Enantioselective, Lewis Base-Catalyzed Carbosulfenylation of Alkenylboronates by 1,2-Boronate Migration

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SUPPORTING INFORMATION

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General Experimental

Reaction solvents tetrahydrofuran (Fisher, HPLC grade, not stabilized) and dichloromethane (Fisher, HPLC grade, not stabilized) were dried by percolation through two columns packed with neutral alumina under positive pressure of argon. Methanol and ethanol were distilled from magnesium turnings under a nitrogen atmosphere. Triethylamine was distilled from calcium hydride under a nitrogen atmosphere. Xylenes (Fisher) was sparged with argon for 15 min before use. Solvents for filtration, transfers, chromatography, and recrystallizations were purchased from commercial sources and used as received. "Brine" refers to a saturated solution of sodium chloride in distilled water. Column chromatography was performed using Merck grade 9385, 60 Å silica gel. Visualization was accomplished by UV light or ceric ammonium molybdate (CAM) solution. Analytical TLC was performed on Merck silica gel plates with F_{254} indicator. R_f values reported were measured using a 10 x 2 cm plate. All reactions were conducted under an atmosphere of dry argon.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz (500 MHz, ^{1}H; 126 MHz, ^{13}C) spectrometer. Spectra are referenced to residual chloroform (δ = 7.26 ppm, ^{1}H; 77.16 ppm, ^{13}C). Chemical shifts are reported in parts per million. Assignments were obtained by reference to COSY, HMQC, HMBC, and TOCSY correlations. Elemental analysis was performed by the University of Illinois Microanalysis Laboratory or Robertson Microlit Laboratories. Mass spectrometry (MS) was performed by the University of Illinois Mass Spectrometry Laboratory. Electron Impact (EI) spectra were performed at 70 eV using methane as the carrier gas on a Finnagin-MAT C5 spectrometer. Electrospray Ionization (ESI) spectra were performed on a Micromass Q-ToF Ultima spectrometer. Data are reported in the form of m/z (intensity relative to the base peak = 100). Infrared spectra (IR) were recorded neat on a Perkin-Elmer FT-IR system and peaks were reported in cm^{-1} with indicated relative intensities: s (strong, 0-33% T); m (medium, 34-66% T); w (weak, 67-100% T). Melting points (m.p.) were determined on a Thomas-Hoover capillary melting point apparatus in sealed tubes and are corrected.

The following organolithium reagents were purchased from Sigma-Aldrich and titrated by the method of Gilman et al.[1-2] prior to use: phenyllithium (1.9 M in dibutyl ether), *n*-butyllithium (1.6 M or 2.5 M in hexanes), and *tert*-butyllithium (1.7 M in pentane). 3-Chloroperbenzoic acid was purchased from Sigma-Aldrich (≤77% by weight) and washed with phosphate buffer by the method of Aggarwal et al.[3] prior to use. *tert*-Butanol was distilled prior to use and stored over

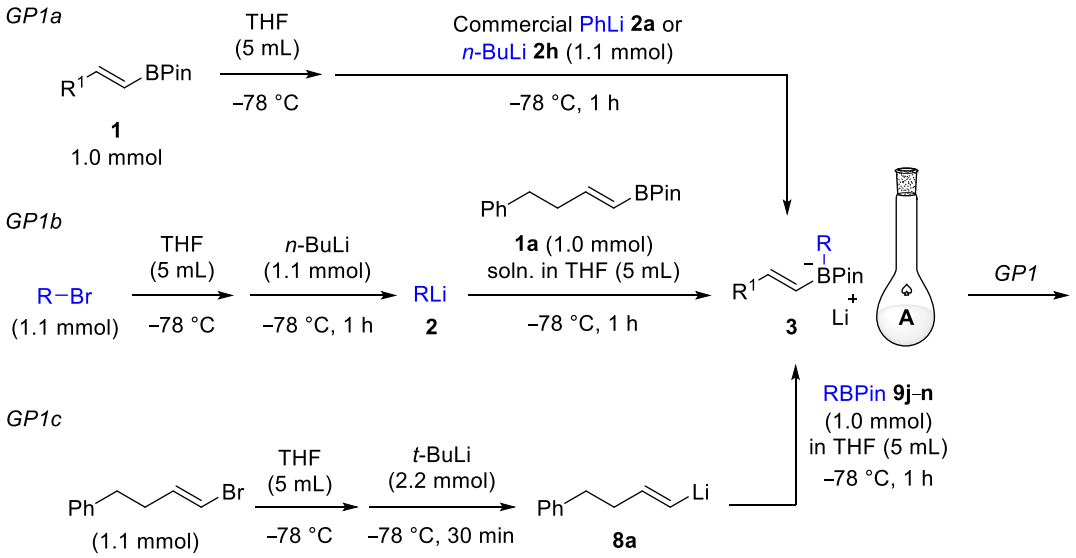
molecular sieves. The following commercial reagents were used as received: 1-bromo-4-methoxybenzene, 1-bromo-4-chlorobenzene, 1-bromo-4-(trifluoromethyl)benzene, 4-bromobenzonitrile, 1-bromo-4-vinylbenzene, 3-(4-bromophenyl)pyridine, 2-bromo-1,3-dimethylbenzene, 1,1,1,2-tetrachloroethane, sodium perborate tetrahydrate, hydrogen peroxide (Sigma-Aldrich, 30% w/w aq.), tetra-*n*-butylammonium chloride (Alfa-Aesar), sodium hydroxide, hexafluoroisopropanol (Oakwood), 2,2,2-trifluoroethanol (Oakwood), sodium carbonate, triphenylphosphine (Oakwood), nitromethane (Sigma-Aldrich), Raney nickel (Oakwood, ®2800 slurry in water, active catalyst), trimethyloxonium tetrafluoroborate (Sigma-Aldrich), lithium wire, *N*,*N*-dimethylnaphthalen-1-amine (Alfa-Aesar), ammonia (compressed gas), isopropoxypinacolborane, methanesulfonic anhydride, and 4-methoxyaniline.

Literature Preparations

The following alkenyl pinacolboranes were prepared by literature methods and the characterization data matched those previously reported: (*E*)-4-phenylbut-1-en-1-yl pinacolborane **1a**,[4] (*E*)-5-chloropent-1-en-1-yl pinacolborane **1c**,[4] (*E*)-6-bromohex-1-en-1-yl pinacolborane **1d**,[4] (*E*)-2-cyclohexylvinyl pinacolborane **1e**,[4] (*Z*)-5-phenylpent-2-en-2-yl pinacolborane **1g**,[5] isopropenyl pinacolborane **1h**,[6-7] and vinyl pinacolborane **1i**.[8] (*E*)-4-(*tert*-Butyldimethylsilyl)oxybut-1-en-1-yl pinacolborane **1b** was prepared from (but-3-yn-1-yloxy)(*tert*-butyl)dimethylsilane using a procedure described for an analogous transformation[4] and the characterization data matched those previously reported.[9] (*E*)-2-Methylhex-1-en-1-yl pinacolborane **1f** was prepared from (*Z*)-(2-bromohex-1-en-1-yl)pinacolborane[10] using a procedure described for an analogous transformation[11] and the characterization data matched those previously reported.[12] (*Z*)-4-Phenylbut-1-en-1-yl pinacolborane **1j** was prepared from 4-phenyl-1-butyne using a procedure described for an analogous transformation[13] and the characterization data matched those previously reported.[14] The following aryl pinacolboranes were prepared by literature methods and the characterization data matched those previously reported: (*o*-tolyl)pinacolboronic ester **9j**,[15] (napthalen-2-yl)pinacolboronic ester **9k**,[15] 5-(pinacolboryl)-1-tosyl-1*H* indole **9l**,[16] and methyl 4-(pinacolboryl)benzoate **9n**.[15] (3-Bromophenyl)pinacolboronic ester **9m** was prepared from (3-bromophenyl)pinacolboronic acid using a procedure described for an analogous transformation[15] and the characterization data matched those previously reported.[17] The precursor to **8a**, (*E*)-(4-bromobut-3-en-1-yl)benzene, was prepared by a literature method and the characterization data matched those previously reported.[18] Sulfenylating agents *N*-(phenylthio)saccharin **4a**[19] and *N*-(phenylthio)phthalimide **4c**[20] were prepared by literature methods and characterization data matched those previously reported. Catalyst (*S*)-**5** was prepared by a literature method and the characterization data matched those previously reported.[21]

Experimental Procedures (General)

GP1: *Carbosulfenylation of Vinyl Boronates by 1,2-Boronate Migration*



General procedures *GP1a*, *GP1b*, and *GP1c* only differ in how the boronate complex **3** is generated. The remaining steps are the same in all cases.

GP1a:

An oven-dried, 25-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (5 mL) and alkenylpinacolborane **1** (1.00 mmol). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A commercial solution of either phenyllithium **2a** in *n*-Bu_2O (1.05 mmol) or *n*-butyllithium **2h** in hexanes (1.10 mmol) was added dropwise over 10 min. After the addition, the resulting solution was stirred at –78 °C for 1 h. *GP1a* was used to generate **3aa**, **3ah**, **3ba**, **3ca**, **3da**, **3ea**, **3fa**, **3ga**, **3ha**, **3ia**, and **3ja**.

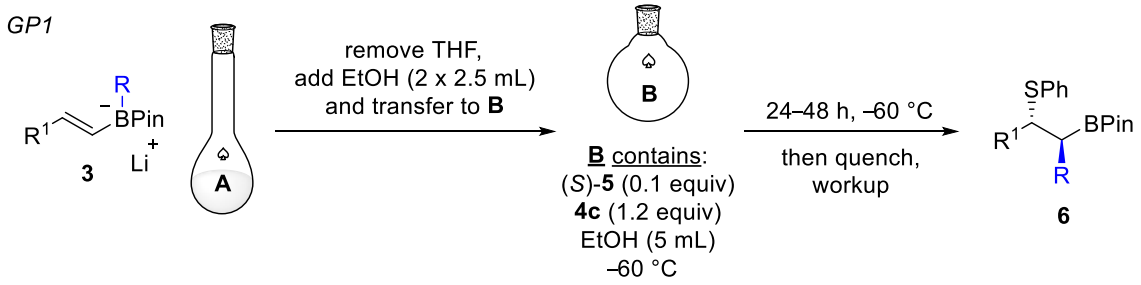
GP1b:

An oven-dried, 25-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (5 mL) and an appropriate bromoarene (1.10 mmol). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *n*-butyllithium in hexanes (1.10 mmol) was added dropwise over 10 min. The resulting solution of aryllithium **2** was stirred at –78 °C for 1 h. A solution of alkenylborane **1a** (1.00 mmol) in THF (5

mL) was added dropwise to flask **A**. The solution was stirred at –78 °C for 1 h. *GP1b* was used to generate **3ab**, **3ac**, **3ad**, **3ae**, **3af**, **3ag**, and **3ai**.

GP1c:

An oven-dried, 25-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (5 mL) and (*E*)-(4-bromobut-3-en-1-yl)benzene (1.10 mmol). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *tert*-butyllithium in pentane (2.20 mmol) was added dropwise over 10 min. The resulting solution of alkenyllithium **8a** was stirred at –78 °C for 30 min. A solution of arylboronic ester **9** (1.00 mmol) in THF (5 mL) was added dropwise to the freshly-prepared alkenyllithium **8a**, and the solution was stirred at –78 °C for 1 h. *GP1c* was used to generate **3aj**, **3ak**, **3al**, **3am**, and **3an**.



GP1:

A separate, oven-dried, 25-mL, Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (52 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. At this point, flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum until all of the THF was removed (typically 20–30 min). The resulting solid boronate complex **3** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate complex. Flask **B** was stirred at –60 °C for 24–48 h. The reaction was quenched by the

addition of sat. aq. NH_4Cl. The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The mixture was extracted three times with Et_2O and the combined organic extracts were dried over magnesium sulfate, filtered, and concentrated to afford the crude α-sulfenylated alkylborane **6**. If desired, the yield of borane **6** could be measured by quantitative ^{1}H-NMR using 1,1,1,2-tetrachloroethane as an internal standard. A Hamilton gastight syringe was used to transfer 1,1,1,2-tetrachloroethane (55 μL, 0.5 mmol) to the flask containing crude **6**, and the mixture was dissolved in chloroform-*d* (approx. 3 mL). An aliquot of this solution (approx. 0.25 mL) was passed through a pipet filter (to remove any insoluble components) into an NMR tube, and the filtrate was diluted with enough chloroform-*d* to reach a typical NMR sample volume. The ^{1}H signal of the internal standard (singlet, 4.31 ppm, 2H) was integrated and normalized to 1.00. Then, the integration value of any non-overlapping (1H) signal of **6** (typically in the 4.00-1.00 ppm region) is equal to the yield of **6**.

GP2: Oxidation of alkylborane **6** *to alcohol* **7** (less sterically encumbered)

A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6**, THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (616 mg, 4.0 mmol) and tetra-*n*-butylammonium chloride (28 mg, 0.1 mmol, optional) were added sequentially to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly at 25 °C and conversion was assessed by TLC (hexanes/EtOAc, 90:10, CAM). Upon completion, the oxidation was quenched with a reducing agent, either sodium bisulfite ($NaHSO_3$) or sodium thiosulfate ($Na_2S_2O_3$), and stirred for 15 min. The mixture was transferred to a separatory funnel and extracted multiple times with Et_2O. The combined organic phases were dried over magnesium sulfate, filtered, and concentrated to afford the crude alcohol **7** which was purified by silica gel chromatography.

GP3: Oxidation of borane **6** *to alcohol* **7** (more sterically encumbered)

A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6** and THF (10 mL). The turbid solution was cooled to 0 °C with an ice bath. To this solution was added a mixture of 30% aq. H_2O_2 (1 mL) and 3 M aq. NaOH (1 mL) also containing EDTA (1.0 mg/mL). The biphasic mixture was stirred rapidly at 0 °C. Conversion was assessed by TLC (hexanes/EtOAc, 90:10, CAM). Upon completion, the oxidation was quenched with a reducing agent, either sodium bisulfite ($NaHSO_3$) or sodium thiosulfate ($Na_2S_2O_3$), and stirred for 15 min.

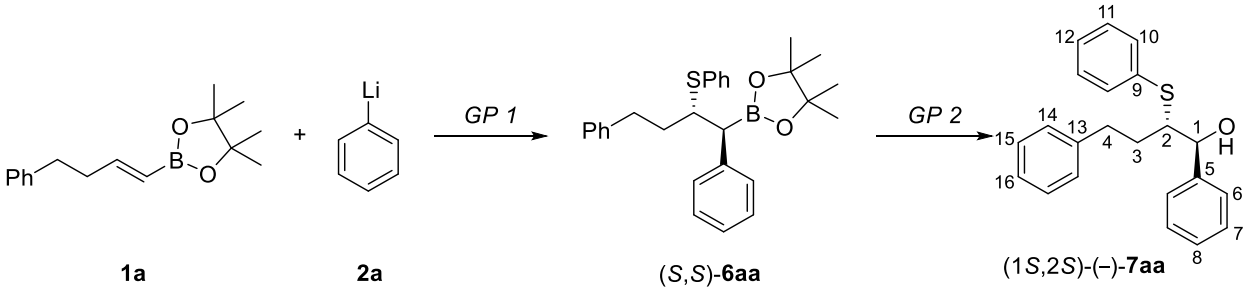
The mixture was transferred to a separatory funnel and diluted with diethyl ether (30 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 x 15 mL). The combined organic phases were washed with brine (25 mL) and then dried over magnesium sulfate, filtered, and concentrated to afford the crude alcohol **7** which was purified by silica gel chromatography.

Preparation of Racemic Standards ((±)-7)

The rapid background reactivity between boronate complexes **3** and reagent **4a** in aprotic solvents enabled an expedient synthesis of racemic products (±)-**7**. The general procedure is as follows. Boronate complex **3** was prepared on a 0.2 mmol scale by *GP1* (according to detailed procedures beginning on p. S9) at –78 °C in THF. Next, a solution of **4a** (1.20 equiv) in THF (1 mL) was added dropwise to the solution of **3** at –78 °C. The reaction mixture was slowly warmed to 25 °C over a period of several hours and stirring was continued at 25 °C for 12 h. The reaction was quenched with sat. aq. NH_4Cl (2.5 mL) and worked up according to *GP1* to afford crude (±)-**6**. The crude alkylboranes were oxidized to (±)-**7** using either *GP2* or *GP3* (according to detailed procedures beginning on p. S9) and purified in analogous fashion to their enantiomerically enriched counterparts.

Experimental Procedures (Detailed)

Preparation of (1*S*,2*S*)-(–)-**1,4-Diphenyl-2-(phenylthio)butan-1-ol (**(1*S*,2*S*)-(–)-**7aa)**



1a **2a** (*S*,*S*)-**6aa** (1*S*,2*S*)-(–)-**7aa**

Alkylborane **6aa** was prepared according to *GP1a*. An oven-dried, 25-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (5 mL) and (*E*)-4-phenylbut-1-en-1-yl pinacolborane **1a** (259.1 mg, 1.00 mmol). The resulting colorless solution was cooled to –78 °C using a dry ice/isopropanol bath, and then stirred for 15 min to allow the temperature to equilibrate. A solution of phenyllithium **2a** in diethyl ether (1.77 M, 595 μL, 1.05 mmol, 1.05 equiv) was added dropwise over 10 min, such that the internal temperature did not exceed –68 °C. The resulting pale, yellow solution was stirred at –78 °C for 1 h. A separate, oven-dried, 25-mL, Schlenk flask (**B**) equipped with a stir bar was charged with chiral (*S*)-catalyst **5** (51.6 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.9 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting beige-colored, foam solid boronate complex **3aa** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 36 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (2.5 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C. The mixture was diluted with Et_2O (5 mL) and water (5

mL) and stirred rapidly to dissolve all solids. The biphasic mixture was transferred to a 60-mL separatory funnel and the layers were separated. The aqueous layer was extracted with Et_2O (2 x 10 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford 551.6 mg of crude alkylborane **6aa** as a red oil. The yield of **6aa** was determined to be 97% by quantitative ^{1}H-NMR as described previously (p. S7).

Borane **6aa** was oxidized to alcohol **7aa** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6aa** (551.6 mg), THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (600.3 mg, 3.9 mmol) and tetra-*n*-butylammonium chloride (28.0 mg, 0.10 mmol) were added sequentially to the rapidly stirred biphasic mixture at 25 °C. The beige-colored mixture was stirred rapidly for 3 h. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of solid sodium bisulfite, $NaHSO_3$ (1.20 g) and the resulting cream-colored mixture was stirred for 15 min. Then, aq. NaOH was added (1 M, 20 mL) and the mixture was stirred for 30 min. The mixture was transferred to a separatory funnel and diluted with Et_2O (30 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (2 x 15 mL). The combined organic phases were washed with brine (25 mL) and then dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford 444.4 mg of crude **7aa** as a red oil. The product was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 90:10 (600 mL)) to afford 299.3 mg of **7aa** as a pink oil. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (135 °C ABT, 4.0 x 10^{-5} mmHg) to afford 283.0 mg (85% yield) of **7aa** as a viscous, pale, yellow oil.

Data for (1*S*,2*S*)-(–)-**7aa**:

b.p.: 135 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.50–7.44 (m, 2H, HC(10)), 7.35–7.26 (m, 8H, HC(6), HC(8), HC(7), HC(11), HC(12)), 7.22–7.17 (m, 2H, HC(15)), 7.16–7.11 (m, 1H, HC(16)), 6.96 (d, *J* = 7.1 Hz, 2H, HC(14)), 4.47 (dd, *J* = 8.4, 2.0 Hz, 1H, HC(1)), 3.39 (d, *J* = 2.0 Hz, 1H, OH), 3.15 (ddd, *J* = 10.0, 8.7, 3.5 Hz, 1H, HC(2)), 2.95 (ddd, *J* = 14.1, 9.4, 4.8 Hz, 1H, H_2C(4)), 2.65 (ddd, *J* = 13.9, 9.2, 7.5 Hz, 1H, H_2C(4)), 1.79–1.69 (m, 1H, H_2C(3)), 1.61 (dtd, *J* = 14.4, 9.7, 4.8 Hz, 1H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

141.3 (C(13)), 141.0 (C(5)), 133.5 (HC(10)), 133.0 (C(9)), 129.2 (HC(11) or HC(14) or HC(15) or HC(7)), 128.53 (two overlapping signals: HC(14) or HC(15) or HC(11) or HC(7)), 128.46 (HC(7) or HC(11) or HC(14) or HC(15)), 128.2 (HC(8)), 127.9 (HC(12)), 127.3 (HC(6)), 126.0 (HC(16)), 75.8 (HC(1)), 58.7 (HC(2)), 33.2 (H_2C(4)), 32.4 (H_2C(3)).

IR: (neat)

3436 (w), 3060 (w), 3026 (w), 2924 (w), 2858 (w), 1948 (w), 1879 (w), 1807 (w), 1602 (w), 1583 (w), 1495 (w), 1479 (w), 1453 (m), 1438 (w), 1383 (w), 1332 (w), 1319 (w), 1298 (w), 1239 (w), 1188 (w), 1156 (w), 1088 (w), 1061 (w), 1025 (m), 1001 (w), 985 (w), 912 (w), 843 (w), 824 (w), 782 (w), 743 (s), 695 (s), 636 (w), 603 (w), 561 (w), 512 (m), 488 (m).

LRMS: (EI, 70 eV)

51.0 (11), 65.1 (14), 77.0 (27), 79.0 (21), 91.0 (100), 92.1 (10), 107.0 (11), 110.0 (12), 115.0 (10), 117.1 (79), 118.1 (21), 123.0 (11), 135.0 (10), 228.1 (49), 334.1 (4), 335.1 (1).

Analysis: $C_{22}H_{22}OS$ (334.48)

Calcd: C, 79.00%; H, 6.63%

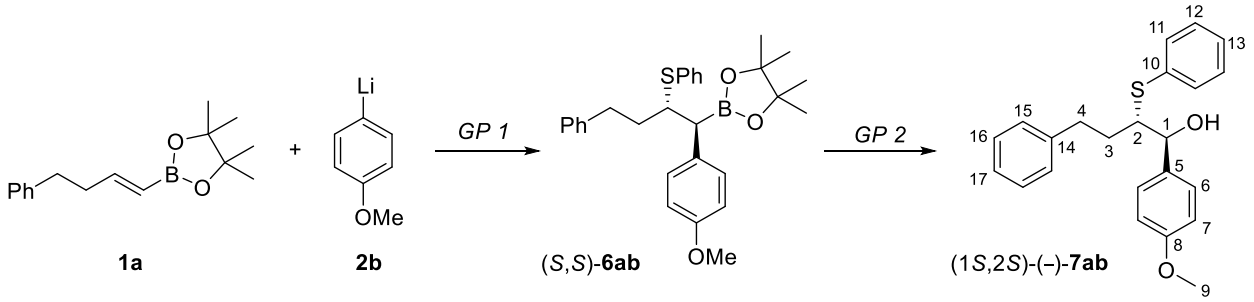
Found: C, 79.14%; H, 6.45%

TLC: R_f 0.14 (hexanes/EtOAc, 90:10, CAM)

HPLC: (1*R*,2*R*)-**7aa** t_R 13.9 min (2%); (1*S*,2*S*)-**7aa** t_R 14.9 min (98%) (Supelco Astec, hexanes/*i*-PrOH, 80:20, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –58.6 (*c* = 1.41 in 95% EtOH) (96% ee)

Preparation of (1*S*,2*S*)-(–)-**1-(4-Methoxyphenyl)-4-phenyl-2-(phenylthio)butan-1-ol (**(1*S*,2*S*)-(–)-**7ab)**



Alkylborane **6ab** was prepared according to *GP1b*. A flame-dried, 25-mL Schlenk flask (**A**) equipped with a magnetic stir bar, septum, and digital thermocouple probe was charged with 1-bromo-4-methoxybenzene (137.7 μL, 1.10 mmol, 1.10 equiv) and THF (5 ml). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *n*-butyllithium in hexanes (667 μL, 1.65 M, 1.10 equiv) was added dropwise over 10 min. The resulting solution of 4-methoxyphenyllithium **2b** was stirred at –78 °C for 1 h. Then, a solution of (*E*)-4-phenylbut-1-en-1-yl pinacolborane **1a** (1.0 mmol, 1.0 equiv, 258.2 mg) in THF (5 ml) was added dropwise to flask **A** over 15 min. The resulting solution of **3ab** was stirred at –78 °C for 1 h. A separate, oven-dried, 25-mL, Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3ab** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to

25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6ab**.

Borane **6ab** was oxidized to alcohol **7ab** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ab**, THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (616 mg, 4.0 mmol) was added to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 3 h. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with Et_2O (4 x 50 mL). The combined organic phases were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7ab**. The product was purified by chromatography (silica gel, 3 x 20 cm, wet load using CH_2Cl_2, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 90:10 (600 mL)) to afford 328.6 mg (90%) of **7ab** as an oil. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (160 °C ABT, 4.0 x 10^{-5} mmHg) to afford 321.6 mg (88% yield) of **7ab** as a viscous oil.

Data for (1*S*,2*S*)-(–)-**7ab**:

b.p.: 160 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.49 (dd, *J* = 7.5, 1.8 Hz, 2H, HC(11)), 7.37 – 7.28 (m, 3H, HC(12) and HC(13)), 7.22 – 7.17 (m, 4H, HC(6) and HC(16)), 7.14 (t, *J* = 7.2 Hz, 1H, HC(17)), 6.97 (d, *J* = 7.2 Hz, 2H, HC(15)), 6.83 (d, *J* = 8.6 Hz, 2H, HC(7)), 4.42 (dd, *J* = 8.6, 1.6 Hz, 1H, HC(1)), 3.80 (s, 3H, H_3C(9)), 3.37 (d, *J* = 1.9 Hz, 1H, OH), 3.12 (td, *J* = 9.8, 3.4 Hz, 1H, HC(2)), 2.95 (ddd, *J* = 14.1, 9.5, 4.7 Hz, 1H, H_2C(4)), 2.65 (ddd, *J* = 13.9, 9.2, 7.4 Hz, 1H, H_2C(4)), 1.72 (dddd, *J* = 13.1, 10.1, 7.3, 3.4 Hz, 1H, H_2C(3)), 1.58 (ddd, *J* = 14.4, 9.6, 4.7 Hz, 1H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

159.5 (C(8)), 141.3 (C(14)), 133.5 (C(11)), 133.0 (C(10)), 133.0 (C(5)), 129.2

(C(12)), 128.6 (C(15)), 128.4 (C(6)), 128.4 (C(16)), 127.9 (C(13)), 126.0 (C(17)), 113.9 (C(7)), 75.4 (C(1)), 58.7 (C(2)), 55.4 (C(9)), 33.2 (C(4)), 32.3 (C(3)).

IR: (neat)

3451 (w), 3025 (w), 2931 (w), 2835 (w), 1742 (w), 1610 (w), 1583 (w), 1511 (m), 1496 (w), 1478 (w), 1454 (w), 1438 (w), 1381 (w), 1302 (w), 1246 (m), 1173 (m), 1111 (w), 1087 (w), 1067 (w), 1029 (m), 908 (w), 832 (m), 734 (m), 695 (m), 647 (w), 609 (w), 574 (w), 540 (w), 516 (w).

LRMS: (ESI, $[M+Na]^+$)

129.1 (19), 237.1 (100), 347.1 (25), 387.1 (16).

HRMS: calcd for $C_{23}H_{24}O_2SNa$ ($[M+Na]^+$): 387.1395, found: 387.1394

Analysis: $C_{23}H_{24}O_2S$ (364.50)

Calcd: C, 75.79; H, 6.64%

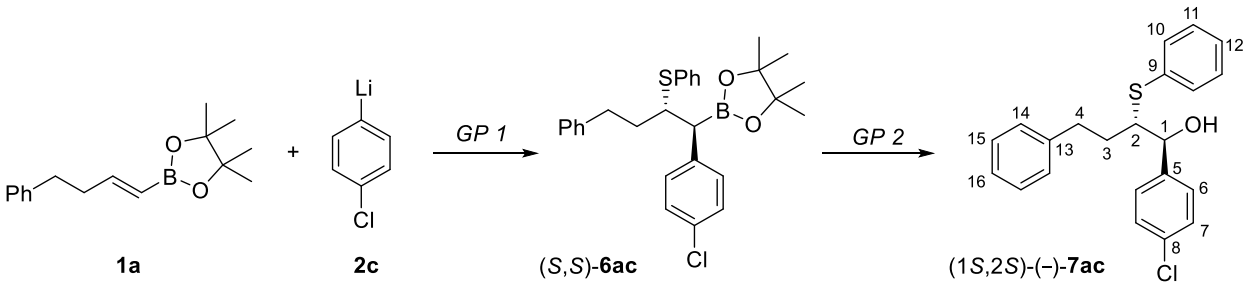
Found: C, 76.19; H, 6.45%

TLC: R_f 0.33 (hexanes/EtOAc, 83:17, CAM)

HPLC: (1*S*,2*S*)-**7ab** t_R 17.3 min (98%); (1*R*,2*R*)-**7ab** t_R 22.5 min (2%) (Regis (*R*,*R*)-Whelk O1, hexanes/*i*-PrOH, 80:20, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –60.2 (*c* = 0.72 in 100% EtOH) (96% ee)

Preparation of (1*S*,2*S*)-(–)-**1-(4-Chlorophenyl)-4-phenyl-2-(phenylthio)butan-1-ol (**(1*S*,2*S*)-(–)-**7ac)**



Alkylborane **6ac** was prepared according to *GP1b*. A flame-dried, 25-mL Schlenk flask (**A**) equipped with a magnetic stir bar, septum, and digital thermocouple probe was charged with 1-bromo-4-chlorobenzene (210.7 mg, 1.10 mmol, 1.10 equiv) and THF (5 ml). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *n*-butyllithium in hexanes (697 μL, 1.58 M, 1.10 equiv) was added dropwise over 10 min. The resulting solution of

4-chlorophenyllithium **2c** was stirred at –78 °C for 1 h. Then, a solution of (*E*)-4-phenylbut-1-en-1-yl pinacolborane **1a** (1.0 mmol, 1.0 equiv, 258.2 mg) in THF (5 ml) was added dropwise to flask **A** over 15 min. The resulting solution of **3ac** was stirred at –78 °C for 1 h. A separate, flame-dried, 50-mL Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3ac** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6ac**.

Borane **6ac** was oxidized to alcohol **7ac** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ac**, THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (616 mg, 4.0 mmol) was added to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 3 h. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with Et_2O (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over

magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7ac**. The product was purified by chromatography (silica gel, 3 x 20 cm, wet load using CH_2Cl_2, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 90:10 (600 mL)) to afford 316.2 mg (85% yield) of **7ac** as an oil. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (160 °C ABT, 4.0 x 10^{-5} mmHg) to afford 312.2 mg (85%) of **7ac** as a viscous oil.

Data for (1*S*,2*S*)-(–)-**7ac**:

b.p.: 160 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.46 (dd, *J* = 6.6, 2.9 Hz, 2H, HC(10)), 7.32 (dd, *J* = 4.7, 1.8 Hz, 3H, HC(11) and HC(12)), 7.28 – 7.15 (m, 7H, HC(6) and HC(7) and HC(15) and HC(16)), 7.00 (d, *J* = 7.2 Hz, 2H, HC(14)), 4.47 (dd, *J* = 8.2, 2.4 Hz, 1H, HC(1)), 3.41 (d, *J* = 2.4 Hz, 1H, OH), 3.10 (ddd, *J* = 9.9, 8.1, 3.5 Hz, 1H, HC(2)), 2.98 (ddd, *J* = 13.9, 9.2, 4.9 Hz, 1H, H_2C(4)), 2.69 (ddd, *J* = 13.9, 9.1, 7.5 Hz, 1H, H_2C(4)), 1.74 (dddd, *J* = 14.1, 9.0, 7.5, 3.5 Hz, 1H, H_2C(3)), 1.62 (dtd, *J* = 14.4, 9.6, 4.8 Hz, 1H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

141.1 (C(13)), 139.6 (C(5)), 133.9 (C(8)), 133.6 (C(10)), 132.6 (C(9)), 129.3 (C(11)), 128.6 (C(15)), 128.6 (C(14)), 128.5 (C(6) and C(7)), 128.1 (C(12)), 126.2 (C(16)), 75.0 (C(1)), 58.5 (C(2)), 33.2 (C(4)), 32.2 (C(3)).

IR: (neat)

3430 (w), 3059 (w), 3025 (w), 2927 (w), 1741 (w), 1599 (w), 1582 (w), 1490 (w), 1480 (w), 1453 (w), 1438 (w), 1409 (w), 1379 (w), 1307 (w), 1264 (w), 1184 (w), 1087 (m), 1068 (w), 1025 (w), 1013 (m), 910 (w), 831 (m), 784 (w), 738 (m), 694 (m), 632 (w), 607 (w), 550 (w), 517 (w), 489 (w).

LRMS: (ESI, $[M+Na]^+$)

216.9(7), 241.1(5), 365.1(4), 391.1(100).

HRMS: calcd for $C_{22}H_{21}ClOSNa$ ($[M+Na]^+$): 391.0899, found: 391.0883

Analysis: $C_{22}H_{21}ClOS$ (368.92)

Calcd: C, 71.63; H, 5.74%

Found: C, 71.65; H, 5.64%

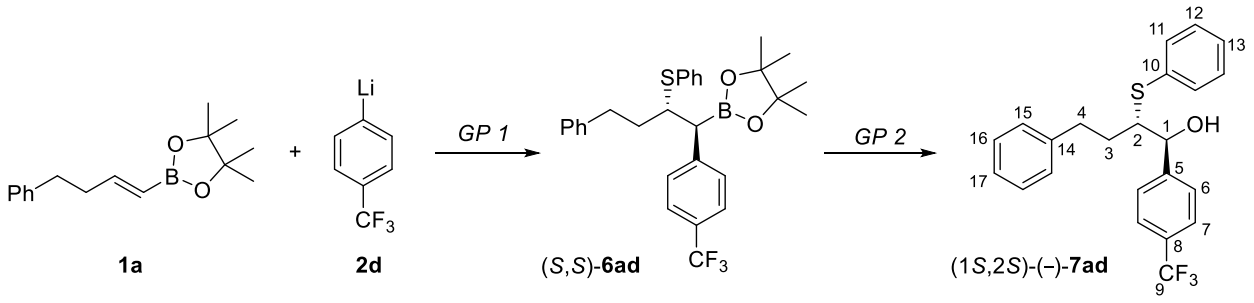
TLC: R_f 0.40 (hexanes/EtOAc, 83:17, CAM)

HPLC: (1*S*,2*S*)-**7ac** t_R 14.8 min (97%); (1*R*,2*R*)-**7ac** t_R 17.5 min (3%) (Regis (*R*,*R*)-Whelk

O1, hexanes/*i*-PrOH, 90:10, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –77.0 (*c* = 1.45 in 100% EtOH) (94% ee)

Preparation of (1*S*,2*S*)-(–)-**4-Phenyl-2-(phenylthio)-1-(4-(trifluoromethyl)phenyl)butan-1-ol (**(1*S*,2*S*)-(–)-**7ad)**



Alkylborane **6ad** was prepared according to *GP1b*. A flame-dried, 25-mL Schlenk flask (**A**) equipped with a magnetic stir bar, septum, and digital thermocouple probe was charged with 1-bromo-4-(trifluoromethyl)benzene (154 μL, 1.10 mmol, 1.10 equiv) and THF (5 ml). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *n*-butyllithium in hexanes (667 μL, 1.65 M, 1.10 equiv) was added dropwise over 10 min. The resulting solution of 4-(trifluoromethyl)phenyllithium **2d** was stirred at –78 °C for 1 h. Then, a solution of (*E*)-4-phenylbut-1-en-1-yl pinacolborane **1a** (258.2 mg, 1.0 mmol, 1.0 equiv) in THF (5 ml) was added dropwise to flask **A** over 15 min. The resulting solution of **3ad** was stirred at –78 °C for 1 h. A separate, flame-dried, 50-mL Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3ad** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5

mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6ad**.

Borane **6ad** was oxidized to alcohol **7ad** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ad**, THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (616 mg, 4.0 mmol) was added to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 2 h. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with Et_2O (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7ad**. The product was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 90:10 (600 mL)) to afford 344.0 mg (85% yield) of **7ad** as an oil. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (160 °C ABT, 4.0 x 10^{-5} mmHg) to afford 333.2 mg (83%) of **7ad** as a viscous oil.

Data for (1*S*,2*S*)-(–)-**7ad**:

b.p.: 160 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.52 (d, *J* = 8.2 Hz, 2H, HC(7)), 7.41 (dd, *J* = 6.5, 3.0 Hz, 2H, HC(11)), 7.36 (d, *J* = 8.1 Hz, 2H, HC(6)), 7.31 – 7.27 (m, 3H, HC(12) and HC(13)), 7.21 (t, *J* = 7.2 Hz, 2H, HC(16)), 7.16 (dd, *J* = 8.6, 5.8 Hz, 1H, HC(17)), 6.99 (d, *J* = 7.2 Hz, 2H, HC(15)), 4.55 (dd, *J* = 7.8, 2.9 Hz, 1H, HC(1)), 3.42 (d, *J* = 2.8 Hz, 1H, OH), 3.14 (ddd, *J* = 9.8, 7.7, 3.7 Hz, 1H, HC(2)), 2.99 (ddd, *J* = 13.8, 8.9, 4.9 Hz, 1H, H_2C(4)),

2.70 (dt, *J* = 13.9, 8.2 Hz, 1H, $H_2C(4)$), 1.75 (dtd, *J* = 16.6, 8.2, 3.7 Hz, 1H, $H_2C(3)$), 1.66 (dtd, *J* = 14.4, 9.5, 4.9 Hz, 1H, $H_2C(3)$).

^{13}C NMR: (126 MHz, $CDCl_3$)

145.2 (C(5)), 140.9 (C(14)), 133.5 (C(11)), 132.5 (C(10)), 130.3 (q, *J* = 32.3 Hz, 1C, C(8)), 129.3 (C(12)), 128.6 (C(15)), 128.5 (C(16)), 128.1 (C(13)), 127.5 (C(6)), 126.2 (C(17)), 125.3 (q, *J* = 3.8 Hz, 1C, C(7)), 124.2 (q, *J* = 272.0 Hz, 1C, C(9)), 75.0 (C(1)), 58.3 (C(2)), 33.2 (C(4)), 32.3 (C(3)).

^{19}F NMR: (471 MHz, $CDCl_3$)

–62.56.

IR: (neat)

3429 (w), 3061 (w), 3026 (w), 2932 (w), 1619 (w), 1602 (w), 1583 (w), 1496 (w), 1479 (w), 1454 (w), 1439 (w), 1416 (w), 1383 (w), 1323 (s), 1162 (m), 1119 (m), 1087 (w), 1066 (s), 1016 (m), 911 (w), 844 (w), 744 (m), 696 (m), 609 (w), 515 (w), 491 (w).

LRMS: (ESI, $[M+Na]^+$)

275.1 (100), 341.1 (59), 425.1 (55).

HRMS: calcd for $C_{23}H_{21}F_3OSNa$ ($[M+Na]^+$): 425.1163, found: 425.1154

Analysis: $C_{23}H_{21}F_3OS$ (402.48)

Calcd: C, 68.64; H, 5.26%

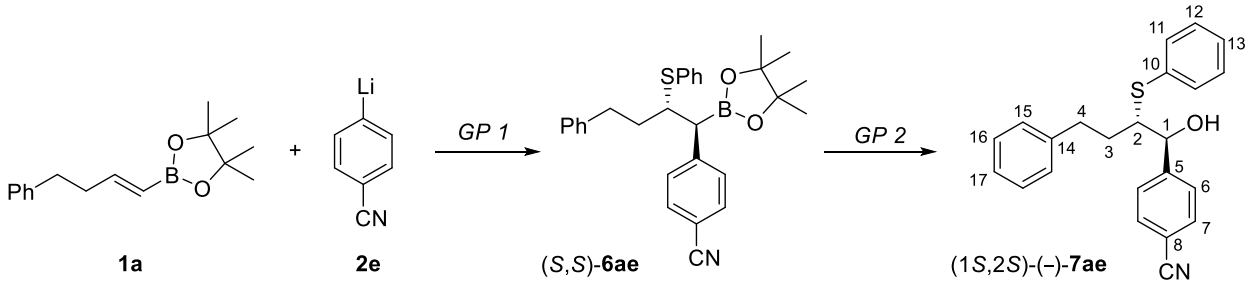
Found: C, 68.36; H, 5.16%

TLC: R_f 0.38 (hexanes/EtOAc, 83:17, CAM)

HPLC: (1*S*,2*S*)-**7ad** t_R 10.8 min (97%); (1*R*,2*R*)-**7ad** t_R 12.5 min (3%) (Regis (*R*,*R*)-Whelk O1, hexanes/*i*-PrOH, 90:10, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –68.2 (*c* = 1.13 in 100% EtOH) (94% ee)

Preparation of 4-((1*S*,2*S*)-(–)-**1-Hydroxy-4-phenyl-2-(phenylthio)butyl)benzonitrile ((**1*S*,2*S*)-(–)-**7ae)**



Alkylborane **6ae** was prepared by a **modification** of *GP1b*. A flame-dried, 25-mL Schlenk flask (**A**) equipped with a magnetic stir bar, septum, and digital thermocouple probe was charged with (*E*)-4-phenylbut-1-en-1-yl pinacolborane **1a** (516.4 mg, 2.0 mmol, 1.0 equiv), 4-bromobenzonitrile (436.8 mg, 2.4 mmol, 1.2 equiv) and THF (10 ml). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *n*-butyllithium in hexanes (1.35 mL, 1.55 M, 1.05 equiv) was added dropwise over 10 min. The resulting solution of **3ae** was stirred at –78 °C for 1 h. A separate, flame-dried, 50-mL Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (104.0 mg, 0.20 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (700.0 mg, 2.40 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (10 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3ae** in flask **A** was taken up in ethanol (5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory

funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6ae**.

Borane **6ae** was oxidized to alcohol **7ae** by a **modification** of *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ae**, THF (20 mL) and sat. aq. NH_4Cl solution (20 mL). Sodium perborate tetrahydrate (1.232 g, 8.0 mmol) was added to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 3 h. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with Et_2O (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7ae**. The product was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 90:10 (600 mL) to 83:17 (600 mL)) to afford 441.1 mg (61% yield) of **7ae** as an oil. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (160 °C ABT, 4.0 x 10^{-5} mmHg) to afford 432.9 mg (60%) of **7ae** as a viscous oil.

Data for (1*S*,2*S*)-(–)-**7ae**:

b.p.: 160 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.54 (d, *J* = 8.2 Hz, 2H, HC(7)), 7.41 – 7.37 (m, 2H, HC(11)), 7.35 (d, *J* = 8.2 Hz, 2H, HC(6)), 7.31 – 7.27 (m, 3H, HC(12) and HC(13)), 7.23 (t, *J* = 7.2 Hz, 2H, HC(16)), 7.18 (t, *J* = 7.2 Hz, 1H, HC(17)), 7.00 (d, *J* = 7.0 Hz, 2H, HC(15)), 4.56 (d, *J* = 7.4 Hz, 1H, HC(1)), 3.43 (s, 1H, OH), 3.12 (ddd, *J* = 9.9, 7.4, 3.8 Hz, 1H, HC(2)), 2.98 (ddd, *J* = 13.9, 8.7, 5.1 Hz, 1H, H_2C(4)), 2.72 (dt, *J* = 14.0, 8.2 Hz, 1H, H_2C(4)), 1.74 (dddd, *J* = 15.2, 11.3, 7.3, 3.3 Hz, 1H, H_2C(3)), 1.70 – 1.63 (m, 1H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

146.6 (C(5)), 140.8 (C(14)), 133.5 (C(11)), 132.3 (C(10)), 132.1 (C(7)), 129.3 (C(12)), 128.6 (C(16)), 128.5 (C(15)), 128.2 (C(13)), 127.9 (C(6)), 126.3 (C(17)),

118.8 (C(9)), 111.8 (C(8)), 74.9 (C(1)), 58.0 (C(2)), 33.1 (C(4)), 32.3 (C(3)).

IR: (neat)

3452 (w), 3059 (w), 3026 (w), 2928 (w), 2228 (w), 1607 (w), 1582 (w), 1496 (w), 1481 (w), 1453 (w), 1438 (w), 1409 (w), 1382 (w), 1265 (w), 1191 (w), 1086 (w), 1068 (w), 1024 (w), 1000 (w), 909 (w), 840 (w), 736 (m), 695 (m), 647 (w), 610 (w), 549 (w), 533 (w), 486 (w).

LRMS: (ESI, $[M+Na]^+$)

196.9 (4), 232.1 (5), 256.8 (4), 382.1 (100).

HRMS: calcd for $C_{23}H_{21}NOSNa$ ($[M+Na]^+$): 382.1242 found: 382.1226

Analysis: $C_{23}H_{21}NOS$ (359.49)

Calcd: C, 76.85; H, 5.89; N, 3.90%

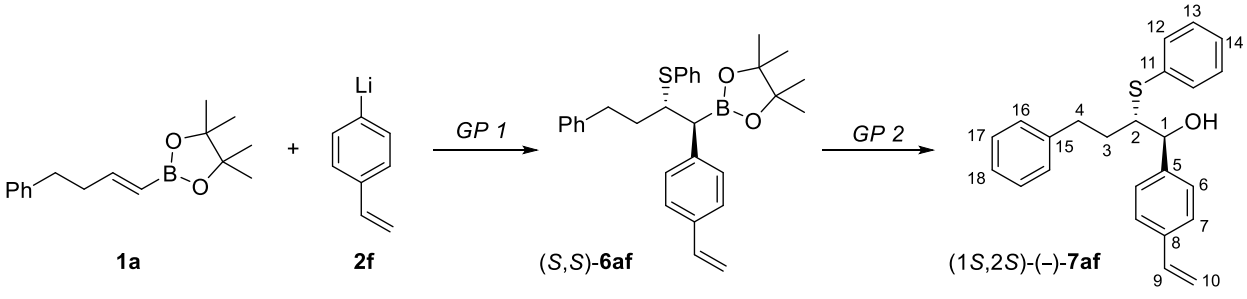
Found: C, 76.72; H, 5.92; N, 3.98%

TLC: R_f 0.28 (hexanes/EtOAc, 80:20, CAM)

HPLC: (1*S*,2*S*)-**7ae** t_R 39.7 min (94%); (1*R*,2*R*)-**7ae** t_R 46.2 min (6%) (Regis (*R*,*R*)-Whelk O1, hexanes/*i*-PrOH, 90:10, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –112.4 (*c* = 0.97 in 100% EtOH) (88% ee)

Preparation of (1*S*,2*S*)-(–)-**4-Phenyl-2-(phenylthio)-1-(4-vinylphenyl)butan-1-ol (**(1*S*,2*S*)-(–)-**7af)**



Alkylborane **6af** was prepared according to *GP1b*. A flame-dried, 25-mL Schlenk flask (**A**) equipped with a magnetic stir bar, septum, and digital thermocouple probe was charged with 1-bromo-4-vinylbenzene (144 μL, 1.10 mmol, 1.10 equiv) and THF (5 ml). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *n*-butyllithium in hexanes (645 μL, 1.58 M, 1.02 equiv) was added dropwise over 10 min. The resulting solution of (4-

vinylphenyl)lithium **2f** was stirred at –78 °C for 1 h. Then, a solution of (*E*)-4-phenylbut-1-en-1-yl pinacolborane **1a** (258.2 mg, 1.0 mmol, 1.0 equiv) in THF (5 ml) was added dropwise to flask **A** over 15 min. The resulting solution of **3af** was stirred at –78 °C for 30 min. A separate, flame-dried, 50-mL Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3af** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6af**.

Borane **6af** was oxidized to alcohol **7af** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6af**, THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (616 mg, 4.0 mmol) was added to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 2 h. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with Et_2O (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over

magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7af**. The product was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 90:10 (600 mL)) to afford 248.8 mg (69% yield) of **7af** as an oil. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (160 °C ABT, 4.0 x 10^{-5} mmHg) to afford 215.3 mg (60%) of **7af** as a viscous oil. A small quantity of polymeric residue formed (and was left behind) during the distillation step.

Data for (1*S*,2*S*)-(–)-**7af**:

b.p.: 160 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.51 – 7.45 (m, 2H, HC(12)), 7.37 – 7.28 (m, 5H, HC(7) and HC(14) and HC(13)), 7.21 (dd, *J* = 17.4, 7.9 Hz, 4H, HC(6) and HC(17)), 7.15 (t, *J* = 7.3 Hz, 1H, HC(18)), 6.98 (d, *J* = 6.9 Hz, 2H, HC(16)), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H, HC(9)), 5.74 (dd, *J* = 17.6, 0.9 Hz, 1H, H_2C(10)), 5.24 (dd, *J* = 10.8, 0.9 Hz, 1H, H_2C(10)), 4.46 (d, *J* = 8.5 Hz, 1H, HC(1)), 3.39 (s, 1H, OH), 3.14 (ddd, *J* = 10.1, 8.5, 3.5 Hz, 1H, HC(2)), 2.97 (ddd, *J* = 13.9, 9.3, 4.6 Hz, 1H, H_2C(4)), 2.66 (ddd, *J* = 13.9, 9.3, 7.4 Hz, 1H, H_2C(4)), 1.74 (dddd, *J* = 13.0, 9.6, 7.3, 3.5 Hz, 1H, H_2C(3)), 1.60 (dtd, *J* = 14.5, 9.8, 4.8 Hz, 1H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

141.2 (C(15)), 140.6 (C(5)), 137.5 (C(8)), 136.6 (C(9)), 133.6 (C(12)), 132.9 (C(11)), 129.2 (C(13)), 128.6 (C(16)), 128.5 (C(17)), 128.0 (C(14)), 127.5 (C(6)), 126.4 (C(7)), 126.1 (C(18)), 114.1 (C(10)), 75.5 (C(1)), 58.6 (C(2)), 33.2 (C(4)), 32.3 (C(3)).

IR: (neat)

3432 (w), 3059 (w), 3024 (w), 2923 (w), 2856 (w), 1629 (w), 1602 (w), 1582 (w), 1510 (w), 1495 (w), 1478 (w), 1453 (w), 1438 (w), 1405 (w), 1381 (w), 1285 (w), 1176 (w), 1116 (w), 1087 (w), 1067 (w), 1025 (w), 1015 (w), 988 (w), 907 (w), 842 (m), 742 (m), 694 (m), 609 (w), 490 (w).

LRMS: (ESI, $[M+Na]^+$)

117.1 (35), 129.1 (21), 233.1 (100), 328.0 (11), 343.2 (28), 383.1 (28).

HRMS: calcd for $C_{24}H_{24}OSNa$ ($[M+Na]^+$): 383.1446, found: 383.1438

Analysis: $C_{24}H_{24}OS$ (360.52)

Calcd: C, 79.96; H, 6.71%

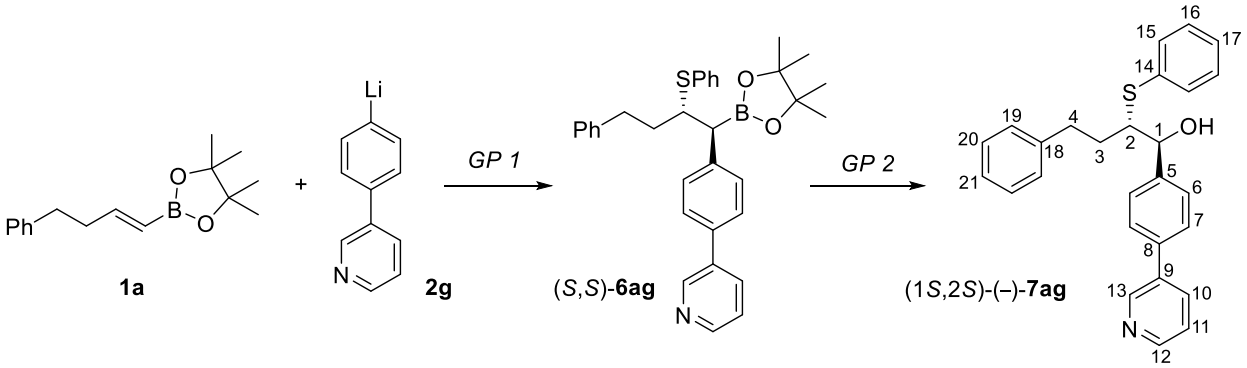
Found: C, 79.81; H, 6.52%

TLC: R_f 0.37 (hexanes/EtOAc, 83:17, CAM)

HPLC: (1*S*,2*S*)-**7af** t_R 20.8 min (98%); (1*R*,2*R*)-**7af** t_R 29.0 min (2%) (Regis (*R*,*R*)-Whelk O1, hexanes/*i*-PrOH, 90:10, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –48.1 (*c* = 1.57 in 100% EtOH) (96% ee)

Preparation of (1*S*,2*S*)-(–)-**4-Phenyl-2-(phenylthio)-1-(4-(pyridin-3-yl)phenyl)butan-1-ol (**(1*S*,2*S*)-(–)-**7ag)**



Alkylborane **6ag** was prepared according to *GP1b*. A flame-dried, 25-mL Schlenk flask (**A**) equipped with a magnetic stir bar, septum, and digital thermocouple probe was charged with 3-(4-bromophenyl)pyridine (327.6 mg, 1.4 mmol, 1.4 equiv) and THF (5 ml). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *n*-butyllithium in hexanes (903 uL, 1.55M, 1.4 equiv) was added dropwise over 10 min. The resulting solution of (4-(pyridin-3-yl)phenyl)lithium **2g** was stirred at –78 °C for 1 h. Then, a solution of (*E*)-4-phenylbut-1-en-1-yl pinacolborane **1a** (1.0 mmol, 1.0 equiv, 258.2 mg) in THF (5 ml) was added dropwise to flask **A** over 15 min. The resulting solution of **3ag** was stirred at –78 °C for 1 h. A separate, flame-dried, 50-mL Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (436.5 mg, 1.50 mmol, 1.50 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool.

Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3ag** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min at –60 °C. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6ag**.

Borane **6ag** was oxidized to alcohol **7ag** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ag**, THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (616 mg, 4.0 mmol) was added to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 3 h. Full conversion was observed by TLC (CH_2Cl_2/EtOAc, 85:15, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with Et_2O (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7ag**. The product was purified by chromatography (silica gel, 3 x 20 cm, wet load with CH_2Cl_2, 25-mL fractions, CH_2Cl_2/EtOAc gradient elution: 95:5 (600 mL) to 90:10 (600 mL)) to afford 320.2 mg (78% yield) of **7ag** as a white solid. Precipitation from hexanes/Et_2O afforded 299.9 mg (73%) of analytically pure **7ag** as a white solid.

Data for (1*S*,2*S*)-(–)-**7ag**:

m.p.: 121–123 °C (hexanes/Et_2O)

^{1}H NMR: (500 MHz, $CDCl_3$)

8.81 – 8.77 (m, 1H, HC(13)), 8.60 – 8.55 (m, 1H, HC(12)), 7.88 – 7.82 (m, 1H,

HC(10)), 7.49 (d, *J* = 8.0 Hz, 2H, HC(7)), 7.48 – 7.43 (m, 2H, HC(15)), 7.38 (d, *J* = 8.5 Hz, 2H, HC(6)), 7.37 – 7.34 (m, 1H, HC(11)), 7.33 – 7.27 (m, 3H, HC(16) and HC(17)), 7.24 – 7.18 (m, 2H, HC(20)), 7.18 – 7.13 (m, 1H, HC(21)), 7.01 (d, *J* = 7.5 Hz, 2H, HC(19)), 4.59 (d, *J* = 7.8 Hz, 1H, HC(1)), 3.63 (bs, 1H, OH), 3.22 (ddd, *J* = 9.6, 7.9, 3.5 Hz, 1H, HC(2)), 3.00 (ddd, *J* = 14.1, 9.3, 4.9 Hz, 1H, H_2C(4)), 2.71 (ddd, *J* = 13.9, 9.2, 7.3 Hz, 1H, H_2C(4)), 1.88 – 1.80 (m, 1H, H_2C(3)), 1.73 – 1.63 (m, 1H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

148.6 (HC(12)), 148.3 (HC(13)), 141.22 (C(18) or C(5)), 141.20 (C(18) or C(5)), 137.5 (C(8)), 136.4 (C(9)), 134.5 (HC(10)), 133.4 (HC(15)), 133.0 (C(14)), 129.2 (HC(16)), 128.6 HC(19)), 128.5 (HC(20)), 128.0 (HC(6)), 127.9 (HC(17)), 127.2 (HC(7)), 126.1 (HC(21)), 123.7 (HC(11)), 75.3 (HC(1)), 58.4 (HC(2)), 33.2 (H_2C(4)), 32.4 (H_2C(3)).

IR: (neat)

3219 (w), 1579 (w), 1495 (w), 1476 (w), 1454 (w), 1434 (w), 1391 (w), 1339 (w), 1302 (w), 1086 (w), 1025 (w), 1003 (w), 939 (w), 857 (w), 799 (w), 739 (m), 698 (m), 688 (m), 649 (w), 624 (w), 607 (w), 592 (w), 557 (w), 494 (w), 476 (w).

LRMS: (ESI, $[M+H]^+$)

302.2 (2), 412.2 (100).

HRMS: calcd for $C_{27}H_{26}NOS$ ($[M+H]^+$): 412.1735, found: 412.1735

Analysis: $C_{27}H_{25}NOS$ (411.56)

Calcd: C, 78.80; H, 6.12%; N, 3.40%

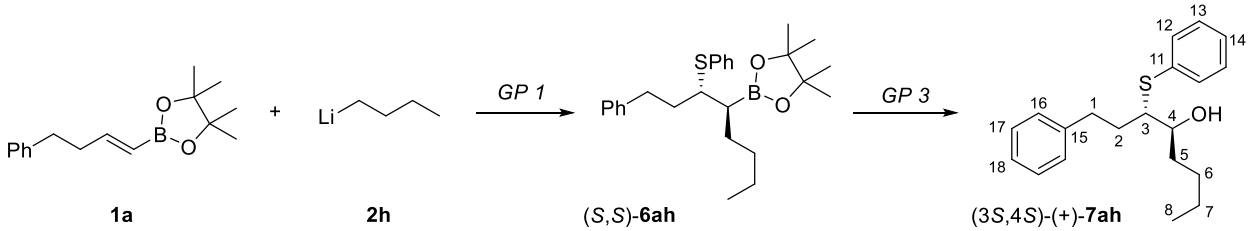
Found: C, 78.44; H, 6.05%; N, 3.53%

TLC: R_f 0.31 (hexanes/EtOAc, 50:50, CAM)

HPLC: (1*R*,2*R*)-**7ag** t_R 45.30 min (19%); (1*S*,2*S*)-**7ag** t_R 48.83 min (81%) (Supelco Astec, hexanes/*i*-PrOH, 80:20, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –64.0 (*c* = 1.07 in 100% EtOH) (62% ee)

Preparation of (3*S*,4*S*)-(+)-**1-Phenyl-3-(phenylthio)octan-4-ol (**(3*S*,4*S*)-(+)-**7ah)**



1a **2h** (*S*,*S*)-**6ah** (3*S*,4*S*)-(+)-**7ah**

Alkylborane **6ah** was prepared according to *GP1a*. A flame-dried, 25-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (5 mL) and (*E*)-4-phenylbut-1-en-1-yl pinacolborane **1a** (258.2 mg, 1.00 mmol). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *n*-butyllithium **2h** in hexanes (696 μL, 1.58 M, 1.10 equiv) was added dropwise over 10 min, and the resulting solution of **3ah** was stirred at –78 °C for 1 h. A separate, flame-dried, 50-mL Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3ah** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –78 °C for 48 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford

crude alkylborane **6ah**.

Borane **6ah** was oxidized to alcohol **7ah** according to *GP3*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ah** and THF (10 mL). The turbid solution was cooled to 0 °C with an ice bath. To this solution was added a mixture of 30% aq. H_2O_2 (1 mL) and 3 M aq. NaOH (1 mL) also containing EDTA (1.0 mg/mL). The biphasic mixture was stirred rapidly at 0 °C for 30 min. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with Et_2O (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7ah**. The product was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 97:3 (600 mL) to 94:6 (600 mL)) to afford 153.9 mg (49% yield) of **7ah** as an oil. The product was purified to analytical standard by diffusion pump Kugelrohr distillation (160 °C ABT, 4.0 x 10^{-5} mmHg) to afford 152.4 mg (48%) of **7ah** as a viscous oil.

Data for (3*S*,4*S*)-(+)-**7ah**:

b.p.: 160 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.61 – 7.56 (m, 2H, HC(10)), 7.48 – 7.38 (m, 5H, HC(15) and HC(12) and HC(11)), 7.37 – 7.29 (m, 3H, HC(16) and HC(14)), 3.81 – 3.70 (m, 1H, HC(4)), 3.17 (dp, *J* = 12.6, 4.0 Hz, 2H, HC(3) and H_2(1)), 2.96 (ddt, *J* = 13.6, 10.3, 4.8 Hz, 1H, H_2C(1)), 2.54 (s, 1H, OH), 2.22 (dtq, *J* = 13.8, 7.4, 3.7 Hz, 1H, H_2C(2)), 2.03 – 1.92 (m, 1H, H_2C(2)), 1.82 – 1.73 (m, 1H, H_2C(5)), 1.67 – 1.51 (m, 2H, H_2C(5) and H_2C(6)), 1.48 – 1.36 (m, 3H, H_2C(6) and H_2C(7)), 1.05 – 0.98 (m, 3H, H_3C(8)).

^{13}C NMR: (126 MHz, $CDCl_3$)

141.6 (C(13)), 134.8 (C(9)), 132.4 (C(10)), 129.1 (C(15)), 128.6 (C(11)), 128.6 (C(14)), 127.3 (C(12)), 126.1 (C(16)), 73.2 (C(4)), 56.8 (C(3)), 34.0 (C(5)), 33.6 (C(1)), 33.3 (C(2)), 28.1 (C(6)), 22.8 (C(7)), 14.1 (C(8)).

IR: (neat)

3428 (w), 3060 (w), 3025 (w), 2929 (w), 2858 (w), 1740 (w), 1602 (w), 1583 (w), 1495 (w), 1479 (w), 1454 (w), 1438 (w), 1378 (w), 1272 (w), 1121 (w), 1088 (w),

1067 (w), 1025 (w), 993 (w), 903. (w), 740 (m), 694 (m), 585 (w), 562 (w), 487 (w).

LRMS: (ESI, $[M+Na]^+$)

187.1 (5), 227.1 (3), 297.2 (3), 337.2 (100), 352. 2(35).

HRMS: calcd for $C_{20}H_{26}OSNa$ ($[M+Na]^+$): 337.1602, found: 337.1589

Analysis: $C_{20}H_{26}OS$ (314.49)

Calcd: C, 76.38; H, 8.33%

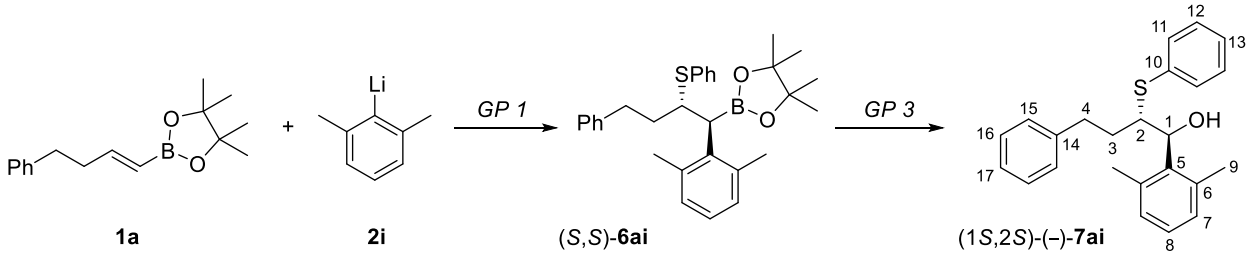
Found: C, 76.35; H, 8.38%

TLC: R_f 0.46 (hexanes/EtOAc, 83:17, CAM)

HPLC: (3*S*,4*S*)-**7ah** t_R 21.5 min (81%); (3*R*,4*R*)-**7ah** t_R 23.8 min (19%) (Supelco Astec, hexanes/*i*-PrOH, 95:5, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ +17.1 (*c* = 1.04 in 100% EtOH) (62% ee)

Preparation of (1*S*,2*S*)-(–)-**1-(2,6-Dimethylphenyl)-4-phenyl-2-(phenylthio)butan-1-ol (**(1*S*,2*S*)-(–)-**7ai)**



Alkylborane **6ai** was prepared according to *GP1b*. A flame-dried, 25-mL Schlenk flask (**A**) equipped with a magnetic stir bar, septum, and digital thermocouple probe was charged with 2-bromo-1,3-dimethylbenzene (147 μL, 1.10 mmol, 1.10 equiv) and THF (5 ml). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *n*-butyllithium in hexanes (667 μL, 1.65 M, 1.10 equiv) was added dropwise over 10 min. The resulting solution of (2,6-dimethylphenyl)lithium **2i** was stirred at –78 °C for 1 h. Then, a solution of (*E*)-4-phenylbut-1-en-1-yl pinacolborane **1a** (258.2 mg, 1.0 mmol, 1.0 equiv) in THF (5 ml) was added dropwise to flask **A** over 15 min. The resulting solution of **3ai** was stirred at –78 °C for 30 min followed by 25 °C for 30 min. A separate, flame-dried, 50-mL Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove

box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h, was returned to –78 °C and placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3ai** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with diethyl ether (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6ai**. As compound **7ai** is difficult to separate from catalyst (*S*)-5 by chromatography, **6ai** was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/CH_2Cl_2 gradient elution: 75:25 (600 mL) to 65:35 (600 mL)) prior to oxidation.

Borane **6ai** was oxidized to alcohol **7ai** according to *GP3*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ai** and THF (10 mL). The turbid solution was cooled to 0 °C with an ice bath. To this solution was added a mixture of 30% aq. H_2O_2 (1 mL) and 3 M aq. NaOH (1 mL) also containing EDTA (1.0 mg/mL). The biphasic mixture was stirred rapidly at 0 °C for 30 min. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with diethyl ether (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over magnesium sulfate, filtered, and

concentrated (30 °C, 50 mmHg) to afford crude **7ai**. The product was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 97:3 (600 mL) to 94:6 (600 mL)) to afford 305.3 mg (84% yield) of **7ai** as an oil. The product was purified to analytical standard by diffusion pump Kugelrohr distillation (160 °C ABT, 4.0 x 10^{-5} mmHg) to afford 300.1 mg (83%) of **7ai** as a viscous oil.

Data for (1*S*,2*S*)-(–)-**7ai**:

b.p.: 160 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.61 – 7.57 (m, 2H, HC(11)), 7.40 – 7.33 (m, 3H, HC(12) and HC(13)), 7.19 – 7.10 (m, 3H, HC(16) and HC(17)), 7.04 (t, *J* = 7.6 Hz, 1H, HC(8)), 6.92 (d, *J* = 7.6 Hz, 2H, HC(7)), 6.89 – 6.86 (m, 2H, HC(15)), 4.92 (d, *J* = 10.5 Hz, 1H, HC(1)), 3.47 (td, *J* = 10.8, 2.9 Hz, 1H, HC(2)), 3.30 (s, 1H, OH), 2.91 (ddd, *J* = 14.0, 7.9, 4.4 Hz, 1H, H_2C(4)), 2.69 (dt, *J* = 14.0, 8.4 Hz, 1H, H_2C(4)), 2.19 (s, 6H, H_3C(9)), 1.58 (dddd, *J* = 14.1, 10.9, 7.8, 4.5 Hz, 1H, H_2C(3)), 1.49 (dtd, *J* = 14.2, 8.7, 2.9 Hz, 1H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

141.0 (C(14)), 137.3 (C(6)), 135.7 (C(5)), 134.4 (C(11)), 132.1 (C(10)), 129.2 (C(12)), 128.6 (C(15)), 128.4 (C(16)), 128.3 (C(13)), 127.7 (C(8)), 126.1 (C(17)), 72.3 (C(1)), 55.8 (C(2)), 32.9 (C(4)), 31.6 (C(3)), 21.0 (C(9)).

IR: (neat)

3465 (w), 3060 (w), 3024 (w), 2933 (w), 2857 (w), 1582 (w), 1495 (w), 1472 (w), 1453 (w), 1438 (w), 1376 (w), 1347 (w), 1302 (w), 1175 (w), 1088 (w), 1069 (w), 1043 (w), 1024 (w), 981 (w), 911 (w), 819 (w), 770 (m), 743 (m), 695 (m), 610. (w), 571 (w), 546 (w), 508 (w).

LRMS: (ESI, $[M+Na]^+$)

216.9 (10), 385.2 (100).

HRMS: calcd for $C_{24}H_{26}OSNa$ ($[M+Na]^+$): 385.1602, found: 385.1596

Analysis: $C_{24}H_{26}OS$ (362.53)

Calcd: C, 79.51; H, 7.23%

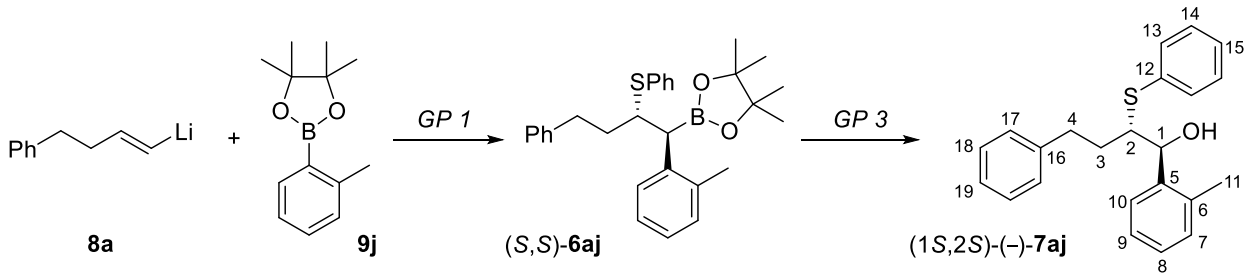
Found: C, 79.55; H, 7.52%

TLC: R_f 0.55 (hexanes/EtOAc, 83:17, CAM)

HPLC: (1*R*,2*R*)-**7ai** t_R 14.2 min (1%); (1*S*,2*S*)-**7ai** t_R 19.8 min (99%) (Supelco Astec, hexanes/*i*-PrOH, 90:10, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –87.1 (*c* = 1.26 in 95% EtOH) (98% ee)

Preparation of (1*S*,2*S*)-(–)-**4-Phenyl-2-(phenylthio)-1-(*o*-tolyl)butan-1-ol (**(1*S*,2*S*)-(–)-**7aj)**



Alkylborane **6aj** was prepared according to *GP1c*. A flame-dried, 25-mL Schlenk flask (**A**) equipped with a magnetic stir bar, septum, and digital thermocouple probe was charged with (*E*)-(4-bromobut-3-en-1-yl)benzene (232.1 mg, 1.10 mmol, 1.10 equiv) and THF (5 ml). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *tert*-butyllithium in pentane (1.23 mL, 1.79 M, 2.20 equiv) was added dropwise over 10 min. The resulting solution of (*E*)-(4-phenylbut-1-en-1-yl)lithium **8a** was stirred at –78 °C for 30 min. Then, a solution of (*o*-tolyl)pinacolboronic ester **9j** (218.1 mg, 1.0 mmol, 1.0 equiv) in THF (5 ml) was added dropwise to flask **A** over 15 min. The resulting solution of **3aj** was stirred at –78 °C for 1 h. A separate, flame-dried, 50-mL Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3aj** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1

mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with diethyl ether (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6aj**.

Borane **6aj** was oxidized to alcohol **7aj** according to *GP3*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6aj** and THF (10 mL). The turbid solution was cooled to 0 °C with an ice bath. To this solution was added a mixture of 30% aq. H_2O_2 (1 mL) and 3 M aq. NaOH (1 mL) also containing EDTA (1.0 mg/mL). The biphasic mixture was stirred rapidly at 0 °C for 30 min. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with diethyl ether (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7aj**. The product was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 90:10 (600 mL)) to afford 298.2 mg (85% yield) of **7aj** as an oil. The product was purified to analytical standard by diffusion pump Kugelrohr distillation (160 °C ABT, 4.0 x 10^{-5} mmHg) to afford 293.2 mg (84%) of **7aj** as a viscous oil.

Data for (1*S*,2*S*)-(–)-**7aj**:

b.p.: 160 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.44 (dd, *J* = 7.3, 2.2 Hz, 2H, HC(13)), 7.34 – 7.27 (m, 4H, HC(10) and HC(14) and HC(19)), 7.23 – 7.12 (m, 5H, HC(8) and HC(9) and HC(15) and HC(18)), 7.10 – 7.08 (m, 1H, HC(7)), 6.95 (d, *J* = 6.9 Hz, 2H, HC(17)), 4.78 (dd, *J* = 8.5, 2.4 Hz, 1H, HC(1)), 3.33 (d, *J* = 2.4 Hz, 1H, OH), 3.26 – 3.15 (m, 1H, HC(2)), 2.97 (dt, *J* = 13.7, 6.8 Hz, 1H, H_2C(4)), 2.68 (dt, *J* = 14.0, 8.3 Hz, 1H, H_2C(4)), 2.20 (s, 3H, H_3C(11)), 1.78 – 1.65 (m, 2H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

141.1 (C(16)), 139.2 (C(6)), 135.8 (C(5)), 133.3 (C(13)), 133.2 (C(12)), 130.6 (C(7)), 129.1 (C(14)), 128.6 (C(18)), 128.4 (C(17)), 127.8 (C(15)), 127.8 (C(8)), 126.8 (C(10)), 126.4 (C(9)), 126.1 (C(19)), 72.2 (C(1)), 58.4 (C(2)), 33.2 (C(4)), 32.6 (C(3)), 19.5 (C(11)).

IR: (neat)

3436 (w), 3059 (w), 3024 (w), 2929 (w), 1740 (w), 1602 (w), 1582 (w), 1495 (w), 1479 (w), 1454 (w), 1438 (w), 1377 (w), 1350 (w), 1303 (w), 1178 (w), 1114 (w), 1048 (w), 1024 (w), 1000 (w), 984 (w), 944 (w), 910 (w), 830 (w), 743 (m), 728 (m), 695 (m), 610 (w), 561 (w), 488 (w).

LRMS: (ESI, $[M+Na]^+$)

105.1 (18), 129.1 (18), 221.1 (100), 239.1 (21), 331.2 (23), 371.1 (20).

HRMS: calcd for $C_{23}H_{24}OSNa$ ($[M+Na]^+$): 371.1446, found: 371.1429

Analysis: $C_{23}H_{24}OS$ (348.50)

Calcd: C, 79.27; H, 6.94%

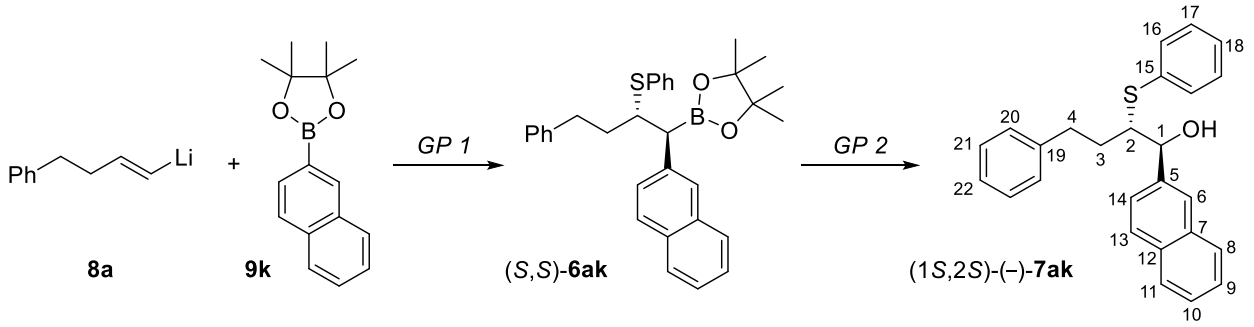
Found: C, 79.10; H, 6.82%

TLC: R_f 0.43 (hexanes/EtOAc, 83:17, CAM)

HPLC: (1*S*,2*S*)-**7aj** t_R 13.6 min (98%); (1*R*,2*R*)-**7aj** t_R 17.8 min (2%) (Regis (*R*,*R*)-Whelk O1, hexanes/*i*-PrOH, 90:10, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –84.6 (*c* = 1.53 in 100% EtOH) (96% ee)

Preparation of (1*S*,2*S*)-(–)-**1-(Naphthalen-2-yl)-4-phenyl-2-(phenylthio)butan-1-ol (**(1*S*,2*S*)-(–)-**7ak)**



Alkylborane **6ak** was prepared according to *GP1c*. A flame-dried, 25-mL Schlenk flask (**A**) equipped with a magnetic stir bar, septum, and digital thermocouple probe was charged with (*E*)-(4-bromobut-3-en-1-yl)benzene (232.1 mg, 1.10 mmol, 1.10 equiv) and THF (5 ml). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *tert*-butyllithium in pentane (1.23 mL, 1.79 M, 2.20 equiv) was added dropwise over 10 min. The resulting solution of (*E*)-(4-phenylbut-1-en-1-yl)lithium **8a** was stirred at –78 °C for 30 min. Then, a solution of (napthalen-2-yl)pinacolboronic ester **9k** (254.1 mg, 1.0 mmol, 1.0 equiv) in THF (5 ml) was added dropwise to flask **A** over 15 min. The resulting solution of **3ak** was stirred at –78 °C for 1 h. A separate, flame-dried, 50-mL Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3ak** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to

a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with diethyl ether (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6ak**.

Borane **6ak** was oxidized to alcohol **7ak** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ak**, THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (616 mg, 4.0 mmol) was added to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 3 h. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with diethyl ether (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7ak**. The product was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 90:10 (600 mL)) to afford 316.9 mg (82% yield) of **7ak** as an oil. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (160 °C ABT, 4.0 x 10^{-5} mmHg) to afford 310.8 mg (81%) of **7ak** as a viscous oil.

Data for (1*S*,2*S*)-(–)-**7ak**:

b.p.: 160 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.82 (dd, *J* = 6.0, 3.4 Hz, 1H, HC(11)), 7.80 – 7.76 (m, 2H, HC(8) and HC(13)), 7.72 (s, 1H, HC(6)), 7.53 – 7.50 (m, 2H, HC(16)), 7.48 (dt, *J* = 6.3, 3.4 Hz, 2H, HC(9) and HC(10)), 7.38 (dd, *J* = 8.5, 1.3 Hz, 1H, HC(14)), 7.31 (dd, *J* = 5.1, 2.0 Hz, 3H, HC(17) and HC(18)), 7.19 – 7.10 (m, 3H, HC(21) and HC(22)), 6.93 (d, *J* = 6.6 Hz, 2H, HC(20)), 4.63 (dd, *J* = 8.5, 1.8 Hz, 1H, HC(1)), 3.54 (d, *J* = 1.9 Hz, 1H, OH), 3.26 (td, *J* = 10.0, 3.5 Hz, 1H, HC(2)), 2.98 (ddd, *J* = 14.0, 9.3, 4.8 Hz, 1H, H_2C(4)), 2.71 – 2.63 (m, 1H, H_2C(4)), 1.76 (dddd, *J* = 12.8, 9.7, 7.5, 3.5 Hz, 1H, H_2C(3)), 1.64 (dtd, *J* = 14.5, 9.7, 4.8 Hz, 1H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

141.2 (C(19)), 138.4 (C(5)), 133.7 (C(16)), 133.4 (C(12)), 133.3 (C(7)), 132.7

(C(5)), 129.2 (C(17)), 128.6 (C(20)), 128.4 (C(21)), 128.4 (C(8)), 128.1 (C(11)), 128.0 (C(18)), 127.8 (C(13)), 126.7 (C(6)), 126.2 (C(9)), 126.1 (C(10)), 126.0 (C(22)), 124.7 (C(14)), 75.9(C(1)), 58.5 (C(2)), 33.2(C(4)), 32.4(C(3)).

IR: (neat)

3432 (w), 3056 (w), 3024 (w), 2928 (w), 2857 (w), 1947 (w), 1805 (w), 1601 (w), 1582 (w), 1508 (w), 1495 (w), 1479 (w), 1453 (w), 1438 (w), 1352 (w), 1270 (w), 1241 (w), 1162 (w), 1122 (w), 1086 (w), 1068 (w), 1025 (w), 1000 (w), 987 (w), 950 (w), 896 (w), 858 (w), 819 (w), 772 (w), 744 (m), 696 (m), 608 (w), 570 (w), 478 (m).

LRMS: (ESI, $[M+Na]^+$)

129.1 (17), 141.1 (21), 239.1 (12), 257.1 (100), 367.2 (14), 407.1 (53).

HRMS: calcd for $C_{26}H_{24}OSNa$ ($[M+Na]^+$): 407.1446, found: 407.1448

Analysis: $C_{26}H_{24}OS$ (384.54)

Calcd: C, 81.21; H, 6.29%

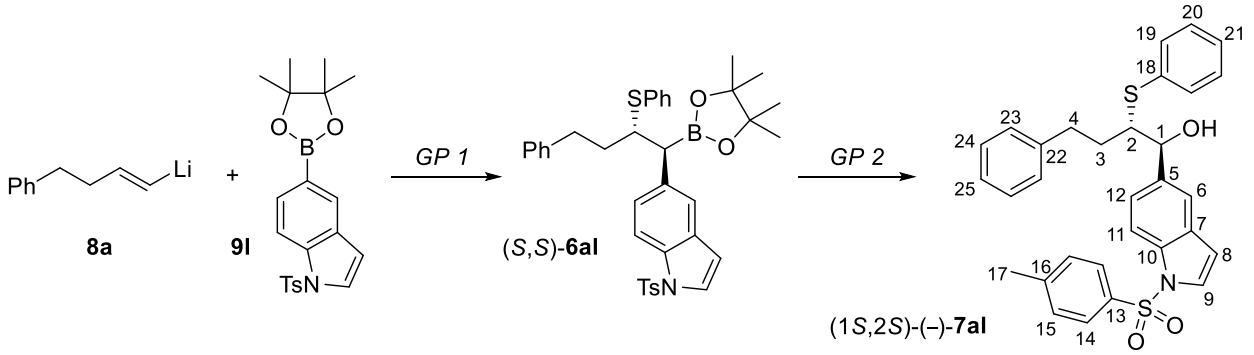
Found: C, 81.21; H, 6.23%

TLC: R_f 0.36 (hexanes/EtOAc, 83:17, CAM)

HPLC: (1*S*,2*S*)-**7ak** t_R 23.0 min (98%); (1*R*,2*R*)-**7ak** t_R 29.1 min (2%) (Regis (*R*,*R*)-Whelk O1, hexanes/*i*-PrOH, 80:20, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –95.4 (*c* = 1.13 in 100% EtOH) (96% ee)

Preparation of (1*S*,2*S*)-(–)-**4-Phenyl-2-(phenylthio)-1-(1-tosyl-1*H*-indol-5-yl)butan-1-ol (**(1*S*,2*S*)-(–)-**7al)**



Alkylborane **6al** was prepared according to *GP1c*. A flame-dried, 25-mL Schlenk flask (**A**) equipped with a magnetic stir bar, septum, and digital thermocouple probe was charged with (*E*)-(4-bromobut-3-en-1-yl)benzene (232.1 mg, 1.10 mmol, 1.10 equiv) and THF (5 mL). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *tert*-butyllithium in pentane (1.27 mL, 1.73 M, 2.20 equiv) was added dropwise over 10 min. The resulting solution of (*E*)-(4-phenylbut-1-en-1-yl)lithium **8a** was stirred at –78 °C for 30 min. Then, a solution of 5-(pinacolboryl)-1-tosyl-1*H* indole **9l** (397.2 mg, 1.0 mmol, 1.0 equiv) in THF (5 mL) was added dropwise to flask **A** over 15 min. The resulting solution of **3al** was stirred at –78 °C for 1 h. A separate, flame-dried, 50-mL Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3al** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min at –60 °C. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of

sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6al**.

Borane **6al** was oxidized to alcohol **7al** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6al**, THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (616 mg, 4.0 mmol) was added to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 3 h. Full conversion was observed by TLC (hexanes/EtOAc, 75:25, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with Et_2O (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7al**. The product was purified by chromatography (silica gel, 3 x 20 cm, wet load with CH_2Cl_2, 25-mL fractions, hexanes/EtOAc gradient elution: 90:10 to 87.5:12.5) to afford 297.8 mg (56% yield) of **7al** as an oil. The oil was triturated with hexanes and dried under vacuum to afford 287.7 mg (55% yield) of analytically pure **7al** as a white, foam solid.

Data for (1*S*,2*S*)-(–)-**7al**:

m.p.: 41–45 °C (hexanes)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.90 (d, *J* = 8.5 Hz, 1H, HC(11)), 7.73 (d, *J* = 8.5 Hz, 2H, HC(14)), 7.54 (d, *J* = 3.7 Hz, 1H, HC(9)), 7.49 – 7.44 (m, 2H, HC(19)), 7.41 – 7.38 (m, 1H, HC(6)), 7.30 – 7.26 (m, 3H, HC(20) and HC(21)), 7.22 – 7.17 (m, 3H, HC(15) and HC(12)), 7.16 – 7.10 (m, 3H, HC(24) and HC(25)), 6.91 – 6.85 (m, 2H, HC(23)), 6.58 (d, *J* = 3.6 Hz, 1H, HC(8)), 4.50 (d, *J* = 8.7 Hz, 1H, HC(1)), 3.60 – 3.35 (bm, 1H, OH), 3.15 (ddd, *J* = 9.9, 8.7, 3.5 Hz, 1H, HC(2)), 2.91 (ddd, *J* = 13.9, 9.1, 4.8 Hz, 1H, H_2C(4)), 2.61 (ddd, *J* = 13.8, 9.0, 7.5 Hz, 1H, H_2C(4)), 2.32 (s, 3H, H_3C(17)), 1.71 – 1.63 (m, 1H, H_2C(3)), 1.62 – 1.54 (m, 1H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

145.1 (C(16)), 141.1 (C(22)), 136.1 (C(5)), 135.4 (C(13)), 134.8 (C(10)), 133.6 (HC(19)), 132.7 (C(18)), 131.0 (C(7)), 130.0 (HC(15)), 129.2 (HC(20)), 128.5 (HC(23)), 128.4 (HC(24)), 128.0 (HC(21)), 127.0 (HC(9)), 126.9 (HC(14)), 126.1 (HC(25)), 123.8 (HC(12)), 120.3 (HC(6)), 113.7 (HC(11)), 109.3 (HC(8)), 75.8 (HC(1)), 58.8 (HC(2)), 33.1 (H_2C(4)), 32.3 (H_2C(3)), 21.7 (H_3C(17)).

IR: (neat)

3024 (w), 1740 (w), 1596 (w), 1494 (w), 1449 (w), 1367 (w), 1271 (w), 1217 (w), 1187 (w), 1169 (w), 1139 (w), 1121 (w), 1091 (w), 1025 (w), 994 (w), 890 (w), 811 (w), 727 (w), 700 (w), 670 (w), 578 (w), 537 (w).

LRMS: (ESI, $[M+Na]^+$)

129.1 (10), 239.1 (24), 400.1 (100), 510.2 (12), 550.1 (33).

HRMS: calcd for $C_{31}H_{29}NO_3S_2Na$ ($[M+Na]^+$): 550.1487, found: 550.1475

Analysis: $C_{31}H_{29}NO_3S_2$ (527.70)

Calcd: C, 70.56; H, 5.54%; N, 2.65%

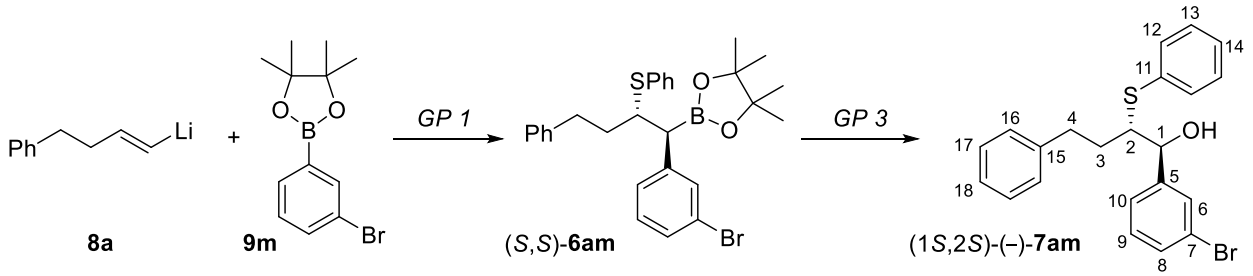
Found: C, 70.21; H, 5.51%; N, 2.78%

TLC: R_f 0.25 (hexanes/EtOAc, 80:20, CAM)

HPLC: (1*S*,2*S*)-**7al** t_R 22.1 min (98%); (1*R*,2*R*)-**7al** t_R 27.2 min (2%) (Supelco Astec, hexanes/*i*-PrOH, 80:20, 1.0 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –60.8 (*c* = 1.11 in 100% EtOH) (96% ee)

Preparation of (1*S*,2*S*)-(–)-**1-(3-Bromophenyl)-4-phenyl-2-(phenylthio)butan-1-ol (**(1*S*,2*S*)-(–)-**7am)**



Alkylborane **6am** was prepared according to *GP1c*. A flame-dried, 25-mL Schlenk flask (**A**) equipped with a magnetic stir bar, septum, and digital thermocouple probe was charged with

(*E*)-(4-bromobut-3-en-1-yl)benzene (232.1 mg, 1.10 mmol, 1.10 equiv) and THF (5 ml). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *tert*-butyllithium in pentane (1.23 mL, 1.79 M, 2.20 equiv) was added dropwise over 10 min. The resulting solution of (*E*)-(4-phenylbut-1-en-1-yl)lithium **8a** was stirred at –78 °C for 30 min. Then, a solution of (3-bromophenyl)pinacolboronic ester **9m** (283.0 mg, 1.0 mmol, 1.0 equiv) in THF (5 ml) was added dropwise to flask **A** over 15 min. The resulting solution of **3am** was stirred at –78 °C for 1 h. A separate, flame-dried, 50-mL Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3am** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with diethyl ether (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6am**.

Borane **6am** was oxidized to alcohol **7am** according to *GP3*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6am** and THF (10 mL). The turbid solution was cooled to 0 °C with an ice bath. To this solution was added a mixture of 30% aq. H_2O_2 (1 mL) and 3 M aq. NaOH (1 mL) also containing EDTA (1.0 mg/mL). The biphasic mixture was stirred rapidly at 0 °C for 30 min. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM).

The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with diethyl ether (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7am**. The product was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 90:10 (600 mL)) to afford 366.6 mg (88% yield) of **7am** as an oil. The product was purified to analytical standard by diffusion pump Kugelrohr distillation (160 °C ABT, 4.0 x 10^{-5} mmHg) to afford 351.7 mg (85%) of **7am** as a viscous oil.

Data for (1*S*,2*S*)-(–)-**7am**:

b.p.: 160 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.45 (dd, *J* = 6.3, 2.8 Hz, 2H, HC(12)), 7.42 (s, 1H, HC(6)), 7.39 (d, *J* = 6.7 Hz, 1H, HC(8)), 7.31 (dd, *J* = 4.9, 1.5 Hz, 3H, HC(13) and HC(14)), 7.22 (t, *J* = 7.4 Hz, 2H, HC(17))), 7.16 (q, *J* = 7.0 Hz, 3H, HC(9) and HC(10) and HC(18)), 6.99 (d, *J* = 7.3 Hz, 2H, HC(16)), 4.43 (dd, *J* = 8.1, 1.9 Hz, 1H, HC(1)), 3.42 (d, *J* = 2.4 Hz, 1H, OH), 3.10 (ddd, *J* = 10.2, 8.1, 3.6 Hz, 1H, HC(2)), 2.97 (ddd, *J* = 13.9, 9.1, 4.9 Hz, 1H, H_2C(4)), 2.69 (dt, *J* = 14.0, 8.3 Hz, 1H, H_2C(4)), 1.73 (ddt, *J* = 17.1, 8.7, 3.7 Hz, 1H, H_2C(3)), 1.62 (dtd, *J* = 14.2, 9.5, 4.8 Hz, 1H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

143.4 (C(5)), 141.0 (C(15)), 133.6 (C(12)), 132.5 (C(11)), 131.3 (C(8)), 130.3 (C(6)), 130.0 (C(9)), 129.3 (C(13)), 128.6 (C(16)), 128.5 (C(17)), 128.1 (C(14)), 126.2 (C(10)), 126.0 (C(18)), 122.7 (C(7)), 75.1 (C(1)), 58.3 (C(2)), 33.1 (C(4)), 32.2 (C(3)).

IR: (neat)

3429 (w), 3059 (w), 3025 (w), 2923 (w), 2856 (w), 1740 (w), 1582 (w), 1570 (w), 1495 (w), 1474 (w), 1453 (w), 1437 (w), 1428 (w), 1375 (w), 1283 (w), 1185 (w), 1069 (w), 1025 (w), 997 (w), 884 (w), 784 (w), 740 (m), 693 (m), 621 (w), 562 (w), 488 (w).

LRMS: (ESI, $[M+Na]^+$)

169.0 (9), 287.0 (27), 357.1 (15), 407.1 (61), 437.0 (100).

HRMS: calcd for $C_{22}H_{21}BrOSNa$ ([M+Na]$^+$): 435.0394, found: 435.0383

Analysis: $C_{22}H_{21}BrOS$ (413.37)

Calcd: C, 63.92; H, 5.12%

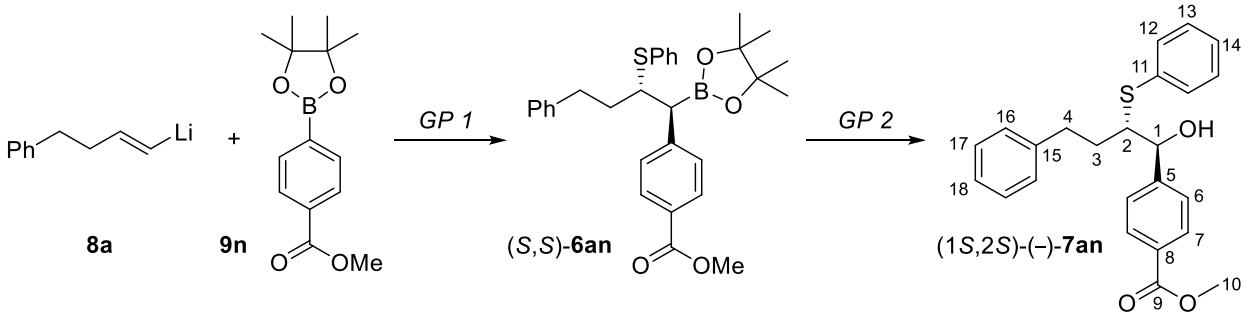
Found: C, 64.10; H, 5.05%

TLC: R_f 0.40 (hexanes/EtOAc, 83:17, CAM)

HPLC: (1*R*,2*R*)-**7am** t_R 22.5 min (3%); (1*S*,2*S*)-**7am** t_R 25.2 min (97%) (Supelco Astec, hexanes/*i*-PrOH, 90:10, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –76.5 (*c* = 0.78 in 100% EtOH) (94% ee)

Preparation of methyl 4-((1*S*,2*S*)-(–)-**1-Hydroxy-4-phenyl-2-(phenylthio)butyl)benzoate (**(1*S*,2*S*)-(–)-**7an)**



Alkylborane **6an** was prepared according to *GP1c*. A flame-dried, 25-mL Schlenk flask (**A**) equipped with a magnetic stir bar, septum, and digital thermocouple probe was charged with (*E*)-(4-bromobut-3-en-1-yl)benzene (464.2 mg, 2.20 mmol, 1.10 equiv) and THF (5 ml). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *tert*-butyllithium in pentane (2.54 mL, 1.73 M, 2.20 equiv) was added dropwise over 10 min. The resulting solution of (*E*)-(4-phenylbut-1-en-1-yl)lithium **8a** was stirred at –78 °C for 30 min. Then, a solution of methyl 4-(pinacolboryl)benzoate **9n** (524.4 mg, 2.0 mmol, 1.0 equiv) in THF (5 ml) was added dropwise to flask **A** over 15 min. The resulting solution of **3an** was stirred at –78 °C for 1 h. A separate, flame-dried, 50-mL Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (104.0 mg, 0.20 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (700.0 mg, 2.40 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (10 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using

a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3an** in flask **A** was taken up in ethanol (7.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with diethyl ether (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6an**.

Borane **6an** was oxidized to alcohol **7an** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6an**, THF (20 mL) and water (20 mL). Sodium perborate tetrahydrate (1.232 mg, 8.0 mmol) was added to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 3 h. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with diethyl ether (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7an**. The product was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, CH_2Cl_2/EtOAc gradient elution: 100:0 (600 mL) to 99:1 (600 mL)) to afford 257.8 mg (33% yield) of **7an** as an oil. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (160 °C ABT, 4.0 x 10^{-5} mmHg) to afford 251.6 mg (32%) of **7an** as a viscous oil.

Data for (1*S*,2*S*)-(–)-**7an**:

b.p.: 160 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.96 (d, *J* = 8.3 Hz, 2H, HC(7)), 7.48 – 7.42 (m, 2H, HC(12)), 7.34 (d, *J* = 8.4 Hz,

2H, HC(6)), 7.30 (dd, *J* = 4.8, 1.9 Hz, 3H, HC(13) and HC(14)), 7.20 (t, *J* = 7.1 Hz, 2H, HC(17)), 7.15 (t, *J* = 7.2 Hz, 1H, HC(18)), 6.97 (d, *J* = 7.0 Hz, 2H, HC(16)), 4.54 (d, *J* = 7.9 Hz, 1H, HC(1)), 3.91 (s, 3H, H_3C(10)), 3.46 (s, 1H, OH), 3.14 (ddd, *J* = 10.0, 8.1, 3.7 Hz, 1H, HC(2)), 2.96 (ddd, *J* = 13.9, 9.1, 4.9 Hz, 1H, H_2C(4)), 2.68 (dt, *J* = 13.9, 8.3 Hz, 1H, H_2C(4)), 1.77 – 1.69 (m, 1H, H_2C(3)), 1.64 (ddt, *J* = 14.4, 9.7, 5.0 Hz, 1H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

167.0 (C(9)), 146.3 (C(5)), 141.0 (C(15)), 133.6 (C(12)), 132.5 (C(11)), 129.9 (C(8)), 129.8 (C(7)), 129.3 (C(13)), 128.5 (C(16)), 128.5 (C(17)), 128.1 (C(14)), 127.3 (C(6)), 126.2 (C(18)), 75.3 (C(1)), 58.4 (C(2)), 52.3 (C(10)), 33.2 (C(4)), 32.3 (C(3)).

IR: (neat)

3457 (w), 3025 (w), 2948 (w), 1715 (m), 1610 (w), 1581 (w), 1496 (w), 1496 (w), 1453 (w), 1436 (m), 1414 (w), 1381 (w), 1310 (w), 1277 (m), 1182 (w), 1107 (m), 1087 (w), 1068 (w), 1018 (m), 965 (w), 908 (w), 861 (w), 810 (w), 766 (w), 731 (m), 697 (m), 647 (w), 607 (w), 563 (w).

LRMS: (ESI, $[M+Na]^+$)

149.1 (23), 215.1 (6), 233.1 (17), 265.1 (100), 343.1 (5), 375.1 (21), 415.1 (66).

HRMS: calcd for $C_{24}H_{24}O_3SNa$ ($[M+Na]^+$): 415.1344, found: 415.1356

Analysis: $C_{24}H_{24}O_3S$ (392.51)

Calcd: C, 73.44; H, 6.16%

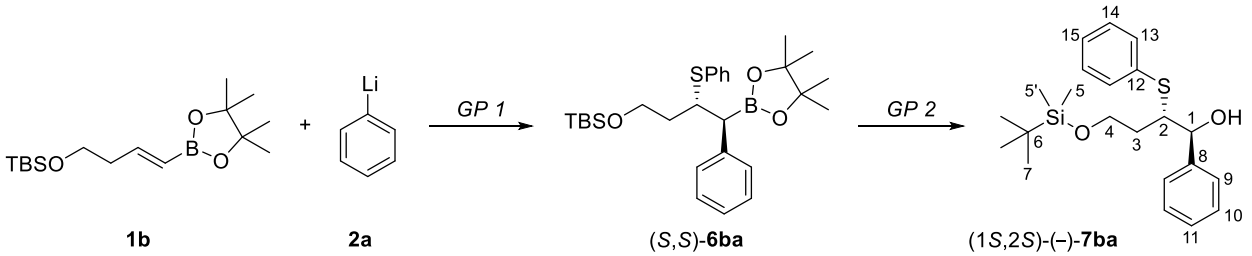
Found: C, 73.29; H, 6.04%

TLC: R_f 0.31 (hexanes/EtOAc, 80:20, CAM)

HPLC: (1*S*,2*S*)-**7an** t_R 10.8 min (87%); (1*R*,2*R*)-**7an** t_R 12.5 min (13%) (Supelco Astec, hexanes/*i*-PrOH, 80:20, 1.0 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –74.2 (*c* = 1.56 in 100% EtOH) (74% ee)

Preparation of (1*S*,2*S*)-(–)-**4-((*tert*-Butyldimethylsilyl)oxy)-1-phenyl-2-(phenylthio)butan-1-ol (**(1*S*,2*S*)-(–)-**7ba)**



1b **2a** (*S*,*S*)-**6ba** (1*S*,2*S*)-(–)-**7ba**

Alkylborane **6ba** was prepared according to *GP1a*. An oven-dried, 25-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (5 mL) and (*E*)-4-(*tert*-butyldimethylsilyl)oxybut-1-en-1-yl pinacolborane **1b** (312.3 mg, 1.00 mmol). The resulting colorless solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of phenyllithium **2a** in diethyl ether (1.77 M, 595 μL, 1.05 mmol, 1.05 equiv) was added dropwise over 10 min, such that the internal temperature did not exceed –68 °C. The dark red color of the phenyllithium solution immediately disappeared upon addition to the reaction mixture. The resulting pale, beige solution was stirred at –78 °C for 1 h. A separate, oven-dried, 25-mL, Schlenk flask (**B**) equipped with a stir bar was charged with chiral (*S*)-catalyst **5** (52.3 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (352.2 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting beige-colored, foam solid boronate complex **3ba** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate complex. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (2.5 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C. The mixture was diluted with diethyl ether (5 mL) and water (5 mL) and stirred rapidly to dissolve all solids. The biphasic mixture was transferred to a 60-mL separatory funnel and the layers were separated. The aqueous layer was washed with diethyl ether (2 x 10 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford

671.7 mg of crude borane **6ba** as a yellow oil. The yield of **6ba** was determined to be 75% by quantitative ^{1}H-NMR as described previously (p. S7).

Borane **6ba** was oxidized to alcohol **7ba** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ba** (671.7 mg), THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (0.60 g, 3.9 mmol) and tetra-*n*-butylammonium chloride (28.0 mg, 0.10 mmol) were added sequentially to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 2.5 h. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of solid sodium bisulfite, $NaHSO_3$ (1.20 g) and the resulting mixture was stirred for 15 min. Then, aq. NaOH was added (1 M, 20 mL) and the mixture was stirred for 30 min. The mixture was transferred to a separatory funnel and diluted with diethyl ether (30 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 x 15 mL). The combined organic phases were washed with brine (25 mL) and then dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford 442.0 mg of crude **7ba** as a yellow oil. The product was purified by chromatography (silica gel, 3 x 25 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 92.5:7.5 (300 mL) to 90:10 (300 mL)) to afford 262.9 mg of **7ba** as a yellow oil. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (120 °C ABT, 3.4 x 10^{-5} mmHg) to afford 253.9 mg (65% yield) of **7ba** as a viscous, pale, yellow oil.

Data for (1*S*,2*S*)-(–)-**7ba**:

b.p.: 120 °C (ABT, 3.4 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.42–7.38 (m, 2H, HC(13)), 7.38–7.34 (m, 2H, HC(9)), 7.33–7.29 (m, 2H, HC(10)), 7.28–7.21 (m, 4H, HC(11), HC(14), HC(15)), 4.60 (dd, *J* = 7.2, 2.7 Hz, 1H, HC(1)), 3.86–3.76 (m, 2H, H_2C(4)), 3.71 (d, *J* = 2.3 Hz, 1H, OH), 3.52 (ddd, *J* = 8.9, 7.4, 4.2 Hz, 1H, HC(2)), 1.78–1.68 (m, 1H, H_2C(3)), 1.63–1.55 (m, 1H, H_2C(3)), 0.84 (s, 9H, H_3C(7)), –0.02 (s, 3H, H_3C(5)), –0.04 (s, 3H, H_3C(5')).

^{13}C NMR: (126 MHz, $CDCl_3$)

141.4 (C(8)), 134.1 (C(12)), 132.8 (HC(13)), 129.1 (HC(14)), 128.4 (HC(10)), 128.0 (HC(11)), 127.4 (HC(15)), 127.2 (HC(9)), 75.9 (HC(1)), 60.1 (H_2C(4)), 56.1 (HC(2)), 34.7 (H_2C(3)), 26.0 (H_3C(7)), 18.3 (C(6)), –5.29 (H_3C(5 or 5')), –5.33 (H_3C(5 or 5')).

IR: (neat)

3435 (w), 3061 (w), 3031 (w), 2953 (w), 2928 (w), 2883 (w), 2856 (w), 1947 (w), 1805 (w), 1584 (w), 1494 (w), 1471 (m), 1463 (w), 1439 (w), 1386 (w), 1361 (w), 1332 (w), 1318 (w), 1296 (w), 1253 (m), 1188 (w), 1156 (w), 1089 (s), 1041 (m), 1025 (m), 1005 (m), 938 (m), 913 (w), 832 (s), 809 (m), 774 (s), 742 (s), 697 (s), 662 (m), 608 (w), 573 (w), 530 (w), 512 (w), 483 (w).

LRMS: (CI, 70 eV)

89.0 (27), 111.0 (19), 129.0 (14), 131.0 (16), 147.0 (18), 213.0 (21), 225.0 (75), 226.0 (13), 239.0 (100), 240.0 (19), 371.1 (29), 388.1 (1), 389.1 (2).

Analysis: $C_{22}H_{32}O_2SSi$ (388.64)

Calcd: C, 67.99%; H, 8.30%

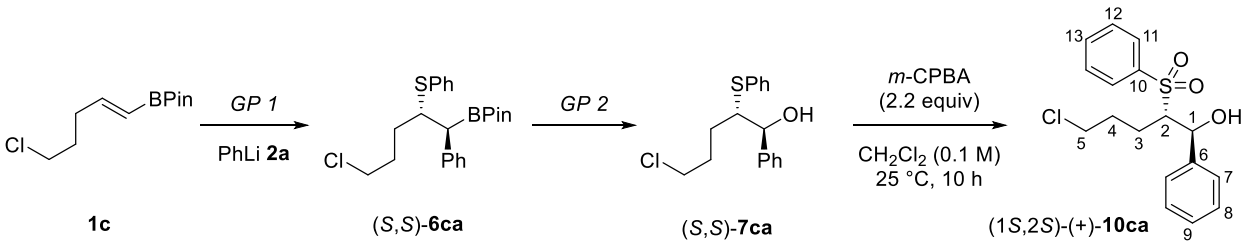
Found: C, 67.87%; H, 8.39%

TLC: R_f 0.23 (hexanes/EtOAc, 90:10, CAM)

HPLC: (1*S*,2*S*)-**7ba** t_R 22.0 min (96%); (1*R*,2*R*)-**7ba** t_R 26.0 min (4%) (Regis (*R*,*R*)-Whelk O1, hexanes/*i*-PrOH, 98:2, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –70.8 (*c* = 1.03 in 95% EtOH) (92% ee)

Preparation of (1*S*,2*S*)-**5-Chloro-1-phenyl-2-(phenylsulfonyl)pentan-1-ol (**(1*S*,2*S*)-(+)-**10ca)**



Alkylborane **6ca** was prepared according to *GP1a*. An oven-dried, 25-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (5 mL) and (*E*)-5-chloropent-1-en-1-yl pinacolborane **1c** (230.5 mg, 1.00 mmol). The resulting colorless solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of phenyllithium **2a** in diethyl ether (1.77 M, 621 μL, 1.1 mmol, 1.1 equiv) was added dropwise over 10 min, such that the internal temperature did not exceed –68 °C. The dark red color of the phenyllithium solution immediately disappeared upon addition to the reaction mixture. The resulting pale, beige solution was stirred at –78 °C for 1 h. A separate, oven-dried, 25-mL, Schlenk

flask (**B**) equipped with a stir bar was charged with chiral (*S*)-catalyst **5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting beige-colored, foam solid boronate complex **3ca** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min at –60 °C. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate complex. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1.0 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6ca**.

Borane **6ca** was oxidized to alcohol **7ca** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ca**, THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (616 mg, 4.0 mmol) was added to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 2.5 h. Full conversion was observed by TLC (hexanes/EtOAc, 10:1, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with Et_2O (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7ca**. The product was purified by chromatography (silica gel, 3 x 20 cm, wet load with CH_2Cl_2, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 90:10 (600 mL)) to afford pure **7ca**. The product

is stable at room temperature for several hours in the presence of trace amounts of solvent. Attempts to rigorously purify **7ca** resulted in extensive decomposition, presumably due to displacement of chloride by the thioether. Consequently, the product was analyzed and characterized as the corresponding sulfone **10ca**.

A 100-mL, round-bottomed flask equipped with a stir bar was charged with thioether **7ca**, CH_2Cl_2 (10 mL), and *m*-CPBA (379.7 mg, 2.2 mmol). The reaction mixture was stirred at 25 °C for 10 h. Full conversion was observed by TLC (hexanes/EtOAc, 80:20, CAM). The reaction was quenched by the addition of sat. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. Then aq. NaOH (1 N, 10 mL) was added to the mixture. The mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (4 x 50 mL). The combined organic phases were washed with aq. NaOH (1 N, 20 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **10ca**. The product was purified by chromatography (silica gel, 3 x 20 cm, wet load with CH_2Cl_2, 25-mL fractions, hexanes/EtOAc gradient elution: 90:10 (600 mL) to 85:15 (600 mL)) to afford 291.4 mg (86%) of pure **10ca** as a white solid. Precipitation from hexanes/Et_2O afforded 287.2 mg (85%) of analytically pure **10ca** as white solid.

Data for (1*S*,2*S*)-(+)-**10ca**:

m.p.: 82–83 °C (hexanes/Et_2O)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.97 – 7.91 (m, 2H, HC(11)), 7.72 – 7.66 (m, 1H, HC(13)), 7.63 – 7.56 (m, 2H, HC(12)), 7.37 – 7.27 (m, 5H, HC(7), HC(8), and HC(9)), 5.02 (dd, *J* = 8.8, 2.3 Hz, 1H, HC(1)), 4.34 (d, *J* = 2.4 Hz, 1H, OH), 3.32 (dt, *J* = 8.8, 5.1 Hz, 1H, HC(2)), 3.19 – 3.06 (m, 2H, H_2C(5)), 1.80 – 1.68 (m, 1H, H_2C(3)), 1.47 – 1.32 (m, 2H, H_2C(3) and H_2C(4)), 1.28 – 1.18 (m, 1H, H_2C(4)).

^{13}C NMR: (126 MHz, $CDCl_3$)

139.4 (C(6)), 138.1 (C(10)), 134.3 (HC(13)), 129.5 (HC(12)), 128.96 (HC(11) or HC(8)), 128.95 (HC(9)), 128.9 (HC(11) or HC(8)), 127.3 (HC(7)), 73.6 (HC(1)), 70.1 (HC(2)), 44.2 (H_2C(5)), 29.9 (H_2C(4)), 24.5 (H_2C(3)).

IR: (neat)

3491 (w), 2923 (w), 1496 (w), 1458 (w), 1448 (w), 1404 (w), 1372 (w), 1352 (w), 1306 (w), 1281 (m), 1252 (w), 1211 (w), 1152 (w), 1133 (m), 1078 (w), 1058 (w),

1028 (w), 997 (w), 919 (w), 836 (w), 760 (w), 748 (w), 728 (w), 704 (w), 691 (m), 681 (w), 636 (w), 606 (w), 562 (m), 522 (m), 485 (w), 458 (w).

LRMS: (ESI, $[M+Na]^+$)

179.1 (20), 321.1 (10), 361.1 (100).

HRMS: calcd for $C_{17}H_{19}ClO_3SNa$ ($[M+Na]^+$): 361.0641, found: 361.0637

Analysis: $C_{17}H_{19}ClO_3S$ (338.85)

Calcd: C, 60.26%; H, 5.65%

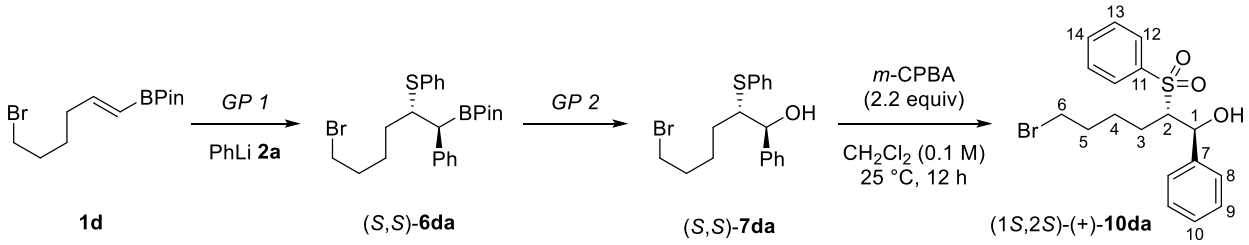
Found: C, 59.91%; H, 5.60%

TLC: R_f 0.38 (hexanes/EtOAc, 67:33, CAM)

HPLC: (1*R*,2*R*)-**10ca**, t_R 12.2 min (1%); (1*S*,2*S*)-**10ca**, t_R 18.7 min (99%) (Supelco Astec, hexanes/*i*-PrOH, 80:20, 1.0 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ +45.3 (*c* = 0.80 in 100% EtOH) (98% ee)

Preparation of (1*S*,2*S*)-**6-Bromo-1-phenyl-2-(phenylsulfonyl)hexan-1-ol (**(1*S*,2*S*)-(+)-**10da)**



Alkylborane **6da** was prepared according to *GP1a*. An oven-dried, 25-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (5 mL) and (*E*)-6-bromohex-1-en-1-yl pinacolborane (289.0 mg, 1.00 mmol). The resulting colorless solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of phenyllithium **2a** in diethyl ether (1.77 M, 621 μL, 1.1 mmol, 1.1 equiv) was added dropwise over 10 min, such that the internal temperature did not exceed –68 °C. The dark red color of the phenyllithium solution immediately disappeared upon addition to the reaction mixture. The resulting pale, beige solution was stirred at –78 °C for 1 h. A separate, oven-dried, 25-mL, Schlenk flask (**B**) equipped with a stir bar was charged with chiral (*S*)-catalyst **5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10

min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting beige-colored, foam solid boronate complex **3da** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min at –60 °C. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate complex. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1.0 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6da**.

Borane **6da** was oxidized to alcohol **7da** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6da**, THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (616 mg, 4.0 mmol) was added to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 3 h. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with Et_2O (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7da**. The product was purified by chromatography (silica gel, 3 x 20 cm, wet load with CH_2Cl_2, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 90:10 (600 mL)) to afford pure **7da**. The product is stable at room temperature for several hours in the presence of trace amounts of solvent. Attempts to rigorously purify **7da** resulted in extensive decomposition, presumably due to displacement of bromide by the thioether. Consequently, the product was analyzed and characterized as the corresponding sulfone **10da**.

A 100-mL, round-bottomed flask equipped with a stir bar was charged with thioether **7da**, CH_2Cl_2 (10 mL), and *m*-CPBA (379.7 mg, 2.2 mmol). The reaction mixture was stirred at 25 °C for 12 h. Full conversion was observed by TLC (hexanes/EtOAc, 80:20, CAM). The reaction was quenched by the addition of sat. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. Then aq. NaOH (1 N, 10 mL) was added to the mixture. The mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (4 x 50 mL). The combined organic phases were washed with aq. NaOH (1 N, 20 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **10da**. The product was purified by chromatography (silica gel, 3 x 20 cm, wet load with CH_2Cl_2, 25-mL fractions, hexanes/EtOAc gradient elution: 90:10 (600 mL) to 85:15 (600 mL)) to afford 336.3 mg (84%) of pure **10da** as a white solid. Precipitation from hexanes/Et_2O afforded 320.3 mg (80%) of analytically pure **10da** as white solid.

Data for (1*S*,2*S*)-(+)-**10da**:

m.p.: 69–70 °C (hexanes/Et_2O)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.96 – 7.89 (m, 2H, HC(12)), 7.73 – 7.65 (m, 1H, HC(14)), 7.61 – 7.57 (m, 2H, HC(13)), 7.36 – 7.27 (m, 5H, HC(8), HC(9), and HC(10)), 5.03 (d, J = 8.7 Hz, 1H, HC(1)), 4.31 (bs, 1H, OH), 3.30 (ddd, J = 8.7, 5.8, 4.5 Hz, 1H, HC(2)), 3.03 (tq, J = 7.0, 3.2 Hz, 2H, H_2C(6)), 1.67 – 1.57 (m, 1H, H_2C(3)), 1.47 – 1.39 (m, 2H, H_2C(5)), 1.34 – 1.26 (m, 1H, H_2C(3)), 1.09 – 0.98 (m, 1H, H_2C(4)), 0.96 – 0.86 (m, 1H, H_2C(4)).

^{13}C NMR: (126 MHz, $CDCl_3$)

139.6 (C(7)), 138.4 (C(11)), 134.2 (HC(14)), 129.5 (HC(13)), 128.92 (HC(10)), 128.88 (HC(9) or HC(12)), 128.85 (HC(9) or HC(12)), 127.3 (HC(8)), 73.6 (HC(1)), 70.5 (HC(2)), 32.7 (H_2C(6)), 32.1 (H_2C(5)), 26.0 (H_2C(3)), 25.8 (H_2C(4)).

IR: (neat)

3494 (w), 2922 (w), 1496 (w), 1478 (w), 1447 (w), 1398 (w), 1376 (w), 1355 (w), 1278 (m), 1247 (w), 1229 (w), 1211 (w), 1147 (w), 1132 (m), 1078 (w), 1070 (w), 1028 (w), 997 (w), 916 (w), 836 (w), 760 (m), 730 (m), 703 (w), 689 (m), 640 (w), 610 (w), 566 (m), 554 (w), 529 (m), 516 (m), 486 (w), 459 (w).

LRMS: (ESI, $[M+Na]^+$)

157.1(11), 237.0(69), 381.0(48), 419.0(96), 421.0(100).

HRMS: calcd for $C_{18}H_{21}BrO_3SNa$ ([M+Na]$^+$): 419.0292, found: 419.0305

Analysis: $C_{18}H_{21}BrO_3S$ (397.33)

Calcd: C, 54.41%; H, 5.33%

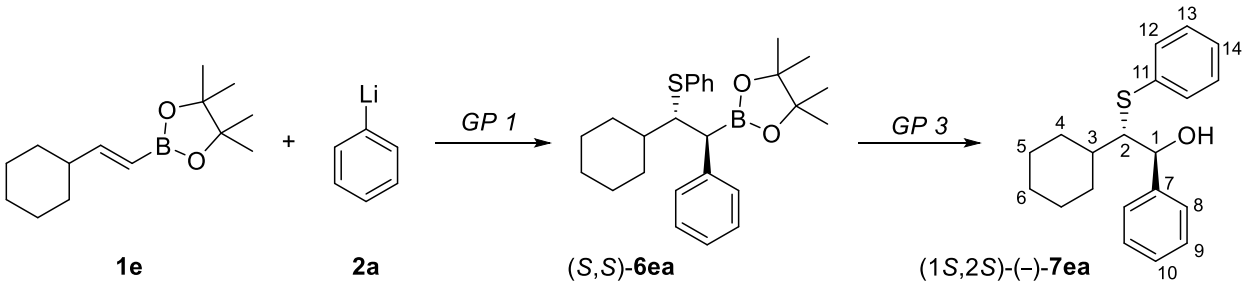
Found: C, 54.38%; H, 5.32%

TLC: R_f 0.41 (hexanes/EtOAc, 67:33, CAM)

HPLC: (1*R*,2*R*)-**10da** t_R 12.1 min (1%); (1*S*,2*S*)-**10da** t_R 17.9 min (99%) (Supelco Astec, hexanes/*i*-PrOH, 80:20, 1.0 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ +41.2 (*c* = 1.00 in 100% EtOH) (98% ee)

Preparation of (1*S*,2*S*)-(–)-**2-Cyclohexyl-1-phenyl-2-(phenylthio)ethan-1-ol (**(1*S*,2*S*)-(–)-**7ea)**



Alkylborane **6ea** was prepared according to *GP1a*. An flame-dried, 25-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (5 mL) and (*E*)-2-cyclohexylvinyl pinacolborane **1e** (236.2 mg, 1.00 mmol). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of phenyllithium **2a** in diethyl ether (1.77 M, 621 μL, 1.10 mmol, 1.10 equiv) was added dropwise over 10 min. The dark red color of the phenyllithium solution immediately disappeared upon addition to the reaction mixture. The resulting solution of boronate **3ea** was stirred at –78 °C for 1 h. A separate, flame-dried, 50-mL, Schlenk flask (**B**) equipped with a stir bar was charged with chiral (*S*)-catalyst **5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. At this point, flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum until all of the THF

was removed (30 min). The resulting solid boronate complex **3ea** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate complex. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with diethyl ether (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6ea**. As **7ea** is difficult to separate from catalyst (*S*)-**5** by chromatography, **6ea** was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/CH_2Cl_2 gradient elution: 75:25 (600 mL) to 65:35 (600 mL)) prior to oxidation.

Borane **6ea** was oxidized to alcohol **7ea** according to *GP3*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ea** and THF (10 mL). The turbid solution was cooled to 0 °C with an ice bath. To this solution was added a mixture of 30% aq. H_2O_2 (1 mL) and 3 M aq. NaOH (1 mL) also containing EDTA (1.0 mg/mL). The biphasic mixture was stirred rapidly at 0 °C for 30 min. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL) and was stirred for 30 min at 25 °C. The mixture was transferred to a separatory funnel and extracted with diethyl ether (4 x 50 mL). The combined organic phases were washed with sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (25 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **7ea**. The product was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 97:3 (600 mL) to 94:6 (600 mL)) to afford 284.7 mg (91% yield) of **7ea** as an oil. The product was purified to analytical standard by diffusion pump Kugelrohr distillation (160 °C ABT, 4.0 x 10^{-5} mmHg) to afford 282.6 mg (90%) of **7ea** as a viscous oil.

Data for (*S*,*S*)-(–)-**7ea**:

b.p.: 160 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.42 – 7.38 (m, 2H, HC(12)), 7.38 – 7.31 (m, 4H, HC(8) and HC(9)), 7.30 – 7.20 (m, 3H, HC(13) and HC(10)), 7.19 – 7.16 (m, 1H, HC(14)), 4.79 (dd, *J* = 8.2, 3.1 Hz, 1H, HC(1)), 3.20 (dd, *J* = 8.2, 3.4 Hz, 1H, HC(2)), 3.18 (d, *J* = 3.2 Hz, 1H, OH), 1.89 – 1.82 (m, 1H, H_2C(4)), 1.79 – 1.70 (m, 1H, H_2C(5)), 1.64 (ddt, *J* = 27.5, 9.7, 2.4 Hz, 2H, H_2C(5)), 1.57 (dd, *J* = 12.1, 3.6 Hz, 1H, H_2C(4)), 1.51 – 1.41 (m, 2H, H_2C(4) and HC(3)), 1.30 (dd, *J* = 12.0, 3.4 Hz, 1H, H_2C(4)), 1.20 – 1.05 (m, 3H, H_2C(5) and H_2C(6)).

^{13}C NMR: (126 MHz, $CDCl_3$)

142.0 (C(7)), 137.5 (C(11)), 131.3 (C(12)), 129.1 (C(13)), 128.6 (C(9)), 128.0 (C(10)), 126.8 (C(8)), 126.7 (C(14)), 74.6 (C(1)), 68.5 (C(2)), 40.3 (C(3)), 32.0 (C(4)), 28.5 (C(4)), 26.4 (C(5)), 26.3 (C(5)), 26.3 (C(6)).

IR: (neat)

3449 (w), 3059 (w), 2922 (m), 2850 (w), 1740 (w), 1581 (w), 1494 (w), 1477 (w), 1449 (w), 1438 (w), 1384 (w), 1348 (w), 1301 (w), 1244 (w), 1188 (w), 1085 (w), 1042 (w), 1025 (w), 1004 (w), 965 (w), 940 (w), 911 (w), 890 (w), 831 (w), 792 (w), 766 (w), 746 (m), 733 (m), 698 (m), 690 (m), 637 (w), 606 (w), 567 (w), 539 (w), 489 (w), 471 (w).

LRMS: (ESI, $[M+Na]^+$)

117.1 (14), 185.1 (100), 199.1 (67), 295.2 (86), 335.1 (31).

HRMS: calcd for $C_{20}H_{24}OSNa$ ($[M+Na]^+$): 335.1446, found: 335.1434

Analysis: $C_{20}H_{24}OS$ (312.47)

Calcd: C, 76.88; H, 7.74%

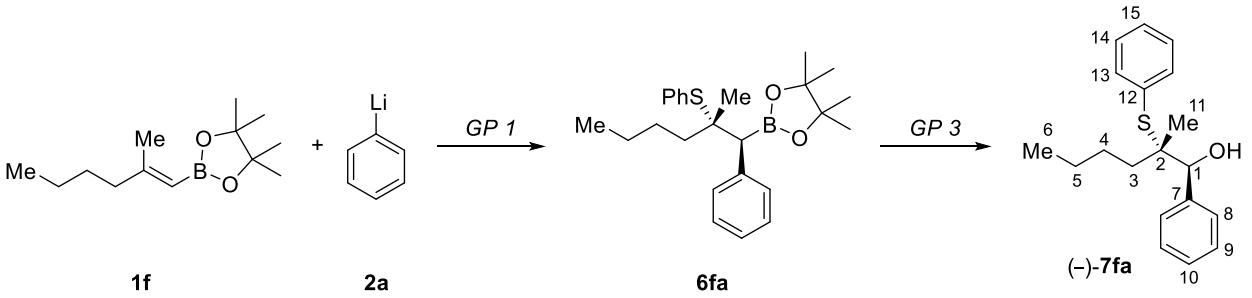
Found: C, 76.88; H, 7.48%

TLC: R_f 0.50 (hexanes/EtOAc, 83:17, CAM)

HPLC: (1*S*,2*S*)-**7ea** t_R 21.1 min (99%); (1*R*,2*R*)-**7ea** t_R 22.4 min (1%) (Supelco Astec, hexanes/*i*-PrOH, 95:5, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –11.9 (*c* = 0.88 in 100% EtOH) (98% ee)

Preparation of (–)**-2-Methyl-1-phenyl-2-(phenylthio)hexan-1-ol (**(–)**-7fa)**



Alkylborane **6fa** was prepared according to *GP1a*. An oven-dried, 50-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (7.5 mL) and (*E*)-2-methylhex-1-en-1-yl pinacolborane **1f** (334.6 mg, 1.49 mmol). The resulting clear, colorless solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of phenyllithium **2a** in diethyl ether (1.77 M, 886 μL, 1.57 mmol, 1.05 equiv) was added dropwise over 10 min, such that the internal temperature did not exceed –68 °C. The dark red color of the phenyllithium solution immediately disappeared upon addition to the reaction mixture. After the addition, the resulting pale, brown solution was stirred at –78 °C for 1 h. A separate, oven-dried, 25-mL, Schlenk flask (**B**) equipped with a stir bar was charged with chiral (*S*)-catalyst **5** (78.3 mg, 0.15 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (527.4 mg, 1.81 mmol, 1.21 equiv). The flask was sealed with a septum and removed from the glove box. Ethanol (7.5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. At this point, flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum until all of the THF was removed (30 min). The resulting white, flaky solid boronate complex **3fa** in flask **A** was taken up in ethanol (3.75 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (3.75 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate complex. Flask **B** was stirred at –60 °C for 40 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (3.75 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C. The mixture was diluted with diethyl ether (7.5 mL) and water (7.5 mL) and stirred rapidly to dissolve all solids. The biphasic mixture was transferred to a

60-mL separatory funnel and the layers were separated. The aqueous layer was washed with diethyl ether (2 x 15 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford the crude borane **6fa** as a pink, oily solid. The yield of **6fa** was determined to be 33% by quantitative ^{1}H-NMR as described previously (p. S7).

Borane **6fa** was oxidized to alcohol **7fa** according to *GP3*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6fa** and THF (15 mL). The turbid solution was cooled to 0 °C with an ice bath. To this solution was added a mixture of 30% aq. H_2O_2 (1.5 mL) and 3 M aq. NaOH (1.5 mL) also containing EDTA (1.0 mg/mL). The biphasic mixture was stirred rapidly at 0 °C for 3 h. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of a sodium bisulfite ($NaHSO_3$) aq. solution (1.80 g in 15 mL water) and stirred for 15 min. The mixture was transferred to a separatory funnel and diluted with diethyl ether (45 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 x 25 mL). The combined organic phases were washed with brine (25 mL) and then dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford 680.4 mg of crude **7fa**. The product was purified by chromatography (silica gel, 3 x 28 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 97.5:2.5 (300 mL) to 95:5 (600 mL) to 92.5:7.5 (300 mL) to 90:10 (300 mL)) to afford 135.1 mg of **7fa** as an oil. The product was purified a second time by chromatography to remove an unidentified impurity (silica gel, 2 x 28 cm, dry load on Celite, 25-mL fractions, hexanes/CH_2Cl_2 gradient elution: 90:10 (200 mL) to 80:20 (200 mL) to 70:30 (200 mL) to 60:40 (200 mL) to 50:50 (200 mL) to 60:40 (200 mL)) to afford 133.6 mg of **7fa**. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (90 °C ABT, 4.0 x 10^{-5} mmHg) to afford 119.0 mg (27% yield) of **7fa** as a viscous, colorless oil.

Data for (–)-**7fa**:

b.p.: 90 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.61–7.54 (m, 2H, HC(13)), 7.45–7.41 (m, 1H, HC(15)), 7.40–7.36 (m, 2H, HC(14)), 7.31–7.23 (m, 5H, HC(8), HC(9) and HC(10)), 4.30 (s, 1H, HC(1)), 3.86 (s, 1H, OH), 1.89–1.78 (m, 1H, H_2C(4)), 1.34–1.25 (m, 1H, H_2C(4)), 1.25–1.14 (m, 4H, H_2C(5) and H_2C(3)), 1.13 (s, 3H, H_3C(11)), 0.87 (t, J = 7.2 Hz, 3H, H_3C(6)).

^{13}C NMR: (126 MHz, $CDCl_3$)

138.9 (C(7)), 137.1 (HC(13)), 130.1 (C(12)), 129.5 (HC(15)), 129.1 (HC(14)), 128.6 (HC(8) or HC(9)), 127.78 (HC(10)), 127.75 (HC(8) or HC(9)), 76.8 (HC(1)), 61.6 (C(2)), 35.5 (H_2C(3)), 26.4 (H_2C(4)), 23.1 (H_2C(5)), 17.7 (H_3C(11)), 14.4 (H_3C(6)).

IR: (neat)

3462 (w), 3061 (w), 3030 (w), 2956 (w), 2933 (w), 2870 (w), 1953 (w), 1886 (w), 1811 (w), 1604 (w), 1583 (w), 1573 (w), 1493 (w), 1474 (w), 1468 (w), 1454 (m), 1438 (m), 1378 (w), 1326 (w), 1303 (w), 1241 (w), 1187 (m), 1155 (w), 1128 (w), 1093 (w), 1044 (m), 1025 (m), 918 (w), 851 (w), 808 (w), 790 (w), 749 (s), 701 (s), 693 (s), 674 (m), 619 (w), 596 (m), 525 (m), 503 (m), 458 (m),

LRMS: (EI, 70 eV)

51.0 (17), 55.1 (69), 57.1 (17), 59.1 (15), 65.1 (22), 66.1 (10), 77.0 (63), 78.1 (13), 79.1 (55), 83.1 (70), 85.1 (10), 91.1 (63), 105.1 (29), 107.1 (35), 109.0 (56), 110.0 (65), 111.0 (18), 115.1 (20), 117.1 (37), 123.0 (70), 129.1 (13), 131.1 (36), 135.0 (10), 137.1 (94), 138.1 (12), 151.1 (25), 173.1 (27), 191.2 (15), 193.1 (100), 194.1 (92), 195.1 (39), 200.1 (14), 300.2 (1).

Analysis: $C_{19}H_{24}OS$ (300.46)

Calcd: C, 75.95%; H, 8.05%

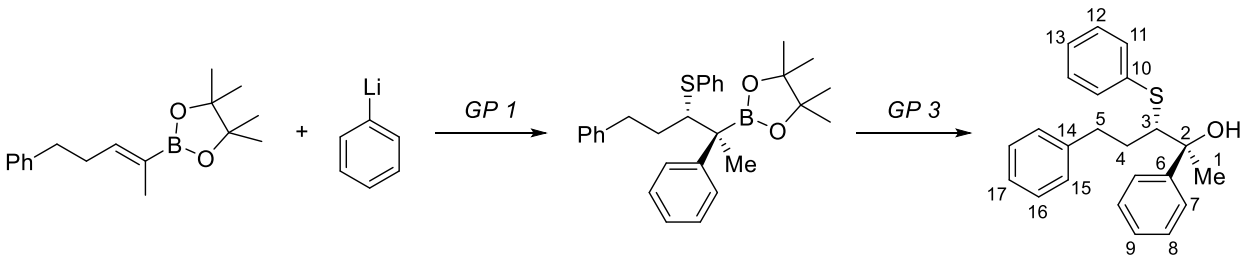
Found: C, 75.79%; H, 7.76%

TLC: R_f 0.35 (hexanes/EtOAc, 90:10, CAM)

HPLC: (–)-**7fa** t_R 12.6 min (54%); (+)-**7fa** t_R 19.7 min (46%) (Regis (*R*,*R*)-Whelk O1, hexanes/*i*-PrOH, 95:5, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –10.2 (*c* = 1.00 in 95% EtOH) (8% ee)

Preparation of (2*S*,3*S*)-(+)-**2,5-Diphenyl-3-(phenylthio)pentan-2-ol (**(2*S*,3*S*)-(+)-**7ga)**



1g **2a** (*S*,*S*)-**6ga** (2*S*,3*S*)-(+)-**7ga**

Alkylborane **6ga** was prepared according to *GP1a*. An oven-dried, 25-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (5 mL) and (*Z*)-5-phenylpent-2-en-2-yl pinacolborane **1g** (273.0 mg, 1.00 mmol). The resulting pale, yellow solution was cooled to –78 °C using a dry ice/isopropanol bath, and then stirred for 15 min to allow the temperature to equilibrate. A solution of phenyllithium **2a** in diethyl ether (1.77 M, 595 μL, 1.05 mmol, 1.05 equiv) was added dropwise over 10 min, such that the internal temperature did not exceed –68 °C. The dark red color of the phenyllithium solution immediately disappeared upon addition to the reaction mixture. The resulting pale, yellow solution was stirred at –78 °C for 1 h. A separate, oven-dried, 25-mL, Schlenk flask (**B**) equipped with a stir bar was charged with chiral (*S*)-catalyst **5** (52.8 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (349.9 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting beige-colored, foam solid boronate complex **3ga** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate complex. Flask **B** was stirred at –60 °C for 48 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (2.5 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C. The mixture was diluted with diethyl ether (5 mL) and water (5 mL) and stirred rapidly to dissolve all solids. The biphasic mixture was transferred to a 60-mL separatory funnel and the layers were separated. The aqueous layer was washed with diethyl ether (2 x 10 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford 0.60 g of crude borane **6ga** as a red oil. The yield of **6ga** was determined to be 81% by quantitative ^{1}H-NMR as described previously (p. S7).

Borane **6ga** was oxidized to alcohol **7ga** according to *GP3*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ga** and THF (10 mL). The turbid, red-

colored solution was cooled to 0 °C with an ice bath. To this solution was added a mixture of 30% aq. H_2O_2 (1 mL) and 3 M aq. NaOH (1 mL) also containing EDTA (1.0 mg/mL). The biphasic mixture was stirred rapidly at 0 °C for 1.5 h. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of a sodium bisulfite ($NaHSO_3$) aq. solution (1.20 g in 10 mL water) and stirred for 15 min. The mixture was transferred to a separatory funnel and diluted with diethyl ether (30 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 x 15 mL). The combined organic phases were washed with brine (25 mL) and then dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford 0.53 g of crude **7ga** as a pink oil. The product was purified by chromatography (silica gel, 3 x 25 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 92.5:7.5 (300 mL) to 90:10 (300 mL)) to afford 307.2 mg of **7ga** as a pink oil which is contaminated with 5-phenylpentan-2-one.[22] **Note:** To remove this ketone impurity prior to distillation, the product mixture was dissolved in absolute ethanol (5 mL) and the resulting solution was cooled to 0 °C with an ice bath. Sodium borohydride (9 mg) was added, and the reaction mixture was stirred at 0 °C for 30 min. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The mixture was diluted with diethyl ether (10 mL) and water (10 mL) and transferred to a 60-mL separatory funnel. The layers were separated. The aqueous layer was extracted with diethyl ether (2 x 10 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg). The residue was purified by chromatography (silica gel, 3 x 25 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 92.5:7.5 (300 mL) to 90:10 (300 mL)) to afford 281.0 mg of **7ga** as an oil. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (120 °C ABT, 4.0 x 10^{-5} mmHg) to afford 265.5 mg (76% yield) of **7ga** as a viscous, colorless oil.

Data for (2*S*,3*S*)-(+)-**7ga**:

b.p.: 120 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.46–7.42 (m, 2H, HC(11)), 7.42–7.39 (m, 2H, HC(7)), 7.30–7.19 (m, 6H, HC(9), HC(8), HC(12), HC(13)), 7.16–7.08 (m, 3H, HC(16), HC(17)), 6.82 (dd, *J* = 7.2, 1.8 Hz, 2H, HC(15)), 3.33 (dd, *J* = 11.3, 2.2 Hz, 1H, HC(3)), 3.13 (s, 1H, OH), 2.97 (ddd, *J* = 13.7, 9.1, 4.4 Hz, 1H, H_2C(5)), 2.50 (ddd, *J* = 13.9, 8.4 Hz, 1H, H_2C(5)),

1.97–1.89 (m, 1H, $H_2C(4)$), 1.78–1.70 (m, 1H, $H_2C(4)$), 1.63 (s, 3H, $H_3C(1)$).

^{13}C NMR: (126 MHz, $CDCl_3$)

145.0 (C(6)), 141.2 (C(14)), 137.2 (C(10)), 131.3 (HC(11)), 129.2 (HC(12)), 128.5 (HC(15) or HC(16)), 128.4 (HC(15) or HC(16)), 128.2 (HC(8)), 127.4 (HC(9)), 126.9 (HC(13)), 126.1 (HC(7)), 125.9 (HC(17)), 76.5 (C(2)), 65.2 (HC(3)), 34.0 ($H_2C(5)$), 33.7 ($H_2C(4)$), 24.1 ($H_3C(1)$).

IR: (neat)

3473 (w), 3059 (w), 3026 (w), 2932 (w), 2857 (w), 1602 (w), 1582 (w), 1495 (w), 1479 (w), 1446 (m), 1439 (m), 1375 (w), 1344 (w), 1182 (w), 1066 (w), 1026 (m), 1001 (w), 937 (w), 908 (m), 875 (w), 792 (w), 764 (m), 738 (s), 695 (s), 616 (m), 594 (w), 563 (w), 488 (m).

LRMS: (EI, 70 eV)

51.0 (13), 65.1 (18), 77.0 (24), 91.1 (88), 92.1 (10), 109.0 (13), 110.0 (41), 115.1 (16), 117.1 (45), 118.1 (55), 121.1 (71), 131.1 (81), 135.0 (12), 222.1 (13), 228.1 (100), 229.1 (23), 348.2 (<1).

Analysis: $C_{23}H_{24}OS$ (348.50)

Calcd: C, 79.27%; H, 6.94%

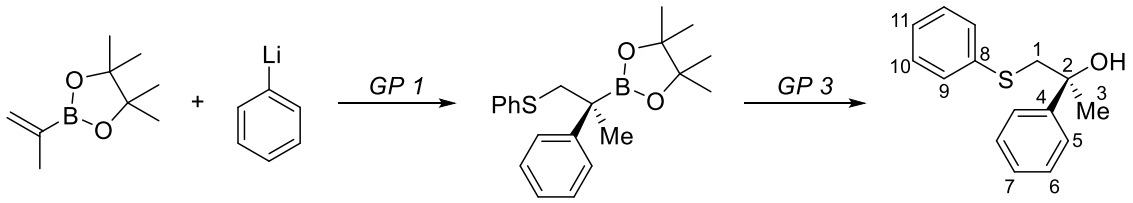
Found: C, 78.98%; H, 6.88%

TLC: R_f 0.28 (hexanes/EtOAc, 90:10, CAM)

HPLC: (2*S*,3*S*)-**7ga** t_R 20.2 min (96%); (2*R*,3*R*)-**7ga** t_R 21.8 min (4%) (Supelco Astec, hexanes/*i*-PrOH, 95:5, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ +17.8 (*c* = 1.30 in 95% EtOH) (92% ee)

Preparation of (*S*)-(–)-**2-Phenyl-1-(phenylthio)propan-2-ol (**(*S*)-(–)-**7ha)**



Alkylborane **6ha** was prepared according to a **modification** of *GP1a*. An oven-dried, 25-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was

charged with THF (5 mL) and isopropenyl pinacolborane **1h** (167.9 mg, 1.00 mmol). The resulting colorless solution was cooled to –78 °C using a dry ice/isopropanol bath, and then stirred for 15 min to allow the temperature to equilibrate. A solution of phenyllithium **2a** in diethyl ether (1.77 M, 595 μL, 1.05 mmol, 1.05 equiv) was added dropwise over 10 min, such that the internal temperature did not exceed –68 °C. The dark red color of the phenyllithium solution immediately disappeared upon addition to the reaction mixture. The resulting *white suspension* was stirred at –78 °C for 10 min, then warmed to 0 °C, resulting in a pale, yellow solution. The solution was maintained at 0 °C for 50 min and then returned to –78 °C, again resulting in a white suspension. A separate, oven-dried, 25-mL, Schlenk flask (**B**) equipped with a stir bar was charged with chiral (*S*)-catalyst **5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The white suspension was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting white, flaky solid boronate complex **3ha** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 36 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (2.5 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C. The mixture was diluted with diethyl ether (5 mL) and water (5 mL) and stirred rapidly to dissolve all solids. The biphasic mixture was transferred to a 60-mL separatory funnel and the layers were separated. The aqueous layer was washed with diethyl ether (2 x 10 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford 466.3 mg of crude borane **6ha** as a red oil. The yield of **6ha** was determined to be 89% by quantitative ^{1}H-NMR as described previously (p. S7).

Borane **6ha** was oxidized to alcohol **7ha** according to *GP3*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ha** and THF (10 mL). The turbid, red-colored solution was cooled to 0 °C with an ice bath. To this solution was added a mixture of 30%

aq. H_2O_2 (1 mL) and 3 M aq. NaOH (1 mL) also containing EDTA (1.0 mg/mL). The biphasic mixture was stirred rapidly at 0 °C for 30 min. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of a sodium bisulfite ($NaHSO_3$) aq. solution (1.20 g in 10 mL water) and stirred for 15 min. The mixture was transferred to a separatory funnel and diluted with diethyl ether (30 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 x 15 mL). The combined organic phases were washed with brine (25 mL) and then dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford 378.4 mg of crude **7ha** as an oil. The product was purified by chromatography (silica gel, 3 x 25 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 90:10 (600 mL)) to afford 194.2 mg of **7ha** as a yellow oil. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (80 °C ABT, 3.4 x 10^{-5} mmHg) to afford 180.3 mg (74% yield) of **7ha** as a viscous, pale, yellow oil.

Data for (*S*)-(–)-**7ha**:

b.p.: 80 °C (ABT, 3.4 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.48–7.43 (m, 2H, HC(5)), 7.36–7.30 (m, 4H, HC(9) and HC(6)), 7.26–7.21 (m, 3H, HC(7) and HC(10)), 7.19–7.14 (m, 1H, HC(11)), 3.54 (d, *J* = 13.3 Hz, 1H, H_2C(1)), 3.36 (d, *J* = 13.3 Hz, 1H, H_2C(1)), 2.85 (s, 1H, OH), 1.62 (s, 3H, H_3C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

146.3 (C(4)), 136.7 (C(8)), 130.2 (HC(9)), 129.1 (HC(10)), 128.4 (HC(6)), 127.3 (HC(7)), 126.6 (HC(11)), 125.0 (HC(5)), 74.1 (C(2)), 49.8 (H_2C(1)), 29.6 (H_3C(3)).

IR: (neat)

3448 (w), 3058 (w), 2976 (w), 2927 (w), 1582 (w), 1493 (w), 1480 (m), 1446 (m), 1439 (m), 1373 (w), 1333 (w), 1269 (w), 1238 (w), 1179 (w), 1087 (m), 1066 (m), 1025 (m), 1000 (w), 940 (w), 911 (w), 842 (w), 765 (m), 737 (s), 716 (m), 697 (s), 689 (s), 608 (m), 581 (m), 541 (m), 473 (m).

LRMS: (EI, 70 eV)

77.1 (24), 78.1 (18), 91.1 (15), 103.1 (18), 109.0 (11), 110.0 (41), 111.0 (82), 115.1 (13), 117.1 (41), 118.1 (24), 119.1 (72), 121.1 (27), 124.1 (37), 125.1 (11), 149.1 (42), 211.1 (13), 226.1 (29), 227.1 (100), 228.1 (14), 244.1 (1), 245.2 (1).

Analysis: $C_{15}H_{16}OS$ (244.35)

Calcd: C, 73.73%; H, 6.60%

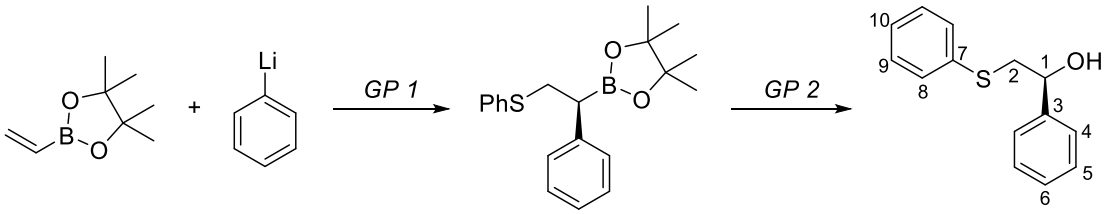
Found: C, 73.70%; H, 6.54%

TLC: R_f 0.19 (hexanes/EtOAc, 90:10, CAM)

SFC: (*S*)-**7ha** t_R 18.9 min (95%); (*R*)-**7ha** t_R 20.0 min (5%) (Chiralpak OD, 5-15% MeOH in CO_2 over 20 min, then hold 15% MeOH in CO_2 for 10 min, 2.0 mL/min, 220 nm, 40 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –23.1 (*c* = 1.33 in 95% EtOH)

Preparation of (*S*)-(–)-**1-Phenyl-2-(phenylthio)ethan-1-ol (**(*S*)-(–)-**7ia)**



1i **2a** (*S*)-**6ia** (*S*)-(–)-**7ia**

Alkylborane **6ia** was prepared according to *GP1a*. An oven-dried, 25-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (5 mL) and vinyl pinacolborane **1i** (154.3 mg, 1.00 mmol). The resulting colorless solution was cooled to –78 °C using a dry ice/isopropanol bath, and then stirred for 15 min to allow the temperature to equilibrate. A solution of phenyllithium **2a** in diethyl ether (1.77 M, 595 μL, 1.05 mmol, 1.05 equiv) was added dropwise over 10 min, such that the internal temperature did not exceed –68 °C. The dark red color of the phenyllithium solution immediately disappeared upon addition to the reaction mixture. The resulting pale, pink-brown solution was stirred at –78 °C for 1 h. A separate, oven-dried, 25-mL, Schlenk flask (**B**) equipped with a stir bar was charged with chiral (*S*)-catalyst **5** (51.9 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting beige-colored, foam solid boronate complex **3ia** in flask **A**

was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 16 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (2.5 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C. The mixture was diluted with diethyl ether (5 mL) and water (5 mL) and stirred rapidly to dissolve all solids. The biphasic mixture was transferred to a 60-mL separatory funnel and the layers were separated. The aqueous layer was washed with diethyl ether (2 x 10 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford 371.0 mg of crude borane **6ia** as a yellow oil. The yield of **6ia** was determined to be 65% by quantitative ^{1}H-NMR as described previously (p. S7).

Borane **6ia** was oxidized to alcohol **7ia** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ia** (371.0 mg), THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (604.3 mg, 3.9 mmol) and tetra-*n*-butylammonium chloride (31.7 mg, 0.11 mmol) were added sequentially to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 2 h at 25 °C. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of solid sodium bisulfite, $NaHSO_3$ (1.20 g) and the resulting mixture was stirred for 15 min. Then, aq. NaOH was added (1 M, 20 mL) and the mixture was stirred for 30 min. The mixture was transferred to a separatory funnel and diluted with diethyl ether (30 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 x 15 mL). The combined organic phases were washed with brine (25 mL) and then dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford 295.7 mg of crude **7ia** as an oil. The product was purified by chromatography (silica gel, 3 x 19 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 90:10 (600 mL) to 85:15 (300 mL)) to afford 144.4 mg of **7ia** as an oil. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (100 °C ABT, 4.2 x 10^{-5} mm Hg) to afford 137.8 mg (60% yield) of **7ia** as a viscous, pale, yellow oil.

Data for (*S*)-(–)-**7ia**:

b.p.: 100 °C (ABT, 4.2 x 10^{-5} mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.45–7.41 (m, 2H, HC(8)), 7.38–7.34 (m, 4H, HC(4) and HC(5)), 7.34–7.28 (m, 3H, HC(9) and HC(6)), 7.26–7.22 (HC(10)), 4.73 (dt, *J* = 9.5, 2.9 Hz, 1H, HC(1)), 3.34 (dd, *J* = 13.8, 3.5 Hz, 1H, H_2C(2)), 3.10 (dd, *J* = 13.8, 9.5 Hz, 1H, H_2C(2)), 2.82 (d, *J* = 2.4 Hz, 1H, OH).

^{13}C NMR: (126 MHz, $CDCl_3$)

142.3 (C(3)), 135.0 (C(7)), 130.4 (HC(8)), 129.3 (HC(9)), 128.7 (HC(5)), 128.2 (HC(6)), 127.0 (HC(10)), 126.0 (HC(4)), 71.8 (HC(1)), 44.3 (H_2C(2)).

IR: (neat)

3395 (w), 3059 (w), 3029 (w), 2961 (w), 2919 (w), 1950 (w), 1881 (w), 1807 (w), 1601 (w), 1582 (w), 1493 (w), 1480 (m), 1453 (w), 1438 (m), 1409 (w), 1331 (w), 1300 (w), 1272 (w), 1232 (w), 1193 (w), 1156 (w), 1086 (w), 1053 (m), 1025 (m), 1001 (m), 989 (m), 914 (w), 857 (w), 769 (w), 736 (s), 691 (s), 612 (m), 523 (m), 474 (m).

LRMS: (EI, 70 eV)

51.0 (41), 65.1 (19), 77.0 (71), 78.0 (25), 79.0 (79), 91.0 (30), 107.0 (41), 109.0 (16), 110.0 (10), 123.0 (16), 124.0 (100), 125.0 (10), 230.1 (9), 231.0 (2).

Analysis: $C_{14}H_{14}OS$ (230.32)

Calcd: C, 73.01%; H, 6.13%

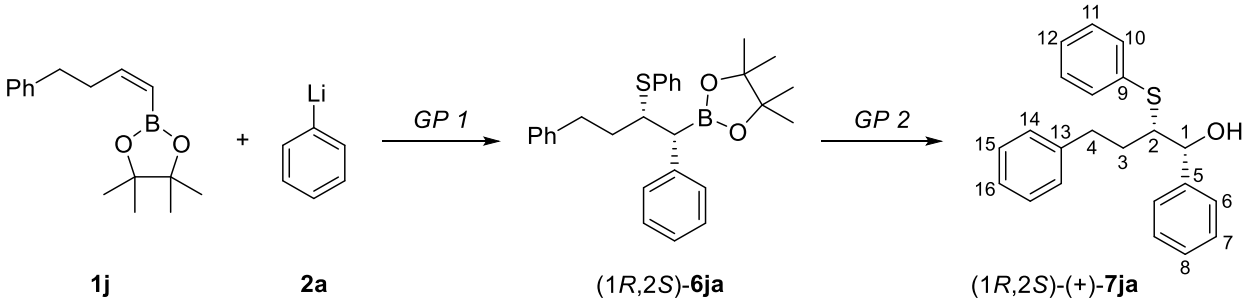
Found: C, 72.81%; H, 5.97%

TLC: R_f 0.14 (hexanes/EtOAc, 90:10, CAM)

HPLC: (*S*)-**7ia** t_R 10.7 min (84%); (*R*)-**7ia** t_R 12.5 min (16%) (Regis (*R*,*R*)-Whelk O1, hexanes/*i*-PrOH, 80:20, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –36.3 (*c* = 1.37 in 95% EtOH) (68% ee)

Preparation of (1*R*,2*S*)-(+)-**1,4-Diphenyl-2-(phenylthio)butan-1-ol (**(1*R*,2*S*)-(+)-**7ja)**



1j **2a** (1*R*,2*S*)-**6ja** (1*R*,2*S*)-(+)-**7ja**

Alkylborane **6ja** was prepared according to *GP1a*. An oven-dried, 25-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (5 mL) and (*Z*)-4-phenylbut-1-en-1-yl pinacolborane **1j** (259.5 mg, 1.01 mmol). The resulting clear, colorless solution was cooled to –78 °C using a dry ice/isopropanol bath, and then stirred for 15 min to allow the temperature to equilibrate. A solution of phenyllithium **2a** in diethyl ether (1.77 M, 596 μL, 1.06 mmol, 1.05 equiv) was added dropwise over 10 min, such that the internal temperature did not exceed –68 °C. The dark red color of the phenyllithium solution immediately disappeared upon addition to the reaction mixture. After the addition, the resulting pale, yellow solution was stirred at –78 °C for 1 h. A separate, oven-dried, 25-mL, Schlenk flask (**B**) equipped with a stir bar was charged with chiral (*S*)-catalyst **5** (52.8 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (352.3 mg, 1.21 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. At this point, flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum until all of the THF was removed (30 min). The resulting white, solid boronate complex **3ja** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 48 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (2.5 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C. The mixture was diluted with diethyl ether

(5 mL) and water (5 mL) and stirred rapidly to dissolve all solids. The biphasic mixture was transferred to a 60-mL separatory funnel and the layers were separated. The aqueous layer was washed with diethyl ether (2 x 10 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford the crude borane **6ja** as a red oil. The yield of **6ja** was determined to be 62% by quantitative ^{1}H-NMR as described previously (p. S7).

Borane **6ja** was oxidized to alcohol **7ja** according to *GP2*. A 100-mL, round-bottomed flask equipped with a stir bar was charged with crude **6ja** (0.65 g), THF (10 mL) and water (10 mL). Sodium perborate tetrahydrate (600 mg, 4.42 mmol) and tetra-*n*-butylammonium chloride (30 mg, 0.11 mmol) were added sequentially to the rapidly stirred biphasic mixture at 25 °C. The mixture was stirred rapidly for 2 h. Full conversion was observed by TLC (hexanes/EtOAc, 90:10, CAM). The oxidation was quenched by the addition of solid sodium bisulfite, $NaHSO_3$ (1.20 g) and the resulting mixture was stirred for 15 min. Then, aq. NaOH was added (1 M, 20 mL) and the mixture was stirred for 30 min. The mixture was transferred to a separatory funnel and diluted with diethyl ether (30 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 x 15 mL). The combined organic phases were washed with brine (25 mL) and then dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford 0.47 g of crude **7ja**. The product was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (600 mL) to 92.5:7.5 (300 mL) to 90:10 (600 mL)) to afford 222.4 mg of **7ja** as an oil. The product was purified to an analytical standard by diffusion pump Kugelrohr distillation (125 °C ABT, 3.4 x 10^{-5} mmHg) to afford 205.1 mg (61% yield) of **7ja** as a viscous, clear, colorless oil.

Data for (1*R*,2*S*)-(+)-**7ja**:

b.p.: 125 °C (ABT, 3.4 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.46–7.40 (m, 2H, HC(10)), 7.34–7.26 (m, 5H, HC(11), HC(12), HC(7)), 7.25–7.23 (m, 1H, HC(8)), 7.23–7.19 (m, 4H, HC(6), HC(15)), 7.18–7.13 (m, 1H, HC(16)), 7.03–6.98 (m, 2H, HC(14)), 4.78 (t, *J* = 3.1 Hz, 1H, HC(1)), 3.34 (dt, *J* = 10.1, 3.2 Hz, 1H, HC(2)), 2.90 (ddd, *J* = 13.8, 9.1, 4.7 Hz, 1H, H_2C(4)), 2.79–2.75 (m, 1H, OH), 2.61 (dt, *J* = 14.0, 8.4 Hz, 1H, H_2C(4)), 1.97–1.86 (m, 1H, H_2C(3)), 1.80–1.69 (m, 1H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

141.4 (C(13)), 140.8 (C(5)), 134.6 (C(9)), 132.5 (HC(10)), 129.4 (HC(11)), 128.6 (HC(14) or HC(15)), 128.4 (HC(14) or HC(15)), 128.3 (HC(7)), 127.6 (HC(8) or HC(12)), 127.5 (HC(8) or HC(12)), 126.1 (HC(6)), 126.0 (HC(16)), 73.6 (HC(1)), 57.2 (HC(2)), 33.5 (H_2C(4)), 29.0 (H_2C(3)).

IR: (neat)

3448 (w), 3060 (w), 3026 (w), 2928 (w), 1602 (w), 1583 (w), 1496 (w), 1480 (w), 1452 (m), 1438 (w), 1388 (w), 1327 (w), 1221 (w), 1186 (w), 1091 (w), 1049 (m), 1025 (m), 918 (w), 845 (w), 742 (s), 695 (s), 604 (w), 561 (w), 544 (w), 492 (m).

LRMS: (EI, 70 eV)

65.0 (13), 77.0 (15), 91.1 (89), 104.1 (15), 109.0 (12), 110.0 (26), 115.1 (41), 116.1 (10), 117.1 (100), 118.1 (14), 128.1 (14), 129.1 (19), 165.1 (11), 169.1 (12), 170.1 (17), 178.1 (15), 179.1 (14), 191.1 (10), 205.1 (10), 206.1 (36), 207.1 (29), 208.1 (24), 228.1 (17), 316.1 (28), 334.1 (2).

Analysis: $C_{22}H_{22}OS$ (334.48)

Calcd: C, 79.00%; H, 6.63%

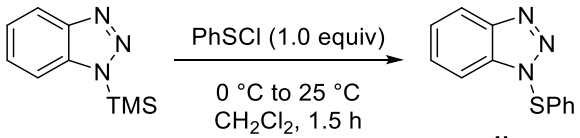
Found: C, 78.77%; H, 6.57%

TLC: R_f 0.23 (hexanes/EtOAc, 90:10, CAM)

HPLC: (1*S*,2*R*)-**7ja** t_R 20.2 min (31%); (1*R*,2*S*)-**7ja** t_R 22.6 min (69%) (Regis (*R*,*R*)-Whelk O1, hexanes/*i*-PrOH, 98:2, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ +7.6 (*c* = 1.18 in 95% EtOH) (38% ee)

Preparation of *N*-(Phenylthio)benzotriazole (4b)



4b

A flame-dried, 50-mL round-bottomed flask equipped with a stir bar was charged with (trimethylsilyl)benzotriazole[23] (2.00 g, 10.45 mmol) and CH_2Cl_2 (10 mL) and the resulting solution was cooled to 0 °C using an ice bath. A solution of phenylsulfenyl chloride[24] (1.51 g, 10.45 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added dropwise over 5 min. The reaction was stirred for 30 min at 0 °C and then for 1 h at 25 °C. Volatile components were removed by rotary evaporation (25

°C, 15 mmHg) and the flask was placed under hi-vacuum (<0.1 mmHg) for 3 h to remove the trimethylsilyl chloride byproduct, at which point crystalline, yellow solid **4b** could be observed. The flask was backfilled with argon, and hexanes (15 mL) were added via syringe. The yellow-colored supernatant was removed by cannula, and the flask was returned to high vacuum (<0.1 mmHg) to remove residual hexanes. This washing protocol was repeated, and the flask was dried under high vacuum (<0.1 mmHg) for 12 h to afford 2.00 g (84%) of yellow-beige solid **4b**. The product undergoes rapid hydrolysis in air and must be stored in the glove box.

Data for **4b**:

^{1}H NMR: (500 MHz, CDCl3)

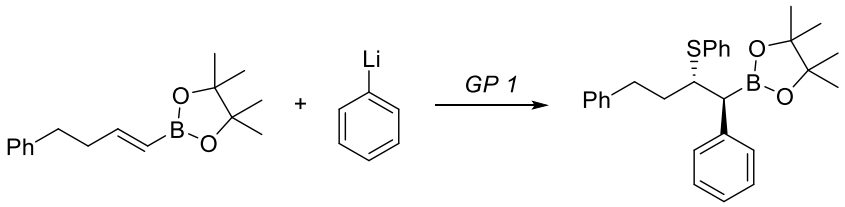
8.09 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.33 – 7.26 (m, 3H).

^{13}C NMR: (126 MHz, $CDCl_3$)

145.8, 137.1, 134.89 129.7, 129.6, 129.4, 129.0, 124.8, 120.5, 110.6.

HRMS: calcd for $C_{12}H_{10}N_3S$ ($[M+H]^+$): 228.0595, found: 228.0588

Gram Scale Preparation of (1*S*,2*S*)-(–)-**6aa**



1a **2a** (1*S*,2*S*)-(–)-**6aa**

Alkylborane **6aa** was prepared according to *GP1a*. An oven-dried, 50-mL, Schlenk flask (**A**) equipped with a stir bar, septum, and digital thermocouple probe was charged with THF (20 mL) and (*E*)-4-phenylbut-1-en-1-yl pinacolborane **1a** (1.29 g, 5.00 mmol). The resulting colorless solution was cooled to –78 °C using a dry ice/isopropanol bath, and then stirred for 15 min to allow the temperature to equilibrate. A solution of phenyllithium **2a** in diethyl ether (1.77 M, 3.10 mL, 5.5 mmol, 5.5 equiv) was added dropwise over 10 min, such that the internal temperature did not exceed –68 °C. The resulting pale, yellow solution was stirred at –78 °C for 1 h. A separate, oven-dried, 100-mL, Schlenk flask (**B**) equipped with a stir bar was charged with chiral (*S*)-catalyst **5** (260 mg, 0.50 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (1.75g, 6.0 mmol, 1.20 equiv). The flask was sealed with a septum and

removed from the glove box. Absolute ethanol (35 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to –78 °C using a dry ice/isopropanol bath. Flask **A**, having been stirred for 1 h at –78 °C, was placed under vacuum (0.01 mmHg) and the cold bath was removed. The solution was stirred rapidly under vacuum for 50 min until all of the THF was removed. The resulting beige-colored, foam solid boronate complex **3aa** in flask **A** was taken up in ethanol (10 mL) at 23 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (5.0 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was then moved into a –60 °C cooling bath and stirred for 36 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (2.0 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6aa**. The product was purified by chromatography (silica gel, 5 x 12 cm, dry load on Celite, 25-mL fractions, hexanes/CH_2Cl_2 gradient elution: 80:20 to 65:35) to afford 1.8002 g (81%) of pure **6aa** as a colorless oil which solidified upon standing. An enantiomeric ratio of 98:2 was measured for the oxidation product **7aa**.

Data for (1*S*,2*S*)-(–)-**6aa**:

^{1}H NMR: (500 MHz, $CDCl_3$)

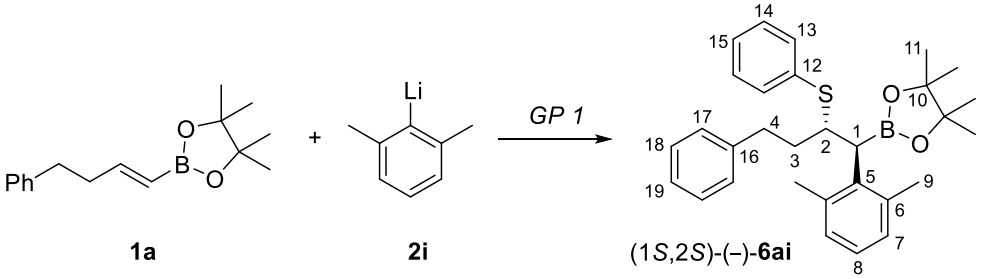
7.64 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.22 (m, 5H), 7.21 – 7.15 (m, 3H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 2H), 3.59 (ddd, *J* = 11.9, 8.5, 3.1 Hz, 1H), 2.83 (ddd, *J* = 14.6, 10.3, 4.7 Hz, 1H), 2.69 – 2.59 (m, 1H), 1.77 (dddd, *J* = 14.0, 10.1, 6.5, 3.2 Hz, 1H), 1.54 (ddt, *J* = 18.9, 9.6, 5.0 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H).

^{13}C NMR: (126 MHz, $CDCl_3$)

142.1, 140.0, 135.0, 133.5, 129.2, 128.9, 128.54, 128.49, 128.2, 127.3, 126.0, 125.7, 83.8, 51.6, 39.1, 34.7, 32.2, 25.0, 24.6.

Opt. Rot.: $[\alpha]_D^{24}$ –32.4 (*c* = 1.46 in $CHCl_3$) (96% ee)

Preparation of (1*S*,2*S*)-(–)-**6ai for X-Ray Analysis**



Alkylborane **6ai** was prepared according to *GP1b*. A flame-dried, 25-mL Schlenk flask (**A**) equipped with a magnetic stir bar, septum, and digital thermocouple probe was charged with 2-bromo-1,3-dimethylbenzene (147 μL, 1.10 mmol, 1.10 equiv) and THF (5 mL). The resulting solution was cooled to –78 °C using a dry ice/isopropanol bath. A solution of *n*-butyllithium in hexanes (667 μL, 1.65 M, 1.10 equiv) was added dropwise over 10 min. The resulting solution of (2,6-dimethylphenyl)lithium **2i** was stirred at –78 °C for 1 h. Then, a solution of (*E*)-4-phenylbut-1-en-1-yl pinacolborane **1a** (258.2 mg, 1.0 mmol, 1.0 equiv) in THF (5 mL) was added dropwise to flask **A** over 15 min. The resulting solution of **3ai** was stirred at –78 °C for 30 min followed by 25 °C for 30 min. A separate, flame-dried, 50-mL Schlenk flask (**B**) equipped with a stir bar was charged with chiral catalyst (*S*)-**5** (52.1 mg, 0.10 mmol, 0.10 equiv) and brought into the glove box. To the flask was added *N*-(phenylthio)saccharin **4a** (350.0 mg, 1.20 mmol, 1.20 equiv). The flask was sealed with a septum and removed from the glove box. Absolute ethanol (5 mL) was added to flask **B**, and the resulting yellow suspension was sonicated under argon for 10 min. Flask **B** was equipped with a digital thermocouple probe and cooled to an internal temperature of –60 °C using a Cryo-Cool. Flask **A**, having been stirred for 1 h, was returned to –78 °C and placed under vacuum (0.01 mmHg). The cold bath was removed, and the solution was stirred rapidly under vacuum for 30 min until all of the THF was removed. The resulting foam solid boronate complex **3ai** in flask **A** was taken up in ethanol (2.5 mL) at 25 °C, and the resulting solution was added dropwise via syringe to flask **B** over 10 min. A white suspension resulted. An additional portion of ethanol (2.5 mL) was added to flask **A** and then transferred to flask **B** as just described, to ensure complete transfer of the boronate. Flask **B** was stirred at –60 °C for 24 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The flask was removed from the cold bath and the biphasic mixture was allowed to warm to 25 °C and stirred rapidly for 15 min. The biphasic

mixture was transferred to a 250-mL round bottom flask (using Et_2O to transfer) and volatile components were removed by rotary evaporation (30 °C, 50 mmHg). The residue was transferred to a separatory funnel with Et_2O (50 mL) and sat. aq. $NaHCO_3$ (25 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 50 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude alkylborane **6ai**. The crude material was purified by chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/CH_2Cl_2 gradient elution: 75:25 to 65:35) to give 396.9 mg (84%) of pure **6ai**. Pure **6ai** was dissolved in hexanes/Et_2O (10 mL, 95:5). Evaporation of solvent afforded colorless crystals.

Data for (1*S*,2*S*)-(–)-**6ai**:

m.p.: 104–105 °C (hexanes/Et_2O)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.69 – 7.62 (m, 2H, HC(13)), 7.34 (t, *J* = 7.2 Hz, 2H, HC(14)), 7.29 (t, *J* = 7.3 Hz, 1H, HC(15)), 7.14 (t, *J* = 7.2 Hz, 2H, HC(18)), 7.09 (t, *J* = 7.2 Hz, 1H, HC(19)), 6.96-6.86 (m, 3H, HC(7) and HC(8)), 6.85 (d, *J* = 7.1 Hz, 2H, HC(17)), 3.83 (ddd, *J* = 12.3, 9.7, 2.7 Hz, 1H, HC(2)), 3.11 (d, *J* = 12.3 Hz, 1H, HC(1)), 2.75 (ddd, *J* = 14.2, 9.7, 4.7 Hz, 1H, HC(4)), 2.66 (ddd, *J* = 13.6, 9.4, 7.1 Hz, 1H, HC(4)), 2.27 (d, *J* = 23.2 Hz, 6H, HC(9)), 1.61 (dddd, *J* = 14.0, 9.8, 7.0, 2.8 Hz, 1H, HC(3)), 1.43 (dtd, *J* = 14.2, 9.5, 4.8 Hz, 1H, HC(3)), 1.23 (s, 6H, HC(11)), 1.17 (s, 6H, HC(11)).

^{13}C NMR: (126 MHz, $CDCl_3$)

142.3 (C(16)), 137.8 (C(6)), 137.3 (C(6)), 136.9 (C(5)), 135.1 (C(12)), 134.1 (C(13)), 129.5 (C(7)), 128.8 (C(14)), 128.7 (C(17)), 128.4 (C(7)), 128.3 (C(18)), 127.4 (C(15)), 125.7 (C(8)), 125.6 (C(19)), 83.5 (C(10)), 49.7 (C(2)), 35.1 (C(3)), 34.3 (C(1)), 32.7 (C(4)), 24.78 (C(11)), 24.77 (C(11)), 22.3 (C(9)), 21.1 (C(9)).

IR: (neat)

2974 (w), 2921 (w), 1740 (w), 1580 (w), 1480 (w), 1438 (w), 1369 (w), 1322 (w), 1269 (w), 1210 (w), 1136 (w), 1102 (w), 1087 (w), 1028 (w), 998 (w), 965 (w), 915 (w), 891 (w), 856 (w), 846 (w), 778 (w), 753 (w), 739 (w), 704 (w), 687 (w), 618 (w), 577 (w), 551 (w), 516 (w), 487 (w), 474 (w).

LRMS: (ESI, $[M+Na]^+$)

173.1 (15), 235.2 (26), 257.2 (67), 437.2 (19), 495.3 (100).

HRMS: calcd for $C_{30}H_{37}BO_2SNa$ ($[M+Na]^+$): 495.2505, found: 495.2516

Analysis: $C_{30}H_{37}BO_2S$ (472.49)

Calcd: C, 76.26%; H, 7.89%

Found: C, 76.26%; H, 7.96%

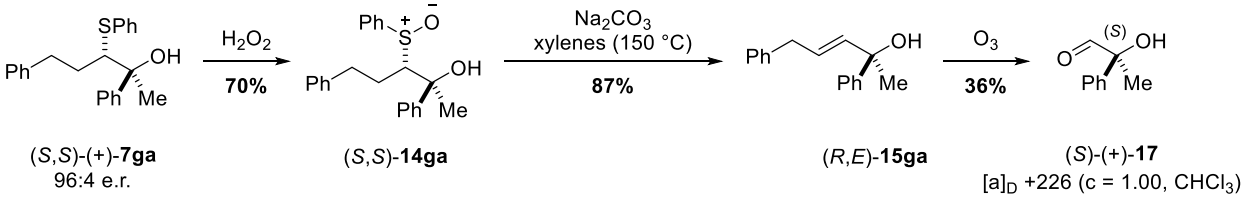
TLC: R_f 0.55 (hexanes/EtOAc, 90:10, CAM)

Opt. Rot.: $[\alpha]_D^{24}$ –61.6 (*c* = 1.14 in $CHCl_3$) (98% ee)

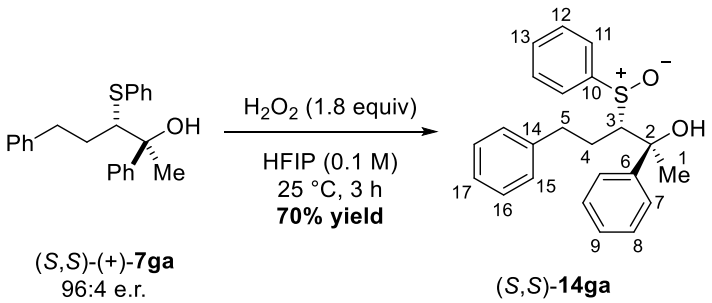
Determinations of Absolute Configuration

The absolute configuration assignments of (1*S*,2*S*)-**7aa**, (1*S*,2*S*)-**7ab**, (1*S*,2*S*)-**7ac**, (1*S*,2*S*)-**7ad**, (1*S*,2*S*)-**7ae**, (1*S*,2*S*)-**7af**, (1*S*,2*S*)-**7ag**, (3*S*,4*S*)-**7ah**, (1*S*,2*S*)-**7aj**, (1*S*,2*S*)-**7ak**, (1*S*,2*S*)-**7al**, (1*S*,2*S*)-**7am**, (1*S*,2*S*)-**7an**, (1*S*,2*S*)-**7ba**, (1*S*,2*S*)-**10ca**, (1*S*,2*S*)-**10da**, and (1*S*,2*S*)-**7ea** were made on the basis of structural analogy to (1*S*,2*S*)-**7ai** for which an X-ray crystal structure of the precursor borane (1*S*,2*S*)-**6ai** was obtained. The remaining compounds (2*S*,3*S*)-**7ga**, (*S*)-**7ha**, (*S*)-**7ia**, and (1*R*,2*S*)-**7ja** were derivatized to known literature compounds for which the absolute configuration is known unambiguously, as outlined below. No attempt was made to determine the absolute configuration of compound (–)-**7fa**, as its observed enantiomeric purity was low (8% ee).

Assignment of (2*S*,3*S*)-(+)-**2,5-Diphenyl-3-(phenylthio)pentan-2-ol (**(2S,3S)-(+)-**7ga)**



Step 1: (2*S*,3*S*)-**2,5-Diphenyl-3-(phenylsulfinyl)pentan-2-ol (**(2*S*,3*S*)-**14ga)**



A 25-mL, round-bottomed flask equipped with a stir bar was charged with (+)-**7ga** (120.2 mg, 0.34 mmol) and hexafluoroisopropyl alcohol (3.4 mL). A colorless solution resulted. Hydrogen peroxide (aq. 30% w/w, 63 μL, 1.8 equiv) was added in one portion, and the mixture was stirred at 25 °C for 3 h. Conversion was assessed by TLC (hexanes/EtOAc, 80:20, CAM). Upon completion, the reaction was quenched by the addition of sat. aq. Na_2SO_3 solution (5 mL). The mixture was diluted with diethyl ether and transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic

extracts were washed with brine, dried over sodium sulfate, filtered, and concentrated to afford 152.5 mg of crude **14ga** as a viscous oil which solidified upon standing. The product was purified by chromatography (silica gel, 2 x 25 cm, dry load on Celite, 10-mL fractions, hexanes/EtOAc, 90:10 (200 mL) to 80:20 (200 mL) to 70:30 (200 mL) to 60:40 (200 mL)) to afford 88.2 mg (70%) of sulfoxide **14ga** as a white powder. Only one sulfoxide diastereomer was observed.

Data for (2*S*,3*S*)-**14ga**:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.82 – 7.76 (m, 2H, HC(11)), 7.61 – 7.52 (m, 5H, HC(13), HC(12) and HC(7)), 7.41 – 7.34 (m, 2H, HC(8)), 7.33 – 7.28 (m, 1H, HC(9)), 7.12 – 6.98 (m, 3H, HC(16) and HC(17)), 6.41 – 6.35 (m, 2H, HC(15)), 6.01 (s, 1H, OH), 3.02 – 2.96 (m, 1H, HC(3)), 1.97 (s, 3H, H_3C(1)), 1.52 – 1.44 (m, 1H, H_2C(4)), 1.33 – 1.23 (m, 2H, H_2C(4) and H_2C(5)), 1.23 – 1.13 (m, 1H, H_2C(5)).

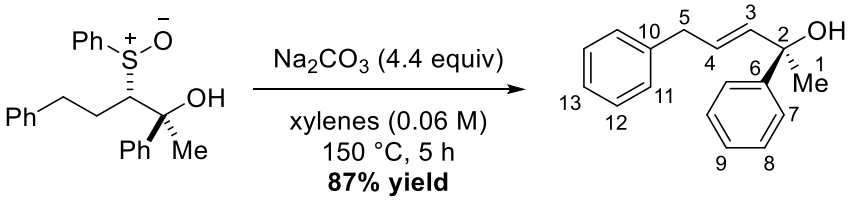
^{13}C NMR: (126 MHz, $CDCl_3$)

144.9 (C(6)), 142.4 (C(10)), 140.2 (C(14)), 132.4 (HC(13)), 129.6 (HC(12)), 128.5 (HC(15) or HC(16)), 128.4 (HC(15) or HC(16)), 128.1 (HC(8)), 128.0 (HC(9)), 126.6 (HC(7)), 126.5 (HC(11)), 126.2 (HC(17)), 77.7 (C(2)), 72.9 (HC(3)), 34.9 (H_2C(5)), 28.1 (H_2C(4)), 23.4 (H_3C(1)).

HRMS: (ES^+, TOF)

Calcd for $C_{23}H_{23}OS$ ($[M–OH]^+$): 347.1470, Found: 347.1471

Step 2: (*R*,*E*)-**2,5-Diphenylpent-3-en-2-ol (**(*R*,*E*)-**15ga)**



(*S*,*S*)-**14ga** (*R*,*E*)-**15ga**

An oven-dried, 25-mL, round-bottomed flask equipped with a stir bar and reflux condenser was charged with sulfoxide **14ga** (87.5 mg, 0.24 mmol), xylenes (4.0 mL), and sodium carbonate (111.3 mg, 1.05 mmol, 4.4 equiv). The colorless suspension was heated to 150 °C for 5 h. Conversion was assessed by TLC (hexanes/EtOAc, 80:20, CAM). Once full conversion was reached, the mixture was cooled to room temperature and directly purified by chromatography

(silica gel, 2 x 25 cm, wet load, 10-mL fractions, hexanes/EtOAc, 95:5 (200 mL) to 90:10 (200 mL) to 85:15 (200 mL)) to afford 52.8 mg (87%) of allylic alcohol **15ga** as a pale, yellow oil. The product contains 6% EtOAc by mass (estimated from relative ^{1}H NMR integrations) and this is accounted for in the reported yield.

Data for (*R*,*E*)-**15ga**:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.49 – 7.45 (m, 2H, HC(7)), 7.36 – 7.32 (m, 2H, HC(8)), 7.31 – 7.27 (m, 2H, HC(12)), 7.26 – 7.19 (m, 2H, HC(9) and HC(13)), 7.19 – 7.16 (m, 2H, HC(11)), 5.91 – 5.82 (m, 2H, HC(3) and HC(4)), 3.41 (d, J = 5.1 Hz, 2H, $H_2C(5)$), 1.83 (s, 1H, OH), 1.65 (s, 3H, $H_3C(1)$).

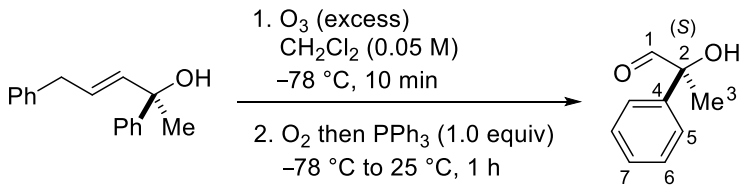
^{13}C NMR: (126 MHz, $CDCl_3$)

147.2 (C(6)), 140.3 (C(10)), 138.5 (HC(3)), 128.7 (HC(11)), 128.6 (HC(12)), 128.3 (HC(8)), 127.8 (HC(4)), 127.0 (HC(9)), 126.3 (HC(13)), 125.3 (HC(7)), 74.6 (C(2)), 38.8 ($H_2C(5)$), 30.1 ($H_3C(1)$).

HRMS: (ES^+, TOF)

Calcd for $C_{17}H_{17}$ ($[M–OH]^+$): 221.1330, Found: 221.1333

Step 3: (*S*)-(+)-**2-Hydroxy-2-phenylpropanal (**(*S*)-(+)-**17)**



(*R*,*E*)-**15ga** **36% yield** (*S*)-(+)-**17**

Note: A lower-than-expected yield was obtained for this reaction, and multiple unidentified by-products were formed. Given the known ability of ozone to oxidize aromatic rings, in retrospect, a much shorter reaction time (e.g. 1 min rather than 10 min) is advisable.

The following ozonolysis procedure is adapted from a published method.[25] A 15-mL, three necked, round bottomed flask equipped with a gas dispersion bubbler, gas outlet adapter, and glass stopper was charged with **15ga** (50.3 mg, 0.21 mmol) and dichloromethane (4 mL). The resulting colorless solution was cooled to –78 °C using a dry ice/isopropanol bath. Ozone was bubbled

through the solution via the gas dispersion bubbler, with outlet line running to ozone trap, for 10 min. The solution became a light blue color. Next, the ozone generator was switched off and oxygen was bubbled through the solution for 10 min. The blue color disappeared. Triphenylphosphine (55.4 mg, 0.21 mmol, 1.0 equiv) was added to the colorless solution in one portion at –78 °C. The mixture was warmed to 25 °C and stirred for 1 h. Volatile components were removed by rotary evaporation to afford a colorless residue containing crude **17**. The product was purified by chromatography (silica gel, 2 x 25 cm, dry load on Celite, 10-mL fractions, hexanes/EtOAc, 95:5 (200 mL) to 90:10 (200 mL) to 85:15 (200 mL) to 80:20 (200 mL)) to afford 15.2 mg (36%) of aldehyde **17** as a pale, yellow oil. Spectroscopic data matched those previously reported.[26] The product contains 15% EtOAc by mass (estimated from relative ^{1}H NMR integrations), as well as multiple unidentified impurities present in trace amounts. The presence of ^{1}H NMR signals unrelated to **17** is particularly evident in the aryl region. The purity of **17** is conservatively estimated as 75% by weight, and this is accounted for in the reported yield.

Data for (*S*)-(+)-**17**:

^{1}H NMR: (500 MHz, $CDCl_3$)
9.56 (d, *J* = 1.1 Hz, 1H, HC(1)), 7.49 – 7.45 (m, 2H, HC(5)), 7.43 – 7.39 (m, 2H, HC(6)), 7.36 – 7.31 (m, 1H, HC(7)), 3.82 (d, *J* = 1.1 Hz, 1H, OH), 1.71 (s, 3H, H_3C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)
199.9 (HC(1)), 139.3 (C(4)), 129.0 (HC(6)), 128.3 (HC(7)), 125.9 (HC(5)), 79.2 (C(2)), 23.8 (H_3C(3)).

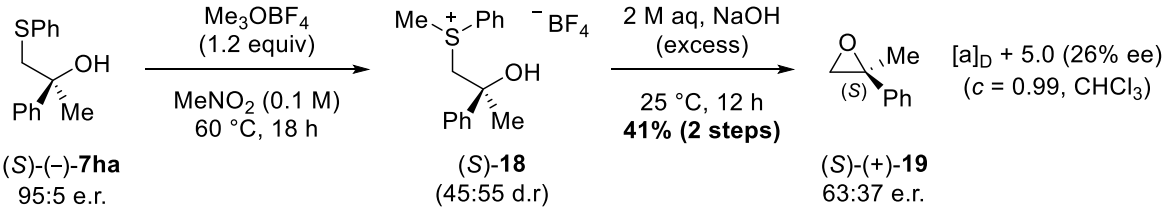
HRMS: (ES^+, TOF)
Calcd for $C_9H_9O_2$ ($[M–H]^+$): 149.0603, Found: 149.0603

Opt. Rot: $[\alpha]_D^{24}$ + 226 (*c* = 1.00 in $CHCl_3$) (92% ee)

Because of the aforementioned uncertainty in the purity of **17**, a small uncertainly also exists in the magnitude of the calculated specific rotation. Despite this, the positive sign of rotation is unambiguous. It has been well-established in the literature that (–)-**17** has the (*R*) configuration[26-29] and (+)-**17** has the (*S*) configuration.[30-31] Therefore, it can be stated with certainty that the carbinol stereogenic center in (+)-**7ga** also has the (*S*) configuration, so the absolute configuration of (2*S*,3*S*)-(+)-**7ga** may be assigned.

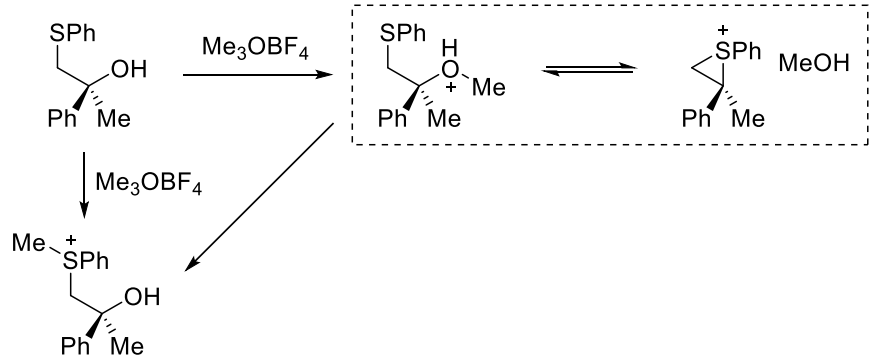
Note: In the course of compiling reported specific rotations of (+)-**17** and (–)-**17** it became clear that the magnitude of specific rotation is heavily concentration dependent in both chloroform and benzene. Reported magnitudes of $[\alpha]_D$ are closer to 250 for sample concentrations of 1.00 g/dL or greater,[26, 28, 30] and closer to 150 for sample concentrations of 0.75 g/dL or lower.[27, 29, 31]

Assignment of (*S*)-(–)-**2-Phenyl-1-(phenylthio)propan-2-ol (**(*S*)-(–)-**7ha)**



Note: Substantial racemization of the oxygen-bearing stereogenic center was observed over this two-step protocol, which likely occurred during treatment of (*S*)-**7ha** with Meerwein salt in nitromethane at high temperatures for an extended period of time. In retrospect, a milder procedure is recommended (dichloromethane, 25 °C, 2 h).[32]

Reasonable mechanism for racemization:



The following methylation procedure is adapted from previously published literature.[33] An oven-dried, 5-mL, round-bottomed flask equipped with a stir bar and reflux condenser was charged with (–)-**7ha** (51.7 mg, 0.21 mmol, 95:5 e.r.), nitromethane (2.0 mL), and trimethyloxonium tetrafluoroborate (38.1 mg, 0.26 mmol, 1.22 equiv). The solution was heated to 60 °C for 18 h. Upon initial heating, a pale, pink suspension resulted, which eventually became a pink-yellow solution after several hours of heating. The reaction mixture was cooled to room temperature and

diluted with methanol (5 mL). Volatile components were removed by rotary evaporation (30 °C, 15 mm Hg) to afford 80.5 mg of crude sulfonium salt **18** as a pink-yellow gum. This intermediate was isolated in 45:55 d.r. and the crude material was directly subjected to the next reaction.

The following procedure is adapted from previously published literature.[34] Compound **18** was suspended in aq. NaOH (2 M, 4 mL) and the mixture was stirred for 12 h at 25 °C. The resulting pale, yellow solution containing orange-brown oil was diluted with water (10 mL) and extracted with Et_2O (3 x 10 mL). The combined organic extracts were washed with brine, dried over sodium sulfate, filtered, and concentrated (25 °C, 100 mm Hg) to afford 53.2 mg of crude oxirane (+)-**19**. The product was purified by chromatography (silica gel, 2 x 25 cm, dry load on Celite, 10-mL fractions, pentane/Et_2O/Et_3N, 98:2:0.5) to afford 11.6 mg (41% yield over two steps) of 2-methyl-2-phenyloxirane (+)-**19** as a colorless oil. Spectroscopic data for (+)-**19** matched those previously reported.[35]

Data for (*S*)-(+)-**19**:

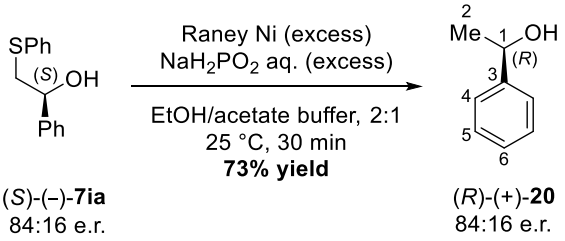
^{1}H NMR: (500 MHz, $CDCl_3$)
7.39 – 7.31 (m, 4H), 7.30 – 7.26 (m, 1H), 2.98 (d, *J* = 5.4 Hz, 1H), 2.81 (d, *J* = 5.4 Hz, 1H), 1.72 (s, 3H).

Opt. Rot: $[\alpha]_D^{24}$ + 5.0 (*c* = 0.99 in $CHCl_3$) (26% ee)

HPLC: t_R 9.4 min (37%); t_R 10.3 min (63%) (Supelco Astec, hexanes/*i*-PrOH, 95:5, 0.5 mL/min, 220 nm, 24 °C)

Despite substantial racemization (*vida supra*), the oxirane **19** was isolated in 41% yield over two steps with 26% ee and a positive sign of rotation. It has been well-established in the literature that (+)-**19** has the (*S*) configuration.[35-36] Therefore, it can be stated with certainty that the carbinol stereogenic center in (–)-**7ha** also has the (*S*) configuration.

Assignment of (*S*)-(–)-**1-Phenyl-2-(phenylthio)ethan-1-ol ((***S***)-(–)-7ia)**



(*S*)-(–)-**7ia**
84:16 e.r.

(*R*)-(+)-**20**
84:16 e.r.

Reference: Node, M. et al. *Tetrahedron Lett.* **1996**, 37(13), 2271-2274

While most literature sources report an (*S*) configuration for known compound (–)-**7ia**, at least one discrepancy was encountered.[37] Therefore, it was deemed prudent to reduce (–)-**7ia** to 1-phenylethan-1-ol **20** to confirm the sign of rotation, using the following procedure described by Node et al. for the exact transformation shown above.[38-39] A scintillation equipped with a stir bar was charged with compound (–)-**7ia** (14.7 mg, 0.064 mmol), ethanol (3 mL) and aq. acetate buffer (1.5 mL, pH ~5.2). A clear, colorless solution resulted. A suspension of Raney nickel (2.5 mL, aq.) was added to the vial in one portion, *followed immediately* by a solution of sodium hypophosphite hydrate ($NaH_2PO_2 \cdot H_2O$) in water (157.3 mg in 1 mL) in one portion. A slight exotherm and mild gas evolution was observed. The dark suspension was stirred at 25 °C for 30 min. Full conversion was observed by TLC (hexanes/EtOAc, 80:20). The suspension was filtered through a pad of Celite (2 cm) to remove nickel, and the pad was rinsed with ethanol (5 mL) and water (5 mL). **[Caution:** Raney nickel is a pyrophoric solid and should not be allowed to dry out completely. After the final rinse, scoop the wet cake into a waste container and store underwater.**]** The filtrate was partitioned between water (15 mL) and dichloromethane (25 mL). The layers were separated, and the aqueous phase was extracted with dichloromethane (2 x 10 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and concentrated (15 mm Hg, 35 °C, 20 min) to afford 1-phenylethan-1-ol **20** (5.7 mg, 73%) as an oil.

Data for (*R*)-(+)-**20**:

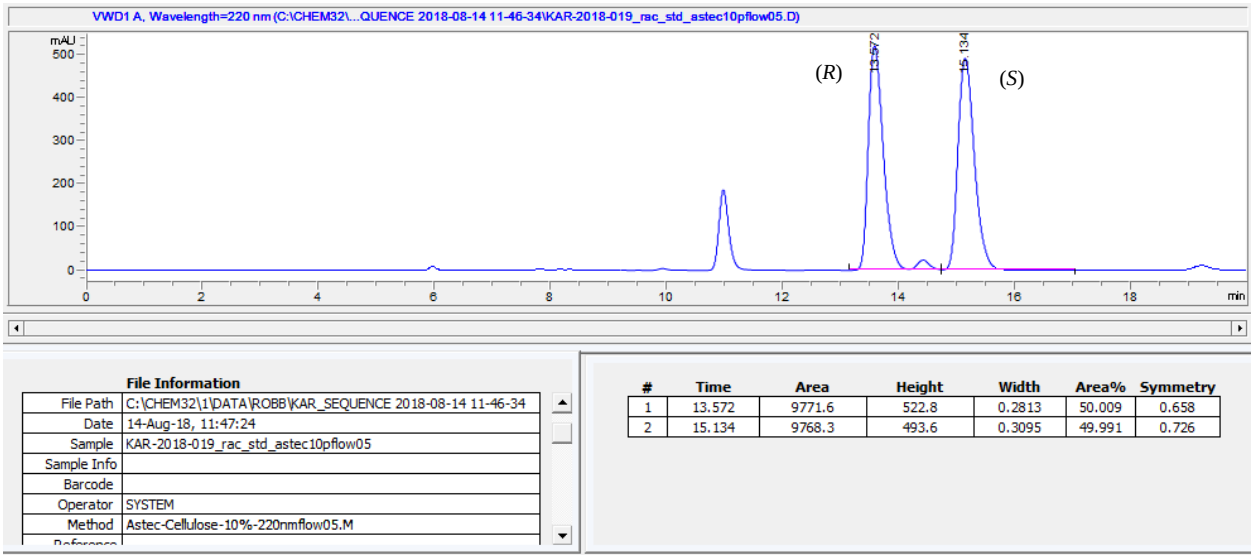
^{1}H NMR: (500 MHz, $CDCl_3$)
7.42 – 7.32 (m, 4H, HC(4) and HC(5)), 7.31 – 7.27 (m, 1H, HC(6)), 4.91 (q, *J* = 6.4 Hz, 1H, HC(1)), 1.76 (s, 1H, OH), 1.51 (d, *J* = 6.5 Hz, 3H, H_3C(2)).

^{13}C NMR: (126 MHz, $CDCl_3$)
146.0 (C(3)), 128.7 (HC(5)), 127.6 (HC(6)), 125.5 (HC(4)), 70.6 (HC(1)), 25.3 (H_3C(2)).

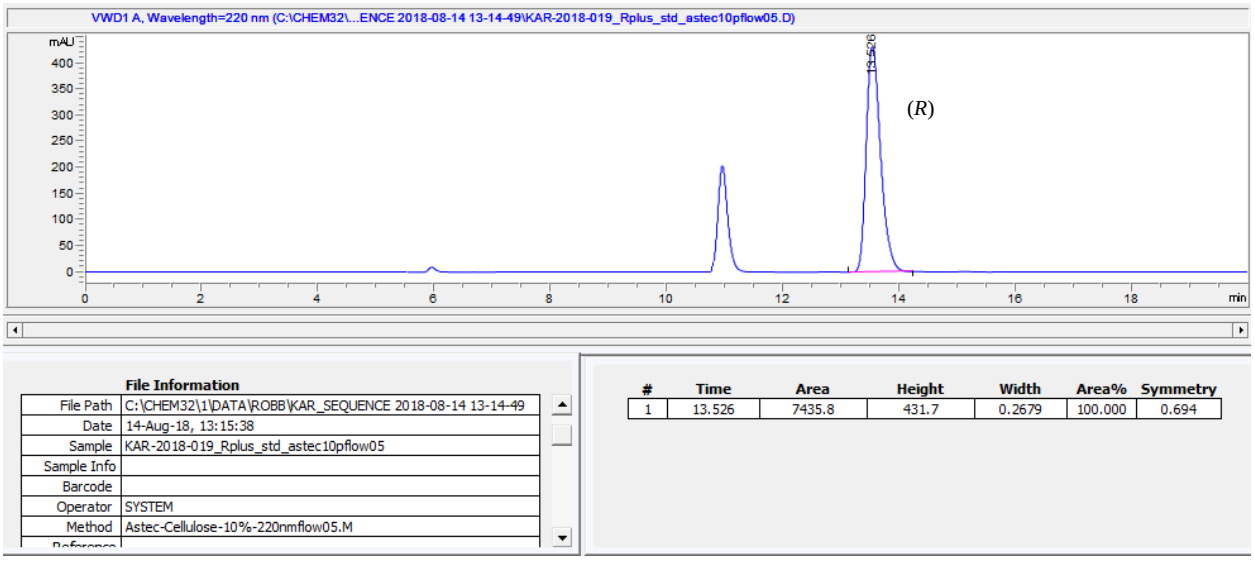
HPLC: t_R 13.5 min (84%); t_R 15.1 min (16%) (Supelco Astec, hexanes/*i*-PrOH, 90:10, 0.5 mL/min, 220 nm, 24 °C)

Given that the isolated material **20** was: (1) present in less than 6 mg, (2) not enantiomerically pure, and (3) appeared from ^{1}H NMR to be contaminated with grease, it was decided that measurement of optical rotation would be unsatisfactory proof of configuration, as the magnitude of observed rotation of the sample would be very small and carry a degree of uncertainty. Instead, the isolated **20** was analyzed by chiral stationary phase HPLC. Comparison of this HPLC trace with those obtained from enantiomerically pure, commercial samples of (*R*)-(+)-**20** and (*S*)-(–)-**20** (*vida infra*) provide unambiguous proof that the isolated **20** from this experiment is of the (*R*)-(+) configuration. Therefore, it can be stated with certainty that the carbinol stereogenic center in (–)-**7ia** is of the (*S*) configuration (Cahn-Ingold-Prelog convention changes due to presence/absence of sulfur atom). This is in agreement with most literature reports.[39-43]

(±)-**20** (commercial sample) * Contaminated with acetophenone (t_R 11.0 min)



(*R*)-(+)-**20** (commercial sample) * Contaminated with acetophenone (t_R 11.0 min)



File Information	
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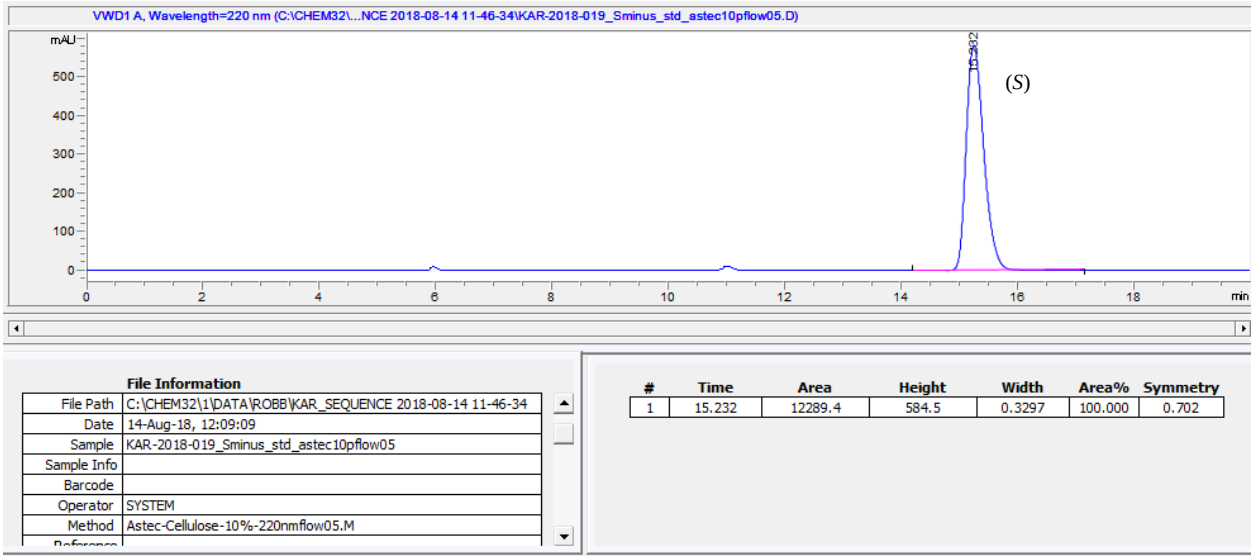
Date	14-Aug-18, 13:15:38
Sample	KAR-2018-019_Rplus_std_astec10pflow05
Sample Info	
Barcode	
Operator	SYSTEM
Method	Astec-Cellulose-10%-220nmflow05.M

#	Time	Area	Height	Width	Area%	Symmetry
1	13.526	7435.8	431.7	0.2679	100.000	0.694

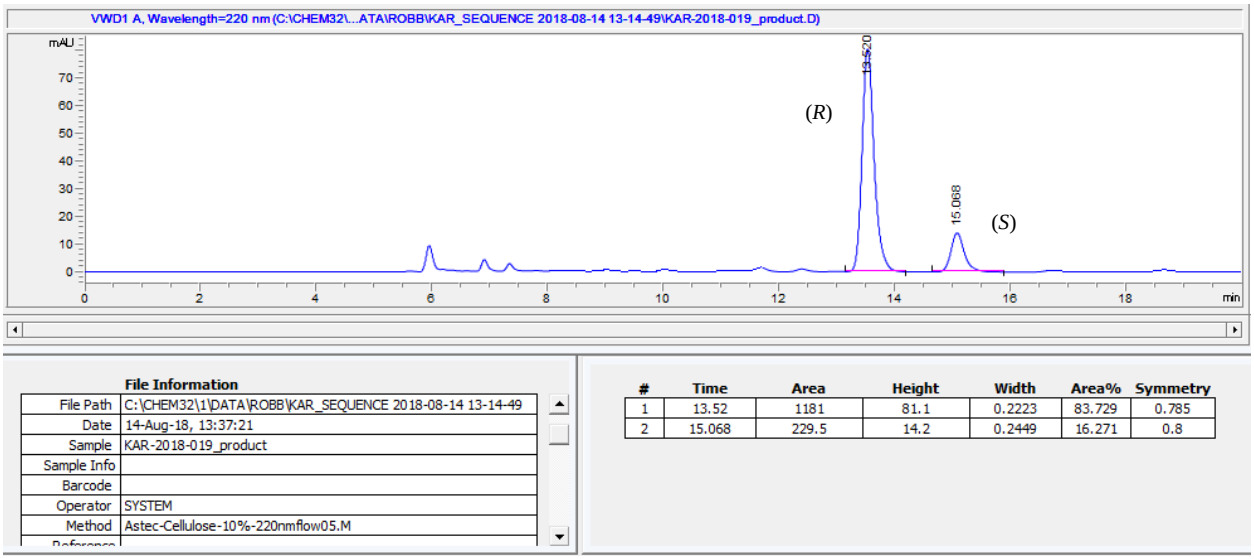
(*S*)-(–)-**20** (commercial sample)



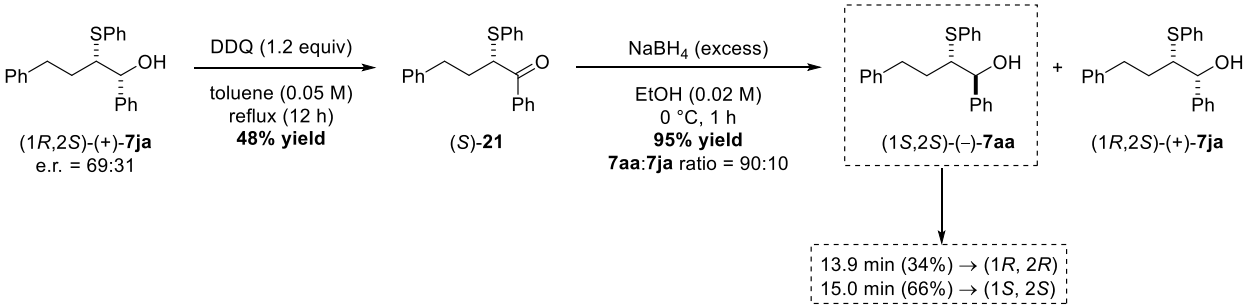
File Information	
File Path	C:\CHEM32\1\DATA\ROBB\KAR_SEQUENCE 2018-08-14 11-46-34
Date	14-Aug-18, 12:09:09
Sample	KAR-2018-019_Sminus_std_astec10pflow05
Sample Info	
Barcode	
Operator	SYSTEM
Method	Astec-Cellulose-10%-220nmflow05.M

#	Time	Area	Height	Width	Area%	Symmetry
1	15.232	12289.4	584.5	0.3297	100.000	0.702

Reduction of (*S*)-(–)-**7ia** to **20**

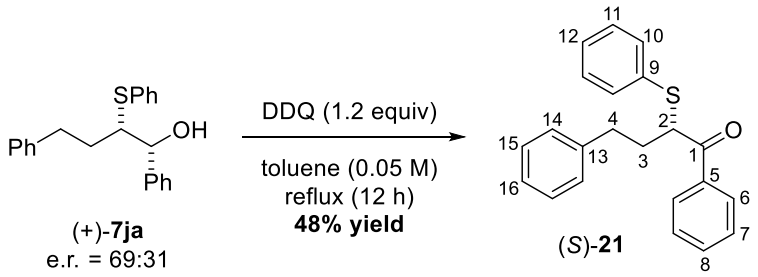


Assignment of (1*R*,2*S*)-(+)-**1,4-Diphenyl-2-(phenylthio)butan-1-ol (**(1*R*,2*S*)-(+)-**7ja)**



The strategy for assigning the absolute configuration of (+)-**7ja** was as follows. Oxidation of (+)-**7ja** to ketone **21**, followed by reduction with sodium borohydride affords a mixture of **7ja** and **7aa**, in which the stereochemistry of the sulfur-bearing carbon atom has been retained. The absolute configuration of **7aa** has already been established and the order of elution of (1*R*,2*R*)-**7aa** and (1*S*,2*S*)-**7aa** on chiral stationary phase HPLC is already known (pp. S9 – S11). Therefore, the stereochemistry of the sulfur-bearing carbon in (+)-**7ja** can be inferred by a comparison of the HPLC trace of **7aa** formed by this oxidation-reduction sequence with the HPLC trace of enantiomerically enriched (*S*,*S*)-(–)-**7aa** formed previously. The stereochemistry of the oxygen-bearing carbon in (+)-**7ja** can then be inferred on the basis of the *anti* diastereomeric relationship.

Step 1: (*S*)-**1,4-Diphenyl-2-(phenylthio)butan-1-one ((*S*)-21)**



An oven-dried, 5 mL, round-bottomed flask equipped with a stir bar and reflux condenser was charged with alcohol (+)-**7ja** (36.4 mg, 0.11 mmol) and toluene (2 mL). To this clear, colorless solution was added 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) (30.2 mg, 0.13 mmol, 1.2 equiv). The resulting red-colored solution was heated to reflux for 12 h. Conversion was monitored by TLC (hexanes/EtOAc, 90:10). Upon completion, the mixture was cooled to 25 °C and volatile components were removed by rotary evaporation (15 mm Hg, 35 °C). The residue was purified by column chromatography (silica gel, 2 x 25 cm, dry load on Celite, 10-mL fractions, hexanes/EtOAc, 97.5:2.5 (200 mL) to 95:5 (200 mL) to 92.5:7.5 (200 mL) to 90:10 (200 mL)) to afford 17.4 mg (48%) of ketone **21** as an oil.

Data for (*S*)-**21**:

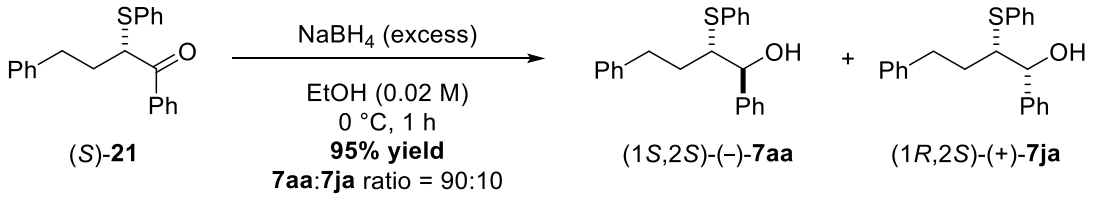
^{1}H NMR: (500 MHz, $CDCl_3$)

7.86 – 7.82 (m, 2H, HC(6)), 7.59 – 7.49 (m, 1H, HC(8)), 7.45 – 7.39 (m, 2H, HC(7)), 7.32 – 7.23 (m, 7H, HC(10), HC(11), HC(12), and HC(15)), 7.22 – 7.18 (m, 1H, HC(16)), 7.17 – 7.13 (m, 2H, HC(14)), 4.40 (t, *J* = 7.2 Hz, 1H, HC(2)), 2.86 – 2.72 (m, 2H, H_2C(4)), 2.39 – 2.30 (m, 1H, H_2C(3)), 2.18 – 2.10 (m, 1H, H_2C(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

195.7 (C(1)), 141.1 (C(13)), 136.3 (C(5)), 134.7 (HC_{om}), 133.2 (HC(8)), 131.7 (C(9)), 129.1 (HC_{om}), 128.8 (HC(12)), 128.73 (HC_{om}), 128.71 (HC_{om}), 128.68 (HC_{om}), 128.6 (HC_{om}), 126.3 (HC(16)), 50.3 (HC(2)), 33.3 (H_2C(4)), 32.5 (H_2C(3)). Deconvolution of the *ortho* and *meta* (HC_{om}) signals was not possible.

Step 2: Reduction of (*S*)-**21 to mixture of** (1*S*,2*S*)-**7aa and** (1*R*,2*S*)-**7ja**



A scintillation vial equipped with a stir bar was charged with ketone **21** (16.6 mg, 0.050 mmol) and ethanol (2 mL). The resulting clear, colorless solution was cooled to 0 °C with an ice bath. Sodium borohydride (41.2 mg, 1.09 mmol, 22 equiv) was added in one portion and the reaction was stirred for 20 min at 0 °C. Conversion was assessed by TLC (hexanes/EtOAc, 90:10). Upon reaching full conversion, the reaction was quenched by the cautious, dropwise addition of sat. aq. ammonium chloride until gas evolution ceased. The mixture was diluted with water (10 mL) and Et_2O (10 mL) and transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic extracts were washed with brine, dried over sodium sulfate, filtered, and concentrated. The residue was purified by column chromatography (silica gel, 1 x 16 cm, dry load on Celite, 5-mL fractions, hexanes/EtOAc, 90:10 (100 mL) to 80:20 (100 mL)) to afford 15.8 mg (95%) of a mixture of **7aa** and **7ja**. The diastereomeric ratio, determined by relative ^{1}H NMR integrations, was 90:10 **7aa**:**7ja**. Spectroscopic data for **7aa** and **7ja** match those reported earlier (pp. S9–S11 and S68–S70).

Data for **7aj**:

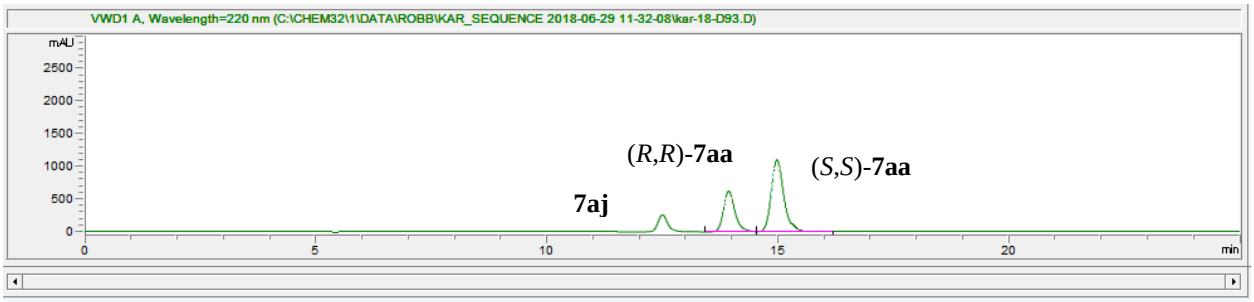
HPLC: t_R 12.5 min (both enantiomers) (Supelco Astec, hexanes/*i*-PrOH, 80:20, 0.5 mL/min, 220 nm, 24 °C)

Data for **7aa**:

HPLC: t_R 13.9 min (34%); t_R 15.0 min (66%) (Supelco Astec, hexanes/*i*-PrOH, 80:20, 0.5 mL/min, 220 nm, 24 °C)

HPLC analysis of this mixture indicated a 66:34 enantiomeric ratio for **7aa**, with the major enantiomer eluting second (*vida infra*). This matches the elution order for (1*S*,2*S*)-**7aa** synthesized earlier (pp. S9 – S11). Therefore, it can be stated with certainty that the absolution configuration of (+)-**7ja** is (1*R*,2*S*).

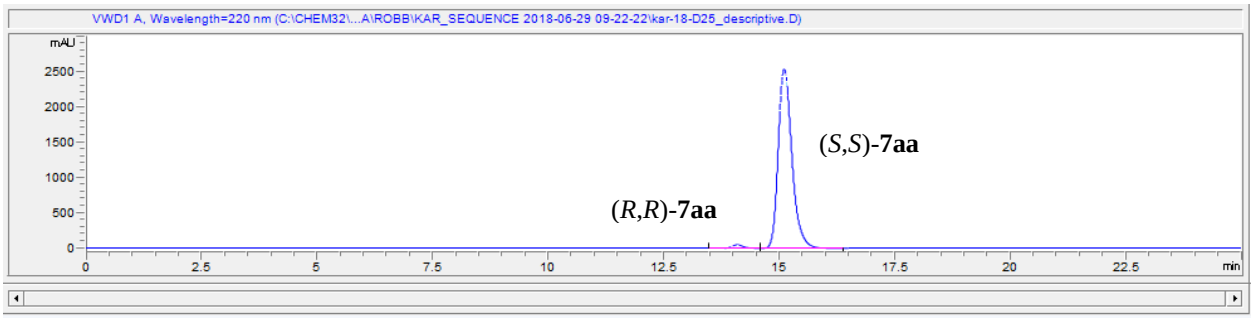
Reduction of **21** to **7aa** and **7aj** (mixture)



File Information	
Date	29-Jun-18, 11:34:24
Sample	kar-18-D93
Sample Info	
Barcode	
Operator	SYSTEM
Method	Astec-Cellulose-20%-220nmflow05.M

#	Time	Area	Height	Width	Area%	Symmetry
1	13.935	10961.3	624.9	0.2687	34.255	0.781
2	14.98	21038	1101.5	0.2927	65.745	0.783

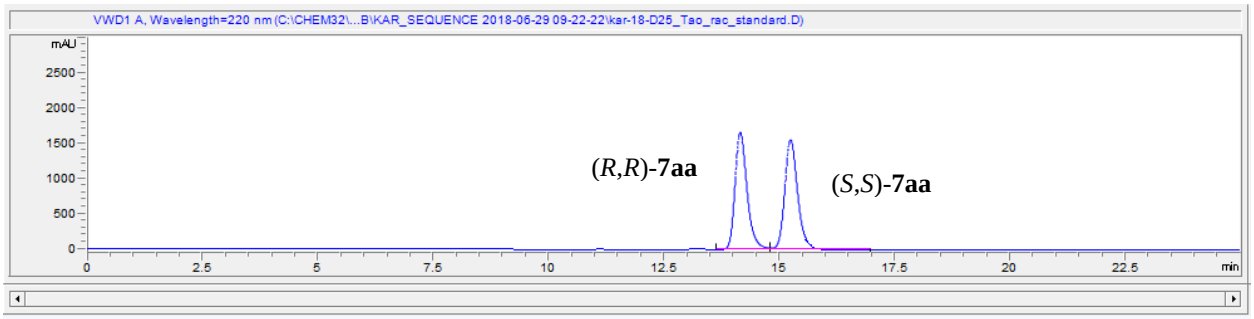
(1*S*,2*S*)-(–)-**7aa** (98:2 e.r.) prepared previously (pp. *S9 – S11*)



File Information	
Date	29-Jun-18, 09:54:59
Sample	kar-18-D25_descriptive
Sample Info	
Barcode	
Operator	SYSTEM
Method	Astec-Cellulose-20%-220nmflow05.M

#	Time	Area	Height	Width	Area%	Symmetry
1	14.082	972.6	52.9	0.2787	1.814	0.805
2	15.111	52634.5	2537.9	0.3177	98.186	0.732

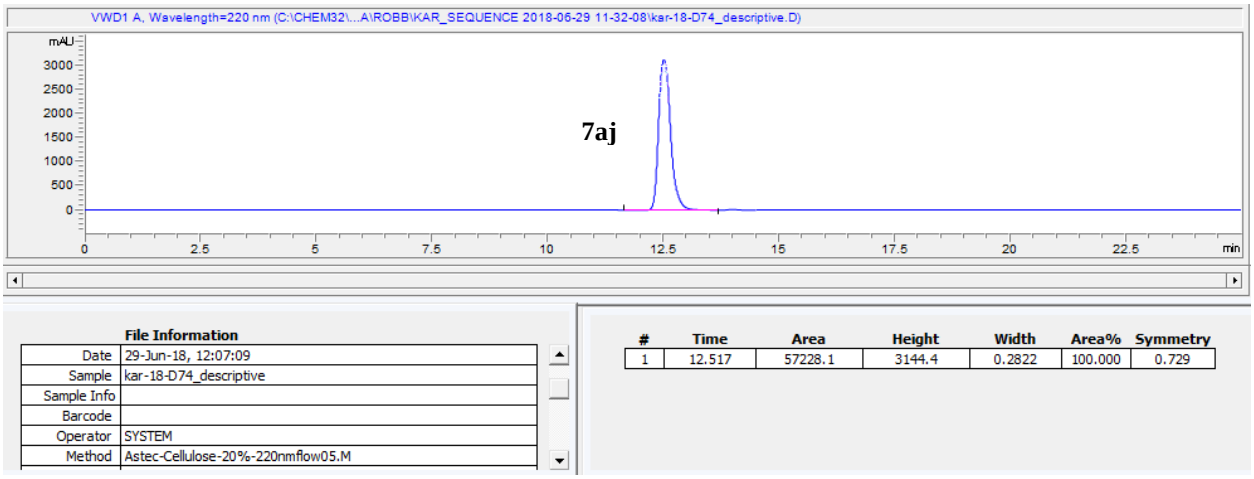
(*rac*)-**7aa**



File Information	
Date	29-Jun-18, 09:24:17
Sample	kar-18-D25_Tao_rac_standard
Sample Info	
Barcode	
Operator	SYSTEM
Method	Astec-Cellulose-20%-220nmflow05.M

#	Time	Area	Height	Width	Area%	Symmetry
1	14.126	30604.3	1667.7	0.2782	49.773	0.726
2	15.215	30883.4	1561.5	0.3006	50.227	0.783

(1*R*,2*S*)-(+)-**7ja** (68:32 e.r.) prepared previously (pp. S67–S70). Under these HPLC conditions, both enantiomers co-elute.



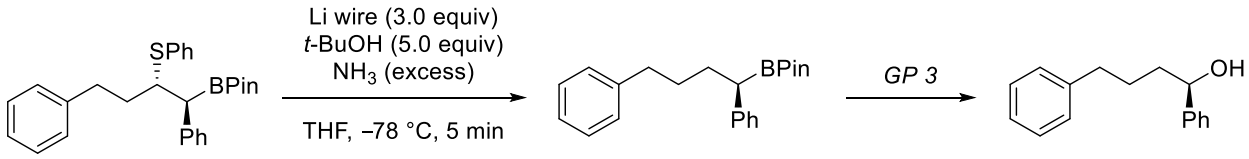
File Information

Date	29-Jun-18, 12:07:09
Sample	kar-18-D74_descriptive
Sample Info	
Barcode	
Operator	SYSTEM
Method	Astec-Cellulose-20%-220nmflow05.M

#	Time	Area	Height	Width	Area%	Symmetry
1	12.517	57228.1	3144.4	0.2822	100.000	0.729

Product Manipulations

Preparation of (*R*)-2-(1,4-Diphenylbutyl)-pinacolborane ((*R*)-(–)-11aa)



(*S*,*S*)-(–)-**6aa** (*R*)-**11aa** (*R*)-**22**

An oven-dried, 100-mL, three necked, round-bottomed flask equipped with a glass-coated stir bar, argon inlet adapter, dry ice condenser, and rubber septum was cooled to –78 °C using a dry ice/acetone bath. Ammonia (approx. 20 mL) was condensed into the flask. Neat *tert*-butanol (475 μL, 5.0 mmol, 5.0 equiv) was added to the flask by syringe (should be done quickly to avoid freezing inside the syringe). A solution of **6aa** (444.5 mg, 1.0 mmol) in THF (5 mL) was added dropwise, and mixture was stirred for 15 min at –78 °C. A single piece of freshly cut lithium wire (21.0 mg, 3.0 mmol, 3.0 equiv) was added to the flask under a stream of argon. The colorless mixture was stirred rapidly at –78 °C until a dark green solution was observed (typically requires less than 5 min). **As soon as the solution color turned dark green, the reaction was quenched immediately** by the addition of sat. aq. NH_4Cl (1 mL). The green color disappeared upon quenching, and the resulting colorless solution was warmed to 25 °C and stirred for an additional 10 min. The mixture was further diluted with sat. aq. NH_4Cl (20 mL) and water (40 mL), transferred to a separatory funnel, and extracted with Et_2O (4 x 50 mL). The combined organic extracts were washed with brine (50 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 25 mmHg) to afford crude 11aa. The product was purified by column chromatography (silica gel, 3 x 25 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 97.5:2.5 (600 mL) to 95:5 (600 mL)) to afford 291.2 mg (87%) of **11aa** as a colorless oil. Spectroscopic data matched those reported previously.[44]

Data for (*R*)-(–)-**11aa**:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.28 – 7.22 (m, 4H), 7.20 (d, *J* = 6.9 Hz, 2H), 7.18 – 7.11 (m, 4H), 2.69 – 2.54 (m, 2H), 2.34 (t, *J* = 7.9 Hz, 1H), 1.96 – 1.86 (m, 1H), 1.77 – 1.68 (m, 1H), 1.61 (p, *J* = 8.0 Hz, 2H), 1.21 (s, 6H), 1.19 (s, 6H).

^{13}C NMR: (126 MHz, $CDCl_3$)

143.3, 142.8, 128.5, 128.5, 128.4, 128.3, 125.7, 125.3, 83.4, 36.1, 32.4, 31.2, 24.8, 24.7.

HRMS: calcd for $C_{22}H_{30}BO_2$ ($[M+H]^+$): 337.2399, found: 337.2354

Opt. Rot.: $[\alpha]_D^{24}$ –22.6 (*c* = 2.5 in $CHCl_3$) (94% ee)

Oxidation of 11aa

11aa was oxidized to alcohol **22** according to *GP3* for analysis of enantiomeric composition. A 25-mL round-bottomed flask equipped with a stir bar was charged with **11aa** (49.7 mg, 0.15 mmol) and THF (1 mL). The turbid solution was cooled to 0 °C with an ice bath. To this solution was added a mixture of 30% aq. H_2O_2 (0.25 mL) and 3 M aq. NaOH (0.5 mL) also containing EDTA (1.0 mg/mL). The biphasic mixture was stirred rapidly at 0 °C and conversion was monitored by TLC (hexanes/EtOAc, 90:10, CAM). Once full conversion was observed, the oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (10 mL) and stirred for 15 min. The mixture was transferred to a separatory funnel and diluted with diethyl ether (30 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (3 x 15 mL). The combined organic phases were washed with brine (25 mL) and then dried over magnesium sulfate, filtered, and concentrated (30 °C, 15 mmHg) to afford crude alcohol **22**. The product was purified by chromatography (silica gel, 2 x 20 cm, dry load on Celite, 10-mL fractions, hexanes/EtOAc, 90:10 (400 mL)) to afford 30.2 mg (90%) of pure alcohol **22** as a colorless oil. Spectroscopic data matched those previously reported.[45]

Data for (*R*)-**22**:

^{1}H NMR: (500 MHz, $CDCl_3$)

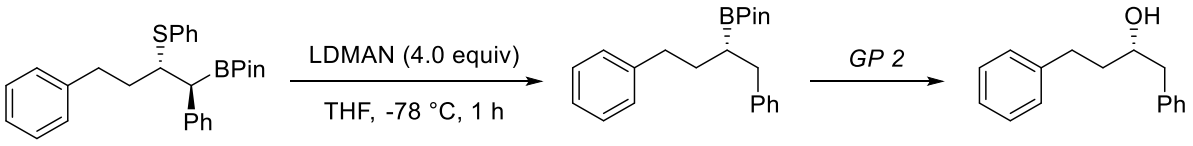
7.24 – 7.17 (m, 4H), 7.17 – 7.11 (m, 3H), 7.07 – 7.01 (m, 3H), 4.55 (dd, *J* = 7.5, 5.0 Hz, 1H), 2.51 (t, *J* = 7.3 Hz, 2H), 1.19 – 1.68 (m, 2H, including OH), 1.68 – 1.58 (m, 2H), 1.55 – 1.43 (m, 1H).

^{13}C NMR: (126 MHz, $CDCl_3$)

144.8, 142.4, 128.6, 128.5, 128.4, 127.7, 126.0, 125.9, 74.7, 38.7, 35.9, 27.7.

HPLC: (*R*)-**22,** t_R 17.5 min (97%); (*S*)-**22,** t_R 20.4 min (3%) (Supelco Astec, hexanes/*i*-PrOH, 80:20, 0.5 mL/min, 220 nm, 24 °C)

Preparation of (*S*)-(1,4-Diphenylbutan-2-yl)pinacolborane ((*S*)-(12aa)) and (*S*)-1,4-Diphenylbutan-2-ol ((*S*)-23)



(*S*,*S*)-(–)-**6aa** (*S*)-**12aa** (*S*)-**23**

A flame-dried, 50-mL Schlenk flask equipped with a glass-coated stir bar was charged with THF (10 mL) and freshly cut lithium wire (28.0 mg, 4.0 mmol, 4.0 equiv). The mixture was cooled to –55 °C using a Cryo-Cool. Neat *N*,*N*-dimethylnaphthalen-1-amine (656 μL, 4.0 mmol, 4.0 equiv) was added dropwise by syringe, and the mixture was stirred at –55 °C for 5 h. Over time, a dark green solution was observed, indicating formation of the LDMAN reagent. A solution of 6aa (444.5 mg, 1.0 mmol) in THF (10 mL) was added dropwise to the LDMAN solution, and the mixture was stirred at –55 °C for 1 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The green color disappeared upon quenching, and the resulting colorless solution was warmed to 25 °C and stirred for an additional 10 min. The mixture was further diluted with aq. 1 N HCl (20 mL), transferred to a separatory funnel, and extracted with Et_2O (4 x 50 mL). The combined organic extracts were washed with brine (50 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 25 mmHg) to afford crude **12aa**. The product was purified by column chromatography (silica gel, 3 x 25 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc, 95:5 (1000 mL)) to afford pure **12aa**[46] which was fully characterized by oxidation to alcohol **23**.

Borane **12aa** was oxidized to alcohol **23** according to *GP2*. A 50-mL, round-bottomed flask equipped with a stir bar was charged with **12aa**, THF (6 mL) and water (6 mL). Sodium perborate tetrahydrate (369.3 mg) was added to the mixture at 25 °C. The mixture was stirred rapidly at 25 °C for 3 h. The oxidation was quenched by the addition of sat. aq. sodium thiosulfate ($Na_2S_2O_3$) solution (10 mL), and the mixture was stirred for 15 min at 25 °C. The mixture was extracted with Et_2O (3 x 30 mL), and the combined organic phases were dried over magnesium sulfate, filtered, and concentrated to afford alcohol **23**. The product was purified by column chromatography (silica gel, 2 x 12 cm, dry load on Celite, 10-mL fractions, hexanes/EtOAc gradient elution: 95:5 (300 mL) to 90:10 (300 mL)) to afford 100.0 mg (44%) of pure **23**. Spectroscopic data matched those reported previously.[47-48] The absolute configuration of (S)-23 was assigned by comparing the sign

of optical rotation to the values reported previously.

Data for (*S*)-**23**:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.34 – 7.27 (m, 4H), 7.25 (d, *J* = 7.3 Hz, 1H), 7.23 – 7.17 (m, 5H), 3.90 – 3.80 (m, 1H), 2.92 – 2.80 (m, 2H), 2.76 – 2.66 (m, 2H), 1.92 – 1.77 (m, 2H), 1.59 (s, 1H).

^{13}C NMR: (126 MHz, $CDCl_3$)

142.2, 138.5, 129.6, 128.7, 128.6, 128.5, 126.6, 126.0, 72.1, 44.3, 38.6, 32.2.

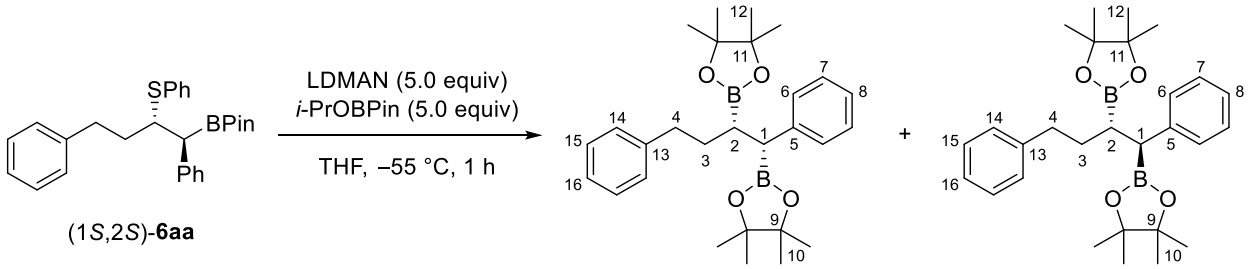
IR: (neat)

3392 (w), 3061 (w), 3026 (w), 2924 (w), 2859 (w), 1602 (w), 1494 (w), 1453 (w), 1179 (w), 1080 (w), 1047 (w), 1030 (w), 908 (w), 857 (w), 731 (m), 697 (m), 647 (w), 613 (w), 526 (w), 492 (w).

HPLC: (*S*)-**23,** t_R 7.4 min (82%); (*R*)-**23,** t_R 9.8 min (18%) (IB-3, hexanes/*i*-PrOH, 90:10, 0.5 mL/min, 220 nm, 24 °C)

Opt. Rot.: $[\alpha]_D^{24}$ –11.0 (*c* = 1.76 in $CHCl_3$)[47-48] (64% ee)

Preparation of (1,4-Diphenylbutane-1,2-diyl)bis(pinacolborane) (13aa)



(1*S*,2*S*)-**6aa**

(1*R*,2*S*)-**13aa** (*syn*)

(1*S*,2*S*)-**13aa** (*anti*)

A flame-dried, 50-mL Schlenk flask equipped with a glass-coated stir bar was charged with THF (5 mL) and freshly cut lithium wire (35.0 mg, 5.0 mmol, 5.0 equiv). The mixture was cooled to –55 °C using a Cryo-Cool. Neat *N*,*N*-dimethylnaphthalen-1-amine (820 μL, 5.0 mmol, 5.0 equiv) was added dropwise by syringe, and the mixture was stirred at –55 °C for 5 h. Over time, a dark green solution was observed, indicating formation of the LDMAN reagent. A solution of **6aa** (444.5 mg, 1.0 mmol) and (isopropoxy)pinacolborane (1.02 mL, 5.0 mmol, 5.0 equiv) in THF (5 mL) was added quickly to the LDMAN solution, and the mixture was stirred at –55 °C for 1 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (1 mL). The green color disappeared upon quenching, and the resulting colorless solution was warmed to 25 °C and stirred for an

additional 10 min. The mixture was further diluted with aq. 1 N HCl (10 mL), transferred to a separatory funnel, and extracted with Et_2O (3 x 30 mL). The combined organic extracts were washed with brine (50 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg) to afford crude **13aa**. The product was purified by column chromatography (silica gel, 3 x 25 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc gradient elution: 97.5:2.5 (600 mL) to 95:5 (600 mL)) to afford 316.0 mg (68%) of white solid **13aa** as a mixture of diastereomers (64:36 *anti*:*syn*). The two diastereomers could be separated by careful column chromatography (hexanes/CH_2Cl_2).

Data for (1*R*,2*S*)-*syn*-**13aa**:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.28 – 7.17 (m, 6H, HC(7) and HC(6) and HC(15)), 7.16 – 7.08 (m, 2H, HC(8) and HC(16)), 7.04 – 6.99 (m, 2H, HC(14)), 2.69 (td, *J* = 12.8, 4.6 Hz, 1H, HC(4)), 2.50 (d, *J* = 12.4 Hz, 1H, HC(1)), 2.38 (td, *J* = 13.3, 12.6, 5.6 Hz, 1H, HC(4)), 1.76 – 1.68 (m, 1H, HC(2)), 1.67 – 1.57 (m, 1H, HC(3)), 1.48 (d, *J* = 11.7 Hz, 1H, HC(3)), 1.34 (s, 12H, HC(12)), 1.20 (d, *J* = 7.2 Hz, 12H, HC(10)).

^{13}C NMR: (126 MHz, $CDCl_3$)

143.4 (C(13)), 142.6 (C(5)), 129.0 (C(6)), 128.4 (C(14)), 128.3 (C(7)), 128.2 (C(15)), 125.5 (C(16)), 125.2 (C(8)), 83.34 (C(9)), 83.27 (C(11)), 34.6 (C(4)), 32.6 (C(1)), 31.4 (C(3)), 25.3 (C(10)), 25.1 (C(10)), 25.0 (C(12)), 24.7 (C(2)), 24.4 (C(12)).

HRMS: calcd for $C_{28}H_{41}B_2O_4$ ($[M+H]^+$): 463.3191, found: 463.3206

TLC: R_f 0.63 (CH_2Cl_2, CAM)

Data for (1*S*,2*S*)-*anti*-**13aa**:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.32 – 7.26 (m, 4H, HC(15) and HC(6)), 7.21 (td, *J* = 7.3, 2.2 Hz, 5H, HC(7) and HC(14) and HC(16)), 7.13 – 7.08 (m, 1H, HC(8)), 2.75 – 2.60 (m, 2H, HC(4)), 2.50 – 2.41 (m, 1H, HC(1)), 1.88 – 1.77 (m, 3H, HC(2) and HC(3)), 1.19 (s, 6H, HC(10)), 1.16 (s, 6H, HC(10)), 1.04 (s, 6H, HC(12)), 1.00 (s, 6H, HC(12))

^{13}C NMR: (126 MHz, $CDCl_3$)

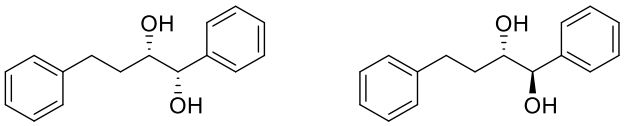
143.2 (C(13)), 142.9 (C(5)), 129.2 (C(6)), 128.5 (C(14)), 128.3 (C(15)), 128.0

(C(7)), 125.6 (C(16)), 125.2 (C(8)), 83.3 (C(9)), 82.9 (C(11)), 36.2 (C(4)), 34.7 (C(1)), 34.4 (C(3)), 27.3 (C(2)), 24.9 (C(12)), 24.8 (C(10)), 24.72 (C(12)), 24.68 (C(10)).

HRMS: calcd for $C_{28}H_{41}B_2O_4$ ($[M+H]^+$): 463.3191, found: 463.3195

TLC: R_f 0.44 (CH_2Cl_2, CAM)

Pure *syn*-**13aa** and *anti*-**13aa** were oxidized to diols *syn*-**24** and *anti*-**24** using *GP3* for determination of enantiomeric composition.



(1*S*,2*S*)-**24** (*syn*) (1*R*,2*S*)-**24** (*anti*)

Data for (1*S*,2*S*)-*syn*-**24**:[49]

^{1}H NMR: (500 MHz, $CDCl_3$)

7.40 – 7.30 (m, 5H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 4.47 (d, *J* = 6.9 Hz, 1H), 3.74 (ddd, *J* = 9.2, 7.0, 3.4 Hz, 1H), 2.95 (s, 1H), 2.85 (ddd, *J* = 14.7, 10.0, 5.3 Hz, 1H), 2.77 (s, 1H), 2.62 (ddd, J = 13.9, 9.7, 6.9 Hz, 1H), 1.74 (ddt, *J* = 13.5, 9.0, 4.7 Hz, 1H), 1.66 (dddd, *J* = 13.8, 10.1, 7.1, 3.7 Hz, 1H).

^{13}C NMR: (126 MHz, $CDCl_3$)

141.9, 141.1, 128.7, 128.50, 128.46, 128.3, 127.0, 125.9, 78.1, 75.4, 34.4, 32.0.

HPLC: (1*R*,2*S*)-**24,** t_R 17.9 min (84%); (1*S*,2*R*)-**24,** t_R 19.4 min (16%) (Supelco Astec, hexanes/*i*-PrOH, 80:20, 0.5 mL/min, 220 nm, 24 °C)

Data for (1*R*,2*S*)-*anti*-**24**:

^{1}H NMR: (500 MHz, $CDCl_3$)

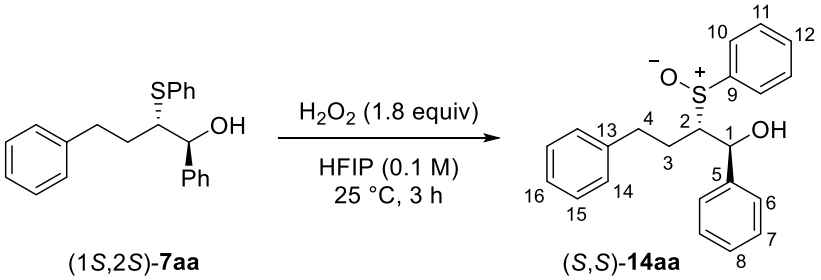
7.41 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 7.24 – 7.15 (m, 2H), 4.71 – 4.63 (m, 1H), 3.91 – 3.81 (m, 1H), 2.85 (ddd, *J* = 14.4, 9.9, 5.2 Hz, 1H), 2.76 – 2.58 (m, 1H), 2.26 – 2.09 (m, 1H), 1.79 (ddd, *J* = 12.7, 10.4, 4.9 Hz, 1H), 1.64 (dtd, *J* = 14.6, 9.6, 5.2 Hz, 1H).

^{13}C NMR: (126 MHz, $CDCl_3$)

142.0, 140.4, 128.6, 128.51, 128.47, 128.0, 126.9, 125.9, 77.2, 74.6, 33.4, 32.2.

HPLC: (1*S*,2*S*)-**24,** t_R 18.1 min (86%); (1*R*,2*R*)-**24,** t_R 20.0 min (14%) (Supelco Astec, hexanes/*i*-PrOH, 80:20, 0.5 mL/min, 220 nm, 24 °C)

Preparation of (1*S*,2*S*)-**1,4-Diphenyl-2-(phenylsulfinyl)butan-1-ol (**(1*S*,2*S*)-**14aa)**



(1*S*,2*S*)-**7aa** (*S*,*S*)-**14aa**

A 100-mL, round-bottomed flask equipped with a stir bar was charged with (1*S*,2*S*)-**7aa** (334.5 mg, 1.0 mmol) and hexafluoroisopropyl alcohol (7.0 mL). A colorless solution resulted. Hydrogen peroxide (aq. 30% w/w, 200 μL, 1.8 equiv) was added in one portion, and the mixture was stirred at 25 °C for 3 h. Conversion was assessed by TLC (hexanes/EtOAc, 50:50, CAM). Upon completion, the reaction was quenched by the addition of sat. aq. $Na_2S_2O_3$ solution (10 mL) and the mixture was stirred at 25 °C for 15 min. Volatile components were removed under reduced pressure (30 °C, 50 mmHg), and the residue was diluted with CH_2Cl_2 and transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with brine, dried over sodium sulfate, filtered, and concentrated to afford crude **14aa**. The product was purified by chromatography (silica gel, 3 x 12 cm, wet load with CH_2Cl_2, 25-mL fractions, hexanes/EtOAc, 65:35 (500 mL) to 50:50 (500 ml)) to afford 333.0 mg (95%) of white, solid sulfoxide **14aa** as a mixture of diastereomers. Precipitation from hexanes/Et_2O afforded 325.2 mg (93%) of analytically pure **14aa** as a mixture of sulfoxide diastereomers (73:27 d.r.).

Data for (1*S*,2*S*)-**14aa**:

^{1}H NMR: (500 MHz, $CDCl_3$)

Major: 7.79 – 7.71 (m, 2H, HC(10)), 7.59 – 7.50 (m, 3H, HC(11) and HC(12)), 7.46 – 7.33 (m, 5H, HC(6) and HC(7) and HC(8)), 7.17 – 7.08 (m, 3H, HC(15) and HC(16)), 6.71 – 6.61 (m, 2H, HC(14)), 5.10 (d, *J* = 9.1 Hz, 1H, HC(1)), 5.07 (s, 1H, OH), 3.15 (ddd, *J* = 9.7, 6.0, 4.3 Hz, 1H, HC(2)), 1.99 (dtd, *J* = 23.7, 13.7, 6.0 Hz, 2H, HC(4)), 1.67 (dddd, *J* = 14.6, 10.5, 6.4, 4.1 Hz, 1H, HC(3)), 1.47 (ddt, *J* =

15.7, 10.0, 5.9 Hz, 1H, HC(3)). **Minor:** 7.60 – 7.55 (m, 2H, HC(10)), 7.55 – 7.51 (m, 3H, HC(11) and HC(12)), 7.39 – 7.30 (m, 5H, HC(6) and HC(7) and HC(8)), 7.14 – 7.08 (m, 3H, HC(15) and HC(16)), 6.69 – 6.61 (m, 2H, HC(14)), 4.99 (d, *J* = 8.0 Hz, 1H, HC(1)), 4.53 (s, 1H, OH), 2.94 – 2.84 (m, 2H, HC(2)), 2.08 (ddd, *J* = 14.9, 9.1, 6.3 Hz, 4H, HC(4)), 2.00 (dt, *J* = 13.9, 7.9 Hz, 4H, HC(4)), 1.77 (ddt, *J* = 12.1, 9.3, 6.3 Hz, 3H, HC(3)), 1.55 (ddt, *J* = 13.0, 8.8, 6.3 Hz, 3H, HC(3)).

^{13}C NMR: (126 MHz, $CDCl_3$)

Major: 142.4 (C(9)), 140.51 (C(5)), 140.2 (C(13)), 131.9 (C(12)), 129.4 (C(11)), 128.71 (C(7)), 128.67 (C(8)), 128.4 (C(15)), 128.2 (C(14)), 127.5 (C(6)), 126.1 (C(16)), 125.8 (C(10)), 76.2 (C(1)), 69.1 (C(2)), 33.1 (C(4)), 27.2 (C(3)). **Minor:** 141.4 (C(5)), 140.45 (C(9)), 140.3 (C(13)), 131.1 (C(12)), 129.3 (C(11)), 128.8 (C(7)), 128.5 (C(8) and C(15)), 128.3 (C(14)), 127.0 (C(6)), 126.2 (C(16)), 125.1 (C(10)), 74.8 (C(1)), 67.6 (C(2)), 33.5 (C(4)), 24.6 (C(3)).

IR: (neat)

3313 (w), 3057 (w), 1602 (w), 1494 (w), 1476 (w), 1444 (w), 1301 (w), 1201 (w), 1079 (w), 1018 (m), 997 (w), 910 (w), 851 (w), 774 (w), 748 (w), 697 (m), 631 (w), 588 (w), 547 (w), 528 (w), 512 (w), 491 (w), 464 (w).

LRMS: (ESI, $[M+H]^+$)

207.1 (100), 351.1 (90), 373.1 (41).

HRMS: calcd for $C_{22}H_{23}O_2S$ ($[M+H]^+$): 351.1419, found: 351.1417

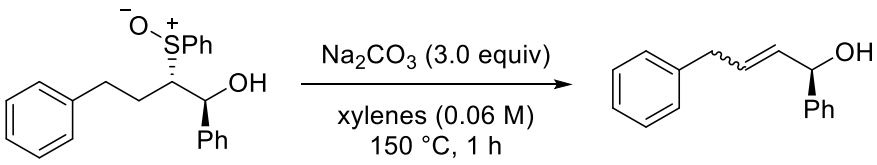
Analysis: $C_{22}H_{22}O_2S$ (350.48)

Calcd: C, 75.40%; H, 6.33%

Found: C, 75.08%; H, 6.29%

TLC: **Major:** R_f 0.49; **Minor:** R_f 0.35 (hexanes/EtOAc, 50:50, CAM)

Preparation of (*R*)-1,4-Diphenylbut-2-en-1-ol ((*R*)-15aa)



(1*S*,2*S*)-**14aa** (*R*)-**15aa**

An oven-dried, 25-mL, round-bottomed flask equipped with a stir bar and reflux condenser

was charged with sulfoxide **14aa** (mixture of diastereomers, 350.0 mg, 1.0 mmol), xylenes (10.0 mL), and sodium carbonate (318.0 mg, 3.0 mmol, 3.0 equiv). The colorless suspension was heated to 150 °C. Full conversion was observed by TLC after 1 h (hexanes/EtOAc, 50:50, CAM). The mixture was cooled to room temperature and directly purified by chromatography (silica gel, 3 x 15 cm, wet load, 25-mL fractions, hexanes/EtOAc gradient elution: 95:5 (400 mL) to 90:10 (400 mL)) to afford 199.4 mg (89%) of allylic alcohol **15aa** as a clear, colorless oil (*E*/*Z* ratio = 8:1). Spectroscopic data matched those previously reported.[50]

Data for (*R*)-**15aa**:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.47 – 7.36 (m, 4.52H, *E* and *Z*), 7.35 – 7.29 (m, 3.39H, *E* and *Z*), 7.26 – 7.18 (m, 3.39H, *E* and *Z*), 5.96 (dt, *J* = 14.0, 6.8 Hz, 1H, *E*), 5.82 – 5.76 (m, 1.26H, *E* and *Z*), 5.69 (d, *J* = 6.2 Hz, 0.13H, *Z*), 5.24 (d, *J* = 6.3 Hz, 1H, *E*), 3.65 (dd, *J* = 15.6, 6.3 Hz, 0.13H, *Z*), 3.57 (dd, *J* = 15.6, 5.9 Hz, 0.13H, *Z*), 3.44 (d, *J* = 6.8 Hz, 2H, *E*), 1.95 (s, 1.13H, *E* and *Z*).

^{13}C NMR: (126 MHz, $CDCl_3$)

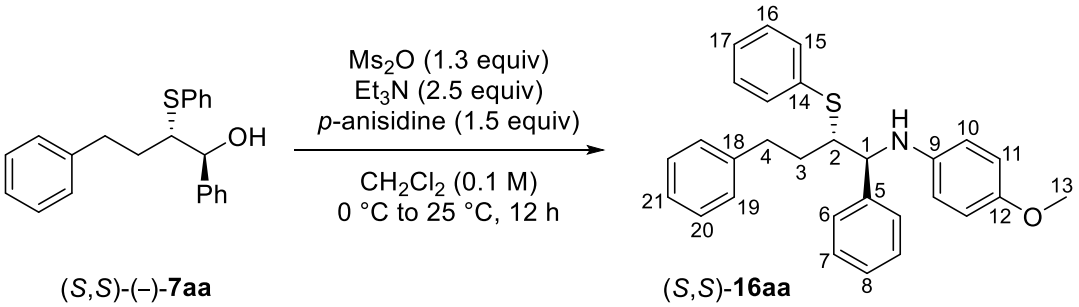
143.6 (*Z*), 143.2 (*E*), 140.1 (*Z*), 140.0 (*E*), 133.8 (*E*), 132.9 (*Z*), 131.1 (*E*), 130.5 (*Z*), 128.8 (Z), 128.71 (*E*), 128.65 (*E*), 128.6 (*E*), 128.5 (*Z*), 127.8 (*Z*), 127.7 (*E*), 126.34 (*E*), 126.29 (*E*), 126.1 (*Z*), 75.1 (*E*), 70.0 (*Z*), 38.7 (*E*), 34.1 (*Z*).

IR: 3345 (w), 3061 (w), 3027 (w), 2900 (w), 1666 (w), 1602 (w), 1493 (w), 1452 (w), 1430 (w), 1231 (w), 1193 (w), 1069 (w), 1029 (w), 1004 (w), 968 (m), 914 (w), 848 (w), 742 (m), 696 (s), 637 (w), 596 (w), 537 (w), 494 (w).

HRMS: calcd for $C_{16}H_{16}ONa$ ($[M+Na]^+$): 247.1099, found: 247.1099

HPLC: (*R*,*E*)-**15aa,** t_R 14.5 min (98%); (*S*,*E*)-**15aa,** t_R 15.8 min (2%) (Supelco Astec, hexanes/*i*-PrOH, 80:20, 0.5 mL/min, 220 nm, 24 °C)

Preparation of *N*-((1*S*,2*S*)-1,4-Diphenyl-2-(phenylthio)butyl)-4-methoxyaniline ((1*S*,2*S*)-(–)-16aa)



A flame-dried, 100-mL, round-bottomed flask equipped with a stir bar was charged with (1*S*,2*S*)-(–)-**7aa** (425.7 mg, 1.27 mmol) and CH_2Cl_2 (6 mL). The resulting colorless solution was cooled to 0 °C with an ice bath. Triethylamine (442 μL, 3.18 mmol, 2.5 equiv) was added to the solution at 0 °C. An oven-dried vial was charged with methanesulfonic anhydride (287 mg, 1.65 mmol, 1.3 equiv) inside the glove box. The vial was removed from the glove box and charged with CH_2Cl_2 (4 mL), and the resulting solution of Ms_2O was added into the reaction by syringe at 0 °C. The mixture was stirred at 0 °C for 1 h. 4-Methoxyaninine (234 mg, 1.9 mmol, 1.5 equiv) was directly added into the mixture. The reaction mixture was warmed to 25 °C and stirred for 12 h at 25 °C. The reaction was then quenched by adding sat. aq. $NaHCO_3$ solution (10 mL). The mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic phases were washed with brine (25 mL), dried over magnesium sulfate, filtered, and concentrated (30 °C, 50 mmHg). The residue was purified by column chromatography (silica gel, 3 x 20 cm, dry load on Celite, 25-mL fractions, hexanes/EtOAc, 95:5 (1000 mL)) to afford 526.3 mg (94%) of **16aa**. Recrystallization from hexanes/Et_2O afforded 483.3 mg (87%) of analytically pure **16aa** as a white solid.

Data for (1*S*,2*S*)-(–)-**16aa**:

m.p.: 74–76 °C (ABT, 4.0 x 10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.33 (d, *J* = 7.3 Hz, 2H, HC(6)), 7.29 – 7.18 (m, 11H, HC(7), HC(8), HC(20), HC(21), HC(15), HC(16), HC(17)), 7.05 (d, *J* = 7.3 Hz, 2H, HC(19)), 6.70 (d, *J* = 8.9 Hz, 2H, HC(11)), 6.49 (d, *J* = 8.9 Hz, 2H, HC(10)), 4.70 (bs, 1H, NH), 4.31 (d, *J* = 6.4 Hz, 1H, HC(1)), 3.72 (s, 3H, H_3C(13)), 3.27 (ddd, *J* = 9.0, 6.4, 4.7 Hz, 1H, HC(2)), 2.98 (ddd, *J* = 14.1, 9.1, 5.3 Hz, 1H, H_2C(4)), 2.82 – 2.70 (m, 1H, H_2C(4)),

2.07 – 1.95 (m, 1H, $H_2C(3)$), 1.84 (ddt, J = 14.0, 9.0, 4.5 Hz, 1H, $H_2C(3)$).

^{13}C NMR: (126 MHz, $CDCl_3$)

152.3 (C(12)), 141.9 (C(18) or C(9) or (C(5)), 141.5 (C(18) or C(9) or (C(5)), 141.3 (C(18) or C(9) or (C(5)), 133.7 (C(14)), 133.1 (HC(15)), 129.0 (HC(16)), 128.6 (HC(7) or HC(19) or HC(20)), 128.54 (HC(7) or HC(19) or HC(20)), 128.52 (HC(7) or HC(19) or HC(20)), 127.7 (HC(6)), 127.6 (HC(8) or HC(17)), 127.5 (HC(8) or HC(17)), 126.1 (HC(21)), 115.1 (HC(10)), 114.9 (HC(11)), 61.9 (HC(1)), 56.5 (HC(2)), 55.8 ($H_3C(13)$), 33.7 ($H_2C(3)$), 33.4 ($H_2C(4)$).

IR: (neat)

3333 (w), 3007 (w), 2947 (w), 1601 (w), 1508 (m), 1475 (w), 1455 (w), 1438 (w), 1406 (w), 1344 (w), 1308 (w), 1296 (w), 1272 (w), 1235 (m), 1174 (w), 1156 (w), 1118 (w), 1099 (w), 1035 (w), 1001 (w), 912 (w), 817 (w), 808 (w), 776 (w), 753 (w), 744 (w), 695 (m), 664 (w), 630 (w), 579 (w), 534 (w), 516 (w), 493 (w).

LRMS: (ESI, $[M+H]^+$)

91.0 (10), 129.1 (15), 207.1 (100), 239.1 (11), 317.1 (18), 440.2 (6).

HRMS: calcd for $C_{29}H_{30}NOS$ ($[M+H]^+$): 440.2048, found: 440.2052

Analysis: $C_{29}H_{29}NOS$ (439.62)

Calcd: C, 79.23%; H, 6.65%; N, 3.19%

Found: C, 78.89%; H, 6.55%; N, 3.21%

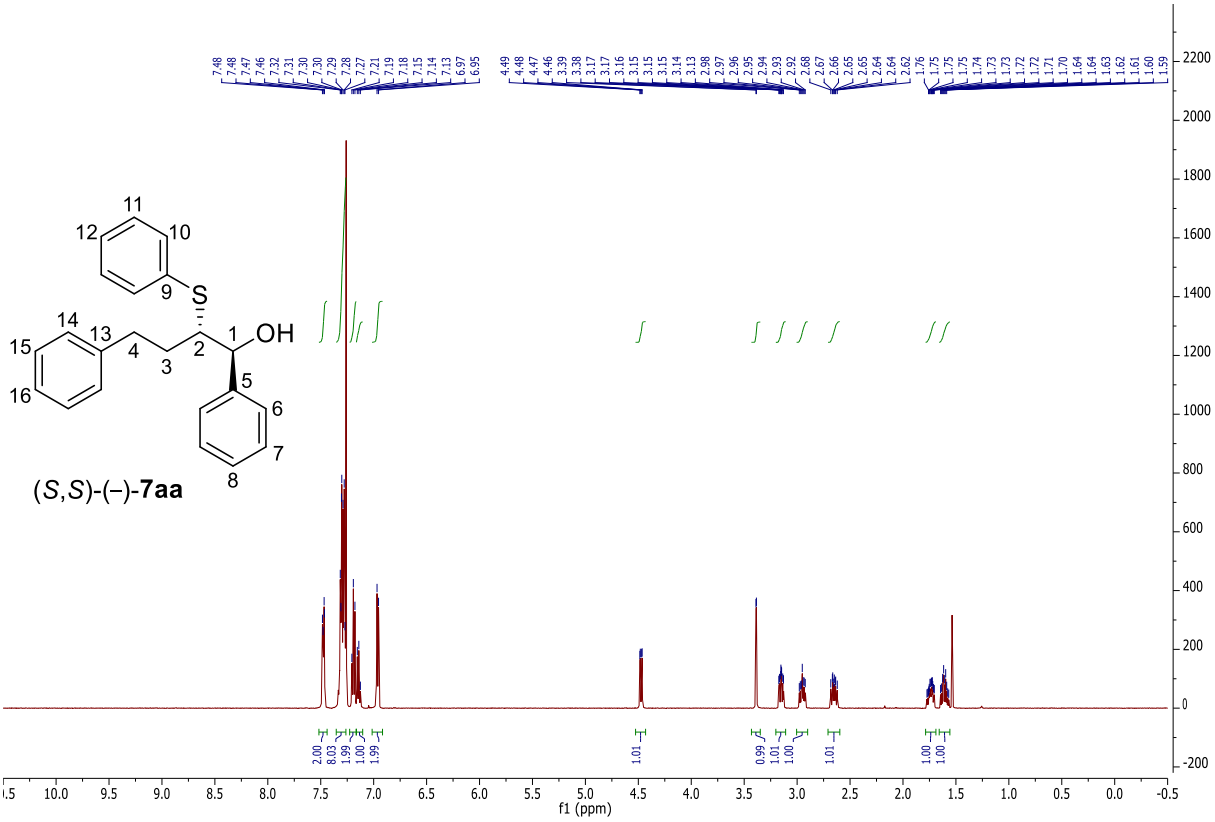
TLC: R_f 0.31 (hexanes/EtOAc, 90:10, CAM)

HPLC: (1*R*,2*R*)-**16aa,** t_R 11.1 min (3%); (1*S*,2*S*)-**16aa,** t_R 15.0 min (97%) (Supelco Astec, hexanes/*i*-PrOH, 80:20, 0.5 mL/min, 220 nm, 24 °C)

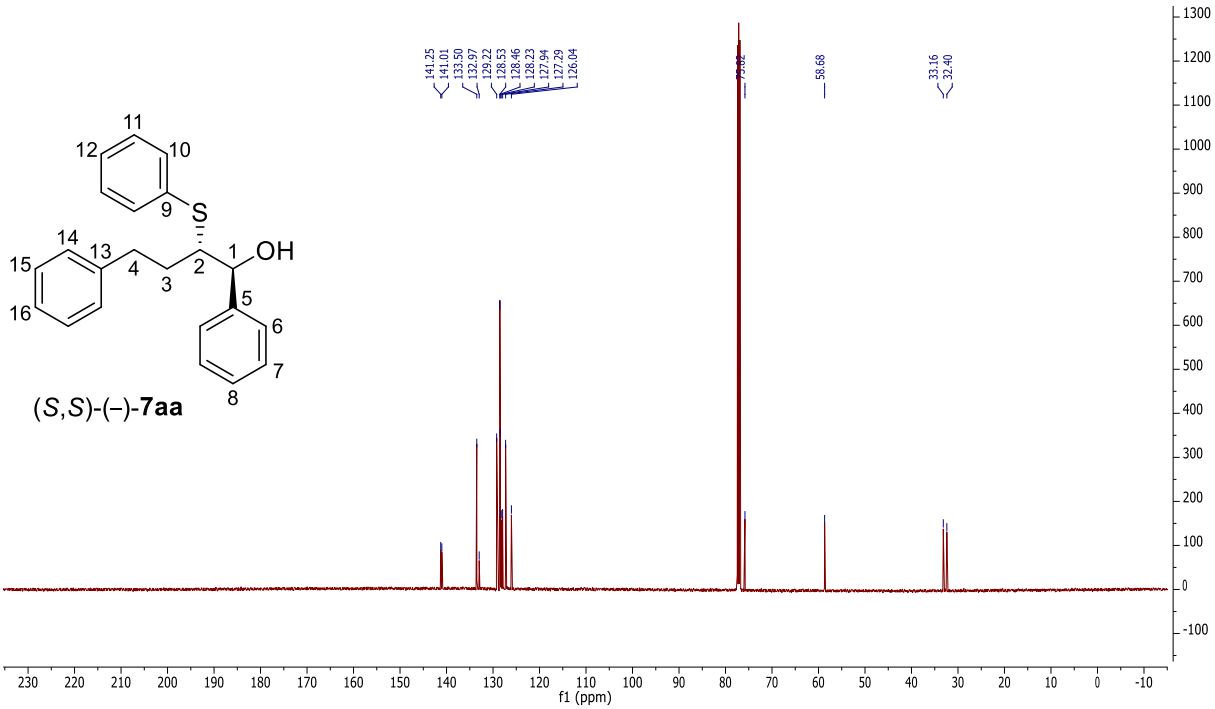
Opt. Rot.: $[\alpha]_D^{24}$ –46.9 (c = 0.85 in 100% EtOH) (94% ee)

NMR Spectra and HPLC Traces

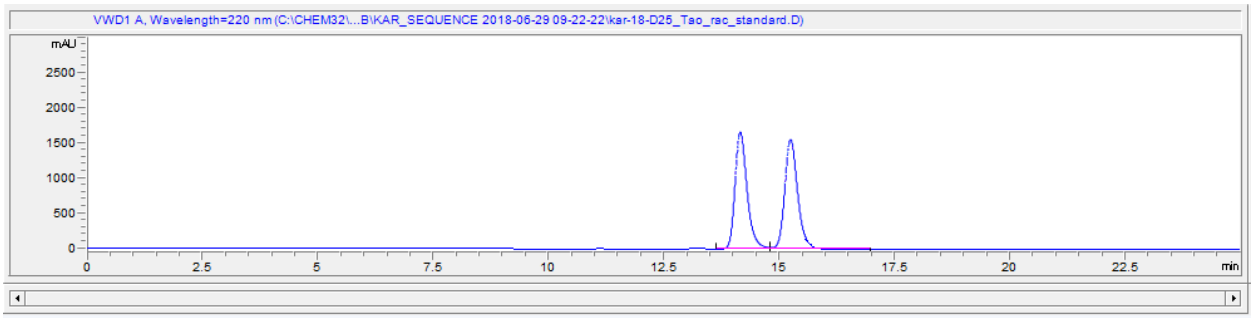
(1*S*,2*S*)-(–)-**7aa** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7aa** ^{13}C NMR (126 MHz, $CDCl_3$)



(±)-7aa



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Sample	kar-18-D25_Tao_rac_standard
Sample Info	
Barcode	
Operator	SYSTEM
Method	Astec-Cellulose-20%-220nmflow05.M
Reference	

#	Time	Area	Height	Width	Area%	Symmetry
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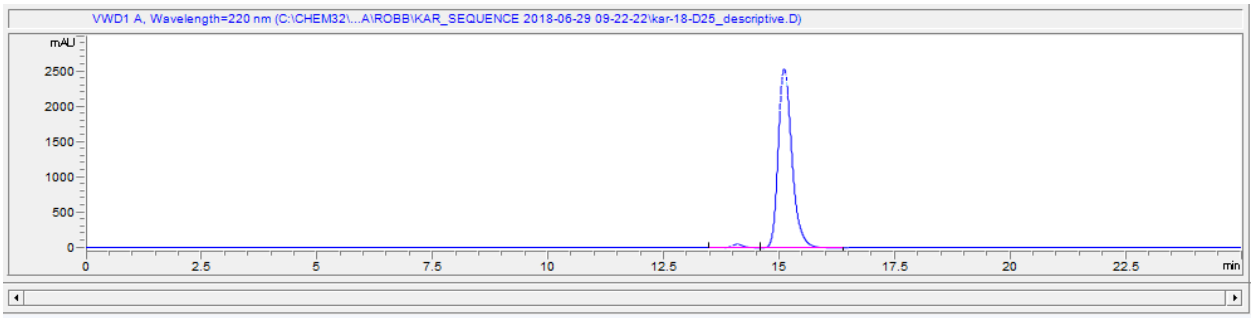
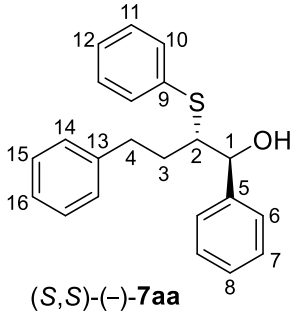
2	15.215	30883.4	1561.5	0.3006	50.227	0.783

(–)-7aa



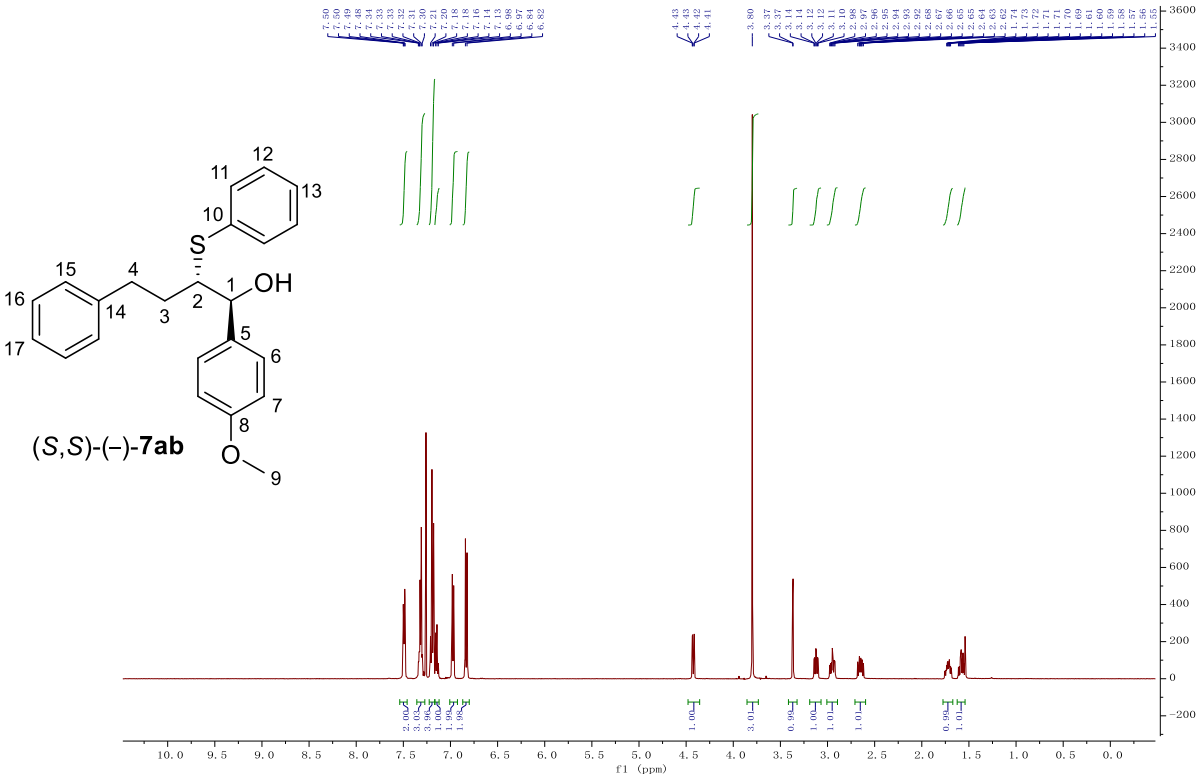
File Information	
Date	29-Jun-18, 09:54:59
Sample	kar-18-D25_descriptive
Sample Info	
Barcode	
Operator	SYSTEM
Method	Astec-Cellulose-20%-220nmflow05.M
Reference	

#	Time	Area	Height	Width	Area%	Symmetry
1	14.082	972.6	52.9	0.2787	1.814	0.805
2	15.111	52634.5	2537.9	0.3177	98.186	0.732

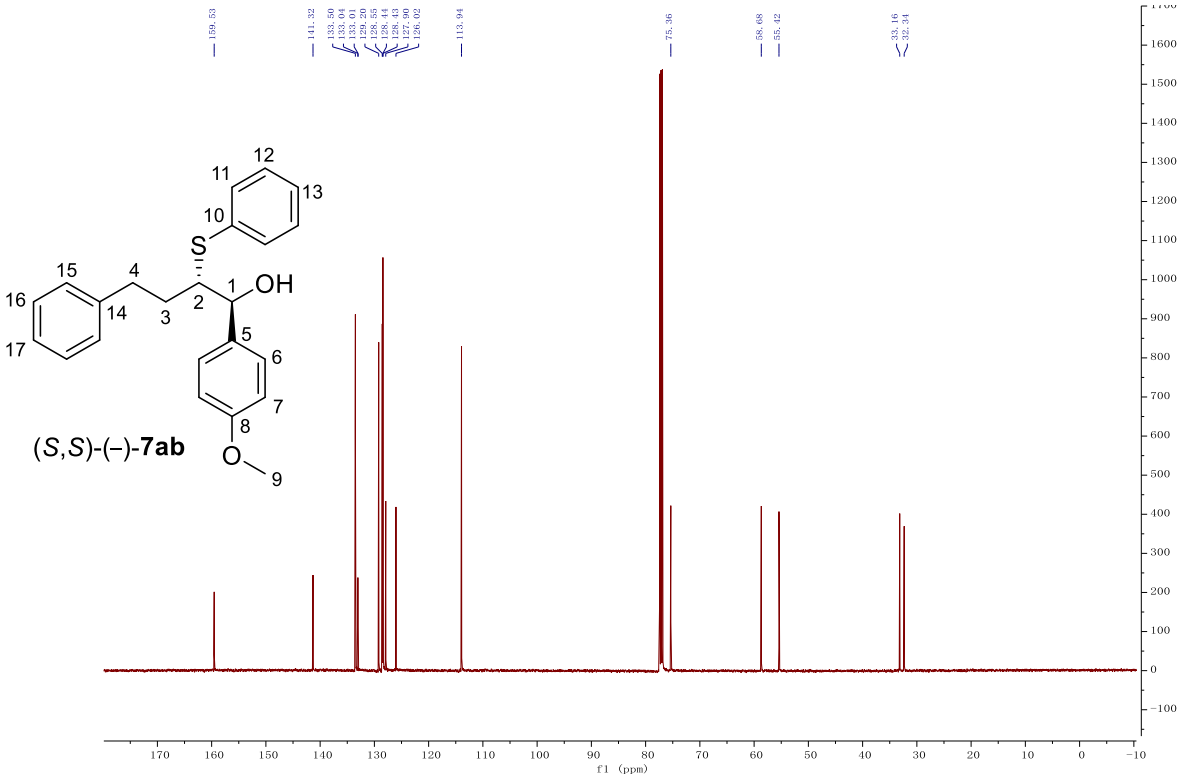


(*S*,*S*)-(–)-**7aa**

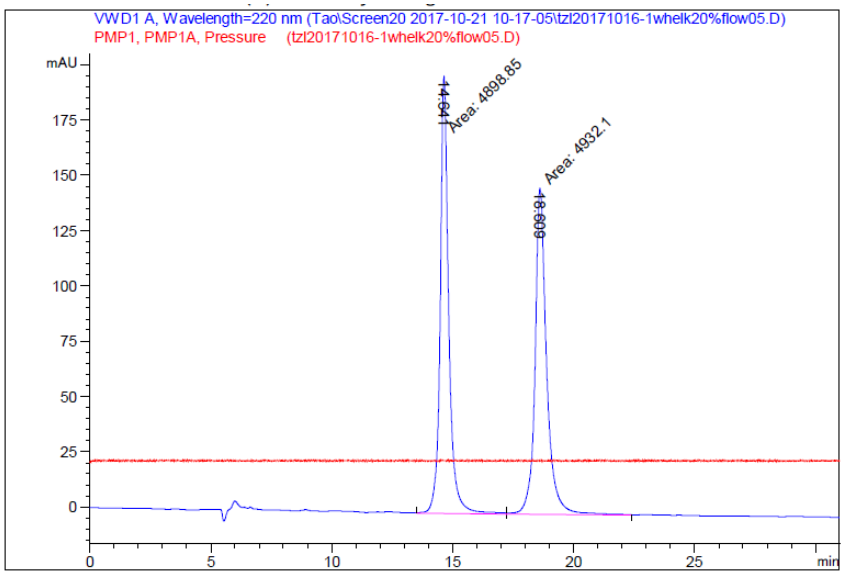
(1*S*,2*S*)-(–)-**7ab** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7ab** ^{13}C NMR (126 MHz, $CDCl_3$)

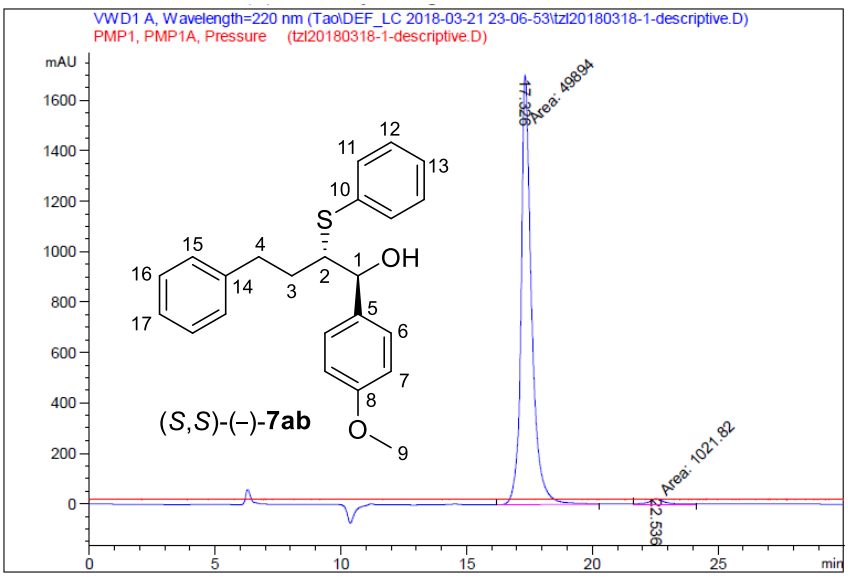


(±)-**7ab**



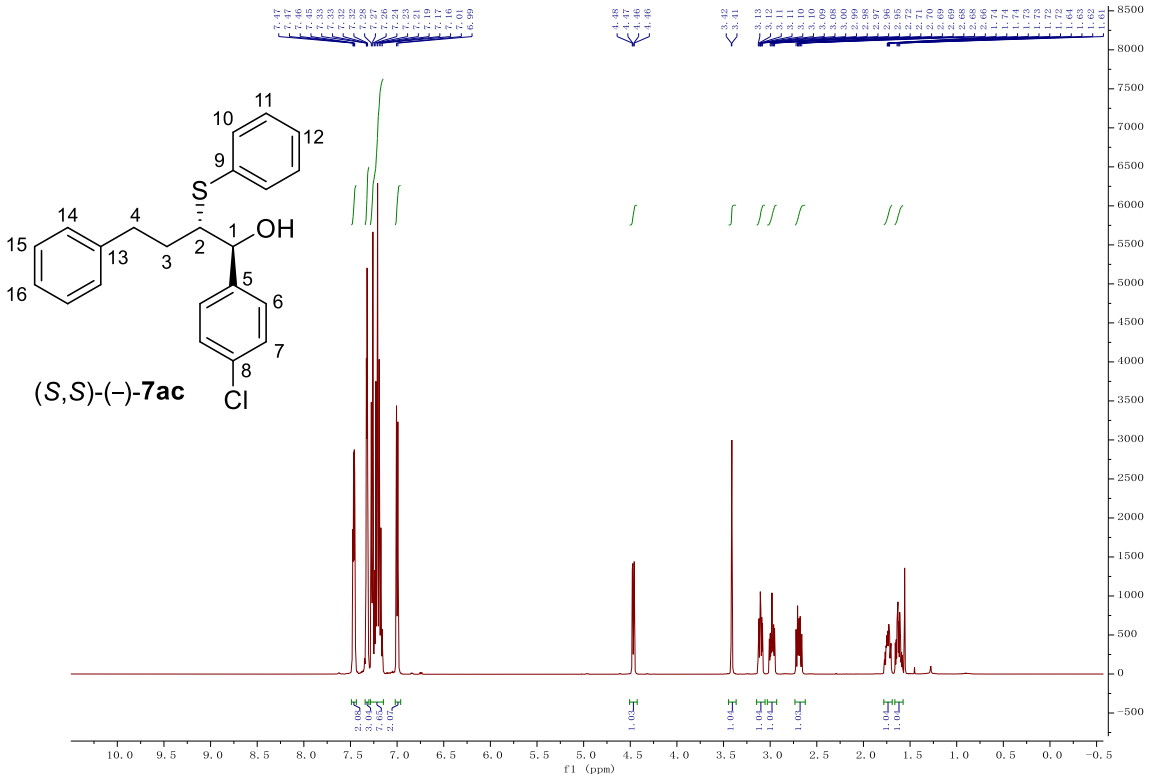
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.641	MF	0.4129	4898.85449	197.72151	49.8309
2	18.609	FM	0.5577	4932.09961	147.40236	50.1691

(1*S*,2*S*)-(–)-**7ab**

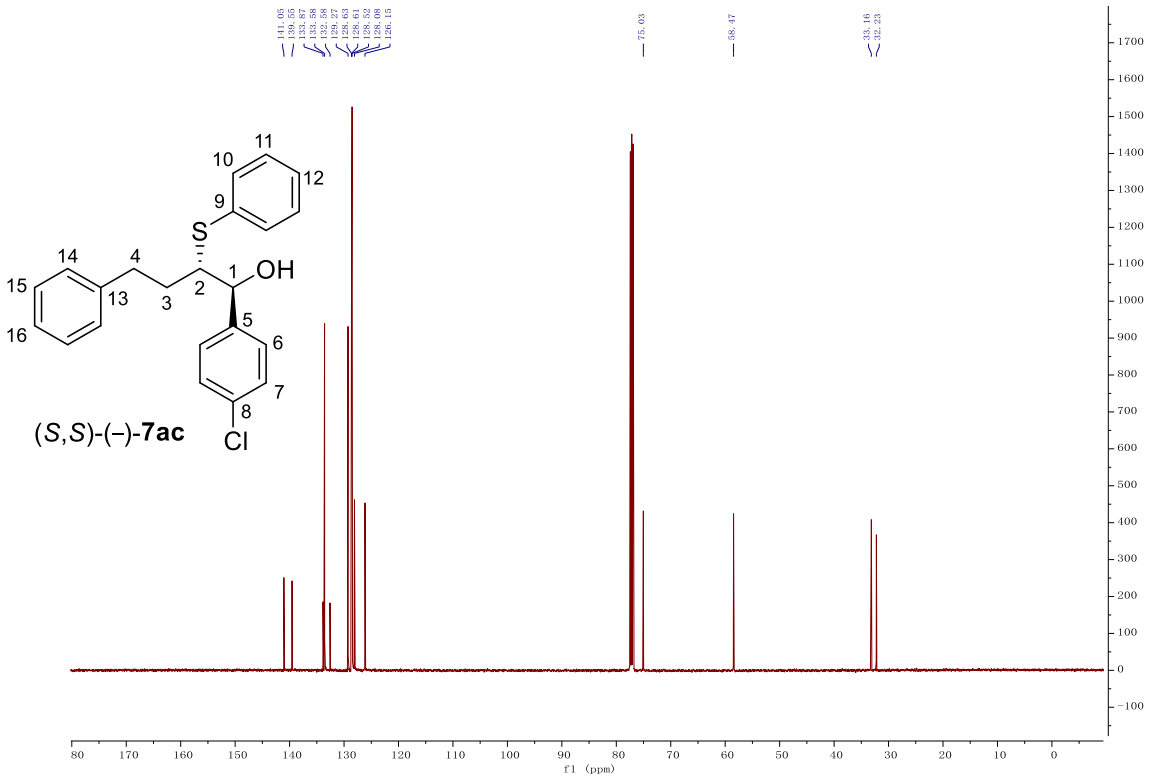


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.326	MM	0.4883	4.98940e4	1703.08862	97.9931
2	22.536	MM	0.7623	1021.82159	22.33975	2.0069

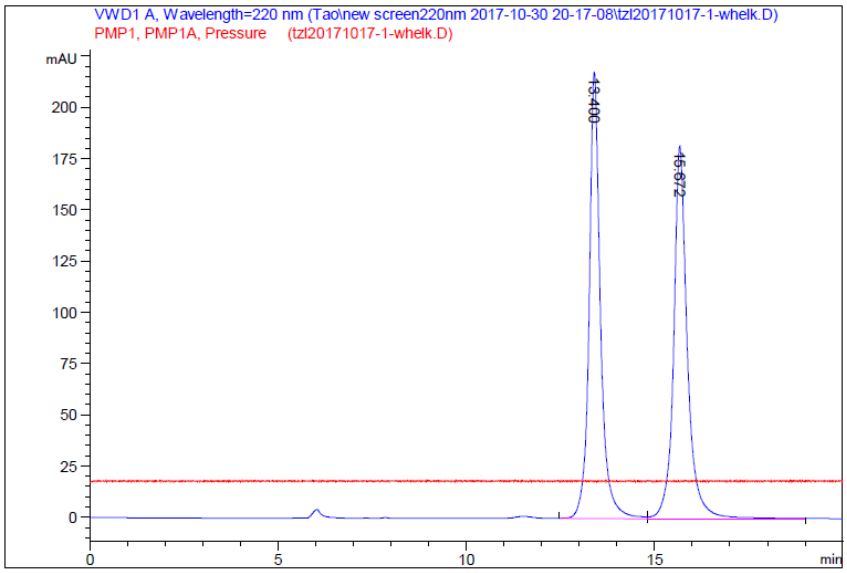
(1*S*,2*S*)-(–)-**7ac** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7ac** ^{13}C NMR (126 MHz, $CDCl_3$)

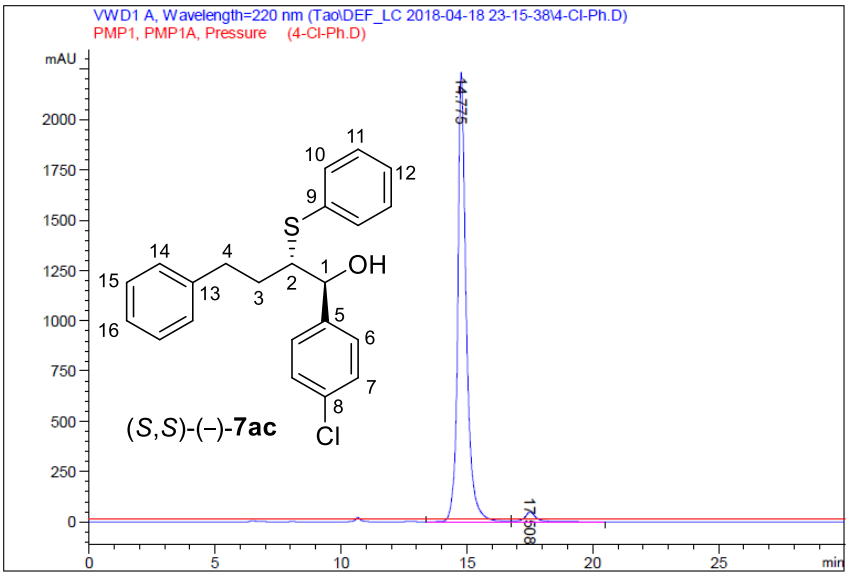


(±)-**7ac**



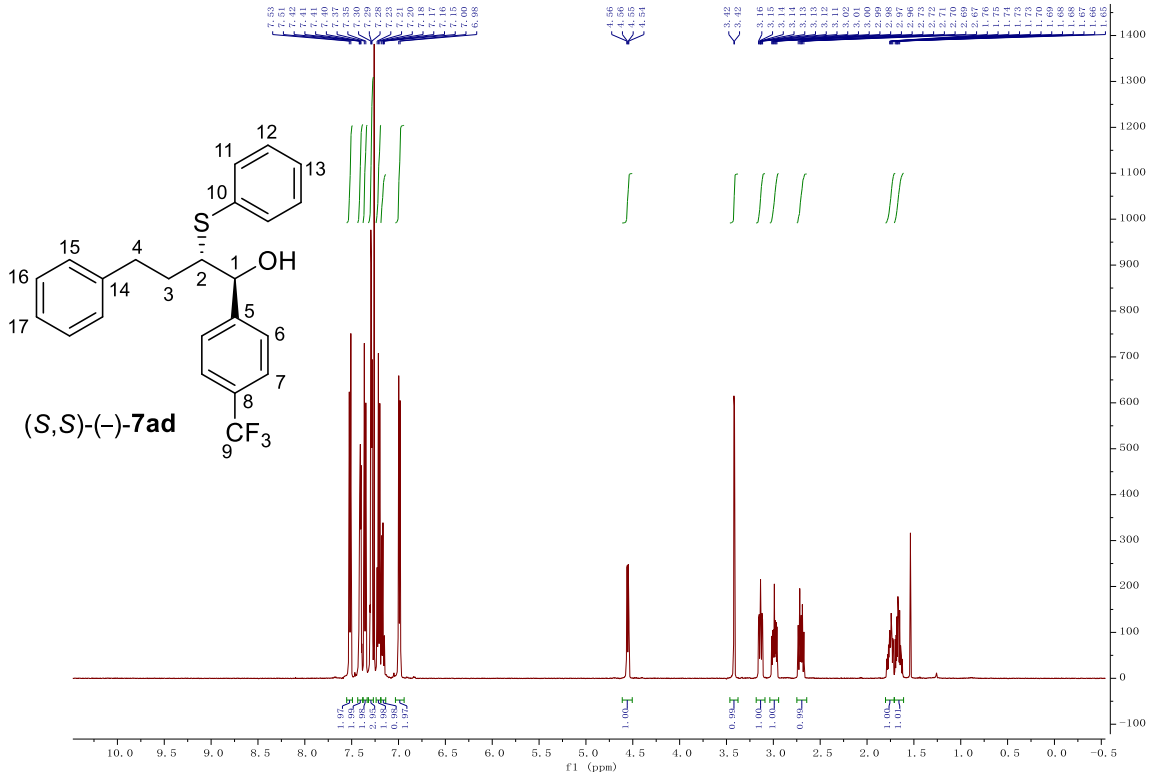
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.400	BV	0.3091	4565.85938	217.39482	49.6680
2	15.672	VV	0.3733	4626.90088	181.41846	50.3320

(1*S*,2*S*)-(–)-**7ac**

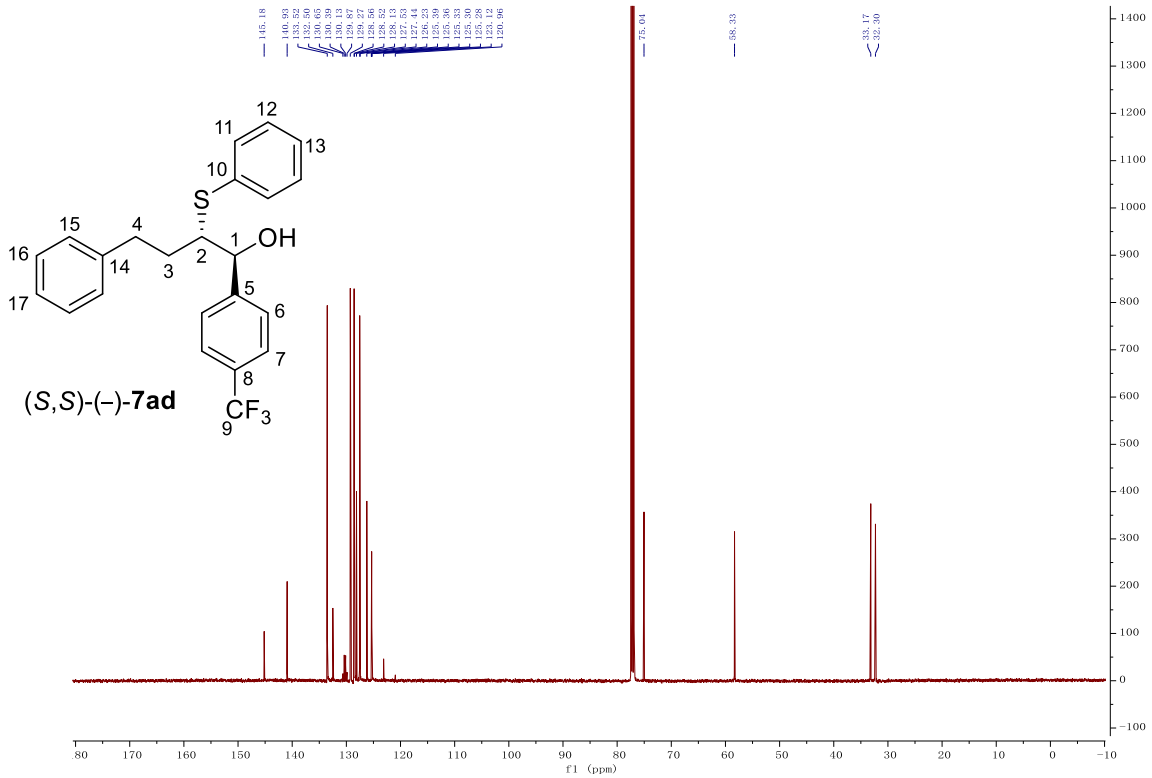


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.775	VV	0.3477	5.30883e4	2229.31250	97.0803
2	17.508	VB	0.4609	1596.62048	49.10498	2.9197

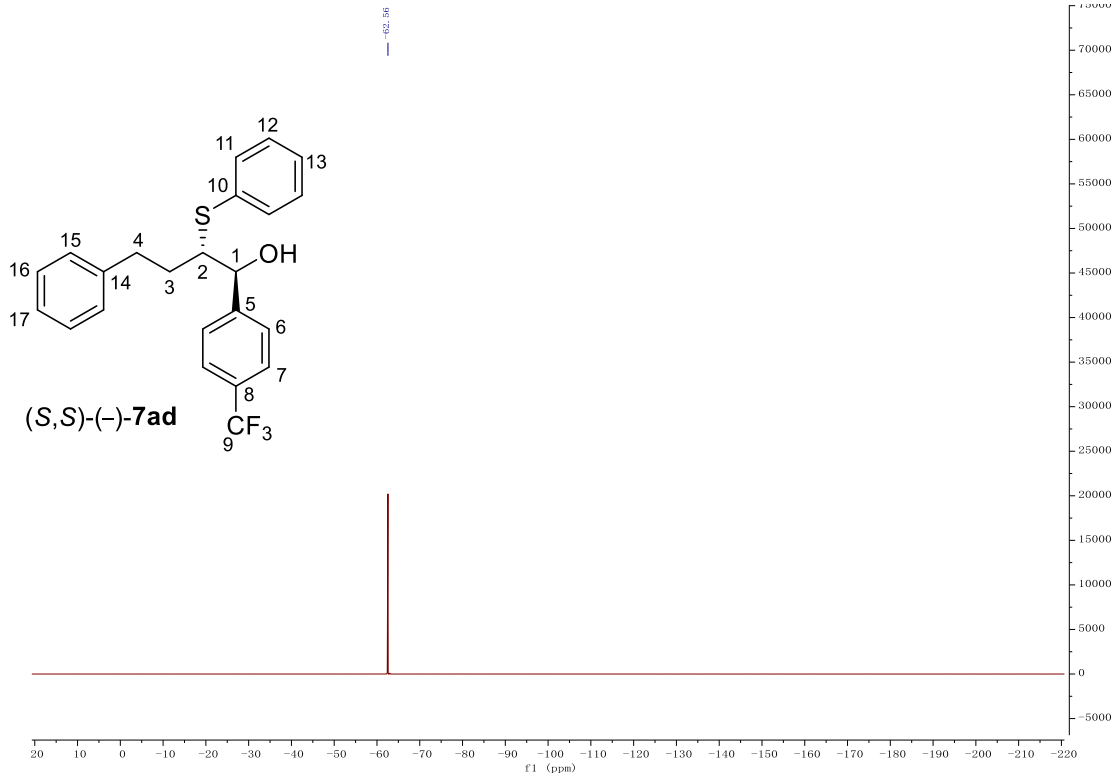
(1*S*,2*S*)-(–)-**7ad** ^{1}H NMR (500 MHz, $CDCl_3$)



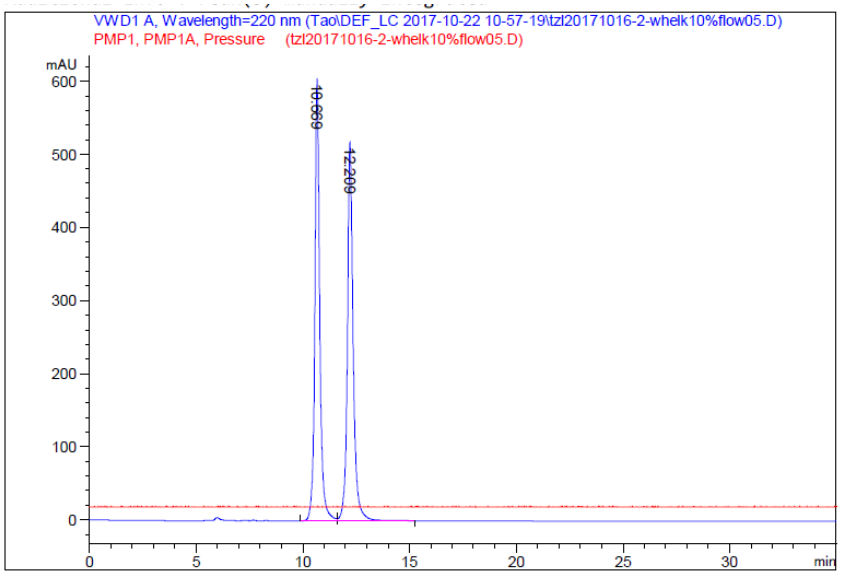
(1*S*,2*S*)-(–)-**7ad** ^{13}C NMR (126 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7ad** ^{19}F NMR (471 MHz, $CDCl_3$)

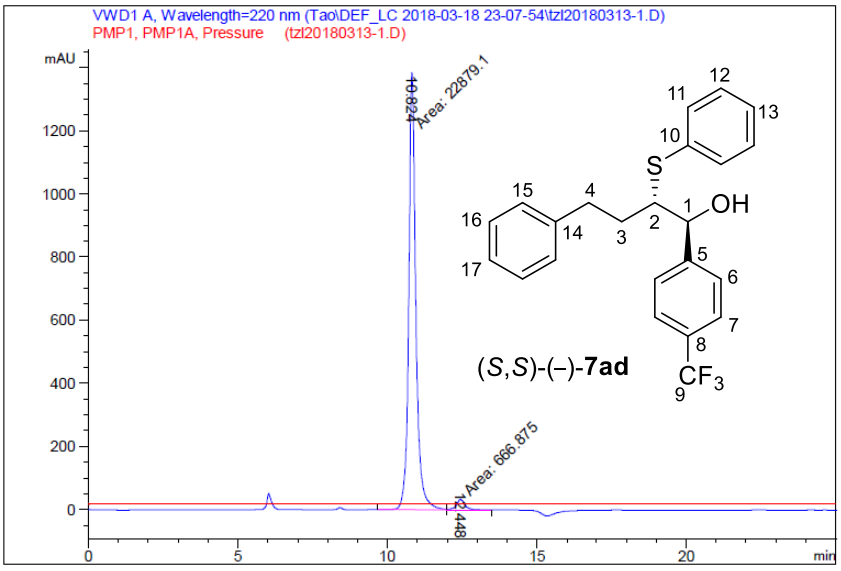


(±)-**7ad**



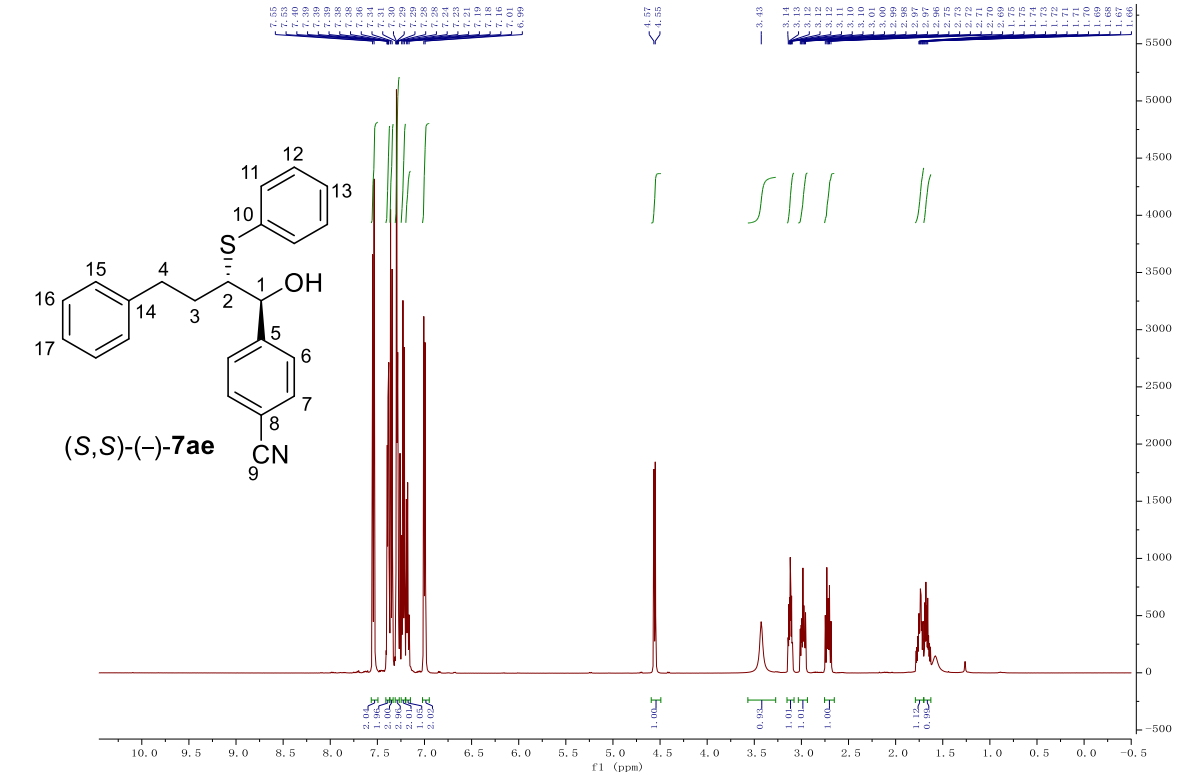
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.669	VV	0.2403	9735.27539	604.49768	49.6393
2	12.209	VV	0.2811	9876.76270	517.08282	50.3607

(1*S*,2*S*)-(–)-**7ad**

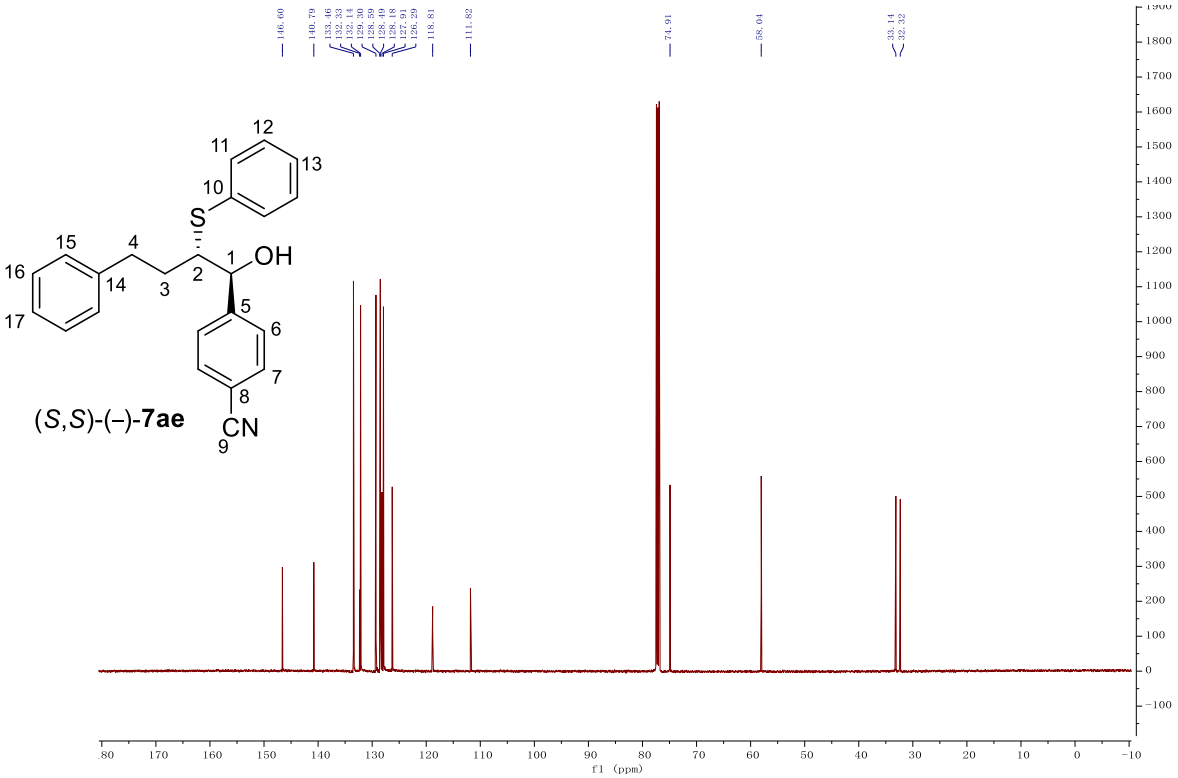


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.824	MF	0.2747	2.28791e4	1388.22302	97.1678
2	12.448	FM	0.3332	666.87476	33.35472	2.8322

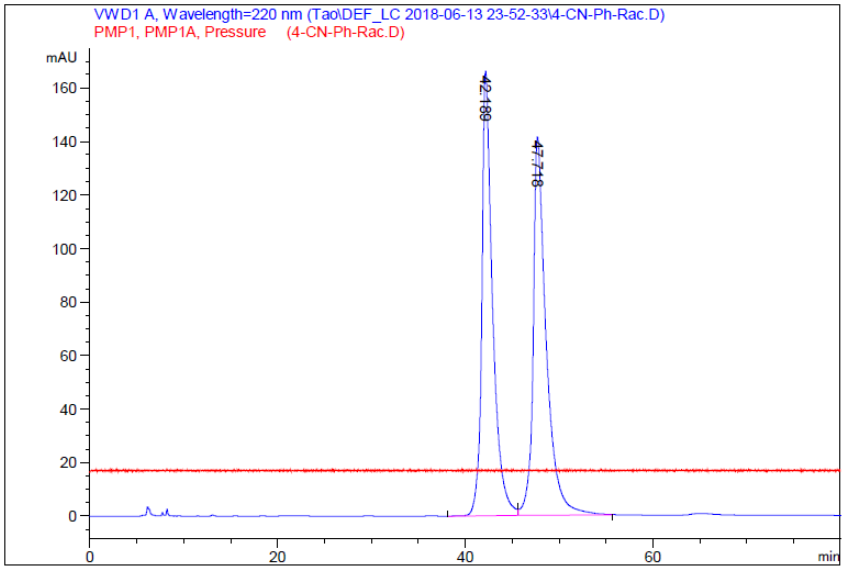
(1*S*,2*S*)-(–)-**7ae** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7ae** ^{13}C NMR (126 MHz, $CDCl_3$)

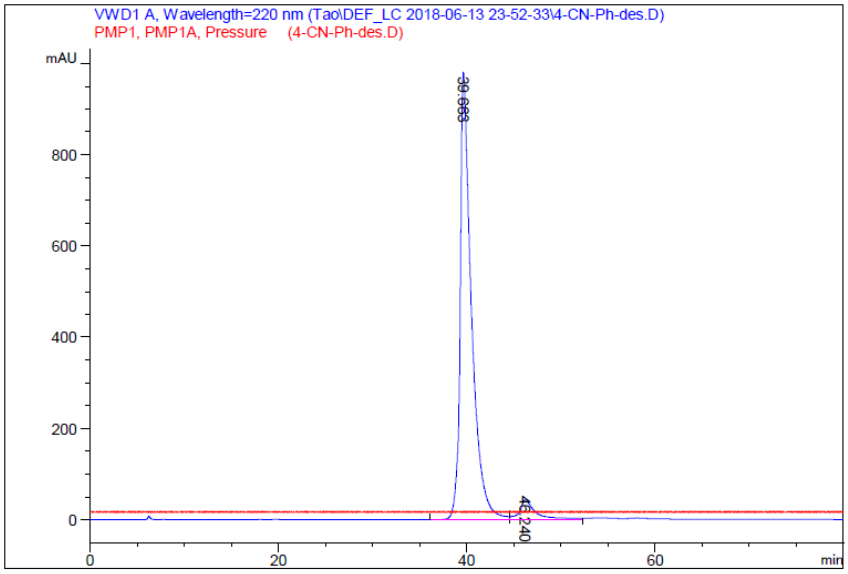


(±)-**7ae**



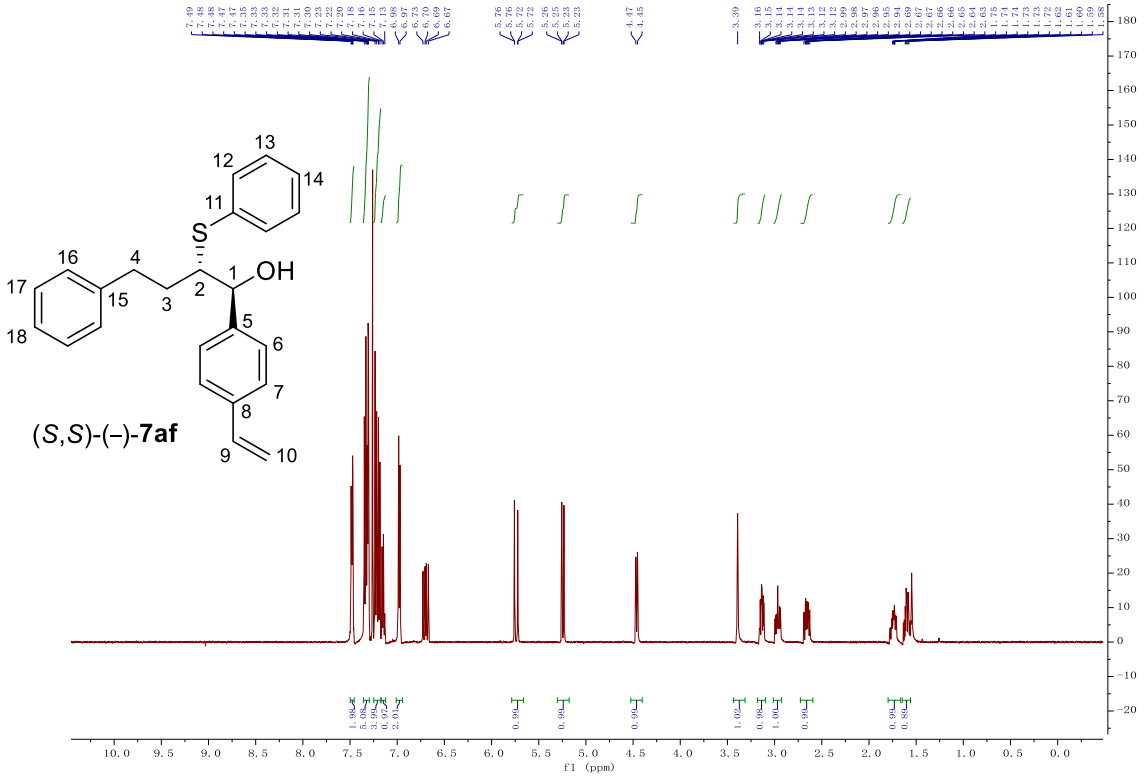
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.189	BV	1.1513	1.33301e4	166.19270	49.3018
2	47.718	VB	1.3683	1.37076e4	141.58827	50.6982

(1*S*,2*S*)-(–)-**7ae**

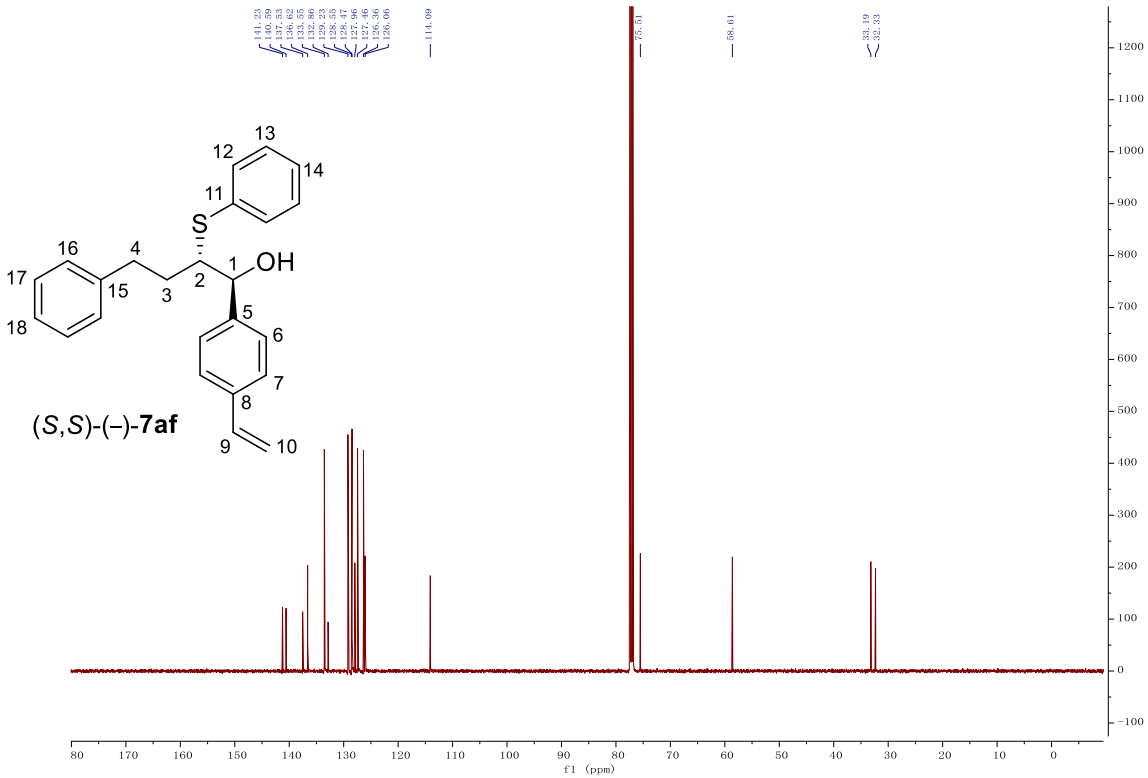


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.663	VV	1.1734	8.15544e4	981.33118	93.9833
2	46.240	VB	1.6542	5221.04688	43.39202	6.0167

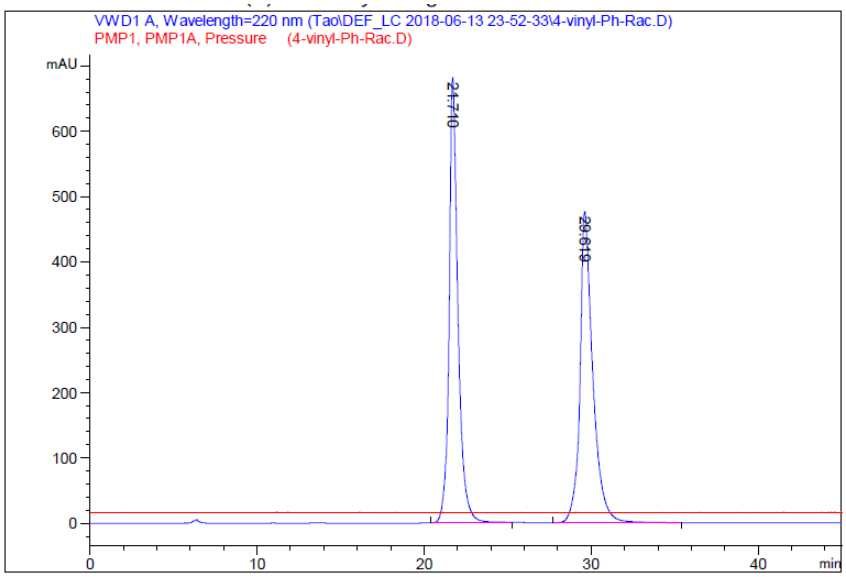
(1*S*,2*S*)-(–)-**7af** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7af** ^{13}C NMR (126 MHz, $CDCl_3$)

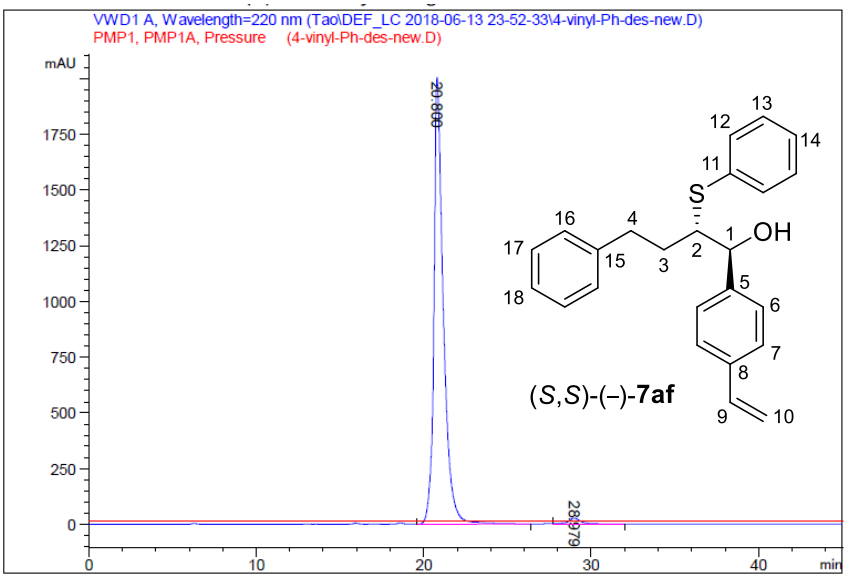


(±)-**7af**



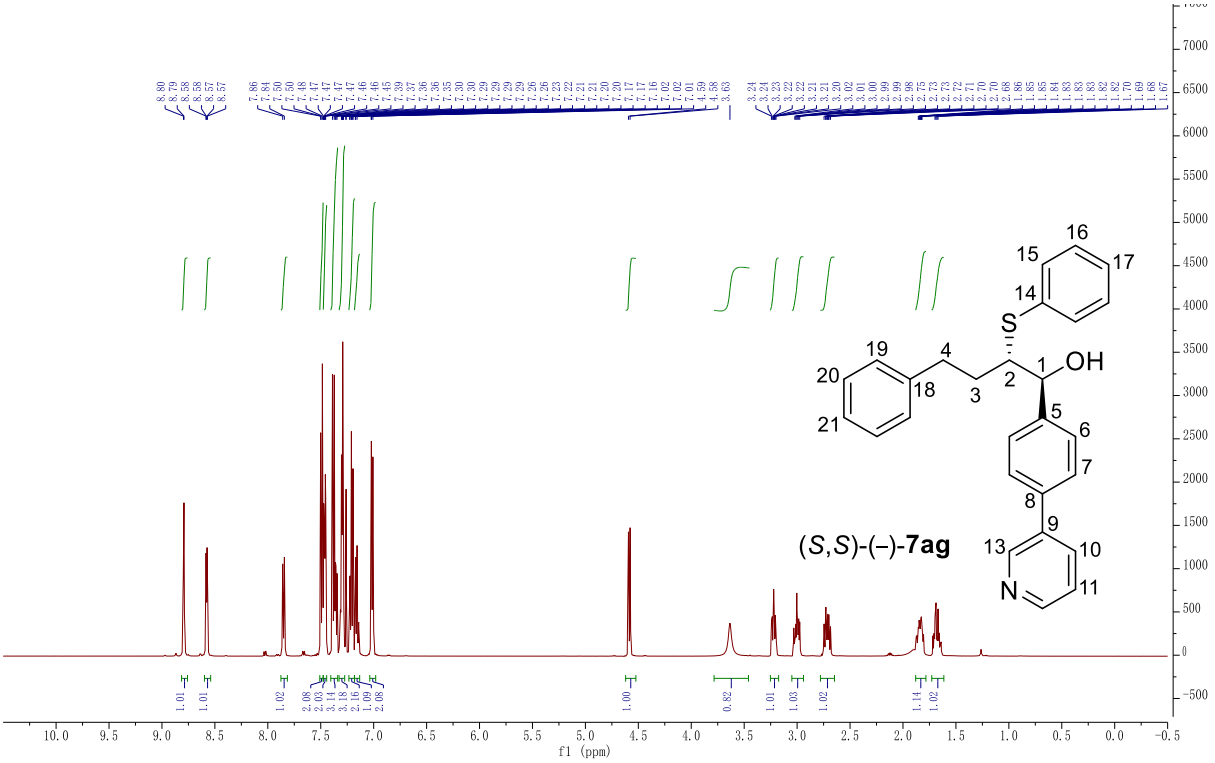
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.710	VB	0.5359	2.51680e4	681.17841	49.6804
2	29.619	BB	0.7642	2.54918e4	476.29169	50.3196

(1*S*,2*S*)-(–)-**7af**

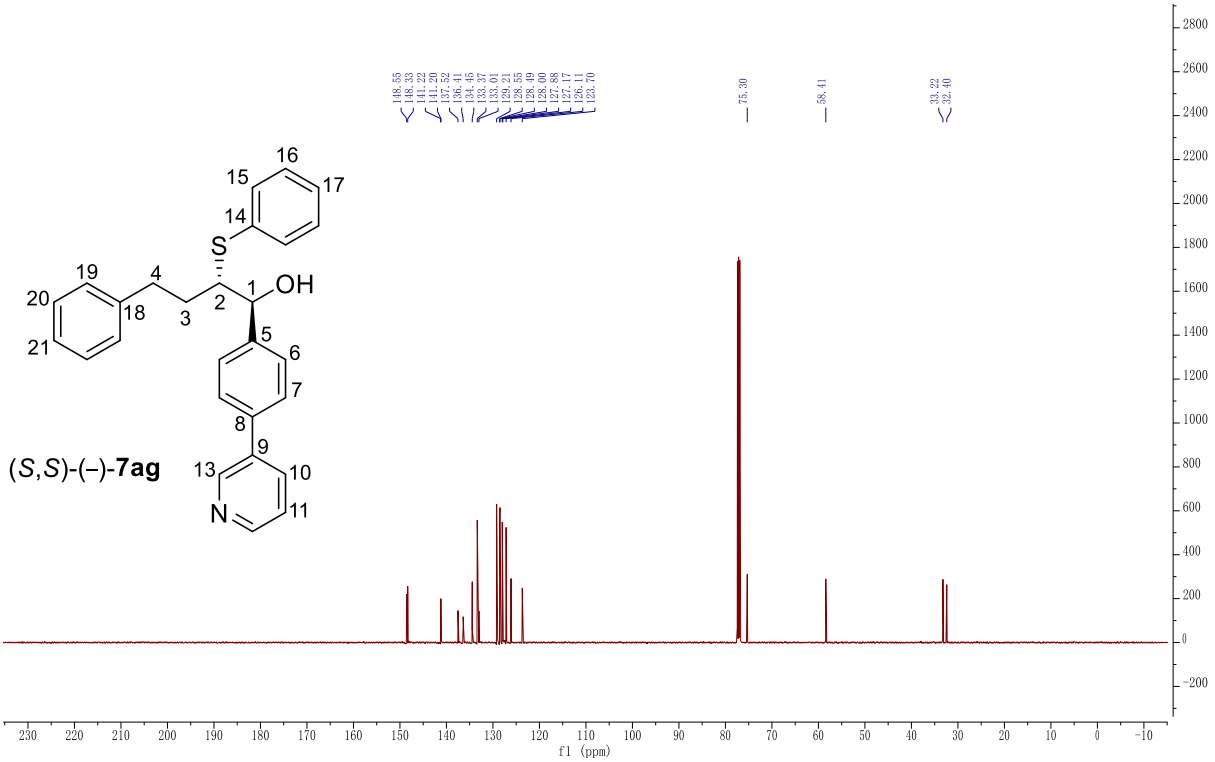


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.800	VV	0.5652	7.90877e4	2004.06567	98.1262
2	28.979	VB	0.7917	1510.24121	27.02501	1.8738

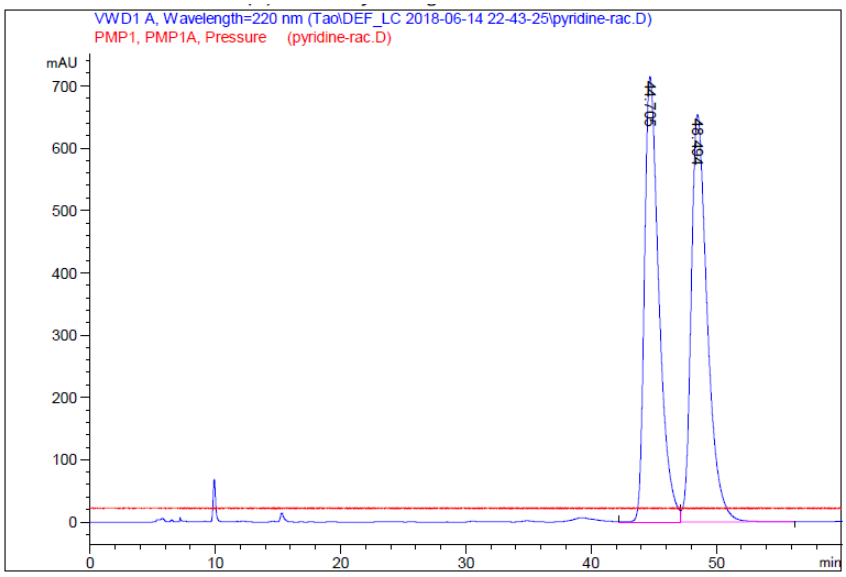
(1*S*,2*S*)-(–)-**7ag** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7ag** ^{13}C NMR (126 MHz, $CDCl_3$)

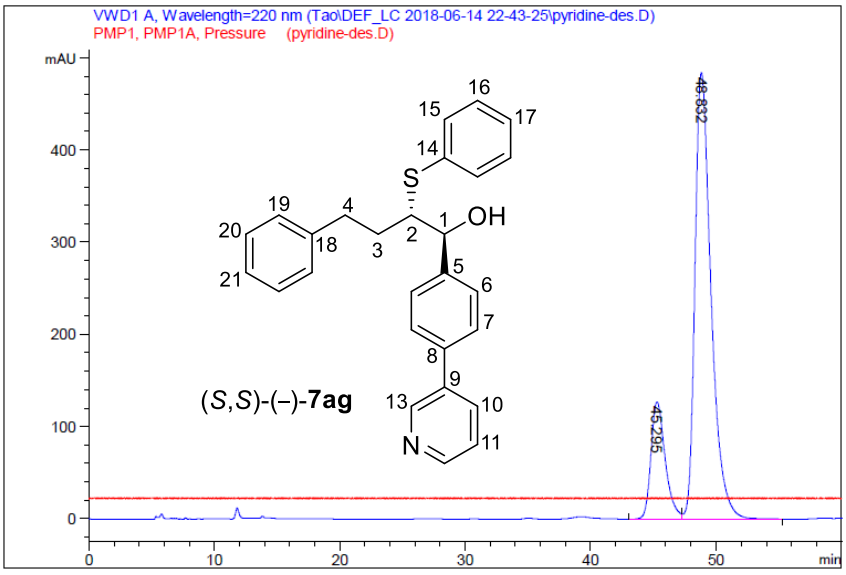


(±)-**7ag**



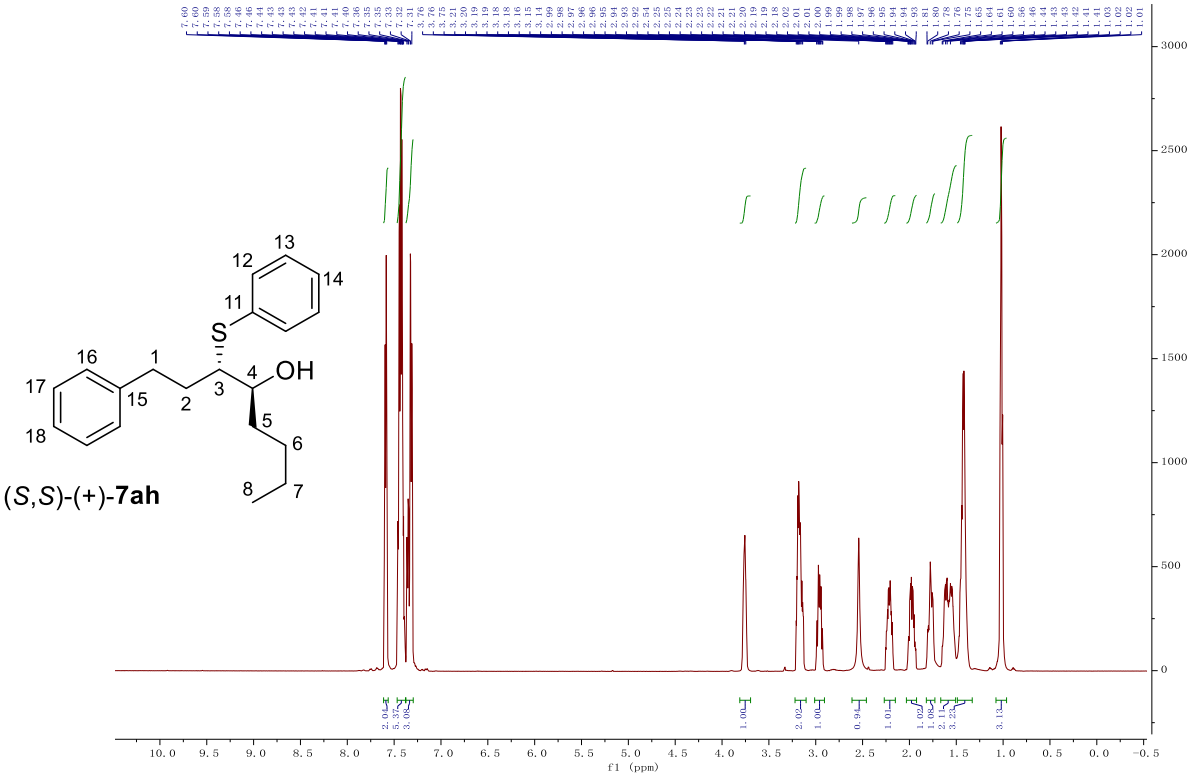
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.705	VV	1.2275	5.77291e4	714.88391	49.5748
2	48.494	VB	1.3621	5.87193e4	653.95715	50.4252

(1*S*,2*S*)-(–)-**7ag**

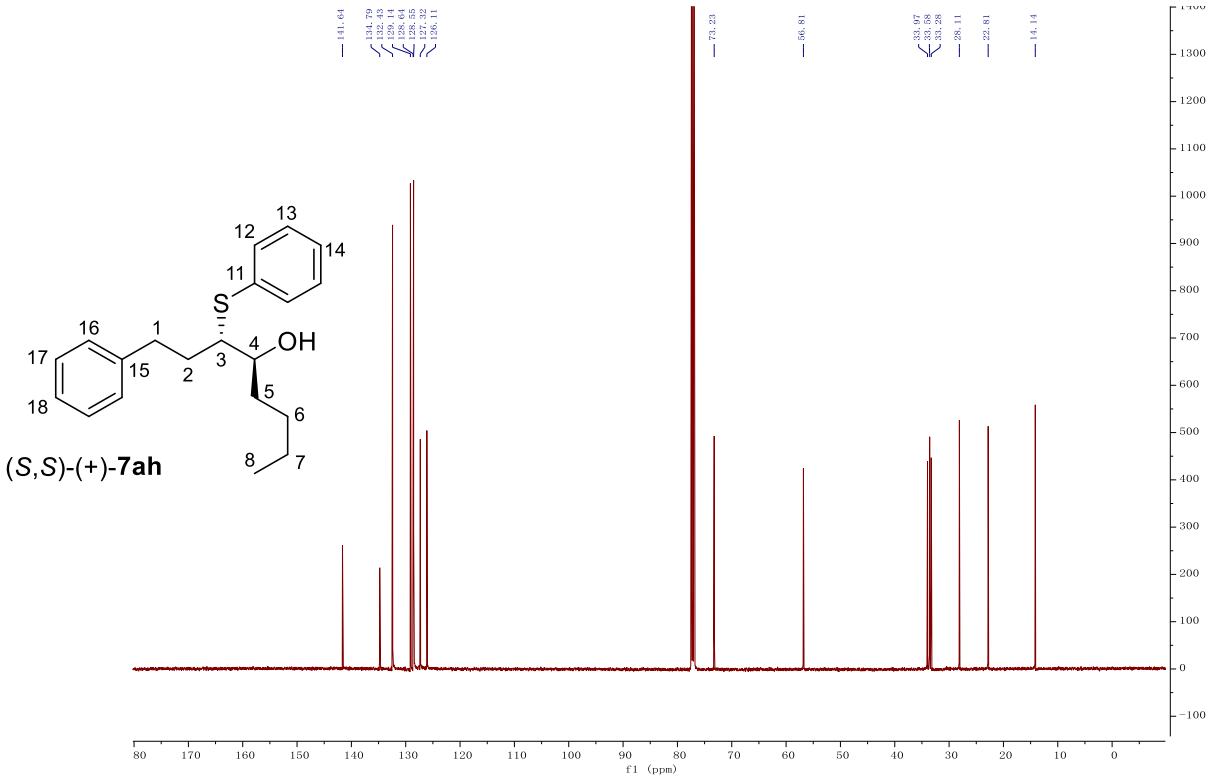


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.295	VV	1.2029	1.00680e4	127.20917	18.8777
2	48.832	VB	1.3565	4.32647e4	484.43036	81.1223

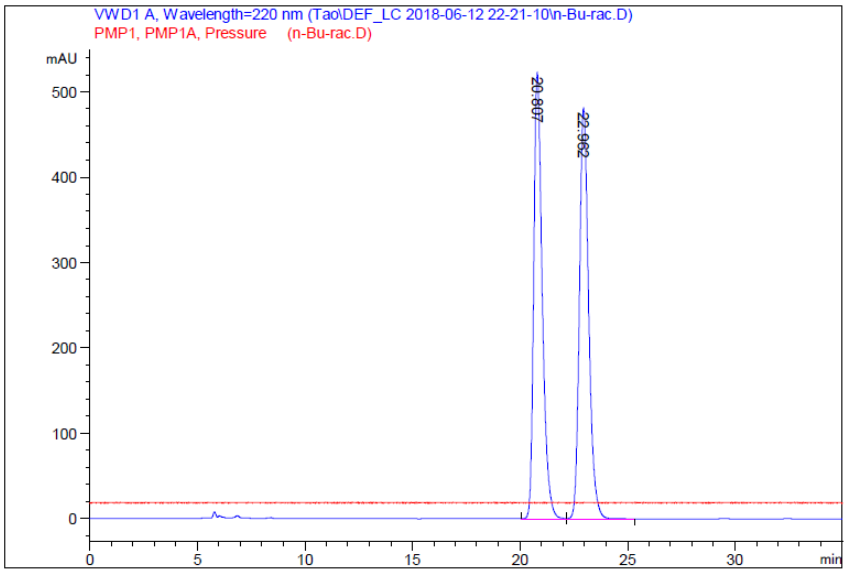
(3*S*,4*S*)-(+)-**7ah** ^{1}H NMR (500 MHz, $CDCl_3$)



(3*S*,4*S*)-(+)-**7ah** ^{13}C NMR (126 MHz, $CDCl_3$)

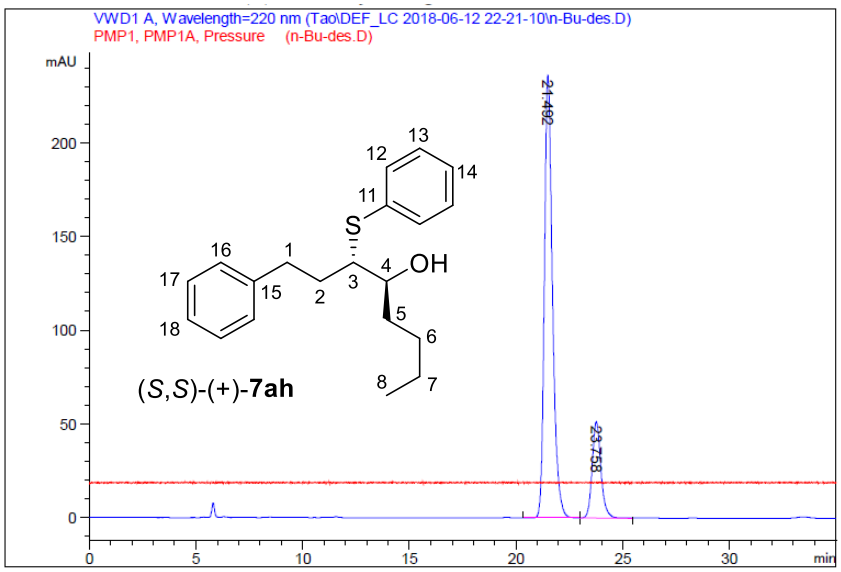


(±)-**7ah**



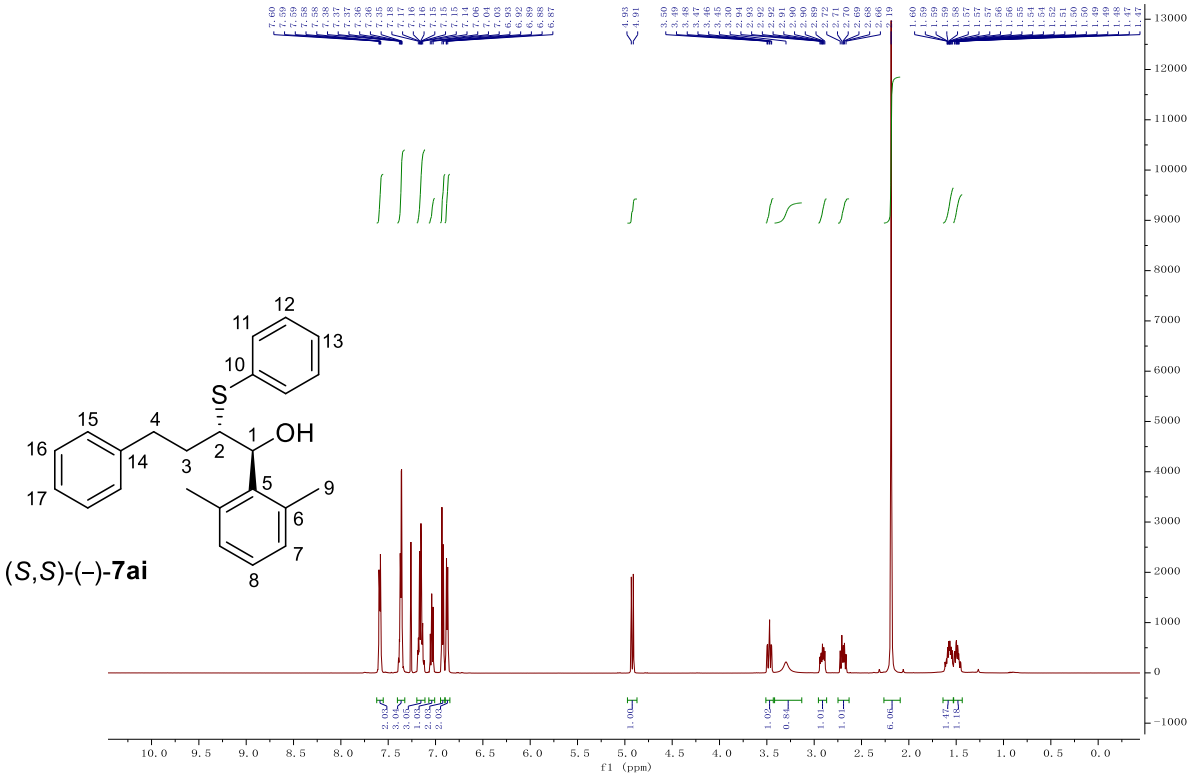
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.807	VV	0.4138	1.43681e4	522.80737	49.9873
2	22.962	VB	0.4530	1.43754e4	481.65756	50.0127

(3*S*,4*S*)-(+)-**7ah**

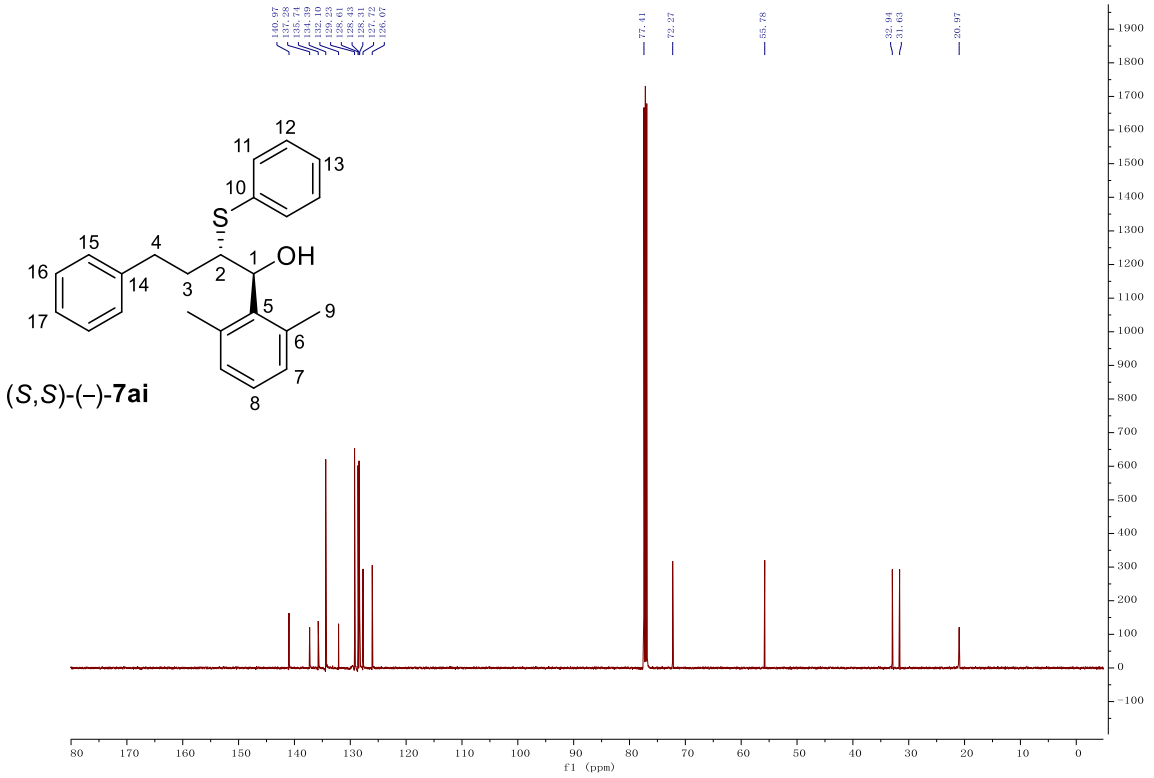


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.492	VV	0.4017	6251.44336	236.41179	80.8290
2	23.758	VB	0.4413	1482.72009	51.40772	19.1710

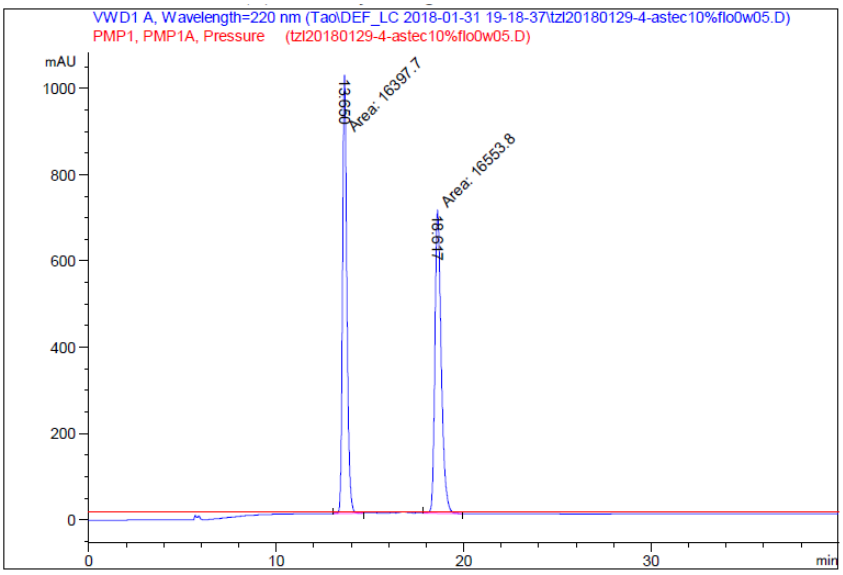
(1*S*,2*S*)-(–)-**7ai** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7ai** ^{13}C NMR (126 MHz, $CDCl_3$)

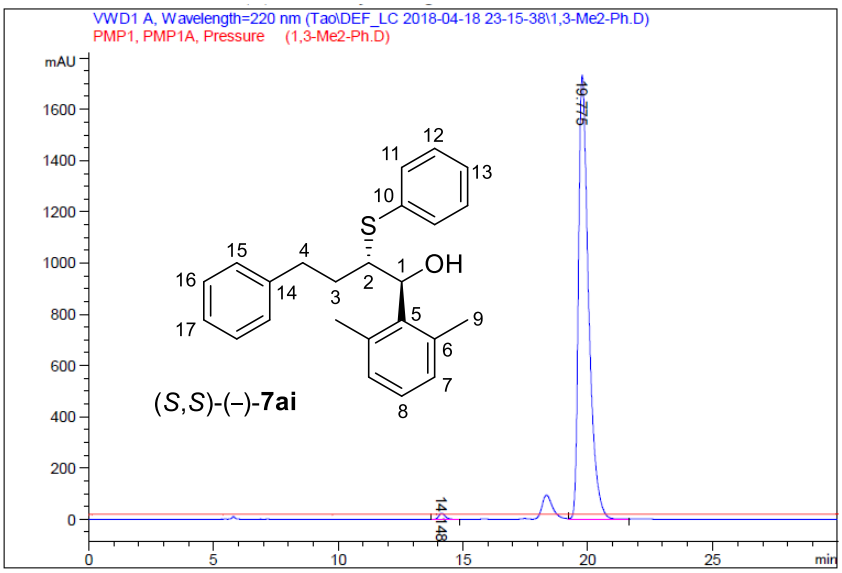


(±)-**7ai**



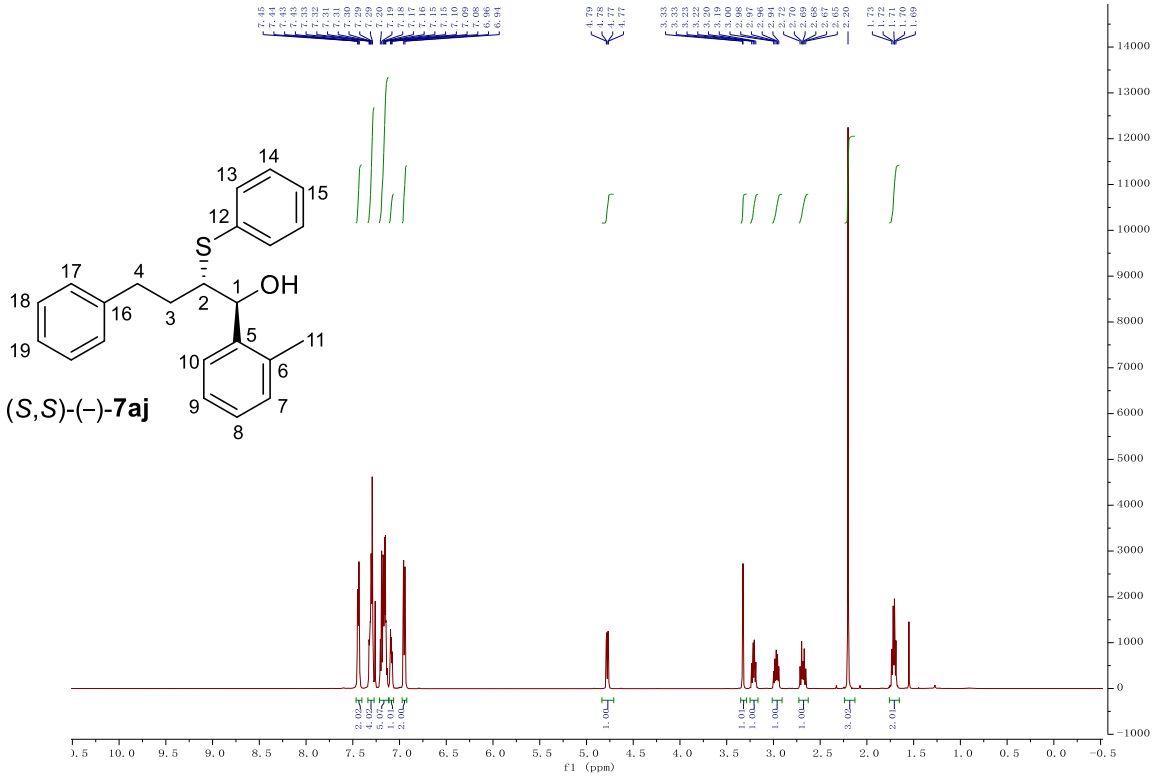
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.650	MM	0.2685	1.63977e4	1017.74811	49.7631
2	18.617	MM	0.3928	1.65538e4	702.31897	50.2369

(1*S*,2*S*)-(–)-**7ai**

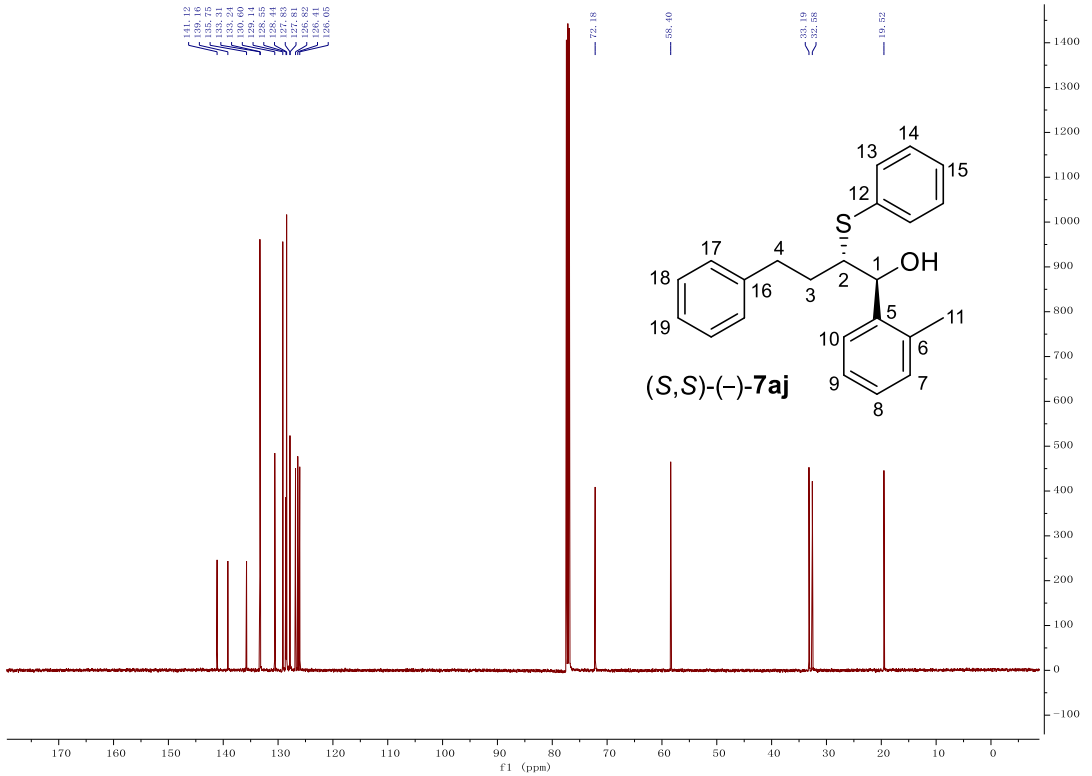


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.148	VV	0.2639	429.90598	24.39105	0.8736
2	19.775	VV	0.4217	4.87823e4	1732.55920	99.1264

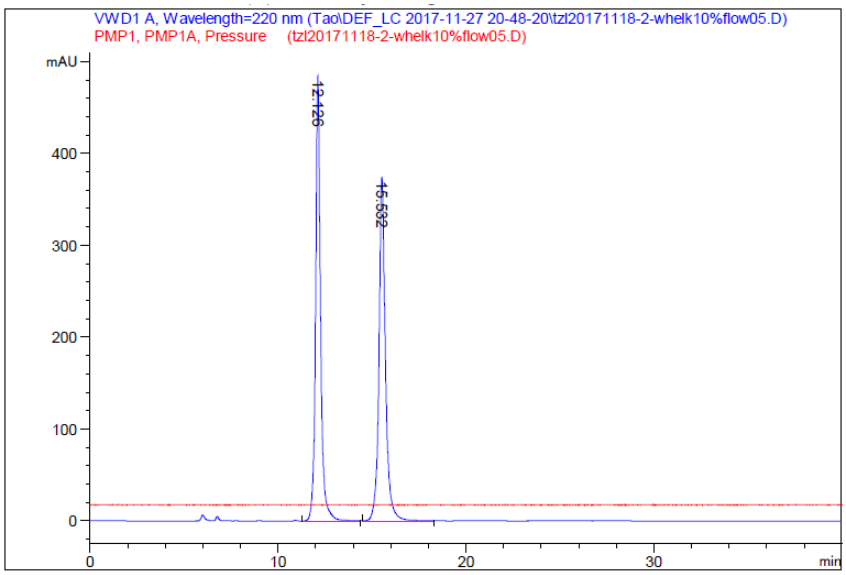
(1*S*,2*S*)-(–)-**7aj** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7aj** ^{13}C NMR (126 MHz, $CDCl_3$)

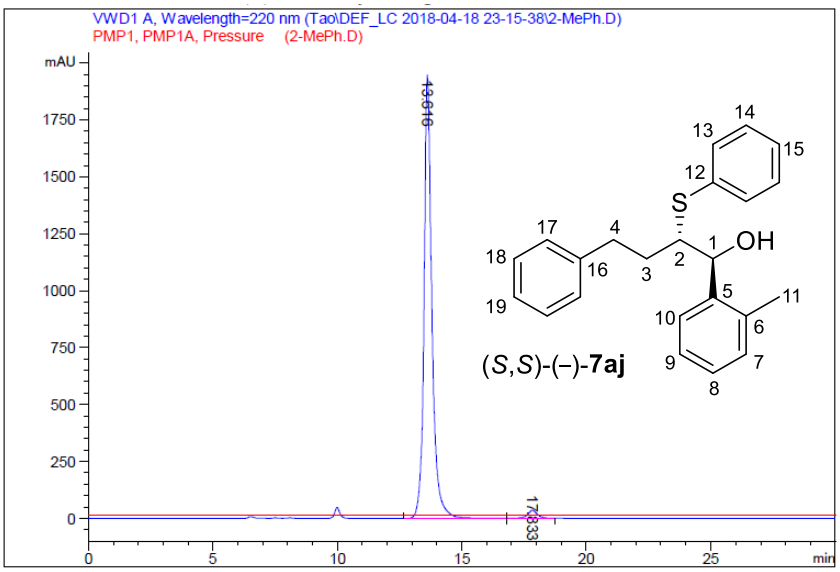


(±)-**7aj**



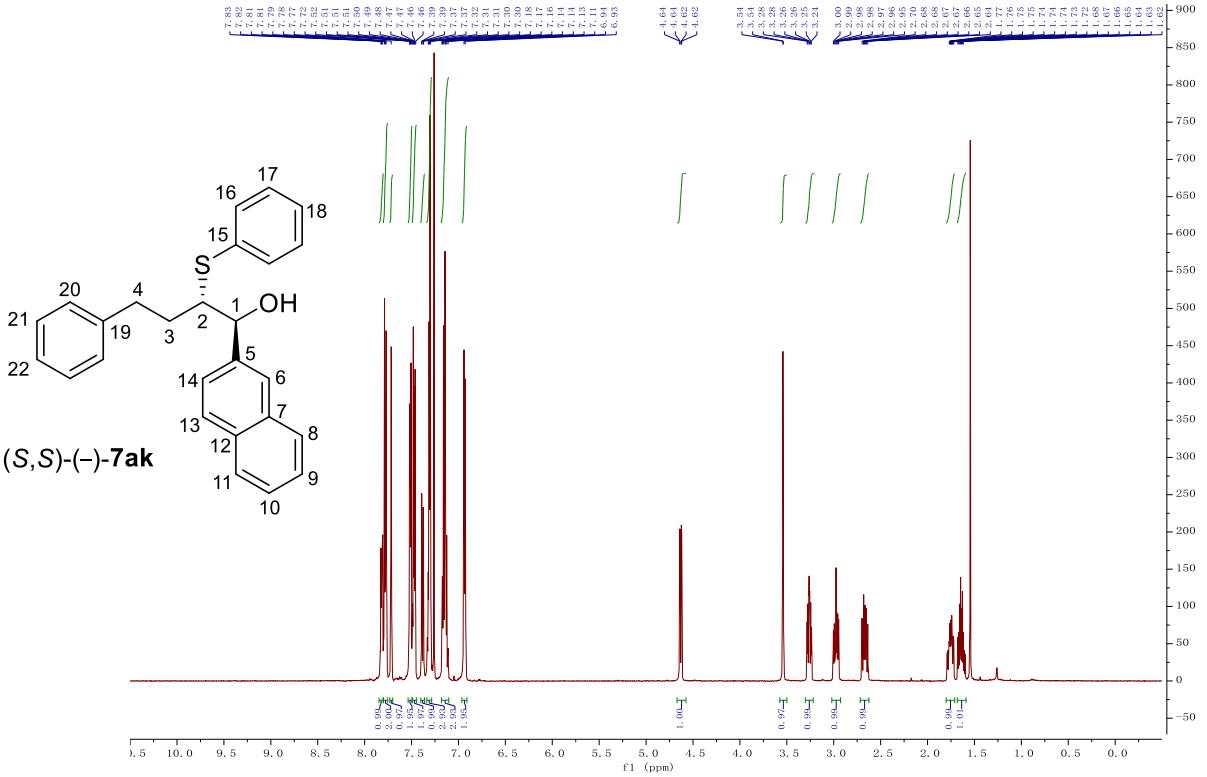
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.126	VB	0.2766	9072.51172	484.67969	49.9995
2	15.532	BV	0.3585	9072.67676	374.28107	50.0005

(1*S*,2*S*)-(–)-**7aj**

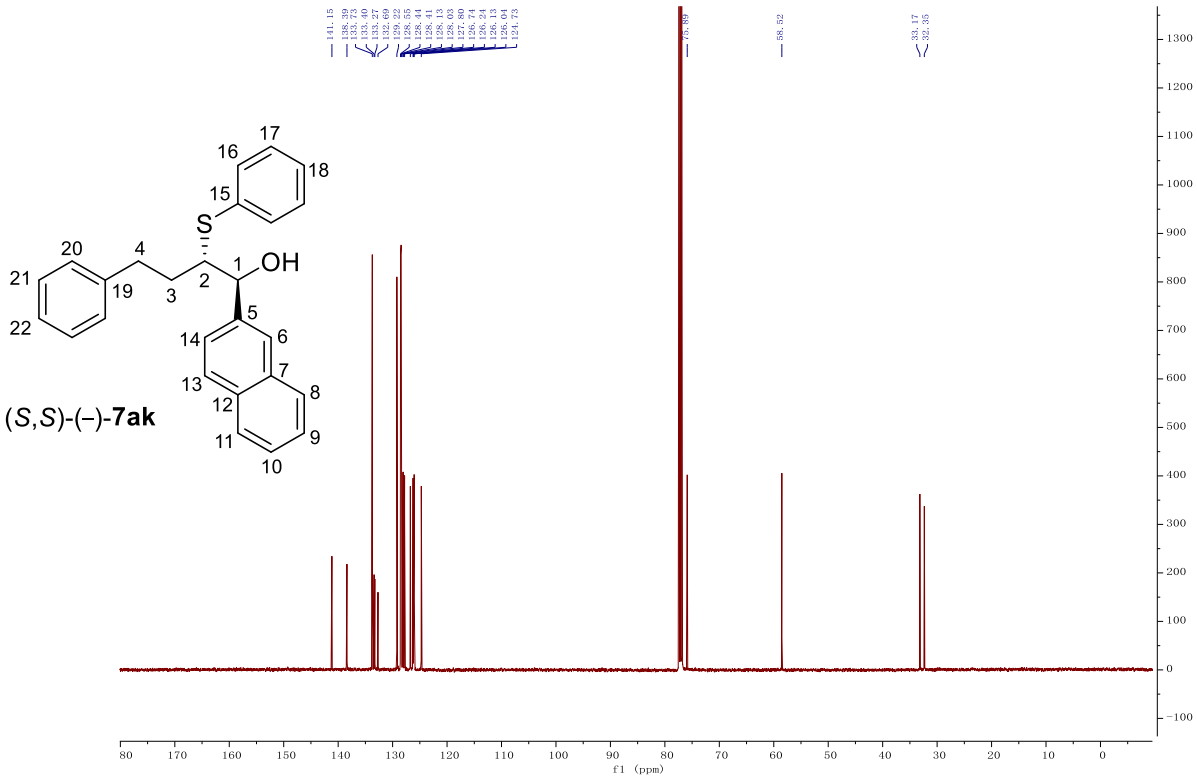


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.616	VV	0.3236	4.32432e4	1943.79797	97.5064
2	17.833	VV	0.4381	1105.90918	36.18745	2.4936

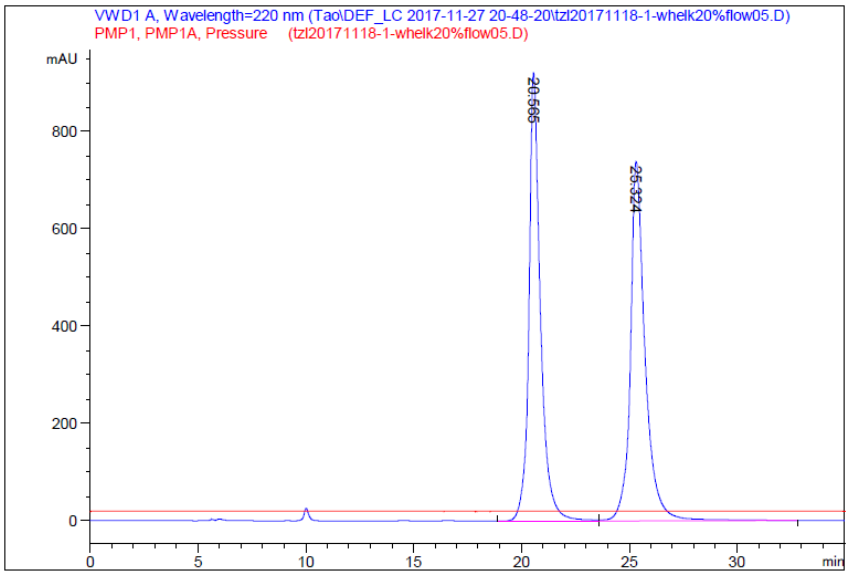
(1*S*,2*S*)-(–)-**7ak** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7ak** ^{13}C NMR (126 MHz, $CDCl_3$)

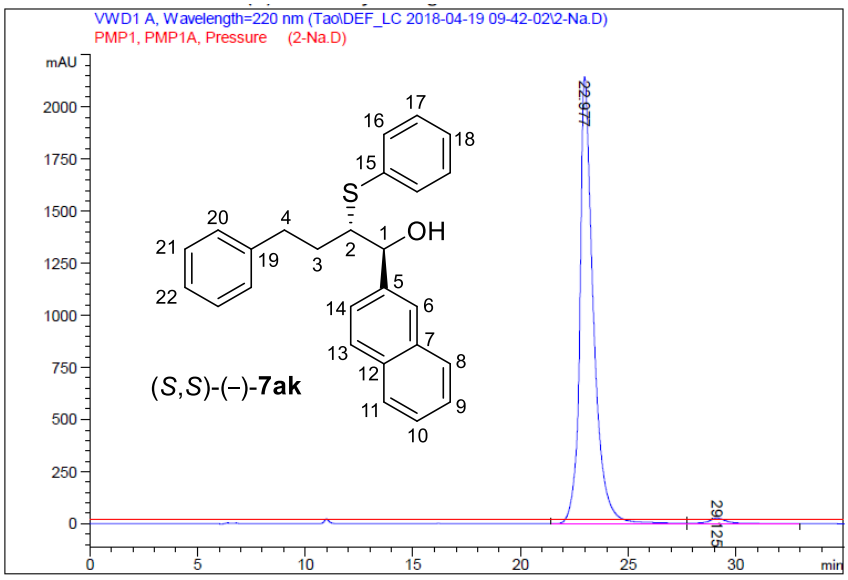


(±)-**7ak**



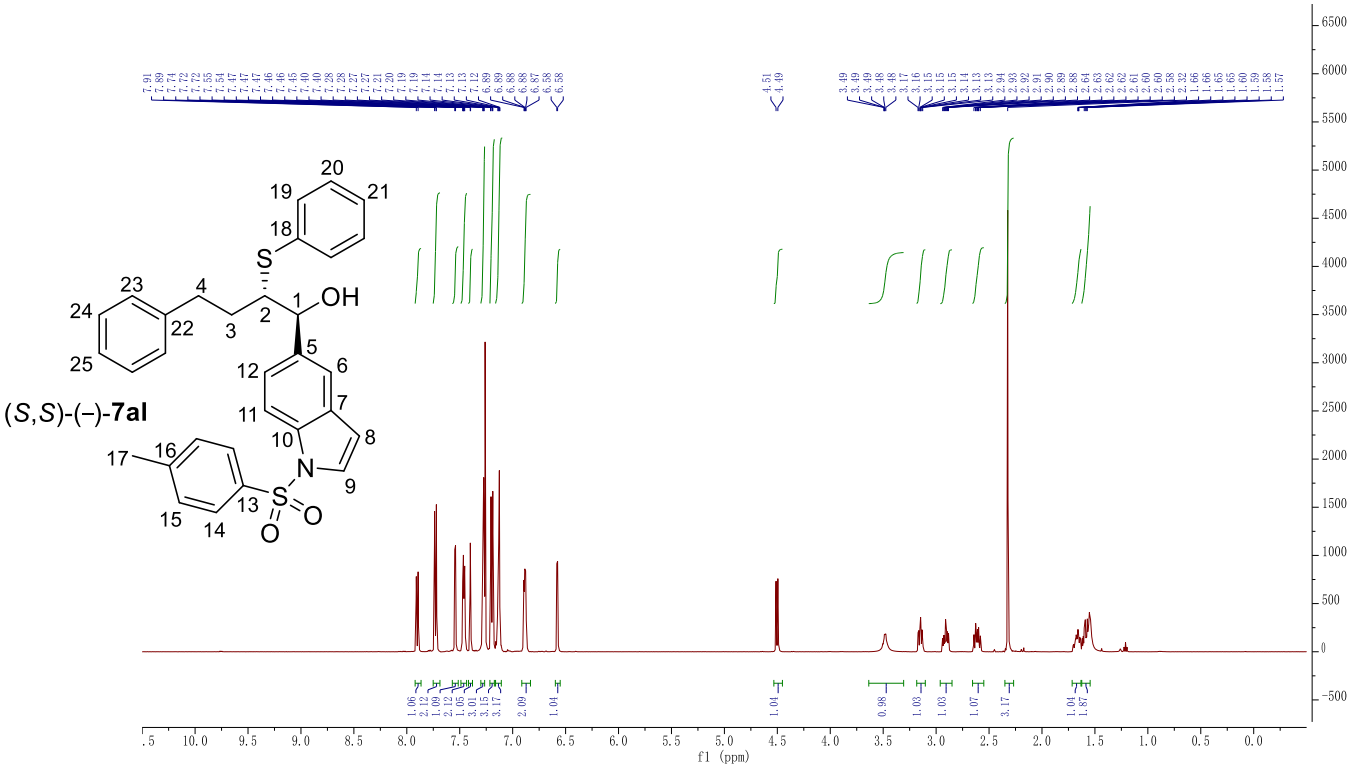
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.565	VV	0.5397	3.43348e4	921.22711	49.3466
2	25.324	VB	0.6909	3.52441e4	738.25415	50.6534

(1*S*,2*S*)-(–)-**7ak**

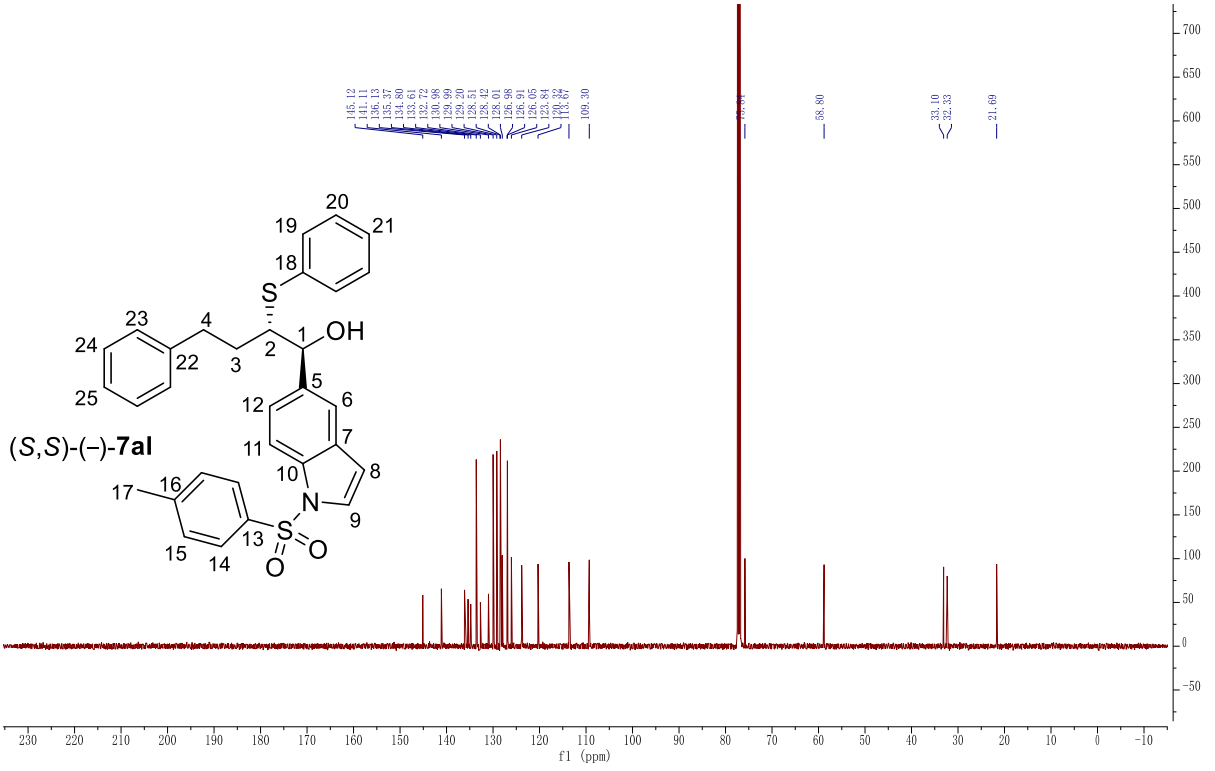


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.977	VV	0.6365	9.46292e4	2147.19995	98.2510
2	29.125	VB	0.8882	1684.48413	27.10070	1.7490

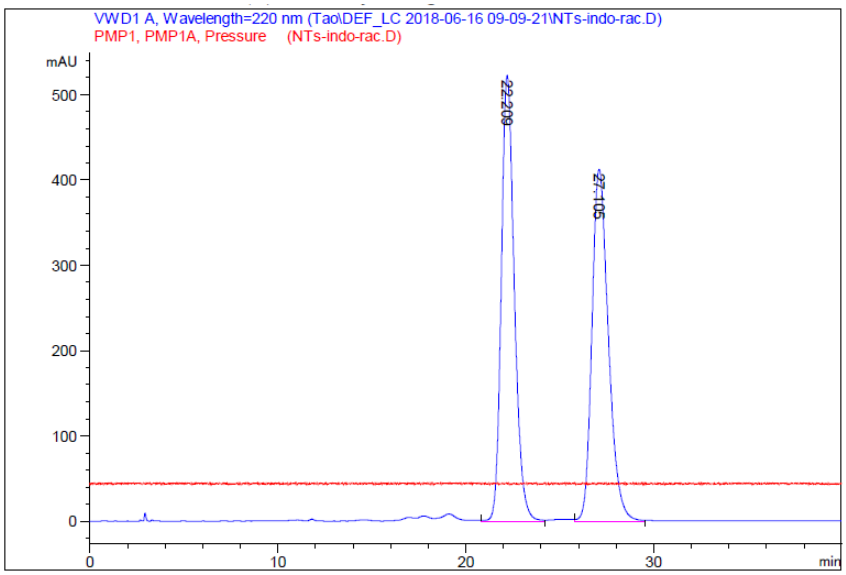
(1*S*,2*S*)-(–)-**7al** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7al** ^{13}C NMR (126 MHz, $CDCl_3$)

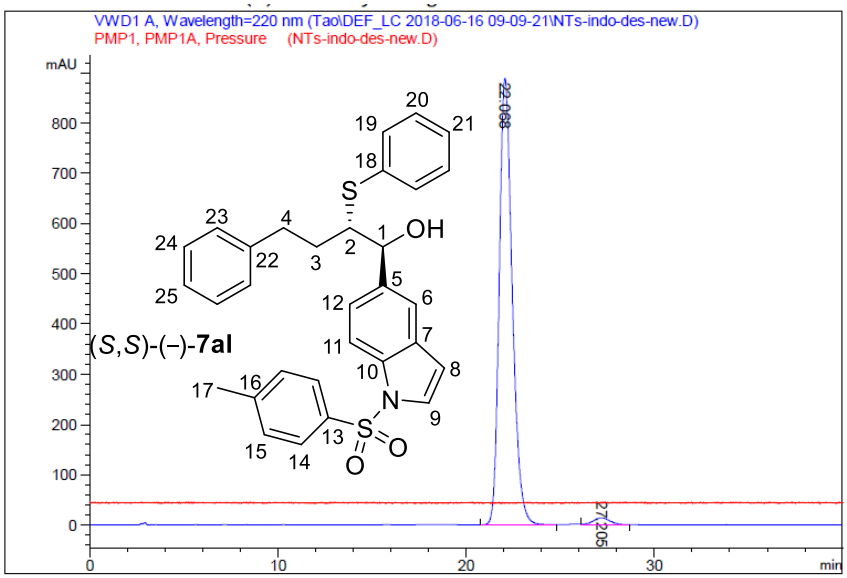


(±)-**7al**



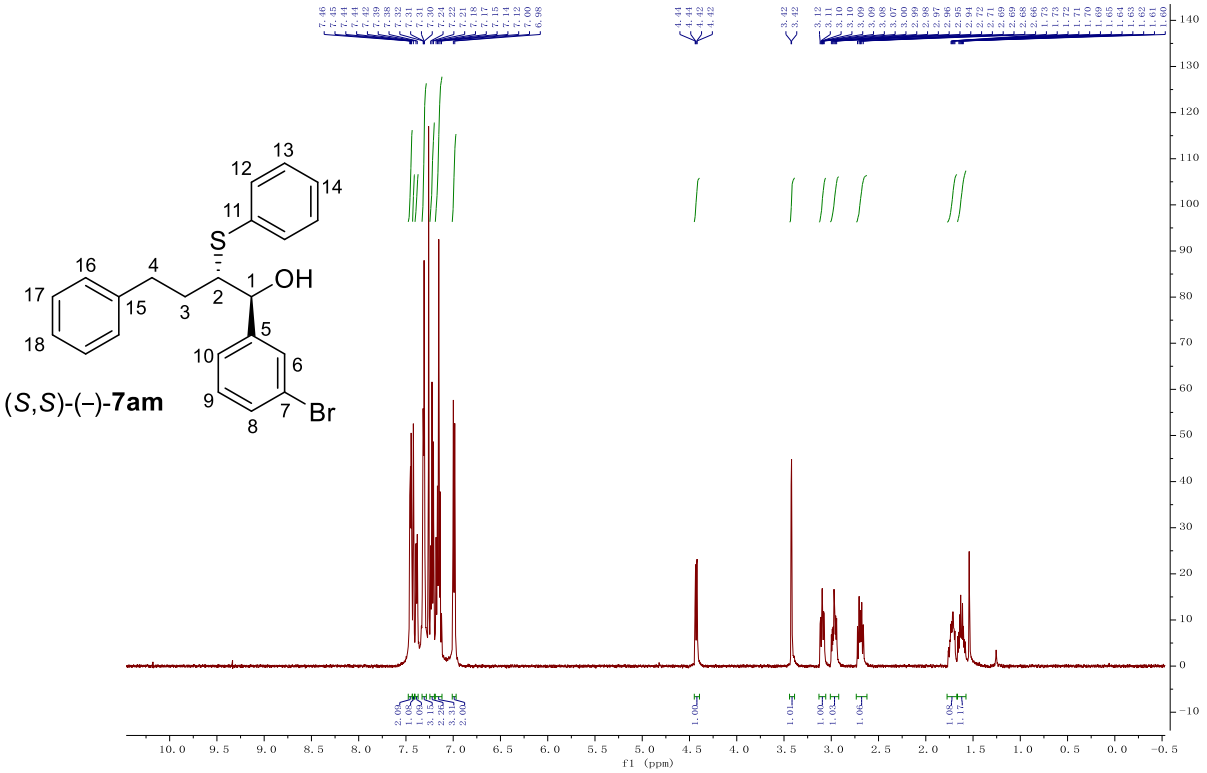
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.209	VV	0.7442	2.52368e4	522.37842	50.1089
2	27.105	VV	0.9143	2.51272e4	412.64096	49.8911

(1*S*,2*S*)-(–)-**7al**

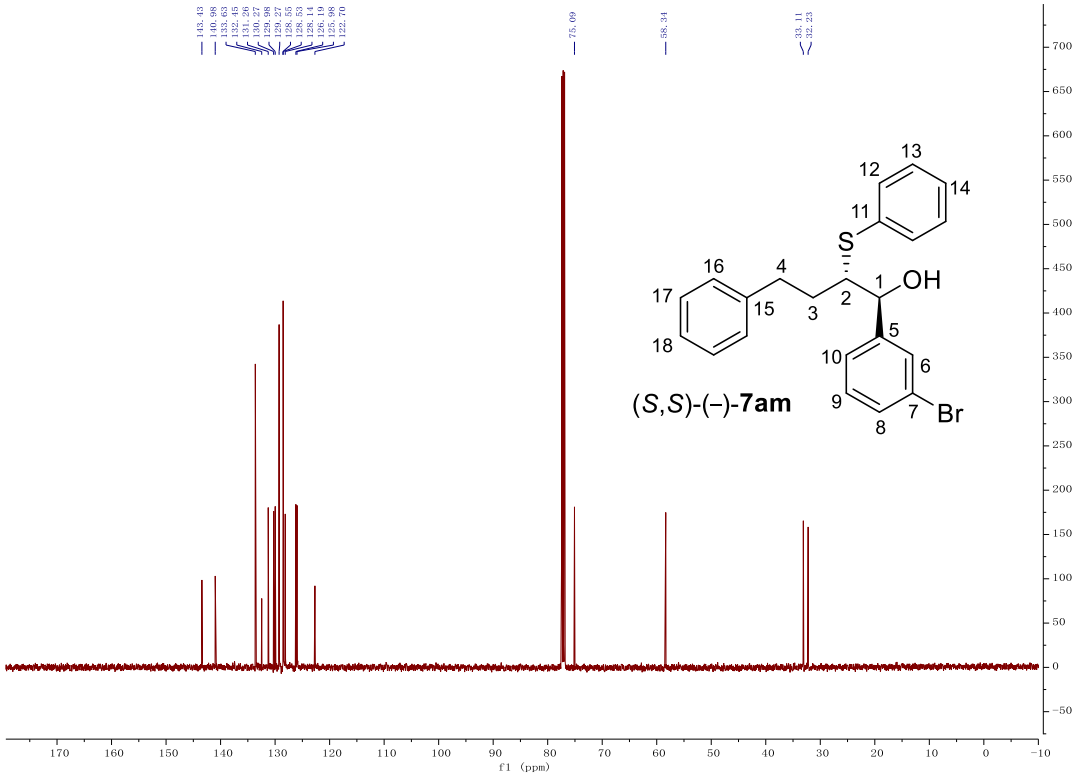


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.068	VV	0.7361	4.28058e4	889.57593	97.8795
2	27.205	VV	0.9758	927.36139	14.45214	2.1205

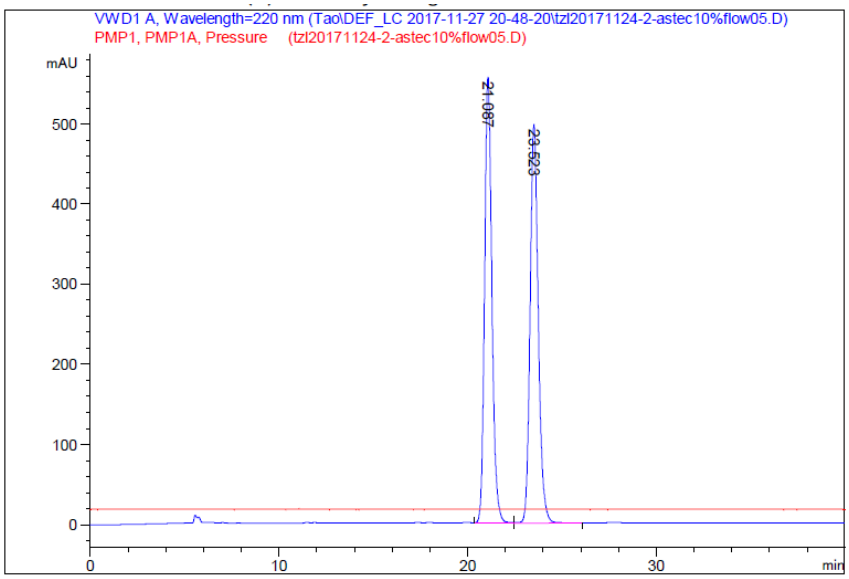
(1*S*,2*S*)-(–)-**7am** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7am** ^{13}C NMR (126 MHz, $CDCl_3$)

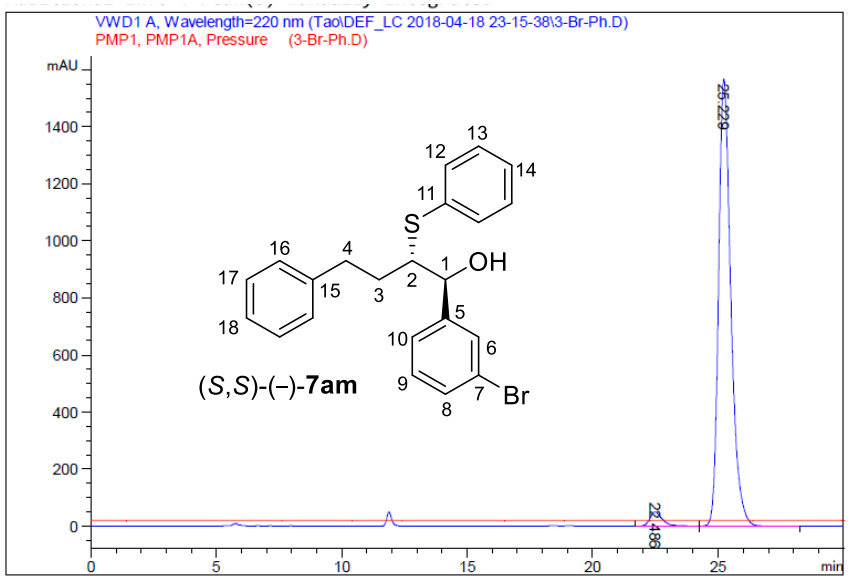


(±)-**7am**



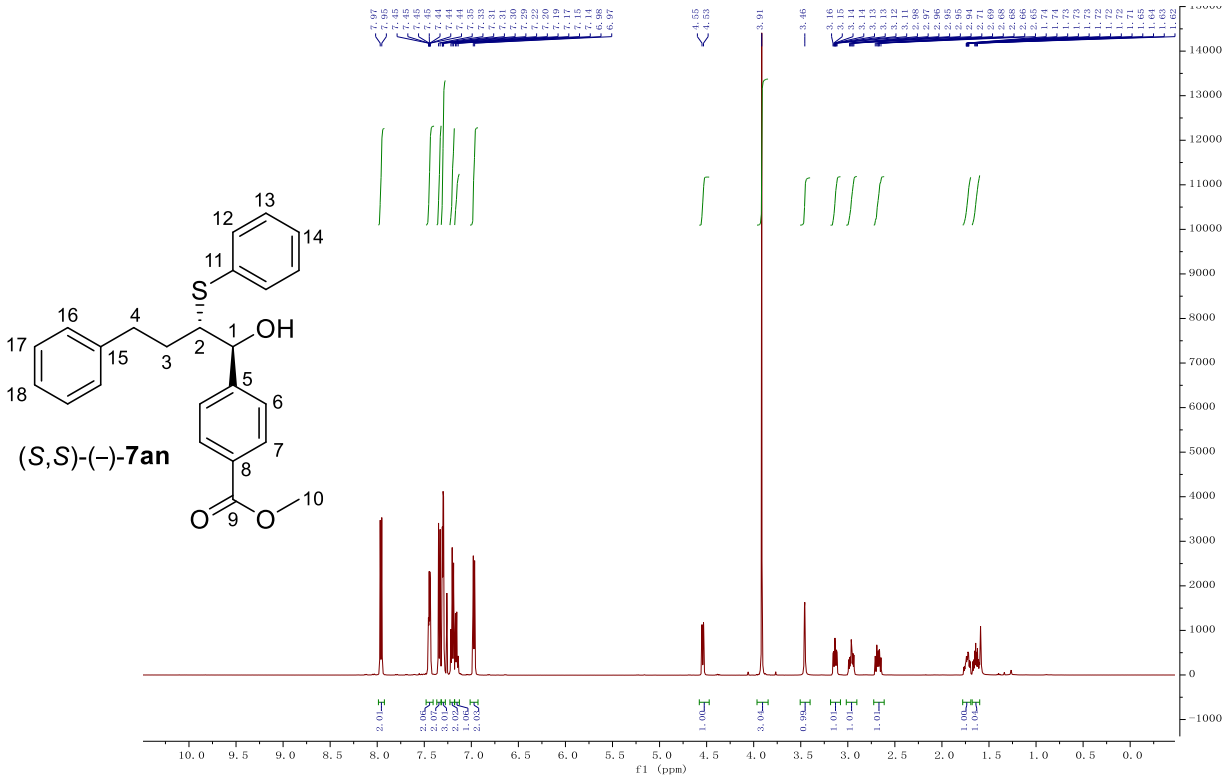
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.087	VV	0.4135	1.49957e4	556.37280	50.0056
2	23.523	VB	0.4628	1.49923e4	496.67096	49.9944

(1*S*,2*S*)-(–)-**7am**

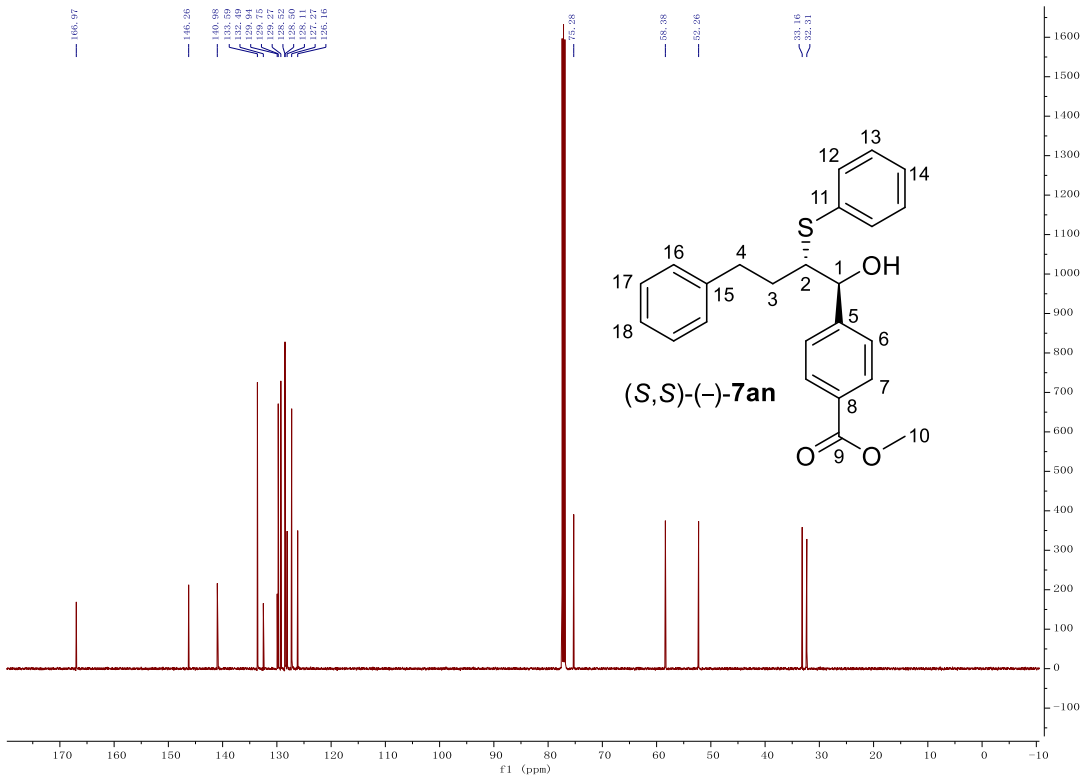


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.486	VV	0.5091	1738.37292	50.17261	3.1500
2	25.229	VB	0.5262	5.34483e4	1566.61670	96.8500

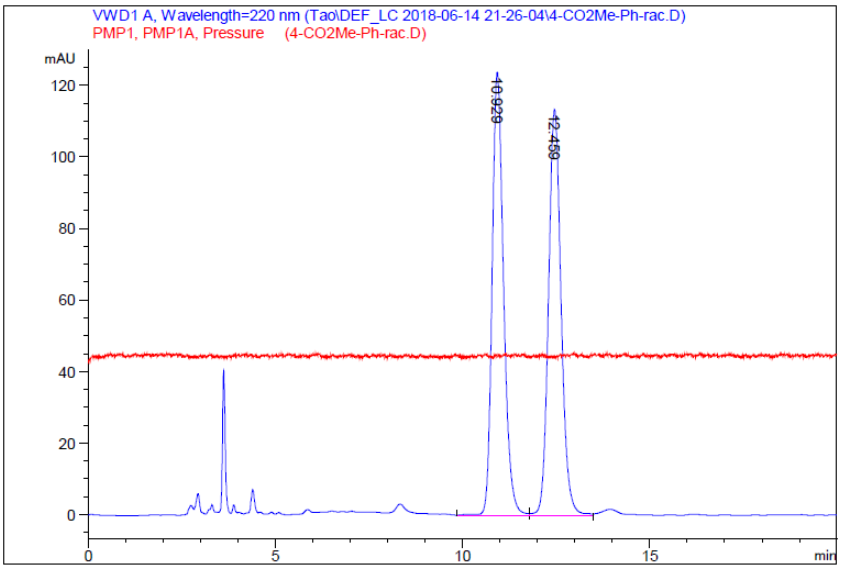
(1*S*,2*S*)-(–)-**7an** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7an** ^{13}C NMR (126 MHz, $CDCl_3$)

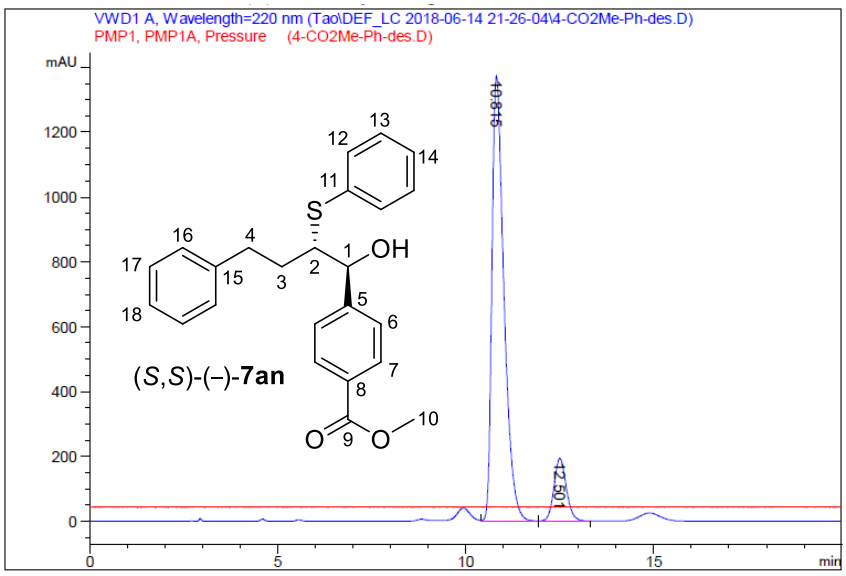


(±)-**7an**



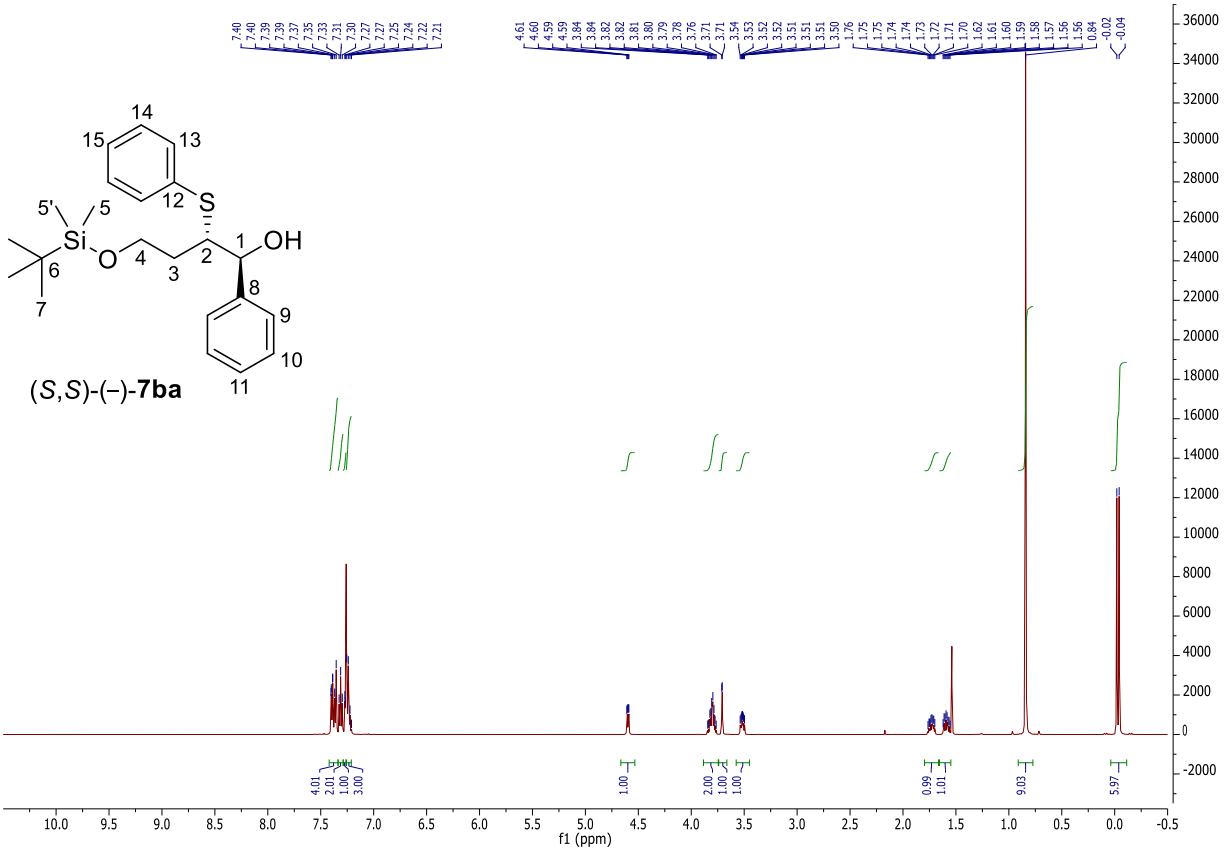
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.929	VV	0.3306	2639.82178	123.63731	49.8346
2	12.459	VV	0.3609	2657.34497	113.34393	50.1654

(1*S*,2*S*)-(–)-**7an**

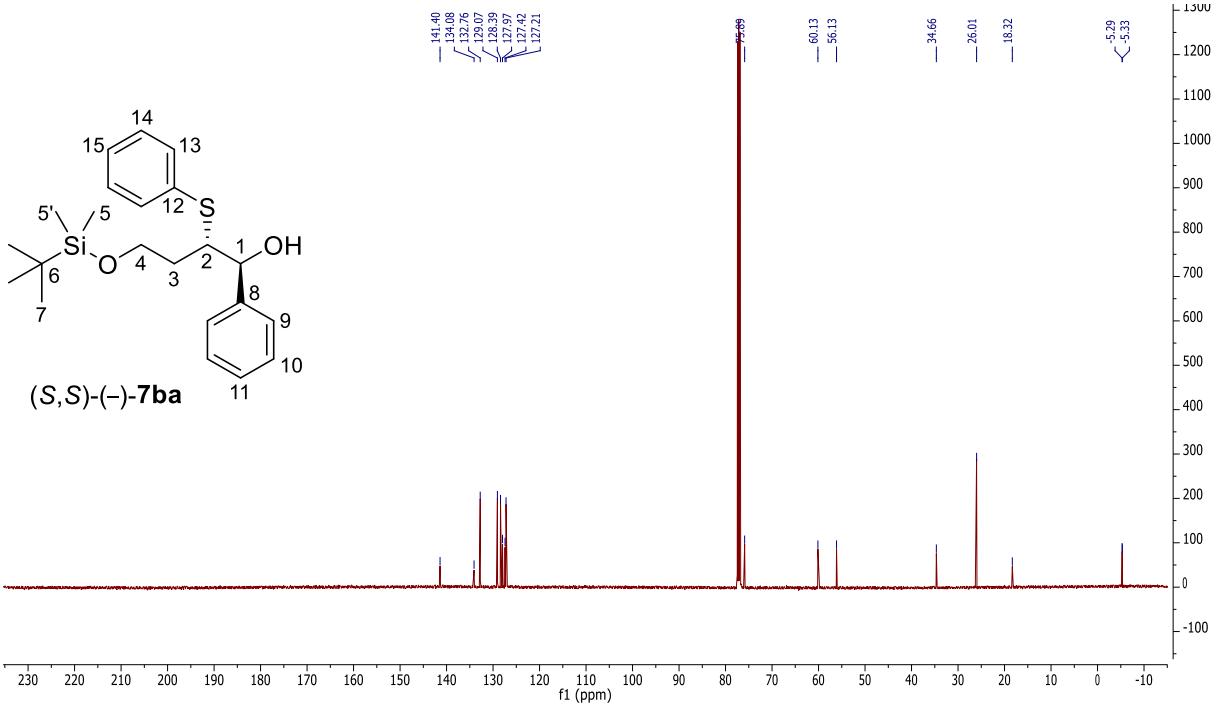


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.815	VV	0.3361	3.06495e4	1373.04602	87.2168
2	12.501	VV	0.3520	4492.22461	193.80582	12.7832

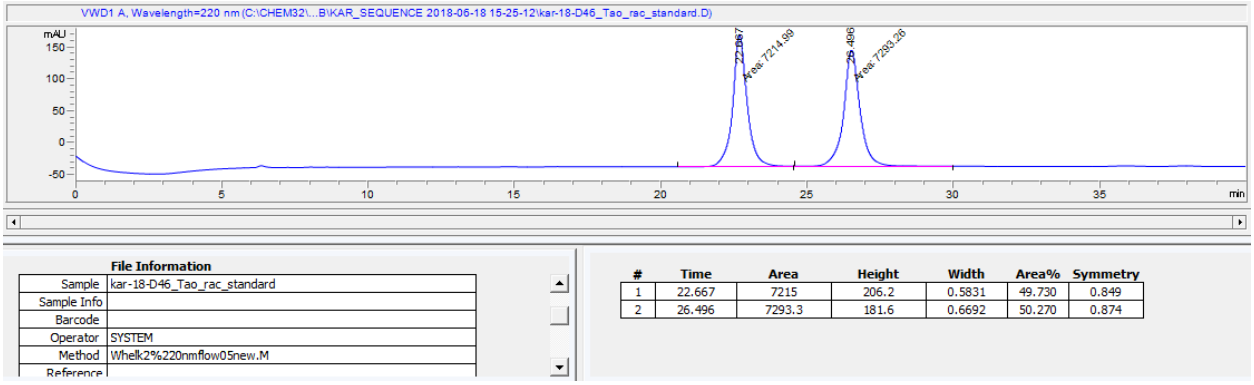
(1*S*,2*S*)-(–)-**7ba** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7ba** ^{13}C NMR (126 MHz, $CDCl_3$)



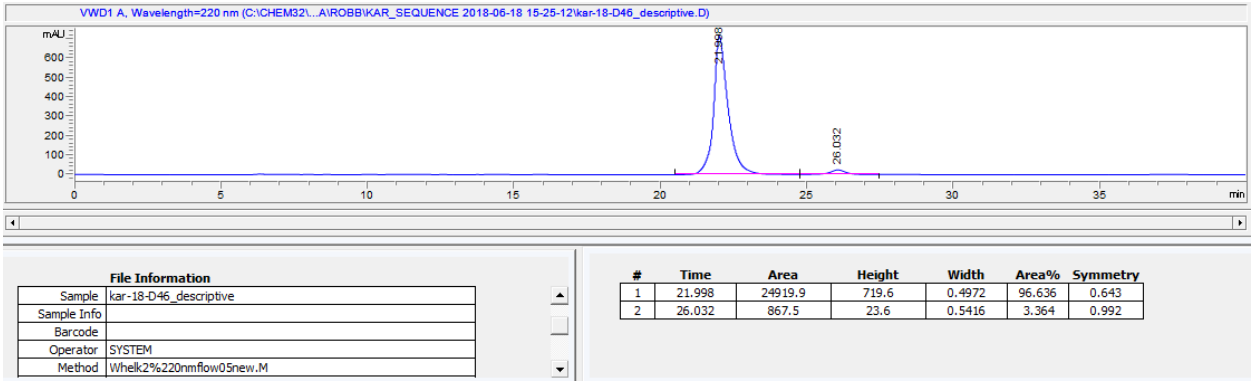
(±)-**7ba**



File Information	
Sample	kar-18-D46_Tao_rac_standard
Sample Info	
Barcode	
Operator	SYSTEM
Method	Whelk2%220nmflow05new.M
Reference	

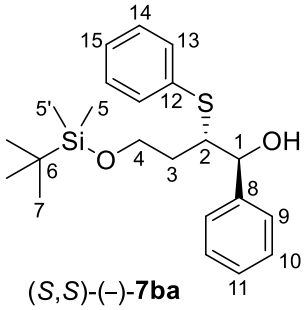
#	Time	Area	Height	Width	Area%	Symmetry
1	22.667	7215	206.2	0.5831	49.730	0.849
2	26.496	7293.3	181.6	0.6692	50.270	0.874

(1*S*,2*S*)-(–)-**7ba**



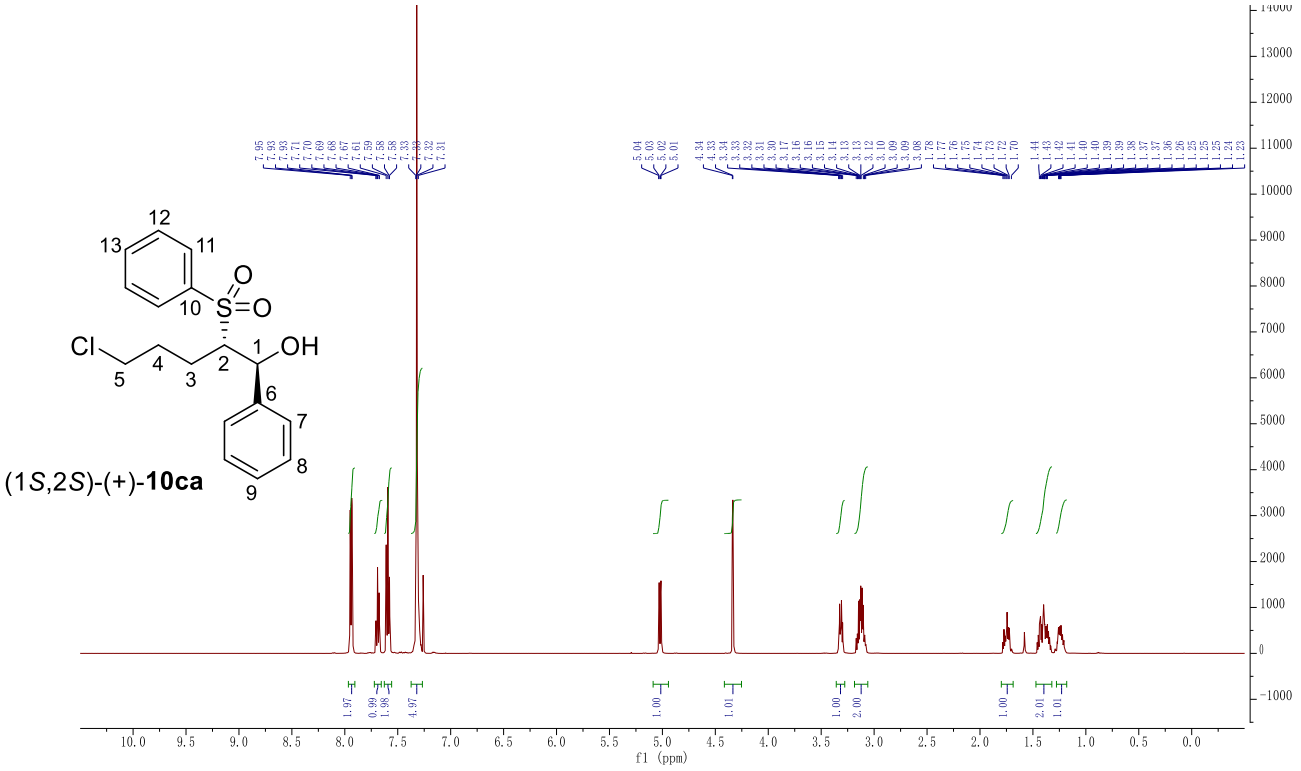
File Information	
Sample	kar-18-D46_descriptive
Sample Info	
Barcode	
Operator	SYSTEM
Method	Whelk2%220nmflow05new.M

#	Time	Area	Height	Width	Area%	Symmetry
1	21.998	24919.9	719.6	0.4972	96.636	0.643
2	26.032	867.5	23.6	0.5416	3.364	0.992

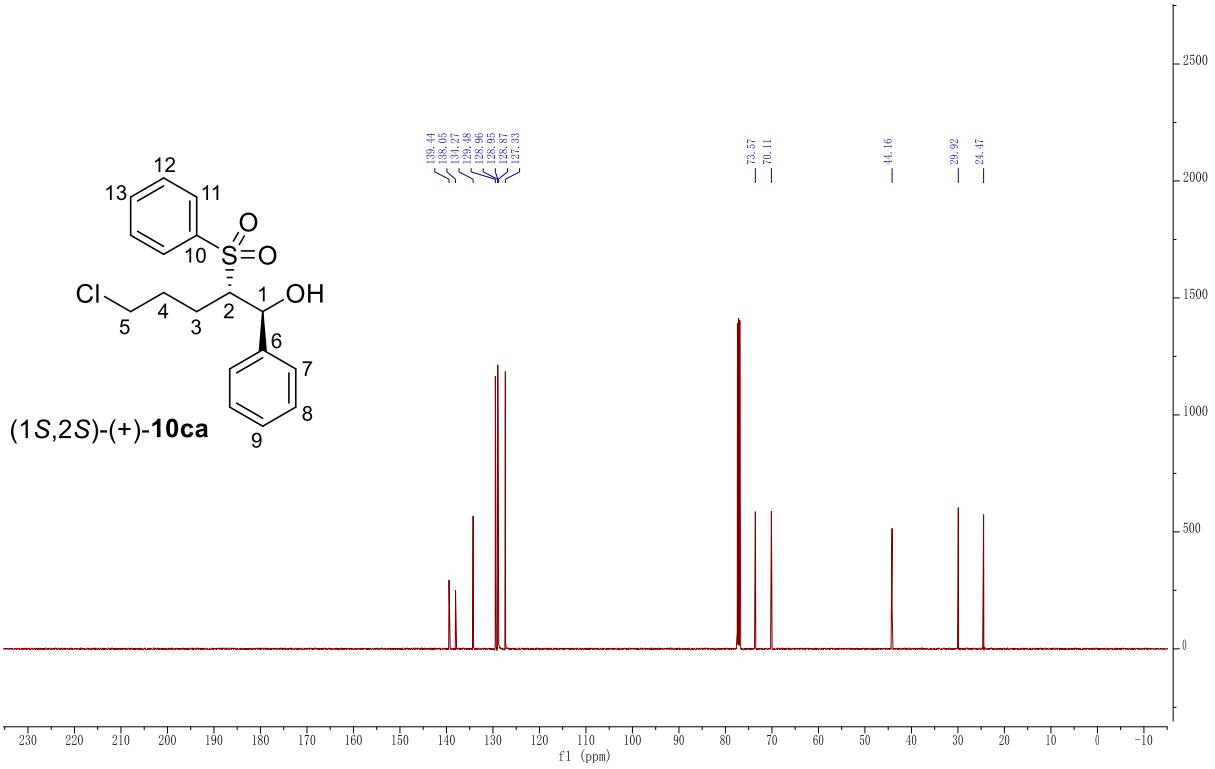


(*S*,*S*)-(–)-**7ba**

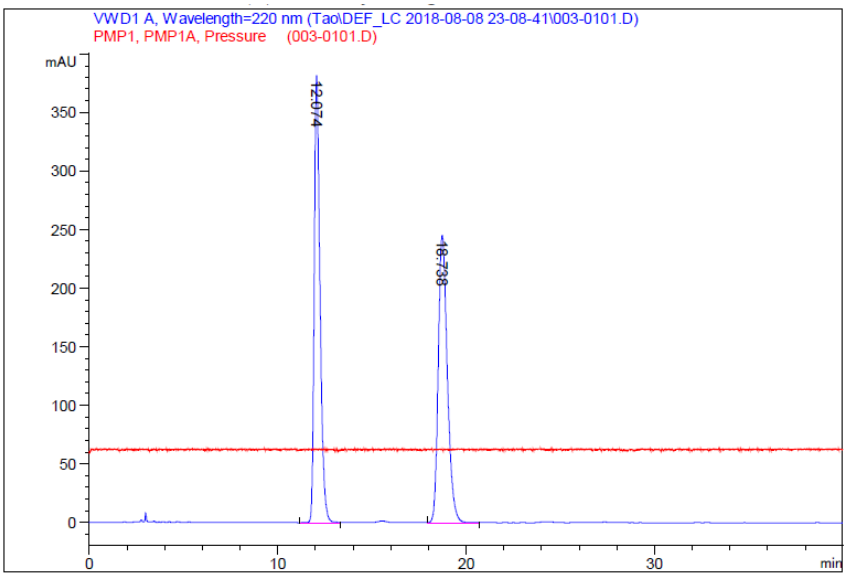
(1*S*,2*S*)-(+)-**10ca** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(+)-**10ca** ^{13}C NMR (126 MHz, $CDCl_3$)

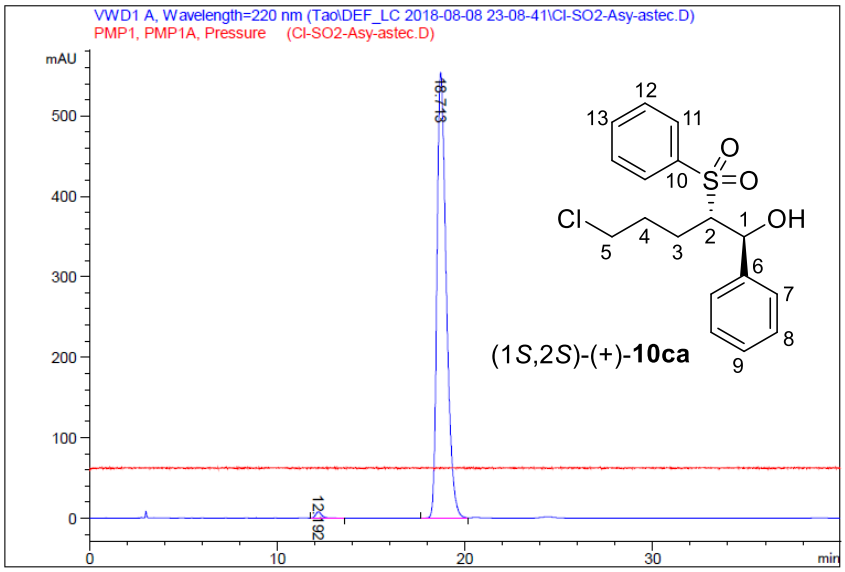


(±)-**10ca**



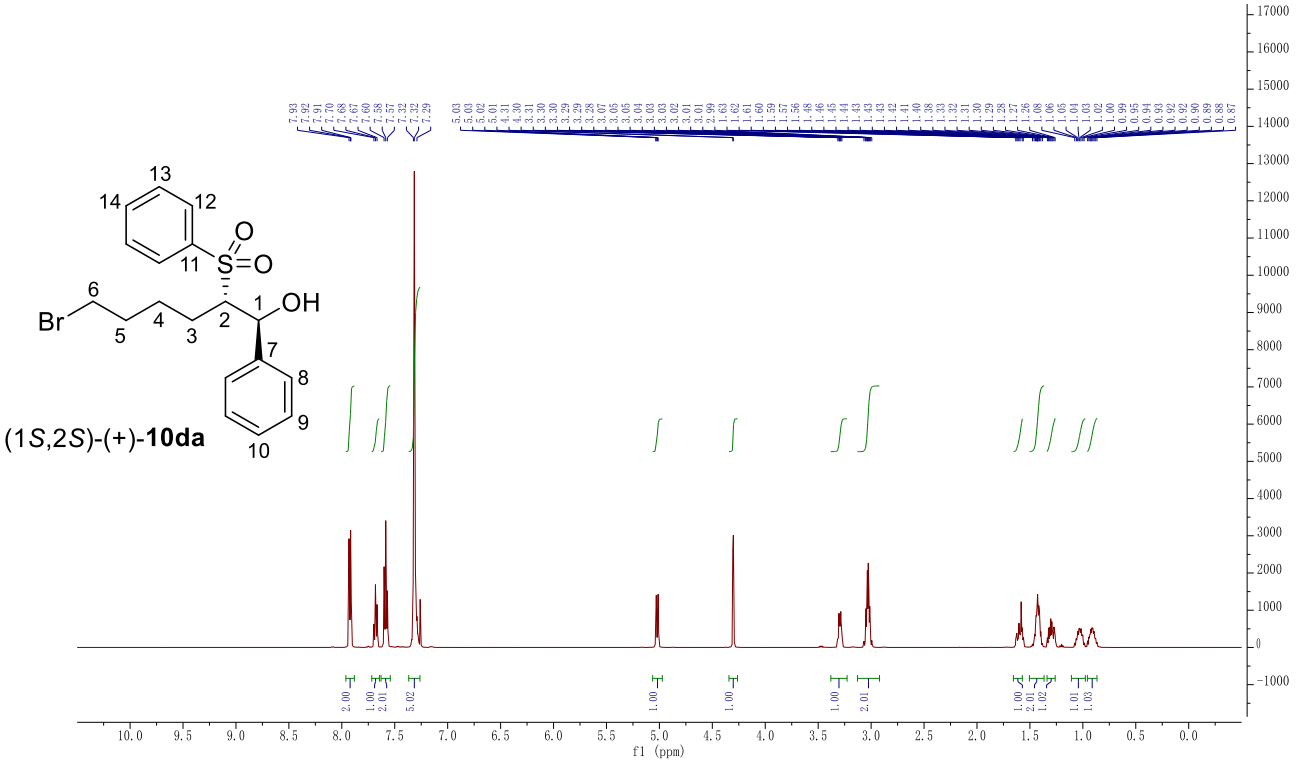
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.074	VV	0.3260	8181.15381	381.36618	49.8064
2	18.738	VV	0.5140	8244.76563	245.59296	50.1936

(1*S*,2*S*)-(+)-**10ca**

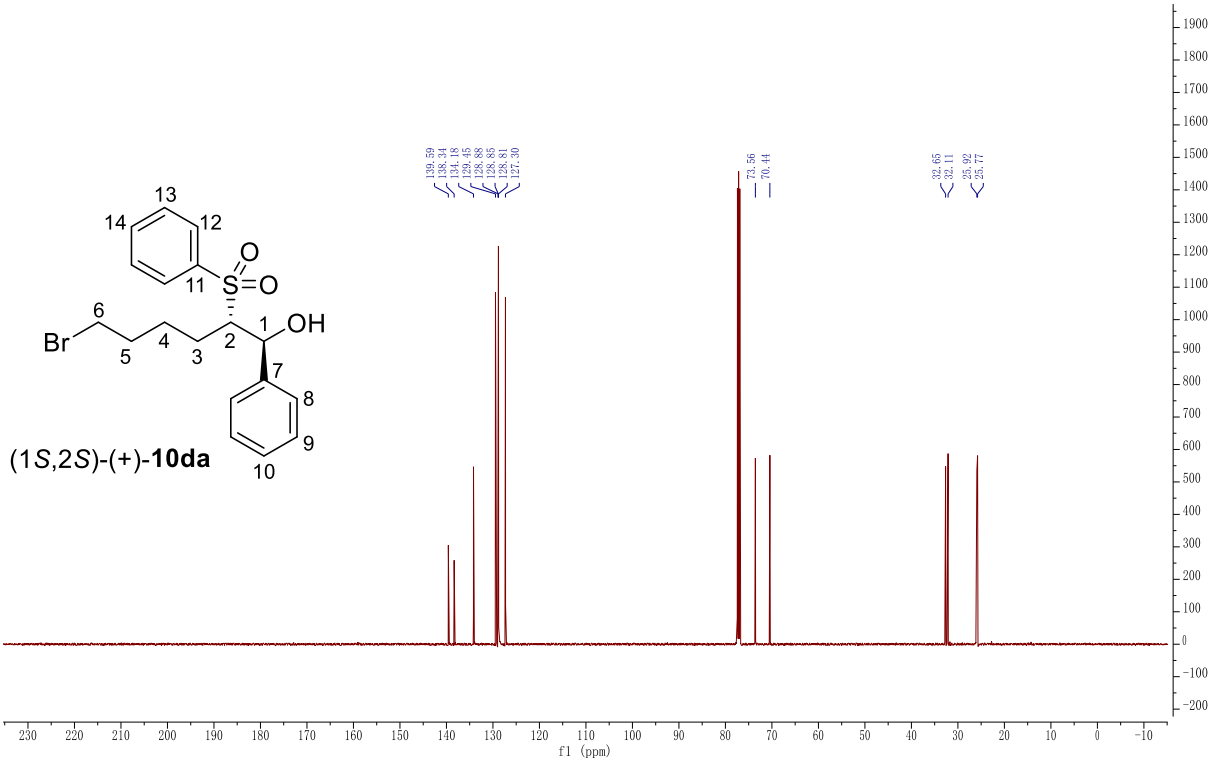


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.192	VV	0.3588	193.58862	8.14644	0.9961
2	18.713	VV	0.5334	1.92406e4	553.92914	99.0039

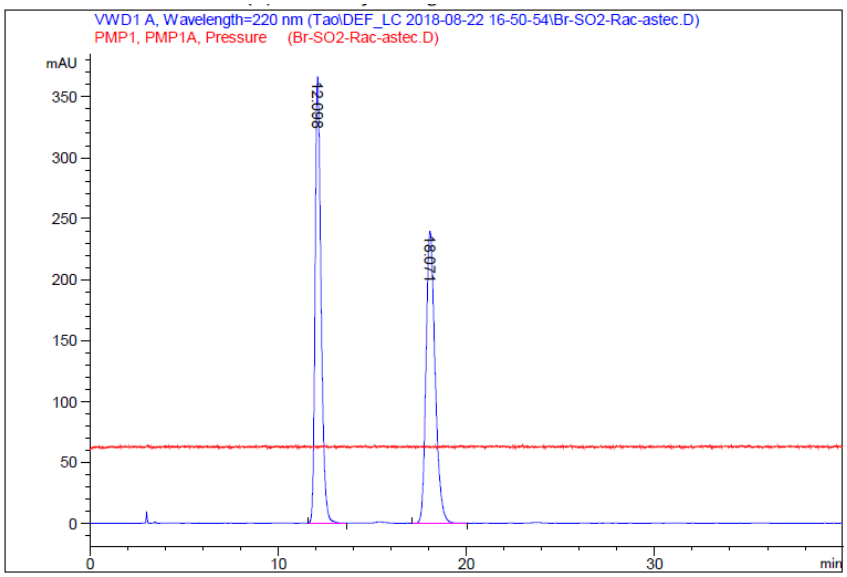
(1*S*,2*S*)-(+)-**10da** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(+)-**10da** ^{13}C NMR (126 MHz, $CDCl_3$)

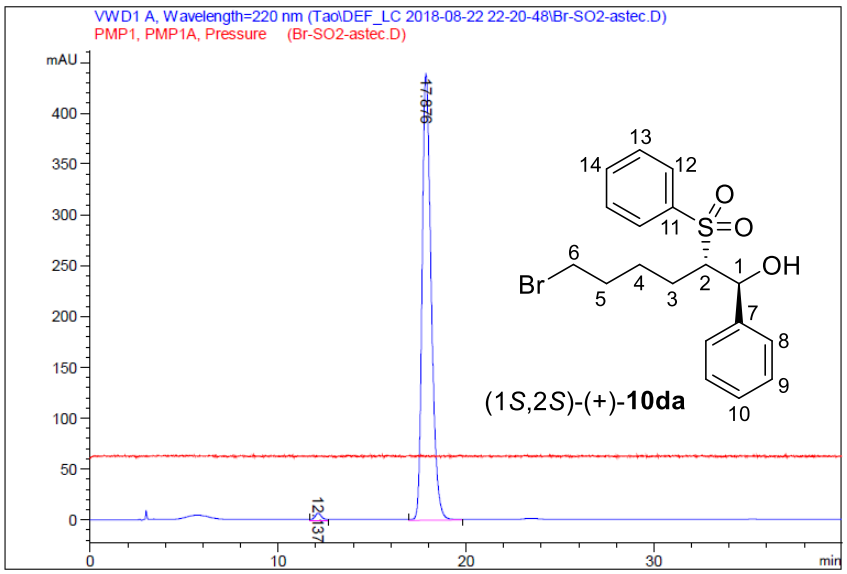


(±)-**10da**



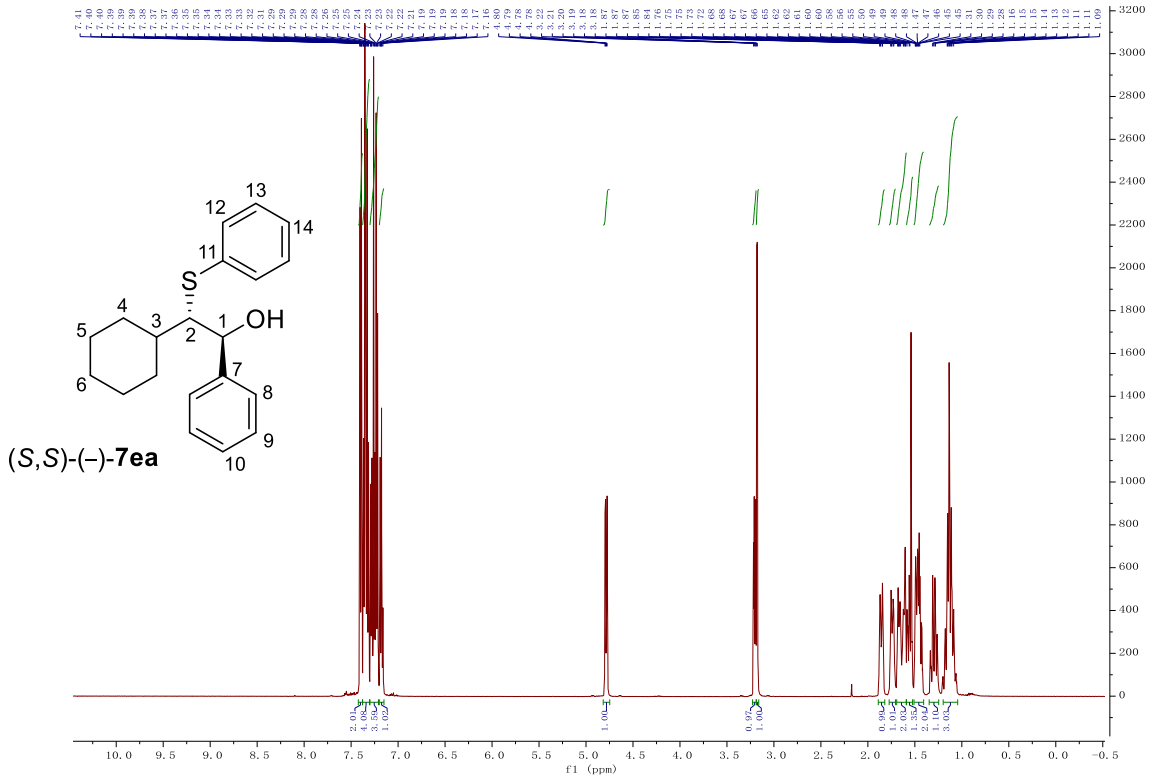
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.098	VV	0.3340	8101.03955	365.97867	50.0447
2	18.071	VB	0.5219	8086.55176	239.56184	49.9553

(1*S*,2*S*)-(+)-**10da**

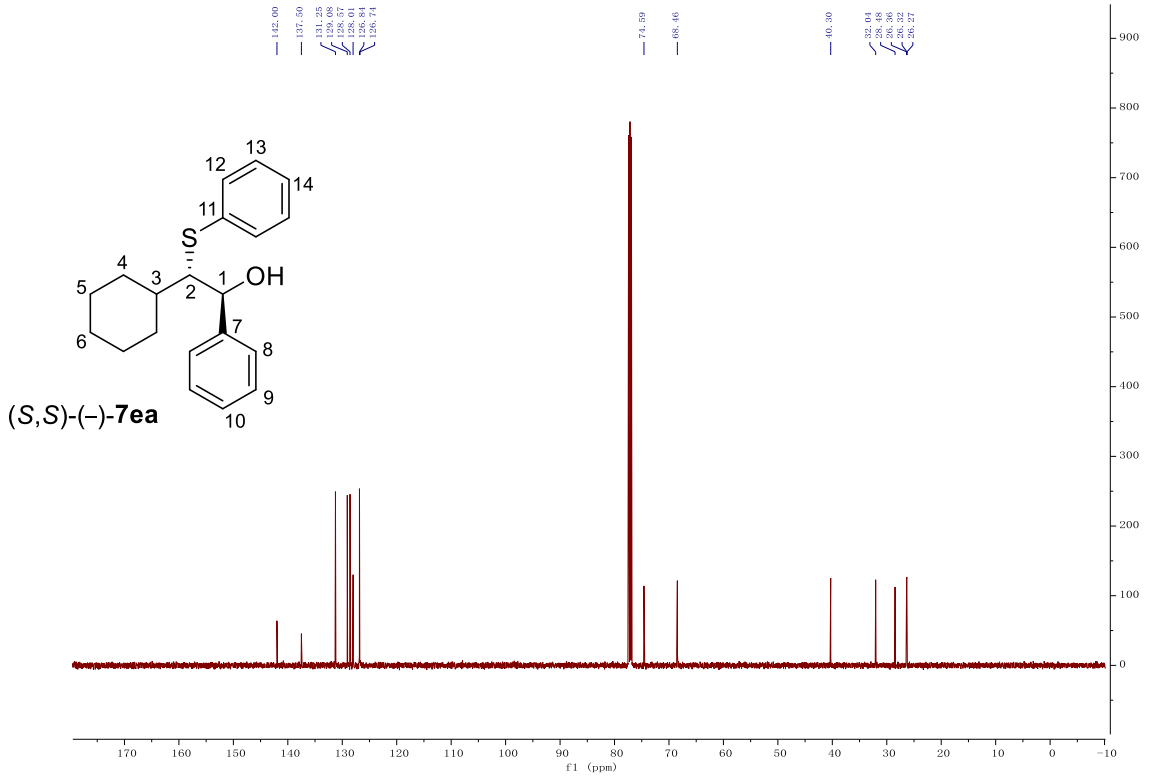


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.137	VV	0.3803	179.01158	6.99122	1.1941
2	17.876	VV	0.5155	1.48117e4	439.45715	98.8059

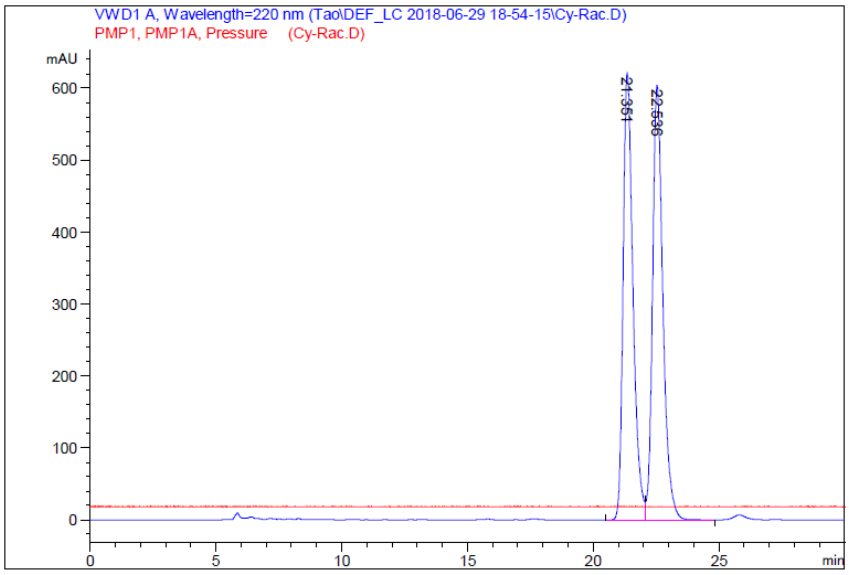
(1*S*,2*S*)-(–)-**7ea** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-(–)-**7ea** ^{13}C NMR (126 MHz, $CDCl_3$)

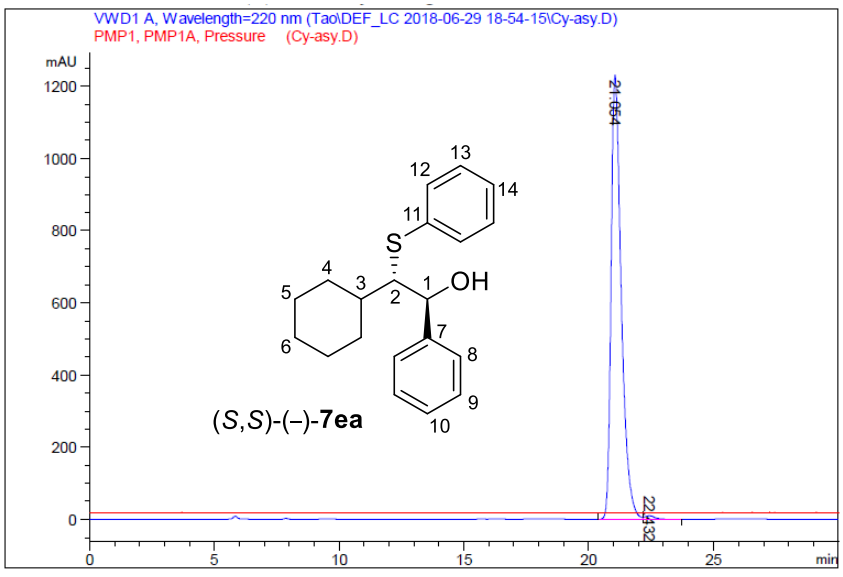


(±)-**7ea**



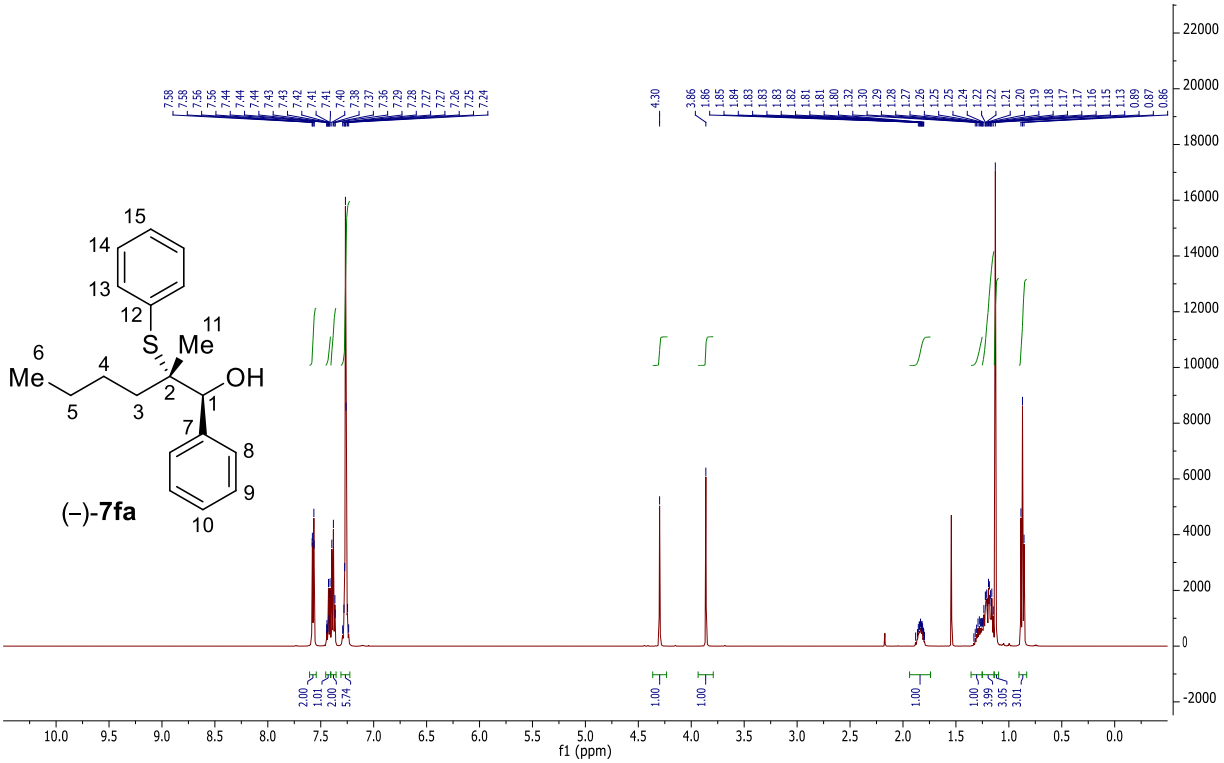
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.351	VV	0.4110	1.69325e4	621.57770	49.5430
2	22.536	VB	0.4380	1.72449e4	603.93933	50.4570

(1*S*,2*S*)-(–)-**7ea**

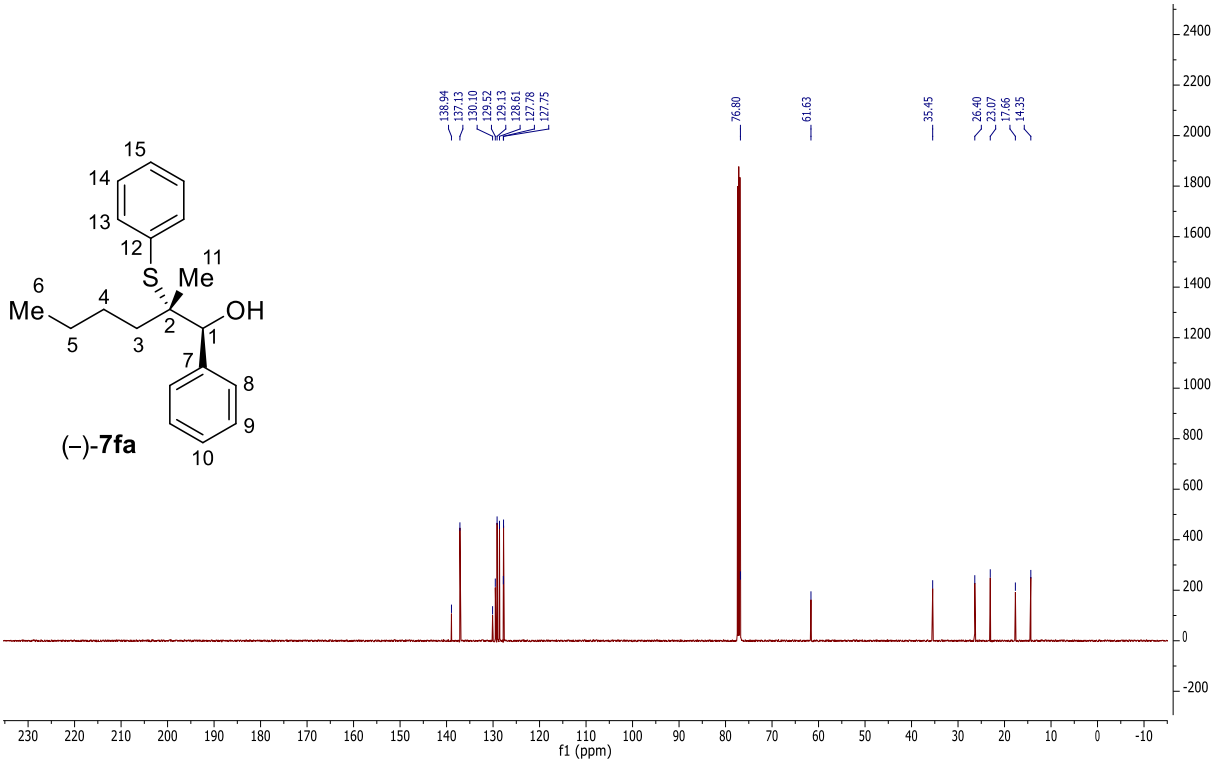


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.054	BV	0.4238	3.48666e4	1230.51086	99.1498
2	22.432	VV	0.4345	298.98199	10.04859	0.8502

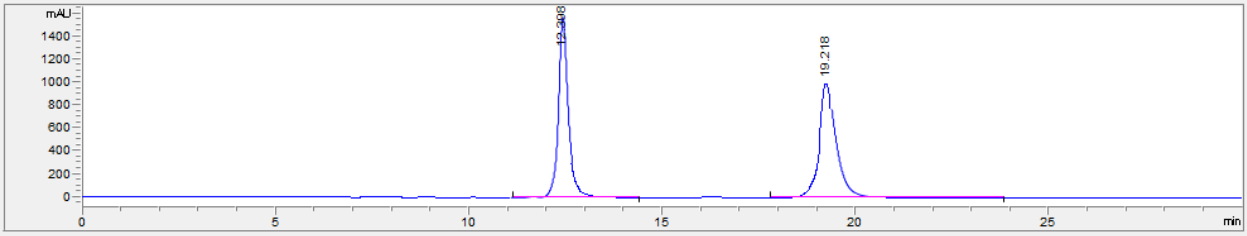
(–)-**7fa** ^{1}H NMR (500 MHz, $CDCl_3$)



(–)-**7fa** ^{13}C NMR (126 MHz, $CDCl_3$)



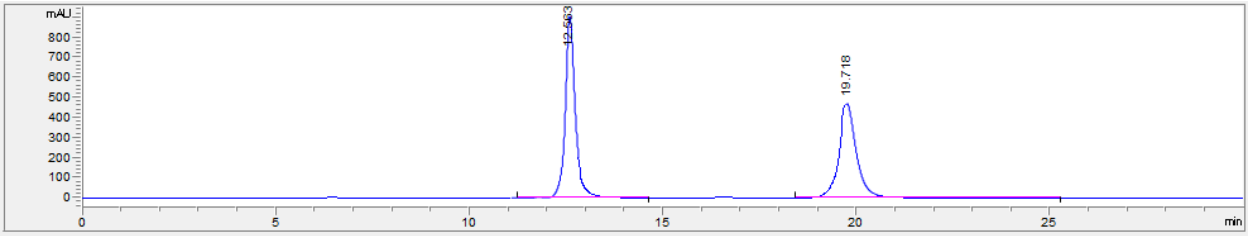
(±)-7fa



File Information	
Date	31-Jul-18, 17:14:57
Sample	KAR-2018-014_Whelk05point5
Sample Info	
Barcode	
Operator	SYSTEM
Method	Whelk5%220nmflow05new.M

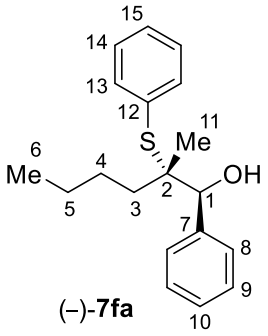
#	Time	Area	Height	Width	Area%	Symmetry
1	12.398	28891	1583.5	0.2656	49.773	0.767
2	19.218	29154	998	0.4209	50.227	0.67

(–)-7fa



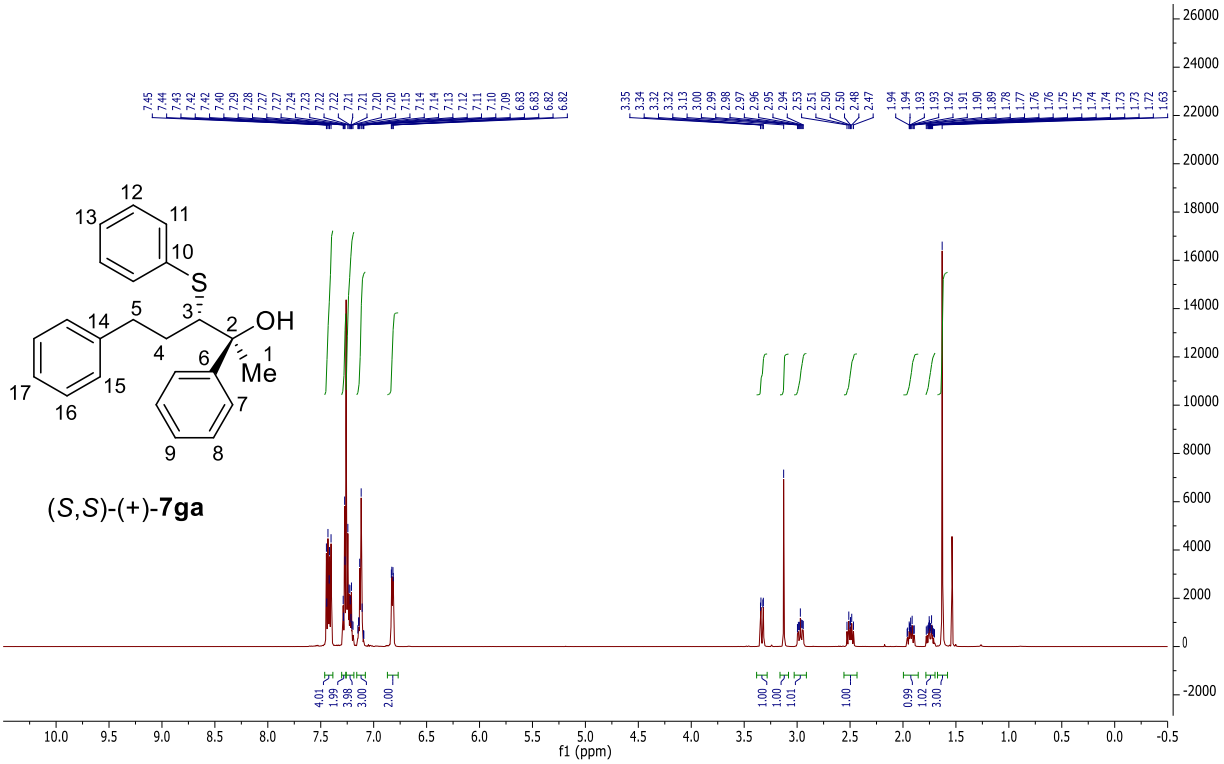
File Information	
Date	01-Aug-18, 09:32:54
Sample	KAR-18-D81_Descriptive_3
Sample Info	
Barcode	
Operator	SYSTEM
Method	Whelk5%220nmflow05new.M

#	Time	Area	Height	Width	Area%	Symmetry
1	12.563	16604.3	905.6	0.267	54.171	0.788
2	19.718	14047.4	472.6	0.4312	45.829	0.744

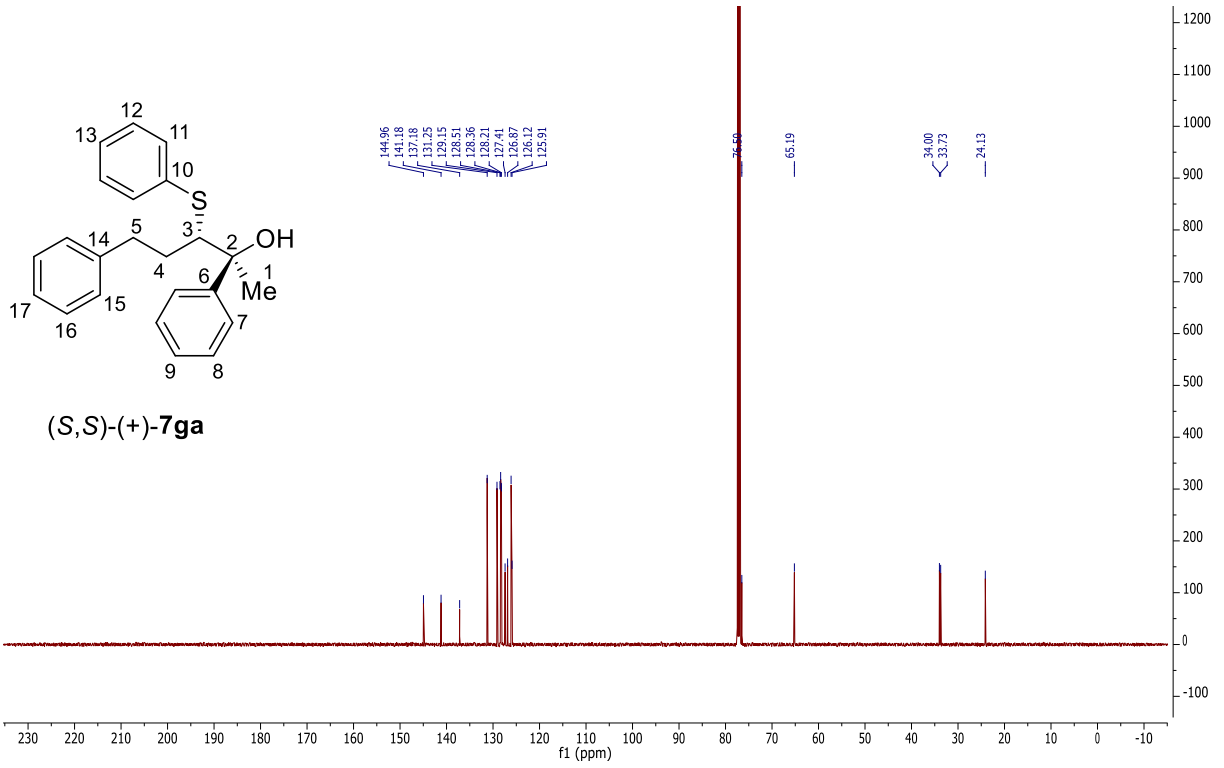


(–)-7fa

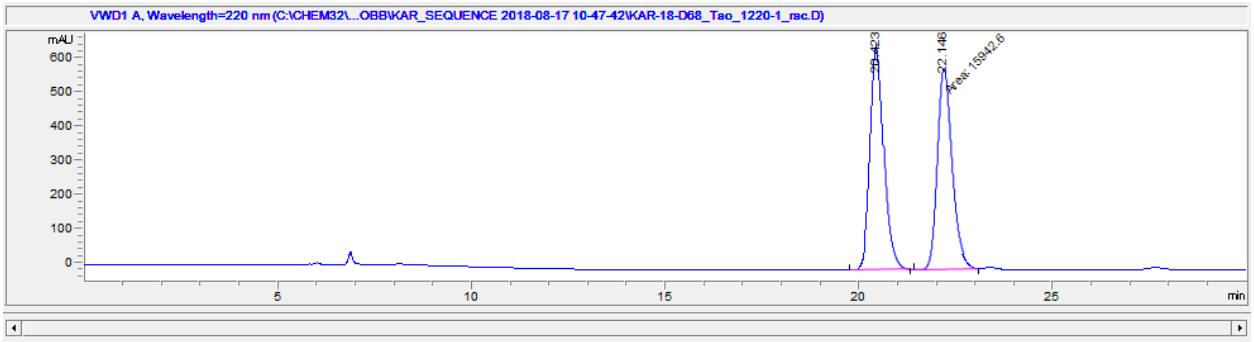
(2*S*,3*S*)-(+)-**7ga** ^{1}H NMR (500 MHz, $CDCl_3$)



(2*S*,3*S*)-(+)-**7ga** ^{13}C NMR (126 MHz, $CDCl_3$)



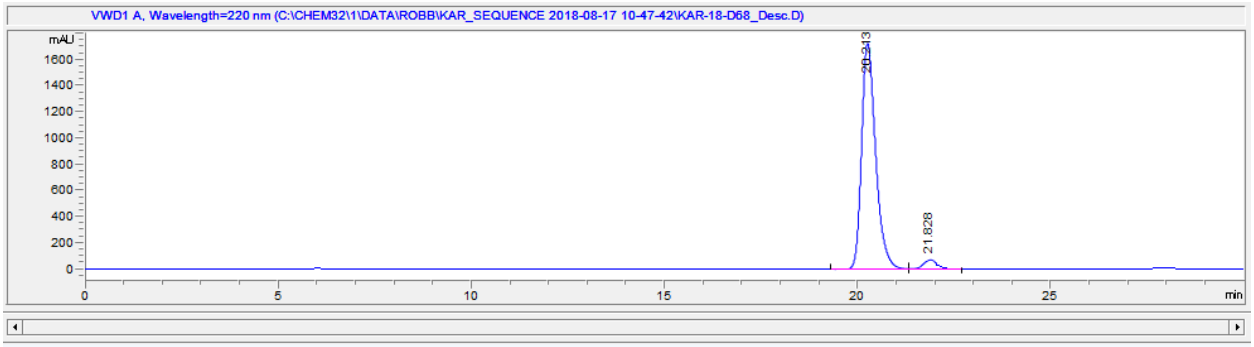
(±)-**7ga**



File Information	
File Path	C:\CHEM32\1\DATA\ROBB\KAR_SEQUENCE 2018-08-17 10-47-42
Date	17-Aug-18, 10:48:30
Sample	KAR-18-D68_Tao_1220-1_rac
Sample Info	
Barcode	
Operator	SYSTEM
Method	Astec-Cellulose-5%-220nmflow05.M

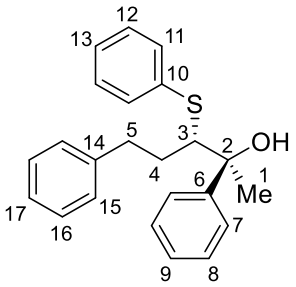
#	Time	Area	Height	Width	Area%	Symmetry
1	20.423	15707.8	660.1	0.3635	49.629	0.778
2	22.146	15942.6	592.3	0.4486	50.371	0.757

(2*S*,3*S*)-(+)-**7ga**



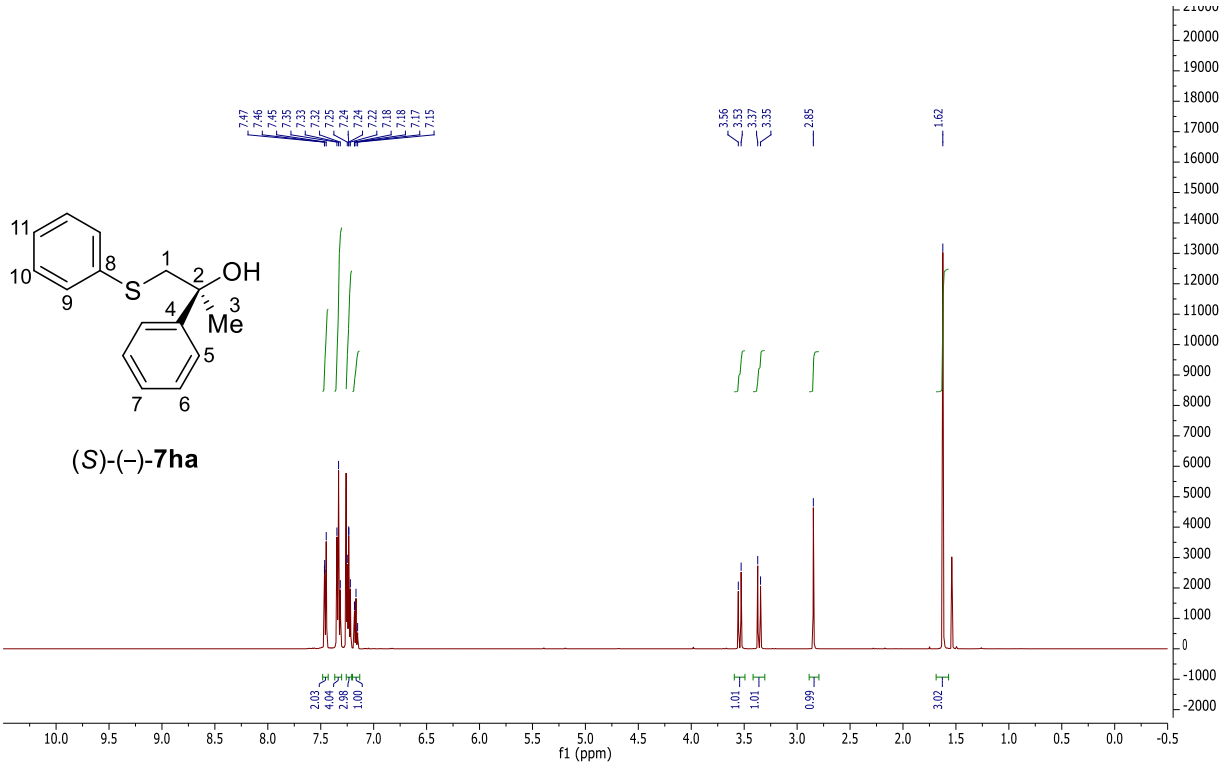
File Information	
File Path	C:\CHEM32\1\DATA\ROBB\KAR_SEQUENCE 2018-08-17 10-47-42
Date	17-Aug-18, 11:20:15
Sample	KAR-18-D68_Desc
Sample Info	
Barcode	
Operator	SYSTEM
Method	Astec-Cellulose-5%-220nmflow05.M

#	Time	Area	Height	Width	Area%	Symmetry
1	20.213	43309.5	1719.5	0.3856	95.829	0.694
2	21.828	1884.9	70.5	0.4065	4.171	0.844

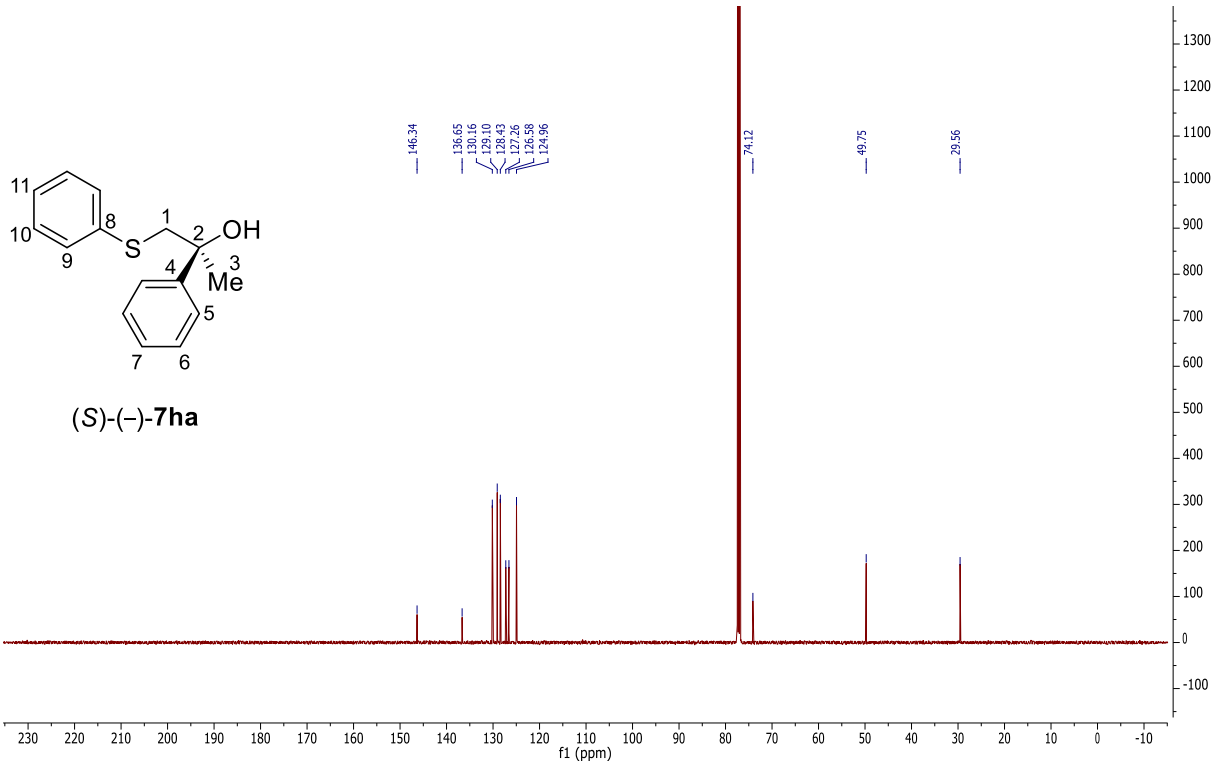


(*S*,*S*)-(+)-**7ga**

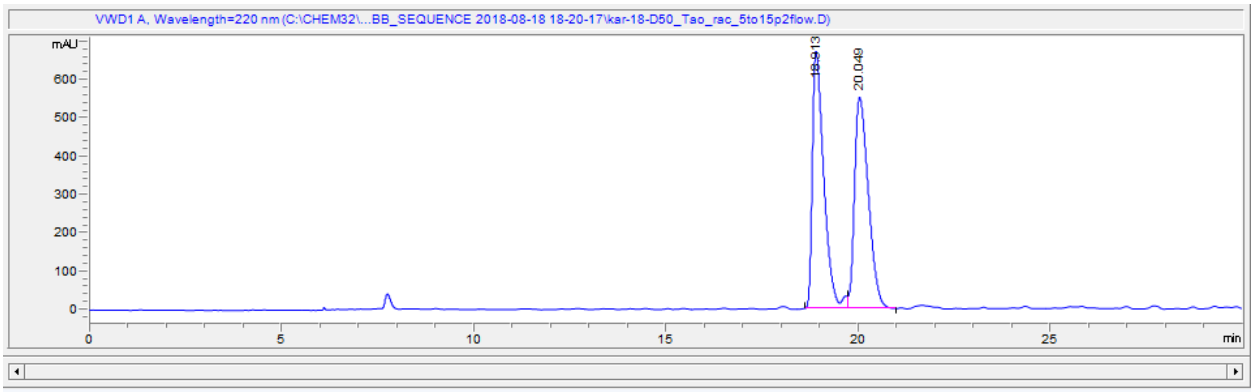
(*S*)-(–)-**7ha** ^{1}H NMR (500 MHz, $CDCl_3$)



(*S*)-(–)-**7ha** ^{13}C NMR (126 MHz, $CDCl_3$)



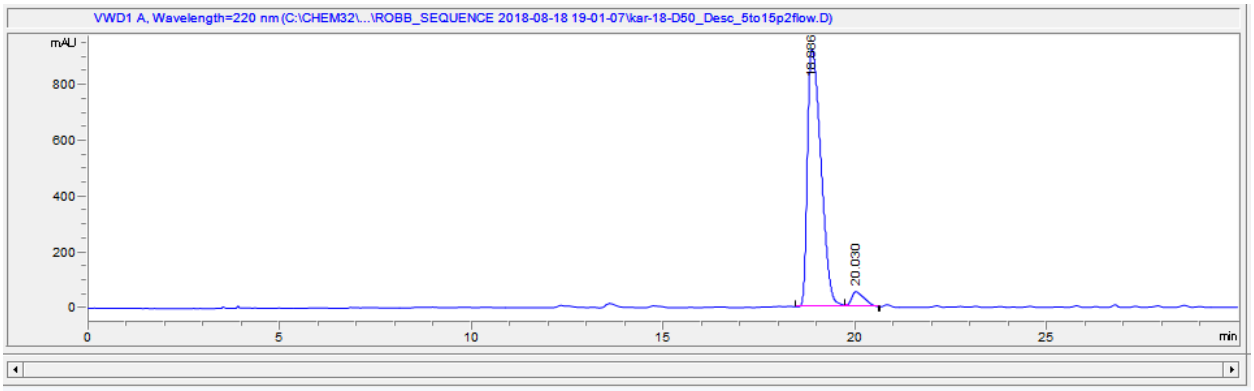
(±)-7ha



File Information	
Date	18-Aug-18, 18:23:23
Sample	kar-18-D50_Tao_rac_5to15p2flow
Sample Info	
Barcode	
Operator	SYSTEM
Method	OD_5to15%_2p0ml-min.M
Reference	

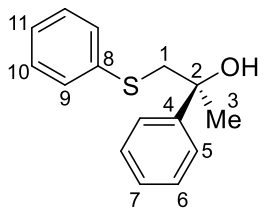
#	Time	Type	Area	Height	Width	Area%	Symm
1	18.913	BV R	13985.5	674.1	0.306	50.136	0.44
2	20.049	VB	13909.7	553.3	0.3879	49.864	0.56

(–)-7ha



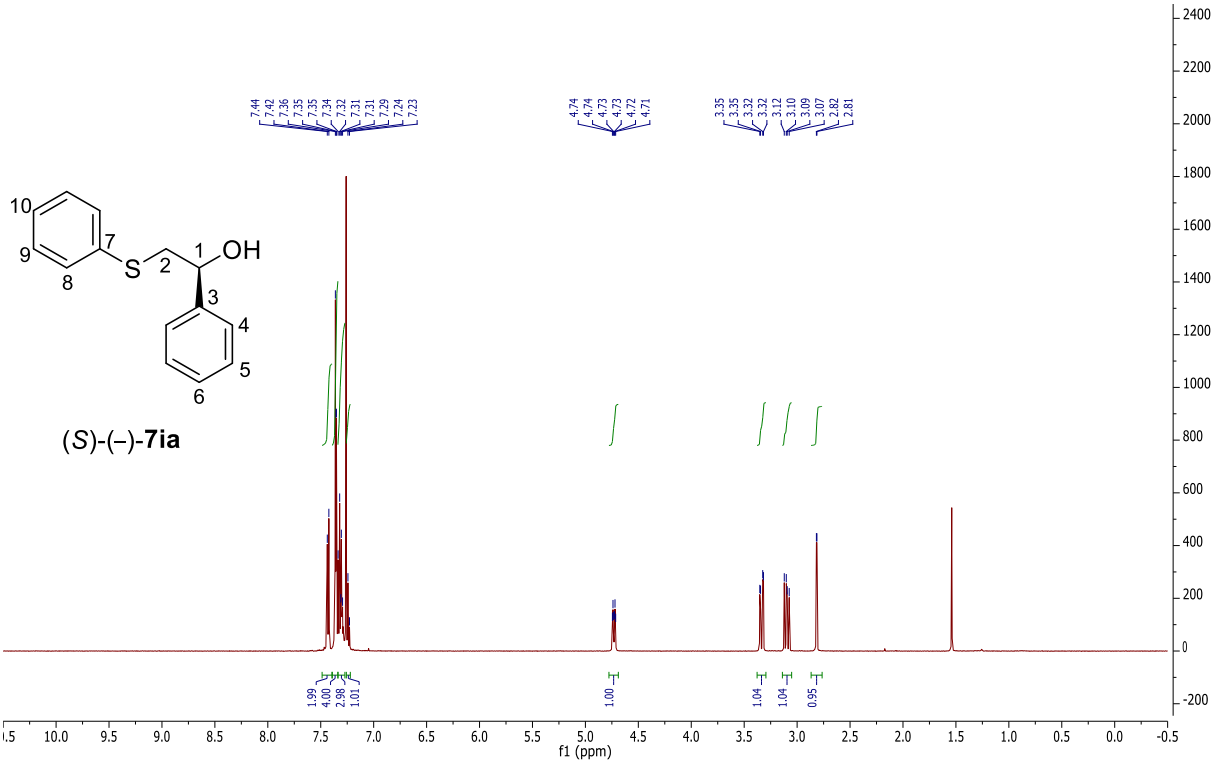
File Information	
Date	18-Aug-18, 19:04:19
Sample	kar-18-D50_Desc_5to15p2flow
Sample Info	
Barcode	
Operator	SYSTEM
Method	OD_5to15%_2p0ml-min.M

#	Time	Type	Area	Height	Width	Area%	Symm
1	18.886	BV R	22734	923.8	0.3978	94.927	0.47
2	20.03	VB E	1215	52.8	0.3251	5.073	0.47

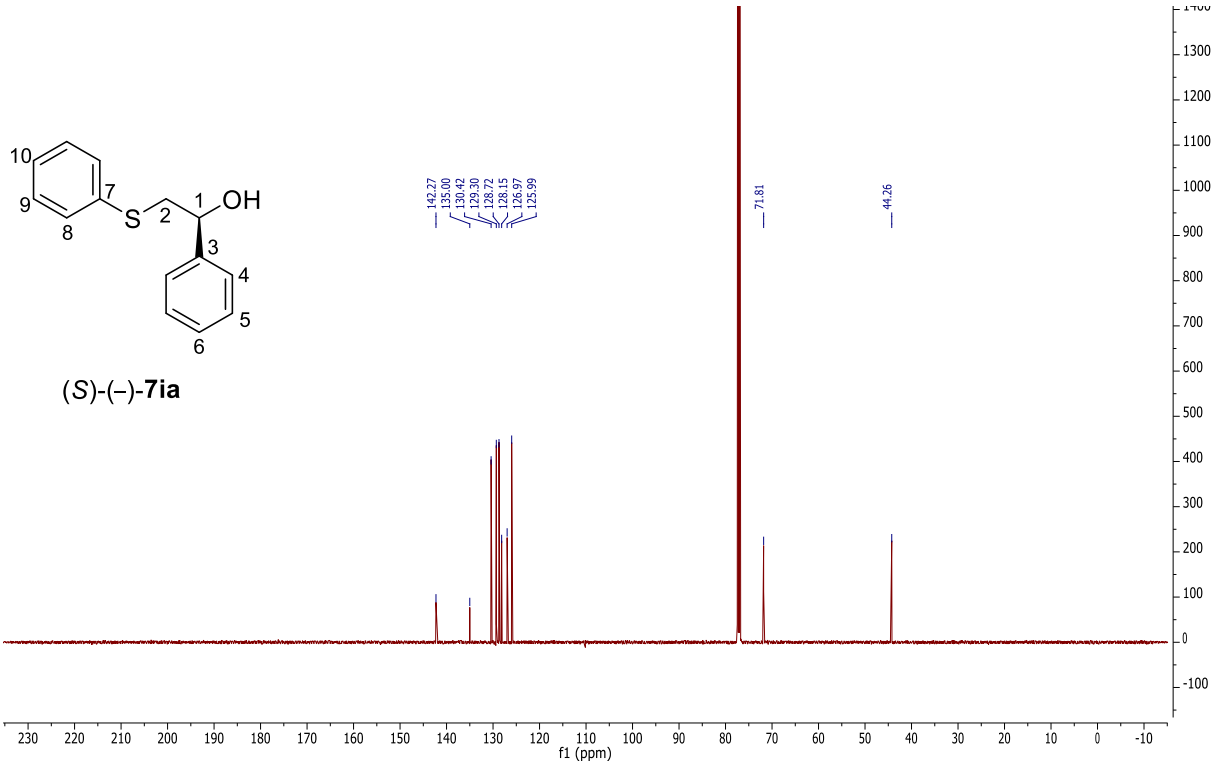


(*S*)-(–)-**7ha**

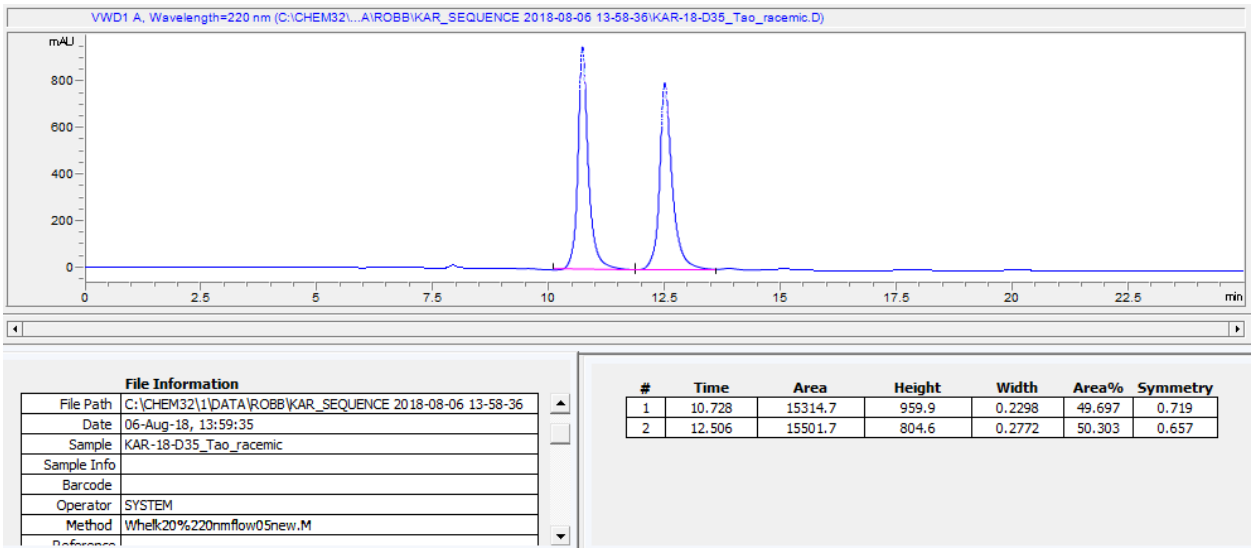
(*S*)-(–)-**7ia** ^{1}H NMR (500 MHz, $CDCl_3$)



(*S*)-(–)-**7ia** ^{13}C NMR (126 MHz, $CDCl_3$)



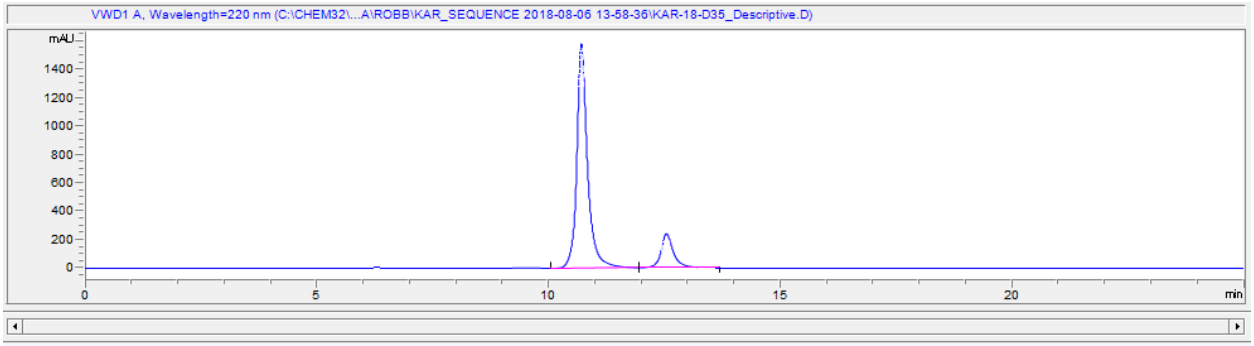
(±)-**7ia**



File Information	
File Path	C:\CHEM32\1\DATA\ROBB\KAR_SEQUENCE 2018-08-06 13-58-36
Date	06-Aug-18, 13:59:35
Sample	KAR-18-D35_Tao_racemic
Sample Info	
Barcode	
Operator	SYSTEM
Method	Whelk20%220nmflow05new.M

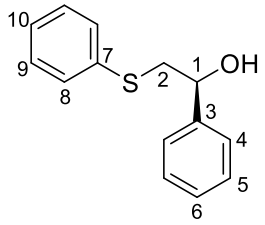
#	Time	Area	Height	Width	Area%	Symmetry
1	10.728	15314.7	959.9	0.2298	49.697	0.719
2	12.506	15501.7	804.6	0.2772	50.303	0.657

(–)-**7ia**



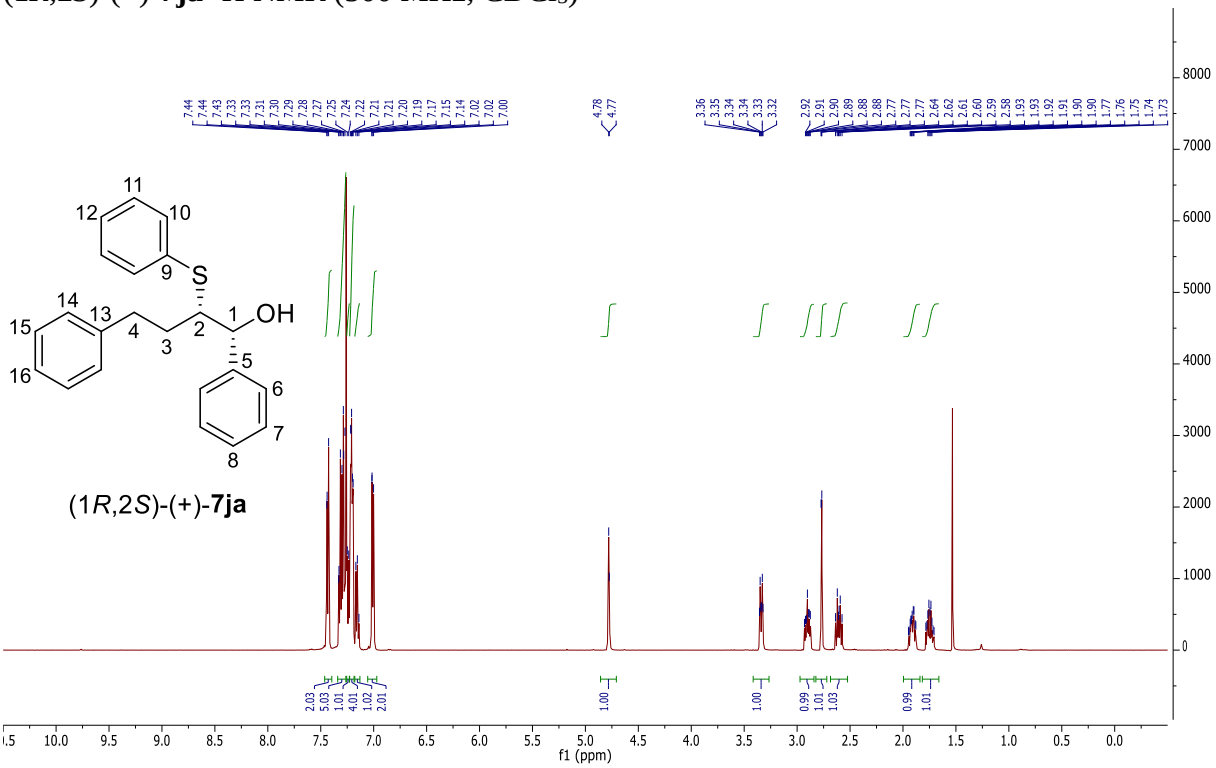
File Information	
File Path	C:\CHEM32\1\DATA\ROBB\KAR_SEQUENCE 2018-08-06 13-58-36
Date	06-Aug-18, 14:29:06
Sample	KAR-18-D35_Descriptive
Sample Info	
Barcode	
Operator	SYSTEM
Method	Whelk20%220nmflow05new.M

#	Time	Area	Height	Width	Area%	Symmetry
1	10.705	25998.3	1586.3	0.2378	83.853	0.694
2	12.541	5006.4	245.9	0.2929	16.147	0.711

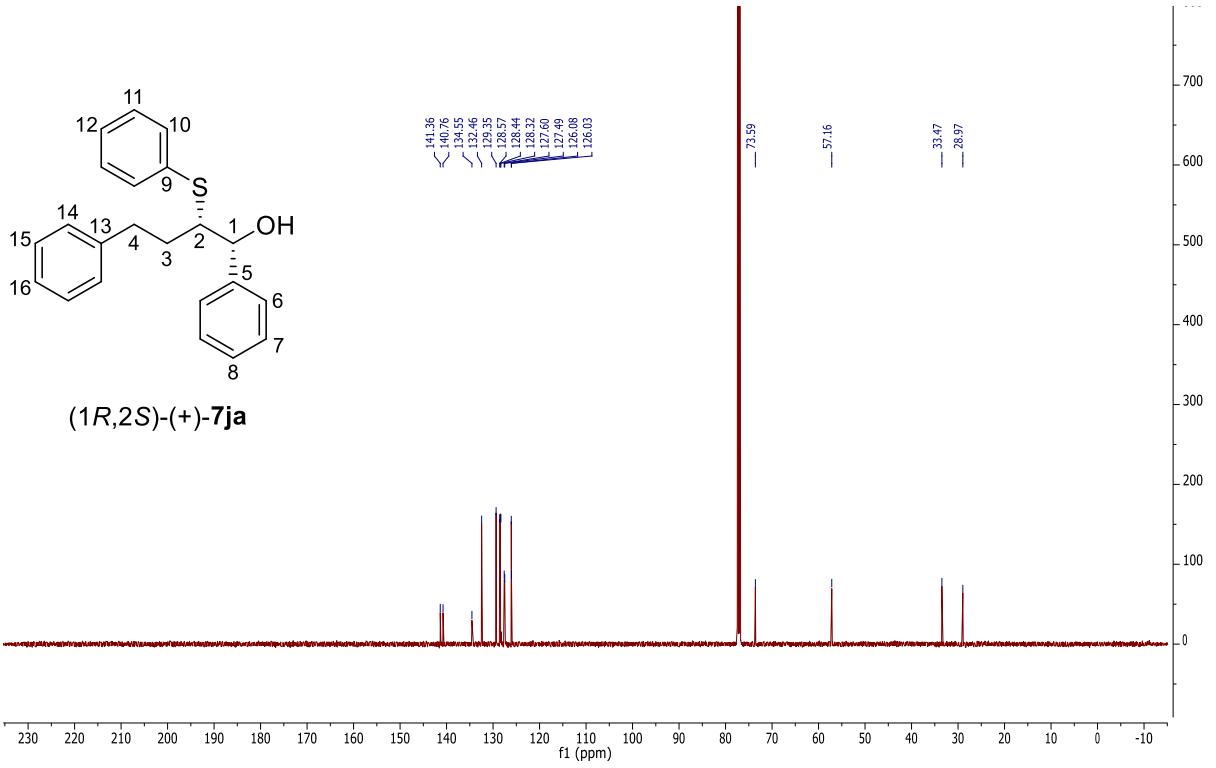


(*S*)-(–)-**7ia**

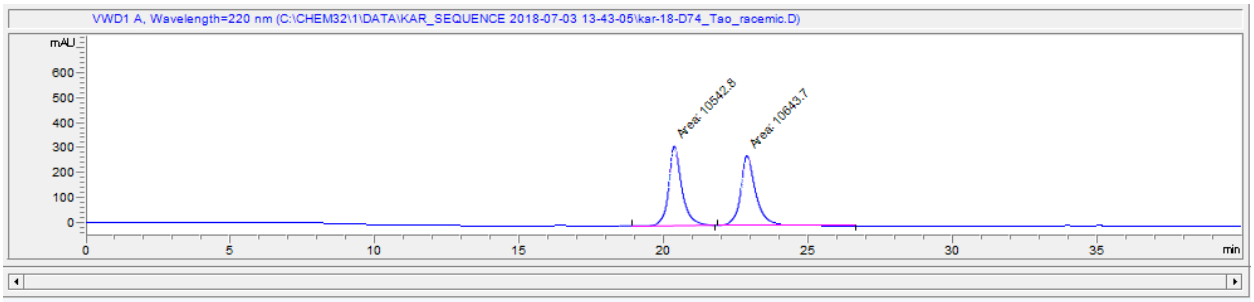
(1*R*,2*S*)-(+)-**7ja** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*R*,2*S*)-(+)-**7ja** ^{13}C NMR (126 MHz, $CDCl_3$)



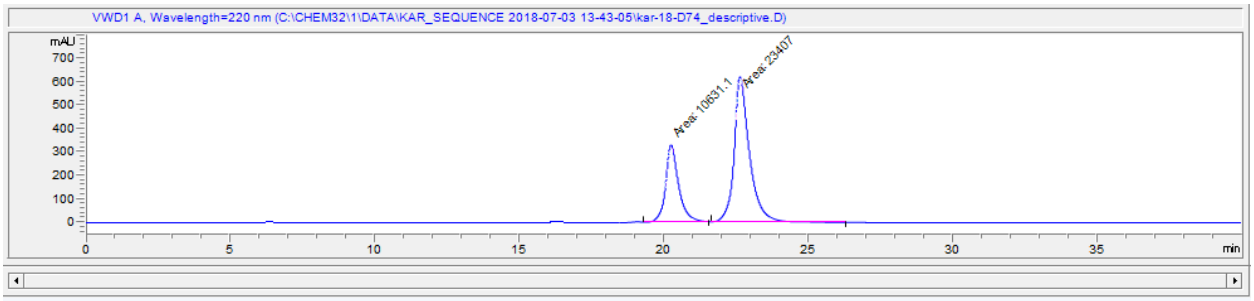
(±)-**7ja**



File Information	
Date	03-Jul-18, 13:43:58
Sample	kar-18-D74_Tao_racemic
Sample Info	
Barcode	
Operator	SYSTEM
Method	Whelk2%220nmflow05new.M

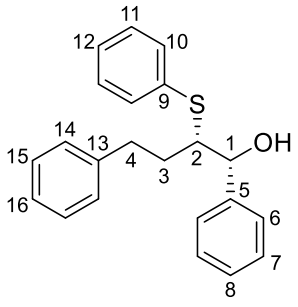
#	Time	Area	Height	Width	Area%	Symmetry
1	20.341	10542.8	323.8	0.8526	49.762	0
2	22.851	10643.7	284.5	0.6234	50.238	0.658

(1*R*,2*S*)-(+)-**7ja**



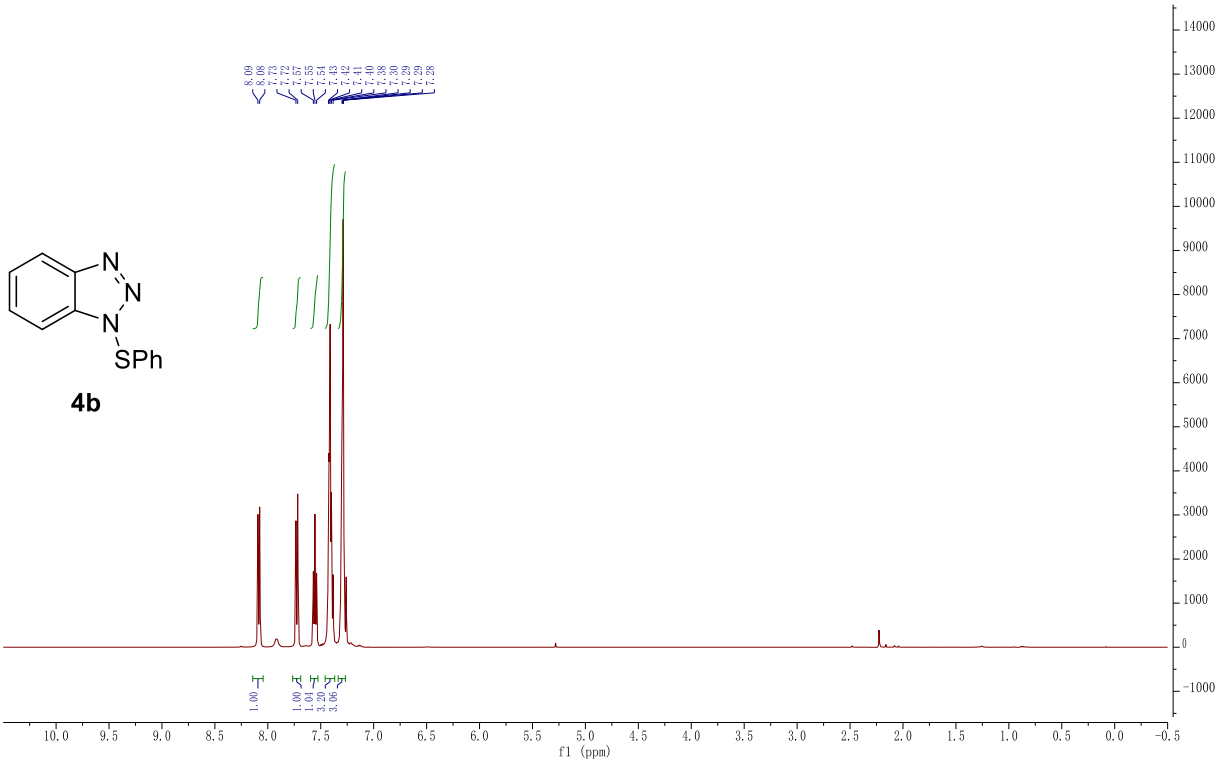
File Information	
Date	03-Jul-18, 14:25:46
Sample	kar-18-D74_descriptive
Sample Info	
Barcode	
Operator	SYSTEM
Method	Whelk2%220nmflow05new.M

#	Time	Area	Height	Width	Area%	Symmetry
1	20.219	10631.1	334.3	0.6916	31.233	1.41E-2
2	22.614	23407	626.2	0.6229	68.767	0.591

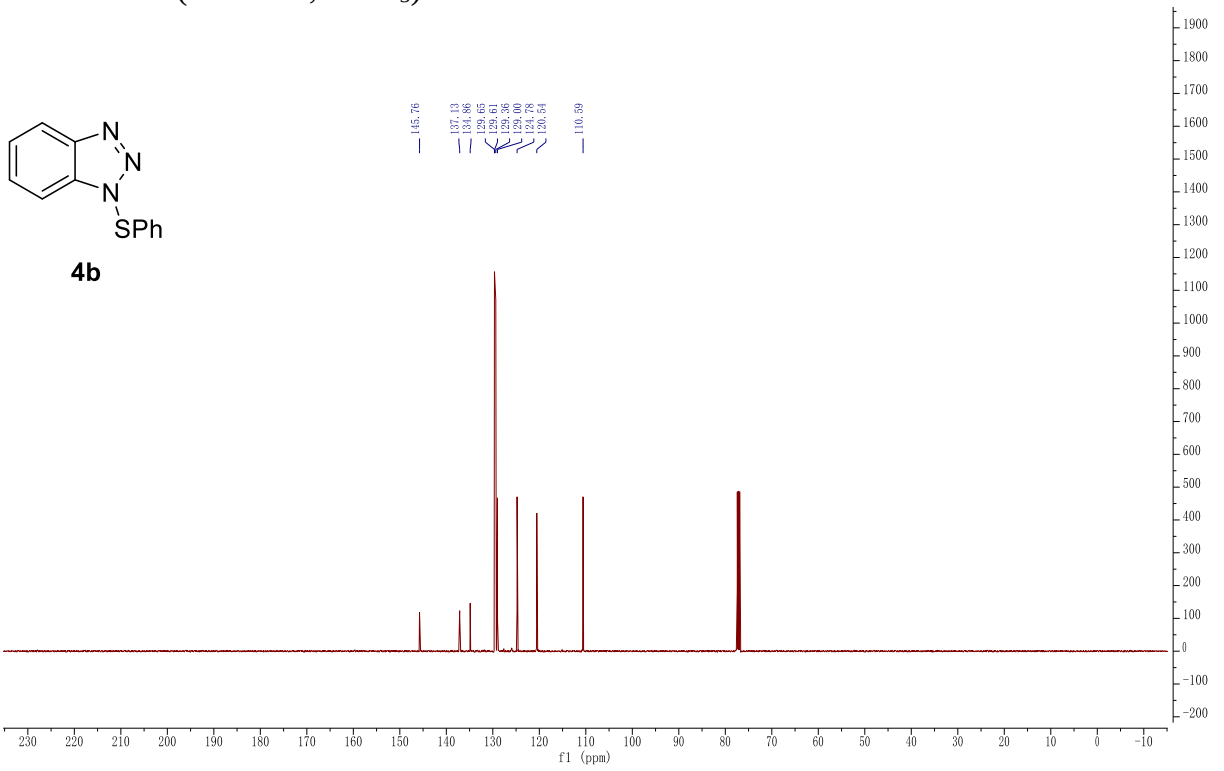


(1*R*,2*S*)-(+)-**7ja**

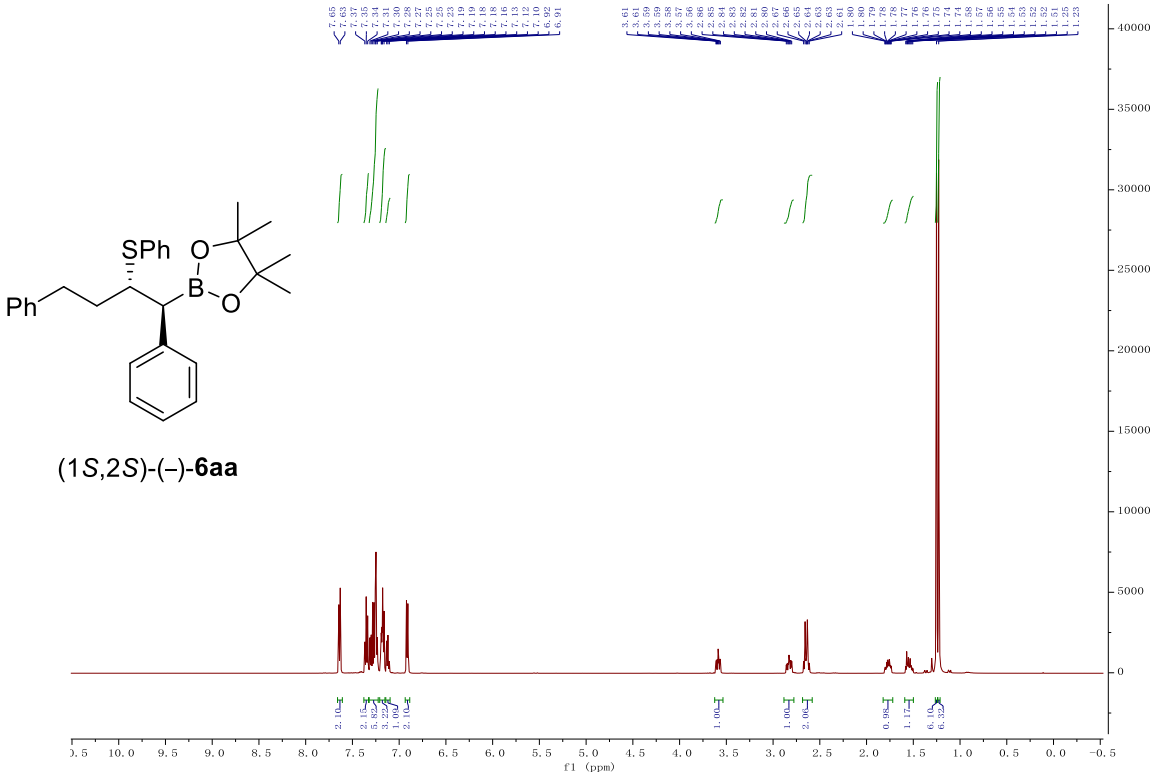
4b ^{1}H NMR (500 MHz, $CDCl_3$)



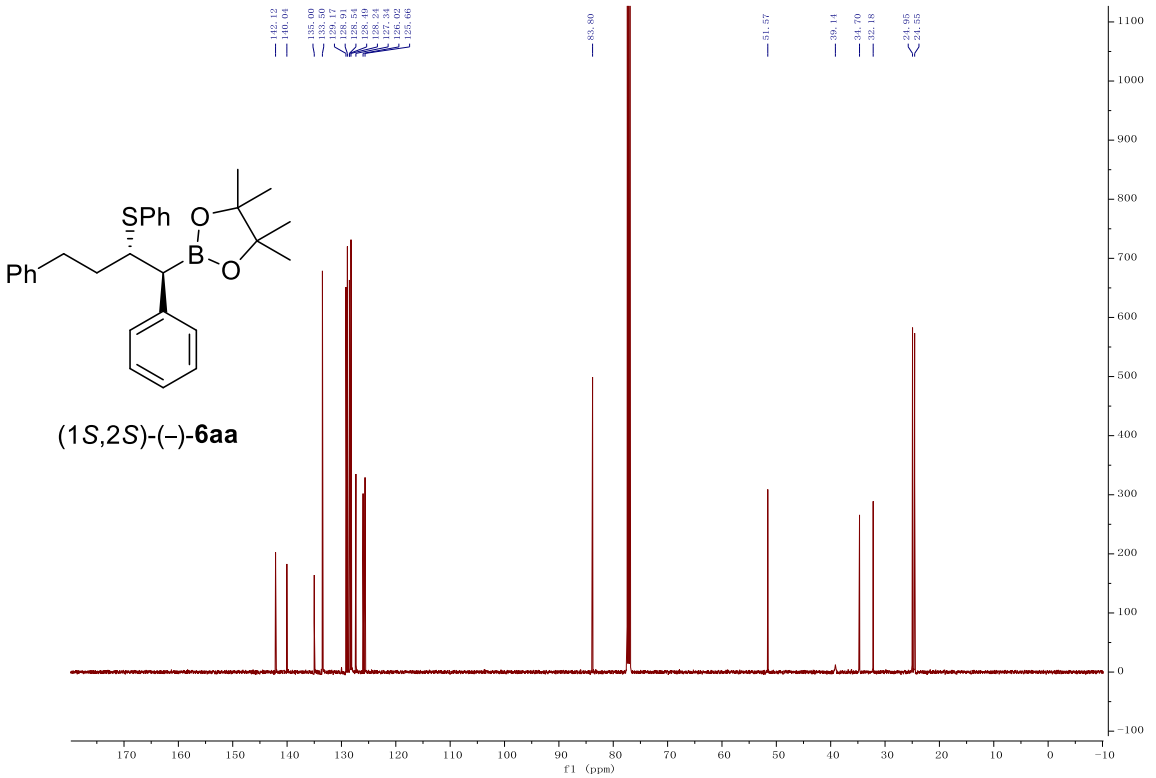
4b ^{13}C NMR (126 MHz, $CDCl_3$)



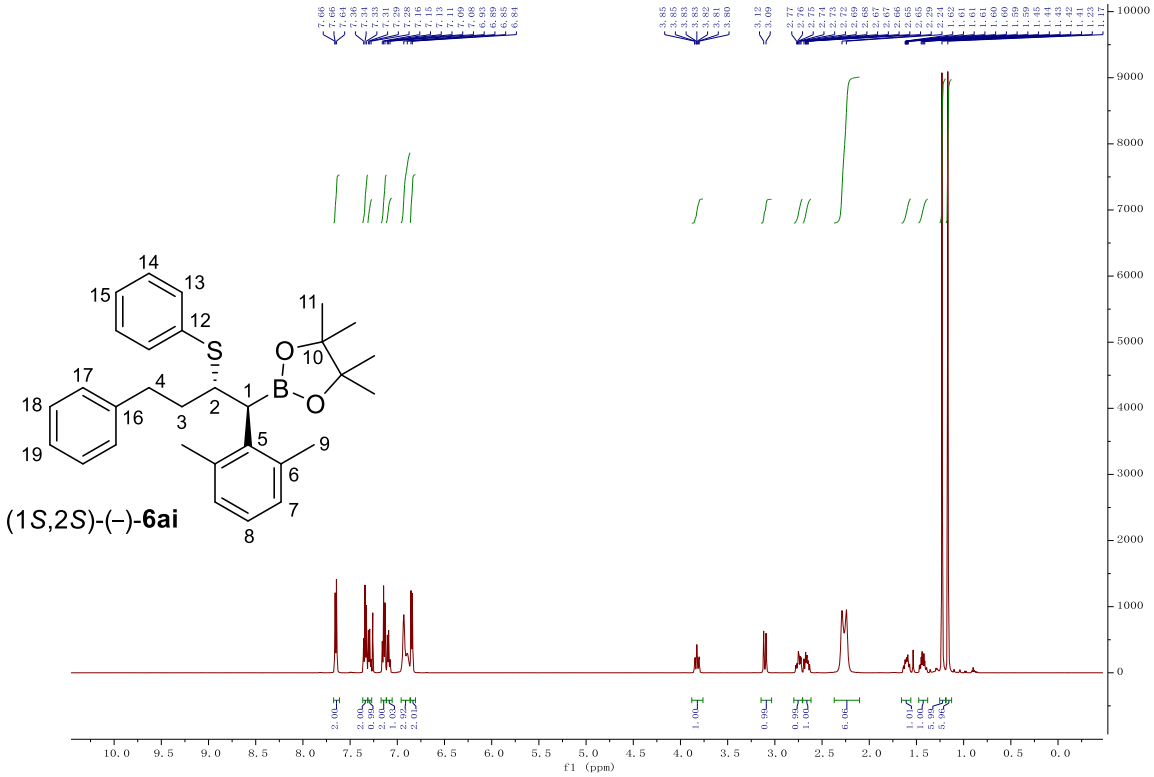
(1*S*,2*S*)-(–)-**6aa** ^{1}H NMR (500 MHz, $CDCl_3$)



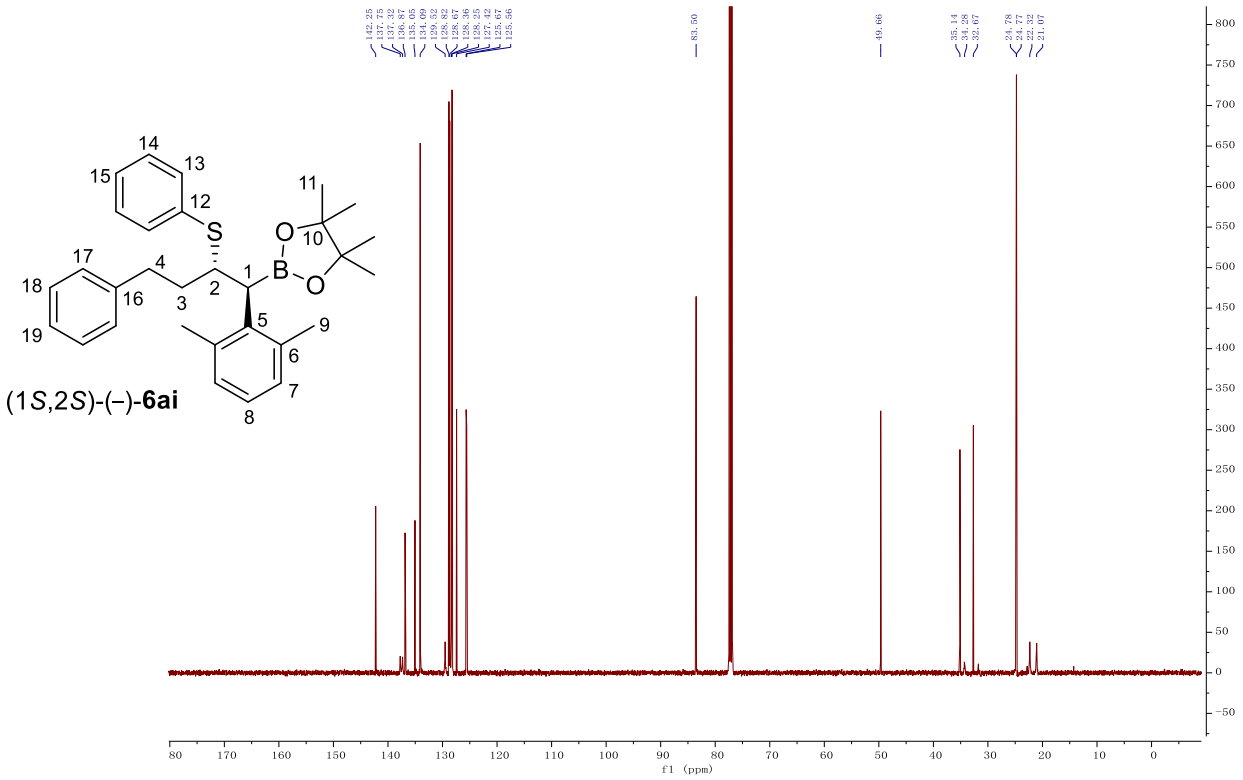
(1*S*,2*S*)-(–)-**6aa** ^{13}C NMR (126 MHz, $CDCl_3$)



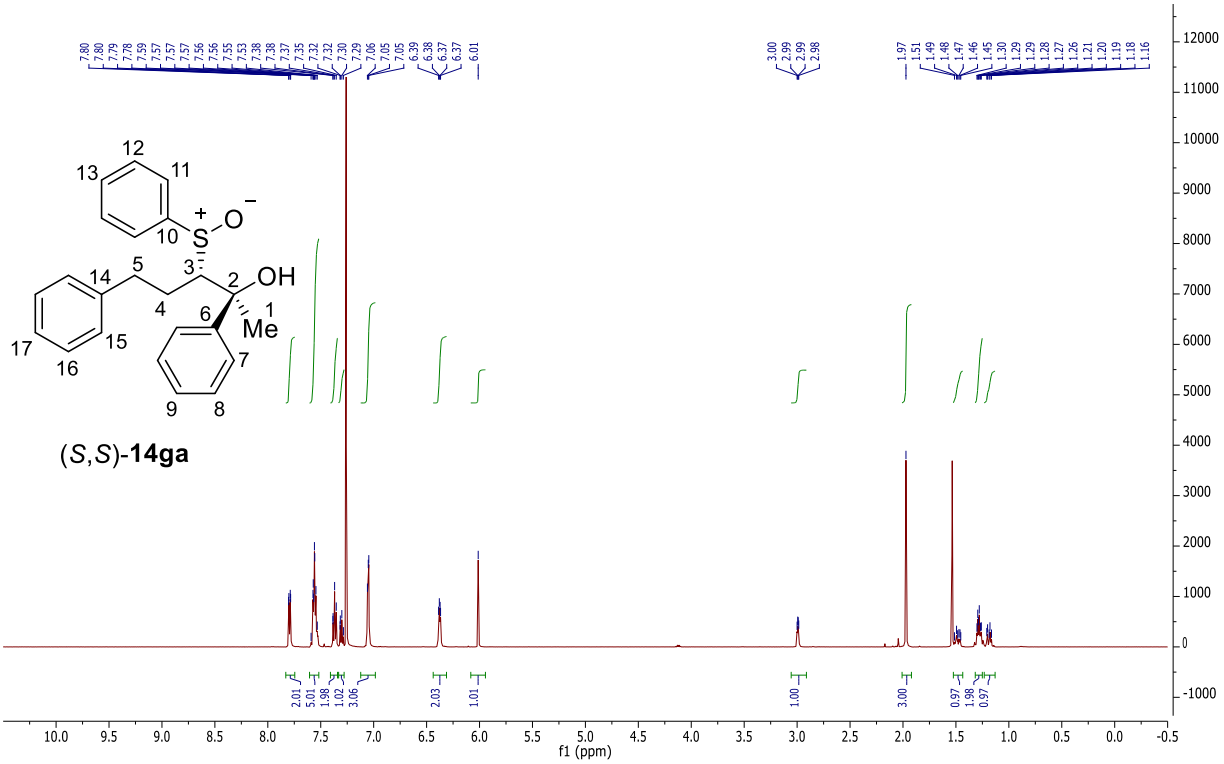
(1*S*,2*S*)-(–)-**6ai** ^{1}H NMR (500 MHz, $CDCl_3$)



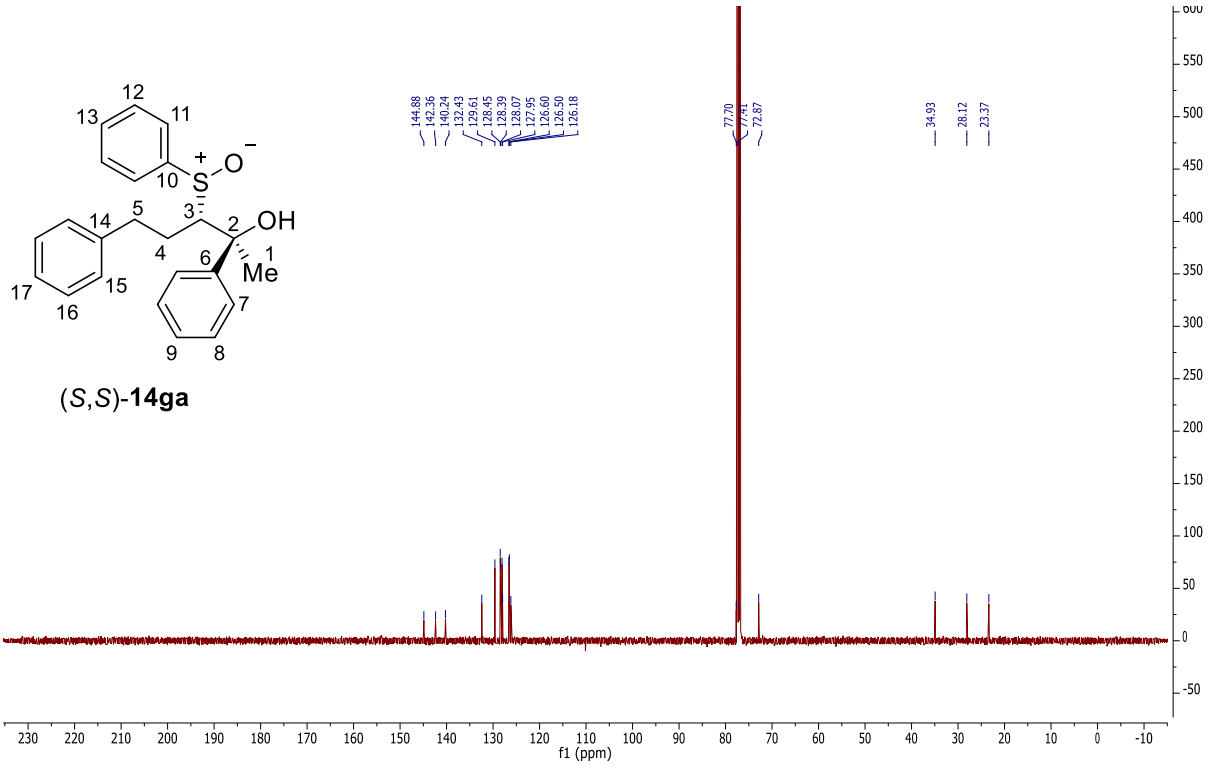
(1*S*,2*S*)-(–)-**6ai** ^{13}C NMR (126 MHz, $CDCl_3$)



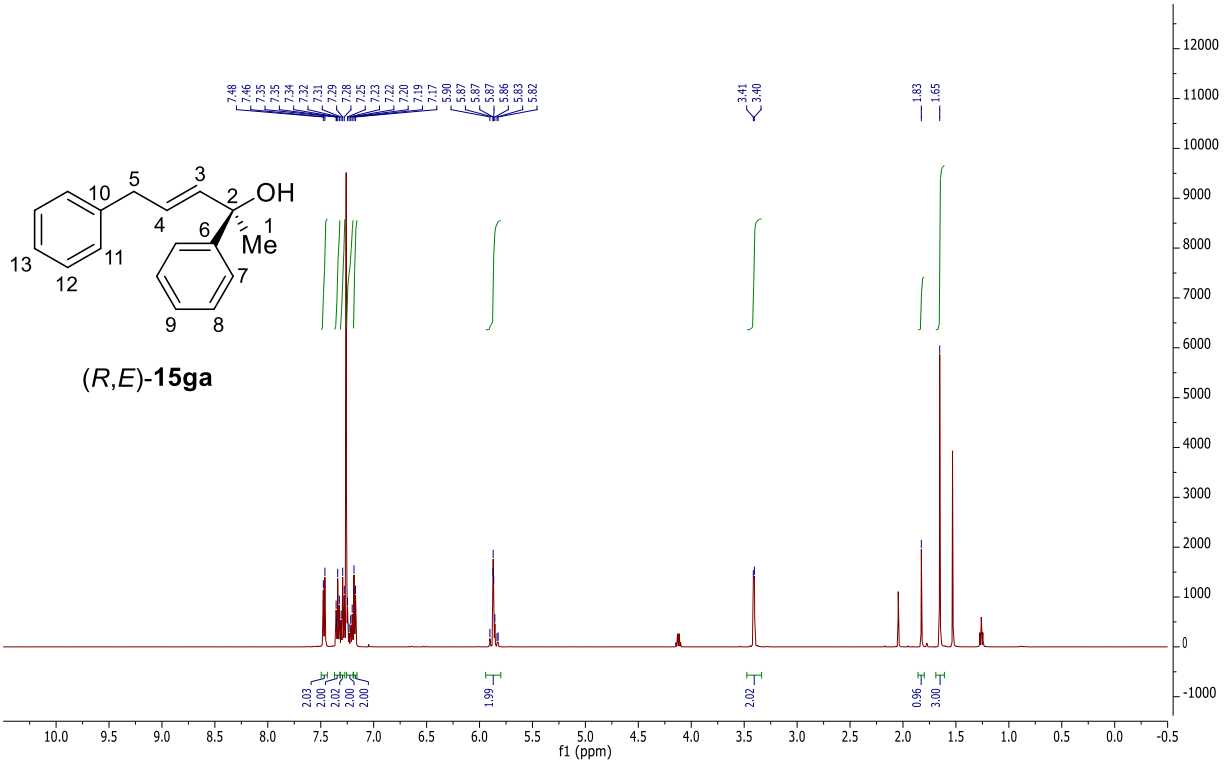
(2*S*,3*S*)-**14ga** ^{1}H NMR (500 MHz, $CDCl_3$)



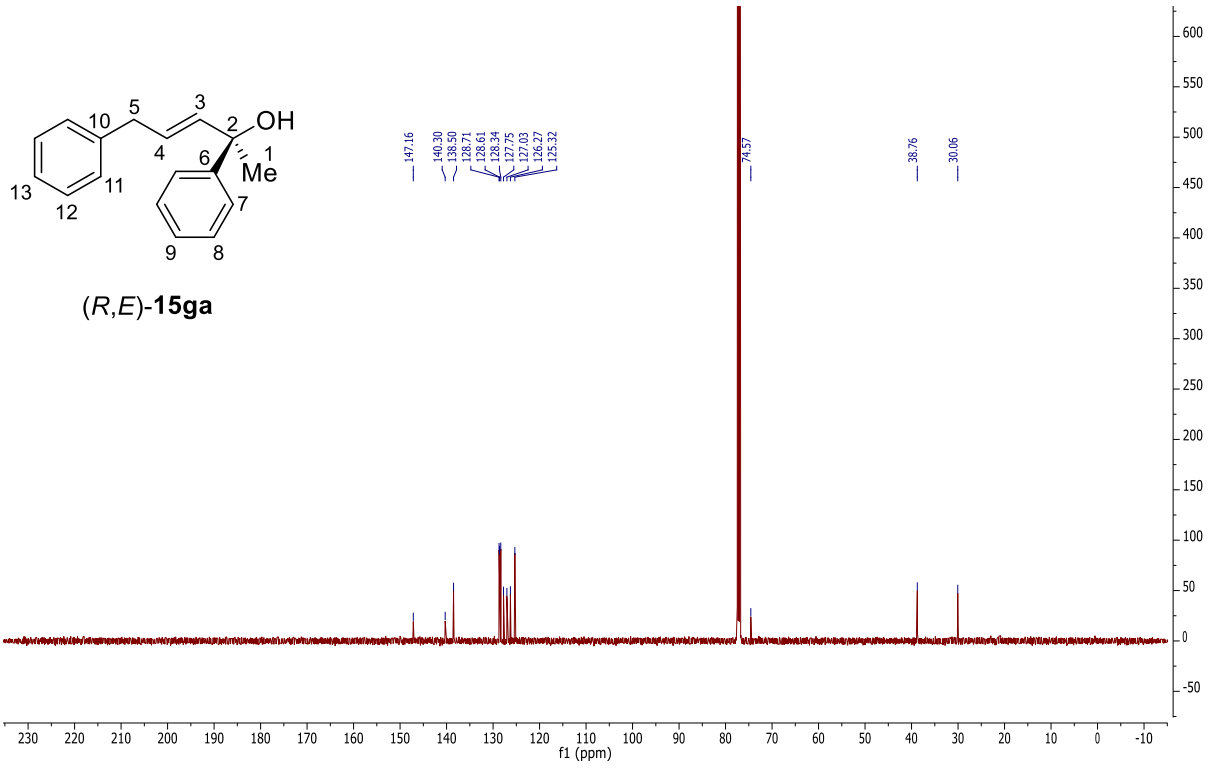
(2*S*,3*S*)-**14ga** ^{13}C NMR (126 MHz, $CDCl_3$)



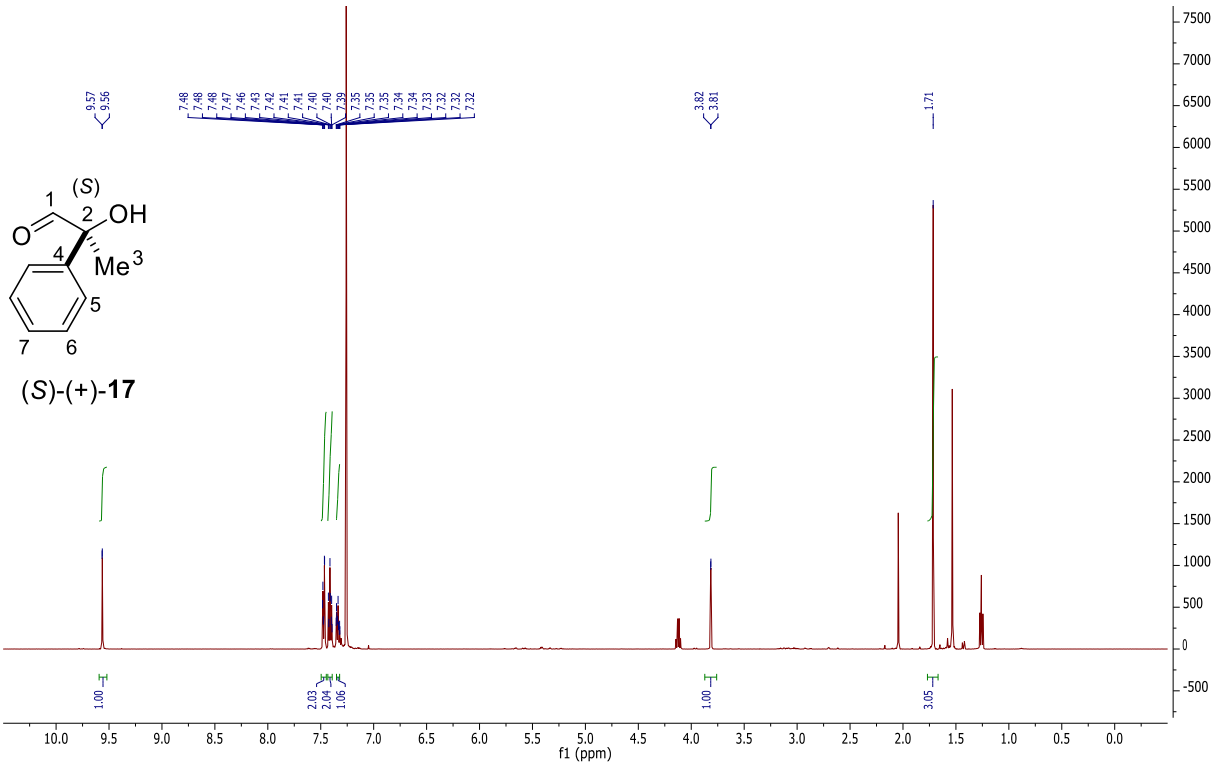
(*R*,*E*)-**15ga** ^{1}H NMR (500 MHz, $CDCl_3$)



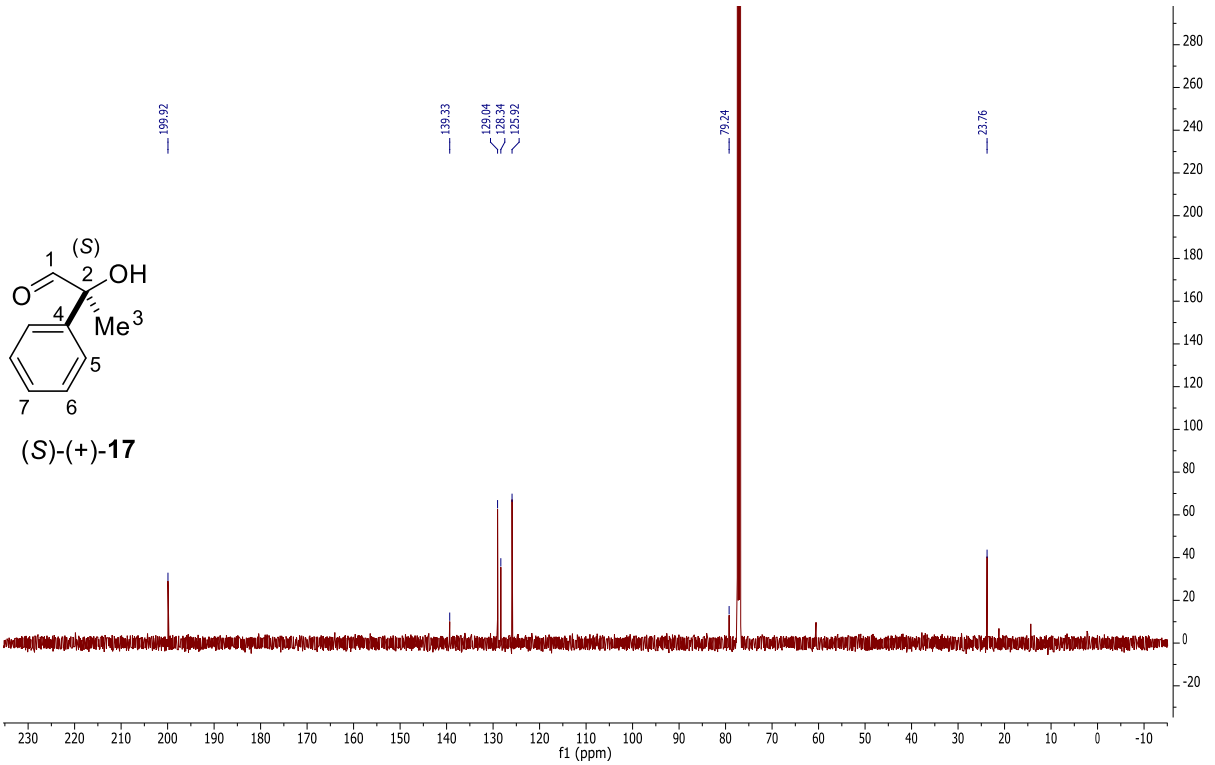
(*R*,*E*)-**15ga** ^{13}C NMR (126 MHz, $CDCl_3$)



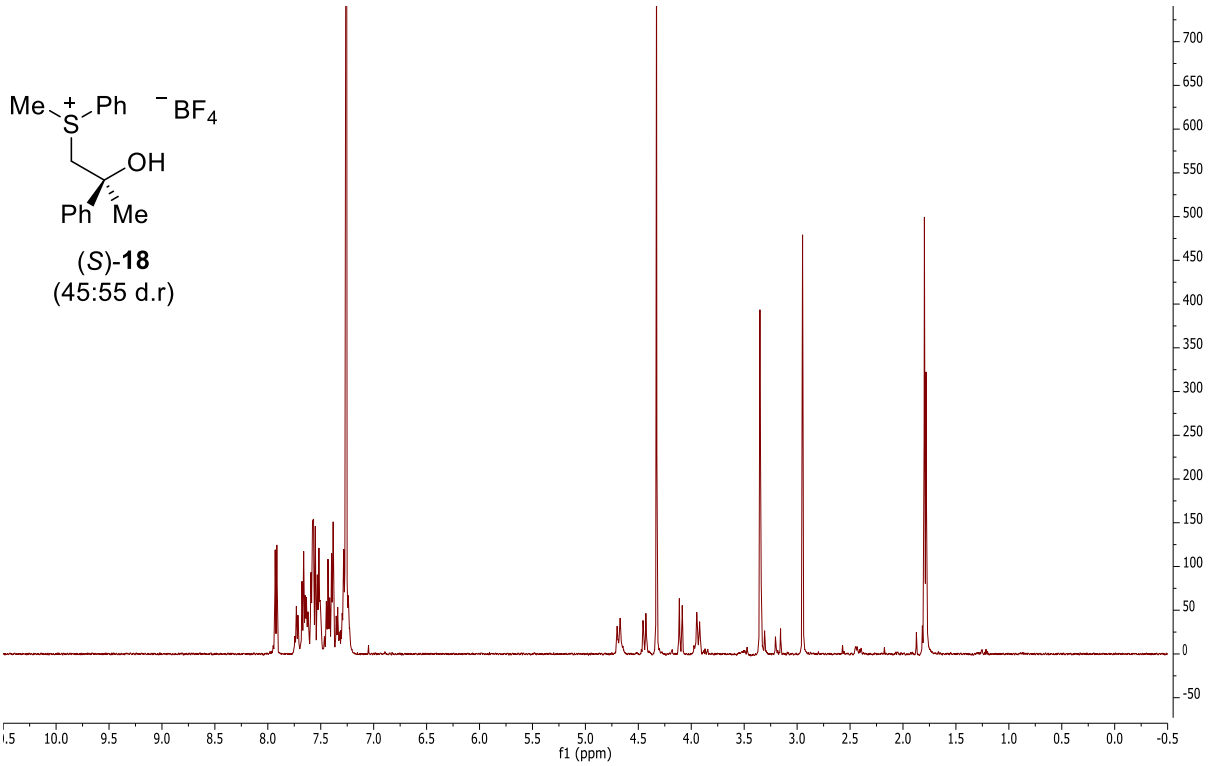
(*S*)-(+)-**17** ^{1}H NMR (500 MHz, $CDCl_3$)



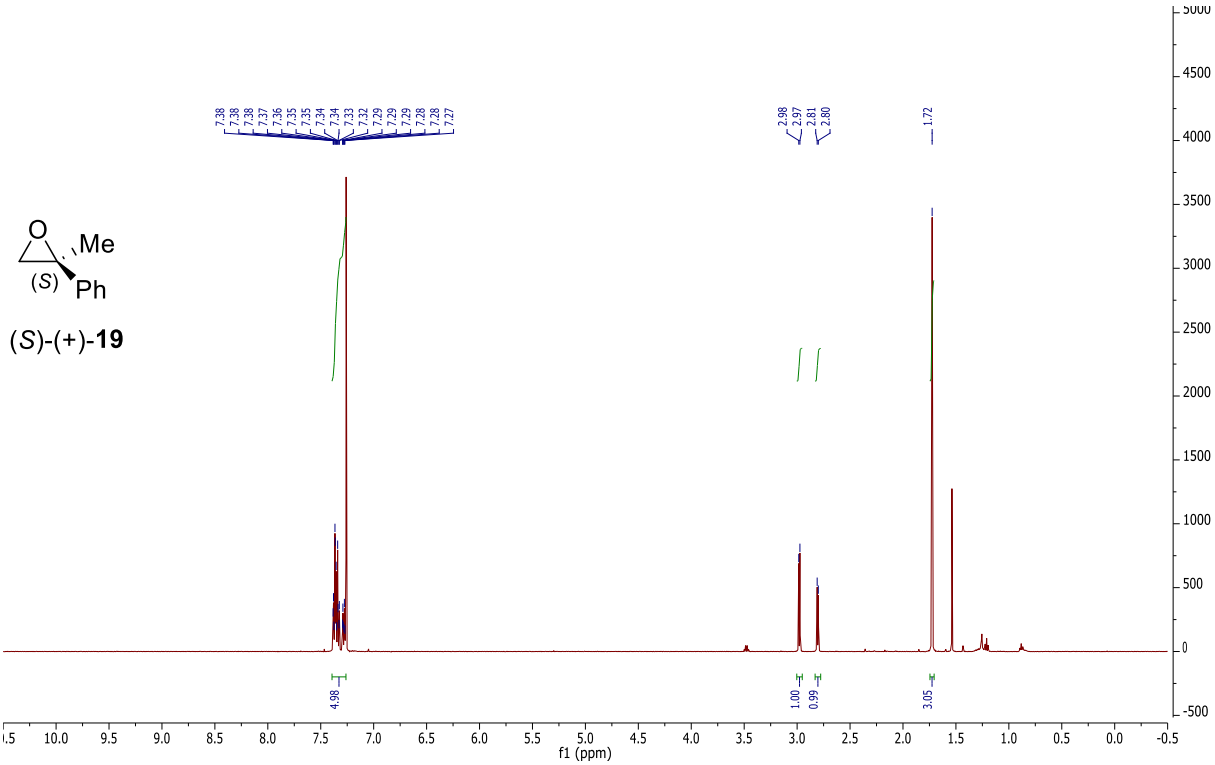
(*S*)-(+)-**17** ^{13}C NMR (126 MHz, $CDCl_3$)



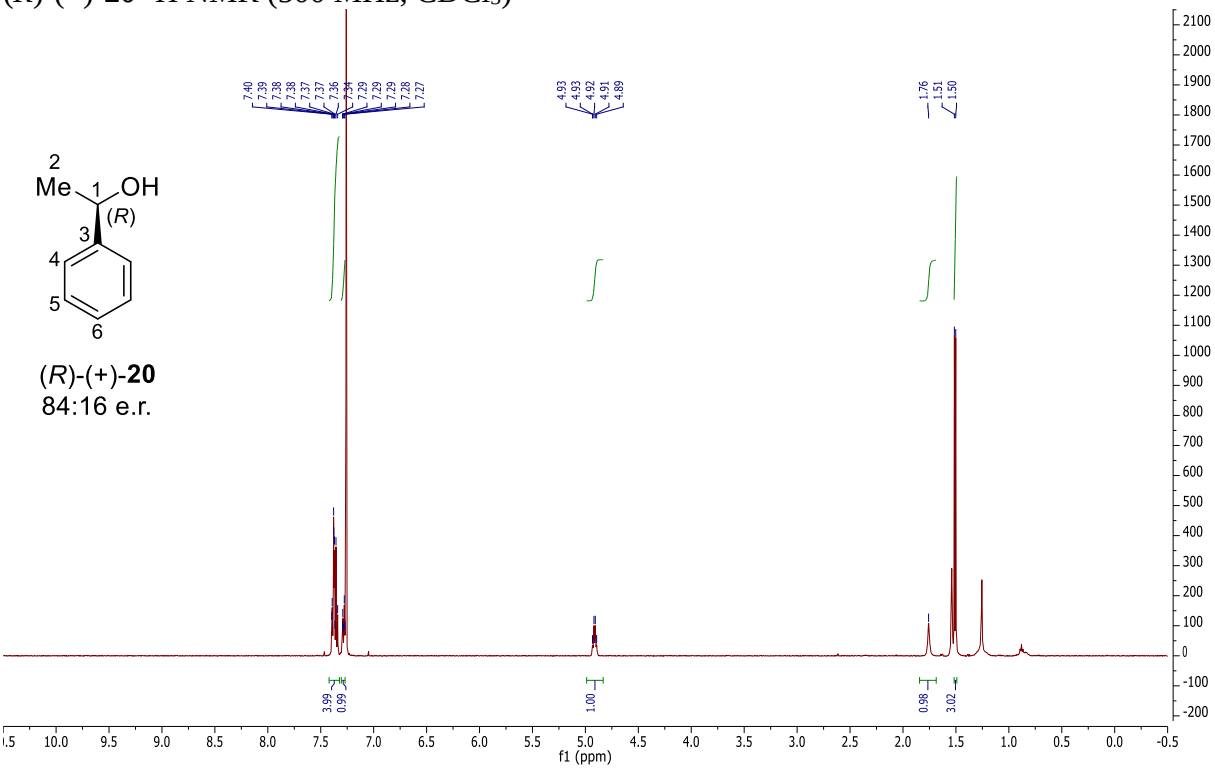
(*S*)-**18** (crude, mixture of diastereomers) ^{1}H NMR (500 MHz, $CDCl_3$)



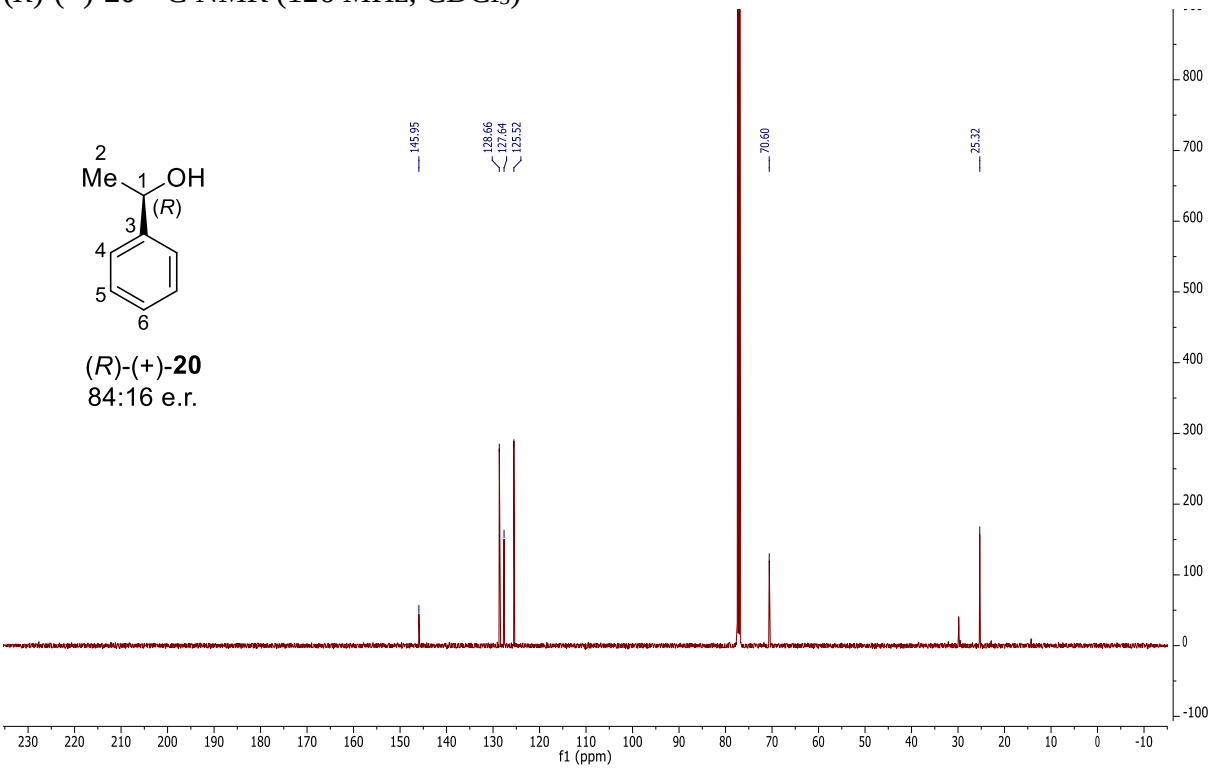
(*S*)-(+)-**19** ^{1}H NMR (500 MHz, $CDCl_3$)



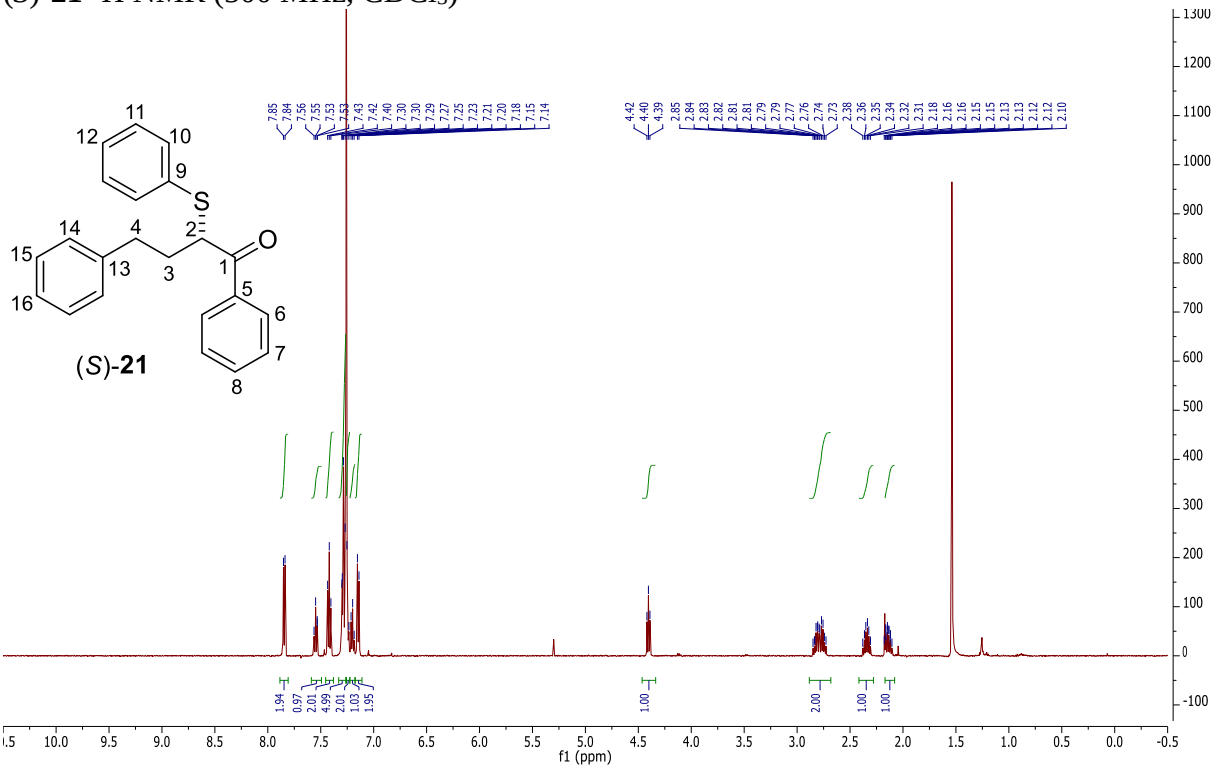
(*R*)-(+)-**20** ^{1}H NMR (500 MHz, $CDCl_3$)



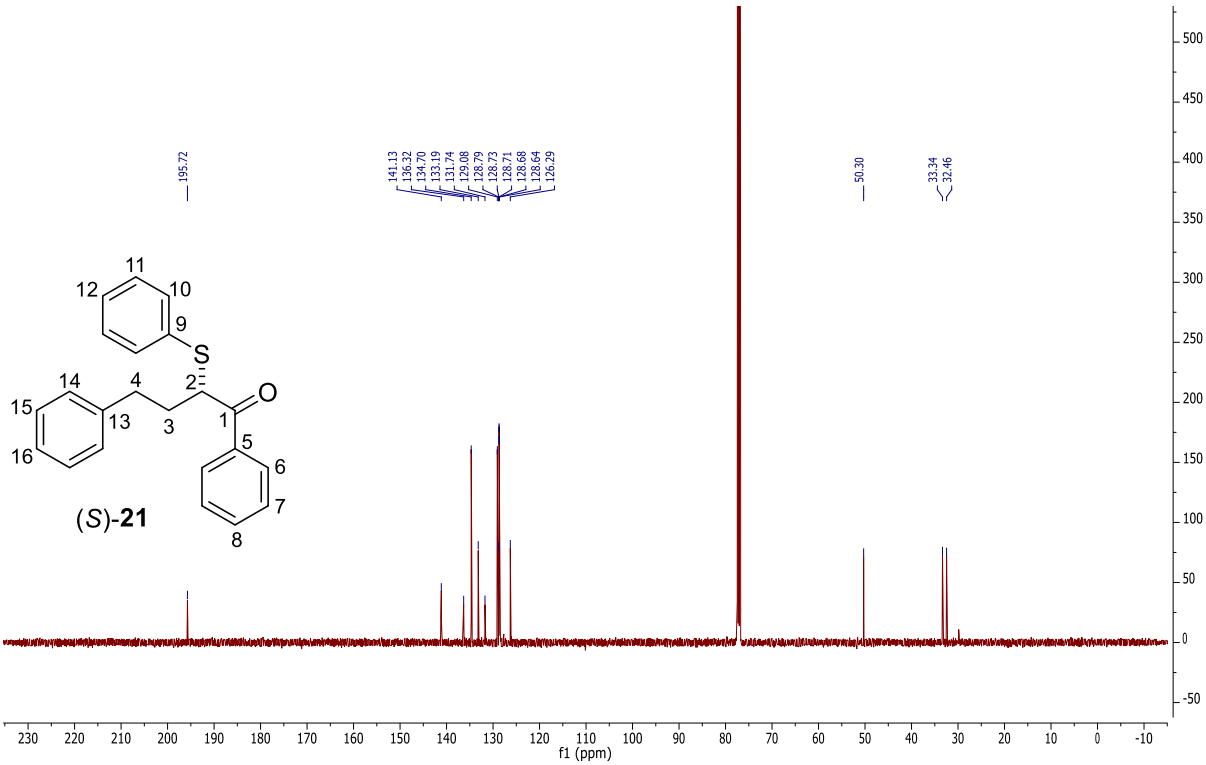
(*R*)-(+)-**20** ^{13}C NMR (126 MHz, $CDCl_3$)



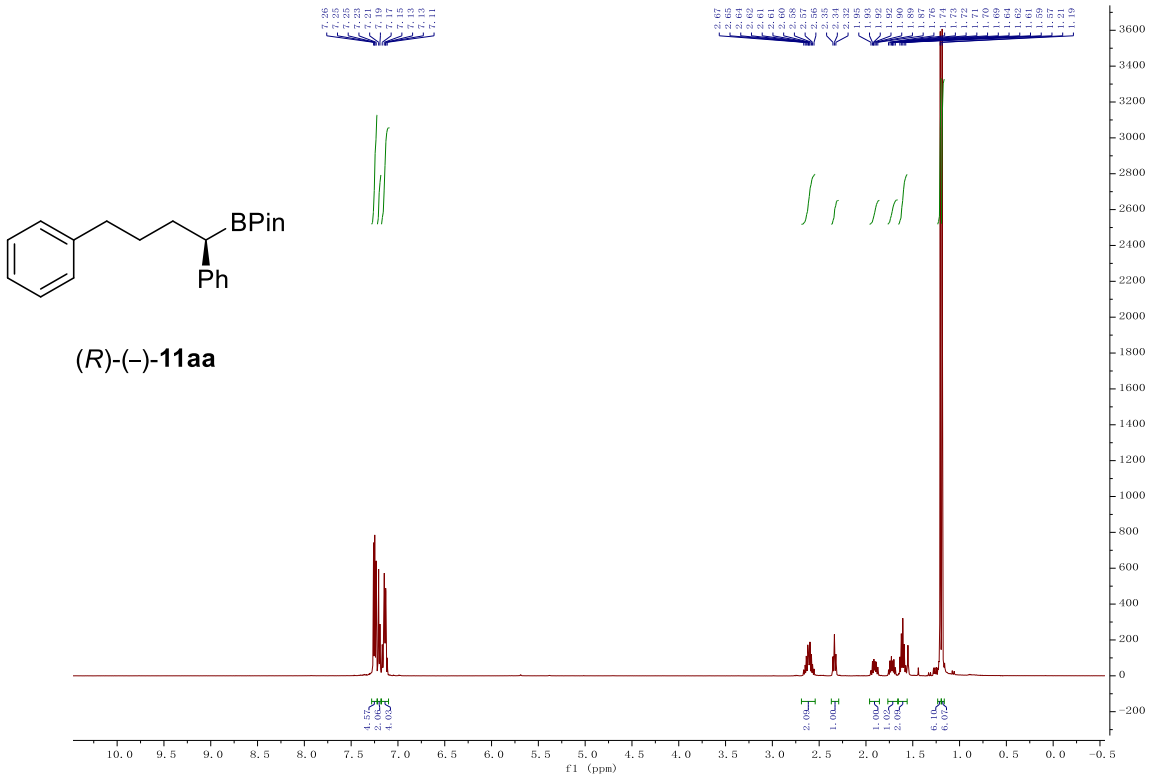
(*S*)-**21** ^{1}H NMR (500 MHz, $CDCl_3$)



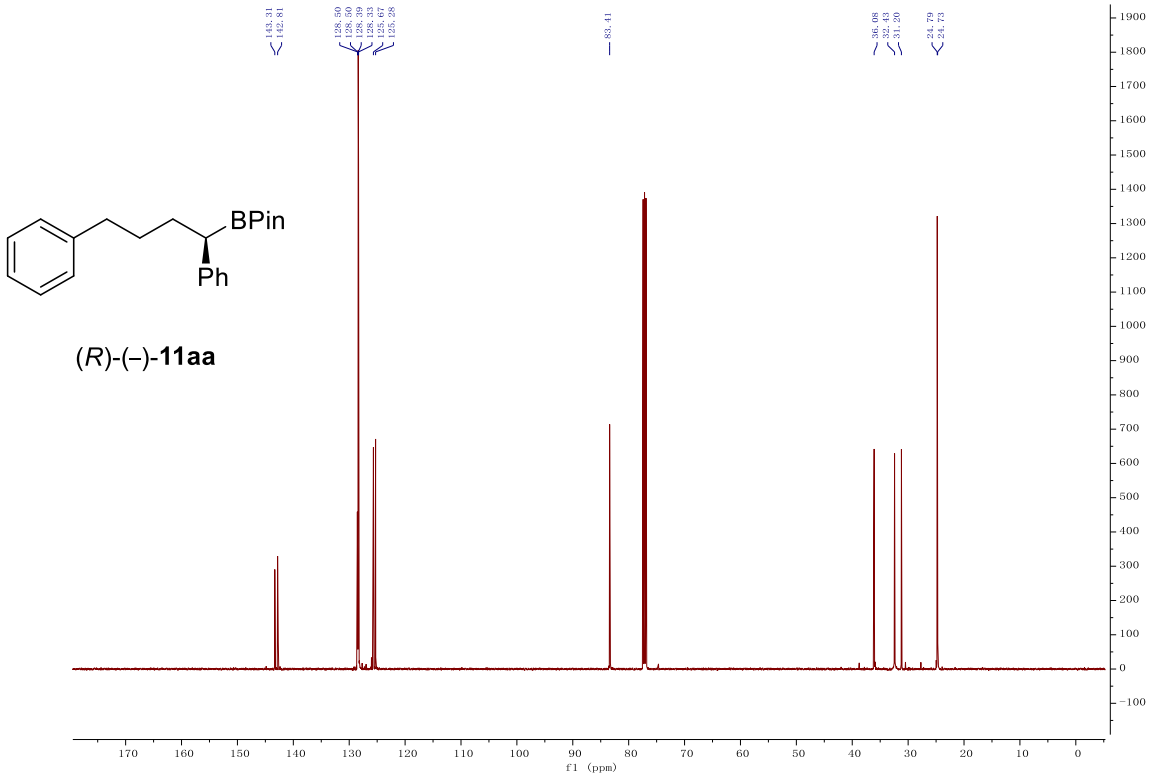
(*S*)-**21** ^{13}C NMR (126 MHz, $CDCl_3$)



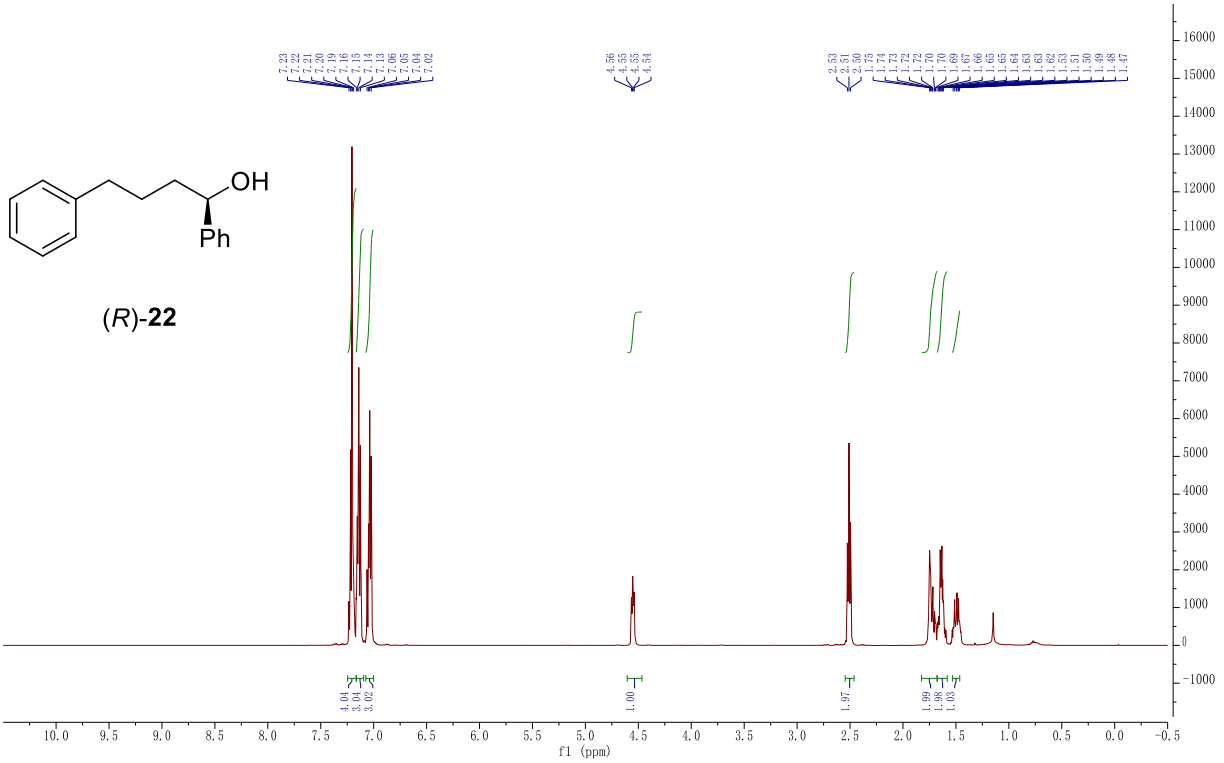
(*R*)-(–)-**11aa** ^{1}H NMR (500 MHz, $CDCl_3$)



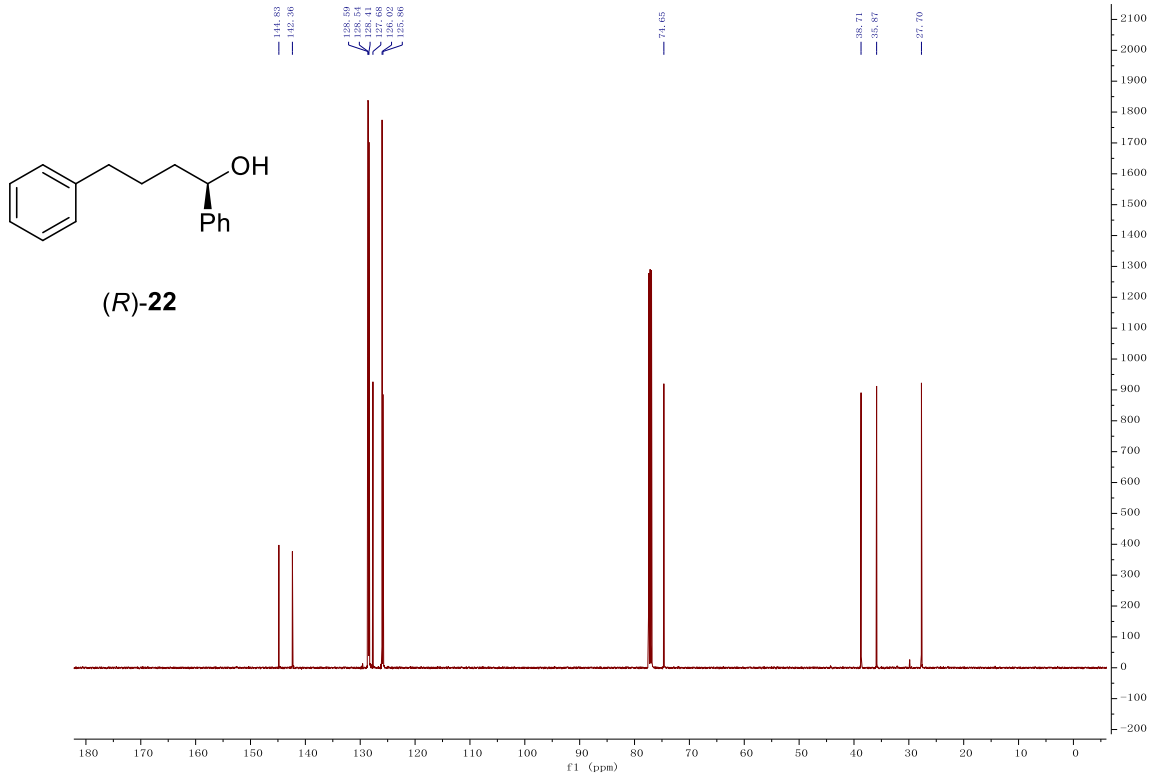
(*R*)-(–)-**11aa** ^{13}C NMR (126 MHz, $CDCl_3$)



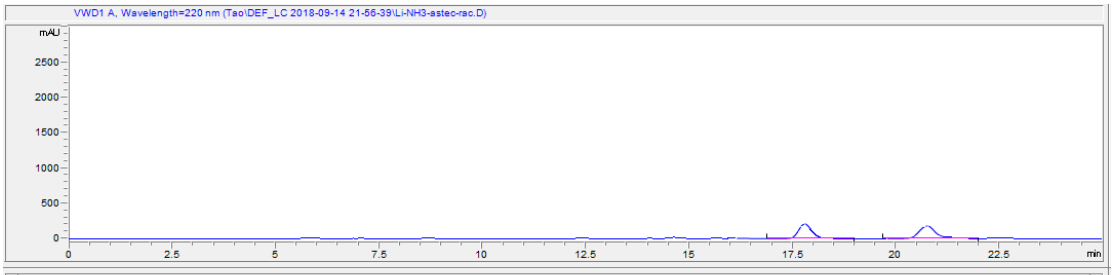
(*R*)-**22** ^{1}H NMR (500 MHz, $CDCl_3$)



(*R*)-**22** ^{13}C NMR (126 MHz, $CDCl_3$)



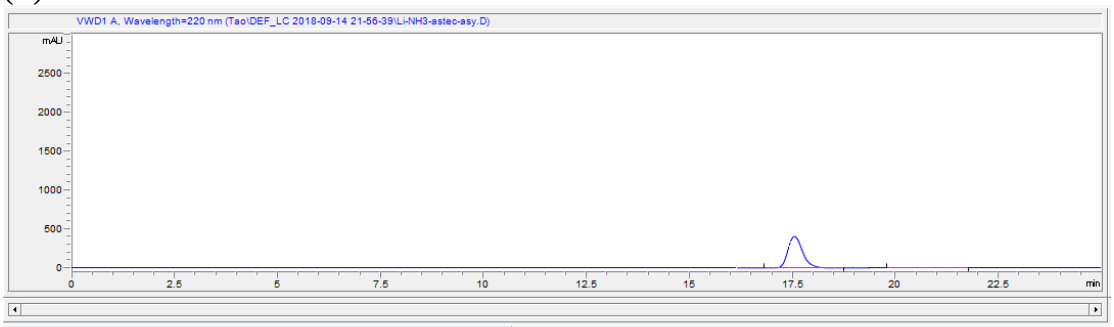
(±)-**22**



File Information	
LC-File	Li-NH3-astec-rac.D
File Path	C:\Chem32\1\Data\Tao\DEF_LC 2018-09-14 21-56-39

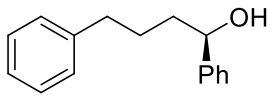
#	Time	Area	Height	Width	Area%	Symmetry
1	17.765	4783	208.5	0.355	47.731	0.793
2	20.722	5237.8	180.6	0.4431	52.269	0.833

(*R*)-**22**



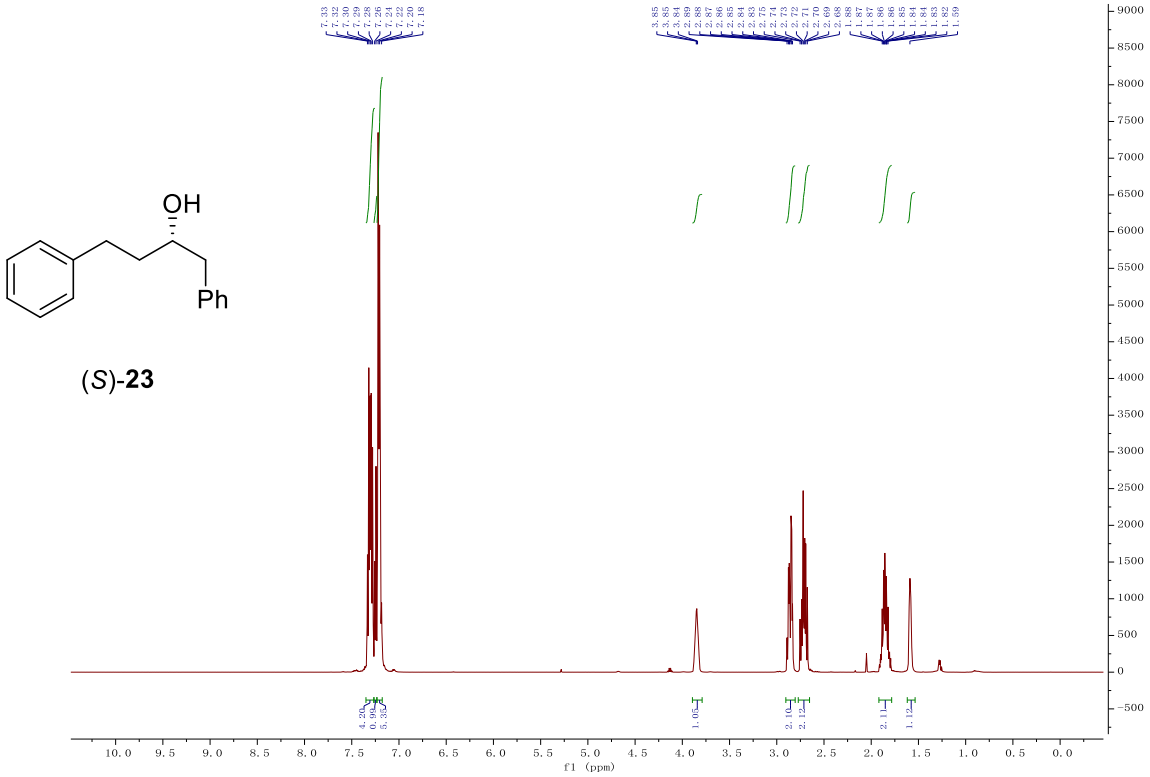
File Information	
LC-File	Li-NH3-astec-asy.D
File Path	C:\Chem32\1\Data\Tao\DEF_LC 2018-09-14 21-56-39

#	Time	Area	Height	Width	Area%	Symmetry
1	17.515	9955	404.8	0.3859	97.431	0.768
2	20.406	262.5	10	0.3929	2.569	0.806

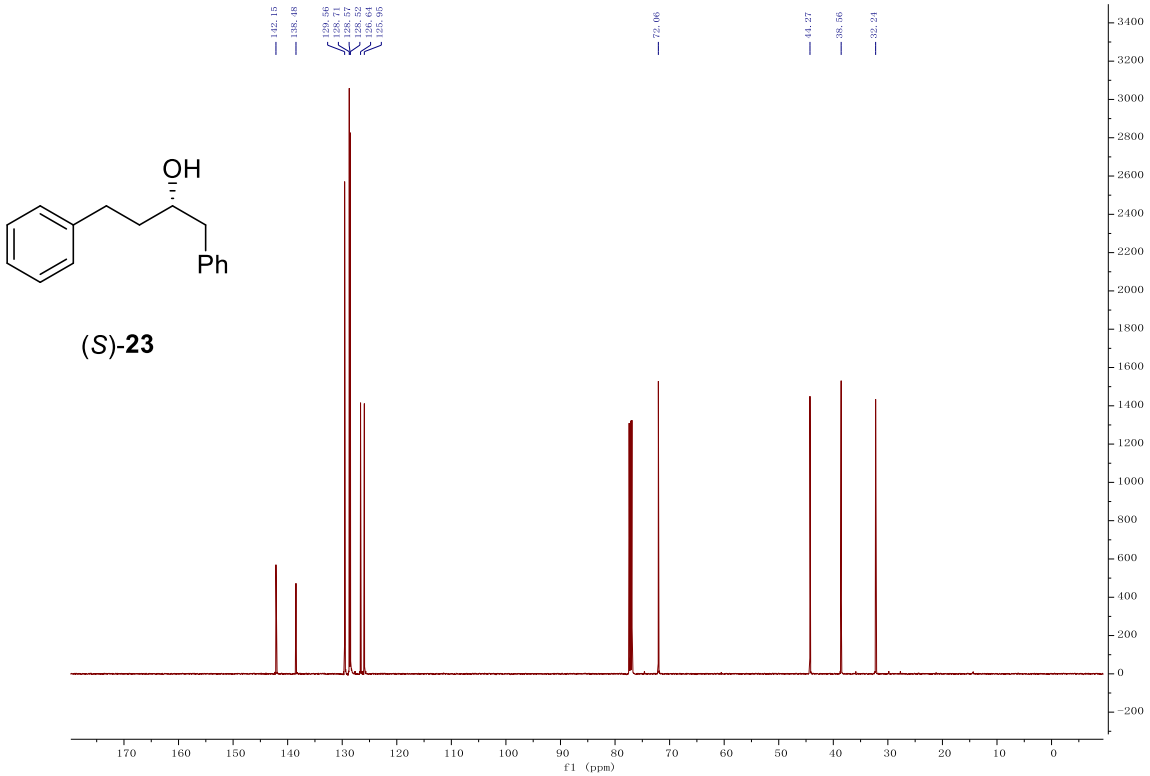


(*R*)-**22**

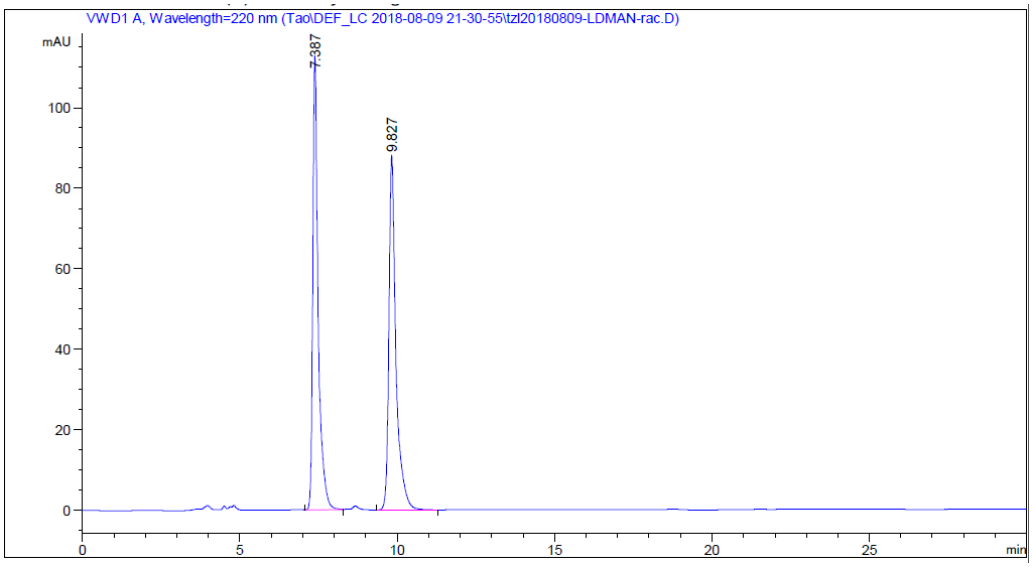
(*S*)-**23** ^{1}H NMR (500 MHz, $CDCl_3$)



(*S*)-**23** ^{13}C NMR (126 MHz, $CDCl_3$)

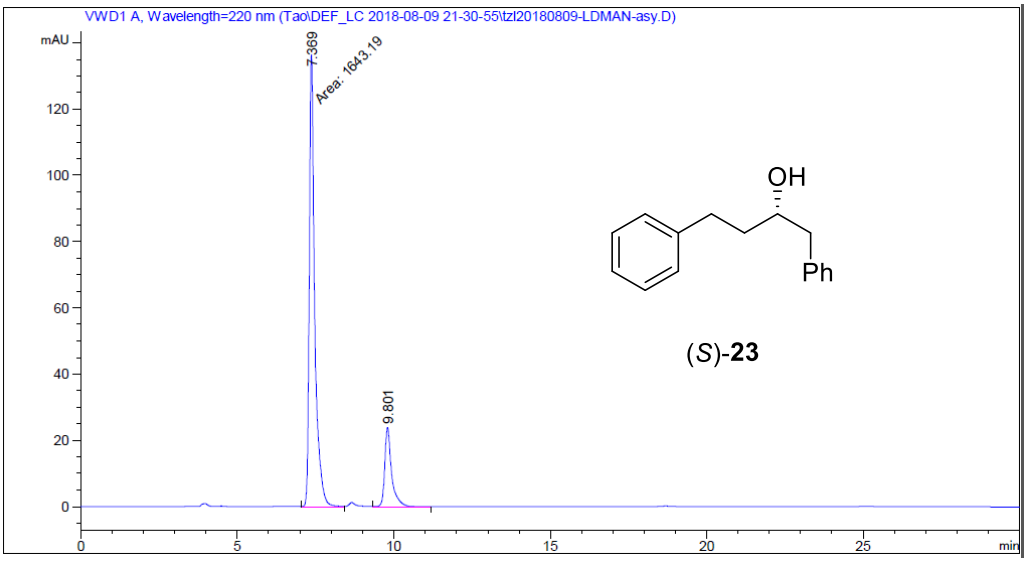


(±)-**23**



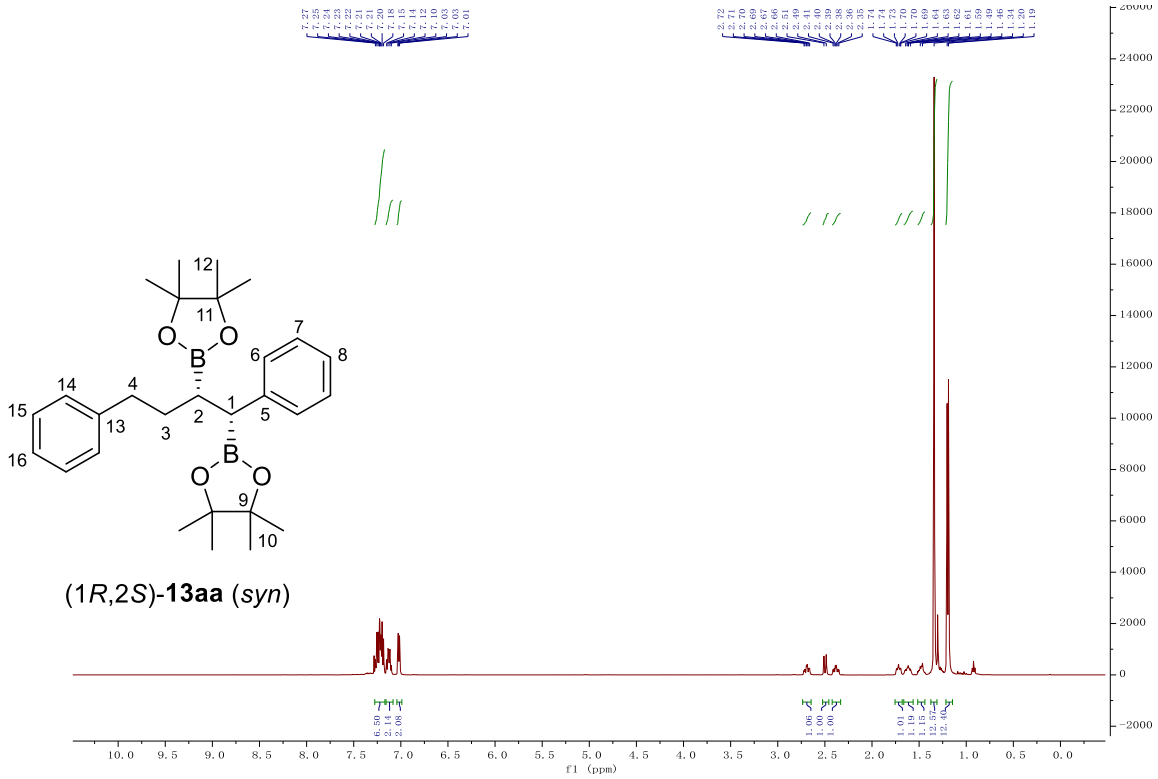
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.387	BB	0.1738	1338.64124	112.43543	49.4394
2	9.827	BB	0.2283	1368.99988	87.91255	50.5606

(*S*)-**23**

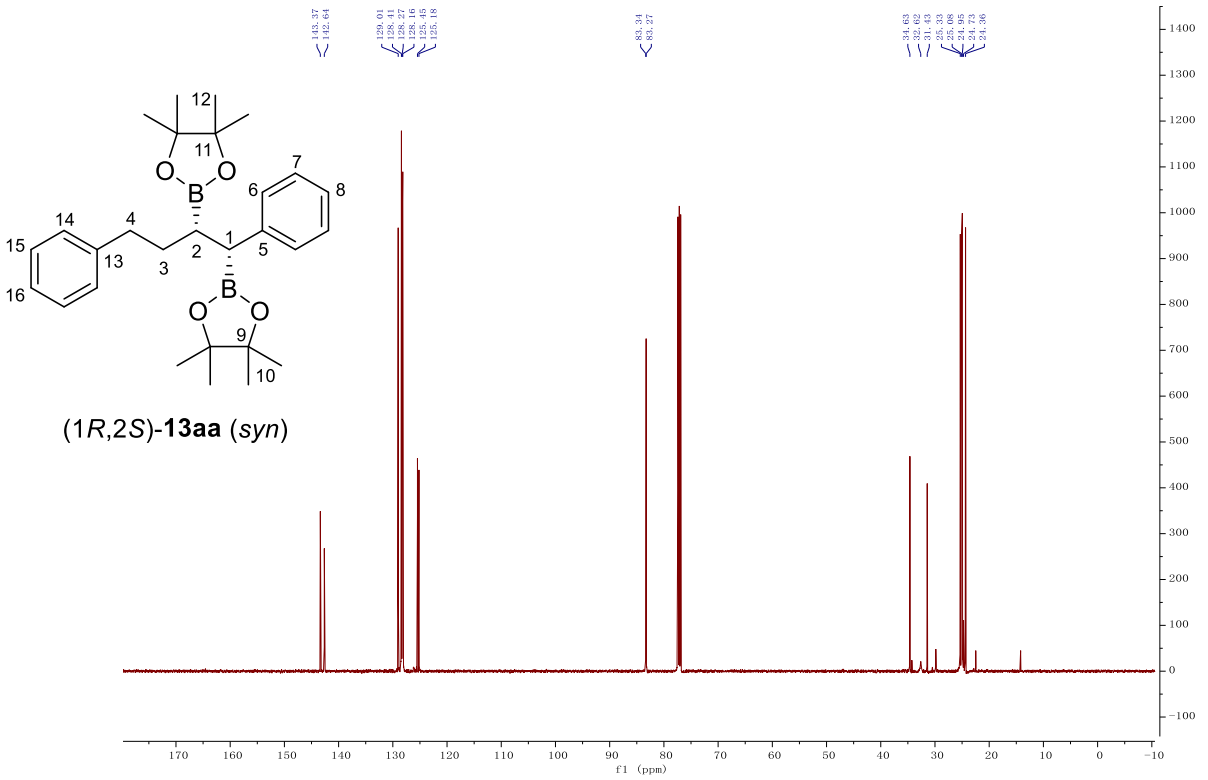


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.369	MF	0.2005	1643.19092	136.62286	81.8902
2	9.801	VB	0.2209	363.38849	23.92654	18.1098

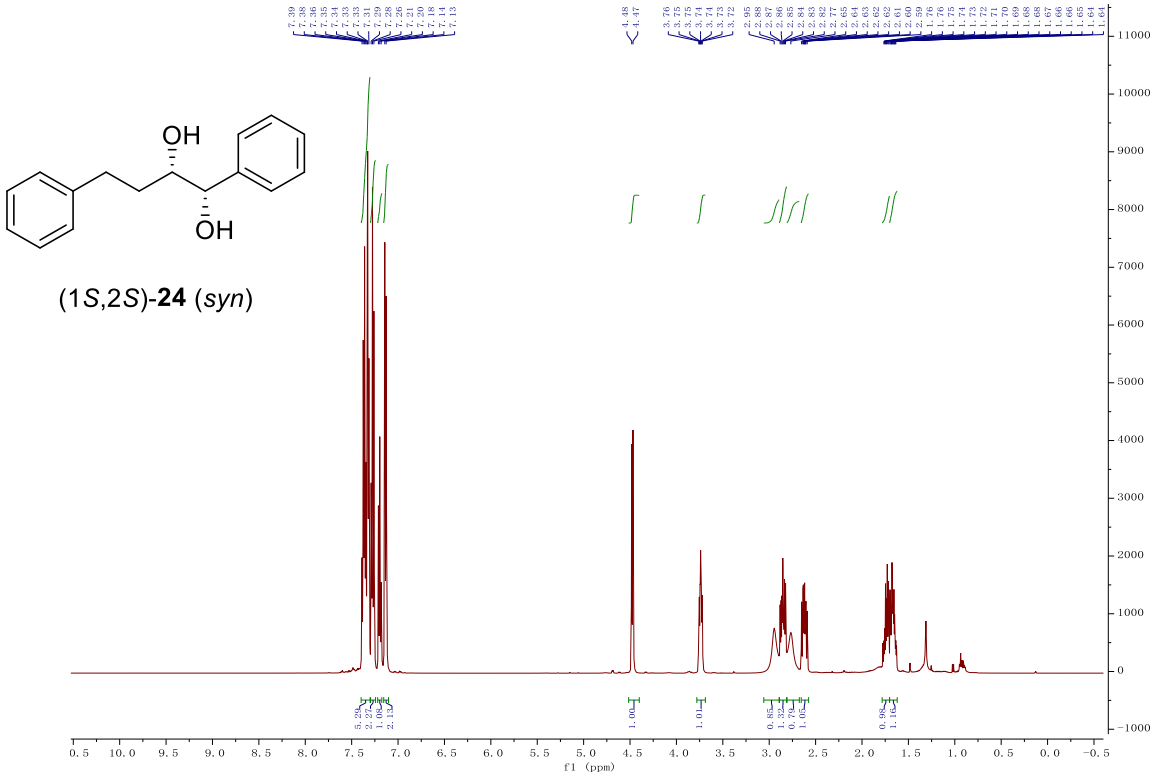
(1*R*,2*S*)-*syn*-**13aa** ^{1}H NMR (500 MHz, $CDCl_3$)



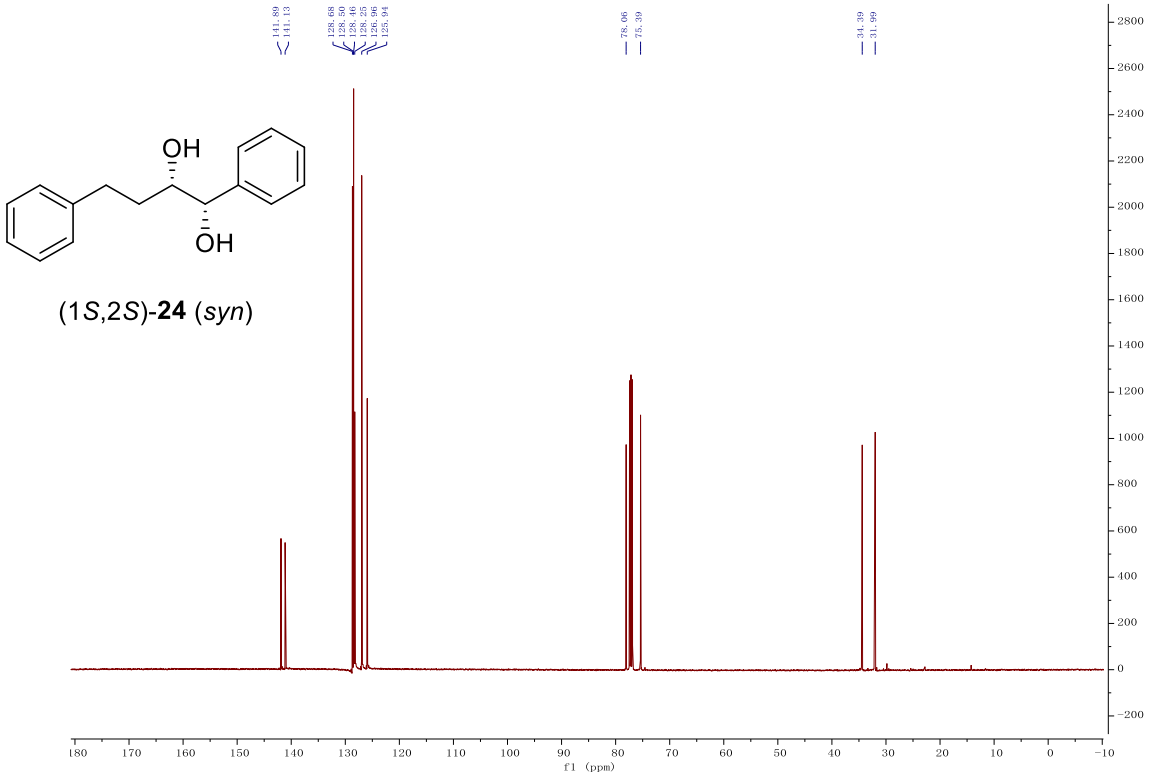
(1*R*,2*S*)-*syn*-**13aa** ^{13}C NMR (126 MHz, $CDCl_3$)



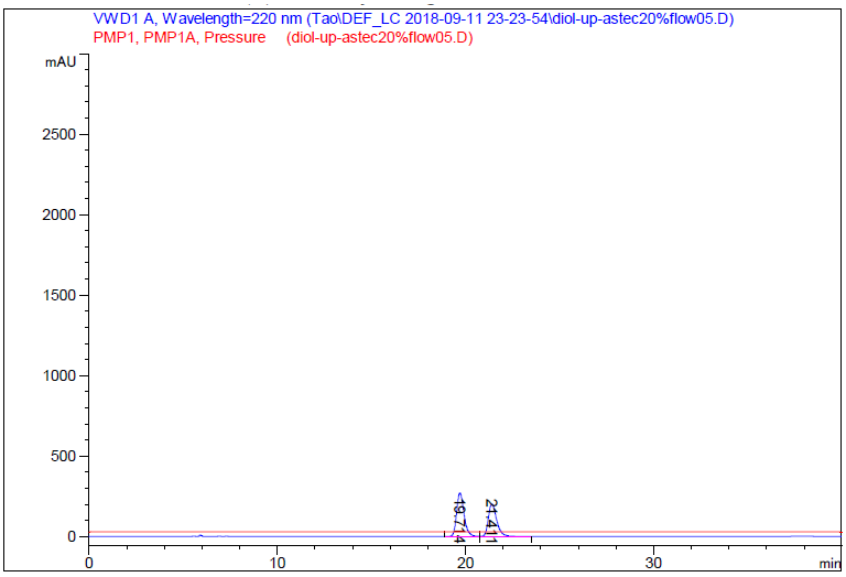
(1*S*,2*S*)-*syn*-**24** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*S*,2*S*)-*syn*-**24** ^{13}C NMR (126 MHz, $CDCl_3$)

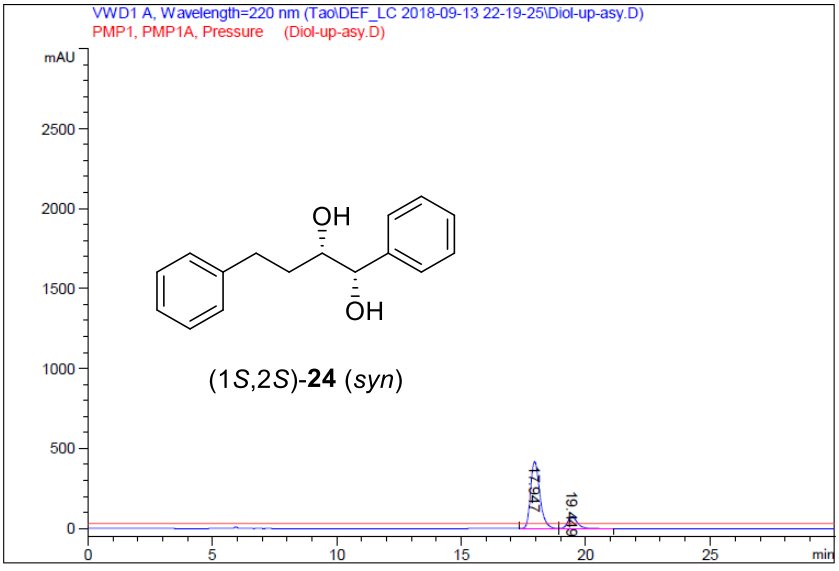


(±)-*syn*-**24**



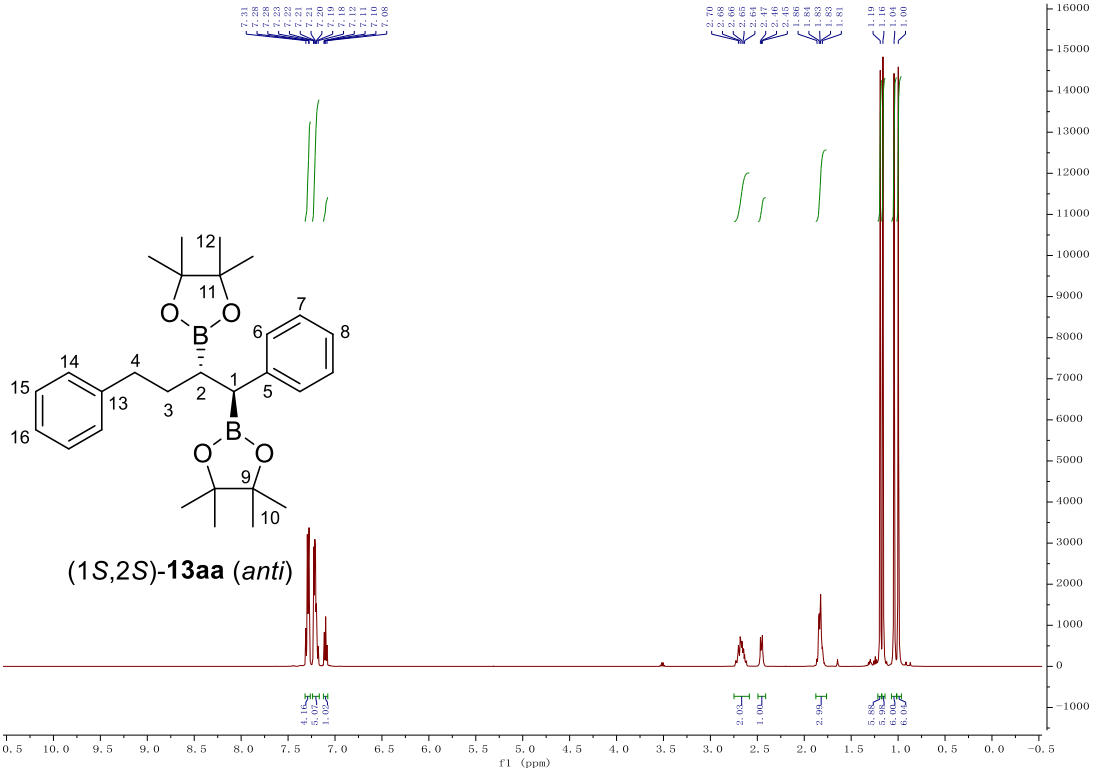
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.714	VV	0.4196	7423.31104	270.16803	54.2779
2	21.411	VB	0.4773	6253.18018	202.16299	45.7221

(1*S*,2*S*)-*syn*-**24**

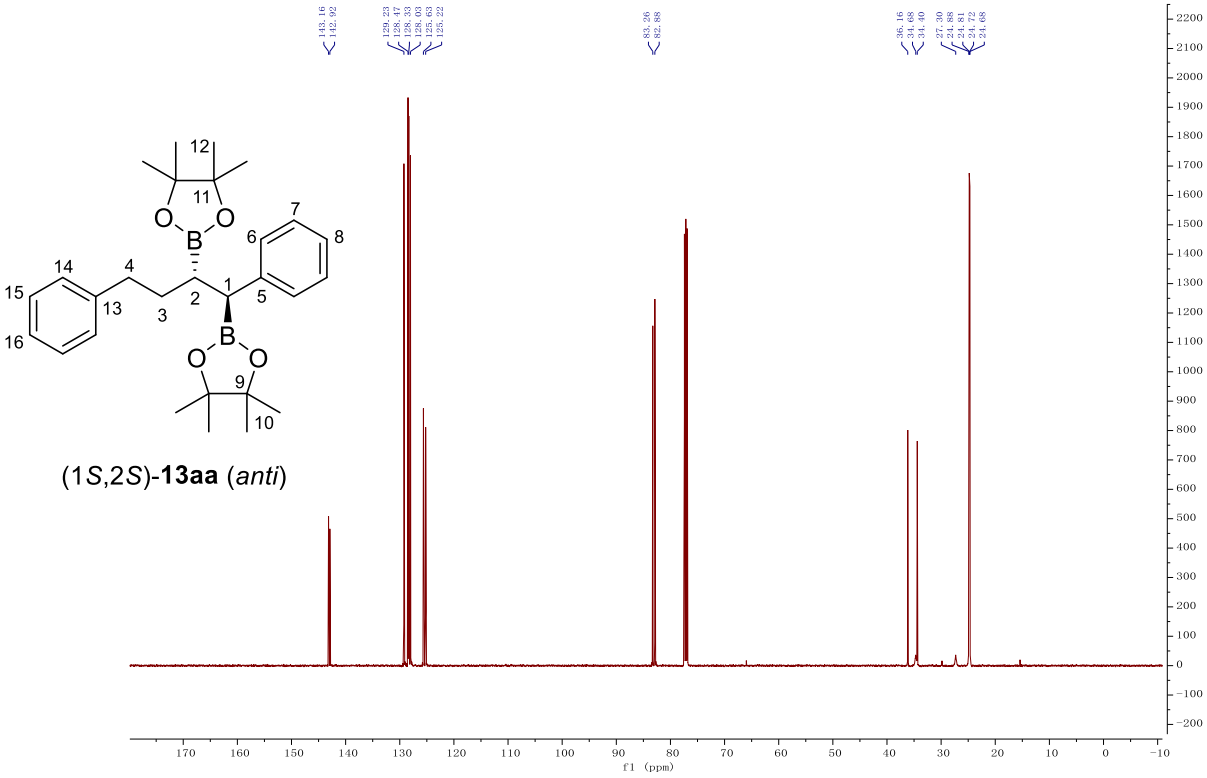


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.947	VV	0.4041	1.09446e4	418.55154	84.0713
2	19.449	VV	0.4122	2073.64014	75.84149	15.9287

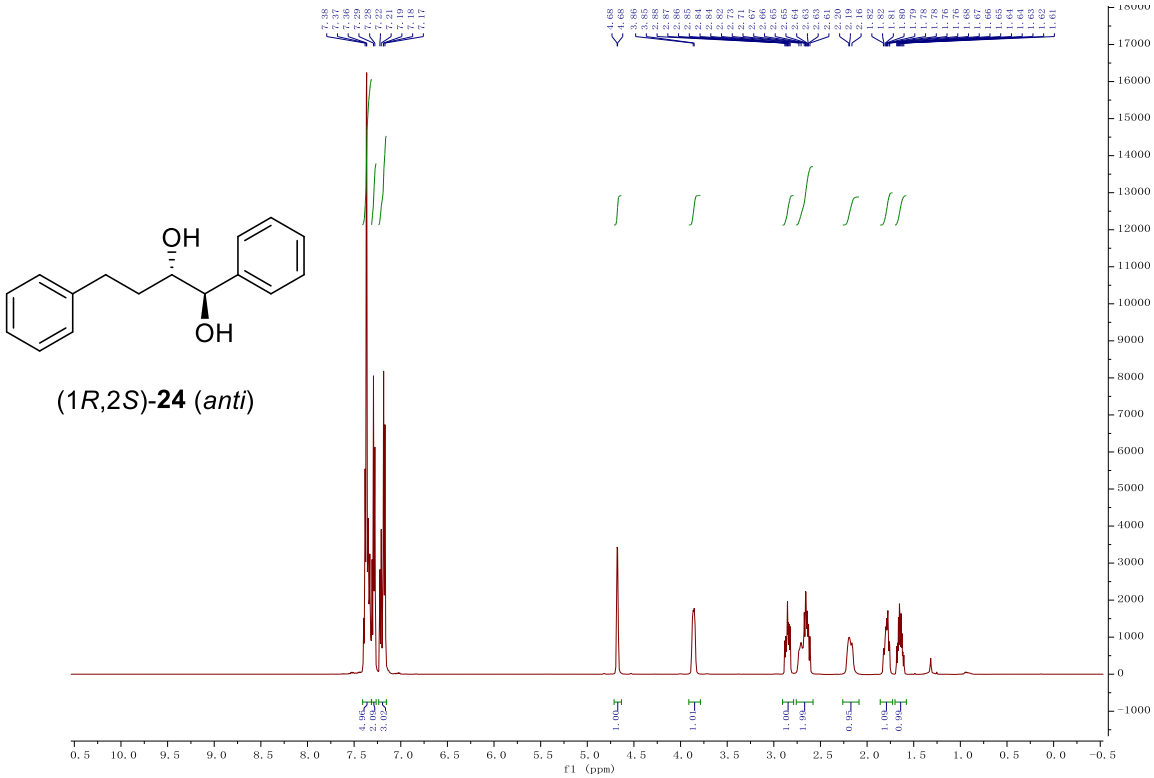
(1*S*,2*S*)-*anti*-**13aa** ^{1}H NMR (500 MHz, $CDCl_3$)



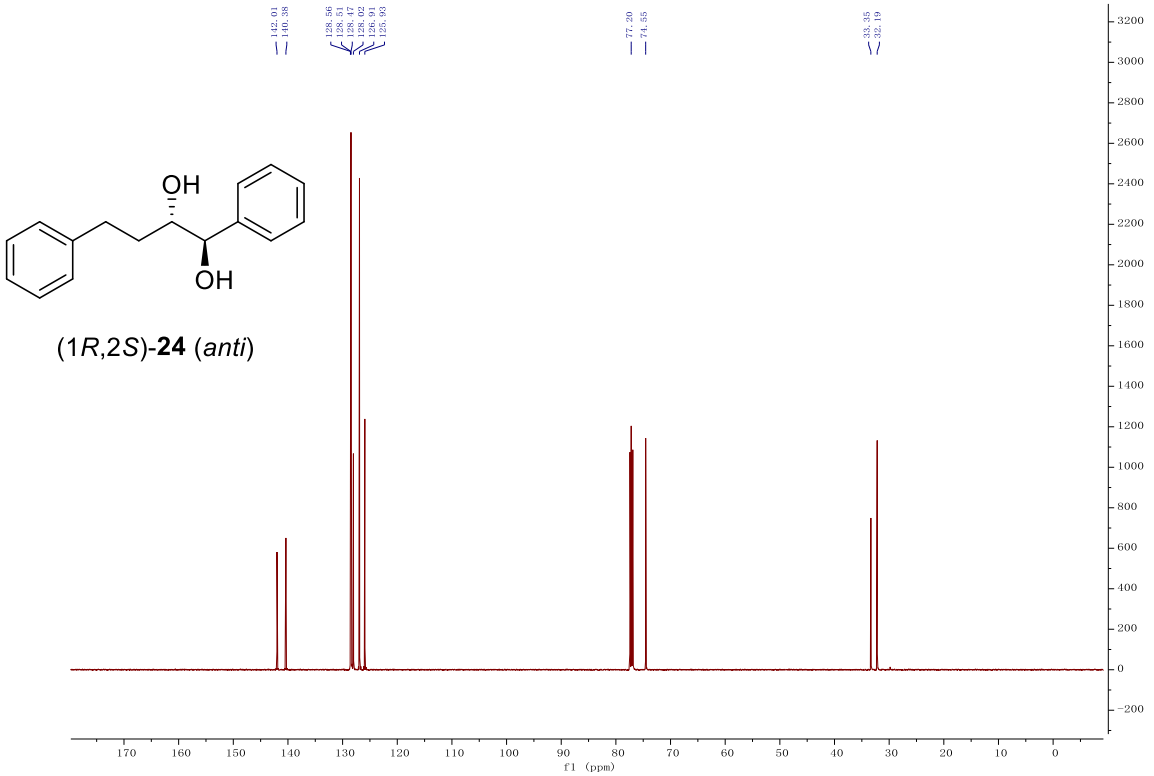
(1*S*,2*S*)-*anti*-**13aa** ^{13}C NMR (126 MHz, $CDCl_3$)



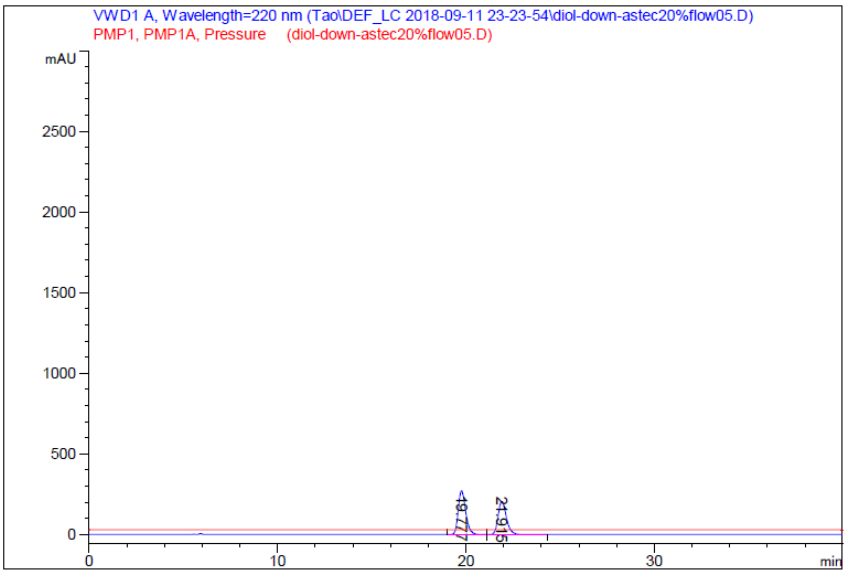
(1*R*,2*S*)-*anti*-**24** ^{1}H NMR (500 MHz, $CDCl_3$)



(1*R*,2*S*)-*anti*-**24** ^{13}C NMR (126 MHz, $CDCl_3$)

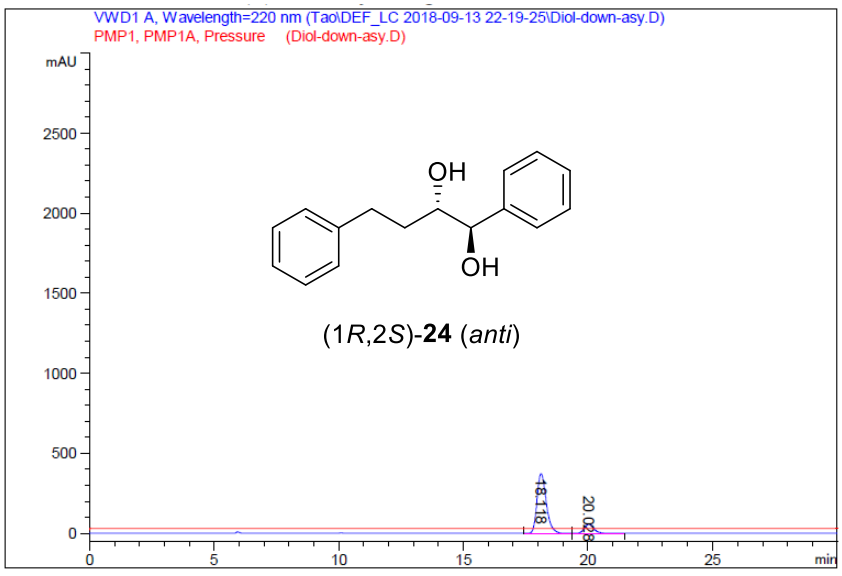


(±)-*anti*-**24**



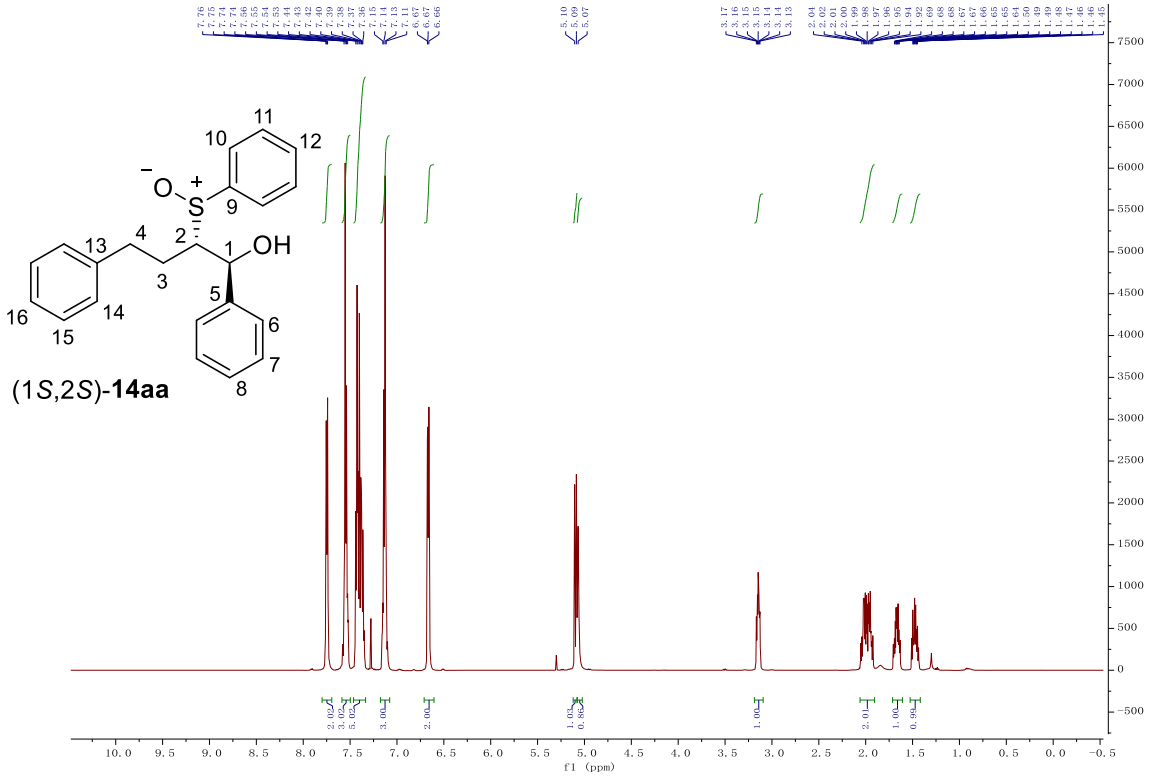
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.777	BV	0.4306	7594.12598	271.94031	54.3374
2	21.915	VB	0.4778	6381.73584	206.06836	45.6626

(1*R*,2*S*)-*anti*-**24**

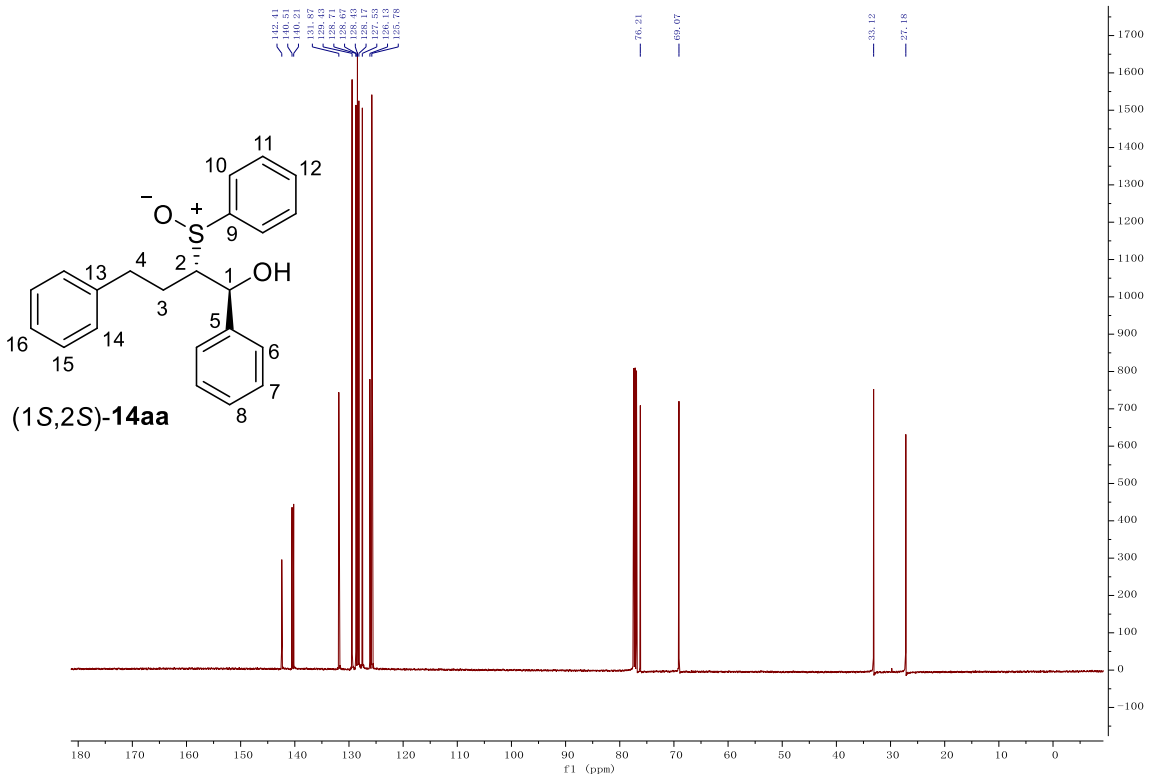


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.118	VV	0.4024	9697.09180	372.87738	85.9655
2	20.028	VB	0.4175	1583.11707	57.98481	14.0345

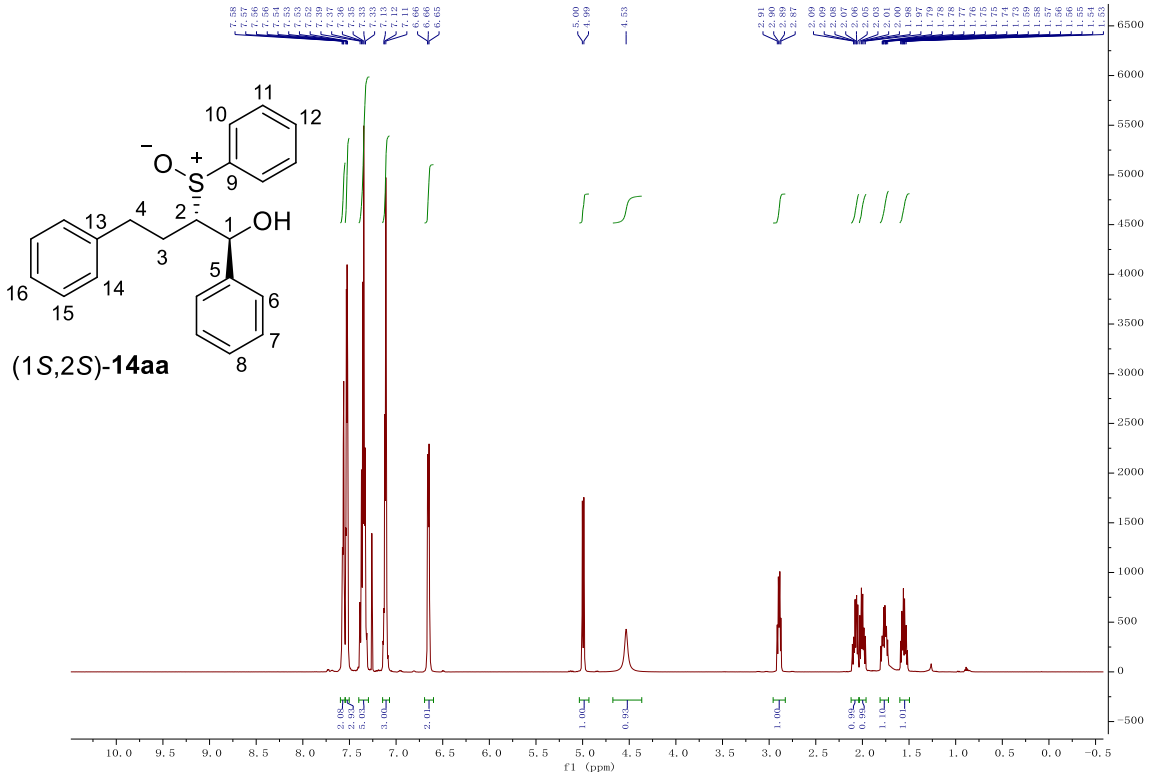
(1*S*,2*S*)-**14aa** (major diastereomer) ^{1}H NMR (500 MHz, $CDCl_3$)



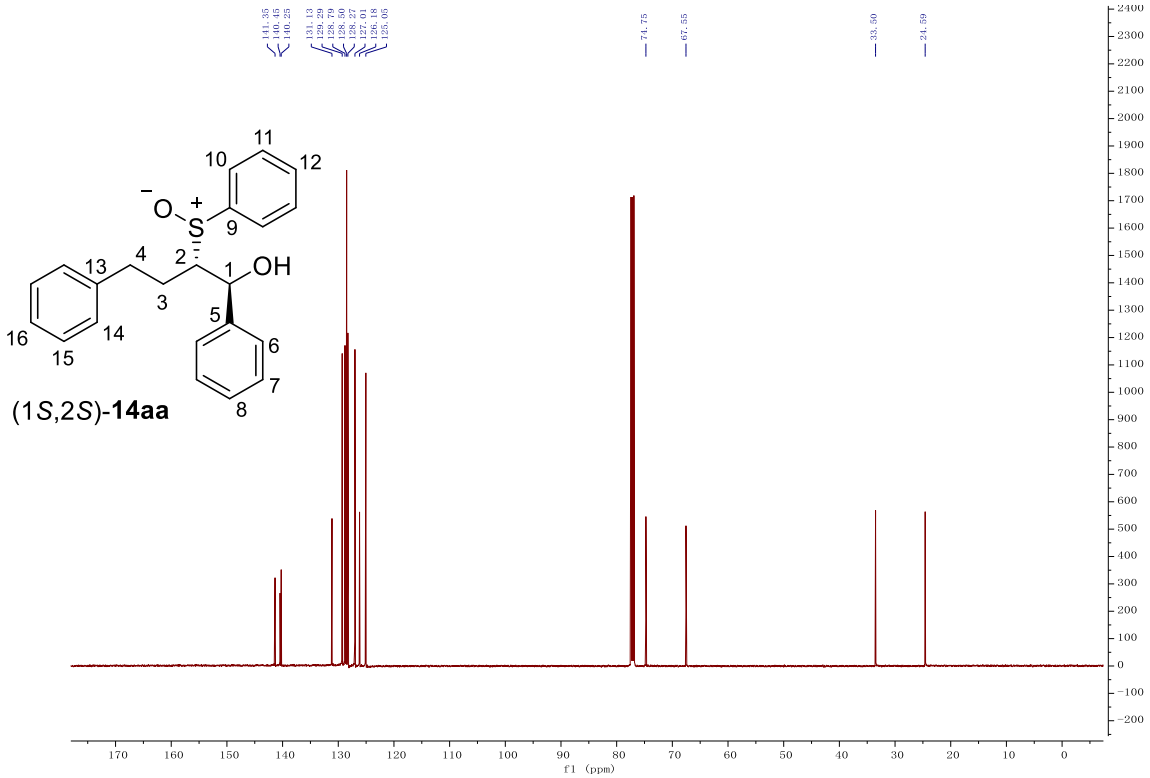
(1*S*,2*S*)-**14aa** (major diastereomer) ^{13}C NMR (126 MHz, $CDCl_3$)



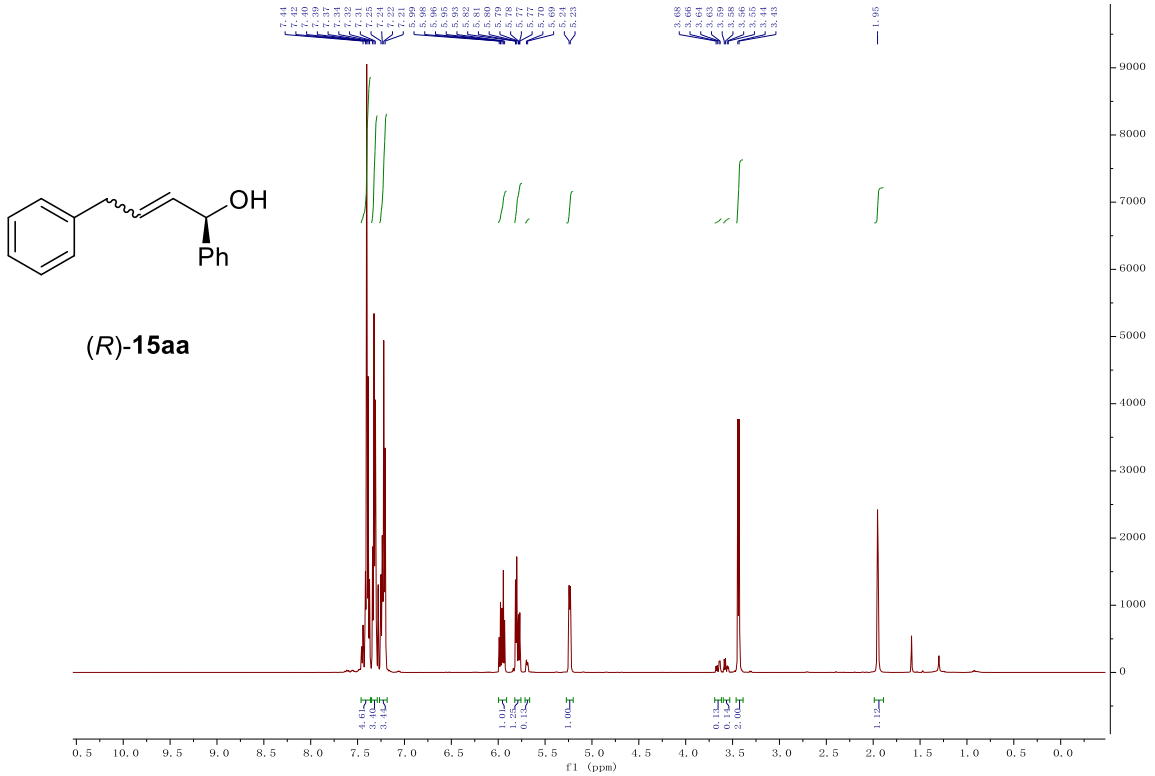
(1*S*,2*S*)-**14aa** (minor diastereomer) ^{1}H NMR (500 MHz, $CDCl_3$)

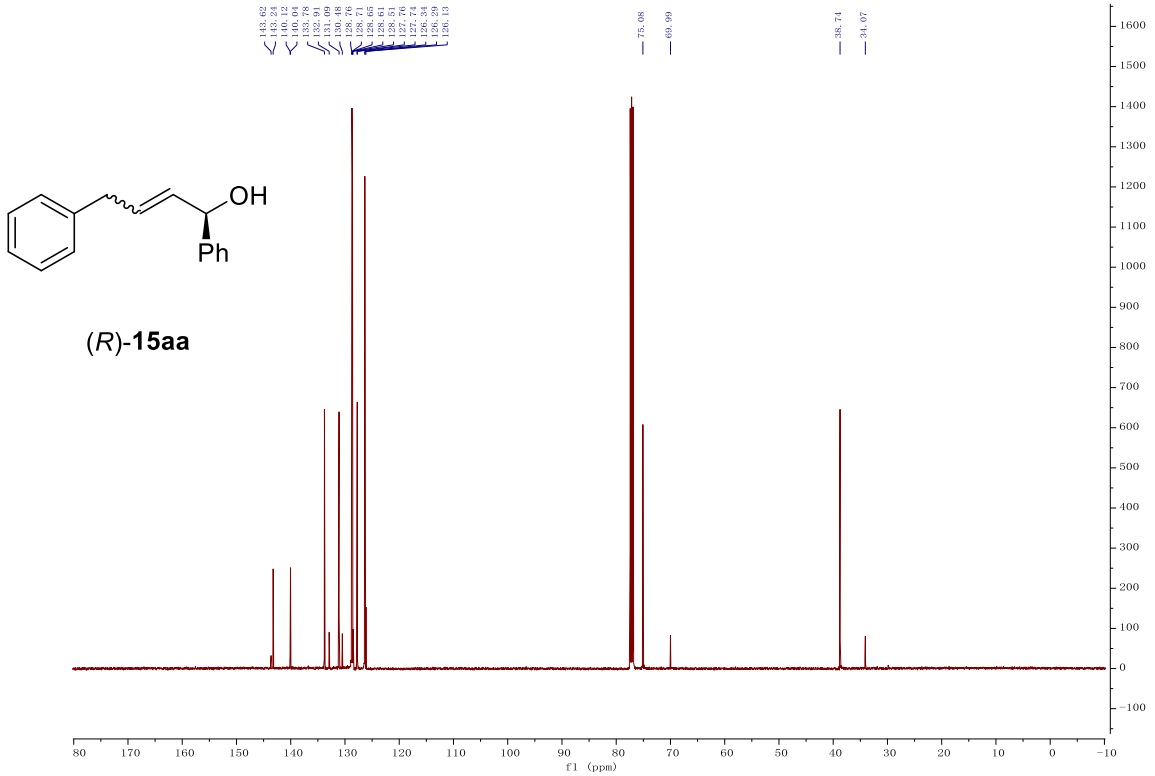


(1*S*,2*S*)-**14aa** (minor diastereomer) ^{13}C NMR (126 MHz, $CDCl_3$)

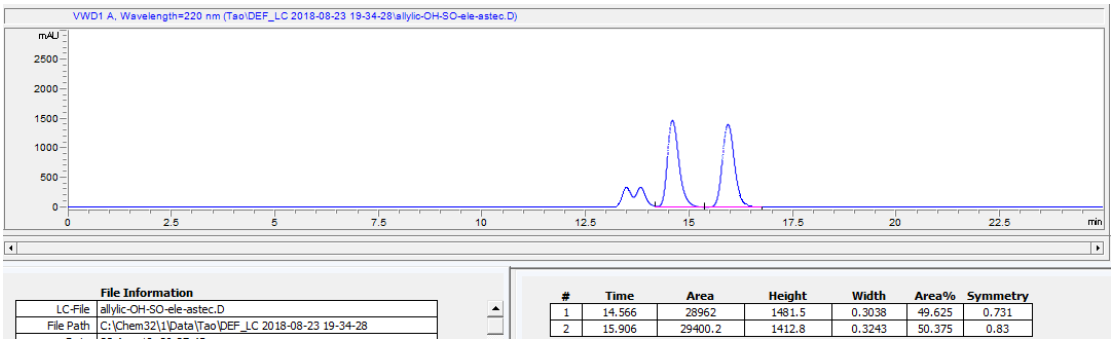


(*R*)-**15aa** (*E*/*Z* 8:1) ^{1}H NMR (500 MHz, $CDCl_3$)





(±)-(*E*)-**15aa**



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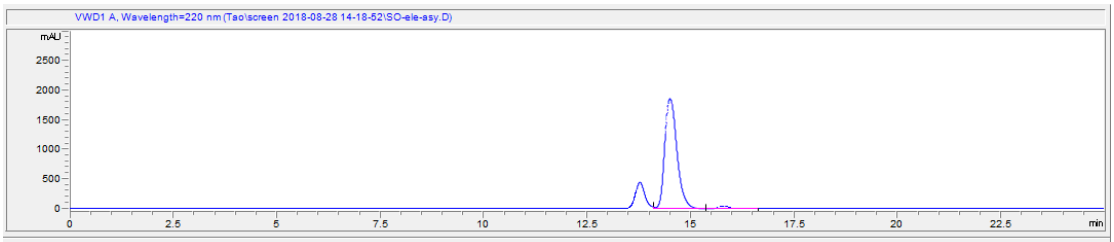
1	14.566	28962	1481.5	0.3038	49.625	0.731
2	15.906	29400.2	1412.8	0.3243	50.375	0.83

(*R*)-(*E*)-**15aa**



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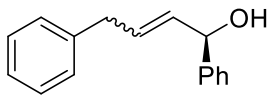
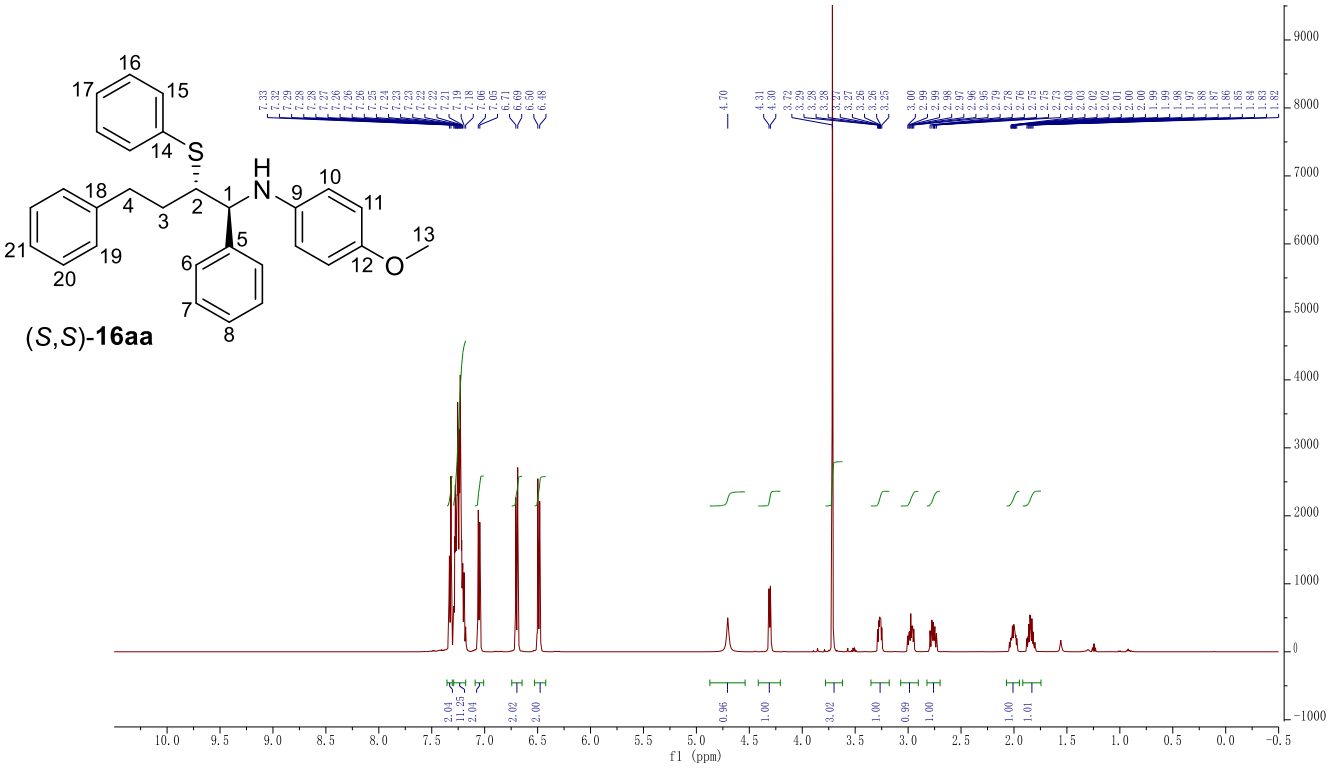
LC-File	SO-ele-asy.D
File Path	C:\Chem32\1\Data\Tao\screen 2018-08-28 14-18-52
Date	28-Aug-18, 14:39:40

#	Time	Area	Height	Width	Area%	Symmetry
1	14.472	38636.5	1873	0.3222	97.843	0.717
2	15.777	851.7	42.8	0.3022	2.157	0.825

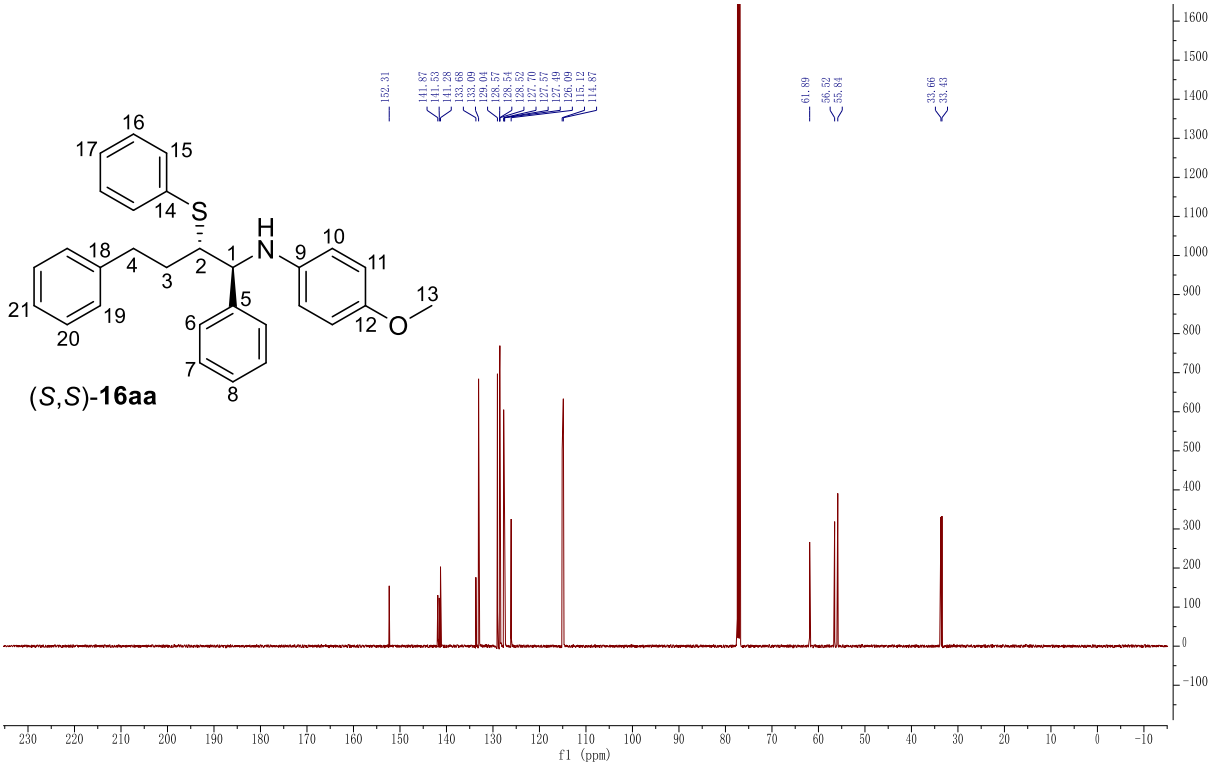


(*R*)-**15aa**

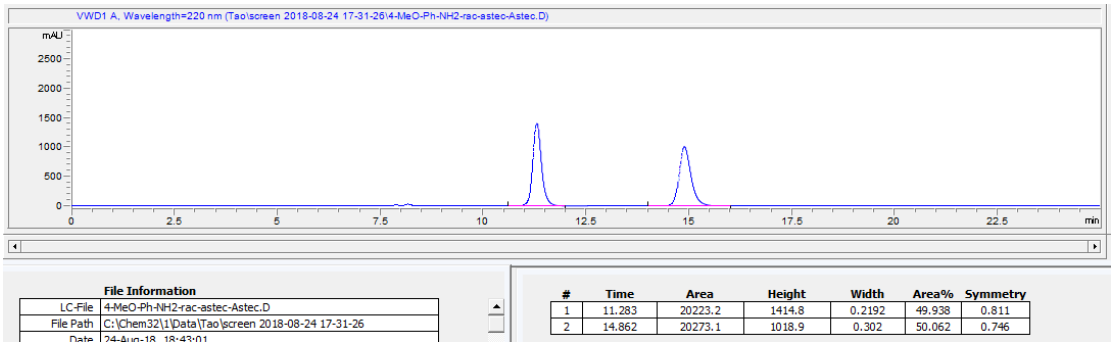
(1*S*,2*S*)-(–)-**16aa** ^{1}H NMR (500 MHz, $CDCl_3$)



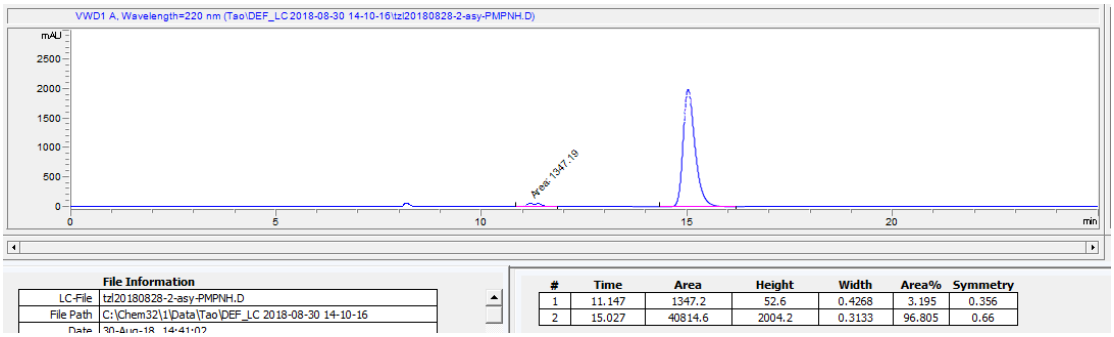
(1*S*,2*S*)-(–)-**16aa** ^{13}C NMR (126 MHz, $CDCl_3$)

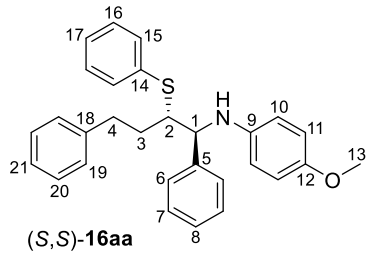


(±)-**16aa**



(1*S*,2*S*)-(–)-**16aa**





(*S*,*S*)-**16aa**

X-Ray data for (*S,S*)-6ai. Crystal data and structure refinement.

Identification code	CCDC 1866767	
Empirical formula	$C_{30}H_{37}BO_2S$	
Formula weight	472.52	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.5200(2) Å	□= 90°.
	b = 13.4283(4) Å	□= 90°.
	c = 20.6016(6) Å	□ = 90°.
Volume	2633.66 (12) $Å^3$	
Z	4	
Density (calculated)	1.192 Mg/m^3	
Absorption coefficient	0.613 mm^{-1}	
F(000)	1016	
Crystal size	0.51 x 0.37 x 0.26 mm	
Theta range for data collection	2.36 to 28.30°.	
Index ranges	-12<=h<=12, -17<=k<=17, -27<=l<=27	
Reflections collected	49428	
Independent reflections	6522 [R(int) = 0.044]	
Completeness to theta = 28.3°	99.8 %	
Absorption correction	Integration	
Max. and min. transmission	0.746 and 0.700	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6522 / 0 / 314	
Goodness-of-fit on F^2	0.995	
Final R indices [I>2sigma(I)]	R1 = 0.0306, wR2 = 0.0733	
Largest diff. peak and hole	0.2864 and -0.1977 e.$Å^{-3}$	

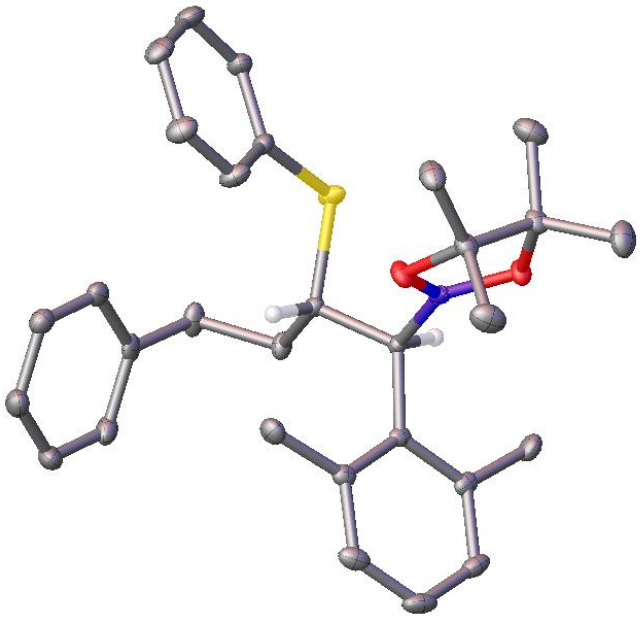


Figure 1. X-ray structure of complex (*S*,*S*)-**6ai.**

The crystals were obtained directly from recrystallization as yellow needles 0.51 x 0.37 x 0.26 mm in size and mounted using oil (Paratone-N, Exxon) to a thin glass fiver with the (1 0 0) scattering planes roughly normal to the spindle axis. Systematic absences for (*S*,*S*)-**6ai** were consistent with the space group $P2_12_12_1$. Unit cell dimensions were a = 9.5200(2) Å, b = 13.4283(4) Å, c = 20.6016(6) Å Å, α= 90°, β= 90°, γ = 90°. Integration absorption correction was applied and maximum and minimum transmission factors were 0.746 and 0.700. The 6522 data points were used in the full-matrix least-squares refinement. The structure was solved using charge flipping by using SHELXTL software package.[51] Hydrogen atoms were placed in "idealized" positions and their displacement parameters were fixed to be 20-50 % larger than those of the attached non-hydrogen atoms.

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Refinement. Omit (060), (012), (110), and (014). No restraints nor constraints

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for (mo_DD48M_0m)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.37901 (4)	0.65733 (2)	0.510290 (15)	0.01819 (8)
O1	0.23720 (9)	0.50566 (7)	0.63213 (5)	0.0178 (2)
O2	0.26085 (9)	0.65401 (7)	0.68593 (4)	0.01567 (18)
C1	0.68061 (15)	0.25499 (11)	0.43328 (7)	0.0222 (3)
H1	0.67861 (15)	0.18487 (11)	0.42727 (7)	0.0267 (3)*
C2	0.79399 (15)	0.29997 (12)	0.46412 (7)	0.0249 (3)
H2	0.87002 (15)	0.26046 (12)	0.47923 (7)	0.0299 (4)*
C3	0.57054 (15)	0.31367 (10)	0.41143 (7)	0.0196 (3)
H3	0.49225 (15)	0.28347 (10)	0.39069 (7)	0.0235 (3)*
C4	0.79636 (14)	0.40235 (11)	0.47285 (6)	0.0223 (3)
H4	0.87379 (14)	0.43219 (11)	0.49448 (6)	0.0268 (4)*
C5	0.57389 (14)	0.41639 (10)	0.41964 (6)	0.0184 (3)
H5	0.49811 (14)	0.45574 (10)	0.40407 (6)	0.0221 (3)*
C6	0.68678 (14)	0.46234 (10)	0.45037 (6)	0.0175 (3)
C7	0.69006 (16)	0.57360 (10)	0.46128 (6)	0.0218 (3)
H7a	0.78459 (16)	0.59923 (10)	0.45024 (6)	0.0262 (3)*
H7b	0.62146 (16)	0.60587 (10)	0.43193 (6)	0.0262 (3)*
C8	0.65522 (13)	0.60158 (10)	0.53187 (6)	0.0166 (3)
H8a	0.72178 (13)	0.56677 (10)	0.56099 (6)	0.0199 (3)*
H8b	0.67005 (13)	0.67404 (10)	0.53747 (6)	0.0199 (3)*
C9	0.50543 (13)	0.57613 (9)	0.55292 (6)	0.0126 (2)
H9	0.48508 (13)	0.50505 (9)	0.54191 (6)	0.0151 (3)*
C10	0.48308 (12)	0.59231 (9)	0.62662 (6)	0.0117 (2)
H10	0.50946 (12)	0.66330 (9)	0.63478 (6)	0.0140 (3)*
C11	0.57330 (12)	0.53103 (10)	0.67380 (6)	0.0128 (2)
C12	0.58838 (12)	0.42669 (10)	0.66956 (6)	0.0151 (2)
C13	0.63367 (13)	0.58072 (10)	0.72772 (6)	0.0155 (2)
C14	0.52427 (14)	0.36410 (9)	0.61617 (7)	0.0189 (3)
H14a	0.5774 (7)	0.3738 (6)	0.57592 (14)	0.0283 (4)*
H14b	0.5275 (10)	0.29369 (12)	0.6286 (2)	0.0283 (4)*
H14c	0.4264 (4)	0.3843 (5)	0.6094 (3)	0.0283 (4)*
C15	0.62111 (16)	0.69221 (10)	0.73714 (6)	0.0209 (3)
H15a	0.6623 (10)	0.71082 (14)	0.7790 (2)	0.0313 (4)*
H15b	0.6711 (9)	0.72661 (10)	0.7021 (3)	0.0313 (4)*
H15c	0.52178 (17)	0.71134 (15)	0.7364 (5)	0.0313 (4)*
C16	0.66380 (13)	0.37535 (11)	0.71756 (7)	0.0203 (3)
H16	0.67580 (13)	0.30536 (11)	0.71382 (7)	0.0243 (3)*
C17	0.70548 (13)	0.52689 (11)	0.77508 (6)	0.0201 (3)
H17	0.74440 (13)	0.56092 (11)	0.81129 (6)	0.0241 (3)*
C18	0.72103 (14)	0.42472 (12)	0.77025 (7)	0.0231 (3)
H18	0.77048 (14)	0.38884 (12)	0.80276 (7)	0.0277 (3)*
C19	0.27465 (13)	0.57724 (10)	0.46143 (6)	0.0157 (2)
C20	0.24599 (14)	0.47803 (11)	0.47566 (7)	0.0210 (3)
H20	0.28421 (14)	0.44860 (11)	0.51369 (7)	0.0253 (3)*

C21	0.21368 (15)	0.61993 (10)	0.40629 (6)	0.0196 (3)
H21	0.23336 (15)	0.68733 (10)	0.39561 (6)	0.0236 (3)*
C22	0.16154 (15)	0.42156 (11)	0.43446 (7)	0.0233 (3)
H22	0.14605 (15)	0.35308 (11)	0.44354 (7)	0.0279 (3)*
C23	0.12431 (16)	0.56429 (11)	0.36693 (6)	0.0243 (3)
H23	0.07980 (16)	0.59474 (11)	0.33074 (6)	0.0292 (3)*
C24	0.10009 (15)	0.46452 (12)	0.38041 (7)	0.0246 (3)
H24	0.04170 (15)	0.42596 (12)	0.35272 (7)	0.0295 (4)*
C25	0.10955 (13)	0.51575 (10)	0.67193 (6)	0.0173 (2)
C26	−0.01545 (14)	0.48278 (11)	0.63209 (7)	0.0239 (3)
H26a	−0.0159 (7)	0.5186 (6)	0.5906 (2)	0.0359 (4)*
H26b	−0.0092 (6)	0.41101 (19)	0.6240 (5)	0.0359 (4)*
H26c	−0.10220 (15)	0.4974 (8)	0.6559 (2)	0.0359 (4)*
C27	0.12852 (17)	0.44748 (11)	0.73029 (8)	0.0283 (3)
H27a	0.1454 (13)	0.3793 (2)	0.71530 (8)	0.0425 (5)*
H27b	0.2089 (8)	0.4702 (6)	0.7561 (3)	0.0425 (5)*
H27c	0.0435 (5)	0.4491 (7)	0.7571 (3)	0.0425 (5)*
C28	0.11140 (13)	0.62884 (9)	0.68967 (6)	0.0164 (2)
C29	0.03659 (16)	0.69350 (11)	0.63938 (8)	0.0271 (3)
H29a	0.0534 (10)	0.76393 (11)	0.6491 (3)	0.0406 (5)*
H29b	0.0729 (9)	0.6780 (6)	0.59602 (10)	0.0406 (5)*
H29c	−0.0645 (2)	0.6800 (6)	0.6407 (4)	0.0406 (5)*
C30	0.05973 (16)	0.65390 (13)	0.75723 (7)	0.0283 (3)
H30a	0.1188 (8)	0.6203 (7)	0.78943 (7)	0.0424 (5)*
H30b	0.0646 (12)	0.72607 (15)	0.7639 (2)	0.0424 (5)*
H30c	−0.0377 (4)	0.6316 (8)	0.7621 (2)	0.0424 (5)*
B1	0.32321 (15)	0.58392 (11)	0.64725 (7)	0.0136 (3)

Atomic displacement parameters (Å²) for (mo_DD48M_0m)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02331 (15)	0.01365 (14)	0.01761 (14)	−0.00035 (12)	−0.00727 (12)	0.00146 (11)
O1	0.0105 (4)	0.0188 (5)	0.0242 (5)	−0.0003 (3)	0.0029 (4)	−0.0052 (4)
O2	0.0108 (4)	0.0171 (4)	0.0191 (4)	−0.0016 (4)	0.0028 (3)	−0.0042 (4)
C1	0.0269 (7)	0.0200 (7)	0.0198 (6)	0.0034 (5)	0.0012 (6)	−0.0025 (5)
C2	0.0218 (7)	0.0299 (7)	0.0231 (7)	0.0105 (6)	−0.0033 (6)	−0.0061 (6)
C3	0.0199 (6)	0.0234 (7)	0.0155 (6)	−0.0015 (5)	0.0001 (5)	−0.0004 (5)
C4	0.0172 (6)	0.0312 (8)	0.0186 (6)	−0.0005 (5)	0.0016 (5)	−0.0087 (5)
C5	0.0194 (6)	0.0227 (7)	0.0131 (6)	0.0031 (5)	0.0025 (5)	0.0012 (5)
C6	0.0217 (6)	0.0200 (7)	0.0109 (5)	−0.0007 (5)	0.0069 (5)	−0.0017 (5)
C7	0.0298 (7)	0.0196 (7)	0.0161 (6)	−0.0054 (6)	0.0092 (5)	−0.0018 (5)
C8	0.0171 (6)	0.0178 (6)	0.0148 (6)	−0.0039 (5)	0.0038 (5)	−0.0031 (5)
C9	0.0140 (5)	0.0124 (6)	0.0113 (5)	0.0000 (4)	−0.0007 (4)	0.0003 (4)
C10	0.0117 (5)	0.0126 (5)	0.0108 (5)	−0.0003 (4)	−0.0008 (4)	−0.0011 (4)
C11	0.0082 (5)	0.0186 (6)	0.0117 (5)	−0.0003 (4)	0.0016 (4)	0.0019 (5)
C12	0.0113 (5)	0.0178 (6)	0.0162 (6)	−0.0002 (4)	0.0025 (4)	0.0028 (5)
C13	0.0108 (5)	0.0239 (6)	0.0117 (5)	−0.0028 (5)	0.0028 (4)	0.0012 (5)
C14	0.0207 (6)	0.0129 (6)	0.0230 (6)	0.0008 (5)	0.0008 (5)	0.0004 (5)
C15	0.0214 (6)	0.0257 (7)	0.0156 (6)	−0.0025 (6)	−0.0027 (5)	−0.0056 (5)
C16	0.0147 (6)	0.0206 (7)	0.0254 (7)	0.0006 (5)	0.0025 (5)	0.0090 (5)
C17	0.0134 (6)	0.0343 (8)	0.0126 (6)	−0.0043 (5)	−0.0013 (5)	0.0032 (5)
C18	0.0144 (6)	0.0345 (8)	0.0204 (6)	0.0011 (6)	−0.0013 (5)	0.0131 (6)

C19	0.0141 (5)	0.0196 (6)	0.0133 (5)	0.0003 (5)	−0.0017 (5)	−0.0021 (5)
C20	0.0211 (6)	0.0236 (7)	0.0184 (6)	−0.0056 (5)	−0.0069 (5)	0.0038 (5)
C21	0.0218 (6)	0.0207 (6)	0.0163 (6)	0.0035 (5)	−0.0024 (5)	0.0011 (5)
C22	0.0223 (7)	0.0236 (7)	0.0238 (7)	−0.0073 (5)	−0.0057 (5)	0.0023 (6)
C23	0.0245 (7)	0.0323 (8)	0.0162 (6)	0.0021 (6)	−0.0067 (6)	0.0021 (5)
C24	0.0200 (7)	0.0346 (8)	0.0192 (6)	−0.0056 (6)	−0.0057 (5)	−0.0030 (6)
C25	0.0122 (5)	0.0184 (6)	0.0213 (6)	0.0000 (5)	0.0023 (5)	−0.0015 (5)
C26	0.0137 (6)	0.0262 (7)	0.0319 (8)	−0.0025 (5)	0.0006 (5)	−0.0090 (6)
C27	0.0247 (7)	0.0276 (7)	0.0327 (8)	0.0005 (6)	0.0035 (6)	0.0108 (6)
C28	0.0100 (5)	0.0181 (6)	0.0212 (6)	−0.0010 (5)	0.0033 (5)	−0.0022 (5)
C29	0.0209 (7)	0.0227 (7)	0.0376 (8)	0.0038 (6)	0.0001 (6)	0.0057 (6)
C30	0.0226 (7)	0.0332 (8)	0.0290 (7)	−0.0040 (6)	0.0092 (6)	−0.0089 (7)
B1	0.0131 (6)	0.0150 (6)	0.0127 (6)	0.0010 (5)	−0.0021 (5)	0.0014 (5)

Geometric parameters (Å, º) for (mo_DD48M_0m)

S1—C9	1.8462 (12)	C14—H14c	0.9800
S1—C19	1.7767 (13)	C15—H15a	0.9800
O1—C25	1.4722 (15)	C15—H15b	0.9800
O1—B1	1.3681 (17)	C15—H15c	0.9800
O2—C28	1.4644 (15)	C16—H16	0.9500
O2—B1	1.3687 (16)	C16—C18	1.384 (2)
C1—H1	0.9500	C17—H17	0.9500
C1—C2	1.390 (2)	C17—C18	1.384 (2)
C1—C3	1.3863 (19)	C18—H18	0.9500
C2—H2	0.9500	C19—C20	1.3911 (19)
C2—C4	1.387 (2)	C19—C21	1.3986 (17)
C3—H3	0.9500	C20—H20	0.9500
C3—C5	1.3900 (19)	C20—C22	1.3934 (19)
C4—H4	0.9500	C21—H21	0.9500
C4—C6	1.397 (2)	C21—C23	1.3927 (19)
C5—H5	0.9500	C22—H22	0.9500
C5—C6	1.3916 (19)	C22—C24	1.384 (2)
C6—C7	1.5111 (18)	C23—H23	0.9500
C7—H7a	0.9900	C23—C24	1.388 (2)
C7—H7b	0.9900	C24—H24	0.9500
C7—C8	1.5381 (17)	C25—C26	1.5120 (18)
C8—H8a	0.9900	C25—C27	1.5227 (19)
C8—H8b	0.9900	C25—C28	1.5620 (18)
C8—C9	1.5291 (16)	C26—H26a	0.9800
C9—H9	1.0000	C26—H26b	0.9800
C9—C10	1.5486 (16)	C26—H26c	0.9800
C10—H10	1.0000	C27—H27a	0.9800
C10—C11	1.5360 (16)	C27—H27b	0.9800
C10—B1	1.5842 (18)	C27—H27c	0.9800
C11—C12	1.4111 (17)	C28—C29	1.5279 (19)
C11—C13	1.4176 (17)	C28—C30	1.5141 (19)
C12—C14	1.5128 (18)	C29—H29a	0.9800
C12—C16	1.4031 (18)	C29—H29b	0.9800
C13—C15	1.5143 (19)	C29—H29c	0.9800
C13—C17	1.3935 (18)	C30—H30a	0.9800
C14—H14a	0.9800	C30—H30b	0.9800
C14—H14b	0.9800	C30—H30c	0.9800

C19—S1—C9	106.05 (6)	H16—C16—C12	119.37 (8)
B1—O1—C25	107.25 (10)	C18—C16—C12	121.26 (13)
B1—O2—C28	107.06 (10)	C18—C16—H16	119.37 (8)
C2—C1—H1	120.39 (8)	H17—C17—C13	119.45 (8)
C3—C1—H1	120.39 (8)	C18—C17—C13	121.09 (13)
C3—C1—C2	119.23 (13)	C18—C17—H17	119.45 (8)
H2—C2—C1	119.91 (8)	C17—C18—C16	119.31 (12)
C4—C2—C1	120.17 (13)	H18—C18—C16	120.35 (8)
C4—C2—H2	119.91 (9)	H18—C18—C17	120.35 (8)
H3—C3—C1	119.76 (8)	C20—C19—S1	124.75 (10)
C5—C3—C1	120.47 (13)	C21—C19—S1	116.36 (10)
C5—C3—H3	119.76 (8)	C21—C19—C20	118.84 (12)
H4—C4—C2	119.45 (9)	H20—C20—C19	119.80 (7)
C6—C4—C2	121.10 (13)	C22—C20—C19	120.39 (13)
C6—C4—H4	119.45 (8)	C22—C20—H20	119.80 (8)
H5—C5—C3	119.56 (8)	H21—C21—C19	119.78 (8)
C6—C5—C3	120.87 (13)	C23—C21—C19	120.43 (13)
C6—C5—H5	119.56 (8)	C23—C21—H21	119.78 (8)
C5—C6—C4	118.15 (12)	H22—C22—C20	119.76 (8)
C7—C6—C4	120.36 (13)	C24—C22—C20	120.48 (14)
C7—C6—C5	121.47 (13)	C24—C22—H22	119.76 (9)
H7a—C7—C6	109.17 (7)	H23—C23—C21	119.90 (8)
H7b—C7—C6	109.17 (8)	C24—C23—C21	120.20 (12)
H7b—C7—H7a	107.9	C24—C23—H23	119.90 (8)
C8—C7—C6	112.19 (11)	C23—C24—C22	119.56 (13)
C8—C7—H7a	109.17 (7)	H24—C24—C22	120.22 (9)
C8—C7—H7b	109.17 (8)	H24—C24—C23	120.22 (8)
H8a—C8—C7	108.64 (8)	C26—C25—O1	108.69 (10)
H8b—C8—C7	108.64 (7)	C27—C25—O1	106.64 (10)
H8b—C8—H8a	107.6	C27—C25—C26	110.22 (12)
C9—C8—C7	114.49 (11)	C28—C25—O1	102.16 (10)
C9—C8—H8a	108.64 (7)	C28—C25—C26	114.87 (11)
C9—C8—H8b	108.64 (7)	C28—C25—C27	113.53 (11)
C8—C9—S1	109.94 (8)	H26a—C26—C25	109.5
H9—C9—S1	109.25 (4)	H26b—C26—C25	109.5
H9—C9—C8	109.25 (7)	H26b—C26—H26a	109.5
C10—C9—S1	107.10 (8)	H26c—C26—C25	109.5
C10—C9—C8	112.01 (10)	H26c—C26—H26a	109.5
C10—C9—H9	109.25 (6)	H26c—C26—H26b	109.5
H10—C10—C9	105.31 (6)	H27a—C27—C25	109.5
C11—C10—C9	117.94 (10)	H27b—C27—C25	109.5
C11—C10—H10	105.31 (6)	H27b—C27—H27a	109.5
B1—C10—C9	112.64 (10)	H27c—C27—C25	109.5
B1—C10—H10	105.31 (7)	H27c—C27—H27a	109.5
B1—C10—C11	109.23 (9)	H27c—C27—H27b	109.5
C12—C11—C10	123.34 (11)	C25—C28—O2	102.89 (10)
C13—C11—C10	118.06 (11)	C29—C28—O2	106.62 (10)
C13—C11—C12	118.34 (11)	C29—C28—C25	112.87 (11)
C14—C12—C11	123.75 (11)	C30—C28—O2	108.22(11)
C16—C12—C11	119.75 (12)	C30—C28—C25	115.31 (11)
C16—C12—C14	116.48 (12)	C30—C28—C29	110.22 (12)
C15—C13—C11	122.26 (12)	H29a—C29—C28	109.5
C17—C13—C11	120.22 (12)	H29b—C29—C28	109.5
C17—C13—C15	117.50 (12)	H29b—C29—H29a	109.5

H14a—C14—C12	109.5	H29c—C29—C28	109.5
H14b—C14—C12	109.5	H29c—C29—H29a	109.5
H14b—C14—H14a	109.5	H29c—C29—H29b	109.5
H14c—C14—C12	109.5	H30a—C30—C28	109.5
H14c—C14—H14a	109.5	H30b—C30—C28	109.5
H14c—C14—H14b	109.5	H30b—C30—H30a	109.5
H15a—C15—C13	109.5	H30c—C30—C28	109.5
H15b—C15—C13	109.5	H30c—C30—H30a	109.5
H15b—C15—H15a	109.5	H30c—C30—H30b	109.5
H15c—C15—C13	109.5	O2—B1—O1	113.65(11)
H15c—C15—H15a	109.5	C10—B1—O1	124.65(11)
H15c—C15—H15b	109.5	C10—B1—O2	121.60(11)

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