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Supporting Information

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Enantioselective Alkylation of Acyclic α,α-Disubstituted Tributyltin Enolates Catalyzed by a Cr(salen) Complex

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Supporting Information

General Procedures. Alkylation reactions were performed in flame-dried 10mL schlenk flasks. All other reactions were performed in flame dried round bottom flasks. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of nitrogen, unless otherwise noted. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids.

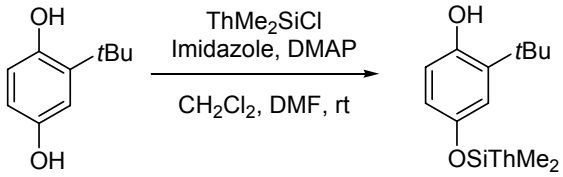
Materials. Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar, or Lancaster, and used as received with the following exceptions: dichloromethane was distilled from calcium hydride at 760 Torr; toluene was distilled from sodium at 760 Torr; *o*-xylene was distilled from calcium chloride at 760 Torr and stored over 4Ä MS; TBME and tetrahydrofuran were distilled from sodium benzophenone ketyl at 760 Torr; ethyl iodoacetate was filtered through a plug of basic alumina before use. Flash chromatography was performed using silica gel 60 (230-400 mesh), purchased from EM Science. Tin enolates were stored at −30 °C under a nitrogen atmosphere for up to 4 weeks and subsequently re-distilled before use.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Varian-Mercury-400 (400 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.16). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). Gas Chromatographic (GC) analyses were performed on Hewlett-Packard 5890 Series II instruments equipped with FID detectors and HP 3396 integrators. Infrared (IR) spectra were obtained using a Mattson Galaxy Series FTIR 3000 spectrophotometer referenced to a polystyrene standard. Data are represented as follows: frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak). Optical rotations were measured using a 1 mL cell with a 0.5 dm path length on a Jasco DIP 370 digital polarimeter. The mass spectral data were obtained at the Harvard University mass spectrometry facility. Chiral gas chromatography (GC) analysis was performed on a Hewlett-Packard 5890 gas chromatograph using a Chiraldex γ-TA (30 m x 0.25 mm). Chiral HPLC analysis was performed on a Shimadzu VP-series instrument.

Representative Experimental Procedures:

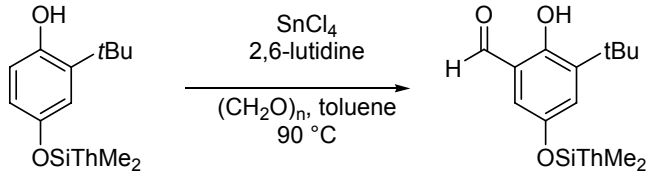
(A) Preparation of catalyst 1e:

Catalyst **1a** was prepared according to the following procedure.[1]
2-*tert*-Butyl-4-thexyldimethylsilanyloxyphenol.



To a flame-dried 100mL round bottom flask was added 1.66 g *t*-butylhydroquinone (10 mmol, 1 equiv.) in 20 mL dichloromethane and 20 mL DMF. To the solution was added 1.38g imidazole (20 mmol, 2 equiv.) and 120 mg DMAP (0.1 mmol, 10 mol %), followed by 2.36 mL $ThMe_2SiCl$ (12 mmol, 1.2 equiv.) via syringe. The reaction was stirred at room temperature for 7 hours at which time the stir bar was removed and the reaction was concentrated *in vacuo* to the DMF solution. The DMF solution was partitioned between 100 mL 25% ethyl acetate/ hexanes and 100 mL water. The organic layer was separated and washed three times with water (100mL), once with saturated aqueous NaCl (100 mL), and once with saturated aqueous $NaHCO_3$ (100 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography on silica gel, eluting with 2% → 5% Et_2O/pentane provided 3.08 g of a light yellow oil (10 mmol, quantitative yield). IR (thin film, cm^{-1}) 3492 (br), 2959 (s), 2870 (m), 1499 (s), 1411 (s), 962 (s), 861 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 6.75 (1H, d, J = 1.2 Hz), 6.52-6.51 (2H, m), 4.47 (1H, s), 1.73 (1H, septet, J = 5.4Hz), 1.38 (9H, s), 0.95-0.94 (12H, m), 0.20 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 148.6, 137.3, 119.2, 117.7, 117.1, 34.7, 34.4, 29.7, 25.2, 20.4, 18.8, -2.3; LRMS (CI): 309 [M+].

3-*tert*-Butyl-2-hydroxy-5-thexyldimethylsilanyloxybenzaldehyde



A flame-dried 100mL 3-neck round bottom flask, equipped with an oven-dried reflux condenser, stir bar, rubber septum, and glass stopper, was charged with 3.08g phenol (10 mmol, 1 equiv.) in 30mL toluene. The solution was cooled to 0 °C (ice-water bath) and 2.33mL 2,6-lutidine (20 mmol, 2 equiv.) was added by syringe in one portion. Tin(IV) chloride (585μL, 5 mmol, 0.5 equiv) was then added over 20 seconds via syringe, resulting in a bright yellow solution. The reaction mixture was stirred for 1 hour under nitrogen atmosphere while the temperature was maintained at 0 °C. Solid paraformaldehyde (2.70g, 90 mmol, 9 equiv.) was then added in one portion. The flow of nitrogen was stopped and replaced by a balloon filled with nitrogen, attached with a needle through the septum. The reaction mixture was heated to 90 °C for 24 hours, then cooled to room temperature and filtered through a frit filled with Celite®. The filter pad was washed with ethyl acetate (100mL). The combined filtrates were concentrated *in vacuo* and the yellow residue was redissolved in ethyl acetate (100mL), washed with water (100mL) and 1M HCl (100mL). The organic phase was dried (Na_2SO_4), filtered and concentrated *in vacuo*. The oil was purified by column chromatography on silica gel eluting with 2% ethyl acetate in hexanes to yield 2.93 g of aldehyde (8.7 mmol, 87% yield). IR (thin film, cm^{-1}) 3035 (w), 2960 (s), 2871 (m), 1657 (s), 1435 (s), 1322 (s), 1256 (m), 1234 (m), 1148 (m), 1001 (m), 857 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 11.41 (1H, s), 9.78 (1H, s), 7.05 (1H, d, J =3.2 Hz), 6.90 (1H, d, J =2.8 Hz), 1.73 (1H, septet, J = 7.0 Hz), 1.40 (9H, s), 0.96-0.95 (12H, m), 0.22 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 156.2, 147.6, 139.8, 128.0, 120.5, 120.5, 35.0, 34.3, 29.3, 25.3, 20.4, 18.8, -2.3; LRMS (CI) 337 (100%) $[M]^+$.

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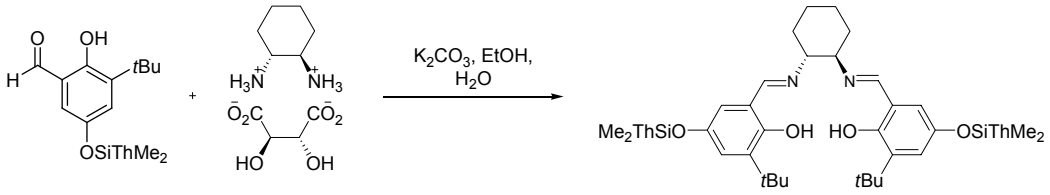
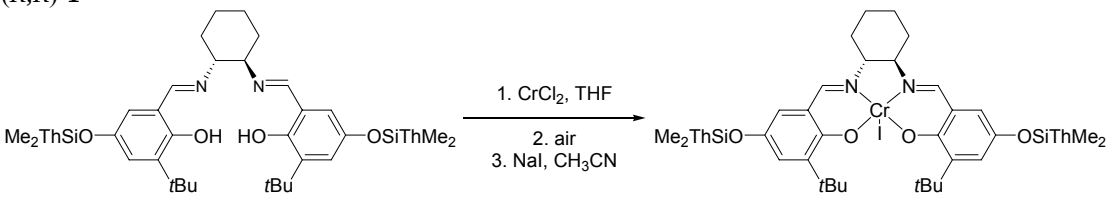
[1] S. E. Schaus, J. Branalt, E. N. Jacobsen, *J. Org. Chem.* **1998**, *63*, 403-405.

(*R*,*R*)-*N*,*N*'-Bis(3-*tert*-butyl-5-thexyldimethylsilanyloxysalicylidene)-1,2-cyclohexanediamine



To a 100 mL 3-neck round bottom flask equipped with a reflux condenser, addition funnel (10mL), glass stopper, and stirbar, was added 1.10g (*R*,*R*)-diaminocyclohexane tartrate salt (4.16 mmol, 1 equiv.), 1.15g K_2CO_3 (8.32 mmol, 2 equiv.), and 5.6 mL H_2O. The solution was stirred at room temperature until all of the solids had dissolved and then 22.3 mL EtOH was added, resulting in a cloudy solution which was heated to 75 °C. A solution of aldehyde (2.80g, 8.32 mmol, 2 equiv.) in 9.3 mL EtOH was added dropwise through the addition funnel over 5 minutes and the addition funnel was rinsed with 2 mL EtOH. The reaction was heated at 80 °C for 2 hours and then cooled slowly to room temperature (1 hour) and further to 4 °C (3 hours). The yellow solid was collected by vacuum filtration, rinsed with cold EtOH and then redissolved in dichloromethane (150 mL). The solution was washed with water (2 x 150 mL) and saturated aqueous NaCl (2 x 150 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Recrystallization from hot EtOH (~ 30 mL) provided 2.50 g of yellow crystals (3.33 mmol, 80% yield). $[\alpha]^{24}_D = -244.1°$ (c=1.0, $CHCl_3$); IR (thin film, cm^{-1}) 2958 (s), 2867 (s), 1632 (s), 1596 (s), 1463 (s), 1438 (s), 1321 (s), 1255 (s), 858 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (2H, s), 6.76 (2H, d, J=2.4 Hz), 6.43 (2H, d, J=2.4 Hz), 3.30-3.27 (2H, m), 1.98-1.62 (8H, m), 1.50-1.41 (2H, m), 1.38 (18H, s), 0.93-0.91 (24H, m), , 0.13 (6H, s), 0.12 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 154.9, 146.6, 138.3, 122.5, 119.4, 118.5, 72.6, 34.9, 34.3, 33.3, 29.5, 25.2, 24.5, 20.4, 18.8, -2.3; LRMS (FAB) 750 (100%) [M-H]+, 773 (80%) [M-H+Na].

(*R*,*R*)-**1**

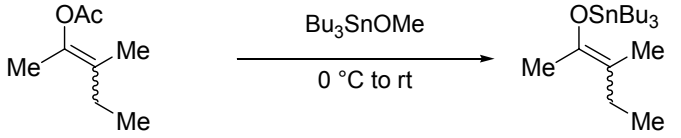


An oven dried 50 mL round bottom flask with stir bar was charged with 270 mg $Cr(II)Cl_2$ (2.2 mmoles, 1.1 equiv.) in an inert atmosphere box. The flask was sealed with a rubber septa and taken out of the box. 5.0 mL THF was added to the flask, followed by a de-gassed solution of 1.50g (*R*,*R*)-*N*,*N*'-Bis(3-*tert*-butyl-5-thexyldimethylsilanyloxysalicylidene)-1,2-cyclohexanediamine (2 mmoles, 1 equiv.) in 22 mL THF (followed by one 5 mL THF rinse of the flask containing the ligand). The solution immediately turned a deep brown color upon addition. The reaction was stirred under nitrogen for 4.5 hours and was then opened to the atmosphere and stirred for an additional 10 hours. The solution was diluted with 100 mL TBME and was washed with sat. aqueous NH_4Cl (4 x 150 mL) and with sat. aqueous NaCl (1 x 150 mL).[2] The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The brown residue was re-dissolved in 100 mL CH_3CN and 750 mg NaI (5 mmoles, 2.5 equiv.) was added. The mixture was stirred for 3 hours and then concentrated in vacuo. The red-brown residue was re-dissolved in TBME (200 mL) and was washed with water (3 x 200 mL). The organic phase was dried (Na_2SO_4), filtered through a pad of Celite®, and concentrated *in vacuo*. The solid was dried overnight on the high vacuum pump to provide a red-brown solid (1.77g, 1.87 mmoles, 94% yield). IR (KBr, cm^{-1}) 3120 (br), 2957 (s), 2867 (s), 1625 (s), 1537 (s), 1466 (s), 1433 (s), 1411 (s), 1337 (s), 1230 (s), 1203 (s), 1006 (m), 875 (s), 856 (s). LRMS (FAB) 800 (100%) [M – I – H_2O].

[2] Note: Shaking the separatory funnel causes significant emulsions. Instead, the funnel was rocked back and forth.

(B) General procedure for the preparation of tributyltin enolates:[3]

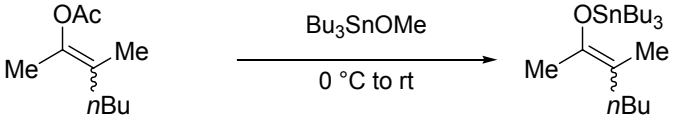
2-Tributylstannyloxy-3-methyl-pent-2-ene (**2a**):



1.8:1 mixture

To tributyltin methoxide (9.30 mL, 33.4 mmol, 1 equiv.) at 0 °C under N_2 was added acetic acid 1,2-dimethyl-but-1-enyl ester (4.75 g, 33.4 mmol, 1.3: 1 mixture, 1 equiv.)[4] dropwise over 5 minutes. After the addition was complete, the mixture was allowed to warm to room temperature and was stirred for 36 hours until ^{1}H NMR analysis of a reaction aliquot showed complete consumption of starting material. The byproduct, methyl acetate, was removed *in vacuo* for 1 hour at 0.2 mmHg. Distillation of the crude material at 0.04 mmHg and 85 °C provided a clear oil (11.02g, 28.3 mmol, 85% yield) as a 1.8: 1 mixture of geometric isomers determined by ^{1}H NMR integration (**minor** δ 2.07 C**H$_2$**CH$_3$ and **major** δ 1.94 C**H$_2$**CH$_3$).[5] ^{1}H NMR (400 MHz, $CDCl_3$): **major** δ 1.94 (2H, q, J = 7.6 Hz), 1.71 (3H, s), 1.62-1.54 (9H, m), 1.39-1.29 (6H, m), 1.16-1.12 (6H, m), 0.91-0.90 (12H, m); **minor** δ 2.07 (2H, q, J = 7.6 Hz), 1.70 (3H, s), 1.62-1.54 (9H, m), 1.39-1.29 (6H, m), 1.16-1.12 (6H, m), 0.91-0.90 (12H, m);: ^{13}C NMR (100 MHz, $CDCl_3$), signals corresponding to both isomers: δ 145.7, 145.1, 111.7, 111.3, 28.1, 27.4, 26.8, 24.1, 20.3, 19.6, 16.6, 16.4, 15.8, 15.0, 13.8, 13.6. Note: tributyltin enolates are TOXIC and extremely air and moisture sensitive; they should be handled with care.

2-Tributylstannyloxy-3-methyl-hept-2-ene (**2b**):



1.5:1 mixture

The general procedure described above was followed on a 20 mmol scale. After 40 hours at ambient temperature, workup as described above and distillation at 0.04 mmHg and 95-100 °C yielded the product as a clear oil (6.6 g, 15.8 mmol, 79%) as a 1.5: 1 mixture of geometric isomers determined by ^{1}H NMR integration (**minor** δ 2.03 C**H$_2$***n*-Pr and **major** δ 1.92 C**H$_2$***n*-Pr). ^{1}H NMR (400 MHz, $CDCl_3$): **major** δ 1.92 (2H, t, J = 7.4 Hz), 1.71 (3H, s), 1.63-1.47 (9H, m), 1.36-1.25 (10H, m), 1.16-1.11 (6H, m), 0.92-0.86 (12H, m); **minor** δ 2.03 (2H, t, J = 7.8 Hz), 1.70 (3H, s),), 1.63-1.47 (9H, m), 1.36-1.25 (10H, m), 1.16-1.11 (6H, m), 0.92-0.86 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$), signals corresponding to both isomers: δ 146.2, 145.5, 110.3, 110.0, 33.6, 31.3, 31.2, 30.6, 28.1, 27.4, 23.3, 22.8, 20.3, 19.8, 17.1, 16.6, 15.8, 15.5, 14.3, 13.8.

2-Tributylstannyloxy-3,4-dimethyl-pent-2-ene (**2c**):

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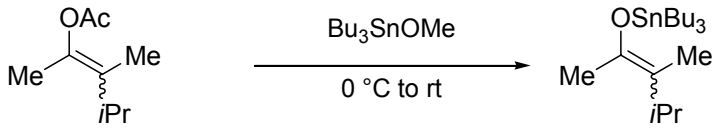
[3] For the general procedure, see: (a) M. Pereyre, B. Bellegarde, J. Mendelsohn, J. Valade, *J. Organomet. Chem.* **1968**, *11*, 97-110. (b) S. S. Labadie, J. K. Stille, *Tetrahedron*, **1984**, *40*, 2329-2336. Note that slight fluctuations in the isomeric ratio of enolate mixtures were observed from batch to batch but the variation did not have an effect on the chromium catalyzed alkylations.

[4] Enol acetates were prepared as described in: (a) S. S. Labadie, J. K. Stille, *Tetrahedron*, **1984**, *40*, 2329-2336; or (b) N. J. Leonard, F. H. Owens, *J. Am. Chem. Soc.* **1958**, *80*, 6039-6045. Characterization data can be found in: (a) W. G. Dauben, R. E. Wolf, *J. Org. Chem.* **1970**, *35*, 2361-2367; (b) T. C. Clarke, R. G. Bergman, *J. Am. Chem. Soc.* **1974**, *96*, 7934. They were distilled immediately prior to use.

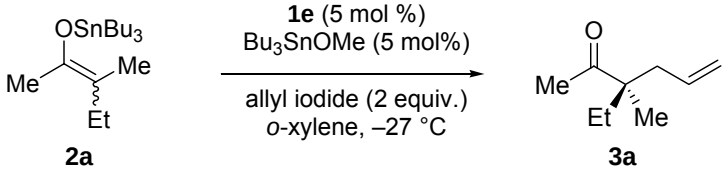
[5] Do not cool the short path distillation head during the tin enolate distillation.



1.2:1 mixture

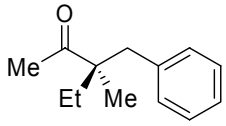
The general procedure described above was followed on a 10 mmol scale. After 40 hours at ambient temperature, workup as described above and distillation at 0.04 mmHg and 85-90 °C yielded the product as a clear oil (2.81 g, 7.0 mmol, 69%) as a 1.2: 1 mixture of geometric isomers determined by ^{1}H NMR integration (**minor** δ 3.18 C**H**Me$_2$ and **major** δ 2.59 C**H**Me$_2$). ^{1}H NMR (400 MHz, $CDCl_3$): **major** δ 2.59 (1H, s, J = 7.2 Hz), 1.74-1.73 (3H, m), 1.64-1.56 (6H, m), 1.49-1.48 (3H, m), 1.38-1.28 (6H, m), 1.16-1.11 (6H, m), 0.92-0.86 (15H, m); **minor** δ 3.18 (1H, s, J = 7.2 Hz), 1.70-1.69 (3H, m),), 1.64-1.56 (6H, m), 1.44-1.42 (3H, m), 1.38-1.28 (6H, m), 1.16-1.11 (6H, m), 0.92-0.86 (15H, m); ^{13}C NMR (100 MHz, $CDCl_3$), signals corresponding to both isomers: δ 144.8, 144.2, 115.4, 114.9, 30.0, 28.0, 27.4, 26.4, 21.5, 20.9, 20.5, 19.6, 15.7, 13.8, 11.3, 9.3.

(C) General procedure for the Cr(salen)Cl-catalyzed alkylation of tributyltin enolates with alkyl halides.
3-Ethyl-3-methyl-hex-5-en-2-one (**3a):**



A 10mL schlenk flask was flame-dried *in vacuo*, cooled to 23 °C and charged with catalyst (*R,R*)-**1e** (23.7 mg, 0.0025 mmol, 5 mol %) under nitrogen. The flask was evacuated for 10 minutes and then flushed with nitrogen. To the schlenk was added *o*-xylene (500 μL) and allyl iodide (91 μL, 1 mmol, 2 equiv.) *via* syringe. The stirred solution was cooled to −27 °C under nitrogen in an immersion cooler for 10 minutes. A solution of tin enolate (195mg, 0.5 mmol, 1 equiv.), tributyltin methoxide (7 μL, 0.025 mmol, 5 mol%) in *o*-xylene (0.75 mL) was prepared in a flame-dried two dram vial. The solution was cooled to −27 °C in an acetone–dry ice bath with vigorous stirring under nitrogen for 5 minutes and was then added in one portion by syringe to the schlenk flask. The rubber septum on the schlenk was exchanged for a greased glass stopper and the nitrogen inlet was sealed shut as the reaction was stirred at −27 °C for 48 hours. The reaction was diluted with pentane (2 mL) and transferred into a 18x150 mm Durex^{TM} borosilicate glass disposable test tube containing saturated NaCl solution (0.5 mL) cooled to 0 °C. Solid potassium fluoride (~1g) was added, accompanied by the formation of white precipitate. The mixture was filtered through a bed of sodium sulfate (rinsing with pentane) into a flask cooled to 0 °C and was concentrated to ~ 1.5 mL by rotary evaporation with a 4 °C bath. The residue was purified by column chromatography on silica gel, eluting with 2% diethyl ether in pentane. Concentration of the desired fractions was again performed with a 4 °C bath yielding the product as a clear oil (58.2 mg, 83% yield). The enantiomeric excess was determined to be 82% by chiral GC analysis (γ-TA 50 °C isothermal, t_r(minor) = 61.1 min, t_r(major) = 58.0 min); $[\alpha]^{24}_D$ = −0.65° (c=6.7, $CHCl_3$); IR (thin film, cm^{-1}) 3070 (w), 2955 (m), 2910 (m), 2860 (w), 1706 (s), 1461 (w), 1355 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71-5.61 (1H, m), 5.07-5.02 (2H, m), 2.34 (1H, dd, J = 14.4, 7.6 Hz), 2.19 (1H, dd, J = 12.8, 7.6 Hz), 2.10 (3H, s), 1.65 (1H, dq, J = 14, 7.6 Hz), 1.50 (1H, dq, J = 14 Hz, 7.6 Hz), 1.07 (3H, s), 0.79 (3H, t, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 134.2, 118.1, 51.8, 42.2, 31.0, 22.6, 20.5, 8.9; LRMS (ES): 141 (100%) $[M+H]^+$.

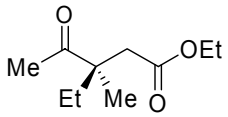
3-Benzyl-3-methyl-pentan-2-one (**3b**):



The reaction was performed on a 0.5 mmol scale using 5 mol % (*R,R*)-**1e** (23.7 mg, 0.025 mmol) and 2 equiv. benzyl bromide (119 μL) at −27 °C for 48 hours. The product was obtained as a clear oil after chromatography on silica gel, eluting with 2% diethyl ether in pentane (81.5 mg, 86% yield). The enantiomeric excess was determined to be 81 % by chiral GC analysis (γ-TA 100 °C isothermal, t_r(minor) = 42.0 min, t_r(major) = 43.2 min); $[\alpha]^{24}_D$ = −3.89° (c=2.5, $CHCl_3$); IR (thin film, cm^{-1}) 3029 (w), 2970 (s), 2937 (m), 2881 (w), 1704 (s), 1496 (m), 1455 (s), 1355 (s), 1117 (w), 749 (m), 703 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.18 (3H, m), 7.09-7.07 (2H, m), 2.94 (1H, d, J = 13.4 Hz), 2.69 (1H, d, J = 13.0 Hz), 2.09 (3H, s), 1.75 (1H, dq, J = 14.4, 7.6 Hz), 1.46 (1H, dq, J = 14.8, 7.2 Hz), 1.06 (3H, s), 0.85 (3H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 138.0, 130.5, 128.2, 126.6, 52.8, 44.1, 31.4, 26.9, 20.6, 9.2; LRMS (ES): 191 (100%) $[M+H]^+$.

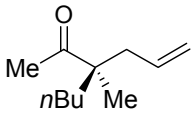
3-Ethyl-3-methyl-4-oxo-pentanoic acid ethyl ester (**3c**):[6]

[6] A. A. Asselin, L. G. Humber, T. A. Dobson, J. Komlossy, R. R. Martel, *J. Med. Chem.* **1976**, *19*, 787-792.



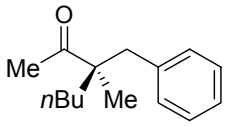
The reaction was performed on a 0.5 mmol scale using 5 mol % (*R*,*R*)-**1e** (23.7 mg, 0.025 mmol) and 2 equiv. ethyl iodoacetate (118 μL) at −27 °C for 48 hours. The product was obtained as a light yellow oil after chromatography on silica gel, eluting with 5% → 10% diethyl ether in pentane (68.0 mg, 73% yield). The enantiomeric excess was determined to be 76 % by chiral GC analysis (γ-TA, 100 °C isothermal, t_r(minor) = 20.1 min, t_r(major) = 18.6 min); $[\alpha]^{24}_D$ = +14.1° (c=3.2, $CHCl_3$); IR (thin film, cm^{-1}) 2974 (m), 2933 (m), 2884 (w), 1735 (s), 1708 (s), 1463 (m), 1369 (m), 1346 (m), 1200 (m), 1163 (m), 1032 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (2H, q, J = 7.2 Hz), 2.75 (1H, d, J = 15.6 Hz), 2.37 (1H, d, J = 15.6 Hz), 2.17 (3H, s), 1.68-1.49 (2H, m), 1.23 (3H, s), 1.23 (3H, t, J = 7.0 Hz), 0.82 (3H, t, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 171.8, 60.6, 49.9, 42.2, 31.7, 26.0, 21.2, 14.4, 8.7; LRMS (ES): 187 (100%) $[M+H]^+$, 141 (30%) $[M-OEt]^+$.

3-Allyl-3-methyl-heptan-2-one (**3d**):



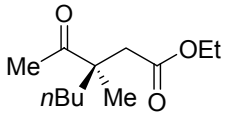
The reaction was performed on a 0.5 mmol scale using 5 mol % (*R*,*R*)-**1e** (23.7 mg, 0.025 mmol) and 2 equiv. allyl iodide (91 μL) at −27 °C for 48 hours. The product was obtained as a clear oil after chromatography on silica gel, eluting with 2% diethyl ether in pentane (78.0 mg, 92% yield). The enantiomeric excess was determined to be 87 % by chiral GC analysis (γ-TA, 80 °C isothermal, t_r(minor) = 19.1 min, t_r(major) = 19.6 min); $[\alpha]^{24}_D$ = −1.03° (c=10.0, $CHCl_3$); IR (thin film, cm^{-1}) 3078 (w), 2960 (m), 2934 (m), 2873 (w), 1706 (s), 1465 (w), 1355 (m), 915 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (1H, m), 5.06-5.01 (2H, m), 2.33 (1H, dd, J = 14.4, 7.2 Hz), 2.18 (1H, dd, J = 14.0, 7.6 Hz), 2.09 (3H, s), 1.58 (1H, ddd, J = 13.0, 12.0, 3.2 Hz), 1.44 (1H, app dt, J = 12.4, 4.8 Hz), 1.31 – 1.00 (4H, m), 1.08 (3H, s), 0.87 (3H, t, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.5, 134.2, 118.1, 51.5, 42.6, 38.3, 26.7, 25.8, 23.5, 21.0, 14.1; LRMS (ES): 169.1 (100%) $[M+H]^+$.

3-Benzyl-3-methyl-heptan-2-one (**3e**):



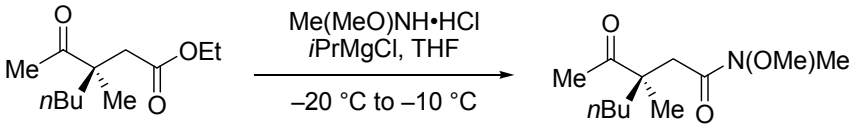
The reaction was performed on a 0.5 mmol scale using 5 mol % (*R*,*R*)-**1e** (23.7 mg, 0.025 mmol) and 2 equiv. benzyl bromide (120 μL) at −27 °C for 48 hours. The product was obtained as a clear oil after chromatography on silica gel, eluting with 2% → 5% diethyl ether in pentane (91.1 mg, 83% yield). The enantiomeric excess was determined to be 86 % by chiral GC analysis (γ-TA, 100 °C isothermal, t_r(minor) = 105.1 min, t_r(major) = 107.3 min); $[\alpha]^{24}_D$ = −0.45° (c=10.0, $CHCl_3$); IR (thin film, cm^{-1}) 3029 (w), 2958 (m), 2933 (m), 2861 (w), 1703 (s), 1465 (m), 1455 (m), 1354 (m), 753 (m), 703 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.18 (3H, m), 7.09-7.06 (2H, m), 2.94 (1H, d, J = 13.6 Hz), 2.68 (1H, d, J = 13.6 Hz), 2.08 (3H, s), 1.68 (1H, ddd, J = 16.8, 12.4, 4.8 Hz), 1.40 (1H, ddd, J = 13.6, 12.0, 4.8 Hz), 1.32-1.11 (4H, m), 1.07 (3H, s), 0.89 (3H, t, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.0, 138.0, 130.5, 128.2, 126.6, 52.5, 44.4, 38.7, 27.0, 26.9, 23.5, 21.0, 14.2; LRMS (ES): 219.2 (100%) $[M+H]^+$.

3-Acetyl-3-methyl-heptanoic acid ethyl ester (**3f**):



The reaction was performed on a 0.5 mmol scale using 5 mol % (*R,R*)-**1e** (23.7 mg, 0.025 mmol) and 2 equiv. ethyl iodoacetate (119 μL) at −27 °C for 48 hours. The product was obtained as a clear oil after chromatography on silica gel, eluting with 5% → 10% diethyl ether in pentane (82.5 mg, 77% yield). The enantiomeric excess was determined to be 84% by chiral HPLC analysis on the corresponding Weinreb amide (see below); $[\alpha]^{24}_{D}$ = +16.7° (c=1.8, $CHCl_3$); IR (thin film, cm^{-1}) 2960 (m), 2936 (m), 2879 (w), 2866 (w), 1735 (s), 1708 (s), 1467 (w), 1369 (w), 1345 (w), 1195 (m), 1160 (m), 1032 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 (2H, q, J = 7.2 Hz), 2.74 (1H, d, J = 15.6 Hz), 2.37 (1H, d, J = 16 Hz), 2.17 (3H, s), 1.60-1.42 (2H, m), 1.30-1.10 (4H, m), 1.24 (3H, s), 1.22 (3H, t, J = 7.6 Hz), 0.87 (3H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.5, 171.8, 60.6, 49.6, 42.6, 38.9, 26.5, 26.0, 23.4, 21.7, 14.3, 14.1; LRMS (ES): 215.1 (100%) $[M+H]^+$, 169.1 (80%) $[M-OEt]^+$.

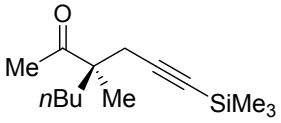
3-Acetyl-3-methyl-heptanoic acid methoxy-methyl-amide:[7]



3f

To a flame-dried 2 dram vial, charged with 20 mg ketone **3f** (0.09 mmol, 1 equiv) in 0.5 mL THF, was added Weinreb amine HCl salt (14 mg, 0.14 mmol, 1.55 equiv.). The solution was cooled to −20 °C (acetone-dry ice bath) and *i*-PrMgCl (135 μL, 2M in THF, 0.27 mmol, 3 equiv) was added dropwise via syringe over 5 minutes. The reaction was stirred at −10 °C for 20 minutes and then 0.5 mL saturated aqueous ammonium chloride was added. The reactions were warmed to room temperature, diluted with 1.0 mL water and 1.0 mL diethyl ether. The organic phase was separated and the aqueous phase was washed with 2 x 1 mL ether. The combined organics were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The material was purified by silica gel chromatography eluting with 25% ethyl acetate in hexanes to provide a clear oil (20.1 mg, 98% yield). The enantiomeric excess was determined to be 84% by chiral HPLC analysis (Chiralcel OD, 99:1 hexane: *i*PrOH, 1.0 mL/min, λ = 208 nm) t_r(minor) = 28.3 min, t_r(major) = 20.9 min); $[\alpha]^{24}_{D}$ = +24.8° (c=1.3, $CHCl_3$); IR (thin film, cm^{-1}) 2959 (s), 2936 (s), 2873 (m), 1705 (s), 1664 (s), 1465 (m), 1421 (m), 1376 (m), 1005 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (3H, s), 3.12 (3H, s), 2.90 (1H, d, J = 16.8 Hz), 2.57 (1H, d, J = 16.4 Hz), 2.20 (3H, s), 1.57 (1H, ddd, J = 13.6, 12.0, 5.2 Hz), 1.46 (1H, app dt, J = 12.0, 4.8 Hz), 1.30-1.10 (4H, m), 1.27 (3H, s), 0.88 (3H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 209.1, 61.3, 48.9, 41.1, 39.6, 31.8, 26.8, 26.4, 23.5, 21.8, 14.2; LRMS (ES): 230.1 (100%) $[M]^+$, 169 (30%) $[M-N(OMe)Me]^+$.

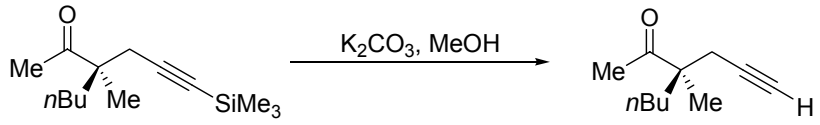
3-Methyl-3-(3-trimethylsilanyl-prop-2-ynyl)-heptan-2-one (**3g**):



The reaction was performed on a 0.5 mmol scale using 5 mol % (*R,R*)-**1e** (23.7 mg, 0.025 mmol) and 2 equiv. TMS propargyl bromide (145 μL) at −27 °C for 48 hours. The product was obtained as a clear oil after chromatography on silica gel, eluting with 2% diethyl ether in pentane (115.2 mg, 97% yield). The enantiomeric excess was determined to be 78 % by chiral GC analysis on the deprotected product (see below). $[\alpha]^{24}_{D}$ = +7.90° (c=3.7, $CHCl_3$); IR (thin film, cm^{-1}) 2960 (s), 2935 (s), 2974 (w), 2862 (w), 2176 (s), 1709 (s), 1250 (m), 1037 (m), 843 (s), 760 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (1H, d, J = 17 Hz), 2.37 (1H, d, J = 16.8 Hz), 2.13 (3H, s), 1.68 (1H, ddd, J = 14.4, 12.0, 5.6 Hz), 1.49 (1H, ddd, J = 14.0, 12.0, 5.2 Hz), 1.31-1.23 (2H, m), 1.19 (3H, s), 1.14-1.01 (2H, m), 0.87 (3H, t, J = 7.2 Hz), 0.11 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.2, 104.2, 87.4, 51.0, 37.4, 27.9, 26.8, 25.9, 23.4, 22.1, 14.0, 0.2; LRMS (ES) 239 (80%) $[M+H]^+$.

3-Methyl-3-prop-2-ynyl-heptan-2-one:

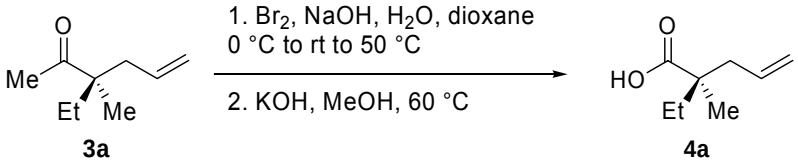
[7] Procedure as described in: J. M. Williams, R. B. Jobson, N. Yasuda, G. Marchesini, U.-H. Dolling, E. J. J. Grabowski, *Tet. Lett.* **1995**, *36*, 5461-5464.



To a scintillation vial containing 27.0 mg TMS ketone (0.12 mmol, 1 equiv.) in 2 mL MeOH was added 33 mg K_2CO_3 (0.24 mmol, 2 equiv.). The reaction was stirred for 2 hours at room temperature and was then diluted with 2 mL water and 2 mL diethyl ether. The organic phase was separated and was washed with saturated aqueous NaCl (2 x 5 mL). The organic phase was dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude material was purified by silica gel chromotagraphy eluting with 2% diethyl ether in pentane to provide a clear oil (18.7 mg, 95% yield). The enantiomeric excess was determined to be 78% by chiral GC analysis (γ-TA, 80 °C isothermal, t_r(minor) = 27.4 min, t_r(major) = 26.4 min); $[\alpha]^{24}_D$ = +12.4° (c=1.0, $CHCl_3$); IR (thin film, cm^{-1}) 3289 (m), 3274 (m), 2960 (m), 2935 (m), 2874 (m), 2862 (m), 2180 (w), 1707 (s), 1462 (m), 1356 (m), 1124 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40-2.36 (2H, m), 2.14 (3H, s), 1.97 (1H, t, J = 2.4 Hz), 1.69 (1H, ddd, J = 13.6, 12.0, 4.8 Hz), 1.53 (1H, ddd, J = 14.0, 12.0, 4.8 Hz), 1.33-1.22 (2H, m), 1.22 (3H, s), 1.19-1.00 (2H, m), 0.88 (3H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.2, 81.4, 70.8, 50.9, 37.4, 26.8, 26.4, 25.7, 23.4, 22.1, 14.1; LRMS (ES): 167 $[M+H]^+$.

Procedures for the elaboration of the methyl ketones

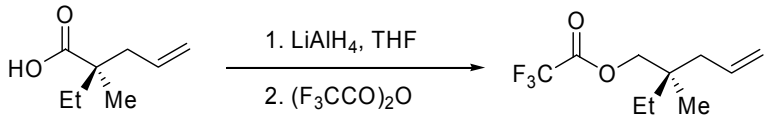
(a) Haloform Reaction
2-Ethyl-2-methyl-pent-4-enoic acid



3a **4a**

To a 50mL round bottom flask containing NaOH (2.70g, 67.5 mmoles, 22 equiv) in 18.8 mL H_2O at 0 °C was added Br_2 (1.42 mL, 27.6 mmoles, 9 equiv) via syringe dropwise over 10 minutes. The bright yellow solution was stirred at 0 °C for 10 minutes and then a solution of 430 mg ketone **3a** (3.07 mmoles, 1 equiv) in 2.13 mL dioxane was added dropwise over 10 minutes. The reaction was stirred at 0 °C for 2 hours, then at room temperature for 5 hours, and finally at 50 °C for 3 hours. The reaction was cooled to room temperature and any residual yellow color was quenched with an aqueous solution of sodium sulfite. The reaction was then acidified to pH 4 with 3N aqueous HCl solution and the solution was extracted with CH_2Cl_2 (3 x 50 mL). The combined organics were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was dissolved in 6 mL MeOH and KOH (1.13g, 9 mmoles, 3 equiv) was added. The solution was heated at 60 °C for 20 hours, then cooled to room temperature and concentrated *in vacuo*. The crude material was acidified to pH 4 with 3N aqueous HCl, and was extracted with diethyl ether (3 x 20 mL); the organic phase was dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography, eluting with 20% Et_2O in pentane provided a clear oil (306 mg, 70% yield). The enantiomeric excess was determined to be 82% by chiral GC analysis on reduced **4a**; $[\alpha]^{24}_D = -5.64°$ (c=0.99, $CHCl_3$); IR (thin film, cm^{-1}) 3305 (br), 3079 (m), 2973 (s), 2940 (s), 2882 (s), 1702 (s), 1463 (m), 1258 (m), 918 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 5.81-5.71 (1H, m), 5.10-5.08 (1H, m), 5.06-5.05 (1H, m), 2.40 (1H, dd, J = 14.0, 6.8 Hz), 2.21 (1H, dd, J = 14.0, 7.6 Hz), 1.69 (1H, dq, J = 14.4, 7.2 Hz), 1.52 (1H, dq, J = 14.0, 7.6 Hz), 1.13 (3H, s), 0.89 (3H, t, J = 7.6 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.5, 134.1, 118.3, 46.4, 42.8, 31.6, 20.8, 9.1; LRMS (ES): 142 (100%) $[M]^+$

ee analysis:

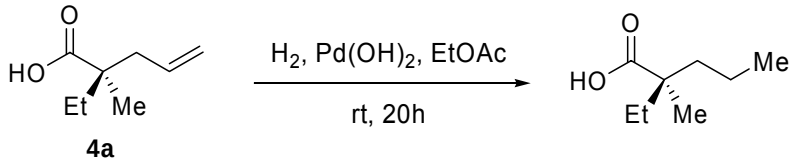


4a

A 1 dram vial was charged with 16mg $LiAlH_4$ (0.42 mmol, 3 equiv) in 0.3mL dry THF. A solution of **4a** (19.8 mg, 0.14 mmol, 1 equiv.) in 0.7mL THF was added via syringe and the reaction was stirred at rt for 5 hours. The reaction was quenched with 10% aqueous H_2SO_4 (1 mL) and was extracted with ether (3 x 2mL). The combined organics were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by silica gel chromatography eluting with 10% Et_2O in pentane to provide a clear oil (17.4 mg, 97% yield). The primary alcohol was treated with 1mL trifluoroacetic anhydride and the solution was concentrated in vacuo. The enantiomeric excess was determined to be 82% by chiral GC analysis (γ-TA, 40 °C isothermal, t_r(minor) = 23.2 min, t_r(major) = 22.2 min).

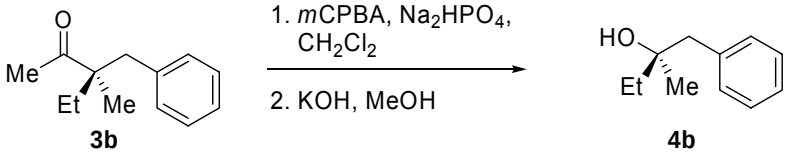
Determination of Absolute Configuration[8]

[8] Procedure taken from: J. M. Manthorpe, J. L. Gleason, *Angew. Chem. Int. Ed.* **2002**, *41*, 2338-2341. For characterization data, see: A. Arpin, J. M. Manthorpe, J. L. Gleason, *Org. Lett.* **2006**, *8*, 1359-1362



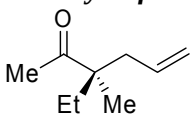
(*R*): 82% ee, $[\alpha]_D$ = +13.3 (c=0.6, 95% EtOH)
(*S*): > 95% ee, Lit $[\alpha]^{20}_D$ = -18 (c=0.6 EtOH)

(b) Baeyer-Villiger Rearrangement
2-Methyl-1-phenyl-butan-2-ol



To a scintillation vial containing ketone **3b** (61.1 mg, 0.32 mmoles, 1 equiv.) in 2.6 mL dichloromethane was added 295 mg *m*CPBA (75 wt. %, 1.28 mmoles, 4 equiv.) and 61.3 mg Na_2HPO_4 (0.32 mmoles, 1 equiv). The reaction was stirred at room temperature for 3 days and then diluted with 20 mL diethyl ether. The solution was washed with saturated aqueous NaCl (2 x 10 mL) and 10% aqueous NaOH (1 x 10 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The material was purified by column chromatography on silica gel eluting with 2% diethyl ether in pentane to provide 63.7 mg of acetate (85% yield, 0.27 mmoles) and 6.0 mg recovered **3b**. The intermediate acetate was dissolved in 1.5 mL MeOH and 252 mg KOH (4.5 mmoles, 18 equiv.) was added. The reaction was stirred at 50 °C for 15 hours and was then diluted with 20 mL dichloromethane and acidified with 3N aqueous HCl to pH 4. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography, eluting with 10% Et_2O in pentane provided a clear oil (43.3 mg, 97% yield). The enantiomeric excess was determined to be 80% by chiral HPLC analysis (Chiralcel AD-H, 99.5:0.5 hexane: *i*PrOH, 1.0 mL/min, λ = 208 nm) t_r(minor) = 40.8 min, t_r(major) = 36.5 min); $[\alpha]^{24}_D$ = -6.5° (c=1.97, $CHCl_3$); IR (thin film, cm^{-1}) 3440 (br), 3028 (m), 2970 (s), 2936 (s), 2881 (m), 1495 (m), 1453 (m), 1377 (m), 1149 (m), 923 (m), 716 (m), 701 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.21 (5H, m), 2.77 (1H, d, J = 13.2 Hz), 2.73 (1H, d, J = 13.2 Hz), 1.51 (2H, q, J = 7.6 Hz), 1.29 (1H, s), 1.14 (3H, s), 0.98 (3H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 130.8, 128.4, 126.6, 72.9, 47.8, 34.4, 26.2, 8.6; LRMS (EI+): 164 (5%) $[M]^+$, 135 (35%) $[M\text{-}CH_2CH_3]^+$, 92 (100%) $[PhCH_2]^+$, 73 (40%) $[M\text{-}PhCH_2]^+$.

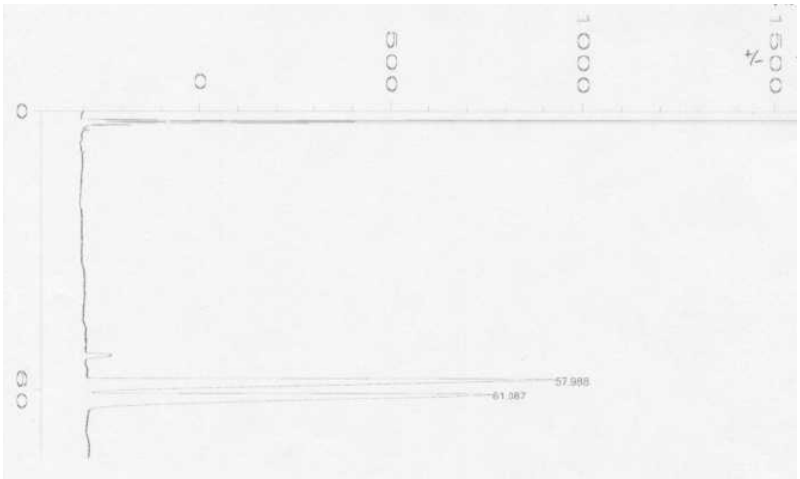
%ee analysis for 3a:



3a

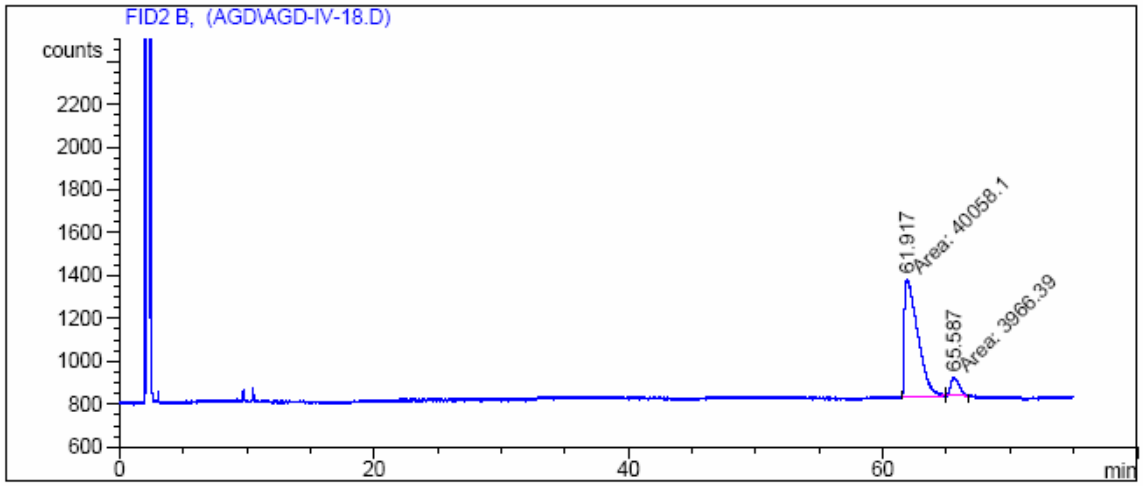
Chiral GC: γ-TA, 50°C isothermal

racemic



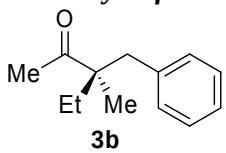
Pk#	Ret Time	Area	Height	Type	Width	Area %
1	57.988	103018	1222	MF	1.405	48.9795
2	61.087	107311	1059	FM	1.689	51.0205

82% ee



Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	61.917	MM	1.2077	4.00581e4	552.81519	90.99049
2	65.587	MM	0.7451	3966.39355	88.71763	9.00951

%ee analysis for 3b:



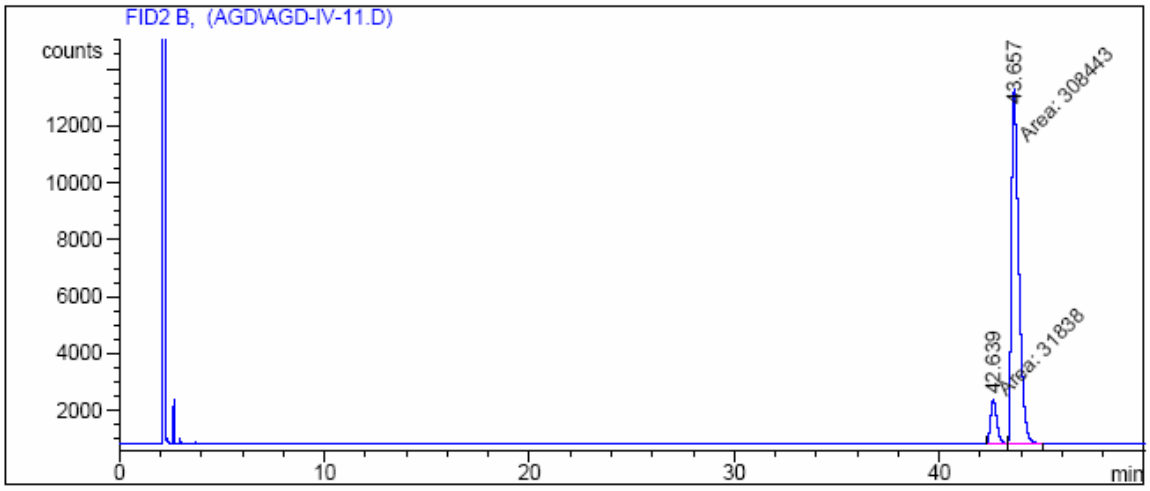
3b

Chiral GC: γ-TA, 100°C isothermal

racemic

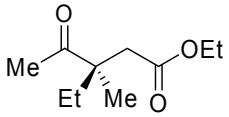
Pk#	Ret Time	Area	Height	Type	Width	Area %
1	42.002	101168	5352	MF	0.315	50.8792
2	43.167	97671	4933	FM	0.330	49.1208

81% ee



Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	42.639	MM	0.3450	3.18380e4	1538.09167	9.35639
2	43.657	MM	0.4131	3.08443e5	1.24453e4	90.64361

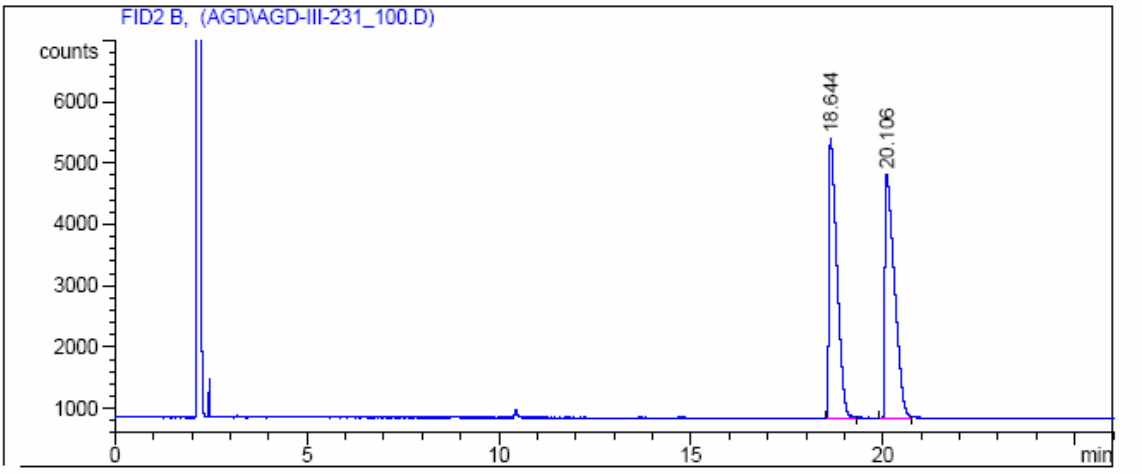
%ee analysis for 3c:



3c

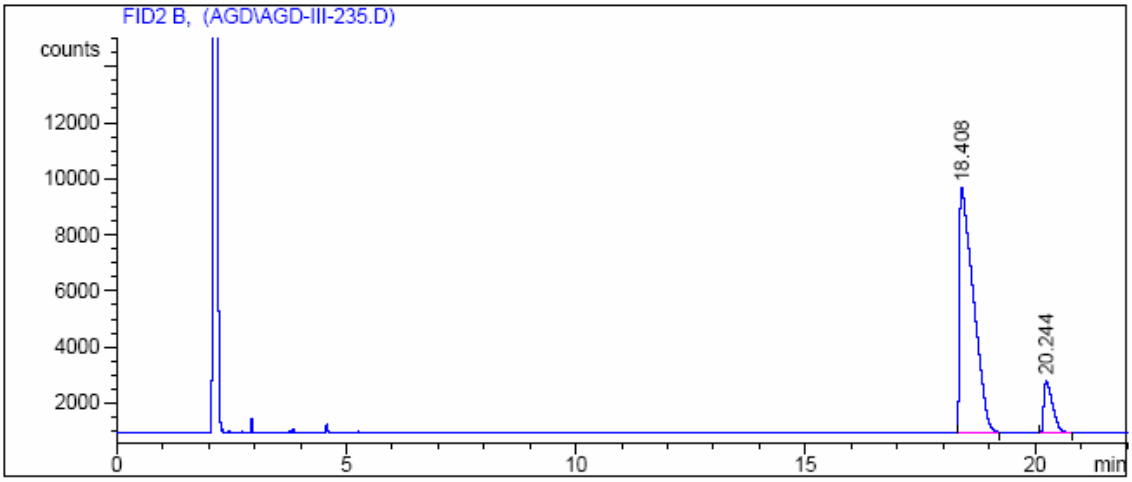
Chiral GC: γ-TA, 100°C isothermal

racemic



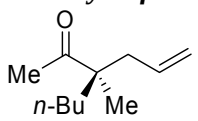
Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	18.644	VV	0.1874	6.59605e4	4570.12451	48.92783
2	20.106	VV	0.2207	6.88513e4	3983.44165	51.07217

76% ee



Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	18.408	VV	0.2518	1.85400e5	8765.32715	88.14772
2	20.244	VV	0.1772	2.49288e4	1861.76123	11.85228

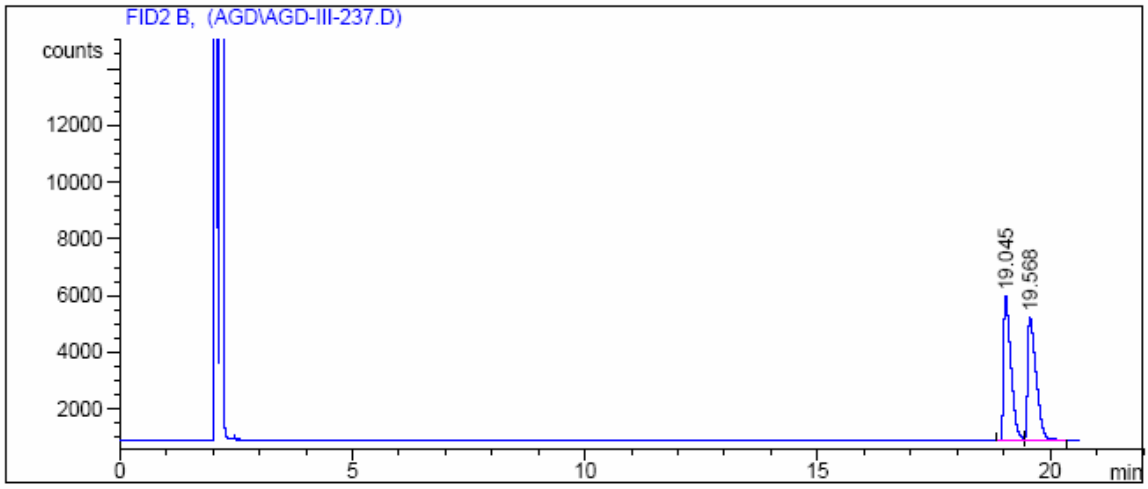
%ee analysis for 3d:



3d

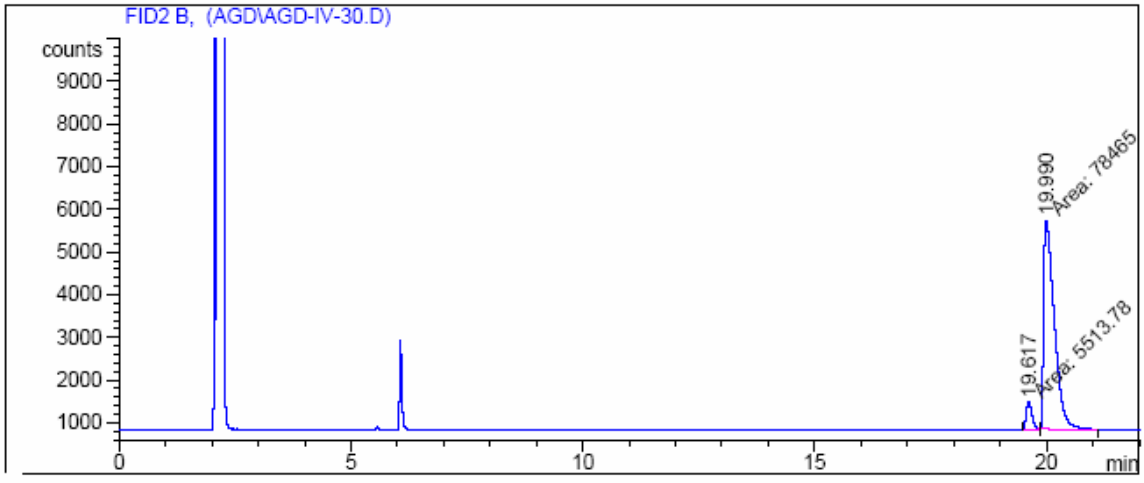
Chiral GC: γ-TA 80°C isothermal

racemic



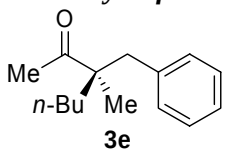
Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	19.045	VV	0.1505	5.59125e4	5077.36084	50.65756
2	19.568	VV	0.1693	5.44609e4	4341.80469	49.34244

87% ee



Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	19.617	MM	0.1442	5513.78369	637.43701	6.56569
2	19.990	MM	0.2676	7.84650e4	4887.84424	93.43431

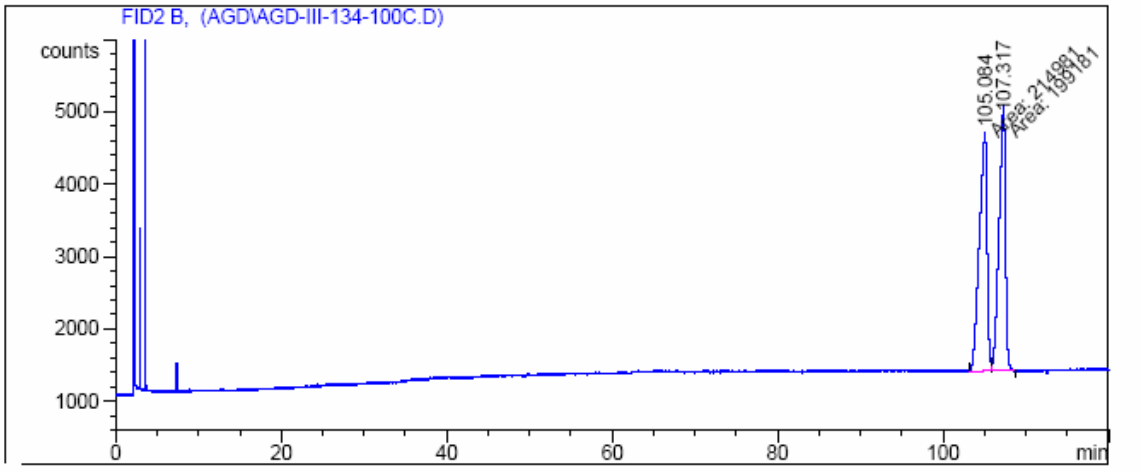
%ee analysis for 3e:



3e

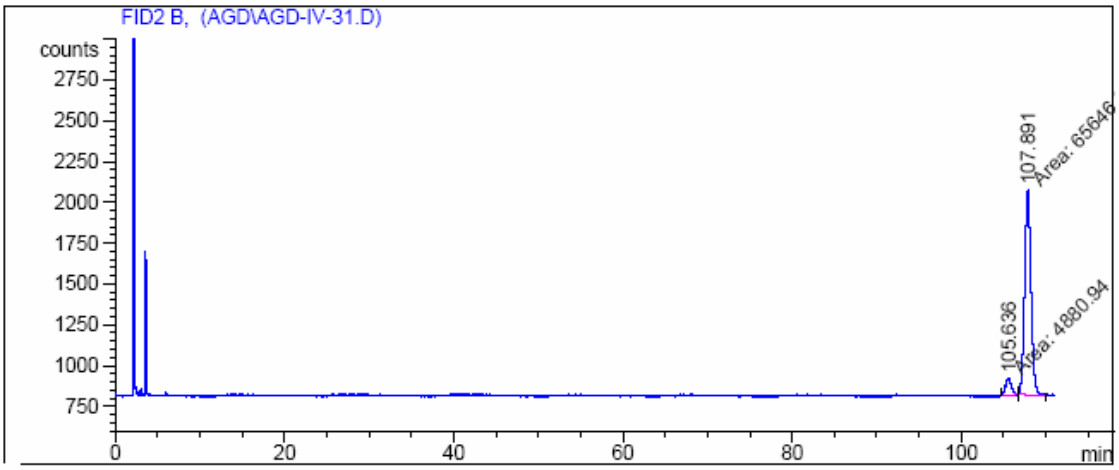
Chiral GC: γ-TA 100°C isothermal

Racemic



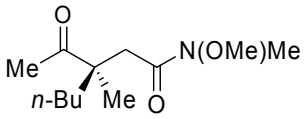
Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	105.084	MF	1.0863	2.14981e5	3298.50269	51.90755
2	107.317	FM	0.9066	1.99181e5	3661.69800	48.09245

86% ee



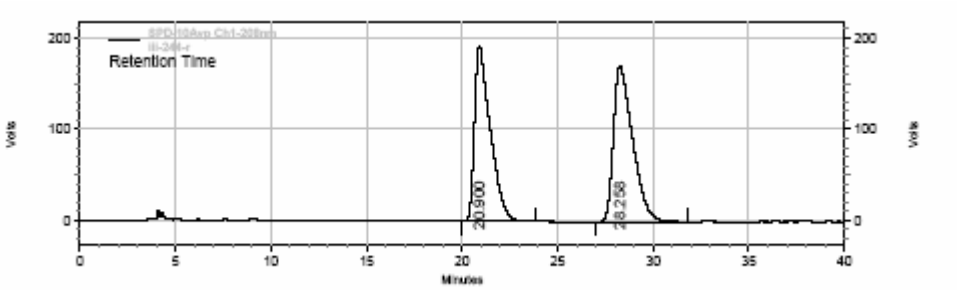
Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	105.636	MM	0.8132	4880.93506	100.03770	6.92061
2	107.891	MM	0.8713	6.56466e4	1255.74939	93.07939

%ee analysis for 3f:



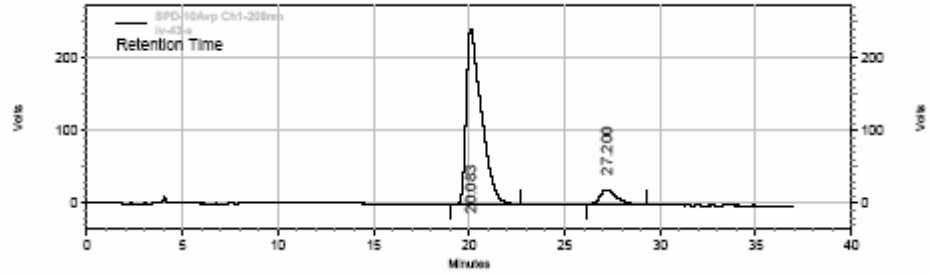
Chiralcel OD-H, 99:1 hexane: *i*PrOH, 1.0 mL/min

racemic



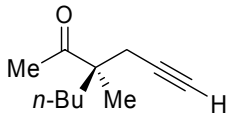
Retention Time	Area	Area %	Height	Height %
20.900	11110355	48.27	193309	53.04
28.258	11905579	51.73	171131	46.96
Totals	23015934	100.00	364440	100.00

84% ee



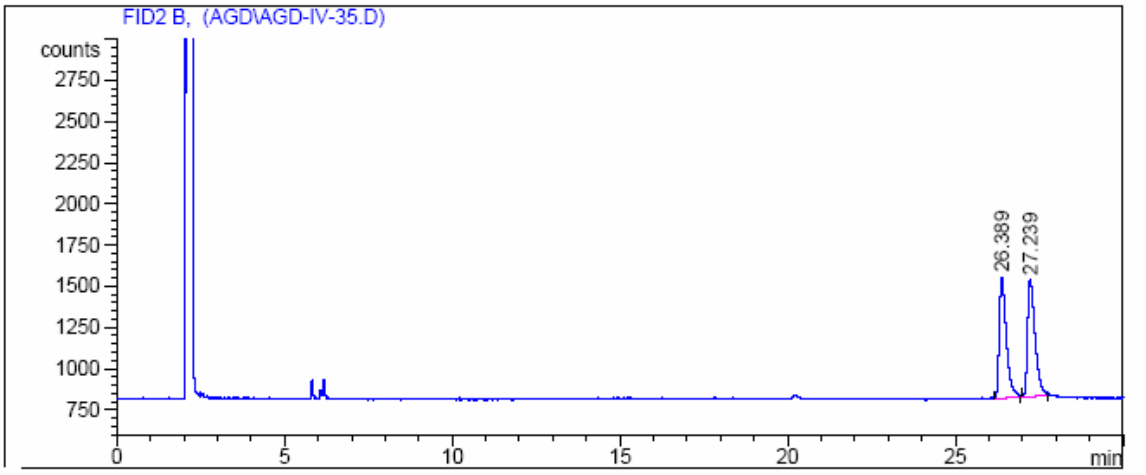
Retention Time	Area	Area %	Height	Height %
20.083	13309150	91.64	242525	92.51
27.200	1213968	8.36	19625	7.49
Totals	14523118	100.00	262150	100.00

%ee analysis for 3g:



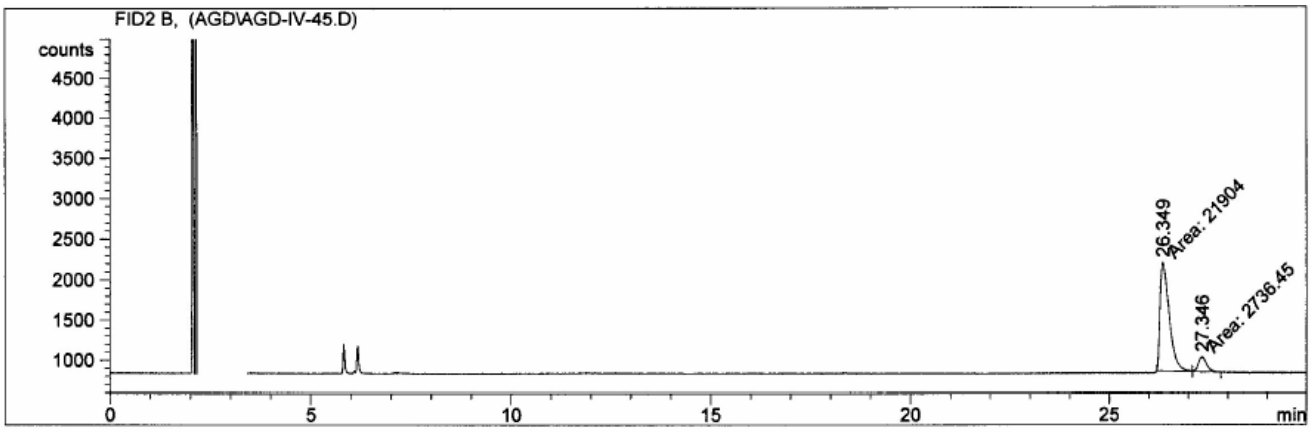
Chiral GC: γ-TA 80°C isothermal

racemic



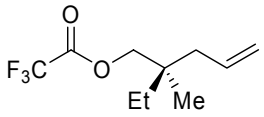
Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	26.389	VV	0.1780	1.07696e4	730.50153	48.96293
2	27.239	VV	0.1883	1.12258e4	706.75403	51.03707

78% ee

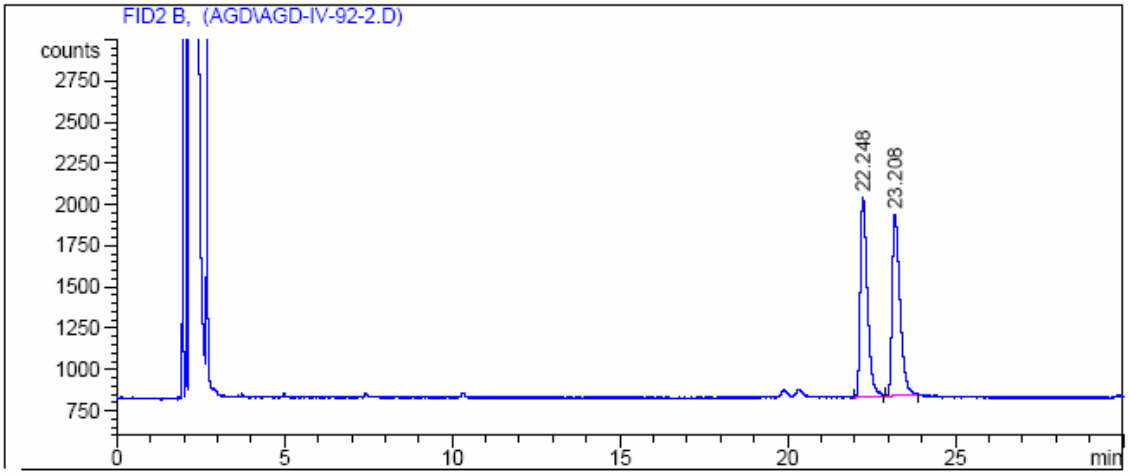


Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	26.349	MF	0.2712	2.19040e4	1345.93799	88.89448
2	27.346	FM	0.2480	2736.45410	183.88284	11.10552

%ee analysis for 4a:

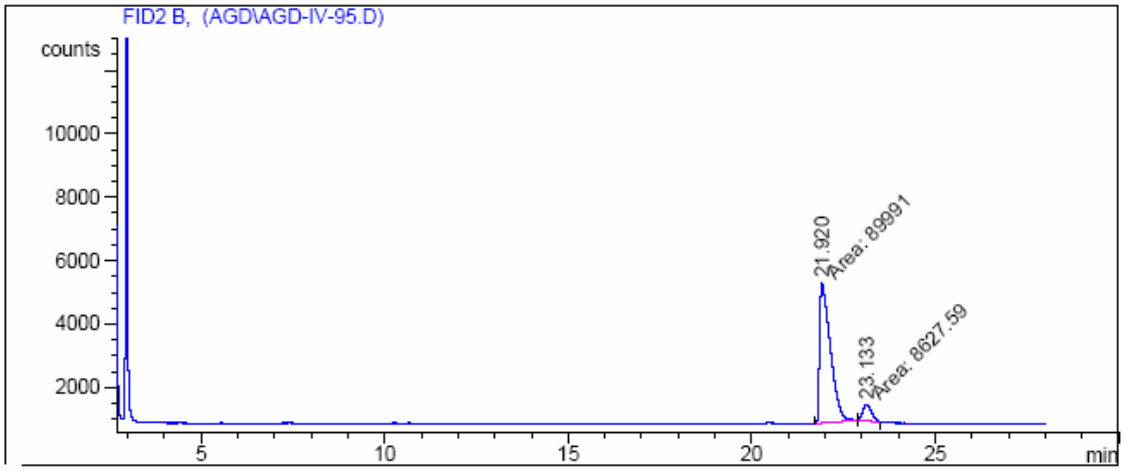


racemic



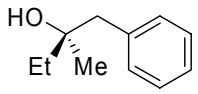
Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	22.248	VB	0.1818	1.79595e4	1212.86633	50.30461
2	23.208	VB	0.1967	1.77420e4	1097.05591	49.69539

82% ee



Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	21.920	MM	0.3396	8.99910e4	4416.27539	91.25156
2	23.133	MM	0.2711	8627.59082	530.32660	8.74844

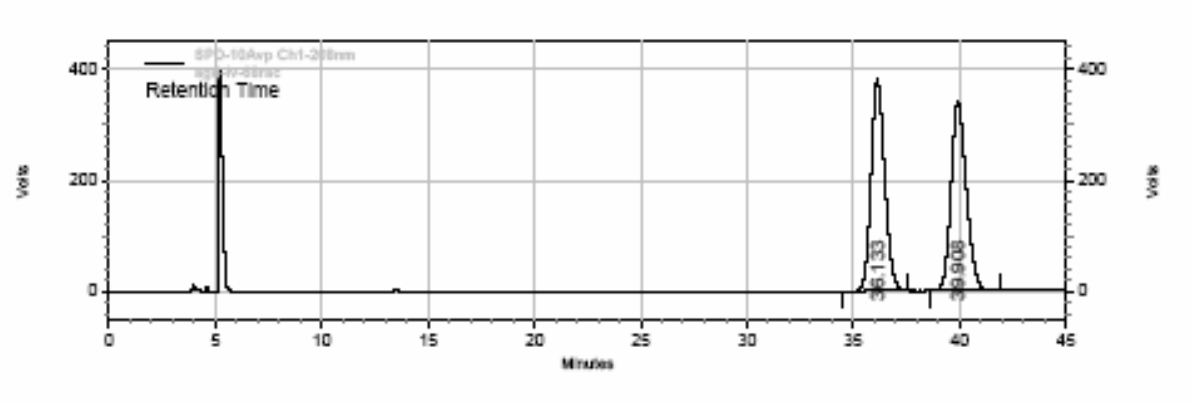
%ee analysis for 4b:



4b

Chiralcel AD-H, 99.5:0.5 hexane: *i*PrOH, 1.0 mL/min

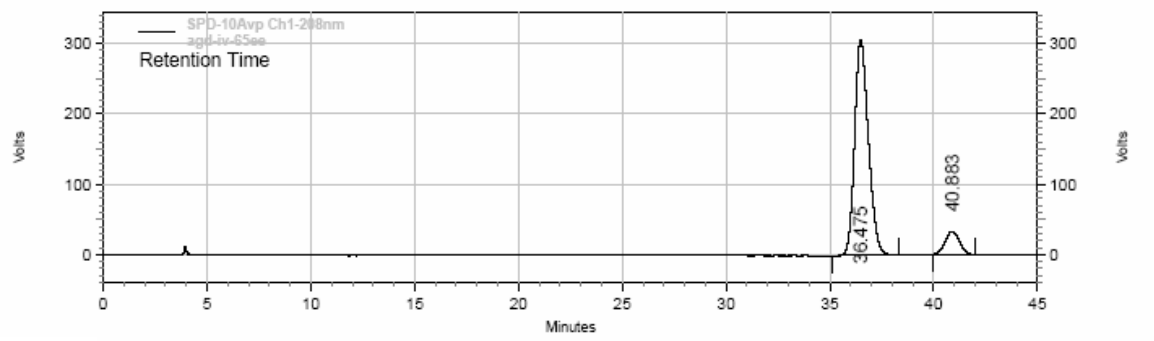
racemic



SPD-10Avp
Ch1-208nm
Results

Retention Time	Area	Area %	Height	Height %
36.133	16913541	49.91	381835	52.91
39.908	16976958	50.09	339838	47.09
Totals	33890499	100.00	721673	100.00

80% ee

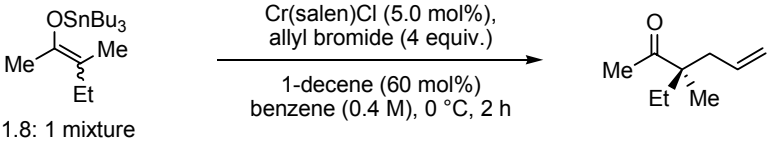


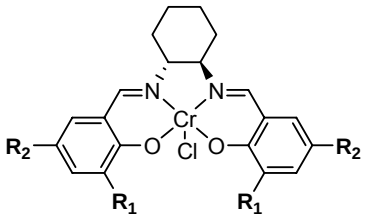
SPD-10Avp
Ch1-208nm
Results

Retention Time	Area	Area %	Height	Height %
36.475	14120927	89.80	306975	90.20
40.883	1604775	10.20	33348	9.80
Totals	15725702	100.00	340323	100.00

Optimization Studies:

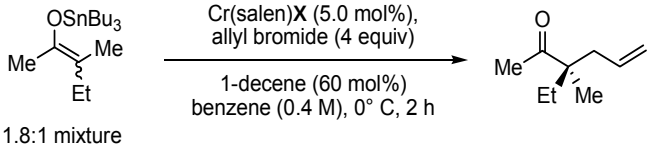
I. Catalyst Structure Optimization



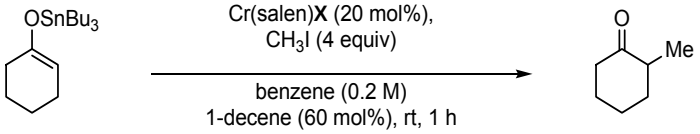


R_1	R_2	*GC Yield*	*ee*
*t*Bu	*t*Bu	80%	21%
*t*Bu	Br	67%	20%
*t*Bu	OPiv	85%	31%
*t*Bu	OMe	61%	20%
***t*Bu**	**OTIPS**	**84%**	**36%**
*t*Bu	NPiv	13%	20%

II. Catalyst Counterion Dependences for Acyclic and Cyclic Tin Enolates

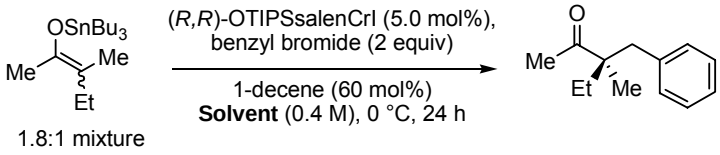


Catalyst	*GC Yield*	*ee*
X = F	46%	**33%**
X = Cl	80%	**21%**
X = Br	>99%	**45%**
X = I	quant	**47%**



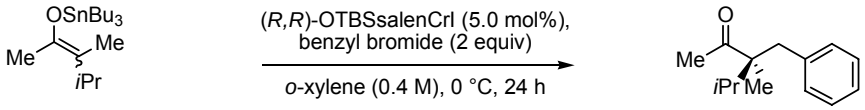
Counterion	*GC Yield*	*ee*
X = BF_4	NR	--
X = PF_6	NR	--
X = F	2%	**--**
X = Cl	57%	**51%**
X = Br	60%	**46%**
X = I	27%	**40%**

III. Solvent Screen



Solvent	*GC Yield*	*ee*
CH_2Cl_2	NR	--
Hexanes	NR	--
TBME	67%	58%
CH_3CN	10%	17%
Et_2O	16%	54%
THF	34%	32%
Benzene	**90%**	**60%**
Toluene	**70%**	**60%**
***o*-Xylene**	**97%**	**62%**

IV. Monitoring the ee and isomeric ratio over time of a poorly enantioselective substrate



1.2: 1 mixture

95% GC yield
32% ee