Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

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Catalytic Enantioselective α-Acylvinyl Anion Reactions of Silyloxyallenes

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General Information

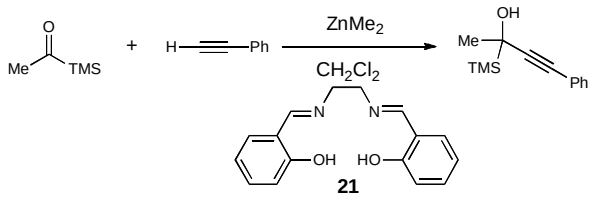
All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring. THF and CH_2Cl_2 were purified by passage through a bed of activated alumina.[1] Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.[2] 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 permangenate stain followed by heating. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. ^{1}H-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] The (salen)Cr(III)-SbF_6 **2** was prepared according to the procedure by Rawal.[4]

General Procedure A for Synthesis of a-Hydroxypropargylsilanes

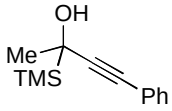
To a flame-dried round bottom flask containing a magnetic stirring bar was added alkyne (2 equiv) and CH_2Cl_2 followed by $ZnMe_2$ (2M solution in toluene, 2 equiv). After stirring for 30 minutes, diimine ligand **21** (0.05 equiv) was added. The suspension was stirred vigorously for 30 minutes and acylsilane (1 equiv, dissolved in CH_2Cl_2) was added. Upon consumption of the acylsilane as determined by thin layer chromatography (20% ethyl acetate/hexanes), the mixture was quenched with saturated aqueous NH_4Cl, diluted with ethyl acetate, and filtered through Celite. The solution was then poured into a separatory funnel, and the layers were separated. The organic layer was washed with water (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated to provide the unpurified propargylsilanes. Purification by flash chromatography on silica gel (5% EtOAc/Hex) provided the desired product.

1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometal.* **1996**, *15*, 1518-1520.
2. D. D. Perrin and W. L. Armarego, *Purification of Laboratory Chemicals*, 3rd Ed., Pergamon Press, Oxford. 1988.
3. (a) C. T. Clark, B. C. Milgram, K. A. Scheidt, *Org. Lett.* **2004**, *6*, 3977-3980. (b) R. B. Lettan II, B. C. Milgram, C. T. Clark, K. A. Scheidt, *Org. Synth.* **2007**. *84*, 22.
4. Y. Huang, T. Iwama, V. H. Rawal, *J. Am. Chem. Soc.* **2000**, *122*, 7843.

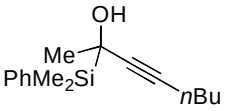


General Procedure B for Synthesis of a**-Hydroxypropargylsilanes**

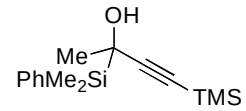
To a flame-dried round bottom flask containing a magnetic stirring bar was added EtMgBr (3M solution in ether) and THF. The alkyne was added slowly via syringe to the Grignard solution. After stirring at room temperature for 1 h, the resulting solution was cooled to –78 °C and acylsilane in THF was added slowly over 5 minutes. Upon consumption of the acylsilane as determined by thin layer chromatography (10% ethyl acetate/hexanes), the mixture was quenched with saturated aqueous NH_4Cl. The mixture was diluted with diethyl ether and the resulting layers were separated. The aqueous layer was extracted with diethyl ether (3 X 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated to provide the unpurified propargylsilane. Purification by flash chromatography on silica gel (5% EtOAc/Hex) provided the title compounds.



4-phenyl-2-(trimethylsilyl)but-3-yn-2-ol: Prepared according to general procedure A using phenylacetylene (5.7 mL, 51.6 mmol), diethylzinc (2M in toluene, 25.8 mL, 51.6 mmol), diimine ligand **21** (350 mg, 1.3 mmol), and acetyltrimethylsilane (3.0 g, 25.8 mmol) to afford 5.0 g (88%) as a yellow liquid. Analytical data: IR (film) 3426, 3058, 2960, 1489, 1443, 1249, 1038, 842, 752, 687 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 4.0 Hz, 2H), 7.29 (m, 3H), 1.55 (s, 4H), 0.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.7, 128.4, 128.1, 123.6, 93.4, 86.5, 61.6, 25.7, –4.3.

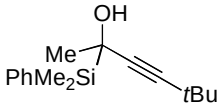


2-(dimethyl(phenyl)silyl)oct-3-yn-2-ol: Prepared according to general procedure B using 1-hexyne (0.65 mL, 5.6 mmol), ethyl Grignard (2M in THF, 2.8 mL, 5.6 mmol), and 1-(dimethyl(phenyl)silyl)ethanone (500 mg, 2.8 mmol) to afford 550 mg (75%) as a yellow liquid. Analytical data: IR (film) 3436, 3050, 2951, 2869, 1428, 1250, 1107, 1057, 822, 780, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 6.6 Hz, 2H), 7.40 - 7.35 (m, 3H), 2.23 (t, *J* = 7.0 Hz, 2H), 1.45 (m, 2H), 1.40 (m, 6H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.43 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 134.9, 129.7, 127.9, 87.6, 84.1, 61.3, 31.2, 26.2, 22.1, 18.8, 13.8, –5.7, –5.9.

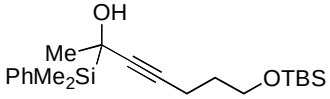


2-(dimethyl(phenyl)silyl)-4-(trimethylsilyl)but-3-yn-2-ol: Prepared according to general procedure B using ethynyltrimethylsilane (0.79 mL, 5.6 mmol), ethyl Grignard (2M in THF, 2.8 mL, 5.6 mmol), and 1-(dimethyl(phenyl)silyl)ethanone (500 mg, 2.8 mmol) to afford 350 mg (45%) as a yellow liquid. Analytical data: IR (film) 3439, 3051, 2961, 2150, 1409, 1250, 1111, 1046, 941, 837, 771, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$)

δ 7.65 (d, *J* = 6.8 Hz, 2H), 7.40 – 7.37 (m, 3H), 1.42 (m, 4H), 0.45 (s, 6H), 0.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.2, 135.0, 129.9, 127.9, 110.3, 91.3, 61.8, 25.6, 0.3, –5.9, –6.0;



2-(dimethyl(phenyl)silyl)-5,5-dimethylhex-3-yn-2-ol: Prepared according to general procedure B using 3,3-dimethyl-1-butyne (460 mg, 5.6 mmol), ethyl Grignard (2M in THF, 2.8 mL, 5.6 mmol), and 1-(dimethyl(phenyl)silyl)ethanone (500 mg, 2.8 mmol) to afford 450 mg (62%) as a yellow liquid. Analytical data: IR (film) 3436, 3050, 2963, 1708, 1428, 1358, 1252, 1100, 1045, 825, 779, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 6.4 Hz, 2H), 7.41 – 7.36 (m, 3H), 1.39 (s, 3H), 1.37 (s, 1H), 1.21 (s, 9H), 0.44 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.7, 134.9, 129.8, 127.9, 95.9, 82.6, 61.1, 31.4, 27.8, 26.1, –5.7, –5.9.



7-(*tert*-butyldimethylsilyloxy)-2-(dimethyl(phenyl)silyl)hept-3-yn-2-ol: Prepared according to general procedure B using TBS-protected 4-pentyn-1-ol (555 mg, 2.8 mmol), ethyl Grignard (2M in THF, 1.4 mL, 2.8 mmol), and 1-(dimethyl(phenyl)silyl)ethanone (250 mg, 1.4 mmol) to afford 360 mg (68%) as a yellow liquid. Analytical data: IR (film) 3443, 3050, 2943, 2858, 1439, 1252, 1103, 960, 829, 778, 701 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 6.4 Hz, 2H), 7.39 – 7.37 (m, 3H), 3.66 (t, *J* = 6.1 Hz, 2H), 2.32 (t, *J* = 7.1 Hz, 2H), 1.70 (triplet of triplets, *J* = 7.1, 6.1 Hz, 2H), 1.41 (s, 4H), 0.91 (s, 9H), 0.44 (s, 6H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 134.9, 129.8, 127.9, 87.1, 84.3, 61.9, 61.3, 32.2, 26.3, 26.2, 18.6, 15.6, –5.1, –5.7, –5.8.

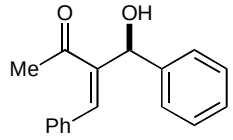
General Procedure for the Synthesis of Silyloxyallenes

To a flame-dried round bottom flask containing α-hydroxypropargylsilane in THF at 0 ºC was added *n*-BuLi (1.6 M in hexanes, 0.05 equiv) dropwise via syringe. Upon consumption of the propargylsilane and rearrangement to the allene as determined by thin layer chromatography (10% ethyl acetate/hexanes), the solution was concentrated *in vacuo* to provide the desired silyloxyallene which was used immediately in the addition to aldehydes. No purification of the silyloxyallene was performed.

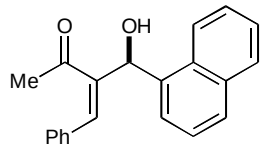
General Procedure for Addition of Silyloxyallenes to Aldehydes

To a 2-dram vial equipped with a magnetic stir bar and (salen)Cr(III)-SbF_6 **2** (0.1 equiv) was added aldehyde (1 equiv.). The vial was cooled to 20 ºC and silyloxyallene (1.5 equiv) dissolved in CH_2Cl_2 (250 μL) was added via syringe in one portion. Upon consumption of aldehyde (24 – 40h) as determined by thin layer chromatography, the solution was concentrated *in vacuo.* The resulting residue was dissolved in THF (5 mL) and treated with 1N HCl (1 mL). After 5-30 minutes, the solution was diluted with water (10 mL) and ether (20 mL) and transferred to 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

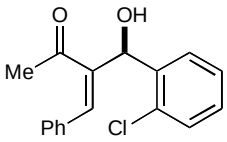
concentrated to provide the unpurified carbinol. The product was purified by flash chromatography to afford the desired product.



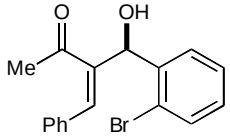
(*Z*)-3-(hydroxy(phenyl)methyl)-4-phenylbut-3-en-2-one (3): Prepared according to general procedure using silyloxyallene **1** (75 mg, 0.34 mmol), benzaldehyde (23 μL, 0.23 mmol) and (salen)Cr(III)-SbF_6 **2** (19 mg, 0.023 mmol) to afford 51 mg (88%) of **3** after flash chromatography (15% EtOAc/hexanes) as a yellow oil. Analytical data for **3**: IR (film) 3426, 3028, 1678, 1485, 1438, 1359, 1189, 1070, 1026, 742, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 8H), 7.23 (m, 2H), 6.94 (s, 1H), 5.58 (d, *J* = 5.3 Hz, 1H), 3.18 (d, *J* = 5.3 Hz, 1H), 1.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.2, 145.1, 141.2, 135.7, 132.5, 128.9, 128.8, 128.7, 128.2, 126.7, 76.5, 31.8; LRMS (electrospray): Exact mass calcd for $C_{17}H_{16}O_2$ $[M-H]^+$, 251.11. Found, 251.6. $[a]_D$: +2.7 (CH_2Cl_2, c = 1.0, ee = 85%). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 5% IPA/Hexanes, Rt_1 = 14.72, Rt_2 = 16.78).



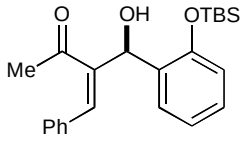
(*Z*)-3-(hydroxy(naphthalen-1-yl)methyl)-4-phenylbut-3-en-2-one (4): Prepared according to general procedure using silyloxyallene **1** (75 mg, 0.34 mmol), 1-naphthaldehyde (31 μL, 0.23 mmol) and (salen)Cr(III)-SbF_6 **2** (19 mg, 0.023 mmol) to afford 58 mg (84%) of **4** after flash chromatography (15% EtOAc/hexanes) as a yellow oil. Analytical data for **4**: IR (film) 3414, 3055, 2922, 1678, 1492, 1355, 1197, 1066, 989, 861, 774, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 7.1 Hz, 1H), 7.54 – 7.49 (m, 3H), 7.29 (m, 3H), 7.16 (m, 2H), 6.73 (s, 1H), 6.39 (d, *J* = 4.6 Hz, 1H), 3.05 (d, *J* = 4.9 Hz, 1H), 1.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3, 145.2, 136.5, 135.7, 134.0, 133.3, 130.9, 129.1, 129.0, 128.8, 128.7, 126.6, 126.0, 125.7, 125.1, 123.9, 73.1, 31.6; LRMS (electrospray): Exact mass calcd for $C_{21}H_{18}O_2$ $[2M+Na]^+$, 627.26. Found, 627.1. $[a]_D$: +45.3 (CH_2Cl_2, c = 1.0, ee = 91%). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 15% IPA/Hexanes, Rt_1 = 8.42, Rt_2 = 13.07).



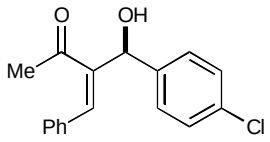
(*Z*)-3-((2-chlorophenyl)(hydroxy)methyl)-4-phenylbut-3-en-2-one (5): Prepared according to general procedure using silyloxyallene **1** (75 mg, 0.34 mmol), 2-chlorobenzaldehyde (26 μL, 0.23 mmol) and (salen)Cr(III)-SbF_6 **2** (19 mg, 0.023 mmol) to afford 65 mg (99%) **of 5** after flash chromatography (15% EtOAc/hexanes) as a yellow oil. Analytical data for **5**: IR (film) 3423, 3061, 2920, 1681, 1431, 1354, 1196, 1028, 755, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.27 (m, 6H), 7.20 (m, 2H), 6.79 (s, 1H), 5.88 (d, *J* = 5.1 Hz, 1H), 3.54 (d, *J* = 5.3 Hz, 1H), 1.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.4, 142.9, 138.3, 135.6, 134.5, 132.7, 129.8, 129.3, 129.0, 128.9, 128.8, 127.4, 72.9, 31.4; LRMS (electrospray): Exact mass calcd for $C_{17}H_{15}O_2Cl$ $[M-H]^+$, 285.07. Found, 285.4. $[a]_D$: +22.2 (CH_2Cl_2, c = 1.0, ee = 94%). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 5% IPA/Hexanes, Rt_1 = 11.86, Rt_2 = 12.41).



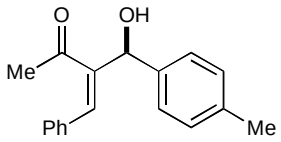
(*Z*)-3-((2-bromophenyl)(hydroxy)methyl)-4-phenylbut-3-en-2-one (6): Prepared according to general procedure using silyloxyallene **1** (75 mg, 0.34 mmol), 2-bromobenzaldehyde (27 μL, 0.23 mmol) and (salen)Cr(III)-SbF_6 **2** (19 mg, 0.023 mmol) to afford 74 mg (98%) of **6** after flash chromatography (15% EtOAc/hexanes) as a yellow oil. Analytical data for **6**: IR (film) 3417, 3059, 1682, 1431, 1353, 1195, 1020, 752, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 6.3 Hz, 1H), 7.57 (d, J = 6.8 Hz, 1H), 7.40 (t, J = 7.0 Hz, 1H), 7.32 (m, 3H), 7.19 (m, 3H), 6.76 (s, 1H), 5.82 (bs, 1H), 3.49 (bs, 1H), 1.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.7, 143.0, 139.8, 135.6, 134.8, 133.1, 129.6, 129.1, 128.9, 128.8, 128.0, 122.9, 74.9, 31.3; LRMS (electrospray): Exact mass calcd for $C_{17}H_{15}O_2Br$ $[2M+Na]^+$, 685.40. Found, 684.9. $[a]_D$: +32.1 (CH_2Cl_2, c = 1.0, ee = 91%). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 5% IPA/Hexanes, Rt_1 = 10.80, Rt_2 = 12.52).



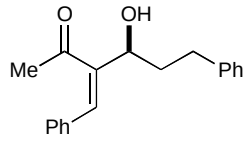
(*Z*)-3-((2-(*tert*-butyldimethylsilyloxy)phenyl)(hydroxy) methyl)-4-phenylbut-3-en-2-one (7): Prepared according to general procedure using silyloxyallene **1** (50 mg, 0.22 mmol), TBS-protected salicylaldehyde (36 mg, 0.15 mmol) and (salen)Cr(III)-SbF_6 **2** (12 mg, 0.015 mmol) to afford 46 mg (79%) of **7** after flash chromatography (15% EtOAc/hexanes) as a yellow oil. Analytical data for **7**: IR (film) 3444, 3028, 2930, 2858, 1681, 1582, 1477, 1361, 1257, 1195, 1099, 1024, 919, 833, 759, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (m, 1H), 7.45-7.41 (m, 2H), 7.33-7.28 (m, 3H), 7.22-7.20 (m, 3H), 7.10 (m, 1H), 6.69 (s, 1H), 5.92 (d, *J* = 5.5 Hz, 1H), 3.29 (d, *J* = 5.8 Hz, 1H), 1.94 (s, 3H), 1.04 (s, 9H), 0.32 (s, 3H), 0.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.9, 153.3, 145.0, 136.0, 134.7, 132.0, 131.0, 130.8, 129.2, 129.1, 128.3, 128.8, 128.6, 127.4, 121.6, 118.5, 71.4, 26.1, 18.6; LRMS (electrospray): Exact mass calcd for $C_{23}H_{30}O_3Si$ $[2M+Na]^+$, 787.40. Found 787.7. $[a]_D$: +35.0 (CH_2Cl_2, c = 1.0, ee = 86%). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 5% IPA/Hexanes, Rt_1 = 4.81, Rt_2 = 5.22).



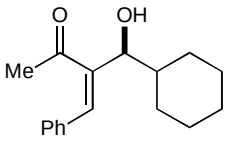
(*Z*)-3-((4-chlorophenyl)(hydroxy)methyl)-4-phenylbut-3-en-2-one (8): Prepared according to general procedure using silyloxyallene **1** (75 mg, 0.34 mmol), 4-chlorobenzaldehyde (32 mg, 0.23 mmol) and (salen)Cr(III)-SbF_6 **2** (19 mg, 0.023 mmol) to afford 64 mg (94%) of **8** after flash chromatography (15% EtOAc/hexanes) as a yellow oil. Analytical data for **8**: IR (film) 3422, 3041, 2922, 1678, 1485, 1359, 1187, 1084, 1026, 825, 754, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 7H), 7.22 (m, 2H), 6.93 (s, 1H), 5.53 (d, *J* = 5.3 Hz, 1H), 3.34 (d, *J* = 5.3 Hz, 1H), 1.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.0, 144.6, 139.9, 135.5, 133.9, 133.4, 129.1, 129.0, 128.9, 128.1, 75.9, 31.8; LRMS (electrospray): Exact mass calcd for $C_{17}H_{15}O_2Cl$ $[M-H]^+$, 285.07. Found [M–H], 285.2. $[a]_D$: –6.5 (CH_2Cl_2, c = 1.0, ee = 88%). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 5% IPA/Hexanes, Rt_1 = 54.11, Rt_2 = 58.15).



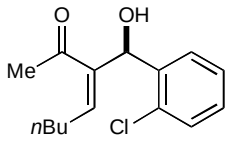
(*Z*)-3-(hydroxy(*p*-tolyl)methyl)-4-phenylbut-3-en-2-one (9): Prepared according to general procedure using silyloxyallene **1** (75 mg, 0.34 mmol), 4-methylbenzaldehyde (27 μL, 0.23 mmol) and (salen)Cr(III)-SbF_6 **2** (19 mg, 0.023 mmol) to afford 45 mg (74%) of **9** after flash chromatography (15% EtOAc/hexanes) as a yellow oil. Analytical data for **9**: IR (film) 3426, 3021, 2921, 1678, 1493, 1408, 1359, 1187, 1030, 821, 760, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 5H), 7.23 (d, *J* = 7.1 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 6.93 (s, 1H), 5.55 (d, *J* = 5.3 Hz, 1H), 3.01 (d, *J* = 5.5 Hz, 1H), 2.34 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.2, 145.3, 138.2, 137.9, 135.8, 132.2, 129.5, 128.9, 128.8, 126.6, 76.3, 31.8, 21.4; LRMS (electrospray): Exact mass calcd for $C_{18}H_{18}O_2$ $[M\text{-}OH]^+$, 249.13. Found, 249.3. $[a]_D$: +18.7 (CH_2Cl_2, c = 1.0, ee = 84%). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 5% IPA/Hexanes, Rt_1 = 45.99, Rt_2 = 50.19).



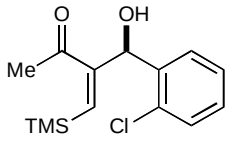
(*Z*)-3-benzylidene-4-hydroxy-6-phenylhexan-2-one (10): Prepared according to general procedure using silyloxyallene **1** (75 mg, 0.34 mmol), hydrocinnamaldehyde (30 μL, 0.23 mmol) and (salen)Cr(III)-SbF_6 **2** (19 mg, 0.023 mmol) to afford 65 mg (95%) of **10** after flash chromatography (15% EtOAc/hexanes) as a yellow oil. Analytical data for **10**: IR (film) 3426, 3026, 2923, 1680, 1489, 1354, 1198, 1062, 750, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 5H), 7.23 – 7.19 (m, 5H), 6.91 (s, 1H), 4.40 (q, *J* = 6.4 Hz, 1H), 2.84 (m, 1H), 2.73 (m, 1H), 2.59 (d, *J* = 6.2 Hz, 1H), 2.02 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.2, 145.3, 141.7, 135.7, 132.5, 128.9, 128.8, 128.7, 128.6, 126.2, 74.7, 38.0, 32.4, 31.8; LRMS (electrospray): Exact mass calcd for $C_{19}H_{20}O_2$ $[M\text{-}H]^+$, 279.15. Found, 279.1. $[a]_D$: +13.1 (CH_2Cl_2, c = 1.0, ee = 61%). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 10% IPA/Hexanes, Rt_1 = 9.52, Rt_2 = 12.55).



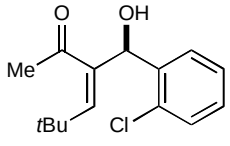
(*Z*)-3-(cyclohexyl(hydroxy)methyl)-4-phenylbut-3-en-2-one (11): Prepared according to general procedure using silyloxyallene **1** (75 mg, 0.34 mmol), cyclohexanecarboxaldehyde (28 μL, 0.23 mmol) and (salen)Cr(III)-SbF_6 **2** (19 mg, 0.023 mmol) to afford 33 mg (57%) of **11** after flash chromatography (15% EtOAc/hexanes) as a yellow oil. Analytical data for **11**: IR (film) 3438, 2925, 2851, 1678, 1439, 1352, 1195, 1099, 1018, 754, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 3H), 7.22 (m, 2H), 6.85 (s, 1H), 4.01 (t, *J* = 7.3 Hz, 1H), 2.58 (d, *J* = 6.8 Hz, 1H), 2.02 (m, 4H), 1.80 – 1.63 (m, 4H), 1.53 (m, 1H), 1.25 (m, 3H), 1.02 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.4, 144.4, 135.8, 133.6, 128.8, 128.7, 128.6, 81.1, 42.5, 31.9, 30.4, 28.9, 26.6, 26.2, 26.1; LRMS (electrospray): Exact mass calcd for $C_{17}H_{22}O_2$ $[M\text{-}H]^+$, 257.16. Found, 257.0. $[a]_D$: +8.5 (CH_2Cl_2, c = 1.0, ee = 34%). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 5% IPA/Hexanes, Rt_1 = 7.68, Rt_2 = 8.19).



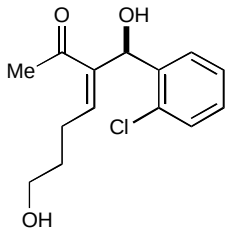
(*Z*)-3-((2-chlorophenyl)(hydroxy)methyl)oct-3-en-2-one (12): Prepared according to general procedure using silyloxyallene prepared from 2-(dimethyl(phenyl)silyl)oct-3-yn-2-ol (75 mg, 0.29 mmol), 2-chlorobenzaldeyde (22 μL, 0.19 mmol) and (salen)Cr(III)-SbF_6 **2** (16 mg, 0.02 mmol) to afford 50 mg (98%) of **12** after flash chromatography (15% EtOAc/hexanes) as a yellow oil. Analytical data for **12**: IR (film) 3407, 2942, 2927, 2865, 1681, 1450, 1370, 1195, 1022, 751 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 5.81 (d, *J* = 5.1 Hz, 1H), 5.72 (t, *J* = 7.7 Hz, 1H), 3.09 (d, *J* = 5.3 Hz, 1H), 2.31 – 2.24 (m, 5H), 1.39 – 1.28 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.7, 141.4, 139.5, 139.0, 132.7, 129.7, 129.1, 128.3, 127.2, 72.2, 31.6, 31.5, 29.5, 22.5, 14.0; LRMS (electrospray): Exact mass calcd for $C_{15}H_{19}O_2Cl$ $[M–H]^+$, 265.11. Found, 265.5. $[a]_D$: –8.2 (CH_2Cl_2, c = 1.0, ee = 80%). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 5% IPA/Hexanes, Rt_1 = 7.92, Rt_2 = 10.98).



(*Z*)-3-((2-chlorophenyl)(hydroxy)methyl)-4-(trimethylsilyl)but-3-en-2-one (13): Prepared according to general procedure using silyloxyallene prepared from 2-(dimethyl(phenyl)silyl)-4-(trimethylsilyl)but-3-yn-2-ol (75 mg, 0.27 mmol), 2-chlorobenzaldeyde (18 μL, 0.18 mmol) and (salen)Cr(III)-SbF_6 **1** (15 mg, 0.018 mmol) to afford 46 mg (90%) of **13** after flash chromatography (15% EtOAc/hexanes) as a yellow oil. Analytical data for **13**: IR (film) 3400, 2953, 1686, 1585, 1425, 1358, 1245, 1180, 1024, 840, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.30 – 7.27 (m, 2H), 6.05 (s, 1H), 5.98 (d, *J* = 4.8 Hz, 1H), 2.46 (d, *J* = 5.1 Hz, 1H), 2.23 (s, 3H), 0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.3, 155.2, 139.9, 138.6, 133.4, 130.0, 129.7, 128.7, 127.6, 72.1, 29.4, –0.3; LRMS (electrospray): Exact mass calcd for $C_{14}H_{19}O_2SiCl$ $[M–OH]^+$, 265.08. Found, 265.3. $[a]_D$: +37.2 (CH_2Cl_2, c = 1.0, ee = 90%). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 5% IPA/Hexanes, Rt_1 = 7.66, Rt_2 = 12.35).



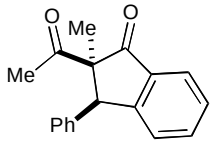
(*Z*)-3-((2-chlorophenyl)(hydroxy)methyl)-5,5-dimethylhex-3-en-2-one (14): Prepared according to general procedure using silyloxyallene prepared from 2-(dimethyl(phenyl)silyl)-5,5-dimethylhex-3-yn-2-ol (75 mg, 0.27 mmol), 2-chlorobenzaldeyde (22 μL, 0.19 mmol) and (salen)Cr(III)-SbF_6 **2** (16 mg, 0.019 mmol) to afford 51 mg (99%) of **14** after flash chromatography (15% EtOAc/hexanes) as a yellow oil. Analytical data for **14**: IR (film) 3417, 2955, 1690, 1456, 1362, 1258, 1180, 1031, 822, 748 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J*= 7.8 Hz, 1H), 7.31 (t, *J* = 7.4 H, 1H), 7.26 (m, 1H), 5.62 (d, *J* = 4.8 Hz, 1H), 5.41 (s, 1H), 2.66 (d, *J* = 4.8 Hz, 1H), 2.15 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3, 141.9, 139.4, 138.4, 132.7, 129.8, 129.3, 128.1, 127.3, 73.4, 33.6, 33.1, 30.3; LRMS (electrospray): Exact mass calcd for $C_{15}H_{19}O_2Cl$ $[M–OH]^+$, 249.11. Found, 249.4. $[a]_D$: –14.0 (CH_2Cl_2, c = 1.0, ee = 90%). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 5% IPA/Hexanes, Rt_1 = 7.66, Rt_2 = 8.54).



(*Z*)-3-((2-chlorophenyl)(hydroxy)methyl)-7-hydroxyhept-3-en-2-one (15): Prepared according to general procedure using silyloxyallene prepared from 7-(*tert*-butyldimethylsilyloxy)-2-(dimethyl(phenyl)silyl)hept-3-yn-2-ol (75 mg, 0.199 mmol), 2-chlorobenzaldeyde (15 μL, 0.133 mmol) and (salen)Cr(III)-SbF_6 **2** (11 mg, 0.013 mmol) to afford 33 mg (92%) of **15** after flash chromatography (50% EtOAc/hexanes) as a yellow oil. Analytical data for **15**: IR (film) 3363, 2926, 2870, 1683, 1431, 1370, 1192, 1023, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.37–7.31 (m, 2H), 7.28 (m, 1H), 5.88 (d, *J* = 4.8 Hz, 1H), 5.63 (t, *J* = 8.1 Hz, 1H), 3.60 (m, 2H), 2.86 (d, *J* = 5.3, 1H), 2.36 – 2.33 (m, 6H), 1.66 – 1.61 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 142.9, 138.9, 138.2, 132.7, 129.8, 129.4, 128.4, 127.4, 71.5, 61.4, 31.4, 30.7, 25.8; LRMS (electrospray): Exact mass calcd for $C_{14}H_{17}O_3Cl$ $[M–H]^+$, 267.09. Found, 267.3. [a]$_D$: –15.6 (CH_2Cl_2, c = 1.0, ee = 87%). Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 10% IPA/Hexanes, Rt_1 = 11.37, Rt_2 = 15.67).

For analytical data for **16**, see reference.[5]

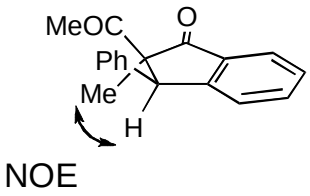
Synthesis of Indanone 19[6]



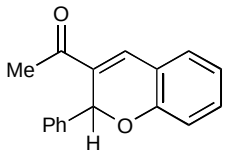
2-ethanoyl-2-methyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (19). To a 2-5 mL microwave vial equipped with a magnetic stir bar was dissolved **6** (200 mg, 0.6 mmol), $(PPh_3)_2PdCl_2$ (2 mg, 0.003 mmol), and Cy_2MeN (0.26 mL, 1.2 mmoL) in DMF (3 mL). The solution was heated in a microwave at 160 ºC for 10 minutes. The solvent was removed and the residue was dissolved in EtOAc (10 mL). This solution was washed with 1N HCl (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was dissolved in DMF (2 mL) and treated with MeI (41 μL, 0.66 mmol) and K_2CO_3 (91 mg, 0.66 mmol). After 1 h, the reaction was quenched with aqueous NH_4Cl, diluted with ether (10 mL), and transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted with ether (2 X 5mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The indanone was purified by flash chromatography (10% EtOAc/Hex) to afford 80 mg (56%) of **19**. Analytical data for **19**: IR (film) 3030, 2973, 2929, 1712, 1597, 1455, 1354, 1219, 1153, 1087, 959, 759, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.33-7.28 (m, 3H), 7.10 (m, 2H), 4.55 (s, 1H), 1.68 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 205.9, 154.2, 138.4, 136.7, 135.7, 129.5, 129.0, 128.9, 128.1, 127.3, 124.6, 68.8, 58.0, 29.5, 21.6; LRMS

[5] T. E. Reynolds, A. R. Bharadwaj, K. A. Scheidt, *J. Am. Chem. Soc.* **2006**, *128*, 15382-15383.
[6] A. Puschl, H. C. Rudbeck, A. Faldt, A. Confante, J. Kehler, *Synthesis* **2005**, 291-295.

(electrospray): Exact mass calcd for $C_{18}H_{16}O_2$ $[2M+Na]^+$, 551.24. Found, 551.5. ee = 70%; Enantiomeric ratio was measured by chiral HPLC (Chiralcel AD-H, 1% IPA/Hexanes, Rt_1 = 28.45, Rt_2 = 32.43). The relative stereochemistry was determined by NOE observed between the benzylic hydrogen and methyl group.

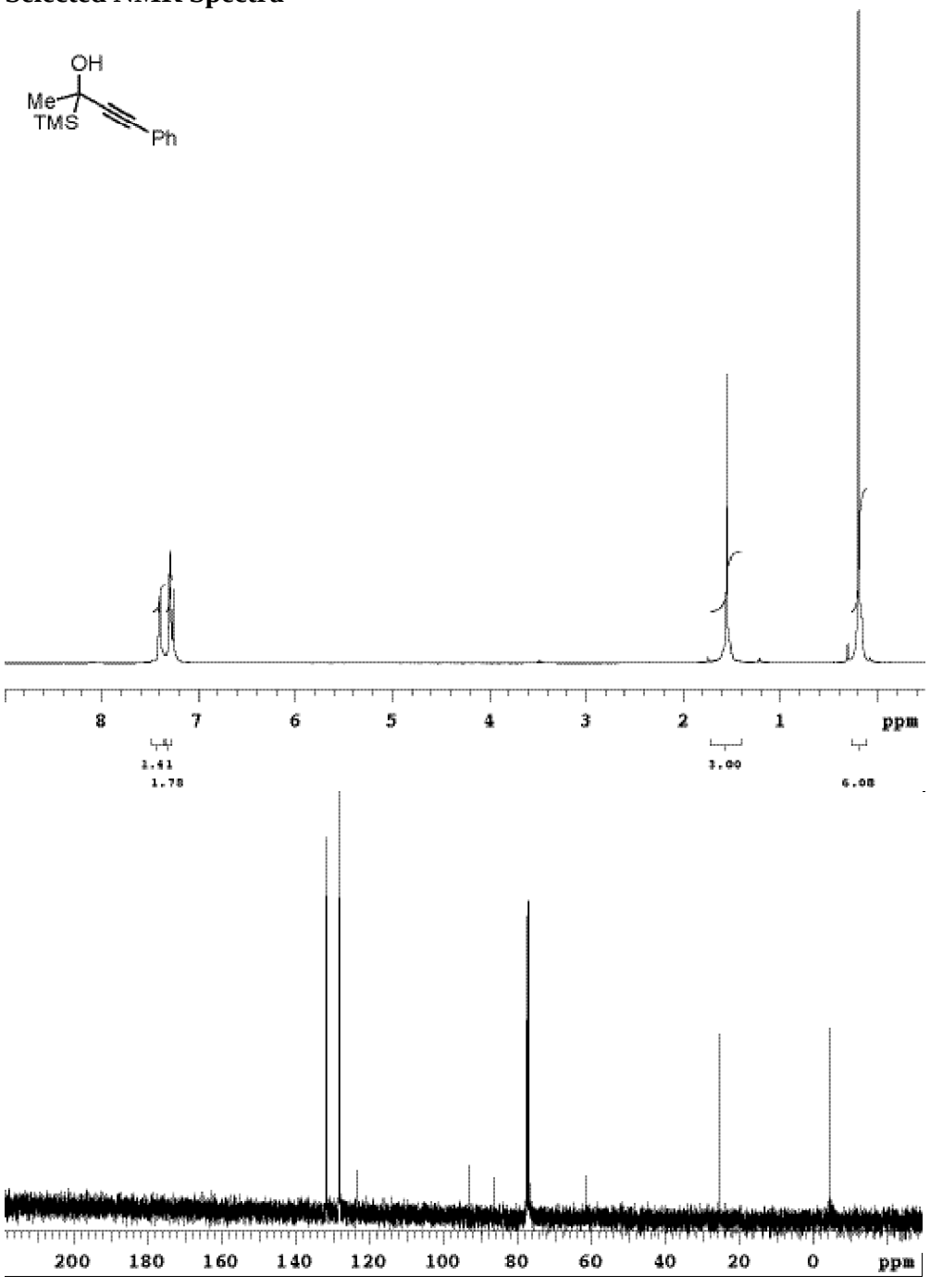


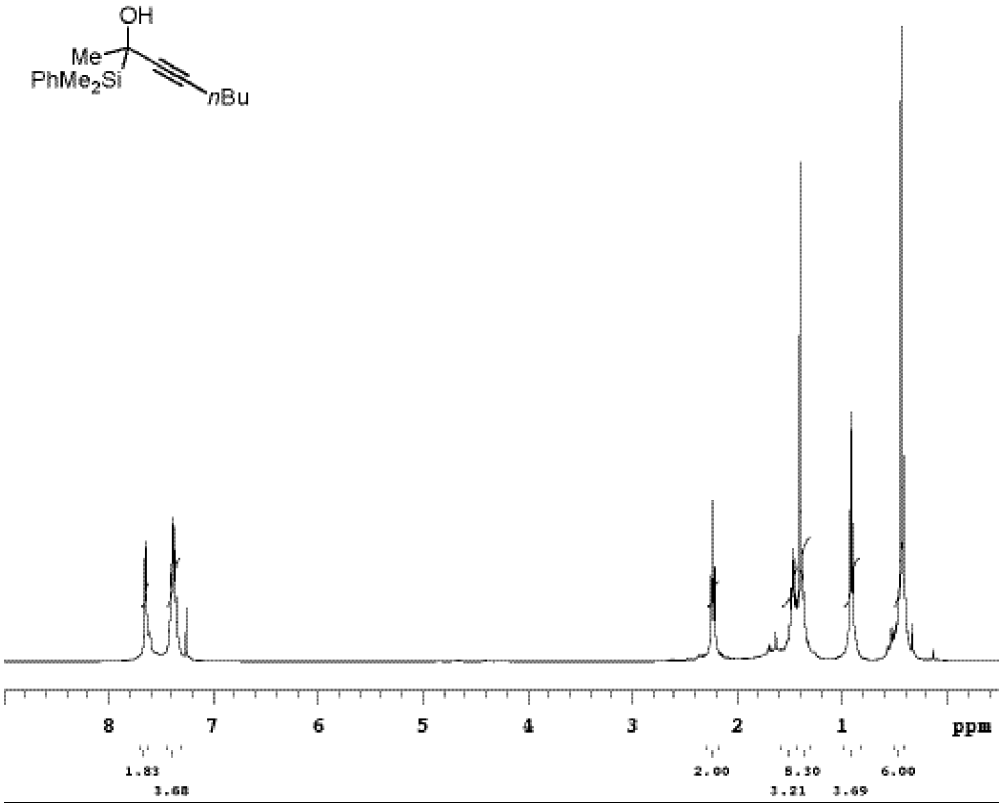
Synthesis of Chromene 20



1-(2-phenyl-2*H*-chromen-3-yl)ethanone (20). To a 2-dram vial equipped with a magnetic stir bar and **7** (25 mg, 0.065 mmol) in THF at 0 ºC was added TBAF (1M in THF, 0.065 mmol). Upon consumption of deprotected **7** (24h) as determined by thin layer chromatography, aqueous NH_4Cl was added to the reaction. The mixture was diluted with ether and transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted with ether (3 X 10 mL). The combined ether layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to provide the unpurified chromene. The product was purified by flash chromatography (10% EtOAc/Hex) to afford 10 mg (61%) of 20. Analytical data for **20**: IR (film) 3047, 1651, 1616, 1445, 1373, 1253, 1207, 1058, 753, 686 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.35 (m, 2H), 7.28- 7.22 (m, 5H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.44 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 154.4, 139.6, 133.9, 133.1, 132.9, 129.4, 127.2, 121.8, 120.5, 99.9, 74.8, 25.6; LRMS (electrospray): Exact mass calcd for $C_{17}H_{14}O_2$ $[M-C_2H_3O+Na]^+$, 230.30. Found [M–H], 230.3. ee = 68%; Enantiomeric ratio was measured by chiral HPLC (Chiralcel OD-H, 1.2% IPA/Hexanes, Rt_1 = 17.56, Rt_2 = 19.11).

Selected NMR Spectra

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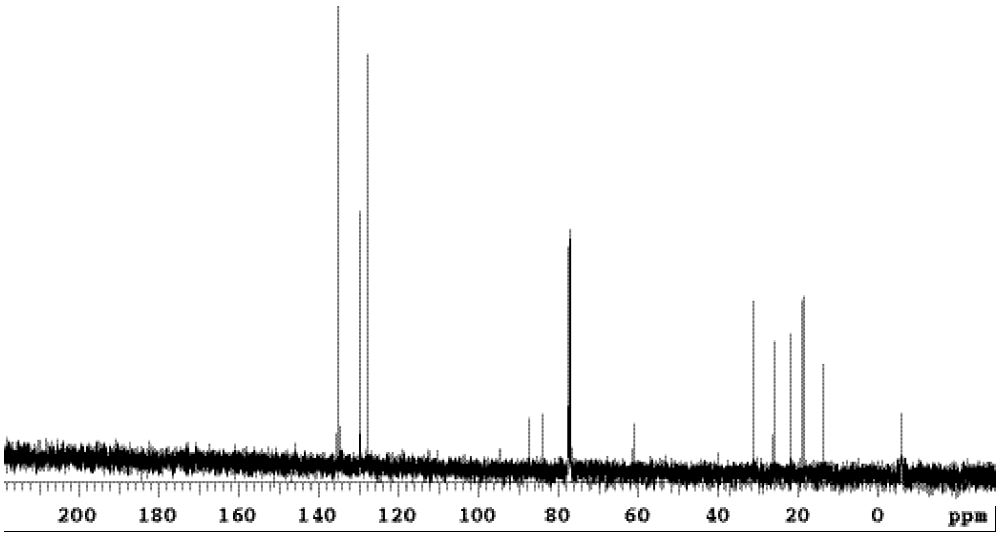
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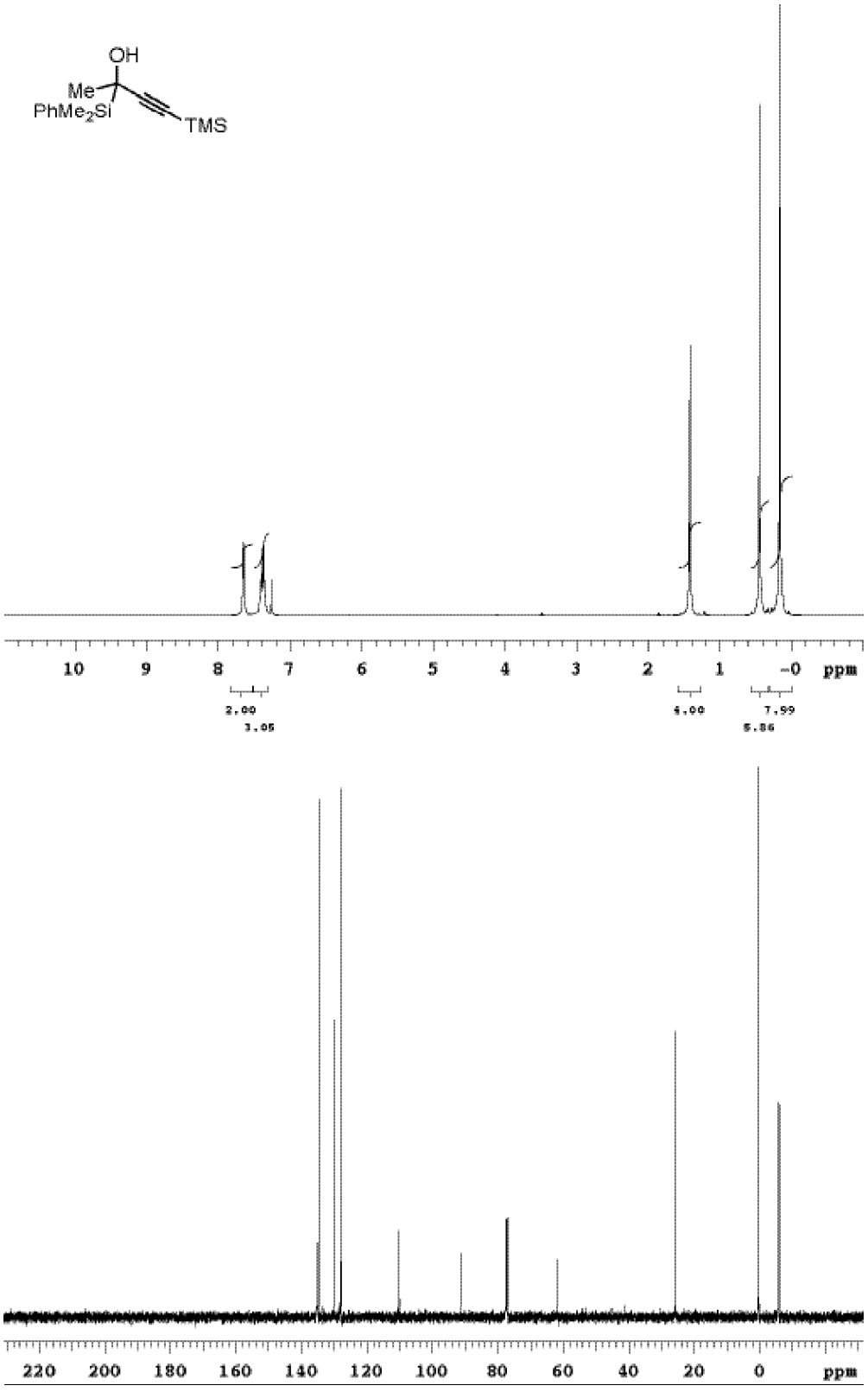
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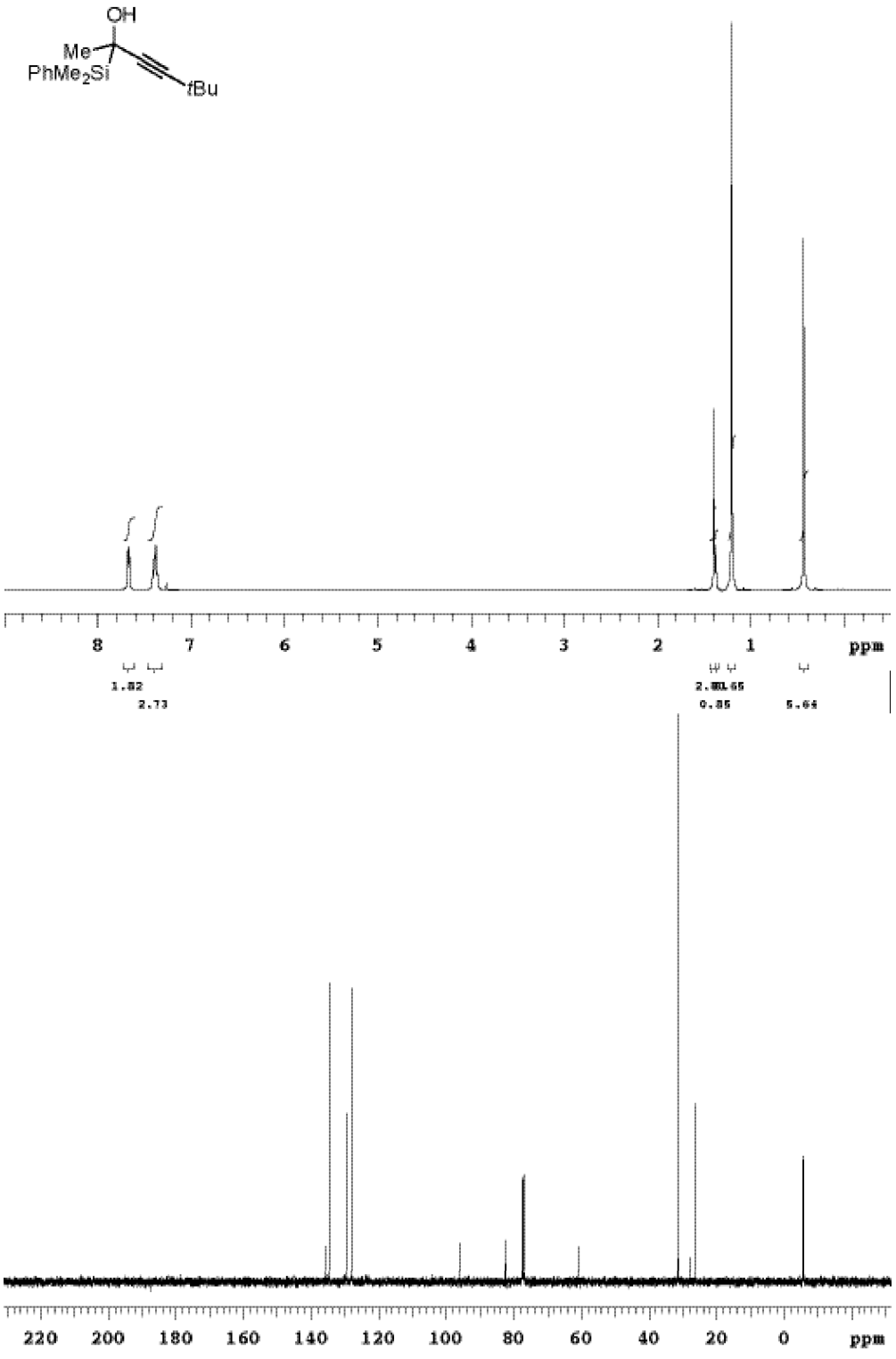
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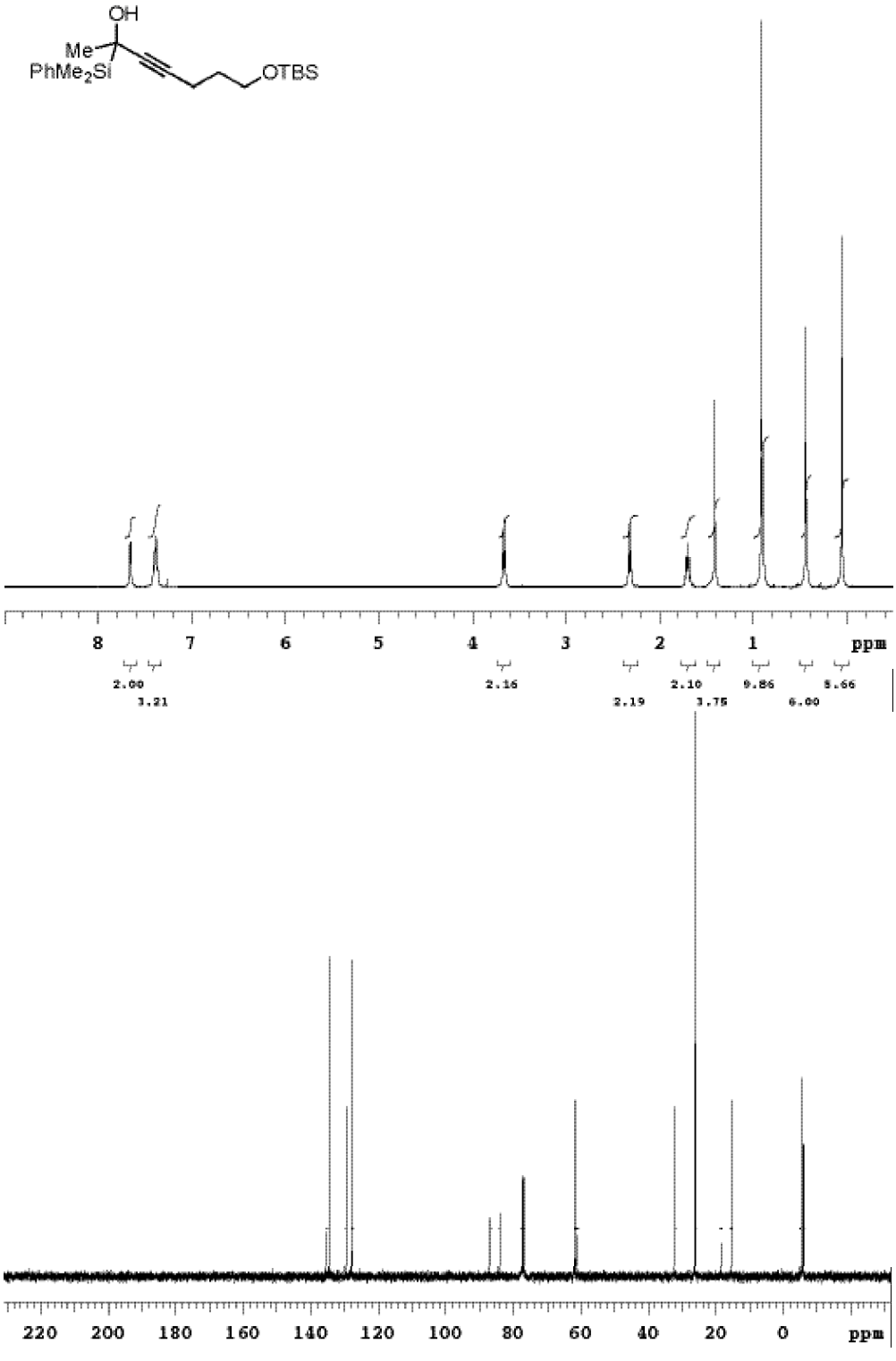
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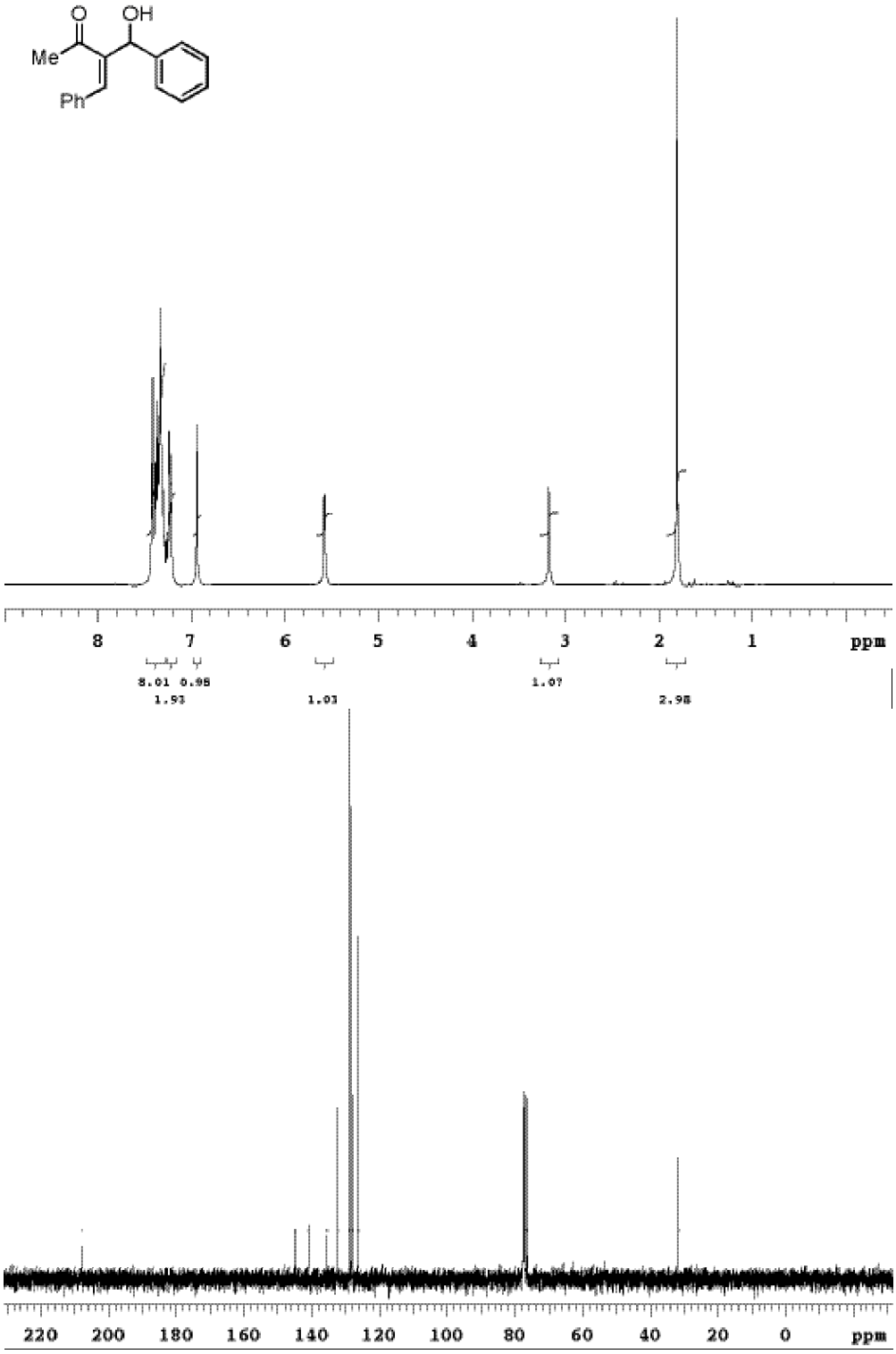
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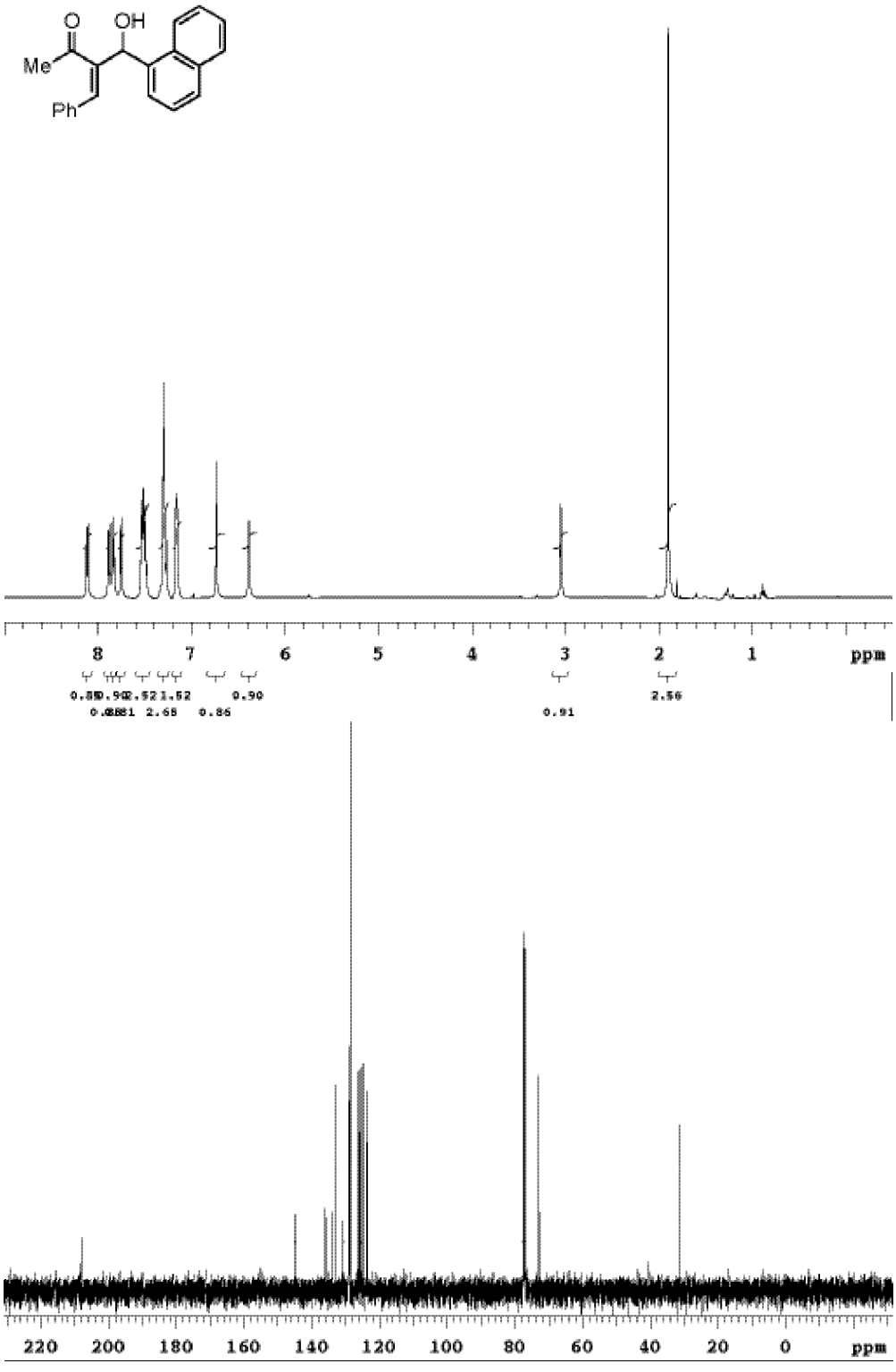
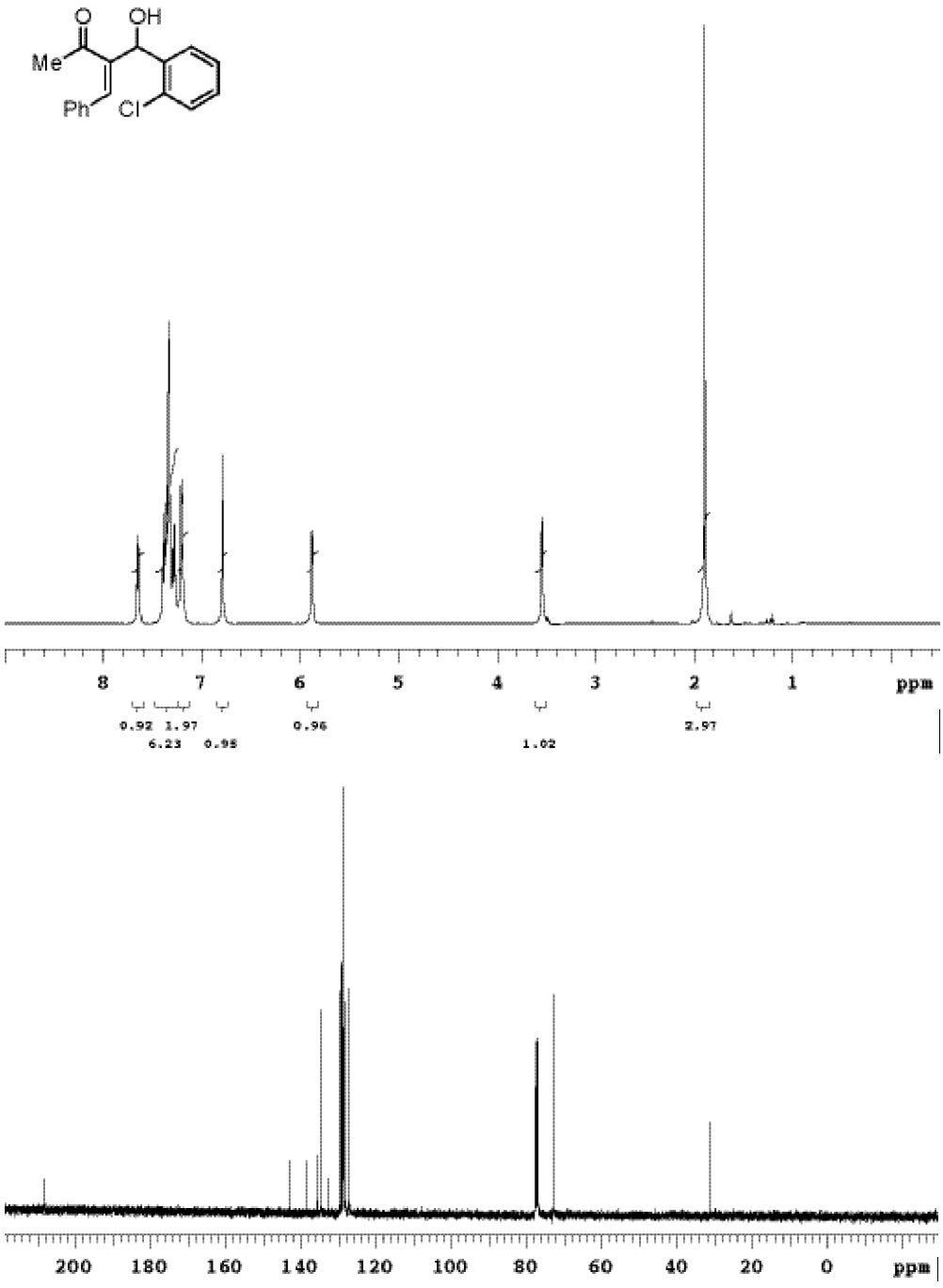
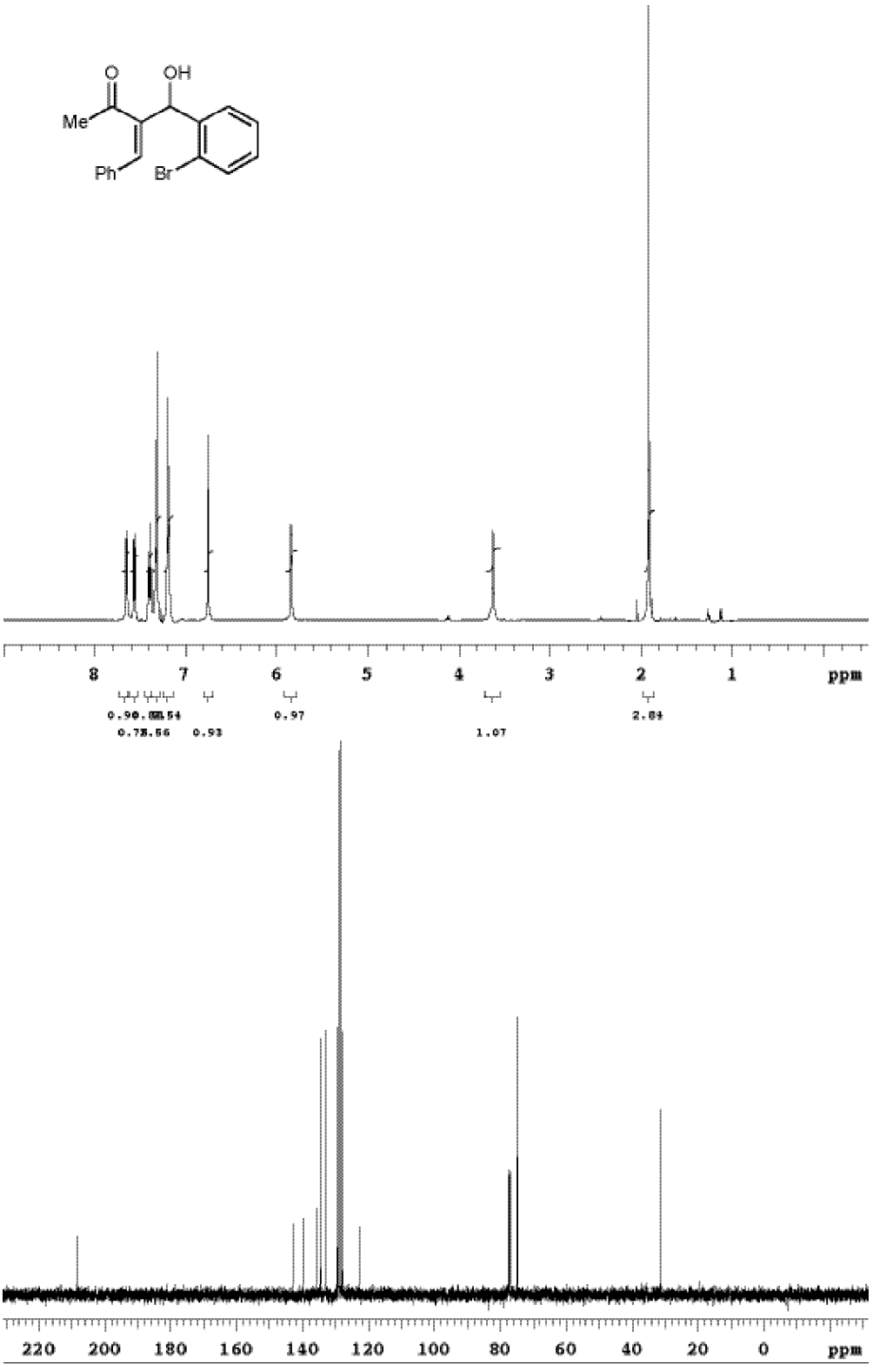
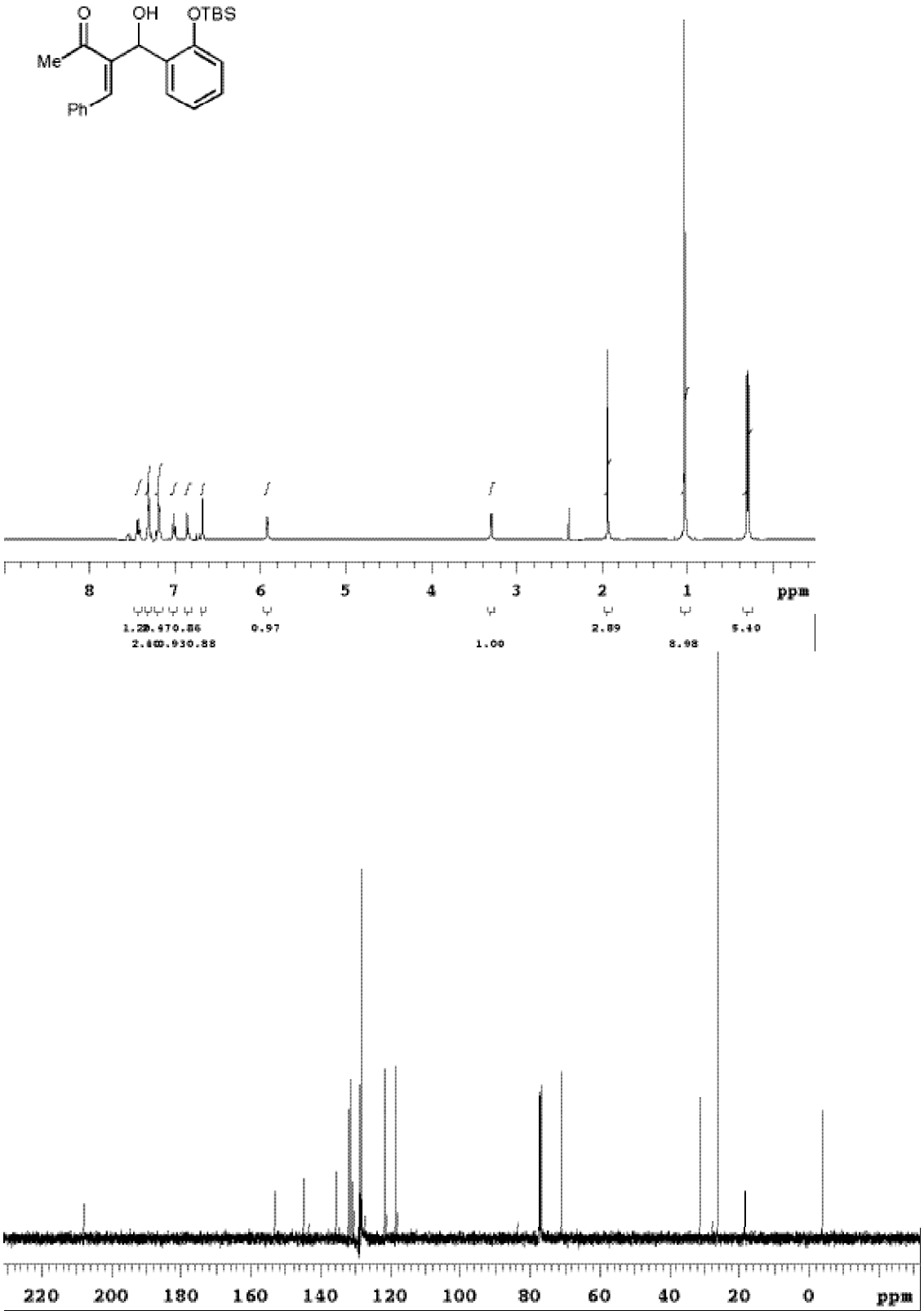
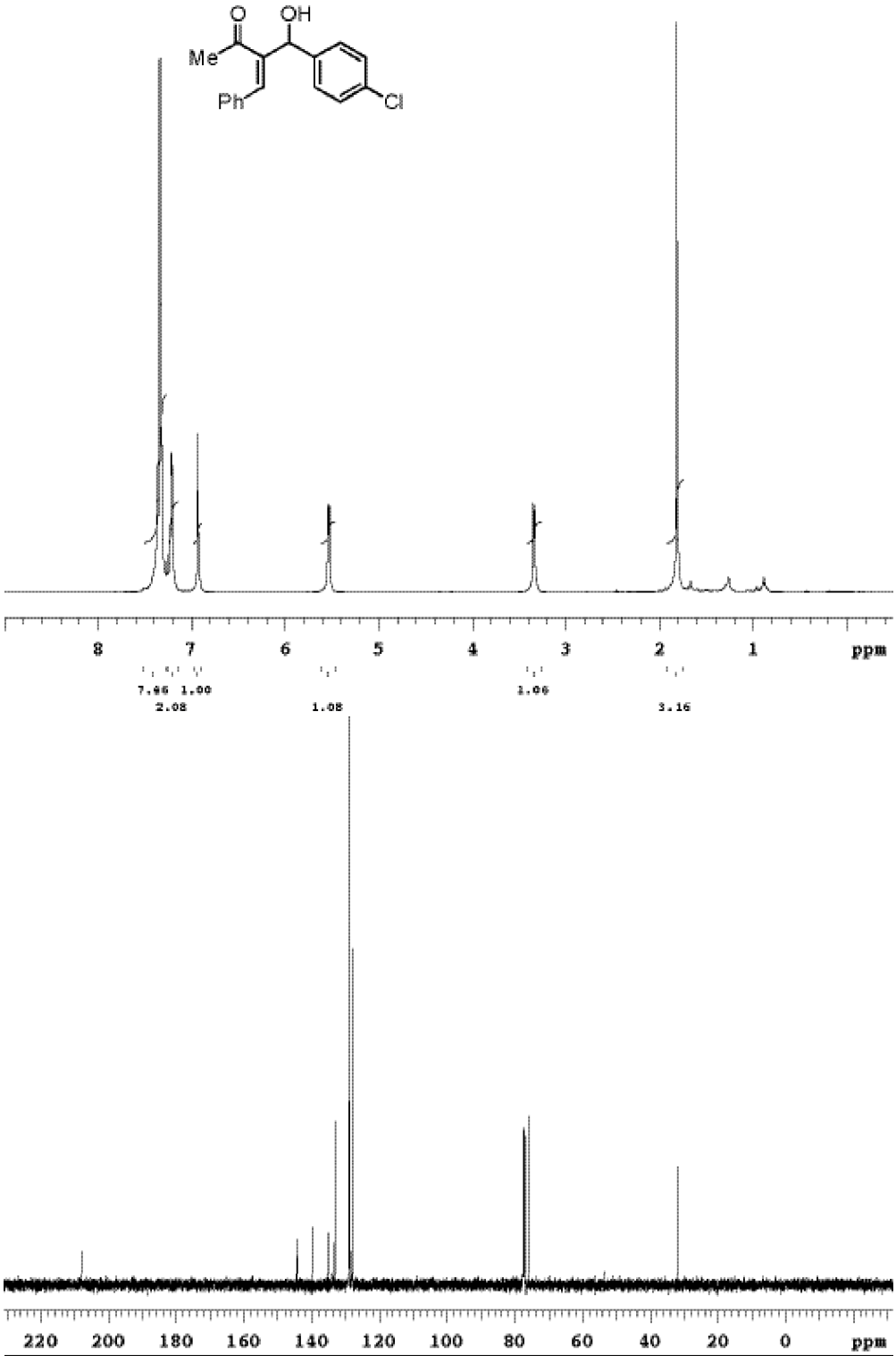
20
0
ppm

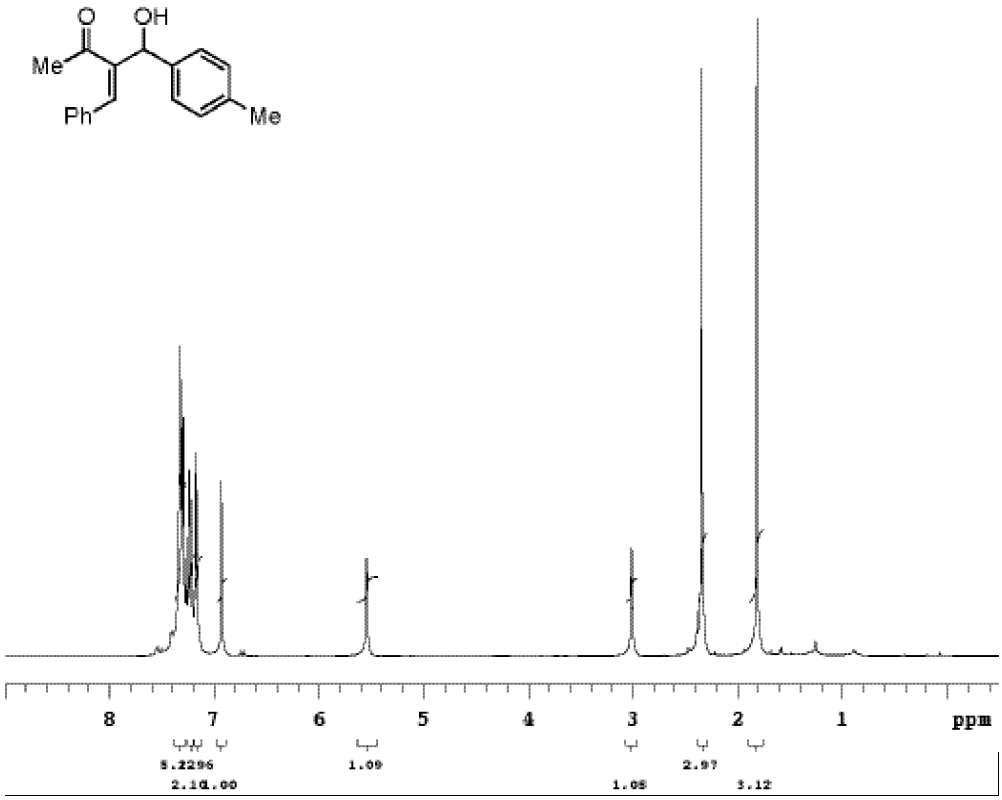

O
OH
Me
Ph
8
7
6
5
4
3
2
1
ppm
0.90
2.56
0.91
220
200
180
160
140
120
100
80
60
40
20
0
ppm

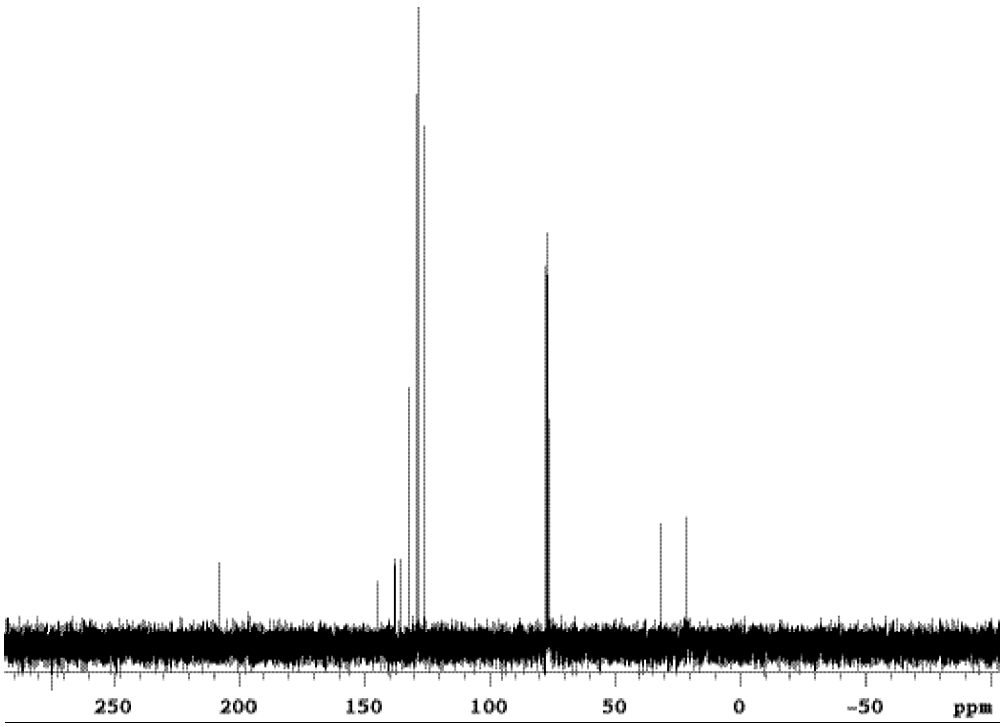

O
OH
Me
Ph
Cl
8
7
6
5
4
3
2
1
ppm
0.92
1.97
6.23
0.98
0.96
1.02
2.97
200
180
160
140
120
100
80
60
40
20
0
ppm

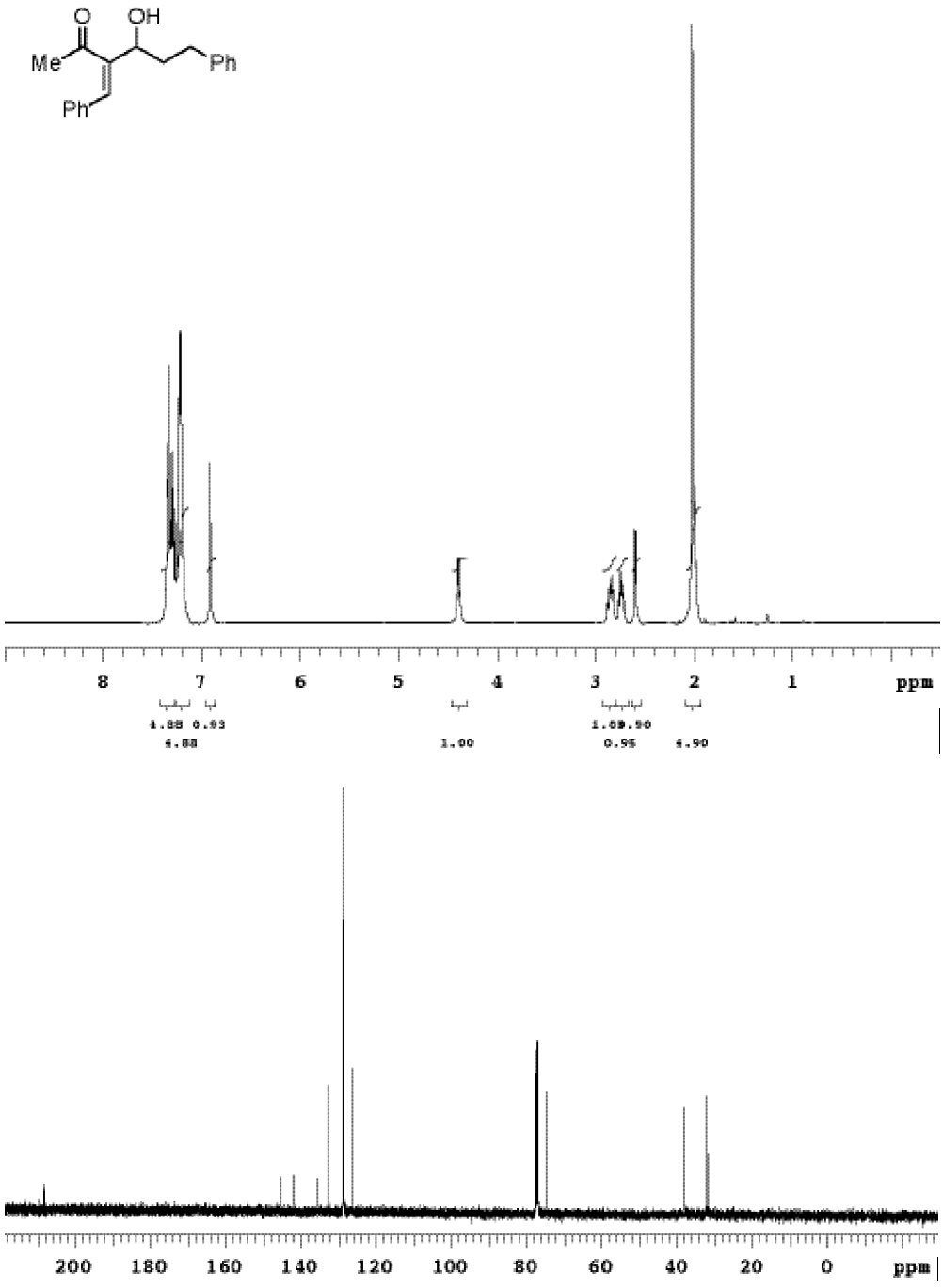

O
OH
Me
Ph
Br
8
7
6
5
4
3
2
1
ppm
0.90
0.78
0.56
0.93
0.97
1.07
2.84
220
200
180
160
140
120
100
80
60
40
20
0
ppm

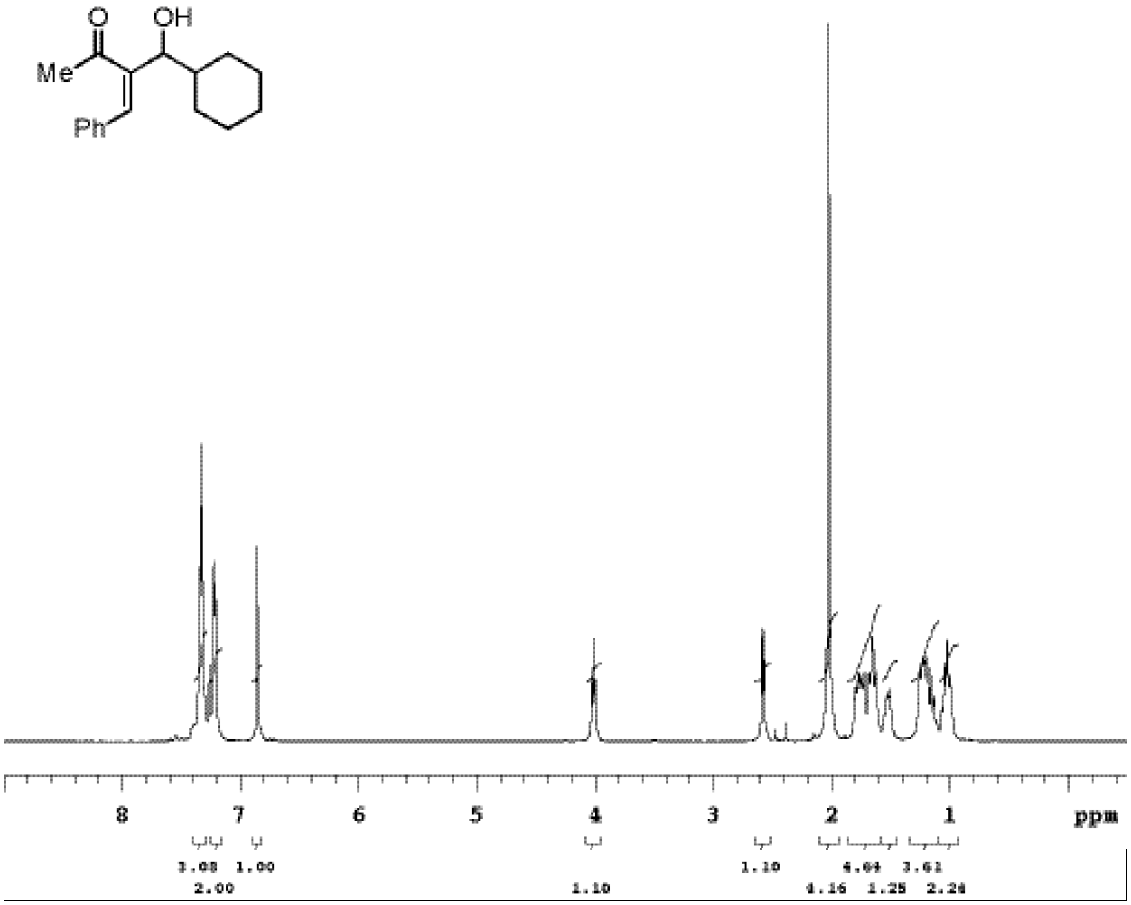

O
OH
OTBS
Me
Ph
8
7
6
5
4
3
2
1
ppm
0.97
1.00
2.89
8.98
5.40
220
200
180
160
140
120
100
80
60
40
20
0
ppm

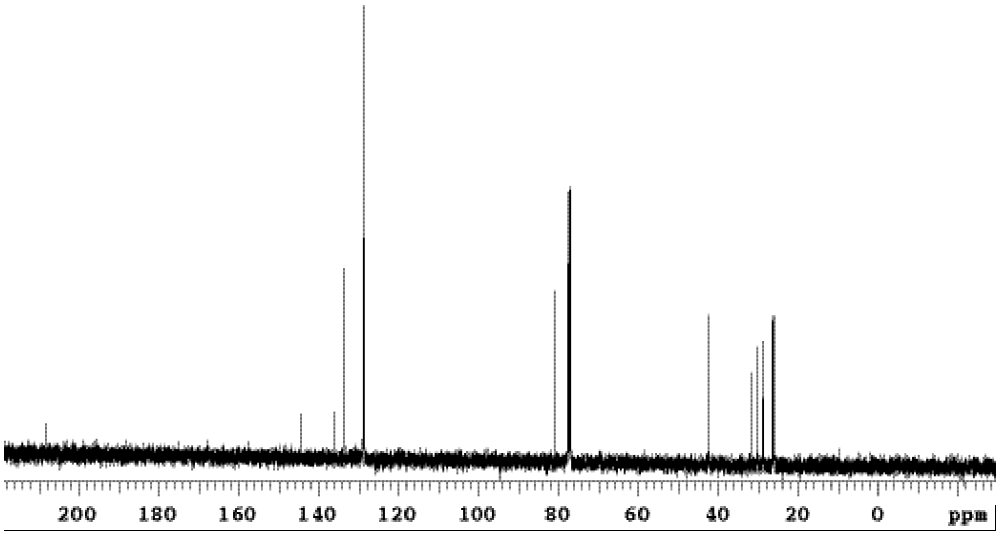

O
OH
Me
Ph
Cl
8
7
6
5
4
3
2
1
ppm
7.46 1.00
2.08
1.08
1.06
3.16
220
200
180
160
140
120
100
80
60
40
20
0
ppm

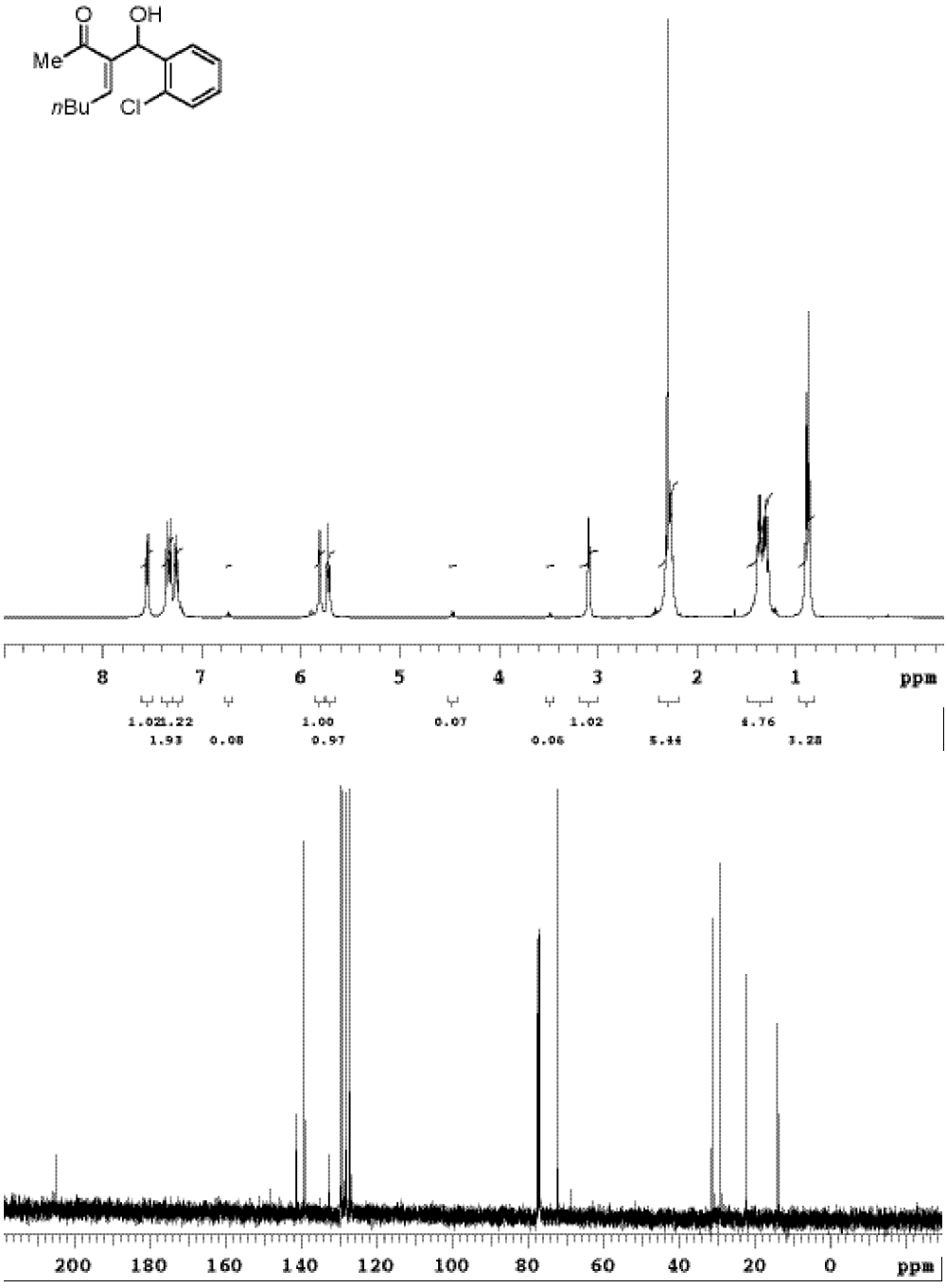

O
OH
Me
Ph
Me
8
7
6
5
4
3
2
1
ppm
5.2296
2.1611.00
1.09
1.08
2.97
3.12

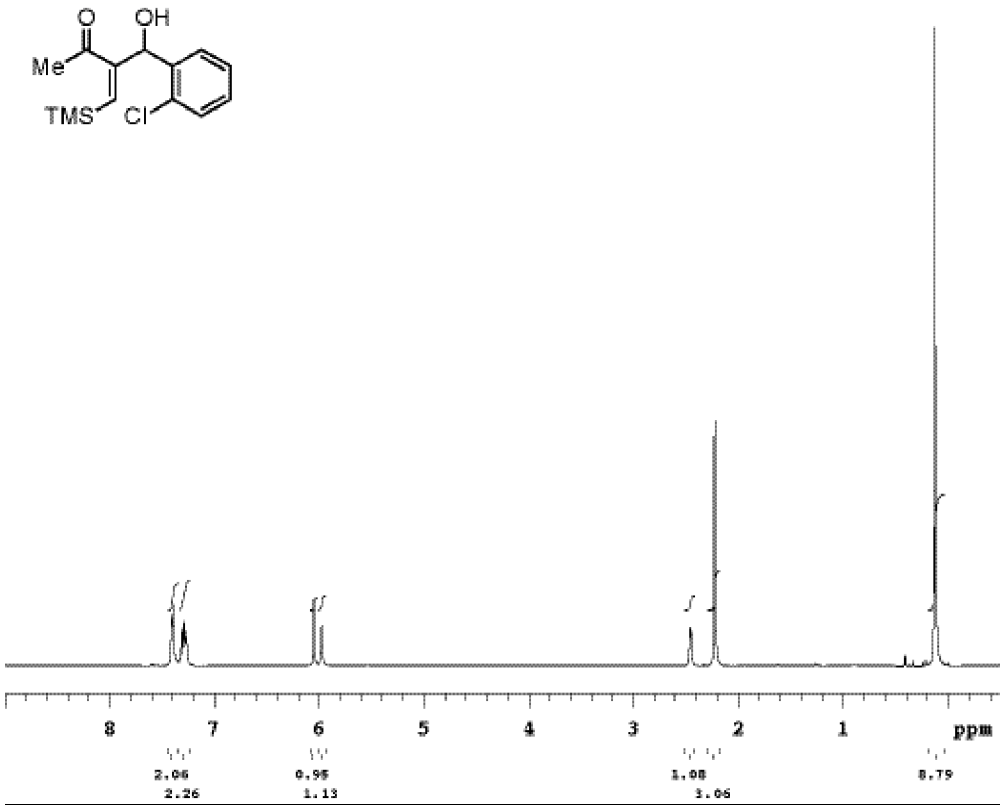

250
200
150
100
50
0
-50
ppm

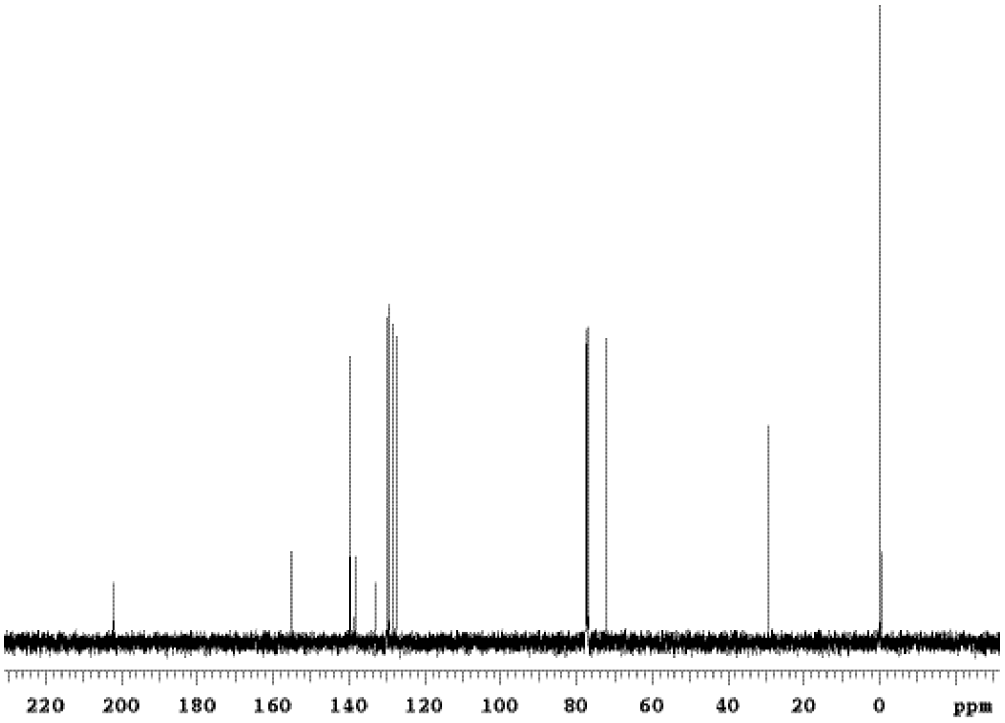

O
OH
Me
Ph
Ph
8
7
6
5
4
3
2
1
ppm
4.88 0.93
4.88
1.00
1.05 0.90
0.95
4.90
200
180
160
140
120
100
80
60
40
20
0
ppm

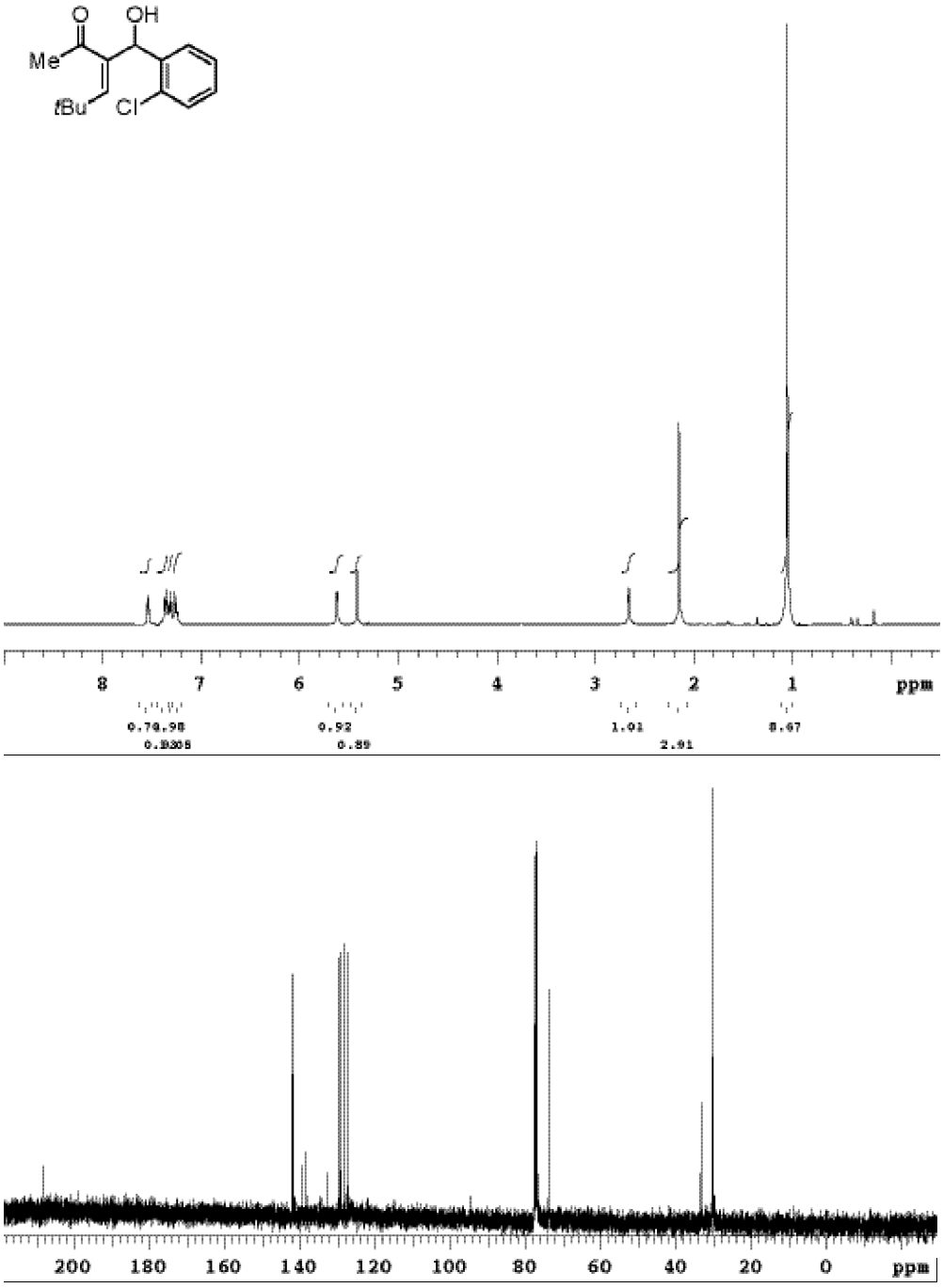

O
OH
Me
Ph
8
7
6
5
4
3
2
1
ppm
3.08 1.00
2.00
1.10
1.10
4.04 3.61
4.16 1.25 2.24

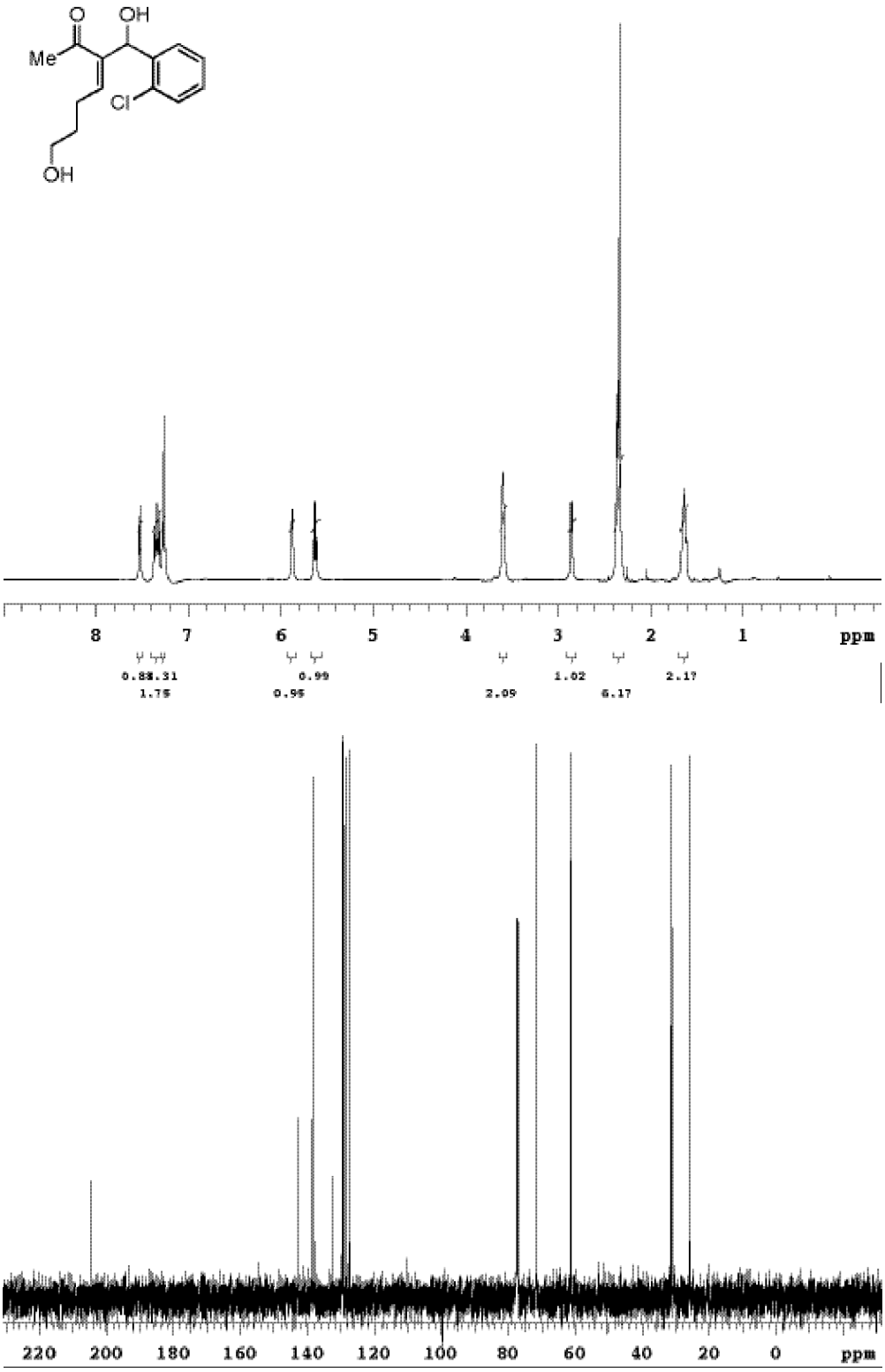

200
180
160
140
120
100
80
60
40
20
0
ppm

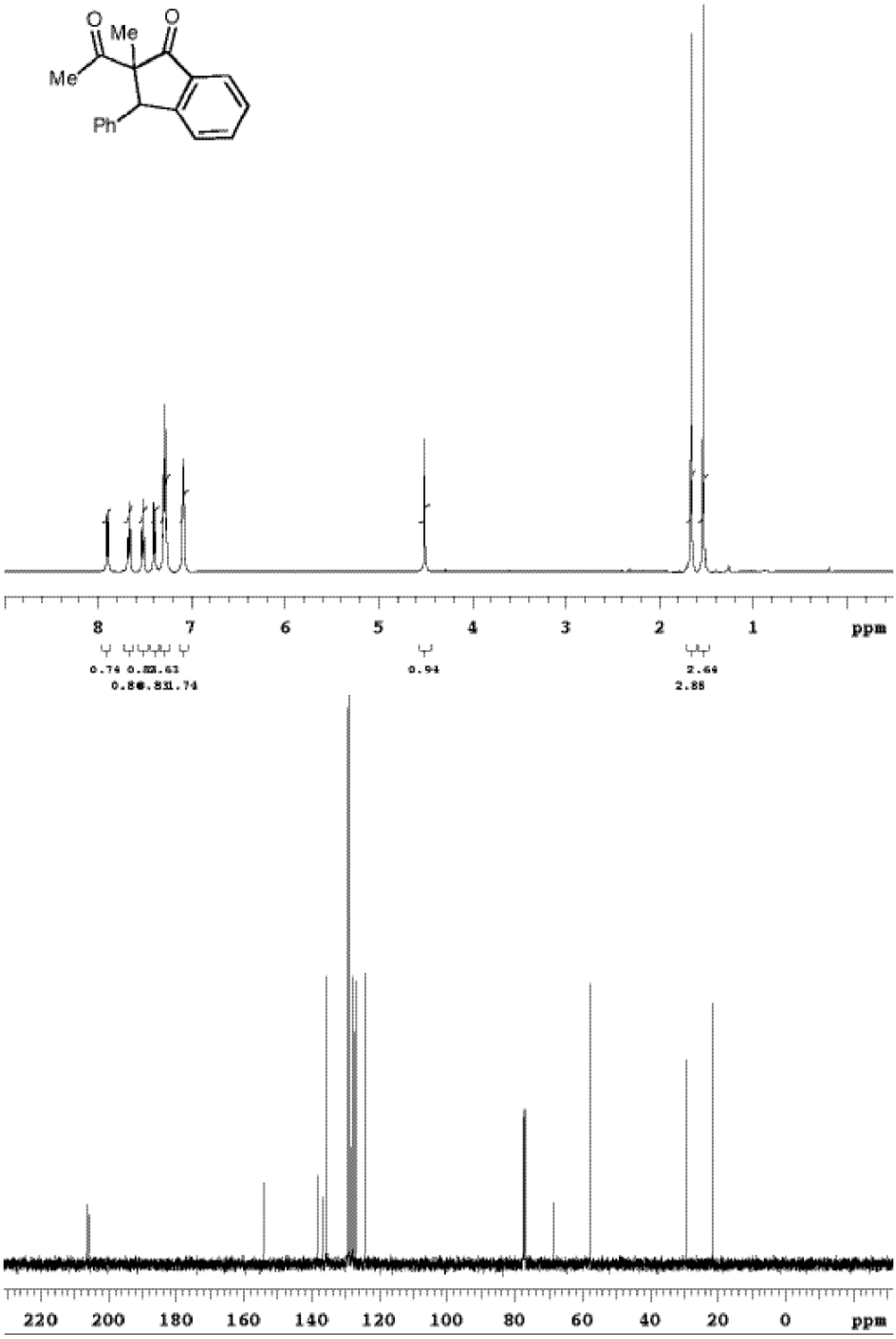

O
OH
Me
nBu
Cl
8
7
6
5
4
3
2
1
ppm
1.02
1.22
1.93
0.08
1.00
0.97
0.07
0.06
1.02
5.44
4.76
3.28
200
180
160
140
120
100
80
60
40
20
0
ppm

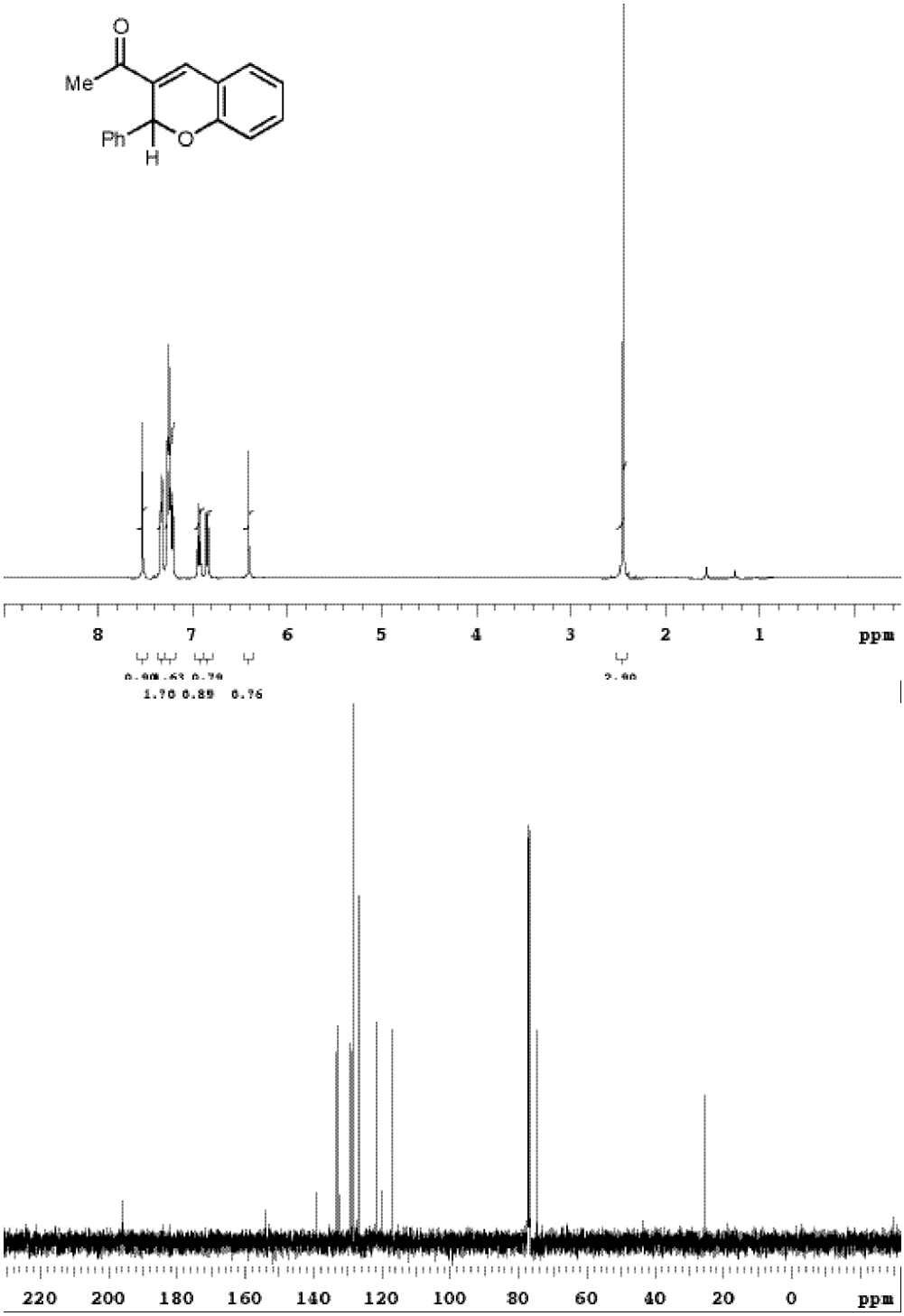

O
OH
Me
TMS
Cl
8
7
6
5
4
3
2
1
ppm
2.06
2.26
0.95
1.13
1.08
3.06
8.79


220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
OH
Me
tBu
Cl
8
7
6
5
4
3
2
1
ppm
0.79
0.92
1.91
0.67
0.89
2.91
200
180
160
140
120
100
80
60
40
20
0
ppm


O
OH
Me
Cl
OH
8
7
6
5
4
3
2
1
ppm
0.88
1.31
1.75
0.99
0.95
2.09
1.02
6.17
2.17
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
Me
O
Me
Ph
8
7
6
5
4
3
2
1
ppm
0.74
0.94
2.44
2.88
220
200
180
160
140
120
100
80
60
40
20
0
ppm

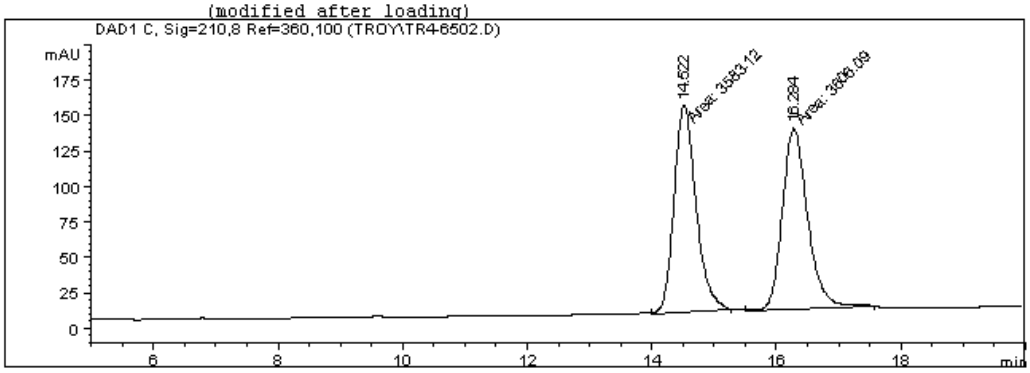

O
Me
Ph
O
H
8
7
6
5
4
3
2
1
ppm
1.76 0.89 0.76
220
200
180
160
140
120
100
80
60
40
20
0
ppm

HPLC Traces

Racemic 3

Data File C:\HPCHEM\2\DATA\TROY\TR4-6502.D Sample Name: TER-IV-65r

```
======================================================================
Injection Date  : 12/14/2006 8:08:55 AM
Sample Name     : TER-IV-65r                    Location : Vial 1
Acq. Operator   : MMB
                                               Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/14/2006 7:56:19 AM by MMB
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/14/2006 8:30:11 AM by MMB
                  (modified after loading)
```

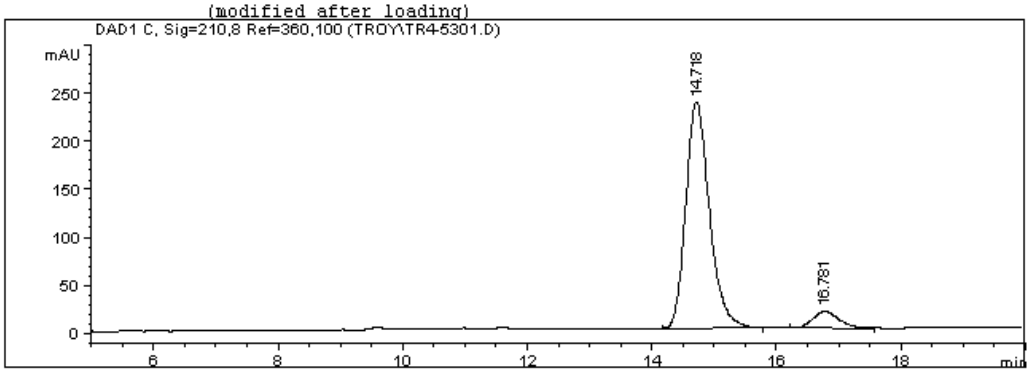



```
======================================================================
                        Area Percent Report
======================================================================

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


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.522 MM    0.4102 3583.11792  145.59479  49.8403
   2  16.284 MM    0.4722 3606.08594  127.27664  50.1597

Totals :                  7189.20386  272.87143

 Results obtained with enhanced integrator!
======================================================================
                          *** End of Report ***
```

Enantioenriched 3

Data File C:\HPCHEM\2\DATA\TROY\TR4-5301.D Sample Name: TER-IV-53

```
==========================================================================
Injection Date  : 12/14/2006 8:35:08 AM
Sample Name     : TER-IV-53                    Location : Vial 1
Acq. Operator   : MMB
                                              Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/14/2006 8:31:57 AM by MMB
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/14/2006 8:57:37 AM by MMB
                  (modified after loading)
```

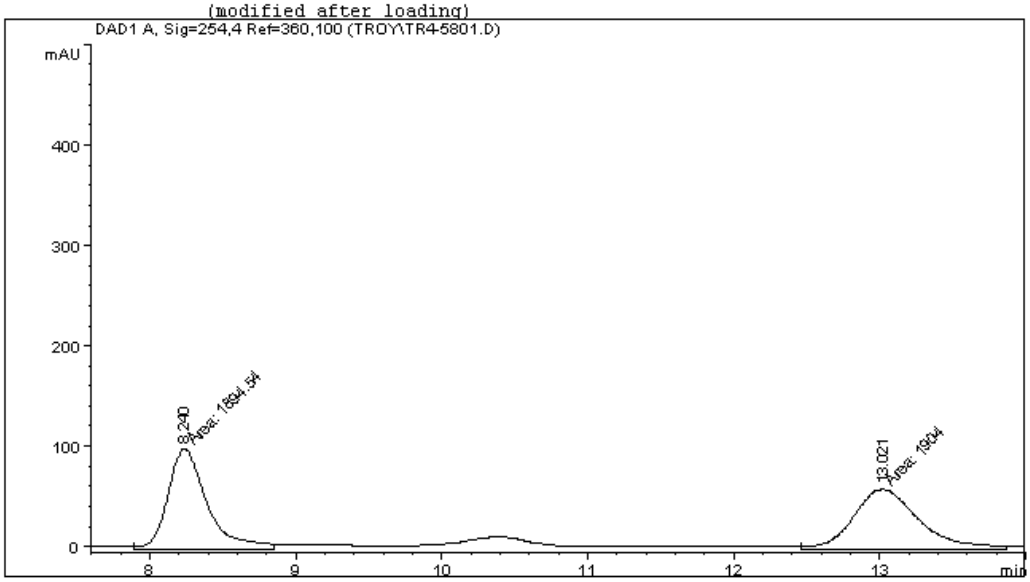



```
==========================================================================
                          Area Percent Report
==========================================================================

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


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.718 BB    0.4089 6280.11230  235.67415  92.2464
   2  16.781 BB    0.4609  527.86652   17.55215   7.7536

Totals :                  6807.97882  253.22630

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Racemic 4

Data File C:\HPCHEM\2\DATA\TROY\TR4-5801.D Sample Name: TER-IV-58

```
==================================================================
Injection Date  : 12/12/2006 1:40:13 PM
Sample Name     : TER-IV-58                    Location : Vial 1
Acq. Operator   : MANABU
                                               Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/12/2006 1:08:34 PM by MANABU
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/5/2007 5:46:37 PM by MANABU
                  (modified after loading)
```

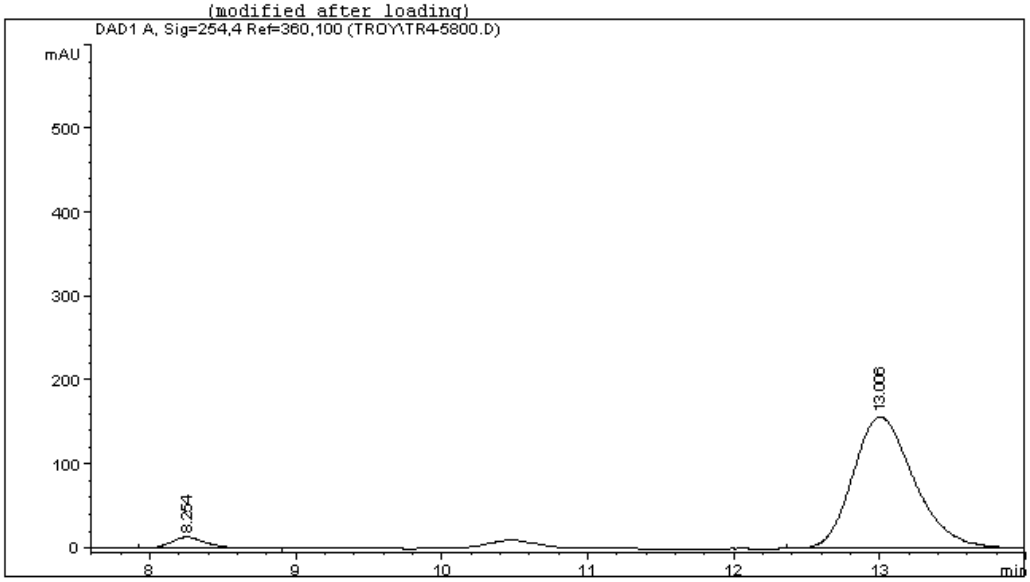



```
==================================================================
                        Area Percent Report
==================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.240 MM    0.3156 1894.53748  100.04969  49.8755
   2  13.021 MM    0.5283 1903.99646   60.07138  50.1245

Totals :                  3798.53394  160.12107

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Enantioenriched 4

Data File C:\HPCHEM\2\DATA\TROY\TR4-5800.D Sample Name: TER-IV-58

```
==================================================================
Injection Date  : 12/12/2006 1:13:40 PM
Sample Name     : TER-IV-58                    Location : Vial 1
Acq. Operator   : MANABU
                                              Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/12/2006 1:08:34 PM by MANABU
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/5/2007 5:45:10 PM by MANABU
                  (modified after loading)
```



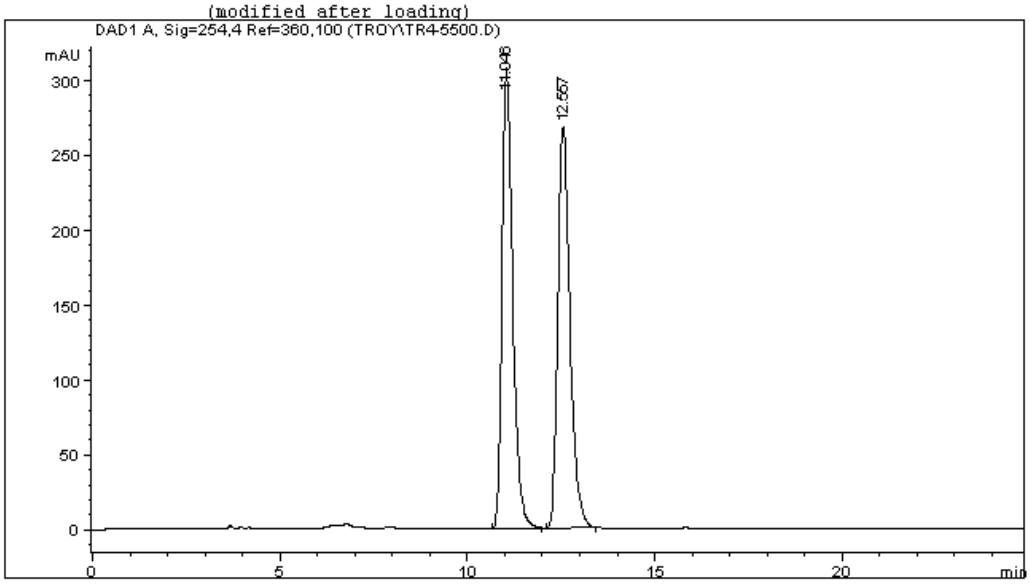

```
==================================================================
                        Area Percent Report
==================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.254 BB    0.2621  220.93944   12.88146   4.6137
   2  13.006 BB    0.4521 4567.78955  156.68053  95.3863

Totals :                   4788.72899  169.56199

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Racemic 5

Data File C:\HPCHEM\2\DATA\TROY\TR4-5500.D Sample Name: TER-IV-55r

racemate

```
======================================================================
Injection Date  : 11/7/2006 4:58:23 PM
Sample Name     : TER-IV-55r                      Location : Vial 2
Acq. Operator   : MANABU
                                                 Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 11/7/2006 5:05:09 PM by MANABU
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 11/9/2006 10:29:20 AM by MANABU
                  (modified after loading)
```



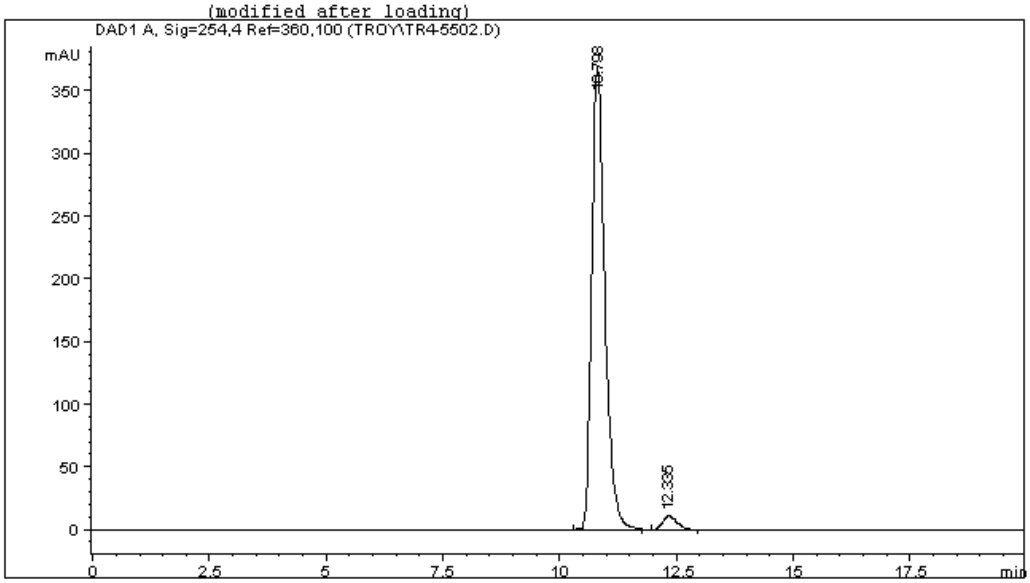

```
======================================================================
                        Area Percent Report
======================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.046 BB    0.3011 6081.13184  307.05020  50.2158
   2  12.557 BB    0.3428 6028.87256  267.64835  49.7842

Totals :                  1.21100e4   574.69855

 Results obtained with enhanced integrator!
======================================================================
                        *** End of Report ***
```

Enantioenriched 5

Data File C:\HPCHEM\2\DATA\TROY\TR4-5502.D Sample Name: TER-IV-55

ee

```
==================================================================
Injection Date  : 11/9/2006 9:53:38 AM
Sample Name     : TER-IV-55                    Location : Vial 2
Acq. Operator   : MANABU
                                              Inj Volume : 5 µl
Method          : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 11/9/2006 8:54:09 AM by MANABU
                  (modified after loading)
```

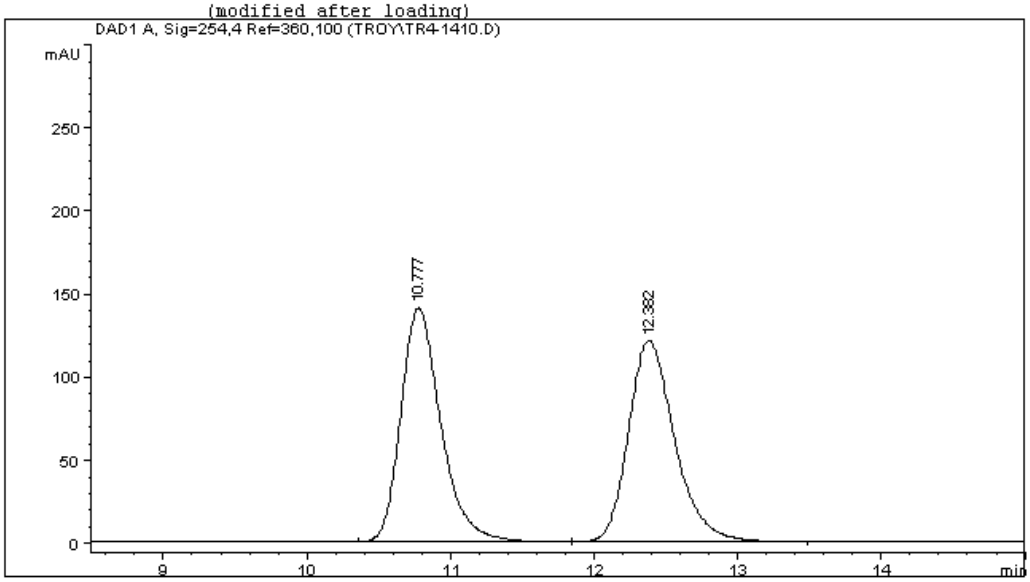



```
==================================================================
                        Area Percent Report
==================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.798 BB    0.2982 7183.58936  367.29581  96.7835
   2  12.335 PB    0.3297  238.74031   11.15417   3.2165

Totals :                  7422.32967  378.44998

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Racemic 6

Data File C:\HPCHEM\2\DATA\TROY\TR4-1410.D Sample Name: TER-IV-141

```
======================================================================
Injection Date  : 2/1/2007 9:19:00 AM
Sample Name     : TER-IV-141                    Location : Vial 1
Acq. Operator   : MANABU
                                                Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 2/1/2007 9:12:00 AM by MANABU
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/5/2007 8:19:43 AM by MANABU
                  (modified after loading)
```

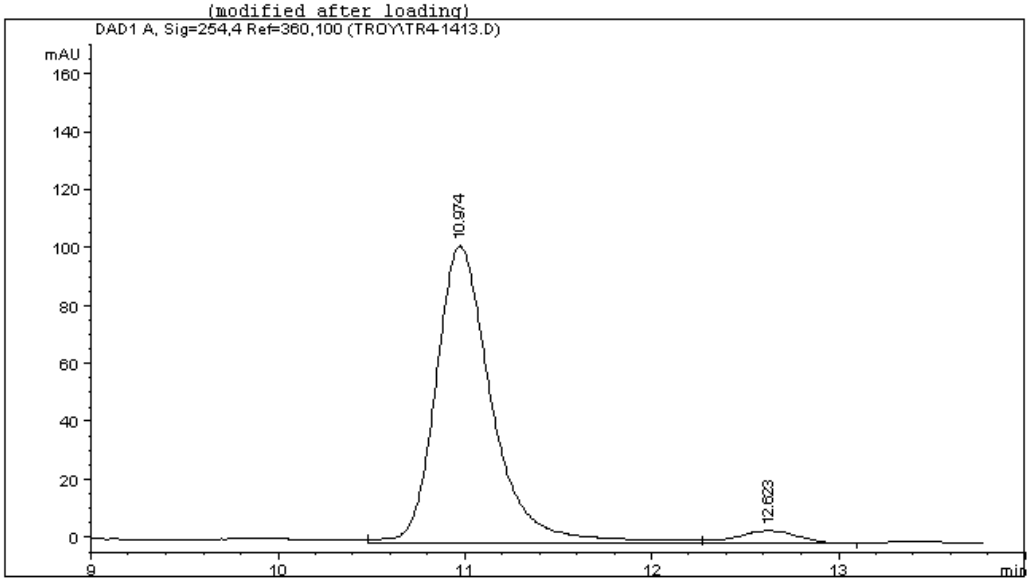



```
======================================================================
                        Area Percent Report
======================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.777 PV    0.2943 2706.43970  140.75478  50.1521
   2  12.382 VB    0.3417 2690.02124  120.84598  49.8479

Totals :                  5396.46094  261.60075

 Results obtained with enhanced integrator!
======================================================================
                        *** End of Report ***
```

Enatioenriched 6

Data File C:\HPCHEM\2\DATA\TROY\TR4-1413.D Sample Name: TER-IV-141

```
==========================================================================
Injection Date  : 4/7/2007 12:45:00 PM
Sample Name     : TER-IV-141                    Location : Vial 1
Acq. Operator   : MANABU
                                               Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/7/2007 12:33:41 PM by MANABU
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/7/2007 1:17:56 PM by MANABU
                  (modified after loading)
```

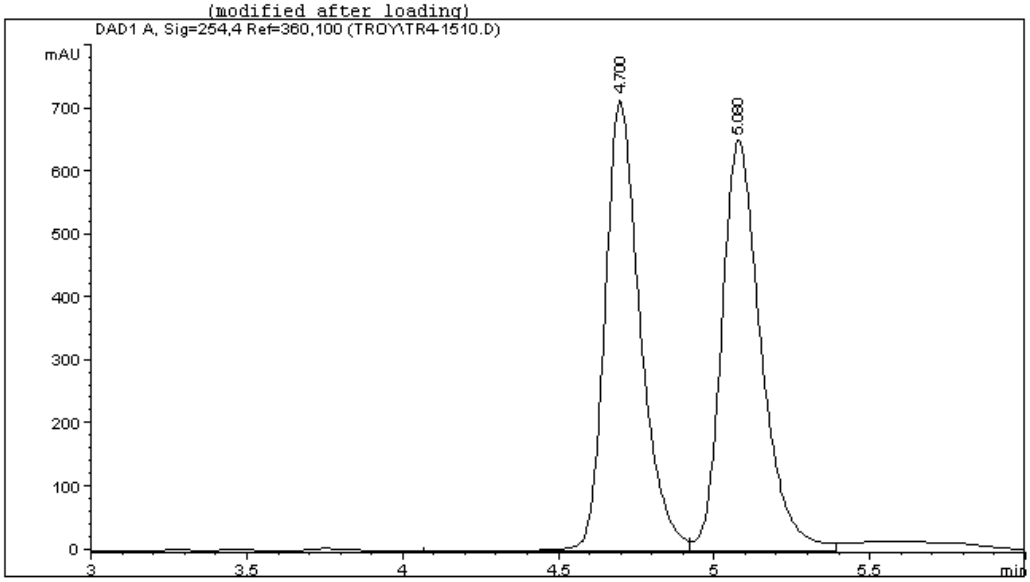



```
==========================================================================
                        Area Percent Report
==========================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.974 VV    0.3142 2148.84399  102.67162  95.3957
   2  12.623 VP    0.3503  103.71458    4.50926   4.6043

Totals :                  2252.55858  107.18087

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Racemic 7

Data File C:\HPCHEM\2\DATA\TROY\TR4-1510.D Sample Name: TR4-151

```
==================================================================
Injection Date  : 2/5/2007 2:05:29 PM
Sample Name     : TR4-151                      Location : Vial 1
Acq. Operator   : Audrey
                                              Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 2/5/2007 2:03:04 PM by Audrey
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/5/2007 8:27:41 AM by MANABU
                  (modified after loading)
```

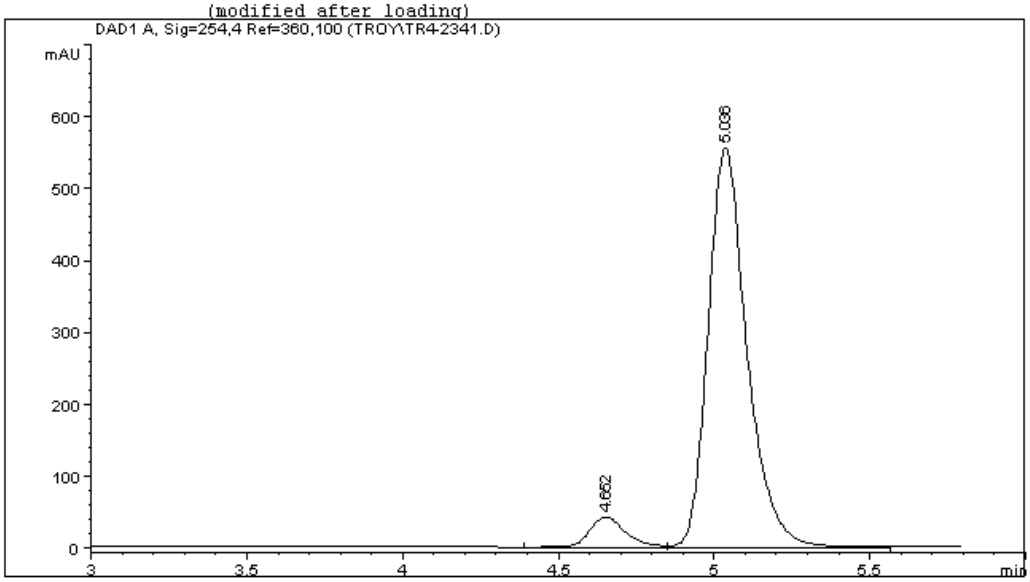



```
==================================================================
                      Area Percent Report
==================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.700 VV    0.1204 5677.51611  716.91150  49.7153
   2   5.080 VV    0.1347 5742.54199  652.04114  50.2847

Totals :                  1.14201e4  1368.95264

 Results obtained with enhanced integrator!
==================================================================
                         *** End of Report ***
```

Enantioenriched 7

Data File C:\HPCHEM\2\DATA\TROY\TR4-2341.D Sample Name: TR4-234

```
==================================================================
Injection Date  : 4/2/2007 3:58:27 PM
Sample Name     : TR4-234                      Location : Vial 1
Acq. Operator   : MANABU
                                               Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/2/2007 3:55:15 PM by MANABU
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/5/2007 8:24:46 AM by MANABU
                  (modified after loading)
```



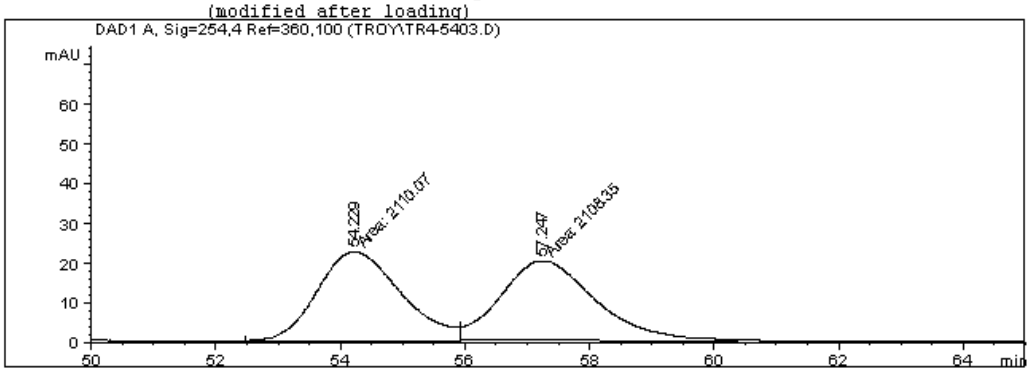

```
==================================================================
                        Area Percent Report
==================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.652 VV    0.1274  371.12250   43.55218   7.1002
   2   5.036 VV    0.1317 4855.79150  556.87250  92.8998

Totals :                   5226.91400  600.42467

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Racemic 8

Data File C:\HPCHEM\2\DATA\TROY\TR4-5403.D Sample Name: TER-IV-54r

racemate

```
==========================================================================
Injection Date  : 12/1/2006 8:51:40 AM
Sample Name     : TER-IV-54r                      Location : Vial 91
Acq. Operator   : mmb
                                                 Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/1/2006 8:50:56 AM by mmb
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/13/2006 10:30:22 AM by MANABU
                  (modified after loading)
```



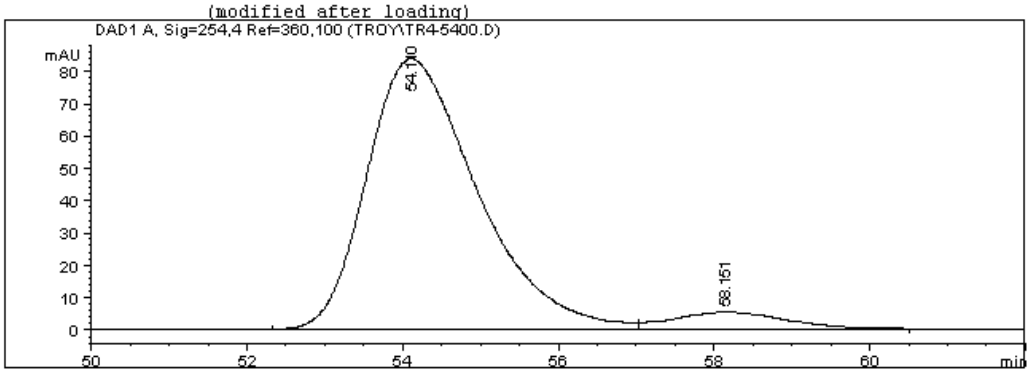

```
==========================================================================
                          Area Percent Report
==========================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  54.229 MM    1.5630 2110.06665   22.49968  50.0203
   2  57.247 MM    1.7613 2108.35205   19.95118  49.9797

Totals :                  4218.41870   42.45086

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Enantioenriched 8

Data File C:\HPCHEM\2\DATA\TROY\TR4-5400.D Sample Name: TER-IV-54

ee

```
==========================================================================
Injection Date  : 12/1/2006 10:39:49 AM
Sample Name     : TER-IV-54                        Location : Vial 91
Acq. Operator   : mmb
                                                  Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/1/2006 9:59:23 AM by mmb
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MMB LC.M
Last changed    : 12/19/2006 9:52:59 AM by MMB
                  (modified after loading)
```



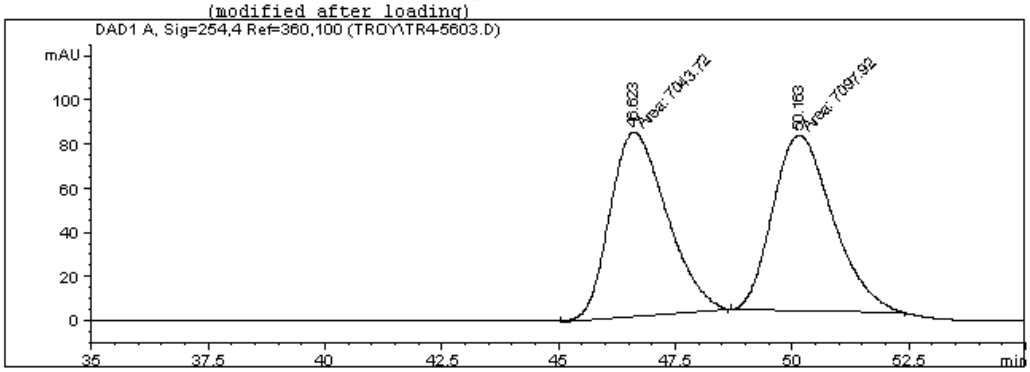

```
==========================================================================
                          Area Percent Report
==========================================================================

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 Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  54.110 BB    1.5034 8259.52539   83.68678  93.8593
   2  58.151 BB    1.2770  540.37085    5.26696   6.1407

Totals :                  8799.89624   88.95373

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Racemic 9

Data File C:\HPCHEM\2\DATA\TROY\TR4-5603.D Sample Name: TER-IV-56r

4-Me-Ph racemate

```
==========================================================================
Injection Date  : 11/30/2006 4:03:44 PM
Sample Name     : TER-IV-56r                      Location : Vial 91
Acq. Operator   : mmb
                                                Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 11/30/2006 4:01:41 PM by mmb
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/13/2006 10:40:29 AM by MANABU
                  (modified after loading)
```



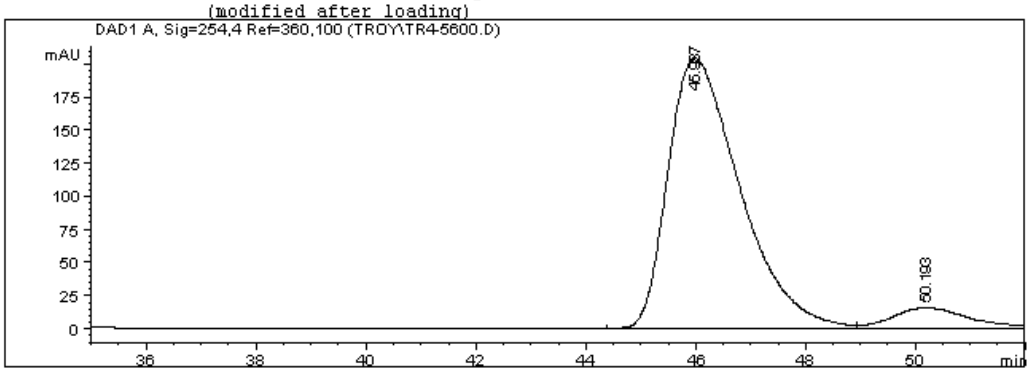

```
==========================================================================
                          Area Percent Report
==========================================================================

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 Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  46.623 MM    1.4081 7043.71826   83.36884  49.8084
   2  50.163 MM    1.4924 7097.91602   79.26981  50.1916

Totals :                  1.41416e4   162.63865

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Enantioenriched 9

Data File C:\HPCHEM\2\DATA\TROY\TR4-5600.D Sample Name: TER-IV-56

ee

```
==========================================================================
Injection Date  : 11/30/2006 5:05:50 PM
Sample Name     : TER-IV-56                    Location : Vial 91
Acq. Operator   : mmb
                                             Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 11/30/2006 5:00:33 PM by mmb
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MMB LC.M
Last changed    : 12/19/2006 10:12:13 AM by MMB
                  (modified after loading)
```



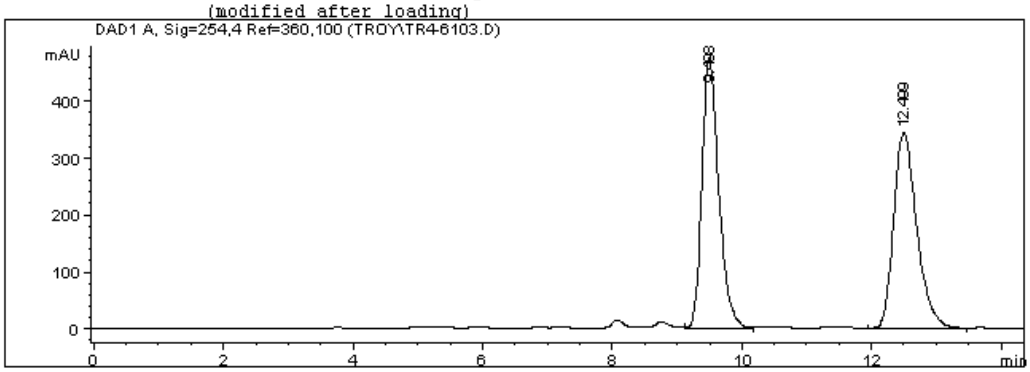

```
==========================================================================
                        Area Percent Report
==========================================================================

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 Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  45.987 BV    1.4108 1.85909e4   204.08107  91.9402
   2  50.193 VBA   1.4571 1629.74231   16.07105   8.0598

Totals :                  2.02207e4   220.15212

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Racemic 10

Data File C:\HPCHEM\2\DATA\TROY\TR4-6103.D Sample Name: TER-IV-61r

racemic

```
==========================================================================
Injection Date  : 11/16/2006 2:31:56 PM
Sample Name     : TER-IV-61r                      Location : Vial 1
Acq. Operator   : Troy
                                                  Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 11/16/2006 2:03:52 PM by Troy
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\EPROCKS.M
Last changed    : 12/12/2006 10:47:45 AM by MANABU
                  (modified after loading)
```

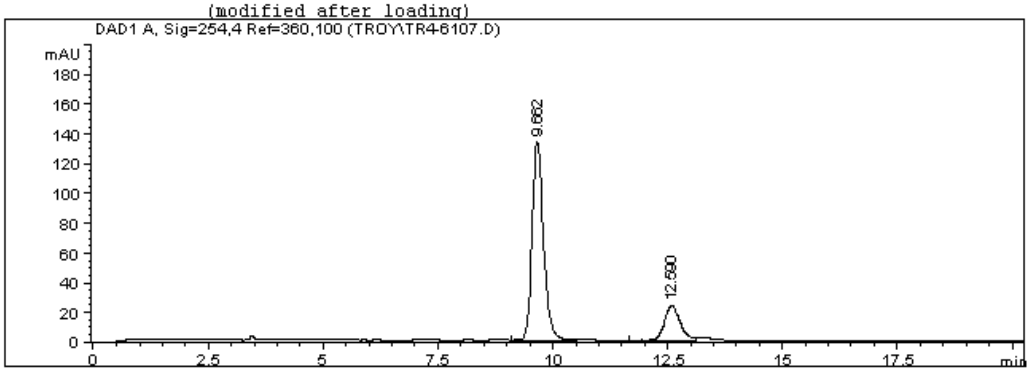



```
==========================================================================
                          Area Percent Report
==========================================================================

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 Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.498 VV    0.2760 8644.07520  475.59396  50.1209
   2  12.499 VV    0.3839 8602.37988  343.79001  49.8791

Totals :                  1.72465e4   819.38397

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Enantioenriched 10

Data File C:\HPCHEM\2\DATA\TROY\TR4-6107.D Sample Name: TER-IV-61

```
======================================================================
Injection Date  : 12/19/2006 2:43:44 PM
Sample Name     : TER-IV-61                    Location : Vial 1
Acq. Operator   : MMB
                                              Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/19/2006 2:40:11 PM by MMB
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/19/2006 3:06:03 PM by MMB
                  (modified after loading)
```



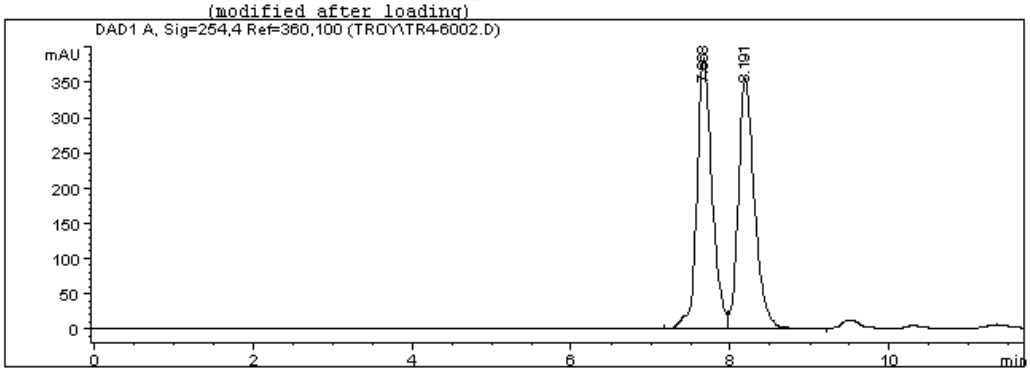

```
======================================================================
                        Area Percent Report
======================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.662 VB    0.2666 2322.12817  133.69525  80.5418
   2  12.590 BV    0.3655  561.00452   23.58904  19.4582

Totals :                  2883.13269  157.28429

 Results obtained with enhanced integrator!
======================================================================
                        *** End of Report ***
```

Racemic 11

Data File C:\HPCHEM\2\DATA\TROY\TR4-6002.D Sample Name: TER-IV-60

rac

```
==========================================================================
Injection Date  : 11/16/2006 4:13:54 PM
Sample Name     : TER-IV-60                      Location : Vial 3
Acq. Operator   : Troy
                                                 Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 11/16/2006 4:06:41 PM by Troy
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\EPROCKS.M
Last changed    : 12/12/2006 10:47:45 AM by MANABU
                  (modified after loading)
```



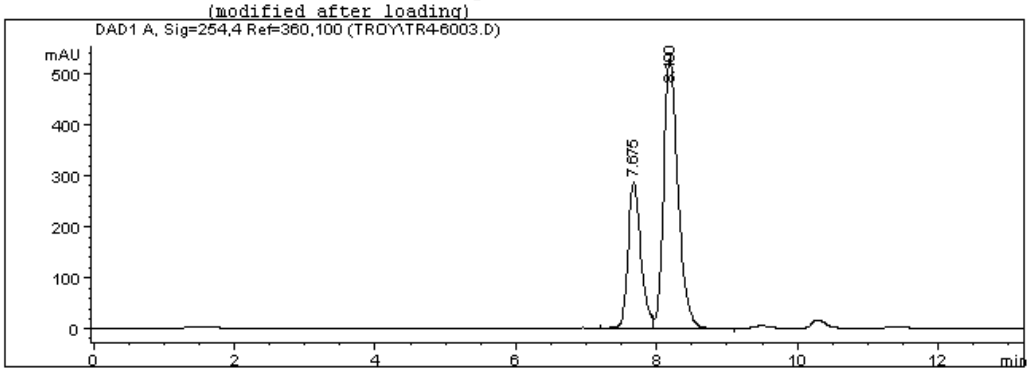

```
==========================================================================
                        Area Percent Report
==========================================================================

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 Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.668 VV    0.2009 5102.55371  384.37640  50.3479
   2   8.191 VV    0.2133 5032.04395  355.13129  49.6521

Totals :                  1.01346e4   739.50769

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Enantioenriched 11

Data File C:\HPCHEM\2\DATA\TROY\TR4-6003.D Sample Name: TER-IV-60

ee

```
==========================================================================
Injection Date  : 11/16/2006 4:27:41 PM
Sample Name     : TER-IV-60                      Location : Vial 4
Acq. Operator   : Troy
                                                 Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 11/16/2006 4:06:41 PM by Troy
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\EPROCKS.M
Last changed    : 12/12/2006 10:47:45 AM by MANABU
                  (modified after loading)
```

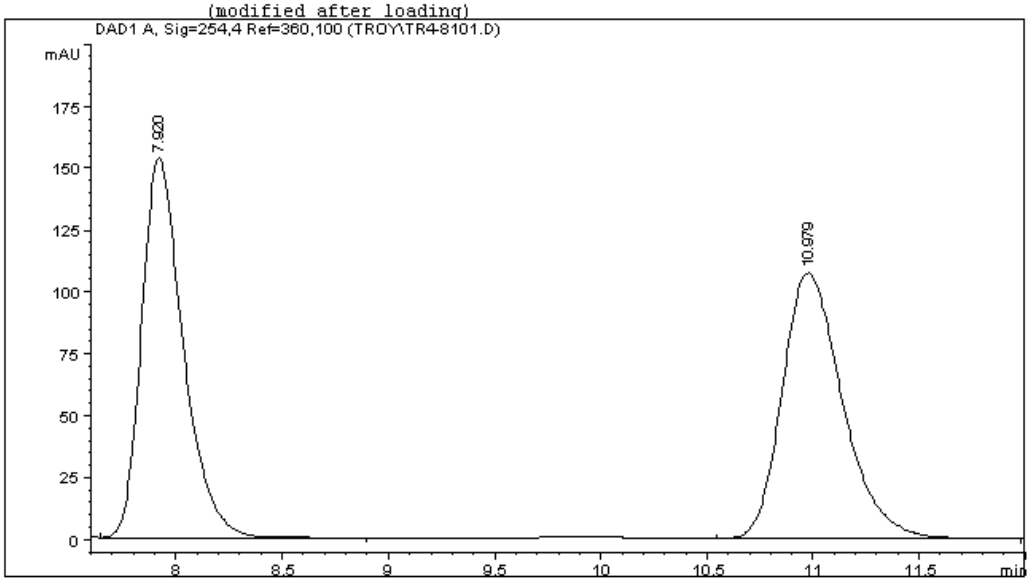



```
==========================================================================
                        Area Percent Report
==========================================================================

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 Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.675 VV    0.1948 3711.07788  287.18552  33.0614
   2   8.190 VV    0.2150 7513.72217  531.19946  66.9386

Totals :                  1.12248e4   818.38498

 Results obtained with enhanced integrator!
==========================================================================
                           *** End of Report ***
```

Racemic 12

Data File C:\HPCHEM\2\DATA\TROY\TR4-8101.D Sample Name: TER-IV-81

```
======================================================================
Injection Date  : 12/12/2006 12:11:11 PM
Sample Name     : TER-IV-81                    Location : Vial 1
Acq. Operator   : MANABU
                                               Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/12/2006 12:20:48 PM by MANABU
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/5/2007 2:33:51 PM by MANABU
                  (modified after loading)
```

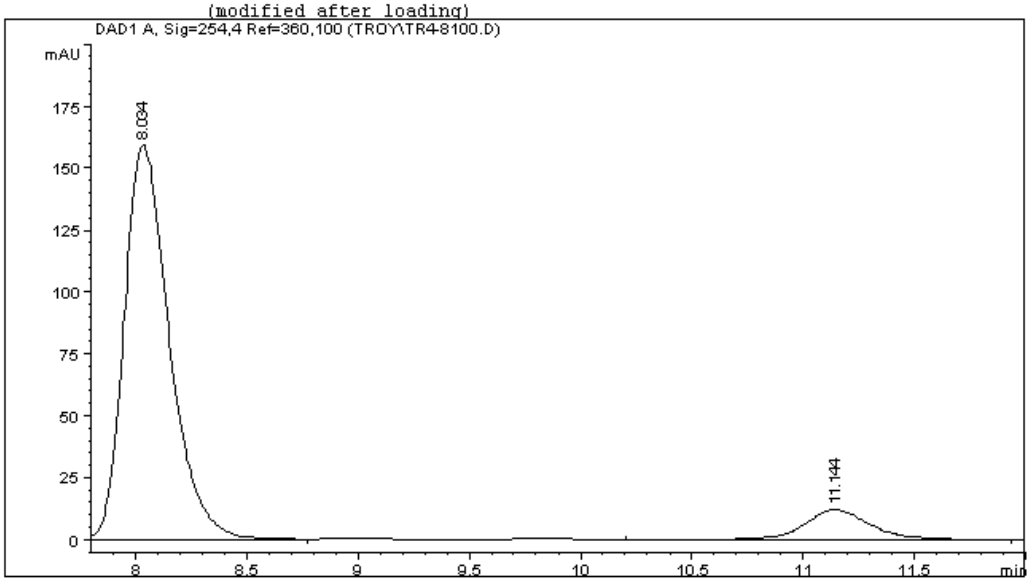



```
======================================================================
                        Area Percent Report
======================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.920 VB    0.2122 2142.18970  154.04074  50.0914
   2  10.979 BB    0.3053 2134.36914  107.67710  49.9086

Totals :                  4276.55884  261.71784

 Results obtained with enhanced integrator!
======================================================================
                        *** End of Report ***
```

Enantioenriched 12

Data File C:\HPCHEM\2\DATA\TROY\TR4-8100.D Sample Name: TER-IV-81

```
======================================================================
Injection Date  : 12/12/2006 11:51:00 AM
Sample Name     : TER-IV-81                    Location : Vial 1
Acq. Operator   : MANABU
                                               Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/12/2006 11:49:34 AM by MANABU
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/5/2007 2:33:03 PM by MANABU
                  (modified after loading)
```

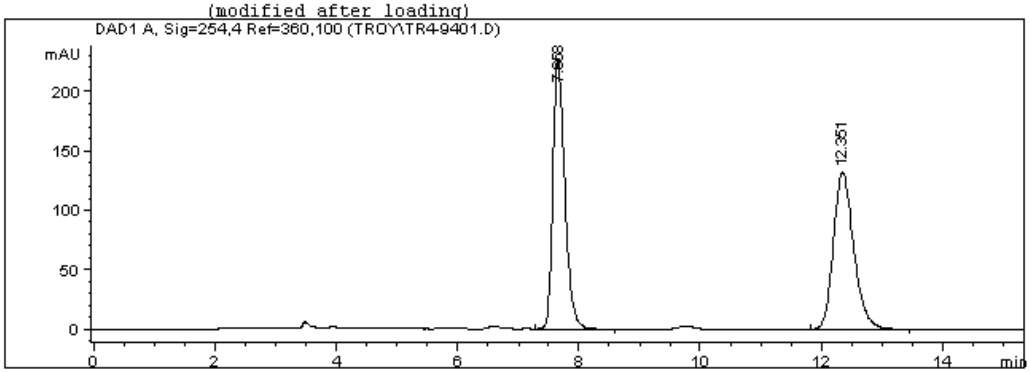



```
======================================================================
                        Area Percent Report
======================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.034 VV    0.2164 2251.06714  159.77780  90.0871
   2  11.144 VP    0.3120  247.70116   12.04223   9.9129

Totals :                  2498.76830  171.82003

 Results obtained with enhanced integrator!
======================================================================
                        *** End of Report ***
```

Racemic 13

Data File C:\HPCHEM\2\DATA\TROY\TR4-9401.D Sample Name: TER-IV-94

```
==================================================================
Injection Date  : 12/12/2006 12:51:42 PM
Sample Name     : TER-IV-94                    Location : Vial 1
Acq. Operator   : MANABU
                                               Inj Volume : 5 µl
Method          : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/12/2006 12:20:48 PM by MANABU
                  (modified after loading)
```

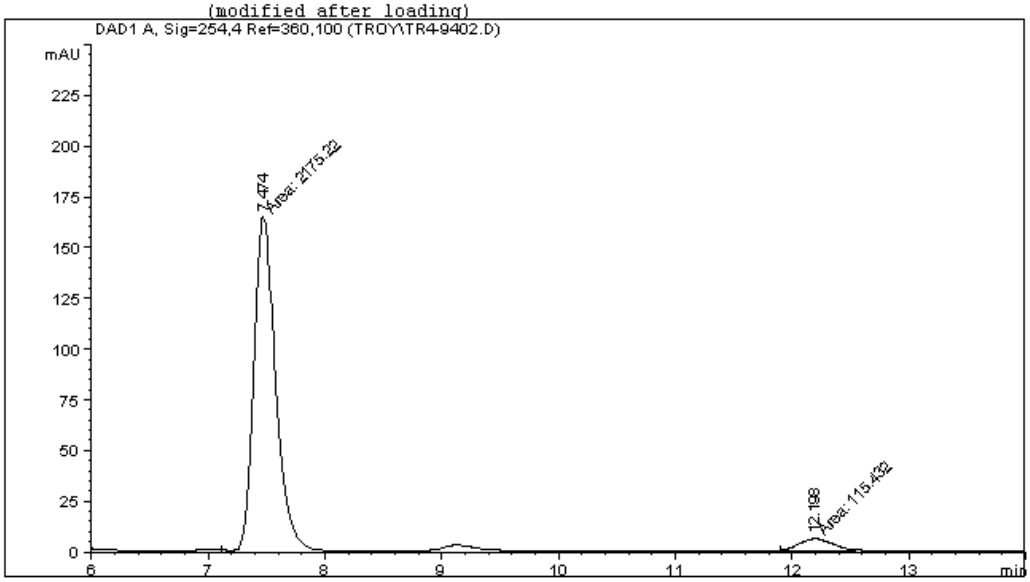



```
==================================================================
                        Area Percent Report
==================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.658 VP    0.2084 3084.74707  227.23563  50.2211
   2  12.351 BB    0.3573 3057.58862  131.46159  49.7789

Totals :                  6142.33569  358.69722

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Enantioenriched 13

Data File C:\HPCHEM\2\DATA\TROY\TR4-9402.D Sample Name: TER-IV-94

```
==========================================================================
Injection Date  : 12/18/2006 10:27:12 AM
Sample Name     : TER-IV-94                    Location : Vial 1
Acq. Operator   : MMB
                                               Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/18/2006 10:19:54 AM by MMB
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/5/2007 7:58:56 AM by MANABU
                  (modified after loading)
```

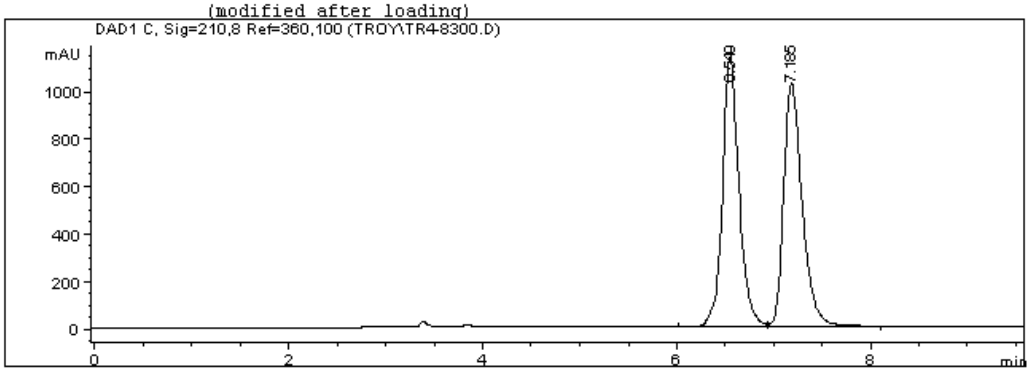



```
==========================================================================
                        Area Percent Report
==========================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.474 MM    0.2195 2175.22192  165.19119  94.9607
   2  12.198 MM    0.3356  115.43202    5.73282   5.0393

Totals :                  2290.65395  170.92402

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Racemic 14

Data File C:\HPCHEM\2\DATA\TROY\TR4-8300.D Sample Name: TER-IV-83

```
==========================================================================
Injection Date  : 12/12/2006 5:05:31 PM
Sample Name     : TER-IV-83                      Location : Vial 1
Acq. Operator   : MANABU
                                                 Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/12/2006 4:51:20 PM by MANABU
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/12/2006 5:16:10 PM by MANABU
                  (modified after loading)
```

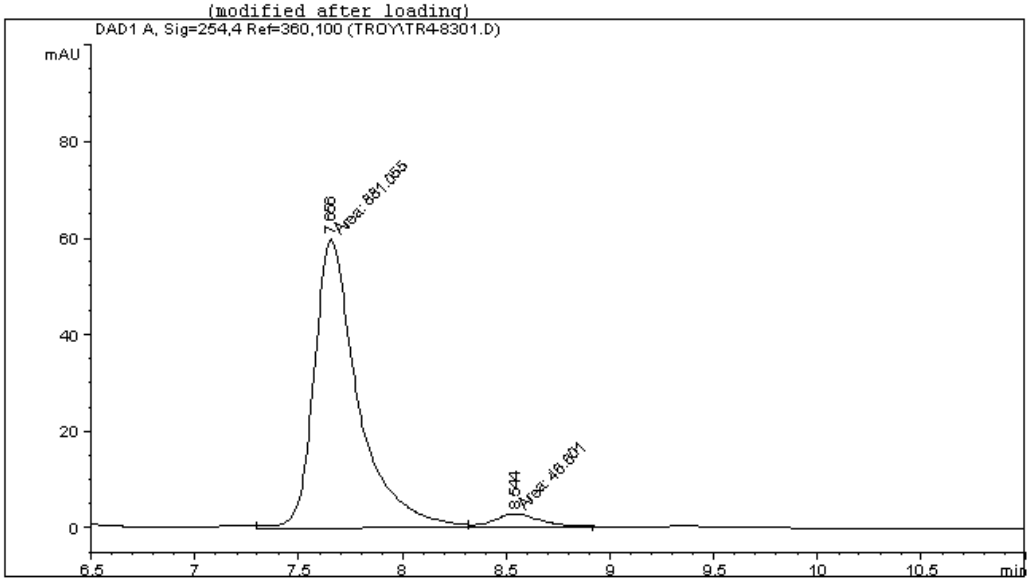



```
==========================================================================
                          Area Percent Report
==========================================================================

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


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.549 VV    0.1794 1.34975e4  1129.23804  49.9495
   2   7.185 VB    0.2000 1.35247e4  1024.54834  50.0505

Totals :                   2.70222e4  2153.78638

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Enantioenriched 14

Data File C:\HPCHEM\2\DATA\TROY\TR4-8301.D Sample Name: TER-IV-83

```
==================================================================
Injection Date  : 11/21/2006 9:08:00 AM
Sample Name     : TER-IV-83                    Location : Vial 1
Acq. Operator   : mmb
                                               Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 11/20/2006 10:47:22 AM by mmb
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/5/2007 8:07:19 AM by MANABU
                  (modified after loading)
```

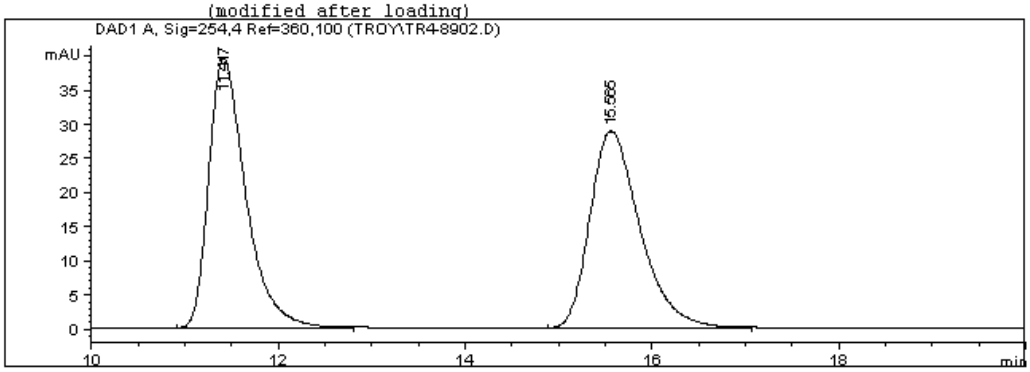



```
==================================================================
                        Area Percent Report
==================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.656 MM    0.2450  881.05505   59.93238  94.9765
   2   8.544 MM    0.2687   46.60097    2.89025   5.0235

Totals :                   927.65602   62.82262

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Racemic 15

Data File C:\HPCHEM\2\DATA\TROY\TR4-8902.D Sample Name: TER-IV-89r

```
==========================================================================
Injection Date  : 12/19/2006 8:41:06 AM
Sample Name     : TER-IV-89r                      Location : Vial 1
Acq. Operator   : Brooks
                                                  Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/19/2006 8:01:30 AM by Brooks
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/19/2006 9:02:14 AM by Brooks
                  (modified after loading)
```



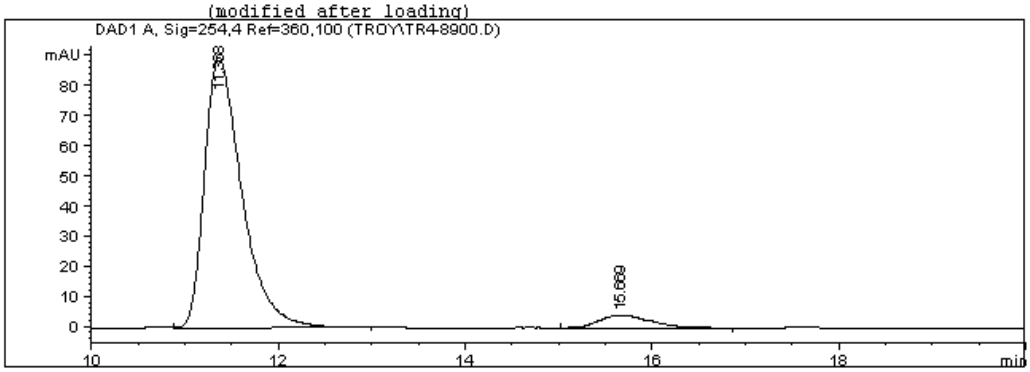

```
==========================================================================
                          Area Percent Report
==========================================================================

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 Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.417 BB    0.4210 1095.65332   39.57635  50.3958
   2  15.565 BB    0.5694 1078.44324   28.89818  49.6042

Totals :                  2174.09656   68.47452

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Enantioenriched 15

Data File C:\HPCHEM\2\DATA\TROY\TR4-8900.D Sample Name: TER-IV-89

ee

```
==========================================================================
Injection Date  : 12/15/2006 4:36:01 PM
Sample Name     : TER-IV-89                      Location : Vial 2
Acq. Operator   : MMB
                                                 Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/15/2006 4:31:39 PM by MMB
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/19/2006 9:02:39 AM by Brooks
                  (modified after loading)
```



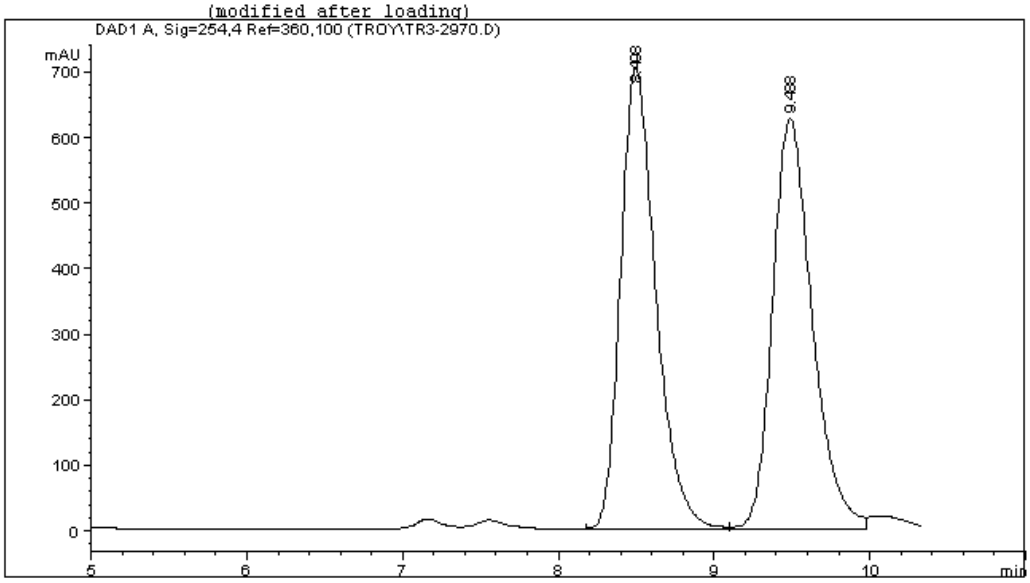

```
==========================================================================
                          Area Percent Report
==========================================================================

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 Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.368 VB    0.4278 2516.09937   89.56007  93.6802
   2  15.669 PB    0.6014  169.74022    4.25541   6.3198

Totals :                  2685.83958   93.81547

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Racemic 16

Data File C:\HPCHEM\2\DATA\TROY\TR3-2970.D Sample Name: TER-III-297r

racemate

```
======================================================================
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)
```

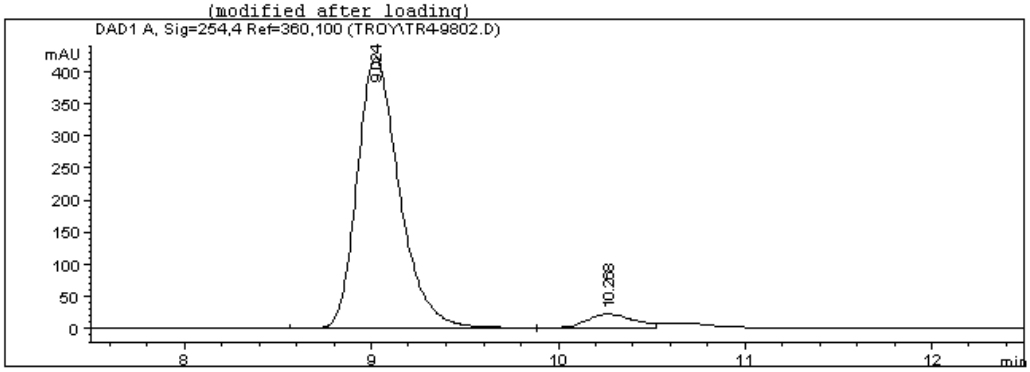



```
======================================================================
                        Area Percent Report
======================================================================

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 Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   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!
======================================================================
                          *** End of Report ***
```

Enantioenriched 16

Data File C:\HPCHEM\2\DATA\TROY\TR4-9802.D Sample Name: TER-IV-98

```
==================================================================
Injection Date  : 12/22/2006 12:21:03 PM
Sample Name     : TER-IV-98                    Location : Vial 1
Acq. Operator   : mmb
                                               Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/22/2006 12:17:44 PM by mmb
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/22/2006 12:47:33 PM by mmb
                  (modified after loading)
```

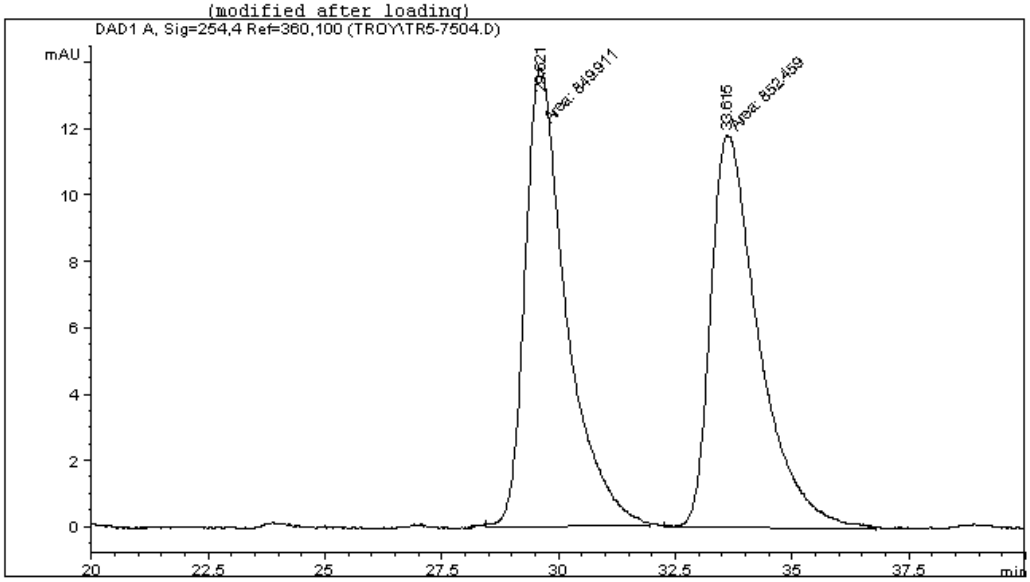



```
==================================================================
                        Area Percent Report
==================================================================

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 Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.024 BV    0.2424 6662.78271  421.53320  94.0074
   2  10.268 VV    0.2767  424.72885   23.07547   5.9926

Totals :                  7087.51157  444.60868

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Racemic 19

Data File C:\HPCHEM\2\DATA\TROY\TR5-7504.D Sample Name: TER-V-75

```
==================================================================
Injection Date  : 6/15/2007 8:44:40 AM
Sample Name     : TER-V-75                      Location : Vial 1
Acq. Operator   : hlee
                                                Inj Volume : 5 µl
Method          : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 6/15/2007 9:16:42 AM by hlee
                  (modified after loading)
```

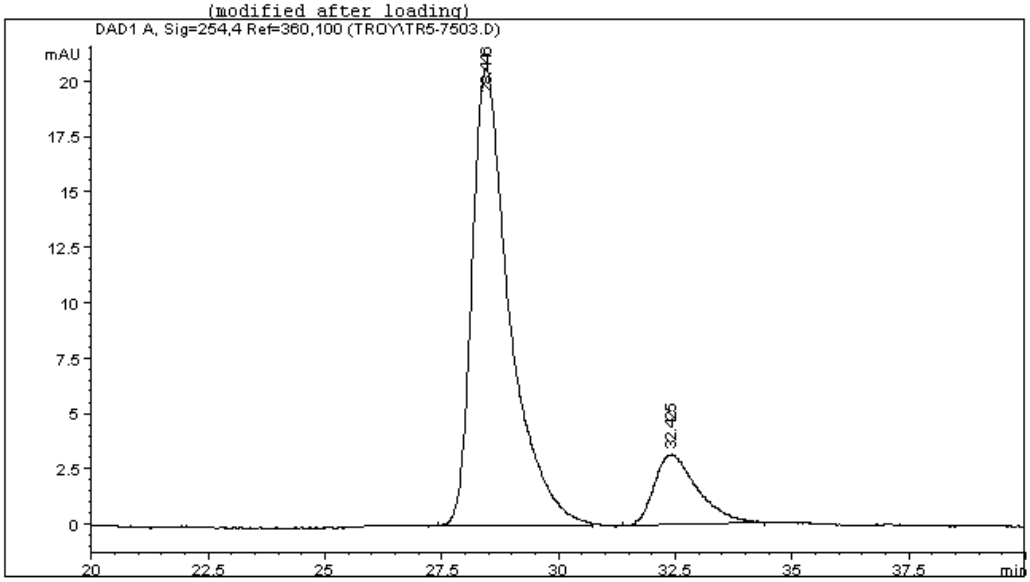



```
==================================================================
                        Area Percent Report
==================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  29.621 MM    1.0235  849.91095   13.84026  49.9252
   2  33.615 MM    1.1973  852.45923   11.86668  50.0748

Totals :                  1702.37018   25.70694

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Enantioenriched 19

Data File C:\HPCHEM\2\DATA\TROY\TR5-7503.D Sample Name: TER-V-75

```
==================================================================
Injection Date  : 6/15/2007 7:36:55 AM
Sample Name     : TER-V-75                      Location : Vial 1
Acq. Operator   : hlee
                                                Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 6/15/2007 7:34:43 AM by hlee
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 6/15/2007 9:16:18 AM by hlee
                  (modified after loading)
```

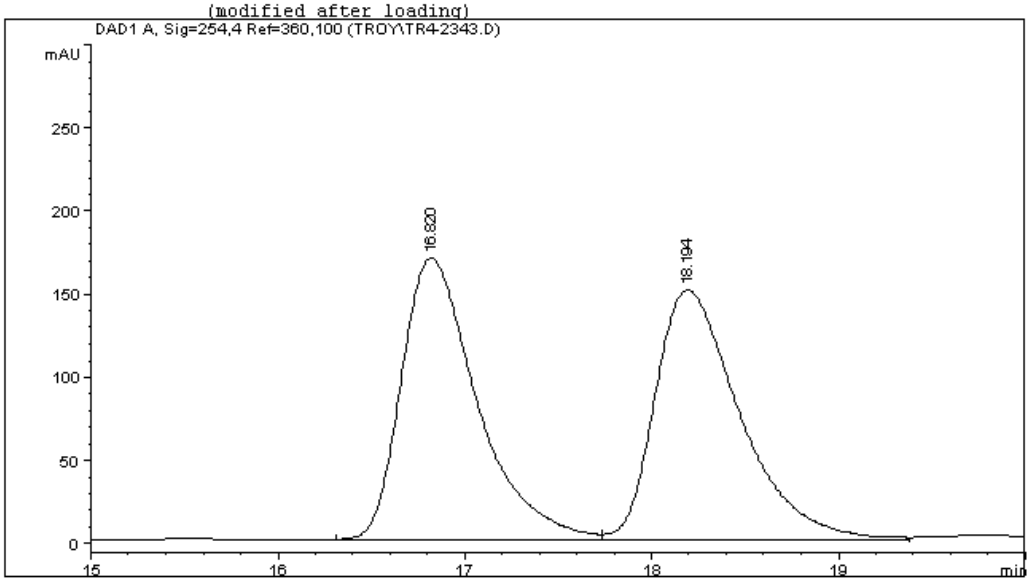



```
==================================================================
                        Area Percent Report
==================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  28.446 BB    0.7936 1151.26563   20.67797  84.8540
   2  32.425 PB    0.7840  205.49474    3.18818  15.1460

Totals :                  1356.76036   23.86615

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Racemic 20

Data File C:\HPCHEM\2\DATA\TROY\TR4-2343.D Sample Name: TER-IV-234r

```
==================================================================
Injection Date  : 4/6/2007 10:20:14 AM
Sample Name     : TER-IV-234r                    Location : Vial 1
Acq. Operator   : MANABU
                                                 Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/6/2007 10:20:28 AM by MANABU
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/6/2007 10:42:55 AM by MANABU
                  (modified after loading)
```

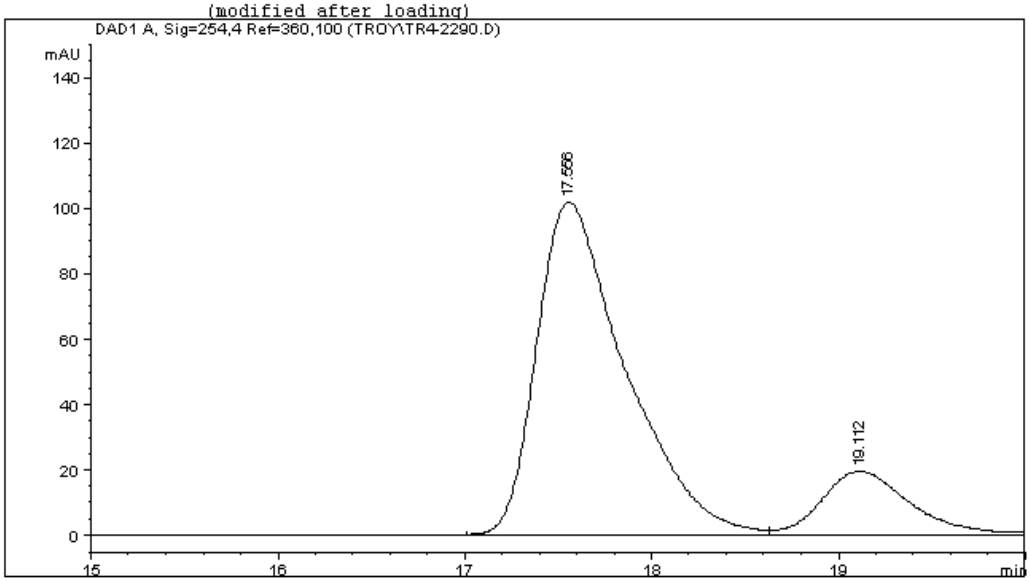



```
==================================================================
                        Area Percent Report
==================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.820 BV    0.4251 4748.37305  169.37079  50.1364
   2  18.194 VV    0.4829 4722.52930  150.15065  49.8636

Totals :                  9470.90234  319.52144

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Enantioenriched 20

Data File C:\HPCHEM\2\DATA\TROY\TR4-2290.D Sample Name: TER-IV-229

```
==========================================================================
Injection Date  : 3/30/2007 10:18:46 AM
Sample Name     : TER-IV-229                    Location : Vial 1
Acq. Operator   : MANABU
                                                Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 3/30/2007 10:08:33 AM by MANABU
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 4/5/2007 8:30:53 AM by MANABU
                  (modified after loading)
```

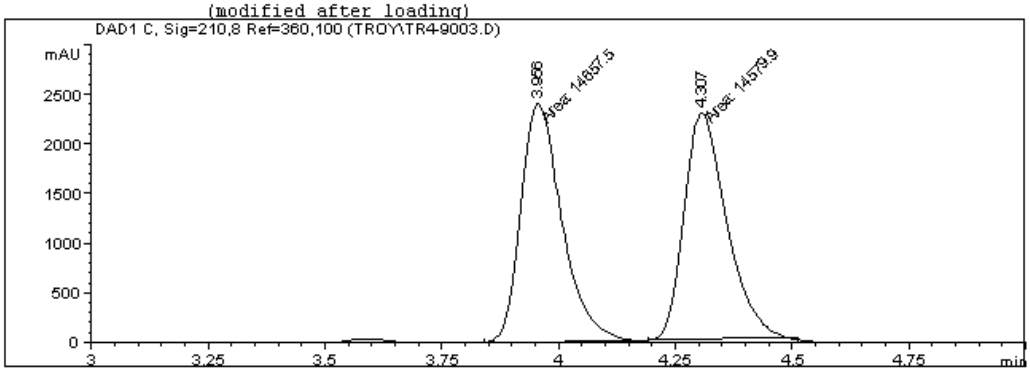



```
==========================================================================
                          Area Percent Report
==========================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.556 BV    0.4822 3348.92187  101.68648  84.0360
   2  19.112 VBA   0.5005  636.18250   19.40361  15.9640

Totals :                  3985.10437  121.09009

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Racemic 1

Data File C:\HPCHEM\2\DATA\TROY\TR4-9003.D Sample Name: TER-IV-90

```
==================================================================
Injection Date  : 12/14/2006 12:04:10 PM
Sample Name     : TER-IV-90                    Location : Vial 1
Acq. Operator   : MMB
                                               Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/14/2006 11:48:38 AM by MMB
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MMB LC.M
Last changed    : 12/21/2006 6:54:53 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 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   3.956 MM    0.1016 1.46575e4  2404.97046  50.1327
   2   4.307 MM    0.1065 1.45799e4  2281.31519  49.8673

Totals :                  2.92374e4  4686.28564

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

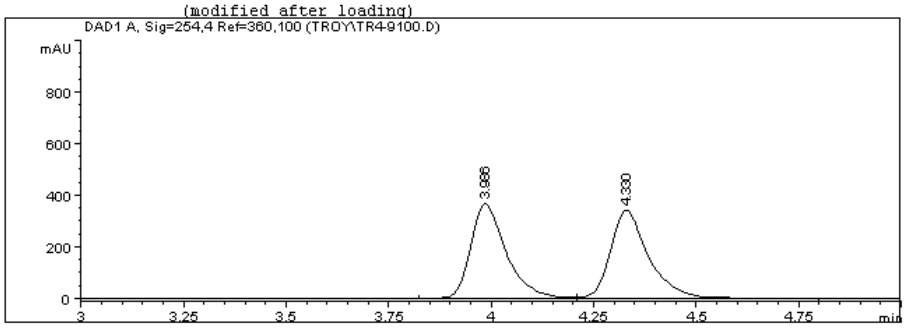
Kinetic Resolution Study

Experiment 1

Followed the general procedure using silyloxyallene **1** (100 mg, 0.46 mmol), 2-chlorobenzaldehyde (26 μL, 0.23 mmol) and (salen)Cr(III)-SbF_6 **2** (19 mg, 0.023 mmol). After consumption of the aldehyde as monitored by TLC (40 h), the mixture was filtered through a plug of silica gel and washed with pentane. The solution was concentrated *in vacuo*. The resulting residue was then analyzed by HPLC with a Chiralcel-OD column. The remaining silyloxyallene **1** was racemic.

Data File C:\HPCHEM\2\DATA\TROY\TR4-9100.D Sample Name: TER-IV-91r

```
==========================================================================
Injection Date  : 11/28/2006 8:19:34 AM
Sample Name     : TER-IV-91r                    Location : Vial 1
Acq. Operator   : MMB
                                               Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 11/28/2006 8:19:49 AM by MMB
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MMB LC.M
Last changed    : 12/21/2006 6:58:26 PM by mmb
                  (modified after loading)
```



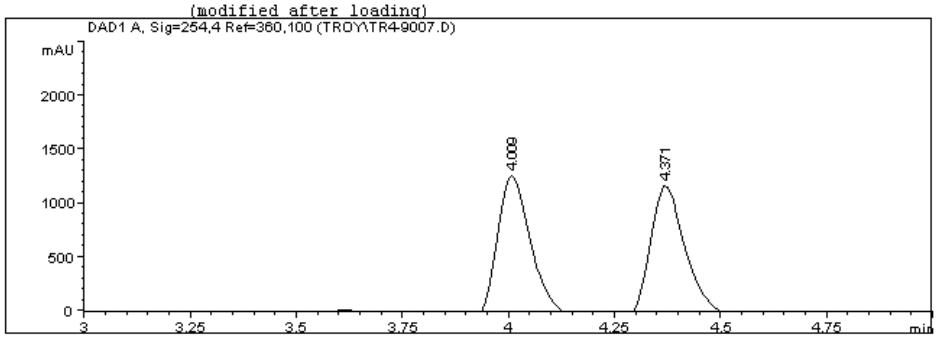

```
==========================================================================
                        Area Percent Report
==========================================================================

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   3.986 VV    0.0876 2192.09204  367.45917  49.7082
   2   4.330 VP    0.0958 2217.83032  341.56226  50.2918

Totals :                   4409.92236  709.02142

 Results obtained with enhanced integrator!
==========================================================================
                           *** End of Report ***
```

Experiment 2

Followed the general procedure using silyloxyallene **1** (50 mg, 0.23 mmol), 2-chlorobenzaldehyde (26 μL, 0.23 mmol) and (salen)Cr(III)-SbF_6 **2** (19 mg, 0.023 mmol). After approximately half of the aldehyde was consumed as monitored by TLC (18 h), the mixture was filtered through a plug of silica gel and washed with pentane. The solution was concentrated *in vacuo*. The resulting residue was then analyzed by HPLC with a Chiralcel-OD column. The remaining silyloxyallene **1** was racemic.

Data File C:\HPCHEM\2\DATA\TROY\TR4-9007.D Sample Name: TER-IV-90

```
==========================================================================
Injection Date  : 12/14/2006 1:08:11 PM
Sample Name     : TER-IV-90                    Location : Vial 1
Acq. Operator   : MMB
                                               Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\SCHWIN1.M
Last changed    : 12/14/2006 12:31:11 PM by MMB
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MMB LC.M
Last changed    : 12/21/2006 6:57:31 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 Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.009 VV    0.0868 8096.12500 1371.98450  50.0474
   2   4.371 VV    0.0958 8080.77832 1277.39111  49.9526

Totals :                  1.61769e4  2649.37561

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Instrument 2 12/21/2006 6:57:44 PM mmb Page 1 of 1

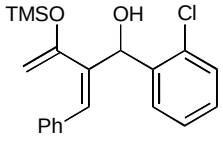
Cr(III)-Catalyzed Competition Experiment

To a 2-dram vial equipped with a magnetic stir bar and (salen)Cr(III)- SbF_6 **2** (19 mg, 0.023 mmol) was added benzaldehyde (23 μL, 0.23 mmol). The vial was cooled to –20 ºC and silyloxyallene **1** (50 mg, 0.23 mmol) and silyl enol ether **17** (30 mg, 0.23 mmol) dissolved in CH_2Cl_2 (250 μL) were added via syringe in one portion. The resulting solution was stirred at –20 °C until the aldehyde was completely consumed (12 h) as determined by thin layer chromatography (20% ethyl acetate/hexanes). The solution was concentrated and the resulting residue was analyzed by 500 MHz ^{1}H NMR spectroscopy. Only product from the addition of silyloxyallene **1** to benzaldehyde was observed. No product derived from the enol silane **17** was witnessed. The residue was then dissolved in THF (5 mL) and treated briefly with 1N HCl (1 mL). After 5 minutes, the solution was diluted with water (10 mL) and ether (20 mL) and transferred to a separatory funnel. The aqueous layer was discarded and the ether layer was washed with saturated $NaHCO_3$ (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated to provide the unpurified reaction mixture. Analysis by 500 MHz ^{1}H NMR spectroscopy revealed **3** as the lone product. Purification by flash chromatography (15% EtOAc/hexanes) afforded 46 mg of **3** (79%) as a yellow oil.

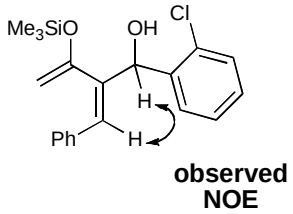
$Sc(OTf)_3$-Catalyzed Competition Experiment

To a flame-dried 10 mL round bottom flask equipped with a magnetic stir bar was dissolved silyloxyallene **1** (50 mg, 0.23 mmol) and silyl enol ether **17** (30 mg, 0.23 mmol) in CH_2Cl_2 (2 mL). Benzaldehyde (23 μL, 0.23 mmol) was added and the flask was cooled to –78 ºC. After stirring for 10 minutes, $Sc(OTf)_3$ (11 mg, 0.023 mmol) was added. The resulting solution was stirred at –78 °C until the aldehyde was completely consumed (15 min) as determined by thin layer chromatography (20% 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 products, which were dissolved in THF (5 mL) and treated with briefly (5 min) with 1N HCl (1mL). This solution was diluted with ether (20 mL) and water (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 NMR spectrum of the unpurified residue revealed a ratio of 1.5 to 1 favoring the aldol product derived from enol silane **17**.

Procedure for Synthesis and Isolation of Hetero-ene Product

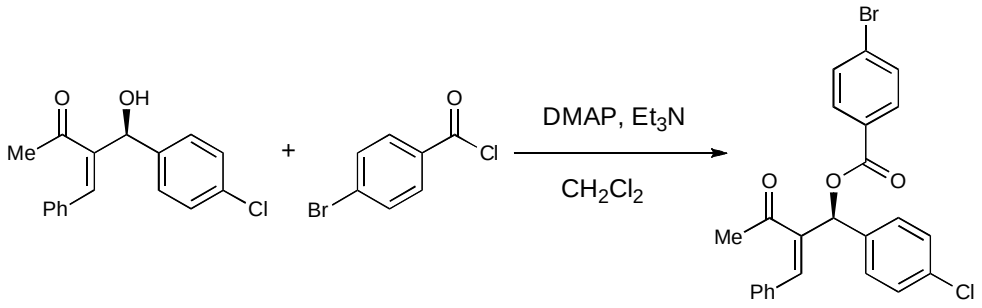


(*Z*)-2-benzylidene-1-(2-chlorophenyl)-3-(trimethylsilyloxy)but-3-en-1-ol: To a 2-dram vial equipped with a magnetic stir bar and (salen)Cr(III)-SbF_6 **2** (19 mg, 0.023 mmol) was added 2-chlorobenzaldehyde (26 μL, 0.23 mmol). The vial was cooled to –20 ºC and silyloxyallene (75 mg, 0.34 mmol) dissolved in CH_2Cl_2 (250 μL) was added via syringe in one portion. Upon consumption of 2-chlorobenzaldehyde (12h) as determined by thin layer chromatography, the solution was concentrated *in vacuo.* The resulting residue was purified by flash chromatography on deactivated silica (15% EtOAc/hexanes) to afford a mixture of the hetero-ene-product (15 mg, 18% yield) and hydrolyzed product **5** (45 mg, 69% yield). Analytical data for hetero-ene-product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.30-7.22 (m, 7H), 6.54 (s, 1H), 5.81 (d, *J* = 4.6 Hz, 1H), 4.19 (s, 1H), 4.11 (s, 1H), 2.80 (d, *J* = 4.8 Hz, 1H), 0.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7, 139.4, 139.3, 137.0, 133.3, 130.3, 129.6, 129.2, 129.0, 128.7, 128.1, 127.5, 127.0, 95.3, 73.8, 0.1. The relative stereochemistry was determined by NOE observed between the vinylic hydrogen and benzylic hydrogen.

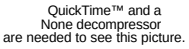


ORTEP and Determination of Absolute Configuration

For the absolute configuration determination, see the X-ray analysis of 4-bromobenzoyl-protected **8**.



X-ray diffraction was performed at –120 °C and raw frame data were processed using SAINT. Molecular structure was solved using direct methods and refined by F2 by full-matrix least-squares techniques. The GOF = 1.04 for 334 variables refined to R1 = 0.0574 for 19743 reflections with I>2α(I). Further information is contained in the CCDC file 631929.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