Synthesis of Quaternary Carbon Stereogenic Center through Enantioselective Copper-Catalyzed Allylic Substitutions with Vinylaluminum Reagents

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SUPPORTING INFORMATION, PART 1

General. Infrared (IR) spectra were recorded on a Nicolet 210 spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm). High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS (positive mode) at the Mass Spectrometry Facility, Boston College. Enantiomer ratios were determined by analytical liquid chromatography (HPLC) on a Shimadzu chromatograph (Chiral Technologies Chiralpak AS (4.6 x 250 mm), Chiral Technologies Chiralcel OD (4.6 x 250 mm), Chiral Technologies Chiralcel OD-R (4.6 x 250 mm), Chiral Technologies Chiralcel OJ-H (4.6 x 250 mm), or Chiral Technologies Chiralcel OD-H (4.6 x 250 mm)) in comparison with authentic racemic materials. Optical rotations were measured on a Rudolph Research Analytical Autopol IV Polarimeter.

Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum-line techniques. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Fisher Inc.) in air.

ν Reagents and Ligands:

3-(*tert*-Butoxy)prop-1-yne: Purchased from Acros and used after distillation from CaH_2 under N_2.

Chlorodiethylphosphate: Purchased from Aldrich and used as received.

5-Chloropent-1-yne: Purchased from Aldrich and used after distillation from CaH_2 under N_2.

Copper (II) chloride dihydrate: Purchased from Aldrich and used without further purification.

Di(*iso*-butyl)aluminum hydride (dibal-H, neat): Purchased from Aldrich and used as received.

4-Dimethylaminopyridine: Purchased from Advanced Chem Tech used as received.

3,3-Dimethylbut-1-yne: Purchased from Aldrich and used after distillation from CaH_2 under N_2.

1-Ethynylcyclohex-1-ene: Purchased from Aldrich and used after distillation from CaH_2 under vacuum.

1-Ethynyl-4-methoxybenzene: Purchased from Aldrich and used after distillation from CaH_2 under vacuum.

1-Ethynyl-2-methylbenzene: Purchased from Aldrich and used after distillation from CaH_2 under vacuum.

1-Ethynyl-4-(trifluoromethyl)benzene: Purchased from Aldrich and used after distillation from CaH_2 under vacuum.

1-Octyne: Purchased from Aldrich and used after distillation from CaH_2 under N_2.

Phenylacetylene: Purchased from Aldrich and used after distillation from CaH_2 under vaccum.

Tetrahydrofuran: Distilled under N_2 from sodium benzophenone ketyl.

Triethylamine: Purchased from Aldrich and distilled from CaH_2 under N_2.

Dichloromethane, diethyl ether, and hexanes: Purified by being passed through two alumina columns under a positive pressure of dry argon with a modified Advanced ChemTech purification system.

Alkyl-substituted vinylaluminum reagents: Prepared according to a known literature procedure. [1]

Chiral NHC-Ag Complex 1a: Prepared based on a previously reported procedure.[2]

Chiral NHC-Ag Complex 1b: Prepared based on a previously reported procedure.[3]

Chiral NHC-Ag Complex 1c: Prepared based on a previously reported procedure.[4]

■ **Preparation of trisubstituted allylic phosphate substrates:** First, the requisite allylic alcohols were synthesized from the corresponding ketones by a two-step Horner-Wadsworth-Emmons olefination[5]/dibal–H reduction sequence.[6] Subsequently, allylic alcohols were converted to the corresponding allylic phosphates based on established methods.[7] Physical attributes of compounds, which have not been reported in the past, are presented below.

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(1) Negishi, E.; Takahashi, T.; Baba, S. *Org. Synth. Coll.* **1993**, *8*, 295–297.

(2) Brown, M. K.; May, T. L.; Baxter, C. A.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2007**, *46*, 1097–1100.

(3) Lee, Y.; Akiyama, K.; Gillingham, D. G.; Brown, M. K.; Hoveyda, A. H.; *J. Am. Chem. Soc.* **2008**, *130*, 446–447.

(4) Akiyama, K.; Gao, F.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2010**, *49*, 419–423.

(5) Nestl, B. M.; Glueck, S. M.; Hall, M.; Kroutil, W.; Stuermer, R.; Hauer, B.; Faber, K. *Eur. J. Org. Chem.* **2006**, *71*, 4573–4577.

(6) Clive, D. L. J.; Stoffman, E. J. L. *Chem. Commum.* **2007**, *21*, 2151–2153.

(7) Luchaco-Cullis, C. A.; Mizutani, H.; Murphy, K. E.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2001**, *40*, 1456–1460.

(*E*)-Diethyl (3-phenylbut-2-en-1-yl) phosphate. IR (neat): 2982 (w), 2908 (w), 1495 (w), 1478 (w), 1445 (w), 1391 (w), 1261 (m), 1165 (w), 1125 (w), 1100 (w), 1062 (w), 1004 (s), 969 (s), 879 (w), 821 (m), 758 (m), 696 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 7.42–7.39 (2H, m), 7.36–7.32 (2H, m), 7.30–7.28 (1H, m), 5.95 (1H, dt, *J* = 6.8, 1.2 Hz), 4.77 (2H, dd, *J* = 8.0, 7.6 Hz), 4.13 (4H, dq, *J* = 7.2, 1.2 Hz), 2.12 (3H, s), 1.36-1.32 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 140.5, 128.5, 127.8, 126.0, 122.0 (d, *J* = 6.7 Hz), 64.5 (d, *J* = 5.2 Hz), 63.9 (d, *J* = 6.0 Hz), 16.35 (d, *J* = 3.0 Hz), 16.27; HRMS (ESI+): Calcd for $C_{14}H_{22}O_5P_1$ $[M+OH]^+$: 301.1205, Found: 301.1207.

(*E*)-Diethyl (3-(*o*-tolyl)but-2-en-1-yl) phosphate. IR (neat): 2982 (w), 2931 (w), 1486 (w), 1445 (w), 1381 (w), 1263 (w), 1263 (m), 1166 (w), 1103 (w), 1029 (s), 1009 (s), 977 (s), 881 (w), 827 (w), 761 (w), 729 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 7.28–7.22 (3H, m), 7.17–7.15 (1H, m), 5.63 (1H, dt, *J* = 6.8, 1.2 Hz), 4.84 (2H, dd, *J* = 8.0, 7.6 Hz), 4.27–4.19 (4H, m), 2.37 (3H, s), 2.10 (3H, s), 1.47–1.43 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$), δ 144.4, 142.5, 134.8, 130.5, 128.1, 127.4, 126.0, 124.0 (d, *J* = 6.7 Hz), 64.3 (d, *J* = 6.0 Hz), 64.0 (d, *J* = 5.9 Hz), 20.0, 18.7, 16.5 (d, *J* = 6.7 Hz); HRMS (ESI+): Calcd for $C_{15}H_{24}O_5P_1$ $[M+OH]^+$: 315.1361, Found: 315.1370.

(*E*)-3-(2-Bromophenyl)but-2-enyl diethyl phosphate. IR (neat): 2983 (w), 2905 (w), 1468 (w), 1426 (w), 1378 (w), 1270 (m), 1166 (w), 1026 (s), 979 (s), 887 (w), 823 (w), 758 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 7.56–7.53 (1H, m), 7.29–7.24 (1H, m), 7.17–7.11 (2H, m), 5.59 (1H, dt, *J* = 5.2, 1.2 Hz), 4.74 (2H, dd, *J* = 6.8, 0.8 Hz), 4.14 (4H dq, *J* = 7.2, 0.8 Hz), 2.05–2.04 (3H, m), 1.37–1.34 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 141.9, 132.9, 129.8, 128.8, 127.5, 125.2 (d, *J* = 6.7 Hz), 121.8, 63.9 (d, *J* = 6.7 Hz), 18.1, 16.3 (d, *J* = 6.7 Hz); HRMS (ESI+): Calcd for $C_{14}H_{21}Br_1O_5P_1$ $[M+OH]^+$: 379.0310, Found: 379.0332.

(*E*)-Diethyl (3-(4-nitrophenyl)but-2-en-1-yl) phosphate. IR (neat): 2984 (w), 2911 (w), 1595 (w), 1515 (m), 1444 (w), 1391 (w), 1369 (w), 1343 (s), 1263 (m), 1165 (w), 1106 (w), 1062 (w), 1005 (s), 974 (s), 853 (s), 818 (m), 747 (m), 695 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 8.21–8.17 (2H, m), 7.56–7.52 (2H, m), 6.07 (1H, dt, *J* = 6.4, 1.2 Hz), 4.78 (2H, dd, *J* = 6.4, 0.8 Hz), 4.18–4.10 (4H, m), 2.14–2.13 (3H, m), 1.37–1.33 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 147.3, 138.2, 126.8, 125.9 (d, *J* = 6.7 Hz), 123.8, 64.1 (d, *J* = 4.5 Hz), 64.1 (d, *J* = 5.2 Hz), 16.3 (d, *J* = 4.5 Hz), 16.3 (d, *J* = 2.2 Hz); HRMS (ESI+): Calcd for $C_{14}H_{24}N_2O_6P$ $[M+NH_4]^+$: 347.1372, Found: 347.1379.

(*E*)-Diethyl (3-(4-(trifluoromethyl)phenyl)but-2-en-1-yl) phosphate. IR (neat): 2986 (w), 2934 (w), 2910 (w), 1616 (w), 1445 (w), 1411 (w), 1394 (w), 1324 (s), 1265 (m), 1164 (m), 1115 (s), 1059 (m), 1006 (s), 975 (s), 847 (m), 819 (m), 749 (w), 724 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 7.60–7.57 (2H, m), 7.50–7.48 (2H, m), 6.00 (1H, dt, *J* = 5.6, 1.6 Hz), 4.79–4.75 (2H, m), 4.17–4.10 (4H, m), 2.12 (3H, s), 1.37–1.32 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$):

δ 146.0, 139.1, 129.7 (q, *J* = 32.0 Hz), 128.8 (q, *J* = 82.1 Hz), 126.3, 125.4 (q, *J* = 3.8 Hz), 124.1 (d, *J* = 6.7 Hz), 64.2 (d, *J* = 5.3 Hz), 64.0 (d, *J* = 5.9 Hz), 17.8, 16.3 (d, *J* = 6.7 Hz); HRMS (ESI+): Calcd for $C_{15}H_{21}F_3O_5P_1$ $[M+OH]^+$: 369.1079, Found: 369.1084.

(*E*)-3-Cyclohexylbut-2-enyl diethyl phosphate. IR (neat): 2982 (w), 2925 (m), 2853 (w), 1663 (w), 1448 (w), 1392 (w), 1369 (w), 1261 (m), 1166 (w), 1098 (w), 1069 (w), 1024 (s), 1001 (s), 972 (s), 881 (w), 852 (w), 830 (w), 801 (m), 747 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 5.37 (1H, ddt, *J* = 6.8, 2.4, 1.2 Hz), 4.57 (2H, t, *J* = 7.6 Hz), 4.14–4.06 (4H, m), 1.87 (1H, t, *J* = 11.6 Hz), 1.77–1.69 (5H, m), 1.67 (3H, s), 1.35–1.30 (6H, m), 1.28–1.11 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 117.4 (d, *J* = 6.7 Hz), 64.4 (d, *J* = 5.9 Hz), 63.7 (d, *J* = 5.2 Hz), 47.3, 31.7, 26.7, 26.4, 16.3 (d, *J* = 6.7 Hz), 15.0; HRMS (ESI+): Calcd for $C_{14}H_{28}O_5P_1$ $[M+OH]^+$: 307.1674, Found: 307.1681.

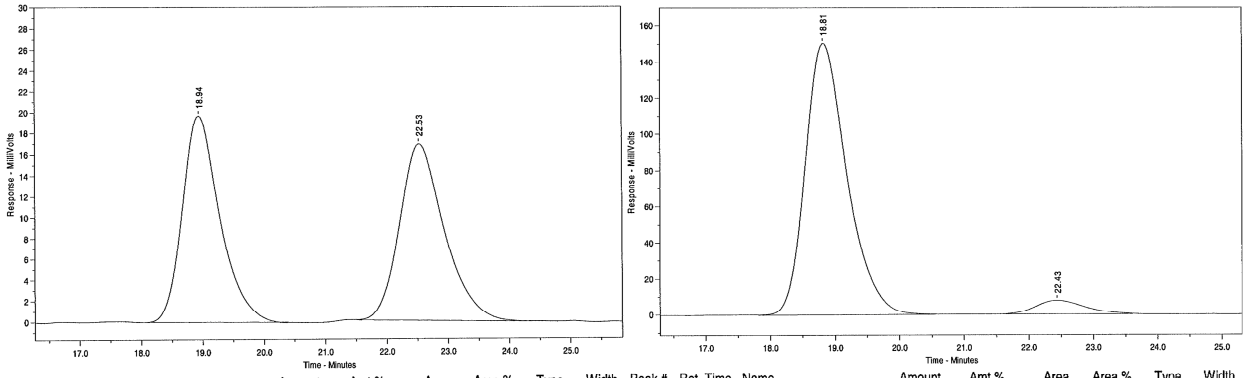
(*E*)-3, 7-Dimethylocta-2, 6-dienyl diethyl phosphate (10, Scheme 4). IR (neat): 2981 (w), 2912 (w), 1669 (w), 1444 (w), 1383 (w), 1261 (m), 1166 (w), 1100 (w), 1027 (s), 972 (s), 886 (w), 818 (m), 801 (m), 746 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 5.41–5.38 (1H, m), 5.10–5.06 (1H, m), 4.56 (2H, t, *J* = 7.6 Hz), 4.14–4.07 (4H, m), 2.13–2.02 (4H, m), 1.69 (6H, d, *J* = 10.0 Hz), 1.60 (3H, s), 1.35–1.31 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 132.0, 123.8, 119.1 (d, *J* = 6.7 Hz), 64.2 (d, *J* = 5.2 Hz), 63.7 (d, *J* = 5.9 Hz), 39.6, 26.4, 25.8, 17.8, 16.6, 16.3 (d, *J* = 6.7 Hz); HRMS (ESI+): Calcd for $C_{14}H_{28}O_5P_1$ $[M+OH]^+$: 307.1674, Found: 307.1673.

(*E*)-*tert*-Butyl 4-((diethoxyphosphoryl)oxy)-2-methylbut-2-enoate. IR (neat): 2980 (w), 2934 (w), 1708 (m), 1657 (w), 1479 (w), 1457 (w), 1392 (w), 1368 (w), 1333 (w), 1252 (m), 1171 (w), 1134 (m), 1100 (w), 1017 (s), 889 (w), 848 (w), 819 (w), 730 (w), 670 (w), 511 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.66–6.63 (1H, m), 4.68–4.63 (2H, m), 4.13–4.05 (4H, m), 1.78 (3H, s), 1.44 (9H, s), 1.33–1.28 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 134.0 (d, *J* = 7.5 Hz), 132.2, 80.9, 64.0 (d, *J* = 6.0 Hz), 63.9 (d, *J* = 5.2 Hz), 28.1, 16.2 (d, *J* = 6.7 Hz), 12.9; HRMS (ESI+): Calcd for $C_{13}H_{26}O_6P_1$ $[M+H]^+$: 309.1467, Found: 309.1453.

ν General Procedure for Cu-catalyzed Enantioselective Allylic Substitutions with Alkyl-substituted Vinylaluminum Reagents (Table 1 and Scheme 3): A 13 x 100 mm test tube equipped with a stir bar is charged with NHC–Ag complex **1a** (1.2 mg, 0.0010 mmol) in an N_2-filled glovebox. The vessel is sealed with a septum and removed from the glovebox. Tetrahydrofuran (1.0 mL) and a solution of $CuCl_2$•$2H_2O$ (0.02M in thf, 100 μL, 0.002 mmol) are added to the test tube at 22 °C. The resulting blue solution is allowed to cool to –78 °C (dry ice/acetone bath), followed by the addition of the vinylaluminum reagent (1.0 M in hexanes, 300 μL, 0.30 mmol) and a solution of (*E*)-diethyl (3-phenylbut-2-en-1-yl) phosphate (56.9 mg, 0.200 mmol) in thf (1.0 mL). The mixture is allowed to warm to –15 °C and sit in a freezer for 3 h, after which time, the reaction is quenched by the addition of a saturated aqueous solution of Rochelle's salt (2.0 mL) at –78 °C and the resulting mixture is allowed to warm to 22 °C and stir for one hour. The layers are separated, and the aqueous layer is washed with Et_2O (2.0 mL x 3).

The combined organic layers are passed through a short plug of $MgSO_4$, and concentrated under reduced pressure. The resulting yellow oil is purified by silica gel chromatography to give the product as colorless oil (39.8 mg, 0.164 mmol, 82% yield). **(*R*,*E*)-(3-Methylundeca-1,4-dien-3-yl)benzene (entry 1, Table 1).** IR (neat): 3083 (w), 2957 (m), 2925 (s), 2871 (m), 2854 (s), 1633 (w), 1599 (w), 1492 (m), 1460 (m), 1445 (m), 975 (m), 914 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36–7.29 (4H, m), 7.22-7.18 (1H, m), 6.09 (1H, dd, *J* = 17.6, 10.8 Hz), 5.67 (1H, dt, *J* = 15.6, 1.6 Hz), 5.43 (1H, dt, *J* = 15.6, 6.8 Hz), 5.12 (1H, dd, *J* = 10.8, 1.6 Hz), 5.02 (1H, dd, *J* = 17.2, 1.6 Hz), 2.09 (2H, dtd, *J* = 6.8, 6.8, 1.2 Hz), 1.49 (3H, s), 1.42–1.27 (8H, m), 0.90 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 146.0, 137.0, 129.1, 128.2, 127.3, 126.1, 112.4, 47.6, 32.9, 31.9, 29.7, 29.1, 25.9, 22.9, 14.3; HRMS (ESI+): Calcd for $C_{18}H_{27}$ $[M+H]^+$: 243.2113, Found: 243.2118. Elemental Analysis: Calcd for $C_{18}H_{26}$: C, 89.19; H, 10.81; Found: C, 89.35; H, 10.60. Optical Rotation: $[\alpha]_D^{20}$ –5.31 (*c* 1.50, $CHCl_3$) for an enantiomerically enriched sample of 94.5:5.5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (94.3:5.7 er shown; Chiralcel OD column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	18.94		0.00	N/A	837687	49.408	BB	0.64
2	22.53		0.00	N/A	857748	50.592	BB	0.77

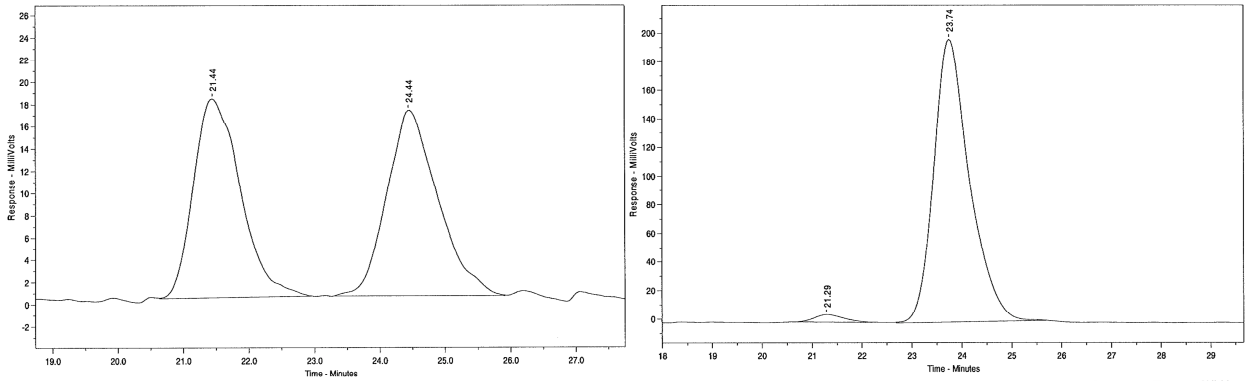
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	18.81		0.00	N/A	6736213	94.343	BB	0.68
2	22.43		0.00	N/A	403892	5.657	BB	0.80

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	18.94	49.4	1	18.81	94.3
2	22.53	50.6	2	22.43	5.7

(*R*,*E*)-1-Bromo-2-(3-methylundeca-1,4-dien-3-yl)benzene (entry 2, Table 1). IR (neat): 2956 (w), 2923 (m), 2853 (w), 1463 (m), 1431 (w), 1267 (w), 1019 (m), 987 (w), 966 (m), 944 (m), 754 (s), 734 (m), 724 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (1H, dd, *J* = 8.0, 1.2 Hz), 7.46 (1H, dd, *J* = 8.0, 1.6 Hz), 7.25 (1H, dt, *J* = 8.0, 0.8 Hz), 7.06 (1H, dq, *J* = 7.2, 0.8 Hz), 6.19 (1H, dd, *J* = 17.2, 10.8 Hz), 5.74 (1H, dt, *J* = 15.6, 0.8 Hz), 5.30 (1H, dt, *J* = 15.6, 6.8 Hz), 5.10 (1H, dt, *J* = 10.8, 0.9 Hz), 4.93 (1H, dd, *J* = 17.6, 0.8 Hz), 2.07 (2H, dtd, *J* = 7.2, 7.2, 1.6 Hz), 1.62 (3H, s), 1.39–1.26 (8H, m), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 145.5, 136.4, 135.6, 129.8, 129.5, 128.0, 127.1, 124.0, 112.8, 48.8, 32.9, 31.9, 29.5, 29.1, 26.3, 22.8, 14.3. Elemental Analysis: Calcd for $C_{18}H_{25}Br_1$: C, 67.29; H, 7.84; Found: C, 67.34; H,

7.84. Optical Rotation: $[\alpha]_D^{20}$ –9.71 (*c* = 1.12, $CHCl_3$) for an enantiomerically enriched sample of 96.5:3.5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (97.9:2.1 er shown; Chiralcel OD column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



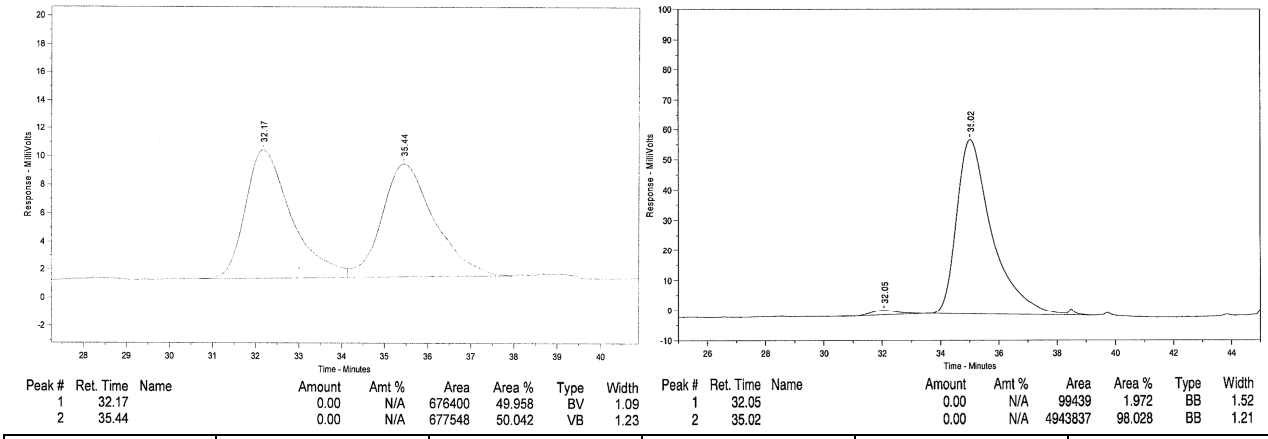
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	21.44		0.00	N/A	892634	49.513	BB	0.78
2	24.44		0.00	N/A	910197	50.487	BB	0.84

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	21.29		0.00	N/A	212838	2.115	BB	0.64
2	23.74		0.00	N/A	9851873	97.885	BB	0.74

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	21.44	49.5	1	21.29	2.1
2	24.44	50.5	2	23.74	97.9

(*R*,*E*)-1-(3-Methylundeca-1,4-dien-3-yl)-2-(trifluoromethyl)benzene (entry 3, Table 1). IR (neat): 2957 (w), 2925 (w), 2855 (w), 1488 (w), 1304 (s), 1268 (m), 1166 (s), 1129 (s), 1034 (s), 912 (m), 765 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (1H, dd, *J* = 8.0, 1.6 Hz), 7.63 (1H, d, *J* = 8.0 Hz), 7.46 (1H, dq, *J* = 8.0, 0.8 Hz), 7.35–7.31 (1H, m), 6.14 (1H, ddd, *J* = 17.6, 10.8, 0.8 Hz), 5.72 (1H, dd, *J* = 15.6, 0.8 Hz), 5.28 (1H, dt, *J* = 15.6, 6.8 Hz), 5.06 (1H, dd, *J* = 10.8, 0.8 Hz), 4.88 (1H, dd, *J* = 17.2, 0.8 Hz), 2.05 (2H, dtd, *J* = 6.8, 6.8, 1.2 Hz), 1.57 (3H, s), 1.38–1.26 (8H, m), 0.89 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 145.9, 137.3, 131.4, 130.6, 129.2 (q, *J* = 30.7 Hz), 128.6, 128.6, 128.5, 124.7 (q, *J* = 272.8 Hz), 111.7, 48.7, 32.9, 31.9, 29.4, 29.1, 27.4, 22.8, 14.3; HRMS (ESI+): Calcd for $C_{19}H_{26}F_3$ $[M+H]^+$: 311.1987, Found: 311.1979. Optical Rotation: $[\alpha]_D^{20}$ –13.3 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (98.0:2.0 er shown; Chiralcel OD column, 99.5/0.5 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



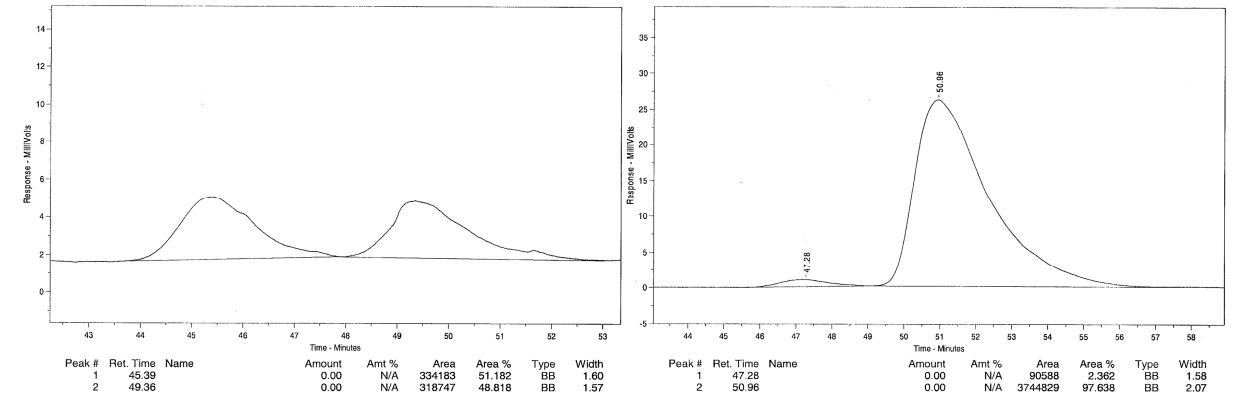
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	32.17		0.00	N/A	676400	49.958	BV	1.09
2	35.44		0.00	N/A	677548	50.042	VB	1.23

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	32.05		0.00	N/A	99439	1.972	BB	1.52
2	35.02		0.00	N/A	4943837	98.028	BB	1.21

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	32.17	50.0	1	32.05	2.0
2	35.44	50.0	2	35.02	98.0

(*R*,*E*)-1-(3-Methylundeca-1,4-dien-3-yl)-2-nitrobenzene (entry 4, Table 1). IR (neat): 2956 (w), 2925 (m), 2855 (w), 1531 (s), 1367 (m), 974 (w), 916 (w), 850 (w), 751 (s), 650 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (1H, dd, *J* = 7.2, 1.2 Hz), 7.47–7.39 (2H, m), 7.32 (1H, dt, *J* = 7.2, 1.2 Hz), 6.01 (1H, dd, *J* = 17.2, 10.6 Hz), 5.58 (1H, d, *J* = 16.4 Hz), 5.44 (1H, dt, *J* = 16.4, 6.0 Hz), 5.13 (1H, d, *J* = 10.6 Hz), 5.02 (1H, d, *J* = 17.6 Hz), 2.01 (2H, dt, *J* = 6.0, 6.0 Hz), 1.62 (3H, s), 1.40–1.24 (8H, m), 0.88 (3H, t, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 143.8, 139.3, 134.3, 131.2, 130.5, 130.2, 127.5, 124.4, 112.9, 47.4, 32.8, 31.9, 29.3, 29.2, 25.7, 22.9, 14.3; HRMS (ESI+): Calcd for $C_{18}H_{26}N_1O_2$ $[M+H]^+$: 288.1964, Found: 288.1961. Elemental Analysis: Anal Calcd for $C_{18}H_{25}N_1O_2$: C, 75.22; H, 8.77; N, 4.87; Found: C, 75.49; H, 9.04; N, 5.05. Optical Rotation: $[\alpha]_D^{20}$ +0.71 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 97.5:2.5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (97.6:2.4 er shown; Chiralcel OD column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	45.39		0.00	N/A	334183	51.182	BB	1.60
2	49.36		0.00	N/A	318747	48.818	BB	1.57

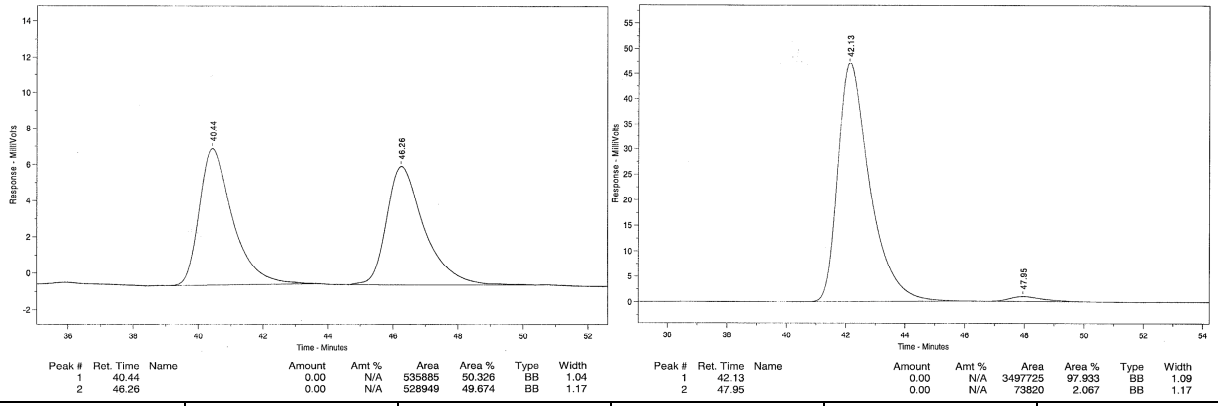
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	47.28		0.00	N/A	90588	2.362	BB	1.58
2	50.96		0.00	N/A	3744829	97.638	BB	2.07

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	45.39	51.2	1	47.28	2.4

2	49.36	48.8	2	50.96	97.6

(*R*,*E*)-1-Methoxy-2-(3-methylundeca-1,4-dien-3-yl)benzene (entry 5, Table 1). IR (neat): 2956 (w), 2924 (m), 2853 (w), 1487 (m), 1461 (m), 1434 (m), 1241 (s), 1031 (m), 967 (w), 909 (m), 748 (s), 670 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.27 (1H, dd, *J* = 7.6, 1.6 Hz), 7.21 (1H, dt, *J* = 7.6, 1.6 Hz), 6.91–6.86 (2H, m), 6.18 (1H, dd, *J* = 17.2, 10.4 Hz), 5.73 (1H, dt, *J* = 15.6, 1.2 Hz), 5.32 (1H, dt, *J* = 15.6, 6.0 Hz), 5.01 (1H, dd, *J* = 10.4, 1.6 Hz,), 4.91 (1H, dd, *J* = 17.2, 1.2 Hz), 3.76 (3H, s), 2.04 (2H, dt, *J* = 6.0, 6.0 Hz), 1.53 (3H, s), 1.35–1.27 (8H, m), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 146.3, 137.1, 135.7, 128.3, 127.9, 127.8, 120.5, 112.3, 111.2, 55.3, 46.5, 33.0, 32.0, 29.9, 29.1, 24.8, 22.9, 14.3; HRMS (ESI+): Calcd for $C_{19}H_{29}O_1$ $[M+H]^+$: 273.2218, Found: 273.2219. Optical Rotation: $[\alpha]_D^{20}$ –3.36 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

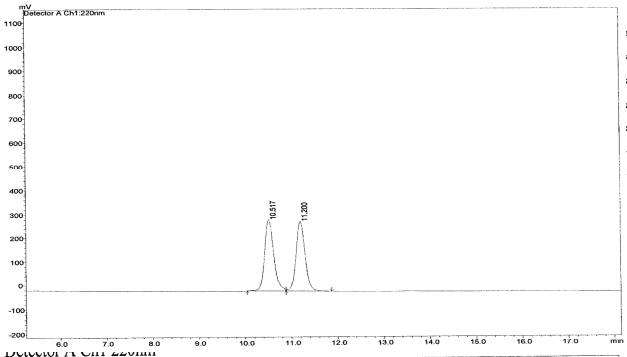
Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (97.9:2.1 er shown; Chiralcel OD-R column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



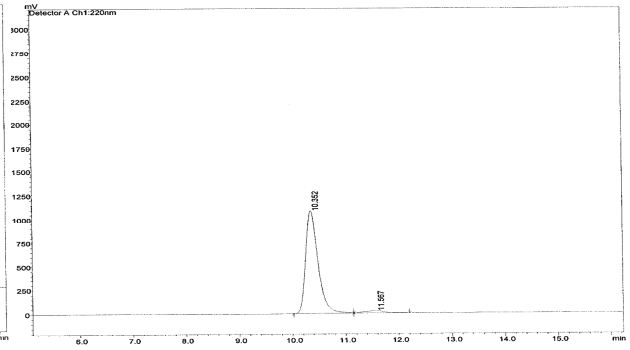
Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	40.44	50.3	1	42.13	97.9
2	46.26	49.7	2	47.95	2.1

(*R*,*E*)-1-Methyl-2-(3-methylundeca-1,4-dien-3-yl)benzene (entry 6, Table 1). IR (neat): 3014 (m), 2957 (m), 2853 (m), 1631 (w), 1485 (w), 1456 (m), 972 (m), 910 (m), 759 (s), 728 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.37 (1H, m), 7.17–7.12 (3H, m), 6.14 (1H, dd, *J* = 17.2, 10.4 Hz), 5.73 (1H, dt, *J* = 15.6, 1.6 Hz), 5.28 (1H, dt, *J* = 15.6, 6.8 Hz), 5.06 (1H, dd, *J* = 10.4, 1.2 Hz), 4.90 (1H, dd, *J* = 17.6, 1.2 Hz), 2.33 (3H, s), 2.05 (2H, dtd, *J* = 6.8, 6.8, 1.6 Hz), 1.53 (3H, s), 1.38–1.27 (8H, m), 0.89 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 144.5, 137.6, 137.2, 132.4, 128.6, 127.6, 126.5, 125.6, 111.9, 48.1, 33.0, 31.9, 29.6, 29.1, 27.5, 22.9, 22.8, 14.3; HRMS (ESI+): Calcd for $C_{19}H_{29}$ $[M+H]^+$: 257.2269, Found: 257.2274. Optical Rotation: $[\alpha]_D^{20}$ –7.58 (*c* 1.26, $CHCl_3$) for an enantiomerically enriched sample of 96.5:3.5 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (96.5:3.5 er shown; Chiralpak OD-H column, 99.8/0.2 hexanes/*i*-PrOH, 0.3 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.517	4119220	303701	50.726	50.567
2	11.200	4001372	296892	49.274	49.433
Total		8120592	600593	100.000	100.000

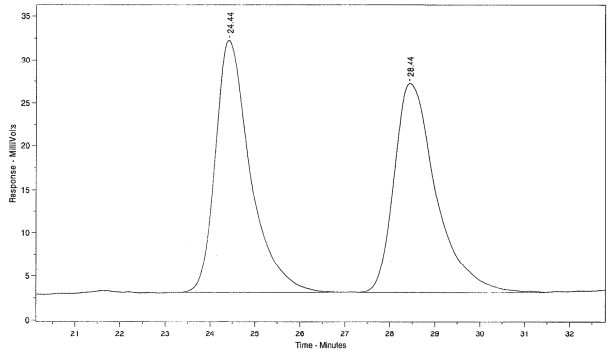


Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.352	17339090	1081398	96.505	97.712
2	11.567	627862	25325	3.495	2.288
Total		17966952	1106724	100.000	100.000

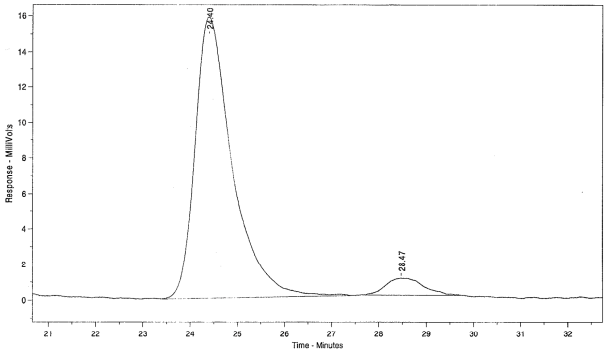
Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	10.52	50.7	1	10.35	96.5
2	11.20	49.3	2	11.57	3.5

(*R*,*E*)-1-(3-Methylundeca-1,4-dien-3-yl)-4-nitrobenzene (entry 7, Table 1). IR (neat): 2956 (w), 2926 (m), 2855 (w), 1597 (w), 1518 (s), 1492 (w), 1459 (w), 1345 (s), 1216 (w), 1111 (w), 1014 (w), 1000 (w), 976 (w), 920 (w), 852 (m), 755 (s), 701 (m), 668 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (2H, d, *J* = 6.8 Hz), 7.48 (2H, d, *J* = 9.2 Hz), 6.03 (1H, dd, *J* = 17.6, 10.6 Hz), 5.62 (1H, d, *J* = 15.6 Hz), 5.43 (1H, dt, *J* = 16.0, 6.8 Hz), 5.18 (1H, d, *J* = 10.6 Hz), 5.03 (1H, d, *J* = 17.6 Hz), 2.08 (2H, dt, *J* = 7.2, 7.2 Hz), 1.50 (3H, s), 1.43–1.27 (8H, m), 0.89 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 146.5, 144.6, 135.7, 130.7, 128.4, 123.5, 113.8, 48.0, 32.9, 31.9, 29.6, 29.1, 26.0, 22.9, 14.3; HRMS (ESI+): Calcd for $C_{18}H_{26}N_1O_2$ $[M+H]^+$: 288.1964, Found: 288.1949. Elemental Analysis: Anal Calcd for $C_{18}H_{25}N_1O_2$: C, 75.22; H, 8.77; N, 4.87; Found: C, 75.49; H, 8.90; N, 4.98. Optical Rotation: $[\alpha]_D^{20}$ –7.54 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 94.5:5.5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (94.4:5.6 er shown; Chiralcel OD-R column, 98/2 hexanes/*i*-PrOH, 1.0 mL/min, 240 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	24.44		0.00	N/A	1576163	50.344	BB	0.78
2	28.44		0.00	N/A	1554601	49.656	BB	0.93



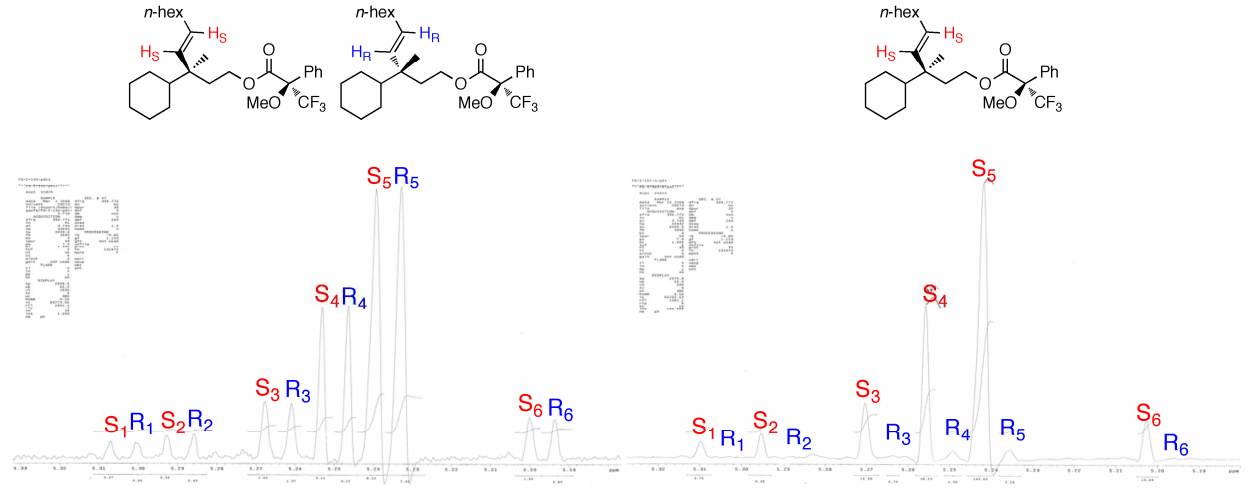
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	24.40		0.00	N/A	866889	94.435	BB	0.78
2	28.47		0.00	N/A	51081	5.565	BB	0.84

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	24.44	50.3	1	24.40	94.4

2	28.44	49.7	2	28.47	5.6

(*S*,*E*)-(3-Methylundeca-1,4-dien-3-yl)cyclohexane (entry 8, Table 1). IR (neat): 2922 (s), 2852 (s), 1450 (m), 1000 (w), 973 (m), 910 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.82 (1H, dd, *J* = 17.6, 10.8 Hz), 5.40 (1H, dt, *J* = 15.6, 1.2 Hz), 5.28 (1H, dt, *J* = 15.6, 6.4 Hz), 4.97 (1H, dd, *J* = 10.8, 1.6 Hz), 4.89 (1H, dd, *J* = 17.6, 1.6 Hz), 2.01 (2H, dt, *J* = 6.4, 6.4 Hz), 1.75-1.69 (4H, m), 1.64–1.61 (1H, m), 1.36–1.19 (8H, m), 1.18–1.05 (4H, m), 1.01 (3H, s), 0.94–0.86 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 137.0, 128.3, 111.6, 47.4, 45.3, 33.2, 31.9, 29.9, 29.2, 28.0, 27.4, 27.0, 22.9, 20.2, 14.3; HRMS (ESI+): Calcd for $C_{18}H_{33}$ $[M+H]^+$: 249.2582, Found: 249.2591. Elemental Analysis: Anal Calcd for $C_{18}H_{32}$: C, 87.02; H, 12.98; Found: C, 87.30; H, 13.26. Optical Rotation: $[\alpha]_D^{20}$ –16.3 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 93:7 er.

Site-selective hydroboration (9-BBN)/oxidation (H_2O_2) of the terminal alkene of the EAS product and generation of the derived Mosher ester, according to published procedures,[8] was performed first. Enantiomeric purity was determined by analysis of the ^1H NMR spectrum in comparison with that of authentic Mosher ester of racemic primary alcohol.[9] (**See ^1H NMR spectra for racemic and enantiomerically enriched Mosher esters in the Appendix, 94.9:5.1 er shown**).



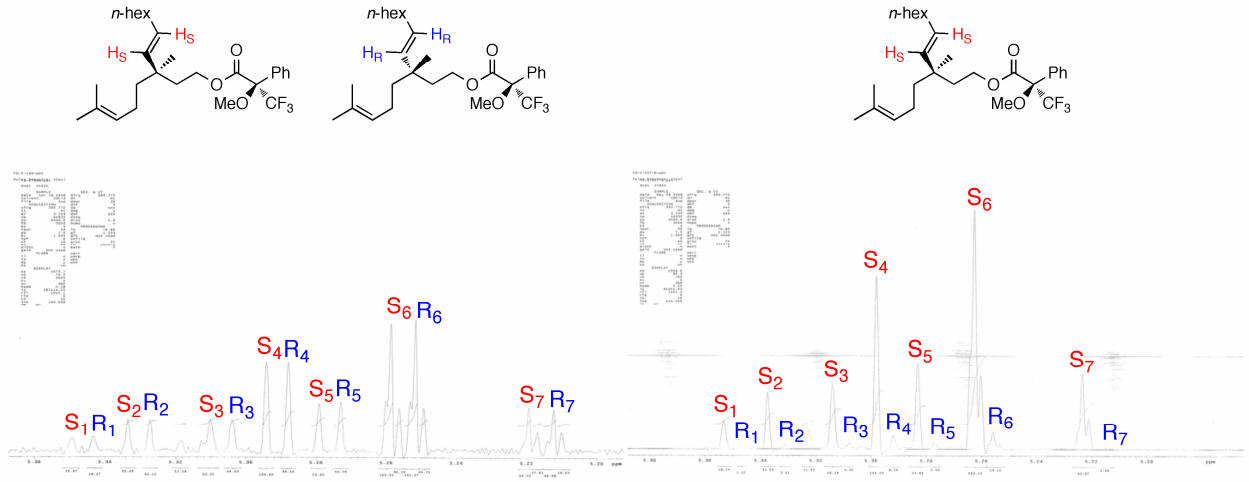
Peak#	ppm	Area%	Peak#	ppm	Area%
S_4	5.253	99.51	S_4	5.254	100.0
R_4	5.246	100.0	R_4	5.247	5.42

(*R*,*E*)-2,6-Dimethyl-6-vinyltetradeca-2,7-diene (entry 9, Table 1). IR (neat): 2960 (m), 2923 (s), 2854 (m), 1634 (w), 1455 (m), 1376 (w), 1459 (w), 972 (s), 911 (s), 837 (w), 724 (w), 681 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.80 (1H, dd, *J* = 17.6, 10.8 Hz), 5.40–5.29 (2H, m), 5.09 (1H, tt, *J* = 7.2, 1.6 Hz), 4.97–4.91 (2H, m), 2.03–1.98 (2H, m), 1.89 (2H, dt, *J* = 6.8, 6.8 Hz), 1.67 (3H, s), 1.58 (3H, s), 1.38–1.27 (10H, m), 1.07 (3H, s), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C

(8) Fujii, M.; Fukumura, M.; Hori, Y.; Hirai, Y.; Akita, H.; Nakamura, K.; Toriizukaa, K.; Idaa, Y. *Tetrahedron; Asymmetry* **2006**, *17*, 2292–2298.
(9) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543–2549.

NMR (100 MHz, $CDCl_3$): δ 146.8, 137.3, 131.4, 128.1, 125.0, 111.3, 42.5, 41.9, 35.2, 34.2, 32.1, 31.3, 28.0, 23.7, 23.6, 23.0, 17.9, 14.6; HRMS (ESI+): Calcd for $C_{18}H_{33}$ $[M+H]^+$: 249.2582, Found: 249.2588. Optical Rotation: $[\alpha]_D^{20}$ –8.37 (*c* 1.48, $CHCl_3$) for an enantiomerically enriched sample of 92.5:7.5 er.

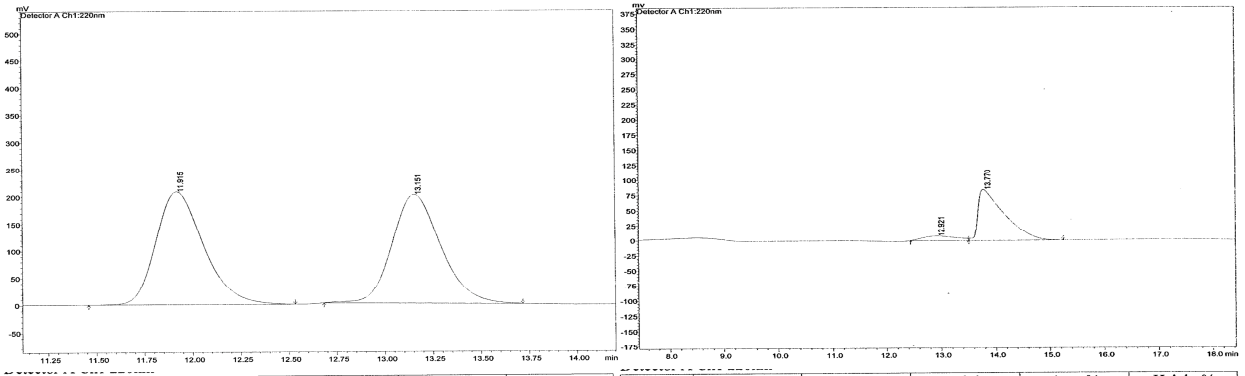
Site-selective hydroboration (9-BBN)/oxidation (H_2O_2) of the terminal alkene of the EAS product and generation of the derived Mosher ester, according to published procedures,[9] was performed first. Enantiomeric purity was determined by analysis of the ^1H NMR spectrum in comparison with that of authentic Mosher ester of racemic primary alcohol.[8] **(See the ^1H NMR spectra for racemic and enantiomerically enriched Mosher esters in the Appendix, 92.2:7.8 er shown).**



Peak#	ppm	Area%	Peak#	ppm	Area%
S_4	5.294	100.0	S_4	5.295	100.0
R_4	5.288	98.16	R_4	5.289	8.50

(*R*,*E*)-*tert*-Butyl 2-methyl-2-vinyldec-3-enoate (entry 10, Table 1). IR (neat): 2958 (w), 2926 (m), 2855 (w), 1726 (s), 1456 (w), 1409 (m), 1250 (s), 1160 (s), 1123 (s), 971 (m), 915 (m), 850 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.04 (1H, dd, *J* = 18.0, 10.0 Hz), 5.60 (1H, dt, *J* = 16.0, 0.8 Hz), 5.47 (1H, dt, *J* = 15.6, 6.8 Hz), 5.08–5.04 (2H, m), 2.03 (2H, dtd, *J* = 7.6, 7.6, 0.8 Hz), 1.42 (9H, s), 1.37–1.24 (8H, m), 1.32 (3H, s), 0.87 (3H, t, *J* = 6.8 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 141.7, 132.6, 130.3, 113.4, 80.7, 51.4, 32.8, 31.9, 29.5, 28.9, 28.1, 22.8, 21.6, 14.3; HRMS (ESI+): Calcd for $C_{17}H_{31}O_2$ $[M+H]^+$: 267.2324, Found: 267.2325. Optical Rotation: $[\alpha]_D^{20}$ –11.4 (*c* 0.91, $CHCl_3$) for an enantiomerically enriched sample of 90:10 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (90.1:9.9 er shown; Chiralcel OD-H column, 99.8/0.2 hexanes/*i*-PrOH, 0.3 mL/min, 220 nm).



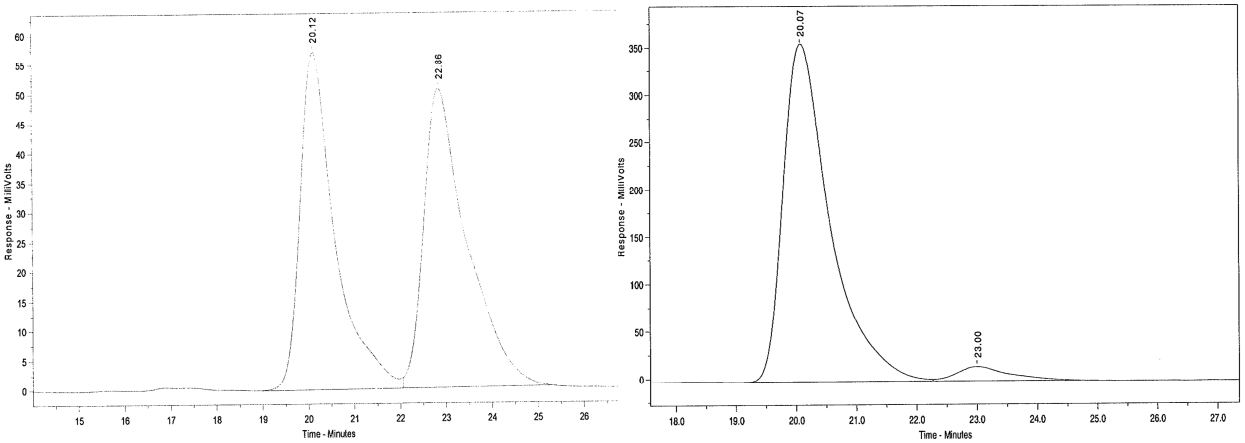
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.915	3599109	208131	50.400	50.959
2	13.151	3541926	200301	49.600	49.041
Total		7141035	408432	100.000	100.000

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.921	311759	7384	9.852	8.059
2	13.770	2852641	84240	90.148	91.941
Total		3164400	91625	100.000	100.000

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	11.92	50.4	1	12.92	9.9
2	13.15	49.6	2	13.77	90.1

(*R*,*E*)-Dimethyl(3-methylundeca-1,4-dien-3-yl)(phenyl)silane (entry 11, Table 1). IR (neat): 2956 (w), 2925 (w), 2856 (w), 1724 (w), 1427 (w), 1251 (w), 1117 (w), 1052 (w), 1026 (w), 998 (w), 829 (m), 811 (m), 790 (m), 773 (m), 698 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49–7.47 (2H, m), 7.39–7.31 (3H, m), 5.93 (1H, dd, *J* = 17.6, 10.8 Hz), 5.54 (1H, dt, *J* = 15.6, 1.2 Hz), 5.16 (1H, dt, *J* = 15.2, 7.2 Hz), 4.92 (1H, dd, *J* = 10.8, 1.2 Hz), 4.75 (1H, dd, *J* =17.2, 0.8 Hz), 2.03 (2H, dt, *J* = 6.8, 6.8 Hz), 1.36–1.23 (8H, m), 1.11 (3H, s), 0.89 (3H, t, *J* = 6.8 Hz), 0.28 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 136.8, 135.0, 133.9, 129.2, 127.4, 126.8, 109.9, 36.2, 33.4, 32.0, 30.2, 29.1, 22.9, 17.9, 14.3, –5.8; HRMS (ESI+): Calcd for $C_{20}H_{33}Si_1$ $[M+H]^+$: 301.2352, Found: 301.2348. Optical Rotation: $[\alpha]_D^{20}$ –3.56 (*c* 0.46, $CHCl_3$) for an enantiomerically enriched sample of 95.5:4.5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (95.5:4.5 er shown; Chiralcel OD column, 99.5/0.5 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



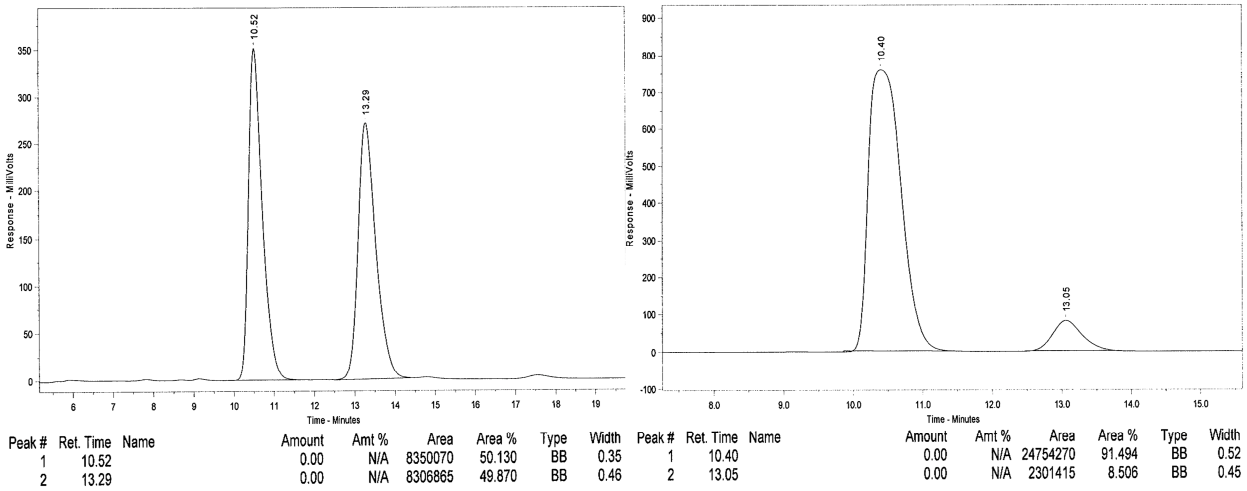
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	20.12		0.00	N/A	3039466	47.917	BV	0.72
2	22.86		0.00	N/A	3303744	52.083	VB	0.92

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	20.07		0.00	N/A	19301500	95.515	BV	0.78
2	23.00		0.00	N/A	906229	4.485	VB	0.86

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	20.12	47.9	1	20.07	95.5
2	22.86	52.1	2	23.00	4.5

(*R*,*E*)-Dimethyl(phenyl)(3,6,6-trimethylhepta-1,4-dien-3-yl)silane (3, Scheme 3). IR (neat): 2956 (m), 1427 (w), 1247 (m), 1113 (m), 976 (m), 894 (m), 810 (s), 772 (s), 734 (s), 698 (s), 473 (m), 404 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.47–7.45 (2H, m), 7.36–7.32 (3H, m), 5.92 (1H, dd, *J* = 17.6, 10.8 Hz), 5.42 (1H, d, *J* = 16.0 Hz), 5.15 (1H, d, *J* = 16.0 Hz), 4.91 (1H, dd, *J* = 10.4, 1.2 Hz), 4.74 (1H, dd, *J* =17.2, 1.2 Hz), 1.09 (3H, s), 0.98 (9H, s), 0.25 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 137.4, 136.8, 134.9, 129.2, 128.6, 127.4, 109.8, 35.8, 33.3, 30.2, 17.8, –6.0; HRMS (ESI+): Calcd for $C_{18}H_{29}Si_1$ $[M+H]^+$: 273.2039, Found: 273.2027. Optical Rotation: $[\alpha]_D^{20}$ +10.82 (*c* 3.58, $CHCl_3$) for an enantiomerically enriched sample of 91:9 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (91.5:8.5 er shown; Chiralcel OD column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	10.52		0.00	N/A	8350070	50.130	BB	0.35
2	13.29		0.00	N/A	8306865	49.870	BB	0.46

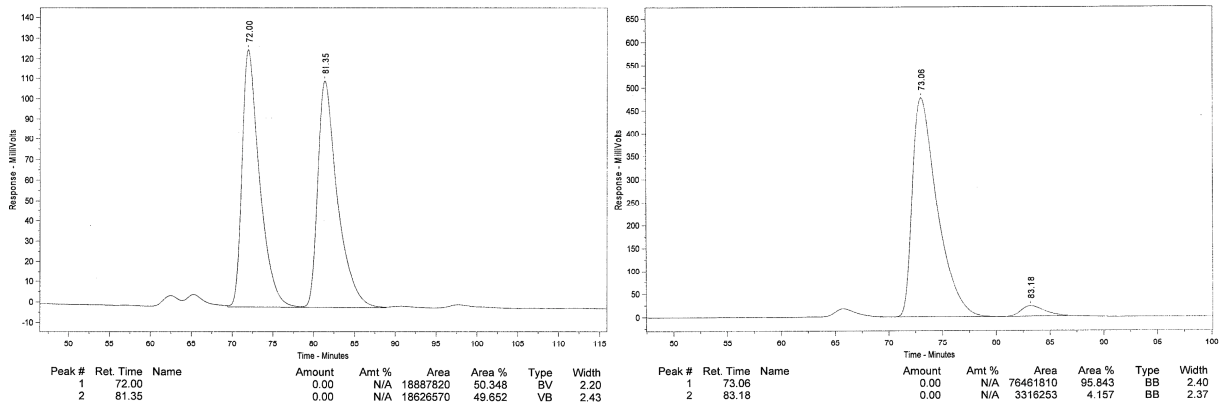
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	10.40		0.00	N/A	24754270	91.494	BB	0.52
2	13.05		0.00	N/A	2301415	8.506	BB	0.45

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	10.52	50.1	1	10.40	91.5
2	13.29	49.9	2	13.05	8.5

(*R*,*E*)-(9-(*tert*-Butoxy)-3-methylnona-1,4-dien-3-yl)dimethyl(phenyl)silane (4, Scheme 3). IR (neat): 2970 (m), 2927 (m), 2860 (w), 1621 (w), 1427 (w), 1361 (m), 1248 (m), 1198 (m), 1081 (m), 972 (m), 894 (m), 830 (s), 810 (s), 773 (s), 735 (s), 699 (s), 654 (m), 472 (m), 409 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48–7.46 (2H, m), 7.36–7.32 (3H, m), 5.91 (1H, dd, *J* = 17.2, 10.8 Hz), 5.54 (1H, d, *J* = 15.6 Hz), 5.15 (1H, dt, *J* = 15.6, 7.2 Hz), 4.91 (1H, dd, *J* = 10.8, 1.2 Hz), 4.74 (1H, dd, *J* = 17.2, 1.2 Hz), 3.33 (2H, t, *J* = 7.6 Hz), 2.04 (2H, dt, *J* = 7.2, 7.2 Hz), 1.54–1.49 (2H, m), 1.43–1.39 (2H, m), 1.20 (9H, s), 1.10 (3H, s), 0.26 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 136.8, 135.0, 134.1, 129.2, 127.5, 126.6, 110.0, 72.6, 61.7, 36.4, 33.3, 30.5, 29.9, 27.8, 26.9, 17.9, –5.8; HRMS (ESI+): Calcd for $C_{22}H_{36}O_1Si_1Na_1$ $[M+Na]^+$: 367.2433,

Found: 367.2420. Optical Rotation: $[\alpha]_D^{20}$ –0.11 (*c* 1.43, $CHCl_3$) for an enantiomerically enriched sample of 96:4 er.

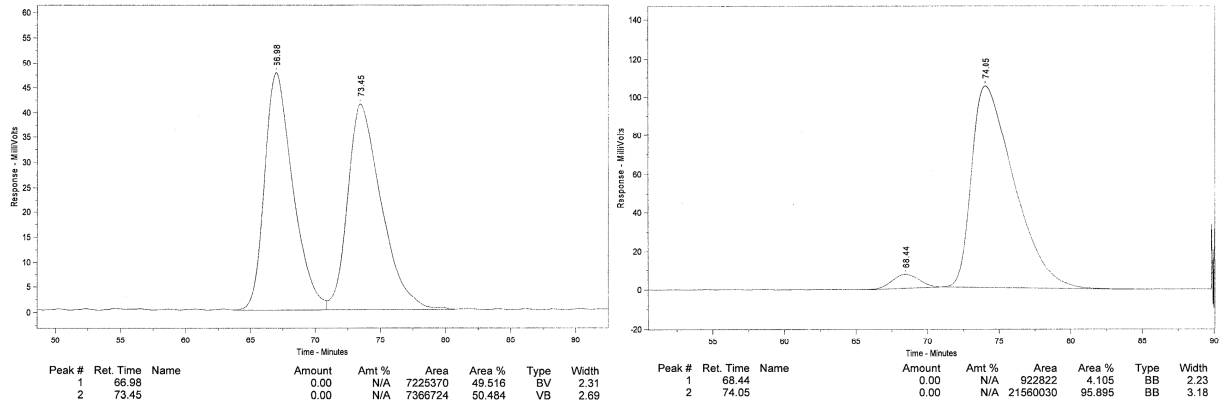
Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (95.8:4.2 er shown; Chiralcel OD column, 99/1 hexanes/*i*-PrOH, 0.2 mL/min, 220 nm).



Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	72.00	50.3	1	72.06	95.8
2	81.35	49.7	2	83.18	4.2

(*R*,*E*)-(8-Chloro-3-methylocta-1,4-dien-3-yl)dimethyl(phenyl)silane (5, Scheme 3). IR (neat): 2957 (w), 1621 (w), 1427 (w), 1247 (m), 1112 (m), 974 (m), 896 (m), 810 (s), 773 (s), 735 (s), 699 (s), 653 (s), 471 (m), 409 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.47–7.45 (2H, m), 7.37–7.33 (3H, m), 5.91 (1H, dd, *J* = 17.6, 11.2 Hz), 5.61 (1H, d, *J* = 15.2 Hz), 5.06 (1H, dt, *J* = 15.6, 6.4 Hz), 4.92 (1H, dd, *J* = 11.2, 1.2 Hz), 4.75 (1H, dd, *J* = 17.6, 1.2 Hz), 3.49 (2H, t, *J* = 6.8 Hz), 2.18 (2H, dt, *J* = 6.4, 6.4 Hz), 1.80 (2H, q, *J* = 7.2 Hz), 1.10 (3H, s), 0.27 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 136.6, 135.8, 134.9, 129.3, 127.6, 124.4, 110.2, 44.7, 36.7, 32.7, 30.4, 17.9, –5.8, –5.8; HRMS (ESI+): Calcd for $C_{17}H_{25}Cl_1Si_1Na_1$ $[M+Na]^+$: 315.1312, Found: 315.1319. Optical Rotation: $[\alpha]_D^{20}$ +0.92 (*c* 2.76, $CHCl_3$) for an enantiomerically enriched sample of 96:4 er.

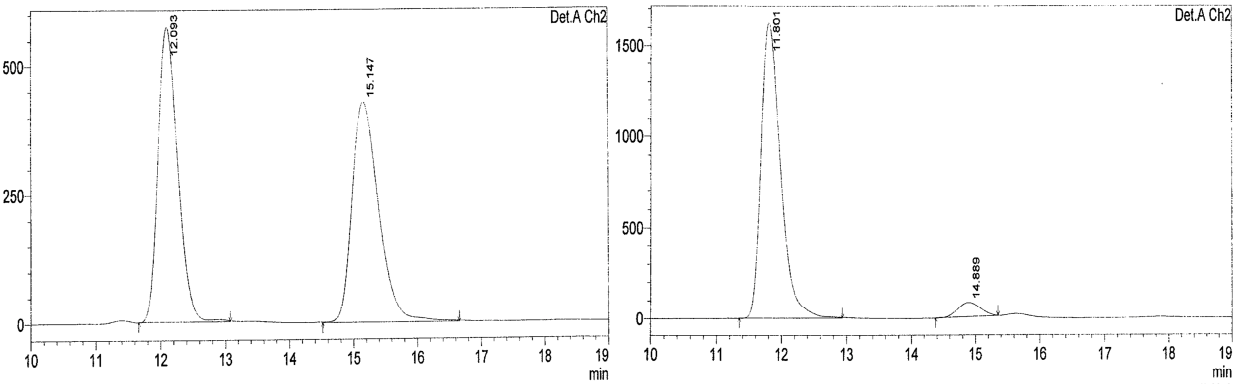
Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (95.9:4.1 er shown; Chiralpak AS column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	66.98	49.5	1	68.44	4.1
2	73.45	50.5	2	74.05	95.9

(*R*,*Z*)-(6-(*tert*-Butoxy)-3-methylhexa-1,4-dien-3-yl)dimethyl(phenyl)silane (6, Scheme 3). IR (neat): 2971 (m), 1363 (m), 1248 (m), 1196 (m), 1111 (m), 1069 (m), 892 (m), 808 (s), 773 (s), 735 (s), 700 (s), 654 (m), 474 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53–7.51 (2H, m), 7.38–7.33 (3H, m), 6.04 (1H, dd, *J* = 17.2, 10.4 Hz), 5.47 (1H, d, *J* = 12.4 Hz), 5.40, (1H, dt, *J* = 11.6, 5.6 Hz), 4.97 (1H, d, *J* = 10.8 Hz), 4.81 (1H, dd, *J* = 17.6, 0.8 Hz), 3.87 (1H, dd, *J* = 11.2, 5.6 Hz), 3.77 (1H, ddd, *J* = 12.0, 6.0, 1.2 Hz), 1.25 (3H, s), 1.14 (9H, s), 0.32 (3H, s), 0.31 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 136.4, 135.0, 133.9, 129.3, 127.9, 127.6, 110.3, 72.9, 58.8, 37.2, 27.8, 19.2, –5.9; HRMS (ESI+): Calcd for $C_{19}H_{30}O_1Si_1Na_1$ $[M+Na]^+$: 325.1964, Found: 325.1973. Optical Rotation: $[\alpha]_D^{20}$ –26.78 (*c* 1.63, $CHCl_3$) for an enantiomerically enriched sample of 94.8:5.2 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (94.8:5.2 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).

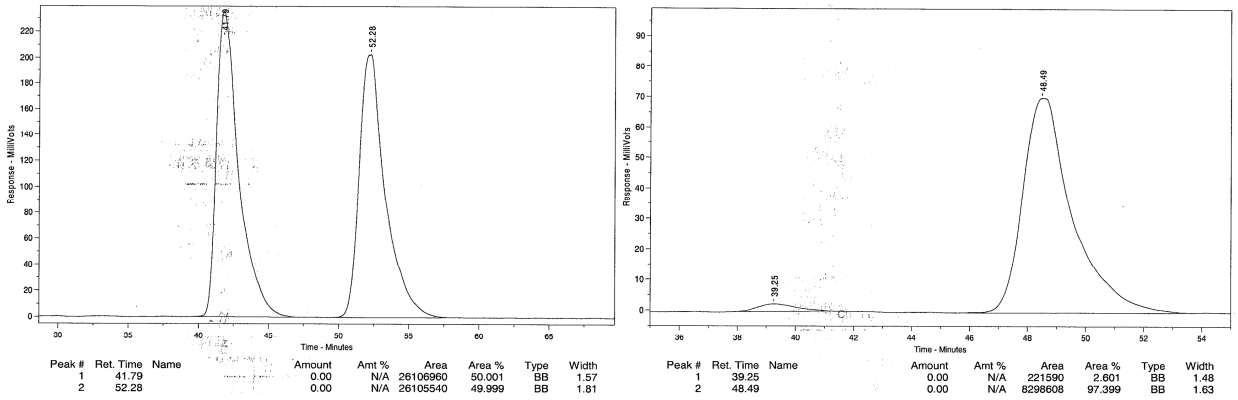


Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	12.09	49.4	1	11.80	94.8

2	15.15	50.6	2	14.89	5.2

(*R*,*E*)-1-Bromo-2-(1-(cyclohex-1-en-1-yl)-3-methylpenta-1,4-dien-3-yl)benzene (7, Scheme 4). IR (neat): 2925 (m), 1463 (m), 1018 (s), 963 (s), 911 (s), 791 (w), 756 (s), 645 (m), 454 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (1H, dd, *J* = 8.0, 1.6 Hz), 7.46 (1H, dd, *J* = 8.0, 1.6 Hz), 7.26 (1H, dt, *J* = 7.6, 1.2 Hz), 7.08 (1H, dt, *J* = 8.0, 1.6 Hz), 6.22 (1H, dd, *J* = 17.2, 10.4 Hz), 5.92 (2H, s), 5.66–5.64 (1H, m), 5.13 (1H, dd, *J* = 10.8, 1.2 Hz), 4.97 (1H, dd, *J* = 17.6, 0.8 Hz), 2.22–2.18 (2H, m), 2.13–2.09 (2H, m), 1.70–1.65 (2H, m), 1.66 (3H, s), 1.63–1.59 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 145.2, 135.9, 135.6, 132.9, 132.2, 129.7, 128.5, 128.1, 127.2, 124.0, 112.9, 48.7, 26.1, 26.0, 24.8, 22.83, 22.78; HRMS (ESI+): Calcd for $C_{18}H_{22}Br_1$ $[M+H]^+$: 317.0905, Found: 317.0906. Optical Rotation: $[\alpha]_D^{20}$ –27.4 (*c* 1.29, $CHCl_3$) for an enantiomerically enriched sample of 97.5:2.5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (97.4:2.6 er shown; Chiralcel OD column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).

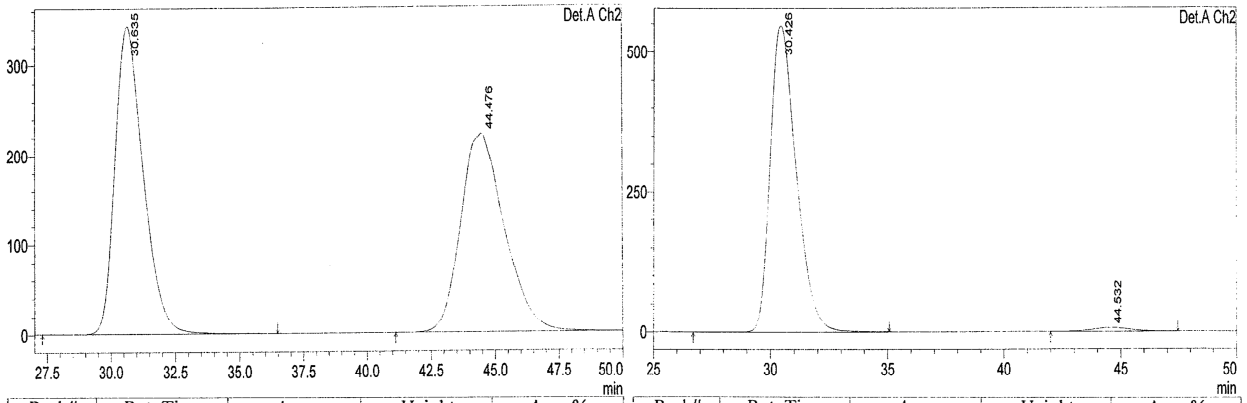


Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	41.79	50.0	1	39.25	2.6
2	52.28	50.0	2	48.49	97.4

(*R*,*E*)-1-Bromo-2-(3-methyl-1-phenylpenta-1,4-dien-3-yl)benzene (8, Scheme 4). IR (neat): 3080 (w), 3057 (w), 3024 (w), 2971 (w), 2918 (w), 2849 (w), 1630 (w), 1597 (w), 1491 (w), 1464 (w), 1427 (w), 1368 (w), 1018 (m), 963 (m), 912 (m), 746 (s), 690 (s), 646 (w), 458 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (1H, dd, *J* = 8.0, 1.6 Hz), 7.51 (1H, dd, *J* = 7.6, 1.6 Hz), 7.38 (2H, dd, *J* = 8.4, 1.2 Hz), 7.32–7.27 (3H, m), 7.21 (1H, tt, *J* = 6.8, 2.0 Hz), 7.11, (1H, dt, *J* = 8.0, 2.0 Hz), 6.57 (1H, d, *J* = 16.0 Hz), 6.33–6.25 (2H, m), 5.19 (1H, dd, *J* = 10.4, 0.8 Hz), 5.04 (1H, dd, *J* = 17.6, 1.2 Hz), 1.75 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 144.6, 137.9, 137.2, 135.6, 131.7, 129.7, 128.7, 128.5, 128.2, 127.2, 126.3, 123.9, 113.4, 49.0, 26.0; HRMS (ESI+): Calcd for $C_{18}H_{18}Br_1$ $[M+H]^+$: 313.0592, Found: 313.0589. Optical Rotation: $[\alpha]_D^{20}$ –31.12 (*c* 0.91, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in

comparison with authentic racemic material (98.2:1.8 er shown; Chiralcel OJ-H column, 95/5 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



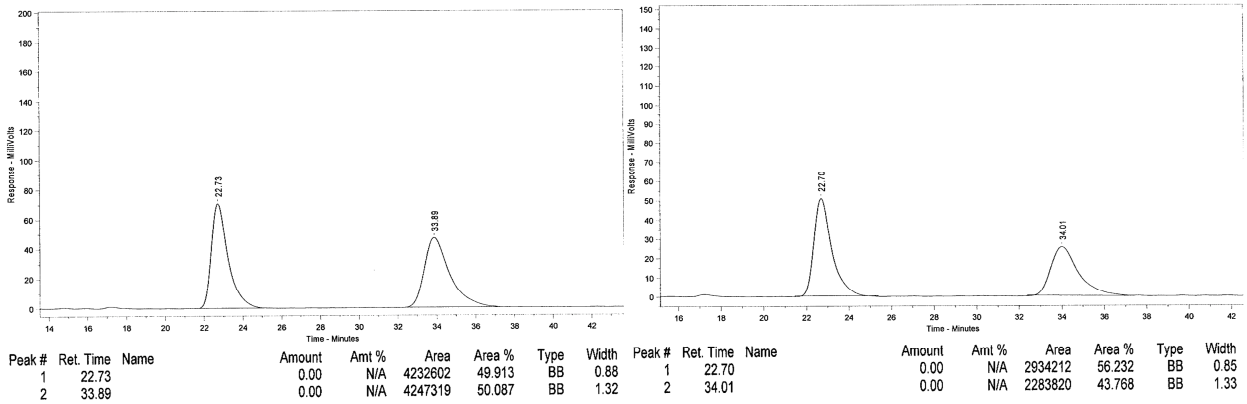
Peak#	Ret. Time	Area	Height	Area %
1	30.635	26267229	342739	50.004
2	44.476	26263306	221259	49.996
Total		52530535	563998	100.000

Peak#	Ret. Time	Area	Height	Area %
1	30.426	41880649	546331	98.173
2	44.532	779598	6637	1.827
Total		42660247	552968	100.000

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	30.64	50.0	1	30.43	98.2
2	44.48	50.0	2	44.53	1.8

(*R*,*Z*)-(1-(4-Methoxyphenyl)-3,7-dimethyl-3-vinylocta-1,6-dien-2-yl)trimethylsilane (11, Scheme 5). IR (neat): 2964 (w), 2929 (w), 2835 (w), 1609 (w), 1505 (s), 1464 (w), 1283 (w), 1244 (s), 1172 (m), 1038 (m), 911 (w), 835 (s), 763 (s), 679 (w), 646 (w), 573 (w), 514 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (1H, s), 7.04 (2H, dd, *J* = 8.8, 1.2 Hz), 6.80 (2H, d, *J* = 8.8 Hz), 5.95 (1H, dd, *J* = 17.6, 10.8 Hz), 5.14–5.09 (1H, m), 5.04–4.97 (2H, m), 3.80 (3H, s), 1.94 (2H, dt, *J* = 8.0, 8.0 Hz), 1.75–1.68 (4H, m), 1.60–1.50 (4H, m), 1.23 (3H, s), –0.09 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 149.5, 148.2, 141.8, 134.1, 131.3, 129.9, 125.1, 113.2, 112.1, 55.4, 47.7, 39.9, 25.9, 25.7, 23.7, 17.9, 3.9; HRMS (ESI+): Calcd for $C_{22}H_{35}O_1Si_1$ $[M+H]^+$: 343.2457, Found: 343.2457.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (56.2:43.8 er shown; Chiralcel OD column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	22.73		0.00	N/A	4232602	49.913	BB	0.88
2	33.89		0.00	N/A	4247319	50.087	BB	1.32

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	22.70		0.00	N/A	2934212	56.232	BB	0.85
2	34.01		0.00	N/A	2283820	43.768	BB	1.33

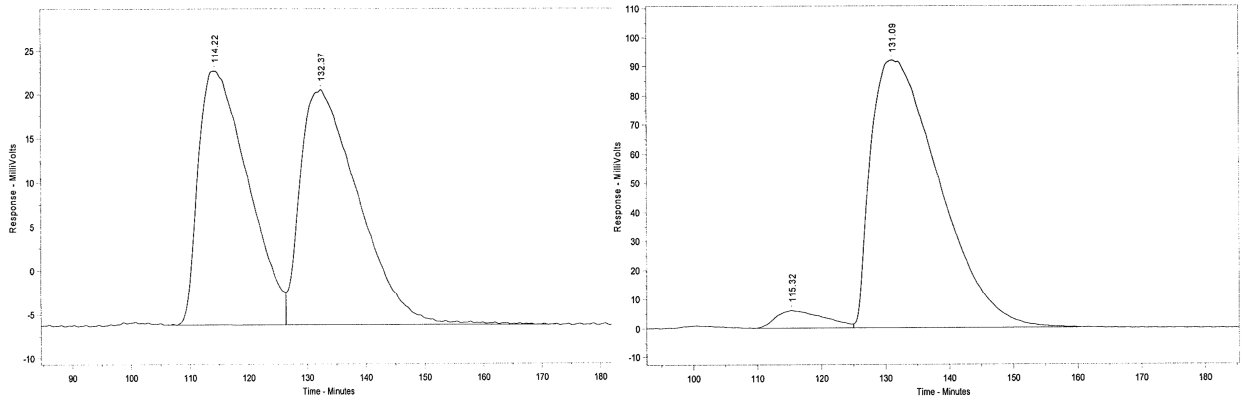
Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%

1	22.73	49.9	1	22.70	56.2
2	33.89	50.1	2	34.01	43.8

■ **General Procedure for Catalytic Hydroalumination of Aryl-substituted Terminal Alkynes with $Ni(PPh_3)_2Cl_2$ (Table 2, Scheme 6 and 7):** Commercial grade bis(triphenylphosphine)nickel dichloride ($Ni(PPh_3)_2Cl_2$, 19.6 mg, 0.0300 mmol) is placed in an oven-dried 13 x 100 mm test tube equipped with a stir bar. The vessel is sealed with a septum and purged with N_2 for approximately ten minutes. Tetrahydrofuran (thf, 1.0 mL) is added through a syringe, followed by dropwise addition of dibal–H (232 μL, 1.3 mmol) at 22 °C (gas evolution occurs as dibal–H is added). The resulting black solution is allowed to cool to 0 °C (ice bath) before phenylacetylene (110 μL, 1.0 mmol) is added slowly over five minutes (reaction is exothermic). The resulting black solution is allowed to warm to 22 °C and stir for additional two hours and used without further purification.

■ **General Procedure for NHC–Cu-catalyzed Enantioselective Allylic Substitutions with Aryl-substituted Vinylaluminum Reagents (Table 2 and Scheme 6 and 7):** A 13 x 100 mm test tube equipped with a stir bar is charged with NHC–Ag complex **1c** (2.3 mg, 0.0020 mmol) in an N_2-filled glovebox. The vessel is sealed with a septum and removed from the glovebox. Tetrahydrofuran (1.0 mL) and a solution of $CuCl_2•2H_2O$ (0.02M in thf, 200 μL, 0.0040 mmol) are added to the test tube at 22 °C. The resulting blue solution is allowed to cool to –78 °C (dry ice/acetone), followed by the addition of the aryl-substituted vinylaluminum reagent (0.745 M in thf, 403 μL, 0.300 mmol) and a solution of (*E*)-diethyl (3-phenylbut-2-en-1-yl) phosphate (56.9 mg, 0.200 mmol) in thf (1.0 mL). The mixture is allowed to warm to –15 °C and sit in a freezer for three hours, after which time, the reaction is quenched by addition of a saturated aqueous solution of Rochelle's salt (2.0 mL) at –78 °C and the resulting mixture is allowed to warm to 22 °C and stir for one hour. The layers are separated, and the aqueous layer is washed with Et_2O (2.0 mL x 3). The combined organic layers are passed through a short plug of $MgSO_4$, and concentrated under reduced pressure. The resulting yellow oil is purified by silica gel chromatography to give the product as colorless oil (36.6 mg, 0.156 mmol, 78% yield). **(*R*,*E*)-(3-Methylpenta-1,4-diene-1,3-diyl)dibenzene (entry 1, Table 2).** IR (neat): 3082 (w), 3057 (w), 3025 (w), 2973 (w), 2917 (w), 2872 (w), 2849 (w), 1633 (w), 1598 (w), 1492 (m), 1445 (m), 1408 (w), 1368 (w), 1072 (w), 1029 (w), 971 (m), 916 (m), 748 (s), 694 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34–7.29 (4H, m), 7.28–7.22 (4H, m), 7.18–7.13 (2H, m), 6.39 (1H, d, *J* = 16.0 Hz), 6.29 (1H, d, *J* = 16.0 Hz), 6.09 (1H, dd, *J* = 17.6, 10.4 Hz), 5.11 (1H, dd, *J* = 10.8, 1.2 Hz), 5.00 (1H, dd, *J* = 17.6, 1.2 Hz), 1.55 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 145.2, 137.7, 137.3, 131.7, 128.7, 128.4, 128.2, 127.4, 127.3, 126.4, 113.2, 48.0, 25.7; HRMS (ESI+): Calcd for $C_{18}H_{19}$ $[M+H]^+$: 235.1487, Found: 235.1476. Optical Rotation: $[\alpha]_D^{20}$ +33.80 (*c* 2.02, $CHCl_3$) for an enantiomerically enriched sample of 96:4 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (95.6:4.4 er shown; Chiralpak AS column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



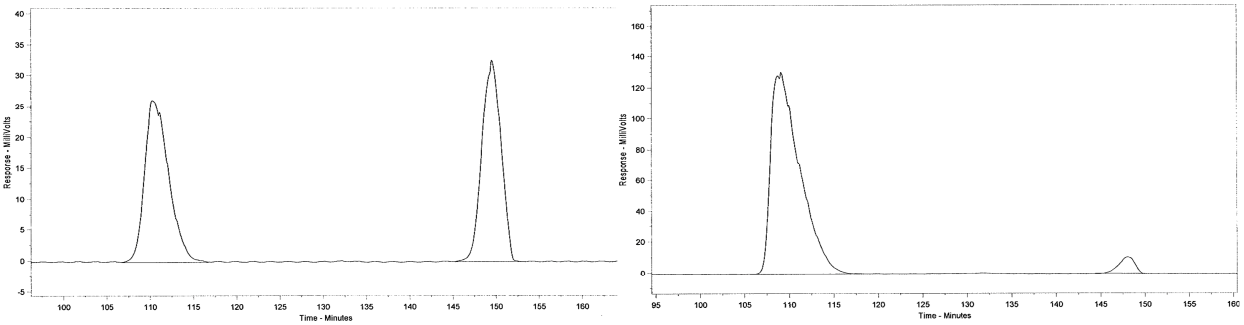
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	114.22		0.00	N/A	17014080	47.981	BV	9.66
2	132.37		0.00	N/A	18446020	52.019	VB	10.87

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	115.32		0.00	N/A	3135952	4.376	BV	9.13
2	131.09		0.00	N/A	68528960	95.624	VB	11.91

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	114.22	48.0	1	115.32	4.4
2	132.37	52.0	2	131.09	95.6

(*R*,*E*)-1-Methyl-2-(3-methyl-3-phenylpenta-1,4-dien-1-yl)benzene (entry 2, Table 2). Spectra were recorded with samples containing 12% alkynyl adduct. IR (neat): 3059 (w), 3021 (w), 2958 (m), 2924 (m), 2854 (m), 1634 (w), 1600 (w), 1490 (m), 1459 (m), 1378 (w), 1029 (w), 951 (m), 916 (m), 747 (s), 698 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48–7.46 (1H, m), 7.42–7.38 (2H, m), 7.37–7.32 (2H, m), 7.26–7.21 (2H, m), 7.19–7.14 (2H, m), 6.59 (1H, d, *J* = 16.0 Hz), 6.33 (1H, d, *J* = 16.0 Hz), 6.20 (1H, dd, *J* = 17.2, 10.4 Hz), 5.21 (1H, dd, *J* = 10.8, 1.2 Hz), 5.10 (1H, dd, *J* = 17.6, 1.2 Hz), 2.33 (3H, s), 1.64 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 145.3, 138.8, 137.0, 135.5, 132.1, 130.3, 128.3, 127.4, 127.3, 126.4, 126.2, 125.8, 113.2, 48.1, 25.8, 20.0; HRMS (ESI+): Calcd for $C_{19}H_{21}$ $[M+H]^+$: 249.1643, Found: 249.1643. Optical Rotation: $[\alpha]_D^{20}$ –29.53 (*c* 1.63, $CHCl_3$) for an enantiomerically enriched sample of 95:5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (95.9:4.1 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	110.25		0.00	N/A	5077918	50.217	BB	2.99
2	149.52		0.00	N/A	5034133	49.784	BB	2.51

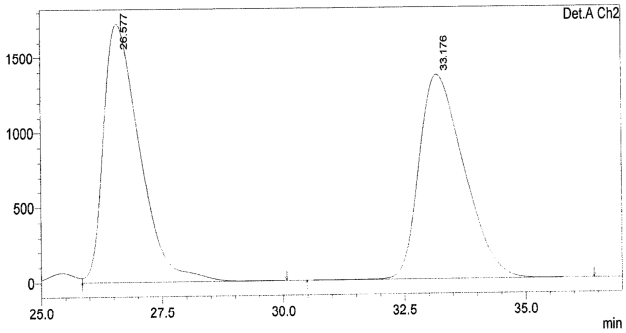
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	109.14		0.00	N/A	29436000	95.854	BB	3.51
2	148.03		0.00	N/A	1273114	4.146	BB	1.99

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	110.25	50.2	1	109.14	95.9

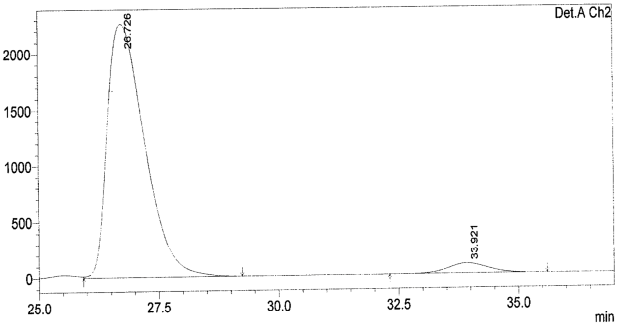
2	149.52	49.8	2	148.03	4.1

(*R*,*E*)-1-Methoxy-4-(3-methyl-3-phenylpenta-1,4-dien-1-yl)benzene (entry 3, Table 2). IR (neat): 3082 (w), 3056 (w), 3030 (w), 3021 (w), 2970 (w), 2933 (w), 2835 (w), 1607 (m), 1510 (s), 1443 (w), 1280 (w), 1246 (s), 1174 (m), 1034 (m), 972 (w), 917 (w), 808 (w), 762 (m), 700 (m), 533 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.30 (6H, m), 7.22 (1H, tt, *J* = 6.4, 2.0 Hz), 6.88–6.84 (2H, m), 6.33 (2H, s), 6.17 (1H, dd, *J* = 17.6, 10.4 Hz), 5.18 (1H, dd, *J* = 10.4, 1.2 Hz), 5.07 (1H, dd, *J* = 17.2, 1.2 Hz), 3.81 (3H, s), 1.60 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 146.7, 145.4, 135.2, 130.4, 128.3, 127.6, 127.5, 127.4, 126.3, 114.1, 113.0, 55.5, 47.9, 25.8; HRMS (ESI+): Calcd for $C_{19}H_{21}O_1$ $[M+H]^+$: 265.1592, Found: 265.1590. Optical Rotation: $[\alpha]_D^{20}$ +24.49 (*c* 1.16, $CHCl_3$) for an enantiomerically enriched sample of 96.5:3.5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (95.9:4.1 er shown; Chiralcel OD-H column, 97/3 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm).



Peak#	Ret. Time	Area	Height	Area %
1	26.577	89643798	1722114	50.446
2	33.176	88057866	1364330	49.554
Total		177701664	3086445	100.000

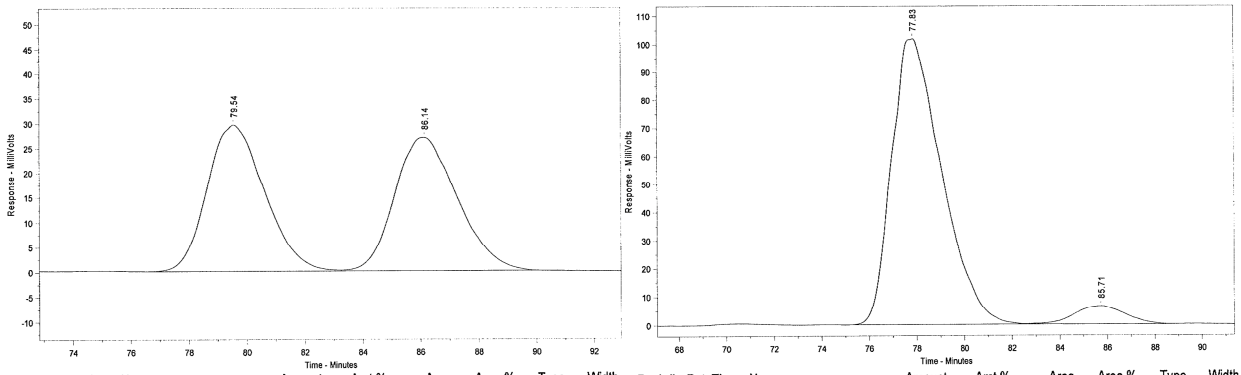


Peak#	Ret. Time	Area	Height	Area %
1	26.726	122902957	2263135	95.916
2	33.921	5233178	90344	4.084
Total		128136135	2353479	100.000

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	26.58	50.4	1	26.73	95.9
2	33.18	49.6	2	33.92	4.1

(*R*,*E*)-1-(3-Methyl-3-phenylpenta-1,4-dien-1-yl)-4-(trifluoromethyl)benzene (entry 4, Table 2). IR (neat): 2924 (m), 2854 (w), 1615 (w), 1323 (s), 1165 (m), 1125 (s), 1067 (s), 1016 (w), 975 (w), 919 (w), 815 (w), 762 (w), 699 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (2H, d, *J* = 8.4 Hz), 7.48 (2H, d, *J* = 8.4 Hz), 7.38–7.32 (4H, m), 7.27–7.22 (1H, m), 6.57 (1H, d, *J* = 16.0 Hz), 6.40 (1H, d, *J* = 16.0 Hz), 6.17 (1H, dd, *J* = 17.6, 10.4 Hz), 5.22 (1H, dd, *J* = 10.8, 1.2 Hz), 5.09 (1H, dd, *J* = 17.6, 1.2 Hz), 1.63 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 144.8 (q, *J* = 5.2 Hz), 141.2 (q, *J* = 1.5 Hz), 140.0 (q, *J* = 3.0 Hz), 132.1, 129.2 (q, *J* = 32.0 Hz), 128.5, 127.3, 127.1 (q, *J* = 3.8 Hz), 126.6 (q, *J* = 4.5 Hz), 125.7 (q, *J* = 10.4 Hz), 124.4 (q, *J* = 270.0 Hz), 113.6 (q, *J* = 3.0 Hz), 48.1, 25.6; HRMS (ESI+): Calcd for $C_{19}H_{18}F_3$ $[M+H]^+$: 303.1361, Found: 303.1373. Optical Rotation: $[\alpha]_D^{20}$ –26.78 (*c* 2.47, $CHCl_3$) for an enantiomerically enriched sample of 94:6 er.

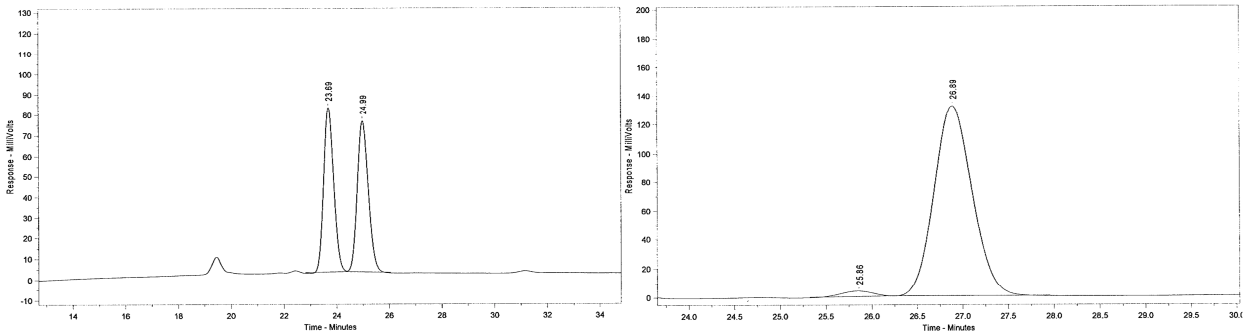
Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (94.0:6.0 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	79.54	50.2	1	77.83	94.0
2	86.14	49.8	2	85.71	6.0

(*R*,*E*)-1-(3-Methyl-1-phenylpenta-1,4-dien-3-yl)-2-nitrobenzene (entry 6, Table 2). IR (neat): 3082 (w), 3026 (w), 2925 (w), 2854 (w), 1528 (s), 1366 (s), 971 (m), 909 (s), 852 (m), 777 (m), 731 (s), 692 (s), 649 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (1H, dd, *J* = 8.0, 1.2 Hz), 7.50–7.46 (2H, m), 7.38–7.29 (5H, m), 7.23 (1H, tt, *J* = 6.4, 1.6 Hz), 6.40 (1H, d, *J* = 16.4 Hz), 6.35 (1H, d, *J* = 16.4 Hz), 6.10 (1H, dd, *J* = 17.6, 10.4 Hz), 5.18 (1H, d, *J* = 10.8 Hz), 5.13 (1H, d, *J* = 17.6 Hz), 1.79 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 142.7, 138.8, 137.2, 134.8, 131.4, 130.4, 128.8, 128.7, 127.8, 127.6, 126.5, 124.5, 113.8, 47.7, 25.6; HRMS (ESI+): Calcd for $C_{18}H_{18}N_1O_2$ $[M+H]^+$: 280.1338, Found: 280.1327. Optical Rotation: $[\alpha]_D^{20}$ –23.19 (*c* 1.71, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

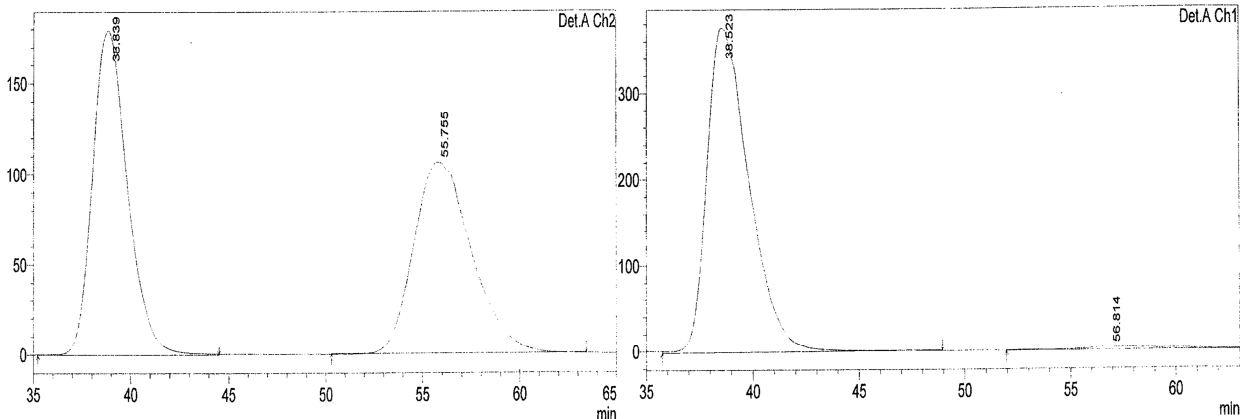
Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (97.8:2.2 er shown; Chiralcel OD-H column, 99.5/0.5 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	23.69	49.7	1	25.86	2.2
2	24.99	50.3	2	28.89	97.8

(*R*,*E*)-1-(1-(4-Methoxyphenyl)-3-methylpenta-1,4-dien-3-yl)-2-methylbenzene (entry 7, Table 2). IR (neat): 3000 (w), 2968 (w), 2932 (w), 2835 (w), 1607 (m), 1510 (s), 1248 (s), 1175 (m), 1036 (m), 972 (w), 915 (w), 815 (w), 759 (w), 730 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.42–7.40 (1H, m), 7.29–7.25 (2H, m), 7.19–7.13 (3H, m), 6.85–6.80 (2H, m), 6.38 (1H, d, *J* = 16.0 Hz), 6.25–6.15 (2H, m), 5.11 (1H, dd, *J* = 10.8, 1.2 Hz), 4.95 (1H, dd, *J* = 17.2, 1.2 Hz), 3.80 (3H, s), 2.33 (3H, s), 1.62 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 145.4, 144.1, 137.4, 135.5, 132.3, 130.5, 127.5, 127.2, 126.9, 126.5, 125.6, 113.9, 112.3, 55.3, 48.2, 27.0, 22.6; HRMS (ESI+): Calcd for $C_{20}H_{21}O_1$ $[M+H]^+$: 277.1592, Found: 277.1598. Optical Rotation: $[\alpha]_D^{20}$ –14.23 (*c* 1.07, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (98.1:1.9 er shown; Chiralcel OJ-H column, 95/5 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm).



Peak#	Ret. Time	Area	Height	Area %
1	38.839	22537602	179456	50.954
2	55.755	21693733	106012	49.046
Total		44231335	285468	100.000

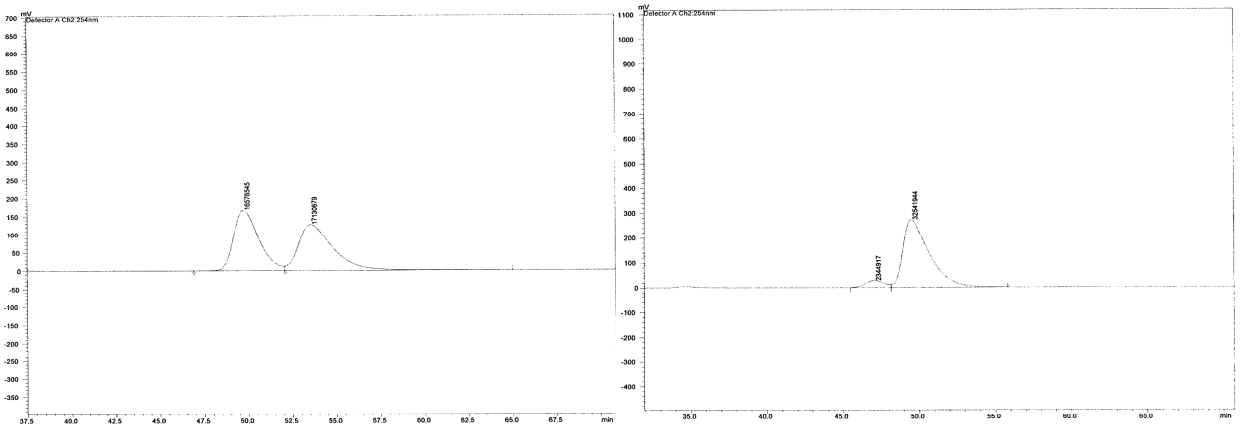
Peak#	Ret. Time	Area	Height	Area %
1	38.523	51401863	376815	98.122
2	56.814	983787	3129	1.878
Total		52385650	379944	100.000

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	38.84	51.0	1	38.52	98.1
2	55.76	49.0	2	56.81	1.9

(*R*,*E*)-1-(3-Methyl-1-phenylpenta-1,4-dien-3-yl)-4-nitrobenzene (entry 8, Table 2). IR (neat): 3082 (w), 3026 (w), 2974 (w), 2931 (w), 2852 (w), 1596 (m), 1514 (s), 1343 (s), 1111 (w), 1068 (w), 971 (m), 919 (m), 852 (s), 748 (s), 735 (s), 692 (s), 613 (w), 537 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.19–8.15 (2H, m), 7.55–7.52 (2H, m), 7.40–7.37 (2H, m), 7.34–7.31 (2H, m), 7.27–7.25 (1H, m), 6.44–6.35 (2H, m), 6.14 (1H, dd, *J* = 17.6, 10.8 Hz), 5.27 (1H, dd, *J* = 10.4, 0.8 Hz), 5.10 (1H, dd, *J* = 17.6, 0.8 Hz), 1.64 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 146.6, 143.8, 137.0, 135.5, 129.5, 128.8, 128.4, 127.8, 126.5, 123.6, 114.5, 48.3, 25.8; HRMS

(ESI+): Calcd for $C_{18}H_{18}N_1O_2$ $[M+H]^+$: 280.1338, Found: 280.1339. Optical Rotation: $[\alpha]_D^{20}$ –20.37 (*c* 2.42, $CHCl_3$) for an enantiomerically enriched sample of 93:7 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (93.7:6.3 er shown; Chiralcel OJ-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm).



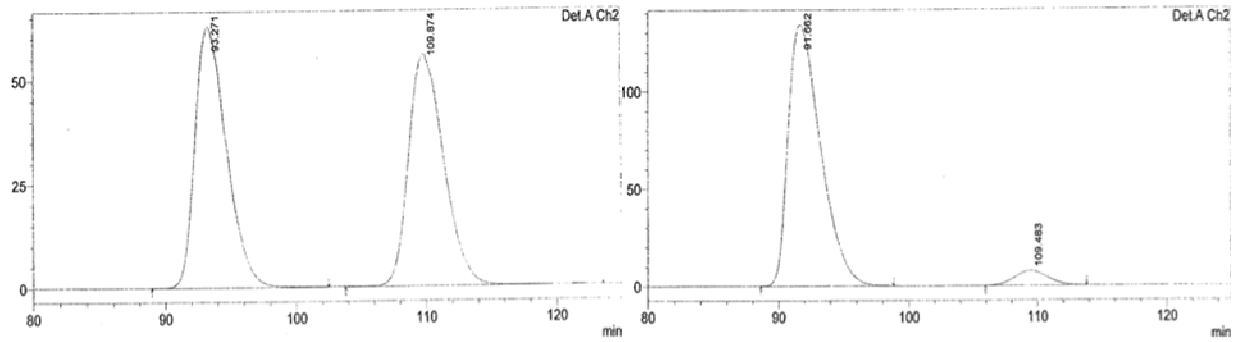
Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.706	16576545	166872	49.178	56.845
2	53.528	17130679	126687	50.822	43.155
Total		33707225	293559	100.000	100.000

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.062	2344917	27231	6.721	9.125
2	49.485	32541944	271196	93.279	90.875
Total		34886861	298427	100.000	100.000

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	49.71	49.2	1	47.06	6.7
2	53.53	50.8	2	49.49	93.3

(*R*,*E*)-1-Methoxy-4-(3-methyl-3-(4-(trifluoromethyl)phenyl)penta-1,4-dien-1-yl)benzene (entry 9, Table 2). IR (neat): 2957 (w), 2926 (w), 2854 (w), 1608 (w), 1511 (m), 1326 (s), 1248 (m), 1165 (m), 1123 (s), 1076 (m), 1036 (w), 1016 (w), 973 (w), 921 (w), 841 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (2H, d, *J* = 8.0 Hz), 7.48 (2H, d, *J* = 8.0 Hz), 7.34–7.30 (2H, m), 6.87–6.84 (2H, m), 6.32 (1H, d, *J* = 16.4 Hz), 6.26 (1H, d, *J* = 16.4 Hz), 6.13 (1H, dd, *J* = 17.2, 10.4 Hz), 5.22 (1H, dd, *J* = 10.8, 1.2 Hz), 5.07 (1H, dd, *J* = 17.6, 1.2 Hz), 3.81 (3H, s), 1.60 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 150.9, 144.6, 134.2, 130.1, 128.6 (q, *J* = 32.0 Hz), 128.4, 127.8, 127.6, 125.2 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 270.1 Hz), 114.2, 113.8, 55.5, 48.0, 25.8; HRMS (ESI+): Calcd for $C_{20}H_{20}F_3O_1$ $[M+H]^+$: 333.1466, Found: 333.1480. Optical Rotation: $[\alpha]_D^{20}$ –22.91 (*c* 1.11, $CHCl_3$) for an enantiomerically enriched sample of 94:6 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (94.0:6.0 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



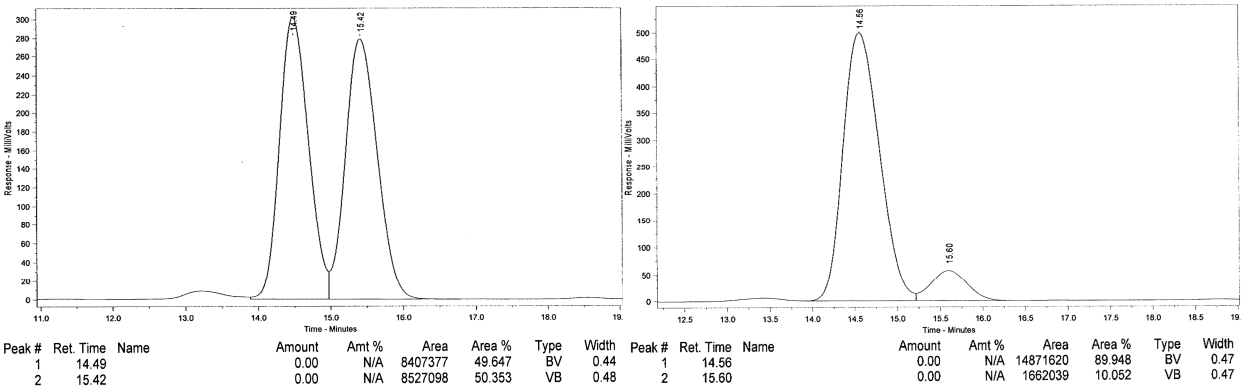
Peak#	Ret. Time	Area	Height	Area %
1	93.271	10594147	62857	50.263
2	109.874	10483365	55838	49.737
Total		21077512	118695	100.000

Peak#	Ret. Time	Area	Height	Area %
1	91.650	18888094	106429	93.976
2	109.481	1210681	6303	6.024
Total		20098775	112731	100.000

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	93.27	50.3	1	91.65	94.0
2	109.87	49.7	2	109.48	6.0

(*R*,*E*)-(3,7-Dimethyl-3-vinylocta-1,6-dien-1-yl)benzene (entry 10, Table 2). IR (neat): 3082 (w), 3059 (w), 3026 (w), 2966 (w), 2915 (w), 2854 (w), 1633 (w), 1598 (w), 1492 (w), 1447 (w), 1374 (w), 968 (m), 912 (m), 831 (w), 745 (s), 691 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.37 (2H, m), 7.33–7.29 (2H, m), 7.21 (1H, tt, *J* = 6.4, 1.6 Hz), 6.34 (1H, d, *J* = 16.8 Hz), 6.22 (1H, d, *J* = 16.0 Hz), 5.91 (1H, dd, *J* = 17.2, 10.8 Hz), 5.15–5.11 (1H, m), 5.08–5.02 (2H, m), 1.98 (2H, dt, *J* = 7.6, 7.6 Hz), 1.69 (3H, s), 1.60 (3H, s), 1.55–1.50 (2H, m), 1.23 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 138.05, 138.03, 131.5, 128.6, 127.4, 127.1, 126.2, 124.9, 112.2, 42.8, 41.4, 25.8, 23.5, 23.4, 17.8; HRMS (ESI+): Calcd for $C_{18}H_{25}$ $[M+H]^+$: 241.1956, Found: 241.1945. Optical Rotation: $[\alpha]_D^{20}$ +23.80 (*c* 1.83, $CHCl_3$) for an enantiomerically enriched sample of 90:10 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (89.9:10.1 er shown; Chiralcel OD-H column, 95/5 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	14.49		0.00	N/A	8407377	49.647	BV	0.44
2	15.42		0.00	N/A	8527098	50.353	VB	0.48

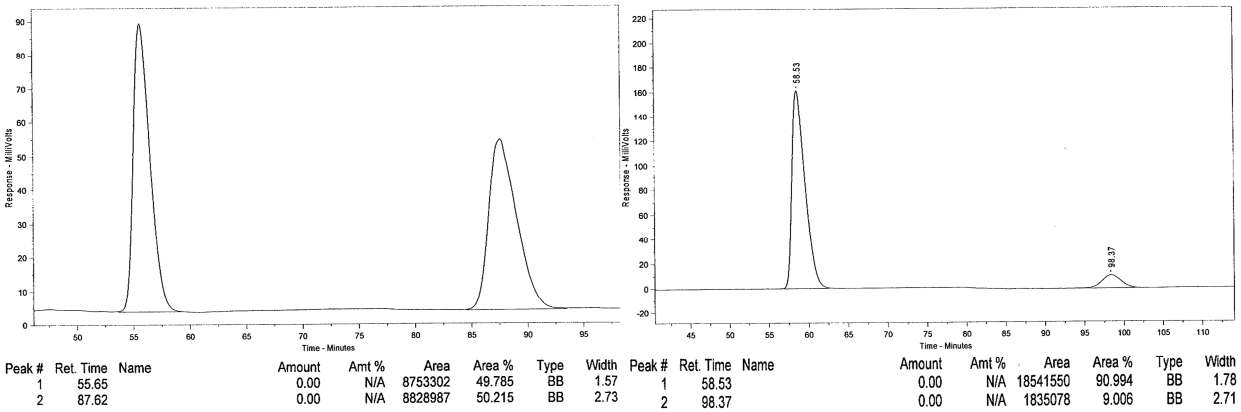
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	14.56		0.00	N/A	14871620	89.948	BV	0.47
2	15.60		0.00	N/A	1662039	10.052	VB	0.47

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	14.49	49.6	1	14.56	89.9

2	15.42	50.4	2	15.60	10.1

(*R*,*E*)-1-(3,7-Dimethyl-3-vinylocta-1,6-dien-1-yl)-2-methylbenzene (entry 11, Table 2). Spectra are taken in the presence of 14% alkynyl adduct. IR (neat): 3019 (w), 2967 (m), 2921 (m), 2856 (w), 1636 (w), 1602 (w), 1511 (w), 1484 (w), 1457 (m), 1376 (w), 1248 (w), 1036 (w), 972 (m), 914 (m), 748 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.43–7.40 (1H, m), 7.20–7.11 (3H, m), 6.53 (1H, d, *J* = 16.4 Hz), 6.07 (1H, d, *J* = 16.4 Hz), 5.92 (1H, dd, *J* = 17.6, 10.8 Hz), 5.16–5.10 (1H, m), 5.08–5.02 (2H, m), 2.34 (3H, s), 1.98 (2H, dt, *J* = 7.6, 7.6 Hz), 1.69 (3H, s), 1.60 (3H, s), 1.53–1.50 (2H, m), 1.23 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 143.6, 139.6, 137.4, 135.3, 132.1, 131.5, 130.2, 127.0, 126.2, 124.9, 112.2, 43.0, 42.4, 41.4, 25.8, 23.7, 23.4, 17.8; HRMS (ESI+): Calcd for $C_{19}H_{27}$ $[M+H]^+$: 255.2113, Found: 255.2115. Optical Rotation: $[\alpha]_D^{20}$ –23.46 (*c* 1.02, $CHCl_3$) for an enantiomerically enriched sample of 91:9 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (91.0:9.0 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	55.65		0.00	N/A	8753302	49.785	BB	1.57
2	87.62		0.00	N/A	8828987	50.215	BB	2.73

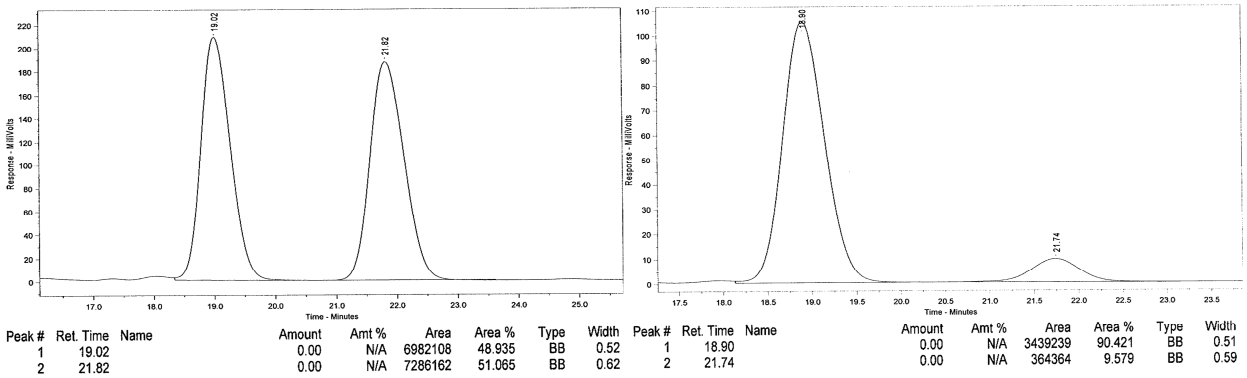
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	58.53		0.00	N/A	18541550	90.994	BB	1.78
2	98.37		0.00	N/A	1835078	9.006	BB	2.71

Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	55.65	49.8	1	58.53	91.0
2	87.62	50.2	2	98.37	9.0

(*R*,*E*)-1-(3,7-Dimethyl-3-vinylocta-1,6-dien-1-yl)-4-methoxybenzene (entry 12, Table 2). IR (neat): 2965 (m), 2916 (m), 1608 (m), 1510 (s), 1456 (w), 1280 (s), 1247 (m), 1037 (m), 970 (w), 913 (w), 815 (w), 527 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31–7.29 (2H, m), 6.86–6.84 (2H, m), 6.27 (1H, d, *J* = 16.4 Hz), 6.07 (1H, d, *J* = 16.4 Hz), 5.89 (1H, dd, *J* = 17.2, 10.8 Hz), 5.14–5.10 (1H, m), 5.06–5.00 (2H, m), 3.81 (3H, s), 1.96 (2H, dt, *J* = 7.6, 7.6 Hz), 1.68 (3H, s), 1.59 (3H, s), 1.53–1.48 (2H, m), 1.21 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 146.2, 136.0, 131.4, 130.9, 127.3, 126.7, 124.9, 114.1, 112.0, 55.5, 42.7, 41.5, 25.8, 23.5, 23.4, 17.8; HRMS (ESI+): Calcd for $C_{19}H_{27}O_1$ $[M+H]^+$: 271.2062, Found: 271.2064. Optical Rotation: $[\alpha]_D^{20}$ –25.16 (*c* 1.91, $CHCl_3$) for an enantiomerically enriched sample of 91:9 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in

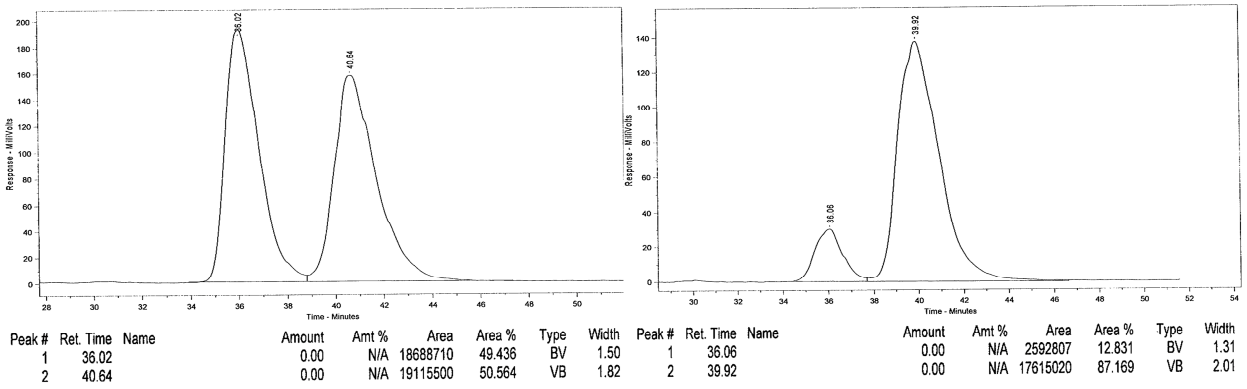
comparison with authentic racemic material (90.4:9.6 er shown; Chiralcel OD-H column, 97/3 hexanes/*i*-PrOH, 0.8 mL/min, 220 nm).



Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%
1	19.02	48.9	1	18.90	90.4
2	21.82	51.1	2	21.74	9.6

(*R*,*E*)-1-(3,7-Dimethyl-3-vinylocta-1,6-dien-1-yl)-4-(trifluoromethyl)benzene (entry 13, Table 2). IR (neat): 2969 (w), 2919 (w), 1616 (w), 1453 (w), 1413 (w), 1376 (w), 1323 (s), 1164 (m), 1124 (s), 1067 (m), 1016 (w), 973 (w), 916 (w), 817 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (2H, d, *J* = 8.4 Hz), 7.44 (2H, d, *J* = 8.4 Hz), 6.36 (1H, d, *J* = 16.0 Hz), 6.30 (1H, d, *J* = 16.0 Hz), 5.89 (1H, ddd, *J* = 17.2, 10.4, 0.8 Hz), 5.12–5.06 (2H, m), 5.03 (1H, dd, *J* = 17.2, 1.2 Hz), 1.96 (2H, dt, *J* = 7.2, 7.2 Hz), 1.68 (3H, s), 1.58 (3H, s), 1.55–1.50 (2H, m), 1.23 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 141.5 (q, *J* = 1.4 Hz), 140.9, 131.7, 128.9 (q, *J* = 32.0 Hz), 126.4, 126.2, 125.6 (q, *J* = 3.7 Hz), 124.7, 124.4 (q, *J* = 270.1 Hz), 112.6, 43.0, 41.3, 25.8, 23.4, 23.3, 17.8; HRMS (ESI+): Calcd for $C_{19}H_{24}F_3$ $[M+H]^+$: 309.1830, Found: 309.1830. Optical Rotation: $[\alpha]_D^{20}$ +13.68 (*c* 1.41, $CHCl_3$) for an enantiomerically enriched sample of 87:13 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (87.2:12.8 er shown; Chiralcel OJ-H column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



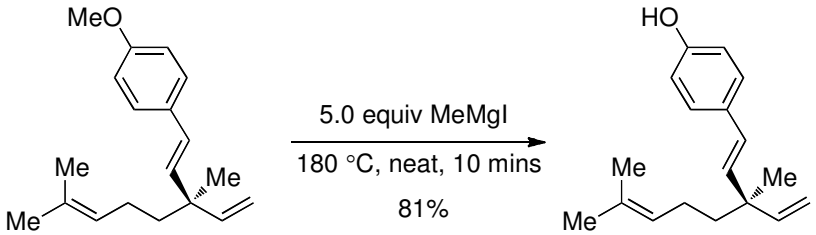
Peak#	Ret. Time	Area%	Peak#	Ret. Time	Area%

1	36.02	49.4	1	36.06	12.8
2	40.64	50.6	2	39.92	87.2

ν Enantioselective Synthesis of *R*-(–)-bakuchiol (Scheme 7): Procedure for Demethylation of Bakuchiol Methyl Ether (Compound in entry 12, Table 2). A flame-dried 6-dram vial is charged with bakuchiol methyl ether (21.4 mg, 0.079 mmol) and a stir bar. The vial is sealed with a septum and purged with N_2 flow for 10 minutes. Freshly prepared MeMgI in diethyl ether (990 μL, 0.396 mmol) is added to the reaction vessel and solvent is carefully removed under reduced pressure. The resulting mixture is heated in a 180 °C oil bath for 10 minutes (white smoke generated as the reaction goes on and disappears in 10 minutes), after which time, it is allowed to cool to 22 °C and diluted with Et_2O (5 mL). A saturated solution of NH_4Cl is added to quench the reaction and layers are separated. The aqueous layer is washed with Et_2O (5 mL x 3) and the combined organic layers are dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford a slightly yellow oil, which is subjected to silica gel chromatography (10:1 hexanes:ethyl acetate) to furnish the desired product as colorless oil (16.4 mg, 0.064 mmol, 81% yield). ***R*-(–)-Bakuchiol.** IR (neat): 3345 (br), 2966 (m), 2919 (m), 2862 (w), 1609 (m), 1511 (s), 1441 (m), 1374 (w), 1235 (m), 1171 (m), 970 (m), 914 (m), 813 (w), 527 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.27–7.24 (2H, m), 6.79–6.76 (2H, m), 6.25 (1H, d, *J* = 16.0 Hz), 6.06 (1H, d, *J* = 16.0 Hz), 5.88 (1H, dd, *J* = 17.2, 10.8 Hz), 5.13–5.09 (1H, m), 5.05–4.99 (2H, m), 4.74 (1H, br), 1.96 (2H, dt, *J* = 7.6, 7.6 Hz), 1.68 (3H, s), 1.58 (3H, s), 1.52–1.47 (2H, m), 1.20 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 146.1, 136.0, 131.5, 131.1, 127.5, 126.6, 125.0, 115.5, 112.0, 42.7, 41.4, 25.8, 23.5, 23.4, 17.8; HRMS (ESI+): Calcd for $C_{18}H_{25}O_1$ $[M+H]^+$: 257.1905, Found: 257.1903. Optical Rotation: $[\alpha]_D^{20}$ –23.81 (*c* 1.14, $CHCl_3$) for an enantiomerically enriched sample of 91:9 er.

ν Correlation of Stereochemistry: The stereochemical identity of bakuchiol derived from bakuchiol methyl ether in entry 12, Table 2 is determined to be *R*-(–)-bakuchiol by comparison with the data previously reported.[10] All the compounds generated in this study therefore are assigned as the *R* enantiomer by inference through analogy with bakuchiol methyl ether in entry 12, Table 2.

Scheme S1. Demethylation of R-(—)–Bakuchiol Methyl Ether and Stereochemistry Proof



R-(—)–bakuchiol methyl ether R-(—)–bakuchiol

(10) Du, X-L.; Chen, H-L.; Feng, H-J.; Li, Y-C. *Helv. Chim. Acta* **2008**, *91*, 371–378.