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

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Supporting Information

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General. NMR spectra were recorded in CDCl$_3$ at ambient temperature. $^1$H NMR spectra were measured at 500 MHz on a Bruker CRYO500 or GN500 and were referenced to residual CHCl$_3$ (7.27 ppm). $^{13}$C NMR spectra were measured at 125 MHz on a Bruker CRYO500 or GN500 and were referenced to the centerline of the CDCl$_3$ triplet (77.23 ppm). $^{31}$P NMR spectra were measured at 162 MHz and referenced externally to 85% H$_3$PO$_4$ (0.0 ppm). The NMR spectral data are reported as follows: chemical shift in ppm on the $\delta$ 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 (SiO$_2$) 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. Et$_2$O 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. 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 H$_2$O-H$_2$O$_2$. Concentrated acid should never be added directly to an alcohol-hydrogen peroxide-H$_2$O mixture, as explosions have been known to occur.

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

(±)-3-Methyl-2-phenylbutan-2-ol (12). 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 Et$_2$O (100 mL) and water (100 mL). The aqueous layer was extracted with Et$_2$O (2 × 50 mL). The combined organic layers were washed with brine (50 mL) and dried over MgSO$_4$. 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:

1H NMR (500 MHz, CDCl$_3$) 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, CDCl$_3$) δ 148.3, 128.3, 126.9, 125.7, 77.0, 39.1, 27.1, 17.9, 17.8. Anal. Calcd for C$_{11}$H$_{16}$O: 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:

1H NMR (500 MHz, CDCl$_3$) 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, CDCl$_3$) δ 148.3, 128.3, 126.9, 125.7, 77.0, 39.1, 27.1, 17.9, 17.8. IR (thin film) 3417, 2935, 1951, 1885, 1447, 1029 cm$^{-1}$. Anal. Calcd for C$_{11}$H$_{16}$O: 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). 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, 1446, 1165, 1028 cm⁻¹; HRMS (ESI) m/z calcd for C₁₄H₂₀O [M+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:¹⁰¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (125 MHz, CDCl₃) δ 144.1, 128.6, 127.1, 126.8, 80.5, 35.7, 19.5, 18.7.

(±)-3,4-Dimethyl-1-phenyl-pentan-3-ol (38). To a cooled solution (0 °C) of 4-phenylbutan-2-one (37) (10.0 mL, 66.7 mmol) in Et₂O (175 mL) was added i-PrMgBr (33 mL, 66 mmol, 2.0 M solution in Et₂O) over one hour. The reaction mixture was stirred for two hours at ambient temperature and diluted with saturated aq NH₄Cl (150 mL) at 0 °C. The aqueous layer was extracted with Et₂O (75 mL) and the combined organic layers were washed with brine (100 mL), dried over MgSO₄, 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:¹¹¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (125 MHz, CDCl₃) 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 C₁₃H₂₀ONa [M+Na]+ 215.1412, found 215.1411. Anal. Calcd for C₁₃H₂₀O: 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 Et₂O (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 NH₄Cl (300 mL). The organic layer was washed with saturated aq NH₄Cl (300 mL), brine (100 mL), dried over MgSO₄, 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: ¹H NMR (500 MHz, CDCl₃) δ 7.28-7.32 (m, 2H), 7.21-7.25 (m, 3H), 2.74 (d, 13.3 Hz, 1H), 2.70 (d, 13.5 Hz, 1H), 1.72 (m, 1H), 1.26 (s, 1H), 1.03 (s, 3H), 1.00 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.9, 130.9, 128.3, 126.6, 74.7, 45.3, 37.2, 23.0, 18.1, 17.4. Anal. Calcd for C₁₂H₁₈O: 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 NaBH₄ (0.70 g, 18 mmol). The slurry was stirred for ten minutes and then was diluted with H₂O (15 mL). The aqueous layer was extracted with Et₂O (3 x 20 mL) and the combined organic layers were washed with brine (100 mL), dried over MgSO₄, 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: ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.42 (m, 5H), 4.42 (d, J = 7.2 Hz, 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); ¹³C NMR (125 MHz, CDCl₃) 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 C₁₃H₁₈O₂Na [M+Na]⁺ 213.1255, found 213.1259. Anal. Calcd for C₁₃H₁₈O₂Na: 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). To a cooled (0 °C) solution of H₂O₂ (65 ml, 1.1 mol, 50% wt in H₂O) and H₂SO₄ (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 Et₂O (100 mL) and water (100 mL). The aqueous layer was extracted with Et₂O (2 x 50 mL) and the combined organic layers were washed with 1 N NaOH (3 x 25 mL) and brine (50 mL). The resulting solution was dried over MgSO₄ and concentrated in vacuo to yield hydroperoxide 11 (6.1 g, 78%) as a clear oil. Spectral data matched those reported in the literature: ¹H NMR (500 MHz, CDCl₃) 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); 13C NMR (125 MHz, CDCl3) 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 C11H16O2: 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 (±)-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:

1H NMR (500 MHz, CDCl3) 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); 13C NMR (125 MHz, CDCl3) δ 144.0, 128.6, 127.5, 125.9, 86.9, 32.5, 22.1, 8.5. HRMS (ESI) m/z calcd for C10H14O2Na [M+Na]+ 189.0892, found 189.0897.

(±)-2-Phenylpent-2-yl hydroperoxide (14). The procedure for the synthesis of hydroperoxide (±)-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:

1H NMR (500 MHz, CDCl3) 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), 0.87 (t, J = 7.4, 3H); 13C NMR (125 MHz, CDCl3) 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 C11H16O: 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 (±)-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:

1H NMR (500 MHz, CDCl3) 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); 13C NMR (125 MHz, CDCl3) δ 144.3, 128.7, 127.5, 125.9, 86.7, 39.8, 26.2, 23.3, 22.6, 14.2. Anal. Calcd for C12H18O2: C, 74.19; H, 9.34. Found: C, 74.02; H, 9.43.
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### (±)-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:

\[ ^1H \text{ NMR (500 MHz, CDCl}_3 \] \( \delta \) 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); \[ ^13C \text{ NMR (125 MHz, CDCl}_3 \] \( \delta \) 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 C\(_{12}\)H\(_{18}\)O\(_2\): 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:

\[ ^1H \text{ NMR (500 MHz, CDCl}_3 \] \( \delta \) 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); \[ ^13C \text{ NMR (125 MHz, CDCl}_3 \] \( \delta \) 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 C\(_{14}\)H\(_{20}\)O\(_2\): 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%): \[ ^1H \text{ NMR (500 MHz, CDCl}_3 \] \( \delta \) 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); \[ ^13C \text{ NMR (125 MHz, CDCl}_3 \] \( \delta \) 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). To a solution of H$_2$O$_2$ (20.0 mL, 320 mmol, 50% wt in H$_2$O) and H$_3$PO$_4$ (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 Et$_2$O (50 mL) and H$_2$O (50 mL). The aqueous layer was extracted with Et$_2$O (2 × 25 mL) and the combined organic layers were washed with brine (50 mL), dried over MgSO$_4$, and concentrated in vacuo. Purification by flash chromatography (hexanes/EtOAc 5:1) yielded hydroperoxide 23 as a clear oil (0.31 g, 31%): $^1$H NMR (500 MHz, CDCl$_3$) 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); $^{13}$C NMR (125 MHz, CDCl$_3$) 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 (2.6 g, 20 mmol) in CH$_2$Cl$_2$ (40 mL) were added t-BuMe$_2$SiCl (3.8 g, 25 mmol) and Et$_3$N (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 CH$_2$Cl$_2$ (100 mL). The organic layer was washed with brine (50 mL), dried over MgSO$_4$ 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%): $^1$H NMR (500 MHz, CDCl$_3$) 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); $^{13}$C NMR (125 MHz, CDCl$_3$) 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 Et$_3$SiH (3.0 mL, 18.8 mmol). The reaction mixture was stirred under O$_2$ (1 atm) for one half hour and then was concentrated in vacuo. The resulting dark green oil was partitioned between H$_2$O (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 MgSO$_4$ and
Supporting Information: Driver, Harris, and Woerpel

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%). $^1$H 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), 0.86 (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 C$_{21}$H$_{40}$O$_3$Si$_2$Na [M+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$_2$O (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%). $^1$H 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 C$_{15}$H$_{26}$O$_3$SiNa [M+Na]$^+$ 305.1536, found 305.1536. Anal. Calcd for C$_{15}$H$_{26}$O$_3$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$_2$O$_2$ (30 ml, 0.50 mol, 50% wt in H$_2$O) and H$_2$SO$_4$ (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$_2$O (20 mL) and water (30 mL). The aqueous layer was extracted with Et$_2$O (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. $^{22}$ $^1$H 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 C$_{8}$H$_{10}$O$_2$Na [M+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.\(^{23}\)\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 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); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 141.0, 129.0, 128.6, 127.4, 90.1, 27.9, 10.6. HRMS (ESI) \(m/z\) calcd for C\(_9\)H\(_{12}\)O\(_2\)Na \([\text{M+Na}]^+\) 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.\(^{23}\)\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90 (s, 1H), 7.26-7.36 (m, 5H), 4.55 (d, \(J = 8.1\), 1H), 1.93-1.99 (m, 1H), 1.03 (d, \(J = 6.7\), 3H), 0.92 (d, \(J = 6.7\), 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 149.0, 128.5, 128.1, 127.5, 93.7, 32.5, 19.4, 19.1. HRMS (ESI) \(m/z\) calcd for C\(_{10}\)H\(_{14}\)O\(_2\)Na \([\text{M+Na}]^+\) 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.\(^{24}\)\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 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 C\(_{13}\)H\(_{18}\)O\(_2\)Na \([\text{M+Na}]^+\) 229.1205, found 229.1200.

III. Preparation of Xylyl-PHANEPHOS 11
**Supporting Information: Driver, Harris, and Woerpel S-11**

**48**

**P**

**O**

**Cl**

**Cl**

49

**P**

**O**

**Cl**

**Et2N**

**Cl**

50

**N,N-Diethylphosphoroamidic dichloride (49).**

To a cooled (0 °C) solution of POCl$_3$ (48) (3.7 mL, 40 mmol) and Et$_3$N (6.3 mL, 45 mmol) in CH$_2$Cl$_2$ (150 mL) was added Et$_2$NH (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 KH$_2$PO$_4$ (50 mL). The resulting mixture was extracted with CH$_2$Cl$_2$ (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:

- $^1$H NMR (500 MHz, CDCl$_3$) δ 3.27-3.35 (m, 4H), 1.20-1.26 (m, 6H);
- $^{13}$C NMR (125 MHz, CDCl$_3$) δ 40.9, 13.4;
- $^{31}$P NMR (162 MHz, CDCl$_3$) δ 14; HRMS (ESI) $m/z$ calcd for C$_4$H$_{10}$ONPCl$_2$Na [M+Na]$^+$ 211.9775, found 211.9769.

50

**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 H$_2$O (100 mL) and saturated aq NH$_4$Cl (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 H$_2$SO$_4$. 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:

- $^1$H NMR (400 MHz, CDCl$_3$) δ 11.75 (s, 1H), 7.36 (d, $J = 12.9$, 4H), 7.07 (s, 2H), 2.28 (s, 12H);
- $^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.1 (d, $J = 14.0$), 133.7, 132.8 (d, $J = 138.2$), 129.0 (d, $J = 11.0$), 21.4; $^{31}$P NMR (162 MHz, CDCl$_3$) δ 32. HRMS (ESI) $m/z$ calcd for C$_{16}$H$_{19}$O$_2$PH [M+H]$^+$ 275.1201, found 275.1198.
Bis(3,5-dimethylphenyl)phosphonyl chloride (51). 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: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (m, 4H), 7.09 (s, 2H), 2.27 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 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; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 27.

(±)-pseudo-o-Bis(di(3,5-dimethylphenyl)phosphinyl)[2.2]paracyclophane (53). 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 Et$_2$O (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: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 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; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 21; IR (thin film) 3233, 2860, 1600, 1454, 1272, 1184 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{48}$H$_{51}$O$_2$P$_2$ [M+H]$^+$ 721.3364, found 721.3369.

Resolution of (R)-pseudo-o-bis(di(3,5-dimethylphenyl)phosphinyl)[2.2]paracyclophane (53). To a slurry of bis(phosphine oxide) (±)-53 (9.4 g, 13 mmol) in acetonitrile
(925 mL) was added (+)-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 MgSO₄ and concentrated in vacuo to yield bis(phosphine oxide) (R)-53 (2.0 g, 43%) as a white solid: [α]D = −112° (c 1.30, CHCl₃).

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 [α]D = −101.5° (c 2.4, CHCl₃).)

(R)-pseudo-α-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 Cl₃SiH (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 H₂O (200 mL). The organic layer was washed with brine (100 mL), dried over MgSO₄, 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 [α]D = −44° (c 1.2, CHCl₃); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (125 MHz, CDCl₃) 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; ³¹P NMR (162 MHz, CDCl₃) δ -2; IR (thin film) 3258, 2918, 2855, 1452, 1123, 1038 cm⁻¹; HRMS (ESI) m/z calcld for C₄₈H₅₀O₂P₂H [M+H]⁺ 721.3364 found 721.3369. Anal. Calcd for C₄₈H₅₀P₂: 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_rel = ln [(1−C)(1−ee)sm]/[(1−C)(1+ee)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 \(^1\)H NMR spectra of the alcohols and hydroperoxides. The values obtained, however, are all within 3% of conversions determined by single pulse \(^1\)H 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)-(+) 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 \(^1\)H NMR spectroscopy (0.55). The reaction mixture was concentrated and filtered through a plug of silica (100% CH\(_2\)Cl\(_2\)) 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 × 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: (++)-11 = 15.1 min (major) and (--)-(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)-10 (18 mg, 0.025 mmol). The reaction mixture was filtered through a plug of silica (100% CH\(_2\)Cl\(_2\)) 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 × 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)-11 = 15.1 min (major) and (--)-(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% CH$_2$Cl$_2$) 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% CH$_2$Cl$_2$) yielding a mixture of hydroperoxide 14 and alcohol 28 (22 mg). The conversion (0.46) was determined by $^1$H 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% CH$_2$Cl$_2$) 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)-10 (24 mg, 0.035 mmol). The reaction mixture was filtered through a plug of silica (100% CH$_2$Cl$_2$) 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 × 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)-16 = 11.3 min (major) and (−)-(S)-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)-10 (100 mg, 0.145 mmol). The reaction mixture was filtered through a plug of silica (100% CH$_2$Cl$_2$) 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 × 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)-17 = 16.2 min (major) and (−)-(S)-17 = 32.0 min (minor)] and correspond to a $k_{rel}$ of 25. A sample of hydroperoxide (R)-(−)-17 was purified by semi-prep HPLC [Alltech Altima column (250 mm × 22 mm i.d.) with EtOAc/hexanes (3:97 v/v), flow rate 10 mL·min$^{-1}$]: $[\alpha]_D^0 = +64^\circ$ ($c = 2.3$, 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)-10 (18 mg, 0.027 mmol). The reaction mixture was filtered through a plug of silica (100% CH$_2$Cl$_2$) yielding a mixture of hydroperoxide 18 and alcohol 54 (25 mg). The conversion (0.49) was determined by $^1$H NMR. The ee of recovered starting material (42%) 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: (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% CH\(_2\)Cl\(_2\)) 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% CH\(_2\)Cl\(_2\)) 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% CH\(_2\)Cl\(_2\)) 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 $^1$H 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 (±)-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 (±)-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 $^1$H NMR spectroscopy (0.71). The reaction mixture was concentrated and filtered through a plug of silica (100% CH$_2$Cl$_2$) 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 × 4.6 mm i.d.) with MeOH:CO$_2$ (3:97 v/v), flow rate 2.5 mL·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 $k_{rel}$ > 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$_2$Cl$_2$ (5 mL) were added Et$_3$SiCl (0.35 mL, 2.1 mmol) and Et$_3$N (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.\(^{32}\) \(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 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); \(^{13}\)C NMR (125 MHz, CDCl₃) \(\delta\) 144.4, 127.6, 126.9, 126.6, 88.2, 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.

\[\text{Me-OOSiEt₃} \rightarrow \text{MeOOH} \]

\((R)-55 \rightarrow (+)-(R)-11\)

\((+)-3\)-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%): \([\alpha]_D = +87^\circ\) (\(c = 3.1\), CHCl₃). NMR spectral data matched previously reported data \((\text{vide supra})\).

\[\text{Me-OOH} \rightarrow \text{Me-OH} \]

\((+)-(R)-11 \rightarrow (+)-(R)-12\)

\((+)-3\)-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%): \([\alpha]_D = +30^\circ\) (\(c = 2.4\), CHCl₃); this data is in contrast to that reported by Walsh et. al., \([\alpha]_D = +6.0^\circ\) (\(c = 0.05\), CHCl₃), for material with 75% ee.\(^{33}\) NMR spectral data matched previously reported data \((\text{vide supra})\).

VI. Resolution with Mono(phosphine oxide) 25.
**Supporting Information: Driver, Harris, and Woerpel S-21**

(R)-pseudo-o-(Di(3,5-dimethylphenyl)phosphino)-(di(3,5-dimethylphenyl)phosphinyl)[2.2]paracyclophane (25). To a cooled (−67 °C) solution of bisphosphine (R)-10 (0.10 g, 0.15 mmol) in CHCl₃ (10 mL) was added a solution of hydroperoxide 17 (0.030 g, 0.15 mmol) in CHCl₃ (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.

**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% CH₂Cl₂) 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 × 4.6
mm i.d. with MeOH:CO$_2$ (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. 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, 30, 34, 36, 41, 42, 46, 49, 47, 48 are known in enantiomeric form and in all cases the R enantiomers are dextrorotary (+) 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

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<sup>a</sup>In all cases the alcohol eluted first and hydroperoxide second using a cellulose-tris(3,5-dimethylphenyl carbamate) solid support. <sup>b</sup>See supporting information text for references. <sup>c</sup>No values have been reported.
21. The procedure employed was adapted from the work of Davies: Davies, A. G.; Foster, R. V.; White, A. M. J. Chem. Soc. 1953, 5, 1541-1547.
Supporting Information: Driver, Harris, Woerpel

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Supporting Information: Driver, Harris, Woerpel

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Supporting Information: Driver, Harris, Woerpel

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Supporting Information: Driver, Harris, Woerpel

VWD1 A, Wavelength=254 nm (JRHKAWJH2013B.D)

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Totals: 2583.89627 133.62177
Supporting Information: Driver, Harris, Woerpel

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acetophenone
Supporting Information: Driver, Harris, Woerpel

Signal 2: VWD1 A, Wavelength=210 nm

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Totals: 2.24567e4 1092.03988
Signal 2: VWD1 A, Wavelength=210 nm

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Totals: 4147.98795 176.02934
Signal 2: VWD1 A, Wavelength=254 nm

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Totals: 3536.49490 156.96894
Signal 2: VWD1 A, Wavelength=254 nm

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<th>Area [mm^2]</th>
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**Current Data Parameters**

**USER** harris  
**NAME** 3077-c2-cf1c  
**EXPNO** 1  
**PROCNO** 1  
**INSTRUM** cryo500  
**PROBHD** 5 mm CPTCI 1H-  
**PULPROG** zg30  
**TD** 81728  
**SOLVENT** CDCl3  
**NS** 8  
**SWH** 8012.820 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  
**MCWRK** 0.01500000 sec

**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

**Supporting Information:** Driver, Harris, Woerpel

---

*Figure S41: 1H NMR spectrum*
Supporting Information: Driver, Harris, Woerpel

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
DETRM     cryo53
FREQUENCY 5 mm CP/3C 1H-
PULPROG    zgdc30
TD         65398
SOLVENT   CDCl3
NS         83
DS        20141.24 Hz
PULRED    0.396248 Hz
F2        1.6219203 sec
RG         14596.5
DW         24.800 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
SFO1    125.7904737 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       125.7804111 MHz
WDW     EM
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
P1       25124.5 Hz
F2P      160.000 ppm
F2       0.00 Hz

PPMCM     7.01754 ppm/cm
HZCM     882.66956 Hz/cm

Supporting Information: Driver, Harris, Woerpel
Supporting Information: Driver, Harris, Woerpel

13C spectrum with 1H decoupling

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

F2 - Acquisition Parameters
Date: 20050308
Time: 8.47
PROBHD: 5 mm QNP H/F
PULPROG: zgdc30
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
TE: 298.0 K
D1: 0.1000000 sec
D11: 0.0300000 sec

F2 - Processing parameters
SI: 65536
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
### Current Data Parameters

**USER**: harris  
**NAME**: 2166-21-cf1  
**EXPNO**: 1  
**PROCNO**: 1

#### F2 - Acquisition Parameters

**Data**: 20060307  
**Tune**: 15.96  
**INSTRUM**: cryo500  
**SOLVENT**: CDCl3T  
**NS**: 8  
**DS**: 2  
**SWH**: 8012.820 Hz  
**FIDRES**: 0.098043 Hz  
**RG**: 35.9  
**DW**: 62.400 usec  
**TE**: 298.0 K  
**MCREST**: 0.0000000 sec  
**MCWRK**: 0.0150000 sec

#### F2 - Processing parameters

**SI**: 65536  
**SF**: 500.2200266 MHz  
**SSB**: 0  
**LB**: 0.00 Hz  
**PC**: 4.00  
**PPMCM**: 0.39474 ppm/cm  
**HZCM**: 197.45528 Hz/cm

---

#### Supporting Information: Driver, Harris, Woerpel

---

**S-45**
13C spectrum with 1H decoupling
1H spectrum

Current Data Parameters
USER  harris
NAME  2146-vol-cfia
EXPNO  1
PROCNO  1

F2 - Acquisition Parameters
Date_ 20060111
Time  8.53
PROBHD  5 mm CPTCI 1H-
PULPROG  zg30
TD  81728
SOLVENT  CDCl3T
NS  8
DS  2
SWH  8012.820 Hz
FIDRES  0.098043 Hz
AQ  5.0998774 sec
RG  18
DW  62.400 usec
DE  6.00 usec
TE  298.0 K
D1  0.10000000 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
F2P  -0.500 ppm
PPMCM  0.39474 ppm/cm
HZCM  197.45528 Hz/cm

Supporting Information: Driver, Harris, Woerpel
13C spectrum with 1H decoupling

13C spectrum with 1H decoupling

Current Data Parameters

USER             harris
NAME       2146-c1-cf1a
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                13C
P1                15.00 usec
PL1               -1.00 dB            SFO1        125.7942548 MHz

======== CHANNEL f2 ========
CPDPDG2         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           PPMCM           7.45614 ppm/cm
HZCM          937.83636 Hz/cm

Supporting Information: Driver, Harris, Woerpel
13C spectrum with 1H decoupling

Current Data Parameters
USER: Harris
NAME: 3031-c2-cf1
PROC: 3

F2 - Acquisition Parameters
Date: 20060821
Time: 18.34
DETNAM: cryo500
PROC: 5 mm CPTCI 1H-
F2P: 30303.031 Hz
TE: 298.0 K
D1: 0.25000000 sec
D2: 0.03000000 sec

===== CHANNEL f1 =====
NUC: 13C
P1: 15.00 ppm
PL1: -1.00 dB
SFO1: 125.7942548 MHz

===== CHANNEL f2 =====
CPDPRG2: waltz16
NUC: 1H
PCPD2: 100.00 ppm
PL2: 1.60 dB
PL12: 23.54 dB
SFO2: 500.2225011 MHz

F2 - Processing parameters
SF: 125.7804080 MHz
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
F2P: -1257.80 Hz
PPCMCM: 8.3333 ppm/cm
MCM: 104.1701 Hz/cm

Supporting Information: Driver, Harris, Woerpel
31P spectrum with 1H decoupling
13C spectrum with 1H decoupling

---

**Current Data Parameters**

**USER**

**NAME**

**EXPNO**

**PROCNO**

**F2 - Acquisition Parameters**

**Date_**

**Time**

**PROBHD**

**PULPROG**

**TD**

**SOLVENT**

**NS**

**DS**

**SWH**

**FIDRES**

**AQ**

**RG**

**DW**

**DE**

**TE**

**D1**

**d11**

**MCREST**

**MCWRK**

**======== CHANNEL f₁ ========**

**NUC1**

**P1**

**PL1**

**SFO1**

**======== CHANNEL f₂ ========**

**CPDPRG2**

**NUC2**

**PCPD2**

**PL2**

**PL12**

**SFO2**

**F2 - Processing parameters**

**SI**

**SF**

**WDW**

**LB**

**GB**

**PC**

**1D NMR plot parameters**

**CX**

**CY**

**F1P**

**F2P**

**F1**

**F2**

**PPCM**

**NUCM**

---

**Supporting Information:** Driver, Harris, Woerpel
**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 CPTCI 1H-
- **SOLVENT**: CDCl3
- **NS**: 8
- **DS**: 2
- **SWH**: 8012.820 Hz
- **FIDRES**: 0.098043 Hz
- **AQ**: 5.0998774 sec
- **RG**: 5
- **DW**: 62.400 usec
- **TE**: 298.0 K
- **D1**: 0.10000000 sec
- **MCREST**: 0.00000000 sec
- **MCWRK**: 0.01500000 sec

---------- CHANNEL f1 ----------

- **NUC1**: 1H
- **P1**: 8.00 usec
- **PL1**: 1.60 dB
- **SP1**: 500.221501 MHz

**F2 - Processing parameters**

- **HF**: 500.2200265 MHz
- **NN**: no
- **LB**: 0.00 Hz
- **DB**: 4.00

1D NMR plot parameters

- **CX**: 22.80 cm
- **CY**: 15.00 cm
- **F1P**: 8.500 ppm
- **F2P**: -0.500 ppm
- **PPMCM**: 0.39474 ppm/cm
- **HZCM**: 197.45528 Hz/cm

Supporting Information: Driver, Harris, Woerpel
13C spectrum with 1H decoupling