Supporting Information

Synthesis of γ,δ-Unsaturated Glycolic Acids via Sequenced Brook and Ireland-Claisen Rearrangements

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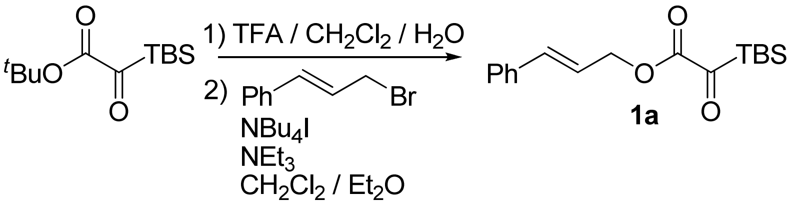
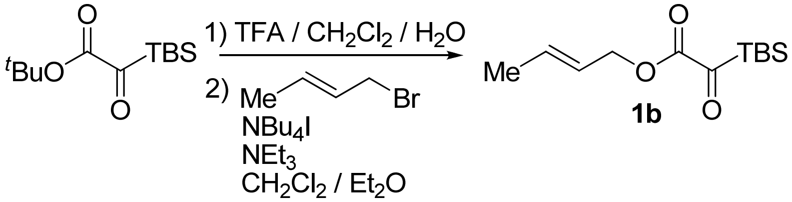
I. Materials and Methods: General. Infrared (IR) spectra were obtained using a Nicolet 560-E.S.P. infrared spectrometer. Proton and carbon nuclear magnetic resonance spectra (^{1}H and ^{13}C NMR) were recorded on either a Bruker model Avance 500 (^{1}H at 500 MHz and ^{13}C NMR at 125 MHz), Bruker model Avance 400 (^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz), or a Varian Gemini 300 (^{1}H NMR at 300 MHz and ^{13}C at 75 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; C_6D_6 at 7.15 ppm and ^{13}C NMR: $CDCl_3$ at 77.0 ppm and C_6D_6 at 128.62 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz), and integration. Analytical thin layer chromatography (TLC) was performed on Whatman 0.25 mm silica gel 60 plates. Visualization was accomplished with UV light and aqueous ceric ammonium molybdate solution followed by heating. Purification of the reaction products was carried out by flash chromatography using Sorbent Technologies silica gel 60 (32-63 µm). All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring. Yield refers to isolated yield of analytically pure material. Yields are reported for a specific experiment and as a result may differ slightly from those found in the tables, which are averages of at least two experiments. Diethyl ether, tetrahydrofuran, and toluene were dried by passage through a column of neutral alumina under nitrogen prior to use.[1] Unless otherwise noted, reagents were obtained from commercial sources and used without further purification. Triethylamine and diisopropylamine were freshly distilled from CaH_2 under Ar prior to use.

II. Synthesis of Silyl Glyoxylates

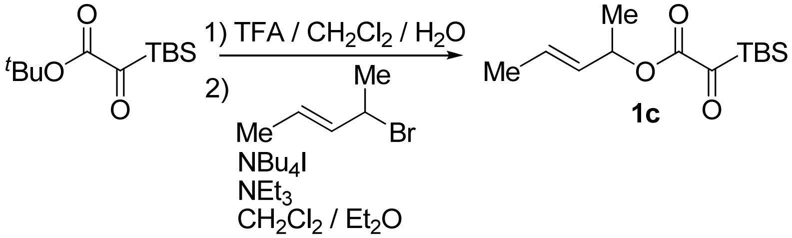
General esterification procedure A for formation of allylic silyl glyoxylates: To *t*-butyl *t*-butyldimethylsilyl glyoxylate,[2] (1.0 equiv) a solution of 20:10:1 CH_2Cl_2:TFA:H_2O (0.5 M) was added. After the yellow solution was stirred at room temperature for 1 h, the reaction mixture was concentrated *in vacuo*. The yellow oil was then dissolved in toluene and again concentrated *in vacuo*. The resulting yellow oil was added to a dry round bottom flask and the allylic bromide (1.3 equiv), and tetrabutylammonium iodide (0.1 equiv) were added. The mixture was dissolved in 1:1 Et_2O:CH_2Cl_2 (0.1 M) and NEt_3 (1.4 equiv) was added. The flask was fitted with a reflux condenser and the solution was heated to reflux for 10-16 h. The reaction was then allowed to cool to room temperature. The reaction was diluted with 30 mL saturated aqueous NH_4Cl solution. The layers were separated and the aqueous layer was extracted with Et_2O (2 X 30 mL) and then CH_2Cl_2 (2 X 30 mL). The organic extracts were combined, dried with $MgSO_4$, and concentrated *in vacuo*. The resulting yellow oil was purified as indicated.



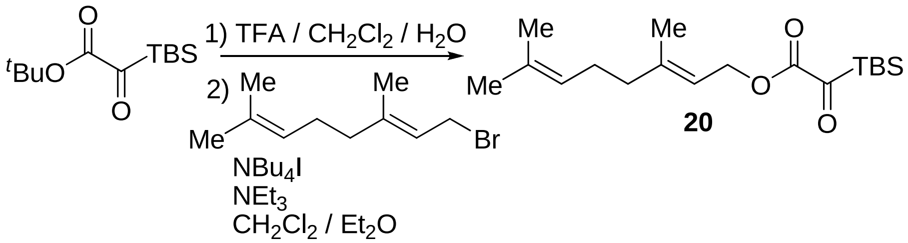
Cinnamyl *tert*-butyldimethylsilyl glyoxylate (1a). The general esterification procedure was performed using *t*-butyl *t*-butyldimethylsilyl glyoxylate (4.96 g, 20.3 mmol), cinnamyl bromide (5.20 g, 26.4 mmol), tetrabutylammonium iodide (750 mg, 2.03 mmol), and NEt_3 (3.95 mL, 28.4 mmol). Purification by flash chromatography (3:97 Et_2O:petroleum ether) furnished 3.07 g (50%) of **1a** as a yellow liquid: **IR** (thin film, cm^{-1}) 3029, 2930, 2860, 1718, 1654, 1558, 1541, 1254, 968; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41-7.28 (m, 5H), 6.73 (d, J = 15.6 Hz, 1H), 6.33 (dt, J = 15.9, 6.6 Hz, 1H), 4.89 (d, J = 6.6 Hz, 2H), 0.97 (s, 9H), 0.30 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 231.9, 162.8, 135.9, 135.7, 128.6, 128.3, 126.7, 121.8, 66.0, 26.4, 17.0, -6.9; **TLC** (5:95 EtOAc: petroleum ether) R_f 0.40. **LRMS** (ESI) exact mass calculated for $C_{17}H_{24}O_3SiNa$: 327.15. Found: 327.13.



Crotyl *tert*-butyldimethylsilyl glyoxylate (1b). The general esterification procedure was performed using *t*-butyl *t*-butyldimethylsilyl glyoxylate (780 mg, 3.19 mmol), *trans*-crotyl bromide[3] (559 mg, 4.14 mmol), tetrabutylammonium iodide (118 mg, 0.319 mmol), and NEt_3 (622 μL, 4.47 mmol). Purification by flash chromatography (3:97 Et_2O:petroleum ether) furnished 335 mg (43%) of **1b** as a yellow liquid: **IR** (thin film, cm^{-1}) 2953, 2931, 2886, 2860, 2360, 1719, 1656, 1465, 1254; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.90-5.84 (m, 1H), 5.67-5.59 (m, 1H), 4.64 (d, *J* = 6.8 Hz, 2H), 1.73 (d, *J* = 6.8 Hz, 3H), 0.96 (s, 9H), 0.27 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 133.0, 124.0, 66.1, 27.9, 26.4, 17.7, 16.9, -7.0; **TLC** (5:95 EtOAc: petroleum ether) R_f 0.52. **LRMS** (ESI) exact mass calculated for $C_{12}H_{22}O_3SiNa$: 265.13. Found: 265.12.



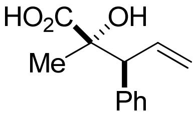
(*E*)-pent-3-en-2-yl-*tert*-butyldimethylsilyl glyoxylate (1c). The general esterification procedure was performed using *t*-butyl *t*-butyldimethylsilyl glyoxylate (1.09 g, 4.46 mmol), (*E*)-4-bromopent-2-ene (864 mg, 5.80 mmol), tetrabutylammonium iodide (165 mg, 0.446 mmol), and NEt_3 (870 μL, 6.24 mmol). Purification by flash chromatography (3:97 Et_2O:petroleum ether) furnished 337 mg (29%) of **1c** as a yellow liquid: **IR** (thin film, cm^{-1}) 2954, 2932, 2886, 2860, 1715, 1658, 1558, 1541, 1254; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.85-5.78 (m, 1H), 5.55-5.40 (m, 2H), 1.70 (d, *J* = 6.6, 3H), 1.38 (d, *J* = 6.3 Hz, 3H), 0.95 (s, 9H), 0.27 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 232.1, 162.6, 129.8, 73.2, 26.4, 20.2, 17.5, 16.9, -6.9; **TLC** (5:95 EtOAc: petroleum ether) R_f 0.54. **LRMS** (ESI) exact mass calculated for $C_{13}H_{24}O_3SiNa$: 279.15. Found: 279.13.



Geranyl *tert*-butyldimethylsilyl glyoxylate (20). The general esterification procedure was performed using *t*-butyl *t*-butyldimethylsilyl glyoxylate (1.21 g, 4.94 mmol), geranyl bromide (1.39 g, 6.42 mmol), tetrabutylammonium iodide (182 mg, 0.494 mmol), and NEt_3 (0.96 mL, 6.92 mmol). Purification by flash chromatography (2:98 Et_2O:petroleum ether) furnished 969 mg (60%) of **20** as a yellow liquid: **IR** (thin film, cm^{-1}) 2930, 2859, 1717, 1660, 1464, 1377, 1365, 1252, 990; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 5.41 (t, *J* = 6.9 Hz, 1H), 5.09-5.07 (m, 1H), 4.75 (d, *J* = 7.5 Hz, 2H), 2.10-2.03 (m, 4H), 1.73 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 0.96 (s, 9H), 0.27 (s, 6H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 231.9, 163.1, 143.9, 131.9, 123.6, 117.3, 62.2, 39.5, 28.0, 26.4, 26.3, 25.6, 17.6, 17.0, 16.5, -6.9; **TLC** (5:95 EtOAc: petroleum ether) R_f 0.53. **LRMS** (ESI) exact mass calculated for $C_{18}H_{32}O_3SiNa$: 347.21. Found: 347.20.

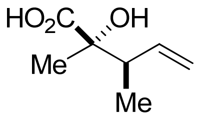
III. Synthesis of Glycolic Acid Derivatives

General procedure B for reaction of silyl glyoxylates with MeMgBr: A solution of MeMgBr (1.7 equiv) in Et_2O (3 M) was diluted with Et_2O to 0.18 M. The solution was cooled to 0 °C and a solution of silyl glyoxylate (1.0 equiv) in Et_2O (0.03 M) was added. The ice bath was removed and the reaction was stirred for 1 min. TMSOTf (2.0 equiv) was added and the reaction was stirred at room temperature for 2-8 h. The reaction was diluted with aqueous HCl (1 M, 5 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 X 10 mL). The organic extracts were combined, dried with $MgSO_4$, and concentrated *in vacuo*. The resulting colorless oil was purified as indicated.

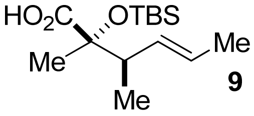


7

2-hydroxy-2-methyl-3-phenylpent-4-enoic acid (7). General procedure B was performed using cinnamyl *tert*-butyldimethylsilyl glyoxylate **1a** (80 mg, 0.263 mmol), MeMgBr (3 M in Et_2O, 0.15 mL, 0.447 mmol), and TMSOTf (95 μL, 0.526 mmol). The reaction was quenched after 2.5 h. Purification by flash chromatography (96:3:1 petroleum ether:Et_2O:HOAc) furnished 30 mg (55%) of **7** as a clear oil that matched analytical data previously reported.[4]

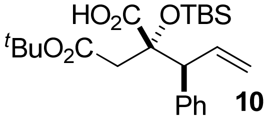

8

2-hydroxy-2,3-dimethylpent-4-enoic acid (8). General procedure B was performed using crotyl *t*-butyldimethylsilyl glyoxylate **1b** (80 mg, 0.33 mmol), MeMgBr (0.19 mL, 0.561 mmol), and TMSOTf (119 µL, 0.66 mmol). The reaction was quenched after 3 h. Purification by flash chromatography (96:3:1 petroleum ether:Et_2O:HOAc) furnished 25 mg (53%) of **8** as a clear oil that matched analytical data previously reported.[5]


9

(E)-2-(tert-butyldimethylsilyloxy)-2,3-dimethylhex-4-enoic acid (9). General procedure B was performed using (*E*)-pent-3-en-2-yl 2-*tert*-butyldimethylsilyl glyoxylate **1c** (70 mg, 0.273 mmol), MeMgBr (0.155 mL, 0.464 mmol), and TMSOTf (99 µL, 0.546 mmol). The reaction was quenched after 7.5 h. Purification by flash chromatography (96:3:1 petroleum ether:Et_2O:HOAc) furnished 48 mg (65%) of **9** as a white solid. Analytical data for **9**: mp 83 °C; **IR** (thin film, cm^{-1}) 2930, 2857, 1715, 1472, 1462, 1410, 1371, 1282, 1198; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.54-5.45 (m, 1H), 5.34-5.26 (m, 1H), 2.46-2.41 (m, 1H), 1.69 (d, J = 6.3 Hz, 3H), 1.44 (s, 3H), 0.99 (d, J = 6.6 Hz, 3H), 0.93 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 130.9, 127.7, 80.8, 46.2, 25.8, 24.2, 18.5, 18.0, 15.7, -2.5, -2.7; **TLC** (10:90 EtOAc: petroleum ether) R_f 0.25. **LRMS** (ESI) exact mass calculated for $C_{14}H_{28}O_3SiNa$: 295.18. Found: 295.17.

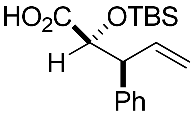
Proof of Stereochemistry: Product stereochemistry was determined by conversion to the known 2-hydroxy-2,3-dimethylhex-4-enoic acid. This was accomplished via TBAF deprotection. Spectral data of the minor diastereomer were identical to those reported in the literature (Wood, J. L.; Moniz, G. A.; Pflum, D. A.; Stoltz, B. M.; Holubec, A. A.; Dietrich, H. *J. Am. Chem. Soc.* **1999**, *121*, 1748-1749). Major diastereomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.63-5.55 (m, 1H), 5.42-5.36 (m, 1H), 2.52-2.47 (m, 1H), 1.72 (d, J = 6.4, 3 H), 1.42 (s, 3H), 1.02 (d, J = 6.8 Hz, 3H). Minor diastereomer: (400 MHz, $CDCl_3$) δ 5.63-5.55 (m, 1H), 5.42-5.36 (m, 1H), 2.52-2.47 (m, 1H), 1.67 (d, J = 6.4, 3 H), 1.42 (s, 3H), 1.08 (d, J = 6.8 Hz, 3H).



10

2-(2-*tert*-butoxy-2-oxoethyl)-2-(*tert*-butyldimethylsilyloxy)-3-phenylpent-4-enoic acid (10). To 56 mg LiCl in 2.2 mL THF at 0 °C was added diisopropylamine (55 μL, 0.395 mmol, 1.5 equiv) followed by ^{n}BuLi (1.5 M in hexanes, 0.245 mL, 0.368 mmol, 1.4 equiv). The solution was stirred for 10 min at 0 °C and then warmed to room temperature and stirred 15 min. The solution was then cooled to -78 °C and ^{t}BuOAc (46 μL, 0.342 mmol, 1.3 equiv) was added. The solution was stirred for 1 h at -78 °C. Cinnamyl silyl glyoxylate **1a** (80 mg, 0.263 mmol, 1.0 equiv) in 2.0 mL Et_2O was then added via syringe. The solution was slowly warmed to room temperature and stirred for 19 h. The reaction was diluted with 5 mL aqueous HCl (1 M). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 X 10 mL). The organic extracts were combined, dried with $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography (93:6:1 petroleum ether:Et_2O:HOAc) furnished 34 mg (31%) of **10** as a white solid. Analytical data for **10**: mp 92 °C; **IR** (thin film, cm^{-1}) 2929, 2855, 1735, 1558, 1541, 1473, 1393, 1368, 1152; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.26-7.20 (m, 5H), 6.36-6.24 (m, 1H), 5.27 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.19 (d, *J* = 17.1, 1H), 3.81 (d, *J* = 9.6 Hz, 1H), 2.92 (d, *J* = 16.8 Hz, 1H), 2.72 (d, *J* = 16.8 Hz, 1H), 1.46 (s, 9H), 0.93 (s, 1H), 0.12 (s, 3H), -0.06 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 138.9, 135.9, 129.4, 128.0, 127.2, 118.9, 82.5, 80.9, 57.5, 44.7, 28.1, 26.2, 19.0, -2.6, -2.9; **TLC** (10:90 EtOAc: petroleum ether) R_f 0.14. **LRMS** (ESI) exact mass calculated for $C_{23}H_{36}O_5SiNa$: 443.23. Found: 443.21.

Proof of Stereochemistry: Product stereochemistry was determined by conversion to the iodolactone **24** and subsequent NOESY analysis. Experimental details are provided below.

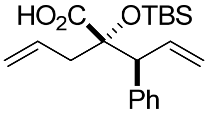


11

2-(*tert*-butyldimethylsilyloxy)-3-phenylpent-4-enoic acid (11). $ZnEt_2$ (1 M in hexanes, 0.39 mL, 0.394 mmol, 1.5 equiv) was diluted with 1.2 mL Et_2O. The solution was cooled to 0 °C and a solution of cinnamyl *tert*-butyldimethylsilyl glyoxylate **1a** (80 mg, 0.263 mmol, 1.0 equiv) in 2.8 mL Et_2O was added. The reaction was warmed to room temperature and allowed to stir for 4 h. The reaction was diluted with 5 mL aqueous HCl (1 M). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 X 10 mL). The organic extracts were combined, dried with $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography (96:3:1 petroleum ether:Et_2O:HOAc) furnished 56 mg (69%) of **11** as a white solid. Analytical data for **11**: mp 82 °C; **IR** (thin film, cm^{-1}) 3031, 2954, 2929, 2896, 2858, 2360, 1724, 1255, 1134; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.32-7.21 (m, 5H), 6.19-6.07 (m, 1H), 5.19 (d, *J* = 3.3 Hz, 1H), 5.14 (s, 1H), 4.44 (d, *J* = 5.7 Hz, 1H), 3.71 (dd, *J* = 8.7, 6.0 Hz, 1H), 0.86 (s, 9H), 0.00 (s, 3H), -0.05 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.0, 139.0, 136.9, 128.9, 128.3, 127.1, 117.5, 76.6, 54.6, 25.6, 18.0, -5.4; **TLC** (10:90 EtOAc: petroleum ether) R_f 0.20. **LRMS** (ESI) exact mass calculated for $C_{17}H_{26}O_3SiNa$: 329.17. Found: 329.15.

Proof of Stereochemistry: Product stereochemistry was determined by conversion to the known 2-hydroxy-3-phenylpent-4-enoic acid. This was accomplished via TBAF deprotection. Spectral data were identical to that reported in the literature (Kaur, P.; Singh, P.; Kumar, S. *Tetrahedron* **2005**, *61*, 8231-8240). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 5H), 6.27-6.18 (m, 1H), 5.27-5.23 (m, 2H), 4.59 (m, 1H), 3.87-3.86 (m, 1H).

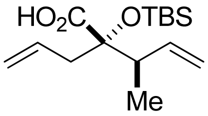
General procedure C for reaction of silyl glyoxylates with allylzinc bromide and methallylzinc bromide: A solution of allylzinc bromide[6] (1.5 equiv) or methallylzinc bromide[7] (1.5 equiv) in THF (0.33 M) was diluted with Et_2O to 0.16 M. The solution was cooled to -78 °C and a solution of silyl glyoxylate (1.0 equiv) in Et_2O (0.10 M) was added. The reaction was allowed to slowly warm to room temperature over 1 h and then stir for 30 min to 3 h at room temperature. The reaction was diluted with 5 mL aqueous HCl (1 M). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 X 10 mL). The organic extracts were combined, dried with $MgSO_4$, and concentrated *in vacuo*. The resulting colorless oil was purified as indicated.



12

2-allyl-2-(*tert*-butyldimethylsilyloxy)-3-phenylpent-4-enoic acid (12). General procedure C was performed using cinnamyl *tert*-butyldimethylsilyl glyoxylate **1a** (40 mg, 0.131 mmol) and allylZnBr (0.33 M, 0.60 mL, 0.197 mmol). The reaction was quenched after 2 h. Purification by flash chromatography (96:3:1 petroleum ether:Et_2O:HOAc) furnished 31 mg (68%) of **12** as a clear oil. Analytical data for **12** (mix of diastereomers): **IR** (thin film, cm^{-1}) 3079, 3031, 2955, 2928, 2895, 1723, 1254, 1158; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.21 (m, 5H), 6.32-6.21 (m, 1H), 5.87-5.74 (m, 1H), 5.25-4.98 (m, 4H), 3.72-3.66 (m, 1H), 2.63-2.24 (m, 3H), 0.96 (s, 9H), 0.11 (s, 3H), -0.10 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.5, 139.9, 137.3, 136.1, 132.8, 129.8, 129.4, 128.0, 126.9, 119.1, 118.4, 83.3, 57.3, 44.1, 26.3, 19.2, -1.7, -2.7; **TLC** (10:90 EtOAc:petroleum ether) R_f 0.20. **LRMS** (ESI) exact mass calculated for $C_{20}H_{30}O_3SiNa$: 369.20. Found: 369.17.

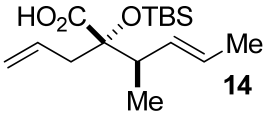
Proof of Stereochemistry: Reaction proceeded with low diastereoselectivity.



13

2-allyl-2-(*tert*-butyldimethylsilyloxy)-3-methylpent-4-enoic acid (13). General procedure C was performed using crotyl *tert*-butyldimethylsilyl glyoxylate **1b** (80 mg, 0.33 mmol) and allylZnBr (0.33 M, 1.52 mL, 0.50 mmol). the reaction was quenched after 1.5 h. Purification by flash chromatography (96:3:1 petroleum ether:Et_2O:HOAc) furnished 54 mg (58%) of **13** as a clear oil. Analytical data for **13**: **IR** (thin film, cm^{-1}) 3079, 2956, 2929, 2857, 1719, 1644, 1558, 1254, 1170; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.84-5.73 (m, 2H), 5.13-5.07 (m, 4H), 2.63-2.60 (m, 1H), 2.48 (d, *J* = 7.2 Hz, 1H), 1.01 (d, *J* = 6.8 Hz, 1H), 0.91 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.0, 138.5, 132.9, 118.8, 116.8, 83.5, 46.2, 43.5, 26.2, 19.1, 16.0, -2.0, -2.5; **TLC** (10:90 EtOAc: petroleum ether) R_f 0.28. **LRMS** (ESI) exact mass calculated for $C_{15}H_{28}O_3SiNa$: 307.18. Found: 307.17.

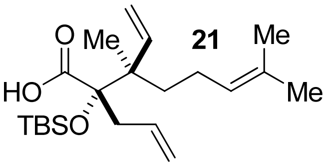
Proof of Stereochemistry: Product stereochemistry was determined by ring closing metathesis and NOESY analysis of the resulting cyclopentene **25**. Experimental details are provided below.



14

2-allyl-2-(*tert*-butyldimethylsilyloxy)-3-methylhex-4-enoic acid (14). General procedure C was performed using (*E*)-pent-3-en-2-yl 2-*tert*-butyldimethylsilyl glyoxylate **1c** (80 mg, 0.312 mmol) and allylZnBr (0.33 M, 1.42 mL, 0.468 mmol). Reaction was quenched after 4 h. Purification by flash chromatography (94:5:1 petroleum ether:Et_2O:HOAc) furnished 61 mg (67%) of **14** as a clear oil. Analytical data for **14**: **IR** (thin film, cm^{-1}) 3080, 2956, 2929, 2857, 1642, 1416, 1377, 1277, 1106; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.82-5.72 (m, 1H), 5.54-5.39 (m, 2H), 5.13-5.07 (m, 2H), 2.59-2.55 (m, 1H), 2.49-2.45 (m, 2H), 1.70 (d, *J* = 6 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.92 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.5, 133.0, 131.0, 127.4, 118.6, 83.8, 45.7, 43.5, 26.2, 19.1, 18.1, 16.4, -2.0, -2.5; **TLC** (10:90 EtOAc: petroleum ether) R_f 0.26. **LRMS** (ESI) exact mass calculated for $C_{16}H_{30}O_3SiNa$: 321.20. Found: 321.18.

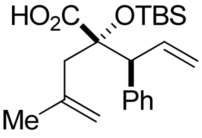
Proof of Stereochemistry: Product stereochemistry was determined by ring closing metathesis, which provided cyclopentene **25.** Experimental details are provided below.



21

2-allyl-2-(*tert*-butyldimethylsilyloxy)-3,7-dimethyl-3-vinyloct-6-enoic acid (21). General procedure C was performed using geranyl *tert*-butyldimethylsilyl glyoxylate 20 (80 mg, 0.247 mmol) and allylZnBr (0.33 M, 1.12 mL, 0.370 mmol). The reaction was quenched after 2.5 h. Purification by flash chromatography (96:3:1 petroleum ether:Et_2O:HOAc) furnished 59 mg (65%) of **21** as a clear oil. Analytical data for **21**: **IR** (thin film, cm^{-1}) 3081, 2956, 2928, 2856, 1714, 1640, 1471, 1415, 1155; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.90 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.77-5.70 (m, 1H), 5.22-5.01 (m, 5H), 2.71 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.43 (dd, *J* = 14.0, 7.2 Hz, 1H), 1.80-1.75 (m, 2H), 1.71-1.61 (m, 1H) 1.67 (s, 3H), 1.56 (s, 3H), 1.40-1.36 (m, 1H), 1.19 (s, 3H), 0.91 (s, 9H), 0.20 (s, 3H), 0.09 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.0, 141.8, 133.9, 133.8, 131.4, 124.6, 119.2, 115.3, 86.9, 48.2, 39.4, 34.7, 26.4, 25.7, 22.9, 19.4, 17.6, 17.1, -1.85, -2.06; **TLC** (10:90 EtOAc: petroleum ether) R_f 0.32. **LRMS** (ESI) exact mass calculated for $C_{21}H_{38}O_3SiNa$: 389.26. Found: 389.24.

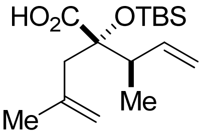
Proof of Stereochemistry: Product stereochemistry was determined by ring closing metathesis followed by $LiAlH_4$ reduction and NOESY analysis of the resulting cyclopentene **27**. See below for experimental details.



17

2-(tert-butyldimethylsilyloxy)-4-methyl-2-(1-phenylallyl)pent-4-enoic acid (17). General procedure C was performed using cinnamyl *tert*-butyldimethylsilyl glyoxylate (80 mg, 0.263 mmol) and methallylZnBr (0.33 M, 1.19 mL, 0.394 mmol). The reaction was quenched after 2 h. Purification by flash chromatography (96:3:1 petroleum ether:Et_2O:HOAc) furnished 70 mg (74%) of **17** as a clear oil. Analytical data for **17** (1:1 mix of diastereomers): **IR** (thin film, cm^{-1}) 3077, 3031, 2957, 2928, 2856, 1721, 1646, 1472, 1151; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.21 (m, 5H), 6.39-6.33 (m, 1H), 6.27-6.18 (m, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 5.17 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 4.0 Hz, 1H), 5.06 (d, *J* = 10.8 Hz, 1H), 4.88 (d, *J* = 14.8 Hz, 2H), 4.76 (d, *J* = 49.6 Hz, 2H), 3.76 (d, *J* = 9.6 Hz, 1H), 3.71 (d, *J* = 9.2 Hz, 1H), 2.69 (d, *J* = 13.6 Hz, 1H) , 2.59 (d, *J* = 13.6 Hz, 1H), 2.56 (d, *J* = 13.6 Hz, 1H), 2.21 (d, *J* = 13.6 Hz, 1H), 1.72 (s, 3H), 1.67 (s, 3H), 0.97 (s, 9H), 0.92 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H), 0.05 (s, 3H), -0.19 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.1, 140.0, 139.9, 137.8, 136.6, 129.8, 129.4, 128.2, 127.9, 127.0, 126.9, 118.7, 117.3, 116.8, 116.5, 83.8, 83.1, 60.1, 58.2, 48.0, 47.4, 27.0, 26.8, 26.7, 23.6, 23.5, 19.5, -1.7, -1.8, -2.1, -2.5; TLC (10:90 EtOAc: petroleum ether) R_f 0.21. **LRMS** (ESI) exact mass calculated for $C_{21}H_{32}O_3SiNa$: 383.21. Found: 383.20.

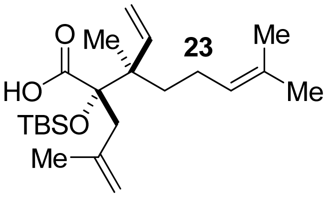
Proof of Stereochemistry: Product was obtained as a 1:1 mixture of diastereomers.



18

2-(2-methyl-2-propen-1-yl)-2-(*tert*-butyldimethylsilyloxy)-4-methylpent-4-enoic acid (18). General procedure C was performed using crotyl tert-butyldimethylsilyl glyoxylate **1b** (40 mg, 0.165 mmol) and methallylZnBr (0.33 M, 0.75 mL, 0.248 mmol). The reaction was quenched after 13 h. Purification by flash chromatography (96:3:1 petroleum ether:Et_2O:HOAc) furnished 30 mg (61%) of **18** as a clear oil. Analytical data for **18**: **IR** (thin film, cm^{-1}) 3078, 2957, 2929, 2856, 2360, 1719, 1646, 1472, 1161; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.90-5.81 (m, 1H), 5.14-5.07 (m, 2H), 4.84 (s, 1H), 4.77 (s, 1H), 2.65-2.61 (m, 1H), 2.55 (d, *J* = 14.0 Hz, 1H), 2.46 (d, *J* = 14.0, 1H), 1.71 (s, 3H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 9H), 0.18 (s, 3H), 0.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.1, 140.4, 138.7, 117.1, 115.7, 83.3, 47.2, 46.8, 26.4, 23.6, 19.3, 16.3, -2.0, -2.1; **TLC** (10:90 EtOAc: petroleum ether) R_f 0.28. **LRMS** (ESI) exact mass calculated for $C_{16}H_{30}O_3SiNa$: 321.20. Found: 321.18.

Proof of Stereochemistry: Product stereochemistry was assigned by analogy to allylzinc example with crotyl silyl glyoxylate.

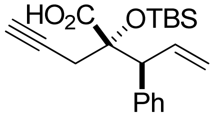


23

2-(*tert*-butyldimethylsilyloxy)-3,7-dimethyl-2-(2-methylallyl)-3-vinyloct-6-enoic acid (23). General procedure C was performed using geranyl *tert*-butyldimethylsilyl glyoxylate **20** (80 mg, 0.247 mmol) and methallylZnBr (0.33 M, 1.12 mL, 0.370 mmol). The reaction was quenced after 2 h. Purification by flash chromatography (96:3:1 petroleum ether:Et_2O:HOAc) furnished 52 mg (55%) of **23** as a clear oil. Analytical data for **23**: **IR** (thin film, cm^{-1}) 2960, 2928, 2856, 1712, 1647, 1471, 1414, 1377, 1145; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.94 (dd, *J* = 17.7, 11.1 Jz, 1H), 5.24 (d, *J* = 11.1 Hz, 1H), 5.08-5.03 (m, 2H), 4.85 (s, 1H), 4.77 (s, 1H), 2.74 (d, *J* = 13.5 Hz, 1H), 2.47 (d, *J* = 13.8 Hz, 1H), 1.79-1.72 (m, 2H), 1.67 (s, 6H), 1.56 (s, 3H), 1.36-1.30 (m, 2H), 1.14 (s, 3H), 0.91 (s, 9H), 0.20 (s, 3H), 0.09 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.0, 142.0, 140.4, 131.3, 124.6, 116.9, 115.5, 86.1, 49.0, 43.0, 34.7, 26.9, 25.6, 23.7, 23.1, 19.9, 17.6, 17.1, -1.4, -1.9; **TLC** (10:90 EtOAc: petroleum ether) R_f 0.32. **LRMS** (ESI) exact mass calculated for $C_{22}H_{40}O_3SiNa$: 403.27. Found: 403.25.

Proof of Stereochemistry: Product stereochemistry was assigned by analogy to allylzinc example with geranyl silyl glyoxylate.

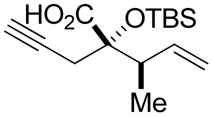
General Procedure D for reaction of silyl glyoxylates with allenylzinc bromide: A solution of allenylzinc bromide[8] (1.5 equiv) in THF (0.33 M) was diluted with Et_2O to 0.10 M. The solution was cooled to -78 °C and a solution of silyl glyoxylate (1.0 equiv) in Et_2O (0.10 M) was added. The reaction was allowed to slowly warm to room temperature over 1 h and then stir for 30 min to 2 h at room temperature. The reaction was diluted with 5 mL aqueous HCl (1 M). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 X 10 mL). The organic extracts were combined, dried with $MgSO_4$, and concentrated *in vacuo*. The resulting colorless oil was purified as indicated.



15

2-(*tert*-butyldimethylsilyloxy)-3-phenyl-2-(prop-2-ynyl)pent-4-enoic acid (15). General procedure D was performed using cinnamyl *tert*-butyldimethylsilyl glyoxylate **1a** (80 mg, 0.263 mmol) and allenylZnBr (0.33 M, 2.39 mL, 0.525 mmol). The reaction was quenched after 1.5 h. Purification by flash chromatography (96:3:1 petroleum ether:Et_2O:HOAc) furnished 53 mg (58%) of **15** as a clear oil. Analytical data for **15**: **IR** (thin film, cm^{-1}) 3310, 3063, 3032, 2954, 2929, 2895, 2856, 1725, 1158; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.21 (m, 5H), 6.31-6.22 (m, 1H), 5.26 (d, J = 1.6 Hz), 5.23 (d, *J* = 8.8 Hz, 1H), 3.84 (d, *J* = 9.6 Hz, 1H), 2.79 (d, *J* = 17.2 Hz, 1H), 2.65 (d, *J* = 16.8 Hz, 1H), 2.10 (t, *J* = 2.8 Hz, 1H), 0.96 (s, 9H), 0.19 (s, 3H), 0.04 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.9, 139.0, 136.5, 135.5, 129.7, 129.2, 128.1, 127.3, 127.2, 118.9, 117.8, 82.4, 79.8, 72.2, 57.6, 29.7, 26.2, 19.0, -2.1, -3.0; **TLC** (10:90 EtOAc: petroleum ether) R_f 0.20. **LRMS** (ESI) exact mass calculated for $C_{20}H_{28}O_3SiNa$: 367.18. Found: 367.16.

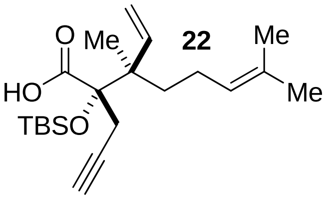
Proof of Stereochemistry: Product was formed with low diastereoselectivity.



16

2-(tert-butyldimethylsilyloxy)-3-methyl-2-(prop-2-ynyl)pent-4-enoic acid (16). General procedure D was performed using crotyl *tert*-butyldimethylsilyl glyoxylate **1b** (80 mg, 0.330 mmol) and allenylZnBr (0.33 M, 3.0 mL, 0.66 mmol). The reaction was quenched after 3.5 h. Purification by flash chromatography (96:3:1 petroleum ether:Et_2O:HOAc) furnished 31 mg (33%) of **16** as a clear oil. Analytical data for **16**: **IR** (thin film, cm^{-1}) 3313, 2955, 2929, 2857, 1725, 1471, 1420, 1254, 1168; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.81-5.72 (m, 1H), 5.14 (d, *J* = 14.0 Hz, 2H), 2.71-2.59 (m, 3H), 2.06 (s, 1H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.93 (s, 9H), 0.24 (s, 3H), 0.22 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.9, 137.6, 117.6, 82.7, 79.8, 72.1, 46.4, 29.1, 26.1, 18.9, 15.7, -2.2, -2.7; **TLC** (10:90 EtOAc: petroleum ether) R_f 0.18. **LRMS** (ESI) exact mass calculated for $C_{15}H_{26}O_3SiNa$: 305.17. Found: 305.12.

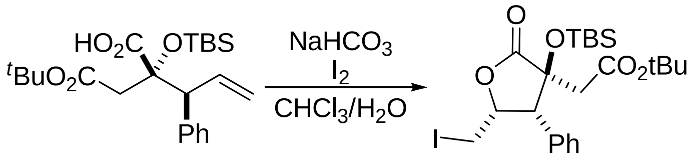
Proof of Stereochemistry: Product stereochemistry was determined by Lindlar reduction to afford 2-allyl-2-(tert-butyldimethylsilyloxy)-3-methylpent-4-enoic acid **13** characterized above.



2-(*tert*-butyldimethylsilyloxy)-3,7-dimethyl-2-(prop-2-ynyl)-3-vinyloct-6-enoic acid (22). General procedure D was performed using geranyl *tert*-butyldimethylsilyl glyoxylate **20** (80 mg, 0.247 mmol) and allenylZnBr (0.30 M, 1.64 mL, 0.493 mmol). The reaction was quenched after 2 h. Purification by flash chromatography (96:3:1 petroleum ether:Et_2O:HOAc) furnished 24 mg (27%) of **22** as a clear oil. Analytical data for **22**: **IR** (thin film, cm^{-1}) 3312, 2956, 2928, 2856, 1717, 1471, 1415, 1378, 1150; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.85 (dd, J = 17.6, 10.8 Hz, 1H), 5.23 (d, *J* = 11.2 Hz, 1H), 5.06-5.02 (m, 2H), 2.94 (dd, *J* = 16.8, 2.4 Hz, 1H), 2.46 (dd, *J* = 16.8, 2.4 Hz, 1H), 2.00-1.98 (m, 1H), 1.78-1.70 (m, 2H), 1.66 (s, 3H), 1.55 (s, 3H), 1.39-1.31 (m, 1H), 1.10 (s, 3H), 0.94 (s, 9H), 0.28 (s, 3H), 0.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.4, 140.8, 131.5, 124.4, 116.0, 86.2, 81.2, 72.1, 48.1, 34.5, 26.3, 25.7, 19.2, 17.6, 17.1, -2.3, -2.4; **TLC** (10:90 EtOAc: petroleum ether) R_f 0.24. **LRMS** (ESI) exact mass calculated for $C_{21}H_{36}O_3SiNa$: 387.24. Found: 387.22.

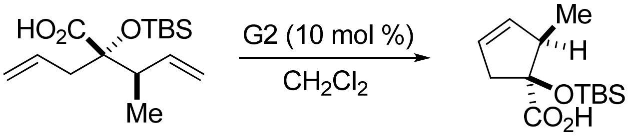
Proof of Stereochemistry: Product stereochemistry was determined by Lindlar reduction to afford 2-allyl-2-(tert-butyldimethylsilyloxy)-3,7-dimethyl-3-vinyloct-6-enoic acid **21** characterized above.

IV. Experimental Details for Cyclizations:



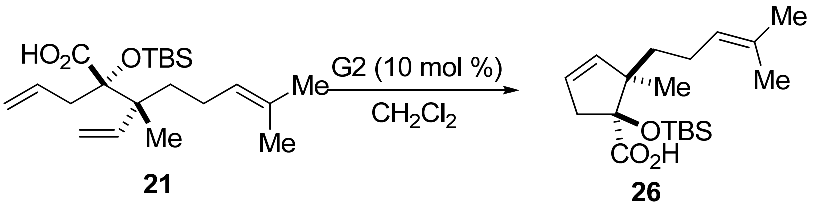
10 **24**

***tert*-Butyl-3-(tert-butyldimethylsilyloxy)-5-(iodomethyl)-2-oxo-4-phenyltetrahydrofuran-3-yl)acetate (24).** To acid **10** (12 mg, 0.0285 mmol, 1.0 equiv) in 2.0 mL $CHCl_3$ was added $NaHCO_3$ (20 mg, 0.239 mmol, 8.4 equiv) in 2.0 mL H_2O. The reaction was cooled to 0 °C and iodine (62 mg, 0.245 mmol, 8.6 equiv) was added. The reaction was allowed to warm to room temperature and stirred 24 h. The reaction was diluted with 5 mL CH_2Cl_2 and the layers were separated. The organic phase was washed with 3 mL 10% $Na_2S_2O_3$ (aq), then 3 mL H_2O, then 3 mL brine. The organic phase was dried with $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (90:10 petroleum ether:EtOAc) furnished 12 mg (77%) of **24**. Analytical data for **24**: **IR** (thin film, cm^{-1}) 2953, 2930, 2857, 1786, 1737, 1558, 1495, 1257, 1153; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.27 (m, 3H), 7.14-7.12 (m, 2H), 5.25-5.20 (m, 1H), 4.15 (d, *J* = 4.8 Hz, 1H), 3.30 (dd, *J* = 10.0, 6.0 Hz, 1H), 2.83-2.79 (m, 2H), 2.19 (d, *J* = 17.6 Hz, 1H), 1.33 (s, 9H), 0.92 (s, 9H), 0.20 (s, 3H), 0.14 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.4, 167.4, 133.0, 128.6, 128.0, 82.1, 80.9, 80.2, 57.6, 38.1, 28.0, 25.5, 18.3, 0.9, -3.3, -4.9; TLC (5:95 EtOAc: petroleum ether) R_f 0.30. **LRMS** (ESI) exact mass calculated for $C_{23}H_{35}IO_5SiNa$: 569.13. Found: 569.11.

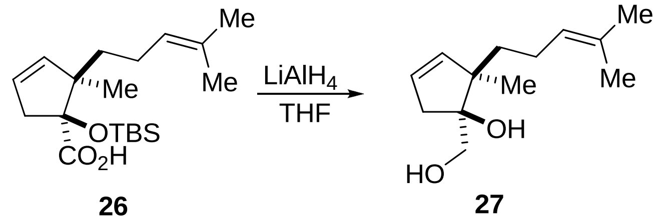


13 **25**

1-(*tert*-butyldimethylsilyloxy)-2-methylcyclopent-3-enecarboxylic acid (25). To diene **13** (12 mg, 0.0421 mmol, 1.0 equiv) in 1.9 mL CH_2Cl_2 was added Grubbs 2^{nd} generation catalyst (3.6 mg, 0.00421 mmol, 0.10 equiv) in 0.90 mL CH_2Cl_2. The reaction was diluted with 2.8 mL CH_2Cl_2 and stirred at room temperature for 50 h. Approximately 200 mg silica was added and the reaction was stirred for 15 min. The slurry was filtered through a silica plug and concentrated *in vacuo* to afford 5 mg (46%) cyclopentene **25**. Analytical data for **25**: **IR** (thin film, cm^{-1}) 2930, 2858, 2349, 1708, 1472, 1256, 1201, 837; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.70-5.69 (m, 1H), 5.56-5.54 (m, 1H), 3.02-2.97 (m, 2H), 2.54 (d, *J* = 18.0 Hz, 1H), 1.05 (d, *J* = 7.5 Hz, 3H), 0.93 (s, 9H), 0.31 (s, 3H), 0.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.5, 133.9, 126.6, 81.9, 49.1, 46.1, 25.4, 17.7, 15.3, 12.6, -4.9, -5.0; **TLC** (10:90 EtOAc: petroleum ether) R_f 0.27. **LRMS** (ESI) exact mass calculated for $C_{13}H_{24}O_3SiNa$: 279.15. Found: 279.13.



1-(*tert*-butyldimethylsilyloxy)-2-methyl-2-(4-methylpent-3-enyl)cyclopent-3-enecarboxylic acid (26). To triene **21** (24 mg, 0.0654 mmol, 1.0 equiv) in 2.9 mL CH_2Cl_2 was added Grubbs 2nd generation catalyst (5.6 mg, 0.00654 mmol, 0.10 equiv) in 1.4 mL CH_2Cl_2. The reaction was diluted with 4.3 mL CH_2Cl_2 and stirred at room temperature for 15 h. Approximately 300 mg silica was added and the reaction was stirred for 15 min. The slurry was filtered through a silica plug (CH_2Cl_2) and concentrated *in vacuo*. Purification by flash chromatography (94:5:1 petroleum ether: Et_2O: HOAc) afforded 13 mg (59%) cyclopentene **26**. Analytical data for **26**: **IR** (thin film, cm^{-1}) 2926, 2349, 1700, 1684, 1653, 1558, 1541, 1507, 1457; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.65-5.58 (m, 2H), 5.11-5.06 (m, 1H), 3.22 (d, *J* = 17.4 Hz, 1H), 2.54 (dd, *J* = 16.8, 6.3 Hz, 1H), 2.04-1.95 (m, 2H), 1.68 (s, 3H), 1.63 (s, 3H), 1.54-1.44 (m, 2H), 1.00 (s, 3H), 0.91 (s, 9H), 0.14 (s, 3H), 0.10 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 137.4, 125.2, 124.9, 100.1, 55.5, 42.7, 35.1, 29.7, 25.9, 25.6, 23.7, 22.7, 21.1, 18.5, 17.7, -3.1, -3.6; **TLC** (10:90 EtOAc: petroleum ether) R_f 0.21. **LRMS** (ESI) exact mass calculated for $C_{19}H_{34}O_3SiCs$: 471.13. Found: 471.27.



1-(hydroxymethyl)-2-methyl-2-(4-methylpent-3-enyl)cyclopent-3-enol (27). To acid **26** (10 mg, 0.0295 mmol, 1.0 equiv) in 0.5 mL THF at 0 °C was added $LiAlH_4$ (44 μL, 0.044 mmol, 1.5 equiv, 1 M in THF). The reaction was allowed to warm to room temperature and stirred 19 h. The reaction was quenched with 1 mL 3 M NaOH (aq). The aqueous layer was extracted with CH_2Cl_2 (3 X 3 mL). The organic extracts were combined, dried with $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography (49:50:1 petroleum ether:Et_2O:HOAc) furnished 5 mg (52%) of **27**. Analytical data for **27**: **IR** (thin film, cm^{-1}) 2958, 2922, 1771, 1732, 1635, 1558, 1489, 1376, 1078; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.69-5.64 (m, 2H), 5.15-5.11 (m, 1H), 3.79-3.75 (m, 1H), 3.66-3.60 (m, 1H), 2.62 (d, *J* = 16.8 Hz, 1H), 2.35 (d, *J* = 16.8 Hz, 1H), 2.10-1.95 (m, 2H), 1.68 (s, 3H), 1.64 (s, 3H), 1.51-1.46 (m, 2H), 0.93 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.2, 131.3, 125.7, 125.1, 84.0, 66.3, 52.1, 43.5, 35.0, 25.6, 23.9, 20.0, 17.6; **TLC** (30:70 EtOAc: petroleum ether) R_f 0.15. **LRMS** (ESI) exact mass calculated for $C_{13}H_{22}O_2Na$: 233.26. Found: 233.12.

V. Literature Cited

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(2) Nicewicz, D. A.; Breteche, G.; Johnson, J. S. *Org. Synth.* **2008**, *85*, 278-286.

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(4) Kaur, P.; Singh, P.; Kumar, S. *Tetrahedron,* **2005**, *61*, 8231-8240.

(5) Bartlett, P. A.; Tanzella, D. J.; Barstow, J. F. *J. Org. Chem.* **1982**, *47*, 3941-3945.

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(7) Methallylzinc bromide was prepared from methallyl bromide using the same procedure as for allylzinc bromide.

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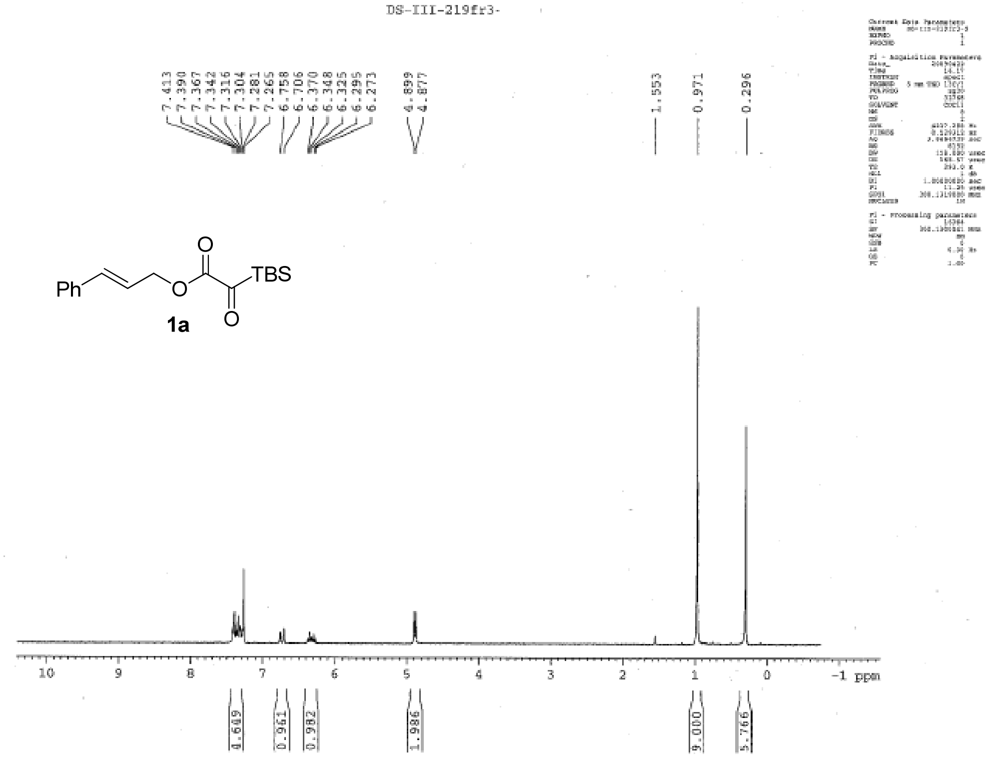
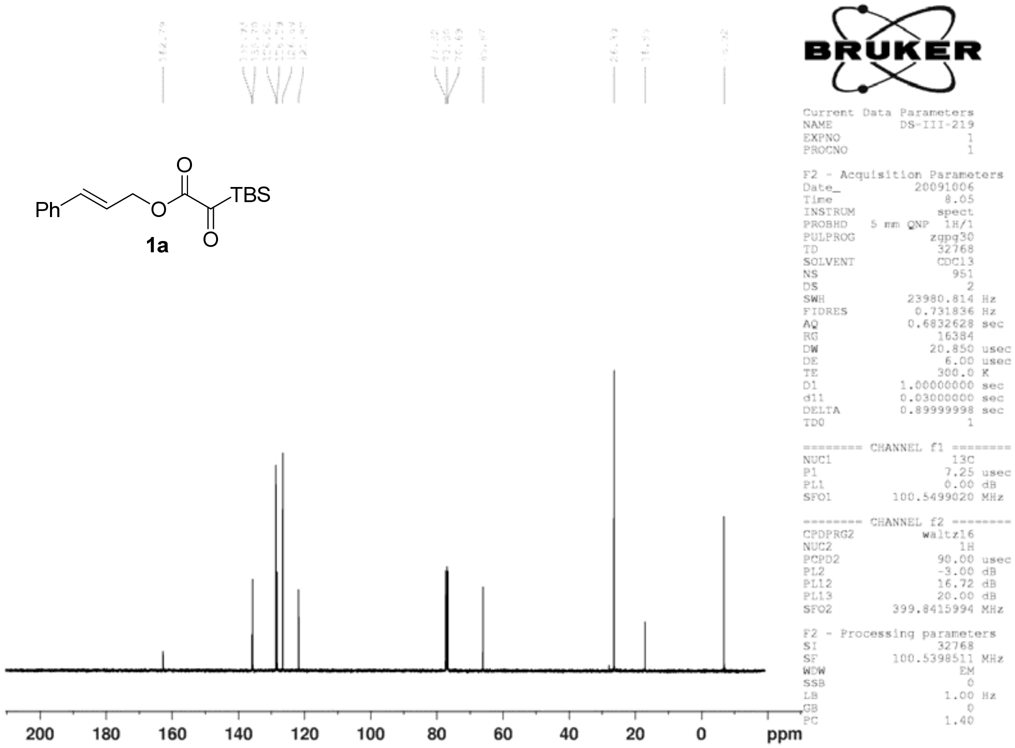
VI. NMR Spectra





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PROCNO                 1

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PULPROG          zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   951
DS                     2
SWH            23980.814 Hz
FIDRES          0.731836 Hz
AQ             0.6832628 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec
d11           0.03000000 sec
DELTA         0.89999998 sec
TD0                    1

======== CHANNEL f1 ========
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P1                  7.25 usec
PL1                 0.00 dB
SFO1         100.5499020 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               16.72 dB
PL13               20.00 dB
SFO2         399.8415994 MHz

F2 - Processing parameters
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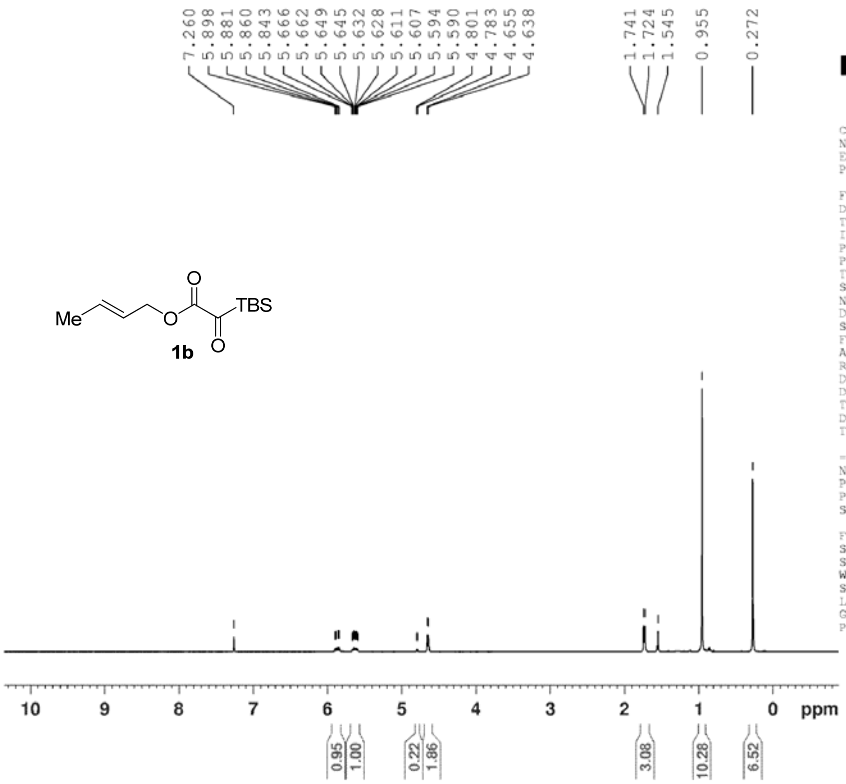

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TD                 32768
SOLVENT            CDCl3
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DS                     2
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RG                 228.1
DW                80.400 usec
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TE                 300.0 K
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TD0                    1

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PL1                -3.00 dB
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SSB                    0
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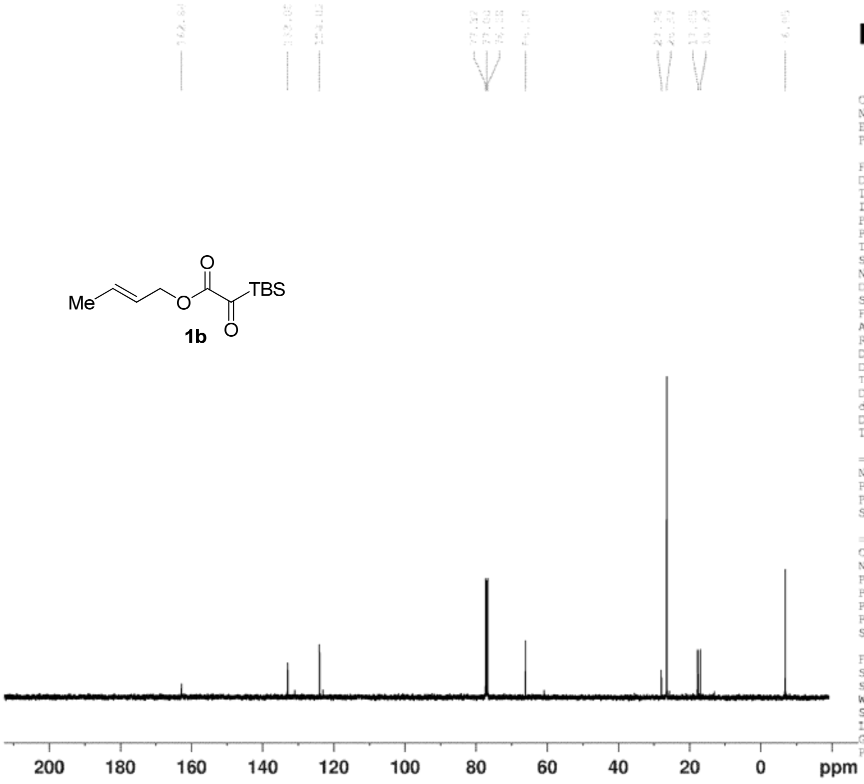

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PROCNO                 1

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TD                 32768
SOLVENT            CDCl3
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DS                     2
SWH            23980.814 Hz
FIDRES          0.731836 Hz
AQ             0.6832628 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec
d11           0.03000000 sec
DELTA         0.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.25 usec
PL1                 0.00 dB
SFO1         100.5499020 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               16.72 dB
PL13               20.00 dB
SFO2         399.8415994 MHz

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SSB                    0
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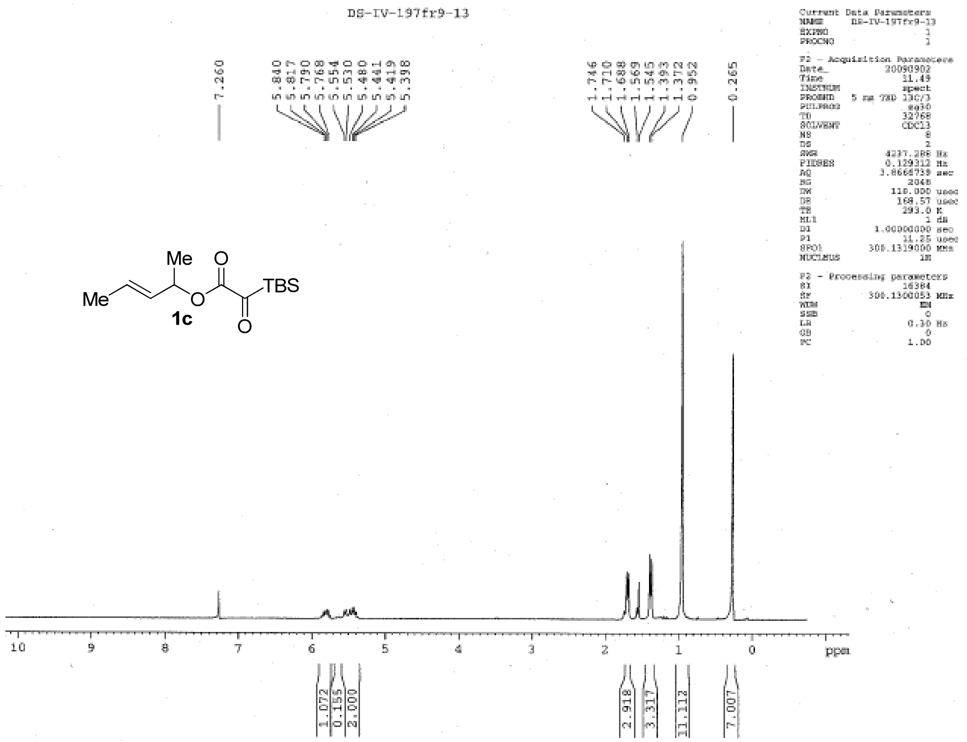
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5.480
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5.398
1.746
1.710
1.688
1.569
1.545
1.393
1.372
0.952
0.265
Me
O
O
O
TBS
Me
1c
10
9
8
7
6
5
4
3
2
1
0
ppm
1.072
0.155
2.000
2.918
3.317
11.112
7.007
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PROCNO 1
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Time 11.49
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 4237.288 Hz
FIDRES 0.129312 Hz
AQ 3.8666739 sec
RG 2048
DW 118.000 usec
DE 168.57 usec
TE 293.0 K
NL1 1 dB
D1 1.00000000 sec
P1 11.25 usec
SFO1 300.1319000 MHz
NUCLEUS 1H
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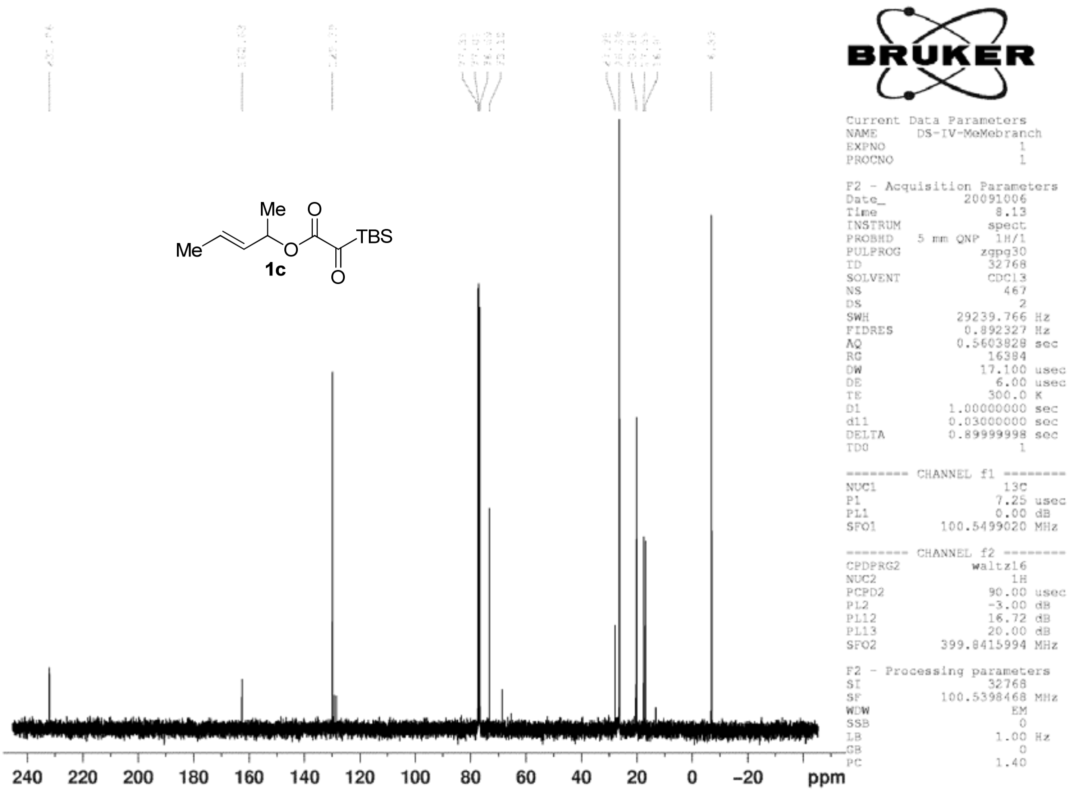
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


Me
O
O
O
TBS
Me
1c
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
ppm
Current Data Parameters
NAME DS-IV-MeMebranch
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091006
Time 8.13
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 467
DS 2
SWH 29239.766 Hz
FIDRES 0.892327 Hz
AQ 0.5603828 sec
RG 16384
DW 17.100 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.25 usec
PL1 0.00 dB
SFO1 100.5499020 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 16.72 dB
PL13 20.00 dB
SFO2 399.8415994 MHz
F2 - Processing parameters
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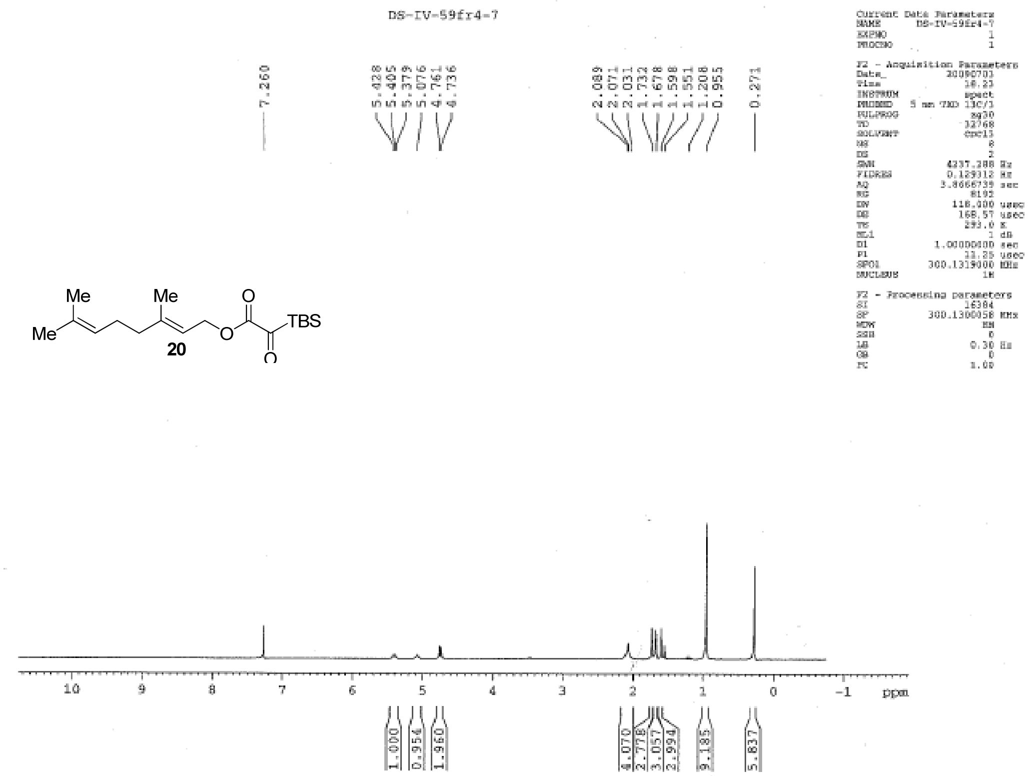
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



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EXPNO                 1
PROCNO                1

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PULPROG            zg30
TD                32768
SOLVENT           cDcl3
NS                    8
DS                    2
SWH            4237.288 Hz
FIDRES         0.129312 Hz
AQ            3.8666739 sec
RG                 8192
DW              118.000 usec
DE               168.57 usec
TE                293.0 K
PL1                   1 dB
D1           1.00000000 sec
P1                11.25 usec
SFO1        300.1319000 MHz
NUCLEUS              1H

F2 - Processing parameters
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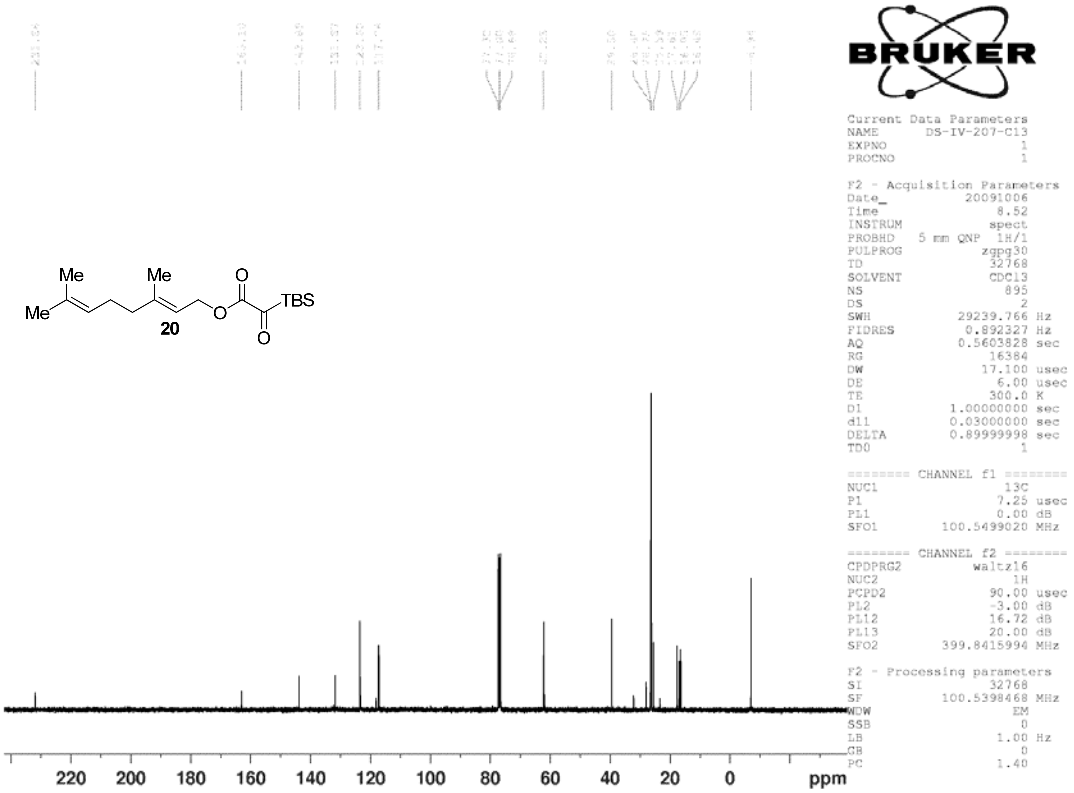

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PROCNO                  1

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PULPROG           zgpg30
TD                  32768
SOLVENT             CDCl3
NS                    895
DS                      2
SWH             29239.766 Hz
FIDRES           0.892327 Hz
AQ              0.5603828 sec
RG                  16384
DW                 17.100 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec
DELTA          0.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.25 usec
PL1                  0.00 dB
SFO1          100.5499020 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -3.00 dB
PL12                16.72 dB
PL13                20.00 dB
SFO2          399.8415994 MHz

F2 - Processing parameters
SI                  32768
SF            100.5398468 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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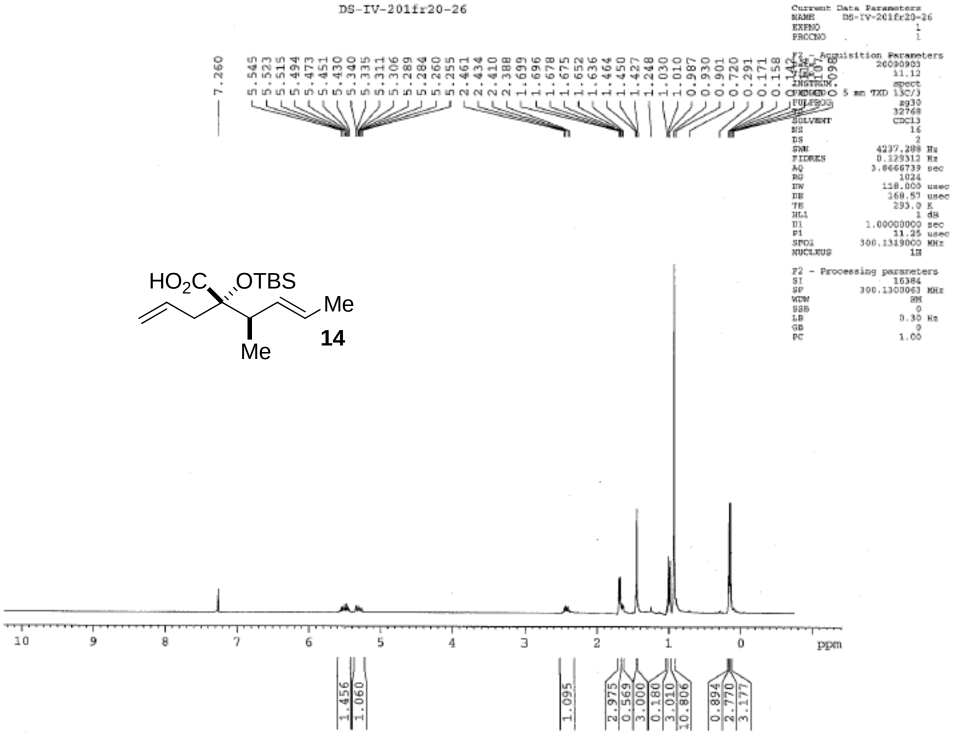

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TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH            4237.288 Hz
FIDRES         0.129312 Hz
AQ            3.8666739 sec
RG                   1024
DW              118.000 usec
DE              168.57 usec
TE               293.0 K
HL1                   1 dB
D1          1.00000000 sec
P1                11.25 usec
SFO1        300.1319000 MHz
NUCLEUS                1H

F2 - Processing parameters
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WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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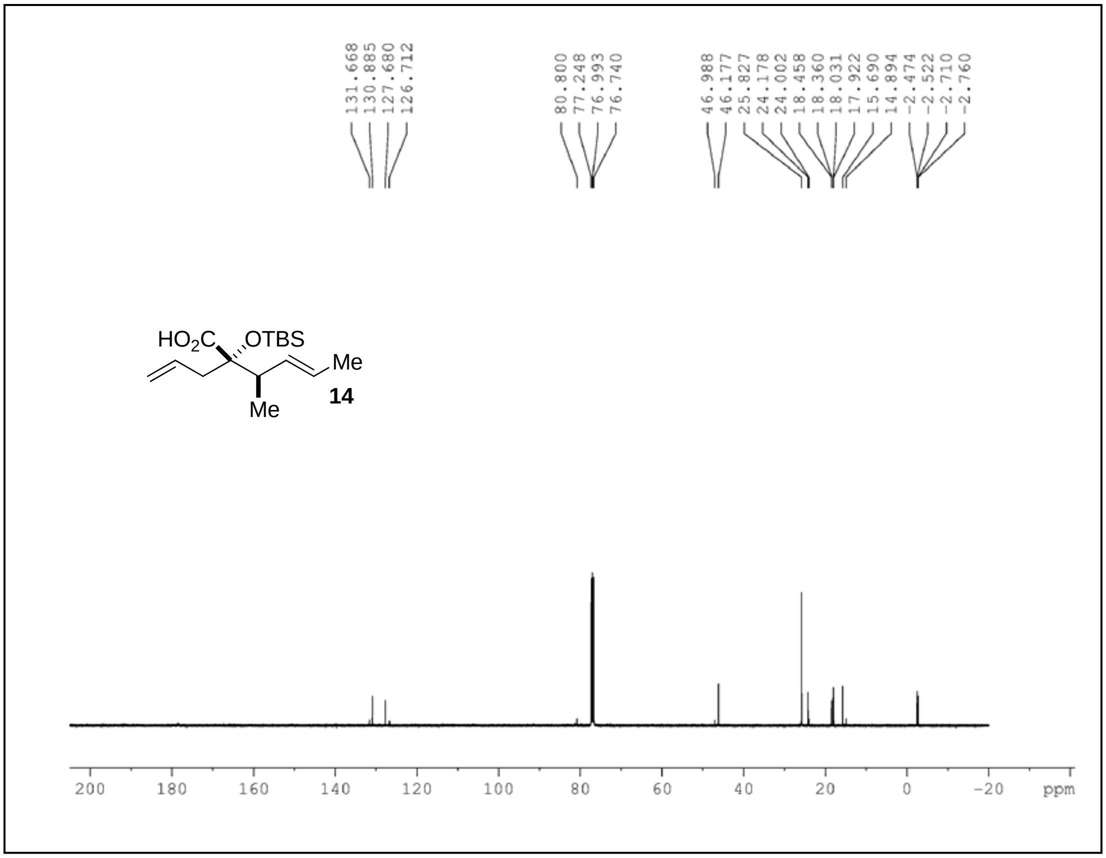

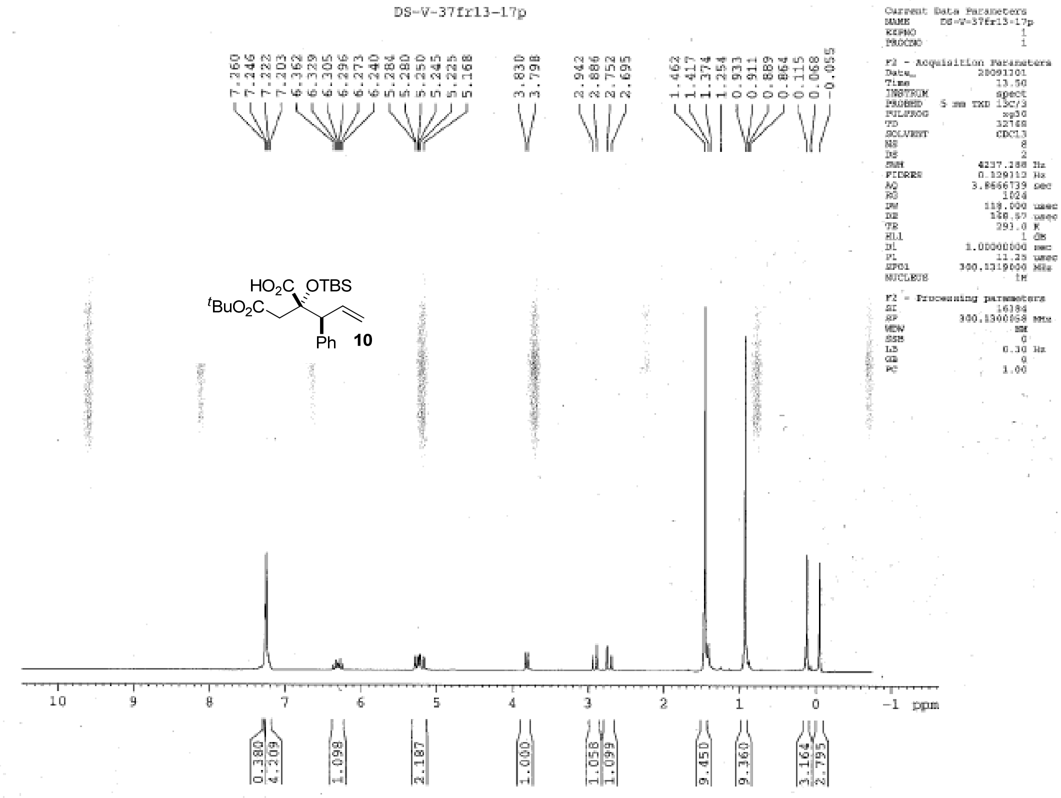

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PROCNO                 1

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TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             4237.288 Hz
FIDRES          0.129312 Hz
AQ             3.8666739 sec
RG                  1024
DW               118.000 usec
DE                140.57 usec
TE                 291.0 K
PL1                    1 dB
D1            1.00000000 sec
P1                 11.25 usec
SFO1         300.1319000 MHz
NUCLEUS               1H

F2 - Processing parameters
SI                 16384
SF           300.1300068 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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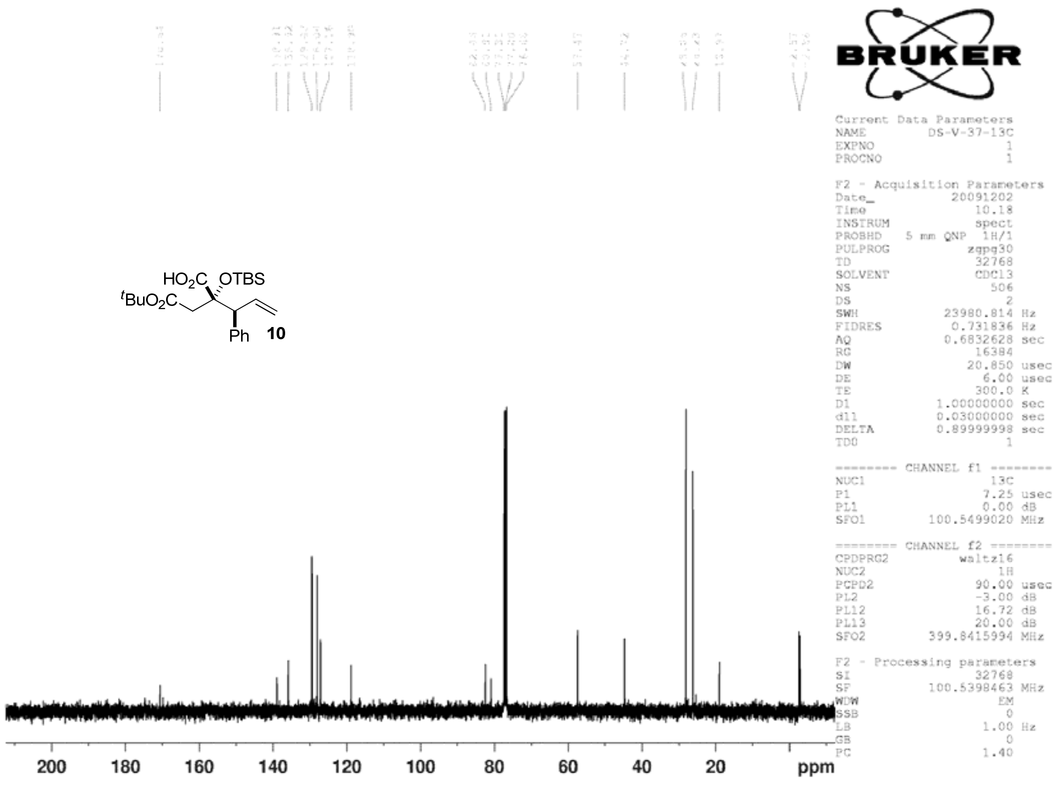

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EXPNO                   1
PROCNO                  1

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PULPROG           zgpg30
TD                  32768
SOLVENT             CDCl3
NS                    506
DS                      2
SWH             23980.814 Hz
FIDRES           0.731836 Hz
AQ              0.6832628 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec
DELTA          0.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.25 usec
PL1                  0.00 dB
SFO1          100.5499020 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -3.00 dB
PL12                16.72 dB
PL13                20.00 dB
SFO2          399.8415994 MHz

F2 - Processing parameters
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SF            100.5398463 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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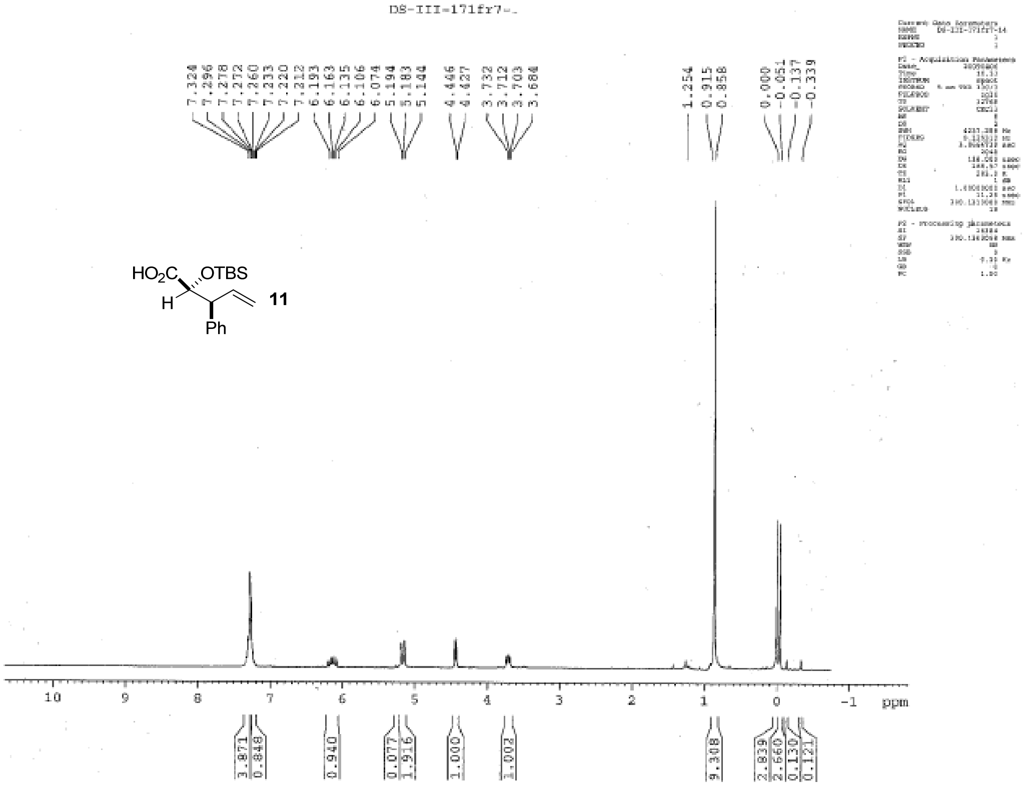
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6.106
6.074
5.194
5.183
5.144
4.446
4.427
3.732
3.712
3.703
3.684
1.254
0.915
0.858
0.000
-0.051
-0.137
-0.339
HO2C
OTBS
H
Ph
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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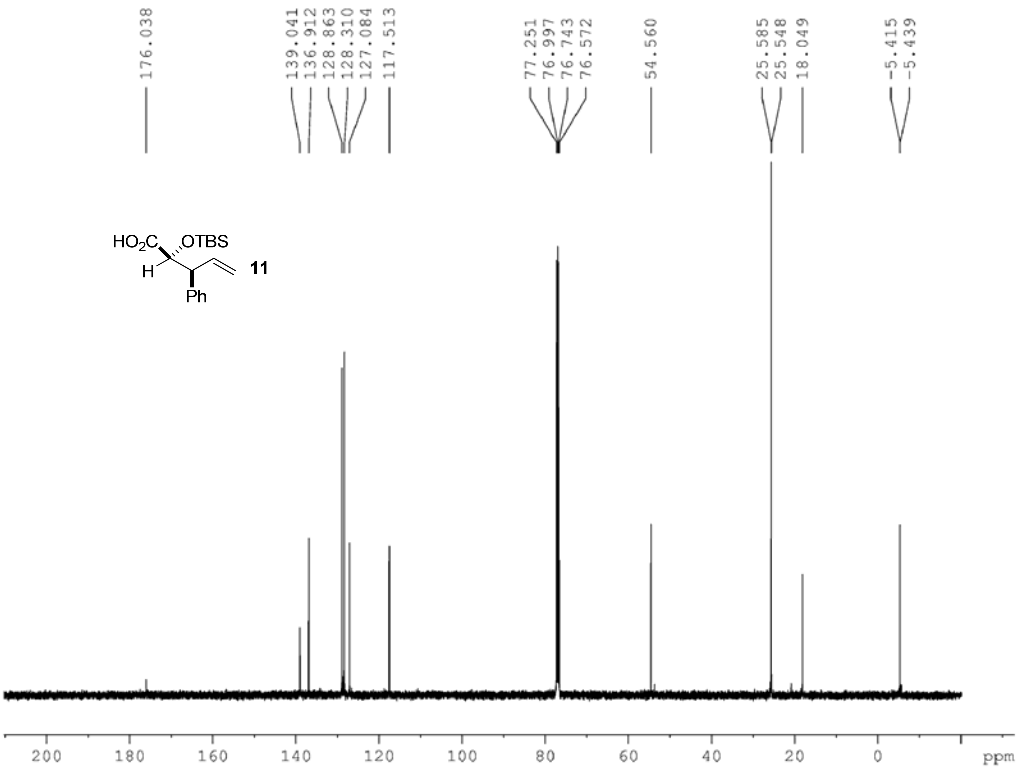
0.121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25.548
18.049
-5.415
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OTBS
H
Ph
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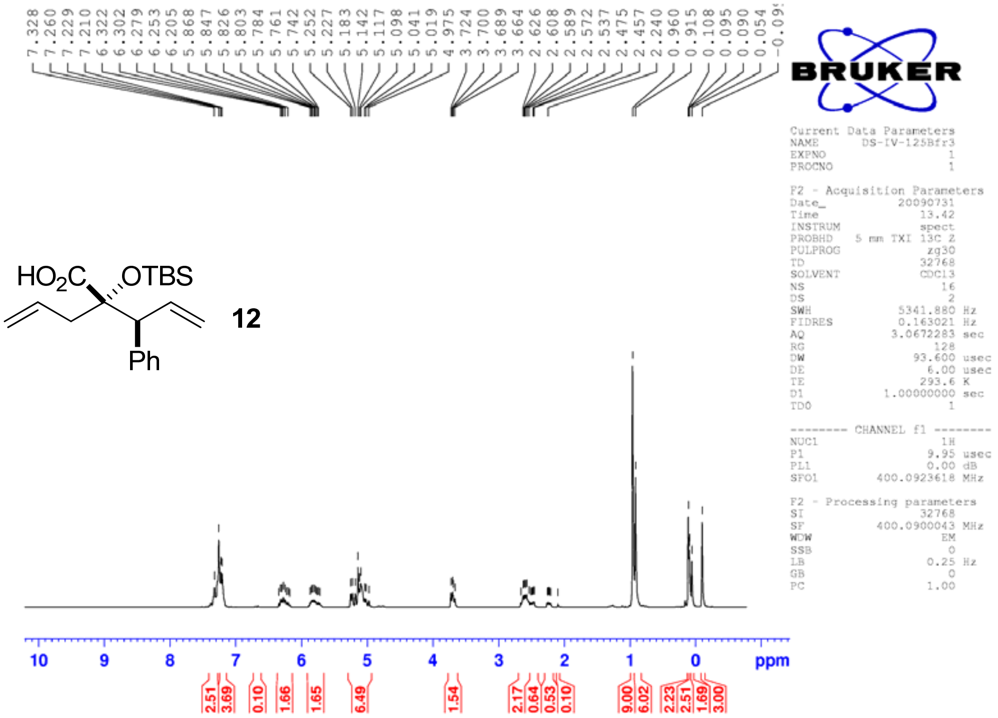
ppm



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PROCNO                   1

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TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
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FIDRES            0.163021 Hz
AQ               3.0672283 sec
RG                     128
DW                  93.600 usec
DE                    6.00 usec
TE                   293.6 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
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P1                    9.95 usec
PL1                   0.00 dB
SFO1           400.0923618 MHz

F2 - Processing parameters
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LB                    0.25 Hz
GB                       0
PC                    1.00
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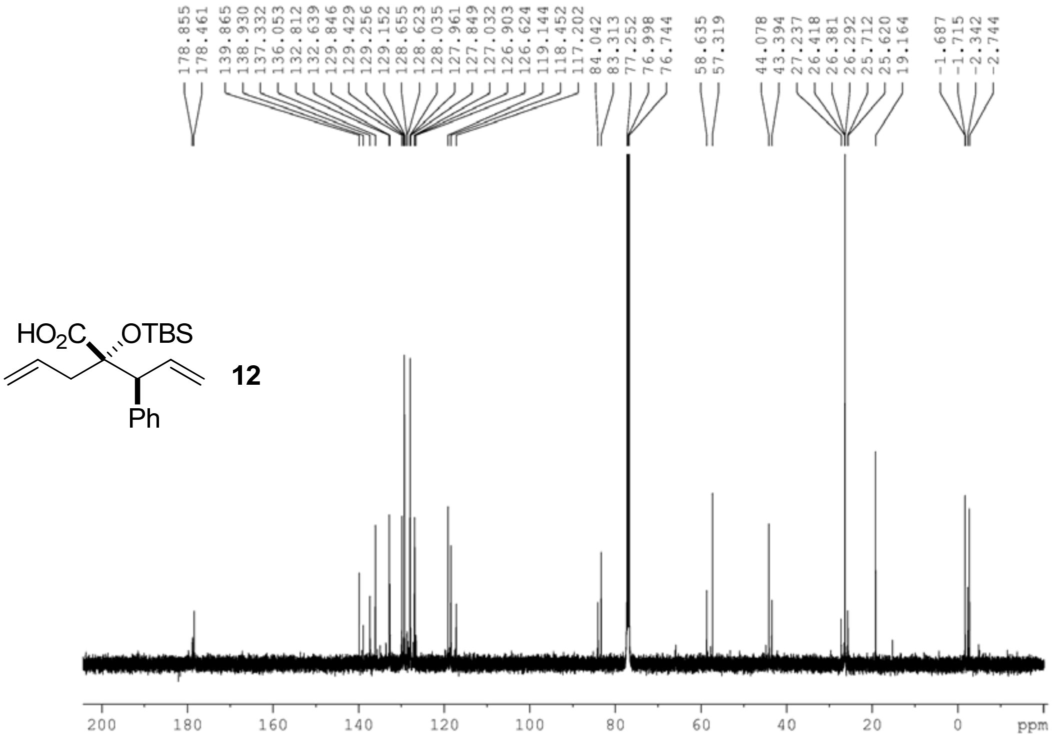
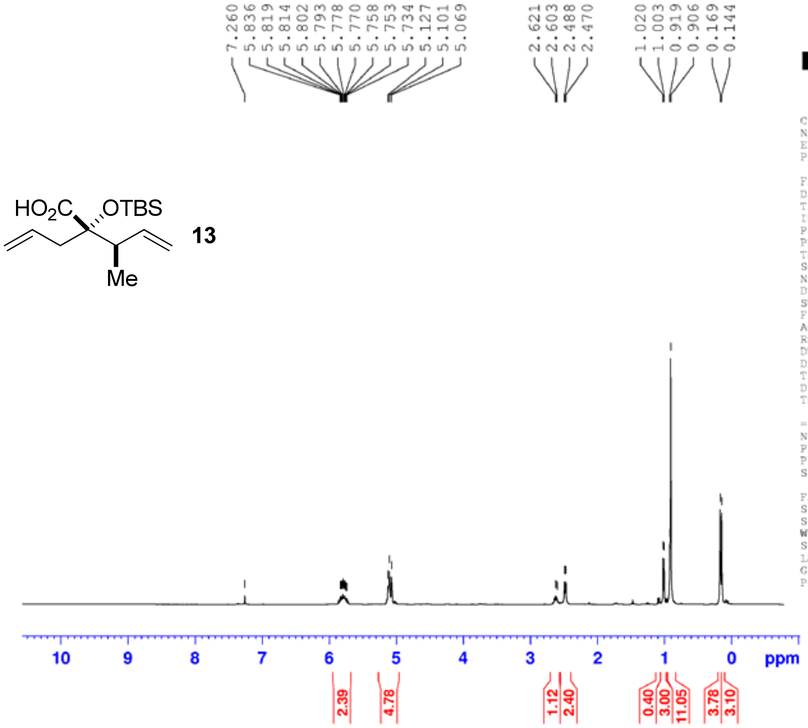


13



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PROCNO                 1

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Time               15.15
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PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
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DS                     2
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FIDRES          0.163021 Hz
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RG                  35.9
DW                93.600 usec
DE                  6.00 usec
TE                 293.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
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PL1                 0.00 dB
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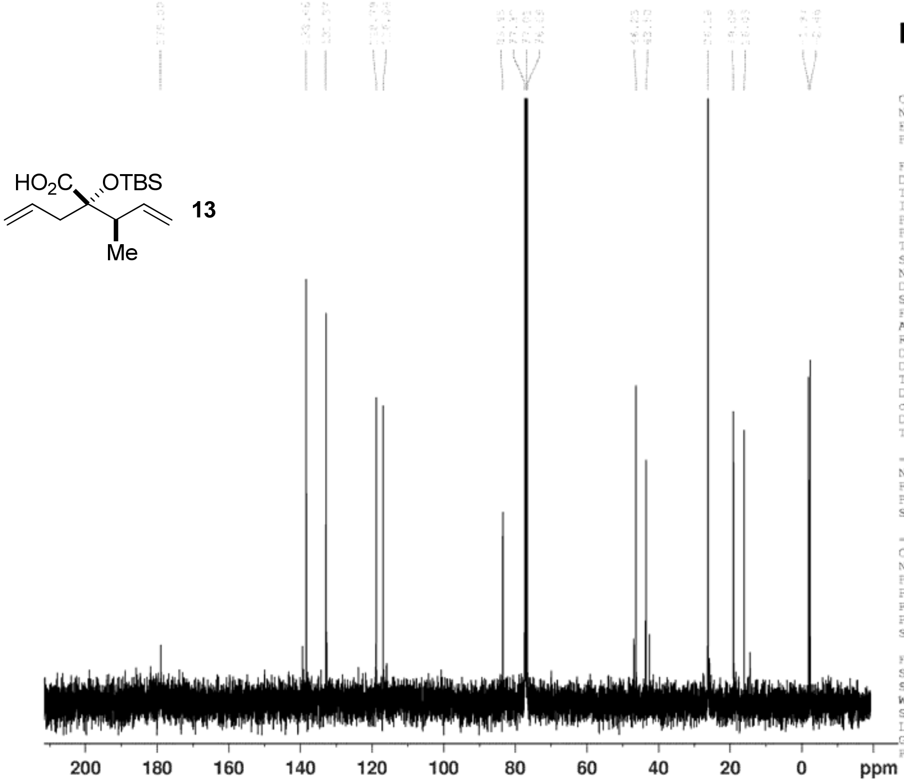
13



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PROCNO                 1

F2 - Acquisition Parameters
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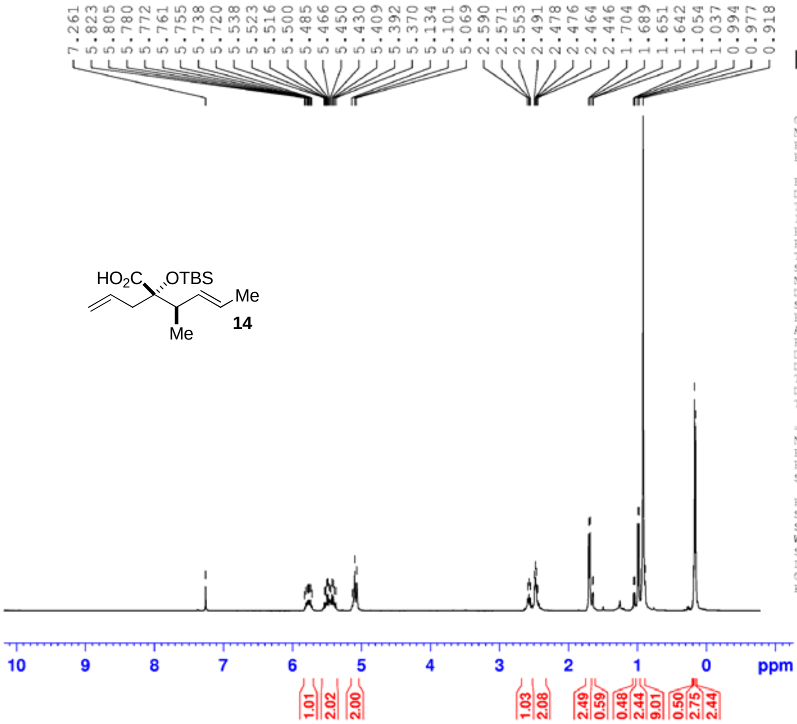
PROBHD   5 mm QNP  1H/1
PULPROG          zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   532
DS                     2
SWH            23980.814 Hz
FIDRES          0.731836 Hz
AQ             0.6832628 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec
d11           0.03000000 sec
DELTA         0.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.25 usec
PL1                 0.00 dB
SFO1         100.5499020 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               16.72 dB
PL13               20.00 dB
SFO2         399.8415994 MHz

F2 - Processing parameters
SI                 32768
SF           100.5398453 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

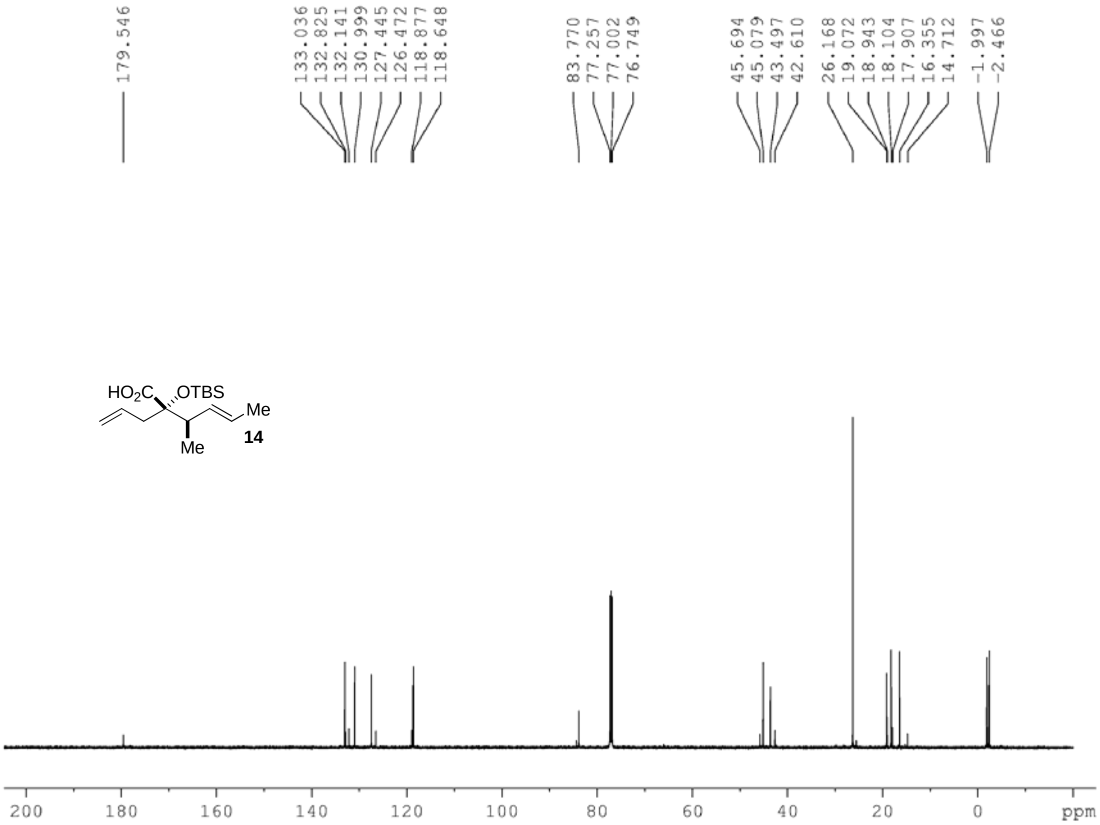


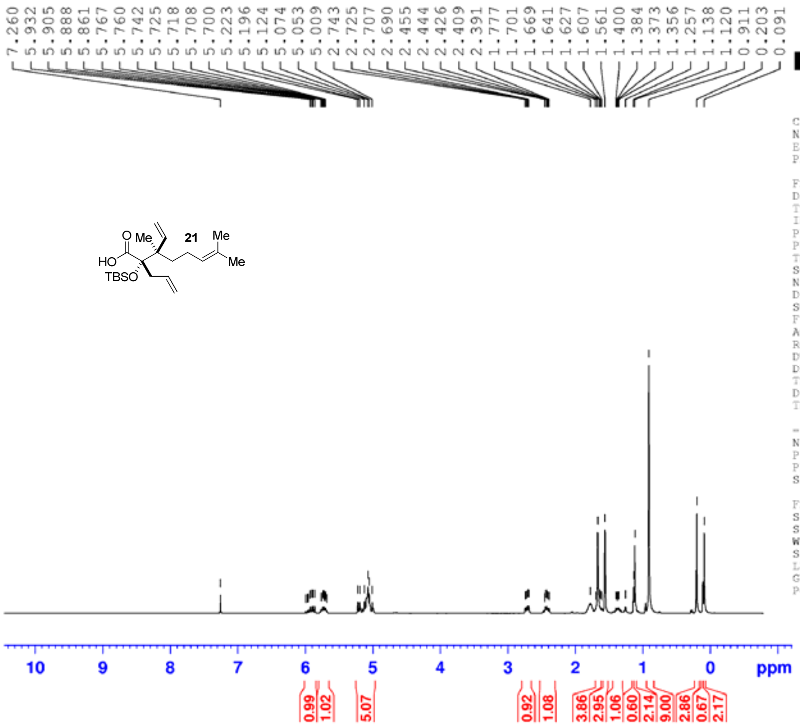
```
Current Data Parameters
NAME       DS-IV-212p-2B
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20091028
Time                8.54
INSTRUM            spect
PROBHD   5 mm TXI 13C Z
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             5341.880 Hz
FIDRES          0.163021 Hz
AQ             3.0672283 sec
RG                    57
DW                93.600 usec
DE                  6.00 usec
TE                 297.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.95 usec
PL1                 0.00 dB
SFO1         400.0923618 MHz

F2 - Processing parameters
SI                 32768
SF           400.0900040 MHz
WDW                   EM
SSB                    0
LB                  0.25 Hz
GB                     0
PC                  1.00
```



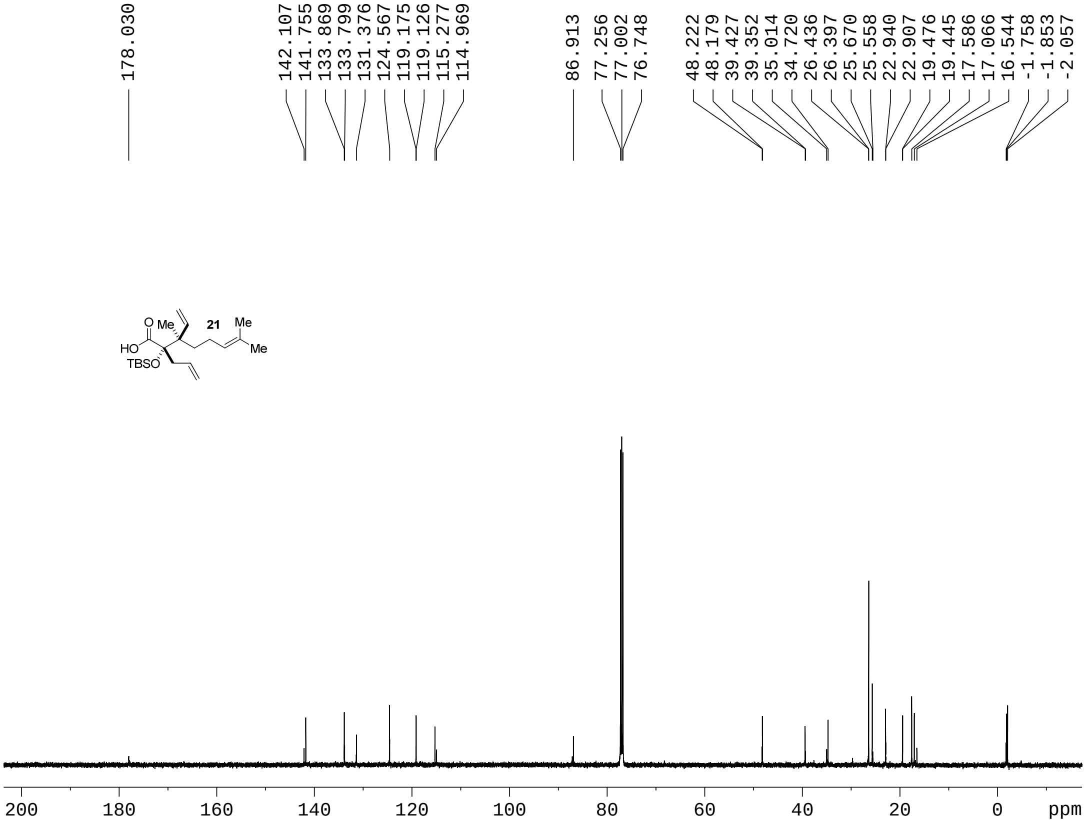


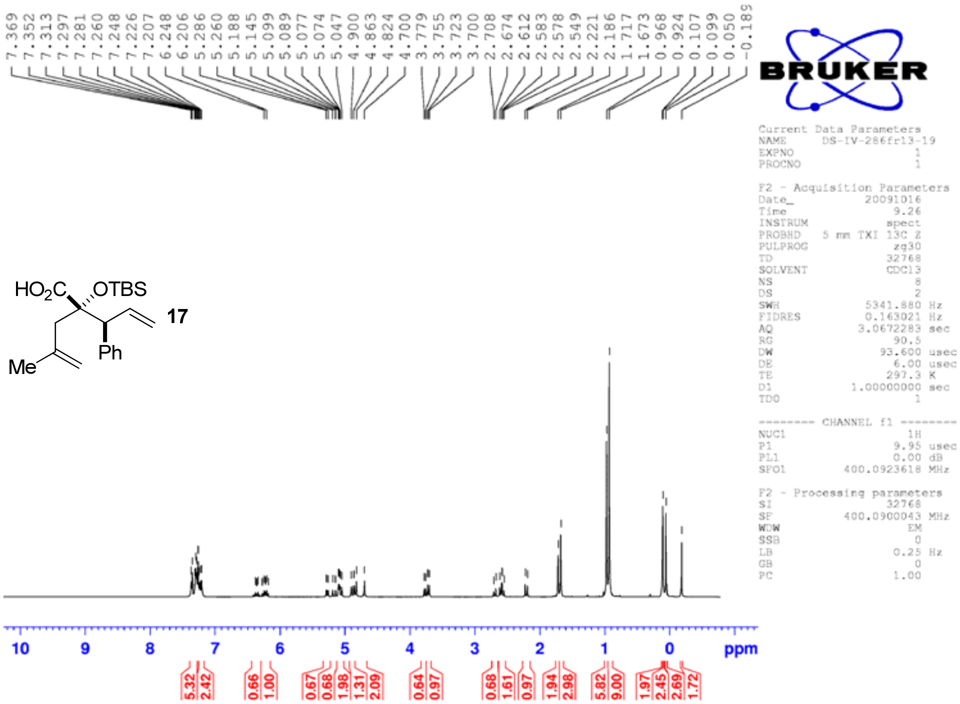
```
Current Data Parameters
NAME          DS-IV-213p
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090909
Time               16.13
INSTRUM            spect
PROBHD   5 mm TXI 13C Z
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5341.880 Hz
FIDRES          0.163021 Hz
AQ             3.0672283 sec
RG                    64
DW                93.600 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.95 usec
PL1                 0.00 dB
SFO1         400.0923618 MHz

F2 - Processing parameters
SI                 32768
SF           400.0900037 MHz
WDW                   EM
SSB                    0
LB                  0.25 Hz
GB                     0
PC                  1.00
```



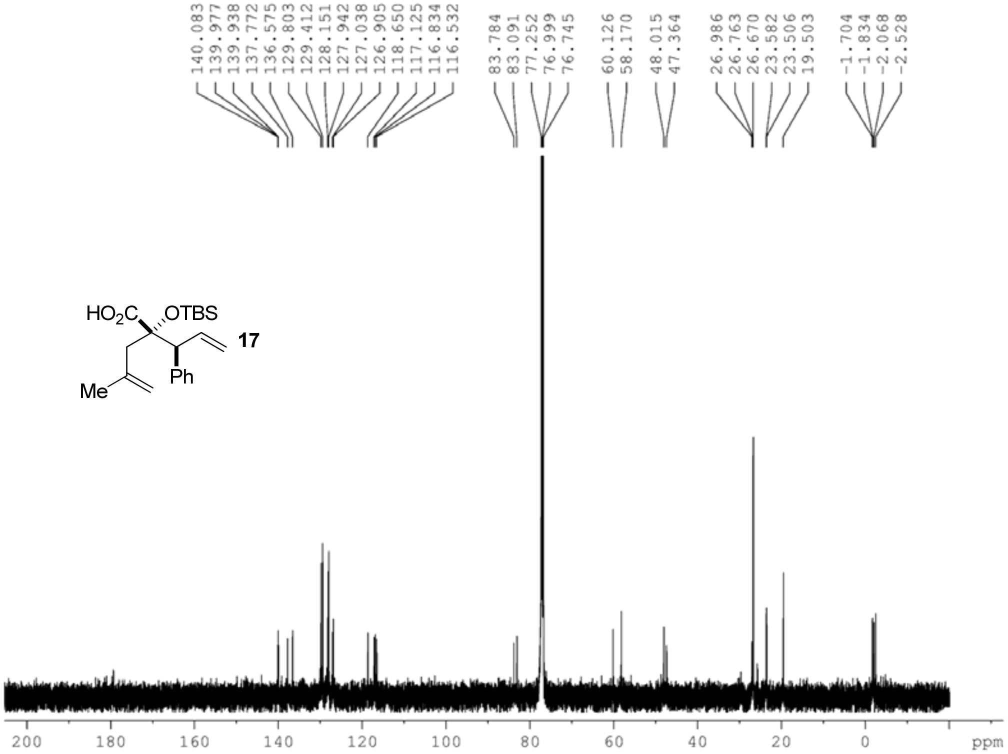


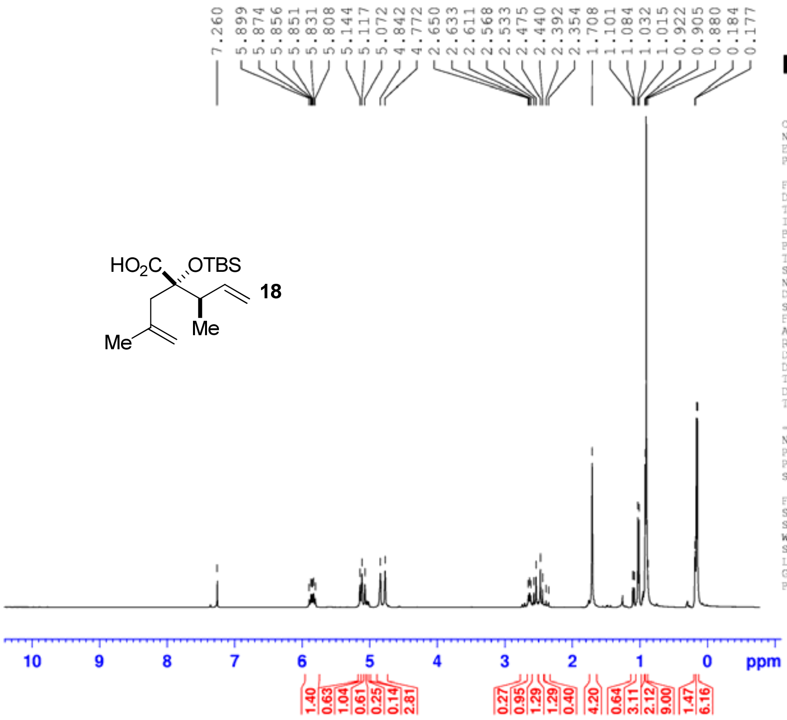
```
Current Data Parameters
NAME     DS-IV-286fr13-19
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20091016
Time                 9.26
INSTRUM             spect
PROBHD   5 mm TXI 13C Z
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              5341.880 Hz
FIDRES           0.163021 Hz
AQ              3.0672283 sec
RG                   90.5
DW                 93.600 usec
DE                   6.00 usec
TE                  297.3 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.95 usec
PL1                  0.00 dB
SFO1          400.0923618 MHz

F2 - Processing parameters
SI                  32768
SF            400.0900043 MHz
WDW                    EM
SSB                     0
LB                   0.25 Hz
GB                      0
PC                   1.00
```



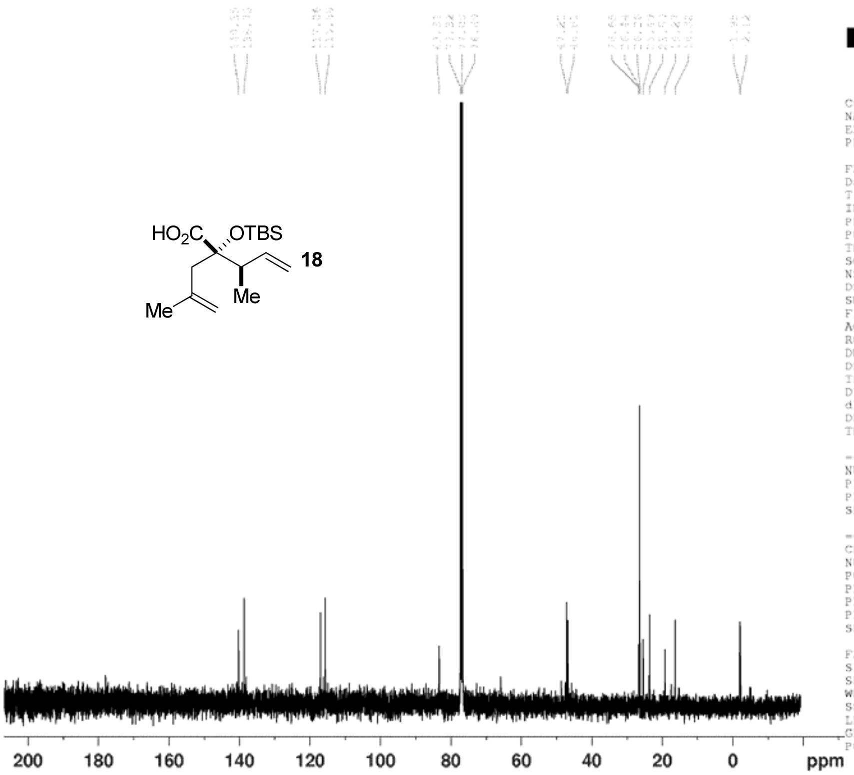


```
Current Data Parameters
NAME      DS-IV-287fr7-14p
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20091027
Time                 18.26
INSTRUM              spect
PROBHD   5 mm TXI 13C Z
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                       8
DS                       2
SWH            5341.880 Hz
FIDRES         0.163021 Hz
AQ            3.0672283 sec
RG                      57
DW              93.600 usec
DE                6.00 usec
TE                296.9 K
D1          1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                9.95 usec
PL1                0.00 dB
SFO1        400.0923618 MHz

F2 - Processing parameters
SI                   32768
SF          400.0900038 MHz
WDW                     EM
SSB                      0
LB                 0.25 Hz
GB                       0
PC                    1.00
```



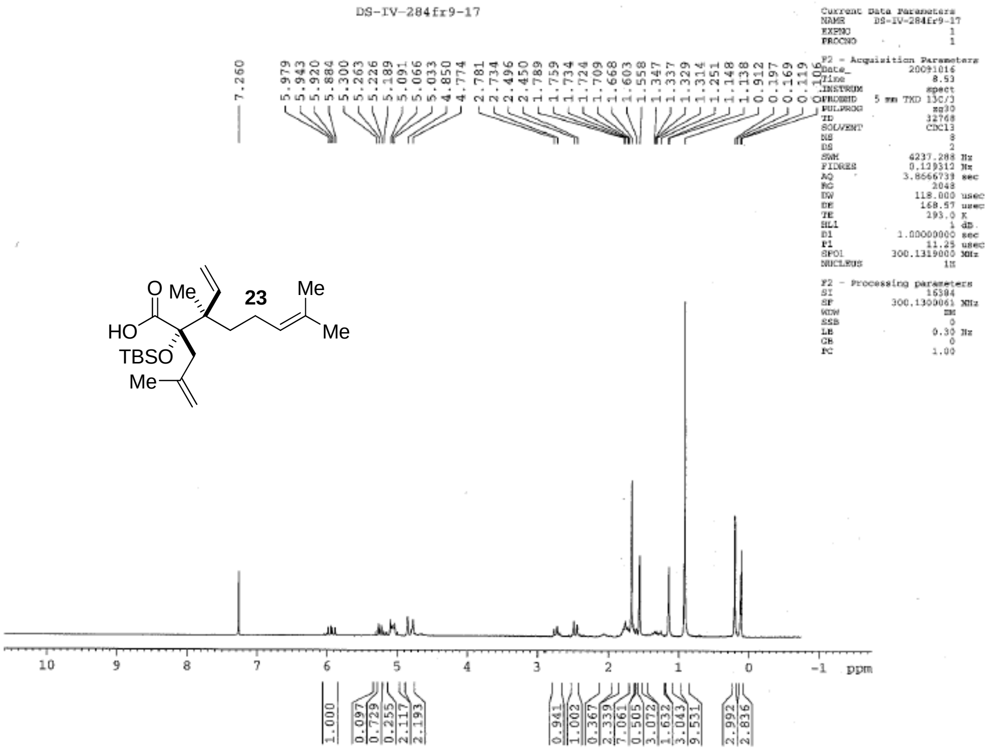
```
Current Data Parameters
NAME        DS-IV-287fr5-6
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20091101
Time                 15.13
INSTRUM              spect
PROBHD   5 mm QNP  1H/1
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                    2916
DS                       2
SWH           23980.814 Hz
FIDRES         0.731836 Hz
AQ            0.6832628 sec
RG                   16384
DW              20.850 usec
DE                6.00 usec
TE                300.0 K
D1          1.00000000 sec
d11         0.03000000 sec
DELTA       0.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                7.25 usec
PL1                0.00 dB
SFO1        100.5499020 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2              90.00 usec
PL2               -3.00 dB
PL12              16.72 dB
PL13              20.00 dB
SFO2        399.8415994 MHz

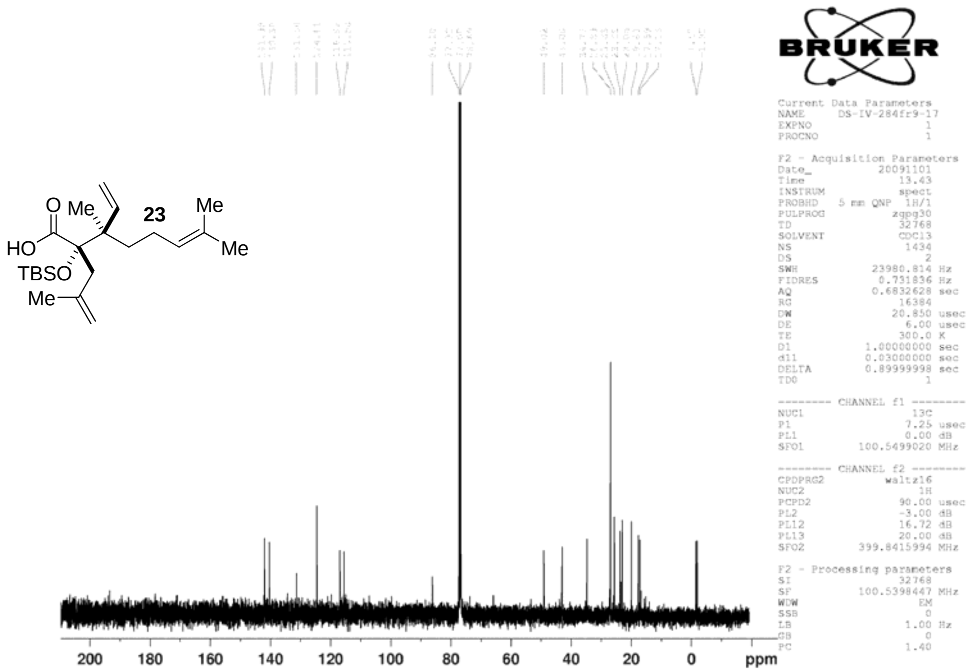
F2 - Processing parameters
SI                   32768
SF          100.5398435 MHz
WDW                     EM
SSB                      0
LB                 1.00 Hz
GB                       0
PC                    1.40
```



```
Current Data Parameters
NAME      DS-IV-284fr9-17
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20091016
Time                 8.53
INSTRUM             spect
PROBHD    5 mm TXD 13C/3
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              4237.288 Hz
FIDRES           0.129312 Hz
AQ              3.8666739 sec
RG                   2048
DW                118.000 usec
DE                 168.57 usec
TE                  293.0 K
HL1                     1 dB
D1             1.00000000 sec
P1                  11.25 usec
SFO1          300.1319000 MHz
NUCLEUS                1H

F2 - Processing parameters
SI                  16384
SF            300.1300061 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



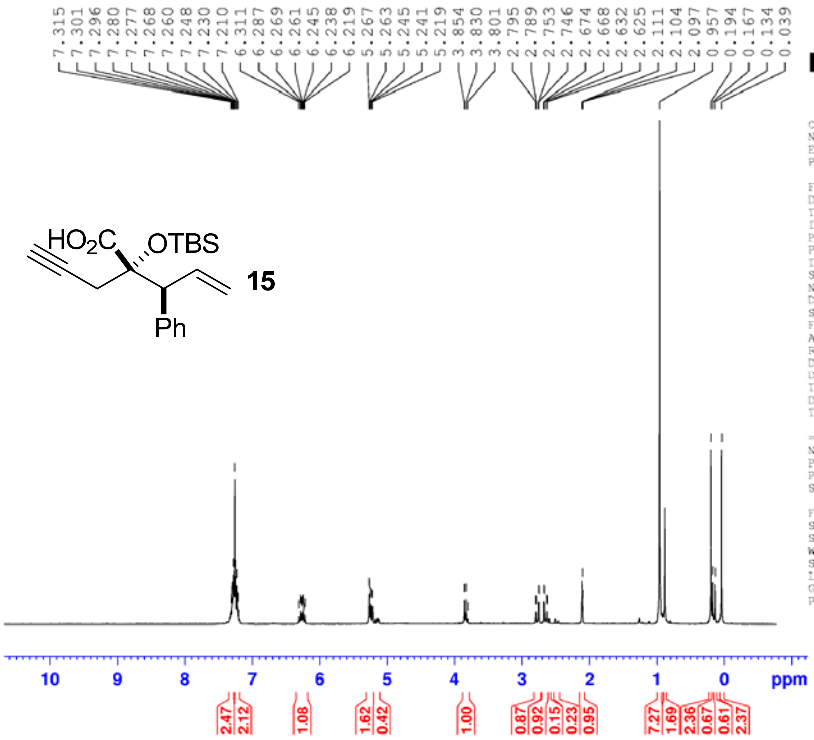
```
Current Data Parameters
NAME      DS-IV-284fr9-17
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20091101
Time                13.43
INSTRUM             spect
PROBHD    5 mm QNP  1H/1
PULPROG            zgpg30
TD                  32768
SOLVENT             CDCl3
NS                   1434
DS                      2
SWH             23980.814 Hz
FIDRES           0.731836 Hz
AQ              0.6832628 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec
DELTA          0.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.25 usec
PL1                  0.00 dB
SFO1          100.5499020 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -3.00 dB
PL12                16.72 dB
PL13                20.00 dB
SFO2          399.8415994 MHz

F2 - Processing parameters
SI                  32768
SF            100.5398447 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

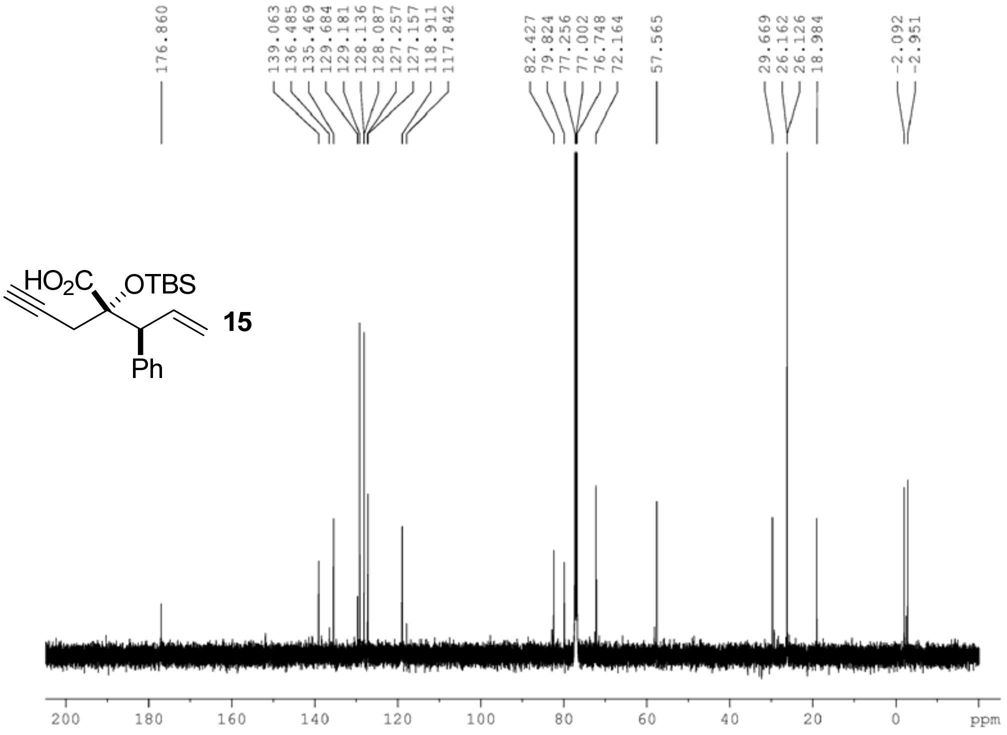


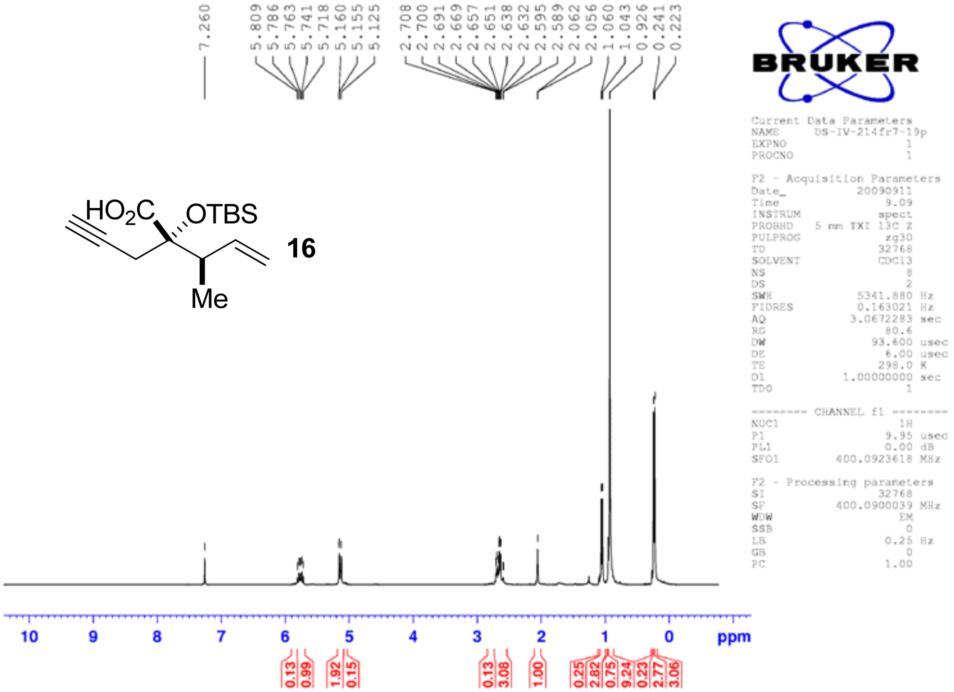
```
Current Data Parameters
NAME      DS-IV-240fr16-31
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090922
Time                 10.40
INSTRUM              spect
PROBHD    5 mm TXI 13C Z
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               5341.880 Hz
FIDRES            0.163021 Hz
AQ               3.0672283 sec
RG                   228.1
DW                  93.600 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    9.95 usec
PL1                   0.00 dB
SFO1           400.0923618 MHz

F2 - Processing parameters
SI                   32768
SF             400.0900043 MHz
WDW                     EM
SSB                      0
LB                    0.25 Hz
GB                       0
PC                    1.00
```



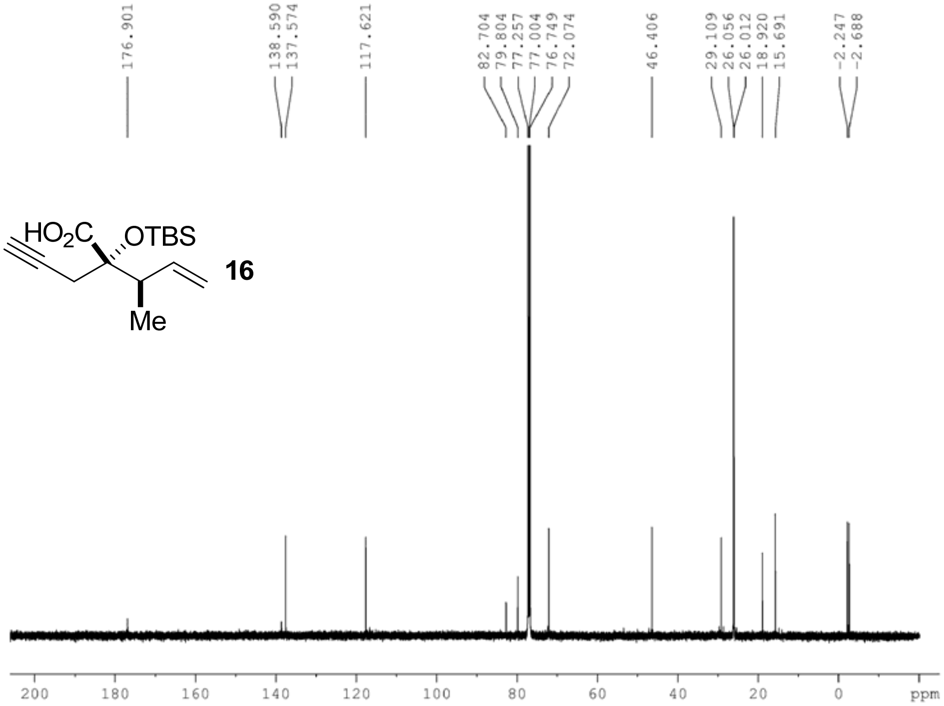


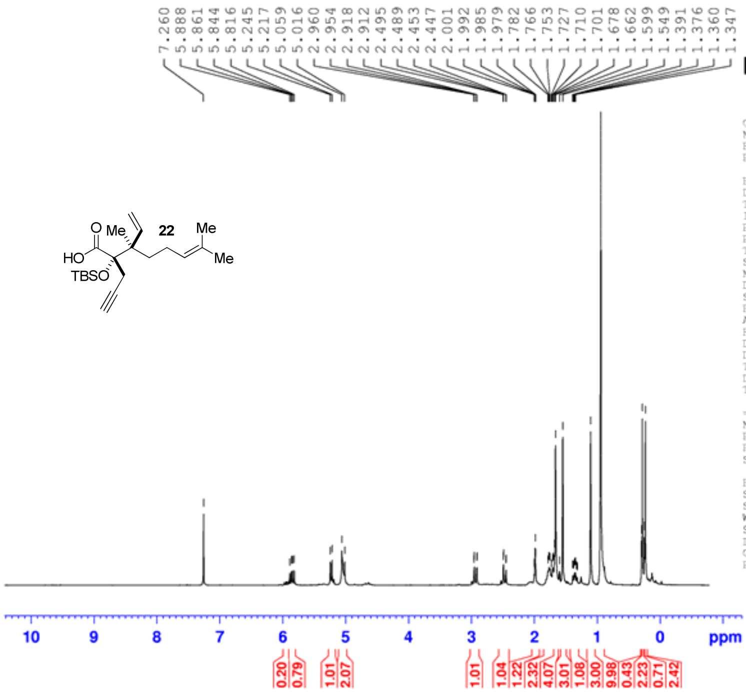
```
Current Data Parameters
NAME     DS-IV-214fr7-19p
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090911
Time                 9.09
INSTRUM             spect
PROBHD   5 mm TXI 13C Z
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              5341.880 Hz
FIDRES           0.163021 Hz
AQ              3.0672283 sec
RG                   80.6
DW                 93.600 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.95 usec
PL1                  0.00 dB
SFO1          400.0923618 MHz

F2 - Processing parameters
SI                  32768
SF            400.0900039 MHz
WDW                    EM
SSB                     0
LB                   0.25 Hz
GB                      0
PC                   1.00
```





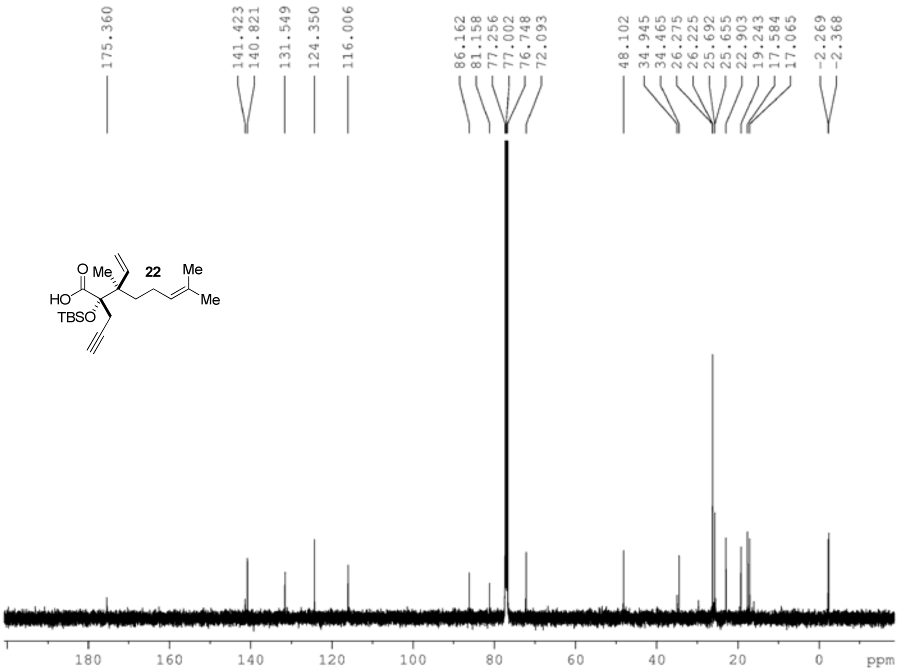
22

```
Current Data Parameters
NAME      DS-IV-215fr10-12p
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090911
Time                   9.12
INSTRUM               spect
PROBHD    5 mm TXI 13C Z
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                5341.880 Hz
FIDRES             0.163021 Hz
AQ                3.0672283 sec
RG                      114
DW                   93.600 usec
DE                     6.00 usec
TE                    298.0 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                     9.95 usec
PL1                    0.00 dB
SFO1            400.0923618 MHz

F2 - Processing parameters
SI                    32768
SF              400.0900039 MHz
WDW                      EM
SSB                       0
LB                     0.25 Hz
GB                        0
PC                     1.00
```



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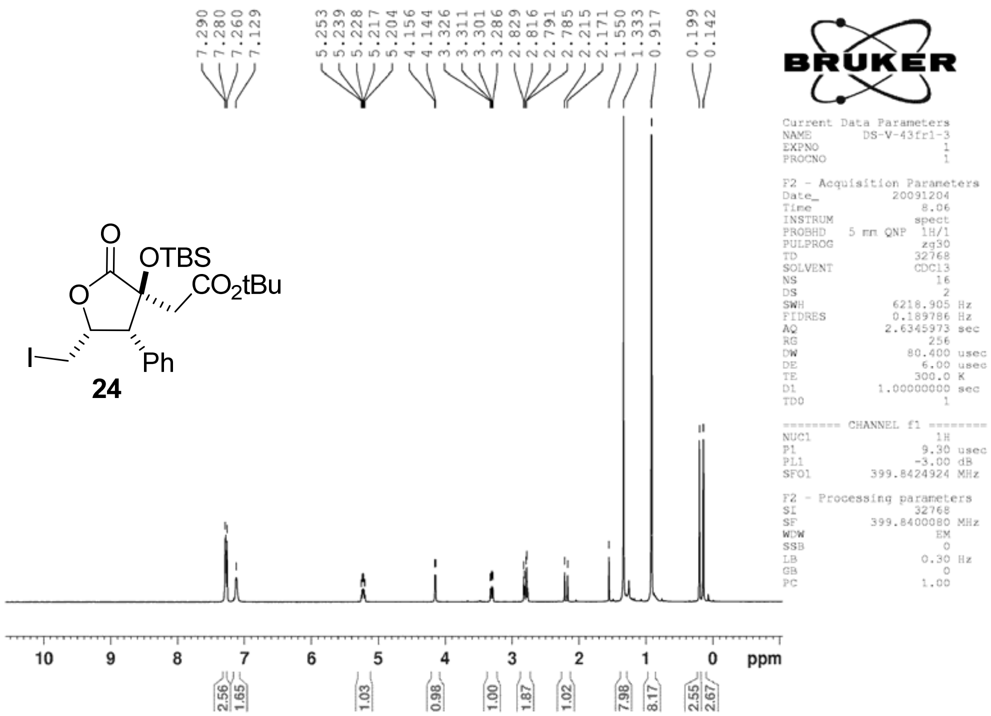


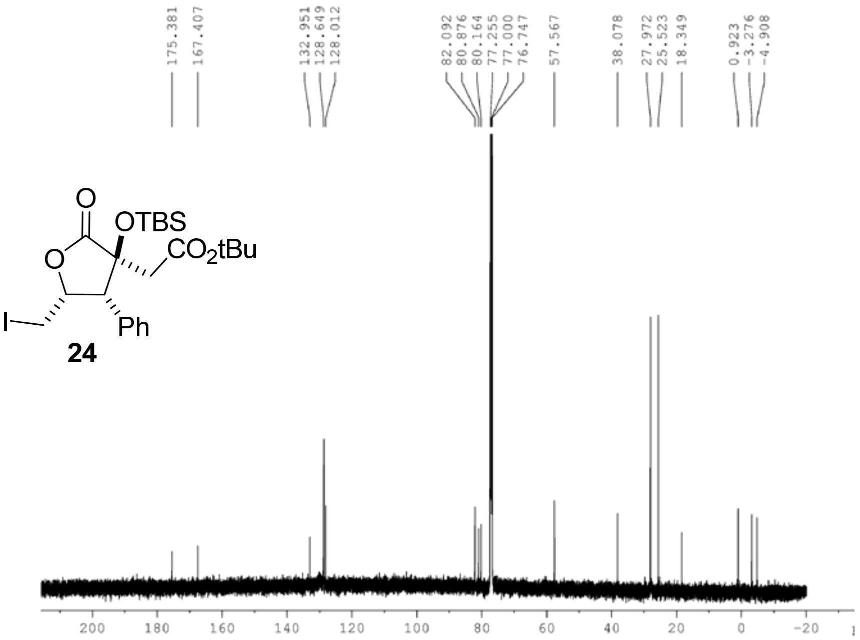
24

```
Current Data Parameters
NAME          DS-V-43fr1-3
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20091204
Time                  8.06
INSTRUM              spect
PROBHD   5 mm QNP  1H/1
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6218.905 Hz
FIDRES            0.189786 Hz
AQ               2.6345973 sec
RG                     256
DW                  80.400 usec
DE                    6.00 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    9.30 usec
PL1                  -3.00 dB
SFO1           399.8424924 MHz

F2 - Processing parameters
SI                   32768
SF             399.8400080 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



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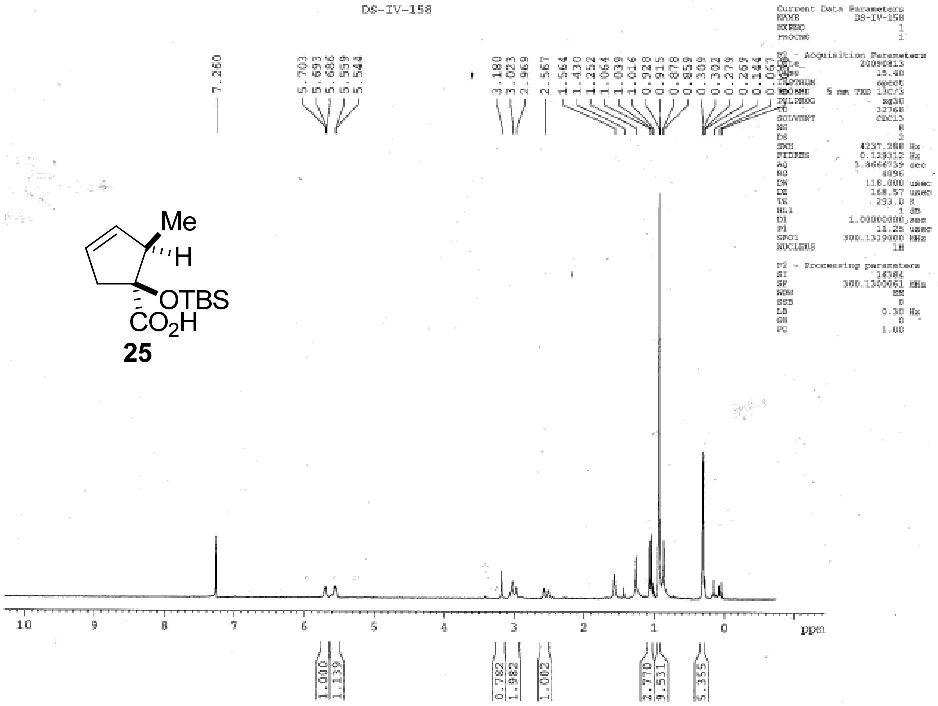
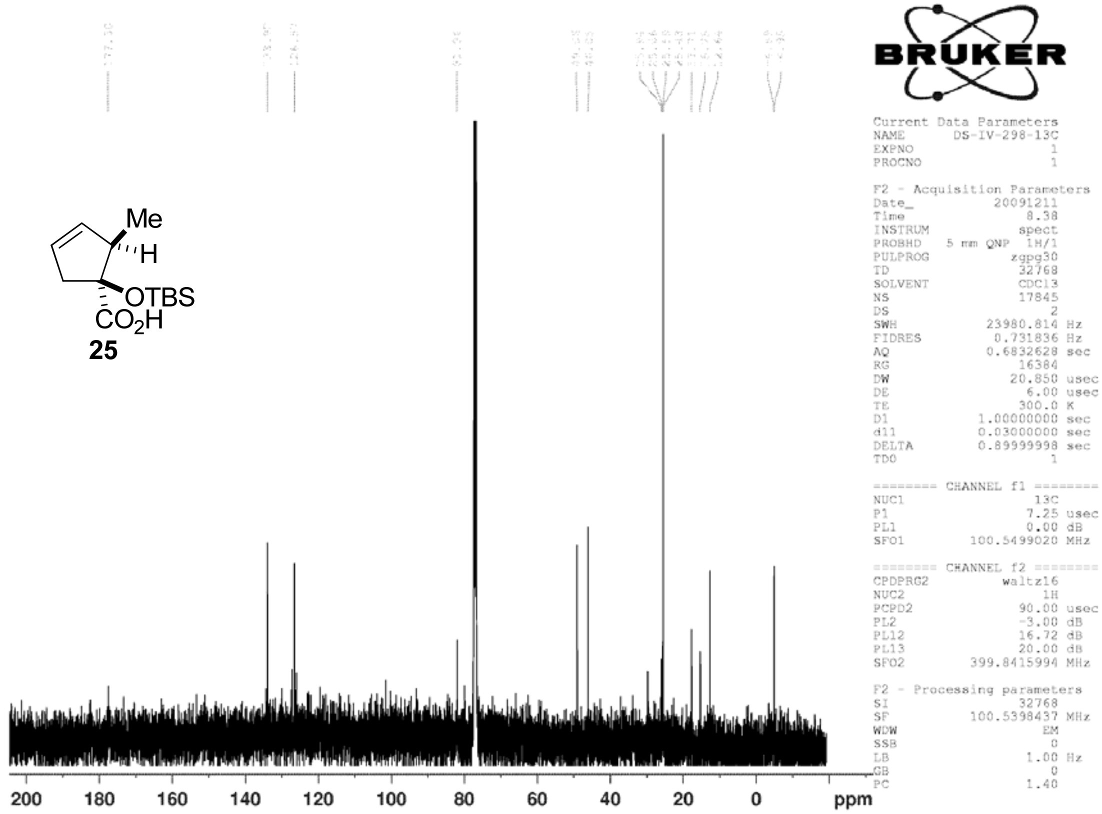


```
Current Data Parameters
NAME          DS-IV-158
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20090813
Time              15.40
INSTRUM           spect
PROBHD   5 mm TXO 13C/3
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            4237.288 Hz
FIDRES         0.129312 Hz
AQ            3.8666739 sec
RG                 4096
DW              118.000 usec
DE               168.57 usec
TE                293.0 K
HL1                   1 dB
D1           1.00000000 sec
P1                11.25 usec
SFO1        300.1319000 MHz
NUCLEUS              1H

F2 - Processing parameters
SI                16384
SF          300.1300061 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



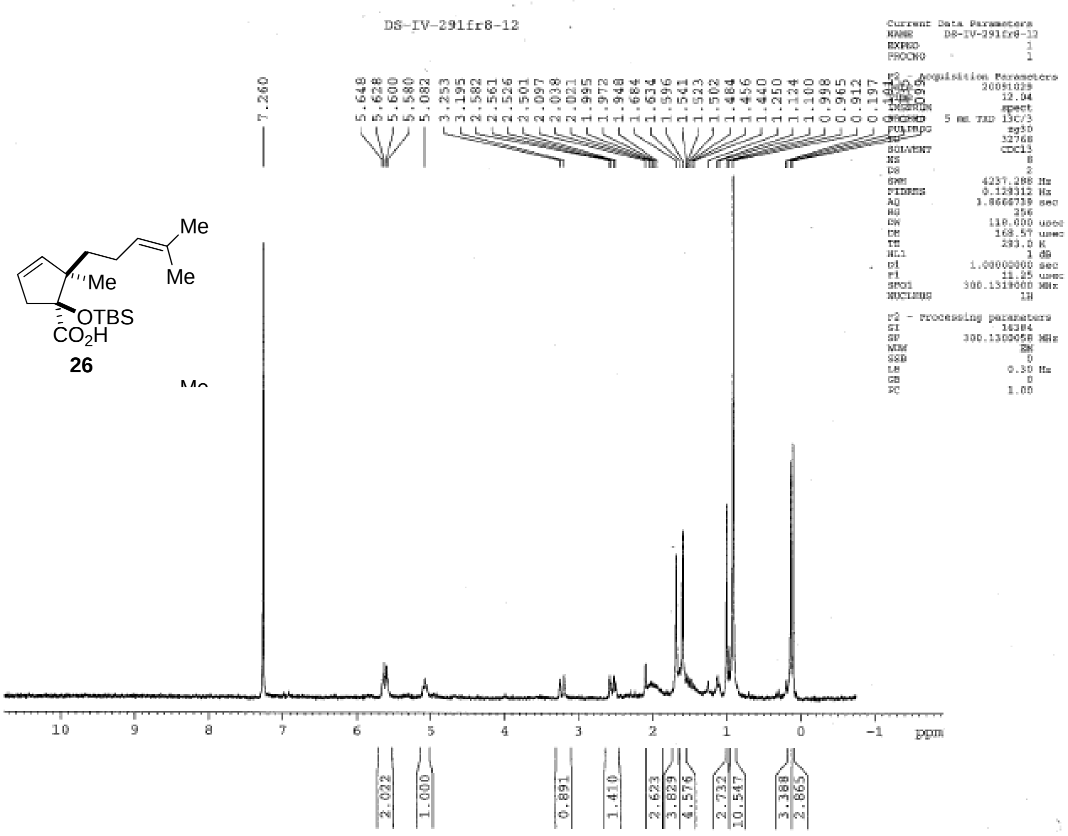
```
Current Data Parameters
NAME      DS-IV-298-13C
EXPNO                 1
PROCNO                1

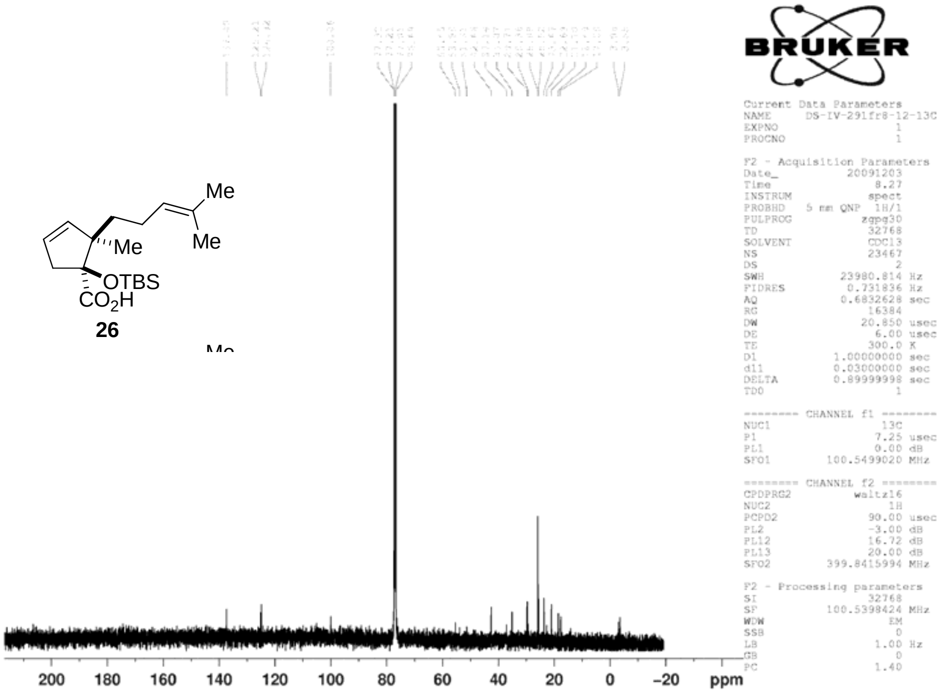
F2 - Acquisition Parameters
Date_          20091211
Time               8.38
INSTRUM           spect
PROBHD   5 mm QNP  1H/1
PULPROG         zgpg30
TD                32768
SOLVENT           CDCl3
NS                17845
DS                    2
SWH           23980.814 Hz
FIDRES         0.731836 Hz
AQ            0.6832628 sec
RG                16384
DW               20.850 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                   1

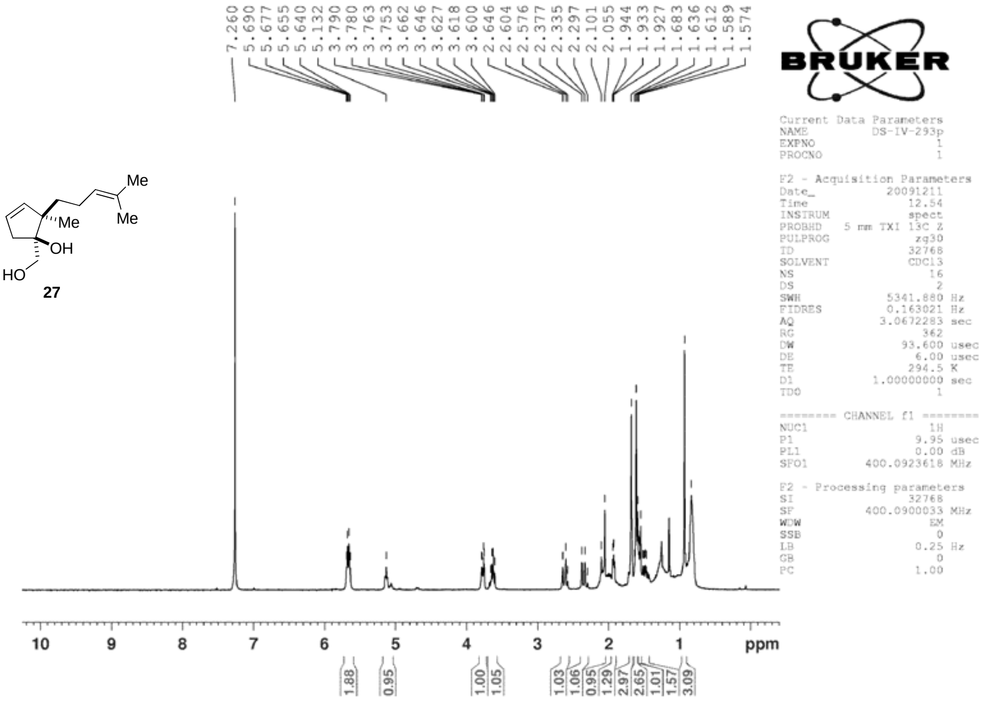
======== CHANNEL f1 ========
NUC1                13C
P1                 7.25 usec
PL1                0.00 dB
SFO1        100.5499020 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2               -3.00 dB
PL12              16.72 dB
PL13              20.00 dB
SFO2        399.8415994 MHz

F2 - Processing parameters
SI                32768
SF          100.5398437 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```


DS-IV-291fr8-12
26
7.260
5.648
5.628
5.600
5.580
5.082
3.253
3.195
2.582
2.561
2.526
2.501
2.097
2.038
2.021
1.995
1.972
1.948
1.684
1.634
1.596
1.541
1.523
1.502
1.484
1.456
1.440
1.250
1.124
1.100
0.998
0.965
0.912
0.197
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.022
1.000
0.891
1.410
2.623
3.829
4.576
2.732
10.547
3.388
2.865
Current Data Parameters
NAME DS-IV-291fr8-12
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
SOLVENT CDCl3
SFO1 300.1319000 MHz
NUCLEUS 1H
F2 - Processing parameters
SF 300.1300058 MHz
LB 0.30 Hz


BRUKER
26
Current Data Parameters
NAME DS-IV-291fr8-12-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091203
Time 8.27
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 23467
DS 2
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 0.6832628 sec
RG 16384
DW 20.850 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.25 usec
PL1 0.00 dB
SFO1 100.5499020 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 16.72 dB
PL13 20.00 dB
SFO2 399.8415994 MHz
F2 - Processing parameters
SI 32768
SF 100.5398424 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
−20
ppm



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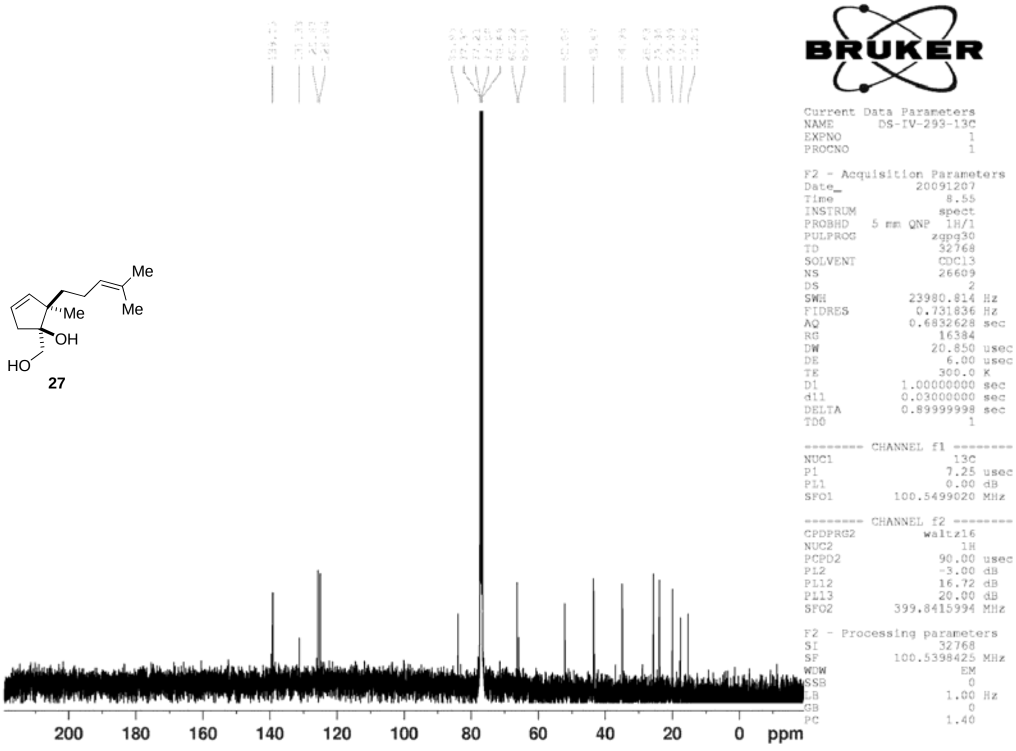
```
Current Data Parameters
NAME          DS-IV-293p
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20091211
Time               12.54
INSTRUM            spect
PROBHD   5 mm TXI 13C Z
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5341.880 Hz
FIDRES          0.163021 Hz
AQ             3.0672283 sec
RG                   362
DW                93.600 usec
DE                  6.00 usec
TE                 294.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.95 usec
PL1                 0.00 dB
SFO1         400.0923618 MHz

F2 - Processing parameters
SI                 32768
SF           400.0900033 MHz
WDW                   EM
SSB                    0
LB                  0.25 Hz
GB                     0
PC                  1.00
```



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```
Current Data Parameters
NAME        DS-IV-293-13C
EXPNO                   1
PROCNO                  1

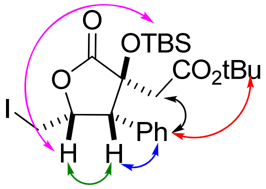
F2 - Acquisition Parameters
Date_            20091207
Time                 8.55
INSTRUM             spect
PROBHD   5 mm QNP  1H/1
PULPROG           zgpg30
TD                  32768
SOLVENT             CDCl3
NS                  26609
DS                      2
SWH             23980.814 Hz
FIDRES           0.731836 Hz
AQ              0.6832628 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec
DELTA          0.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.25 usec
PL1                  0.00 dB
SFO1          100.5499020 MHz

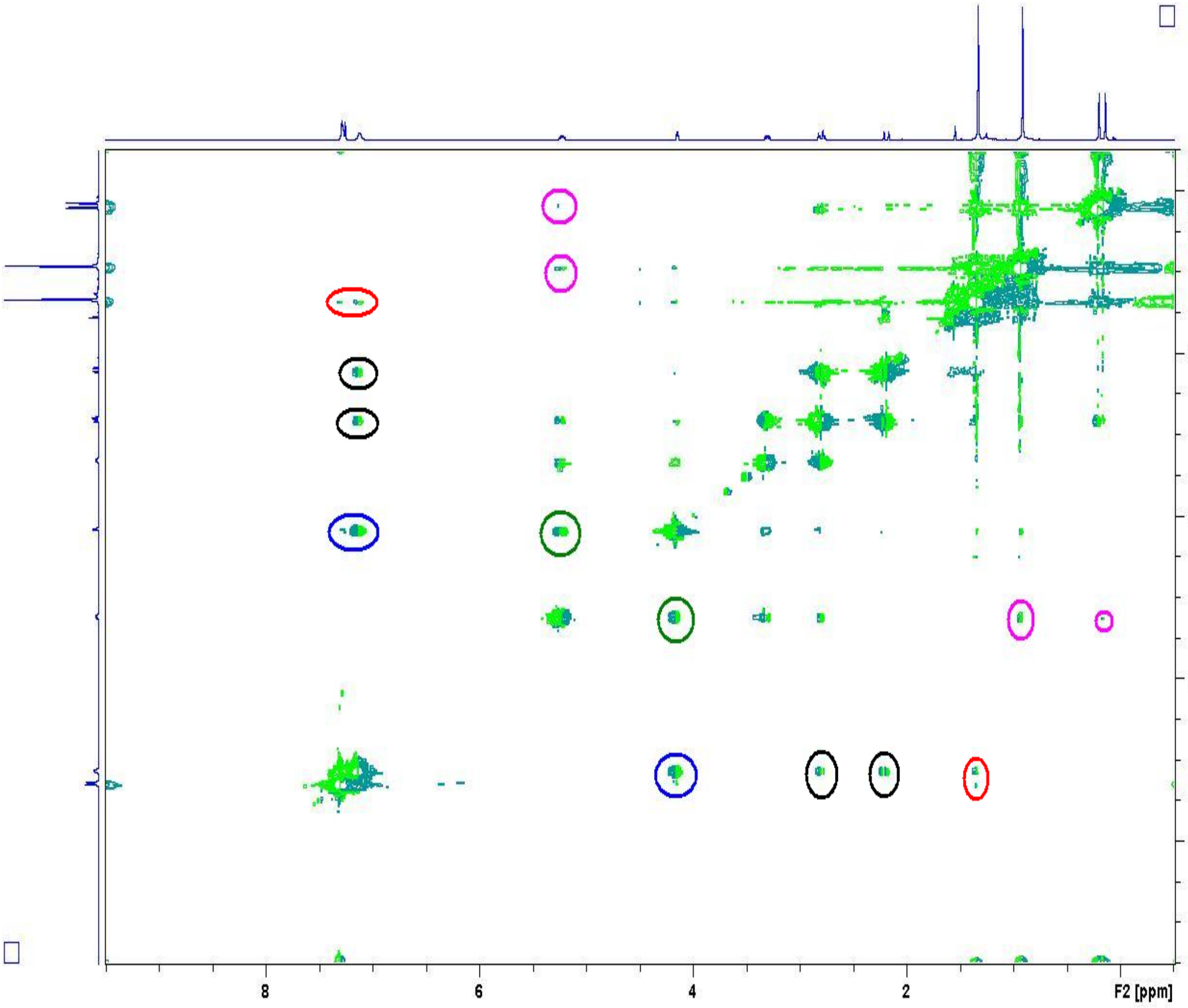
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -3.00 dB
PL12                16.72 dB
PL13                20.00 dB
SFO2          399.8415994 MHz

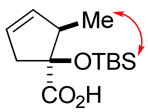
F2 - Processing parameters
SI                  32768
SF            100.5398425 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

VII. 2D NOESY for Cyclized Products

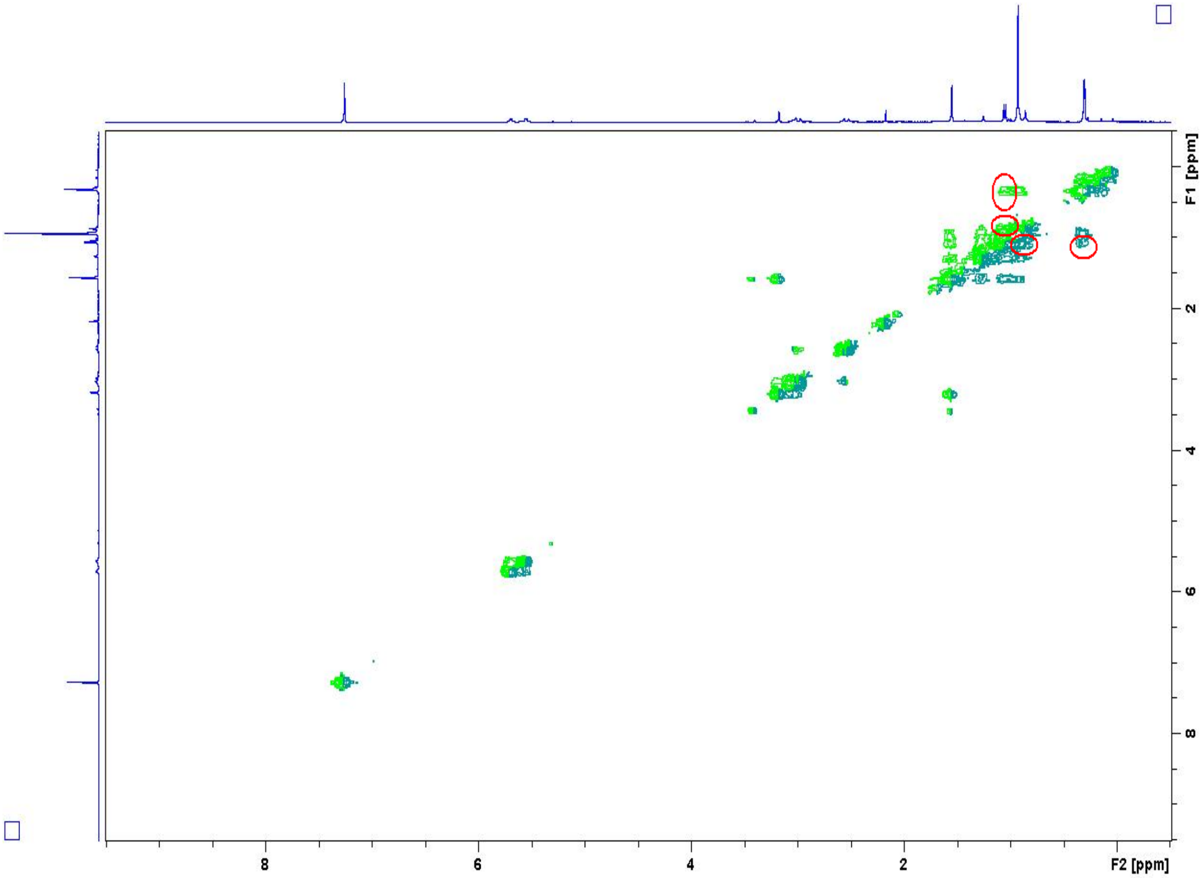


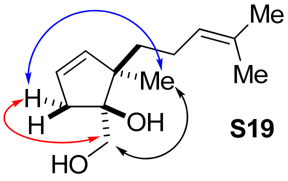
S16





S17





S19