

The Use of an Aminosilyllithium for the Diastereoselective Synthesis of Diphenyl Oxasilacyclopentane Acetals and Polyols

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A. Experimental Data

S-2

B. GCMS and Spectral Data for Stereochemical Proofs

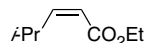
S-17

Experimental Section

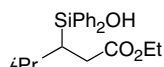
General: ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature at 400 or 500 MHz, and 100 or 125 MHz, respectively, using a Bruker DRX400 or DRX500 spectrometer. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, and m = multiplet), coupling constants in Hz, and integration. High resolution mass spectra were acquired on a VG Analytical 7070E or Fisons Autospec spectrometer and were obtained by peak matching. Microanalyses were performed by Atlantic Microlab, Atlanta, GA. Analytical gas-liquid chromatography (GLC) was performed on a Hewlett Packard 5890 Level 4 chromatograph equipped with a split mode injection system and a flame ionization detector. Fused silica capillary columns (30 m \times 0.32 mm) wall-coated with DB-1 (J & W Scientific) were used with helium as the carrier gas (16 psi column head pressure). GC-MS analyses were conducted on a Finnigan Trace-MS from 50 $^{\circ}\text{C}$ for 1 min then ramped 10 $^{\circ}\text{C}$ / min to 290 $^{\circ}\text{C}$. Fused silica capillary columns (30 \times 0.32 mm) wall-coated with DB-5 (J&W Scientific) were used with ammonia as the reagent gas for chemical impact (CI) analysis. Unless otherwise stated, all reactions were carried out under an atmosphere of nitrogen in glassware which had been flame-dried under a stream of nitrogen. Air-sensitive compounds were stored in an Innovative Technologies nitrogen atmosphere drybox. THF, CH_2Cl_2 , Et_2O , and toluene were purified by filtration through activated alumina according to the method of Grubbs.¹ Hexane, benzene, and $\text{BF}_3\cdot\text{Et}_2\text{O}$ were purified by distillation from CaH_2 . NaH was washed with hexanes and dried under reduced pressure

prior to use. Ethyl crotonate, and isobutyraldehyde were purified by distillation over CaCl_2 . All other reagents were used as received.

A. Experimental Data

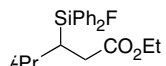


Ethyl Z-4-methyl-pent-2-eneoate (10). To a cooled ($-78\text{ }^{\circ}\text{C}$) suspension of NaH (0.96 g, 40 mmol, 60% dispersion in oil, washed with hexanes) in 65 mL of THF was added a cooled ($-78\text{ }^{\circ}\text{C}$) solution of ethyl (di-*o*-tolylphosphono)acetate² (10 g, 29 mmol) in 50 mL of THF. The reaction mixture was stirred for 15 min at $-78\text{ }^{\circ}\text{C}$. A cooled ($-78\text{ }^{\circ}\text{C}$) solution of isobutyraldehyde (2.9 mL, 32 mmol) in 29 mL of THF was added to the reaction mixture. After the mixture was warmed to $0\text{ }^{\circ}\text{C}$ for 2.75 h, 30 mL of ammonium chloride (saturated aqueous) was added. After the reaction mixture was warmed to $22\text{ }^{\circ}\text{C}$, the mixture was diluted with 100 mL of H_2O and 50 mL of Et_2O . The organic layer was separated, and the aqueous layer was extracted with Et_2O ($3 \times 100\text{ mL}$). The combined organic layers were washed with H_2O ($3 \times 200\text{ mL}$) and brine ($3 \times 200\text{ mL}$). The organic layer was dried over MgSO_4 , filtered, and concentrated *in vacuo* to give a colorless oil as a 90:10 mixture of diastereomers as determined by GCMS-EI. The resulting oil was purified by flash column chromatography (4:96 EtOAc/hexanes) to give a single diastereomer of the product as a colorless oil (2.7 g, 66%): ^1H NMR (500 MHz, CDCl_3) δ 5.99 (dd, $J = 11.4, 10.0$, 1H), 5.64 (d, $J = 11.5$, 1H), 4.16 (q, $J = 7.1$, 2H), 3.60 (m, 1H), 1.29 (t, $J = 7.1$, 3H), 1.02 (d, $J = 6.6$, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.2, 156.8, 117.4, 59.6, 27.5, 22.2, 14.2; HRMS (EI-GCMS) m/z calcd for $\text{C}_8\text{H}_{14}\text{O}_2$ (M^+) 142.0994, found 142.0995.



Ethyl 4-methyl-3-(diphenylsilanol)pentanoate (8). To a solution of chloro(diethylamino)diphenylsilane³ (2.0 g, 6.9 mmol) in 28 mL of THF was added Li° wire (0.39 g, 56 mmol, 0.5 to 1.0% Na° content) cut into small pieces ($<5\text{ mm}$). The suspension was cooled to $0\text{ }^{\circ}\text{C}$ and stirred vigorously for 3 h to give a solution of

(diethylamino)diphenylsilyllithium **5**.⁴ The cooled (0 °C) solution of the silyllithium was added to a cooled (−78 °C) solution of Me₂Zn (3.4 mL, 6.9 mmol, 2.0 M in toluene) in 46 mL of THF. The solution was warmed to 0 °C for 5 min and then re-cooled to −78 °C. To a separate flask, MeLi (0.49 mL, 0.69 mmol, 1.4 M in Et₂O) was added to a cooled (−78 °C) suspension of CuCN (0.034 g, 0.38 mmol) in 8.5 mL of THF. The suspension was warmed to −30 °C, stirred for 5 min, cooled to −78 °C, and stirred for 5 min. The cuprate solution was added to the zincate solution, and the mixture was stirred at −78 °C for 10 min. To the reaction solution was added a cooled (−78 °C) solution of enoate **7** (0.93 g, 6.6 mmol) in 3.9 mL of THF. After 2 h at −78 °C, 15 mL of ammonium chloride (saturated aqueous) was added, and the mixture was warmed to 22 °C. The mixture was diluted with 100 mL of H₂O and 100 mL of Et₂O. The organic layer was separated and the aqueous layer was extracted with Et₂O (3 × 100 mL). The combined organic layers were dried with MgSO₄, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (3:97 to 10:90 EtOAc/hexanes) to give the product as a white solid (1.5 g, 68%): ¹H NMR (500 MHz, CDCl₃) δ 7.69 (m, 2H), 7.64 (m, 2H), 7.36 (m, 6H), 3.99 (dq, *J* = 7.1, 2.2, 2H), 3.59 (br s, 1H), 2.59 (dd, *J* = 16.6, 6.2, 1H), 2.44 (dd, *J* = 16.6, 5.7, 1H), 2.06 (tt, *J* = 11.8, 6.8, 1H), 1.67 (dd, *J* = 10.8, 5.8, 1H), 1.17 (t, *J* = 7.1, 3H), 0.93 (d, *J* = 6.8, 3H), 0.85 (d, *J* = 6.8, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 175.6, 136.6, 136.1, 134.3, 134.1, 129.53, 129.47, 127.8, 60.7, 31.2, 29.3, 27.8, 23.3, 20.8, 14.0; IR (thin film): 3462, 3070, 2960, 1711, 1590, 856 cm^{−1}; HRMS (CI+/NH₃) *m/z* calcd for C₂₀H₂₅O₃Si (M-H)⁺ 341.1573, found 341.1563. Anal. Calcd for C₂₀H₂₆O₃Si: C, 70.13; H, 7.65. Found: C, 70.21; H, 7.64.



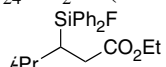
Ethyl 4-methyl-3-(fluorodiphenylsilyl)pentanoate (9). *One step formation from silanol*

8: To a cooled (−78 °C) solution of ester **8** (1.4 g, 4.1 mmol) in 27 mL of CH₂Cl₂ was added BF₃•OEt₂ (0.62 mL, 4.9 mmol). After the solution was stirred for 15 min at −78 °C, 10 mL of sodium bicarbonate (saturated aqueous) was added. The mixture was

diluted with 50 mL of H₂O. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 40 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (1:99 EtOAc/hexanes) to give the product as a colorless oil (1.1 g, 78%).

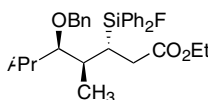
Two step formation from enoate 7: To a solution of chloro(diethylamino)diphenylsilane³ (2.0 g, 6.9 mmol) in 28 mL of THF was added Li⁰ wire (0.38 g, 55 mmol, 0.5 to 1.0% Na⁰ content) cut into small pieces (<5 mm). The suspension was cooled to 0 °C and stirred vigorously for 3 h to give a solution of (diethylamino)diphenylsilyllithium **5**.⁴ The cooled (0 °C) solution of the silyllithium was added to a cooled (−78 °C) solution of Me₂Zn (3.4 mL, 6.9 mmol, 2.0 M in toluene) in 46 mL of THF. The solution was warmed to 0 °C for 5 min and then re-cooled to −78 °C. To a separate flask, MeLi (0.49 mL, 0.69 mmol, 1.4 M in Et₂O) was added to a cooled (−78 °C) suspension of CuCN (0.030 g, 0.33 mmol) in 8.5 mL of THF. The suspension was warmed to −30 °C, stirred for 5 min, cooled to −78 °C, and stirred for 5 min. The cuprate solution was added to the zincate solution, and the mixture was stirred at −78 °C for 10 min. To the reaction solution was added a cooled (−78 °C) solution of enoate **7** (0.93 g, 6.5 mmol) in 4 mL of THF. After 6 h at −78 °C, 15 mL of ammonium chloride (saturated aqueous) was added, and the mixture was warmed to 22 °C. The mixture was diluted with 100 mL of H₂O and 100 mL of Et₂O. The organic layer was separated and the aqueous layer was extracted with Et₂O (3 × 100 mL). The combined organic layers were dried with MgSO₄, filtered, and concentrated *in vacuo*. The resulting oil was dissolved in 46 mL of CH₂Cl₂ and cooled to −78 °C. BF₃•OEt₂ (1.1 mL, 8.7 mmol) was added to the cooled solution. After the solution was stirred for 15 min at −78 °C, 10 mL of sodium bicarbonate (saturated aqueous) was added. The mixture was diluted with 50 mL of H₂O. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 40 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography

(0.5:99.5 to 1:99 EtOAc/hexanes) to give the product as a colorless oil (1.5 g, 68% over two steps): ^1H NMR (500 MHz, CDCl_3) δ 7.68 (m, 2H), 7.64 (m, 2H), 7.41 (m, 6H), 3.94 (m, 2H), 2.46 (m, 2H), 2.04 (m, 2H), 1.14 (t, $J = 7.1$, 3H), 0.97 (d, $J = 6.6$, 3H), 0.92 (d, $J = 6.6$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.9, 134.3 (d, $J = 2.5$), 134.2 (d, $J = 2.5$), 133.4 (d, $J = 15.0$), 133.1 (d, $J = 15.0$), 130.4, 130.3, 128.02, 127.95, 60.4, 31.2, 28.6 (d, $J = 13.8$), 28.3, 22.5, 21.1, 14.0; IR (thin film): 3051, 2960, 1731, 1591, 1429, 841 cm^{-1} ; HRMS (CI+/ NH_3) m/z calcd for $\text{C}_{20}\text{H}_{24}\text{FO}_2\text{Si}$ (M-H) $^+$ 343.1530, found 343.1524.



Ethyl 4-methyl-3-(fluorodiphenylsilyl)pentanoate (9). To a solution of chloro(diethylamino)diphenylsilane³ (2.4 g, 8.3 mmol) in 30 mL of THF was added Li $^\circ$ wire (0.40 g, 58 mmol, 0.5 to 1.0% Na $^\circ$ content) cut into small pieces (<5 mm). The suspension was cooled to 0 $^\circ\text{C}$ and stirred vigorously for 3 h to give a solution of (diethylamino)diphenylsilyllithium **5**.⁴ The cooled (0 $^\circ\text{C}$) solution of the silyllithium was added to a cooled (-78 $^\circ\text{C}$) solution of Me_2Zn (3.9 mL, 7.8 mmol, 2.0 M in toluene) in 50 mL of THF. The solution was warmed to 0 $^\circ\text{C}$ for 5 min and then re-cooled to -78 $^\circ\text{C}$. To a separate flask, MeLi (0.56 mL, 0.78 mmol, 1.4 M in Et_2O) was added to a cooled (-78 $^\circ\text{C}$) suspension of CuCN (0.032 g, 0.36 mmol) in 10 mL of THF. The suspension was warmed to -30 $^\circ\text{C}$, stirred for 5 min, cooled to -78 $^\circ\text{C}$, and stirred for 5 min. The cuprate solution was added to the zincate solution, and the mixture was stirred at -78 $^\circ\text{C}$ for 10 min. To the reaction solution was added a cooled (-78 $^\circ\text{C}$) solution of enoate **10** (1.0 g, 7.0 mmol) in 4 mL of THF. After 6 h at -78 $^\circ\text{C}$, 15 mL of ammonium chloride (saturated aqueous) was added, and the mixture was warmed to 22 $^\circ\text{C}$. The mixture was diluted with 100 mL of H_2O and 100 mL of Et_2O . The organic layer was separated and the aqueous layer was extracted with Et_2O (3×100 mL). The combined organic layers were dried with MgSO_4 , filtered, and concentrated *in vacuo*. The resulting oil was dissolved in 50 mL of CH_2Cl_2 and cooled to -78 $^\circ\text{C}$. $\text{BF}_3 \cdot \text{OEt}_2$ (1.1 mL, 8.7 mmol) was added to the cooled solution. After the solution was stirred for 15 min at -78 $^\circ\text{C}$, 10 mL

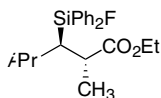
of sodium bicarbonate (saturated aqueous) was added. The mixture was diluted with 50 mL of H₂O. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 40 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (1:99 EtOAc/hexanes) to give the product as a colorless oil (1.5 g, 63% over two steps): ¹H NMR (500 MHz, CDCl₃) δ 7.68 (m, 2H), 7.64 (m, 2H), 7.41 (m, 6H), 3.94 (m, 2H), 2.46 (m, 2H), 2.04 (m, 2H), 1.14 (t, *J* = 7.1, 3H), 0.97 (d, *J* = 6.6, 3H), 0.92 (d, *J* = 6.5, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.9, 134.3 (d, *J* = 2.5), 134.2 (d, *J* = 2.5), 133.4 (d, *J* = 15.0), 133.0 (d, *J* = 15.0), 130.4, 130.3, 128.03, 127.95, 60.4, 31.2, 28.6 (d, *J* = 13.0), 28.3, 22.5, 21.9, 14.0; HRMS (CI+/NH₃) *m/z* calcd for C₂₀H₂₄FO₂Si (M-H)⁺ 343.1530, found 343.1523.



Ethyl (3*R,4*S**,5*R**)-5-benzyloxy-3-(fluorodiphenylsilyl)-4,6-dimethylheptanoate**

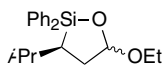
(12). To a solution of chloro(diethylamino)diphenylsilane³ (2.8 g, 9.6 mmol) in 36 mL of THF was added Li[°] wire (0.54 g, 78 mmol, 0.5 to 1.0% Na[°] content) cut into small pieces (<5 mm). The suspension was cooled to 0 °C and stirred vigorously for 3 h to give a solution of (diethylamino)diphenylsilyllithium **5**.⁴ The cooled (0 °C) solution of the silyllithium was added to a cooled (−78 °C) solution of Me₂Zn (4.8 mL, 9.6 mmol, 2.0 M in toluene) in 64 mL of THF. The solution was warmed to 0 °C for 5 min and then re-cooled to −78 °C. To a separate flask, MeLi (0.68 mL, 0.96 mmol, 1.4 M in Et₂O) was added to a cooled (−78 °C) suspension of CuCN (0.042 g, 0.47 mmol) in 12 mL of THF. The suspension was warmed to −30 °C, stirred for 5 min, cooled to −78 °C, and stirred for 5 min. The cuprate solution was added to the zincate solution, and the mixture was stirred at −78 °C for 10 min. To the reaction solution was added a cooled (−78 °C) solution of ethyl enoate **11**⁶ (2.5 g, 8.6 mmol) in 5 mL of THF. After 1 h at −78 °C, 15 mL of ammonium chloride (saturated aqueous) was added, and the mixture was warmed

to 22 °C. The mixture was diluted with 100 mL of 9:1 ammonium chloride/ammonium hydroxide and 100 mL of Et₂O. The organic layer was separated and the aqueous layer was extracted with Et₂O (3 × 100 mL). The combined organic layers were dried with MgSO₄, filtered, and concentrated *in vacuo*. The resulting oil was re-dissolved in 57 mL of CH₂Cl₂ and cooled to –78 °C. BF₃•OEt₂ (1.3 mL, 10 mmol) was added to the cooled solution. After the solution was stirred for 10 min at –78 °C, 10 mL of sodium bicarbonate (saturated aqueous) was added. The mixture was diluted with 50 mL of H₂O. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 40 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo* to give a pale yellow oil as a 99:1 mixture of diastereomers as determined by GCMS-EI. The resulting oil was purified by flash column chromatography (0.5:99.5 to 2:98 EtOAc/hexanes) to give the product as a pale yellow oil (3.2 g, 76% over two steps): ¹H NMR (500 MHz, CDCl₃) δ 7.67 (dd, *J* = 7.9, 1.4, 4H), 7.40 (m, 7H), 7.31 (m, 4H), 4.56 (d, *J* = 11.2, 1H), 4.53 (d, *J* = 11.2, 1H), 3.87 (dq, *J* = 10.8, 7.2, 1H), 3.79 (dq, *J* = 10.8, 7.2, 1H), 3.12 (dd, *J* = 6.3, 4.5, 1H), 2.62 (dd, *J* = 16.6, 5.5, 1H), 2.52 (dd, *J* = 16.6, 7.7, 1H), 2.17 (m, 2H), 2.00 (ddt, *J* = 13.8, 6.8, 4.5, 1H), 1.08 (t, *J* = 7.1, 3H), 0.98 (d, *J* = 6.8, 3H), 0.89 (d, *J* = 6.8, 3H), 0.81 (d, *J* = 6.7, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.9, 139.1, 135.5 (d, *J* = 36.3), 134.3 (d, *J* = 2.5), 134.1 (d, *J* = 2.5), 132.8 (d, *J* = 15.0), 132.5 (d, *J* = 16.3), 130.4 (d, *J* = 13.8), 128.2, 128.1, 127.9, 127.3, 127.2, 88.6, 75.0, 60.3, 33.8, 30.5, 30.0, 24.8 (d, *J* = 13), 20.3, 16.8, 13.9, 13.1; IR (thin film): 3052, 2965, 1731, 1590, 1429, 1119 cm⁻¹; HRMS (CI+/NH₃) *m/z* calcd for C₃₀H₃₇O₃Si (M-F)⁺ 473.2512, found 473.2494. Anal. Calcd for C₃₀H₃₇FO₃Si: C, 73.13; H, 7.57. Found: C, 72.97; H, 7.62.



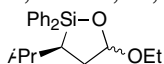
(2S*,3R*)-Ethyl 2,4-dimethyl-3-(fluorodiphenylsilyl)pentanoate (13). To a cooled (–78 °C) solution of *i*-Pr₂NH (0.36 mL, 2.6 mmol) in 2.5 mL of THF was added *n*-BuLi

(1.2 mL, 2.4 mmol, 2.0 M in hexanes). After the solution was stirred at 0 °C for 30 min, it was re-cooled to –78 °C. To the reaction solution was added a cooled (–78 °C) solution of β -fluorosilyl ester **9** (0.70 g, 2.0 mmol) in 10 mL of THF and DMPU (1.2 mL, 10 mmol). After the reaction solution was stirred at –78 °C for 1 h, CH₃I (0.25 mL, 4.0 mmol) was added. After the reaction solution was stirred at –78 °C for 2 h, 4 mL of ammonium chloride (saturated aqueous) was added. The mixture was diluted with 50 mL of H₂O and 50 mL of MTBE. The organic layer was separated, and the aqueous layer was extracted with MTBE (3 \times 50 mL). The combined organic layers were washed with H₂O (4 \times 50 mL) and brine (4 \times 50 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated *in vacuo* to give a colorless oil as a 90:10 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash column chromatography (20:80 CH₂Cl₂/hexanes) to give a single diastereomer of the product as a colorless oil (0.46 g, 65%): ¹H NMR (500 MHz, CDCl₃) δ 7.78 (dd, *J* = 7.7, 1.6, 2H), 7.69 (dd, *J* = 8.0, 1.5, 2H), 7.39 (m, 6H), 4.00 (dq, *J* = 10.8, 7.1, 1H), 3.91 (dq, *J* = 10.8, 7.1, 1H), 2.76 (m, 1H), 2.16 (dq, *J* = 13.6, 6.8, 1H), 1.86 (dt, *J* = 9.2, 5.0, 1H), 1.15 (t, *J* = 7.1, 3H and d, *J* = 7.3, 3H), 1.03 (d, *J* = 6.8, 3H), 0.89 (d, *J* = 6.9, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 177.6, 134.7 (d, *J* = 2.5), 134.4 (d, *J* = 2.5), 130.0 (d, *J* = 6.3), 127.8 (d, *J* = 10.0), 60.7, 38.6, 36.8 (d, *J* = 13.6), 27.2, 22.7, 22.4, 16.8, 14.0; IR (thin film): 3071, 2978, 1721, 1590, 1117, 700 cm⁻¹; HRMS (CI+/NH₃) *m/z* calcd for C₂₁H₂₆FO₂Si (M-H)⁺ 357.1686, found 357.1679. Anal. Calcd for C₂₁H₂₇FO₂Si: C, 70.35; H, 7.59. Found: C, 70.39; H, 7.64.



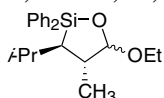
1-Oxa-3-(1-methylethyl)-5-ethoxy-2,2-(diphenyl)silacyclopentane (14). To a solution of β -fluorosilyl ester **9** (0.39 g, 1.1 mmol) and LiBH₄ (1.6 mL, 3.2 mmol, 2.0 M in THF) in 4.5 mL of Et₂O was added MeOH (0.13 mL, 3.2 mmol) dropwise. After 15 h at 22 °C, the solution was cooled to 0 °C, and 1 mL of ammonium chloride (saturated aqueous) was added dropwise. The solution was diluted with 50 mL of H₂O and 50 mL of CH₂Cl₂.

The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3×60 mL). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo* to give a colorless oil as a 56:44 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash column chromatography (0.5:99.5 EtOAc/hexanes) to give the product as a colorless oil (0.31 g, 86%). The product was characterized as a mixture of diastereomers: ^1H NMR (500 MHz, CDCl_3) δ 7.72 (m, 3.6H), 7.68 (m, 2.7H), 7.59 (m, 2.7H), 7.41 (m, 13H), 5.43 (d, $J = 3.9$, 1H), 5.23 (dd, $J = 7.7$, 4.3, 0.7H), 4.02 (m, 0.8H), 3.70 (dq, $J = 9.5$, 7.1, 1H), 3.60 (dq, $J = 9.6$, 7.0, 0.8H), 3.44 (dq, $J = 9.6$, 7.1, 1H), 2.46 (m, 1.3H), 2.34 (dd, $J = 11.6$, 6.3, 1H), 1.75 (m, 2.9H), 1.49 (m, 2.2H), 1.29 (t, $J = 7.1$, 2.6H), 1.06 (t, $J = 7.1$, 3H), 0.93 (m, 12H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.6, 135.3, 134.91, 134.89, 130.2, 130.1, 130.05, 130.02, 127.9, 127.74, 127.69, 102.6, 101.7, 64.0, 62.3, 38.5, 37.8, 33.1, 30.6, 29.2, 25.1, 24.9, 23.1, 23.0, 15.3, 14.9; IR (thin film): 3071, 2955, 1729, 1590, 1429, 1118 cm^{-1} ; HRMS (CI^+/NH_3) m/z calcd for $\text{C}_{20}\text{H}_{25}\text{O}_2\text{Si}$ (M-H) $^+$ 325.1624, found 325.1620. Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2\text{Si}$: C, 73.57; H, 8.03. Found: C, 73.68; H, 7.85.



1-Oxa-3-(1-methylethyl)-5-ethoxy-2,2-(diphenyl)silacyclopentane (14). To a cooled (-78 °C) solution of β -fluorosilyl ester **9** (0.39 g, 1.1 mmol) in 9 mL of CH_2Cl_2 was added $i\text{-Bu}_2\text{AlH}$ (0.73 mL, 1.1 mmol, 1.5 M in toluene). After 3 h at -78 °C, 1 mL of EtOH was added. After 2 h at 22 °C, the mixture was diluted with 20 mL of sodium potassium tartrate (saturated aqueous), 50 mL of H_2O , and 50 mL of CH_2Cl_2 . The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3×40 mL). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo* to give a colorless oil as a 62:38 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash column chromatography (0.5:99.5 EtOAc/hexanes) to give the product as a colorless oil (0.35g, 97%). The product was characterized as a mixture of diastereomers: ^1H NMR (500 MHz, CDCl_3) δ 7.72 (m, 3H),

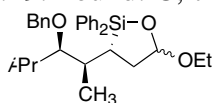
7.65 (m, 2.3H), 7.59 (m, 2.7H), 7.41 (m, 12H), 5.43 (d, $J = 4.0$, 1H), 5.23 (dd, $J = 7.7$, 4.3, 0.5H), 4.02 (dq, $J = 9.6$, 7.1, 0.5H), 3.69 (dq, $J = 9.6$, 7.1, 1H), 3.60 (dq, $J = 9.6$, 7.0, 0.5H), 3.44 (dq, $J = 9.6$, 7.0, 1H), 2.46 (m, 1H), 2.34 (dd, $J = 11.8$, 6.5, 1H), 1.75 (m, 2.7H), 1.50 (m, 2.3H), 1.29 (t, $J = 7.1$, 1.6H), 1.05 (t, $J = 7.1$, 3H), 0.93 (m, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.5, 135.3, 134.96, 134.94, 130.3, 130.12, 130.09, 130.05, 128.0, 127.8, 127.7, 102.6, 101.8, 64.1, 62.3, 38.6, 37.9, 33.2, 30.7, 29.2, 25.1, 24.9, 23.1, 23.0, 15.3, 15.0; IR (thin film): 3069, 2954, 1728, 1589, 1428, 1118 cm^{-1} ; HRMS (CI+/NH₃) m/z calcd for $\text{C}_{20}\text{H}_{25}\text{O}_2\text{Si}$ (M-H)⁺ 325.1624, found 325.1628. Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2\text{Si}$: C, 73.57; H, 8.03. Found: C, 73.73; H, 7.96.



(3R*,4S*)-1-Oxa-3-(1-methylethyl)-5-ethoxy-4-methyl-2,2-

(diphenyl)silacyclopentane (15). To a solution of β -fluorosilyl ester **13** (0.55 g, 1.5 mmol) and LiBH_4 (2.4 mL, 4.8 mmol, 2.0 M in THF) in 6.5 mL of Et_2O was added MeOH (0.19 mL, 4.8 mmol) dropwise. After 15 h at 22 °C, the solution was cooled to 0 °C, and 2 mL of ammonium chloride (saturated aqueous) was added dropwise. The solution was diluted with 50 mL of H_2O and 50 mL of Et_2O . The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 \times 50 mL). The combined organic layers were dried over MgSO_4 , filtered, and concentrated *in vacuo* to give a colorless oil as a 60:40 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash column chromatography (0.5:99.5 EtOAc/hexanes) to give the product as a colorless oil (0.47 g, 87%). The product was characterized as a mixture of diastereomers: ^1H NMR (500 MHz, CDCl_3) δ 7.73 (m, 3.8H), 7.67 (m, 2H), 7.62 (m, 2H), 7.40 (m, 12H), 5.16 (d, $J = 4.2$, 0.65H), 4.78 (d, $J = 6.0$, 1H), 4.01 (dq, $J = 9.7$, 7.1, 1H), 3.60 (m, 1.7H), 3.37 (dq, $J = 9.6$, 7.0, 0.64H), 2.19 (m, 0.65H), 2.11 (m, 1H), 1.87 (m, 2H), 1.70 (dd, $J = 12.2$, 7.0, 0.67H), 1.30 (t, $J = 7.1$, 3H and m, 1.35H), 1.12 (d, $J = 6.7$, 3H and d, $J = 6.6$, 2.1H), 1.02 (d, $J = 5.3$ H), 0.97 (t, $J = 7.1$, 3H), 0.62 (t, $J = 6.9$, 5.1 H);

^{13}C NMR (125 MHz, CDCl_3) δ 135.8, 135.7, 135.0, 134.8, 130.1, 130.0, 129.9, 127.9, 127.7, 127.6, 108.4, 104.6, 64.3, 62.5, 42.9, 42.0, 40.3, 36.4, 27.6, 26.9, 24.6, 24.3, 22.0, 21.3, 18.3, 15.3, 15.2, 14.8; IR (thin film): 3050, 2959, 1429, 1116, 982, 701 cm^{-1} ; HRMS (CI^+/NH_3) m/z calcd for $\text{C}_{21}\text{H}_{27}\text{O}_2\text{Si}$ ($\text{M}-\text{H}$) $^+$ 339.1780, found 339.1772. Anal. Calcd for $\text{C}_{21}\text{H}_{28}\text{O}_2\text{Si}$: C, 74.07; H, 8.29. Found: C, 74.35; H, 8.36.

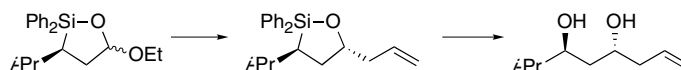


(3R*)-1-Oxa-3-[(1S*,2R*)-2-benzyloxy-1,3-dimethylbutyl]-5-ethoxy-2,2-

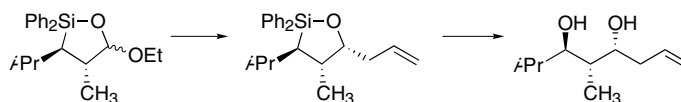
(diphenyl)silacyclopentane (16). To a solution of β -fluorosilyl ester **12** (1.0 g, 2.0 mmol) and LiBH_4 (3.0 mL, 6.0 mmol, 2.0 M in THF) in 8 mL of Et_2O was added MeOH (0.24 mL, 6.0 mmol) dropwise. After 15 h at 22 $^\circ\text{C}$, the solution was cooled to 0 $^\circ\text{C}$, and 2 mL of ammonium chloride (saturated aqueous) was added dropwise. The solution was diluted with 50 mL of H_2O and 50 mL of CH_2Cl_2 . The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were dried over MgSO_4 , filtered, and concentrated *in vacuo* to give a pale yellow oil as a 56:44 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash column chromatography (0.5:99.5 EtOAc /hexanes) to give the product as a pale yellow oil (0.66 g, 70%). The product was characterized as a mixture of diastereomers:

^1H NMR (500 MHz, CDCl_3) δ 7.73 (m, 7H), 7.44 (m, 7H), 7.32 (m, 7H), 7.22 (m, 5H), 5.43 (d, $J = 4.3$, 1H), 5.26 (dd, $J = 6.7$, 4.3, 0.5H), 4.41 (d, $J = 11.8$, 0.5H), 4.31 (d, $J = 11.7$, 1H), 4.19 (d, $J = 11.7$, 1H and d, $J = 11.8$, 0.5H), 4.02 (dq, $J = 9.6$, 7.1, 0.5H), 3.61 (m, 1.5H), 3.40 (dq, $J = 9.6$, 7.1, 1H), 2.90 (dd, $J = 7.8$, 1.9, 1H), 2.87 (dd, $J = 7.7$, 2.0, 0.5H), 2.36 (m, 2.5H), 2.00 (m, 0.5H), 1.76 (m, 5H), 1.29 (t, $J = 7.1$, 1.5H), 1.06 (t, $J = 7.1$, 3H), 0.92 (d, $J = 6.8$, 3H and d, $J = 6.7$, 1.5H), 0.78 (d, $J = 6.7$, 3H and d, $J = 6.7$, 1.5H), 0.52 (d, $J = 6.9$, 1.5H), 0.45 (d, $J = 6.9$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 139.5, 139.4, 135.8, 135.7, 135.5, 135.01, 134.99, 134.1, 134.0, 132.8, 132.1, 130.4, 130.31, 130.27, 130.2, 128.1, 128.0, 127.90, 127.85, 127.79, 126.93, 126.86, 126.6, 126.5, 102.5,

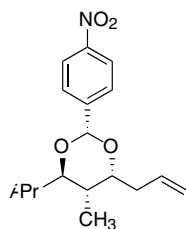
101.6, 89.8, 89.5, 74.0, 73.8, 63.9, 62.3, 38.6, 37.2, 36.6, 36.0, 31.7, 31.5, 28.4, 26.4, 19.62, 19.59, 19.4, 19.3, 15.3, 14.9, 13.49, 13.46; IR (thin film): 3070, 2970, 1590, 1428, 1119, 699 cm^{-1} ; HRMS (CI+/ NH_3) m/z calcd for $\text{C}_{30}\text{H}_{37}\text{O}_3\text{Si}$ (M-H) $^+$ 473.2512, found 473.2494.



7-Methyl-1-octene-4,6-diol (18).⁵ To a cooled ($-78\text{ }^{\circ}\text{C}$) solution of acetal **14** (0.54 g, 1.6 mmol) and allyltrimethylsilane (0.51 mL, 3.2 mmol) in 50 mL of CH_2Cl_2 was added $\text{BF}_3\cdot\text{OEt}_2$ (0.20 mL, 1.6 mmol). After the reaction mixture was warmed to $0\text{ }^{\circ}\text{C}$ for 3 h, 10 mL of sodium bicarbonate (saturated aqueous) was added. The mixture was diluted with 50 mL of H_2O . The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 ($3 \times 50\text{ mL}$). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo* to give oxasilacyclopentane **17** as a 99:1 mixture of diastereomers as determined by GCMS-EI. The oil was dissolved in 7 mL of 1:1 THF/MeOH. To the solution was added KF (0.16 g, 2.8 mmol), KHCO_3 (0.28 g, 2.8 mmol), and H_2O_2 (2.9 mL, 28 mmol, 30 % by weight in H_2O). The reaction mixture was heated to reflux for 1 h. After the mixture was cooled to $22\text{ }^{\circ}\text{C}$, solid $\text{Na}_2\text{S}_2\text{O}_3$ (0.1 g) was added. After the mixture was stirred for 1 h, it was filtered through Celite, and the filtrate was washed with Et_2O ($3 \times 25\text{ mL}$). The solution was concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (10:90 to 20:90 EtOAc/hexanes) to give the product as a colorless oil (0.14 g, 56% over two steps): ^1H NMR (500 MHz, CDCl_3) δ 5.83 (m, 1H), 5.15 (m, 2H), 4.00 (qd, $J = 7.7, 3.2$, 1H), 3.68 (ddd, $J = 8.8, 6.1, 2.5$, 1H), 2.29 (m, 3H), 2.22 (br s, 1H), 1.69 (m, 2H), 1.60 (m, 1H), 0.95 (d, $J = 6.7$, 3H), 0.91 (d, $J = 6.8$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 134.7, 118.1, 73.8, 68.3, 42.0, 38.9, 33.8, 18.6, 17.9; HRMS (CI+/ NH_3) m/z calcd for $\text{C}_9\text{H}_{19}\text{O}_2$ (M+H) $^+$ 159.1385, found 159.1388.

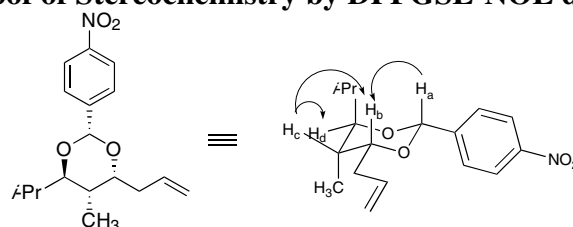


(4*R,5*S**,6*R**)-5,7-Dimethyl-1-octene-4,6-diol (20).** To a cooled ($-78\text{ }^{\circ}\text{C}$) solution of acetal **15** (0.45 g, 1.3 mmol) and allyltrimethylsilane (0.44 mL, 2.8 mmol) in 45 mL of CH_2Cl_2 was added $\text{BF}_3\cdot\text{OEt}_2$ (0.18 mL, 1.4 mmol). After the reaction mixture was warmed to $0\text{ }^{\circ}\text{C}$ for 3 h, 10 mL of sodium bicarbonate (saturated aqueous) was added. The mixture was diluted with 50 mL of H_2O . The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 ($3 \times 50\text{ mL}$). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo* to give oxasilacyclopentane **19** as a colorless oil as a 91:9 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash column chromatography (20:80 CH_2Cl_2 /hexanes) to give oxasilacyclopentane **19** as a colorless oil (0.27 g, 63%). The oil (0.27 g, 0.80 mmol) was dissolved in 4 mL of 1:1 THF/MeOH. To the solution was added KF (0.093 g, 1.6 mmol), KHCO_3 (0.16 g, 1.6 mmol), and H_2O_2 (1.6 mL, 16 mmol, 30 % by weight in H_2O). The reaction mixture was heated to reflux for 1.5 h. After the mixture was cooled to $22\text{ }^{\circ}\text{C}$, solid $\text{Na}_2\text{S}_2\text{O}_3$ (0.1 g) was added. After the mixture was stirred for 1 h, it was filtered through Celite, and the filtrate was washed with Et_2O ($3 \times 25\text{ mL}$). The solution was concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (10:90 EtOAc/hexanes) to give the product as a colorless oil (0.080 g, 62%): ^1H NMR (500 MHz, CDCl_3) δ 5.82 (ddt, $J = 17.1, 10.2, 6.9$, 1H), 5.13 (m, 2H), 3.99 (m, 1H), 3.33 (dd, $J = 10.5, 5.7$, 1H), 2.64 (m, 2H), 2.30 (m, 1H), 2.22 (m, 1H), 1.83 (dq, $J = 13.3, 6.7$, 2H), 0.97 (d, $J = 6.9$, 6H), 0.91 (d, $J = 6.8$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.3, 117.5, 80.7, 71.6, 38.6, 37.5, 30.7, 19.5, 17.2, 11.3; IR (thin film): 3357, 2965, 1642, 1462, 1081, 913 cm^{-1} ; HRMS (CI+/NH₃) m/z calcd for $\text{C}_{10}\text{H}_{21}\text{O}_2$ (M+H)⁺ 173.1541, found 173.1545.

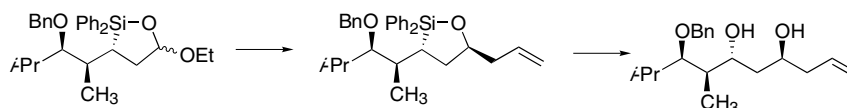


(2R*,4R*,5S*,6R*)-4-Allyl-5-methyl-6-(1-methylethyl)-2-(4-nitrophenyl)-1,3-

dioxane. A flask fitted with a Dean-Stark trap and reflux condenser was charged with diol **20** (0.070 g, 0.41 mmol) and 4-nitrobenzaldehyde (0.088 g, 0.58 mmol) in 20 mL of benzene. CSA (<0.010 g) was added and the solution was heated to reflux for 15 h. The solution was cooled to 22 °C and a few drops of Et₃N were added. The solution was concentrated *in vacuo* to afford a yellow oil as a 70:30 mixture of diastereomers. The resulting oil was purified by flash column chromatography (hexanes to 0.5:99.5 EtOAc/hexanes) to give the product as a yellow oil (0.11 g, 92%): ¹H NMR (500 MHz, CDCl₃) major diastereomer: δ 8.21 (d, *J* = 8.7, 2H), 7.68 (d, *J* = 8.8, 2H), 5.83 (m, 1H), 5.76 (s, 1H), 5.17 (m, 2H), 4.12 (ddd, *J* = 8.2, 5.8, 2.2, 1H), 3.35 (d, *J* = 10.8, 1H), 2.48 (m, 2H), 2.21 (dt, *J* = 14.1, 7.0, 1H), 1.76 (dq, *J* = 7.0, 2.1, 1H), 1.21 (d, *J* = 7.0, 3H), 1.06 (d, *J* = 6.5, 3H), 0.94 (d, *J* = 6.5, 3H); minor diastereomer: δ 8.20 (d, *J* = 8.7, 2H), 7.64 (d, *J* = 8.8, 2H), 5.92 (m, 1H), 5.79 (s, 1H), 5.11 (m, 2H), 4.16 (dt, *J* = 11.0, 4.6, 1H), 3.64 (dd, *J* = 10.3, 2.4, 1H), 2.81 (ddd, *J* = 19.3, 11.5, 3.5, 1H), 2.31 (m, 2H), 1.93 (ddt, *J* = 13.8, 6.9, 2.5, 1H), 1.08 (d, *J* = 6.9, 3H), 0.97 (d, *J* = 6.9, 3H), 0.83 (d, *J* = 7.1, 3H); ¹³C NMR (125 MHz, CDCl₃) major diastereomer: δ 147.96, 145.9, 134.0, 127.1, 123.4, 117.3, 93.7, 86.7, 74.8, 37.0, 30.9, 26.0, 19.6, 19.2, 13.2; minor diastereomer: δ 147.86, 146.2, 134.9, 127.0, 123.2, 116.9, 92.5, 81.2, 76.1, 34.1, 30.2, 28.8, 19.9, 14.6, 12.4; IR (thin film): 3077, 2966, 1642, 1609, 1524, 1348 cm⁻¹; HRMS (CI⁺/NH₃) *m/z* calcd for C₁₇H₂₂NO₄ (M-H)⁺ 304.1549, found 304.1550. Anal. Calcd for C₁₇H₂₃NO₄: C, 66.86; H, 7.59. Found: C, 67.00; H, 7.71.

Proof of Stereochemistry by DPGSE-NOE data:**(2*R**,4*R**,5*S**,6*R**)-4-Allyl-5-methyl-6-(1-methylethyl)-2-(4-nitrophenyl)-1,3-dioxane****H_a** irradiated: H_b (3.5%)**H_c** irradiated: H_b (2.5%)H_d (1.8%)

Note: To minimize unfavorable gauche and diaxial interactions, the 1,3-dioxane adopts the above-pictured conformer, leading to the observed NOEs. There was no NOE observed between H_a or H_b and H_d. If the 1,3-cis diol were obtained, an NOE would be observed between H_b, H_a, and H_d. If the C5 methyl were inverted, no NOE would be visible between H_c and H_b. (Mixing time was 0.5 s)



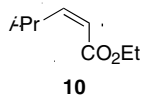
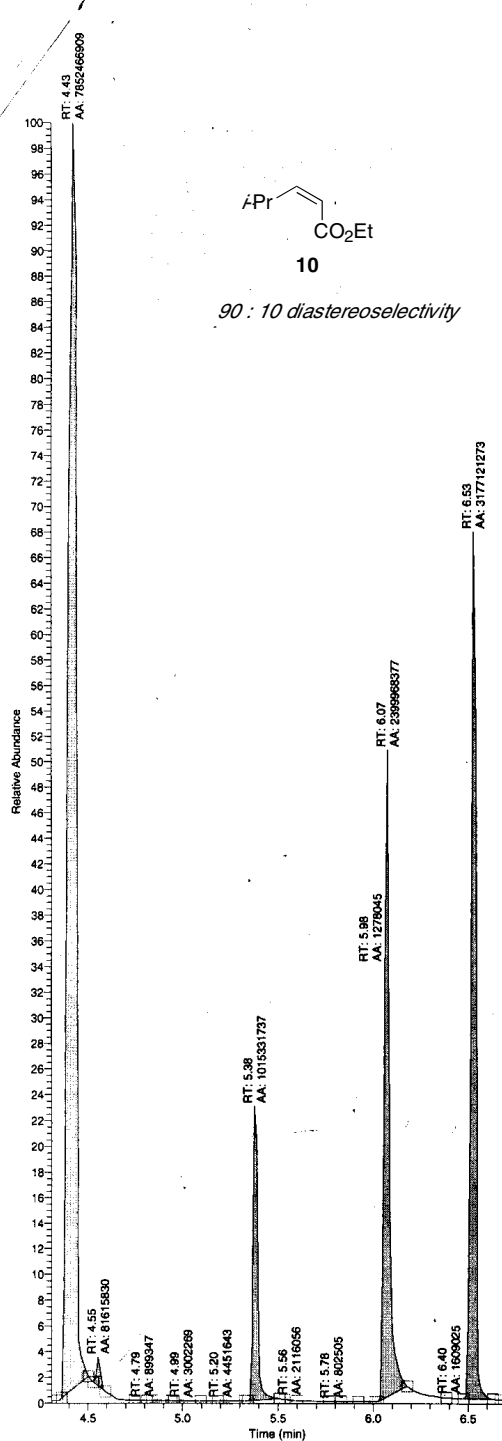
(3*R,4*R**,5*R**,7*S**)-3-benzyloxy-2,4-dimethyl-dec-9-ene-5,7-diol (**22**).⁷** To a cooled (−78 °C) solution of acetal **16** (0.97 g, 2.0 mmol) and allyltrimethylsilane (0.67 mL, 4.2 mmol) in 70 mL of toluene was added SnCl₄ (2.1 mL, 2.1 mmol, 1.0 M in CH₂Cl₂). After the reaction mixture was stirred at −78 °C for 9 h, 20 mL of sodium bicarbonate (saturated aqueous) was added. The reaction mixture was concentrated *in vacuo*. The mixture was diluted with 100 mL of sodium potassium tartrate and 100 mL of CH₂Cl₂. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 100 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo* to give oxasilacyclopentane **21** as a 93:7 mixture of diastereomers as determined by GCMS-EI. The oil was dissolved in 10.6 mL of 1:1 THF/MeOH. To the solution was added KF (0.25 g, 4.3 mmol), KHCO₃ (0.50 g, 5.0 mmol), and H₂O₂ (4.3 mL, 42 mmol, 30 % by weight in H₂O). The reaction mixture was heated to reflux for 5 h. After the mixture was cooled to 22 °C, solid Na₂S₂O₃ (0.5 g) was added. After the

mixture was stirred for 1 h, the mixture was filtered through Celite, and the filtrate was washed with Et₂O (3 × 75 mL). The solution was concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (10:90 to 20:80 EtOAc/hexanes) to give the product as a pale yellow oil (0.360 g, 56% over two steps): ¹H NMR (500 MHz, CDCl₃) δ 7.35 (m, 4H), 7.29 (m, 1H), 5.82 (ddt, *J* = 18.0, 10.6, 7.1, 1H), 5.13 (m, 2H), 4.68 (d, *J* = 11.4, 1H), 4.62 (d, *J* = 11.3, 1H), 4.00 (m, 1H), 3.91 (m, 1H), 3.46 (dd, *J* = 7.4, 2.5, 1H), 3.41 (br s, 1H), 2.73 (br s, 1H), 2.27 (t, *J* = 6.8, 2H), 1.94 (m, 2H), 1.68 (m, 2H), 1.07 (d, *J* = 6.7, 3H), 0.92 (d, *J* = 6.8, 3H), 0.88 (d, *J* = 7.0, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 138.7, 134.7, 128.4, 127.6, 127.4, 117.8, 85.4, 73.9, 71.3, 68.2, 42.0, 39.8, 39.4, 30.5, 20.2, 19.6, 11.3; IR (thin film): 3384, 3067, 2960, 1641, 1069, 734 cm⁻¹; HRMS (CI+/NH₃) *m/z* calcd for C₁₉H₃₁O₃ (M+H)⁺ 307.2273, found 307.2273. Anal. Calcd for C₁₉H₃₀O₃: C, 74.47; H, 9.87. Found: C, 74.36; H, 9.84.

References.

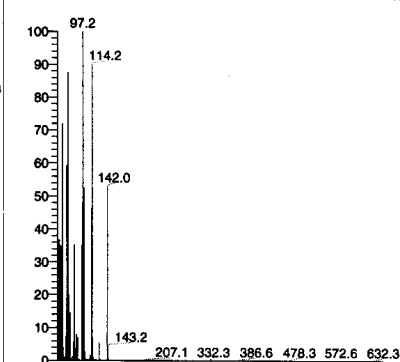
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- (5) Proof of stereochemistry was accomplished by chemical correlation with previously prepared 7-methyl-1-octene-4,6-diol. Bear, T. J.; Shaw, J. T.; Woerpel, K. A. *J. Org. Chem.* **2002**, *67*, 2056-2064.
- (6) Powell, S. A.; Tenenbaum, J. M.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 12648-12649.
- (7) Proof of stereochemistry was accomplished by chemical correlation with previously prepared (3R*,4R*,5R*,7S*)-3-benzyloxy-2,4-dimethyl-dec-9-ene-5,7-diol. Powell, S. A.; Tenenbaum, J. M.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 12648-12649.

B. GCMS and Spectral Data for Stereochemical Proofs

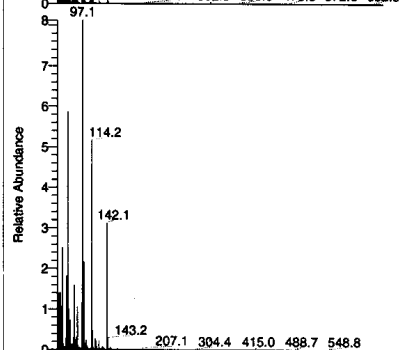


90 : 10 diastereoselectivity

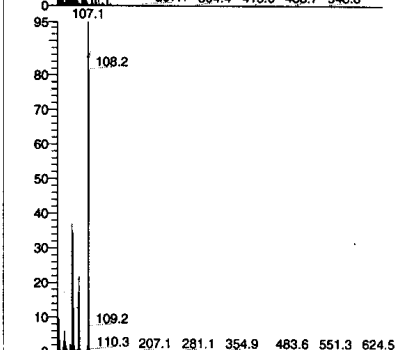
NL:
2.55E9
TIC MS
ICIS
jmt-v-
4304220064
_113324



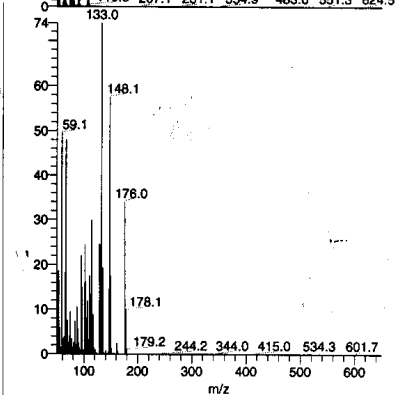
jmt-v-
4304220064_113324#110
RT: 4.41 AV: 1 NL: 2.25E8
T: (0,0) + c EI det=349.00
Full ms [50.00-650.00]



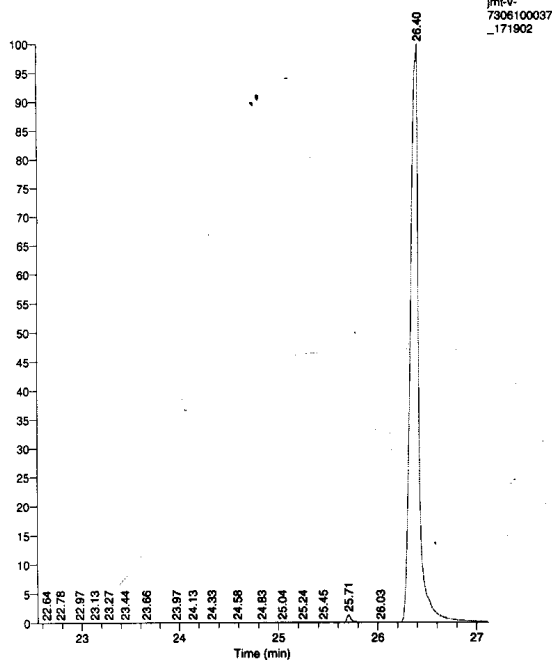
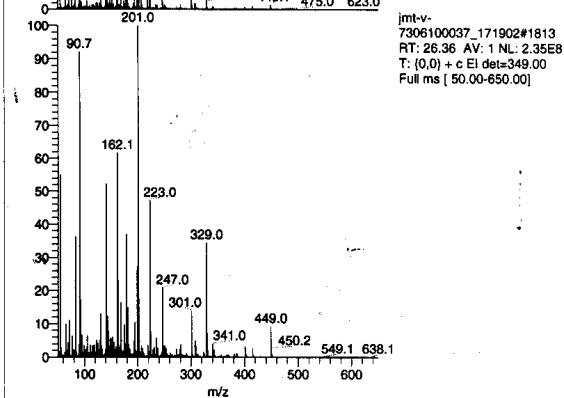
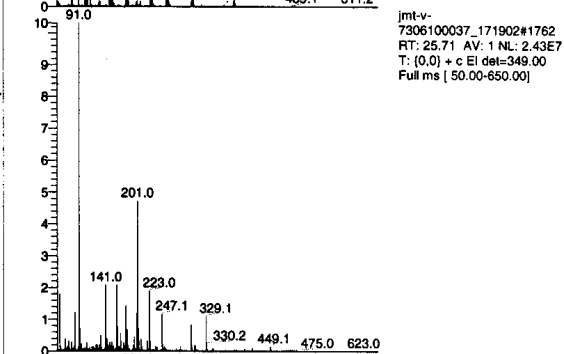
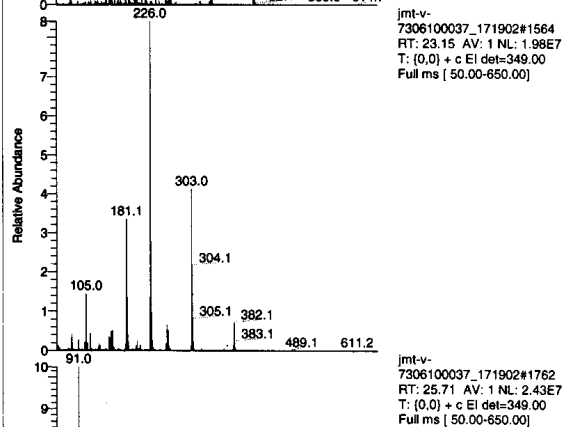
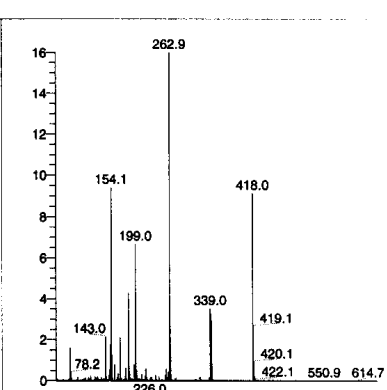
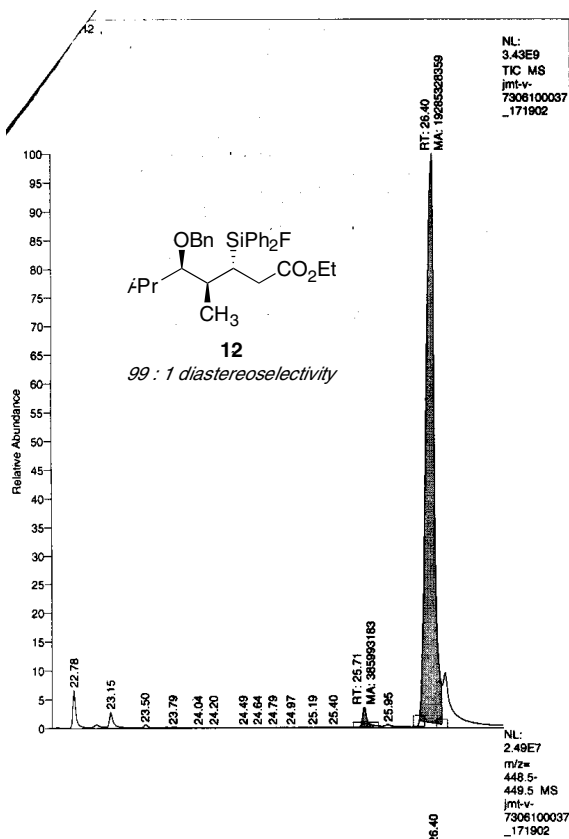
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4304220064_113324#184
RT: 5.37 AV: 1 NL: 1.82E7
T: (0,0) + c EI det=349.00
Full ms [50.00-650.00]

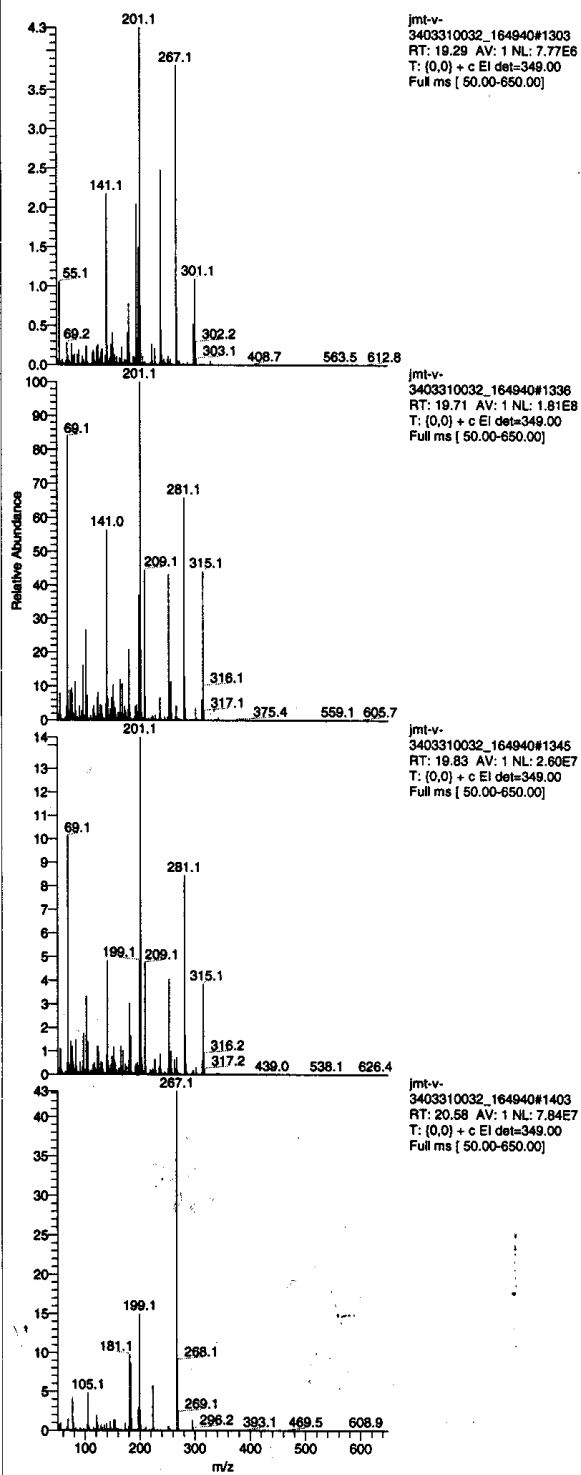
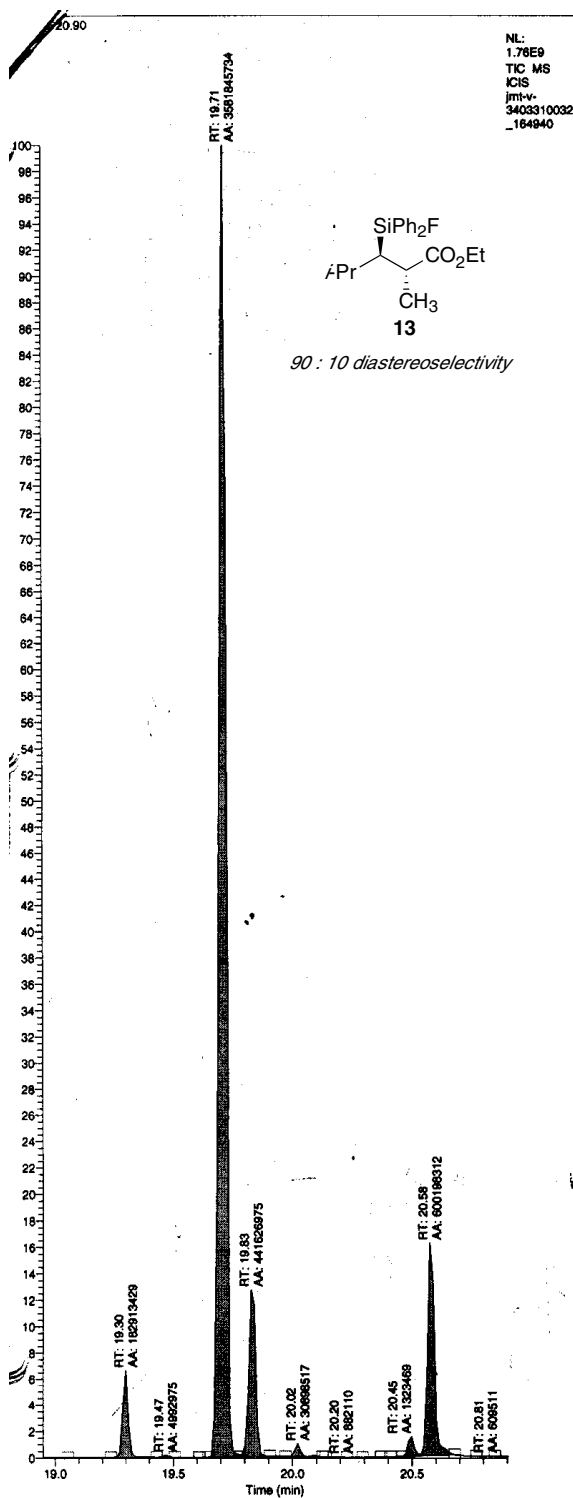


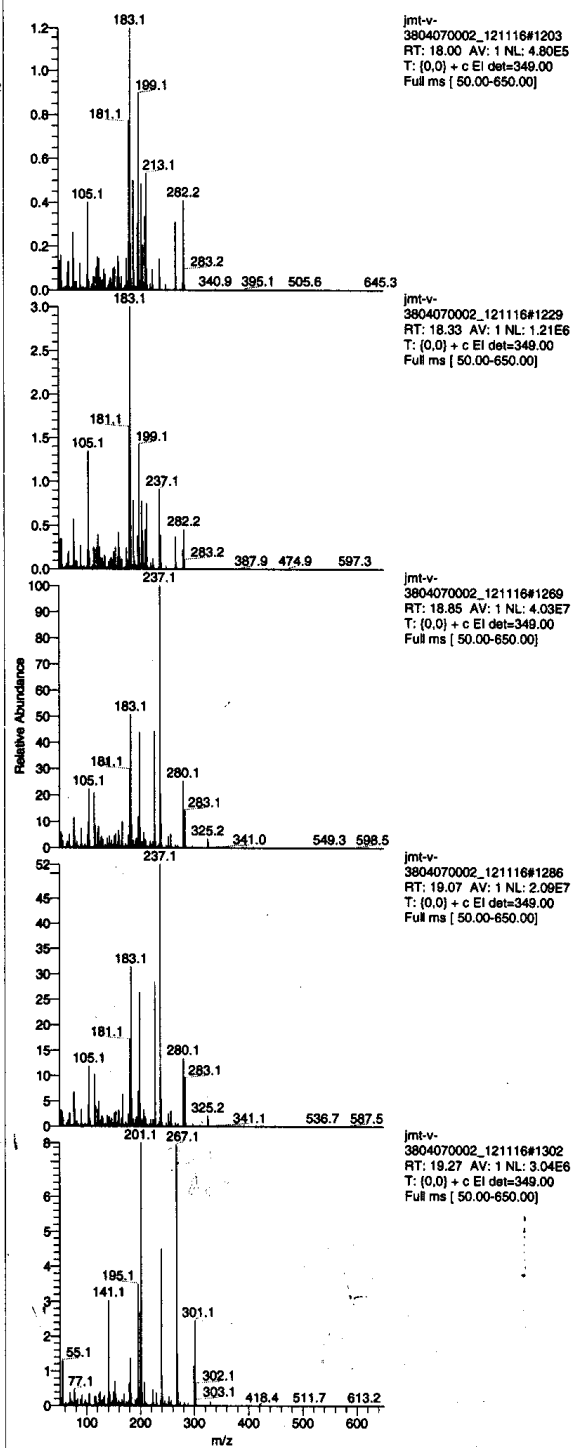
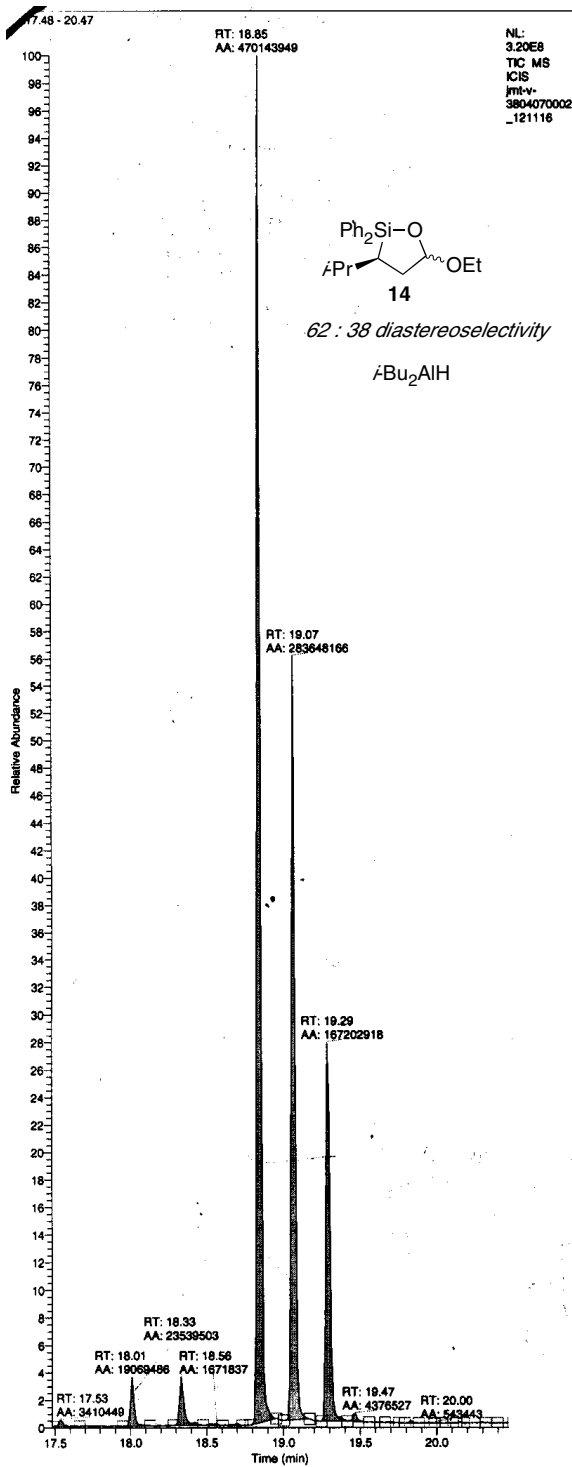
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4304220064_113324#238
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T: (0,0) + c EI det=349.00
Full ms [50.00-650.00]

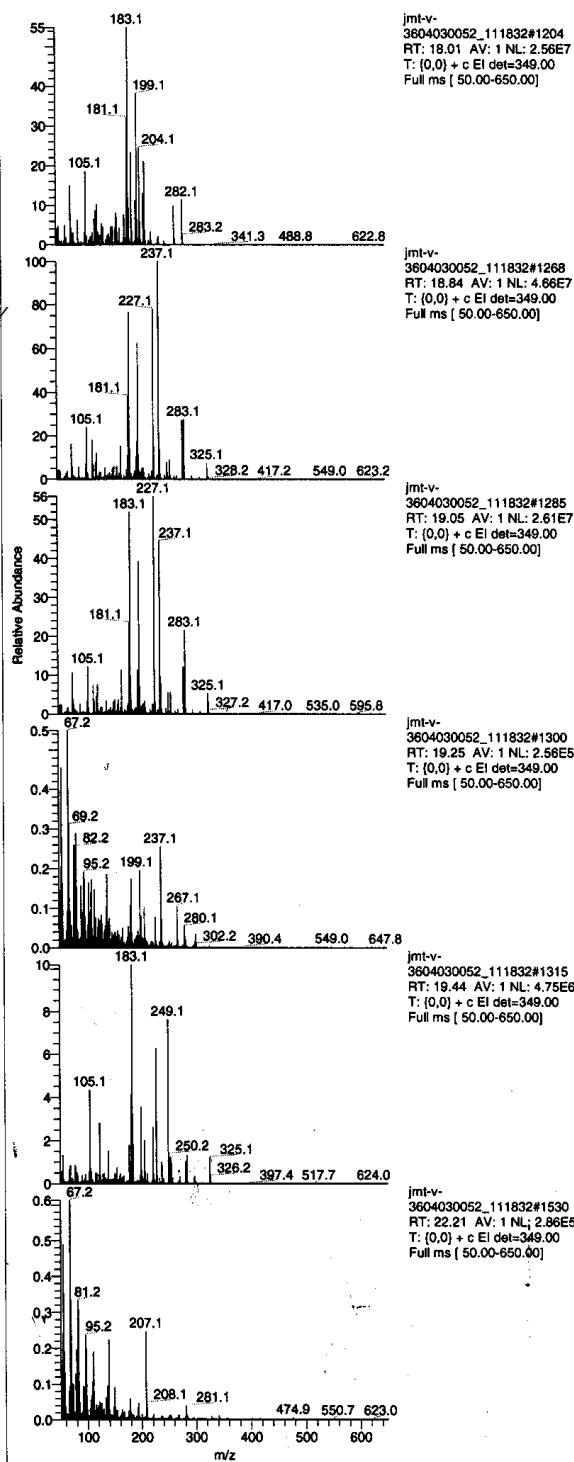
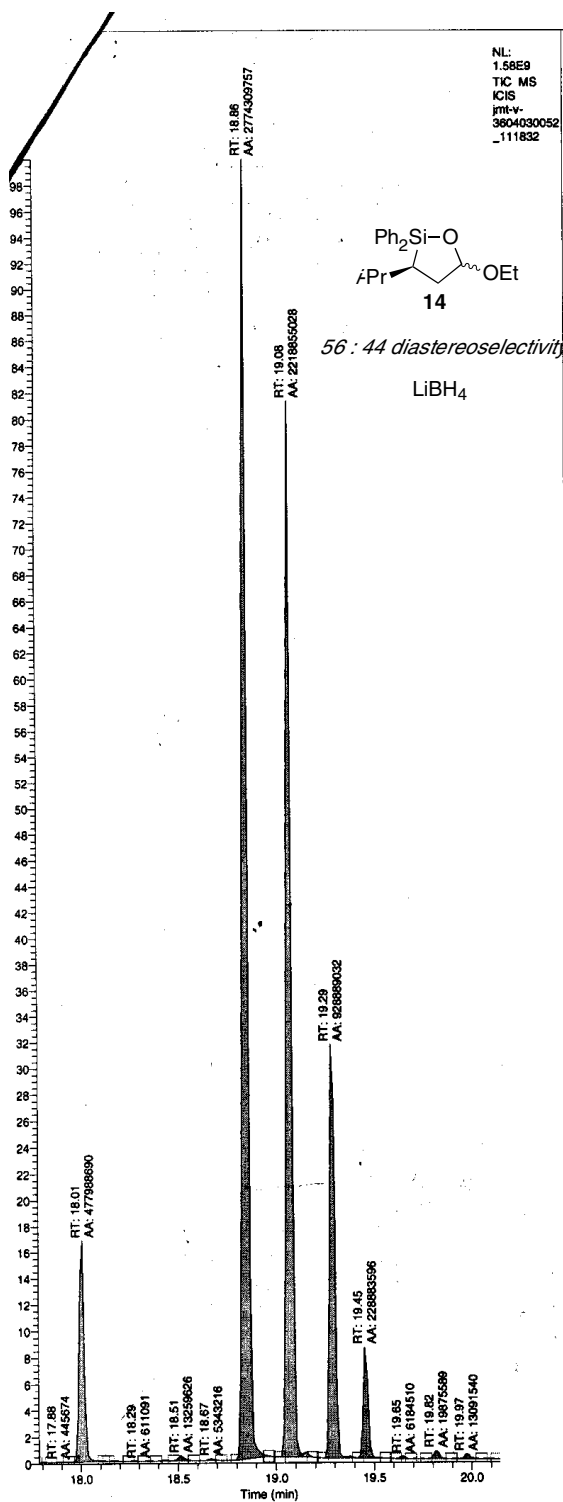


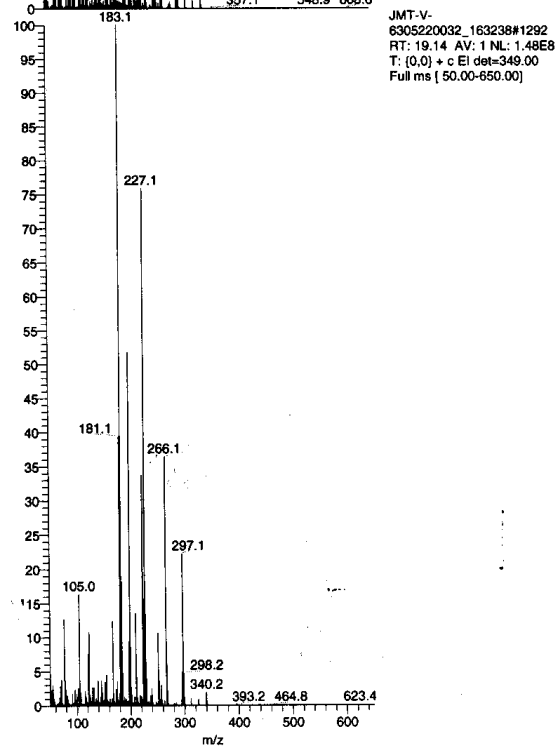
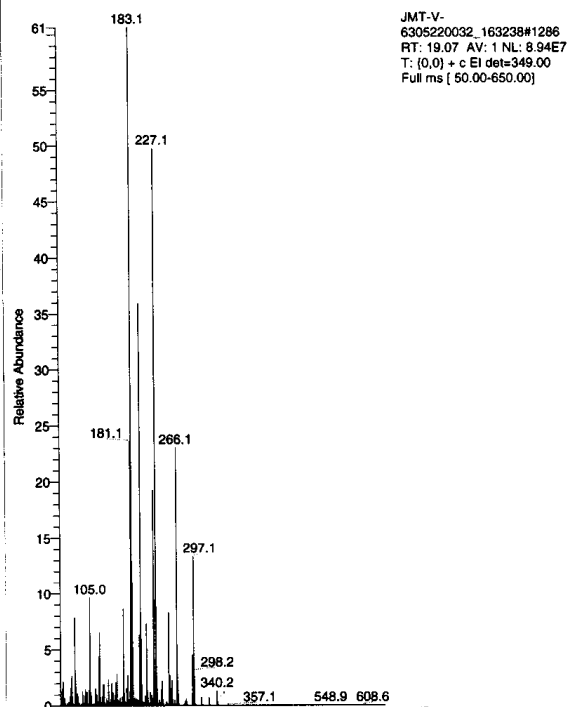
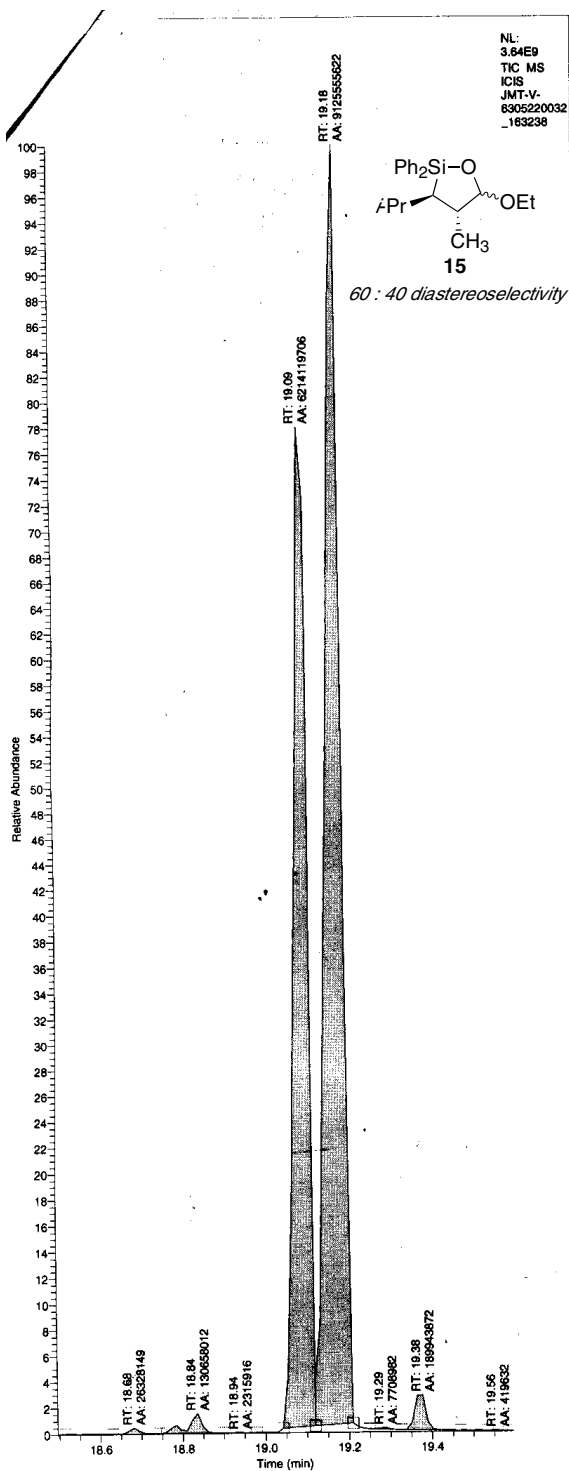
jmt-v-
4304220064_113324#274
RT: 6.53 AV: 1 NL: 1.66E8
T: (0,0) + c EI det=349.00
Full ms [50.00-650.00]

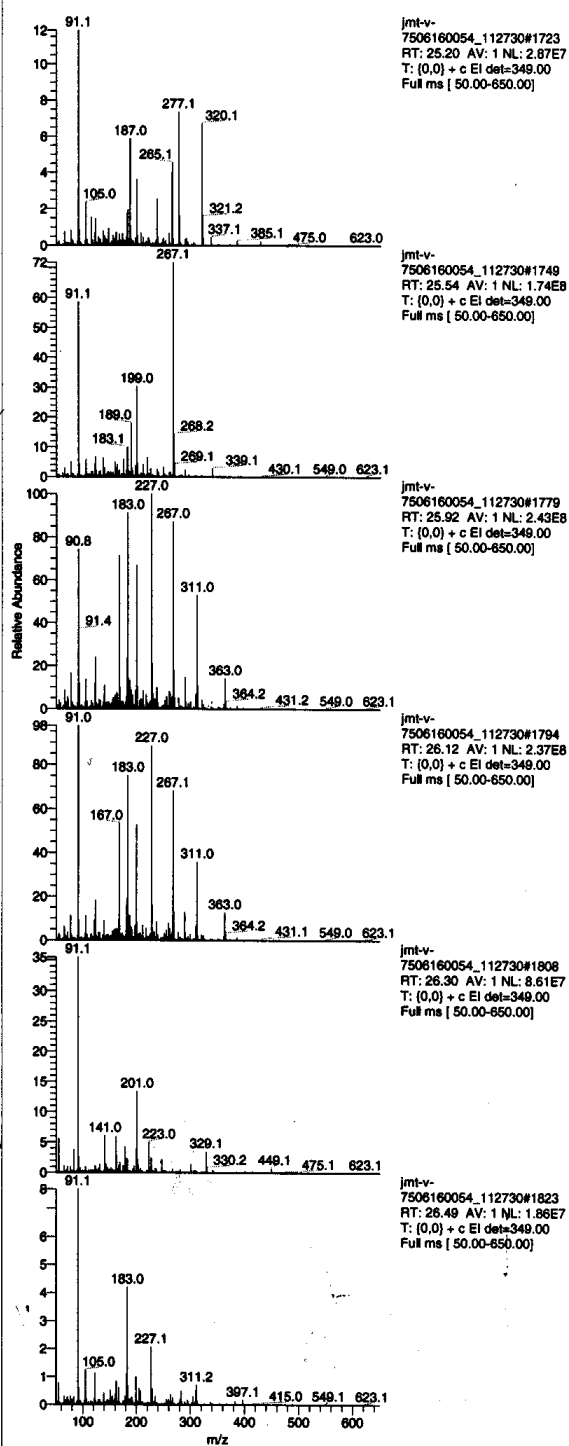


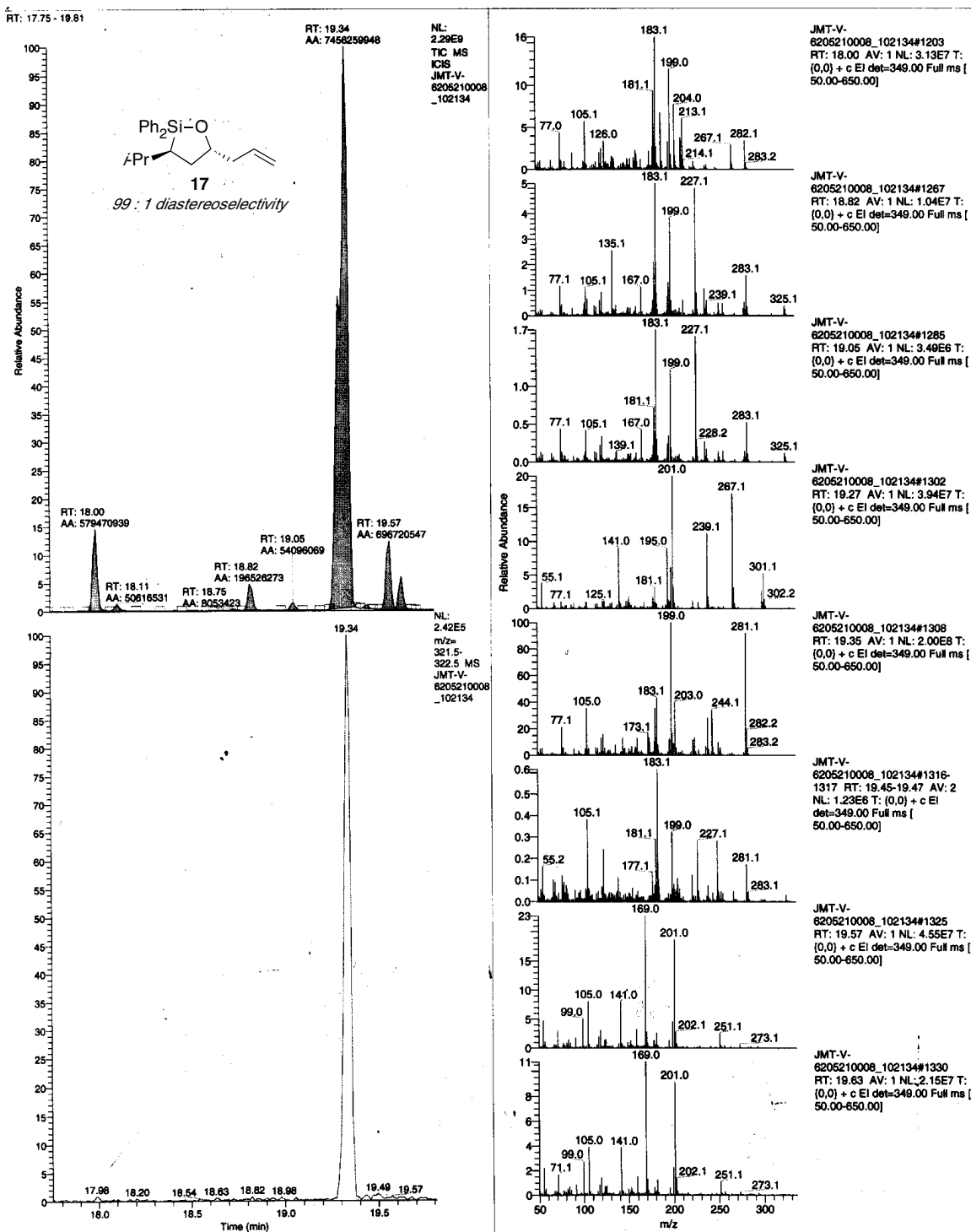


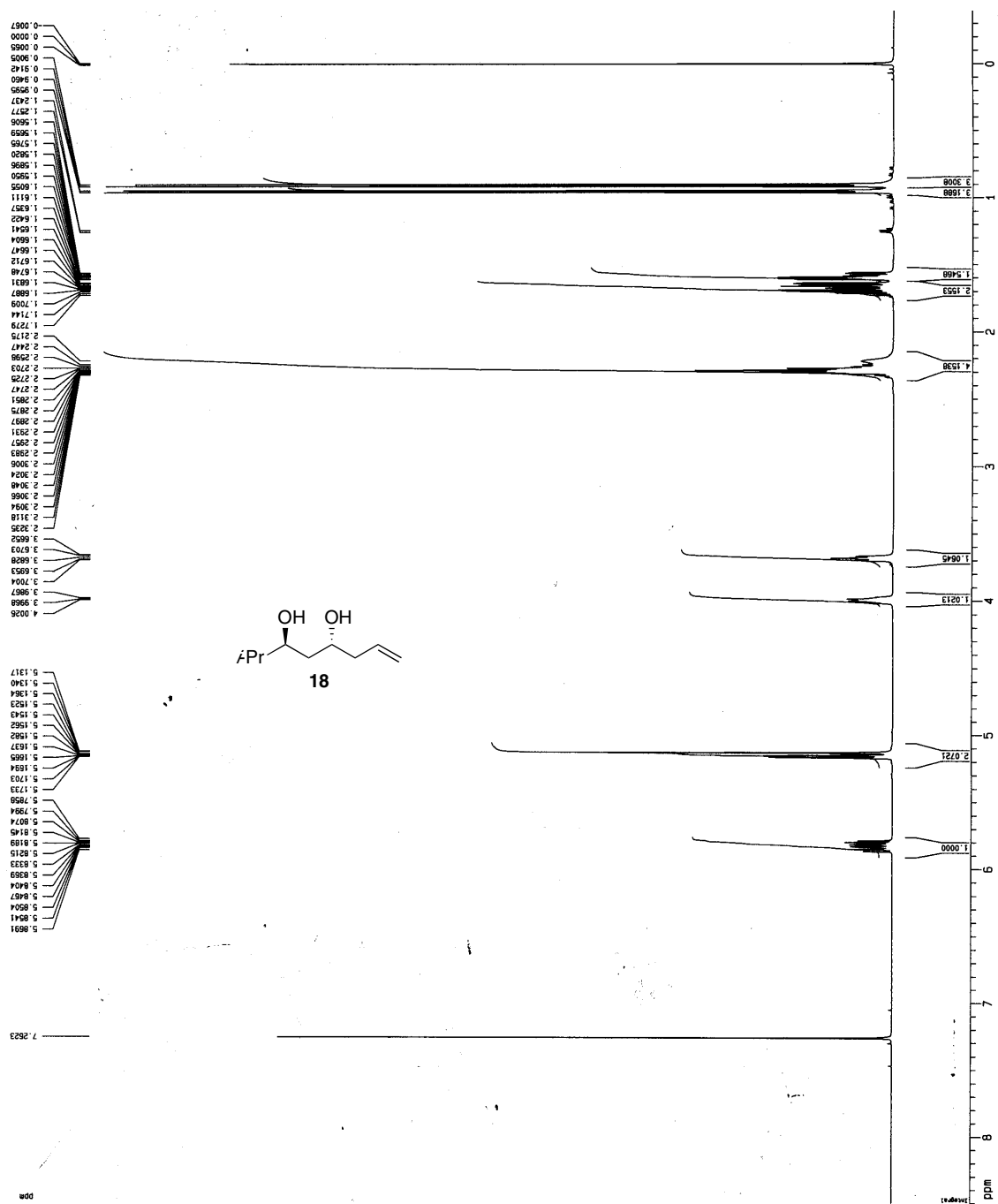


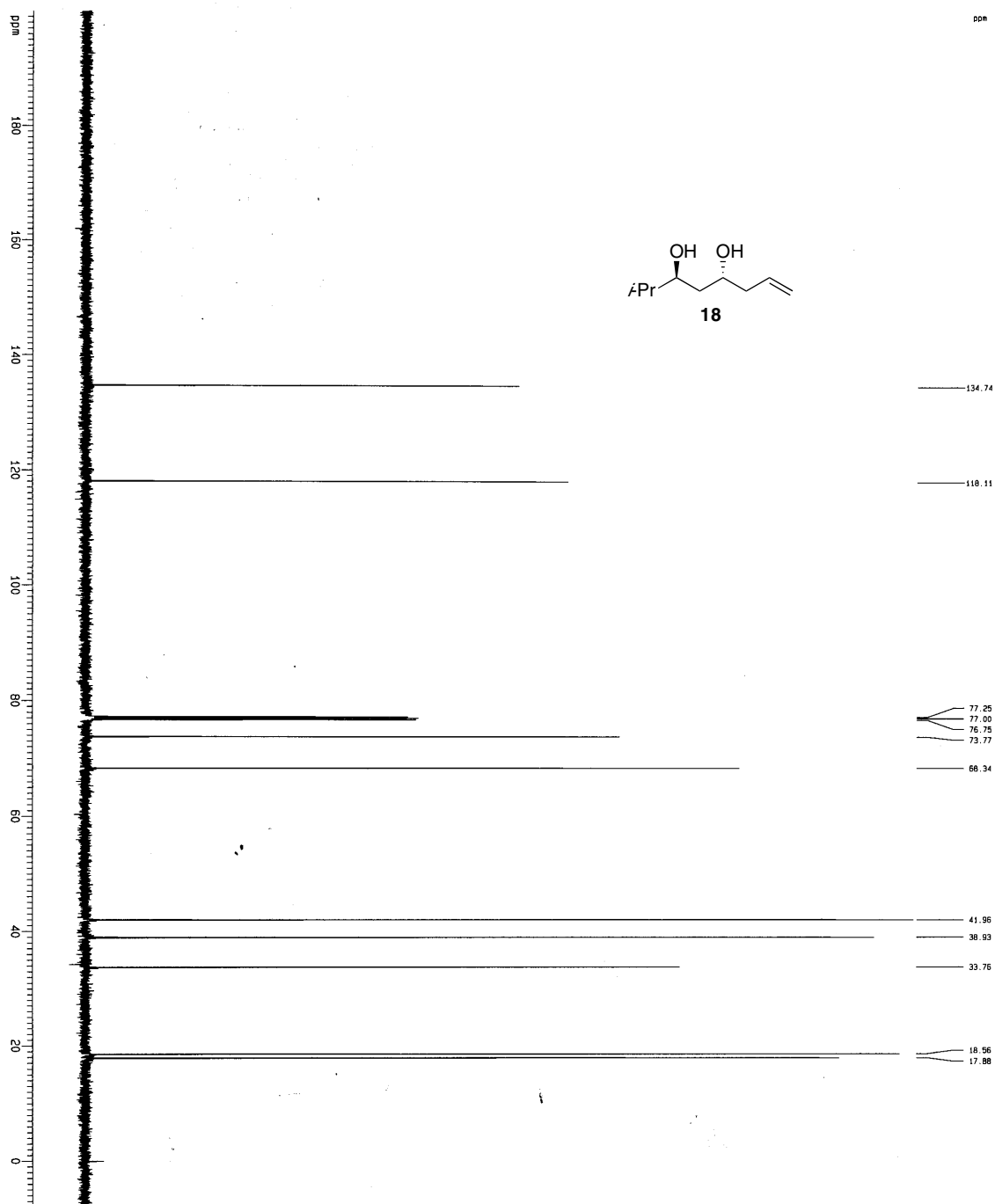


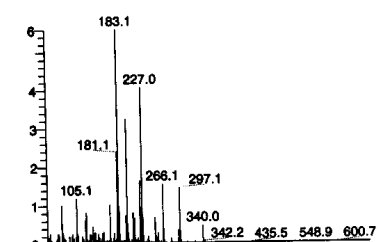
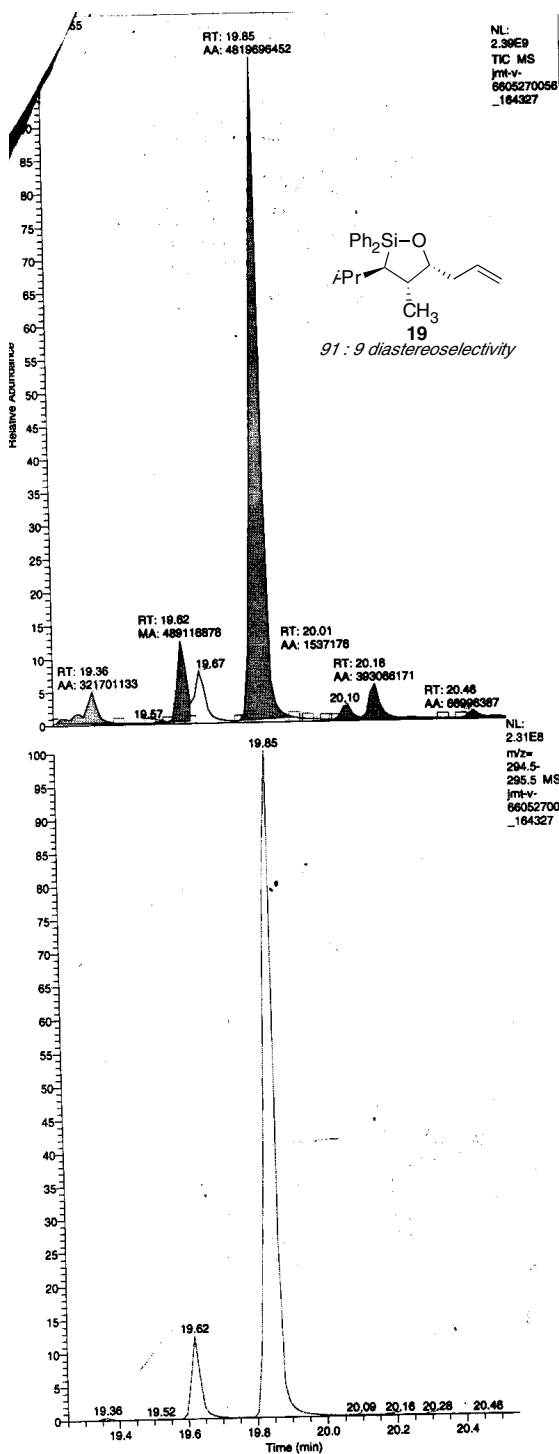




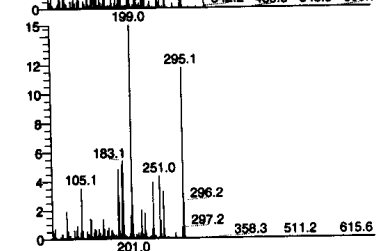




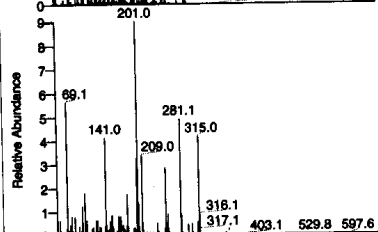




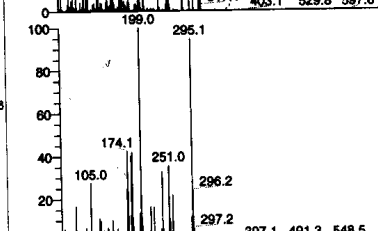
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T: (0,0) + c EI det=349.00
Full ms [50.00-650.00]



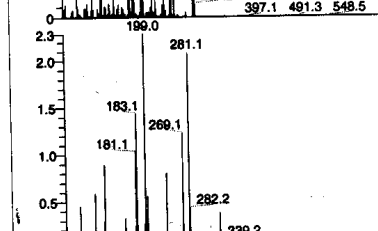
jmt-v-
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T: (0,0) + c EI det=349.00
Full ms [50.00-650.00]



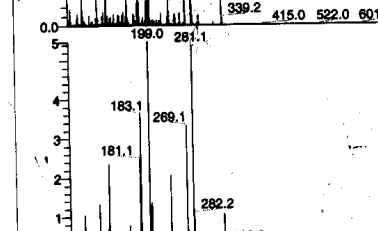
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Full ms [50.00-650.00]



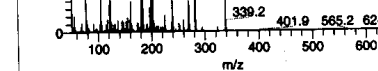
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RT: 19.85 AV: 1 NL: 2.43E8
T: (0,0) + c EI det=349.00
Full ms [50.00-650.00]



jmt-v-
6605270056_164327#1368
RT: 20.10 AV: 1 NL: 5.56E6
T: (0,0) + c EI det=349.00
Full ms [50.00-650.00]



jmt-v-
6605270056_164327#1372
RT: 20.18 AV: 1 NL: 1.33E7
T: (0,0) + c EI det=349.00
Full ms [50.00-650.00]



jmt-v-
6605270056_164327#1372
RT: 20.18 AV: 1 NL: 1.33E7
T: (0,0) + c EI det=349.00
Full ms [50.00-650.00]

