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Supporting Information

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Oxidative Cleavage in the Construction of Complex Molecules. Synthesis of the Leucascandrolide A Macrolactone

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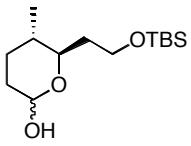
General

Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded on Bruker Avance 300 spectrometers at 300 MHz and 75 MHz, respectively; or Bruker Avance 500 spectrometers at 500 MHz and 125 MHz if specified. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak or the internal standard tetramethylsilane were used as reference values. For ^{1}H NMR: $CDCl_3$ = 7.26 ppm, C_6D_6 = 7.15 ppm, TMS = 0.00 ppm. For ^{13}C NMR: $CDCl_3$ = 77.23, C_6D_6 = 128.0, TMS = 0.00. For proton data: s = singlet; d = doublet; t = triplet; q = quartet; p = pentet; dd = doublet of doublets; dt = doublet of triplets; ddd = doublet of doublet of doublets; dddd = doublet of doublet of doublet of doublets; ddt = doublet of doublet of triplets; ddq = doublet of doublet of quartets; br = broad; m = multiplet; app t = apparent triplet; app q = apparent quartet; app p = apparent pentet. High resolution and low resolution mass spectra were recorded on a VG 7070 spectrometer. Infrared (IR) spectra were collected on a Mattson Gygnus 100 spectrometer. Analytical gas chromatography (GC) was performed using a Hewlett-Packard 6850 Series Gas Chromatograph fitted with a flame ionization detector. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Analytical thin layer chromatography (TLC) was performed on E. Merck pre-coated (25 nm) silica gel 60F-254 plates. Visualization was done under UV (254 nm). Flash column chromatography was preformed using ICN SiliTech 32-63 60Å silica gel. Reagent grade ethyl acetate and hexanes (commercial mixture) were purchased from EM Science and used as is for chromatography. Reagent grade methylene chloride (CH_2Cl_2) was distilled from CaH_2. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were dried by passing through aluminum drying column. Anhydrous methanol (CH_3OH), and acetonitrile (CH_3CN) were purchased from Aldrich and used as is. All reactions were conducted under argon or nitrogen atmosphere, unless otherwise specified.

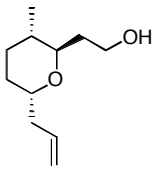


(5*S*,6*R*)-6-(2-(*tert*-Butyldimethylsilyloxy)ethyl)-5-methyltetrahydro-2*H*-pyran-2-ol (8).

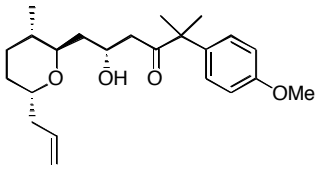
In a two neck round-bottom flask connected to a three way adapter were placed $[Rh(CO)_2acac]$ (42.2 mg, 0.164 mmol), 6-diphenylphosphanyl-2-pyridone (6-DPPon)[1] (229 mg, 0.818 mmol), and THF (5 mL). After stirring at room temperature for 10 min under an atmosphere of Ar gas, a solution of **7** (800 mg, 3.27 mmol) in THF (2.0 mL) was added. A CO balloon and a H_2 balloon were individually fitted into the three way adapter. The reaction mixture was saturated with a mixture of CO and H_2 gases applying three cycles of careful evacuation and refilling with a mixture of gases. The brown mixture was vigorously stirred at room temperature for 3 days. Then solvent was removed under a reduced pressure. The crude was purified by flash column chromatography on silica gel (1:10 to 1:4, EtOAc/Hexanes) to afford **8** (809 mg, 2.95 mmol, 90%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.27 (dd, *J* = 4.8, 2.7 Hz, 0.5H), 4.67 (ddd, *J* = 9.3, 5.7, 2.1 Hz, 0.5H), 3.78-3.67 (m, 2.5H), 3.20 (td, *J* = 9.6, 2.4 Hz, 0.5H), 2.79 (m, 0.5H), 2.33 (m, 0.5H), 1.93–1.23 (m, 7H), 0.89 (s, 9H), 0.86 (d, *J* = 6.3 Hz, 1.5H), 0.83 (d, *J* = 6.3 Hz, 1.5H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ

[1] B. Breit, W. Seiche, *J. Am. Chem. Soc.* **2003**, *125*, 6608.

96.3, 91.4, 78.2, 71.3, 59.8, 59.4, 36.2, 36.1, 35.0, 34.4, 33.3, 31.6, 30.2, 26.3, 26.0, 18.3, 18.1, 17.2, –5.22, –5.24, –5.27, –5.32; IR (neat): 3402 (br), 2954, 2929, 2857, 1472, 1462, 1256, 1087 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{14}H_{29}O_2Si$ $(M–OH)^+$ 257.1937 found 257.1945; $[\alpha]_D^{23}$ +56.2 (*c* 1.54, $CHCl_3$).



2-((2*R*,3*S*,6*S*)-6-Allyl-3-methyltetrahydro-2*H*-pyran-2-yl)ethanol (6). To a solution of **8** (3.00 g, 10.9 mmol) in acetonitrile (50 mL) was added allyltrimethylsilane (8.68 mL, 54.6 mmol). After stirring at room temperature for 5 min, bismuth(III) bromide (2.45 g, 5.45 mmol) was added with a portion. The clear yellow mixture was stirred at room temperature for 20 min. Aqueous saturated $NaHCO_3$ solution (20 mL) was then added. The resulting solution was stirred at same temperature for additional 20 min. The organic layer was extracted. The aqueous layer was reextracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (1:4 to 1:2, EtOAc/hexanes) gave **6** (2.00 g, 10.9 mmol, 99%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 5.81 (m, 1H), 5.10 (m, 2H), 3.96 (m, 1H), 3.73 (m, 2H), 3.45 (td, *J* = 9.0, 3.0 Hz, 1H), 2.95 (m, 1H), 2.60 (m, 1H), 2.17 (m, 1H), 1.85-1.32 (m, 7H), 0.87 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.3, 116.8, 76.4, 71.6, 61.6, 35.7, 34.8, 34.7, 27.7, 26.9, 18.0; IR (neat): 3421 (br), 3075, 2930, 2873, 1459, 1439, 1379, 1355, 1236, 1053 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{11}H_{21}O_2$ $(M+H)^+$ 185.1541 found 185.1537; $[\alpha]_D^{23}$ +45.7 (*c* 1.64, $CHCl_3$).



(*S*)-6-((2*S*,3*R*,6*R*)-6-Allyl-3-methyltetrahydro-2*H*-pyran-2-yl)-5-hydroxy-2-(4-methoxyphenyl)-2-methylhexan-3-one (10). To a solution of **6** (413 mg, 2.24 mmol) in CH_2Cl_2 (5 mL) was added pyridine (0.73 mL, 9.02 mmol) followed by the addition of Dess-Martin periodinane (1.90 g, 4.48 mmol) at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 30 min. The reaction was quenched with a mixture of aqueous saturated $Na_2S_2O_3$ solution and aqueous saturated $NaHCO_3$ solution (*v*/*v* 1:5, 20 mL). The resulting milky solution was then stirred vigorously until the solution became clear (ca. 30 min). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 times). The combined organic layers were washed with aqueous saturated NH_4Cl solution and then brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Without further purification, the resulting residue was dissolved in CH_2Cl_2. To a cooled solution of the crude aldehyde in CH_2Cl_2 at –78 °C was added freshly distilled $BF_3{\cdot}OEt_2$ (0.43 mL, 3.4 mmol) dropwise followed by the addition of enolsilane **9**[2] (1.18 g, 4.46 mmol) dropwise. The reaction mixture was then stirred at –78 °C for 2 h and quenched with aqueous saturated NH_4Cl. The resulting mixture was warmed to room temperature. The mixture was then poured into water. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 times). The combined organic layers were washed with water and then brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified *via* flash chromatography on silica gel (1:4, EtOAc/hexanes) to provide ketone **10** (658 mg, 1.76 mmol, 78% over two steps) as an inseparable 4.5:1 mixture of diastereomers. ^1H NMR (300 MHz, $CDCl_3$): δ 7.16 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0, 2H), 5.76 (m, 1H), 5.05 (m, 2H), 4.17 (m, 1H), 3.83 (m, 1H), 3.79 (s, 3H), 3.39 (td, *J* = 8.6, 2.7 Hz, 1H), 2.45 (m, 1H), 2.40 (m, 2H), 2.13 (m, 1H), 1.69 (m, 1H), 1.60-1.25 (m, 6H), 1.48 (s, 3H), 1.43 (s, 3H), 0.83 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 213.7, 158.5, 135.6, 127.2, 116.5, 114.1, 72.7, 71.7, 65.0, 55.2, 51.5, 44.3, 38.7, 35.6, 34.5, 27.6, 26.9, 25.4, 24.8, 18.0; ^{13}C NMR (75 MHz, C_6D_6): δ 212.7, 159.0, 136.22, 136.19, 127.5, 116.4, 114.4, 73.0, 71.6, 65.4, 54.7, 51.7, 45.0, 39.5, 36.1, 34.7, 27.9, 27.2, 25.6, 24.9, 18.1; IR (neat): 3489 (br), 2932, 1702, 1513, 1463, 1253, 1035 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{23}H_{34}O_4$ $(M)^+$ 374.2457 found 374.2445.

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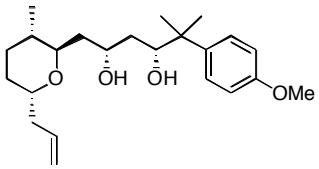
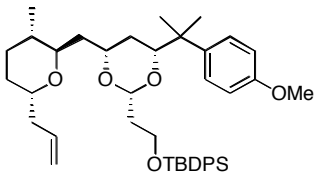
[2] A. Jönsson, *Acta Chim. Scand.* **1954**, *8*, 1206.



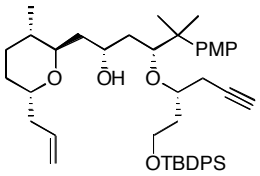
(2*S*,4*R*)-1-((2*R*,3*S*,6*S*)-6-Allyl-3-methyltetrahydro-2*H*-pyran-2-yl)-5-(4-methoxyphenyl)-5-methylhexane-2,4-diol (11).

To a solution of **10** (1.65 g, 4.40 mmol) in THF/CH_3OH (*v*/*v* 10:1, 55 mL) at –78 °C was added Et_2BOMe (0.87 mL, 6.6 mmol) dropwise. The clear solution was stirred at the same temperature for 1 h and $NaBH_4$ (501 mg, 13.2 mmol) was then added with several portions. The reaction mixture was stirred at –78 °C for 1 h and poured into an ice-cooled pH 7 buffer solution (100 mL) with caution (bubbling and eruption). After stirring at 0 °C for 30 min, hydrogen peroxide (wt. 30% solution in water, 10 mL) was added dropwise. The resulting mixture was vigorously stirred at room temperature overnight (*ca.* 10 h). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 times). The combined organic layers were washed with water, aqueous saturated Na_2SO_3 solution and then brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified *via* flash column chromatography (1:4, EtOAc/hexanes) to afford **11** (1.27 g, 3.37 mmol, 76%) as a single stereoisomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 9.0, 2H), 5.81 (m, 1H), 5.09 (m, 2H), 3.97 (m, 2H), 3.87 (m, 1H), 3.78 (s, 3H), 3.75 (s, 1H), 3.60 (s, 1H), 3.40 (td, *J* = 8.7, 3.0 Hz, 1H), 2.57 (m, 1H), 2.13 (m, 1H), 1.78 (m, 1H), 1.66-1.30 (m, 8H), 1.31 (s, 3H), 1.29 (s, 3H), 0.81 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.6, 139.4, 136.0, 127.5, 116.8, 113.4, 80.2, 72.3, 71.9, 70.0, 55.2, 41.6, 39.9, 37.3, 35.2, 35.0, 27.9, 27.0, 25.2, 23.1, 17.9; IR (neat): 3444 (br), 3074, 2931, 1641, 1611, 1513, 1251, 1185 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{36}O_4Na$ $(M+Na)^+$ 399.2511 found 399.2530; $[\alpha]_D^{23}$ +33.2 (*c* 1.49, $CHCl_3$).



(2-((2*R*,4*R*,6*R*)-4-(((2*R*,3*S*,6*S*)-6-Allyl-3-methyltetrahydro-2*H*-pyran-2-yl)methyl)-6-(2-(4-methoxyphenyl)propan-2-yl)-1,3-dioxan-2-yl)ethoxy)(*tert*-butyl)diphenylsilane (13).

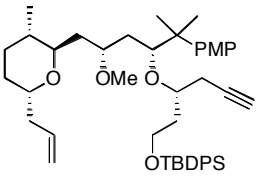
To a cooled solution of diol **11** (1.32 g, 3.50 mmol) in CH_2Cl_2 (35 mL) at –78 °C was added 2,6-lutidine (1.63 mL, 14.0 mmol) followed by the dropwise addition of TMSOTf (1.59 mL, 8.76 mmol). The reaction mixture was stirred at –78 °C for 2 h and poured into water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 times). The combined organic layers were washed with HCl (wt. 10% solution in water), water and then brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Without further purification, the resulting residue was dissolved in CH_2Cl_2 (20 mL) and cooled down to –78 °C. Aldehyde **12** (1.31 g, 4.21 mmol) was added followed by the addition of TMSOTf (64 μL, 0.35 mmol). The reaction mixture was then slowly warmed to –45 °C and stirred for 2 h. The reaction was quenched with pyridine (43 μL, 0.52 mmol) and poured into water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 times). The combined organic layers were washed with water and then brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified *via* flash column chromatography (1:20, EtOAc/hexanes) to afford **13** (2.05 g, 3.05 mmol, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (m, 4H), 7.40 (m, 6H), 7.23 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0, 2H), 5.72 (m, 1H), 5.01 (m, 2H), 4.69 (dd, *J* = 6.6, 4.2 Hz, 1H), 3.85-3.65 (m, 4H), 3.77 (s, 3H), 3.52 (m, 1H), 3.42 (app t, *J* = 8.2 Hz, 1H), 2.49 (m, 1H), 2.08-1.82 (m, 3H), 1.73-1.55 (m, 3H), 1.46 (m, 1H), 1.34-1.27 (m, 3H), 1.28 (s, 3H), 1.26 (s, 3H), 1.07 (m, 2H), 1.05 (s, 9H), 0.84 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.6, 138.7, 135.54, 135.52, 135.47, 134.02, 133.99, 129.5, 127.7, 127.6, 116.4, 113.1, 99.1, 83.8, 72.9, 71.6, 71.2, 59.9, 55.1, 40.5, 39.6, 38.1, 35.9, 34.7, 32.2, 27.9, 27.1, 26.9, 26.1, 22.8, 19.2, 18.1; IR (neat): 3071, 2930, 1641, 1612, 1513, 1361, 1251, 1185 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{42}H_{58}O_5SiNa$ $(M+Na)^+$ 693.3951 found 693.3951; $[\alpha]_D^{23}$ +24.6 (*c* 1.71, $CHCl_3$).



(2*R*,4*R*)-1-((2*R*,3*S*,6*S*)-6-Allyl-3-methyltetrahydro-2*H*-pyran-2-yl)-4-((*R*)-1-(*tert*-butyldiphenylsilyloxy)hex-5-yn-3-yloxy)-5-(4-methoxyphenyl)-5-methylhexan-2-ol (14).

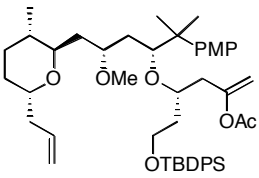
To a cooled solution of acetal **13** (200 mg, 0.298 mmol) and allenyltributyltin (294 mg, 0.894 mmol) in CH_2Cl_2 (3 mL) at –78 °C was added a freshly prepared

mixture of $TiCl_4$ (286 μL, 2.61 mmol) and $Ti(O^iPr)_4$ (260 μL, 0.89 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at same temperature for 1 h and quenched with CH_3OH. The resulting mixture was poured into aqueous saturated $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 times). The combined organic layers were washed with water and KF (wt. 10% solution in water), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was then purified *via* flash column chromatography (1:20 to 1:10, EtOAc/hexanes) to give **14** (188 mg, 0.265 mmol, 89%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (m, 4H), 7.40 (m, 6H), 7.27 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0, 2H), 5.74 (m, 1H), 5.02 (m, 2H), 3.83-3.72 (m, 3H), 3.75 (s, 3H), 3.68 (m, 2H), 3.33 (m, 2H), 3.17 (d, *J* = 3.0 Hz, 1H), 2.45 (m, 1H), 2.39 (ddd, *J* = 16.5, 5.7, 3.0 Hz, 1H), 2.29 (ddd, *J* = 16.5, 3.6, 3.0 Hz, 1H), 2.07 (m, 1H), 1.96 (t, *J* = 2.6 Hz, 1H), 1.91 (app q, *J* = 6.3 Hz, 2H), 1.67 (m, 1H), 1.57-1.23 (m, 8H), 1.33 (s, 3H), 1.26 (s, 3H), 1.04 (s, 9H), 0.72 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.6, 139.7, 135.8, 135.6, 135.5, 133.9, 129.5, 127.7, 127.63, 127.61, 116.4, 113.2, 81.7, 81.5, 72.8, 71.8, 71.6, 70.1, 66.7, 60.6, 55.1, 42.2, 39.6, 39.5, 36.3, 35.4, 34.1, 27.8, 27.0, 26.9, 26.7, 23.2, 22.9, 19.2, 18.0; IR (neat): 3497 (br), 3309, 3071, 3031, 2118, 1611, 1513, 1428, 1251, 1098 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{45}H_{62}O_5SiNa$ $(M+Na)^+$ 733.4264 found 733.4268.



((*R*)-3-((3*R*,5*R*)-6-((2*R*,3*S*,6*S*)-6-Allyl-3-methyltetrahydro-2*H*-pyran-2-yl)-5-methoxy-2-(4-methoxyphenyl)-2-methylhexan-3-yloxy)hex-5-ynyloxy)(*tert*-butyl)diphenylsilane.

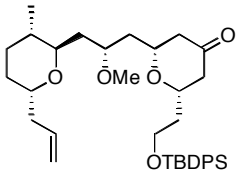
To a solution of alcohol **14** (369 mg, 0.519 mmol) in CH_2Cl_2 (4 mL) at 0 °C was added 2,6-di-*tert*-butylpyridine (459 mg, 2.08 mmol) followed by the addition of MeOTf (176 μL, 1.56 mmol). The reaction was then slowly warmed to room temperature and stirred for 24 h. The reaction was quenched with aqueous saturated $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 times). The combined organic layers were washed with water and then brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Flash chromatography on silica gel (1:20 to 1:10, EtOAc/hexanes) afforded the desired product (329 mg, 0.454 mmol, 87%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (m, 4H), 7.38 (m, 6H), 7.26 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0, 2H), 5.72 (m, 1H), 5.01 (m, 2H), 3.78 (m, 3H), 3.76 (s, 3H), 3.67 (m, 1H), 3.41 (app t, *J* = 4.6 Hz, 1H), 3.24 (m, 1H), 3.16 (s, 3H), 2.94 (m, 1H), 2.41-2.27 (m, 3H), 2.17 (m, 1H), 1.95 (t, *J* = 2.6 Hz, 1H), 1.92 (m, 2H), 1.60-1.15 (m, 9H), 1.31 (s, 3H), 1.26 (s, 3H), 1.05 (s, 9H), 0.82 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.6, 139.6, 135.7, 135.6, 135.5, 134.0, 129.5, 127.9, 127.6, 116.3, 113.1, 81.9, 80.3, 72.8, 71.8, 70.9, 69.8, 60.9, 57.2, 55.1, 42.3, 38.5, 37.8, 37.2, 36.9, 34.0, 27.1, 26.9, 26.7, 26.5, 23.1, 23.0, 19.2, 18.2; IR (neat): 3309, 3071, 2930, 2119, 1611, 1513, 1428, 1251, 1111 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{46}H_{64}O_5SiNa$ $(M+Na)^+$ 747.4421 found 747.4431.



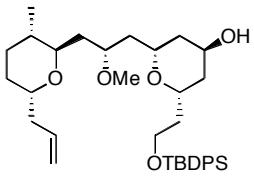
(*S*)-4-((3*R*,5*R*)-6-((2*R*,3*S*,6*S*)-6-Allyl-3-methyl-tetrahydro-2*H*-pyran-2-yl)-5-methoxy-2-(4-methoxyphenyl)-2-methylhexan-3-yloxy)-6-(*tert*-butyldiphenylsilyloxy)hex-1-en-2-yl acetate.

To a solution of the alkyne (316 mg, 0.435 mmol) in toluene (10 mL) was added Na_2CO_3 (7.0 mg, 66 μmol) followed by the addition of acetic acid (50 μL, 0.87 mmol) under an atmosphere of Ar gas. The mixture was stirred at room temperature for 10 min, and $[Ru(p\text{-cymene})Cl_2]_2$ (5.3 mg, 8.7 μmol), tri(2-furyl)phosphine (4.0 mg, 17 μmol). The brown reaction mixture was stirred at 80 °C for 36 h. The color of reaction was slowly changed to green over 6 h. The mixture was cooled to room temperature and the solvent was then removed under reduced pressure. The resulting residue was purified *via* flash column chromatography (1:20 to 1:10, EtOAc/hexanes) to give **15** (245 mg, 0.312 mmol, 72%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (m, 4H), 7.37 (m, 6H), 7.25 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7, 2H), 5.71 (m, 1H), 5.01 (m, 2H), 4.78 (s, 1H), 4.73 (s, 1H), 3.77 (m, 3H), 3.76 (s, 3H), 3.67 (m, 1H), 3.39 (app t, *J* = 4.6 Hz, 1H), 3.22 (m, 1H), 3.15 (s, 3H), 2.90 (m, 1H), 2.55 (dd, *J* = 14.7, 4.2 Hz, 1H), 2.33 (m, 1H), 2.23-2.05 (m, 2H), 2.11 (s, 3H), 1.90-1.71 (m, 2H), 1.60-1.15 (m, 9H), 1.28 (s, 3H), 1.24 (s, 3H), 1.05 (s, 9H), 0.80 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz,

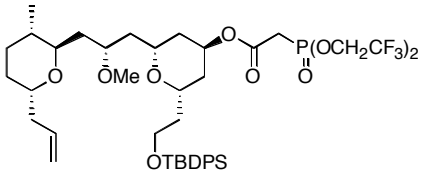
$CDCl_3$): δ 169.1, 157.6, 153.7, 139.7, 135.7, 135.6, 135.5, 134.0, 129.50, 129.48, 127.9, 127.6, 116.3, 113.1, 103.51, 80.0, 76.4, 72.6, 71.0, 60.8, 57.2, 55.1, 42.3, 38.7, 37.9, 37.7, 37.1, 36.7, 34.2, 27.0, 26.9, 26.7, 26.6, 23.0, 21.1, 19.2, 18.2; IR (neat): 3071, 2931, 2858, 1757, 1665, 1513, 1428, 1368, 1200, 1109 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{48}H_{68}O_7SiNa$ $(M+Na)^+$ 807.4632 found 807.4608; $[\alpha]_D^{23}$ +2.82 (*c* 1.42, $CHCl_3$).



(2*R*,6*S*)-2-((*S*)-3-((2*R*,3*S*,6*S*)-6-Allyl-3-methyltetrahydro-2*H*-pyran-2-yl)-2-methoxypropyl)-6-(2-(*tert*-butyldiphenylsilyloxy)ethyl)tetrahydropyran-4-one.
To a solution of enol acetate **15** (236 mg, 0.301 mmol) in 1,2-dichloroethane (6 mL) was added $NaHCO_3$ (472 mg) and 4 Å molecular sieves (472 mg). After stirring at room temperature for 20 min, a dark orange colored solution of ceric ammonium nitrate (CAN) (659 mg, 1.20 mmol) in acetonitrile (1 mL) was added dropwise. The dull green colored reaction mixture was stirred at room temperature for an additional 2 h. The resulting mixture was filtered through a small silica plug and washed with EtOAc. The filtrate was then concentrated under reduced pressure and the residue was purified *via* flash column chromatography (1:10 to 1:4, EtOAc/hexanes) to provide **17** (121 mg, 0.204 mmol, 68%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (app d, *J* = 7.2 Hz, 4H), 7.40 (m, 6H), 5.78 (m, 1H), 5.05 (m, 2H), 3.87-3.68 (m, 5H), 3.56-3.44 (m, 2H), 3.30 (s, 3H), 2.48-2.34 (m, 3H), 2.30-2.16 (m, 3H), 1.98-1.84 (m, 2H), 1.81-1.44 (m, 7H), 1.40-1.23 (m, 2H), 1.03 (s, 9H), 0.89 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.4, 135.6, 135.5, 133.7, 133.6, 129.63, 129.62, 127.7, 116.4, 74.3, 73.91, 73.87, 72.6, 71.2, 60.1, 56.8, 48.1, 47.8, 40.6, 39.3, 38.6, 36.8, 34.2, 27.3, 26.8, 26.6, 19.1, 18.3; IR (neat): 3071, 2929, 2857, 1720, 1460, 1427, 1147, 1109, 1090 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{36}H_{52}O_5SiNa$ $(M+Na)^+$ 615.3482 found 615.3455; $[\alpha]_D^{23}$ +22.2 (*c* 2.00, $CHCl_3$).

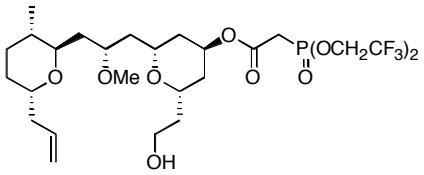


(2*S*,4*S*,6*S*)-2-((*S*)-3-((2*S*,3*S*,6*S*)-6-Allyl-3-methyltetrahydro-2*H*-pyran-2-yl)-2-methoxypropyl)-6-(2-(*tert*-butyldiphenylsilyloxy)ethyl)tetrahydro-2*H*-pyran-4-ol.
To a cooled solution of ketone **17** (349 mg, 0.589 mmol) in THF (30 mL) at –90 °C was slowly added L-Selectride® (1.0 M solution in THF, 0.88 mL, 0.88 mmol) over 5 min. The reaction mixture was stirred at –90 °C for 1 h and quenched with aqueous saturated potassium sodium tartrate solution (30 mL). The solution was allowed to warm to room temperature. Diethyl ether (30 mL) was added and the resulting mixture was vigorously stirred for 1 h. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 times). The combined organic layers were washed with water and then brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel (1:2, EtOAc/hexanes) to afford **18** (266 mg, 0.447 mmol, 76%) and the epimer (30 mg, 0.050 mmol, 8%). **S**^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (m, 4H), 7.38 (m, 6H), 5.79 (m, 1H), 5.04 (m, 2H), 4.20 (m, 1H), 3.95-3.81 (m, 2H), 3.79 (t, *J* = 6.6 Hz, 2H), 3.74 (m, 1H), 3.52 (m, 2H), 3.30 (s, 3H), 2.40 (m, 1H), 2.21 (m, 1H), 1.86-1.25 (m, 15H), 1.05 (s, 9H), 0.91 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.7, 135.5, 134.1, 134.0, 129.5, 127.6, 116.3, 74.4, 72.7, 70.8, 68.6, 68.4, 64.8, 60.8, 56.8, 40.4, 39.3, 39.0, 38.7, 38.5, 37.2, 33.9, 27.1, 26.9, 26.5, 19.2, 18.4; IR (neat): 3436 (br), 3071, 2931, 2858, 1460, 1428, 1109 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{36}H_{54}O_5SiNa$ $(M+Na)^+$ 617.3638 found 617.3591; $[\alpha]_D^{23}$ +25.8 (*c* 2.05, $CHCl_3$).



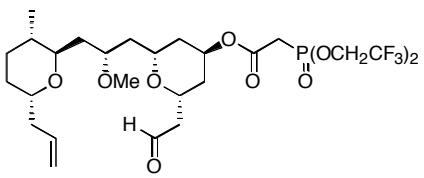
(2*R*,4*S*,6*S*)-2-((*S*)-3-((2*R*,3*S*,6*S*)-6-Allyl-3-methyltetrahydro-2*H*-pyran-2-yl)-2-methoxypropyl)-6-(2-(*tert*-butyldiphenylsilyloxy)ethyl)tetrahydro-2*H*-pyran-4-yl 2-((bis(2,2,2-trifluoroethoxy))phosphoryl)acetate.

To a mixture of alcohol **18** (80.1 mg, 0.135 mmol) and bis-(2,2,2-trifluoroethyl)phosphonoacetic acid[3] (82 mg, 0.27 mmol) in CH_2Cl_2 (10 mL) were added $HOBt{\cdot}H_2O$ (9.1 mg, 0.067 mmol) and then EDC·HCl (51.6 mg, 0.269 mmol). The reaction mixture was stirred at room temperature for 1.5 h and quenched with aqueous saturated $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 times). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified *via* flash chromatography on silica gel (1:3, EtOAc/hexanes) to afford **19** (109 mg, 0.124 mmol, 92%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (m, 4H), 7.39 (m, 6H), 5.77 (m, 1H), 5.24 (m, 1H), 5.04 (m, 2H), 4.47 (qd, $^3J(^1H,^{19}F)$ = 8.1 Hz, $^3J(^1H,^{31}P)$ = 3.6 Hz, 2H), 4.44 (qd, $^3J(^1H,^{19}F)$ = 8.1 Hz, $^3J(^1H,^{31}P)$ = 3.6 Hz, 2H), 3.77 (m, 5H), 3.49 (m, 2H), 3.27 (s, 3H), 3.15 (d, $^2J(^1H,^{31}P)$ = 21.0 Hz, 1H), 3.14 (d, $^2J(^1H,^{31}P)$ = 21.0 Hz, 1H), 2.40 (m, 1H), 2.21 (m, 1H), 1.85-1.44 (m, 13H), 1.29 (m, 2H), 1.03 (s, 9H), 0.88 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.1 (d, $^2J(^{13}C,^{31}P)$ = 4 Hz), 135.7, 135.5, 133.94, 133.89, 129.6, 127.6, 122.5 (q, $^1J(^{13}C,^{19}F)$ = 274 Hz), 122.4 (q, $^1J(^{13}C,^{19}F)$ = 274 Hz), 116.3, 74.4, 72.5, 71.0, 70.8, 69.2, 68.9, 62.6 (qm, $^2J(^{13}C,^{19}F)$ = 37 Hz), 62.5 (qm, $^2J(^{13}C,^{19}F)$ = 37 Hz), 60.6, 56.7, 40.1, 39.0, 38.5, 36.9, 35.7, 35.3, 34.2 (d, $^1J(^{13}C,^{31}P)$ = 143 Hz), 34.1, 27.2, 26.8, 26.6, 19.2, 18.3; IR (neat): 3072, 2931, 2858, 1737, 1460, 1427, 1299, 1269, 1175, 1101 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{42}H_{59}O_9F_6PSiNa$ $(M+Na)^+$ 903.3468 found 903.3495; $[\alpha]_D^{23}$ 17.0 (*c* 2.56, $CHCl_3$).



(2*R*,4*S*,6*S*)-2-((*S*)-3-((2*R*,3*S*,6*S*)-6-Allyl-3-methyltetrahydro-2*H*-pyran-2-yl)-2-methoxypropyl)-6-(2-hydroxyethyl)tetrahydro-2*H*-pyran-4-yl 2-((bis(2,2,2-trifluoroethoxy))phosphoryl)acetate.

A solution of **19** (108 mg, 0.122 mmol) in 3% HCl in CH_3OH (10 mL) was stirred at room temperature for 2 h. The reaction was quenched with aqueous saturated $NaHCO_3$. After adding EtOAc, the organic layer was separated and the aqueous layer was extracted with EtOAc (2 times). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified *via* flash chromatography on silica gel (1:1, EtOAc/hexanes) to give alcohol (77 mg, 0.12 mmol, 98%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.80 (m, 1H), 5.25 (m, 1H), 5.07 (m, 2H), 4.48 (q, $^3J(^1H,^{19}F)$ = 8.1 Hz, 2H), 4.45 (q, $^3J(^1H,^{19}F)$ = 8.1 Hz, 2H), 3.96-3.79 (m, 3H), 3.73-3.60 (m, 3H), 3.48 (tm, *J* = 8.1 Hz, 1H), 3.35 (br s, 1H), 3.32 (s, 3H), 3.19 (d, $^2J(^1H,^{31}P)$ = 21.3 Hz, 2H), 2.56 (m, 1H), 2.20 (m, 1H), 1.90 (m, 1H), 1.81-1.47 (m, 11H), 1.34 (m, 3H), 0.88 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.9 (d, $^2J(^{13}C,^{31}P)$ = 5 Hz), 135.6, 122.4 (q, $^1J(^{13}C,^{19}F)$ = 275 Hz), 122.3 (q, $^1J(^{13}C,^{19}F)$ = 275 Hz), 116.5, 74.2, 72.1, 71.9, 70.6, 70.1, 69.6, 62.6 (qm, $^2J(^{13}C,^{19}F)$ = 37 Hz), 62.5 (qm, $^2J(^{13}C,^{19}F)$ = 37 Hz), 58.6, 56.6, 38.9, 37.9, 37.5, 35.8, 35.6, 35.4, 35.1, 34.4 (d, $^1J(^{13}C,^{31}P)$ = 143 Hz), 27.8, 27.1, 18.2; IR (neat): 3467 (br), 2927, 2858, 1737, 1459, 1269, 1174, 1073 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{26}H_{41}O_9F_6PNa$ $(M+Na)^+$ 665.2290 found 665.2281; $[\alpha]_D^{23}$ +25.3 (*c* 1.70, $CHCl_3$).



(2*R*,4*R*,6*R*)-2-((*S*)-3-((2*R*,3*S*,6*S*)-6-Allyl-3-methyltetrahydro-2*H*-pyran-2-yl)-2-methoxypropyl)-6-(2-oxoethyl)tetrahydro-2*H*-pyran-4-yl 2-((bis(2,2,2-trifluoroethoxy))phosphoryl)acetate.

To a solution of alcohol (100 mg, 0.156 mmol) in CH_2Cl_2 was added pyridine (50 μL, 0.62 mmol) followed by the addition of Dess-Martin periodinane (132 mg, 0.311 mmol). The reaction mixture was stirred at room temperature for 2 h. The mixture was filtered through a short silica plug and washed with EtOAc.

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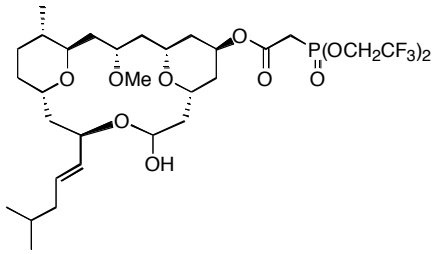
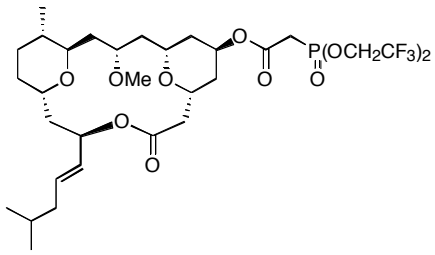
[3] A. K. Ghosh, Y. Wang, J. T. Kim, *J. Org. Chem.* **2001**, *66*, 8973 .

The filtrate was concentrated. The crude was purified *via* flash chromatography on silica gel (1:1, EtOAc/hexanes) to afford **20** (95 mg, 0.148 mmol, 95%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.77 (dd, *J* = 1.8, 2.7 Hz, 1H), 5.81 (m, 1H), 5.27 (m, 1H), 5.06 (m, 2H), 4.50 (qd, $^3J(^1H,^{19}F)$ = 8.1 Hz, $^3J(^1H,^{31}P)$ = 1.2 Hz, 2H), 4.47 (qd, $^3J(^1H,^{19}F)$ = 8.1 Hz, $^3J(^1H,^{31}P)$ = 1.2 Hz, 2H), 4.22 (m, 1H), 3.82 (m, 2H), 3.51 (m, 2H), 3.29 (s, 3H), 3.20 (d, $^2J(^1H,^{31}P)$ = 21.3 Hz, 2H), 2.55 (ddd, *J* = 16.2, 8.4, 2.7 Hz, 1H), 2.51-2.41 (m, 1H), 2.39 (ddd, *J* = 16.2, 4.5, 1.8 Hz, 1H), 2.28-2.17 (m, 1H), 1.87-1.47 (m, 11H), 1.35 (m, 2H), 0.93 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.8, 163.8 (d, $^2J(^{13}C,^{31}P)$ = 5 Hz), 135.7, 122.4 (q, $^1J(^{13}C,^{19}F)$ = 276 Hz), 122.3 (q, $^1J(^{13}C,^{19}F)$ = 276 Hz), 116.3, 74.3, 72.5, 71.2, 70.1, 69.2, 67.6, 62.6 (qd, $^2J(^{13}C,^{19}F)$ = 37 Hz, $^2J(^{13}C,^{31}P)$ = 2 Hz), 62.5 (qd, $^2J(^{13}C,^{19}F)$ = 37 Hz, $^2J(^{13}C,^{31}P)$ = 2 Hz), 56.6, 49.3, 39.6, 38.5, 36.7, 35.4, 34.9, 34.4 (d, $^1J(^{13}C,^{31}P)$ = 142 Hz), 34.3, 27.4, 26.7, 18.3; IR (neat): 2928, 2876, 1731, 1420, 1299, 1270, 1174, 1074 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{26}H_{39}O_9F_6PNa$ $(M+Na)^+$ 663.2134 found 663.2106; $[\alpha]_D^{23}$ +25.1 (*c* 1.60, $CHCl_3$).



Macrocyclic lactol 23.

To a solution of alkene **20** (20 mg, 31 μmol) and (*S*)-5-methylhex-1-en-3-ol[4] (18 mg, 160 μmol) in CH_2Cl_2 (3 mL) was added Hoveyda-Grubbs (2nd generation) (3.9 mg, 6.2 μmol) followed by the addition of 1,4-benzoquinone (1.3 mg, 12 μmol). The flask was fitted with a condenser and refluxed at 45 °C for 6 h under an atmosphere of N_2 gas. The greenish crude mixture was then concentrated under reduced pressure and purified by flash chromatography on silica gel (1:1 to 2:1, EtOAc/hexanes) to give **22** (15.9 mg, 21.9 μmol, 70%) as a colorless oil that was used directly for the next reaction. To a solution of allylic alcohol **22** (14.5 mg, 19.9 μmol) in diethyl ether (2 mL) was added Re_2O_7 (0.9 mg, 2 μmol). The reaction mixture was stirred at room temperature for 2.5 h and then concentrated under reduced pressure. The resulting residue was purified *via* flash chromatography on silica gel (1:2 to 1:1, EtOAc/hexanes) to give **23** (10 mg, 14 μmol, 69%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.73 (dt, *J* = 15.3, 7.2 Hz, 1H), 5.26 (m, 1H), 5.10 (dd, *J* = 15.3, 8.7 Hz, 1H), 4.92 (dm, *J* = 10.2 Hz, 1H), 4.70 (m, 1H), 4.47 (q, $^3J(^1H,^{19}F)$ = 8.1 Hz, 2H), 4.44 (q, $^3J(^1H,^{19}F)$ = 8.1 Hz, 2H), 4.25 (m, 1H), 3.94 (dm, *J* = 11.4 Hz, 1H), 3.83 (m, 1H), 3.74 (tm, *J* = 11.7 Hz, 1H), 3.65 (tm, *J* = 11.7 Hz, 1H), 3.37 (s, 3H), 3.22 (d, $^2J(^1H,^{31}P)$ = 21.0 Hz, 1H), 3.21 (d, $^2J(^1H,^{31}P)$ = 21.0 Hz, 1H), 2.55 (ddm, *J* = 14.1, 12.6 Hz, 1H), 2.02_1.36 (m, 18H), 1.19 (d, *J* = 7.2 Hz, 3H), 1.05 (ddd, *J* = 14.1, 11.0, 2.1 Hz, 1H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): _ 163.8 (d, $^2J(^{13}C,^{31}P)$ = 5 Hz), 134.1, 130.7, 122.4 (q, $^1J(^{13}C,^{19}F)$ = 276 Hz), 122.3 (q, $^1J(^{13}C,^{19}F)$ = 276 Hz), 90.94, 74.0, 73.8, 71.4, 70.7, 70.3, 68.8, 63.1, 62.6 (qd, $^2J(^{13}C,^{19}F)$ = 37 Hz, $^2J(^{13}C,^{31}P)$ = 2 Hz), 62.5 (qd, $^2J(^{13}C,^{19}F)$ = 37 Hz, $^2J(^{13}C,^{31}P)$ = 2 Hz), 57.1, 44.2, 41.7, 39.8, 38.7, 35.8, 35.6, 35.5, 34.4 (d, $^1J(^{13}C,^{31}P)$ = 142 Hz), 31.2, 28.1, 27.3, 24.2, 22.3, 22.2, 18.4; IR (neat): 3487 (br), 2927, 1740, 1457, 1271, 1173, 1097, 1075 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{31}H_{49}O_{10}F_6PNa$ $(M+Na)^+$ 749.2865 found 749.2833; $[\alpha]_D^{23}$ +39.3 (*c* 1.20, $CHCl_3$).



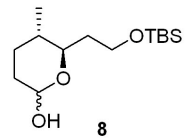
Macrocyclic lactone 24.

To a solution of lactol **23** (8.2 mg, 11 μmol) in CH_2Cl_2 (3 mL) was added 4 Å molecular sieves (8.2 mg). After gently stirring for 10 min, pyridinium chlorochromate (PCC) (4.9 mg, 23 μmol) was added with a portion. The resulting mixture was stirred at room temperature for 2 h and concentrated under reduced pressure. The resulting residue was purified *via* flash chromatography on silica gel (1:10 to 1:4, EtOAc/hexanes) to provide **24** (6.6 mg, 9.1 μmol, 81%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.70 (m, 1H), 5.37 (m, 1H), 5.36 (m, 1H), 5.27 (m, 1H), 4.46 (m, 4H), 4.01 (tm, *J* = 11.5 Hz, 1H), 3.89 (dm, *J* = 11.5 Hz, 1H), 3.61 (tm, *J* = 11.5 Hz, 2H), 3.53 (tm, *J* = 11.0 Hz,

[4] M. Bessodes, M. Saiah, K. Antonakis, *J. Org. Chem.* **1992**, *57*, 4441.

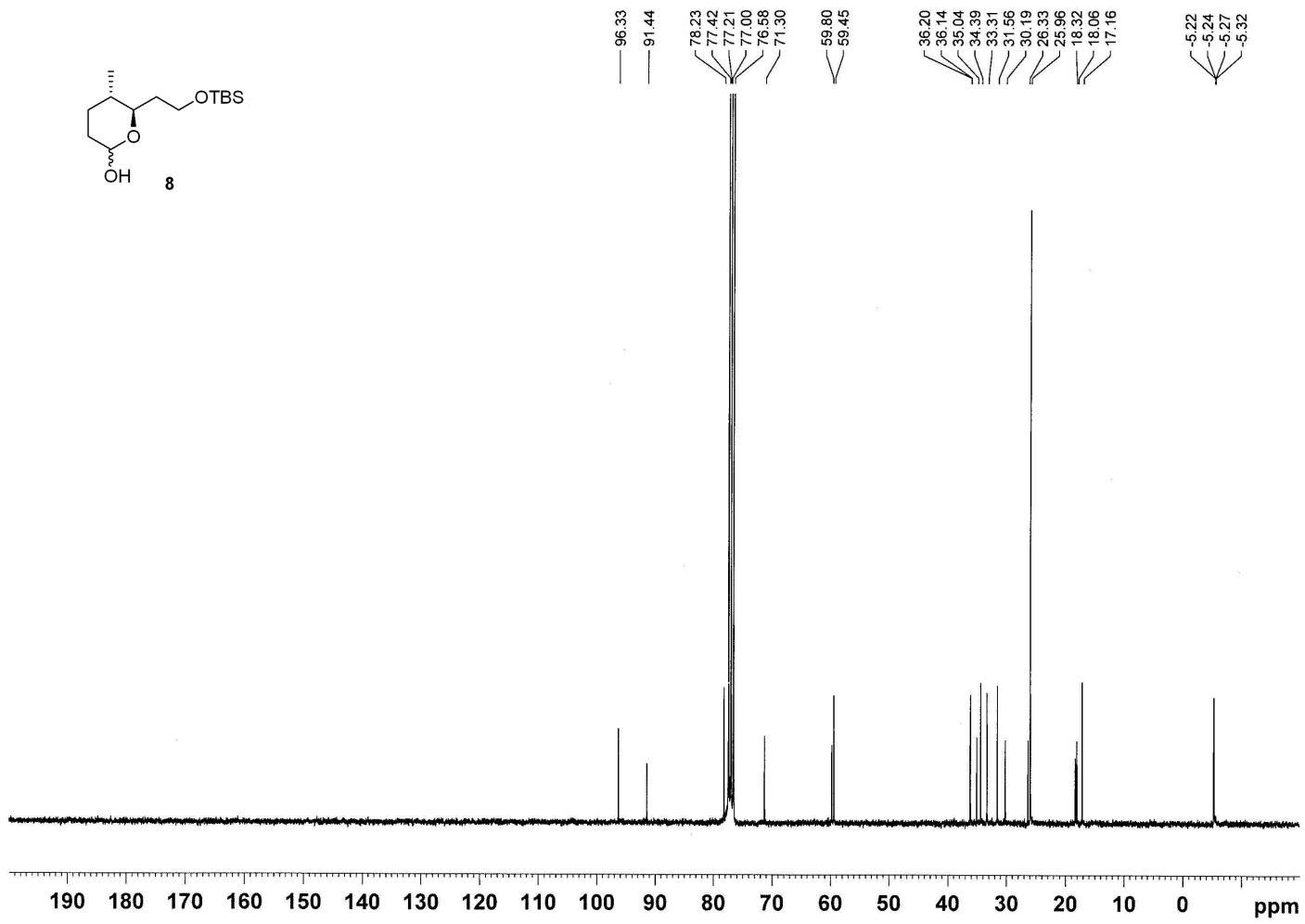
1H), 3.35 (s, 3H), 3.23 (d, $^{2}J(^{1}H,^{31}P)$ = 21.0 Hz, 1H), 3.22 (d, $^{2}J(^{1}H,^{31}P)$ = 21.0 Hz, 1H), 2.52 (dd, *J* = 13.0, 4.0 Hz, 1H), 2.45 (m, 1H), 2.31 (dd, *J* = 13.0, 12.0 Hz, 1H), 2.01-1.84 (m, 4H), 1.76-1.65 (m, 2H), 1.63-1.49 (m, 7H), 1.42 (dm, *J* = 13.0 Hz, 1H), 1.32 (dm, *J* = 13.0 Hz, 1H), 1.17 (d, *J* = 7.0 Hz, 3H), 1.01 (m, 1H), 0.85 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2, 163.7 (d, $^{2}J(^{13}C,^{31}P)$ = 5 Hz), 132.4, 130.1, 122.4 (q, $^{1}J(^{13}C,^{19}F)$ = 276 Hz), 122.3 (q, $^{1}J(^{13}C,^{19}F)$ = 276 Hz), 73.7, 73.3, 70.9, 70.4, 69.7, 69.3, 63.0, 62.6 (m), 62.5 (m), 57.3, 43.2, 42.8, 41.6, 39.1, 35.5, 35.2, 35.1, 34.4 (d, $^{1}J(^{13}C,^{31}P)$ = 142 Hz), 31.0, 28.1, 27.2, 24.0, 22.2, 18.3; IR (neat): 2927, 1739, 1459, 1271, 1171, 1073 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{31}H_{47}O_{10}F_6PNa$ $(M+Na)^+$ 747.2709 found 747.2685; $[\alpha]_D^{23}$ +40 (*c* 0.67, $CHCl_3$).

HHJ-3-106 02-17-07

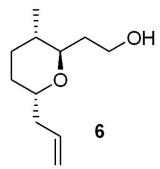


8

HHJ-3-106 02-17-07

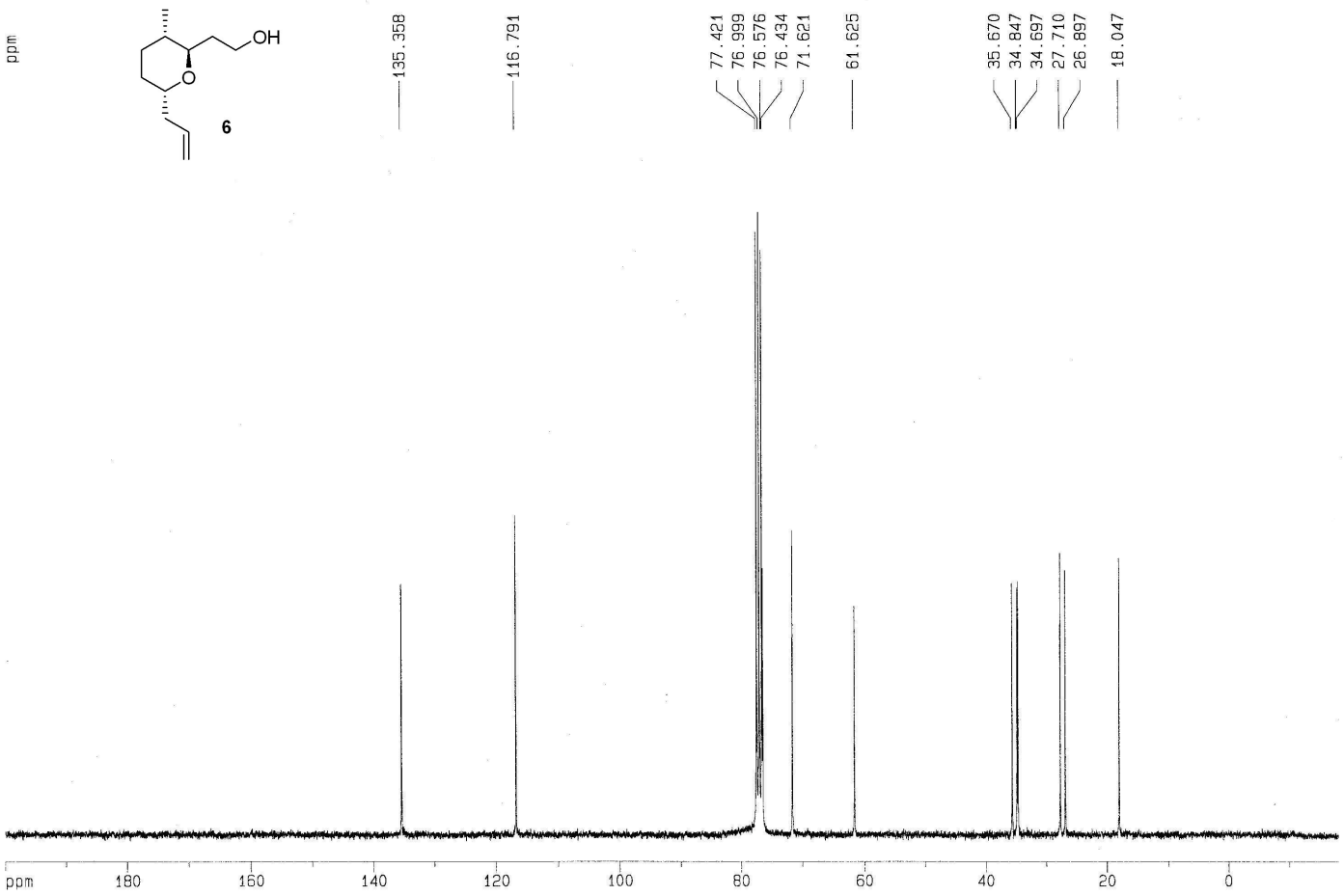


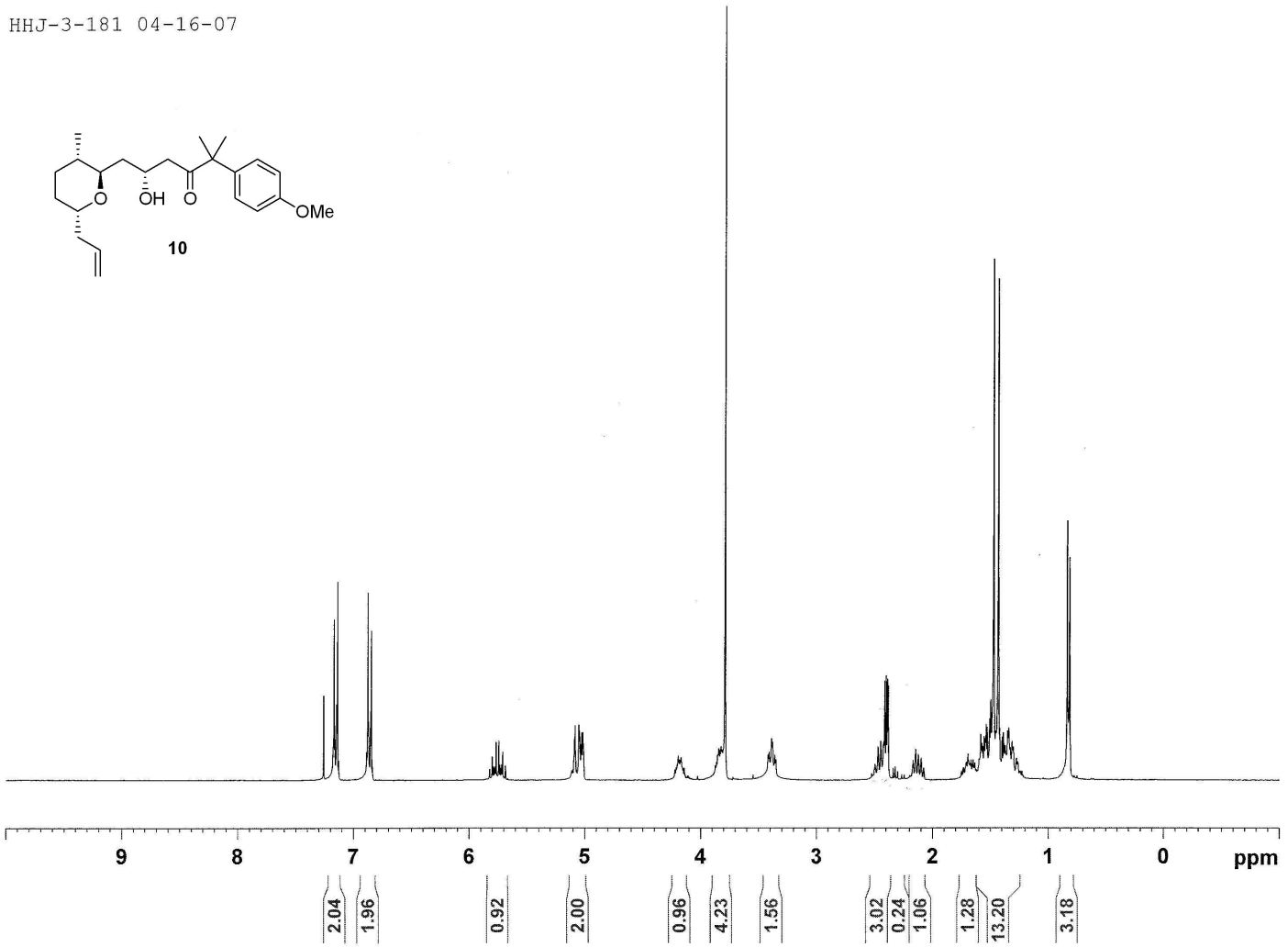
HHJ-3-125 03-02-07



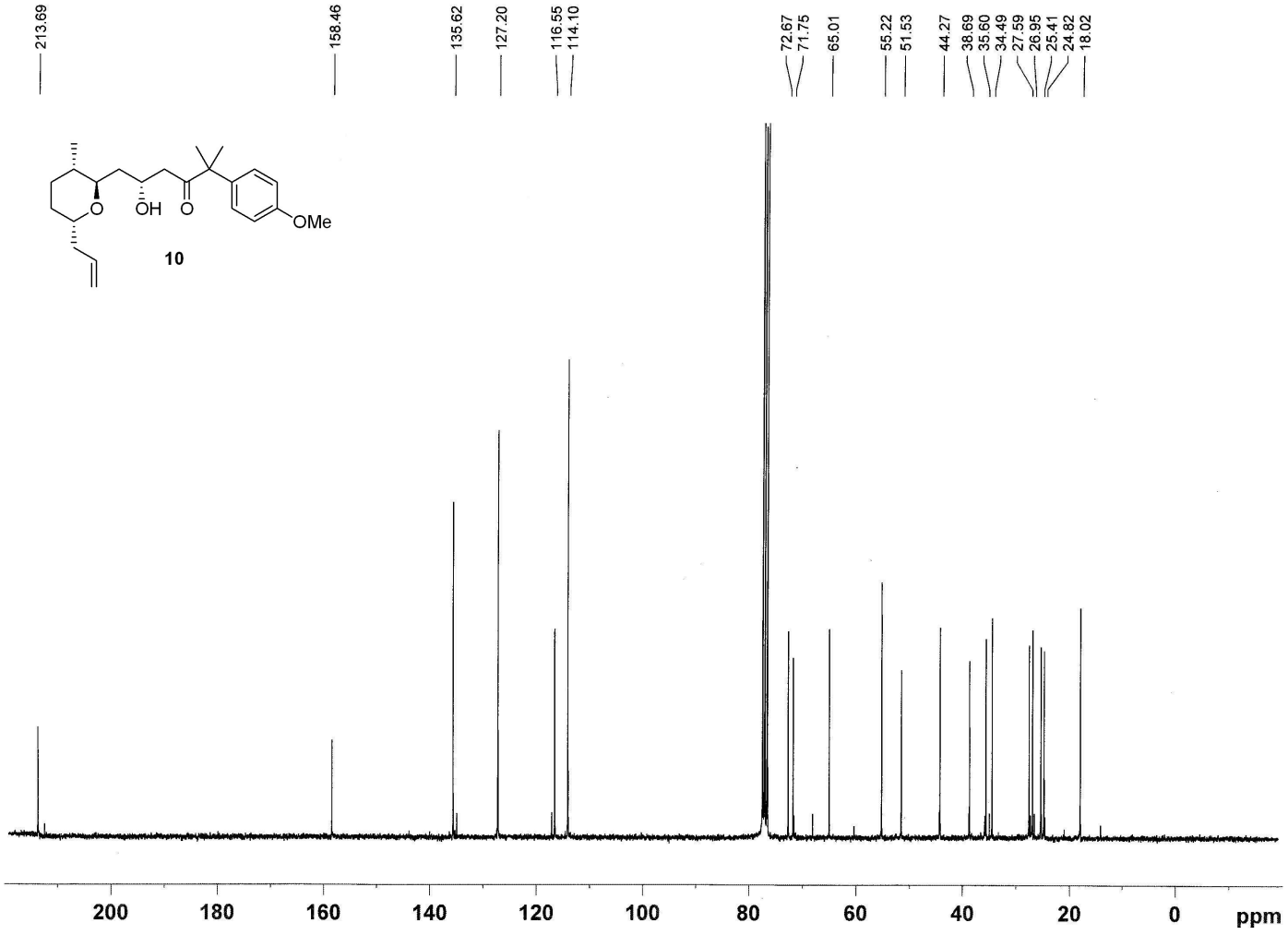
6

HHJ-3-28 08-16-06



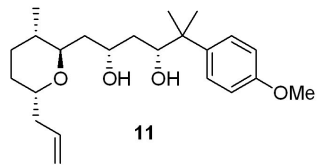

HHJ-3-181 04-16-07
OH
O
O
OMe
10
9
8
7
6
5
4
3
2
1
0
ppm
2.04
1.96
0.92
2.00
0.96
4.23
1.56
3.02
0.24
1.06
1.28
13.20
3.18

HHJ-3-181 (CDCl3) 04-17-07



10

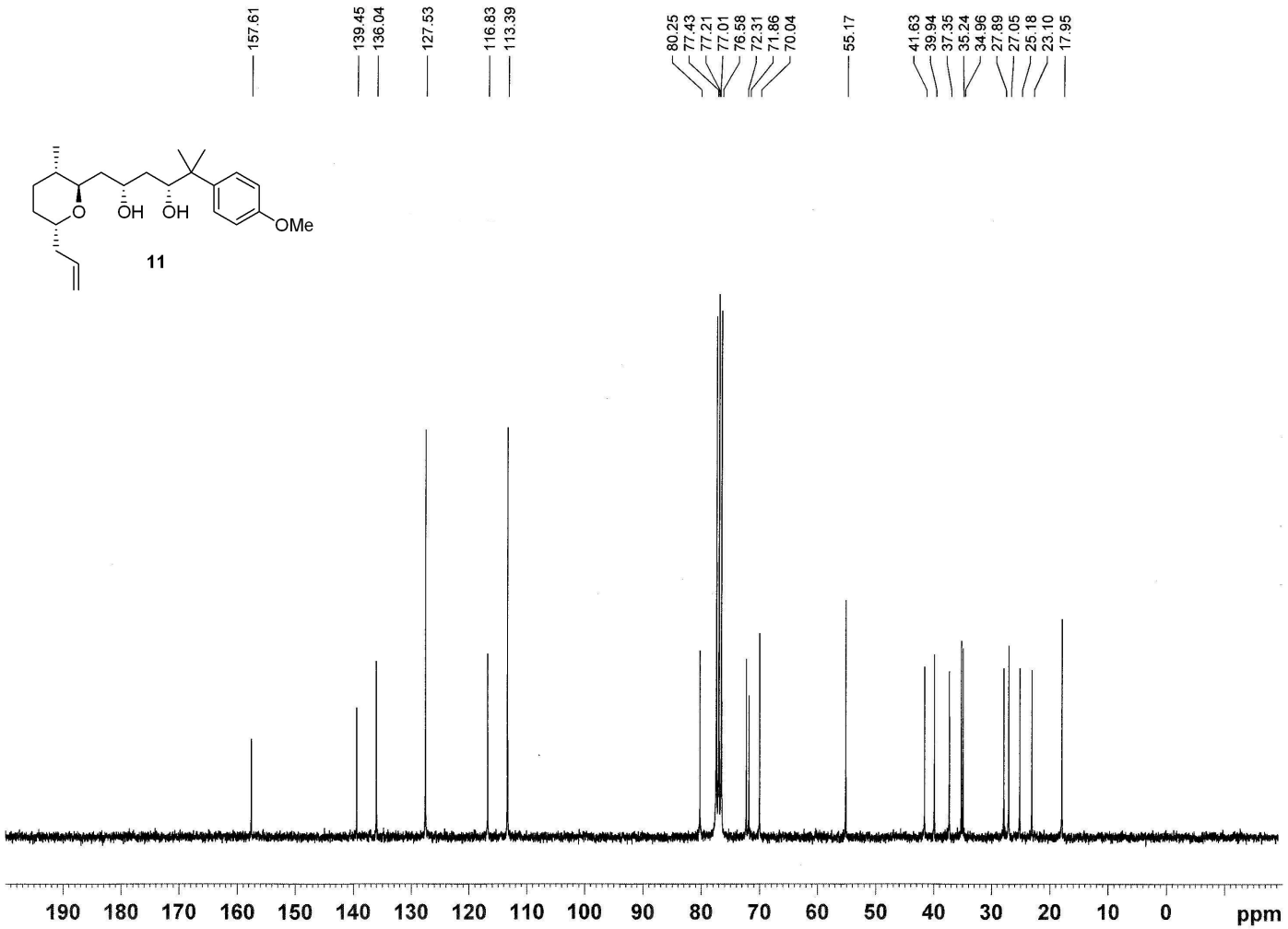
HHJ-3-141


O
OH
OH
OMe

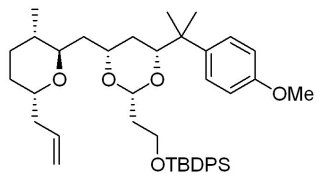
11

9
8
7
6
5
4
3
2
1
0
ppm
2.08
1.91
0.97
2.00
2.09
1.04
3.88
0.88
0.99
0.98
1.01
1.31
4.18
10.86
2.96

HHJ-3-192 04-27-07

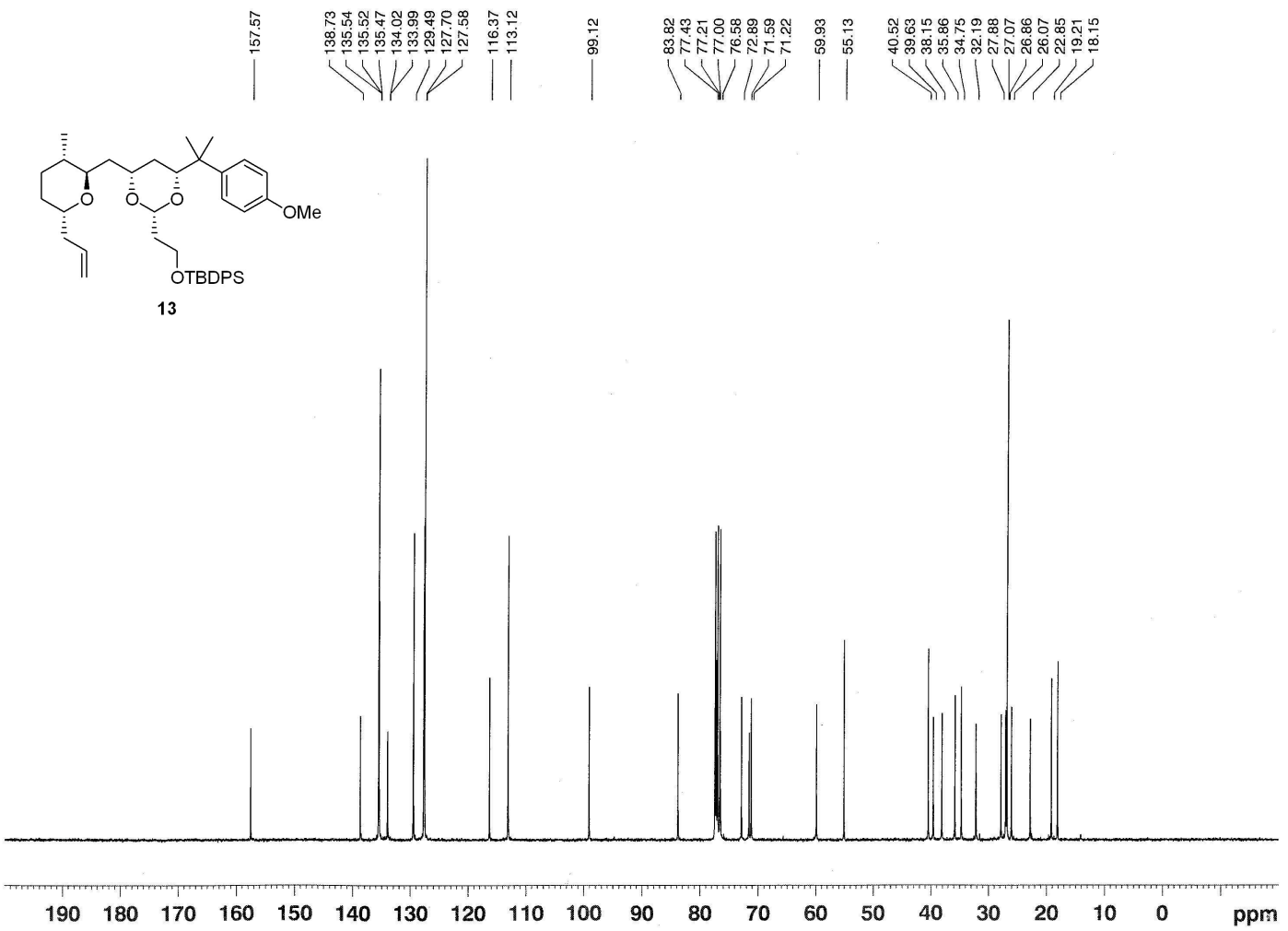


HHJ-3-141 03-17-07



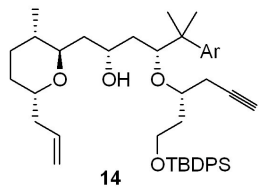
13

HHJ-3-193 05-01-07



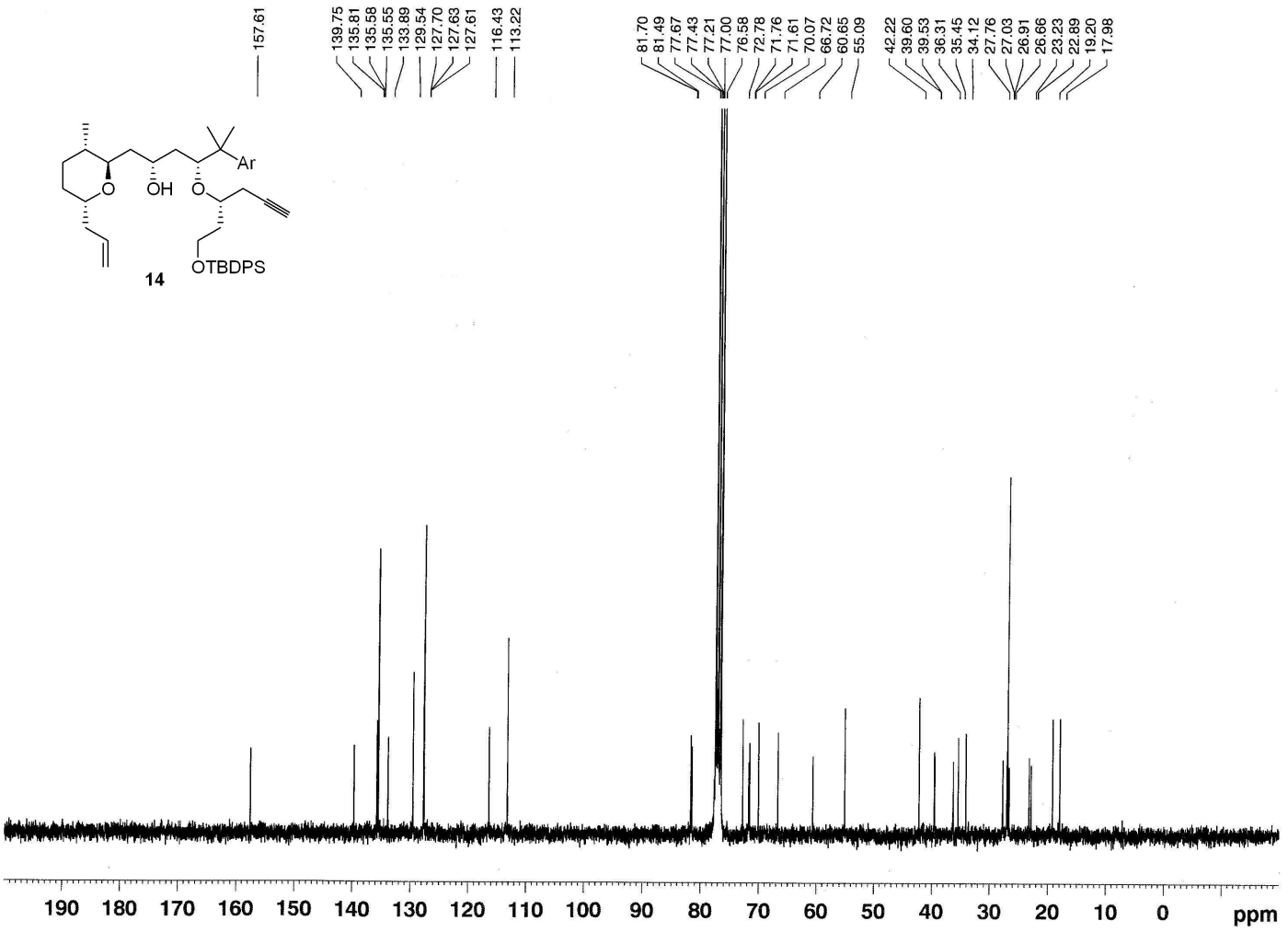
13

HHJ-3-143 03-19-07

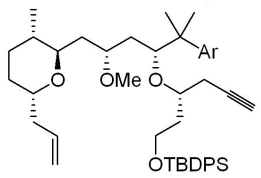


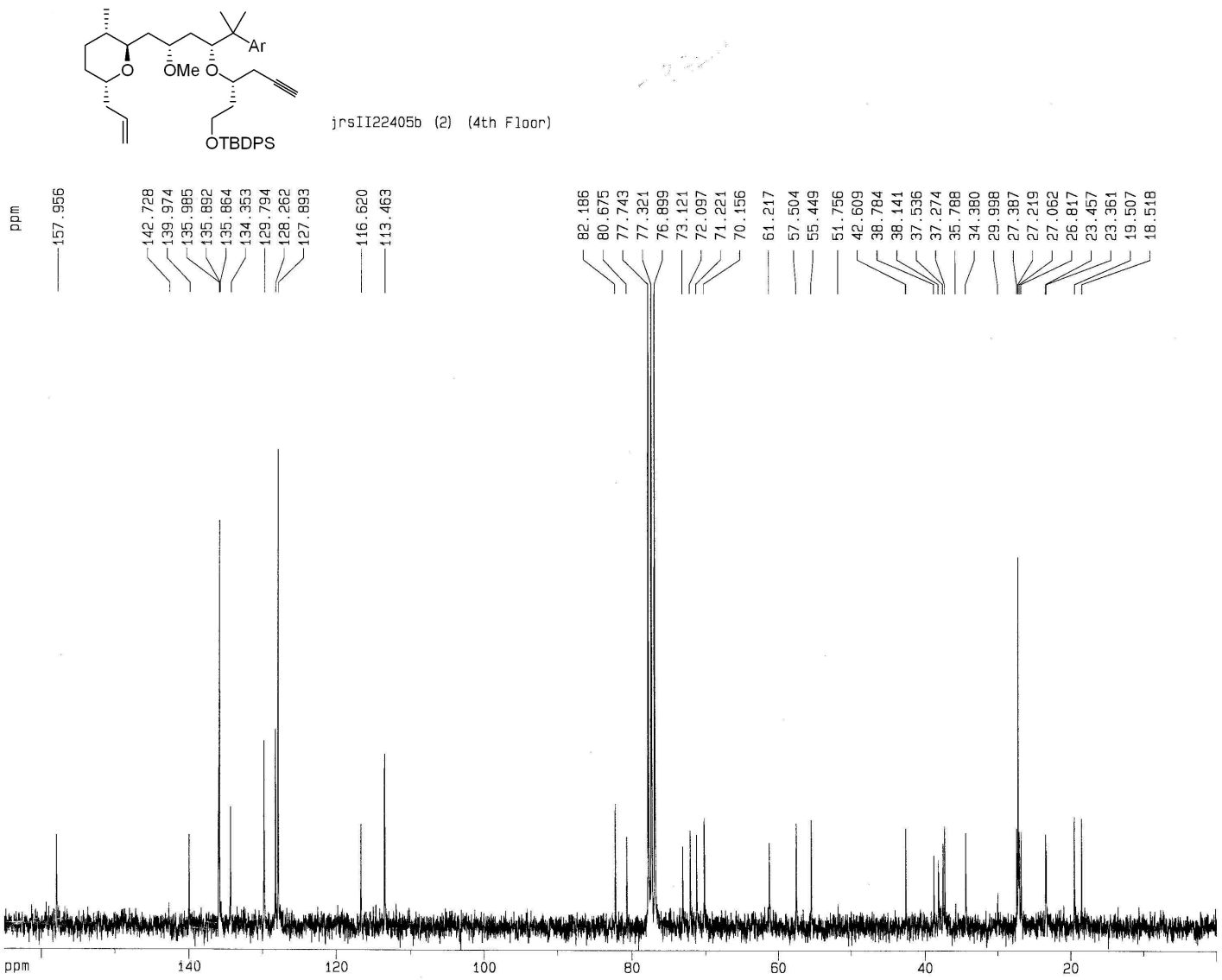
14

HHJ-3-143 03-19-07

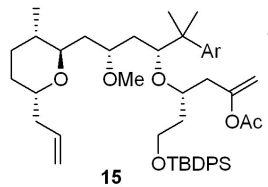


HHJ-3-144 03-21-07



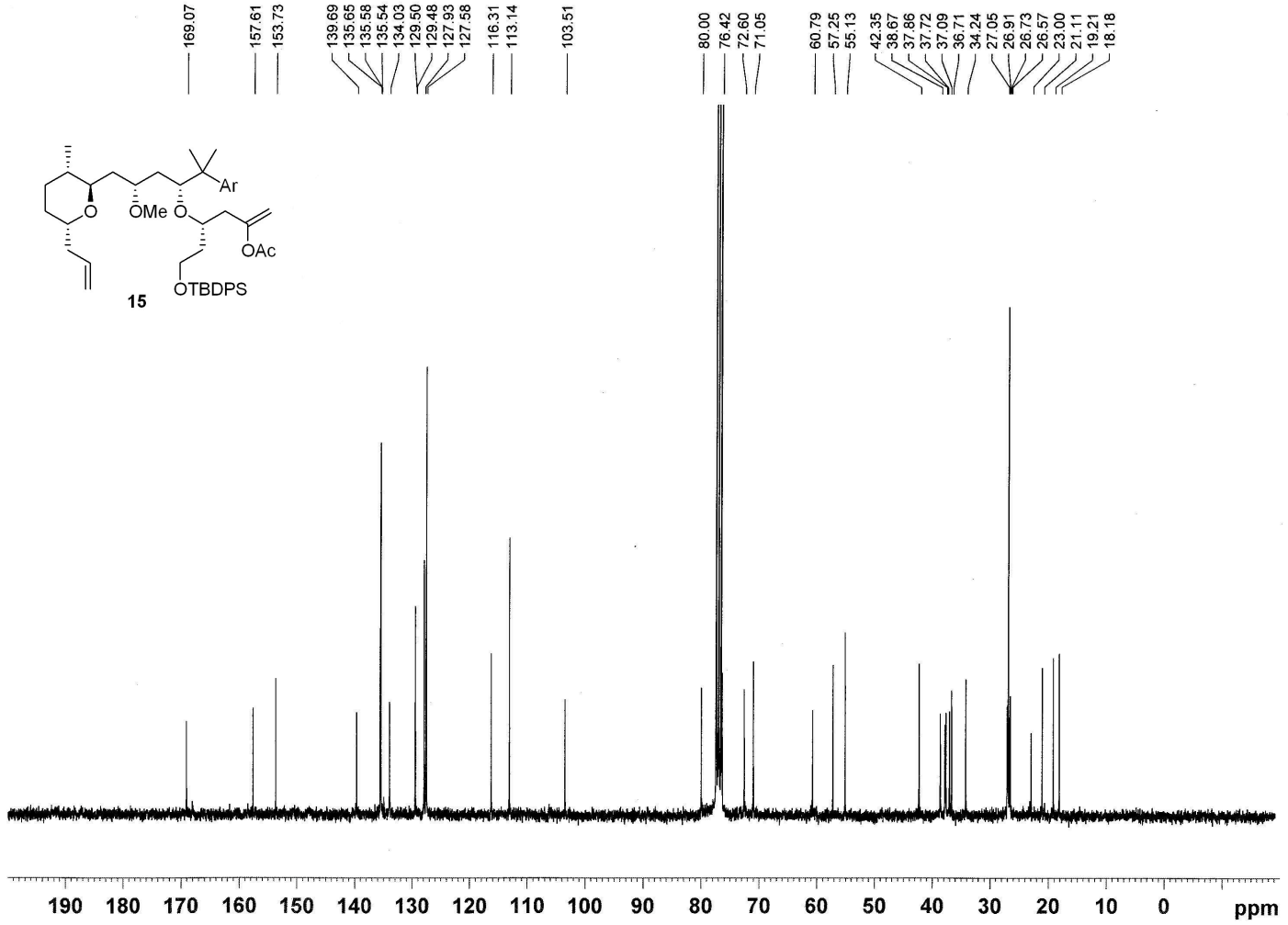

Ar
OMe
O
O
OTBDPS
jrsII22405b (2) (4th Floor)
ppm
157.956
142.728
139.974
135.985
135.892
135.864
134.353
129.794
128.262
127.893
116.620
113.463
82.186
80.675
77.743
77.321
76.899
73.121
72.097
71.221
70.156
61.217
57.504
55.449
51.756
42.609
38.784
38.141
37.536
37.274
35.788
34.380
29.998
27.387
27.219
27.062
26.817
23.457
23.361
19.507
18.518
ppm
140
120
100
80
60
40
20

HHJ-3-196 05-10-07



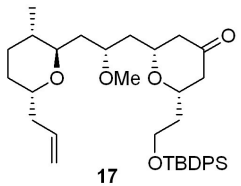
15

HHJ-3-196 05-10-07



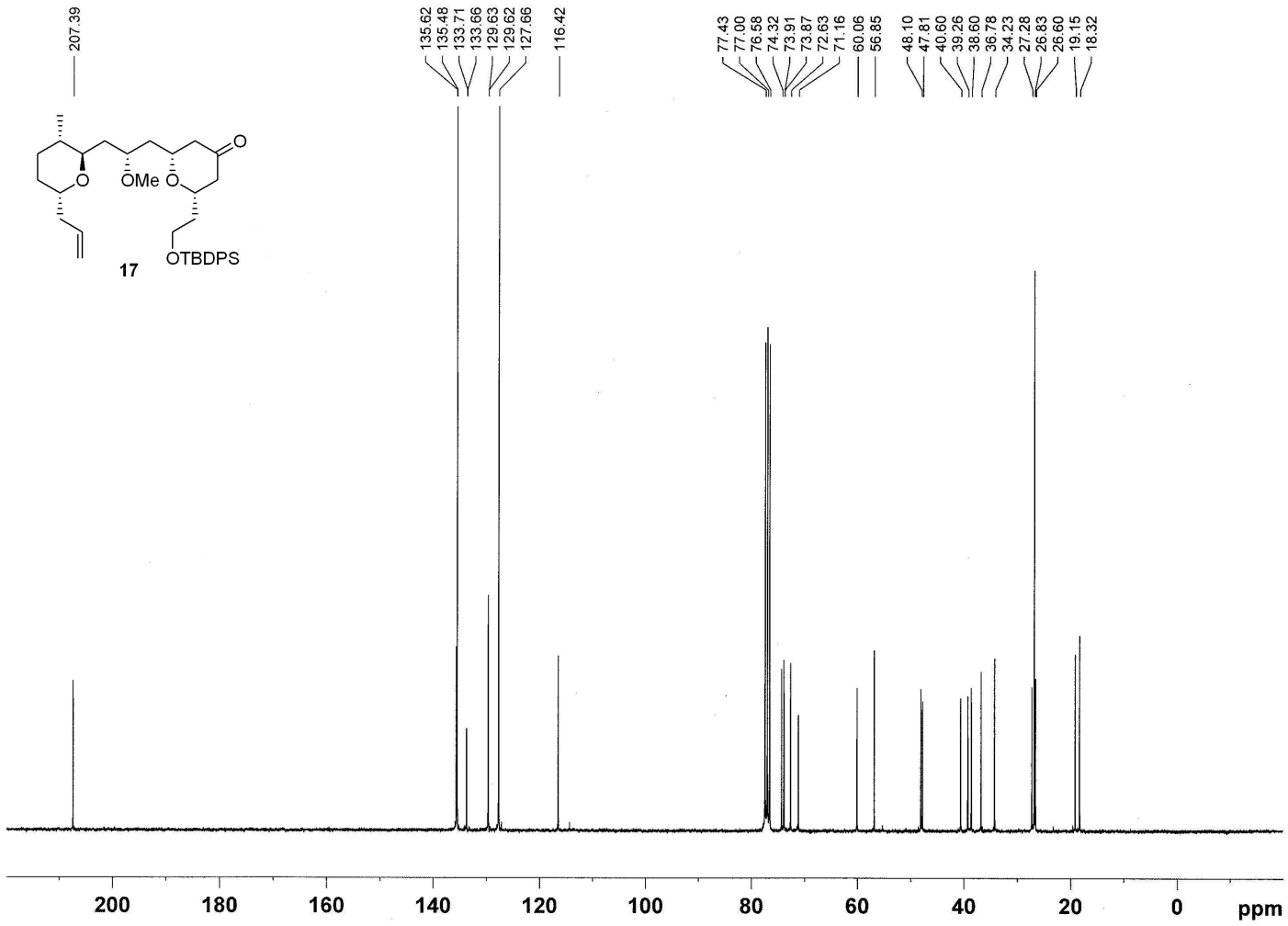
15

HHJ-3-197 05-12-07

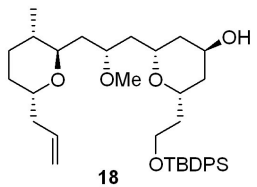


17

HHJ-3-197 05-12-07

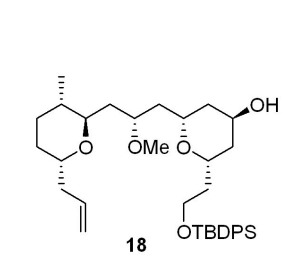


HHJ-3-198 05-14-07



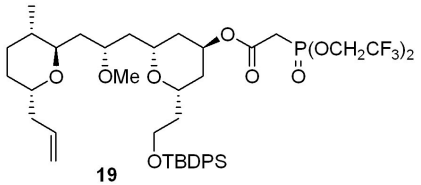
18

HHJ-3-198 05-14-07

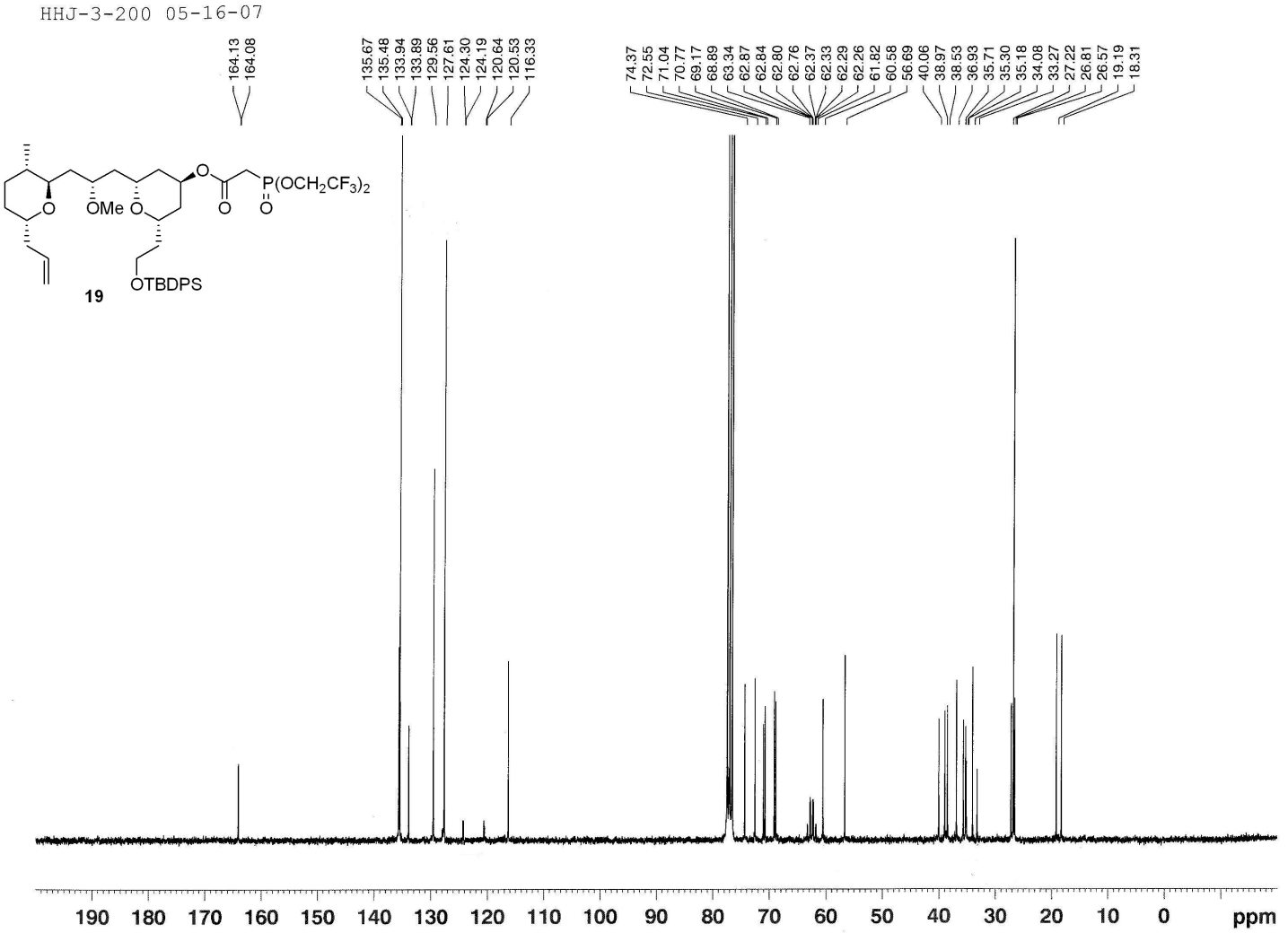


18

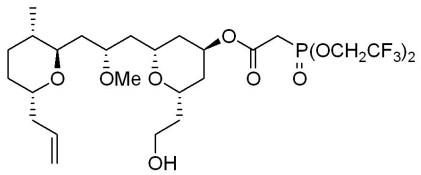
HHJ-3-200 05-16-07

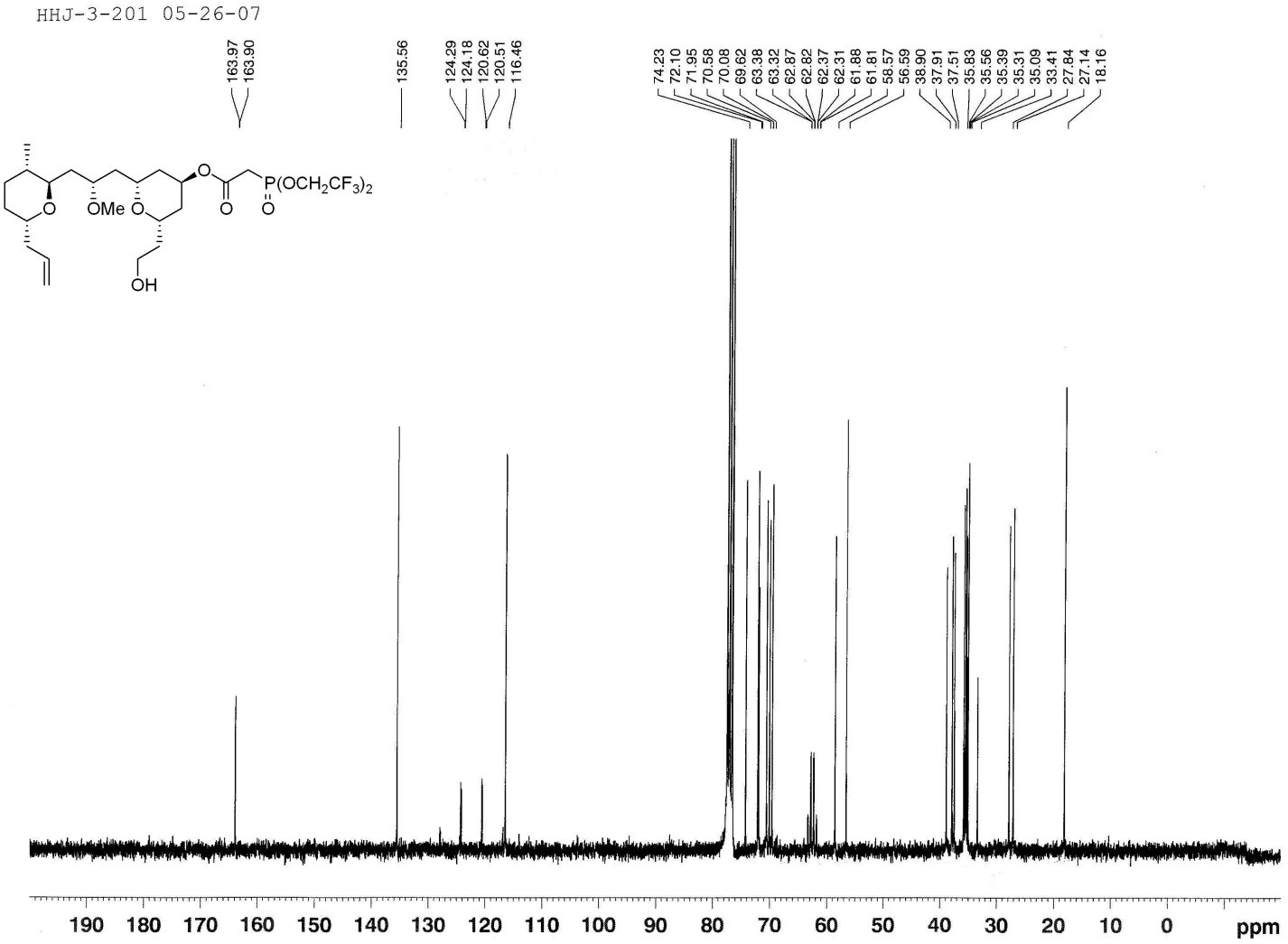


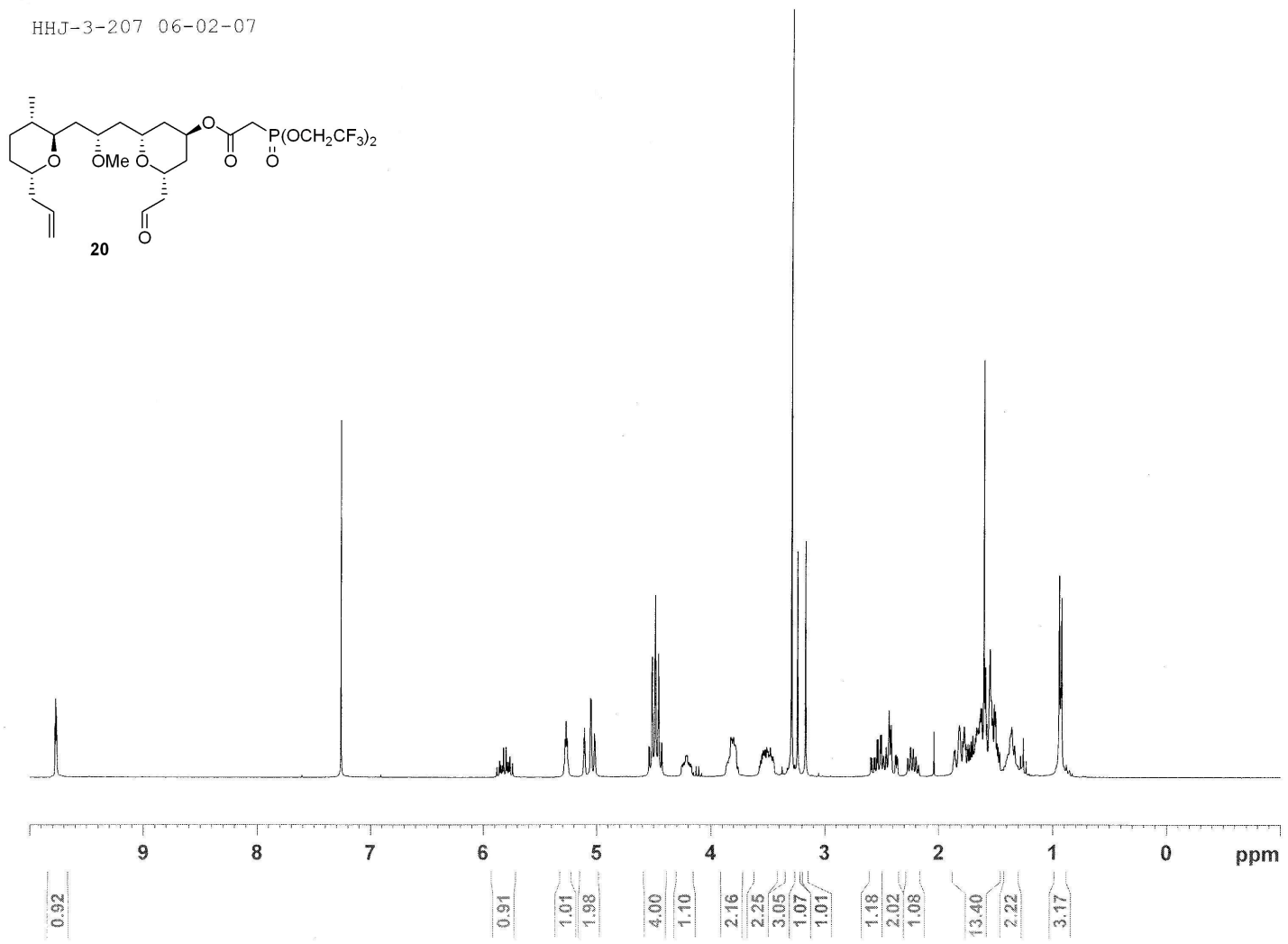
19

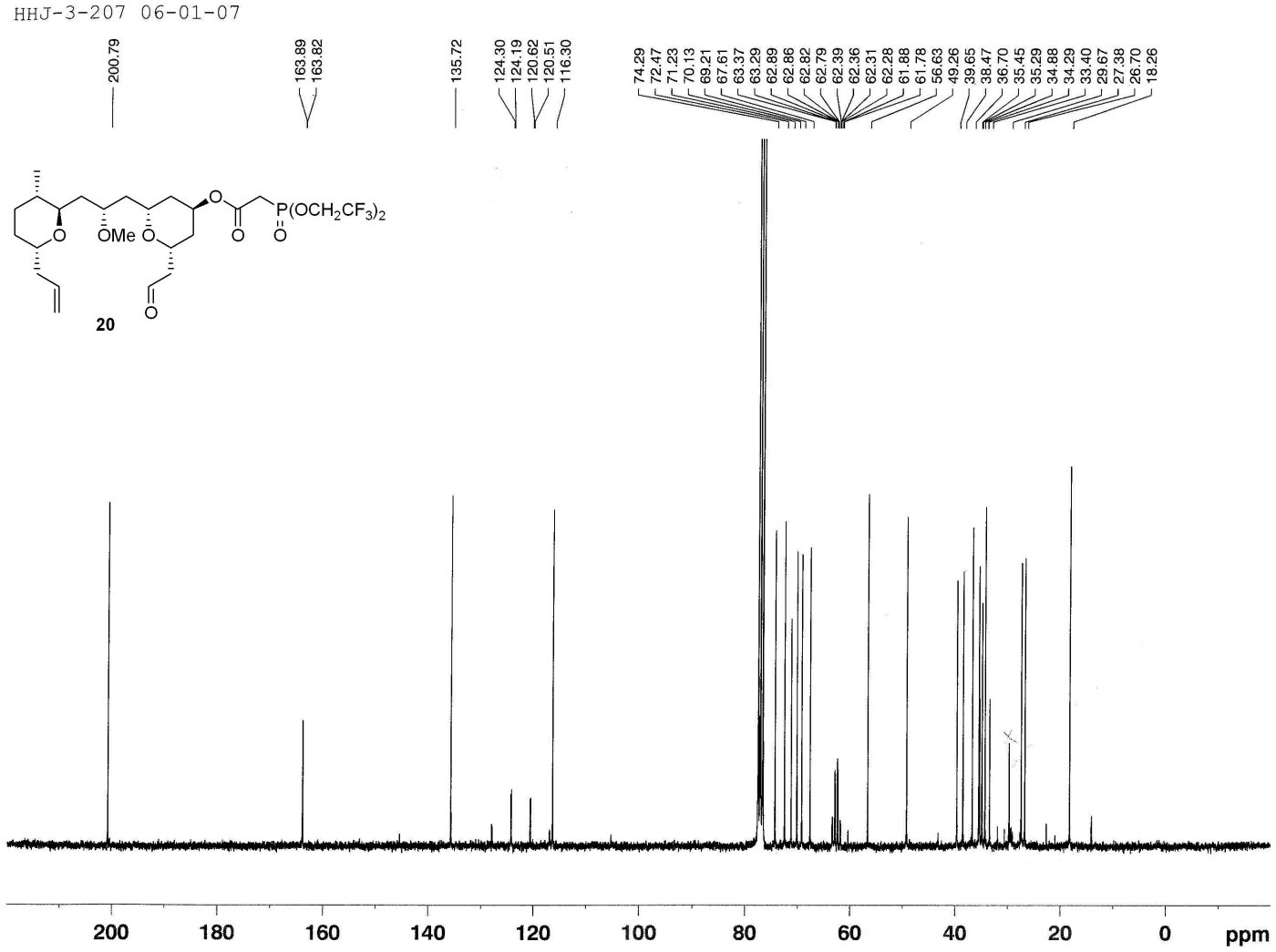

HHJ-3-200 05-16-07
164.13
164.08
135.67
135.48
133.94
133.89
129.56
127.61
124.30
124.19
120.64
120.53
116.33
74.37
72.55
71.04
70.77
69.17
68.89
63.34
62.87
62.84
62.80
62.76
62.37
62.33
62.29
62.26
61.82
60.58
56.69
40.06
38.97
38.53
36.93
35.71
35.30
35.18
34.08
33.27
27.22
26.81
26.57
19.19
18.31
O
OMe
O
O
O
P(OCH2CF3)2
O
OTBDPS
19
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

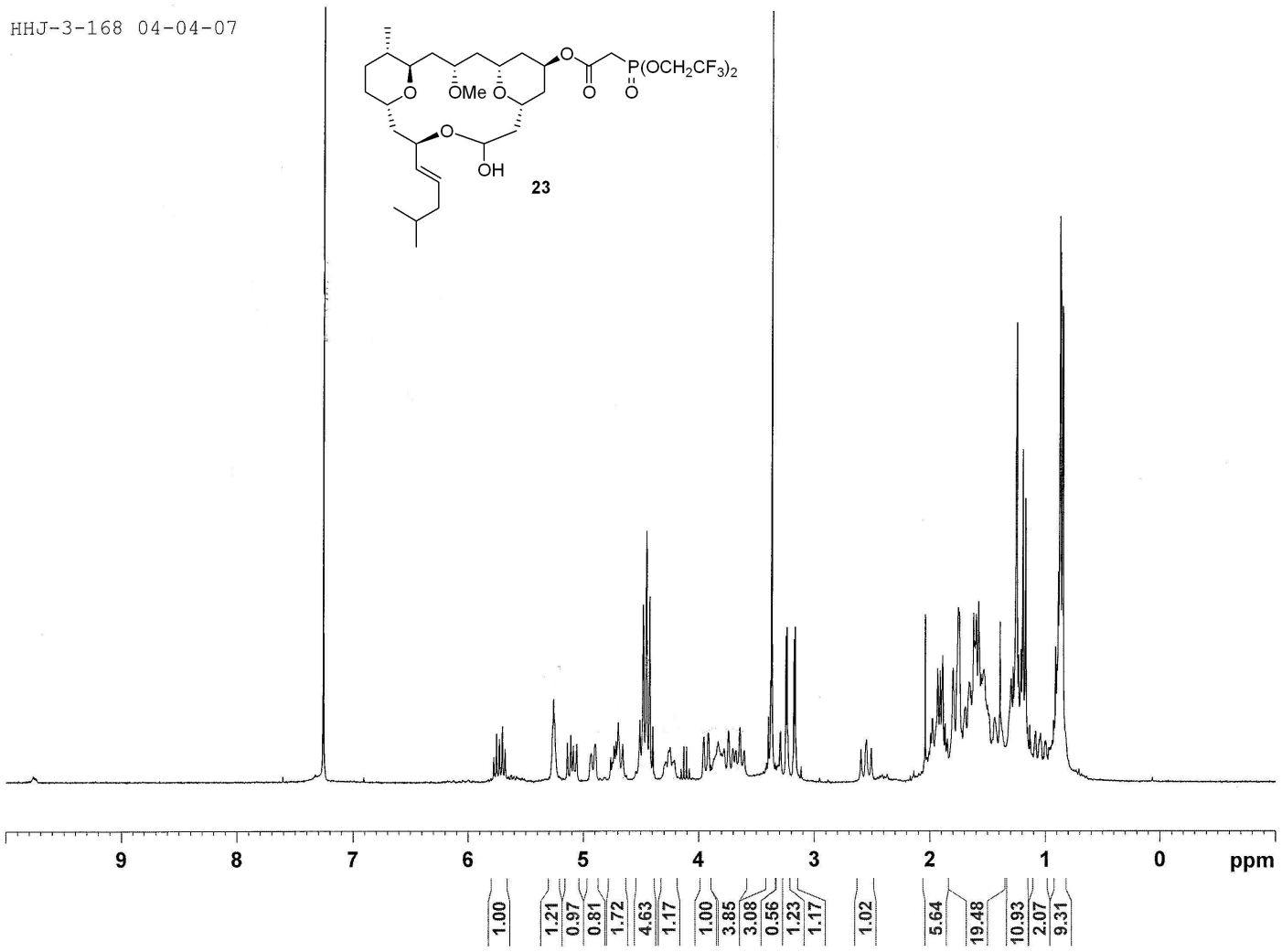
HHJ-3-160 03-29-07

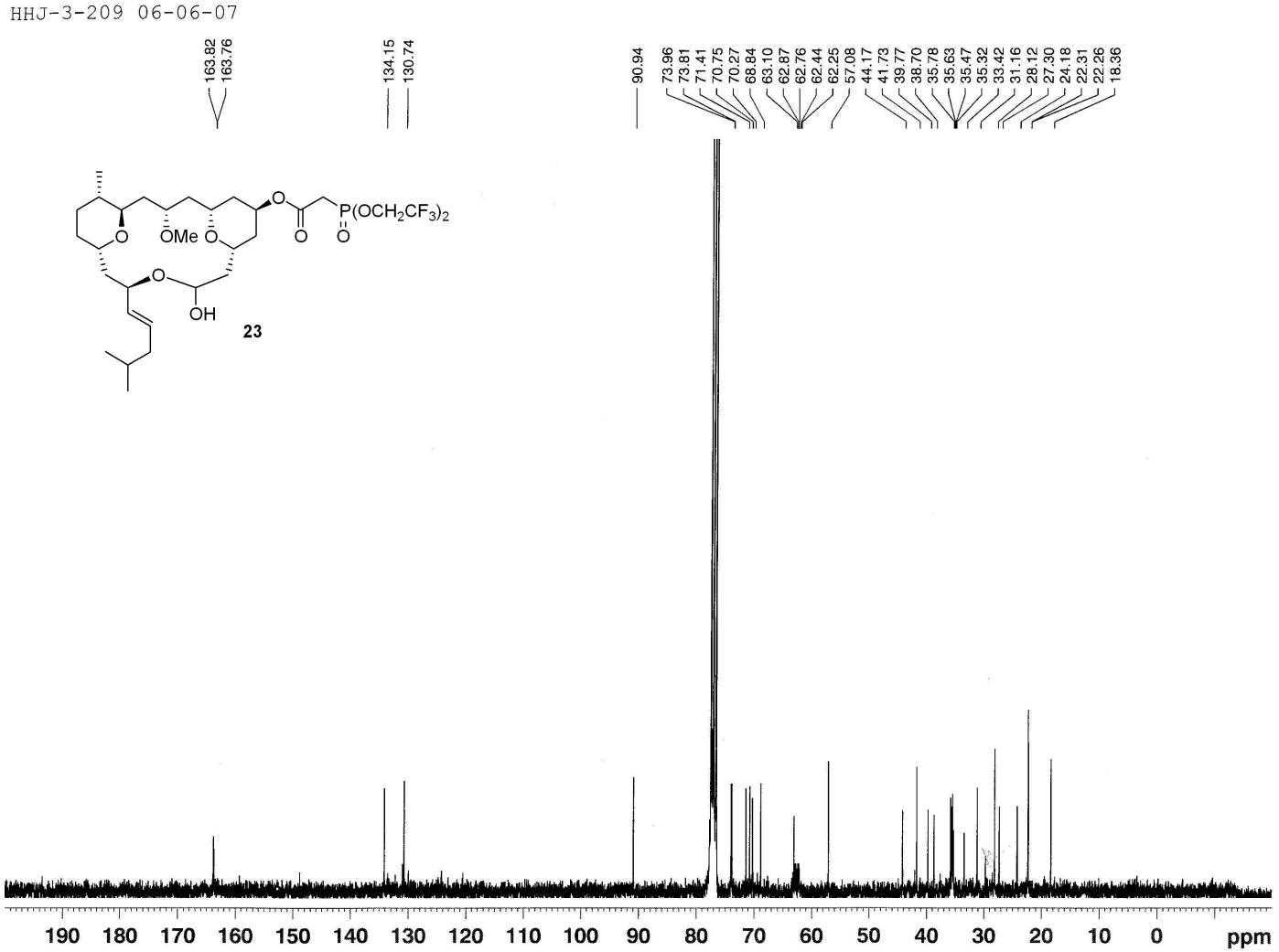



HHJ-3-201 05-26-07
163.97
163.90
135.56
124.29
124.18
120.62
120.51
116.46
74.23
72.10
71.95
70.58
70.08
69.62
63.38
63.32
62.87
62.82
62.37
62.31
61.88
61.81
58.57
56.59
38.90
37.91
37.51
35.83
35.56
35.39
35.31
35.09
33.41
27.84
27.14
18.16
OMe
P(OCH2CF3)2
OH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

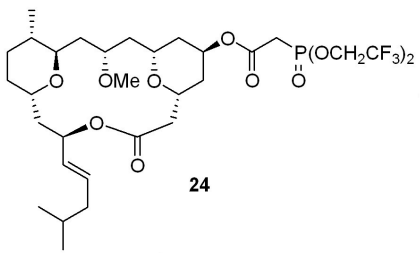

HHJ-3-207 06-02-07
OMe
P(OCH2CF3)2
20
9
8
7
6
5
4
3
2
1
0
ppm
0.92
0.91
1.01
1.98
4.00
1.10
2.16
2.25
3.05
1.07
1.01
1.18
2.02
1.08
13.40
2.22
3.17


HHJ-3-207 06-01-07
200.79
163.89
163.82
135.72
124.30
124.19
120.62
120.51
116.30
74.29
72.47
71.23
70.13
69.21
67.61
63.37
63.29
62.89
62.86
62.82
62.79
62.39
62.36
62.31
62.28
61.88
61.78
56.63
49.26
39.65
38.47
36.70
35.45
35.29
34.88
34.29
33.40
29.67
27.38
26.70
18.26
OMe
P(OCH2CF3)2
20
200
180
160
140
120
100
80
60
40
20
0
ppm


HHJ-3-168 04-04-07
OMe
P(OCH2CF3)2
OH
23
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.21
0.97
0.81
1.72
4.63
1.17
1.00
3.85
3.08
0.56
1.23
1.17
1.02
5.64
19.48
10.93
2.07
9.31


HHJ-3-209 06-06-07
163.82
163.76
134.15
130.74
90.94
73.96
73.81
71.41
70.75
70.27
68.84
63.10
62.87
62.76
62.44
62.25
57.08
44.17
41.73
39.77
38.70
35.78
35.63
35.47
35.32
33.42
31.16
28.12
27.30
24.18
22.31
22.26
18.36
P(OCH2CF3)2
OMe
OH
23
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

HHJ-3-210 06-08-07



24

BRUKER

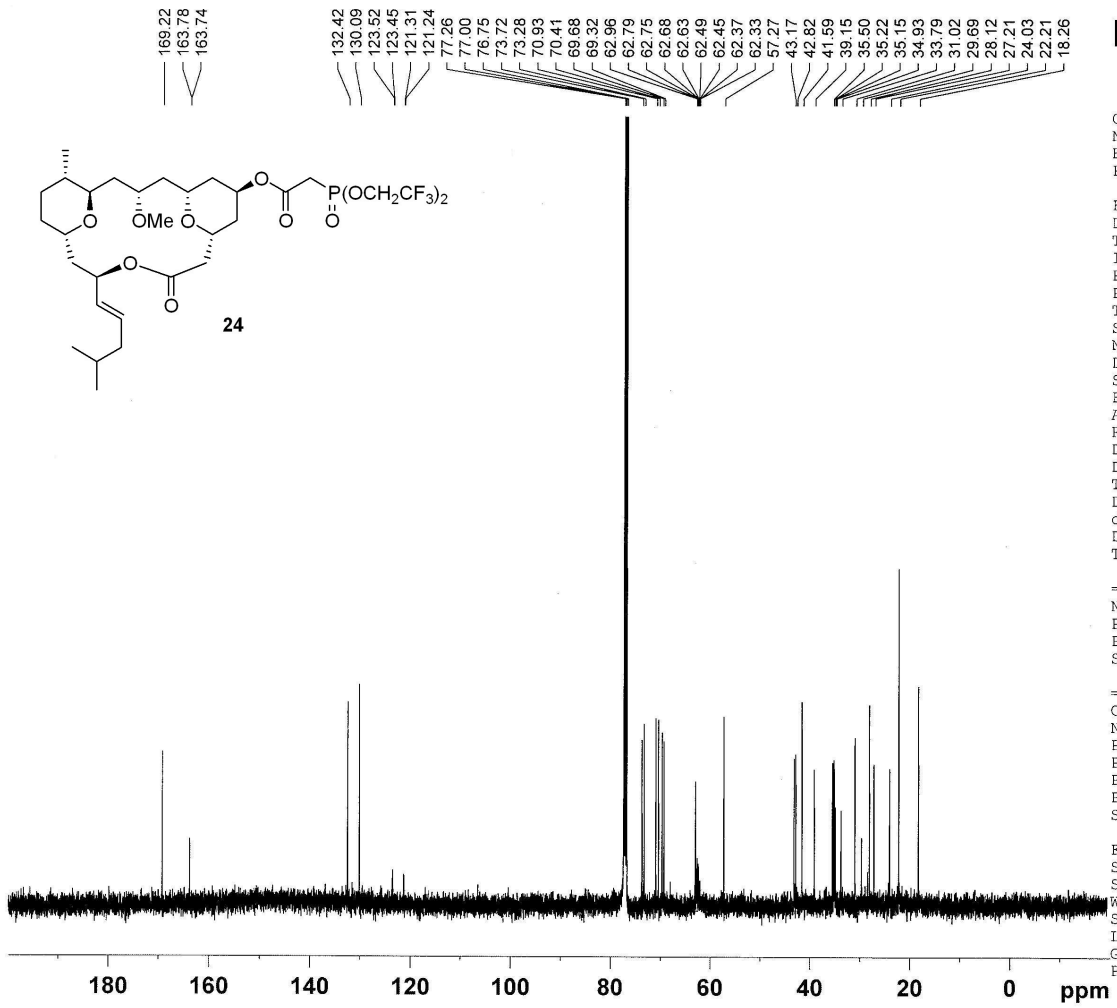
Current Data Parameters
NAME HHJ-3-210
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070608
Time 21.21
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 80.6
DW 48.400 usec
DE 6.00 usec
TE 298.2 K
D1 6.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300135 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

HHJ-3-210 06-08-07



BRUKER

Current Data Parameters

NAME	HHJ-3-210
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

Date_	20070609
Time	9.37
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg
TD	65536
SOLVENT	CDCl3
NS	6144
DS	2
SWH	30030.029 Hz
FIDRES	0.458222 Hz
AQ	1.0912244 sec
RG	7298.2
DW	16.650 usec
DE	6.00 usec
TE	298.2 K
D1	6.00000000 sec
d11	0.03000000 sec
DELTA	5.90000010 sec
TD0	1

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

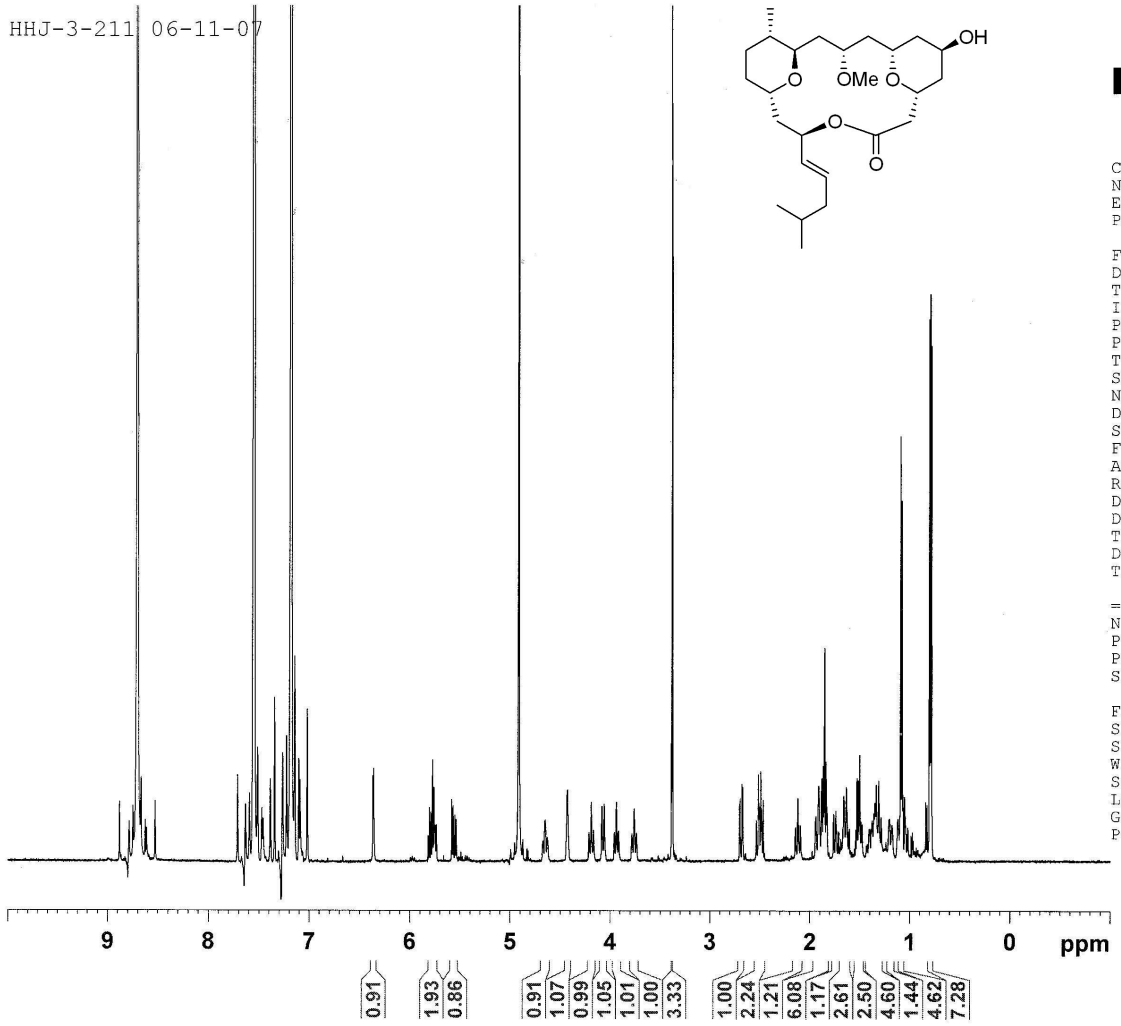
NUC1	13C
P1	11.00 usec
PL1	-2.00 dB
SFO1	125.7703643 MHz

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

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	20.00 dB
PL12	20.00 dB
PL13	20.00 dB
SFO2	500.1320005 MHz

F2 - Processing parameters

SI	32768
SF	125.7577919 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



BRUKER

Current Data Parameters

NAME	HHJ-3-211
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20070611
Time	16.50
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	65536
SOLVENT	Pyr
NS	32
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	101.6
DW	48.400 usec
DE	6.00 usec
TE	298.2 K
D1	2.00000000 sec
TD0	1

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

NUC1	1H
P1	9.00 usec
PL1	0.00 dB
SFO1	500.1330885 MHz

F2 - Processing parameters

SI	32768
SF	500.1305753 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00