Supplementary Information

'Vinylogous reactivity of silver(I)-vinylcarbenoids'

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Table of Contents

1. Experimental Section..... S-2

1.1 General Considerations..... S-2

1.2 Procedures and Characterization Data..... S-3

2. Computational Studies.....S-17

2.1 General Computational Considerations.....S-17

2.2 Calculated Structures and Properties.....S-18

2.3 Single Point Energy Calculations.....S-29

3. NMR Data for Selected New Compounds.....S-30

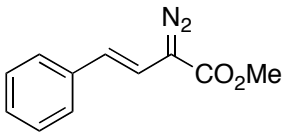
References.....S-75

1. Experimental Section

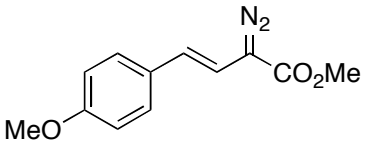
1.1 General Considerations

All reactions were conducted in flame-dried glassware under an inert atmosphere of dry argon. All reagents were used as received from commercial suppliers, unless otherwise stated. Dichloromethane solvent was obtained from drying columns (Grubbs type solvent purifier) and degassed by bubbling argon through the solvent for >15 min prior to use. Flash chromatography was performed on silica gel (230-400 mesh). Thin layer chromatography (TLC) was performed on aluminium-backed plates, pre-coated with silica gel (0.25 mm, 60 F_{254}), which were developed using standard visualizing agents: UV fluorescence (254 nm) and phosphomolybdic acid/Δ. Melting points were determined using a Mel-Temp electrothermal melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Varian Nuclear Magnetic Resonance spectrometers at 600, 500, 400 or 300 MHz. Tetramethylsilane (TMS) (δ = 0.00 ppm), or residual protonated solvent peak of chloroform (δ = 7.26 ppm), were used as internal standards and data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, m = multiplet, and br = broad), integration and coupling constants in Hz. ^{13}C NMR spectra were recorded at 150, 125, 100 or 75 MHz. The solvent was used as internal standard ($CDCl_3$ δ =77.0) and spectra were obtained with complete proton decoupling. Infrared (IR) spectra were aquired using a Thermo Scientific Nicolet iS10 FTIR spectrometer and the wavenumbers are reported in reciprocal centimeters (cm^{-1}). Diastereomer and regioisomer ratios were determined by integration of the ^{1}H NMR spectra of crude reaction mixtures.

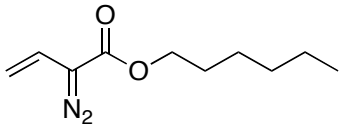
1.2 Procedures and Characterization Data



(*E*)-Methyl 2-diazo-4-phenylbut-3-enoate (1): Synthesized by published procedure.[1] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.29 (m, 4H), 7.20 (t, 1H, *J* = 7 Hz), 6.48 (d, 1H, *J* = 16 Hz), 6.20 (d, 1H, *J* =16 Hz), 3.85 (s, 3H). The spectroscopic properties were consistent with published data.[1]

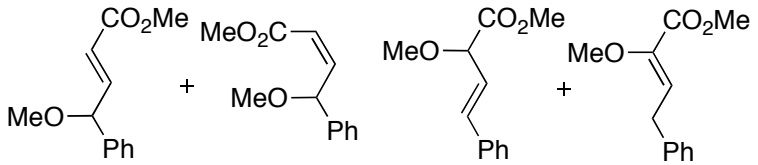


(*E*)-Methyl 2-diazo-4-(4-methoxy)phenylbut-3-enoate (7). Synthesized by published procedure.[1] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, 2H, *J* = 8.8 Hz), 6.86 (d, 2H, *J* = 8.8 Hz), 6.29 (d, 1H, *J* = 16.0 Hz), 6.14 (d, 1H, *J* = 16.0 Hz), 3.84 (s, 3H), 3.80 (s, 3H). The spectroscopic properties were consistent with published data.[1]



Hexyl 2-diazo-3-butenoate (10). According to published procedures.[2] A solution of 2,2,6-trimethyl-1,3-dioxolan-4-one (53.5 g, 0.38 mol) and hexanol (47 mL, 38.2 g, 0.37 mol, 1 equiv.) in xylenes (300 mL) was heated to 130-140°C for 1-1.5 h until all acetone was distilled off. The solvent was then removed *in vacuo*. The residue was diluted with MeCN (400 mL) and added *p*-ABSA (107 g, 0.45 mol, 1.2 equiv.) and NEt_3 (108 mL, 0.77 mol, 2.1 equiv.). The mixture was stirred vigorously for 10 h at ambient temperature. The thick suspension was then filtered, and the filtrate was concentrated *in*

vacuo. The resulting residue was triturated with a 1:1 mixture of Et_2O/pet.ether (3 X 200 mL), dried over Na_2SO_4 and concentrated *in vacuo* to afford a yellow/orange oil. The oil was dissolved in a 1:1 mixture of CH_2Cl_2 and MeOH (500 mL) and cooled to 0°C in an ice bath. $NaBH_4$ was added in portions over 1.5 h and the mixture was stirred for several hours at ambient temperature. The mixture was then concentrated *in vacuo* and diluted with CH_2Cl_2. The organic phase was washed with water (3X), dried over Na_2SO_4 and concentrated *in vacuo* to afford a yellow oil. To a dry flask was added the oil, NEt_3 and CH_2Cl_2. The mixture was cooled to 0°C and added trifluoroacetic anhydride drop-wise over 30 min and stirred for further 2-3 h after addition at ambient temperature. The solvent was removed *in vacuo* and the residue was purified by column chromatography (5-10% Et_2O/pet.ether) to afford an orange liquid **10**. Data for **10**: FTIR (neat): ν_{max}/cm^{-1} 2958, 2932, 2860, 2085, 1705, 1616, 1468, 1389, 1308, 1267, 1158, 1108. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.16 (dd, 1H, J = 17.2, 11.2 Hz), 5.11 (d, 1H, J = 11.2 Hz), 4.85 (d, 1H, J = 17.2 Hz), 4.20 (t, 2H, J = 6.4 Hz), 1.66 (m, 2H), 1.31 (m, 6H), 0.89 (t, 3H, J = 6.4 Hz). Consistent with previously reported data.[2]

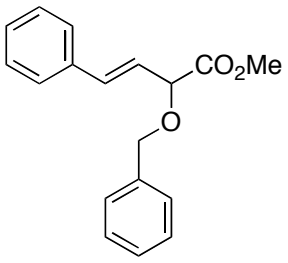


***E*-3.11** ***Z*-3.11** **3.10a** **3.10b**

Data for **(Z)-methyl 4-methoxy-4-phenylbut-2-enoate (*Z*-4).** ^{1}HNMR (500 MHz, $CDCl_3$): δ 7.47-7.28 (m, 5H), 6.32 (dd, 1H, J = 11.5, 9 Hz), 5.97 (d, 1H, J = 9 Hz), 5.87 (d, 1H, J = 11.5 Hz), 3.75 (s, 3H), 3.34 (s, 3H). Data for **(*E*)-methyl 4-methoxy-4-phenylbut-2-enoate (*E*-4)**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.29 (m, 5H), 6.97 (dd, 1H, J = 6, 15.5 Hz), 6.10 (d, 1H, J = 15.5 Hz), 4.78 (d, 1H, J = 6 Hz), 3.72 (s, 3H), 3.33

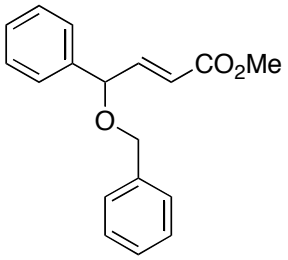
(s, 3H). Data for **(*E*)-methyl 2-methoxy-4-phenylbut-3-enoate (5) and (Z)-methyl 2-methoxy-4-phenylbut-2-enoate (6)**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41-7.28 (m, 5H), 6.77 (d, 1H, J = 15.5), 6.20 (dd, 1H, J = 7, 15.5), 4.43 (d, 1H, J = 7), 3.79 (s, 3H), 3.46 (s, 3H). Consistent with previously reported results.[3]

General Procedure for X–H insertions with Ag-catalyst: To a flame dry round-bottom flask, covered with Al-foil, was added Ag(I)-catalyst (0.05-0.1 equiv.), CH_2Cl_2 (5 mL) and substrate (1.5-2.1 equiv.). The reaction mixture was kept under an inert and dry argon-atmosphere. The mixture was then cooled to 0 °C with an ice/water bath. The vinyldiazoacetate (0.5 mmol, 1.0 equiv.) in CH_2Cl_2 (5 mL, 0.1 M) was added to the former solution drop-wise by syringe pump addition over 1-2 h. The reaction was then allowed to slowly reach ambient temperature and stirred for further 2-12 h until TLC analysis showed full conversion of the diazo compound. The solvent was then removed *in vacuo* and the residue purified by flash column chromatography (SiO_2, Et_2O/pentane mixtures) to afford the product(s).

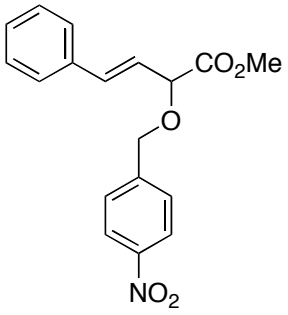


(*E*)-Methyl 2-benzyloxy-4-phenylbut-3-enoate (3). Colourless oil. FTIR (neat): ν_{max}/cm^{-1} 3028, 2951, 1748, 1450, 1435, 1199, 1096, 967, 734, 693. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.25 (m, 10H), 6.77 (d, 1H, J = 16 Hz), 6.25 (dd, 1H, J = 16, 7.2 Hz), 4.66 (q AB, 2H), 4.60 (d, 1H, J = 7.2 Hz), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ

171.1, 137.1, 135.8, 134.4, 128.6, 128.5, 128.2, 128.0, 127.9, 126.7, 123.6, 78.5, 71.3, 52.3. HRMS (ESI): *m/z* 300.1592 ($C_{18}H_{18}O_3$+NH_4 requires 300.1594).

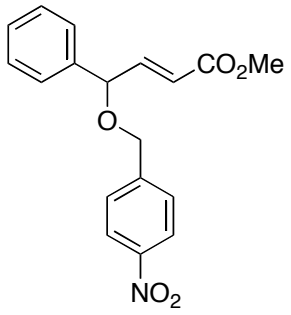


(*E*)-Methyl 4-benzyloxy-4-phenylbut-3-enoate (2). Colourless oil. TLC (20% Et_2O/pentane): R_f = 0.46. FTIR (neat): ν_{max}/cm^{-1} 3087, 3063, 3030, 2949, 2864, 1720, 1658, 1494, 1454, 1435, 1392, 1273, 1195, 1168, 1102, 1040, 1027. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.28 (m, 10H), 7.01 (dd, 1H, *J* = 16.0, 5.5 Hz), 6.15 (d, 1H, *J* = 16.0, 1.5 Hz), 4.98 (dd, 1H, *J* = 5.0, 1.5 Hz), 4.53 (d AB, 1H), 4.45 (d AB, 1H), 3.71 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 147.7, 138.9, 137.9, 137.8, 128.8, 128.4, 128.3, 127.7, 127.6, 127.2, 120.5, 79.7, 70.4, 51.6. HRMS (EI): *m/z* 282.1261 ($C_{18}H_{18}O_3$ requires 282.1250).

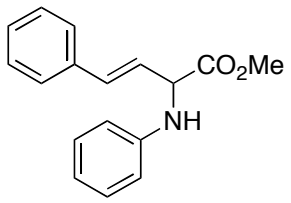


(*E*)-methyl 2-((4-nitrobenzyl)oxy)-4-phenylbut-3-enoate (9a). TLC (10% Et_2O/hexane): R_f = 0.27. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22 (d, 2H, *J* = 9 Hz), 7.57 (d, 2H, *J* = 8.4 Hz), 7.41 (d, 2H, *J* = 7.8 Hz), 7.34 (t, 2H, *J* = 8.4 Hz), 7.29 (t, 1H, *J* = 5.4 Hz), 6.79 (d, 1H, *J* = 16.2 Hz), 6.27 (dd, 1H, *J* = 16.2, 7.2 Hz), 4.78 (d AB, 1H, *J* = 13.2 Hz), 4.72 (d AB, 1H, *J* = 13.2 Hz), 4.64 (dd, 1H, *J* = 7.2, 1.2 Hz), 3.81 (s, 3H). ^{13}C NMR

(150 MHz, $CDCl_3$): δ 170.6, 147.5, 144.9, 135.5, 134.9, 128.7, 128.5, 126.8, 123.7, 123.7, 123, 79.4, 70.0, 52.5. FTIR (film): ν_{max}/cm^{-1} 2924, 1747, 1518, 1344, 1107, 736, 691. MS (neg-APCI): *m/z* 326 (100%, M-H). HRMS (neg-APCI): *m/z* 326.10328 ($C_{18}H_{17}O_5N$-H requires 326.1034).

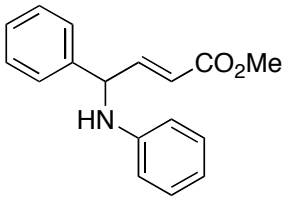


(*E*)-methyl 4-((4-nitrobenzyl)oxy)-4-phenylbut-2-enoate (8a). ^{1}H NMR (400 MHz; $CDCl_3$) δ 2 (12, dH,), 2 (12, dH,), 5 (mH,), 1 (16, 5.2, ddH,), 1 (16, 4.0, ddH,), 1 (16, 4.0, ddH,), 2 (t ABH,), 3 (sH,). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 147.2, 146.9, 145.4, 138.1, 128.8, 128.6, 127.5, 127.1, 123.5, 120.5, 80.5, 69.1, 51.6. FTIR (film): ν_{max}/cm^{-1} 2950, 1720, 1519, 1344, 729, 699. HRMS (pos-APCI): *m/z* 328.11844 ($C_{18}H_{17}O_5N$+H requires 328.11795).

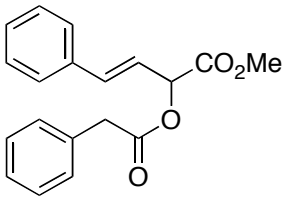


(*E*)-methyl 4-phenyl-2-(phenylamino)but-3-enoate (9b). White solid. Mp = 64-66 °C. FTIR (film): ν_{max}/cm^{-1} 3396, 3024, 2952, 1735, 1601, 1504, 1432, 1202, 1158, 968, 748, 691. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (dm, 2H, J = 7.2 Hz), 7.31 (tm, 2H, J = 6.8 Hz), 7.26-7.23 (m, 1H), 7.20-7.16 (tm, 2H), 6.81-6.73 (m, 2H), 6.66 (dm, 1H, J = 7.6 Hz), 6.29 (dd, 1H, J = 16, 6.0 Hz), 4.74 (br t, 1H, J = 6.0 Hz), 4.66 (br s, 1H), 3.80 (s, 3H). ^{13}C

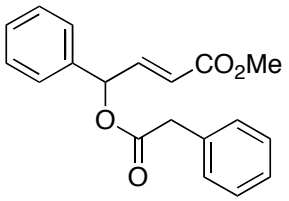
NMR (100 MHz, $CDCl_3$): δ 172.2, 146.2, 136.0, 133.0, 129.3, 128.6, 128.0, 126.7, 124.8, 118.3, 113.5, 58.8, 52.8. HRMS (ESI): *m/z* 268.13309 *(*$C_{17}H_{17}O_2N$+H requires 268.13321).



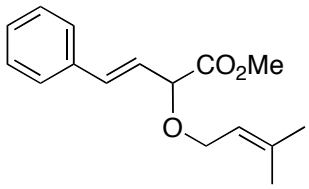
(*E*)-methyl 4-phenyl-4-(phenylamino)but-2-enoate (8b). Colourless oil. FTIR (film): ν_{max}/cm^{-1} 3384, 3027, 2949, 1713, 1657, 1600, 1501, 1434, 1275, 1168. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.30 (m, 5H), 7.18-7.13 (m, 2.5H), 7.09 (d, 0.5H, *J* = 5.6 Hz), 6.74 (t, 1H, *J* = 7.6 Hz), 6.59 (d, 1H, *J* = 7.6 Hz), 6.10 (dd, 1H, *J* = 16.0, 1.6 Hz), 5.06 (d, 1H, *J* = 4.4 Hz), 4.05 (bs, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 148.0, 146.6, 139.9, 129.2, 129.1, 128.2, 127.4, 121.4, 118.2, 113.5, 59.5, 51.6. HRMS (ESI): *m/z* 268.13315 ($C_{17}H_{17}O_2N$+H requires 268.13321).



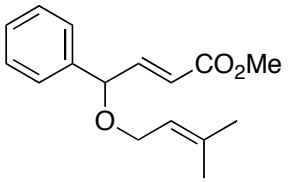
(*E*)-methyl 4-phenyl-2-(2-phenylacetoxy)but-3-enoate (9c). Colourless oil. FTIR (neat): ν_{max}/cm^{-1} 3029, 2953, 1740, 1497, 1454, 1436, 1206, 1142, 1029, 967. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.25 (m, 10H), 6.73 (d, 1H, *J* = 16 Hz), 6.25 (dd, 1H, *J* = 16, 7.2 Hz), 5.65 (dd, 1H, *J* = 7.2, 1.2 Hz), 3.79 (bs, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 168.9, 135.4, 135.2, 133.3, 129.4, 128.6, 128.6, 127.2, 126.8, 120.5, 73.3, 52.7, 40.9. HRMS (ESI): *m/z* 328.15422 (M+NH_4 requires 328.15433).



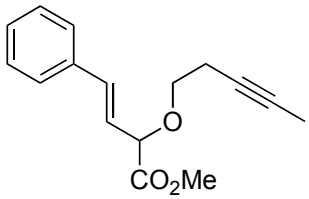
(*E*)-methyl 4-phenyl-4-(2-phenylacetoxy)but-2-enoate (8c). Colourless oil. TLC (20% EtOAc/hexane): R_f = 0.42. FTIR (neat): ν_{max}/cm^{-1} 3031, 2950, 1722, 1661, 1243, 1170, 1139, 978, 696. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.25 (m, 10H), 6.98 (dd, 1H, *J* = 15.6, 5.2 Hz), 6.39 (dd, 1H, *J* = 5.2, 1.6 Hz), 5.94 (dd, 1H, *J* = 15.6, 1.6 Hz), 3.71 (s, 3H), 3.69 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 166.2, 144.6, 136.9, 133.4, 129.2, 128.7, 128.7, 128.6, 127.2, 121.2, 74.4, 51.7, 41.3 LRMS (ESI): *m/z* 328 (100), 278 (4). HRMS (ESI): *m/z* 328.15431 (M+NH_4 requires 328.15433).



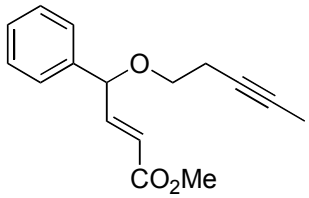
(*E*)-Methyl 2-(3-methylbut-2-enoxy)-4-phenylbut-3-enoate (9d). TLC (20% Et_2O/hexane): R_f = 0.24. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.39 (m, 2H), 7.35-7.31 (m, 2H), 7.28-7.24 (m, 1H), 7.76 (d, 1H, *J* = 16 Hz), 6.23 (dd, 1H, *J* = 16, 6.8 Hz), 5.40 (tt, 1H, *J* = 7.2, 1.2 Hz), 4.57 (dd, 1H, *J* = 7.2, 1.6 Hz), 4.10 (m AB, 2H), 3.78 (s, 3H), 1.77 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.4, 138.4, 135.9, 134.1, 128.6, 128.2, 126.7, 124, 120.1, 78.5, 65.9, 52.3, 25.8, 18.1. FTIR (film): ν_{max}/cm^{-1} 2915, 1750, 1198, 967, 736, 691. HRMS (pos-APCI): *m/z* 261.14851 ($C_{16}H_{20}O_3$+H requires 261.14852).



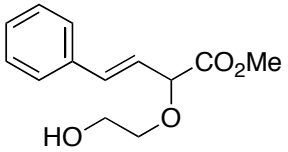
(*E*)-Methyl 4-(3-methylbut-2-enoxy)-4-phenylbut-2-enoate (8d). Yellow oil. FTIR (neat film): ν_{max} (cm^{-1}) 3063, 3029, 2973, 2949, 2858, 1724, 1659, 1493, 1453, 1436, 1378, 1303, 1271, 1245, 1195, 1168, 1115, 1061, 1026. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.30 (m, 5H), 6.99 (dd, 1H, J = 15.5, 5.5 Hz), 6.07 (d, 1H, J = 15.5 Hz), 5.36 (m, 1H), 4.94 (d, 1H, J = 5.5 Hz), 3.95 (d, 2H, J = 7.0 Hz), 3.72 (s, 3H), 1.74 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 148.0, 139.3, 137.4, 128.6, 128.1, 127.1, 120.7, 120.4, 79.6, 65.2, 51.5, 25.7, 18.0. HRMS (ESI): *m/z* 260.1406 ($C_{16}H_{20}O_3$ requires 260.1407).



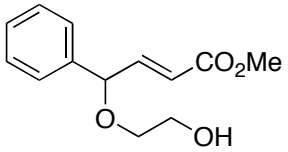
(*E*)-Methyl 2-(pent-3-ynoxy)-4-phenylbut-2-enoate (9e). TLC (20% Et_2O/hexane): R_f= 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.38 (m, 2H), 7.35-7.31 (m, 2H), 7.29-7.25 (m, 1H), 6.78 (d, 1H, J = 16 Hz), 6.22 (dd, 1H, J = 16, 7.2 Hz), 4.59 (dd, 1H, J = 7.2, 1.6 Hz), 3.78 (s, 3H), 3.70-3.59 (m, 2H), 2.54-2.48 (m, 2H), 1.77 (t, 3H, J = 2.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171 (4°), 135.8 (4°), 134.2 (3°), 128.6 (3°), 128.2 (3°), 126.7 (3°), 123.6 (3°), 79.9 (3°), 77 (4°), 75.2 (4°), 68.4 (2°), 52.3 (1°), 20 (2°), 3.5 (1°). FTIR (film): ν_{max}/cm^{-1} 2919, 1749, 1198, 1107, 967, 736, 691. MS (neg-APCI): *m/z* 257 (100%, M-H), 219 (4%), 197 (3%), 190 (11%). HRMS (neg-APCI): *m/z* 257.11823 ($C_{16}H_{18}O_3$-H requires 257.11832).



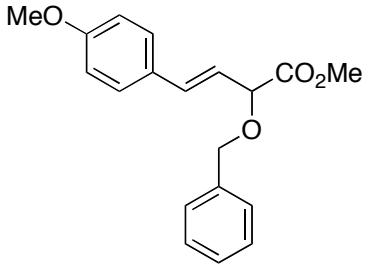
(*E*)-Methyl 4-(pent-3-ynoxy)-4-phenylbut-2-enoate (8e). TLC (15% Et_2O/pentane): R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.29 (m, 5H), 6.97 (dd, 1H, *J* = 15.6, 5.6 Hz), 6.12 (dd, 1H, *J* = 15.6, 1.6 Hz), 4.95 (dd, 1H, *J* = 5.2, 1.6 Hz), 3.72 (s, 3H), 3.55-3.46 (m, 2H), 2.46-2.40 (m, 2H), 1.77 (t, 3H, *J* = 2.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 147.6, 138.9, 128.7, 128.3, 127.1, 120.4, 80.8, 76.8, 75.6, 67.6, 51.6, 20.1, 3.4. FTIR (film): ν_{max}/cm^{-1} 2918, 1722, 1271, 1167, 1103, 699. MS (negAPCI): m/z 257 (100%), 219 (5%), 190 (5%). HRMS (neg-APCI): m/z 257.11827 ($C_{16}H_{18}O_3$-H requires 257.11832).



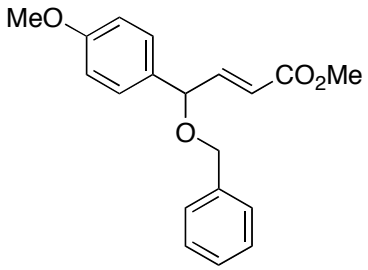
(*E*)-methyl 2-(2-hydroxyethoxy)-4-phenylbut-3-enoate (9f). TLC (40% EtOAc/hexanes): R_f = 0.16. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, 2H, *J* = 7.6 Hz), 7.35-7.26 (m, 3H), 6.78 (d, 1H, *J* = 15.6 Hz), 6.23 (dd, 1H, *J* = 16.4, 7.2 Hz), 4.60 (dd, 1H, *J* = 7.2, 1.6 Hz), 3.83-3.74 (m, 3H), 3.79 (s, 3H), 3.68-3.62 (m, 1H), 2.57 (t, 1H, *J* = 6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.4, 135.7, 134.3, 128.6, 128.3, 126.7, 123.4, 79.9, 71.4, 61.7, 52.4. FTIR (film): ν_{max}/cm^{-1} 3456 (OH), 2952, 1736, 1065, 969, 738, 692. HRMS (ESI): *m/z* 259.09393 ($C_{13}H_{16}O_4$+Na requires 259.09408).



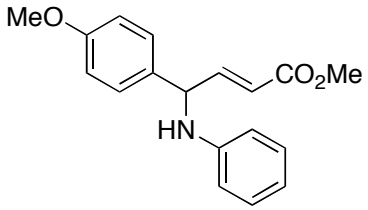
(*E*)-methyl 4-(2-hydroxyethoxy)-4-phenylbut-2-enoate (8f). TLC (40% EtOAc/hexanes): R_f = 0.25. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (t, 2H, *J* = 6.6 Hz), 7.33-7.30 (m, 3H), 6.99 (dd, 1H, *J* = 15.6, 5.4 Hz), 6.10 (dd, 1H, *J* = 15.6, 1.8 Hz), 4.96 (dd, 1H, *J* = 5.4, 1.2 Hz), 3.75 (bs, 2H), 3.73 (s, 3H), 3.73-3.55 (m, 1H), 3.53-3.50 (m, 1H), 2.06 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 147.3, 138.7, 128.8, 128.4, 127.1, 120.5, 81.2, 70.1, 61.9, 51.6. FTIR (film): ν_{max}/cm^{-1} 3428 (OH), 2950, 1719, 1274, 1169, 1042, 699. MS (ESI): *m/z* 259 (100%, M+Na). HRMS (ESI): *m/z* 259.09395 ($C_{13}H_{16}O_4$+Na requires 259.09408).



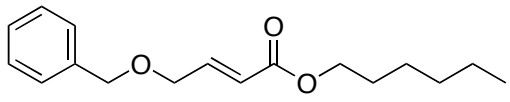
(*E*)-methyl 2-(benzyloxy)-4-(4-methoxyphenyl)but-3-enoate (9g). TLC (20% EtOAc/hexanes): R_f = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.29 (m, 7H), 6.86 (dt, 2H, *J* = 8.8, 2.8 Hz), 6.70 (d, 1H, *J* = 16 Hz), 6.11 (dd, 1H, *J* = 16, 6.8 Hz), 4.64 (q AB, 2H), 4.57 (dd, 1H, *J* = 7.6, 0.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 159.7, 137.2, 134.2, 128.6, 128.5, 128, 128, 127.9, 121.4, 114, 78.8, 71.1, 55.3, 52.3. FTIR (film): ν_{max}/cm^{-1} 2923, 1747, 1511, 1251, 1174, 1028, 698.



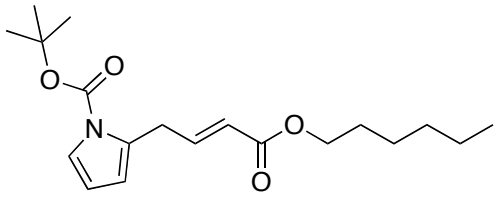
(*E*)-Methyl 4-benzyloxy-4-(4-methoxyphenyl)but-2-enoate (8g). TLC (20% Et_2O/pentane): R_f = 0.21. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.28 (m, 5H), 7.25 (dt, 2H, *J* = 8.8, 2.0 Hz), 7.00 (dd, 1H, *J* = 15.6, 5.2 Hz), 6.90 (dt, 2H, *J* = 8.8, 2.0 Hz), 6.13 (dd, 1H, *J* = 15.6, 2.0 Hz), 4.94 (dd, 1H, *J* = 5.2, 1.6 Hz), 4.47 (q AB, 2H), 3.81 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 159.6, 147.9, 137.9, 130.8, 128.6, 128.4, 127.6, 127.6, 120.1, 114.1, 79.2, 70.1, 55.3, 51.6. FTIR (film): ν_{max}/cm^{-1} 2950, 1721, 1510, 1246, 1167, 1028, 831. MS (neg-APCI): *m/z* 311 (100%, M-H), 279 (20%), 264 (9%). HRMS (neg-APCI): *m/z* 311.1287 ([$C_{19}H_{20}O_4$-H] requires 311.12888).



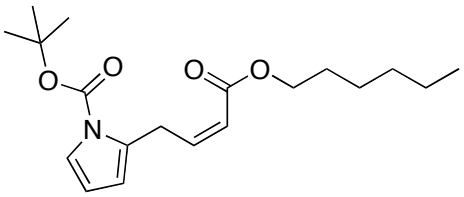
(*E*)-methyl 4-(4-methoxyphenyl)-4-(phenylamino)but-2-enoate (8h). TLC (30% Et_2O/hexanes): R_f = 0.25. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82 (d, 2H, *J* = 7.8 Hz), 7.70 (s, 1H), 7.48 (t, 1H, *J* = 7.8 Hz), 7.35 (t, 2H, *J* = 7.8 Hz), 7.21 (bs, 5H), 3.85 (s, 3H), 6.07 (dd, 1H, *J* = 15.6, 1.2 Hz), 4.99 (bt, 1H, *J* = 4.8 Hz), 4.02 (bd, 1H, *J* = 3.6 Hz), 3.78 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 159.4, 148.3, 146.6, 131.9, 129.1, 128.6, 121.1, 118.0, 114.3, 113.4, 58.9, 55.2, 51.5. FTIR (film): ν_{max}/cm^{-1} 3385, 2950, 1713, 1600, 1502, 1246, 1168. MS (neg-APCI): *m/z* 296 (100%, M-H), 264 (26%, M-H-OMe). HRMS (neg-APCI): *m/z* 296.12923 ($C_{18}H_{19}O_3N$-H requires 296.12922).



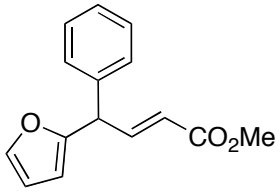
(*E*)-Hexyl 4-benzyloxybut-2-enoate (13). TLC (10% Et_2O/hex): R_f = 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 5H), 6.98 (dt, 1H, *J* = 15.6, 4.4 Hz), 6.14 (dt, 1H, *J* = 15.6, 2.0 Hz), 4.57 (s, 2H), 4.19 (dd, 2H, *J* = 4.4, 2.0 Hz), 4.14 (t, 2H, *J* = 6.4 Hz), 1.69-1.62 (m, 2H), 1.40-1.27 (m, 6H), 0.89 (t, 3H, *J* = 6.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.3, 144.1, 137.7, 128.4, 127.8, 127.6, 121.4, 72.7, 68.6, 64.6, 31.4, 28.6, 25.5, 22.5, 14. IR (film): ν_{max}/cm^{-1} 2930, 1718, 1271, 1169, 1119, 1022, 697. HRMS (pos-APCI): m/z 277.17979 (M+H requires 277.17982).



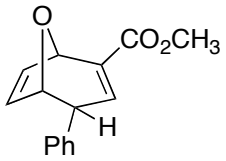
(*E*)-*tert*-butyl 2-(4-(hexyloxy)-4-oxobut-2-en-1-yl)-1*H*-pyrrole-1-carboxylate (*E*-14). Colourless oil. FTIR (neat): ν_{max}/cm^{-1} 2956, 2932, 2859, 1740, 1720, 1655, 1493, 1330, 1313, 1266, 1161, 1121, 1061. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.23 (dd, 1H, *J* = 3.2, 1.6 Hz), 7.11 (dt, 1H, *J* = 16.0, 6.4 Hz), 6.10 (t, 1H, *J* = 3.2 Hz), 5.99 (m, 1H), 5.78 (dt, 1H, *J* = 15.6, 1.6 Hz), 4.12 (t, 2H, *J* = 6.8 Hz), 3.76 (d, 2H, *J* = 6.4 Hz), 1.64 (m, 2H), 1.58 (s, 9H), 1.37 (m, 6H), 0.89 (t, 3H, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 166.7, 149.2, 146.1, 131.1, 122.3, 121.5, 112.7, 110.1, 83.8, 64.4, 31.5, 31.4, 28.6, 27.9, 25.6, 22.5, 14.0. HRMS (pos-APCI): *m/z* 336.2155 ([$C_{19}H_{28}O_4N$] requires 336.2169).



(*Z*)-*tert*-butyl 2-(4-(hexyloxy)-4-oxobut-2-en-1-yl)-1*H*-pyrrole-1-carboxylate (*Z*-14). Colourless oil. FTIR (neat): ν_{max}/cm^{-1} 2957, 2932, 2860, 1743, 1720, 1644, 1493, 1458, 1406, 1371, 1337, 1319, 1236, 1172, 1124, 1064. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (bs, 1H), 6.40 (dt, 1H, J = 11, 7.0 Hz), 6.08 (bs, 1H), 6.01 (bs, 1H), 5.85 (d, 1H, J = 12.0 Hz), 4.23 (d, 2H, J = 6.5 Hz), 4.12 (t, 2H, J = 7.0 Hz), 1.67 (m, 2H), 1.58 (s, 9H), 1.37 (m, 2H), 1.31 (m, 4H), 0.89 (t, 3H, J = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 149.4, 146.5, 132.7, 121.2, 120.0, 112.0, 110.1, 83.7, 64.2, 31.4, 28.7, 28.6, 27.9, 25.6, 22.5, 14.0. MS (EI): *m/z* (rel. int) 336 (19), 252 (31), 236 (100). HRMS (EI): *m/z* 336.2168 ([$C_{19}H_{28}O_4N$+H] requires 336.2169).



(*E*)-methyl 4-(furan-2-yl)-4-phenylbut-2-enoate (15). FTIR (neat): ν_{max}/cm^{-1} 3029, 2950, 1723, 1654, 1495, 1454, 1435, 1314, 1272, 1236, 1195, 1166, 1038, 1010, 982, 913, 742, 700. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.25 (m, 5H), 7.20 (d, 2H, J = 7.0 Hz), 6.32 (m, 1H), 6.07 (d, 1H, J = 3.0 Hz), 5.79 (dd, 1H, J = 15.5, 1.0 Hz), 4.88 (d, 1H, J = 7.0 Hz), 3.72 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 154.0, 147.3, 142.2, 139.0, 128.8, 128.3, 127.4, 122.6, 110.3, 107.3, 51.6, 47.5. MS (EI): *m/z* 242, 210, 183, 153. HRMS (EI): *m/z* 242.0944 ([$C_{15}H_{14}O_3$] requires *m/z* 242.0937).



(±)-Methyl 4-phenyl-8-oxabicyclo[3.2.1]octa-2,6-diene-2-carboxylate (16). FTIR (neat): ν_{max}/cm^{-1} 3028, 2993, 2951, 1712, 1633, 1494, 1452, 1437, 1355, 1337, 1294, 1276, 1203, 1076, 1042. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.26 (m, 3H), 7.09 (d, 2H, J = 7.0 Hz), 6.74 (bs, 1H), 6.66 (dd, 1H, J = 6.0, 1.5 Hz), 5.53 (dd, 1H, J = 5.5, 1.5 Hz), 5.21 (bs, 1H), 5.12 (d, 1H, J = 4.5 Hz), 4.10 (dd, 1H, J = 6.5, 2.5 Hz), 3.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2, 139.5, 139.0, 136.3, 135.7, 128.7, 128.1, 127.7, 127.4, 82.4, 75.9, 51.8, 42.9. MS (EI): *m/z* 242, 210, 183, 153. HRMS (EI): *m/z* 242.0941 ($C_{15}H_{14}O_3$ requires *m/z* 242.0937).

2. Computational Studies

2.1 General Computational Considerations

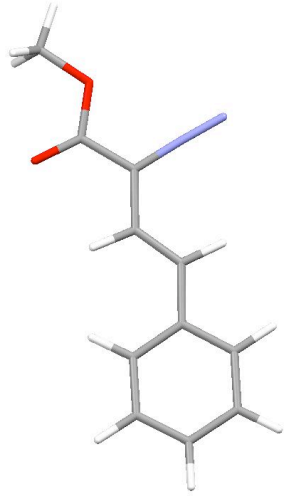
All calculations were performed with the Gaussian '09 software package.[5] Density Functional Theory was employed with the 3-parameter hybrid functional B3LYP[6,7] to locate stationary points on the potential energy surface (PES). The structures were subjected to full geometry optimization with a basis set consisting of the 1997 Stuttgart relativistic small-core effective core-potential [Stuttgart RSC 1997 ECP][8-10] for Ag, augmented with two 4f-functions (ζf(Ag) = 2.5 and 0.7).[11,12] The Ag f-exponents were obtained from Reference 11.[11] The split valence basis set 6-31G* was used in the optimization and frequency calculations for all other atoms (C, H, O, F, N and S). This composite basis set is abbreviated 6-31G*[Ag-RSC+4f].[13]. The main discussion in this chapter is based on single-point energies obtained at the B3LYP/6-311+G(2d,2p)[Ag-RSC+4f]//B3LYP/6-31G*[Ag-RSC+4f] level, corrected with zero-point energies from B3LYP/6-31G*[Ag-RSC+4f] calculations. Heavy-atom basis set definitions and corresponding pseudopotential parameters were obtained from the EMSL basis set exchange library.[14,15] All stationary points were characterized by normal coordinate analysis at the B3LYP/6-31G*[Ag-RSC+4f] level of theory. For transition states TS-IIIa and TS-IIIb, full geometry optimization was also carried out at the B3LYP/6-311+G(2d,2p)[Ag-RSC+4f] level of theory at temperature=273.15 K, also including the effects of dichloromethane as solvent (ε = 8.93) through the Integral Equation Formalism Polarizable Continuum Model (IEFPCM).[5,16] All transition states were confirmed to have only one imaginary vibrational mode corresponding to movement along the reaction coordinate.[17] Equilibrium structures were confirmed to have zero imaginary vibrational

modes.[17] Transition states were further characterized by intrinsic reaction coordinate (IRC) analysis using default parameters, followed by geometry optimization, to confirm that the stationary points were smoothly connected to each other.[7] The calculated harmonic zero-point vibrational energies (ZPVE) are reported unscaled. Calculated structures have been visualized using Mercury.[18-21]

2.2 Calculated Structures and Properties

The structure and properties of dinitrogen $\mathbf{N_2}$ has been reported prevously.[13]

Structure 1



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ZPE=0.192102 Hartree
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Free Energy=-684.925867 Hartree
Entropy=122.234 cal/mol-K

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C	-2.34334700	0.24352200	0.00017400
C	-3.46440300	1.19519200	0.00016700
C	-4.84540200	0.74138500	0.00019700
C	-5.95071200	1.51481500	0.00000400
H	-5.83196600	2.59889600	-0.00023000
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C	-10.0605500	0.28624200	0.00018800
C	-9.05034600	-0.68153100	0.00019000
C	-7.71098900	-0.30515700	0.00013000
H	-6.94521800	-1.07537100	0.00011500
H	-9.30961400	-1.73708800	0.00023500
H	-11.1051270	-0.01266000	0.00022900
H	-10.4872250	2.40097800	0.00009300
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N	-3.17734000	2.47980800	0.00019100
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O	-2.48871700	-0.96321200	0.00017800
H	0.00021200	-0.63394600	0.89056200
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AgOTf

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ZPE=0.027984 Hartree
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Free Energy=-1108.435123 Hartree
Entropy=100.527 cal/mol-K

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F	-2.02450100	-1.29090400	-1.08842700
F	-0.62600500	-2.55745200	-0.00010400
F	-2.02435300	-1.29085600	1.08839700
O	0.83992200	-0.30533700	1.22535900
Ag	2.65949800	-1.01978100	-0.00004000
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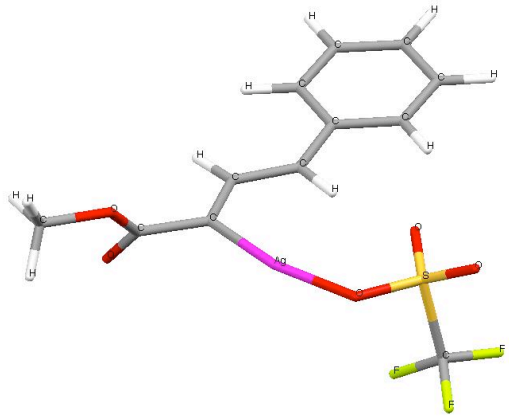
O	0.84001100	-0.30513800	-1.22543800

Ag-carbenoid VC, *s-cis*



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ZPE=0.212141 Hartree
Conditions=298K, 1.00000 atm
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Enthalpy=-1683.799328 Hartree
Free Energy=-1683.882131 Hartree
Entropy=174.273 cal/mol-K

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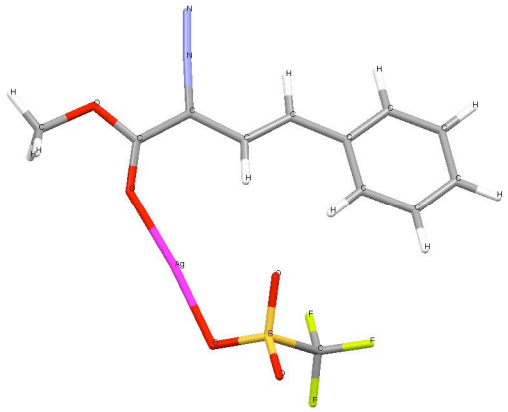
C	-0.75891600	0.16976700	1.69140200
F	-1.88543700	-0.53965000	1.77817100
F	0.10277100	-0.27665000	2.62630500
F	-1.02926700	1.45450700	1.94591300
O	-1.02154100	0.42944400	-0.94963000
O	1.25020600	0.79428700	0.09088500
Ag	2.28610900	-1.97792500	0.48186100
O	0.28245500	-1.50195000	-0.04685500
C	4.29961900	-1.99943600	0.93474800
C	5.03088200	-3.25915100	1.21420400
O	5.00391600	-4.12114500	0.18641600
C	5.66374300	-5.38316600	0.41268100
H	6.71113300	-5.22590400	0.68234700
H	5.58431600	-5.92241100	-0.53052400
H	5.16240300	-5.93077100	1.21460300
O	5.54652900	-3.47827900	2.29505700
C	5.05167700	-0.82678700	1.02590200
C	4.44152600	0.40257600	0.77770900
H	3.37080600	0.38068600	0.57274100
C	5.03329500	1.70503700	0.74533600
C	4.17081700	2.79690400	0.46904900
C	4.67102500	4.09275800	0.43231000
C	6.03083800	4.31777500	0.66846400
C	6.89834100	3.24831300	0.94145100
C	6.40965800	1.95234000	0.97889100
H	7.08224300	1.12660100	1.18736600
H	7.95207300	3.43800200	1.12159800
H	6.42255200	5.33085800	0.63939400
H	4.00799900	4.92574500	0.22059800
H	3.11720800	2.59886500	0.28785500
H	6.11238700	-0.87339100	1.27424100

Lewis Acid complex LA-I

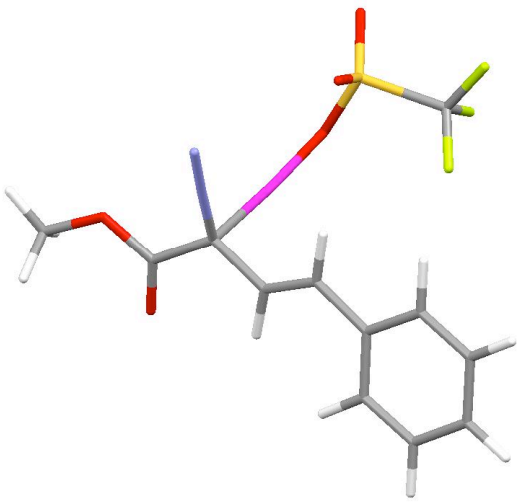


Route= #N b3lyp/gen pseudo=read gfprint OPT FREQ
RB3LYP Energy=-1793.54344838 Hartree
ZPE=0.221452 Hartree
Conditions=298K, 1.00000 atm
Internal Energy=-1793.296804 Hartree
Enthalpy=-1793.295859 Hartree
Free Energy=-1793.383213 Hartree
Entropy=183.850 cal/mol-K

C	0.00000000	0.00000000	0.00000000
Ag	2.39926400	-2.88368000	-0.41383400
F	7.04389700	-2.59168300	-1.36390600
F	5.47220100	-1.09006300	-1.50418600
F	7.03677100	-0.89473500	-0.00103700
O	6.15287100	-3.46128600	1.40049800
O	4.34544000	-1.69890500	1.17003500
C	6.26483400	-1.77157500	-0.65860400
O	4.40527200	-3.61231600	-0.39586400
C	-2.26357300	-2.86190800	-0.34747600
O	-1.75219000	-1.52778000	-0.14528300
C	-0.42596300	-1.36876700	-0.20281000
S	5.22126700	-2.72707700	0.55089800
C	1.38383900	0.48044600	0.01914800
C	1.74346800	1.76422600	-0.19235000
H	0.96113500	2.48385200	-0.43842100
C	3.09027100	2.33508100	-0.14661200
C	3.25373400	3.68601200	-0.50770200
C	4.51264300	4.28289600	-0.50498100
C	5.63564900	3.53747500	-0.14168000
C	5.48774500	2.19542100	0.22395600
C	4.23074100	1.59831000	0.22943400
H	4.14466200	0.56082700	0.53566300
H	6.35417000	1.60425300	0.50389500
H	6.61984800	3.99795100	-0.14058800
H	4.61620100	5.32705900	-0.78745800
H	2.38163300	4.26847200	-0.79730200
H	2.12572700	-0.27674800	0.25959200
N	-0.98427700	0.87376500	0.16880300
N	-1.79033000	1.66058200	0.30561400
O	0.32333400	-2.33487300	-0.41944300
H	-1.98613900	-3.22833400	-1.33839500
H	-3.34496500	-2.76346700	-0.26147900
H	-1.87474700	-3.53695200	0.41808600

Diazocomplex LA-II

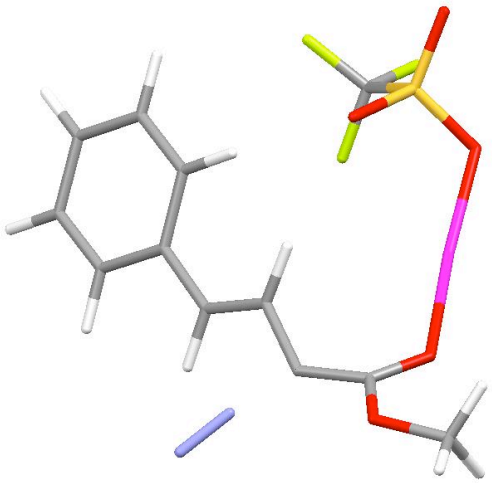
C	0.00000000	0.00000000	0.00000000
Ag	1.89330400	-1.01426300	-0.73937500
F	4.15058900	-5.23900300	0.38447900
F	2.53451400	-4.54105000	-0.89783000
F	4.54022300	-4.78730400	-1.70862000
O	5.67395000	-2.60432600	0.06598400
O	3.75710400	-1.90490700	-1.40772000
C	3.84804700	-4.42252100	-0.62809700



Route= #N b3lyp/gen pseudo=read gfprint OPT FREQ
RB3LYP Energy=-1793.52861111 Hartree
ZPE=0.220344 Hartree
Conditions=298K, 1.00000 atm
Internal Energy=-1793.282657 Hartree
Enthalpy=-1793.281713 Hartree
Free Energy=-1793.372585 Hartree
Entropy=191.256 cal/mol-K

O	3.31444300	-2.37206800	0.97083400
C	0.72235100	3.52900000	-0.82612800
O	0.60069800	2.27752900	-0.11407600
C	0.02163300	1.27490500	-0.79469100
S	4.23455800	-2.66059400	-0.16552600
C	-0.93255700	-1.08222700	-0.40918800
C	-1.23576600	-2.18814400	0.30032600
H	-0.74451800	-2.34834400	1.26082600
C	-2.16725100	-3.24895200	-0.09155100
C	-2.25556100	-4.39621900	0.71841700
C	-3.11692500	-5.44188600	0.39187800
C	-3.91263100	-5.36000900	-0.75153000
C	-3.84043900	-4.22354900	-1.56432500
C	-2.98158900	-3.17892900	-1.23894300
H	-2.95021700	-2.30078300	-1.87760700
H	-4.46035200	-4.15094300	-2.45364900
H	-4.58616400	-6.17253500	-1.00883700
H	-3.16510100	-6.31963000	1.03014700
H	-1.63448000	-4.46713400	1.60827600
H	-1.35791100	-0.88207700	-1.38824000
N	0.21522400	0.16685900	1.32658100
N	0.39641100	0.26320900	2.43578700
O	-0.42546500	1.34946900	-1.91796600
H	1.34405200	3.39484600	-1.71432700
H	1.19603500	4.21172000	-0.12212400
H	-0.26428500	3.89361600	-1.11955700

N_2 extrusion **TS-I**



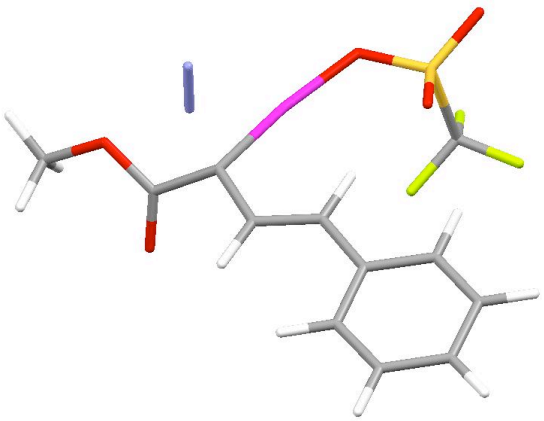
Route= #N b3lyp/gen pseudo=read gfprint OPT=(TS,CalcFC,NoEigenTest) freq
RB3LYP Energy=-1793.50054591 Hartree

C	0.00000000	0.00000000	0.00000000
F	0.72485500	-0.86033900	-0.71511200
F	-0.69856500	0.78232700	-0.84423200
F	0.82734000	0.78194900	0.70993300
S	-1.16250800	-0.89737800	1.14379000
O	-0.32667000	-1.77859900	1.95301900
O	-1.91552200	0.18637100	1.82051200
O	-2.04457100	-1.63788400	0.13763200
Ag	-3.95262900	-0.74367900	-0.07427200
O	-5.95889800	-0.03086800	-0.13579100
C	-6.41779300	1.05224700	0.32376500
C	-5.70422400	2.26812400	0.16561400
C	-4.35681000	2.52696200	0.52412600
C	-3.71708400	3.61810800	-0.01229300
H	-4.30341600	4.22278500	-0.70421500
C	-2.37460300	4.09054800	0.23981600
C	-1.96977600	5.30027900	-0.36881600

ZPE=0.218060 Hartree
Conditions=298K, 1.00000 atm
Internal Energy=-1793.256992 Hartree
Enthalpy=-1793.256047 Hartree
Free Energy=-1793.344194 Hartree
Entropy=185.520 cal/mol-K

C	-0.68776700	5.80088900	-0.17518200
C	0.21777500	5.09409200	0.62235900
C	-0.16347700	3.88872800	1.22362600
C	-1.44737100	3.38845000	1.04446600
H	-1.71922200	2.44461700	1.50543000
H	0.54591400	3.33115900	1.82668800
H	1.22274300	5.47929200	0.77185200
H	-0.39082000	6.73390900	-0.64504000
H	-2.67607800	5.84144800	-0.99376100
H	-3.83168500	1.88126900	1.23124100
O	-7.66648900	1.09712300	0.80220200
C	-8.44000500	-0.11426200	0.70502700
H	-8.57004500	-0.40354100	-0.34084100
H	-9.40100800	0.13040800	1.15718400
H	-7.95544500	-0.92644500	1.25163200
N	-6.83424100	3.53009200	1.00078900
N	-7.31572300	4.53243600	0.93771500

N_2 extrusion TS-II

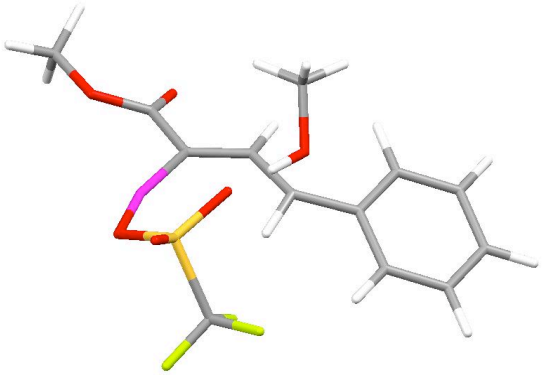


Route= #N b3lyp/gen pseudo=read gfprint
OPT=(TS,CalcFC,NoEigenTest) freq
RB3LYP Energy=-1793.51738041 Hartree
ZPE=0.218744 Hartree
Conditions=298K, 1.00000 atm
Internal Energy=-1793.273272 Hartree
Enthalpy=-1793.272328 Hartree
Free Energy=-1793.360288 Hartree
Entropy=185.128 cal/mol-K

C	0.00000000	0.00000000	0.00000000
Ag	-2.05191100	-0.58050400	0.19248700
F	-5.99489000	2.05331000	-1.09238000
F	-4.33948100	0.88806200	-1.89615300
F	-6.26409900	-0.06194400	-1.52790100
O	-6.06636100	0.31443700	1.45518700
O	-4.13650300	-0.89599400	0.42143600
C	-5.40712400	0.85332400	-1.07283000
O	-3.88489300	1.51160300	0.99096600
C	1.76715600	-3.04021900	-1.18478100
O	1.15035700	-2.07269600	-0.31053900
C	0.75796300	-0.92753100	-0.90173300
S	-4.85226500	0.43881200	0.65570300
C	0.25465700	1.43155800	-0.17824700
C	-0.67681000	2.36544600	0.14673100
H	-1.63039500	2.01529600	0.54203600
C	-0.58254900	3.81095600	0.00476800
C	-1.73563500	4.56950400	0.29459200
C	-1.72181800	5.95635300	0.16793300
C	-0.55744900	6.60661300	-0.24610000
C	0.59590100	5.86607900	-0.53413300
C	0.58653800	4.48211300	-0.41017300
H	1.48876100	3.91942700	-0.63084100
H	1.50155400	6.37379900	-0.85359500
H	-0.54413000	7.68864700	-0.34394400
H	-2.61755400	6.52830900	0.39147200

H	-2.63972100	4.05452600	0.61010400
H	1.21006000	1.71597800	-0.61567100
N	0.60413500	-0.38844600	1.54021200
N	0.75559400	-0.42403000	2.64147600
O	0.91908800	-0.66296500	-2.07388000
H	1.05467500	-3.36552900	-1.94671500
H	2.04840800	-3.87199400	-0.53981200
H	2.64611800	-2.60905500	-1.66931300

Vinylogous addition TS-IIIb



Route= #N b3lyp/gen pseudo=read gfprint OPT=(TS,CalcFC,NoEigenTest) FREQ
RB3LYP Energy=-1799.75858898 Hartree
ZPE=0.266859 Hartree
Conditions=298K, 1.00000 atm
Internal Energy=-1799.466018 Hartree
Enthalpy=-1799.465074 Hartree
Free Energy=-1799.553452 Hartree
Entropy=186.007 cal/mol-K

O	0.00000000	0.00000000	0.00000000
C	0.77396400	0.38132900	-1.60498500
F	-4.51555600	-0.78953400	-3.22044200
F	-2.37377700	-0.82219600	-2.82727900
F	-3.69811800	-2.18392600	-1.76294600
O	-5.11853900	0.04925900	-0.31517500
O	-2.62737300	0.08228600	-0.04564000
O	-3.73992300	1.62062900	-1.68044100
Ag	-1.76070800	2.43853900	-1.93129200
C	0.28300000	2.77612500	-1.87174000
C	0.88464600	4.14883200	-1.91996900
O	-0.05731600	5.10423000	-1.74241600
C	0.42501900	6.45696900	-1.75730100
H	1.16473900	6.61055500	-0.96661900
H	-0.45237100	7.08183900	-1.59034300
H	0.88513700	6.68621900	-2.72226500
O	2.06081100	4.40913400	-2.09999700
C	1.17647700	1.78115000	-1.62178200
C	-3.60236600	-0.95203200	-2.26601100
H	-0.15693000	0.18975100	-2.13203400
C	1.75240000	-0.71611000	-1.72288000
C	1.31370500	-1.94253000	-2.25403500
C	2.19671900	-3.00896800	-2.39676200
C	3.52970300	-2.86578500	-2.00207600
C	3.97605000	-1.65434300	-1.46662600
C	3.09551200	-0.58394900	-1.32843300
H	3.45600700	0.35355500	-0.91747200
H	5.01238000	-1.54282300	-1.16140800
H	4.22100700	-3.69649400	-2.11328400
H	1.84818300	-3.94896000	-2.81417700
H	0.27406700	-2.04955300	-2.55356400
H	2.22931900	2.01856400	-1.47153700
S	-3.81990000	0.31679700	-0.91735900
C	0.40934800	0.76876800	1.14767100
H	-0.22714900	0.47084100	1.98362500

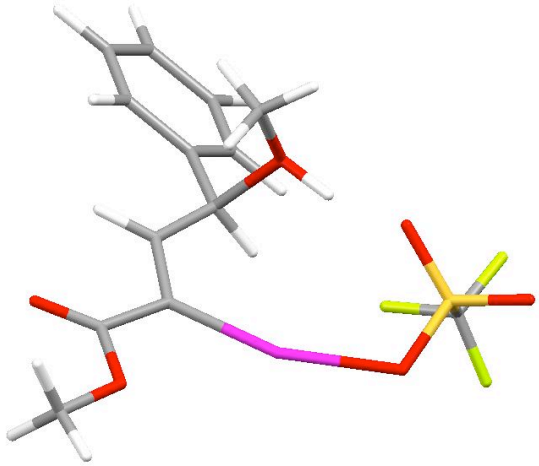
H	1.44840900	0.50945000	1.35623600
H	0.31219100	1.84088000	0.95616500
H	-0.99958200	0.08571800	-0.11548500

Vinylogous addition TS-IIIb in DCM@0°C

Route= #N b3lyp/gen pseudo=read gfprint temperature=273.15
OPT=(TS,CalcFC,NoEigenTest) freq
SCRF=(PCM,Solvent=dichloromethane)
RB3LYP Energy=-1799.77810003 Hartree
ZPE=0.266453 Hartree
Conditions=273K, 1.00000 atm
Internal Energy=-1799.489191 Hartree
Enthalpy=-1799.488326 Hartree
Free Energy=-1799.566623 Hartree
Entropy=179.872 cal/mol-K

O	0.00000000	0.00000000	0.00000000
C	0.80130800	0.38750900	-1.57650500
F	-4.67078400	-0.84608600	-3.05475100
F	-2.51788500	-0.88609600	-2.73346400
F	-3.82150900	-2.14717000	-1.52870200
O	-5.19284600	0.21145600	-0.24344500
O	-2.70413300	0.20625100	0.02353300
O	-3.79040400	1.65189200	-1.71475800
Ag	-1.76466500	2.44051100	-1.98723800
C	0.28299900	2.77968000	-1.88390900
C	0.84296300	4.15644200	-1.95472100
O	0.06742300	5.04929400	-1.29855700
C	0.53655800	6.41105100	-1.30211600
H	1.53186200	6.47657900	-0.85549400
H	-0.18607700	6.96952300	-0.70791000
H	0.57235600	6.79707000	-2.32401800
O	1.86088700	4.47305100	-2.54928900
C	1.17614100	1.79872400	-1.59051200
C	-3.71827900	-0.95833700	-2.12728300
H	-0.10676500	0.17171700	-2.13439100
C	1.81645300	-0.67858700	-1.66658100
C	1.44542100	-1.90508100	-2.24812000
C	2.36893000	-2.94002200	-2.36815500
C	3.67392800	-2.76612400	-1.89742700
C	4.05220200	-1.55530800	-1.30940400
C	3.13245500	-0.51497400	-1.19572800
H	3.44200700	0.41980800	-0.73982400
H	5.06542600	-1.42058800	-0.94315200
H	4.39592900	-3.57237900	-1.98963600
H	2.07371400	-3.87901400	-2.82638100
H	0.42853400	-2.03867100	-2.60782900
H	2.22067600	2.04046700	-1.39642500
S	-3.88220600	0.40415300	-0.86777600
C	0.50113700	0.66339000	1.18484900
H	-0.10565200	0.32821400	2.02767900
H	1.53366600	0.33972100	1.31581800
H	0.44587200	1.74884900	1.07542400
H	-0.98077700	0.17076400	-0.09138100

Vinylogous Ylide YL-IIb

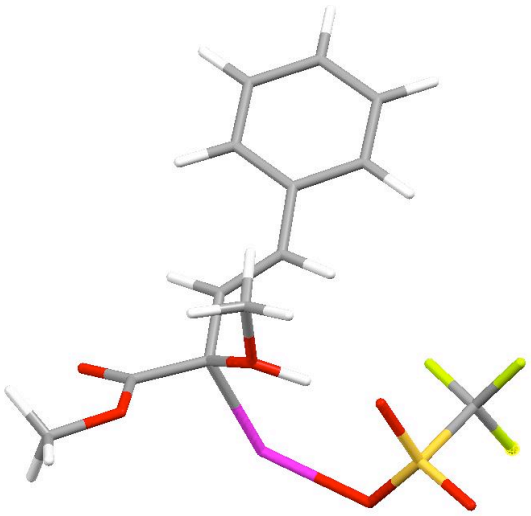


Route= #N b3lyp/gen pseudo=read gfprint OPT FREQ
RB3LYP Energy=-1799.75921383 Hartree
ZPE=0.267225 Hartree
Conditions=298K, 1.00000 atm
Internal Energy=-1799.466034 Hartree
Enthalpy=-1799.465090 Hartree
Free Energy=-1799.553743 Hartree
Entropy=186.586 cal/mol-K

O	0.00000000	0.00000000	0.00000000
C	0.76515000	0.39447400	-1.36596700
F	-4.46492200	-0.86410500	-2.98605600
F	-2.31786400	-0.86818600	-2.61771700
F	-3.61102400	-2.25046000	-1.54166500
O	-5.01709600	-0.06576900	-0.03692400
O	-2.52718200	0.03965400	0.15089100
O	-3.73310600	1.55104800	-1.44714400
Ag	-1.77857800	2.46388600	-1.69991000
C	0.26157500	2.81803200	-1.60465500
C	0.84948500	4.19761200	-1.60932900
O	-0.11890000	5.14489700	-1.64778400
C	0.34728200	6.50233200	-1.65019300
H	0.92873000	6.71104200	-0.74772600
H	-0.55036500	7.12027200	-1.68083200
H	0.97507500	6.68947300	-2.52572700
O	2.03487200	4.47830600	-1.58430000
C	1.15444000	1.83005700	-1.37134800
C	-3.53690600	-1.01812500	-2.04552000
H	-0.06906000	0.20723000	-2.04110700
C	1.82874100	-0.64889900	-1.51695800
C	1.49159500	-1.85654900	-2.14849500
C	2.43846100	-2.86691200	-2.30104000
C	3.73623600	-2.68448300	-1.81677500
C	4.08155300	-1.48931300	-1.18275800
C	3.13524700	-0.47499100	-1.03471400
H	3.42302100	0.45295800	-0.55040400
H	5.09054900	-1.34240900	-0.80827200
H	4.47709300	-3.47009100	-1.93625000
H	2.16553600	-3.79352800	-2.79760100
H	0.47904200	-1.99914400	-2.51851900
H	2.20627800	2.07210600	-1.22026500
S	-3.75595300	0.24617200	-0.69250400
C	0.47590000	0.54491200	1.25795500
H	-0.19863200	0.16414900	2.02496600
H	1.48562400	0.16379400	1.41100100
H	0.46439100	1.63567200	1.22753100
H	-1.02821300	0.10772000	-0.07562600

Carbenoid Ylide YL-IIa

O	0.00000000	0.00000000	0.00000000
C	0.56888200	0.45968900	-1.31284800
F	-0.96399100	-5.35402000	-2.34611800
F	0.64244200	-3.91396500	-2.04253000

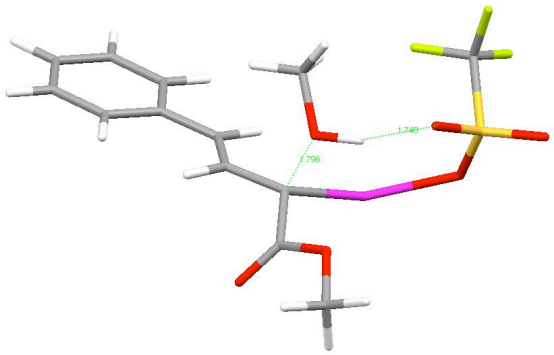


Route= #N b3lyp/gen pseudo=read gfprint OPT FREQ
RB3LYP Energy=-1799.75997515 Hartree
ZPE=0.266276 Hartree
Conditions=298K, 1.00000 atm
Internal Energy=-1799.467784 Hartree
Enthalpy=-1799.466839 Hartree
Free Energy=-1799.554658 Hartree
Entropy=184.829 cal/mol-K

F	-0.01467100	-5.17704200	-0.39493300
O	-2.79404100	-3.90302400	-0.37981900
O	-0.85789900	-2.34946600	-0.04699800
O	-1.96196100	-2.52502100	-2.30035400
Ag	-0.74284700	-0.69303200	-2.65033300
C	2.53412900	-1.10988600	-1.08154800
C	0.31417200	1.91107900	-1.51291900
O	-0.63440500	2.41462100	-0.68446700
C	-0.97605300	3.79178700	-0.91996300
H	-0.09853900	4.43320600	-0.80547300
H	-1.73160100	4.03413100	-0.17225600
H	-1.38006000	3.91800300	-1.92791400
O	0.88296400	2.57383100	-2.36160300
C	1.96733200	0.03266400	-1.52383800
C	-0.42308500	-4.50640400	-1.47294300
H	1.91489600	-1.83058000	-0.54776300
C	3.92427800	-1.53091600	-1.28799600
C	4.26920700	-2.87201300	-1.03433000
C	5.57066000	-3.33085900	-1.22949400
C	6.56230400	-2.45632600	-1.67764500
C	6.23838900	-1.11872100	-1.92553000
C	4.93912800	-0.65931800	-1.72866100
H	4.71297400	0.38871000	-1.90458000
H	7.00553800	-0.42779800	-2.26533100
H	7.57876100	-2.80991000	-1.82682300
H	5.80972000	-4.37242600	-1.03169400
H	3.49754000	-3.56036400	-0.69673100
H	2.53425800	0.73725700	-2.12868700
S	-1.66869700	-3.21002800	-0.98950700
C	0.65587900	0.34709100	1.26156400
H	1.71682200	0.10566200	1.19971500
H	0.48632500	1.41148400	1.41366800
H	0.15482500	-0.24273500	2.02908300
H	-0.36656900	-0.98006200	-0.04227100

Carbenoid addition TS-IIIa

O	0.00000000	0.00000000	0.00000000
C	0.83381400	0.33232800	-1.55664000
F	-3.33970800	-4.21338300	-2.17876200
F	-1.46921200	-3.56162000	-1.27323000
F	-3.26847300	-3.73257800	-0.05723800
O	-4.68329300	-1.52964900	-1.63545800
O	-2.49516800	-0.87179200	-0.58692500
O	-2.60110000	-1.45217600	-3.02264100
Ag	-0.61403000	-0.58804200	-2.81845400



Route= #N b3lyp/gen pseudo=read gfprint
OPT=(TS,CalcFC,NoEigenTest) freq
RB3LYP Energy=-1799.75390321 Hartree
ZPE=0.266259 Hartree
Conditions=298K, 1.00000 atm
Internal Energy=-1799.461766 Hartree
Enthalpy=-1799.460822 Hartree
Free Energy=-1799.548490 Hartree
Entropy=184.513 cal/mol-K

C	2.66025700	-1.30448500	-1.85738500
C	0.70028900	1.82405800	-1.59128800
O	-0.48760800	2.27761300	-1.14799500
C	-0.69505400	3.69658400	-1.26396600
H	0.07124500	4.24245300	-0.70777600
H	-1.68257100	3.87871500	-0.84091200
H	-0.66256400	4.00066700	-2.31345000
O	1.56492900	2.53502500	-2.06836000
C	2.21289000	-0.11971000	-1.38117400
C	-2.81319800	-3.39819600	-1.26657700
H	1.94113000	-1.92489600	-2.39328300
C	4.00836200	-1.86185400	-1.75632400
C	4.25565500	-3.12477300	-2.32742800
C	5.52023800	-3.70609300	-2.26555300
C	6.56557200	-3.03253600	-1.63142300
C	6.33781600	-1.77537000	-1.06038500
C	5.07518800	-1.19571600	-1.11959700
H	4.91706500	-0.21804600	-0.67476200
H	7.14976700	-1.24696000	-0.56865800
H	7.55362500	-3.48155500	-1.58216500
H	5.68969800	-4.68153000	-2.71253500
H	3.44300400	-3.64951200	-2.82433800
H	2.89891800	0.56074400	-0.87722300
S	-3.22944500	-1.62361100	-1.65079900
C	0.38687500	-1.19751800	0.71585100
H	0.22916100	-2.08867600	0.10385200
H	1.43599500	-1.09533800	0.98537700
H	-0.23558900	-1.23763400	1.61186400
H	-0.95941000	-0.12237800	-0.25859600

Carbenoid addition TS-IIIa in DCM@0°C

Route= #N b3lyp/gen pseudo=read gfprint
temperature=273.15
OPT=(TS,CalcFC,NoEigenTest) freq
SCRF=(PCM,Solvent=dichloromethane)
RB3LYP Energy=-1799.77458523 Hartree
ZPE=0.265645 Hartree
Conditions=273K, 1.00000 atm
Internal Energy=-1799.486307 Hartree
Enthalpy=-1799.485442 Hartree
Free Energy=-1799.562567 Hartree
Entropy=177.179 cal/mol-K

O	0.00000000	0.00000000	0.00000000
C	0.85372100	0.36008800	-1.64844900
F	-3.30657700	-4.24352500	-2.22810000
F	-1.47559200	-3.56796200	-1.26326000
F	-3.30871800	-3.76533900	-0.10359400
O	-4.72203600	-1.61466800	-1.70503700
O	-2.58609900	-0.87656900	-0.61855700
O	-2.63041900	-1.47189500	-3.05681500
Ag	-0.60644000	-0.56231000	-2.89413000
C	2.63455800	-1.31615100	-1.92147600
C	0.71245700	1.84557600	-1.65698100
O	-0.41253000	2.31968300	-1.09953900
C	-0.61715000	3.74300700	-1.20934300
H	0.21286900	4.28496400	-0.75044200

H	-1.54589100	3.94191200	-0.67613700
H	-0.70743300	4.03312400	-2.25906400
O	1.53157100	2.54530300	-2.23370700
C	2.21546000	-0.10742500	-1.46705500
C	-2.81373200	-3.42380300	-1.29620700
H	1.90245600	-1.92629800	-2.45062100
C	3.96492100	-1.90381800	-1.80448000
C	4.19770600	-3.15580100	-2.40855200
C	5.44937700	-3.76365500	-2.33823000
C	6.49364000	-3.12991500	-1.66057100
C	6.27870000	-1.88672400	-1.05280000
C	5.02955400	-1.27907500	-1.12092200
H	4.87892800	-0.31753100	-0.64040500
H	7.08896700	-1.39360300	-0.52365000
H	7.47094500	-3.60062100	-1.60344200
H	5.60997100	-4.72833700	-2.81056100
H	3.38545300	-3.64847100	-2.93722600
H	2.91627400	0.55711500	-0.96232700
S	-3.25688800	-1.65993200	-1.69328400
C	0.43603800	-1.18532500	0.70349400
H	0.32170700	-2.07741600	0.08259900
H	1.48037800	-1.04078700	0.97285700
H	-0.17529600	-1.26880900	1.60471600
H	-0.94323200	-0.14938400	-0.26522400

MeOH

Route= #N B3LYP/6-31G(d) 5d OPT FREQ
RB3LYP Energy=-115.712204002 Hartree
ZPE=0.051473 Hartree
Conditions=298K, 1.00000 atm
Internal Energy=-115.657440 Hartree
Enthalpy=-115.656496 Hartree
Free Energy=-115.683451 Hartree
Entropy=56.733 cal/mol-K

C	0.00000000	0.00000000	0.00000000
O	-1.41021400	0.14214000	0.00001300
H	-1.79812400	-0.74538000	-0.00002400
H	0.37469100	-0.52481100	-0.89294500
H	0.41788400	1.01051900	-0.00077500
H	0.37512500	-0.52369400	0.89342500

2.3 Single Point Energy Calculations

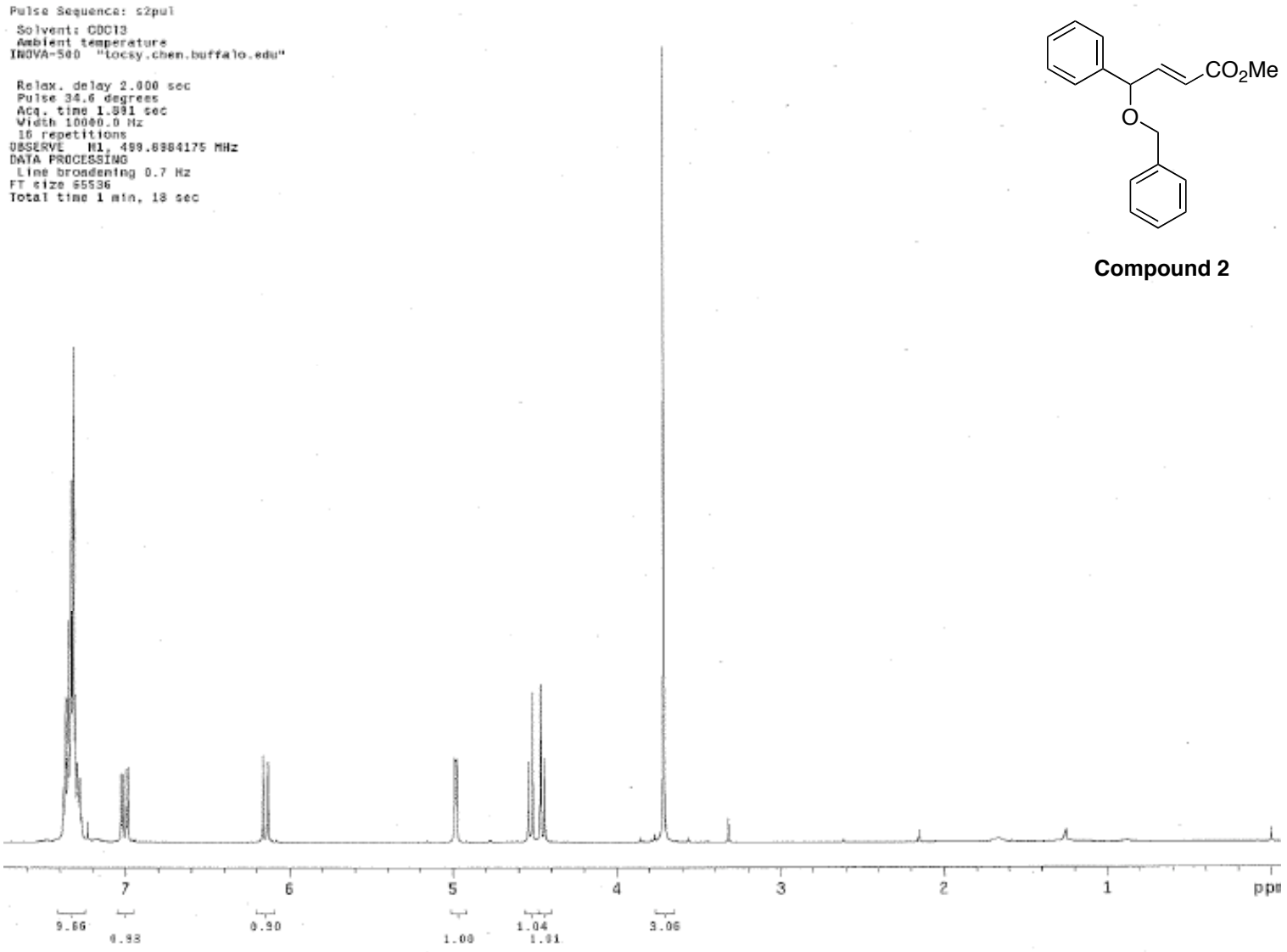
Single-point energies were calculated for the structures at the B3LYP/6-311+G(2d,2p)[Ag-RSC+2(4f)]//B3LYP/6-31G*[Ag-RSC+2(4f)] level of theory. The results are summarized in Table S-1 below.

Table S-1: Single point energies and calculated E+ZPE.

Structure	**Single pt Energy (Hartree)**	**ZPE from 6-31G* (Hartree)**	**E+ZPE (Hartree)**
Ag_CrbndInsTS **TS-IIIa**	-1800.244639	0.266259	-1799.97838
Ag_LAcoor_synN2lossTS	-1793.972281	0.266276	-1793.706005
Ag_CrbndYlide **YL-IIa**	-1800.252006	0.266276	-1799.98573
Ag_PVCrbnd_sTrans **VC**	-1684.470259	0.211753	-1684.258506
Ag_MeoH_Crbnd_COMPLEX	-1800.25491	0.265394	-1799.989516
Ag_VnlgsYLIDE **YL-IIb**	-1800.249796	0.267225	-1799.982571
Ag_VnlgADDTS_ **TS-IIIb**	-1800.249531	0.266859	-1799.982672
Ag_N2TS **TS-II**	-1793.998863	0.218744	-1793.780119
Ag_LAcmpxAN2DISSTS **TS-I**	-1793.981735	0.21806	-1793.763675
AgOTf_MPVD_N2Ccoord **LA-II**	-1794.009475	0.220344	-1793.789131
AgOTf_MPVD_LAcoord1 **LA-I**	-1794.02295	0.221452	-1793.801498
Ag_CrbndsCis s-*cis* **VC**	-1684.480248	0.212141	-1684.268107
MPVD **1**	-685.3004567	0.192102	-685.1083547
AgOTf	-1108.688454	0.027984	-1108.66047
N2	-109.5629655	0.0056	-109.5573655
MeOH	-115.769755	0.051473	-115.718282

3. NMR Data for Selected New Compounds

This section contains ^{1}H and ^{13}C NMR data for new compounds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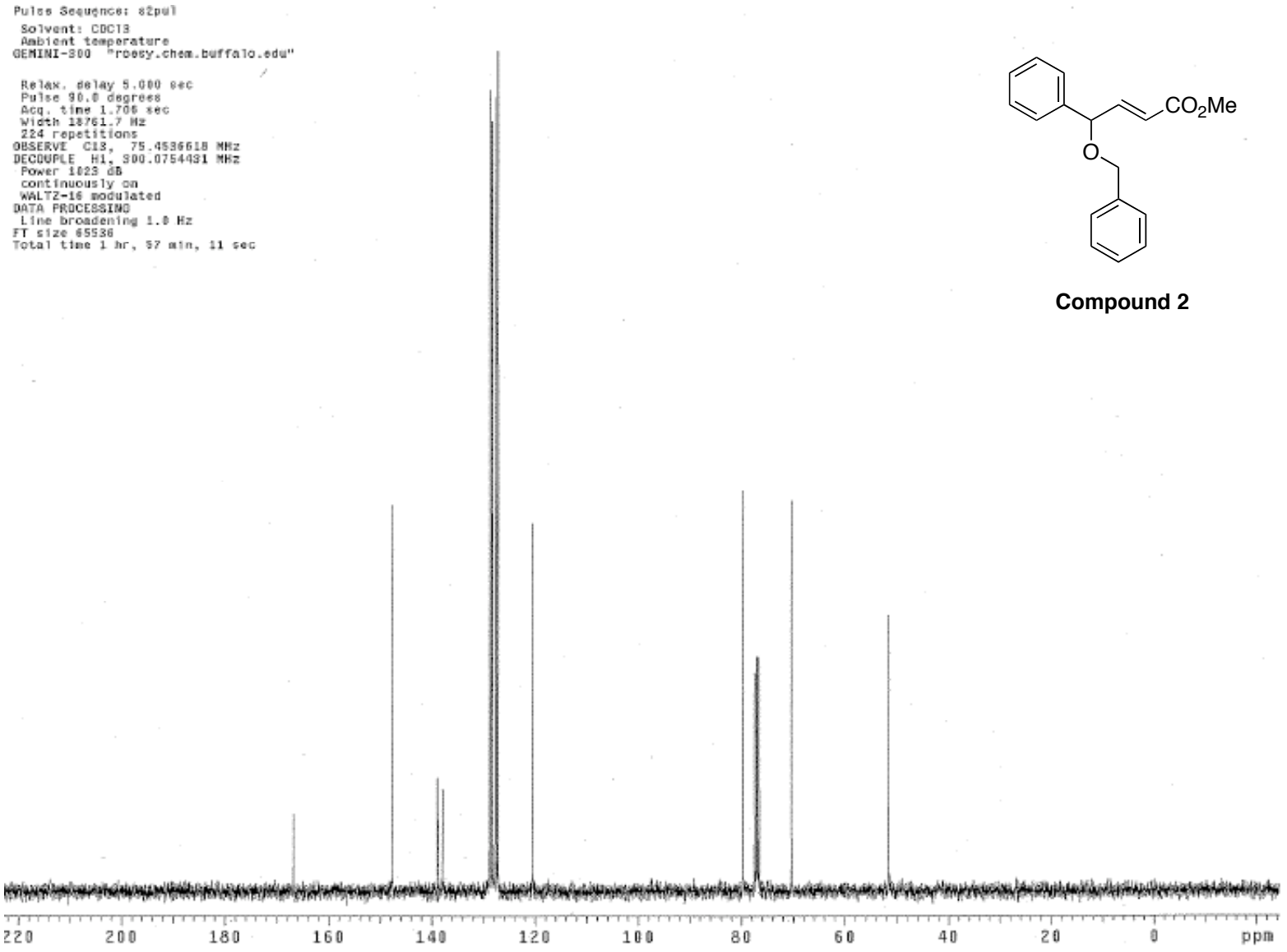
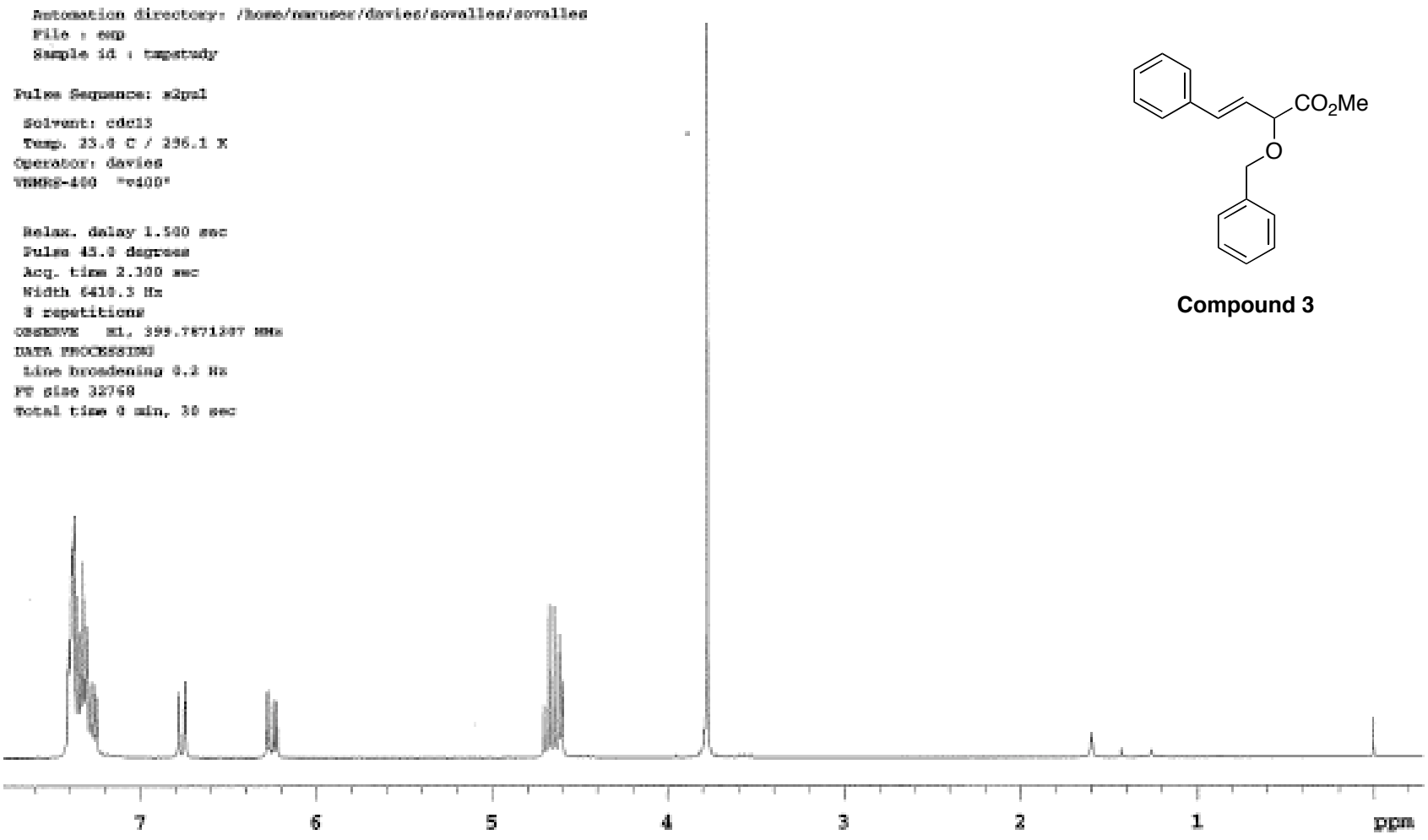
Solvent: CDCl3
Ambient temperature
INOVA-500 "tocsy.chem.buffalo.edu"
Relax. delay 2.000 sec
Pulse 34.6 degrees
Acq. time 1.891 sec
Width 10000.0 Hz
16 repetitions
OBSERVE H1, 499.8984175 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 1 min, 18 sec
CO2Me
O
7
6
5
4
3
2
1
ppm
9.66
0.93
0.90
1.00
1.04
1.01
3.06

Compound 2


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"
Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
224 repetitions
OBSERVE C13, 75.4536618 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 57 min, 11 sec
CO2Me
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm

Compound 2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Sample id : tempstudy
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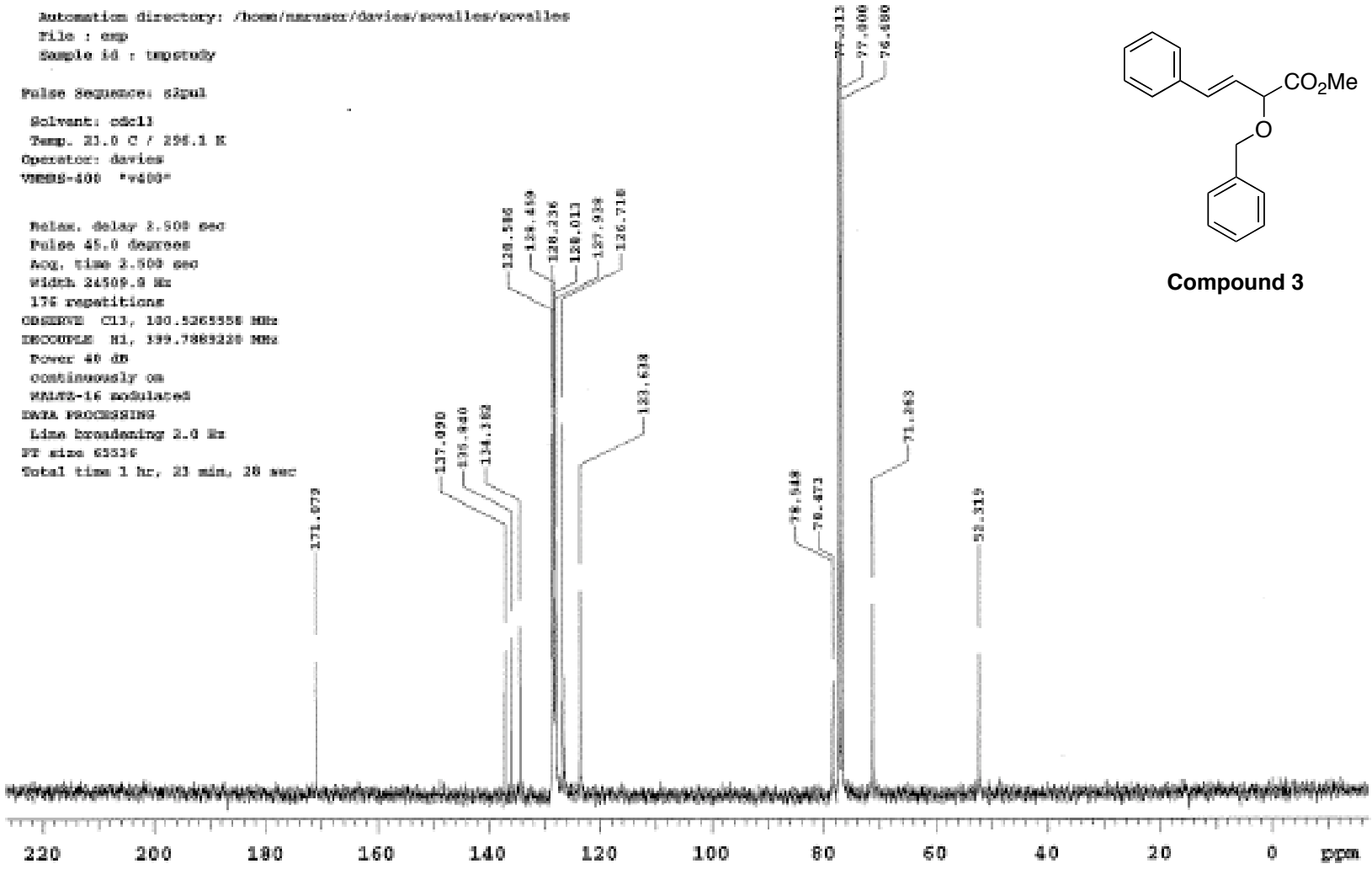
Solvent: cdcl3
Temp. 23.0 C / 296.1 K
Operator: davies
VNMRS-400 "v400"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 2.300 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7871207 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 30 sec
7
6
5
4
3
2
1
ppm

CO2Me
O

Compound 3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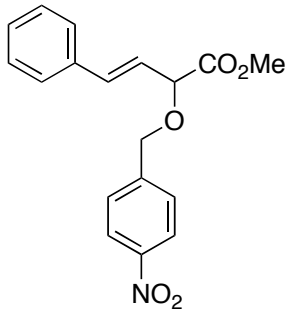
File : exp
Sample id : tmpstudy
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 21.0 C / 294.1 K
Operator: davies
VNMRS-400 "v400"
Relax. delay 2.500 sec
Pulse 45.0 degrees
Acq. time 2.509 sec
Width 24509.8 Hz
176 repetitions
OBSERVE C13, 100.5265558 MHz
DECOUPLE H1, 399.7889220 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 23 min, 28 sec
171.679
137.090
135.440
134.382
128.585
128.459
128.236
128.013
127.938
126.718
123.638
77.313
77.000
76.688
76.548
76.473
71.383
52.319
220
200
180
160
140
120
100
80
60
40
20
0
ppm

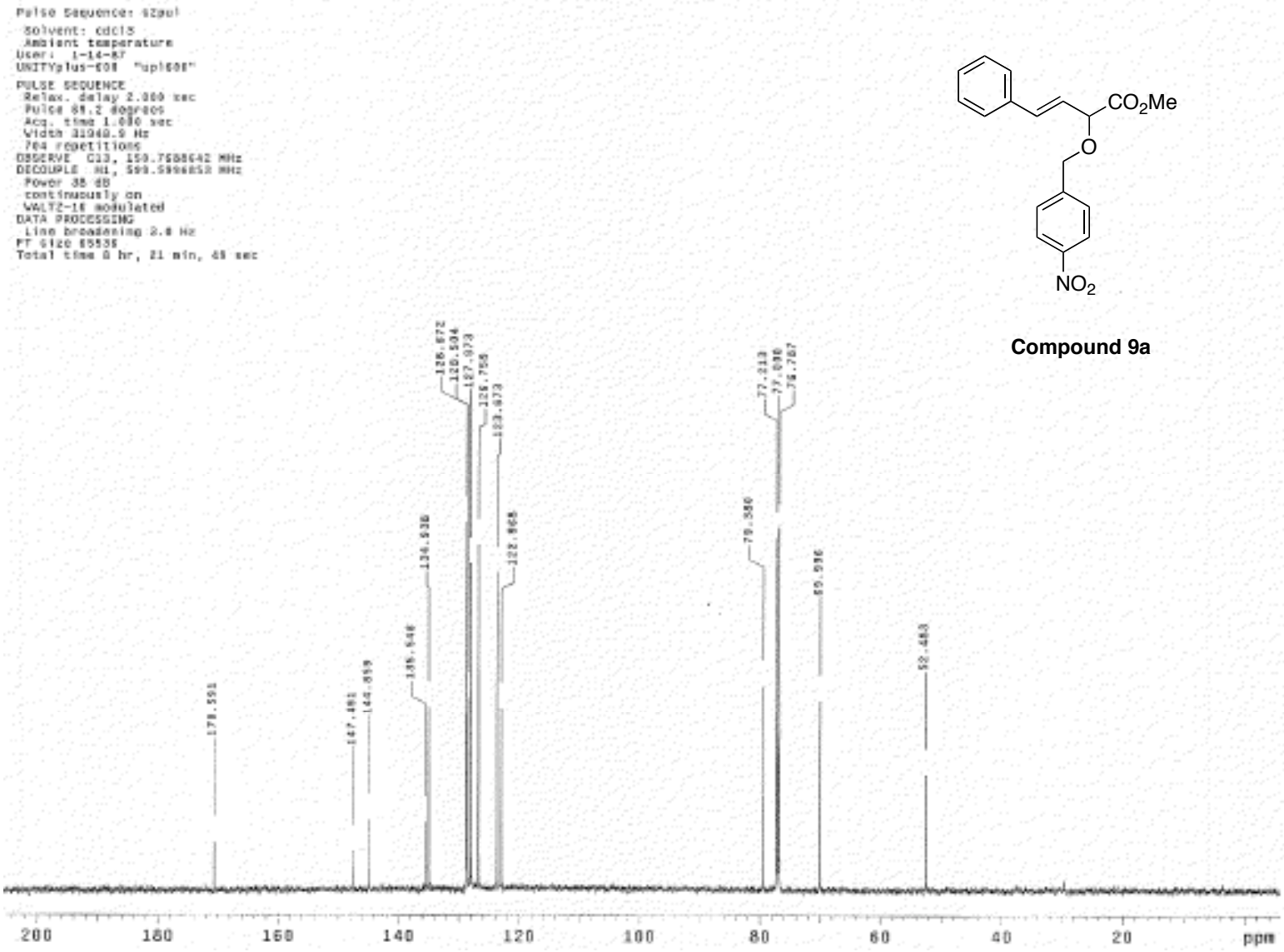
CO2Me
O

Compound 3


CO2Me
O
NO2

Compound 9a

1.68
1.80
1.98
3.06
0.92
0.94
2.10
0.93
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)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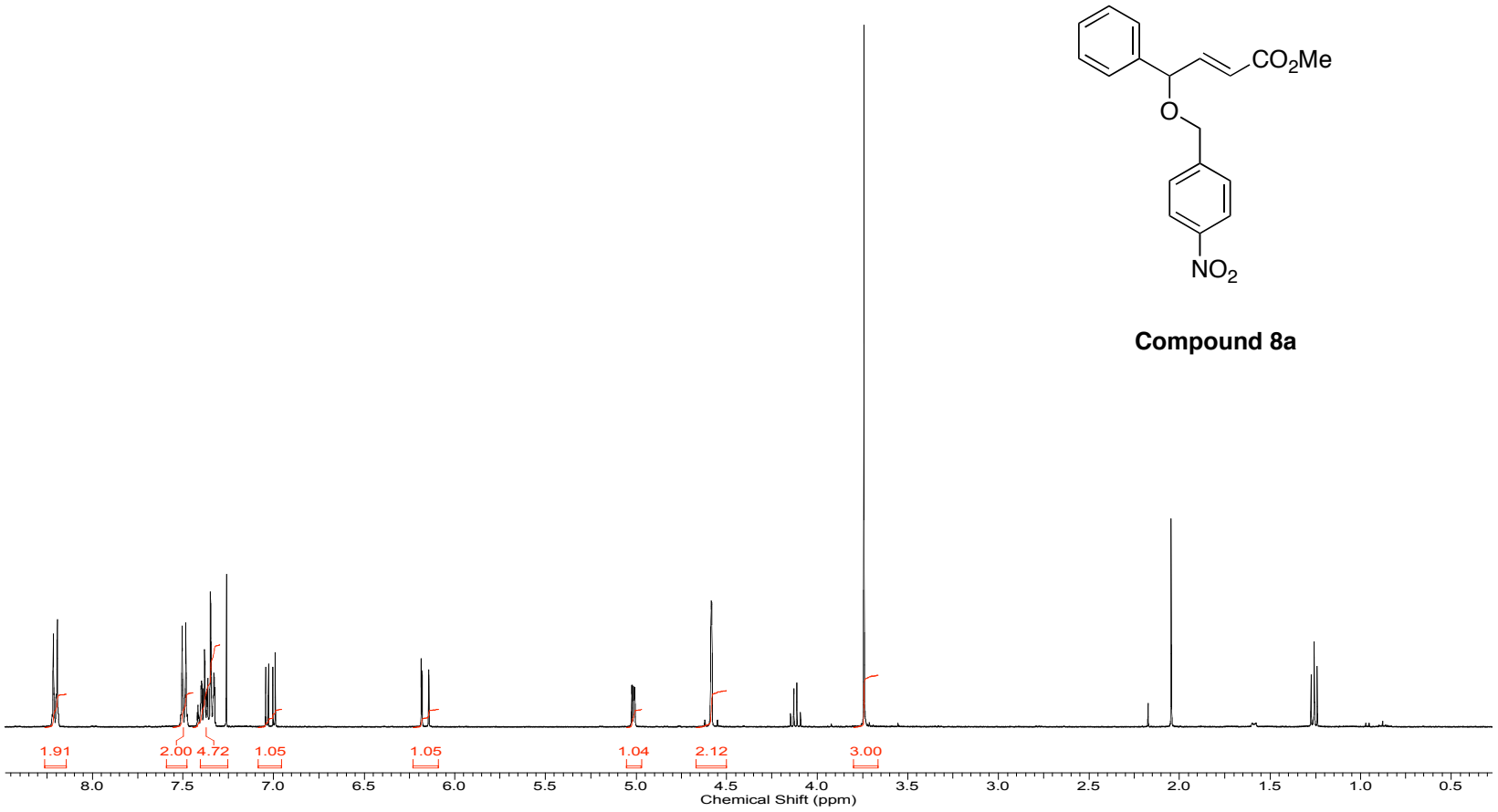
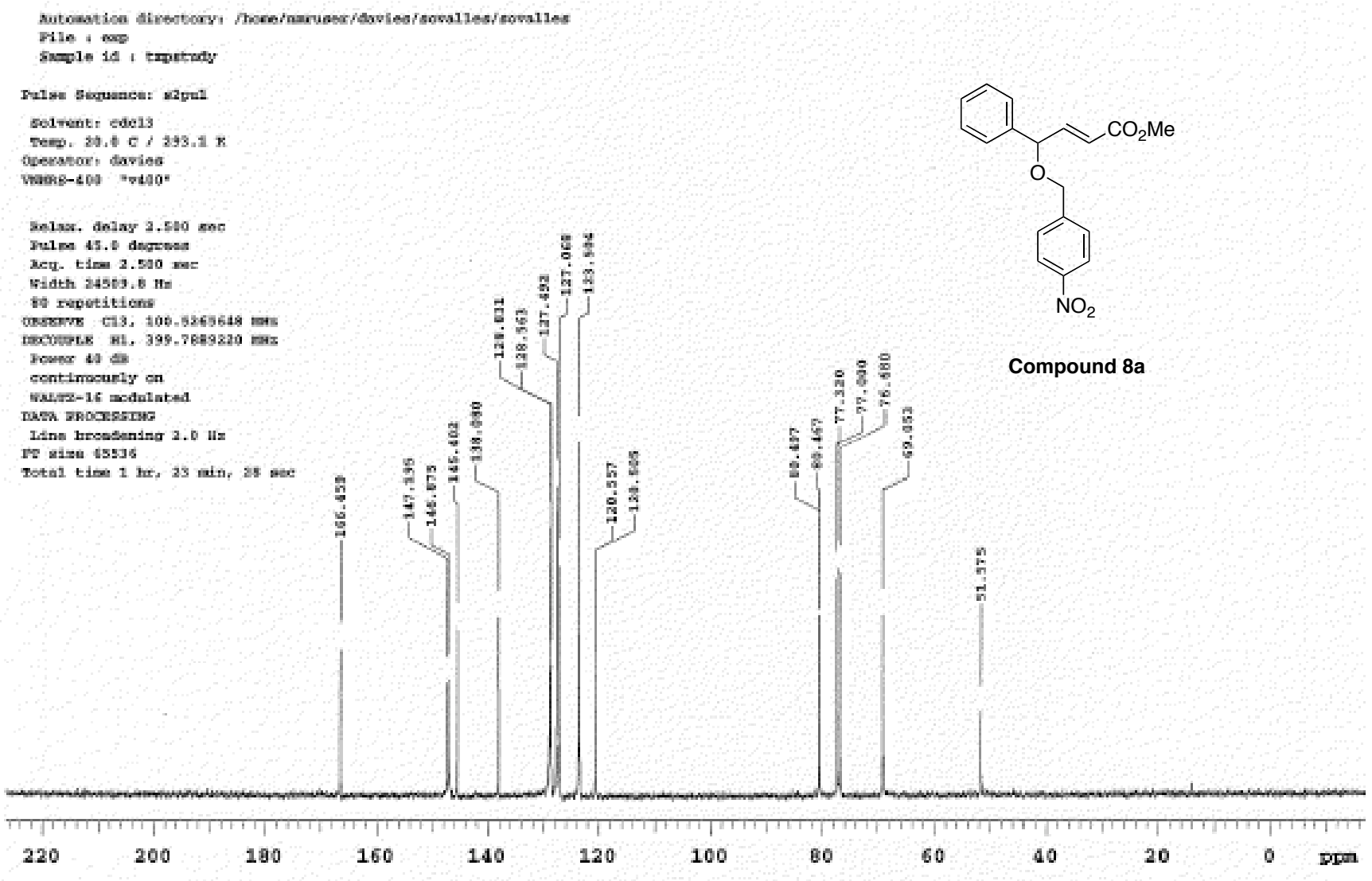
Solvent: cdcl3
Ambient temperature
User: 1-14-87
UNITYplus-600 "upl600"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 84.2 degrees
Acq. time 1.000 sec
Width 31948.9 Hz
764 repetitions
OBSERVE C13, 150.7588642 MHz
DECOUPLE H1, 599.5996853 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 0 hr, 21 min, 45 sec
CO2Me
O
NO2
Compound 9a
170.591
147.481
144.859
135.648
134.538
128.672
128.594
127.973
126.758
123.473
122.968
77.313
77.000
76.787
70.386
59.936
52.483
200
180
160
140
120
100
80
60
40
20
ppm


CO2Me
O
NO2
1.91
2.00
4.72
1.05
1.05
1.04
2.12
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

Compound 8a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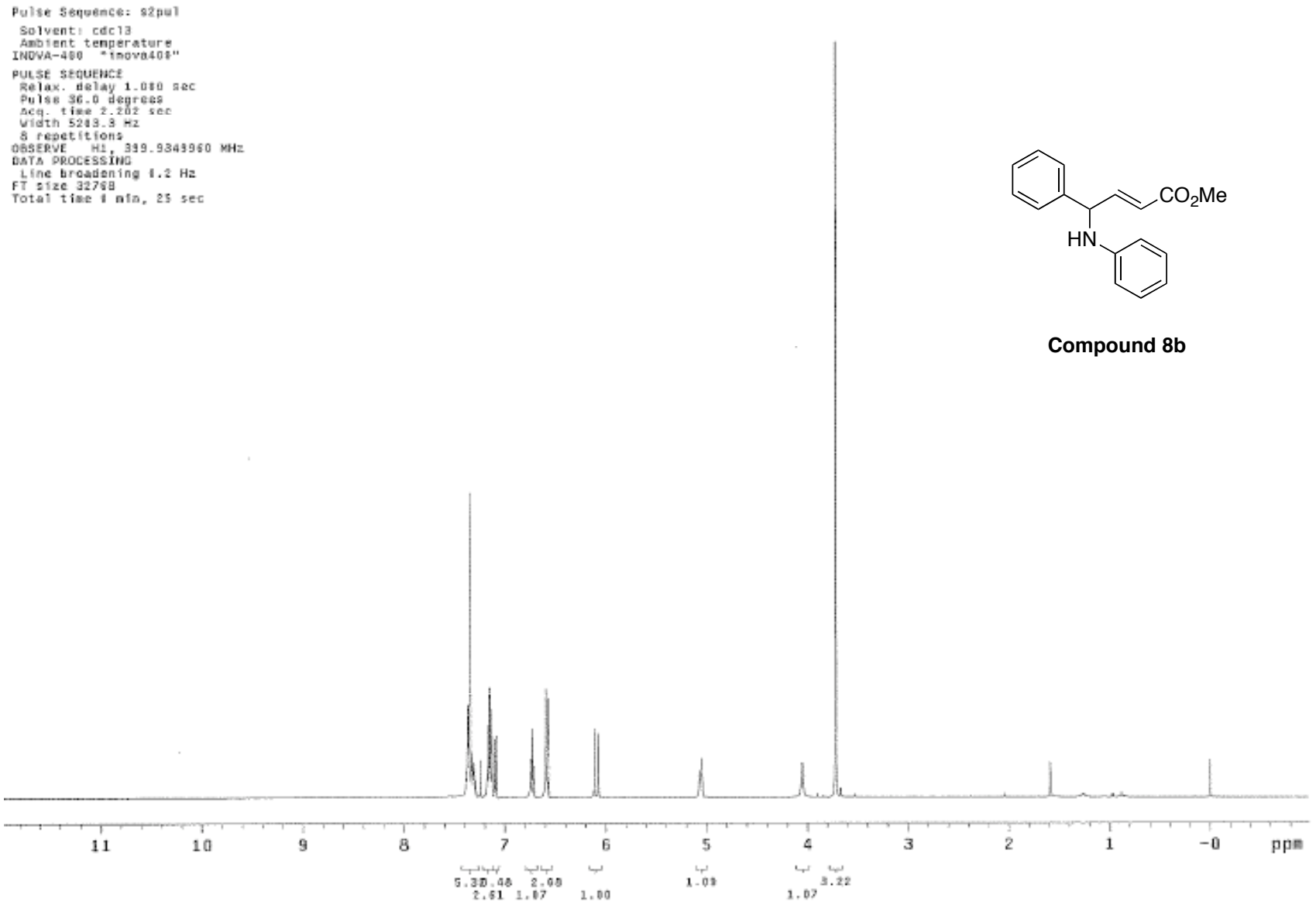
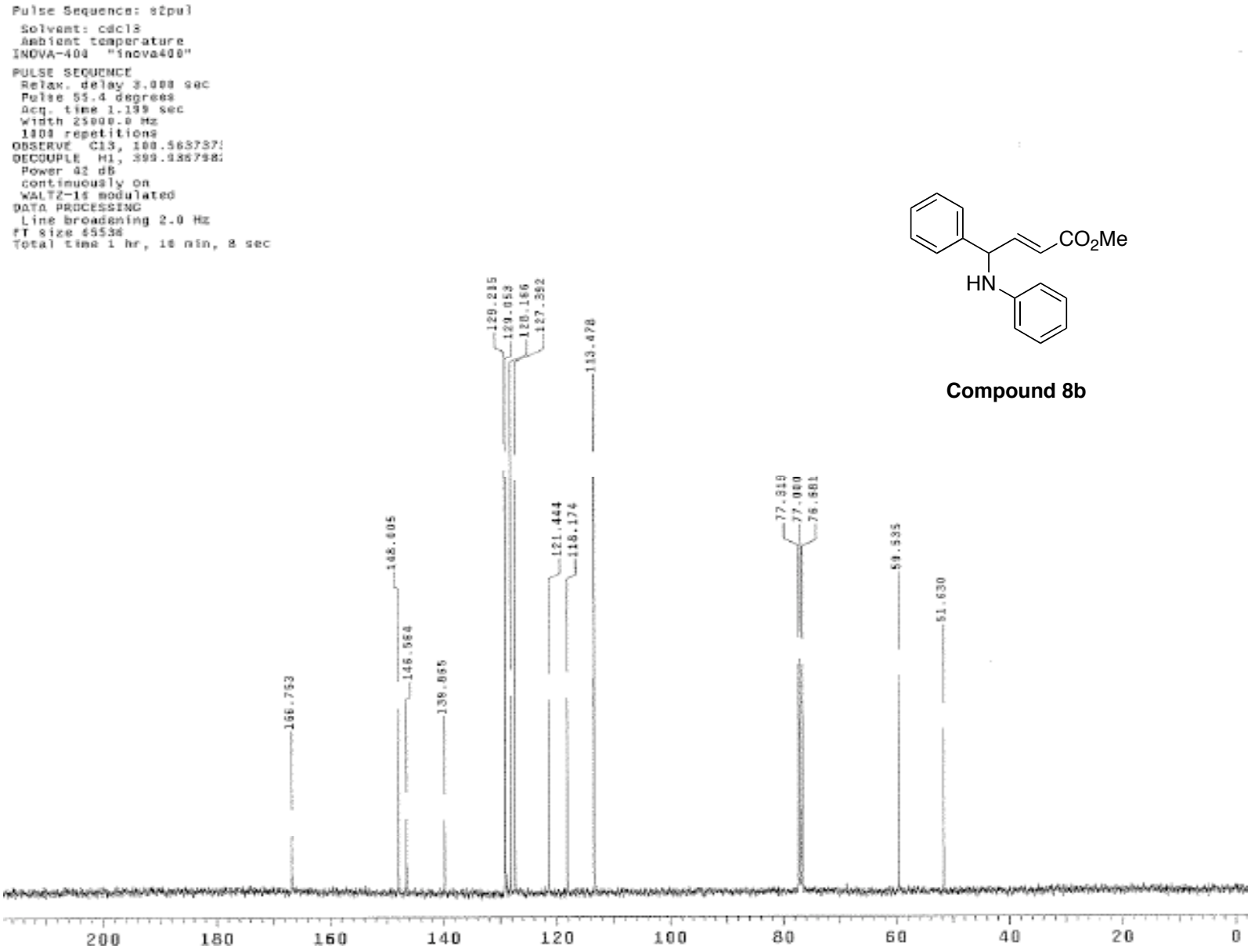
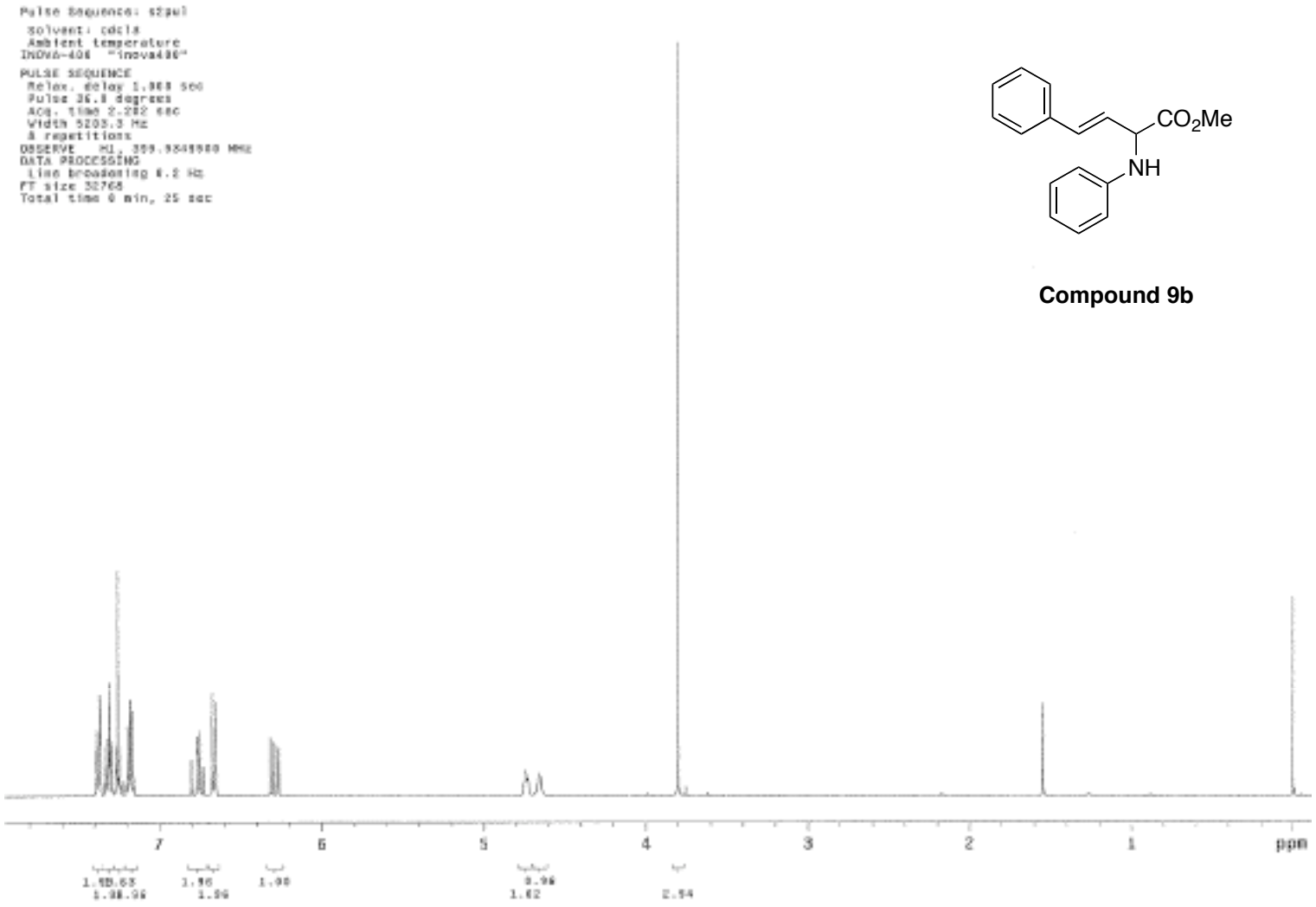
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K
Operator: davies
VNMRS-400 "v400"
Relax. delay 2.500 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 24509.8 Hz
80 repetitions
OBSERVE C13, 100.5265648 MHz
DECOUPLE H1, 399.7689220 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 33 min, 28 sec
166.459
147.135
145.873
145.402
130.690
128.831
128.563
127.492
127.068
123.584
120.357
120.026
88.497
88.467
77.320
77.000
76.680
69.053
51.575
220
200
180
160
140
120
100
80
60
40
20
0
ppm
CO2Me
O
NO2

Compound 8a

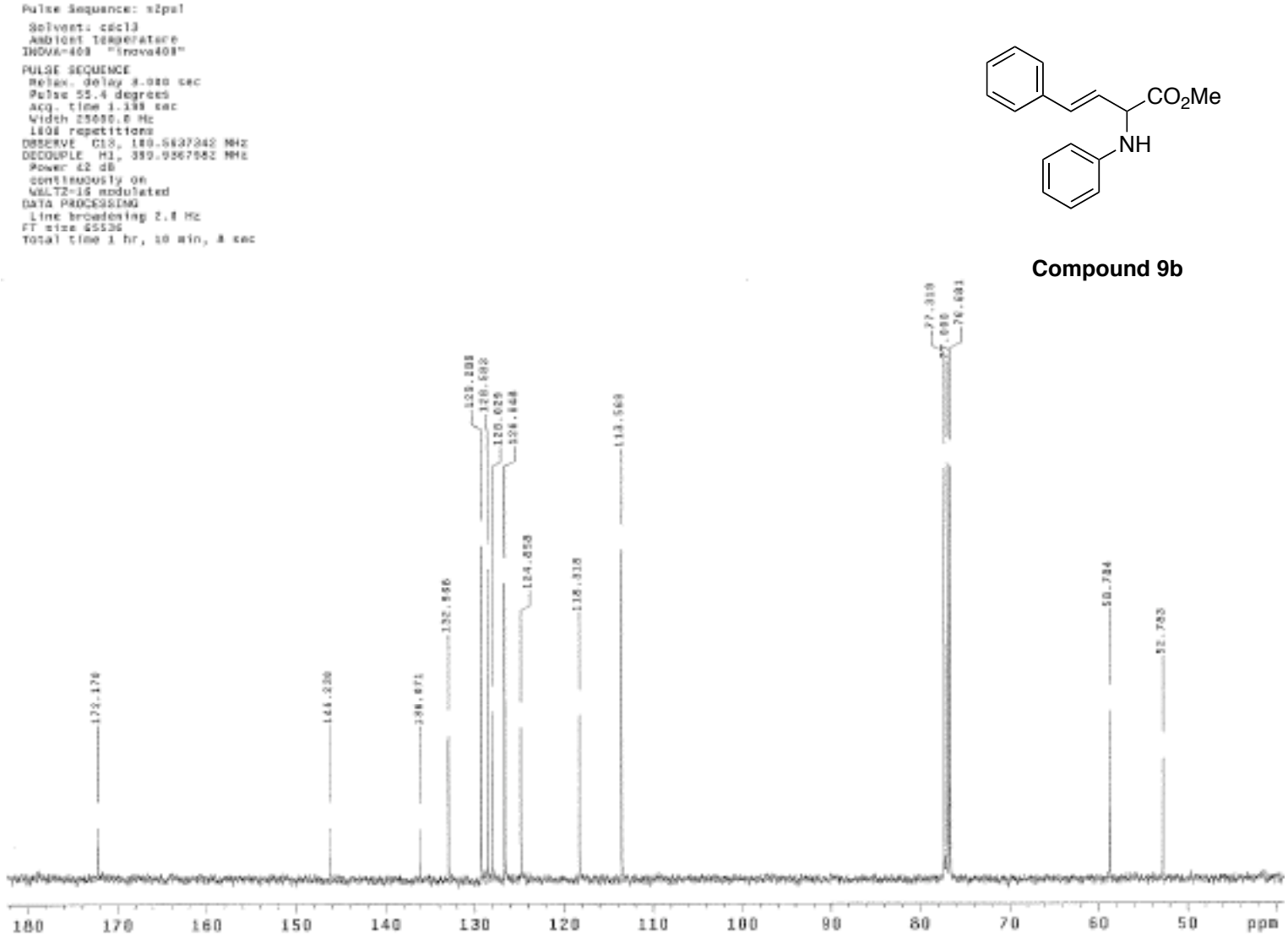

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
INOVA-400 "inova400"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 36.0 degrees
Acq. time 2.202 sec
Width 5283.8 Hz
8 repetitions
OBSERVE H1, 399.9349960 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 25 sec
CO2Me
HN
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
5.30
2.61
0.48
1.87
2.00
1.00
1.09
1.07
3.22

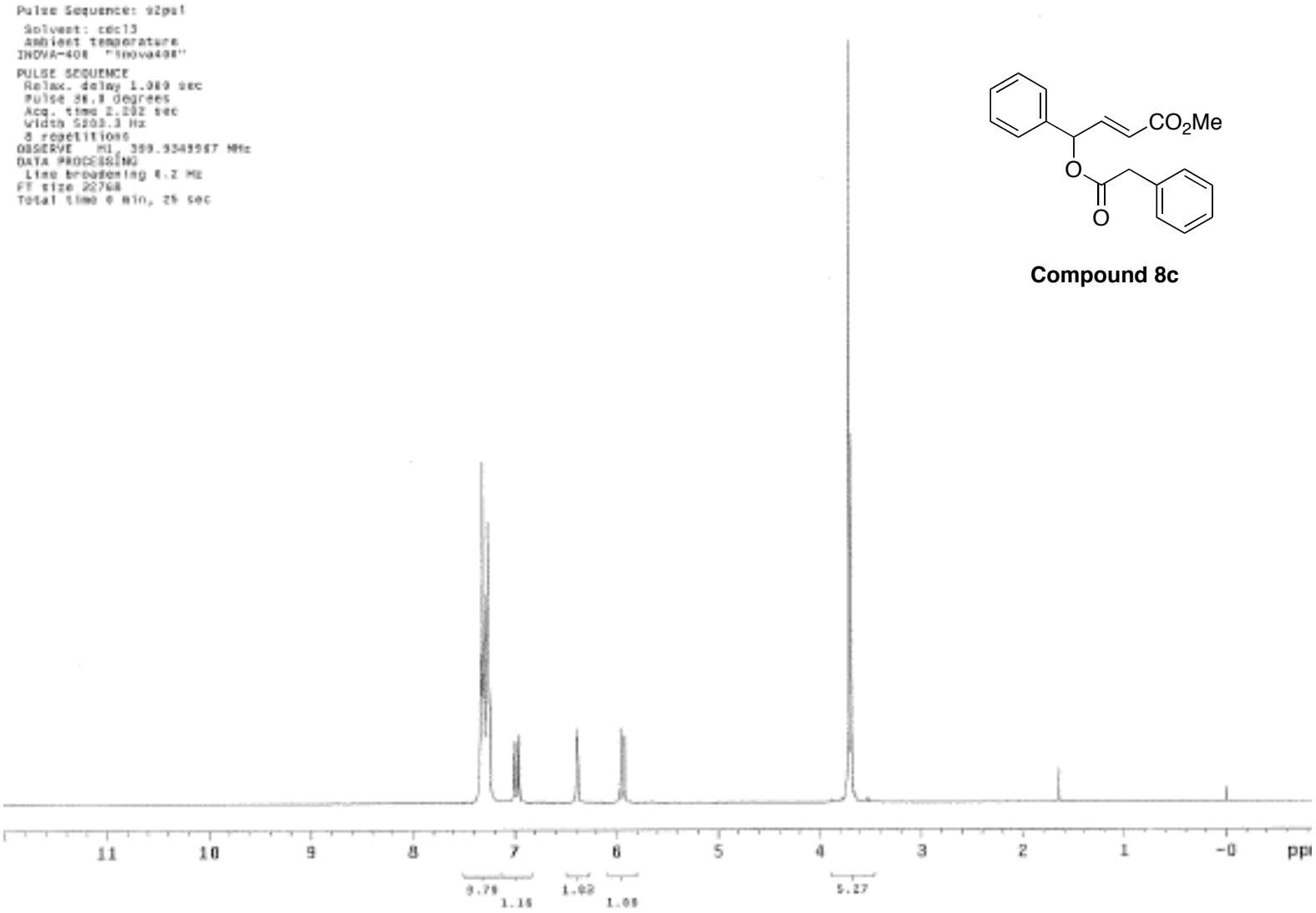
Compound 8b


Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
INOVA-400 "inova400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 55.4 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
1808 repetitions
OBSERVE C13, 100.5637371
DECOUPLE H1, 399.9367981
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 18 min, 8 sec
CO2Me
HN
Compound 8b
129.215
129.053
128.166
127.382
113.478
148.605
146.564
139.055
121.444
118.174
77.319
77.000
76.681
59.535
51.630
166.753
200
180
160
140
120
100
80
60
40
20
0

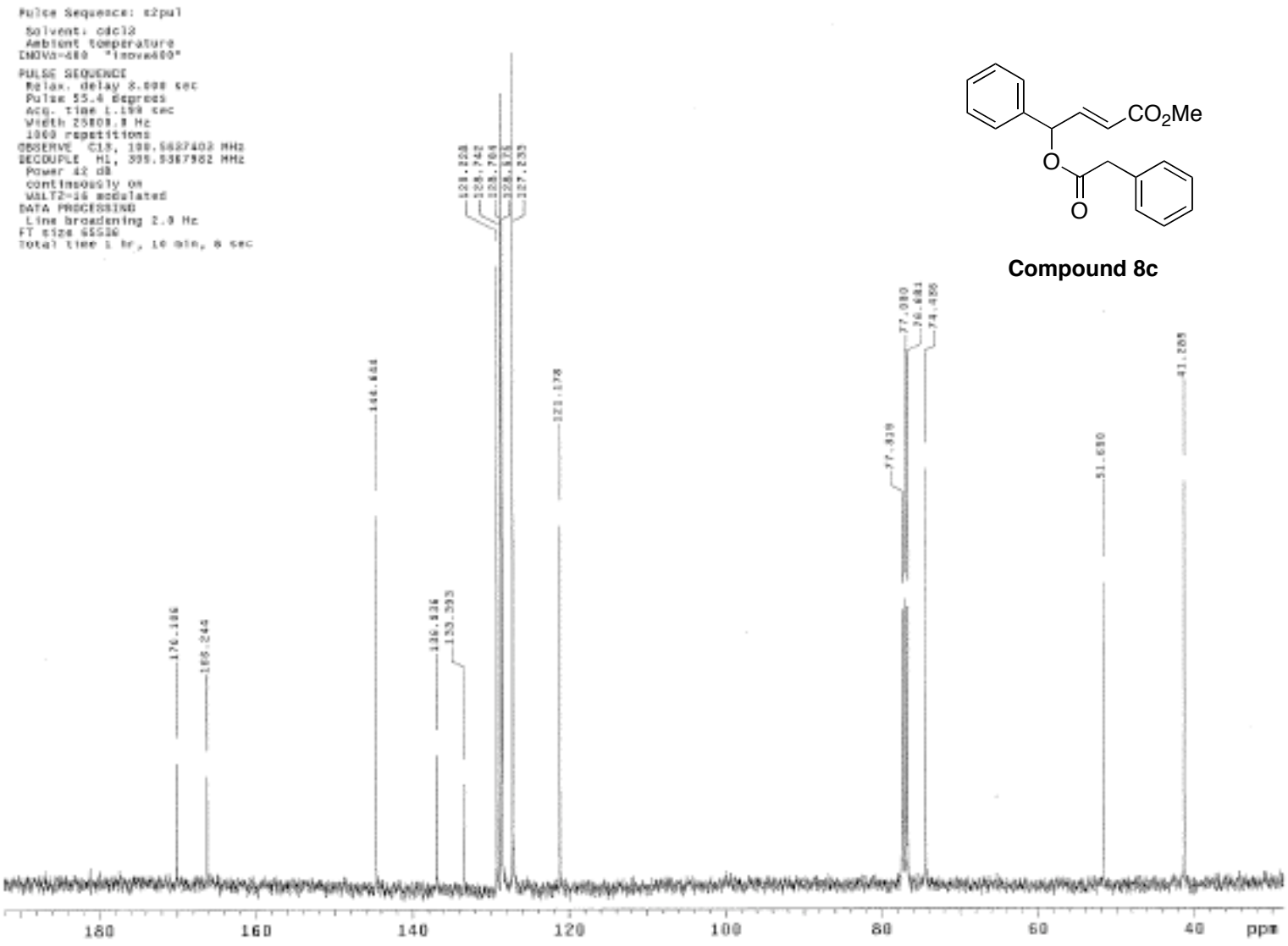

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
INOVA-400 "inova400"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 35.8 degrees
Acq. time 2.282 sec
Width 5203.3 Hz
8 repetitions
OBSERVE H1, 399.9849580 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 25 sec
CO2Me
NH
7
6
5
4
3
2
1
ppm
1.98.65
1.38.96
1.96
1.96
1.98
8.96
1.62
2.54

Compound 9b

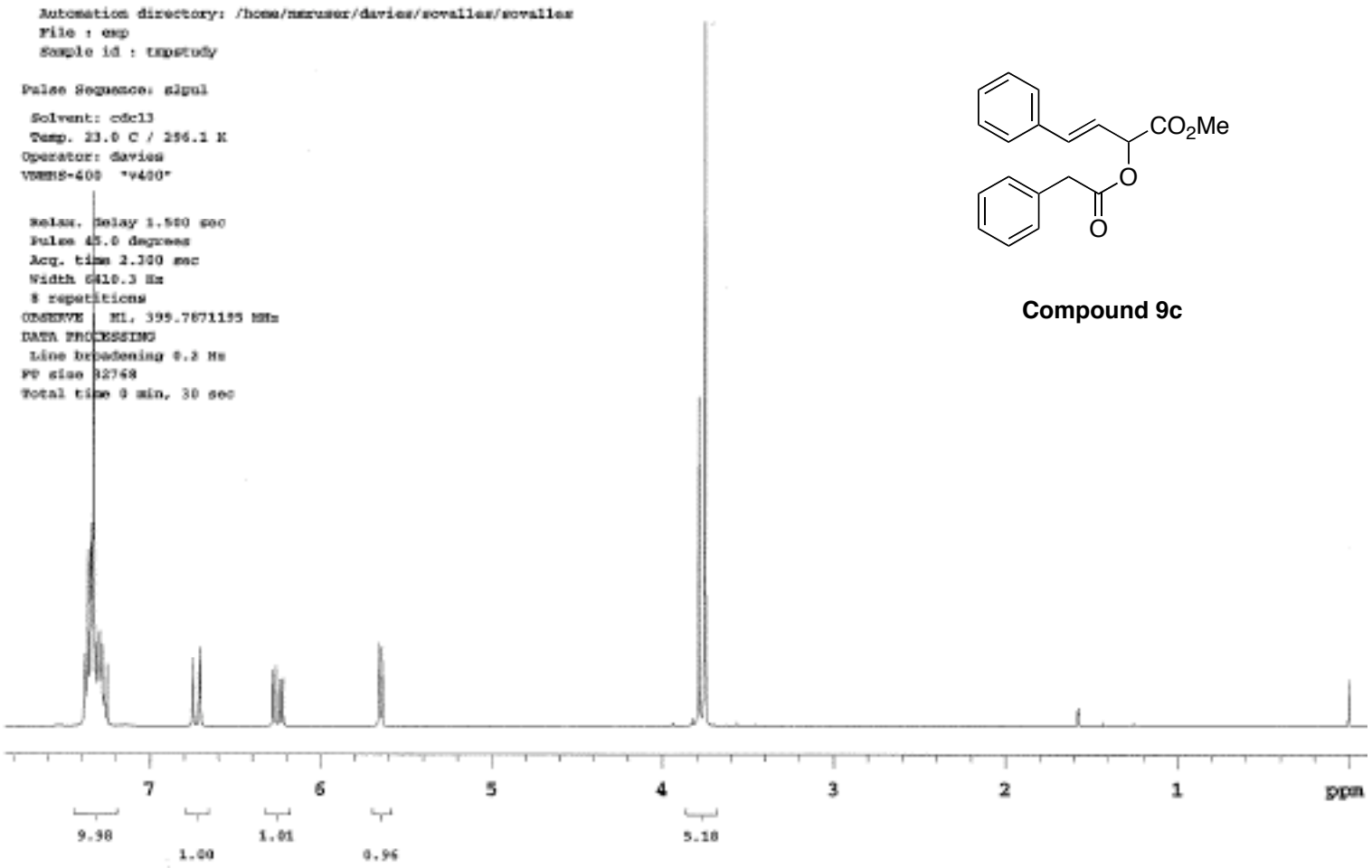

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
INOVA-400 "inova400"
PULSE SEQUENCE
Relax. delay 8.000 sec
Pulse 55.4 degrees
Acq. time 1.198 sec
Width 25000.0 Hz
1608 repetitions
OBSERVE C13, 100.5637242 MHz
DECOUPLE H1, 399.9367582 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.8 Hz
FT size 65536
Total time 1 hr, 10 min, 8 sec
CO2Me
NH
Compound 9b
172.170
144.230
136.671
132.586
128.288
128.082
126.629
126.448
124.858
118.318
113.569
77.319
77.000
76.681
59.784
52.783
180
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm


Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
INOVA-400 "inova400"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 2.202 sec
Width 5203.3 Hz
8 repetitions
OBSERVE H1, 399.9349567 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 25 sec
CO2Me
O
O
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.79
1.16
1.02
1.08
5.27

Compound 8c

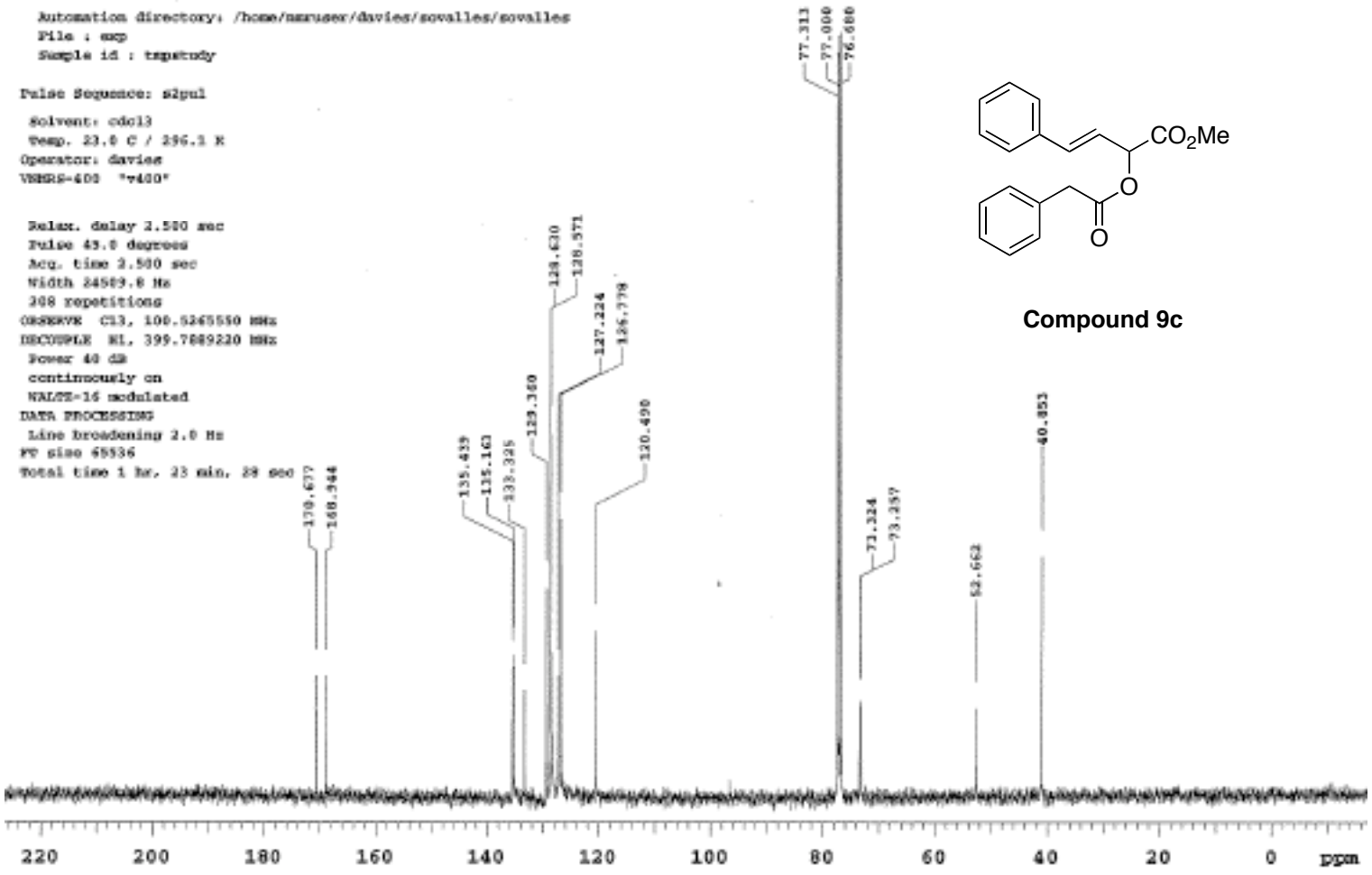

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
INOVA-400 "inova400"
PULSE SEQUENCE
Relax. delay 8.000 sec
Pulse 55.4 degrees
Acq. time 1.199 sec
Width 25809.8 Hz
1000 repetitions
OBSERVE C13, 100.5627402 MHz
DECOUPLE H1, 399.9387982 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 10 min, 8 sec
128.858
128.742
128.704
128.575
128.253
144.444
121.178
77.080
76.684
74.488
77.439
51.630
41.265
176.186
166.244
136.436
133.393
180
160
140
120
100
80
60
40
ppm
CO2Me
O
O

Compound 8c


Automation directory: /home/nmruser/davies/sovalles/sovalles
File : exp
Sample id : tmpstudy
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 23.0 C / 296.1 K
Operator: davies
VNMRS-400 "v400"
Relax. Delay 1.500 sec
Pulse 45.0 degrees
Acq. time 2.300 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7871135 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 30 sec
7
6
5
4
3
2
1
ppm
9.38
1.00
1.01
0.96
5.18

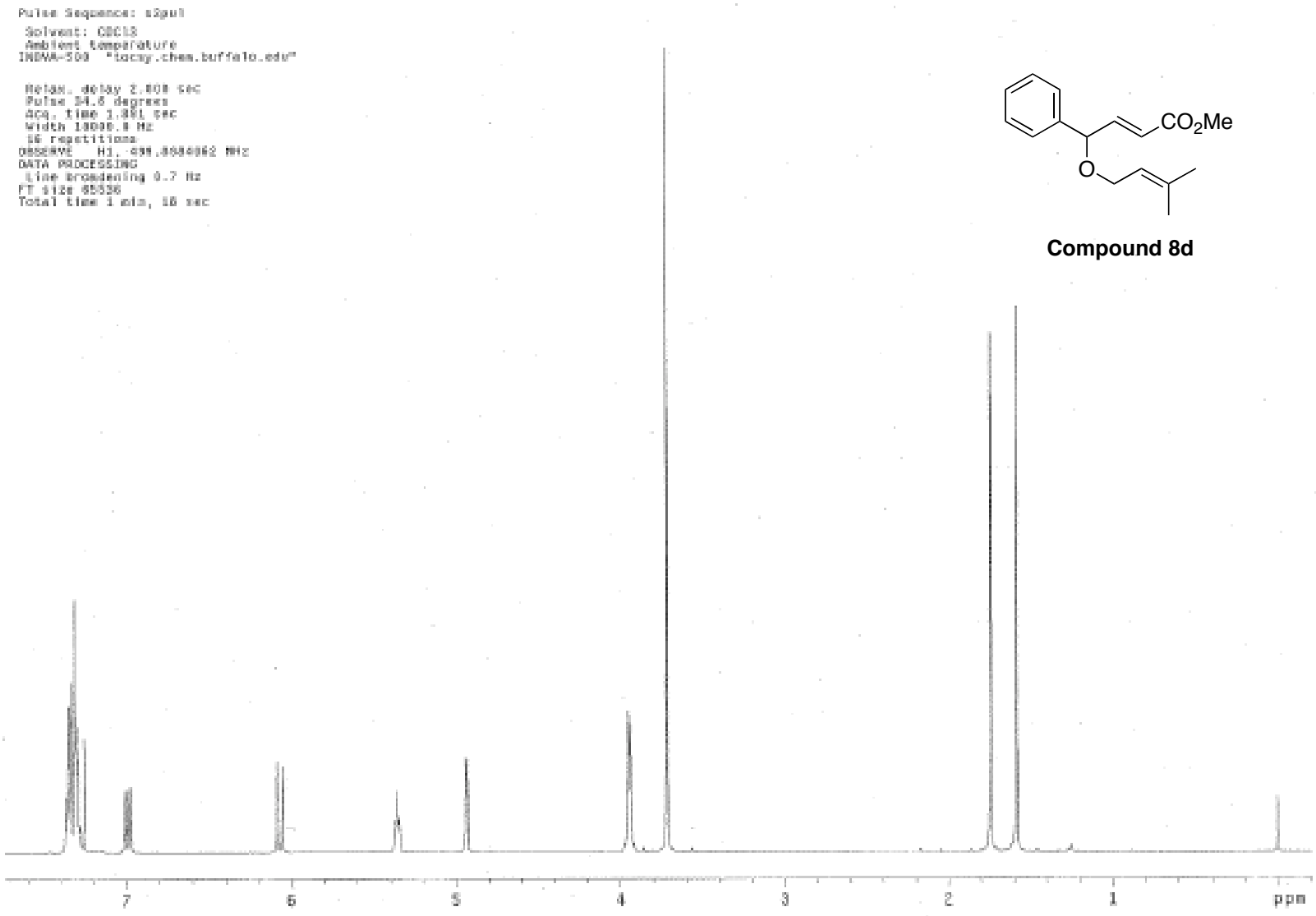
CO2Me
O
O

Compound 9c

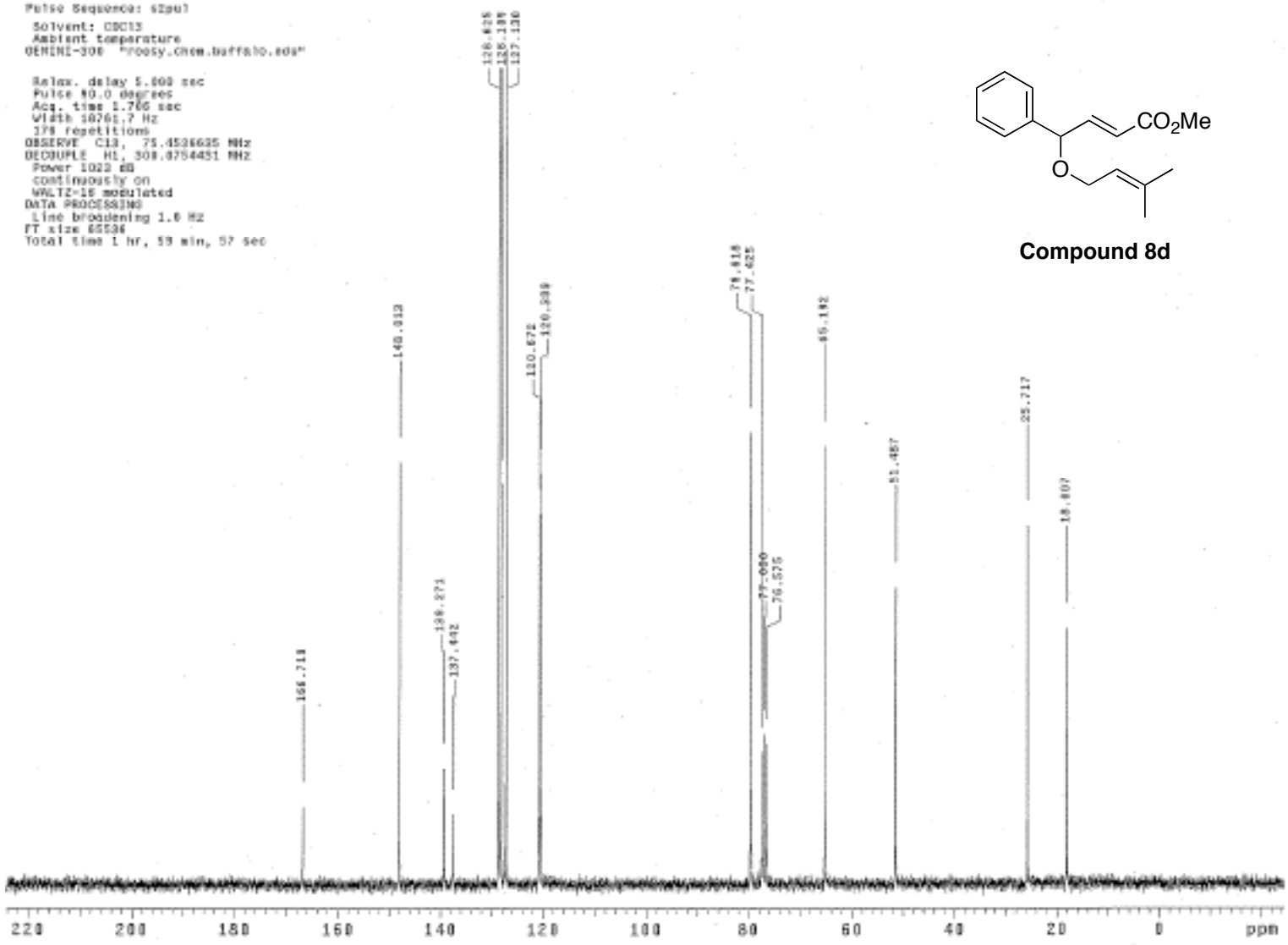

Automation directory: /home/nmruser/davies/sovalles/sovalles
File : exp
Sample id : tmpstudy
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 23.0 C / 296.1 K
Operator: davies
VNMRS-400 "v400"
Relax. delay 2.500 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 24509.8 Hz
308 repetitions
OBSERVE C13, 100.5265550 MHz
DECOUPLE H1, 399.7889220 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 23 min, 28 sec
170.677
168.344
135.439
135.163
133.325
129.360
128.630
128.371
127.224
126.778
120.490
77.313
77.000
76.686
73.324
73.257
62.662
40.353
220
200
180
160
140
120
100
80
60
40
20
0
ppm

CO2Me
O
O

Compound 9c

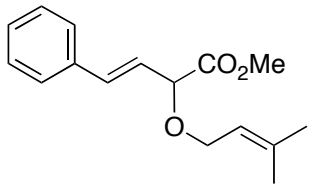

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "tacoy.chem.buffalo.edu"
Relax. delay 2.808 sec
Pulse 34.8 degrees
Acq. time 1.891 sec
Width 10000.8 Hz
16 repetitions
OBSERVE H1, 499.8584062 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 1 min, 18 sec
CO2Me
O
7
6
5
4
3
2
1
ppm

Compound 8d


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roosy.chem.buffalo.edu"
Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
178 repetitions
OBSERVE C13, 75.4536635 MHz
DECOUPLE H1, 308.0754451 MHz
Power 1022 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 59 min, 57 sec
166.718
140.013
136.873
137.442
128.425
128.139
127.130
120.672
120.839
79.818
77.425
77.050
76.675
65.182
51.457
25.717
18.007
220
200
180
160
140
120
100
80
60
40
20
0
ppm

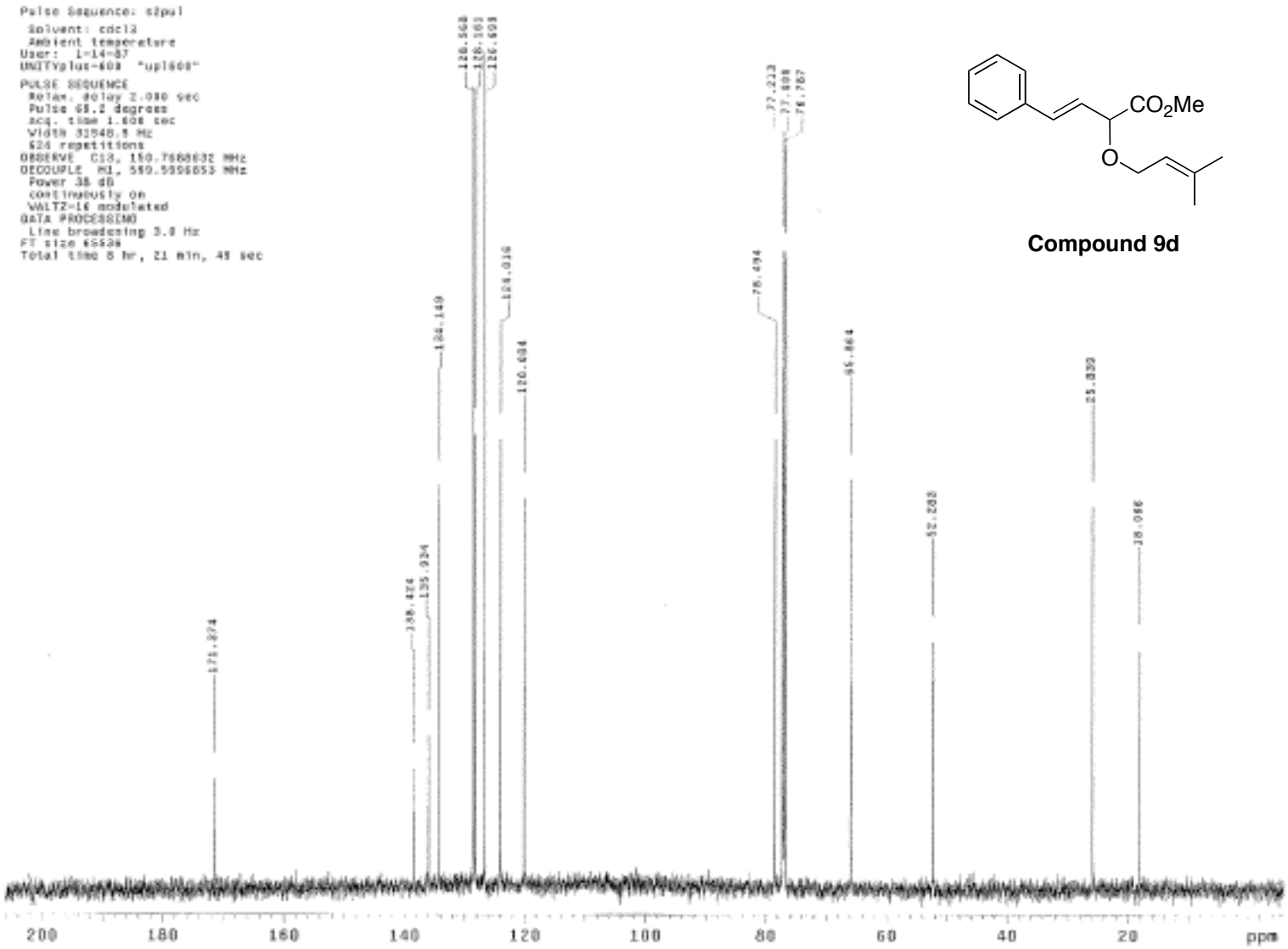
CO2Me
O

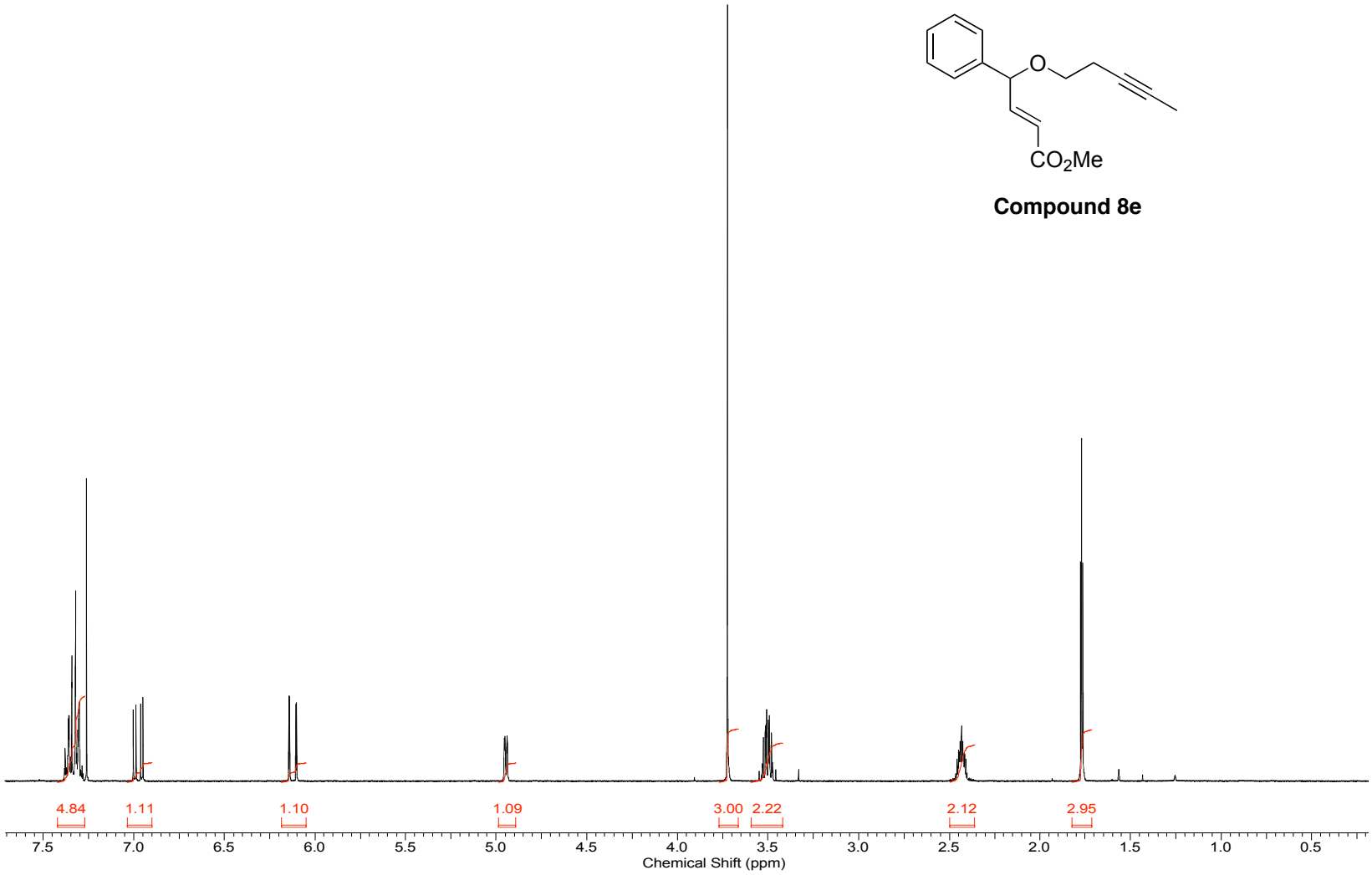
Compound 8d


CO2Me
O

Compound 9d

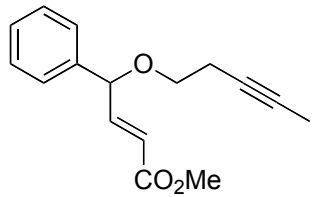
6.02
1.16
1.15
1.11
1.12
2.23
2.99
3.02
2.99
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: l-14-87
UNITYplus-400 "upl600"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 68.2 degrees
acq. time 1.608 sec
Width 31548.5 Hz
524 repetitions
OBSERVE C13, 150.7868632 MHz
DECOUPLE H1, 599.5959855 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 65536
Total time 8 hr, 21 min, 45 sec
CO2Me
O
Compound 9d
200
180
160
140
120
100
80
60
40
20
ppm

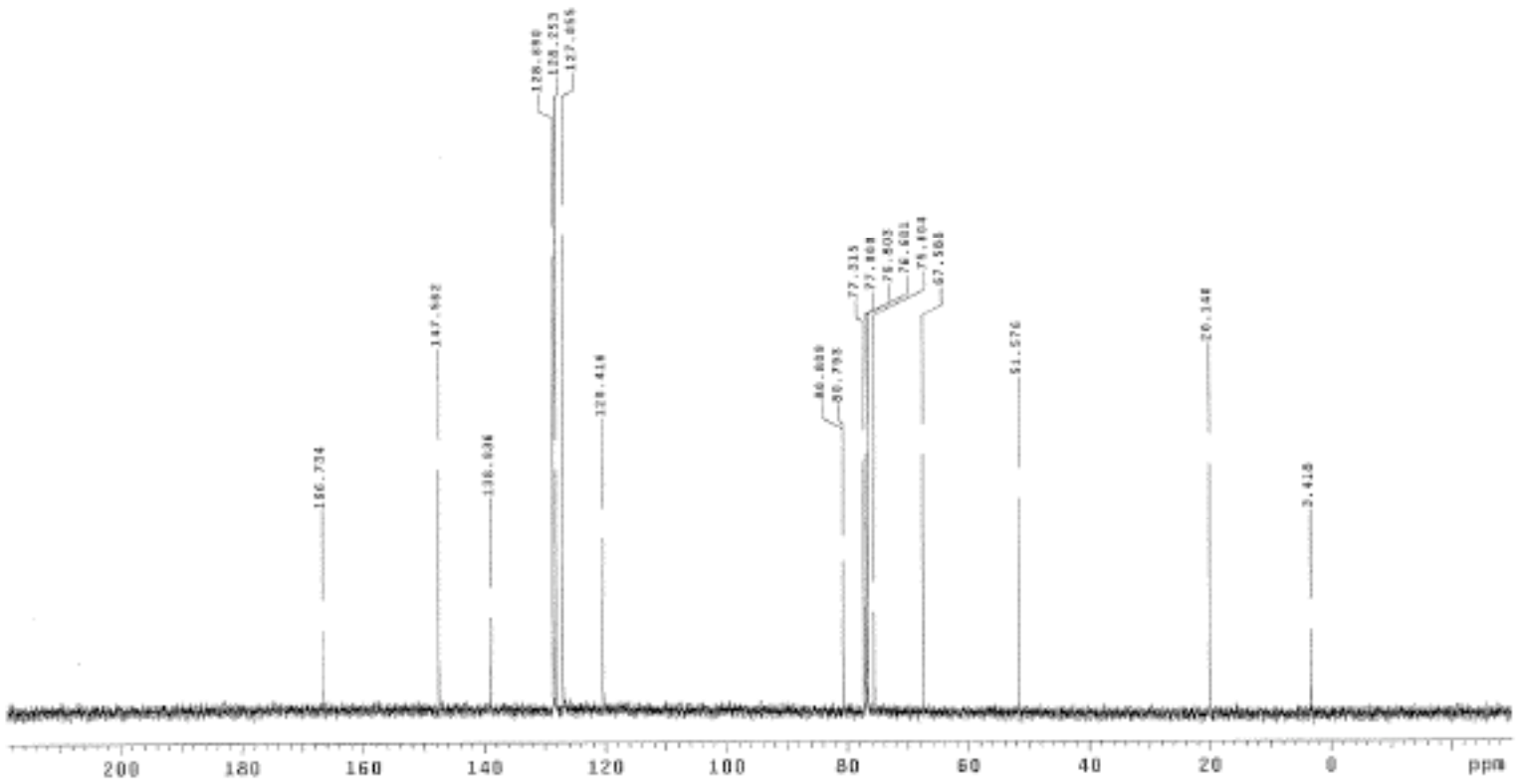

O
CO2Me
4.84
1.11
1.10
1.09
3.00
2.22
2.12
2.95
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

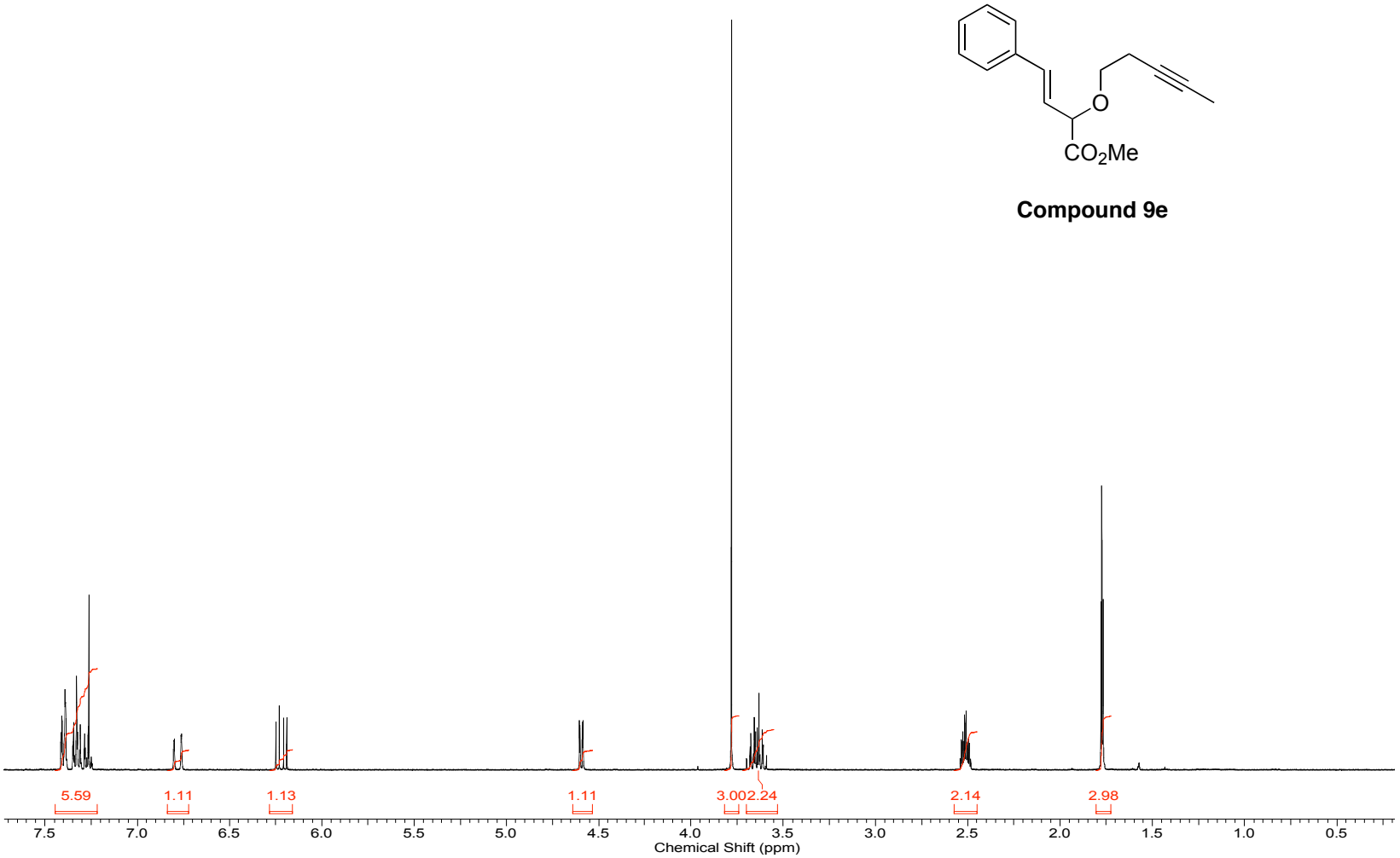
Compound 8e


Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
INOVA-400 "1600data"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 69.2 degrees
Acq. time 2.801 sec
Width 25808.8 Hz
224 repetitions
OBSERVE C13, 100.5614488 MHz
DECOUPLE H1, 399.5270768 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line Broadening 1.8 Hz
FT Size 131072
Total time 11 hr, 8 min, 14 sec

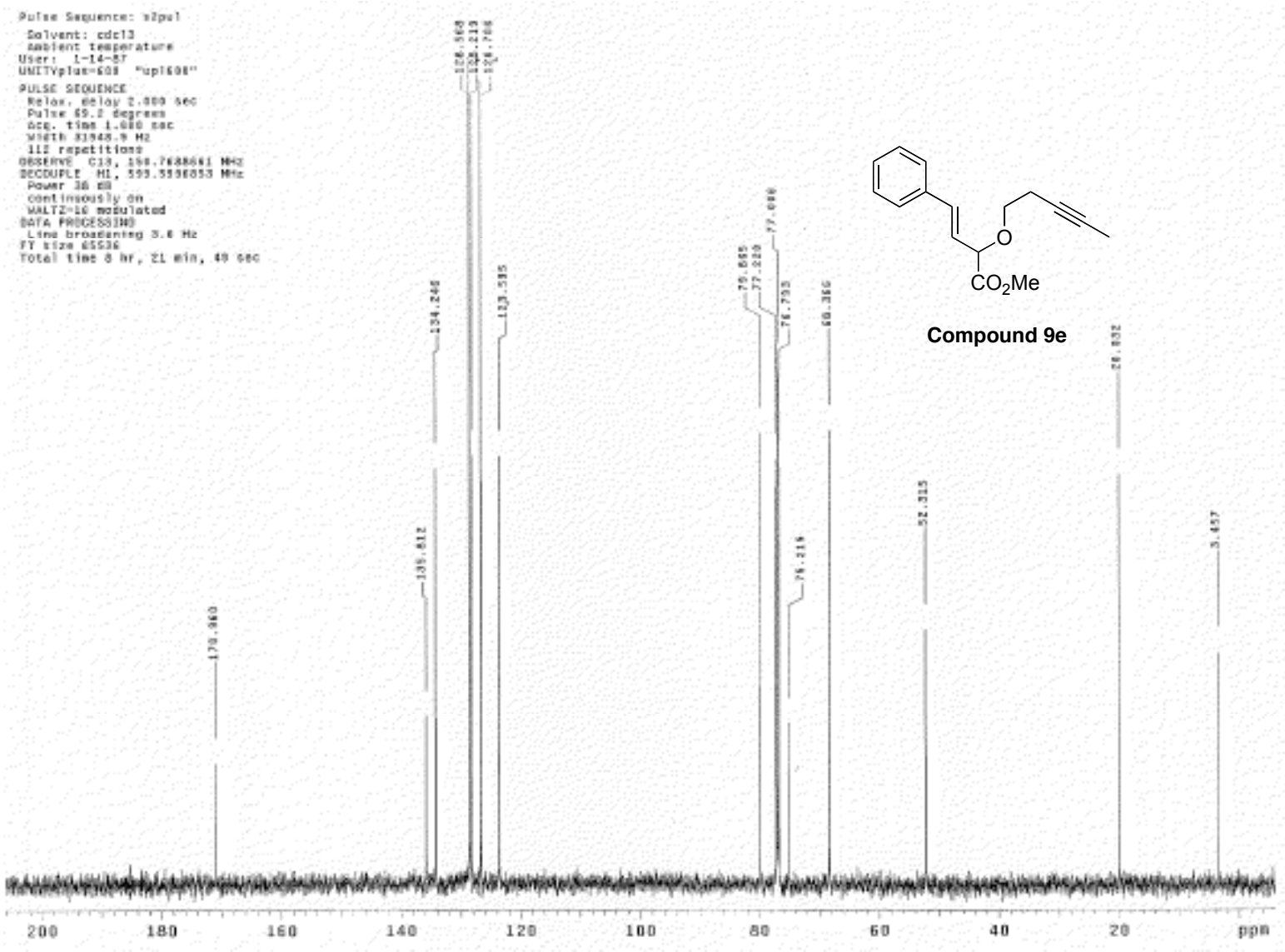

O
CO2Me

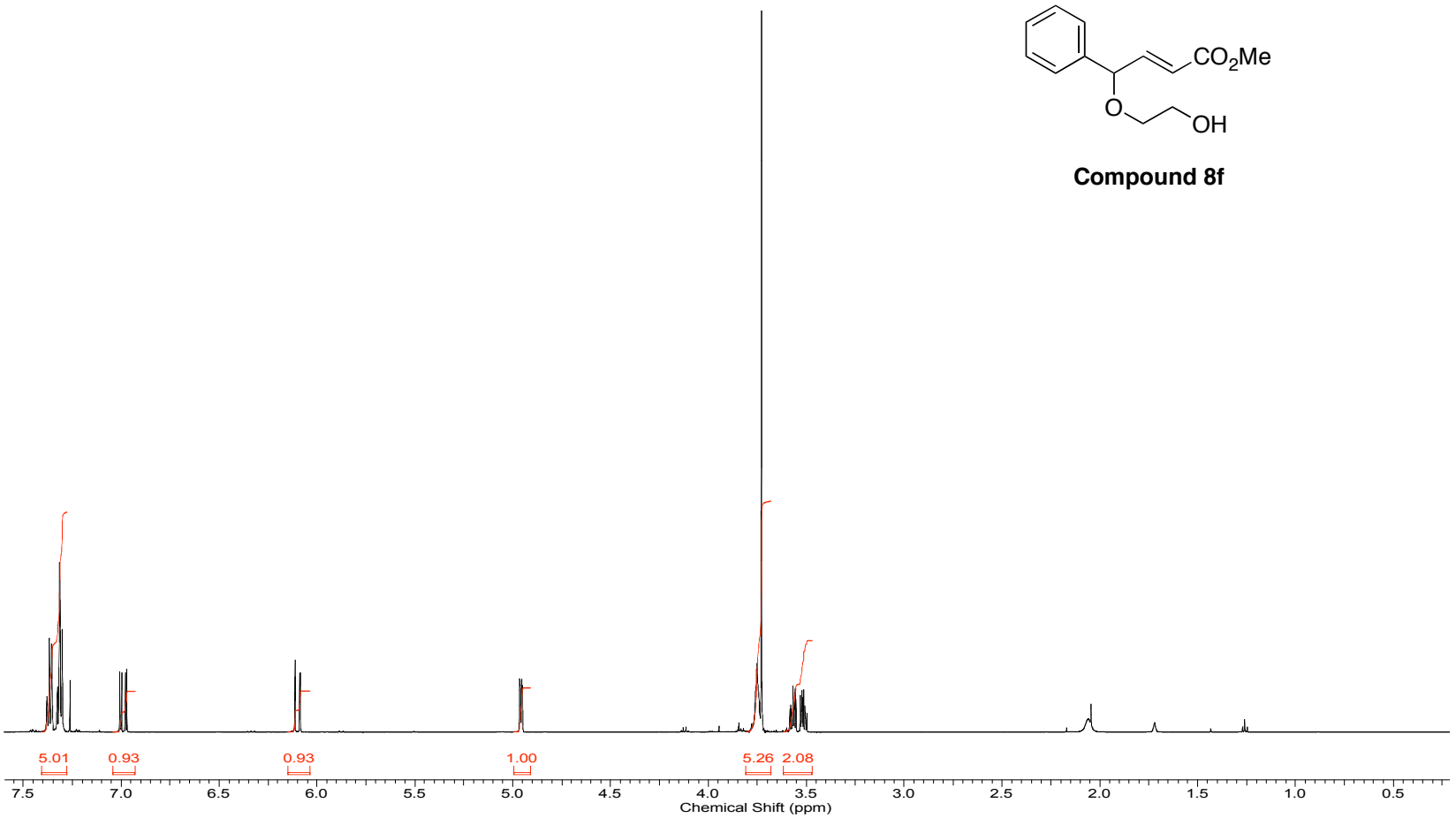
Compound 8e


166.734
147.692
138.636
128.698
128.253
127.855
128.418
80.609
80.793
77.315
77.000
76.803
76.601
76.404
67.568
51.576
20.144
3.418
200
180
160
140
120
100
80
60
40
20
0
ppm

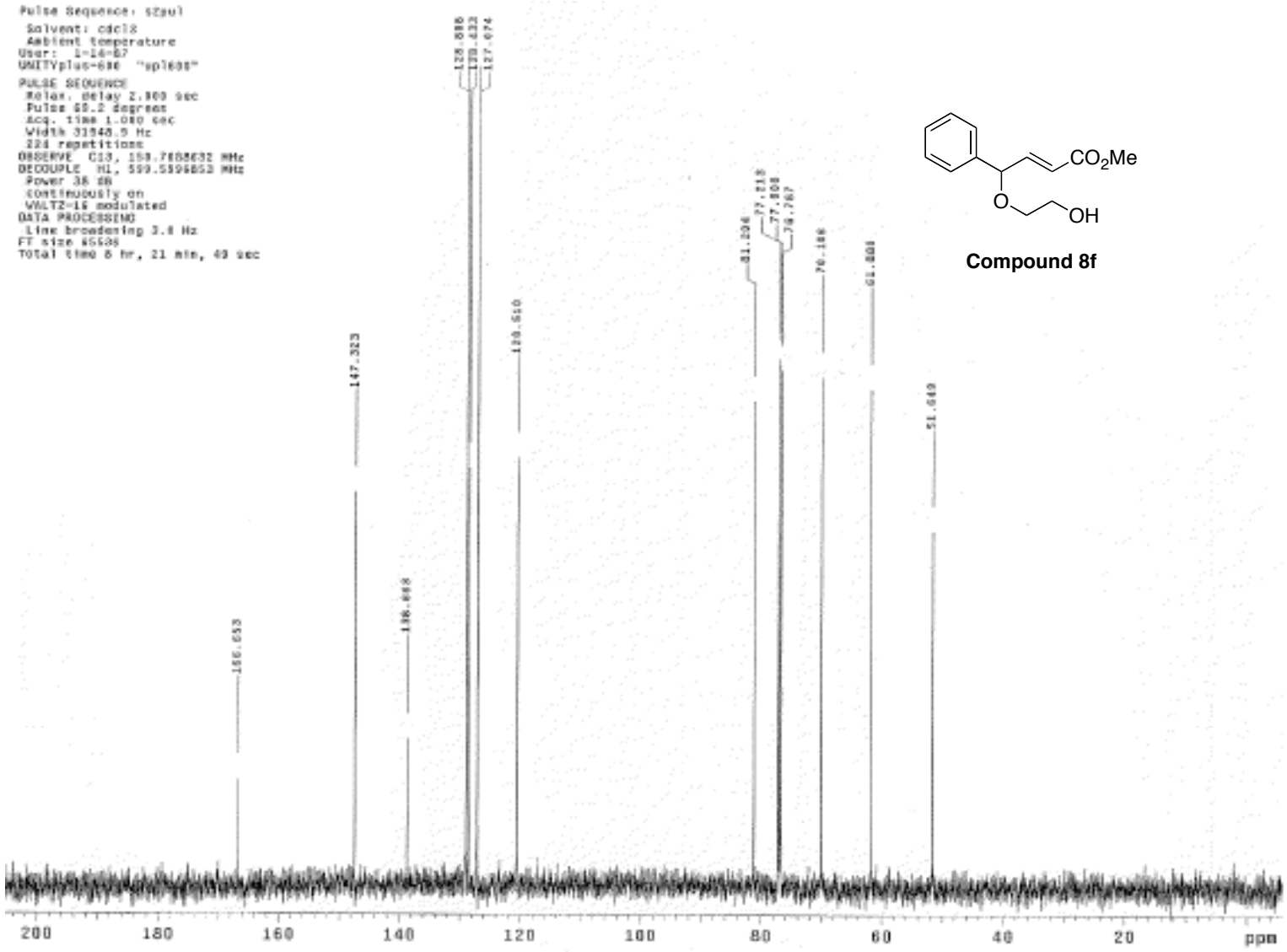

O
CO2Me
5.59
1.11
1.13
1.11
3.00
2.24
2.14
2.98
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

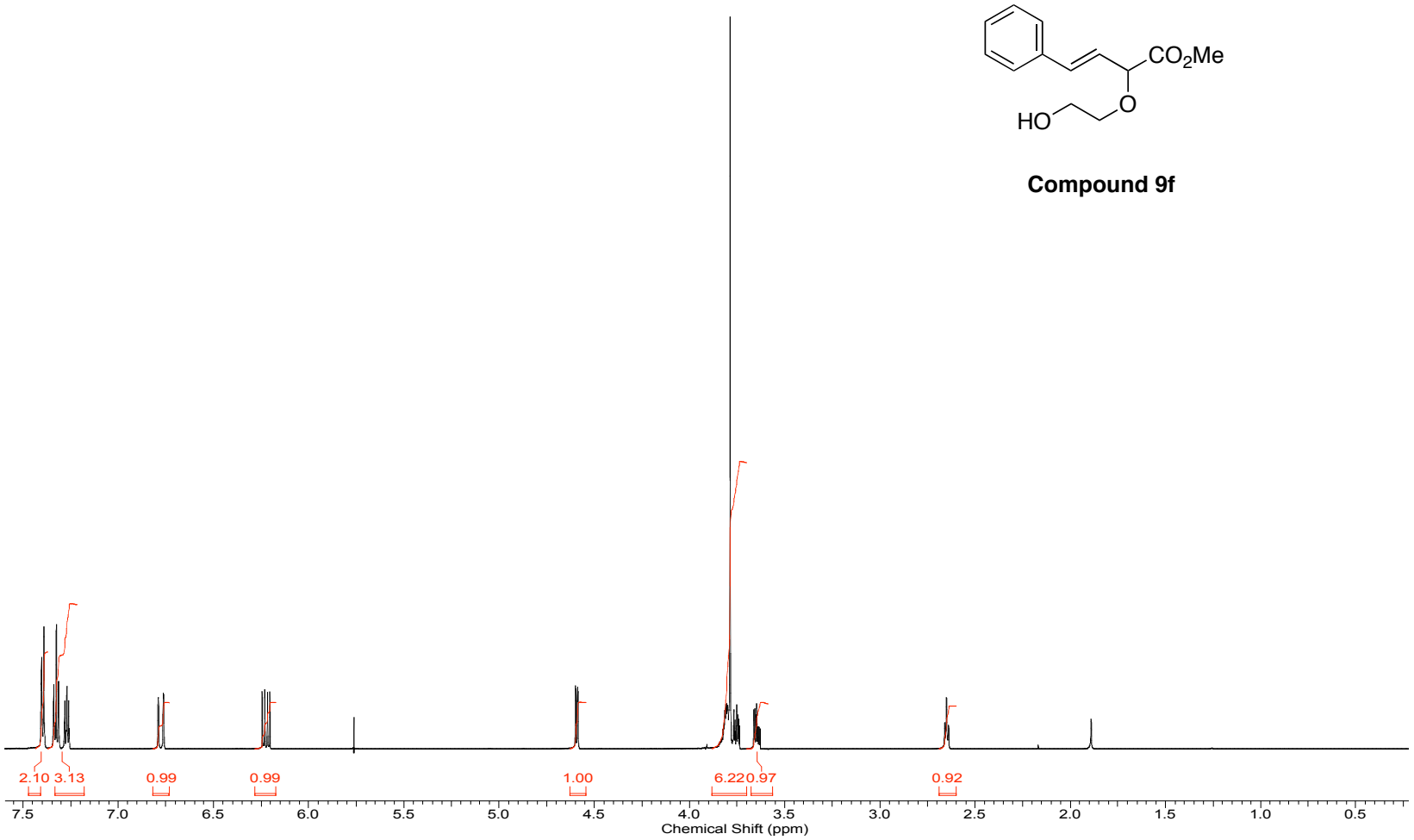
Compound 9e


Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: l-14-87
UNITYplus-600 "upl600"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 69.2 degrees
Acq. time 1.000 sec
Width 31948.9 Hz
112 repetitions
OBSERVE C13, 150.7688661 MHz
DECOUPLE H1, 599.5536853 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 65536
Total time 0 hr, 21 min, 49 sec
170.960
135.812
134.248
128.568
128.219
127.766
123.595
79.655
77.320
77.000
76.793
76.319
68.366
52.315
20.832
14.457
O
CO2Me
Compound 9e
200
180
160
140
120
100
80
60
40
20
ppm

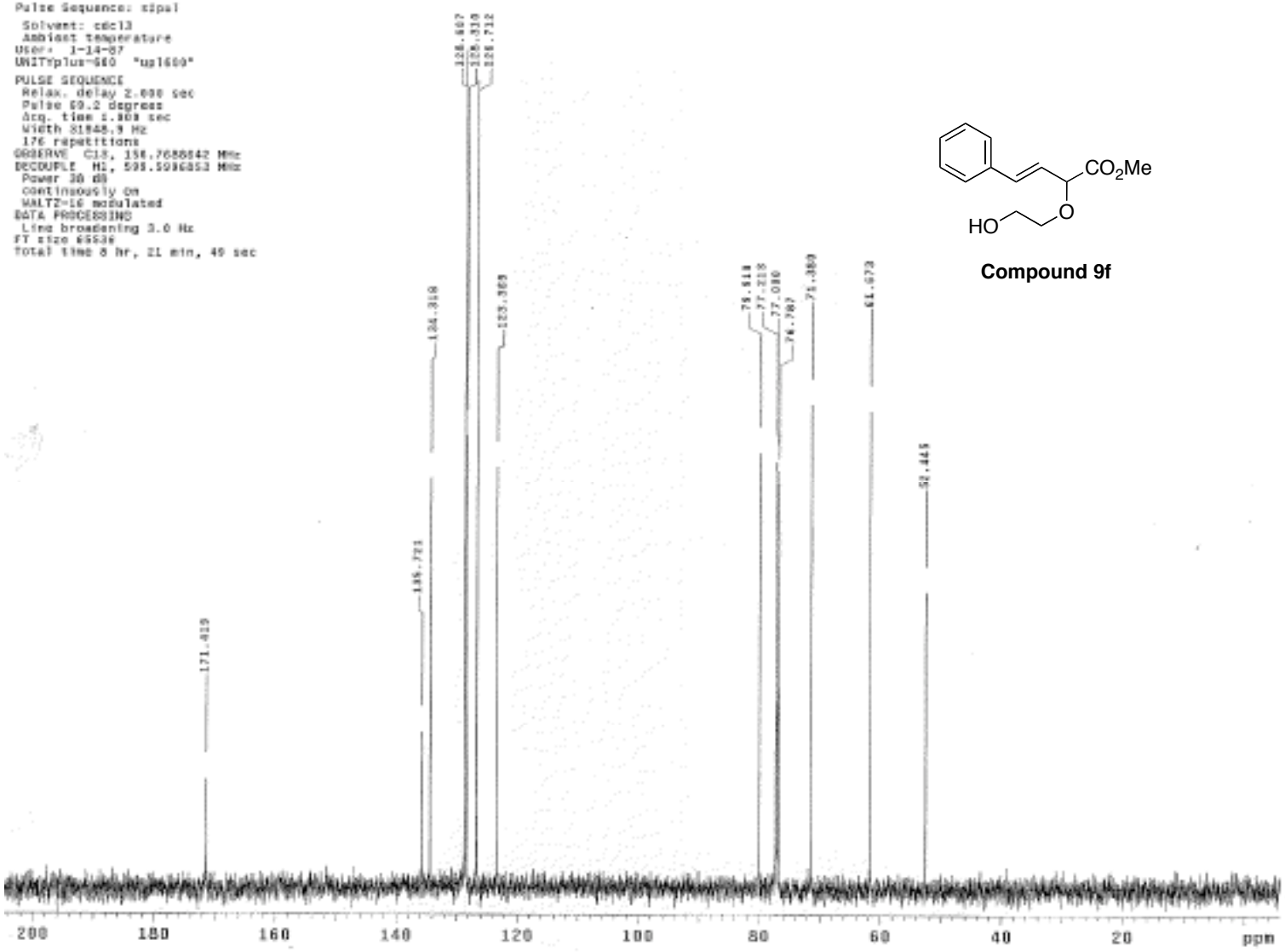

CO2Me
O
OH
5.01
0.93
0.93
1.00
5.26
2.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

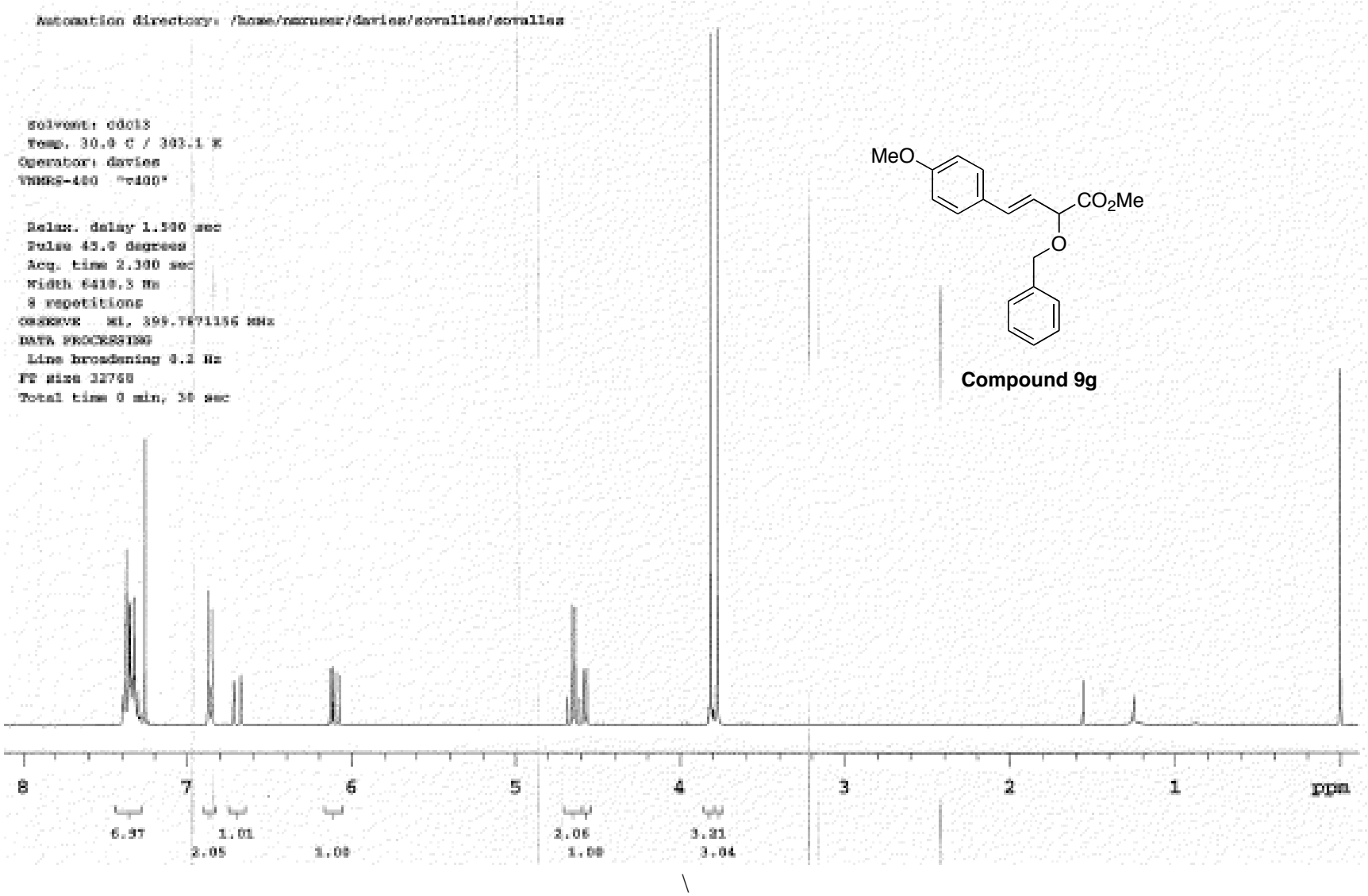
Compound 8f

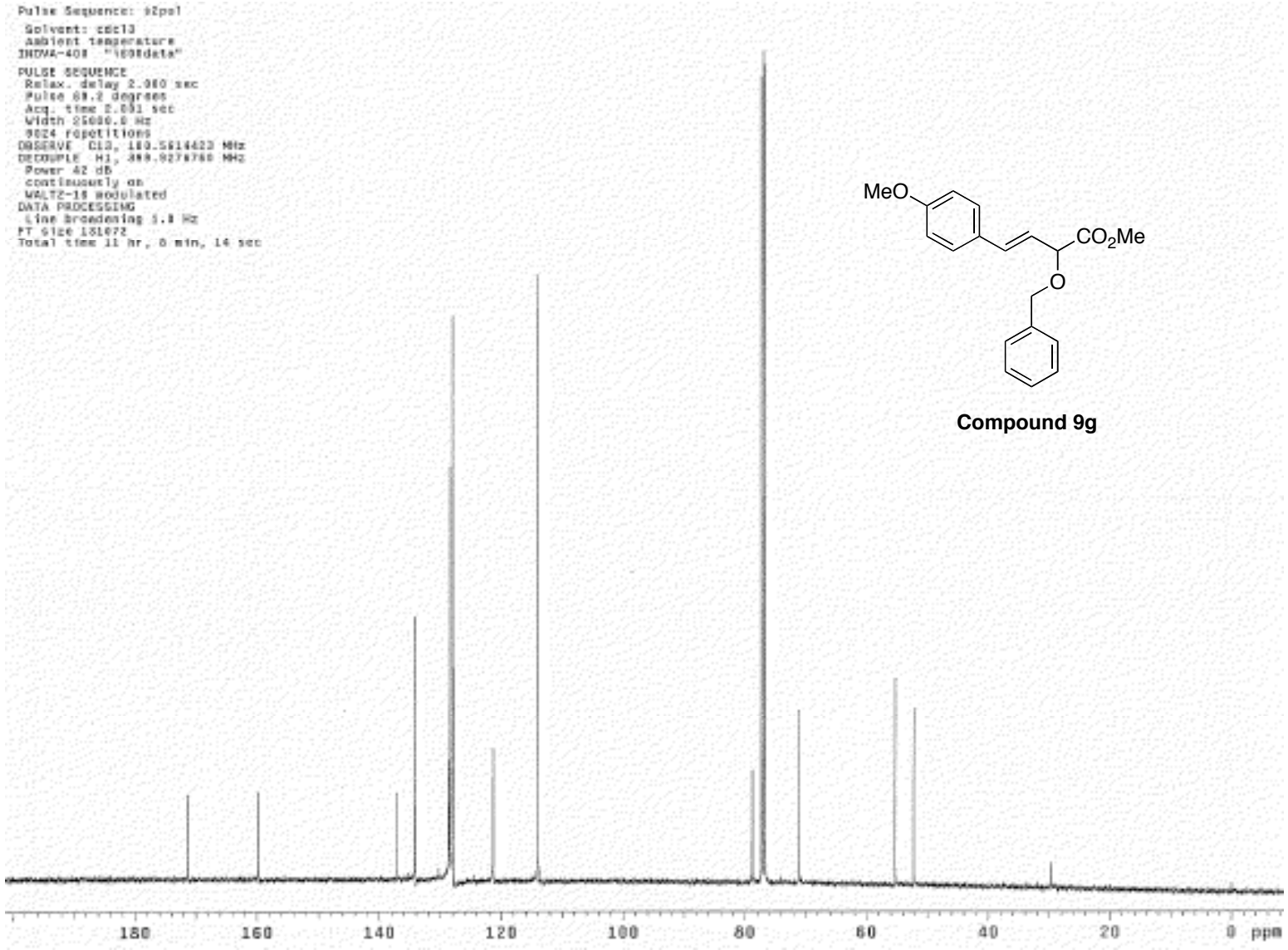

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-07
UNITYplus-600 "sp1600"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 60.2 degrees
Acq. time 1.080 sec
Width 31948.9 Hz
224 repetitions
OBSERVE C13, 150.7658632 MHz
DECOUPLE H1, 599.5596853 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.8 Hz
FT size 65536
Total time 8 hr, 21 min, 49 sec
128.686
128.433
127.674
147.323
120.610
81.204
77.215
77.000
76.787
70.186
61.808
51.649
166.653
136.668
CO2Me
O
OH
Compound 8f
200
180
160
140
120
100
80
60
40
20
ppm


CO2Me
O
HO
2.10
3.13
0.99
0.99
1.00
6.22
0.97
0.92
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

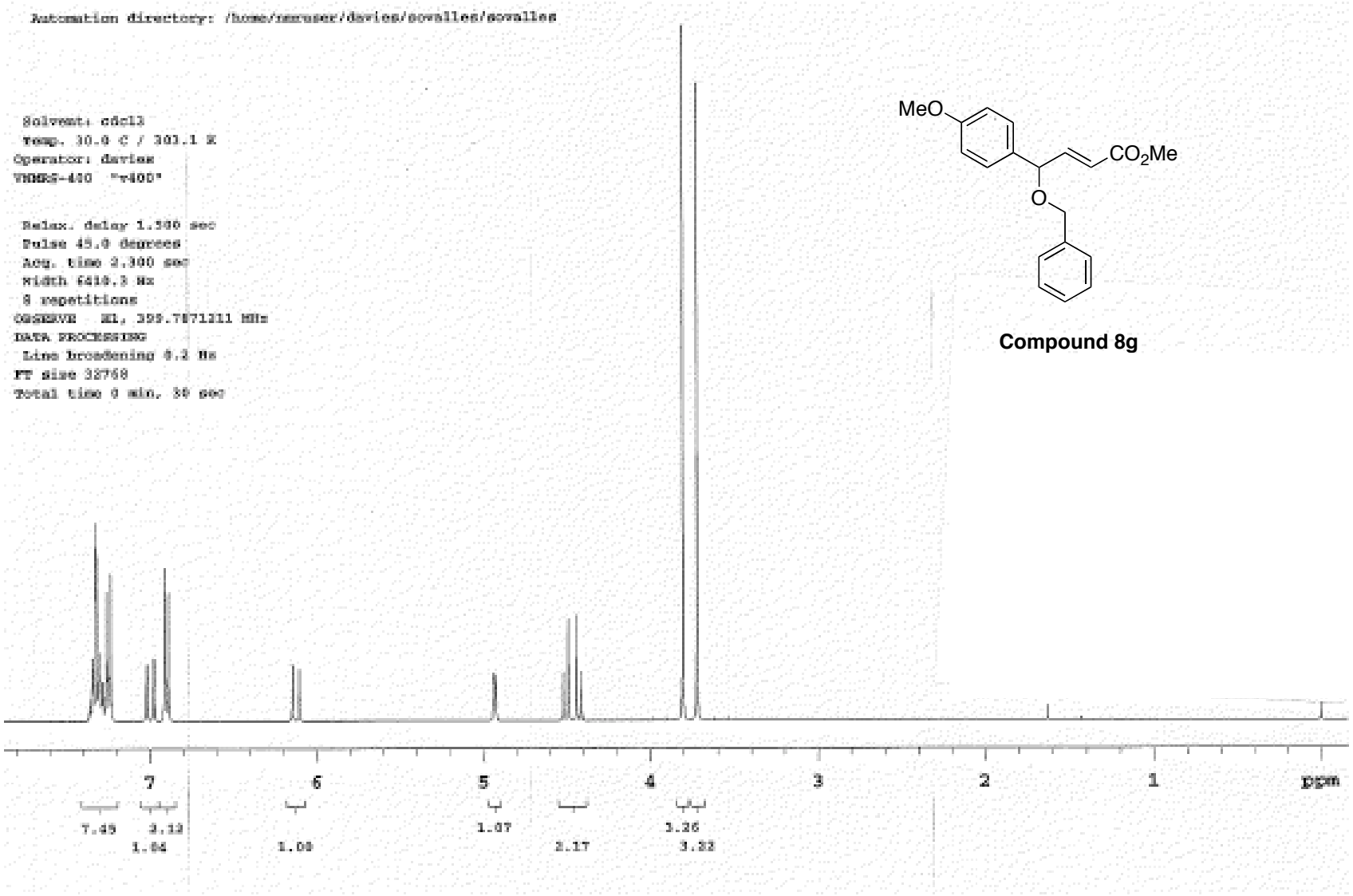
Compound 9f


Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-07
UNITYplus-600 "up1600"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 69.2 degrees
Acq. time 1.909 sec
Width 31848.9 Hz
176 repetitions
OBSERVE C13, 150.7686842 MHz
DECOUPLE H1, 599.5996853 MHz
Power 38 dB
continously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 65536
Total time 8 hr, 21 min, 49 sec
171.419
145.721
134.368
128.687
128.318
128.712
123.369
79.514
77.218
77.000
76.782
71.389
61.673
52.445
200
180
160
140
120
100
80
60
40
20
ppm
CO2Me
O
HO
Compound 9f

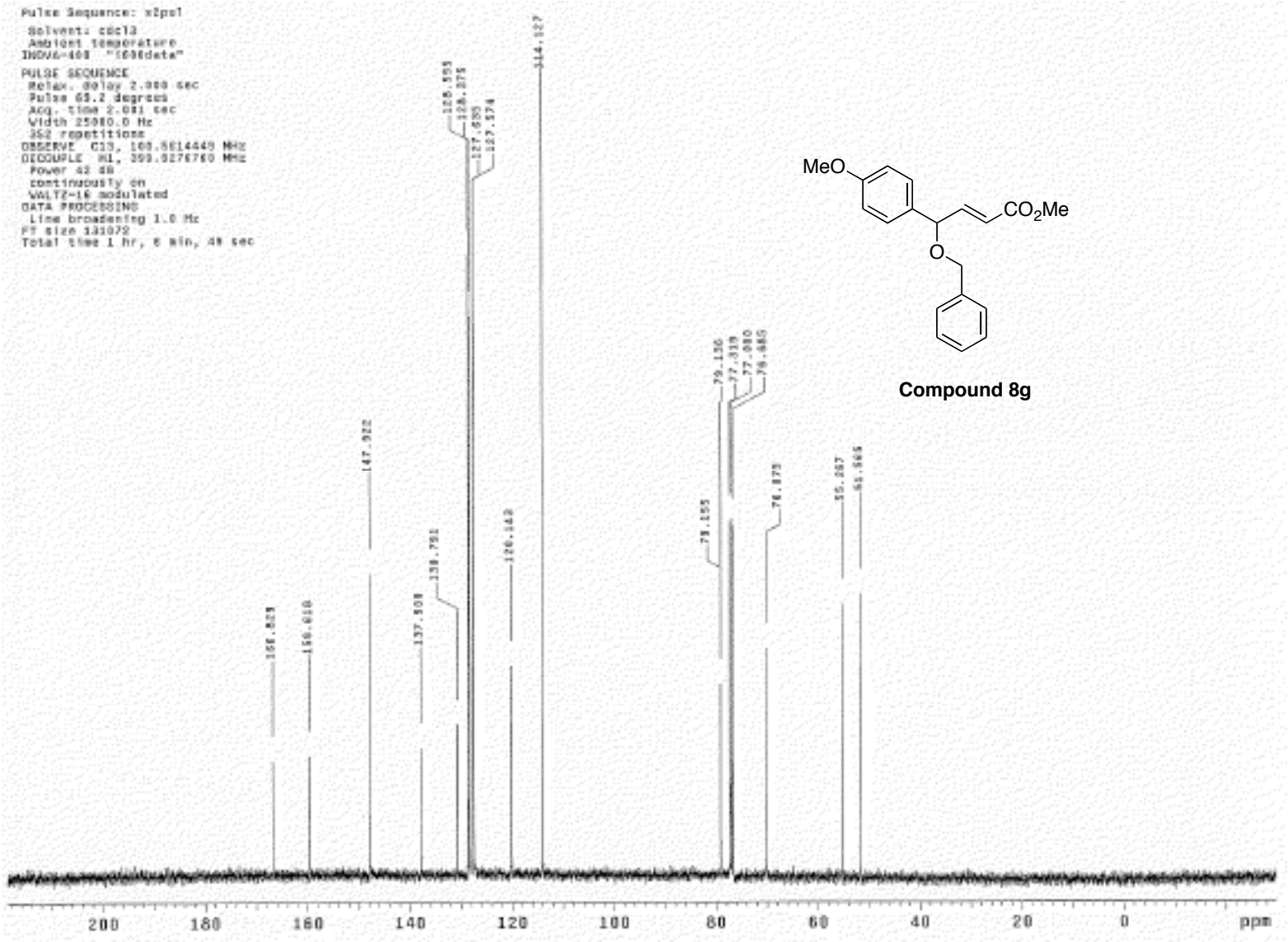

Automation directory: /home/nmruser/davies/sovallas/sovallas
Solvent: cdcl3
Temp. 30.0 C / 303.1 K
Operator: davies
VNMRS-400 "vd400"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 2.300 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7871156 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 30 sec
MeO
CO2Me
O
Compound 9g
8
7
6
5
4
3
2
1
ppm
6.97
2.05
1.01
1.09
2.06
1.08
3.21
3.04

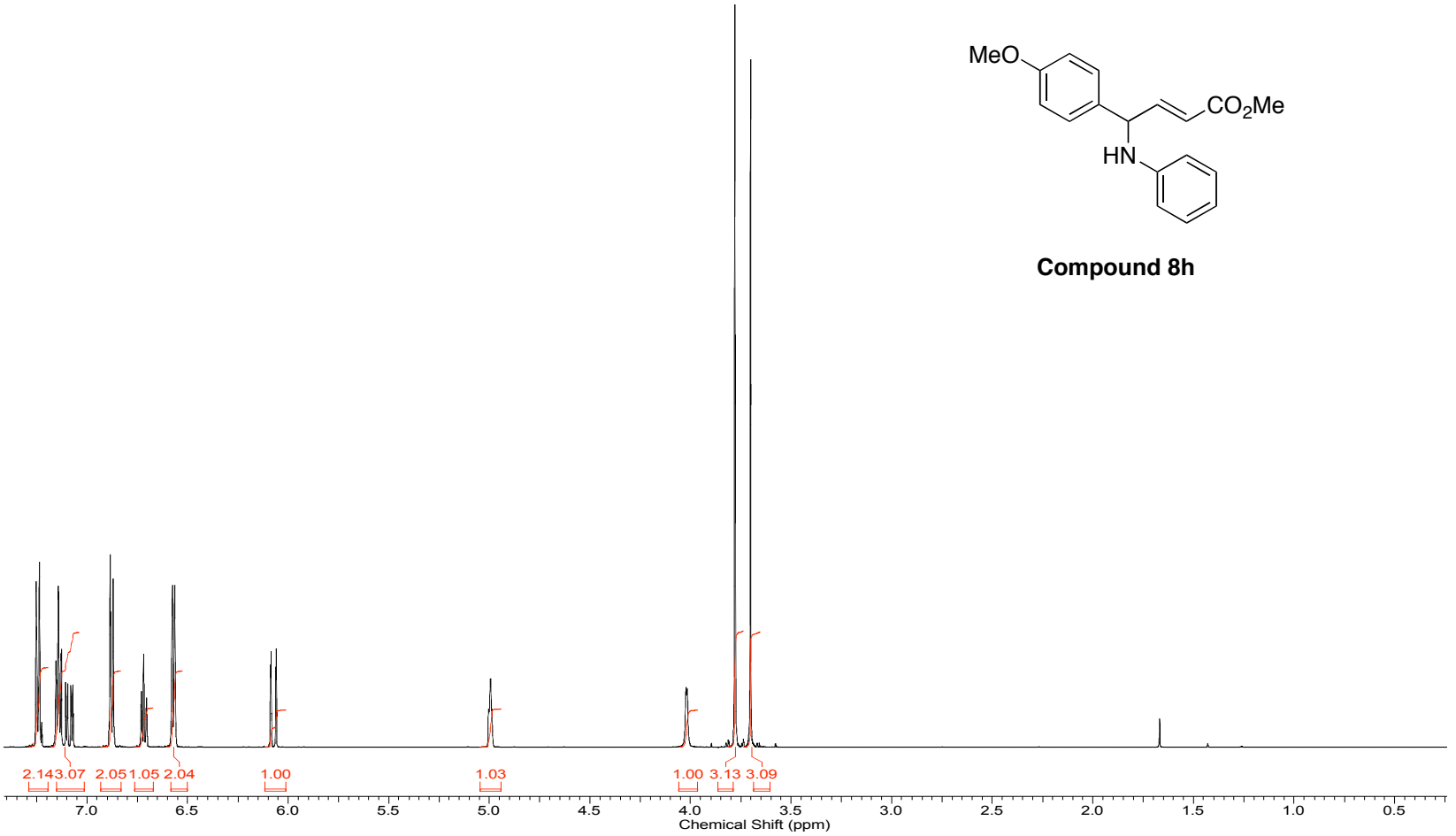

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
INOVA-400 "1698data"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 69.2 degrees
Acq. time 2.551 sec
Width 25600.0 Hz
8024 repetitions
OBSERVE C13, 100.5614423 MHz
DECOUPLE H1, 399.9276760 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 11 hr, 6 min, 14 sec
MeO
CO2Me
O
180
160
140
120
100
80
60
40
20
0 ppm

Compound 9g

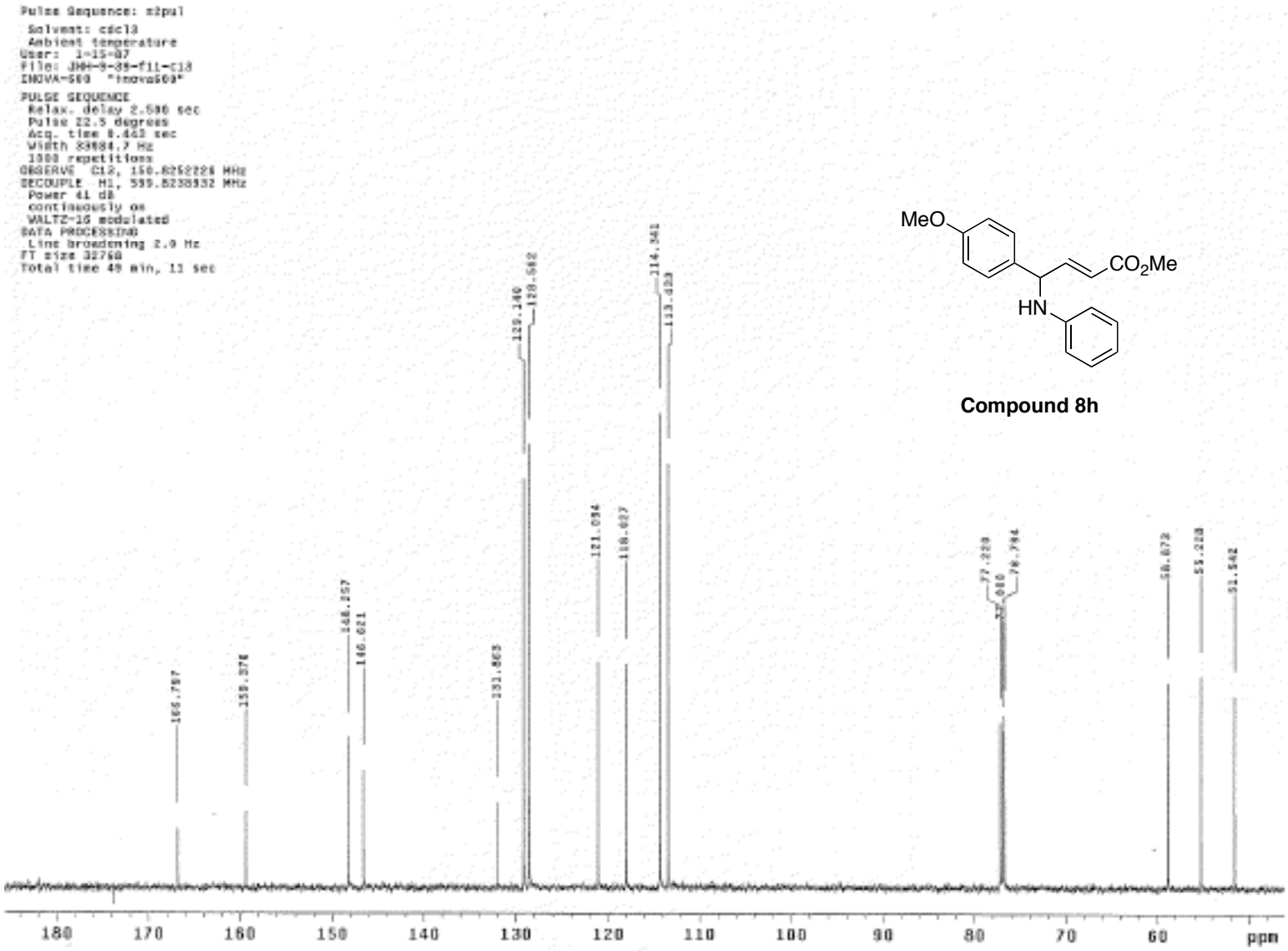

Automation directory: /home/nmruser/davies/govalles/govalles
Solvent: cdcl3
Temp. 30.0 C / 303.1 K
Operator: davies
VNMRS-400 "v400"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 2.300 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7871211 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min. 39 sec
MeO
CO2Me
O
7
6
5
4
3
2
1
ppm
7.49
2.12
1.84
1.00
1.07
2.17
3.26
3.22

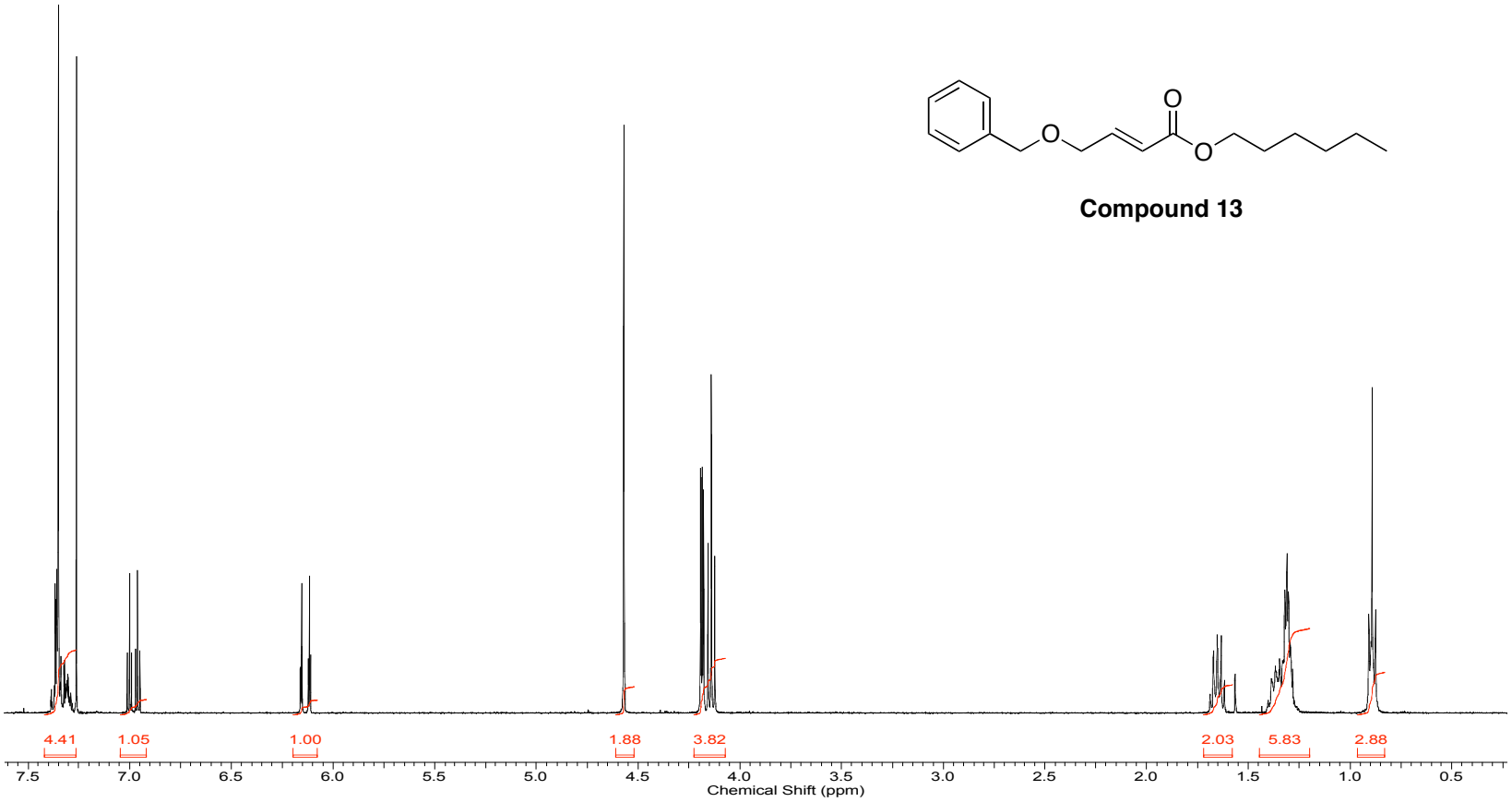
Compound 8g


Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
INOVA-400 "1698data"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 68.2 degrees
Acq. time 2.081 sec
Width 25080.0 Hz
352 repetitions
OBSERVE C13, 100.5614449 MHz
DECOUPLE H1, 399.9276760 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 6 min, 49 sec
MeO
CO2Me
O
Compound 8g
200
180
160
140
120
100
80
60
40
20
0
ppm

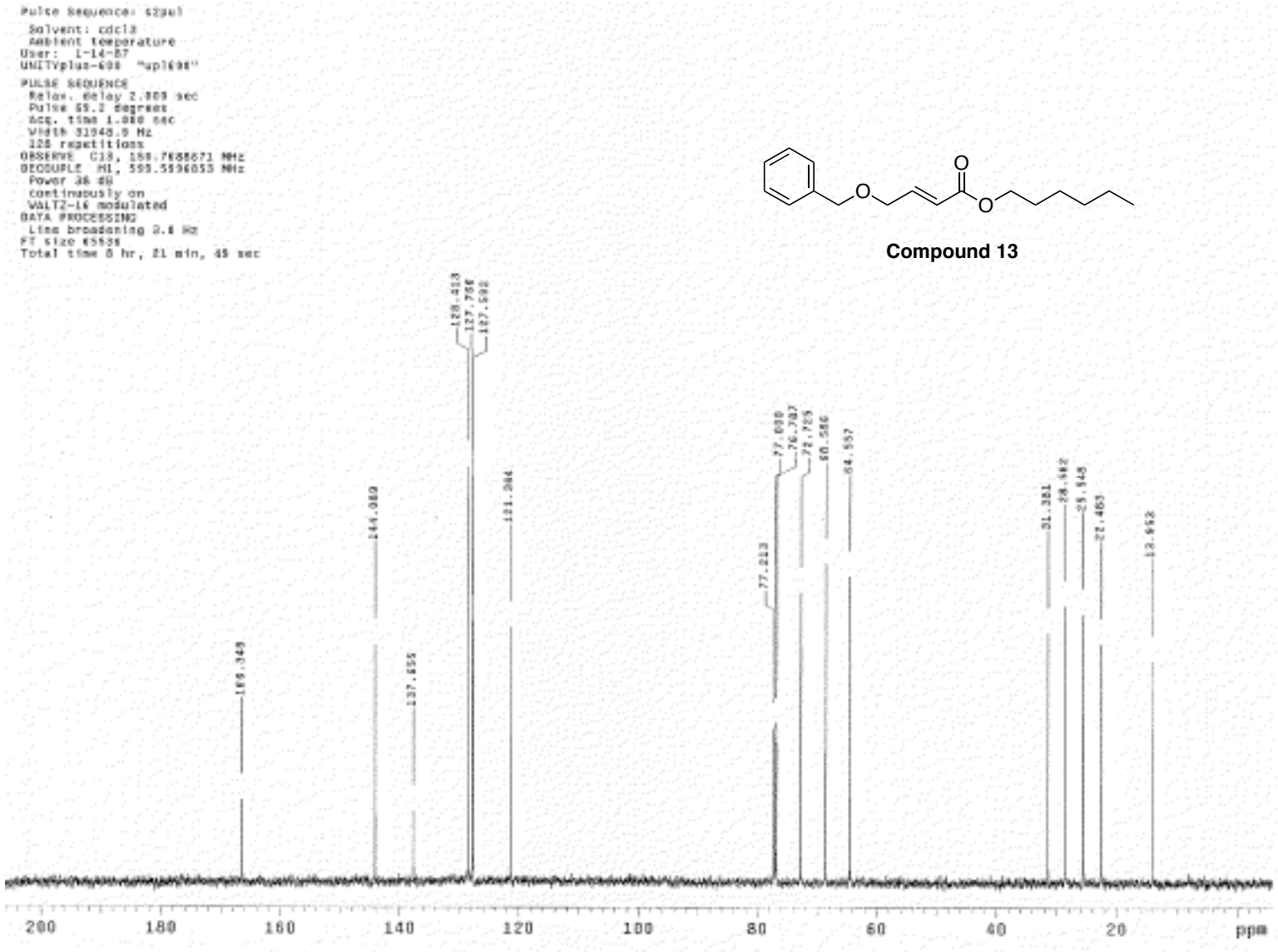

MeO
CO2Me
HN
2.14
3.07
2.05
1.05
2.04
1.00
1.03
1.00
3.13
3.09
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

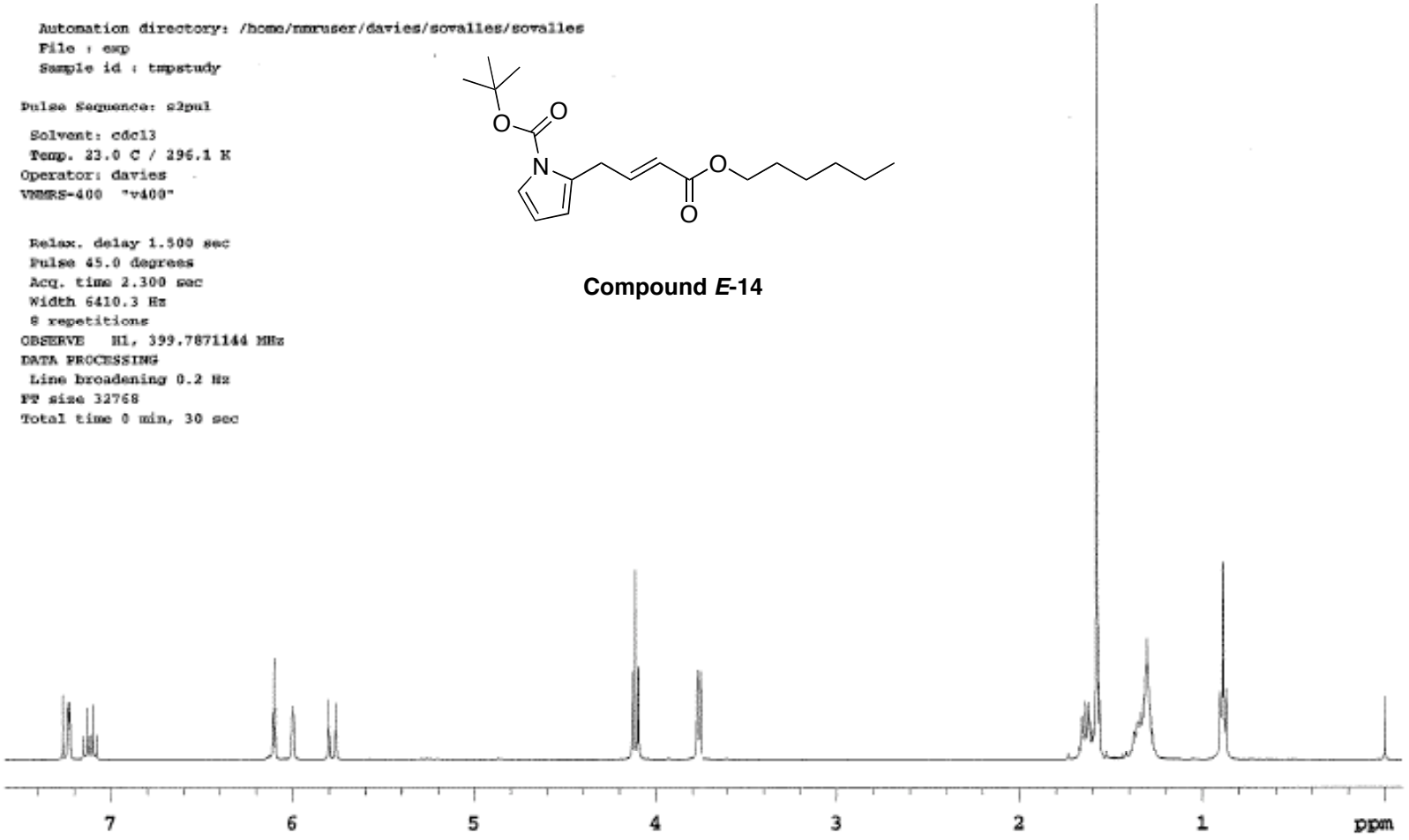
Compound 8h


Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-15-07
File: JHH-9-38-f11-c13
INOVA-500 "inova500"
PULSE SEQUENCE
Relax. delay 2.500 sec
Pulse 22.5 degrees
Acq. time 0.443 sec
Width 33884.7 Hz
1000 repetitions
OBSERVE C13, 150.8252226 MHz
DECOUPLE H1, 599.8238832 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 32768
Total time 49 min, 11 sec
MeO
CO2Me
HN
Compound 8h
165.787
159.378
148.357
146.021
131.863
129.146
128.582
121.054
118.627
114.341
113.429
77.320
77.000
76.784
58.672
55.228
51.542
180
170
160
150
140
130
120
110
100
90
80
70
60
ppm

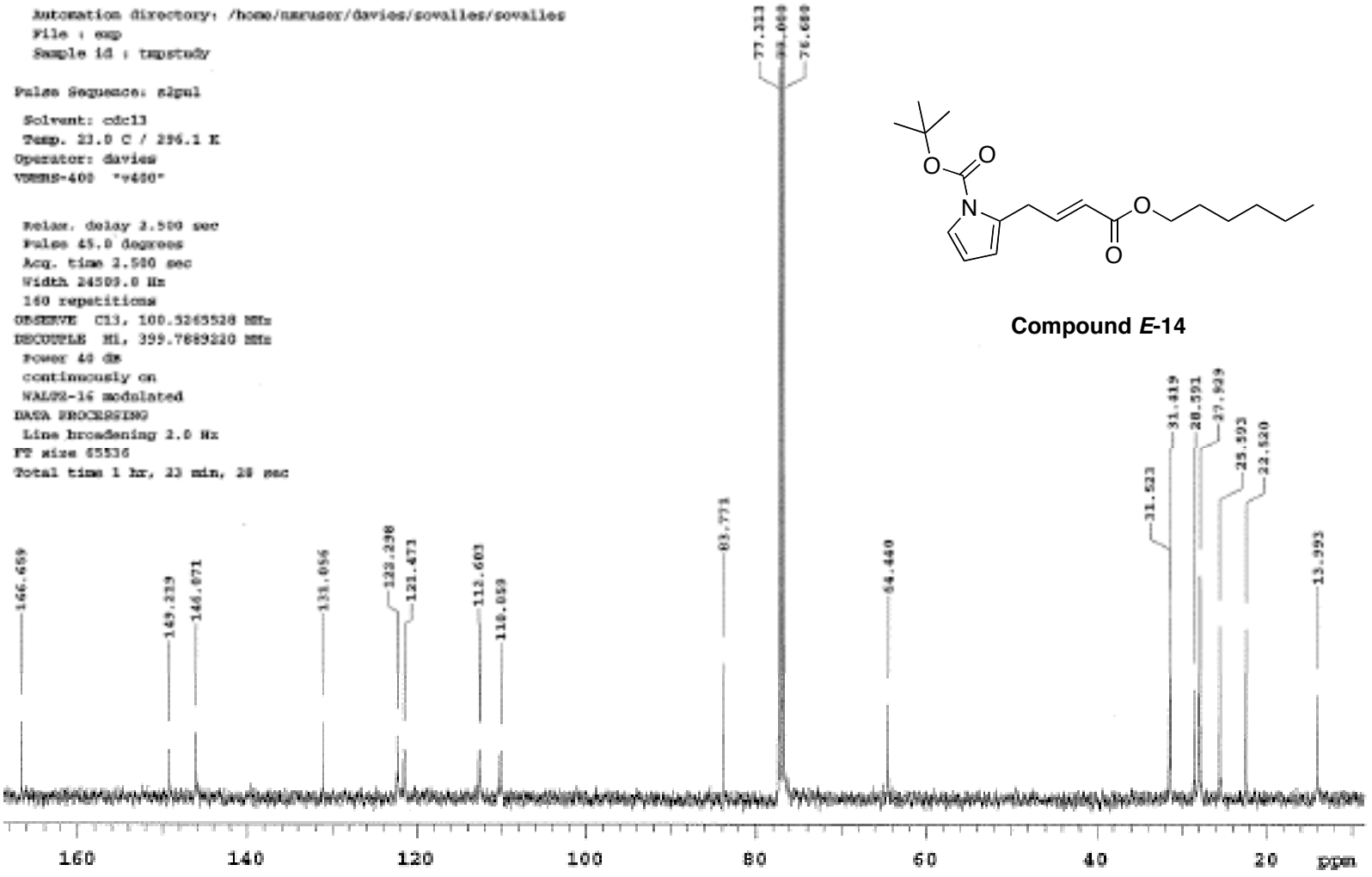

O
O
O
4.41
1.05
1.00
1.88
3.82
2.03
5.83
2.88
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

Compound 13

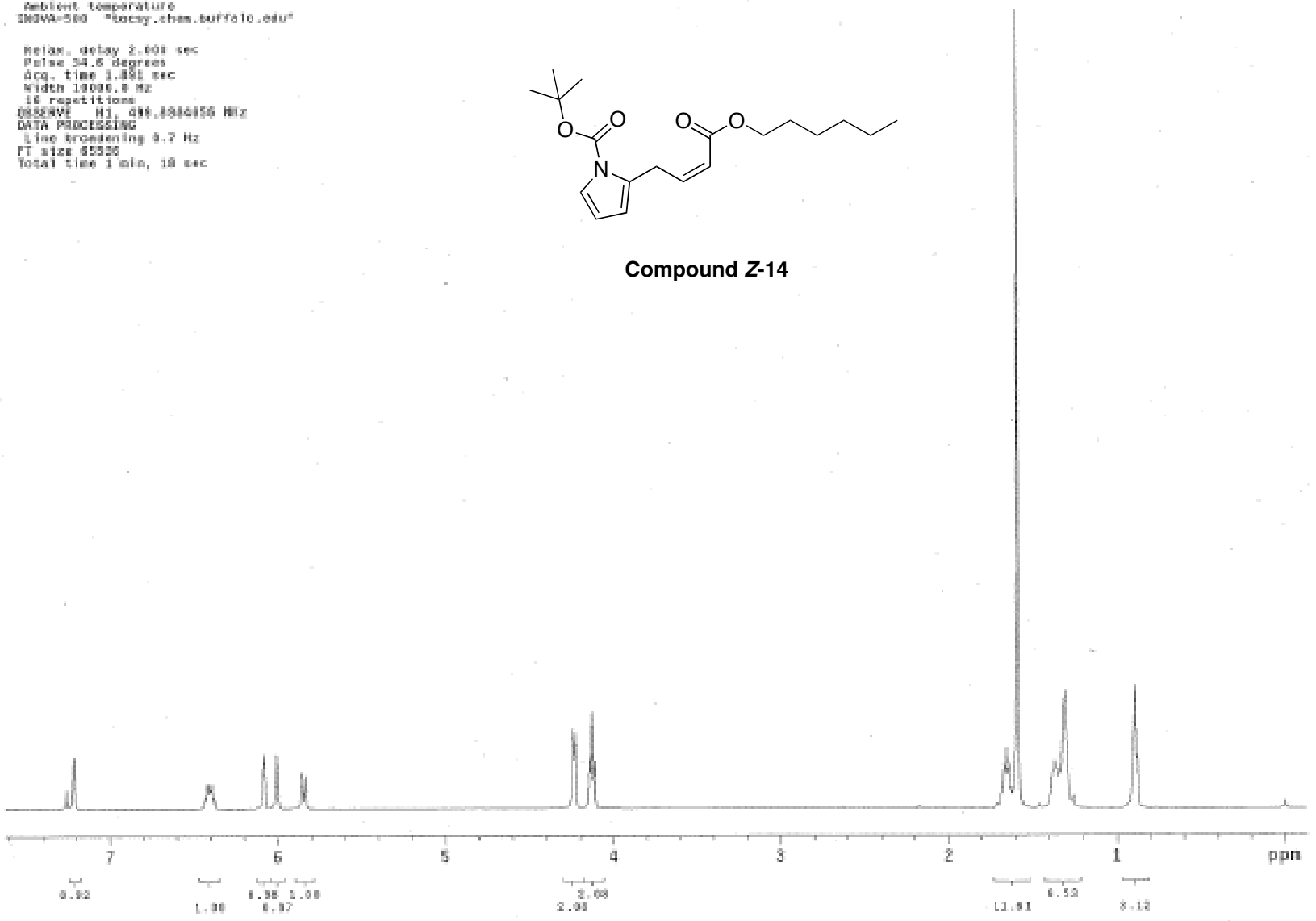

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: l-14-87
UNITYplus-600 "upl600"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 55.2 degrees
Acq. time 1.000 sec
Width 31948.9 Hz
128 repetitions
OBSERVE C13, 150.7688671 MHz
DECOUPLE H1, 599.5596053 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.4 Hz
FT size 65536
Total time 0 hr, 21 min, 45 sec
O
O
O
Compound 13
166.349
144.089
137.655
128.413
127.758
127.698
121.284
77.213
77.000
76.787
72.725
60.586
64.557
31.381
28.582
25.648
22.463
13.952
200
180
160
140
120
100
80
60
40
20
ppm



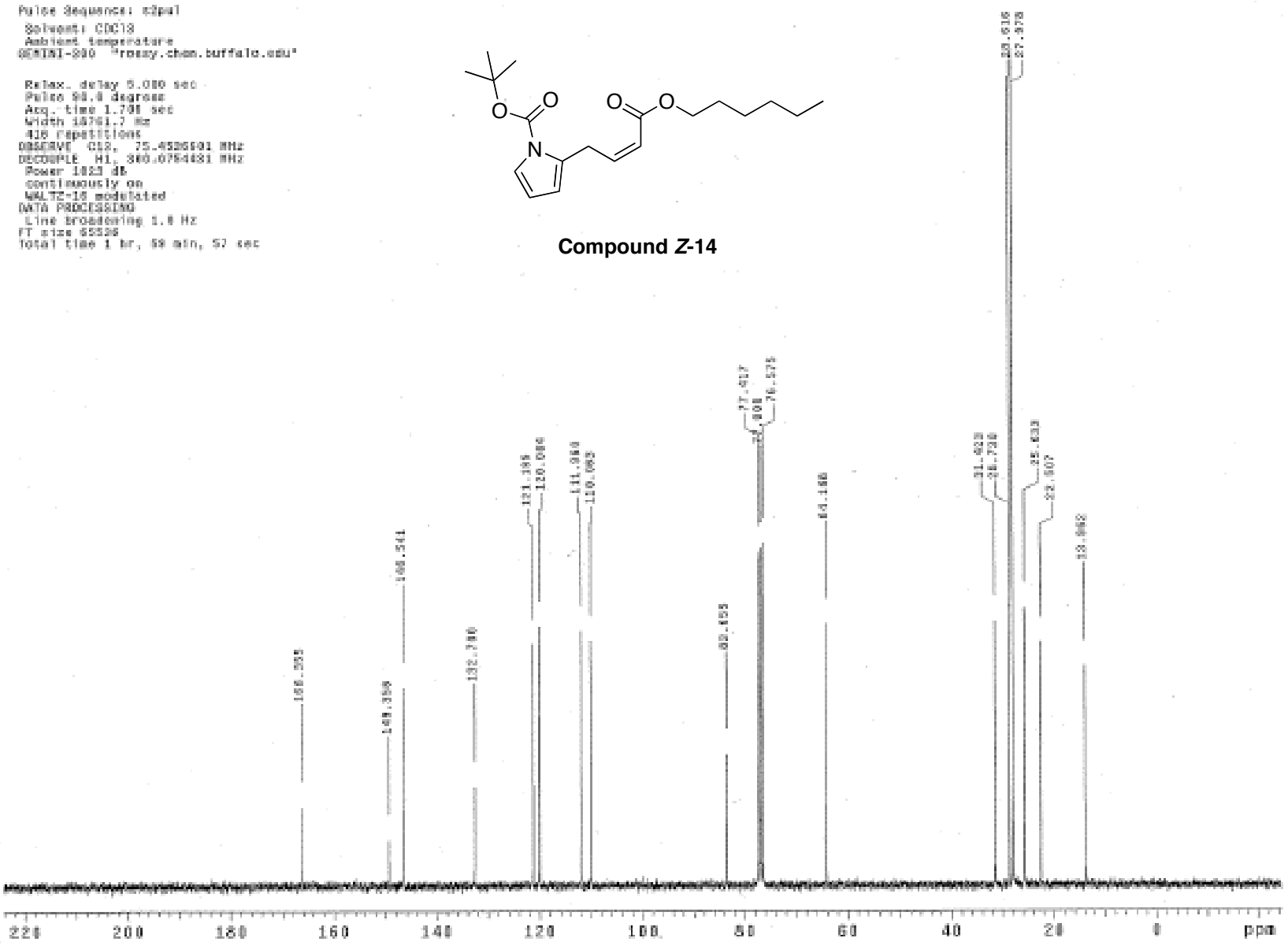
Compound *E*-14



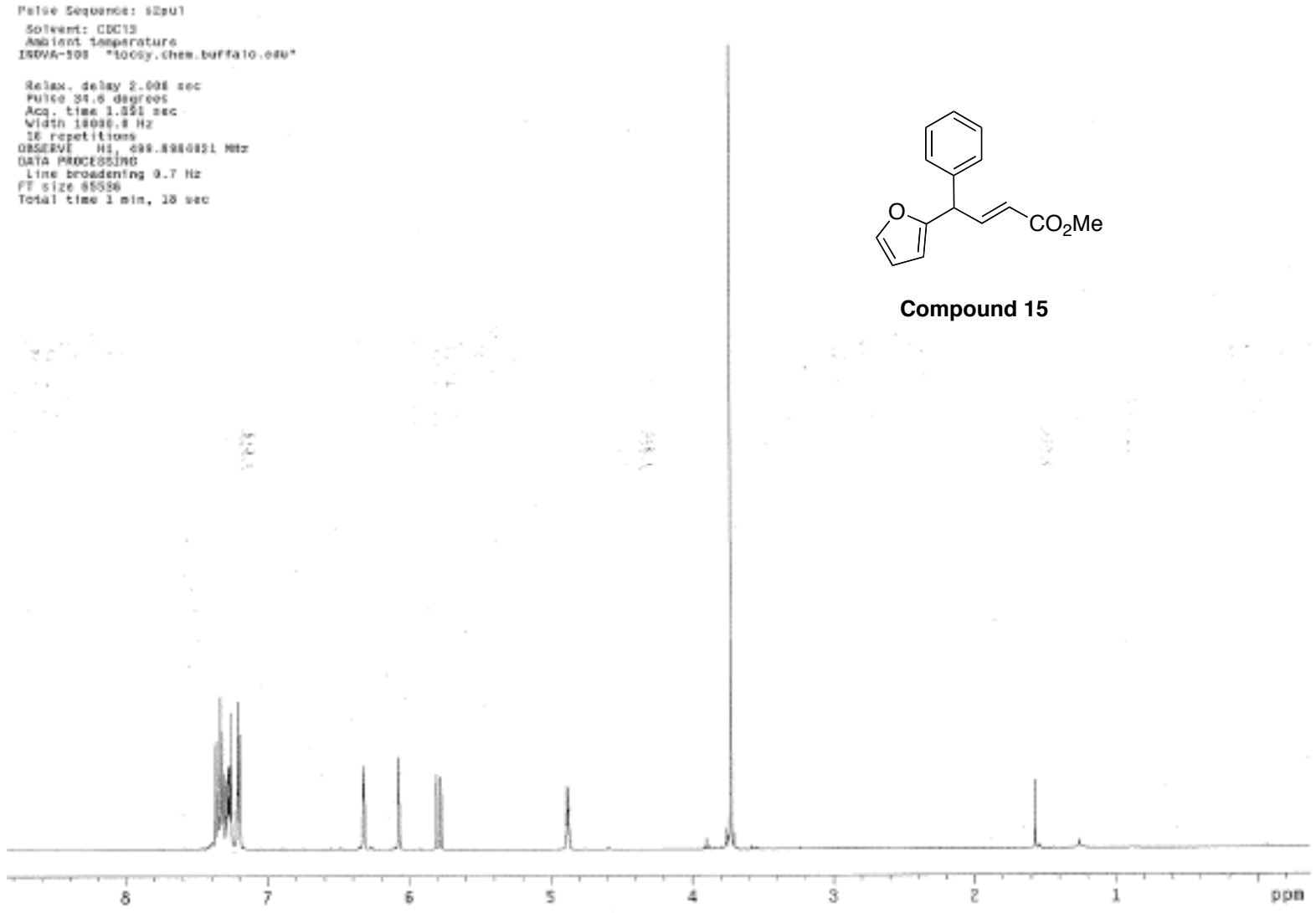
Compound *E*-14



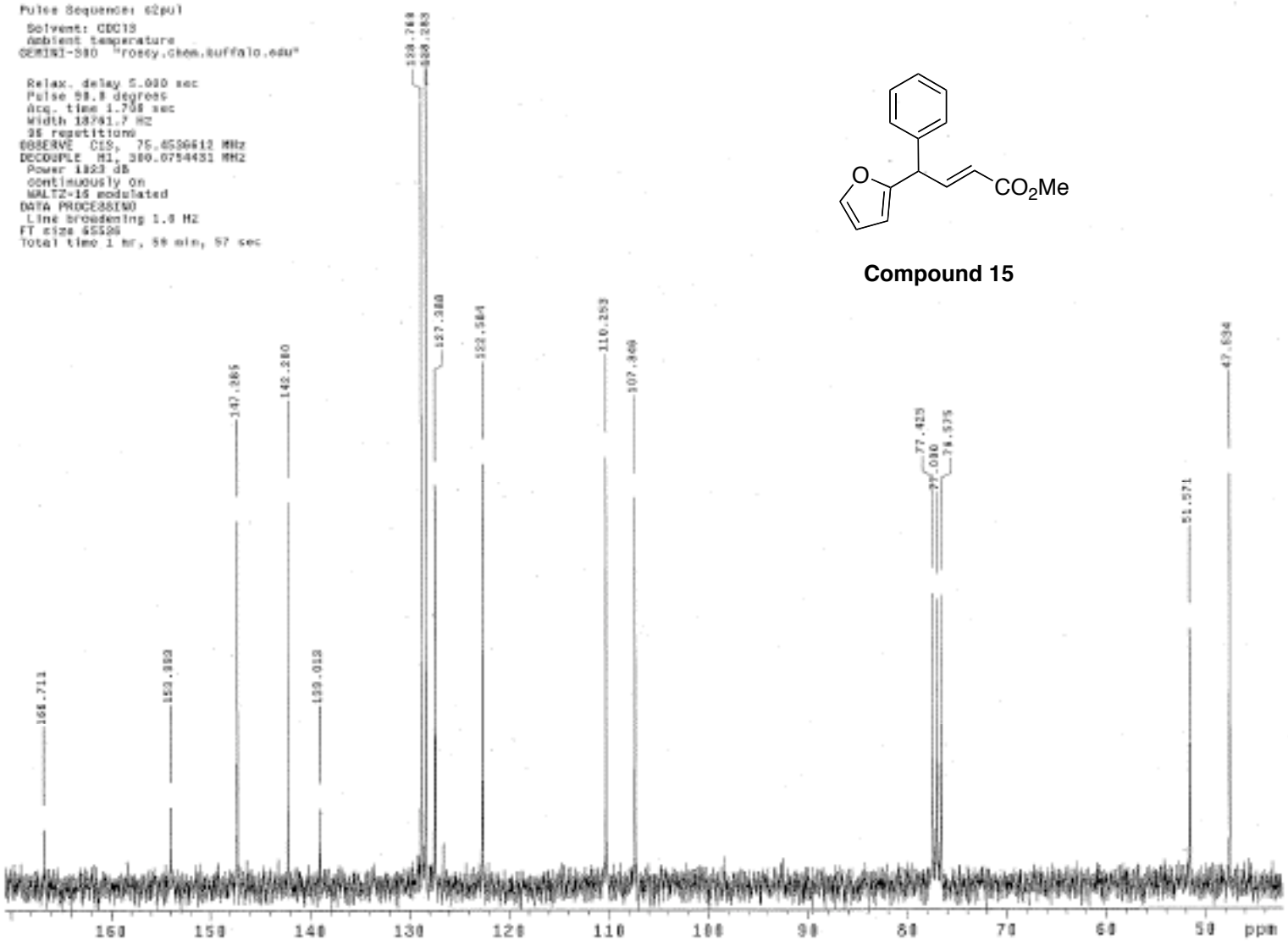
Compound *Z*-14

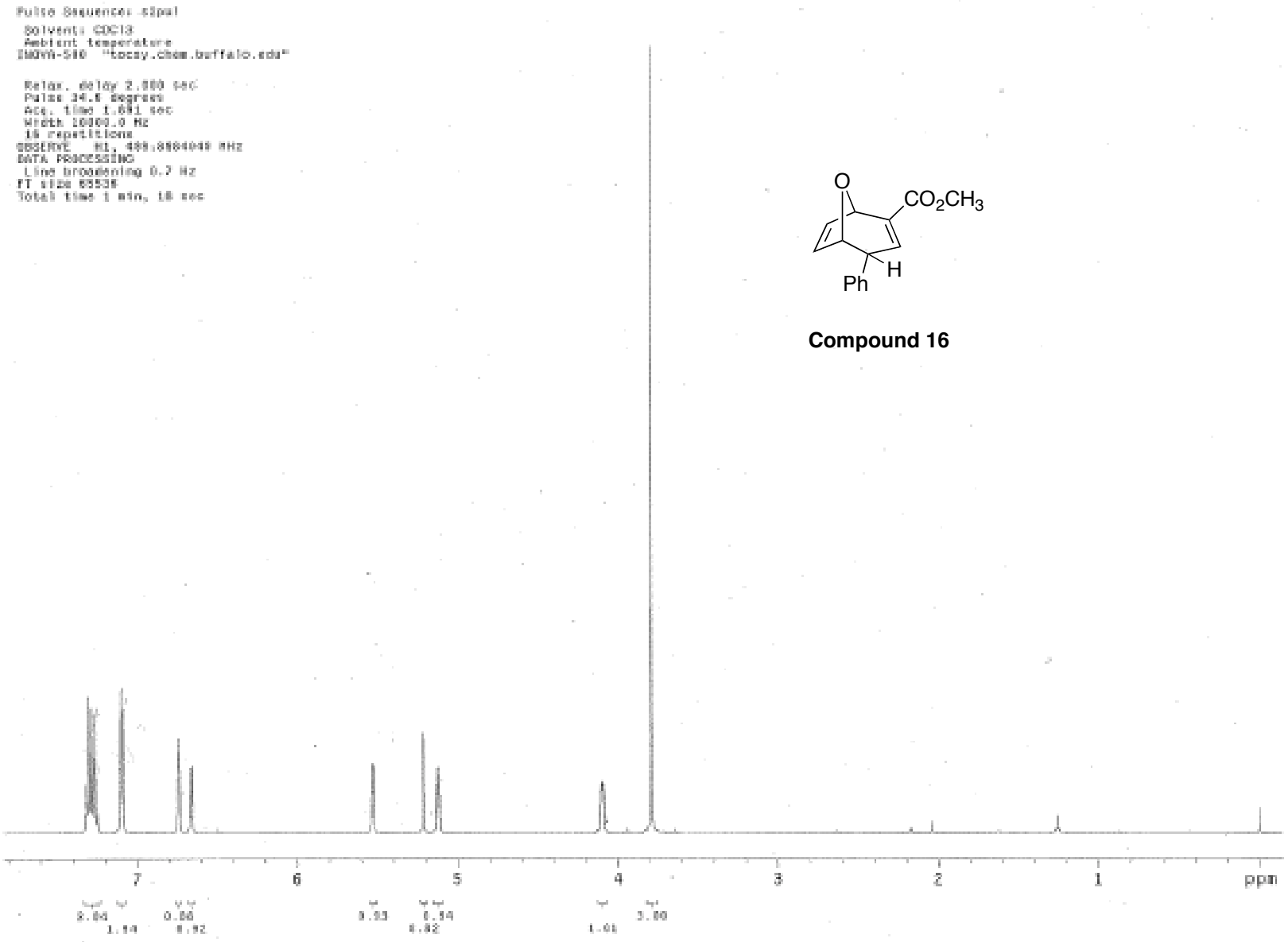


Compound *Z*-14

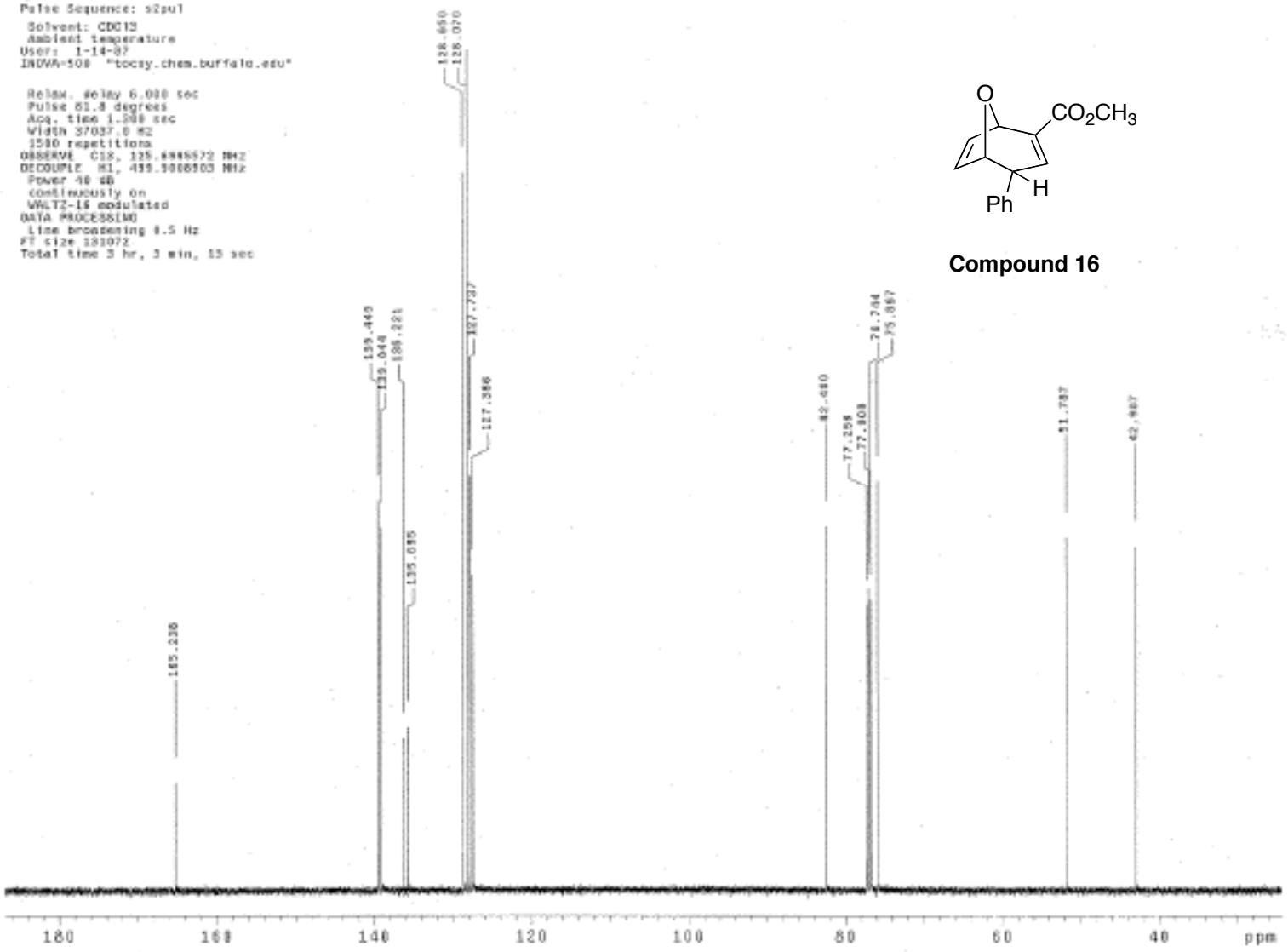

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "tocsy.chem.buffalo.edu"
Relax. delay 2.000 sec
Pulse 34.6 degrees
Acq. time 1.851 sec
Width 10000.8 Hz
16 repetitions
OBSERVE H1, 499.8986831 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 1 min, 18 sec
O
CO2Me
8
7
6
5
4
3
2
1
ppm

Compound 15


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "rossy.chem.buffalo.edu"
Relax. delay 5.000 sec
Pulse 58.8 degrees
Acq. time 1.708 sec
Width 18761.7 HZ
96 repetitions
OBSERVE C13, 75.4536612 MHz
DECOUPLE H1, 300.0754451 MHz
Power 1823 dB
continuously On
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 59 min, 57 sec
O
CO2Me
Compound 15
166.711
153.883
147.265
142.280
139.018
128.748
128.283
117.388
122.584
110.253
107.368
77.423
77.000
76.575
51.571
47.634
160
150
140
130
120
110
100
90
80
70
60
50
ppm


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "tocsy.chem.buffalo.edu"
Relax. delay 2.000 sec
Pulse 24.6 degrees
Acq. time 1.691 sec
Width 10000.0 Hz
16 repetitions
OBSERVE H1, 499.8884049 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 1 min, 18 sec
O
CO2CH3
H
Ph
7
6
5
4
3
2
1
ppm
2.04
1.14
0.86
0.92
3.33
1.14
0.82
1.01
3.00

Compound 16


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-07
INOVA-500 "tocsy.chem.buffalo.edu"
Relax. delay 6.000 sec
Pulse 61.8 degrees
Acq. time 1.200 sec
Width 37037.0 Hz
1580 repetitions
OBSERVE C13, 125.6886572 MHz
DECOUPLE H1, 499.9988503 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 3 hr, 3 min, 15 sec
128.650
128.070
127.737
127.386
139.449
139.044
136.221
135.035
185.230
83.680
77.256
77.000
76.744
75.987
51.757
42.487
180
160
140
120
100
80
60
40
ppm

O
CO2CH3
H
Ph

Compound 16

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