

Synthesis of α -Hydroxy Acids by Silylene Transfer to α -Keto Esters

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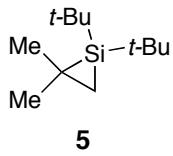
Supporting Information

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Experimental Section

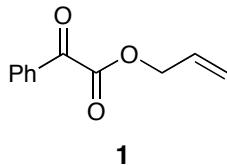
General. Melting points were obtained using a Büchi 510 melting point apparatus and are reported uncorrected. Chiral gas chromatography was performed using a Hewlett-Packard 5890 series II gas chromatograph with a G-TA γ -cyclodextrin, trifluoroacetyl column (20 m x 0.25 mm, 100:1 split ratio), with helium as the carrier gas. Chiral HPLC was accomplished using a Varian Prostar 320 UV-Vis detector in combination with 2 Varian Prostar 210 solvent delivery modules and a Daicel Chemical Industries LTD. Chiralcel OD-H column (25 cm x 0.46 cm). Method of chromatography is as follows: 199:1 hexanes:IPA, flow rate 0.6 mL/min. Analytical thin later chromatography was performed on EMD Silical Gel 60 F₂₅₄ precoated plates. Liquid chromatography utilized force flow (flash chromatography) of the indicated solvent system on Silacycle Sila-P silica gel (SiO₂) 60Å pore size, 40-63 μ m mesh. Infrared spectroscopy was performed on an Applied Systems React IR 1000. High-resolution mass spectra were acquired on a Walters LCT Premier and were obtained by peak matching. Microanalyses were performed by Atlantic Microlabs, Atlanta, GA. ¹H NMR and ¹³C NMR spectra were recorded at 25 °C at 400 and 100, and 500 and 125 MHz respectively, using Bruker DRX 400 or DRX 500 spectrometers as indicated. These data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Silacyclopropanes were stored and manipulated in an Innovative Technologies nitrogen-atmosphere dry box. All reactions were performed under an atmosphere of nitrogen or argon in glassware that had been flame-dried under vacuum prior to use. Solvents were distilled or filtered before use. Cyclohexenesilacyclop propane (**6**) was constructed by known methods.¹



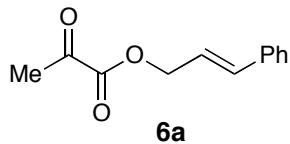
1,1-di-*tert*-butyl-2,2-dimethylsilirane (5). To a cooled (-78°C) solution of lithium granules (3.9 g, 470 mmol) in THF (23 mL), isobutylene (14.5 g, 259 mmol) and di-*tert*-butyldichlorosilane (10 g, 47 mmol) were added. After warming to room temperature and stirring for 72 h, the reaction mixture was concentrated *in vacuo* and filtered through a Celite pad using Schlenk technique. The Celite was rinsed with hexanes (4 \times 50 mL) and the filtrate was concentrated. The reaction mixture was then purified by bulb to bulb distillation to give **5** (4.7 g, 50% yield) as a colorless oil: ^1H NMR (500 MHz, CDCl_3) δ 1.54 (s, 6H), 1.24 (s, 18H), 0.66 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 32.0, 29.2, 20.5, 17.9, 15.3; IR (thin film) 2936, 2857, 1475 cm^{-1} .

I. Synthesis of Substituted α -Keto Esters

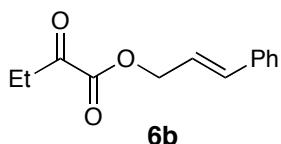
General Coupling Procedure for the Formation of α -Keto Esters: To a solution of the α -hydroxy acid (1.5–2.0 equiv) in CH_2Cl_2 (0.1 M) was added the allylic alcohol (1.0 equiv) and DMAP (0.1 equiv). The solution was cooled to 0°C and stirred for 15 min prior to the addition of DCC (1.5–2.0 equiv). After stirring for 3–6 h, the reaction mixture was filtered, diluted with 20 mL of saturated aqueous NaHCO_3 , and extracted three times with CH_2Cl_2 (30 mL per mmol of alcohol). The organic layers were combined, dried with Na_2SO_4 , and concentrated *in vacuo*. The resulting oil was purified as indicated.



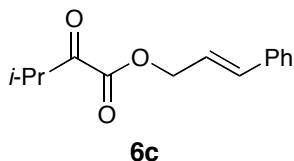
Allyl 2-oxo-2-phenylacetate (1). The general coupling procedure was performed on benzoyl formic acid (3.30 g, 22.0 mmol) and allyl alcohol (0.748 mL, 11.0 mmol). Purification of the concentrated reaction mixture by flash chromatography (10:1 hexanes:EtOAc) gave **1** (1.01 g, 48%) as a yellow oil: ^1H NMR (500 MHz, CDCl_3) δ 8.00–7.97 (m, 2H), 7.63–7.60 (m, 1H), 7.49–7.46 (m, 2H), 5.99 (ddt, $J = 17.0, 10.4, 5.9, 1\text{H}$), 5.42 (m, 1H), 5.31 (m, 1H), 4.85 (dt, $J = 5.9, 1.3, 2\text{H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 186.3, 163.7, 135.2, 132.6, 131.0, 130.2, 129.2, 120.1, 66.7; IR (thin film) 3070, 1737, 1686, 1598, 1451, 1194, 1175 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{10}\text{NaO}_3$ ($\text{M} + \text{Na}$) $^+$ 213.0528, found 213.0529. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{O}_3$: C, 69.46; H, 5.30. Found: C, 69.10; H, 5.26.



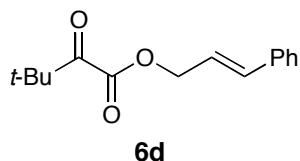
Cinnamyl 2-oxopropanoate (6a). The general coupling procedure was performed on pyruvic acid (0.557 mL, 8.00 mmol) and cinnamyl alcohol (0.537 g, 4.00 mmol). Purification of the concentrated reaction mixture by flash chromatography (10:1 hexanes:EtOAc) gave **6a** (0.434 g, 53%) as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 7.42–7.27 (m, 5H), 6.74 (d, $J = 15.9, 1\text{H}$), 6.33 (dt, $J = 15.6, 6.7, 1\text{H}$), 4.91 (dd, $J = 6.7, 1.1, 2\text{H}$), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.0, 160.7, 136.3, 136.0, 128.9, 128.7, 127.0, 121.6, 67.2, 27.0; IR (thin film) 3369 (br), 2939, 1727, 1677, 1135 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{12}\text{NaO}_3$ ($\text{M} + \text{Na}$) $^+$ 227.0684, found 227.0687. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_3$: C, 70.57; H, 5.92. Found: C, 70.56; H, 6.02.



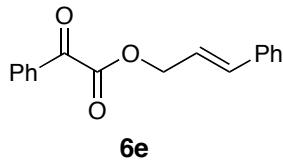
Cinnamyl 2-oxobutanoate (6b). The general coupling procedure was performed on 2-ketobutyric acid (0.817 g, 8.00 mmol) and cinnamyl alcohol (0.537 g, 4.00 mmol). Purification of the concentrated reaction mixture by column chromatography (10:1 hexanes:EtOAc) gave **6b** (0.667 g, 76%) as a pale yellow oil: ¹H NMR (500 MHz, CDCl₃) δ 7.41–7.27 (m, 5H), 6.72 (d, *J* = 15.9, 1H), 6.32 (dt, *J* = 15.9, 6.6, 1H), 4.9 (dd, *J* = 6.6, 1.1, 2H), 2.88 (q, *J* = 7.2, 2H), 1.13 (t, *J* = 7.2, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 194.3, 160.5, 135.5, 135.2, 128.3, 128.0, 126.4, 121.3, 66.2, 32.4, 6.5; IR (thin film) 3451, 2940, 1731, 1269 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₃H₁₄NaO₃ (M + Na)⁺ 241.0841, found 241.0845.



Cinnamyl 3-methyl-2-oxobutanoate (6c). The general coupling procedure was performed on 2-ketovaline (0.318 g, 2.75 mmol) and cinnamyl alcohol (0.184 g, 1.37 mmol). Purification of the concentrated reaction mixture by column chromatography (10:1 hexanes:EtOAc) gave **6c** (0.254 g, 80%) as a light yellow oil: ¹H NMR (500 MHz, CDCl₃) δ 7.42–7.27 (m, 5H), 6.74 (d, *J* = 15.9, 1H), 6.34 (m, 1H), 4.92 (d, *J* = 6.7, 2H), 3.30 (septet, *J* = 7.0, 1H), 1.19 (dd, *J* = 7.0, 0.7, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 198.0, 161.5, 135.85, 135.79, 128.6, 128.4, 126.7, 121.5, 66.6, 37.1, 17.1; IR (thin film) 2977, 2937, 1729, 1449, 1264, 1027 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₄H₁₆NaO₃ (M + Na)⁺ 255.0997, found 255.0996. Anal. Calcd for C₁₄H₁₆O₃: C, 72.39; H, 6.94. Found: C, 72.32; H, 7.08.

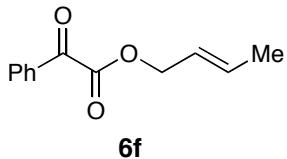


Cinnamyl 3,3-dimethyl-2-oxobutanoate (6d). The general coupling procedure was performed on 3,3-dimethyl-2-oxobutanoic acid (0.484 g, 3.73 mmol) and cinnamyl alcohol (0.250 g, 1.86 mmol). Purification of the concentrated reaction mixture by column chromatography (10:1 hexanes:EtOAc) gave **6d** (0.408 g, 90%) as a white solid: mp 45 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.43–7.30 (m, 5H), 6.74 (d, *J* = 15.9, 1H), 6.33 (dt, *J* = 15.9, 6.7, 1H), 4.91 (dd, *J* = 6.7, 1.2, 2H), 1.29 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 202.1, 163.8, 136.1, 128.9, 128.7, 127.0, 121.8, 66.4, 43.0, 26.0; IR (thin film) 2973, 1733, 1717, 1480, 1449, 1287, 1233 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₅H₁₈NaO₃ (M + Na)⁺ 269.1154, found 269.1157. Anal. Calcd for C₁₅H₁₈O₃: C, 73.15; H, 7.37. Found: C, 73.44; H, 7.40.

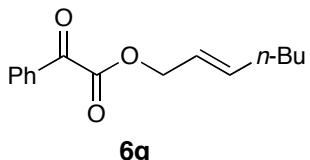


Cinnamyl 2-oxo-2-phenylacetate (6e). The general coupling procedure was performed on benzoylformic acid (0.60 g, 4.0 mmol) and cinnamyl alcohol (0.268 g, 2.00 mmol). Purification of the concentrated reaction

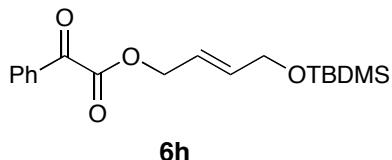
mixture by column chromatography (10:1 hexanes:EtOAc) gave **6e** (0.481 g, 90%) as a yellow oil: ¹H NMR (500 MHz, CDCl₃) δ 8.07–8.04 (m, 2H), 7.70–7.65 (m, 1H), 7.55–7.50 (m, 2H), 7.47–7.41 (m, 2H), 7.38–7.28 (m, 3H), 6.80 (d, *J* = 15.9, 1H), 6.40 (dt, *J* = 15.9, 6.6, 1H), 5.06 (dd, *J* = 6.6, 1.2, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 186.4, 163.8, 136.2, 136.1, 135.2, 132.7, 130.3, 129.2, 128.9, 128.7, 127.0, 121.8, 66.9; IR (thin film) 3060, 3028, 1735, 1686, 1596, 1449, 1195 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₇H₁₄NaO₃ (M + Na)⁺ 289.0841, found 289.0837. Anal. Calcd for C₁₇H₁₄O₃: C, 76.68; H, 5.30. Found: C, 76.25; H, 5.27.



Crotyl 2-oxo-2-phenylacetate (6f). The general coupling procedure was performed on benzoyl formic acid (3.36 g, 22.4 mmol) and crotyl alcohol (0.941 mL, 11.2 mmol). Purification of the concentrated reaction mixture by column chromatography (10:1 hexanes:EtOAc) gave **6f** (1.11 g, 49%) as a yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 7.96–7.94 (m, 2H), 7.61–7.56 (m, 1H), 7.46–7.42 (m, 2H), 5.91–5.82 (m, 1H), 5.64 (dtq, *J* = 15.1, 6.7, 1.6, 1H), 4.76 (dt, *J* = 6.8, 1.2, 2H), 1.70–1.67 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 186.5, 163.9, 135.1, 133.7, 132.7, 130.2, 129.1, 124.0, 67.0, 18.0; IR (thin film) 3031, 1735, 1686, 1598, 1451, 1194, 1173 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₂H₁₂NaO₃ (M + Na)⁺ 227.0684, found 227.0685. Anal. Calcd for C₁₂H₁₂O₃: C, 70.57; H, 5.92. Found: C, 70.59; H, 6.00.

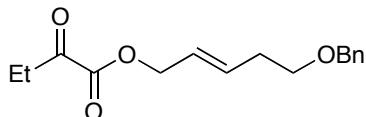


(E)-Hept-2-enyl 2-oxo-2-phenylacetate (6g). The general coupling procedure was performed on benzoyl formic acid (0.500 g, 3.33 mmol) and (*E*)-hept-2-en-1-ol (0.253 g, 2.22 mmol). Purification of the concentrated reaction mixture by column chromatography (20:1 hexanes:EtOAc) gave **6g** (0.497 g, 91%) as a light yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 8.03–8.00 (m, 2H), 7.69–7.64 (m, 1H), 7.55–7.49 (m, 2H), 5.96–5.88 (m, 1H), 5.75–5.64 (m, 1H), 4.83 (d, *J* = 6.7, 2H), 2.10 (q, *J* = 6.9, 2H), 1.45–1.28 (m, 4H), 0.91 (t, *J* = 7.1, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 186.6, 163.9, 139.0, 135.1, 132.7, 130.3, 129.1, 122.7, 67.2, 32.2, 31.1, 22.4, 14.1; IR (thin film) 2958, 2931, 1735, 1688, 1598, 1451, 1194 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₅H₁₈NaO₃ (M + Na)⁺ 269.1154, found 269.1154. Anal. Calcd for C₁₅H₁₈O₃: C, 73.15; H, 7.37. Found: C, 73.39; H, 7.42.



(E)-4-(tert-butyldimethylsilyloxy)but-2-enyl 2-oxo-2-phenylacetate (6h). The general coupling procedure was performed on benzoyl formic acid (0.500 g, 3.33 mmol) and (*E*)-4-(tert-butyldimethylsilyloxy)but-2-en-1-ol (0.449 g, 2.22 mmol). Purification of the concentrated reaction mixture by column chromatography (20:1 hexanes:EtOAc) gave **6h** (0.676 g, 91%) as a light yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 8.04–8.00 (m, 2H), 7.70–7.64 (m, 1H), 7.55–7.48 (m, 2H), 6.04–5.87 (m, 2H), 4.90 (d, *J* = 5.6, 2H), 4.23 (dd, *J* = 3.7, 1.3, 2H), 0.92 (s, 9H), 0.09 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 186.4, 163.8, 136.3, 135.1, 132.7, 130.3, 129.1,

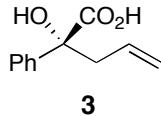
122.2, 66.3, 62.8, 26.1, 18.6, -5.1; IR (thin film) 2931, 2858, 1737, 1690, 1598, 1451, 1194 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{26}\text{NaO}_4\text{Si} (\text{M} + \text{Na})^+$ 357.1498, found 357.1502.

**6i**

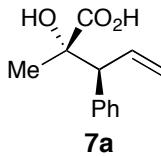
(E)-5-(benzyloxy)pent-2-enyl 2-oxobutanoate (6i). The general coupling procedure was performed on 2-ketobutyric acid (0.153 g, 1.50 mmol) and (E)-5-(benzyloxy)pent-2-en-1-ol (0.192 g, 1.00 mmol). Purification of the concentrated reaction mixture by column chromatography (20:1 hexanes:EtOAc) gave **6i** (0.186 g, 67%) as a light yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 7.36–7.24 (m, 5H), 5.94–5.85 (m, 1H), 5.74–5.64 (m, 1H), 4.68 (d, $J = 6.6$, 2H), 4.50 (s, 2H), 3.52 (t, $J = 6.6$, 2H), 2.84 (q, $J = 7.2$, 2H), 2.39 (q, $J = 6.5$, 2H), 1.11 (t, $J = 7.2$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.1, 161.1, 138.6, 134.7, 128.6, 127.9, 127.8, 124.7, 73.1, 69.3, 66.9, 33.1, 32.9, 7.2; IR (thin film) 3029, 2860, 1727, 1455, 1218, 1100 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{24}\text{NO}_4 (\text{M} + \text{NH}_4)^+$ 294.1705, found 294.1700.

II. Synthesis of α -Hydroxy Acids

Procedure for the Formation of α -Hydroxy Acids: Silacyclopropane **5** (1.25–1.65 equiv) was added to a solution of the α -keto ester (1.0 equiv) in toluene (0.1 M) inside an inert atmosphere glove box. Upon cooling to -24°C , silver tosylate (10 mol%) was added, and the reaction mixture was kept at -24°C . After 3 h, the reaction mixture was removed from the glove box and warmed to ambient temperature under nitrogen atmosphere over 1 h, then HF•Pyr (70% HF solution in pyridine, 4.0 equiv of HF) was added. After an additional 1 h, the reaction mixture was diluted with 20 mL of saturated aqueous NaHCO_3 and washed with CH_2Cl_2 (3×25 mL). The aqueous layer was then acidified to pH 1 with 1M aqueous HCl and extracted with CH_2Cl_2 (5×20 mL). The organic layers were combined, dried with Na_2SO_4 , and concentrated *in vacuo* to provide pure products.

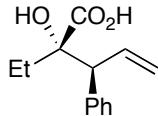
**3**

2-hydroxy-2-phenylpent-4-enoic acid (3). The general transfer procedure was performed on **1** (0.190 g, 1.00 mmol), silacyclopropane **5** (0.277 g, 1.40 mmol), and AgOTs (0.028 g, 0.10 mmol) to give **3** (0.092 g, 48%) as a white solid: mp 100 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.65–7.63 (m, 2H), 7.40–7.32 (m, 3H), 5.81 (ddt, $J = 17.2, 10.1, 7.2, 1\text{H}$), 5.23 (dd, $J = 17.2, 1.3, 1\text{H}$), 5.19 (d, $J = 10.2, 1\text{H}$), 3.03 (dd, $J = 14.0, 7.4, 1\text{H}$), 2.81 (dd, $J = 14.1, 6.9, 1\text{H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 179.0, 140.2, 131.7, 128.4, 128.2, 125.5, 120.4, 77.8, 44.1; IR (thin film) 3435 (br), 3062, 2981, 1713, 1449, 1229, 1189 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{NaO}_3 (\text{M} + \text{Na})^+$ 215.0684, found 215.0683. Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3$: C, 68.74; H, 6.29. Found: C, 68.48; H, 6.21.

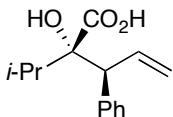
**7a**

2-Hydroxy-2-methyl-3-phenylpent-4-enoic acid (7a). The general transfer procedure was performed on **6a** (0.204 g, 1.00 mmol), silacyclopropane **5** (0.287 g, 1.45 mmol), and AgOTs (0.028 g, 0.10 mmol) to give **7a**

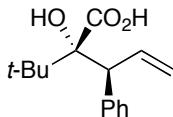
(0.126 g, 62%) as a light yellow oil, single diastereomer (as determined by ^1H NMR spectroscopy): ^1H NMR (500 MHz, CDCl_3) δ 7.33–7.29 (m, 5H), 6.32 (dt, J = 17.0, 10.0, 1H), 5.33 (dd, J = 10.2, 1.7, 1H), 5.27 (dd, J = 17.0, 1.1, 1H), 3.64 (d, J = 9.8, 1H), 1.55 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 181.2, 139.6, 135.6, 128.8, 128.7, 127.5, 119.1, 77.5, 57.9, 24.7; IR (thin film) 3450 (br), 3064, 2983, 1713, 1455, 1148 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{NaO}_3$ ($\text{M} + \text{Na}$) $^+$ 229.0841, found 229.0844. Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.88; H, 6.84. Found: C, 69.70; H, 6.80.

**7b**

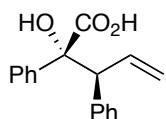
2-Ethyl-2-hydroxy-3-phenylpent-4-enoic acid (7b). The general transfer procedure was performed on **6b** (0.050 g, 0.23 mmol), silacyclopropane **5** (0.072 g, 1.6 mmol), and AgOTs (0.006 g, 0.02 mmol) to give **7b** (0.038 g, 84%) as a white solid, single diastereomer (as determined by ^1H NMR spectroscopy): mp 80 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.27–7.22 (m, 5H), 6.26 (dt, J = 17.0, 10.0, 1H), 5.23 (dd, J = 10.2, 1.7, 1H), 5.19 (dd, J = 17.1, 1.1, 1H), 3.57 (d, J = 9.8, 1H), 1.95–1.74 (m, 2H), 0.88 (t, J = 7.4, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 180.8, 139.8, 135.9, 128.8, 128.6, 127.4, 118.7, 80.7, 57.9, 30.7, 8.3; IR (thin film) 3460 (br), 2973, 1710, 1231, 1135 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{16}\text{NaO}_3$ ($\text{M} + \text{Na}$) $^+$ 243.0997, found 243.0995. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3$: C, 70.89; H, 7.32. Found: C, 70.80; H, 7.39.

**7c**

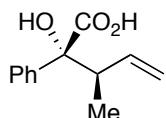
2-Hydroxy-2-isopropyl-3-phenylpent-4-enoic acid (7c). The general transfer procedure was performed on **6c** (0.232 g, 1.00 mmol), silacyclopropane **5** (0.287 g, 1.45 mmol), and AgOTs (0.028 g, 0.10 mmol) to give **7c** (0.127 g, 54%) as a white solid, single diastereomer (as determined by ^1H NMR spectroscopy): mp 125 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.37–7.20 (m, 5H), 6.31 (dt, J = 16.9, 9.8, 1H), 5.22 (m, 2H), 3.86 (d, J = 9.6, 1H), 2.12 (septet, J = 6.9, 1H), 1.14 (d, J = 6.9, 3H), 0.96 (d, J = 6.9, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 179.3, 140.0, 135.8, 129.0, 128.3, 127.0, 118.0, 82.4, 54.0, 34.6, 17.2, 16.9; IR (thin film) 3489 (br), 2973, 1706, 1231, 1140, 1073 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{18}\text{NaO}_3$ ($\text{M} + \text{Na}$) $^+$ 257.1154, found 257.1159. Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3$: C, 71.77; H, 7.74. Found: C, 71.47; H, 7.70.

**7d**

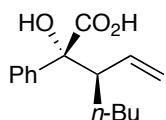
2-tert-Butyl-2-hydroxy-3-phenylpent-4-enoic acid (7d). The general transfer procedure was performed on **6d** (0.246 g, 1.00 mmol), silacyclopropane **5** (0.287 g, 1.45 mmol), and AgOTs (0.028 g, 0.10 mmol) to give **7d** (0.115 g, 47%) as a white solid, single diastereomer (as determined by ^1H NMR spectroscopy): mp 123 °C; ^1H NMR (400 MHz, acetone- d_6) δ 7.43–7.30 (m, 5H), 6.47 (d, J = 15.9, 1H), 6.25 (ddd, J = 15.8, 8.1, 6.3, 1H), 2.76 (dd, J = 13.6, 8.2, 1H), 2.56 (ddd, J = 13.6, 6.2, 0.9, 1H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, acetone- d_6) δ 176.2, 137.9, 133.3, 128.6, 127.2, 126.2, 125.7, 81.8, 37.3, 36.9, 25.3; IR (thin film) 3435 (br), 2960, 1702, 1368, 1212, 1106 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{NaO}_3$ ($\text{M} + \text{Na}$) $^+$ 271.1310, found 271.1317. Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3$: C, 72.55; H, 8.12. Found: C, 72.33; H, 8.08.

**7e**

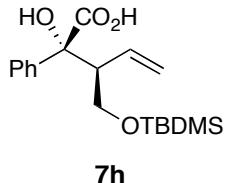
2-Hydroxy-2,3-diphenylpent-4-enoic acid (7e). The general transfer procedure was performed on **6e** (0.266 g, 1.00 mmol), silacyclopropane **5** (0.277 g, 1.40 mmol), and AgOTs (0.028 g, 0.10 mmol) to give **7e** (0.189 g, 71%) as a white solid, single diastereomer (as determined by ¹H NMR spectroscopy): mp 183 °C; ¹H NMR (500 MHz, acetone-*d*₆) δ 7.89–7.86 (m, 2H), 7.57–7.56 (m, 2H), 7.40–7.36 (m, 2H), 7.30–7.26 (m, 3H), 7.23–7.19 (m, 1H), 6.03 (ddd, *J* = 17.2, 10.4, 8.6, 1H), 4.84–4.78 (m, 2H), 4.38 (d, *J* = 8.6, 1H); ¹³C NMR (125 MHz, acetone-*d*₆) δ 174.8, 141.7, 140.8, 137.4, 130.1, 128.5, 128.01, 127.98, 127.5, 126.9, 126.8, 116.8, 80.7, 57.6; IR (thin film) 3423, 3064 (br), 3029, 1721, 1694, 1449, 1100 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₇H₁₆NaO₃ (M + Na)⁺ 291.0997, found 291.1000. Anal. Calcd for C₁₇H₁₆O₃: C, 76.10; H, 6.01. Found: C, 75.82; H, 6.19.

**7f**

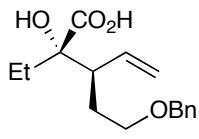
2-Hydroxy-3-methyl-2-phenylpent-4-enoic acid (7f). The general transfer procedure was performed on **6f** (0.204 g, 1.00 mmol), silacyclopropane **5** (0.287 g, 1.45 mmol), and AgOTs (0.028 g, 0.10 mmol) to give **7f** (0.126 g, 62%) as a white solid, single diastereomer (as determined by ¹H NMR spectroscopy): mp 119 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.66–7.64 (m, 2H), 7.38–7.28 (m, 3H), 5.58 (ddd, *J* = 17.5, 10.6, 7.2, 1H), 4.98 (d, *J* = 8.4, 1H), 4.95 (s, 1H), 3.26 (quintet, *J* = 6.7, 1H), 1.19 (d, *J* = 6.7, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 179.0, 139.8, 137.2, 128.3, 128.0, 126.0, 117.1, 80.5, 45.1, 14.5; IR (thin film) 3481 (br), 3072, 2977, 1706, 1449, 1241, 1192, 1135 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₂H₁₄NaO₃ (M + Na)⁺ 229.0841, found 229.0841. Anal. Calcd for C₁₂H₁₄O₃: C, 69.88; H, 6.84. Found: C, 69.49; H, 6.93.

**7g**

2-Hydroxy-2-phenyl-3-vinylheptanoic acid (7g). The general transfer procedure was performed on **6g** (0.150 g, 0.609 mmol), silacyclopropane **5** (0.174 g, 1.45 mmol), and AgOTs (0.017 g, 0.061 mmol) to give **7g** (0.110 g, 72%) as a white solid with 98:2 diastereoselectivity (as determined by ¹H NMR spectroscopy): mp 110 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.64–7.59 (m, 2H), 7.37–7.25 (m, 3H), 5.45 (dt, *J* = 17.1, 10.1, 1H), 4.94 (dd, *J* = 10.3, 1.8, 1H), 4.82 (dd, *J* = 17.3, 1.6, 1H), 2.96 (t, *J* = 9.6, 1H), 1.68–1.55 (m, 1H), 1.43–1.18 (m, 5H), 0.89 (t, *J* = 6.6, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 180.3, 140.2, 136.0, 128.3, 128.0, 126.3, 119.0, 81.3, 52.1, 29.8, 29.3, 22.7, 14.2; IR (thin film) 3450 (br), 3074, 2958, 2933, 1706, 1449, 1131 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₅H₁₉O₃ (M – H)[−] 247.1334, found 247.1333. Anal. Calcd for C₁₅H₂₀O₃: C, 72.55; H, 8.12. Found: C, 72.53; H, 8.14.

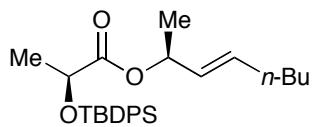


3-((*tert*-Butyldimethylsilyloxy)methyl)-2-hydroxy-2-phenylpent-4-enoic acid (7h). The general transfer procedure was performed on **6h** (0.100 g, 0.299 mmol), silacyclopropane **5** (0.071 g, 0.36 mmol), and AgOTs (0.008g, 0.03 mmol). The reaction mixture was concentrated *in vacuo* and purified by column chromatography (80:18:2 hexanes:EtOAc:AcOH) to give **7h** (0.071 g, 71%) as a white solid, single diastereomer (as determined by ¹H NMR spectroscopy): mp 91–93 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.62–7.58 (m, 2H), 7.37–7.25 (m, 3H), 5.72 (ddd, *J* = 17.4, 10.5, 8.5, 1H), 5.05–4.95 (m, 2H), 4.09 (dd, *J* = 10.3, 3.1, 1H), 3.92 (dd, *J* = 10.3, 3.8, 1H), 3.24 (m, 1H), 0.90 (s, 9H), 0.07 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 176.3, 139.4, 133.5, 128.4, 128.1, 125.8, 119.3, 81.6, 66.1, 50.7, 25.9, 18.3, –5.6, –5.7; IR (thin film) 3529, 2950, 2931, 2858, 1698, 1259, 1098 cm^{–1}; HRMS (ESI) *m/z* calcd for C₁₈H₂₇O₄Si (M – H)[–] 335.1679, found 335.1672.



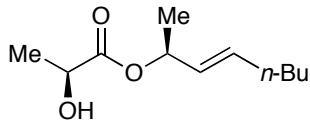
3-(2-(benzyloxy)ethyl)-2-Ethyl-2-hydroxypent-4-enoic acid (7i). The general transfer procedure was performed on **6i** (0.050 g, 0.18 mmol), silacyclopropane **5** (0.061 g, 0.31 mmol), and AgOTs (0.005g, 0.02 mmol) to give **7i** (0.038 g, 75%) as a white solid, single diastereomer (as determined by ¹H NMR spectroscopy): mp 81–82 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.26 (m, 5H), 5.62 (dt, *J* = 17.2, 10.1, 1H), 5.18 (dd, *J* = 10.2, 1.8, 1H), 5.06 (dd, *J* = 17.2, 1.7, 1H), 4.57 (d, *J* = 11.8, 1H), 4.50 (d, *J* = 11.8, 1H), 3.63–3.58 (m, 1H), 3.50–3.45 (m, 1H), 2.63 (td, *J* = 10.3, 3.2, 1H), 1.78–1.54 (m, 4H), 0.81 (t, *J* = 7.4, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.8, 137.3, 136.0, 128.7, 128.4, 128.2, 119.5, 79.8, 73.4, 68.0, 48.3, 31.0, 29.4, 8.0; IR (thin film) 3438 (br), 2971, 2937, 2879, 1719, 1237 cm^{–1}; HRMS (ESI) *m/z* calcd for C₁₆H₂₃O₄ (M + H)⁺ 279.1596, found 279.1588. Anal. Calcd for C₁₆H₂₂O₄: C, 69.04; H, 7.97. Found: C, 69.07; H, 7.98.

III. Chiral α -Keto Ester Synthetic Intermediates and Products

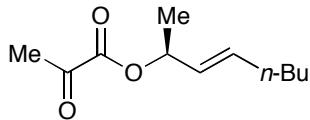
**S-1**

Lactate S-1. (*S*)-2-(*tert*-Butyldiphenylsilyloxy)propanoic acid² (0.20 g, 0.61 mmol) was added to 10 mL of CH₂Cl₂ followed by oxalyl chloride (0.058 mL, 0.67 mmol) and DMF (1 drop). After stirring for 11 h, pyridine (0.072 mL, 0.91 mmol) and (*S,E*)-oct-3-en-2-ol³ (0.097 g, 0.76 mmol, ee > 97% as determined by chiral GC) were then added. After 3 h, the reaction mixture was diluted with 15 mL of aqueous saturated ammonium chloride and extracted with CH₂Cl₂ (3 × 20 mL). The organic layers were combined, dried with Na₂SO₄, and concentrated *in vacuo*. The resultant yellow oil was purified by column chromatography (20:1 hexanes:EtOAc) to give **S-1** (0.106 g, 40%) as a colorless oil: [α]²³_D –55.3 (*c* 5.29, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.77–7.69 (m, 4H), 7.47–7.36 (m, 6H), 5.71–5.65 (m, 1H), 5.37 (ddt, *J* = 15.3, 6.9, 1.3, 1H), 5.27 (pentet, *J* = 6.5,

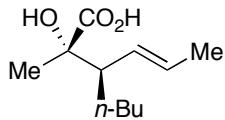
1H), 4.28 (q, $J = 6.7$, 1H), 2.02 (q, $J = 6.6$, 2H), 1.39 (d, $J = 6.7$, 3H), 1.34–1.29 (m, 4H), 1.19 (d, $J = 6.4$, 3H), 1.13 (s, 9H), 0.91 (t, $J = 7.2$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.2, 136.2, 136.0, 134.0, 133.8, 133.5, 129.96, 129.95, 129.5, 127.9, 127.8, 71.8, 69.3, 32.1, 31.3, 27.1, 22.4, 21.5, 20.5, 19.5, 14.1; IR (thin film) 3074, 2960, 2933, 2860, 1750, 1428 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{42}\text{NO}_3\text{Si} (\text{M} + \text{NH}_4)^+$ 456.2934, found 456.2936. Anal. Calcd for $\text{C}_{27}\text{H}_{38}\text{O}_3\text{Si}$: C, 73.92; H, 8.73. Found: C, 73.97; H, 8.89.

**S-2**

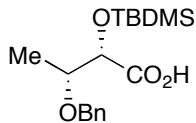
(S)-((S,E)-oct-3-en-2-yl) 2-Hydroxypropanoate (S-2). To a cooled solution (-20°C) of **S-1** (1.77 g, 4.03 mmol) in 40 mL THF was added $n\text{-Bu}_4\text{NF}$ (6.05 mL of a 1M solution in THF, 6.05 mmol) dropwise. After 48 h, 10 mL of aqueous saturated NH_4Cl was added and the reaction mixture was warmed to room temperature.⁴ The mixture was then extracted with CH_2Cl_2 (3×30 mL). The organic layers were combined, dried with Na_2SO_4 , and concentrated *in vacuo*. The resultant oil was purified by column chromatography (5:1 hexanes:EtOAc) affording **S-2** (0.597 g, 74%) as a colorless oil: $[\alpha]^{23}_D -67.2$ (*c* 3.44, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 5.73–5.68 (m, 1H), 5.45–5.32 (m, 2H), 4.25–4.18 (m, 1H), 3.00 (d, $J = 4.4$, 1H), 2.01 (q, $J = 7.0$, 2H), 1.38 (d, $J = 6.9$, 3H), 1.36–1.25 (m, 7H), 0.88 (t, $J = 7.0$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.1, 134.2, 128.8, 77.8, 66.8, 31.8, 31.0, 22.1, 20.39, 20.35, 13.9; IR (thin film) 3464 (br), 2958, 2929, 2858, 1735, 1214, 1129 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{20}\text{NaO}_3 (\text{M} + \text{Na})^+$ 223.1310, found 223.1302. Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{O}_3$: C, 65.97; H, 10.07. Found: C, 65.77; H, 10.21.

**13**

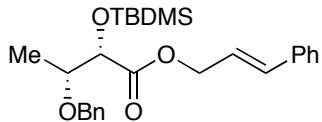
(S,E)-Oct-3-en-2-yl 2-oxopropanoate (13). To **S-2** (0.50 g, 2.5 mmol) in 25 mL of CH_2Cl_2 was added pyridine (1.0 mL, 12 mmol) followed by Dess-Martin periodinane (1.6 g, 3.7 mmol).⁵ After 3 h, the reaction mixture was diluted with 15 mL of saturated aqueous Na_2SO_3 and extracted with CH_2Cl_2 (3×20 mL). The organic layers were combined, dried with Na_2SO_4 , and concentrated *in vacuo*. The resultant oil was purified by column chromatography (5:1 hexanes:EtOAc) to give **13** (0.23 g, 84%) as a pale yellow oil: $[\alpha]^{23}_D -32.9$ (*c* 1.70, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 5.79 (td, $J = 6.7$, 15.0, 1H), 5.50 (ddt, $J = 15.1$, 7.3, 1.3, 1H), 5.42 (quintet, $J = 6.5$, 1H), 2.45 (s, 3H), 2.03 (q, $J = 6.8$, 2H), 1.42–1.23 (m, 7H), 0.89 (t, $J = 7.1$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.6, 160.4, 135.6, 128.3, 74.5, 32.0, 31.1, 26.9, 22.4, 20.5, 14.1; IR (thin film) 2960, 2933, 2861, 1725, 1430, 1295, 1144 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{18}\text{NaO}_3 (\text{M} + \text{Na})^+$ 221.1154, found 221.1148. Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}_3$: C, 66.64; H, 9.15. Found: C, 66.92; H, 9.08.

**14**

α -Hydroxy acid 14. The general transfer procedure was performed on **13** (0.498 g, 2.51 mmol), silacyclopropane **5** (0.871 g, 4.40 mmol), and AgOTs (0.07 g, 0.3 mmol) to give **14** (0.389 g, 77%, 97% ee based on HPLC data on the derived benzyl ester, absolute and relative stereochemistry determined from phenylethylamine salt *vida infra*) as a white solid: mp 105 °C; $[\alpha]^{23}_D +10.6$ (*c* 0.38, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 5.60–5.49 (m, 1H), 5.21 (ddd, *J* = 15.3, 9.7, 1.5, 1H), 2.23 (t, *J* = 10.2, 1H), 1.73 (dd, *J* = 6.4, 1.4, 3H), 1.43–1.09 (m, 9H), 0.87 (t, *J* = 6.9, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 182.2, 130.3, 129.2, 51.4, 29.9, 29.3, 24.6, 22.7, 18.3, 14.2; IR (thin film) 3440 (br), 2958, 2933, 2860, 1717, 1453, 1239 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₁H₂₀NaO₃ (M + Na)⁺ 223.1310, found 223.1301. Anal. Calcd for C₁₁H₂₀O₃: C, 65.97; H, 10.07. Found: C, 65.91; H, 10.09.

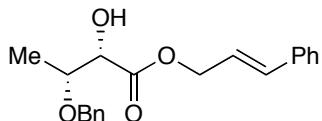
**S-3**

(2*S*,3*R*)-3-(BenzylOxy)-2-(*tert*-Butyldimethylsilyloxy)butanoic acid (S-3). (2*S*,3*R*)-3-(benzylOxy)-2-hydroxybutanoic acid⁶ (0.61 g, 2.9 mmol) was combined with imidazole (0.40 g, 5.8 mmol) and *tert*-butyldimethylsilyl chloride (1.7 g, 11 mmol) in 2 mL of DMF.⁷ The reaction mixture was stirred overnight then diluted with 50 mL of 1:1 Et₂O:EtOAc. This solution was washed with 15 mL of 10% aqueous citric acid, 15 mL of H₂O, and 15 mL of saturated aqueous Na₂SO₄. The mixture was then concentrated *in vacuo*, and dilute with in 20 mL of MeOH. K₂CO₃ (0.69 g, 5.0 mmol) in 6 mL of H₂O was then added dropwise. After stirring for 16 h, the solution was concentrated, diluted with 20 mL of H₂O, and acidified with 10% aqueous citric acid (about 15 mL) to pH 2. The mixture was then extracted with EtOAc (3 × 25 mL), the organic layers were combined, dried with MgSO₄, and concentrated *in vacuo* to give a viscous oil which was purified by column chromatography (80:18:2 hexanes:EtOAc:AcOH) to give **S-3** (0.83 g, 88%) as a colorless oil. **S-3** decomposed rapidly and was carried on to the next synthetic step immediately after isolation: ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.25 (m, 5H), 4.64 (d, *J* = 11.6, 1H), 4.49 (d, *J* = 11.6, 1H), 4.10 (d, *J* = 3.0, 1H), 4.06–3.97 (m, 1H), 1.31 (d, *J* = 6.4, 3H), 0.92 (s, 9H), 0.11 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 175.7, 137.5, 128.7, 128.3, 128.1, 75.1, 73.6, 71.6, 25.8, 18.3, 15.6, -3.4; IR (thin film) 3355 (br), 2971, 1380, 1129 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₇H₂₇O₄Si (M – H)⁻ 323.1679, found 323.1688.

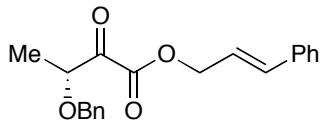
**S-4**

(2*S*,3*R*)-Cinnamyl 3-(benzylOxy)-2-(*tert*-butyldimethylsilyloxy)butanoate (S-4). To a solution of **S-3** (1.89 g, 5.83 mmol) in 58 mL of benzene, were added cinnamyl alcohol (0.601 g, 4.49 mmol), triethylamine (1.68 mL, 12.1 mmol) and DMAP (0.680 g, 5.57 mmol).⁷ After stirring for 30 min, 2,4,6-trichlorobenzoyl chloride (1.43 mL, 9.15 mmol) was added dropwise. After stirring for 16 h, the solution was diluted with 20 mL of 10% aqueous citric acid and extracted with EtOAc (3 × 25 mL). The organic layers were combined, dried with Na₂SO₄, and concentrated *in vacuo* to give an oil which was purified by column chromatography (20:1 hexanes:EtOAc) to give **S-4** (1.08 g, 54%) as a colorless oil: $[\alpha]^{23}_D -12.6$ (*c* 0.55, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.24 (m, 10H), 6.67 (d, *J* = 15.9, 1H), 6.26 (dt, *J* = 15.9, 6.5, 1H), 4.78 (dt, *J* = 6.5, 1.5, 2H), 4.65 (d, *J* = 12.0, 1H), 4.58 (d, *J* = 12.0, 1H), 4.27 (d, *J* = 4.6, 1H), 3.88 (dq, *J* = 6.4, 4.7, 1H), 1.24 (d, *J* = 6.4, 3H), 0.93 (s, 9H), 0.12 (s, 3H), 0.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 138.8, 136.4, 134.8, 128.5, 128.0, 126.8, 123.1, 76.5, 76.3, 71.5, 65.6, 26.0, 18.7, 15.9, -4.7, -5.0; IR (thin film) 2954, 2858, 1752, 1254,

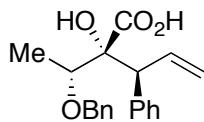
1162, 1123 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{40}\text{NO}_4\text{Si} (\text{M} + \text{NH}_4)^+$ 458.2727, found 458.2735. Anal. Calcd for $\text{C}_{26}\text{H}_{36}\text{O}_4\text{Si}$: C, 70.87; H, 8.23. Found: C, 71.20; H, 8.27.

**S-5**

(2S,3R)-Cinnamyl 3-(benzyloxy)-2-hydroxybutanoate (S-5). **S-4** (0.624 g, 1.42 mmol) was added to 15 mL of THF and cooled to -20°C . After stirring for 30 min, $n\text{-Bu}_4\text{NF}$ (2.12 mL of a 1 M solution in THF, 2.12 mmol) was added dropwise. After 48 h, 5 mL of aqueous saturated NH_4Cl was added and the reaction mixture was warmed to room temperature.⁴ The mixture was then extracted with CH_2Cl_2 (3×20 mL). The organic layers were combined, dried with Na_2SO_4 , and concentrated *in vacuo*. The resultant oil was purified by column chromatography (5:1 hexanes:EtOAc) to give **S-5** (0.303 g, 66%) as a colorless oil: $[\alpha]^{23}_D -62.9$ (c 0.781, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.37–7.24 (m, 10H), 6.65 (d, $J = 15.9$, 1H), 6.22 (dt, $J = 15.9, 6.6$, 1H), 4.83 (ddd, $J = 12.6, 6.7, 1.1$, 1H), 4.75 (ddd, $J = 12.6, 6.6, 1.2$, 1H), 4.62 (d, $J = 11.9$, 1H), 4.41 (d, $J = 11.9$, 1H), 4.12 (dd, $J = 8.4, 2.3$, 1H), 3.98 (qd, $J = 6.4, 2.3$, 1H), 2.95 (d, $J = 8.4$, 1H), 1.35 (d, $J = 6.4$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 138.2, 136.2, 135.4, 128.9, 128.6, 128.5, 127.9, 126.9, 122.6, 75.3, 74.7, 71.1, 66.4, 15.8; IR (thin film) 3489 (br), 3029, 2935, 2875, 1742, 1266, 1198 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{22}\text{NaO}_4 (\text{M} + \text{Na})^+$ 349.1416, found 349.1429.

**15**

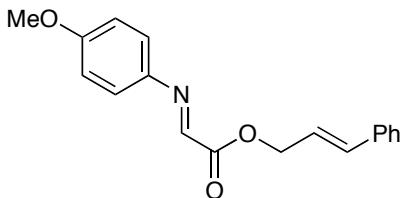
(R)-Cinnamyl 3-(benzyloxy)-2-oxobutanoate (17). To **S-5** (0.280 g, 0.858 mmol) in 10 mL of CH_2Cl_2 was added pyridine (0.345 mL, 4.28 mmol) followed by Dess-Martin periodinane (0.545 g, 1.28 mmol).⁵ After 3 h, the reaction mixture was diluted with 8 mL of saturated aqueous Na_2SO_3 and extracted with CH_2Cl_2 (3×20 mL). The organic layers were combined, dried with Na_2SO_4 , and concentrated *in vacuo*. The resultant oil was purified by column chromatography (5:1 hexanes:EtOAc) to give **15** (0.233 g, 84%) as a yellow oil: $[\alpha]^{23}_D +27.3$ (c 1.15, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.42–7.26 (m, 10H), 6.74 (d, $J = 15.9$, 1H), 6.31 (dt, $J = 15.9, 6.7$, 1H), 4.94 (ddd, $J = 6.7, 2.5, 1.2$, 2H), 4.70 (d, $J = 11.5$, 1H), 4.62–4.54 (m, 2H), 1.49 (d, $J = 6.9$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.5, 162.6, 137.4, 136.2, 136.0, 128.9, 128.7, 128.6, 128.3, 128.2, 127.0, 121.6, 77.7, 72.8, 67.0, 16.8; IR (thin film) 3477 (br), 3031, 2985, 2939, 2873, 1729, 1272 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{28}\text{NO}_5 (\text{M} + \text{NH}_4 + \text{CH}_3\text{OH})^+$ 374.1967, found 374.1957. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{D}_3\text{H}_{21}\text{NaO}_5 (\text{M} + \text{Na} + \text{CD}_3\text{OH})^+$ 382.1710, found 382.1704.

**16**

2-((R)-1-(Benzyloxy)ethyl)-2-Hydroxy-3-phenylpent-4-enoic acid (16). The general transfer procedure was performed on **15** (0.050 g, 0.15 mmol), silacyclopropane **5** (0.050 g, 1.65 mmol), and AgOTs (0.004 g, 0.02 mmol) to give **16** (0.032 g, 63%, 80% diastereoselectivity as determined by ^1H NMR spectroscopy. The

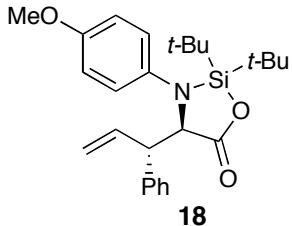
product is predominantly one diastereomer, but 20% of other compounds can be observed by ¹H NMR spectroscopy. These materials are likely to be isomers because the compound exhibits satisfactory elementary analysis.) as a viscous light yellow oil. The relative stereochemistry of the product was assigned based upon analogies to similar systems, as described in the text: ¹H NMR major diastereomer (400 MHz, CDCl₃) δ 7.47–7.24 (m, 10H), 6.36 (td, *J* = 10.0, 17.1, 1H), 5.27 (dd, *J* = 10.1, 1.7, 1H), 5.21 (dd, *J* = 17.1, 1.2, 1H), 4.81 (d, *J* = 10.9, 1H), 4.55 (d, *J* = 10.9, 1H), 4.06 (q, *J* = 6.3, 1H), 3.98 (d, *J* = 9.7, 1H), 1.34 (d, *J* = 6.3, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.9, 138.9, 136.7, 136.1, 129.1, 128.9, 128.80, 128.76, 128.7, 128.4, 127.7, 118.8, 81.2, 76.4, 72.3, 54.0, 14.0; IR (thin film) 3460 (br), 3006, 2917, 1710, 1420, 1360 cm⁻¹; HRMS (ESI) *m/z* calcd for C₂₀H₂₂NaO₄ (M + Na)⁺ 349.1416, found 349.1414. Anal. Calcd for C₂₀H₂₂O₄: C, 73.60; H, 6.79. Found: C, 73.24; H, 6.85.

IV. α-Imino Ester Synthesis and Silylene Transfer



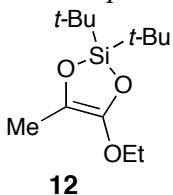
17

Cinnamyl 2-(4-methoxyphenylimino)acetate (17). To a solution of anisidine (0.073 g, 0.60 mmol) in 3 mL of CH₂Cl₂ was added cinnamyl 2-oxoacetate (obtained as a mixture of aldehyde, hydrate, and hydrate oligomers⁸, 0.136 g, 0.654 mmol) and MgSO₄ (about 0.2 g).⁹ After stirring for 2 h, the reaction mixture was filtered and concentrated *in vacuo* to give **17** (0.172 g, 98%) as a yellow-green solid: mp 76–81 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.98 (s, 1H), 7.43–7.25 (m, 7H), 6.97–6.92 (m, 2H), 6.76 (d, *J* = 15.9, 1H), 6.41 (dt, *J* = 15.9, 6.6, 1H), 5.01 (dd, *J* = 6.6, 1.0, 2H), 3.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 160.9, 147.9, 141.5, 136.3, 135.7, 128.9, 128.6, 127.0, 124.0, 122.6, 114.8, 66.6, 55.8; IR (thin film) 3054, 2919, 2840, 1740, 1717, 1590 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₈H₁₇NNaO₃ (M + Na)⁺ 318.1106, found 318.1096.



18

Azasilalactone (18). The general transfer procedure was performed on **17** (0.082 g, 0.28 mmol), silacyclopropane **5** (0.079 g, 0.40 mmol), and AgOTs (0.008 g, 0.03 mmol) to give **18** (0.059 g, 48%) as a tan viscous oil: ¹H NMR (400 MHz, CDCl₃) δ 7.45–7.21 (m, 5H), 6.88 (s, 4H), 6.16 (dt, *J* = 16.9, 9.7, 1H), 5.10 (dd, *J* = 10.0, 1.6, 1H), 5.01 (d, *J* = 16.9, 1H), 4.79 (d, *J* = 1.8, 1H), 3.83–3.80 (m, 4H), 1.21 (s, 9H), 0.90 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 171.8, 154.9, 141.8, 137.3, 128.9, 128.7, 128.6, 127.0, 121.5, 118.8, 115.2, 67.2, 55.8, 52.0, 28.5, 27.3, 24.1, 21.5; IR (thin film) 2937, 2861, 1766, 1509, 1474, 1243 cm⁻¹; HRMS (ESI) *m/z* calcd for C₂₆H₃₅NNaO₃Si (M + Na)⁺ 460.2284, found 460.2275.

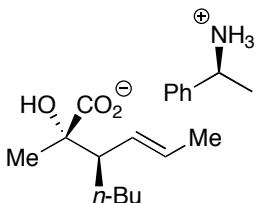


Silyl ketene acetal (12). Ethyl pyruvate (0.022 g, 0.19 mmol) was added to a solution of silirane **5** (0.045 g, 0.23 mmol) in benzene-*d*₆ (0.65 mL). The solution was left under an inert atmosphere for several minutes before the addition of AgOTs (0.005 g, 0.02 mmol). This reaction was performed to determine the viability of **12** as an intermediate; no product was collected: ¹H NMR (500 MHz, benzene-*d*₆) δ 3.89 (q, *J* = 5.7, 2H), 1.98 (s, 3H), 1.16-1.14 (m, 21H); ²⁹Si NMR (100 MHz, benzene-*d*₆) δ 14.2.

V. References

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VI. X-Ray Crystallographic Data



SI-6

Phenylethylamine Salt (SI-6): To a solution of **14** (0.050 mg, 0.25 mmol) in benzene (2 mL) was added S-phenylethylamine (0.030 mg, 0.25 mmol). The mixture was left at 4 °C for 21 d, at which point crystals had formed and were submitted for X-ray crystallographic analysis.

X-ray Data Collection, Structure Solution and Refinement for **SI-6**.

A colorless crystal of approximate dimensions 0.14 x 0.19 x 0.35 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹ program package was used to determine the unit-cell parameters and for data collection (40 sec/frame scan time for a hemisphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space groups *P*2₁ and *P*2₁/m. It was later determined that the noncentrosymmetric space group *P*2₁ was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were either located from a difference-Fourier map and refined (x, y, z and U_{iso}) or were included using a riding model. There were two molecules of the formula unit present ($Z = 4$).

Least-squares analysis yielded $wR2 = 0.1698$ and $GOF = 1.050$ for 434 variables refined against 5903 data (0.85 Å), $R1 = 0.0597$ for those 4209 data with $I > 2.0\sigma(I)$. The absolute structure could not be assigned by inversion of the model or by refinement of the Flack parameter.⁶ Although the quality of the structure was not high, the data establishes the relative stereochemistry between the acid and the amine.

References.

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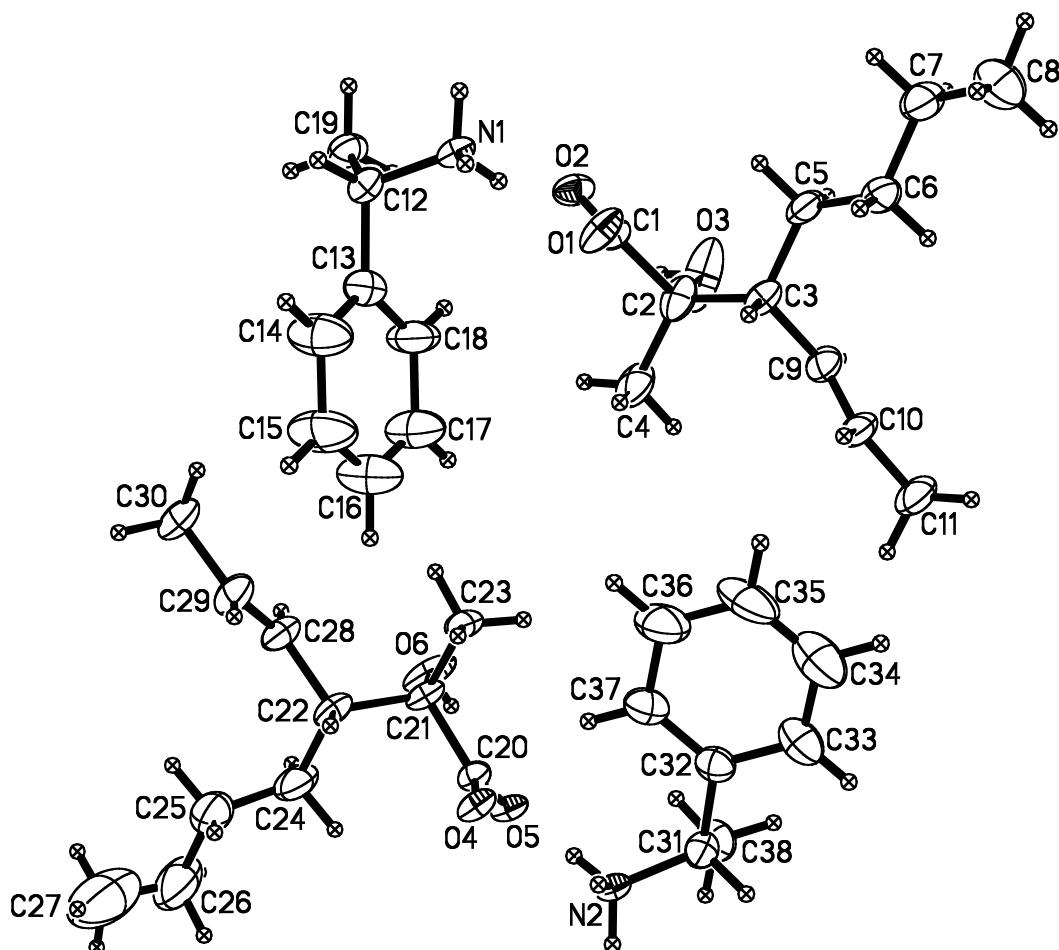
Definitions:

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

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

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

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

Table 1. Crystal data and structure refinement for **SI-6**.

Identification code	kaw109 (Brett Howard)		
Empirical formula	$C_{19} H_{31} N O_3$		
Formula weight	321.45		
Temperature	153(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	$P2_1$		
Unit cell dimensions	$a = 17.558(3) \text{ Å}$	$\alpha = 90^\circ.$	
	$b = 5.4049(9) \text{ Å}$	$\beta = 92.475(3)^\circ.$	
	$c = 20.711(3) \text{ Å}$	$\gamma = 90^\circ.$	

Volume	1963.6(6) Å ³
Z	4
Density (calculated)	1.087 Mg/m ³
Absorption coefficient	0.072 mm ⁻¹
F(000)	704
Crystal color	colorless
Crystal size	0.35 x 0.19 x 0.14 mm ³
Theta range for data collection	1.49 to 24.79°
Index ranges	-20 ≤ <i>h</i> ≤ 20, -6 ≤ <i>k</i> ≤ 6, -24 ≤ <i>l</i> ≤ 23
Reflections collected	12061
Independent reflections	5903 [R(int) = 0.0366]
Completeness to theta = 24.79°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9899 and 0.9751
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5903 / 1 / 434
Goodness-of-fit on F ²	1.050
Final R indices [I>2sigma(I) = 4209 data]	R1 = 0.0597, wR2 = 0.1453
R indices (all data; 0.85Å)	R1 = 0.0945, wR2 = 0.1698
Absolute structure parameter	-0.8(15)
Extinction coefficient	0.005(2)
Largest diff. peak and hole	0.392 and -0.255 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **SI-6**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	1343(1)	9490(5)	526(1)	38(1)
O(2)	887(1)	5696(5)	425(1)	35(1)
O(3)	2276(2)	3699(6)	360(2)	74(1)
N(1)	-3(1)	11643(5)	688(1)	26(1)
C(1)	1430(2)	7213(7)	505(2)	26(1)
C(2)	2236(2)	6164(7)	607(2)	39(1)
C(3)	2806(2)	7673(7)	219(2)	32(1)
C(4)	2426(2)	6257(13)	1331(2)	71(2)
C(5)	2589(2)	7671(8)	-505(2)	35(1)
C(6)	3015(2)	9559(8)	-892(2)	36(1)
C(7)	2780(2)	9619(9)	-1605(2)	45(1)
C(8)	3174(3)	11607(10)	-1983(2)	62(1)
C(9)	3608(2)	6731(8)	345(2)	35(1)
C(10)	4182(2)	8080(8)	581(2)	39(1)
C(11)	4976(2)	7147(10)	722(2)	52(1)
C(12)	-440(2)	11092(7)	1270(2)	29(1)
C(13)	104(2)	11229(7)	1865(2)	35(1)
C(14)	105(3)	13202(9)	2278(2)	62(1)
C(15)	626(3)	13328(11)	2815(2)	73(2)
C(16)	1137(3)	11548(10)	2921(2)	64(1)
C(17)	1175(3)	9617(11)	2514(2)	67(1)
C(18)	657(2)	9416(10)	1980(2)	57(1)
C(19)	-826(2)	8580(7)	1179(2)	36(1)
O(4)	3692(1)	8360(5)	4564(1)	31(1)
O(5)	4018(1)	4387(4)	4630(1)	29(1)
O(6)	2657(2)	2772(5)	4218(2)	49(1)
N(2)	5021(1)	10580(5)	4332(1)	25(1)
C(20)	3547(2)	6104(7)	4506(2)	27(1)
C(21)	2736(2)	5369(6)	4261(2)	30(1)
C(22)	2166(2)	6429(7)	4735(2)	34(1)
C(23)	2594(2)	6460(8)	3588(2)	36(1)
C(24)	2323(2)	5433(11)	5426(2)	59(1)
C(25)	1901(2)	6730(17)	5936(2)	93(2)

C(26)	2064(3)	5730(30)	6619(3)	176(6)
C(27)	1623(4)	5980(30)	7053(3)	207(8)
C(28)	1352(2)	5913(8)	4525(2)	38(1)
C(29)	821(2)	7588(9)	4418(2)	50(1)
C(30)	-2(2)	7078(13)	4227(2)	73(2)
C(31)	5431(2)	9915(7)	3742(2)	31(1)
C(32)	5012(2)	10820(7)	3136(2)	33(1)
C(33)	5429(3)	11399(8)	2608(2)	48(1)
C(34)	5075(3)	12157(10)	2035(2)	67(1)
C(35)	4289(3)	12369(11)	1995(2)	70(2)
C(36)	3866(3)	11814(11)	2511(2)	64(1)
C(37)	4229(2)	11021(9)	3089(2)	46(1)
C(38)	5579(2)	7152(8)	3740(2)	42(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for **SI-6**.

O(1)-C(1)	1.241(4)
O(2)-C(1)	1.262(4)
O(3)-C(2)	1.430(5)
N(1)-C(12)	1.487(4)
C(1)-C(2)	1.532(5)
C(2)-C(4)	1.523(6)
C(2)-C(3)	1.544(5)
C(3)-C(9)	1.508(4)
C(3)-C(5)	1.531(5)
C(5)-C(6)	1.516(5)
C(6)-C(7)	1.515(5)
C(7)-C(8)	1.515(6)
C(9)-C(10)	1.321(5)
C(10)-C(11)	1.500(5)
C(12)-C(19)	1.526(5)
C(12)-C(13)	1.527(5)
C(13)-C(14)	1.368(6)
C(13)-C(18)	1.392(6)
C(14)-C(15)	1.411(6)
C(15)-C(16)	1.326(7)
C(16)-C(17)	1.345(7)
C(17)-C(18)	1.405(6)
O(4)-C(20)	1.251(4)
O(5)-C(20)	1.262(4)
O(6)-C(21)	1.413(5)
N(2)-C(31)	1.488(4)
C(20)-C(21)	1.543(4)
C(21)-C(23)	1.523(5)
C(21)-C(22)	1.544(5)
C(22)-C(28)	1.502(5)
C(22)-C(24)	1.541(5)
C(24)-C(25)	1.492(7)
C(25)-C(26)	1.529(8)
C(26)-C(27)	1.219(8)
C(28)-C(29)	1.311(6)
C(29)-C(30)	1.508(6)

C(31)-C(32)	1.509(5)
C(31)-C(38)	1.516(5)
C(32)-C(37)	1.377(5)
C(32)-C(33)	1.379(5)
C(33)-C(34)	1.379(6)
C(34)-C(35)	1.384(7)
C(35)-C(36)	1.361(7)
C(36)-C(37)	1.399(5)

O(1)-C(1)-O(2)	123.8(3)
O(1)-C(1)-C(2)	118.4(3)
O(2)-C(1)-C(2)	117.8(3)
O(3)-C(2)-C(4)	111.8(4)
O(3)-C(2)-C(1)	110.7(3)
C(4)-C(2)-C(1)	106.6(3)
O(3)-C(2)-C(3)	105.3(3)
C(4)-C(2)-C(3)	112.1(3)
C(1)-C(2)-C(3)	110.4(3)
C(9)-C(3)-C(5)	111.1(3)
C(9)-C(3)-C(2)	110.6(3)
C(5)-C(3)-C(2)	111.7(3)
C(6)-C(5)-C(3)	114.2(3)
C(7)-C(6)-C(5)	114.2(3)
C(8)-C(7)-C(6)	114.1(3)
C(10)-C(9)-C(3)	124.7(4)
C(9)-C(10)-C(11)	125.1(4)
N(1)-C(12)-C(19)	108.7(3)
N(1)-C(12)-C(13)	108.5(3)
C(19)-C(12)-C(13)	113.7(3)
C(14)-C(13)-C(18)	117.3(4)
C(14)-C(13)-C(12)	121.7(4)
C(18)-C(13)-C(12)	120.8(4)
C(13)-C(14)-C(15)	120.9(4)
C(16)-C(15)-C(14)	120.4(5)
C(15)-C(16)-C(17)	120.7(4)
C(16)-C(17)-C(18)	120.3(5)
C(13)-C(18)-C(17)	120.2(5)
O(4)-C(20)-O(5)	124.6(3)

O(4)-C(20)-C(21)	117.6(3)
O(5)-C(20)-C(21)	117.7(3)
O(6)-C(21)-C(23)	108.4(3)
O(6)-C(21)-C(20)	111.3(3)
C(23)-C(21)-C(20)	108.3(3)
O(6)-C(21)-C(22)	110.1(3)
C(23)-C(21)-C(22)	110.7(3)
C(20)-C(21)-C(22)	108.0(3)
C(28)-C(22)-C(24)	109.5(3)
C(28)-C(22)-C(21)	112.4(3)
C(24)-C(22)-C(21)	111.5(3)
C(25)-C(24)-C(22)	114.8(4)
C(24)-C(25)-C(26)	114.2(6)
C(27)-C(26)-C(25)	122.9(7)
C(29)-C(28)-C(22)	125.5(4)
C(28)-C(29)-C(30)	125.8(5)
N(2)-C(31)-C(32)	111.6(3)
N(2)-C(31)-C(38)	109.2(3)
C(32)-C(31)-C(38)	113.2(3)
C(37)-C(32)-C(33)	119.2(3)
C(37)-C(32)-C(31)	122.3(3)
C(33)-C(32)-C(31)	118.4(3)
C(34)-C(33)-C(32)	121.0(4)
C(33)-C(34)-C(35)	119.1(4)
C(36)-C(35)-C(34)	120.8(4)
C(35)-C(36)-C(37)	119.7(4)
C(32)-C(37)-C(36)	120.1(4)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **SI-6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	20(1)	23(2)	71(2)	-2(1)	-3(1)	-1(1)
O(2)	32(1)	35(2)	37(1)	2(1)	-9(1)	-9(1)
O(3)	51(2)	26(2)	148(3)	14(2)	46(2)	6(2)
N(1)	20(1)	24(2)	33(2)	-1(1)	-7(1)	1(1)
C(1)	21(2)	27(2)	31(2)	1(2)	-2(1)	-3(2)
C(2)	28(2)	29(2)	60(2)	10(2)	8(2)	12(2)
C(3)	21(2)	29(2)	44(2)	0(2)	-3(2)	3(2)
C(4)	28(2)	129(5)	58(3)	46(3)	2(2)	20(3)
C(5)	19(2)	44(2)	43(2)	-4(2)	-5(2)	-1(2)
C(6)	30(2)	40(2)	38(2)	-1(2)	-4(2)	-6(2)
C(7)	33(2)	55(3)	48(2)	-2(2)	-5(2)	5(2)
C(8)	71(3)	66(3)	48(2)	15(2)	3(2)	-1(3)
C(9)	25(2)	42(2)	38(2)	6(2)	0(2)	9(2)
C(10)	21(2)	49(3)	45(2)	6(2)	-7(2)	1(2)
C(11)	24(2)	76(3)	56(3)	20(2)	-6(2)	2(2)
C(12)	23(2)	30(2)	35(2)	0(2)	0(1)	4(2)
C(13)	39(2)	35(2)	32(2)	3(2)	-4(2)	-6(2)
C(14)	81(3)	47(3)	57(3)	-6(2)	-25(2)	16(3)
C(15)	86(4)	62(3)	68(3)	-26(3)	-33(3)	5(3)
C(16)	79(3)	54(3)	57(3)	-1(3)	-29(2)	2(3)
C(17)	63(3)	77(4)	57(3)	2(3)	-25(2)	5(3)
C(18)	52(3)	72(3)	44(2)	-10(2)	-22(2)	14(3)
C(19)	28(2)	44(2)	36(2)	5(2)	-4(2)	-9(2)
O(4)	19(1)	30(2)	45(1)	0(1)	-7(1)	-1(1)
O(5)	21(1)	29(1)	36(1)	-2(1)	-10(1)	1(1)
O(6)	30(1)	26(2)	89(2)	0(1)	-26(1)	-2(1)
N(2)	20(1)	26(2)	28(2)	1(1)	-7(1)	1(1)
C(20)	21(2)	27(2)	31(2)	-1(2)	-3(1)	2(2)
C(21)	19(2)	26(2)	43(2)	2(2)	-10(2)	-1(1)
C(22)	20(2)	35(2)	46(2)	6(2)	-5(2)	-7(2)
C(23)	25(2)	46(2)	35(2)	-4(2)	-10(2)	2(2)
C(24)	30(2)	98(4)	46(2)	24(3)	-10(2)	-6(2)
C(25)	39(3)	197(8)	43(3)	13(4)	2(2)	-12(4)

C(26)	43(3)	432(19)	53(3)	44(7)	0(3)	14(6)
C(27)	78(5)	460(20)	83(5)	96(9)	-12(4)	-59(9)
C(28)	22(2)	44(2)	47(2)	6(2)	-6(2)	-3(2)
C(29)	28(2)	65(3)	56(3)	3(2)	-2(2)	13(2)
C(30)	25(2)	129(5)	65(3)	0(3)	-7(2)	22(3)
C(31)	27(2)	32(2)	34(2)	3(2)	3(2)	1(2)
C(32)	38(2)	29(2)	31(2)	-4(2)	-2(2)	3(2)
C(33)	64(3)	47(3)	33(2)	5(2)	7(2)	6(2)
C(34)	93(4)	66(3)	42(3)	7(2)	10(2)	23(3)
C(35)	99(4)	81(4)	29(2)	2(2)	-12(2)	39(3)
C(36)	63(3)	86(4)	41(3)	-4(2)	-16(2)	26(3)
C(37)	47(2)	59(3)	31(2)	3(2)	-6(2)	4(2)
C(38)	47(2)	40(2)	40(2)	-1(2)	3(2)	11(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **SI-6**.

	x	y	z	U(eq)
H(4)	1970(30)	2800(110)	560(20)	78(17)
H(1)	-307	11401	327	39
H(2)	408	10622	679	39
H(3)	157	13244	702	39
H(3A)	2789	9424	374	38
H(4A)	2052	5279	1559	107
H(4B)	2411	7978	1480	107
H(4C)	2937	5576	1421	107
H(5A)	2687	6004	-681	42
H(5B)	2035	7997	-563	42
H(6A)	2932	11221	-706	44
H(6B)	3568	9197	-847	44
H(7A)	2892	7988	-1796	54
H(7B)	2222	9882	-1649	54
H(8A)	3004	11505	-2440	92
H(8B)	3727	11365	-1943	92
H(8C)	3045	13238	-1813	92
H(9A)	3706	5046	248	42
H(10A)	4084	9774	668	46
H(11A)	5338	8163	491	78
H(11B)	5013	5424	579	78
H(11C)	5097	7243	1188	78
H(12A)	-843	12383	1311	35
H(14A)	-250	14507	2203	75
H(15A)	612	14695	3102	87
H(16A)	1478	11637	3288	77
H(17A)	1555	8385	2587	80
H(18A)	683	8037	1698	68
H(19A)	-1168	8622	793	54
H(19B)	-1121	8203	1558	54
H(19C)	-438	7300	1129	54
H(8)	3020(30)	2100(130)	4360(30)	100(20)

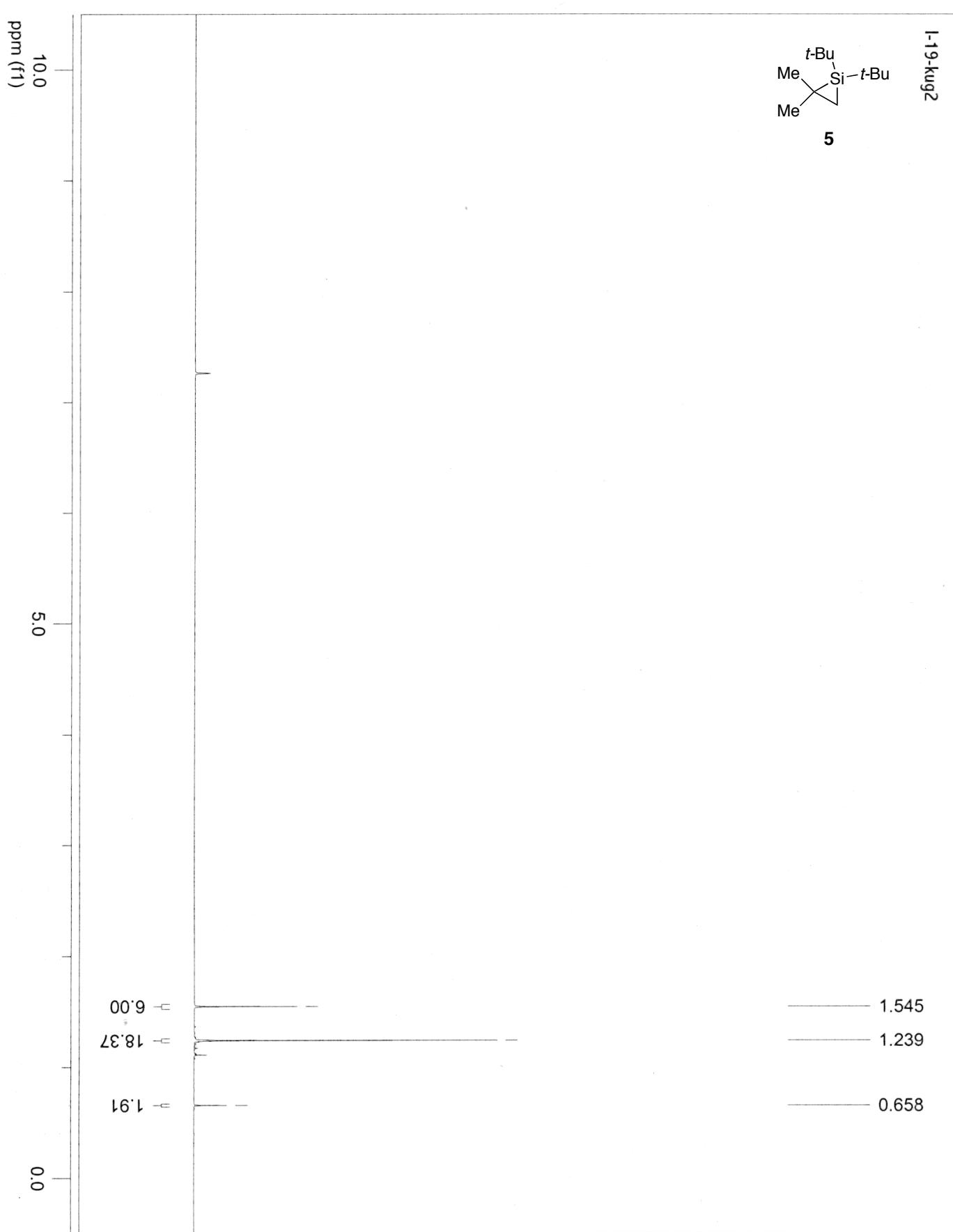
H(5)	5342	10419	4686	37
H(6)	4614	9556	4369	37
H(7)	4856	12173	4300	37
H(22A)	2235	8265	4749	40
H(23A)	2989	5883	3304	54
H(23B)	2608	8270	3614	54
H(23C)	2093	5928	3413	54
H(24A)	2187	3656	5433	70
H(24B)	2876	5565	5534	70
H(25A)	1347	6592	5831	112
H(25B)	2035	8508	5930	112
H(26A)	2152	3929	6575	211
H(26B)	2555	6461	6775	211
H(27A)	1857	5332	7457	311
H(27B)	1151	5081	6945	311
H(27C)	1509	7745	7107	311
H(28A)	1210	4230	4464	45
H(29A)	969	9271	4465	59
H(30A)	-129	7852	3809	110
H(30B)	-329	7764	4555	110
H(30C)	-83	5288	4195	110
H(31A)	5937	10765	3771	37
H(33A)	5969	11274	2640	58
H(34A)	5368	12528	1671	80
H(35A)	4042	12909	1603	84
H(36A)	3327	11964	2479	77
H(37A)	3936	10621	3449	55
H(38A)	5894	6731	3377	64
H(38B)	5093	6265	3696	64
H(38C)	5846	6673	4146	64

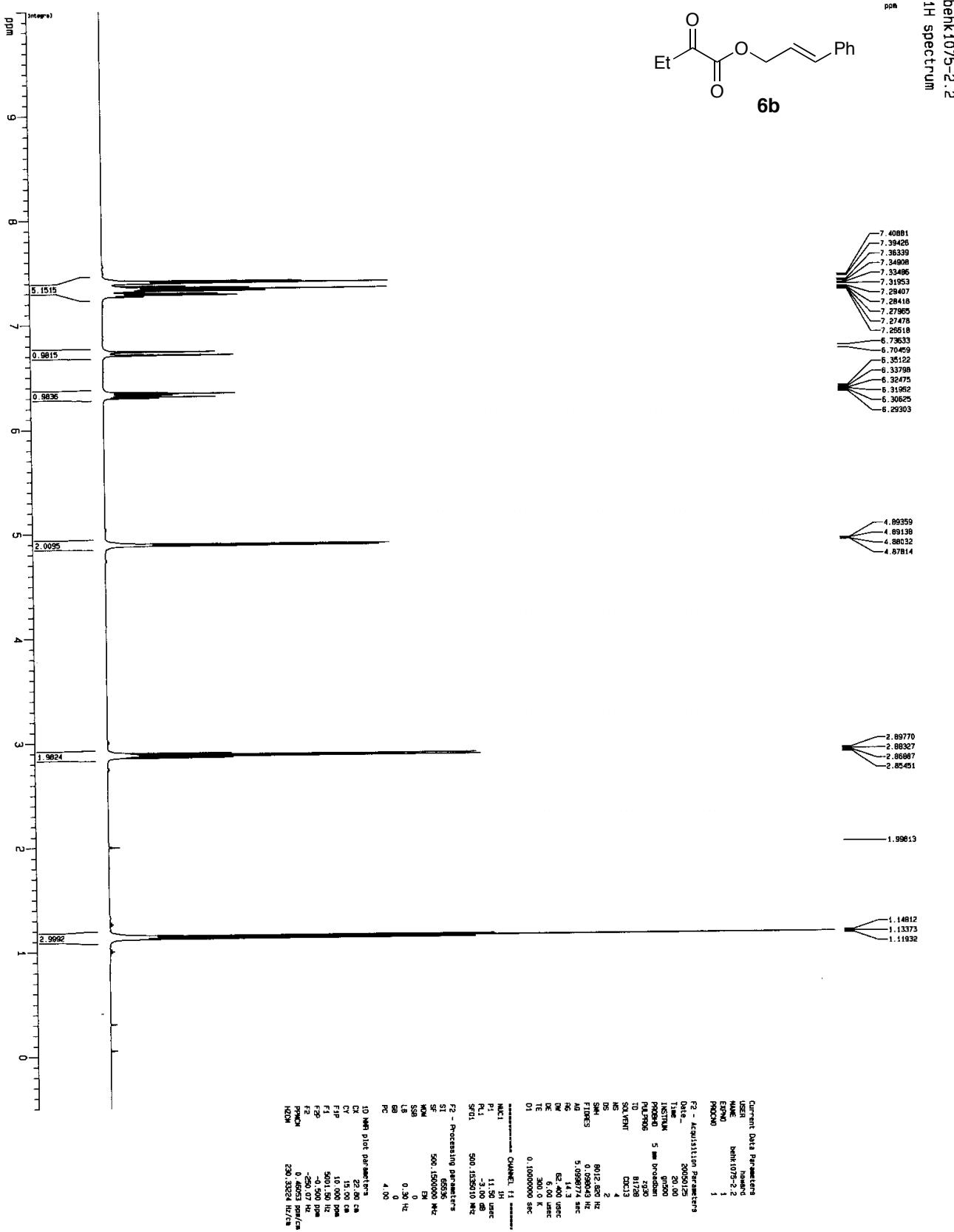
Table 6. Torsion angles [°] for **SI-6**.

O(1)-C(1)-C(2)-O(3)	-160.7(3)
O(2)-C(1)-C(2)-O(3)	21.7(4)
O(1)-C(1)-C(2)-C(4)	77.5(4)
O(2)-C(1)-C(2)-C(4)	-100.1(4)
O(1)-C(1)-C(2)-C(3)	-44.5(5)
O(2)-C(1)-C(2)-C(3)	137.9(3)
O(3)-C(2)-C(3)-C(9)	-63.4(4)
C(4)-C(2)-C(3)-C(9)	58.4(4)
C(1)-C(2)-C(3)-C(9)	177.1(3)
O(3)-C(2)-C(3)-C(5)	61.0(4)
C(4)-C(2)-C(3)-C(5)	-177.2(3)
C(1)-C(2)-C(3)-C(5)	-58.5(4)
C(9)-C(3)-C(5)-C(6)	-68.8(4)
C(2)-C(3)-C(5)-C(6)	167.1(3)
C(3)-C(5)-C(6)-C(7)	-178.0(3)
C(5)-C(6)-C(7)-C(8)	176.6(4)
C(5)-C(3)-C(9)-C(10)	113.9(4)
C(2)-C(3)-C(9)-C(10)	-121.4(4)
C(3)-C(9)-C(10)-C(11)	178.5(3)
N(1)-C(12)-C(13)-C(14)	104.2(4)
C(19)-C(12)-C(13)-C(14)	-134.7(4)
N(1)-C(12)-C(13)-C(18)	-71.3(4)
C(19)-C(12)-C(13)-C(18)	49.8(5)
C(18)-C(13)-C(14)-C(15)	-2.6(7)
C(12)-C(13)-C(14)-C(15)	-178.2(4)
C(13)-C(14)-C(15)-C(16)	1.3(8)
C(14)-C(15)-C(16)-C(17)	1.2(9)
C(15)-C(16)-C(17)-C(18)	-2.2(9)
C(14)-C(13)-C(18)-C(17)	1.6(7)
C(12)-C(13)-C(18)-C(17)	177.3(4)
C(16)-C(17)-C(18)-C(13)	0.7(8)
O(4)-C(20)-C(21)-O(6)	179.8(3)
O(5)-C(20)-C(21)-O(6)	0.4(4)
O(4)-C(20)-C(21)-C(23)	60.7(4)
O(5)-C(20)-C(21)-C(23)	-118.7(3)
O(4)-C(20)-C(21)-C(22)	-59.3(4)

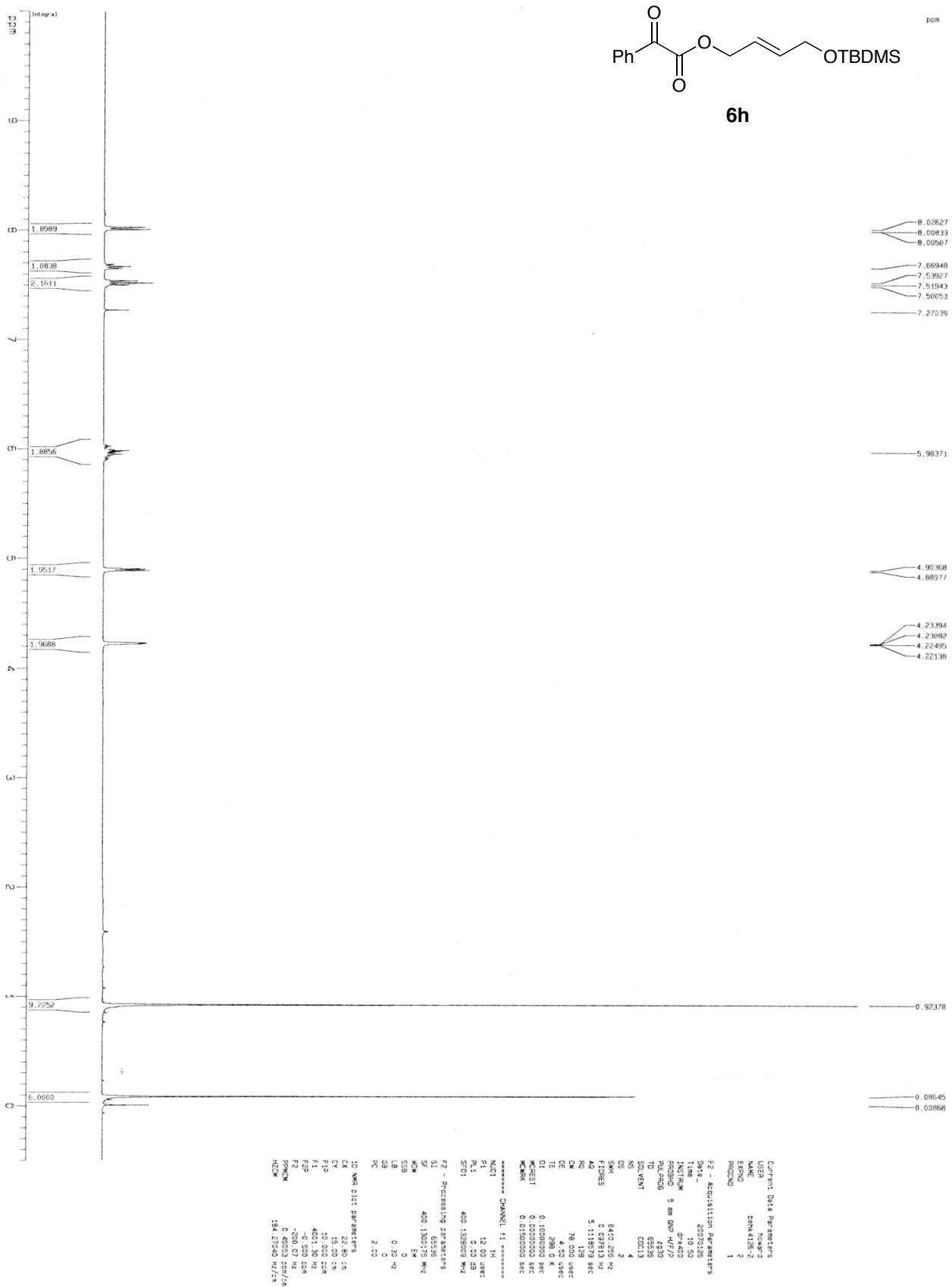
O(5)-C(20)-C(21)-C(22)	121.3(3)
O(6)-C(21)-C(22)-C(28)	-60.8(4)
C(23)-C(21)-C(22)-C(28)	59.0(4)
C(20)-C(21)-C(22)-C(28)	177.5(3)
O(6)-C(21)-C(22)-C(24)	62.6(4)
C(23)-C(21)-C(22)-C(24)	-177.5(3)
C(20)-C(21)-C(22)-C(24)	-59.1(4)
C(28)-C(22)-C(24)-C(25)	-66.4(5)
C(21)-C(22)-C(24)-C(25)	168.5(4)
C(22)-C(24)-C(25)-C(26)	-179.8(6)
C(24)-C(25)-C(26)-C(27)	-156.7(12)
C(24)-C(22)-C(28)-C(29)	113.1(5)
C(21)-C(22)-C(28)-C(29)	-122.4(4)
C(22)-C(28)-C(29)-C(30)	-177.9(4)
N(2)-C(31)-C(32)-C(37)	-31.0(5)
C(38)-C(31)-C(32)-C(37)	92.7(4)
N(2)-C(31)-C(32)-C(33)	150.8(3)
C(38)-C(31)-C(32)-C(33)	-85.5(4)
C(37)-C(32)-C(33)-C(34)	-0.4(6)
C(31)-C(32)-C(33)-C(34)	177.8(4)
C(32)-C(33)-C(34)-C(35)	0.9(7)
C(33)-C(34)-C(35)-C(36)	-0.7(8)
C(34)-C(35)-C(36)-C(37)	0.1(8)
C(33)-C(32)-C(37)-C(36)	-0.2(7)
C(31)-C(32)-C(37)-C(36)	-178.5(4)
C(35)-C(36)-C(37)-C(32)	0.4(8)

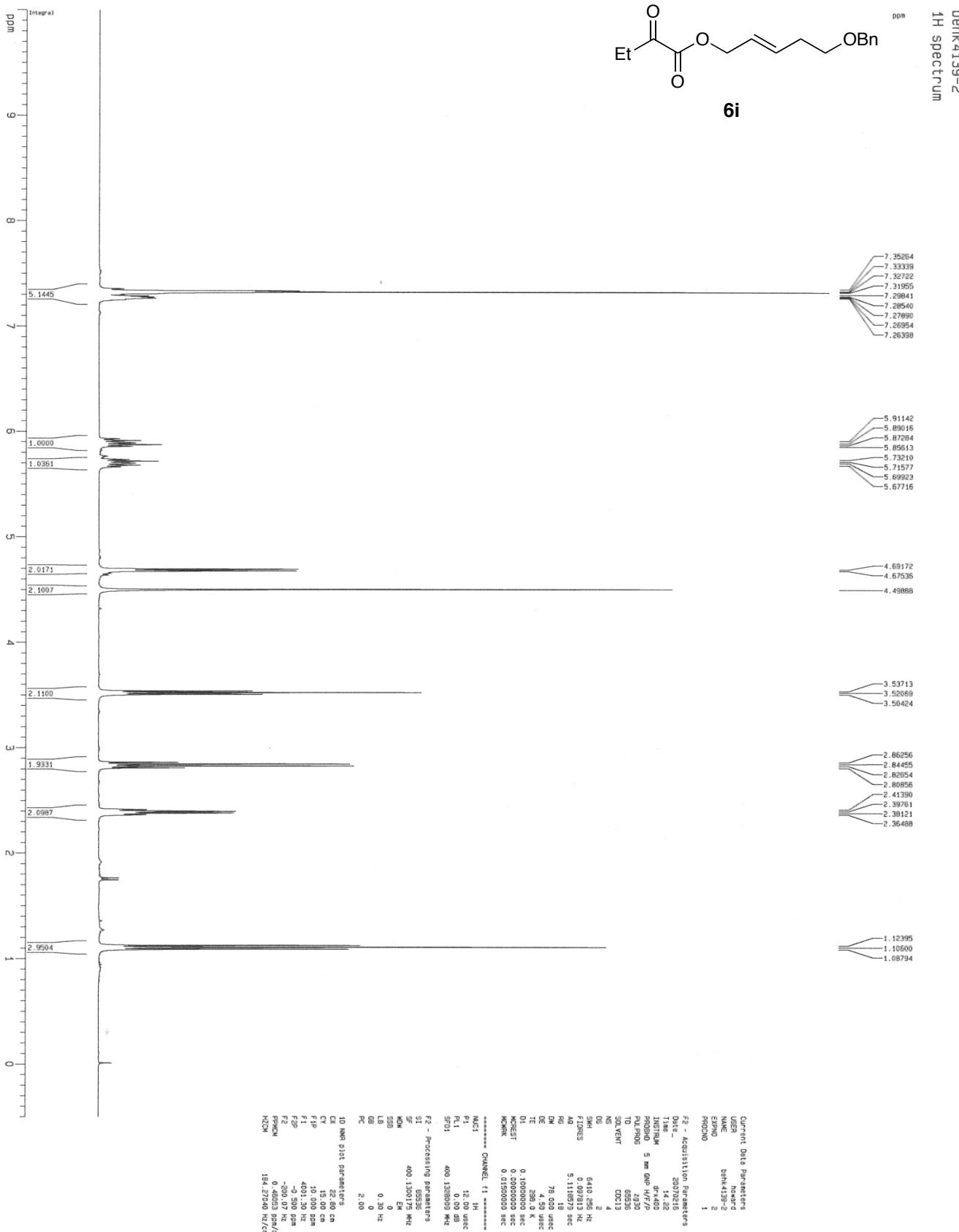
VII. Selected Spectra

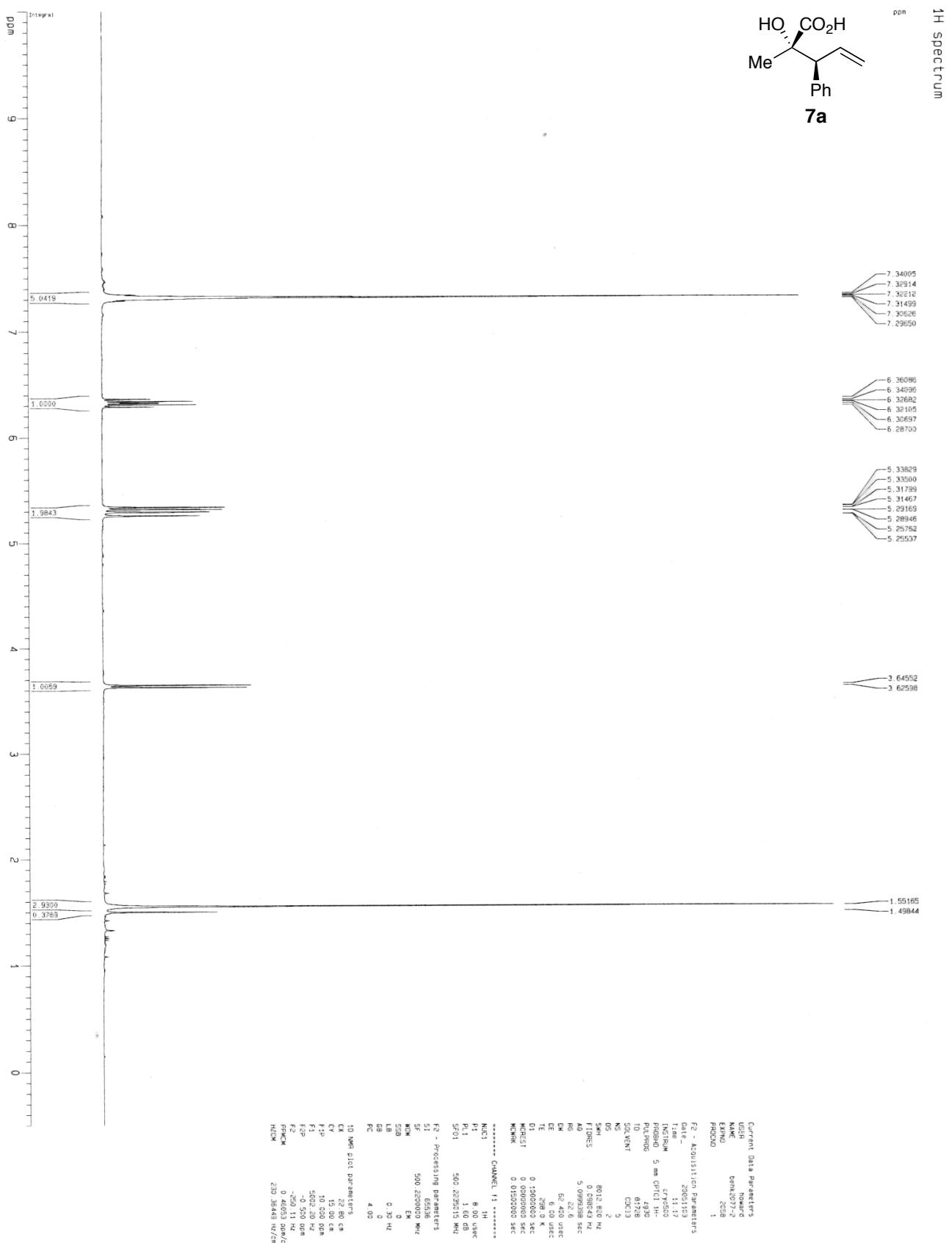


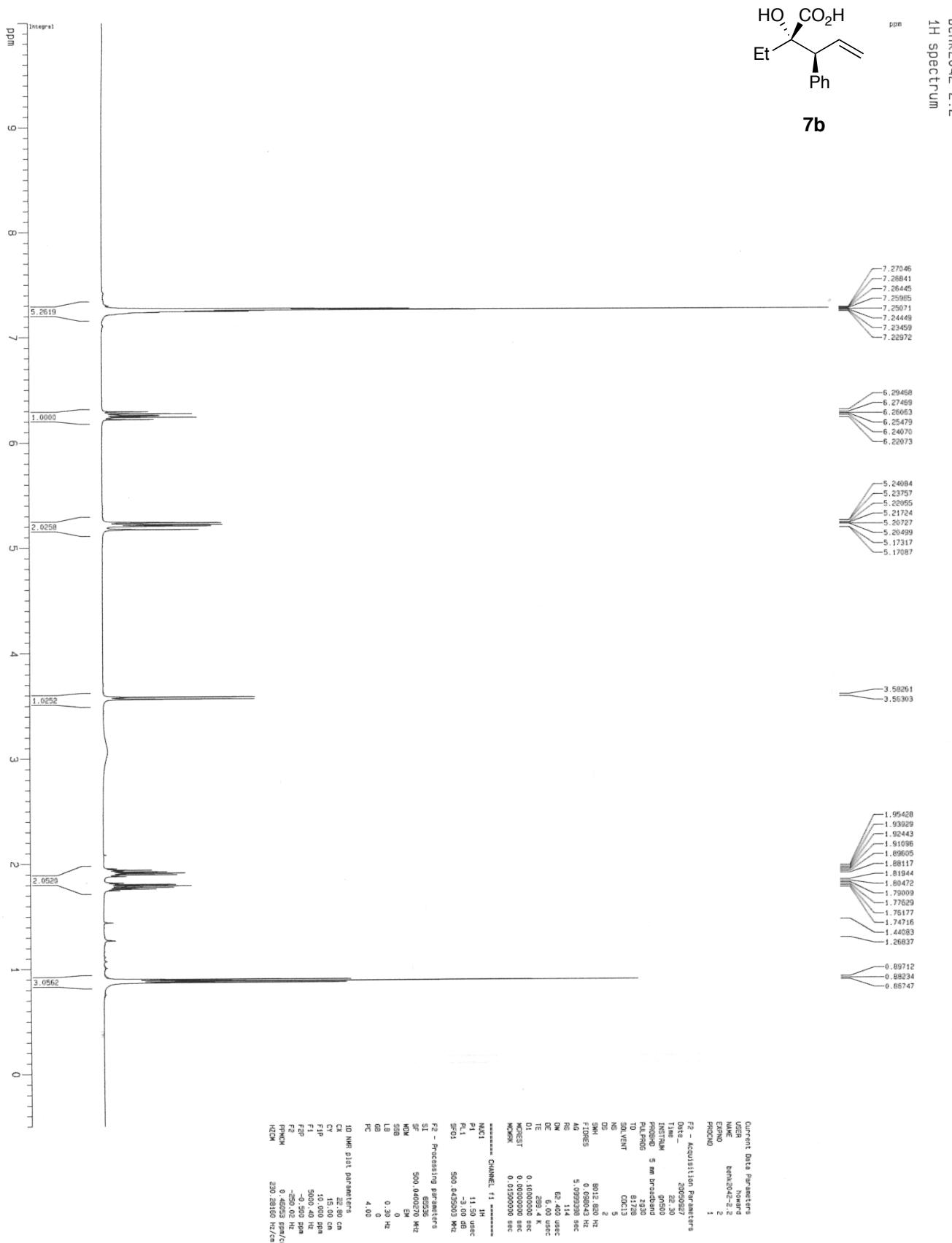


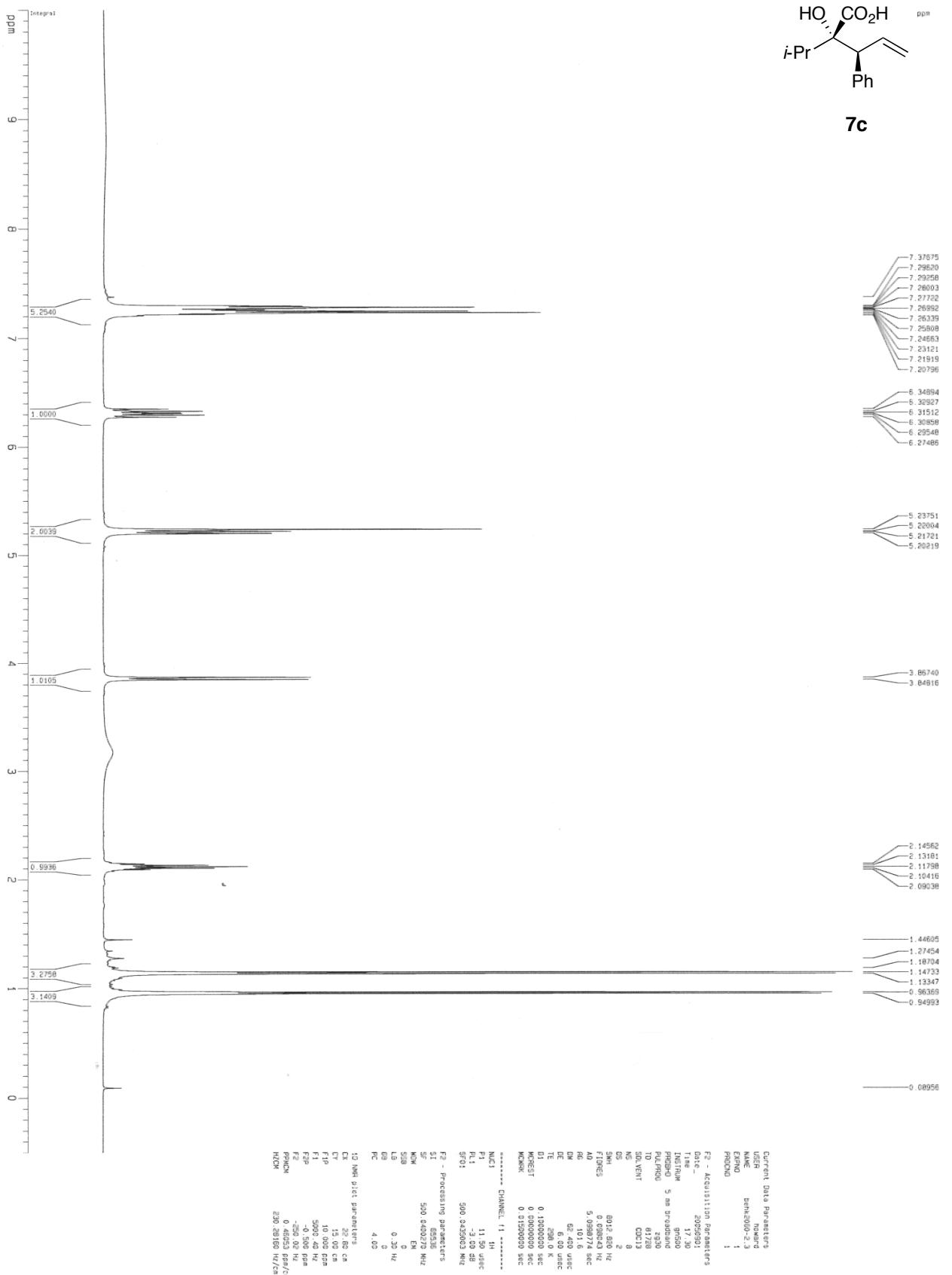
Dehk126-2
1H spectrum

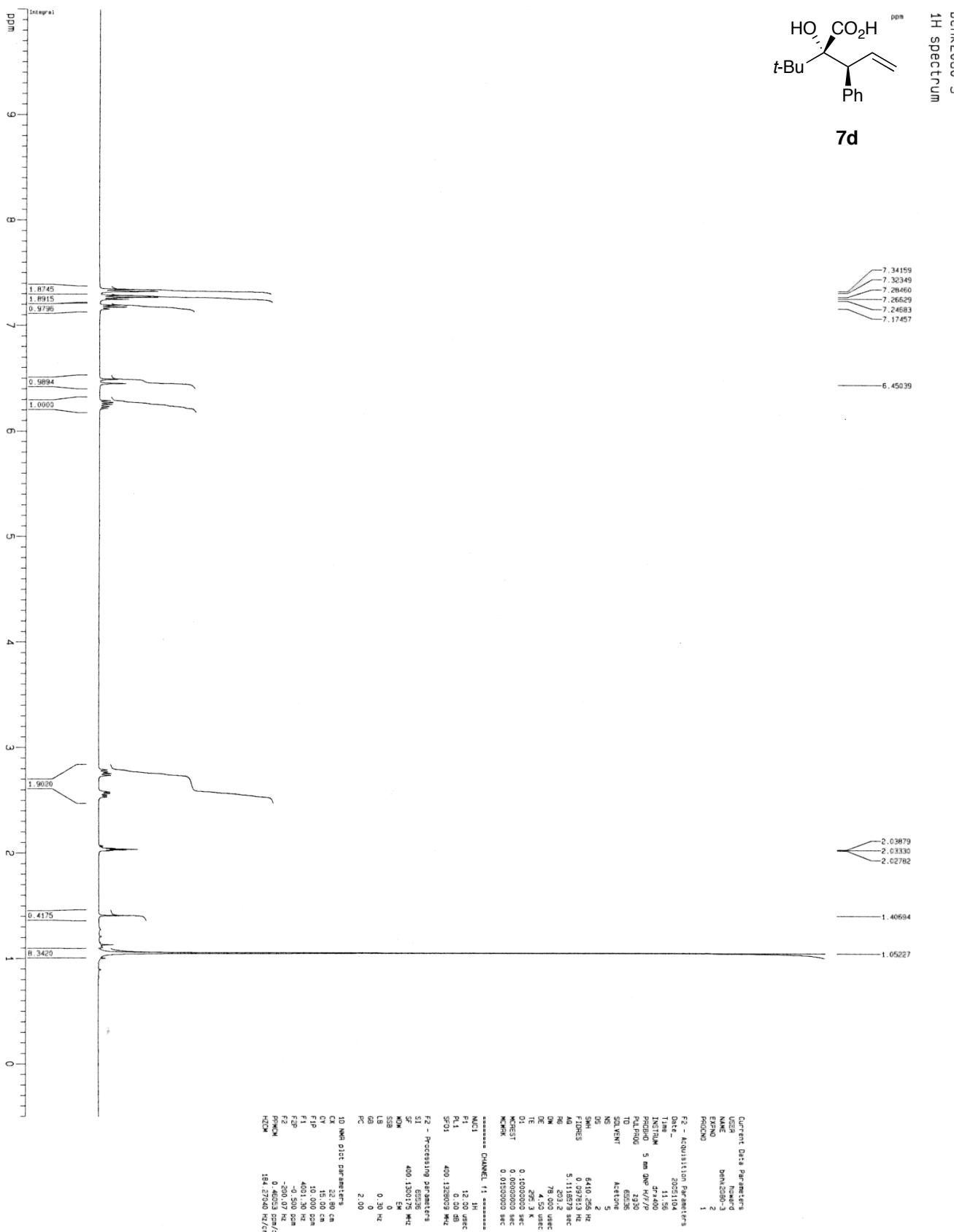


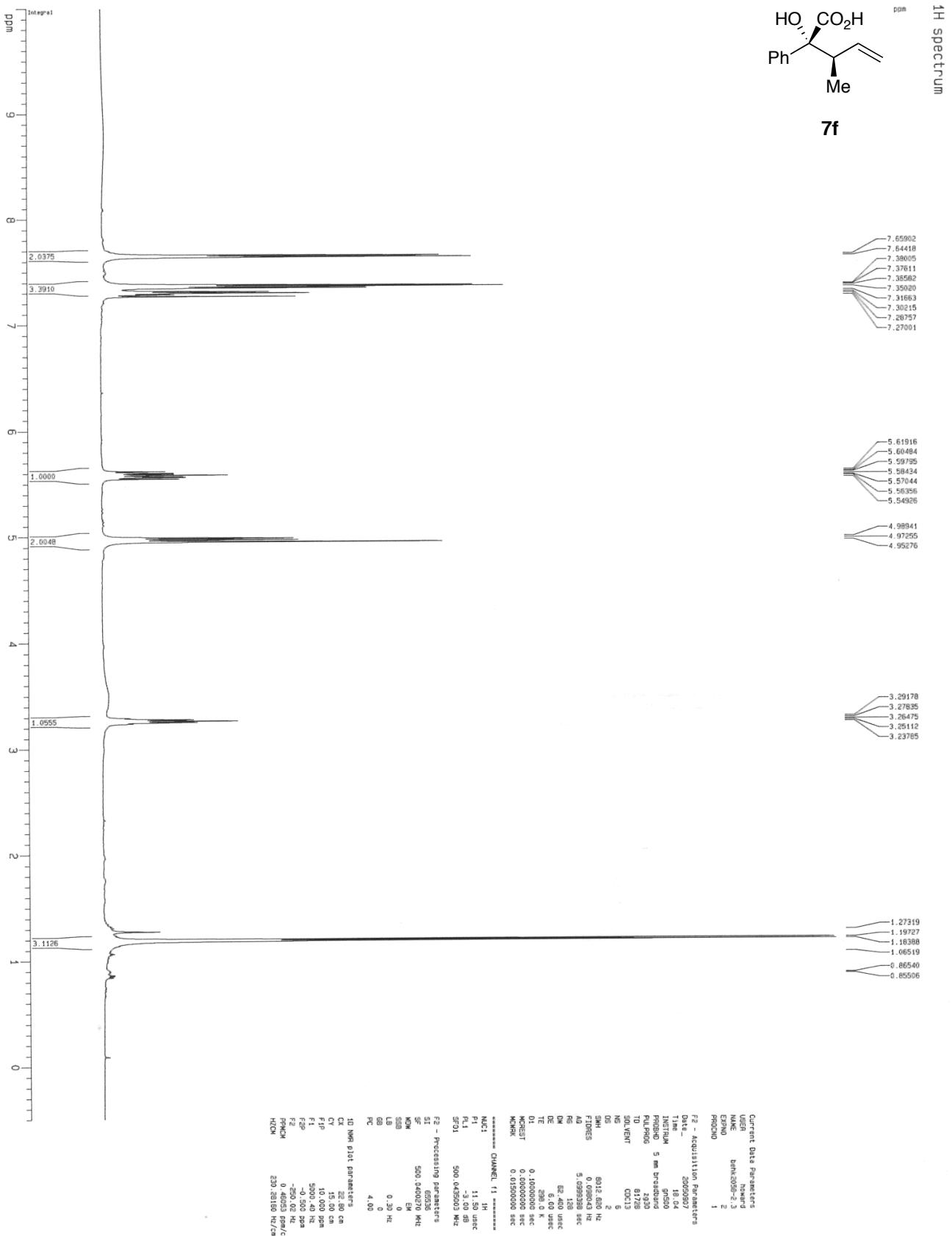


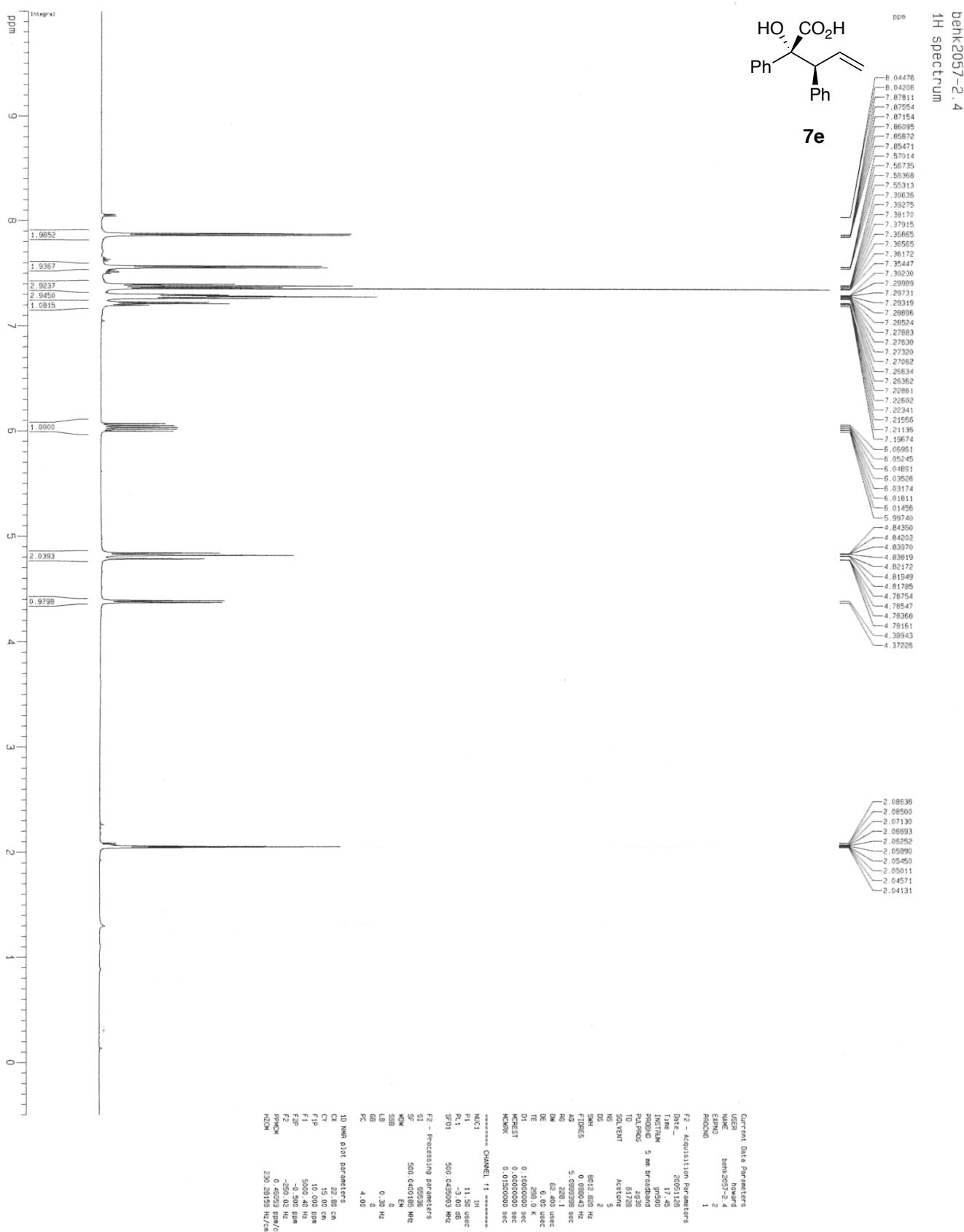


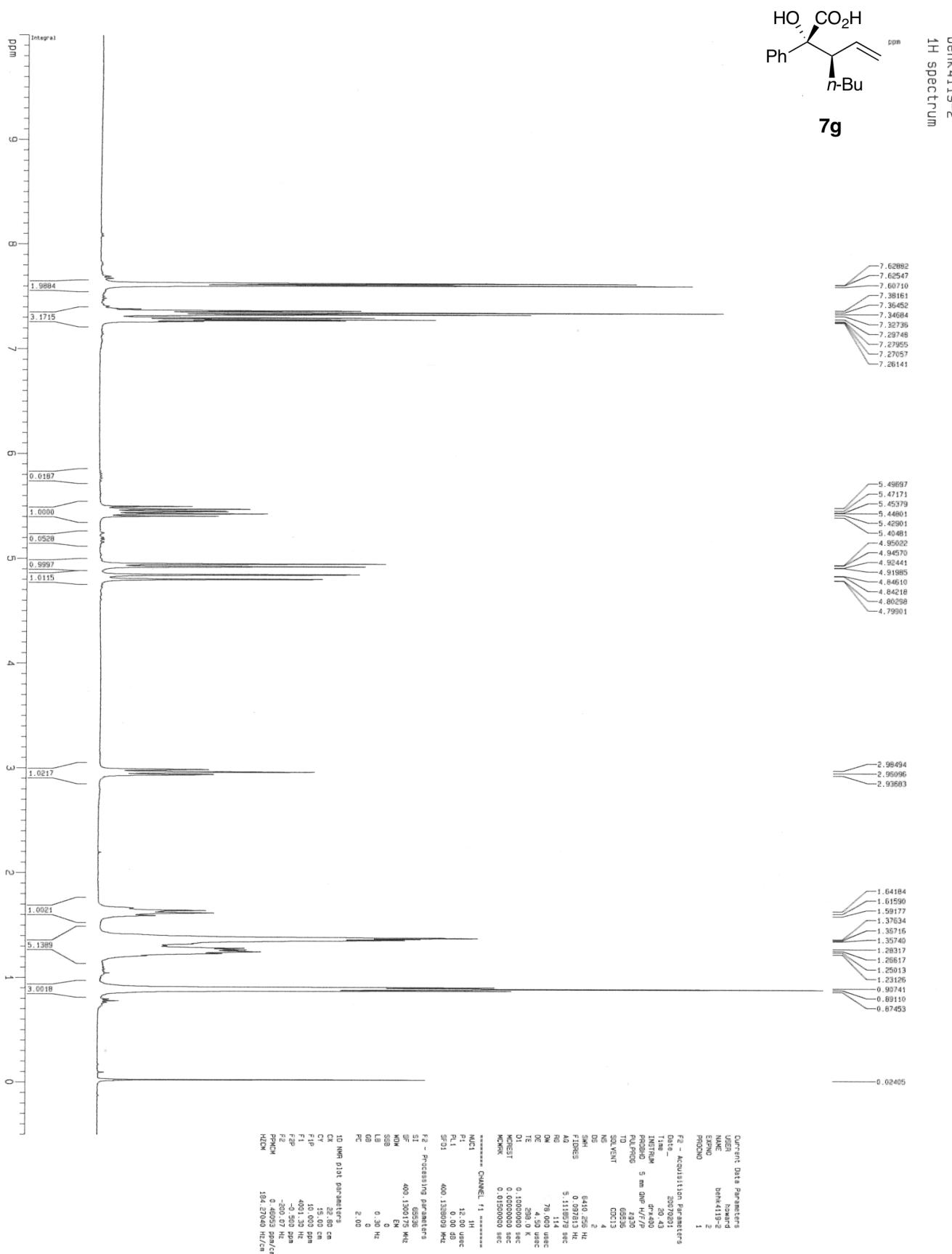


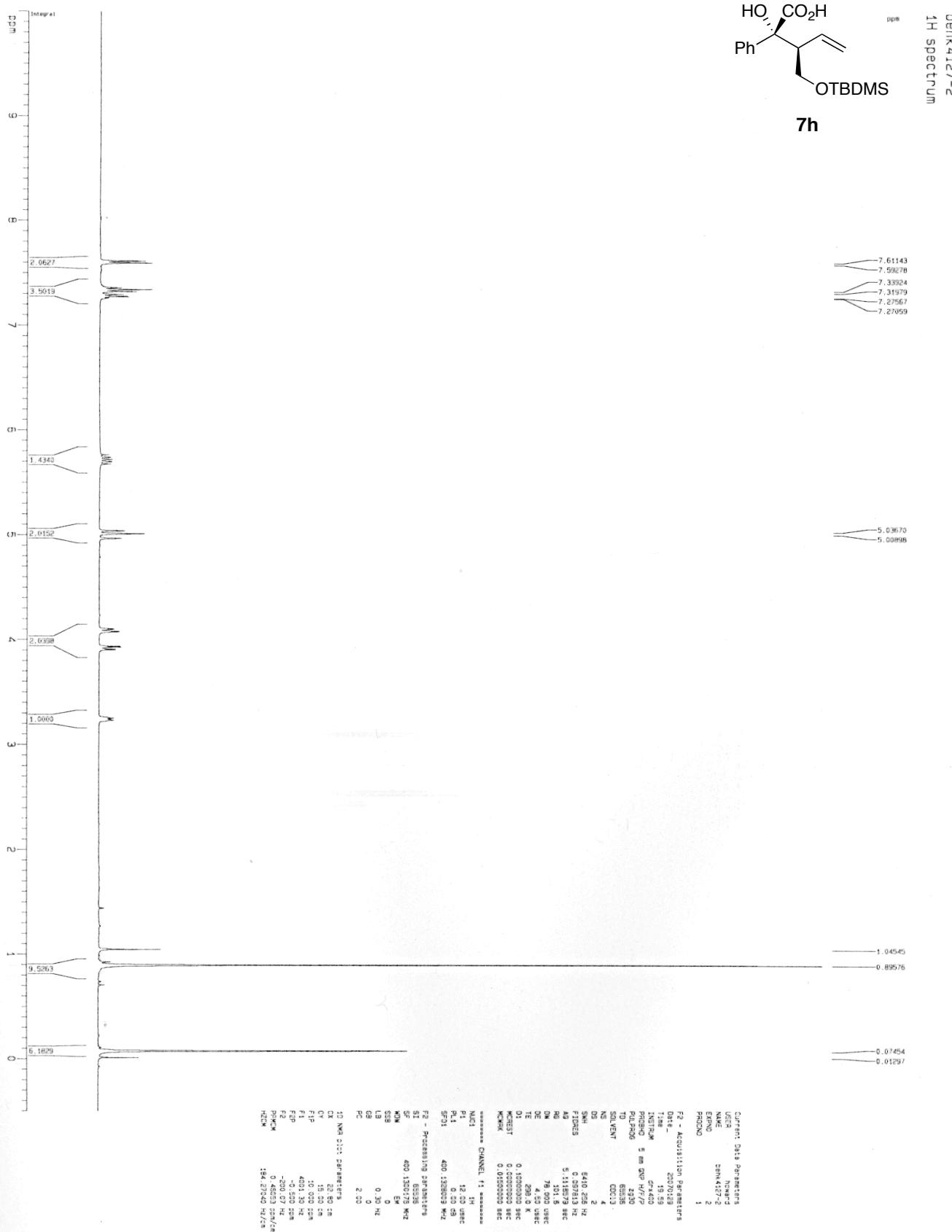


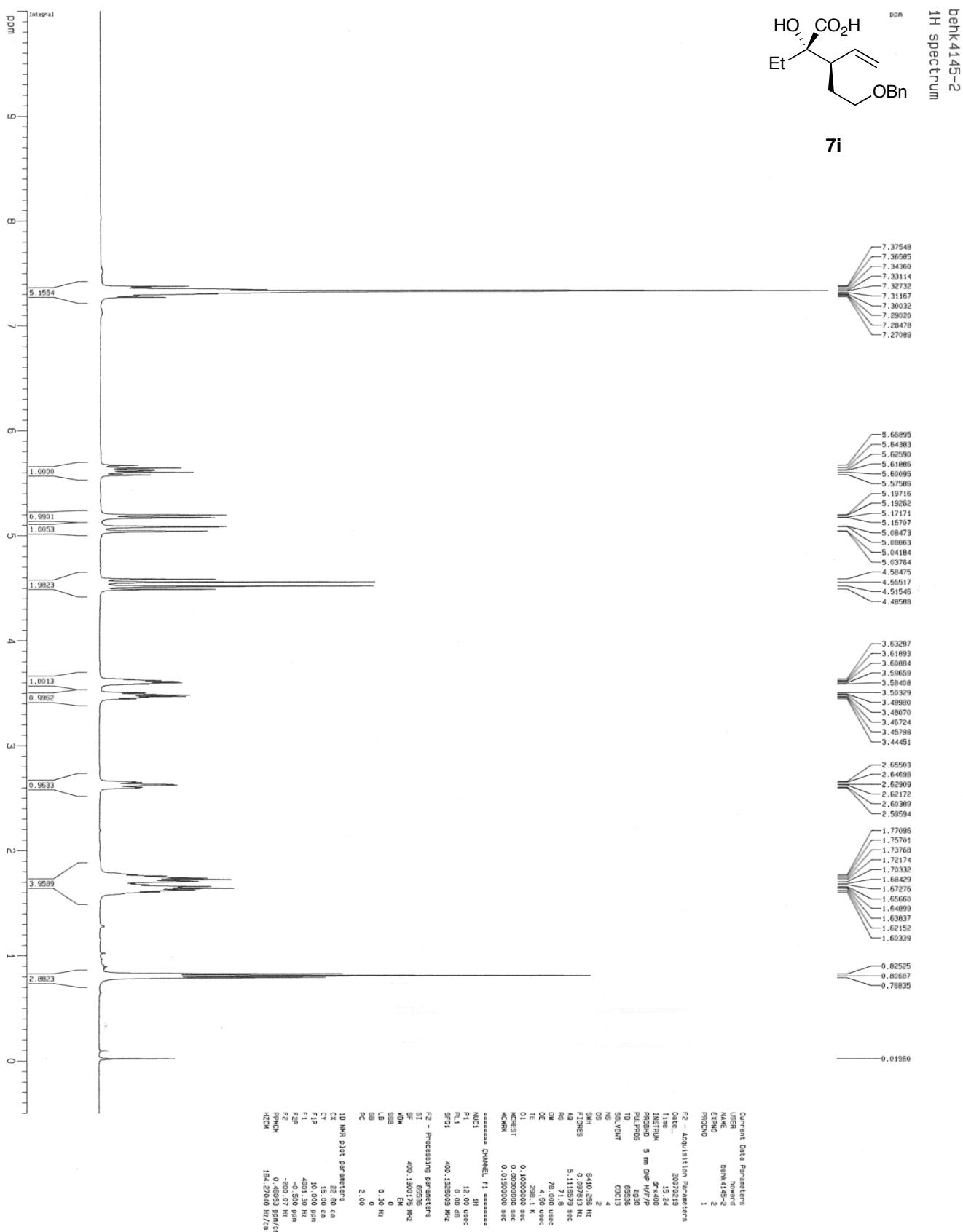


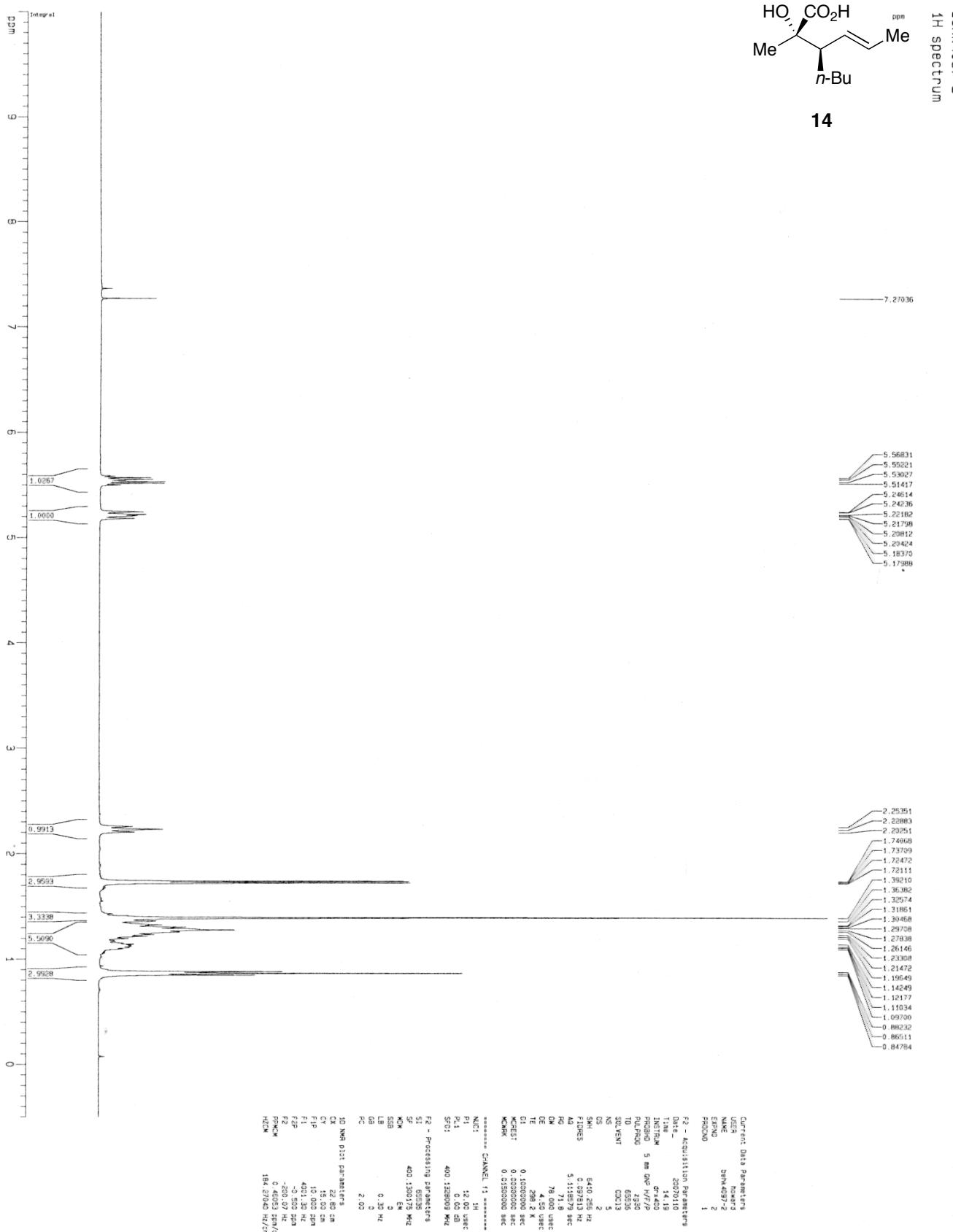




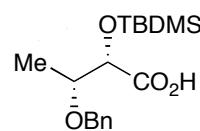








benk4078-2
1H spectrum



S-3

