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Supporting Material

Rhodium Catalyzed Asymmetric Ring-Opening of Oxabicyclic Alkenes with Sulfur Nucleophiles

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General. All flasks were flame-dried under a stream of nitrogen and cooled before use. Solvents and solutions were transferred with syringes and cannulae using standard inert atmosphere techniques. Analytical TLC was performed using EM separations precoated silica gel 0.2 mm layer UV fluorescent sheets. Column chromatography was carried out as “flash chromatography” as reported by Still using Merck 60 (230-400 mesh) silica gel.¹ Unless otherwise specified, crude reaction mixtures were concentrated on a rotary evaporator at aspirator pressure.

Tetrahydrofuran (THF) was distilled under N₂ from Na/benzophenone immediately prior to use. Oxabenzonornbornadiene was prepared according to a literature procedure.² All other reagents, metal catalysts and ligands were obtained from commercial sources and used as received unless otherwise noted.

IR spectra were obtained on a FT-IR spectrometer as thin films on NaCl plates. High-resolution mass spectra were obtained at 70 eV. ¹H spectra were referenced to tetramethylsilane (TMS, 0 ppm); ¹³C spectra were referenced to solvent carbons (77.23 ppm for CDCl₃); trichlorofluoromethane (CFCl₃, 0 ppm) was used an external reference for ¹⁹F spectra. Spectral features are tabulated in the following order: chemical shift (δ, ppm); number of protons; multiplicity (s-singlet, d-doublet, t-triplet, q-quartet, m-complex multiplet); coupling constants (J, Hz). Optical rotations were measured on a polarimeter using the sodium D line with spectrograde CHCl₃ in a 1 dm cell. Enantiomeric excess was determined on an analytical HPLC using a Chiracel OD column.

¹ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

² Gillespie, D.G.; Walker, B.J.; Stevens, D.; McAuliffe, C.A. *J. Chem. Soc. Perkin Trans. 1* **1983**, *8*, 1697-1703.

Catalyst Preparation. To a flame dried round bottom flask was added $[\text{Rh}(\text{COD})\text{Cl}]_2$ (2.5 mol%) and (*S,R*)-PPF- P^tBu_2 (6 mol%) followed by the addition of THF. After stirring at room temperature for 5 minutes (dark red), the solution was transferred *via* cannula to a second flask containing AgOTf (7 mol%) and stirred vigorously for an additional 5 minutes in the dark (brown). This mixture was subsequently transferred *via* cannula to a third flask containing NH_4I (1.7 equiv) and stirred for 5 minutes (dark red). This solution was then used in the asymmetric ring opening (ARO) reactions.

General Procedure for the ARO Reactions with Sulfur Nucleophiles.

Method 1: To a flame dried flask was added **1** (100 mg, 0.69 mmol) and galvinoxyl (14.6 mg, 0.035 mmol) in THF (2 mL) at room temperature. Thiol (1.5 equiv) was added and stirred for 5 minutes prior to the addition of the catalyst. This mixture was then heated to reflux (85°C oil bath temperature) until the reaction was complete as judged by thin layer chromatography. The solvent was removed *in vacuo* and the crude mixture was purified by flash chromatography.

Method 2: To a flame dried flask was added catalyst and thiol (1.5 equiv) in THF (3 mL). This mixture was heated to reflux (85°C oil bath temperature) and a solution of **1** in THF (2 mL) was added dropwise *via* syringe pump over a period of 2 hours. After the addition was complete, the reaction mixture was heated for an additional 45 minutes. The solvent was removed *in vacuo* and the crude mixture was purified by flash chromatography.

Method 3: As with method 2, except galvinoxyl was added to the catalyst and thiol.

2-Phenylsulfanyl-1,2-dihydro-naphthalen-1-ol (**2**)

Method 1 or 2. Yield = 92 %. The ee was determined to be 94 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 14.4 min (major) and 9.8 min; $R_f = 0.28$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = +403$, ($c = 5$, CHCl_3); IR (Thin Film) ν 3358, 3056, 2925, 1582, 1479, 1438 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.37 (2H, m), 7.31-7.21 (6H, m), 7.08-7.05 (1H, m), 6.6 (1H, d, $J = 9.6$ Hz), 6.0 (1H, dd, $J = 9.6$, 4.4 Hz), 4.7 (1H, dd, $J = 6.0$, 4.4 Hz), 2.2 (1H, d, $J = 6.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 134.1, 133.3, 132.6, 131.2, 129.1, 129.1, 129.0, 128.9, 128.6, 128.0, 127.6, 125.1, 71.1, 48.9; HRMS (EI) m/e calcd ($[\text{M}]^+$) 254.0765, found 254.0761.

2-o-Tolylsulfanyl-1,2-dihydro-naphthalen-1-ol (**5**)

Method 1. Yield = 92 %. The ee was determined to be 93 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 13.9 min (major) and 9.2 min; $R_f = 0.44$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = +360$, ($c = 1.7$, CHCl_3); IR (Thin Film) ν 3357, 3057, 2362, 1588, 1467, 1454 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.47-7.44 (1H, m), 7.35-7.27 (3H, m), 7.20-7.13 (4H, m), 6.6 (1H, d, $J = 9.3$ Hz), 6.1 (1H, dd, $J = 9.3, 5.5$ Hz), 4.7 (1H, dd, $J = 6.6, 3.0$ Hz), 4.2 (1H, dd, $J = 5.5, 3.0$ Hz), 2.4 (3H, s), 2.0 (1H, d, $J = 6.6$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 140.2, 134.2, 133.0, 132.2, 131.1, 130.6, 129.2, 129.1, 129.0, 128.6, 127.6, 127.4, 126.6, 124.8, 71.0, 48.2, 20.8; HRMS (EI) m/e calcd ($[\text{M}]^+$) 268.0922, found 268.0916.

2-(2,6-Dimethyl-phenylsulfanyl)-1,2-dihydro-naphthalen-1-ol (**6**)

Method 1. Yield = 79 %. The ee was determined to be 98 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 9.8 min (major) and 7.4 min; $R_f = 0.39$ (EtOAc:hexanes; 2:8); mp 73-74 $^\circ\text{C}$ (hexanes); $[\alpha]_D^{25} = +281$, ($c = 4.8$, CHCl_3); IR (Thin Film) ν 3329, 3054, 2923, 1460, 1376 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.30 (3H, m), 7.21-7.11 (4H, m), 6.6 (1H, d, $J = 9.3$ Hz), 6.0 (1H, dd, $J = 9.3, 5.5$ Hz), 4.5 (1H, dd, $J = 6.9, 4.9$ Hz), 4.0 (1H, dd, $J = 5.5, 4.9$ Hz), 2.5 (6H, s), 1.8 (1H, d, $J = 6.9$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 143.7, 134.2, 131.4, 131.2, 129.4, 129.2, 128.8, 128.6, 128.4, 127.5, 124.9, 71.1, 48.7, 22.2; HRMS (EI) m/e calcd ($[\text{M}]^+$) 282.1078, found 282.1074.

2-(Naphthalen-1-ylsulfanyl)-1,2-dihydro-naphthalen-1-ol (**7**)

Method 1. Yield = 66 %. The ee was determined to be 92 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 22.4 min (major) and 13.2 min; $R_f = 0.30$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = +364$, ($c = 3.5$, CHCl_3); IR (Thin Film) ν 3368, 3054, 2927, 1563, 1502, 1380, 1246 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 8.46-8.42 (1H, m), 7.85-7.78 (2H, m), 7.73-7.70 (1H, m), 7.56-7.47 (2H, m), 7.41-7.36 (1H, m), 7.31-7.20 (3H, m), 7.12-7.09 (1H, m), 6.6 (1H, d, $J = 9.3$ Hz), 6.1 (1H, dd, $J = 9.3, 5.5$ Hz), 4.6 (1H, dd, $J = 6.9, 2.5$ Hz), 4.2 (1H, dd, $J = 5.5, 2.5$ Hz), 2.0 (1H, d, $J = 6.9$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 134.6, 134.2, 134.1, 133.2, 131.1, 130.5, 129.3, 129.2, 129.1, 129.0, 128.7, 128.6, 127.3, 126.9, 126.4, 125.8, 125.6, 124.8, 71.1, 49.4; HRMS (EI) m/e calcd ($[\text{M}]^+$) 304.0922, found 304.0918.

2-(2-Chloro-phenylsulfanyl)-1,2-dihydro-naphthalen-1-ol (**8**)

Method 1. Yield = 91 %. The ee was determined to be 91 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 16.9 min (major) and 11.3 min; $R_f = 0.22$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = +331$, ($c = 3$, CHCl_3); IR (Thin Film) ν 3357, 3058, 2362, 2344, 1451, 1035 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.46-7.07 (8H, m), 6.6 (1H, d, $J = 9.3$ Hz), 6.0 (1H, dd, $J = 9.3, 5.5$ Hz), 4.7 (1H, dd, $J = 5.5, 4.4$ Hz), 4.2 (1H, dd, $J = 5.5, 4.4$ Hz), 2.2 (1H, d, $J = 5.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 136.6, 134.0, 133.0, 132.9, 131.1, 130.2, 129.4, 129.2, 129.1, 128.7, 128.6, 127.4, 127.3, 124.2, 71.0, 47.8; HRMS (EI) m/e calcd ($[\text{M}]^+$) 288.0376, found 288.0378.

2-(2-Methoxy-phenylsulfanyl)-1,2-dihydro-naphthalen-1-ol (**9**)

Method 1. Yield = 65 %. The ee was determined to be 95 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 27.5 min (major) and 13.3 min; $R_f = 0.21$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = +302$, ($c = 2$, CHCl_3); IR (Thin Film) ν 3398, 3060, 2936, 2835, 2361, 2343, 1578, 1475, 1244 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.43-7.24 (5H, m), 7.10-7.07 (1H, m), 6.93-6.84 (2H, ddd, $J = 16.2, 7.4, 1.1$ Hz), 6.6 (1H, d, $J = 9.3$ Hz), 6.1 (1H, dd, $J = 9.3, 4.7$ Hz), 4.7 (1H, dd, $J = 6.0, 5.5$ Hz), 4.2 (1H, dd, $J = 5.5, 4.7$ Hz), 3.9 (3H, s), 2.4 (1H, d, $J = 6.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 159.4, 135.2, 134.7, 131.4, 129.8, 128.8, 128.7, 128.4, 128.2, 127.0, 126.1, 121.1, 120.7, 111.0, 71.2, 55.9, 48.4; HRMS (EI) m/e calcd ($[\text{M}]^+$) 284.0871, found 284.0863.

2-(3-Methoxy-phenylsulfanyl)-1,2-dihydro-naphthalen-1-ol (**10**)

Method 3. Yield = 75 %. The ee was determined to be 94 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 19.2 min (major) and 12.1 min; $R_f = 0.24$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = +331$, ($c = 5.2$, CHCl_3); IR (Thin Film) ν 3394, 3018, 2936, 2834, 2361, 2344, 1589, 1574, 1479, 1247, 1230 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.10 (5H, m), 7.03-6.94 (2H, m), 6.8 (1H, m), 6.6 (1H, d, $J = 9.6$ Hz), 6.1 (1H, dd, $J = 9.6, 5.2$ Hz), 4.8 (1H, dd, $J = 6.6, 3.6$ Hz), 4.2 (1H, dd, $J = 5.2, 3.6$ Hz), 3.8 (3H, s), 2.0 (1H, d, $J = 6.6$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 159.8, 134.6, 134.1, 131.2, 129.9, 129.1, 129.0, 128.4, 128.6, 127.3, 125.0, 124.4, 117.5, 113.4, 71.1, 55.4, 48.8; HRMS (EI) m/e calcd ($[\text{M}]^+$) 284.0871, found 284.0858.

2-(4-Methoxy-phenylsulfanyl)-1,2-dihydro-naphthalen-1-ol (**11**)

Method 1. Yield = 81 %. The ee was determined to be 92 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 18.3 min (major) and 12.5 min; $R_f = 0.21$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = +413$, ($c = 2.3$, CHCl_3); IR (Thin Film) ν 3406, 3037, 2938, 2836, 2364, 2345, 1591, 1493, 1286, 1246 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.23 (5H, m), 7.04-7.02 (1H, m), 6.8 (1H, m), 6.5 (1H, d, $J = 9.3$ Hz), 6.0 (1H, dd, $J = 9.3, 4.9$ Hz), 4.7 (1H, dd, $J = 6.2, 0.7$ Hz), 4.0 (1H, dd, $J = 4.9, 0.7$ Hz), 3.8 (3H, s), 2.2 (1H, d, $J = 6.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 159.9, 136.3, 134.3, 131.3, 128.9, 128.7, 128.6, 128.4, 127.1, 125.4, 122.8, 114.5, 71.2, 55.4, 50.2; HRMS (EI) m/e calcd ($[\text{M}]^+$) 284.0871, found 284.0871.

2-(4-Fluoro-phenylsulfanyl)-1,2-dihydro-naphthalen-1-ol (**12**)

Method 1. Yield = 90 %. The ee was determined to be 90 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 14.9 min (major) and 10.5 min; $R_f = 0.27$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = +444$, ($c = 1.4$, CHCl_3); IR (Thin Film) ν 3373, 3038, 2360, 1588, 1489, 1224 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.25 (5H, m), 7.06-7.03 (1H, m), 6.94-6.88 (2H, m), 6.6 (1H, d, $J = 9.6$ Hz), 6.0 (1H, dd, $J = 9.6, 4.7$ Hz), 4.7 (1H, dd, $J = 6.6, 3.3$ Hz), 4.0 (1H, dd, $J = 4.7, 3.3$ Hz), 2.0 (1H, d, $J = 6.6$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 162.8 (d, $J = 248.0$ Hz), 136.2, 136.0, 134.1, 131.2, 129.1, 129.0, 128.8, 128.6, 127.5, 127.4, 127.2, 124.8, 115.9 (d, $J = 22.0$ Hz), 71.4, 49.5; ^{19}F NMR (282 MHz, CDCl_3) δ -113.2; HRMS (EI) m/e calcd ($[\text{M}]^+$) 272.0671, found 272.0663.

2-(4-Nitro-phenylsulfanyl)-1,2-dihydro-naphthalen-1-ol (**13**)

Method 1. Yield = 88 %. The ee was determined to be 96 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 34.5 min (major) and 29.3 min; $R_f = 0.19$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = +16$, ($c = 0.6$, CHCl_3); IR (Thin Film) ν 3056, 2923, 2851, 1362, 1576, 1513, 1337 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 8.1 (2H, dd, $J = 6.7, 1.9$ Hz), 7.4 (2H, dd, $J = 6.7, 1.9$ Hz), 7.35-7.30 (3H, m), 7.17-7.14 (1H, m), 6.7 (1H, d, $J = 9.6$ Hz), 6.1 (1H, dd, $J = 9.6, 5.5$ Hz), 4.8 (1H, dd, $J = 6.6, 2.7$ Hz), 4.4 (1H, dd, $J = 5.5, 2.7$ Hz), 2.1 (1H, d, $J = 6.6$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 145.9, 144.7, 133.6, 130.8, 130.1, 129.6, 129.2, 129.0, 128.9, 127.6, 124.0, 123.1, 71.0, 46.9; HRMS (EI) m/e calcd ($[\text{M}-\text{H}_2\text{O}]^+$) 281.0511, found 281.0514.

2-Benzylsulfanyl-1,2-dihydro-naphthalen-1-ol (**14**)

Method 1. Yield = 75 %. The ee was determined to be 96 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 13.1 min (major) and 10.5 min; $R_f = 0.30$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = +468$, ($c = 1.8$, CHCl_3); IR (Thin Film) ν 3061, 2928, 2363, 1493, 1453, 1407, 1290 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.33-7.25 (8H, m), 7.1 (1H, m), 6.6 (1H, d, $J = 9.3$ Hz), 5.9 (1H, dd, $J = 9.3, 4.9$ Hz), 4.8 (1H, dd, $J = 6.0, 4.9$ Hz), 3.7 (2H, s), 3.7 (1H, m), 2.0 (1H, d, $J = 6.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 138.1, 134.4, 131.4, 129.1, 129.0, 128.7, 128.5, 128.2, 128.2, 127.2, 127.1, 125.9, 71.9, 45.9, 34.9; HRMS (EI) m/e calcd ($[\text{M}]^+$) 268.0922, found 268.0931.

2-(Furan-2-ylmethylsulfanyl)-1,2-dihydro-naphthalen-1-ol (**15**)

Method 1. Yield = 52 %. The ee was determined to be 96 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 12.5 min (major) and 10.7 min; $R_f = 0.17$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = +425$, ($c = 2.4$, CHCl_3); IR (Thin Film) ν 3148, 2926, 1500, 1451, 1407, 1290, 1148 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.26 (4H, m), 7.15-7.12 (1H, m), 6.6 (1H, d, $J = 9.6$ Hz), 6.3 (1H, dd, $J = 3.0, 1.9$ Hz), 6.2 (1H, dd, $J = 3.0, 0.5$ Hz), 6.0 (1H, dd, $J = 9.6, 5.0$ Hz), 4.7 (1H, dd, $J = 6.0, 5.0$ Hz), 3.8 (1H, dd, $J = 5.0, 5.0$ Hz), 3.7 (2H, s), 2.1 (1H, d, $J = 6.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 151.4, 142.3, 134.3, 131.4, 129.1, 128.5, 128.4, 127.1, 125.7, 110.6, 107.8, 71.8, 46.2, 27.1; HRMS (EI) m/e calcd ($[\text{M}-\text{H}_2\text{O}]^+$) 240.0609, found 240.0611.

(1-Hydroxy-1,2-dihydro-naphthalen-2-ylsulfanyl)-acetic acid methyl ester (**16**)

Method 1. Yield = 63 %. The ee was determined to be 97 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 16.9 min (major) and 14.2 min; $R_f = 0.10$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = +497$, ($c = 5.6$, CHCl_3); IR (Thin Film) ν 3428, 3036, 2952, 1732, 1435, 1285, 1154, 1004 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.44-7.41 (1H, m), 7.31-7.28 (2H, m), 7.15-7.12 (1H, m), 6.6 (1H, d, $J = 9.3$ Hz), 6.0 (1H, dd, $J = 9.3, 4.9$ Hz), 4.8 (1H, dd, $J = 6.0, 5.0$ Hz), 3.8 (1H, dd, $J = 5.0, 4.9$ Hz), 3.7 (3H, s), 3.2 (2H, dd, $J = 26.4, 15.7$ Hz), 2.5 (1H, d, $J = 6.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 171.3, 134.6, 131.5, 129.3, 129.1, 128.8, 128.4, 127.2, 125.5, 72.1, 52.8, 47.2, 31.9; HRMS (EI) m/e calcd ($[\text{M}-\text{H}_2\text{O}]^+$) 232.0558, found 232.0561.

3-(1-Hydroxy-1,2-dihydro-naphthalen-2-ylsulfanyl)-propionic acid ethyl ester (**17**)

Method 1. Yield = 64 %. The ee was determined to be 96 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 14.9 min (major) and 12.5 min; $R_f = 0.08$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = +479$, ($c = 2.9$, CHCl_3); IR (Thin Film) ν 3423, 2980, 2932, 2363, 1731, 1372, 1246, 1187, 1010 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.42 (1H, m), 7.31-7.28 (2H, m), 7.15-7.13 (1H, m), 6.6 (1H, d, $J = 9.5$ Hz), 6.0 (1H, dd, $J = 9.5, 4.9$ Hz), 4.8 (1H, dd, $J = 5.9, 4.9$ Hz), 4.1 (2H, q, $J = 7.1$ Hz),

3.7 (1H, dd, $J = 5.9, 5.9$ Hz), 2.7 (2H, t, $J = 6.8$ Hz), 2.5 (2H, t, $J = 6.8$ Hz), 2.3 (1H, d, $J = 5.9$ Hz), 1.2 (3H, t, $J = 7.1$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 171.8, 134.5, 131.4, 128.9, 128.5, 128.3, 128.2, 127.0, 126.0, 72.3, 60.8, 46.7, 35.1, 23.0, 14.2; HRMS (EI) m/e calcd ($[\text{M}-\text{H}_2\text{O}]^+$) 260.0871, found 260.0874.

2-(trimethoxysilylpropyl-3-sulfanyl)-1,2-dihydro-naphthalen-1-ol (**18**)

Method 3. Note: (R,S)-PPF- P^tBu_2 was used. Yield = 64 %. The ee was determined to be 96 % using HPLC analysis on a CHIRACEL OD column, $\lambda = 254$ nm. Retention times in 10 % isopropanol in hexanes were 10.3 min (major) and 9.4 min; $R_f = 0.17$ (EtOAc:hexanes; 2:8); $[\alpha]_D^{25} = -395$, ($c = 8.1$, CHCl_3); IR (Thin Film) ν 3423, 3036, 2942, 2840, 1453, 1190, 1085 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.44-7.40 (1H, m), 7.32-7.27 (2H, m), 7.16-7.12 (1H, m), 6.6 (1H, d, $J = 9.6$ Hz), 6.0 (1H, dd, $J = 9.6, 4.9$ Hz), 4.8 (1H, dd, $J = 5.8, 5.1$ Hz), 3.7 (1H, dd, $J = 5.1, 4.9$ Hz), 3.6 (9H, s), 2.5 (2H, t, $J = 7.1$ Hz), 2.2 (1H, d, $J = 5.8$ Hz), 1.6 (2H, tt, $J = 8.5, 7.1$ Hz), 0.7 (2H, t, $J = 8.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 134.5, 131.5, 128.9, 128.5, 128.3, 127.9, 127.0, 126.5, 72.2, 50.6, 46.4, 33.1, 23.4, 8.7; HRMS (EI) m/e calcd ($[\text{M}-\text{H}_2\text{O}]^+$) 322.1059, found 322.1060.