Stereoselective Lewis Acid-Catalyzed α -Acylvinyl Additions

Troy E. Reynolds and Karl A. Scheidt*

*Department of Chemistry, Northwestern University,
2145 Sheridan Road, Evanston, Illinois 60208*

Supporting Information

Table of Contents

General Information.....	S2
General Procedure for Racemic α -Hydroxypropargyl Silanes.....	S2
General Procedure to Access Siloxyallenes	S4
General Procedure for Addition of Silyloxyallenes to Aldehydes.....	S5
General Procedure for Enantioselective Addition of Alkynes to Acylsilanes.....	S9
Base-Catalyzed Rearrangement of Enantioenriched 22	S10
Procedure for Chirality Transfer Reaction	S11
Selected NMR Spectra	S12
HPLC Traces.....	S33

General Information

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring. THF and CH_2Cl_2 were purified by passage through a bed of activated alumina.¹ Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.² Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and ceric ammonium nitrate stain or potassium permanganate stain followed by heating. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. ^1H -NMR spectra were recorded on a Varian Inova 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl_3 at 7.26 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C -NMR spectra were recorded on a Varian Inova 500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl_3 at 77.0 ppm). Mass spectra data were obtained on a Varian 1200 Quadrupole Mass Spectrometer and Micromass Quadro II Spectrometer.

Acylsilanes were prepared using the procedure developed in our laboratory.³

General Procedure for Racemic α -Hydroxypropargyl Silanes

To a flame-dried round bottom flask containing a magnetic stirring bar was added EtMgBr (3M solution in ether) and THF. The alkyne was added slowly via syringe to the Grignard solution. After stirring at room temperature for 1 h, the resulting solution was cooled to -78°C and acylsilane in THF was added slowly over 5 minutes. This solution was allowed to slowly warm up to room temperature over 3 h. Upon consumption of the acylsilane as determined by TLC (20% ethyl acetate/hexanes), the mixture was cooled to -78°C then quenched with saturated aqueous NH_4Cl . The mixture was diluted with ethyl acetate and the resulting layers were separated. The aqueous layer was extracted with EtOAc (3 X 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered and concentrated to provide the unpurified propargyl silanes. Purification by flash chromatography on silica gel (5% EtOAc/Hex) provided the title compounds.

3-(dimethyl(phenyl)silyl)non-4-yn-3-ol (4): Prepared according to general procedure using 1-(dimethyl(phenyl)silyl)propan-1-one (1.25 g, 6.5 mmol), 1-hexyne (1.5 mL, 13 mmol), and ethylmagnesium

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometal.* **1996**, *15*, 1518-1520.
2. Perrin, D. D. and Armarego, W. L. *Purification of Laboratory Chemicals*; 3rd Ed., Pergamon Press, Oxford. 1988.
3. (a) Clark, C. T.; Milgram, B. C.; Scheidt, K. A. *Org. Lett.* **2004**, *6*, 3977-3980. (b) Lettan II, R. B.; Milgram, B. C.; Clark, C. T.; Scheidt, K. A. *Org. Syn.* **2006**, in press.

bromide (4.3 mL, 13 mmol) to afford **1.5 g (84%) of 4** as a colorless oil. Analytical data for **4**: IR (film) cm^{-1} 3447, 3069, 2961, 2932, 2872, 1456, 1428, 1246, 1111, 935, 833, 805, 778, 735, 701, 652; ^1H NMR (500 MHz, CDCl_3) δ 7.65 (m, 2H), 7.40 (m, 3H), 2.26 (t, $J = 7.1$ Hz, 2H), 1.63 (doublet of quartets, $J = 21.5, 7.3$ Hz, 2H), 1.52 (m, 2H), 1.43 (m, 3H), 1.02 (t, $J = 7.0$ Hz, 3H), 0.93 (t, $J = 7.3$ Hz), 0.45 (s, 3H), 0.44 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.9, 134.9, 129.7, 127.9, 84.1, 81.5, 65.4, 30.7, 8.0, 4.1, -5.0;

3-(dimethyl(phenyl)silyl)hex-4-yn-3-ol: Prepared according to general procedure using 1-(dimethyl(phenyl)silyl)propan-1-one (5 g, 26 mmol) and propyne magnesium bromide (60 mL, 31 mmol) to afford **5.1 g (84%)** as a colorless oil. Analytical data: IR (film) cm^{-1} 3445, 2958, 2919, 2850, 1725, 1284, 1257, 1118, 1070, 1036, 786; ^1H NMR (500 MHz, CDCl_3) δ 7.65 (m, 2H), 7.40 (m, 3H), 1.91 (s, 3H), 1.58 (doublets of quartets, $J = 20.5, 7.3$ Hz, 2H), 1.40 (s, 1H), 1.02 (t, $J = 7.3$ Hz, 3H), 0.45 (s, 3H), 0.44 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.9, 134.9, 129.7, 127.9, 84.1, 81.5, 65.4, 30.7, 8.0, 4.1, -5.0;

3-(dimethyl(phenyl)silyl)-1-phenylpent-1-yn-3-ol: Prepared according to general procedure using 1-(dimethyl(phenyl)silyl)propan-1-one (1 g, 5.2 mmol), phenylacetylene (1.1 mL, 10.4 mmol), and ethylmagnesium bromide (3.5 mL, 10.4 mmol) to afford **0.85 g (55%)** as a yellow oil. Analytical data: IR (film) 3445, 3069, 2964, 1489, 1427, 1306, 1247, 1112, 935, 815, 778, 755, 735, 692 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.69 (m, 2H), 7.40 (m, 5H), 7.30 (m, 3H), 1.74 (doublets of quartets, $J = 10.4, 7.3$ Hz, 2H), 1.58 (s, 1H), 1.09 (t, $J = 7.3$, 3H), 0.50 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 135.6, 135.0, 131.7, 129.9, 128.5, 128.2, 128.0, 123.6, 91.9, 88.2, 65.6, 53.7, 30.7, 8.3;

3-(dimethyl(phenyl)silyl)-1-(trimethylsilyl)pent-1-yn-3-ol: Prepared according to general procedure using 1-(dimethyl(phenyl)silyl)propan-1-one (1 g, 5.2 mmol), trimethylsilylacetylene (1.5 mL, 10.4 mmol), and ethylmagnesium bromide (3.5 mL, 10.4 mmol) to afford **1.2 g (80%)** as a colorless oil. Analytical data: IR (film) 3564, 3444, 3070, 3050, 2963, 2153, 1456, 1428, 1409, 1302, 1250, 1114, 988, 939, 841, 812, 778, 759, 700, 651, 629 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.65 (m, 2H), 7.37 (m, 3H), 1.63 (doublets of quartets, $J = 23.7, 7.3$ Hz, 2H), 1.47 (s, 1H), 1.01 (t, $J = 7.3$ Hz, 3H), 0.45 (s, 6H), 0.17 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.5, 135.0, 129.8, 127.9, 108.6, 92.6, 65.9, 30.4, 8.1, 0.68, -0.1;

Prepared according to general procedure using 1-(dimethyl(phenyl)silyl)propan-1-one (1 g, 5.2 mmol), TBDPS-protected propargyl alcohol (3 g, 10.4 mmol), and ethylmagnesium bromide (3.5 mL, 10.4 mmol) to afford **3.2 g (87%)** as a yellow oil. Analytical data: IR (film) 3447, 3070, 2961, 2931, 2857, 1427, 1371, 1248, 1110, 1064, 997, 939, 823, 806, 779, 737, 701 cm^{-1} ; ^1H NMR (500 MHz,

CDCl₃) δ 7.72 (m, 4H), 7.64 (m, 1H), 7.44 – 7.33 (m, 10H), 4.41 (s, 2H), 1.60 (doublets of quartets, $J = 24.2, 7.3$ Hz, 2H), 1.35 (s, 1H), 1.07 (s, 9H) 0.96 (t, $J = 7.3$ Hz, 3H), 0.43 (s, 3H), 0.42 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 135.9, 135.7, 135.1, 135.0, 133.5, 133.4, 130.1, 130.0, 129.9, 129.8, 127.9, 87.5, 86.7, 65.1, 53.1, 30.5, 26.9, 26.8, 19.4, 8.1;

6,6-dimethyl-3-(dimethyl(phenyl)silyl)hept-4-yn-3-ol:

Prepared according to general procedure using 1-(dimethyl(phenyl)silyl)propan-1-one (1 g, 5.2 mmol), *tert*-butylacetylene (1.3 mL, 10.4 mmol), and ethylmagnesium bromide (3.5 mL, 10.4 mmol) to afford **1.2 g (84%)** as a colorless oil. Analytical data: IR (film) 3567, 3446, 3070, 3050, 2966, 2931, 2867, 1456, 1428, 1361, 1302, 1247, 1203, 1112, 1061, 1009, 935, 908, 862, 809, 777, 735, 701, 650 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.65 (m, 2H), 7.38 (m, 3H), 1.60 (doublets of quartets, $J = 23.2, 7.3$ Hz, 2H), 1.36 (bs, 1H), 1.22 (s, 9H) 0.99 (t, $J = 7.3$ Hz, 3H), 0.43 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 136.1, 135.0, 129.7, 127.8, 97.1, 80.8, 65.1, 31.5, 31.4, 30.7, 27.9, 8.1, -5.5;

1-cyclopropyl-1-(dimethyl(phenyl)silyl)hept-2-yn-1-ol:

Prepared according to general procedure using cyclopropyl(dimethyl(phenyl)silyl)methanone (1 g, 4.9 mmol), 1-hexyne (1.1 mL, 9.8 mmol), and ethylmagnesium bromide (3.5 mL, 9.8 mmol) to afford **1.3 g (93%)** as a colorless oil. Analytical data: IR (film) 3444, 3070, 3003, 2959, 2931, 2871, 1457, 1427, 1300, 1247, 1112, 1052, 1023, 986, 959, 913, 831, 797, 777, 735, 701, 652 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.68 (m, 2H), 7.37 (m, 3H), 2.20 (t, $J = 6.4$ Hz, 2H), 1.52 (bs, 1H), 1.44 (m, 2H), 1.37 (m, 2H), 1.02 (m, 1H), 0.90 (t, $J = 7.0$ Hz, 3H), 0.57 (m, 2H), 0.46 (s, 3H), 0.45 (s, 3H), 0.34 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 136.1, 135.0, 129.6, 127.8, 89.4, 79.0, 66.9, 31.3, 21.1, 18.8, 16.9, 13.8, -5.3;

General Procedure to Access Siloxyallenes

To a flame-dried 10 mL round bottom flask containing a magnetic stirring bar was added α -hydroxypropargyl silane in THF. The solution was cooled to 0 °C and *n*-BuLi (1.5 M in THF) was added. The resulting solution was quenched with saturated NaHCO₃. This solution was poured into a separatory funnel and diluted with pentane (10 mL). After mixing, the layers were separated. The aqueous layer was then extracted with pentane (3 X 5 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated to provide the unpurified silylallenol ethers. Purification by Kugelrohr distillation provided **5**. Additional siloxyallenes were used without purification.

Dimethyl(nona-3,4-dien-3-yloxy)(phenyl)silane (5):

Prepared according to general procedure using 3-(dimethyl(phenyl)silyl)non-4-yn-3-ol (1 g, 3.64 mmol) and *n*-BuLi (1.5 M in THF, 0.12 mL, 0.18 mmol) to afford **0.90 g (90%) of 5** as a colorless oil. Analytical data for

5: IR (film) cm^{-1} 3412, 3069, 2958, 2931, 2873, 1693, 1675, 1625, 1459, 1427, 1252, 1118, 1062, 871, 829, 786, 699; ^1H NMR (500 MHz, CDCl_3) δ 7.59 (m, 2H), 7.38 (m, 3H), 5.46 (t, $J = 3.0$ Hz, 1H), 2.13 (doublets of quartets, $J = 7.3, 3.1$ Hz, 2H), 1.83 (m, 2H), 1.26 (m, 4H), 0.97 (t, $J = 7.3$ Hz, 3H), 0.87 (t, $J = 6.4$ Hz, 3H), 0.45 (s, 3H), 0.43 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 194.4, 138.2, 133.7, 129.7, 128.6, 127.9, 103.3, 31.2, 31.0, 27.5, 22.6, 14.2, 11.3, -0.6 ;

General Procedure for Addition of Silyloxyallenes to Aldehydes

To a flame-dried 10 mL round bottom flask containing a magnetic stirring bar and 4Å molecular sieves was added $\text{Sc}(\text{OTf})_3$ under an inert atmosphere. The flask was fitted with septum, removed from the inert atmosphere box and charged with solvent (2 mL CH_2Cl_2). Aldehyde was added and the resulting suspension was stirred rapidly at room temperature. After 15 minutes, the flask was cooled to -78°C and the silyloxyallene in CH_2Cl_2 (0.5 mL) was added slowly via syringe. The resulting solution was stirred at -78°C until the aldehyde was completely consumed (15 min to 18 h) as determined by TLC (10% ethyl acetate/hexanes). After consumption of the aldehyde, the reaction mixture was then filtered through a plug of silica gel with ether (40 mL). The ether solution was concentrated giving the unpurified silyl protected product, which was dissolved in THF (5 mL) and treated with 1N HCl (1 mL). After stirring at room temperature for 1-5 h, this solution was diluted with ether (20 mL) and H_2O (10 mL) and poured into a separatory funnel. The aqueous layer was discarded and the ether layer was washed with saturated NaHCO_3 (10 mL) and brine (10 mL). The resulting ether layer was dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuo to provide the unpurified carbinols. The products were purified by flash chromatography (10% EtOAc/hexanes).

(Z)-4-(1-hydroxy-3-phenylpropyl)non-4-en-3-one (6): Prepared according to general procedure using dimethyl(nona-3,4-dien-3-yloxy)(phenyl)silane (200 mg, 0.73 mmol), hydrocinnamaldehyde (48 μL , 0.36 mmol) and $\text{Sc}(\text{OTf})_3$ (18 mg, 0.036 mmol) to afford **78 mg (78%) of 6** as a colorless oil. Analytical data for **6**: IR (film) 3445, 3026, 2957, 2931, 2860, 1684, 1496, 1455, 1377, 1181, 1049, 748, 699 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.30 (m, 2H), 7.22 (m, 3H), 5.81 (t, $J = 7.0$ Hz, 1H), 4.24 (bs, 1H), 2.7 (m, 1H), 2.65 – 2.59 (m, 3H), 2.38 (bs, 1H), 2.17 (quartet, $J = 7.3$ Hz, 2H), 1.90 (m, 2H), 1.44 – 1.32 (m, 4H), 1.11 (t, $J = 7.3$, 3H), 0.92 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 208.8, 143.8, 141.9, 135.4, 128.7, 128.6, 126.2, 74.3, 38.2, 37.8, 32.5, 31.9, 29.4, 22.6, 14.1, 8.0; LRMS (electrospray): Exact mass calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2$ $[\text{M}]^+$, 274.19. Found $[\text{M}+\text{Na}]$, 297.5.

(Z)-4-(hydroxy(phenyl)methyl)hex-4-en-3-one (7): Prepared according to general procedure using the silyloxyallene from 3-(dimethyl(phenyl)silyl)hex-4-yn-3-ol (55 mg, 0.24 mmol), benzaldehyde (16 mL, 0.16 mmol) and $\text{Sc}(\text{OTf})_3$ (8 mg, 0.016 mmol) to afford **32 mg (99%) of 7** as a colorless oil. Analytical data for **7**: IR (film) 3436, 2976, 1684, 1492, 1452, 1377, 1187, 1112, 1013, 927, 701 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.35 (m,

4H), 7.28 (m, 1H), 5.94 (q, $J = 7.3$ Hz, 1H), 5.44 (d, $J = 5.5$ Hz, 1H), 2.96 (d, $J = 5.5$ Hz, 1H), 2.53 (doublet of quartets, $J = 26.3, 7.3$ Hz, 2H), 1.87 (d, $J = 7.3$ Hz, 3H), 0.96 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 208.3, 144.6, 141.9, 131.4, 128.6, 127.9, 126.6, 76.3, 37.5, 15.6, 7.8; LRMS (electrospray): Exact mass calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$, 204.12. Found $[\text{M}+\text{Na}]^+$, 431.

(Z)-2-(hydroxy(phenyl)methyl)-1-phenylpent-1-en-3-one (8): Prepared according to general procedure using the siloxyallene from 3-(dimethyl(phenyl)silyl)-1-phenylpent-1-yn-3-ol (160 mg, 0.55 mmol), benzaldehyde (37 μL , 0.36 mmol) and $\text{Sc}(\text{OTf})_3$ (18 mg, 0.036 mmol) to afford **95 mg (98%) of 8** as a yellow oil. Analytical data for **8**: IR (film) 3436, 3060, 3028, 2975, 2936, 2878, 1681, 1600, 1492, 1405, 1376, 1235, 1154, 1071, 1027, 947, 871, 746, 700 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.43 – 7.30 (m, 8H), 7.20 (m, 2H), 6.90 (s, 1H), 5.57 (d, $J = 5.5$ Hz, 1H), 3.22 (d, $J = 5.5$ Hz, 1H), 2.01 (doublet of quartets, $J = 7.0, 2.4$ Hz, 2H), 0.76 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 211.7, 145.3, 141.2, 135.8, 131.4, 128.8, 128.7, 126.7, 37.4, 8.0; LRMS (electrospray): Exact mass calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$ $[\text{M}]^+$, 266.13. Found $[\text{M}+\text{Na}]^+$, 289.9.

(Z)-2-(hydroxy(phenyl)methyl)-1-(trimethylsilyl)pent-1-en-3-one (9): Prepared according to general procedure using the siloxyallene from 3-(dimethyl(phenyl)silyl)-1-(trimethylsilyl)pent-1-yn-3-ol (160 mg, 0.55 mmol), benzaldehyde (37 μL , 0.36 mmol) and $\text{Sc}(\text{OTf})_3$ (18 mg, 0.036 mmol) to afford **94 mg (98%) of 9** as a colorless oil. Analytical data for **9**: IR (film) 3427, 3063, 3029, 2952, 2898, 1687, 1592, 1492, 1453, 1407, 1357, 1246, 1133, 1075, 1045, 978, 866, 841, 760 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.30 (m, 5H), 6.09 (s, 1H), 5.51 (d, $J = 4.3$ Hz, 1H), 2.50 (d, $J = 4.3$ Hz, 1H), 2.37 (doublet of quartets, $J = 8.2, 7.3$ Hz, 2H), 0.92 (t, $J = 7.3$ Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 211.0, 142.2, 141.5, 140.7, 128.7, 128.1, 128.0, 126.5, 77.3, 39.2, 33.6, 30.5, 9.0; LRMS (electrospray): Exact mass calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{Si}$ $[\text{M}]^+$, 262.14. Found $[\text{M}+\text{Na}]^+$, 547.2.

(Z)-4-(hydroxy(phenyl)methyl)non-4-en-3-one (10): Prepared according to general procedure using dimethyl(nona-3,4-dien-3-yloxy)(phenyl)silane (150 mg, 0.55 mmol), benzaldehyde (37 μL , 0.36 mmol) and $\text{Sc}(\text{OTf})_3$ (18 mg, 0.036 mmol) to afford **82 mg (91%) of 10** as a colorless oil. Analytical data for **10**: IR (film) 3428, 3063, 3028, 2957, 2929, 2857, 1684, 1492, 1453, 1377, 1336, 1251, 1176, 1118, 1017, 876, 828, 780, 701 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.34 (m, 4H), 7.29 (m, 1H), 5.83 (t, $J = 7.5$ Hz, 1H), 5.42 (bs, 1H), 3.00 (bs, 1H), 2.42 (doublet of quartets, $J = 20.5, 7.0$ Hz, 2H), 2.21 (dt, $J = 7.3$ Hz, 2H), 1.42 (m, 2H), 1.34 (m, 2H), 0.95 – 0.90 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 208.5, 143.5, 142.0, 136.5, 128.7, 127.9, 126.6, 76.3, 37.5, 31.8, 29.5, 22.6, 14.1, 7.8; LRMS (electrospray): Exact mass calcd for $\text{C}_{16}\text{H}_{22}\text{O}_2$ $[\text{M}]^+$, 246.16. Found $[\text{M}-\text{OH}]$, 229.4.

(11): Prepared according to general procedure using the appropriate siloxyallene (200 mg, 0.41 mmol), benzaldehyde (28 μL , 0.27 mmol) and

Sc(OTf)₃ (13 mg, 0.027 mmol) to afford **122 mg (97%) of 11** as a yellow oil. Analytical data for **11**: IR (film) 3441, 3069, 2958, 2932, 2892, 2857, 1684, 1628, 1470, 1453, 1428, 1378, 1254, 1167, 1110, 1044, 1007, 823, 739, 701 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.65 (m, 4H), 7.46 – 7.30 (m, 11H), 6.12 (t, *J* = 5.2 Hz, 1H), 5.48 (d, *J* = 4.6 Hz, 1H), 4.51 (d, *J* = 5.2 Hz, 2H), 2.44 (d, *J* = 4.6 Hz, 1H), 2.26 (doublet of quartets, *J* = 11.1, 7.3 Hz, 2H), 1.06 (s, 9H), 0.81 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 205.5, 141.7, 141.4, 139.3, 135.8, 133.6, 133.5, 130.0, 128.8, 128.2, 128.0, 126.8, 75.2, 62.6, 36.1, 27.0, 19.4; LRMS (electrospray): Exact mass calcd for C₂₉H₃₄O₃Si [M]⁺, 458.23. Found [M+Na]⁺, 481.82.

(Z)-4-(hydroxy(phenyl)methyl)-6,6-dimethylhept-4-en-3-one (12):

Prepared according to general procedure using the siloxyallene from 6,6-dimethyl-3-(dimethyl(phenyl)silyl)hept-4-yn-3-ol (150 mg, 0.55 mmol), benzaldehyde (37 μL, 0.36 mmol) and Sc(OTf)₃ (18 mg, 0.036 mmol) to afford **88 mg (98%) of 12** as a colorless oil. Analytical data for **12**: IR (film) 3432, 3063, 3029, 2958, 2905, 2871, 1687, 1450, 1404, 1377, 1362, 1251, 1200, 1142, 1089, 1034, 942, 920, 877, 829, 782, 741, 701 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.35 (m, 5H), 5.53 (s, 1H), 5.28 (d, *J* = 3.4 Hz, 1H), 2.92 (d, *J* = 4.0 Hz, 1H), 2.38 (doublet of quartets, *J* = 19.0, 7.3 Hz, 1H), 2.14 (doublet of quartets, *J* = 19.0, 7.3 Hz, 1H), 1.07 (s, 9H), 0.81 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 206.5, 157.7, 141.1, 136.6, 129.0, 128.4, 128.1, 127.2, 76.4, 35.8, 7.6; LRMS (electrospray): Exact mass calcd for C₁₆H₂₂O₂ [M]⁺, 246.16. Found [M–OH]⁺, 229.5.

(Z)-1-cyclopropyl-2-(hydroxy(phenyl)methyl)hept-2-en-1-one (13):

Prepared according to general procedure using the siloxyallene from 1-cyclopropyl-1-(dimethyl(phenyl)silyl)hept-2-yn-1-ol (156 mg, 0.55 mmol), benzaldehyde (37 μL, 0.36 mmol) and Sc(OTf)₃ (18 mg, 0.036 mmol) to afford **91 mg (97%) of 13** as a colorless oil. Analytical data for **13**: IR (film) 3431, 3061, 3028, 3007, 2957, 2928, 2859, 1665, 1493, 1451, 1392, 1249, 1220, 1192, 1115, 1029, 1004, 875, 825, 745, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.35 (m, 5H), 7.28 (m, 1H), 5.92 (t, *J* = 7.6 Hz, 1H), 5.41 (d, *J* = 6.1 Hz, 1H), 3.41 (d, *J* = 6.1 Hz, 1H), 2.37 (quartet, *J* = 7.0 Hz, 2H), 2.04 (m, 1H), 1.45 (m, 2H), 1.37 (m, 2H), 1.06 (m, 1H), 0.97 (m, 1H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.88 (m, 1H), 0.83 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 208.5, 143.9, 142.2, 136.9, 128.5, 126.5, 76.5, 31.7, 29.5, 23.1, 22.6, 14.1, 12.9, 12.8; LRMS (electrospray): Exact mass calcd for C₁₇H₂₂O₂ [M]⁺, 258.16. Found [M+Na]⁺, 281.9.

(Z)-4-((4-chlorophenyl)(hydroxy)methyl)non-4-en-3-one (14):

Prepared according to general procedure using dimethyl(nona-3,4-dien-3-yloxy)(phenyl)silane (150 mg, 0.56 mmol), 4-chlorobenzaldehyde (51 mg, 0.36 mmol) and Sc(OTf)₃ (18 mg, 0.036 mmol) to afford **98 mg (96%) of 14** as a colorless oil. Analytical data for **14**: IR (film) 3419, 2957, 2932, 2872, 1684, 1593, 1490, 1458, 1404, 1377, 1251, 1171, 1118, 1090, 1014, 874, 827, 783, 727, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.33 (m, 4H), 7.28 (m, 2H), 5.83 (t, *J* = 7.6 Hz, 1H), 5.41 (d, *J* = 5.5 Hz, 1H), 2.88 (d, *J* = 5.5 Hz, 1H), 2.41 (doublet of quartets, *J* = 30.5, 7.3 Hz, 2H), 2.20 (dt, *J* = 7.3 Hz, 2H), 1.44 – 1.31 (m,

4H), 0.94 – 0.89 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 208.3, 143.1, 140.6, 137.4, 133.6, 128.8, 127.9, 75.8, 37.7, 31.8, 29.5, 22.6, 14.1, 7.8; LRMS (electrospray): Exact mass calcd for $\text{C}_{16}\text{H}_{21}\text{O}_2\text{Cl}$ $[\text{M}]^+$, 280.12. Found $[\text{M}+\text{Na}]^+$, 303.6.

(Z)-4-(hydroxy(4-methoxyphenyl)methyl)non-4-en-3-one

(15): Prepared according to general procedure using dimethyl(nona-3,4-dien-3-yloxy)(phenyl)silane (150 mg, 0.55 mmol), *para*-anisaldehyde (44 μL , 0.36 mmol) and $\text{Sc}(\text{OTf})_3$ (18 mg, 0.036 mmol) to afford **98 g (97%) of 15** as a colorless oil. Analytical data for **15**: IR (film) 3447, 2957, 2932, 2872, 1684, 1611, 1511, 1459, 1377, 1302, 1249, 1173, 1116, 1034, 836 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.25 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 5.81 (t, J = 7.3 Hz, 1H), 5.39 (d, J = 5.2 Hz, 1H), 3.81 (s, 3H), 2.79 (d, J = 5.2 Hz, 1H), 2.43 (doublet of quartets, J = 20.7, 7.0 Hz, 2H), 2.21 (dt, J = 7.3 Hz, 2H), 1.44 – 1.32 (m, 4H), 0.95 (t, J = 7.0 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 208.5, 159.3, 143.7, 135.8, 134.0, 127.9, 114.0, 113.9, 75.7, 55.5, 37.5, 31.9, 29.4, 22.6, 14.1, 7.8; LRMS (electrospray): Exact mass calcd for $\text{C}_{17}\text{H}_{24}\text{O}_3$ $[\text{M}]^+$, 276.17. Found $[\text{M}+\text{Na}]^+$, 299.8.

(Z)-4-(hydroxy(naphthalen-3-yl)methyl)non-4-en-3-one (16):

Prepared according to general procedure using dimethyl(nona-3,4-dien-3-yloxy)(phenyl)silane (150 mg, 0.55 mmol), 2-naphthaldehyde (57 mg, 0.36 mmol) and $\text{Sc}(\text{OTf})_3$ (18 mg, 0.036 mmol) to afford **106 mg (98%) of 16** as a colorless oil. Analytical data for **16**: IR (film) 3430, 3055, 2956, 2930, 2871, 1684, 1507, 1457, 1405, 1376, 1250, 1178, 1119, 1051, 1019, 950.4, 897, 859, 822, 778, 751 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.84 (m, 4H), 7.50 (m, 2H), 7.42 (m, 1H), 5.87 (t, J = 7.6 Hz, 1H), 5.58 (d, J = 3.6 Hz, 1H), 3.23 (d, J = 4.9 Hz, 1H), 2.44 (doublet of quartets, J = 24.4, 7.3 Hz, 2H), 2.23 (dt, J = 7.3 Hz, 2H), 1.42 (m, 2H), 1.35 (m, 2H), 0.96 – 0.91 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 208.6, 143.4, 139.3, 136.9, 133.5, 133.1, 128.4, 128.3, 127.9, 126.5, 126.3, 125.3, 124.7, 76.4, 37.6, 31.8, 29.5, 22.6, 14.1, 7.8; LRMS (electrospray): Exact mass calcd for $\text{C}_{20}\text{H}_{24}\text{O}_2$ $[\text{M}]^+$, 296.18. Found $[\text{M}+\text{Na}]$, 320.1.

(Z)-4-(1-hydroxy-2,2-dimethylpropyl)non-4-en-3-one (17):

Prepared according to general procedure using dimethyl(nona-3,4-dien-3-yloxy)(phenyl)silane (150 mg, 0.55 mmol), trimethylacetaldehyde (40 μL , 0.36 mmol) and $\text{Sc}(\text{OTf})_3$ (36 mg, 0.073 mmol) to afford **78 mg (95%) of 17** as a colorless oil. Analytical data for **17**: IR (film) 3496, 2957, 2934, 2872, 1723, 1684, 1590, 1480, 1460, 1396, 1365, 1271, 1172, 1100, 1011, 971, 850, 756 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.81 (t, J = 7.3 Hz, 1H), 4.02 (d, J = 5.2 Hz, 1H), 2.81 (d, J = 5.2 Hz, 1H), 2.67 (doublet of quartets, J = 13.5, 7.3 Hz, 2H), 2.15 (dt, J = 7.3 Hz, 1H), 1.40 (m, 2H), 1.33 (m, 2H), 1.10 (t, J = 7.3 Hz, 3H), 0.90 (t, J = 7.3 Hz, 3H), 0.85 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 209.5, 142.0, 137.8, 83.3, 37.5, 36.4, 32.0, 29.4, 26.4, 22.6, 14.1, 8.4; LRMS (electrospray): Exact mass calcd for $\text{C}_{14}\text{H}_{26}\text{O}_2$ $[\text{M}]^+$, 226.19. Found $[\text{M}+\text{Na}]$, 249.6.

(Z)-methyl 2-hydroxy-2-phenyl-3-propanoyloct-3-enoate (19):

Prepared according to general procedure using dimethyl(nona-3,4-dien-3-yloxy)(phenyl)silane (150 mg, 0.55 mmol), methyl benzoylformate (52 μ L, 0.36 mmol) and $\text{Sc}(\text{OTf})_3$ (36 mg, 0.073 mmol) to afford **20 mg (18%) of 19** as a colorless oil. Analytical data for **19**: IR (film) cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.55 (m, 2H), 7.36 (m, 3H), 5.51 (t, $J = 7.6$ Hz, 1H), 4.35 (s, 1H), 3.80 (s, 3H), 2.64 (doublet of quartets, $J = 12.5, 7.3$ Hz, 2H), 2.16 (dt, $J = 7.3$ Hz, 2H), 1.55 (s, 1H), 1.28 (m, 4H), 1.09 (t, $J = 7.3$ Hz, 3H), 0.85 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 208.7, 174.6, 144.2, 139.2, 128.5, 128.4, 127.1, 81.6, 53.6, 37.8, 31.5, 29.7, 22.5, 14.1, 8.2; LRMS (electrospray): Exact mass calcd for $\text{C}_{18}\text{H}_{24}\text{O}_4$ $[\text{M}]^+$, 304.17. Found $[\text{M}+\text{M}+\text{Na}]$, 631.5.

General Procedure for Enantioselective Addition of Alkynes to Acylsilanes

To a flame-dried round bottom flask with alkyne in toluene was added diethylzinc (2M in toluene). The solution was stirred at room temperature for 1 h after which ligand **21** in toluene was added. After stirring for another 1 h, the acylsilane dissolved in toluene was added. The bright yellow solution was stirred rapidly until consumption (4 to 8h) of acylsilane was detected by TLC (10% EtOAc/hexanes). The reaction was then quenched with saturated NH_4Cl . The mixture was filtered through Celite with EtOAc (60 mL). The solution was washed with brine (30 mL), dried over anhydrous Na_2SO_4 , filtered and concentrated to give the unpurified propargyl silane. The product was purified by flash chromatography (5% EtOAc/hexanes).

3-(dimethyl(phenyl)silyl)-1-phenylpent-1-yn-3-ol (22):

Prepared according to general procedure using 1-(dimethyl(phenyl)silyl)propan-1-one (200 mg, 1.04 mmol), phenylacetylene (230 μ L, 2.08 mmol), ZnEt_2 (1.04 mL, 2.08 mmol), and ligand **21** (77 mg, 0.21 mmol) to afford **290 mg (95%) of 22** as a colorless oil. $[\alpha]_D : -9.6$ (MeOH, $c = 0.9$, $er = 87:13$). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 5% IPA/Hexanes, $\text{Rt}_1 = 4.95$, $\text{Rt}_2 = 5.56$).

3-(dimethyl(phenyl)silyl)undec-4-yn-3-ol (23):

Prepared according to general procedure using 1-(dimethyl(phenyl)silyl)propan-1-one (200 mg, 1.04 mmol), 1-octyne (310 μ L, 2.08 mmol), ZnEt_2 (1.04 mL, 2.08 mmol), and ligand **21** (77 mg, 0.21 mmol) to afford **265 mg (84%) of 23** as a colorless oil. Analytical data for **22**: IR (film) 3451, 3069, 3049, 2960, 2931, 2857, 1457, 1427, 1376, 1303, 1246, 1112, 1037, 936, 832, 806, 778, 734, 701, 652 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.65 (m, 2H), 7.38 (m, 3H), 2.24 (t, $J = 7.0$ Hz, 2H), 1.62 (doublet of quartets, $J = 21.0, 7.0$ Hz, 2H), 1.50 (m, 2H), 1.41 (m, 3H), 1.30 (m, 4H), 1.01 (t, $J = 7.3$ Hz, 3H), 0.91 (t, $J = 7.0$ Hz, 3H), 0.44 (s, 3H), 0.43 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 136.1, 134.9, 129.7, 127.9, 88.8, 82.4, 65.3, 31.6, 30.8, 29.2, 28.8, 22.9, 19.3, 14.3, 8.1, -5.5 ; $[\alpha]_D : +4.8$ (MeOH, $c = 1.0$, $er = 89:11$). Enantiomeric ratio was measured by chiral HPLC (Chiralcel AD-H, 5% IPA/Hexanes, $\text{Rt}_1 = 5.01$, $\text{Rt}_2 = 7.20$).

Base-Catalyzed Rearrangement of Enantioenriched **22**

To a flame-dried round bottom flask with enantioenriched **22** in THF at –78 °C was slowly added *n*-BuLi (1.5M in THF) via syringe. The resulting solution was quenched with saturated NaHCO₃. This solution was poured into a separatory funnel and diluted with pentane (10 mL). After mixing, the layers were separated. The aqueous layer was then extracted with pentane (3 X 5 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated to provide the unpurified silylallenol **24**. The product was used without purification in the next step. [α]_D: +24.6 (MeOH, c = 1.0, er = 86:14). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 0.3% IPA/Hexanes, Rt₁ = 4.67, Rt₂ = 5.21).

Addition of Enantioenriched **24 to Benzaldehyde**

Prepared according to general procedure using the enantioenriched siloxyallene **24**. er = 68:32. Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 5% IPA/Hexanes, $R_{t1} = 7.73$, $R_{t2} = 9.41$).

Procedure for Enantioselective Addition of Racemic Silyloxyallene **24**

(Z)-2-((2-chlorophenyl)(hydroxy)methyl)-1-phenylpent-1-en-3-one (24) Cr complex **25** (28 mg, 0.034 mmol) and 4Å molecular sieves (100 mg) were combined in a 2 dram vial equipped with a stir bar. Acetone (125 μ L) was added followed by 2,6-lutidine (20 μ L, 0.17 mmol) and benzaldehyde (17 μ L, 0.17 mmol). The vial was cooled to -78°C and **($\pm$)-23** (100 mg, 0.34 mmol) dissolved in acetone (125 μ L) was added dropwise. The reaction was stirred for 56h at which time it was diluted with ether and filtered through a small pad of Celite to remove the molecular sieves. The solvent was removed *in vacuo*. The resulting residue was dissolved in THF (5 mL) and treated with 1N HCl (1mL). After stirring at room temperature for 30 min, this solution was diluted with ether (10 mL) and H_2O (10 mL) and poured into a separatory funnel. The aqueous layer was discarded and the ether layer was washed with saturated NaHCO_3 (10 mL) and brine (10 mL). The resulting ether layer was dried over anhydrous Na_2SO_4 , filtered, and concentrated *in vacuo* to provide the unpurified carbinol. The resulting residue was purified by flash chromatography (SiO_2 , 10% EtOAc/hexanes) to afford **41 mg (80%)** of **24** as a light yellow oil. Analytical data for **24**: IR (film) 3439, 3060, 3026, 2971, 2934, 1682, 1574, 1460, 1440, 1405, 1376, 1309, 1263, 1158, 1030, 951, 874, 753, 699 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.63 (m, 1H), 7.39 – 7.26 (m, 7H), 7.18 (m, 2H), 6.78 (s, 1H), 5.84 (d, $J = 5.2$ Hz, 1H), 3.68 (d, $J = 5.2$ Hz, 1H), 2.18 (doublet of quartets, $J = 14.4, 7.3$, 1H) 2.00 (doublet of quartets, $J = 14.4, 7.3$, 1H), 0.81 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 212.0, 142.7, 138.4, 135.6, 133.6, 132.7, 129.8, 129.3, 128.9, 128.9, 128.8, 128.4, 127.3, 73.4, 37.0, 9.0; LRMS (electrospray): Exact mass calcd for $\text{C}_{18}\text{H}_{17}\text{O}_2\text{Cl}$ $[\text{M}]^+$, 300.8. Found $[\text{M}+\text{M}+\text{Na}]$, 623.5. $[\alpha]_D^{25}$: +20.6 (MeOH, $c = 1.0$, er = 96:4). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 5% IPA/Hexanes, $R_{t1} = 8.70$, $R_{t2} = 9.81$).

Selected NMR Spectra

HPLC Traces

Racemic 22

Data File C:\HPCHEM\1\DATA\SCHWIN\ARB-RAC0.D

Sample Name: ARB-RAC

Racemate

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Injection Date   : 12/15/2004 5:06:03 PM
Sample Name      : ARB-RAC                      Location : Vial 3
Acq. Operator    : Troy
Acq. Instrument  : Instrument 1                  Inj Volume : 5 µl
Acq. Method      : C:\HPCHEM\1\METHODS\SCHWIN.M
Last changed     : 12/15/2004 4:28:14 PM by Troy
Analysis Method  : C:\HPCHEM\1\METHODS\REVERS~1\RP109025.M
Last changed     : 7/14/2006 8:46:27 AM by Audrey
                  (modified after loading)
Zorbax XBD-C8, 4.6x 150mm, 10% ACN/90% 0.1% HClO4 to 90%ACN/10% HClO4 over 25 min, hold 90%
ACN 10 min, 5 min post time, 1 mL/min, column temp 35C
DAD1 A, Sig=254,4 Ref=360,100 (SCHWIN\ARB-RAC0.D)
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Area Percent Report

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.978	VV	0.1000	6307.58887	968.68048	49.8957
2	5.621	VB	0.1159	6333.95947	840.70752	50.1043

Totals : 1.26415e4 1809.38800

Results obtained with enhanced integrator!

*** End of Report ***

Enantioenriched 22

Data File C:\HPCHEM\1\DATA\TROY\TER29A00.D

Sample Name: TER-I-29A

RED0 OF TER29A

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Injection Date   : 12/16/2004 1:03:33 PM
Sample Name      : TER-I-29A                      Location : Vial 1
Acq. Operator    : Troy
Acq. Instrument  : Instrument 1                    Inj Volume : 5 µl
Acq. Method      : C:\HPCHEM\1\METHODS\SCHWIN.M
Last changed     : 12/15/2004 4:28:14 PM by Troy
Analysis Method  : C:\HPCHEM\1\METHODS\REVERS-1\RP109025.M
Last changed     : 7/14/2006 8:55:51 AM by Audrey
                  (modified after loading)
Zorbax XBD-C8, 4.6x 150mm, 10% ACN/90% 0.1% HC104 to 90%ACN/10% HC104 over 25 min, hold 90%
ACN 10 min, 5 min post time, 1 mL/min, column temp 35C
DAD1 A, Sig=254,4 Ref=360,100 (TROY\TER29A00.D)
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Area Percent Report

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Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.946	VV	0.1019	1.18184e4	1816.36145	86.4481
2	5.566	VV	0.1146	1852.68201	249.65088	13.5519

Totals : 1.36711e4 2066.01233

Results obtained with enhanced integrator!

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*** End of Report ***

Racemic 24

Data File C:\HPCHEM\2\DATA\TROY\TR400010.D

Sample Name: TER-IV

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Injection Date   : 10/12/2006 3:03:57 PM
Sample Name      : TER-IV                      Location : Vial 81
Acq. Operator    : mmb
Method           : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed     : 10/12/2006 2:56:15 PM by mmb
                  (modified after loading)
Inj Volume       : 5 µl
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Area Percent Report
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Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Tvpe	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.865	BV	0.1225	1.08413e4	1338.29761	49.7592
2	5.466	VB	0.1634	1.09463e4	1018.73840	50.2408

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Totals :                2.17876e4  2357.03601
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Results obtained with enhanced integrator!

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*** End of Report ***
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Enantioenriched 24

Data File C:\HPCHEM\2\DATA\TROY\TR4-1010.D

Sample Name: TR4-1

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Injection Date   : 10/14/2006 10:57:15 AM
Sample Name      : TR4-1                      Location : Vial 81
Acq. Operator    : mmb                      Inj Volume : 5 µl
Acq. Method      : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed     : 10/14/2006 10:51:27 AM by mmb
                  (modified after loading)
Analysis Method  : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed     : 10/14/2006 11:13:30 AM by mmb
                  (modified after loading)
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Area Percent Report
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Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.946	VV	0.1184	708.64929	89.49261	15.1035
2	5.551	VB	0.1568	3983.29932	384.67273	84.8965

Totals : 4691.94861 474.16534

Results obtained with enhanced integrator!

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*** End of Report ***
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Racemic 8

Data File C:\HPCHEM\2\DATA\TROY\TR3-2902.D

Sample Name: TER-III-29

racemic

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Injection Date   : 7/14/2006 4:42:29 PM
Sample Name      : TER-III-29                Location : Vial 51
Acq. Operator    : MMB                      Inj Volume : 5 µl
Acq. Method      : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed     : 7/14/2006 4:41:18 PM by MMB
                  (modified after loading)
Analysis Method   : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed     : 7/14/2006 4:59:43 PM by MMB
                  (modified after loading)
=====
```

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=====
                          Area Percent Report
=====
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```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.573	BB	0.2000	4176.54004	316.41101	50.0451
2	9.371	BB	0.2636	4169.01221	243.67401	49.9549

Totals : 8345.55225 560.08502

Results obtained with enhanced integrator!

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*** End of Report ***
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Enantioenriched 8

Data File C:\HPCHEM\2\DATA\TROY\TR3-5900.D

Sample Name: TER-III-59

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Injection Date   : 4/3/2006 6:53:48 PM
Sample Name      : TER-III-59                Location : Vial 83
Acc. Operator    : Troy                      Inj Volume : 5 µl
Acc. Method      : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed     : 4/3/2006 6:46:29 PM by Troy
                  (modified after loading)
Analysis Method  : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed     : 7/13/2006 3:24:11 PM by MMB
                  (modified after loading)
=====
```

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Area Percent Report
=====

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.726	VV	0.2224	2.70213e4	1872.33923	37.7674
2	9.412	VV	0.2883	4.45253e4	2379.94653	62.2326

Totals : 7.15465e4 4252.28577

Results obtained with enhanced integrator!

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*** End of Report ***

Racemic 24

Data File C:\HPCHEM\2\DATA\TROY\TR3-2970.D

Sample Name: TER-III-297r

racemate

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=====
Injection Date   : 10/10/2006 1:31:55 PM
Sample Name      : TER-III-297r           Location : Vial 62
Acq. Operator    : mmb                   Inj Volume : 5 µl
Acq. Method      : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed     : 10/10/2006 1:29:51 PM by mmb
                  (modified after loading)
Analysis Method  : C:\HPCHEM\2\METHODS\MMB LC.M
Last changed     : 10/12/2006 5:36:57 PM by mmb
                  (modified after loading)
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=====
Area Percent Report
=====
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```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.498	BV	0.2392	1.10406e4	703.10413	49.9480
2	9.488	VV	0.2706	1.10636e4	624.87714	50.0520

Totals : 2.21043e4 1327.98126

Results obtained with enhanced integrator!

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*** End of Report ***
```

Enantioenriched 24

Data File C:\HPCHEM\2\DATA\TROY\TR3-2962.D

Sample Name: TER-III-296

2-Cl-benzaldehyde

```
=====
Injection Date   : 10/9/2006 1:51:09 PM
Sample Name      : TER-III-296           Location : Vial 61
Acq. Operator    : mmb
Inj Volume       : 5 µl

Acq. Method      : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed     : 10/9/2006 1:35:18 PM by mmb
                  (modified after loading)
Analysis Method  : C:\HPCHEM\2\METHODS\MMB LC.M
Last changed     : 10/12/2006 5:34:16 PM by mmb
                  (modified after loading)
=====
```

```
=====
                          Area Percent Report
=====
```

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.700	BB	0.2350	2531.71704	163.14244	96.0541
2	9.813	PB	0.2603	104.00401	6.11922	3.9459

Totals : 2635.72105 169.26166

Results obtained with enhanced integrator!

```
=====
*** End of Report ***
=====
```