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

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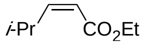
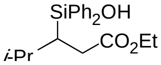
Experimental Section

General: ^{1}H 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 × 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 ˚C for 1 min then ramped 10 ˚C / min to 290 ˚C. Fused silica capillary columns (30 × 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 $BF_3•Et_2O$ 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.

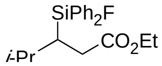
A. Experimental Data



Ethyl *Z*-4-methyl-pent-2-eneoate (10). To a cooled (–78 °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 °C) solution of ethyl (di-*o*-tolylphosphono)acetate[2] (10 g, 29 mmol) in 50 mL of THF. The reaction mixture was stirred for 15 min at –78 °C. A cooled (–78 °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 °C for 2.75 h, 30 mL of ammonium chloride (saturated aqueous) was added. After the reaction mixture was warmed to 22 °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 × 100 mL). The combined organic layers were washed with H_2O (3 × 200 mL) and brine (3 × 200 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 $C_8H_{14}O_2$ (M^+) 142.0994, found 142.0995.

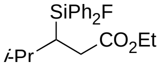


Ethyl 4-methyl-3-(diphenylsilanol)pentanoate (8). To a solution of chloro(diethylamino)diphenylsilane[3] (2.0 g, 6.9 mmol) in 28 mL of THF was added Li° wire (0.39 g, 56 mmol, 0.5 to 1.0% Na° content) cut into small pieces (<5 mm). The suspension was cooled to 0 °C and stirred vigorously for 3 h to give a solution of (diethylamino)diphenylsilyllithium **5**.[4] The cooled (0 °C) solution of the silyllithium was added to a cooled (–78 °C) solution of Me_2Zn (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 Et_2O) 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 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 purified by flash column chromatography (3:97 to 10:90 EtOAc/hexanes) to give the product as a white solid (1.5 g, 68%): ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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+/NH_3) m / z calcd for $C_{20}H_{25}O_3Si$ $(M\text{-}H)^+$ 341.1573, found 341.1563. Anal. Calcd for $C_{20}H_{26}O_3Si$: C, 70.13; H, 7.65. Found: C, 70.21; H, 7.64.

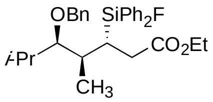


Ethyl 4-methyl-3-(fluorodiphenylsilyl)pentanoate (9). *One step formation from silanol **8***: To a cooled (–78 °C) solution of ester **8** (1.4 g, 4.1 mmol) in 27 mL of CH_2Cl_2 was added BF_3•OEt_2 (0.62 mL, 4.9 mmol). After the solution was stirred for 15 min at –78 °C, 10 mL of sodium bicarbonate (saturated aqueous) was added. The mixture was diluted with 50 mL of H_2O. 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*. 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)diphenylsilane[3] (2.0 g, 6.9 mmol) in 28 mL of THF was added Li° wire (0.38 g, 55 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 Me_2Zn (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 Et_2O) 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 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 46 mL of CH_2Cl_2 and cooled to –78 °C. BF_3•OEt_2 (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 H_2O. 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*. The resulting oil was purified by flash column chromatography

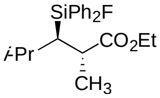
(0.5:99.5 to 1:99 EtOAc/hexanes) to give the product as a colorless oil (1.5 g, 68% over two steps): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (m, 2H), 7.64 (m, 2H), 7.41 (m, 6H), 3.94 (m, 2H), 2.46 (m, 2H), 2.04 (m, 2H), 1.14 (t, *J* = 7.1, 3H), 0.97 (d, *J* = 6.6, 3H), 0.92 (d, *J* = 6.6, 3H); ^{13}C NMR (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 $C_{20}H_{24}FO_2Si$ $(M-H)^+$ 343.1530, found 343.1524.



Ethyl 4-methyl-3-(fluorodiphenylsilyl)pentanoate (9). To a solution of chloro(diethylamino)diphenylsilane[3] (2.4 g, 8.3 mmol) in 30 mL of THF was added Li° wire (0.40 g, 58 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 Me_2Zn (3.9 mL, 7.8 mmol, 2.0 M in toluene) in 50 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 (0.56 mL, 0.78 mmol, 1.4 M in Et_2O) was added to a cooled (–78 °C) suspension of CuCN (0.032 g, 0.36 mmol) in 10 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 **10** (1.0 g, 7.0 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 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 °C. BF_3•OEt_2 (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 H_2O. 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*. 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): ^{1}H 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* = 6.5, 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), 133.0 (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+/NH_3) *m* / *z* calcd for $C_{20}H_{24}FO_2Si$ $(M-H)^+$ 343.1530, found 343.1523.

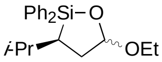


Ethyl (3*R,4*S**,5*R**)-5-benzyloxy-3-(fluorodiphenylsilyl)-4,6-dimethylheptanoate (12).** To a solution of chloro(diethylamino)diphenylsilane[3] (2.8 g, 9.6 mmol) in 36 mL of THF was added Li° wire (0.54 g, 78 mmol, 0.5 to 1.0% Na° content) cut into small pieces (<5 mm). The suspension was cooled to 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 Me_2Zn (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 Et_2O) 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 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 re-dissolved in 57 mL of CH_2Cl_2 and cooled to –78 °C. $BF_3{\bullet}OEt_2$ (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 H_2O. 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 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): ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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+/NH_3) *m* / *z* calcd for $C_{30}H_{37}O_3Si$ (M-F)$^+$ 473.2512, found 473.2494. Anal. Calcd for $C_{30}H_{37}FO_3Si$: C, 73.13; H, 7.57. Found: C, 72.97; H, 7.62.



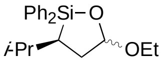
(2*S,3*R**)-Ethyl 2,4-dimethyl-3-(fluorodiphenylsilyl)pentanoate (13).** To a cooled (–78 °C) solution of *i*-Pr_2NH (0.36 mL, 2.6 mmol) in 2.5 mL of THF was added *n*-BuLi

(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, CH_3I (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 H_2O and 50 mL of MTBE. The organic layer was separated, and the aqueous layer was extracted with MTBE (3 × 50 mL). The combined organic layers were washed with H_2O (4 × 50 mL) and brine (4 × 50 mL). The organic layer was dried over Na_2SO_4, 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 CH_2Cl_2/hexanes) to give a single diastereomer of the product as a colorless oil (0.46 g, 65%): ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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+/NH_3) *m* / *z* calcd for $C_{21}H_{26}FO_2Si$ (M-H)$^+$ 357.1686, found 357.1679. Anal. Calcd for $C_{21}H_{27}FO_2Si$: C, 70.35; H, 7.59. Found: C, 70.39; H, 7.64.

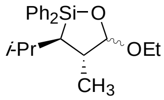


1-Oxa-3-(1-methylethyl)-5-ethoxy-2,2-(diphenyl)silacyclopentane (14). To a solution of β-fluorosilyl ester **9** (0.39 g, 1.1 mmol) and $LiBH_4$ (1.6 mL, 3.2 mmol, 2.0 M in THF) in 4.5 mL of Et_2O was added MeOH (0.13 mL, 3.2 mmol) dropwise. After 15 h at 22 °C, the solution was cooled to 0 °C, and 1 mL of ammonium chloride (saturated aqueous) was added dropwise. The solution was diluted with 50 mL of 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 × 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 $C_{20}H_{25}O_2Si$ $(M-H)^+$ 325.1624, found 325.1620. Anal. Calcd for $C_{20}H_{26}O_2Si$: C, 73.57; H, 8.03. Found: C, 73.68; H, 7.85.

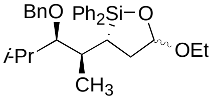


1-Oxa-3-(1-methylethyl)-5-ethoxy-2,2-(diphenyl)silacyclopentane (14). To a cooled (–78 °C) solution of β-fluorosilyl ester **9** (0.39 g, 1.1 mmol) in 9 mL of CH_2Cl_2 was added *i*-Bu_2AlH (0.73 mL, 1.1 mmol, 1.5 M in toluene). After 3 h at –78 °C, 1 mL of EtOH was added. After 2 h at 22 °C, the mixture 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+/NH_3) *m* / *z* calcd for $C_{20}H_{25}O_2Si$ $(M-H)^+$ 325.1624, found 325.1628. Anal. Calcd for $C_{20}H_{26}O_2Si$: C, 73.57; H, 8.03. Found: C, 73.73; H, 7.96.

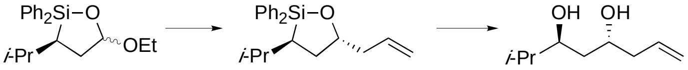


(3*R,4*S**)-1-Oxa-3-(1-methylethyl)-5-ethoxy-4-methyl-2,2-(diphenyl)silacyclopentane (15).** To a solution of β-fluorosilyl ester **13** (0.55 g, 1.5 mmol) and $LiBH_4$ (2.4 mL, 4.8 mmol, 2.0 M in THF) in 6.5 mL of Et_2O was added MeOH (0.19 mL, 4.8 mmol) dropwise. After 15 h at 22 °C, the solution was 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 × 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: ^{1}H 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);

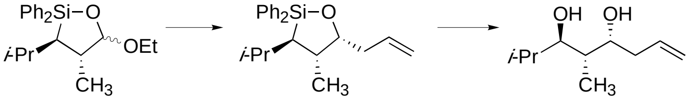
^{13}C NMR (125 MHz, $CDCl_3$) δ 135.8, 135.7, 135.0, 134.8, 130.1, 130.0, 129.9, 127.9, 127.7, 127.6, 108.4, 104.6, 64.3, 62.5, 42.9, 42.0, 40.3, 36.4, 27.6, 26.9, 24.6, 24.3, 22.0, 21.3, 18.3, 15.3, 15.2, 14.8; IR (thin film): 3050, 2959, 1429, 1116, 982, 701 cm^{-1}; HRMS (CI+/NH_3) *m* / *z* calcd for $C_{21}H_{27}O_2Si$ $(M-H)^+$ 339.1780, found 339.1772. Anal. Calcd for $C_{21}H_{28}O_2Si$: C, 74.07; H, 8.29. Found: C, 74.35; H, 8.36.



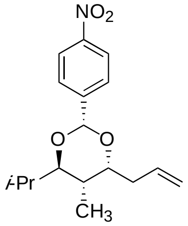
(3*R)-1-Oxa-3-[(1*S**,2*R**)-2-benzyloxy-1,3-dimethylbutyl]-5-ethoxy-2,2-(diphenyl)silacyclopentane (16).** To a solution of β-fluorosilyl ester **12** (1.0 g, 2.0 mmol) and $LiBH_4$ (3.0 mL, 6.0 mmol, 2.0 M in THF) in 8 mL of Et_2O was added MeOH (0.24 mL, 6.0 mmol) dropwise. After 15 h at 22 °C, the 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 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: ^{1}H 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 $C_{30}H_{37}O_3Si$ (M-H)$^+$ 473.2512, found 473.2494.



7-Methyl-1-octene-4,6-diol (18).[5] To a cooled (–78 °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 BF_3•OEt_2 (0.20 mL, 1.6 mmol). After the reaction mixture was warmed to 0 °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 × 50 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 °C, solid $Na_2S_2O_3$ (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 × 25 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): ^{1}H 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 $C_9H_{19}O_2$ (M+H)$^+$ 159.1385, found 159.1388.

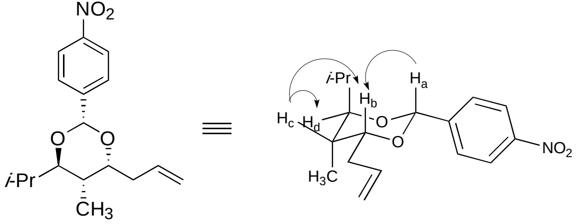


(4*R,5*S**,6*R**)-5,7-Dimethyl-1-octene-4,6-diol (20).** To a cooled (–78 °C) solution of acetal **15** (0.45 g, 1.3 mmol) and allyltrimethylsilane (0.44 mL, 2.8 mmol) in 45 mL of CH_2Cl_2 was added BF_3•OEt_2 (0.18 mL, 1.4 mmol). After the reaction mixture was warmed to 0 °C for 3 h, 10 mL of sodium 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 × 50 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 purifed 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 °C, solid $Na_2S_2O_3$ (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 × 25 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%): ^{1}H 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+/NH_3) *m* / *z* calcd for $C_{10}H_{21}O_2$ $(M+H)^+$ 173.1541, found 173.1545.



(2*R,4*R**,5*S**,6*R**)-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 Et_3N 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%): ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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+/NH_3) *m* / *z* calcd for $C_{17}H_{22}NO_4$ $(M-H)^+$ 304.1549, found 304.1550. Anal. Calcd for $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59. Found: C, 67.00; H, 7.71.

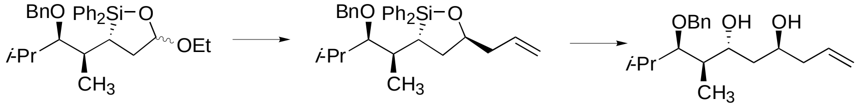
Proof of Stereochemistry by DPFGSE-NOE data:



(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 $SnCl_4$ (2.1 mL, 2.1 mmol, 1.0 M in CH_2Cl_2). 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 CH_2Cl_2. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, 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), $KHCO_3$ (0.50 g, 5.0 mmol), and H_2O_2 (4.3 mL, 42 mmol, 30 % by weight in H_2O). The reaction mixture was heated to reflux for 5 h. After the mixture was cooled to 22 °C, solid $Na_2S_2O_3$ (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 Et_2O (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): ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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+/NH_3) *m* / *z* calcd for $C_{19}H_{31}O_3$ $(M+H)^+$ 307.2273, found 307.2273. Anal. Calcd for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87. Found: C, 74.36; H, 9.84.

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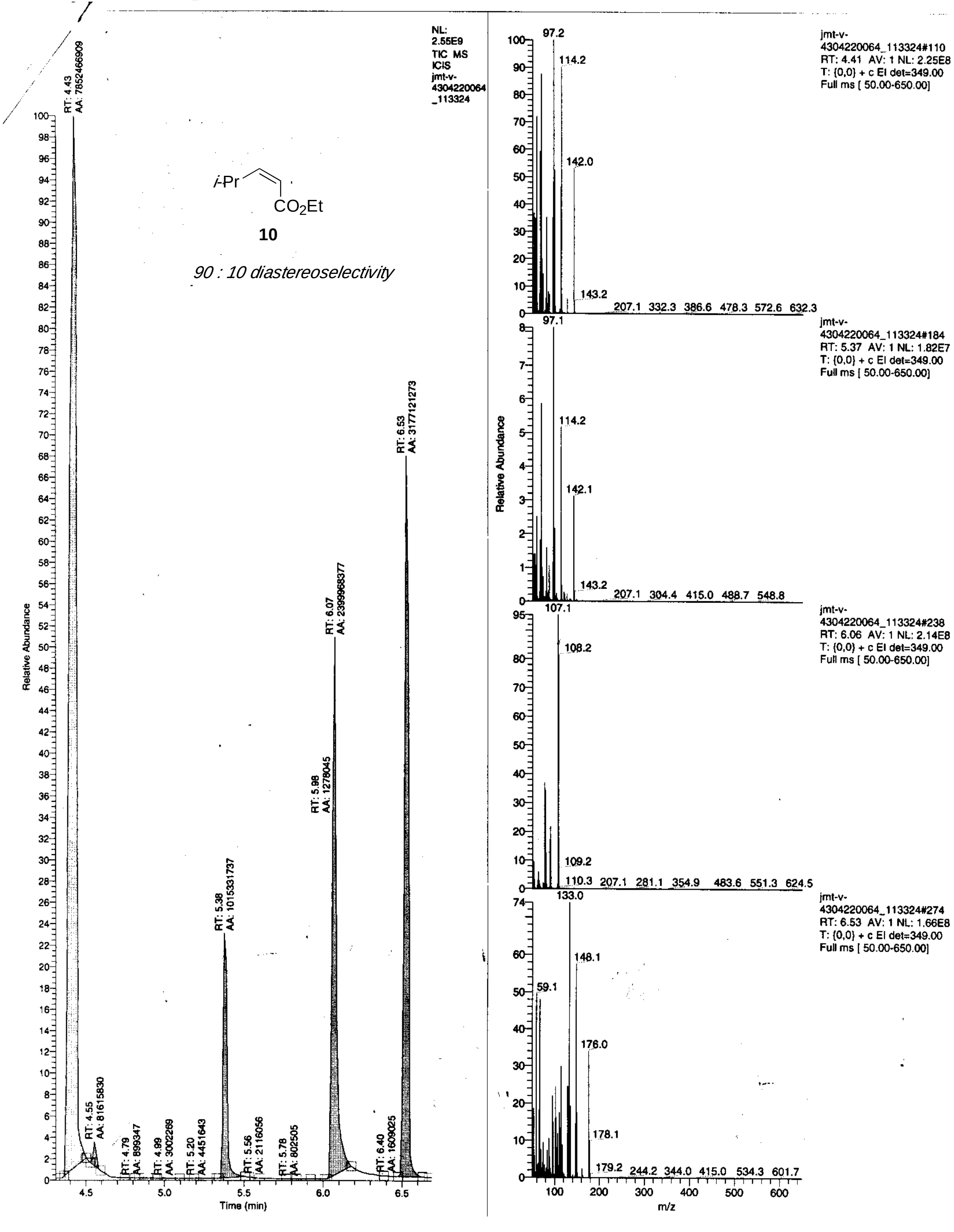
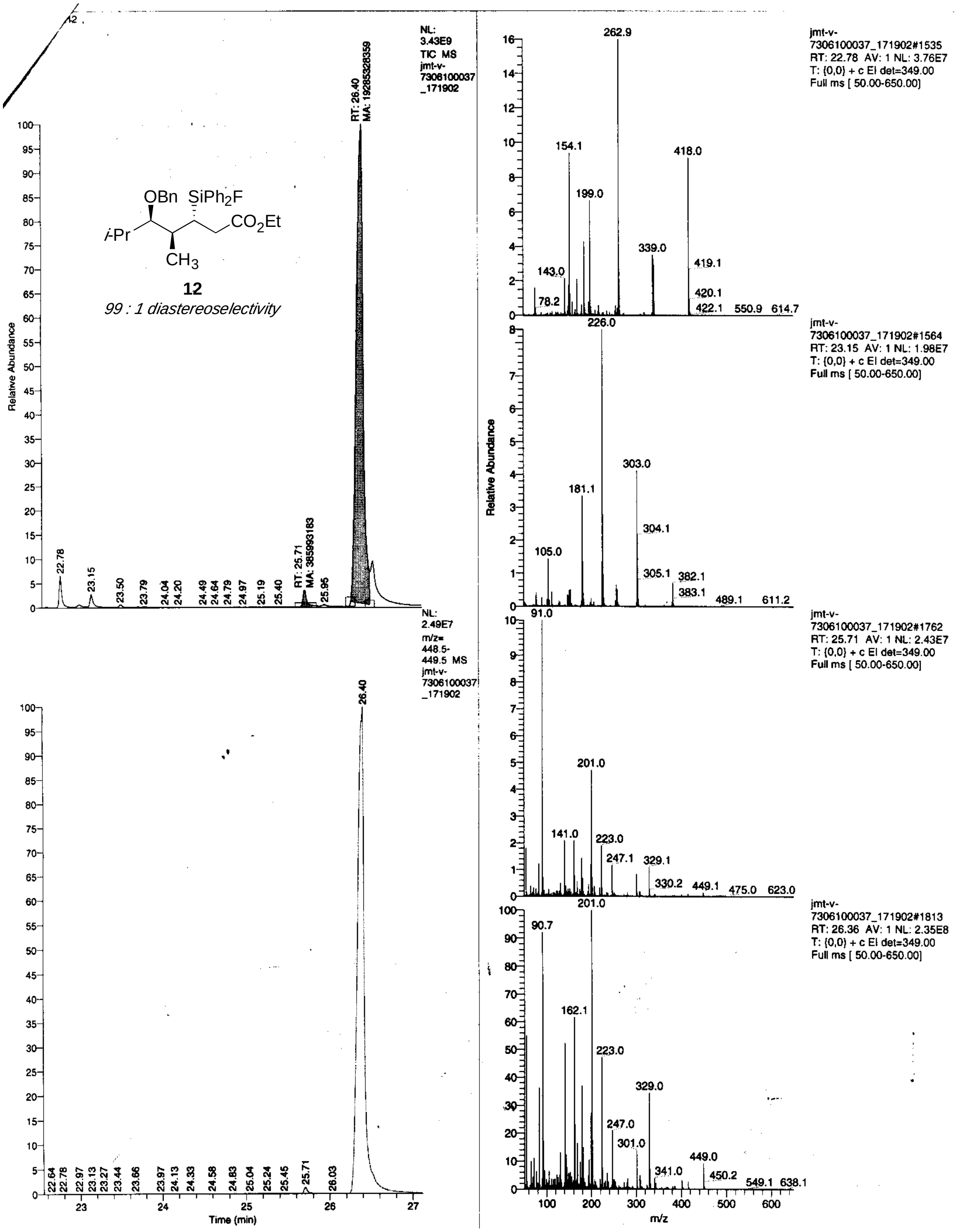
(7) Proof of stereochemistry was accomplished by chemical correlation with previously prepared (3R*,4R*,5R*,7S*)-3-benzyloxy-2,4-dimethyl-dec-9-ene-5,7-diol. Powell, S. A.; Tenenbaum, J. M.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 12648-12649.

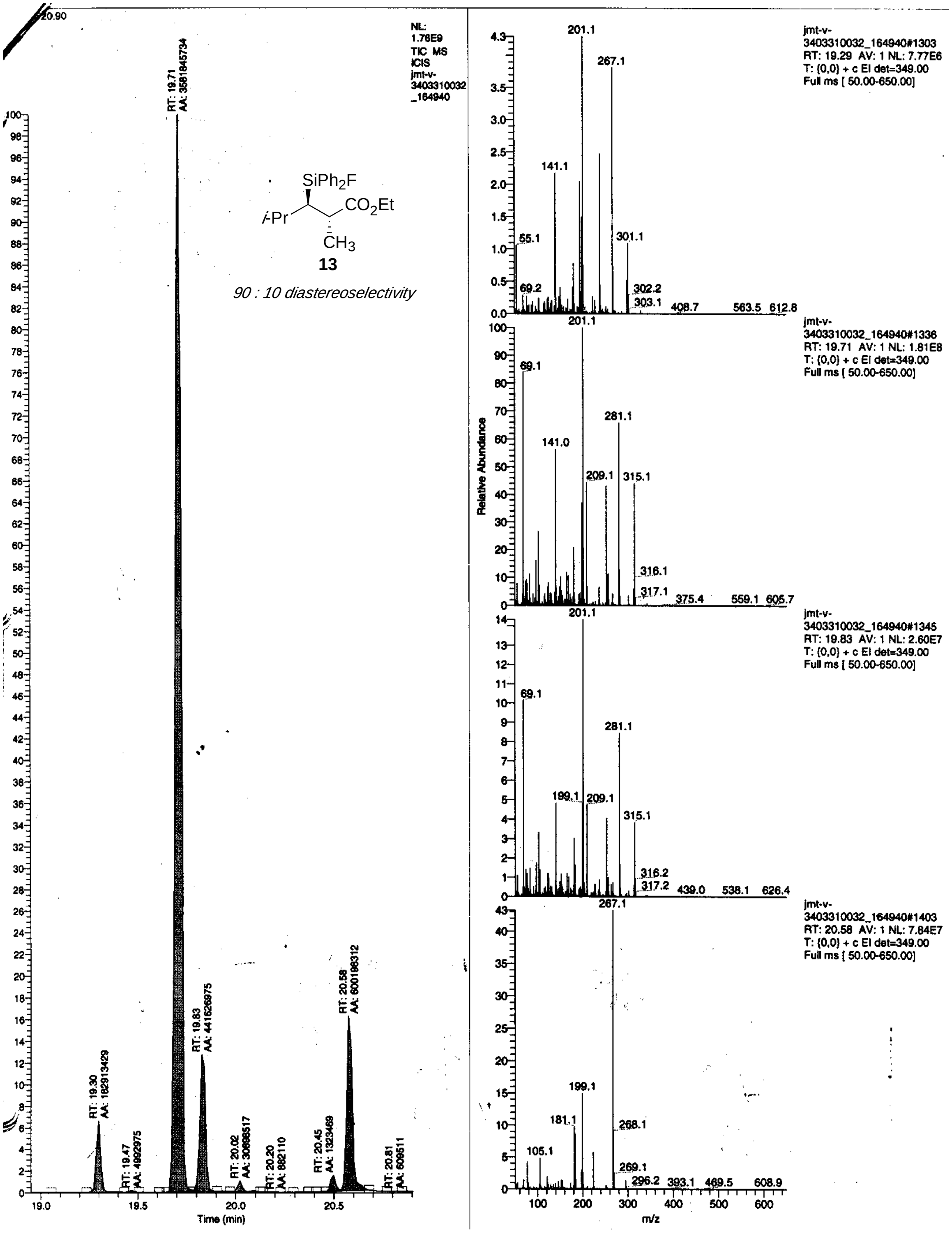
B. GCMS and Spectral Data for Stereochemical Proofs





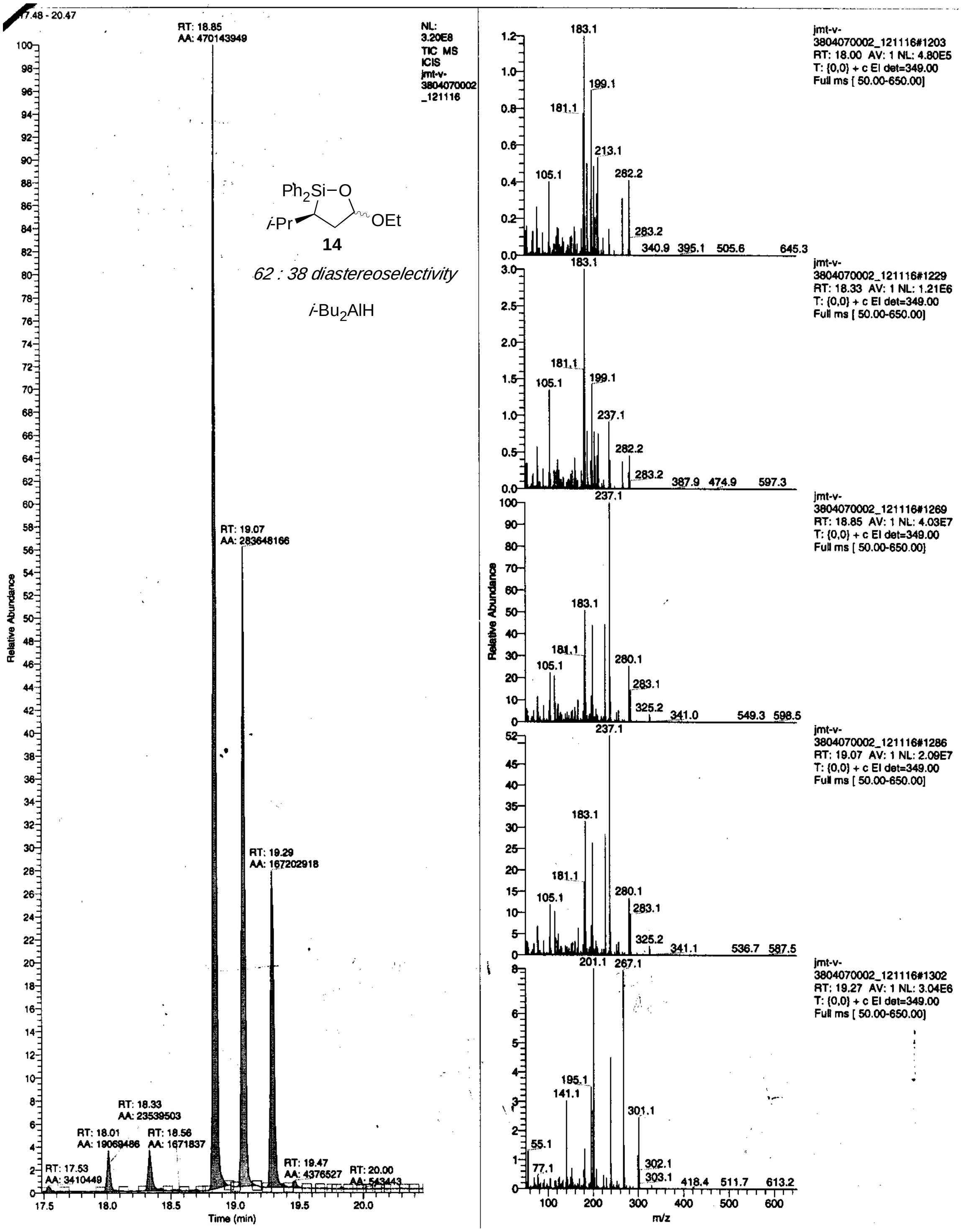
12

99 : 1 diastereoselectivity



13

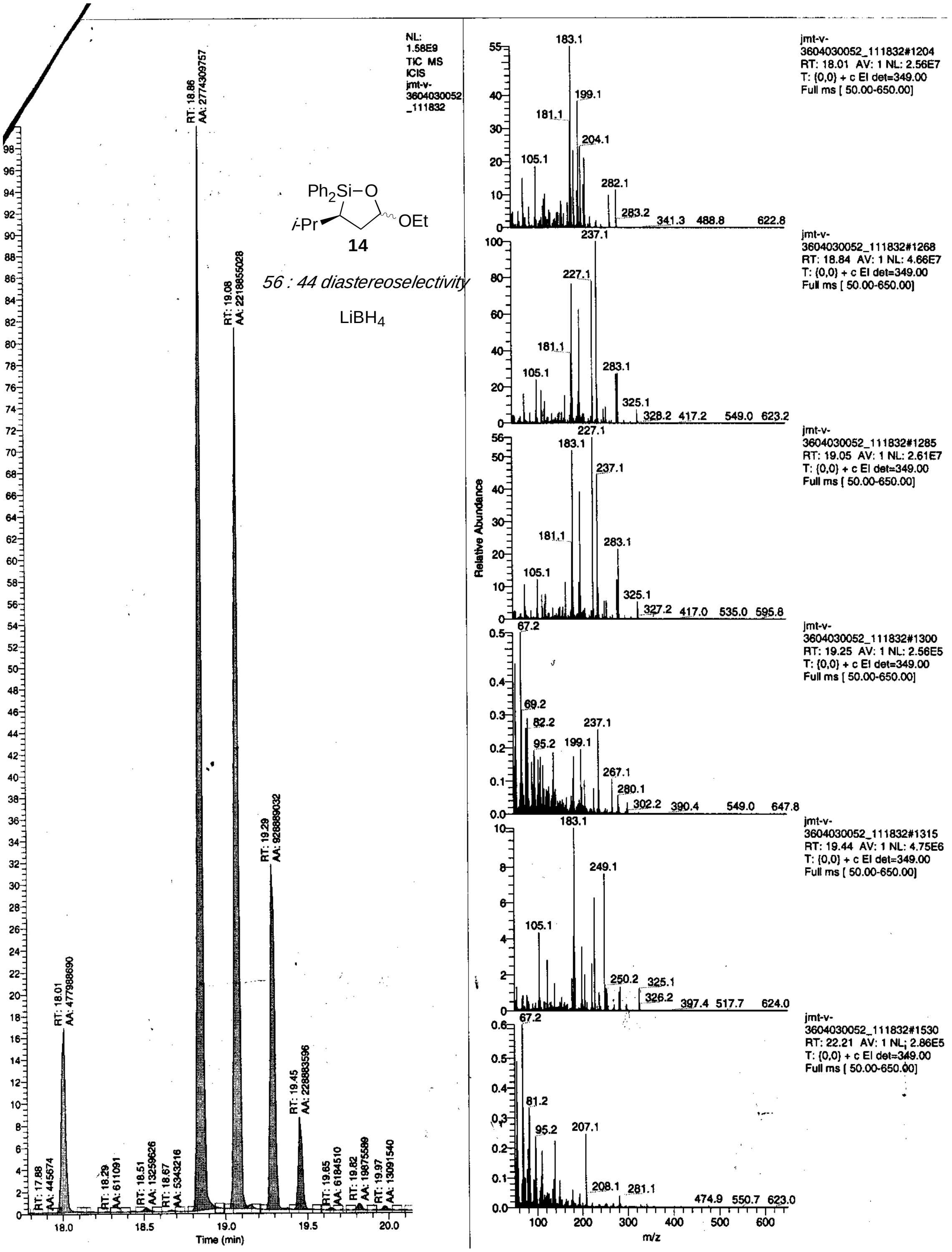
90 : 10 diastereoselectivity

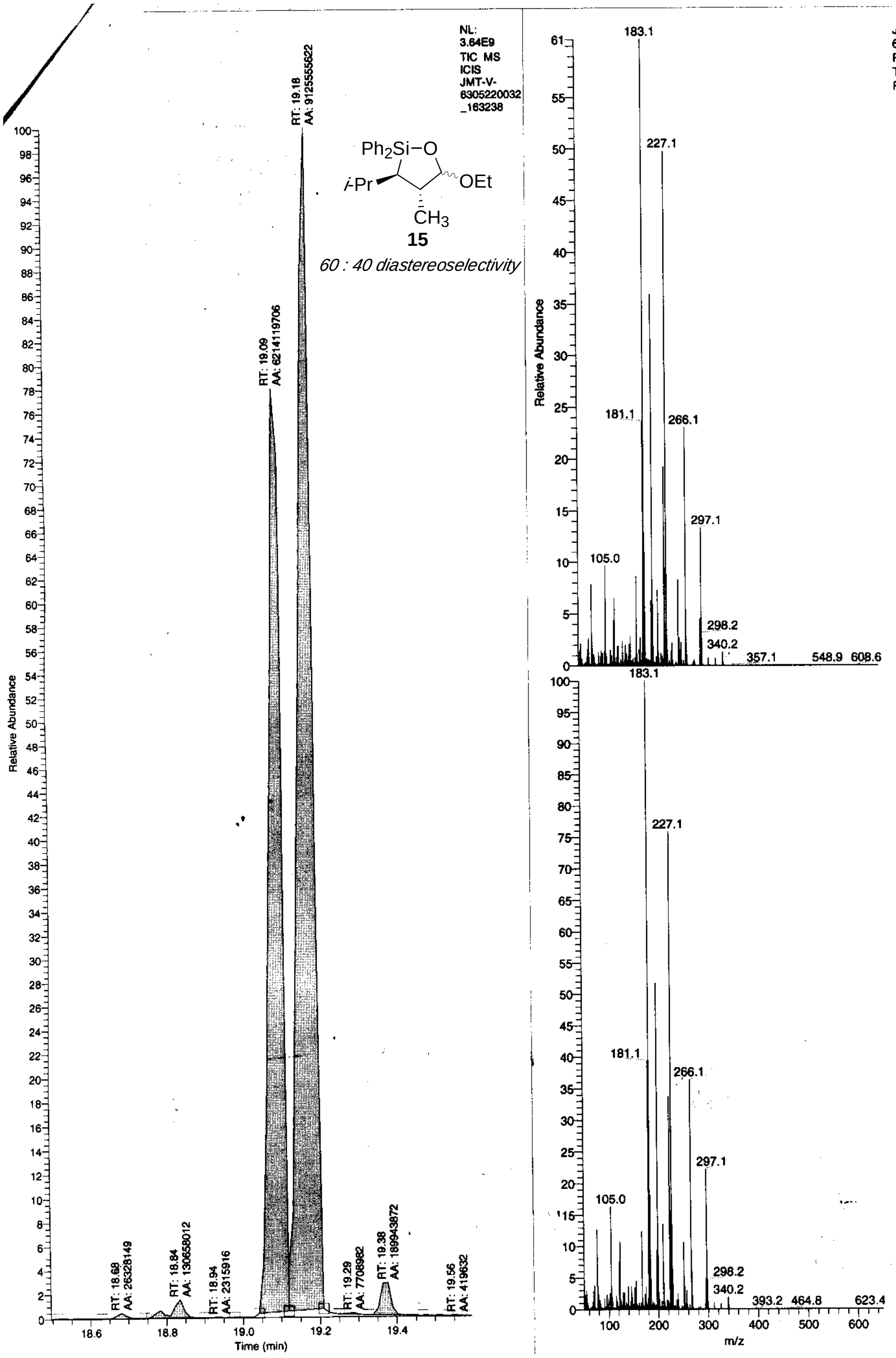


14

62 : 38 diastereoselectivity

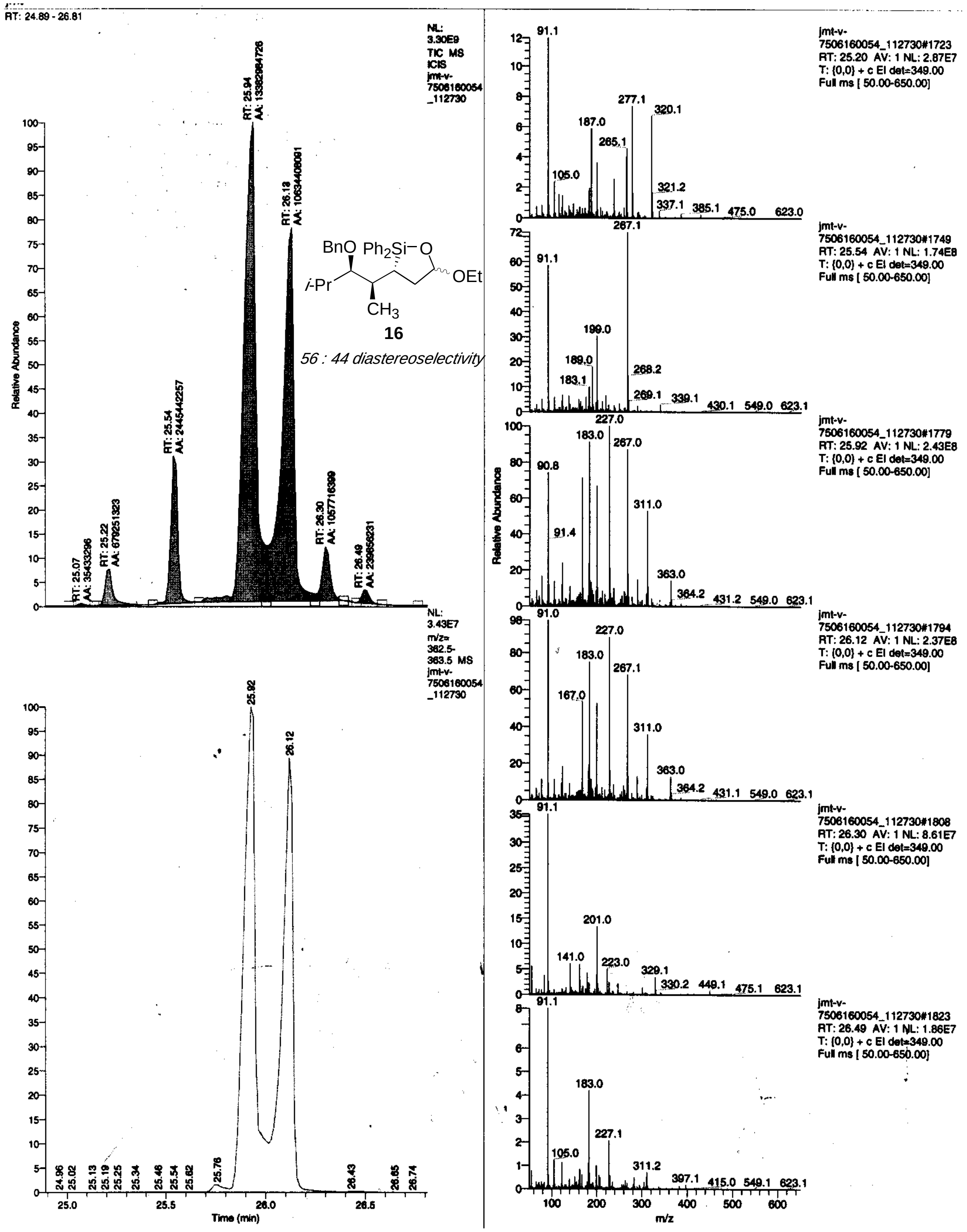
i-Bu_2AlH


NL: 1.58E9
TIC MS
ICIS
jmt-v-3604030052_111832
Ph2Si–O
i-Pr
OEt
14
56 : 44 diastereoselectivity
LiBH4
RT: 17.88 AA: 445674
RT: 18.01 AA: 477988690
RT: 18.29 AA: 611091
RT: 18.51 AA: 13259626
RT: 18.67 AA: 5343216
RT: 18.86 AA: 2774309757
RT: 19.08 AA: 2218855028
RT: 19.29 AA: 928889032
RT: 19.45 AA: 228883596
RT: 19.65 AA: 6184510
RT: 19.82 AA: 19875589
RT: 19.97 AA: 13091540
Time (min)
18.0
18.5
19.0
19.5
20.0
Relative Abundance
m/z
jmt-v-3604030052_111832#1204
RT: 18.01 AV: 1 NL: 2.56E7
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]
183.1
199.1
181.1
204.1
105.1
282.1
283.2
341.3
488.8
622.8
jmt-v-3604030052_111832#1268
RT: 18.84 AV: 1 NL: 4.66E7
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]
237.1
227.1
181.1
105.1
283.1
325.1
328.2
417.2
549.0
623.2
jmt-v-3604030052_111832#1285
RT: 19.05 AV: 1 NL: 2.61E7
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]
227.1
183.1
237.1
181.1
283.1
105.1
325.1
327.2
417.0
535.0
595.8
jmt-v-3604030052_111832#1300
RT: 19.25 AV: 1 NL: 2.56E5
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]
67.2
69.2
82.2
237.1
95.2
199.1
267.1
280.1
302.2
390.4
549.0
647.8
jmt-v-3604030052_111832#1315
RT: 19.44 AV: 1 NL: 4.75E6
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]
183.1
249.1
105.1
250.2
325.1
326.2
397.4
517.7
624.0
jmt-v-3604030052_111832#1530
RT: 22.21 AV: 1 NL: 2.86E5
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]
67.2
81.2
95.2
207.1
208.1
281.1
474.9
550.7
623.0
100
200
300
400
500
600



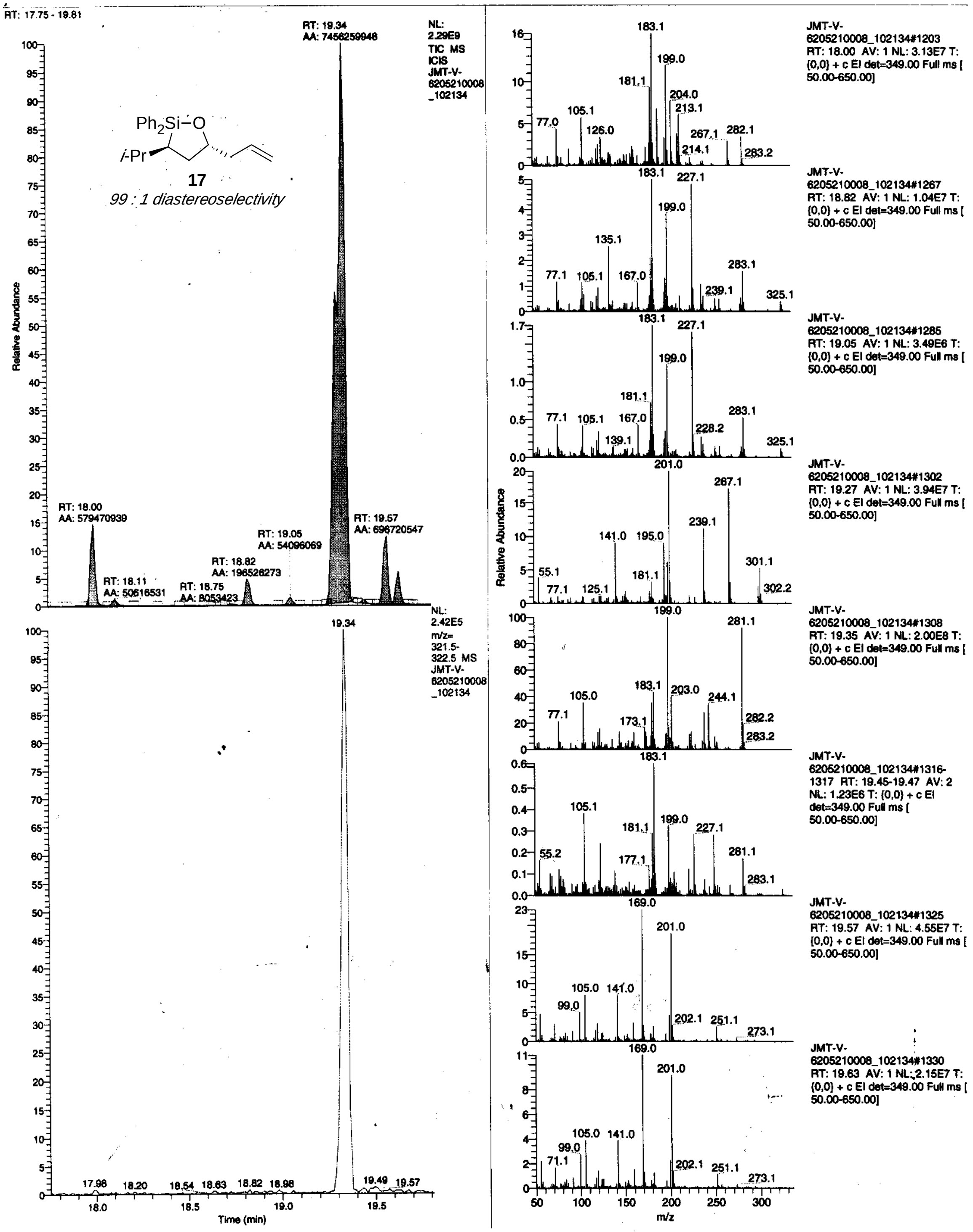
15

60 : 40 diastereoselectivity



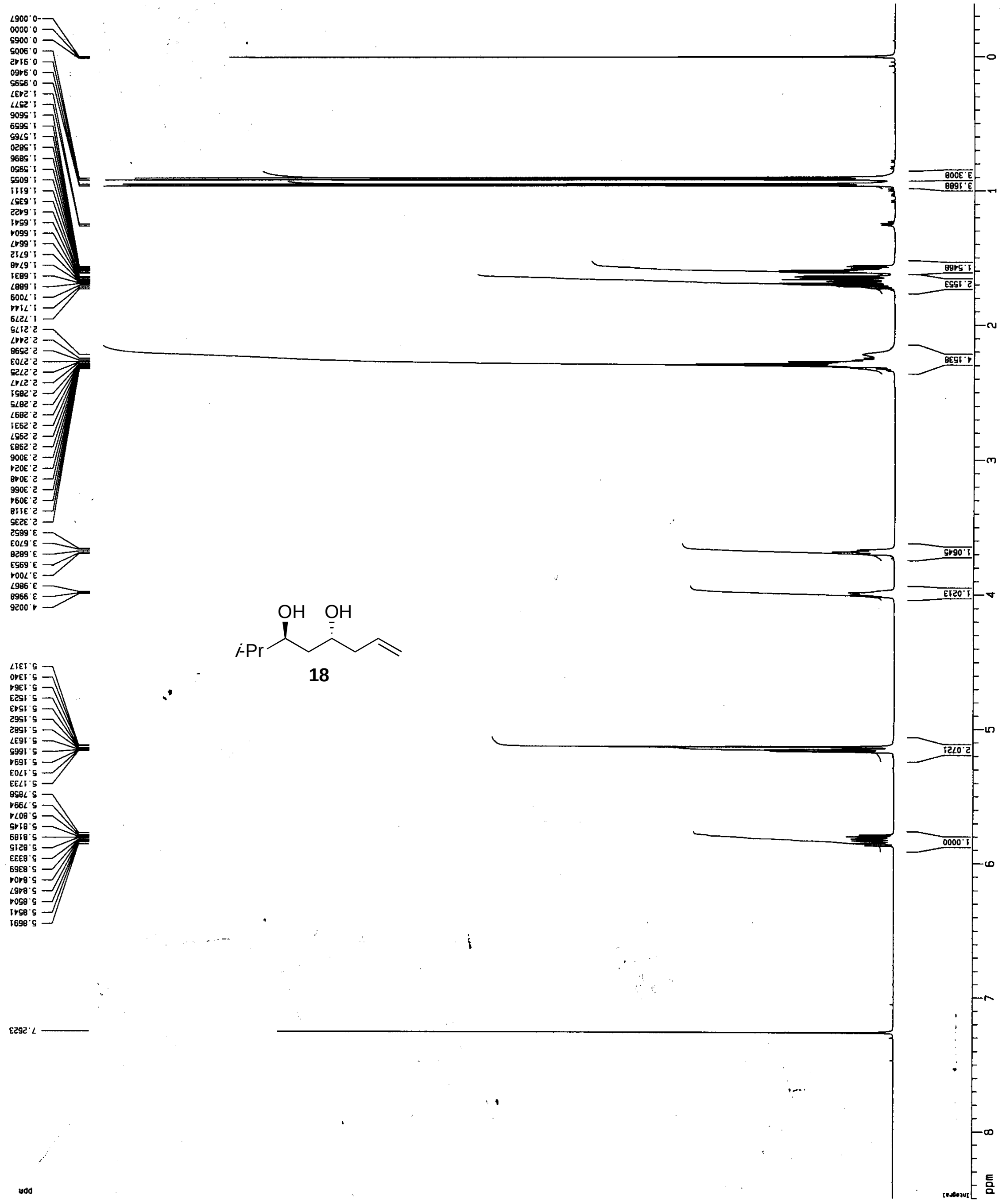
16

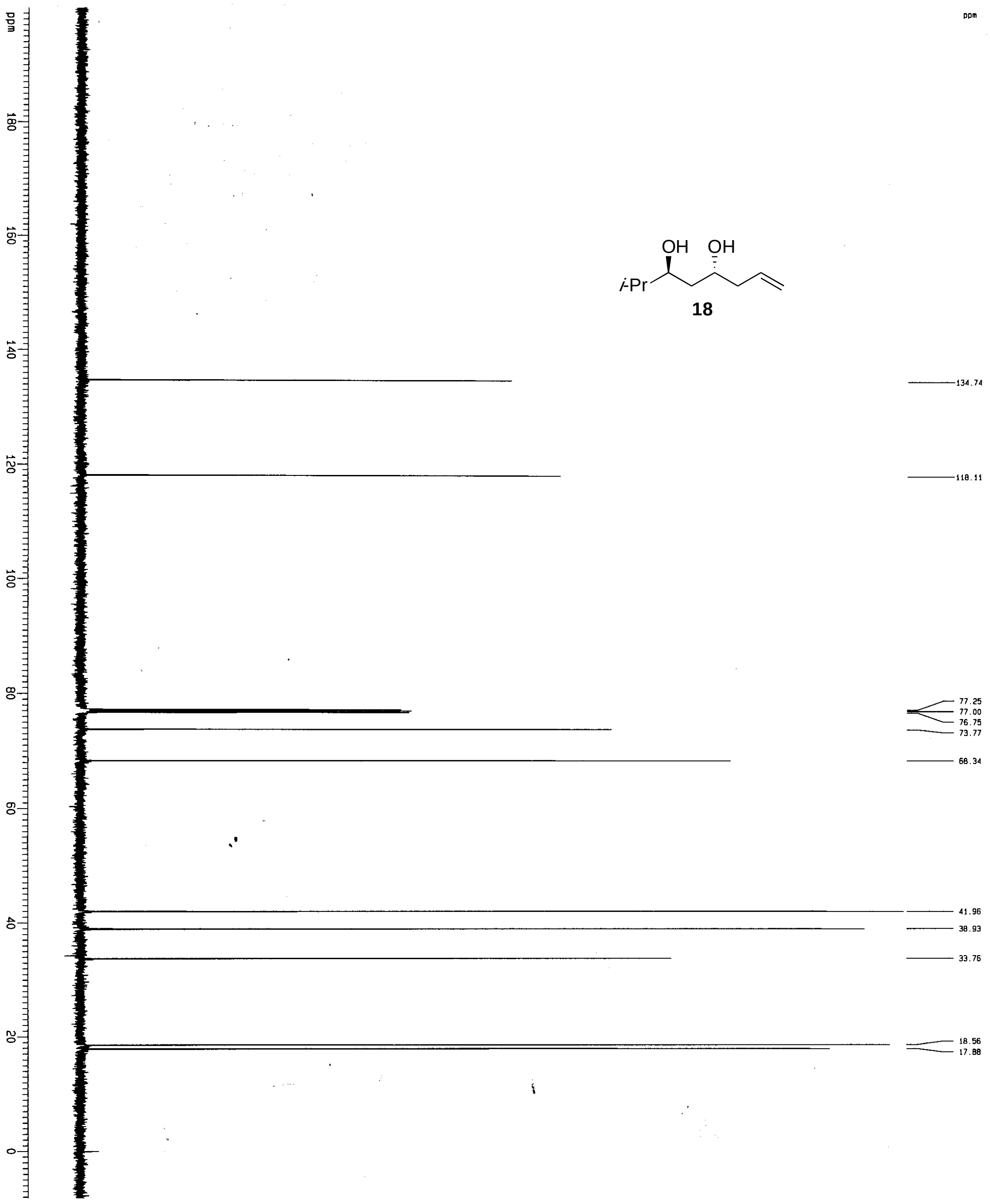
56 : 44 diastereoselectivity

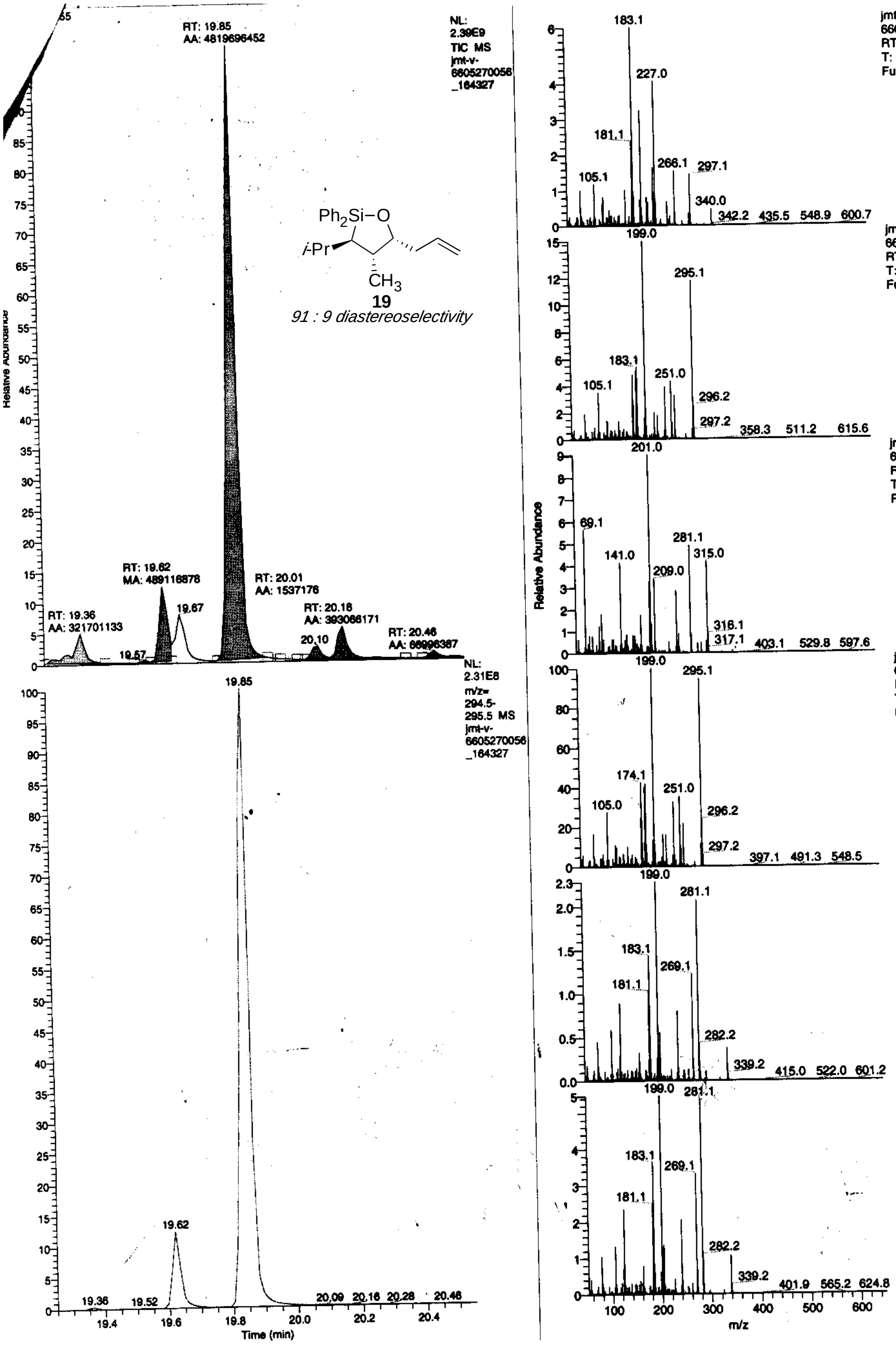


17

99 : 1 diastereoselectivity

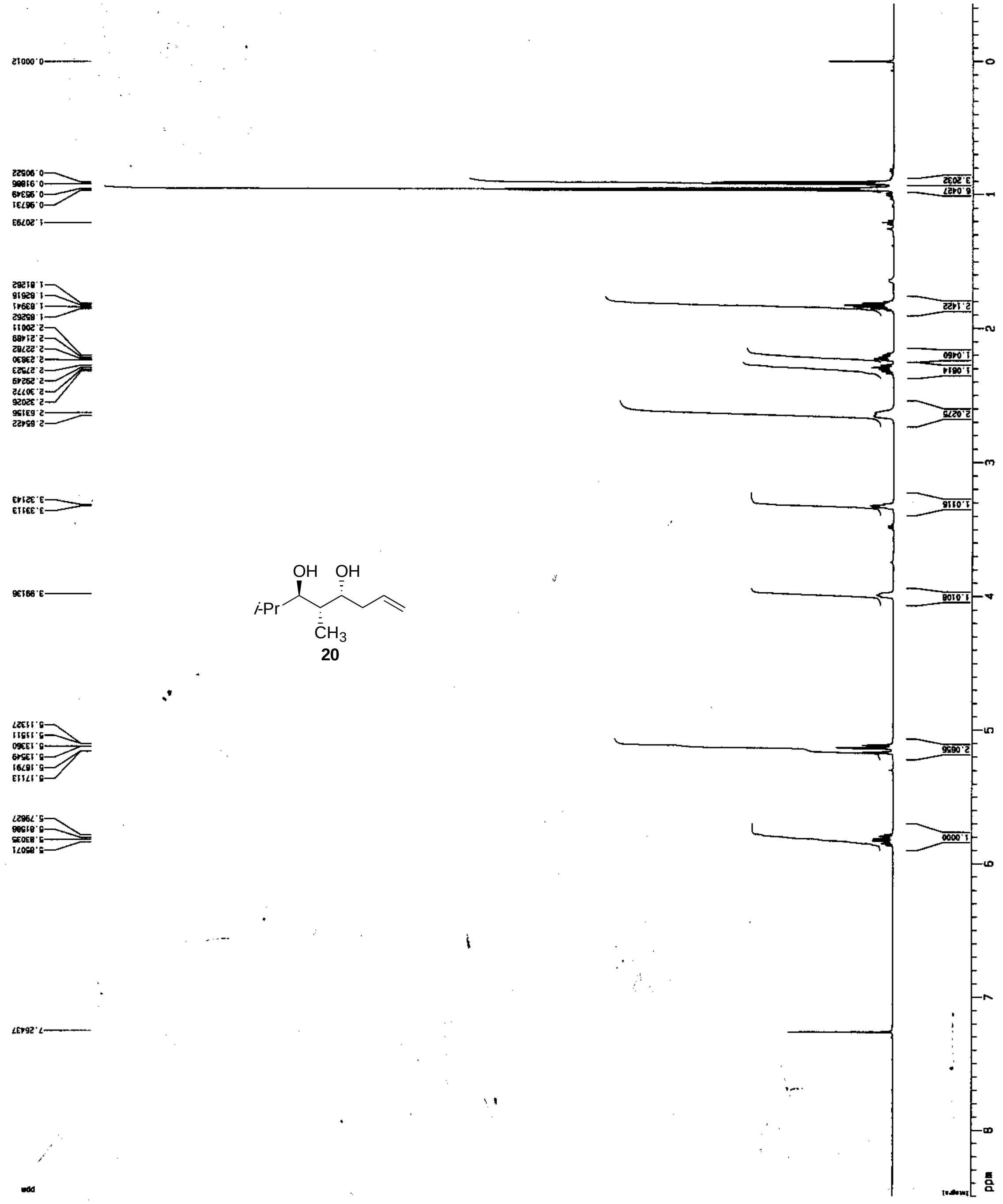

OH
OH
i-Pr
18
ppm

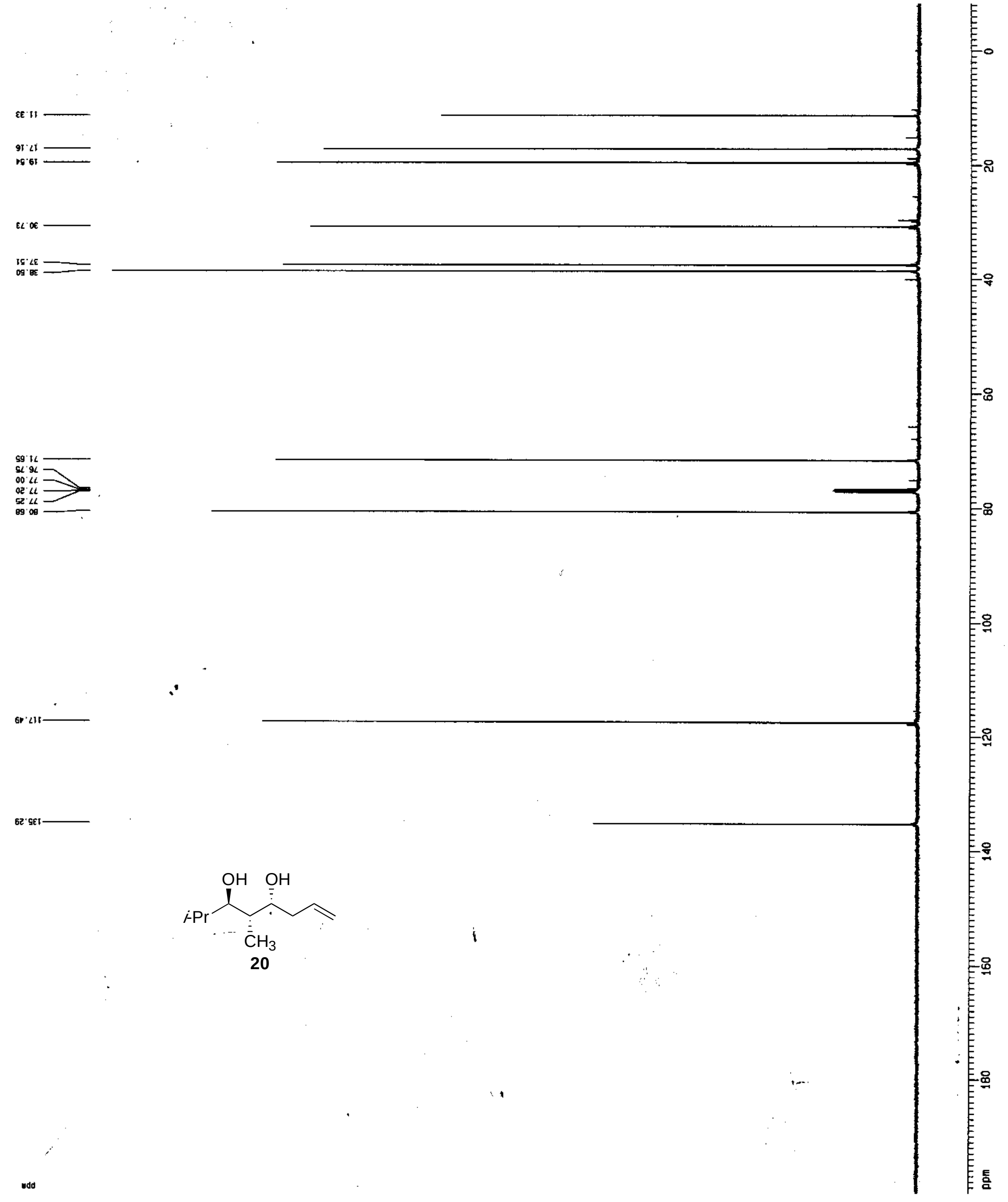

ppm
180
160
140
120
100
80
60
40
20
0
ppm
OH
OH
i-Pr
18
134.74
118.11
77.25
77.00
76.75
73.77
68.34
41.96
38.93
33.76
18.56
17.88



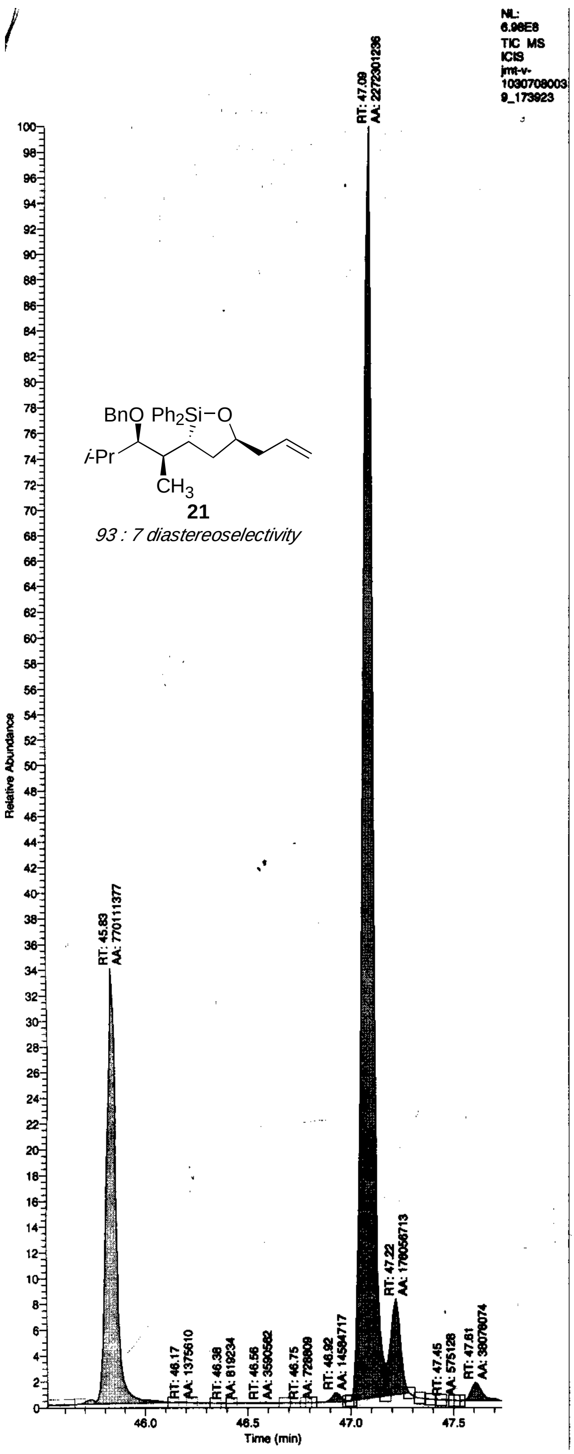
19

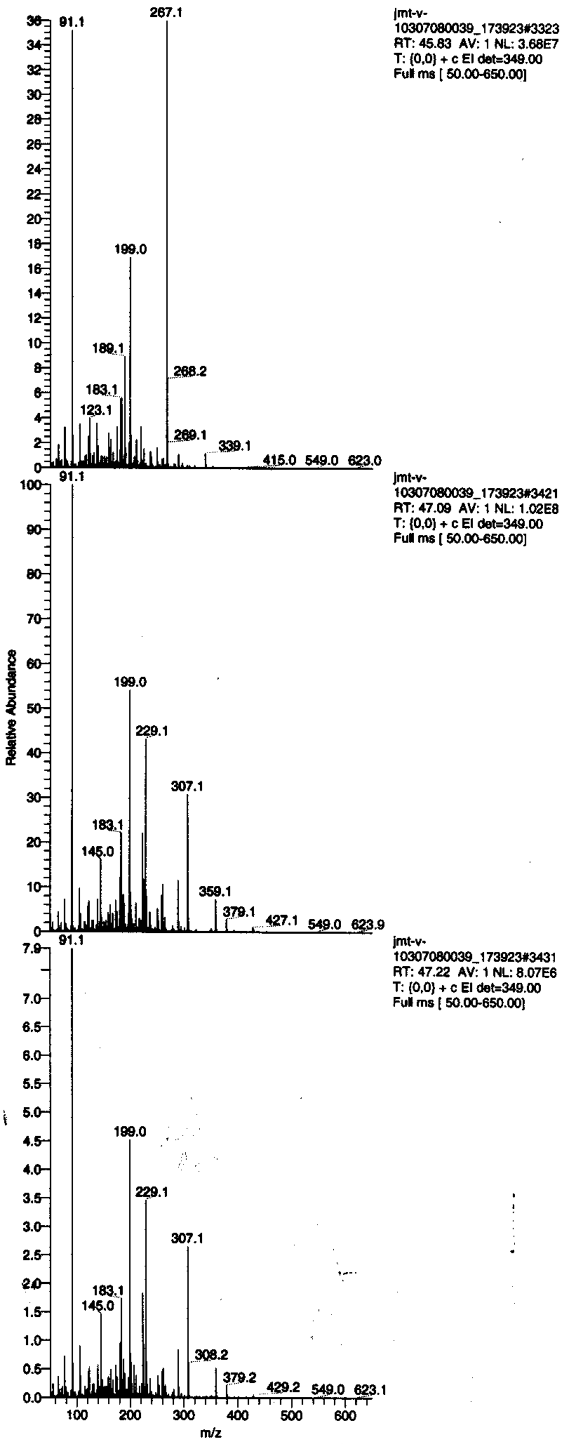
91 : 9 diastereoselectivity

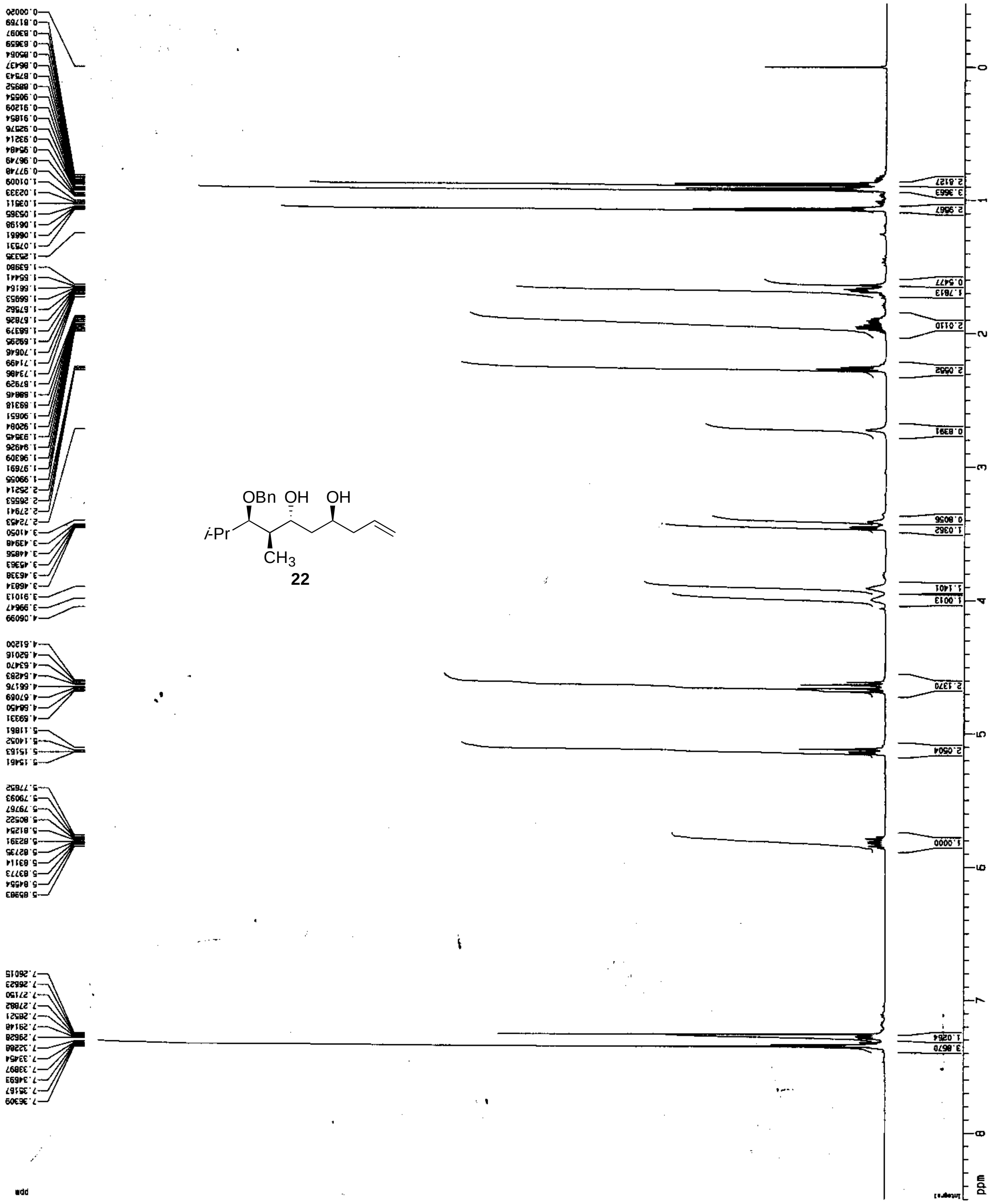

0.00012
0.90522
0.91886
0.95349
0.96731
1.20793
1.81282
1.82616
1.83941
1.85262
2.20011
2.21489
2.22782
2.23930
2.27523
2.29249
2.30772
2.32026
2.63156
2.65422
3.32143
3.33113
3.99136
5.11327
5.11511
5.13360
5.13549
5.16791
5.17113
5.79627
5.81586
5.83035
5.85071
7.26437
ppm
3.2032
6.0427
2.1422
1.0460
1.0614
2.0275
1.0116
1.0108
2.0656
1.0000
Integral
0
1
2
3
4
5
6
7
8
ppm
OH
OH
i-Pr
CH3
20


11.33
17.16
19.54
30.73
37.51
38.60
71.65
76.75
77.00
77.20
77.25
80.68
117.49
135.29
ppm
OH
OH
i-Pr
CH3
0
20
40
60
80
100
120
140
160
180
ppm

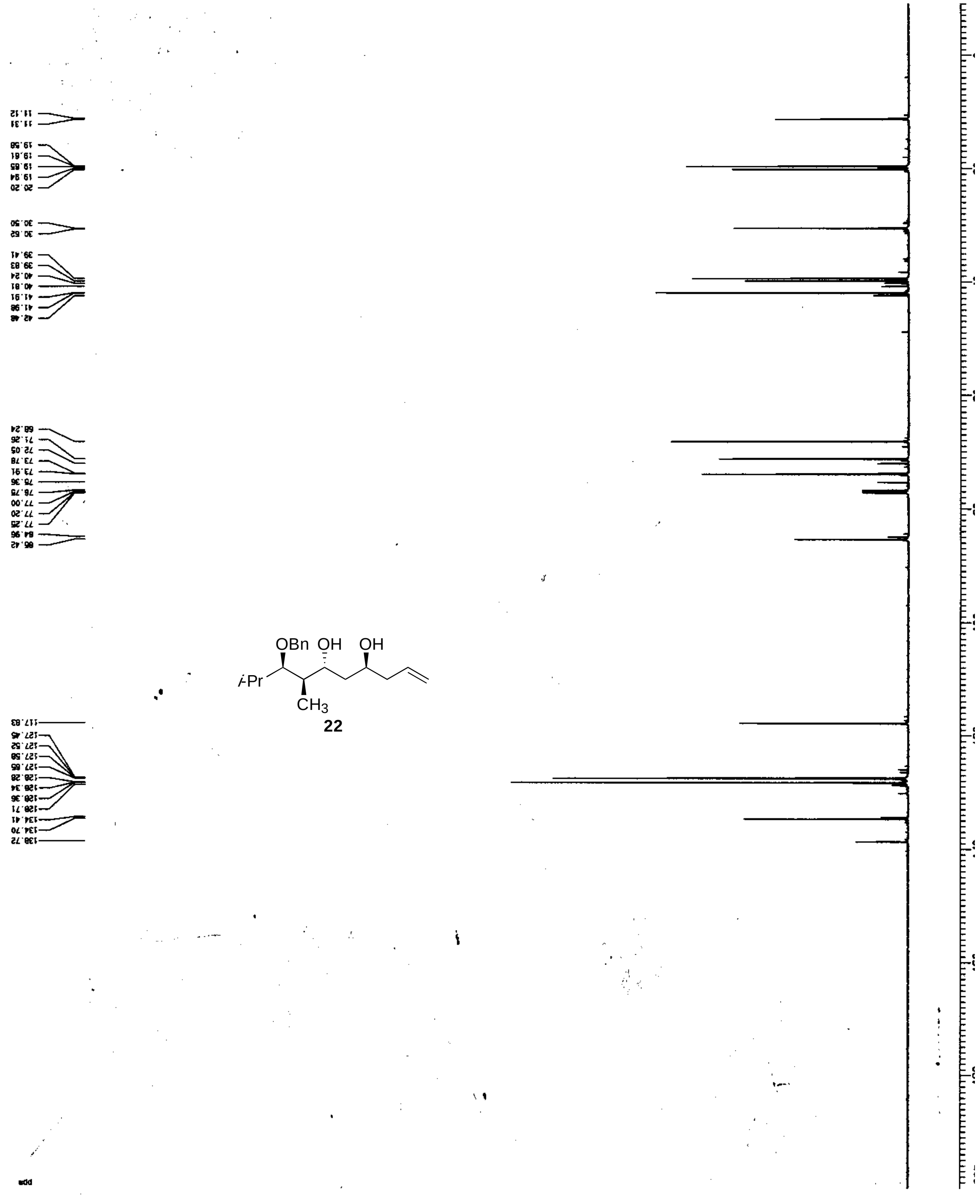
20


NL: 6.98E8
TIC MS
ICIS
jmt-v-10307080039_173923
RT: 47.09 AA: 2272301236
RT: 45.83 AA: 770111377
RT: 46.17 AA: 1375610
RT: 46.38 AA: 619234
RT: 46.56 AA: 3590562
RT: 46.75 AA: 728609
RT: 46.92 AA: 14564717
RT: 47.22 AA: 176056713
RT: 47.45 AA: 575128
RT: 47.61 AA: 38076074
Relative Abundance
Time (min)
46.0
46.5
47.0
47.5
BnO Ph2Si–O
i-Pr
CH3
21
93 : 7 diastereoselectivity

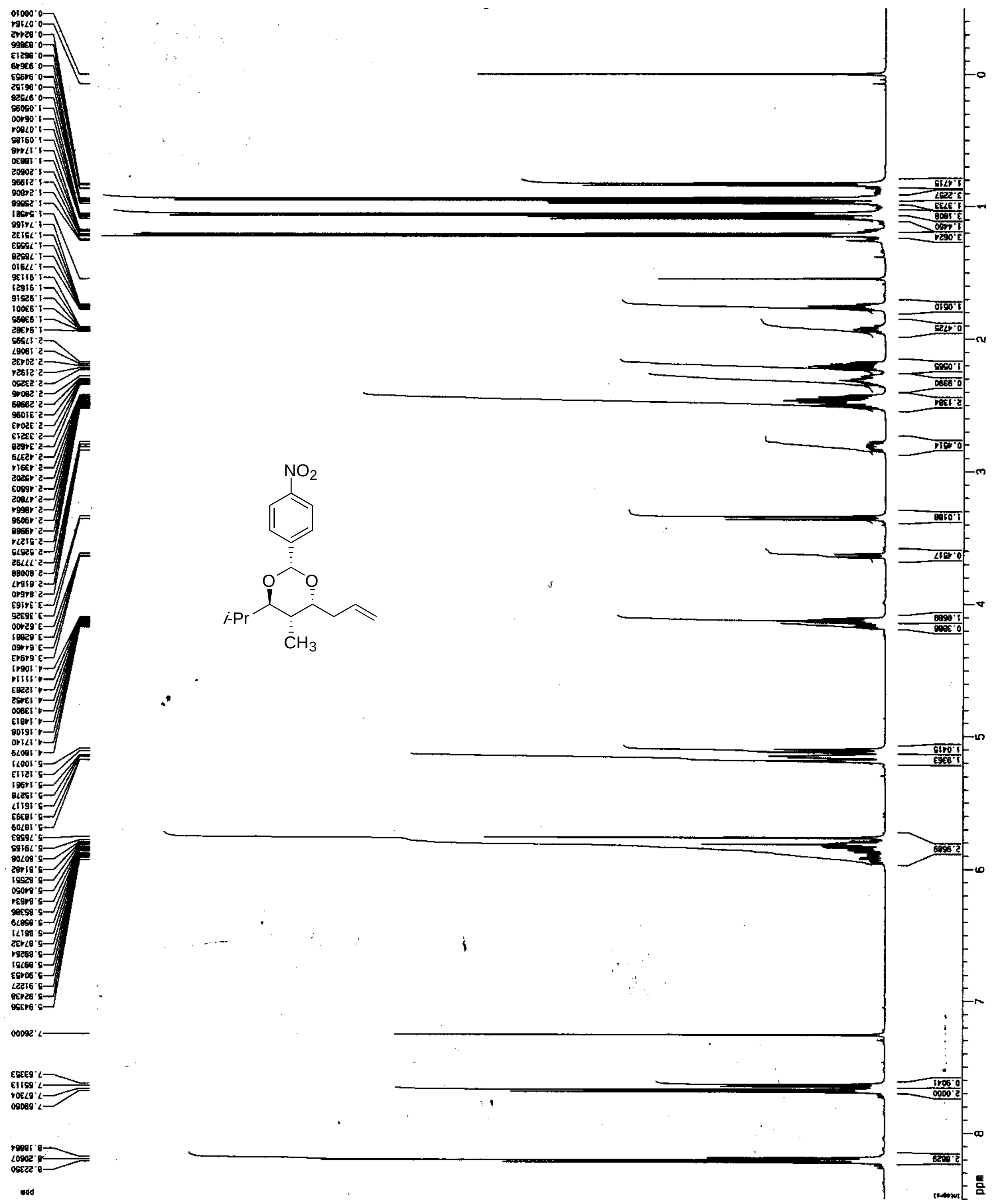

jmt-v-10307080039_173923#3323
RT: 45.83 AV: 1 NL: 3.68E7
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]
91.1
267.1
199.0
189.1
268.2
183.1
123.1
269.1
339.1
415.0
549.0
623.0
jmt-v-10307080039_173923#3421
RT: 47.09 AV: 1 NL: 1.02E8
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]
91.1
199.0
229.1
307.1
183.1
145.0
359.1
379.1
427.1
549.0
623.9
jmt-v-10307080039_173923#3431
RT: 47.22 AV: 1 NL: 8.07E6
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]
91.1
199.0
229.1
307.1
183.1
145.0
308.2
379.2
429.2
549.0
623.1
Relative Abundance
m/z
100
200
300
400
500
600

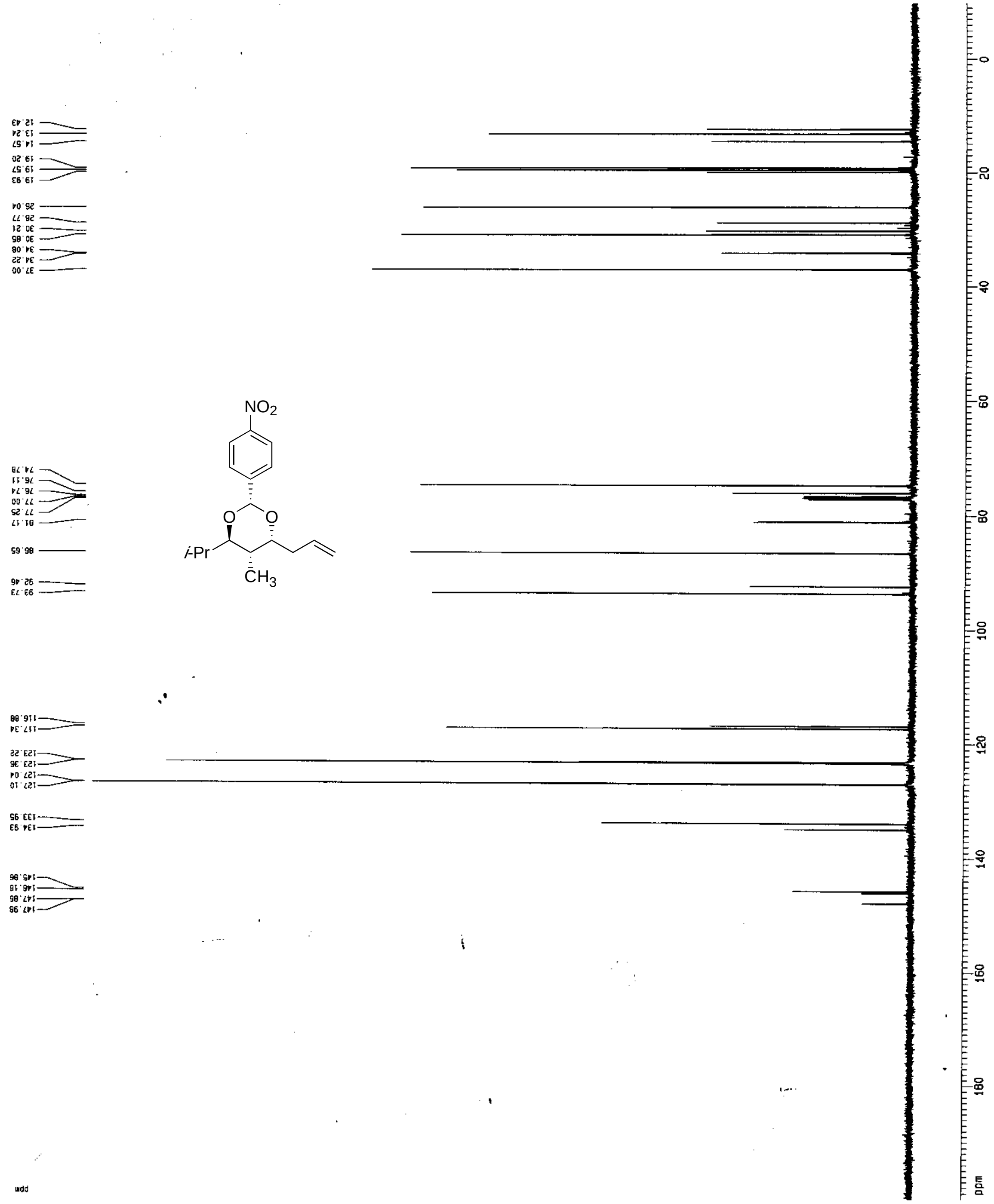

OBn
OH
OH
i-Pr
CH3
0.00020
0.81769
0.83097
0.83659
0.85064
0.86437
0.87843
0.88952
0.90654
0.91209
0.91854
0.92376
0.93214
0.95484
0.96749
0.97748
1.01009
1.02333
1.03511
1.05365
1.06198
1.06661
1.07331
1.25339
1.53980
1.65441
1.66164
1.66953
1.67562
1.67826
1.68379
1.69295
1.70646
1.71499
1.73486
1.82929
1.88846
1.89318
1.90651
1.92084
1.93545
1.94926
1.96309
1.97691
1.99055
2.25214
2.26553
2.27941
2.72453
3.41050
3.43948
3.44856
3.45393
3.46338
3.46834
3.91013
3.99647
4.06099
4.61200
4.62016
4.63470
4.64283
4.66176
4.67069
4.68450
4.69331
5.11861
5.14052
5.15153
5.15461
5.77852
5.79093
5.79767
5.80522
5.81254
5.82291
5.82735
5.83114
5.83773
5.84554
5.85983
7.26015
7.26623
7.27150
7.27882
7.28521
7.29148
7.29628
7.32268
7.33454
7.33897
7.34693
7.35167
7.36309
ppm
2.6127
3.3663
2.9567
0.5477
1.7813
2.0110
2.0562
0.8391
0.8056
1.0362
1.1401
1.0013
2.1370
2.0504
1.0000
1.0264
3.8670
Integral
0
1
2
3
4
5
6
7
8
ppm

22


11.12
11.31
19.58
19.61
19.65
19.84
20.20
30.50
30.62
39.41
39.83
40.24
40.81
41.91
41.98
42.48
68.24
71.26
72.05
73.78
73.91
76.36
76.78
77.00
77.20
77.25
84.96
86.42
117.63
127.46
127.52
127.58
127.65
128.28
128.34
128.36
128.71
134.41
134.70
138.72
ppm
OBn
OH
OH
i-Pr
CH3

22


NO2
O
O
i-Pr
CH3
ppm
0
1
2
3
4
5
6
7
8


12.43
13.24
14.57
19.20
19.57
19.93
26.04
26.77
30.21
30.85
34.08
34.22
37.00
74.78
76.11
76.74
77.00
77.25
81.17
86.65
92.46
93.73
116.88
117.34
123.22
123.36
127.04
127.10
133.95
134.93
145.96
146.18
147.86
147.98
ppm
NO2
O
O
i-Pr
CH3
0
20
40
60
80
100
120
140
160
180
ppm