Stereospecific Cross Couplings to Set Benzylic, All-Carbon Quaternary Stereocenters in High Enantiopurity

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Supplementary Materials

General Information ........................................................................................................................................... S2
Optimization of Benzylic Arylation.................................................................................................................. S3
Stereospecific Arylation to Prepare Diaryl and Triarylalkanes .......................................................... S4
  General Procedure A: Stereospecific Arylation of Tertiary Benzylic Acetates........................ S4
Preparation of Enantioenriched Tertiary Benzylic Acetates ............................................................. S14
  General Procedure B: Preparation of (S)-2-(Naphthalen-2-yl)butan-2-yl Acetate (1a)..... S14
  Preparation of (S,E)-2-(Naphthalen-2-yl)-5-(o-tolyl)pent-4-en-2-yl acetate ((S)-1g). .... S18
Preparation of Tertiary Benzylic Alcohols (S-1a – S-1j)................................................................. S19
  Preparation of S-1a – S-1d. .................................................................................................................. S20
  Preparation of S-1e .......................................................................................................................... S22
  Preparation of S-1f and S-1h........................................................................................................... S22
  Preparation of S-1i, S-1j. .................................................................................................................. S24
Evidence for Stereoretention ......................................................................................................................... S25
Crystal Structure Data for (R)-10 ............................................................................................................. S25
Crystal Structure Data for 1a ..................................................................................................................... S32
Crystal Structure Data for S-1d .................................................................................................................. S36
References .................................................................................................................................................. S41
NMR Spectral Data ........................................................................................................................................ S42
HPLC and SFC Spectral Data ................................................................................................................... S126
General Information

Reactions were performed in oven-dried vials with Teflon-lined caps or in oven-dried round-bottomed flasks unless otherwise noted. On occasions when a viscous mixture formed in the reaction vials, a higher speed of stirring or shaking was performed to guarantee sufficient mixing. Flasks were fitted with rubber septa, and reactions were conducted under a positive pressure of N₂. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed on silica gel 60 (40-63 μm, or 5-20 μm 60Å) unless otherwise noted. Commercial reagents were purchased from Sigma Aldrich, Acros, Fisher, Strem, TCI, Combi Blocks, Alfa Aesar, or Cambridge Isotopes Laboratories and used as received with the following exceptions: sodium methoxide, anhydrous 2-methylytetrahydrofuran, diethyl zinc, dimethyl zinc (1.0 M in PhMe) were purchased from vendors and immediately placed in a N₂-atmosphere glovebox for storage. Acetic anhydride and Ti(O-iPr)₄ were distilled before use and stored under N₂. Toluene, CH₂Cl₂, and THF were dried by passing through drying columns and stored over activated 4Å MS in a N₂-atmosphere glovebox.¹ (R,R)-Bis(sulfonamide) diol ligand L₁ was prepared according to reported literature procedure.² Bis(4-((tert-butyldimethylsilyl)oxy)butyl)zinc was prepared according to reported literature procedure and used immediately.³ Oven-dried potassium carbonate was added into CDCl₃ to remove trace amount of acid. Proton nuclear magnetic resonance (¹H NMR) spectra and carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on both 400 MHz and 600 MHz spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl₃ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl₃ = δ 77.2). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = doublet of doublets, h = heptet), coupling constants in Hertz (Hz), integration. Infrared (IR) spectra were obtained using FTIR spectrophotometers with material loaded onto a NaCl plate. The mass spectral and X-ray crystallography data were obtained at the University of Delaware facilities. Optical rotations were measured using a 2.5 mL cell with a 0.1 dm path length. Melting points were taken on a Stuart SMP10 instrument. Enantiomeric excess (ee) was determined using chiral HPLC analysis at the University of Delaware or chiral SFC analysis at Lotus Separations, Inc.

\[ \text{L1} \]

\[ \text{bis(4-((tert-butyldimethylsilyl)oxy)butyl)zinc} \]
## Optimization of Benzylic Arylation

### Detailed Optimization Table

| entry | [Ni]        | ligand (mol %) | temp (°C) | solvent  | time (h) | 4 | 5 | ee of 4 (%) | es (%) |
|-------|-------------|----------------|-----------|----------|----------|---|---|-------------|--------|
| 1     | Ni(cod)₂    | none           | 80        | PhMe     | 2        | 93| 2 | 20          | 21     |
| 2     | Ni(cod)₂    | PhPCy₂ (11)   | 80        | PhMe     | 2        | 74| 22| 87          | 90     |
| 3     | Ni(cod)₂    | PhPCy₂ (11)   | 60        | PhMe     | 5        | 72| 25| 90          | 93     |
| 4     | Ni(cod)₂    | PhPCy₂ (11)   | 60        | THF      | 5        | 63| 24| 93          | 96     |
| 5     | Ni(cod)₂    | CyJohnPhos (11)| 40       | THF      | 16       | 57| 9 | 96          | 99     |
| 6     | Ni(cod)₂    | CyJohnPhos (5)| 40        | THF      | 16       | 81| 6 | 96          | 99     |
| 7     | Ni(cod)₂    | CyJohnPhos (5)| 40        | 1,4-dioxane | 39   | 97| 5 | 97          | >99    |
| 8     | Ni(cod)₂    | CyJohnPhos (5)| 40        | THF      | 22       | 92| 8 | 96          | 99     |
| 9     | NiCl₂·DME   | CyJohnPhos (5)| 40        | THF      | 22       | 90| 6 | 95          | 98     |
| 10    | NiCl₂·DME   | CyJohnPhos (5)| 40        | 2-Me-THF | 22       | 99| ≤3| 97          | >99    |

**Conditions:** 1a (0.10 mmol), 2a (1.0 equiv), [Ni] (5 mol %), ligand, NaOMe (2.0 equiv), solvent (0.4 M), unless otherwise noted. *a* Determined by ¹H NMR analysis using an internal standard. Total yields over 100% reflect the inherent error bar of ¹H NMR yields, particularly for minor products. *b* Determined by HPLC analysis using a chiral stationary phase. *c* es = enantiospecificity = (ee product)/(ee starting material). *d* Boronate ester 3a used in place of boroxine 2a.

## Evaluation of Aryl Boronate Reagents

| Entry | Ar–BX₂ (equiv) | 4 | S-1a | ee of 1a (%) | ee of 4 (%) | es (%) |
|-------|----------------|---|------|--------------|-------------|--------|
| 1     | (ArBO)₃ (2a) (1.0) | 90| —    | 97           | 95          | 98     |
| 2     | Ar–BO (2.0)     | 99| —    | 97           | 97          | >99    |
| 3     | Ar–B(OH)₂ (2.0) | 86| 5    | 94           | 92          | 98     |
| 4     | Ar–Bpin (2.0)   | 80| 0    | 94           | 92          | 98     |
| 5     | Ar–BF₃K (2.0)   | 0 | 90   | 94           | —           | —      |

**Conditions:** 1a (0.10 mmol), ArBX₂, NiCl₂·DME (5 mol %), CyJohnPhos (5 mol %), NaOMe (2.0 equiv), 2-Me-THF (0.4 M), 40 °C, 22 h. *a* Determined by ¹H NMR analysis using an internal standard. Total yields over 100%.
reflect the inherent error bar of $^1$H NMR yields, particularly for minor products. b Determined by HPLC analysis using a chiral stationary phase. c \( e_s = \text{enantiospecificity} = (\text{ee}_{\text{product}}) / (\text{ee}_{\text{starting material}}) \).

### Stereospecific Arylation to Prepare Diaryl and Triarylalkanes

#### General Procedure A: Stereospecific Arylation of Tertiary Benzylic Acetates

\[(S)-2-(2-((3\text{-methoxyphenyl})\text{butan-2-yl})\text{naphthalene}\ ((S)-4). \]

In a N\textsubscript{2}-atmosphere glovebox, NiCl\textsubscript{2}·DME (4.4 mg, 0.020 mmol, 5 mol %), CyJohnPhos (7.0 mg, 0.020 mmol, 5 mol %), and NaOMe (43 mg, 0.80 mmol, 2.0 equiv) were weighed into a 1-dram vial fitted with a magnetic stir bar. 2-(3-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (3a, 176 mg, 0.800 mmol, 2.0 equiv) and (S)-2-(naphthalen-2-yl)butan-2-yl acetate (1a, prepared in 95% ee, 97 mg, 0.40 mmol, 1.0 equiv) were added, followed by 2-Me-THF (1.0 mL, 0.4 M). The vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at 40 °C for 22 h. Please note that these reactions are heterogeneous and vigorous stirring is critical. The reaction mixture was then diluted with Et\textsubscript{2}O (5 mL) and filtered through a plug of silica gel and Celite®, which was then rinsed with Et\textsubscript{2}O (~ 15 mL). The filtrate was concentrated and then purified by silica gel chromatography (0–2% Et\textsubscript{2}O/hexanes) to give the compound 4 (run 1: 100.3 mg, 86%; run 2: 105.7 mg, 91%) as a colorless sticky oil. The enantiomeric excess was determined to be 93% (run 1: 93% ee; run 2: 92% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.6 mL/min, 0.1% \( i \)-PrOH/hexane, \( \lambda = 254 \) nm); \( t_R(\text{major}) = 12.058 \) min, \( t_R(\text{minor}) = 14.930 \) min. \( \alpha_D^{24} = -102.0^\circ \) (c 4.25, CHCl\textsubscript{3}); $^1$H NMR (600 MHz, CDCl\textsubscript{3}) \( \delta 7.85 – 7.81 \) (m, 1H), 7.81 – 7.77 (m, 2H), 7.49 – 7.42 (m, 2H), 7.21 – 7.16 (m, 2H), 6.38 – 6.79 (m, 2H), 6.76 – 6.69 (m, 1H), 3.75 (s, 3H), 2.31 – 2.20 (m, 2H), 1.70 (s, 3H), 0.77 (t, \( J = 7.3 \) Hz, 3H); $^{13}$C NMR (151 MHz, CDCl\textsubscript{3}) \( \delta 159.4, 151.5, 146.9, 133.3, 131.9, 128.9, 128.1, 127.6, 127.5, 127.2, 125.9, 125.5, 124.9, 120.4, 114.3, 110.3, 55.3, 46.8, 33.9, 26.9, 9.4; FTIR (NaCl/thin film) 3054, 2967, 2934, 2877, 1599, 1582, 1485, 1457, 1430, 1290, 1254, 1053, 819, 749, 703, 477 cm\textsuperscript{-1}; HRMS (CI+) [M+H]+ calculated for C\textsubscript{21}H\textsubscript{23}O: 291.1749, found: 291.1773.

\[(R)-2-(2-\text{Phenylbutan-2-yl})\text{naphthalene}\ ((R)-6). \]

Prepared via General Procedure A using 1a (prepared in 96% ee) as a colorless oil (run 1: 100 mg, 96%; run 2: 96.8 mg, 93%). The enantiomeric excess was determined to be 95% (run 1: 95% ee; run 2: 95% ee) by chiral SFC
analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.0 mL/min, 15% EtOH(0.1% diethylamine)/CO₂ (100 bar), λ=220 nm); \( t_R \) (major) = 6.25 min, \( t_R \) (minor) = 7.32 min. \([α]_D^{24} = +13.3° \) (c 1.02, CHCl₃): \(^1\)H NMR (400 MHz, CDCl₃) \( δ \) 7.88 – 7.78 (m, 3H), 7.71 (d, \( J = 8.7 \) Hz, 1H), 7.53 – 7.43 (m, 2H), 7.33 – 7.18 (m, 6H), 2.36 – 2.22 (m, 2H), 1.73 (s, 3H), 0.79 (t, \( J = 7.4 \) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl₃) \( δ \) 149.7, 147.0, 133.2, 131.8, 128.10, 128.07, 127.63, 127.61, 127.5, 127.3, 126.0, 125.7, 125.6, 124.9, 46.8, 33.8, 26.9, 9.4; FTIR (NaCl/thin film) 3055, 2968, 2934, 2876, 1599, 1494, 1444, 1380, 1273, 1131, 1029, 948, 897, 770 cm⁻¹; HRMS (EI+) [M]+ calculated for C₂₀H₂₀: 260.1565, found: 260.1558.

(R)-N,N-Dimethyl-4-(2-(naphthalen-2-yl)butan-2-yl)aniline ((R)-7). Prepared via General Procedure A using 1a (prepared in 96% ee) as a white solid (mp 64–66 °C; 99 mg, 82%). The enantiomeric excess was determined to be 96% by chiral SFC analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.5 mL/min, 55% MeOH(0.1% diethylamine)/CO₂ (100 bar), λ=220 nm); \( t_R \) (major) = 11.68 min, \( t_R \) (minor) = 17.66 min. \([α]_D^{24} = +22.6° \) (c 3.8, CHCl₃): \(^1\)H NMR (600 MHz, CDCl₃) \( δ \) 7.81 (dd, \( J = 8.0, 1.3 \) Hz, 1H), 7.79 – 7.74 (m, 2H), 7.67 (d, \( J = 8.7 \) Hz, 1H), 7.48 – 7.38 (m, 2H), 7.21 (dd, \( J = 8.7, 1.9 \) Hz, 1H), 7.11 – 7.05 (m, 2H), 6.68 – 6.63 (m, 2H), 2.91 (s, 6H), 2.28 – 2.15 (m, 2H), 1.67 (s, 3H). 0.76 (t, \( J = 7.3 \) Hz, 3H); \(^{13}\)C NMR (151 MHz, CDCl₃) \( δ \) 148.6, 147.6, 137.8, 133.3, 131.8, 128.2, 128.1, 127.50, 127.46, 127.4, 125.8, 125.4, 124.8, 112.3, 45.9, 40.8, 34.0, 27.0, 9.4; FTIR (NaCl/thin film) 3431, 3054, 2966, 2934, 2876, 1613, 1519, 1444, 1348, 1201, 1166, 948, 818, 746, 569, 476 cm⁻¹; HRMS (LIFDI) [M]⁺ calculated for C₂₂H₂₅N: 303.1987, found: 303.1966.

(R)-2-(2-(4-Methoxyphenyl)butan-2-yl)naphthalene ((R)-8). Prepared via General Procedure A using 1a (prepared in 96% ee) as a colorless oil (run 1: 110 mg, 95%; run 2: 105.7 mg, 91%). The enantiomeric excess was determined to be 96% (run 1: 96% ee; run 2: 96% ee) by chiral SFC analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.0 mL/min, 25% i-PrOH(0.1% diethylamine)/CO₂ (100 bar), λ=220 nm); \( t_R \) (major) = 4.89 min, \( t_R \) (minor) = 6.27 min. \([α]_D^{24} = +12.4° \) (c 0.98, CHCl₃): \(^1\)H NMR (400 MHz, CDCl₃) \( δ \) 7.89 – 7.83 (m, 1H), 7.83 – 7.77 (m, 2H), 7.54 – 7.43 (m, 2H), 7.23 – 7.13 (m, 3H), 6.87 – 6.80 (m, 2H), 3.81 (s, 3H), 2.35 – 2.16 (m, 2H), 1.71 (s, 3H). 0.79 (t, \( J = 7.3 \) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl₃) \( δ \) 157.5, 147.2, 141.8, 133.2, 131.8, 128.6, 128.1, 127.6, 127.5, 127.3, 125.9, 125.5, 124.8, 113.3, 55.3, 46.1, 34.0, 27.1, 9.4; FTIR (NaCl/thin film) 3055, 2967, 2932, 2876, 1511, 1463, 1441, 1298, 1248, 1182, 1034, 852, 745 cm⁻¹; HRMS (Cl+) [M+H]⁺ calculated for C₂₁H₂₃O: 291.1749, found: 291.1768.
\((R)-2-(2-(4-	ext{Chlorophenyl})\text{butan-2-yl})\text{naphthalene ((R)-9)}\). Prepared via General Procedure A using 1a (prepared in 95\% ee) as a colorless oil (run 1: 62.1 mg, 53\%; run 2: 70.4 mg, 60\%). The enantiomeric excess was determined to be 92\% (run 1: 92\% ee; run 2: 92\% ee) by chiral SFC analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.0 mL/min, 15\% EtOH(0.1\% diethylamine)/CO₂ (100 bar), \(\lambda=220\) nm); \(t_R\)(major) = 6.18 min, \(t_R\)(minor) = 6.97 min. \([\alpha]_D^{24} = +10.8^\circ\) (c 1.66, CHCl₃); \(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) 7.86 (d, \(J = 8.0\) Hz, 1H), 7.85 – 7.79 (m, 2H), 7.73 (d, \(J = 8.7\) Hz, 1H), 7.55 – 7.45 (m, 2H), 7.31 – 7.25 (m, 2H), 7.20 – 7.13 (m, 3H), 2.35 – 2.19 (m, 2H), 1.72 (s, 3H), 0.80 (t, \(J = 7.4\) Hz, 3H); \(^13\)C NMR (151 MHz, CDCl₃) \(\delta\) 148.3, 146.4, 134.6, 133.2, 131.9, 128.1, 127.7, 127.6, 127.5, 127.2, 126.3, 126.0, 125.7, 125.1, 46.9, 43.4, 39.3, 33.8, 26.9, 14.4, 13.0, 9.3; FTIR (NaCl/thin film) 3055, 2969, 2934, 2887, 1599, 1509, 1489, 1092, 817, 746, 477 cm\(^{-1}\); HRMS (EI\(^+\)) [M]+ calculated for C\(_{20}\)H\(_{19}\)Cl 294.1775, found: 294.1189.

\((R)-\text{N,N-Diethyl-4-(2-(naphthalen-2-yl)\text{butan-2-yl})benzamide ((R)-10)}\). Prepared via General Procedure A using 1a (prepared in 96\% ee) except that the reaction mixture was heated at 60 °C for 12 h. Compound 10 was obtained as white solid (mp 96–100 °C; run 1: 125 mg, 87\%; run 2: 122 mg, 85\%). The enantiomeric excess was determined to be 94\% (run 1: 94\% ee, run 2: 94\% ee) by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 8\% \(i\)-PrOH/hexane, \(\lambda=254\) nm); \(t_R\)(major) = 11.038 min, \(t_R\)(minor) = 10.179 min. \([\alpha]_D^{24} = +18.9^\circ\) (c 1.16, CHCl₃); \(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) 7.82 (d, \(J = 8.0\) Hz, 1H), 7.80 – 7.76 (m, 2H), 7.69 (d, \(J = 8.7\) Hz, 1H), 7.50 – 7.42 (m, 2H), 7.29 (d, \(J = 8.1\) Hz, 2H), 7.24 (d, \(J = 8.4\) Hz, 2H), 7.15 (dd, \(J = 8.7, 1.9\) Hz, 1H), 3.54 (br s, 2H), 3.28 (br s, 2H), 2.33 – 2.18 (m, \(J = 7.1\) Hz, 2H), 1.70 (s, 3H), 1.23 (br s, 3H), 1.12 (br s, 3H), 0.77 (t, \(J = 7.3\) Hz, 3H); \(^13\)C NMR (151 MHz, CDCl₃) \(\delta\) 171.5, 150.9, 146.5, 134.6, 133.2, 131.9, 128.1, 127.7, 127.6, 127.5, 127.2, 126.3, 126.0, 125.7, 125.1, 46.9, 43.4, 39.3, 33.8, 26.9, 14.4, 13.0, 9.3; FTIR (NaCl/thin film) 3053, 2970, 2934, 2876, 1630, 1457, 1424, 1288, 1098, 1019, 819, 748, 478 cm\(^{-1}\); HRMS (CI\(^+\)) [M+H]+ calculated for C\(_{25}\)H\(_{30}\)NO: 360.2327, found: 360.2347.

X-ray quality crystals were obtained from slow evaporation of 10 in EtOAc. The crystal structure demonstrates that the absolute configuration is \(R\) (Figure S1). The enantiomeric excess of the crystal was determined to be 96\% ee by chiral HPLC analysis, with the major enantiomer matching that of the bulk material isolated as described above.
Figure S1. Molecular diagram of (R)-10 with ellipsoids at 50% probability. H-atoms omitted for clarity. (CCDC 1424635)

(R)-Methyl-4-(2-(naphthalen-2-yl)butan-2-yl)benzoate ((R)-11). Prepared via General Procedure A using 1a (prepared in 96% ee) except that 3.0 equiv of 3 were used and the reaction mixture was heated at 60 °C for 12 h. Compound 11 was obtained as a colorless oil (run 1: 114.5 mg, 90%; run 2: 105.6 mg, 83%). The enantiomeric excess was determined to be 96% (run 1: 96% ee, run 2: 96% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.6 mL/min, 1% i-PrOH/hexane, λ=254 nm); t_R(major) = 30.604 min, t_R(minor) = 33.299 min. [α]_D^24 = +8.1° (c 1.23, CHCl₃); \(^1\)H NMR (600 MHz, CDCl₃) δ 7.98 – 7.90 (m, 2H), 7.85 – 7.81 (m, 1H), 7.81 – 7.76 (m, 2H), 7.69 (d, J = 8.7 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.34 – 7.28 (m, 2H), 7.12 (dd, J = 8.6, 1.9 Hz, 1H), 3.90 (s, 3H), 2.34 – 2.22 (m, 2H), 1.72 (s, 3H), 0.77 (t, J = 7.4 Hz, 3H); \(^{13}\)C NMR (151 MHz, CDCl₃) δ 167.2, 155.1, 146.2, 133.3, 131.9, 129.4, 128.1, 127.84, 127.75, 127.7, 127.6, 127.0, 126.1, 125.8, 125.0, 52.1, 47.2, 33.8, 26.8, 9.3; FTIR (NaCl/thin film) 3055, 2969, 2878, 1718, 1608, 1435, 1279, 1188, 1115, 1018, 854, 819, 747, 477 cm⁻¹; HRMS (Cl⁺) [M+H]^⁺ calculated for C₂₂H₂₃O₂: 319.1698, found: 319.1708.
(R)-2-(2-(4-(Trifluoromethyl)phenyl)butan-2-yl)naphthalene ((R)-12). Prepared via General Procedure A using \(1a\) (prepared in 96% ee) as a colorless oil (117 mg, 89%). The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK IB, 0.2 mL/min, 0% i-PrOH/hexane, \(\lambda=210\) nm); \(t_R\)(major) = 39.173 min, \(t_R\)(minor) = 35.980 min. A second run using \(1a\) (prepared in 95% ee) gave 12 (95 mg, 72%) in 95% ee. \([\alpha]_D^{24} = +9.9^\circ\) (c 1.1, CHCl\(_3\)):

\(\text{H NMR (400 MHz, CDCl}_3\) \(\delta 7.91 – 7.84 (m, 1H), 7.84 – 7.79 (m, 2H), 7.73 (d, \(J = 8.6\) Hz, 1H), 7.58 – 7.45 (m, 4H), 7.35 (d, \(J = 8.2\) Hz, 2H), 7.13 (dd, \(J = 8.7, 1.9\) Hz, 1H), 2.38 – 2.21 (m, 2H), 1.74 (s, 3H), 0.79 (t, \(J = 7.4\) Hz, 3H); \(\text{13C NMR (101 MHz, CDCl}_3\) \(\delta 153.9, 145.9, 133.2, 131.9, 128.1, 128.02 (q, \(J_{C-F} = 32.9\) Hz), 128.0, 127.9, 127.6, 126.9, 126.2, 125.8, 125.1, 125.0 (q, \(J_{C-F} = 3.8\) Hz), 124.4 (q, \(J_{C-F} = 272.9\) Hz), 47.0, 33.8, 26.8, 9.25; \(\text{19F NMR (377 MHz, CDCl}_3\) \(\delta -62.2; FTIR (NaCl/thin film) 3057, 2971, 2937, 2880, 1921, 1617, 1504, 1409, 1325, 1273, 1122, 1068, 1016, 948, 841, 748 \text{ cm}^{-1}; HRMS (EI+) [M]+ calculated for C\(_{21}\)H\(_{19}\)F\(_3\): 328.1439, found: 328.1447.

(S)-2-(2-(3-Fluorophenyl)butan-2-yl)naphthalene ((S)-13). Prepared via General Procedure A using \(1a\) (prepared in 96% ee) as a colorless oil (run 1: 103.5 mg, 93%; run 2: 106.4 mg, 96%). The enantiomeric excess was determined to be 94% (run 1: 94% ee; run 2: 94% ee) by chiral SFC analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.0 mL/min, 8% EtOH/0.1% diethylamine)/CO\(_2\) (100 bar, \(\lambda=220\) nm); \(t_R\)(major) = 5.22 min, \(t_R\)(minor) = 5.57 min. \([\alpha]_D^{24} = +7.5^\circ\) (c 1.19, CHCl\(_3\)):

\(\text{H NMR (600 MHz, CDCl}_3\) \(\delta 7.83 (d, \(J = 7.9\) Hz, 1H), 7.81 – 7.75 (m, 2H), 7.70 (d, \(J = 8.7\) Hz, 1H), 7.52 – 7.41 (m, 2H), 7.21 (td, \(J = 8.0, 6.3\) Hz, 1H), 7.15 (dd, \(J = 8.7, 1.9\) Hz, 1H), 6.98 (dt, \(J = 8.0, 1.2\) Hz, 1H), 6.95 (dt, \(J = 11.1, 2.2\) Hz, 1H), 6.87 (td, \(J = 8.5, 2.7\) Hz, 1H), 2.32 – 2.17 (m, 2H), 1.70 (s, 3H), 0.77 (t, \(J = 7.3\) Hz, 3H); \(\text{13C NMR (151 MHz, CDCl}_3\) \(\delta 162.9 (d, \(J_{C-F} = 245\) Hz), 152.6 (d, \(J_{C-F} = 6.4\) Hz), 146.3, 133.3, 131.9, 129.4 (d, \(J_{C-F} = 8.2\) Hz), 128.1, 127.8, 127.5, 127.0, 126.1, 125.7, 125.0, 123.4 (d, \(J_{C-F} = 2.7\) Hz), 114.7 (d, \(J_{C-F} = 21.7\) Hz), 112.7 (d, \(J_{C-F} = 21.2\) Hz), 46.8 (d, \(J_{C-F} = 1.5\) Hz), 33.8, 26.8, 9.3; \(\text{19F NMR (565 MHz, CDCl}_3\) \(\delta -113.6); FTIR (NaCl/thin film) 3056, 2970, 2878, 1612, 1585, 1485, 1433, 1243, 1163, 917, 818, 783, 477 \text{ cm}^{-1}; HRMS (EI+) [M]+ calculated for C\(_{20}\)H\(_{19}\)F: 278.1471, found: 278.1479.
(S)-5-(2-(Naphthalen-2-yl)butan-2-yl)benzo-[1,3]-dioxole ((S)-14). Prepared via General Procedure A using 1a (prepared in 95% ee) as a colorless oil (run 1: 110 mg, 90%; run 2: 100 mg, 82%). The enantiomeric excess was determined to be 92% (run 1: 92% ee; run 2: 92% ee) by chiral SFC analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.0 mL/min, 30% EtOH(0.1% diethylamine)/CO₂ (100 bar), λ=220 nm); tᵣ(major) = 4.19 min, tᵣ(minor) = 4.93 min. [α]D²⁴ = +3.9° (c 4.57, CHCl₃): ¹H NMR (600 MHz, CDCl₃) δ 7.83 (dd, J = 8.0, 1.5 Hz, 1H), 7.81 – 7.77 (m, 2H), 7.70 (d, J = 8.7 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.19 (dd, J = 8.7, 1.9 Hz, 1H), 6.74 (d, J = 1.3 Hz, 2H), 6.70 – 6.65 (m, 1H), 5.91 (s, 2H), 2.31 – 2.14 (m, 2H), 1.67 (s, 3H), 0.78 (t, J = 7.3 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 147.6, 147.1, 145.4, 143.8, 133.3, 131.9, 128.1, 127.7, 127.5, 127.1, 126.0, 125.6, 124.8, 120.4, 108.7, 107.6, 100.9, 46.6, 34.1, 27.1, 9.4; FTIR (NaCl/thin film) 3055, 2968, 2933, 2877, 1631, 1599, 1485, 1430, 1303, 1039, 817, 746 cm⁻¹; HRMS (EI+) [M]+ calculated for C₂₁H₂₀O: 304.1463 found: 304.1482.

(2)-2-(2-(2,4-Dimethylphenyl)butan-2-yl)naphthalene ((S)-15). Prepared via General Procedure A using 1a (prepared in 96% ee) as a colorless oil (run 1: 103.8 mg, 90%; run 2: 100.4 mg, 87%). The enantiomeric excess was determined to be 95% (run 1: 95% ee; run 2: 95% ee) by chiral SFC analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.0 mL/min, 8% EtOH(0.1% diethylamine)/CO₂ (100 bar), λ=220 nm); tᵣ(major) = 7.83 min, tᵣ(minor) = 8.59 min. [α]D²⁴ = −16.3° (c 1.02, CHCl₃): ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.75 (m, 2H), 7.73 (d, J = 1.9 Hz, 1H), 7.67 (d, J = 8.6 Hz, 1H), 7.45 (dtd, J = 14.9, 7.5, 7.0, 5.4 Hz, 3H), 7.15 (dd, J = 8.6, 1.9 Hz, 1H), 7.11 – 7.06 (m, 1H), 6.91 – 6.85 (m, 1H), 2.46 – 2.30 (m, 4H), 2.27 – 2.14 (m, 1H), 1.71 (s, 3H), 1.68 (s, 3H), 0.71 (t, J = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 148.2, 142.8, 137.2, 135.7, 133.5, 133.4, 131.7, 128.0, 127.7, 127.6, 127.5, 126.3, 126.1, 125.8, 125.3, 124.2, 46.9, 32.8, 28.0, 21.9, 20.9, 9.5; FTIR (NaCl/thin film) 3054, 2969, 2934, 2876 1630, 1598, 1502, 1455, 1376, 1265, 1130, 1040, 948, 894, 769, 476 cm⁻¹; HRMS (EI+) [M]+ calculated for C₂₂H₂₄: 288.1878, found: 288.1896.

(S)-2-Methoxy-6-(2-(3-methoxyphenyl)butan-2-yl)naphthalene (16). Prepared via General Procedure A using 1b (prepared in 92% ee) as a colorless sticky oil (run 1: 120 mg, 94%; run 2:
124.9 mg, 98%). The enantiomeric excess was determined to be 90% (run 1: 90% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.6 mL/min, 0.1% i-ProOH/hexane, λ=254 nm); tR(major) = 16.688 min, tR(minor) = 18.948 min. [α]D24 = +7.7° (c 4.28, CHCl3): 1H NMR (600 MHz, CDCl3) δ 7.75 – 7.69 (m, 2H), 7.59 (d, J = 8.6 Hz, 1H), 7.21 – 7.12 (m, 3H), 7.10 (d, J = 2.5 Hz, 1H), 6.84 – 6.79 (m, 2H), 6.75 – 6.70 (m, 1H), 3.91 (s, 3H), 3.75 (s, 3H), 2.30 – 2.18 (m, 2H), 1.68 (s, 3H), 0.77 (t, J = 7.4 Hz, 3H); 13C NMR (151 MHz, CDCl3) δ 159.4, 157.6, 151.7, 144.6, 132.9, 125.6, 128.9, 128.7, 126.6, 124.8, 120.4, 118.6, 114.3, 110.2, 105.7, 55.5, 55.2, 46.7, 33.9, 26.9, 9.4; FTIR (NaCl/thin film) 3057, 2967, 2936, 2834, 1609, 1488, 1456, 1388, 1264, 1198, 1032, 852, 779 cm−1; HRMS (CI+) [M+H]+ calculated for C22H25O: 321.1855, found: 321.1859.

(R)-1-(2-(3-Methoxyphenyl)butan-2-yl)napthalene (17). Prepared via General Procedure A using 1c (prepared in 90% ee), except on a 0.30 mmol scale. Product 17 was isolated as a colorless sticky oil (58.6 mg, 67%). The enantiomeric excess was determined to be 88% by chiral HPLC analysis (CHIRALPAK IB, 0.6 mL/min, 0.1% i-ProOH/hexane, λ=254 nm); tR(major) = 11.227 min, tR(minor) = 14.389 min. A duplicate run was performed via General Procedure A using 1c (prepared in 84% ee), except on a 0.3 mmol scale, to give 17 as a colorless oil (70.1 mg, 80%) in 83% ee. [α]D24 = +17.1° (c 3.09, CHCl3): 1H NMR (600 MHz, CDCl3) δ 7.81 – 7.77 (m, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.30 (ddd, J = 8.0, 6.7, 1.1 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.84 – 6.80 (m, 1H), 6.80 – 6.75 (m, 1H), 6.71 – 6.66 (m, 1H), 3.71 (s, 3H), 2.52 (dq, J = 14.6, 7.4 Hz, 1H), 2.25 (dq, J = 13.0, 7.3 Hz, 1H), 1.73 (s, 3H), 0.58 (t, J = 7.3 Hz, 3H); 13C NMR (151 MHz, CDCl3) δ 159.7, 153.1, 143.3, 135.0, 131.6, 129.3, 127.9, 127.3, 125.3, 124.9, 124.8, 124.7, 119.4, 113.1, 110.0, 55.2, 47.5, 33.6, 29.4, 9.4; FTIR (NaCl/thin film) 3048, 2969, 2936, 2833, 1604, 1580, 1289, 1043, 877, 777, 705 cm−1; HRMS (CI+) [M+H]+ calculated for C21H23O: 291.1745, found: 291.1749.

(S)-6-(2-(3-Methoxyphenyl)butan-2-yl)-2-methylquinoline ((S)-18). Prepared via General Procedure A using 1d (prepared in 99% ee), except that 2a (133 mg, 0.332 mmol, 0.83 equiv) was used in place of 3a and the reaction mixture was heated at 60 °C. Product 18 was isolated as a pale yellow oil (run 1: 91 mg, 74%; run 2: 102.9 mg, 84%). The enantiomeric excess was determined to be 97% (run 1: 97% ee; run 2: 97% ee) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 5% i-ProOH/hexane, λ=254 nm); tR(major) = 8.758 min, tR(minor) = 9.969 min. [α]D24 = +5.7° (c 3.68, CHCl3): 1H NMR (600 MHz, CDCl3) δ 8.01 (d, J = 8.4 Hz, 1H), 7.86 (d, J
= 8.8 Hz, 1H), 7.68 (d, J = 2.1 Hz, 1H), 7.40 (dd, J = 8.8, 2.2 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.19 (t, J = 7.9 Hz, 1H), 6.82 – 6.76 (m, 2H), 6.75 – 6.69 (m, 1H), 3.74 (s, 3H), 2.73 (s, 3H), 2.30 – 2.16 (m, 2H), 1.68 (s, 3H), 0.76 (t, J = 7.3 Hz, 3H); 13C NMR (151 MHz, CDCl3) δ 159.5, 158.6, 151.1, 146.9, 146.6, 136.4, 130.7, 129.0, 128.3, 126.1, 126.4, 125.4, 122.0, 120.3, 114.3, 110.4, 55.2, 46.8, 26.9, 25.4, 9.3; FTIR (NaCl/thin film) 3053, 2968, 2936, 2833, 1599, 1488, 1431, 1291, 1254, 1173, 1052, 837, 703 cm⁻¹; HRMS (LIFDI) [M]+ calculated for C21H23NO: 305.1780, found: 305.1759.

(S)-tert-Butyl((5-(3-methoxyphenyl)-5-(naphthalen-2-yl)hexyl)oxy)dimethylsilane ((S)-19). Prepared via General Procedure A using 1e (prepared in 99% ee) as a colorless sticky oil (159.8 mg, 89%). The enantiomeric excess was determined to be 99% by chiral HPLC analysis (CHIRALPAK IB, 0.4 mL/min, 100% hexane, λ=254 nm); tR(major) = 33.672 min, tR(minor) = 26.337 min. [α]D²⁴ = −11.0° (c 5.22, CHCl₃): 1H NMR (600 MHz, CDCl₃) δ 7.82 (d, J = 8.0 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.68 (d, J = 8.6 Hz, 1H), 7.45 (ddd, J = 19.3, 8.1, 6.8, 1.4 Hz, 2H), 7.21 – 7.15 (m, 2H), 6.83 – 6.78 (m, 2H), 6.75 – 6.70 (m, 1H), 3.75 (s, 3H), 3.55 (t, J = 6.6 Hz, 2H), 2.26 – 2.15 (m, 2H), 1.72 (s, 3H), 1.56 – 1.49 (m, 2H), 1.22 – 1.09 (m, 2H), 0.84 (s, 9H), −0.01 (s, 6H); 13C NMR (151 MHz, CDCl₃) δ 159.4, 151.6, 147.0, 133.3, 131.9, 129.0, 128.1, 127.7, 127.5, 127.1, 125.9, 125.5, 124.7, 120.3, 114.2, 110.3, 63.2, 55.2, 46.6, 41.4, 33.7, 27.6, 26.1, 21.3, 18.4, −5.1; FTIR (NaCl/thin film) 3055, 2934, 2856, 1606, 1283, 1099, 1046, 836, 775, 705, 476 cm⁻¹; HRMS (LIFDI) [M]+ calculated for C29H40O2Si: 448.2798, found: 448.2790.

(S)-2-(2-(3-Methoxyphenyl)-4-phenylbutan-2-yl)naphthalene ((S)-20). Prepared via General Procedure A using 1f (prepared in 99% ee), except that the reaction was run for 48 h. Product 20 was obtained as a colorless oil (run 1: 171.5 mg, 90%; run 2: 137.8 mg, 94%). The enantiomeric excess was determined to be 94% (run1: 94% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 100% hexane, λ=210 nm); tR(major) = 34.901 min, tR(minor) = 31.785 min. [α]D²⁴ = −25.9° (c 4.54, CHCl₃): 1H NMR (600 MHz, CDCl₃) δ 7.87 – 7.83 (m, 2H), 7.81 (dd, J = 7.8, 1.5 Hz, 1H), 7.73 (d, J = 8.7 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.17 – 7.13 (m, 2H), 6.88 – 6.85 (m, 2H), 6.76 (ddd, J = 8.3, 2.4, 1.0 Hz, 1H), 3.76 (t, J = 6.9 Hz, 2H), 2.49 – 2.47 (m, 2H), 2.18 (s, 3H), 0.76 (t, J = 7.3 Hz, 3H); 13C NMR (151 MHz, CDCl₃) δ 159.5, 151.1, 146.9, 146.6, 143.0, 133.3, 130.7, 129.1, 128.5, 128.0, 127.9, 127.5, 127.0, 126.1, 125.9, 125.7, 124.8, 120.2, 114.2, 110.5, 55.3, 46.7, 131.5, 27.5; FTIR (NaCl/thin film) 3056, 3024, 2946, 2867, 1600, 1283, 1494, 1291, 1047, 908, 818, 760 cm⁻¹; HRMS (EI+) [M]+ calculated for C₂₇H₂₆O: 366.1984, found: 366.1967.
Please note: The absolute configuration of 20 is tentatively assigned. The absolute configuration resulting from the method used in the preparation of its alcohol precursor S-1f has not been reported in the literature. Please see the experimental for S-1f below.

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\text{(E)-2-(2-(3-Methoxyphenyl)-5-(o-tolyl)pent-4-en-2-yl)naphthalene (21). Prepared via General Procedure A using 1g (prepared in 96% ee), except that 2a (133 mg, 0.332 mmol, 0.83 equiv) was used in place of 3a. Product 21 was isolated as a colorless sticky oil (run 1: 125.6 mg, 80%; run 2: 119.7 mg, 76%). The enantiomeric excess was determined to be 95% (run 1: 95% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.6 mL/min, 0.1% hexane, λ=210 nm); \tau_R(\text{major}) = 13.480 \text{ min}, \tau_R(\text{minor}) = 15.096 \text{ min}. [\alpha]_D^{24} = +3.7^\circ (c 4.84, \text{CHCl}_3); ^1H \text{ NMR (600 MHz, CDCl}_3) \delta 7.85 – 7.81 (m, 2H), 7.81 – 7.76 (m, 1H), 7.71 (d, \text{ }J = 8.6 \text{ Hz, 1H}), 7.50 – 7.42 (m, 2H), 7.24 (dd, \text{ }J = 8.7, 2.0 \text{ Hz, 1H}), 7.20 (t, \text{ }J = 7.9 \text{ Hz, 1H}), 7.17 (d, \text{ }J = 7.3 \text{ Hz, 1H}), 7.10 – 7.01 (m, 3H), 6.88 – 6.82 (m, 2H), 6.77 – 6.72 (m, 1H), 6.57 (d, \text{ }J = 15.6 \text{ Hz, 1H}), 5.76 (dt, \text{ }J = 15.6, 7.2 \text{ Hz, 1H}), 3.74 (s, 3H), 3.21 – 3.10 (m, 2H), 2.20 (s, 3H), 1.76 (s, 3H); ^{13}C \text{ NMR (151 MHz, CDCl}_3) \delta 159.5, 151.0, 146.5, 137.1, 135.1, 133.3, 132.0, 131.1, 130.1, 129.1, 128.5, 128.2, 127.8, 127.5, 127.1, 127.0, 126.04, 126.02, 125.9, 125.7, 124.8, 120.3, 114.2, 110.6, 55.3, 46.8, 45.6, 27.7, 19.8; \text{FTIR (NaCl/thin film) 3054, 2965, 2933, 1599, 1485, 1431, 1254, 1047, 967, 818, 754 cm}^{-1}; \text{HRMS (LIFDI) [M]+ calculated for C}_{29}H_{28}O: 392.2140, found: 392.2137.}
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Please note: The absolute configuration of 21 is tentatively assigned. The absolute configuration resulting from the method used in the preparation of its acetate precursor 1g has not been reported in the literature. Please see the experimental for 1g below.

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\text{(S)-2-(1,3-Bis(3-methoxyphenyl)pentan-3-yl)naphthalene (S)-22). Prepared via General Procedure A using 1h (prepared in 89% ee), except that 2a (133 mg, 0.332 mmol, 0.83 equiv) was used in place of 3a. Product 22 was isolated as a colorless sticky oil (127 mg, 77%). The enantiomeric excess was determined to be 87% by chiral SFC analysis (CHIRALCEL OJ-H(25 x 0.46 cm), 3.0 mL/min, 20% \text{MeOH(0.1% diethylamine)/CO}_2 (100 \text{bar}, \lambda=220 \text{nm}); \tau_R(\text{major}) = 9.10 \text{ min}, \tau_R(\text{minor}) = 7.81 \text{ min. A duplicate experiment was conducted with 1h (prepared in 87% ee) to give 22 (103 mg, 63%) in 86% ee. [\alpha]_D^{24} = -30.5^\circ (c 3.04, \text{CHCl}_3); ^1H \text{ NMR (600 MHz, CDCl}_3) \delta 7.87 – 7.81 (m, 2H), 7.78 (d, \text{ }J = 7.8 \text{ Hz, 1H}), 7.68 (d, \text{ }J = 8.7 \text{ Hz, 1H}), 7.51 – 7.41 (m, 2H), 7.19 (td, \text{ }J = 7.9, 4.1 \text{ Hz, 2H}), 7.14 (dd, \text{ }J = 8.7, 1.9 \text{ Hz, 1H}), 6.86 – 6.81 (m, 2H), 6.77 – 6.72 (m, 3H), 6.65 – 6.61 (m, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 2.50 – 2.44 (m, 2H), 2.36 – 2.22 (m, 4H), 0.75 (t, \text{ }J = 7.3 \text{ Hz, 3H}); ^{13}C \text{ NMR (151 MHz, CDCl}_3) \delta 159.5, 159.4, 150.1, 145.7, 144.8, 133.2, 131.9, 129.5, 128.9, 128.2, 127.7, 127.51, 127.48, 126.0, 125.6, 125.5, 120.93, 120.92, 114.9, 114.4, 111.0, 110.4, 55.29, 55.28, 50.0, 38.9, 30.9, 29.5, 8.6; \text{FTIR}}
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(R)-2-(1-(3-Methoxyphenyl)-1-phenylethyl)naphthalene ((R)-23). Prepared via General Procedure A using 1i (prepared in 96% ee) as a colorless oil (run 1: 95 mg, 70%; run 2: 101 mg, 75%). The enantiomeric excess was determined to be 94% (run 1: 94%; run 2: 94%) by chiral HPLC analysis (CHIRALPAK IB, 0.2 mL/min, 0.1% hexane, λ=210 nm); t_R(minor) = 52.102 min. [α]_D²⁴ = +15.0° (c 0.86, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.82 – 7.79 (m, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.49 – 7.41 (m, 3H), 7.32 (dd, J = 8.6, 2.0 Hz, 1H), 7.28 (t, J = 7.4 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.19 – 7.14 (m, 2H), 6.81 – 6.74 (m, 2H), 6.72 (t, J = 2.1 Hz, 1H), 3.72 (s, 3H), 2.27 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 159.4, 150.6, 148.8, 146.5, 133.2, 132.0, 130.6, 128.94, 128.91, 128.3, 128.1, 127.8, 127.5, 127.0, 126.2, 126.0, 125.9, 121.7, 115.6, 110.9, 55.3, 52.9, 30.6; FTIR (NaCl/thin film) 3054, 2978, 2833, 1597, 1486, 1254, 1044, 820, 745, 701 cm⁻¹; HRMS (CI+) [M+H]+ calculated for C₂₂H₂₂O: 339.1749, found: 339.1742.

(R)-4-(1-(3-Methoxyphenyl)-1-phenylethyl)-1,1'-biphenyl ((R)-24). Prepared via General Procedure A using 1j (prepared as 91% ee), except with 10 mol % NiCl₂·DME, 10 mol % CyJohnPhos, 60 °C, 48 h. Product 24 was isolated as a colorless oil (run 1: 84.4 mg, 58%; run 2: 96.2 mg, 66%). The enantiomeric excess was determined to be 91% (run 1: 91% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.6 mL/min, 0.1% hexane, λ=254 nm); t_R(minor) = 18.913 min, t_R(minor) = 18.288 min. [α]_D²⁴ = +31.5° (c 1.68, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.60 (dd, J = 8.1, 1.4 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.43 (t, J = 7.7 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.29 (dd, J = 8.4, 6.9 Hz, 2H), 7.22 (td, J = 7.6, 4.0 Hz, 2H), 7.20 – 7.14 (m, 4H), 6.80 – 6.73 (m, 2H), 6.71 (t, J = 2.1 Hz, 1H), 3.74 (s, 3H), 2.22 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 159.4, 150.8, 149.0, 148.2, 140.9, 138.8, 129.3, 128.90, 128.86, 128.85, 128.0, 127.3, 127.1, 126.6, 126.2, 121.6, 115.6, 110.8, 55.3, 52.5, 30.6; FTIR (NaCl/thin film) 3055, 3028, 2979, 2833, 1598, 1486, 1290, 1254, 1040, 845, 735, 699 cm⁻¹; HRMS (CI+) [M+H]+ calculated for C₂₇H₂₅O: 365.1905, found: 365.1907.
Preparation of Enantioenriched Tertiary Benzyl Acetates

General Procedure B: Preparation of (S)-2-(Naphthalen-2-yl)butan-2-yl Acetate (1a).

In an oven-dried 100-mL round-bottomed flask, was placed 2-(naphthalen-2-yl)butan-2-ol (S-1a, prepared in 96% ee, 1.5 g, 7.5 mmol, 1.0 equiv), 4-pyrrolidinopyridine (PPY, 168 mg, 1.13 mmol, 0.150 equiv), and CH$_2$Cl$_2$ (25 mL, 0.3 M). Then flask was then placed in an ice/water bath. Et$_3$N (3.1 mL, 23 mmol, 3.0 equiv) was added, followed by acetic anhydride (1.4 mL, 15 mmol, 2.0 equiv). The solution was then stirred at room temperature for 14 h. Sat. NaHCO$_3$ (100 mL) was added, and the product was extracted with CH$_2$Cl$_2$ (3 x 25 mL). The combined organic layers were washed with sat. NaCl, dried (Na$_2$SO$_4$), filtered and concentrated. The crude mixture was purified by silica gel chromatography (0–20% EtOAc/hexanes) to give 1a as a viscous oil (1.45 g, 80%). The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK IB, 1 mL/min, 1% i-PrOH/hexane, $\lambda$=254 nm); $t_R$(major) = 8.234 min, $t_R$(minor) = 6.313 min. $[\alpha]_D^{24}$ = +5.0° (c 3.59, CHCl$_3$): $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.86 – 7.78 (m, 3H), 7.77 – 7.74 (m, 1H), 7.51 – 7.39 (m, 3H), 2.18 – 2.08 (m, 5H), 1.92 (s, 3H), 0.81 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 169.8, 142.4, 133.2, 132.5, 128.3, 128.1, 127.6, 126.2, 125.9, 123.6, 123.2, 84.6, 35.1, 24.5, 22.4, 8.3; FTIR (NaCl/thin film) 3057, 2977, 2938, 2880, 1734, 1458, 1366, 1246, 1128, 1017, 817, 747, 477 cm$^{-1}$; HRMS (EI+) [M]$^+$ calculated for C$_{16}$H$_{18}$O$_2$: 242.1307, found: 242.1309.

This type of compound decomposed to olefins quickly in pure form at room temperature, but is relatively stable in cold solution. Our suggestion is to immediately dissolve in anhydrous 2-Me-THF and store in fridge under N$_2$.

A crystal suitable for X-ray diffraction analysis was obtained upon cooling the viscous oil isolated above neat at –35 °C. The crystal structure demonstrates that the absolute configuration is S (Figure S2).

**Figure S2.** Molecular diagram of (S)-1a with ellipsoids at 50% probability, H-atoms omitted for clarity. (CCDC 1502353)
(S)-2-(6-Methoxynaphthalen-2-yl)butan-2-yl acetate ((S)-1b). Prepared via General Procedure B using S-1b (prepared as 92% ee) as a colorless oil (75%). The enantiomeric excess was assumed to be 92% based on the starting material (S-1b). \([\alpha]^2_{D} = +42^\circ\) (c 1.5, CHCl₃): \(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) 7.74 – 7.66 (m, 3H), 7.40 (dd, \(J = 8.6, 1.9\) Hz, 1H), 7.14 (dd, \(J = 8.8, 2.5\) Hz, 1H), 7.11 (d, \(J = 2.5\) Hz, 1H), 3.91 (s, 3H), 2.16 – 2.06 (m, 5H), 1.90 (s, 3H), 0.80 (t, \(J = 7.4\) Hz, 3H); \(^1^3\)C NMR (151 MHz, CDCl₃) \(\delta\) 169.9, 157.8, 140.1, 133.6, 129.8, 128.7, 126.9, 123.8, 123.5, 119.0, 105.7, 84.7, 55.5, 35.1, 24.5, 22.4, 8.3; FTIR (NaCl/thin film) 2975, 2937, 1734, 1608, 1367, 1247, 1204, 1164, 1031, 850 cm\(^{-1}\); HRMS (CI+) [M]+H calculated for C₁₇H₂₁O₃: 273.1491, found: 273.1501.

(\textit{S})-2-(Naphthalen-1-yl)butan-2-yl acetate ((\textit{S})-1c). Prepared via General Procedure B using S-1c (90% ee) as a colorless oil (58%). The enantiomeric excess was determined to be 90% by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 1.0% i-PrOH/hexanes, \(\lambda = 254\) nm); \(t_R\)(major) = 9.214 min, \(t_R\)(minor) = 8.322 min. \([\alpha]^2_{D} = +10.2^\circ\) (c 0.88, CHCl₃): \(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) 8.55 (dd, \(J = 8.5, 1.5\) Hz, 1H), 7.87 (dd, \(J = 7.7, 1.9\) Hz, 1H), 7.78 (d, \(J = 8.1\) Hz, 1H), 7.52 (dd, \(J = 7.3, 1.3\) Hz, 1H), 7.50 – 7.41 (m, 3H), 2.48 (dq, \(J = 14.7, 7.5\) Hz, 1H), 2.25 (dq, \(J = 14.6, 7.5\) Hz, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 0.87 (t, \(J = 7.5\) Hz, 3H); \(^1^3\)C NMR (151 MHz, CDCl₃) \(\delta\) 169.5, 139.9, 134.9, 130.4, 129.7, 125.6, 125.5, 125.1, 125.0, 124.3, 85.6, 34.0, 24.6, 21.8, 8.7; FTIR (NaCl/thin film) 2979, 2940, 1734, 1653, 1558, 1507, 1538, 1107, 1015, 804, 776 cm\(^{-1}\); HRMS (EI+) [M]+ calculated for C₁₆H₁₈O₂: 242.1307, found: 242.1316.

(\textit{S})-2-(2-Methylquinolin-6-yl)butan-2-yl acetate ((\textit{S})-1d). Prepared via General Procedure B using S-1d (99% ee) as a yellow oil (87%). The enantiomeric excess was determined to be 99% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 6.0% i-PrOH/hexanes, \(\lambda = 254\) nm); \(t_R\)(major) = 13.331 min, \(t_R\)(minor) = 9.787 min. \([\alpha]^2_{D} = +7.8^\circ\) (c 1.51, CHCl₃): \(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) 8.01 (d, \(J = 8.4\) Hz, 1H), 7.97 (d, \(J = 8.8\) Hz, 1H), 7.67 (d, \(J = 2.1\) Hz, 1H), 7.63 (dd, \(J = 8.8, 2.2\) Hz, 1H), 7.27 (s, 1H), 2.72 (s, 3H), 2.10 (s, 5H), 1.90 (s, 3H), 0.79 (t, \(J = 7.4\) Hz, 3H); \(^1^3\)C NMR (151 MHz, CDCl₃) \(\delta\) 169.8, 159.0, 147.0, 142.1, 136.5, 128.7, 128.7, 125.6, 125.5, 125.1, 125.0, 124.3, 85.6, 34.0, 24.6, 21.8, 8.7; FTIR (NaCl/thin film) 2977, 2938, 1734, 1653, 1558, 1507, 1538, 1107, 1015, 804, 776 cm\(^{-1}\); HRMS (CI+) [M]+H calculated for C₁₆H₂₀N O₂: 258.1494, found: 258.1488.
(S)-6-((tert-Butyldimethylsilyl)oxy)-2-(naphthalen-2-yl)hexan-2-yl acetate ((S)-1e). Prepared via General Procedure B using S-1e (99% ee) as a colorless oil (75%). The enantiomeric excess was determined to be 99% by chiral HPLC analysis (CHIRLCEL OD-H, 1.0 mL/min, 0.5% i-PrOH/hexanes, λ=254 nm); tR(major) = 21.535 min, tR(minor) = 14.469 min. [α]D24 = +15.4° (c 4.73, CHCl3); 1H NMR (600 MHz, CDCl3) δ 7.81 (dd, J = 11.1, 8.5 Hz, 3H), 7.76 – 7.71 (m, 1H), 7.48 – 7.41 (m, 3H), 3.53 (t, J = 6.4 Hz, 2H), 2.14 – 2.03 (m, 5H), 1.93 (s, 3H), 1.46 (p, J = 7.0 Hz, 2H), 1.31 – 1.22 (m, 2H), 0.83 (s, 9H), –0.01 (s, 6H); 13C NMR (101 MHz, CDCl3) δ 169.9, 142.5, 133.2, 132.5, 128.3, 128.1, 127.6, 126.1, 125.9, 123.5, 121.84, 63.0, 42.4, 33.0, 26.0, 24.8, 22.4, 20.3, 18.4, –5.2; FTIR (NaCl/thin film) 3058, 2952, 2929, 2857, 1739, 1366, 1248, 1101, 775 cm⁻¹; HRMS (LIFDI) [M]+ calculated for C24H36O3Si: 400.2434, found: 400.2435.

(S)-2-(Naphthalen-2-yl)-4-phenylbutan-2-yl acetate ((S)-1f). Prepared via General Procedure B as a colorless oil (96%). The enantiomeric excess was determined to be 94% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 0.5% i-PrOH/hexanes, λ=254 nm); tR(major) = 11.227 min, tR(minor) = 12.577 min. [α]D24 = −74.8° (c 1.1, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.89 – 7.77 (m, 4H), 7.52 – 7.43 (m, 3H), 7.26 – 7.21 (m, 2H), 7.16 (d, J = 7.3 Hz, 1H), 7.13 – 7.07 (m, 2H), 2.58 – 2.34 (m, 4H), 2.12 (s, 3H), 2.01 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 169.9, 142.2, 141.8, 133.2, 132.5, 128.49, 128.46, 128.4, 128.3, 127.6, 126.3, 126.0, 124.5, 123.6, 123.0, 84.0, 44.1, 30.4, 25.3, 22.4; FTIR (NaCl/thin film) 3059, 3025, 2937, 1734, 1717, 1652, 1558, 1506, 1244, 747 cm⁻¹; HRMS (LIFDI) [M]+ calculated for C22H22O2: 318.1620, found: 318.1648.

Please note: The absolute configuration of 1f is tentatively assigned. The absolute configuration resulting from the method used in the preparation of its alcohol precursor S-1f has not been reported in the literature. Please see the experimental for S-1f below.

(S)-1-(3-Methoxyphenyl)-3-(naphthalen-2-yl)pentan-3-yl acetate ((S)-1h). Prepared via General Procedure B using S-1h (89% ee) as a colorless oil (80%). The enantiomeric excess was assumed to be 89% based on the starting material. [α]D24 = +30.5° (c 1.50, CHCl3); 1H NMR (600 MHz, CDCl3) δ 7.91 – 7.84 (m, 4H), 7.55 – 7.46 (m, 3H), 7.16 (t, J = 7.9 Hz, 1H), 6.70 (ddd, J = 13.7, 7.8, 2.0 Hz, 2H), 6.65 – 6.61 (m, 1H), 3.76 (s, 3H), 2.97 – 2.85 (m, 1H), 2.62 (dq, J = 14.6, 7.3 Hz, 1H), 2.51 – 2.41 (m, 2H), 2.39 – 2.29 (m, 1H), 2.27 – 2.16 (m, 4H), 0.74 (t, J = 7.4 Hz, 3H); 13C NMR (151 MHz, CDCl3) δ 169.7, 159.7, 143.6, 140.6, 134.1, 130.4, 25.3, 22.4; FTIR (NaCl/thin film) 3056, 3070, 2937, 1734, 1652, 1558, 1506, 1244, 747 cm⁻¹; HRMS (LIFDI) [M]+ calculated for C24H26O3: 362.1882, found: 362.1906.
Please note: The absolute configuration of **1h** is tentatively assigned. The absolute configuration resulting from the method used in the preparation of its alcohol precursor **S-1h** has not been reported in the literature. Please see the experimental for **S-1h** below.

**\((R)-1-(Naphthalen-2-yl)-1-phenylethyl acetate (\((R)-1i)\).** Prepared via General Procedure B using **S-1i** (96% ee) as a colorless sticky oil (54%). The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRLPAK IB, 1.0 mL/min, 1.0% i-PrOH/hexanes, λ=254 nm); \(t_R\) (major) = 8.923 min, \(t_R\) (minor) = 7.511 min. \([\alpha]^D_{24} = +15.3^\circ\) (c 4.1, CHCl₃); \(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) 7.89 – 7.87 (m, 1H), 7.84 (dd, \(J = 7.4, 1.8\) Hz, 1H), 7.79 (dd, \(J = 7.4, 1.7\) Hz, 1H), 7.75 (d, \(J = 8.7\) Hz, 1H), 7.50 – 7.44 (m, 2H), 7.38 – 7.29 (m, 5H), 7.26 – 7.23 (m, 1H), 2.30 (s, 3H), 2.16 (s, 3H); \(^13\)C NMR (151 MHz, CDCl₃) \(\delta\) 169.4, 145.6, 142.9, 133.0, 132.6, 128.5, 128.3, 128.1, 127.7, 127.3, 126.3, 126.2, 126.1, 124.6, 124.5, 84.8, 27.0, 22.6; FTIR (NaCl/thin film) 3056, 3024, 2981, 1739, 1368, 1241, 1188, 749, 699 cm\(^{-1}\); HRMS (LIFDI) \([M]^+\) calculated for C\(_{20}\)H\(_{18}\)O\(_2\): 290.1307, found: 290.1328.

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\begin{align*}
\text{Me} &\quad \text{OAc} \\
\end{align*}
\]

**\((R)-1-(1,1'-Biphenyl)-4-yl)-1-phenylethyl acetate (\((R)-1j)\).** Prepared via General Procedure B using **S-1j** (91% ee) as a colorless oil (61%). The enantiomeric excess was assumed to be 91% based on the starting material. \([\alpha]^D_{24} = -17.8^\circ\) (c 0.84, CHCl₃); \(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) 7.61 – 7.57 (m, 2H), 7.57 – 7.53 (m, 2H), 7.44 (t, \(J = 7.7\) Hz, 2H), 7.42 – 7.32 (m, 7H), 7.29 – 7.26 (m, 1H), 2.25 (s, 3H), 2.16 (s, 3H); \(^13\)C NMR (151 MHz, CDCl₃) \(\delta\) 169.4, 145.7, 144.8, 140.8, 140.1, 128.9, 128.3, 127.4, 127.3, 127.2, 127.0, 126.5, 126.0, 84.6, 27.0, 22.6; FTIR (NaCl/thin film) 3057, 3029, 2939, 1739, 1600, 1582, 1487, 1446, 1368, 1238, 1057, 875, 761 cm\(^{-1}\); HRMS (LIFDI) \([M]^+\) calculated for C\(_{22}\)H\(_{20}\)O\(_2\): 316.1463, found: 316.1485.
Preparation of (S,E)-2-(Naphthalen-2-yl)-5-(o-tolyl)pent-4-en-2-yl acetate ((S)-1g).

2-(Naphthalen-2-yl)pent-4-en-2-ol. This procedure was adapted from that reported in the literature.4 In an oven-dried, 50-mL, round-bottomed flask was placed (R)-BINOL (312 mg, 1.09 mmol, 0.30 equiv) in CH2Cl2 (9.0 mL). Ti(O-iPr)4 (0.33 mL, 1.1 mmol, 0.30 equiv) was added at room temperature. The mixture was stirred for 10 min. Then iPrOH (5.6 mL, 73 mmol, 20 equiv) was added, followed by a solution of 2-acetonaphthone (618 mg, 3.63 mmol, 1.00 equiv) and CH2Cl2 (3.0 mL), and then tetraallyltin (0.96 mL, 4.0 mmol, 1.1 equiv). The orange solution was stirred at room temperature for 22 h and quenched with sat. NaHCO3 (40 mL). To remove solids, the mixture was filtered through Celite®, which was then washed with CH2Cl2. The layers were separated, and the organic layer was washed with sat. NaCl, dried (Na2SO4), filtered, and concentrated. The crude mixture was purified on silica gel chromatography (0–20% EtOAc/hexanes) to give a 2-(naphthalen-2-yl)pent-4-en-2-ol as a clear oil (634.2 mg, 82%). The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 3% i-PrOH/hexane, λ = 254 nm); tR(major) = 12.164 min, tR(minor) = 10.175 min. The spectral data of this compound matches that reported in the literature.5 Please note: The absolute configuration of 2-(naphthalene-2-yl)pent-4-en-2-ol is tentatively assigned. The absolute configuration resulting from this allylation procedure has not been reported in the literature.[REF: Walsh ACIE 2002]

2-(Naphthalen-2-yl)pent-4-en-2-yl acetate. Using General Procedure B, 2-(naphthalen-2-yl)pent-4-en-2-yl acetate was obtained as a colorless oil (632.5 mg, 86%) from 2-(naphthalen-2-yl)pent-4-en-2-ol (611 mg, 2.88 mmol, 96% ee): 1H NMR (600 MHz, CDCl3) δ 7.90 – 7.80 (m, 3H), 7.79 – 7.72 (m, 1H), 7.46 (ddt, J = 9.2, 6.9, 5.4 Hz, 3H), 5.63 (ddt, J = 17.3, 10.2, 7.2 Hz, 1H), 5.11 – 4.95 (m, 2H), 2.94 (dd, J = 14.0, 7.1 Hz, 1H), 2.85 (dd, J = 14.0, 7.3 Hz, 1H), 2.09 (s, 3H), 1.91 (s, 3H); 13C NMR (151 MHz, CDCl3) δ 169.8, 142.2, 133.2, 133.0, 123.6, 132.6, 128.4, 128.2, 127.6, 126.2, 126.0, 123.6, 123.1, 118.8, 83.4, 46.4, 25.1, 22.4.

(S,E)-2-(Naphthalen-2-yl)-5-(o-tolyl)pent-4-en-2-yl acetate ((S)-1g). The procedure was adapted from reported literature.6 In 25-mL, round-bottomed flask was placed 2-(naphthalen-2-yl)pent-4-en-2-yl acetate (632 mg, 2.49 mmol, 1.00 equiv), 2-methylphenylboronic acid (677 mg, 5.00 mmol, 2.00 equiv), N-methylmorpholine (0.55 mL, 5.0 mmol, 2.0 equiv), and MeCN (10 mL). The flask was exposed to open air. Pd(OAc)2 (335 mg, 0.498 mmol, 2.0 mol %) and neocuproine (125 mg, 0.598 mmol, 24 mol %) were added. The mixture was heated at 80 °C for 22 h. The mixture was cooled to room temperature and diluted with CH2Cl2 (30 mL). The solid was removed by filtration through a pad of Celite® and the organic layer was
concentrated. The crude mixture was purified via silica gel chromatography (0–15% EtOAc/hexanes) to give \textbf{1g} as a colorless oil (351 mg, 41%). The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 1% i-PrOH/hexane, λ=254 nm); \textbf{t}ₘₐᵣᵢₜ (major) = 15.924 min, \textbf{t}ₘᵦₜ (minor) = 21.866 min. [\(\alpha\)]\textsubscript{D}\textsuperscript{24} = +10.7° (c 1.12, CHCl₃): \(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) 7.85 – 7.78 (m, 4H), 7.52 – 7.44 (m, 3H), 7.28 (dd, \(J\) = 7.4, 2.2 Hz, 1H), 7.14 – 7.07 (m, 3H), 6.62 – 6.56 (m, 1H), 5.87 (dt, \(J\) = 15.3, 7.4 Hz, 1H), 3.12 – 2.99 (m, 2H), 2.22 (s, 3H), 2.10 (s, 3H), 1.97 (s, 3H); \(^1\)C NMR (151 MHz, CDCl₃) \(\delta\) 169.8, 142.2, 136.8, 135.3, 133.2, 132.6, 132.1, 130.2, 128.4, 128.2, 127.6, 127.3, 126.3, 126.1, 126.05, 126.03, 125.9, 123.6, 123.2, 83.8, 45.9, 25.3, 22.4, 19.8; FTIR (NaCl/thin film) 2955, 2921, 2850, 1713, 1464, 1364, 1232, 1076, 748 cm\(^{-1}\); HRMS (LIFDI) [M]⁺ calculated for C\(_{24}\)H\(_{24}\)O\(_2\): 344.1776, found: 344.1769.

Please note: The absolute configuration of \textbf{1g} is tentatively assigned. The absolute configuration resulting from the method used in the preparation of its alcohol precursor has not been reported in the literature, as discussed above.

### Preparation of Tertiary Benzyl Alcohols (S-1a – S-1j).

In addition to the reactions described below, a number of other methods are available for the preparation of highly enantioenriched tertiary benzylic alcohols. Notable examples are described in the following references:

1) Jeon, S.-J., Li, H. & Walsh, P. J. A Green Chemistry Approach to a More Efficient Asymmetric Catalyst: Solvent-Free and Highly Concentrated Alkyl Additions to Ketones. \textit{J. Am. Chem. Soc.} \textbf{127}, 16416-16425 (2005).

2) García, C., LaRochelle, L. K. & Walsh, P. J. A Practical Catalytic Asymmetric Addition of Alkyl Groups to Ketones. \textit{J. Am. Chem. Soc.} \textbf{124}, 10970-10971 (2002).

3) Li, H. & Walsh, P. J. Catalytic Asymmetric Vinylation of Ketones. \textit{J. Am. Chem. Soc.} \textbf{126}, 6538-6539 (2004).

4) García, C. & Walsh, P. J. Highly Enantioselective Catalytic Phenylation of Ketones with a Constrained Geometry Titanium Catalyst. \textit{Org. Lett.} \textbf{5}, 3641-3644 (2003).

5) Waltz, K. M., Gavenonis, J. & Walsh, P. J. A Simple, Reliable, Catalytic Asymmetric Allylation of Ketones. \textit{Angew. Chem., Int. Ed.} \textbf{41}, 3697-3699 (2002).

6) Watson, C. G. & Aggarwal, V. K. Asymmetric Synthesis of 1-Heteroaryl-1-arylalkyl Tertiary Alcohols and 1-Pyridyl-1-arylethenes by Lithiation–Borylation Methodology. \textit{Org. Lett.} \textbf{15}, 1346-1349 (2013).

7) Cozzi, P. G. Enantioselective Alkynylation of Ketones Catalyzed by Zn(Salen) Complexes. \textit{Angew. Chem., Int. Ed.} \textbf{42}, 2895-2898 (2003).

8) Zhou, Y., Wang, R., Xu, Z., Yan, W., Liu, L., Kang, Y. & Han, Z. Highly Enantioselective Phenylacctetylene Additions to Ketones Catalyzed by (S)-BINOL–Ti Complex. \textit{Org. Lett.} \textbf{6}, 4147-4149 (2004).
Preparation of S-1a – S-1d.

(S)-2-(Naphthalen-2-yl)butan-2-ol ((S)-S-1a). This procedure was adapted from that reported in the literature.7a In an oven-dried, 100-mL, round-bottomed flask was placed L1 (33 mg, 0.060 mmol, 0.010 equiv) and Et2Zn (0.73 mL, 7.2 mmol, 1.2 equiv). Ti(O-iPr)4 (2.1 mL, 7.2 mmol, 1.2 equiv) was added. The resulting greenish solution was stirred at room temperature for 5 min. 2-Acetonaphthalone (1.02 g, 6.00 mmol, 1.00 equiv) was added into the flask in one portion. The mixture was stirred at room temperature for 17 h. The resulting brown sticky oil was diluted with EtOAc (50 mL) and quenched with HCl (1 N). The product was extracted from the aqueous layer with EtOAc (25 mL x 2). The combined organic layers were washed with sat. NaCl, dried (MgSO4), filtered, and concentrated. The residue was purified via silica gel chromatography (5–10% Et2O/hexanes) to give (S)-S-1a (470 mg, 39%) as a colorless oil. The enantiomeric excess was determined to be 97% by chiral HPLC analysis (CHIRLPAK IB, 1.0 mL/min, 3.0% i-PrOH/hexanes, λ=254 nm); tR(major) = 10.269 min, tR(minor) = 11.370 min. Based on the optical rotation, [α]D24 = −9.5° (c 1.0, MeOH) (Literature data: [α]D24 = +16.3° (c 1.0, MeOH) for R configuration), 7b the absolute configuration of S-1a was assigned as S. The spectral data of this compound matched that reported in the literature.7

(S)-2-(6-Methoxynaphthalen-2-yl)butan-2-ol ((S)-S-1b). Prepared via the procedure described above for preparation of (S)-S-1a as a colorless oil (32%). The enantiomeric excess was determined to be 92% by chiral HPLC analysis (CHIRLPAK IC, 1.0 mL/min, 3.0% i-PrOH/hexanes, λ=254 nm); tR(major) = 21.219 min, tR(minor) = 16.516 min. [α]D24 = +5.1° (c 3.02, CHCl3); 1H NMR (600 MHz, CDCl3) δ 7.83 (d, J = 1.9 Hz, 1H), 7.73 (dd, J = 12.2, 8.7 Hz, 2H), 7.50 (dd, J = 8.6, 1.9 Hz, 1H), 7.16 – 7.11 (m, 2H), 3.92 (s, 3H), 1.99 – 1.85 (m, 2H), 1.79 (d, J = 3.6 Hz, 1H), 1.63 (s, 3H), 0.82 (td, J = 7.4, 1.0 Hz, 3H); 13C NMR (151 MHz, CDCl3) δ 157.7, 143.0, 133.4, 129.7, 128.8, 124.4, 123.3, 118.9, 105.7, 75.2, 55.5, 36.7, 29.9, 8.5; FTIR (NaCl/thin film) 3447 (br s), 3059, 2969, 2935, 1634, 4606, 1504, 1485, 1462, 1388, 1265, 1199, 1033, 852, 810 cm−1; HRMS (CI+) [M]+H calculated for C15H19O2: 231.1385, found: 231.1400.
**((S)-2-(Naphthalen-1-yl)butan-2-ol ((S)-S-1c)**. Prepared via the procedure described above for preparation of **((S)-S-1a** as a colorless oil (9%). The enantiomeric excess was determined as 90% by chiral HPLC analysis (CHIRLPAK IB, 0.7 mL/min, 2.0% i-PrOH/hexanes, λ=254 nm); t_R(major) = 15.085 min, t_R(minor) = 17.287 min. [α]_D^{24} = +33.7° (c 1.91, CHCl3): ¹H NMR (600 MHz, CDCl₃) δ 8.79 – 8.75 (m, 1H), 7.87 (dd, J = 7.8, 1.9 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.58 (dd, J = 7.3, 1.3 Hz, 1H), 7.48 (pd, J = 6.8, 1.6 Hz, 2H), 7.42 (t, J = 7.7 Hz, 1H), 2.30 – 2.17 (m, 2H), 2.02 (s, 1H), 1.82 (s, 3H), 0.83 (t, J = 7.5 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 142.4, 135.0, 131.1, 129.3, 128.6, 127.1, 125.3, 125.2, 124.9, 124.0, 76.9, 35.4, 29.5, 9.0; FTIR (NaCl/thin film) 3420 (brs), 3048, 2971, 2936, 2877, 1653, 1508, 1456, 1374, 1117, 804, 777 cm⁻¹; HRMS (EI+ ) [M]+H calculated for C₁₄H₁₆O: 200.1201, found: 200.1205.

**((S)-2-(2-Methylquinolin-6-yl)butan-2-ol ((S)-S-1d)**. Prepared via the procedure described above for preparation of **((S)-S-1a** as a pale yellow solid (mp 86–89°, 41%). The enantiomeric excess was determined as 99% by chiral HPLC analysis (CHIRLPAK IC, 1 mL/min, 8.0% i-PrOH/hexanes, λ=230 nm); t_R(major) = 23.228 min, t_R(minor) = 19.313 min. [α]_D^{24} = +33° (c 1.03, CHCl3): ¹H NMR (600 MHz, CDCl₃) δ 8.04 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 2.1 Hz, 1H), 7.71 (dd, J = 8.9, 2.1 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 2.74 (s, 3H), 1.93 (ddt, J = 27.2, 14.1, 7.1 Hz, 2H), 1.64 (s, 3H), 0.81 (t, J = 7.5 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 158.9, 147.0, 145.1, 136.5, 128.6, 127.4, 126.2, 123.1, 122.3, 75.1, 36.7, 30.0, 25.5, 8.4; FTIR (NaCl/thin film) 3355 (brs), 3048, 2971, 2936, 2877, 1653, 1508, 1456, 1374, 1117, 804, 837, 755 cm⁻¹; HRMS (Cl+) [M]+H calculated for C₁₄H₁₈NO: 216.1388, found: 216.1398.

A crystal suitable for X-ray diffraction analysis was obtained via diffusion of hexanes into a solution of **S-1d** in EtOAc at –18 °C. The crystal structure demonstrates that the absolute configuration is S (Figure S3).

**Figure S3.** Molecular diagram of **(S)-S-1d** with ellipsoids at 50% probability, all non-oxygen bound H-atoms omitted for clarity. (CCDC 1424634)
Preparation of S-1e.

\[(\text{S})-6-((\text{tert-Butyldimethylsilyl})\text{oxy})-2-(\text{4-nitrophenyl})\text{hexan-2-ol (}\text{S}-\text{S-1e})\]. Prepared via the procedure described above for preparation of \((\text{S})-\text{S-1a}\), except that bis(4-((\text{tert-butyldimethylsilyl})\text{oxy})butyl)zinc was used instead of Et_2Zn, as a colorless oil (30%). The enantiomeric excess was determined to be 99% by chiral HPLC analysis (CHIRLPAK IA, 0.6 mL/min, 3.0% \text{i-PrOH/hexanes}, \(\lambda=254\) nm); \(t_R(\text{major}) = 14.468\) min, \(t_R(\text{minor}) = 13.695\) min. \([\alpha]_D^{24} = +10.2^\circ (c 2.63, \text{CHCl}_3)\): \(^1\)H NMR (600 MHz, CDCl_3) \(\delta 7.93 – 7.89\) (m, 1H), 7.86 – 7.79 (m, 3H), 7.52 (dd, \(J = 8.6, 1.9\) Hz, 1H), 7.50 – 7.42 (m, 2H), 3.54 (t, \(J = 6.5\) Hz, 2H), 2.01 – 1.84 (m, 3H), 1.65 – 1.45 (m, 2H), 1.40 – 1.28 (m, 1H), 1.27 – 1.17 (m, 1H), 0.83 (s, 9H), –0.01 (d, \(J = 2.3\) Hz, 6H); \(^{13}\)C NMR (151 MHz, CDCl_3) \(\delta 145.5, 133.3, 132.4, 128.3, 128.0, 127.6, 126.1, 125.8, 123.8, 123.3, 75.1, 63.1, 43.8, 33.1, 30.4, 26.1, 20.6, 18.4, –5.16, –5.17; FTIR (NaCl/thin film) 3432 (brs), 3056, 2952, 2929, 2857, 1471, 1254, 1101, 836, 775, 476 cm\(^{-1}\); HRMS (LIFDI) \([\text{M}]^+\) calculated for \text{C}_{24}\text{H}_{26}\text{O}_3: 358.2328, found: 358.2343.

Preparation of S-1f and S-1h.

\((\text{S})-2-(\text{naphthalen-2-yl})-4-\text{phenylbutan-2-ol (}\text{S}-\text{S-1f})\). The procedure for formation of the allylic alcohol was adapted from a reported procedure.\(^3\) For preparation the vinylzinc reagent, in an oven-dried, round-bottomed flask was placed \text{Cp}_2\text{ZrHCl} (346 mg, 1.20 mmol, 1.20 equiv) and CH\(_2\)Cl\(_2\) (4.0 mL). At room temperature, phenylacetylene (0.13 mL, 1.2 mmol, 1.2 equiv) was added into the flask and stirred for 10 min. The solvent was removed, and the orange solid was dissolved in PhMe (4.0 mL). The solution was cooled to –78 °C, before Me\(_2\)Zn (1.0 mL, 1.2 mmol, 1.2 equiv, 1.2 M in PhMe) was added. The mixture was stirred at –78 °C for 10 min. The resulting solution was assumed to be the vinylzinc in PhMe solution. In a separate flask was placed \text{L1} (54.5 mg, 0.100 mmol, 0.100 equiv), Me\(_2\)Zn (0.33 mL, 0.40 mmol, 0.40 equiv, 1.2 M in PhMe), and PhMe (2.0 mL). To this mixture was added Ti(O-iPr)\(_4\) (0.36 mL, 1.2 mmol, 1.2
equiv) at room temperature. The mixture was stirred at room temperature for 15 min, then the solution was added into the pre-formed vinylzinc solution at –78 °C via cannula. The combined solution was warmed to 0 °C, and treated with a solution of 2-acetylnaphthalone (170 mg, 1.0 mmol, 1.0 equiv) and PhMe (1.0 mL). The resulting reddish solution was stirred at room temperature for 16 h and then quenched with sat. NaHCO₃ aq. (20 mL). The solid was removed via filtration through a pad of Celite®. The product was extracted with EtOAc. The combined organic layers were washed with sat. NaCl, dried (Na₂SO₄), filtered, and concentrated. The residue was purified via silica gel chromatography (0–10% EtOAc/hexanes) to give (E)-2-(naphthalen-2-yl)-4-phenylbut-3-en-2-ol as a colorless oil (202 mg, 77%), which was used directly in next step.

Please note: We assume the same absolute configuration using these homemade vinylzinc reagents as when Et₂Zn is used. However, the absolute configuration obtained for this procedure has not been reported in the literature.8

(E)-2-(Naphthalen-2-yl)-4-phenylbut-3-en-2-ol (202 mg, 0.736 mmol) was dissolved in THF (7 mL) at room temperature. Pd/C (39 mg, 0.037 mmol, 10% w) was added. The headspace of the flask was evacuated and refilled with H₂ three times. The mixture was then stirred at room temperature for 12 h under H₂ (1 atm). The solid was removed via filtration through a tight-packed pad of Celite®. The filtrate was concentrated and purified via silica gel chromatography (0–10% EtOAc/hexanes) to give (S)-1f (189 mg, 93%) as a white solid (mp 76–79°). [α]D²⁴ = +43.6° (c 2.2, CHCl₃): 1H NMR (600 MHz, CDCl₃) δ 8.02 – 7.98 (m, 1H), 7.92 – 7.86 (m, 3H), 7.60 (dd, J = 8.6, 1.9 Hz, 1H), 7.52 (pd, J = 6.8, 1.5 Hz, 2H), 7.29 – 7.21 (m, 2H), 7.21 – 7.16 (m, 1H), 7.16 – 7.13 (m, 2H), 2.69 (ddd, J = 13.7, 11.8, 5.6 Hz, 1H), 2.48 (ddd, J = 13.6, 11.8, 4.9 Hz, 1H), 2.33 – 2.20 (m, 2H), 1.93 (s, 1H), 1.73 (s, 3H); 13C NMR (151 MHz, CDCl₃) δ 145.0, 142.3, 133.4, 132.4, 128.51, 128.46, 128.3, 128.2, 127.6, 126.3, 125.90, 125.89, 123.7, 123.4, 75.1, 45.9, 30.8, 30.7; FTIR (NaCl/thin film) 3446 (brs), 3057, 3024, 2972, 2932, 1601, 1496, 1469, 1455, 819, 747, 700, 487 cm⁻¹; HRMS (EI+) [M]+ calculated for C₂₀H₂₀O: 276.1514, found: 276.1514.

(S)-1-(3-methoxyphenyl)-3-(naphthalen-2-yl)pentan-3-ol ((S)-S-1h). Following a similar procedure as for the preparation of (S)-S-1f above, (S)-S-1h was prepared as a colorless oil (40% overall yield from 1-(naphthalene-2-yl)propan-1-one). The enantiomeric excess was determined to be 89% ee by chiral HPLC analysis (CHIRLPAK IC, 1.0 mL/min, 5.0% i-PrOH/hexanes, λ=254 nm); tₘ(major) = 9.989 min, tₘ(minor) = 10.700 min. [α]D²⁴ = +41.3° (c 0.92, CHCl₃): 1H NMR (600 MHz, CDCl₃) δ 7.98 – 7.93 (m, 1H), 6.71 (dd, J = 8.0, 2.1 Hz, 2H), 6.66 (t, J = 2.0 Hz, 1H), 3.76 (s, 3H), 2.66 (ddd, J = 13.6, 11.7, 5.5 Hz, 1H), 2.35 (ddd, J = 13.6, 11.8, 4.7 Hz, 1H), 2.32 – 2.17 (m, 2H), 2.03 (dq, J = 14.9, 7.4 Hz, 1H), 1.95 (dq, J = 14.5, 7.4 Hz, 1H), 1.88 (s, 1H), 0.81 (t, J = 7.4 Hz, 3H); 13C NMR (151 MHz, CDCl₃) δ 159.8, 144.2, 143.0, 133.3, 132.3, 129.5, 128.3, 128.1, 127.6, 126.2, 125.8, 124.4, 123.9, 120.8, 114.2, 111.2, 77.6, 55.2, 44.5, 35.9, 30.3, 7.9; FTIR (NaCl/thin film) 3486 (brs), 3054, 2964, 2936, 1680, 1489, 1455, 1258, 1152, 1048, 819, 748, 698, 477 cm⁻¹; HRMS (EI+) [M]+ calculated for C₂₂H₂₄O₂: 320.1776, found: 320.1753.

Please note: We assume the same absolute configuration using these homemade vinylzinc reagents as when Et₂Zn is used. However, the absolute configuration obtained for this procedure has not been reported in the literature.8
Preparation of S-1i, S-1j.

\[
\begin{align*}
\text{Ar} & \quad \text{Me} \\
\text{Ti(O-i-Pr)}_4 & \quad \text{L1} \\
\text{Ph}_2\text{Zn} & \quad \text{PhMe, rt} \\
\text{S-1i, S-1j} & \quad \text{HO} \quad \text{Me} \\
\end{align*}
\]

\((R)-1-(\text{naphthalen}-2-\text{yl})-1-\text{phenylethan}-1-\text{ol} ((R)-S-1i)\). The procedure was adapted from that reported in the literature. In an oven-dried, 50-mL, round-bottomed flask was placed L1 (54.5 mg, 0.100 mmol, 0.100 equiv), Ph2Zn (351 mL, 1.60 mmol, 1.60 equiv), and PhMe (10 mL) at room temperature. Ti(O-i-Pr)4 (0.18 mL, 0.60 mmol, 0.60 equiv) was added. The mixture was stirred at room temperature for 15 min. A solution of 2-acetonaphthalone (170 mg, 1.0 mmol, 1.0 equiv) and PhMe (5 mL) was added into the flask. The mixture was stirred at room temperature for 17 h. The reaction was then quenched with sat. NH4Cl aq. (20 mL). The solids were removed via filtration through a pad of Celite®. The mixture was extracted with EtOAc (25 mL x 2). The combined organic layers were washed with sat. NaCl, dried (Na2SO4), filtered, and concentrated. The residue was purified via silica gel chromatography (5–15% Et2O/hexanes) to give \((R)-S-1i\) (203.7 mg, 82%) as a colorless oil. The enantiomeric excess was determined to be 95% by chiral HPLC analysis (CHIRLPAK IB, 1.0 mL/min, 4.0% i-PrOH/hexanes, \(\lambda=254\) nm); \(t_R\)(major) = 13.183 min, \(t_R\)(minor) = 14.119 min. [\(\alpha\]D\)\(24 = +10.7^\circ\) (c 0.82, CHCl3): \(^1H\) NMR (600 MHz, CDCl3) \(\delta 8.00 – 7.95 (m, 1H), 7.87 – 7.83 (m, 1H), 7.81 (dd, \(J = 7.5, 1.8 \text{ Hz, 1H}), 7.77 (d, J = 8.6 \text{ Hz, 1H}), 7.52 – 7.44 (m, 4H), 7.42 (dd, J = 8.6, 1.9 Hz, 1H), 7.33 (dd, J = 8.5, 7.0 Hz, 2H), 7.27 (d, J = 6.6 Hz, 1H), 2.22 (s, 1H), 2.06 (s, 3H); \(^13C\) NMR (151 MHz, CDCl3) \(\delta 147.9, 145.4, 133.1, 132.5, 128.40, 128.38, 128.1, 127.6, 127.2, 126.3, 126.10, 126.09, 125.1, 123.9, 76.5, 30.9\); FTIR (NaCl/thin film) 3560 (brs), 3056, 2978, 2931, 1599, 1505, 1493, 14461, 1372, 1126, 1065, 909, 858 cm\(^{-1}\); HRMS (EI+) [M]+ calculated for C\(_{18}\)H\(_{16}\)BO: 248.1201, found: 248.1193.

\((R)-1-(\text{[1,1'-biphenyl]-4-yl})-1-\text{phenylethan}-1-\text{ol} ((R)-S-1j)\). Following a similar procedure as described for \((R)-S-1i\) above, compound \((R)-S-1j\) was prepared as a white solid (mp 108–111 °C, 72%). The enantiomeric excess was determined to be 91% by chiral HPLC analysis (CHIRLPAK IB, 1.0 mL/min, 2.0% i-PrOH/hexanes, \(\lambda=254\) nm); \(t_R\)(major) = 34.792 min, \(t_R\)(minor) = 18.929 min. [\(\alpha\]D\)\(24 = +9.0^\circ\) (c 1.0, CHCl3): \(^1H\) NMR (600 MHz, CDCl3) \(\delta 7.61 – 7.57 (m, 2H), 7.57 – 7.54 (m, 2H), 7.51 – 7.46 (m, 4H), 7.43 (dd, J = 8.4, 7.0 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.29 – 7.26 (m, 1H), 2.22 (s, 1H), 2.00 (s, 3H); \(^13C\) NMR (151 MHz, CDCl3) \(\delta 148.0, 147.2, 140.9, 140.0, 128.9, 128.4, 127.4, 127.21, 127.17, 127.1, 126.4, 126.0, 76.3, 31.0\); FTIR (NaCl/thin film) 3458 (brs), 3056, 2978, 2931, 1599, 1505, 1493, 14461, 1372, 1126, 1065, 909, 858 cm\(^{-1}\); HRMS (CI+) [M]+H calculated for C\(_{20}\)H\(_{19}\)O: 275.1436, found: 275.1444.
Evidence for Stereoretention

As discussed above, the absolute configurations of S-1d, (S)-1a, and (R)-10 were determined by X-ray crystallography. The arylation of (S)-1a produced (R)-10, demonstrating that this arylation proceeds with overall retention of absolute stereochemistry.

Crystal Structure Data for (R)-10

Table S1. Sample and crystal data for (R)-10.

| Identification code | mary029 |
|---------------------|---------|
| Chemical formula    | C_{25}H_{29}NO |
| Formula weight      | 359.49 |
| Temperature         | 200(2) K |
| Wavelength          | 1.54178 Å |
| Crystal size        | 0.248 x 0.378 x 0.487 mm |
| Crystal system      | orthorhombic |
| Space group         | P 21 21 21 |
Unit cell dimensions

\[ a = 8.1727(3) \, \text{Å} \quad \alpha = 90^\circ \]
\[ b = 12.9877(5) \, \text{Å} \quad \beta = 90^\circ \]
\[ c = 19.1341(7) \, \text{Å} \quad \gamma = 90^\circ \]

Volume

\[ 2030.98(13) \, \text{Å}^3 \]

\[ Z \]
4

Density (calculated)

1.176 g/cm³

Absorption coefficient

0.540 mm⁻¹

\[ F(000) \]
776

Table S2. Data collection and structure refinement for (R)-10.

| Description | Value |
|-------------|-------|
| Theta range for data collection | 4.11 to 59.90° |
| Index ranges | -8<=h<=9, -14<=k<=13, -21<=l<=19 |
| Reflections collected | 6276 |
| Independent reflections | 2630 [R(int) = 0.0365] |
| Coverage of independent reflections | 95.1% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.8780 and 0.7080 |
| Refinement method | Full-matrix least-squares on F² |
| Refinement program | SHELXL-2014/7 (Sheldrick, 2014) |
| Function minimized | \( \sum w(F_o^2 - F_c^2)^2 \) |
| Data / restraints / parameters | 2630 / 0 / 249 |
| Goodness-of-fit on F² | 0.860 |
| Final R indices | 2423 data; I>2σ(I) R1 = 0.0373, wR2 = 0.1046 all data R1 = 0.0407, wR2 = 0.1084 |
| Weighting scheme | \( w=1/\left[\sigma^2(F_o^2)+(0.1000P)^2\right] \) where \( P=(F_o^2+2F_c^2)/3 \) |
| Absolute structure parameter | 0.0(3) |
| Extinction coefficient | 0.0058(9) |
| Largest diff. peak and hole | 0.135 and -0.151 eÅ⁻³ |
| R.M.S. deviation from mean | 0.037 eÅ⁻³ |

Table S3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for (R)-10.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

|   | x/a     | y/b         | z/c         | U(eq)   |
|---|---------|-------------|-------------|---------|
| O1| 0.4981(3) | 0.50887(17) | 0.01225(10) | 0.0528(6) |
| N1| 0.5202(3) | 0.39117(18) | 0.09868(13) | 0.0412(6) |
| C1| 0.6431(3) | 0.61242(19) | 0.24991(13) | 0.0288(6) |
| C2| 0.5755(3) | 0.5641(2)   | 0.30982(14) | 0.0311(7) |
|   |   |   |   |   |
|---|---|---|---|---|
| C3 | 0.4047(4) | 0.5453(2) | 0.31633(15) | 0.0364(7) |
| C4 | 0.3434(4) | 0.4997(2) | 0.37492(16) | 0.0445(8) |
| C5 | 0.4486(4) | 0.4689(2) | 0.42913(16) | 0.0455(8) |
| C6 | 0.6129(4) | 0.4850(2) | 0.42429(15) | 0.0403(7) |
| C7 | 0.6800(3) | 0.5343(2) | 0.36502(14) | 0.0334(7) |
| C8 | 0.8496(3) | 0.5562(2) | 0.35893(14) | 0.0305(6) |
| C9 | 0.9094(3) | 0.6044(2) | 0.30127(14) | 0.0306(7) |
| C10 | 0.8070(3) | 0.6340(2) | 0.24435(13) | 0.0377(7) |
| C11 | 0.8828(3) | 0.6988(2) | 0.20884(16) | 0.0396(7) |
| C12 | 0.9236(4) | 0.7444(2) | 0.14805(14) | 0.0343(8) |
| C13 | 0.7628(3) | 0.6988(2) | 0.12206(14) | 0.0355(7) |
| C14 | 0.8307(4) | 0.7444(2) | 0.10319(12) | 0.0295(6) |
| C15 | 0.3068(3) | 0.5282(2) | 0.11035(13) | 0.0305(6) |
| C16 | 0.3106(3) | 0.6850(2) | 0.13789(13) | 0.0303(6) |
| C17 | 0.3068(3) | 0.6345(2) | 0.15721(13) | 0.0290(6) |
| C18 | 0.4492(4) | 0.4735(2) | 0.06861(14) | 0.0354(7) |
| C19 | 0.6428(4) | 0.3346(3) | 0.05765(18) | 0.0536(9) |
| C20 | 0.5677(6) | 0.2525(3) | 0.1140(3) | 0.0894(15) |
| C21 | 0.2106(4) | 0.3501(2) | 0.16769(16) | 0.0459(8) |
| C22 | 0.6199(4) | 0.3331(3) | 0.21548(18) | 0.0530(9) |

**Table S4.** Bond lengths (Å) for (R)-10.
Table S5. Bond angles (°) for (R)-10.

C21-N1-C24 124.5(2) C21-N1-C22 117.6(2)
C24-N1-C22 117.8(2) C10-C1-C2 122.2(2)
C10-C1-H1 118.9 C2-C1-H1 118.9
C7-C2-C1 119.3(2) C7-C2-C3 118.8(3)
C1-C2-C3 121.9(3) C4-C3-C2 120.5(3)
C4-C3-H3 119.8 C2-C3-H3 119.8
C3-C4-C5 120.4(3) C3-C4-H4 119.8
C5-C4-H4 119.8 C6-C5-C4 120.6(3)
C6-C5-H5 119.7 C4-C5-H5 119.7
C5-C6-C7 120.5(3) C5-C6-H6 119.8
C7-C6-H6 119.8 C2-C7-C6 119.3(3)
C2-C7-C8 118.3(2) C6-C7-C8 122.4(3)
C9-C8-C7 120.7(3) C9-C8-H8 119.7
C7-C8-H8 119.7 C8-C9-C10 122.2(3)
C8-C9-H9 118.9 C10-C9-H9 118.9
C1-C10-C9 117.3(2) C1-C10-C11 123.7(2)
C9-C10-C11 118.9(2) C10-C11-C20 109.7(2)
C10-C11-C12 106.9(2) C20-C11-C12 111.8(2)
C10-C11-C13 111.5(2) C20-C11-C13 107.5(2)
C12-C11-C13 109.4(2) C11-C12-H12A 109.5
C11-C12-H12B 109.5 H12A-C12-H12B 109.5
C11-C12-H12C 109.5 H12A-C12-H12C 109.5
H12B-C12-H12C 109.5 C14-C13-C11 116.3(2)
C14-C13-H13A 108.2 C11-C13-H13A 108.2
C14-C13-H13B 108.2 C11-C13-H13B 108.2
H13A-C13-H13B 107.4 C13-C14-H14A 109.5
C13-C14-H14B 109.5 H14A-C14-H14B 109.5
C13-C14-H14C 109.5 H14A-C14-H14C 109.5
H14B-C14-H14C 109.5 C16-C15-C20 121.8(3)
C16-C15-H15 119.1 C20-C15-H15 119.1
C15-C16-C17 120.4(3) C15-C16-H16 119.8
C17-C16-H16 119.8 C18-C17-C16 118.1(2)
C18-C17-C21 118.4(2) C16-C17-C21 123.2(2)
C17-C18-C19 121.4(3) C17-C18-H18 119.3
### Table S6. Torsion angles (°) for (R)-10.

| Bond/Geometric Angle | Value (°) | Bond/Geometric Angle | Value (°) |
|----------------------|-----------|----------------------|-----------|
| C19-C18-H18          | 119.3     | C18-C19-C20          | 121.1(2)  |
| C18-C19-H19          | 119.5     | C20-C19-C11          | 122.8(2)  |
| C19-C20-C15          | 117.3(2)  | C19-C20-C11          | 122.8(2)  |
| C15-C20-C11          | 119.8(2)  | O1-C21-N1            | 121.9(3)  |
| O1-C21-C17           | 117.8(3)  | N1-C21-C17           | 120.4(2)  |
| N1-C22-C23           | 112.1(3)  | N1-C22-H22A          | 109.2     |
| C23-C22-H22A         | 109.2     | N1-C22-H22B          | 109.2     |
| C23-C22-H22B         | 109.2     | H22A-C22-H22B        | 107.9     |
| C22-C23-H23A         | 109.5     | C22-C23-H23B         | 109.5     |
| H23A-C23-H23B        | 109.5     | C23-C23-H23C         | 109.5     |
| H23A-C23-H23C        | 109.5     | H23B-C23-H23C        | 109.5     |
| N1-C24-C25           | 114.1(3)  | N1-C24-H24A          | 108.7     |
| C25-C24-H24A         | 108.7     | N1-C24-H24B          | 108.7     |
| C25-C24-H24B         | 108.7     | H24A-C24-H24B        | 107.6     |
| C24-C25-H25A         | 109.5     | C24-C25-H25B         | 109.5     |
| H25A-C25-H25B        | 109.5     | C24-C25-H25C         | 109.5     |
| H25A-C25-H25C        | 109.5     | H25B-C25-H25C        | 109.5     |

Table continued...
Table S7. Anisotropic atomic displacement parameters (Å²) for (R)-10.
The anisotropic atomic displacement factor exponent takes the form: -2π² [ h² a² U₁₁ + ... + 2 h k a^ b^ b' U₁₂ ]

|   | U₁₁     | U₂₂     | U₃₃     | U₂₃     | U₁₃     | U₁₂     |
|---|---------|---------|---------|---------|---------|---------|
| O1| 0.0573(14) | 0.0621(14) | 0.0391(12) | 0.0079(11) | 0.0201(12) | 0.0140(12) |
| N1| 0.0358(14) | 0.0424(14) | 0.0453(14) | 0.0030(12) | 0.0100(12) | 0.0097(12) |
| C1| 0.0289(14) | 0.0312(14) | 0.0262(14) | 0.0003(12) | -0.0029(12) | 0.0033(11) |
| C2| 0.0331(15) | 0.0278(15) | 0.0323(16) | -0.0029(12) | 0.0014(13) | -0.0010(12) |
| C3| 0.0313(15) | 0.0395(17) | 0.0384(17) | 0.0019(14) | 0.0009(14) | -0.0025(13) |
| C4| 0.0386(17) | 0.0449(18) | 0.0499(19) | 0.0010(16) | 0.0045(15) | -0.0121(14) |
| C5| 0.0537(19) | 0.0443(18) | 0.0385(18) | 0.0054(14) | 0.0095(15) | -0.0116(15) |
| C6| 0.0464(14) | 0.0413(17) | 0.0332(16) | 0.0040(13) | 0.0004(15) | -0.0025(14) |
| C7| 0.0356(15) | 0.0325(15) | 0.0319(15) | -0.0034(13) | -0.0005(13) | 0.0001(12) |
| C8| 0.0315(15) | 0.0515(18) | 0.0301(15) | 0.0065(14) | -0.0023(14) | 0.0056(13) |
| C9| 0.0252(15) | 0.0516(19) | 0.0360(17) | 0.0004(14) | -0.0015(13) | 0.0014(13) |
| C10| 0.0276(13) | 0.0337(15) | 0.0302(14) | 0.0024(12) | 0.0000(13) | 0.0047(12) |
| C11| 0.0230(13) | 0.0367(15) | 0.0295(14) | 0.0017(12) | 0.0004(12) | 0.0030(11) |
| C12| 0.0370(16) | 0.0366(16) | 0.0453(17) | -0.0011(14) | 0.0076(14) | 0.0029(13) |
| C13| 0.0297(15) | 0.0412(16) | 0.0353(16) | 0.0038(13) | 0.0005(12) | 0.0052(13) |
| C14| 0.0436(19) | 0.0510(17) | 0.0359(15) | 0.0077(15) | 0.0006(15) | 0.0077(15) |
| C15| 0.0274(14) | 0.0372(17) | 0.0379(15) | 0.0044(13) | 0.0035(13) | -0.0020(12) |
| C16| 0.0367(16) | 0.0305(15) | 0.0392(16) | -0.0013(13) | 0.0041(13) | 0.0014(13) |
| C17| 0.0300(14) | 0.0378(16) | 0.0207(13) | 0.0026(12) | 0.0005(12) | 0.0046(13) |
| C18| 0.0255(13) | 0.0392(16) | 0.0269(13) | 0.0054(12) | -0.0017(12) | -0.0016(12) |
| C19| 0.0290(15) | 0.0312(14) | 0.0309(14) | 0.0011(12) | 0.0013(13) | 0.0009(12) |
| C20| 0.0278(14) | 0.0329(16) | 0.0262(14) | 0.0039(12) | -0.0015(12) | 0.0009(11) |
| C21| 0.0330(15) | 0.0413(17) | 0.0319(16) | -0.0020(13) | 0.0045(13) | 0.0039(13) |
| C22| 0.0482(19) | 0.0486(19) | 0.064(2) | -0.0055(18) | 0.0122(18) | 0.0142(16) |
| C23| 0.092(3) | 0.063(2) | 0.113(4) | -0.035(3) | 0.027(3) | -0.003(2) |
| C24| 0.0411(17) | 0.0452(18) | 0.0513(18) | 0.0145(15) | 0.0062(16) | 0.0087(14) |
| C25| 0.051(2) | 0.0470(19) | 0.061(2) | 0.0045(16) | -0.0059(18) | 0.0073(16) |

Table S8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for (R)-10.

|   | x/a   | y/b   | z/c   | U(eq) |
|---|-------|-------|-------|-------|
| H1| -0.4274 | 0.6304 | 0.2124 | 0.035  |
| H3| -0.6672 | 0.5646 | 0.2796 | 0.044  |
|   |   |   |
|---|---|---|
| H4 | -0.7711 | 0.4887 |
| H5 | -0.5952 | 0.4366 |
| H6 | -0.3172 | 0.4629 |
| H8 | -0.0780 | 0.5370 |
| H9 | 0.0232  | 0.6188 |
| H12A| -0.1767 | 0.8350 |
| H12B| -0.0286 | 0.8413 |
| H12C| 0.0021  | 0.7970 |
| H13A| -0.2777 | 0.6285 |
| H13B| -0.3326 | 0.7405 |
| H14A| -0.1280 | 0.8139 |
| H14B| -0.2562 | 0.7477 |
| H14C| -0.0799 | 0.7010 |
| H15 | -0.0653 | 0.4918 |
| H16 | 0.1570  | 0.4016 |
| H18 | 0.4054  | 0.6682 |
| H19 | 0.1871  | 0.7575 |
| H22A| 0.7236  | 0.3032 |
| H22B| 0.7019  | 0.3834 |
| H23A| 0.5062  | 0.2051 |
| H23B| 0.6538  | 0.2145 |
| H23C| 0.4934  | 0.2837 |
| H24A| 0.4182  | 0.2838 |
| H24B| 0.3992  | 0.3985 |
| H25A| 0.6849  | 0.2750 |
| H25B| 0.5805  | 0.3181 |
| H25C| 0.6879  | 0.3953 |

Note: The table entries represent values with varying decimal places.
Crystal Structure Data for 1a

Table S9. Sample and crystal data for (S)-1a.

| Identification code       | mary035         |
|--------------------------|-----------------|
| Chemical formula         | C_{16}H_{18}O_{2} |
| Formula weight           | 242.30 g/mol    |
| Temperature              | 200(2) K        |
| Wavelength               | 1.54178 Å       |
| Crystal size             | 0.144 x 0.196 x 0.269 mm |
| Crystal system           | monoclinic      |
| Space group              | C 1 2 1         |
| Unit cell dimensions     | a = 21.7695(7) Å, α = 90° |
|                         | b = 5.8807(2) Å, β = 97.282(2)° |
|                         | c = 10.4637(3) Å, γ = 90° |
| Volume                   | 1328.76(7) Å³   |
| Z                        | 4               |
| Density (calculated)     | 1.211 g/cm³     |
| Absorption coefficient   | 0.620 mm⁻¹      |
| F(000)                   | 520             |

Table S10. Data collection and structure refinement for (S)-1a.

| Theta range for data collection | 4.09 to 75.07° |
| Index ranges                   | -27<=h<=26, -7<=k<=7, -13<=l<=12 |
| Reflections collected          | 13728           |
| Independent reflections        | 2708 [R(int) = 0.0319] |
| Coverage of independent reflections | 99.4%          |
| Absorption correction          | multi-scan      |
| Max. and min. transmission     | 0.7539 and 0.6441 |
| Structure solution technique   | direct methods  |
| Structure solution program     | SHELXS-97 (Sheldrick 2008) |
Refinement method: Full-matrix least-squares on $F^2$
Refinement program: SHELXL-2014/7 (Sheldrick, 2014)
Function minimized: $\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters: 2708 / 1 / 166
Goodness-of-fit on $F^2$: 1.035
Final R indices:
- I>2$\sigma$(I): R1 = 0.0349, wR2 = 0.0937
- All data: R1 = 0.0359, wR2 = 0.0948
Weighting scheme:
$$w = \frac{1}{[\sigma^2(F_o^2) + (0.0638P)^2 + 0.1971P]}$$
where P = (F_o^2 + 2F_c^2)/3
Absolute structure parameter: -0.1(1)
Largest diff. peak and hole: 0.193 and -0.164 eÅ$^{-3}$
R.M.S. deviation from mean: 0.034 eÅ$^{-3}$

Table S11. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for (S)-1a.

|       | x/a        | y/b        | z/c        | U(eq)   |
|-------|------------|------------|------------|---------|
| O1    | 0.40605(5) | 0.6779(2)  | 0.16441(11)| 0.0352(3)|
| O2    | 0.32500(7) | 0.4448(3)  | 0.10507(15)| 0.0560(4)|
| C1    | 0.44069(7) | 0.5057(3)  | 0.24545(16)| 0.0324(4)|
| C2    | 0.45441(10)| 0.3005(3)  | 0.1639(2)  | 0.0452(4)|
| C3    | 0.50055(7) | 0.6315(3)  | 0.29722(16)| 0.0353(4)|
| C4    | 0.54151(8) | 0.6990(4)  | 0.19539(19)| 0.0444(4)|
| C5    | 0.35048(8) | 0.6252(4)  | 0.09814(17)| 0.0407(4)|
| C6    | 0.32655(9) | 0.8226(5)  | 0.0164(2)  | 0.0528(5)|
| C7    | 0.40667(7) | 0.4437(3)  | 0.35920(16)| 0.0324(4)|
| C8    | 0.42021(8) | 0.2325(3)  | 0.42318(19)| 0.0378(4)|
| C9    | 0.39467(8) | 0.1768(3)  | 0.53140(18)| 0.0398(4)|
| C10   | 0.35368(8) | 0.3262(3)  | 0.58396(18)| 0.0358(4)|
| C11   | 0.32657(9) | 0.2747(4)  | 0.69691(19)| 0.0445(4)|
| C12   | 0.28692(9) | 0.4252(4)  | 0.74387(19)| 0.0481(5)|
| C13   | 0.27174(9) | 0.6322(4)  | 0.67982(19)| 0.0453(5)|
| C14   | 0.29716(8) | 0.6866(3)  | 0.57105(18)| 0.0381(4)|
| C15   | 0.33914(7) | 0.5370(3)  | 0.52055(17)| 0.0325(4)|
| C16   | 0.36692(7) | 0.5906(3)  | 0.40857(16)| 0.0327(3)|

Table S12. Bond lengths (Å) for (S)-1a.

|       |               |               |           |          |
|-------|---------------|---------------|-----------|----------|
| C1-O1 | 1.352(2)      | O1-C1         | 1.466(2)  |          |
| O2-C5 | 1.204(3)      | C1-C7         | 1.524(2)  |          |
| C1-C2 | 1.529(2)      | C1-C3         | 1.536(2)  |          |
| C2-H2A| 0.98          | C2-H2B        | 0.98      |          |
| C2-H2C| 0.98          | C3-C4         | 1.526(2)  |          |
| C3-H3A| 0.99          | C3-H3B        | 0.99      |          |
| C4-H4A| 0.98          | C4-H4B        | 0.98      |          |
C4-H4C  0.98  C5-C6  1.496(3)
C6-H6A  0.98  C6-H6B  0.98
C6-H6C  0.98  C7-C16  1.369(2)
C7-C8  1.424(2)  C8-C9  1.363(3)
C8-H8  0.95  C9-C10  1.413(3)
C9-H9  0.95  C10-C11  1.419(3)
C10-C15  1.423(2)  C11-C12  1.370(3)
C11-H11  0.95  C12-C13  1.409(3)
C12-H12  0.95  C13-C14  1.365(3)
C13-H13  0.95  C14-C15  1.418(2)
C14-H14  0.95  C15-C16  1.420(2)
C16-H16  0.95

Table S13. Bond angles (°) for (S)-1a.

| Bond Angle | Value (°) |
|------------|-----------|
| C5-O1-C1   | 119.98(14)|
| O1-C1-C2   | 110.15(14)|
| O1-C1-C3   | 102.86(13)|
| C2-C1-C3   | 111.09(14)|
| C1-C2-H2B  | 109.5     |
| C1-C2-H2C  | 109.5     |
| H2B-C2-H2C | 109.5     |
| C4-C3-H3A  | 108.5     |
| C4-C3-H3B  | 108.5     |
| H3A-C3-H3B | 107.5     |
| C3-C4-H4B  | 109.5     |
| C3-C4-H4C  | 109.5     |
| H4B-C4-H4C | 109.5     |
| O2-C5-C6   | 126.06(18)|
| C5-C6-C7   | 110.59(12)|
| C7-C1-C2   | 113.31(15)|
| C7-C1-C3   | 108.33(13)|
| C1-C2-H2A  | 109.5     |
| C1-C2-H2C  | 109.5     |
| H2A-C2-H2B | 109.5     |
| H2A-C2-H2C | 109.5     |
| C4-C3-H3A  | 108.5     |
| C4-C3-H3B  | 108.5     |
| C3-C4-H4A  | 109.5     |
| C3-C4-H4B  | 109.5     |
| C3-C4-H4C  | 109.5     |
| H4B-C4-H4C | 109.5     |
| O2-C5-O1   | 124.07(19)|
| C5-C6-C7   | 110.59(12)|
| C7-C1-C2   | 113.31(15)|
| C7-C1-C3   | 108.33(13)|
| C1-C2-H2A  | 109.5     |
| C1-C2-H2C  | 109.5     |
| H2A-C2-H2B | 109.5     |
| H2A-C2-H2C | 109.5     |
| C4-C3-H3A  | 108.5     |
| C4-C3-H3B  | 108.5     |
| C3-C4-H4A  | 109.5     |
| C3-C4-H4B  | 109.5     |
| C3-C4-H4C  | 109.5     |
| H4B-C4-H4C | 109.5     |
| O2-C5-O1   | 124.07(19)|
| C5-C6-C7   | 110.59(12)|
| C7-C1-C2   | 113.31(15)|
| C7-C1-C3   | 108.33(13)|
| C1-C2-H2A  | 109.5     |
| C1-C2-H2C  | 109.5     |
| H2A-C2-H2B | 109.5     |
| H2A-C2-H2C | 109.5     |
| C4-C3-H3A  | 108.5     |
| C4-C3-H3B  | 108.5     |
| C3-C4-H4A  | 109.5     |
| C3-C4-H4B  | 109.5     |
| C3-C4-H4C  | 109.5     |
| H4B-C4-H4C | 109.5     |
| O2-C5-O1   | 124.07(19)|
Table S14. Torsion angles (°) for (S)-1a.

|       | C5-O1-C1-C7 | C5-O1-C1-C2 | C15-C16-H16 | C15-C16-H16 |
|-------|-------------|-------------|-------------|-------------|
| Angles | -66.62(18)  | 59.41(19)   | 119.1       | 119.1       |
|        | 177.89(14)  | -64.92(17)  |             |             |
|        | 177.97(16)  | 52.9(2)     |             |             |
|        | 3.6(3)      | -176.21(14) | -52.9(2)    | -52.9(2)    |
|        | -26.1(2)    | -150.35(16) | -89.05(18)  | -89.05(18)  |
|        | 85.91(18)   | 158.93(14)  |             |             |
|        | 34.7(2)     |             |             |             |
|        | -0.3(3)     |             | 174.88(16)  | 174.88(16)  |
|        | 0.2(3)      |             | -179.53(18) | -179.53(18) |
|        | 0.5(3)      |             | -179.82(18) | -179.82(18) |
|        | -1.0(3)     |             |             |             |
|        | -179.14(16) |             |             |             |
|        | 0.2(2)      |             |             |             |
|        | -0.2(2)     |             |             |             |
|        | -178.95(15) |             |             |             |

Table S15. Anisotropic atomic displacement parameters (Å²) for (S)-1a.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 \left[ h^2 a^2 U_{11} + \ldots + 2hk a^* b^* U_{12} \right]$

| Atom | $U_{11}$  | $U_{22}$  | $U_{33}$  | $U_{23}$  | $U_{13}$  | $U_{12}$  |
|------|------------|------------|------------|------------|------------|------------|
| O1   | 0.0306(6)  | 0.0377(6)  | 0.0366(6)  | 0.0034(5)  | 0.0016(4)  | -0.0007(5) |
| O2   | 0.0427(7)  | 0.0672(10) | 0.0555(8)  | -0.0023(8) | -0.0033(6) | -0.0155(8) |
| C1   | 0.0318(7)  | 0.0301(8)  | 0.0353(8)  | -0.0008(7) | 0.0035(6)  | 0.0007(6)  |
| C2   | 0.0510(11) | 0.0386(10) | 0.0478(10) | -0.0099(8) | 0.0134(8)  | -0.0023(8) |
| C3   | 0.0299(8)  | 0.0387(9)  | 0.0368(8)  | -0.0010(7) | 0.0029(6)  | -0.0005(7) |
| C4   | 0.0357(9)  | 0.0512(11) | 0.0472(10) | -0.0004(9) | 0.0085(7)  | -0.0061(8) |
| C5   | 0.0320(8)  | 0.0560(12) | 0.0341(8)  | -0.0024(8) | 0.0037(6)  | -0.0019(8) |
| C6   | 0.0387(9)  | 0.0745(15) | 0.0443(10) | 0.0088(10) | 0.0016(8)  | 0.0103(10) |
| C7   | 0.0308(7)  | 0.0296(8)  | 0.0363(8)  | -0.0022(7) | 0.0025(6)  | -0.0018(6) |
| C8   | 0.0376(8)  | 0.0283(8)  | 0.0479(10) | -0.0003(7) | 0.0071(7)  | 0.0030(7)  |
| C9   | 0.0420(9)  | 0.0291(8)  | 0.0478(10) | 0.0037(8)  | 0.0036(7)  | 0.0002(7)  |
| C10  | 0.0334(8)  | 0.0342(8)  | 0.0391(8)  | 0.0004(7)  | 0.0025(6)  | -0.0048(7) |
| C11  | 0.0469(10) | 0.0434(10) | 0.0432(10) | 0.0055(8)  | 0.0059(8)  | -0.0062(8) |
| C12  | 0.0482(10) | 0.0577(12) | 0.0407(9)  | -0.0002(9) | 0.0146(8)  | -0.0094(9) |
| C13  | 0.0395(9)  | 0.0528(12) | 0.0448(10) | -0.0086(8) | 0.0100(7)  | -0.0004(8) |
| C14  | 0.0337(8)  | 0.0379(9)  | 0.0425(9)  | -0.0033(8) | 0.0036(6)  | 0.0010(7)  |
| C15  | 0.0287(7)  | 0.0307(8)  | 0.0374(8)  | -0.0006(6) | 0.0013(6)  | -0.0029(6) |
| C16  | 0.0320(7)  | 0.0282(8)  | 0.0374(8)  | 0.0006(6)  | 0.0024(6)  | -0.0005(6) |
Table S16. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for (S)-1a.

|   | x/a | y/b | z/c | U(eq) |
|---|-----|-----|-----|-------|
| H2A | 0.4184 | 0.1992 | 0.1532 | 0.068 |
| H2B | 0.4904 | 0.2184 | 0.2070 | 0.068 |
| H2C | 0.4633 | 0.3526 | 0.0791 | 0.068 |
| H3A | 0.4894 | 0.7708 | 0.3422 | 0.042 |
| H3B | 0.5249 | 0.5333 | 0.3617 | 0.042 |
| H4A | 0.5574 | 0.5617 | 0.1577 | 0.067 |
| H4B | 0.5763 | 0.7908 | 0.2354 | 0.067 |
| H4C | 0.5172 | 0.7877 | 0.1276 | 0.067 |
| H6A | 0.3521 | 0.8435 | -0.0533 | 0.079 |
| H6B | 0.3282 | 0.9605 | 0.0693 | 0.079 |
| H6C | 0.2836 | 0.7932 | -0.0204 | 0.079 |
| H8  | 0.4476 | 0.1286 | 0.3898 | 0.045 |
| H9  | 0.4046 | 0.0348 | 0.5722 | 0.048 |
| H11 | 0.3360 | 0.1347 | 0.7403 | 0.053 |
| H12 | 0.2695 | 0.3896 | 0.8202 | 0.058 |
| H13 | 0.2437 | 0.7343 | 0.7124 | 0.054 |
| H14 | 0.2866 | 0.8267 | 0.5286 | 0.046 |
| H16 | 0.3577 | 0.7322 | 0.3668 | 0.039 |

Crystal Structure Data for S-1d

Table S17. Sample and crystal data for S-1d.

| Identification code | mary026 |
|---------------------|--------|
| Chemical formula    | C_{14}H_{17}NO |
| Formula weight      | 215.28 |
| Temperature         | 200(2) K |
| Wavelength          | 1.54178 Å |
Crystal size
0.216 x 0.425 x 0.545 mm

Crystal system
orthorhombic

Space group
P 21 21 21

Unit cell dimensions
\[ a = 5.9000(2) \, \text{Å} \quad \alpha = 90° \]
\[ b = 8.4404(3) \, \text{Å} \quad \beta = 90° \]
\[ c = 23.7442(10) \, \text{Å} \quad \gamma = 90° \]

Volume
1182.42(8) Å³

Z
4

Density (calculated)
1.209 g/cm³

Absorption coefficient
0.591 mm⁻¹

F(000)
464

Table S18. Data collection and structure refinement for S-1d.

| Parameter Description | Value |
|-----------------------|-------|
| Theta range for data collection | 3.72 to 74.70° |
| Index ranges | -7<=h<=7, -10<=k<=10, -29<=l<=29 |
| Reflections collected | 19673 |
| Independent reflections | 2415 [R(int) = 0.0388] |
| Max. and min. transmission | 0.8830 and 0.7390 |
| Refinement method | Full-matrix least-squares on F² |
| Refinement program | SHELXL-2014/7 (Sheldrick, 2014) |
| Function minimized | \( \sum \frac{w(F_o^2 - F_c^2)}{} \) |
| Data / restraints / parameters | 2415 / 0 / 150 |
| Goodness-of-fit on F² | 1.020 |
| \( \Delta/\sigma_{\text{max}} \) | 0.001 |
| Final R indices | 2389 data; I>2σ(I) R1 = 0.0333, wR2 = 0.0953 |
| | all data R1 = 0.0337, wR2 = 0.0976 |
| Weighting scheme | w=1/[(σ²(Fo^2)+(0.0716P)^2+0.1296P)] |
| | where P=(Fo^2+2Fc^2)/3 |
| Absolute structure parameter | -0.1(1) |
| Extinction coefficient | 0.0143(18) |
| Largest diff. peak and hole | 0.213 and -0.198 eÅ⁻³ |
| R.M.S. deviation from mean | 0.044 eÅ⁻³ |

Table S19. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for S-1d.

U(eq) is defined as one third of the trace of the orthogonalized Uₐₗₖ tensor.

| Atomic Symbol | x/a | y/b | z/c | U(eq) |
|---------------|-----|-----|-----|-------|
| N1            | 0.7994(2) | 0.02782(15) | 0.06577(6) | 0.0283(3) |
| O1            | 0.37311(19) | 0.72139(14) | 0.84869(5) | 0.0341(3) |
| C1            | 0.7123(4) | 0.1740(2) | 0.15036(7) | 0.0426(4) |
| C2            | 0.6518(3) | 0.12030(18) | 0.09177(6) | 0.0297(3) |
| C3            | 0.4435(3) | 0.16671(18) | 0.06700(7) | 0.0309(4) |
### Table S20. Bond lengths (Å) for S-1d.

|       | Length (Å)       |       | Length (Å)       |
|-------|------------------|-------|------------------|
| N1-C2 | 1.322(2)         | N1-C10| 1.376(2)         |
| O1-C11| 1.4365(19)       | O1-H1 | 0.84             |
| C1-C2 | 1.506(2)         | C1-H1A| 0.98             |
| C1-H1B| 0.98             | C1-H1C| 0.98             |
| C2-C3 | 1.418(2)         | C3-C4 | 1.365(2)         |
| C3-H3 | 0.95             | C4-C5 | 1.419(2)         |
| C4-H4 | 0.95             | C5-C6 | 1.416(2)         |
| C5-C10| 1.420(2)         | C6-C7 | 1.379(2)         |
| C6-H6 | 0.95             | C7-C8 | 1.417(2)         |
| C7-C11| 1.5335(19)       | C8-C9 | 1.373(2)         |
| C8-H8 | 0.95             | C9-C10| 1.409(2)         |
| C9-H9 | 0.95             | C11-C12| 1.522(2)       |
| C11-C13| 1.537(2)        | C12-H12A| 0.98         |
| C12-H12B| 0.98        | C12-H12C| 0.98         |
| C13-C14| 1.512(3)        | C13-H13A| 0.99         |
| C13-H13B| 0.99        | C14-H14A| 0.98         |
| C14-H14B| 0.98        | C14-H14C| 0.98         |

### Table S21. Bond angles (°) for S-1d.

|       | Angle (°)       |       | Angle (°)       |
|-------|-----------------|-------|-----------------|
| C2-N1-C10| 118.39(14)   | C11-O1-H1| 109.5          |
| C2-C1-H1A| 109.5         | C2-C1-H1B| 109.5          |
| H1A-C1-H1B| 109.5        | C2-C1-H1C| 109.5          |
| H1A-C1-H1C| 109.5        | H1B-C1-H1C| 109.5       |
| N1-C2-C3| 122.71(14)    | N1-C2-C1| 116.91(15)     |
| C3-C2-C1| 120.37(15)    | C4-C3-C2| 119.84(14)     |
| C4-C3-H3| 120.1         | C2-C3-H3| 120.1          |
| C3-C4-C5| 119.22(14)    | C3-C4-H4| 120.4          |
| C5-C4-H4| 120.4         | C6-C5-C4| 123.29(14)     |
Table S22. Torsion angles (°) for S-1d.

| Torsion Angle                  | Value         |
|--------------------------------|---------------|
| C10-N1-C2-C3                  | 1.4(2)        |
| N1-C2-C3-C4                   | 0.3(2)        |
| C2-C3-C4-C5                   | -1.1(2)       |
| C3-C4-C5-C10                  | 0.2(2)        |
| C10-C5-C6-C7                  | -1.5(2)       |
| C5-C6-C7-C11                  | 176.90(12)    |
| C11-C7-C8-C9                  | -175.20(13)   |
| C2-N1-C10-C9                  | 178.04(13)    |
| C8-C9-C10-C11                 | 178.33(13)    |
| C6-C5-C10-N1                  | -177.24(13)   |
| C6-C5-C10-C9                  | 2.4(2)        |
| C6-C7-C11-O1                  | -47.66(18)    |
| C6-C7-C11-C12                 | -168.19(14)   |
| O1-C11-C13-C14                | 174.47(15)    |
| C7-C11-C13-C14                | 58.1(2)       |

Table S23. Anisotropic atomic displacement parameters (Å²) for S-1d.

The anisotropic atomic displacement factor exponent takes the form: 

\[-2\pi^2 \left( a^2 U_{11} + ... + 2 \ h \ k \ a^* \ b^* \ U_{12} \right) \]
Table S24. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for S-1d.

|  | x/a   | y/b   | z/c   | U(eq) |
|---|-------|-------|-------|-------|
| H1 | 0.3743 | 0.6477 | 0.8725 | 0.051 |
| H1A | 0.6046 | 1.1287 | 1.1773 | 0.064 |
| H1B | 0.7057 | 1.2898 | 1.1523 | 0.064 |
| H1C | 0.8659 | 1.1382 | 1.1596 | 0.064 |
| H3  | 0.3423 | 1.2337 | 1.0870 | 0.037 |
| H4  | 0.2483 | 1.1439 | 0.9976 | 0.033 |
| H6  | 0.3605 | 0.9797 | 0.9123 | 0.031 |
| H8  | 0.9754 | 0.7673 | 0.9108 | 0.033 |
| H9  | 1.0488 | 0.8570 | 1.0008 | 0.033 |
| H12A | 0.7689 | 0.5794 | 0.8539 | 0.061 |
| H12B | 0.9111 | 0.7106 | 0.8205 | 0.061 |
| H12C | 0.7085 | 0.6189 | 0.7898 | 0.061 |
| H13A | 0.5308 | 0.8720 | 0.7642 | 0.045 |
| H13B | 0.4402 | 0.9903 | 0.8116 | 0.045 |
| H14A | 0.8085 | 1.0824 | 0.8275 | 0.091 |
| H14B | 0.7473 | 1.1013 | 0.7622 | 0.091 |
| H14C | 0.9062 | 0.9587 | 0.7825 | 0.091 |
References

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QZ-P5-4
C13CPD256 CDCl3 /opt/nmrdata qzhou 39

102030405060708090100110120130140150160170180190200

f1 (ppm)

9.3558
26.8875
33.8547
46.8485
55.2578
77.1600

110.2683
114.3107
120.3919
124.8795
125.5433
125.9296
127.2206
127.5148
127.6187
128.1257
128.9424
131.8831
133.3013
146.8718
151.4786
159.4347

127.5148
127.6187
128.1257
128.9424
131.8831
133.3013
146.8718
151.4786
159.4347

CH
3

O
C
H
3

4

S43
S43

H5C
QZ-8-058-1

9

\begin{align*}
&\text{Cl} \\
&\text{H}_2\text{C} \\
&\text{CH}_3
\end{align*}
QZ-8-TYT-052-2
C13CPD256 CDC13 /opt/nmrdata qzhou 10

10

[Chemical structure image]

[Chemical shifts table]

| f1 (ppm) |
|----------|
| 9.2957   |
| 13.0286  |
| 14.3885  |
| 26.8962  |
| 33.8364  |
| 39.3409  |
| 43.4313  |
| 46.8535  |
| 77.1600  |
| 125.0523 |
| 125.6545 |
| 126.0286 |
| 126.2791 |
| 126.7610 |
| 127.1704 |
| 127.6805 |
| 128.0922 |
| 131.8799 |
| 133.2420 |
| 134.5783 |
| 146.4565 |
| 150.9162 |
| 171.4812 |
QZ-P5-1D
PROTON CDCl3 /opt/nmrdata qzhou 31

1.000
0.993
0.957
0.998
0.7784
0.7908
0.8032
1.9044
2.0959
2.7217
7.2556
7.2595
7.2696
7.6209
7.6245
7.6356
7.6392
7.6641
7.6677
7.9636
7.9784
8.0062
8.0202

NC H
3
O
O
C H
3
CH
3

1d
| f (ppm) | 169.8193 | 158.9881 | 147.0698 | 136.5306 | 128.7441 | 128.7441 | 128.7441 | 128.7441 | 123.2382 | 123.2382 | 122.2677 | 121.0361 | 121.0361 | 119.8049 | 118.6136 | 117.3224 | 116.1312 | 114.9399 | 113.7487 | 112.6482 | 111.4471 | 110.2459 | 109.0448 |
|---------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 22.3340 | 24.4015   | 25.4306   | 35.1011   | 77.1600 CDCl3 | 84.2808 | 8.2693 | 35.1011 | 77.1600 CDCl3 | 84.2808 | 8.2693 | 35.1011 | 77.1600 CDCl3 | 84.2808 | 8.2693 | 35.1011 | 77.1600 CDCl3 | 84.2808 | 8.2693 | 35.1011 | 77.1600 CDCl3 | 84.2808 | 8.2693 |

The image contains a chemical structure labeled as 1d and a 1D NMR spectrum with peaks indicated. The structure shows a molecule with multiple groups and functional groups, including methyl groups (CH₃), a carbonyl group (C=O), and other chemical bonds. The NMR spectrum is likely used to determine the chemical shifts and assignments for the various protons and carbons in the molecule.
**QZ-8-113-1.2.fid**

**QZ-8-113-1**

C13CPD2048 CDCl3 /opt/nmrdata qzhou 60

| ppm  | Value   |
|------|---------|
| 19.81| 162.11  |
| 22.42| 163.24  |
| 25.25| 160.98  |
| 45.93| 159.34  |
| 77.16| 158.04  |
| 83.75| 157.34  |
| 123.16|156.87   |
| 123.63|156.87   |
| 125.88|156.87   |
| 126.03|156.87   |
| 126.05|156.87   |
| 126.13|156.87   |
| 126.25|156.87   |
| 130.24|157.34   |
| 130.25|157.34   |
| 132.06|157.34   |
| 136.81|157.34   |
| 137.19|157.34   |
| 142.19|157.34   |
| 169.82|157.34   |

**[Diagram]**

![Diagram of a chemical structure](image)
\[ \text{QZ-P5-1i} \]

\[ \text{PROTON CDCl}_3 / \text{opt/nmrdata qzhou} 41 \]

\[ f_1 (\text{ppm}) \]

\[ 0.0 \quad 0.5 \quad 1.0 \quad 1.5 \quad 2.0 \quad 2.5 \quad 3.0 \quad 3.5 \quad 4.0 \quad 4.5 \quad 5.0 \quad 5.5 \quad 6.0 \quad 6.5 \quad 7.0 \quad 7.5 \quad 8.0 \]

\[ 2.1641 \quad 2.3020 \quad 7.2336 \quad 7.2358 \quad 7.2380 \quad 7.2444 \quad 7.2479 \quad 7.2512 \quad 7.2601 \quad 7.2968 \quad 7.2995 \quad 7.3072 \quad 7.3101 \quad 7.3194 \quad 7.3226 \quad 7.3339 \quad 7.3371 \quad 7.3518 \quad 7.3536 \quad 7.3560 \quad 7.3623 \quad 7.3656 \quad 7.3684 \quad 7.4466 \quad 7.4491 \quad 7.4579 \quad 7.4607 \quad 7.4676 \quad 7.4699 \quad 7.4718 \quad 7.4737 \quad 7.4808 \quad 7.4837 \quad 7.4925 \quad 7.4951 \quad 7.7433 \quad 7.7577 \quad 7.7850 \quad 7.7880 \quad 7.7974 \quad 7.8001 \quad 7.8299 \quad 7.8330 \quad 7.8423 \quad 7.8453 \quad 7.8801 \quad 7.8820 \quad 7.8837 \]

\[ \text{Ma}, \text{OAc} \]

\[ \text{ni} \]
$\text{MeOAc}$

$\text{C}_8\text{H}_{16}$

$\text{f}_1 (\text{ppm})$

- 22.5618
- 27.0452
- 77.1600 CDCl$_3$
- 84.6092
- 126.0054
- 126.4792
- 126.9822
- 127.2013
- 127.3051
- 127.4047
- 128.2998
- 128.8545
- 140.0508
- 140.7828
- 144.7504
- 145.6906
- 169.4257

$\text{1j}$
O
CH₃

S-1b

H
CH₃

CH₃

O

C13CPD256 CDCl3 /opt/nmrdata qzhou

8.5278
29.8643
36.6918
55.4721
75.1719
77.1600 CDCl₃
105.6573
118.9297
123.2888
124.3844
126.8258
128.7678
129.7329
133.4354
142.9931
157.7226

30 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

f1 (ppm)
QZ-P5-S-1c
C13CPD256 CDCl3 /opt/nmrdata qzhou 30

[Chemical structure image]

9.0241
29.5194
35.4490
76.8875
77.1600 CDCl3
124.0180
124.8693
125.2173
125.3139
127.0880
128.5970
129.2640
131.0965
135.0227
142.4264

O H CH₃

CH₃
C13CPD256 CDCl3 /opt/nmrdata qzhou 13

-145.4855
133.3377
132.3813
128.2711
127.9678
127.5865
126.1199
125.7516
124.2979

-77.1600 CDCl3
63.1386
-43.8020
-33.9862
-26.0814
-20.5840
-18.4401
-5.1695
-5.1578
18.4401
20.5840
26.0814
33.9862
63.1386
77.1600

S-1e
The attached image contains a chemical structure and a 1D NMR spectrum. The chemical structure shows a molecule with a carboxylic acid group (COOH) and a methylene group (CH₂). The NMR spectrum displays various peaks at different ppm values, indicating the presence of different chemical shifts. The peaks correspond to the protons of the molecule, with assignments at 29.8853, 74.9959, 77.1600, 123.5550, 124.3358, 126.0618, 126.2704, 126.7191, 127.6343, 127.8209, 128.1632, 128.2210, 128.3293, 128.7216, 132.5838, 133.2540, 136.2397, 136.7448, and 143.9726 ppm. These values likely correspond to the chemical shifts of the protons in different environments within the molecule.
QZ-P5-S-IJ
C13CPD256 CDCl3 /opt/nmrdata qzhou 35

Me OH

S-1j

[Chemical Structure Image]

148.0478, 147.1863, 140.8793, 138.8843, 128.3748, 127.3964, 126.4287, 125.9744, 127.2080, 127.1727, 127.2080, 127.0501, 127.1727, 126.4287, 125.9744, 128.3748, 128.8843, 139.9642, 140.8793, 147.1863, 148.0478, 31.0363, 76.2695, 77.1600 CDCl3
Racemic 4

Detector A Ch1 254nm

| Peak# | Ret. Time | Area  | Height | Area %  | Height % |
|-------|-----------|-------|--------|---------|----------|
| 1     | 11.674    | 264030| 18609  | 50.155  | 53.657   |
| 2     | 14.231    | 262397| 16073  | 49.845  | 46.343   |
| Total |           | 526427| 34682  | 100.000 | 100.000  |

Enantioenriched 4, 93% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area  | Height | Area %  | Height % |
|-------|-----------|-------|--------|---------|----------|
| 1     | 12.058    | 138560| 9748   | 96.319  | 96.759   |
| 2     | 14.930    | 5295  | 326    | 3.681   | 3.241    |
| Total |           | 143855| 10075  | 100.000 | 100.000  |
Racemic 6

Enantioenriched 6, 95% ee
Racemic 7

Enantioenriched 7, 96% ee
### Racemic 8

(A = 220 nm, B = 254 nm, C = 280 nm)

| Index | Name       | Start | Time | End | RT Offset | Quantity | Height | Area  | Area  |
|-------|------------|-------|------|-----|-----------|----------|--------|-------|-------|
| 1     | UNKNOWN    | 4.69  | 4.91 | 5.25| 0.00      | 49.78    | 396.5  | 55.7  | 49.783|
| 2     | UNKNOWN    | 6.01  | 6.29 | 6.67| 0.00      | 50.22    | 308.1  | 56.2  | 50.217|
| Total |            |       |      |     |           | 100.00   | 704.6  | 112.0 | 100.00|

### Enantioenriched 8, 96% ee

(A = 220 nm, B = 254 nm, C = 280 nm)

| Index | Name       | Start | Time | End | RT Offset | Quantity | Height | Area  | Area  |
|-------|------------|-------|------|-----|-----------|----------|--------|-------|-------|
| 1     | UNKNOWN    | 6.09  | 6.27 | 6.47| 0.00      | 1.95     | 13.5   | 2.3   | 1.949 |
| 2     | UNKNOWN    | 4.65  | 4.89 | 5.30| 0.00      | 98.05    | 790.5  | 114.5 | 98.051|
| Total |            |       |      |     |           | 100.00   | 804.0  | 116.8 | 100.00|
### Racemic 9

![Graph](image1.png)

| Index | Name      | Start | Time | End  | RT Offset | Quantity | Height | Area  | Area  |
|-------|-----------|-------|------|------|-----------|----------|--------|-------|-------|
|       | UNKNOW   | 5.82  | 6.17 | 6.52 | 0.00      | 49.58    | 1197.4 | 201.8 | 49.580|
| 1     | UNKNOW   | 6.64  | 6.96 | 7.47 | 0.00      | 50.42    | 1078.7 | 205.2 | 50.420|
| 2     | Total    |       |      |      |           | 100.00   | 2276.1 | 407.0 | 100.000|

### Enantioenriched 9, 92% ee

![Graph](image2.png)

| Index | Name      | Start | Time | End  | RT Offset | Quantity | Height | Area  | Area  |
|-------|-----------|-------|------|------|-----------|----------|--------|-------|-------|
|       | UNKNOW   | 5.89  | 6.18 | 6.52 | 0.00      | 96.01    | 1087.1 | 180.0 | 96.009|
| 1     | UNKNOW   | 6.79  | 6.97 | 7.30 | 0.00      | 3.99     | 41.2   | 7.5   | 3.991 |
| 2     | Total    |       |      |      |           | 100.00   | 1128.3 | 187.4 | 100.000|

- \( A = 220 \text{ nm}, B = 254 \text{ nm}, C = 280 \text{ nm} \)
**Racemic 10**

![Racemic 10 diagram]

**Detector A Ch1 254nm**

| Peak# | Ret. Time | Area   | Height  | Area %  | Height % |
|-------|-----------|--------|---------|---------|----------|
| 1     | 10.471    | 1653101| 109872  | 50.507  | 52.247   |
| 2     | 11.483    | 1619926| 100424  | 49.493  | 47.753   |
| Total |           | 3273026| 210296  | 100.000 | 100.000  |

**Enantioenriched 10, 94% ee**

![Enantioenriched 10 diagram]

**Detector A Ch1 254nm**

| Peak# | Ret. Time | Area   | Height  | Area %  | Height % |
|-------|-----------|--------|---------|---------|----------|
| 1     | 10.179    | 9333   | 548     | 2.832   | 2.609    |
| 2     | 11.038    | 320214 | 20472   | 97.168  | 97.391   |
| Total |           | 329548 | 21021   | 100.000 | 100.000  |
Enantioenriched (R)-10, 96% ee (crystal used for X-ray diffraction analysis)
Racemic 11

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height | Area %  | Height % |
|-------|-----------|--------|--------|---------|----------|
| 1     | 31.758    | 1728236| 44032  | 49.845  | 52.134   |
| 2     | 34.546    | 1738977| 40427  | 50.155  | 47.866   |
| Total |           | 3467213| 84459  | 100.000 | 100.000  |

Enantioenriched 11, 96% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height | Area %   | Height % |
|-------|-----------|--------|--------|----------|----------|
| 1     | 30.604    | 251321 | 6477   | 97.885   | 98.017   |
| 2     | 33.299    | 5430   | 131    | 2.115    | 1.983    |
| Total |           | 256751 | 6608   | 100.000  | 100.000  |
Racemic 12

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height | Area %  | Height % |
|-------|-----------|--------|--------|---------|----------|
| 1     | 33.885    | 1587788| 36919  | 49.856  | 51.534   |
| 2     | 36.489    | 1596950| 34721  | 50.144  | 48.466   |
| Total |           | 3184738| 71640  | 100.000 | 100.000  |

Enantioenriched 12, 96% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height | Area %  | Height % |
|-------|-----------|--------|--------|---------|----------|
| 1     | 35.980    | 18779  | 442    | 2.148   | 2.424    |
| 2     | 39.173    | 855635 | 17798  | 97.852  | 97.576   |
| Total |           | 874414 | 18241  | 100.000 | 100.000  |
Racemic 13

![Graph showing rac-13 with retention times and UV absorbance.](image)

| Index | Name      | Start | Time | End | RT Offset | Quantity | Height | Area | Area [%] |
|-------|-----------|-------|------|-----|-----------|----------|--------|------|---------|
| 1     | UNKNOWN   | 5.01  | 5.21 | 5.41| 0.00      | 49.95    | 599.1  | 80.3 | 49.946  |
| 2     | UNKNOWN   | 5.41  | 5.55 | 5.88| 0.00      | 50.05    | 555.9  | 80.5 | 50.054  |
| Total |           |       |      |     |           | 100.00   | 1155.0 | 160.8| 100.000 |

Enantioenriched 13, 94% ee

![Graph showing 13 with retention times and UV absorbance.](image)

| Index | Name      | Start | Time | End | RT Offset | Quantity | Height | Area | Area [%] |
|-------|-----------|-------|------|-----|-----------|----------|--------|------|---------|
| 1     | UNKNOWN   | 5.05  | 5.22 | 5.47| 0.00      | 97.13    | 303.5  | 40.2 | 97.132  |
| 2     | UNKNOWN   | 5.47  | 5.57 | 5.83| 0.00      | 2.87     | 7.8    | 1.2  | 2.868   |
| Total |           |       |      |     |           | 100.00   | 311.3  | 41.4 | 100.000 |
**Racemic 14**

![Graph of racemate 14 with traces and mAU readings.](image)

| Index | Name     | Start [Min] | Time [Min] | End [Min] | RT Offset [Min] | Quantity [% Area] | Height [μV] | Area [μV.Min] | Area [%] |
|-------|----------|-------------|------------|-----------|-----------------|-------------------|-------------|---------------|----------|
| 1     | UNKNOWN  | 3.99        | 4.18       | 4.45      | 0.00            | 49.67             | 950.2      | 114.9         | 49.670   |
| 2     | UNKNOWN  | 4.70        | 4.91       | 5.27      | 0.00            | 50.33             | 814.4      | 115.4         | 50.330   |
| Total |          |             |            |           |                 | 100.00            | 1764.6     | 231.2         | 100.000  |

**Enantioenriched 14, 92% ee**

![Graph of enantiomer 14 with traces and mAU readings.](image)

| Index | Name     | Start [Min] | Time [Min] | End [Min] | RT Offset [Min] | Quantity [% Area] | Height [μV] | Area [μV.Min] | Area [%] |
|-------|----------|-------------|------------|-----------|-----------------|-------------------|-------------|---------------|----------|
| 1     | UNKNOWN  | 3.98        | 4.19       | 4.43      | 0.00            | 96.07             | 1130.0     | 139.5         | 96.066   |
| 2     | UNKNOWN  | 4.75        | 4.93       | 5.16      | 0.00            | 3.93              | 41.1        | 5.7           | 3.934    |
| Total |          |             |            |           |                 | 100.00            | 1171.2      | 145.2         | 100.000  |
Racemic 15

Enantioenriched 15, 95% ee
Racemic 16

| Peak# | Ret. Time | Area   | Height | Area %  | Height % |
|-------|-----------|--------|--------|---------|----------|
| 1     | 17.916    | 330741 | 14782  | 49.859  | 50.395   |
| 2     | 20.200    | 332617 | 14550  | 50.141  | 49.605   |
| Total | 663357    | 29332  | 100.000| 100.000 |          |

Detector A Ch1 254nm

Enantioenriched 16, 90% ee

| Peak# | Ret. Time | Area   | Height | Area %  | Height % |
|-------|-----------|--------|--------|---------|----------|
| 1     | 16.688    | 147777 | 7132   | 94.789  | 94.386   |
| 2     | 18.948    | 8124   | 424    | 5.211   | 5.614    |
| Total | 155901    | 7556   | 100.000| 100.000 |          |
Racemic 17

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height | Area % | Height % |
|-------|-----------|--------|--------|--------|----------|
| 1     | 11.933    | 192477 | 12599  | 50.018 | 54.934   |
| 2     | 15.440    | 192342 | 10336  | 49.982 | 45.066   |
| Total |           | 384819 | 22934  | 100.000| 100.000  |

Enantioenriched 17, 88% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height | Area % | Height % |
|-------|-----------|--------|--------|--------|----------|
| 1     | 11.227    | 378067 | 26292  | 93.832 | 94.517   |
| 2     | 14.389    | 24853  | 1525   | 6.168  | 5.483    |
| Total |           | 402920 | 27817  | 100.000| 100.000  |
Racemic 18

| Peak# | Ret. Time | Area    | Height  | Area % | Height % |
|-------|-----------|---------|---------|--------|----------|
| 1     | 8.753     | 355326  | 28276   | 50.038 | 52.795   |
| 2     | 9.949     | 354785  | 25282   | 49.962 | 47.205   |
| Total |           | 710111  | 53557   | 100.000| 100.000  |

Enantioenriched 18, 97% ee

| Peak# | Ret. Time | Area    | Height  | Area % | Height % |
|-------|-----------|---------|---------|--------|----------|
| 1     | 8.758     | 310956  | 24796   | 98.496 | 98.455   |
| 2     | 9.969     | 4747    | 389     | 1.504  | 1.545    |
| Total |           | 315703  | 25185   | 100.000| 100.000  |
Racemic 19

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height  | Area %  | Height % |
|-------|-----------|--------|---------|---------|----------|
| 1     | 26.232    | 416026 | 11202   | 50.139  | 56.329   |
| 2     | 33.767    | 413712 | 8684    | 49.861  | 43.671   |
| Total |           | 829738 | 19886   | 100.000 | 100.000  |

Enantioenriched 19, 99% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height  | Area %  | Height % |
|-------|-----------|--------|---------|---------|----------|
| 1     | 26.337    | 2073   | 64      | 0.625   | 0.925    |
| 2     | 33.672    | 329423 | 6878    | 99.375  | 99.075   |
| Total |           | 331496 | 6942    | 100.000 | 100.000  |
Racemic 20

Detector A Ch2 220nm

| Peak# | Ret. Time | Area     | Height   | Area % | Height % |
|-------|-----------|----------|----------|--------|----------|
| 1     | 53.803    | 3938543  | 65377    | 49.786 | 50.537   |
| 2     | 56.351    | 3972469  | 63987    | 50.214 | 49.463   |
| Total |           | 7911011  | 129364   | 100.000| 100.000  |

Enantioenriched 20, 94% ee

Detector A Ch2 220nm

| Peak# | Ret. Time | Area       | Height   | Area % | Height % |
|-------|-----------|------------|----------|--------|----------|
| 1     | 53.025    | 977426     | 19027    | 2.811  | 3.355    |
| 2     | 53.798    | 33790474   | 548101   | 97.189 | 96.645   |
| Total |           | 34767901   | 567128   | 100.000| 100.000  |
### Racemic 21

![Racemic 21 Chromatogram](image)

| Peak# | Ret. Time | Area  | Height | Area %  | Height %  |
|-------|-----------|-------|--------|---------|-----------|
| 1     | 13.506    | 1981293 | 87791  | 49.645  | 56.359    |
| 2     | 15.101    | 2009656 | 67980  | 50.355  | 43.641    |
| Total |           | 3990949 | 155771 | 100.000 | 100.000   |

### Enantioenriched 21, 94% ee

![Enantioenriched 21 Chromatogram](image)

| Peak# | Ret. Time | Area  | Height | Area %  | Height %  |
|-------|-----------|-------|--------|---------|-----------|
| 1     | 13.480    | 1845100 | 76078  | 97.047  | 97.444    |
| 2     | 15.096    | 56141  | 1996   | 2.953   | 2.556     |
| Total |           | 1901241 | 78073  | 100.000 | 100.000   |
Racemic 22

Enantioenriched 22, 87% ee
Racemic 23

Detector A Ch1 254nm

| Peak# | Ret. Time | Area    | Height   | Area %   | Height %  |
|-------|-----------|---------|----------|----------|-----------|
| 1     | 40.045    | 1348999 | 27748    | 49.573   | 50.539    |
| 2     | 41.650    | 1372253 | 27157    | 50.427   | 49.461    |
| Total |           | 2721252 | 54905    | 100.000  | 100.000   |

Enantioenriched 23, 94% ee

Detector A Ch2 210nm

| Peak# | Ret. Time | Area    | Height   | Area %   | Height %  |
|-------|-----------|---------|----------|----------|-----------|
| 1     | 49.084    | 15876695| 242733   | 97.073   | 97.378    |
| 2     | 52.102    | 478750  | 6535     | 2.927    | 2.622     |
| Total |           | 16355444| 249267   | 100.000  | 100.000   |
Co-injection of racemic 23 and enantioenriched 23

Detector A Ch2 210nm

| Peak# | Ret. Time | Area   | Height  | Area %  | Height % |
|-------|-----------|--------|---------|---------|----------|
| 1     | 40.491    | 38652729 | 74641   | 60.136  | 61.431   |
| 2     | 42.469    | 25623023 | 468626  | 39.864  | 38.569   |
| Total |           | 64275752 | 1215037 | 100.000 | 100.000  |
Racemic 24

Detector A Ch1 254nm

| Peak# | Ret. Time | Area  | Height | Area %   | Height % |
|-------|-----------|-------|--------|----------|----------|
| 1     | 17.947    | 146239| 7340   | 49.779   | 42.872   |
| 2     | 18.756    | 147539| 9781   | 50.221   | 57.128   |
| Total |           | 293778| 17120  | 100.000  | 100.000  |

Enantioenriched 24, 91% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area  | Height | Area %   | Height % |
|-------|-----------|-------|--------|----------|----------|
| 1     | 18.288    | 179299| 9861   | 4.531    | 3.984    |
| 2     | 18.913    | 3777644| 237657| 95.469   | 96.016   |
| Total |           | 3956943| 247518| 100.000  | 100.000  |
Racemic $1a$

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area      | Height   | Area % | Height % |
|-------|-----------|-----------|----------|--------|----------|
| 1     | 6.328     | 491674    | 54209    | 49.939 | 57.391   |
| 2     | 8.318     | 492882    | 40246    | 50.061 | 42.609   |
| Total |           | 984556    | 94456    | 100.000| 100.000  |

Enantioenriched $1a$, 96% ee

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area      | Height   | Area %  | Height % |
|-------|-----------|-----------|----------|---------|----------|
| 1     | 6.313     | 8728      | 1084     | 2.011   | 3.036    |
| 2     | 8.234     | 425380    | 34633    | 97.989  | 96.964   |
| Total |           | 434108    | 35717    | 100.000 | 100.000  |
Racemic 1c

Enantioenriched 1c, 90% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height  | Area %  | Height % |
|-------|-----------|--------|---------|---------|----------|
| 1     | 7.879     | 542497 | 54132   | 49.894  | 54.318   |
| 2     | 8.702     | 544812 | 45525   | 50.106  | 45.682   |
| Total |           | 1087309| 99658   | 100.000 | 100.000  |
Racemic 1d

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height | Area %  | Height % |
|-------|-----------|--------|--------|---------|----------|
| 1     | 9.793     | 255341 | 8840   | 49.841  | 55.369   |
| 2     | 13.431    | 256972 | 7126   | 50.159  | 44.631   |
| Total |           | 512313 | 15966  | 100.000 | 100.000  |

Enantioenriched 1d, 99% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height | Area %  | Height % |
|-------|-----------|--------|--------|---------|----------|
| 1     | 9.787     | 2432   | 82     | 0.716   | 0.847    |
| 2     | 13.331    | 337293 | 9599   | 99.284  | 99.153   |
| Total |           | 339725 | 9681   | 100.000 | 100.000  |
Racemic 1e

| Peak# | Ret. Time | Area       | Height     | Area %  | Height % |
|-------|-----------|------------|------------|---------|----------|
| 1     | 14.150    | 6717068    | 118892     | 49.889  | 55.245   |
| 2     | 21.445    | 6746910    | 96316      | 50.111  | 44.765   |
| Total |           | 13463978   | 215209     | 100.000 | 100.000  |

Detector A Ch2 220nm

Enantioenriched 1e, 99% ee

| Peak# | Ret. Time | Area       | Height | Area %  | Height % |
|-------|-----------|------------|--------|---------|----------|
| 1     | 14.469    | 10257      | 216    | 0.521   | 0.711    |
| 2     | 21.535    | 1957089    | 30206  | 99.479  | 99.289   |
| Total |           | 1967346    | 30422  | 100.000 | 100.000  |
Racemic 1f

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height | Area %   | Height % |
|-------|-----------|--------|--------|----------|----------|
| 1     | 11.685    | 259259 | 14975  | 49.898   | 50.568   |
| 2     | 12.976    | 260324 | 14639  | 50.102   | 49.432   |
| Total |           | 519583 | 29614  | 100.000  | 100.000  |

Enantoienriched 1f, 94% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height | Area %   | Height % |
|-------|-----------|--------|--------|----------|----------|
| 1     | 11.227    | 154894 | 9370   | 97.078   | 96.964   |
| 2     | 12.577    | 4663   | 293    | 2.922    | 3.036    |
| Total |           | 159557 | 9664   | 100.000  | 100.000  |
Racemic 1g

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height  | Area %  | Height % |
|-------|-----------|--------|---------|---------|----------|
| 1     | 15.074    | 682100 | 29840   | 49.883  | 65.138   |
| 2     | 20.792    | 685307 | 15970   | 50.117  | 34.862   |
| Total |           | 136708 | 45811   | 100.000 | 100.000  |

Enantioenriched 1g, 96% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area    | Height  | Area %  | Height % |
|-------|-----------|---------|---------|---------|----------|
| 1     | 15.924    | 789682  | 35965   | 98.270  | 99.044   |
| 2     | 21.866    | 13905   | 347     | 1.730   | 0.956    |
| Total |           | 803587  | 36312   | 100.000 | 100.000  |
Racemic 1i

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area    | Height | Area % | Height % |
|-------|-----------|---------|--------|--------|----------|
| 1     | 7.600     | 291470  | 28014  | 50.165 | 56.265   |
| 2     | 9.034     | 289554  | 21776  | 49.835 | 43.735   |
| Total |           | 581024  | 49790  | 100.000| 100.000  |

Enantioenriched 1i, 96% ee

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area    | Height | Area % | Height % |
|-------|-----------|---------|--------|--------|----------|
| 1     | 7.511     | 7964    | 824    | 1.915  | 2.731    |
| 2     | 8.923     | 407977  | 29359  | 98.085 | 97.269   |
| Total |           | 415942  | 30183  | 100.000| 100.000  |
Racemic S-1a

Detector A Ch1 254nm

| Peak# | Ret. Time | Area  | Height | Area %  | Height % |
|-------|-----------|-------|--------|---------|----------|
| 1     | 10.353    | 144648| 11554  | 49.962  | 51.955   |
| 2     | 11.468    | 144869| 10684  | 50.038  | 48.045   |
| Total |           | 289518| 22238  | 100.000 | 100.000  |

Enantioenriched 1a, 96% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area  | Height | Area %  | Height % |
|-------|-----------|-------|--------|---------|----------|
| 1     | 10.269    | 283433| 22977  | 98.493  | 98.537   |
| 2     | 11.370    | 4338  | 341    | 1.507   | 1.463    |
| Total |           | 287771| 23318  | 100.000 | 100.000  |
**Racemic S-1b**

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height | Area %  | Height % |
|-------|-----------|--------|--------|---------|----------|
| 1     | 16.534    | 73547  | 3522   | 50.022  | 56.460   |
| 2     | 21.305    | 73483  | 2716   | 49.978  | 43.540   |
| Total |           | 147031 | 6238   | 100.000 | 100.000  |

**Enantioenriched S-1b, 91% ee**

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height | Area %  | Height % |
|-------|-----------|--------|--------|---------|----------|
| 1     | 16.516    | 6536   | 328    | 4.672   | 6.201    |
| 2     | 21.219    | 13384  | 4962   | 95.328  | 93.799   |
| Total |           | 139920 | 5291   | 100.000 | 100.000  |
Racemic S-1c

Detector A Ch1 254nm

| Peak# | Ret. Time | Area    | Height  | Area %  | Height % |
|-------|-----------|---------|---------|---------|----------|
| 1     | 15.186    | 337510  | 20102   | 49.967  | 52.913   |
| 2     | 17.346    | 337952  | 17889   | 50.033  | 47.087   |
| Total |           | 675461  | 37991   | 100.000 | 100.000  |

Enantioenriched S-1c, 90% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area    | Height  | Area %  | Height % |
|-------|-----------|---------|---------|---------|----------|
| 1     | 15.085    | 379069  | 22316   | 94.789  | 95.245   |
| 2     | 17.287    | 20837   | 1114    | 5.211   | 4.755    |
| Total |           | 399906  | 23430   | 100.000 | 100.000  |
**Racemic S-1d**

Detector A Ch2 230nm

| Peak# | Ret. Time | Area   | Height | Area % | Height % |
|-------|-----------|--------|--------|--------|----------|
| 1     | 19.343    | 830508 | 27995  | 49.756 | 54.100   |
| 2     | 23.296    | 838670 | 23752  | 50.244 | 45.900   |
| Total |           | 1669178| 51747  | 100.000| 100.000  |

**Enantoienriched S-1d, 99% ee**

Detector A Ch2 230nm

| Peak# | Ret. Time | Area   | Height | Area % | Height % |
|-------|-----------|--------|--------|--------|----------|
| 1     | 19.313    | 10754  | 429    | 0.510  | 0.708    |
| 2     | 23.228    | 2099723| 60224  | 99.490 | 99.292   |
| Total |           | 2110477| 60653  | 100.000| 100.000  |
Racemic S-1e

Detector A Ch1 254nm

| Peak# | Ret. Time | Area  | Height | Area %  | Height % |
|-------|-----------|-------|--------|---------|----------|
| 1     | 13.737    | 525563| 30811  | 49.594  | 50.552   |
| 2     | 14.503    | 534166| 30139  | 50.406  | 49.448   |
| Total |           | 1059729| 60950  | 100.000 | 100.000  |

Enantioenriched S-1e, 99% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area  | Height | Area %  | Height % |
|-------|-----------|-------|--------|---------|----------|
| 1     | 13.695    | 2096  | 141    | 0.553   | 0.651    |
| 2     | 14.468    | 376900| 21525  | 99.447  | 99.349   |
| Total |           | 378996| 21666  | 100.000 | 100.000  |
Racemic 2-(Naphthalen-2-yl)pent-4-en-2-ol (used in preparation of S-1g)

Enantioenriched 2-(Naphthalen-2-yl)pent-4-en-2-ol (used in preparation of S-1g), 96% ee
Racemic S-1h

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area  | Height | Area % | Height % |
|-------|-----------|-------|--------|--------|----------|
| 1     | 9.944     | 89648 | 6313   | 50.174 | 55.701   |
| 2     | 10.699    | 89026 | 5021   | 49.826 | 44.299   |
| Total |           | 178674| 11333  | 100.000| 100.000  |

Enantioenriched S-1h, 89% ee

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area  | Height | Area % | Height % |
|-------|-----------|-------|--------|--------|----------|
| 1     | 9.989     | 678937| 47129  | 94.701 | 95.414   |
| 2     | 10.700    | 37992 | 2265   | 5.299  | 4.586    |
| Total |           | 716930| 49394  | 100.000| 100.000  |
Racemic S-1i

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height  | Area %  | Height % |
|-------|-----------|--------|---------|---------|----------|
| 1     | 12.591    | 110150 | 7219    | 50.024  | 51.378   |
| 2     | 13.419    | 110043 | 6832    | 49.976  | 48.622   |
| Total |           | 220194 | 14051   | 100.000 | 100.000  |

Enantioenriched S-1i, 96% ee

Detector A Ch1 254nm

| Peak# | Ret. Time | Area   | Height  | Area %  | Height % |
|-------|-----------|--------|---------|---------|----------|
| 1     | 13.183    | 429320 | 27232   | 97.819  | 98.017   |
| 2     | 14.119    | 9571   | 551     | 2.181   | 1.983    |
| Total |           | 438890 | 27783   | 100.000 | 100.000  |
Racemic S-1j

**Detector A Ch1 254nm**

| Peak# | Ret. Time | Area  | Height | Area %    | Height % |
|-------|-----------|-------|--------|-----------|----------|
| 1     | 17.830    | 116347| 54572  | 49.994    | 63.499   |
| 2     | 32.340    | 1163916| 31370  | 50.006    | 36.501   |
| Total |           | 2327563| 85942  | 100.000   | 100.000  |

Enantioenriched S-1j, 91% ee

**Detector A Ch1 254nm**

| Peak# | Ret. Time | Area  | Height | Area %    | Height % |
|-------|-----------|-------|--------|-----------|----------|
| 1     | 18.929    | 11129 | 512    | 4.454     | 8.053    |
| 2     | 34.792    | 238760| 5845   | 95.546    | 91.947   |
| Total |           | 249889| 6357   | 100.000   | 100.000  |