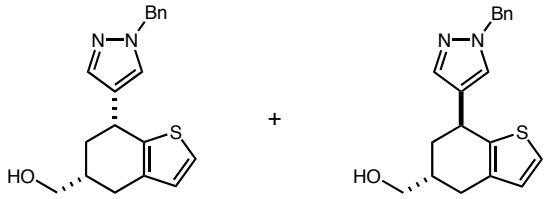
for $C_{24}H_{24}NO_3S_2$ ([M+H]$^+$) 438.1192, found 438.1192; $[\alpha]_D$ +31.0 (*c* = 2.00, CH_2Cl_2, 24 °C); Chiral SFC analysis (OJ-H, 5-50% MeOH/CO_2, 4.0 mL/min, 254 nm) indicated 92% ee, t_R(major) = 6.19 min, t_R(minor) = 7.50 min.

Table 3, entry 5:



(5*R*,7*R*)-7-(1-benzyl-1*H*-pyrazol-4-yl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carbaldehyde and (5*R*,7*S*)-7-(1-benzyl-1*H*-pyrazol-4-yl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carbaldehyde. According to the general procedure, 3-(thiophen-3-yl)propanal (51.0 μL, 0.40 mmol, 1.0 equiv), 1-benzyl-4-vinyl-1*H*-pyrazole (158.3 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (1.03 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -40 °C for 12 h to afford a colorless solid after workup. Analysis by ^{1}H NMR indicated a diastereomeric ratio of 4.0:1.0. Purification by silica gel column chromatography (30% EtOAc/hexanes) afforded the (5*R*)-7-(1-benzyl-1*H*-pyrazol-4-yl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carbaldehydes as an inseparable 4.0:1 mixture of diastereomers as a clear colorless syrup (88.4 mg, 69% yield). **(5*R*,7*R*)-7-(1-benzyl-1*H*-pyrazol-4-yl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carbaldehyde**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (d, *J* = 0.9 Hz, 1H, C**H**O), 7.50 (s, 1H, Ar**H**), 7.38-7.28 (m, 4H, Ar**H**), 7.20 (d, *J* = 7.2 Hz, 2H, Ar**H**), 7.12 (d, *J* = 5.2 Hz, 1H, Ar**H**), 6.81 (d, *J* = 5.2 Hz, 1H, Ar**H**), 5.27 (s, 2H, ArC**H**$_2$N), 4.18 (dd, *J* = 11.3, 4.6 Hz, 1H, ArC**H**Ar), 2.99-2.75 (m, 3H, ArC**H**$_2$CH, C**H**CHO), 2.56-2.50 (m, 1H, CHC**H**$_2$CH), 1.78 (dd (app q), *J* = 11.6 Hz, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.8, 140.1, 138.5, 136.5, 133.3, 128.9, 128.1, 127.7, 127.6, 127.4, 125.4, 123.8, 56.1, 48.0, 33.5 (2C), 25.0. **(5*R*,7*S*)-7-(1-benzyl-1*H*-pyrazol-4-yl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carbaldehyde (minor diastereomer, characteristic signals)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.75 (s, 1H, C**H**O), 7.39 (s, 1H, Ar**H**), 5.25 (s,

2H, ArC**H**$_2$N), 4.29 (t, *J* = 5.2 Hz, 1H, ArC**H**Ar), 2.23 (t, *J* = 6.4 Hz, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.7, 138.2, 133.5, 128.0, 127.1, 126.2, 43.7, 32.2, 30.6. **For the mixture of diastereomers**: R_f 0.19 (30% EtOAc/hexanes); IR (film) 2921, 2844, 1720, 1496, 1446, 1398, 1168, 994, 847, 719, 701, 673 cm^{-1}, HRMS (ESI-TOF) m/z calculated for $C_{19}H_{19}N_2OS$ ($[M+H]^+$) 323.1213, found 323.1215.

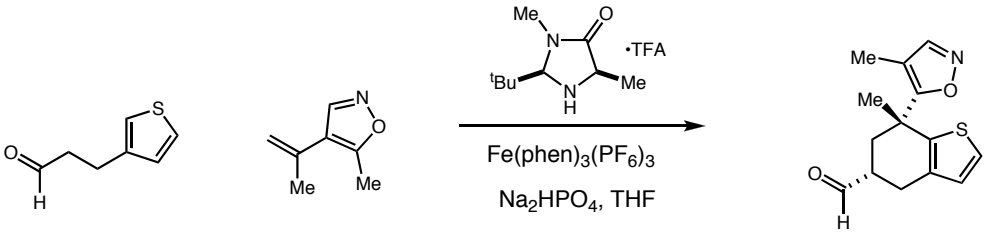


major minor

((5*R*,7*R*)-7-(1-benzyl-1*H*-pyrazol-4-yl)-4,5,6,7-tetrahydrobenzo[*b*]thiophen-5-yl)methanol and ((5*R*,7*S*)-7-(1-benzyl-1*H*-pyrazol-4-yl)-4,5,6,7-tetrahydrobenzo[*b*]thiophen-5-yl)methanol. According to the general procedure, 33.6 mg (0.10 mmol, 1.0 equiv) of the diastereomeric mixture obtained above was dissolved in 4:1 (CH_2Cl_2:EtOH, 10 ml) and treated with $NaBH_4$ (7.6 mg, 0.20 mmol, 2.0 equiv). Upon complete consumption of the aldehydes as indicated by TLC analysis, the reaction was quenched with saturated aqueous NH_4Cl, the product extracted (CH_2Cl_2), dried over Na_2SO_4, filtered, and concentrated to afford a white solid after workup. Purification by silica gel column chromatography (50% EtOAc/hexanes) afforded the alcohols as an inseparable 4.0:1 mixture of diastereomers as a white solid (30.5 mg, 90% yield). Chiral SFC analysis of the mixture (OD-H, 30% iPrOH/CO_2, 4.0 mL/min, 220nm) indicated 90% ee for the major diastereomer (t_R(major) = 4.97 min, t_R(minor) = 6.94 min) and 80% ee for the minor diastereomer (t_R(major) = 3.54 min, t_R(minor) = 3.92 min). Preparative chiral SFC (OD-H, 30% iPrOH/CO_2, 4.0 mL/min) gave an analytically pure sample of each diastereomer, both as clear colorless oils. **((5*R*,7*R*)-7-(1-benzyl-1*H*-pyrazol-4-yl)-4,5,6,7-tetrahydrobenzo[*b*]thiophen-5-yl)methanol (major diastereomer)**: R_f 0.22 (50% EtOAc/hexanes); IR (film) 3345, 2915, 2865, 1455, 1446, 1029, 998, 719, 701 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (s, 1H, Ar**H**), 7.37-7.28 (m, 4H, Ar**H**), 7.20 (d, *J* = 7.3 Hz, 2H, Ar**H**), 7.08 (d, *J* = 4.9 Hz, 1H, Ar**H**), 6.77 (d, *J* = 4.9 Hz, 1H, Ar**H**), 5.27 (s, 2H, ArC**H**$_2$N), 4.15-4.08 (m, 1H, ArC**H**Ar), 3.72-3.62 (m, 2H, C**H**$_2$OH), 2.84 (dd, *J* =

15.9, 5.2 Hz, 1H, ArC**H**$_2$CH), 2.38 (ddd, *J* = 15.4, 14.5, 2.8 Hz, 1H, ArC**H**$_2$CH), 2.31-2.24 (m, 1H, CHC**H**$_2$CH), 2.18-2.06 (m, 1H, C**H**CH$_2$OH), 1.56 (q, *J* = 12.5 Hz, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 138.5, 136.7, 134.8, 128.9, 128.0, 127.6 (2C), 127.5, 126.3, 123.2, 67.5, 56.1, 38.1, 37.2, 33.8, 28.7; HRMS (ESI-TOF) calculated for $C_{19}H_{21}N_2OS$ ([M+H]$^+$) 325.1369, found 325.1368; $[\alpha]_D$ +28.3 (*c* = 1.92, CH_2Cl_2, 24 °C). **((5*R*,7*S*)-7-(1-benzyl-1*H*-pyrazol-4-yl)-4,5,6,7-tetrahydrobenzo[*b*]thiophen-5-yl)methanol (minor diastereomer)**: R_f 0.22 (50% EtOAc/hexanes); IR (film) 3341, 2922, 1455, 1399, 1170, 1076, 1035, 733, 701 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (s, 1H, Ar**H**), 7.36-7.27 (m, 3H, Ar**H**), 7.18 (d, *J* = 7.0 Hz, 2H, Ar**H**), 7.13-7.10 (m, 2H, Ar**H**), 6.77 (d, *J* = 5.2 Hz, 1H, Ar**H**), 5.23 (s, 2H, ArC**H**$_2$N), 4.26 (t, *J* = 4.3 Hz, 1H, ArC**H**Ar), 3.64-3.60 (m, 2H, C**H**$_2$OH), 2.84 (dd, *J* = 16.5, 5.5 Hz, 1H, ArC**H**$_2$CH), 2.39 (dd, *J* = 16.5, 10.4 Hz, 1H, ArC**H**$_2$CH), 2.14-2.05 (m, 1H, C**H**CH$_2$OH), 2.05-1.99 (m, 1H, CHC**H**$_2$CH), 1.96 (dd, *J* = 10.7, 5.5 Hz, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 137.9, 136.7, 134.9, 128.8, 128.0 (2C), 127.6, 127.3, 127.2, 123.3, 67.0, 56.0, 35.0, 33.0, 30.8, 28.6; HRMS (ESI-TOF) calculated for $C_{19}H_{21}N_2OS$ ([M+H]$^+$) 325.1369, found 325.1369; $[\alpha]_D$ -3.18 (*c* = 0.32, CH_2Cl_2, 25 °C).

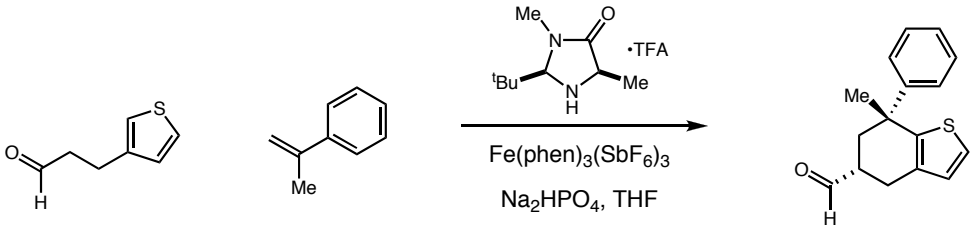
Table 3, entry 6:



(5*S*,7*R*)-4,5,6,7-tetrahydro-7-methyl-7-(5-methylisoxazol-4-yl)benzo[*b*]thiophene-5-carbaldehyde. According to the general procedure, 3-(thiophen-3-yl)propanal (51.0 μL, 0.40 mmol, 1.0 equiv), 5-methyl-4-vinylisoxazole (154.4 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (1.03 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -20 °C for 12 h to afford a colorless syrup after workup. Analysis by ^{1}H NMR indicated a diastereomeric ratio of >20:1. Purification by silica gel column chromatography (15-20%

EtOAc/hexanes) afforded the title compound as a single diastereomer as a clear colorless oil (75.1 mg, 72% yield). R_f 0.39 (30% EtOAc/hexanes); IR (film) 2928, 1721, 1472, 1446, 1229, 1149, 933, 885, 714 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.66 (s, 1H, C**H**O), 8.17 (s, 1H, Ar**H**), 7.18 (d, *J* = 5.2 Hz, 1H, Ar**H**), 6.79 (d, *J* = 5.2 Hz, 1H, Ar**H**), 2.97-2.86 (m, 3H, ArC**H**$_2$CH, C**H**CHO), 2.28 (d, *J* = 12.8 Hz, 1H, CHC**H**$_2$CH), 2.03-1.97 (m, 1H, CHC**H**$_2$CH), 1.91 (s, 3H, ArC**H**$_3$), 1.76 (s, 3H, ArC(C**H**$_3$)Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.2, 165.4, 149.6, 143.0, 133.4, 127.0, 124.3, 122.7, 45.1, 39.5, 35.1, 30.7, 24.8, 11.7; HRMS (EI) m/z calculated for $C_{14}H_{14}NO_2S$ ($[M]^+$) 261.0824, found 261.0825; $[\alpha]_D$ +105.4 (*c* = 2.27, CH_2Cl_2, 25 °C); Chiral SFC analysis of the corresponding alcohol (IC, 25% iPrOH (0.1% $HNEt_2$)/CO_2, 3.0 mL/min, 220 nm) indicated 88% ee, t_R(major) = 2.26 min, t_R(minor) = 3.41 min.

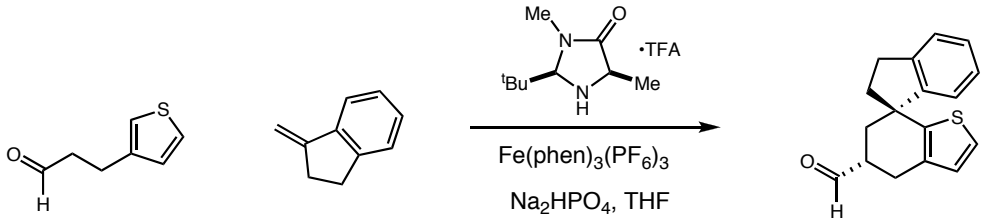
Table 3, entry 7;



(5*S*,7*R*)-4,5,6,7-tetrahydro-7-methyl-7-phenylbenzo[*b*]thiophene-5-carbaldehyde. According to the general procedure, 3-(thiophen-3-yl)propanal (51.0 μL, 0.40 mmol, 1.0 equiv), α-methylstyrene (155.9 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (1.304 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -20 °C for 12 h to afford a colorless syrup after workup. Analysis by ^1H NMR indicated a diastereomeric ratio of >20:1. Purification by silica gel column chromatography (5% EtOAc/hexanes) afforded the title compound as a single diastereomer as a clear colorless oil (92.5 mg, 90% yield). R_f 0.31 (10% EtOAc/hexanes); IR (film) 2969, 2926, 1722, 1495, 1444, 1376, 1027, 980, 761 cm^{-1} ;^1H NMR (500 MHz, $CDCl_3$) δ 9.55 (s, 1H, C**H**O), 7.31-7.26 (m, 4H, Ar**H**), 7.24-7.21 (m, 1H, Ar**H**), 7.17 (d, *J* = 5.2 Hz, 1H Ar**H**), 6.82 (d, *J* = 5.2 Hz, 1H, Ar**H**), 2.97-2.91 (m, 3H, C**H**CHO, C**H**$_2$Ar), 2.28 (dd, *J* = 13.4, 3.4 Hz, 1H, C**H$_2$**CHAr$_2$), 2.18 (dd, *J* = 13.4, 10.1 Hz, 1H, C**H**$_2$CHAr$_2$), 1.82 (s, 3H, C**H$_3$**CAr); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 202.8, 149.1, 145.0, 133.5, 128.1, 126.9, 126.8, 126.6, 123.9, 45.5, 42.0, 41.7, 29.7, 24.8; HRMS (ESI-TOF) m/z calculated for $C_{16}H_{17}OS$ ($[M+H]^+$) 257.0995, found 257.0995; $[\alpha]_D$ +79.6 (*c* = 2.18, CH_2Cl_2, 24 °C); Chiral SFC analysis of the corresponding alcohol (AS-H, 5-25% MeOH/CO_2, 4.0 mL/min, 254 nm) indicated 90% ee, t_R(minor) = 7.04 min, t_R(major) = 8.46 min.

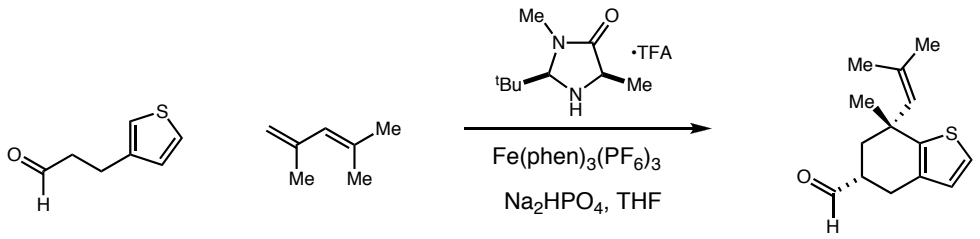
Table 3, entry 8:



(1'*R*,5*S*)-2',3',5,6-tetrahydro-4H-spiro[benzo[b]thiophene-7,1'-indene]-5-carbaldehyde. According to the general procedure, 3-(thiophen-3-yl)propanal (51.0 μL, 0.40 mmol, 1.0 equiv), 2,3-dihydro-1-methylene-1*H*-indene (161.1 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (1.031 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -40 °C for 12 h to afford a colorless solid after workup. Analysis by ^{1}H NMR indicated a diastereomeric ratio of 12.8:1. Purification by silica gel column chromatography (5-7.5% EtOAc/hexanes) afforded the title compound as a single diastereomer as a white solid (77.1 mg, 72% yield). R_f 0.43 (10% EtOAc/hexanes); IR (film) 2925, 2848, 1721, 1477, 1445, 759, 712 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.91 (d, *J* = 1.2 Hz, 1H, C**H**O), 7.31 (d, *J* = 7.4 Hz, 1H, Ar**H**), 7.27 (t, *J* = 7.4 Hz, 1H, Ar**H**), 7.21 (t, *J* = 7.4 Hz, 1H, Ar**H**), 7.17 (d, *J* = 5.1 Hz, 1H, Ar**H**), 7.06 (d, *J* = 7.4 Hz, 1H, Ar**H**), 6.85 (d, *J* = 5.1 Hz, 1H, Ar**H**), 3.08-2.90 (m, 4H, ArC**H**$_2$CH, ArC**H**$_2$CH$_2$, C**H**CHO), 2.84 (dd, *J* = 15.1, 10.8 Hz, 1H, ArC**H**$_2$), 2.43-2.26 (m, 3H, ArCH$_2$C**H**$_2$, CHC**H**$_2$CH), 1.80 (t, *J* = 13.5 Hz, 1H, CHC**H**$_2$CAr$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.2, 150.4, 144.6, 143.1, 133.7, 127.6, 127.0, 126.8, 124.7, 124.0, 123.9, 51.0, 46.2, 42.7, 36.2, 30.1, 25.4; HRMS (ESI-TOF) m/z calculated for $C_{17}H_{17}OS$ ($[M+H]^+$) 269.0995, found 269.0996; $[\alpha]_D$ +122.5 (*c* = 1.76, CH_2Cl_2, 24 °C); Chiral SFC analysis of the corresponding alcohol (OH-H, 5-25% iPrOH/CO_2, 4.0 mL/min, 254 nm) indicated 84% ee, t_R(minor) = 7.05 min, t_R(major) = 8.10 min. **(1'*S*,5*S*)-2',3',5,6-tetrahydro-4H-**

spiro[benzo[b]thiophene-7,1'-indene]-5-carbaldehyde (minor diastereomer, characteristic signals): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.72 (s, 1H, C**H**O), 6.88 (d, *J* = 5.2 Hz, 1H, Ar**H**), 1.89 (t, *J* = 12.3 Hz, 1H, CHC**H**$_2$CAr$_2$).

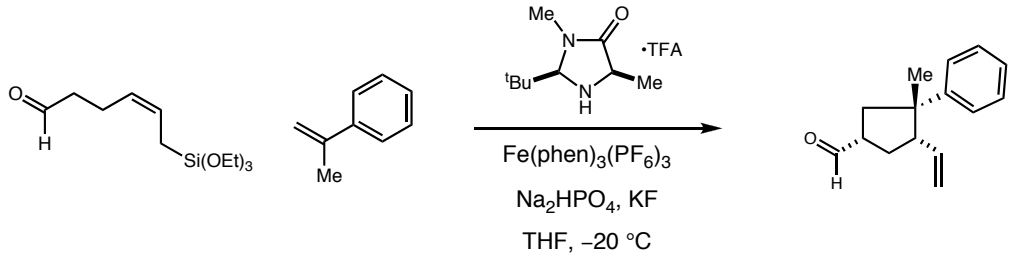
Table 3, entry 9:



(5*S*,7*R*)-4,5,6,7-tetrahydro-7-methyl-7-(2-methylprop-1-enyl)benzo[*b*]thiophene-5-carbaldehyde. According to the general procedure, 3-(thiophen-3-yl)propanal (51.0 μL, 0.40 mmol, 1.0 equiv), 2,4-dimethyl-1,3-pentadiene (155.2 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (1.031 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -20 °C for 12 h to afford a colorless syrup after workup. Analysis by ^{1}H NMR indicated a diastereomeric ratio of 5.5:1. Purification by silica gel column chromatography (5% Et_2O/hexanes) afforded the (5*S*)-4,5,6,7-tetrahydro-7-methyl-7-(2-methylprop-1-enyl)benzo[*b*]thiophene-5-carbaldehydes as a 5.4:1 mixture of diastereomers as a clear colorless oil (80.9 mg, 86% yield). **(5*S*,7*R*)-4,5,6,7-tetrahydro-7-methyl-7-(2-methylprop-1-enyl)benzo[*b*]thiophene-5-carbaldehyde**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (d, *J* = 1.1 Hz, 1H, C**H**O), 7.17 (d, *J* = 5.2 Hz, 1H, Ar**H**), 6.77 (d, *J* = 5.2 Hz, 1H, Ar**H**), 5.20 (m, 1H, $(CH_3)_2$CC**H**), 2.90 (dd, *J* = 15.0, 4.6 Hz, 1H, ArC**H**$_2$), 2.86-2.78 (m, 1H, C**H**CHO), 2.5 (dd, *J* = 15.0, 10.7 Hz, 1H, ArC**H**$_2$), 2.21 (dq, *J* = 12.8, 1.5 Hz, 1H, CHOCHC**H**$_2$CAr), 1.68 (d, *J* = 1.2 Hz, 3H, (C**H**$_3$)$_2$CCH), 1.58 (t, *J* = 12.8 Hz, 1H, CHOCHC**H**$_2$CAr), 1.50 (s, 3H, ArCC**H**$_3$), 1.15 (d, *J* = 1.2 Hz, 3H, (C**H**$_3$)$_2$CCH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.9, 144.7, 133.2, 132.9, 132.4, 127.0, 123.6, 45.2, 39.6, 38.8, 32.7, 28.7, 25.3, 16.7. **(5*S*,7*S*)-4,5,6,7-tetrahydro-7-methyl-7-(2-methylprop-1-enyl)benzo[*b*]thiophene-5-carbaldehyde (minor diastereomer, characteristic signals)**: ^{1}H NMR (500MHz, $CDCl_3$) δ 9.77 (d, *J* = 0.8 Hz, 1H, C**H**O), 7.10 (d, *J* = 5.2 Hz, 1H, Ar**H**), 6.71 (d, *J* = 5.2 Hz, 1H, Ar**H**), 5.53-5.50 (m, 1H, $(CH_3)_2$CC**H**), 2.09 (d, *J*

= 13.2 Hz, 1H, CHOCHC**H**$_2$CAr), 1.87 (t, *J* = 12.6 Hz, 1H, CHOCHC**H**$_2$CAr), 1.85 (s, 3H, (C**H**$_3$)$_2$CCH), 1.45 (s, 3H, ArCC**H**$_3$), 1.23 (s, 3H, (C**H**$_3$)$_2$CCH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.5, 135.3, 133.9, 131.8, 126.6, 123.2, 114.8, 37.4, 33.6, 27.1, 25.1, 18.4. **For the mixture of diastereomers**: R_f 0.44 (10% EtOAc/hexanes); IR (film) 2920, 1723, 1446, 977, 836; HRMS (ESI-TOF) m/z calculated for $C_{14}H_{19}OS$ ($[M+H]^+$) 235.1151, found 235.1151. Chiral SFC analysis (OJ-H, 5% (isopropanol/heptane)/CO_2, 3.0 mL/min, 220 nm) of the corresponding mixture of alcohols indicated 70% ee for the major diastereomer (t_R(minor) = 2.36 min, t_R(major) = 3.01 min).

Equation 3:

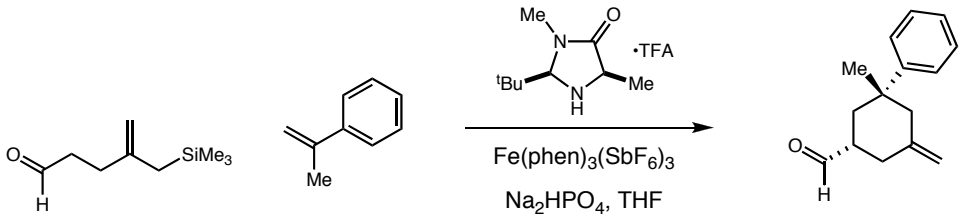


(1*S*,3*S*,4*S*)-3-methyl-3-phenyl-4-vinylcyclopentanecarbaldehyde:

According to the general procedure, 6-(triethoxysilyl)hex-4-enal (104.2 mg, 0.40 mmol, 1.0 equiv), prop-1-en-2-ylbenzene (155.9 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (1.03 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -20 °C for 12 h to afford a colorless oil after workup. Analysis by ^{1}H NMR indicated a diastereomeric ratio of 80:11:9:<5. Purification by silica gel column chromatography (5% EtOAc/hexanes) afforded the **(1*S*)-3-methyl-3-phenyl-4-vinylcyclopentanecarbaldehydes** as a 80:11:9 mixture of diastereomers as a clear colorless oil (58.3 mg, 68% yield). **(1*S*,3*S*,4*S*)-3-methyl-3-phenyl-4-vinylcyclopentanecarbaldehyde**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (s, 1H, C**H**O), 7.30-7.27 (m, 2H, Ar**H**), 7.21-7.17 (m, 3H, Ar**H**), 5.25 (ddd, *J* = 17.1, 10.3, 8.3 Hz, 1H, CHC**H**CH$_2$), 4.91 (ddd, *J* = 17.1, 1.8, 1.2 Hz, 1H, CHC**H**$_2$), 4.80 (ddd, *J* = 10.3, 1.8. 0.9 Hz, 1H, CHC**H**$_2$), 3.12-3.04 (m, 1H, CHOC**H**), 2.81-2.77 (m, 1H, C**H**CHCH$_2$), 2.49 (dd, *J* = 12.9, 9.0 Hz, 1H, C**H**$_2$CHCHO), 2.38 (ddd, *J* = 13.8, 10.5, 7.1 Hz, 1H, C**H**$_2$CHO), 2.07 (dd, *J* = 13.1, 9.1 Hz, 1H, C**H**$_2$CHCHO), 1.98 (ddd, *J* = 13.8, 6.5, 4.6 Hz, 1H, C**H**$_2$CHO), 1.39 (s, 3H, CC**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.4,

146.5, 139.9, 127.9, 127.2, 125.8, 114.9, 53.6, 49.1, 38.0, 36.4, 31.1, 30.1. **(1*S*)-3-methyl-3-phenyl-4-vinylcyclopentanecarbaldehyde (minor diastereomers, characteristic signals)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (s, 0.1H, C**H**O), 9.72 (s, 0.1H, C**H**O), 5.81-5.73 (m, 0.2H, ArC**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.5, 203.1. **For the mixture of diastereomers:** R_f 0.39 (10% EtOAc/hexanes); IR (solid) 2961, 1721, 1684, 1638, 1601, 1497, 1445, 1377, 1084, 1030, 995, 914, 765, 700 cm^{-1}; HRMS (ESI-TOF) exact mass calculated for $[M+Na]^+$ ($C_{15}H_{18}NaO$) requires *m/z* 237.1250, found *m/z* 237.1250. Chiral SFC analysis (AD-H, 5% (0.1% Et_2NH/MeOH)/CO_2, 3.0 mL/min, 220 nm) of the corresponding mixture of alcohols indicated 88% ee for the major diastereomer (t_r (major) = 3.32 min, t_R (minor) = 3.96 min).

Equation 4:

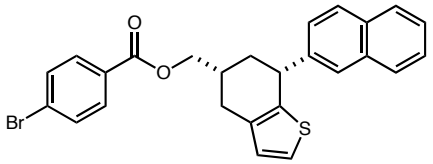


(1*S*,3*S*)-3-methyl-5-methylene-3-phenylcyclohexanecarbaldehyde. According to the general procedure, 4-((trimethylsilyl)methyl)pent-4-enal (80.1 μL, 0.40 mmol, 1.0 equiv), styrene (137.4 μL, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (1.304 g, 1.00 mmol, 2.5 equiv), anhydrous potassium fluoride[20] (34.9 mg, 0.60 mmol, 1.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -20 °C for 12 h to afford a colorless oil after workup. Analysis by ^{1}H NMR indicated a diastereomeric ratio of 4.0:1. Purification by silica gel column chromatography (3-5% Et_2O/hexanes) afforded the (1*S*)-3-methyl-5-methylene-3-phenylcyclohexanecarbaldehydes as a 4.0:1 mixture of diastereomers as a clear colorless oil (63.2 mg, 74% yield). **(1*S*,3*S*)-3-methyl-5-methylene-3-phenylcyclohexanecarbaldehyde**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (d, *J* = 1.5 Hz, 1H, C**H**O), 7.42 (d, *J* = 7.9 Hz, 2H, Ar**H**), 7.35 (t, *J* = 8.2 Hz, 2H, Ar**H**), 7.23 (t, *J* = 7.3 Hz, 1H, Ar**H**), 4.94 (s, 1H, C**H**$_2$=C$(CH_2)_2$), 4.84 (s, 1H, C**H**$_2$=C$(CH_2)_2$), 2.72-2.58 (m,

[20] The use of KF was found to increase reaction efficiency, presumably by sequestering TMS cation.

2H, CHOCHC**H**$_2$C=CH$_2$), 2.42 (s, 2H, ArC(CH$_3$)C**H**$_2$C=CH$_2$), 2.18-2.03 (m, 2H, CHOC**H**, CHOCHC**H**$_2$CAr), 1.69 (t, *J* = 12.8 Hz, 1H, CHOCHC**H**$_2$CAr), 1.26 (s, 3H, ArCC**H**$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 203.7, 150.0, 143.8, 128.4, 126.2, 125.1, 111.9, 47.6, 46.3, 37.8, 37.4, 33.9, 24.5. **(1*S*,3*R*)-3-methyl-5-methylene-3-phenylcyclohexanecarbaldehyde (minor diastereomer, characteristic signals)**: ^{1}H NMR (500 MHz CDCl$_3$) δ 9.63 (d, *J* = 0.9 Hz, 1H, C**H**O), 7.39 (d, *J* = 7.6 Hz, 2H, Ar**H**), 7.31 (t, *J* = 7.6 Hz, 2H, Ar**H**), 7.18 (t, *J* = 7.3 Hz, 1H, Ar**H**), 3.0 (d, *J* = 14.0 Hz, 1H), 2.50-2.46 (m, 1H), 1.29 (s, 3H, ArCC**H**$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 203.8, 146.1, 143.4, 126.4, 125.9, 47.2, 45.3, 38.6, 34.0, 33.8. **For the mixture of diastereomers**: R_f 0.50 (10% EtOAc/hexanes); IR (film) 2928, 1725, 1497, 1444, 1263; HRMS (ESI-TOF) m/z calculated for $C_{15}H_{19}O$ ([M+H]$^+$) 215.1430, found 215.1431; Chiral HPLC analysis (OJ-H, 2% (iPrOH)/hexanes, 1.0 mL/min, 214 nm) of the corresponding mixture of alcohols indicated 89% ee for the major diastereomer (t_r (major) = 25.5 min, t_R (minor) = 26.4 min) and 85% ee for the minor diastereomer (t_r (major) = 22.7 min, t_R (minor) = 28.8 min).

6. Proof of absolute configuration

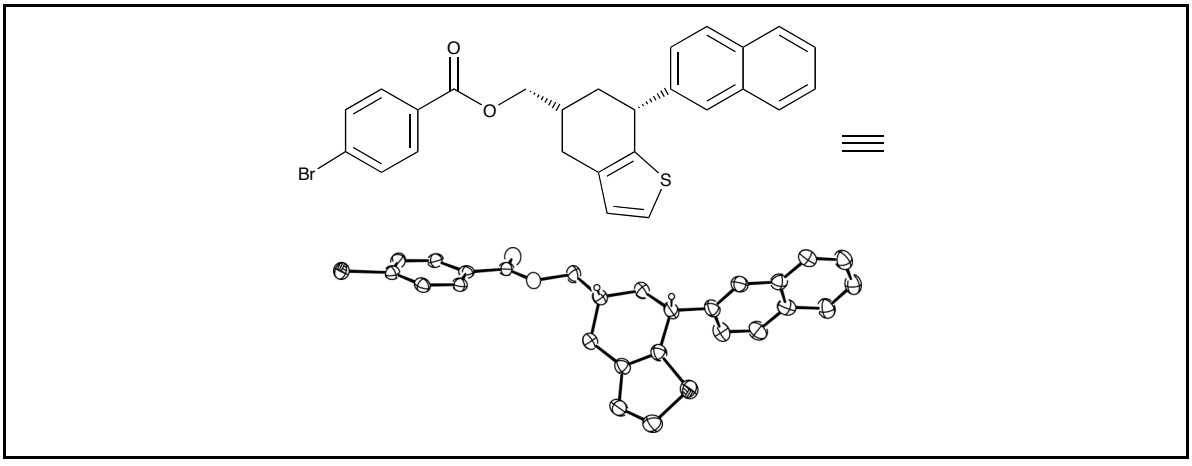


X-ray crystal structure obtained

(5*R*,7*R*)-7-(naphthalen-2-yl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carbaldehyde. According to the general procedure, 3-(thiophen-3-yl)propanal (56.1 mg, 0.40 mmol, 1.0 equiv), 2-vinylnapthalene (185.0 mg, 1.20 mmol, 3.0 equiv), catalyst **1** (22.7 mg, 0.08 mmol, 0.20 equiv), Fe(phen)$_3$(SbF$_6$)$_3$ (1.304 g, 1.00 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 1.0 equiv) in THF (5.3 mL) were stirred at -10 °C for 12 h to afford a white solid after workup. Analysis by ^{1}H NMR indicated a diastereomeric ratio of >20:1. Purification by silica gel column chromatography (5% EtOAc/ hexanes) afforded a 20.0:1 mixture of diastereomers as a white solid (88.0 mg, 75% yield). An analytically pure sample of the major diastereomer was obtained by column chromatography under

the conditions outlined above omitting the leading fractions. A sample of the diastereomerically pure aldehyde (63.0 mg, 0.215 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (4.0 mL) and $NaBH_4$ (15.2 mg, 0.4 mmol, 2.0 equiv) was added followed by EtOH (1.0 mL). Upon complete consumption of the aldehyde, saturated aqueous NH_4Cl (5 mL) was added, the product extracted with CH_2Cl_2, organics dried over Na_2SO_4, filtered, and concentrated. Purification by silica gel column chromatography (15% EtOAc/hexanes) afforded the corresponding alcohol as a white solid (46.2 mg, 73%) which was dissolved in CH_2Cl_2 (1.7 mL) and treated with NEt_3 (26.0 μL, 0.19 mmol, 1.2 equiv), DMAP (5.7 mg, 0.05 mmol, 0.3 equiv), and 4-bromobenzoyl chloride (24.8 μL, 0.19 mmol, 1.2 equiv). After stirring at room temperature for 1 h, the reaction mixture was quenched with H_2O (2 mL), extracted with CH_2Cl_2, the extracts dried over Na_2SO_4, filtered, and concentrated to a white solid. Purification by silica gel column chromatography (10% EtOAc/hexanes) afforded the title compound as a white solid. Recrystallization from EtOAc/hexanes (slow evaporation technique) afforded crystals suitable for X-ray crystallographic analysis (see data below).

X-ray Structure Determination of Compound (5*R*,7*R*)-7-(naphthalen-2-yl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carbaldehyde



Compound 99109, $C_{26}H_{21}SO_2Br$, crystallizes in the orthorhombic space group $P2_12_12_1$ (systematic absences h00: h=odd, 0k0: k=odd, and 00l: l=odd) with a=6.9696(7)Å, b=10.6475(11)Å, c=29.860(3)Å, V=2215.8(4)Å^3, Z=4, and d_{calc}=1.431 g/cm^3 . X-ray intensity

data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at a temperature of 150(1)K. Preliminary indexing was performed from a series of twelve 0.5° rotation images with exposures of 30 seconds. A total of 990 rotation images were collected with a crystal to detector distance of 35 mm, a 2θ swing angle of -12°, rotation widths of 0.5° and exposures of 30 seconds: scan no. 1 was a ϕ-scan from 45° to 225° at ω = 10° and χ = 20°; scan no. 2 was a ϕ-scan from 195° to 390° at ω = 0° and χ = -30°; scan no. 3 was an ω-scan from -20° to 20° at χ = -90° and ϕ = 0°; scan no. 4 was an ω-scan from -20° to 20° at χ = -90° and ϕ = 120°; scan no. 5 was an ω-scan from -20° to 20° at χ = -90° and ϕ = 240°. Rotation images were processed using CrystalClear[i], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the CrystalStructure[ii] program package for further processing and structure solution on a Dell Pentium 4 computer. A total of 31556 reflections were measured over the ranges $2.73 \leq \theta \leq 27.48°$, $-9 \leq h \leq 7$, $-13 \leq k \leq 13$, $-38 \leq l \leq 38$ yielding 5048 unique reflections (Rint = 0.0363). The intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB[iii] (minimum and maximum transmission 0.8061, 1.0000).

The structure was solved by direct methods (SIR97[iv]). Refinement was by full-matrix least squares based on F^2 using SHELXL-97.[v] All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ 0.0685P^2 + 0.5104P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0488 and wR2=0.1237 for 4339 observed reflections for which $F > 4\sigma(F)$ and R1=0.0582 and wR2=0.1306 and GOF =1.084 for all 5048 unique, non-zero reflections and 273 variables.[vi] The maximum Δ/σ in the final cycle of least squares was 0.532 and the two most prominent peaks in the final difference Fourier were +0.582 and -0.537 e/Å^3. The Flack absolute structure parameter[vii] refined to a value of 0.000(11) which corroborates the assignment of the absolute structure (the correct enantiomer will have a Flack parameter of 0; the incorrect enantiomer will have a Flack

parameter of 1).

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2. and 3. Anisotropic thermal parameters are in Table 4. Tables 5. and 6. list bond distances and bond angles. Figure 1. is an ORTEP[viii] representation of the molecule with 30% probability thermal ellipsoids displayed.

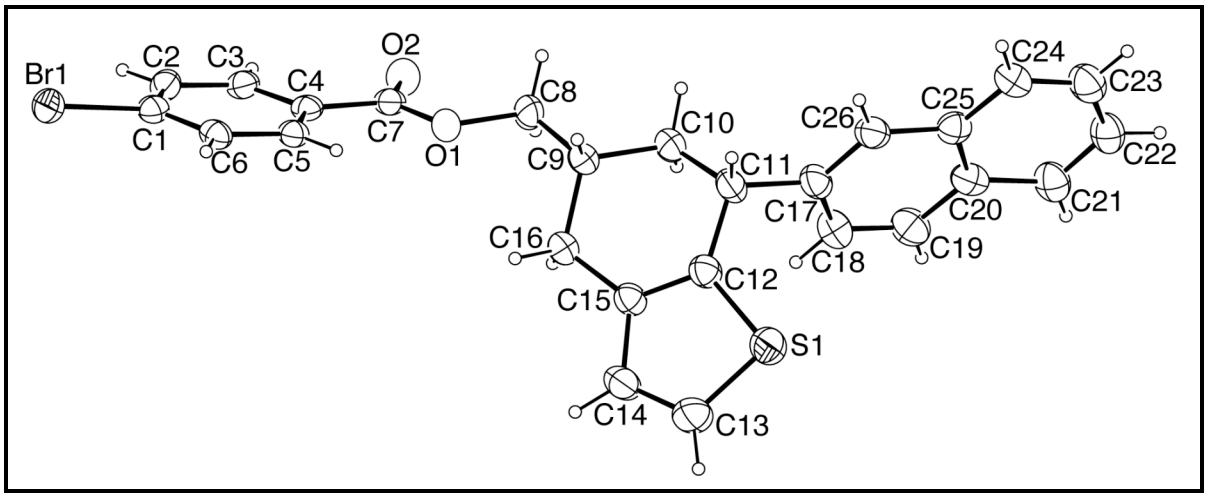


Figure 1. ORTEP drawing of the title compound with 30% probability thermal ellipsoids.

Table 1. Summary of Structure Determination of Compound 99109

Empirical formula	$C_{26}H_{21}SO_2Br$
Formula weight	477.40
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Cell constants:	
a	6.9696(7) Å
b	10.6475(11) Å
c	29.860(3) Å
Volume	2215.8(4) $Å^3$
Z	4
Density (calculated)	1.431 Mg/m^3
Absorption coefficient	1.969 mm^{-1}
F(000)	976
Crystal size	0.38 x 0.15 x 0.12 mm^3
Theta range for data collection	2.73 to 27.48°
Index ranges	$-9 \le h \le 7$, $-13 \le k \le 13$, $-38 \le l \le 38$
Reflections collected	31556
Independent reflections	5048 [R(int) = 0.0363]
Completeness to theta = 27.48°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8061
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5048 / 0 / 273
Goodness-of-fit on F^2	1.084
Final R indices [I>2sigma(I)]	R1 = 0.0488, wR2 = 0.1237
R indices (all data)	R1 = 0.0582, wR2 = 0.1306
Absolute structure parameter	0.000(11)
Largest diff. peak and hole	0.582 and -0.537 $e.Å^{-3}$
Flack Absolute Structure Parameter	0.000(11)

Table 2. Refined Positional Parameters for Compound 99109

Atom	x	y	z	U_{eq},Å^2
C1	0.2799(5)	0.1655(3)	0.47017(12)	0.0485(8)
C2	0.2933(5)	0.2473(3)	0.43429(12)	0.0510(8)
C3	0.2910(5)	0.3753(3)	0.44239(12)	0.0486(8)
C4	0.2758(5)	0.4208(3)	0.48584(11)	0.0425(7)
C5	0.2669(5)	0.3370(3)	0.52166(12)	0.0440(7)
C6	0.2692(5)	0.2080(3)	0.51387(12)	0.0484(7)
C7	0.2631(5)	0.5597(3)	0.49238(11)	0.0452(7)
C8	0.2136(6)	0.7255(3)	0.54363(13)	0.0587(9)
C9	0.2469(5)	0.7504(3)	0.59250(12)	0.0501(8)
C10	0.2104(7)	0.8905(4)	0.60143(14)	0.0612(10)
C11	0.2273(6)	0.9235(4)	0.65128(13)	0.0558(9)
C12	0.4123(6)	0.8691(4)	0.66896(13)	0.0547(9)
C13	0.7047(8)	0.8116(5)	0.71099(15)	0.0832(14)
C14	0.6833(7)	0.7427(5)	0.67283(16)	0.0732(13)
C15	0.5125(6)	0.7758(4)	0.64890(12)	0.0512(8)
C16	0.4537(5)	0.7170(3)	0.60525(12)	0.0503(8)
C17	0.2206(7)	1.0672(4)	0.65764(12)	0.0604(10)
C18	0.3790(7)	1.1425(4)	0.64382(16)	0.0680(11)
C19	0.3773(7)	1.2713(5)	0.64946(16)	0.0706(12)
C20	0.2211(6)	1.3291(4)	0.66961(12)	0.0587(9)
C21	0.2255(7)	1.4649(4)	0.67911(14)	0.0680(11)
C22	0.0678(7)	1.5166(4)	0.69834(14)	0.0663(11)
C23	-0.0916(8)	1.4429(5)	0.70965(17)	0.0740(12)
C24	-0.1007(6)	1.3182(4)	0.70225(15)	0.0659(11)
C25	0.0552(6)	1.2604(4)	0.68250(12)	0.0537(9)
C26	0.0660(6)	1.1243(4)	0.67513(14)	0.0588(10)
O1	0.2482(4)	0.5919(2)	0.53526(8)	0.0504(5)
O2	0.2637(4)	0.6335(2)	0.46188(9)	0.0600(6)
S1	0.5215(2)	0.91718(13)	0.71802(4)	0.0765(4)
Br1	0.27215(6)	-0.00930(3)	0.459065(16)	0.06607(16)

$U_{eq}={}^1/_3[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha]$

Table 3. Positional Parameters for Hydrogens in Compound 99109

Atom	x	y	z	U_{iso},Å^2
H2	0.3037	0.2168	0.4052	0.068
H3	0.2997	0.4312	0.4186	0.065
H5	0.2595	0.3673	0.5508	0.058
H6	0.2636	0.1516	0.5376	0.064
H8a	0.0828	0.7471	0.5356	0.078
H8b	0.3001	0.7761	0.5257	0.078
H9	0.1577	0.6998	0.6104	0.067
H10a	0.3023	0.9400	0.5846	0.081
H10b	0.0830	0.9123	0.5909	0.081
H11	0.1195	0.8856	0.6674	0.074
H13	0.8066	0.8024	0.7308	0.111
H14	0.7695	0.6814	0.6634	0.097
H16a	0.4657	0.6265	0.6076	0.067
H16b	0.5397	0.7453	0.5818	0.067
H18	0.4853	1.1044	0.6308	0.090
H19	0.4807	1.3193	0.6398	0.094
H21	0.3324	1.5133	0.6722	0.090
H22	0.0655	1.6024	0.7041	0.088
H23	-0.1965	1.4821	0.7229	0.098
H24	-0.2089	1.2723	0.7102	0.088
H26	-0.0392	1.0753	0.6829	0.078

Table 4. Refined Thermal Parameters (U's) for Compound 99109

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0370(16)	0.0444(17)	0.064(2)	-0.0022(14)	-0.0050(15)	-0.0023(14)
C2	0.0479(19)	0.0514(18)	0.054(2)	-0.0084(15)	-0.0007(16)	-0.0047(16)
C3	0.0415(18)	0.0520(18)	0.0522(19)	0.0000(15)	-0.0074(14)	-0.0036(16)
C4	0.0323(15)	0.0411(15)	0.0542(18)	0.0052(13)	-0.0053(14)	-0.0043(14)
C5	0.0351(16)	0.0450(16)	0.0518(17)	0.0007(13)	-0.0026(14)	0.0006(14)
C6	0.0380(17)	0.0429(16)	0.064(2)	0.0062(14)	0.0013(15)	0.0005(15)
C7	0.0372(18)	0.0439(16)	0.0545(19)	0.0029(14)	-0.0079(15)	-0.0003(15)
C8	0.072(2)	0.0389(16)	0.065(2)	-0.0038(15)	-0.015(2)	0.0093(16)
C9	0.050(2)	0.0446(17)	0.0558(19)	0.0015(13)	-0.0023(16)	0.0070(16)
C10	0.065(2)	0.0509(19)	0.068(2)	-0.0071(17)	-0.0124(19)	0.0158(19)
C11	0.055(2)	0.0522(19)	0.060(2)	-0.0036(15)	0.0034(18)	0.0144(19)
C12	0.056(2)	0.060(2)	0.048(2)	-0.0019(17)	0.0003(16)	0.0087(18)
C13	0.082(3)	0.107(4)	0.061(3)	-0.012(2)	-0.020(2)	0.025(3)
C14	0.063(3)	0.085(3)	0.072(3)	-0.009(2)	-0.008(2)	0.027(2)
C15	0.052(2)	0.055(2)	0.0463(19)	0.0015(15)	0.0023(15)	0.0080(17)
C16	0.052(2)	0.0458(18)	0.053(2)	0.0018(15)	0.0023(15)	0.0057(16)
C17	0.064(2)	0.068(2)	0.0485(19)	-0.0088(17)	-0.0022(18)	0.020(2)
C18	0.068(3)	0.064(3)	0.071(3)	-0.002(2)	0.009(2)	0.012(2)
C19	0.061(3)	0.077(3)	0.073(3)	0.003(2)	0.011(2)	0.004(2)
C20	0.053(2)	0.081(3)	0.0419(18)	0.0051(16)	0.0023(16)	0.010(2)
C21	0.084(3)	0.057(2)	0.064(2)	0.0104(17)	-0.001(2)	0.011(2)
C22	0.084(3)	0.049(2)	0.066(2)	0.0055(19)	0.002(2)	0.006(2)
C23	0.079(3)	0.064(3)	0.079(3)	0.005(2)	-0.003(2)	0.015(2)
C24	0.055(2)	0.070(3)	0.073(3)	0.001(2)	0.0018(19)	0.010(2)
C25	0.055(2)	0.062(2)	0.0447(19)	0.0019(16)	-0.0026(15)	0.0005(18)
C26	0.053(2)	0.068(2)	0.055(2)	-0.0021(19)	-0.0043(17)	0.0084(19)
O1	0.0583(15)	0.0376(11)	0.0554(13)	-0.0013(9)	-0.0060(12)	0.0049(10)
O2	0.0778(18)	0.0423(12)	0.0600(14)	0.0085(11)	-0.0069(17)	0.0011(12)
S1	0.0819(8)	0.0923(8)	0.0552(6)	-0.0159(6)	-0.0093(5)	0.0229(7)
Br1	0.0571(2)	0.0437(2)	0.0974(3)	-0.01003(18)	-0.00843(19)	-0.00435(16)

The form of the anisotropic displacement parameter is:

$\exp[-2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$

Table 5. Bond Distances in Compound 99109, Å

C1-C6	1.383(5)	C1-C2	1.384(5)	C1-Br1	1.891(3)
C2-C3	1.384(5)	C3-C4	1.389(5)	C4-C5	1.394(5)
C4-C7	1.494(4)	C5-C6	1.393(5)	C7-O2	1.203(4)
C7-O1	1.330(4)	C8-O1	1.464(4)	C8-C9	1.501(5)
C9-C16	1.533(5)	C9-C10	1.536(5)	C10-C11	1.534(5)
C11-C12	1.510(6)	C11-C17	1.542(6)	C12-C15	1.353(5)
C12-S1	1.728(4)	C13-C14	1.364(7)	C13-S1	1.714(5)
C14-C15	1.433(6)	C15-C16	1.503(5)	C17-C26	1.343(6)
C17-C18	1.426(7)	C18-C19	1.382(6)	C19-C20	1.387(6)
C20-C25	1.421(6)	C20-C21	1.474(6)	C21-C22	1.357(6)
C22-C23	1.402(7)	C23-C24	1.348(7)	C24-C25	1.381(6)
C25-C26	1.467(6)				

Table 6. Bond Angles in Compound 99109, °

C6-C1-C2	121.8(3)	C6-C1-Br1	119.1(3)	C2-C1-Br1	119.1(3)
C3-C2-C1	118.9(3)	C2-C3-C4	120.5(3)	C3-C4-C5	119.8(3)
C3-C4-C7	118.1(3)	C5-C4-C7	122.0(3)	C6-C5-C4	120.1(3)
C1-C6-C5	118.8(3)	O2-C7-O1	124.1(3)	O2-C7-C4	123.2(3)
O1-C7-C4	112.7(3)	O1-C8-C9	108.2(3)	C8-C9-C16	110.2(3)
C8-C9-C10	108.3(3)	C16-C9-C10	109.7(3)	C11-C10-C9	112.2(3)
C12-C11-C10	108.5(3)	C12-C11-C17	111.3(4)	C10-C11-C17	110.2(3)
C15-C12-C11	124.6(4)	C15-C12-S1	111.5(3)	C11-C12-S1	124.0(3)
C14-C13-S1	111.9(4)	C13-C14-C15	112.0(4)	C12-C15-C14	112.9(4)
C12-C15-C16	123.3(3)	C14-C15-C16	123.8(3)	C15-C16-C9	112.0(3)
C26-C17-C18	118.6(4)	C26-C17-C11	121.4(4)	C18-C17-C11	119.9(4)

C19-C18-C17	121.1(4)	C18-C19-C20	120.0(5)	C19-C20-C25	121.8(4)
C19-C20-C21	120.1(4)	C25-C20-C21	118.0(4)	C22-C21-C20	117.6(4)
C21-C22-C23	121.1(4)	C24-C23-C22	123.3(5)	C23-C24-C25	118.2(4)
C24-C25-C20	121.8(4)	C24-C25-C26	123.0(4)	C20-C25-C26	115.2(4)
C17-C26-C25	123.1(4)	C7-O1-C8	115.3(3)	C13-S1-C12	91.7(2)

[i]CrystalClear: Rigaku Corporation, 1999.

[ii]CrystalStructure: Crystal Structure Analysis Package, Rigaku Corp. Rigaku/MSC (2002).

[iii]REQAB4: R.A. Jacobsen, (1994). Private Communication.

[iv]SIR97: Altomare, A., M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori & R. Spagna (1999). J. Appl. Cryst., 32, 115-119.

[v]SHELXL-97: Sheldrick, G.M. (2008) Acta Cryst., A64,112-122.

[vi]$R1 = \Sigma||F_o| - |F_c|| / \Sigma |F_o|$

$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$

$GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{½}$

where n = the number of reflections and p = the number of parameters refined.

[vii] Flack Parameter: Flack, H.D. (1983) Acta. Cryst., A39, 876-881.

[viii]"ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations". C.K. Johnson (1976) ORNL-5138.