

Supporting Information

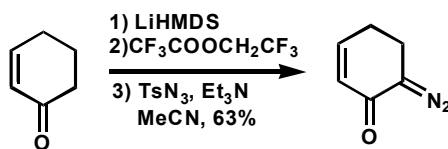
Studies of Stereochemistry of [2+2]-Photocycloaddition Reactions of 2-Cyclohexenones with Olefins

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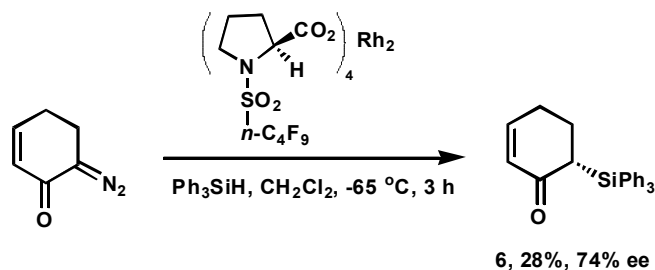
General Procedures: Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of nitrogen using freshly distilled dry solvents. NMR spectra were recorded on Varian Mercury-300 and Varian Mercury-400 instruments and calibrated using residual undeuterated solvent as an internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad. IR spectra were recorded either on Thermo-Nicolet Avatar 360 FT-IR on a diamond crystal or Applied Systems (ASI) ReactIR 1000 spectrometers. Optical rotations were measured on Perkin-Elmer 241 polarimeter using Na lamp in a 1 mL cell having 1 decimeter length. Low-resolution and high-resolution mass spectral analyses were performed at the Harvard University Mass Spectrometry Center.



6-Diazo-cyclohex-2-enone. The compound was prepared by a modified Danheiser's protocol.¹ To a solution of hexamethyldisilazane (8.0 mL, 38.1 mmol) in THF (60 mL) at 0 °C was added 21 mL of *n*-BuLi (1.6 M in hexane). The resulting solution was stirred at 0 °C for 10 min, cooled to -78 °C, and treated dropwise with 2-cyclohexen-1-one (2.5 mL, 25.4 mmol). After stirring at -78 °C for 30 min, 2,2,2-trifluoroethyl trifluoroacetate (5.8 mL, 43 mmol) was added. The solution was stirred at -78 °C for 10 min, and poured into a mixture of 80 mL of Et₂O and 80 mL of *aq.* 5% HCl. The aqueous layer was washed

¹ Danheiser, R. L.; Miller, R. F.; Brisbois, R. G.; Park, S. Z. *J. Org. Chem.* **1990**, 55, 1959.

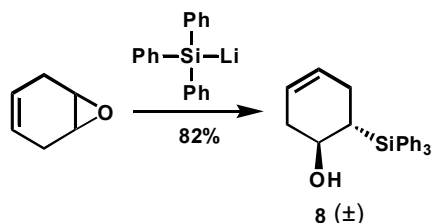
with Et₂O (40 mL × 2). The organic layers were combined, washed with brine, and concentrated at 1 atm at 67 °C until no more solvent condensed in the recovery flask. The crude solution was re-dissolved in 35 mL of MeCN and Et₃N (4.3 mL, 30.9 mmol) and treated dropwise with a solution of TsN₃ (4870 mg, 24.7 mmol) in MeCN (15 mL) over 30 min. The reaction mixture was stirred for 30 min after addition, and concentrated *in vacuo*. Purification of the crude product on Et₃N-buffered silica gel with hexane–EtOAc (4:1) provided 6-diazo-cyclohex-2-enone in 63% yield (1.95 g), which was used immediately for the next step reaction. ¹H NMR (400 MHz, CDCl₃) δ 6.72 (1H, dt, *J* = 10.4, 4.4 Hz), 6.07 (1H, d, *J* = 10.4 Hz), 2.88 (2H, t, *J* = 6.4 Hz), 2.46 (2H, m).



(*S*)-6-Triphenylsilyl-cyclohex-2-enone (6). Triphenylsilane (2642 mg, 10.16 mmol) and the *N*-nonafluorobutanesulfonylproline–Rh(II) complex² (136 mg, 0.076 mmol) were dissolved in 5.0 mL of CH₂Cl₂. The resulting solution was cooled to –65 °C and a solution of 6-diazo-cyclohex-2-enone (620 mg, 5.08 mmol) in 5.0 mL of CH₂Cl₂ was added dropwise *via* a syringe pump over 3.0 h with the temperature of the reaction solution maintained at –65 °C. The reaction mixture was stirred for additional 15 min and then warmed to 23 °C. The reaction mixture was filtered through a SiO₂ plug, and concentrated *in vacuo*. Purification of the crude product by SiO₂ chromatography provided 501 mg of (*S*)-6-triethylsilyl-2-cyclohexen-1-one (28%) with 74% ee. Analytical HPLC conditions: (*S,S*) Whelk O1 column (4.6 mm × 25 cm), 225 nm, 10% *i*-PrOH–hexane, 1.0 mL/min, *R*_t_{major} = 8.6 min (**6**); *R*_t_{minor} = 23.3 min (*ent*-**6**). M.p. 109–111 °C; [*α*]_D²³ –81.3° (*c* 2.88, CHCl₃); IR (film) 3074, 1656, 1430, 1109 cm^{–1}; ¹H NMR (300 MHz, CDCl₃) δ 7.59 (6H, d, *J* = 8.1 Hz), 7.43–7.35 (9H, m), 6.79 (1H, br d, *J* = 10.5

² (a) Ge, M.; Corey, E. J. *Tetrahedron Lett.* **2006**, 47, 2319–2321. (b) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; John Wiley: New York, 1998. Page 79. For preparation of a similar Rh(II) catalyst, see (c) Biffis, A.; Braga, M.; Cadamuro, S.; Tubaro, C.; Basato, M. *Org. Lett.* **2005**, 7, 1841–1844.

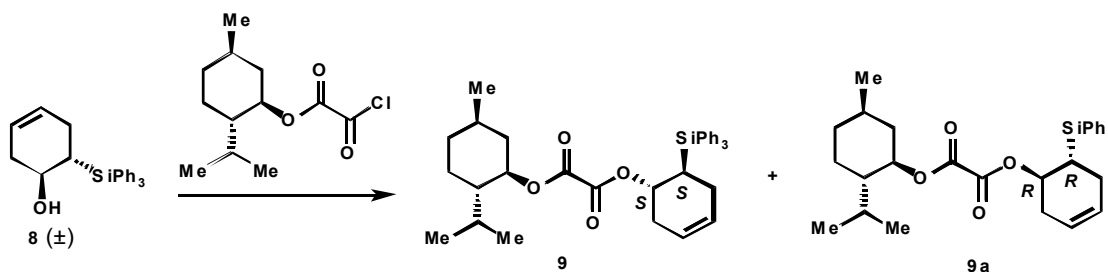
Hz), 5.96 (1H, d, $J = 10.2$ Hz), 3.07 (1H, dd, $J = 7.5, 5.7$ Hz), 2.17 (4H, br s). ^{13}C NMR (100 MHz, CDCl_3) δ 200.1, 149.1, 136.2 (6C), 133.5 (3C), 130.9, 129.5 (3C), 127.7 (6C), 38.0, 25.3, 24.8. LRMS(ES $^{+}$): calcd. for $[\text{M}+\text{H}]^{+}$ $\text{C}_{24}\text{H}_{23}\text{OSi}$ 355.2, found 355.3; calcd. for $[\text{M}+\text{NH}_4]^{+}$ $\text{C}_{24}\text{H}_{26}\text{NOSi}$ 372.2, found 372.3.



(\pm)-2-Triphenylsilyl-4-cyclohexen-1-ol (8**).** To an oven-dried flask charged with finely cut lithium (4500 mg, 642 mmol, washed with hexane prior to use) was added triphenylsilyl chloride (9475 mg, 32.1 mmol) and 80 mL THF. The resulting solution was stirred at 23 °C for 3 h. A white precipitate formed in 20 minutes. The color of the suspension gradually changed from white to yellow to green and finally to clear dark brown. The resulting triphenylsilyllithium solution was added dropwise at 23 °C to a solution of 1,4-cyclohexadiene monoxide³ (3236 mg, 33.7 mmol) in THF (45 mL). After stirring for 30 min, the reaction solution was slowly quenched with saturated *aq.* NH_4Cl and extracted 3 times with ether. The organic layers were combined, washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was redissolved in 100 mL of 1,2-dichloroethane at 60 °C on storage at 23 °C for 24 h, the alcohol **8** precipitated as white needles. The supernatant was decanted and the remaining solid was washed with hexane and dried *in vacuo* to afford pure **8** (6.87 g, 60%). The mother liquor and the washings were combined and concentrated *in vacuo*. Washing of the resulting light-yellow crude product repeatedly with MeOH afforded the alcohol **8** as white solid (2.43 g, 22%, 82% total yield). M.p. 194–196 °C; IR (film) 3575, 3066, 3024, 2900, 1486, 1428, 1216, 1108, 1065 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.62 (6H, d, $J = 7.2$ Hz), 7.41 (3H, dd, $J = 7.2, 7.2$ Hz), 7.37 (6H, dd, $J = 7.2, 7.2$ Hz), 5.60 (2H, br s), 3.92 (1H, m), 2.30 (2H, m), 2.17 (2H, m), 2.08 (1H, ddd, $J = 10.8, 10.8, 4.8$ Hz), 1.51 (1H, d, $J = 5.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 136.2 (6C), 134.5 (3C), 129.4 (3C), 127.9 (6C), 127.4,

³ Perlman, N.; Albeck, A. *Synth. Commun.* **2000**, *30*, 4443.

124.8, 69.7, 35.9, 28.6, 28.4. LRMS (ES⁺): calcd. for [M+NH₄]⁺ C₂₄H₂₈NOSi 374.2, found 374.4.



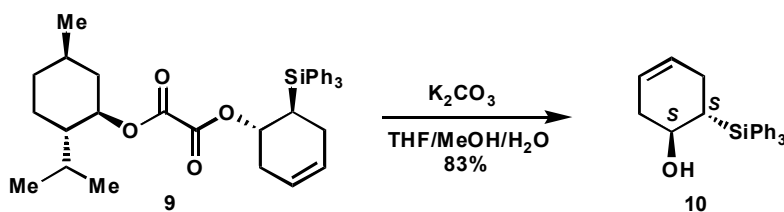
Diastereomeric Oxalates 9 and 9a. (±)-2-Triphenylsilyl-4-cyclohexen-1-ol (**8**) (5000 mg, 14.0 mmol) was dissolved in 47 mL of CH₂Cl₂. To the solution was added Et₃N (2.34 mL, 16.8 mmol) and (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 2-chloro-2-oxoacetate⁴ (3626 mg, 14.7 mmol) dropwise. The resulting mixture was stirred at 23 °C for 1 hour and quenched with 20 mL of H₂O. The organic layer was washed with water and brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The light-yellow crude oil (9.4 g) was dissolved in 40 mL of isopropyl alcohol and stored at −20 °C for 24 h. A large amount of white precipitate was formed. The supernatant was decanted. The remaining solid was washed with hexane at 60 °C. The diastereomeric oxalate **9** (2.37g) was obtained with 90% de. Further recrystallization of both **9** and the mother liquor using *i*-PrOH provided the oxalate diastereomer **9** (3.05g, 99% de) in 38% yield and diastereomer **9a** (1.32 g, 99% de) in 17% yield. Analytical HPLC conditions: Chiralpak AD column (4.6 mm × 25 cm), 225 nm, 1% *i*-PrOH–hexane, 1.0 mL/min, Rt = 4.5 min (**9**) and 5.1 min (**9a**).

Oxalate 9. M.p. 148–150 °C; [α]_D²³ +4.1° (*c* 1.10, CHCl₃); IR (film) 3070, 2956, 2871, 1760, 1735, 1428, 1314, 1175, 1109 cm^{−1}; ¹H NMR (400 MHz, CDCl₃) δ 7.58 (6H, d, *J* = 8.0 Hz), 7.40 (3H, dd, *J* = 7.6, 7.2 Hz), 7.34 (6H, dd, *J* = 7.6, 7.2 Hz), 5.62 (1H, br d, *J* = 10.0 Hz), 5.50 (1H, br d, *J* = 9.6 Hz), 5.13 (1H, m), 4.70 (1H, ddd, *J* = 11.2, 10.8, 4.4 Hz), 2.44 (1H, m), 2.40 (1H, m), 2.30 (1H, br d, *J* = 14.0 Hz), 2.23 (2H, m), 1.79 (1H, br d, *J* = 12.0 Hz), 1.74 (1H, m), 1.66 (2H, m), 1.44 (1H, br s), 1.30 (1H, br t, *J* = 12.0 Hz), 1.02–0.86 (3H, m), 0.91 (3H, d, *J* = 6.0 Hz), 0.81 (3H, d, *J* = 7.2 Hz), 0.70 (3H, d, *J* = 7.2

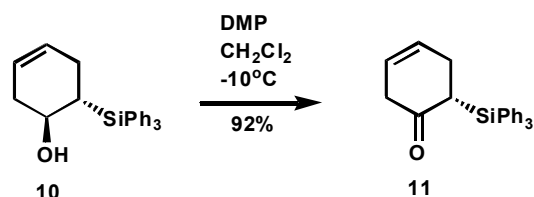
⁴ Blanco, J. M.; Caamano, O.; Fernandez, F.; Garcia-Mera, X.; Lopez, C.; Rodriguez-Borges, J. E.; Hergueta, A. R. *Synthesis*, **1998**, 1590–1592.

Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 157.4, 157.1, 136.0 (6C), 133.6 (3C), 129.5 (3C), 127.8 (6C), 127.1, 123.6, 77.1, 75.7, 46.3, 40.0, 33.9, 31.4, 31.3, 27.6, 25.8, 23.7, 23.0, 21.9, 20.6, 16.0. LRMS(ES $^{+}$): calcd. for $[\text{M}+\text{NH}_4]^{+} \text{C}_{36}\text{H}_{46}\text{NO}_4\text{Si}$ 584.3, found 584.6.

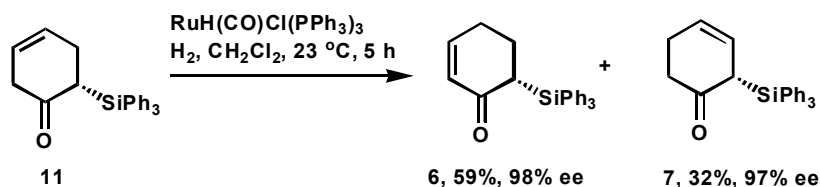
Oxalate 9a. M.p. 113–114 °C; $[\alpha]_{\text{D}}^{23} -53.5^{\circ}$ (c 1.41, CHCl_3); IR (film) 3072, 2958, 1758, 1737, 1428, 1314, 1177, 1150, 1109 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (6H, d, $J = 8.0$ Hz), 7.41 (3H, dd, $J = 7.6, 7.2$ Hz), 7.35 (6H, dd, $J = 8.0, 7.2$ Hz), 5.63 (1H, br d, $J = 10.0$ Hz), 5.51 (1H, br d, $J = 10.0$ Hz), 5.09 (1H, ddd, $J = 10.0, 8.0, 5.2$ Hz), 4.68 (1H, ddd, $J = 11.2, 10.8, 4.4$ Hz), 2.42 (2H, m), 2.35–2.19 (3H, m), 1.83 (1H, br d, $J = 12.0$ Hz), 1.73 (1H, m), 1.67 (2H, m), 1.44 (2H, m), 1.01 (1H, m), 0.89 (3H, d, $J = 6.8$ Hz), 0.87 (3H, d, $J = 7.2$ Hz), 0.79 (2H, m), 0.67 (3H, d, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 156.9, 156.7, 136.0 (6C), 133.6 (3C), 129.5 (3C), 127.8 (6C), 127.3, 123.6, 77.2, 75.8, 46.3, 39.8, 33.8, 31.5, 31.2, 28.0, 26.0, 23.8, 23.3, 21.8, 20.6, 16.1. LRMS(AP $^{+}$): calcd. for $[\text{M}+\text{NH}_4]^{+} \text{C}_{36}\text{H}_{46}\text{NO}_4\text{Si}$ 584.3, found 584.0.



(1*S*,2*S*)-2-Triphenylsilyl-4-cyclohexen-1-ol (10). To a mixture of oxalate **9** (2290 mg, 4.04 mmol) and K_2CO_3 (1393 mg, 10.1 mmol) was added THF (15 mL), MeOH (15 mL) and H_2O (5 mL). The resulting mixture was vigorously stirred at 23 °C for 2 h and the solvent was removed *in vacuo*. The crude product was taken up in H_2O and extracted 3 times with CH_2Cl_2 . The organic layers were combined, washed with brine, dried over Na_2SO_4 , filtered through SiO_2 , and concentrated *in vacuo*. The obtained white solid (1.67 g) was washed with MeOH and dried *in vacuo* to provide (1*S*,2*S*)-2-triphenylsilyl-4-cyclohexen-1-ol (**10**) (1.0 g) of 99% ee. Concentration of the MeOH solution followed by sublimation *in vacuo* (5 mm Hg) at 100 °C provided compound **10** (200 mg) (83% total yield). M.p. 196–198 °C; $[\alpha]_{\text{D}}^{23} +46.6^{\circ}$ (c 1.03, CHCl_3). HPLC conditions: Chiralcel OD column (4.6 mm \times 25 cm), 225 nm, 2% *i*-PrOH–hexane, 1.0 mL/min, $\text{Rt}_{\text{major}} = 9.9$ min (**10**); $\text{Rt}_{\text{minor}} = 7.9$ min (*ent*-**10**).



β,γ -enone 11. (1*S*,2*S*)-2-triphenylsilyl-4-cyclohexen-1-ol (**10**) (99% ee, 500 mg, 1.41 mmol) was dissolved in 10 mL of CH₂Cl₂. To the solution at –10 °C was added dropwise 7.2 mL of Dess–Martin periodinane solution (0.3 M in CH₂Cl₂) over 1 h. After additional stirring for 10 min, the reaction mixture was quenched with 10% *aq.* NaHCO₃ (5 mL), warmed to 23 °C, and extracted with CH₂Cl₂ (3 ×). The organic layers were combined, filtered, dried over Na₂SO₄, and concentrated to about 5 mL. The crude product solution was filtered through a silica plug, and eluted with a mixture of hexane–EtOAc (4:1). Concentration of the filtrate *in vacuo* provided β,γ -enone **11** in 92% yield (459 mg) with 98% ee. Analytical HPLC conditions: (*S,S*) Whelk O1 column (4.6 mm × 25 cm), 225 nm, 10% *i*-PrOH/hexane, 1.0 mL/min, *R*_t_{major} = 7.2 min (**11**); *R*_t_{minor} = 13.2 min (*ent*-**11**). M.p. 99–101°C; [α]_D²³ +99.6° (*c* 1.03, CHCl₃); IR (film) 3074, 1683, 1430, 1109 cm^{–1}; ¹H NMR (400 MHz, CDCl₃) δ 7.59 (6H, d, *J* = 8.0 Hz), 7.43 (3H, dd, *J* = 7.2, 7.2 Hz), 7.36 (6H, dd, *J* = 8.0, 8.0 Hz), 5.70 (1H, m), 5.48 (1H, m), 3.36 (1H, ddd, *J* = 5.2, 5.2, 1.6 Hz), 2.74 (2H, br s), 2.72 (1H, br d, *J* = 21.6 Hz), 2.41 (1H, br d, *J* = 21.6 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 210.4, 136.2 (6C), 132.7 (3C), 129.8 (3C), 127.8 (6C), 126.3, 124.3, 40.4, 39.9, 27.9. LRMS(AP⁺): calcd. for [M+NH₄]⁺ C₂₄H₂₆NOSi 372.2, found 372.1.

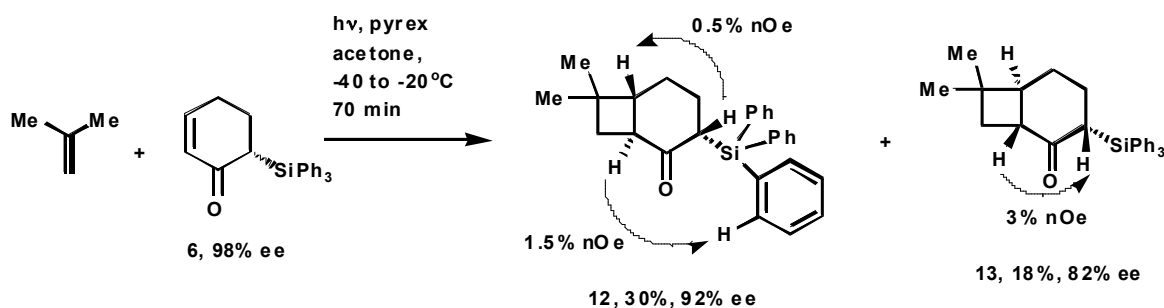


6-(*S*)-Triphenylsilyl-2-cyclohexenone (6). β,γ -enone **11** (98% ee, 336 mg, 0.95 mmol) was dissolved in 7 mL of CH₂Cl₂ and treated with RuH(CO)Cl(PPh₃)₃ (45 mg, 0.047 mmol). The resulting solution was stirred under H₂ (1 atm) at 23 °C for 5 h. The resulting solution was concentrated *in vacuo*. Purification of the crude product by SiO₂ chromatography provided 6-(*S*)-triphenylsilyl-2-cyclohexenone (**6**) as a white solid in

59% yield (199 mg, 98% ee) and 2-(*S*)-triphenylsilyl-3-cyclohexenone (**7**) as colorless oil in 32% yield (107 mg, 97% ee). Analytical HPLC conditions: (*S,S*) Whelk O1 column (4.6 mm × 25 cm), 225 nm, 10% *i*-PrOH–hexane, 1.0 mL/min, $R_{t\text{major}} = 8.6$ min (**6**); $R_{t\text{minor}} = 23.3$ min (*ent*-**6**); $R_{t\text{major}} = 6.7$ min (**7**); $R_{t\text{minor}} = 13.6$ min (*ent*-**7**).

6-(*S*)-Triphenylsilyl-2-cyclohexenone (6). M.p. 109–111 °C; $[\alpha]_{\text{D}}^{23} -81.3^\circ$ (*c* 2.88, CHCl₃); IR (film) 3074, 1656, 1430, 1109 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.59 (6H, d, *J* = 8.1 Hz), 7.43–7.35 (9H, m), 6.79 (1H, br d, *J* = 10.5 Hz), 5.96 (1H, d, *J* = 10.2 Hz), 3.07 (1H, dd, *J* = 7.5, 5.7 Hz), 2.17 (4H, br s). ¹³C NMR (100 MHz, CDCl₃) δ 200.1, 149.1, 136.2 (6C), 133.5 (3C), 130.9, 129.5 (3C), 127.7 (6C), 38.0, 25.3, 24.8. LRMS(ES⁺): calcd. for $[M+H]^+$ C₂₄H₂₃OSi 355.2, found 355.3; calcd. for $[M+NH_4]^+$ C₂₄H₂₆NOSi 372.2, found 372.3.

2-(*S*)-Triphenylsilyl-3-cyclohexenone (7). $[\alpha]_{\text{D}}^{23} +59.6^\circ$ (*c* 1.07, CHCl₃); IR (film) 3047, 2923, 1690, 1428, 1109 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (6H, d, *J* = 7.6 Hz), 7.44 (3H, dd, *J* = 7.6, 7.6 Hz), 7.38 (6H, dd, *J* = 7.6, 7.6 Hz), 5.73 (2H, s), 3.79 (1H, s), 2.29 (1H, m), 2.15 (2H, m), 1.86 (1H, m). ¹³C NMR (100 MHz, CDCl₃) δ 210.0, 136.2 (6C), 132.2 (3C), 130.0 (3C), 127.9 (6C), 125.4, 125.1, 45.5, 38.5, 25.8. LRMS(AP⁺): calcd. for $[M+NH_4]^+$ C₂₄H₂₆NOSi 372.2, found 372.2.

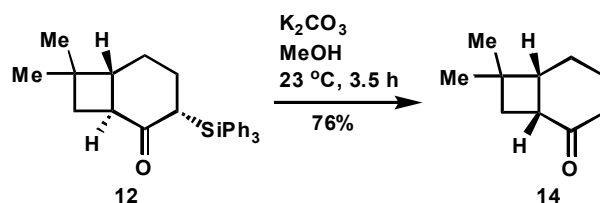


[2+2] cycloadducts 12 and 13. A solution of 6-(*S*)-triphenylsilyl-2-cyclohexenone (**6**) (98% ee, 199 mg, 0.56 mmol) in acetone (80 mL) was placed under a positive pressure of N₂ in a Hanovia[®] photochemical reaction vessel fitted with a Pyrex[®] immersion well and a magnetic stir bar. The running water used to cool the immersion well was first passed through a 50 inch copper coil (1/4" O.D. × 0.030" wall) immersed in ice. The reaction vessel was cooled with an external dry ice–acetone bath at -40°C (internal temperature,

measured by a thermocouple immersed into the solution). 2-Methylpropene (10 mL) was condensed into the reaction vessel with stirring at the same time. A medium pressure mercury lamp 450W Hanovia[®] UV lamp was installed to the immersion well and the irradiation was started. During the irradiation the internal temperature was maintained between -40°C and -20°C . The irradiation was stopped as soon as TLC analysis of an aliquot showed complete consumption of the enone compound **6** (70 min). The reaction mixture was slowly warmed to room temperature and concentrated *in vacuo*. Purification of the crude product by flash chromatography over silica gel (hexanes/EtOAc = 20 : 1) provided 68 mg (30%, 92% ee) of cycloadduct **12** as a white solid, and a non-polar fraction as a colorless oil. Further purification of the non-polar fraction by Chiralpak AD column (2 cm \times 25 cm) using 5% *i*-PrOH–hexane provided 40 mg of cycloadduct **13** (18%, 82% ee) as colorless oil. Analytical HPLC conditions: (S,S) Whelk O1 column (4.6 mm \times 25 cm), 2%-30% *i*-PrOH–hexane over 30 min, 1.0 mL/min, 225 nm, $R_{t\text{major}} = 11.8$ min (**12**); $R_{t\text{minor}} = 19.0$ (*ent*-**12**); $R_{t\text{major}} = 7.3$ min (**13**); $R_{t\text{minor}} = 8.9$ min (*ent*-**13**).

Cycloadduct 12. M.p. 90–92 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{23} +56.8^{\circ}$ (*c* 1.01, CHCl_3); IR (film) 2956, 2867, 1686, 1430, 1109 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (6H, dd, $J = 8.0, 1.6$ Hz), 7.44–7.36 (9H, m), 3.20 (1H, dd, $J = 8.0, 2.8$ Hz), 2.44 (1H, ddd, $J = 12.8, 10.4, 6.8$ Hz), 2.38 (1H, m), 2.25 (1H, m), 1.85 (1H, ddd, $J = 12.8, 12.8, 4.4$ Hz), 1.79 (1H, dd, $J = 10.4, 10.0$ Hz), 1.44 (1H, dd, $J = 10.4, 6.4$ Hz), 1.32 (1H, m), 1.07 (1H, dddd, $J = 22.8, 12.0, 6.4, 1.6$ Hz), 0.96 (3H, s), 0.72 (3H, s). ^{13}C NMR (100 MHz, CDCl_3) δ 210.5, 136.2 (6C), 133.3 (3C), 129.9 (3C), 128.0 (6C), 55.2, 46.9, 40.6, 38.4, 35.3, 29.7, 29.4, 23.6, 20.1. LRMS(AP⁺): calcd. for $[\text{M}+\text{H}]^+ \text{C}_{28}\text{H}_{31}\text{OSi}$ 411.2, found 411.3.

Cycloadduct 13. $[\alpha]_{\text{D}}^{23} +51.3^{\circ}$ (*c* 0.87, CHCl_3); IR (film) 3070, 2933, 2863, 1702, 1428, 1108, 909 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.56 (6H, dd, $J = 8.0, 1.6$ Hz), 7.39–7.32 (9H, m), 2.98 (1H, ddd, $J = 11.2, 10.7, 7.2$ Hz), 2.76 (1H, dd, $J = 12.8, 6.0$ Hz), 2.31 (1H, m), 1.99 (1H, ddd, $J = 25.2, 12.4, 5.2$ Hz), 1.91 (1H, ddd, $J = 12.4, 12.4, 3.2$ Hz), 1.88 (1H, dd, $J = 10.4, 10.4$ Hz), 1.64 (1H, m), 1.61 (1H, dd, $J = 10.4, 6.8$ Hz), 1.55 (1H, m), 1.15 (3H, s), 1.03 (3H, s). ^{13}C NMR (100 MHz, CDCl_3) δ 209.9, 136.2 (6C), 134.3 (3C), 129.2 (3C), 127.7 (6C), 58.3, 49.9, 40.2, 39.4, 36.0, 32.4, 29.4, 27.6, 20.4. LRMS(AP⁺): calcd. for $\text{M}^+ \text{C}_{28}\text{H}_{30}\text{OSi}$ 410.2, found 410.3.



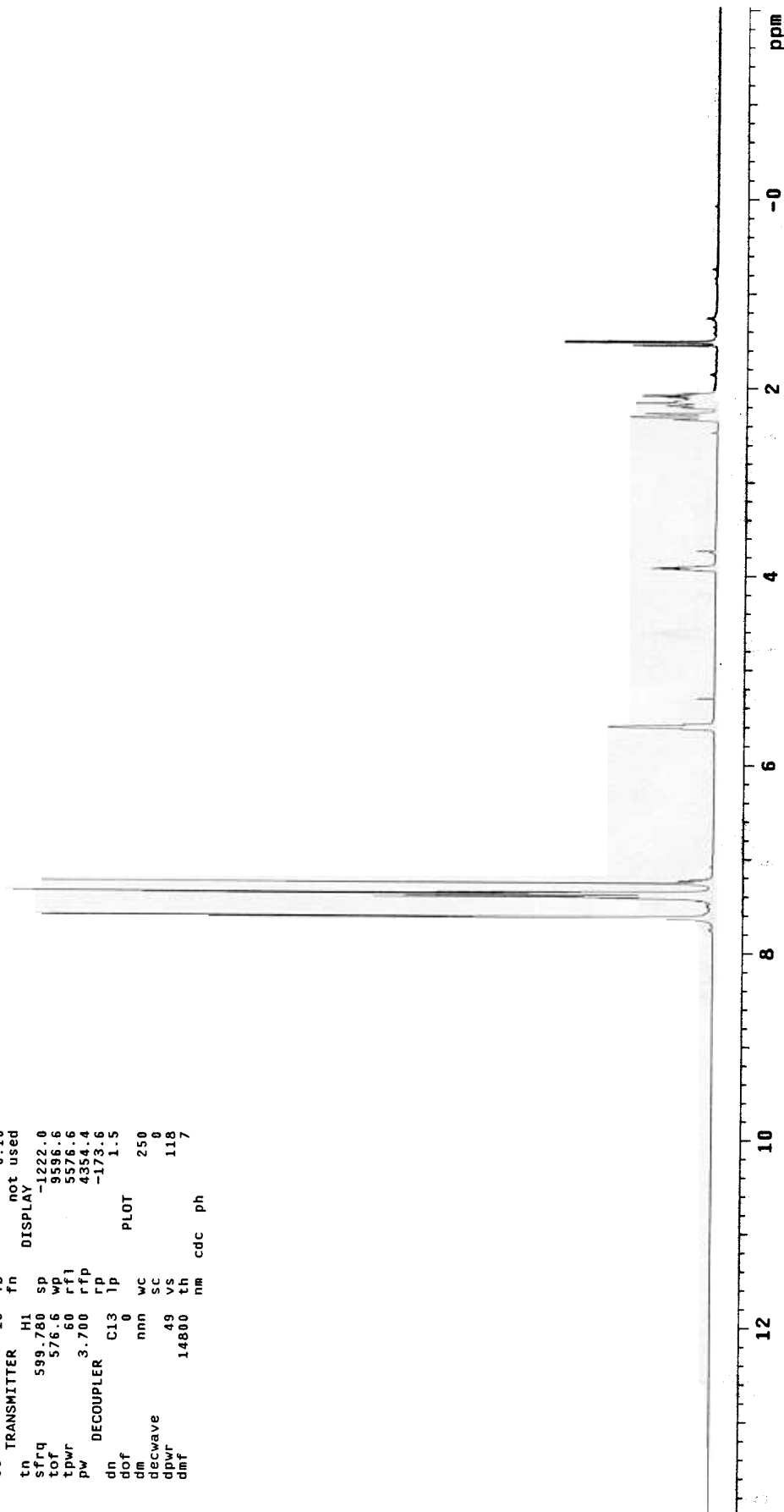
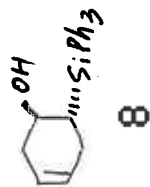
(*R,R*)-(-)-7,7-Dimethyl-bicyclo[4.2.0]octan-2-one (14**)**. Cycloadduct **12** (92% ee, 54 mg, 0.13 mmol) was dissolved in 1.5 mL of MeOH followed by addition of K_2CO_3 (36 mg, 0.26 mmol). The resulting mixture was stirred at $23\text{ }^\circ\text{C}$ for 3.5 h, followed by filtration to remove the solid. The filtrate was concentrated and purified on silica gel using hexane–ether (10 : 1). (*R,R*)-(-)-7,7-Dimethyl-bicyclo[4.2.0]octan-2-one (**14**) was obtained in 76% yield (15 mg) in 92% ee. $[\alpha]_{\text{D}}^{23} -152.8^\circ$ (c 1.41, CHCl_3). The NMR and IR spectra of **14** are consistent with the data reported in literature.⁵ Analytical HPLC conditions: Chiralpak IA column (4.6 mm \times 25 cm), 20% CH_2Cl_2 –hexane, 1.0 mL/min, 280 nm, $\text{Rt}_{\text{major}} = 8.7\text{ min}$ (**14**); $\text{Rt}_{\text{minor}} = 7.2\text{ min}$ (*ent*-**14**).

⁵ (a) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, 86, 5570–5583. (b) Liu, D.; Hong, S.; Corey, E. J. *J. Am. Chem. Soc.* **2006**, 128, 8160–8161.

STANDARD PROTON PARAMETERS

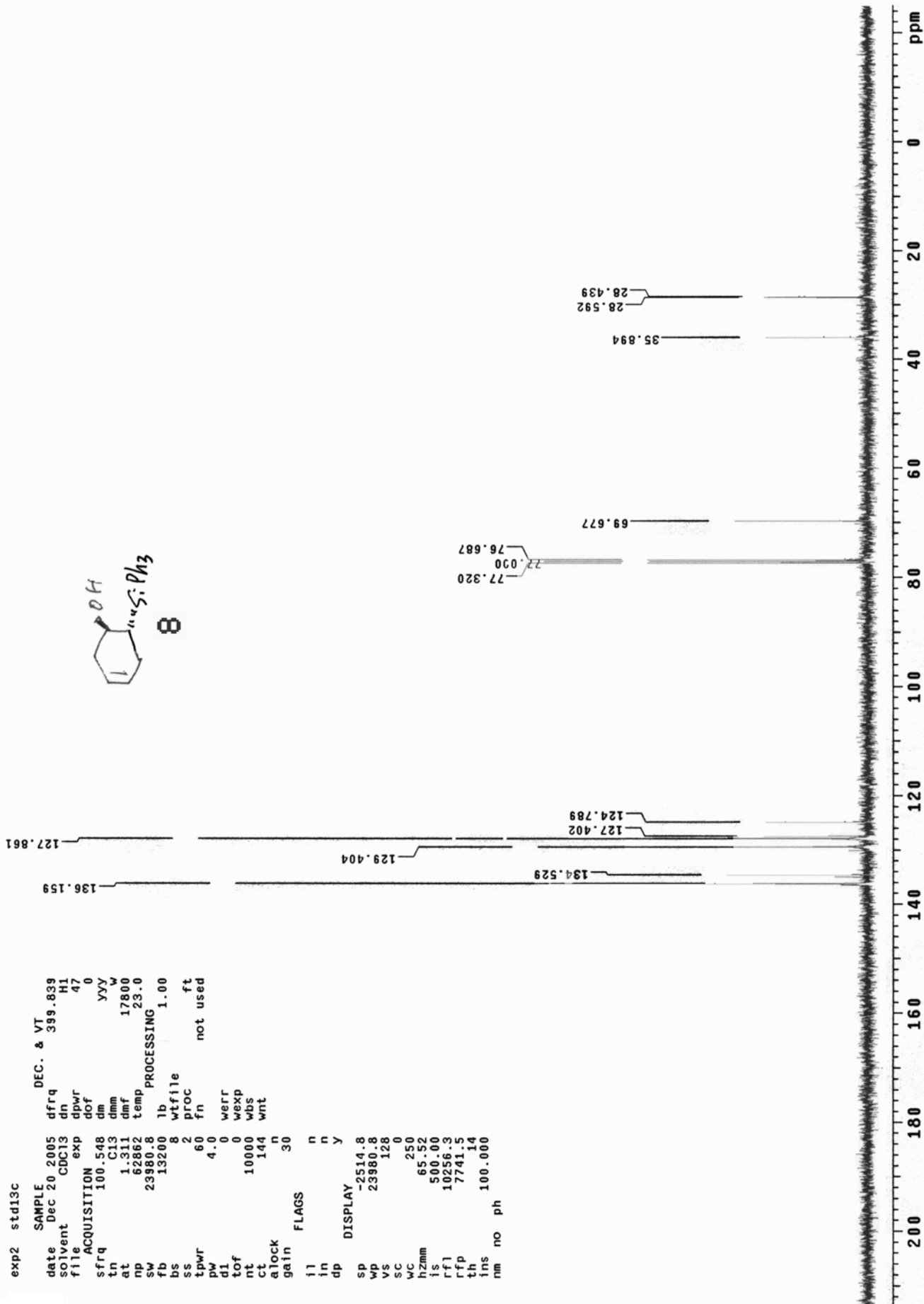
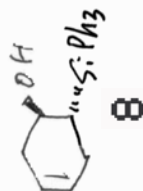
exp1 PROTON

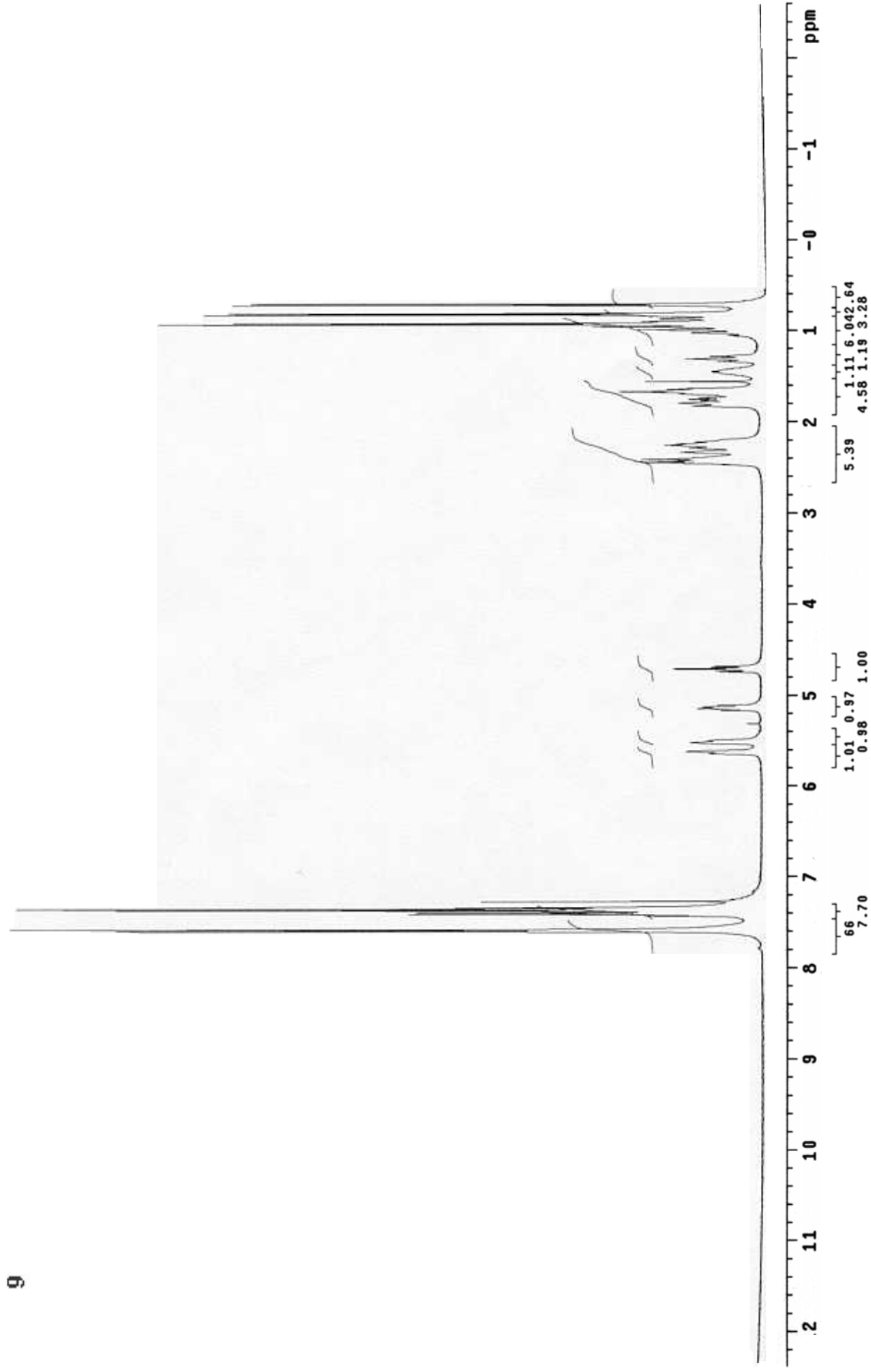
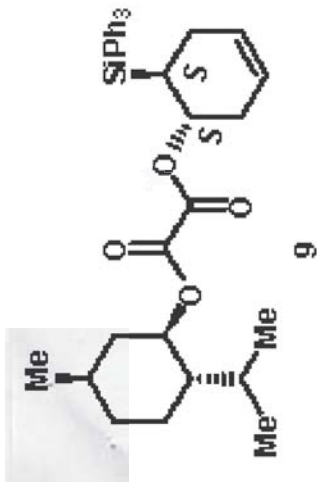
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solvent	CDCl3	gain	not used
file	exp	spin	0
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sw	9596.9	pw90	7.400
at	2.048	alfa	0
np	39310	il	FLAGS
fb	5000	in	n
bs	4	in	n
ss	2	dp	y
dl	1.000	hs	PROCESSING
nt	128	lb	0.10
ct	16	fn	not used
TRANSMITTER		h1	DISPLAY
to	599.750	sp	-1222.0
sfrq	576.6	wp	9596.6
tofr	60	rfl	5576.6
tpwr	3.700	rfp	4354.4
pw	DECOUPLER	rp	-173.6
dn	C13	lp	1.5
dof	0	plot	
dm	nnn	wc	250
decwave	49	sc	0
dpwr	14800	vs	118
dmf		th	7
		nm	cdc ph



exp2 std13c

SAMPLE		DEC. & VT	
date	Dec 20 2005	dfrq	399.839
solvent	CDC13	dn	H1
exp		dpwr	47
file		dof	0
ACQUISITION			
sfrq	100.548	dm	yyy
tn	C13	dmm	w
at	1.311	dmf	17800
temp	62862	temp	23.0
sw	23980.8	PROCESSING	
sf	13200	lb	1.00
bs	8	wfile	
ss	2	proc	ft
tpwr	60	fn	not used
pw	4.0		
wd		werr	
tof	0	wexp	
nt	10000	wbs	
ct	144	wnt	
alock	n		
gain	30		

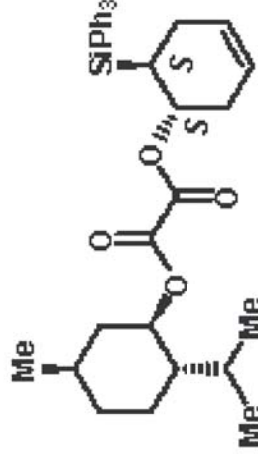




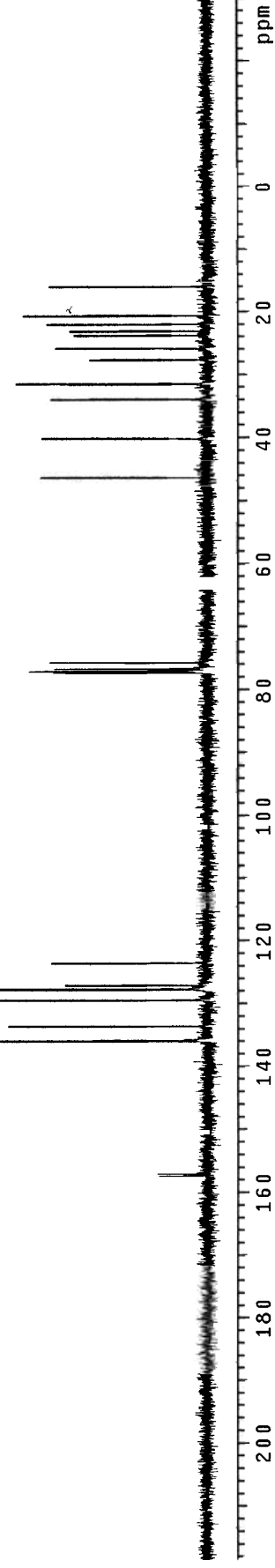
13C OBSERVE

exp5 std13c

SAMPLE		DEC. & VT	
date	Aug 1 2006	dfrq	400.021
solvent	CDCl3	dn	H1
file	exp	dpwr	46
ACQUISITION		dof	0
tn	100.594	dm	yyv
at	1.311	dmm	w
np	65536	dmf	9999
sw	25000.0	temp	22.0
fb	13800	lb	1.00
bs	8	wfile	not used
tpwr	61	proc	ft
dl	3.2	fn	0
tof	0	werr	svf(nl)
nt	1000	wexp	
ct	96	wbs	
alock	n	wnt	
gain	not used	flags	
il	n		
in	n		
dp	y		
DISPLAY			
sp	-3023.1		
wp	24999.2		
vs	152		
sc	0		
wc	250		
hzm	0.79		
is	500.00		
rfl	10788.9		
rtp	7745.0		
th	6		
ins	100.000		
nm			
ph			

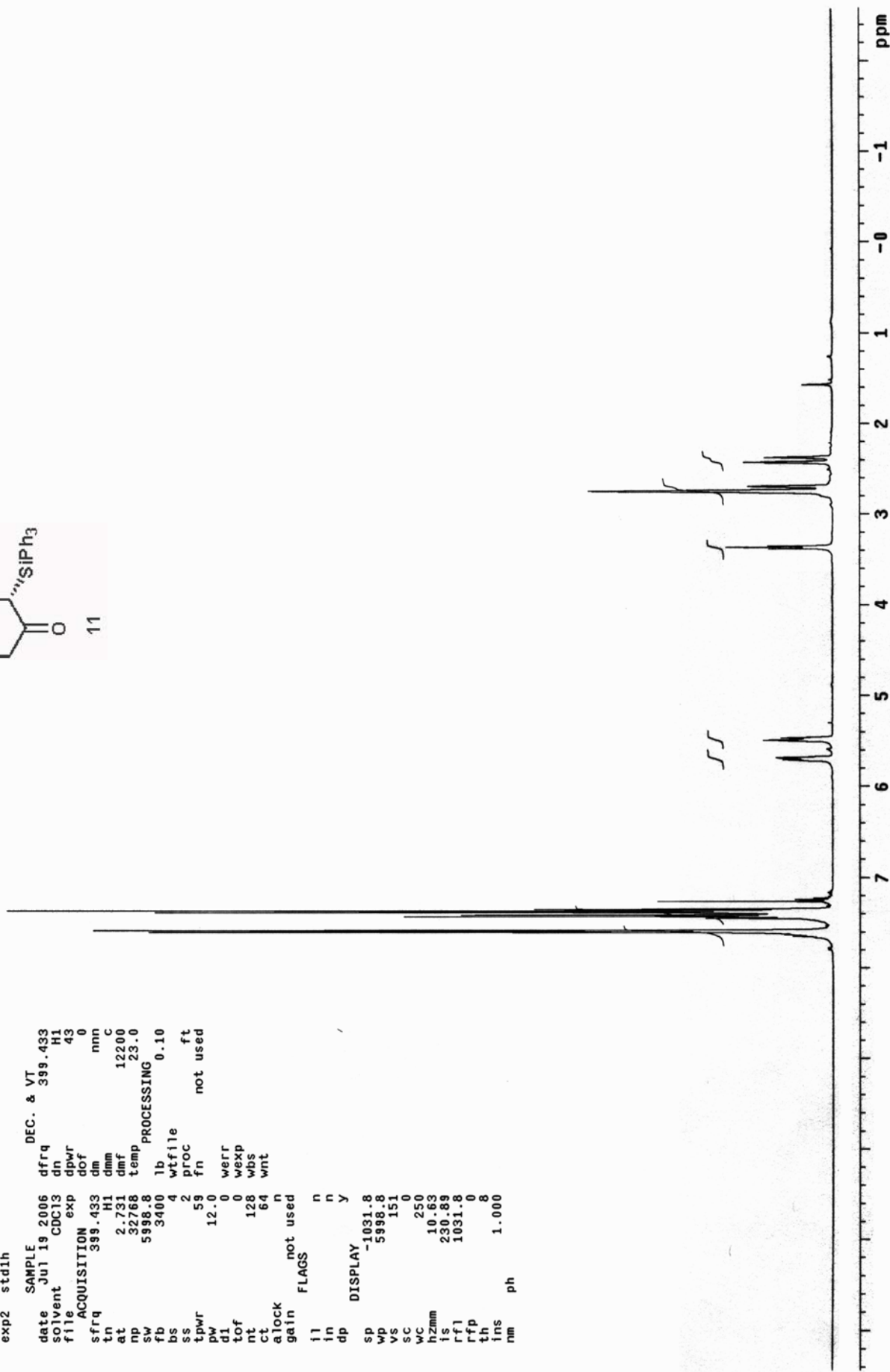
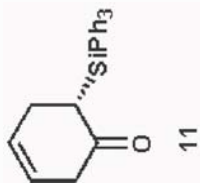


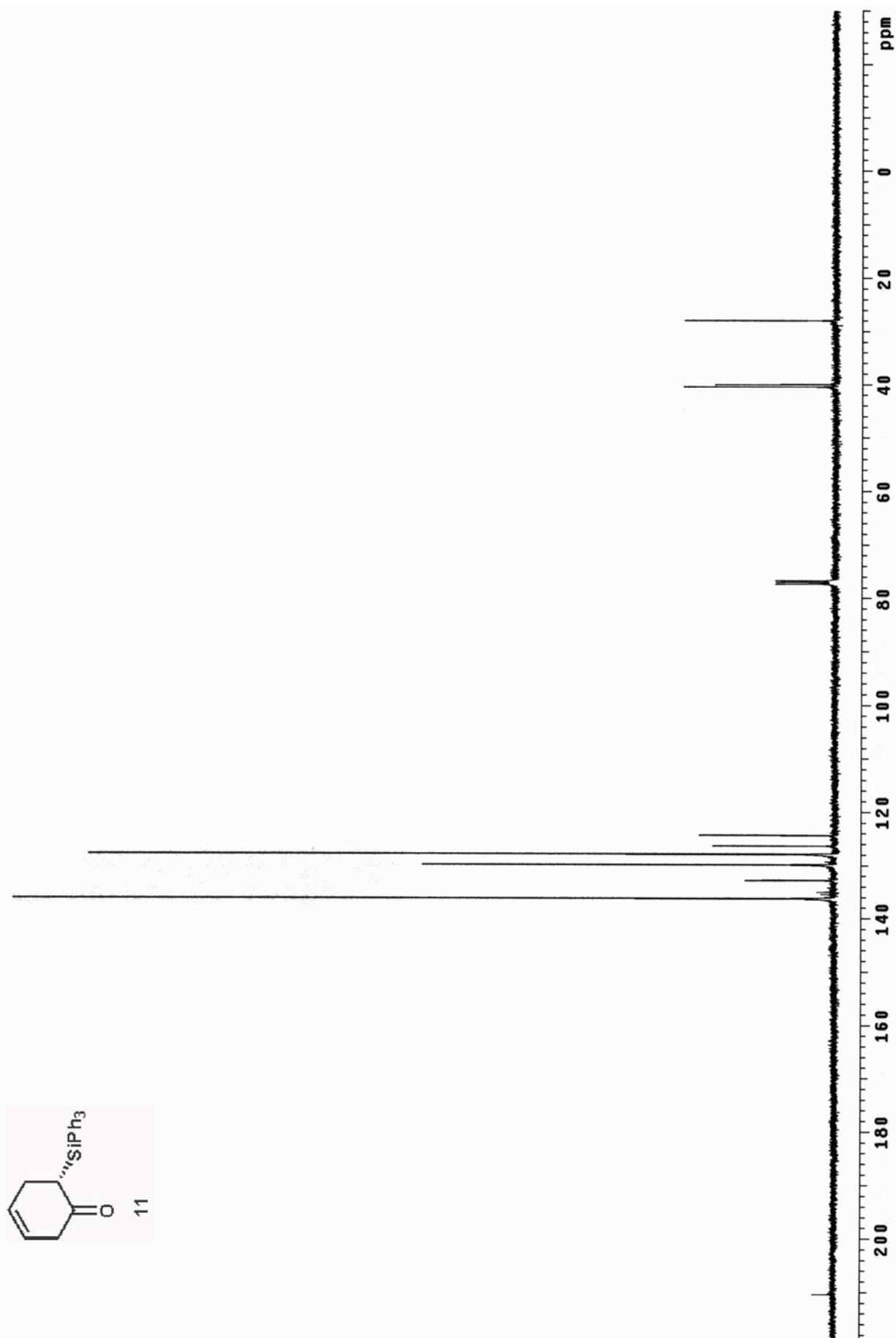
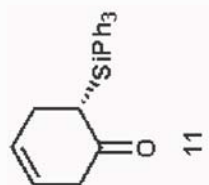
9

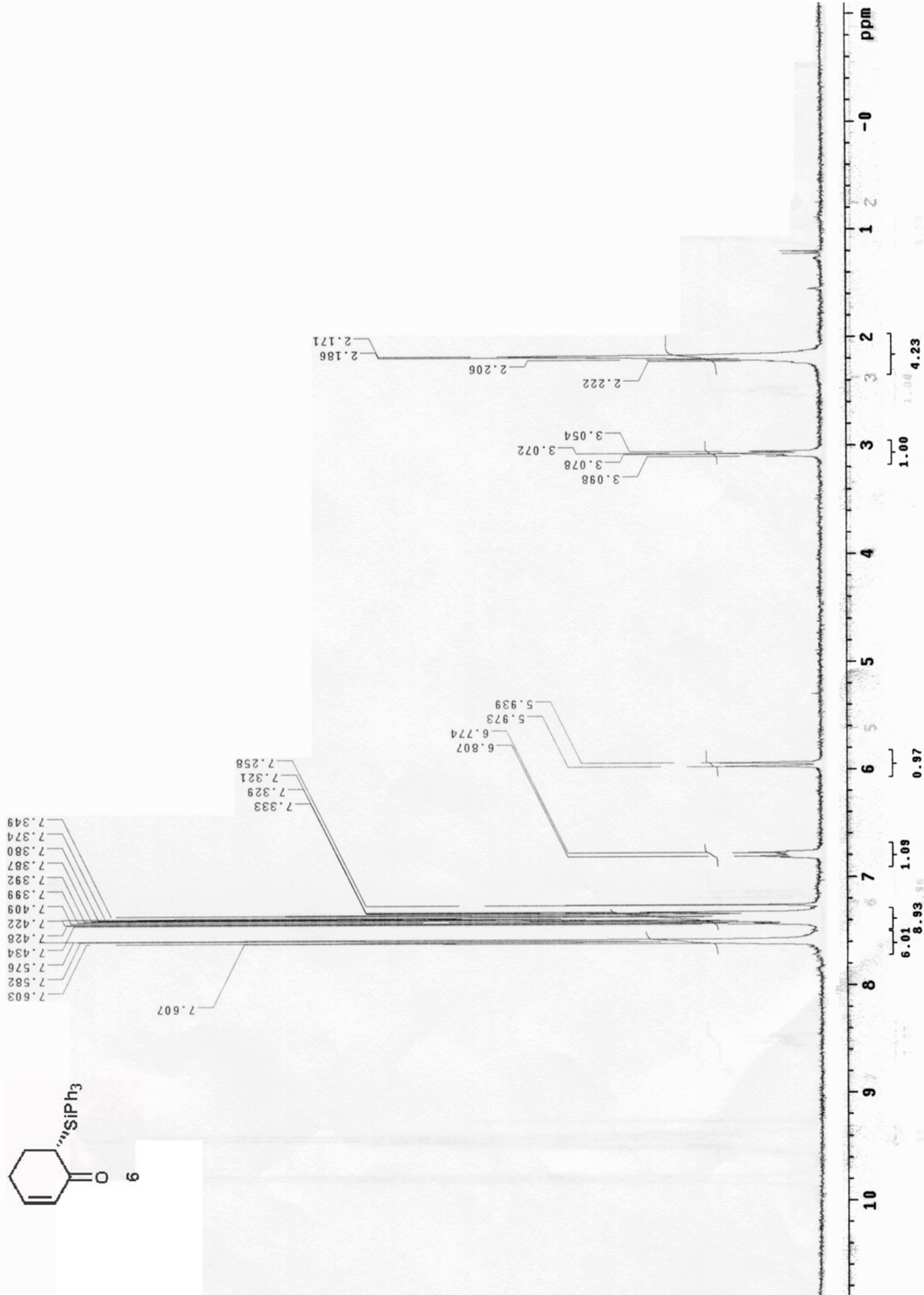
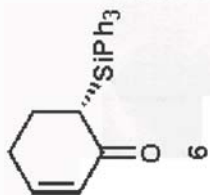


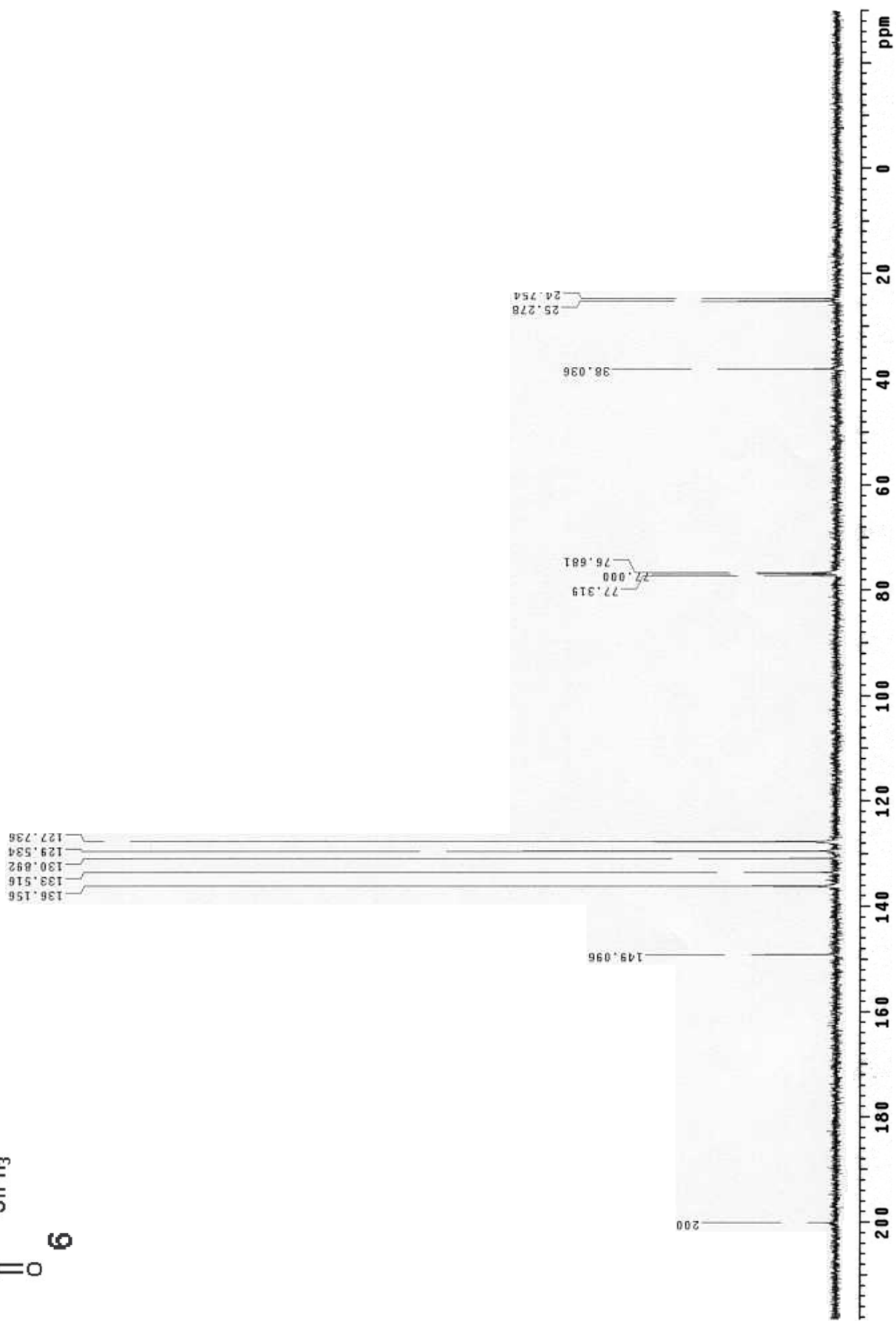
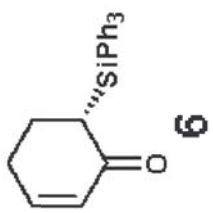
exp2 std1h

SAMPLE		DEC. & VT	
date	Jul 19 2006	dfrq	399.433
solvent	CDC13	dn	H1
file	exp	dpwr	43
		dof	0
ACQUISITION			
sfrq	399.433	dm	nnn
tn	H1	dmm	C
at	2.731	dmf	12200
np	32768	temp	23.0
sw	5998.8	PROCESSING	
fb	3400	lb	0.10
bs	4	wtfile	
ss	2	proc	ft
tpwr	59	fn	not used
pw	12.0		
d1	0	werr	
tof	0	wexp	
nt	128	wbs	
ct	64	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-1031.8		
wp	5998.8		
vs	151		
sc	0		
wc	250		
hzmm	10.83		
is	230.89		
rfl	1031.8		
rtp	0		
th	8		
ins	1.000		
nm	ph		







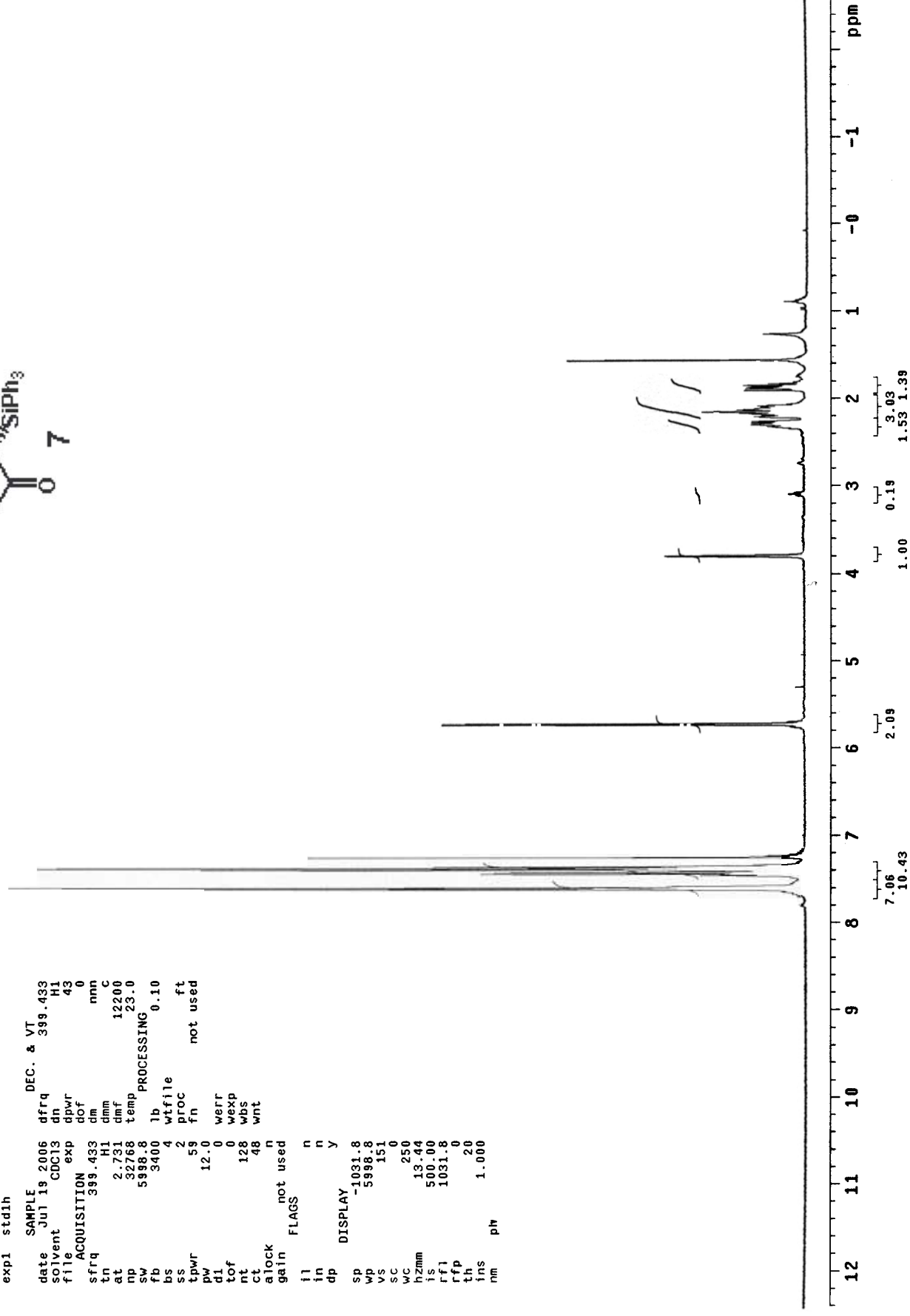
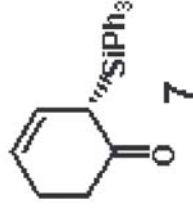


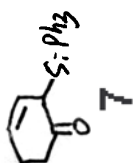
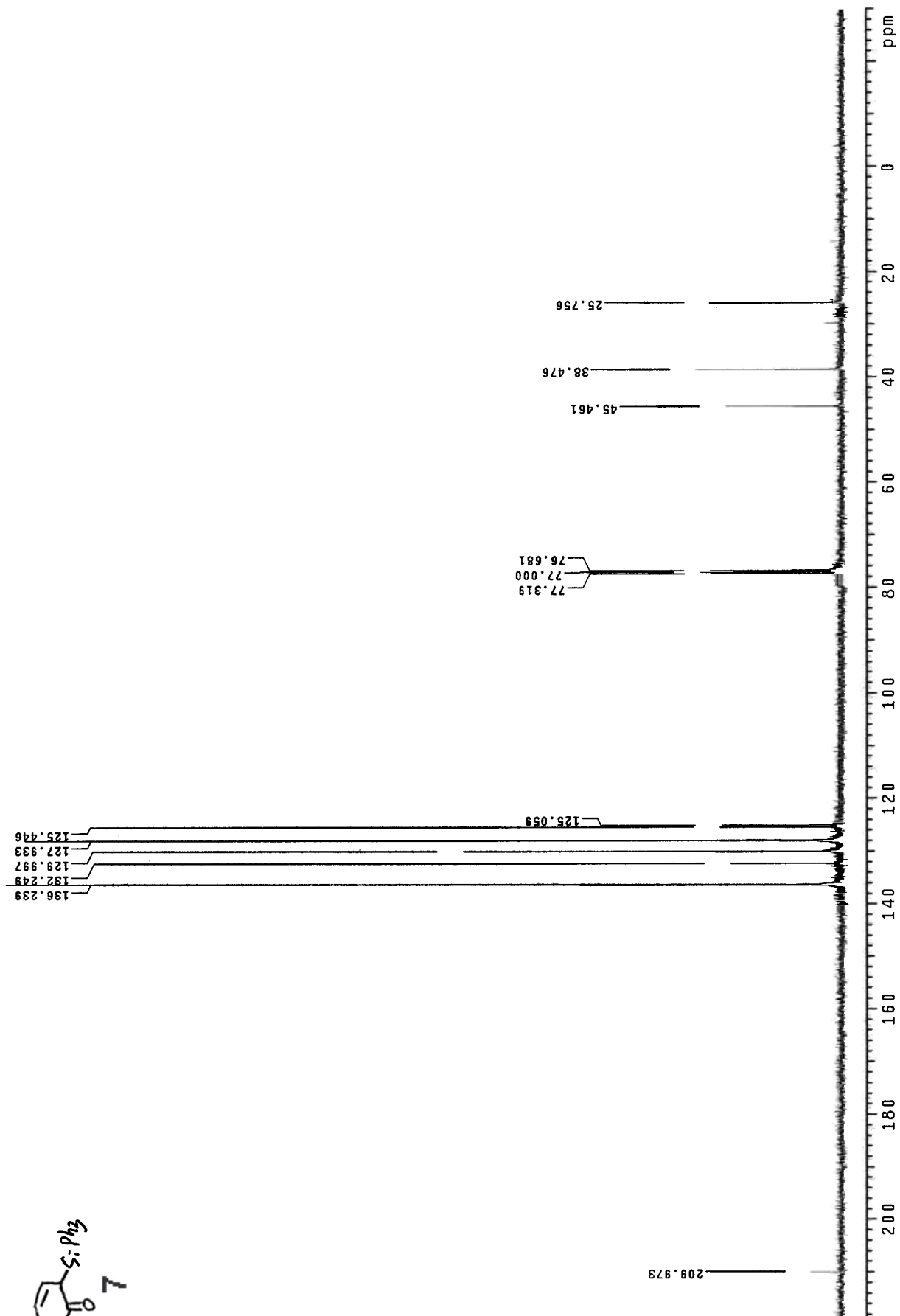
STANDARD 1H OBSERVE

exp1 std1h

SAMPLE
 date Jul 19 2006
 solvent CDCl3
 file ACQUISITION
 sfrq 399.433
 tn H1
 at 2.731
 np 32768
 sw 5998.8
 fb 3400
 bs 4
 ss 2
 tpwr 59
 pw 12.0
 dl 0
 tof 0
 nt 128
 ct 48
 alock not used
 gain n
 flags n
 il n
 in n
 dp y
 sp -1031.8
 wp 5998.8
 vs 151
 sc 0
 wc 250
 hzmm 13.44
 is 500.00
 rfl 1031.8
 rfp 0
 th 20
 ins 1.000
 nm ph

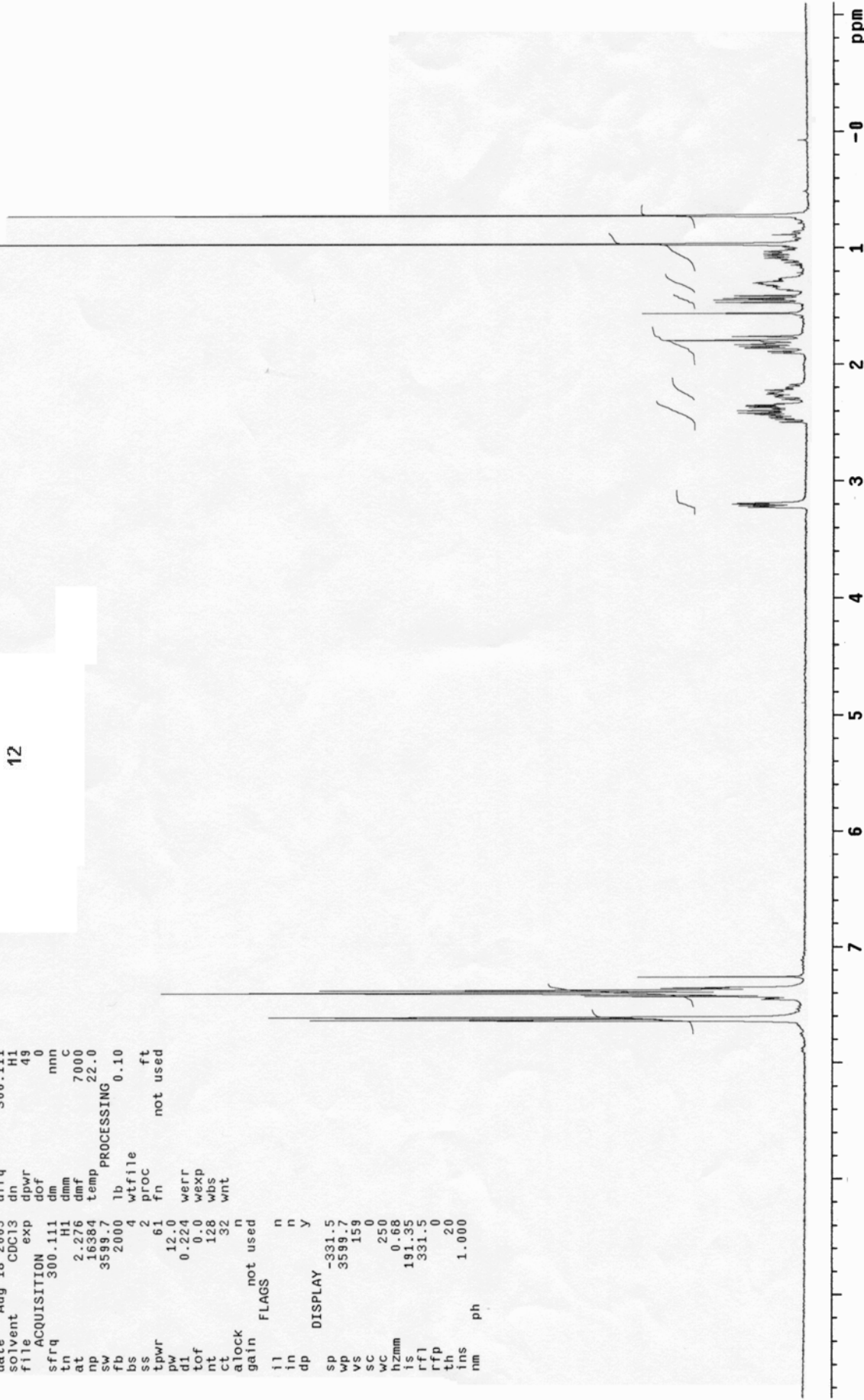
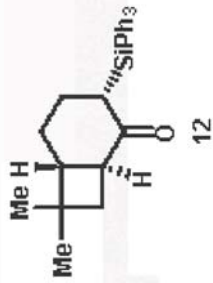
DEC. & VT
 dfrq 399.433
 dn H1
 dpwr 43
 dof 0
 dm nm
 dmm C
 dmf 12200
 temp 23.0
 PROCESSING
 lb 0.10
 wfile
 4
 2
 proc not used
 fn ft
 12.0
 werr
 0
 wexp
 128
 wbs
 48
 wnt





exp6 s2pul

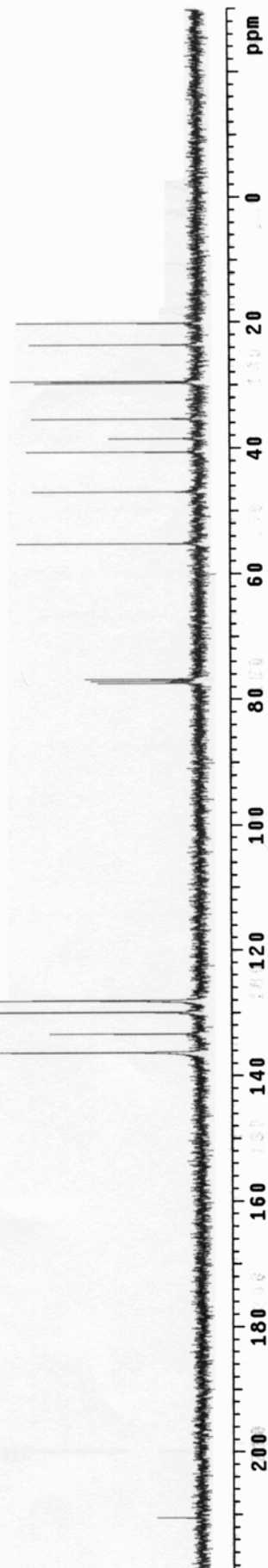
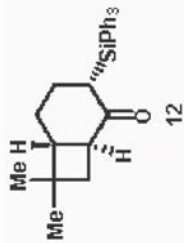
ph

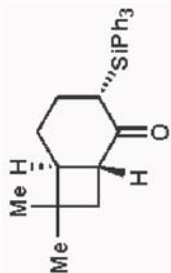


13C OBSERVE

exp3 std13c

date	Jul 31 2006	DEC. & VT	400.021
solvent	CDCl3	dn	H1
file	ACQUISITION	dpwr	46
exp	exp	dof	0
sfreq	100.594	dm	yyy
tn	C13	dmm	w
at	1.311	dmf	9993
np	65536	temp	22.0
sw	25000.0	PROCESSING	
fb	13800	lb	1.00
bs	8	wtfile	
tpwr	61	proc	ft
d1	3.2	fn	not used
tof	0	werr	
nt	10000	wexp	svf(n1)
ct	56	wbs	
alock	n	wnt	
gain	not used		
il	n		
in	n		
dp	y		
sp	-3019.3	DISPLAY	
wp	24999.2		
vs	158		
sc	0		
wc	250		
hzm	26.26		
is	500.00		
rfl	3020.0		
rfl	0		
th	5		
ins	100.000		
nm	ph		





13

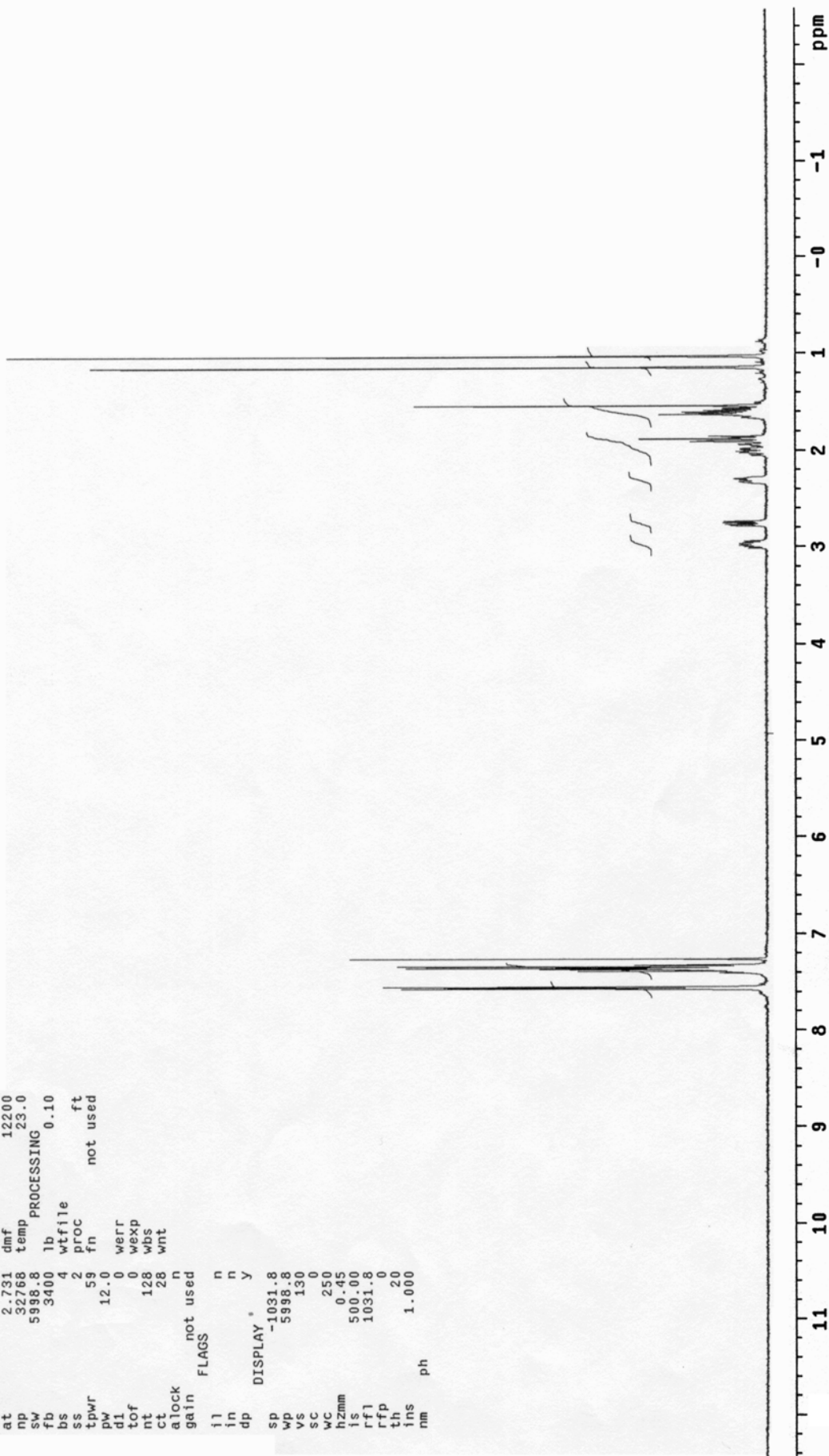
STANDARD 1H OBSERVE

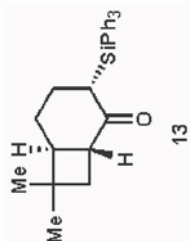
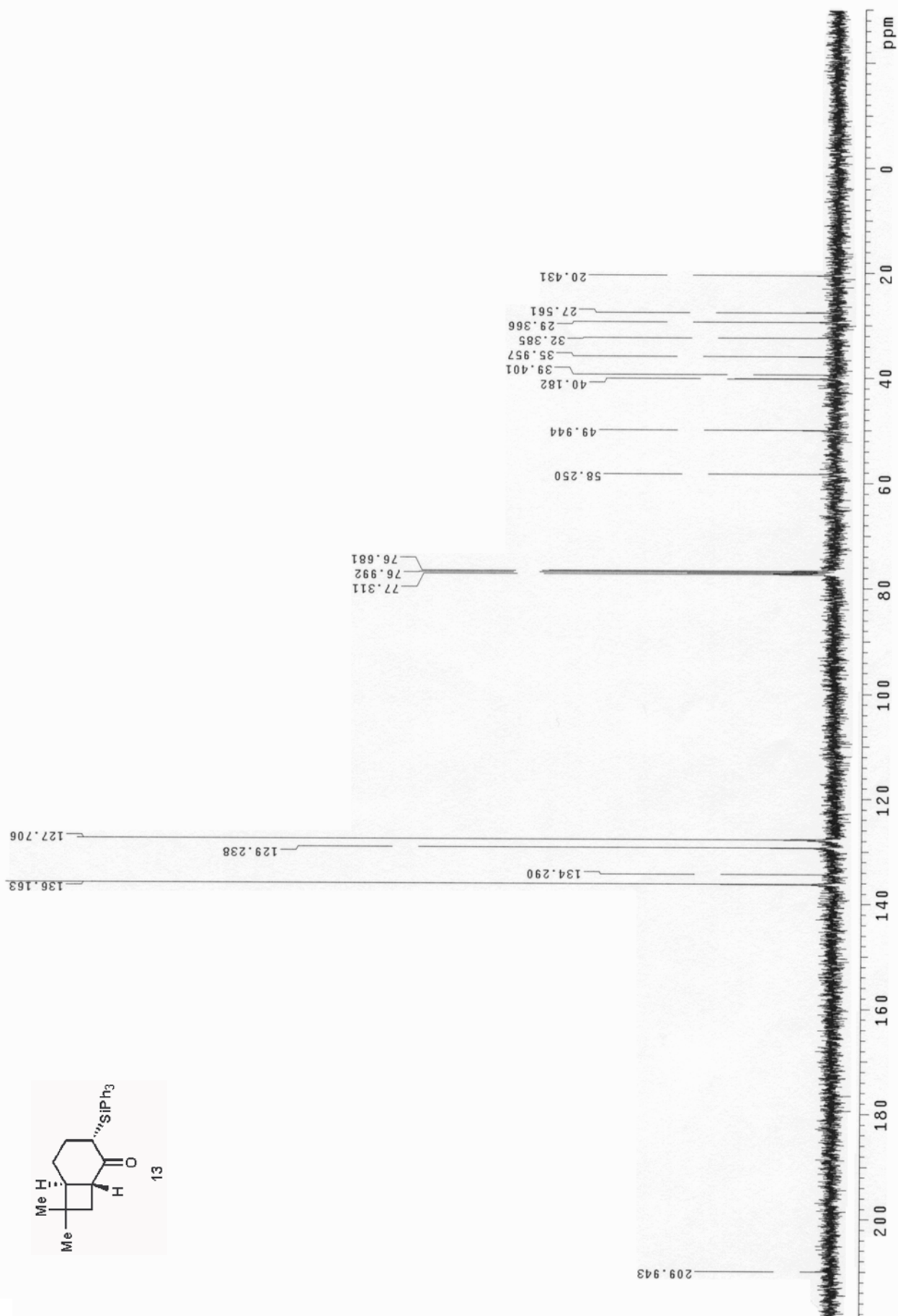
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exp5 stdih
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date Jul 28 2006
solvent CDC13
file exp
ACQUISITION
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tn H1
at 2.731
np 32768
sw 5998.8
fb 3400
bs 4
ss 2
tpwr 59
pw 12.0
d1 0
nt 128
ct 28
alock not used
gain not used
il n
in n
dp y
DISPLAY
sp -1031.8
wp 5998.8
vs 130
sc 0
wc 250
hzm 0.45
is 500.00
rfl 1031.8
rfp 0
th 20
ins 1.000
nm ph
  
```

```

DEC. & VT
dfrq 399.433
dn H1
dpr 43
dof 0
dm nnn
dmm C
dmf 12200
temp 23.0
PROCESSING
lb 0.10
wtfile
2 proc
fn not used
werr 0
wexp 0
wbs 28
wnt 28
  
```





exp1 std1h

SAMPLE		DEC. & VT	
date	Aug 7 2006	dfrq	400.021
solute	CDC13	dn	H1
file	exp	dpwr	40
ACQUISITION		dof	0
sfrq	400.021	dm	nnn
tn	H1	dmm	C
at	2.731	dmf	7500
np	32748	temp	22.0
sw	5995.2	PROCESSING	
fb	3400	lb	0.10
bs	8	wtfile	
ss	2	proc	not used
tpwr	60	fn	ft
pw	15.0	werr	
d1	0.120	wexp	svf(n1)
tof	0	wbs	
nt	256	wnt	
ct	16		
alock	not used		
gain	n		
fl	n		
in	n		
dp	y		
DISPLAY			
sp	-1041.9		
wp	5994.8		
vs	138		
sc	0		
wc	250		
hzm	19.56		
is	124.01		
rfl	3846.4		
rff	2304.1		
th	20		
ins	2.000		
nm	cdc	ph	

