Supplementary information for 'Iminium Salt Catalysts for Asymmetric Epoxidation: The First High Enantioselectivities'

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General Experimental:

All infrared spectra were obtained using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer; thin film spectra were acquired using sodium chloride plates.

All ¹H and ¹³C NMR spectra were measured at 250.13 and 62.86 MHz using a Bruker AC 250 MHz spectrometer or at 400.13 and 100.62 MHz using a Bruker DPX 400 MHz spectrometer. The solvent used for NMR spectroscopy was CDCl₃ (unless stated otherwise) using TMS (tetramethylsilane) as the internal reference. Chemical shifts are given in parts per million (ppm) and *J* values are given in Hertz (Hz).

The mass spectra were recorded using a Jeol-SX102 instrument utilising electron impact (E.I.), fast atom bombardment (F.A.B.) and by the EPSRC national mass spectrometry service at the University of Wales, Swansea, utilising electrospray (ES.). Analysis by GCMS utilised a Fisons GC 8000 series (AS 800), using a 15 m x 0.25 mm DB-5 column and an electron impact low resolution mass spectrometer.

Melting points were recorded using an Electrothermal-IA 9100 melting point instrument and are uncorrected.

Optical rotation values were measured with an Optical Activity-polAAar 2001 instrument, operating at λ=589 nm, corresponding to the sodium line, (D), at the temperatures indicated. The solvents used for these measurements were of spectrophotometric grade. The solutions for these measurements were prepared in volumetric flasks for maximum accuracy of the volume of solvent used.

Microanalyses were performed on a Perkin Elmer Elemental Analyser 2400 CHN.

All chromatographic manipulations used silica gel as the adsorbent. Reactions were monitored using thin layer chromatography (TLC) on aluminium backed plates with Merck Kiesel 60 F254 silica gel. TLC visualised by UV radiation at a wavelength of 254 nm, or stained by exposure to an ethanolic solution of phosphomolybdic acid (acidified with concentrated sulphuric acid), followed by charring where appropriate. Purification by column chromatography used Merck Kiesel 60 H silica adsorbent.

The reactions requiring anhydrous conditions were carried out using glassware dried overnight at 150 °C, under a nitrogen atmosphere unless otherwise stated. Reaction solvents were obtained commercially dry,

except light petroleum (b.p. 40-60 °C) which was distilled from calcium chloride prior to use. Ethyl acetate was distilled over calcium sulphate or chloride. Dichloromethane was distilled over calcium hydride. Tetrahydrofuran (THF), was distilled under a nitrogen atmosphere from the sodium/benzophenone ketyl radical or from lithium aluminium hydride.

Enantiomeric excesses were determined by either proton nuclear magnetic resonance ($^1\text{H-NMR}$), or by chiral HPLC.

The proton nuclear magnetic resonance spectra were recorded in deuteriated chloroform on a Bruker AC 250, operating at 250.13 MHz, in the presence of europium (III) tris [3-(heptafluoropropylhydroxymethylene)-(+)-camphorate], [(+)-Eu(hfc)₃], as the chiral shift reagent and tetramethylsilane as the internal standard.

The chiral column used for the determination of enantiomeric excesses (ee), of non-racemic mixtures by chiral HPLC, was Chiracel OD on a TSP Thermo-Separating-Products Spectra Series P200 instrument, with TSP Spectra Series UV100 ultra-violet absorption detector set at 254 nm and a Chromojet integrator. Both solvents used to gain measurements (hexane and isopropanol), were of HPLC grade.

(*R*)-Trifluoro-methanesulfonic acid 2'-trifluoromethanesulfonyloxy [1,1']binaphthalenyl-2-yl ester:

(*R*)-[1,1']Binaphthalenyl-2,2'-diol (1.70 g, 5.9 mmol) was dissolved in dichloromethane (40 ml) and cooled to $-30\text{ }^{\circ}\text{C}$. To this was added 4-dimethylaminopyridine (0.289 g, 2.4 mmol), 2,6-lutidine (2.06 ml, 17.7 mmol) and triflic anhydride (2.98 ml, 17.7 mmol). The solution was allowed to warm to room temperature and stirred for 4 h. Silica gel was added to the solution and the solvent evaporated under reduced pressure. The compound adsorbed on silica was transferred to a fritted glass funnel and washed with ethyl acetate/light petroleum until the title compound had eluted. Solvents were removed under reduced pressure to yield a crude colourless solid, which was recrystallized from hexane to give colourless crystals (3.20 g, 99%), m.p. 68-70 °C; $[\alpha]_{\text{D}}^{20} -145.3$ (c 1.08, CHCl_3) [$\text{Lit}^1 +142.0$ (c 1.04, CHCl_3), for (*S*)-enantiomer]; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3062, 1508, 1424, 1246, 1140, 1065, 963, 865; δ_{H} (250 MHz; CDCl_3) 7.25 (2 H, m), 7.40 (2 H, m), 7.59 (4 H, m), 8.00 (2 H, d, J 8.2 Hz), 8.13 (2 H, d, J 9.0 Hz); δ_{C} (100 MHz; CDCl_3) 118.12, 119.33, 123.46, 126.76, 127.33, 127.99, 128.36, 132.00, 132.37, 133.17, 145.41; m/z (EI) 549.9974; $\text{C}_{22}\text{H}_{12}\text{F}_6\text{O}_6\text{S}_2$ (M^+) requires 549.9980.

(*S*)-Trifluoro-methanesulfonic acid 2'-trifluoromethanesulfonyloxy [1,1']binaphthalenyl-2-yl ester:

Prepared in an identical manner to the (*R*)-enantiomer above, from (*S*)-[1,1']binaphthalenyl-2,2'-diol (6.76 g, 24.0 mmol). Colourless crystals (13.0 g, 99%); $[\alpha]_D^{20} +140.6$ (*c* 1.09, CHCl₃).

(*R*)-2,2'-Dimethyl-[1,1']binaphthalenyl:

(*R*)-Trifluoromethanesulfonic acid 2'-trifluoromethanesulfonyloxy [1,1']binaphthalenyl-2-yl ester (13.0 g, 23.6 mmol) and 1,3-bis(diphenylphosphino)propane nickel(II)chloride (1.10 g, 1.7 mmol) were dissolved in anhydrous diethyl ether (100 ml). The reaction was cooled to $-10\text{ }^{\circ}\text{C}$ in a ice/salt bath and methylmagnesium bromide (3 M in Et₂O, 31.5 ml, 94.4 mmol) was added dropwise over 30 min. The reaction was allowed to attain ambient temperature and stirred over night. The dark green/brown solution was diluted with diethyl ether (150 ml) and filtered through celite (to remove the nickel catalyst). The filtrate was washed with 0.5 M hydrochloric acid (2 x 50 ml) and brine (50 ml). Removal of solvent under reduced pressure yielded a red/orange crude oil, which was purified by column chromatography eluting with hexane to give a pale yellow oil. Crystallization from methanol afforded the product as colourless crystals (6.00 g, 90%); m.p. 68-72 $^{\circ}\text{C}$ (Lit² 67-71 $^{\circ}\text{C}$); $[\alpha]_D^{20} -39.0$ (*c* 1.12, CHCl₃) [Lit³ $[\alpha]_D^{21} +37.7$ (*c* 1.00, CHCl₃) for (*S*)-enantiomer]; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3053, 2246, 1594, 1506, 1421, 1379, 1351, 1221, 1143, 1027, 913, 865; δ_{H} (250 MHz; CDCl₃) 2.03 (6 H, s), 7.04 (2 H, d, *J* 8.4 Hz), 7.19 (2 H, m), 7.35 (2 H, m), 7.37 (2 H, d, *J* 8.3 Hz), 7.86 (2 H, d, *J* 8.4 Hz), 7.88 (2 H, d, *J* 8.4 Hz); δ_{C} (100 MHz; CDCl₃) 20.01, 124.87, 125.62, 126.06, 127.41, 127.90, 128.70, 132.20, 132.75, 134.25, 135.11; *m/z* (EI) 282 (*M*⁺), 300.1747; C₂₂H₂₂N (*M*⁺+NH₄) requires 300.1752.

(*S*)-2,2'-Dimethyl-[1,1']binaphthalenyl:

Prepared in an identical manner to the (*R*)-enantiomer above, from (*S*)-trifluoro-methanesulfonic acid 2'-trifluoromethanesulfonyloxy [1,1']binaphthalenyl-2-yl ester (5.00 g, 9.0 mmol). Colourless crystals (2.33 g, 92%); m.p. 71-73 °C; $[\alpha]_D^{20} +37.0$ (*c* 1.01, CHCl₃).

(*R*)-2,2'-Dibromomethyl-[1,1']binaphthalenyl:

(*R*)-2,2'-Dimethyl-[1,1']binaphthalenyl (4.00 g, 14.2 mmol), *N*-bromosuccinimide (5.06 g, 28.4 mmol) and AIBN (10 mol%, 0.221 g, 1.4 mmol) were stirred in cyclohexane (35 ml). The solution was irradiated with visible light (150 Watt Philips tungsten bulb) for 5 h. The reaction mixture was filtered through a fritted glass funnel and a scoop of silica added. The solvent was removed under reduced pressure to give the reaction mixture adsorbed onto silica. Immediately chromatographed eluting with light petroleum/ethyl acetate (97:3) to afford a colourless solid, recrystallized from chloroform/hexane. Colourless crystals (5.50 g, 88%). m.p. 185-187 °C; $[\alpha]_D^{20} +164.4$ (*c* 1.04, benzene); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3049, 2360, 1506, 1431, 1210, 818, 749, 684; δ_{H} (400 MHz; CDCl₃) 4.25 (4 H, s), 7.07 (2 H, d, *J* 8.0 Hz), 7.25 (2 H, m), 7.46 (2 H, m), 7.74 (2 H, d, *J* 8.0 Hz), 7.91 (2 H, d, *J* 8.0 Hz), 8.00 (2 H, d, *J* 8.0 Hz); δ_{C} (100 MHz; CDCl₃) 32.61, 126.78, 126.80, 127.61, 127.74, 128.02, 129.35, 132.50, 133.25, 134.07, 134.17; *m/z* 437.9614; C₂₂H₁₆Br₂ (M⁺) requires 437.9619.

(*S*)-2,2'-Dibromomethyl-[1,1']binaphthalenyl:

Prepared in an identical manner to the (*R*)-enantiomer above, from (*S*)-2,2'-dimethyl-[1,1']binaphthalenyl (2.00 g, 7.1 mmol). Colourless crystals (1.87 g, 60%); m.p. 181-183 °C (lit³ 183-184 °C); $[\alpha]_D^{20} -159.0$ (*c* 1.17, benzene) [lit³ $[\alpha]_D^{20} -160.0$ (*c* 1.00, benzene)].

(*R*)-3,5-Dihydro-4-oxa-cyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene:

(*R*)-2,2'-Dibromomethyl-[1,1']binaphthalenyl (0.50 g, 1.1 mmol) was suspended in a mixture of sat. aq. sodium carbonate solution and 1,4-dioxane (1:1, 60 ml). The solution was heated under reflux for 12 h. Upon cooling the mixture was extracted with diethyl ether (3 x 30 ml), washed with brine (2 x 20 ml) and dried. Removal of the solvent under reduced pressure afforded a yellow oil (TLC visualised using UV shows product as bright blue spot). Column chromatography eluting with ethyl acetate/light petroleum (0:100-10:90) gave a colourless solid, recrystallized from chloroform/hexane, (0.21 g 65%); m.p. 187-188 °C (lit.⁴ 188-189 °C); $[\alpha]_D^{20}$ -551.2 (*c* 1.12, CHCl₃); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3052, 2983, 2926, 1594, 1508, 1465, 1420, 1368, 1265, 1158, 1056, 895; δ_{H} (250 MHz; CDCl₃) 4.18 (2 H, d, *J* 11.3 Hz), 4.64 (2 H, d, *J* 11.3), 7.29 (2 H, m), 7.50 (4 H, m), 7.61 (2 H, d, *J* 8.33 Hz), 7.97 (4 H, dd, *J* 7.99 Hz); δ_{C} (100 MHz; CDCl₃) 67.44, 125.85, 125.94, 127.35, 127.59, 128.35, 129.15, 131.16, 133.55, 133.64, 135.46; *m/z* (FAB) 296 (*M*⁺ 40%), 267 (100%), 252 (35%); 296.1205; C₂₂H₁₆O (*M*⁺) requires 296.1201.

(*S*)-3,5-Dihydro-4-oxa-cyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene:

Prepared in an identical manner to the (*R*)-enantiomer above, from (*S*)-2,2'-dibromomethyl-[1,1']binaphthalenyl (7.00 g, 15.9 mmol). Colourless crystals (3.10 g, 66%); m.p. 186-188 °C; $[\alpha]_D^{20}$ +572.6 (*c* 1.04, CHCl₃).

(*R*)-2'-Bromomethyl-[1,1']binaphthalenyl-2-carbaldehyde:

To an ice-cooled solution of (*R*)-3,5-dihydro-4-oxa-cyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene (3.0 g, 9.6 mmol) in cyclohexane (50 ml), molecular bromine (1.24 g, 7.8 mmol) as a solution in cyclohexane (5 ml) was added over a period of 5 min (solution turned dark red). After a further 5 min the ice bath was removed and the reaction mixture heated under reflux until it became pale yellow (*ca* 1 h). The solvent was removed under reduced pressure and the residue obtained dissolved in diethyl ether. The organic solvents were washed with sat. aq. sodium hydrogen carbonate (2 x 50 ml) and brine (2 x 30 ml). The organic solution was dried (MgSO₄) and solvents were removed under reduced pressure to yield a orange oil. Crystallization from ethyl acetate afforded the product as colourless crystals (2.33 g, 65%); m.p. 151-153 °C; $[\alpha]_D^{20}$ +144.7 (*c* 1.02, CHCl₃); Found: C, 70.04; H, 3.78. C₂₂H₁₅BrO requires C, 70.41; H, 4.03.; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3058, 1688, 1594, 1430, 1324, 1212, 1027, 821, 749; δ_{H} (250 MHz; CDCl₃) 4.07 (1 H, d, *J* 10.2 Hz), 4.27 (1 H, d, *J* 10.2

Hz), 7.01 (1 H, dq, J 8.4, 2.0 Hz) 7.22-7.38 (3 H, m), 7.50 (1 H, m), 7.63 (1 H, m), 7.72 (1 H, d, J 8.6 Hz), 7.93-8.12 (4 H, m), 8.22 (1 H, d, J 8.6 Hz), 9.56 (1 H, d, J 0.9 Hz); δ_{C} (100 MHz; CDCl_3) 31.92, 122.38, 126.56, 126.94, 127.03, 127.39, 127.40, 128.17, 128.48, 129.20, 129.34, 129.85, 132.41, 132.42, 132.53, 132.97, 133.56, 134.63, 136.29, 141.59, 191.81; m/z (EI) 374.0310; $\text{C}_{22}\text{H}_{15}\text{BrO}$ (M^+) requires 374.0306; HPLC retention time (Chiracel OD column) 12.75 min; Hex:IPA (90:10), Flow 1.0.

(*S*)-2'-Bromomethyl-[1,1']binaphthalenyl-2-carbaldehyde:

Prepared in an identical manner to the (*R*)-enantiomer above, from (*S*)-3,5-dihydro-4-oxa-cyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene (2.30 g, 7.8 mmol). Colourless crystals (1.87 g, 64%); m.p. 154-155 °C; $[\alpha]_{\text{D}}^{20}$ –140.3 (c 1.13, CHCl_3); HPLC retention time (Chiracel OD column) 11.71 min; Hex:IPA (90:10), Flow 1.0.

General procedure for the synthesis of 3*H*-4-azapinium-cyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene salts from (*R*) or (*S*)-2'-Bromomethyl-[1,1']binaphthalenyl-2-carbaldehyde and primary amines:

A solution of the amine in ethanol, (10 ml per g of amine, 1 equivalent), was added dropwise via a stoppered, pressure equalising, dropping funnel, to a one-neck flask, containing a solution of (*R*) or (*S*)-2'-Bromomethyl-[1,1']binaphthalenyl-2-carbaldehyde, (1.10 equiv.) in ethanol (10 ml/g carbaldehyde) warmed at 35 °C. After the addition was complete the dropping funnel was removed and replaced by a stopper to contain the hydrogen bromide generated temporarily in the reaction. The reaction mixture was stirred overnight while attaining ambient temperature. Sodium tetraphenylborate, (or any other anion exchanging salt, 1.10 equivalents), in the minimum amount of acetonitrile, was added in one portion to the reaction mixture and after 5 minutes of stirring, the organic solvents are removed under reduced pressure. Ethanol was added to the residue, followed by water. The resulting solid was collected by filtration and washed with additional ethanol followed by hexane. If no solid materialises after the addition of the water the suspension is allowed to settle and the ethanol/water phase is decanted off. The gummy residue which may be obtained, is macerated in hot ethanol or methanol. The organic salt may then precipitate but in some rare cases it does so upon slow cooling of the hot alcoholic solution. If solubility problems do arise, small amounts of acetonitrile may be added during this process.

(*R*)-[(4*S*,5*S*)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl]-3*H*-4-azapinium-cyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene tetraphenylborate (7a**):**

Prepared according to the general procedure from (+)-(4*S*,5*S*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-amine (**4**) (0.15 g, 0.72 mmol). The product was isolated as yellow plates (0.39 g, 66%); m.p. 111-113 °C (dec.); $[\alpha]_D^{20}$ -98.5 (*c* 1.04, acetone); Found: C, 84.44; H, 5.97; N, 1.71. $C_{58}H_{50}BNO_2 \cdot 1.0H_2O$ requires C, 84.73; H, 6.13; N, 1.71.; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3055, 2986, 1626, 1610, 1593, 1548, 1478, 1450, 1382, 1266, 1203, 1110, 846, 817, 735, 704; $\delta_H(400 \text{ MHz; acetone-}d_6)$ 1.79 (3 H, s), 1.85 (3 H, s), 4.43 (1 H, d, *J* 13.2 Hz), 4.51 (1 H, d, *J* 13.6 Hz), 4.86 (2 H, m), 5.98 (2 H, m), 6.76 (4 H, t, *J* 7.2 Hz), 6.93 (8 H, t, *J* 7.6 Hz), 6.95-7.10 (5 H, m), 7.18-7.32 (2 H, m), 7.34 (8 H, m), 7.45 (3 H, m), 7.45-7.65 (2 H, m), 7.78 (1 H, m), 7.88 (1 H, d, *J* 8.4 Hz), 8.10 (1 H, d, *J* 8.4 Hz), 8.17 (1 H, d, *J* 8.4 Hz), 8.23 (1 H, dd, *J* 8.4, 2.4 Hz), 9.29 (1 H, s); $\delta_C(400 \text{ MHz; acetone-}d_6)$ 19.34, 29.69, 57.00, 62.26, 68.42, 72.94, 102.06, 120.51, 122.67, 126.33, 126.40, 126.58, 127.30, 128.11, 128.15, 128.38, 129.05, 129.19, 129.88, 130.04, 130.12, 130.57, 130.65, 131.70, 132.16, 132.57, 132.92, 133.25, 135.25, 136.61, 137.43, 142.75, 165.25, 171.37; *m/z* (FAB⁺) 484 (M⁺, 100%) 320 (76%), 293 (72%), 277 (69%), 265 (79%), 252 (49%), 165 (44%), 133 (41%); 484.2275; $C_{34}H_{30}NO_2$ (cation) requires 484.2277.

(*S*)-[(4*R*,5*R*)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl]-3*H*-4-azapinium-cyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene tetraphenylborate (*ent*-7a**):**

Prepared according to the general procedure from (-)-(4*R*,5*R*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-amine (*ent*-**4**) (0.16 g, 0.77 mmol). The product was isolated as yellow plates (0.40 g, 64%); m.p. 109-112 °C (dec.); $[\alpha]_D^{20}$ +95.3 (*c* 1.01, acetone).

(*S*)-[(4*S*,5*S*)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl]-3*H*-4-azapinium-cyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene tetraphenylborate (7b**):**

Prepared according to the general procedure from (+)-(4*S*,5*S*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-amine (**4**) (0.20 g, 0.97 mmol). The product was isolated as yellow plates (0.50 g, 64%); m.p. 218 °C (dec.); $[\alpha]_D^{20} +360.4$ (*c* 1.10, acetone); Found: C, 84.33; H, 6.06; N, 1.64. $C_{58}H_{50}BNO_2 \cdot 1.0H_2O$ requires C, 84.73; H, 6.13; N, 1.71.; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3054, 2998, 1626, 1609, 1579, 1545, 1477, 1458, 1383, 1266, 1201, 1110, 840, 817, 733, 704; δ_H (250 MHz; acetone- d_6) 1.72 (3 H, s), 1.78 (3 H, s), 4.23 (1 H, d, *J* 13.4 Hz), 4.31 (1 H, d, *J* 13.9 Hz), 4.73 (1 H, dd, *J* 13.8, 3.0 Hz), 4.90 (1 H, bs), 5.35 (1 H, d, *J* 13.5 Hz), 5.86 (1 H, d, *J* 2.3 Hz) 6.76 (4 H, t, *J* 7.1 Hz), 6.93 (8 H, t, *J* 7.1 Hz), 6.90-6.95 (5 H, m), 7.21 (8 H, m), 7.26-7.33 (3 H, m), 7.44 (1 H, m), 7.58 (1 H, m), 7.77 (1 H, m), 7.93 (2 H, dd, *J* 8.6, 2.2 Hz), 8.13 (1 H, d, *J* 7.9 Hz), 8.17 (1 H, d, *J* 8.4 Hz), 8.29 (2 H, dd, *J* 8.6, 5.3 Hz), 9.30 (1 H, s); δ_H (400 MHz; acetone- d_6) 19.13, 29.75, 57.29, 61.31, 67.00, 71.47, 100.64, 115.57, 121.88, 125.47, 125.66, 126.47, 126.94, 127.04, 127.31, 127.77, 127.88, 128.13, 128.67, 128.87, 129.28, 129.49, 130.56, 130.89, 131.09, 131.15, 131.98, 133.42, 133.70, 134.43, 141.08, 163.75, 170.82; *m/z* (FAB⁺) 484 (M^+ , 100%); 320 (35%), 292 (35%), 277 (62%), 265 (84%), 252 (25%), 165 (15%), 133 (25%); 484.2282; $C_{34}H_{30}NO_2$ (cation) requires 484.2277.

(-)-(R)-6-[(1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]-3*H*-4-azapinium-cyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene tetraphenylborate (7c**):**

Prepared according to the general procedure from (-)-isopinocampheylamine (**5**) (0.25 g, 1.6 mmol). The product was isolated as yellow plates (0.82 g, 73%), mp 219-221 °C (dec); $[\alpha]_D^{20} -318.8$ (*c* 1.37, acetone); Found: C, 88.22; H, 6.81; N, 1.79%. $C_{48}H_{48}BN \cdot 0.5H_2O$ requires C, 88.61; H, 6.91; N, 1.85%; $\nu_{\max}(\text{nujol})/\text{cm}^{-1}$ 3055, 2997, 1629, 1612, 1588, 1551, 1155, 818, 734, 706; δ_H (400 MHz; acetone- d_6) 1.10 (3 H, s), 1.21 (3 H, d, *J* 6.8 Hz), 1.32 (3 H, s), 1.53 (1 H, d, *J* 10.4 Hz), 2.01-2.08 (1 H, m), 2.15-2.17 (1 H, m) 2.42 (1 H, m), 2.63-2.70 (3 H, m), 4.80 (1 H, dd, *J* 13.6, 1.2 Hz) 5.06 (1 H, q, *J* 7.6 Hz), 5.48 (1 H, d, *J* 14.0 Hz) 6.73 (4 H, t, *J* 8.0 Hz), 6.88 (8 H, t, *J* 8.0 Hz), 7.06 (1 H, d, *J* 8.4 Hz), 7.27 (8 H, t, *J* 8.0 Hz), 7.45-7.49 (3 H, m), 7.56-7.63 (1 H, m), 7.77-7.80 (1 H, m), 7.99 (1 H, d, *J* 8.8 Hz), 8.03 (1 H, d, *J* 8.4 Hz), 8.08 (1 H, d, *J* 8.4 Hz), 8.20 (1 H, d, *J* 8.4 Hz), 8.26 (1 H, d, *J* 8.4 Hz), 8.31 (1 H, d, *J* 8.4 Hz), 9.62 (1 H, s); δ_C (100

MHz; acetone- d_6) 20.32, 23.86, 28.78, 34.07, 35.22, 40.64, 42.09, 42.60, 48.59, 54.24, 75.64, 122.69, 126.45, 127.17, 127.56, 128.15, 128.33, 128.58, 129.05, 129.99, 130.07, 130.14, 130.60, 130.76, 131.64, 132.81, 132.92, 133.14, 133.26, 135.15, 135.38, 136.74, 137.47, 142.81, 165.35, 170.77; m/z (ES^+) 430 (M^+ , 100%), 355 (30%), 154 (15%), 119 (13%); 430.2540; $C_{32}H_{32}N$ (cation) requires 430.2535.

(+)-(S)-6-[(1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]- 3*H*-4-azapinium-cyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene tetraphenylborate (7d**):**

Prepared according to the general procedure from (–)-isopinocampheylamine (**5**) (0.25 g, 1.6 mmol). The product was isolated as yellow plates (0.82 g, 73%), mp 225–227 °C (dec); $[\alpha]_D^{20} +359.1$ (c 1.31, acetone); Found: C, 88.38; H, 6.86; N, 1.80%. $C_{48}H_{48}BN \cdot 0.5H_2O$ requires C, 88.61; H, 6.91; N, 1.85%; ν_{max} (nujol)/ cm^{-1} 3053, 2996, 1627, 1610, 1580, 1549, 1206, 750, 705; δ_H (400 MHz; acetone- d_6) 0.84 (3 H, d, J 4.0 Hz), 1.13 (3 H, s), 1.32 (3 H, s), 1.51 (1 H, d, J 8.0 Hz), 2.04 (1 H, m), 2.18 (1 H, m), 2.35 (1 H, m), 2.67 (1 H, m), 2.78 (2 H, m), 4.80 (1 H, dd, J 13.6, 1.2 Hz), 5.14 (1 H, q, J 7.6 Hz), 5.50 (1 H, d, J 14.0 Hz), 6.74 (4 H, t, J 8.0 Hz), 6.89 (8 H, t, J 8.0 Hz), 7.06 (1 H, d, J 8.4 Hz), 7.33 (8 H, t, J 8.0 Hz), 7.50 (3 H, m), 7.75 (1 H, m), 7.77–7.80 (1 H, m), 7.94 (1 H, d, J 8.8 Hz), 7.99 (1 H, d, J 8.4 Hz), 8.08 (1 H, d, J 8.4 Hz), 8.20 (1 H, d, J 8.4 Hz), 8.24 (1 H, d, J 8.4 Hz), 8.29 (1 H, d, J 8.4 Hz), 9.72 (1 H, s); δ_C (100 MHz; acetone- d_6) 19.35, 23.36, 28.45, 33.78, 35.05, 40.22, 41.63, 42.26, 48.23, 54.65, 75.38, 122.23, 125.94, 125.97, 126.00, 126.01, 126.03, 126.38, 127.87, 127.93, 128.00, 128.04, 128.07, 128.57, 129.57, 129.63, 130.21, 130.24, 131.19, 132.33, 137.01, 137.04, 142.38, 164.90, 171.15; m/z (FAB $^+$) 430 (M^+ , 100%), 294 (55%), 277 (52%), 265 (61%), 263 (32%), 252 (20%); 430.2536; $C_{32}H_{32}N$ (cation) requires 430.2535.

Representative epoxidation procedure:

To an ice cooled solution of sodium carbonate (0.26 g, 2.52 mmol), in water (2.1 ml), OxoneTM (0.77 g, 1.26 mmol), was added with stirring and the resulting foaming solution left to stir for 5–10 minutes, so that most of the initial effervescence subsided. The iminium salt (**6a**), (0.5 mol %, 0.0025 g, 0.0032 mmol), was then added as a solution in acetonitrile, (1.05 ml), followed by 1-phenylcyclohexene, (1 equivalent, 0.10 g, 0.63 mmol), also as a solution in acetonitrile (1.05 ml). The suspension was stirred at the same temperature until the substrate was completely consumed by TLC (2.0 h). The reaction mixture was then diluted with ice cooled diethyl ether (20 ml) and immediately followed by the addition of water (20 ml). The aqueous phase was washed with diethyl ether (4 x 20 ml) and the organics were combined, washed with brine and dried

(MgSO₄). Filtration and evaporation of the solvents furnished a light brown residue. Column chromatography eluting with ethyl acetate : light petroleum (1:99) afforded pure 1-phenylcyclohexene oxide as a colourless oil (0.071 g, 65 %, 91 % ee, (–)-1*S*,2*S*). Colourless oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3084, 1602, 1495, 1446, 1359, 1249, 1173, 1132, 1079, 1030, 993, 974; $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$ 1.22-1.35 (1H, m), 1.53-1.64 (3H m), 1.99-2.06 (2H, m) 2.16-2.18 (1H, m), 2.26-2.32 (1H, m), 3.10 (1 H, t, *J* 2.0 Hz), 7.28-7.44 (5 H, m); $\delta_{\text{C}}(62.5 \text{ MHz}; \text{CDCl}_3)$ 19.8, 20.1, 24.7, 28.2, 60.1, 61.8, 125.3, 127.1, 128.2, 142.8.

Control Epoxidation Reaction:

To an ice cooled solution of sodium carbonate (0.26 g, 2.5 mmol), in water (2.1 ml), Oxone™ (0.77 g, 1.3 mmol), was added with stirring and the resulting foaming solution left to stir for 5-10 minutes, so that most of the initial effervescence subsided. 1-Phenylcyclohexene (1 equivalent, 0.10 g, 0.63 mmol) was then added as a solution in acetonitrile (2.1 ml). The suspension was stirred at the same temperature for 8 h at which point 1-phenylcyclohexene oxide became detectable by tlc analysis. The reaction mixture was diluted with ice cooled diethyl ether (20 ml), immediately followed by the addition of water (20 ml). The aqueous phase was washed with diethyl ether (4 x 20 ml) and the organics were combined, washed with brine and dried (MgSO₄). Filtration and evaporation of the solvents furnished a colourless oil. Analysis by ¹H-NMR spectroscopy showed less than 5% conversion to epoxide (conversion was evaluated by integration of epoxide versus alkene).

2-Methyl-(*E*)-2,3-diphenyloxirane:

Trans-(α -Methyl)-stilbene oxide:⁵ Colourless oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3061, 1602, 1495, 1449, 1381, 1279, 1157, 1118, 1065, 1027, 980; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 1.46 (3 H, s), 3.96 (1 H, s), 7.30-7.46 (10 H, m); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 17.1, 63.5, 67.5, 125.6, 126.9, 127.7, 127.9, 128.6, 129.2, 136.4, 142.8.

2,2,3-Triphenyloxirane:

Triphenylethylene oxide:^{Error! Bookmark not defined.,6} Colourless oil which slowly solidified; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3062, 3030, 2957, 2925, 2856, 1605, 1596, 1499, 1471, 1448, 1262, 1221, 741, 698, 621; $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$ 4.40 (1 H, s), 7.10-7.47 (15 H, m); $\delta_{\text{C}}(62.5 \text{ MHz}; \text{CDCl}_3)$ 68.0, 68.3, 126.3, 126.8, 127.5, 127.6, 127.7, 127.8 128.0, 128.2, 128.6, 135.42, 135.9, 141.1.

7b-Phenyl-1a,2,3,7b-tetrahydro-1-oxa-cyclopropa[*a*]naphthalene:

1-Phenyl-3,4-dihydronaphthalene oxide:^{Error! Bookmark not defined.,7} Pale yellow solid; $\nu_{\max}(\text{nujol})/\text{cm}^{-1}$ 1602, 1486, 1307, 1155, 1074, 1042, 953; $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$ 2.10 (1 H, td, *J* 5.8, 13.7 Hz), 2.49-2.60 (1 H, m), 2.77 (1 H, dd, *J* 5.6, 15.5 Hz), 2.98-3.06 (1 H, m), 3.71 (1 H, d, *J* 3.1 Hz), 7.11-7.31 (4 H, m), 7.45-7.61 (5 H, m); $\delta_{\text{C}}(62.5 \text{ MHz}; \text{CDCl}_3)$ 22.1, 25.4, 60.9, 63.0, 126.0, 127.7, 127.9, 128.1, 128.2, 128.6, 129.8, 135.0, 137.5, 138.8.

(E)-2,3-Diphenyloxirane:

Trans-stilbene oxide:**Error! Bookmark not defined.**⁸ Colourless solid; $\nu_{\max}(\text{nujol})/\text{cm}^{-1}$ 1601, 1492, 1284, 1176, 1157, 1094, 1072, 1025; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 3.84 (2 H, s), 7.28-7.37 (10 H m); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 63.3, 126.0, 128.6, 129.3, 137.6.

2-Biphenyl-4-yl-oxirane:

para-Phenylstyrene oxide:⁹ Colourless solid; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 2.85 (1 H, dd, J 2.6, 5.5 Hz), 3.91 (1 H, dd, J 2.5, 4.0 Hz), 7.30-7.68 (9 H, m); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 51.2, 52.2, 126.0, 127.1, 127.3, 127.4, 128.8, 136.6, 140.7, 141.2.

1-tert-Butyl-7-oxa-bicyclo[4.1.0]heptane:

1-tert-Butyl-cyclohex-1-ene oxide:¹⁰ Colourless oil; $\nu_{\max}(\text{nujol})/\text{cm}^{-1}$ 2938, 2868, 1481, 1433, 1363, 1036, 921, 767; $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$ 0.73 (9 H, s), 0.91-1.10 (2 H, m), 1.12-1.36 (2 H, m), 1.46-1.61 (2 H, m), 1.64-1.81 (2 H, m), 2.91-2.93 (1 H, m); $\delta_{\text{C}}(62.5 \text{ MHz}; \text{CDCl}_3)$ 19.69, 21.09, 24.82, 25.29, 25.53, 44.77, 55.16, 64.66.

1a,2,3,7b-Tetrahydro-1-oxa-cyclopropa[a]naphthalene:

1,2-Dihydronaphthylene oxide:¹¹ Colourless oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3059, 3028, 2930, 2850, 1602, 1493, 1316, 1129, 1088, 1030, 964; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 1.65-1.73 (1 H, m), 2.30-2.36 (1 H, m), 2.45 (1 H, dd, J 15.6, 5.6 Hz), 2.67-2.74 (1 H, m), 3.65 (1 H, t, J 4.0 Hz), 3.78 (1 H, d, J 4.4 Hz), 7.01 (1 H, d, J 7.2 Hz), 7.10-7.20 (2 H, m), 7.33 (1 H, d, J 7.2 Hz); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 22.2, 24.8, 55.2, 55.6, 126.5, 128.8, 128.8, 129.9, 132.9, 137.1.

(3-Phenyl-oxiranyl)-methanol:

Trans-Cinnamyl alcohol oxide:¹² Colourless solid; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3322, 3266, 2863, 1664, 1494, 1449, 1091, 1007, 733; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 1.92 (1 H, s), 3.2 (1 H, ddt, J 0.1, 2.0, 3.8 Hz), 3.8 (1 H, dd, J 3.8, 12.7 Hz), 3.9 (1 H, d, J 2.1 Hz), 4.04 (1 H, dd, J 2.3, 12.7 Hz), 7.26-7.41 (5 H, m); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 55.7, 61.3, 62.6, 125.8, 128.3, 128.5, 136.7.

1-Phenyl-8-oxa-bicyclo[5.1.0]octane:

1-Phenylcyclohept-1-ene oxide:¹³ Colourless oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3084, 1602, 1494, 1445, 1358, 1255, 1166, 1128, 1088, 1030, 964, 855, 738; $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$ 1.50-1.85 (6 H, m), 1.90-2.20 (2 H, m), 2.38-2.50 (2 H, m), 3.04 (1 H, q, J 3.8 Hz), 7.25-7.40 (5 H, m); $\delta_{\text{C}}(62.5 \text{ MHz}; \text{CDCl}_3)$ 24.9, 25.5, 29.9, 31.7, 33.9, 63.4, 65.8, 125.4, 127.3, 128.5, 142.0.

Determination of enantiomeric excess for 1-Phenyl-7-oxa-bicyclo[4.1.0]heptane:

^1H -NMR conditions: 8-10 mg substrate
3-5 mg (+)-Eu(hfc)₃

Racemic: Literature Ref: Tu, Y.; Wang, Z.-X.; Shi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9806.

Reaction material: Table 2 Catalyst *ent*-7a:

Determination of enantiomeric excess for 1-Phenyl-7-oxa-bicyclo[4.1.0]heptane:

^1H -NMR conditions: 8-10 mg substrate
3-5 mg (+)-Eu(hfc)₃

Reaction material: Table 2, Catalyst 7b:

Determination of enantiomeric excess for 1-Phenyl-7-oxa-bicyclo[4.1.0]heptane:

^1H -NMR conditions: 8-10 mg substrate
3-5 mg (+)-Eu(hfc)₃

Reaction material: Table 2, Catalyst 7c:

Determination of enantiomeric excess for 1-Phenyl-7-oxa-bicyclo[4.1.0]heptane:

^1H -NMR conditions: 8-10 mg substrate
3-5 mg (+)-Eu(hfc)₃

Reaction material: Table 2, Catalyst 7d:

Determination of enantiomeric excess for 1-Phenyl-7-oxa-bicyclo[4.1.0]heptane:

^1H -NMR conditions: 8-10 mg substrate
3-5 mg (+)-Eu(hfc)₃

Reaction material: Table 4 and 5 Catalyst 7a (1 mol%):

Determination of enantiomeric excess for 1-Phenyl-7-oxa-bicyclo[4.1.0]heptane:

^1H -NMR conditions: 8-10 mg substrate
 3-5 mg (+)-Eu(hfc)₃

Reaction material: Table 5: Catalyst 7a (0.5 mol%):

Determination of enantiomeric excess for 1-Phenyl-7-oxa-bicyclo[4.1.0]heptane:

^1H -NMR conditions: 8-10 mg substrate
 3-5 mg (+)-Eu(hfc)₃

Reaction material: Table 5: Catalyst 7a (0.1 mol%):

Determination of enantiomeric excess for 2-Methyl-(*E*)-2,3-diphenyloxirane:

¹H-NMR conditions: 8-10 mg substrate
3-5 mg (+)-Eu(hfc)₃

Racemic: Literature Ref: Tu, Y.; Wang, Z.-X.; Shi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9806.

Reaction material: Reaction Material: Table 2, Catalyst 7a:

Determination of enantiomeric excess for 2,2,3-Triphenyloxirane:

¹H-NMR conditions: 8-10 mg substrate
3-5 mg (+)-Eu(hfc)₃

Racemic: Literature Ref: Tu, Y.; Wang, Z.-X.; Shi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9806.

Reaction Material: Table 2, Catalyst 7a:

Determination of enantiomeric excess for 1a,2,3,7b-Tetrahydro-1-oxa-cyclopropa[*a*]naphthalene:

¹H-NMR conditions: 8-10 mg substrate
3-5 mg (+)-Eu(hfc)₃

Racemic: Literature Ref: Wong, M.-K.; Ho, L.-M.; Zheng, Y.-S.; Ho, C.-Y.; Yang, D. *Org. Lett.* **2001**, 3, 2587.

Reaction Material: Table 3, Catalyst 7a:

Determination of enantiomeric excess for 7b-Phenyl-1a,2,3,7b-tetrahydro-1-oxa-cyclopropa[a]naphthalene:

HPLC conditions: Flow : 1.0
 Hex:IPA : 90:10

Racemic: Literature Ref: Wang, Z.-X.; Tu, Y.; Frohn, M.; Zhang, J.-R.; Shi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11224.

Retention times: (1*S*,2*R*) = 9.88; (1*R*,2*S*) = 12.16.

CHANNEL A INJECT 25-10-02 15:01:00 REPLAYED FROM BIN # 5

25-10-02 15:01:00 CH= "A" PS= 1.

FILE 1.	METHOD	0.	RUN	6	INDEX	6	BIN	5
PEAK#	AREA	RT	AREA	BC				
1	0.756	0.54	113010	02				
2	1.345	4.67	200934	02				
3	2.335	5.26	348844	03				
4	0.206	7.01	30819	01				
5	0.139	8.7	20816	01				
6	47.351	9.88	7074664	01				
7	0.28	11.23	41760	02				
8	46.666	12.16	7005163	03				
9	0.709	15.02	104929	01				
TOTAL	100.		1454666					

Reaction Material, Table 3, Catalyst 7a:

Retention times: (1*S*,2*R*) = 9.78; (1*R*,2*S*) = 11.81.

CHANNEL A INJECT 25-10-02 17:16:37 STORED TO BIN # 10

DATA SAVED TO BIN # 10

1RUN2306 25-10-02 17:16:37 CH= "A" PS= 1. BIN 10

FILE 1. METHOD 0. RUN 14 INDEX 14

PEAK# AREA% RT AREA BC

1	10.814	4.6	3682926	02
2	22.79	5.2	8183042	02
3	1.965	6.49	705462	02
4	2.485	6.9	892284	02
5	2.936	7.65	1034270	02
6	1.797	9.12	645212	02
7	55.736	9.78	20012539	08
8	1.477	11.81	530426	05

TOTAL 100. 35906161

Determination of enantiomeric excess for 2-Biphenyl-4-yl-oxirane:

HPLC conditions: Flow : 1.5
Hex:IPA : 95:5

Racemic: Literature Ref: Wang, Z.-X.; Shi, Y. *J. Org. Chem.* **1997**, 62, 8622.

Retention times: (*R*) = 6.54; (*S*) = 7.41.

DATA SAVED TO BIN # 3

09-03-02 15:54:37 CH= 'A' PS= 1.

FILE 1. METHOD 0. RUN 3 INDEX 3 BIN 3

PEAK#	AREA	RT	AREA BC
1	2.825	3.23	580662.01
2	0.398	4.88	99966.01
3	0.094	5.57	23606.02
4	0.191	5.92	47959.02
5	45.62	6.54	1145725.08
6	42.921	7.41	10779857.06
7	1.619	7.92	406733.06
8	2.18	8.38	547570.07
9	4.101	17.36	1030066.02
10	0.95	17.74	213448.03

Reaction Material, Table 3, Catalyst 7a:

Retention times: (*R*) = 6.60; (*S*) = 7.49.

CHANNEL A INJECT 09-03-02 18:20:28 STORED TO BIN # 10

DATA SAVED TO BIN # 10

09-03-02 18:20:28 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 11 INDEX 11 BIN 10

PEAK#	AREA%	RT	AREA BC
1	4.037	4.83	842514 01
2	32.761	6.46	6837145 02 -
3	0.697	7.01	145491 02
4	59.582	7.3	12434436 08 -
5	0.923	8.2	192675 05
6	1.03	9.71	214979 01
7	0.167	11.12	34797 01
8	0.803	19.39	167490 01

TOTAL 100. 20869527

Determination of enantiomeric excess for 1-*tert*-Butyl-7-oxa-bicyclo[4.1.0]heptane:

¹H-NMR conditions:

8-10 mg substrate

3-5 mg (+)-Eu(hfc)₃

Racemic: Literature Ref: Wang, Z.-X.; Tu, Y.; Frohn, M.; Zhang, J.-R.; Shi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11224.

Reaction Material, Table 3, Catalyst 7a:

Determination of enantiomeric excess for (3-Phenyl-oxiranyl)-methanol

¹H-NMR conditions:

8-10 mg substrate
3-5 mg (+)-Eu(hfc)₃

Racemic: Literature Ref: Tu, Y.; Wang, Z.-X.; Shi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9806.

Reaction Material, Table 3, Catalyst 7a:

Determination of enantiomeric excess for 1-Phenyl-6-oxa-bicyclo[3.1.0]hexane:

¹H-NMR conditions: 8-10 mg substrate
3-5 mg (+)-Eu(hfc)₃

Racemic: Literature Ref: Brandes, B. D.; Jacobsen, E. N. *J. Org. Chem.* **1994**, *59*, 4378.

Reaction Material, Table 4, Catalyst 7a:

Determination of enantiomeric excess for: 1-Phenyl-6-oxa-bicyclo[3.1.0]hexane:

¹H-NMR conditions: 8-10 mg substrate
3-5 mg (+)-Eu(hfc)₃

Racemic: Literature Ref: Sethi, S. C.; Natu, A. D.; Wadia, M. S. *Heterocycles* **1982**, 221.

Reaction Material, Table 4, Catalyst 7a:

¹ Vondenhof, M.; Mattay, J. *Tetrahedron Lett.*, **1990**, 31, 985.

² Maigrot, N.; Mazaleyrat, J-P. *Synthesis*, **1985**, 317.

³ Mecca, T.; Superchi, S.; Giorgio, E.; Rosini, C. *Tetrahedron: Asymmetry*, **2001**, 1225.

⁴ Mislow, K.; Glass, M. A. W.; O'Brien, R. E.; Rutkin, P.; Steinberg, D. H.; Weiss, J.; Djerassi, C. *J. Am. Chem. Soc.*, **1962**, 84, 1455.

⁵ Brandes, B. D.; Jacobsen, E. N. *J. Org. Chem.* **1994**, 59, 4378.

⁶ Fleiser, R.; Galle, D.; Braun, M. *Liebigs Ann.* **1997**, 6, 1189.

⁷ Padwa, A.; Owens, D. *J. Org. Chem.* **1977**, 42, 3076.

⁸ Solladié-Cavallo, A.; Diep-Vohuule, A.; Sunjic, V.; Vinkovic, V. *Tetrahedron: Asymmetry* **1996**, 7, 1783.; Chang, H.-T.; Sharpless, K. B.; *J. Org. Chem.* **1996**, 60, 6456.

⁹ Miao, G.; Rossiter, B. E. *J. Org. Chem.* **1995**, 60, 8424.

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- ¹⁰ Wang, Z.-X.; Tu, Y.; Frohn, M.; Zhang, J.-R.; Shi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11224.
- ¹¹ Akhtar, M. N.; Boyd, D. R.; Hamilton, J. G. *J. Chem. Soc. Perkin Trans. 1* **1979**, 2437.
- ¹² Melloni, P.; Della Torre, A.; Lazzari, E.; Mazzini, G.; Meroni, M. *Tetrahedron* **1985**, *41*, 1393.
- ¹³ Sethi, S. C.; Natu, A. D.; Wadia, M. S. *Heterocycles* **1982**, 221.