Supporting Information

Construction of Bridged and Fused Ring Systems via Intramolecular Michael Reactions of Vinylnitroso Compounds

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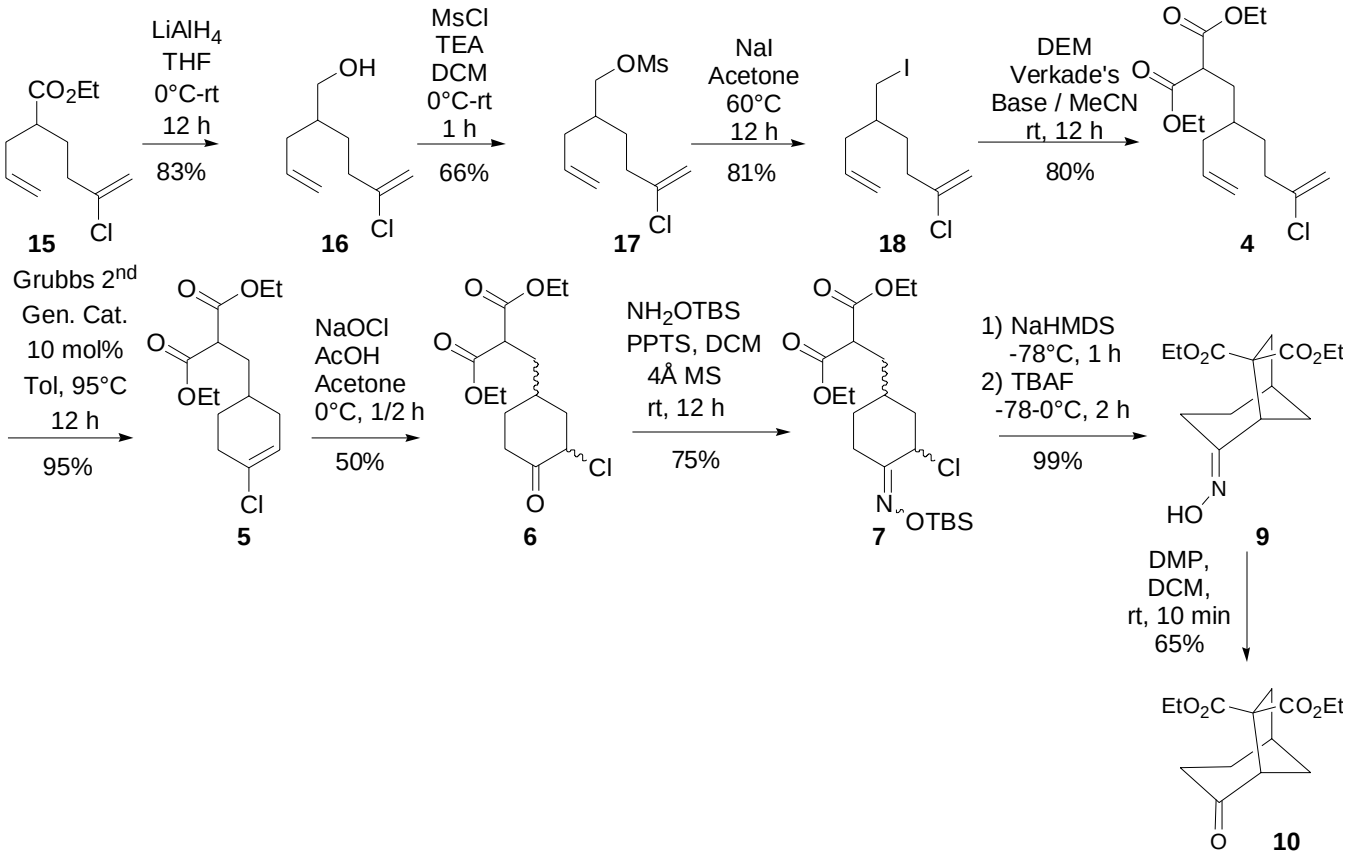
General Methods. All non-aqueous reactions were carried out under an inert atmosphere of argon in flame-dried glassware. Air and moisture sensitive liquid reagents were added via a dry syringe or canula. All solvents and reagents were used as obtained from commercial sources without further purification. Flash column chromatography was performed using EM Science silica gel 60 (230-400 mesh). Analytical and preparative thin layer chromatography (TLC) were performed on EM Science silica gel 60 PF_{254} plates. ^{1}H and ^{13}C NMR spectral data were recorded on Bruker DPX-300, CDPX-300, AMX-360, or DRX 400 MHz spectrometers. Infrared spectral data were obtained using a Perkin-Elmer 1600 FTIR spectrometer.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81%
DEM
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Base / MeCN
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16
17
18
4
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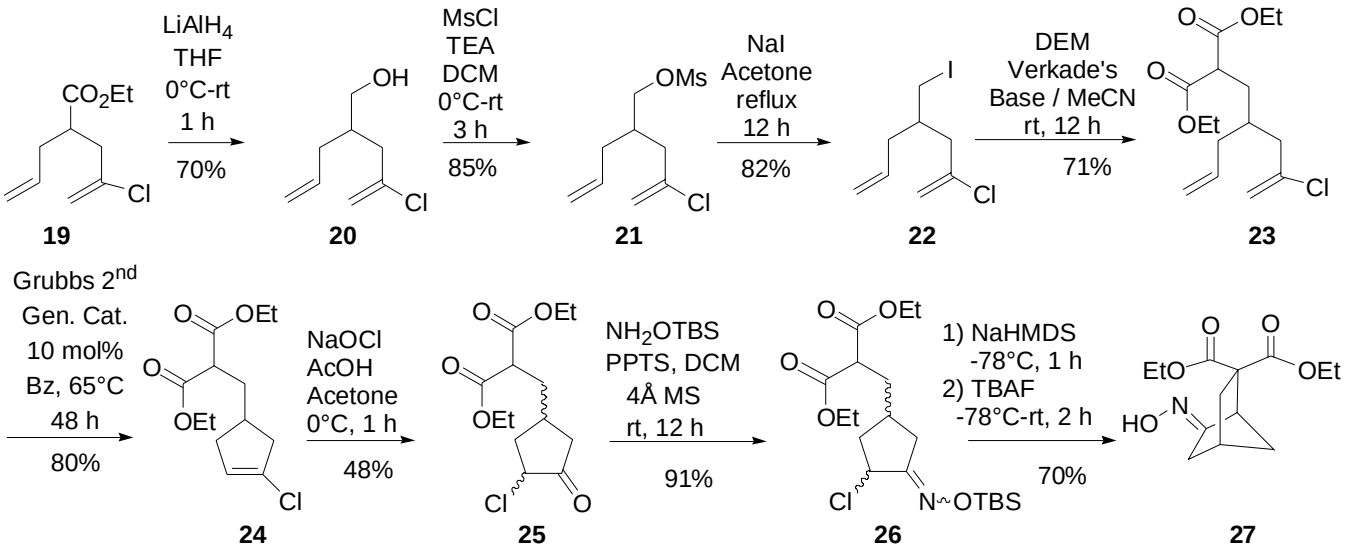
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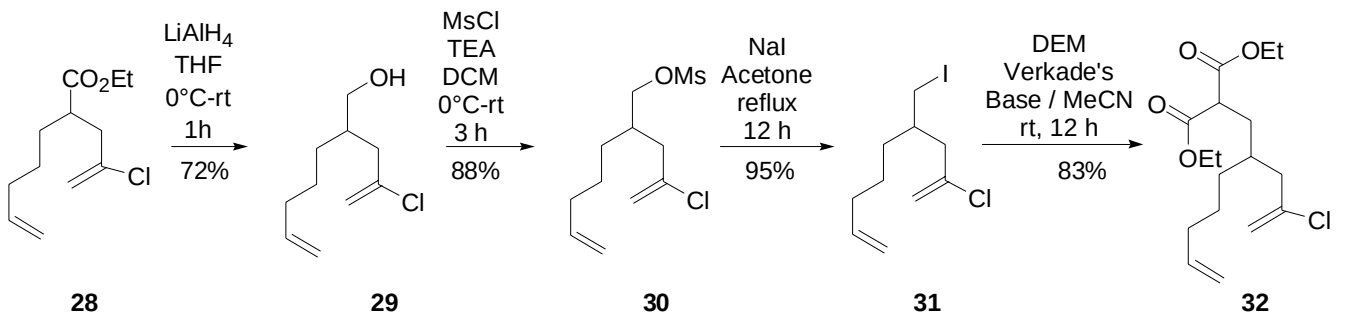
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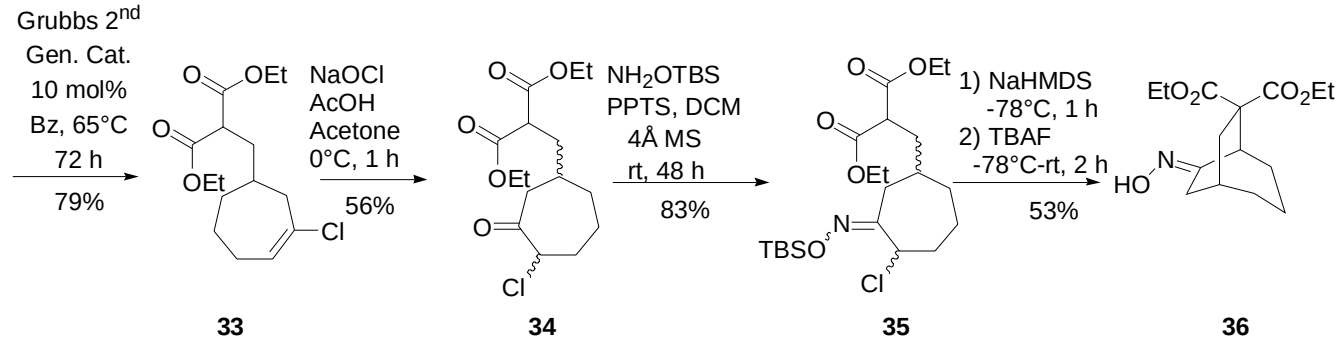
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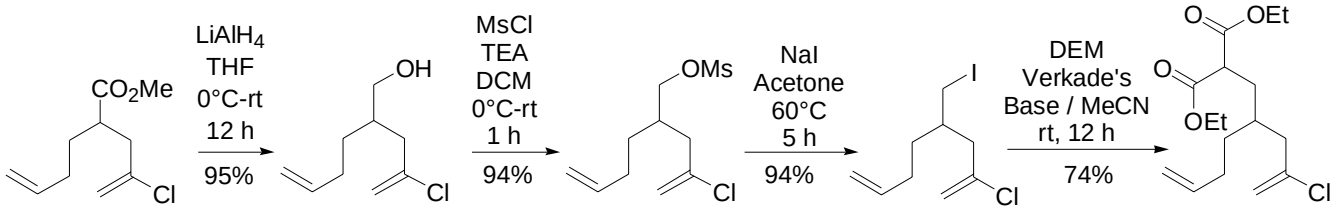
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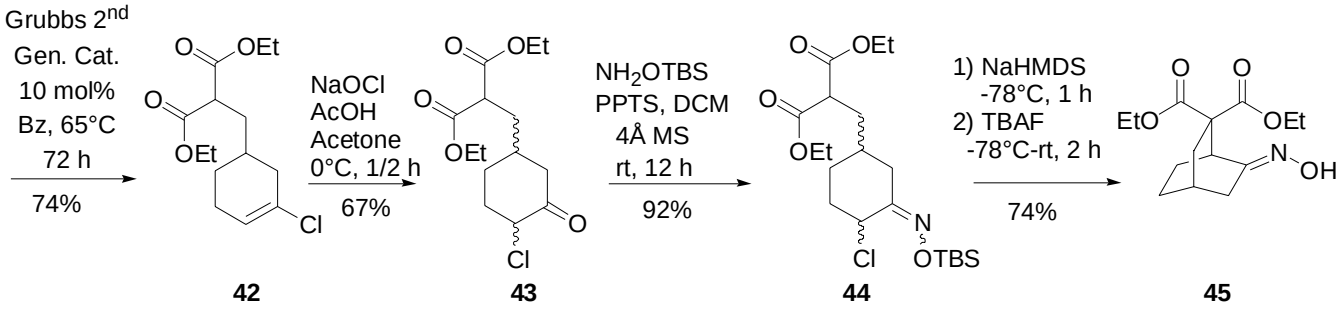
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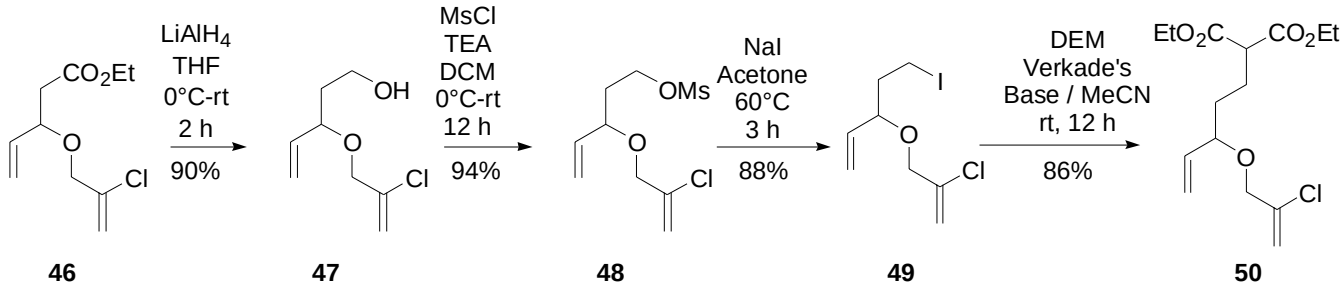
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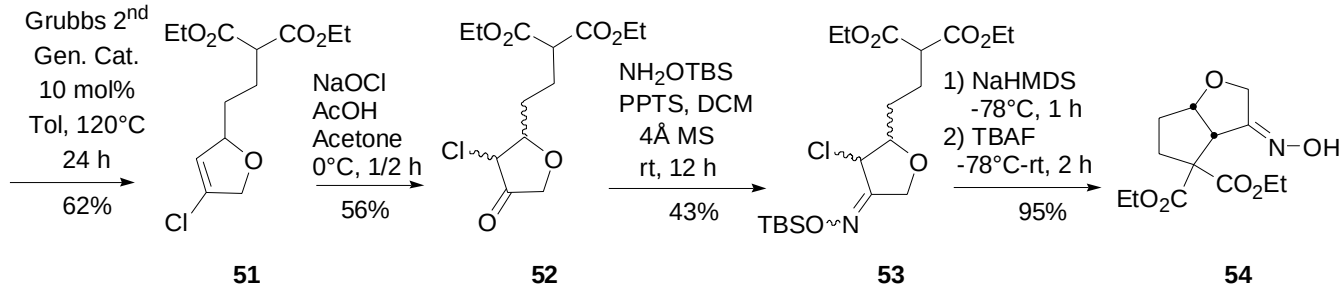
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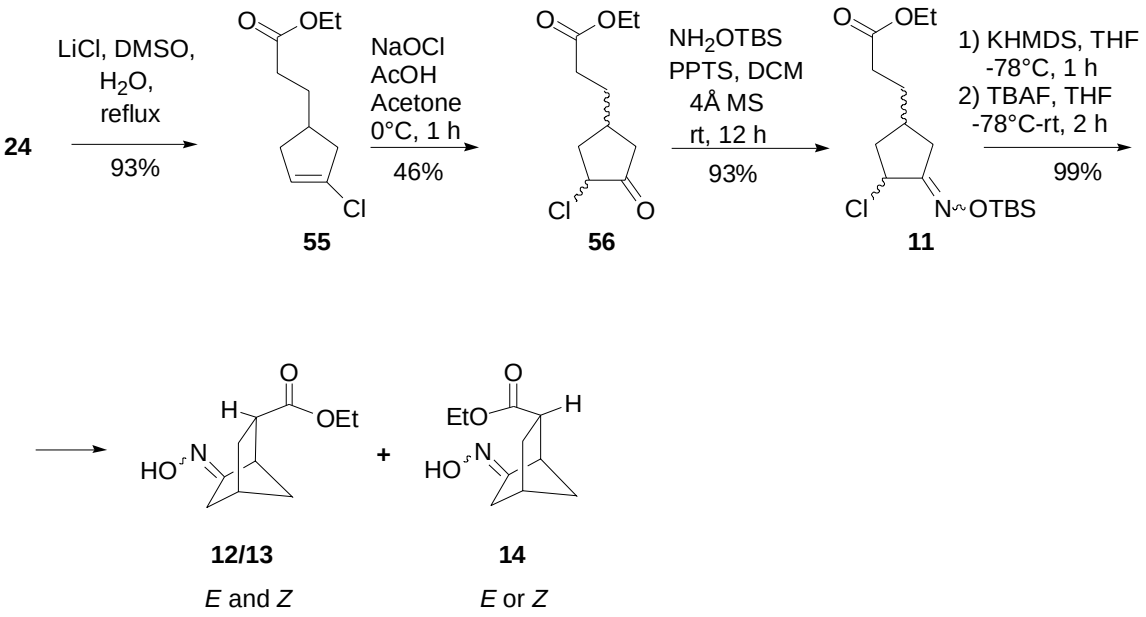
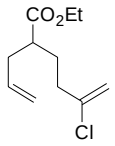
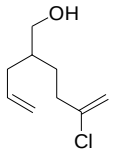


2-Allyl-5-chlorohex-5-enoic Acid Ethyl Ester (15). To a solution of

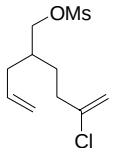


2-allyl-2-(3-chlorobut-3-enyl)-malonic acid diethyl ester (710 mg, 2.46 mmol) in DMSO (10 mL) were added LiCl (228 mg, 5.42 mmol) and water (0.4 mL). The mixture was heated in an oil bath at 190 °C for 12 h, and cooled to rt. Aqueous NH_4OAc (10 mL) was added and the mixture was then extracted with ether (30 mL x 3). The organic layers were combined and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (5-10% ether/pentane gradient) to afford the title compound **15** as a clear oil (250 mg, 64%, 73% brsm). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78-5.64 (m, 1H), 5.14-4.99 (m, 4H), 4.12 (dd, *J* = 7.1, 14.2 Hz, 2H), 3.45 (dd, *J* = 7.0, 14.0 Hz, 1H), 2.45-2.20 (m, 5H), 1.84-1.57 (m, 2H), 1.25-1.16 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3, 142.2, 135.4, 117.4, 113.1, 60.7, 44.4, 37.2, 36.8, 29.4, 14.7; HRMS-AP $[M + H]^+$ calcd for $C_{11}H_{18}O_2Cl$, 217.1000; found, 217.0995.

2-Allyl-5-chlorohex-5-en-1-ol (16). To a suspension of $LiAlH_4$ (79 mg, 2.07 mmol) in THF (5 mL) at 0 °C was added dropwise ester **15** (250 mg, 1.15 mmol) in THF (5 mL). The mixture was stirred for 12 h at rt, and then diluted with EtOAc (20 mL). The mixture was poured into 1 M HCl solution (10 mL), and saturated aqueous NH_4Cl (10 mL) and EtOAc (10 mL) were added. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (10-20% ether/pentane gradient) to afford the title compound **16** as a clear oil (166 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82-5.73 (m, 1H), 5.18-5.06 (m, 4H), 4.18-3.96 (m, 2H), 3.50 (dd, *J* = 7.0, 14.0 Hz, 1H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.17-2.07 (m, 2H), 1.88-1.76 (m, 1H), 1.67-1.59 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.9, 117.4, 112.7, 66.6, 36.8, 35.9, 28.8, 21.3, 14.4; HRMS-ES $[M + Na]^+$ calcd for $C_9H_{15}ClO$, 174.0811; found, 174.0815.

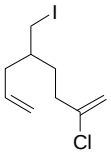


Methanesulfonic Acid 2-Allyl-5-chlorohex-5-enyl Ester (17). To a solution of alcohol **16** (166 g, 0.95 mmol) in dichloromethane (3.0 mL) at 0 °C was added portionwise triethylamine (0.13 mL, 0.87 mmol) and mesyl chloride (0.042 mL, 0.57 mmol). The mixture was stirred at 0 °C for 30 min, and then at rt for 30 min. The organic phase was diluted with dichloromethane (18 mL) and washed consecutively with brine (10 mL), 1 M aqueous $KHSO_4$ (10 mL), brine (10 mL), 5% aqueous $NaHCO_3$ (10 mL), brine (10 mL), and dried over Na_2SO_4 overnight. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (10-20% EtOAc/hexanes gradient) to afford the title compound **17** as a

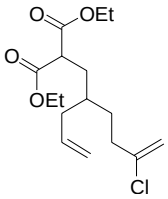


clear oil (159 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81-5.73 (m, 1H), 5.20-5.10 (m, 4H), 4.21-4.15 (m, 2H), 3.03 (s, 3H), 2.43 (t, *J* = 7.5 Hz, 2H), 2.19 (t, *J* = 6.0 Hz, 2H), 1.94-1.86 (m, 1H), 1.73-1.63 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 135.2, 118.2, 113.1, 71.6, 37.6, 36.9, 35.2, 30.1, 28.2; HRMS-ES $[M+Na]^+$ calcd for $C_{10}H_{17}ClO_3SNa$, 275.0485; found, 275.0480.

2-Chloro-5-iodomethylocta-1,7-diene (18). To a solution of mesylate **17** (155 mg, 0.62 mmol) in acetone (5 mL) was added sodium iodide (369 mg, 2.96 mmol) and the mixture was stirred at 60 °C for 12 h. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography (pentane) to afford the title compound **18** as a clear oil (140 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79-5.65 (m, 1H), 5.19-4.91 (m, 4H), 3.27 (d, *J* = 3.7 Hz, 2H), 2.41-2.34 (m, 2H), 2.19-2.06 (m, 2H), 1.68-1.61 (m, 1H), 1.35-1.22 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 135.5, 117.9, 112.9, 38.7, 37.6, 36.6, 32.0, 15.0; HRMS-EI $[M]^+$ calcd for $C_9H_{14}ClI$, 283.9829; found, 283.9841.



2-(2-Allyl-5-chlorohex-5-enyl)-malonic Acid Diethyl Ester (4). To a solution of iodide **18** (44 mg, 0.15 mmol) and diethyl malonate (26 mg, 0.16 mmol) in acetonitrile (5 mL) was added Verkade's base (37 mg, 0.17 mmol), and the reaction mixture was stirred at rt for 24 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (5-20% ether/pentane gradient) to afford the title compound **4** as a clear oil (38 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81-5.68 (m, 1H), 5.14-5.04 (m, 4H), 4.20 (q, *J* =6.8 Hz,



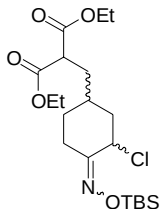
4H), 3.46 (t, J = 7.5 Hz, 1H), 2.37 (t, J = 6.0 Hz, 2H), 2.10-2.08 (m 3H), 1.89 (t, J = 6.0 Hz, 2H), 1.63-1.39 (m, 3H), 1.27 (t, J = 7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 143.0, 135.9, 117.4, 112.5, 61.8, 50.2, 37.7, 36.5, 34.7, 32.7, 31.0, 14.5; HRMS-ES $[M + H]^+$ calcd for $C_{16}H_{26}ClO_4$, 317.1520; found, 317.1512.

2-(4-Chlorocyclohex-3-enylmethyl)-malonic Acid Diethyl Ester (5). A flame dried 50 mL two necked flask equipped with a condenser and a magnetic stirring bar was charged with ester **4** (48 mg, 0.15 mmol) and benzene (20 mL). The mixture was deaerated with argon for 1 h. Grubbs 2nd generation catalyst (12 mg, 0.02 mmol) in benzene (2 mL) was added *via* syringe. The combined mixture was deaerated with argon for another 20 min, and then heated at 65 °C for 12 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (2-5% ether/pentane gradient) to afford the title compound **5** as a yellow oil (42 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83-5.66 (m, 1H), 4.20 (dd, J = 7.0, 14.0 Hz, 4H), 3.42 (t, J = 7.5 Hz, 1H), 2.56-2.26 (m, 4H), 1.97-1.84 (m, 4H), 1.51-1.50 (m, 2H), 1.49-1.39 (m, 1H), (t, J = 6.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 132.1, 123.6, 61.8, 50.1, 34.7, 32.7, 32.3, 30.8, 29.8, 14.4; HRMS-ES $[M + H]^+$ calcd for $C_{14}H_{22}ClO_4$, 289.1207; found, 289.1202.

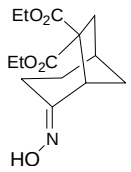
2-(3-Chloro-4-oxocyclohexylmethyl)-malonic Acid Diethyl Ester (6). To a solution of ester **5** (30 mg, 0.10 mmol), acetone (0.40 mL), and glacial acetic acid (0.17 mL) at 0 °C was added dropwise aqueous sodium hypochlorite (68 μL of 10% solution, 0.10 mmol) *via* syringe. The reaction mixture was stirred at 0 °C for 30 min and quenched by addition of aqueous

saturated Na_2CO_3 solution. The mixture was then extracted with dichloromethane (20 mL x 2). The organic layers were combined, washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (10% ether/pentane) to afford the title compound **6** as a yellow oil containing a 1:1 mixture of diastereomers (16 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (0.2 H), 4.33-4.06 (m, 4.8H), 3.47-3.7 (m, 1H), 3.03-2.94 (m, 0.6H), 2.99-2.96 (m, 1H), 2.35-2.22 (m, 2H), 2.13-2.07 (m, 2H), 1.97-1.86 (m, 3H), 1.81-1.79 (m, 1H), 1.32-1.27 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.6, 169.7, 169.6, 169.5, 168.0, 62.1, 62.0, 59.8, 50.2, 50.0, 41.0, 37.2, 35.8, 34.2, 33.9, 32.6, 30.1, 29.1, 28.9, 22.4, 14.5; HRMS-ES $[M + Na]^+$ calcd for $C_{14}H_{21}ClO_5Na$, 327.0975; found, 327.0984.

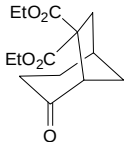
2-(3-Chloro-4-*tert*-butyldimethylsilyloxyimino-cyclohexylmethyl)-malonic Acid Diethyl Ester (7). To a solution of α-chloroketone **6** (11 mg, 0.037 mmol) in dichloromethane (0.5 mL) were added *O*-(*t*-butyldimethylsilyl)-hydroxylamine (11 mg, 0.075 mmol), 4Å molecular sieves (crushed), and a catalytic amount of PPTS. The mixture was stirred at rt for 12 h, and then filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (10-20% ether/pentane gradient) to afford the title compound **7** as a clear oil containing a complex mixture of stereoisomers (12 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68 (brs, 0.4H), 5.14 (brs, 0.6H), 4.24 (q, J = 7.0 Hz, 4H), 3.45 (t, J = 7.7 Hz, 1H), 3.36-3.23 (m, 0.6H), 2.60-2.58 (m, 0.4H), 2.41-1.85 (m, 6H), 1.66-1.53 (m, 1H), 1.31 (t, J = 7.0, 6H), 0.91 (s,



9H), 0.18 (s, 6H); HRMS-ES $[M + H]^+$ calcd for $C_{20}H_{37}NClO_5Si$, 434.2130; found, 434.2132.

4-Hydroxyiminobicyclo[3.2.1]octane-6,6-dicarboxylic Acid Diethyl Ester (9). 

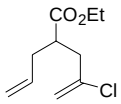
To a solution of oxime **7** (8 mg, 0.018 mmol) in THF (0.5 mL) at -78 °C was added dropwise NaHMDS (2 M in THF, 12 μL, 0.025 mmol). After 1 h at -78 °C, TBAF (1 M in THF, 24 μL, 0.024 mmol) was added and the reaction mixture was warmed to rt over 2 h. Saturated NH_4Cl was added and the mixture was extracted with EtOAc (10 mL x 2). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (20% EtOAc/hexanes) to afford the title compound **9** as a white crystalline solid (5 mg, 99%) which was recrystallized from chloroform to afford colorless crystals suitable for X-ray analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (brs, 1H), 4.23-4.14 (m, 4H), 3.49 (d, J = 4.4 Hz, 1H), 3.03 (q, J = 8.0 Hz, 1H), 2.6 (d, J = 14.5 Hz, 1H), 2.44 (brs, 1H), 2.27 (q, J = 7.4 Hz, 1H), 2.15-2.03 (m, 2H), 1.75-1.85 (m, 1H), 1.66-1.61 (m, 2H), 1.27-1.20 (m, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 171.9, 170.2, 160.0, 63.4, 62.0, 61.9, 49.3, 38.3, 36.3, 34.3, 30.4, 18.3, 14.4, 14.3; HRMS-ES $[M + H]^+$ calcd for $C_{14}H_{22}NO_5$, 284.1498; found, 284.1504.

4-Oxobicyclo[3.2.1]octane-6,6-dicarboxylic Acid Diethyl Ester (10). 

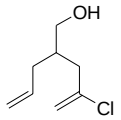
To a solution of oxime **9** (23 mg, 0.084 mmol) in dichloromethane (0.5 mL) at rt was added DMP (20 mg, 0.088 mmol). After stirring the mixture for 10 min at rt, dichloromethane (10 mL) and aqueous $NaHSO_4$ (10 mL) were added. The mixture was shaken for 5 min and extracted with dichloromethane (10 mL x 2). The

combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (10% EtOAc/hexanes) to afford the title compound **10** as a clear oil (15 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25-4.41 (m, 4H), 3.31 (d, *J* = 4.6 Hz, 1H), 2.75-2.67 (m, 1H), 2.65-2.55 (m, 1H), 2.49-2.44 (m, 1H), 2.43-2.34 (m, 2H), 2.28-2.23 (m, 1H), 1.92-1.89 (m, 1H), 1.80-1.76 (m, 1H), 1.29-1.22 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.5, 171.3, 170.5, 77.6, 62.8, 62.49, 62.45, 58.8, 38.3, 36.6, 35.9, 34.3, 32.0, 30.1, 14.39, 14.31.

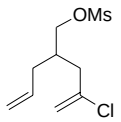
2-Allyl-4-chloro-4-enoic Acid Ethyl Ester (19). To a stirred solution of LDA (2 M in THF, 1.2 mL, 2.4 mmol) and DMPU (0.67 mL) in THF (5 mL) was added dropwise ethyl 4-pentenoate (256 mg, 2 mmol) in THF (1 mL) at –78 °C. The resulting mixture was stirred for 30 min at –78 °C and 2-chloro-3-iodopropene (486 mg, 2.4 mmol) was added. The reaction mixture was warmed to rt over 8 h. Saturated aqueous NH_4Cl (10 mL) and ether (10 mL) were added. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (10% ether/pentane) to afford the ester **19** as a colorless oil (309 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.73-5.59 (m, 1H), 5.13 (d, *J* = 1.2 Hz, 1H), 5.11 (d, *J* = 1.0 Hz, 1H), 5.05-4.96 (m, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.82-2.70 (m, 1H), 2.62 (dd, *J* = 8.3, 14.7 Hz, 1H), 2.38 (dd, *J* = 6.3, 14.5 Hz, 1H), 2.31-2.17 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 140.1, 134.8, 117.8, 114.6, 60.8, 43.1, 41.0, 35.8, 14.6; HRMS-AP $[M + H]^+$ calcd for $C_{10}H_{16}ClO_2$, 203.0839; found, 203.0835.



2-Allyl-4-chloropent-4-en-1-ol (20). To a stirred suspension of $LiAlH_4$ (84 mg, 2.21 mmol) in THF (5 mL) at 0 °C was added dropwise ester **19** (250 mg, 1.23 mmol) in ether (5 mL). The mixture was stirred for 1 h at rt, and then diluted with ethyl acetate (10 mL). The mixture was poured into 1 M HCl solution. Saturated aqueous NH_4Cl (10 mL) and EtOAc (10 mL) were then added. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (30% ether/pentane) to afford the alcohol **20** as a colorless oil (140 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81-5.67 (m, 1H), 5.15 (d, *J* = 1.1 Hz, 1H), 5.10 (d, *J* = 1.0 Hz, 1H), 5.05-4.97 (m, 2H), 3.53 (d, *J* = 4.8 Hz, 2H), 2.36 (dd, *J* = 7.4, 14.4 Hz, 1H), 2.25 (dd, *J* = 6.7, 14.4 Hz, 1H), 2.10-2.05 (m, 2H), 2.01-1.90 (m, 1H), 1.47 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 134.9, 115.6, 112.7, 62.9, 39.3, 36.5, 33.6; HRMS-EI $[M]^+$ calcd for $C_8H_{13}ClO$, 160.0655; found, 160.0654.

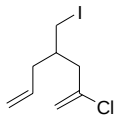


Methanesulfonic Acid 2-Allyl-4-chloropent-4-enyl Ester (21). To a stirred solution of alcohol **20** (132 mg, 0.82 mmol) in dichloromethane (5 mL) at 0 °C was added portionwise triethylamine (0.36 mL, 2.46 mmol) and mesyl chloride (0.20 mL, 2.46 mmol). The mixture was stirred at 0 °C for 30 min, and then at rt for 3 h. The organic phase was diluted with dichloromethane (10 mL) and washed consecutively with brine (10 mL), 1 M aqueous $KHSO_4$ (10 mL), brine (10 mL), 5% aqueous $NaHCO_3$ (10 mL), brine (10 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (30% ether/pentane) affording the mesylate **21** as a clear oil (166 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76-5.62 (m, 1H), 5.20 (d, *J* = 1.2 Hz, 1H), 5.16 (d, *J* = 1.0 Hz, 1H),

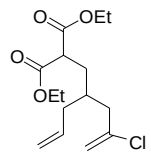


5.07-5.01 (m, 2H), 4.11 (d, J = 4.4 Hz, 2H), 2.93 (s, 3H), 2.43-2.29 (m, 2H), 2.23-2.09 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.1, 135.0, 118.5, 115.4, 70.8, 40.5, 37.5, 35.5, 34.6; LRMS-ES $[M + Na]^+$ calcd for $C_9H_{15}ClNaO_3S$, 261.0; found, 261.0.

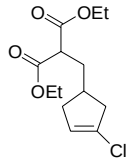
2-Chloro-4-iodomethylhepta-1,6-diene (22). To a solution of mesylate **21** (156 mg, 0.65 mmol) in acetone (5 mL) was added sodium iodide (491 mg, 3.25 mmol), and the mixture was stirred at reflux for 12 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (pentane) to produce the iodide **22** as a clear oil (145 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.71-5.58 (m, 1H), 5.21 (d, J = 1.2 Hz, 1H), 5.19 (d, J = 1.0 Hz, 1H), 5.13-5.02 (m, 2H), 3.21 (dq, J = 3.9, 7.6 Hz, 2H), 2.29-2.26 (m, 2H), 2.09-1.97 (m, 2H), 1.57-1.50 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 135.3, 118.2, 115.3, 44.1, 38.3, 35.4, 15.0; HRMS-EI $[M]^+$ calcd for $C_8H_{12}ClI$, 269.9672; found, 269.9669.

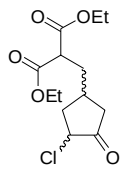


2-(2-Allyl-4-chloropent-4-enyl)-malonic Acid Diethyl Ester (23). To a stirred solution of diethyl malonate (90 mg, 0.56 mmol) in acetonitrile (3 mL) was added Verkade's base (122 mg, 0.56 mmol), and the mixture was stirred for 30 min at rt. Iodide **22** (138 mg, 0.51 mmol) was then added and the mixture was stirred for 12 h at rt. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (20% ether/hexanes) to afford the diene **23** as a colorless oil (109 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.73-5.60 (m, 1H), 5.15 (d, J = 1.2 Hz, 1H), 5.09 (d, J = 1.0 Hz, 1H), 5.02-4.95 (m, 2H), 4.12 (dq, J = 1.9, 7.1 Hz, 4H), 3.40 (t, J = 7.8 Hz, 1H), 2.27 (dd, J = 6.1, 14.3 Hz, 1H), 2.17 (dd, J =



5.6, 14.3 Hz, 1H), 2.06-2.01 (m, 2H), 1.88-1.77 (m, 3H), 1.20 (dt, *J* = 1.0, 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 169.7, 141.2, 135.4, 117.9, 114.6, 61.8, 50.2, 43.7, 37.1, 33.2, 32.2, 14.4; HRMS-ES $[M + H]^+$ calcd for $C_{15}H_{24}ClO_4$, 303.1363; found, 303.1360.

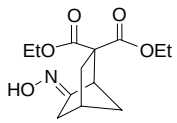
2-(3-Chlorocyclopent-3-enylmethyl)-malonic Acid Diethyl Ester (24).  A flame dried 250 mL two necked flask equipped with a magnetic stirring bar and a condenser was charged with diene **23** (106 mg, 0.35 mmol) and benzene (100 mL). The solution was deaerated by bubbling argon through the mixture for 2 h. The second-generation Grubbs catalyst (30 mg, 0.035 mmol) in 2 mL of benzene was added and the argon bubbling was continued for an additional 30 min. The mixture was heated and stirred at 65 °C for 2-3 days until TLC showed the reaction was complete. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (20% ether/hexanes) to afford the vinyl chloride **24** as a pale yellow oil (77 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.53-5.50 (m, 1H), 4.13 (dq, *J* = 3.7, 7.2 Hz, 4H), 3.27 (t, *J* = 7.6 Hz, 1H), 2.60-2.42 (m, 2H), 2.34-2.30 (m, 1H), 2.21-2.15 (m, 1H), 2.02-1.93 (m, 3H), 1.19 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 168.6, 130.4, 124.7, 60.8, 50.0, 42.5, 36.8, 34.8, 34.2, 13.4; HRMS-ES $[M + H]^+$ calcd for $C_{13}H_{20}ClO_4$, 275.1050; found, 275.1052.

2-(3-Chloro-4-oxocyclopentylmethyl)-malonic Acid Diethyl Ester (25).  To a solution of vinyl chloride **24** (60 mg, 0.22 mmol), acetone (2.5 mL) and glacial acetic acid (1 mL) at 0 °C was added dropwise sodium hypochlorite (0.16 mL of 10% solution, 0.22 mmol) via syringe. The reaction mixture

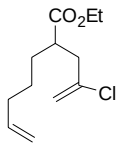
was stirred at 0 °C for 1 h and quenched by addition of saturated aqueous $NaHCO_3$ solution. The mixture was then extracted with dichloromethane (10 mL x 2). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (50% ether/hexanes) affording the α-chloroketone **25** as a clear oil (30 mg, 48%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.13 (dq, *J* = 1.1, 7.1 Hz, 4H), 4.10-4.06 (m, 1H), 3.31 (t, *J* = 7.6 Hz, 1H), 2.64-2.43 (m, 2H), 2.33-2.24 (m, 1H), 2.08-1.99 (m, 2H), 1.97-1.79 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.7, 169.3, 169.3, 62.1, 57.5, 50.8, 42.3, 39.9, 34.2, 32.2, 14.4; HRMS-AP $[M + H]^+$ calcd for $C_{13}H_{20}ClO_5$, 291.0999; found, 291.0992.

2-(3-Chloro-4-*tert*-butyldimethylsilyloxyimino-cyclopentylmethyl)-malonic Acid Diethyl Ester (26). To a solution of α-chloroketone **25** (23 mg, 0.079 mmol) in dichloromethane (3 mL) were added *O*-(*tert*-butyldimethylsilyl)-hydroxylamine (24 mg, 0.16 mmol), 4Å molecular sieves (crushed), and a catalytic amount of PPTS. The mixture was stirred at rt for 12 h and then filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (20% ether/hexanes) to afford the α-chloroketoxime **26** as a complex mixture of stereoisomers (colorless oil, 31 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.80 (d, *J* = 5.7 Hz, 1H, *minor*), 4.62 (d, *J* = 5.1 Hz, 1H, *major*), 4.04 (q, *J* = 7.2 Hz, 4H, *major and minor*), 3.21 (t, *J* = 7.6 Hz, 1H, *major and minor*), 2.75-2.60 (m, 1H, *major and minor*), 2.38-2.25 (m, 1H, *major and minor*), 2.10-2.04 (m, 1H, *major and minor*), 1.90-1.79 (m, 3H, *major and*

minor), 1.60-1.50 (m, 1H, *major and minor*), 1.11 (t, *J* = 7.2 Hz, 6H, *major and minor*), 0.76 (s, 9H, *minor*), 0.74 (s, 9H, *major*), 0.00 (s, 6H, *major*), -0.01 (s, 6H, *minor*); HRMS-ES $[M + H]^+$ calcd for $C_{19}H_{35}ClNO_5Si$, 420.1973; found, 420.1955.

6-Hydroxyiminobicyclo[2.2.1]heptane-2,2-dicarboxylic Acid Diethyl Ester (27). 

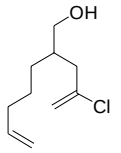
To a stirred solution of oxime **26** (14.0 mg, 0.033 mmol) in THF (2 mL) at –78 °C was added dropwise NaHMDS (1M in THF, 0.033 mL, 0.033 mmol) via syringe, and the reaction mixture was stirred at –78 °C for 1 h. TBAF (1 M in THF, 0.049 mL, 0.049 mmol) was then added dropwise via syringe, and the mixture was warmed to rt over 2 h. Saturated aqueous NH_4Cl (5 mL) was then added. The mixture was extracted with ether (10 mL x 3), and the combined extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (50% ether/pentane) to afford the bridged bicyclic oxime **27** as a clear oil (6.3 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (s, 1H), 4.18-3.98 (m, 4H), 3.37 (d, *J* = 0.9 Hz, 1H), 2.49 (d, *J* = 1.4 Hz, 1H), 2.37-2.20 (m, 2H), 2.11 (dd, *J* = 3.4, 17.6 Hz, 1H), 1.87 (m, 1H), 1.73 (m, 1H), 1.58 (m, 1H), 1.19-1.14 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 170.3, 163.2, 62.2, 61.8, 60.3, 49.7, 40.2, 37.6, 35.3, 33.7, 14.4, 14.3; HRMS-ES $[M + H]^+$ calcd for $C_{13}H_{20}NO_5$, 270.1341; found, 270.1354.

2-(2-Chloroallyl)-hept-6-enoic Acid Ethyl Ester (28). 

To a stirred solution of LDA (2 M in THF, 9 mL, 18 mmol) and DMPU (4 mL) in THF (50 mL) was added dropwise ethyl 6-heptenoate (1.87 g, 12 mmol) in THF (5 mL) at –78

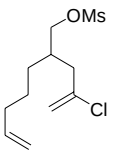
°C. The resulting mixture was stirred for 45 min at –78 °C and 2-chloro-3-iodopropene (3.17 g, 15.6 mmol) was added. The reaction mixture was warmed to rt over 8 h. Saturated aqueous NH_4Cl (50 mL) and ether (50 mL) were added. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (5% EtOAc/hexanes) to afford the ester **28** as a colorless oil (1.95 g, 71%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.77-5.63 (m, 1H), 5.12 (d, *J* = 1.2 Hz, 1H), 5.10 (d, *J* = 1.0 Hz, 1H), 4.97-4.86 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.71-2.58 (m, 2H), 2.38-2.32 (m, 1H), 1.99 (dq, *J* = 1.4, 7.3 Hz, 2H), 1.58-1.43 (m, 2H), 1.41-1.27 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 175.3, 140.3, 138.6, 115.2, 114.5, 60.8, 43.5, 42.0, 33.8, 31.4, 26.6, 14.6; HRMS-AP $[M + H]^+$ calcd for $C_{12}H_{20}ClO_2$, 231.1152; found, 231.1151.

2-(2-Chloroallyl)-hept-6-en-1-ol (29). To a stirred suspension of $LiAlH_4$ (1.05 g, 27.9 mmol) in THF (50 mL) was added dropwise ester **28** (3.58 g, 15.5 mmol) in ether (25 mL) at 0 °C. The mixture was stirred for 1 h at rt, and then diluted with ethyl acetate (15 mL). The mixture was poured into 1 M HCl solution. Saturated aqueous NH_4Cl (20 mL) and EtOAc (20 mL) were then added. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (25% ether/pentane) to afford the alcohol **29** as a colorless oil (2.11 g, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87-5.73 (m, 1H), 5.20 (d, *J* = 1.1 Hz, 1H), 5.16 (d, *J* = 1.0 Hz, 1H), 5.04-4.92 (m, 2H), 3.57 (br s, 2H), 2.46 (dd, *J* = 0.6, 7.3 Hz, 1H), 2.34 (s, 1H), 2.28 (dd, *J* = 0.6, 6.8 Hz, 1H), 2.09-2.02 (m, 2H), 1.92-1.85 (m, 1H), 1.49-1.30 (m, 4H); ^{13}C NMR (75 MHz,



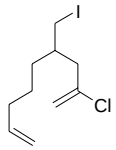
$CDCl_3$) δ 142.0, 139.0, 115.0, 114.1, 64.7, 41.5, 38.4, 34.3, 30.1, 26.5; HRMS-EI $[M]^+$ calcd for $C_{10}H_{17}ClO$, 188.0968; found, 188.0959.

Methanesulfonic Acid 2-(2-Chloroallyl)-hept-6-enyl Ester (30). To



a solution of alcohol **29** (30 mg, 0.15 mmol) in dichloromethane (3 mL) at 0 °C was added portionwise triethylamine (0.065 mL, 0.45 mmol) and mesyl chloride (0.037 mL, 0.45 mmol). The mixture was stirred at 0 °C for 30 min, and then at rt for 3 h. The organic phase was diluted with dichloromethane (10 mL) and washed consecutively with brine (10 mL), 1 M aqueous $KHSO_4$ (10 mL), brine (10 mL), 5% aqueous $NaHCO_3$ (10 mL), brine (10 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (30% ether/pentane) affording the mesylate **30** as a clear oil (37 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78-5.65 (m, 1H), 5.19 (d, J = 1.2 Hz, 1H), 5.15 (d, J = 1.0 Hz, 1H), 4.98-4.87 (m, 2H), 4.11 (d, J = 4.5 Hz, 2H), 2.93 (s, 3H), 2.42-2.26 (m, 2H), 2.09-1.97 (m, 3H), 1.43-1.32 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 138.6, 115.4, 115.3, 71.1, 41.1, 37.6, 35.8, 34.0, 29.9, 26.2; LRMS-ES $[M + Na]^+$ calcd for $C_{11}H_{19}ClNaO_3S$, 289.1; found, 289.1.

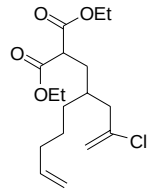
2-Chloro-4-iodomethylnona-1,8-diene (31). To a stirred solution of



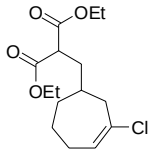
mesylate **30** (2.00 g, 7.49 mmol) in acetone (20 mL) was added sodium iodide (5.62 g, 37.45 mmol) and the mixture was stirred at reflux for 12 h. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography (pentane) to produce the iodide **31** as a clear oil (2.12 g, 95%). ^{1}H NMR

(300 MHz, $CDCl_3$) δ 5.79-5.66 (m, 1H), 5.19 (d, J = 0.7 Hz, 1H), 5.17 (d, J = 1.0 Hz, 1H), 4.98-4.87 (m, 2H), 3.21 (dq, J = 3.7, 10.1 Hz, 2H), 2.31-2.17 (m, 2H), 2.01 (q, J = 6.8 Hz, 2H), 1.43-1.18 (m, 5H); ^{13}C- NMR (75 MHz, $CDCl_3$) δ 140.5, 138.7, 115.3, 115.2, 44.7, 35.4, 34.0, 33.7, 26.1, 15.8; HRMS-EI $[M]^+$ calcd for $C_{10}H_{16}ClI$, 297.9985; found, 297.9987.

2-[2-(2-Chloroallyl)-hept-6-enyl]-malonic Acid Diethyl Ester (32). To a stirred solution of diethyl malonate (0.59 g, 3.69 mmol) in acetonitrile (50 mL) was added Verkade's base (0.8 g, 3.69 mmol) and the mixture was stirred for 30 min at rt. Iodide **31** (1.00 g, 3.35 mmol) was then added and the resulting solution was stirred at rt for 12 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (15% ether/hexanes) to afford the diene **32** as a colorless oil (0.92 g, 83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78-5.64 (m, 1H), 5.13 (d, J = 1.1 Hz, 1H), 5.08 (d, J = 0.9 Hz, 1H), 4.96-4.84 (m, 2H), 4.12 (q, J = 7.1 Hz, 4H), 3.37 (t, J = 7.5 Hz, 1H), 2.27-2.14 (m, 2H), 1.96 (q, J = 6.9 Hz, 2H), 1.82 (t, J = 7.1 Hz, 2H), 1.74-1.63 (m, 1H), 1.40-1.24 (m, 4H), 1.19 (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 169.7, 141.5, 138.9, 115.0, 114.3, 61.8, 50.2, 44.1, 34.1, 33.4, 32.6, 32.4, 25.6, 14.4; HRMS-ES $[M + H]^+$ calcd for $C_{17}H_{28}ClO_4$, 331.1676; found, 331.1674.



2-(3-Chlorocyclohept-3-enylmethyl)-malonic Acid Diethyl Ester (33). A flame dried 250 mL two necked flask equipped with a magnetic stirring bar and a condenser was charged with diene **32** (250 mg, 0.76 mmol)

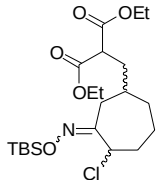


and benzene (200 mL). The resulting solution was deaerated by bubbling argon through the mixture for 2 h. The second-generation Grubbs catalyst (66 mg, 0.076 mmol) in 2 mL of benzene was added and the argon bubbling was continued for an additional 30 min. The mixture was heated and stirred at 65 °C for 6-7 days until TLC showed the reaction was complete. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (10% EtOAc/hexanes) to afford the vinyl chloride **33** as a yellow oil (180 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.89 (t, J = 6.5 Hz, 1H), 4.12 (dq, J = 1.9, 7.0 Hz, 4H), 3.37 (t, J = 7.7 Hz, 1H), 2.44-2.42 (m, 2H), 2.04-1.95 (m, 2H), 1.84-1.78 (m, 3H), 1.65-1.57 (m, 2H), 1.45-1.32 (m, 2H), 1.21 (dt, J = 0.9, 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 169.8, 133.9, 129.6, 61.8, 50.2, 43.2, 37.0, 34.9, 34.0, 27.9, 24.8, 14.4; HRMS-ES $[M + H]^+$ calcd for $C_{15}H_{24}ClO_4$, 303.1363; found, 303.1358.

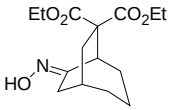
2-(4-Chloro-3-oxocycloheptylmethyl)-malonic Acid Diethyl Ester (34). To a stirred solution of vinyl chloride **33** (94 mg, 0.31 mmol) in acetone (5 mL) and glacial acetic acid (2 mL) at 0 °C was added dropwise sodium hypochlorite (0.23 mL of 10% solution, 0.31 mmol) via syringe. The reaction mixture was stirred at 0 °C for 1 h and quenched by addition of saturated aqueous $NaHCO_3$ solution. The mixture was then extracted with dichloromethane (10 mL x 2). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (50% ether/hexanes) affording the α-chloroketone **34** as a clear oil (56 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$, 2:1 diastereomeric mixture) δ 4.26 (t, J =

4.8 Hz, 1H, *minor*), 4.06-3.94 (m, 5H *major*, 4H *minor*), 3.19 (t, *J* = 7.7 Hz, 1H, *major and minor*), 2.71-2.65 (m, 1H, *minor*), 2.46-2.38 (m, 1H, *major*), 2.29-2.05 (m, 3H, *major and minor*), 1.82-1.51 (m, 5H, *major and minor*), 1.08-1.02 (m, 8H, *major and minor*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.7, 204.7, 169.6, 169.5, 169.4, 65.4, 62.4, 62.0, 62.0, 50.0, 50.0, 46.0, 44.9, 36.1, 35.9, 35.9, 35.4, 35.2, 35.2, 34.2, 33.2, 25.1, 23.2, 14.4; HRMS-ES $[M + Na]^+$ calcd for $C_{15}H_{23}ClNaO_5$, 341.1132; found, 341.1141.

2-(4-Chloro-3-*tert*-butyldimethylsilyloxyimino-cycloheptylmethyl)-malonic Acid Diethyl Ester (35). To a solution of α-chloroketone **34** (48 mg, 0.15 mmol) in dichloromethane (3 mL) were added *O*-(*tert*-butyldimethylsilyl)-hydroxylamine (45 mg, 0.30 mmol), 4Å molecular sieves (crushed), and a catalytic amount of PPTS. The mixture was stirred at rt for 48 h and then filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (20% ether/hexanes) to afford the α-chloroketoxime **35** (colorless oil) as a complex mixture of stereoisomers (57 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$,) δ 5.47 (s, 0.02H), 5.26 (dd, *J* = 4.4, 8.1 Hz, 0.28H), 5.09 (dd, *J* = 6.3, 10.7 Hz, 0.18H), 4.75-4.72 (m, 0.11H), 4.57-4.39 (m, 0.27H), 4.10-3.92 (m, 4H), 3.43-3.28 (m, 1H), 3.22-3.16 (m, 0.25H), 2.86 (d, *J* = 11.8 Hz, 0.33H), 2.60-1.49 (m, 9H), 1.32-1.27 (m, 1.5H), 1.16-1.07 (m, 6H), 0.77 (s, 9H), 0.00 (s, 6H); HRMS-ES $[M + H]^+$ calcd for $C_{21}H_{39}ClNO_5Si$, 448.2286; found, 448.2274.

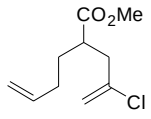


9-Hydroxyiminobicyclo[3.2.2]nonane-6,6-dicarboxylic Acid Diethyl Ester (36). To a stirred solution of oxime **35** (20.0 mg, 0.044



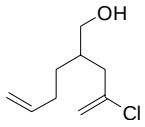
mmol) in THF (2 mL) at –78 °C was added dropwise NaHMDS (1 M in THF, 0.044 mL, 0.044 mmol) via syringe, and the reaction mixture was stirred at –78 °C for 1 h. TBAF (1 M in THF, 0.067 mL, 0.067 mmol) was added dropwise via syringe, and the mixture was warmed to rt over 2 h. Saturated aqueous NH_4Cl (5 mL) was then added. The mixture was extracted with ether (10 mL x 3), and the combined extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (50% ether/hexanes) to afford the bridged bicyclic oxime **36** as a colorless oil (6.9 mg, 53%). ^{1}H NMR (300 MHz, $CDCl_3$, 5:1 geometrical isomer mixture) δ 7.62 (br s, 1H, *major and minor*), 4.10-3.88 (m, 4H, *major and minor*), 3.18 (t, *J* = 4.7 Hz, 1H, *major*), 2.91 (t, *J* = 2.8 Hz, 1H, *minor*), 2.55-2.45 (m, 1H, *major*), 2.32-2.09 (m, 4H, *major and minor*), 1.98-1.94 (m, 1H, *minor*), 1.86-1.75 (m, 2H, *minor*), 1.64 (q, J = 5.9 Hz, 2H, *major*), 1.54-1.48 (m, 2H, *major and minor*), 1.41-1.19 (m, 2H, *major and minor*), 1.12-1.02 (m, 6H, *major and minor*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 171.6, 171.5, 171.2, 161.5, 161.2, 62.1, 62.0, 57.0, 55.3, 42.5, 37.6, 34.9, 33.1, 32.9, 30.5, 30.4, 30.1, 28.6, 27.5, 25.7, 24.4, 21.6, 21.0, 14.4, 14.4, 14.3; HRMS-ES $[M + H]^+$ calcd for $C_{15}H_{24}NO_5$, 298.1654; found, 298.1662.

2-(2-Chloroallyl)-hex-5-enoic Acid Methyl Ester (37). To a solution of LDA (2 M in THF, 10 mL, 20.0 mmol) and DMPU (2.8 mL, 21.8 mmol) in THF (15 mL) was added 5-hexenoic acid methyl ester (2.00 g, 15.6 mmol) in THF (15 mL) dropwise at -78 °C. The mixture was stirred for 45 min at -78 °C. 2-Chloro-3-iodopropene (4.0 g, 19.8 mmol) was added, and the reaction mixture was allowed to warm to 0 °C over 3 h. Saturated aqueous NH_4Cl (30 mL) and EtOAc (50

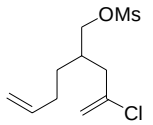


mL) were added. The organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford the title compound **37** as a yellow oil (2.52 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (m, 1H), 5.12 (dd, *J* = 1.1, 8.9 Hz, 2H), 4.99-4.93 (m, 0.5H), 4.95-4.93 (m, 1H), 4.91-4.90 (m, 0.5H), 3.61 (s, 3H), 2.63-2.60 (m, 1H), 2.64 (dd, *J* = 8.3, 22.6 Hz, 2H), 2.38 (dd, *J* = 6.2, 14.3 Hz, 1H), 2.01-1.98 (m, 2H), 1.63-1.72 (m 1H), 1.59-1.61 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5, 140.2, 137.7, 115.7, 114.6, 51.9, 43.1, 41.9, 31.6, 31.1.

2-(2-Chloroallyl)-hex-5-en-1-ol (38). To a suspension of $LiAlH_4$ (1.5 g, 39.8 mmol) in THF (50 mL) at 0 °C was added dropwise ester **37** (4.50 g, 22.3 mmol) in ether (50 mL) over 10 min. The mixture was stirred for 12 h at rt, and diluted with EtOAc (20 mL). The mixture was then poured into 1 M HCl solution (30 mL) and saturated aqueous NH_4Cl (10 mL) and EtOAc (10 mL) were added. The organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (10-30% EtOAc/hexanes gradient) to afford the title compound **38** as a clear oil (3.09 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81-5.68 (m, 1H), 5.13 (dd, *J* =0.9, 11.7 Hz, 2H), 5.01-4.88 (m, 2H), 3.55 (t, *J* = 4.3 Hz, 2H), 2.40 (dd, *J* = 7.5, 14.3 Hz, 1H), 2.25 (dd, *J* = 6.7, 14.2 Hz, 1H), 2.12-1.99 (m, 2H), 1.93-1.80 (m, 1H), 1.49-1.30 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.9, 138.9, 115.2, 114.3, 64.5, 41.5, 37.9, 31.4, 29.8; HRMS-EI $[M]^+$ calcd for $C_9H_{15}ClO$, 174.0811; found, 175.0815.

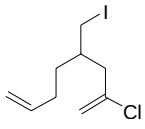


Methanesulfonic Acid 2-(2-Chloroallyl)-hex-5-enyl Ester (39).



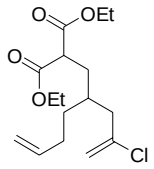
To a solution of alcohol **38** (152 mg, 0.87 mmol) in dichloromethane (3 mL) at 0 °C was added portionwise triethylamine (117 μL, 0.79 mmol) and mesyl chloride (40 μL, 0.54 mmol). The mixture was stirred at 0 °C for 30 min, and then at rt for 30 min. The organic phase was washed consecutively with brine (10 mL), 1 M aqueous $KHSO_4$ (10 mL), brine (10 mL), 5% aqueous $NaHCO_3$ (10 mL), brine (10 mL), and dried over Na_2SO_4 overnight. The solvent was removed under reduced pressure to afford the title compound **39** as a clear oil which was used for the next step without further purification (206 mg, 94%). ^{1}H NMR (75 MHz, $CDCl_3$) δ 5.81-5.72 (m, 1H), 5.20-5.09 (m, 4H), 4.21-4.19 (m, 2H), 3.03 (s, 3H), 2.45-2.40 (m, 2H), 2.21-2.17 (m, 2H), 1.92-1.86 (m, 1H), 1.73-1.70 (m, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 142,4, 135.2, 118.2, 113.1, 71.6, 37.6, 36.9, 36.6, 35.2, 28.2; HRMS-ES $[M + Na]^+$ calcd for $C_{10}H_{17}O_3SClNa$, 275.0485; found, 275.0487.

2-Chloro-4-iodomethylocta-1,7-diene (40). To a solution of mesylate **39** (3.09 g, 12.30 mmol) in acetone (30 mL) was added sodium iodide (5.51 g, 36.70 mmol), and the mixture was stirred at 60 °C for 5 h.

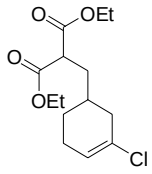


The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography (pentane) to afford the title compound **40** as a clear oil (3.29 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87-5.78 (m, 1H), 5.29 (dd, J = 0.7, 7.6 Hz, 2H), 5.10-5.00 (m, 2H), 3.50 (ddd, J = 0.9, 7.0, 14.1 Hz, 1H), 3.32 (ddd, J = 3.7, 10.1, 21.6 Hz, 2H), 2.14 (dd, J = 21.8, 25.1, 1H), 2.04 (dd, J = 21.8, 25.1, 1H), 1.46-1.49 (m, 4H), 1.22-1.21 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 138.1, 115.7, 115.3,

44.6, 34.7, 33.4, 31.0, 15.6; HRMS-EI $[M]^+$ calcd for $C_9H_{14}ClI$, 283.9822; found, 283.9829.

2-[2-(2-Chloroallyl)-hex-5-enyl]-malonic Acid Diethyl Ester (41). 

To a solution of iodide **40** (816 mg, 2.90 mmol) and diethyl malonate (486 mg, 3.04 mmol) in acetonitrile (50 mL) was added Verkade's base (656 mg, 3.04 mmol), and the reaction mixture was stirred at rt for 24 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (5-20% EtOAc/hexanes gradient) to afford the title compound **41** as a clear oil (653 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87-5.73 (m, 1H), 5.22 (d, J = 16.2 Hz, 2H), 5.08-4.97 (m, 2H), 4.22 (dd, J = 7.1, 14.2 Hz, 4H), 3.54-3.45 (m, 1H), 2.39-2.26 (m, 2H), 2.14-2.04 (m, 2H), 1.96-1.91 (m, 2H), 1.84-1.76 (m, 1H), 1.60 (s, 1H), 1.49-1.32 (m, 1H), 1.30 (t, J = 5.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 115.2, 114.5, 61.8, 50.2, 44.0, 33.1, 32.6, 32.0, 30.6, 14.4; HRMS-ES $[M + Na]^+$ calcd for $C_{16}H_{25}ClNaO_4$, 339.1339; found, 339.1349.

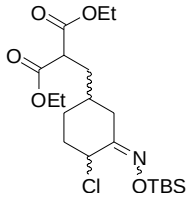
2-(3-Chlorocyclohex-3-enylmethyl)-malonic Acid Diethyl Ester (42). 

A flame dried 50 mL two necked flask equipped with a condenser and a magnetic stirring bar was charged with ester **41** (100 mg, 0.32 mmol) and benzene (40 mL). The mixture was deaerated with argon for 1 h. Grubbs 2nd generation catalyst (20 mg, 0.03 mmol) in benzene (10 mL) was added *via* syringe. The mixture was deaerated with argon for another 20 min and then heated at 65 $^{\circ}$C for three days. The solvent was removed under reduced pressure, and the residue was purified by flash

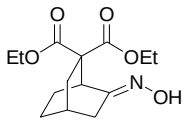
column chromatography (2 - 5% ether/pentane gradient) to afford the title compound **42** as a yellow oil (67 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72-5.70 (m, 1H), 4.18-4.08 (m, 4H), 2.31-2.26 (m, 1H), 2.09-1.80 (m, 5.5H), 1.67-5.58 (m, 2.5H), 1.20 (t, *J* = 8.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 128.7, 122.5, 59.7, 47.8, 36.9, 32.8, 31.1, 25.4, 23.7, 12.3; HRMS-AP $[M + H]^+$ calcd for $C_{14}H_{22}O_4Cl$, 289.1207; found, 289.1214.

2-(4-Chloro-3-Oxocyclohexylmethyl)-malonic Acid Diethyl Ester (43). To a solution of ester **42** (280 mg, 0.97 mmol), acetone (3.39 mL), glacial acetic acid (1.60 mL) at 0 °C was added dropwise aqueous sodium hypochlorite (638 μL of 10% solution, 0.97 mmol) *via* syringe. The reaction mixture was stirred at 0 °C for 30 min, and quenched by addition of aqueous saturated Na_2CO_3 solution. The mixture was then extracted with dichloromethane (20 mL x 2). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (10% EtOAc/hexanes) to afford the title compound **43** (yellow oil) as a 4:6 mixture of diastereomers (139 mg, 47%, 67% brsm). For characterization purposes the two diastereomers were separated by column chromatography. *More polar major diastereomer:* ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75-4.74 (m, 1H), 4.18-4.08 (m, 4H), 3.37-3.31 (m, 1H), 2.65-2.60 (m, 1H), 2.17-1.94 (m, 4H), 1.82-1.77 (m, 2H), 1.52-1.40 (m, 1H), 1.23-1.17 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.9, 169.6, 169.4, 62.2, 62.0, 61.9, 60.5, 49.6, 42.7, 37.1, 35.0, 34.8, 33.8, 32.7, 30.6 ,25.9, 22.3, 14.4. *Less polar minor diastereomer:* ^{1}H NMR (400 MHz, $CDCl_3$) δ (m, 4.40-4.33, 1H), 4.16-4.09

(m, 4H), 3.30 (t, J = 4.0 Hz, 1H), 2.68-2.63 (m, 1H), 2.48-2.44 (m, 1H), 2.06-1.79 (m, 6H), 1.50-1.49 (m, 1H), 1.23-1.17 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.5, 170.4, 64.9, 63.2, 50.9, 47.9, 38.7, 37.9, 36.1, 32.3, 15.5; HRMS-ES $[M + Na]^+$ calcd for $C_{14}H_{21}ClNaO_5$, 327.0975; found, 327.0984.

2-(4-Chloro-3-*tert*-butyldimethylsilyloxyimino-cyclohexylmethyl)-malonic Acid Diethyl Ester (44). 

To a solution of α-chloroketone **43** (131 mg, 0.43 mmol) in dichloromethane (0.7 mL) were added *O*-(*tert*-butyldimethylsilyl)-hydroxylamine (127 mg, 0.86 mmol), 4Å molecular sieves (crushed), and a catalytic amount of PPTS. The mixture was stirred at rt for 12 h and then filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (10% EtOAc/hexanes) to afford the title compound **44** as a clear oil which was an inseparable complex mixture of diastereomers (171 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.51 (brs, 0.3H), 4.95 (brs, 0.6H), 4.11-3.95 (m, 4H), 3.34-3.06 (m, 1H), 2.12-2.00 (m, 1H), 1.91-1.71 (m, 2H), 1.67-1.48 (m, 3H), 1.43-1.27 (m, 2H), 1.11 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H), 0.74 (s, 9H), 0.00 (s, 6H); HRMS-ES $[M + H]^+$ calcd for $C_{20}H_{37}NO_5SiCl$, 434.2130; found, 434.2130.

6-Hydroxyiminobicyclo[2.2.2]octane-2,2-dicarboxylic Acid Diethyl Ester (45). 

To a solution of oxime **44** (20 mg, 0.046 mmol) in THF (0.5 mL) at -78 °C was added dropwise NaHMDS (2 M in THF, 31 μL, 0.062 mmol) *via* syringe, and the reaction mixture was stirred at -78 °C for 1 h. TBAF (1 M in

THF, 62 μL, 0.062 mmol) was added dropwise *via* syringe, and the mixture was warmed to rt over 2 h. Saturated aqueous NH_4Cl (5 mL) was then added. The mixture was extracted with ether (10 mL x 3), and the combined extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (50% ether/pentane) to afford the title compound **45** as a clear oil (10 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (m, 1H), 4.25-4.11 (m, 4H), 3.07 (m, 1H), 2.41 (m, 2H), 2.25 (m, 2H), 2.21-1.97 (m, 1H), 1.96-1.90 (m, 1H), 1.65-1.47 (m, 3H), 1.28-1.19 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 171.2, 161.0, 62.1, 62.0, 55.3, 37.6, 32.9, 30.4, 25.7, 24.3, 21.6, 14.4, 14.3; HRMS-ES $[M + H]^+$ calcd for $C_{14}H_{22}NO_5$, 284.1498; found, 284.1496.

2-(2-Chloroallyloxy)-but-3-en-1-ol (47). To a suspension of $LiAlH_4$ (0.18 g, 4.73 mmol) in THF (20 mL) at 0 °C was added dropwise ester **46** (1.00 g, 4.73 mmol) in ether (20 mL) over 5 min. The mixture was stirred for 2 h at rt, and diluted with EtOAc (10 mL). The mixture was then poured into saturated aqueous NH_4Cl (10 mL) and extracted with EtOAc (10 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (10-30% EtOAc/hexanes gradient) to afford the title compound **47** as a clear oil (0.75 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.18-5.45 (m, 1H), 5.49 (d, J = 1.2Hz, 1H), 5.39 (d, J = 0.6 Hz, 1H), 5.29 (dd, J = 0.6, 0.7 Hz, 1H), 5.26 (dd, J = 3.8, 0.8 Hz, 1H), 4.16-4.01 (m, 3H), 3.96-3.79 (m, 2H), 2.35 (m, 1H), 1.90-1.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 137.8, 118.5, 114.4, 80.2, 70.9, 60.7, 38.2; HRMS-ES $[M + Na]^+$ calcd for $C_8H_{13}ClO_2Na$, 199.0502; found 199.0500.

Methanesulfonic Acid 2-(2-Chloroallyloxy)-but-3-enyl Ester (48). To a solution of alcohol **47** (1.22 g, 6.90 mmol) in dichloromethane (21 mL) at 0 °C was added triethylamine (928 μL, 6.27 mmol) and mesyl chloride (562 μL, 7.59 mmol) portionwise. The mixture was stirred at 0 °C for 30 min, and then at rt for 30 min. The organic phase was washed consecutively with brine (10 mL), 1 M aqueous $KHSO_4$ (10 mL), brine (10 mL), 5% aqueous $NaHCO_3$ (10 mL), brine (10 mL), and dried over Na_2SO_4 overnight. The solvent was removed under reduced pressure to afford the title compound **48** as a clear oil used for the next step without further purification (206 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70-5.67 (m, 1H), 5.45 (s, 1H), 5.44 (s, 1H), 5.37-5.27 (m, 2H), 4.43-4.33 (m, 2H), 4.13-4.08 (m, 1H), 3.97-3.93 (m, 2H), 3.02 (s, 3H), 2.06-1.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 137.2, 119.4, 114.4, 77.4, 71.0, 67.1, 37.6, 35.4; HRMS-ES $[M + H]^+$ calcd for $C_9H_{16}ClO_4S$, 254.0458; found 255.0463.

3-(2-Chloroallyloxy)-5-iodopent-1-ene (49). To a solution of mesylate **48** (400 mg, 1.60 mmol) in acetone (10 mL) was added sodium iodide (964 mg, 6.40 mmol), and the mixture was stirred at 60 °C for 5 h. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography (pentane) to afford the title compound **49** as a clear oil (399 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77-5.65 (m, 1H), 5.47 (dd, J = 1.3, 2.6 Hz, 1H), 5.39-5.29 (m, 3H), 4.15-3.80 (m, 3H), 3.76-3.22 (m, 2H), 2.23-1.94 (m, 2H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 137.2, 119.0, 114.0, 80.8, 71.1, 39.5, 2.3; HRMS-AP $[M+H]^+$ calcd for $C_8H_{13}ClIO$, 286.9700; found, 286.9706.

2-[3-(2-Chloroallyloxy)-pent-4-enyl]-malonic Acid Diethyl Ester (50). To a solution of iodide **49** (881 mg, 3.09 mmol) and diethyl malonate (520 mg, 3.24 mmol) in acetonitrile (40 mL) was added Verkade's base (700 mg, 3.24 mmol), and the reaction mixture was stirred at rt for 24 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (5-20% EtOAc/hexanes gradient) to afford the title compound **50** as a clear oil (827 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.73-5.61 (m, 1H), 5.45-5.20 (m, 4H), 4.25-4.17 (m, 4H), 4.00 (dd, *J* = 13.8, 44.4 Hz, 2H), 3.77 (q, *J* = 7.1 Hz, 1H), 3.37 (m, 1H), 2.09-1.89 (m, 2H), 1.80-1.46 (m, 2H), 1.27 (t, *J*=6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 138.8, 138.0, 118.5, 113.5, 80.6, 70.7, 61.6, 52.0, 33.1, 25.0, 14.4; HRMS-ES $[M+H]^+$ calcd for $C_{15}H_{24}ClO_5$, 319.1312; found, 319.1310.

2-[2-(4-Chloro-2,5-dihydrofuran-2-yl)-ethyl]-malonic Acid Diethyl Ester (51). A flame dried 50 mL two necked flask equipped with a condenser and a magnetic stirring bar was charged with ester **50** (100 mg, 0.35 mmol) and toluene (60 mL). The mixture was deaerated with argon for 1 h. Grubbs 2nd generation catalyst (30 mg, 0.03 mmol) in toluene (10 mL) was added *via* syringe. The combined mixture was deaerated with argon for another 20 min and then heated at 120 °C for 24 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (2-5% ether/pentane gradient) to

afford the title compound **51** as a yellow oil (63 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78-5.74 (m, 1H), 4.92-4.87 (m, 1H), 4.55-4.50 (m, 2H), 4.23-4.17 (m, 4H), 3.36 (t, *J* = 6.0 Hz, 1H), 1.98-1.93 (m, 2H), 1.65-1.60 (m, 2H), 1.27 (t, *J* = 9.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 129.0, 124.9, 85.9, 76.1, 61.8, 52.1, 33.6, 24.5, 14.4; HRMS-ES $[M+H]^+$ calcd for $C_{13}H_{20}ClO_5$, 291.0999; found, 291.0995.

2-[2-(3-Chloro-4-oxotetrahydrofuran-2-yl)-ethyl]-malonic Acid Diethyl Ester (52). To a solution of ester **51** (125 mg, 0.43 mmol), in acetone (1.86 mL), and glacial acetic acid (0.75 mL) at 0 °C was added dropwise aqueous sodium hypochlorite (300 μL of 10% solution, 0.47 mmol) *via* syringe. The reaction mixture was stirred for 20 min at 0 °C and quenched by addition of aqueous saturated Na_2CO_3 solution. The mixture was then extracted with dichloromethane (20 mL x 2). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (10% EtOAc/hexanes) to afford the title compound **52** (yellow oil) as an inseparable 1:1 mixture of diastereomers (73 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38-3.92 (m, 6H), 3.91-3.82 (m, 1H), 3.42-3.35 (m, 1H), 2.31-1.67 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.3, 169.7, 169.4, 124.9, 85.9, 80.6, 77.8, 77.4, 69.6, 61.9, 61.8, 57.7, 52.1, 52.0, 51.9, 51.0, 42.9, 41.7, 38.3, 33.6, 28.1, 24.8, 24.5, 22.8, 17.0, 14.4, 14.3; HRMS-ES $[M+H]^+$ calcd for $C_{13}H_{20}ClO_6$, 307.0948; found, 307.0943.

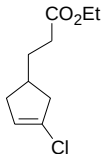
2-[2-(3-Chloro-4-*tert*-butyldimethylsilyloxyimino-tetrahydrofuran-2-yl)-ethyl]-malonic Acid Diethyl Ester (53). To

a solution of α-chloroketone **52** (10 mg, 0.03 mmol) in dichloromethane (0.5 mL) were added *O*-(*tert*-butyldimethylsilyl)-hydroxylamine (10 mg, 0.07 mmol), 4Å molecular sieves (crushed) and a catalytic amount of PPTS. The mixture was stirred at rt for 24 h and then filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (10% EtOAc/hexanes) to afford the title compound **53** (clear oil) as an inseparable complex mixture of stereoisomers (6 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76-4.36 (m, 3H), 4.30-4.18 (m, 4H), 4.21-4.01 (m, 1H), 4.47-4.36 (m, 3H), 4.30-4.19 (m, 4H), 3.43-3.37 (m, 6H), 1.33-1.24 (m, 6H), 0.94 (s, 9H), 0.16 (s, 6H); HRMS-ES $[M+H]^+$ calcd for $C_{19}H_{35}ClNO_6Si$, 436.1922; found, 436.1928.

3-Hydroxyiminohexahydrocyclopenta[b]furan-4,4-dicarboxylic Acid Diethyl Ester (54). To a solution of oxime **53** (8 mg, 0.018 mmol) in THF (0.5 mL) at -78 °C was added dropwise NaHMDS (2 M in THF, 24 μL, 0.024 mmol) *via* syringe, and the reaction mixture was stirred at -78 °C for 1 h. TBAF (1 M in THF, 48 μL, 0.048 mmol) was then added dropwise *via* syringe, and the mixture was warmed to 0 °C over 2 h. Saturated aqueous NH_4Cl (5 mL) was then added. The mixture was extracted with ether (10 mL x 3), and the combined extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (50% ether/pentane) to afford the title compound **54** as a clear oil (6 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 (t, J = 5.2Hz, 1H), 4.52 (dd, J = 15.2, 41.1 Hz, 2H), 4.45-4.02 (m, 5H), 2.64 (td, J = 6.7, 13.3 Hz, 2H), 2,26 (q, J = 6.8 Hz, 1H), 2.04 (q, J = 7.2 Hz, 1H), 1.72-1.62 (m, 1H), 1.29 (m,

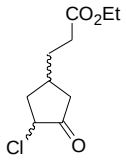
6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 169.4, 164.2, 85.5, 77.6, 67.7, 65.5, 62.4, 62.0, 50.9, 33.0, 32.2, 30.1, 14.3; HRMS-ES $[M+H]^+$ calcd for $C_{13}H_{20}NO_6$, 286.1291; found, 286.1290.

3-(3-Chlorocyclopent-3-enyl)-propionic Acid Ethyl Ester (55).



To a stirred solution of diester **24** (100 mg, 0.36 mmol) and water (0.05 mL) in DMSO (3 mL) was added LiCl (35 mg, 0.79 mmol). The reaction mixture was heated at reflux for 5 h, and then cooled to rt. Saturated aqueous NH_4Cl (10 mL) was added and the aqueous phase was extracted with ether (10 mL x 3). The combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (15% ether/hexanes) to afford the monoester **55** as a clear oil (68 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.53-5.50 (m, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.57-2.41 (m, 2H), 2.35-2.30 (m, 1H), 2.23 (t, *J* = 5.2 Hz, 2H), 2.20-2.12 (m, 1H), 1.99-1.90 (m, 1H), 1.70 (q, *J* = 7.3 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 130.1, 124.4, 59.3, 42.1, 36.3, 35.7, 31.6, 30.2, 13.1; HRMS-AP $[M+H]^+$ calcd for $C_{10}H_{16}ClO_2$, 203.0839; found, 203.0838.

3-(3-Chloro-4-Oxocyclopentyl)-propionic Acid Ethyl Ester (56).

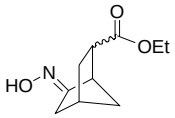


To a solution of vinyl chloride **55** (121 mg, 0.59 mmol), acetone (2.5 mL) and glacial acetic acid (1 mL) at 0 °C was added dropwise sodium hypochlorite (0.48 mL of 10% solution, 0.59 mmol) via syringe. The reaction mixture was stirred at 0 °C for 1 h and quenched by addition of saturated aqueous $NaHCO_3$ solution. The

mixture was then extracted with dichloromethane (10 mL x 2). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (50% ether/hexanes) affording the α-chloroketone **56** as a clear oil (60 mg, 46%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.07 (q, *J* = 7.1 Hz, 3H), 2.63-2.43 (m, 2H), 2.30 (t, *J* = 7.2 Hz, 2H), 2.28-2.23 (m, 1H), 1.94-1.69 (m, 4H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.2, 173.3, 61.0, 57.7, 42.4, 39.9, 33.5, 32.9, 30.5 14.6; HRMS-ES $[M + Na]^+$ calcd for $C_{10}H_{15}ClNaO_3$, 241.0607; found, 241.0604.

3-(3-Chloro-4-*tert*-butyldimethylsilyloxyiminocyclopentyl)-propionic Acid Ethyl Ester (11). To a solution of α-chloroketone **56** (52 mg, 0.23 mmol) in dichloromethane (3 mL) were added *O*-(*tert*-butyldimethylsilyl)-hydroxylamine (50 mg, 0.34 mmol), 4Å molecular sieves (crushed), and a catalytic amount of PPTS. The mixture was stirred at rt for 12 h and then filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (20% ether/hexanes) to afford the α-chloroketoxime **11** as a colorless oil (76 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$, 2:1 geometrical isomer mixture) δ 4.84 (d, *J* = 5.6 Hz, 1H, *minor*), 4.62 (d, *J* = 5.1 Hz, 1H, *major*), 3.97 (q, *J* = 7.1 Hz, 2H, *major and minor*), 2.75-2.60 (m, 1H, *major and minor*), 2.35-2.30 (m, 1H, *major and minor*), 2.22-2.15 (m, 2H, *major and minor*), 2.10-2.03 (m, 1H, *major and minor*), 1.88-1.78 (m, 1H, *major and minor*), 1.63-1.48 (m, 3H, *major and minor*), 1.09 (t, *J* = 7.1 Hz, 3H, *major and minor*), 0.77 (s, 9H, *minor*), 0.75 (s, 9H,

major), 0.00 (s, 6H, *major*), -0.01 (s, 6H, *minor*); HRMS-ES $[M + H]^+$ calcd for $C_{16}H_{31}ClNO_3Si$, 348.1762; found, 348.1760.

6-Hydroxyiminobicyclo[2.2.1]heptane-2-carboxylic Acid Ethyl Ester (12, 13, 14). 

To a stirred solution of oxime **11** (20.0 mg, 0.057 mmol) in THF (3 mL) at –78 °C was added dropwise KHMDS (0.5 M in toluene, 0.15 mL, 0.068 mmol) via syringe, and the reaction mixture was stirred at –78 °C for 1 h. The reaction mixture was diluted with 9 mL of THF. TBAF (1 M in THF, 0.057 mL, 0.057 mmol) was added dropwise via syringe, and the mixture was warmed to rt over 2 h and stirred at rt for 12 h. Saturated aqueous NH_4Cl (5 mL) was then added. The mixture was extracted with ether (10 mL x 3), and the combined extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (50% ether/hexanes) to afford the bridged bicyclic oxime **12, 13, 14** (8:7:10 by NMR integration) as a clear oil (10.9 mg, 99%)**.** One oxime geometric isomer of the *anti* ester **12** or **13** was isolated in pure form, while **14** and the other *anti* isomer **12** or **13** were obtained as an inseparable mixture. More polar isomer (inseparable 2:1 mixture of **14** and **12** or **13**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (s, 1H, *major*), 7.69 (s, 1H, *minor*), 4.04-3.93 (m, 2H, *major and minor*), 3.65 (s, 1H, *major*), 2.98-2.96 (m, 1H, *minor*), 2.83-2.76 (m, 1H, *minor*), 2.44-2.40 (m, 2H *major,* 1H *minor*), 2.24-2.01 (m, 2H, *major*), 1.91-1.83 (m, 2H, *major*), 1.71-1.65 (m, 2H, *minor*), 1.56-1.44 (m, 2H, *major and minor*), 1.30-1.26 (m, 2H, *minor*), 1.14-1.07 (m, 3H, *major and minor*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7, 173.8, 165.1, 164.4, 61.2, 61.1, 46.7, 45.2, 42.7, 42.2, 40.7, 37.0, 36.5, 35.9, 35.6, 34.6, 32.6, 31.0, 14.6; HRMS-ES $[M + H]^+$ calcd for $C_{10}H_{16}NO_3$, 198.1130; found, 198.1132. Less polar isomer **12** or **13** (single geometrical isomer): ^{1}H

NMR (300 MHz, $CDCl_3$) δ 7.40 (s, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.99 (s, 1H), 2.48-2.44 (m, 2H), 2.21-2.13 (m, 1H), 1.97 (dd, *J* = 3.4, 17.6 Hz, 1H), 1.90-1.82 (m, 1H), 1.56-1.45 (m, 2H), 1.34-1.27(m, 1H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 166.4, 61.2, 46.5, 44.0, 37.4, 35.6, 34.5, 33.0, 14.6; HRMS-ES $[M + H]^+$ calcd for $C_{10}H_{16}NO_3$, 198.1130; found, 198.1134.

Crystal Structure Information for compound 9

A colorless brick shaped crystal of **9** (C14 H22 N O5) with approximate dimensions 0.07 x 0.10 x 0.15 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 103(2) K, cooled by Rigaku-MSC X-Stream 2000, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of 0.3º in ω and an exposure time of 40 seconds/frame. The total data collection time was about 24 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Monoclinic unit cell yielded a total of 21513 reflections to a maximum θ angle of 28.34° (0.90 Å resolution), of which 6959 were independent, completeness = 98.1%, R_{int} = 0.0582, R_{sig} = 0.0754 and 4723 were greater than 2σ(I). The final cell constants: a = 12.467(3)Å, b = 15.301(4)Å, c = 14.892(4)Å, α = 90°, β = 90.615(5)°, γ = 90°, volume = 2840.6(12)$Å^3$, are based upon the refinement of the XYZ-centroids of 7040 reflections above 20σ(I) with 2.501° <θ <28.324° . Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.7006.

The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P2(1)/n, with Z = 8 for the formula unit, C14 H22 N O5 . The final anisotropic full-matrix least-squares refinement on F^2 with 367 variables converged at R1 = 10.72%, for the observed data and wR2 = 24.00% for all data. The goodness-of-fit was 1.193. The largest peak on the final difference map was 0.569 $e^-/Å^3$ and the largest hole was -0.580 $e^-/Å^3$. Based on the final model, the calculated density of the crystal is 1.330 g/cm^3 and F(000) amounts to 1224 electrons.

Note to users: The small molecule crystallographic facility was establish using funds from an NSF Chemistry Research Instrumentation and Facilities grant CHE-0131112.

Table 1. Sample and crystal data for 9.

Identification code	9	
Compound number	IK3-186	
X-ray lab-book	IK3	
Crystallization lab-book	IK3	
Crystallization solvents	CDCl3	
Crystallization method	slow evaporation	
Empirical formula	C14 H22 N O5	
Formula weight	284.33	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.15 x 0.10 x 0.07 mm	
Crystal habit	colorless brick	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.467(3) Å	α= 90°
	b = 15.301(4) Å	β= 90.615(5)°
	c = 14.892(4) Å	γ = 90°
Volume	2840.6(12) $Å^3$	
Z	8	
Density (calculated)	1.330 g/cm^3	
Absorption coefficient	0.100 mm^{-1}	
F(000)	1224	

Table 2. Data collection and structure refinement for 9.

Diffractometer	CCD area detector
Radiation source	fine-focus sealed tube, MoKα
Generator power	1600 watts (50 kV, 32mA)
Detector distance	5.8 cm
Data collection method	phi and omega scans
Theta range for data collection	1.91 to 28.34°
Index ranges	$-16 \leq h \leq 12$, $-20 \leq k \leq 20$, $-19 \leq l \leq 18$

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 9.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C1	0.7571(3)	0.2316(2)	0.4429(2)	0.0207(8)
C2	0.8689(3)	0.2068(2)	0.4775(2)	0.0193(8)
C3	0.8872(3)	0.1098(3)	0.4606(3)	0.0239(8)
C4	0.8040(3)	0.0520(2)	0.5075(3)	0.0212(8)
C5	0.6936(3)	0.0917(2)	0.5067(2)	0.0160(7)
C6	0.6858(3)	0.1894(2)	0.5148(2)	0.0137(7)
C7	0.8629(3)	0.2288(2)	0.5784(2)	0.0162(7)
C8	0.7415(3)	0.2222(2)	0.6019(2)	0.0123(7)
C9	0.6965(3)	0.3118(2)	0.6274(2)	0.0147(7)
C10	0.6987(3)	0.4168(2)	0.7458(3)	0.0276(9)
C11	0.5983(3)	0.3975(3)	0.7972(3)	0.0317(10)
C12	0.7184(3)	0.1640(2)	0.6823(2)	0.0143(7)
C13	0.5777(3)	0.1178(3)	0.7773(3)	0.0271(9)
C14	0.4586(3)	0.1241(3)	0.7804(3)	0.0293(9)
C15	0.7762(3)	0.2222(3)	-0.0484(2)	0.0230(8)
C16	0.8778(3)	0.1943(2)	0.0011(2)	0.0218(8)
C17	0.8957(3)	0.0969(3)	-0.0131(3)	0.0251(9)
C18	0.8018(3)	0.0411(2)	0.0213(3)	0.0218(8)
C19	0.6950(3)	0.0843(2)	0.0077(2)	0.0157(7)
C20	0.6903(3)	0.1829(2)	0.0125(2)	0.0168(7)
C21	0.8532(3)	0.2174(2)	0.0994(2)	0.0178(7)
C22	0.7285(3)	0.2156(2)	0.1059(2)	0.0150(7)
C23	0.6837(3)	0.3073(2)	0.1232(3)	0.0188(7)
C24	0.6782(3)	0.4194(2)	0.2347(3)	0.0309(10)
C25	0.5747(3)	0.4127(3)	0.2837(3)	0.0323(10)
C26	0.6855(3)	0.1580(2)	0.1810(2)	0.0164(7)
C27	0.5186(4)	0.1147(3)	0.2463(3)	0.0322(10)

C28	0.4774(3)	0.1740(3)	0.3166(3)	0.0281(9)
N1	0.6063(2)	0.04967(19)	0.5012(2)	0.0194(7)
N2	0.6066(2)	0.04498(18)	-0.00337(19)	0.0159(6)
O1	0.6196(2)	-0.04165(17)	0.4923(2)	0.0300(7)
O2	0.61353(19)	0.16676(16)	0.69987(16)	0.0177(5)
O3	0.7821(2)	0.12183(16)	0.72455(17)	0.0222(6)
O4	0.7407(2)	0.33676(16)	0.70567(17)	0.0207(6)
O5	0.6313(2)	0.35278(16)	0.58618(18)	0.0227(6)
O6	0.6172(2)	-0.04694(16)	-0.00743(19)	0.0242(6)
O7	0.7375(2)	0.11439(18)	0.23114(18)	0.0279(6)
O8	0.5786(2)	0.16400(17)	0.18027(18)	0.0241(6)
O9	0.6297(2)	0.34882(17)	0.0724(2)	0.0281(6)
O10	0.7140(2)	0.33312(16)	0.20516(18)	0.0248(6)

Table 4. Bond lengths (Å) for 9.

C1-C2	1.529(5)	C1-C6	1.541(5)
C1-H1B	0.9900	C1-H1C	0.9900
C2-C3	1.523(5)	C2-C7	1.541(5)
C2-H2	1.0000	C3-C4	1.536(5)
C3-H3A	0.9900	C3-H3B	0.9900
C4-C5	1.505(5)	C4-H4A	0.9900
C4-H4B	0.9900	C5-N1	1.266(4)
C5-C6	1.503(5)	C6-C8	1.548(4)
C6-H6	1.0000	C7-C8	1.561(5)
C7-H7A	0.9900	C7-H7B	0.9900
C8-C12	1.521(5)	C8-C9	1.531(4)
C9-O5	1.192(4)	C9-O4	1.339(4)
C10-O4	1.462(4)	C10-C11	1.504(6)
C10-H10A	0.9900	C10-H10B	0.9900
C11-H11A	0.9800	C11-H11B	0.9800
C11-H11C	0.9800	C12-O3	1.197(4)
C12-O2	1.337(4)	C13-O2	1.449(4)
C13-C14	1.490(5)	C13-H13A	0.9900
C13-H13B	0.9900	C14-H14A	0.9800
C14-H14B	0.9800	C14-H14C	0.9800
C15-C16	1.520(5)	C15-C20	1.533(5)
C15-H15A	0.9900	C15-H15B	0.9900
C16-C17	1.522(5)	C16-C21	1.541(5)
C16-H16	1.0000	C17-C18	1.541(5)
C17-H17A	0.9900	C17-H17B	0.9900
C18-C19	1.499(5)	C18-H18A	0.9900
C18-H18B	0.9900	C19-N2	1.266(4)
C19-C20	1.511(5)	C20-C22	1.549(5)
C20-H20	1.0000	C21-C22	1.559(5)
C21-H21A	0.9900	C21-H21B	0.9900
C22-C26	1.525(5)	C22-C23	1.533(5)
C23-O9	1.191(4)	C23-O10	1.333(5)
C24-O10	1.462(4)	C24-C25	1.493(6)
C24-H24A	0.9900	C24-H24B	0.9900
C25-H25A	0.9800	C25-H25B	0.9800
C25-H25C	0.9800	C26-O7	1.188(4)
C26-O8	1.336(4)	C27-O8	1.454(4)
C27-C28	1.481(6)	C27-H27A	0.9900
C27-H27B	0.9900	C28-H28A	0.9800
C28-H28B	0.9800	C28-H28C	0.9800
N1-O1	1.414(4)	N1-H1A	0.8800
N2-O6	1.414(4)	N2-H2A	0.8800
O1-H1	0.8400	O6-H6A	0.8400

Symmetry transformations used to generate equivalent atoms (if any):

Table 5. Bond angles (°) for 9.

C2-C1-C6	101.1(3)	C2-C1-H1B	111.6
C6-C1-H1B	111.6	C2-C1-H1C	111.6
C6-C1-H1C	111.6	H1B-C1-H1C	109.4
C3-C2-C1	108.9(3)	C3-C2-C7	112.5(3)
C1-C2-C7	102.8(3)	C3-C2-H2	110.8
C1-C2-H2	110.8	C7-C2-H2	110.8
C2-C3-C4	112.4(3)	C2-C3-H3A	109.1
C4-C3-H3A	109.1	C2-C3-H3B	109.1
C4-C3-H3B	109.1	H3A-C3-H3B	107.8
C5-C4-C3	112.7(3)	C5-C4-H4A	109.0
C3-C4-H4A	109.0	C5-C4-H4B	109.0
C3-C4-H4B	109.0	H4A-C4-H4B	107.8
N1-C5-C6	117.0(3)	N1-C5-C4	125.6(3)
C6-C5-C4	117.4(3)	C5-C6-C1	108.8(3)
C5-C6-C8	111.1(3)	C1-C6-C8	100.9(3)
C5-C6-H6	111.8	C1-C6-H6	111.8
C8-C6-H6	111.8	C2-C7-C8	105.2(3)
C2-C7-H7A	110.7	C8-C7-H7A	110.7
C2-C7-H7B	110.7	C8-C7-H7B	110.7
H7A-C7-H7B	108.8	C12-C8-C9	104.8(3)
C12-C8-C6	112.5(3)	C9-C8-C6	109.6(3)
C12-C8-C7	114.0(3)	C9-C8-C7	110.9(3)
C6-C8-C7	105.1(3)	O5-C9-O4	124.8(3)
O5-C9-C8	126.4(3)	O4-C9-C8	108.9(3)
O4-C10-C11	110.3(3)	O4-C10-H10A	109.6
C11-C10-H10A	109.6	O4-C10-H10B	109.6
C11-C10-H10B	109.6	H10A-C10-H10B	108.1
C10-C11-H11A	109.5	C10-C11-H11B	109.5
H11A-C11-H11B	109.5	C10-C11-H11C	109.5
H11A-C11-H11C	109.5	H11B-C11-H11C	109.5
O3-C12-O2	124.0(3)	O3-C12-C8	126.8(3)
O2-C12-C8	109.2(3)	O2-C13-C14	107.9(3)
O2-C13-H13A	110.1	C14-C13-H13A	110.1
O2-C13-H13B	110.1	C14-C13-H13B	110.1
H13A-C13-H13B	108.4	C13-C14-H14A	109.5
C13-C14-H14B	109.5	H14A-C14-H14B	109.5
C13-C14-H14C	109.5	H14A-C14-H14C	109.5
H14B-C14-H14C	109.5	C16-C15-C20	100.8(3)
C16-C15-H15A	111.6	C20-C15-H15A	111.6
C16-C15-H15B	111.6	C20-C15-H15B	111.6
H15A-C15-H15B	109.4	C15-C16-C17	109.2(3)
C15-C16-C21	102.9(3)	C17-C16-C21	112.8(3)
C15-C16-H16	110.5	C17-C16-H16	110.5
C21-C16-H16	110.5	C16-C17-C18	112.6(3)

C16-C17-H17A	109.1	C18-C17-H17A	109.1
C16-C17-H17B	109.1	C18-C17-H17B	109.1
H17A-C17-H17B	107.8	C19-C18-C17	112.7(3)
C19-C18-H18A	109.0	C17-C18-H18A	109.0
C19-C18-H18B	109.0	C17-C18-H18B	109.0
H18A-C18-H18B	107.8	N2-C19-C18	125.4(3)
N2-C19-C20	116.6(3)	C18-C19-C20	118.0(3)
C19-C20-C15	109.6(3)	C19-C20-C22	110.7(3)
C15-C20-C22	101.3(3)	C19-C20-H20	111.6
C15-C20-H20	111.6	C22-C20-H20	111.6
C16-C21-C22	105.3(3)	C16-C21-H21A	110.7
C22-C21-H21A	110.7	C16-C21-H21B	110.7
C22-C21-H21B	110.7	H21A-C21-H21B	108.8
C26-C22-C23	105.9(3)	C26-C22-C20	111.4(3)
C23-C22-C20	109.7(3)	C26-C22-C21	114.5(3)
C23-C22-C21	111.1(3)	C20-C22-C21	104.3(3)
O9-C23-O10	125.2(3)	O9-C23-C22	125.9(3)
O10-C23-C22	108.9(3)	O10-C24-C25	110.7(3)
O10-C24-H24A	109.5	C25-C24-H24A	109.5
O10-C24-H24B	109.5	C25-C24-H24B	109.5
H24A-C24-H24B	108.1	C24-C25-H25A	109.5
C24-C25-H25B	109.5	H25A-C25-H25B	109.5
C24-C25-H25C	109.5	H25A-C25-H25C	109.5
H25B-C25-H25C	109.5	O7-C26-O8	125.5(3)
O7-C26-C22	126.2(3)	O8-C26-C22	108.2(3)
O8-C27-C28	110.2(3)	O8-C27-H27A	109.6
C28-C27-H27A	109.6	O8-C27-H27B	109.6
C28-C27-H27B	109.6	H27A-C27-H27B	108.1
C27-C28-H28A	109.5	C27-C28-H28B	109.5
H28A-C28-H28B	109.5	C27-C28-H28C	109.5
H28A-C28-H28C	109.5	H28B-C28-H28C	109.5
C5-N1-O1	114.0(3)	C5-N1-H1A	123.0
O1-N1-H1A	123.0	C19-N2-O6	113.4(3)
C19-N2-H2A	123.3	O6-N2-H2A	123.3
N1-O1-H1	109.5	C12-O2-C13	116.7(3)
C9-O4-C10	116.7(3)	N2-O6-H6A	109.5
C26-O8-C27	118.7(3)	C23-O10-C24	117.3(3)

Symmetry transformations used to generate equivalent atoms (if any):

Table 6. Torsion angles (°) for 9.

C6-C1-C2-C3	73.3(3)	C6-C1-C2-C7	-46.2(3)
C1-C2-C3-C4	-59.5(4)	C7-C2-C3-C4	53.8(4)
C2-C3-C4-C5	37.3(4)	C3-C4-C5-N1	146.0(4)
C3-C4-C5-C6	-35.3(4)	N1-C5-C6-C1	-128.4(3)
C4-C5-C6-C1	52.8(4)	N1-C5-C6-C8	121.3(3)
C4-C5-C6-C8	-57.5(4)	C2-C1-C6-C5	-68.5(3)
C2-C1-C6-C8	48.5(3)	C3-C2-C7-C8	-91.4(3)
C1-C2-C7-C8	25.6(3)	C5-C6-C8-C12	-41.7(4)
C1-C6-C8-C12	-157.0(3)	C5-C6-C8-C9	-157.9(3)
C1-C6-C8-C9	86.9(3)	C5-C6-C8-C7	82.9(3)
C1-C6-C8-C7	-32.4(3)	C2-C7-C8-C12	128.1(3)
C2-C7-C8-C9	-113.9(3)	C2-C7-C8-C6	4.4(3)
C12-C8-C9-O5	-123.4(4)	C6-C8-C9-O5	-2.4(5)
C7-C8-C9-O5	113.2(4)	C12-C8-C9-O4	55.3(3)
C6-C8-C9-O4	176.3(3)	C7-C8-C9-O4	-68.2(3)
C9-C8-C12-O3	-124.8(4)	C6-C8-C12-O3	116.2(4)
C7-C8-C12-O3	-3.4(5)	C9-C8-C12-O2	55.0(3)
C6-C8-C12-O2	-64.0(3)	C7-C8-C12-O2	176.5(3)
C20-C15-C16-C17	73.8(4)	C20-C15-C16-C21	-46.3(3)
C15-C16-C17-C18	-59.5(4)	C21-C16-C17-C18	54.3(4)
C16-C17-C18-C19	35.5(4)	C17-C18-C19-N2	151.5(3)
C17-C18-C19-C20	-32.2(4)	N2-C19-C20-C15	-132.8(3)
C18-C19-C20-C15	50.5(4)	N2-C19-C20-C22	116.3(3)
C18-C19-C20-C22	-60.3(4)	C16-C15-C20-C19	-67.7(3)
C16-C15-C20-C22	49.3(3)	C15-C16-C21-C22	25.3(4)
C17-C16-C21-C22	-92.3(3)	C19-C20-C22-C26	-41.1(4)
C15-C20-C22-C26	-157.2(3)	C19-C20-C22-C23	-158.0(3)
C15-C20-C22-C23	85.9(3)	C19-C20-C22-C21	82.9(3)
C15-C20-C22-C21	-33.2(3)	C16-C21-C22-C26	127.1(3)
C16-C21-C22-C23	-113.0(3)	C16-C21-C22-C20	5.1(4)
C26-C22-C23-O9	-122.0(4)	C20-C22-C23-O9	-1.7(5)
C21-C22-C23-O9	113.2(4)	C26-C22-C23-O10	57.4(3)
C20-C22-C23-O10	177.7(3)	C21-C22-C23-O10	-67.5(4)
C23-C22-C26-O7	-124.9(4)	C20-C22-C26-O7	116.0(4)
C21-C22-C26-O7	-2.1(5)	C23-C22-C26-O8	55.8(3)
C20-C22-C26-O8	-63.4(3)	C21-C22-C26-O8	178.5(3)
C6-C5-N1-O1	179.0(3)	C4-C5-N1-O1	-2.2(5)
C18-C19-N2-O6	-3.7(5)	C20-C19-N2-O6	179.9(3)
O3-C12-O2-C13	2.5(5)	C8-C12-O2-C13	-177.4(3)
C14-C13-O2-C12	-175.7(3)	O5-C9-O4-C10	5.1(5)
C8-C9-O4-C10	-173.6(3)	C11-C10-O4-C9	82.7(4)
O7-C26-O8-C27	0.8(5)	C22-C26-O8-C27	-179.9(3)
C28-C27-O8-C26	105.8(4)	O9-C23-O10-C24	-0.2(5)
C22-C23-O10-C24	-179.6(3)	C25-C24-O10-C23	91.9(4)

Symmetry transformations used to generate equivalent atoms (if any):

Table 7. Anisotropic atomic displacement parameters (Å^2) for 9.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2} U_{11} + ... + 2hka^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13} U_{12}
C1	0.0219(19)	0.0230(19)	0.0173(18)	0.0035(14)	-0.0020(14) -0.0067(15)
C2	0.0192(18)	0.0242(19)	0.0145(17)	-0.0001(14)	0.0036(14) -0.0097(14)
C3	0.0198(19)	0.029(2)	0.023(2)	-0.0083(16)	0.0036(15) -0.0024(16)
C4	0.0217(19)	0.0140(17)	0.028(2)	-0.0057(15)	-0.0011(15) -0.0003(14)
C5	0.0181(17)	0.0165(17)	0.0133(17)	-0.0025(13)	-0.0014(13) -0.0010(14)
C6	0.0120(16)	0.0147(16)	0.0145(17)	-0.0008(13)	-0.0018(13) -0.0015(12)
C7	0.0154(17)	0.0160(17)	0.0171(18)	-0.0011(13)	0.0025(13) -0.0033(13)
C8	0.0108(15)	0.0107(15)	0.0154(17)	-0.0008(12)	0.0000(12) 0.0010(12)
C9	0.0159(16)	0.0077(15)	0.0206(18)	0.0037(13)	0.0061(14) -0.0053(12)
C10	0.030(2)	0.0162(18)	0.037(2)	-0.0125(17)	0.0026(17) 0.0026(16)
C11	0.028(2)	0.031(2)	0.036(2)	-0.0117(19)	0.0026(18) 0.0050(17)
C12	0.0172(16)	0.0094(15)	0.0162(17)	-0.0044(13)	0.0006(13) -0.0021(13)
C13	0.028(2)	0.029(2)	0.025(2)	0.0155(17)	-0.0014(16) -0.0093(17)
C14	0.028(2)	0.032(2)	0.028(2)	0.0120(18)	0.0098(17) 0.0009(17)
C15	0.0206(19)	0.031(2)	0.0171(18)	0.0029(15)	0.0016(14) -0.0101(16)
C16	0.0156(17)	0.027(2)	0.023(2)	-0.0056(15)	0.0053(15) -0.0099(15)
C17	0.0189(18)	0.028(2)	0.028(2)	-0.0166(17)	0.0077(15) -0.0018(15)
C18	0.0186(18)	0.0206(19)	0.026(2)	-0.0099(15)	0.0029(15) -0.0012(14)
C19	0.0178(17)	0.0197(17)	0.0096(16)	-0.0028(13)	0.0020(13) -0.0016(14)
C20	0.0142(16)	0.0194(18)	0.0166(18)	0.0025(14)	0.0006(13)

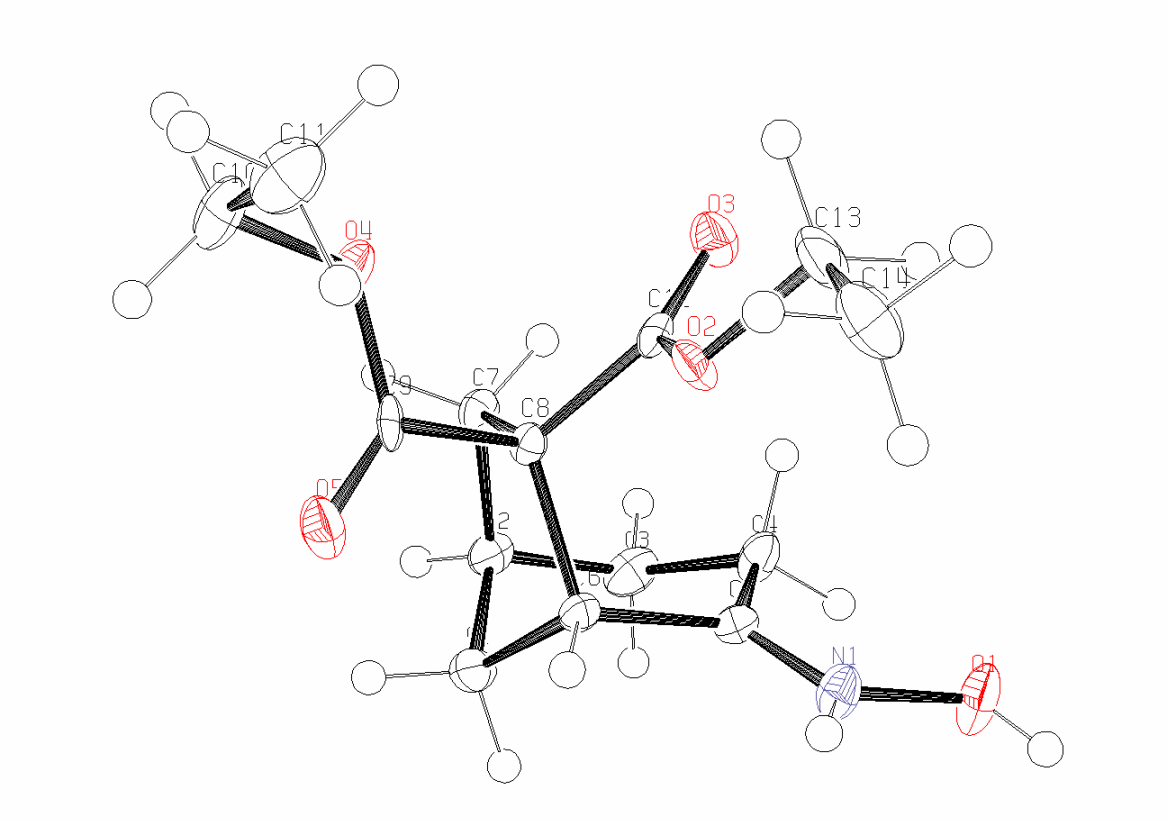
	-0.0030(13)				
C21	0.0129(16)	0.0177(17)	0.0226(19)	-0.0057(14)	-0.0004(14)
	-0.0018(13)				
C22	0.0162(17)	0.0138(16)	0.0150(17)	-0.0018(13)	0.0011(13)
	0.0006(13)				
C23	0.0143(16)	0.0146(17)	0.028(2)	0.0006(15)	0.0065(14)
	-0.0029(13)				
C24	0.037(2)	0.0113(18)	0.045(3)	-0.0102(17)	0.0109(19)
	0.0021(16)				
C25	0.029(2)	0.023(2)	0.045(3)	-0.0140(19)	0.0018(19)
	0.0048(17)				
C26	0.0270(19)	0.0078(15)	0.0144(17)	-0.0049(13)	0.0048(14)
	0.0017(13)				
C27	0.039(2)	0.0173(19)	0.041(3)	0.0084(17)	0.016(2)
	-0.0060(17)				
C28	0.027(2)	0.036(2)	0.021(2)	0.0050(17)	0.0044(16)
	-0.0019(17)				
N1	0.0184(15)	0.0133(14)	0.0267(17)	-0.0038(12)	0.0008(13)
	0.0013(12)				
N2	0.0157(14)	0.0148(14)	0.0173(15)	0.0007(11)	0.0008(11)
	-0.0010(11)				
O1	0.0257(15)	0.0150(13)	0.0492(19)	-0.0048(12)	0.0005(13)
	-0.0056(11)				
O2	0.0185(12)	0.0181(12)	0.0165(13)	0.0089(10)	0.0010(10)
	-0.0014(10)				
O3	0.0231(13)	0.0181(13)	0.0254(14)	0.0052(11)	-0.0012(11)
	0.0033(11)				
O4	0.0248(13)	0.0129(12)	0.0243(14)	-0.0074(10)	-0.0002(11)
	0.0004(10)				
O5	0.0228(13)	0.0146(13)	0.0306(15)	0.0059(11)	-0.0010(11)
	0.0021(10)				
O6	0.0214(13)	0.0146(13)	0.0367(16)	-0.0038(11)	0.0046(12)
	-0.0054(10)				
O7	0.0384(16)	0.0238(14)	0.0214(14)	0.0053(11)	-0.0027(12)
	0.0066(12)				
O8	0.0242(14)	0.0185(13)	0.0300(15)	0.0066(11)	0.0129(11)
	0.0022(11)				
O9	0.0268(15)	0.0152(13)	0.0424(17)	0.0065(12)	-0.0027(13)
	0.0014(11)				
O10	0.0310(15)	0.0140(13)	0.0294(15)	-0.0067(11)	0.0044(12)
	0.0026(11)				

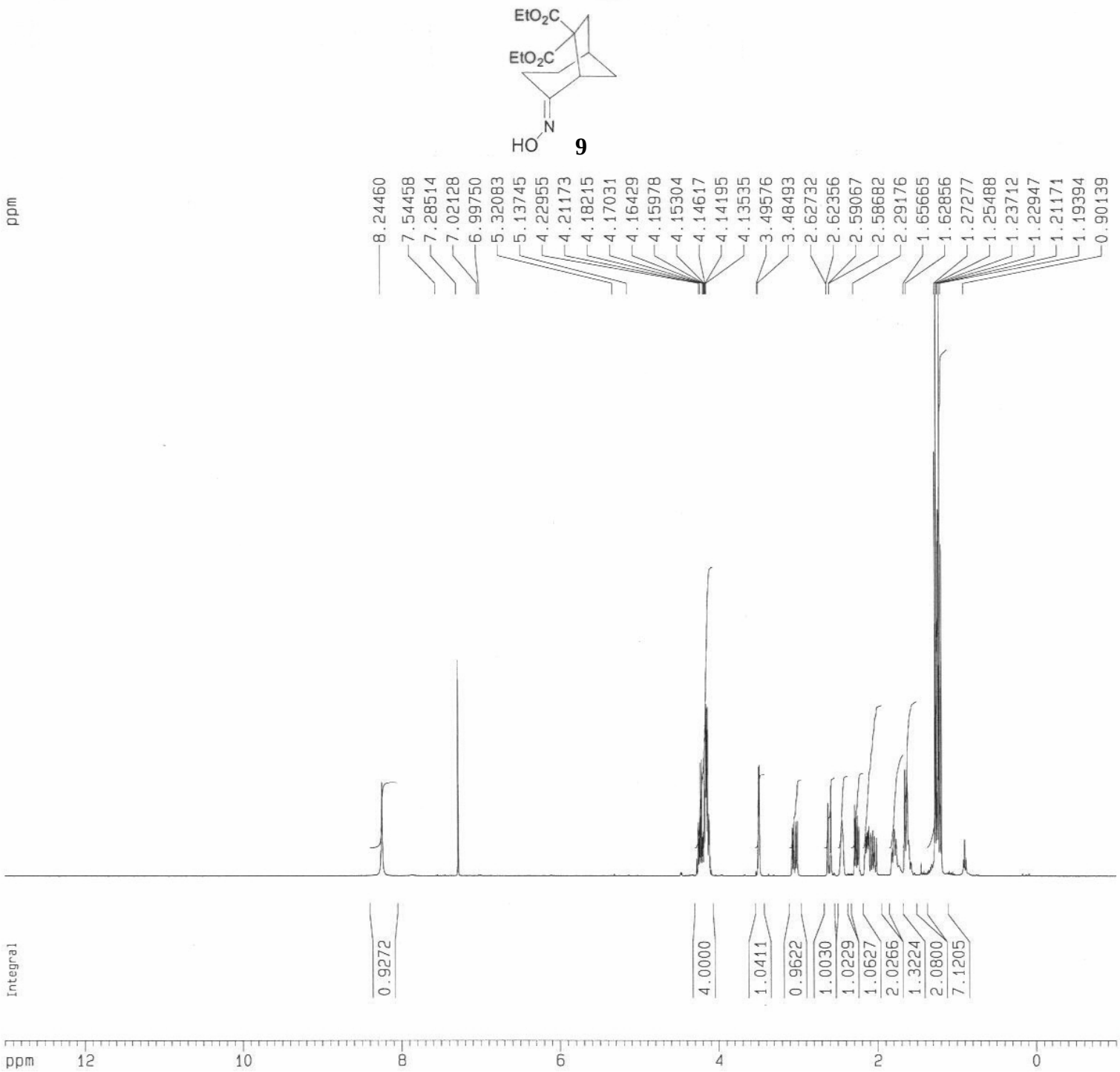
Table 8. Hydrogen atom coordinates and isotropic atomic displacement parameters (Å^2) for 9.

	x/a	y/b	z/c	U
H1B	0.7425	0.2067	0.3827	0.025
H1C	0.7474	0.2958	0.4407	0.025
H2	0.9251	0.2427	0.4477	0.023
H3A	0.9598	0.0936	0.4823	0.029
H3B	0.8839	0.0986	0.3951	0.029
H4A	0.8011	-0.0056	0.4773	0.025
H4B	0.8272	0.0423	0.5705	0.025
H6	0.6099	0.2101	0.5102	0.016
H7A	0.8903	0.2885	0.5901	0.019
H7B	0.9057	0.1867	0.6143	0.019
H10A	0.6827	0.4600	0.6980	0.033
H10B	0.7533	0.4424	0.7868	0.033
H11A	0.5437	0.3733	0.7563	0.048
H11B	0.5713	0.4515	0.8241	0.048
H11C	0.6143	0.3550	0.8447	0.048
H13A	0.6098	0.1424	0.8329	0.032
H13B	0.6000	0.0560	0.7722	0.032
H14A	0.4375	0.1853	0.7882	0.044
H14B	0.4321	0.0894	0.8308	0.044
H14C	0.4277	0.1017	0.7241	0.044
H15A	0.7725	0.1972	-0.1097	0.028
H15B	0.7701	0.2866	-0.0520	0.028
H16	0.9409	0.2285	-0.0205	0.026
H17A	0.9624	0.0791	0.0185	0.030
H17B	0.9053	0.0856	-0.0780	0.030
H18A	0.8017	-0.0158	-0.0105	0.026
H18B	0.8129	0.0293	0.0861	0.026
H20	0.6172	0.2054	-0.0031	0.020
H21A	0.8814	0.2761	0.1147	0.021
H21B	0.8859	0.1741	0.1408	0.021
H24A	0.6687	0.4580	0.1818	0.037
H24B	0.7334	0.4456	0.2745	0.037
H25A	0.5185	0.3914	0.2427	0.048
H25B	0.5547	0.4704	0.3066	0.048
H25C	0.5829	0.3719	0.3341	0.048
H27A	0.5656	0.0699	0.2742	0.039
H27B	0.4578	0.0844	0.2164	0.039
H28A	0.5378	0.2000	0.3497	0.042
H28B	0.4326	0.1408	0.3582	0.042
H28C	0.4345	0.2204	0.2885	0.042
H1A	0.5430	0.0750	0.5029	0.023

H2A	0.5445	0.0721	-0.0080	0.019
H1	0.5592	-0.0656	0.4874	0.045
H6A	0.5561	-0.0701	-0.0067	0.036

Figure 1: Ortep Diagram of X-ray Diffraction Structure of 9.





Current Data Parameters

NAME	ik3-166
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20070329
Time	10.40
INSTRUM	spect
PROBHD	5 mm BBI 1H-B
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	203.2
DW	60.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 =======

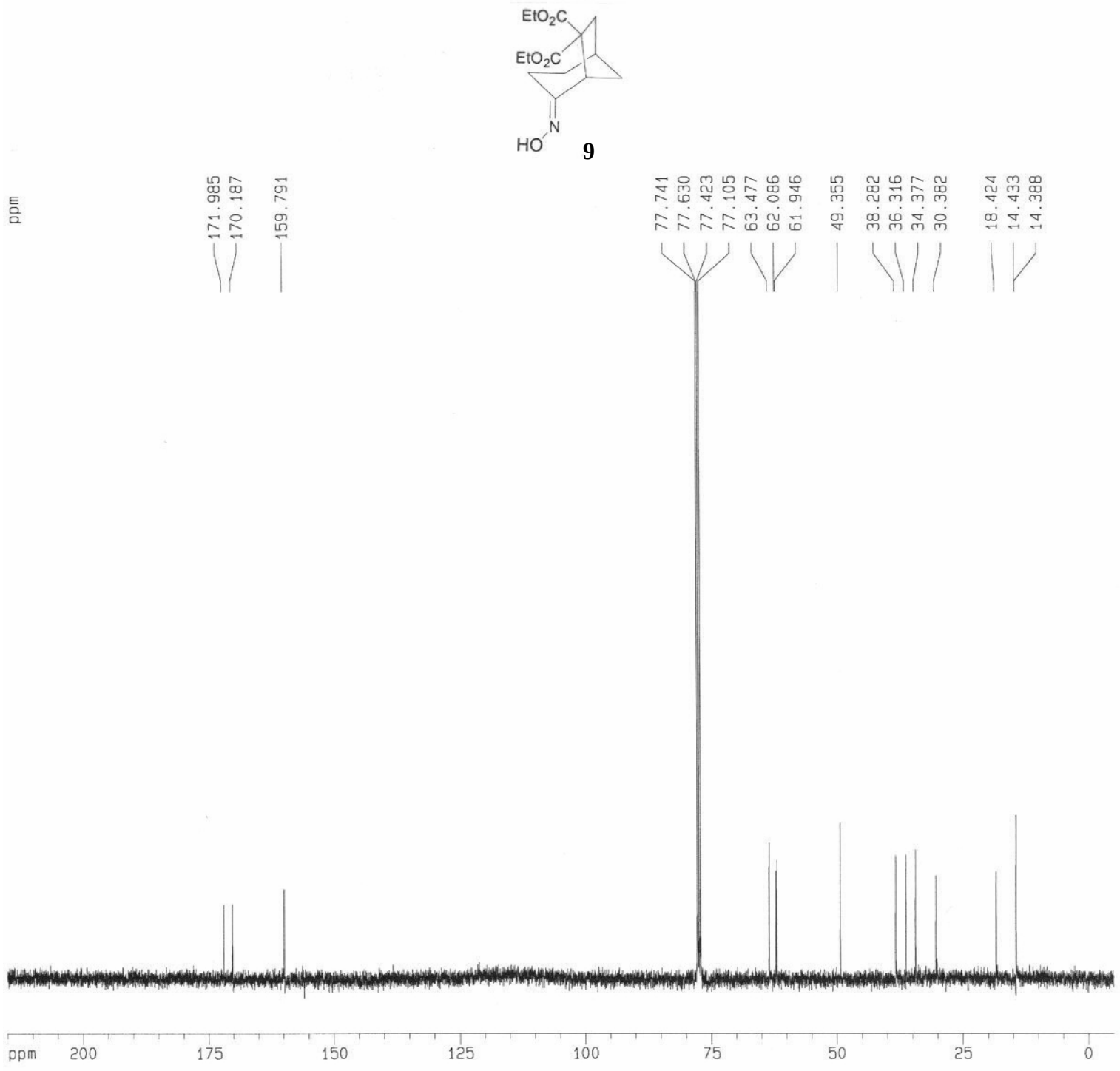
NUC1	1H
P1	6.45 usec
PL1	0.00 dB
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300000 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	13.000 ppm
F1	5201.69 Hz
F2P	-1.000 ppm
F2	-400.13 Hz
PPMCM	0.70000 ppm/cm
HZCM	280.09100 Hz/cm



Current Data Parameters

NAME	ik3-166
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20070329
Time	10.48
INSTRUM	spect
PROBHD	5 mm BBI 1H-B
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	25125.629 Hz
FIDRES	0.383387 Hz
AQ	1.3042164 sec
RG	5160.6
DW	19.900 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

========== CHANNEL f1 =======

NUC1	13C
P1	16.35 usec
PL1	-6.00 dB
SFO1	100.6237959 MHz

========== CHANNEL f2 =======

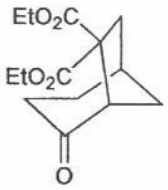
CPDPRG2	waltz16
NUC2	1H
PCPD2	114.00 usec
PL2	0.00 dB
PL12	24.00 dB
PL13	24.00 dB
SFO2	400.1316005 MHz

F2 - Processing parameters

SI	32768
SF	100.6127290 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	215.000 ppm
F1	21631.74 Hz
F2P	-5.000 ppm
F2	-503.06 Hz
PPMCM	11.00000 ppm/cm
HZCM	1106.73999 Hz/cm



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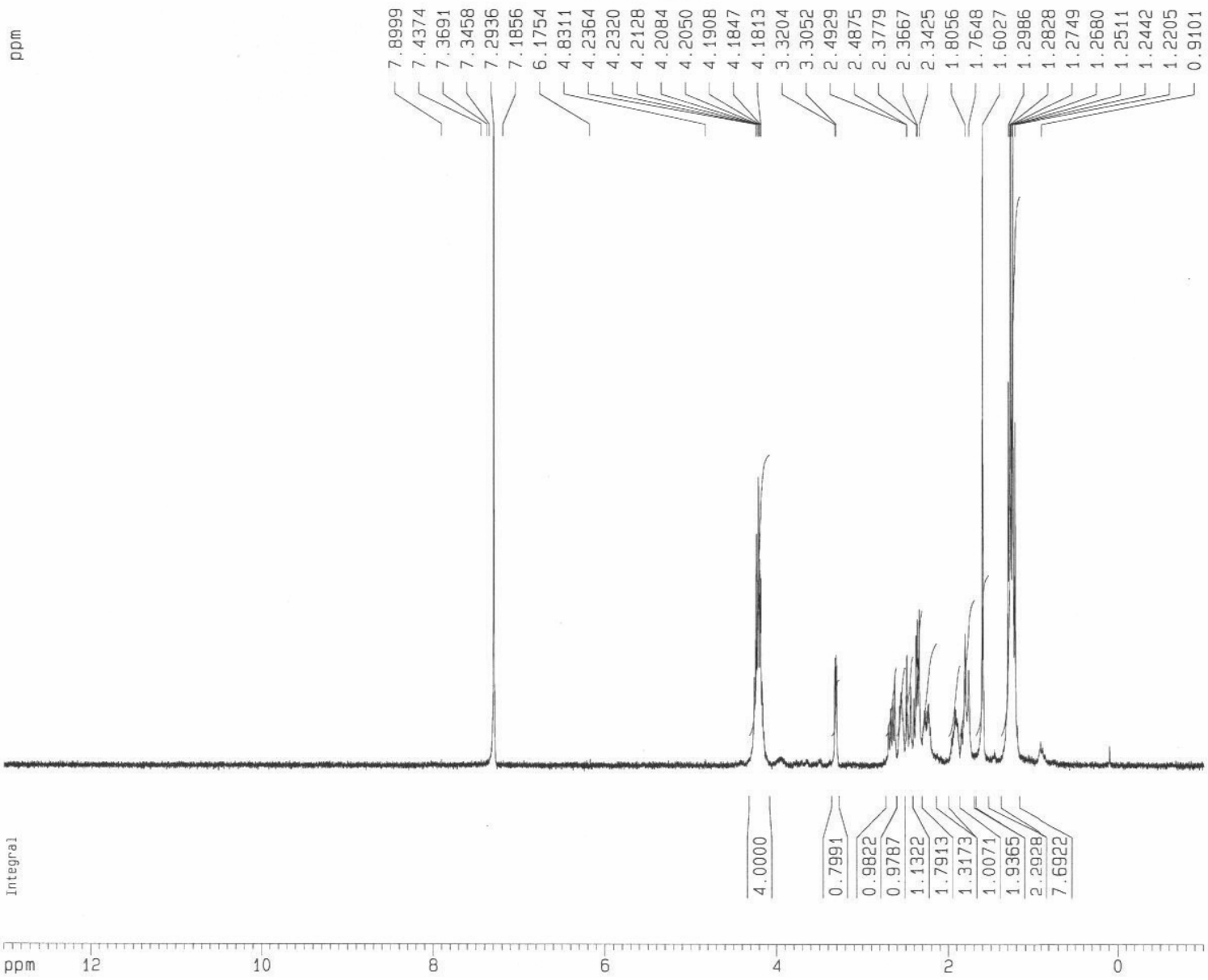


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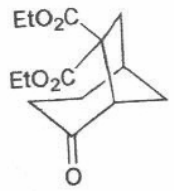
Current Data Parameters
NAME                  ik4-15
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20070510
Time                  14.15
INSTRUM               spect
PROBHD     5 mm QNP 1H/1
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ                5.3084660 sec
RG                   912.3
DW                  81.000 usec
DE                   6.00 usec
TE                  300.0 K
D1                1.00000000 sec

========== CHANNEL f1 =======
NUC1                      1H
P1                     11.70 usec
PL1                     0.00 dB
SFO1             299.8718518 MHz

F2 - Processing parameters
SI                     32768
SF               299.8700000 MHz
WDW                       no
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
F1P                   13.000 ppm
F1                  3898.31 Hz
F2P                   -1.000 ppm
F2                  -299.87 Hz
PPMCM                0.70000 ppm/cm
HZCM               209.90900 Hz/cm
```



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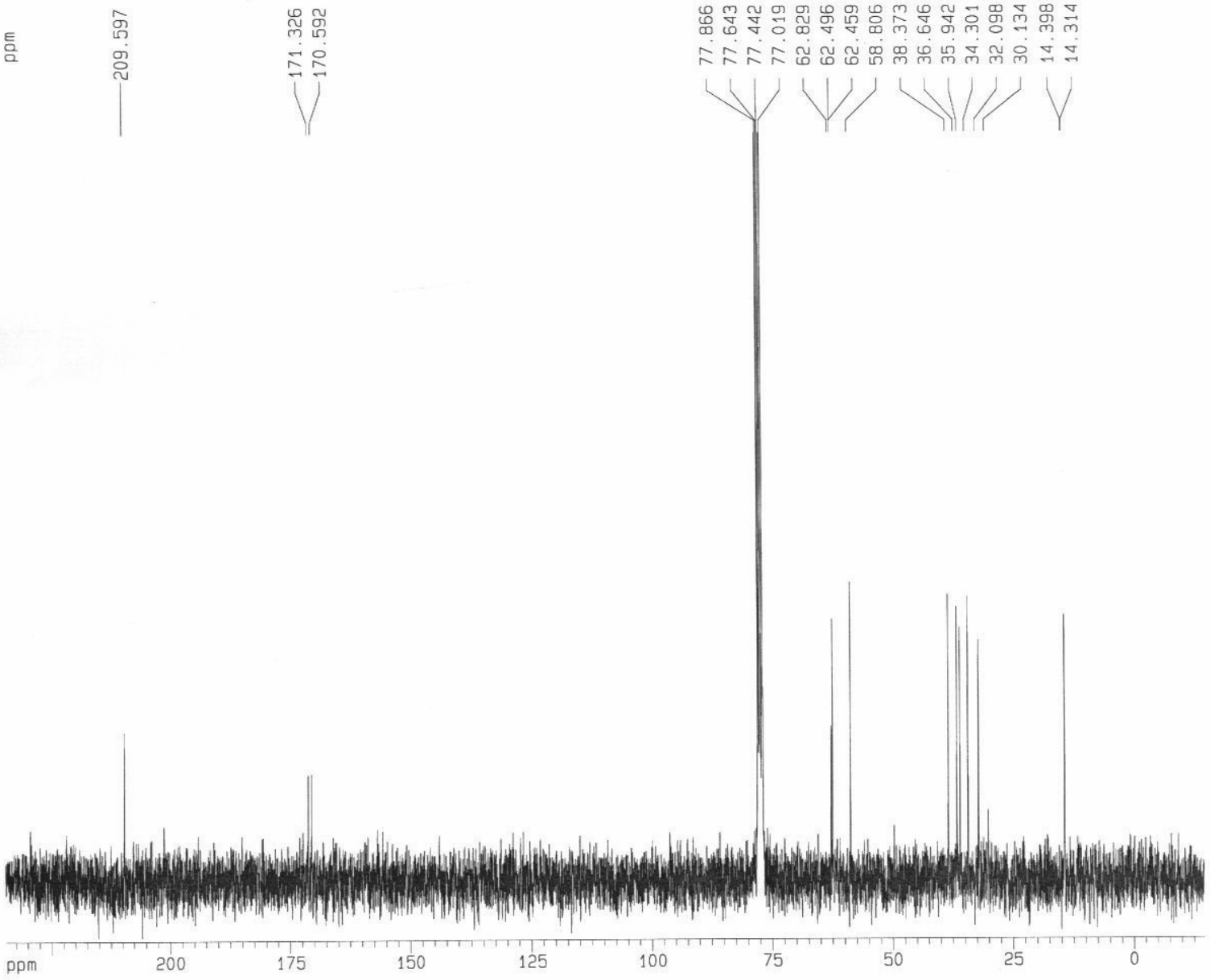


Current Data Parameters

NAME	ik4-15
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

Date_	20070510
Time	17.10
INSTRUM	spect
PROBHD	5 mm QNP 1H/1
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1621
DS	4
SWH	18796.992 Hz
FIDRES	0.286819 Hz
AQ	1.7433076 sec
RG	1024
DW	26.600 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
D11	0.03000000 sec
D12	0.00002000 sec

========== CHANNEL f1 =======

NUC1	13C
P1	5.40 usec
PL1	-6.00 dB
SFO1	75.4106357 MHz

========== CHANNEL f2 =======

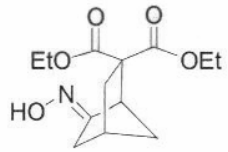
CPDPRG2	waltz16
NUC2	1H
PCPD2	115.00 usec
PL2	0.00 dB
PL12	20.00 dB
PL13	20.00 dB
SFO2	299.8711995 MHz

F2 - Processing parameters

SI	32768
SF	75.4023410 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	234.651 ppm
F1	17693.24 Hz
F2P	-14.638 ppm
F2	-1103.75 Hz
PPMCM	12.46446 ppm/cm
HZCM	939.84967 Hz/cm



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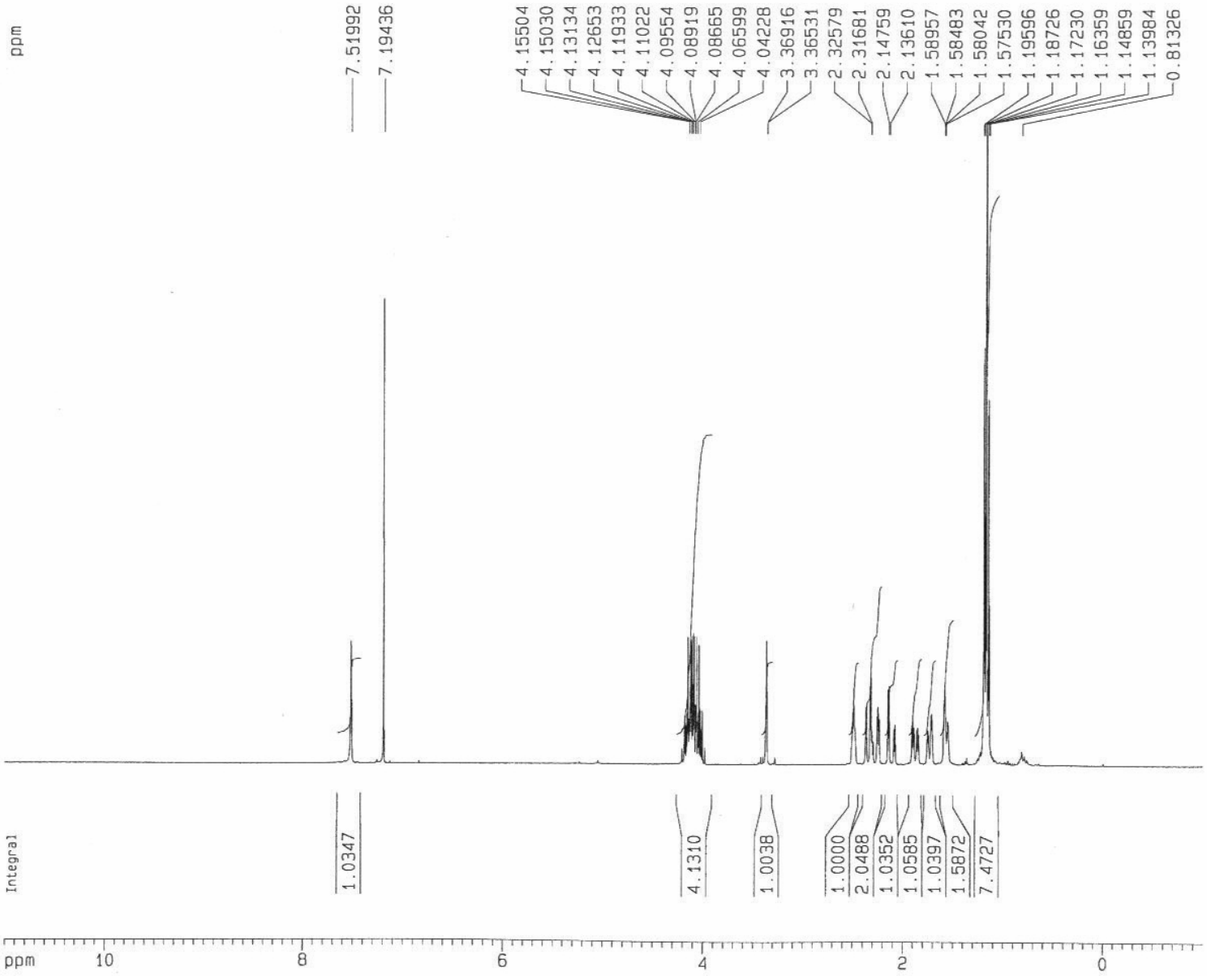


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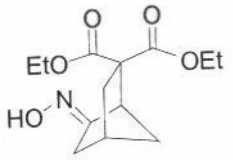
Current Data Parameters
NAME      May05-2007-Wein
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070505
Time               23.12
INSTRUM            spect
PROBHD     5 mm Multinu
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    0
SWH            6172.839 Hz
FIDRES         0.094190 Hz
AQ             5.3084660 sec
RG                645.1
DW               81.000 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec

============ CHANNEL f1 =======
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300261 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               11.000 ppm
F1              3301.43 Hz
F2P               -1.000 ppm
F2              -300.13 Hz
PPMCM           0.60000 ppm/cm
HZCM          180.07802 Hz/cm
```



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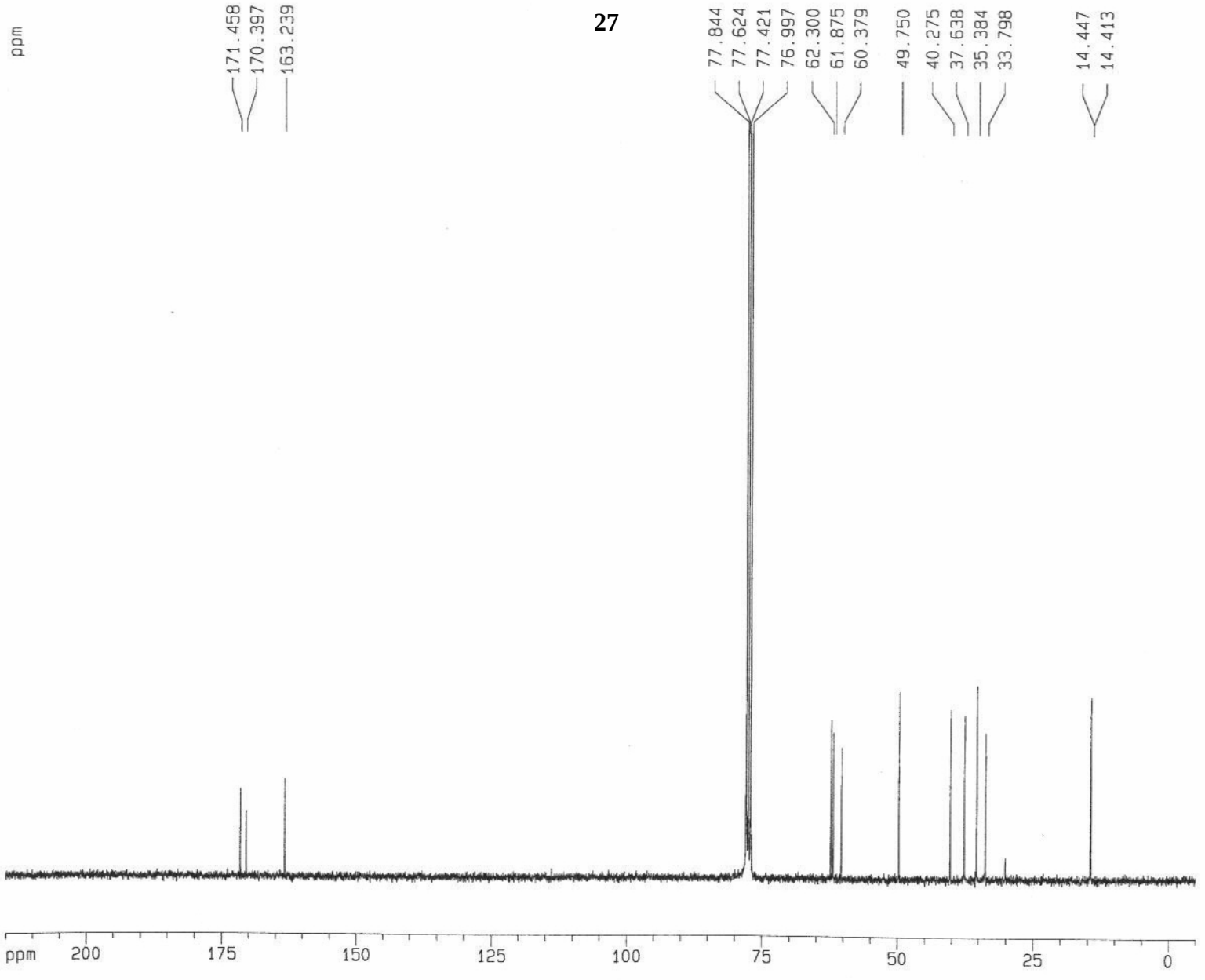


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Current Data Parameters
NAME      pka-144-05-05-
EXPNO                  1
PROCNO                 1

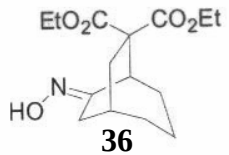
F2 - Acquisition Parameters
Date_           20070506
Time                0.44
INSTRUM            spect
PROBHD     5 mm Multinu
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 7300
DS                    4
SWH           18832.393 Hz
FIDRES        0.287360 Hz
AQ            1.7400308 sec
RG              11585.2
DW               26.550 usec
DE                6.00 usec
TE               300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1                11.80 usec
PL1                0.00 dB
SFO1         75.4760200 MHz

============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                1H
PCPD2           110.00 usec
PL2                0.00 dB
PL12              17.50 dB
PL13              17.50 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677190 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P              215.000 ppm
F1             16225.56 Hz
F2P               -5.000 ppm
F2              -377.34 Hz
PPMCM          11.00000 ppm/cm
HZCM           830.14490 Hz/cm
```



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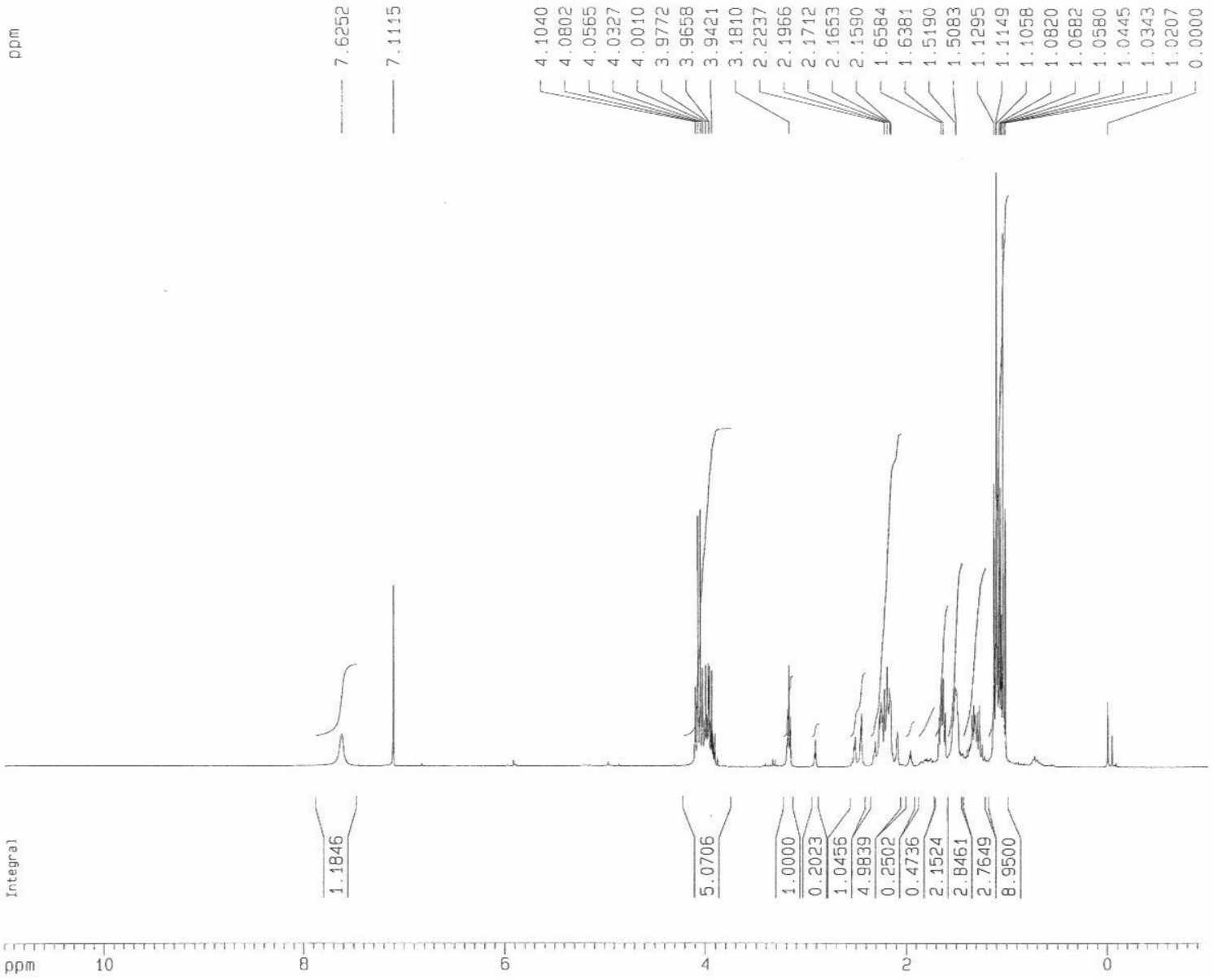


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Current Data Parameters
NAME      Nov21-2006-Wein
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20061121
Time               23.03
INSTRUM            spect
PROBHD     5 mm QNP 1H/1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6172.839 Hz
FIDRES        0.094190 Hz
AQ            5.3084660 sec
RG                456.1
DW               81.000 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                11.70 usec
PL1                0.00 dB
SFO1         299.8718518 MHz

F2 - Processing parameters
SI                32768
SF          299.8700545 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P              11.000 ppm
F1              3298.57 Hz
F2P              -1.000 ppm
F2              -299.87 Hz
PPMCM          0.60000 ppm/cm
HZCM          179.92203 Hz/cm
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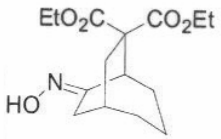

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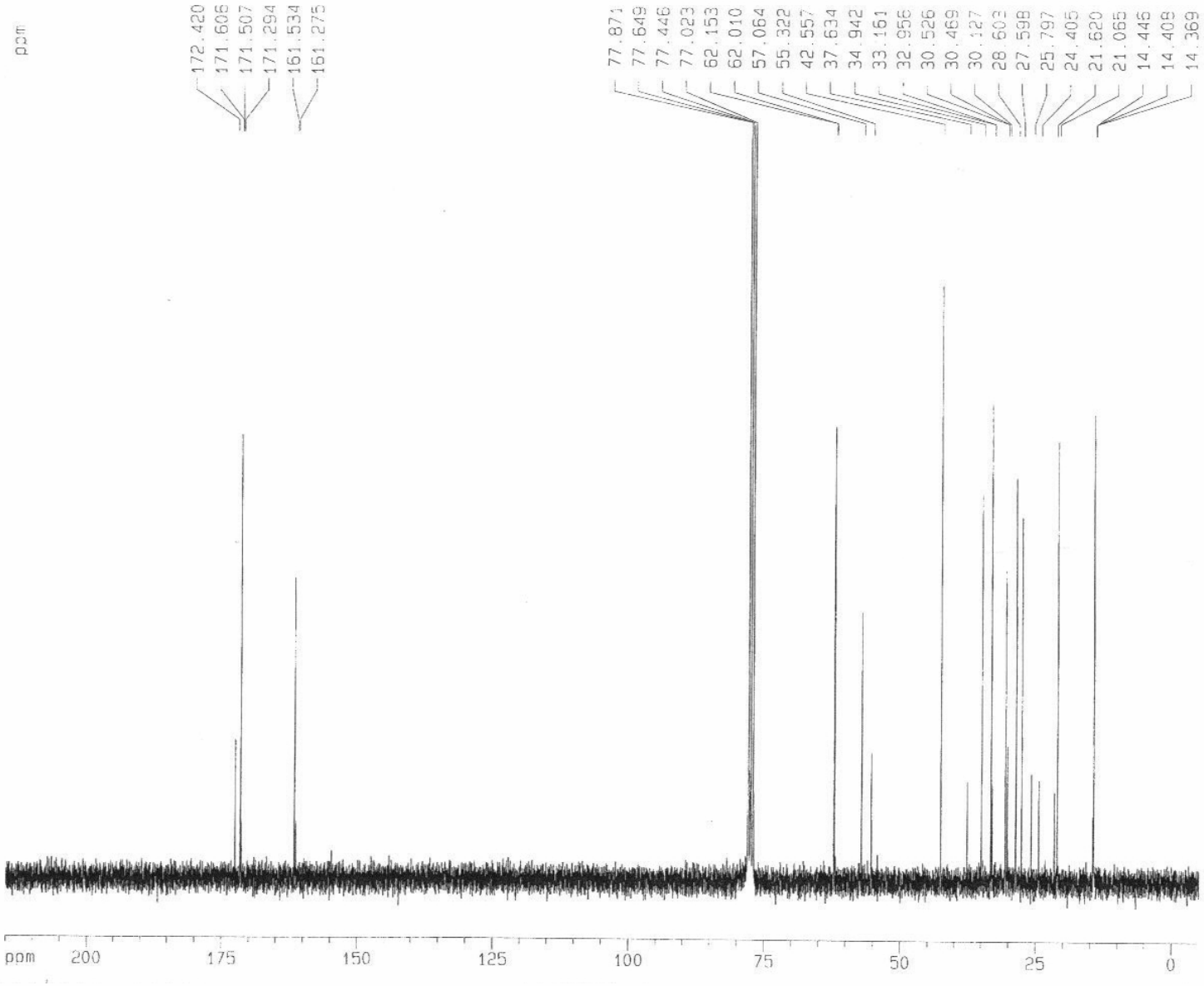



```
Current Data Parameters
NAME                  pst_163
EXPNO                       1
PROCNO                      1

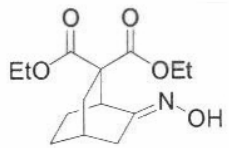
F2 - Acquisition Parameters
Date_              20061219
Time                  21.00
INSTRUM               spect
PROBHD     5 mm QNP 1H/1
PULPROG               zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    12270
DS                        4
SWH               18796.992 Hz
FIDRES            0.286819 Hz
AQ                1.7433076 sec
RG                    2048
DW                   26.600 usec
DE                    6.00 usec
TE                   300.0 K
D1                2.00000000 sec
D11               0.03000000 sec
D12               0.00002000 sec

========== CHANNEL f1 ==========
NUC1                    13C
P1                    5.40 usec
PL1                  -6.00 dB
SFO1              75.4106357 MHz

========== CHANNEL f2 ==========
CPDPRG2              waltz16
NUC2                    1H
PCPD2                115.00 usec
PL2                   0.00 dB
PL12                 20.00 dB
PL13                 20.00 dB
SFO2             299.8711995 MHz

F2 - Processing parameters
SI                      32768
SF                75.4023410 MHz
WDW                       no
SSB                        0
LB                    0.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                 215.000 ppm
F1                  16211.50 Hz
F2P                  -5.000 ppm
F2                   -377.01 Hz
PPMCM               11.00000 ppm/cm
HZCM                629.42578 Hz/cm
```



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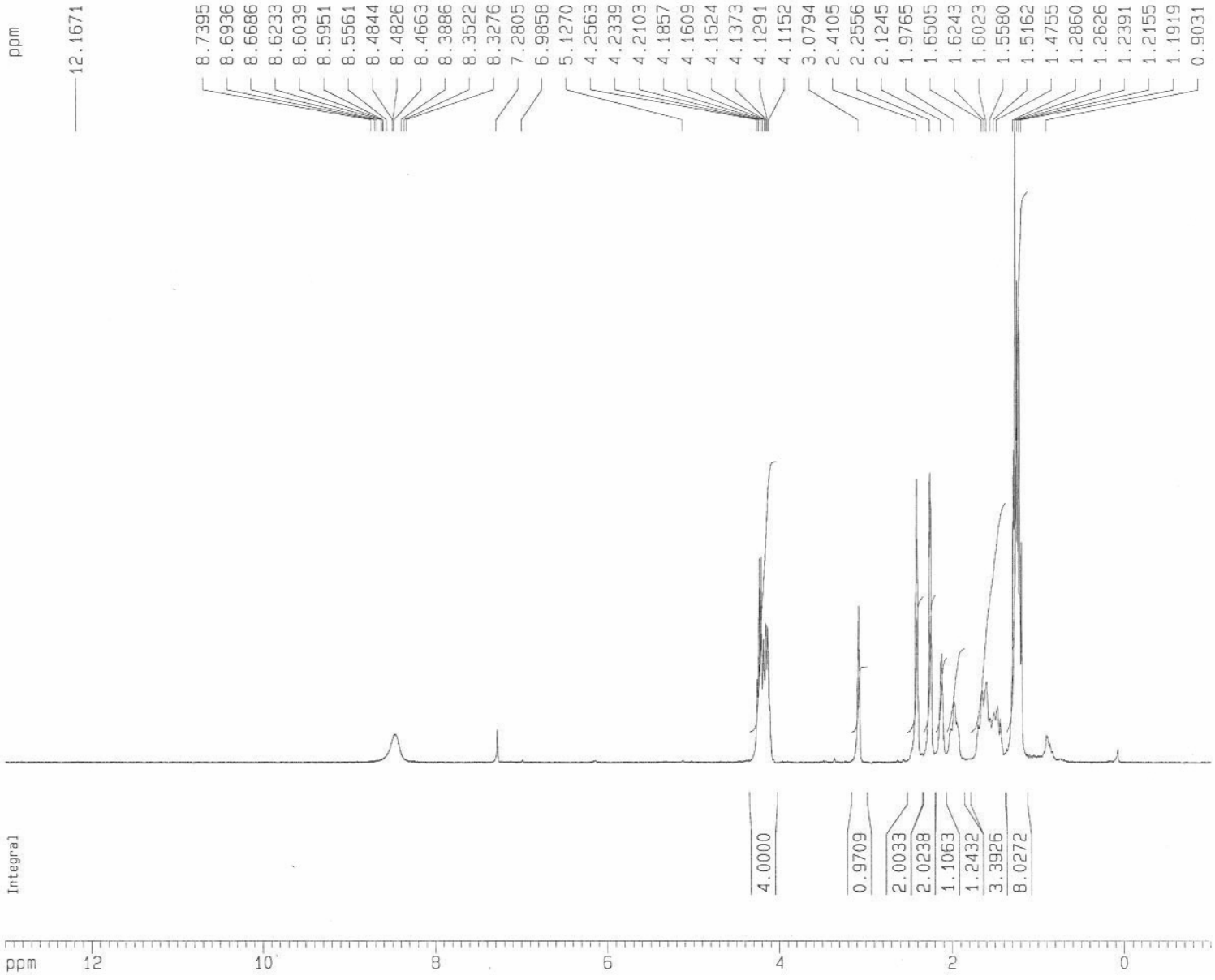


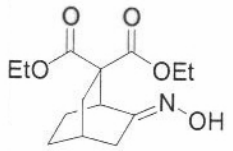

```
Current Data Parameters
NAME      Nov13-2006-Wein
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20061113
Time               11.02
INSTRUM            spect
PROBHD     5 mm Multinu
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6172.839 Hz
FIDRES         0.094190 Hz
AQ             5.3084660 sec
RG                228.1
DW               81.000 usec
DE                6.00 usec
TE                300.0 K
D1             1.00000000 sec

============ CHANNEL f1 =======
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                32768
SF          300.1300000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               13.000 ppm
F1              3901.69 Hz
F2P               -1.000 ppm
F2              -300.13 Hz
PPMCM          0.70000 ppm/cm
```



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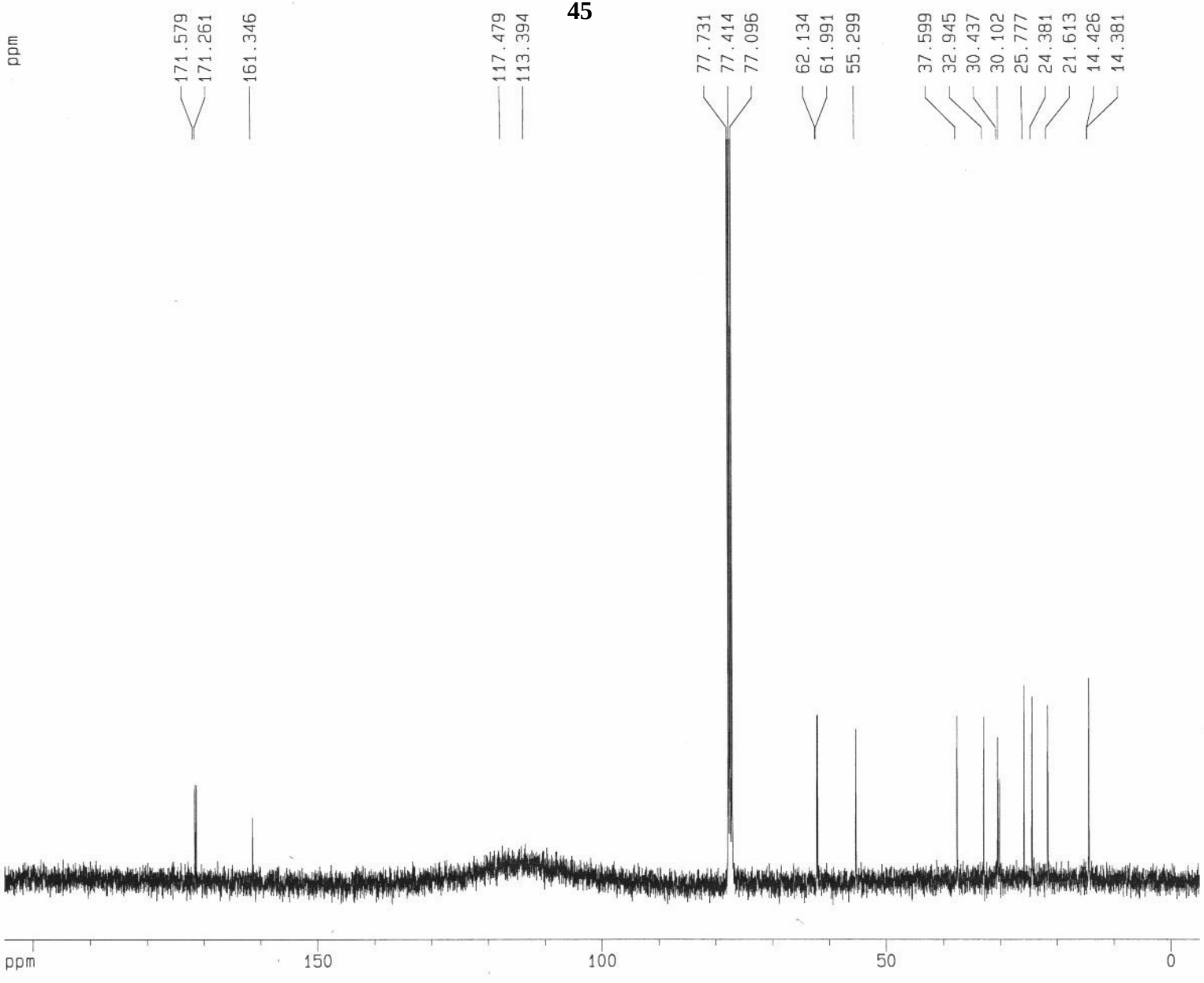



```
Current Data Parameters
NAME          ik09072006
EXPNO                  2
PROCNO                 1

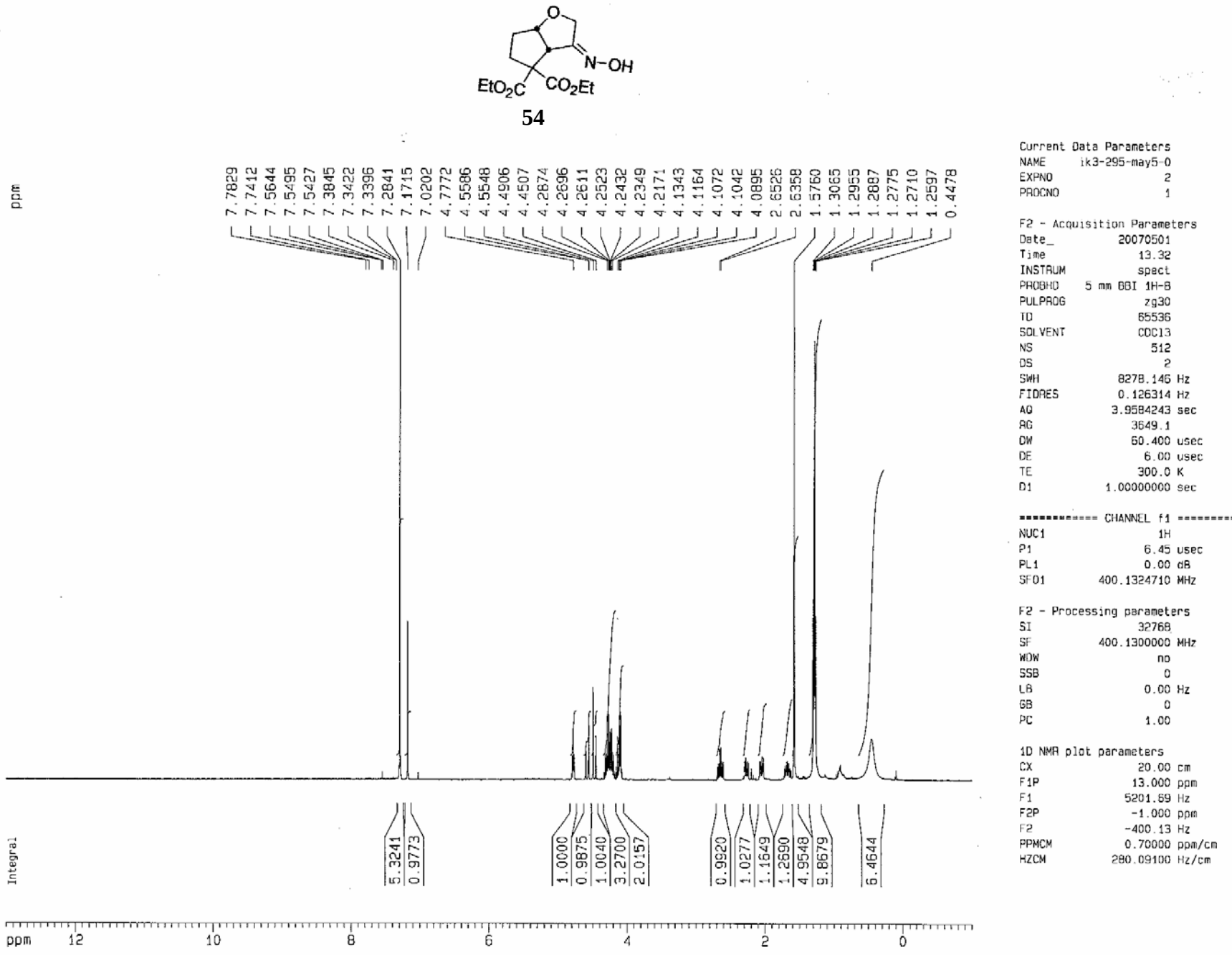
F2 - Acquisition Parameters
Date_           20060907
Time               22.03
INSTRUM            spect
PROBHD     5 mm BBI 1H-B
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 7168
DS                    4
SWH           25125.629 Hz
FIDRES        0.383387 Hz
AQ            1.3042164 sec
RG                16384
DW               19.900 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

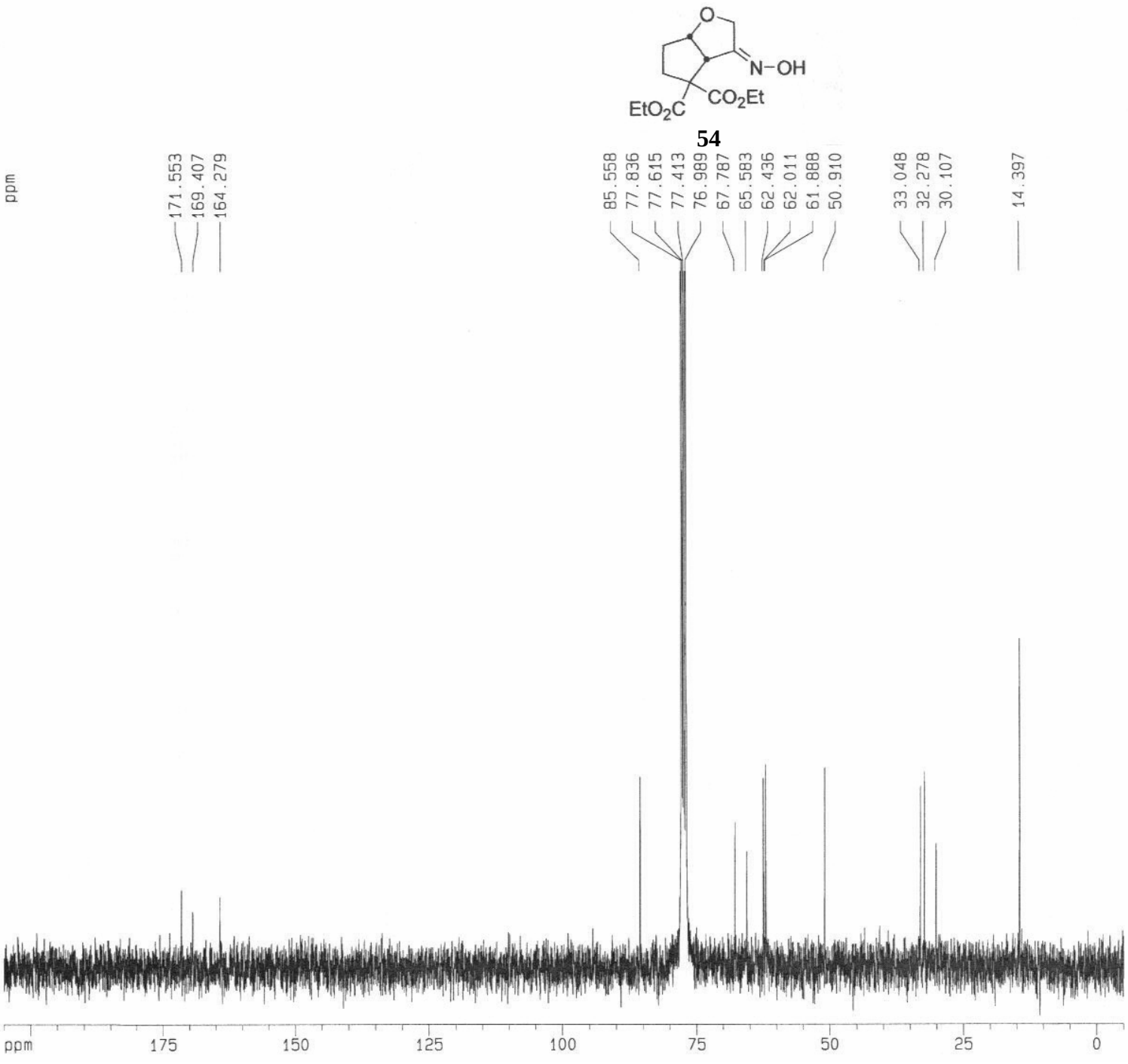
============ CHANNEL f1 =======
NUC1                13C
P1                16.35 usec
PL1               -6.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 =======
CPDPRG2         waltz16
NUC2                1H
PCPD2           114.00 usec
PL2               0.00 dB
PL12             24.00 dB
PL13             24.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127290 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P               205.000 ppm
F1              20625.61 Hz
F2P               -5.000 ppm
F2              -503.06 Hz
PPMCM           10.50000 ppm/cm
HZCM          1056.43372 Hz/cm
```


N–OH
EtO2C
CO2Et
54
ppm
7.7829
7.7412
7.5644
7.5495
7.5427
7.3845
7.3422
7.3396
7.2841
7.1715
7.0202
4.7772
4.5586
4.5548
4.4906
4.4507
4.2874
4.2696
4.2611
4.2523
4.2432
4.2349
4.2171
4.1343
4.1164
4.1072
4.1042
4.0895
2.6526
2.6358
1.5760
1.3065
1.2955
1.2887
1.2775
1.2710
1.2597
0.4478
Integral
5.3241
0.9773
1.0000
0.9875
1.0040
3.2700
2.0157
0.9920
1.0277
1.1649
1.2690
4.9548
9.8679
6.4644
ppm
12
10
8
6
4
2
0
Current Data Parameters
NAME ik3-295-may5-0
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070501
Time 13.32
INSTRUM spect
PROBHD 5 mm BBI 1H-B
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 3649.1
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 13.000 ppm
F1 5201.69 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.70000 ppm/cm
HZCM 280.09100 Hz/cm



Current Data Parameters
NAME ik3-289overnig
EXPNO 1
PROCNO 1

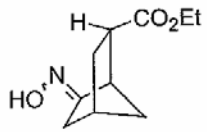
F2 - Acquisition Parameters
Date_ 20070605
Time 9.11
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10240
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 13004
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

========== CHANNEL f1 =======
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz

========== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 205.000 ppm
F1 15470.88 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 10.50000 ppm/cm
HZCM 792.41107 Hz/cm



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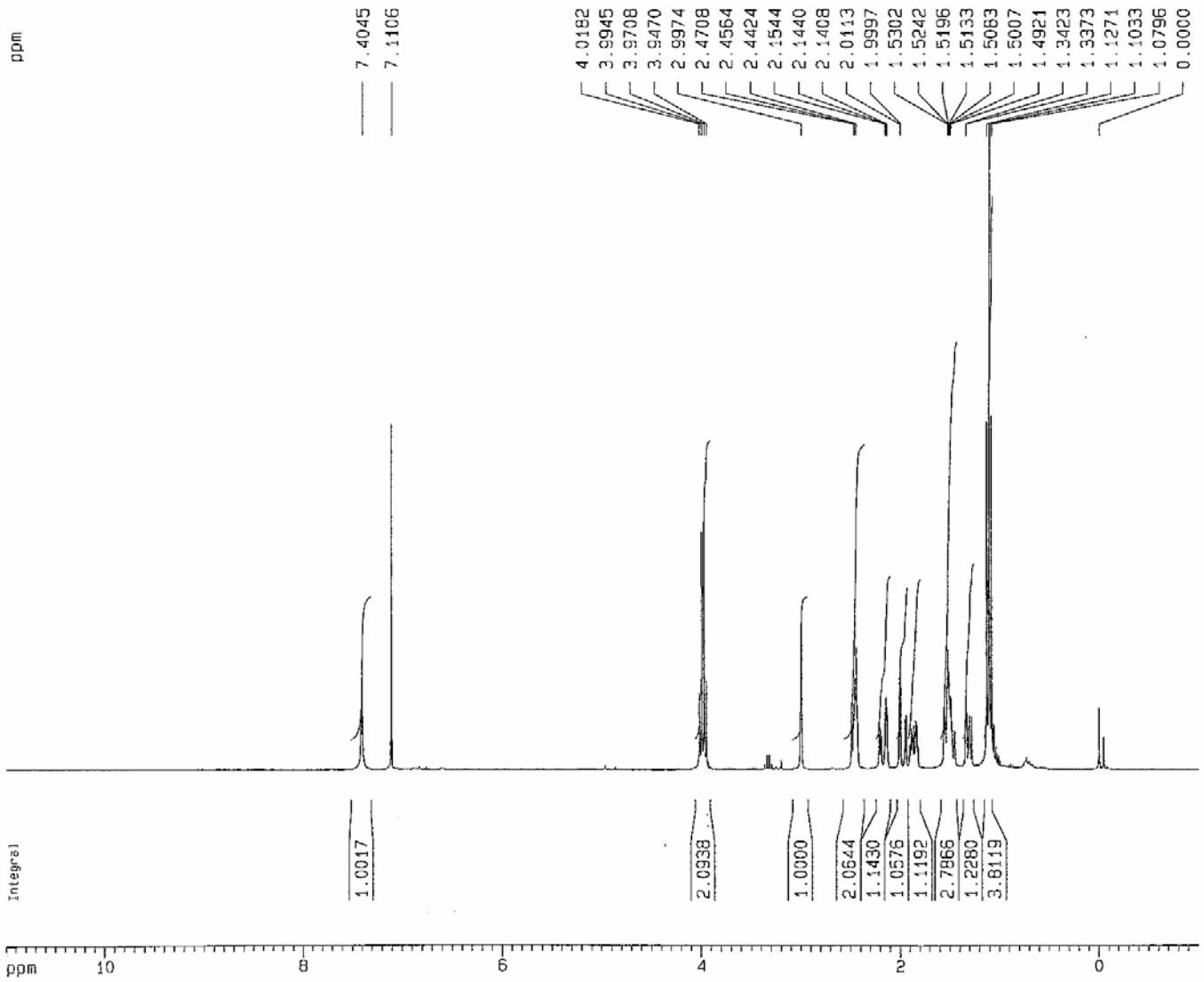


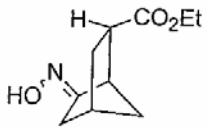

```
Current Data Parameters
NAME      May29-2007-Wein
EXPNO                 90
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070529
Time               20.11
INSTRUM            spect
PROBHD     5 mm QNP 1H/1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    0
SWH           6172.839 Hz
FIDRES        0.094190 Hz
AQ            5.3084660 sec
RG                574.7
DW               81.000 usec
DE                6.00 usec
TE               300.0 K
D1           2.00000000 sec

========== CHANNEL f1 ========
NUC1                  1H
P1                11.70 usec
PL1                0.00 dB
SFO1         299.8718518 MHz

F2 - Processing parameters
SI                32768
SF           299.8700547 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               11.000 ppm
F1              3298.57 Hz
F2P               -1.000 ppm
F2              -299.87 Hz
PPMCM          0.60000 ppm/cm
HZCM         179.92203 Hz/cm
```



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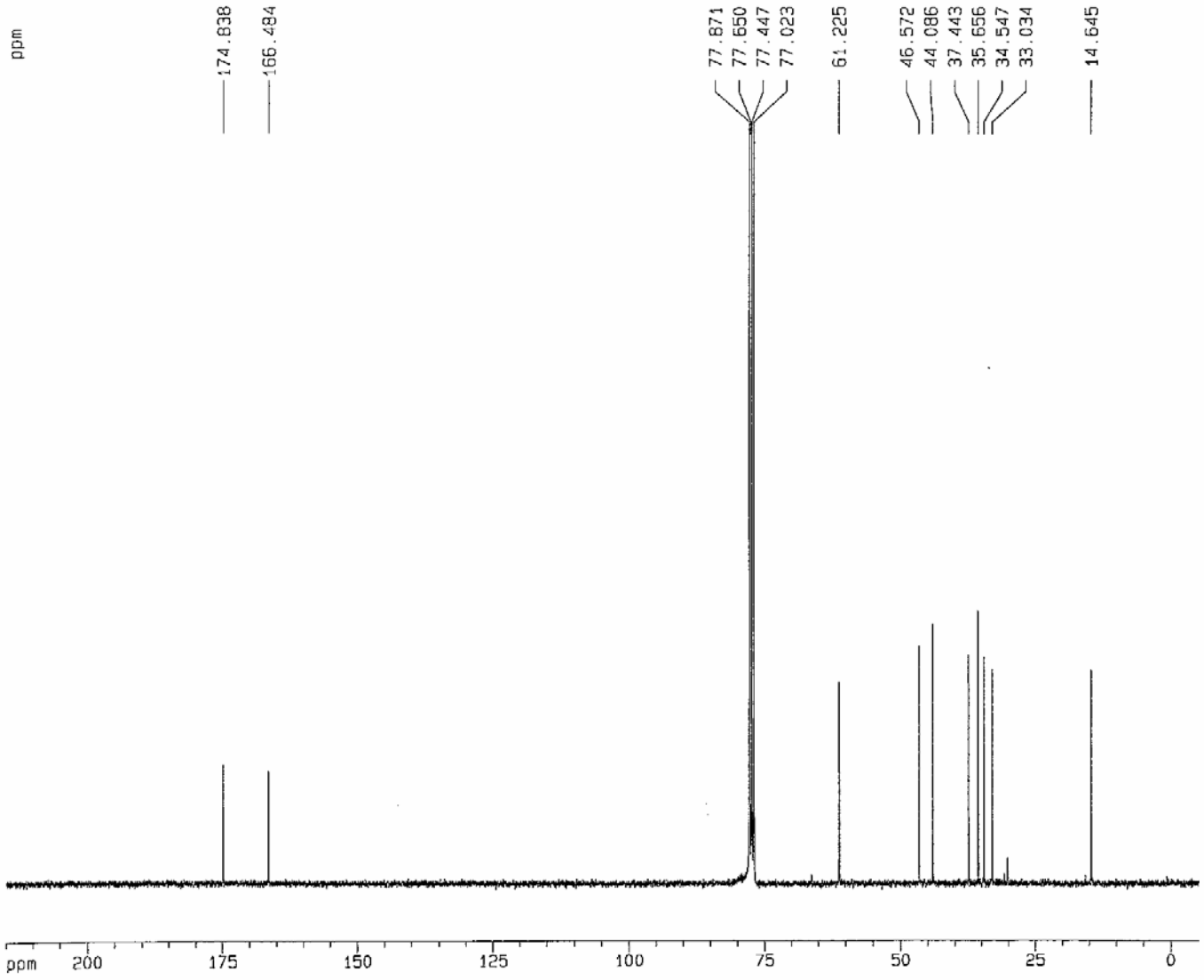



```
Current Data Parameters
NAME      May29-2007-Wein
EXPNO                  92
PROCNO                  1

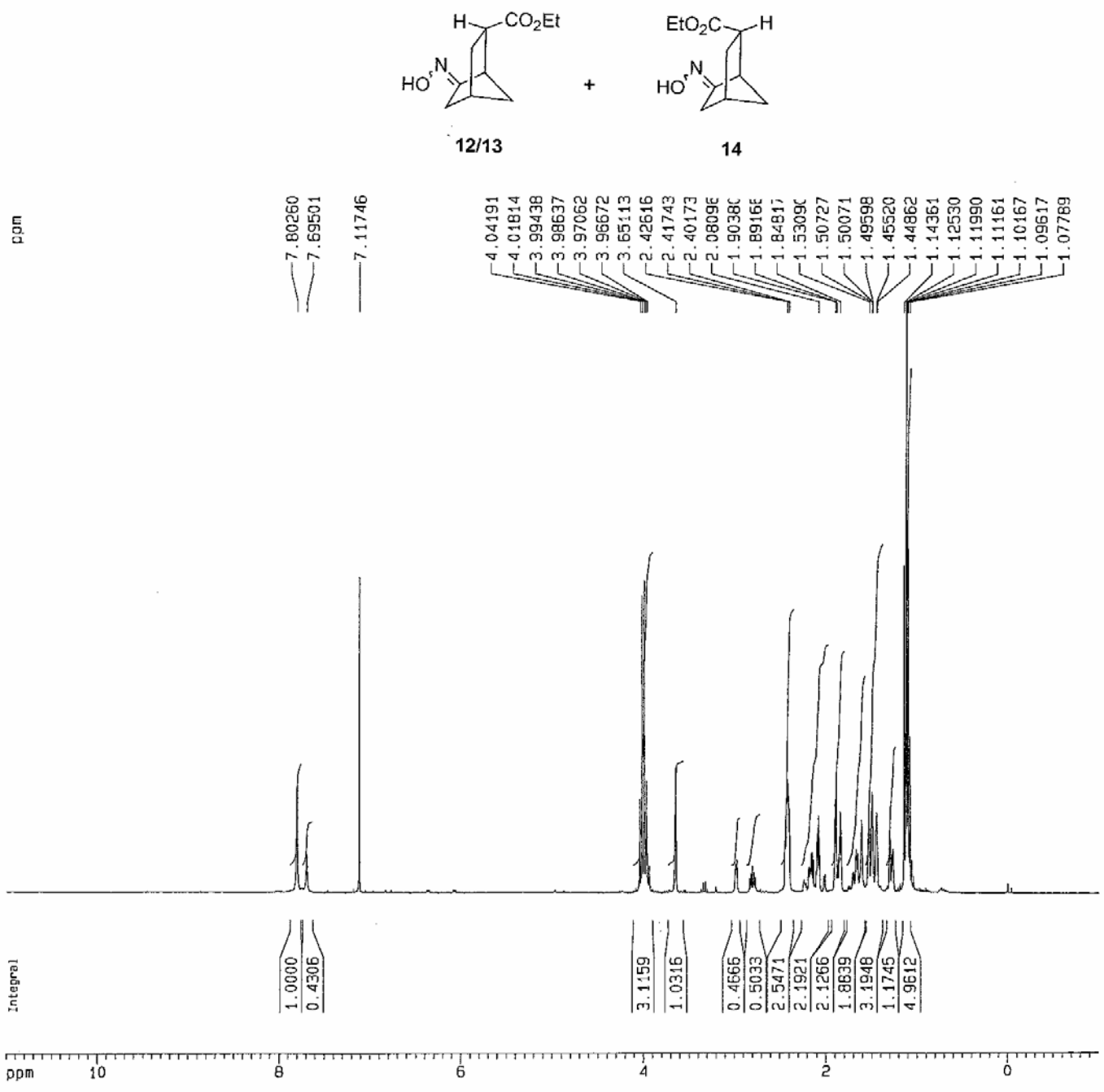
F2 - Acquisition Parameters
Date_            20070529
Time                20.49
INSTRUM             spect
PROBHD    5 mm QNP 1H/1
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                  11641
DS                      4
SWH            18796.992 Hz
FIDRES         0.286819 Hz
AQ             1.7433076 sec
RG                   2048
DW                26.600 usec
DE                 6.00 usec
TE                300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec

========== CHANNEL f1 ==========
NUC1                 13C
P1                  5.40 usec
PL1                -6.00 dB
SFO1          75.4106357 MHz

========== CHANNEL f2 ==========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             115.00 usec
PL2                0.00 dB
PL12              20.00 dB
PL13              20.00 dB
SFO2         299.8711995 MHz

F2 - Processing parameters
SI                   32768
SF            75.4023410 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                  20.00 cm
F1P                215.000 ppm
F1               16211.50 Hz
F2P                 -5.000 ppm
F2                -377.01 Hz
PPMCM             11.00000 ppm/cm
HZCM           829.42578 Hz/cm
```



Current Data Parameters

NAME	May30-2007-Wein
EXPNO	10
PROCNO	1

F2 - Acquisition Parameters

Date_	20070530
Time	18.25
INSTRUM	spect
PROBHD	5 mm Multinu
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	456.1
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 =========

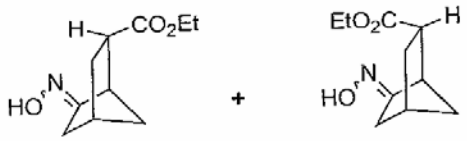
NUC1	1H
P1	9.60 usec
PL1	-6.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	32768
SF	300.1300492 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	11.000 ppm
F1	3301.43 Hz
F2P	-1.000 ppm
F2	-300.13 Hz
PPMCM	0.60000 ppm/cm
HZCM	180.07802 Hz/cm



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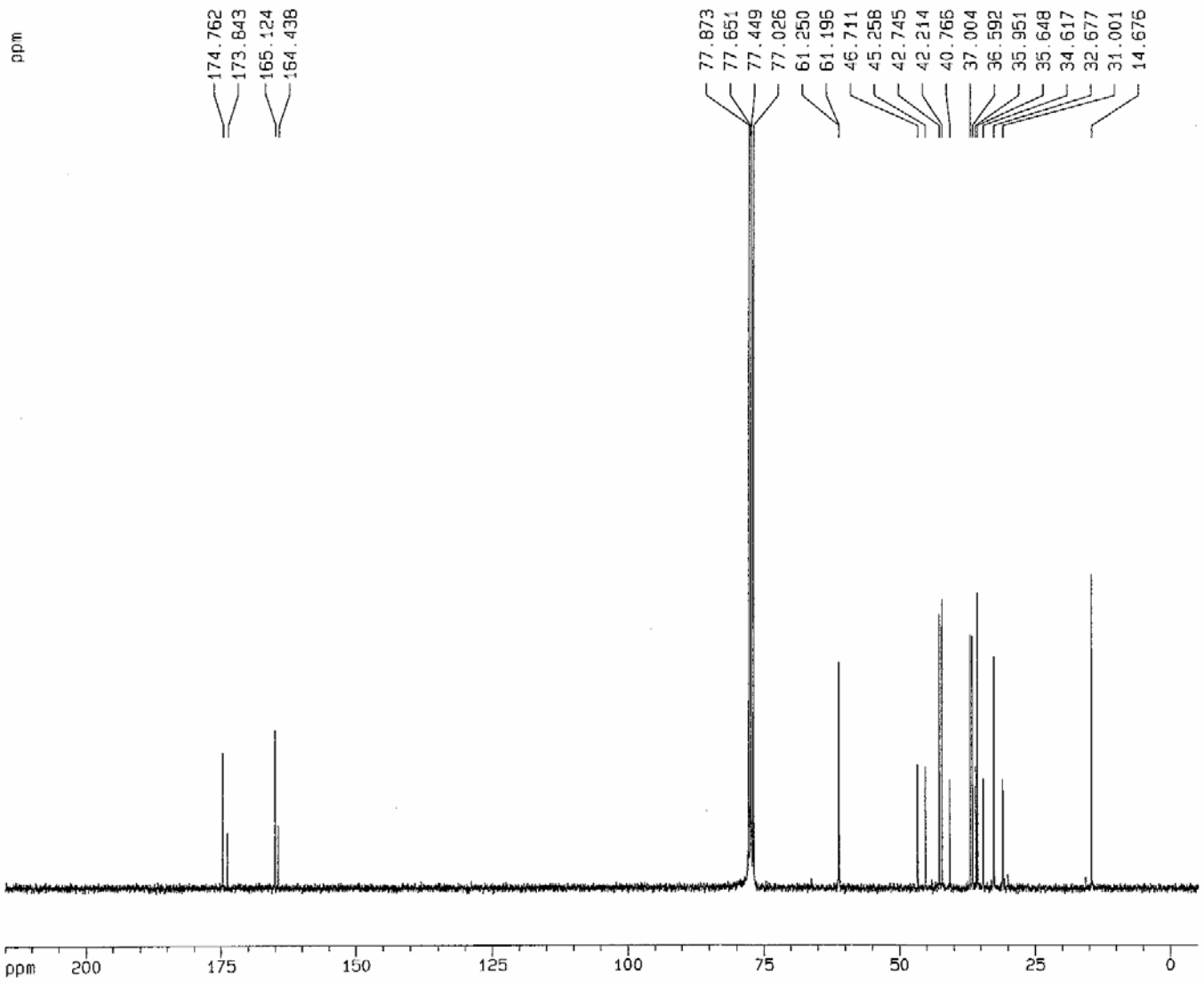


```
Current Data Parameters
NAME      May30-2007-Wein
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070531
Time                0.34
INSTRUM            spect
PROBHD    5 mm CNP 1H/1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  9075
DS                     4
SWH            18796.992 Hz
FIDRES         0.286819 Hz
AQ             1.7433076 sec
RG                   512
DW                26.600 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec

========== CHANNEL f1 ==========
NUC1                13C
P1                 5.40 usec
PL1               -6.00 dB
SFO1          75.4106357 MHz

========== CHANNEL f2 ==========
CPDPRG2          waltz16
NUC2                1H
PCPD2             115.00 usec
PL2                0.00 dB
PL12              20.00 dB
PL13              20.00 dB
SFO2         299.8711995 MHz

F2 - Processing parameters
SI                 32768
SF            75.4023410 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P               215.000 ppm
F1              16211.50 Hz
F2P                -5.000 ppm
F2               -377.01 Hz
PPMCM           11.00000 ppm/cm
HZCM          829.42578 Hz/cm
```