Kinetic Resolution of Hydroperoxides with Enantiopure Phosphines: Preparation of Enantioenriched Tertiary Hydroperoxides

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General. NMR spectra were recorded in CDCl₃ at ambient temperature. ¹H NMR spectra were measured at 500 MHz on a Bruker CRYO500 or GN500 and were referenced to residual CHCl₃ (7.27 ppm). ¹³C NMR spectra were measured at 125 MHz on a Bruker CRYO500 or GN500 and were referenced to the centerline of the CDCl₃ triplet (77.23 ppm). ³¹P NMR spectra were measured at 162 MHz and referenced externally to 85% H₃PO₄ (0.0 ppm). The NMR spectral data are reported as follows: chemical shift in ppm on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qu = quintuplet, sp = septet, m = multiplet), coupling constants (Hz) and integration. Infrared (IR) spectra were obtained using a MIDAC Prospect FT-IR spectrometer. High-resolution mass spectra were acquired on a VG Analytical 7070E or Fisions Autospec spectrometer, and were obtained by peak matching. Atlantic Microlab, Atlanta, GA, performed microanalyses. Melting points are reported uncorrected. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system in EM Reagents silica gel (SiO₂) 60 (230-400 mesh). Enantiomeric excess was determined using a Berger SFC Analytix or a Hewlett Packard series 1100 HPLC, and the enantiomerically enriched material was compared to racemic material (see note below). Optical rotations were measured on a JASCO P-1010 polarimeter. Unless otherwise noted, all reactions were performed open to air and all reagents were obtained from commercial sources and used without further purification. Et₂O and THF were dried by filtration through alumina according to the procedure of Grubbs.¹

Caution: Although we have not had any incidents exploring this chemistry, caution should be exercised when handling organic peroxides: scales should be minimized, safety shields should always be employed and precautions should be taken to minimize exposure to light, heat and metal salts.² In addition, in the syntheses of hydroperoxides, the order of addition of the reagents is crucial to avoid uncontrollable chain reactions; alcohols should be added to a mixture of dilute acid in H₂O-H₂O₂. Concentrated acid should never be added directly to an alcohol-hydrogen peroxide-H₂O mixture, as explosions have been known to occur.³

I. Preparation of Alcohols **12**, **28**, **30**, **32**, **34**, **36**, **38**, **39**, **41**

(±)-3-Methyl-2-phenylbutan-2-ol (12**).**⁴ To a cooled (−78 °C) solution of bromobenzene (7.9 mL, 75 mmol) in THF (250 mL) was added *n*-BuLi (32 mL, 79 mmol, 2.5 M solution in hexane). The mixture was stirred for one hour and 3-methylbutan-2-one (**26**) (9.7 mL, 90 mmol) was added over one-half hour. The reaction mixture was stirred at ambient temperature for one hour and partitioned between Et₂O (100 mL) and water (100 mL). The aqueous layer was extracted with Et₂O (2 × 50 mL). The combined organic layers were washed with brine (50 mL) and dried over MgSO₄. The resulting mixture was filtered and the filtrate was concentrated *in vacuo*. The resulting oil was purified by flash chromatography (hexanes/EtOAc 9:1) yielding alcohol **12** (8.0 g, 65%) as a clear oil. Spectral data matched those reported in the literature:⁵ ¹H NMR (500 MHz, CDCl₃) δ 7.49-7.51 (m, 2H), 7.32-7.42 (m, 2H), 7.23-7.29 (m, 1H), 2.08-2.11 (m, 1H), 1.78 (s, 1H), 1.59 (s, 3H), 0.97 (d, *J* = 6.7, 3H), 0.88 (d, *J* = 6.8, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 148.3, 128.3, 126.9, 125.7, 77.0, 39.1, 27.1, 17.9, 17.8. Anal. Calcd for C₁₁H₁₆O: C, 80.44; H, 9.82. Found: C, 80.27; H, 10.03.

(±)-2-Phenylpentan-2-ol (28**).** The procedure for the synthesis of alcohol (±)-**12** was followed using 2-pentanone (**27**) (5.1 mL, 48 mmol), bromobenzene (5.0 mL, 48 mmol), *n*-BuLi (34 mL, 48 mmol, 1.4 M solution in hexane) to afford alcohol **28** as a clear oil (5.2 g, 67%) after purification by flash chromatography (hexanes/EtOAc 19:1). Spectral data matched those reported in the literature:⁶ ¹H NMR (500 MHz, CDCl₃) δ 7.49-7.51 (m, 2H), 7.39-7.42 (m, 2H), 7.28-7.32 (m, 1H), 1.79-1.87 (m, 2H), 1.79 (s, 1H), 1.62 (s, 3H), 1.22-1.37 (m, 2H), 0.93 (t, *J* = 7.5, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 148.1, 128.2, 126.5, 124.8, 74.8, 46.6, 30.2, 17.3, 14.5; IR (thin film) 3417, 2935, 1951, 1885, 1447, 1029 cm^{−1}. Anal. Calcd for C₁₁H₁₆O: C, 80.44; H, 9.82. Found: C, 80.41; H, 10.10.

(±)-2-Phenylhexan-2-ol (30). The procedure for the synthesis of alcohol (±)-**12** was followed using 2-pentanone (**29**) (4.8 g, 48 mmol), bromobenzene (5.0 mL, 48 mmol), *n*-BuLi (19 mL, 48 mmol, 2.5 M solution in hexane) to afford alcohol **30** as a clear oil (5.3 g, 63%) after purification by flash chromatography (hexanes/EtOAc 19:1). Spectral data matched those reported in the literature:⁷ ¹H NMR (500 MHz, CDCl₃) δ 7.43-7.45 (m, 2H), 7.33-7.37 (m, 2H), 7.23-7.26 (m, 1H), 1.78-1.84 (m, 2H), 1.72 (s, 1H), 1.57 (s, 3H), 1.23-1.30 (m, 3H), 1.11-1.14 (m, 1H), 0.86 (t, *J* = 7.0, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 148.1, 128.2, 126.5, 124.8, 74.8, 44.0, 30.2, 26.2, 23.2, 14.1; IR (thin film) 3417, 3027, 2958, 1603, 1495, 1028 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₂H₁₈O [M+Na]⁺ 201.1255, found 201.1253.

(±)-4-Methyl-2-phenylpentan-2-ol (32). The procedure for the synthesis of alcohol (±)-**12** was followed using 4-methyl-2-pentanone (**31**) (5.9 mL, 48 mmol), bromobenzene (5.0 mL, 48 mmol), *n*-BuLi (20 mL, 48 mmol, 1.4 M solution in hexane) to afford alcohol **32** as a clear oil (4.3 g, 50%) after purification by flash chromatography (hexanes/EtOAc 19:1). Spectral data matched those reported in the literature:⁸ ¹H NMR (500 MHz, CDCl₃) δ 7.45-7.46 (m, 2H), 7.33-7.37 (m, 2H), 7.23-7.27 (m, 1H), 1.69-1.83 (m, 4H), 1.57 (s, 3H), 0.89 (d, *J* = 6.6, 3H), 0.77 (d, *J* = 6.5, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 148.3, 128.1, 126.5, 124.9, 75.3, 52.8, 31.4, 24.5, 24.4; IR (thin film) 3449, 2956, 2717, 1602, 1446, 1028 cm⁻¹. Anal. Calcd for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 80.59; H, 10.28.

(±)-1-Cyclohexyl-1-phenylethanol (34). The procedure for the synthesis of alcohol (±)-**12** was followed using 1-cyclohexylethanone (**33**) (6.0 mL, 48 mmol), bromobenzene (5.0 mL, 48 mmol), *n*-BuLi (37 mL, 52 mmol, 2.4 M solution in hexane) to afford alcohol **34** as a clear oil (4.1 g, 46%) after purification by flash chromatography (hexanes/EtOAc 19:1). Spectral data matched those reported in the literature:⁹ ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.43 (m, 2H), 7.32-7.36 (m, 2H), 7.23-7.26 (m, 1H), 2.14 (s, 1H), 1.54-1.77 (m, 5H), 1.54 (s, 3H), 0.89-1.22 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 148.1, 128.0, 126.5, 125.5, 76.8, 49.2, 27.4, 27.2, 26.8, 26.71, 26.70, 26.5; IR (thin film)

3449, 2956, 1602, 1446, 1165, 1028 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{20}\text{O}$ $[\text{M}+\text{Na}]^+$ 227.1412, found 227.1401.

(±)-2-Methyl-1-phenylpropan-1-ol (36). The procedure for the synthesis of alcohol (±)-**12** was followed using with 2-methylpropionaldehyde (**35**) (4.3 mL, 48 mmol), bromobenzene (5.0 mL, 48 mmol), *n*-BuLi (22 mL, 47 mmol, 2.1 M solution in hexane) to afford alcohol **36** as a clear oil (3.7 g, 52%) after purification by flash chromatography (hexanes/EtOAc 19:1). Spectral data matched those reported in the literature:¹⁰ ^1H NMR (500 MHz, CDCl_3) δ 7.23-7.33 (m, 5H), 4.31 (d, $J = 6.9$, 1H), 2.05 (s, 1H), 1.89-1.96 (m, 1H), 0.98 (d, $J = 6.7$, 3H), 0.77 (d, $J = 6.7$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.1, 128.6, 127.1, 126.8, 80.5, 35.7, 19.5, 18.7.

(±)-3,4-Dimethyl-1-phenylpentan-3-ol (38). To a cooled solution (0 °C) of 4-phenylbutan-2-one (**37**) (10.0 mL, 66.7 mmol) in Et_2O (175 mL) was added *i*-PrMgBr (33 mL, 66 mmol, 2.0 M solution in Et_2O) over one hour. The reaction mixture was stirred for two hours at ambient temperature and diluted with saturated aq NH_4Cl (150 mL) at 0 °C. The aqueous layer was extracted with Et_2O (75 mL) and the combined organic layers were washed with brine (100 mL), dried over MgSO_4 , and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (hexanes/EtOAc 19:1) yielding alcohol **38** (4.7 g, 24.5 mmol). Spectral data matched those reported in the literature:¹¹ ^1H NMR (500 MHz, CDCl_3) δ 7.20-7.33 (m, 5H), 2.70-2.77 (m, 2H), 1.77-1.84 (m, 3H), 1.31 (s, 1H), 1.22 (s, 3H), 1.00 (d, $J = 6.8$, 3H), 0.97 (d, $J = 6.9$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.1, 128.7, 128.6, 126.0, 74.9, 42.1, 37.3, 30.2, 23.3, 17.8, 17.2; IR (thin film) 3419, 2877, 1603, 1497, 1374, 1094 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{20}\text{ONa}$ $[\text{M}+\text{Na}]^+$ 215.1412, found 215.1411. Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{O}$: C, 81.20; H, 10.48. Found: C, 81.16; H, 10.56.

(±)-2,3-Dimethyl-1-phenylbutan-2-ol (39).¹² Benzyl chloride (23.7 mL, 205 mmol) was added to a slurry of magnesium (5.00 g, 205 mmol) in refluxing Et_2O (200 mL) over one hour. The reaction mixture was stirred at reflux for two hours and 3-methylbutan-2-one

(**26**) (17.7 mL, 165 mmol) was added over one hour. The reaction mixture was stirred for 18 hours at ambient temperature and then was diluted with saturated aq NH_4Cl (300 mL). The organic layer was washed with saturated aq NH_4Cl (300 mL), brine (100 mL), dried over MgSO_4 , and concentrated *in vacuo*. The resulting oil was purified by distillation (bp 72-74 °C, 0.5 mm Hg) yielding alcohol **39** (12.3 g, 42%). Spectral data matched those reported in the literature:¹² ^1H NMR (500 MHz, CDCl_3) δ 7.28-7.32 (m, 2H), 7.21-7.25 (m, 3H), 2.74 (d, 13.3, 1H), 2.70 (d, 13.5 1H), 1.72 (m, 1H), 1.26 (s, 1H), 1.03 (s, 3H), 1.00 (d, $J = 6.8$, 3H), 0.97 (d, $J = 6.8$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 137.9, 130.9, 128.3, 126.6, 74.7, 45.3, 37.2, 23.0, 18.1, 17.4. Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}$: C, 80.85; H, 10.18. Found: C, 80.69; H, 10.21.

(±)-Cyclohexylphenylmethanol (**41**). To a slurry of cyclohexylphenylmethanone (**40**) (3.5 g, 18 mmol) in MeOH (20 mL) was added NaBH_4 (0.70 g, 18 mmol). The slurry was stirred for ten minutes and then was diluted with H_2O (15 mL). The aqueous layer was extracted with Et_2O (3×20 mL) and the combined organic layers were washed with brine (100 mL), dried over MgSO_4 , and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (hexanes/ EtOAc 19:1) yielding alcohol **41** (3.5 g, 73%). Spectral data matched those reported in the literature:¹³ ^1H NMR (500 MHz, CDCl_3) δ 7.32-7.42 (m, 5H), 4.42 (d, $J = 7.2$, 1H), 2.04-2.07 (m, 1H), 1.95 (s, 1H), 1.80-1.87 (m, 1H), 1.60-1.79 (m, 3H), 1.42-1.46 (m, 1H), 1.24-1.33 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.8, 128.4, 127.6, 126.8, 79.6, 45.1, 29.5, 29.0, 26.6, 26.3, 26.2; IR (thin film) 3409, 2852, 1603, 1493, 1451, 1015 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{ONa}$ $[\text{M}+\text{Na}]^+$ 213.1255, found 213.1259. Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}$: C, 82.06; H, 9.53. Found: C, 82.08; H, 9.53.

II. Preparation of Hydroperoxides 11, 13-24

(±)-3-Methyl-2-phenylbut-2-yl hydroperoxide (**11**).¹⁴ To a cooled (0 °C) solution of H_2O_2 (65 mL, 1.1 mol, 50% wt in H_2O) and H_2SO_4 (1.0 mL, 19 mmol) was added 3-methyl-2-phenylbutan-2-ol (**12**) (6.9 g, 42 mmol). The reaction mixture was stirred vigorously at ambient temperature for 14 hours and then was partitioned between Et_2O (100 mL) and water (100 mL). The aqueous layer was extracted with Et_2O (2×50 mL) and the combined organic layers were washed with 1 N NaOH (3×25 mL) and brine (50 mL). The resulting solution was dried over MgSO_4 and concentrated *in vacuo* to yield hydroperoxide **11** (6.1 g, 78%) as a clear oil. Spectral data matched those reported in the literature:¹⁵ ^1H NMR (500 MHz, CDCl_3) δ 7.42-7.48 (m, 4H), 7.37 (tt, $J = 6.8, 1.8$, 1H),

7.32 (s, 1H), 2.00 (sp, $J = 6.9$, 1H), 1.66 (s, 3H), 0.96 (d, $J = 6.8$, 3H), 0.69 (d, $J = 6.9$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.3, 128.3, 127.2, 126.3, 89.1, 37.0, 17.9, 17.4, 17.3; IR (thin film) 3422, 2965, 2878, 1446, 1030 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 73.30; H, 8.95. Found: C, 73.04; H, 8.93.

(±)-2-Phenylbut-2-yl hydroperoxide (13). The procedure for the synthesis of hydroperoxide ($\pm$)-**11** was followed using alcohol **42** (5.0 g, 33.3 mmol) to afford hydroperoxide **13** as a clear oil (4.2 g, 76%) after purification by flash chromatography (hexanes/EtOAc 19:1). Previous literature report does not provide NMR spectral data.¹⁶ ^1H NMR (500 MHz, CDCl_3) δ 7.54 (s, 1H), 7.36-7.48 (m, 4H), 7.29-7.35 (m, 1H), 1.85-1.92 (m, 2H), 1.68 (s, 3H), 0.87 (t, $J = 7.4$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.0, 128.6, 127.5, 125.9, 86.9, 32.5, 22.1, 8.5. HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{14}\text{O}_2\text{Na}$ [$\text{M}+\text{Na}$] $^+$ 189.0892, found 189.0897.

(±)-2-Phenylpent-2-yl hydroperoxide (14). The procedure for the synthesis of hydroperoxide ($\pm$)-**11** was followed using alcohol **28** (1.0 mL, 5.9 mmol) to afford hydroperoxide **14** as a clear oil (0.48 g, 46%) after purification by flash chromatography (hexanes/EtOAc 19:1). Spectral data matched those reported in the literature:¹⁷ ^1H NMR (500 MHz, CDCl_3) δ 7.38-7.45 (m, 4H), 7.29-7.32 (m, 1H), 7.21 (s, 1H), 1.75-1.80 (m, 2H), 1.67 (s, 3H), 1.30-1.35 (m, 1H), 1.18-1.20 (m, 1H), 0.88 (t, $J = 7.4$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.1, 128.6, 127.4, 125.7, 86.6, 42.2, 22.5, 17.3, 14.5; IR (thin film) 3427, 2960, 2873, 1447, 1314, 1028 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}$: C, 73.30; H, 8.95. Found: C, 73.26; H, 9.07.

(±)-2-Phenylhex-2-yl hydroperoxide (15). The procedure for the synthesis of hydroperoxide ($\pm$)-**11** was followed using alcohol **30** (1.0 g, 5.6 mmol) to afford hydroperoxide **15** as a clear oil (0.70 g, 65%) after purification by flash chromatography (hexanes/EtOAc 19:1). Spectral data matched those reported in the literature:¹⁸ ^1H NMR (500 MHz, CDCl_3) δ 7.45-7.46 (m, 2H), 7.39-7.44 (m, 2H), 7.27-7.33 (m, 1H), 7.28 (s, 1H), 1.75-1.82 (m, 2H), 1.68 (s, 3H), 1.24-1.31 (m, 3H), 1.11-1.16 (m, 1H), 0.88 (t, $J = 7.3$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.3, 128.7, 127.5, 125.9, 86.7, 39.8, 26.2, 23.3, 22.6, 14.2. Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2$: C, 74.19; H, 9.34. Found: C, 74.02; H, 9.43.

(±)-4-Methyl-2-phenylpent-2-yl hydroperoxide (16). The procedure for the synthesis of hydroperoxide (±)-**11** was followed using alcohol **32** (3.2 mL, 5.9 mmol) to afford hydroperoxide **16** as a clear oil (1.9 g, 57%) after purification by flash chromatography (hexanes/EtOAc 19:1). Spectral data matched those reported in the literature:⁸ ¹H NMR (500 MHz, CDCl₃) δ 7.38-7.47 (m, 4H), 7.29-7.32 (m, 1H), 7.29 (s, 1H), 1.65-1.74 (m, 6H), 0.90 (d, *J* = 6.6, 3H), 0.78 (d, *J* = 6.6, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 144.5, 128.5, 127.3, 125.8, 87.0, 49.0, 24.5, 24.4, 24.3, 22.8; IR (thin film) 3418, 2950, 1951, 1603, 1447, 1029 cm⁻¹. Anal. Calcd for C₁₂H₁₈O₂: C, 74.19; H, 9.34. Found: C, 74.12; H, 9.36.

(±)-1-Cyclohexyl-1-phenyleth-1-yl hydroperoxide (17). The procedure for the synthesis of hydroperoxide (±)-**11** was followed using alcohol **34** (1.0 g, 4.9 mmol) to afford hydroperoxide **17** as a clear oil (0.5 g, 42%) after purification by flash chromatography (hexanes/EtOAc 19:1). Spectral data matched those reported in the literature:¹⁷ ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.40 (m, 4H), 7.30-7.32 (m, 1H), 7.09 (s, 1H), 1.60-1.69 (m, 8H), 0.91-1.09 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 143.7, 128.5, 127.4, 126.5, 89.7, 47.8, 28.0, 27.8, 26.8, 26.7, 26.6, 18.6; IR (thin film) 3419, 2929, 1603, 1447, 1059, 1028 cm⁻¹. Anal. Calcd for C₁₄H₂₀O₂: C, 76.33; H, 9.15. Found: C, 76.60; H, 9.22.

(±)-3,4-Dimethyl-1-phenylpent-3-yl hydroperoxide (24). The procedure for the synthesis of hydroperoxide (±)-**11** was followed using alcohol **38** (1.0 g, 4.9 mmol) to afford hydroperoxide **24** as a clear oil (0.30 g, 30%) after purification by flash chromatography (hexanes/EtOAc 19:1) as a clear oil (0.30 g, 30%): ¹H NMR (500 MHz, CDCl₃) δ 7.31-7.33 (m, 2H), 7.24-7.30 (m, 2H), 7.19-7.23 (m, 1H), 9.98 (s, 1H), 2.69-2.73 (m, 2H), 2.10-2.15 (m, 1H), 1.90-1.94 (m, 2H), 1.16 (s, 3H), 0.93-0.97 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 143.2, 128.6, 128.5, 126.0, 87.0, 37.0, 32.8, 29.8, 17.9, 17.2, 17.1; IR (thin film) 3406, 2962, 1603, 1497, 1096, 1030 cm⁻¹.

(±)-2,3-Dimethyl-1-phenylbut-2-yl hydroperoxide (23).¹⁹ To a solution of H₂O₂ (20.0 mL, 320 mmol, 50% wt in H₂O) and H₃PO₄ (8.0 mL, 18 mmol) was added alcohol **39** (1.0 g, 4.9 mmol). The reaction mixture was heated (40 °C) for 18 hours and then was partitioned between Et₂O (50 mL) and H₂O (50 mL). The aqueous layer was extracted with Et₂O (2 × 25 mL) and the combined organic layers were washed with brine (50 mL), dried over MgSO₄, and concentrated *in vacuo*. Purification by flash chromatography (hexanes/EtOAc 5:1) yielded hydroperoxide **23** as a clear oil (0.31 g, 31%): ¹H NMR (500 MHz, CDCl₃) δ 7.22-7.32 (m, 5H), 7.08 (s, 1H), 2.95 (d, *J* = 14.2, 1H), 2.85 (d, *J* = 14.2, 1H), 2.06-2.12 (m, 1H), 1.03 (s, 3H), 1.01 (d, *J* = 6.9, 3H), 0.97 (d, *J* = 6.9, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.9, 130.8, 128.2, 126.3, 87.4, 40.1, 32.9, 18.1, 17.4, 17.2.

tert-Butyl-dimethyl-(2-phenyl-allyloxy)-silane (44). To a cooled (0 °C) solution of alcohol **43**²⁰ (2.6 g, 20 mmol) in CH₂Cl₂ (40 mL) were added *t*-BuMe₂SiCl (3.8 g, 25 mmol) and Et₃N (8.2 mL, 59 mmol) over one half hour. The reaction mixture was stirred at ambient temperature for 12 hours and then partitioned between water (100 mL) and CH₂Cl₂ (100 mL). The organic layer was washed with brine (50 mL), dried over MgSO₄ and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (hexanes/EtOAc 50:1) to yield *tert*-butyl-dimethyl-(2-phenyl-allyloxy)-silane **44** as a clear oil (4.1 g, 84%): ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.48 (m, 2H), 7.35-7.41 (m, 2H), 7.30-7.34 (m, 1H), 5.47 (d, *J* = 10.8 Hz, 2H), 4.58 (s, 2H), 0.99 (s, 9H), 0.16 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 147.2, 139.4, 128.5, 127.8, 126.2, 111.5, 64.9, 26.1, 18.6, -5.1; IR (thin film) 3245, 3033, 2858, 1254, 1129, 1082 cm⁻¹.

1-(tert-Butyl-dimethyl-silanyloxy)-2-phenyl-prop-2-yl-hydroperoxytriethylsilyl ether (45). To a solution of silyl ether **44** (2.3 g, 9.4 mmol) in anhydrous EtOH (20 mL) were added Co(acac)₂ (0.24 g, 0.94 mmol) and Et₃SiH (3.0 mL, 18.8 mmol). The reaction mixture was stirred under O₂ (1 atm) for one half hour and then was concentrated *in vacuo*. The resulting dark green oil was partitioned between H₂O (50 mL) and EtOAc (50 mL) and the aqueous layer was extracted with EtOAc (2 × 25 mL). The organic layers were combined and washed with brine (50 mL), dried with MgSO₄ and

concentrated *in vacuo*. Purification by flash chromatography (hexanes/EtOAc 33:1) afforded 1-(*tert*-butyl-dimethyl-silanyloxy)-2-phenyl-prop-2-yl-hydroperoxytriethylsilyl ether (**45**) as a clear oil (1.8 g, 49%): ^1H NMR (500 MHz, CDCl_3) δ 7.44-7.48 (m, 2H), 7.30-7.35 (m, 2H), 7.23-7.28 (m, 1H), 3.78 (d, $J = 10.4$, 1H), 3.74 (d, $J = 10.4$, 1H), 1.64 (s, 3H), 1.00 (t, $J = 7.8$, 9H), 0.86 (s, 9H), 0.72 (q, $J = 7.7$, 6H), -0.02 (s, 3H), -0.05 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.3, 127.9, 127.2, 126.6, 86.4, 68.6, 26.0, 20.4, 18.4, 7.0, 4.0, -5.4, -5.5; IR (thin film) 2956, 2931, 1727, 1472, 1252, 1109 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{40}\text{O}_3\text{Si}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 419.2414, found 419.2415.

1-(*tert*-Butyl-dimethyl-silanyloxy)-2-phenyl-prop-2-yl-hydroperoxide (18**).** A solution of silylperoxy ether (**45**) (0.50 g, 1.3 mmol) in 2 M NaOH/MeOH (5:95) was stirred at ambient temperature for 45 minutes. The reaction mixture was then diluted with H_2O (20 mL) and extracted with EtOAc (2×20 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO_4 , and concentrated *in vacuo*. Purification by flash chromatography (hexanes/EtOAc 9:1) yielded 1-(*tert*-butyl-dimethyl-silanyloxy)-2-phenyl-prop-2-yl-hydroperoxide (**18**) as a clear oil (0.06 g, 17%): ^1H NMR (500 MHz, CDCl_3) δ 8.15 (s, 1H), 7.47-7.51 (m, 2H), 7.37-7.41 (m, 2H), 7.30-7.33 (m, 1H), 3.94 (d, $J = 10.6$, 1H), 3.88 (d, $J = 10.6$, 1H), 1.65 (s, 3H), 0.91 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 142.1, 128.5, 127.8, 126.2, 86.3, 68.9, 26.0, 21.2, 18.5, -5.4, -5.5; IR (thin film) 3417, 2931, 1472, 1447, 1254, 1111 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{26}\text{O}_3\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 305.1549, found 305.1536. Anal. Calcd for $\text{C}_{15}\text{H}_{26}\text{O}_3\text{Si}$: C, 63.78; H, 9.28. Found: C, 64.03; H, 9.38.

(±)-1-Phenyleth-1-yl hydroperoxide (19**).**²¹ To a cooled (0 °C) solution of H_2O_2 (30 mL, 0.50 mol, 50% wt in H_2O) and H_2SO_4 (0.5 mL, 9 mmol) was added 1-phenylethanol (**46**) (2.3 g, 18 mmol). The reaction mixture was stirred vigorously for 72 hours at ambient temperature and partitioned between Et_2O (20 mL) and water (30 mL). The aqueous layer was extracted with Et_2O (2×20 mL) and the combined organic layers were washed with 1 N aq NaOH (2×10 mL) and brine (20 mL). The resulting solution was dried over MgSO_4 , concentrated *in vacuo* and was purified by flash chromatography (hexanes/EtOAc 9:1) to yield hydroperoxide **19** (1.7 g, 76%). Spectral data matched those reported in literature:²² ^1H NMR (500 MHz, CDCl_3) δ 8.03 (s, 1H), 7.38-7.47 (m, 5H), 5.13 (q, $J = 6.6$, 1H), 1.54 (d, $J = 6.6$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.9, 129.1, 128.7, 127.0, 84.2, 20.5. HRMS (ESI) m/z calcd for $\text{C}_8\text{H}_{10}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 161.0578, found 161.0585.

(±)-1-Cyclohexyl-1-phenyleth-1-yl hydroperoxide (20). The procedure for the synthesis of hydroperoxide (±)-**19** was followed using alcohol **47** (2.2 g, 16 mmol) to afford hydroperoxide **20** as a clear oil (1.3 g, 52%) after purification by flash chromatography (hexanes/EtOAc 19:1). Previous literature report does not provide NMR spectral data.²³ ¹H NMR (500 MHz, CDCl₃) δ 7.92 (s, 1H), 7.32-7.42 (m, 5H), 4.83 (t, *J* = 6.9, 1H), 1.87-1.96 (m, 1H), 1.65-1.74 (m, 1H), 0.92 (t, *J* = 7.5, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 141.0, 129.0, 128.6, 127.4, 90.1, 27.9, 10.6. HRMS (ESI) *m/z* calcd for C₉H₁₂O₂Na [M+Na]⁺ 175.0735, found 175.0739.

(±)-2-Methyl-1-phenylprop-1-yl hydroperoxide (21). The procedure for the synthesis of hydroperoxide (±)-**19** was followed using alcohol **38** (1.0 g, 16 mmol) to afford hydroperoxide **21** as a clear oil (0.50 g, 44%) after purification by flash chromatography (hexanes/EtOAc 19:1). Previous literature report does not provide NMR spectral data.²³ ¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 1H), 7.26-7.36 (m, 5H), 4.55 (d, *J* = 8, 1H), 1.93-1.99 (m, 1H), 1.03 (d, *J* = 6.7, 3H), 0.92 (d, *J* = 6.7, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 128.5, 128.1, 127.5, 93.7, 32.5, 19.4, 19.1. HRMS (ESI) *m/z* calcd for C₁₀H₁₄O₂Na [M+Na]⁺ 189.0892, found 189.0899.

(±)-Cyclohexylphenylmethyl hydroperoxide (22). The procedure for the synthesis of hydroperoxide (±)-**19** was followed using alcohol **41** (0.90 g, 16 mmol) to afford hydroperoxide **22** as a clear oil (0.30 g, 33%) after purification by flash chromatography (hexanes/EtOAc 19:1). Previous literature report does not provide NMR spectral data.²⁴ ¹H NMR (400 MHz, CDCl₃) δ 7.72 (s, 1H), 7.30-7.42 (m, 5H), 4.66 (d, *J* = 8.1, 1H), 2.04-2.08 (m, 1H), 1.61-1.78 (m, 4H), 0.91-1.34 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 140.0, 128.6, 128.2, 127.5, 93.0, 42.2, 29.8, 29.4, 26.5, 26.2, 26.0. HRMS (ESI) *m/z* calcd for C₁₃H₁₈O₂Na [M+Na]⁺ 229.1205, found 229.1200.

III. Preparation of Xylyl-PHANEPHOS 11

***N,N*-Diethylphosphoramidic dichloride (49).**²⁵ To a cooled (0 °C) solution of POCl₃ (**48**) (3.7 mL, 40 mmol) and Et₃N (6.3 mL, 45 mmol) in CH₂Cl₂ (150 mL) was added Et₂NH (4.1 mL, 40 mmol) over one hour. The reaction mixture was stirred at ambient temperature for 24 hours and then was diluted with 10% aq KH₂PO₄ (50 mL). The resulting mixture was extracted with CH₂Cl₂ (2 × 50 mL) and the combined organic layers were washed with brine (50 mL) and concentrated *in vacuo*. Purification by distillation (bp: 62-64 °C; 0.5 mm Hg) yielded compound **49** as a clear oil (6.1 g, 81%). Spectral data matched those reported in literature:²⁵ ¹H NMR (500 MHz, CDCl₃) δ 3.27-3.35 (m, 4H), 1.20-1.26 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 40.9, 13.4; ³¹P NMR (162 MHz, CDCl₃) δ 14; HRMS (ESI) *m/z* calcd for C₄H₁₀ONPCl₂Na [M+Na]⁺ 211.9775, found 211.9769.

Bis(3,5-dimethylphenyl)phosphinic acid (50). To a cooled (−78 °C) solution of 3,5-dimethylbromobenzene (10.0 mL, 73.5 mmol) in THF (100 mL) was added *n*-BuLi (37 mL, 77 mmol, 2.1 M solution in hexane) over one hour. The reaction mixture was stirred at ambient temperature for one-half hour then cooled (−78 °C). Electrophile **49** (5.6 mL, 37 mmol) was added over one-half hour to the mixture and the resulting solution was heated to reflux for two hours and then was diluted with H₂O (100 mL) and saturated aq NH₄Cl (50 mL). The layers were separated and then the organic layer was diluted with concentrated aq HCl (100 mL) and heated (80 °C) for five hours. The resulting precipitate was isolated by filtration and added to 0.5 M aq NaOH (300 mL). The slurry was then filtered to remove insoluble matter and the resulting solution was acidified with 20% aq H₂SO₄. The resulting precipitate was isolated by filtration to provide phosphinic acid **50** (14.5 g, 72%) as a white solid. Spectral data matched those reported in literature:²⁶ ¹H NMR (400 MHz, CDCl₃) δ 11.75 (s, 1H), 7.36 (d, *J* = 12.9, 4H), 7.07 (s, 2H), 2.28 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 138.1 (d, *J* = 14.0), 133.7, 132.8 (d, *J* = 138.2), 129.0 (d, *J* = 11.0), 21.4; ³¹P NMR (162 MHz, CDCl₃) δ 32. HRMS (ESI) *m/z* calcd for C₁₆H₁₉O₂PH [M+H]⁺ 275.1201, found 275.1198.

Bis(3,5-dimethylphenyl)phosphonyl chloride (51).²⁶ To a heated (50 °C) slurry of phosphinic acid **50** (2.5 g, 9.2 mmol) in toluene (20 mL) was added thionyl chloride (1.3 mL, 18 mmol) over two hours. The reaction mixture was filtered and then was diluted with hexanes (50 mL). The resulting precipitate was filtered to yield phosphonyl chloride **51** (2.7 g, 99%) as a white solid. Spectral data matched those reported in literature:²⁷ ¹H NMR (400 MHz, CDCl₃) δ 7.39 (m, 4H), 7.09 (s, 2H), 2.27 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 138.2 (d, *J* = 7.7), 138.1 (d, *J* = 7.7), 134.3, 130.9 (d, *J* = 147.4), 130.8 (d, *J* = 147.8), 129.44 (d, *J* = 5.9), 129.36 (d, *J* = 5.9), 21.4; ³¹P NMR (162 MHz, CDCl₃) δ 27.

(±)-pseudo-o-Bis(di(3,5-dimethylphenyl)phosphinyl)[2.2]paracyclophane (53).²⁸ To a cooled (−78 °C) solution of dibromide **52** (1.7 g, 4.5 mmol) in THF (45 mL) was added *t*-BuLi (12 mL, 18 mmol, 1.5 M solution in pentane) over one-half hour. Magnesium bromide diethyl etherate (2.7 g, 10 mmol) was added and the reaction mixture was allowed to warm (10 °C) before adding phosphonyl chloride **51**. The resulting reaction mixture was stirred at ambient temperature for 18 hours and then diluted with Et₂O (150 mL). The resulting precipitate was collected by filtration. Recrystallization (EtOH) provided bis(phosphine oxide) **53** (2.4 g, 74%) as a white crystalline solid. Previous literature report does not provide NMR spectral data:²⁹ ¹H NMR (500 MHz, CDCl₃) δ 7.35 (d, *J* = 11.8, 4H), 7.11-7.20 (m, 6H), 7.10 (s, 2H), 7.01 (s, 2H), 6.75 (d, *J* = 7.1, 2H), 6.63-6.65 (m, 2H), 3.24-3.27 (m, 2H), 3.13-3.15 (m, 2H), 2.96-3.00 (m, 2H), 2.70-2.73 (m, 2H), 2.40 (s, 12H), 2.23 (s, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 145.6 (d, *J* = 8.3), 139.7 (d, *J* = 13.0), 138.8 (d, *J* = 13.0), 137.5 (d, *J* = 12.5), 137.3 (d, *J* = 12.5), 136.9 (d, *J* = 101.3), 136.3 (d, *J* = 2.9), 134.5 (d, *J* = 11.8), 133.5 (d, *J* = 2.8), 132.6 (d, *J* = 2.6), 132.3 (d, *J* = 103.4), 131.5 (d, *J* = 104.2), 129.7 (d, *J* = 9.1), 128.5 (d, *J* = 9.3), 36.2 (d, *J* = 5.1), 34.8, 21.8, 21.5; ³¹P NMR (162 MHz, CDCl₃) δ 21; IR (thin film) 3233, 2860, 1600, 1454, 1272, 1184 cm^{−1}; HRMS (ESI) *m/z* calcd for C₄₈H₅₁O₂P₂ [M+H]⁺ 721.3364, found 721.3369.

Resolution of (R)-pseudo-o-bis(di(3,5-dimethylphenyl)phosphinyl)[2.2]paracyclophane (53).³⁰ To a slurry of bis(phosphine oxide) (±)-**53** (9.4 g, 13 mmol) in acetonitrile

(925 mL) was added (+)-D-dibenzoyltartaric acid (2.1 g, 5.9 mmol). The reaction mixture was heated to reflux and allowed to cool slowly (five hours). The resulting precipitate was isolated by filtration and then was dissolved in chloroform (150 mL). This solution was washed with 1 N aq NaOH (2×75 mL) and then with brine (100 mL). The organic layer was dried over MgSO_4 and concentrated *in vacuo* to yield bis(phosphine oxide) (*R*)-**53** (2.0 g, 43%) as a white solid: $[\alpha]_{\text{D}} = -112^\circ$ (c 1.30, CHCl_3). Repeating this procedure with (–)-L-dibenzoyltartaric acid provides access to (*S*)-**53**. (Note: Oxidation of a commercial sample of (*R*)-**10**, labeled as “>95% ee”, to bis(phosphine oxide) (*R*)-**53** gave a rotation of $[\alpha]_{\text{D}} = -101.5^\circ$ (c 2.4, CHCl_3).

(*R*)-pseudo-*o*-Bis(di(3,5-dimethylphenyl)phosphino)[2.2]paracyclophane (10**).**²⁸ To a solution of bis(phosphine oxide) (*R*)-**53** (2.2 g, 3.1 mmol) in *m*-xylene (50 mL) was added Cl_3SiH (5.9 mL, 59 mmol) and the reaction vessel was sealed. The reaction mixture was heated (140°C) for 18 hours and then was partitioned between EtOAc (250 mL) and H_2O (200 mL). The organic layer was washed with brine (100 mL), dried over MgSO_4 , and concentrated *in vacuo*. Purification by flash chromatography (hexanes/EtOAc 19:1) yielded bisphosphine **10** (1.9 g, 90%) as a white solid. Previous literature report does not provide NMR spectral data:²⁹ $[\alpha]_{\text{D}} = -44^\circ$ (c 1.2, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.23 (d, $J = 8.5$, 4H), 7.10 (d, $J = 8.2$, 4H), 7.02 (s, 2H), 6.90 (s, 2H), 6.60 (d, $J = 9.2$, 2H), 6.53–6.57 (m, 4H), 2.97–3.02 (m, 2H), 2.86–2.92 (m, 4H), 2.59–2.62 (m, 2H), 2.37 (s, 12H), 2.23 (s, 12H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.4 (d, $J = 13.8$), 139.3 (d, $J = 11.3$), 139.1 (d, $J = 2.5$), 138.4 (d, $J = 11.3$), 137.9 (d, $J = 11.3$), 137.7 (d, $J = 8.8$), 137.6 (d, $J = 8.8$), 134.2 (d, $J = 2.5$), 133.5 (d, $J = 3.8$), 133.4 (d, $J = 21.3$), 133.3 (d, $J = 3.8$), 132.5, 131.1 (d, $J = 21.3$), 131.0 (d, $J = 94$), 35.9 (d, $J = 6.3$), 33.4, 21.7, 21.5 ^{31}P NMR (162 MHz, CDCl_3) δ -2; IR (thin film) 3258, 2918, 2855, 1452, 1123, 1038 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{48}\text{H}_{50}\text{O}_2\text{P}_2\text{H}$ $[\text{M}+\text{H}]^+$ 721.3364 found 721.3369. Anal. Calcd for $\text{C}_{48}\text{H}_{50}\text{P}_2$: C, 83.69; H, 7.32. Found: C, 83.58; H, 7.43.

IV. Kinetic Resolutions

All reactions were run in triplicate and the experiments shown here are typical. Values for k_{rel} were calculated using the equation reported by Kagan: $k_{\text{rel}} = \ln [((1-C)(1-\text{ee}_{\text{sm}}))/((1-C)(1+\text{ee}_{\text{sm}}))]$, in which C is the fractional conversion of the starting material and ee_{sm} is the enantiomeric excess of the recovered starting material.³¹

(Note: In most cases, conversions were determined by HPLC analysis due to overlapping peaks in the ^1H NMR spectra of the alcohols and hydroperoxides. The values obtained, however, are all within 3% of conversions determined by single pulse ^1H NMR analysis. The error-bars associated with the k_{rel} 's obtained from this type of analysis are unsymmetrical and large due to the logarithmic nature of the equations used (*vide supra*). For example: a resolution with a measured ee of 63 % and conversion of 43 % correlates to a k_{rel} of 21. When the same equation is utilized to determine the k_{rel} from the error limits, 40% and 46%, the values are 13 and 68, respectively. We feel the values reported in this communication are representative of the values that would be obtained from calculating the k_{rel} 's from re-isolated starting material.)

Representative procedure for kinetic resolution; Table 1, Entry 8: To a cooled (-67°C) solution of 3-methyl-2-phenylbut-2-yl hydroperoxide (**11**) (49 mg, 0.27 mmol) in CDCl_3 (0.7 mL) was added a solution of $(R)\text{-(+)-4,12-bis(diphenylphosphino)-[2.2]-paracyclophane}$ (**9**) (39 mg, 0.070 mmol) in CDCl_3 (0.2 mL) by cannula. The phosphine residue-containing vessel was washed with CDCl_3 (0.3 mL) and the resulting solution was transferred by cannula. After 16 hours, the reaction mixture was allowed to warm (25°C) and the fractional conversion was measured by ^1H NMR spectroscopy (0.55). The reaction mixture was concentrated and filtered through a plug of silica (100% CH_2Cl_2) yielding a mixture of 3-methyl-2-phenylbut-2-yl hydroperoxide (**11**) and 3-methyl-2-phenylbutan-2-ol (**12**) (45 mg). The ee of recovered starting material (75%) was determined by HPLC [Chiracel OD-H column (250 mm $\times$ 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate $0.8\text{ mL}\cdot\text{min}^{-1}$, detection by UV absorbance at 254 nm, retention times: $(+)\text{-(R)-11}$ = 15.1 min (major) and $(-)\text{-(S)-11}$ = 22.2 min (minor)]. An ee of 75% with a conversion of 0.55 corresponds to a k_{rel} of 4.2.

Table 1, Entry 9: The representative procedure was followed using compound **11** (11 mg, 0.060 mmol) and compound $(R)\text{-10}$ (18 mg, 0.025 mmol). The reaction mixture was filtered through a plug of silica (100% CH_2Cl_2) yielding a mixture of hydroperoxide **11** and alcohol **12** (9 mg). The conversion (0.50) and ee of recovered starting material (86%) were determined by HPLC [Chiracel OD-H column (250 mm $\times$ 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate $0.8\text{ mL}\cdot\text{min}^{-1}$, detection by UV absorbance at 254 nm, retention times: $(+)\text{-(R)-11}$ = 15.1 min (major) and $(-)\text{-(S)-11}$ = 22.2 min (minor)] and correspond to a k_{rel} of 36.

Table 2, Entry 1: The representative procedure was followed using compound **13** (9.0 mg, 0.054 mmol) and compound **(R)-10** (9.3 mg, 0.014 mmol). The reaction mixture was filtered through a plug of silica (100% CH₂Cl₂) yielding a mixture of hydroperoxide **13** and alcohol **42** (8 mg). The conversion (0.43) and ee of recovered starting material (63%) were determined by HPLC [Chiracel OD-H column (250 mm × 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate 0.8 mL·min⁻¹, detection by UV absorbance at 210 nm, retention times: (+)-**(R)-13** = 15.3 min (major) and (-)-**(S)-13** = 21.1 min (minor)] and correspond to a *k*_{rel} of 21.

Table 2, Entry 2: The representative procedure was followed using compound **14** (32 mg, 0.18 mmol) and compound **(S)-10** (30 mg, 0.044 mmol). The reaction mixture was filtered through a plug of silica (100% CH₂Cl₂) yielding a mixture of hydroperoxide **14** and alcohol **28** (22 mg). The conversion (0.46) was determined by ¹H NMR and ee of recovered starting material (71%) was determined by HPLC [Chiracel OD-H column (250 mm × 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate 0.8 mL·min⁻¹, detection by UV absorbance at 254 nm, retention times: (+)-**(R)-14** = 12.2 min (minor) and (-)-**(S)-14** = 16.4 min (major)] and correspond to a *k*_{rel} of 23.

Table 2, Entry 3: The representative procedure was followed using compound **15** (14 mg, 0.073 mmol) and compound **(R)-10** (13 mg, 0.018 mmol). The reaction mixture was filtered through a plug of silica (100% CH₂Cl₂) yielding a mixture of hydroperoxide **15** and alcohol **30** (13 mg). The conversion (0.57) and ee of recovered starting material (90%) were determined by HPLC [Chiracel OD-H column (250 mm × 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate 0.8 mL·min⁻¹, detection by UV absorbance at 254 nm, retention times: (+)-**(R)-15** = 14.1 min (major) and (-)-**(S)-15** = 18.9 min (minor)] and correspond to a *k*_{rel} of 16.

Table 2, Entry 4: The representative procedure was followed using compound **16** (27 mg, 0.14 mmol) and compound $(R)\text{-10}$ (24 mg, 0.035 mmol). The reaction mixture was filtered through a plug of silica (100% CH_2Cl_2) yielding a mixture of hydroperoxide **16** and alcohol **32** (25 mg). The conversion (0.39) and ee of recovered starting material (58%) were determined by HPLC [Chiracel OD-H column (250 mm $\times$ 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate 0.8 mL $\cdot$ min $^{-1}$, detection by UV absorbance at 254 nm, retention times: (+)- $(R)\text{-16}$ = 11.3 min (major) and (–)- $(S)\text{-16}$ = 17.1 min (minor)] and correspond to a k_{rel} of 37.

Table 2, Entry 5: The representative procedure was followed using compound **17** (96 mg, 0.43 mmol) and compound $(R)\text{-10}$ (100 mg, 0.145 mmol). The reaction mixture was filtered through a plug of silica (100% CH_2Cl_2) yielding a mixture of hydroperoxide **17** and alcohol **34** (25 mg). The conversion (0.56) and ee of recovered starting material (95%) were determined by HPLC [Chiracel OD-H column (250 mm $\times$ 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate 0.8 mL $\cdot$ min $^{-1}$, detection by UV absorbance at 254 nm, retention times: (+)- $(R)\text{-17}$ = 16.2 min (major) and (–)- $(S)\text{-17}$ = 32.0 min (minor)] and correspond to a k_{rel} of 25. A sample of hydroperoxide $(R)\text{-}(+)\text{-17}$ was purified by semi-prep HPLC [Alltech Altima column (250 mm $\times$ 22 mm i.d.) with EtOAc/hexanes (3:97 v/v), flow rate 10 mL $\cdot$ min $^{-1}$]: $[\alpha]_{\text{D}}^{25} = +64^\circ$ ($c = 2.3$, CHCl_3). NMR spectral data matched previously reported data (*vide supra*).

Table 2, Entry 6: The representative procedure was followed using compound **18** (30 mg, 0.11 mmol) and compound $(R)\text{-10}$ (18 mg, 0.027 mmol). The reaction mixture was filtered through a plug of silica (100% CH_2Cl_2) yielding a mixture of hydroperoxide **18** and alcohol **54** (25 mg). The conversion (0.49) was determined by ^1H NMR. The ee of recovered starting material (42%) was determined by HPLC [Chiracel OD-H column (250 mm $\times$ 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate 0.8 mL $\cdot$ min $^{-1}$, detection by UV absorbance at 254 nm, retention times: (major)-**18** = 9.5 min and (minor)-**18** = 11.7 min] and the two correspond to a k_{rel} of 3.8.

Table 2, Entry 7: The representative procedure was followed using compound **19** (10 mg, 0.075 mmol) and compound (*R*)-**10** (17 mg, 0.025 mmol). The reaction mixture was filtered through a plug of silica (100% CH₂Cl₂) yielding a mixture of hydroperoxide **19** and alcohol **46** (7 mg). The conversion (0.84) and ee of recovered starting material (77%) were determined by HPLC [Chiracel OD-H column (250 mm × 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate 0.8 mL·min⁻¹, detection by UV absorbance at 210 nm, retention times: (+)-(*R*)-**19** = 16.6 min (major) and (-)-(*S*)-**19** = 24.7 min (minor)] and correspond to a *k*_{rel} of 2.6.

Table 2, Entry 8: The representative procedure was followed using compound **20** (9.0 mg, 0.057 mmol) and compound (*R*)-**10** (10 mg, 0.014 mmol). The reaction mixture was filtered through a plug of silica (100% CH₂Cl₂) yielding a mixture of hydroperoxide **20** and alcohol **47** (7 mg). The conversion (0.75) and ee of recovered starting material (76%) were determined by HPLC [Chiracel OD-H column (250 mm × 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate 0.8 mL·min⁻¹, detection by UV absorbance at 210 nm, retention times: (+)-(*R*)-**20** = 18.7 min (major) and (-)-(*S*)-**20** = 23.4 min (minor)] and correspond to a *k*_{rel} of 3.4.

Table 2, Entry 9: The representative procedure was followed using compound **21** (18 mg, 0.11 mmol) and compound (*R*)-**10** (24 mg, 0.035 mmol). The reaction mixture was filtered through a plug of silica (100% CH₂Cl₂) yielding a mixture of hydroperoxide **21** and alcohol **38** (14 mg). The conversion (0.47) and ee of recovered starting material (54%) were determined by HPLC [Chiracel OD-H column (250 mm × 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate 0.8 mL·min⁻¹, detection by UV absorbance at 254 nm, retention times: (+)-(*R*)-**21** = 14.5 min (major) and (-)-(*S*)-**21** = 24.3 min (minor)] and correspond to a *k*_{rel} of 6.9.

Table 2, Entry 10: The representative procedure was followed using compound **22** (21 mg, 0.10 mmol) and compound (*R*)-**10** (20 mg, 0.029 mmol). The reaction mixture was filtered through a plug of silica (100% CH₂Cl₂) yielding a mixture of hydroperoxide **22** and alcohol **41** (19 mg). The conversion (0.43) and ee of recovered starting material (42%) were determined by HPLC [Chiracel OD-H column (250 mm × 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate 0.8 mL·min⁻¹, detection by UV absorbance at 210 nm, retention times: (+)-(*R*)-**22** = 14.9 min (major) and (-)-(*S*)-**22** = 22.9 min (minor)] and correspond to a *k*_{rel} of 5.2.

Scheme 1, entry 1: The representative procedure was followed using compound **23** (23 mg, 0.11 mmol) and compound (*R*)-**10** (20 mg, 0.028 mmol). The reaction mixture was concentrated and conversion was measured with ¹H NMR (.45). Purification by chromatography (hexanes/EtOAc 19:1) yielded hydroperoxide **23** (9 mg) as a clear oil. The ee of recovered starting material (51%) was determined by HPLC [Chiracel OB-H column (2 × 250 mm × 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate 0.8 mL·min⁻¹, detection by UV absorbance at 254 nm, retention times: major = 10.6 min and minor = 11.9 min] and correspond to a *k*_{rel} of 7.1.

Scheme 1, entry 2: The representative procedure was followed using compound **24** (38 mg, 0.13 mmol) and compound (*S*)-**10** (42 mg, 0.030 mmol). The reaction mixture was purified by chromatography (hexanes/EtOAc 19:1) yielding hydroperoxide **24** (13 mg). The conversion (0.64) and ee of recovered starting material (0%) were determined by HPLC [Chiracel OB-H column (2 × 250 mm × 4.6 mm i.d.) with *i*-PrOH/hexanes (5:95 v/v), flow rate 0.8 mL·min⁻¹, detection by UV absorbance at 254 nm, retention times: minor = 20.4 min and major = 22.3 min] and correspond to a *k*_{rel} of 1.0.

V. Isolation of Enantiopure Hydroperoxide

The information in this section describes efforts to utilize the resolution conditions to isolate appreciable amounts of enantiopure hydroperoxides (Scheme 4). The resolution of hydroperoxide ($\pm$)-**11** with (*R*)-xylyl-PHANEPHOS (**10**) was taken to ~70% conversion to ensure recovered starting material with >99% ee. In the course of developing this methodology, it became apparent that isolation of the recovered starting material by flash chromatography was not a viable option for all substrates; however, selective protection of the hydroperoxide in the presence of the alcohol was possible. After isolation of the silylperoxyether **55** by chromatography and subsequent deprotection, enantiopure hydroperoxide (+)-(*R*)-**11** was obtained. Reduction of hydroperoxide (+)-(*R*)-**11** with PPh_3 provided enantiopure alcohol (+)-(*R*)-**12**.

Scheme 2.

Large-scale resolution of ($\pm$)-3-methyl-2-phenylbut-2-yl hydroperoxide (11**).** To a cooled (-67°C) solution of 3-methyl-2-phenylbut-2-yl hydroperoxide (**11**) (1.0 g, 5.6 mmol) in CDCl_3 (12 mL) was added a cooled (-67°C) solution of (*R*)-xylyl PHANEPHOS (**10**) (1.3 g, 1.8 mmol) in CDCl_3 (4.0 mL) by cannula. Additional CDCl_3 (4.0 mL) was used to rinse the phosphine residue-containing vessel, and the resulting solution was transferred by cannula to the reaction mixture. The reaction mixture was stirred at -67°C for 16 hours and the fractional conversion was measured by ^1H NMR spectroscopy (0.71). The reaction mixture was concentrated and filtered through a plug of silica (100% CH_2Cl_2) yielding a mixture of 3-methyl-2-phenylbut-2-yl hydroperoxide (**11**) and 3-methyl-2-phenylbutan-2-ol (**12**) (0.90 g). The ee of recovered starting material (>99%) was determined by SFC [Chiracel OD-H column (250 mm $\times$ 4.6 mm i.d.) with $\text{MeOH}:\text{CO}_2$ (3:97 v/v), flow rate $2.5\text{ mL}\cdot\text{min}^{-1}$, detection by UV absorbance at 210 nm, retention times: (+)-(*R*)-**11** = 6.4 min (major) and (–)-(*S*)-**11** = 10.8 min (minor)] and corresponds to a $k_{\text{rel}} > 11$.

3-Methyl-2-phenylbut-2-ylhydroperoxytrimethylsilyl ether (55**).** To a cooled (0°C) solution of hydroperoxide (+)-(*R*)-**11** (0.26 g, 1.4 mmol) and alcohol (–)-(*S*)-**12** (0.64 g, 3.9 mmol) in CH_2Cl_2 (5 mL) were added Et_3SiCl (0.35 mL, 2.1 mmol) and Et_3N (0.58 mL, 4.2 mmol). The reaction mixture was stirred for two hours and then diluted with

EtOAc (40 mL). The solution was washed with H₂O (3 × 20 mL) and brine (30 mL), dried over MgSO₄, and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (100% hexanes) to yield silylperoxy ether **55** (0.40 g, 95%). Previous literature report does not provide NMR spectral data:³² ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.40 (m, 2H), 7.30-7.34 (m, 2H), 7.22-7.26 (m, 1H), 1.97- 2.03 (m, 1H), 1.63 (s, 3H), 1.00 (t, *J* = 7.8, 9H), 0.88 (d, 3H, *J* = 6.9), 0.76 (d, *J* = 6.9, 3H), 0.68-0.73 (q, *J* = 8.0, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 144.4, 127.6, 126.9, 126.6, 88.2, 37.8, 19.3, 17.9, 17.8, 7.0, 4.1. Anal. Calcd for C₁₇H₃₀O₂Si: C, 69.33; H, 10.27. Found: C, 69.34; H, 10.50.

(+)-3-Methyl-2-phenylbut-2-yl hydroperoxide (11). To a cooled (−10 °C) solution of silylperoxy ether **55** (0.40 g, 1.4 mmol) in THF (10 mL) was added *n*-Bu₄NF (1.5 mL, 1.5 mmol, 1.0 M in THF). The reaction mixture was diluted with 1 N aq HCl (20 mL) and was then extracted with EtOAc (3 × 25 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄, and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (hexanes/EtOAc 19:1) to yield enantiopure hydroperoxide (+)-(R)-**11** (0.24 g, 99%): [α]_D = +87° (*c* = 3.1, CHCl₃). NMR spectral data matched previously reported data (*vide supra*).

(+)-3-Methyl-2-phenylbutan-2-ol (12). To a cooled (0 °C) solution of hydroperoxide (+)-**11** (0.09 g, 0.5 mmol) in CHCl₃ (4.0 mL) was added PPh₃ (0.13 g, 0.50 mmol). The reaction mixture was stirred for one-half hour, concentrated *in vacuo* and purified by flash chromatography (hexanes/EtOAc 19:1) to yield enantiopure alcohol (+)-(R)-**12** (0.070, 95%): [α]_D = +30° (*c* = 2.4, CHCl₃); this data is in contrast to that reported by Walsh et. al., [α]_D = +6.0° (*c* = 0.05, CHCl₃), for material with 75% ee.³³ NMR spectral data matched previously reported data (*vide supra*).

VI. Resolution with Mono(phosphine oxide) **25**.

(*R*)-pseudo-*o*-(Di(3,5-dimethylphenyl)phosphino)-(di(3,5-dimethylphenyl)phosphinyl)[2.2]paracyclophane (25). To a cooled ($-67\text{ }^{\circ}\text{C}$) solution of bisposphine (*R*)-10 (0.10 g, 0.15 mmol) in CHCl_3 (10 mL) was added a solution of hydroperoxide 17 (0.030 g, 0.15 mmol) in CHCl_3 (5 mL). The reaction mixture was stirred for one-half hour and concentrated *in vacuo*. Purification by flash chromatography (hexanes/EtOAc 19:1) yielded mono(phosphine oxide) (*R*)-25 (0.050 g, 48%) as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.43 (d, $J = 11.6$, 2H), 7.09-7.22 (m, 8H), 7.03 (s, 1H), 6.97 (s, 1H), 6.89 (s, 1H), 6.73 (d, $J = 7.7$, 1H), 6.67 (dd, $J = 7.6$, 4.1, 1H), 6.55-6.60 (m, 2H), 6.48-6.54 (m, 1H), 3.10-3.14 (m, 3H), 2.91-3.00 (m, 3H), 2.50-2.78 (m, 2H), 2.41 (s, 6H), 2.36 (s, 6H), 2.25 (s, 6H), 2.21 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 146.0 (d, $J = 7.5$), 142.8 (d, $J = 12.5$), 139.2 (d, $J = 2.5$), 139.2 (d, $J = 13.8$), 139.0, 138.9, 138.8, 137.7, 137.6 (d, $J = 11.3$), 137.53, 137.51, 137.45 (d, $J = 2.5$), 137.1 (d, $J = 7.5$), 136.9 (d, $J = 101.3$), 136.8 (d, $J = 2.5$), 136.7 (d, $J = 8.8$), 135.2 (d, $J = 11.3$), 134.2 (d, $J = 3.8$), 134.1 (d, $J = 3.8$), 133.5 (d, $J = 2.5$), 133.18 (d, $J = 2.5$), 133.17 (d, $J = 21.2$), 132.8 (d, $J = 2.5$), 131.5 (d, $J = 26.3$), 131.1 (d, $J = 21.3$), 130.5, 129.8 (d, $J = 7.5$), 129.7, 36.0 (d, $J = 7.5$), 35.0, 32.7 (d, $J = 3.8$), 21.6; ^{31}P NMR (162 MHz, CDCl_3) δ 21, -2 ; IR (thin film) 3316, 2859, 1454, 1265, 1183, 1068 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{48}\text{H}_{50}\text{OP}_2$ $[\text{M}+\text{H}]^+$ 721.3364, found 721.3369.

Scheme 3, Entry 1: The representative procedure was followed using compound 11 (11 mg, 0.060 mmol) and compound (*R*)-25 (18 mg, 0.025 mmol). The reaction mixture was filtered through a plug of silica (100% CH_2Cl_2) yielding a mixture of hydroperoxide (+)-(*R*)-11 and alcohol (−)-(*S*)-12 (15 mg). The conversion (0.51) and ee of recovered starting material (81%) were determined by SFC [Chiracel OD-H column (250 mm $\times$ 4.6

mm i.d.) with MeOH:CO₂ (1:99 v/v), flow rate 1.0 mL·min⁻¹, detection by UV absorbance at 210 nm, retention times: (+)-(*R*)-**11** = 5.8 min (major) and (-)-(*S*)-**11** = 8.4 min (minor)] and correspond to a k_{rel} of 25.

VII. Determination of Absolute Configuration and Rotation.

The literature data regarding the absolute configuration and optical rotation of the compounds included in this communication are scattered and to facilitate the flow we have made extrapolations based on the available data. Kunath et. al. have reported HPLC traces of hydroperoxides **11**, **13**, **14** and **17** and the corresponding alcohols using a cellulose-tris(3,5-dimethylphenyl carbamate) solid support.³⁴ This support is similar to Chiracel's OD and OD-H columns that we utilized in our research. In all cases the elution order was (+)-alcohol, (–)-alcohol, (+)-hydroperoxide, (–)-hydroperoxide. In addition, alcohols **28**,³⁵ **30**,³⁵ **34**,³⁶ **36**,¹⁰ **41**,³⁷ **42**,³⁸ **46**,³⁹ **47**,⁴⁰ are known in enantioenriched form and in all cases the *R* enantiomers are dextrarotary (+) and the *S* enantiomers are levorotary (–). We surmise, for all benzylic compounds, the hydroperoxide enantiomer eluting first corresponds to the *R*-(+) enantiomer and the second peak corresponds to the *S*-(–) enantiomer.

Table 3. Absolute stereochemistry and Optical Rotation Data

entry	R ¹	R ²	substrate	ROH and ROOH elution order ^a	absolute configuration ^b
1	Me	Et	42	1 st -(+), 2 nd -(-)	(<i>S</i>)-(-)
2	Me	<i>i</i> -Pr	12	1 st -(+), 2 nd -(-)	(<i>R</i>)-(+)
3	Me	<i>n</i> -Pr	28	1 st -(+), 2 nd -(-)	(<i>S</i>)-(-)
4	Me	<i>n</i> -Bu	30	nd ^c	(<i>S</i>)-(-)
5	Me	<i>i</i> -Bu	32	nd ^c	nd ^c
6	Me	<i>c</i> -C ₆ H ₁₁	34	1 st -(+), 2 nd -(-)	(<i>R</i>)-(+)
7	H	Me	46	1 st -(+), 2 nd -(-)	(<i>R</i>)-(+)
8	H	Et	47	nd ^c	(<i>R</i>)-(+)
9	H	<i>i</i> -Pr	38	nd ^c	(<i>R</i>)-(+)
10	H	<i>c</i> -C ₆ H ₁₁	41	nd ^c	(<i>S</i>)-(-)

^a In all cases the alcohol eluted first and hydroperoxide second using a cellulose-tris(3,5-dimethylphenyl carbamate) solid support. ^b See supporting information text for references. ^c No values have been reported.

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Signal 2: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.880	MM	0.2147	4285.30762	332.63324	5.8928
2	9.886	MM	0.2683	3.23324e4	2008.20044	44.4612
3	14.954	MM	0.4303	3.36249e4	1302.41113	46.2386
4	27.969	MM	0.8147	2477.90112	50.69005	3.4074

Totals : 7.27206e4 3693.93486

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	9.243	MM	0.2263	2866.09741		211.09280	4.8253
2	10.027	MM	0.2631	2.28464e4		1447.07007	38.4634
3	15.335	MM	0.4294	2.73823e4		1062.78259	46.0999
4	21.137	MM	0.5964	6302.93359		176.15292	10.6114

Totals : 5.93978e4 2897.09839

Signal 2: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	7.157	VV	0.2353	29.96621	1.97427	1.3254
2	7.786	VV	0.1868	825.20050	65.93339	36.4976
3	8.446	VB	0.1955	119.62459	9.10492	5.2908
4	12.216	BB	0.3303	185.32639	8.44287	8.1968
5	16.446	BB	0.4798	1100.85571	34.65535	48.6895

Totals : 2260.97339 120.11080

Signal 2: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.432	MF	0.1461	37.19296	4.24358	1.1691
2	8.719	MF	0.2154	365.24826	28.26128	11.4806
3	9.221	FM	0.2364	1433.92200	101.10966	45.0714
4	14.148	MM	0.3988	1279.68286	53.48181	40.2233
5	18.898	MM	0.5082	65.39918	2.14486	2.0556

Totals : 3181.44525 189.24118

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	4.994	BV	0.1664	62.20807		5.07065	0.7597
2	5.374	VB	0.1605	57.15961		4.91371	0.6981
3	8.997	BB	0.1993	505.36670		37.53416	6.1719
4	10.486	BB	0.2580	2707.00610		154.74670	33.0598
5	14.239	BB	0.3941	3831.74585		143.69745	46.7958
6	22.128	BP	0.6080	1024.73376		25.61493	12.5147

Totals :	8188.22010	371.57760

Signal 2: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	9.129	MM	0.2220	189.61459	14.23364	7.3383
2	10.147	MM	0.2616	1258.96057	80.19722	48.7233
3	16.245	MM	0.4773	1105.03162	38.58365	42.7661
4	31.959	MM	0.8313	30.28949	6.07260e-1	1.1722

Totals : 2583.89627 133.62177

Analysis: Channel A

Peak No.	Time	Type	Height(μ V)	Area(μ V-sec)	Area%
1	5.091	N25	618944	5439242	8.140
2	5.370	Err!	1608319	15854866	23.727
3	7.441	N34	210244	1985839	2.971
4	9.526	Err!	1804918	30877622	46.210
5	11.746	N45	748573	12662284	18.949
Total Area				66819853	99.997

Signal 2: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	11.851	MM	0.3002	7783.91309		432.12027	34.6619
2	13.563	MM	0.3446	1.09723e4		530.60834	48.8598
3	16.588	MM	0.4608	3270.66919		118.30054	14.5644
4	24.691	MM	0.6506	429.79272		11.01073	1.9139

Totals :   2.24567e4   1092.03988

Signal 2: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.601	VP	0.2903	1479.83167	75.34127	35.6759
2	15.147	BP	0.3494	1635.34729	69.70401	39.4251
3	18.747	PP	0.4881	911.40149	27.63652	21.9721
4	23.406	BB	0.5440	121.40751	3.34754	2.9269

Totals : 4147.98795 176.02934

Signal 2: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.417	MM	0.3071	1679.26318	91.12174	47.4838
2	14.488	MM	0.4274	1433.51794	55.90548	40.5350
3	24.250	MM	0.7103	423.71378	9.94172	11.9812

Totals : 3536.49490 156.96894

Signal 2: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	11.913	VB	0.3385	1941.12097	80.38700	43.1016
2	14.866	BB	0.3947	1814.14124	68.55012	40.2821
3	22.896	BB	0.8965	748.32928	13.66760	16.6163

Totals : 4503.59149 162.60472

Signal 2: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	10.641	MM	0.2737	3503.24292		213.30818	66.6478
2	11.876	MM	0.3191	1753.10510		91.57590	33.3522

Totals : 5256.34802 304.88408

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	[%]
1	UNKNOWN	2.93	3.05	3.16	0.00	19.80	393.0	34.3	19.799
2	UNKNOWN	3.24	3.42	3.58	0.00	49.91	780.0	86.5	49.910
3	UNKNOWN	6.40	6.64	6.91	0.00	30.29	276.9	52.5	30.291
Total						100.00	1449.8	173.4	100.000

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	[%]
1	UNKNOWN	2.66	2.73	2.89	0.00	100.00	2695.5	249.2	100.000
Total						100.00	2695.5	249.2	100.000

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	[%]
1	UNKNOWN	4.44	4.57	4.66	0.00	5.35	255.9	24.6	5.349
4	UNKNOWN	4.66	4.76	4.92	0.00	41.48	1724.8	190.6	41.478
2	UNKNOWN	5.82	6.02	6.29	0.00	48.82	1664.4	224.3	48.818
3	UNKNOWN	8.40	8.57	8.77	0.00	4.36	119.1	20.0	4.355
Total						100.00	3764.2	459.5	100.000

¹H spectrum

Current Data Parameters
USER harris
NAME 3077-c2-cf1c
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061030
Time 14.02
INSTRUM cryo500
PROBHD 5 mm CPTCL 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0999398 sec
RG 2.8
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWREX 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

F2 - Processing parameters
SI 65536
SF 500.2200261 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.500 ppm
F1 4251.87 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.39474 ppm/cm
HZCM 197.45528 Hz/cm

¹³C spectrum with ¹H decoupling

Current Data Parameters
USER harris
NAME 3077-c2-cf1c
EXPNO 8
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061030
Time 14.10
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65398
SOLVENT CDCl3
NS 83
DS 4
SWH 20161.291 Hz
FIDRES 0.308286 Hz
AQ 1.6219203 sec
RG 14596.5
DW 24.800 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SF01 125.7904737 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SF02 500.2225011 MHz

F2 - Processing parameters
SI 65536
SF 125.7804111 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 160.000 ppm
F1 20124.87 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 7.01754 ppm/cm
HZCM 882.66956 Hz/cm

¹H spectrum

Current Data Parameters
USER harris
NAME 1205c-01-01
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050309
Time 8.44
INSTRUM drx400
PROBHD 5 mm QNP H/F
PULPROG zg30
TD 65536
SOLVENT CDCl3T
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 64
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SF01 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300172 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
FLP 8.500 ppm
F1 3401.10 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.39474 ppm/cm
HZCM 157.94606 Hz/cm

¹³C spectrum with ¹H decoupling

Current Data Parameters
USER harris
NAME 1205c-01-01
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050309
Time 8.47
INSTRUM drx400
PROBHD 5 mm QNP H/F
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 238
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 1290.2
DW 20.700 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 10.12 usec
PL1 0.00 dB
SF01 100.6237964 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 17.00 dB
PL12 17.90 dB
SF02 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 100.6127554 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 160.000 ppm
F1 16098.04 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 7.45614 ppm/cm
HZCM 750.18286 Hz/cm

¹H spectrum

Current Data Parameters
USER harris
NAME 2166-c2-cf1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060307
Time 15.08
INSTRUM cryo500
PROBHD 5 mm CPTCL 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 35.9
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWREX 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

F2 - Processing parameters
SI 65536
SF 500.2200266 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.500 ppm
F1 4251.87 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.39474 ppm/cm
HZCM 197.45528 Hz/cm

^{13}C spectrum with ^1H decoupling

Current Data Parameters
USER harris
NAME 2166-c2-cf1
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060307
Time 15.13
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT CDCl3
NS 398
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794470 sec
RG 9195.2
DN 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 ^{13}C
P1 15.00 usec
PL1 -1.00 dB
SF01 125.7942548 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 ^1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SF02 500.2225011 MHz

F2 - Processing parameters
SI 65536
SF 125.7804011 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 160.000 ppm
F1 20124.87 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 7.45614 ppm/cm
HZCM 937.83636 Hz/cm

¹H spectrum

^{13}C spectrum with ^1H decoupling

Current Data Parameters
USER harris
NAME 2146-cl-cfla
EXPNO 100
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060111
Time 8.57
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT CDCl3
NS 210
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794470 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 ^{13}C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 ^1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

F2 - Processing parameters
SI 65536
SF 125.7804025 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 160.000 ppm
F1 20124.87 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 7.45614 ppm/cm
HZCM 937.83636 Hz/cm

¹H spectrum

¹³C spectrum with ¹H decoupling

Current Data Parameters
USER harris
NAME 3031-c2-cf1
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060821
Time 18.34
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT CDCl3T
NS 322
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794470 sec
RG 9195.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SF01 125.7942548 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SF02 500.2225011 MHz

F2 - Processing parameters
SI 65536
SF 125.7804080 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 180.000 ppm
F1 22640.47 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 8.33333 ppm/cm
HZCM 1048.17017 Hz/cm

31P spectrum with 1H decoupling

Current Data Parameters
USER harris
NAME 2170-cl-cf3
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060215
Time 13.34
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 319
DS 4
SWH 75187.969 Hz
FIDRES 1.147277 Hz
AQ 0.4358644 sec
RG 9195.2
DN 6.650 usec
DE 4.50 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 31P
P1 16.00 usec
PL1 0.00 dB
SF01 161.9753930 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 17.00 dB
PL12 17.70 dB
SF02 400.1324008 MHz

F2 - Processing parameters
SI 65536
SF 161.9759620 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 228.583 ppm
F1 37024.93 Hz
F2P -235.609 ppm
F2 -38163.04 Hz
PPMCM 20.35930 ppm/cm
HZCM 3297.71802 Hz/cm

¹H spectrum

Current Data Parameters
USER harris
NAME 3095-c3-cf1-500
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070105
Time 17.41
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 4.5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWREX 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SF01 500.2235015 MHz

F2 - Processing parameters
SI 65536
SF 500.2200266 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.500 ppm
F1 4251.87 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.39474 ppm/cm
HZCM 197.45528 Hz/cm

¹³C spectrum with ¹H decoupling

Current Data Parameters
USER harris
NAME 3095-c3-cf1-500
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070105
Time 17.43
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT CDCl3
NS 401
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794470 sec
RG 13004
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SF01 125.7942548 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SF02 500.2225011 MHz

F2 - Processing parameters
SI 65536
SF 125.7804002 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50366 Hz/cm

¹H spectrum

Current Data Parameters
USER harris
NAME 3099-c4-cf1-500
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070104
Time 15.45
INSTRUM cryo500
PROBHD 5 mm CPTCL 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWREX 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SF01 500.2235015 MHz

F2 - Processing parameters
SI 65536
SF 500.2200265 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.500 ppm
F1 4251.87 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.39474 ppm/cm
HZCM 197.45528 Hz/cm

¹³C spectrum with ¹H decoupling

Current Data Parameters
 USER harris
 NAME 3099-c4-cf1-500
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070104
 Time 15.53
 INSTRUM cryo500
 PROBHD 5 mm CPTCI 1H-
 PULPROG zgdc30
 TD 65418
 SOLVENT CDC13
 NS 354
 DS 4
 SWH 30303.031 Hz
 FIDRES 0.463222 Hz
 AQ 1.0794470 sec
 RG 13004
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 MCREST 0.00000000 sec
 MCWRE 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 15.00 usec
 PL1 -1.00 dB
 SF01 125.7942548 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 1.60 dB
 PL12 23.54 dB
 SF02 500.2225011 MHz

F2 - Processing parameters
 SI 65536
 SF 125.7803992 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 2.00

1D NMR plot parameters
 CX 22.80 cm
 CY 15.65 cm
 F1P 180.000 ppm
 F1 22640.47 Hz
 F2P -10.000 ppm
 F2 -1257.80 Hz
 PPMCM 8.33333 ppm/cm
 HZCM 1048.17004 Hz/cm