Cu-Catalyzed Asymmetric Conjugate Additions of Dialkyl- and Diarylzinc Reagents to Acyclic β-Silyl-α,β-Unsaturated Ketones. Synthesis of Allylsilanes in High Diastereo- and Enantiomeric Purity

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SUPPORTING INFORMATION

GENERAL. Infrared (IR) spectra were recorded on a Nicolet 210 spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), or weak (w). ^{1}H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad and m = multiplet), coupling constants (Hz), and assignment. ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16). Enantiomer ratios are determined by chiral GLC analysis (Supleco Betadex 120 column (30 m x 0.25 mm) or Alltech Associated Chiraldex GTA column (30 m x 0.25 mm)) or by chiral HPLC analysis (Chiral Technologies Chiralpak AS (4.6 x 250 mm), Chiral Technologies Chiralcel OD (4.6 x 250 mm) or Chiral Technologies Chiralpak AD (4.6 x 250 mm)) in comparison with authentic racemic materials. Elemental analysis was performed by Robertson Microlit Laboratories (Madison, New Jersey). High resolution mass spectrometry was performed by the University of Illinois Mass Spectrometry Laboratories (Urbana, Illinois) or by the Boston College Mass Spectrometry Laboratories. Optical rotation values were recorded on a Rudolph Research Analytical Autopol IV Polarimeter.

MATERIALS. Unless otherwise stated, all reactions were conducted in oven (135 °C) and flame-dried glassware under an inert atmosphere of nitrogen. All work-up and purification procedures were carried out with reagent solvents in air. All reagent solvents were purchased from Doe and Ingalls.

Benzene: Purified by being passed through Cu and alumina columns under a positive pressure of dry argon by a modified Advanced ChemTech purification system.

Chloroform: Purchased from Aldrich and used as received.
Dichloromethane: Purified through two alumina columns under a positive pressure of dry argon by a modified Advanced ChemTech purification system.
Diethyl ether: Purified through two alumina columns under a positive pressure of dry argon by a modified Advanced ChemTech purification system.
Dimethoxyethane: Purified by distillation from sodium benzophenone ketal immediately prior to use.
Benzaldehyde: Purchased from Aldrich and distilled over $CaCl_2$ prior to use.
***n*-Butyl lithium (1.6 M solution in hexane):** Purchased from Strem and used without further purification.
Chlorodimethylphenylsilane: Purchased from Aldrich and used as received.
Chlorotrimethylsilane: Purchased from Aldrich and used as received.
3-Chloroperbenzoic acid: Purchased from Aldrich and washed with phosphate buffer (pH 7.5), extracted with benzene, dried over $MgSO_4$, and concentrated prior to use.
Chlorosulfonyl isocyanate (CSI): Purchased from Aldrich and distilled over K_2CO_3 prior to use.
Copper (I) iodide: Purchased from Strem and used without further purification.
Copper (I) triflate (benzene complex, 2:1): Prepared according to known methods.[1]
Copper (I) triflate (toluene complex, 2:1): Purchased from Aldrich and used without further purification.
Dess-Martin Periodinane: Purchased from Atlantic Scientific Company and used as received.
Dibutylzinc (1 M solution in heptane): Purchased from Fluka and used as received.
Diethylzinc: Purchased from Aldrich and used as received.
Di-4-acetoxybutylzinc: Prepared according to known literature procedure.[2]
Di-4-methoxyphenylzinc: Prepared from commercially available starting materials by a known literature procedure.[3]
Dimethylzinc: Purchased from Strem and used as received.
Diphenylzinc: Purchased from Strem and used as received.[4]
Di-4-trifluoromethylphenylzinc: Prepared from commercially available starting materials by a known literature procedure.[5]
Palladium (II) acetate: Purchased from Aldrich and used without further purification.
Phenylboronic acid: Purchased from Aldrich and recrystallized from hot H_2O prior to use.
Sodium bis(2-methoxyethoxy) aluminum hydride (Red-Al, 3.33 M solution in toluene): Purchased from Aldrich and used without further purification.

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(1) (a) Salomon, R. G.; Kochi. J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889-1897. (b) Salomon, R. G.; Kochi. J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300-3310.
(2) Knochel, P.; Singer, R. *Chem. Rev.* **1993**, *93*, 2177-2188 and references cited therein.
(3) Lee, K-s; Brown, M.K.; Hird, A. W.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 7182-7184.
(4) It is critical that fresh and high quality Ph_2Zn is used.
(5) Chisholm, M. H.; Galluci, J. C.; Yin, H.; Zhen, H. *Inorg. Chem.* **2005**, *44*, 4777-4785.

Tetrabutyl ammonium fluoride (1 M solution in THF): Purchased from Acros and used as received.

Tetrahydrofuran: Purified by distillation from sodium benzophenone ketal immediately prior to use.

Titanium (IV) chloride: Purchased from Aldrich and used without further purification.

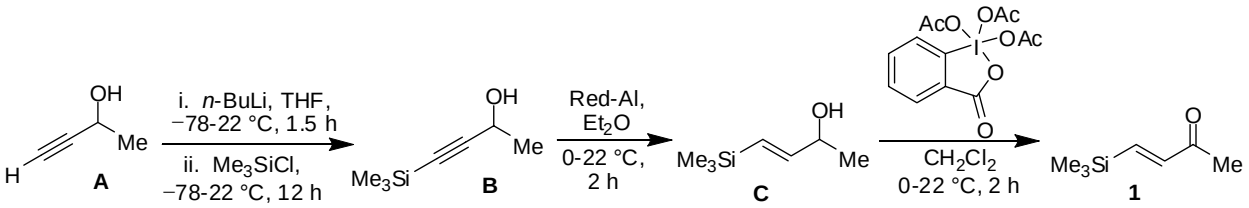
Toluene: Purified by being passed through Cu and alumina columns under a positive pressure of dry argon by a modified Advanced ChemTech purification system.

Trifluoroacetic anhydride: Purchased from Aldrich and distilled over P_2O_5 prior to use.

Triphenylphosphine: Purchased from Aldrich and recrystallized from hot hexanes prior to use.

Zinc (II) chloride, ultra dry: Purchased from Strem and used without further purification.

Representative experimental procedures for synthesis of α,β-unsaturated ketones:



4-(Trimethylsilyl)-but-3-yn-2-ol (B).[6] To a solution of propargyl alcohol **A** (1.50 mL, 19.1 mmol) in THF (95.5 mL) was added *n*-BuLi (26.4 mL of a 1.52 M solution in hexanes, 40.1 mmol) through a syringe at -78 °C (dry ice/actone bath). After addition was complete, the solution was allowed to warm to 22 °C. After 1.5 h at 22 °C, the mixture was allowed to cool to -78 °C (dry ice/acetone bath) and chlorotrimethylsilane (4.82 mL, 38.2 mmol) was added dropwise through a syringe. The solution was allowed to slowly warm to 22 °C over 12 h, and the reaction was quenched by the addition of an aqueous solution of HCl (200 mL, 1.00 M) and diluted with Et_2O (100 mL). The layers were separated and the aqueous layer was washed with Et_2O (3 x 100 mL). The combined organic layers were washed with a saturated solution of NaCl (100 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The yellow oil was purified by silica gel chromatography (6:1 hexanes:EtOAc, R_f = 0.5) to afford the desired product **B** as a pale yellow oil (1.87 g, 13.1 mmol, 69%). This spectral data is in accordance with the reported literature data.

(*E*)-4-(Trimethylsilyl)-3-buten-2-ol (C).[7] To a solution of **B** (1.87 g, 13.1 mmol) in Et_2O (29.1 mL) was slowly added Red-Al (7.88 mL of a 3.33 M solution in toluene, 26.2 mmol) as a solution in Et_2O (6.99 mL) at 0 °C (ice bath). The mixture was allowed to warm to 22 °C over 2 h and then quenched by the addition of H_2O (1 mL) and H_2SO_4 (2.0 mL, 3.6 M) at 0 °C. The resulting solution was diluted with Et_2O (100 mL) and H_2O (100 mL). The layers were separated and the aqueous layer was washed with Et_2O (3 x 100 mL). The combined organic

(6) Jung, M. E.; Piizzi, G. *J. Org. Chem.* **2002**, *67*, 3911-3914.
(7) Hwu, J. R.; Furth, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 8834-8841.

layers were washed with a saturated solution of NaCl (100 mL), dried over Na_2SO_4, filtered and concentrated in vacuo to afford desired product **C** without purification as a pale yellow oil (1.84 g, 12.8 mmol, 13:1 E:Z, 97%). This spectral data is in accordance with reported literature data.[7]

(*E*)-4-(Trimethylsilyl)-3-buten-2-one (1).[8] To a solution of **C** (1.84 g, 12.8 mmol) in CH_2Cl_2 (128 mL) was added Dess-Martin periodinate (DMP) in three equal portions (8.10 g, 19.1 mmol) at 30 minute intervals at 22 °C. The mixture was allowed to stir for 30 min after the final addition of DMP. The mixture was diluted with 15% aqueous solution of NaOH (50 mL) and Et_2O (50 mL) and allowed to stir for 10 min. At this time, the layers were separated and the aqueous layer was washed with Et_2O (3 x 100 mL). The combined organic layers were washed with a saturated solution of NaCl (100 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The remaining yellow oil was purified by silica gel chromatography (25:1 hexanes:Et_2O, R_f = 0.3) to afford the desired product **1** as a pale yellow oil (1.06 g, 7.44 mmol, 59%).IR (neat): 3005 (w), 2968 (m), 2899 (w), 1678 (s), 1363 (m), 1256 (s), 1218 (m), 1193 (m), 992 (m), 866 (s), 856 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.01 (1H, d, *J* = 19.6 Hz, C**H**=CH), 6.43 (1H, d, *J* = 19.6 Hz, CH=C**H**), 2.26 (3H, s, C$\mathbf{H}_3$), 0.13 (9H, s, Si(C$\mathbf{H}_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 147.8, 143.2, 26.4, -1.7. Anal Calcd. for $C_7H_{14}OSi$: C, 59.09; H, 9.92. Found: C, 59.34; H, 10.14.

(*E*)-4-(Dimethylphenylsilyl)-3-buten-2-one (15). IR (neat): 3068 (s), 3050 (s), 3006 (m), 2955 (m), 2904 (s), 1684 (s), 1590 (s), 1432 (m), 1363 (m), 1250 (s), 1225 (m), 1193 (m), 1117 (m), 998 (s), 834 (s), 734 (m), 702 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.51-7.36 (5H, m, Ar**H**), 7.11 (1H, d, *J* = 19.2 Hz, C**H**=CH), 6.48 (1H, d, *J* = 19.2 Hz, CH=C**H**), 2.27 (3H, s, C$\mathbf{H}_3$), 0.42 (6H, s, Si(C$\mathbf{H}_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 145.7, 144.3, 136.5, 134.0, 129.7, 128.2, 26.5, -3.1. HRMS Calcd. for $C_{12}H_{15}OSi$ ($M\text{-}H^+$): 203.0892. Found: 203.0895.

(*E*)-2-Methyl-5-(trimethylsilyl)-4-penten-3-one (D). IR (neat): 2968 (s), 2905 (w), 1715 (s), 1671 (s), 1470 (m), 1250 (s), 1212 (m), 1061 (m), 1011 (m), 878 (s), 865 (s), 759 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.11 (1H, d, *J* = 19.2 Hz, C**H**=CH), 6.55 (1H, d, *J* = 19.2 Hz, CH=C**H**), 2.95 (1H, dq, *J* = 6.8, 6.8 Hz, C**H**$(CH_3)_2$), 1.12 (6H, d, *J* = 6.8 Hz, CH(C$\mathbf{H}_3$)$_2$), 0.15 (9H, s, Si(C$\mathbf{H}_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 146.7, 140.7, 37.9, 18.6, -1.6. HRMS Calcd. for $C_{13}H_{18}OSi$: 170.1127. Found: 170.1124.

(*E*)-1-Phenyl-3-(trimethylsilyl)-prop-2-enone (E). IR (neat): 3062 (w), 3031 (w), 2955 (m), 2892 (w), 1665 (s), 1608 (m), 1576 (m), 1451 (m), 1243 (s), 1180 (m), 1010 (m), 872 (s), 853 (s), 749 (m), 690 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.93-7.91 (2H, m, Ar**H**), 7.57-7.44 (3H, m, Ar**H**), 7.32-7.21 (2H, m, C**H**=CH and CH=C**H**), 0.18 (9H, s, Si(C$\mathbf{H}_3$)$_3$). ^{13}C NMR

(8) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155-4156.

(100 MHz, $CDCl_3$): δ 201.1, 149.9, 138.2, 137.7, 132.9, 129.0, 128.7, -1.6. Anal. Calcd. for $C_{12}H_{16}OSi$: C, 70.53; H, 7.89. Found: C, 70.49; H, 7.65.

Representative procedure for Cu-catalyzed enantioselective conjugate addition of dialkylzinc reagents to (*E*)-4-(dimethylphenylsilyl)-3-buten-2-one (15):

(*S*)-(+)-4-(Dimethylphenylsilyl)-2-pentanone (7). In a N_2 filled glove box, a 13 x 100 mm test tube was charged with $(CuOTf)_2 \cdot C_6H_6$ (2.41 mg, 4.80 x 10^{-3}mmol) and Schiff base **4** (5.33 mg, 1.20 x 10^{-2} mmol), sealed with a septum, wrapped with parafilm and Telfon tape and removed from the glovebox. A solution of enone **15** (98.1 mg, 0.480 mmol) in toluene (4.80 mL) was added through a syringe at 22 °C, followed by the addition of Me_2Zn (99.0 μL, 1.44 mmol) (CAUTION: Me_2Zn is pyrophoric! Use extreme caution). The mixture was allowed to stir for 3 h at 22 °C, at which time the reaction was quenched with the addition of a saturated solution of NH_4Cl (2.0 mL) and diluted with Et_2O (1.0 mL). The layers were separated and the aqueous layer was washed with Et_2O (3 x 2.0 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The resulting residue was purified by silica gel chromatography (25:1 petroleum ether: EtOAc, R_f = 0.5) to afford the desired product **7** (98.0 mg, 0.421 mmol, 93%) as a colorless oil. IR (neat): 3075 (m), 3018 (w), 2968 (s), 2905 (m), 2867 (m), 1722 (s), 1445 (s), 1357 (s), 1250 (s), 1202 (m), 1124 (s), 815 (s), 771 (s), 734 (s), 696 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.51-7.35 (5H, m, Ar**H**), 2.42 (1H, dd, *J* = 16.0, 3.6 Hz, C(O)C**H**H), 2.18 (1H, dd, *J* = 16.0, 11.2 Hz, COCH**H**), 2.07 (3H, s, C(O)C$\mathbf{H}_3$), 1.49 (1H, dq, *J* = 11.2, 3.6 Hz, CH_3C**H**), 0.93 (3H, d, *J* = 7.2 Hz, CHC$\mathbf{H}_3$), 0.28 (3H, s, SiC$\mathbf{H}_3$), 0.28 (3H, s, SiC$\mathbf{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.4, 137.6, 134.0, 129.2, 127.9, 46.0, 30.0, 15.3, 14.6, -4.7, -5.2. Anal. Calcd. for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15. Found: C, 70.97; H, 8.86. $[\alpha]_D^{20}$ +22.5 (*c* = 1.84, $CHCl_3$).

Enantiomeric purity was determined by chiral GLC analysis (Chiraldex-GTA, 100 °C, 15 psi) of the derived alcohol, obtained by protodesilylation and oxidation under the reaction conditions reported by Fleming.[9]

(*S*)-(+)-4-Hydroxy-2-pentanone (F). ^1H NMR (400 MHz, $CDCl_3$): δ 4.24-4.20 (1H, m, C**H**OH), 3.02 (1H, br s, O**H**), 2.63 (1H, dd, *J* = 14.4, 2.4 Hz, CH_3C(O)C**H**H), 2.54 (1H, dd, *J* = 14.4, 6.8 Hz, CH_3C(O)CH**H**), 2.17 (3H, s, C$\mathbf{H}_3$C(O)), 1.19 (3H, d, *J* = 4.8 Hz, CH(OH)C$\mathbf{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.0, 63.9, 51.5, 30.8, 22.4. Spectral data is in accordance with literature data.[10] $[\alpha]_D^{20}$ +63.4 (*c* = 0.347, $CHCl_3$) for a 96% ee sample, indicating the *S*-isomer.[11] The corresponding chromatograms are illustrated below:

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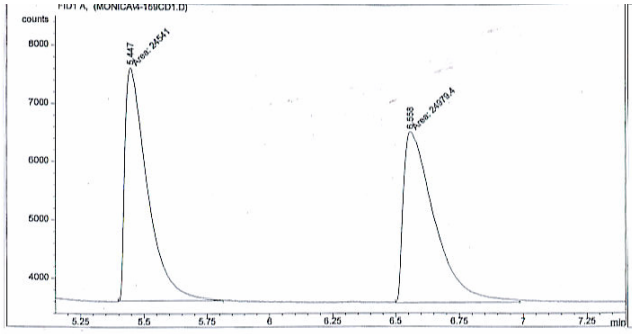
(13) Fleming, I.; Henning, R.; Parker, D. C.; Plaut, H. E.; Sanderson, P. E. J. *J. Chem. Soc. Perkin Trans. 1* **1995**, 317-337.

(14) Fauve, A.; Veschambre, H. *J. Org. Chem.* **1988**, *53*, 5213-5219.

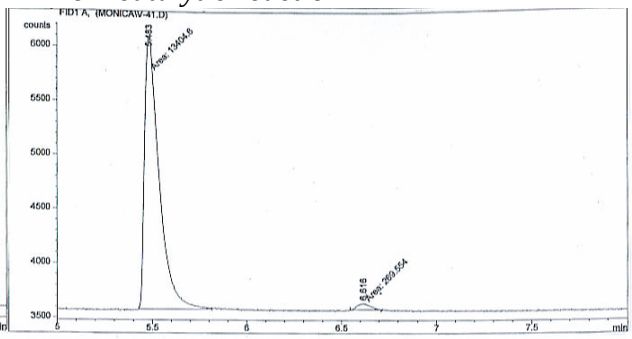
(15) Bolte, J.; Gourcy, J-G.; Veschambre, H. *Tetrahedron Lett.* **1986**, *27*, 565-568. Reported values: $[\alpha]_D^{25}$ +55 (*c* = 0.050, $CHCl_3$) for (*S*)-4-hydroxy-2-pentanone.

Authentic racemic



peak #	time	area	height	width	area %
1	5.447	24541.0	4011.35	0.1020	49.55739
2	6.558	24979.4	2961.14	0.1406	50.44261

From catalytic reaction

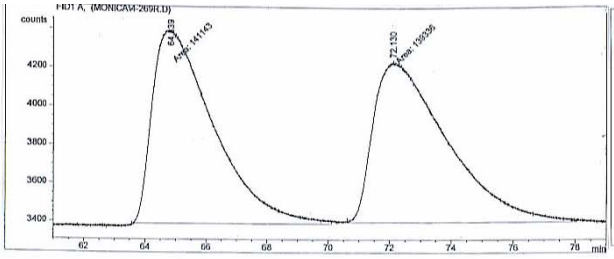


peak #	time	area	height	width	area %
1	5.163	73404.6	2511.61	0.0890	98.0288
2	6.816	269.554	6.97854	0.0725	1.97127

(*S*)-(+)-4-(Trimethylsilyl)-2-hexanone (2). IR (neat): 2967 (s), 2905 (m), 2880 (w), 1728 (s), 1363 (m), 1256 (s), 1193 (m), 847 (s), 759 (w), 702 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.40-2.33 (2H, m, C(O)C**H**$_2$), 2.15 (3H, s, C**H**$_3$C(O)), 1.55-1.13 (3H, m, aliphatic C**H**), 0.88 (3H, t, *J* = 7.6 Hz, $CH_2C\mathbf{H}_3$), -0.02 (9H, s, Si(C**H**$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.8, 44.2, 30.0, 23.3, 22.8, 13.8, -2.3. HRMS Calcd. for $C_9H_{19}OSi$ ($M\text{-}H^+$): 171.1205. Found: 171.1207. $[\alpha]_D^{20}$ +27.6 (*c* = 1.17, $CHCl_3$) for a 96% ee sample.

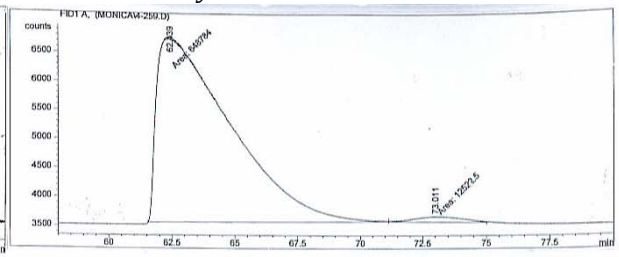
Enantiomeric purity was determined by chiral GLC analysis (Chiraldex-GTA, 50 °C, 15 psi); chromatograms are illustrated below:

Authentic racemic



peak #	time	area	height	width	area %
1	64.839	141343	1015.04	2.3175	50.32219
2	72.130	139336	851.323	2.7278	49.67781

From catalytic reaction



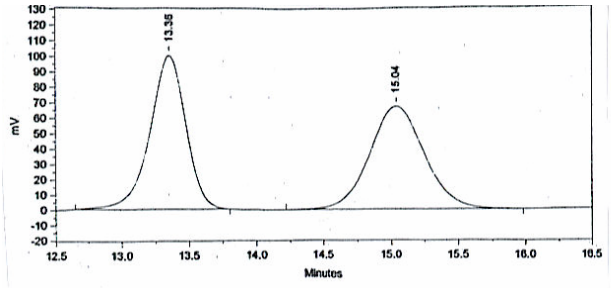
peak #	time	area	height	width	area %
1	62.439	648784	3242.69	3.3346	98.10640
2	73.011	125225	101.542	2.0554	1.89360

(*S*)-(+)-4-(Dimethylphenylsilyl)-2-hexanone (5). IR (neat): 3075 (m), 2955 (s), 2911 (m), 2873 (m), 1715 (s), 1439 (s), 1369 (s), 1256 (s), 1187 (m), 1124 (s), 834 (s), 809 (s), 790 (s), 740 (s), 715 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.51-7.33 (5H, m, Ar**H**), 2.44-2.30 (2H, m, C(O)C**H**$_2$), 2.04 (3H, s, C(O)C**H**$_3$), 1.58-1.23 (3H, m, aliphatic C**H**), 0.84 (3H, t, *J* = 7.2 Hz, $CH_2C\mathbf{H}_3$), 0.29 (3H, s, SiC**H**$_3$), 0.28 (3H, s, SiC**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.3, 138.3, 134.0, 129.1, 127.9, 44.2, 30.0, 23.4, 22.3, 13.9, -3.7, -4.2. HRMS Calcd. for $C_{14}H_{22}OSi$: 234.1440. Found: 234.1436. $[\alpha]_D^{20}$ +24.3 (*c* = 2.13, $CHCl_3$) for a 96% ee sample.

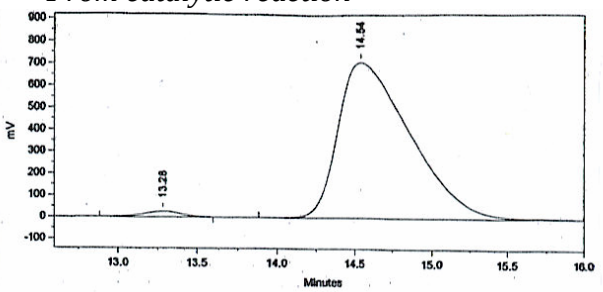
Enantiomeric purity was determined by chiral HPLC analysis (Chiral Technologies

Chiralpak AS, 220 nm, 99.5% hexanes:0.5% *i*-PrOH, 1.0 mL/min); chromatograms are illustrated below:

Authentic racemic



From catalytic reaction



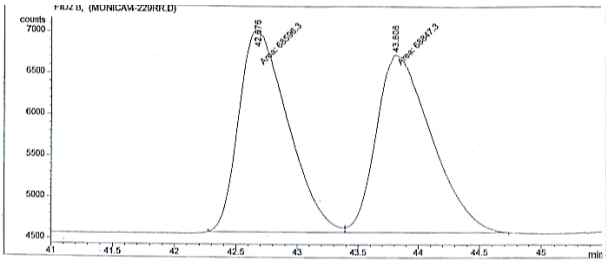
peak #	time	area	height	width	area %
1	13.355	1874723.0	100156.50	0.312	59.829
2	15.039	1907473.0	67248.15	0.473	40.171

peak #	time	area	height	width	area %
1	13.284	429832.53	25832.53	0.277	3.525
2	14.536	23247950.0	706929.80	0.548	96.475

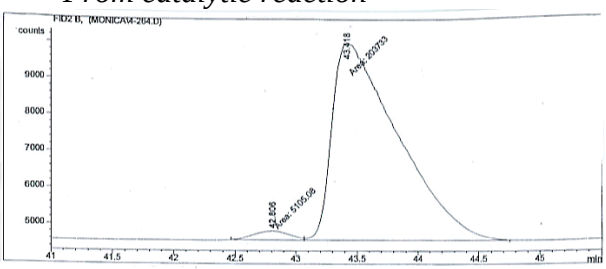
(*S*)-(+)-4-(Trimethylsilyl)-2-pentanone (6). IR (neat): 2967 (s), 2911 (m), 2867 (m), 1728 (s), 1369 (m), 1262 (s), 1193 (m), 853 (s), 752 (m), 690 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.44 (1H, dd, *J* = 16.0, 3.6 Hz, C(O)C**H**H), 2.21-2.13 (4H, m, COCH**H** and C(O)C**H**$_3$), 1.21 (1H, dq, *J* = 11.2, 3.6 Hz), 0.90 (3H, d, *J* = 3.6 Hz, CHC**H**$_3$), -0.03 (9H, s, Si(C**H**$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.8, 46.1, 30.0, 15.8, 14.5, -3.39. HRMS Calcd. for $C_8H_{18}OSi$ ($M\text{-}H^+$): 157.1055. Found: 157.1049. $[\alpha]_D^{20}$ +24.9 (*c* = 0.667, $CHCl_3$) for a 95% ee sample.

Enantiomeric purity was determined by chiral GLC analysis (β-dex, 60 °C, 15 psi); chromatograms are illustrated below:

Authentic racemic



From catalytic reaction



peak #	time	area	height	width	area %
1	42.676	68596.3	2459.54	0.4648	49.90869
2	43.808	68847.3	2161.86	0.5308	50.09131

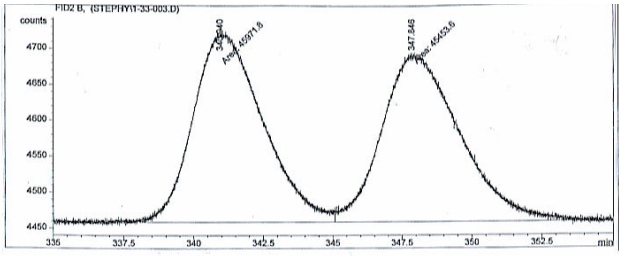
peak #	time	area	height	width	area %
1	42.806	5105.08	251.42	0.3384	2.44452
2	43.418	2.03733	5469.0	0.6209	97.5555

(*S*)-(+)-2-Methyl-5-(trimethylsilyl)-3-heptanone (8). IR (neat): 2968 (s), 2899 (m), 2873 (w), 1715 (s), 1470 (m), 1382 (w), 1250 (s), 1048 (m), 834 (s), 752 (m), 683 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.62 (1H, dq, *J* = 7.0, 7.0 Hz, C(O)C**H**$(CH_3)_2$), 2.42-2.40 (2H, m, C(O)C**H**$_2$), 1.52-1.16 (3H, m, aliphatic C**H**), 1.09 (6H, dd, *J* = 7.0, 1.6 Hz, CH(C**H**$_3$)$_2$), 0.87 (3H, t, *J* = 7.6 Hz, CH_2C**H**$_3$), -0.02 (9H, s, Si(C**H**$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.2, 40.9,

40.8, 23.5, 22.3, 18.7, 18.5, 13.8, -2.2. Anal. Calcd. for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07. Found: C, 65.95; H, 12.29. $[\alpha]_D^{20}$ +9.23 (*c* = 0.953, $CHCl_3$) for a 95% ee sample.

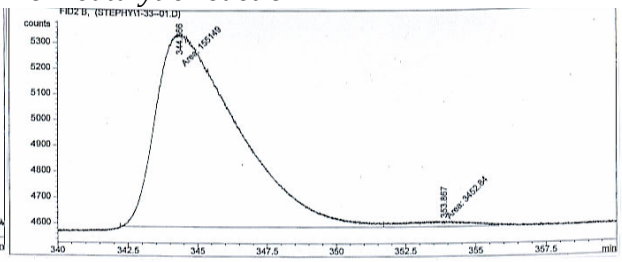
Enantiomeric purity was determined by chiral GLC analysis (β-dex, 50 °C, 15 psi); chromatograms are illustrated below:

Authentic racemic



peak #	time	area	height	width	area %
1	340.940	45971.6	270.53	2.8323	50.28343
2	347.846	4.5453.6	237.39	3.1912	49.71657

From catalytic reaction

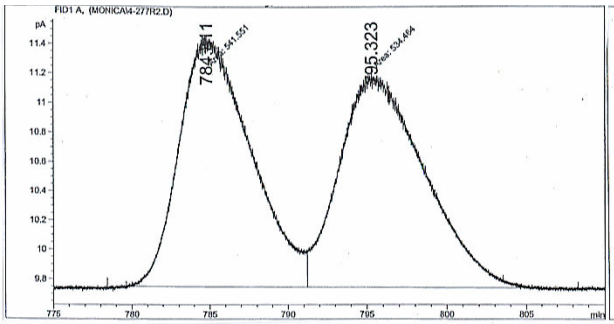


peak #	time	area	height	width	area %
1	17.352	344.366	155149	3.4036	97.8230
2	28.331	353.867	3452.84	2.4382	2.17704

(*S*)-(+)-1-Phenyl-3-(trimethylsilyl)-1-pentanone (9). IR (neat): 3056 (w), 2955 (m), 2899 (m), 2892 (m), 1696 (s), 1602 (m), 1451 (m), 1250 (s), 1231 (m), 1017 (w), 954 (m), 853 (s), 759 (s), 696 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.97-7.44 (5H, m, Ar**H**), 3.00-2.87 (2H, m C(O)C**H**$_2$), 1.50-1.30 (3H, m, aliphatic C**H**) 0.91 (3H, t, *J* = 7.2 Hz, CHC**H**$_3$), 0.03 (9H, s, Si(C**H**$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 137.5, 132.9, 128.7, 128.2, 38.9, 23.4, 23.2, 13.9, -2.17. HRMS Calcd. for $C_{14}H_{22}OSi$ (M-H^+): 233.1368. Found: 233.1361. $[\alpha]_D^{20}$ +7.72 (*c* = 0.933, $CHCl_3$) for a 89% ee sample.

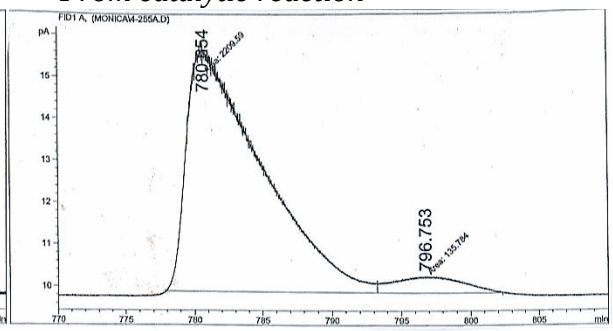
Enantiomeric purity was determined by chiral GLC analysis (β-dex, 85 °C, 15 psi); chromatograms are illustrated below:

A*uthentic racemic*



peak #	time	area	height	width	area %
1	784.811	541.55	1.72547	5.2310	50.32932
2	795.323	534.46	1.48650	5.9844	49.67068

From catalytic reaction



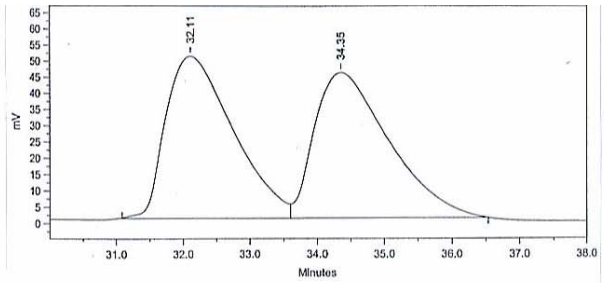
peak #	time	area	height	width	area %
1	780.654	2209.59	5.98165	6.1566	94.2106
2	796.753	135.783	0.395120	5.7275	5.78943

(*S*)-(+)-1-Phenyl-3-(trimethylsilyl)-butan-1-one (10). IR (neat): 3100 (w), 3075 (m), 3037 (w), 2961 (s), 2905 (m), 2873 (m), 1703 (s), 1596 (m), 1577 (m), 1451 (s), 1350 (m), 1256 (s), 1231 (s), 985 (m), 841 (s), 746 (s), 683 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (2H,

d, *J* = 7.2 Hz, Ar**H**), 7.52 (1H, d, *J* = 7.2 Hz, Ar**H**), 7.46 (2H, t, *J* = 7.2 Hz, Ar**H**), 3.03 (1H, dd, *J* = 16.0, 3.6 Hz, COC**H**H), 2.69 (1H, dd, *J* = 16.0, 10.8 Hz, COCH**H**), 1.41-1-32 (1H, m, C**H**CH_3), 0.95 (3H, d, *J* = 7.2 Hz, CHC**H**$_3$), 0.03 (9H, s, Si(C**H**$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.0, 137.5, 132.9, 128.7, 128.2, 40.9, 16.3, 14.6, -3.2. HRMS Calcd. for $C_{13}H_{20}OSi$ (M-H$^+$): 219.1198. Found: 219.1192. $[\alpha]_D^{20}$ –4.28 (*c* = 1.73, $CHCl_3$) for a 93% ee sample.

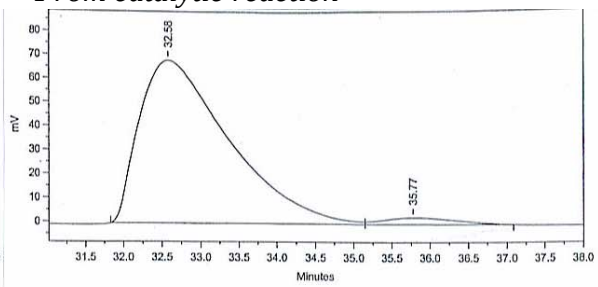
Enantiomeric purity was determined by chiral HPLC analysis (Chiral Technologies Chiralpak OD, 220 nm, 100% hexanes, 1.0 mL/min); chromatograms are illustrated below:

Authentic racemic



peak #	time	area	height	width	area %
1	32.109	3517018.0	50155.23	1.109	50.78806
2	34.350	3407873.0	45041.67	1.283	49.21194

From catalytic reaction



peak #	time	area	height	width	area %
1	32.576	5530494	68556.9	1.345	96.7453
2	35.773	186056.4	2850.85	1.088	3.25470

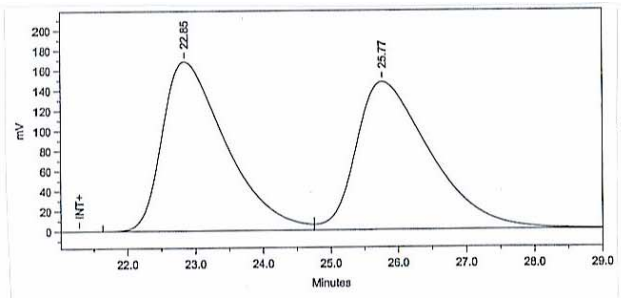
Representative procedure for Cu-catalyzed enantioselective conjugate addition of diarylzinc reagents to (*E*)-4-(dimethylphenylsilyl)-3-buten-2-one (15):

(*R*)-(+)-4-(Dimethylphenylsilyl)-4-phenyl-2-butanone (12). In a N_2-filled glove box, a 13 x 100 mm test tube was charged with $(CuOTf)_2{\cdot}C_6H_6$ (0.800 mg, 1.60 x 10^{-3} mmol), Schiff-based ligand **4** (1.8 mg, 4.0 x 10^{-4} mmol), and Ph_2Zn (52.3 mg, 2.40 x 10^{-4} mmol), sealed with a septum, and removed from the glovebox. The mixture was allowed to cool to 0 °C in a ice bath before a solution of **15** (33.6 mg, 1.60 x 10^{-1} mmol) in DME (0.800 mL) was added. The resulting solution was allowed to stir for 8 h at 0 ^{o}C (ice bath), at which time the reaction was quenched with the addition of a saturated solution of NH_4Cl (2.0 mL) and the mixture was diluted with Et_2O. The layers were separated and the aqueous layer was washed with Et_2O (3 x 2.0 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The pale yellow oil was purified by silica gel chromatography (20:1 petroleum ether: ethyl acetate, R_f = 0.4) to afford the desired product **12 (**35.9 mg, 1.27 x 10^{-1} mmol, 79.0%) as a colorless oil. IR (neat): 3075 (m), 3024 (m), 2962 (m), 2892 (m), 1722 (s), 1621 (m), 1489 (m), 1438 (s), 1357 (s), 1243 (s), 1111 (s), 841 (s), 809 (s), 740 (s), 721 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-6.94 (10H, m, Ar**H**), 2.96-2.86 (2H, m, aliphatic C**H**), 2.65 (1H, dd, *J* = 22.8, 10.8 Hz, C(O)C**H**$_2$), 1.95 (3H, s, C**H**$_3$C(O)), 0.25 (3H, s, SiC**H**$_3$), 0.22 (3H, s, SiC**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.3, 142.1, 136.7, 134.3, 129.4, 128.3, 127.9, 127.7, 125.9, 44.1, 31.5,

30.2, -3.9, -5.3. Anal. Calcd. for $C_{18}H_{22}OSi$: C, 76.56; H, 7.85. Found: C, 76.32; H, 7.55. $[\alpha]_D^{20}$ +14.0 (*c* = 1.97, $CHCl_3$) for a 94% ee sample, indicating the prevalence of the *R* isomer.[12]

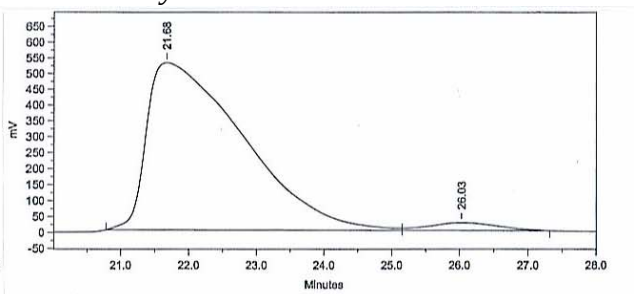
Enantiomeric purity was determined by chiral HPLC analysis (Chiral Technologies Chiralpak AS, 220 nm, 99.5% hexanes:0.5% *i*-PrOH, 0.6 mL/min); chromatograms are illustrated below:

Authentic racemic



peak #	time	area	height	width	area %
1	22.846	11020940.0	168652.50	1.089	49.4381
2	22.772	11271460.0	147209.10	1.276	50.5619

From catalytic reaction

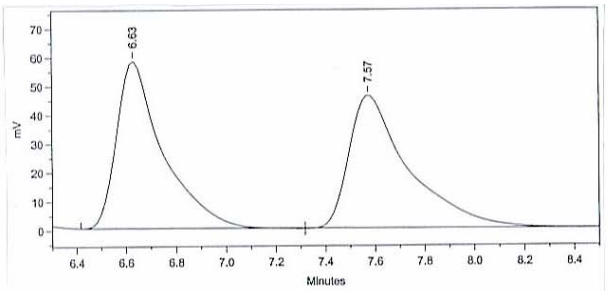


peak #	time	area	height	width	area %
1	21.676	52124100	527350.2	1.647	96.794
2	26.031	1726255.0	25686.53	1.165	3.2057

(*R*)-(–)-4-(Trimethylsilyl)-4-phenyl-2-butanone (11). IR (neat): 3068 (m), 3018 (m), 2955 (s), 2899 (m), 1741 (s), 1596 (m), 1495 (m), 1463 (m), 1438 (m), 1237 (s), 1174 (s), 853 (s), 721 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.24-7.05 (5H, m, Ar**H**), 2.97 (1H, ddd, *J* = 16.0, 10.4, 0.4 Hz, aliphatic C**H**), 2.73-2.63 (2H, m, aliphatic C**H**), 2.03 (3H, s, C**H**$_3$C(O)), -0.05 (9H, s, Si(C**H**$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.6, 142.8, 128.4, 127.5, 124.9, 44.2, 31.9, 30.1, -2.9. HRMS Calcd. for $C_{13}H_{20}OSi$: 220.1291. Found: 220.1283. $[\alpha]_D^{20}$ –1.5 (*c* = 1.2, $CHCl_3$) for a 92% ee sample.

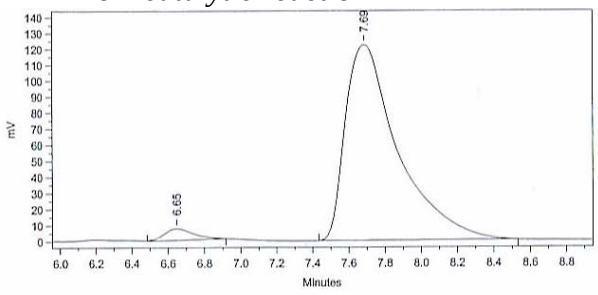
Enantiomeric purity was determined by chiral HPLC analysis (Chiral Technologies Chiralpak OD, 220 nm, 99.0% hexanes:1.0% *i*-PrOH, 1.0 mL/min); chromatograms are illustrated below:

Authentic racemic



peak #	time	area	height	width	area %
1	6.630	742939.9	58252.31	0.213	49.4262
2	7.574	760190.9	46067.04	0.275	50.5738

From catalytic reaction



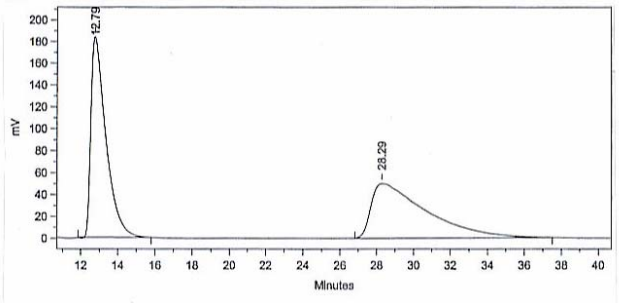
peak #	time	area	height	width	area %
1	6.617	100326.6	8359.80	0.200	96.148
2	7.576	2504413.0	133760.50	0.312	3.8517

(12) Matsumoto, Y.; Hayashi, T.; Ito, Y. *Tetrahedron* **1994**, *50*, 335-346; Reported: $[\alpha]_D^{20}$ +9.2 (*c* = 1.1, $CHCl_3$) for (*R*)-(+)-4-(dimethylphenylsilyl)-4-phenyl-2-butanone.

(*R*)-(+)-4-(Dimethylphenylsilyl)-4-(4-methoxyphenyl)-2-butanone (13). IR (neat): 3068 (m), 3012 (m), 2973 (m), 2842 (m), 1721 (s), 1614 (m), 1507 (s), 1432 (m), 1350 (m), 1255 (s), 1111 (s), 1048 (m), 827(m), 770 (m), 739 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41-7.32 (5H, m, Ar**H**), 6.85 (2H, d, *J* = 8.8 Hz, Ar**H**), 6.75 (2H, d, *J* = 8.8 Hz, Ar**H**), 3.76 (3H, s, OC**H**$_3$), 2.89-2.77 (2H, m, aliphatic C**H**), 2.65-2.55 (1H, m, aliphatic C**H**), 1.94 (3H, s, C**H**$_3$C(O)), 0.23 (3H, s, SiC**H**$_3$), 0.21 (3H, s, SiC**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.6, 157.2, 136.9, 134.3, 133.9, 129.4, 128.6, 127.9, 113.8, 55.3, 44.3, 30.5, 30.1, -3.9, -5.2. HRMS Calc for $C_{19}H_{24}O_2Si$: 312.1554. Found: 312.1546. $[\alpha]_D^{20}$ +0.635 (*c* = 1.26, $CHCl_3$) for a 87% ee sample.

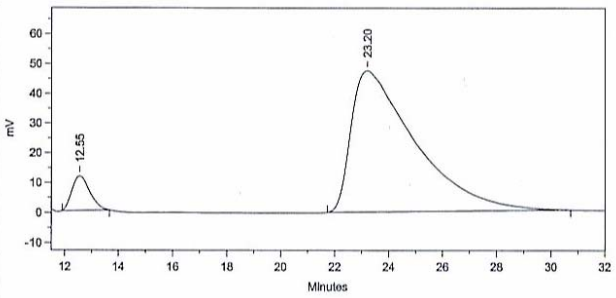
Enantiomeric purity was determined by chiral HPLC analysis (Chiral Technologies Chiralpak AS, 220 nm, 99.0% hexanes:1.0% *i*-PrOH, 1.0 mL/min); chromatograms are illustrated below:

Authentic racemic



peak #	time	area	height	width	area %
1	12.789	10167990.0	183745.80	0.922	49.395
2	28.287	10416950.0	50074.99	3.467	50.605

From catalytic reaction

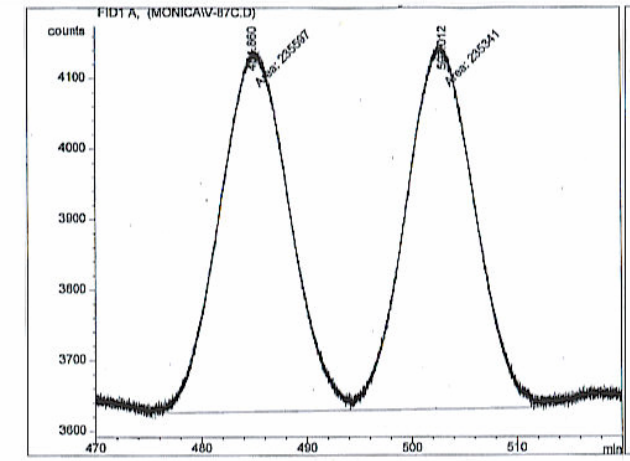


peak #	time	area	height	width	area %
1	12.554	527635.9	11527.51	0.763	6.310
2	23.203	7834330	47458.99	2.751	93.69

(*R*)-(+)-4-(Dimethylphenylsilyl)-4-(4-trifluoromethylphenyl)-2-butanone (14). IR (neat): 3075 (m), 3050 (m), 3020 (w), 2962 (m), 2912 (m), 1734 (s), 1621 (s), 1432 (m), 1325 (s), 1250 (m), 1174 (s), 1124 (s), 1079 (s), 1017 (m), 853 (m), 834 (m), 809 (m), 746 (m), 702 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.41-7.32 (5H, m, Ar**H**), 7.1 (2H, d, *J* = 8.0 Hz, Ar**H**), 3.01-2.89 (2H, m, aliphatic C**H**), 2.68 (1H, dd, *J* = 15.6, 2.4 Hz, aliphatic C**H**), 1.97 (3H, s, C**H**$_3$C(O)), 0.24 (3H, s, SiC**H**$_3$), 0.23 (3H, s, SiC**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 146.9, 135.9, 134.2, 129.7, 128.3, 127.7, 127.3 (q, *J* = 32.1 Hz), 125.2 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 270.2 Hz), 43.8, 31.7, 30.1, -4.1, -5.2. HRMS Calcd. for $C_{19}H_{21}F_3OSi$: 350.1314. Found: 350.1307. $[\alpha]_D^{20}$ +7.58 (*c* = 1.24, $CHCl_3$) for a 85% ee sample.

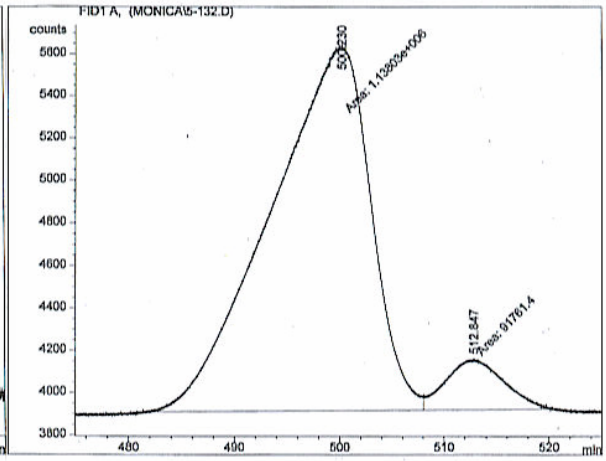
Enantiomeric purity was determined by chiral GLC analysis (Chiraldex-GTA, 110 °C, 25 psi); chromatograms are illustrated below:

Authentic racemic



peak #	time	area	height	width	area %
1	484.860	235597	517.1139	7.5933	50.02719
2	503.012	235341	519.1823	7.5549	49.97281

From catalytic reaction



peak #	time	area	height	width	area %
1	500.230	1138030	1735.61	10.928	92.5385
2	512.847	91761.4	247.3768	6.1923	7.46151

(*S*)-4-(Dimethylphenylsilyl)-2-(trifluoromethylsulfonyloxy)-2-hexene (16). In a N_2 filled glove box, a flame-dried 10-mL flask was charged with $(CuOTf)_2 \cdot C_6H_6$ (7.04 mg, 1.40 x 10^{-2} mmol) and Schiff base **4** (16.2 mg, 3.60 x 10^{-2} mmol), sealed with a septum, wrapped with parafilm and Telfon tape and removed from the glovebox. A solution of enone **15** (294 mg, 1.44 mmol) in toluene (14.4 mL) was added through a syringe at 22 ^{o}C, followed by the addition of Et_2Zn (450 μL, 4.32 mmol) (CAUTION: Et_2Zn is pyrophoric! Use extreme caution). The mixture was allowed to stir for 1 h at 22 ^{o}C, at which time it was cooled to 0 ^{o}C with an ice bath. Triflic anhydride (1.12 mg, 6.62 mmol) was added dropwise to the mixture, which was allowed to warm to 22 ^{o}C and stir for 12 h at 22 ^{o}C. At this time, the solution was cooled to 0 ^{o}C and the reaction was quenched through the addition of a saturated solution of $NaHCO_3$ (15 mL) and the resulting mixture was diluted with EtOAc (15 mL). The resulting layers were separated and the aqueous layer was washed with EtOAc (3 x 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to furnish a yellow oil. The residue was purified by silica gel chromatography (100:1 hexanes:Et_2O, R_f = 0.5) to afford the desired product **16** (491 mg, 1.34 mmol, 6.6:1 E:Z ratio, 93%) as a colorless oil. IR (neat): 3068 (w), 3050 (w), 2962 (m), 2930 (m), 2873 (m), 1413 (s), 1250 (m), 1212 (s), 1143 (s), 1086 (m), 972 (s), 887 (s), 885 (s), 834 (s), 778 (m) cm^{-1}. ^{1}H NMR only *E*-isomer reported (400 MHz, $CDCl_3$): δ 7.50-7.35 (5H, m, Ar**H**), 5.29 (1H, d, J = 12.0 Hz, C=C**H**), 1.83 (3H, s, C$\mathbf{H}_3$), 1.67-1.20 (3H, m, aliphatic C**H**), 0.86 (3H, t, J = 7.2 Hz, $CH_2C\mathbf{H}_3$), 0.34 (3H, s, SiC$\mathbf{H}_3$), 0.32 (3H, s, SiC$\mathbf{H}_3$). ^{13}C NMR both *E*- and *Z*-olefin isomers reported (100 MHz, $CDCl_3$): δ 144.6, 144.3, 136.6, 134.1, 129.5, 129.4, 128.0, 127.9, 124.5, 123.8, 120.3, 117.1, 30.8, 29.6, 22.9, 22.9, 19.7, 16.3, 14.6, -4.1, -4.6, -5.1, -5.1. Anal. Calcd. for $C_{15}H_{21}F_3O_3SSi$: C, 49.16; H, 5.78. Found: C, 49.44; H, 5.57.

(*S*)-4-(Dimethylphenylsilyl)-2-phenyl-2-hexene (17).[13] In a N_2 filled glove box, a flame-dried 25-mL flask was charged with $Pd(OAc)_2$ (22.4 mg, 0.100 mmol), PPh_3 (57.6 mg, 0.220 mmol), and $PhB(OH)_2$ (153 mg, 1.25 mmol), wrapped with parafilm and Telfon tape and removed from the glovebox. A solution of **16** (366 mg, 1.00 mmol) in THF (2.0 mL) was added at 22 ^oC to the flask. After 10 min, an aqueous solution of KOH (0.50M, 2.0 mL) was added to the mixture. After allowing the solution to stir for 45 min, distilled H_2O (2.0 mL) was added and the mixture was washed with EtOAc (3 x 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the volatiles were concentrated in vacuo to furnish a yellow oil, which was purified by silica gel chromatography (150:1 petroleum ether:Et_2O) to afford **17** as a colorless oil (198 mg, 0.672 mmol, 67%, 81% based on conversion of *E*-olefin isomer). IR (neat): 3069 (m), 3018 (m), 2962 (s), 2917 (m), 2870 (m), 1640 (w), 1596 (m), 1495 (s), 1432 (s), 1381 (m), 1250 (s), 1111 (s), 1079 (m), 1030 (m), 834 (s), 759 (s), 696 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55-7.20 (10H, m, Ar**H**), 5.57 (1H, dd, *J* = 11.2, 1.2 Hz, C=C**H**), 2.03 (1H, dt, *J* = 11.2, 3.2 Hz, aliphatic C**H**), 1.86 (3H, s, C$\mathbf{H}_3$), 1.70-1.34 (2H, m, aliphatic C**H**), 0.89 (3H, t, *J* = 7.2 Hz, $CH_2C\mathbf{H}_3$), 0.35 (3H, s, SiC$\mathbf{H}_3$), 0.32 (3H, s, SiC$\mathbf{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 138.2, 134.2, 133.3, 130.8, 129.1, 128.2, 127.8, 126.2, 125.6, 32.6, 23.5, 16.4, 14.9, -4.1, -4.8. Anal. Calcd. for $C_{15}H_{21}F_3O_3SSi$: C, 49.16; H, 5.78. Found: C, 49.44; H, 5.57.

(2*S*,3*R*,4*S*)-4-(Dimethylphenylsilyl)-2,3-oxiranyl-2-phenyl-hexane (G).[14] To a solution of **17** (20.0 mg, 6.80 x 10^{-2} mmol) and $NaHCO_3$ (6.80 mg, 8.10 x 10^{-2} mmol) in CH_2Cl_2 (230 μL) at -78 ^oC (dry ice/acetone bath) was added a solution of *m*-CPBA (15.2 mg, 8.80 x 10^{-2} mmol) in CH_2Cl_2 (440 μL) through cannula. The resulting solution was allowed to warm to 0 ^oC and allowed to stir for 2 h, at which time the reaction was quenched by the addition of Et_2O (2 mL) and a saturated aqueous $NaHCO_3$ solution (2 mL). The layers were separated and the aqueous layer was washed with Et_2O (3 x 2 mL). The combined organic layers were washed with a saturated aqueous NaCl solution (2 mL), dried over anhydrous $MgSO_4$, and the volatiles were concentrated in vacuo to furnish a colorless oil, which was purified by silica gel chromatography (50:1 petroleum ether:Et_2O) to afford **G** as a colorless oil (21.0 mg, 6.80 x 10^{-2} mmol, 24:1 dr, >98%). IR (neat): 3069 (m), 2968 (s), 2924 (m), 2873 (m), 1608 (w), 1500 (s), 1451 (s), 1432 (s), 1382 (s), 1250 (s), 1111 (s), 1067 (s), 841 (s), 702 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (2H, d, *J* = 7.6 Hz, Ar**H**), 7.36-7.26 (6H, m, Ar**H**), 7.15 (2H, d, *J* = 7.6 Hz), 2.78 (1H, d, *J* =11.2 Hz, OC**H**), 1.77-1.61 (2H, m, aliphatic C**H**), 1.34 (3H, s, CC$\mathbf{H}_3$), 1.09 (3H, t, *J* = 7.6 Hz, $CH_2C\mathbf{H}_3$), 1.00 (1H, ddd, *J* = 10.8, 8.0, 5.2 Hz, aliphatic C**H**), 0.36 (3H, s, SiC$\mathbf{H}_3$), 0.34 (3H, s, SiC$\mathbf{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 137.7, 134.1, 129.4, 128.3, 128.0, 127.1, 125.1, 70.4, 60.4, 29.3, 23.0, 18.6, 15.1, -3.7, -3.9. HRMS Calcd. for $C_{20}H_{26}OSi$: 310.1753. Found: 310.1751.

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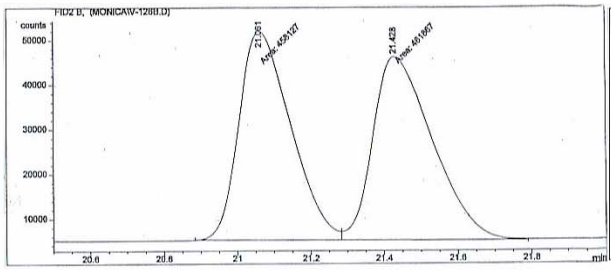
(13) Willis, M. C.; Claverie, C. K. *Tetrahedron Lett.* **2001**, *42*, 5105-5107.
(14) For a review on substrate directed reactions, see: Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307-1370.

(*S*)-(+)-2-Phenyl-3-hexen-2-ol (18). To a solution of **G** (10 mg, 3.2 x 10^{-2} mmol) in THF (65 μL) at 23 °C was added TBAF (65 μL, 1.0 M). The mixture was allowed to stir for 0.5 h at which time it was filtered through a pad of silica gel with CH_2Cl_2. The silica gel pad was washed with CH_2Cl_2 (3 x 5 mL) and the volatiles were concentrated in vacuo to furnish a colorless oil, which was purified by silica gel chromatography (25:1 petroleum ether:EtOAc) to afford **18** as a colorless oil (5.3 mg, 3.0 x 10^{-2} mmol, 94%). IR (neat): 3456 (br), 3031 (w), 2961 (m), 2924 (m), 2867 (m), 1464 (s), 1376 (m), 1029 (m), 979 (m), 708 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48-7.24 (5H, m, Ar**H**), 5.80-5.72 (2H, m, C**H**=CH and CH=C**H**), 2.08 (2H, m, C**H**$_2$CH$_3$), 1.83 (1H, s, O**H**), 1.64 (3H, s, C**H**$_3$), 1.01 (3H, t, *J* = 7.6 Hz, CH$_2$C**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 136.0, 130.8, 128.3, 126.9, 125.3, 74.5, 30.1, 25.4, 13.7. HRMS Calc for $C_{14}H_{16}O$: 176.1201. Found: 176.1204. $[\alpha]_D^{20}$ +4.53 (*c* = 0.352, $CHCl_3$) for a 96% ee sample.

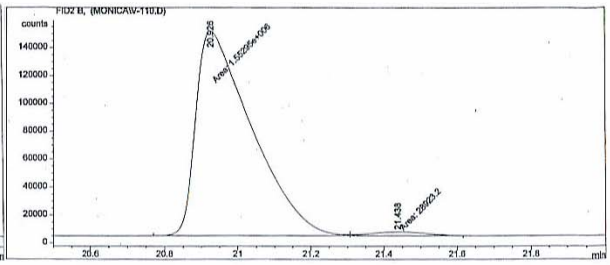
Enantiomeric purity was determined by chiral GLC analysis (β-dex, 85 °C, 15 psi); chromatograms are illustrated below:

Authentic racemic



peak #	time	area	height	width	area %
1	21.061	458127	46794.8	0.1632	49.79672
2	21.428	461867	41107.3	0.1873	50.20328

From catalytic reaction



peak #	time	area	height	width	area %
1	20.926	1552950	146975	0.1761	98.1716
2	21.438	28923.4	2687.18	0.1794	1.82842

(*S*)-3-(Dimethylphenylsilyl)-5-methyl-4-nonene (19).[15] In a N_2 filled glove box, a flame-dried 25-mL flask was charged with CuI (477 mg, 2.50 mmol), wrapped with parafilm and Telfon tape and removed from the glovebox. Tetrahydrofuran (5 mL) was added to the flask, and the mixture was allowed to cool to -15 °C with a dry ice/acetone bath. To the cooled solution was added *n*-BuLi (2.3 mL, 3.6 mmol) in a dropwise fashion, followed by the addition of **16** (270 mg, 0.74 mmol) in a solution of THF (1.7 mL). After allowing to stir for 16 h, the mixture was diluted with petroleum ether (20 mL) and filtered through a pad of celite, which was then washed with petroleum ether (3 x 20 mL). The volatiles were concentrated in vacuo to furnish a colorless oil. The oil was purified by silica gel chromatography (100% petroleum ether) to afford **19** as a colorless oil (169 mg, 0.616 mmol, 83%). IR (neat): 3081 (w), 2975 (s), 2930 (s), 2886 (m), 1464 (m), 1432 (m), 1256 (s), 1117 (s), 834 (s), 809 (m), 740 (m), 702 (s) cm^{-1}. ^1H

(15) McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1980**, *21*, 4313-4316.

NMR (400 MHz, $CDCl_3$): δ 7.51-7.33 (5H, m, Ar**H**), 5.57 (1H, dd, *J* = 11.2, 1.2 Hz, C=C**H**), 2.01-1.98 (2H, m, aliphatic C**H**), 1.77 (1H, dt, *J* =11.2, 3.2 Hz, aliphatic C**H**), 1.58-1.47 (1H, m, aliphatic C**H**), 1.45 (3H, s, C$\mathbf{H}_3$), 1.41-1.13 (5H, m, aliphatic C**H**), 0.90 (3H, t, *J* = 6.8 Hz, $CH_2C\mathbf{H}_3$), 0.81 (3H, t, *J* = 7.6 Hz, $CH_2C\mathbf{H}_3$) 0.26 (3H, s, SiC$\mathbf{H}_3$), 0.24 (3H, s, SiC$\mathbf{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 134.0, 133.9, 128.7, 127.5, 125.6, 40.0, 30.8, 30.7, 23.5, 22.6, 16.6, 14.7, 14.3, -3.9, -4.8. Anal. Calcd. for $C_{18}H_{30}Si$: C, 78.75; H, 11.02. Found: C, 78.73; H, 10.90. HRMS Calc for $C_{18}H_{30}Si$: 274.2117. Found: 274.2110.

(3*R*,4*S*,5*R*)-3-Butyl-1-chlorosulfonyl-4-(dimethylphenylsilyl)-5-ethyl-3-methylpyrrolidin-2-one (H).[16] A solution of **19** (10 mg, 3.6 x 10^{-2} mmol) in toluene (360 μL) was allowed to cool to 0 °C with an ice bath. To this mixture was added CSI (15.5 μL, 18.0 x 10^{-2} mmol) and the reaction was allowed to warm to 22 °C. After 3 h, the reaction was quenched by the addition of a saturated aqueous $NaHCO_3$ solution (2 mL) and CH_2Cl_2 (2 mL). The layers were separated and the aqueous layer was washed with CH_2Cl_2 (3 x 2 mL). The organic layers were combined, dried over anhydrous $MgSO_4$, and the volatiles were concentrated in vacuo to furnish a colorless oil. The oil was purified by silica gel chromatography (25:1 petroleum ether:Et_2O) to afford **20** as a colorless oil (11.6 mg, 2.89 x 10^{-2} mmol, 97:3 dr, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.39 (5H, m, Ar**H**), 4.28 (1H, ddd, *J* = 9.2, 6.0, 2.0, NC**H**), 2.17 (1H, dddd, *J* = 14.8, 13.2, 7.2, 7.2 Hz, aliphatic C**H**), 1.84 (1H, d, *J* = 9.2 Hz, aliphatic C**H**), 1.72-1.07 (8H, m, aliphatic C**H**), 1.20 (3H, s, C$\mathbf{H}_3$), 0.90 (3H, t, *J* = 7.2 Hz, $CH_2C\mathbf{H}_3$), 0.71 (3H, t, *J* = 7.2 Hz, $CH_2C\mathbf{H}_3$), 0.49 (3H, s, SiC$\mathbf{H}_3$), 0.48 (3H, s, SiC$\mathbf{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 136.9, 133.6, 129.9, 128.3, 62.6, 48.8, 37.3, 29.3, 27.2, 25.2, 23.1, 23.1, 14.2, 7.1, -1.5, -2.0. Anal Calcd. for $C_{19}H_{30}ClNO_3SSi$: C, 54.85; H, 7.27. Found: C, 54.55; H, 7.27.

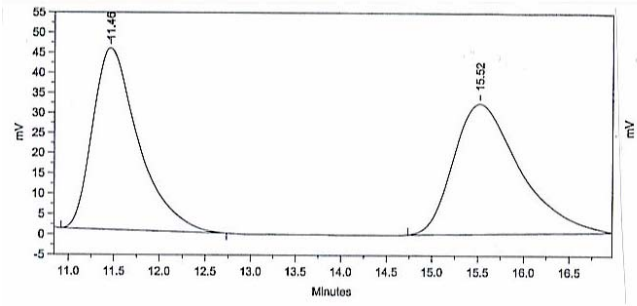
(3*R*,4*S*,5*R*)-(+)-3-Butyl-4-(dimethylphenylsilyl)-5-ethyl-3-methyl-pyrrolidin-2-one (20). To a solution of **H** (10.0 mg, 2.50 x 10^{-2} mmol) in THF (250 μL) was added a saturated aqueous $NaHCO_3$ solution (100 μL) and a saturated aqueous Na_2SO_3 solution (100 μL). The mixture was allowed to heat to 50 °C for 0.5 h at which time the solution was allowed to cool to 22 °C and EtOAc (2 mL) was added and the layers were separated. The aqueous layer was washed with EtOAc (3 x 2 mL) and the organic layers were combined, dried over anhydrous $MgSO_4$, and the volatiles removed *in vacuo* to furnish a colorless oil. The oil was purified by silica gel chromatography (1:1 petroleum ether:Et_2O) to afford **20** as a colorless oil (6.60 mg, 2.20 x 10^{-2} mmol, 87%). IR (neat): 3194 (s), 3081 (s), 2961 (s), 2936 (s), 2880 (m), 1697 (s), 1470 (s), 1426 (m), 1388 (m), 1331 (m), 1262 (s), 1111 (s), 840 (s), 822 (s), 746 (w), 702 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.36 (5H, m, Ar**H**), 5.78 (1H, br s, N**H**), 3.51 (1H, dt, *J* = 9.2, 2.4 Hz, NC**H**), 1.61-1.10 (9H, m, aliphatic C**H**), 1.13 (3H, s, C$\mathbf{H}_3$), 0.88 (3H, t, *J* = 7.2 Hz, $CH_2C\mathbf{H}_3$), 0.81 (3H, t, *J* = 7.6 Hz, $CH_2C\mathbf{H}_3$), 0.43 (3H, s, Si(C$\mathbf{H}_3$)), 0.42 (3H, s, Si(C$\mathbf{H}_3$)).

(16) For a recent example of [3+2] cycloaddition of an allylsilane and CSI, see: Woerpel, K. A.; Romero, A. *Org. Lett.* **2006**, *8*, 2127-2130 and references therein.

^{13}C NMR (100 MHz, $CDCl_3$): δ 182.2, 138.3, 133.7, 129.3, 127.9, 54.6, 48.2, 37.4, 35.4, 29.2, 27.5, 23.8, 23.4, 14.3, 10.4, -1.5, -1.7. HRMS Calc for $C_{19}H_{32}NOSi$ ($M+H^+$): 318.2253. Found: 318.2259. $[a]_D^{20}$ +31.8 (*c* = 0.440, $CHCl_3$) for a 94% ee sample.

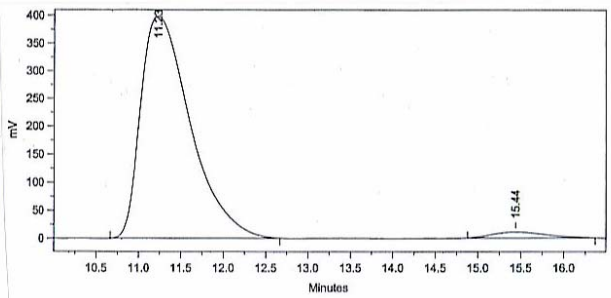
Enantiomeric purity was determined by chiral HPLC analysis (Chiral Technologies OD(B), 220 nm, 95.0% hexanes:5.0% *i*-PrOH, 1.0 mL/min) of product **20**; chromatograms are illustrated below:

Authentic racemic



peak #	time	area	height	width	area %
1	11.456	1573511.0	45009.54	0.583	49.25767
2	15.519	1620938.0	32285.78	0.837	50.74233

From catalytic reaction

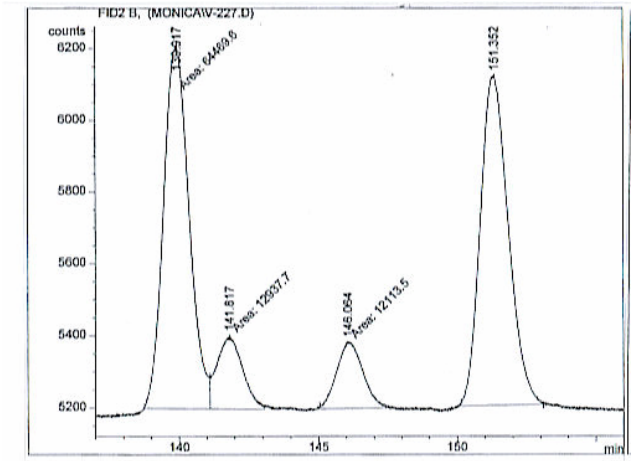


peak #	time	area	height	width	area %
1	11.228	16174180	398190.0	0.677	97.1907
2	15.437	467507.7	10850.10	0.718	2.80926

(1*S*,2*S*)-(+)-2-Butyl-2-methyl-1-phenyl-3*E*-hexen-1-ol (21). To a solution of **19** (15.0 mg, 5.50 x 10^{-2} mmol) and benzaldehyde (8.60 μL, 8.30 x 10^{-2} mmol) in CH_2Cl_2 (270 μL) at -50 ^oC was added a solution of $TiCl_4$ (9.00 μL, 8.30 x 10^{-2} mmol) in CH_2Cl_2 (270 μL). The mixture was allowed to stir for 5 h at -50 ^oC (dry ice/acetone bath), after which the reaction was quenched by the addition of a saturated aqueous $NaHCO_3$ solution (2 mL) and allowed to warm to 22 ^oC. The layers were separated and the aqueous layer was washed with EtOAc (3 x 2 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and volatiles were concentrated in vacuo to furnish a colorless oil. The resulting oil was purified by silica gel chromatography (20:1 petroleum ether:EtOAc) to afford **21** as a colorless oil (10.2 mg, 4.1 x 10^{-2} mmol, 87:13 dr, 76%). IR (neat): 3465 (br), 3031 (w), 2962 (s), 2923 (s), 2867 (m), 1464 (s), 1376 (m), 1029 (s), 979 (m), 708 (s) cm^{-1}. ^{1}H NMR of the major diastereomer (400 MHz, $CDCl_3$): δ 7.31-7.22 (5H, m, Ar**H**), 5.41 (1H, dt, *J* = 16.0, 6.0 Hz, C**H**=CH), 5.31 (1H, dt, *J* = 16.0, 1.2 Hz, CH=C**H**), 4.40 (1H, d, *J* = 4.4 Hz, C**H**OH), 2.09-2.03 (2H, m, aliphatic C**H**), 1.31-1.11 (6H, m, aliphatic C**H**), 1.03 (3H, s, C**H**$_3$), 0.98 (3H, t, *J* = 7.2 Hz, CH_2C**H**$_3$), 0.85 (3H, t, *J* = 7.2 Hz, CH_2C**H**$_3$). ^{13}C NMR of both diastereomers (100 MHz, $CDCl_3$): δ 141.7, 140.8, 134.7, 133.7, 133.4, 132.9, 128.3, 128.0, 127.5, 127.5, 127.4, 127.4, 81.1, 80.4, 45.1, 44.4, 38.0, 36.8, 26.5, 26.5, 26.2, 26.1, 23.7, 23.6, 20.0, 17.2, 14.3, 14.3, 14.2. HRMS Calc for $C_{17}H_{27}O$ ($M+H^+$): 247.2063. Found: 247.2058. $[\alpha]_D^{20}$ +18.9 (*c* = 0.666, $CHCl_3$) for 95% ee (major) and 50% ee (minor) samples.

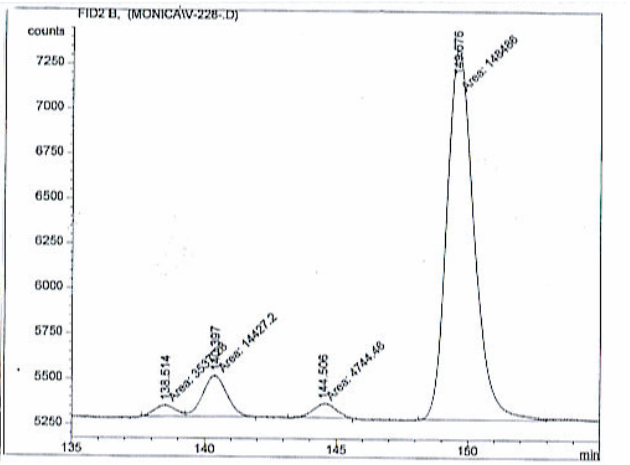
Enantiomeric purity was determined by chiral GLC analysis (β-dex, 140 ^oC, 15 psi); chromatograms are illustrated below:

Authentic racemic



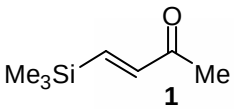
peak #	time	area	height	width	area %
1	139.917	64469.6	1013.39	1.060	41.9709
2	141.837	12937.7	207.923	1.037	8.42272
3	146.064	12113.5	188.714	1.070	7.88612
4	151.352	6.4084.5	922.580	0.8144	41.7202

From catalytic reaction



peak #	time	area	height	width	area %
1	138.514	3537.28	69.0850	0.8534	2.06623
2	150.397	14427.2	233.619	1.029	8.42735
3	144.506	4744.46	83.1967	0.9504	2.77136
4	149.576	148486	2063.48	1.199	86.7350

^{1}H NMR SPECTRA



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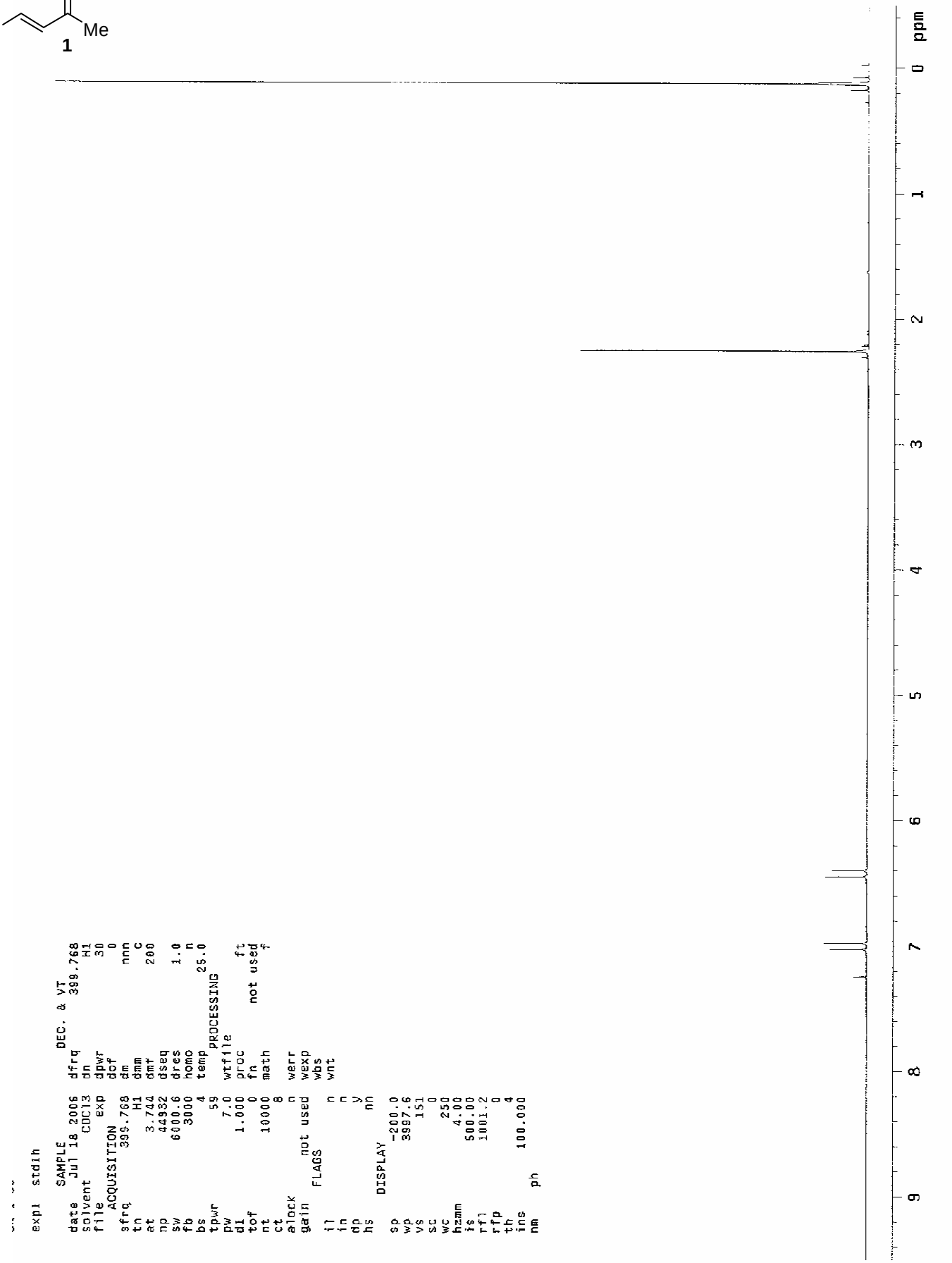

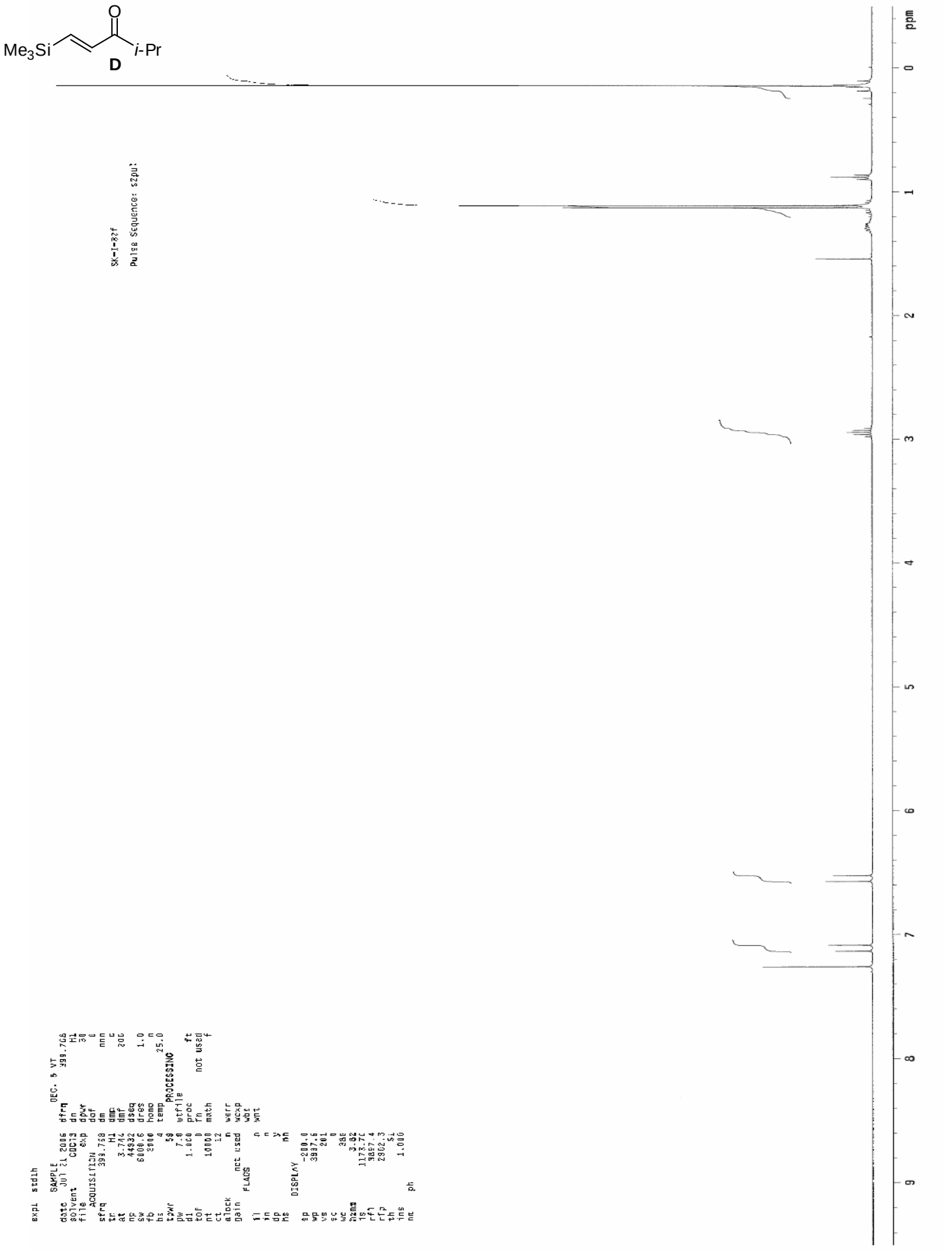
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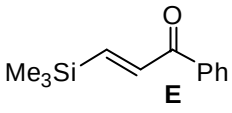
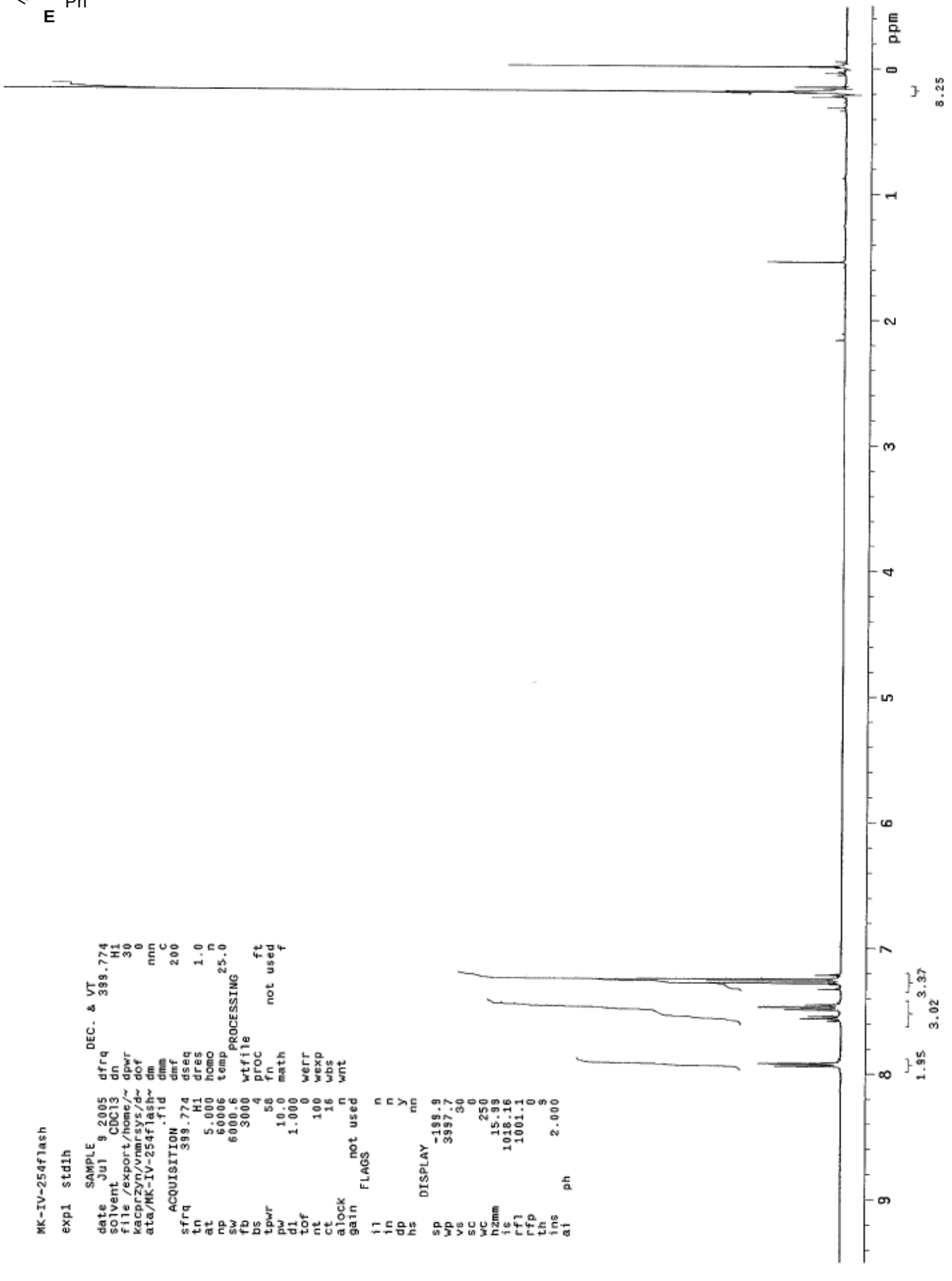
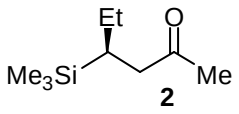
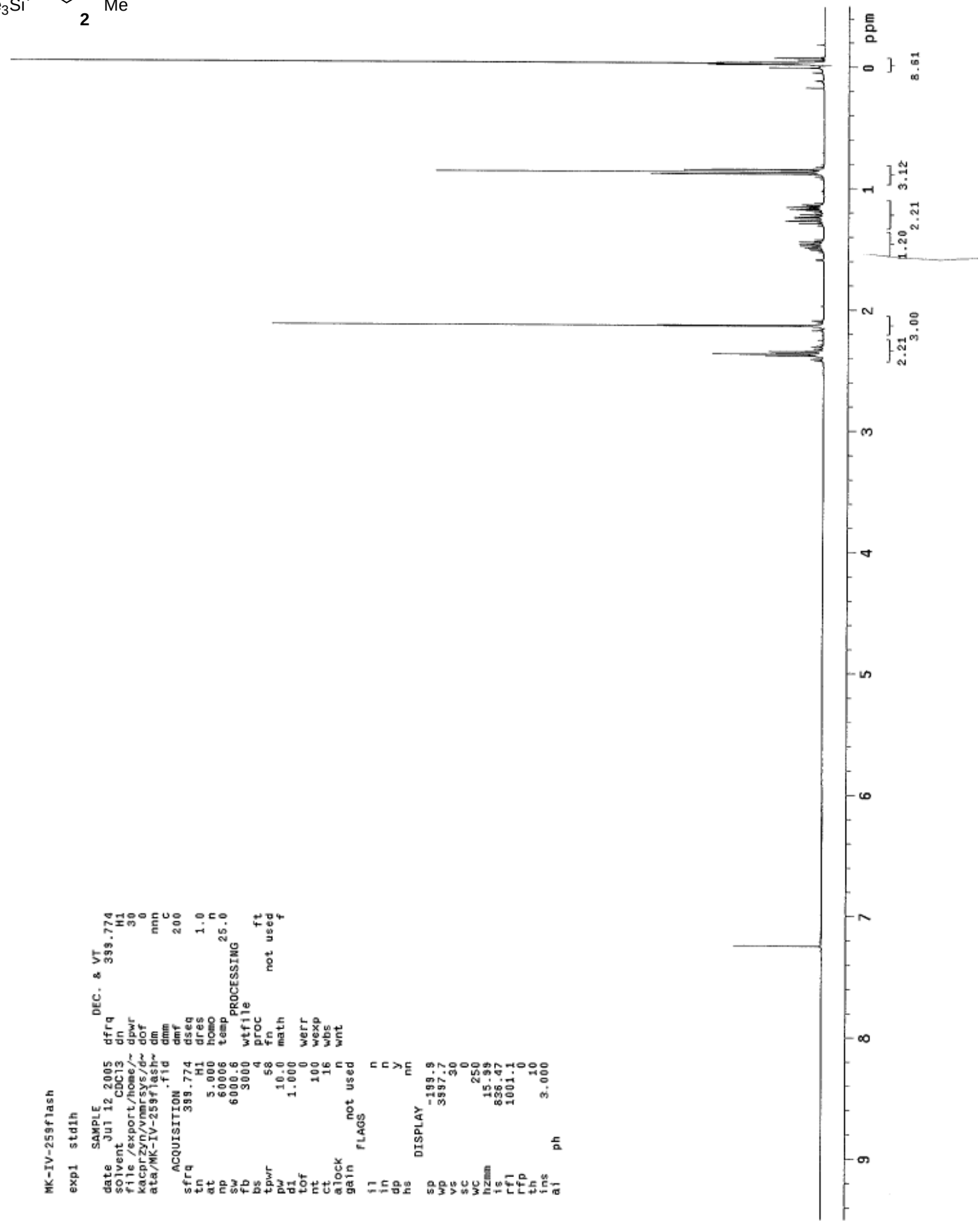

O
Me3Si
Ph

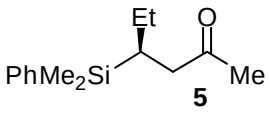
E


MK-IV-254flash
exp1 std1h
SAMPLE
date Jul 9 2005
solvent CDCl3
file /export/home/~
kacprzyn/vnmrsys/d~
ata/MK-IV-254flash~
.fid
ACQUISITION
sfrq 399.774
tn H1
at 5.000
np 60006
sw 6000.6
fb 3000
bs 4
tpwr 58
pw 10.0
d1 1.000
tof 0
nt 100
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -189.9
wp 3997.7
vs 30
sc 0
wc 250
hzmm 15.99
is 1018.16
rfl 1001.1
rfp 0
th 9
ins 2.000
ai ph
DEC. & VT
dfrq 399.774
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
ppm
1.95
3.37
3.02
8.25

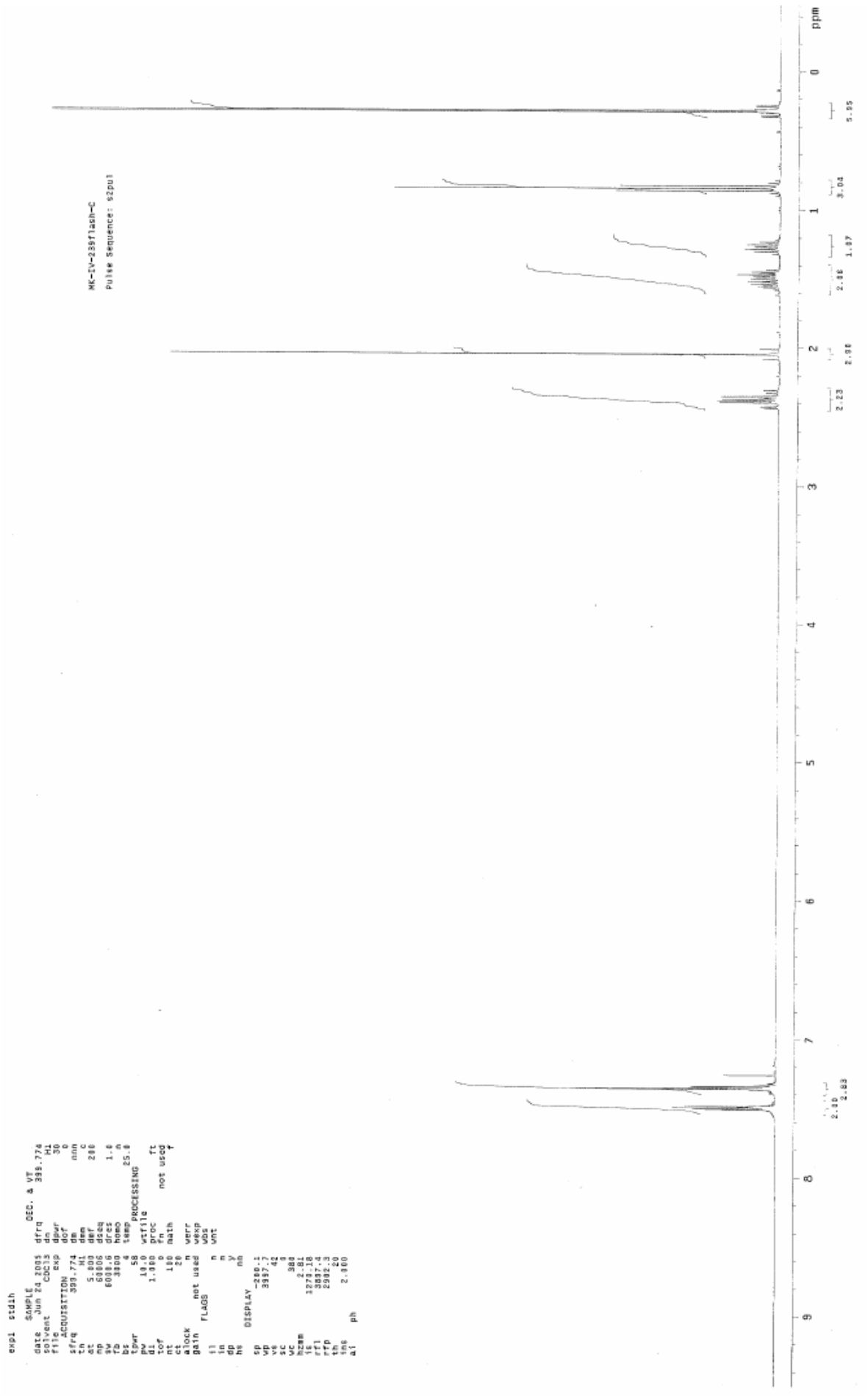

Et
O
Me3Si
Me

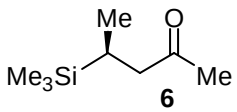
2


MK-IV-259flash
expl stdih
SAMPLE
date Jul 12 2005
solvent CDCl3
file /export/home/~
kacprzyn/vnmrsys/d~
ata/MK-IV-259flash~
.fid
ACQUISITION
sfrq 399.774
tn H1
at 5.000
np 60006
sw 60006.6
fb 3000
bs 4
tpwr 58
pw 10.0
d1 1.000
tof 0
nt 100
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -199.8
wp 3997.7
vs 30
sc 0
wc 250
hzmm 15.99
is 886.47
rfl 1001.1
rfp 0
th 10
ins 3.000
ai ph
DEC. & VT
dfrq 399.774
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
ppm
0
1
2
3
4
5
6
7
8
9
8.61
3.12
2.21
1.20
2.21
3.00

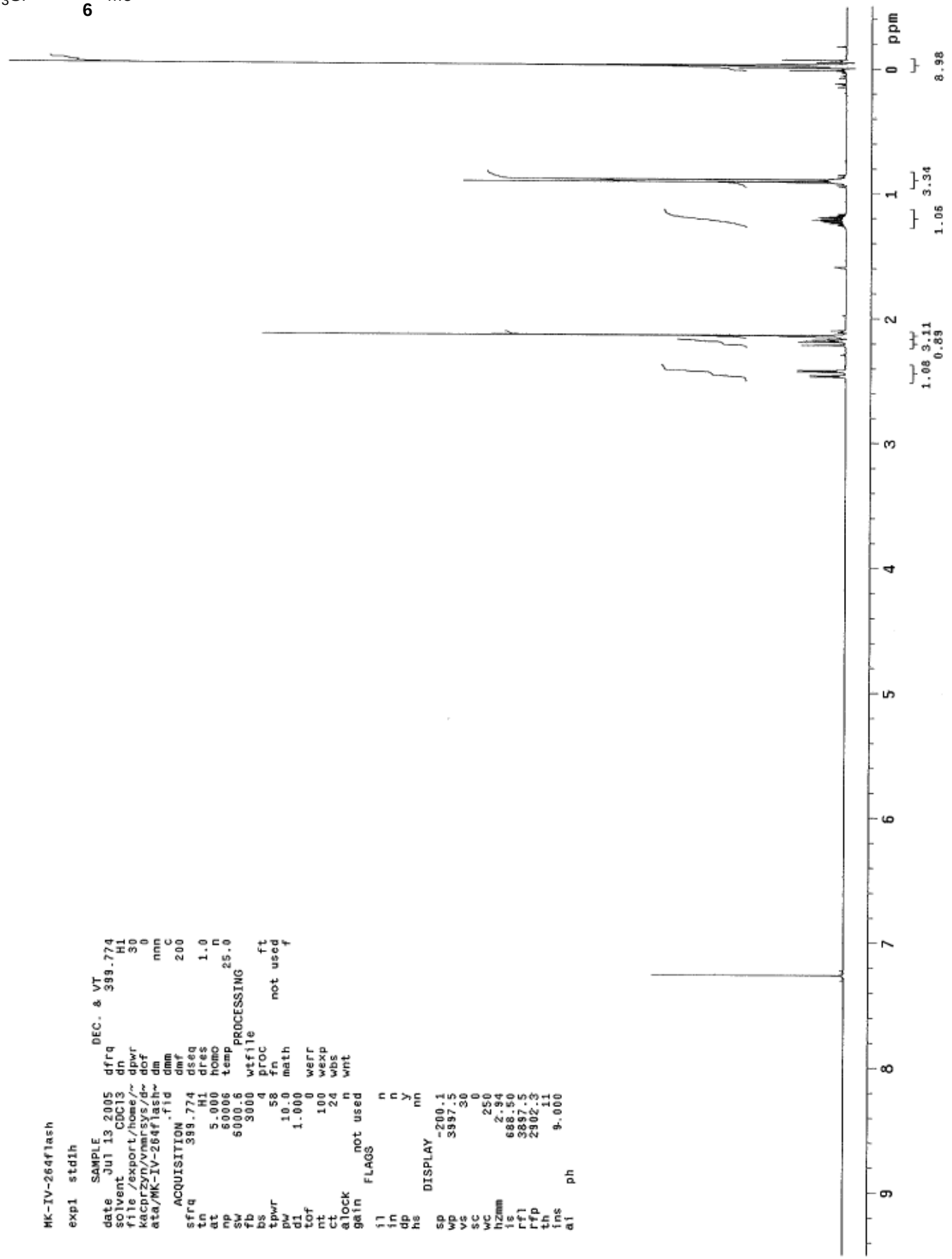

Et
O
PhMe2Si
Me

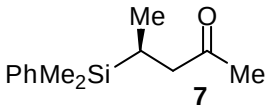
5


MK-IV-259flash-C
Pulse Sequence: s2pul
ppm
5.95
3.04
1.87
2.86
2.23
2.00
2.10
2.03
expl stdih
SAMPLE
date Jun 24 2005
solvent CDCl3
file exp
ACQUISITION
sfrq 399.774
tn H1
at 5.800
np 46506
sw 8009.6
fb 3800
bs 4
tpwr 58
pw 10.0
pl 1.960
tof 180
nt 20
ct n
alock not used
gain FLAGS
fl n
in n
dp y
hs nn
DISPLAY
sp -280.1
wp 3937.7
vs 42
sc 0
wc 388
hzcm 2.81
hs 3273.18
rfl 3937.4
rfp 2982.3
th 20
ins 2.000
ai ph
DEC. & VT
dfrq 399.774
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dres 1.0
homo n
temp 25.0
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt

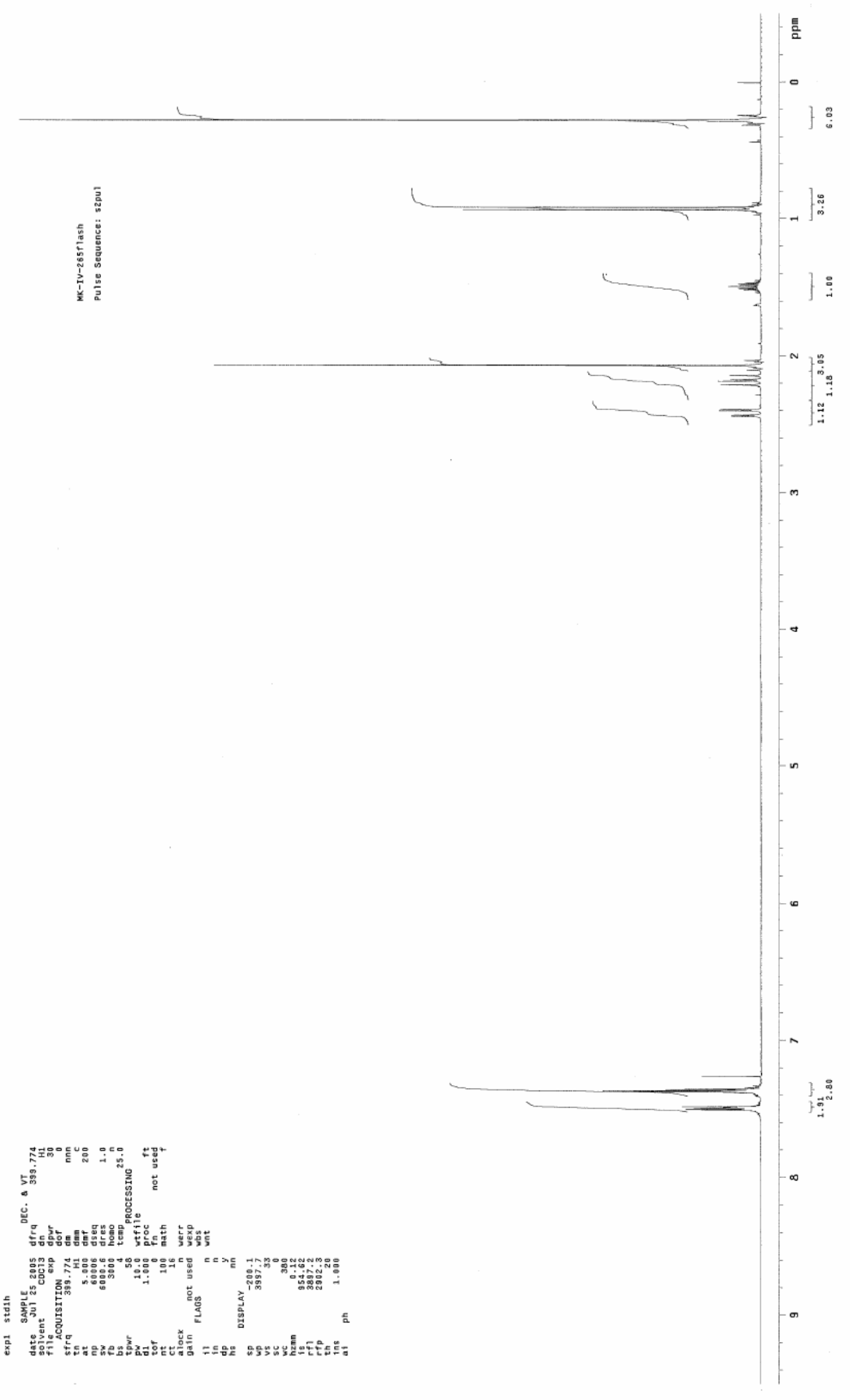

Me
O
Me3Si
Me

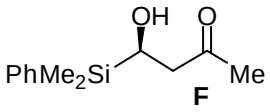
6


MK-IV-264flash
exp1 stdih
SAMPLE
date Jul 13 2005
solvent CDCl3
file /export/home/~
kacprzyn/vnmrsys/d~
ata/MK-IV-264flash~
.fid
ACQUISITION
sfrq 399.774
tn H1
at 5.000
np 60006
sw 60000.6
fb 3000
bs 4
tpwr 58
pw 10.0
d1 1.000
tof 0
nt 100
ct 24
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -200.1
wp 3997.5
vs 30
sc 0
wc 250
hzmm 2.94
is 688.50
rfl 3857.5
rfp 2902.3
th 11
ins 9.000
ai ph
DEC. & VT
dfrq 399.774
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
ppm
1.08
3.11
0.89
1.06
3.34
8.98

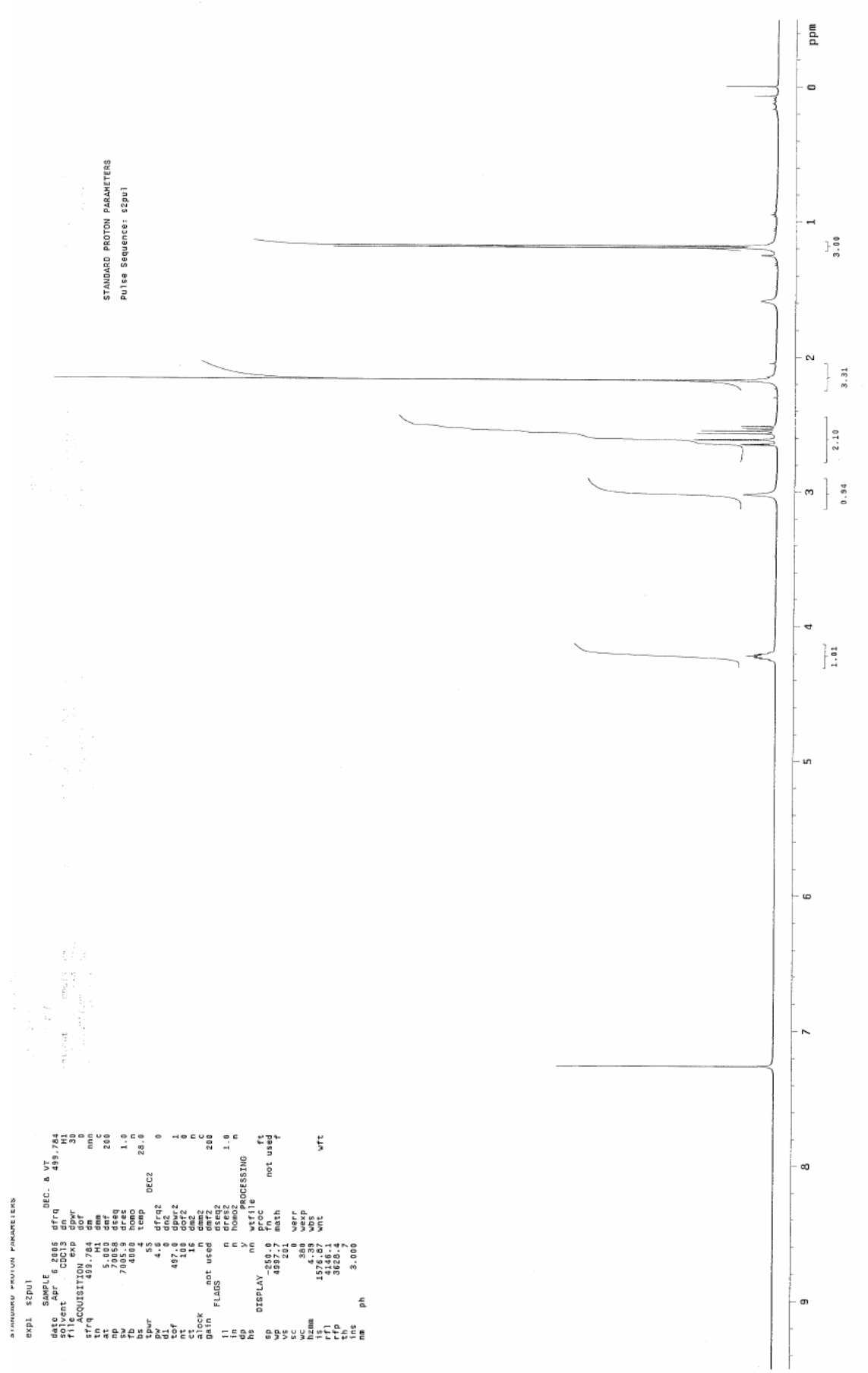

Me
O
PhMe2Si
Me

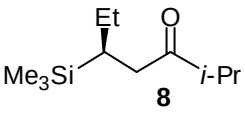
7


MK-IV-265flash
Pulse Sequence: s2pul
ppm
6.03
3.26
1.00
3.05
1.18
1.12
2.00
1.91

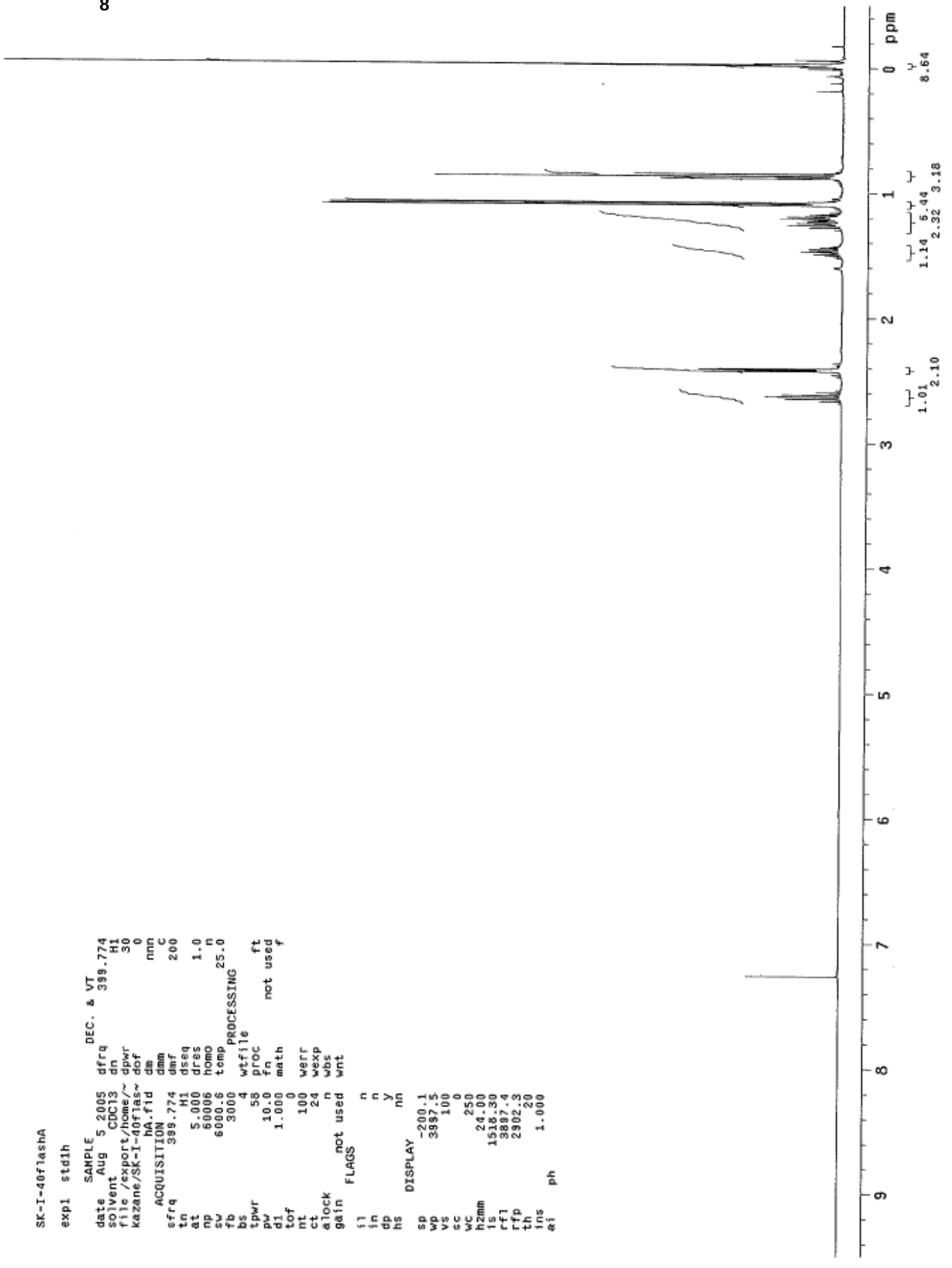

OH
O
PhMe2Si
Me

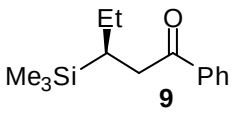
F


STANDARD PROTON PARAMETERS
Pulse Sequence: s2pul
ppm
3.00
3.31
2.10
0.94
1.01

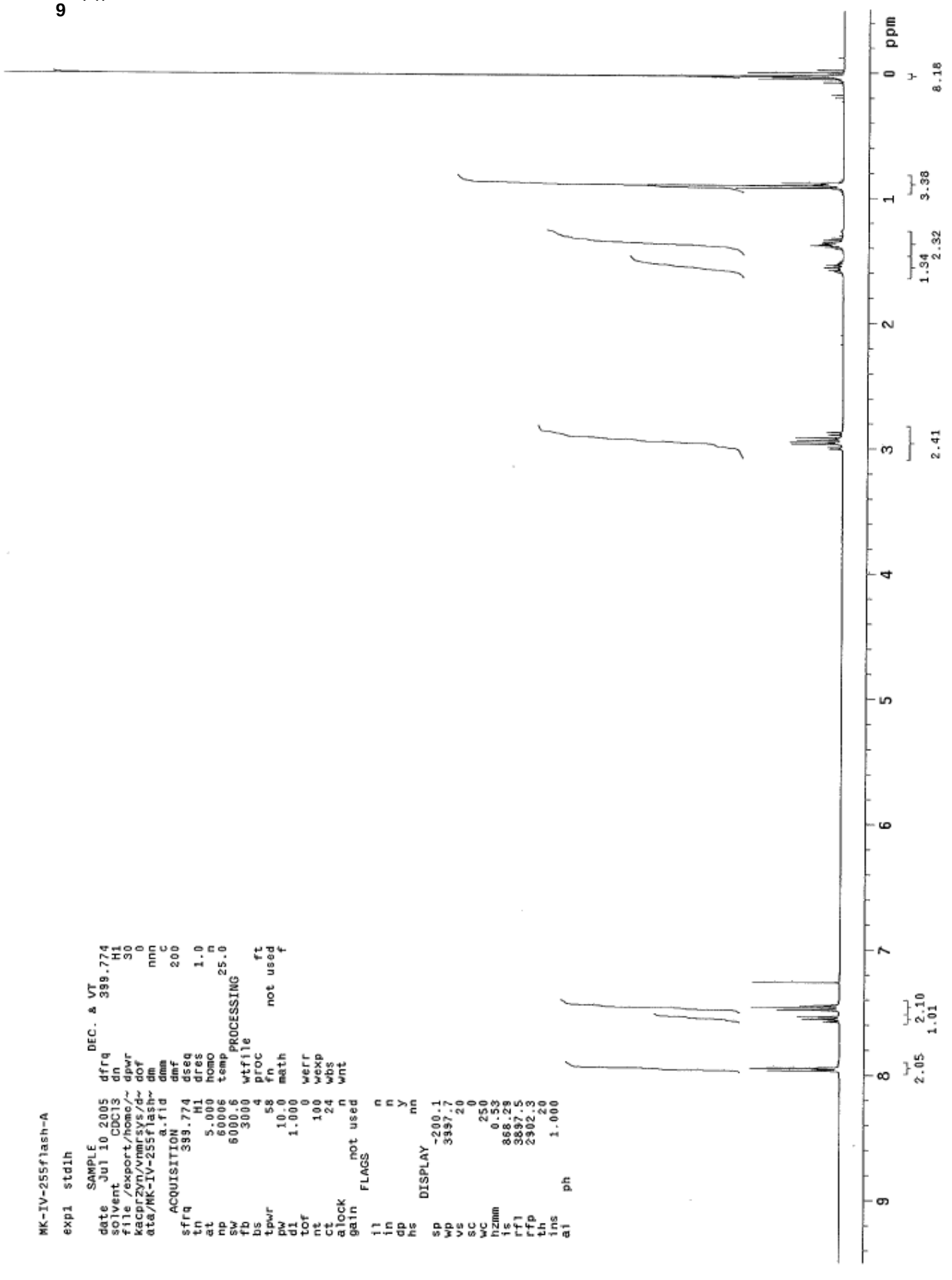

Et
O
Me3Si
i-Pr

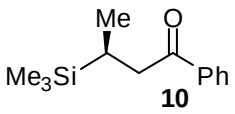
8


SK-I-40flashA
expl std1h
DEC. & VT
SAMPLE
date Aug 5 2005 dfrq 399.774
solvent CDCl3 dn H1
file /export/home/~ dpwr 30
kazane/SK-I-40flas~ dof 0
hA.fid dm nnn
ACQUISITION dmm c
sfrq 399.774 dmf 200
tn H1 dseq
at 5.000 dres 1.0
np 60006 homo n
sw 6000.6 temp 25.0
fb 3000 PROCESSING
bs 4 wtfile
tpwr 58 proc ft
pw 10.0 fn not used
d1 1.000 math f
tof 0
nt 100 werr
ct 24 wexp
alock n wbs
gain not used wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -200.1
wp 3997.5
vs 100
sc 0
wc 250
hzmm 24.00
is 1518.30
rfl 3887.4
rfp 2302.3
th 20
ins 1.000
ph
ppm
8.64
1.14
5.44
2.32
3.18
1.01
2.10

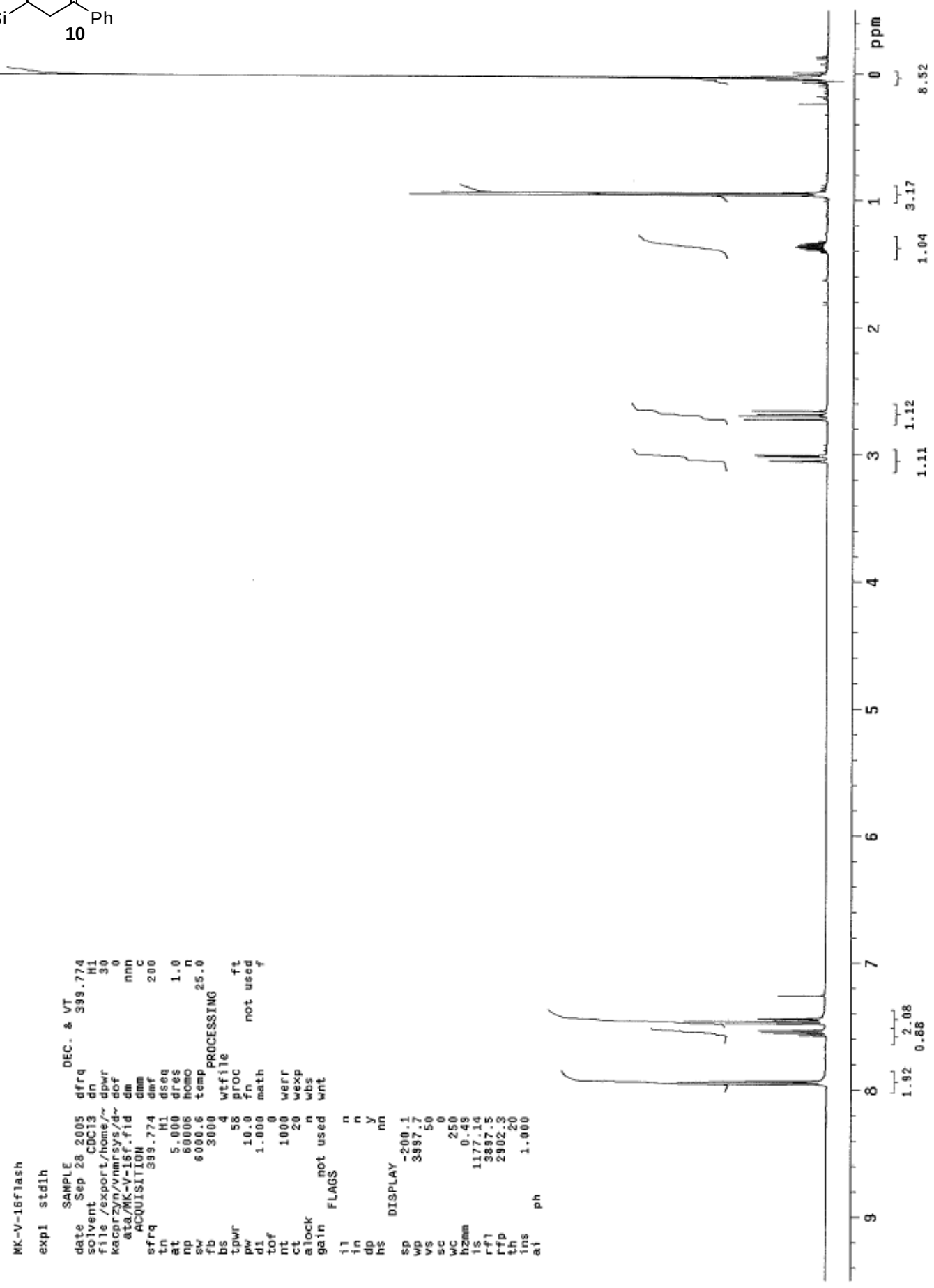

Et
O
Me3Si
Ph

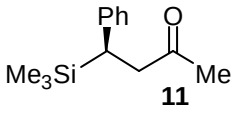
9


MK-IV-255flash-A
expl stdlh
SAMPLE
date Jul 10 2005
solvent CDCl3
file /export/home/~
kacprzyn/vnmrsys/d~
data/MK-IV-255flash~
a.fid
ACQUISITION
sfrq 399.774
tn H1
at 5.000
np 60006
sw 6000.6
fb 3000
bs 4
tpwr 58
pw 10.0
d1 1.000
tof 0
nt 100
ct 24
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -200.1
wp 3997.7
vs 20
sc 0
wc 250
hzmm 0.53
is 868.29
rfl 3897.5
rfp 2902.3
th 20
ins 1.000
al ph
DEC. & VT
dfrq 399.774
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
ppm
2.05
2.10
1.01
1.34
2.32
2.41
3.38
8.18

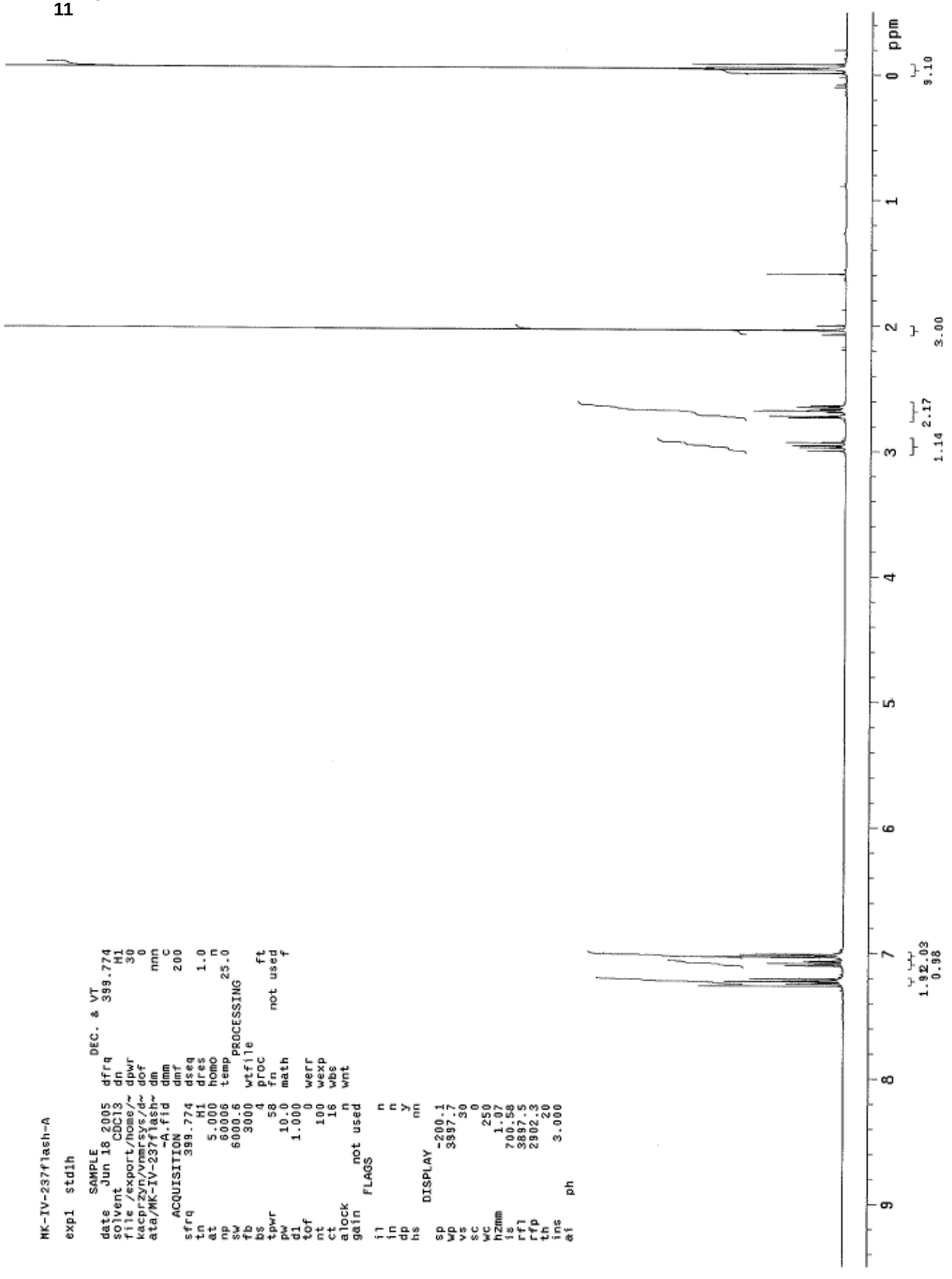

Me
O
Me3Si
Ph

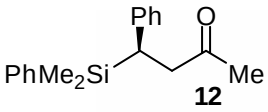
10


MK-V-16flash
expl std1h
SAMPLE
date Sep 28 2005
solvent CDCl3
file /export/home/~
kacprzyn/vnmrsys/d~
data/MK-V-16f.fid
ACQUISITION
sfrq 399.774
tn H1
at 5.000
np 60006
sw 6000.6
fb 3000
bs 4
tpwr 58
pw 10.0
d1 1.000
tof 0
nt 1000
ct 20
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -200.1
wp 3997.7
vs 50
sc 0
wc 250
hzmm 0.49
is 1177.14
rfl 3897.5
rfp 2902.3
th 20
ins 1.000
ai ph
DEC. & VT
dfrq 399.774
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
ppm
1.92
2.08
0.88
1.11
1.12
1.04
3.17
8.52

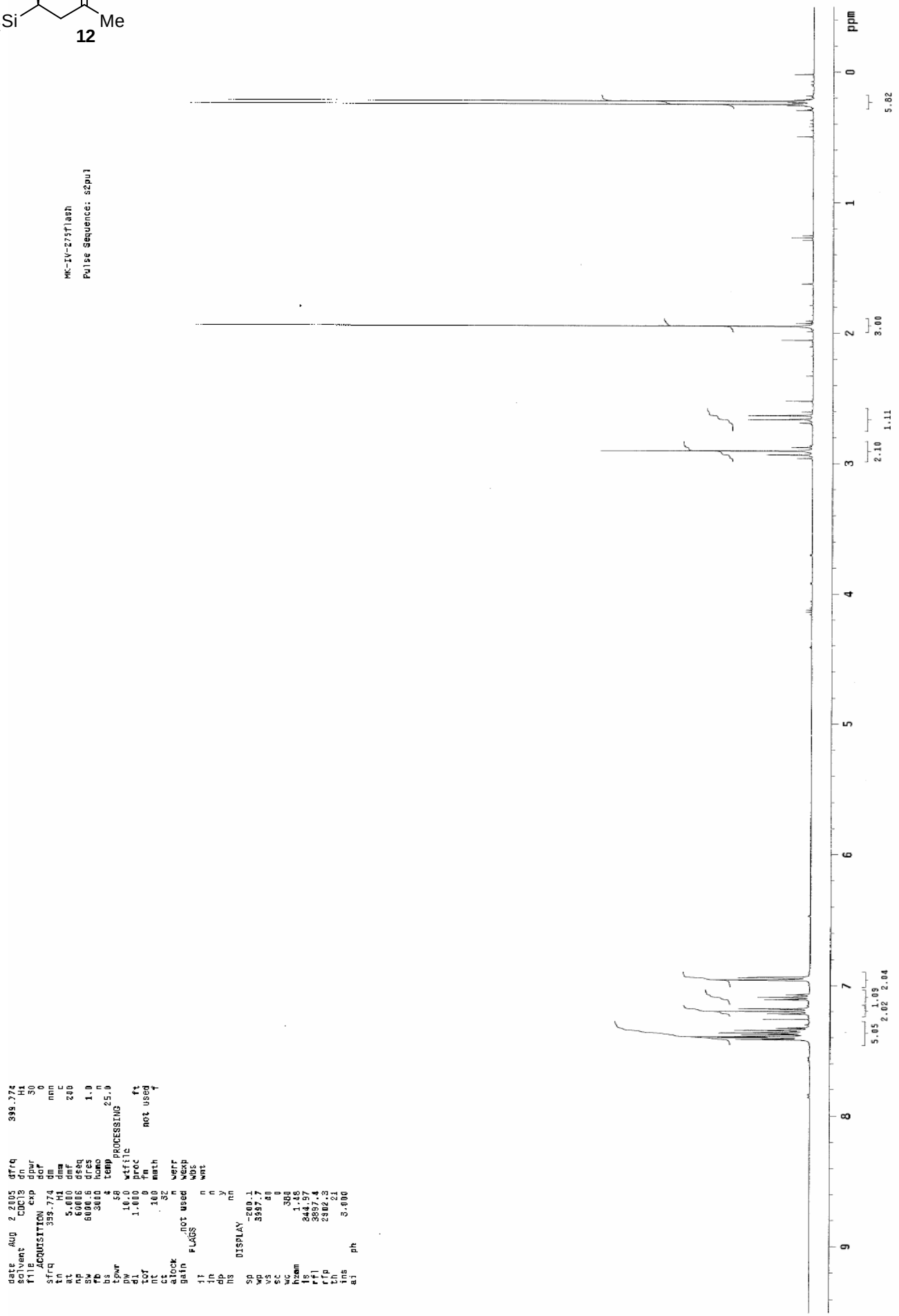

Ph
O
Me3Si
Me

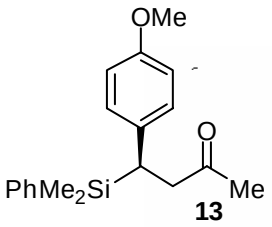
11


MK-IV-237flash-A
exp1 stdih
SAMPLE
date Jun 18 2005
solvent CDCl3
file /export/home/~
kacprzyn/vnmrsys/d~
ata/MK-IV-237flash~
-A.fid
ACQUISITION
sfrq 399.774
tn H1
at 5.000
np 60006
sw 6000.6
fb 3000
bs 4
tpwr 58
pw 10.0
d1 1.000
tof 0
nt 100
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -200.1
wp 3997.7
vs 30
sc 0
wc 250
hzmm 1.07
is 700.58
rfl 3897.5
rfp 2902.3
th 20
ins 3.000
af ph
DEC. & VT
dfrq 399.774
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
ppm
9.10
3.00
2.17
1.14
2.03
1.92
0.98

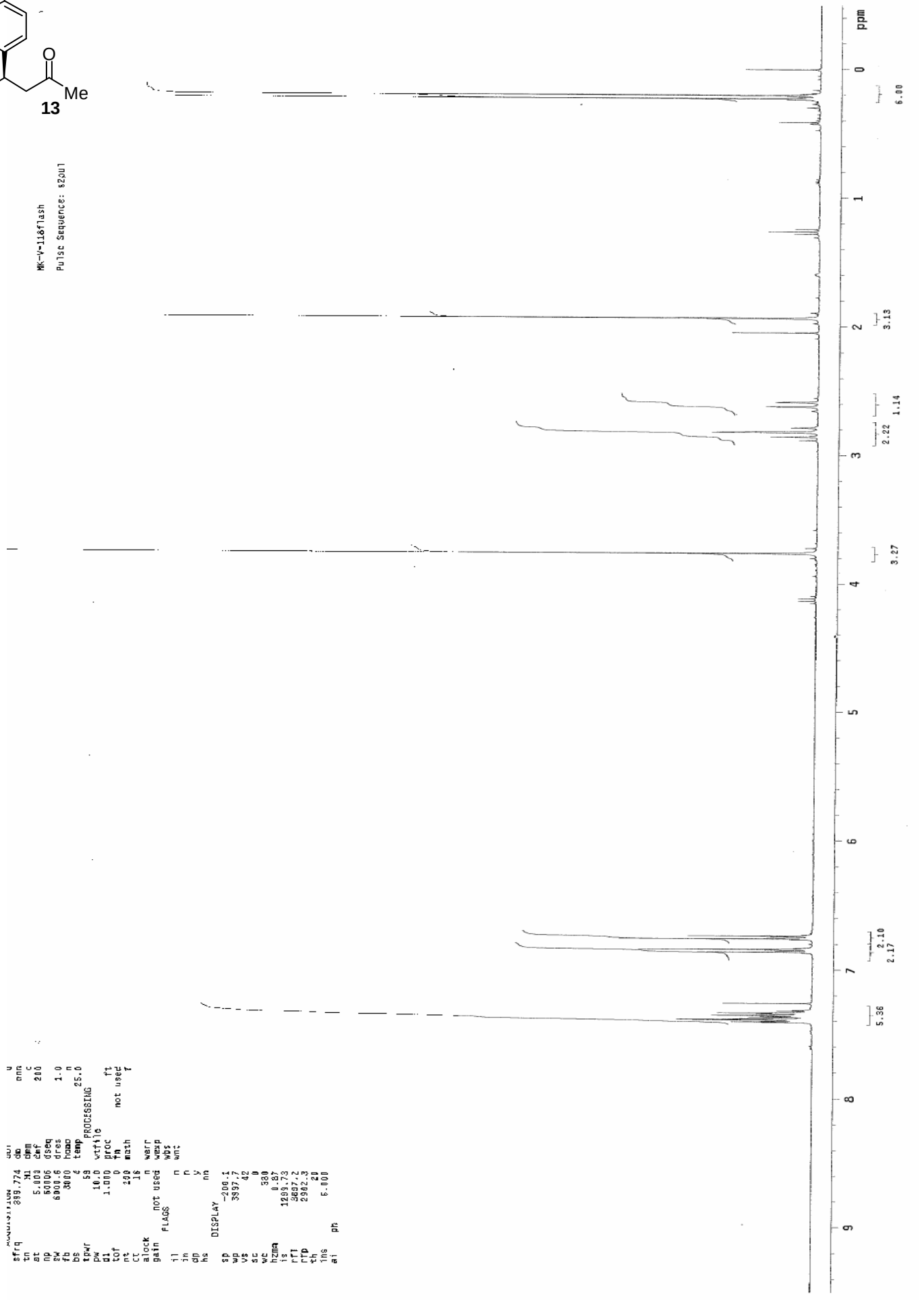

Ph
O
PhMe2Si
Me

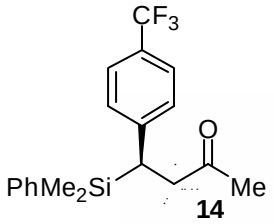
12


MK-IV-275flash
Pulse Sequence: s2pul
ppm
5.82
3.00
2.10
1.11
5.05
1.09
2.02
2.04
date Aug 2 2005
solvent CDCl3
file ACQUISITION
sfrq 399.774
tn H1
at 5.000
np 60008
sw 6000.6
fb 3000
bs 4
tpwr 58
pw 10.0
d1 1.000
tof 0
nt 100
ct 32
alock n
gain not used
PROCESSING
wtfile
proc ft
fn not used
math
werr
wexp
wbs
wnt
FLAGS
DISPLAY
sp -200.1
wp 3997.7
vs 40
sc 0
wc 360
hzcm 1.48
hs 2844.97
fl 3997.4
fp 2902.3
th 21
ins 3.000
ai ph

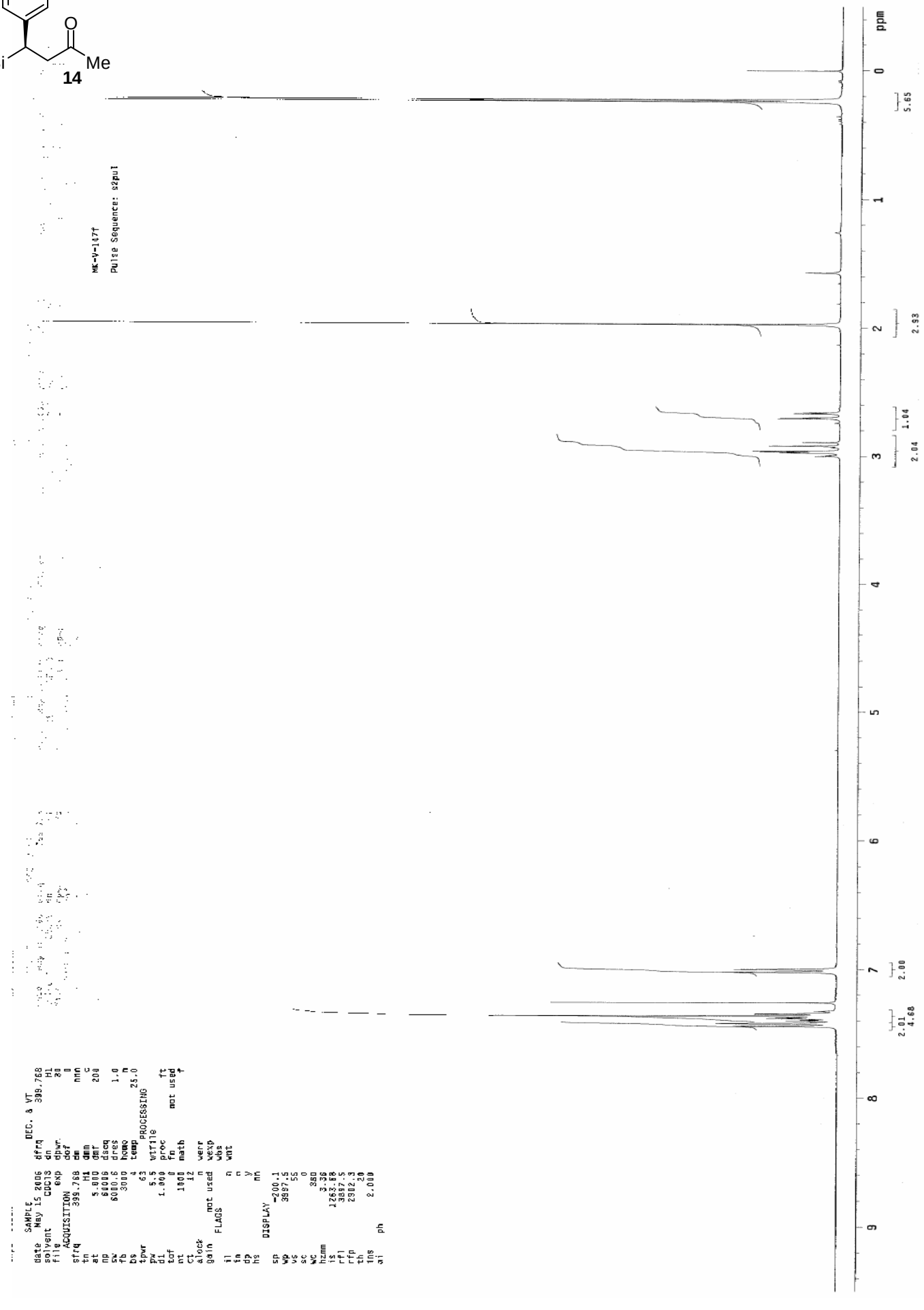

OMe
O
PhMe2Si
Me

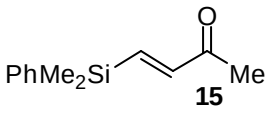
13


MK-V-116flash
Pulse Sequence: s2pul
ppm
6.00
3.13
1.14
3.27
2.10
2.17
5.36

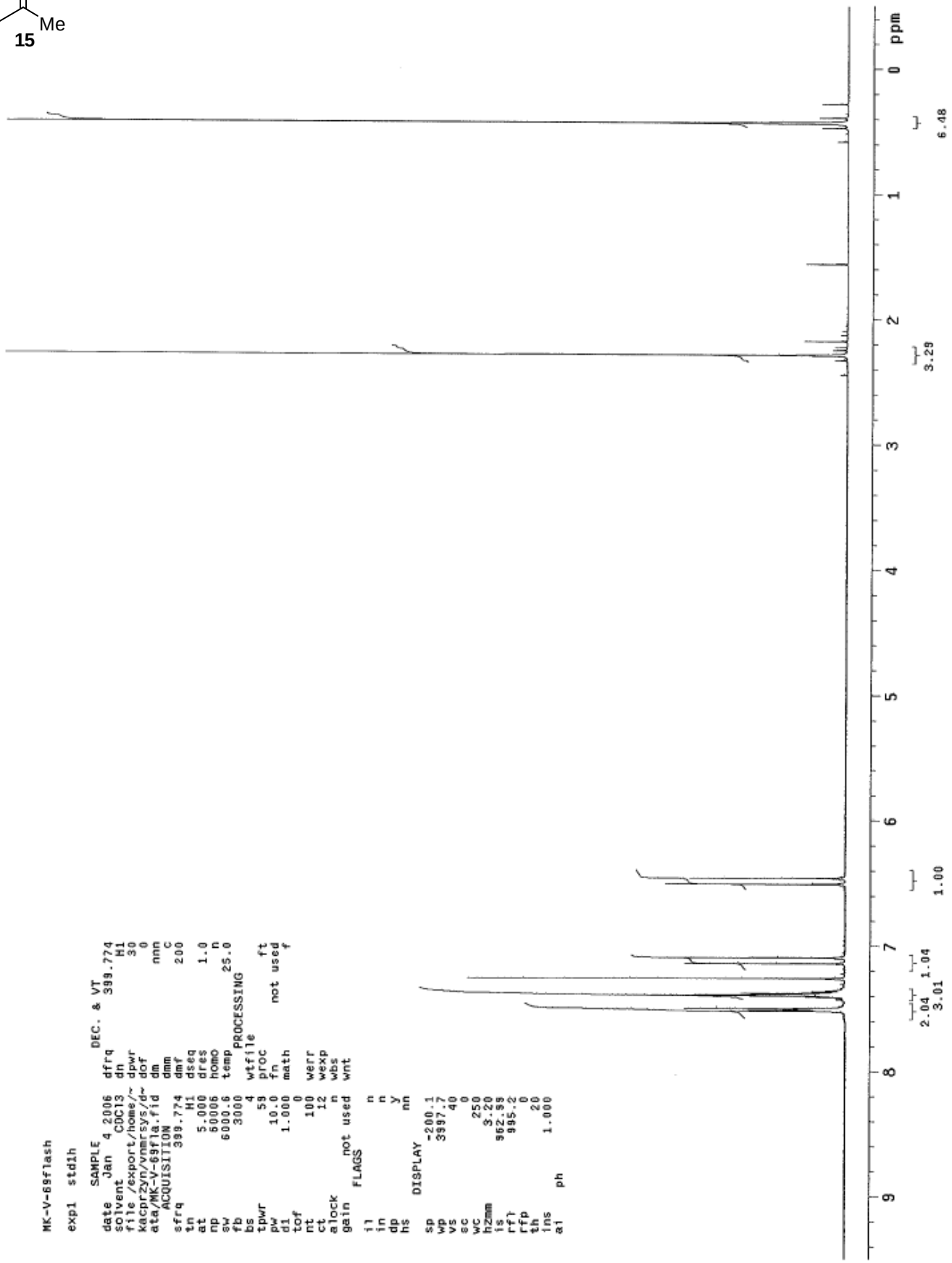

CF3
O
PhMe2Si
Me

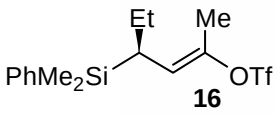
14


MK-V-147f
Pulse Sequence: s2pul
ppm
5.65
2.93
1.04
2.04
2.00
2.01
4.68

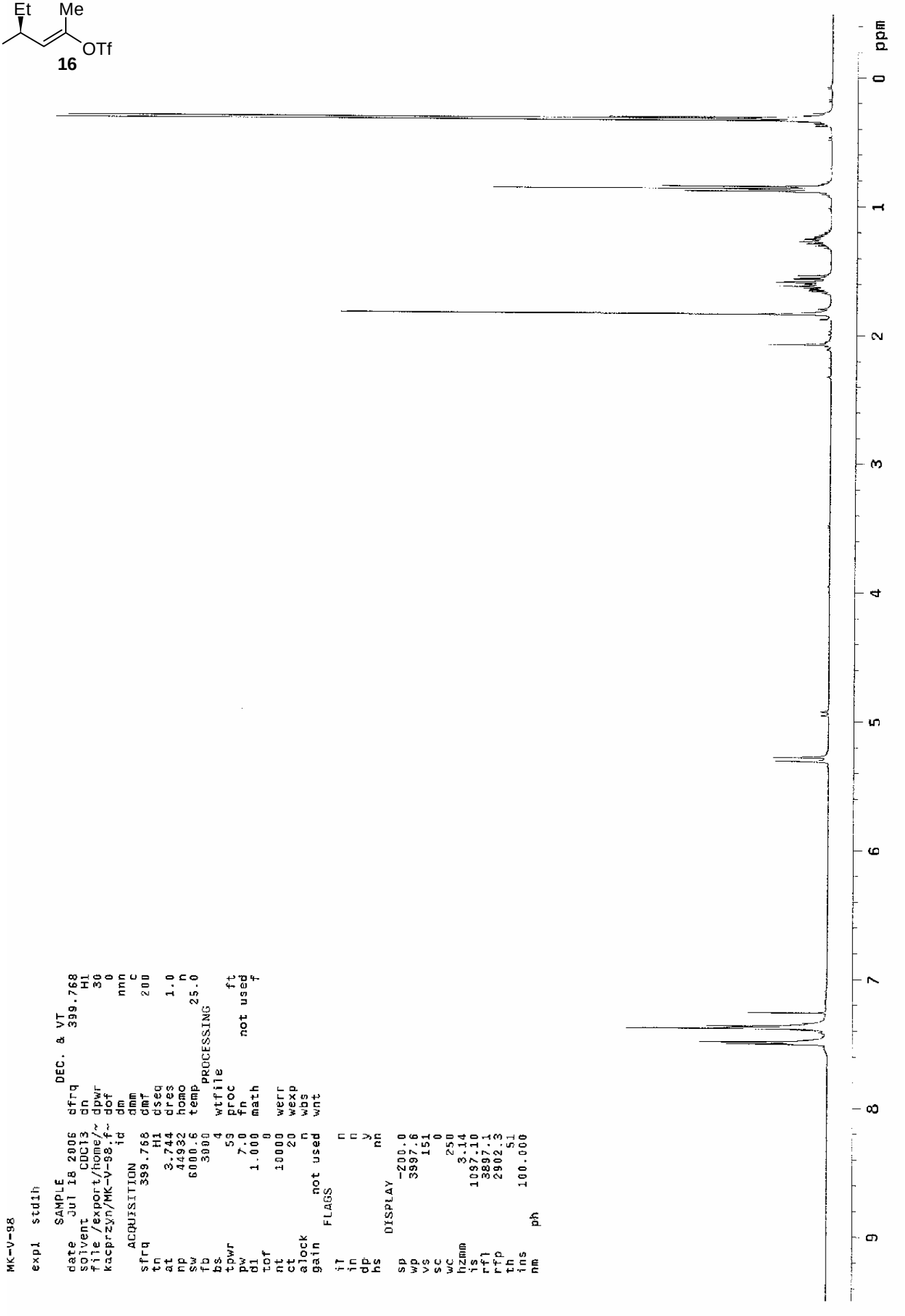

PhMe2Si
O
Me

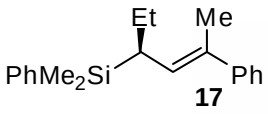
15


MK-V-69flash
exp1 stdih
SAMPLE
date Jan 4 2006
solvent CDCl3
file /export/home/~
kacprzyn/vnmrsys/d~
ata/MK-V-69fla.fid
ACQUISITION
sfrq 399.774
tn H1
at 5.000
np 60006
sw 6000.6
fb 3000
bs 4
tpwr 59
pw 10.0
d1 1.000
tof 0
nt 100
ct 12
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -200.1
wp 3997.7
vs 40
sc 0
wc 250
hzmm 3.20
is 962.9
rfl 995.2
rfp 0
th 20
ins 1.000
ai ph
DEC. & VT
dfrq 399.774
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
ppm
2.04
1.04
3.01
1.00
3.29
6.48

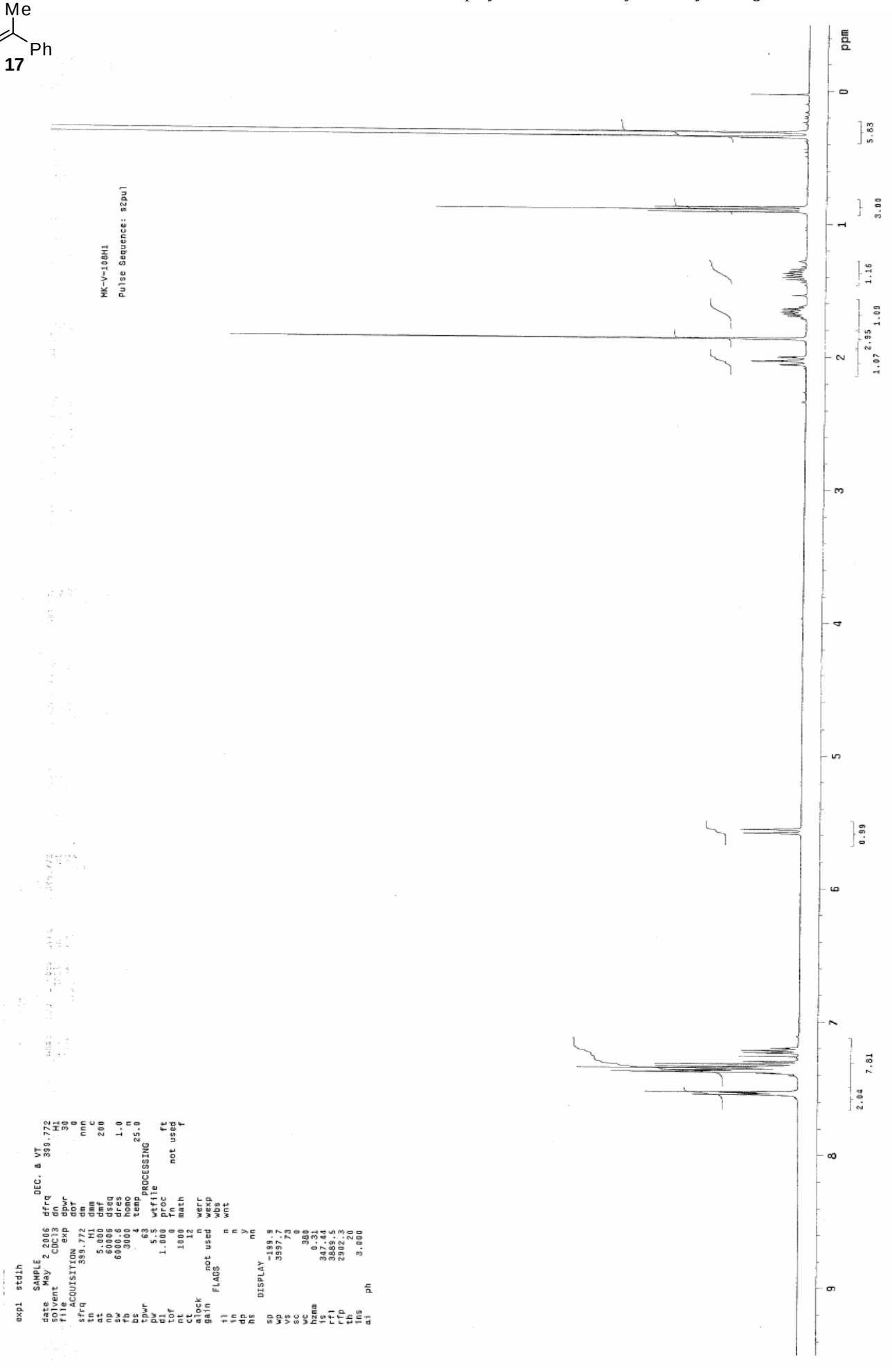

Et
Me
PhMe2Si
OTf

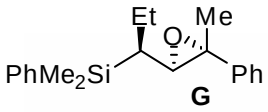
16


MK-V-98
expl std1h
SAMPLE
date Jul 18 2006
solvent CDCl3
file /export/home/~
kacprzyn/MK-V-98.fi
ACQUISITION
sfrq 399.768
tn H1
at 3.744
np 44932
sw 6000.6
fb 3000
bs 4
tpwr 59
pw 7.0
d1 1.000
tof 0
nt 10000
ct 20
alock n
gain not used
FLAGS
DISPLAY
sp -200.0
wp 3997.6
vs 151
sc 0
wc 250
hzmm 3.14
is 1097.10
rfl 3897.1
rfp 2902.3
th 51
ins 100.000
nm ph
DEC. & VT
dfrq 399.768
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
ppm


Et
Me
PhMe2Si
Ph

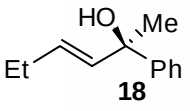
17


MK-V-108H1
Pulse Sequence: s2pul
ppm
5.83
3.00
1.16
1.08
2.95
1.07
0.99
7.81
2.04


Et
Me
O
PhMe2Si
Ph

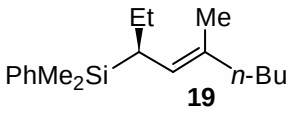
G

MK-V-186flash
Pulse Sequence: szpul
ppm
0
1
2
3
4
5
6
7
8
9
5.98
3.15
1.18
3.16
2.44
1.00
0.04
9.27
2.00
Date_ Feb 7 2006
solvent CDCl3
file ACQUISITION
sfrq 391.774
tn H1
at 5.000
np 60006
sw 6000.6
fb 3003
bs 4
tpwr 53
pw 10.0
pl 1.000
tof 0
nt 100
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -280.1
wp 3997.7
vs 71
sc 0
wc 308
hzcm 1.38
fs 1178.11
rtl 3807.2
rfp 2702.3
rh 21
ins 1.000
ai ph
dfrq 399.774
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
wtfile
proc ft
ffn not used f
math
wexp
wbs
wnt

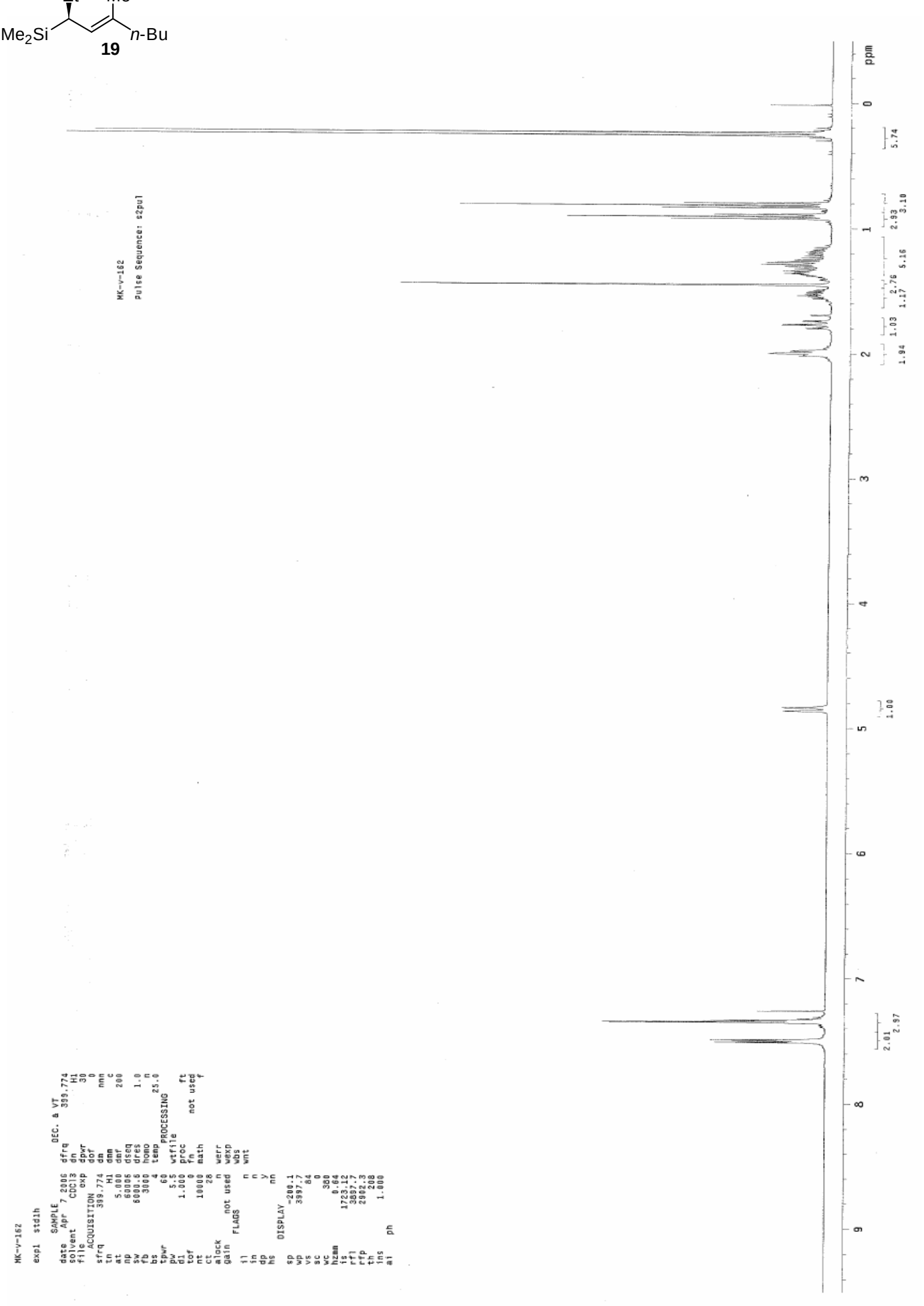

HO
Me
Et
Ph

18

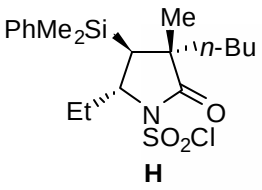
MK-V-110flash
Pulse Sequence: s2pul
ppm
3.17
3.42
0.91
2.19
2.00
1.48
2.07
1.84
exp1 stdih
DEC. & VT
SAMPLE
date Feb 19 2006
solvent CDCl3
file
ACQUISITION
sfrq 399.774
tn H1
at 5.000
np 60006
sw 6000.6
fb 8000
bs 4
tpwr 59
pw 10.0
d1 1.000
tof 0
nt 100
ct 12
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -260.1
wp 3997.7
vs 45
sc 0
wc 250
hzmm 1.11
is 2244.30
rfl 999.4
rfp 0
th 6
ins 2.000
ai ph
dfrq 399.774
dn H1
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
wtfile
proc ft
ft not used
fn f
math
werr
wexp
wbs
wnt



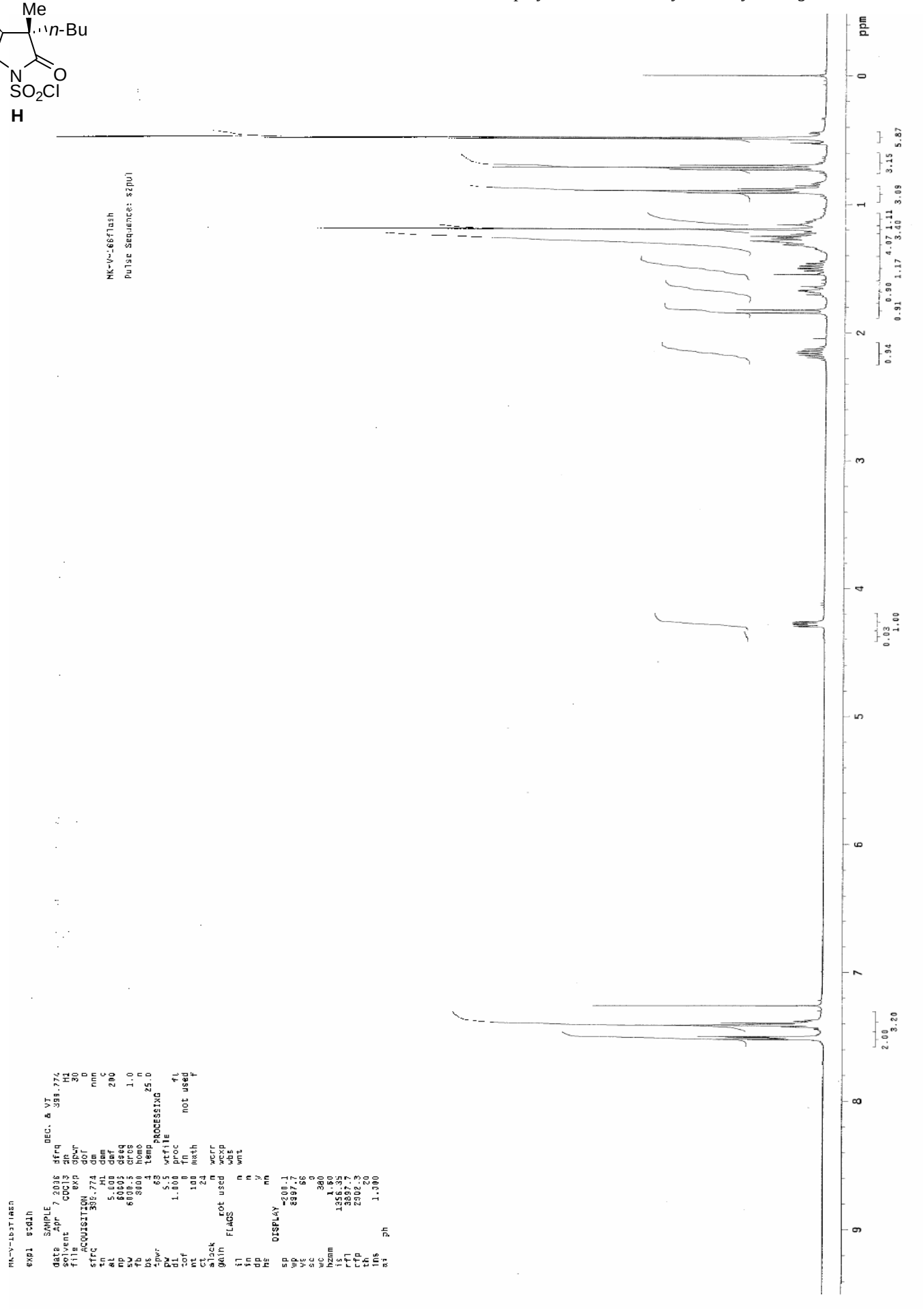
19

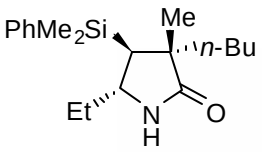



```
MK-v-162
expl  std1h
                    DEC. & VT
      SAMPLE
date   Apr  7 2006  dfrq      399.774
solvent    CDCl3    dn           H1
file          exp   dpwr           30
   ACQUISITION      dof            0
sfrq      399.774   dm           nnn
tn             H1   dmm            c
at          5.000   dmf          200
np          60005   dseq
sw           6000.6 dres           1.0
fb           3000   homo           n
bs              4   temp        25.0
tpwr           60    PROCESSING
pw            5.5   wtfile
d1          1.000   proc           ft
tof             0   fn       not used
nt          10000   math           f
ct             28
cl              n   werr
alock      not used  wexp
gain      FLAGS      wbs
                n    wnt
il              n
in              y
dp             nn
hs      DISPLAY
                    -200.1
sp                  3997.7
wp                      84
vs                       0
sc                     300
wc                    0.64
hzmm               1723.12
is                 3897.7
rfl                2902.3
rfp                   208
th                  1.000
ins
ai      ph
```

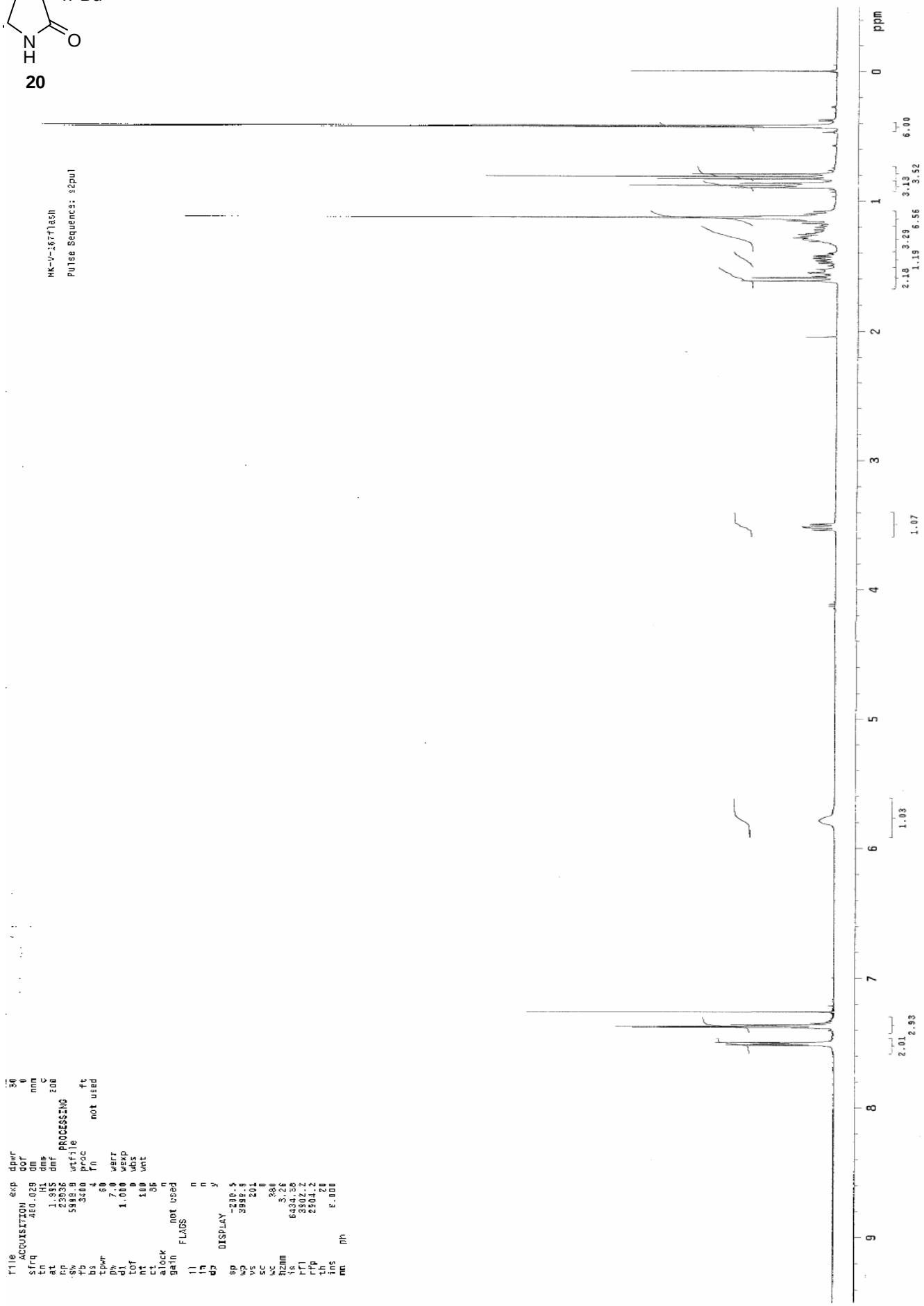

PhMe2Si
Me
n-Bu
Et
N
O
SO2Cl

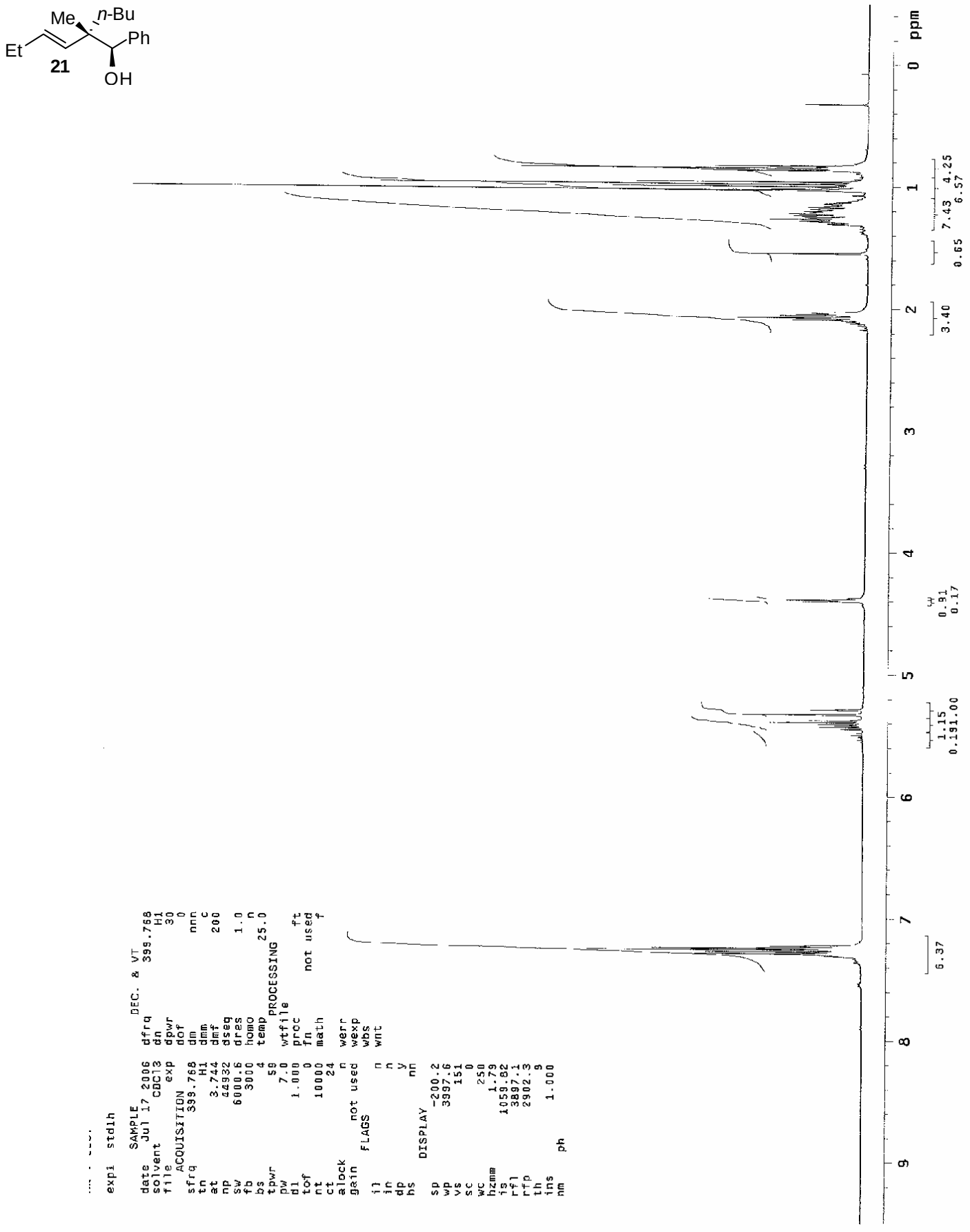
H


MK-V-166flash
Pulse Sequence: szpul
ppm
0
1
2
3
4
5
6
7
8
9
0.94
2.00
3.20
0.03
1.00
0.91
0.90
1.17
4.07
1.11
3.00
3.09
3.15
5.87


PhMe2Si
Me
n-Bu
Et
N
H
O

20


MK-V-167flash
Pulse Sequence: s2pul
ppm
0
1
2
3
4
5
6
7
8
9
6.00
3.52
3.13
3.29
6.56
2.18
1.19
1.07
1.03
2.01
2.93
file exp
ACQUISITION
sfrq
tn H1
at 1.995
np 23936
sw 5988.8 wtfile
fb 3400 proc ft
bs 4 fn not used
tpwr 60
pw 7.0 werr
d1 1.000 wexp
tof 0 wbs
nt 100 wnt
ct 36
alock n
gain not used
ll n
in n
dp y
DISPLAY
sp -230.5
wp 3999.8
vs 201
sc 0
wc 380
hzmm 3.26
is 6434.38
rfl 3902.2
rfp 2904.2
th 20
ins 1.000
nm nh


Me
n-Bu
Et
Ph
21
OH
ppm