Stereoselective Synthesis of Substituted γ-Butyrolactones by the [3 + 2] Annulation of Allylic Silanes with Chlorosulfonyl Isocyanate: Enantioselective Total Synthesis of (+)-Blastmycinone

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Supporting Information

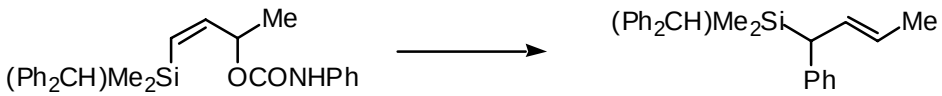
Contents:

General. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature at 500 MHz and 125 MHz, respectively, using a Bruker DRX 500 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, m = multiplet), coupling constants (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 column (30 m × 0.32 mm) wall-coated with DB-1 (J & W Scientific) was used with helium as the carrier gas. Melting points are reported uncorrected. Analytical thin layer chromatography was performed using EM Reagents 0.25 mm silica gel 60–F plates. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on EM Reagents silica gel (SiO_2) 60 (230–400) mesh. Enantiomeric excess was determined by HPLC analysis on a Hewlett Packard series 1100 using a Chiralcel OD-H column, and the enantiomerically enriched material was compared with racemic material. All reactions were carried out under an atmosphere of nitrogen in glassware which had been flame-dried under a stream of nitrogen. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Toluene, THF, Et_2O, and CH_2Cl_2 were dried by filtration through alumina according to the procedure of Grubbs.[1] Methanol was distilled over CaH_2 prior to use. LiCl was dried at 150 °C at 0.05 mmHg for 8 h, then stored in an Innovative Technologies nitrogen atmosphere drybox. Chlorosulfonyl isocyanate was purchased from Aldrich and distilled over K_2CO_3 prior to use. Alkyllithium and Grignard reagents were purchased from Aldrich or were prepared from the corresponding alkyl halides, and were titrated using salicylaldehyde phenylhydrazone as an indicator.[2]

I. Syntheses of Allylsilanes 2

The syntheses of allylsilanes **2a** and **2b** have been reported.[3]

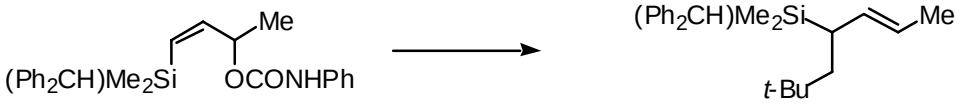
A. Allylsilanes **2c** and **2d**



17 **2c**

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.
[2] Love, B. E.; Jones, E. G. *J. Org. Chem.* **1999**, 64, 3755 -3756.
[3] Peng, Z.-H.; Woerpel, K. A. *Org. Lett.* **2000**, *2*, 1379-1381.

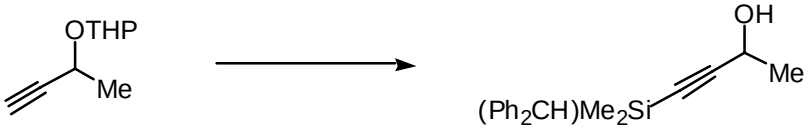
(±)-(*E*)-1-Benzhydryldimethylsilyl-1-phenyl-2-butene (2c). The general procedure for the copper-mediated S_N2' reaction was followed.[3,4] The reagents used were: **17**[3] (0.415 g, 1.00 mmol), *n*-BuLi (1.40 M solution in hexanes, 0.710 mL, 1.00 mmol), CuI (0.190 g, 1.00 mmol), LiCl (0.085 g, 2.0 mmol), and phenylmagnesium bromide (0.970 M solution in THF, 1.03 mL, 1.00 mmol). Purification by flash chromatography (hexanes) afforded **2c** as a colorless oil (0.314 g, 88%) with a *E*/*Z* ratio > 99:1 and γ:α ratio of 97:3 as indicated by capillary GC analysis of the unpurified reaction mixture: GC t_R 7.1 min (DB-1, 1 min at 200 °C then ramped to 275 °C at 10 °C / min, 16 psi); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40-7.24 (m, 10H), 7.20 (t, *J* = 7.3 Hz, 3H), 7.03 (d, *J* = 7.3 Hz, 2H), 5.83 (ddq, *J* = 14.9, 10.0, 1.5 Hz, 1H), 5.33 (dq, *J* = 14.9, 6.4 Hz, 1H), 3.64 (s, 1H), 3.07 (d, *J* = 10.2 Hz, 1H), 1.78 (dd, *J* = 6.5, 1.4 Hz, 3H), 0.20 (s, 3H), 0.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.6, 142.53, 142.49, 129.9, 129.22, 129.17, 128.43, 128.38, 127.6, 125.41, 125.36 124.8, 124.5, 43.8, 41.1, 18.7, –3.6, –4.0; IR (thin film) 3023, 1596, 1493, 1248 cm^{-1}; HRMS (CI/NH_3) *m* / *z* calcd for $C_{25}H_{28}Si$ (M^+) 356.1960, found 356.1960. Anal. Calcd for $C_{25}H_{28}Si$: C, 84.22; H, 7.92. Found: C, 84.24; H, 7.98.



17 **2d**

(±)-(*E*)-4-(Benzhydryldimethylsilyl)-6,6-dimethyl-2-heptene (2d). The general procedure was followed with carbamate **17** (1.25 g, 3.00 mmol), *n*-BuLi (2.10 M solution in hexanes, 1.43 mL, 3.00 mmol), CuI (0.571 g, 3.00 mmol), LiCl (0.254 g, 6.00 mmol), and neopentylmagnesium bromide (0.350 M solution in THF, 8.57 mL, 3.00 mmol). Purification by flash chromatography (hexanes) afforded **2d**, as a colorless oil (0.986 g, 94%) with a *E*/*Z* ratio of 98:2 and γ:α ratio of > 99:1 as indicated by capillary GC analysis of the unpurified reaction mixture: GC t_R 5.8 min (DB-1, 1 min at 200 °C then ramped to 250 °C at 5 °C / min, 16 psi); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29 (m, 8H), 7.17 (m, 2H), 5.09 (ddq, *J* = 15.2, 9.8, 1.4 Hz, 1H), 4.98 (dq, *J* = 15.2, 6.2 Hz, 1H), 3.66 (s, 1H), 1.68 (td, *J* = 9.9, 2.5 Hz, 1H), 1.52 (dd, *J* = 6.2, 1.2 Hz, 3H), 1.22 (dd, *J* = 14.0, 2.7 Hz, 1H), 1.18 (dd, *J* = 14.0, 10.0 Hz, 1H), 0.78 (s, 9H), 0.08 (s, 3H), 0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.3, 143.2, 134.8, 129.5, 129.4, 128.7, 128.6, 125.6, 125.5, 122.0, 43.8, 42.8, 32.8, 30.3, 28.4, 18.5, –4.3, –4.5; IR (thin film) 2953, 1597, 1494, 1248 cm^{-1}; HRMS (CI/isobutane) *m* / *z* calcd for $C_{24}H_{34}Si$ (M^+) 350.2430, found 350.2427. Anal. Calcd for $C_{24}H_{34}Si$: C, 82.23; H, 9.78. Found: C, 82.34; H, 9.83.

B. Allylsilane **2e**



18 **19**

(±)-4-(Benzhydryldimethylsilyl)-3-butyn-2-ol (19). To a cooled (–78 °C) solution of **18**[3] (0.771 g, 5.00 mmol) in 5 mL of THF was added *n*-BuLi (1.45 M solution in hexanes, 3.45 mL, 5.00 mmol) dropwise by syringe. After 5 min, the mixture was allowed to warm to 0 °C. A solution of chlorobenzhydryldimethylsilane[3] (1.43 g, 5.50 mmol) in 5 mL of THF was added dropwise. The ice/H_2O bath was removed, and after 30 min, 20 mL of 10% aqueous NaCl and 20 mL of hexanes were added to the reaction mixture. The layers were separated, and the aqueous layer was extracted with 3 × 20 mL of hexanes. The combined organic layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was diluted with 10 mL of MeOH, and TsOH (0.190 g, 0.100 mmol) was added. After 2 h at 22 °C, 5 mL of saturated aqueous Na_2CO_3 was added to the reaction mixture. The resultant suspension was stirred for an additional 10 min, then the mixture was concentrated *in*

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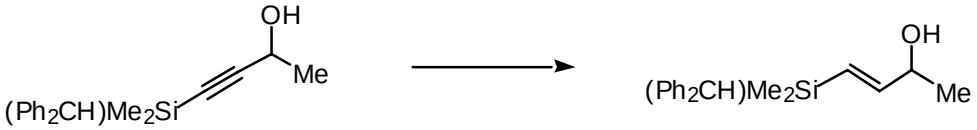
[4] (a) Smitrovich, J. H.; Woerpel, K. A. *J. Am. Chem. Soc.* **1998**, *120*, 12998-12999. (b) Smitrovich, J. H.; Woerpel, K. A. *J. Org. Chem.* **2000**, *65*, 1601-1614.

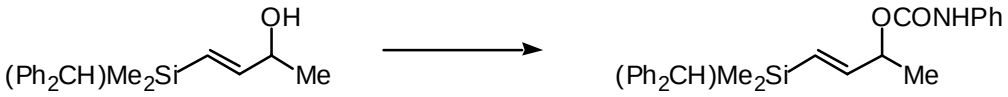
vacuo to remove most of the MeOH. The residue was transferred to a separatory funnel containing 10 mL of 10% aqueous NaCl. The mixture was extracted with 3 × 20 mL of 1:1 hexane/EtOAc. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash chromatography (10:90 EtOAc/hexanes) afforded **19** as a colorless oil (1.31 g, 89%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33 (d, *J* = 7.9 Hz, 4H), 7.26 (t, *J* = 7.5 Hz, 4H), 7.14 (t, *J* = 7.3 Hz, 2H), 4.45 (m, 1H), 3.59 (s, 1H), 2.03 (d, *J* = 5.0 Hz, 1H), 1.39 (d, *J* = 6.6 Hz, 3H), 0.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.3, 129.5, 128.8, 126.0, 110.0, 87.3, 59.1, 45.2, 24.5, –1.45, –1.46. IR (thin film) 3347, 2174, 1250 cm^{-1}; HRMS (CI/isobutane) *m* / *z* calcd for $C_{19}H_{22}OSi$



19 **20**

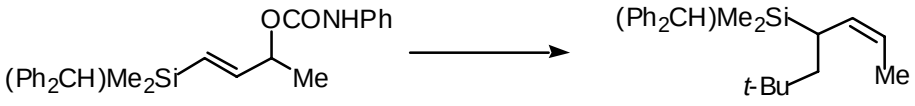
(M^+) 294.1440, found 294.1440. Anal. Calcd for $C_{19}H_{22}OSi$: C, 77.51; H, 7.54. Found: C, 77.41; H, 7.49.

(±)-(*E*)-1-(Benzhydryldimethylsilyl)-1-buten-3-ol (20). To a cooled (–20 °C) solution of sodium bis-(2-methoxyethoxy)aluminum hydride (Red-Al®, 65+ wt% solution in toluene, 3.00 mL, 9.90 mmol) in 10 mL of Et_2O was slowly added a solution of **19** (1.93 g, 6.60 mmol) in 5 mL of Et_2O by cannula. After the addition, the reaction mixture was allowed to warm to 22 °C and stirred for 4 h. The reaction mixture was cooled to 0 °C and a H_2SO_4 solution (3.60 M, 4.00 mL, 14.4 mmol) was cautiously added. Then 30 mL of Et_2O and 5 mL of water were added, the layers were separated and the aqueous layer was extracted with 3 × 20 mL of Et_2O. The combined organic layers were washed with 10 mL of brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash chromatography (4:96 to 10:90 EtOAc/hexanes) afforded **20** as a colorless oil (1.83 g, 94%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34 (m, 8H), 7.22 (m, 2H), 6.08 (dd *J* = 18.8, 5.0 Hz, 1H), 5.91 (dd, *J* = 18.8, 1.3 Hz, 1H), 4.31 (m, 1H), 3.68 (s, 1H), 1.80 (d, *J* = 3.8 Hz, 1H), 1.29 (d, *J* = 6.5 Hz, 3H), 0.21 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.3, 143.0, 129.41, 129.38, 128.7, 125.75, 125.68, 70.9, 46.0, 23.3, –2.7; IR (thin film) 3356, 1597, 1494, 1249 cm^{-1}; HRMS (CI/isobutane) *m* / *z* calcd for $C_{19}H_{24}OSi$ (M^+) 296.1596, found 296.1606. Anal. Calcd for $C_{19}H_{24}OSi$: C, 76.99; H, 8.17. Found: C, 76.90; H, 8.26.



20 **21**

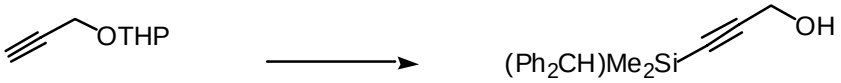
(±)-(*E*)-1-(Benzhydryldimethylsilyl)-1-buten-3-ol *N*-phenylcarbamate (21). Phenyl isocyanate (0.704 mL, 6.50 mmol) was added to alcohol **20** (1.60 g, 5.40 mmol) at 22 °C. After stirring for 12 h, the resultant slurry was diluted with hexanes and then filtered. The filtrate was concentrated *in vacuo*. Purification by flash chromatography (5:95 EtOAc/hexanes) afforded **21** as a colorless oil (2.05 g, 92%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48-7.12 (m, 15H), 6.73 (s, 1H), 6.02 (dd, *J* = 18.9, 4.5 Hz, 1H), 5.96 (d, *J* = 18.9 Hz, 1H), 5.40 (m, 1H), 3.64 (s, 1H), 1.37 (d, *J* = 6.6 Hz, 3H), 0.17 (s, 3H), 0.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.3, 147.4, 142.8, 138.5, 129.54, 129.46, 129.45, 129.3, 128.9, 128.7, 128.2, 125.7, 123.8, 119.0, 73.6, 45.9, 20.5, –2.8, –2.9; IR (thin film) 3316, 1715, 1598, 1538, 1313 cm^{-1}; HRMS (FAB) *m* / *z* calcd for $C_{26}H_{29}NO_2SiNa$ (M + Na)$^+$ 438.1865, found 438.1869. Anal. Calcd for $C_{26}H_{29}NO_2Si$: C, 75.40; H, 7.03; N, 3.37. Found: C, 75.30; H, 7.11; N, 3.42.



21 **2e**

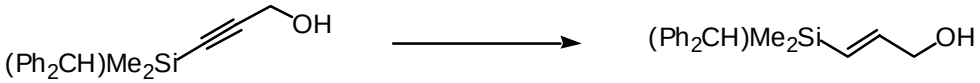
(±)-(*Z*)-4-(Benzhydryldimethylsilyl)-6,6-dimethyl-2-heptene (2e). The general procedure was followed with carbamate **21** (0.332 g, 0.80 mmol), *n*-BuLi (1.4 M solution in hexanes, 0.57 mL, 0.80 mmol), CuI (0.152 g, 0.80 mmol), LiCl (0.067 g, 1.6 mmol), and neopentylmagnesium bromide (0.20 M solution in THF, 4.0 mL, 0.80 mmol). Purification by flash chromatography (hexanes) afforded **2e** as a colorless oil (0.255 g, 91%) with a *Z*/*E* ratio of 96:4 and γ:α ratio of > 99:1 as indicated by capillary GC analysis of the unpurified reaction mixture: GC t_R 6.3 min (DB-1, 1 min at 200 °C then ramped to 250 °C at 5 °C / min, 16 psi); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34 (m, 8H), 7.18 (m, 2H), 5.24 (m, 2H), 3.73 (s, 1H), 2.14 (m, 1H), 1.51 (d, *J* = 5.1 Hz, 3H), 1.39 (dd, *J* = 13.8, 1.4 Hz, 1H), 1.24 (dd, *J* = 13.8, 11.0 Hz, 1H), 0.76 (s, 9H), 0.11 (s, 3H), 0.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.3, 143.1, 135.2, 129.7, 129.1, 128.8, 128.7, 125.8, 125.5, 120.1, 43.9, 43.6, 32.7, 30.2, 23.8, 13.8, –4.2, –4.7; IR (thin film) 2952, 1597, 1494, 1248 cm^{-1}; HRMS (CI/isobutane) *m* / *z* calcd for $C_{24}H_{34}Si$ (M^+) 350.2430, found. 350.2429. Anal. Calcd for $C_{24}H_{34}Si$: C, 82.23; H, 9.78. Found: C, 82.26; H, 9.82.

C. Allylsilanes **2f** and **2g**



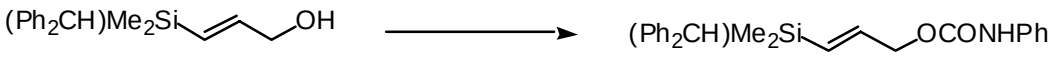
10 **22**

3-(Benzhydryldimethylsilyl)-2-propyn-1-ol (22). The same procedure given for **19** was followed. The reagents used were: **10** (2.10 g, 15.0 mmol), *n*-BuLi (2.50 M solution in hexanes, 6.00 mL, 15.0 mmol), chlorobenzhydryldimethylsilane (4.04 g, 15.5 mmol), and *p*-TsOH (0.190 g, 1.00 mmol). Purification by flash chromatography (10:90 to 20:80 EtOAc/hexanes) afforded **22** as a colorless oil (3.94 g, 94%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.32 (d, *J* = 7.6 Hz, 4H), 7.25 (t, *J* = 7.9 Hz, 4H), 7.13 (t, *J* = 7.3 Hz, 2H), 4.17 (d, *J* = 5.8 Hz, 2H), 3.59 (s, 1H), 1.83 (t, *J* = 5.8 Hz, 1H), 0.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.3, 129.5, 128.9, 126.0, 106.8, 89.5, 52.1, 45.2, –1.4; IR (thin film) 3404, 2175, 1251 cm^{-1}; HRMS (CI/isobutane) *m* / *z* calcd for $C_{18}H_{20}OSi$ (M^+) 280.1283, found 280.1291. Anal. Calcd for $C_{18}H_{20}OSi$: C, 77.09; H, 7.19. Found: C, 77.15; H, 7.29.



22 **23**

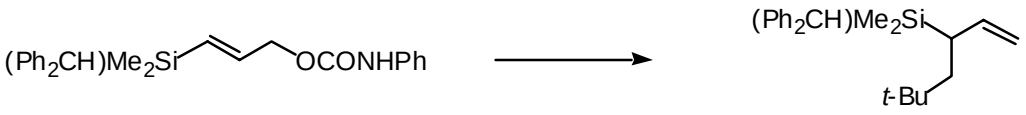
(*E*)-3-(Benzhydryldimethylsilyl)-2-propen-1-ol (23). The same procedure given for **20** was followed with **22** (3.94 g, 14.0 mmol) and sodium bis-(2-methoxyethoxy)aluminum hydride (Red-Al®, 65+ wt% solution in toluene, 6.30 mL, 21.0 mmol). Purification by flash chromatography (10:90 to 20:80 EtOAc/hexanes) afforded **23** as a colorless oil (3.45 g, 87%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33 (m, 8H), 7.22 (m, 2H), 6.17 (dt, *J* = 18.9, 4.3 Hz, 1H), 5.98 (dt, *J* = 18.9, 1.7 Hz, 1H), 4.17 (t, *J* = 4.0 Hz, 2H), 3.68 (s, 1H), 1.83 (t, *J* = 5.6 Hz, 1H), 0.19 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.4, 143.1, 129.4, 128.8, 127.0, 125.7, 65.8, 45.9, –2.7; IR (thin film) 3331, 1597, 1494, 1248 cm^{-1}; HRMS (CI/isobutane) *m* / *z* calcd for $C_{18}H_{22}OSi$ (M^+) 282.1440, found 282.1439. Anal. Calcd for $C_{18}H_{22}OSi$: C, 76.56; H, 7.86. Found: C, 76.35; H, 7.87.



23 **24**

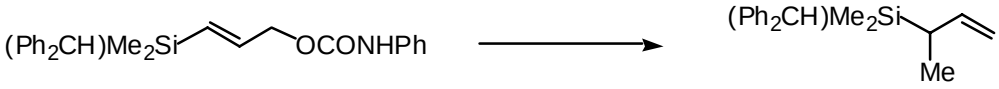
(*E*)-1-(Benzhydryldimethylsilyl)-1-propen-3-ol *N*-phenylcarbamate (24). Phenyl isocyanate (1.35 mL, 12.4 mmol) was added to alcohol **23** (3.20 g, 11.3 mmol) at 22 °C. After stirring for 12 h, the resultant slurry was diluted with hexanes and then filtered. The filtrate was concentrated *in vacuo*. Purification by flash chromatography (5:95 EtOAc/hexanes) afforded **24** as a pale yellow oil (4.38 g, 97%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.49-7.13 (m, 15H), 6.85 (s, 1H), 6.13 (dt, *J* = 18.9, 4.6 Hz, 1H), 6.05 (d, *J* = 18.9 Hz, 1H), 4.75 (m,

2H), 3.67 (s, 1H), 0.19 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.7, 142.9, 142.1, 138.3, 130.7, 129.6, 129.4, 128.8, 125.7, 124.0, 119.2, 67.7, 45.8, –2.8; IR (thin film) 3328, 1713, 1599, 1537, 1494, 1219 cm^{-1}; HRMS (CI/isobutane) *m* / *z* calcd for $C_{25}H_{27}NO_2Si$ (M^+) 401.1811, found 401.1806. Anal. Calcd for $C_{25}H_{27}NO_2Si$: C, 74.77; H, 6.78; N, 3.49. Found: C, 75.03; H, 6.80; N, 3.56.



24 **2f**

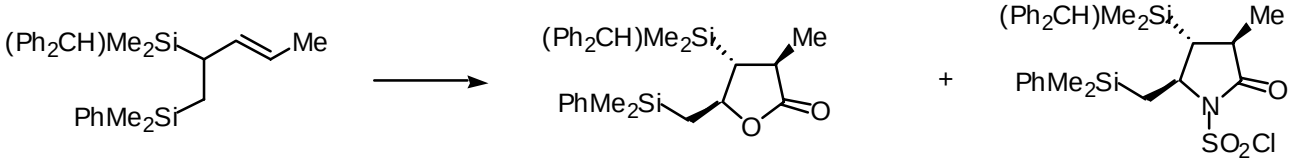
(±)-3-(Benzhydryldimethylsilyl)-5,5-dimethyl-1-hexene (2f). Following the general procedure with carbamate **24** (0.401 g, 1.00 mmol), *n*-BuLi (2.00 M solution in hexanes, 0.500 mL, 1.00 mmol), CuI (0.190 g, 1.00 mmol), LiCl (0.085 g, 2.0 mmol), and neopentylmagnesium bromide (0.320 M solution in THF, 3.20 mL, 1.00 mmol) afforded **2f**, after purification by flash chromatography (hexanes), as a colorless oil (0.297 g, 88%) with a γ:α ratio of 96:4 as indicated by capillary GC analysis of the unpurified reaction mixture: GC t_R 5.5 min (DB-1, 1 min at 200 °C then ramped to 250 °C at 5 °C / min, 16 psi); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34 (m, 8H), 7.22 (m, 2H), 5.66 (dt, *J* = 17.1, 10.1 Hz, 1H), 4.85 (dd, *J* = 10.3, 1.8 Hz, 1H), 4.77 (ddd, *J* = 17.1, 1.8, 0.9 Hz, 1H), 3.75 (s, 1H), 1.89 (m, 1H), 1.36 (m, 2H), 0.81 (s, 9H), 0.15 (s, 3H), 0.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.2, 143.0, 142.8, 129.6, 129.4, 128.82, 128.75, 125.7, 125.6, 111.8, 43.6, 42.5, 33.0, 30.4, 30.3, –4.4, –4.6; IR (thin film) 1622, 1597, 1494 cm^{-1}; HRMS (CI/isobutane) *m* / *z* calcd for $C_{23}H_{32}Si$ (M^+) 336.2273, found 336.2264. Anal. Calcd for $C_{23}H_{32}Si$: C, 82.09; H, 9.59. Found: C, 82.14; H, 9.66.



24 **2g**

(±)-3-(Benzhydryldimethylsilyl)-1-butene (2g). Following the general procedure with carbamate **24** (0.401 g, 1.00 mmol), *n*-BuLi (2.00 M solution in hexanes, 0.500 mL, 1.00 mmol), CuI (0.190 g, 1.00 mmol), LiCl (0.085 g, 2.0 mmol), and methyllithium (0.910 M solution in Et_2O, 1.10 mL, 1.00 mmol) afforded **2g**, after purification by flash chromatography (hexanes), as a colorless oil (0.245 g, 88%) with a γ:α ratio of > 99:1 as indicated by capillary GC analysis of the unpurified reaction mixture: GC t_R 3.6 min (DB-1, 1 min at 200 °C then ramped to 250 °C at 5 °C / min, 16 psi); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34 (m, 8H), 7.21 (m, 2H), 5.86 (ddd, *J* = 17.5, 10.4, 7.5 Hz, 1H), 4.93 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.82 (dt, *J* = 17.2, 1.6 Hz, 1H), 3.72 (s, 1H), 1.89 (quintet, *J* = 7.3 Hz, 1H), 1.06 (d, *J* = 7.2 Hz, 3H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.0, 141.5, 129.4, 128.8, 125.7, 111.3, 44.0, 26.2, 13.6, –4.9, –5.1; IR (thin film) 1626, 1597, 1484 cm^{-1}; HRMS (CI/isobutane) *m* / *z* calcd for $C_{19}H_{24}Si$ (M^+) 280.1647, found 280.1643. Anal. Calcd for $C_{19}H_{24}Si$: C, 81.38; H, 8.63. Found: C, 81.36; H, 8.64.

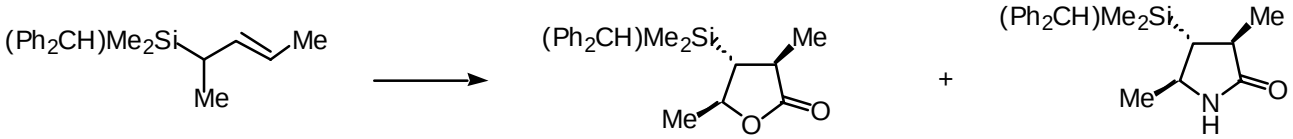
II. [3 + 2] Annulation of Allysilanes 2 with Chlorosulfonyl Isocyanate



2a **5a** **4a**

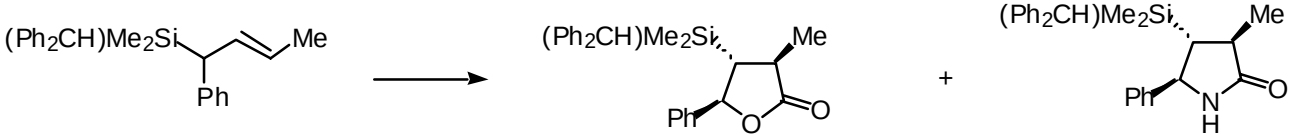
(4*R,3*S**,5*S**)-4-Benzhydryldimethylsilyl-5-dimethylphenylsilylmethyl-3-methyl-2-furanone (5a) and (4*R**,3*S**,5*S**)-4-Benzhydryldimethylsilyl-1-chlorosulfonyl-5-dimethylphenylsilylmethyl-3-methyl-2-pyrrolidinone (4a).** To a cooled (0 °C) solution of (*E*)-2-(benzhydryldimethylsilyl)-1-(dimethylphenylsilyl)-3-pentene **2a** (0.128 g, 0.300 mmol) in 4 mL of CH_2Cl_2 was added chlorosulfonyl isocyanate (0.065 mL, 0.75

mmol). After stirring at 0 °C for 2 h, 3 mL of saturated aqueous $NaHCO_3$ was added. The mixture was extracted with 3 × 15 mL of EtOAc. The combined organic layers were washed with 5 mL of brine, dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was then dissolved in 4 mL of THF, and then 0.3 mL of HCl (1.0 N, 0.30 mmol) was added. After 12 h at 22 °C, 2 mL of saturated aqueous $NaHCO_3$ was added, the mixture was extracted with 3 × 20 mL of CH_2Cl_2. The combined organic layers were washed with 5 mL of brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by flash chromatography (5:95 EtOAc/hexanes) afforded **4a** (0.014 g, 8%) and **5a** (0.113 g, 79%), both as white solids. **4a**: mp 104–106 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.46-7.10 (m, 15H), 4.38 (dt, *J* = 11.2, 2.5 Hz, 1H), 3.39 (s, 1H), 2.29 (qd, *J* = 7.4, 3.7 Hz, 1H), 1.77 (dd, *J* = 14.4, 2.1 Hz, 1H), 1.46 (dd, *J* = 14.3, 11.2 Hz, 1H), 0.94 (t, *J* = 3.3 Hz, 1H), 0.85 (d, *J* = 7.4, 3H), 0.31 (s, 3H), 0.29 (s, 3H), 0.05 (s, 3H), –0.12 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 175.7, 141.6, 141.5, 137.4, 134.3, 130.1, 129.4, 129.3, 129.2, 128.7, 128.6, 126.4, 126.2, 62.5, 43.9, 39.9, 31.1, 25.9, 19.5, –1.4, –1.6, –3.7, –5.0; IR (KBr) 1752, 1403 cm^{-1}; HRMS (CI/isobutane) *m* / *z* calcd for $C_{29}H_{37}ClNO_3SSi_2$ $(M + H)^+$ 570.1721, found 570.1716. Anal. Calcd for $C_{29}H_{36}ClNO_3SSi_2$: C, 61.14; H, 6.37; N, 2.46. Found: C, 61.28; H, 6.51; N, 2.46. **5a**: mp 132–133 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.49-7.12 (m, 15H), 4.23 (td, *J* = 10.1, 3.0 Hz, 1H), 3.47 (s, 1H), 2.31 (dq, *J* = 12.2, 7.0 Hz, 1H), 1.17 (dd, *J* = 12.2, 10.3 Hz, 1H), 1.06 (d, *J* = 7.0 Hz, 3H), 0.98 (dd, *J* = 15.1, 3.1 Hz, 1H), 0.87 (dd, *J* = 15.1, 10.1 Hz, 1H), 0.33 (s, 3H), 0.30 (s, 3H), 0.09 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 180.2, 142.04, 142.01, 138.8, 134.2, 129.6, 129.3, 129.26, 129.2, 129.1, 128.4, 126.32, 126.28, 79.8, 44.8, 40.4, 39.1, 25.3, 17.2, –1.4, –2.3, –3.1, –3.2; IR (KBr) 1759, 1255 cm^{-1}; HRMS (CI/isobutane) *m* / *z* calcd for $C_{29}H_{37}O_2Si_2$ $(M + H)^+$ 473.2332, found 473.2326. Anal. Calcd for $C_{29}H_{36}O_2Si_2$: C, 73.68; H, 7.68. Found: C, 73.39; H, 7.69.



2b **5b** **4b**

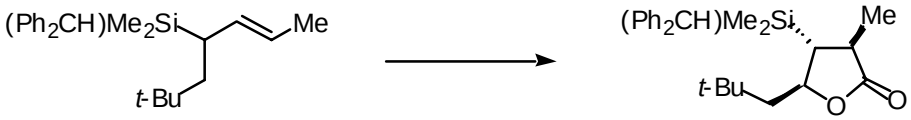
(4*R,3*S**,5*S**)-4-Benzhydryldimethylsilyl-3,5-methyl-2-furanone (5b) and (4*R**,3*S**,5*S**)-4-Benzhydryldimethylsilyl-3,5-methyl-2-pyrrolidinone (4b).** To a cooled (0 °C) solution of **2b** (0.060 g, 0.20 mmol) in 5 mL of CH_2Cl_2 was added chlorosulfonyl isocyanate (0.021 mL, 0.24 mmol). After 2 h, 2 mL of 25% aqueous Na_2SO_3 was added. The reaction mixture was then stirred vigorously at 22 °C for 12 h. The layers were separated and the aqueous layer was extracted with 3 × 10 mL of CH_2Cl_2. The combined organic layers were washed with 5 mL of brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by flash chromatography (10:90 to 80:20 EtOAc/hexanes) afforded **5b** as a colorless oil (0.011 g, 16%, 95:5 diastereomer ratio as determined by GC analysis of the unpurified reaction mixture) and **4b**[3] as a white solid (0.178 g, 77%, 98:2 diastereomer ratio as determined by GC analysis of the unpurified reaction mixture). **5b**: GC t_R 9.2 min (DB-1, 1 min at 200 °C then ramped to 250 °C at 5 °C / min, 16 psi); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26 (m, 8H), 7.15 (m, 2H), 4.28 (dq, *J* = 10.3, 6.0 Hz, 1H), 3.58 (s, 1H), 2.41 (dq, *J* = 12.2, 7.1 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.13 (d, *J* = 7.0 Hz, 3H and m, 1H), 0.16 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 180.2, 141.9, 129.25, 129.21, 129.16, 126.3, 77.8, 44.8, 39.3, 38.6, 22.4, 17.3, –3.3, –3.4; IR (thin film) 2974, 1769 cm^{-1}; HRMS (FAB) *m* / *z* calcd for $C_{21}H_{27}O_2Si$ $(M + H)^+$ 339.1780, found 339.1782. Anal. Calcd for $C_{21}H_{26}O_2Si$: C, 74.52; H, 7.75. Found: C, 74.59; H, 7.92.



2c **5c** **4c**

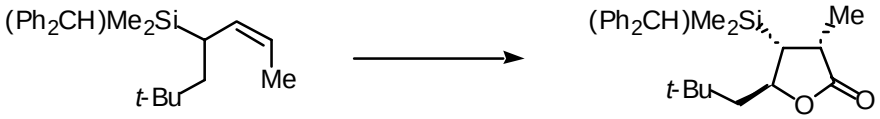
(4*R,3*S**,5*S**)-4-Benzhydryldimethylsilyl-3-methyl-5-phenyl-2-furanone (5c) and (4*R**,3*S**,5*S**)-4-Benzhydryldimethylsilyl-3-methyl-5-phenyl-2-pyrrolidinone (4c).** To a cooled (0 °C) solution of **2c** (0.107 g, 0.300 mmol) in 3 mL of CH_2Cl_2 was added chlorosulfonyl isocyanate (0.065 mL, 0.75 mmol). After 3 h, 3

mL of saturated aqueous $NaHCO_3$ was added. The mixture was extracted with 3 × 10 mL of EtOAc. The combined organic layers were washed with 5 mL of brine, dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was diluted with 3 mL of CH_2Cl_2, and 3 mL of 25% aqueous Na_2SO_3 was added. The reaction mixture was then stirred vigorously at 22 °C for 12 h. The layers were separated and the aqueous layer was extracted with 3 × 10 mL of CH_2Cl_2. The combined organic layers were washed with 5 mL of brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was dissolved in 3 mL of THF, and 0.3 mL of HCl (1.0 N, 0.30 mmol) was added. The reaction mixture was stirred at 22 °C for 12 h, and 2 mL of saturated aqueous $NaHCO_3$ was added, the mixture was extracted with 3 × 20 mL of CH_2Cl_2. The combined organic layers were washed with 5 mL of brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by flash chromatography (5:95 to 80:20 EtOAc/hexanes) afforded **5c** as a colorless viscous oil (0.036 g, 30%, 98:2 diastereomer ratio as determined by GC analysis of the unpurified reaction mixture) and **4c** as a white solid (0.068 g, 57%, ≥ 99:1 diastereomer ratio as determined by GC analysis of the unpurified reaction mixture). **5c**: GC t_R 11.3 min (DB-1, 1 min at 200 °C then ramped to 275 °C at 10 °C / min, 16 psi); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.45-7.15 (m, 13H), 7.01 (d, *J* = 7.0 Hz, 2H), 5.13 (d, *J* = 11.1 Hz, 1H), 3.44 (s, 1H), 2.60 (dq, *J* = 12.4, 7.0 Hz, 1H), 1.68 (dd, *J* = 12.2, 11.1 Hz, 1H), 1.27 (d, *J* = 7.0 Hz, 3H), 0.12 (s, 3H), 0.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 179.4, 141.5, 141.2, 138.5, 129.3, 128.8, 128.7, 128.6, 127.6, 125.8, 125.7, 83.1, 44.2, 39.4, 38.7, 17.0, –2.9, –3.1; IR (thin film) 3025, 2969, 1770 cm^{-1}; HRMS (CI/NH_3) *m* / *z* calcd for $C_{26}H_{29}O_2Si$ $(M + H)^+$ 401.1937, found 401.1936. Anal. Calcd for $C_{26}H_{28}O_2Si$: C, 77.96; H, 7.05. Found: C, 77.57; H, 7.15. **4c**: GC t_R 12.8 min (DB-1, 1 min at 200 °C then ramped to 275 °C at 10 °C / min, 16 psi); mp 142–144 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34-7.06 (m, 13H), 6.94 (d, *J* = 7.4 Hz, 2H), 6.04 (s, 1H), 4.39 (d, *J* = 8.4 Hz, 1H), 3.45 (s, 1H), 2.33 (dq, *J* = 9.9, 7.0 Hz, 1H), 1.34 (dd, *J* = 9.7, 8.6 Hz, 1H), 1.09 (d, *J* = 7.0 Hz, 3H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 180.2, 142.8, 141.9, 141.7, 128.9, 128.7, 128.6, 128.5, 128.3, 127.1, 125.6, 125.5, 59.0, 44.1, 39.4, 38.9, 18.5, –3.1, –3.5; IR (KBr) 3186, 1686 cm^{-1}; HRMS (CI/NH_3) *m* / *z* calcd for $C_{26}H_{30}ONSi$ $(M + H)^+$ 400.2096, found 400.2097. Anal. Calcd for $C_{26}H_{29}ONSi$: C, 78.15; H, 7.31; N, 3.51. Found: C, 77.95; H, 7.38; N, 3.40.



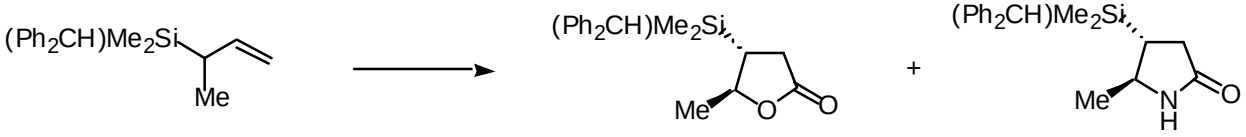
2d **5d**

(4*R,3*S**,5*S**)-4-Benzhydryldimethylsilyl-3-methyl-5-(2,2-dimethylpropyl)-2-furanone (5d).** To a solution of chlorosulfonyl isocyanate (0.065 mL, 0.75 mmol) in 1 mL of CH_2Cl_2 was added 4-methyl-2,6-di-*tert*-butylpyridine (0.020 g, 0.10 mmol) at 22 °C. After 10 min, this mixture was added to a solution of **2d** (0.105 g, 0.300 mmol) in 2 mL of CH_2Cl_2 at –50 °C. After 24 h, 3 mL of saturated aqueous $NaHCO_3$ was added. The mixture was extracted with 3 × 10 mL of EtOAc. The combined organic layers were washed with 5 mL of brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was then dissolved in 3 mL of THF, and 0.3 mL of HCl (1.0 N, 0.30 mmol) was added and the reaction mixture was stirred at 22 °C. After 12 h, 2 mL of saturated aqueous $NaHCO_3$ was added. The mixture was extracted with 3 × 20 mL of CH_2Cl_2. The combined organic layers were washed with 5 mL of brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by flash chromatography (3:97 to 5:95 EtOAc/hexanes) afforded **5d** as a white solid (0.073 g, 61%, 97:3 diastereomer ratio as determined by GC analysis of the unpurified reaction mixture): GC t_R 11.8 min (DB-1, 1 min at 200 °C then ramped to 250 °C at 5 °C / min, 16 psi); mp 96–98 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29-7.22 (m, 8H), 7.16 (m, 2H), 4.27 (td, *J* = 10.0, 1.0 Hz, 1H), 3.56 (s, 1H), 2.36 (dq, *J* = 12.1, 7.0 Hz, 1H), 1.32 (dd, *J* = 15.1, 9.6 Hz, 1H), 1.24 (dd, *J* = 15.1, 1.0 Hz, 1H), 1.13 (m, 1H and d, *J* = 7.0 Hz, 3H), 0.91 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 180.5, 142.0, 129.3, 129.24, 129.20, 129.14, 126.4, 126.3, 79.0, 50.9, 44.8, 38.2, 37.2, 31.0, 30.4, 17.4, –3.0, –3.2; IR (KBr) 2958, 1762 cm^{-1}; HRMS (CI/isobutane) *m* / *z* calcd for $C_{25}H_{35}O_2Si$ $(M + H)^+$ 395.2406, found 395.2406. Anal. Calcd for $C_{25}H_{34}O_2Si$: C, 76.10; H, 8.69. Found: C, 76.22; H, 8.83.



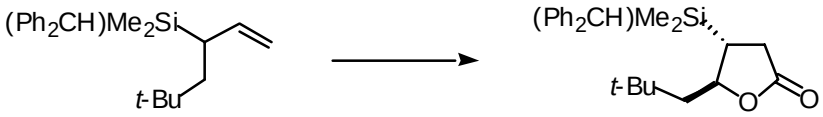
2e **5e**

(3*R,4*R**,5*S**)-4-Benzhydryldimethylsilyl-3-methyl-5-(2,2-dimethylpropyl)-2-furanone (5e).** Using the procedure given for **5a** with **2e** (0.105 g, 0.300 mmol), chlorosulfonyl isocyanate (0.065 mL, 0.75 mmol) and HCl (1.0 N, 0.30 mL, 0.30 mmol) afforded **5e**, after purification by flash chromatography (3:97 to 5:95 EtOAc/hexanes), as a colorless oil (0.096 g, 81%, 94:6 diastereomer ratio as determined by GC analysis of the unpurified reaction mixture): GC t_R 12.7 min (DB-1, 1 min at 200 °C then ramped to 250 °C at 5 °C / min, 16 psi); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29-7.14 (m, 10H), 4.55 (td, *J* = 9.5, 1.3 Hz, 1H), 3.68 (s, 1H), 2.36 (quintet, *J* = 7.8 Hz, 1H), 1.50 (dd, *J* = 9.3, 8.3 Hz, 1H), 1.42 (dd, *J* = 15.0, 9.6 Hz, 1H), 1.26 (m, 1H and d, *J* = 7.5 Hz, 3H), 0.93 (s, 9H), 0.21 (s, 3H), 0.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 180.0, 140.99, 140.98, 128.45, 128.43, 128.39, 125.6, 125.5, 79.2, 49.3, 44.6, 38.0, 35.0, 30.6, 30.1, 14.9, –1.8, –2.2; IR (thin film) 2955, 1770 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{25}H_{35}O_2Si$ $(M + H)^+$ 395.2406, found 395.2397. Anal. Calcd for $C_{25}H_{34}O_2Si$: C, 76.10; H, 8.69. Found: C, 75.95; H, 8.85.



2f **5f** **4f**

(4*R,5*S**)-4-Benzhydryldimethylsilyl-5-methyl-2-furanone (5f) and (4*R**,5*S**)-4-Benzhydryldimethylsilyl-5-methyl-2-pyrrolidinone (4f).** The procedure given for **5b** and **4b** with **2f** (0.140 g, 0.500 mmol), chlorosulfonyl isocyanate (0.108 mL, 1.25 mmol) and 25% Na_2SO_3 (5 mL) was followed. Purification by flash chromatography (10:90 to 80:20 EtOAc/hexanes) afforded **5f** as a colorless oil (0.060 g, 37%, 91:9 diastereomer ratio as determined by GC analysis of the unpurified reaction mixture) and **4f** as a white solid (0.066 g, 42%, 91:9 diastereomer ratio as determined by GC analysis of the unpurified reaction mixture). **5f**: GC t_R 9.2 min (DB-1, 1 min at 200 °C then ramped to 250 °C at 5 °C / min, 16 psi); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24 (m, 8H), 7.10 (m, 2H), 4.38 (dq, *J* = 10.1, 6.0 Hz, 1H), 3.54 (s, 1H), 2.24 (dd, *J* = 17.7, 9.8 Hz, 1H), 2.20 (dd, *J* = 17.8, 11.8 Hz, 1H), 1.38 (m, 1H), 1.26 (d, *J* = 6.0 Hz, 3H), 0.14 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 177.0, 141.4, 141.3, 128.81, 128.79, 128.7, 128.6, 125.9, 80.0, 44.7, 32.6, 30.8, 22.2, –3.3, –4.6; IR (thin film) 2901, 1768 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{20}H_{24}O_2Si$ (M^+) 324.1545, found 324.1540. Anal. Calcd for $C_{20}H_{24}O_2Si$: C, 74.03; H, 7.45. Found: C, 74.29; H, 7.55. **4f**: GC t_R 11.0 min (DB-1, 1 min at 200 °C then ramped to 250 °C at 5 °C / min, 16 psi); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (m, 8H), 7.20 (m, 2H), 6.95 (s, 1H), 3.62 (m, 2H), 2.24 (dd, *J* = 17.2, 10.2 Hz, 1H), 2.12 (dd, *J* = 17.2, 10.2 Hz, 1H), 1.24 (td, *J* = 10.3, 7.9 Hz, 1H), 1.12 (d, *J* = 6.1 Hz, 3H), 0.17 (s, 3H), 0.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 178.1, 141.83, 141.79, 128.7, 128.6, 125.7, 52.4, 44.6, 33.5, 28.8, 23.7, –3.6, –4.7; IR (KBr) 3180, 1697 cm^{-1}; HRMS (CI/NH_3) *m* / *z* calcd for $C_{20}H_{26}ONSi$ $(M + H)^+$ 324.1784, found 324.1784. Anal. Calcd for $C_{20}H_{25}ONSi$: C, 74.26; H, 7.80; N, 4.33. Found: C, 74.15; H, 7.82; N, 4.34.

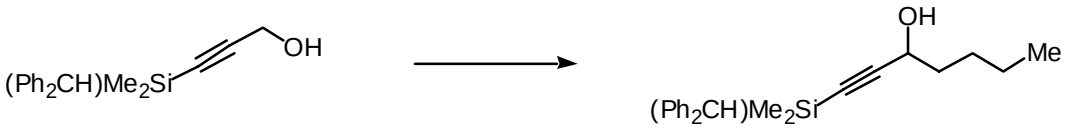


2g **5g**

(4*R,5*S**)-4-Benzhydryldimethylsilyl-5-(2,2-dimethylpropyl)-2-furanone (5g).** The same procedure given for **5a** was followed. The reagents used were: **2g** (0.101 g, 0.300 mmol), *N*-chlorosufonyl isocyanate (0.039 mL, 0.45 mmol), 1.0 N HCl (0.45 mL, 0.45 mmol). Purification by flash chromatography (3:97 to 5:95

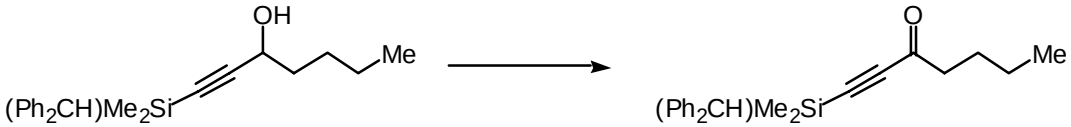
EtOAc/hexanes) afforded **5g** as a white solid (0.094 g, 82%, 96:4 diastereomer ratio as determined by GC analysis of the unpurified reaction mixture): GC t_R 8.7 min (DB-1, 1 min at 200 °C then ramped to 275 °C at 10 °C / min, 16 psi); mp 64–66 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31–7.15 (m, 10H), 4.39 (t, J = 9.7 Hz, 1H), 3.54 (s, 1H), 2.18 (m, 2H), 1.47 (dd, J = 15.1, 9.6 Hz, 1H), 1.39 (q, J = 10.7 Hz, 1H), 1.29 (d, J = 15.1 Hz, 1H), 0.92 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 177.9, 141.80, 141.76, 129.3, 129.2, 129.01, 128.96, 126.33, 126.31, 81.4, 50.7, 44.8, 31.8, 30.9, 30.3, 29.5, –3.1, –4.5; IR (thin film) 2956, 1769 cm^{-1}; HRMS (CI/isobutane) m / z calcd for $C_{24}H_{33}O_2Si$ $(M + H)^+$ 381.2249, found 381.2251. Anal. Calcd for $C_{24}H_{32}O_2Si$: C, 75.75; H, 8.48. Found: C, 75.71; H, 8.56.

III. Enantioselective Synthesis of (+)-Blastmycinone



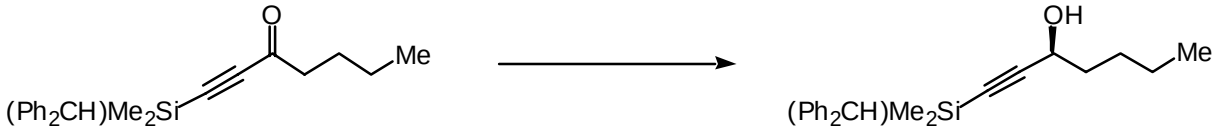
22 (±)-**12**

(±)-1-(Benzhydryldimethylsilyl)-1-heptyn-3-ol (12). To a solution of **22** (3.70 g, 13.2 mmol) in 30 mL of CH_2Cl_2 was added PCC (8.60 g, 40.0 mmol) and NaOAc (0.164 g, 2.00mmol). After 4 h at 22 °C, 100 mL of Et_2O was added. The mixture was filtered through a plug of silica gel, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was dissolved in 30 mL of dry Et_2O and was added slowly through syringe pump over 20 min to a cooled (–78 °C) solution of *n*-BuLi (2.10 M solution in hexanes, 6.90 mL, 14.5 mmol) in 40 mL of dry Et_2O. After the addition, the reaction mixture was allowed to warm to –30 °C. After 3 h, 30 mL of saturated aqueous NH_4Cl was added. The layers were separated, and the aqueous layer was extracted with 3 × 50 mL of Et_2O. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash chromatography (3:97 to 5:95 EtOAc/hexanes) afforded (±)-**12** as a colorless oil (3.15 g, 71%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.32 (m, 4H), 7.25 (m, 4H), 7.14 (m, 2H), 4.31 (m, 1H), 3.59 (s, 1H), 1.82 (s, 1H), 1.65 (m, 2H), 1.41-1.31 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H), 0.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.3, 129.5, 128.8, 126.0, 109.9, 88.1, 63.4, 45.3, 37.7, 27.7, 22.9, 14.5, –1.4; IR (thin film) 3355, 2171, 1598, 1494, 1250 cm^{-1}; HRMS (CI/NH_3) m / z calcd for $C_{22}H_{32}ONSi$ $(M + NH_4)^+$ 354.2253, found 354.2254. Anal. Calcd for $C_{22}H_{28}OSi$: C, 78.53; H, 8.39. Found: C, 78.45; H, 8.44.



(±)-**12** **11**

1-(Benzhydryldimethylsilyl)-1-heptyn-3-one (11). A solution of (±)-**12** (0.800 g, 2.37 mmol) in 5 mL of CH_2Cl_2 was added to a suspension of PDC (1.34 g, 3.56 mmol) in 5 mL of CH_2Cl_2 at 22 °C. After 12 h, 20 mL of Et_2O was added. The mixture was filtered through a plug of silica gel, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by flash chromatography (2:98 EtOAc/hexanes) afforded **11** as a colorless oil (0.719 g, 91%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29 (m, 8H), 7.15 (m, 2H), 3.66 (s, 1H), 2.49 (t, J = 7.5 Hz, 2H), 1.60 (quintet, J = 7.5 Hz, 2H), 1.32 (sextet, J = 7.5 Hz, 2H), 0.91 (t, J = 7.3 Hz, 3H), 0.22 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 187.3, 140.7, 128.2, 125.5, 103.7, 95.7, 45.1, 44.2 26.2, 22.2, 14.0, –2.2; IR (thin film) 2959, 2150, 1682, 1494, 1253 cm^{-1}; HRMS (CI/NH_3) m / z calcd for $C_{22}H_{26}OSi$ (M^+) 334.1753, found 334.1741. Anal. Calcd for $C_{22}H_{26}OSi$: C, 79.00; H, 7.84. Found: C, 78.77; H, 7.89.

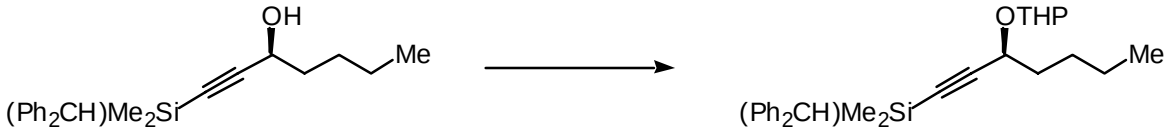


11 (*S*)-**12**

(–)-(*S*)-1-(Benzhydryldimethylsilyl)-1-heptyn-3-ol (12). A 50 mL of Schlenk flask was charged with Noyori's ruthenium catalyst[5] (0.032 g, 0.054 mmol), **11** (0.600 g, 1.79 mmol), and *i*-PrOH (18 mL). The orange-brown reaction mixture was stirred for 2 h at 22 °C, then transferred to a round bottom flask and concentrated *in vacuo* to afford a brown oil. Purification by flash chromatography (5:95 to 10:90 EtOAc/hexanes) afforded (*S*)-**12** as a colorless oil (0.596 g, 99%). The product was identical to (±)-**12** by ^{1}H NMR and ^{13}C NMR spectroscopic analyses (*vide supra*): $[\alpha]^{23}_D$ –5.9 (*c* 1.25, $CHCl_3$).

Preparation of Mosher Ester[6] of (±)-12. To a solution of (±)-**12** (0.013 g, 0.040 mmol) in 0.50 mL of CH_2Cl_2 was added successively 4-(*N*,*N*-dimethylamino)pyridine (0.005 g, 0.04 mmol), triethylamine (0.028 mL, 0.20 mmol) and (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (0.015 mL, 0.080 mmol). The reaction mixture was stirred at 22 °C for 3 h, and ethanolamine (0.027 mL, 0.44 mmol) was added. The resultant mixture was filtered through a plug of silica gel, washing with 25:75 EtOAc/hexanes. The filtrate was concentrated *in vacuo*. ^{1}H NMR spectroscopic and capillary GC analyses indicated a 1:1 ratio of diastereomers: t_R 11.2 min; t_R 11.3 min, DB-1, 1 min at 200 °C then ramped at 10 °C/min to 275 °C, 16 psi.

Preparation of Mosher Ester[6] of (–)-(*S*)-12. The procedure given for the preparation of the Mosher ester of (±)-**12** was followed. The reagents used were: (S)-**12** (0.013 g, 0.040 mmol), 4-(*N*,*N*-dimethylamino)pyridine (0.005 g, 0.04 mmol), triethylamine (0.028 mL, 0.20 mmol), (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (0.015 mL, 0.080 mmol) and ethanolamine (0.027 mL, 0.44 mmol). ^{1}H NMR spectroscopic and capillary GC analyses indicated a 98.7:1.3 ratio of diastereomers: (*S*, *S*)-isomer: t_R 11.2 min; (*S*, *R*)- isomer: t_R 11.3 min, DB-1, 1 min at 200 °C then ramped at 10 °C/min to 275 °C, 16 psi.



(*S*)-**12** **25**

2-[3-(Benzyhydryldimethylsilyl)-1-butyl-2-propynyloxy)tetrahydropyran (25). To a cooled (0 °C) solution of (*S*)-**12** (1.60 g, 4.74 mmol) and CSA (0.012 g, 0.05 mmol) in 10 mL of CH_2Cl_2 was added 3,4-dihydro-2*H*-pyran (0.48 mL, 5.22 mmol) dropwise by addition funnel over a period of 1 h. Upon completion of the addition, the ice bath was removed and the reaction mixture was allowed to warm to 22 °C. After 2 h, the reaction mixture was transferred to a separatory funnel with 5 mL of saturated aqueous $NaHCO_3$. The organic layer was separated and washed with 5 mL of brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash chromatography (3:97 to 5:95 EtOAc/hexanes) afforded **25** as a colorless oil (1.91 g, 96%). ^{1}H NMR spectroscopic analysis indicated that the acetal was an approximately 60:40 mixture of diastereomers: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35 (m, 8H, major+minor), 7.24 (m, 8H, major+minor), 4.88 (t, *J* = 3.5 Hz, 1H, minor), 4.76 (t, *J* = 3.2 Hz, 1H, major), 4.39 (t, *J* = 6.8 Hz, 1H, minor), 4.26 (t, *J* = 6.8 Hz, 1 H, major), 3.95 (td, *J* = 10.8, 2.8 Hz, 1H, major), 3.79 (ddd, *J* = 11.4, 8.5, 2.9 Hz, 1H, minor), 3.57 (s, 1H, major), 3.56 (s, 1H, minor), 3.50 (m, 1H, minor), 3.43 (m, 1H, major), 1.87–1.29 (m, 24H, major+minor), 0.91 (t, *J* = 7.2 Hz, 3H, minor), 0.90 (t, *J* = 7.2 Hz, 3H, major), 0.132 (s, 6H, minor), 0.130 (s, 6H, major); ^{13}C NMR ($CDCl_3$, 125 MHz) major isomer: δ 141.9, 128.96, 128.15, 125.28, 108.3, 97.8, 87.1, 67.6, 61.8, 44.7, 35.3, 30.4, 27.3, 25.4, 22.4, 18.8, 14.0, –1.9. Characteristic signals of the minor isomer: 141.8, 128.91, 128.17, 125.32, 107.3, 95.4, 87.9, 65.3, 62.2, 35.19, 30.45, 27.5, 19.3; IR (thin film) 2955, 2170, 1597, 1494 cm^{-1}; HRMS (FAB) *m* / *z* calcd for $C_{27}H_{37}O_2Si$ $(M + H)^+$ 421.2562, found 421.2573. Anal. Calcd for $C_{27}H_{36}O_2Si$: C, 77.10; H, 8.63. Found: C, 76.93; H, 8.65.

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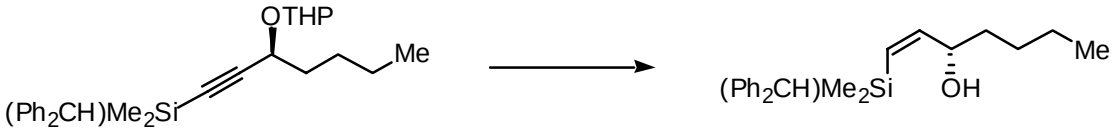
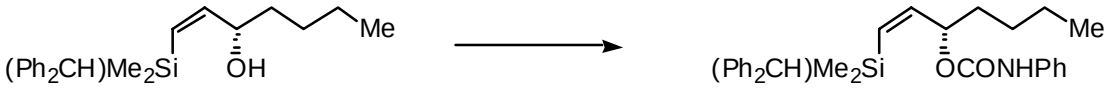
[5] Hashiguchi, S.; Fujii, A.; Haack, K.-J.; Matsumura, K.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 288-290.

[6] Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543–2549.



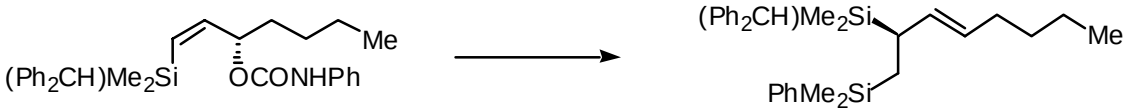
25 **26**

(–)-(*S*)-(*Z*)-1-(Benzhydryldimethylsilyl)-1-hepten-3-ol (26). Following the previous procedure[3] with **25** (1.90 g, 4.52 mmol), BH_3·DMS (0.640 mL, 6.78 mmol), cyclohexene (1.37 mL, 13.6 mmol), acetic acid (0.65 mL, 11.3 mmol) and *p*-TsOH (0.085 g, 0.045 mmol) afforded **26**, after purification by flash chromatography (3:97 to 5:95 EtOAc/hexanes), as a colorless oil (1.38 g, 90%) with a *Z*/*E* ratio > 99:1 as indicated by capillary GC analysis of the unpurified reaction mixture: GC t_R 6.2 min (DB-1, 1 min at 200 °C then ramped to 250 °C at 5 °C / min, 16 psi); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25 (m, 8H), 7.14 (m, 2H), 6.21 (dd, *J* = 14.2, 9.0 Hz, 1H), 5.63 (d, *J* = 14.2 Hz, 1H), 3.82 (m, 1H), 3.62 (s, 1H), 1.44 (m, 1H), 1.28 (m, 4H), 1.16 (m, 1H), 1.03 (d, *J* = 3.1 Hz, 1 H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.22 (s, 3H), 0.12 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.6, 142.2, 142.1, 128.7, 128.6, 128.13, 128.12, 127.9, 125.2, 125.1, 72.4, 46.0, 36.5, 27.7, 22.9, 14.3, –0.5, –0.8; IR (thin film) 3416, 2956, 2859, 1597 cm^{-1}; $[\alpha]^{23}_D$ –33.0 (*c* 1.03, $CHCl_3$); HRMS (FAB) *m* / *z* calcd for $C_{22}H_{30}OSiNa$ $(M + Na)^+$ 361.1964, found 361.1957. Anal. Calcd for $C_{22}H_{30}OSi$: C, 78.06; H, 8.94. Found: C, 77.89; H, 8.99.



26 **13**

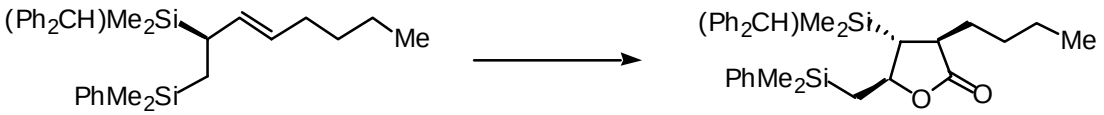
(+)-(*S*)-(*Z*)-1-(Benzhydryldimethylsilyl)-1-hepten-3-ol *N*-phenylcarbamate (13). Phenyl isocyanate (0.487 mL, 4.50 mmol) was added to **26** (1.38 g, 4.07 mmol) at 22 °C. After stirring for 18 h, the resultant slurry was diluted with hexanes and then filtered. The filtrate was concentrated *in vacuo*. Purification by flash chromatography (5:95 EtOAc/hexanes) afforded **13** as a pale yellow oil (1.83 g, 98%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37-7.01 (m, 15H), 6.57 (s, 1H), 6.23 (dd, *J* = 14.5, 9.3 Hz, 1H), 5.70 (dd, *J* = 14.5, 0.5 Hz, 1H), 5.33 (m, 1H), 3.72 (s, 1H), 1.64 (m, 1H), 1.40 (m, 1H), 1.34-1.24 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.26 (s, 3H), 0.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.8, 146.5, 142.5, 142.4, 138.0, 130.6, 129.1, 129.0, 128.9, 128.8, 128.5, 128.3, 128.27, 125.3, 125.2, 123.2, 118.5, 75.3, 45.4, 34.8, 27.2, 22.6, 14.0, –1.3, –1.4; IR (thin film) 3401, 3334, 1728, 1600, 1217 cm^{-1}; $[\alpha]^{23}_D$ +15.8 (*c* 1.10, $CHCl_3$); HRMS (CI/NH_3) *m* / *z* calcd for $C_{29}H_{36}NO_2Si$ $(M + H)^+$ 458.2515, found 458.2518. Anal. Calcd for $C_{29}H_{35}NO_2Si$: C, 76.11; H, 7.71; N, 3.06. Found: C, 75.97; H, 7.89; N, 3.03.



13 **14**

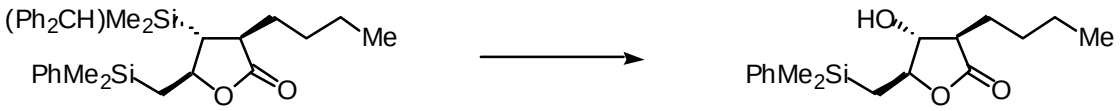
(–)-(*S*)-(*E*)-2-(Benzhydryldimethylsilyl)-1-dimethylphenylsilyl-3-octene (14). The general procedure[3,4] was followed with **13** (1.81 g, 4.00 mmol), *n*-BuLi (1.20 M solution in hexanes, 3.33 mL, 4.00 mmol), CuI (0.762 g, 4.00 mmol), LiCl (0.337 g, 8.00 mmol), and (dimethylphenylsilyl)methylmagnesium chloride (0.730 M solution in THF, 6.03 mL, 4.40 mmol). Purification by flash chromatography (hexanes) afforded **14** as a colorless oil (1.66 g, 88%) with a *E*/*Z* ratio of 98:2 and γ:α ratio of > 99:1 as indicated by capillary GC analysis of the unpurified reaction mixture and an ee of 95% as determined by chiral HPLC analysis: GC t_R 11.0 min (DB-1, 1 min at 200 °C then ramped to 275 °C at 10 °C / min, 16 psi); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.53-7.20 (m, 15H), 5.19 (m, 2H), 3.79 (s, 1H), 2.05 (m, 2H), 1.78 (m, 1H), 1.44 (m, 4H), 1.05 (t, *J* = 6.7 Hz, 3H), 0.92 (dd, *J* = 14.7, 3.9 Hz, 1H), 0.86 (d, *J* = 14.7 Hz, 1H), 0.33 (s, 3H), 0.26 (s, 3H), 0.16 (s, 3H), 0.13 (s, 3H); ^{13}C NMR

($CDCl_3$, 125 MHz) δ 142.8, 142.7, 140.1, 133.6, 132.0, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 127.6, 125.2, 125.1, 43.4, 32.5, 32.0, 26.0, 22.4, 14.5, 14.1, –1.8, –2.7, –5.0, –5.5; IR (thin film) 2923, 1596, 1247, 1113 cm^{-1}; $[\alpha]^{23}_D$ –3.90 (*c* 1.07, $CHCl_3$); HRMS (FAB) *m* / *z* calcd for $C_{31}H_{43}Si_2$ $(M + H)^+$ 471.2903, found 471.2916. Anal. Calcd for $C_{31}H_{42}Si_2$: C, 79.10; H, 9.00. Found: C, 78.80; H, 8.96.



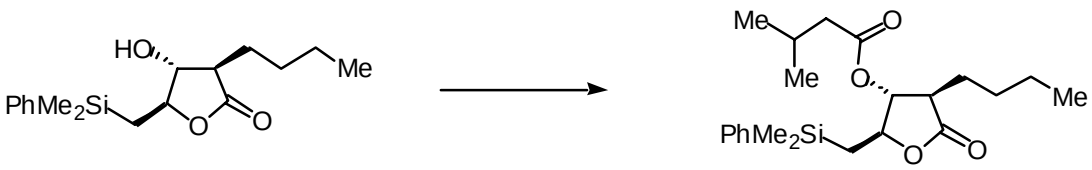
14 **15**

(–)-(4*R*,3*S*,5*S*)-4-Benzhydryldimethylsilyl-3-butyl-5-dimethylphenylsilylmethyl-2-furanone (15). The procedure given for **5a** was followed with **14** (0.775 g, 1.65 mmol), chlorosulfonyl isocyanate (0.360 mL, 4.10 mmol), and HCl (1.0 N, 3.2 mL, 3.2 mmol). Purification by flash chromatography (3:97 to 5:95 EtOAc/hexanes) afforded **15** as a colorless oil (0.606 g, 72%, 97:3 diastereomer ratio as determined by GC analysis of the unpurified reaction mixture, 94% ee as determined by chiral HPLC analysis): GC t_R 17.4 min (DB-1, 1 min at 200 °C then ramped to 275 °C at 10 °C / min, 16 psi); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.50-7.12 (m, 15H), 4.24 (m, 1H), 3.47 (s, 1H), 2.36 (ddd, *J* = 10.8, 7.3, 4.5 Hz, 1H), 1.50 (m, 1H), 1.42 (m, 1H), 1.31 (dd, *J* = 10.7, 8.9 Hz, 1H), 1.17 (m, 3H), 1.07 (m, 1H), 0.92 (m, 2H), 0.85 (t, *J* = 6.9 Hz, 3H), 0.34 (s, 3H), 0.31 (s, 3H), 0.06 (s, 3H), 0.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 179.2, 141.52, 141.50, 138.3, 133.6, 129.1, 128.74, 128.72, 128.6, 127.8, 125.8, 79.1, 44.1, 43.0, 35.6, 30.7, 28.0, 25.6, 22.7, 13.9, –2.0, –2.9, –3.95, –4.04; IR (thin film) 2955, 1760, 1252 cm^{-1}; $[\alpha]^{23}_D$ –15.0 (*c* 1.07, $CHCl_3$); HRMS (FAB) *m* / *z* calcd for $C_{32}H_{43}O_2Si_2$ $(M + H)^+$ 515.2801, found 515.2803. Anal. Calcd for $C_{32}H_{42}O_2Si_2$: C, 74.65; H, 8.22. Found: C, 74.76; H, 8.28.



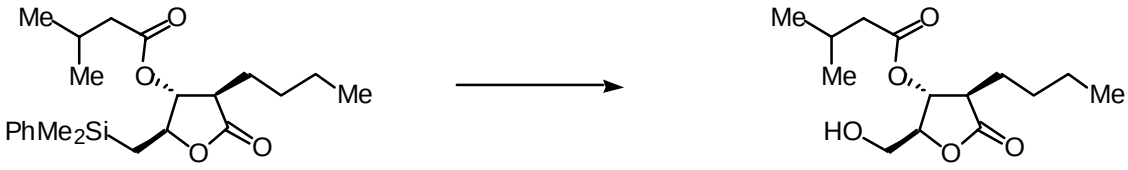
15 **27**

(–)-(3*R*,4*R*,5*S*)-3-Butyl-5-dimethylphenylsilylmethyl-4-hydroxy-2-furanone (27). A round-bottom flask was charged with CsF (0.880 g, 5.90 mmol). The flask was then heated under vacuum with a heat gun for 5 min. After cooling to room temperature, the flask was backfilled with nitrogen and the dry methanol (5 mL) and THF (5 mL) were sequentially added to the flask. A solution of **15** (0.606 g, 1.18 mmol) in 5 mL of THF was then added. After 6 h at 22 °C, the reaction mixture was partitioned between 10 mL of water and 20 mL of CH_2Cl_2, the layers were separated, and the aqueous layer was extracted with 3 × 20 mL of CH_2Cl_2. The combined organic layers were washed with 10 mL of brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was then dissolved in 5 mL of THF, and then MeOH (2 mL), $KHCO_3$ (0.118 g, 1.18 mmol), KF (0.137 g, 2.36 mmol), and H_2O_2 (30 %, 2.70 mL, 23.6 mmol) were sequentially added. The reaction mixture was vigorously stirred at 22 °C for 12 h, and then partitioned between 5 mL of water and 10 mL of CH_2Cl_2. The layers were separated and the aqueous layer was extracted with 3 × 20 mL of CH_2Cl_2. The combined organic layers were washed with 10 mL of brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash chromatography (5:95 to 10:90 EtOAc/hexanes) afforded **27** as a colorless oil (0.293 g, 81%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55 (m, 2H), 7.39 (m, 3H), 4.16 (dd, *J* = 14.5, 7.1 Hz, 1H), 3.67 (dd, *J* = 8.5, 7.1 Hz, 1H), 2.44 (ddd, *J* = 8.6, 7.5, 5.7 Hz, 1H), 2.24 (br, 1H), 1.76 (m, 1H), 1.50 (m, 1H), 1.45-1.25 (m, 6H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.42 (s, 3H), 0.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 176.4, 137.9, 133.5, 129.5, 128.1, 82.5, 79.5, 48.4, 28.7, 28.0, 22.6, 21.3, 13.8, –1.8, –3.1; IR (thin film) 3453, 1748 cm^{-1}; $[\alpha]^{23}_D$ –17.1 (*c* 0.94, $CHCl_3$); HRMS (CI/NH_3) *m* / *z* calcd for $C_{17}H_{25}O_2Si$ $(M - OH)^+$ 289.1624, found 289.1626. Anal. Calcd for $C_{17}H_{26}O_3Si$: C, 66.62; H, 8.55. Found: C, 66.42; H, 8.52.



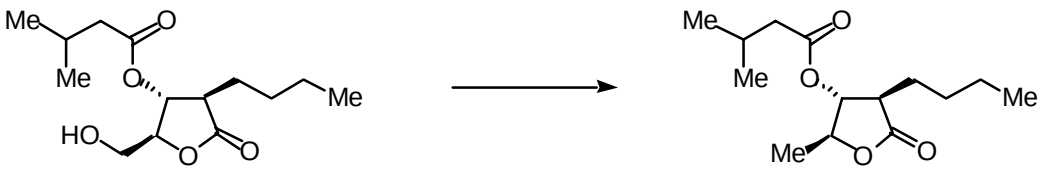
27 **16**

(–)-(3*R*,4*R*,5*S*)-3-Butyl-5-dimethylphenylsilylmethyl-4-(3-methylbutyryloxy)-2-furanone (16). To a solution of **27** (0.260 g, 0.850 mmol) in 10 mL of CH_2Cl_2 were added triethylamine (0.296 mL, 2.10 mmol), 4-(*N*,*N*-dimethylamino)pyridine (0.021 g, 0.085 mmol), and isovaleroyl chloride (0.256 mL, 2.10 mmol). After stirring at 22 °C for 12 h, 5 mL of saturated aqueous $NaHCO_3$ and 10 mL of CH_2Cl_2 were added. The layers were separated, and the aqueous layer was washed with 3 × 10 mL of CH_2Cl_2. The combined organic layers were washed with 10 mL of brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford a yellow oil. Purification by flash chromatography (3:97 to 5:95 EtOAc/hexanes) afforded **16** as a colorless oil (0.296 g, 89%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (m, 2H), 7.36 (m, 3H), 4.91 (dd, *J* = 5.1, 4.3 Hz, 1H), 4.33 (ddd, *J* = 9.6, 5.2, 4.3 Hz, 1H), 2.55 (dt, *J* = 8.2, 5.6 Hz, 1H), 2.16 (d, *J* = 7.2 Hz, 2H), 2.06 (m, 1H), 1.80 (m, 1H), 1.57 (m, 1H), 1.43-1.28 (m, 4H and dd, *J* = 14.9, 5.3 Hz, 1H), 1.25 (dd, *J* = 14.9, 9.7 Hz, 1H), 0.93 (d, *J* = 6.6 Hz, 6H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.40 (s, 3H), 0.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.0, 172.2, 137.4, 133.5, 129.3, 127.9, 81.6, 79.3, 46.6, 43.0, 29.1, 28.9, 25.6, 22.3, 22.23, 22.17, 13.7, –2.1, –2.9; IR (thin film) 2959, 1778, 1742 cm^{-1}; $[\alpha]^{23}_D$ –13.3 (*c* 1.18, $CHCl_3$); HRMS (CI/NH_3) *m* / *z* calcd for $C_{21}H_{31}O_4Si$ $(M - Me)^+$ 375.1991, found 375.1991. Anal. Calcd for $C_{22}H_{34}O_4Si$: C, 67.65; H, 8.77. Found: C, 67.91; H, 8.71.



16 **28**

(+)-(3*R*,4*R*,5*S*)-3-Butyl-5-hydroxymethyl-4-(3-methylbutyryloxy)-2-furanone (28). Potassium bromide (0.183 g, 1.54 mmol) and anhydrous NaOAc (0.238 g, 2.90 mmol) were added to a stirred solution of **16** (0.376 g, 0.960 mmol) in 4.0 mL of AcOH (glacial). The reaction mixture was cooled to 0 °C and AcOOH (32%, 1.21 mL, 5.76 mmol) was added dropwise, during which time Br_2 was generated and the reaction mixture became orange. After the addition, more anhydrous NaOAc (0.709 g, 8.64 mmol) and AcOOH (32%, 3.64 mL, 17.3 mmol) were added. After 18 h at 22 °C, the reaction mixture was diluted with 100 mL of Et_2O, and 10 g of $Na_2S_2O_3$ was added. The reaction mixture was stirred vigorously for 30 min, filtered through Celite, washed with Et_2O, and concentrated *in vacuo*. The residue was dissolved in 50 mL of EtOAc, washed with 5 mL of saturated aqueous $NaHCO_3$ and 5 mL of brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by flash chromatography (10:90 to 20:80 EtOAc/hexanes) afforded **28** as a colorless oil (0.192 g, 73%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.20 (dd, *J* = 5.9, 4.7 Hz, 1H), 4.30 (dt, *J* = 4.6, 3.4 Hz, 1H), 3.94 (ddd, *J* = 12.4, 6.0, 3.1 Hz, 1H), 3.86 (ddd, *J* = 12.4, 7.0, 3.7 Hz, 1H), 2.75 (dt, *J* = 9.0, 5.6 Hz, 1H), 2.23 (d, *J* = 7.2 Hz, 2H), 2.20 (m, 1H), 2.11 (m, 1H), 1.87 (m, 1H), 1.69 (m, 1H), 1.46-1.32 (m, 4H), 0.97 (d, *J* = 7.7 Hz, 6H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 175.9, 172.8, 83.1, 74.4, 61.9, 46.0, 43.0, 28.9, 28.3, 25.7, 22.2, 13.7; IR (thin film) 3478, 2959, 1770, 1738, 1183 cm^{-1}; $[\alpha]^{23}_D$ +10.7 (*c* 1.16, $CHCl_3$); HRMS (CI/NH_3) *m* / *z* calcd for $C_{14}H_{25}O_5$ $(M + H)^+$ 273.1702, found 273.1703. Anal. Calcd for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.45; H, 8.91.

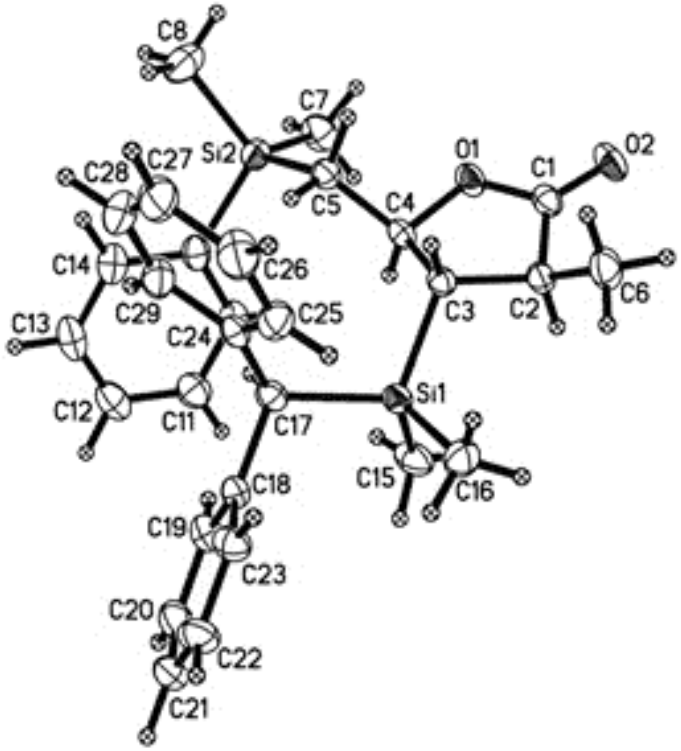


28 **1**

(+)-(3*R*,4*R*,5*S*)-3-Butyl-5-methyl-4-(3-methylbutyryloxy)-2-furanone [(+)-blastmycinone] (1). To a solution of **28** (0.108 g, 0.400 mmol) in 4 mL of dry CH_3CN was added PPh_3 (0.210 g, 0.800 mmol) and CBr_4 (0.265 g, 0.800 mmol). After stirring at 22 °C for 12 h, the reaction mixture was concentrated *in vacuo*. The residue was dissolved in 10 mL of Et_2O. The suspension was filtered and the filtrate was evaporated. The unpurified bromide was dissolved in 4 mL of degassed toluene, and AIBN (0.006 g, 0.04 mmol) and tributyltin hydride (0.108 mL, 0.400 mmol) were added. The mixture was heated at reflux for 7 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo*. Purification by flash chromatography (5:95 EtOAc/hexanes) afforded **1** as a colorless oil (0.081 g, 79%). Spectral data were identical to that reported in the literature[7]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.94 (dd, *J* = 5.7, 4.7 Hz, 1H), 4.36 (qd, *J* = 6.6, 4.6 Hz, 1H), 2.68 (dt, *J* = 8.4, 5.8 Hz, 1H), 2.22 (d, *J* = 7.0 Hz, 2H), 2.10 (m, 1H), 1.86 (m, 1H), 1.64 (m, 1H), 1.47 (d, 6.6 Hz, 3H), 1.45-1.25 (m, 4H), 0.97 (d, *J* = 6.6 Hz, 6H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 175.4, 172.0, 79.2, 78.3, 46.4, 43.2, 29.1, 29.0, 25.8, 22.5, 22.4, 19.4, 13.9; IR (thin film) 2960, 1784, 1742 cm^{-1}; $[\alpha]^{23}_D$ +10.4 (*c* 1.39, $CHCl_3$) {lit.[7] $[\alpha]^{20}_D$ +11.3 (*c* 1.18, $CHCl_3$)}; HRMS (CI/isobutane) *m* / *z* calcd for $C_{14}H_{25}O_4$ $(M + H)^+$ 257.1753, found 257.1746.

IV. X-ray Analysis of Compound 5a

[7] Sibi, M. P.; Lu, J.; Talbacka, C. L. *J. Org. Chem.* **1996**, *61*, 7848-7855.



X-ray Data Collection, Structure Solution and Refinement for 5a. A colorless crystal of approximate dimensions 0.19 x 0.30 x 0.32 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[1] program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group P1 was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}). At convergence, wR2 = 0.0974 and GOF = 1.031 for 442 variables refined against 6293 unique data. As a comparison for refinement on F, R1 = 0.0359 for those 5306 data with $I > 2.0\sigma(I)$.

References.

1. SMART Software Users Guide, Version 5.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.

2. SAINT Software Users Guide, Version 6.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.

3. Sheldrick, G. M. SADABS, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1997.

4. Sheldrick, G. M. SHELXTL Version 5.10, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1997.

5. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer AcademicPublishers.

Definitions:

$wR2 = [\Sigma[w(F_o^2-F_o^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

Goof = $S = [\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

Table 1. Crystal data and structure refinement for 5a.

Empirical formula	$C_{29}\ H_{36}\ O_2\ Si_2$	
Formula weight	472.76	
Temperature	158(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.2736(10) Å	α= 92.620(2)°.
	b = 11.0058(11) Å	β= 108.969(2)°.
	c = 12.7257(13) Å	γ = 98.752(2)°.
Volume	1337.9(2) Å^3	
Z	2	
Density (calculated)	1.174 Mg/m^3	
Absorption coefficient	0.156 mm^{-1}	
F(000)	508	
Crystal size	0.32 x 0.30 x 0.19 mm^3	
Theta range for data collection	1.70 to 28.27°.	
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $-16 \le l \le 16$	
Reflections collected	14372	
Independent reflections	6293 [R(int) = 0.0234]	
Completeness to theta = 28.27°	94.9 %	
Absorption correction	None	
Max. and min. transmission	0.9710 and 0.9519	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6293 / 0 / 442	
Goodness-of-fit on F^2	1.031	
Final R indices [I > 2sigma(I)]	R1 = 0.0359, wR2 = 0.0915	
R indices (all data)	R1 = 0.0446, wR2 = 0.0974	
Largest diff. peak and hole	0.332 and -0.229 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 5a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	2521(1)	6422(1)	1906(1)	22(1)
Si(2)	7358(1)	8712(1)	4349(1)	25(1)
O(1)	5012(1)	6601(1)	5150(1)	26(1)
O(2)	3826(1)	5489(1)	6071(1)	33(1)
C(1)	3847(1)	5915(1)	5218(1)	24(1)
C(2)	2654(1)	5778(1)	4113(1)	23(1)
C(3)	3150(1)	6813(1)	3480(1)	20(1)
C(4)	4748(1)	7056(1)	4036(1)	21(1)
C(5)	5455(1)	8403(1)	4217(1)	24(1)
C(6)	1263(2)	5817(2)	4290(1)	35(1)
C(7)	8324(2)	7673(2)	5311(1)	35(1)
C(8)	8040(2)	10377(2)	4866(2)	42(1)
C(9)	7487(1)	8360(1)	2931(1)	26(1)
C(10)	7349(2)	7133(1)	2501(1)	29(1)
C(11)	7362(2)	6842(2)	1427(1)	33(1)
C(12)	7518(2)	7778(2)	761(1)	38(1)
C(13)	7666(2)	8992(2)	1165(1)	40(1)
C(14)	7652(2)	9284(2)	2237(1)	34(1)
C(15)	3259(2)	5058(2)	1578(1)	36(1)
C(16)	573(2)	6018(2)	1388(1)	34(1)
C(17)	3199(1)	7763(1)	1210(1)	23(1)
C(18)	2703(1)	7427(1)	-52(1)	24(1)
C(19)	3552(2)	6905(1)	-540(1)	31(1)
C(20)	3117(2)	6566(1)	-1684(1)	37(1)
C(21)	1828(2)	6755(1)	-2364(1)	38(1)
C(22)	970(2)	7277(1)	-1895(1)	37(1)
C(23)	1402(2)	7610(1)	-750(1)	29(1)
C(24)	2966(1)	9034(1)	1541(1)	24(1)
C(25)	1719(2)	9246(1)	1661(1)	31(1)
C(26)	1553(2)	10427(2)	1970(2)	42(1)
C(27)	2642(2)	11412(2)	2181(2)	46(1)
C(28)	3881(2)	11222(2)	2064(1)	44(1)
C(29)	4041(2)	10049(1)	1737(1)	34(1)

Table 3. Bond lengths [Å] and angles [°] for 5a.

Si(1)-C(16)	1.8661(16)
Si(1)-C(15)	1.8702(16)

Si(1)-C(3)	1.8994(12)
Si(1)-C(17)	1.9122(13)
Si(2)-C(7)	1.8648(16)
Si(2)-C(8)	1.8656(17)
Si(2)-C(9)	1.8794(14)
Si(2)-C(5)	1.8826(14)
O(1)-C(1)	1.3451(16)
O(1)-C(4)	1.4792(14)
O(2)-C(1)	1.2067(15)
C(1)-C(2)	1.5190(18)
C(2)-C(6)	1.5234(19)
C(2)-C(3)	1.5435(17)
C(2)-H(2)	0.974(15)
C(3)-C(4)	1.5368(17)
C(3)-H(3)	0.966(15)
C(4)-C(5)	1.5200(18)
C(4)-H(4)	0.993(14)
C(5)-H(5A)	0.974(16)
C(5)-H(5B)	0.930(17)
C(6)-H(6A)	1.001(19)
C(6)-H(6B)	0.975(19)
C(6)-H(6C)	0.96(2)
C(7)-H(7A)	0.95(2)
C(7)-H(7B)	0.97(2)
C(7)-H(7C)	0.89(2)
C(8)-H(8A)	1.00(2)
C(8)-H(8B)	0.94(2)
C(8)-H(8C)	0.95(2)
C(9)-C(10)	1.402(2)
C(9)-C(14)	1.4032(19)
C(10)-C(11)	1.394(2)
C(10)-H(10)	0.961(16)
C(11)-C(12)	1.387(2)
C(11)-H(11)	0.963(18)
C(12)-C(13)	1.378(2)
C(12)-H(12)	0.991(19)
C(13)-C(14)	1.392(2)
C(13)-H(13)	0.946(19)
C(14)-H(14)	0.955(18)
C(15)-H(15A)	0.96(2)
C(15)-H(15B)	0.91(3)
C(15)-H(15C)	0.97(3)
C(16)-H(16A)	0.96(2)
C(16)-H(16B)	0.93(2)
C(16)-H(16C)	0.97(2)

C(17)-C(24)	1.5188(18)
C(17)-C(18)	1.5259(17)
C(17)-H(17)	0.987(16)
C(18)-C(23)	1.3946(19)
C(18)-C(19)	1.3956(19)
C(19)-C(20)	1.391(2)
C(19)-H(19)	0.968(19)
C(20)-C(21)	1.379(2)
C(20)-H(20)	0.963(19)
C(21)-C(22)	1.388(2)
C(21)-H(21)	0.980(18)
C(22)-C(23)	1.3912(19)
C(22)-H(22)	0.972(18)
C(23)-H(23)	0.939(17)
C(24)-C(25)	1.391(2)
C(24)-C(29)	1.3960(19)
C(25)-C(26)	1.392(2)
C(25)-H(25)	0.920(17)
C(26)-C(27)	1.381(3)
C(26)-H(26)	0.95(2)
C(27)-C(28)	1.374(3)
C(27)-H(27)	0.94(2)
C(28)-C(29)	1.389(2)
C(28)-H(28)	0.98(2)
C(29)-H(29)	0.968(17)
C(16)-Si(1)-C(15)	109.13(8)
C(16)-Si(1)-C(3)	108.67(6)
C(15)-Si(1)-C(3)	109.00(6)
C(16)-Si(1)-C(17)	112.58(6)
C(15)-Si(1)-C(17)	107.01(7)
C(3)-Si(1)-C(17)	110.38(6)
C(7)-Si(2)-C(8)	112.10(9)
C(7)-Si(2)-C(9)	108.21(7)
C(8)-Si(2)-C(9)	110.98(8)
C(7)-Si(2)-C(5)	110.03(7)
C(8)-Si(2)-C(5)	107.26(7)
C(9)-Si(2)-C(5)	108.20(6)
C(1)-O(1)-C(4)	110.96(10)
O(2)-C(1)-O(1)	121.57(13)
O(2)-C(1)-C(2)	127.52(13)
O(1)-C(1)-C(2)	110.91(10)
C(1)-C(2)-C(6)	111.41(11)
C(1)-C(2)-C(3)	103.33(10)
C(6)-C(2)-C(3)	116.17(11)
C(1)-C(2)-H(2)	102.9(9)

C(6)-C(2)-H(2)	110.8(9)
C(3)-C(2)-H(2)	111.1(9)
C(4)-C(3)-C(2)	103.42(10)
C(4)-C(3)-Si(1)	114.37(8)
C(2)-C(3)-Si(1)	113.94(9)
C(4)-C(3)-H(3)	108.2(9)
C(2)-C(3)-H(3)	107.3(9)
Si(1)-C(3)-H(3)	109.2(9)
O(1)-C(4)-C(5)	107.35(10)
O(1)-C(4)-C(3)	105.55(9)
C(5)-C(4)-C(3)	115.63(10)
O(1)-C(4)-H(4)	104.4(8)
C(5)-C(4)-H(4)	111.7(8)
C(3)-C(4)-H(4)	111.2(8)
C(4)-C(5)-Si(2)	116.65(9)
C(4)-C(5)-H(5A)	108.0(9)
Si(2)-C(5)-H(5A)	109.4(9)
C(4)-C(5)-H(5B)	108.9(10)
Si(2)-C(5)-H(5B)	106.4(10)
H(5A)-C(5)-H(5B)	107.0(14)
C(2)-C(6)-H(6A)	109.1(11)
C(2)-C(6)-H(6B)	111.0(11)
H(6A)-C(6)-H(6B)	108.7(15)
C(2)-C(6)-H(6C)	110.4(12)
H(6A)-C(6)-H(6C)	110.0(16)
H(6B)-C(6)-H(6C)	107.6(16)
Si(2)-C(7)-H(7A)	111.8(13)
Si(2)-C(7)-H(7B)	110.9(13)
H(7A)-C(7)-H(7B)	103.4(18)
Si(2)-C(7)-H(7C)	112.7(15)
H(7A)-C(7)-H(7C)	105.8(19)
H(7B)-C(7)-H(7C)	111.8(19)
Si(2)-C(8)-H(8A)	112.1(13)
Si(2)-C(8)-H(8B)	107.5(14)
H(8A)-C(8)-H(8B)	110.1(19)
Si(2)-C(8)-H(8C)	113.0(14)
H(8A)-C(8)-H(8C)	106.7(18)
H(8B)-C(8)-H(8C)	107.4(19)
C(10)-C(9)-C(14)	117.13(13)
C(10)-C(9)-Si(2)	120.30(10)
C(14)-C(9)-Si(2)	122.50(11)
C(11)-C(10)-C(9)	121.47(13)
C(11)-C(10)-H(10)	117.9(9)
C(9)-C(10)-H(10)	120.6(9)
C(12)-C(11)-C(10)	119.89(15)

C(12)-C(11)-H(11)	121.4(10)
C(10)-C(11)-H(11)	118.7(10)
C(13)-C(12)-C(11)	119.87(14)
C(13)-C(12)-H(12)	121.2(11)
C(11)-C(12)-H(12)	118.9(11)
C(12)-C(13)-C(14)	120.28(14)
C(12)-C(13)-H(13)	117.7(11)
C(14)-C(13)-H(13)	122.0(11)
C(13)-C(14)-C(9)	121.35(15)
C(13)-C(14)-H(14)	119.3(10)
C(9)-C(14)-H(14)	119.3(10)
Si(1)-C(15)-H(15A)	110.4(13)
Si(1)-C(15)-H(15B)	112.5(15)
H(15A)-C(15)-H(15B)	107.3(19)
Si(1)-C(15)-H(15C)	111.2(14)
H(15A)-C(15)-H(15C)	105.4(18)
H(15B)-C(15)-H(15C)	110(2)
Si(1)-C(16)-H(16A)	112.8(12)
Si(1)-C(16)-H(16B)	109.9(13)
H(16A)-C(16)-H(16B)	109.2(17)
Si(1)-C(16)-H(16C)	110.8(12)
H(16A)-C(16)-H(16C)	106.4(16)
H(16B)-C(16)-H(16C)	107.4(17)
C(24)-C(17)-C(18)	113.42(10)
C(24)-C(17)-Si(1)	116.47(9)
C(18)-C(17)-Si(1)	109.77(9)
C(24)-C(17)-H(17)	107.6(9)
C(18)-C(17)-H(17)	105.6(9)
Si(1)-C(17)-H(17)	102.8(9)
C(23)-C(18)-C(19)	117.80(12)
C(23)-C(18)-C(17)	122.05(12)
C(19)-C(18)-C(17)	120.15(12)
C(20)-C(19)-C(18)	121.47(14)
C(20)-C(19)-H(19)	120.2(11)
C(18)-C(19)-H(19)	118.3(11)
C(21)-C(20)-C(19)	120.02(15)
C(21)-C(20)-H(20)	121.9(11)
C(19)-C(20)-H(20)	118.0(11)
C(20)-C(21)-C(22)	119.42(13)
C(20)-C(21)-H(21)	122.1(11)
C(22)-C(21)-H(21)	118.5(11)
C(21)-C(22)-C(23)	120.57(15)
C(21)-C(22)-H(22)	120.1(10)
C(23)-C(22)-H(22)	119.3(11)
C(22)-C(23)-C(18)	120.71(14)

C(22)-C(23)-H(23)	119.4(10)
C(18)-C(23)-H(23)	119.9(10)
C(25)-C(24)-C(29)	117.59(13)
C(25)-C(24)-C(17)	123.05(12)
C(29)-C(24)-C(17)	119.36(13)
C(24)-C(25)-C(26)	121.09(15)
C(24)-C(25)-H(25)	121.0(10)
C(26)-C(25)-H(25)	117.9(11)
C(27)-C(26)-C(25)	120.24(16)
C(27)-C(26)-H(26)	119.9(13)
C(25)-C(26)-H(26)	119.9(13)
C(28)-C(27)-C(26)	119.56(15)
C(28)-C(27)-H(27)	121.5(12)
C(26)-C(27)-H(27)	119.0(12)
C(27)-C(28)-C(29)	120.33(16)
C(27)-C(28)-H(28)	121.5(12)
C(29)-C(28)-H(28)	118.2(12)
C(28)-C(29)-C(24)	121.16(16)
C(28)-C(29)-H(29)	118.9(10)
C(24)-C(29)-H(29)	120.0(10)

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for 5a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	26(1)	21(1)	18(1)	3(1)	6(1)	5(1)
Si(2)	24(1)	24(1)	26(1)	2(1)	8(1)	2(1)
O(1)	28(1)	30(1)	19(1)	8(1)	7(1)	6(1)
O(2)	47(1)	35(1)	24(1)	12(1)	19(1)	13(1)
C(1)	32(1)	23(1)	23(1)	4(1)	14(1)	9(1)
C(2)	29(1)	22(1)	22(1)	4(1)	12(1)	4(1)
C(3)	23(1)	19(1)	20(1)	3(1)	9(1)	5(1)
C(4)	24(1)	24(1)	17(1)	6(1)	8(1)	7(1)
C(5)	26(1)	23(1)	22(1)	3(1)	8(1)	5(1)
C(6)	29(1)	44(1)	35(1)	8(1)	16(1)	2(1)
C(7)	30(1)	44(1)	30(1)	7(1)	7(1)	9(1)
C(8)	38(1)	31(1)	55(1)	-7(1)	16(1)	-4(1)
C(9)	23(1)	30(1)	29(1)	8(1)	11(1)	5(1)
C(10)	30(1)	30(1)	31(1)	9(1)	14(1)	7(1)
C(11)	34(1)	36(1)	33(1)	4(1)	14(1)	10(1)
C(12)	37(1)	52(1)	29(1)	10(1)	16(1)	10(1)
C(13)	43(1)	45(1)	38(1)	21(1)	20(1)	9(1)
C(14)	35(1)	30(1)	41(1)	11(1)	16(1)	5(1)

C(15)	59(1)	28(1)	26(1)	3(1)	16(1)	16(1)
C(16)	30(1)	36(1)	30(1)	6(1)	4(1)	-4(1)
C(17)	22(1)	26(1)	19(1)	4(1)	5(1)	6(1)
C(18)	29(1)	22(1)	20(1)	5(1)	8(1)	3(1)
C(19)	33(1)	35(1)	29(1)	6(1)	15(1)	6(1)
C(20)	51(1)	34(1)	33(1)	3(1)	25(1)	4(1)
C(21)	60(1)	30(1)	21(1)	2(1)	15(1)	-1(1)
C(22)	46(1)	35(1)	22(1)	5(1)	0(1)	7(1)
C(23)	34(1)	29(1)	24(1)	4(1)	7(1)	11(1)
C(24)	31(1)	24(1)	17(1)	7(1)	6(1)	5(1)
C(25)	36(1)	25(1)	34(1)	3(1)	15(1)	5(1)
C(26)	58(1)	32(1)	49(1)	7(1)	31(1)	15(1)
C(27)	78(1)	23(1)	47(1)	5(1)	33(1)	9(1)
C(28)	59(1)	27(1)	42(1)	7(1)	17(1)	-5(1)
C(29)	36(1)	30(1)	31(1)	9(1)	10(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 5a.

	x	y	z	U(eq)
H(2)	2662(15)	4966(14)	3779(12)	25(4)
H(3)	2805(16)	7540(14)	3651(12)	25(4)
H(4)	5190(15)	6529(13)	3649(11)	20(3)
H(5A)	5341(16)	8783(15)	4880(13)	31(4)
H(5B)	4992(17)	8807(15)	3617(14)	34(4)
H(6A)	1284(19)	6661(18)	4630(15)	46(5)
H(6B)	1094(19)	5213(17)	4789(16)	45(5)
H(6C)	510(20)	5625(19)	3590(18)	59(6)
H(7A)	7970(20)	6820(20)	5045(18)	64(6)
H(7B)	8180(20)	7750(20)	6023(19)	66(6)
H(7C)	9230(30)	7790(20)	5389(19)	70(7)
H(8A)	7480(20)	10930(20)	4379(18)	65(6)
H(8B)	8010(20)	10490(20)	5600(20)	71(7)
H(8C)	8980(30)	10630(20)	4905(18)	68(6)
H(10)	7256(16)	6465(15)	2947(13)	27(4)
H(11)	7281(18)	5988(17)	1171(14)	40(5)
H(12)	7502(19)	7554(17)	-7(16)	46(5)
H(13)	7790(19)	9608(17)	694(15)	47(5)
H(14)	7719(18)	10127(17)	2494(14)	37(4)
H(15A)	2850(20)	4770(20)	800(20)	70(7)
H(15B)	3090(20)	4410(20)	1960(20)	75(7)
H(15C)	4250(30)	5280(20)	1718(19)	77(7)
H(16A)	150(20)	6565(19)	1726(16)	51(5)
H(16B)	230(20)	6025(18)	618(18)	57(6)

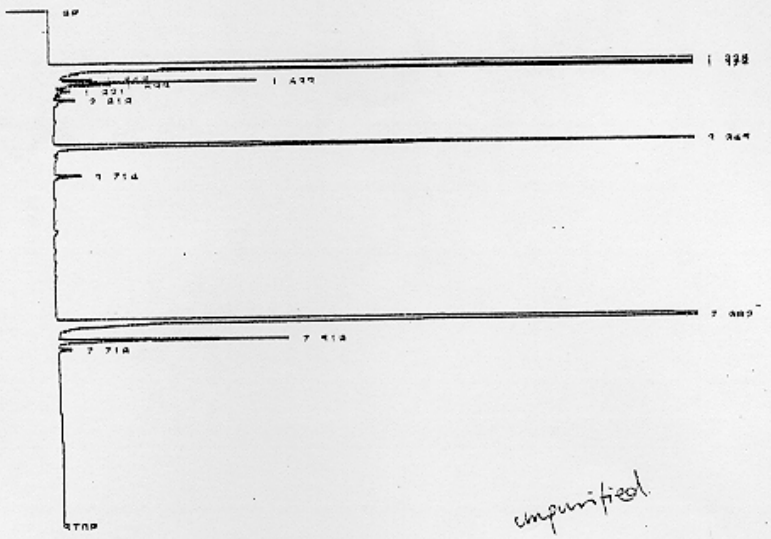
H(16C)	270(20)	5191(19)	1555(16)	54(5)
H(17)	4217(17)	7774(14)	1472(13)	28(4)
H(19)	4470(20)	6794(17)	-63(15)	45(5)
H(20)	3740(20)	6205(17)	-1976(15)	46(5)
H(21)	1496(19)	6537(17)	-3174(15)	46(5)
H(22)	55(19)	7406(16)	-2366(15)	42(5)
H(23)	801(17)	7948(15)	-446(13)	31(4)
H(25)	978(18)	8609(16)	1541(14)	35(4)
H(26)	700(20)	10552(19)	2053(17)	59(6)
H(27)	2520(20)	12198(19)	2399(16)	52(5)
H(28)	4670(20)	11905(19)	2193(17)	59(6)
H(29)	4919(18)	9939(15)	1650(14)	37(4)

Table 6. Torsion angles [°] for 5a.

C(4)-O(1)-C(1)-O(2)	-177.51(12)
C(4)-O(1)-C(1)-C(2)	2.70(14)
O(2)-C(1)-C(2)-C(6)	37.95(19)
O(1)-C(1)-C(2)-C(6)	-142.27(12)
O(2)-C(1)-C(2)-C(3)	163.38(13)
O(1)-C(1)-C(2)-C(3)	-16.84(13)
C(1)-C(2)-C(3)-C(4)	23.15(12)
C(6)-C(2)-C(3)-C(4)	145.46(12)
C(1)-C(2)-C(3)-Si(1)	147.90(8)
C(6)-C(2)-C(3)-Si(1)	-89.79(13)
C(16)-Si(1)-C(3)-C(4)	174.93(9)
C(15)-Si(1)-C(3)-C(4)	56.10(11)
C(17)-Si(1)-C(3)-C(4)	-61.16(10)
C(16)-Si(1)-C(3)-C(2)	56.26(11)
C(15)-Si(1)-C(3)-C(2)	-62.58(11)
C(17)-Si(1)-C(3)-C(2)	-179.83(9)
C(1)-O(1)-C(4)-C(5)	136.69(11)
C(1)-O(1)-C(4)-C(3)	12.81(13)
C(2)-C(3)-C(4)-O(1)	-22.23(12)
Si(1)-C(3)-C(4)-O(1)	-146.71(8)
C(2)-C(3)-C(4)-C(5)	-140.72(10)
Si(1)-C(3)-C(4)-C(5)	94.81(11)
O(1)-C(4)-C(5)-Si(2)	85.86(11)
C(3)-C(4)-C(5)-Si(2)	-156.65(9)
C(7)-Si(2)-C(5)-C(4)	-45.76(12)
C(8)-Si(2)-C(5)-C(4)	-167.94(10)
C(9)-Si(2)-C(5)-C(4)	72.28(10)
C(7)-Si(2)-C(9)-C(10)	41.51(13)
C(8)-Si(2)-C(9)-C(10)	164.90(12)

C(5)-Si(2)-C(9)-C(10)	-77.68(12)
C(7)-Si(2)-C(9)-C(14)	-141.76(12)
C(8)-Si(2)-C(9)-C(14)	-18.38(15)
C(5)-Si(2)-C(9)-C(14)	99.04(12)
C(14)-C(9)-C(10)-C(11)	-0.5(2)
Si(2)-C(9)-C(10)-C(11)	176.35(11)
C(9)-C(10)-C(11)-C(12)	0.2(2)
C(10)-C(11)-C(12)-C(13)	0.3(2)
C(11)-C(12)-C(13)-C(14)	-0.3(2)
C(12)-C(13)-C(14)-C(9)	-0.1(2)
C(10)-C(9)-C(14)-C(13)	0.5(2)
Si(2)-C(9)-C(14)-C(13)	-176.32(12)
C(16)-Si(1)-C(17)-C(24)	71.40(11)
C(15)-Si(1)-C(17)-C(24)	-168.71(10)
C(3)-Si(1)-C(17)-C(24)	-50.23(11)
C(16)-Si(1)-C(17)-C(18)	-59.21(11)
C(15)-Si(1)-C(17)-C(18)	60.68(11)
C(3)-Si(1)-C(17)-C(18)	179.16(8)
C(24)-C(17)-C(18)-C(23)	-46.54(17)
Si(1)-C(17)-C(18)-C(23)	85.68(14)
C(24)-C(17)-C(18)-C(19)	134.29(13)
Si(1)-C(17)-C(18)-C(19)	-93.49(13)
C(23)-C(18)-C(19)-C(20)	-0.6(2)
C(17)-C(18)-C(19)-C(20)	178.61(13)
C(18)-C(19)-C(20)-C(21)	0.7(2)
C(19)-C(20)-C(21)-C(22)	-0.5(2)
C(20)-C(21)-C(22)-C(23)	0.1(2)
C(21)-C(22)-C(23)-C(18)	0.0(2)
C(19)-C(18)-C(23)-C(22)	0.2(2)
C(17)-C(18)-C(23)-C(22)	-178.95(13)
C(18)-C(17)-C(24)-C(25)	86.40(15)
Si(1)-C(17)-C(24)-C(25)	-42.47(16)
C(18)-C(17)-C(24)-C(29)	-93.61(14)
Si(1)-C(17)-C(24)-C(29)	137.52(11)
C(29)-C(24)-C(25)-C(26)	-0.2(2)
C(17)-C(24)-C(25)-C(26)	179.79(13)
C(24)-C(25)-C(26)-C(27)	-1.1(2)
C(25)-C(26)-C(27)-C(28)	1.3(3)
C(26)-C(27)-C(28)-C(29)	-0.1(3)
C(27)-C(28)-C(29)-C(24)	-1.3(2)
C(25)-C(24)-C(29)-C(28)	1.4(2)
C(17)-C(24)-C(29)-C(28)	-178.59(13)

V. Analytic Data:



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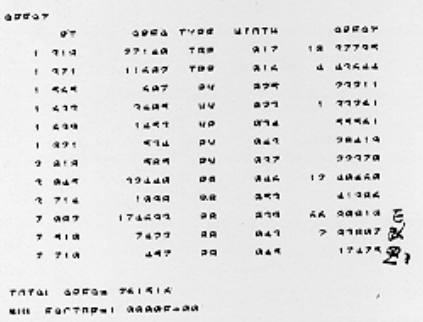
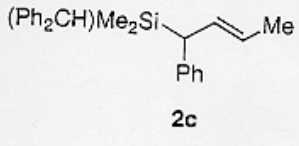


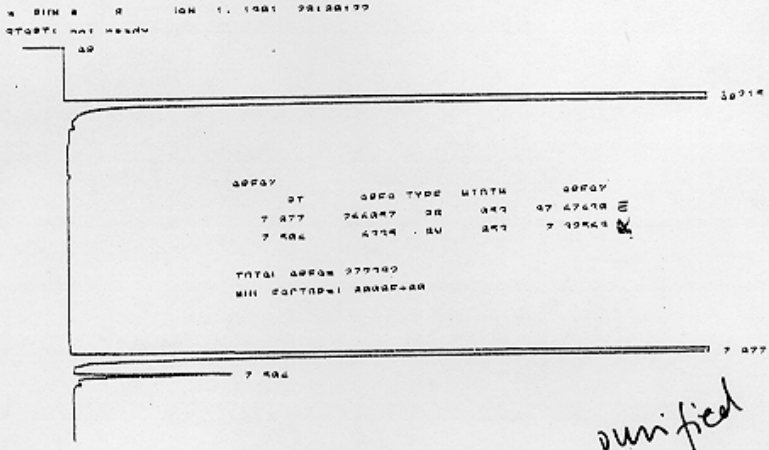


2c

E/Z ≥ 99/1

SN2'/SN2 ≥ 98/2

ZPI-94-8



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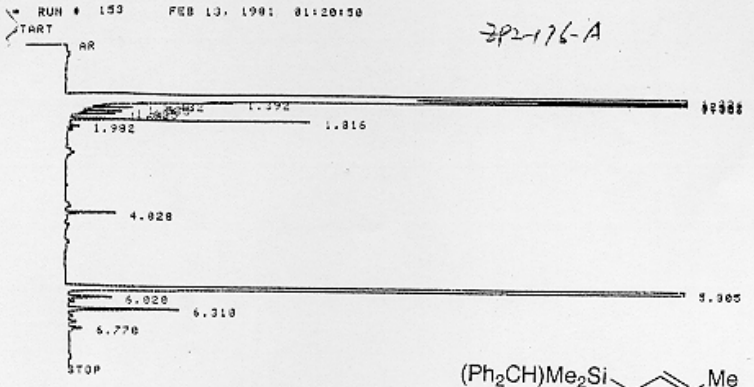

ZP2-176-A

$(Ph_2CH)Me_2Si$, Me, *t*-Bu

2d

RUN# 153 FEB 13, 1901 01:20:50

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1.392	634	TPP	.017	.22143
1.432	213	TPV	.015	.07439
1.535	627	BP	.018	.21898
1.625	588	PV	.018	.20536
1.691	505	VB	.016	.17637
1.816	3364	BB	.018	1.17488
1.982	244	BP	.027	.08522
4.328	1206	PB	.031	.42120
5.385	186638	PB	.040	65.18374 E
6.020	1385	BV	.040	.48371 Z
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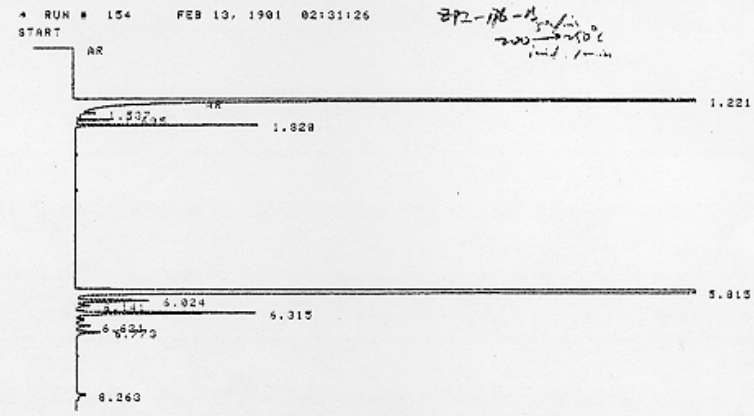
unpurified

E/Z = 98:2

γ/α > 99/1



ZP2-176-A, 200 → 250°C

AREA%

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6.024	2376	BV	.043	.74795 Z
6.141	432	VB	.043	.13597
6.315	6223	BV	.045	1.95870 Z
6.521	495	PP	.047	.15580
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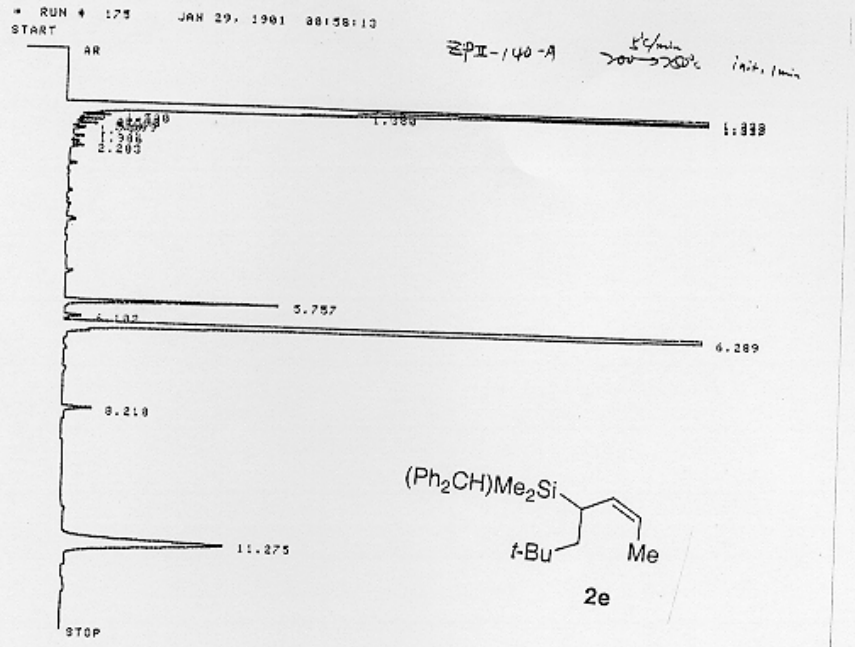
MUL FACTOR=1.0000E+00

purified

E/Z = 98/2

γ/α > 99/1



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1.598	373	VP	.021	.11544
1.699	447	VP	.025	.13834
1.797	393	PP	.041	.12163
1.986	121	PB	.016	.03745
2.203	310	VB	.033	.09842
5.757	8081	PB	.050	2.58104
6.102	663	BP	.053	.20520
6.289	216078	PB	.051	66.87280
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E/Z = 96:4 Y/N > 99:1

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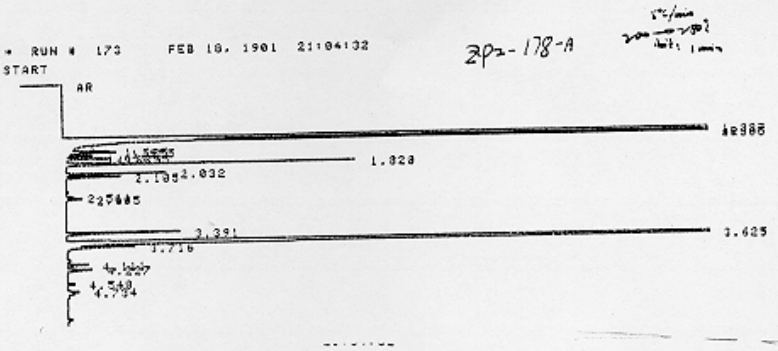

2pz-178-A

AREA%

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1.555	1262	VV	.018	.23079	
1.617	657	VP	.018	.12015	
1.675	1002	PV	.018	.18324	
1.695	1196	VP	.018	.21872	
1.820	9401	VB	.022	1.73306	
2.032	3152	BV	.021	.57643	
2.105	1875	VB	.023	.34289	
2.561	267	VV	.023	.04883	
2.605	701	VB	.028	.12820	
3.391	5204	PB	.030	.95163	
3.625	400839	PB	.031	73.15789	γ
3.716	2114	PB	.024	.38660	α
4.111	1846	VV	.032	.19129	
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4.734	655	PV	.034	.11978	
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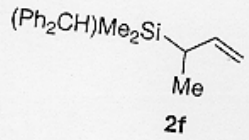
TOTAL AREA= 546816

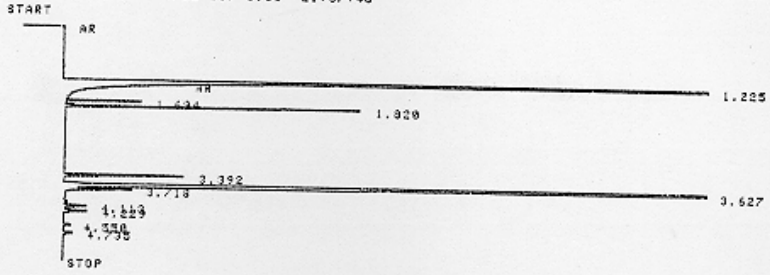
unpurified

γ/α > 99/1



2f

2pz-178-B



RUN# 175 FEB 18, 1901 21:37:46

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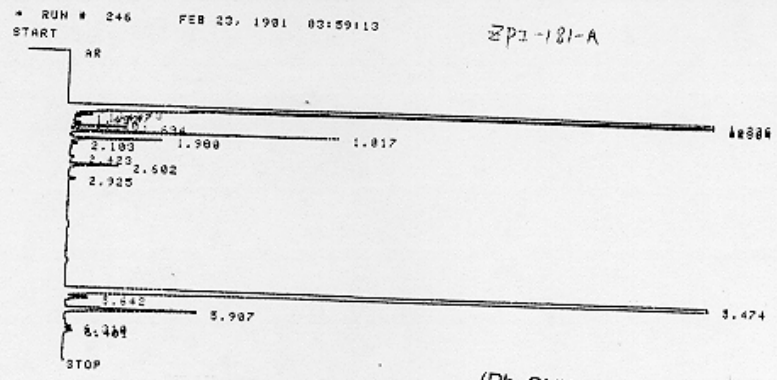
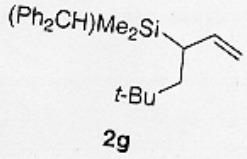
3.392	5702	PB	.031	1.27183	
3.627	424310	PV	.032	94.64432	γ
3.718	3236	VB	.032	.72179	α
4.113	1101	PB	.033	.24558	
4.229	1283	BB	.036	.28617	
4.550	403	PB	.036	.08999	
4.735	582	BB	.038	.12982	

TOTAL AREA= 448329
MUL FACTOR=1.0000E+00

purified





2g

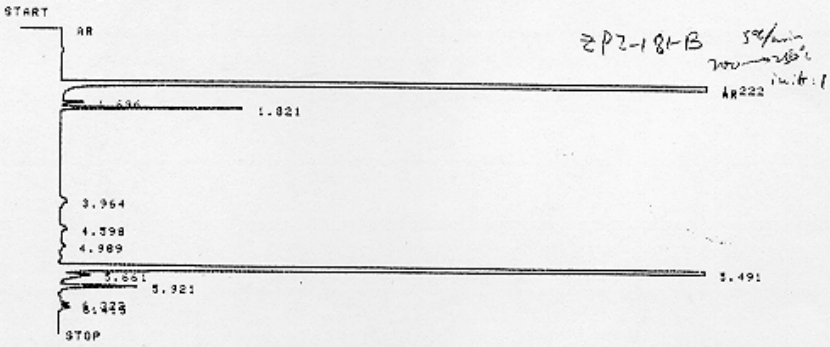
AREA%

RT	AREA	TYPE	WIDTH	AREA%
1.384	94180	TBV	.018	21.85430
1.373	332	TPP	.015	.08619
1.447	524	BP	.019	.13604
1.492	197	PB	.019	.05114
1.620	306	BV	.025	.07944
1.694	2184	VP	.026	.56708
1.817	10263	PB	.026	2.66443
1.900	4040	BB	.030	1.04884
2.103	332	BV	.035	.08619
2.423	303	PB	.043	.07866
2.502	2776	BB	.038	.72069
2.925	367	BB	.037	.09528
3.474	265630	PB	.053	68.96147 γ
3.642	1550	BP	.048	.40240
3.907	10582	PB	.054	2.74724 α
6.310	763	VV	.071	.19809
6.401	857	VB	.067	.22249

96/4

unpurified

TOTAL AREA= 385136
MUL FACTOR=1.0000E+00

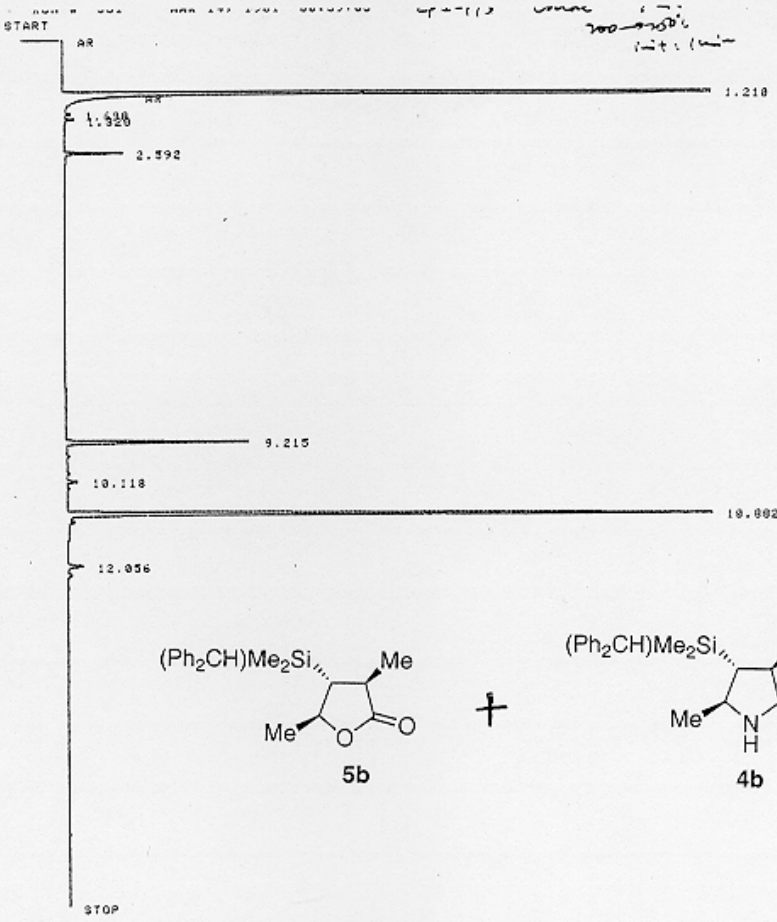


AREA%

RT	AREA	TYPE	WIDTH	AREA%
1.696	1186	BP	.036	.32463
1.821	10253	PB	.038	2.80973
3.964	1467	BP	.134	.40155
4.398	1517	VV	.138	.41523
4.989	1202	VV	.133	.32901
5.491	338445	PB	.057	92.63888 γ
5.661	3223	BP	.083	.88220
5.921	6546	PB	.057	1.79177 α
6.322	624	BV	.054	.17088
6.415	863	VB	.059	.23622

purified

TOTAL AREA= 365338
MUL FACTOR=1.0000E+00

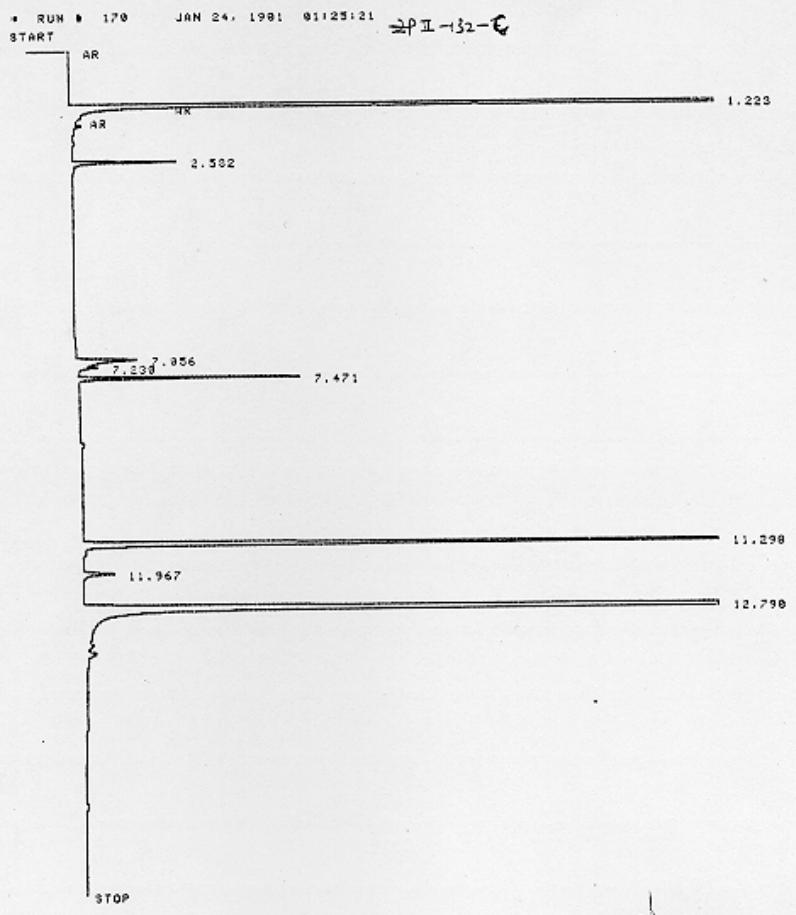


RUN# 351 MAR 14, 1991 08:59:00

AREA%

RT	AREA	TYPE	WIDTH	AREA%	
1.698	289	PB	.029	.36907	
1.828	395	BB	.027	.50444	
2.592	2664	PB	.031	3.40212	
9.215	13332	BB	.049	17.02594	] 95% lactone
10.118	799	BB	.048	1.02039	]
10.882	59453	PB	.055	75.92589	] 98% lactam
12.056	1372	PB	.060	1.75215	]

TOTAL AREA= 78304
MUL FACTOR=1.0000E+00



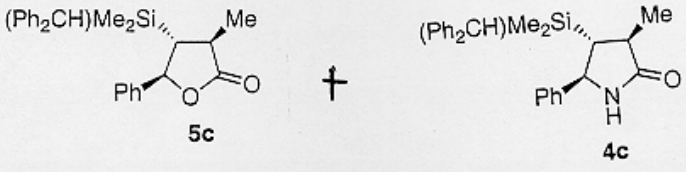
RUN# 170 JAN 24, 1991 01:25:21 unpurified

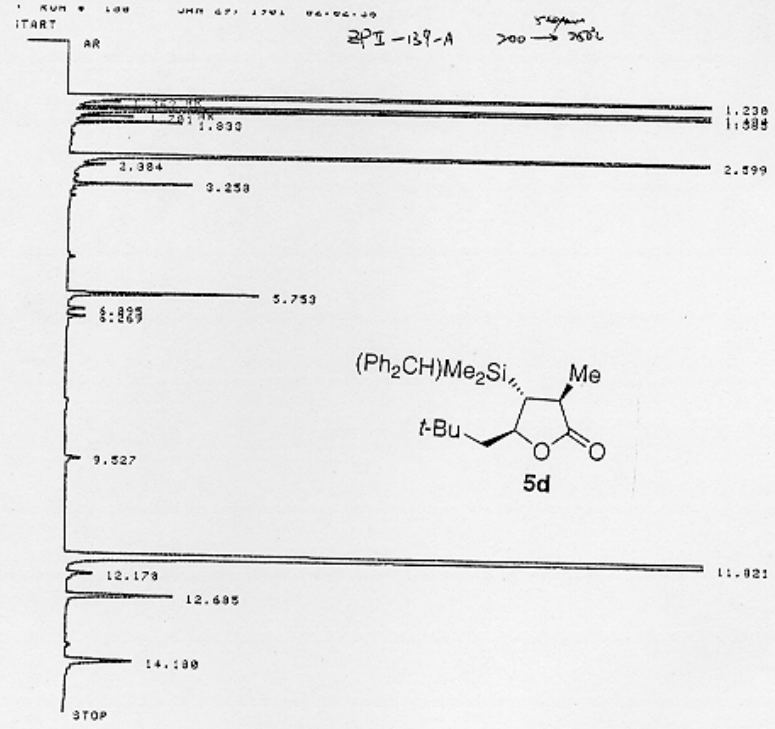
AREA%

RT	AREA	TYPE	WIDTH	AREA%
2.532	3085	BB	.040	1.97711
7.856	4069	PV	.089	2.58773
7.230	808	VB	.053	.51793
7.471	6621	PB	.040	4.24325
11.298	45893	PB	.058	29.41181
11.967	1453	BB	.062	.93128
12.798	94107	PB	.073	60.31110

97/3 lactone lactam

TOTAL AREA= 156036
MUL FACTOR=1.0000E+00





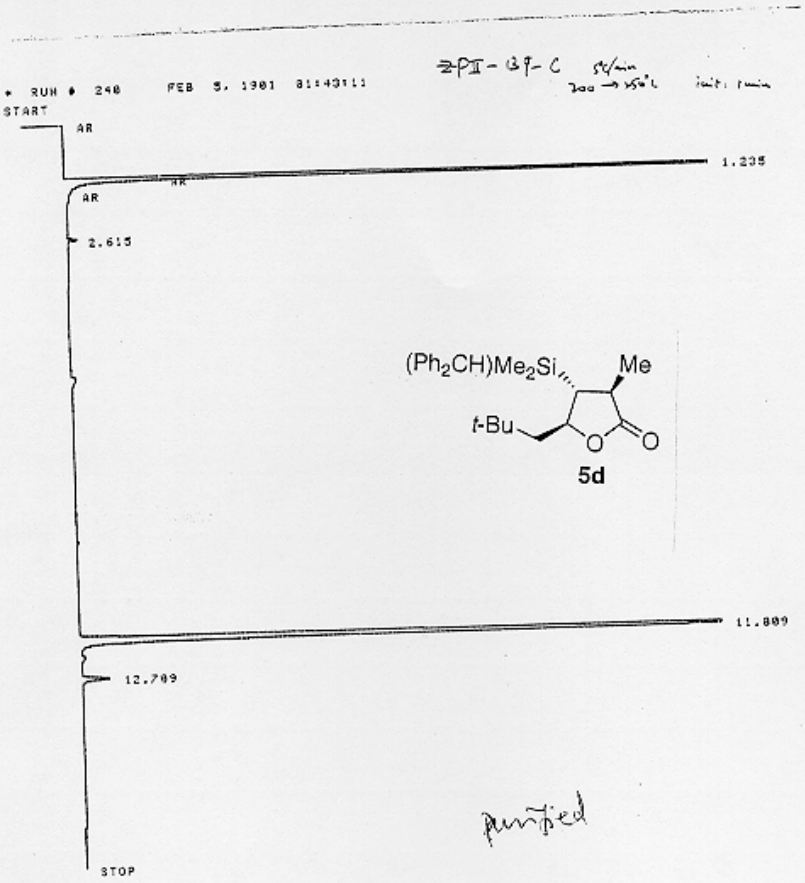
RUN# 180 JAN 29, 1901 02:02:36

AREA%

RT	AREA	TYPE	WIDTH	AREA%
1.362	288	TBB	.015	.06713
1.484	37429	BB	.016	8.72396
1.565	63081	BB	.019	14.70939
1.701	873	BP	.021	.20348
1.833	2118	VB	.026	.49366
2.599	125256	PB	.026	29.19469
2.804	636	PB	.034	.14824
3.258	2643	VB	.029	.61603
5.753	6338	PB	.044	1.47726
6.095	603	PP	.045	.14055
6.269	682	PB	.049	.15896
9.527	614	BB	.057	.14311
11.021	177303	PB	.065	41.32591
12.178	998	PB	.056	.23075
12.685	5330	BV	.066	1.24418
14.180	4045	PB	.082	.94281

97:3

TOTAL AREA= 429837
MUL FACTOR=1.0000E+00



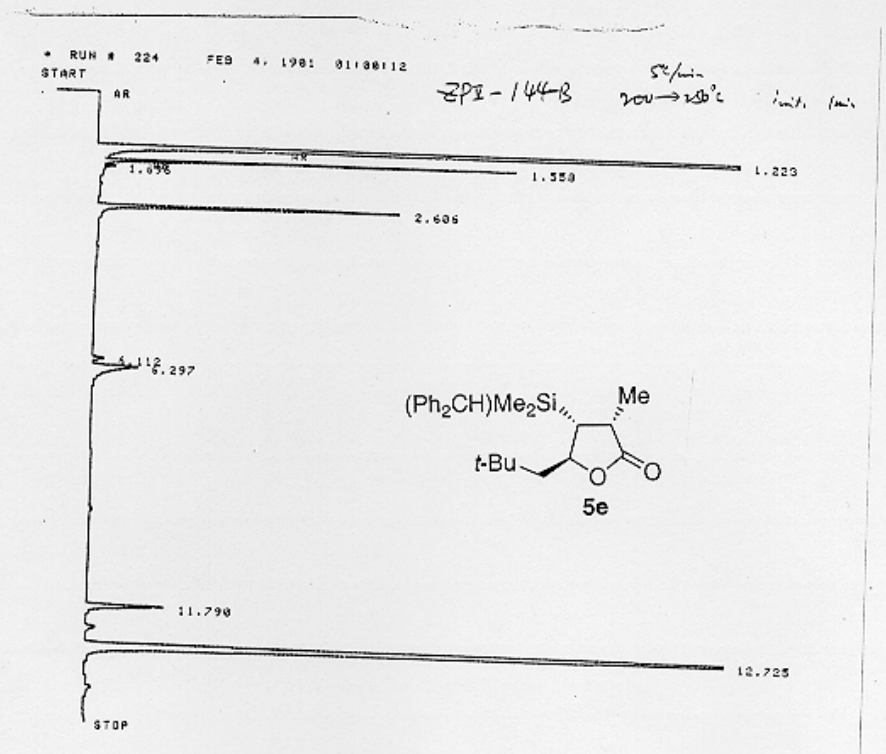
purified

RUN# 240 FEB 5, 1901 81:43:11

AREA%

RT	AREA	TYPE	WIDTH	AREA%
2.615	398	BB	.051	.57185
11.309	67571	PB	.870	97.08618
12.709	1630	BB	.077	2.34199

TOTAL AREA= 69599
MUL FACTOR=1.0000E+00



RUN# 224 FEB 4, 1981 01:08:12

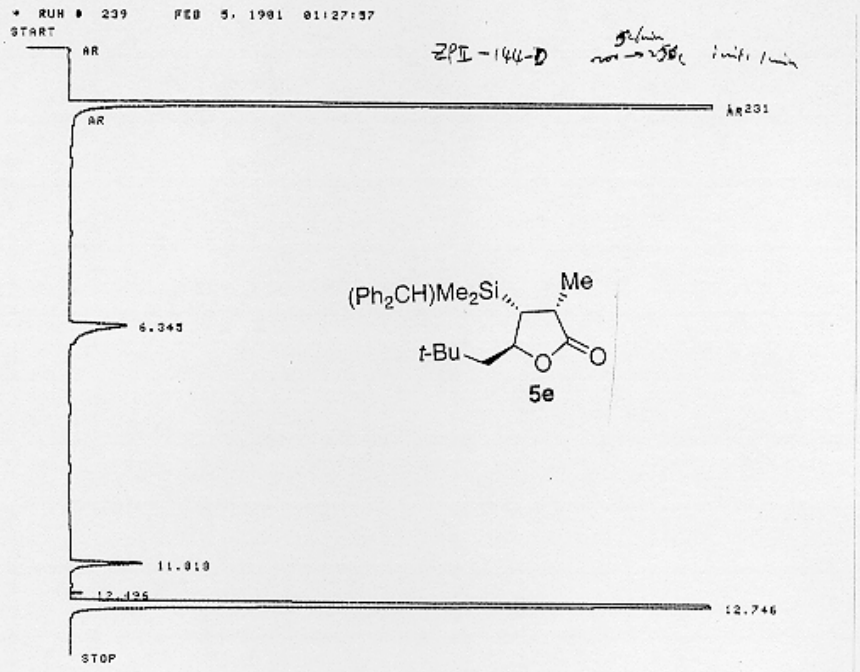
AREA%

RT	AREA	TYPE	WIDTH	AREA%
1.558	8752	PB	.029	8.66964
1.596	309	PB	.038	.30609
2.606	10659	PB	.048	10.55069
6.112	523	BP	.059	.51806
6.297	4818	PB	.138	4.76473
11.790	4507	PB	.077	4.46459
12.725	71398	PB	.079	78.71818

unpurified

94:6

TOTAL AREA= 100950
MUL FACTOR=1.0000E+00



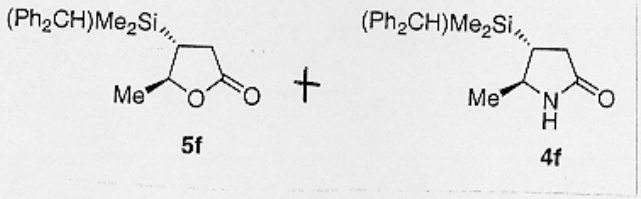
RUN# 239 FEB 5, 1901 01:27:37

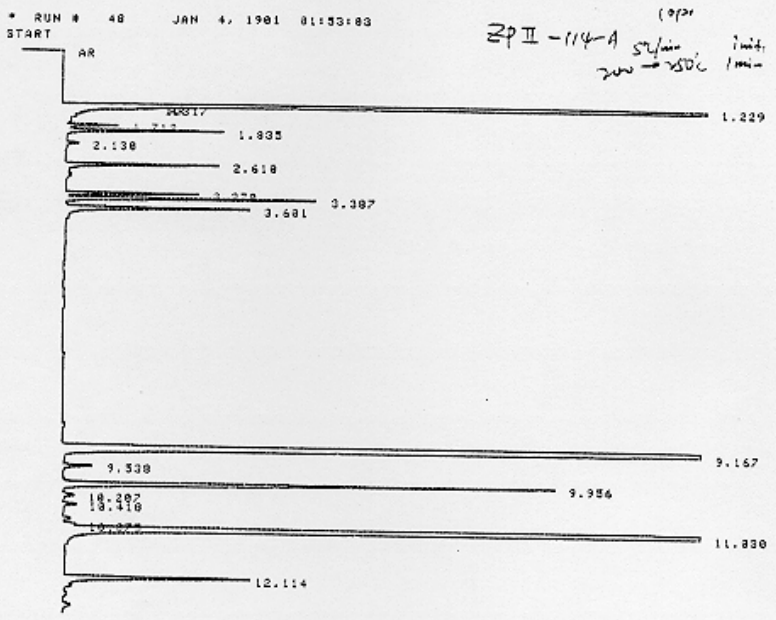
purified

AREA%

RT	AREA	TYPE	WIDTH	AREA%	
6.345	8524	BB	.199	9.21374	
11.818	4991	BB	.091	5.39486	94:6
12.496	52	BB	.085	.05621	
12.746	78947	PB	.088	85.33520	

TOTAL AREA= 92514
MUL FACTOR=1.0000E+00





AREA%

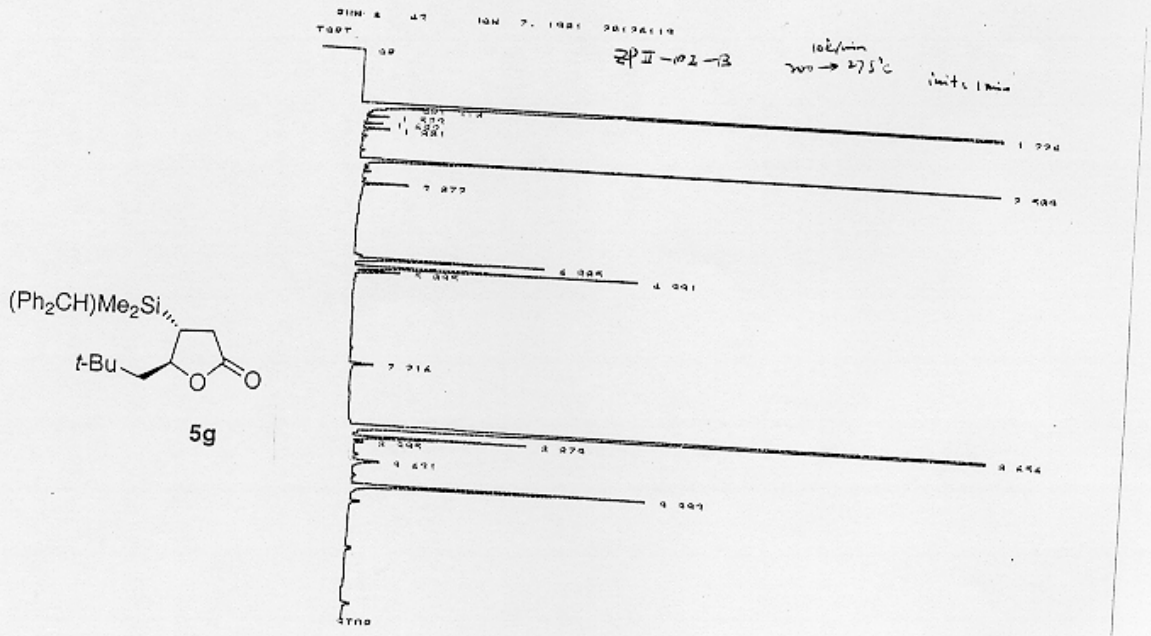
RT	AREA	TYPE	WIDTH	AREA%	
1.317	526	TBP	.023	.14086	
1.712	1258	BB	.034	.33497	
1.835	4343	BB	.037	1.15642	
2.138	488	BB	.043	.10864	
2.618	4937	PB	.043	1.31459	
3.270	3947	BV	.039	1.05098	
3.387	8562	VB	.045	2.27983	
3.681	6927	BB	.051	1.84447	
9.167	210369	PB	.061	56.01550	lactone
9.538	1195	BB	.054	.31920	
9.956	20617	BB	.056	5.48974	
10.207	644	BP	.069	.17140	
10.418	614	PB	.057	.16349	
10.875	171	PV	.039	.04553	
11.830	101439	VB	.066	27.01042	lactam
12.114	9598	BV	.069	2.55568	

TOTAL AREA= 375555
MUL FACTOR=1.0000E-00

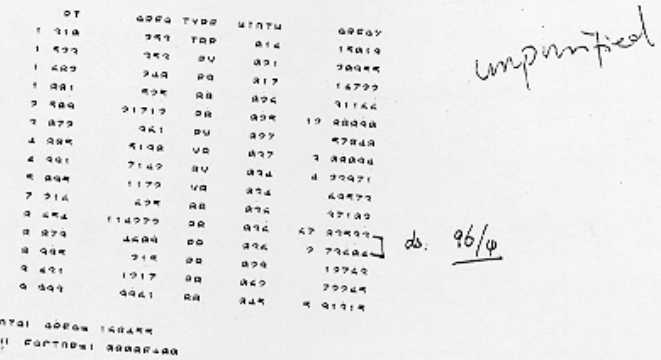
unpurified

91/9

97/9

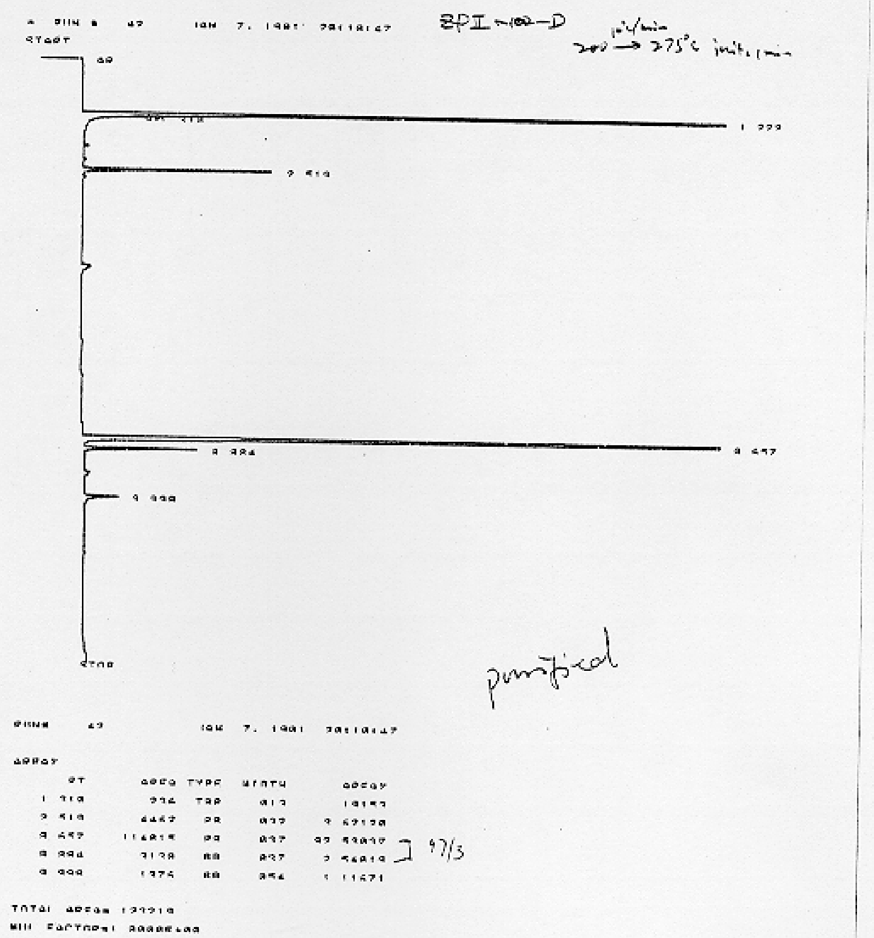


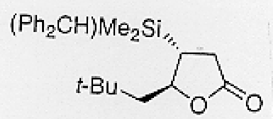
5g



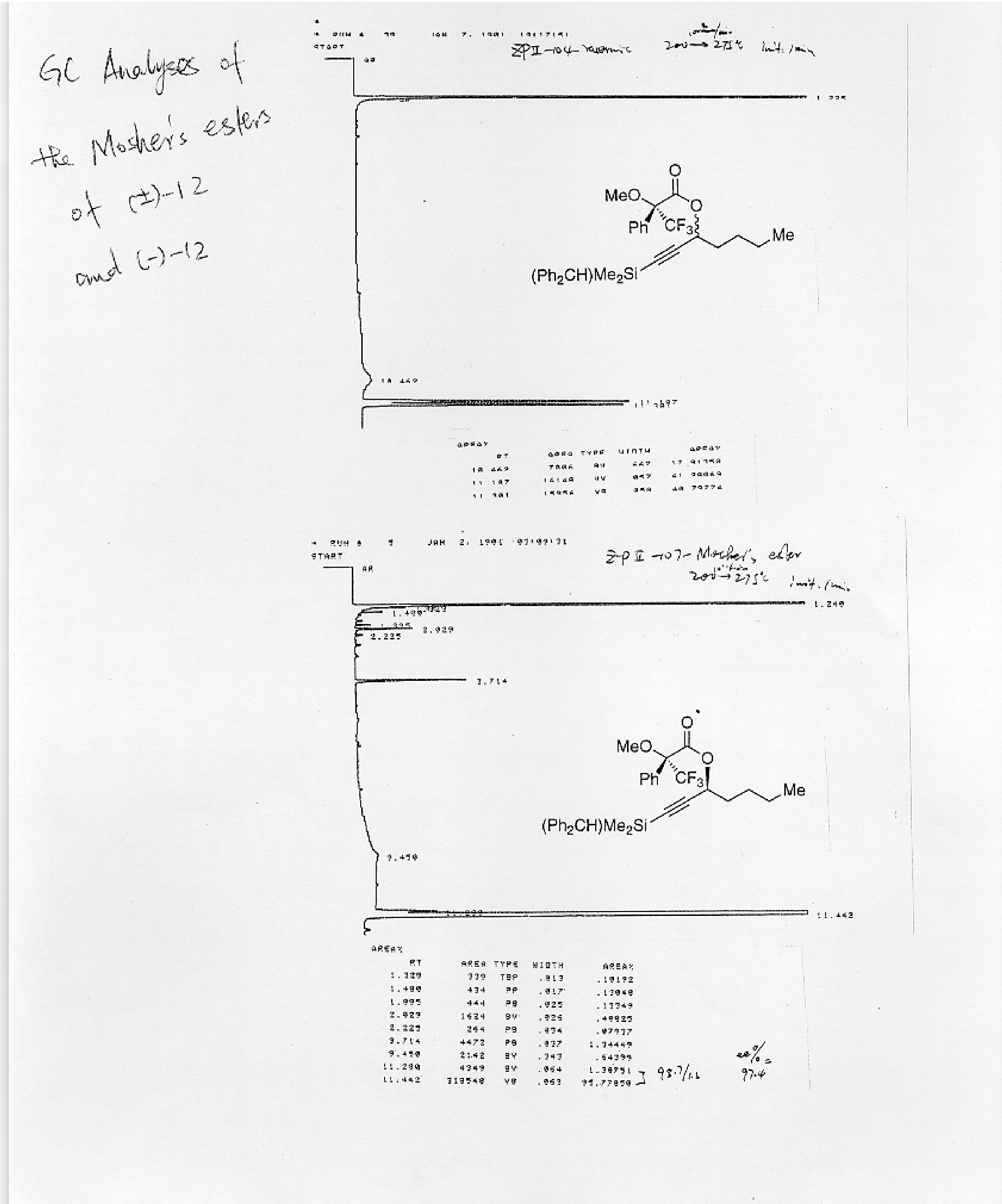
unpurified

ds. 96/4


START
STOP
purified
AREA%
RT AREA TYPE WIDTH AREA%
97/3

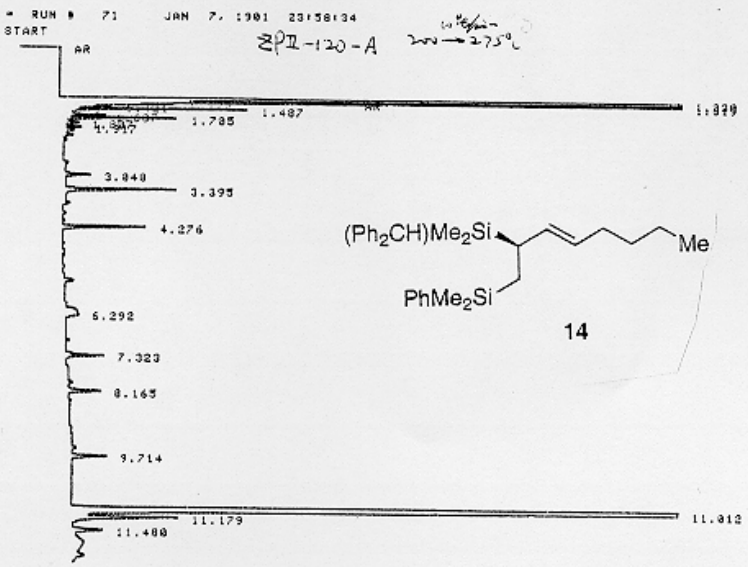

(Ph2CH)Me2Si
t-Bu
O
O

5g



RT	AREA	TYPE	WIDTH	AREA%
1.320	339	TBP	.013	.10192
1.490	434	PP	.017	.13048
1.995	444	PB	.025	.13349
2.029	1624	BV	.025	.49925
2.225	264	PB	.034	.07937
3.714	4472	PB	.037	1.34449
9.450	2142	BV	.243	.64399
11.280	4349	BV	.064	1.30751
11.442	318548	VB	.053	95.77850

98.7/1.1 ee% = 97.4

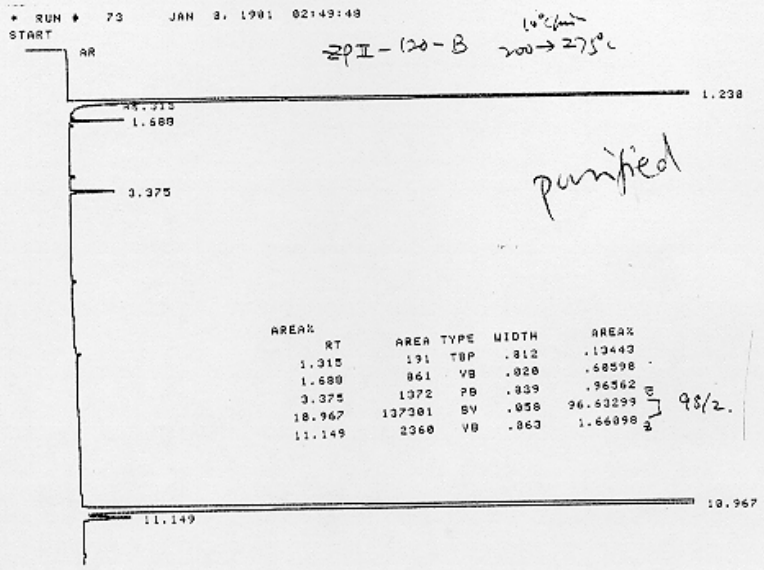


AREA%

RT	AREA	TYPE	WIDTH	AREA%	
1.319	101270	TBV	.022	24.87977	
1.372	914	TVP	.021	.21732	
1.421	421	TPB	.023	.10818	
1.487	3444	BB	.026	.81887	
1.637	769	BP	.028	.18284	
1.785	2387	PP	.029	.56755	
1.887	545	PP	.036	.12958	
1.917	419	PV	.032	.09962	
3.040	995	VB	.049	.23658	
3.395	3392	PB	.040	.80651	
4.276	2746	BB	.042	.65291	
6.292	1857	BB	.100	.44154	
7.323	1279	VB	.043	.30411	
8.165	1510	PB	.061	.36893	
9.714	1489	BB	.055	.35404	
11.812	290424	PB	.061	68.57882	E
11.179	3945	BB	.053	.93799	a
11.488	1686	BV	.072	.40088	α
13.650	1557	VB	.087	.37020	
16.445	1521	BB	.116	.36165	

unpurified

E/Z = 99%
Z/α >99/1



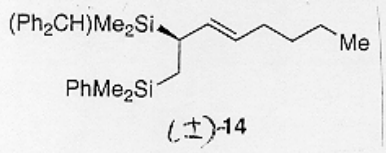
purified

AREA%

RT	AREA	TYPE	WIDTH	AREA%	
1.315	191	TBP	.012	.13443	
1.688	861	VB	.020	.60598	
3.375	1372	PB	.039	.96562	
18.967	137301	BV	.058	96.63299	E
11.149	2360	VB	.063	1.66098	Z

98/2.

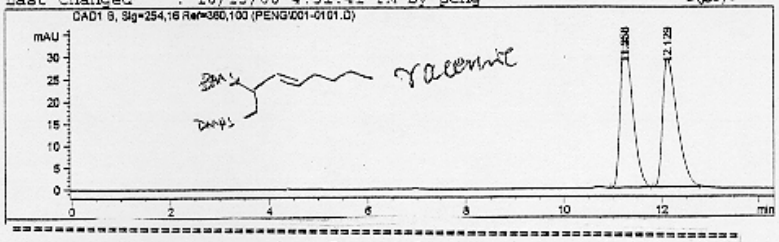
HPLC Analysis of 14



(±)-14

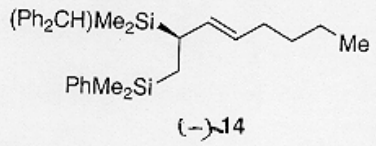
```
Injection Date   : 10/13/00 4:54:00 PM          Seq. Line :   1
Sample Name      : ZPII-78-B                       Vial :   1
Acq. Operator    : peng                            Inj :   1
                                                Inj Volume : 5 ul
Sequence File    : D:\HPCHEM\1\SEQUENCE\BURKE.S
Method           : D:\HPCHEM\1\METHODS\PENG.M
Last changed     : 10/13/00 4:51:41 PM by peng
```

flow rate: 0.7 mL/min
hexanes



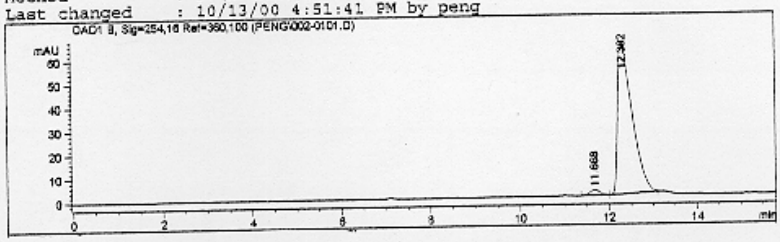
Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.258 PB    0.2688  608.01276   34.63831  50.0737
   2  12.129 BB    0.3114  606.22308   29.29762  49.9263

Totals :                  1214.23584   63.93593

 Results obtained with enhanced integrator!
```



(–)-14

```
Injection Date   : 10/13/00 5:10:06 PM          Seq. Line :   1
Sample Name      : ZPII-120-B                      Vial :   2
Acq. Operator    : peng                            Inj :   1
                                                Inj Volume : 5 ul

Sequence File    : D:\HPCHEM\1\SEQUENCE\BURKE.S
Method           : D:\HPCHEM\1\METHODS\PENG.M
Last changed     : 10/13/00 4:51:41 PM by peng
```

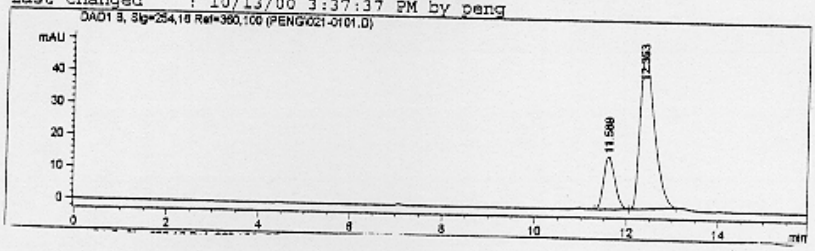


Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.668 PP    0.2478   36.87790    2.31541   2.4436
   2  12.302 VB    0.3356 1472.28589   64.66972  97.5564

Totals :                  1509.16379   66.98513

 Results obtained with enhanced integrator!
```

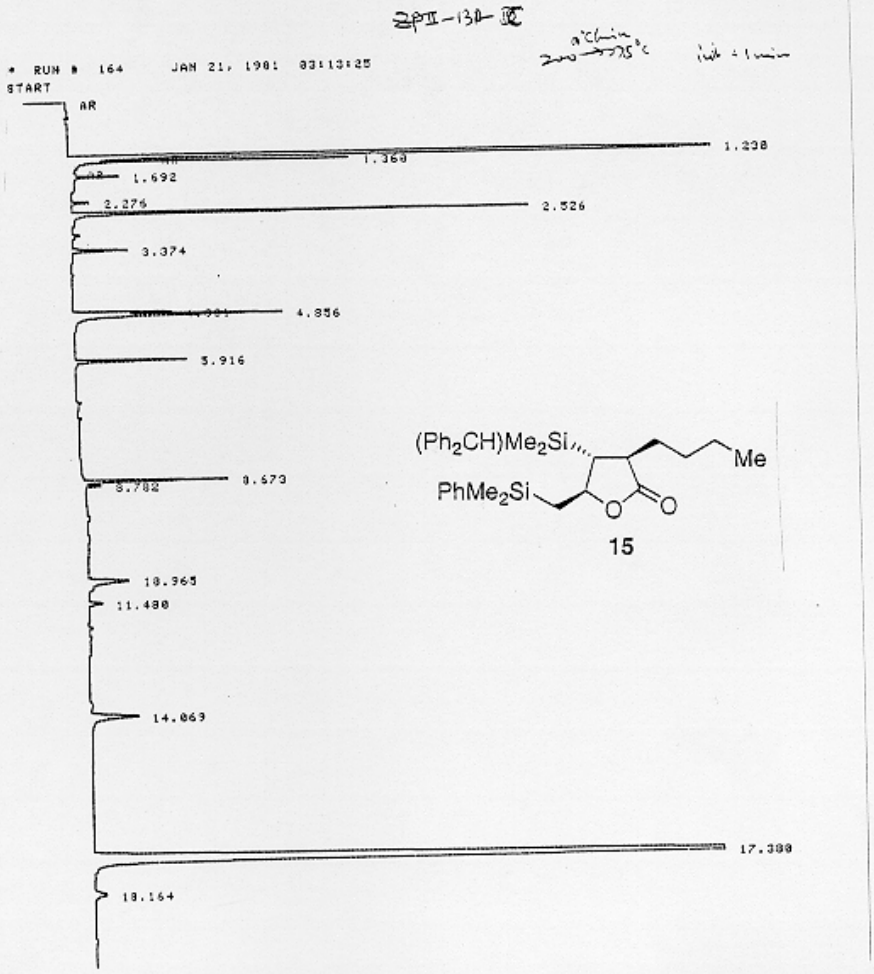
95% e.e.

```
Injection Date   : 10/13/00 4:34:18 PM          Seq. Line :   1
Sample Name      : Co-INJECTION                    Vial :  21
Acq. Operator    : peng                            Inj :   1
                                                Inj Volume : 5 ul
Sequence File    : D:\HPCHEM\1\SEQUENCE\BURKE.S
Method           : D:\HPCHEM\1\METHODS\PENG.M
Last changed     : 10/13/00 3:37:37 PM by peng
```




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.589 PB    0.2649  279.93228   16.41660  20.7058
   2  12.353 PB    0.3296 1072.02026   48.93918  79.2942

Totals :                  1351.95255   65.35578

 Results obtained with enhanced integrator!
```

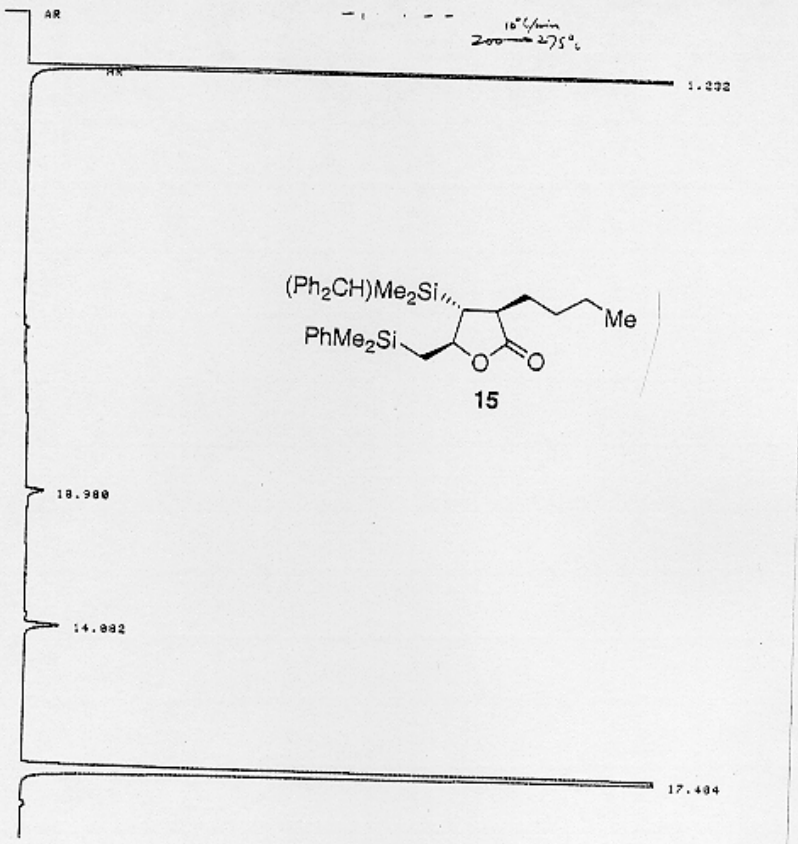
Coinjection of (±)-14 and (−)-14



AREA% RT	AREA	TYPE	WIDTH	AREA%
1.360	3854	TBB	.016	2.89395
1.692	810	BB	.025	.55537
2.276	415	BB	.031	.28454
2.526	11691	PB	.034	9.01582
3.374	1849	BB	.044	1.26775
4.881	2559	PV	.035	1.75455
4.856	8155	VB	.052	5.59140
5.916	3223	PB	.039	2.28992
8.673	4212	BV	.039	2.88792
8.782	492	VB	.039	.33734
10.965	3381	PB	.108	2.31815
11.480	676	BB	.063	.46349
14.069	3809	BB	.106	2.61160
17.380	92294	PB	.110	63.27368
19.164	1061	BB	.115	.72746

Unpurified

97/3



15

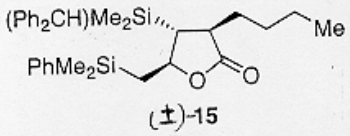
AREA%

RT	AREA	TYPE	WIDTH	AREA%
18.980	1373	BB	.185	1.42376
14.882	2712	VB	.185	2.82213
17.404	92012	PB	.112	95.74989

purified

97/3

HPLC Analysis of lactone 15



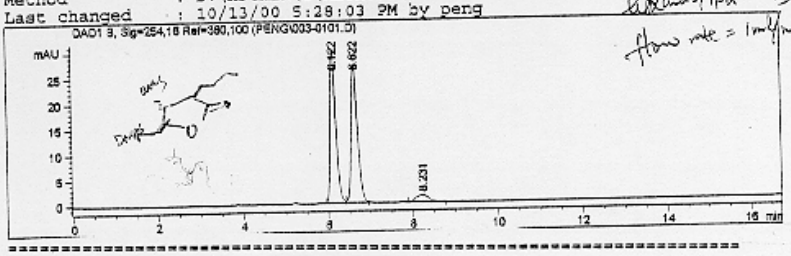
(±)-15

racemic

```
Injection Date  : 10/13/00 5:55:35 PM          Seq. Line :  1
Sample Name     : ZPII-124-D                      Vial :  3
Acq. Operator   : peng                            Inj :  1
                                                  Inj Volume : 5 ul

Sequence File   : D:\HPCHEM\1\SEQUENCE\BURKE.S
Method          : D:\HPCHEM\1\METHODS\PENG.M
Last changed    : 10/13/00 5:28:03 PM by peng
```

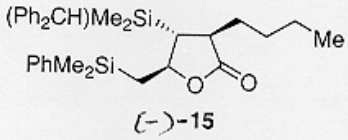
hexanes/IPA = 97/3

flow rate = 1 mL/min



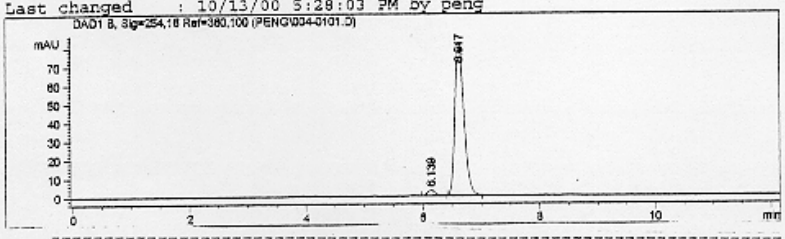
Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.122 BB    0.1420  280.95212   30.34309  47.1807
   2   6.622 BB    0.1622  286.13968   27.30785  48.0519
   3   8.231 PB    0.2902   28.38878    1.33468   4.7674

Totals :                   595.48058   58.98562

 Results obtained with enhanced integrator!
```



(−)-15

```
Injection Date  : 10/13/00 6:14:07 PM          Seq. Line :  1
Sample Name     : ZPII-130-D                      Vial :  4
Acq. Operator   : peng                            Inj :  1
                                                  Inj Volume : 5 ul

Sequence File   : D:\HPCHEM\1\SEQUENCE\BURKE.S
Method          : D:\HPCHEM\1\METHODS\PENG.M
Last changed    : 10/13/00 5:28:03 PM by peng
```



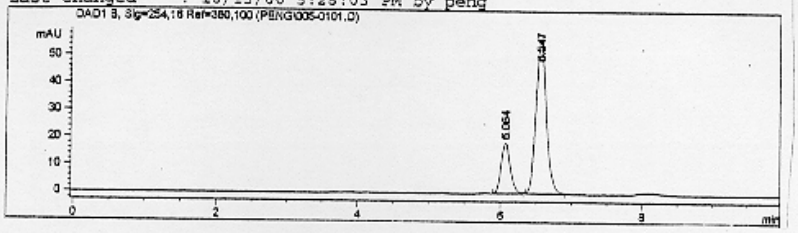
Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.139 PB    0.1418   26.67774    2.94052   2.9657
   2   6.617 BB    0.1610  872.87085   82.78935  97.0343

Totals :                   899.54859   85.72987

 Results obtained with enhanced integrator!
```

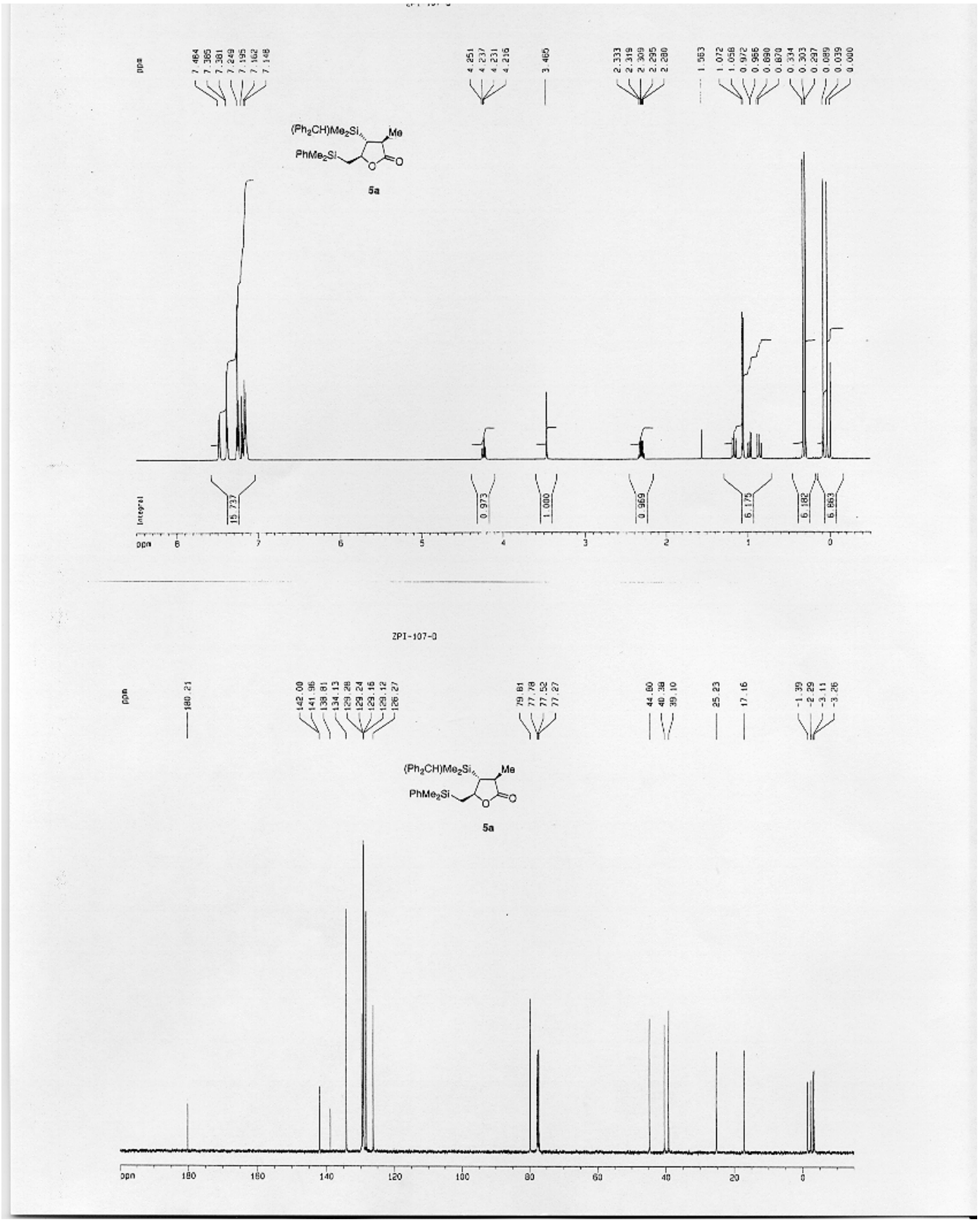
94% e.e.

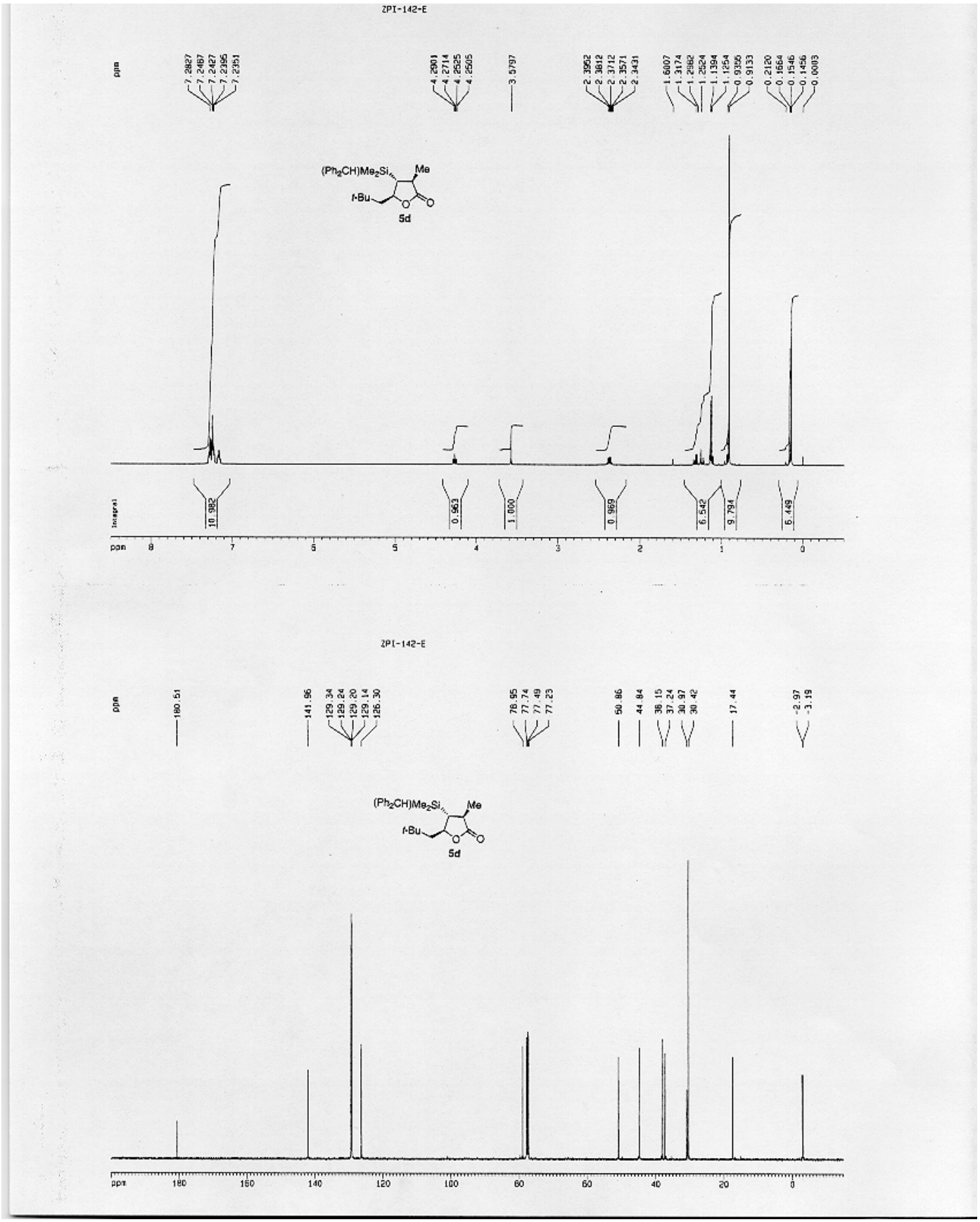
Coinjection of (±)-15 and (−)-15

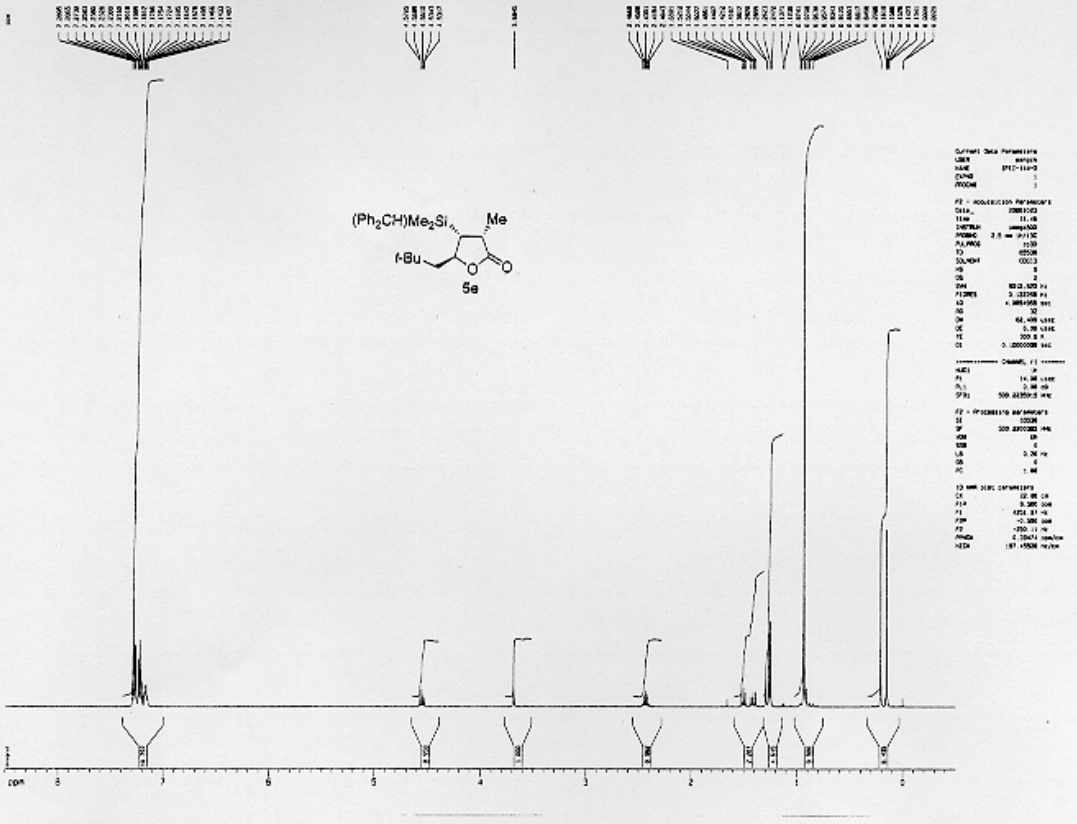
```
Injection Date   : 10/13/00 6:28:35 PM          Seq. Line :   1
Sample Name      : Co-INJECTION                     Vial :   5
Acq. Operator    : peng                             Inj :   1
                                                Inj Volume : 5 ul
Sequence File    : D:\HPCHEM\1\SEQUENCE\BURKE.S
Method           : D:\HPCHEM\1\METHODS\PENG.M
Last changed     : 10/13/00 5:28:03 PM by peng
```



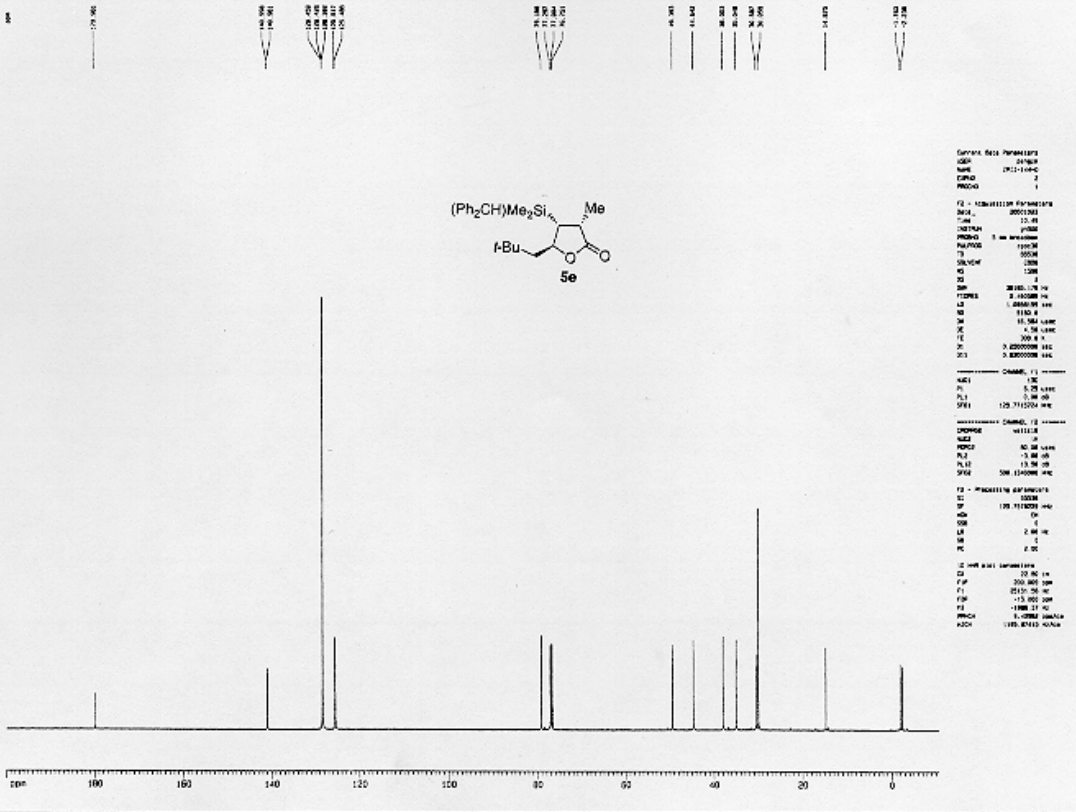

```
                    Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.064 BB    0.1384  167.82301   18.75358  22.4089
   2   6.547 BB    0.1575  581.08826   56.71854  77.5911

Totals :                   748.91127   75.47211

 Results obtained with enhanced integrator!
```

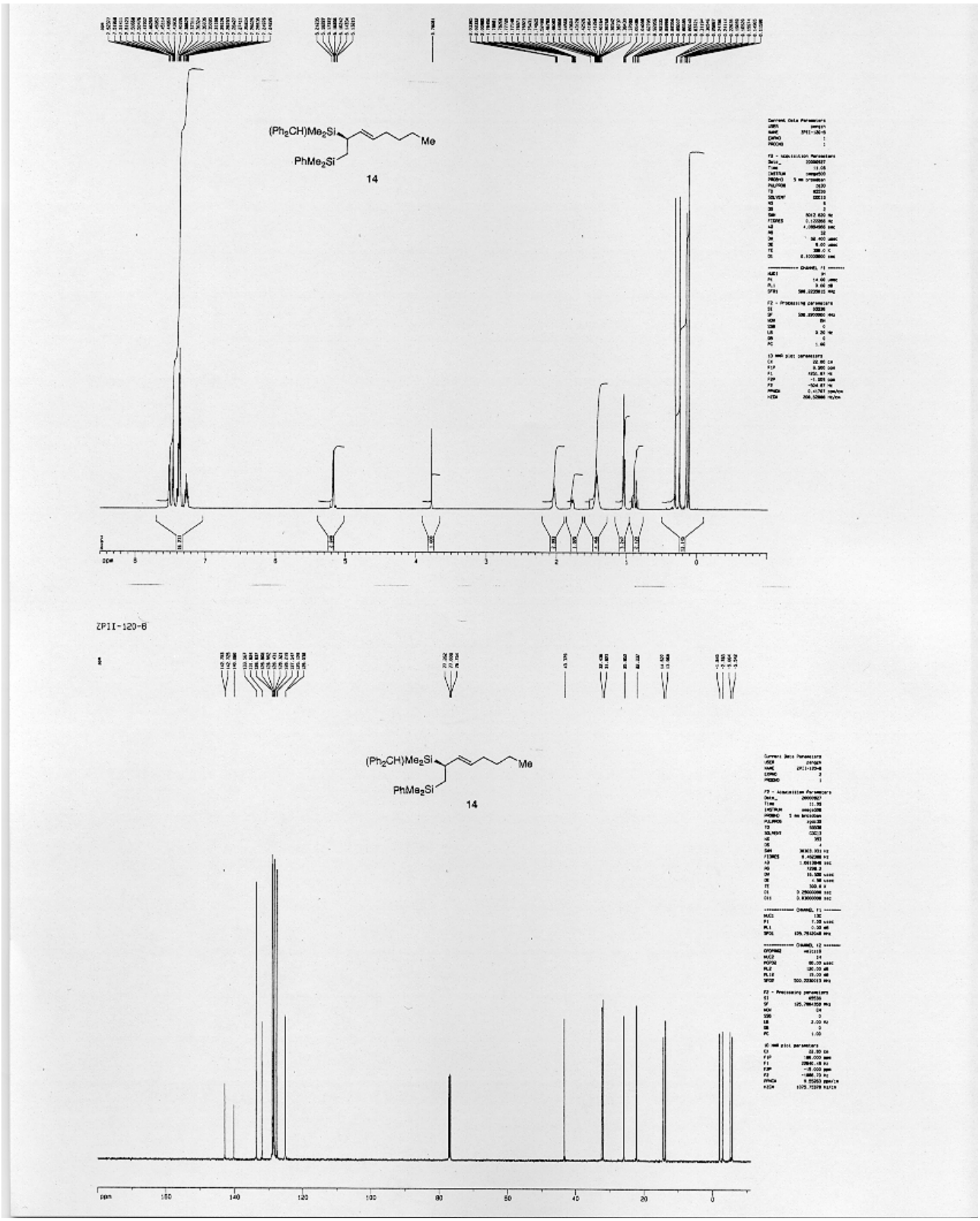

ppm
7.464
7.365
7.361
7.249
7.195
7.162
7.148
4.251
4.237
4.231
4.216
3.465
2.333
2.319
2.309
2.295
2.280
1.563
1.072
1.058
0.972
0.966
0.890
0.870
0.334
0.303
0.297
0.089
0.039
0.000
(Ph2CH)Me2Si
Me
PhMe2Si
O
5a
Integral
15.737
0.973
1.000
0.969
6.175
6.182
6.863
ppm
ZPI-107-3
180.21
142.00
141.96
138.81
134.13
129.28
129.24
129.16
129.12
126.27
79.81
77.78
77.52
77.27
44.80
40.38
39.10
25.23
17.16
-1.39
-2.29
-3.11
-3.26

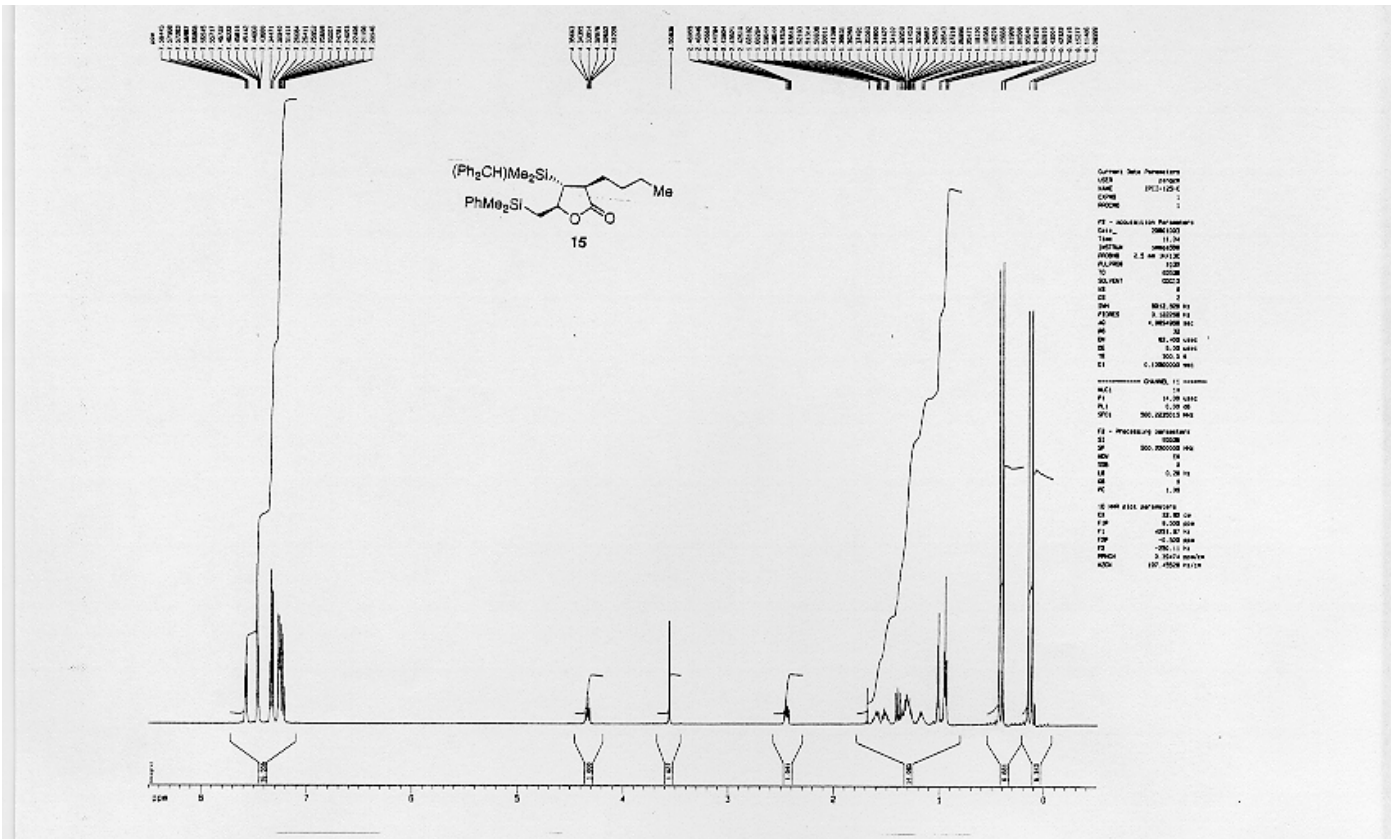

ZPI-142-E
(Ph2CH)Me2Si
Me
t-Bu
5d
ZPI-142-E
(Ph2CH)Me2Si
Me
t-Bu
5d



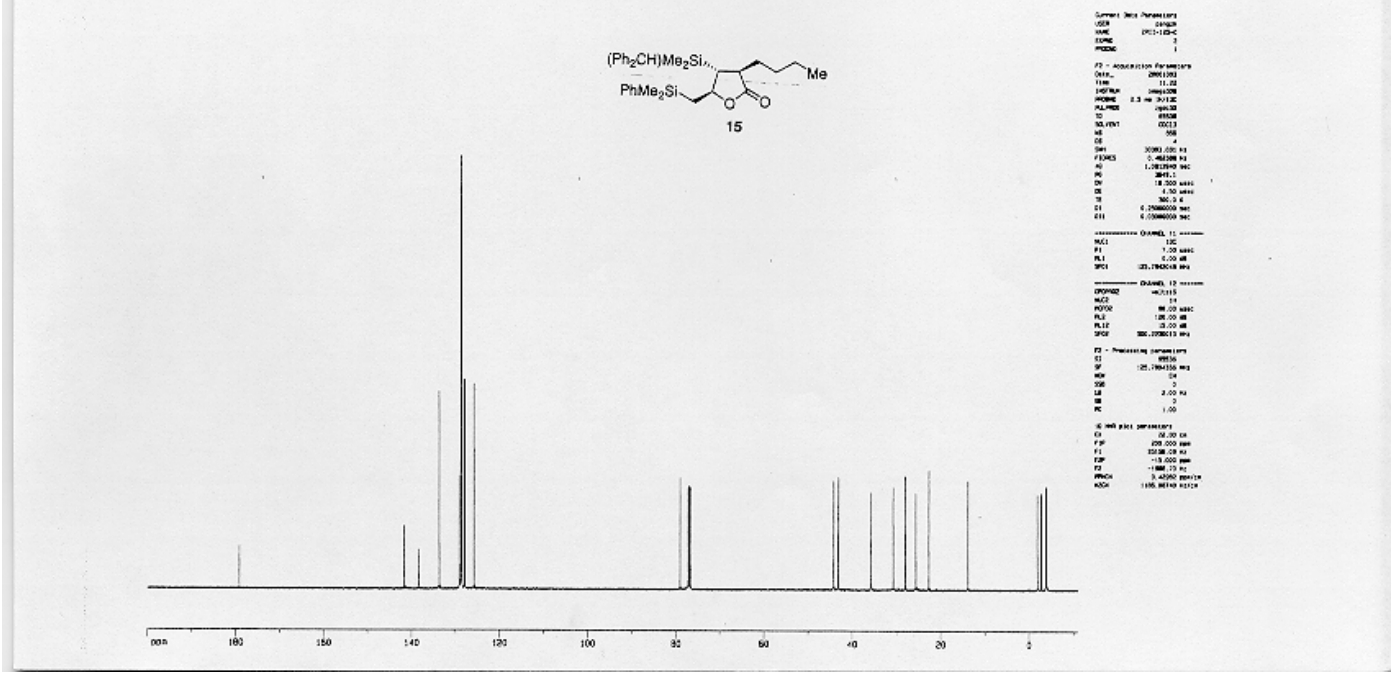
ZPII-144-D

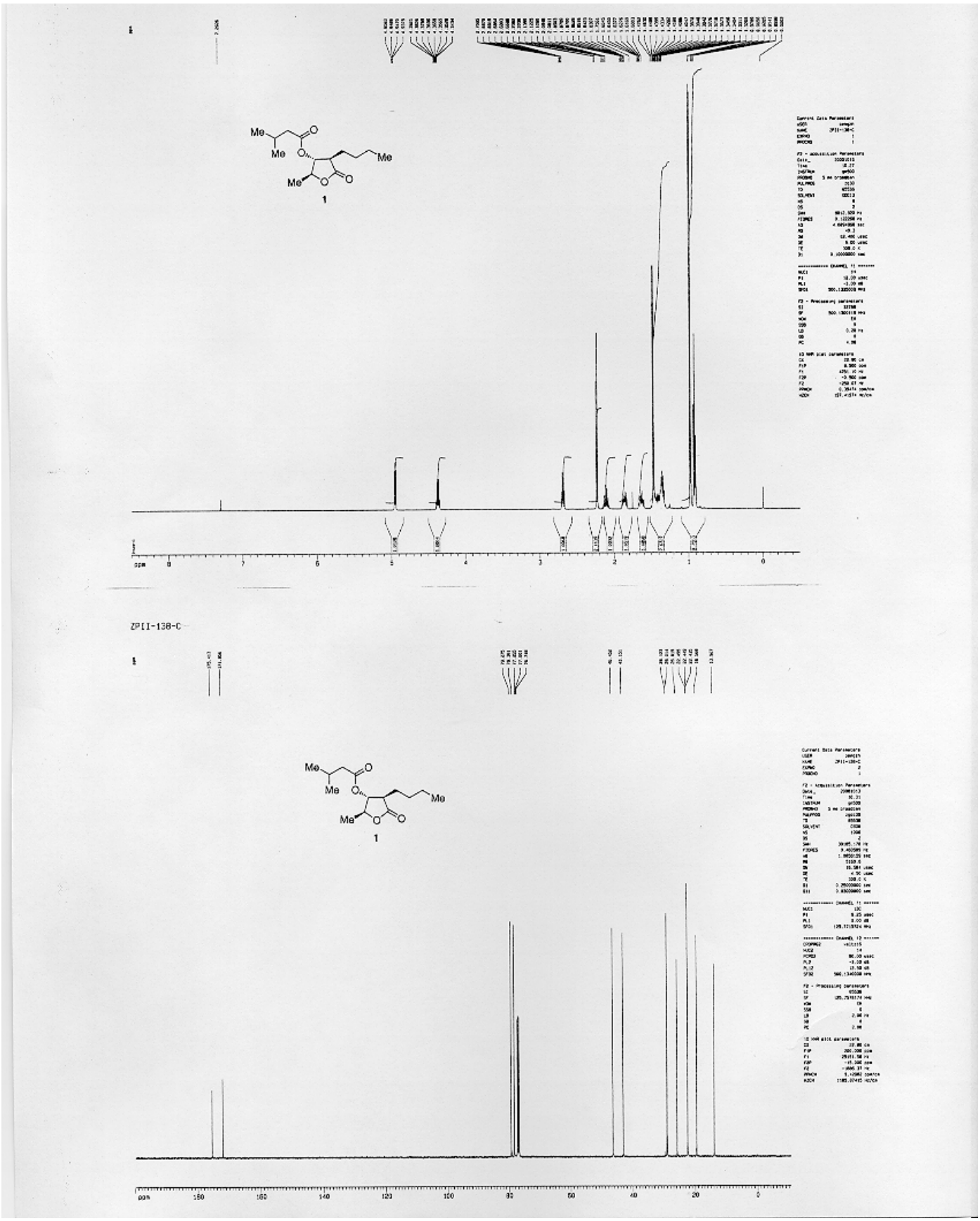



(Ph2CH)Me2Si
Me
PhMe2Si
14
ZPII-120-B
(Ph2CH)Me2Si
Me
PhMe2Si
14



ZPII-125-D




Me
Me
Me
Me
O
O
O
1
ZPII-138-C
Me
Me
Me
Me
O
O
O
1
ppm