Table of Contents

General Information

^{1}H NMR spectra were recorded on either a Varian Gemini-500 (500 MHz), Varian Gemini-600 (600 MHz), or Varian Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, app = apparent), and coupling constants (Hz). ^{13}C NMR spectra were recorded on either a Varian Gemini-500 (125 MHz), Varian Gemini-600 (150 MHz) or a Varian Inova-500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). ^{11}B NMR spectra were recorded on a Varian Gemini-500 (128 MHz) spectrometer. Chemical shifts are reported in ppm using boron trifluoride diethyl etherate as the external standard (BF_3•$O(C_2H_5)_2$: 0.0 ppm). Infrared (IR) spectra were recorded on a Bruker alpha-P Spectrometer. Frequencies are reported in wavenumbers (cm^{-1}) as follows: strong (s), broad (br), medium (m), and weak (w). Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter. High-resolution mass spectrometry (DART) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA. Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230 x 450 Mesh) purchased from Silicycle, or with a Biotage Isolera One equipped with full wavelength scan. Thin layer chromatography (TLC) was performed on 25 μm silica gel aluminum backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm), ceric ammonium molybdate in water/sulfuric acid (CAM), phosphomolybdic acid in ethanol (PMA), phosphomolybdic acid and cerium sulfate in water/sulfuric acid (Seebach), or potassium permanganate ($KMnO_4$). Analytical chiral supercritical fluid chromatography (SFC) was performed on a TharSFC Method Station II equipped with Waters 2998 Photodiode Array Detector with isopropanol as the modifier.

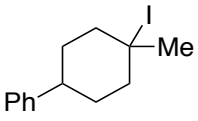
All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (DCM) and toluene were purified using Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after purging with argon. N,N-dimethyl acetamide (DMA) was purchased from Sigma Aldrich, distilled over 4Å molecular sieves under reduced pressure and stored under argon atmosphere. Nickel(II) dibromide • glyme was purchased from STREM. (*S*,*S*)-*N*,*N*′-dimethyl-1,2-diphenylethane-1,2-diamine **(*S*,*S*)-L1** (as well as **(*R*,*R*)-L1** and racemic **L1**) was synthesized from the corresponding commercially available (*S*,*S*)-1,2-diphenylethylenediamine (Oakwood Chemicals) following literature methods.[1] All other reagents were purchased from Sigma Aldrich, Alfa Aesar, Oakwood Chemicals, Combi-Blocks, or Acros Organics and used without further purification.

[1] V. F. Kuznetsov, G. R. Jefferson, G. P. A. Yap, H. Alper, *Organometallics* **2002**, *21*, 4241

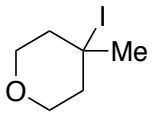
Experimental Procedures

I. Procedure for Preparation of Tertiary Alkyl Iodides

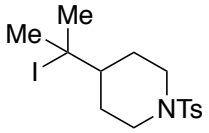
The corresponding tertiary alcohol (1.0 equiv.) and sodium iodide (2.0 equiv.) were dissolved in acetonitrile and cooled to 0º C. Methanesulfonic acid (2 equiv.) was added dropwise to the reaction mixture, which was then warmed to room temperature and stirred for an additional 30 minutes. Minimizing light exposure, the mixture was then concentrated on a rotary evaporator, re-dissolved in diethyl ether and washed with aqueous saturated $NaHCO_3$ solution followed by a wash with saturated $Na_2S_2O_3$. The organic layer was dried over $MgSO_4$ and concentrated. Purification by silica gel column chromatography was generally carried out rapidly (prolonged residence on the stationary phase resulted in H-I elimination). The compounds were stored in a freezer in the dark under N_2 atmosphere.



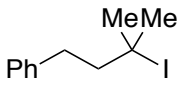
(4-iodo-4-methylcyclohexyl)benzene (SI-1). The title compound was obtained through the general procedure from the corresponding alcohol 1-methyl-4-phenylcyclohexan-1-ol (1.08 g, 5.7mmol). The product was isolated by silica gel chromatography (pentane, stain in CAM) to afford a white solid (1.4 g, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42-7.17 (m, 5H), 2.51 (tt, *J* = 12.4, 3.8 Hz, 1H), 2.29-2.23 (m, 2H), 2.19 (s, 3H), 2.10-1.98 (m, 2H), 1.88 (dd, *J* = 14.2, 3.7 Hz, 2H), 1.07 (ddd, *J* = 15.4, 12.4, 3.6 Hz, 2H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.7, 128.6, 127.1, 126.3, 58.6, 46.1, 43.7, 39.6, 32.8. **IR** (neat) ν_{max} 2952.20 (m), 2905.07 (m), 2853.6 (m), 1463.3 (w), 1441.3 (w), 1102.4 (s), 1013.6 (s), 979.7 (s), 775.6 (s), 614.3 (s), 476.6 (s). **HRMS** (DART) for $C_{13}H_{17}$ $(M+H-HI)^+$: Calc'd: 173.1325, found: 173.1318.



4-iodo-4-methyltetrahydro-2*H*-pyran (SI-2). The title compound was obtained through the general procedure from the corresponding alcohol 1-methyl-4-phenylcyclohexan-1-ol (780 mg, 6.7 mmol) . The product was isolated by silica gel chromatography (1% ethyl acetate in pentane, stain in CAM) to afford a clear yellow oil (986 mg, 67% yield). Clear yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.95-3.88 (m, 2H), 3.77-3.69 (m, 2H), 2.15 (s, 3H), 2.03 (dd, *J* = 14.7, 2.3 Hz, 2H), 1.31 (ddd, *J* = 15.1, 10.8, 4.4 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 66.4, 52.9, 44.9, 39.1. **IR** (neat) ν_{max} 2952.2 (m), 2905.0 (m), 2853.6 (m), 1463.3 (w), 1441.3 (w), 1102.4 (s), 1013.6 (s), 979.7 (s), 775.6 (s), 614.3 (s), 476.6 (s). **HRMS** (DART) for $C_6H_{22}OI$ $(M+H)^+$: Calc'd: 226.9922, found: 226.9927.

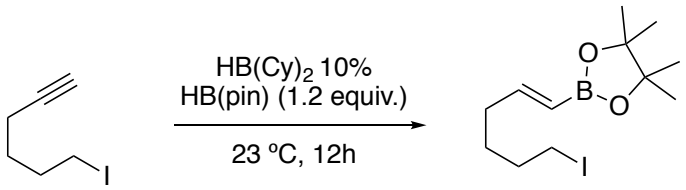


4-(2-iodopropan-2-yl)-1-tosylpiperidine (SI-3). The title compound was synthesized from the corresponding alcohol (2-(1-tosylpiperidin-4-yl)propan-2-ol) which was obtained in turn through standard procedures starting from commercially available ethyl isonipecotate. All spectral data was in accordance with the literature.[2]



(3-iodo-3-methylbutyl)benzene (SI-4). The title compound was synthesized from the corresponding alcohol 2-methyl-4-phenylbutan-2-ol. All spectral data was in accordance with the literature. [3]

II. Procedure for Preparation of Cyclizing Substrates



(*E*)-2-(6-iodohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20). In the glovebox a 2 dram vial was charged with neat 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.88 g, 22.5 mmol, 1.2 equiv.) and dicyclohexylborane (333.9 mg, 1.87 mmol, 0.10 equiv.). The vial was cooled inside the glovebox freezer for 30 min and 6-iodohex-1-yne (3.90 g, 18.8 mmol, 1.0 equiv.) was added to the cold mixture. The vial was sealed and the mixture was stirred for 12 hours at room temperature. The reaction mixture was quenched by bubbling air through the solution for 2 h at room temperature. to oxidize the dicyclohexylborane. The resulting mixture was diluted with hexane, washed with water, dried over Na_2SO_4, and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel with 2% ethyl acetate in hexanes as eluent (5.32 g, 84% yield). All spectra for the isolated product was in accordance with the literature. [4]

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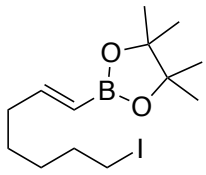
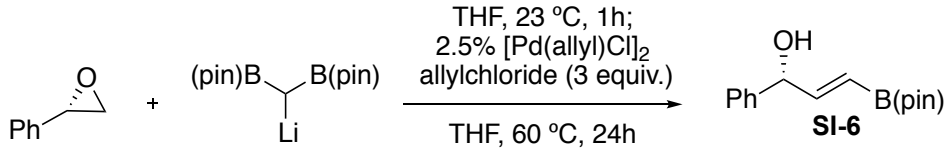
[2] Soulard, V.; Villa, G.; Vollmar, D. P. *J. Am. Chem. Soc.* **2018**, *140*, 155.

[3] Zhao, S.; Mankad, N. P. *Angew. Chem. Int. Ed* **2018**, *57*, 5867.

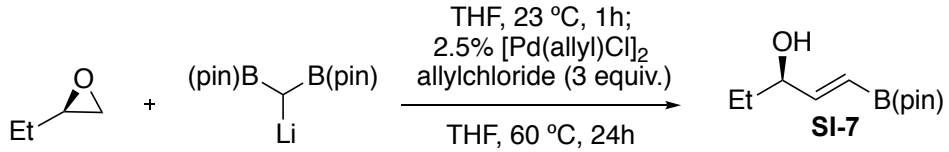
[4] N. Guennouni, F. Lhermitte, S. Cochard, B. Carboni, Tetrahedron **1995**, *51,* 6999.



(*E*)-2-(7-iodohept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (SI-5) was synthesized using the same procedure as for substrate **20** from 7-Iodohept-1-yne. The crude product was isolated by silica gel chromatography (2% ethyl acetate in hexanes, stain in CAM), as a colorless oil (78% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.59 (dt, *J* = 17.9, 6.4 Hz, 1H), 5.42 (dt, *J* = 17.9, 1.4 Hz, 1H), 3.16 (t, *J* = 7.1 Hz, 2H), 2.15 (q, *J* = 6.6 Hz, 2H), 1.81 (p, *J* = 7.1 Hz, 2H), 1.47-1.34 (m, 4H), 1.25 (s, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.0, 83.2, 35.6, 33.5, 30.2, 27.2, 24.9, 6.9. **IR** (neat) ν_{max} 2974.1 (w), 2926.4 (w), 2853.3 (w), 1636.4 (m), 1359.4 (s), 1317.2 (s), 1143.0 (s), 994.9 (w), 969.2 (w), 848.5 (w). **HRMS** (DART) for $C_{13}H_{25}BO_2I$ $(M+H)^+$: Calc'd: 351.0987, found: 351.0967.



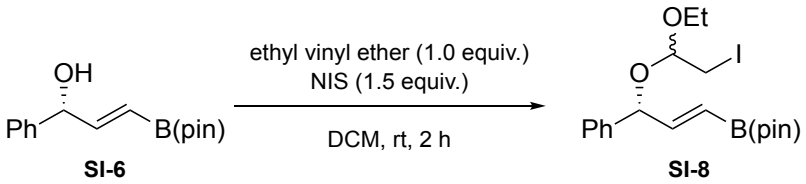
(*R*,*E*)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-ol (SI-6) was generated from commercial (*S*)-styrene oxide following the method reported by Meek.[5] All spectral data matched previously published results.[5]



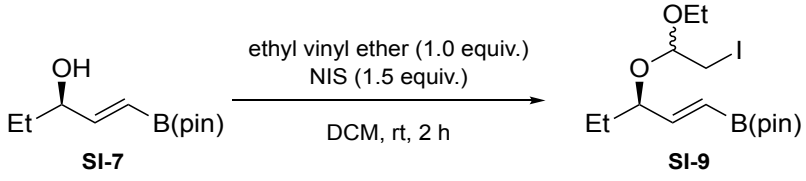
(*R*,*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-3-ol (SI-7) was generated from commercial (*R*)-1,2-epoxybutanestyrene (434 mg, 6.00 mmol, 1.0 equiv.) following the method reported by Meek.[5] The product was isolated by silica gel column chromatography (15% ethyl acetate in hexanes, stain in CAM) as a colorless oil (1.27 g, 77 % yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.59 (dd, *J* = 18.1, 5.3 Hz, 1H), 5.60 (d, *J* = 18.1 Hz, 1H), 4.06 (s, 1H), 1.77 (s, 1H), 1.55 (dt, *J* = 21.1, 14.3, 7.4 Hz, 2H), 1.25 (s, 11H), 0.92 (t, *J* = 7.5 Hz, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.1, 117.7, 83.4, 75.1, 29.5, 24.8, 9.7. **IR** (neat) ν_{max} 3432.2 (br), 2974.1 (w),

[5] S. A. Murray, E. C. M. Luc, S. J. Meek, *Org. Lett.* **2018**, *20*, 469.

2928.7 (w), 2874.5 (w), 1640.5(m), 1356.0 (s), 1317.8 (s), 1142.4 (s), 997.0 (m), 965.7 (m), 898.8 (m), 647.3 (w). **HRMS** (DART) for $C_{11}H_{25}BNO_3$ $(M+NH_4)^+$: Calc'd: 230.1922, found: 230.1926. $\mathbf{[\alpha]_D^{20}}$ = -12.40 (*c* = 1.0, $CHCl_3$, *l* = 50 mm).

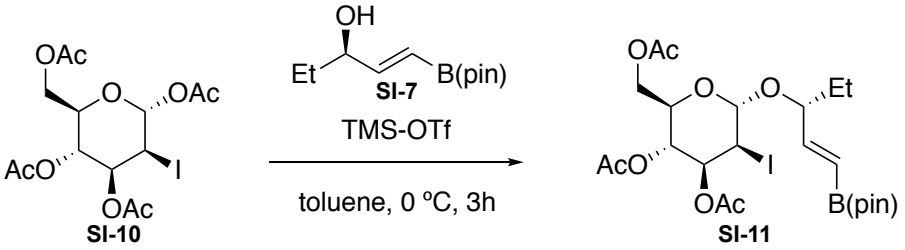


2-((*3R,E*)-3-(1-ethoxy-2-iodoethoxy)-3-phenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (SI-8). A mixture of **SI-6** (156.1 mg, 0.6 mmol) and ethyl vinyl ether (43.3 mg, 0.6 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of N-iodosuccinimide (202.5 mg, 0.9 mmol) in CH_2Cl_2 (10 mL) at 0 °C over 5 minutes. After stirring at room temperature for 2 hours, water (10 mL) was added, and the stirring was continued for one additional hour. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2×15 mL). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash chromatography (10% ethyl acetate in hexanes, stain in CAM) afforded **SI-8** as a 1:1 mixture of diastereomers (clear yellow oil, 0.21 g, 77% yield).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36-7.26 (m, 10H), 6.66 (ddd, *J* = 39.0, 18.0, 5.8 Hz, 2H), 5.69 (t, *J* = 19.2, 19.2 Hz, 2H), 5.14 (dd, *J* = 18.9, 5.8 Hz, 2H), 4.78 (t, *J* = 5.5, 5.5 Hz, 1H), 4.56 (t, 1H), 3.79-3.69 (m, 2H), 3.60-3.52 (m, 3H), 3.43 (dq, *J* = 9.0, 7.1, 7.1, 6.9 Hz, 1H), 3.23-3.18 (m, 4H), 1.86-1.84 (m, 2H), 1.25 (d, *J* = 6.7 Hz, 24H), 1.20 (t, *J* = 7.0, 7.0 Hz, 3H), 1.13 (t, *J* = 7.0, 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.0, 151.6, 140.4, 139.5, 128.6, 128.5, 128.2, 127.9, 127.7, 127.1, 100.2, 99.4, 83.5, 83.4, 80.1, 79.8, 68.0, 61.7, 61.2, 25.7, 24.9, 24.9, 24.9, 15.2, 15.1, 5.9, 5.6. **IR** (neat) ν_{max} 2973.5 (m), 2925.1 (w), 1636.7 (m), 1352.8 (s), 1323.0 (s), 1266.5 (w), 1141.2 (s), 1107.9 (m), 1055.3 (m), 994.4 (s), 968.5 (s), 847.3 (m), 759.1 (m), 698.2 (m), 658.9 (w). **HRMS** (DART) for $C_{19}H_{32}BNO_4I$ $(M+NH_4)^+$: Calc'd: 476.1464, found: 476.1463.



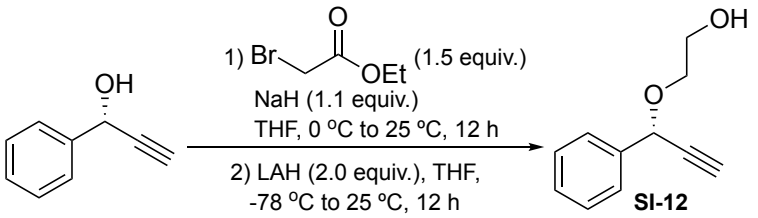
2-((*3R,E*)-3-(1-ethoxy-2-iodoethoxy)pent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3-dioxolane (SI-9) was synthesized using the same procedure for the synthesis of **SI-8** using **SI-7** (200 mg, 0.94 mmol, 1 equiv.**)** as starting material. The product consisting of a 1:1 inseparable mixture of diastereomers was isolated by silica gel chromatography (10% ethyl acetate in hexanes, stain in CAM) as a clear yellow oil (240 mg, 62% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.46 (ddd, *J* =

45.5, 18.1, 7.1 Hz, 2H), 5.58 (dd, *J* = 18.2, 2.9 Hz, 2H), 4.59 (dt, *J* = 14.7, 5.6, 5.6 Hz, 2H), 3.99 (q, *J* = 6.7, 6.7, 6.7 Hz, 1H), 3.88 (q, *J* = 6.5, 6.5, 6.5 Hz, 1H), 3.69-3.44 (m, 4H), 3.20 (dt, *J* = 5.0, 2.9, 2.9 Hz, 4H), 1.70-1.50 (m, 5H), 1.32-1.24 (m, 24H), 1.22 (t, *J* = 7.0, 7.0 Hz, 3H), 1.17 (t, *J* = 7.0, 7.0 Hz, 3H), 0.92 (t, *J* = 7.5, 7.5 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.1, 152.4, 100.9, 99.6, 83.5, 83.4, 81.2, 80.5, 62.2, 61.5, 28.2, 27.8, 25.0, 24.9, 24.9, 24.8, 15.3, 15.0, 9.8, 9.7, 6.3, 6.3. **IR** (neat) ν_{max} 2972.9 (m), 2927.8 (w), 2874.6 (w), 1639.6 (m), 1365.7 (s), 1323.9 (s), 1141.9 (s), 1101.4 (s), 1047.4 (s), 998.4 (s), 968.6 (s), 847.9 (m), 648.5 (w), 577.4 (w). **HRMS** (DART) for $C_{15}H_{32}BNO_4I$ $(M+NH_4)^+$: Calc'd: 428.1464, found: 428.1467.

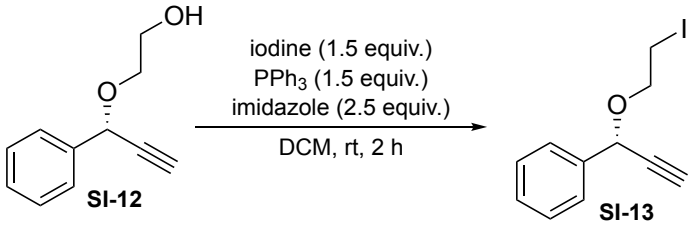


(2*R*,3*R*,4*S*,5*S*,6*S*)-2-(acetoxymethyl)-5-iodo-6-(((*R*,*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-3-yl)oxy)tetrahydro-2*H*-pyran-3,4-diyl diacetate (SI-11) was synthesized starting from (2*R*,3*S*,4*S*,5*R*,6*R*)-6-(acetoxymethyl)-3-iodotetrahydro-2*H*-pyran-2,4,5-triyl triacetate (**SI-10**) (1.07 g, 2.34 mmol, 1.1 equiv.) and **SI-7** (452 mg, 2.13 mmol, 1.0 equiv.) following the method described by Wan.[6] The crude product was isolated by silica gel chromatography (30% ethyl acetate in hexanes, UV) to afford a white a solid (1.12 g, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.33 (dd, *J* = 18.1, 7.2 Hz, 1H), 5.59 (d, *J* = 18.1 Hz, 1H), 5.37 (t, *J* = 9.8 Hz, 1H), 5.16 (s, 1H), 4.66 (dd, *J* = 9.5, 4.3 Hz, 1H), 4.50 (d, *J* = 4.3 Hz, 1H), 4.21 (dd, *J* = 12.2, 5.0 Hz, 1H), 4.16-4.12 (m, 1H), 4.08-4.05 (m, 1H), 3.99 (q, *J* = 6.8 Hz, 1H), 2.11 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 1.72-1.50 (m, 4H), 1.28 (d, *J* = 2.5 Hz, 13H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.8, 169.9, 169.7, 150.4, 98.7, 98.6, 83.6, 80.8, 69.4, 69.2, 67.9, 62.5, 30.4, 28.1, 25.0, 24.9, 24.8, 21.1, 20.9, 20.8, 10.2. **IR** (neat) ν_{max} 2973.9 (m), 2933.1 (m), 1744.3 (s), 1641.1 (m), 1453.5 (w), 1366.3 (m), 1328.9 (w), 1222.2 (s), 1142.9 (s), 1114.6 (s), 1030.7 (s). **HRMS** (DART) for $C_{23}H_{40}BNOI$ $(M+NH_4)^+$: Calc'd: 628.1785, found: 628.1779. **$[\alpha]_D^{20}$** = 47.39 (*c* =1.0, $CHCl_3$, *l* = 50 mm).

[6] H. Wang, J. Tao, X. Cai, W. Chen, Y. Zhao, Y. Xu, W. Yao, J. Zeng, Q. Wan, *Chem. Eur. J.* **2014**, *20*, 17319.



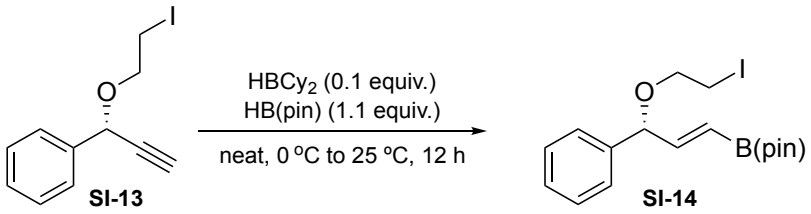
(*R*)-2-((1-phenylprop-2-yn-1-yl)oxy)ethan-1-ol (SI-12). Commercial (*R*)-1-phenylprop-2-yn-1-ol (981.0 mg, 7.42 mmol, 1.0 equiv.) was added dropwise to a suspension of sodium hydride (217.6 mg, 8.16 mmol, 90% purity, 1.1 equiv.) in THF (6 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 1 h. After the mixture was cooled to 0 °C, ethyl 2-bromoacetate (1.86 g, 11.13 mmol, 1.5 equiv.) was added dropwise to the mixture. The mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was quenched by saturated NH_4Cl aq. solution (10 mL) and extracted with Et_2O (3 x 20 mL). The combined organic layer was then dried over anhydrous Na_2SO_4. After filtration, the material was concentrated under reduced pressure. The corresponding crude ether was dissolved in THF (20 mL) and added dropwise to a solution of LAH in THF (1 M, 15.0 mL) at −78 °C under a nitrogen atmosphere. The reaction was allowed to warm to room temperature and stir for 12 h, after which it was cooled to 0ºC and quenched by careful addition of H_2O (1.0 mL) and then aqueous NaOH (3 M, 3.0 mL). After stirring at room temperature for 20 min $MgSO_4$ was added to the reaction mixture and the suspension was filtered through celite. The solvent was removed in vacuo and the crude product was purified by flash column chromatography (20% ethyl acetate in hexanes) to obtain **SI-12** (0.78 g, 44% yield over two steps) as a colorless oil. All spectral data is in accordance with the literature.[7]



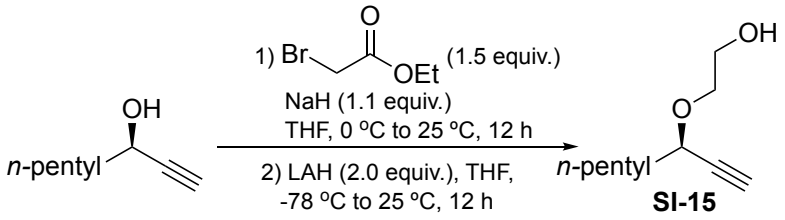
(*R*)-(1-(2-iodoethoxy)prop-2-yn-1-yl)benzene (SI-13). A solution of triphenylphosphine (1.03 g, 3.92 mmol) and iodine (0.99 g, 3.92 mmol) in dichloromethane (20 mL) was allowed to stir for 10 min at ambient temperature. Imidazole (0.44 g, 6.53 mmol) was added to the resulting mixture. After a 10 min stir, **SI-12** (0.46 g, 2.61 mmol) was added and the resulting mixture was stirred for 2 h. The mixture was quenched by the addition of saturated sodium metabisulfite (10 mL). The aqueous and organic layers were separated followed by extraction of the aqueous with dichloromethane (3 x 20 mL). The combined organic extracts were dried (anhydrous Na_2SO_4)

[7] J. Bucher, T. Wurm, K. S. Nalivela, M. Rudolph, F. Rominger, A. S. K. Hashmi *Angew. Chem. Int. Ed.* **2014**, *53*, 3854.

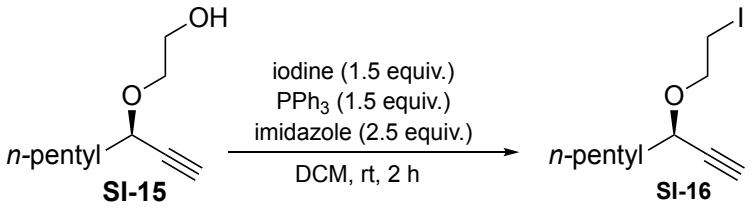
and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (5% ethyl acetate in hexanes) to afford the **SI-13** (0.45 g, 60% yield) as a light-yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.44-7.32 (m, 3H), 5.28 (d, *J* = 2.2 Hz, 1H), 3.95-3.89 (m, 1H), 3.84-3.77 (m, 1H), 3.31-3.28 (m, 2H), 2.69 (d, *J* = 2.2 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 137.7, 128.8, 128.7, 127.5, 81.1, 76.4, 71.4, 68.9, 2.5. **IR** (neat) ν_{max} 3284.2 (m), 3059.1 (w), 3027.0 (w), 2914.6 (w), 2850.9 (w), 1491.4 (w), 1451.3 (m), 1261.2 (m), 1189.5 (w), 1170.2 (w), 1094.3 (s), 1054.1 (s), 1027.2 (m), 990.3 (m), 740.0 (m), 696.4 (s), 652.8 (s). **HRMS** (DART) for $C_{11}H_{12}OI$ $(M+H)^+$: Calc'd: 286.9927, found: 286.9929.



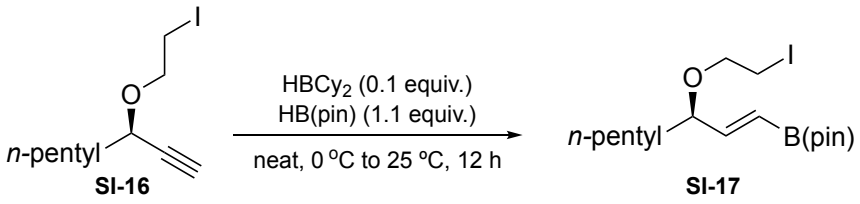
(*R*,*E*)-2-(3-(2-iodoethoxy)-3-phenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (SI-14). In the glovebox a 2-dram vial is charged with neat dicyclohexylborane (19.1 mg, 0.11 mmol), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (164.5 mg, 1.30 mmol) and **SI-13** (306.4 mg, 1.1 mmol) was added at 0 °C and the mixture was stirred for a 12 hours at room temperature. The reaction mixture was quenched by bubbling air through the solution with tube pump for 2 hours at room temperature to oxidize the dicyclohexylboryl group. The resulting mixture was diluted with hexane, washed with water, dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (5% ethyl acetate in hexanes, stain in CAM) to afford the title compound (0.25 g, 56% yield) as a clear yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H, 6.66 (dd, *J* = 18.0, 5.8 Hz, 1H), 5.70 (d, *J* = 17.8 Hz, 1H), 4.86 (d, *J* = 5.7 Hz, 1H), 3.79-3.71 (m, 2H), 3.67-3.63 (m, 1H), 3.28-3.24 (m, 2H), 1.87-1.84 (m, 1H), 1.25 (s, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 151.9, 140.1, 128.7, 128.0, 127.2, 84.0, 83.5, 69.5, 24.9, 3.0. **IR** (neat) ν_{max} 2974.2 (w), 1637.3 (m), 1355.7 (s), 1355.7 (s), 1265.3 (w), 1142.6 (s), 1106.9 (w), 995.4 (w), 969.3 (w), 847.8 (m), 669.2 (m). **HRMS** (DART) for $C_{17}H_{23}BO_3I$ $(M+H)^+$: Calc'd: 413.0779, found: 413.0788. **$[\alpha]_D^{20}$**= 19.11 (*c* =1.0, $CHCl_3$, *l* = 50 mm).



(*R*)-2-(oct-1-yn-3-yloxy)ethan-1-ol (SI-15) was synthesized using the same procedure for the synthesis of **SI-13**, using commercially available (*R*)-oct-1-yn-3-ol. The product was isolated by silica gel chromatography (20% ethyl acetate in hexanes, stain in CAM) to afford a colorless oil (37% yield over two steps). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.08 (td, *J* = 6.7, 6.6, 2.0 Hz, 1H), 3.88-3.83 (m, 1H), 3.80-3.75 (m, 2H), 3.56-3.51 (m, 1H), 2.45 (t, *J* = 1.9, 1.9 Hz, 1H), 1.93 (t, *J* = 6.3, 6.3 Hz, 1H), 1.81-1.69 (m, 2H), 1.50-1.44 (m, 2H), 1.36-1.31 (m, 4H), 0.91 (t, *J* = 7.0, 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 83.0, 74.0, 70.2, 70.1, 62.1, 35.7, 31.6, 25.0, 22.7, 14.1. **IR** (neat) ν_{max} 3423.7 (br), 3306.2 (m), 2950.9 (s), 2927.2 (s), 2858.8 (m), 1460.8 (w), 1333.3 (w), 1105.5 (s), 1070.6 (m), 657.9 (w), 629.3 (w). **HRMS** (DART) for $C_{10}H_{19}O_2$ $(M+H)^+$: Calc'd: 171.1380, found: 171.1376.



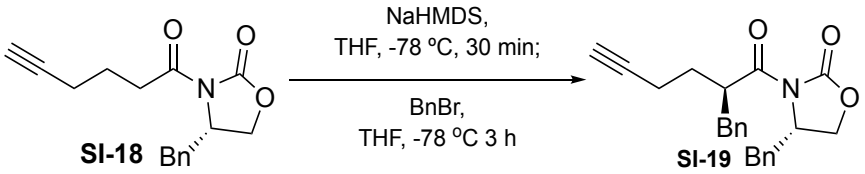
(*R*)-3-(2-iodoethoxy)oct-1-yne was synthesized using the same procedure for the synthesis of **2c**. All spectral data is in accordance with the literature.[8]



2-((*R,E*)-3-(2-iodoethoxy)oct-1-en-1-yl)-4,4,5-trimethyl-1,3,2-dioxaborolane (SI-17) was synthesized using the same procedure for the synthesis of **SI-14**. Isolated by silica gel chromatography (10% ethyl acetate in hexanes, stain CAM) to afford the product as a clear

[8] H. Iwamoto, Y. Ozawa, K. Kubota, H. Ito, *J. Org. Chem*. **2017**, *82*, 10563.

yellow oil (60% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.42 (dd, *J* = 18.1, 6.6 Hz, 1H), 5.57 (d, *J* = 18.1 Hz, 1H), 3.77-3.71 (m, 2H), 3.58-3.46 (m, 1H), 3.21 (t, *J* = 7.0, 7.0 Hz, 2H), 1.59-1.38 (m, 4H), 1.33-1.22 (d, 16H), 0.87 (t, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.2, 83.4, 82.5, 69.7, 35.2, 31.9, 25.2, 24.9, 22.7, 14.2, 3.4. **IR** (neat) ν_{max} 2973.9 (w), 2953.2 (w), 2926.2 (m), 2855.6 (w), 1639.1 (m), 1464.4 (w), 1356.5 (s), 1327.2 (s), 1265.6 (m), 1142.9 (s), 1107.2 (m), 1107.2 (m), 998.2 (m), 968.8 (m), 848.5 (m). **HRMS** (DART) for $C_{16}H_{34}BNO_3I$ $(M+NH_4)^+$: Calc'd: 426.1671, found: 426.1669. **$[\alpha]_D^{20}$** = 26.05 (*c* =1.0, $CHCl_3$, *l* = 50 mm).

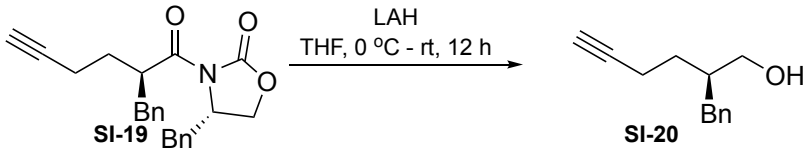


(*S*)-4-benzyl-3-(hex-5-ynoyl)oxazolidin-2-one (SI-18) was synthesized using reported method. All spectral data is in accordance with the literature.[9]

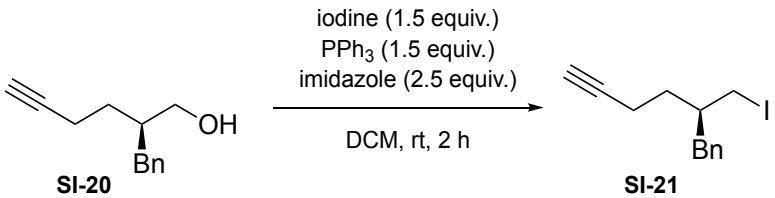
(*S*)-4-benzyl-3-((*R*)-2-benzylhex-5-ynoyl)oxazolidin-2-one (SI-19). In a flame-dried round bottom flask, under an atmosphere of N_2, a solution of sodium bis(trimethylsilyl)amide (11.6 mL, 1.00 M in THF, 11.6 mmol) was further diluted with THF (20 mL) and cooled to -78 °C. To it was added a solution of (4S)-4-benzyl-3-hex-5-ynoyl-oxazolidin-2-one (**SI-18**) (1.8 g, 6.63 mmol) in THF (10 mL) by syringe over 10 min. After stirring for 30 min, benzylbromide (3.40 g, 19.9 mmol) was added neat. The solution was then stirred at -78 °C temperature for 2.5 h at which point the reaction was quenched with 100 mL of 0.5 M HCl (aq.). The mixture was extracted with ethyl acetate (50 mL x 2) and the combined organic extracts were washed with water (100 mL), brine (100 mL) and dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (15% ethyl acetate in hexanes, UV active) to afford the product as a colorless oil (1.41 g, 59% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34-7.16 (m, 8H), 7.12-7.03 (m, 2H), 4.66-4.62 (m, 1H), 4.39-4.30 (m, 1H), 4.13 (t, *J* = 8.4 Hz, 1H), 4.07 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.13-3.00 (m, 2H), 2.79 (dd, *J* = 13.4, 7.5 Hz, 1H), 2.46 (dd, *J* = 13.4, 9.6 Hz, 1H), 2.25-2.22 (m, 2H), 2.06-1.99 (m, 1H), 1.94-1.93 (m, 1H), 1.78-1.70 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.4, 153.1, 138.6, 135.3, 129.5, 129.5, 129.0, 128.5, 127.4, 126.7, 83.4, 69.2, 66.0, 55.3, 43.8,

[9] C. R. Moyes, R. Berger, S. D. Goble, B. Harper, D.-M. Shen, L. Wang, A. Bansal, P. N. Brown, A. S. Chen, K. H. Dingley, J. Di Salvo, A. Fitzmaurice, L. N. Gichuru, D. Hrenuik, A. L. Hurley, N. Jochnowitz, S. Mistry, H. Nagabukuro, G. M. Salituro, A. Sanfiz, A. S. Stevenson, K. Villa, B. Zamlynny, M. Struthers, S. D. Edmondson, *J. Med. Chem.* **2014**, *57*, 1437.

38.8, 37.8, 30.1, 16.6. **IR** (neat) ν_{max} 3284.2 (m), 3059.2 (w), 3025.4 (w), 2921.6 (m), 2856.9 (w), 1772.4 (s), 1691.1 (s), 1385.3 (s), 1348.1 (s), 1239.9 (s), 1210.1 (s), 1193.1 (s), 739.9 (s). **HRMS** (DART) for $C_{23}H_{24}NO3$ $(M+H)^+$: Calc'd: 362.1751, found: 362.1761. $\mathbf{[\alpha]_D^{20}}$ = 18.20 (*c* =1.0, $CHCl_3$, *l* = 50 mm).

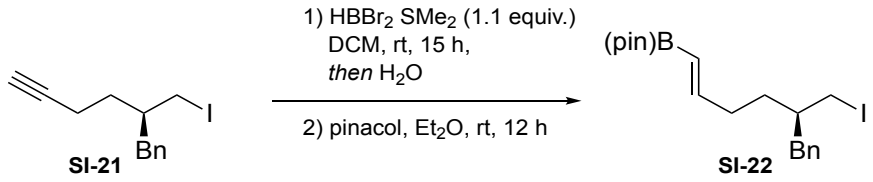


(*R*)-2-benzylhex-5-yn-1-ol (SI-20). To a solution of LAH (220.5 mg, 5.8 mmol) in THF (30 mL) was added a solution of **SI-19** (0.70 g, 1.94 mmol) in 20 mL THF at -78 °C. The mixture was allowed to warm to room temperature over the course of a several hours and stirred for 12 hours. The mixture was cooled to 0 ºC and H_2O (0.6 mL) was carefully added, followed by 3 M NaOH (0.6 mL). The suspension was stirred at room temperature for 20 min after which $MgSO_4$ was added. The resulting mixture was filtered through a pad of celite and concentrated in vacuo. The crude product was purified by silica gel column chromatography (15% ethyl acetate in hexanes) to afford **SI-20** (0.25 g, 68% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.23-7.21 (m, 3H), 3.63-3.53 (m, 2H), 2.67 (d, *J* = 7.3 Hz, 2H), 2.30-2.27 (m, 2H), 2.02-1.97 (m, 2H), 1.72-1.57 (m, 2H), 1.31 (td, *J* = 5.6, 5.6, 2.2 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.4, 129.3, 128.5, 126.2, 84.5, 68.8, 64.3, 41.6, 37.5, 29.7, 16.4. **IR** (neat) ν_{max} 3288.6 (m), 3023.4 (w), 3025.4 (w), 2921.3 (m), 1600.8 (w), 1493.5 (m), 1451.5 (m), 1029.0 (s), 981.9 (s), 736.3 (s), 699.3 (s), 631.8 (s), 493.4 (w). **HRMS** (DART) for $C_{13}H_{17}O$ $(M+H)^+$: Calc'd:189.1274, found: 189.1268. $\mathbf{[\alpha]_D^{20}}$ = 1.19 (*c* =1.0, $CHCl_3$, *l* = 50 mm).



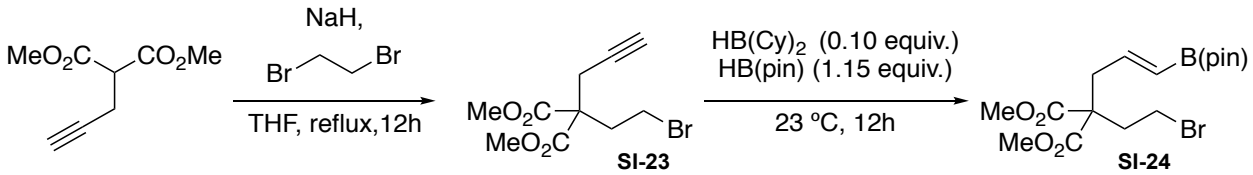
(*R*)-(2-(iodomethyl)hex-5-yn-1-yl)benzene (SI-21). A solution of triphenylphosphine (0.53 g, 2.0 mmol) and iodine (0.51 g, 2.0 mmol) in dichloromethane (5 mL) was allowed to stir for 10 min at ambient temperature. Imidazole (0.23 g, 3.3 mmol) was added to the resulting mixture. After stirring for 10 min, **SI-20** (.25 g, 1.3 mmol) was added and the resulting mixture was stirred for 2 h. The mixture was quenched by the addition of saturated sodium metabisulfite aq. solution (5 mL). The aqueous and organic layers were separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic extracts were dried over

Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (5% ethyl acetate in hexane, stain in CAM) to afford the title compound (0.3 g, 75%) as a light-yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2H), 7.28-7.24 (m, 3H), 3.27 (dd, *J* = 10.3, 3.1 Hz, 1H), 3.16 (dd, *J* = 10.2, 2.9 Hz, 1H), 2.71 (dd, *J* = 13.8, 4.1 Hz, 1H), 2.56 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.37-2.19 (m, 2H), 2.00 (t, *J* = 2.6, 2.6 Hz, 1H), 1.71-1.56 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.5, 129.3, 128.6, 126.5, 83.4, 69.3, 40.2, 39.1, 33.1, 15.9, 15.5. **IR** (neat) ν_{max} 3290.6 (m), 3058.8 (w), 2920.0 (m), 2851.4 (w), 1601.0 (w), 1493.7 (m), 1451.2 (m), 1220.8 (m), 735.9 (s), 699.1 (s), 634.9 (s), 491.3 (w). **HRMS** (DART) for $C_{13}H_{16}I$ $(M+H)^+$: Calc'd: 299.0291, found: 299.0292. **$[\alpha]_D^{20}$** = -45.02 (*c* =1.0, $CHCl_3$, *l* = 50 mm).



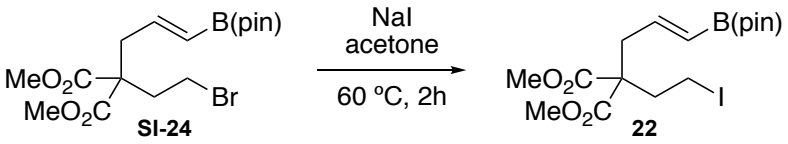
SI-21 SI-22

(*R,E*)-2-(5-benzyl-6-iodohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (SI-22). To a solution of **SI-21** (0.30 g, 1.0 mmol) in 10 mL of anhydrous dichloromethane was added 1.1 mL of a 1.0 M solution of $HBBr_2$•SMe_2 (1.1 mmol) in dichloromethane. After 15 h at room temperature, the mixture was cooled to 0 ºC and water (5 mL) was slowly added. The aqueous phase was extracted with 2 x 20 mL of ether. Addition of pinacol (0.12 g, 1.0 mmol) to the combined organic phases was followed by stirring for 12 hours at room temperature. The reaction mixture is concentrated under reduced pressure, and purified by flash chromatography (5% ethyl acetate in hexane, stain in CAM) to afford **SI-22** (0.35 g, 82%) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.24-7.19 (m, 3H), 6.63 (dt, *J* = 17.9, 6.4, 6.4 Hz, 1H), 5.49 (d, *J* = 17.9 Hz, 1H), 3.23 (dd, *J* = 10.0, 4.2 Hz, 1H), 3.13 (dd, *J* = 10.0, 3.7 Hz, 1H), 2.67 (dd, *J* = 13.8, 5.5 Hz, 1H), 2.55 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.30-2.21 (m, 1H), 2.18-2.11 (m, 1H), 1.59-1.46 (m, 2H), 1.46-1.37 (m, 1H), 1.29 (s, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.4, 139.7, 129.2, 128.5, 126.4, 83.2, 40.4, 39.9, 33.1, 32.8, 24.9, 15.9. **IR** (neat) ν_{max} 3022.6 (m), 2974.1 (m), 2923.5 (w), 1636.3 (m), 1452.0 (w), 1396.3 (m), 1360.6 (s), 1320.1 (s), 1143.0 (s), 999.4 (w), 969.5 (w), 848.7 (w), 738.3 (w), 699.7 (m). **HRMS** (DART) for $C_{19}H_{29}BO_2I$ $(M+H)^+$: Calc'd: 427.1300, found: 427.1315. **$[\alpha]_D^{20}$** = -18.64 (*c* = 1.0, $CHCl_3$, *l* = 50 mm).



Dimethyl(E)-2-(2-bromoethyl)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)malonate (SI-24). Sodium hydride (260 mg, 10.75 mmol, 1.15 equiv.) was placed in a flame dried round bottom flask under Ar atmosphere and dissolved in 10 mL of THF. The flask was cooled to 0 ºC and a solution of dimethyl 2-prop-2-ynylpropanedioate (1.59 g, 9.34 mmol, 1.0 equiv.) in 10 mL of THF was added dropwise. The mixture was stirred for 20 min at 0 ºC after which time neat 1,2-dibromoethane (5.27 g, 28.03 mmol, 3.0 equiv.) was added. The mixture was then heated to reflux for 12 hours. The suspension was then cooled to 0 ºC and the reaction was quenched with 10 mL of saturated NH_4Cl aq. solution. The organic layer was extracted with ethyl acetate three times, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. The crude material was filtered through a silica plug with 20% ethyl acetate in hexanes and carried to the next step.

Inside an argon filled glovebox a 4 dram vial was charged with neat 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (637.32 mg, 5.00 mmol, 1.15 equiv.) and dicyclohexylborane (77.13 mg, 0.43 mmol, 0.10 equiv.). The vial was placed inside the glove box freezer to cool for 30 minutes. Dimethyl-2-(2-bromoethyl)-2-prop-2-ynyl-propanedioate (**SI-23)** (1.20 g, 4.33 mmol, 1.0 equiv.) was added to the cool suspension and the vial was then sealed and stirred for 12 hours at room temperature. Finally, the reaction mixture was quenched by bubbling air through the solution for 2 hours at room temperature to oxidize the dicyclohexylborane. The resulting mixture was diluted with diethyl ether, washed with water, dried over Na_2SO_4, and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (10% ethyl acetate in hexanes, stain in $KMnO_4$) to afford the product **SI-24** as a colorless oil (862 mg, 49% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.35 (dt, J = 17.7, 7.2 Hz, 1H), 5.53 (dt, J = 17.7, 1.2 Hz, 1H), 3.74 (s, 6H), 3.34 (t, 2H), 2.76 (dd, J = 7.2, 1.3 Hz, 2H), 2.45 (t, 2H), 1.25 (s, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.7, 146.1, 121.9, 83.5, 57.5, 52.9, 40.1, 36.4, 27.2, 24.9. **IR** (neat) ν_{max} 2975.4 (w), 1732.4 (s), 1637.6 (w), 1436.1 (w), 1390.7 (m), 1362.6 (m), 1268.9 (m), 1166.2 (m), 998.4 (w), 970.4 (w), 643.0 (w). **HRMS** (DART) for $C_{16}H_{26}BIO_6$ $(M+H)^+$: Calc'd: 405.1079, found: 405.1075.



Dimethyl(E)-2-(2-iodoethyl)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)malonate (22). To a round bottom flask containing **SI-24** (400 mg, 0.99 mmol, 1.0 equiv.) was added a solution of sodium iodide (592.04 mg, 3.95 mmol, 4.0 equiv.) in acetone (22 mL). The reaction mixture was heated to reflux for 2 hours. The mixture was cooled to room temperature, diluted with diethyl ether (100 mL), and washed with water and brine. The organic layer was dried over Na_2SO_4, and concentrated under reduced pressure. The product was isolated after silica gel chromatography (10% ethyl acetate in hexanes, stain in CAM) as a clear yellow oil (395 mg, 89% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.34 (dt, *J* = 17.7, 7.2 Hz, 1H), 5.52 (d, *J* = 17.7 Hz, 1H), 3.73 (s, 6H), 3.14-3.00 (m, 2H), 2.73 (d, *J* = 7.2 Hz, 2H), 2.52-2.38 (m, 2H), 1.25 (s, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.47, 146.12, 83.43, 59.05, 52.85, 39.82, 37.97, 24.88, 2.42. **IR** (neat) ν_{max} 2975.24 (br), 1732.1 (s), 1637.31 (w), 1436.06 (w), 1390.18 (m), 1324.55 (m), 1143.48 (m), 997.73 (w), 970.29 (w), 848.74 (w). **HRMS** (DART) for $C_{16}H_{26}BIO_6$ $(M+H)^+$: Calc'd: 453.0940, found: 453.0949.

III. Procedures for the Preparation of Organozinc Reagents:

Alkyl zinc bromide synthesis by zinc insertion into C-Br bond.
A 20 mL vial was charged with zinc powder (1.26 g, 19.31 mmol, 2.50 equiv.) and a stir bar. The vial was capped with a PTFE-lined pierceable screwcap and he system was heated at 80 °C under high vacuum for 2 hours with stirring. The vial is then cooled to room temperature and backfilled with N_2. At this point the vial is brought into an Ar filled glove box, a solution of iodine (95.84 mg, 0.38 mmol, 0.02 equiv.) in DMA (1 mL) and the suspension was stirred until the red color subsided. In turn, alkyl bromide (7.60 mmol, 1.00 equiv.) and an additional 4 mL of DMA were added. The vial was capped with a Teflon screwcap, taped and the suspension was heated at 80 °C for 12 hours. Next, the mixture was cooled to room temperature, brought inside the glovebox and filtered through a syringe filter (pore-size: 0.45 μM, PTFE). The resulting organo-zinc solution was titrated following the Knochel method (I_2 in a 0.5 M THF solution of LiCl).[10]

The solutions could be stored in a freezer under inert atmosphere for several weeks without deleterious effects.

[10] A. Krasovskiy, P. Knochel, *Synthesis* **2006**, *5*, 890.

Note: for the three-component cross-coupling reactions (**Procedure A**, see below) the alkyl zinc bromide solution (0.4 mmol, 2.0 equiv.) was transferred under inert atmosphere into a flame dried vial containing LiCl (35.6 mg, 0.84 mmol, 4.20 equiv.) in 0.5 mL of THF. The mixture was stirred vigorously for 1 hour at room temperature prior to being used in the cross-coupling reaction.

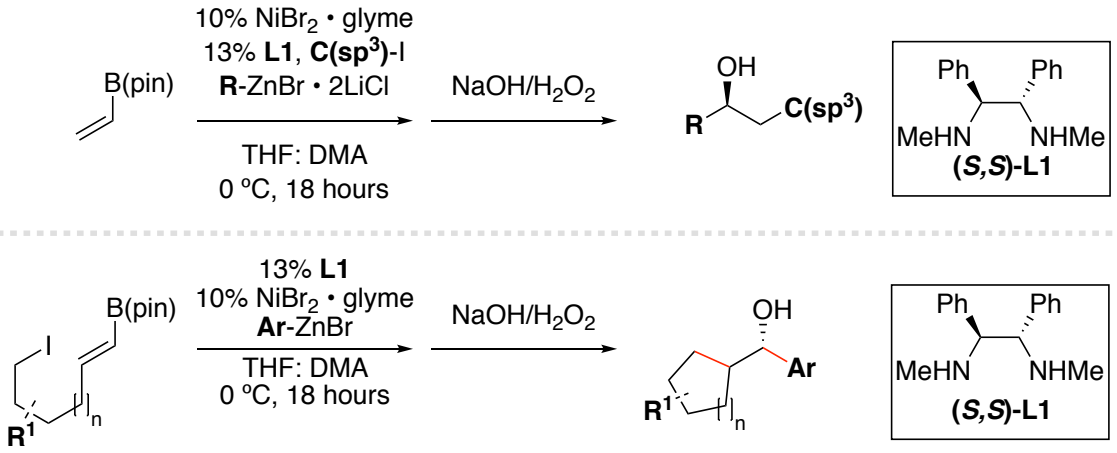
Organozinc Chloride synthesis by addition of organolithium reagents to $ZnCl_2$.

Organolithium reagents were generated by lithium-halogen exchange with *tert*-butyllithium using the following procedure: an aryl bromide or alkyl iodide (1.0 mmol) was placed in a flame-dried 20 mL vial under N_2 atmosphere and dissolved 5 mL of dry diethyl ether. The vial was sealed with a pierceable PTFE-lined cap and a septum was taped over it (this second septum was backfilled with N_2 and creates a buffer zone to prevent air from entering the vial). The solution was cooled to -78 ºC and *tert*-butyllithium (1.18 mL, 1.7 M, 2.0 equiv.) was added dropwise. The solution was stirred at -78°C for 30-40 min after which a solution of $ZnCl_2$ in THF was added (2.4 mL, 0.5 M, 1.2 equiv.). The mixture was warmed to room temperature and stirred for 45 minutes after which time the solvent was carefully removed under vacuum through the Schlenck line. The concentrated residue was brought inside an argon filled glovebox and re-dissolved in 2 mL of THF. The resulting solution was titrated following the Knochel method.[10]

Note: phenyllithium and methyllithium solutions purchased from commercial sources (Sigma Aldrich) were added to $ZnCl_2$ solutions in THF (0.5 M, 1.2 equiv.) at 0 ºC, stirred for 45 min, and used directly in the reaction.

IV. Representative Procedure for Cross-Coupling

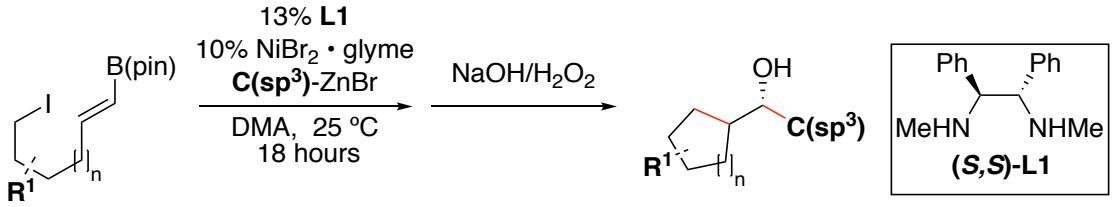
Procedure A, for the three component cross-coupling (alkyl or aryl ZnX) and two component cyclization/cross-coupling with aryl ZnX reagents.



In an argon-filled glovebox, an oven-dried 2 dram vial equipped with a magnetic stirrer was charged with **$NiBr_2$ • glyme** (6.17 mg, 0.02 mmol), (*S*,*S*)-N,N-dimethyl-1,2-diphenyl-ethane-1,2-diamine **(*S*,*S*)-L1** (6.25 mg, 0.026 mmol) and dissolved in 1.0 mL of THF. The catalyst solution was stirred for 1 hour at ambient temperature. **Vinylboronic acid pinacol ester** (30.80 mg, 0.20 mmol, 1.00 equiv.) and **alkyl iodide** (0.40 mmol, 2.00 equiv.), or **cyclizing alkenyl boron** substrate (0.20 mmol, 1.00 equiv.) were added to the catalyst solution (alternatively, the reactants could be weighed out in a separate vial and the catalyst solution added to the latter). At this point, THF and DMA were added so as to reach a final volume (taking into account the volume of the organozinc solution) of 2.00 mL of THF and 0.40 mL DMA. The vial was sealed with a PTFE-lined pierceable cap, taped, and brought outside the glovebox where it was placed in a CryoCool set at 0 ºC. The vial was cooled for 20-30 minutes before addition of the **organozinc** solution (0.40 mmol, 2.00 equiv.) (***Note:*** for the three component reactions with alkyl-ZnBr reagents, the organozinc reagent was stirred with LiCl (35.6 mg, 0.84 mmol, 4.20 equiv.), in 0.50 mL of THF for 1 hour at room temperature before addition). The puncture hole was taped over and the reaction mixture was stirred at 0 ºC for 18 hours. Oxidation was then carried out by adding 0.50 mL of 30% H_2O_2 and 0.50 mL of 3.0 M aqueous NaOH solution to the cold reaction mixture (the vial was vented to prevent pressure build-up). The mixture was stirred vigorously for 2-3 hours and allowed to slowly warm to room temperature. At this point the reaction mixture was cooled to 0 ºC once more and the oxidation was quenched by addition of 0.50 mL of saturated aqueous $Na_2S_2O_3$ .The organic layer was extracted four times with ethyl acetate, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography.

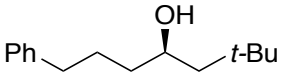
Note: In order to isolate the boronic ester product prior to oxidation, the work-up was carried out by adding 0.30 mL of saturated aqueous NH_4Cl solution to the reaction mixture at 0 ºC. The mixture was then transferred to a separatory funnel using ethyl acetate, and the organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The crude product was then purified by silica gel chromatography.

Procedure B, **for intramolecular cyclization/cross-coupling reactions using alkyl-ZnBr.**



In an argon-filled glovebox, an oven-dried 2 dram vial equipped with a magnetic stirrer was charged with **$NiBr_2$ • glyme** (6.17 mg, 0.02 mmol), (*S,S*)-N,N-dimethyl-1,2-diphenyl-ethane-1,2-diamine **(*S,S*)-L1** (6.25 mg, 0.026 mmol) and dissolved in 1.0 mL of DMA. The catalyst solution was stirred for 1 hour at ambient temperature. The **cyclizing alkenyl-boron** substrate (0.20 mmol, 1.00 equiv.) was added to the catalyst solution (alternatively, the substrated could be weighed out in a separate vial and the catalyst solution added to the latter). DMA was added so as to reach a final volume (taking into account the volume of the organozinc solution) of 2.00 mL. The vial was sealed with a PTFE-lined pierceable cap, taped, and brought outside the glovebox where it was placed in an ice-bath. The vial was cooled for a few minutes before addition of the organozinc solution (0.40 mmol, 0.20 equiv.). The puncture hole was taped over and the reaction mixture was taken off the ice bath and stirred at room temperature for 18 hours. Finally, the mixture was cooled to 0 ºC and 0.30 mL of saturated aqueous NH_4Cl solution were added. The mixture was then transferred to a separatory funnel using ethyl acetate and the organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The crude product could then be isolated as the boronic ester by silica gel chromatography, or re-dissolved in 1.0 mL of THF and oxidized following the method outlined in **procedure B**.

V. Procedures and Characterization for Cross-Coupling Product



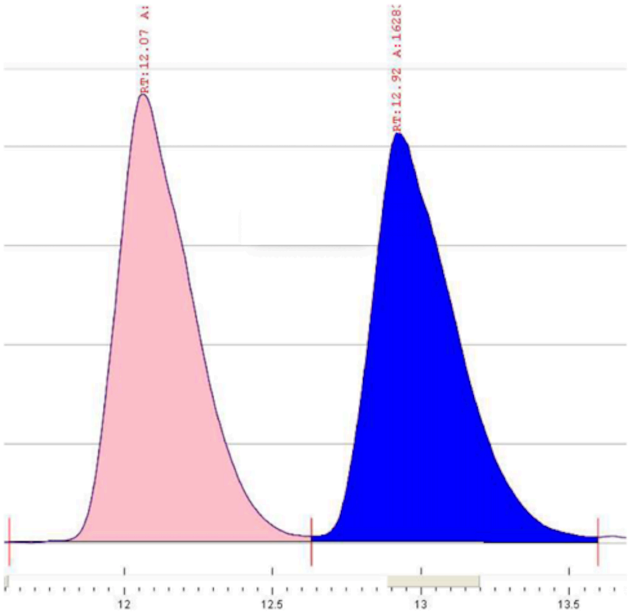
(*R*)-6,6-dimethyl-1-phenylheptan-4-ol (**2**) The reaction was performed according to general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyl iodide (73.6 mg, 0.40 mmol, 2.0 equiv.), and (3-phenylpropyl)zinc bromide • 2LiCl solution in DMA (0.24 mL, 1.68 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (24.3 mg, 55% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29-7.26 (m, 3H), 7.19-7.18 (m, 2H), 3.80-3.75 (m, 1H), 2.67-2.60 (m, 2H), 1.82-1.69 (m, 1H), 1.7-1.60 (m, 1H), 1.52-1.42 (m, 2H), 1.38-1.30 (m, 2H), 0.95 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.56, 128.55, 128.44, 125.87, 69.64, 51.49, 39.33, 36.04, 30.41, 30.30, 27.59. **IR** (neat) ν_{max} 3358.9 (br), 3023.7 (w), 2945.4 (s), 2931.7 (s), 2859.3 (m), 1602.2 (w), 1494.4 (m), 1452.2 (m), 1362.2 (m),1089.6 (m), 746.89 (m), 697.6 (s). **HRMS** (DART) for $C_{15}H_{28}NO$ $(M+NH_4)^+$: Calc'd: 238.2165, found: 238.2166. $[\alpha]_D^{20}$ = 8.60 (*c* =1.0, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned analogy (see product **7** and **21**).

Chiral SFC (Chiracel AD-H, 2% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*R*)-6,6-dimethyl-1-phenylheptan-4-ol**.

Racemic Material



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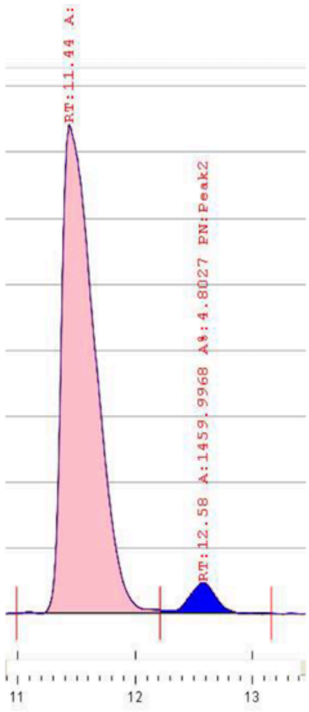
Enantioenriched Material



Peak Info			
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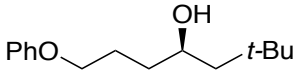
Total:	100	30399.5276	



(*R*)-6,6-dimethyl-1-phenoxyheptan-4-ol (3). The reaction was performed according to general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyl iodide (73.6 mg, 0.40 mmol, 2.0 equiv.), and (3-phenoxypropyl)zinc bromide • 2LiCl solution in DMA (0.360 mL, 1.1 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The

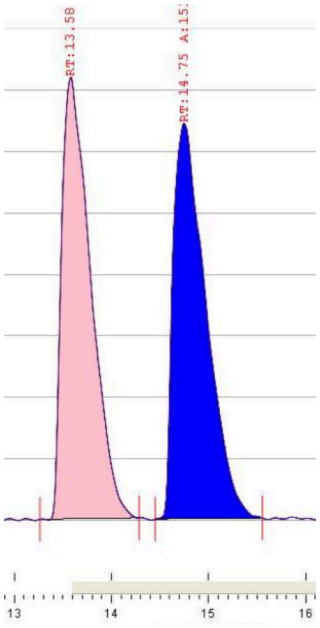
crude mixture was purified by silica gel column chromatography (20% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (33.1 mg,70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.21 (m, 2H), 6.99-6.84 (m, 3H), 4.08-3.91 (m, 2H), 3.91-3.75 (m, 1H), 2.00-1.76 (m, 2H), 1.71-1.55 (m, 2H), 1.40 (d, J = 5.1 Hz, 2H), 0.98 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.0, 129.6, 120.8, 114.6, 69.2, 68.1, 51.5, 36.4, 30.4, 30.3, 25.7. **IR** (neat) ν_{max} 3394.5 (br), 2947.5 (m), 1598.8 (m), 1495.5 (m), 1471.1 (m), 1360.4 (w), 1247.9 (s), 1034.4 (w), 757.1 (m), 690.7 (m). **HRMS** (DART) for $C_{15}H_{25}O_2$ $(M+H)^+$: Calc'd: 237.18491, found: 237.18571. **$[\alpha]_D^{20}$** = -6.898 (c = 1.0, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

Chiral SFC (Chiracel AD-H, 1% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*R*)-6,6-dimethyl-1-phenoxyheptan-4-ol**.

Racemic Material



Peak No	% Area	Area	RT (min)
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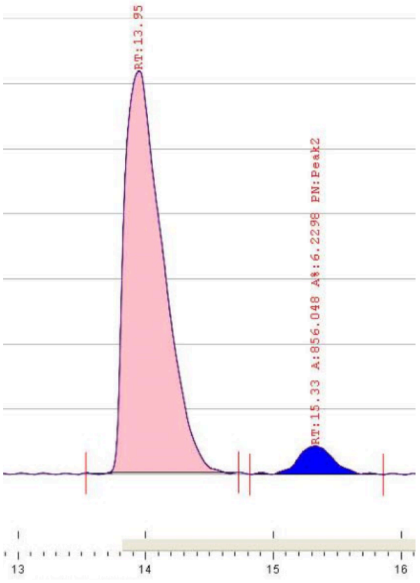
Enantioenriched Material



Peak No	% Area	Area	RT (min)
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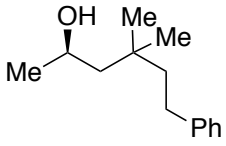
Total:	100	13741.2181	



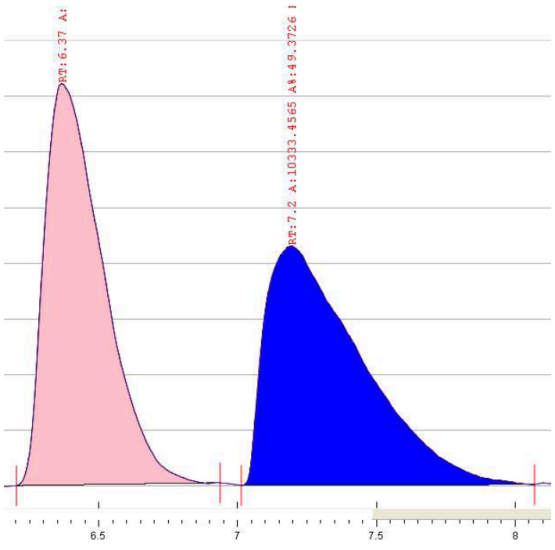
(*R*)-4,4-dimethyl-6-phenylhexan-2-ol (4). The reaction was performed according to general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), (3-iodo-3-methylbutyl)benzene (109.7 mg, 0.40 mmol, 2.0 equiv.), and methylzinc chloride • 2LiCl solution in THF (1.01 mL, 0.40 M, 0.40 mmol, 2.0 equiv.) (**note:** the organozinc reagent was obtained by addition of commercial MeLi (130 µL, 3.1 M in DME, 0.4 mmol, 2.0 equiv.) to $ZnCl_2$ in THF (880 µL, 0.5 M, 0.44 mmol, 2.2 equiv.). After stirring for 30 min at room temperature additional LiCl (18.7 mg, 0.44 mmol, 2.2 equiv.) was added to improve yield and selectivity of the reaction), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as colorless oil (48.9 mg, 55% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30-7.23 (m, 2H), 7.21-7.14 (m, 3H), 4.03-4.00 (m, 1H), 2.65-2.50 (m, 2H), 1.65-1.52 (m, 2H), 1.50 (dd, *J* = 14.5, 7.9 Hz, 1H), 1.41 (dd, *J* = 14.6, 2.9 Hz, 1H), 1.22 (d, *J* = 6.2 Hz, 3H), 1.02 (s, 3H), 1.01 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.5, 128.5, 125.7, 65.7, 51.0, 45.3, 33.1, 30.9, 27.9, 27.8, 26.3. **IR** (neat) ν_{max} 3363.6 (br), 3023.3 (w), 2955.9 (s), 2924.5 (s), 2863.2 (m), 1494.9 (m), 1467.25 (m), 1259.0 (m), 1072.9 (s), 1051.5 (s), 1029.7 (s), 737.7 (s) 697.4 (s). **HRMS** (DART) for $C_{14}H_{26}NO$ $(M+NH_4)^+$: Calc'd: 224.2007, found: 224.2009. $\mathbf{[\alpha]_D^{20}}$ = 11.80 (*c* =1.0, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

Chiral SFC (Chiracel AS-H, 1% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*R*)-4,4-dimethyl-6-phenylhexan-2-ol.**

Racemic Material



Peak Info			
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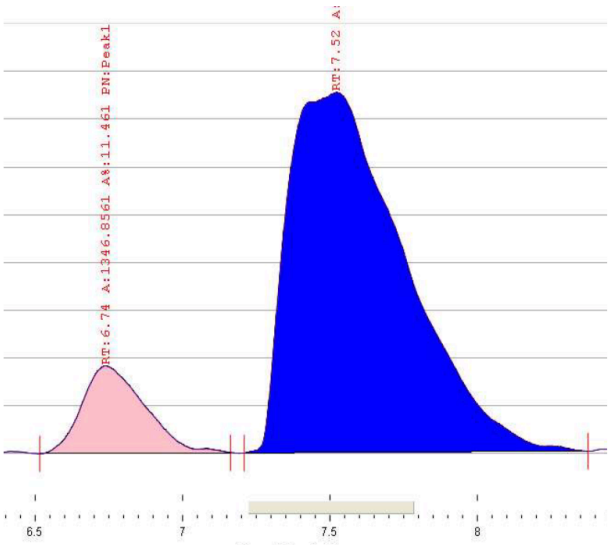
Enantioenriched Material



Peak Info			
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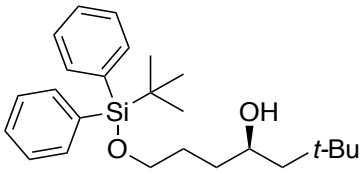
Total:	100	11751.6019	



(*R*)-1-((*tert*-butyldiphenylsilyl)oxy)-6,6-dimethylheptan-4-ol (5). The reaction was performed according to general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyl iodide (73.6 mg, 0.40 mmol, 2.0 equiv.), and (3-((*tert*-butyldiphenylsilyl)oxy)propyl)zinc bromide• 2LiCl solution in DMA (0.425 mL, 0.94 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography

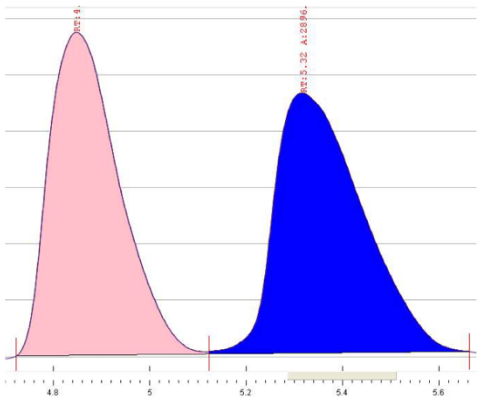
(10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (56 mg, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69-7.67 (m, 3H), 7.48-7.36 (m, 5H), 3.82-3.76 (m, 1H), 3.71-3.68 (m, 2H), 1.83 (s, 1H), 1.73-1.61 (m, 2H), 1.60-1.47 (m, 2H), 1.42 -1.32 (m, 2H), 1.06 (s, 9H), 0.97 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 135.7, 135.7, 133.9, 133.9, 129.8, 127.8, 69.3, 64.3, 51.4, 36.6, 30.4, 30.3, 28.9, 27.0, 19.3. **IR** (neat) ν_{max} 3385.9 (br), 3067.8 (w), 3047.8 (w), 2948.0 (s), 2928.7 (s), 2856.3 (s), 1471.1 (m), 1426.3 (m), 1388.8 (m), 1108.8 (s), 700.3 (s), 613.0 (m), 504.4 (s). **HRMS** (DART) for $C_{25}H_{39}O_2Si$ $(M+H)^+$: Calc'd: 399.2714, found: 399.2723. **$[\alpha]_D^{20}$** = -3.60 (*c* =1.0, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

Chiral SFC (Chiracel OJ-H, 3% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*R*)-1-((*tert*-butyldiphenylsilyl)oxy)-6,6-dimethylheptan-4-ol.**

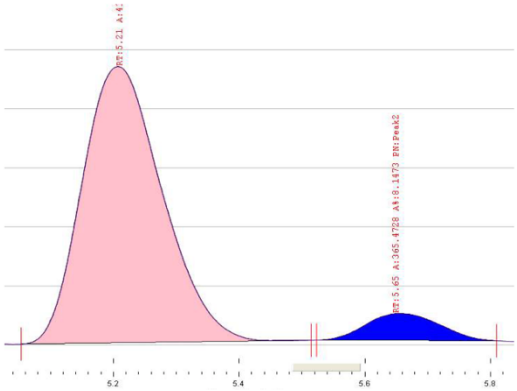
Racemic Material



Peak Info

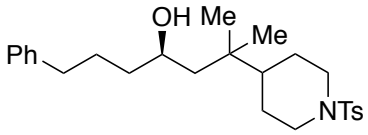
Peak No	% Area	Area	RT (min)
1	49.8877	2883.1671	4.85
2	50.1123	2896.1481	5.32
Total:	100	5779.3152	

Enantioenriched Material



Peak Info

Peak No	% Area	Area	RT (min)
1	91.8527	4120.3358	5.21
2	8.1473	365.4728	5.65
Total:	100	4485.8086	



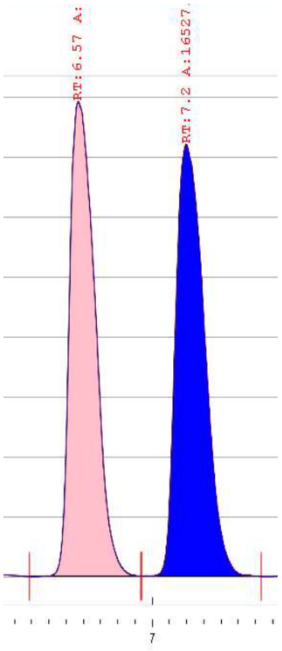
(*R*)-6-methyl-1-phenyl-6-(1-tosylpiperidin-4-yl)heptan-4-ol (6). The reaction was performed according to general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), 4-(2-iodopropan-2-yl)-1-tosylpiperidine (162.92 mg, 0.40 mmol, 2.0 equiv.), and (3-phenylpropyl)zinc bromide • 2LiCl solution in DMA (0.24 mL, 1.68 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (20% ethyl acetate in hexanes, stain in CAM) to afford the product as white solid (48.9 mg, 55% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65-7.63(m, 2H), 7.33-7.26 (m, 4H), 7.19-7.17 (m, 3H), 3.84 (apparent d, J = 11.2 Hz, 2H), 3.70-3.67 (m, 1H), 2.69-2.55 (m, 2H), 2.43 (s, 3H), 2.20-1.99 (m, 2H), 1.79-1.58 (m, 4H), 1.45-1.25 (m, 6H), 1.11-1.07 (m, 2H), 0.87 (s, 3H), 0.84 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5, 142.3, 133.2, 129.6, 128.5, 128.4, 127.9, 125.9, 69.0, 47.3, 47.2, 44.7, 39.6, 35.9, 34.7, 27.5, 26.1, 25.3, 25.1, 21.6. **IR** (neat) ν_{max} 3541.5 (br), 3023.0 (m), 2926.1 (s), 2850.8 (m), 1715.6 (w), 1596.4 (w), 1493.2 (m),1464.6 (s), 1450.4 (s), 1353.5 (s), 1334.5 (s), 1303.2 (s), 1054.5 (s), 930.8 (s), 862.3 (s), 813.0 (s), 724.1 (s), 698.9 (s), 649.2 (s), 573.8 (s). **HRMS** (DART) for $C_{26}H_{38}NO_3S$ $(M+H)^+$: Calc'd: 444.2565, found: 444.2567. $\mathbf{[\alpha]_D^{20}}$ = 4.60 (c =1.0, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

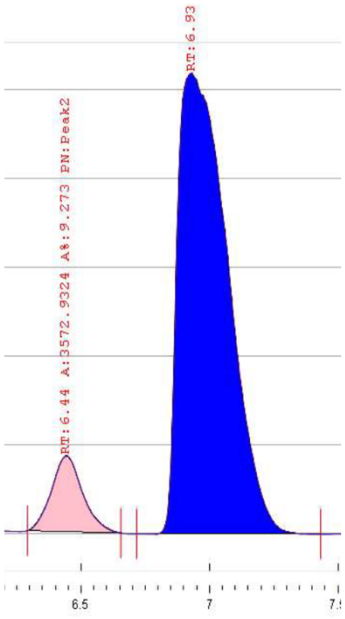
Chiral SFC (Chiracel OJ-H, 15% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*R*)-6-methyl-1-phenyl-6-(1-tosylpiperidin-4-yl)heptan-4-ol.**

Racemic Material

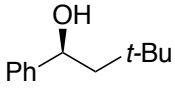


Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
1	49.3844	16125.6078	6.57
2	50.6156	16527.6547	7.2
Total:	100	32653.2625	

Enantioenriched Material



Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
1	9.273	3572.9324	6.44
2	90.727	34957.4911	6.93
Total:	100	38530.4235	



(*S*)-3,3-dimethyl-1-phenylbutan-1-ol (7). The reaction was performed according to general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyl iodide (73.6 mg, 0.40 mmol, 2.0 equiv.), and phenylzinc chloride solution in THF (1.0 mL, 0.4 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a white solid (25.1 mg, 70% yield). **HRMS** (DART) for $C_{26}H_{38}NO3S$ $(M+H-H_2O)^+$: Calc'd: 161.1321,

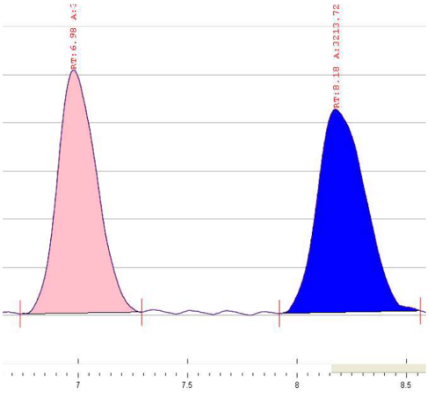
found: 161.1325. $[\alpha]_D^{20}$ = -52.39 (*c* = 0.5, $CHCl_3$, *l* = 50 mm). (lit: $[\alpha]_D^{20}$ = -71.2 (*c* = 1.9, THF, *l* = 100mm, ≤ 99% *ee*, (*S*)-enantiomer)). All spectral data was in accordance with the literature. [11]

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was determined from the X-ray crystal structure of the unoxidized boronic ester product obtained using **(*S*,*S*)-L1** as ligand.

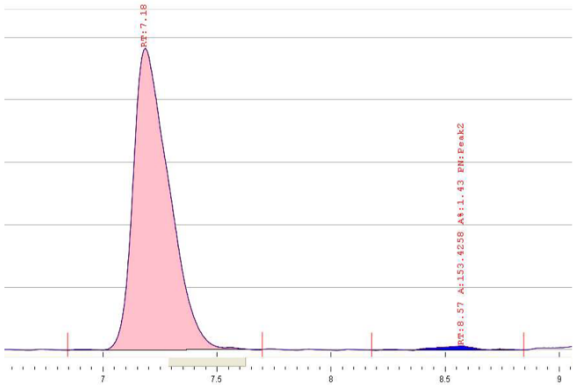
Chiral SFC (Chiracel ODR-H, 1% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*S*)-3,3-dimethyl-1-phenylbutan-1-ol.**

Racemic Material

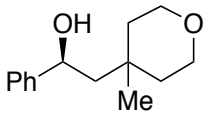


Peak Info			
Peak No	% Area	Area	RT (min)
1	49.3436	3130.442	6.98
2	50.6564	3213.7248	8.18
Total:	100	6344.1668	

Enantioenriched Material



Peak Info			
Peak No	% Area	Area	RT (min)
1	98.57	10575.7422	7.18
2	1.43	153.4258	8.57
Total:	100	10729.168	



(*S*)-2-(4-methyltetrahydro-2*H*-pyran-4-yl)-1-phenylethan-1-ol (8). The reaction was performed according to general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), 4-iodo-4-methyltetrahydro-2*H*-pyran (90.0 mg, 0.40 mmol, 2.0 equiv.), and phenylzinc chloride solution in THF (1.0 mL, 0.4 M, 0.4 mmol, 2.0 equiv.), in a

[11] R. Scholz, G. Hellmann, S. Rohs, D. Özdemir, G, Raabe, C. Vermeeren, H.-J. Gais, *Eur. J. Org. Chem.* **2010**, 4588.

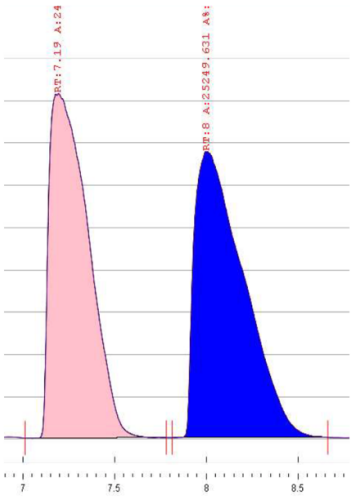
mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (20% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (32.2 mg, 73% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36-7.35 (m, 3H), 7.29-7.26 (m, 2H), 4.90 (dd, *J* = 8.8, 3.5 Hz, 1H), 3.84-3.70 (m, 1H), 3.71-3.59 (m, 2H), 1.91 (dd, *J* = 14.7, 8.7 Hz, 1H), 1.75-1.58 (m, 3H), 1.56-1.44 (m, 2H), 1.37-1.30 (m, 1H), 1.26 (s, 1H), 1.14 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.4, 128.8, 127.7, 125.8, 71.8, 64.1, 64.0, 51.5, 38.5, 38.4, 31.0, 24.5. **IR** (neat) ν_{max} 3410.3 (br), 2950.7 (s), 2919.2 (s), 2853.8 (s), 1452.7 (m), 1102.3 (s), 1060.0 (m), 1036.0 (m), 1017.1 (m), 699.3 (m). **HRMS** (DART) for $C_{14}H_{19}O$ $(M+H-H_2O)^+$: Calc'd: 203.1424, found: 203.1430. **$[\alpha]_D^{20}$** = 40.78 (*c* = 0.5, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

Chiral SFC (Chiracel OJ-H, 5% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*S*)-2-(4-methyltetrahydro-2*H*-pyran-4-yl)-1-phenylethan-1-ol.**

Racemic Material



Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
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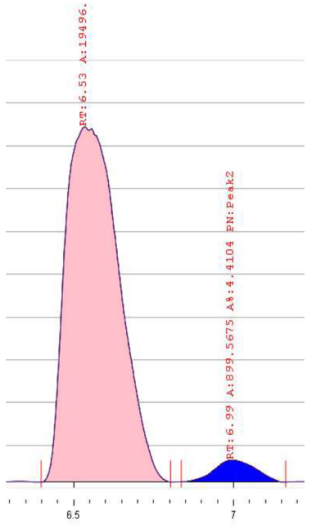
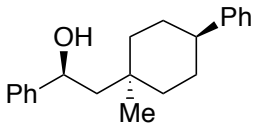
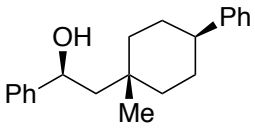
2	51.0988	25249.631	8
Total:	100	49413.3685	

Enantioenriched Material



Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
1	95.5896	19496.8917	6.53
2	4.4104	899.5675	6.99
Total:	100	20396.4592	



and


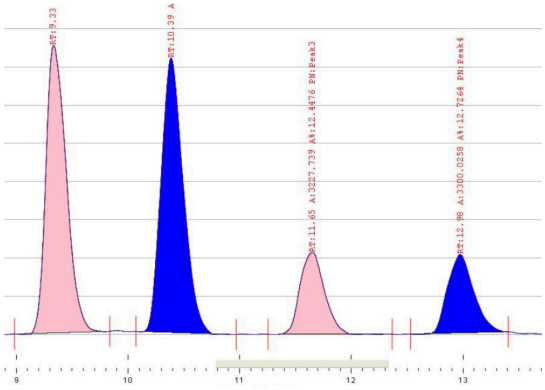
(*S*)-2-((1*s*,4*R*)-1-methyl-4-phenylcyclohexyl)-1-phenylethan-1-ol (9 and **9')**. The reaction was performed according to general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), (4-iodo-4-methylcyclohexyl)benzene (120.1 mg, 0.40 mmol, 2.0 equiv.), and phenylzinc chloride solution in THF (1.0 mL, 0.4 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil consisting of a 1:2.7 mixture of diastereomers (30.6 mg, 52% yield). The diastereomeric ratio was determined by ^{1}H NMR integration. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44-7.34 (m, 13H), 7.34-7.26 (m, 12H), 7.26-7.16 (m, 11H), 4.97 (dd, *J* = 8.4, 2.9 Hz, 1H, minor diastereomer), 4.88 (dd, *J* = 8.2, 3.2 Hz, 3H, major diastereomer), 2.55-2.37 (m, 5H), 2.00 (m, 4H), 1.94-1.85 (m, 4H), 1.84-1.52 (m, 32H), 1.39-1.24 (m, 9H), 1.14 (s, 3H), 1.09 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.7, 147.6, 146.8, 146.8, 128.7, 128.7, 128.4, 128.4, 127.6, 127.5, 127.0, 126.9, 126.0, 126.0, 125.9, 72.4, 71.8, 55.4, 45.2, 44.7, 44.4, 39.1, 38.7, 38.7, 38.6, 32.8, 32.4, 30.5, 29.9, 29.8, 29.8, 29.7, 22.3. **IR** (neat) ν_{max} 412.6 (br), 2919.3 (m), 2857.4 (w), 1491.2 (w), 1053.4 (w), 718.5 (m), 697.2 (s), 533.78 (w). **HRMS** (DART) for $C_{15}H_{25}O_2$ $(M+H-H_2O)^+$: Calc'd: 277.1951, found: 277.1951.

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

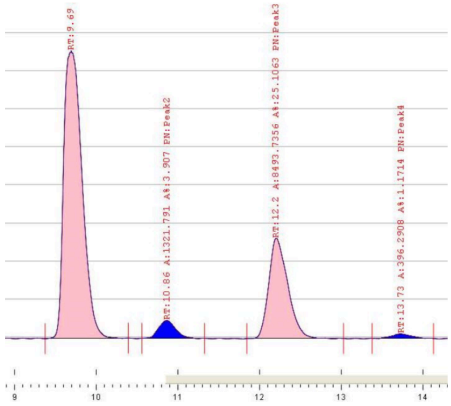
Chiral SFC (Chiracel OJ-H, 4% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*S*)-2-(1-methyl-4-phenylcyclohexyl)-1-phenylethan-1-ol**.

Racemic Material



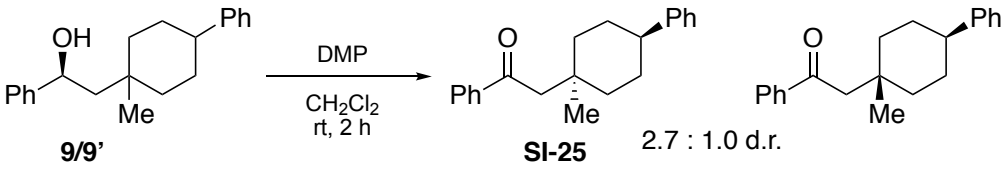
Peak No	% Area	Area	RT (min)
1	36.764	9533.1123	9.33
2	38.062	9869.7005	10.39
3	12.4476	3227.739	11.65
4	12.7264	3300.0258	12.98
Total:	100	25930.5776	

Enantioenriched Material

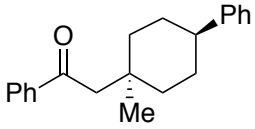


Peak No	% Area	Area	RT (min)
1	69.8153	23619.2332	9.69
2	3.907	1321.791	10.86
3	25.1063	8493.7356	12.2
4	1.1714	396.2908	13.73
Total:	100	33831.0506	

The stereochemical configuration was determined by COSY and NOESY analysis of compound **SI-25** which was isolated as a single stereoisomer from the mixture obtained after oxidation of product **9**.



9/9' **SI-25** 2.7 : 1.0 d.r.

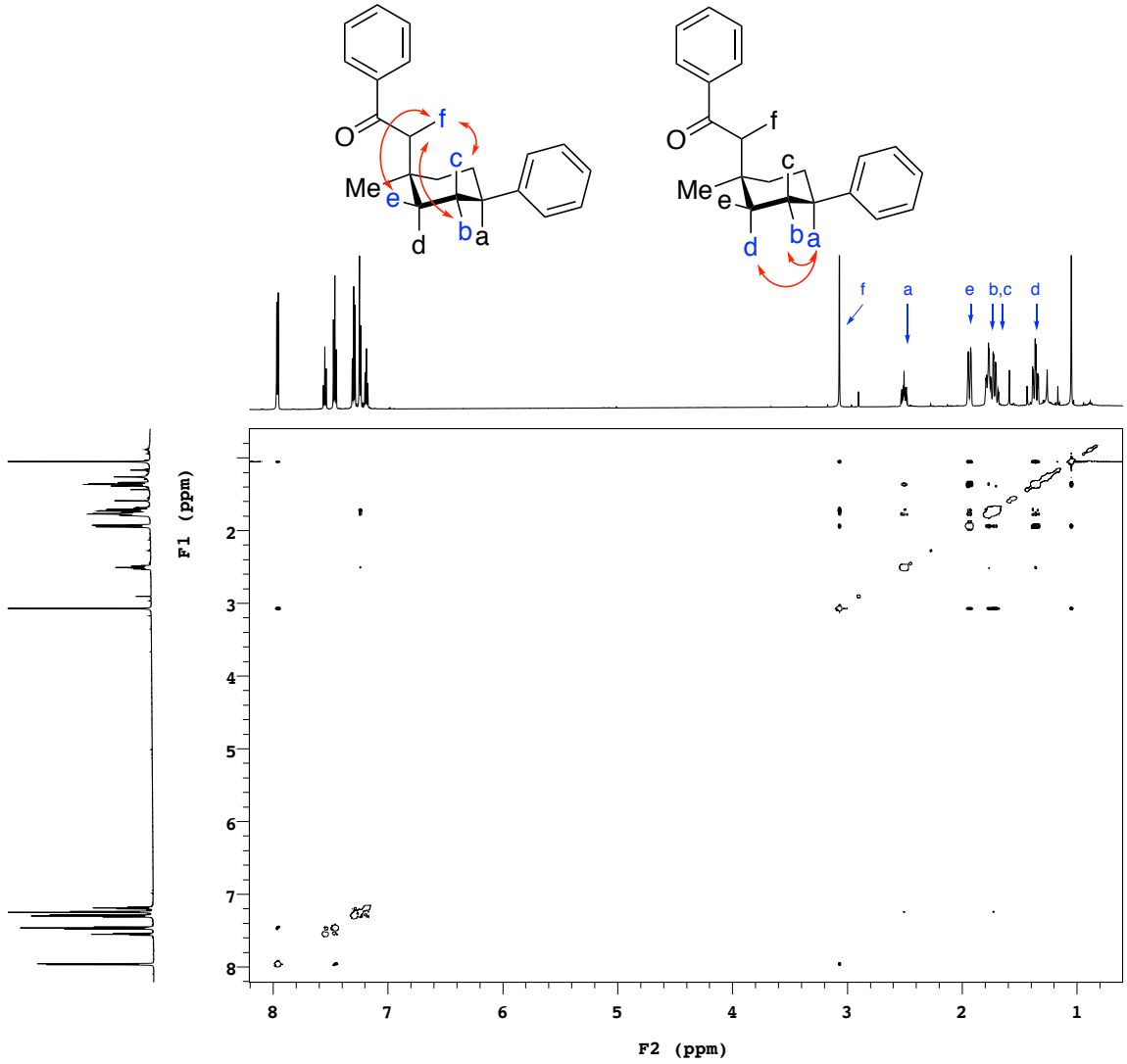


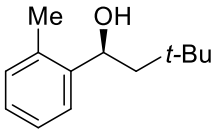
2-((1*s*,4*s*)-1-methyl-4-phenylcyclohexyl)-1-phenylethan-1-one (SI-25)

Diastereomeric mixture **9** (40.7 mg, 0.14 mmol, 1.0 equiv.) was placed in a scintillation vial equipped with a stirr-barr, and dissolved in 5 mL of dichloromethane. Sodium bicarbonate (47

mg, 0.56 mmol, 4.0 equiv.) was added to the solution followed by Dess-Martin periodinane (88.0 mg, 0.21 mmol, 1.5 equiv.) and the mixture was stirred at room temperature for 2 hours. The reaction was quenched with 2 mL of 10% sodium thiosulfate aq. solution followed by 2 mL of sat. sodium bicarbonate aq. solution. The organic layer was extracted twice with dichloromethane and twice with diethyl ether, the combined organic layers were dried over MgSO4 and concentrated in vacuo. The major diastereomer was isolated by silica gel chromatography (1-5% ethyl acetate in pentanes, UV) as a colorless oil (22 mg, 55% yield). **^{1}H NMR** (600 MHz, $CDCl_3$(600 MHz, Chloroform-*d*) δ 7.99-7.94 (m, 2H), 7.58-7.52 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.26-7.23 (m, 2H), 7.21-7.17 (m, 1H), 3.07 (s, 2H), 2.51 (tt, *J* = 12.0, 4.1 Hz, 1H), 1.94 (app. d, *J* = 11.3 Hz, 2H), 1.82 – 1.66 (m, 4H), 1.36 (td, *J* = 13.4, 4.1 Hz, 2H), 1.05 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.1, 147.2, 139.0, 132.7, 128.5, 128.3, 128.3, 128.2, 128.1, 126.8, 125.9, 44.1, 42.6, 38.6, 33.6, 29.9, 29.8. **IR** (neat) ν_{max} 3056.3 (w), 3023.3 (w), 2921.7 (s), 2858.7 (s), 1686.2 (s), 1671.2 (s), 1596.3 (w), 1447.0 (m), 1375.0 (m), 1252.8 (m), 750.0 (s), 728.2 (s).

Relevant NOESY correlations are illustrated below.





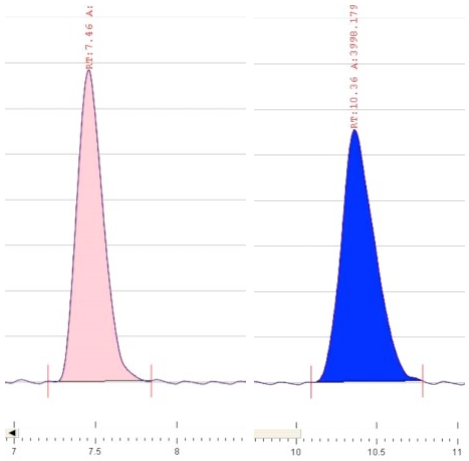
(*S*)-3,3-dimethyl-1-(o-tolyl)butan-1-ol (10) The reaction was performed according to the general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyl iodide (73.6 mg, 0.40 mmol, 2.0 equiv.), and (o-tolyl) zinc chloride (0.89 mL, 0.45 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and **(*S*,*S*)-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (27.6 mg, 56% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.7, 1.5 Hz, 1H), 7.23 (t, *J* = 7.4, 7.4 Hz, 1H), 7.17-7.11 (m, 2H), 5.10 (dt, *J* = 9.3, 2.9, 2.9 Hz, 1H), 2.34 (s, 3H), 1.68 (dd, *J* = 14.9, 9.1 Hz, 1H), 1.58 (dt, *J* = 3.5, 1.2 Hz, 1H), 1.51 (dd, *J* = 14.8, 1.4 Hz, 1H), 1.04 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.8, 133.8, 130.5, 127.1, 126.5, 125.3, 68.8, 52.1, 30.9, 30.4, 19.3. **IR** (neat) ν_{max} 2953.0 (m), 2922.3 (s), 2850.9 (w), 1462.4 (w), 1363.0 (w), 1337.35 (w), 1079.7 (w), 1026.27 (w), 425.5 (w). **HRMS** (DART) for $C_{13}H_{19}$ $(M+H-H_2O)^+$: Calc'd: 175.1481, found: 175.1473. $[\alpha]_D^{20}$ = 17.00 (*c* = 0.20, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

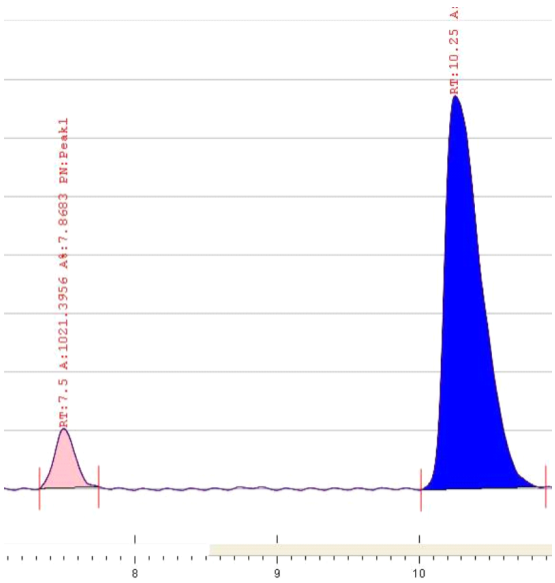
Chiral SFC (Chiracel ODR-H, 1% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*S*)-1-(4-methoxyphenyl)-3,3-dimethylbutan-1-ol.**

Racemic Material

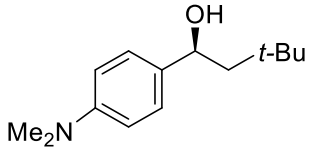


Peak No	% Area	Area	RT (min)
1	49.0177	3844.1176	7.46
2	50.9823	3998.1798	10.36
Total:	100	7842.2974	

Enantioenriched Material



Peak No	% Area	Area	RT (min)
1	7.8683	1021.3956	7.5
2	92.1317	11959.7606	10.25
Total:	100	12981.1562	



(*S*)-1-(4-(dimethylamino)phenyl)-3,3-dimethylbutan-1-ol (11) The reaction was performed according to the general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyl iodide (73.6 mg, 0.40 mmol, 2.0 equiv.), and (4-(dimethylamino)phenyl) zinc chloride (1.11 mL, 0.36 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using NiBr2 • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and **(*S*,*S*)-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (20% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (20.4 mg, 46% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 (d, 2H), 6.72 (d, 2H), 4.74 (dd, *J* = 8.3, 4.1 Hz, 1H), 2.95 (s, 6H), 1.82-1.74 (m, 1H), 1.63-1.54 (m, 2H), 0.97 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.3, 134.6, 127.0, 112.8,

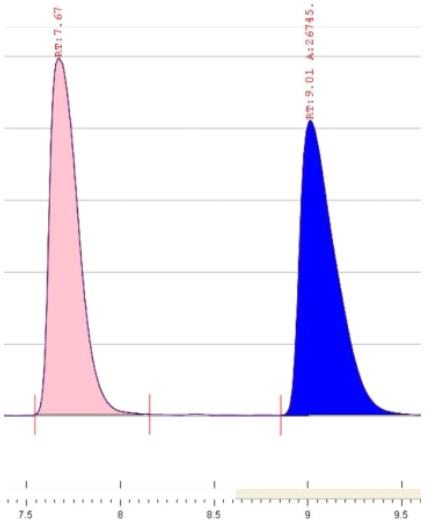
72.4, 52.5, 40.8, 30.5, 30.4. **IR** (neat) ν_{max} 3256.4 (br), 2947.6 (m), 2915.3 (w), 2882.2 (w), 2027.4 (w), 1614.0 (m), 1521.8 (m), 1468.3 (w), 1360.7 (w), 1348.2 (w), 1224.4 (w), 1059.5 (w), 1018.6 (w), 988.7 (w), 819.1 (w). **HRMS** (DART) for $C_{14}H_{22}N$ $(M+H-H_2O)^+$: Calc'd: 204.1747, found: 204.1743. $[\alpha]_D^{20} = 28.98$ ($c = 0.35$, $CHCl_3$, $l = 50$ mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

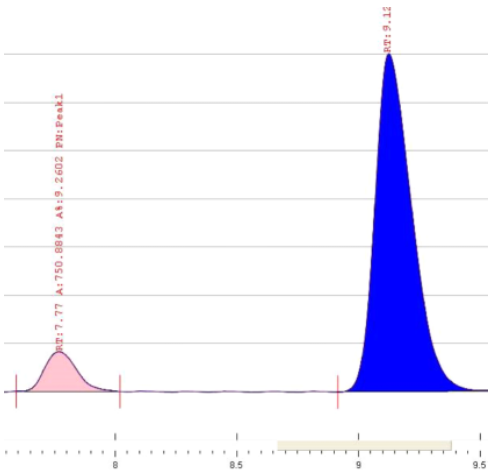
Chiral SFC (Chiracel OJ-H, 5% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*S*)-1-(4-(dimethylamino)phenyl)-3,3-dimethylbutan-1-ol.**

Racemic Material

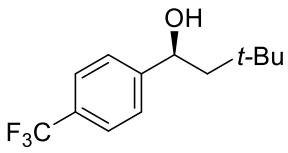


Peak No	% Area	Area	RT (min)
1	49.3028	26010.3074	7.67
2	50.6972	26745.8883	9.01
Total:	100	52756.1957	

Enantioenriched Material



Peak No	% Area	Area	RT (min)
1	9.2602	750.8843	7.77
2	90.7398	7357.8656	9.12
Total:	100	8108.7499	



(*S*)-3,3-dimethyl-1-(4-(trifluoromethyl)phenyl)butan-1-ol (12). The reaction was performed according to the general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyl iodide (73.6 mg, 0.40 mmol, 2.0 equiv.), and 4-(trifluoromethyl)phenylzinc chloride (0.52 mL, 0.77 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and **(*S*,*S*)-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain

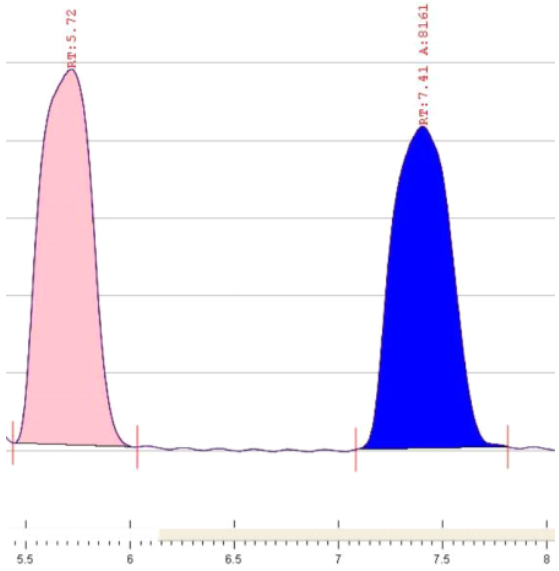
in CAM) to afford the product as a colorless oil (27.6 mg, 56% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 4.91 (d, J = 8.0 Hz, 1H), 1.77– 1.71 (m, 2H), 1.56 (dd, J = 14.7, 3.1 Hz, 1H), 1.02 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.5, 126.1, 125.6, 125.6, 125.6, 125.6, 72.1, 53.3, 30.8, 30.3. **IR** (neat) ν_{max} 3396.7 (br), 2952.3 (m), 2866.9 (w), 1324.8 (s), 1164.2 (m), 1126.6 (m), 1067.7 (m), 1016.6 (w), 843.7 (w). **HRMS** (DART) for $C_{13}H_{16}F_3$ $(M+H-H_2O)^+$: Calc'd: 229.1199, found: 229.1204. **$[\alpha]_D^{20}$** = 28.66 (c = 0.30, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

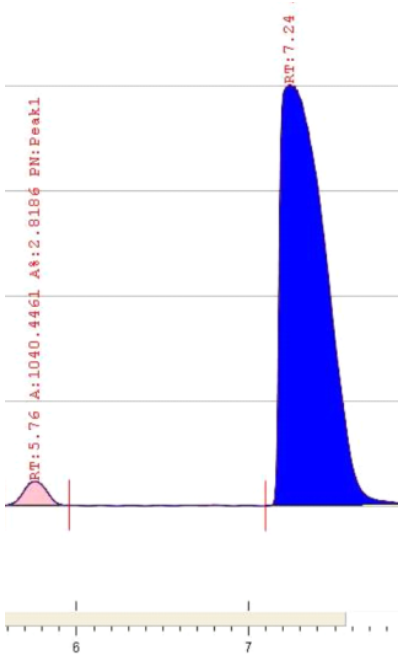
Chiral SFC (Chiracel OJ-H, 1% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(S)-3,3-dimethyl-1-(4-(trifluoromethyl)phenyl)butan-1-ol**

Racemic Material

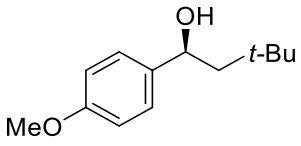


Peak No	% Area	Area	RT (min)
1	50.6036	8360.4958	5.72
2	49.3964	8161.0401	7.41
Total:	100	16521.5359	

Enantioenriched Material



Peak No	% Area	Area	RT (min)
1	2.8186	1040.4461	5.76
2	97.1814	35873.3607	7.24
Total:	100	36913.8068	



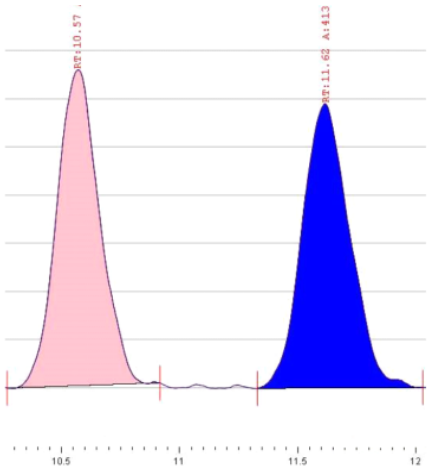
(*S*)-1-(4-methoxyphenyl)-3,3-dimethylbutan-1-ol (13). The reaction was performed according to the general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyl iodide (73.6 mg, 0.40 mmol, 2.0 equiv.), and (4-methoxyphenyl)zinc chloride (0.23 mL, 1.74 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and **(*S*,*S*)-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (26.2 mg, 63% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28-7.26 (m, 2H), 6.90-6.83 (d, J = 8.6 Hz, 2H), 4.79 (dt, J = 7.9, 3.8 Hz, 1H), 3.80 (s, 3H), 1.77 (dd, J = 14.3, 8.1 Hz, 1H), 1.60 (dd, 2H), 0.97 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.1, 138.8, 127.2, 114.0, 72.2, 55.4, 52.9, 30.6, 30.3. **IR** (neat) ν_{max} 3408.8 (br), 2948.4 (m), 2864.8 (w), 2833.9 (w), 1610.5 (w), 1510.3 (s), 1244.4 (s), 1173 (m), 1035.3 (m), 830.6 (m), 587.3 (w). **HRMS** (DART) for $C_{13}H_{19}O$ $(M+H-H_2O)^+$: Calc'd: 191.1430, found: 191.1420. **$[\alpha]_D^{20}$** = 39.72 (c =0.59, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

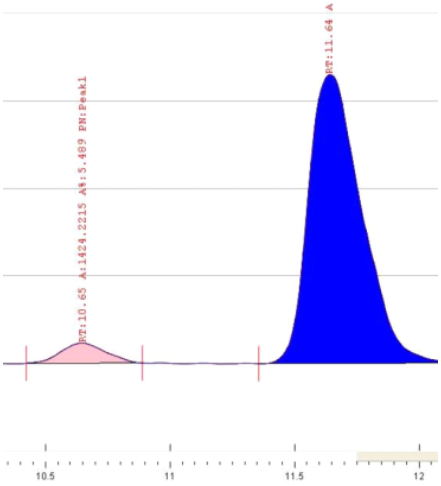
Chiral SFC (Chiracel OJ-H, 2% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(S)-1-(4-methoxyphenyl)-3,3-dimethylbutan-1-ol.**

Racemic Material

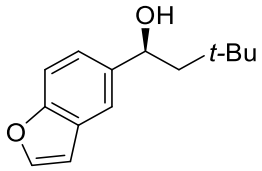


Peak No	% Area	Area	RT (min)
1	49.9828	4128.837	10.57
2	50.0172	4131.6767	11.62
Total:	100	8260.5137	

Enantioenriched Material



Peak No	% Area	Area	RT (min)
1	5.489	1424.2215	10.65
2	94.511	24522.3855	11.64
Total:	100	25946.607	



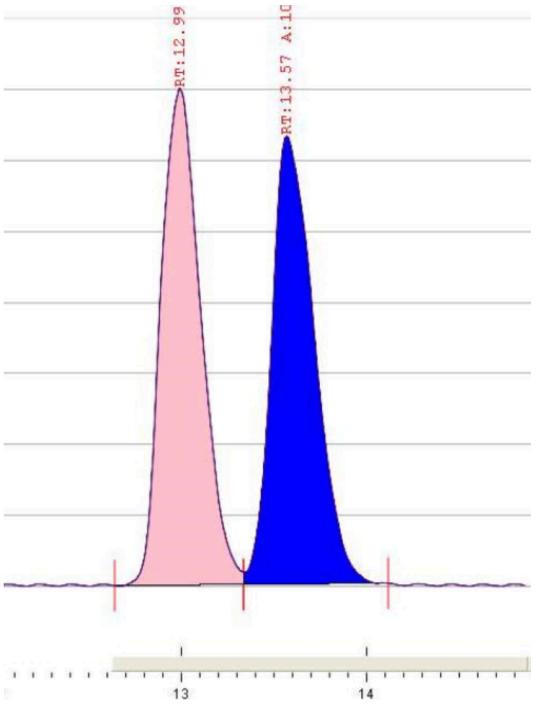
(S)-1-(benzofuran-5-yl)-3,3-dimethylbutan-1-ol (14). The reaction was performed according to general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyl iodide (73.6 mg, 0.40 mmol, 2.0 equiv.), and (3- benzofuran-5-ylzinc chloride solution in THF (1.0 mL, 0.4 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, UV active) to afford the product as a colorless oil (23.1 mg, 52% yield).**^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.1 Hz, 1H), 7.59 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.29 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.75 (d, *J* = 2.2 Hz, 1H), 4.93 (dd, *J* = 8.9, 3.3 Hz, 1H), 1.82 (dd, *J* = 14.5, 8.3 Hz, 1H), 1.74 (s, 1H), 1.66 (dd, *J* = 14.5, 3.7 Hz, 1H), 1.00 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.5, 145.6, 141.4, 127.6, 122.54, 118.5, 111.5, 106.8, 72.8, 53.4, 30.7, 30.4. **IR** (neat) ν_{max} 3377.6 (br), 2948.9 (s), 2864.0 (m), 1466.2 (m), 1362.9 (m), 1158.8 (m), 1106.2 (m), 767.5 (m), 747.2 (m), 734.3 (m), 699.5 (m). **HRMS** (DART) for $C_{14}H_{17}O$ $(M+H-H_2O)^+$: Calc'd: 201.1274, found: 201.1268. **$[\alpha]_D^{20}$** = -47.687 (*c* = 1.0, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

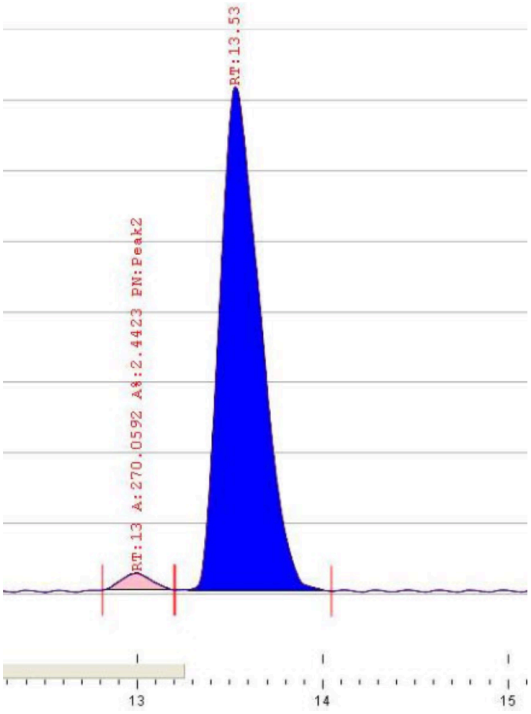
Chiral SFC (Chiracel OJ-H, 2% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(S)-1-(benzofuran-5-yl)-3,3-dimethylbutan-1-ol**.

Racemic Material

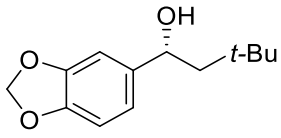


Peak No	% Area	Area	RT (min)
1	50.839	10492.7555	12.99
2	49.161	10146.4396	13.57
Total:	100	20639.1951	

Enantioenriched Material



Peak No	% Area	Area	RT (min)
1	2.4423	270.0592	13
2	97.5577	10787.3117	13.53
Total:	100	11057.3709	



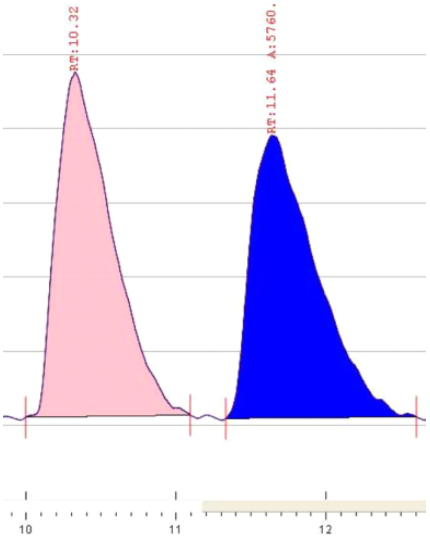
(S)-1-(benzo[d][1,3]dioxol-5-yl)-3,3-dimethylbutan-1-ol (15). The reaction was performed according to the general **procedure A** with vinylboronic acid pinacol ester (30.8 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyl iodide (73.6 mg, 0.40 mmol, 2.0 equiv.), and (benzo[d][1,3]dioxol-5-yl) zinc bromide • 2LiCl (1.11 mL, 0.36 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using NiBr2 • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and **(*R*,*R*)-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (29.3 mg, 66% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.93-6.86 (s, 1H), 6.80-6.74(m, 2H), 5.94 (s, 2H), 4.74 (dd, J = 8.2, 3.9 Hz, 1H), 1.74 (dd, J = 14.4, 8.2 Hz, 1H), 1.64 (s, 1H), 1.57 (dd, J = 14.4, 3.9 Hz, 1H), 0.97 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.9, 146.9, 140.8, 119.2, 108.2, 106.5, 101.1, 72.5, 53.0, 30.6, 30.5, 30.3. **IR** (neat) ν_{max} 3378.6 (br), 2948.8 (s), 2901.2 (m), 1502.1 (m), 1485.9 (s), 1440.4 (m), 1363.4 (w), 1243.2 (s), 1039.5 (s), 934.0 (w), 810.7 (w). **HRMS** (DART) for $C_{13}H_{17}O_2$ $(M+H-H_2O)^+$: Calc'd: 205.1223, found: 205.1219. $\mathbf{[\alpha]_D^{20}}$ = 31.17 (c = 0.34, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

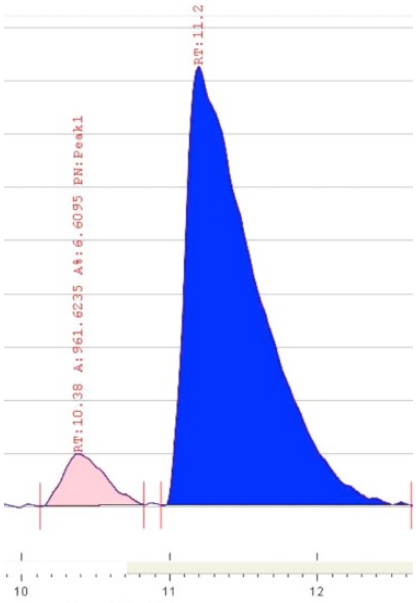
Chiral SFC (Chiracel AS-H, 1% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*S*)-1-(benzo[d][1,3]dioxol-5-yl)-3,3-dimethylbutan-1-ol.**

Racemic Material

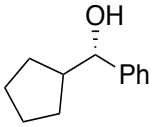


Peak No	% Area	Area	RT (min)
1	50.8722	5964.8104	10.32
2	49.1278	5760.2832	11.64
Total:	100	11725.0936	

Enantioenriched Material



Peak No	% Area	Area	RT (min)
1	6.6095	961.6235	10.38
2	93.3905	13587.4501	11.2
Total:	100	14549.0736	



(*S*)-cyclopentyl(phenyl)methanol (21). The reaction was performed according to general **procedure A** with (*E*)-2-(6-iodohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (67.2 mg, 0.20 mmol, 1.0 equiv.), and phenylzinc chloride solution in THF (1.00 mL, 0.4 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (24.6 mg, 70% yield). **HRMS** (DART) for $C_{12}H_{15}$ $(M+H-H_2O)^+$: Calc'd: 159.1166, found: 151.1168. $[\alpha]_D^{20}$ = -

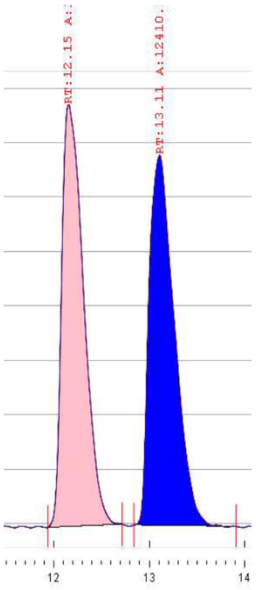
51.03 (*c* = 1.0, $CHCl_3$, *l* = 50 mm (lit: $[\alpha]_D^{20}$ = - 40.08 (*c* = 0.8, $CHCl_3$, 78% *ee*, (*S*)-enantiomer)). All spectral data was in accordance with the literature.[12]

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by comparison with the optical rotation reported in the literature for the same compound.[12] The stereochemical assignment was found to be in accordance with product **7** (determined through X-ray crystallography).

Chiral SFC (Chiracel OJ-H, 2% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*S*)-cyclopentyl(phenyl)methanol.**

Racemic Material



Peak Info			
Peak No	% Area	Area	RT (min)
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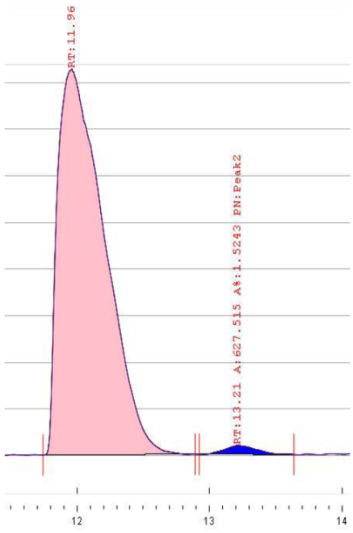
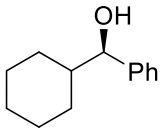
2	50.1865	12410.1565	13.11
Total:	100	24728.0733	

Enantioenriched Material



Peak Info			
Peak No	% Area	Area	RT (min)
1	98.4757	40539.7235	11.96
2	1.5243	627.515	13.21
Total:	100	41167.2385	

[12] D. J. Morris, A. M. Hayes, M. Wills *J. Org. Chem.* **2006**, 7035.



(*R*)-cyclohexyl(phenyl)methanol (24). The reaction was performed according to general **procedure A** with (*E*)-2-(7-iodohept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (70.0 mg, 0.20 mmol, 1.0 equiv.), and phenylzinc chloride solution in THF (1.00 mL, 0.4 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(R,R)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (19.0 mg, 52% yield). **HRMS** (DART) for $C_{13}H_{17}$ $(M+H-H_2O)^+$: Calc'd: 173.1325, found: 173.1329. $\mathbf{[\alpha]_D^{20}}$ = 28.27 (*c* = 0.29, $CHCl_3$, *l* = 50 mm (lit: $\mathbf{[\alpha]_D^{20}}$ = -21.4 (*c* = 1.01, $CHCl_3$, 91% *ee*, (*S*)-enantiomer)). All spectral data was in accordance with the literature.[13]

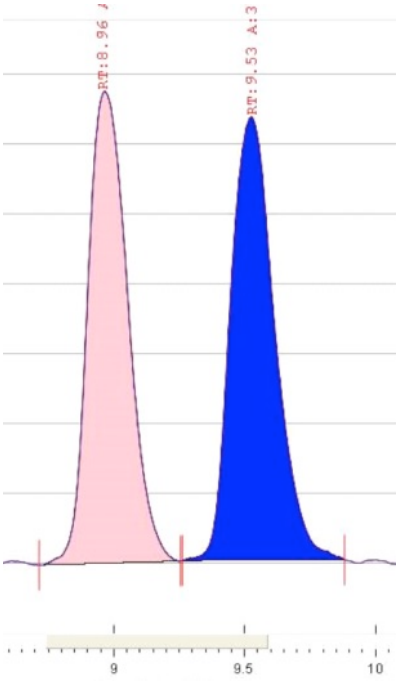
[13] I. Arenas, O. Boutureira, M. I. Matheu, Y. Díaz, S. Castillón, *Eur. J. Org. Chem.* **2015**, 3666.

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**) and comparison of optical rotation reported in the literature for the same compound.[13]

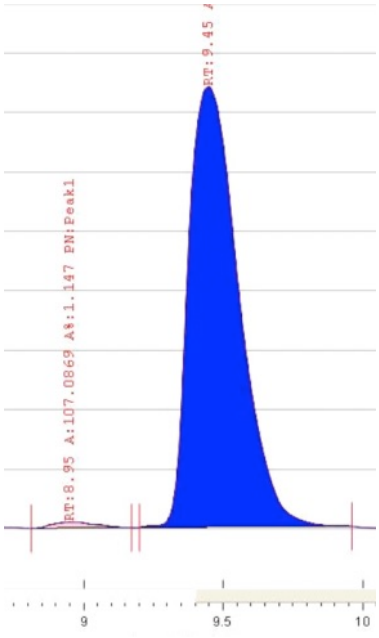
Chiral SFC (Chiracel OJ-H, 3% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*S*)-cyclohexyl(phenyl)methanol.**

Racemic Material

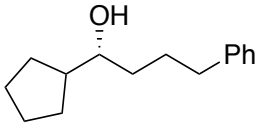


Peak No	% Area	Area	RT (min)
1	49.1136	3580.9512	8.96
2	50.8864	3710.2034	9.53
Total:	100	7291.1546	

Enantioenriched Material



Peak No	% Area	Area	RT (min)
1	1.147	107.0869	8.95
2	98.853	9229.2502	9.45
Total:	100	9336.3371	



(*R*)-1-cyclopentyl-4-phenylbutan-1-ol (25). The reaction was performed according to general **procedure B** with (*E*)-2-(6-iodohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (67.2 mg, 0.20 mmol, 1.0 equiv.), and (3-phenylpropyl)zinc bromide solution in DMA (0.24 mL, 1.68 M, 0.4 mmol, 2.0 equiv.), with (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol,

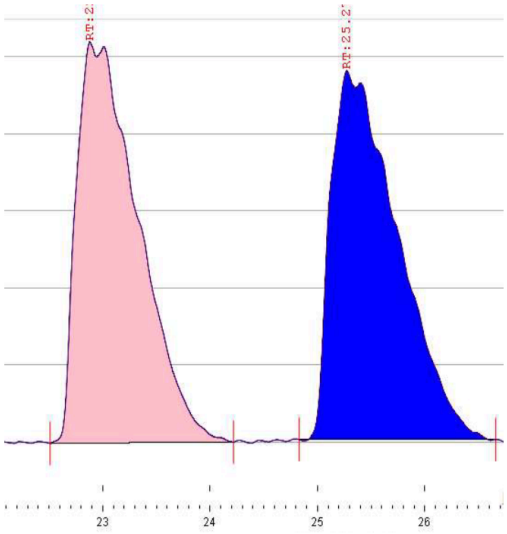
0.13 equiv.) in DMA (2.40 mL). The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (25.3 mg, 58% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29-7.26 m, 2H), 7.20-7.18(m, 3H), 3.43 (td, J = 8.0, 3.2 Hz, 1H), 2.72-2.53 (m, 2H), 1.89-1.50 (m, 10H), 1.46-1.28 (m, 2H), 1.29 -1.15 (m, 1H).**^{13}C NMR** (151 MHz, $CDClz_3$) δ 142.6, 128.5, 128.4, 125.8, 75.9, 46.5, 36.1, 35.9, 29.3, 28.6, 27.7, 25.8, 25.7. **IR** (neat) ν_{max} 3357.1 (br), 3082.2 (w), 3057. 3022.8 (w), 2938.7 (s), 2861.2 (s), 1494.2 (m), 1450.8 (m), 1094.4 (m), 1053.8 (m), 1028.9 (m), 920.6 (m), 800.8 (s), 746.5 (s). **HRMS** (DART) for $C_{15}H_{21}$ $(M+H-H_2O)^+$: Calc'd: 201.1634, found: 201.1638. **$[\alpha]_D^{20}$** = -5.66 (c = 1.0, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

Chiral SFC (Chiracel OJ-H, 2% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*R*)-1-cyclopentyl-4-phenylbutan-1-ol.**

Racemic Material



Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
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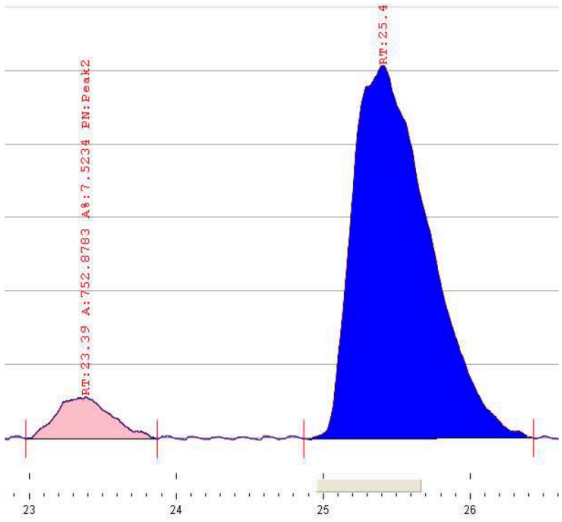
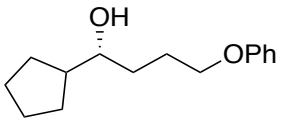
2	49.926	20827.4806	25.27
Total:	100	41716.7121	

Enantioenriched Material



Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
1	7.5234	752.8783	23.39
2	92.4766	9254.2799	25.41
Total:	100	10007.1582	



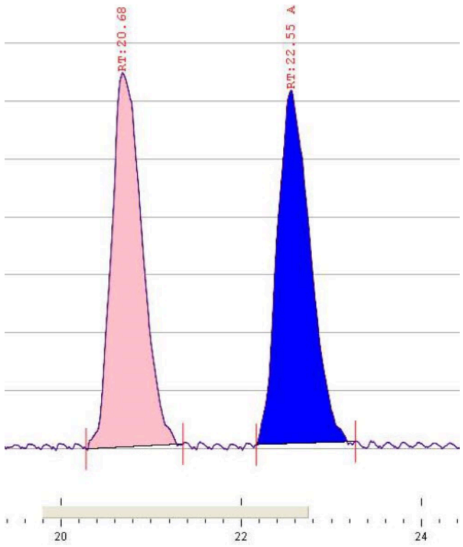
(*R*)-1-cyclopentyl-4-phenoxybutan-1-ol (27). The reaction was performed according to general **procedure B** with (*E*)-2-(6-iodohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (67.2 mg, 0.20 mmol, 1.0 equiv.), and (3-phenoxypropyl)zinc bromide solution in DMA (0.360 mL, 1.1 M, 0.4 mmol, 2.0 equiv.), with (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) in DMA (2.40 mL). The crude mixture was purified by silica gel column chromatography (15% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (30.1 mg, 64% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.18 (m, 2H), 7.05-6.76 (m, 3H), 4.00 (ddd, *J* = 5.8, 3.0 Hz, 2H), 3.59-3.35 (m, 1H), 2.14-1.43 (m, 12H), 1.43-1.30 (m, 1H), 1.27-1.17 (m, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.1, 129.6, 120.8, 114.7, 75.8, 68.1, 46.7, 33.0, 29.3, 28.8, 25.9, 25.8 (one diastereotopic carbon peak not observed). **IR** (neat) ν_{max} 3408.7 (Br), 2946.9 (m), 2865.0 (m), 1598.1 (w), 1495.6 (m), 1299.5 (w), 1244.0 (s), 1040.7 (w), 1012.4 (w), 752.3 (m), 690.7 (m). **HRMS** (DART) for $C_{15}H_{23}O_2$ $(M+H)^+$: Calc'd: 235.1694, found: 235.1704. **$[\alpha]_D^{20}$** = 4.159 (*c* = 1.0, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

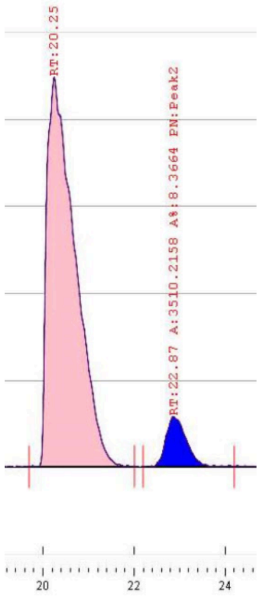
Chiral SFC (Chiracel OJ-H, 4% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*R*)-1-cyclopentyl-4-phenoxybutan-1-ol.**

Racemic Material

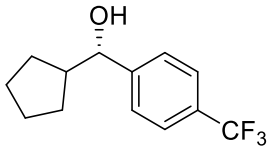


Peak No	% Area	Area	RT (min)
1	49.9026	3070.2661	20.68
2	50.0974	3082.2568	22.55
Total:	100	6152.5229	

Enantioenriched Material



Peak No	% Area	Area	RT (min)
1	91.6336	38445.685	20.25
2	8.3664	3510.2158	22.87
Total:	100	41955.9008	



(*S*)-cyclopentyl(4-(trifluoromethyl)phenyl)methanol (27). The reaction was performed according to general **procedure A** with (E)-2-(6-iodohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (67.2 mg, 0.20 mmol, 1.0 equiv.), and 4-(trifluoromethyl)phenyl zinc chloride solution in THF (0.52 mL, 0.77 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (27.0 mg, 55% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, J = 7.9 Hz, 2H), 7.46 (d, J = 7.8 Hz, 2H), 4.50 (d, J = 8.2 Hz, 1H), 2.18 (h, J =

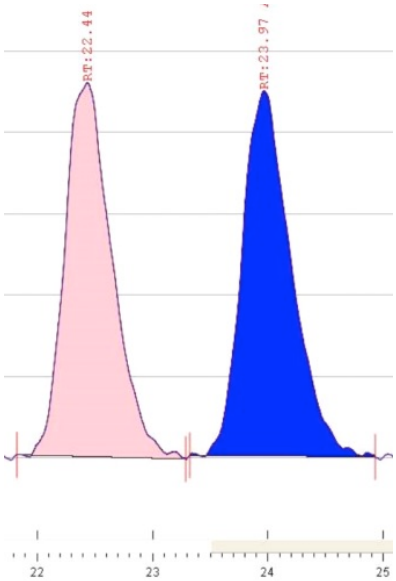
8.9, 8.9, 8.9, 8.3, 8.3 Hz, 1H), 1.93 (dd, *J* = 3.3, 1.2 Hz, 1H), 1.85 (h, td, *J* = 12.4, 12.2, 7.3 Hz, 1H), 1.71-1.55 (m, 3H), 1.55-1.45 (m, 2H), 1.43-1.36 (m, 1H), 1.22-1.14 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.5, 126.9, 125.4, 125.4, 125.4, 125.4, 78.4, 47.9, 29.5, 29.2, 25.6, 25.5. **IR** (neat) ν_{max} 3374.5 (br), 2953.1 (w), 2867.0 (w), 1618.6 (w), 1417.4 (w), 1323.9 (s), 1162.2 (m), 1123.4 (s), 1065.9 (s), 1016.1 (w), 836.9 (w), 758.6 (w). **HRMS** (DART) for $C_{13}H_{14}F_3$ $(M+H-H_2O)^+$: Calc'd: 227.1042, found: 227.1048. **$[\alpha]_D^{20}$** = -29.83 (*c* = 1.00, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

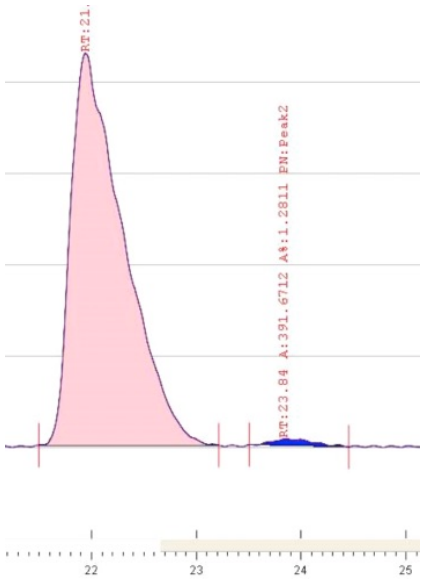
Chiral SFC (Chiracel AD-H, 1% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*S*)-cyclopentyl(4-(trifluoromethyl)phenyl)methanol.**

Racemic Material

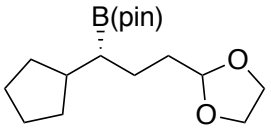


Peak No	% Area	Area	RT (min)
1	49.6834	6573.1351	22.44
2	50.3166	6656.9053	23.97
Total:	100	13230.0404	

Enantioenriched Material



Peak No	% Area	Area	RT (min)
1	98.7189	30182.1448	21.94
2	1.2811	391.6712	23.84
Total:	100	30573.816	



(*R*)-2-(1-cyclopentyl-3-(1,3-dioxolan-2-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28). The reaction was performed according to general **procedure B** with (*E*)-2-(6-iodohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (67.2 mg, 0.20 mmol, 1.0 equiv.), and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide solution in DMA (0.330 mL, 1.23 M, 0.4 mmol, 2.0 equiv.), with (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) in DMA (2.40 mL). ***Note:*** product was isolated and characterized as the boronic ester prior to oxidation since the corresponding alcohol was prone to decomposition. The crude mixture was purified by silica gel column chromatography (15% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (40.8 mg, 66% yield). **^{1}H NMR** (600 MHz, $CDCl_3$)) δ 4.83 (t, J = 4.8 Hz, 1H), 3.99-3.91 (m, 2H), 3.87-3.78 (m, 2H), 1.88-1.77 (m, 2H), 1.77-1.64 (m, 2H), 1.62-1.54 (m, 4H), 1.53-1.40 (m, 3H), 1.24 (s, 12H), 1.17-1.05 (m, 2H), 0.96-0.85 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 104.9, 83.0, 65.0, 42.0, 33.9, 32.6, 32.2, 25.4, 25.3, 25.1, 25.0. **IR** (neat) ν_{max} 2974.1 (m), 2943.9 (m), 2864.7 (m), 1455.5 (w), 1378.4 (m), 1316.5 (m), 1213.3 (w), 1143.8 (s), 1033.6 (w), 966.8 (w), 842.5 (w). **HRMS** (DART) for $C_{17}H_{32}BO_4$ $(M+H)^+$: Calc'd:311.2388, found: 311.2386. $\mathbf{[\alpha]_D^{20}}$ = 6.67 (c = 1.0, $CHCl_3$, l = 50 mm).

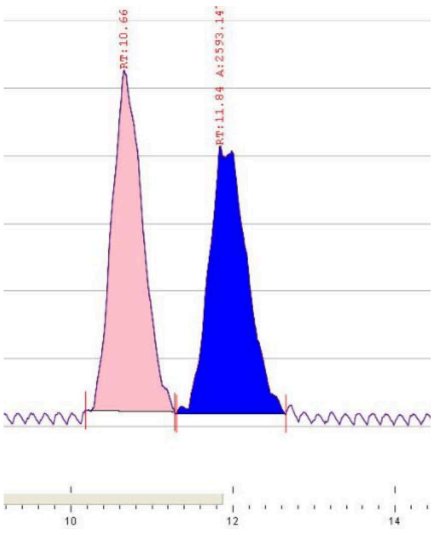
Analysis of Stereochemistry:

Racemic compound was prepared according to the general **procedure A** with racemic **L1** as ligand. Absolute stereochemistry was assigned by analogy (see product **7** and **21**).

Note: the analysis of stereochemistry was performed on the corresponding TBDPS protected silyl ether. The boronic ester (both the enriched sample and the racemate) was oxidized under standard conditions and the crude alcohol was promptly protected with TBDPS-Cl following standard procedures.

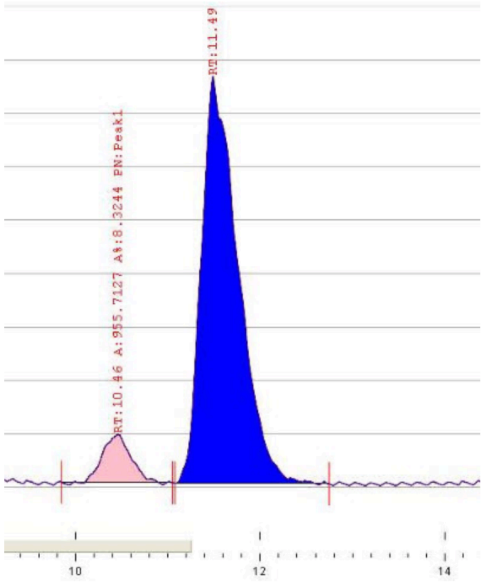
Chiral SFC (Chiracel AD-H, 1% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)-analysis of **(*R*)-1-cyclopentyl-3-(1,3-dioxolan-2-yl)propan-1-ol**.

Racemic Material

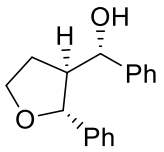


Peak No	% Area	Area	RT (min)
1	50.5782	2653.8255	10.66
2	49.4218	2593.1472	11.84
Total:	100	5246.9727	

Enantioenriched Material



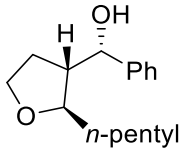
Peak No	% Area	Area	RT (min)
1	8.3244	955.7127	10.46
2	91.6756	10525.088	11.49
Total:	100	11480.8007	



(*S*)-phenyl((*2R*,*3R*)-2-phenyltetrahydrofuran-3-yl)methanol (29). The reaction was performed according to the general **procedure A** with (*R,E*)-2-(3-(2-iodoethoxy)-3-phenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82.8 mg, 0.20 mmol, 1.0 equiv.), and phenylzinc chloride solution in THF (1.00 mL, 0.4 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using NiBr2 • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and **(*S*,*S*)-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel /column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a white solid (35.8 mg, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33-7.22 (m, 8H), 7.10 (d, *J* = 6.8 Hz, 2H), 4.72 (d, *J* = 6.6 Hz, 2H), 4.11 (q, *J* = 8.1, 8.1, 8.1 Hz, 1H), 4.00 (q, *J* = 8.0, 8.1, 8.1 Hz, 1H), 2.53-2.48 (m, 1H), 2.26 (m, 2H), 2.05-1.95 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.4, 142.6, 128.6, 128.4, 127.9, 127.4, 126.4, 126.1, 82.6, 74.0, 68.3, 55.3, 27.5. **IR** (neat) ν_{max} 3400.0 (br), 3081.8 (w), 3058.3 (w), 2921.4 (w), 2872.1 (w), 1600.9 (w), 1491.9 (m), 1452.0 (m), 1059.6 (m), 1040.6 (m), 1024.8 (m), 756.3 (m), 699.3 (s). **HRMS** (DART) for $C_{17}H_{19}O_2$ $(M+H)^+$: Calc'd: 255.1380, found: 255.1383 $\mathbf{[\alpha]_D^{20}}$ = 23.05 (*c* = 0.85, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

In order to assign the stereochemical configuration of the title compound, the substrate was first protected with TBSCl through standard methods. All spectra for the resulting TBS-ether was found to match that obtained for compound **SI-26** for which the stereochemical configuration has been determined through NOESY correlation (see below).

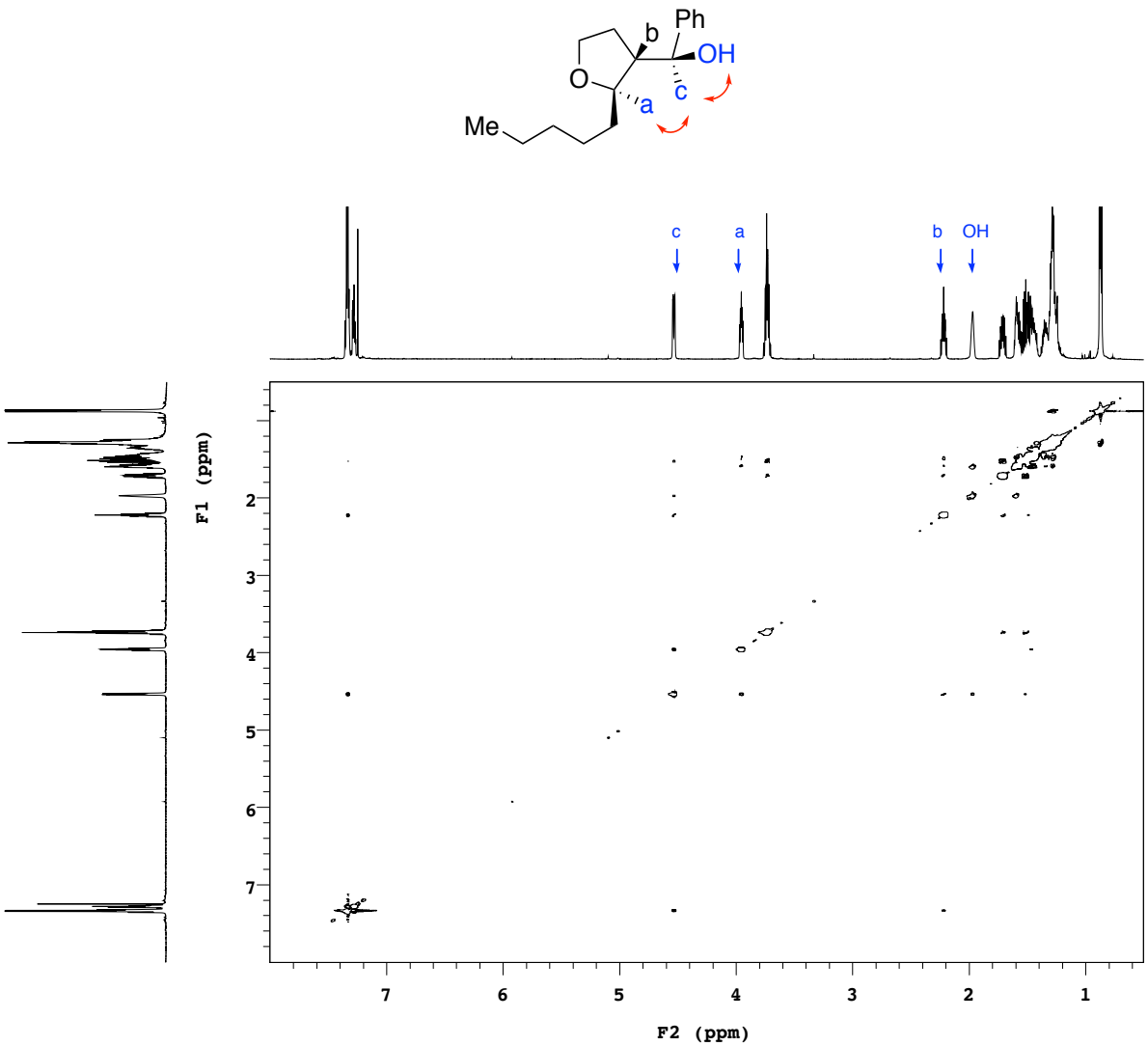


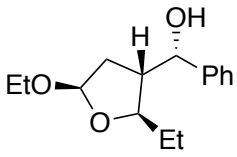
(*S*)-((*2R*,*3R*)-2-pentyltetrahydrofuran-3-yl)(phenyl)methanol (30). The reaction was performed according to the general **procedure A** with (*R,E*)-2-(3-(2-iodoethoxy)oct-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (81.6 mg, 0.20 mmol, 1.0 equiv.), and phenylzinc chloride solution in THF (1.00 mL, 0.4 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using NiBr2 • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and **(*S*,*S*)-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (17.6 mg, 45% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33-7.23 (m, 5H), 4.52 (dd, 1H), 3.96-3.92 (m, 1H), 3.74-3.70 (m, 2H), 2.23-2.17 (m, 1H), 1.94 (d, *J* = 3.4 Hz, 1H), 1.73-1.63 (m, 1H), 1.60-1.36 (m, 4H), 1.32-1.12 (m, 5H), 0.86 (t, *J* = 6.5, 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.9, 128.7, 128.0, 126.7, 82.6, 77.5, 66.7,

51.4, 36.0, 32.1, 30.1, 26.2, 22.8, 14.2. **IR** (neat) ν_{max} 3407.6 (br), 3061.1 (w), 3027.4 (w), 2951.6 (s), 2925.5 (s), 2855.4 (s), 1452.7 (w), 1074.5 (m), 1034.4 (m), 904.6 (w), 761.9 (m), 700.8 (s). **HRMS** (DART) for $C_{16}H_{25}O_2$ $(M+H)^+$: Calc'd: 249.1849, found: 249.1848 $\mathbf{[\alpha]_D^{20}}$ = 31.80 (*c* = 0.64, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

The stereochemistry of the carbon skeleton was assigned through NOESY correlation analysis. The absolute configuration at the B(pin)/OH containing stereocenter was assigned by analogy (see substrates: **7** and **21**). Relevant NOESY correlations are illustrated below.





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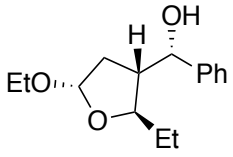
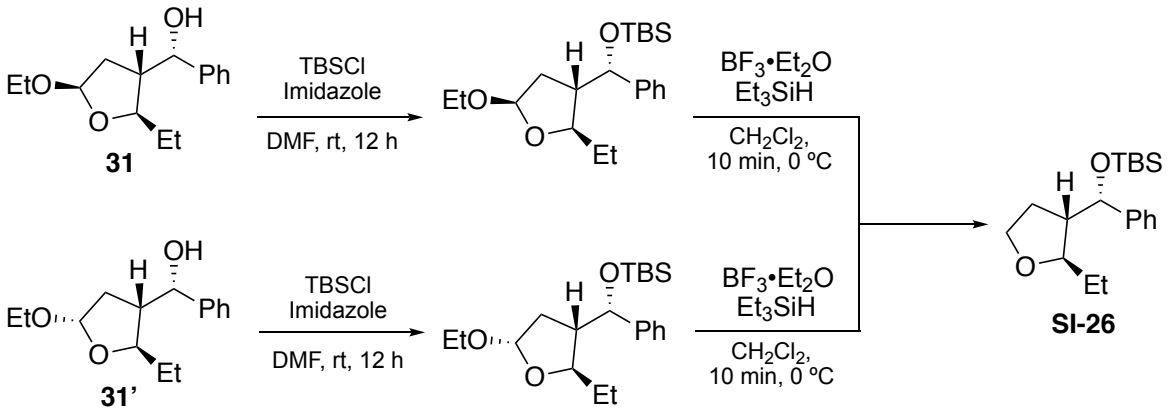
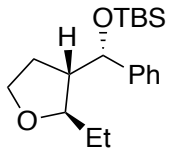


(*1S*)-((*2R*,*3R*)-5-ethoxy-2-ethyltetrahydrofuran-3-yl)(phenyl)methanol (31 and 31'). The reaction was performed according to the general **procedure A** with 2-((3*R,E*)-3-(1-ethoxy-2-iodoethoxy)pent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82.0 mg, 0.20 mmol, 1.0 equiv.), and phenylzinc chloride solution in THF (1.00 mL, 0.4 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using NiBr2 • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and **(*S,S*)-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel /column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (25.0 mg, 50% yield). The product was obtained as a pair of separable diastereomers. *Diastereomer 1:* **^{1}H NMR** (500 MHz, $CDCl_3$) 7.37-7.36 (m, 2H), 7.33-7.30 (m, 2H), 7.23-7.19 (m, 1H), 5.12 (d, *J* = 4.6 Hz, 1H), 4.90 (d, *J* = 4.3 Hz, 1H), 4.12 (q, *J* = 5.1, 5.1, 4.9 Hz,1H), 4.05 (s, 1H), 3.82 (dq, *J* = 9.3, 7.2, 7.2, 7.1 Hz, 1H), 3.50 (dq, *J* = 9.2, 9.2, 6.1, 6.1 Hz, 1H), 2.28-2.25 (m, 1H), 2.20 (ddd, *J* = 13.3, 11.1, 4.9 Hz, 1H), 1.88 (dd, *J* = 13.5, 2.2 Hz, 1H), 1.26-1.21 (m, 5H), 0.66 (t, *J* = 7.4, 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.6, 128.4, 127.3, 126.1, 102.7, 79.9, 75.4, 62.2, 49.4, 37.7, 28.9, 15.2, 9.5. **IR** (neat) ν_{max} 3423.0 (br), 3059.3 (w), 3026.7 (w), 2968.8 (m), 2920.7 (s), 2873.5 (m), 1492.0 (w), 1452.3 (m), 1202.9 (w), 1082.4 (s), 1072.3 (s), 979.0 (s), 758.2 (w), 701.0 (s). **HRMS** (DART) for $C_{15}H_{21}O_3$ $(M+H)^+$: Calc'd: 249.1485, found: 249.1483. **$[\alpha]_D^{20}$** = 22.40 (*c* =1.00, $CHCl_3$, *l* = 50 mm). *Diastereomer 2:* **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33-7.25 (m, 5H), 4.99 (d, *J* = 2.9 Hz, 1H), 4.51 (dd, *J* = 8.5, 3.0 Hz, 1H), 4.03 (ddd, *J* = 9.5, 6.3, 3.7 Hz, 1H), 3.72 (dq, *J* = 9.4, 7.1, 7.1, 7.0 Hz, 1H), 3.36 (dq, *J* = 9.6, 7.2, 7.1, 7.1 Hz, 1H), 2.55-2.46 (m, 1H), 1.90 (d, *J* = 3.4 Hz, 1H), 1.74-1.63 (m, 3H), 1.57 (ddd, *J* = 13.5, 8.6, 6.9 Hz, 1H), 1.14 (t, *J* = 7.1, 7.1 Hz, 3H), 0.99 (t, *J* = 7.4, 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.6, 128.7, 128.1, 126.5, 103.2, 103.2, 85.2, 77.9, 62.4, 49.5, 37.3, 31.1, 15.3, 11.1. **IR** (neat) ν_{max} 3433.0 (br), 2968.7 (m), 2927.1 (m), 2872.2 (m), 1452.9 (m), 1372.2 (w), 1343.9 (w), 1309.5 (w), 1190.3 (w), 1092.5 (s), 1064.9 (s), 1023.0 (s), 971.8 (s), 760.1 (w), 701.4 (s), 624.9 (w). **HRMS** (DART) for $C_{15}H_{21}O_3$ $(M+H)^+$: Calc'd: 249.1485, found: 249.1490. **$[\alpha]_D^{20}$**= -108.38 (*c* = 1.00, $CHCl_3$, *l* = 50 mm).

Analysis of stereochemistry:

The transformations below were carried out on the isolated compounds **31** and **31'** separately in order to assess the stereochemistry of the isolated compounds. Upon reduction all spectral data of the two separate products was found to be identical. The stereochemical assignment was determined through NOESY correlation analysis of the resulting products. The absolute configuration at the B(pin)/silyl ether containing stereocenter was assigned by analogy (see substrates **7** and **21**).

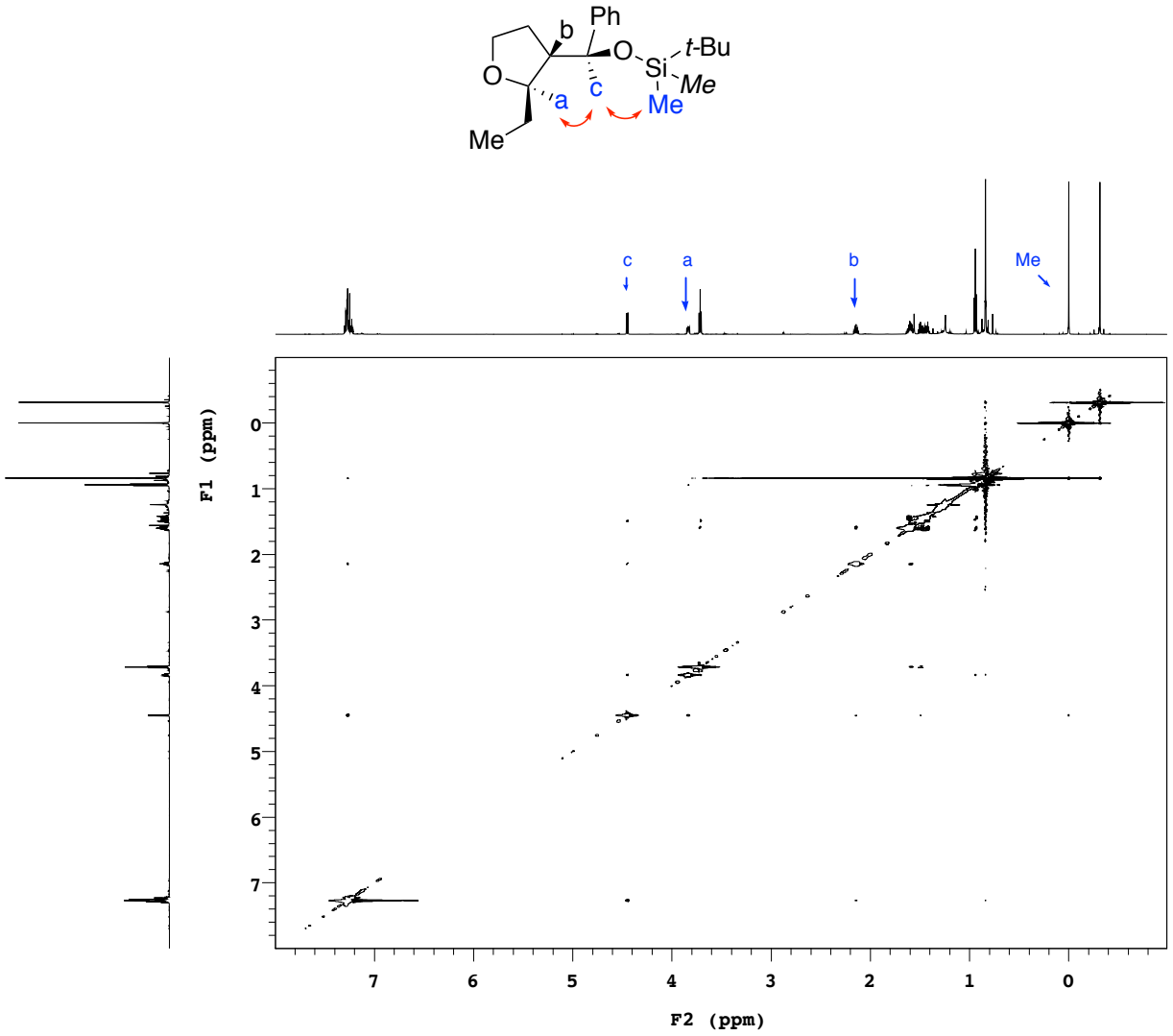


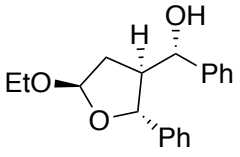


***Tert*-butyl((*S*)-((*2R,3S*)-2-ethyltetrahydrofuran-3-yl)(phenyl)methoxy)dimethylsilane (SI-26)**. Compound **31** (12 mg, 0.048 mmol) was dissolved in anhydrous DMF (4 mL), followed by addition of imidazole (9.8 mg, 0.14 mmol), and TBSCl (5.9 mg, 0.072 mmol). The resulting mixture was stirred overnight at room temperature, diluted with diethyl ether, washed twice with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture is filtered through silica gel (3% ethyl in hexanes). The resulting mixture was dissolved in CH_2Cl_2 (5 mL) and triethylsilane (17.5 μL, 0.1 mmol) was added, followed by dropwise addition of BF_3•Et_2O (6.8 μL, 0.055 mmol) at 0 °C. The reaction mixture was stirred for 10 min at the same temperature, then saturated aqueous sodium bicarbonate solution (5 mL) was added, and the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined extracts were dried over anhydrous sodium sulfate and concentrated in vacuo. Purification by flash column chromatography provided **SI-25** (8.2 mg, 93% over two steps) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31-7.19 (m, 5H), 4.45 (d, *J* = 8.5 Hz, 1H), 3.84 (ddd, *J* = 8.3, 5.8, 3.7 Hz, 1H), 3.72 (t, *J* = 6.7, 6.7 Hz, 2H), 2.17-2.12 (m, 1H), 1.65-1.55 (m, 2H), 1.53-1.39 (m, 2H), 0.95 (t, *J* = 7.4, 7.4 Hz, 3H), 0.84 (s, 9H), 0.00 (s, 3H), -0.31 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.4, 128.2, 127.5, 126.9, 84.0, 78.4, 67.0, 52.7, 30.2, 29.0, 25.9, 18.2, 10.8, -4.4, -4.8. **IR** (neat) ν_{max} 2953.9 (s), 2926.3 (s), 2853.9 (s), 1460.2 (w),

1251.7 (m), 1107.9 (m), 1080.2 (m), 851.6 (s), 836.2 (s), 775.0 (s). **HRMS** (DART) for $C_{19}H_{33}O_2Si$ $(M+H)^+$: Calc'd: 321.2244, found: 321.2232. $[\alpha]_D^{20}$ = -42.66 (*c* = 0.38, $CHCl_3$, *l* = 50 mm).

Relevant NOESY correlations are illustrated below.





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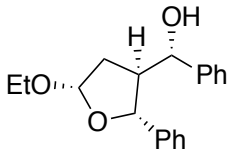
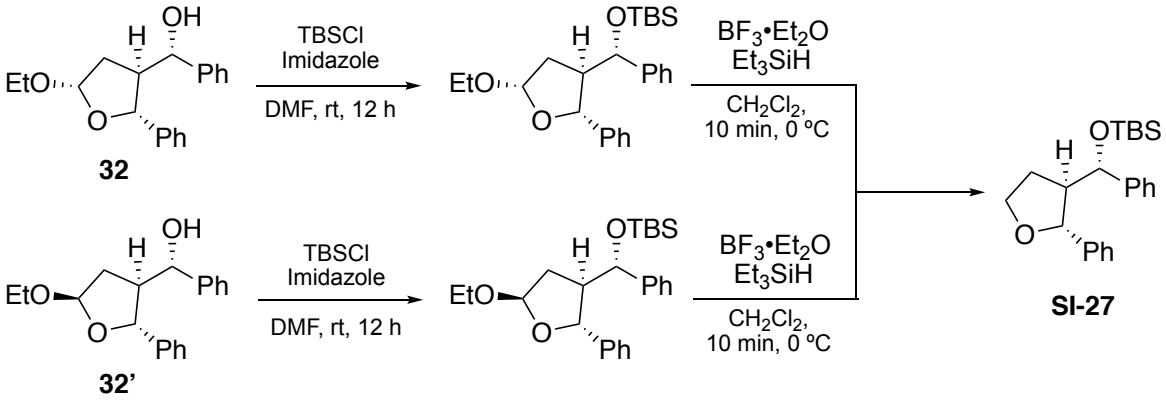
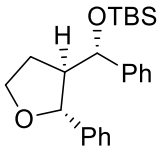


(*1S*)-((*2R*,*3S*)-5-ethoxy-2-phenyltetrahydrofuran-3-yl)(phenyl)methanol (32 and 32') . The reaction was performed according to the general **procedure A** with 2-((*3R*,*E*)-3-(1-ethoxy-2-iodoethoxy)-3-phenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (91.6 mg, 0.20 mmol, 1.0 equiv.), and phenylzinc chloride solution in THF (1.00 mL, 0.4 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using NiBr2 • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and **(*S*,*S*)-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (30.4 mg, 51% yield). The product is a pair of separable diastereomers. *Diastereomer 1 (up):* **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36-7.23 (m, 9H), 7.23-7.18 (m, 1H), 5.34 (d, *J* = 4.9 Hz, 1H), 5.12 (d, *J* = 5.8 Hz, 1H), 4.94 (t, *J* = 4.9, 4.9 Hz, 1H), 3.99 (d, *J* = 5.8 Hz, 1H), 3.93-3.86 (m, 1H), 3.61-3.58 (m, 1H), 2.58-2.54 (m, 1H), 2.12-2.07 (m, 1H), 2.01 (dd, *J* = 14.0, 3.2 Hz, 1H), 1.30 (td, *J* = 7.1, 7.1, 1.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.1, 142.3, 128.7, 128.4, 127.8, 127.2, 126.0, 126.0, 103.3, 103.3, 82.1, 82.1, 73.3, 62.6, 54.1, 33.3, 15.2. **IR** (neat) ν_{max} 3424.6 (br), 3060.1 (w), 3029.2 (w), 2971.0 (w), 2923.0 (w), 1492.5 (w), 1452.4 (w), 1197.7 (w), 1097.0 (m), 1046.2 (s), 1022.8 (s), 759.1 (w), 699.6 (s). **HRMS** (DART) for $C_{19}H_{26}NO_3$ $(M+NH_4)^+$: Calc'd: 316.1907, found: 316.1906. **$[\alpha]_D^{20}$** = 72.04 (*c* =1.00, $CHCl_3$, *l* = 50 mm). *Diastereomer 2 (down):* **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27-7.15 (m, 10H), 5.18 (d, *J* = 5.2 Hz, 1H), 4.91 (d, *J* = 8.9 Hz, 1H), 4.69 (s, 1H), 3.84 (dq, *J* = 9.8, 7.2, 7.1, 7.1 Hz, 1H), 3.47 (dq, *J* = 9.8, 7.1, 7.1, 7.1 Hz, 1H), 2.74-2.69 (m, 1H), 2.32 (ddd, *J* = 12.9, 11.4, 5.3 Hz, 1H), 1.99-1.94 (m, 2H), 1.23 (t, *J* = 7.1, 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.1, 142.3, 128.4, 128.2, 127.7, 127.4, 127.2, 125.9, 103.7, 84.1, 77.3, 77.0, 76.8, 72.7, 62.8, 53.4, 34.3, 15.1. **IR** (neat) ν_{max} 3434.9 (br), 3059.9 (w), 3027.7 (w), 2972.1 (w), 2923.4 (w), 1492.4 (w), 1453.4 (w), 1190.9 (w), 1094.9 (m), 1041.2 (m), 974.1 (m), 908.4 (w), 754.9 (w), 700.6 (s). **HRMS** (DART) for $C_{19}H_{26}NO_3$ $(M+NH_4)^+$: Calc'd: 316.1907, found: 316.1894. **$[\alpha]_D^{20}$** = 57.75 (*c* =1.00, $CHCl_3$, *l* = 50 mm).

Analysis of stereochemistry:

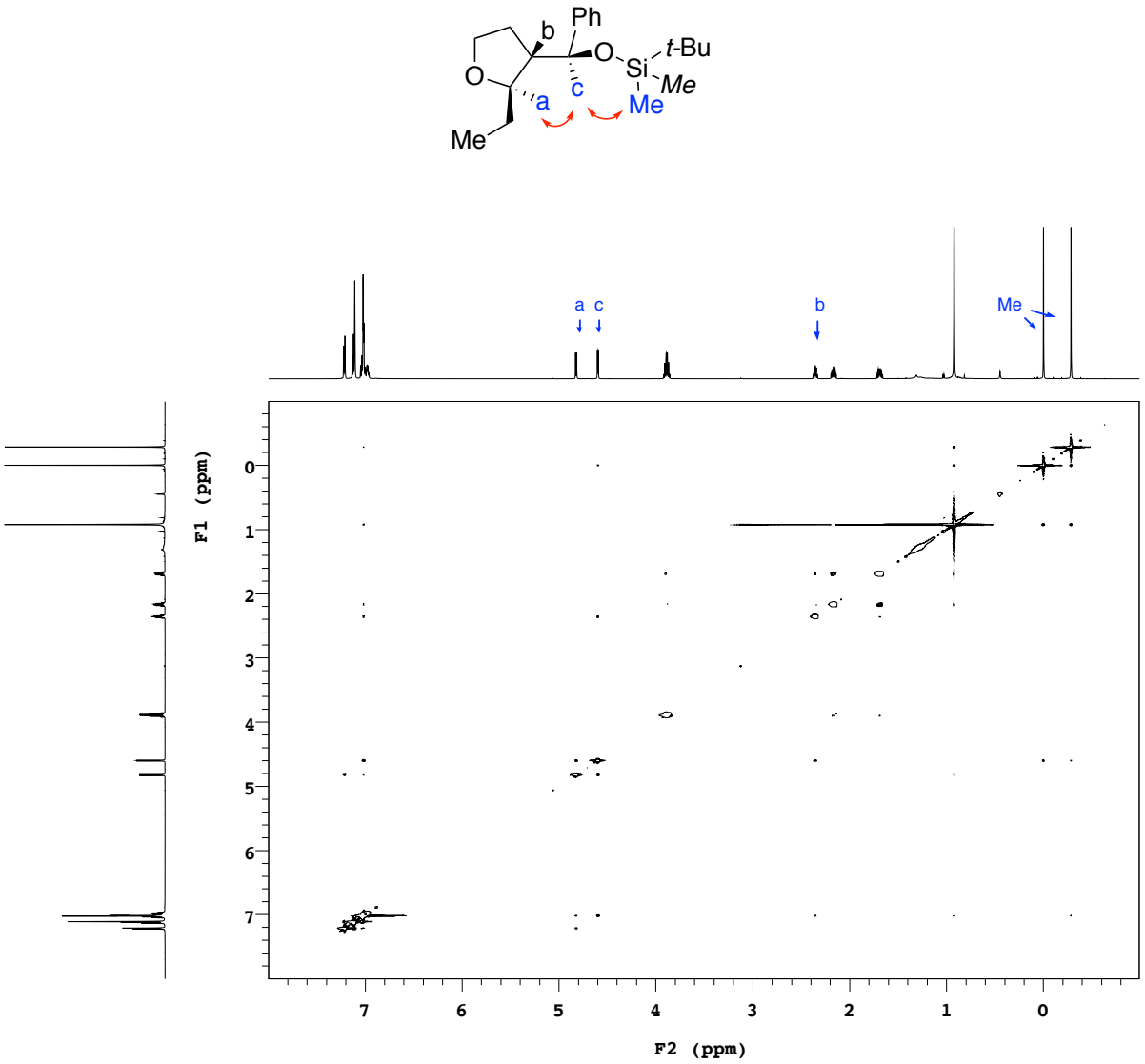
The transformations below were carried out on the isolated compounds **32** and **32'** separately in order to assess the stereochemistry of the isolated compounds. Upon reduction all spectral data of the two separate products was found to be identical. The stereochemical assignment was determined through NOESY correlation analysis of the resulting products. The absolute configuration at the B(pin)/silyl ether containing stereocenter was assigned by analogy (see substrates **7** and **21**).

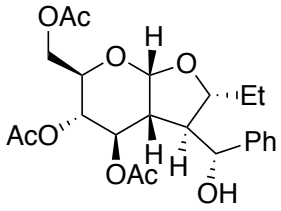




***tert*-butyldimethyl((*S*)-phenyl((*2R,3R*)-2-phenyltetrahydrofuran-3-yl)methoxy)silane (SI-27).** The title compound was generated through the same procedure used to synthesize **SI-25** and isolated by silica gel chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (17.0 mg, 81% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28-7.21 (m, 8H), 7.15-7.14 (m, 2H), 4.68 (dd, *J* = 15.2, 5.9 Hz, 2H), 4.08 (td, *J* = 7.8, 7.7, 6.1 Hz, 1H), 3.97 (td, *J* = 8.0, 7.9, 6.4 Hz, 1H), 2.43-2.40 (m, 1H), 2.33-2.27 (m, 1H), 1.95-1.89 (m, 1H), 0.93 (s, 9H), 0.08 (s, 3H), -0.25 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.2, 143.0, 128.4, 128.2, 127.4, 127.4, 126.6, 126.3, 82.5, 82.4, 74.3, 74.3, 68.5, 57.0, 27.4, 26.0, 18.3, -4.1, -4.2, -4.8, -4.8. **IR** (neat) ν_{max} 3026.5 (w), 2880.3 (w), 2853.3 (w), 1452.1 (w), 1250.7 (w), 1060.6 (m), 1003.2 (w), 834.1(s), 773.9 (m), 698.4 (s). **HRMS** (DART) for $C_{23}H_{33}O_2Si$ $(M+NH_4)^+$: Calc'd: 386.2515, found: 386.2510. **$[\alpha]_D^{20}$** = -49.60 (*c* = 0.90, $CHCl_3$, *l* = 50 mm).

NOESY was carried out in C_6D_6. Relevant NOESY correlations are illustrated below.

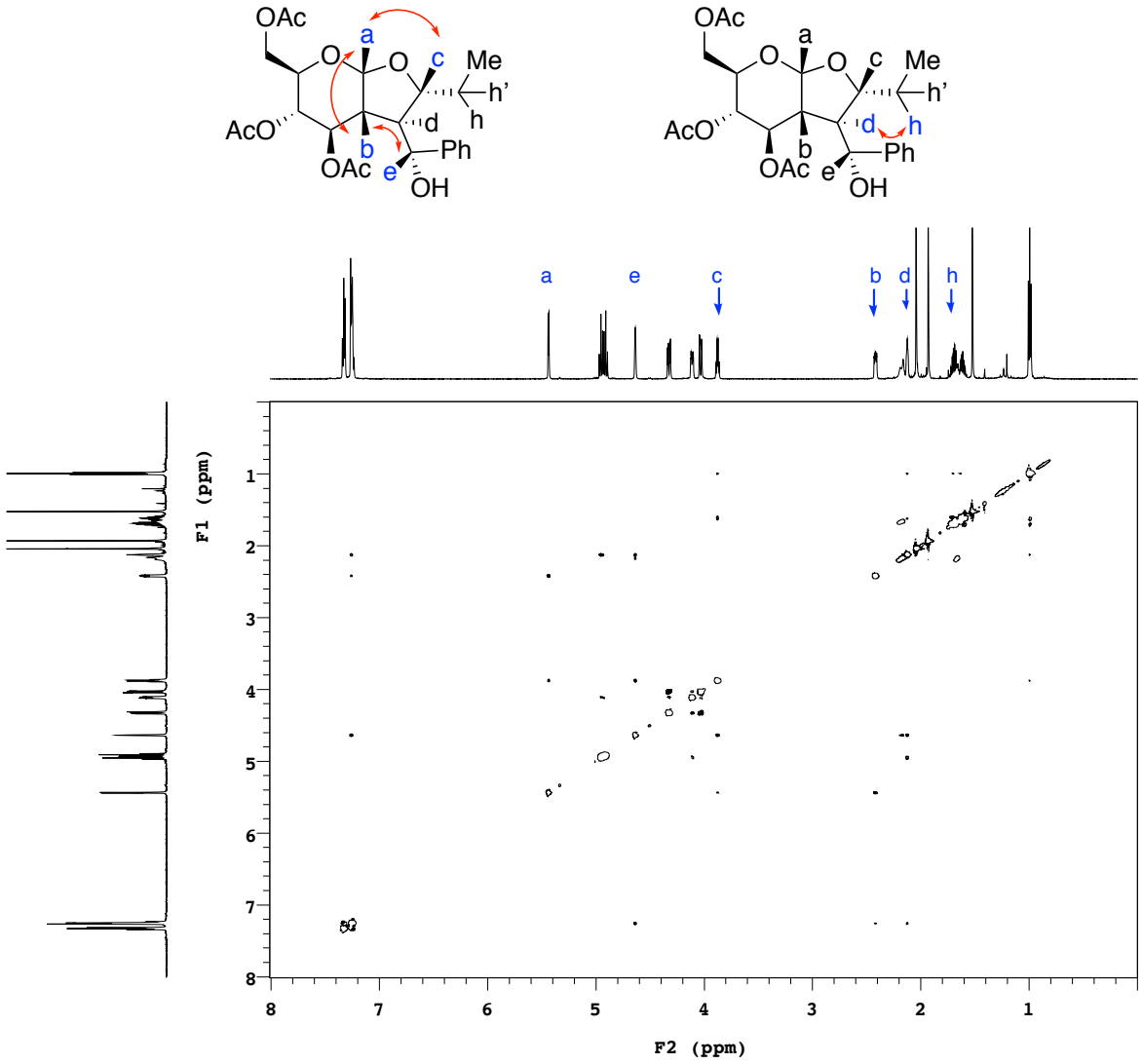


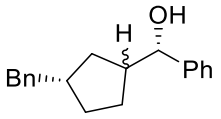


(2*R*,3*R*,3a*R*,4*R*,5*S*,6*R*,7a*S*)-6-(acetoxymethyl)-2-ethyl-3-((*R*)-hydroxy(phenyl)methyl)hexahydro-4*H*-furo[2,3-*b*]pyran-4,5-diyl diacetate (33). The reaction was performed according to general **procedure A** with (2*R*,3*R*,4*S*,5*S*,6*S*)-2-(acetoxymethyl)-5-iodo-6-(((*R*,*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-3-yl)oxy)tetrahydro-2*H*-pyran-3,4-diyl diacetate (122.1 mg, 0.20 mmol, 1.0 equiv.), and phenylzinc chloride solution in THF (1.00 mL, 0.4 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(R,R)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. ^{1}H NMR of the boronic ester isolated prior to oxidation indicated a 5:1 diastereomeric ratio in the reaction product. ***Note:*** the oxidation was carried out under buffered conditions by using pH7 phosphate buffer solution (0.50 mL) in place of 3M NaOH solution, and carrying out the oxidation for 12 hours. The crude mixture was purified by silica gel column chromatography (30% ethyl acetate in hexanes, stain in CAM) to afford the product as a single diastereomer. White solid (59.6 mg, 66% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37-7.30 (m, 2H), 7.27-7.22 (m, 3H), 5.44 (d, *J* = 4.6 Hz, 1H), 5.00-4.88 (m, 2H), 4.64-4.63 (m, 1H), 4.33 (dd, *J* = 12.3, 4.2 Hz, 1H), 4.11 (ddd, *J* = 9.6, 4.3, 2.2 Hz, 1H), 4.03 (dd, *J* = 12.3, 2.2 Hz, 1H), 3.88 (q, *J* = 6.1 Hz, 1H), 2.42 (ddd, *J* = 9.0, 4.6, 1.8 Hz, 1H), 2.17-2.09 (m, 2H), 2.05 (s, 3H), 1.93 (s, 3H), 1.75-1.56 (m, 2H), 1.53 (s, 3H), 1.00 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDClz_3$) δ 171.0, 170.8, 169.7, 143.0, 128.7, 127.7, 125.6, 100.8, 79.4, 74.3, 73.7, 69.5, 68.2, 62.2, 54.5, 43.1, 28.8, 20 .9, 20.7, 20.5, 10.3. **IR** (neat) ν_{max} 3506.0 (br), 2960.8 (m), 2931.6 (m), 2876.70 (w), 1744.4 (s), 1451.8 (m), 1230.9 (s), 1036.4 (s), 795.2 (w) 763.7 (w). **HRMS** (DART) for $C_{23}H_{34}NO_9$ $(M+NH_4)^+$: Calc'd 468.2228:, found: 468.2248. **$[\alpha]_D^{20}$** = 78.38 (*c* = 0.5, $CHCl_3$, *l* = 50 mm).

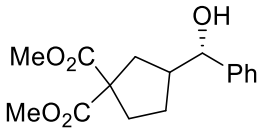
Analysis of Stereochemistry:

The stereochemistry of the carbon skeleton was assigned through NOESY correlation analysis. The absolute configuration at the B(pin)/OH containing stereocenter was assigned by analogy (see substrates **7** and **21**). Relevant NOESY correlations are illustrated below (assignment of the ^{1}H NMR shifts was aided by COSY analysis. The COSY spectrum is included along with the other spectral data).





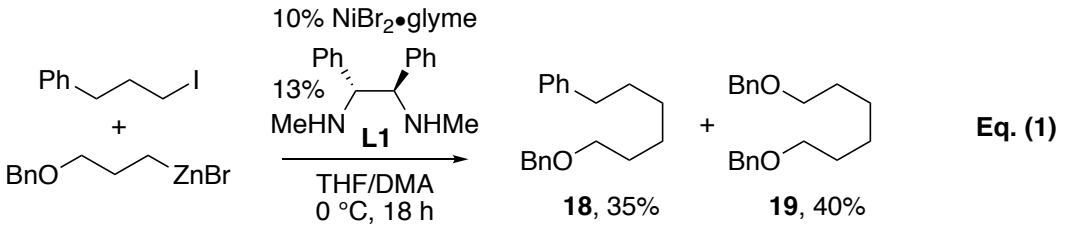
(*1S*)-((*3S*)-3-benzylcyclopentyl)(phenyl)methanol **(34).** The reaction was performed according to the general **procedure A** with (*R*,*E*)-2-(5-benzyl-6-iodohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (85.2 mg, 0.20 mmol, 1.0 equiv.), and phenylzinc chloride solution in THF (1.00 mL, 0.4 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using NiBr2 • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and **(*S*,*S*)-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. The crude mixture was purified by silica gel /column chromatography (10% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (30.9 mg, 58% yield). The product is a diastereomeric mixture (d.r. = 1.2:1) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 (m, 8H), 7.30-7.24 (m, 7H), 7.19-7.12 (m, 7H), 4.43 (d, *J* = 8.2 Hz, 1H), 4.38 (d, *J* = 8.5 Hz, 1H), 2.68-2.56 (m, 5H), 2.43-2.38 (m, 2H), 2.32-2.23 (m, 2H), 2.14-2.08 (m, 1H), 1.88-1.66 (m, 8H), 1.63-1.43 (m, 5H), 1.39-1.14 (m, 5H), 0.97 (q, *J* = 11.1, 11.1, 11.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.3, 144.3, 142.1, 142.0, 128.9, 128.8, 128.5, 128.3, 128.3, 127.7, 127.7, 126.7, 126.6, 125.8, 125.8, 79.3, 79.2, 47.4, 46.3, 42.4, 42.3, 42.1, 41.3, 37.0, 35.1, 32.9, 31.7, 29.6, 28.1. **IR** (neat) ν_{max} 3022.8 (w), 2922.3 (w), 2852.0 (w), 1492.5 (m), 1450.5 (m), 1028.6 (w), 741.5 (m), 697.0 (s), 599.3 (w), 542.1 (w), 479.9 (m). **HRMS** (DART) for $C_{19}H_{21}$ $(M+H-H_2O)^+$: Calc'd: 249.1638, found: 249.1627. **Note**: the product was obtained as a mixture of diastereomers and an optical rotation was not obtained



dimethyl 3-((S)-hydroxy(phenyl)methyl)cyclopentane-1,1-dicarboxylate (23). The reaction was performed according to general **procedure A** dimethyl (*E*)-2-(2-iodoethyl)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)malonate (90.4 mg, 0.20 mmol, 1.0 equiv.), and phenylzinc chloride solution in THF (1.00 mL, 0.4 M, 0.4 mmol, 2.0 equiv.), in a mixture of THF/DMA (2.00 mL THF and 0.40 mL DMA overall) using $NiBr_2$ • glyme (6.17 mg, 0.020 mmol, 0.10 equiv.) and ***(S,S)*-L1** (6.25 mg, 0.026 mmol, 0.13 equiv.) as catalyst. **Note** the oxidation was carried out under buffered conditions by using pH7 phosphate buffer solution (0.50 mL) in place of 3M NaOH solution, and carrying out the oxidation for 12 hours. The crude mixture was purified by silica gel column chromatography (20% ethyl acetate in hexanes, stain in CAM) to afford the product as a colorless oil (36.0 mg, 62% yield).
^{1}H NMR (600 MHz, C_6D_6) δ 7.15-7.12 (m, 2H), 7.10-7.04 (m, 6H), 7.04-6.99 (m, 2H), 4.18 (d, *J* = 7.1 Hz, 1H), 4.11 (d, *J* = 6.7 Hz, 1H), 3.27 (s, 3H), 3.24 (s, 3H), 3.22 (s, 3H), 3.19 (s, 3H), 2.70-2.62 (m, 1H), 2.41-2.36 (m, 1H), 2.35-2.29 (m, 3H), 2.25-2.19 (m, 2H), 2.19-2.12 (m, 1H), 2.12-2.05 (m, 1H), 1.83-1.73 (m, 1H), 1.73-1.63 (m, 1H), 1.35 (s, 1H), 1.35-1.29 (m, 3H), 0.39 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.3, 173.1, 172.9, 172.8, 144.0, 143.8, 128.6, 128.5, 127.80, 127.8, 126.4, 126.3, 77.9, 77.7, 60.2, 60.1, 52.9, 52.8, 52.8, 52.8, 46.9, 46.8, 37.2, 37.2,

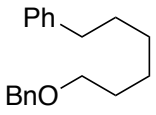
34.2, 34.0, 28.8, 28.3. **IR** (neat) ν_{max} 3522.2 (br), 3026.2 (w), 1726.3 (s), 1492.2 (w), 1267.0 (m), 1197.0 (w), 1158.7 (w), 1102.6 (w), 763.8 (w), 702.4 (w). **HRMS** (DART) for $C_{16}H_{19}O_5$ $(M+H)^+$: Calc'd: 291.1227, found: 291.1226. **Note**: the product was obtained as a mixture of diastereomers and an optical rotation was not obtained. The diastereomeric ratio was determined by the integration of the ^1H NMR in C_6D_6.

VI. Background Reaction Experiments

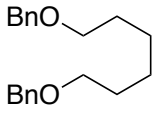


Eq. (1)

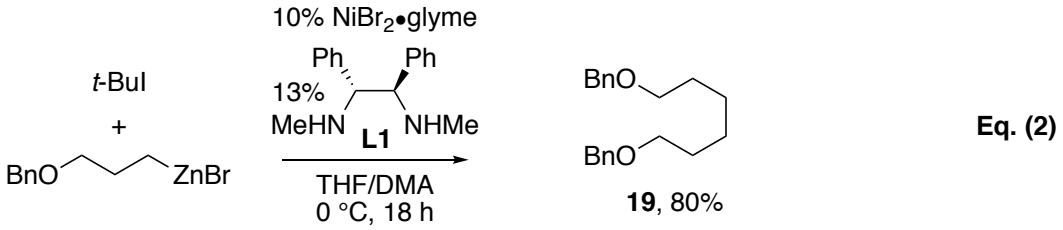
Equation (1). In an argon-filled glovebox, an oven-dried 2 dram vial equipped with a magnetic stirrer was charged with **$NiBr_2$ • glyme** (6.17 mg, 0.02 mmol), (*S,S*)-N,N-dimethyl-1,2-diphenyl-ethane-1,2-diamine (***S,S*)-L1** (6.25 mg, 0.026 mmol) and dissolved in 2.0 mL of THF. The catalyst solution was stirred for 1 hour at ambient temperature. **(3-iodopropyl)benzene** (98.4 mg, 0.40 mmol, 1.0 equiv.) was added to the catalyst solution. The vial was sealed with a PTFE-lined pierceable cap, taped, and brought outside the glovebox where it was placed in a CryoCool set at 0 ºC. The vial was cooled for 30 minutes before addition of **(3-(benzyloxy)propyl)zinc bromide** solution (0.410 mL, 0.97M 0.40 mmol, 1.0 equiv.). The puncture hole was taped over and the reaction mixture was stirred at 0 ºC for 18 hours. The reaction was quenched with 0.40 mL of saturated NH_4Cl aq. solution, diluted with diethyl ether and washed with water and brine sequentially. The organic layer was dried over magnesium sulfate and concentrated. The crude material was then submitted to silica gel chromatography.



(6-(benzyloxy)hexyl)benzene (18). The product of the reaction was isolated by silica gel column chromatography (25% CH_2Cl_2 in hexane, stain in CAM) as a colorless oil (37.8 mg, 35% yield). **^1H NMR** (600 MHz, $CDCl_3$) δ 7.36-7.34 (m, 4H), 7.32-7.23 (m, 3H), 7.20-7.13 (m, 3H), 4.50 (s, 2H), 3.46 (t, *J* = 6.6 Hz, 2H), 2.84-2.53 (m, 2H), 1.69-1.55 (m, 4H), 1.45-1.34 (m, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.9, 138.8, 128.5, 128.5, 128.4, 127.7, 127.6, 125.7, 73.0, 70.6, 36.0, 31.6, 29.8, 29.3, 26.2. **IR** (neat) ν_{max} 3082.6 (w), 3060.2 (w), 3024.1 (w), 2925.8 (s), 2851.7 (s), 1494.1 (m), 1452.2 (m), 1360.8 (m), 1202.6 (s), 734.2 (s), 696.4 (s). **HRMS** (DART) for $C_{19}H_{25}O$ $(M+H)^+$: Calc'd: 269.1900 , found: 269.1901.

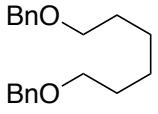


1,6-bis(benzyloxy)hexane (19) was isolated by silica gel column chromatography (40% CH_2Cl_2 in hexane, stain in CAM) as a colorless oil (24.1 mg, 40% yield based on 0.50 equiv. of starting material). All spectral data were in accordance with the literature.[14]



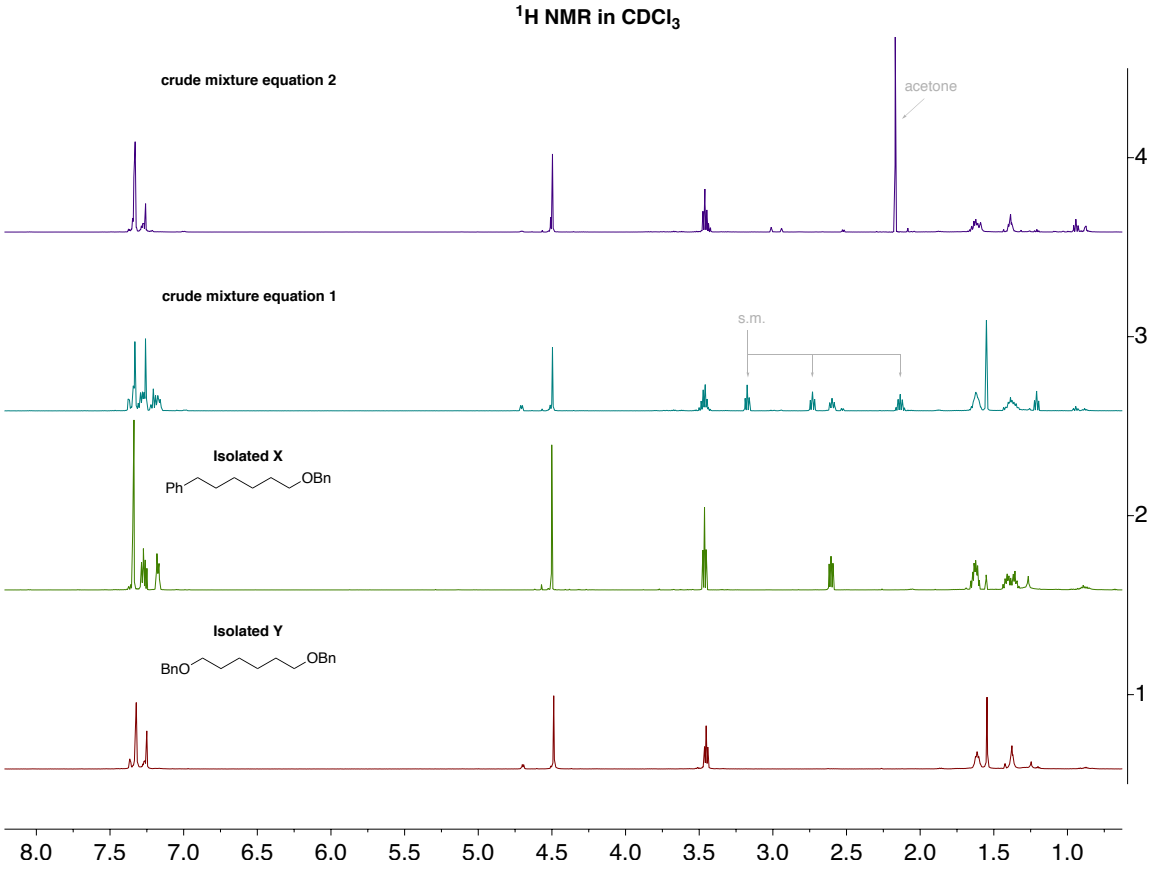
Eq. (2)

Equation (2). The experiment was carried out following the same procedure as for equation (1) by replacing **(3-iodopropyl)benzene** with ***t*-butyl iodide** (73.6 mg, 0.40 mmol, 1.00 equiv.).



1,6-bis(benzyloxy)hexane (19) was isolated by silica gel column chromatography (40% CH_2Cl_2 in hexane, stain in CAM) as a colourless oil (47.8 mg 80% yield based on 0.50 equiv. of starting material) All spectral data were in accordance with the literature.[14]

[14] E. A. Mash, L. T. A. Kantor, Liza, S. C. Waller, *Synth. Commun.* **1997**, *27*, 507.



Comparison of the ^{1}H NMR for the crude mixtures from eq. (1) and eq.(2) with the corresponding isolated products ^{1}H NMR spectra for reference. The starting material (s. m.) corresponds to unreacted (3-iodopropyl)benzene.

Crystallographic Data

Table 1. Crystal data and structure refinement for C18H29BO2.

Identification code	C18H29BO2	
Empirical formula	C18 H29 B O2	
Formula weight	288.22	
Temperature	100(2) K	
Wavelength	1.54178 ≈	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.0566(4) ≈	α= 90∞.
	b = 10.7760(5) ≈	β= 107.7390(10)∞.
	c = 9.4198(5) ≈	γ = 90∞.
Volume	875.61(7) $≈^3$	
Z	2	
Density (calculated)	1.093 Mg/m^3	
Absorption coefficient	0.522 mm^{-1}	
F(000)	316	
Crystal size	0.580 x 0.420 x 0.360 mm^3	
Theta range for data collection	4.929 to 68.271∞.	
Index ranges	-10<=h<=10, -12<=k<=12, -11<=l<=9	
Reflections collected	14858	
Independent reflections	3144 [R(int) = 0.0228]	
Completeness to theta = 67.679∞	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6809	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3144 / 14 / 245	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0280, wR2 = 0.0735	
R indices (all data)	R1 = 0.0280, wR2 = 0.0735	
Absolute structure parameter	-0.08(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.167 and -0.120 $e.≈^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for C18H29BO2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8186(1)	5807(1)	2777(1)	21(1)
O(2)	8459(1)	3705(1)	2668(1)	21(1)
B(1)	7556(2)	4665(2)	2851(2)	19(1)
C(1)	8049(2)	4992(2)	6243(2)	25(1)
C(2)	6278(2)	5031(2)	5837(2)	22(1)
C(3)	5540(2)	5361(1)	4178(2)	20(1)
C(4)	5893(2)	4478(1)	3037(2)	19(1)
C(5)	4744(2)	4630(2)	1472(2)	20(1)
C(6)	4362(2)	3600(2)	534(2)	24(1)
C(7)	3334(2)	3702(2)	-895(2)	30(1)
C(8)	2674(2)	4834(2)	-1412(2)	31(1)
C(9)	3052(2)	5868(2)	-504(2)	30(1)
C(10)	4088(2)	5766(2)	929(2)	24(1)
C(11)	5702(2)	3786(2)	6231(2)	30(1)
C(12)	5807(2)	6053(2)	6744(2)	28(1)
C(13)	9498(6)	5560(5)	2212(5)	22(1)
C(14)	9930(6)	4183(4)	2645(6)	20(1)
C(15)	10730(3)	6536(3)	2885(4)	31(1)
C(16)	8898(3)	5746(3)	522(3)	30(1)
C(17)	11046(3)	4070(3)	4230(3)	31(1)
C(18)	10519(3)	3466(3)	1572(3)	29(1)
C(13X)	9807(11)	5702(9)	2730(11)	27(2)
C(14X)	9711(12)	4360(10)	2164(10)	26(2)
C(15X)	10873(5)	5789(6)	4330(6)	33(1)
C(16X)	10133(7)	6654(5)	1756(8)	36(2)
C(17X)	11159(6)	3538(5)	2730(7)	31(1)
C(18X)	9138(7)	4254(5)	444(6)	31(1)

Table 3. Bond lengths [≈] and angles [∞] for C18H29BO2.

O(1)-B(1)	1.367(2)
O(1)-C(13)	1.466(5)
O(2)-B(1)	1.362(2)
O(2)-C(14)	1.435(6)
B(1)-C(4)	1.582(2)
C(1)-C(2)	1.532(2)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(11)	1.525(2)
C(2)-C(12)	1.532(2)
C(2)-C(3)	1.543(2)
C(3)-C(4)	1.540(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.5328(19)
C(4)-H(4)	1.0000
C(5)-C(10)	1.389(2)
C(5)-C(6)	1.395(2)
C(6)-C(7)	1.388(2)
C(6)-H(6)	0.9500
C(7)-C(8)	1.381(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.382(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.394(2)
C(9)-H(9)	0.9500
C(10)-H(10)	0.9500
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800

C(13)-C(15)	1.524(5)
C(13)-C(16)	1.531(5)
C(13)-C(14)	1.556(7)
C(14)-C(18)	1.494(6)
C(14)-C(17)	1.532(5)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800

B(1)-O(1)-C(13)	104.6(2)
B(1)-O(2)-C(14)	109.0(2)
O(2)-B(1)-O(1)	113.65(14)
O(2)-B(1)-C(4)	123.10(14)
O(1)-B(1)-C(4)	123.16(14)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(11)-C(2)-C(12)	108.83(13)
C(11)-C(2)-C(1)	108.93(14)
C(12)-C(2)-C(1)	109.20(13)
C(11)-C(2)-C(3)	112.02(13)
C(12)-C(2)-C(3)	106.92(13)
C(1)-C(2)-C(3)	110.88(12)
C(4)-C(3)-C(2)	116.49(12)

C(4)-C(3)-H(3A)	108.2
C(2)-C(3)-H(3A)	108.2
C(4)-C(3)-H(3B)	108.2
C(2)-C(3)-H(3B)	108.2
H(3A)-C(3)-H(3B)	107.3
C(5)-C(4)-C(3)	112.35(12)
C(5)-C(4)-B(1)	105.68(11)
C(3)-C(4)-B(1)	113.94(13)
C(5)-C(4)-H(4)	108.2
C(3)-C(4)-H(4)	108.2
B(1)-C(4)-H(4)	108.2
C(10)-C(5)-C(6)	118.18(14)
C(10)-C(5)-C(4)	122.52(14)
C(6)-C(5)-C(4)	119.28(14)
C(7)-C(6)-C(5)	121.04(16)
C(7)-C(6)-H(6)	119.5
C(5)-C(6)-H(6)	119.5
C(8)-C(7)-C(6)	120.11(16)
C(8)-C(7)-H(7)	119.9
C(6)-C(7)-H(7)	119.9
C(7)-C(8)-C(9)	119.72(14)
C(7)-C(8)-H(8)	120.1
C(9)-C(8)-H(8)	120.1
C(8)-C(9)-C(10)	120.12(17)
C(8)-C(9)-H(9)	119.9
C(10)-C(9)-H(9)	119.9
C(5)-C(10)-C(9)	120.82(16)
C(5)-C(10)-H(10)	119.6
C(9)-C(10)-H(10)	119.6
C(2)-C(11)-H(11A)	109.5
C(2)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(2)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(2)-C(12)-H(12A)	109.5

C(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(1)-C(13)-C(15)	107.2(3)
O(1)-C(13)-C(16)	106.5(3)
C(15)-C(13)-C(16)	109.0(4)
O(1)-C(13)-C(14)	104.2(4)
C(15)-C(13)-C(14)	117.1(4)
C(16)-C(13)-C(14)	112.2(4)
O(2)-C(14)-C(18)	110.4(3)
O(2)-C(14)-C(17)	107.2(3)
C(18)-C(14)-C(17)	110.6(3)
O(2)-C(14)-C(13)	100.7(4)
C(18)-C(14)-C(13)	115.4(4)
C(17)-C(14)-C(13)	111.7(4)
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(14)-C(18)-H(18A)	109.5

C(14)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(14)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\approx^2$x 10^3) for C18H29BO2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	16(1)	24(1)	26(1)	1(1)	9(1)	2(1)
O(2)	16(1)	23(1)	25(1)	-1(1)	7(1)	-1(1)
B(1)	17(1)	24(1)	14(1)	0(1)	3(1)	0(1)
C(1)	22(1)	32(1)	19(1)	-1(1)	4(1)	4(1)
C(2)	20(1)	28(1)	19(1)	0(1)	8(1)	2(1)
C(3)	16(1)	23(1)	21(1)	0(1)	7(1)	2(1)
C(4)	17(1)	20(1)	20(1)	1(1)	6(1)	-1(1)
C(5)	12(1)	28(1)	21(1)	-1(1)	9(1)	-4(1)
C(6)	23(1)	27(1)	27(1)	-1(1)	12(1)	-4(1)
C(7)	27(1)	41(1)	25(1)	-10(1)	12(1)	-13(1)
C(8)	18(1)	56(1)	19(1)	0(1)	4(1)	-4(1)
C(9)	21(1)	40(1)	28(1)	7(1)	7(1)	6(1)
C(10)	20(1)	28(1)	25(1)	-2(1)	7(1)	0(1)
C(11)	35(1)	32(1)	28(1)	4(1)	15(1)	1(1)
C(12)	28(1)	34(1)	24(1)	-1(1)	9(1)	8(1)
C(13)	13(2)	23(2)	36(3)	-7(2)	14(2)	-7(1)
C(14)	16(2)	16(2)	30(3)	3(2)	9(2)	2(1)
C(15)	22(1)	31(2)	42(2)	-5(1)	14(1)	-9(1)
C(16)	29(1)	35(2)	27(1)	6(1)	13(1)	4(1)
C(17)	16(1)	43(2)	30(2)	2(1)	3(1)	4(1)
C(18)	23(1)	30(2)	36(2)	-5(1)	13(1)	4(1)
C(13X)	18(4)	22(4)	45(6)	-7(4)	15(4)	1(3)
C(14X)	13(4)	32(4)	37(6)	23(4)	13(4)	6(3)
C(15X)	17(2)	50(3)	33(3)	-14(3)	10(2)	-6(2)
C(16X)	29(3)	33(3)	53(4)	7(3)	23(3)	4(2)
C(17X)	23(3)	32(3)	41(3)	2(2)	14(2)	4(2)
C(18X)	32(3)	40(3)	24(3)	-7(2)	12(2)	-3(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (≈^{2}x 10 ^{3}) for C18H29BO2.

	x	y	z	U(eq)
H(1A)	8429	5789	5993	37
H(1B)	8495	4835	7313	37
H(1C)	8356	4326	5681	37
H(3A)	4401	5397	3971	24
H(3B)	5890	6204	4011	24
H(4)	5819	3605	3372	22
H(6)	4813	2818	877	29
H(7)	3083	2990	-1518	36
H(8)	1964	4903	-2386	38
H(9)	2604	6650	-858	36
H(10)	4349	6483	1542	29
H(11A)	5998	3125	5656	45
H(11B)	6168	3625	7298	45
H(11C)	4571	3808	5992	45
H(12A)	6172	6858	6499	43
H(12B)	4675	6070	6504	43
H(12C)	6273	5886	7810	43
H(15A)	11629	6400	2531	46
H(15B)	10303	7364	2583	46
H(15C)	11052	6472	3975	46
H(16A)	9738	5590	91	45
H(16B)	8044	5167	90	45
H(16C)	8526	6600	302	45
H(17A)	12067	4389	4256	46
H(17B)	10646	4551	4916	46
H(17C)	11140	3196	4533	46
H(18A)	11523	3802	1568	43
H(18B)	10642	2592	1874	43
H(18C)	9778	3532	570	43
H(15D)	10606	5134	4931	49

H(15E)	11952	5688	4343	49
H(15F)	10745	6602	4745	49
H(16D)	11205	6568	1740	54
H(16E)	9424	6551	744	54
H(16F)	9987	7478	2132	54
H(17D)	12015	3907	2443	47
H(17E)	11452	3473	3818	47
H(17F)	10934	2709	2290	47
H(18D)	9885	4657	28	47
H(18E)	9038	3377	157	47
H(18F)	8127	4662	57	47

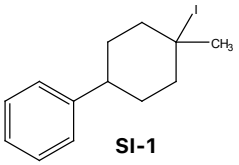
Table 6. Torsion angles [∞] for C18H29BO2.

C(14)-O(2)-B(1)-O(1)	7.6(3)
C(14)-O(2)-B(1)-C(4)	-175.7(2)
C(13)-O(1)-B(1)-O(2)	11.4(2)
C(13)-O(1)-B(1)-C(4)	-165.3(2)
C(11)-C(2)-C(3)-C(4)	-62.57(18)
C(12)-C(2)-C(3)-C(4)	178.29(13)
C(1)-C(2)-C(3)-C(4)	59.35(18)
C(2)-C(3)-C(4)-C(5)	162.02(13)
C(2)-C(3)-C(4)-B(1)	-77.84(17)
O(2)-B(1)-C(4)-C(5)	-94.99(16)
O(1)-B(1)-C(4)-C(5)	81.33(17)
O(2)-B(1)-C(4)-C(3)	141.19(14)
O(1)-B(1)-C(4)-C(3)	-42.50(19)
C(3)-C(4)-C(5)-C(10)	33.69(19)
B(1)-C(4)-C(5)-C(10)	-91.12(17)
C(3)-C(4)-C(5)-C(6)	-147.96(14)
B(1)-C(4)-C(5)-C(6)	87.22(16)
C(10)-C(5)-C(6)-C(7)	-1.2(2)
C(4)-C(5)-C(6)-C(7)	-179.60(14)
C(5)-C(6)-C(7)-C(8)	0.3(2)
C(6)-C(7)-C(8)-C(9)	0.5(3)
C(7)-C(8)-C(9)-C(10)	-0.3(3)
C(6)-C(5)-C(10)-C(9)	1.4(2)
C(4)-C(5)-C(10)-C(9)	179.72(14)
C(8)-C(9)-C(10)-C(5)	-0.6(2)
B(1)-O(1)-C(13)-C(15)	-148.7(3)
B(1)-O(1)-C(13)-C(16)	94.8(3)
B(1)-O(1)-C(13)-C(14)	-24.0(3)
B(1)-O(2)-C(14)-C(18)	-144.0(2)
B(1)-O(2)-C(14)-C(17)	95.4(3)
B(1)-O(2)-C(14)-C(13)	-21.6(4)
O(1)-C(13)-C(14)-O(2)	27.6(4)
C(15)-C(13)-C(14)-O(2)	145.7(3)
C(16)-C(13)-C(14)-O(2)	-87.2(4)

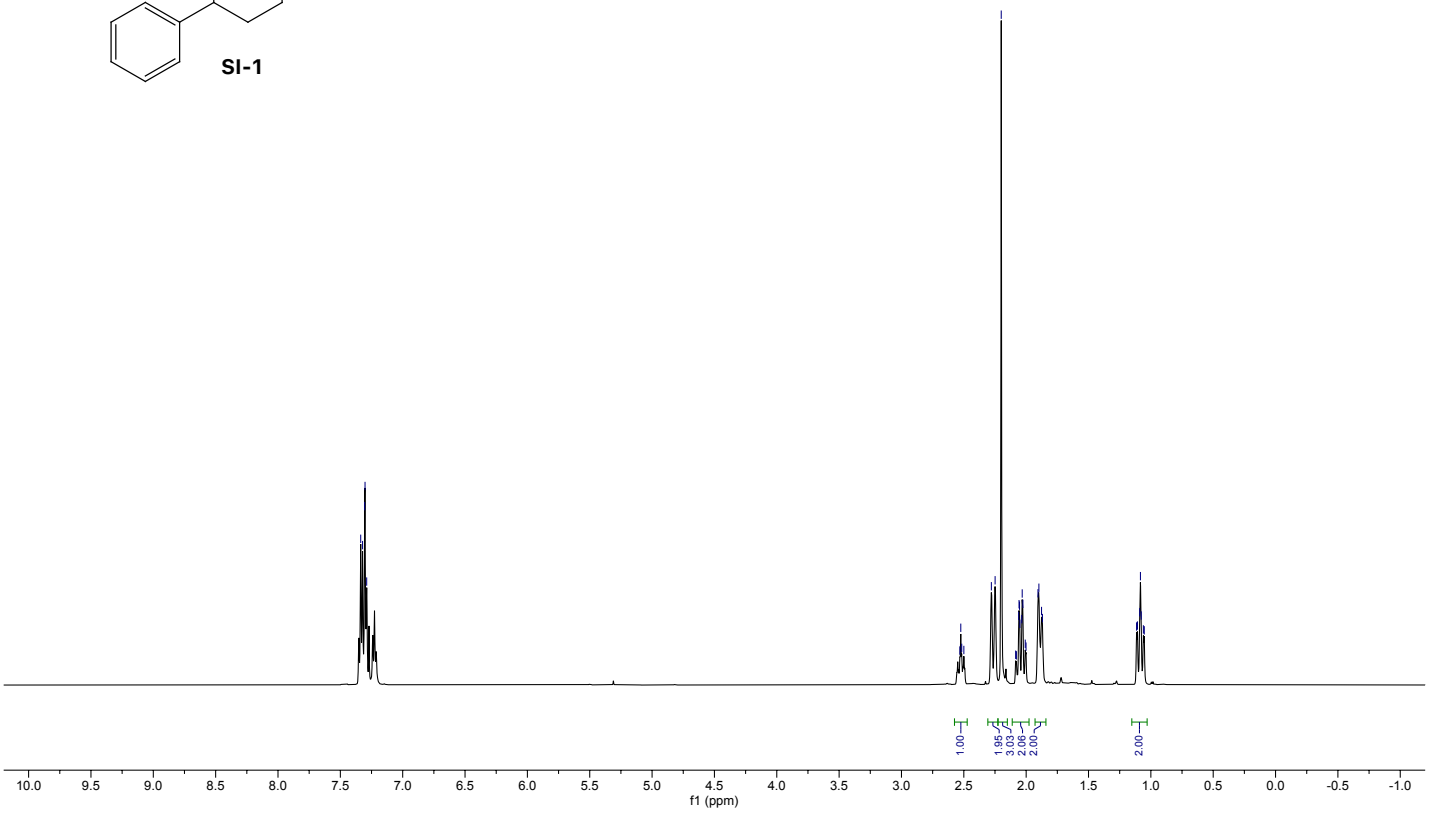
O(1)-C(13)-C(14)-C(18)	146.5(3)
C(15)-C(13)-C(14)-C(18)	-95.4(5)
C(16)-C(13)-C(14)-C(18)	31.7(5)
O(1)-C(13)-C(14)-C(17)	-86.0(4)
C(15)-C(13)-C(14)-C(17)	32.1(6)
C(16)-C(13)-C(14)-C(17)	159.2(4)

Symmetry transformations used to generate equivalent atoms:

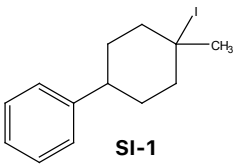
^{1}H NMR (500 MHz, $CDCl_3$)



SI-1

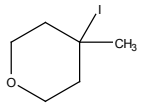


^{13}C NMR (151 MHz, $CDCl_3$)



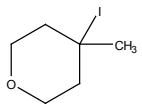
SI-1

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



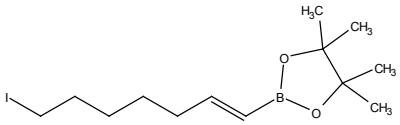
SI-2

^{13}C NMR (151 MHz, $CDCl_3$)



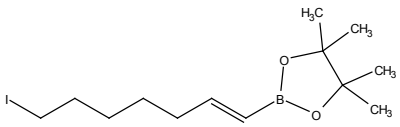
SI-2

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



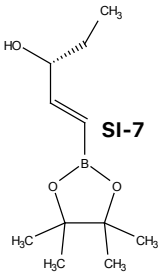
SI-5

^{13}C NMR (151 MHz, $CDCl_3$)



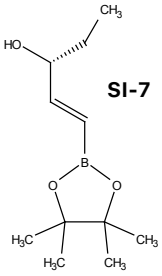
SI-5

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



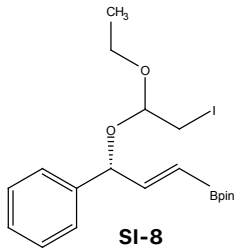
SI-7

^{13}C NMR (151 MHz, $CDCl_3$)



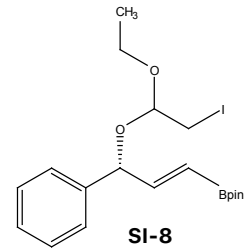
SI-7

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



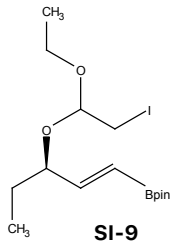
SI-8

^{13}C NMR (151 MHz, $CDCl_3$)



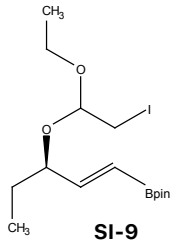
SI-8

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



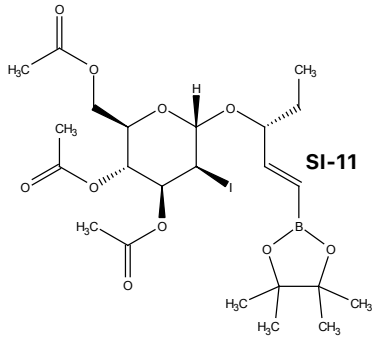
SI-9

^{13}C NMR (151 MHz, $CDCl_3$)

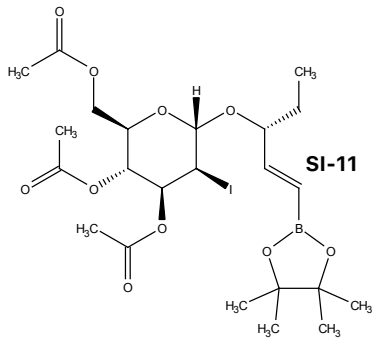


SI-9

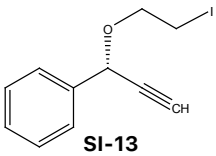
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

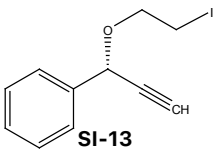


^{1}H NMR (500 MHz, $CDCl_3$)



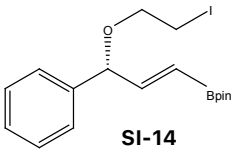
SI-13

^{13}C NMR (151 MHz, $CDCl_3$)



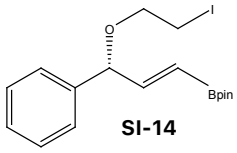
SI-13

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



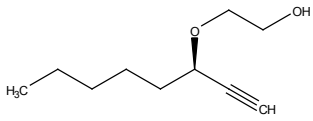
SI-14

^{13}C NMR (151 MHz, $CDCl_3$)



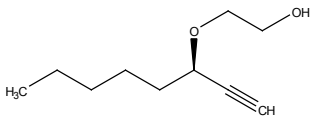
SI-14

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



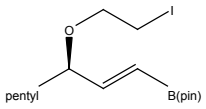
SI-15

^{13}C NMR (151 MHz, $CDCl_3$)



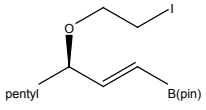
SI-15

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



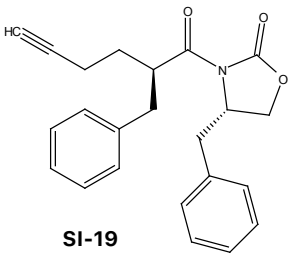
SI-17

^{13}C NMR (151 MHz, $CDCl_3$)



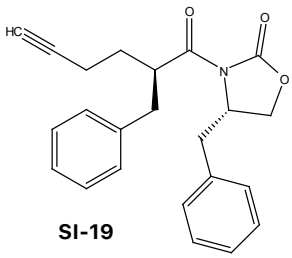
SI-17

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



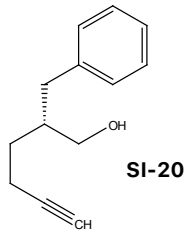
SI-19

^{13}C NMR (151 MHz, $CDCl_3$)



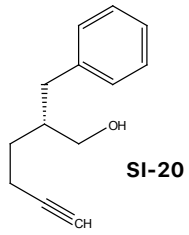
SI-19

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



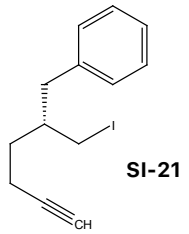
SI-20

^{13}C NMR (151 MHz, $CDCl_3$)



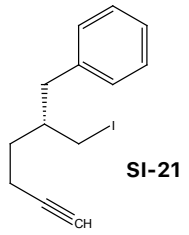
SI-20

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



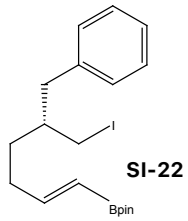
SI-21

^{13}C NMR (151 MHz, $CDCl_3$)



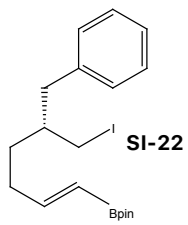
SI-21

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



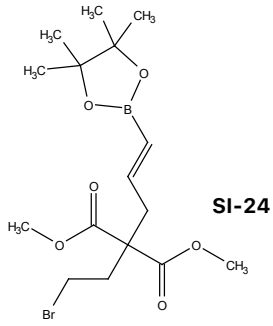
SI-22

^{13}C NMR (151 MHz, $CDCl_3$)



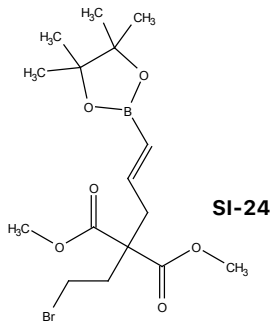
SI-22

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



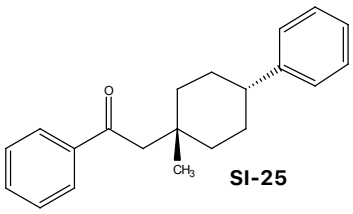
SI-24

^{13}C NMR (151 MHz, $CDCl_3$)



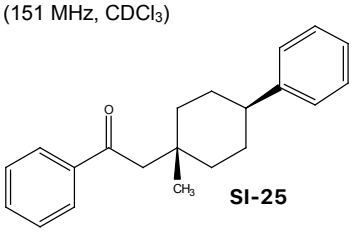
SI-24

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



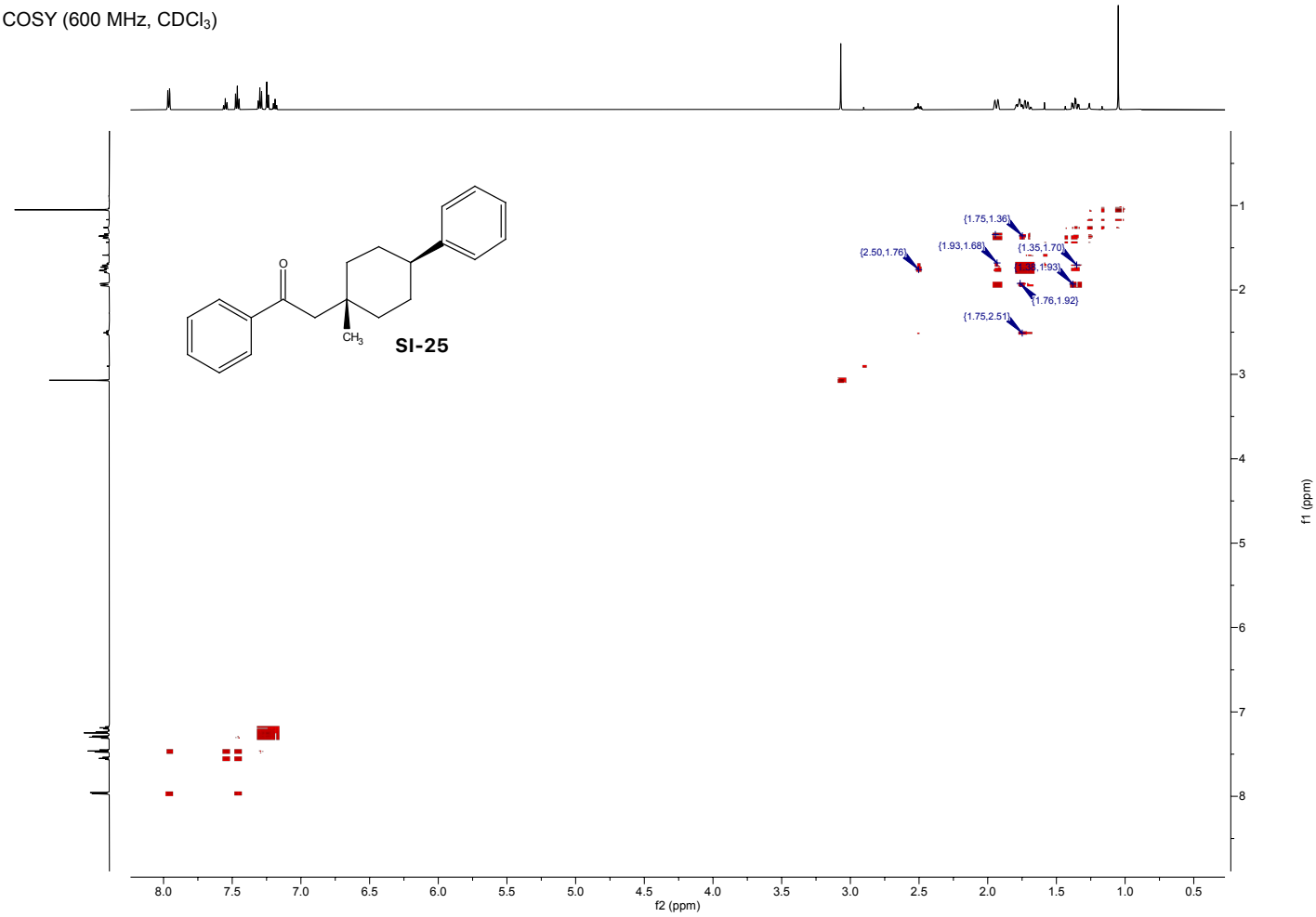
SI-25

^{13}C NMR (151 MHz, $CDCl_3$)

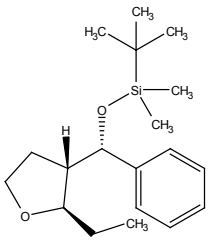


SI-25

COSY (600 MHz, $CDCl_3$)

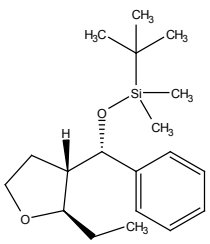


^{1}H NMR (500 MHz, $CDCl_3$)



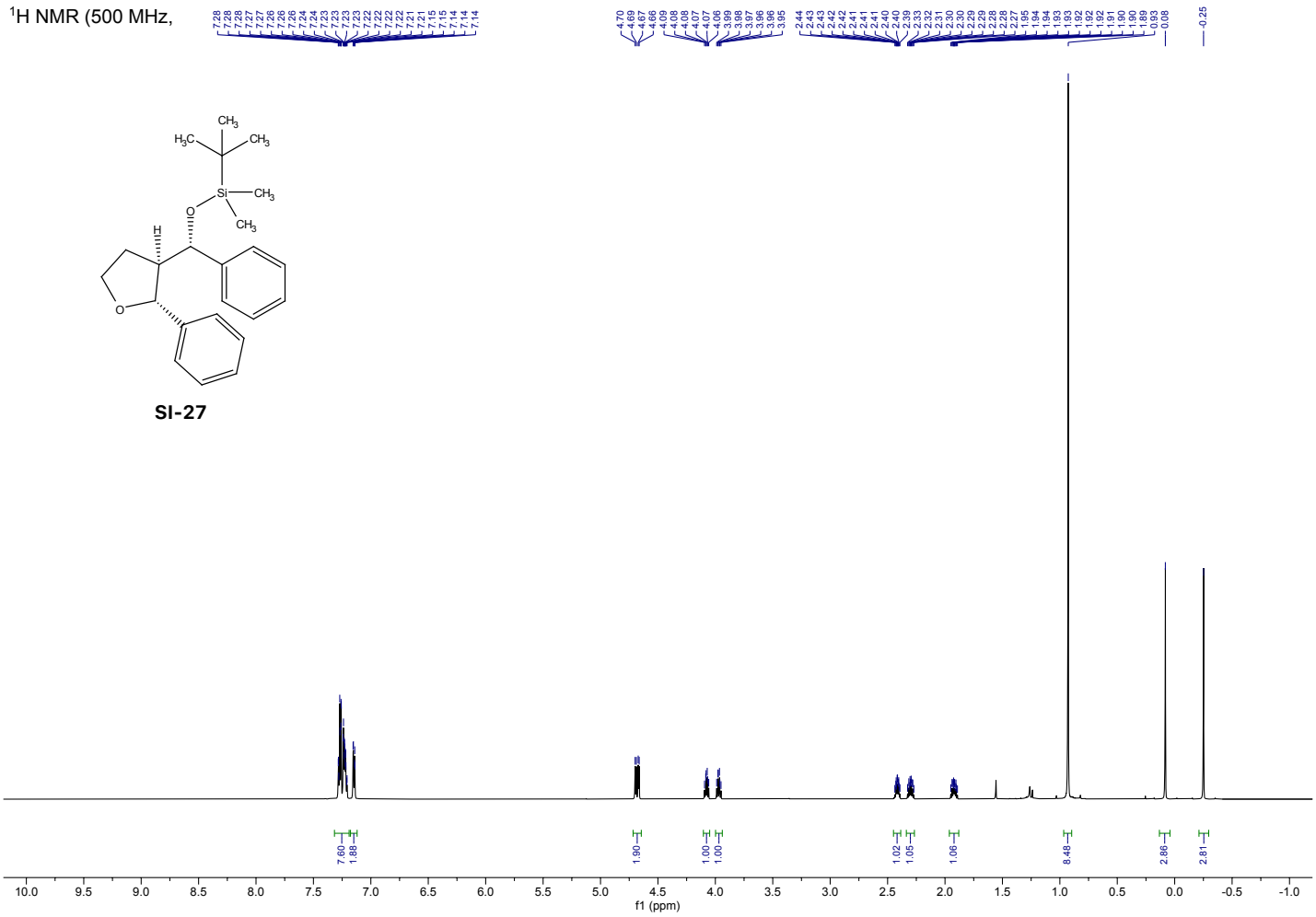
SI-26

^{13}C NMR (151 MHz, $CDCl_3$)



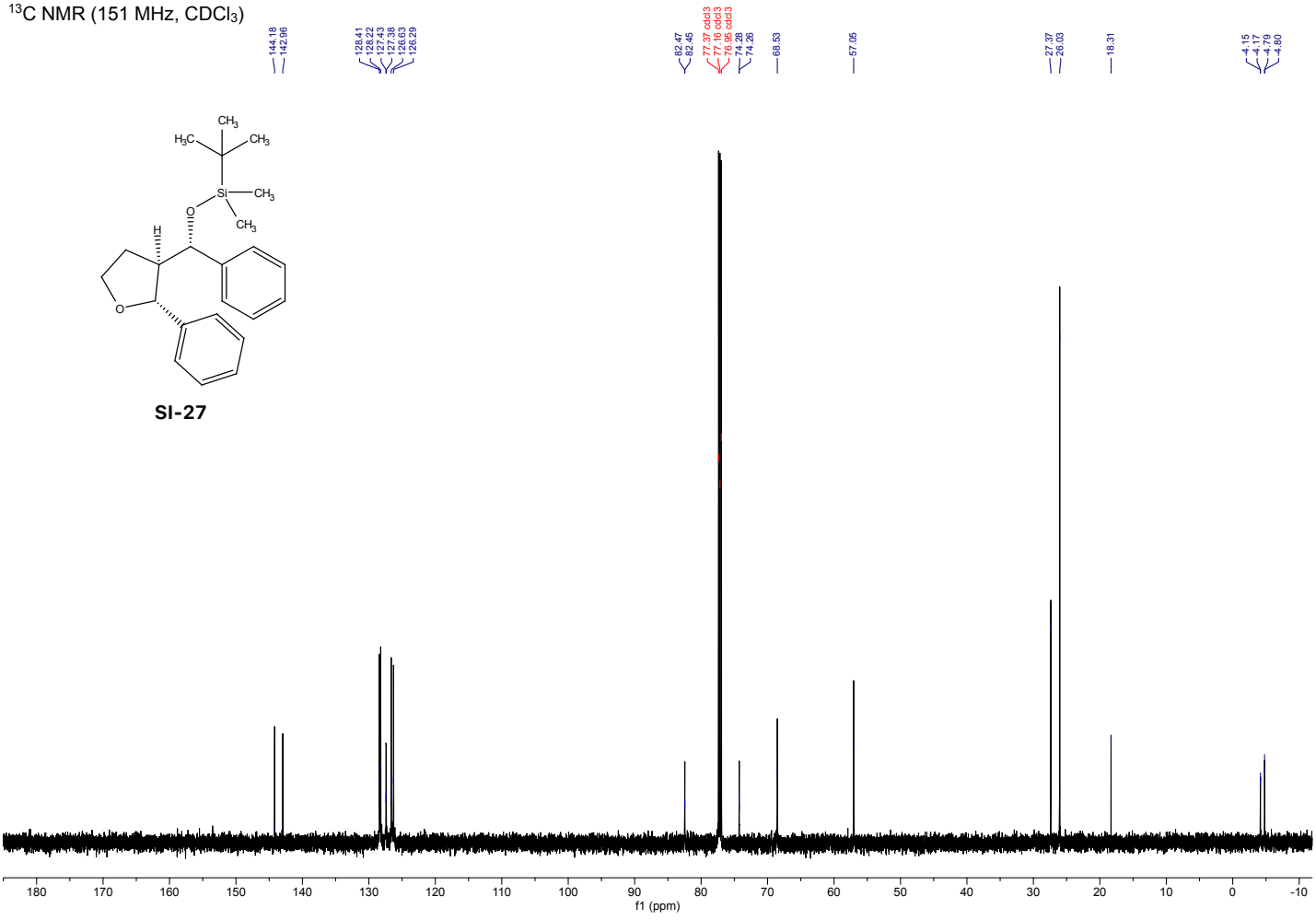
SI-26

^{1}H NMR (500 MHz,



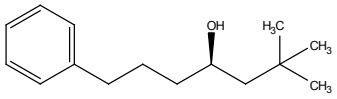
SI-27

^{13}C NMR (151 MHz, $CDCl_3$)



SI-27

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

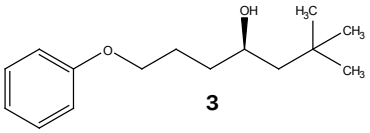


2

^{13}C NMR (151 MHz, $CDCl_3$)

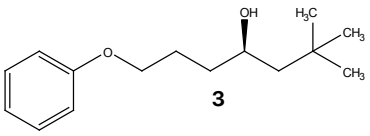
2

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



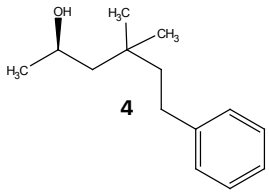
3

^{13}C NMR (151 MHz, $CDCl_3$)



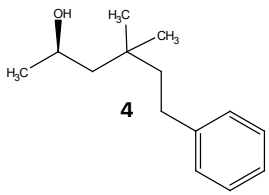
3

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



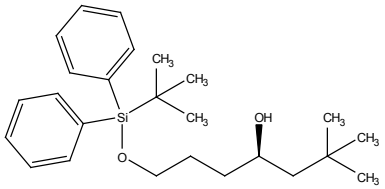
4

^{13}C NMR (151 MHz, $CDCl_3$)



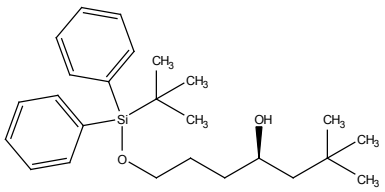
4

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



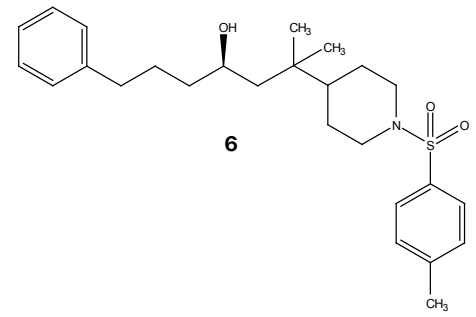
5

^{13}C NMR (151 MHz, $CDCl_3$)



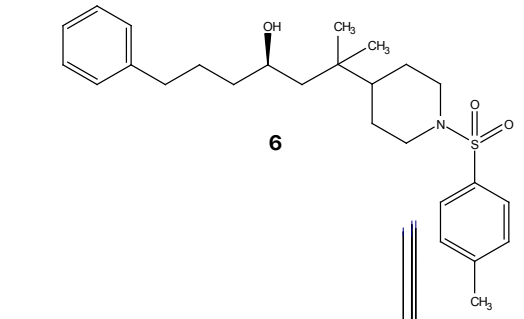
5

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



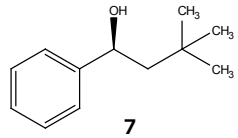
6

^{13}C NMR (151 MHz, $CDCl_3$)



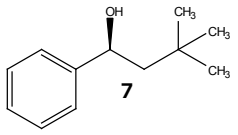
6

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



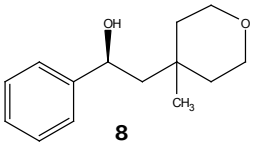
7

^{13}C NMR (151 MHz, $CDCl_3$)



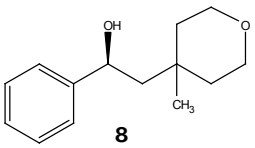
7

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



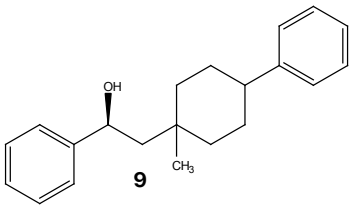
8

^{13}C NMR (151 MHz, $CDCl_3$)



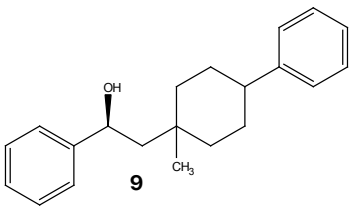
8

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



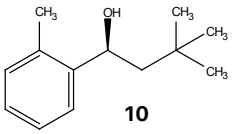
9

^{13}C NMR (151 MHz, $CDCl_3$)



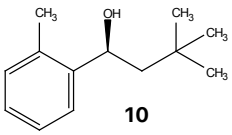
9

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



10

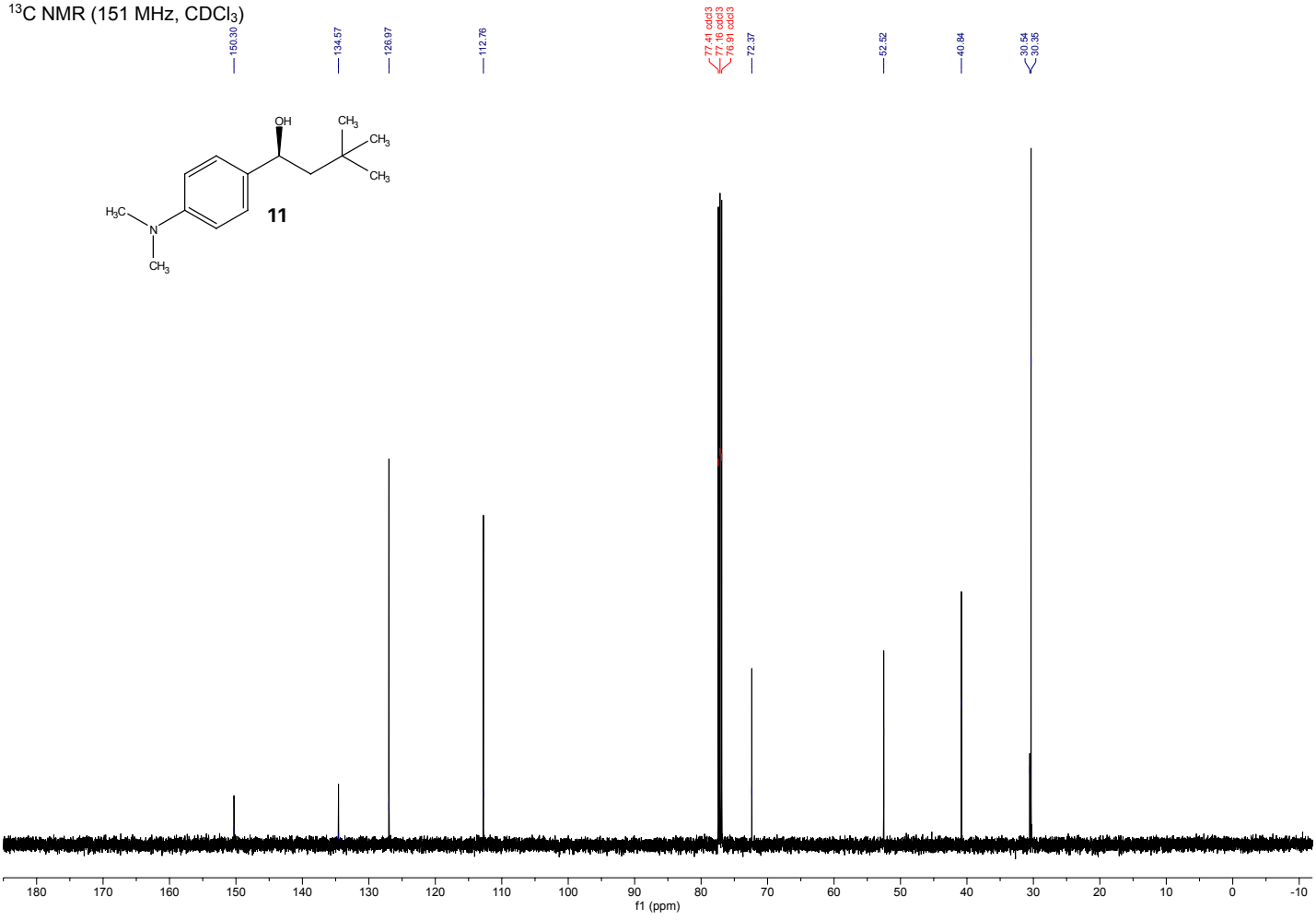
^{13}C NMR (151 MHz, $CDCl_3$)



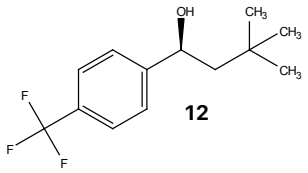
10

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

^{13}C NMR (151 MHz, $CDCl_3$)

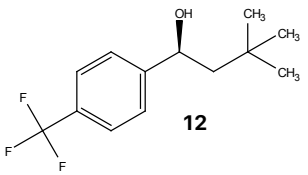


^{1}H NMR (500 MHz, $CDCl_3$)



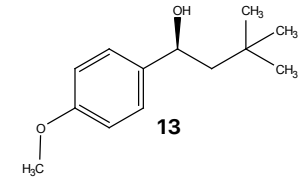
12

^{13}C NMR (151 MHz, $CDCl_3$)

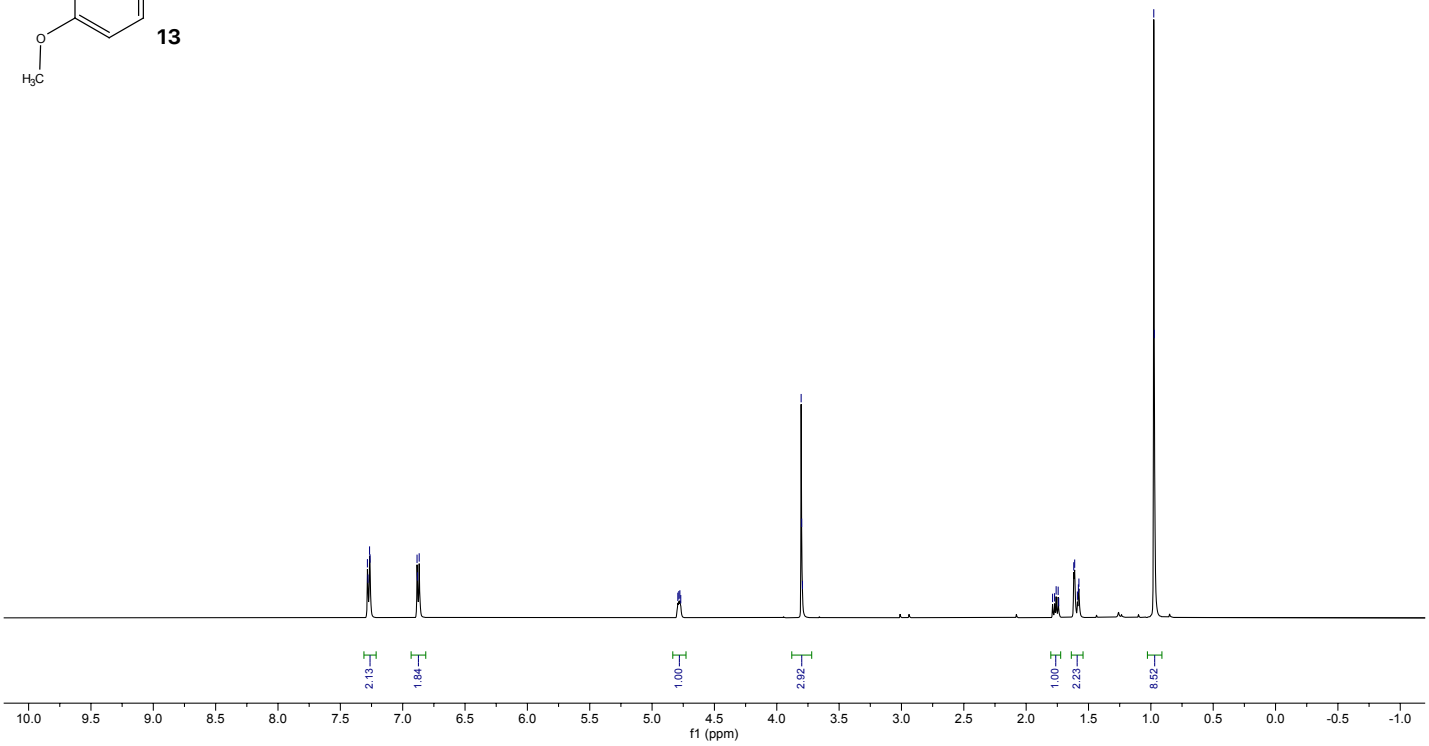


12

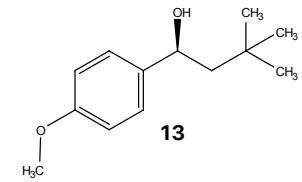
^{1}H NMR (500 MHz, $CDCl_3$)



13

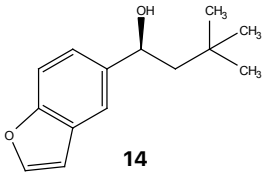


^{13}C NMR (151 MHz, $CDCl_3$)



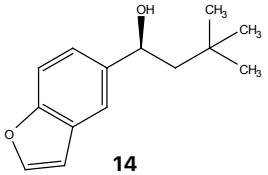
13

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



14

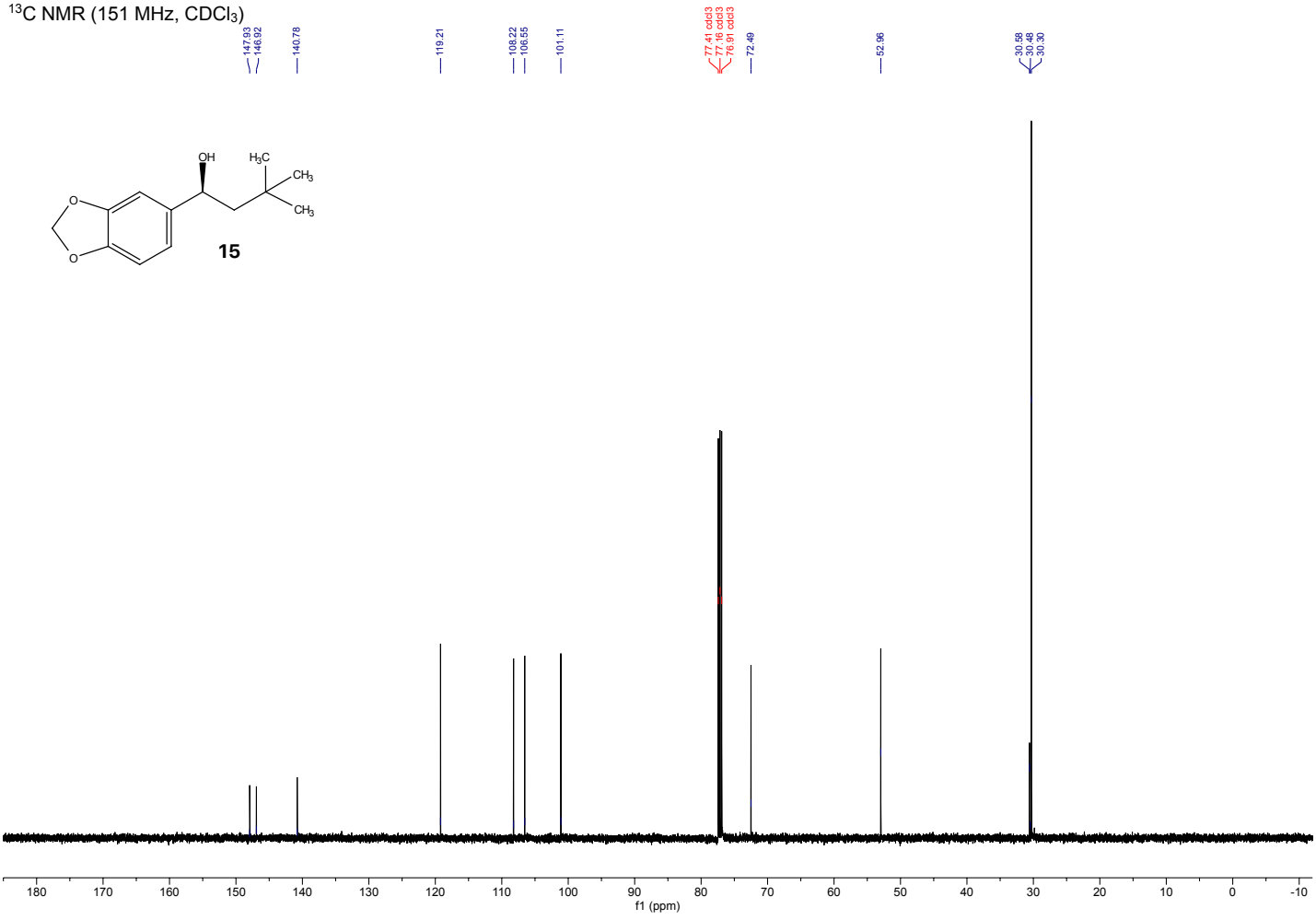
^{13}C NMR (151 MHz, $CDCl_3$)



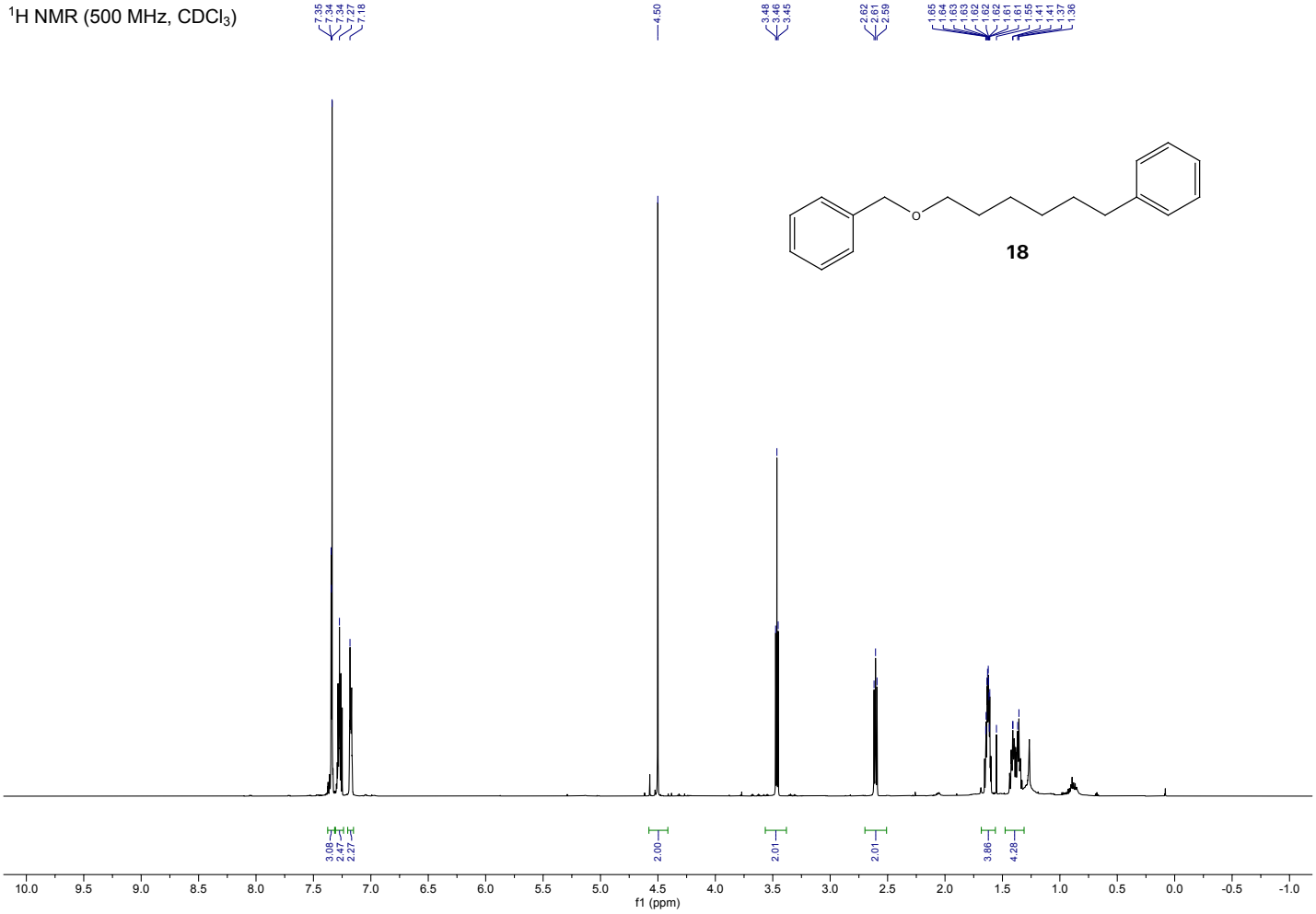
14

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

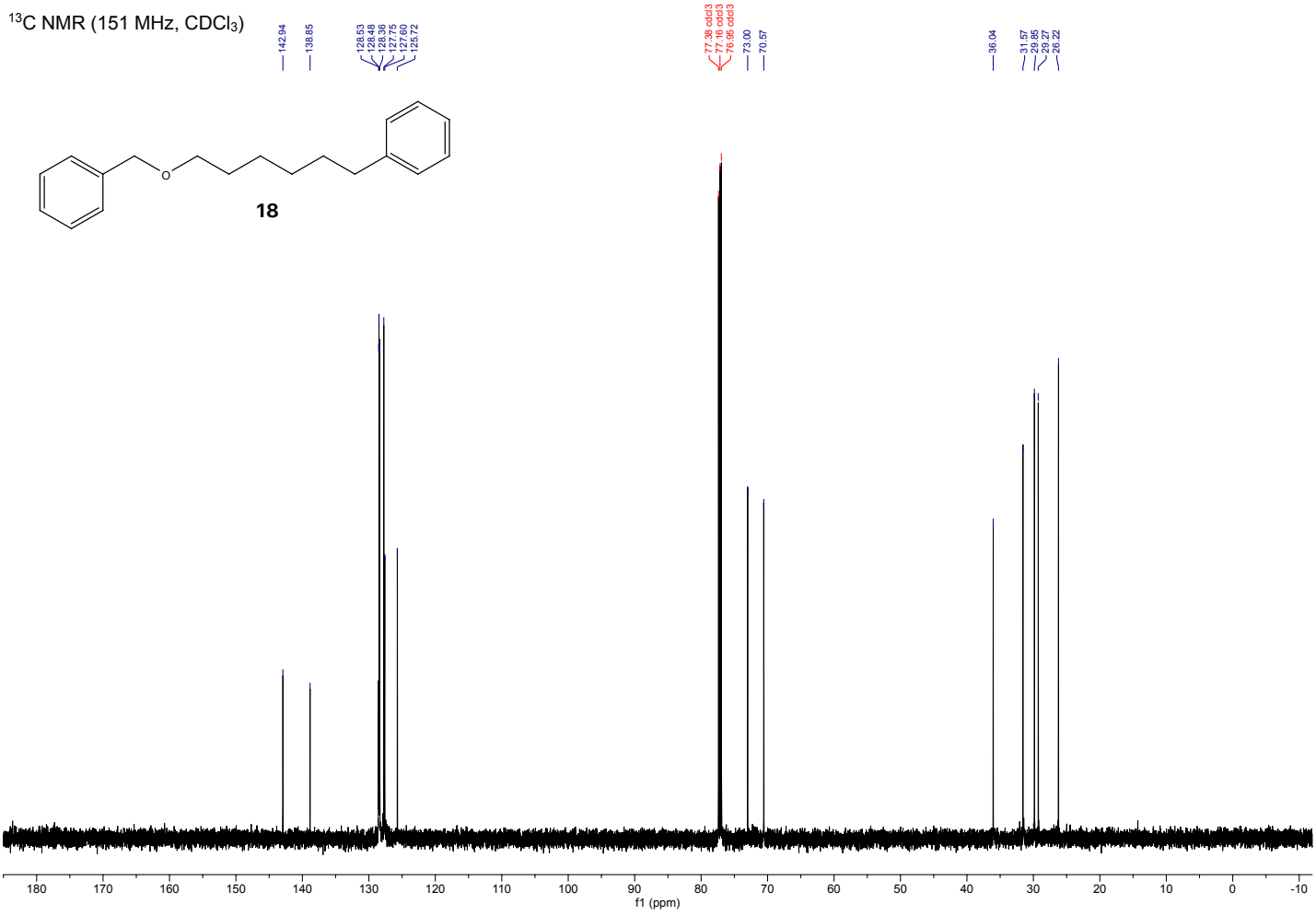
^{13}C NMR (151 MHz, $CDCl_3$)



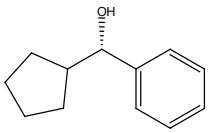
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

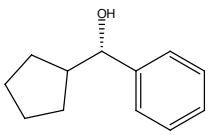


^{1}H NMR (500 MHz, $CDCl_3$)



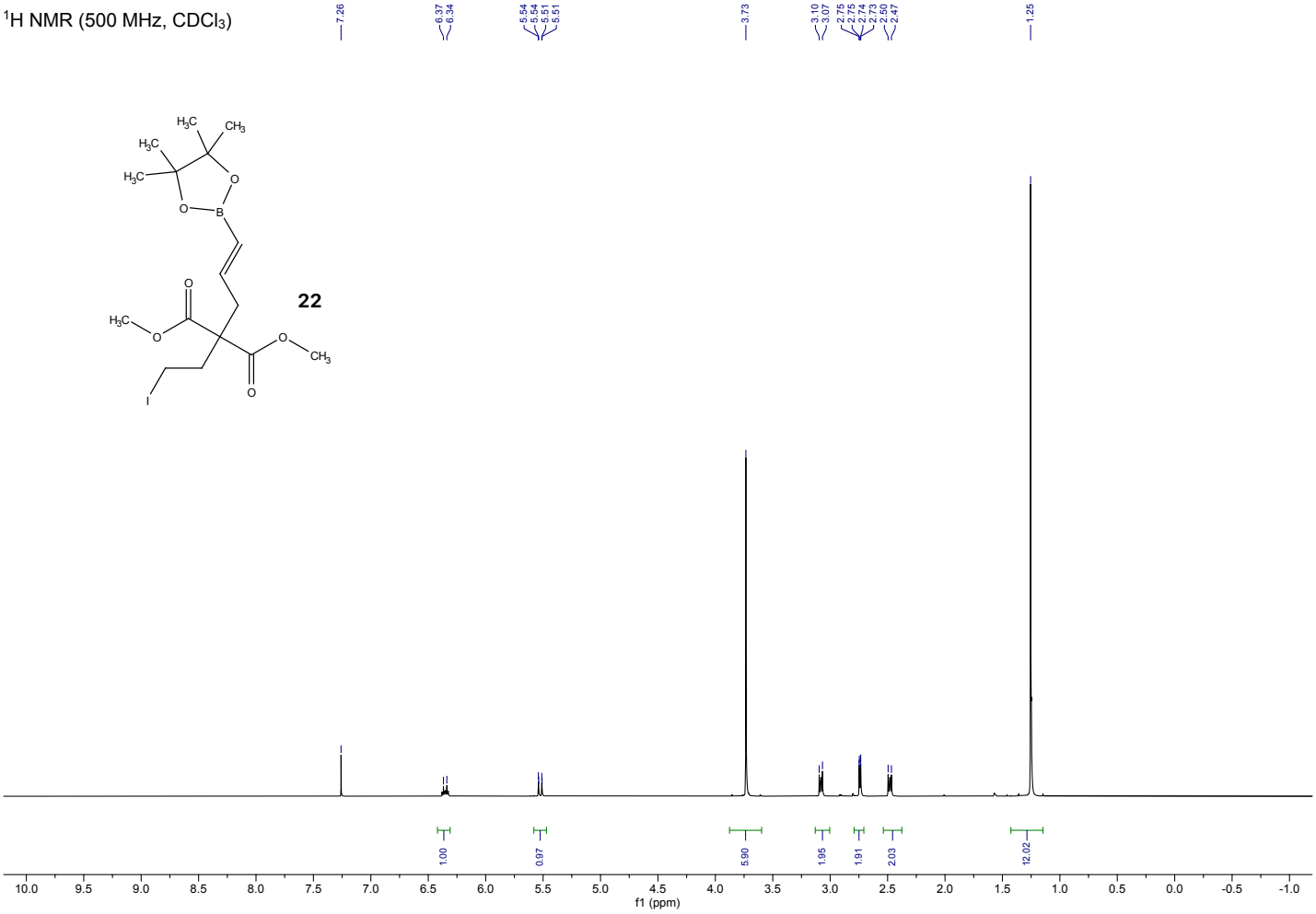
21

^{13}C NMR (151 MHz, $CDCl_3$)

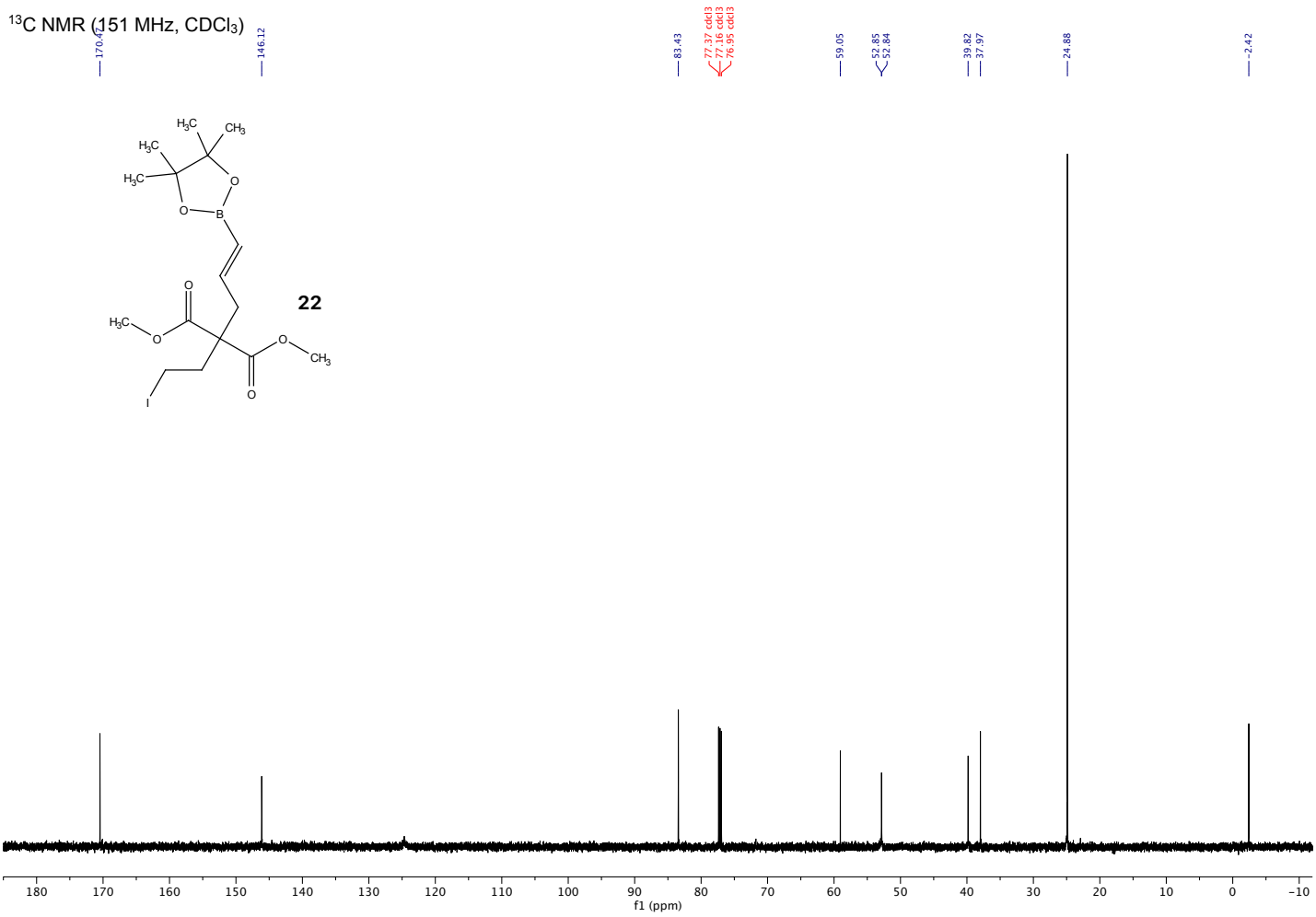


21

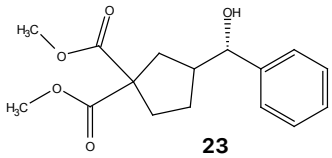
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

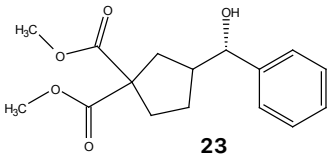


^{1}H NMR (500 MHz, C_6D_6)



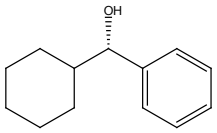
23

^{13}C NMR (151 MHz, $CDCl_3$)



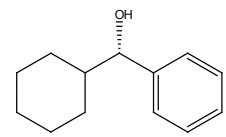
23

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



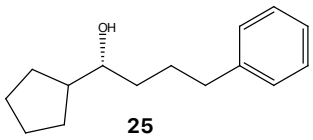
24

^{13}C NMR (151 MHz, $CDCl_3$)



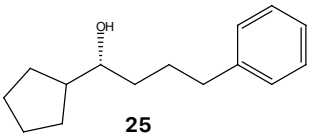
24

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



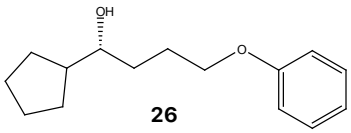
25

^{13}C NMR (151 MHz, $CDCl_3$)



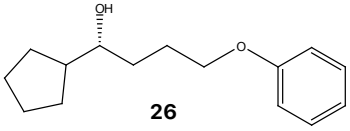
25

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



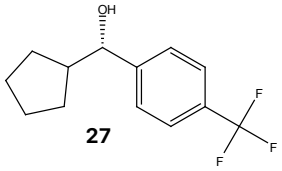
26

^{13}C NMR (151 MHz, $CDCl_3$)



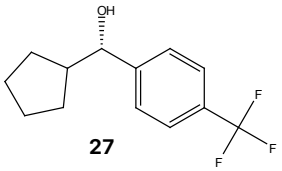
26

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



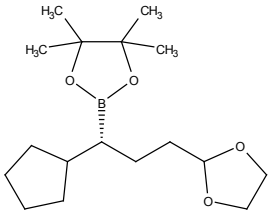
27

^{13}C NMR (151 MHz, $CDCl_3$)



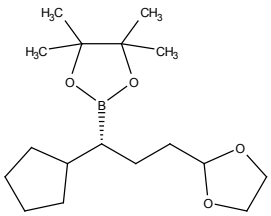
27

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



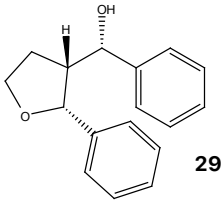
28

^{13}C NMR (151 MHz, $CDCl_3$)

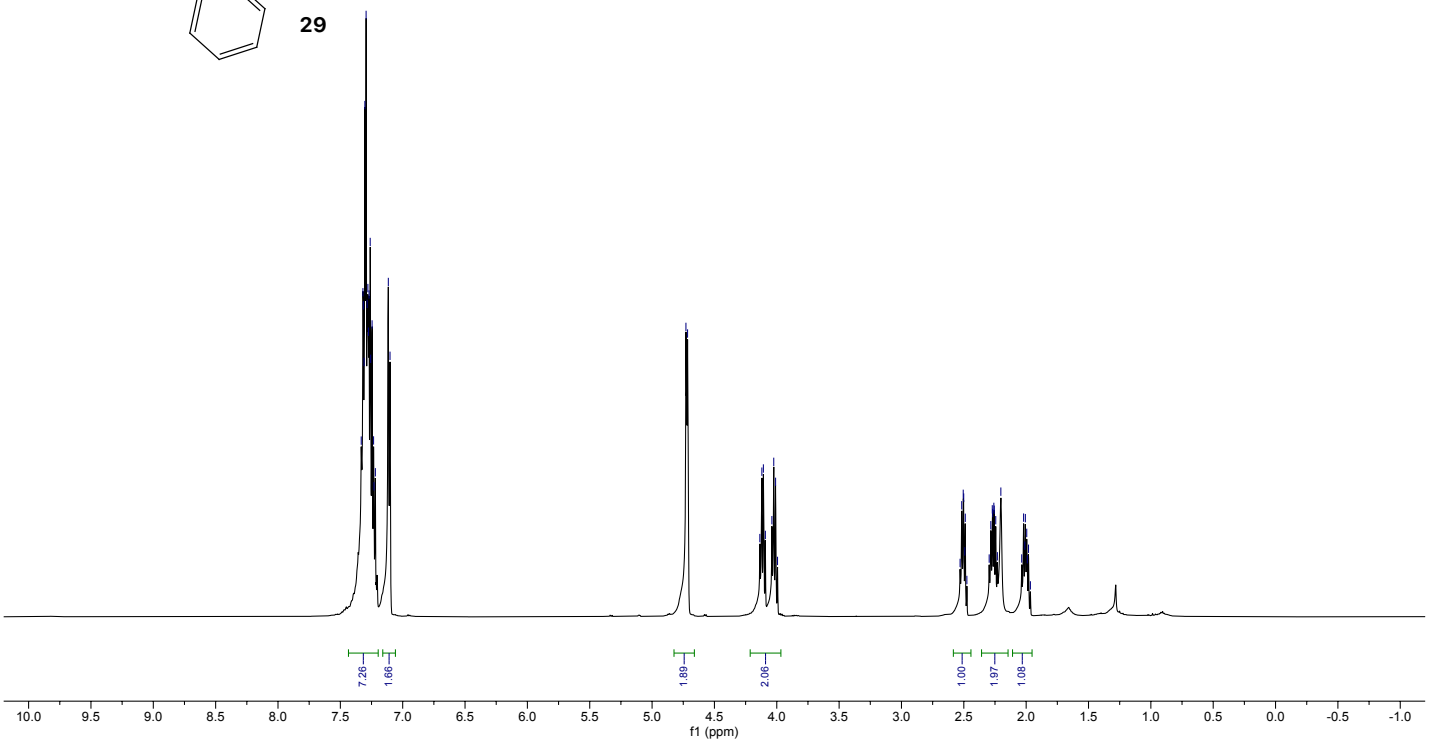


28

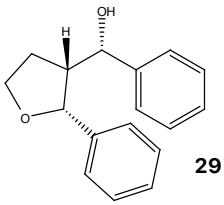
^{1}H NMR (500 MHz, $CDCl_3$)



29

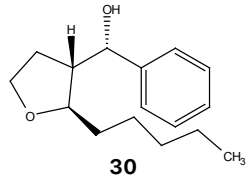


^{13}C NMR (151 MHz, $CDCl_3$)



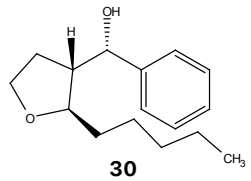
29

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



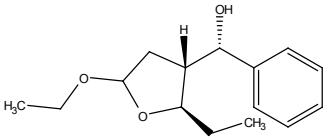
30

^{13}C NMR (151 MHz, $CDCl_3$)



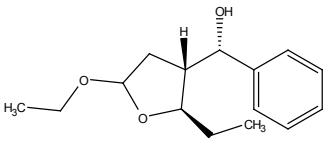
30

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



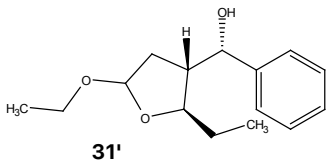
31

^{13}C NMR (151 MHz, $CDCl_3$)



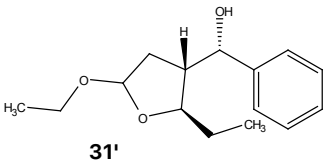
31

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



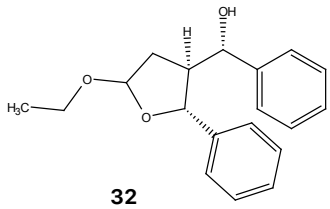
31'

^{13}C NMR (151 MHz, $CDCl_3$)



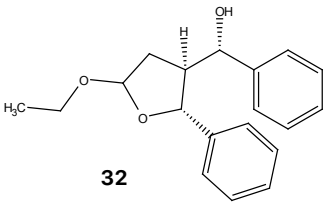
31'

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



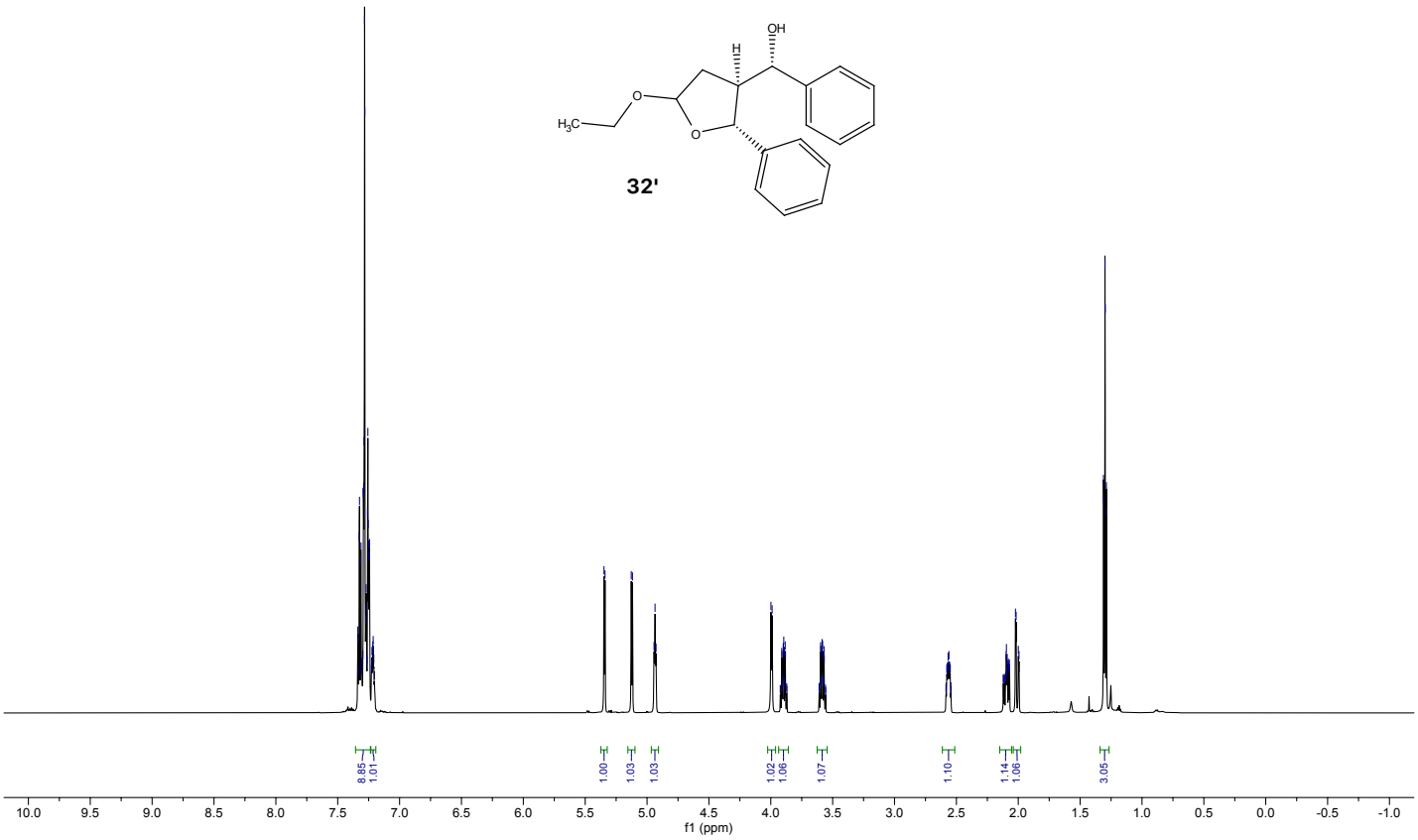
32

^{13}C NMR (151 MHz, $CDCl_3$)

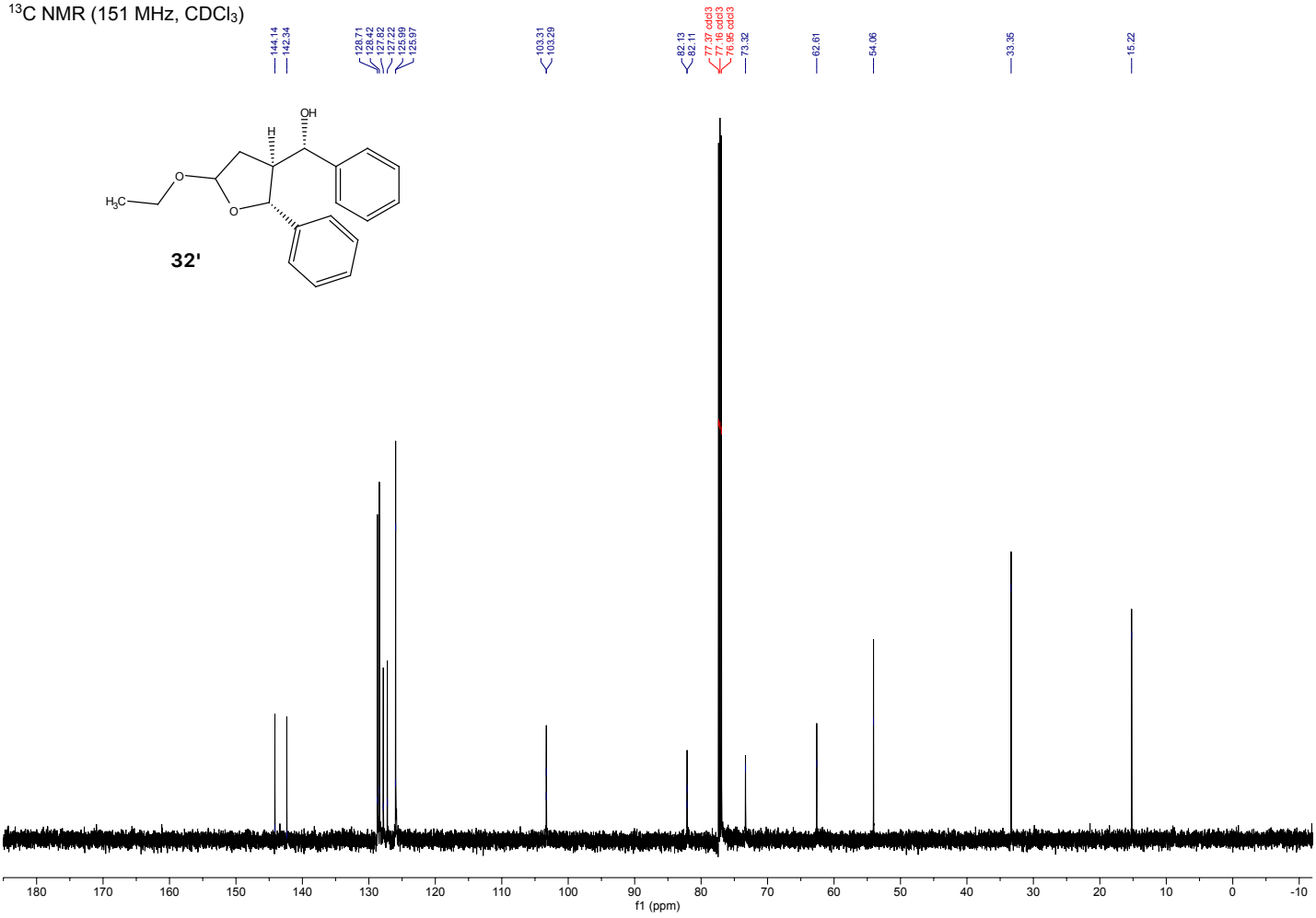


32

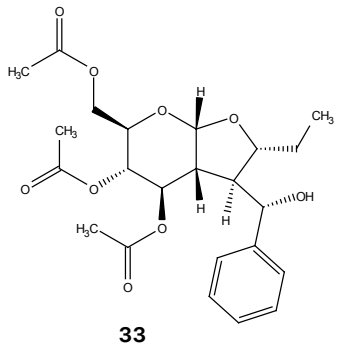
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

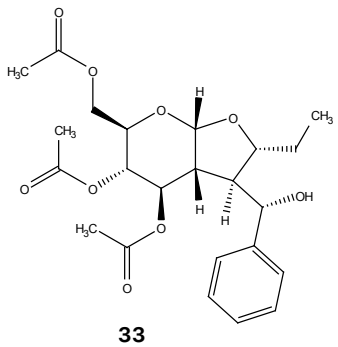


^{1}H NMR (500 MHz, $CDCl_3$)



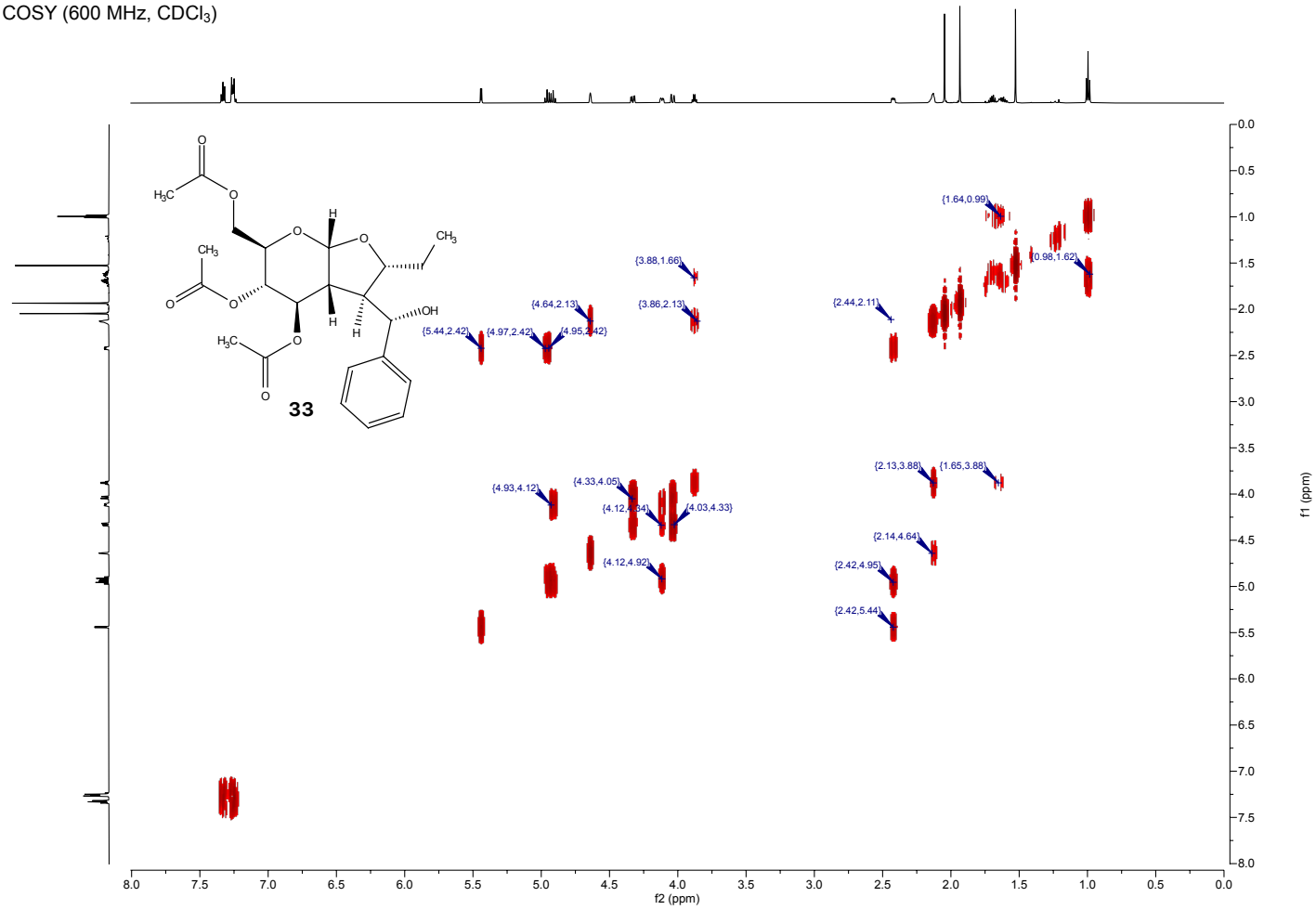
33

^{13}C NMR (151 MHz, $CDCl_3$)

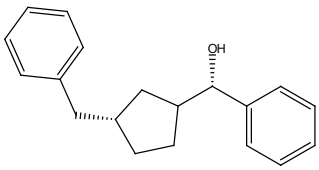


33

COSY (600 MHz, $CDCl_3$)

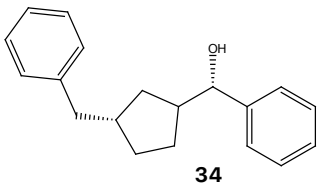


^{1}H NMR (500 MHz, $CDCl_3$)



34

^{13}C NMR (151 MHz, $CDCl_3$)



34