Supporting Information

Total and Syntheses of Fostriecin

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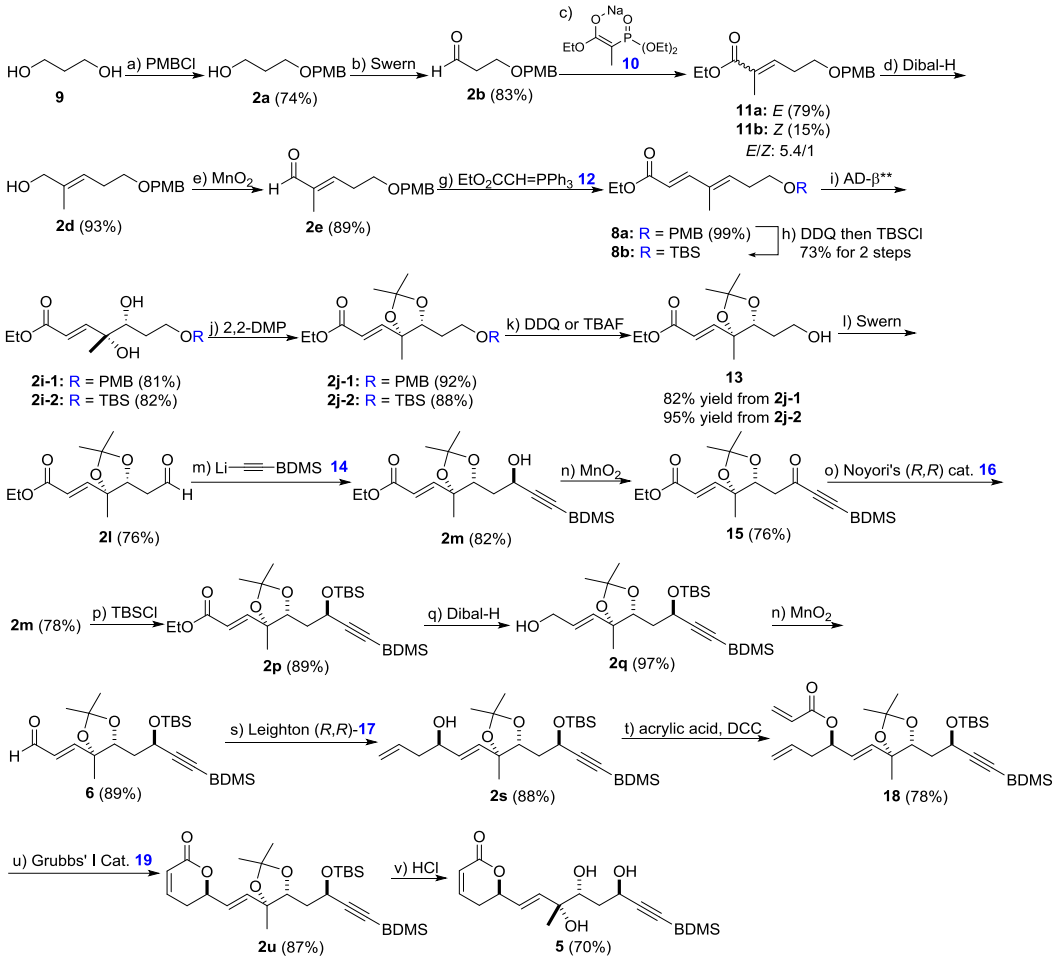
General Methods

All reagents were purchased from commercial sources and used without further purification. Dichloromethane, DMF and THF used in reactions were taken from a solvent purification system in which the solvents are purified by successive passage through columns of alumina and copper under argon. Methanol used in reactions was dried in a sealed bottle over activated 3 Å molecular sieves. Air and/or moisture-sensitive reactions were carried out under an atmosphere of argon/nitrogen using oven/flamed-dried glassware and standard syringe/septa techniques. Unless stated otherwise, all reactions were monitored by thin layer chromatography on silica gel 60 F254 (0.25 mm, Merck) glass plates and visualized by quenching of fluorescence and by charring after treatment with *p*-anisaldehyde or phosphomolybdic acid or potassium permanganate stain. R_f values were obtained by elution in the stated solvent ratios (v/v). In the reaction work-up involving extractions, solutions of organic solvents were washed with equal amounts of aqueous solutions, unless otherwise noted. All column chromatography was performed on silica gel 60 (40–60 μm). Melting points were measured on an Electrothermal Mel-Temp apparatus and were not corrected. Optical rotations were measured on a Jasco DIP-370 digital polarimeter in the solvent specified. FTIR spectra were run on Thermo Nicolet (Madison Wisconsin, USA) 8700 main bench with a Continuum FTIR microscope attached, and samples cast from a chloroform solution onto an IR-transparent silicon wafer. ^{1}H NMR spectra were recorded at 270, 500 and 600 MHz, while ^{13}C NMR spectra were recorded at 67.5, 150 and 500 MHz correspondingly. Chemical shifts of both ^{1}H and ^{13}C NMR were referenced to internal tetramethylsilane (0.00 ppm) or $CHCl_3$ (7.26 ppm, $CDCl_3$). High resolution electrospray mass spectra were recorded on an Agilent Technologies 6220 Accurate-Mass TOF spectrometer with samples dissolved in a suitable solvent.

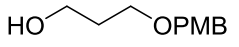
The following experimental section outlines the synthetic and spectroscopic details for the all the synthetic pathways explored in the manuscript. Of the experimental

detailed, the one for the following compounds are being disclosed for the first time: **24**, **27**-**37**, **39**, **43**-**51** and accordingly the procedures include, R_f, ^{1}H NMR, ^{13}C NMR, IR, HRMS, melting points, and optical rotation when relevant.

Intermediates related to Scheme 2:



3-((4-methoxybenzyl)oxy)propan-1-ol (2a)[1]



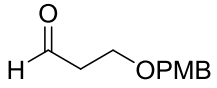
(2a)

Propane-1,3-diol **9** (2 g, 26.28 mmol) was taken in 100 mL of anhydrous THF and NaH (60% dispersion in mineral oil, 1.16 g, 28.91 mmol) was added to it portion wise at 0 °C. The reaction mixture was stirred at 0 °C for 30 min. Tetrabutylammonium iodide (TBAI, 1.07 g, 2.89 mmol) was added to it followed by the addition of 4-methoxybenzylchloride (PMBCl) (4.12 g, 26.28 mmol) in THF (10 mL). The reaction mixture was stirred for a further 8 h at room temperature. H_2O was added carefully to the reaction mixture to quench any excess of NaH. The reaction mixture was then extracted with EtOAc. The organic solution was washed with water, brine,

[1] Spectral data matched which was previously reported, see: (a) Shibahara, S.; Fujino, M.; Tashiro, Y.; Okamoto, N.; Esumi, T.; Takahashi, K.; Ishihara, J.; Hatakeyama S. Total Synthesis of (+)-Fostriecin and (+)-Phoslactomycin B. *Synthesis*, **2009**, *17*, 293. (b) Kretschmer, M.; Menche, D. Stereocontrolled Synthesis of the C8-C22 Fragment of Rhizopodin. *Org. Lett.* **2012**, *14*, 382.

dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 3:2 (v/v) hexane/EtOAc) to afford the PMB mono-protecting compound **2a** (3.80 g, 74% yield) as a yellow liquid. R_f = 0.214 (6:4 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3521, 2905, 2856, 1650, 1463, 1366, 1172, 1086, 1033, 819; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.25 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 4.44 (s, 2H), 3.79 (s, 3H), 3.74 (t, *J* = 5.8 Hz, 2H), 3.62 (t, *J* = 5.9 Hz, 2H), 2.71 (s, 1H), 1.84 (p, *J* = 5.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 158.8, 130.0, 128.9 (2C), 113.4 (2C), 72.4, 67.8, 60.1, 54.5, 32.3; HRMS (ESI+) calculated for $[C_{11}H_{16}O_3 + H]^+$: 197.1172, Found: 197.1176.

3-((4-methoxybenzyl)oxy)propanal (2b)[2]



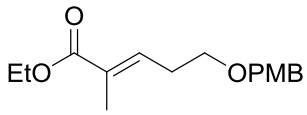
(2b)

To a 5mL anhydrous CH_2Cl_2 solution, DMSO (0.24 g, 3.06 mmol) was added, and the mixture was cooled to –78 °C under argon, followed by the dropwise addition of oxalylchloride (0.26 g, 2.04 mmol). After 30 min, PMB-propanol **2a** (200 mg, 1.02 mmol) in anhydrous CH_2Cl_2 (1 mL) was added and the reaction was stirred at –78 °C for additional 1.5 h under argon. Et_3N (0.52 g, 5.10 mmol) was then added and the reaction mixture was allowed to react 6 h under room temperature. 1 M $NaHSO_4$ (10 mL) was added carefully to the reaction mixture to quench the excessive Et_3N and oxalylchloride, and the reaction mixture was then extracted with Et_2O. The combined organic phases were washed with saturated aqueous solution of $NaHCO_3$, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 8:1 (v/v) hexane/EtOAc) to afford the PMB-propanal **2b** (165.0 mg, 83% yield) as a yellow liquid. R_f = 0.237 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2980, 2905, 2856, 1706, 1463, 1366, 1172, 1086, 1033, 819; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.78 (s, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 6.88

[2] Spectral data matched which was previously reported, see: (a) Hayashi, Y.; Yamaguchi, H.; Toyoshima, M.; Okado, K.; Toyo, T.; Shoji, M. Formal Total Synthesis of Fostriecin via 1,4-Asymmetric Induction Using Alkyne-Cobalt Complex. *Chem. Eur. J.* **2010**, *16*, 10150. (b) Hernandez, D.; Lindsay, K.B.; Nielsen, L.; Mittag, T.; Bjerglund, K.;Friis, S.; Mose, R.; Skrydstrup, T. Further Studies toward the Stereocontrolled Synthesis of Silicon-Containing Peptide Mimics. *J. Org. Chem.* **2010**, *75*, 3283.

(d, J = 8.5 Hz, 2H), 4.46 (s, 2H), 3.80 (s, 3H), 3.78 (t, J = 6.2 Hz, 2H), 2.68 (td, J = 6.1, 1.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 201.3, 159.4, 130.0, 129.4 (2C), 113.9 (2C), 73.0, 63.6, 55.3, 43.9. HRMS (ESI+) calculated for $[C_{11}H_{14}O_3 + Na]^+$: 217.0841, Found: 217.0842.

Ethyl (*E*)-5-((4-methoxybenzyl)oxy)-2-methylpent-2-enoate (11a)[3]

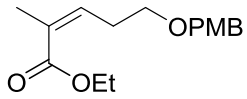


(11a)

Triethyl 2-phosphonopropionate **10** (220.77 mg, 0.93 mmol) was added dropwise to a suspension of NaH 60% weight in mineral oil (37.07 mg, 0.93 mmol) in anhydrous THF (7 mL) at 0 °C under an argon atmosphere. After 1 h stirring, PMB-propanal **2b** (150 mg, 0.77 mmol) was added, and the reaction was stirred at room temperature for another 2 h. The reaction mixture was quenched by saturated aqueous solution of NH_4Cl, and was then extracted with Et_2O. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 20:1 (v/v) hexane/EtOAc) to afford the PMB-enoate **11a** in (142.4 mg, 79% yield) as a colorless oil. R_f = 0.216 (10:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2931, 2905, 2856, 1706, 1612, 1512, 1366, 1244, 1086, 1033, 819; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 6.77 (t, J = 7.2 Hz, 1H), 4.45 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 3.53 (t, J = 6.8 Hz, 2H), 2.47 (q, J = 6.9 Hz, 2H), 1.84 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 168.1, 159.3, 138.4, 130.4, 129.5, 129.4 (2C), 113.9 (2C), 72.8, 68.4, 60.6, 55.4, 29.5, 14.4, 12.7. HRMS (MALDI-TOF/CCA) calculated for $[C_{16}H_{22}O_4 + H]^+$: 279.1591, Found: 279.1593.

Ethyl (*Z*)-5-((4-methoxybenzyl)oxy)-2-methylpent-2-enoate (11b)

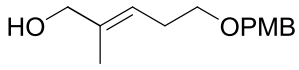
[3] Spectral data matched which was previously reported, see: Hayashi, Y.; Yamaguchi, H.; Toyoshima, M.; Okado, K.; Toyo, T.; Shoji, M. Formal Total Synthesis of Fostriecin via 1,4-Asymmetric Induction Using Cobalt-Alkyne Complex. *Org. Lett.* **2008**, *10*, 1405.



(11b)

Triethyl 2-phosphonopropionate **10** (220.77 mg, 0.93 mmol) was added dropwise to a suspension of NaH 60% weight in mineral oil (37.07 mg, 0.93 mmol) in anhydrous THF (7 mL) at 0 °C under an argon atmosphere. After 1 h stirring, PMB-propanal **2b** (150 mg, 0.77 mmol) was added, then stirred at room temperature for another 2 h. The reaction mixture was quenched by saturated aqueous solution of NH_4Cl, and was then extracted with Et_2O. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 20:1 (v/v) hexane/EtOAc) to afford the PMB-enoate **11b** in (26.4 mg, 15% yield) as a colorless oil. R_f = 0.378 (10:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2931, 2905, 2856, 1706, 1612, 1512, 1463, 1366, 1244, 1086, 1033, 819; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.06 – 5.97 (m, 1H), 4.45 (s, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.51 (t, *J* = 6.5 Hz, 2H), 2.77 (q, *J* = 6.5 Hz, 2H), 1.91 – 1.89 (m, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 168.0, 159.3, 139.5, 130.6, 129.4, 128.7 (2C), 113.9 (2C), 72.6, 69.3, 60.2, 55.4, 30.3, 20.8, 14.4. HRMS (MALDI-TOF/CCA) calculated for $[C_{16}H_{22}O_4 + H]^+$: 279.1591, Found: 279.1593.

(*E*)-5-((4-methoxybenzyl)oxy)-2-methylpent-2-en-1-ol (2d)[4]



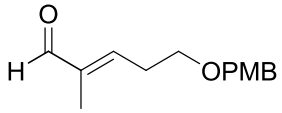
(2d)

To a solution of enoate **11a** (350 mg, 1.26 mmol) in CH_2Cl_2 (5.0 mL) was dropwise added diisobutylaluminum hydride (*i*-Bu)$_2$AlH (1.0 M in CH_2Cl_2, 8.80 mL, 8.80 mmol) at –78 °C under an argon atmosphere. After stirring for 2 h at –78 °C, the reaction mixture was allowed warming up to 0 °C and kept stirring for 1 h. Then the reaction mixture was diluted with Et_2O and was quenched with saturated aqueous solution of potassium sodium tartrate (Rochelle's salt, 15 mL). The biphasic mixture

[4] Spectral data matched which was previously reported, see: Chakraborty, T. K.; Purkait, S.; Das, S. Synthesis of chiral 4-hydroxy-2,3-unsaturated carbonyl compounds from 3,4-epoxy alcohols by oxidation: application in the formal synthesis of macrosphelide A. *Tetrahedron* **2003**, *59*, 9127.

was stirred until two layers separated once stopped stirring. The aqueous layer was extracted with Et_2O. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 3:1 (v/v) hexane/EtOAc) to afford the primary alcohol **2d** (277.30 mg, 93% yield) as a colorless oil. R_f = 0.219 (6:4 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3523, 2903, 2857, 1649, 1461, 1367, 1175, 1085, 819; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.26 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 5.43 (t, *J* = 7.0 Hz, 1H), 4.45 (s, 2H), 3.99 (s, 2H), 3.80 (s, 3H), 3.46 (t, *J* = 7.0 Hz, 2H), 2.36 (q, *J* = 7.0 Hz, 2H), 1.67 (s, 3H), 1.65 (s, 1H); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 159.2, 136.8, 130.5, 129.4 (2C), 122.0, 113.8 (2C), 72.6, 69.5, 68.6, 55.3, 28.4, 13.9. HRMS (MALDI-TOF/CCA) calculated for $[C_{14}H_{20}O_3 + H]^+$: 237.1485, Found: 237.1482.

5-((4-methoxybenzyl)oxy)-2-methylpent-2-enal (2e)[4]

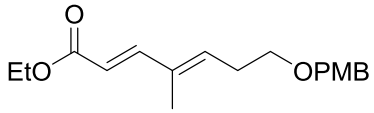


(2e)

To a solution of the Dibal-H reduction product alcohol **2d** (100 mg, 0.423 mmol) in 5.0 mL of anhydrous CH_2Cl_2 was added activated MnO_2 (551.8 mg, 6.348 mmol), and the mixture stirred vigorously for 24 h at room temperature, the reaction mixture was filtered through celite, and the celite was washed with CH_2Cl_2 and ethyl acetate. The filtrate was then dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 12:1 (v/v) hexane/EtOAc) to afford the enal **2e** (88.2 mg, 89% yield) as a colorless oil. Fortunately, at this point we were able to convert the undesired *Z*-isomer to the desired *E*-isomer **2e** by treating the crude mixture with 10 mol % trifluoacetic acid (TFA) in CH_2Cl_2 at room temperature, which gave an 81% yield. R_f = 0.284 (6:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2931, 2857, 1706, 1649, 1612, 1461, 1367, 1175, 1085, 819; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.41 (s, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.55 (t, *J* = 6.9 Hz, 1H), 4.47 (s, 2H), 3.81 (s, 3H), 3.60 (t, *J* = 6.4 H, 2H), 2.64 (q, *J* = 6.6 Hz, 2H), 1.75 (s, 3H). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 195.3, 159.4, 151.2, 140.7, 130.2, 129.5 (2C),

114.0 (2C), 72.9, 68.0, 55.4, 29.8, 9.5. HRMS (MALDI-TOF/CCA) calculated for $[C_{14}H_{18}O_3 + H]^+$: 235.1392, Found: 235.1394.

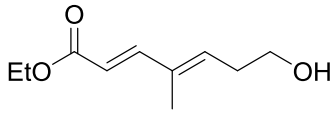
Ethyl (2*E*,4*E*)-7-((4-methoxybenzyl)oxy)-4-methylhepta-2,4-dienoate (8a)



(8a)

To a solution of MnO_2 oxidative enal **2e** (100 mg, 0.427 mmol) in 2.0 mL of anhydrous THF was added (Carboethoxymethylene)-triphenylphosphorane **12** (297.4 mg, 0.854 mmol), the reaction was stirred for 48 h at room temperature. The crude was concentrated in vacuo, then purified by column chromatography (silica gel, 50:1 (v/v) hexane/EtOAc) to afford dienoate **8a** (129.5 mg, 99% yield) as a colorless oil. R_f = 0.289 (15:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3413, 2935, 1714, 1612, 1512, 1444, 1244, 1085, 1033; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32 (d, *J* = 15.7 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 5.91 (t, *J* = 7.3 Hz, 1H), 5.80 (d, *J* = 15.7 Hz, 1H), 4.44 (s, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.50 (t, *J* = 6.8 Hz, 2H), 2.50 (q, *J* = 6.9 Hz, 2H), 1.78 (d, *J* = 1.6 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 167.5, 159.2, 149.2, 137.8, 134.2, 130.3, 129.3 (2C), 116.0, 113.8 (2C), 72.7, 68.7, 60.2, 55.3, 29.5, 14.3, 12.3. HRMS (MALDI-TOF/CCA) calculated for $[C_{18}H_{24}O_4 + H]^+$: 305.1747, Found: 305.1744.

(2*E*,4*E*)-ethyl 7-hydroxy)-4-methylhepta-2,4-dienoate (2h)

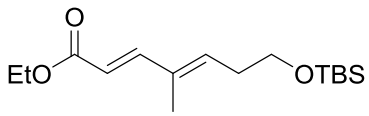


(2h)

To 0.55 ml of CH_2Cl_2-H_2O (10:1 (v/v)) solution, dienoate **8a** (25.0 mg, 0.082 mmol) was added and stirred at room temperature for 10 min, then 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (28.0 mg, 0.123 mmol) was added and the resulting solution was allowed to stir for 3 h at room temperature, during which time it turned dark green, brown, dark pink and ultimately, pink. The reaction mixture was extracted with Et_2O, and was then washed with saturated aqueous

solution of $NaHCO_3$, brine. The combined organic fraction was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford crude product. The crude was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the deprotected dienoate **2h** (13.3 mg, 88% yield) as a colorless liquid. R*f* = 0.282 (2:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3546, 3454, 3372, 2922, 2909, 1733, 1168; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.32 (d, *J* = 15.7 Hz, 1H), 5.91 (t, *J* = 7.4 Hz, 1H), 5.81 (d, *J* = 15.7 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.72 (t, *J* = 6.5 Hz, 2H), 2.48 (q, *J* = 6.8 Hz, 2H), 1.87 (s, 1H), 1.80 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 167.6, 149.2, 137.3, 135.2, 116.4, 61.9, 60.4, 32.4, 14.4, 12.5. HRMS (MALDI-TOF/CCA) calculated for $[C_{10}H_{16}O_3 + H]^+$: 185.1172, Found: 185.1171.

(2*E*,4*E*)-ethyl 7-(*tert*-butyldimethylsilyloxy)-4-methylhepta-2,4-dienoate (8b)[5]



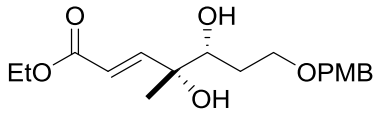
(8b)

To a solution of previous deprotected dienoate **2h** (30.0 mg, 0.16 mmol) in dry DMF (1.0 mL), imidazole (33.3 mg, 0.48 mmol) was added in one portion, and the reaction mixture was stirred at room temperature for 30 min. Then *tert*-Butyldimethylsilyl chloride (49.1 mg, 0.32 mmol) was added into the above solution and stirred for 10 h at room temperature. The reaction mixture was quenched by H_2O, extracted by Et_2O, and was then washed with brine. The combined organic fraction was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the yellow liquid crude product. The crude was purified by column chromatography (silica gel, 249:1 (v/v) hexane/EtOAc) to afford the TBS-protected dienoate **8b** (40.3 mg, 83% yield) as a colorless liquid. R*f* = 0.430 (40:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2928, 2857, 1698; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.31 (d, *J* = 15.7 Hz, 1H), 5.91 (t, *J* = 7.3 Hz, 1H), 5.80 (d, *J* = 15.7 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.67 (t, *J* = 6.7 Hz, 2H), 2.42 (q, *J* = 6.8 Hz, 2H), 1.78 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.04

[5] Spectral data matched which was previously reported, see: Clarke, P. A.; Davie, R. L.; Peace, S. Synthesis of the B-ring of FR182877. Investigation of the reactions of 6-fumaryl 1,3,8-nonatrienes. *Tetrahedron*, **2005**, *61*, 2335.

(s, 6H). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 167.7, 149.5, 138.2, 134.4, 116.0, 62.2, 60.3, 32.7, 26.0 (3C), 18.4, 14.5, 12.5, –5.2 (2C). HRMS (MALDI-TOF/CCA) calculated for $[C_{16}H_{30}O_3Si + H]^+$: 299.2037, Found: 299.2035.

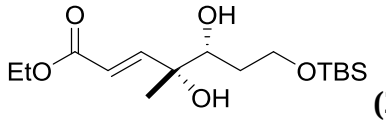
(*E*,4*R*,5*R*)-ethyl-7-(4-methoxybenzyloxy)-4,5-dihydroxy-4-methylhept-2-enoate (2i-1)



(2i-1)

To a 250 mL round bottom flask was added 1:1 *t*-butyl alcohol (30 mL)/H_2O (30 mL), $K_3Fe(CN)_6$ (9.81 g, 30.0 mmol), K_2CO_3 (4.14 g, 30.0 mmol), $KHCO_3$ (3.01 g, 30.0 mmol), $CH_3SO_2NH_2$ (0.95 g, 10.0 mmol), $(DHQD)_2$-PHAL (401 mg, 0.5 mmol, 2 mol %) and OsO_4 (51 mg, 0.2 mmol, 1 mol %). The mixture was stirred at room temperature for 15 min and then cooled to 0 ^oC. To this solution was added solution of dienoate **8a** (3.00 g, 16.8 mmol) in 2 mL of CH_2Cl_2 dropwise and the reaction was stirred vigorously at 0 ^oC overnight. Saturated aqueous solution of Na_2SO_3 was added to quench the reaction while stirring vigorously. EtOAc was added to the reaction mixture, and after separation of the layers, the aqueous layer was further extracted with EtOAc. The combined organic phases were washed with 2 M KOH and brine to remove the methanesulfonamide, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford compound **2i-1** (2.74 g, 81% yield). R_f = 0.20 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3510, 2989, 1736; $[\alpha]^{25}{}_D$ –6^o (*c* 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.22 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 15.8 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.10 (d, *J* = 15.6 Hz, 1H), 4.43 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 3.74-3.59 (m, 3H), 1.81-1.75 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.6, 159.3, 152.1, 129.4 (2C), 120.2, 113.8 (2C), 76.6, 74.7, 73.0, 68.7, 60.4, 55.2, 30.2, 22.8, 14.2; HRMS (CI) calcd for $[C_{18}H_{26}O_6 + Na]^+$: 361.1627, Found: 361.1621.

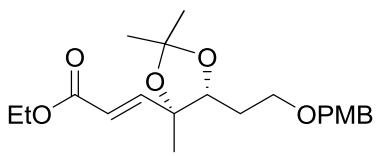
(*E*,4*R*,5*R*)-ethyl-4,5-dihydroxy-7-*tert*-butyldimethylsilyl-4-methylhept-2-enoate (2i-2)



(2i-2)

To a 250 mL round bottom flask was added 1:1 *t*-butyl alcohol (50 mL)/H_2O (50 mL), $K_3Fe(CN)_6$ (16.5 g, 50.3 mmol), K_2CO_3 (6.94 g, 50.3 mmol), $KHCO_3$ (5.08 g, 50.3 mmol), $CH_3SO_2NH_2$ (1.59 g, 16.8 mmol), $(DHQD)_2$-PHAL (270 mg, 0.34 mmol, 2 mol %) and OsO_4 (43 mg, 0.17 mmol, 1 mol %). The mixture was stirred at room temperature for 15 min and then cooled to 0 ^oC. To this solution was added enoate **8b** (5.01 g, 16.8 mmol) dropwise and the reaction was stirred vigorously at 0 ^oC overnight. Saturated aqueous solution of Na_2SO_3 was added to quench the reaction while stirring vigorously. EtOAc was added to the reaction mixture, and after separation of the layers, the aqueous layer was further extracted with EtOAc. The combined organic phases were washed with 2 M KOH and brine to remove the methanesulfonamide, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford compound **2i-2** (4.57 g, 82% yield). R_f = 0.25 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3430, 2980, 1758; $[\alpha]^{25}{}_D$ –11^o (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 6.99 (d, *J* = 15.6 Hz, 1H), 6.11 (d, *J* = 15.8 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.95-3.72 (m, 4H), 2.94 (bs, 1H), 1.74-1.67 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.25 (s, 3H), 0.87 (s, 9H), 0.06 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.6, 152.3, 120.2, 77.2, 74.6, 62.6, 60.3, 32.1, 25.8 (3C), 26.8, 18.0, 14.2, –5.64 (2C); HRMS (CI) calcd for $[C_{16}H_{32}O_6Si + Na]^+$: 371.1806, Found: 371.1861.

(*E*)-ethyl-3-((4*R*,5*R*)-5-(2-(4-methoxybenzyloxy)ethyl-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate (2j-1)

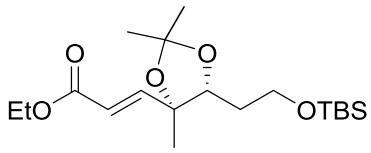


(2j-1)

To a solution of diol **2i-1** (3.38 g, 10.0 mmol) in 30 mL acetone was added

2,2-dimethoxypropane (10.42 g, 100.0 mmol) and CSA (223 mg, 1.0 mmol) at room temperature. In an hour, the reaction was quenched by adding saturated solution of $NaHCO_3$ and the mixture was filtered through a pad of celite. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, (9:1 (v/v) hexane/EtOAc) to afford compound **2j-1** (3.48 g, 92% yield) as a colorless oil. R_f = 0.25 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2990, 1728; $[\alpha]^{25}_D$ –15° (*c* 2.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 7.25 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 15.8 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.10 (d, *J* = 15.6 Hz, 1H), 4.44 (s, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.95 (dd, *J* = 8.9, 3.9 Hz, 1H), 3.80 (s, 3H), 3.64-3.49 (m, 2H), 1.93-1.72 (m, 2H), 1.46 (s, 3H), 1.36 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.4, 159.1, 149.4, 130.2, 129.2 (2C), 120.3, 113.7 (2C), 108.0, 81.6, 78.8, 72.7, 67.0, 60.5, 55.2, 29.5, 28.3, 26.3, 20.8, 14.2; HRMS (CI) calcd for $[C_{21}H_{30}O_6 + Na]^+$: 401.1934, Found: 401.1940.

(*E*)-ethyl-3-((4*R*,5*R*)-5-(2-*tert*-butyldimethylsilylethyl-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate (2j-2)

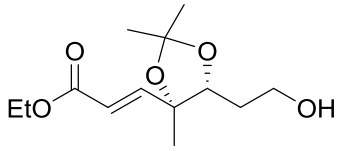


(2j-2)

To a solution of diol **2i-2** (2.20 g, 6.62 mmol) in 25 mL acetone was added 2,2-dimethoxypropane (13.80 g, 132.5 mmol) and CSA (0.15 g, 0.66 mmol) at room temperature. In an hour, the reaction was quenched by adding saturated aqueous solution of $NaHCO_3$ and the mixture was filtered through a pad of celite. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afforded compound **2j-2** (2.17 g, 88% yield) as a colorless oil. R_f = 0.60 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2980, 1710; $[\alpha]^{25}_D$ –14° (*c* 1.0,

$CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 6.89 (d, *J* = 15.8 Hz, 1H), 6.04 (d, *J* = 15.8 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.96 (dd, *J* = 8.9, 3.7 Hz, 1H), 3.81-3.65 (m, 2H), 1.83-1.68 (m, 2H), 1.46 (s, 3H), 1.36 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.21 (s, 3H), 0.88 (s, 9H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.4, 149.5, 120.3, 107.9, 81.5, 78.3, 60.5, 60.1, 32.2, 28.3, 26.3, 25.9 (3C), 20.9, 18.3, 14.2, –5.4, –5.4; HRMS (CI) calcd for $[C_{19}H_{36}O_5Si + Na]^+$: 395.2224, Found: 395.2229.

(*E*)-ethyl-3-((4*R*,5*R*)-5-(2-hydroxyethyl-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate (13)

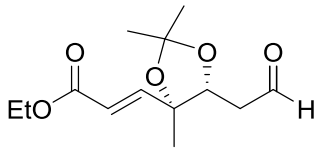


(13)

To a 10 mL round bottom flask was added 2.75 ml of 10:1 CH_2Cl_2 (2.50 mL)/H_2O (0.25 mL) and ether **2j-1** (155.2 mg, 0.41 mmol) at room temperature and stirred for 10 min, then 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (140.3 mg, 0.62 mmol) was added and the resulting solution was stirred at room temperature for 3 h. The reaction mixture was extracted by Et_2O. The combined organic phases were washed with saturated aqueous solution of $NaHCO_3$, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to afford crude product. The crude was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford compound **13** (93.2 mg, 88% yield) as a colorless liquid. Similarly, to a solution of silyl ether **2j-2** (2.45 g, 6.58 mmol) in 20 mL THF was added TBAF (9.87 mL, 9.87 mmol) at 0 ^oC. In two hour, the reaction was quenched by adding saturated aqueous solution of NH_4Cl. The aqueous layer was separated, extracted with Et_2O. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford compound **13** (1.61 g, 95% yield) as a colorless oil. R_f = 0.30 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3498, 2980, 1720; $[\alpha]^{25}_D$ –25^o (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 6.89 (d, *J* = 15.6 Hz, 1H), 6.10 (d, *J* = 15.6 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.95 (dd, *J* = 10.1, 2.7 Hz, 1H),

3.79 (dd, *J* = 6.4, 5.2 Hz, 2H), 2.22 (bs, 1H), 1.91-1.65 (m, 2H), 1.46 (s, 3H), 1.37 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.7, 149.1, 120.5, 108.5, 81.8, 80.5, 60.9, 60.6, 31.4, 28.3, 26.4, 20.9, 14.2; HRMS (CI) calcd for $[C_{13}H_{22}O_5 + Na]^+$: 281.1359, Found: 281.1368.

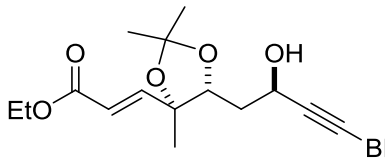
(*E*)-ethyl-3-((4*R*,5*R*)-5-(formylethyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate (2l)



(2l)

To a solution of oxalyl chloride (0.98 g, 7.7 mmol) in 30 mL of CH_2Cl_2 was added DMSO (0.69 g, 8.85 mmol) at –78 ^{o}C. After stirring for 30 min, alcohol **13** (1.52 g, 5.9 mmol) in 5 mL of CH_2Cl_2 was added dropwise. The mixture was stirred for another 90 min, and then Et_3N (1.98 g, 19.5 mmol) was added. In 2 h, the reaction was quenched with saturated aqueous solution of $NaHCO_3$, and the reaction mixture was extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford compound **2l** (1.14 g, 76% yield) as a colorless oil. R_f = 0.51 (1:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2986, 1720; $[\alpha]^{25}{}_D$ –26^o (*c* 1.0, $CHCl_3$): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 9.78 (t, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 15.6 Hz, 1H), 6.11 (d, *J* = 15.6 Hz, 1H), 4.31 (dd, *J* = 9.4, 3.5 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.74 (ddd, *J* = 16.8, 9.4, 2.2 Hz, 1H), 2.52 (ddd, *J* = 16.6, 3.5, 1.5 Hz, 1H), 1.46 (s, 3H), 1.39 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 198.9, 166.2, 148.4, 121.0, 108.9, 81.3, 76.2, 60.6, 43.2, 28.1, 26.3, 21.0, 14.2; HRMS (CI) calcd for $[C_{13}H_{20}O_5Si + Na]^+$: 279.1203, Found: 279.1205.

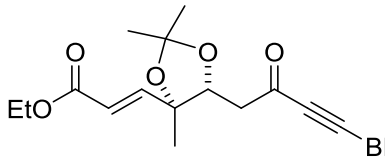
(*E*)-ethyl-3-((4*R*,5*R*)-5-((*R*)-4-(benzyldimethylsilyl)-2-hydroxybut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate (2m)



(2m)

To a solution of benzyldimethylsilane **14** (0.13 g, 0.75 mmol) in 4 mL of THF was added *n*-BuLi (0.31 mL, 0.75 mmol) at –78 ^{o}C, and the reaction was stirred for 0.5 h. Then a solution of aldehyde **2l** (0.18 g, 0.68 mmol) in 1 mL THF was added into the above mixture at –78 ^{o}C. After stirring for 2 h, the reaction was quenched with saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The crude product was purified by column chromatography (silica gel, 7:3 (v/v) hexane/EtOAc) to afford compound **2m** and its enantiomer (0.14 g, 82% yield) as a yellow oil. R_f = 0.35 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3432, 2986, 1718; $[\alpha]^{25}{}_{D}$ –15^{o} (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.23-7.17 (m, 2H), 7.10-7.03 (m, 3H), 6.88 (d, *J* = 15.8 Hz, 1H), 6.10 (d, *J* = 15.6 Hz, 1H), 4.56 (bs, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.74 (d, *J* = 7.2 Hz, 1H), 2.15 (s, 2H), 1.95 (ddd, *J* = 17.3, 10.6, 3.2 Hz, 1H), 1.77 (ddd, *J* = 14.1, 7.4, 2.2 Hz, 1H), 1.46 (s, 3H), 1.36 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.23 (s, 3H), 0.11 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.3, 148.8, 138.7, 128.3 (2C), 128.1 (2C), 124.4, 120.6, 108.6, 107.0, 88.1, 81.5, 78.1, 60.5, 60.3, 36.0, 28.2, 26.3, 26.0, 21.1, 14.2, –2.3 (2C); HRMS (CI) calcd for $[C_{24}H_{34}O_5Si + Na]^{+}$: 453.2073, Found: 453.2067.

(*E*)-ethyl-3-((4*R*,5*R*)-5-(4-(benzyldimethylsilyl)-2-oxobut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate (15)

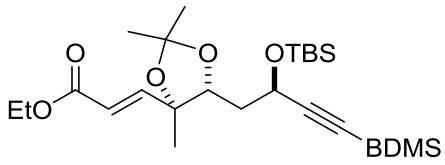


(15)

To a mixture alcohol **2m** and its enantiomer (105 mg, 0.25 mmol) in 2 mL of CH_2Cl_2 was added MnO_2 (213 mg, 2.45 mmol) at room temperature. In 24 h, the reaction

mixture was filtered through a pad of celite and washed with EtOAc. The organic phases were washed with brine and dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford ketone **15** (80 mg, 76% yield) as a colorless oil. R_f = 0.45 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2989, 1680; $[\alpha]^{25}{}_D$ –15° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 7.24-7.21 (m, 2H), 7.14-7.04 (m, 3H), 6.89 (d, *J* = 15.6 Hz, 1H), 6.12 (d, *J* = 15.6 Hz, 1H), 4.38 (dd, *J* = 9.2, 3.7 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.87 (dd, *J* = 16.6, 9.2 Hz, 1H), 2.64 (dd, *J* = 16.8, 4.0 Hz, 1H), 2.26 (s, 2H), 1.46 (s, 3H), 1.38 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.22 (s, 3H), 0.21 (s, 3H), 0.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 183.1, 166.2, 148.6, 137.7, 128.4 (2C), 128.3 (2C), 124.8, 120.9, 102.4, 98.1, 81.2, 76.8, 60.6, 44.7, 28.2, 26.2, 25.2, 21.1, 14.2, –2.8, –2.9; HRMS (CI) calcd for $[C_{24}H_{32}O_5Si + Na]^+$: 451.1911, Found: 451.1928.

(*E*)-ethyl-3-((4*R*,5*R*)-5-((*R*)-4-(benzyldimethylsilyl)-2-*tert*-butyldimethylsiloxy-but-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate (2p)

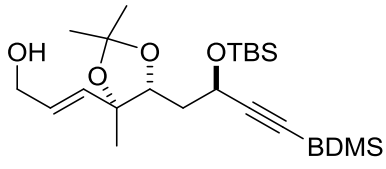


(2p)

To a solution of **2m** (220 mg, 0.51 mmol) in dry DMF (5.0 mL), imidazole (104.2 mg, 1.53 mmol) was added in one portion, and the reaction mixture was allowed to stir at room temperature for 30 min. Then *tert*-butyldimethylsilyl chloride (153.7 mg, 1.02 mmol) was added into the above solution and stirred for 3 h at room temperature. The reaction mixture was quenched by H_2O, extracted by Et_2O, and was then washed with brine. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the crude product. The residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford compound **2p** (213 mg, 89% yield) as a colorless oil. R_f = 0.32 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2986, 1752; $[\alpha]^{25}{}_D$ +62° (*c* 1.0, $CHCl_3$); ^1H NMR

($CDCl_3$, 270 MHz): δ 7.26-7.19 (m, 2H), 7.11-7.05 (m, 3H), 6.90 (d, *J* = 15.6 Hz, 1H), 6.08 (d, *J* = 15.6 Hz, 1H), 4.54-4.49 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.04-3.99 (m, 1H), 2.19 (s, 2H), 1.83 (ddd, *J* = 7.9, 4.5, 4.5 Hz, 2H), 1.46 (s, 3H), 1.34 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.22 (s, 3H), 0.89 (s, 9H) 0.11 (s, 6H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.3, 149.1, 138.1, 128.3 (2C), 128.1 (2C), 124.3, 120.4, 108.5, 108.2, 81.3, 77.2, 60.5, 60.1, 38.2, 28.3, 26.4, 26.0, 25.7 (3C), 21.1, 18.2, 14.2, –2.3 (2C), –4.6, –5.1; HRMS (CI) calcd for $[C_{30}H_{48}O_5Si_2 + Na]^+$: 567.2932, Found: 567.2934.

(*R*)-4-(benzyldimethylsilyl)-1-((*4R*,*5R*)-5-((*E*)-3-tert-butyldimethylsiloxyprop-1-enyl)-2,2,5-trimethyl-1,3-dioxolan-4-yl)but-3-yn-2-ol (2q)

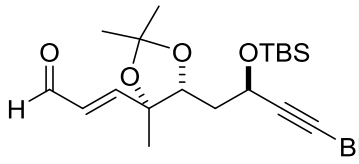


(2q)

To a solution of ester **2p** (380 mg, 0.70 mmol) in 3 mL of THF was added DIBAL-H (1.61 ml, 1.0 M in hexanes, 1.61 mmol) dropwise at –78 °C. In 1 h, the reaction was quenched by adding 1 mL of acetone and saturated aqueous solution of sodium potassium tartrate solution (Rochelle's salt, 10 mL), warmed to room temperature, diluted with ether and stirred for 1 h. The aqueous layer was extracted with Et_2O. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, 7:3 (v/v) hexane/EtOAc) to afford the allylic alcohol **2q** (341 mg, 97% yield) as a colorless oil. R_f = 0.24 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3402, 2989; $[\alpha]^{25}_{D}$ +76° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz): 7.24-7.19 (m, 2H), 7.11-7.04 (m, 3H), 5.93 (ddd, *J* = 15.6, 5.2, 5.2 Hz, 1H), 5.71 (d, *J* = 15.8 Hz, 1H), 4.54-4.49 (m, 1H), 4.15 (d, *J* = 4.5 Hz, 2H), 4.01-3.96 (m, 1H), 2.18 (s, 2H), 1.83 (ddd, *J* = 7.9, 3.5, 3.5 Hz, 2H), 1.45 (s, 3H), 1.34 (s, 3H), 1.21 (s, 3H), 0.90 (s, 9H) 0.13 (s, 3H), 0.11 (s, 6H), 0.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 138.8, 133.7, 129.7, 128.3 (2C), 128.1 (2C), 124.3, 108.7, 107.6, 81.3, 77.9, 63.1,

60.2, 38.0, 28.4, 26.7, 26.0, 25.8 (3C), 20.9, 18.2, –2.3 (2C), –4.6, –5.1; HRMS (CI) calcd for $[C_{28}H_{46}O_4Si_2 + Na]^+$: 525.2827, Found: 525.2835.

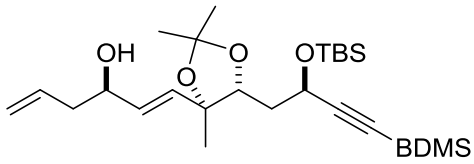
(*E*)-3-((4*R*,5*R*)-5-((*R*)-4-(benzyldimethylsilyl)-2-*tert*-butyldimethylsiloxybut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylaldehyde (6)



(6)

To a solution of alcohol **2q** (336 mg, 0.69 mmol) in 3 mL of CH_2Cl_2 was added MnO_2 (0.6 g, 6.9 mmol) at room temperature. In 8 h, the reaction mixture was filtered through a pad of celite. The filtrate was concentrated to afford the crude product. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford compound **6** (307 mg, 89% yield) as a colorless oil. R_f = 0.58 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2986, 1758; $[\alpha]^{25}{}_D$ +84° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 9.56 (d, *J* = 7.7 Hz, 1H), 7.24-7.19 (m, 2H), 7.11-7.05 (m, 3H), 6.73 (d, *J* = 15.6 Hz, 1H), 6.35 (dd, *J* = 15.6, 7.9 Hz, 1H), 4.52 (dd, *J* = 10.1, 3.0 Hz, 1H), 4.05 (dd, *J* = 9.9, 2.5 Hz, 1H), 2.19 (s, 2H), 1.85-1.75 (m, 2H), 1.48 (s, 3H), 1.35 (s, 3H), 1.27 (s, 3H), 0.89 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 193.2, 157.7, 138.7, 130.7, 128.3 (2C), 128.1 (2C), 124.3, 108.4, 108.2, 87.3, 81.3, 77.1, 60.0, 38.2, 28.2, 26.2, 25.9, 25.6 (3C), 20.8, 18.1, –2.3, –2.3, –4.6, –5.1; HRMS (CI) calcd for $[C_{28}H_{44}O_4Si_2 + Na]^+$: 523.2670, Found: 523.2665.

(*R*,*E*)-1-((4*R*,5*R*)-5-((*R*)-4-(benzyldimethylsilyl)-2-*tert*-butyldimethylsiloxybut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)hexa-1,5-dien-3-ol (2s)

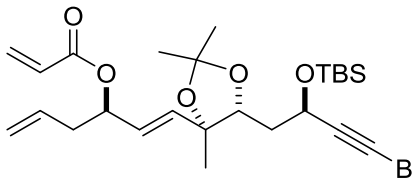


(2s)

To a solution of (*R*,*R*)-**17** (983 mg, 1.78 mmol) in 5 mL of CH_2Cl_2 was added a

solution of aldehyde **6** (297 mg, 0.60 mmol) in 4 mL of CH_2Cl_2 dropwise at –10 °C. The reaction flask was stirred at –10 °C for 48 h, was then diluted with EtOAc and quenched by adding 1 M $NaHSO_4$. The mixture was vigorously stirred at room temperature for 30 min, and filtered through a pad of celite. The filtrate was extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford compound **2s** (283 mg, 88% yield) as a light yellow oil. R_f = 0.32 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3630, 2932; $[\alpha]^{25}{}_D$ +55° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.22-7.20 (m, 2H), 7.10-7.06 (m, 3H), 5.81 (dd, *J* = 15.6, 6.0 Hz, 1H), 5.82-5.76 (m, 1H), 5.70 (d, *J* = 15.6 Hz, 1H), 5.15 (d, *J* = 6.0 Hz, 1H), 5.12 (s, 1H), 4.52 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.19 (dd, *J* = 6.0, 6.0 Hz, 1H), 3.97 (dd, *J* = 9.6, 2.4 Hz, 1H), 2.33 (ddd, *J* = 13.2, 6.6, 6.6 Hz, 1H), 2.28 (ddd, *J* = 13.8, 7.2, 6.6 Hz, 1H), 2.19 (s, 2H), 1.83-1.74 (m, 2H), 1.45 (s, 3H), 1.34 (s, 3H), 1.20 (s, 3H), 0.91 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 138.9, 134.0, 133.4, 132.3, 128.4 (2C), 128.2 (2C), 124.3, 118.3, 108.8, 107.6, 87.1, 81.3, 78.0, 71.1, 60.2, 41.8, 38.1, 28.4, 26.6, 26.1, 25.8 (3C), 21.1, 18.2, –2.3, –2.3, –4.6, –5.1; HRMS (CI) calcd for $[C_{31}H_{50}O_4Si_2 + Na]^+$: 565.3140, Found: 565.3132.

(*R*,*E*)-1-((4*R*,5*R*)-5-((*R*)-4-(benzyldimethylsilyl)-2-*tert*-butyldimethylsiloxybut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)hexa-1,5-dien-3-ylacrylate (18)

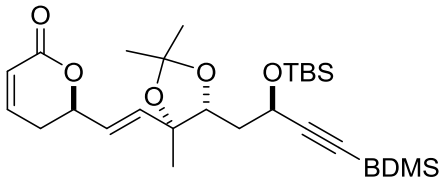


(18)

To a solution of alcohol **2s** (317 mg, 0.59 mmol) in 5 mL of CH_2Cl_2 was added acrylic acid (127 mg, 1.76 mmol), DCC (362 mg, 1.76 mmol) and catalytic amount of DMAP (5 mg, 7 mmol %). In 5 h, the reaction mixture was diluted with Et_2O and filtered through a pad of celite and washed with Et_2O. The organic phase was washed with saturated aqueous solution of $NaHSO_4$, saturated aqueous solution of $NaHCO_3$, brine

and dried over anhydrous Na_2SO_4. The organic phase was then concentrated under reduced pressure to afford the crude product. The crude was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to provide the ester **18** (274 mg, 78% yield) as a colorless oil. R_f = 0.71 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2987, 1727; $[\alpha]^{25}{}_D$ +50° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.22-7.20 (m, 2H), 7.10-7.06 (m, 3H), 6.39 (dd, *J* = 17.4, 1.2 Hz, 1H), 6.10 (dd, *J* = 17.4, 10.2 Hz, 1H), 5.81 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.79 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.76-5.69 (m, 1H), 5.75 (s, 1H), 5.41 (dd, *J* = 6.6, 6.0 Hz, 1H), 5.10 (dd, *J* = 3.0, 1.2 Hz, 1H), 5.08-5.06 (m, 1H), 5.51 (dd, *J* = 10.2, 2.4 Hz, 1H), 3.96 (dd, *J* = 10.2, 2.4 Hz, 1H), 2.42 (ddd, *J* = 6.9, 6.9, 1.2 Hz, 1H), 2.19 (s, 2H), 1.82-1.72 (m, 2H), 1.45 (s, 3H), 1.33 (s, 3H), 1.17 (s, 3H), 0.90 (s, 9H), 0.12 (s, 3H), 0.12 (s, 3H), 0.10 (s, 3H), 0.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 165.2, 138.9, 135.7, 132.9, 130.6, 128.7, 128.4 (2C), 128.2 (2C), 127.4, 124.4, 118.1, 108.7, 107.6, 87.0, 81.3, 78.0, 73.1, 60.2, 39.1, 38.3, 34.9, 28.4, 26.5, 26.1, 25.8 (3C), 21.4, 18.2, –2.2, –2.3, –4.6, –5.1; HRMS (CI) calcd for $[C_{34}H_{52}O_5Si_2 + Na]^+$: 619.3245, Found: 619.3234.

(*R*)-6-((*E*)-2-((4*R*,5*R*)-5-((*R*)-4-(benzyldimethylsilyl)-2-*tert*-butyldimethylsiloxybut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)vinyl-5,6-dihydropyran-2-one (2u)

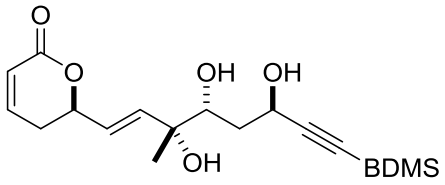


(2u)

To a solution of triene **18** (177 mg, 0.30 mmol) in 15 mL CH_2Cl_2 was added Grubbs catalyst I **19** (25 mg, 10 mmol %) in 15 mL CH_2Cl_2. The reaction was refluxed for 2 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, 7:3 (v/v) hexane/EtOAc) to afford the lactone **2u** (142 mg, 87% yield) as a colorless oil. R_f = 0.16 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2930, 1731; $[\alpha]^{25}{}_D$ +137° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.22-7.20 (m, 2H), 7.10-7.06 (m, 3H), 6.88-6.85 (m, 1H), 6.05 (d, *J* = 9.6 Hz, 1H), 5.91 (dd, *J* = 15.6, 5.4 Hz, 1H), 5.84 (dd, *J* = 15.6 Hz, 1H), 4.94 (ddd, *J* = 10.2, 5.4, 4.8 Hz, 1H),

4.51 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.97 (dd, *J* = 9.6, 2.4 Hz, 1H), 2.44-2.41 (m, 2H), 2.19 (s, 2H), 1.82-1.75 (m, 2H), 1.45 (s, 3H), 1.33 (s, 3H), 1.20 (s, 3H), 0.90 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 163.7, 144.4, 138.9, 130.6, 128.7, 128.4 (2C), 128.2 (2C), 126.8, 124.4, 121.7, 109.8, 107.8, 81.2, 77.9, 77.1, 60.1, 38.1, 29.8, 28.4, 26.6, 26.1, 25.8 (3C), 21.0, 18.2, –2.2, –2.3, –4.5, –5.1; HRMS (CI) calcd for $[C_{32}H_{48}O_5Si_2 + Na]^+$: 591.2932, Found: 591.2930.

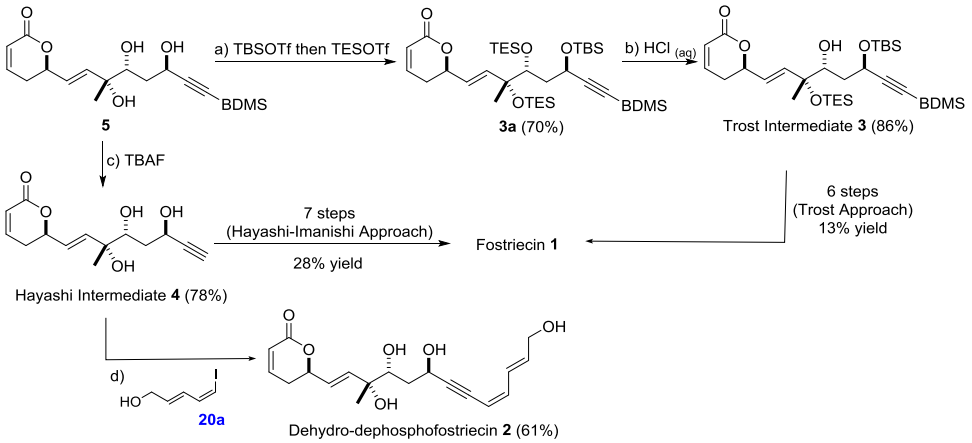
(*R*)-6-((*E*,3*R*,4*R*,5*R*)-8-(benzyldimethylsilyl)-3,4,6-trihydroxy-3-methyloct-1-en-7-ynyl)-5,6-dihydropyran-2-one (5)



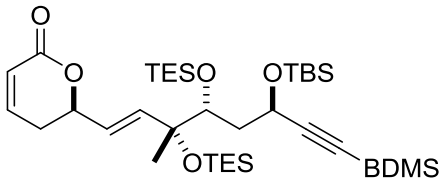
(5)

To a 10 mL round bottom flask was added acetonide **2u** (53 mg, 0.093 mmol) and 10 mol % aqueous solution of 1:1 HCl (0.7 mL)/THF (0.7 mL). The mixture was stirred at 65 ^{o}C for 0.5 h, then cooled down to room temperature and quenched by saturated aqueous solution of $NaHCO_3$. The solution was extracted with Et_2O, and combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 1:4 (v/v) hexane/EtOAc) to provide the pyranone **5** (27 mg, 70% yield) as a colorless oil. R_f = 0.31 (2:8 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3407, 2981, 1742; $[\alpha]^{25}_{D}$ +66^{o} (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.24-7.21 (m, 2H), 7.11-7.06 (m, 3H), 6.88 (ddd, *J* = 9.0, 6.0, 3.0 Hz, 1H), 6.05 (dd, *J* = 9.6, 2.4 Hz, 1H), 5.97-5.94 (m, 2H), 4.97 (ddd, *J* = 10.2, 4.8, 4.2 Hz, 1H), 4.60 (dd, *J* = 4.8, 4.2 Hz, 1H), 3.69 (d, *J* = 9.6 Hz, 1H), 3.13 (d, *J* = 2.4 Hz, 1H), 2.76 (s, 1H), 2.46 (dddd, *J* = 18.6, 14.4, 5.4, 4.8 Hz, 2H), 2.21 (s, 2H), 1.93-1.80 (m, 2H), 1.28 (s, 3H), 0.14 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 164.1, 145.0, 138.8, 137.9, 128.3 (2C), 128.2 (2C), 126.6, 124.4, 121.4, 107.5, 88.3, 77.3, 74.5, 74.0, 60.8, 37.1, 29.8, 26.0, 22.4, –2.2 (2C); HRMS (CI) calcd for $[C_{23}H_{30}O_5Si + Na]^+$: 437.1755, Found: 437.1756.

Intermediates related to Scheme 3:



(*R*)-6-((*E*,3*R*,4*R*,5*R*)-8-(benzyldimethylsilyl)-3,4-bistrimethylsiloxy-6-*tert*-butyl dimethylsiloxybut-3-methyloct-1-en-7-ynyl)-5,6-dihydropyran-2-one (3a)

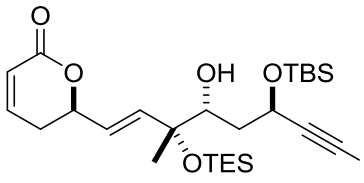


(3a)

To a solution of lactone **5** (22 mg, 0.053 mmol) in 1.0 mL of CH_2Cl_2 was added 2,6-lutidine (62 µl, 0.53 mmol) at –78 ºC and stirred for 10 min. TBSOTf (34.4 mg, 0.13 mmol) was added to the reaction mixture, and monitored by the TLC. After the spot representing for the starting material disappeared, TESOTf (113.7 mg, 0.43 mmol) was added into the reaction. The reaction was stirred at –78 ºC for 1 h, was then diluted with CH_2Cl_2 and quenched by saturated aqueous solution of $NaHCO_3$. The reaction mixture was extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 1:4 (v/v) hexane/EtOAc) to provide compound **3a** (28 mg, 70% yield) as a colorless oil. R_f = 0.88 (3:7 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2956, 1736; $[\alpha]^{25}{}_D$ +38º (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.22-7.19 (m, 2H), 7.09-7.06 (m, 3H), 6.86 (ddd, *J* = 8.4, 4.8, 3.0 Hz, 1H), 6.05 (ddd, *J* = 10.2, 1.8, 1.8 Hz, 1H), 5.91 (dd, *J* = 16.2, 1.2 Hz, 1H), 5.79 (dd, *J* = 15.6, 6.0 Hz, 1H), 4.97 (ddd, *J* = 9.6, 6.0, 1.2 Hz, 1H), 4.50 (dd, *J* = 7.8, 6.6 Hz, 1H), 3.68 (dd, *J* = 6.0, 5.4 Hz, 1H), 2.47-2.42 (m, 2H), 2.19 (s, 2H), 1.97 (ddd, *J* = 13.2, 7.8, 2.4 Hz, 2H), 1.37 (s, 3H), 0.97 (t, *J* = 8.4 Hz, 18H),

0.89 (s, 9H), 0.67-0.63 (m, 12H), 0.13 (s, 3H), 0.11 (s, 3H), 0.10 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 164.0, 144.4, 138.9, 138.2, 128.3 (2C), 128.2 (2C), 125.9, 124.3, 121.7, 109.5, 87.6, 78.1, 77.9, 76.0, 61.0, 43.6, 30.0, 26.1, 25.9 (3C), 25.7, 18.2, 7.3 (3C), 7.1 (3C), 7.0 (3C), 5.4 (3C), –2.3 (2C), –3.9, –4.4; HRMS (CI) calcd for $[C_{41}H_{72}O_5Si_4 + Na]^+$: 779.4349, Found: 779.4354.

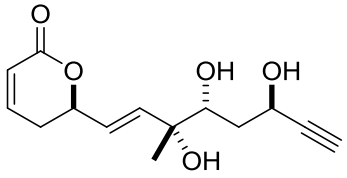
(*R*)-6-((*E*,3*R*,4*R*,5*R*)-8-(benzyldimethylsilyl)-3-trimethylsiloxy-4-hydroxy-6-*tert*-butyldimethylsiloxybut-3-methyloct-1-en-7-ynyl)-5,6-dihydropyran-2-one (3)



(3)

A solution of silyl ether **3a** (23 mg, 0.03 mmol) in a mixture of 1M HCl/THF/CH_3CN : 1/3/6 was stirred at –10 ^{o}C. In 1.5 h, the reaction was then diluted with EtOAc and quenched by saturated aqueous solution of $NaHCO_3$. The reaction mixture was extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 1:9 (v/v) hexane/EtOAc) to provide compound **3** (17 mg, 86% yield) as a colorless oil. R_f = 0.51 (3:7 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3511, 2957, 1726; $[\alpha]^{25}_D$ +54^o (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.22-7.20 (m, 2H), 7.10-7.05 (m, 3H), 6.88 (ddd, *J* = 9.8, 4.8, 3.0 Hz, 1H), 6.06 (ddd, *J* = 9.6, 1.8, 1.8 Hz, 1H), 5.91 (dd, *J* = 16.2, 1.2 Hz, 1H), 5.82 (dd, *J* = 16.2, 6.0 Hz, 1H), 4.97 (dddd, *J* = 9.6, 6.0, 6.0, 1.2 Hz, 1H), 4.66 (dd, *J* = 7.2, 3.0 Hz, 1H), 3.75 (dd, *J* = 10.8, 1.2 Hz, 1H), 2.95 (d, *J* = 2.4 Hz, 1H), 2.46-2.43 (m, 2H), 2.19 (s, 2H), 1.84 (ddd, *J* = 14.4, 7.8, 1.2 Hz, 1H), 1.51 (ddd, *J* = 14.4, 10.8, 3.6 Hz, 1H), 1.37 (s, 3H), 0.95 (t, *J* = 8.4 Hz, 9H), 0.90 (s, 9H), 0.60 (q, *J* = 8.4 Hz, 6H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 163.9, 144.4, 138.9, 137.7, 128.3 (2C), 128.2 (2C), 126.7, 124.3, 121.7, 108.2, 87.8, 77.5, 76.9, 75.1, 61.7, 38.9, 29.6, 26.1, 25.8 (3C), 22.6, 18.1, 7.1 (3C), 6.75 (3C), –2.3, –2.4, –4.6, –5.2; HRMS (CI) calcd for $[C_{35}H_{58}O_5Si_3 + Na]^+$: 665.3484, Found: 665.3469.

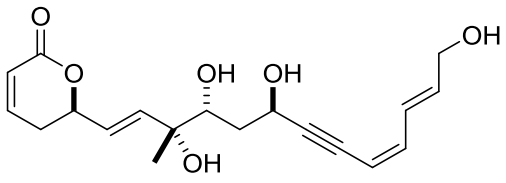
(*R*)-5,6-dihydro-6-((*E*,3*R*,4*R*,6*R*)-3,4,6-trihydroxy-3-methyloct-1-en-7-ynyl)pyran-2-one (4)



(4)

To a solution of lactone **5** (37 mg, 0.089 mmol) in 0.5 mL of THF was added TBAF (0.13 mL, 1.0 M in THF) at 0 ^{o}C. After stirring at 0 ^{o}C for 2 h, the reaction was quenched by saturated aqueous solution of $NaHCO_3$. The reaction mixture was extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 1:9 (v/v) hexane/EtOAc) to provide compound **4** (18 mg, 78% yield) as a colorless oil. R_f = 0.21 (1:9 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3406, 2907, 1739; $[\alpha]^{25}{}_{D}$ +33^{o} (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.88 (ddd, *J* = 8.4, 6.0, 3.0 Hz, 1H), 6.04 (dd, *J* = 9.6, 1.2 Hz, 1H), 5.96 (d, *J* = 15.6 Hz, 1H), 5.93 (ddd, *J* = 15.6, 4.8, 4.8 Hz, 1H), 4.97 (ddd, *J* = 9.6, 4.8, 4.8 Hz, 1H), 4.68 (bs, 1H), 4.00 (d, *J* = 9.0 Hz, 1H), 3.4 (d, *J* = 9.6 Hz, 1H), 2.53-2.41 (m, 3H), 1.91-1.82 (m, 2H), 1.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 164.1, 145.1, 138.6, 126.8, 121.4, 84.4, 77.2, 74.6, 74.2, 73.4, 60.4, 36.8, 29.8, 22.5; HRMS (CI) calcd for $[C_{14}H_{18}O_5 + Na]^{+}$: 289.1046, Found: 289.1045.

(*R*)-5,6-dihydro-6-((1*E*,3*R*,4*R*,6*R*,9*Z*,11*E*)-3,4,6,13-tetrahydroxy-3-methyltrideca-1,9,11-trien-7-ynyl)-pyran-2-one (2)

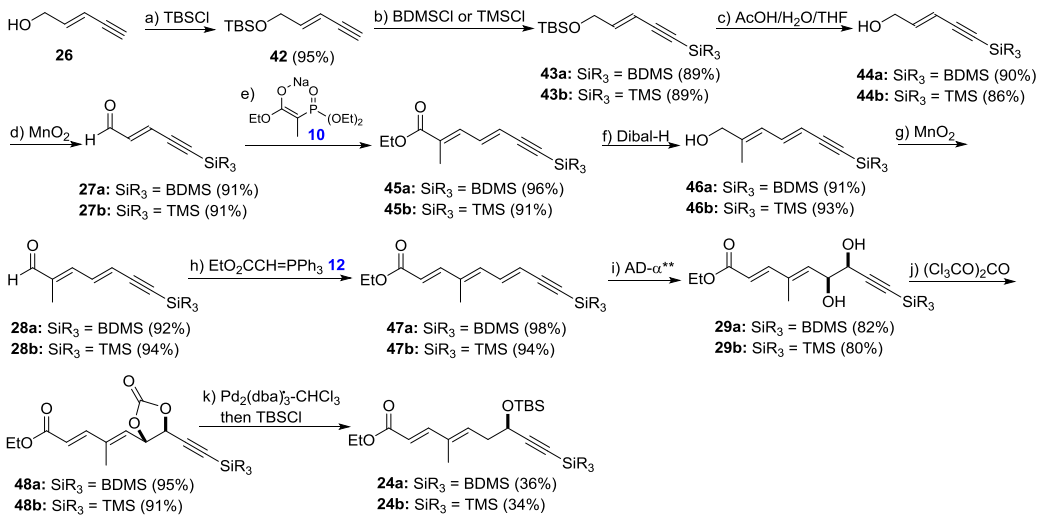


(2)

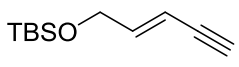
To a solution of vinyl iodide **20a** (27 mg, 0.13 mmol) in 0.5 mL of Et_3N was added $Pd_2(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol) and CuI (7 mg, 0.026 mmol) at room temperature. After 10 min, alkyne **4** (17 mg, 0.064 mmol) in 0.5 mL of Et_3N was added into the reaction and kept stirring at room temperature for 2 h. Then the reaction was diluted

with EtOAc and quenched by saturated aqueous solution of NH_4Cl. The reaction mixture was extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 1:9 (v/v) hexane/EtOAc) to provide compound **2** (13 mg, 61% yield) as a colorless oil. R_f = 0.35 (9:1 (v/v) CH_2Cl_2/MeOH); IR (neat, cm^{-1}): 3486, 2942, 1712; $[\alpha]^{25}{}_D$ +52º (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 6.90-6.84 (m, 2H), 6.40 (dd, *J* = 10.8, 10.8 Hz, 1H), 6.01-5.92 (m, 3H), 5.89 (ddd, *J* = 15.6, 6.0, 6.0 Hz, 1H), 5.40 (d, *J* = 10.2 Hz, 1H), 4.97 (dddd, *J* = 9.6, 6.0, 6.0, 1.2 Hz, 1H), 4.95 (ddd, *J* = 15.6, 10.2, 4.8 Hz, 1H), 4.80 (d, *J* = 2.4 Hz, 1H), 4.26 (d, *J* = 2.4 Hz, 1H), 4.09 (ddd, *J* = 7.2, 3.0, 3.0 Hz, 1H), 3.53 (ddd, *J* = 7.2, 7.2, 7.2 Hz, 1H), ^{13}C NMR ($CDCl_3$, 150 MHz): δ 164.4, 145.3, 140.1, 139.6, 137.9, 136.0, 134.3, 126.3, 121.3, 108.3, 95.6, 82.5, 74.8, 62.2, 61.6, 36.2, 29.9, 29.7, 22.4; HRMS (CI) calcd for $[C_{19}H_{24}O_6 + Na]^+$: 371.1465, Found: 371.1458.

Intermediates related to Scheme 5:



((*E*)-pent-2-en-4-ynyloxy)(*tert*-butyl)dimethylsiane (42)

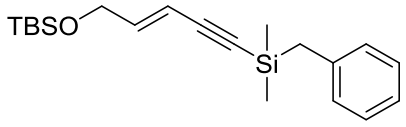


(42)

To the solution of 2-penten-4-yn-1-ol **26** (10.0 g, 121.8 mmol) in 100 mL of CH_2Cl_2, Et_3N (30.8 g, 304.5 mmol), TBSCl (23.8 g, 158.4 mmol) and DMAP (0.73 g, 6.1 mmol)

were added at room temperature. The reaction mixture was stirred at room temperature for 15 h, and quenched with saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2, and the combined organic solution was washed with brine, dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the TBS protecting alkyne **42** (22.7g, 95% yield) as a viscous oil. R_f = 0.59 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2955, 1740, 1463; ^1H NMR ($CDCl_3$, 270 MHz): δ 6.30 (ddd, *J* = 15.8, 4.0, 4.0 Hz, 1H), 5.75 (dddd, *J* = 15.8, 2.2, 2.2, 2.2 Hz, 1H), 4.23 (dd, *J* = 3.7, 2.5 Hz, 2H), 2.87 (d, *J* = 1.7 Hz, 1H), 0.91 (s, 9H), 0.69 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 144.3, 107.5, 82.1, 77.3, 62.7, 25.8 (3C), 18.3, –5.4 (2C); HRMS (CI) calcd for $[C_{11}H_{20}OSi + Na]^+$: 219.1175, Found: 219.1181.

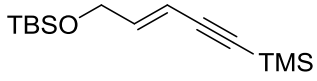
(*E*)- 5-(benzyldimethylsilyl)pent-2-en-4-ynyloxy)(*tert*-butyl)dimethylsiane (43a)



(43a)

To a solution of alkyne **42** (5.0 g, 25.5 mmol) in 60 mL of THF flask was added *n*-BuLi (1.7 g, 26.8 mmol) at –78 °C. BDMSCl (5.0 g, 27.6 mmol) was dissolved in 5 mL of THF and then added dropwise into the previous solution. The reaction mixture was stirred at –78 °C for 2 h and quenched with saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with EtOAc, and the combined organic solution was washed with brine, dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the silyl ether **43a** (7.81 g, 89% yield) as a viscous oil. R_f = 0.56 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2959, 1600, 1494; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.28-7.23 (m, 2H), 7.15-7.10 (m, 3H), 6.30 (ddd, *J* = 15.8, 4.2, 4.0 Hz, 1H), 5.84 (ddd, *J* = 15.8, 2.2, 2.2 Hz, 1H), 4.27 (dd, *J* = 4.0, 2.2 Hz, 2H), 2.26 (s, 2H), 0.96 (s, 9H), 0.18 (s, 6H), 0.11 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 143.9, 138.9, 128.3 (2C), 128.1 (2C), 124.3, 108.5, 104.9, 92.9, 62.7, 26.3, 25.8 (3C), 18.3, –2.2 (2C), –5.4 (2C); HRMS (CI) calcd for $[C_{20}H_{32}OSi_2 + Na]^+$: 219.1175, Found: 219.1171.

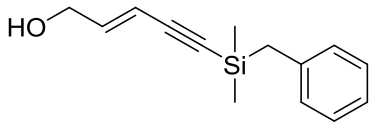
(*E*)- 5-(benzyldi methylsilyl)pent-2-en-4-ynyloxy)(tert-butyl)dimethylsilane (43b)



(43b)

To a solution of alkyne **42** (25.1 g, 128.1 mmol) in 150 mL of THF flask was added *n*-BuLi (9.8 g, 153.0 mmol) at –78 °C. TMSCl (18.1 g, 166.4 mmol) was dissolved in 30 mL of THF and then added dropwise into the previous solution. The reaction mixture was stirred at –78 °C for 2 h and quenched with saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with EtOAc, and the combined organic solution was washed with brine, dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the silyl ether **43b** (30.6 g, 89% yield) as a viscous oil. R_f = 0.58 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2980; ^1H NMR ($CDCl_3$, 270 MHz): δ 6.25 (ddd, *J* = 15.8, 4.2, 4.0 Hz, 1H), 5.79 (ddd, *J* = 15.8, 2.2, 2.0 Hz, 1H), 4.21 (dd, *J* = 4.2, 2.2 Hz, 2H), 0.90 (s, 9H), 0.18 (s, 9H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 143.6, 108.6, 103.6, 94.4, 62.7, 25.8 (3C), 18.3, –0.07 (3C), –5.4 (2C); HRMS (CI) calcd for $[C_{14}H_{20}OSi_2 + Na]^+$: 291.1571, Found: 291.1577.

(*E*)-5-(benzyldimethylsilyl)pent-2-en-4-yn-1-ol (44a)

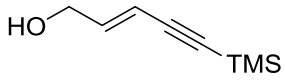


(44a)

A mixture of 50 mL AcOH/H_2O/THF: 3/1/1 was added to silyl ether **43a** (2.98 g, 8.65 mmol) at room temperature. The reaction was stirred at room temperature for 12 h and quenched with saturated aqueous solution of K_2CO_3. The aqueous layer was extracted with Et_2O and the combined organic solution was washed with brine, dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the primary alcohol **44a** (1.79 g, 90% yield) as a colorless oil. R*f* = 0.16 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3363, 2959, 1600, 1494; ^1H NMR ($CDCl_3$, 270 MHz):

δ 7.27-7.21 (m, 2H), 7.13-7.07 (m, 3H), 6.30 (ddd, *J* = 16.1, 5.0, 4.9 Hz, 1H), 5.77 (ddd, *J* = 16.1, 2.0, 1.7 Hz, 1H), 4.20 (dd, *J* = 4.9, 2.0 Hz, 2H), 2.23 (s, 2H), 0.16 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 143.0, 138.8, 128.3 (2C), 128.1 (2C), 124.3, 110.0, 104.2, 93.5, 62.5, 26.1, 20.7, –2.3 (2C); HRMS (CI) calcd for $[C_{14}H_{18}OSi + Na]^+$: 253.1019, Found: 253.1022.

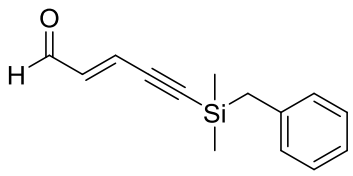
(*E*)-5-(trimethylsilyl)pent-2-en-4-yn-1-ol (44b)



(44b)

A mixture of 150 mL AcOH/H_2O/THF: 3/1/1 was added to silyl ether **43b** (26.8 g, 100 mmol) at room temperature. The reaction was stirred at room temperature for 12 h and quenched with saturated aqueous solution of K_2CO_3. The aqueous layer was extracted with Et_2O and the combined organic solution was washed with brine, dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the primary alcohol **44b** (13.2 g, 86% yield) as a colorless oil. R*f* = 0.25 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3363, 2959, 1600, 1494; ^{1}H NMR ($CDCl_3$, 270 MHz): δ 6.27 (ddd, *J* = 15.8, 5.2, 5.0 Hz, 1H), 5.74 (ddd, *J* = 16.1, 2.0, 1.8 Hz, 1H), 4.20 (dd, *J* = 4.4, 3.7 Hz, 2H), 2.20 (bs, 1H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 142.9, 110.2, 103.0, 95.2, 62.6, –0.2 (3C) ; HRMS (CI) calcd for $[C_{14}H_{18}OSi + Na]^+$: 176.2722, Found: 176.2727.

(*E*)-5-(benzyldimethylsilyl)pent-2-en-4-yna1 (27a)

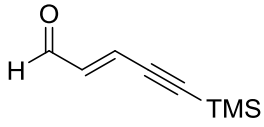


(27a)

To a solution of primary alcohol **44a** (1.79 g, 7.79 mmol) in 20 mL of CH_2Cl_2 was added MnO_2 (6.78 g, 77.85 mmol) at room temperature. The reaction mixture was stirred at room temperature for 16 h and then filtered through a pad of celite and washed

with Et_2O. The filtrate was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the aldehyde **27a** (1.62 g, 91% yield) as a colorless oil. R_f = 0.53 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2989, 1710, 1456; ^1H NMR ($CDCl_3$, 270 MHz): δ 9.56 (d, *J* = 7.2, Hz, 1H), 7.28-7.22 (m, 2H), 7.15-7.06 (m, 3H), 6.57 (d, *J* = 16.1 Hz, 1H), 6.46 (dd, *J* = 15.8, 7.2 Hz, 1H), 2.27 (s, 2H), 0.21 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 193.1, 140.2, 138.2, 131.8, 128.3 (4C), 124.6, 109.6, 101.7, 25.6, –2.6 (2C); HRMS (CI) calcd for $[C_{14}H_{16}OSi + Na]^+$: 251.0862, Found: 251.0855.

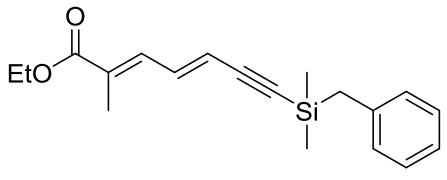
(*E*)-5-(trimethylsilyl)pent-2-en-4-yna1 (27b)



(27b)

To a solution of primary alcohol **44b** (10.4 g, 67.5 mmol) in 100 mL of CH_2Cl_2 was added MnO_2 (58.0 g, 672 mmol) at room temperature. The reaction mixture was stirred at room temperature for 16 h and then filtered through a pad of celite and washed with Et_2O. The filtrate was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the aldehyde **27b** (9.3 g, 91% yield) as a colorless oil. R_f = 0.23 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3369, 2989, 1680; ^1H NMR ($CDCl_3$, 270 MHz): δ 9.54 (d, *J* = 7.2, Hz, 1H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.44 (dd, *J* = 15.8, 7.4 Hz, 1H), 0.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 193.1, 140.1, 132.1, 111.4, 100.6, –0.6 (3C); HRMS (CI) calcd for $[C_8H_{12}OSi + H]^+$: 153.0736, Found: 153.0730.

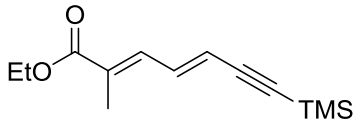
(2*E*, 4*E*)-ethyl-7-(benzyldimethylsilyl)-2-methylhepta-2,4-dien-ynoate (45a)



(45a)

Triethyl 2-phosphonopropionate **10** (2.07 g, 8.67 mmol) was added dropwise to *n*-BuLi (0.56 g, 2.3 M, 8.67 mmol) in THF (30 mL) at –78 °C under an argon atmosphere. After 30 min stirring, aldehyde **27a** (1.52 g, 6.67 mmol) in 1 mL of THF was added dropwise, and the reaction was stirred at room temperature for another 2 h. The reaction mixture was quenched by saturated aqueous solution of NH_4Cl, and was then extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the dienynoate **45a** (1.99 g, 96% yield) as a colorless oil. R_f = 0.63 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2982, 1705; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.26-7.18 (m, 2H), 7.13-7.07 (m, 3H), 6.90 (d, *J* = 15.3 Hz, 1H), 6.88 (d, *J* = 15.3 Hz, 1H), 5.91 (d, *J* = 15.3 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.25 (s, 2H), 1.99 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.17 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 167.8, 137.7, 136.4, 130.1, 128.3 (2C), 128.1 (2C), 124.4, 117.2, 105.3, 99.4, 82.6, 60.8, 26.1, 14.2, 13.0, –2.3 (2C); HRMS (CI) calcd for $[C_{19}H_{24}O_2Si + Na]^+$: 335.1438, Found: 335.1433.

(2E, 4E)-ethyl-2-methyl-7-(trimethylsilyl)hepta-2,4-dien-6-ynoate (45b)

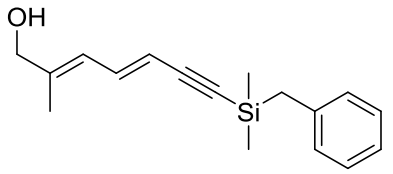


(45b)

Triethyl 2-phosphonopropionate **10** (15.6 g, 65.7 mmol) was added dropwise to *n*-BuLi (3.86 g, 2.3 M, 60.2 mmol) in THF (200 mL) at –78 °C under an argon atmosphere. After 30 min stirring, aldehyde **27b** (8.32 g, 54.8 mmol) in 10 mL of THF was added dropwise, and the reaction was stirred at room temperature for another 2 h. The reaction mixture was quenched by saturated aqueous solution of NH_4Cl, and was then extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the dienynoate **45b** (12.2 g, 91% yield) as a colorless oil. R_f = 0.32 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2986, 1708; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.14 (dd, *J*

= 11.9, 1.2 Hz, 1H), 6.90 (dd, *J* = 15.3, 11.9 Hz, 1H), 5.90 (d, *J* = 15.3 Hz, 1H), 4.20 (q, *J* = 7.2, 2H), 1.96 (d, *J* = 1.2 Hz, 3H), 1.29 (t, *J* = 7.2, 3H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 167.8, 137.4, 136.5, 129.9, 117.3, 103.9, 100.8, 60.8, 14.2, 12.9, –0.3 (3C); HRMS (CI) calcd for $[C_{13}H_{20}O_2Si + H]^+$: 237.1311, Found: 237.1306.

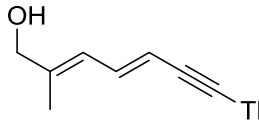
(2*E*,4*E*)-7-(benzyldimethylsilyl)-2-methylhepta-2,4-dien-6-yn-1-ol (46a)



(46a)

To a solution of dienynoate **45a** (1.68 g, 5.38 mmol) in CH_2Cl_2 (15 mL) was dropwise added diisobutylaluminum hydride (*i*-Bu)$_2$AlH (1.0 M in CH_2Cl_2, 16.1 mL, 16.1 mmol) at –78 °C under an argon atmosphere. After stirring for 30 min at –78 °C, the reaction mixture was allowed warming up to 0 °C and kept stirring for 30 min. Then the reaction mixture was diluted with Et_2O and was quenched with saturated aqueous solution of potassium sodium tartrate (Rochelle's salt, 15 mL). The biphasic mixture was stirred until two layers separated once stopped stirring. The aqueous layer was extracted with Et_2O. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the primary alcohol **46a** (443 mg, 91% yield) as a colorless oil. R_f = 0.21 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3429, 2982; ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.26-7.21 (m, 2H), 7.12-7.07 (m, 3H), 6.90 (dd, *J* = 15.6, 11.4 Hz, 1H), 6.14 (d, *J* = 11.4 Hz, 1H), 5.61 (d, *J* = 15.6 Hz, 1H), 4.11 (s, 2H), 2.24 (s, 2H), 1.82 (s, 3H), 0.16 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 141.2, 138.7, 128.4 (2C), 128.1 (2C), 124.3, 123.5, 110.3, 106.2, 95.4, 67.8, 26.3, 14.4, 13.0, –2.1 (2C); HRMS (CI) calcd for $[C_{17}H_{22}OSi + Na]^+$: 293.1332, Found: 293.1327.

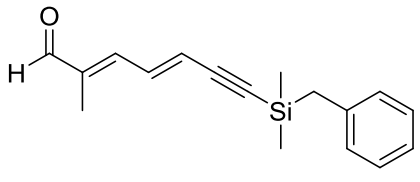
(2*E*, 4*E*)-2-methyl-7-(trimethylsilyl)hepta-2,4-dien-6-yn-1-ol (46b)



(46b)

To a solution of dienynoate **45b** (8.69 g, 36.8 mmol) in CH_2Cl_2 (100 mL) was dropwise added diisobutylaluminum hydride $(i\text{-Bu})_2AlH$ (1.0 M in CH_2Cl_2, 92.0 mL, 92.0 mmol) at –78 °C under an argon atmosphere. After stirring for 30 min at –78 °C, the reaction mixture was allowed warming up to 0 °C and kept stirring for 30 min. Then the reaction mixture was diluted with Et_2O and was quenched with saturated aqueous solution of potassium sodium tartrate (Rochelle's salt, 150 mL). The biphasic mixture was stirred until two layers separated once stopped stirring. The aqueous layer was extracted with Et_2O. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the primary alcohol **46b** (6.66 g, 93% yield) as a colorless oil. R_f = 0.20 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3429, 2982; ^1H NMR ($CDCl_3$, 270 MHz): δ 6.88 (dd, *J* = 15.3, 11.1 Hz, 1H), 6.13-6.07 (m, 1H), 5.58 (d, *J* = 15.6 Hz, 1H), 4.05 (s, 2H), 1.71 (d, *J* = 0.8 Hz, 3H), 0.80 (s, 1H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 141.0, 138.4, 123.4, 110.4, 104.8, 96.9, 67.7, 14.3, –0.1 (3C); HRMS (CI) calcd for $[C_{11}H_{18}OSi + H]^+$: 195.1205, Found: 195.1216.

(2*E*,4*E*)-7-(benzyldimethylsilyl)-2-methylhepta-2,4-dien-6-ynal (28a)

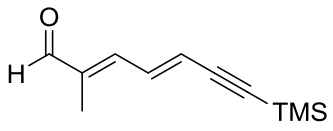


(28a)

To a solution of primary alcohol **46a** (342 mg, 1.26 mmol) in 10 mL of CH_2Cl_2 was added MnO_2 (1.10 g, 12.6 mmol) at room temperature. The reaction mixture was stirred at room temperature for 18 h and then filtered through a pad of celite and washed with Et_2O. The filtrate was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the ynal **28a** (310 mg, 92% yield) as a colorless oil. R_f = 0.60 (4:1 (v/v) hexane/EtOAc); IR (neat,

cm^{-1}): 3370, 2990, 1456; ^1H NMR ($CDCl_3$, 270 MHz): δ 9.47 (s, 1H), 7.27-7.22 (m, 2H), 7.14-7.07 (m, 3H), 7.04 (dd, *J* = 15.3, 11.6 Hz, 1H), 6.83 (d, *J* = 11.6 Hz, 1H), 6.04 (d, *J* = 15.3 Hz, 1H), 2.25 (s, 2H), 1.89 (s, 3H), 0.19 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 194.3, 146.2, 139.7, 138.6, 128.4 (2C), 128.2 (2C), 124.5, 119.3, 100.6, 100.2, 26.0, 9.8, –2.3 (2C); HRMS (CI) calcd for $[C_{17}H_{20}OSi + Na]^+$: 291.1175, Found: 291.1179.

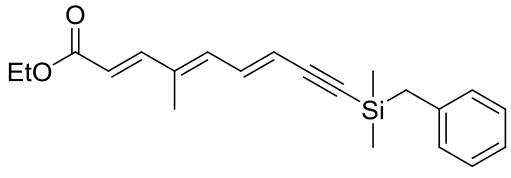
(2*E*, 4*E*)-2-methyl-7-(trimethylsilyl)hepta-2,4-dien-6-ynal (28b)



(28b)

To a solution of primary alcohol **46b** (6.66 g, 34.3 mmol) in 80 mL of CH_2Cl_2 was added MnO_2 (29.9 g, 343.3 mmol) at room temperature. The reaction mixture was stirred at room temperature for 18 h and then filtered through a pad of celite and washed with Et_2O. The filtrate was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the ynal **28b** (6.24 mg, 94% yield) as a colorless oil. R_f = 0.64 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3370, 2990, 1456; ^1H NMR ($CDCl_3$, 270 MHz): δ 9.45 (s, 1H), 7.04 (dd, *J* = 15.3, 11.4 Hz, 1H), 6.82 (d, *J* = 11.4 Hz, 1H), 6.04 (d, *J* = 15.3 Hz, 1H), 1.87 (d, *J* = 1.0 Hz, 3H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 194.4, 146.3, 139.5, 136.7, 119.5, 103.5, 103.0, 9.7, –0.3 (3C); HRMS (CI) calcd for $[C_{11}H_{16}OSi + Na]^+$: 215.0862, Found: 215.0865.

(2*E*,4*E*,6*E*)-ethyl-9-(benzyldimethylsilyl)-4-methylnona-2,4,6-trien-8-ynoate (47a)

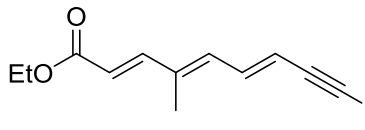


(47a)

To a solution of MnO_2 oxidative ynal **28a** (1.50 g, 5.6 mmol) in 15 mL of toluene was added (Carboethoxymethylene)-triphenylphosphorane **12** (2.54 g, 7.28 mmol), the

reaction was refluxed for 3 h. After cooling down to room temperature, the solvent was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the trienoate **47a** (1.78 g, 98% yield) as a colorless oil. R_f = 0.36 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2988, 1719; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.33 (d, *J* = 15.6 Hz, 1H) 7.27-7.21 (m, 2H), 7.13-7.07 (m, 3H), 6.97 (dd, *J* = 15.3, 11.6 Hz, 1H), 6.40 (d, *J* = 11.6 Hz, 1H), 5.96 (d, *J* = 15.6 Hz, 1H), 5.79 (d, *J* = 15.3 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.25 (s, 2H), 1.93 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.17 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 167.0, 147.9, 138.7, 138.2, 136.8, 136.2, 128.3 (2C), 128.1 (2C), 124.3, 118.6, 114.7, 105.6, 99.0, 60.3, 26.1, 14.3, 12.7, –2.2 (2C); HRMS (CI) calcd for $[C_{21}H_{26}O_2Si + Na]^+$: 361.1594, Found: 361.1589.

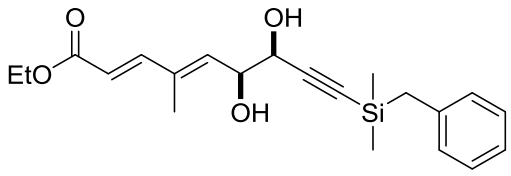
(2*E*,4*E*,6*E*)-ethyl-4-methyl-9-(trimethylsilyl)nona-2,4,6-trien-8-ynoate (47b)



(47b)

To a solution of MnO_2 oxidative ynal **28b** (5.57 g, 29.0 mmol) in 70 mL of toluene was added (Carboethoxymethylene)-triphenylphosphorane **12** (13.13 g, 37.7 mmol), the reaction was refluxed for 5 h. After cooling down to room temperature, the solvent was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the trienoate **47b** (7.15 g, 94% yield) as a colorless oil. R_f = 0.60 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2988, 1719; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.30 (d, *J* = 15.6 Hz, 1H), 6.96 (dd, *J* = 15.3, 11.6 Hz, 1H), 6.38 (d, *J* = 11.6 Hz, 1H), 5.93 (d, *J* = 15.6 Hz, 1H), 5.78 (d, *J* = 15.3 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.93 (d, *J* = 0.73 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 167.0, 147.9, 137.9, 136.9, 136.1, 118.5, 114.9, 104.4, 100.1, 60.3, 14.3, 12.7, –0.2 (3C); HRMS (CI) calcd for $[C_{15}H_{22}O_2Si + Na]$+: 285.1281, Found: 285.1287.

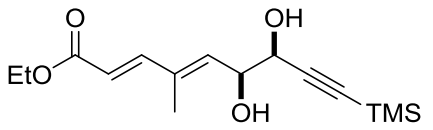
(2*E*,4*E*,6*S*,7*S*)-ethyl-9-(benzyldimethylsilyl)-6,7-dihydroxy-4-methylnona-2,4-die n-8-ynoate (29a)



(29a)

To a 50 mL round bottom flask was added 1:1 *t*-butyl alcohol (40 mL)/H_2O (40 mL), $K_3Fe(CN)_6$ (9.67 g, 29.5 mmol), K_2CO_3 (4.08 g, 29.5 mmol), $CH_3SO_2NH_2$ (0.94 g, 9.85 mmol), $(DHQ)_2$-PHAL (152 mg, 0.20 mmol, 2 mol %) and OsO_4 (25 mg, 0.10 mmol, 1 mol %). The mixture was stirred at room temperature for 15 min and then cooled to 0 ^oC. To this solution was added trienoate **47a** (3.33 g, 9.85 mmol) in 2 mL CH_2Cl_2 dropwise and the reaction was stirred vigorously at 0 ^oC overnight. Saturated aqueous solution of Na_2SO_3 was added to quench the reaction while stirring vigorously. EtOAc was added to the reaction mixture, and after separation of the layers, the aqueous layer was further extracted with EtOAc. The combined organic phases were washed with 2 M KOH and brine to remove the methanesulfonamide, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, 1:1 (v/v) hexane/EtOAc) to afford the diol **29a** (3.00 g, 82% yield) as a colorless oil. R_f = 0.15 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}) 3446, 2983, 1762; $[\alpha]^{25}{}_D$ –13.8^o (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 7.26-7.21 (m, 2H), 7.12-7.07 (m, 3H), 6.89 (dd, *J* = 15.6, 11.4 Hz, 1H), 6.18 (d, *J* = 11.4 Hz, 1H), 5.63 (d, *J* = 15.3 Hz, 1H), 4.34-4.24 (m, 4H), 2.23 (s, 2H), 1.88 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 172.9, 139.5, 138.9, 138.2, 128.3 (2C), 128.1 (2C), 125.4, 124.3, 111.3, 105.9, 95.9, 76.6, 72.2, 62.2, 26.2, 14.1, 13.9, –2.2 (2C); HRMS (CI) calcd for $[C_{21}H_{28}O_4Si + Na]^+$: 395.1649, Found: 395.1653.

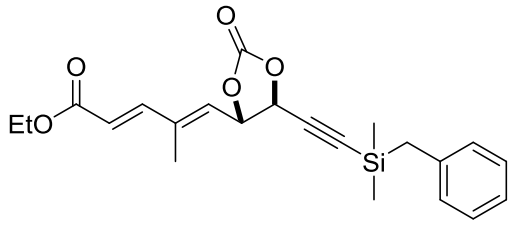
(2*E*,4*E*,6*S*,7*S*)-ethyl-6,7-dihydroxy-4-methyl-9-(trimethylsilyl)nona-2,4-dien-8-yn oate (29b)



(29b)

To a 500 mL round bottom flask was added 1:1 *t*-butyl alcohol (100 mL)/H_2O (100 mL), $K_3Fe(CN)_6$ (26.8 g, 81.9 mmol), K_2CO_3 (11.31 g, 81.9 mmol), $KHCO_3$ (8.24 g, 81.9 mmol), $CH_3SO_2NH_2$ (0.85 g, 27.3 mmol), $(DHQ)_2$-PHAL (0.42 g, 0.55 mmol, 2 mol %) and OsO_4 (69 mg, 0.27 mmol, 1 mol %). The mixture was stirred at room temperature for 15 min and then cooled to 0 ^oC. To this solution was added trienoate **47b** (7.15 g, 27.3 mmol) in 5 mL CH_2Cl_2 dropwise and the reaction was stirred vigorously at 0 ^oC overnight. Saturated aqueous solution of Na_2SO_3 was added to quench the reaction while stirring vigorously. EtOAc was added to the reaction mixture, and after separation of the layers, the aqueous layer was further extracted with EtOAc. The combined organic phases were washed with 2 M KOH and brine to remove the methanesulfonamide, dried over anhydrous Na_2SO_4, and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, 1:1 (v/v) hexane/EtOAc) to afford the diol **29b** (6.47 g, 80% yield) as a colorless oil. R_f = 0.19 (19:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}) 3446, 2983, 1762; $[\alpha]^{25}{}_D$ +14^o (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 6.88 (dd, *J* = 15.3, 11.1 Hz, 1H), 6.15 (d, *J* = 12.1 Hz, 1H), 5.62 (d, *J* = 15.6 Hz, 1H), 4.30-4.21 (m, 4H), 1.84 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.18 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 172.9, 139.3, 138.0, 125.4, 111.5, 104.5, 97.5, 76.7, 72.2, 62.2, 14.1, 13.8, –0.1 (3C); HRMS (CI) calcd for $[C_{15}H_{24}O_4Si + Na]^+$: 319.1336, Found: 319.1332.

(2*E*,4*E*)-ethyl-5-((4*S*,5*S*)-5-(2-(benzyldimethylsilyl)ethynyl)-2-oxo-1,3-dioxolan-4-yl)-4-ethylpenta-2,4-dienoate (48a)

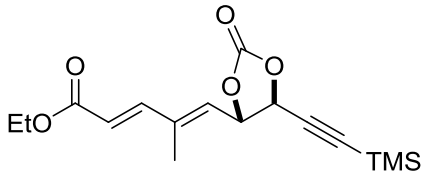


(48a)

To a solution of diol **29a** (506 mg, 1.36 mmol) in 6 mL of CH_2Cl_2 was added pyridine (0.45 mL, 5.44 mmol) and $(Cl_3CO)_2CO$ (484 mg, 1.63 mmol) in 2 mL of CH_2Cl_2 at 0 ^oC. After stirring for 2 h at 0 ^oC, the reaction mixture was quenched by saturated aqueous

solution of NH_4Cl and extracted with Et_2O. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the carbonate **48a** (440 mg, 95% yield) as a colorless oil. R_f = 0.57 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2989, 1714; $[\alpha]^{25}{}_D$ –101° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 7.23-7.21 (m, 2H), 7.13-7.06 (m, 3H), 6.81 (dd, *J* = 15.3, 11.1 Hz, 1H), 6.22 (d, *J* = 11.1 Hz, 1H), 5.75 (d, *J* = 15.6 Hz, 1H), 5.04 (d, *J* = 5.2 Hz, 1H), 4.71 (d, *J* = 5.5 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.23 (s, 2H), 1.86 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 0.16 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 167.0, 153.0, 138.7, 136.4, 132.6, 128.8, 128.3 (2C), 128.2 (2C), 124.4, 114.9, 104.9, 98.1, 82.6, 76.0, 63.0, 26.1, 14.0, 11.7, –2.3 (2C); HRMS (CI) calcd for $[C_{22}H_{26}O_5Si + Na]^+$: 421.1442, Found: 421.1439.

(2*E*,4*E*)-ethyl-4-methyl-((4*S*,5*S*)-5-(2-(trimethylsilyl)ethynyl)-2-oxo-1,3-dioxolan-4-yl)penta-2,4-dienoate (48b)

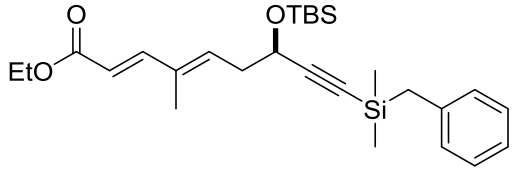


(48b)

To a solution of diol **29b** (4.81 g, 16.2 mmol) in 60 mL of CH_2Cl_2 was added pyridine (4.68 mL, 56.9 mmol) and $(Cl_3CO)_2CO$ (5.78 g, 19.5 mmol) in 10 mL of CH_2Cl_2 at 0 °C. After stirring for 3 h at 0 °C, the reaction mixture was quenched by saturated aqueous solution of NH_4Cl and extracted with Et_2O. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 19:1 (v/v) hexane/EtOAc) to afford the carbonate **48b** (4.76 g, 91% yield) as a colorless oil. R_f = 0.61 (19:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2989, 1714; $[\alpha]^{25}{}_D$ –80° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 6.81 (dd, *J* = 15.6, 11.4 Hz, 1H), 6.21 (d, *J* = 11.4 Hz, 1H), 5.74 (d, *J* = 15.6 Hz, 1H), 5.02 (d, *J* = 5.2 Hz, 1H), 4.70 (d, *J* = 5.4 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.84 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.5 MHz):

δ 166.9, 153.1, 136.2, 132.4, 128.9, 115.0, 103.7, 99.7, 82.7, 75.9, 62.9, 14.0, 11.6, –0.2 (3C); HRMS (CI) calcd for $[C_{16}H_{22}O_5Si + H]^+$: 323.1310, Found: 322.1306.

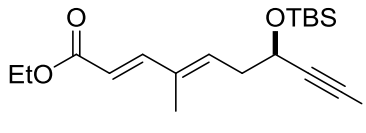
(*R*,2*E*,4*E*)-ethyl-9-(benzyldimethylsilyl)-7-hdroxy-4-methylnona-2,4-dien-8-ynoat e (24a)



(24a)

To a solution of carbonate **48a** (193 mg, 0.48 mmol) in 4 mL of CH_2Cl_2 was added $Pd_2(dba)_3{\cdot}CHCl_3$ (25 mg, 0.024 mmol), PPh_3 (12 mg, 0.048 mmol), Et_3N (245 mg, 2.24 mmol) and HCO_2H (111 mg, 2.42 mmol) at room temperature. After stirring at room temperature for 4 h, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl and extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude alcohol. To a solution of the above crude alcohol in 0.5 mL of DMF was added imidazole (104 mg, 1.52 mmol) and TBSCl (114 mg, 0.76 mmol) at room temperature. In 0.5 h, the reaction mixture was purified by chromatography (silica gel, 19:1 (v/v) hexane/EtOAc) without work up to provide the ester **24a** (82 mg, 36% yield for two steps) as a colorless oil with 32% of the recovered starting material. R*f* = 0.35 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3410, 2968, 1690; $[\alpha]^{25}{}_D$ +36° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.23-7.21 (m, 2H), 7.10-7.08 (m, 3H), 6.84 (dd, *J* = 15.6, 11.4 Hz, 1H), 5.94 (d, *J* = 11.4 Hz, 1H), 5.51 (d, *J* = 15.6 Hz, 1H), 4.29 (dd, *J* = 8.4, 4.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.48 (dd, *J* = 13.2, 4.2 Hz, 1H), 2.43 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.23 (s, 2H), 1.85 (s, 3H), 1.27 (t, *J* = 6.6 Hz, 3H), 0.89 (s, 9H) 0.15 (s, 6H), 0.05 (s, 3H), 0.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 173.2, 139.1, 138.2, 128.4 (2C), 128.1 (2C), 127.9, 124.3, 109.3, 94.9, 71.4, 60.8, 45.6, 26.3, 25.7, 25.6 (3C), 21.0, 18.2, 17.5, 14.2, –2.1 (2C), –5.1, –5.3; HRMS (CI) calcd for $[C_{27}H_{42}O_3Si_2 + Na]^+$: 493.2564, Found: 493.2559.

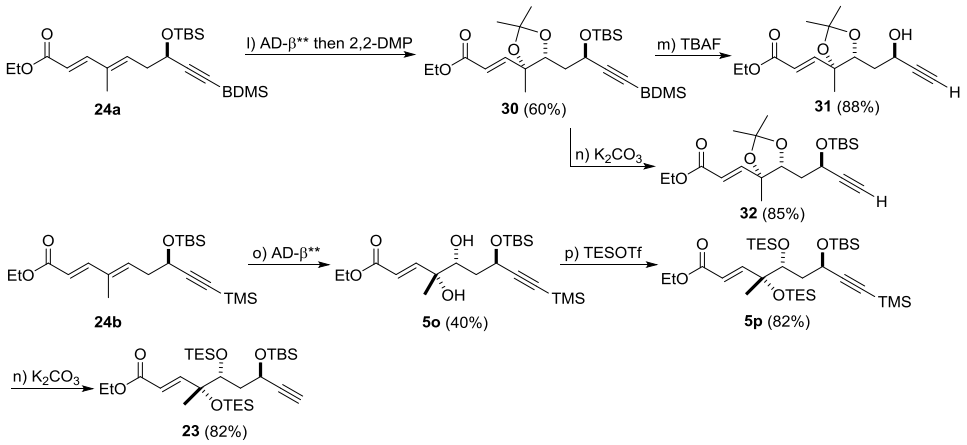
(*R*,2*E*,4*E*)-ethyl-7-*tert*-butyldimethylsiloxy-4-methyl-9-(trimethylsilyl)nona-2,4-di en-8-ynoate (24b)



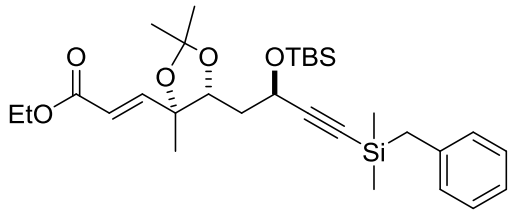
(24b)

To a solution of carbonate **48b** (103 mg, 0.32 mmol) in 5 mL of CH_2Cl_2 was added $Pd_2(dba)_3{\cdot}CHCl_3$ (7 mg, 0.007 mmol), PPh_3 (4 mg, 0.13 mmol), Et_3N (98 mg, 0.97 mmol) and HCO_2H (46 mg, 0.97 mmol) at room temperature. After stirring at room temperature for 4 h, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl and extracted with EtOAc. The organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford the crude alcohol. To a solution of the above crude alcohol in 0.5 mL of DMF was added imidazole (66 mg, 0.97 mmol) and TBSCl (72 mg, 0.48 mmol) at room temperature. In 0.5 h, the reaction mixture was purified by chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) without work up to provide the ester **24b** (43 mg, 34% yield for two steps) as a colorless oil with 30% of the recovered starting material. R_f = 0.36 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2968, 1690; $[\alpha]^{25}{}_D$ –20° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 6.84 (dd, *J* = 15.3, 11.4 Hz, 1H), 5.92 (d, *J* = 11.4 Hz, 1H), 5.51 (d, *J* = 15.3 Hz, 1H), 4.27 (dd, *J* = 7.7, 4.7 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.49-2.41 (m, 2H), 1.83 (s, 3H), 1.27 (t, *J* = 6.6 Hz, 3H), 0.89 (s, 9H), 0.19 (s, 9H), 0.04 (s, 3H), 0.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 173.2, 138.8 138.0, 128.0, 109.4, 105.0, 96.3, 71.4, 60.8, 45.6, 25.7 (3C), 18.2, 17.5, 14.2, –0.03 (3C), –5.1, –5.3; HRMS (CI) calcd for $[C_{21}H_{38}O_3Si_2 + Na]^+$: 417.2251, Found: 417.2247.

Intermediates related to Scheme 5:



(*E*)-ethyl-3-((4*R*,5*R*)-5-((*R*)-4-(benzyldimethylsilyl)-2-*tert*-butyldimethylsiloxy-but-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate (30)

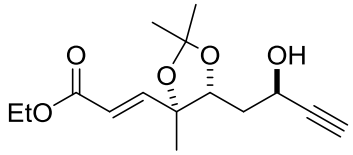


(30)

To a 50 mL round bottom flask was added 1:1 *t*-butyl alcohol (10 mL)/H_2O (10 mL), $K_3Fe(CN)_6$ (4.35 g, 13.2 mmol), K_2CO_3 (1.82 g, 13.2 mmol), $CH_3SO_2NH_2$ (0.42 g, 4.4 mmol), $(DHQD)_2$-PHAL (137 mg, 0.18 mmol, 4 mol %) and OsO_4 (22 mg, 0.09 mmol, 2 mol %). The mixture was stirred at room temperature for 30 min and then cooled to 0 ^oC. To this solution was added compound **24a** (2.07 g, 4.4 mmol) in 1 mL CH_2Cl_2 dropwise and the reaction was stirred vigorously at 0 ^oC overnight. Saturated aqueous solution of Na_2SO_3 was added to quench the reaction while stirring vigorously. EtOAc was added to the reaction mixture, and after separation of the layers, the aqueous layer was further extracted with EtOAc. The combined organic phases were washed with 2 M KOH and brine to remove the methanesulfonamide, dried over anhydrous Na_2SO_4, and concentrated to afford the crude diol. To a solution of the above crude diol in 5 mL of acetone was added 2,2-dimethoxypropane (9.17 g, 88 mmol) and CSA (0.10 g, 10 mol %) at room temperature. After stirring at room temperature for 3 h, the reaction was quenched with saturated aqueous solution of $NaHCO_3$ and extracted with Et_2O. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4,

and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the acetonide **30** (1.440 g, 60% yield for two steps) as a colorless oil. R_f = 0.32 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2986, 1752; $[\alpha]^{25}_D$ +62° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 7.26-7.19 (m, 2H), 7.11-7.05 (m, 3H), 6.90 (d, *J* = 15.6 Hz, 1H), 6.08 (d, *J* = 15.6 Hz, 1H), 4.54-4.49 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.04-3.99 (m, 1H), 2.19 (s, 2H), 1.83 (ddd, *J* = 7.9, 4.5, 4.5 Hz, 2H), 1.46 (s, 3H), 1.34 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.22 (s, 3H), 0.89 (s, 9H) 0.11 (s, 6H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.3, 149.1, 138.1, 128.3 (2C), 128.1 (2C), 124.3, 120.4, 108.5, 108.2, 81.3, 77.2, 60.5, 60.1, 38.2, 28.3, 26.4, 26.0, 25.7 (3C), 21.1, 18.2, 14.2, –2.3 (2C), –4.6, –5.1; HRMS (CI) calcd for $[C_{30}H_{48}O_5Si_2 + Na]^+$: 567.2932, Found: 567.2934.

(*E*)-ethyl-3-((4*R*,5*R*)-5-((*R*)-2-hydroxybut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)-acrylate (31)

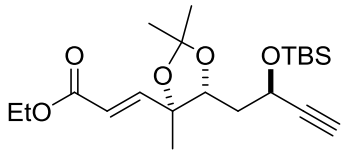


(31)

To a solution of compound **30** (665 mg, 1.55 mmol) in 5 mL of THF was added TBAF (607 mg, 2.32 mL, 2.32 mmol) at 0 °C. After stirring at 0 °C for 4 h, the reaction was quenched with saturated aqueous solution of NH_4Cl and extracted with Et_2O. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the allylic alcohol **31** (385 mg, 88% yield) as a colorless oil. R_f = 0.33 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3489, 2989, 1752; $[\alpha]^{25}_D$ –3° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 6.87 (d, *J* = 15.6 Hz, 1H), 6.11 (d, *J* = 15.6 Hz, 1H), 4.65-4.58 (m, 1H), 4.26 (dd, *J* = 10.9, 2.5 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.89 (d, *J* = 8.2 Hz, 1H), 2.49 (d, *J* = 2.0 Hz, 1H), 2.00 (ddd, *J* = 14.1, 10.6, 3.5 Hz, 1H), 1.80 (ddd, *J* = 14.3, 6.9, 2.5 Hz, 1H), 1.47 (s, 3H), 1.39 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.4, 148.7, 120.6,

108.7, 83.8, 81.5, 78.0, 73.3, 60.6, 59.8, 35.8, 28.2, 26.3, 21.0, 14.1; HRMS (CI) calcd for $[C_{15}H_{22}O_5 + Na]^+$: 305.1359, Found: 305.1385.

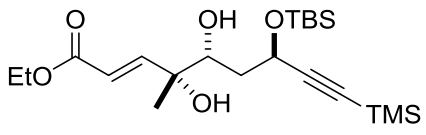
(*E*)-ethyl-3-((4*R*,5*R*)-5-((*R*)-2-tert-butyldimethylsiloxybut-3-ynyl)-2,2,4-trimethyl -1,3-dioxolan-4-yl)-acrylate (32)



(32)

To a solution of compound **30** (330 mg, 0.61 mmol) in 5 mL of EtOH was added K_2CO_3 (251 mg, 1.82 mmol) at room temperature. The reaction was stirred at room temperature for 24 h, then diluted with EtOAc and quenched by 1 M $NaHSO_4$. The reaction mixture was extracted with Et_2O, and the combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the silyl ether **32** (204 mg, 85% yield) as a colorless oil. R_f = 0.66 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2989, 1752; $[\alpha]^{25}{}_D$ +33° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 6.84 (d, *J* = 15.6 Hz, 1H), 6.05 (d, *J* = 15.6 Hz, 1H), 4.52-4.46 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.01-3.96 (m, 1H), 2.39 (d, *J* = 8.2 Hz, 1H), 1.85-1.80 (m, 2H), 1.43 (s, 3H), 1.31 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.17 (s, 3H), 0.86 (s, 9H), 0.12 (s, 3H), 0.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.3, 149.0, 120.3, 108.1, 85.2, 81.2, 77.1, 72.2, 60.4, 59.4, 38.3, 28.3, 26.3, 25.6 (3C), 21.0, 18.1, 14.1, –4.7, –5.3; HRMS (CI) calcd for $[C_{21}H_{36}O_5Si + Na]^+$: 419.2224, Found: 419.2197.

(*E*,4*R*,5*R*,7*R*)-ethyl-4,5-dihydroxy-7-*tert*-butyldimethylsiloxy-4-methyl-9-(trimeth ylsilyl)non-2-en-8-ynoate (5o)

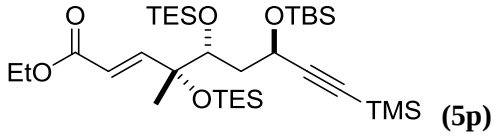


(5o)

To a 100 mL round bottom flask was added 1:1 *t*-butyl alcohol (20 mL)/H_2O (20 mL), $K_3Fe(CN)_6$ (3.03 g, 9.22 mmol), K_2CO_3 (1.27 g, 9.22 mmol), $KHCO_3$ (0.93 g, 9.22

mmol), $CH_3SO_2NH_2$ (0.29 g, 3.07 mmol), $(DHQD)_2$-PHAL (99 mg, 0.13 mmol, 4 mol %) and OsO_4 (16 mg, 0.062 mmol, 2 mol %). The mixture was stirred at room temperature for 30 min and then cooled to 0 °C. To this solution was added dienoate **24b** (1.18 g, 3.07 mmol) in 2 mL CH_2Cl_2 dropwise and the reaction was stirred vigorously at 0 °C for 8 h. Saturated aqueous solution of Na_2SO_3 was added to quench the reaction while stirring vigorously. EtOAc was added to the reaction mixture, and after separation of the layers, the aqueous layer was further extracted with EtOAc. The combined organic phases were washed with 2 M KOH and brine to remove the methanesulfonamide, dried over anhydrous Na_2SO_4, and concentrated to afford the crude diol. The crude product was purified by column chromatography (silica gel, 1:1 (v/v) hexane/EtOAc) to afford the diol **5o** (0.53 g, 40% yield) as a colorless oil. R_f = 0.46 (1:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3446, 2983, 1762; $[\alpha]^{25}{}_D$ +52° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 7.01 (d, *J* = 15.8 Hz, 1H), 6.13 (d, *J* = 15.6 Hz, 1H), 4.73 (dd, *J* = 4.7, 4.5 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 4.06-4.02 (m, 1H), 3.64 (bs, 1H), 2.58 (s, 1H), 1.84-1.80 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.26 (s, 3H), 0.88 (s, 9H), 0.16 (s, 12H), 0.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.6, 152.3, 120.3, 105.5, 90.7, 74.7, 74.0, 62.5, 60.4, 37.6, 25.7 (3C), 22.6, 18.0, 14.2, –0.3 (3C), –4.6, –5.3; HRMS (CI) calcd for $[C_{21}H_{40}O_5Si_2 + Na]^+$: 451.2306, Found: 451.2307.

(*E*,4*R*,5*R*,7*R*)-ethyl-4,5-bistriethylsilyl-7-*tert*-butyldimethylsilyl-4-methyl-9-(trimethylsilyl)non-2-en-8-ynoate (5p)

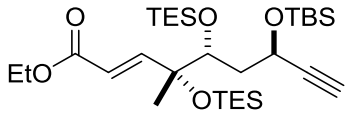


(5p)

To a solution of diol **5o** (43 mg, 0.10 mmol) in 1 mL of CH_2Cl_2 was added 2,6-lutidine (0.12 mL, 1.0 mmol) and TESOTf (159 mg, 0.6 mmol) at –78 °C. The reaction mixture was warmed up to –10 °C and stirred for 2 h. Then the reaction was quenched with saturated aqueous solution of NH_4Cl and extracted with Et_2O. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v)

hexane/EtOAc) to afford compound **5p** (54 mg, 82% yield) as a colorless oil. R_f = 0.52 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2986, 1752; $[\alpha]^{25}_{D}$ +14° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 7.00 (d, *J* = 15.8 Hz, 1H), 5.97 (d, *J* = 15.6 Hz, 1H), 4.47 (dd, *J* = 7.7, 7.2 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.73 (dd, *J* = 5.9, 5.9 Hz, 1H), 1.98-1.88 (m, 1H), 1.59-1.49 (m, 1H), 1.49 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.88 (s, 9H), 0.65 (q, *J* = 7.9 Hz, 6H), 0.52 (q, *J* = 7.9 Hz, 6H), 0.15 (s, 9H), 0.13 (s, 3H), 0.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.7, 152.1, 120.0, 108.2, 89.1, 78.7, 76.0, 60.8, 60.2, 43.6, 25.9 (3C), 25.3, 18.2, 14.2, 7.2 (3C), 7.0 (3C), 6.9 (3C), 5.4 (3C), –0.3 (3C), –4.1, –4.4; HRMS (CI) calcd for $[C_{33}H_{68}O_5Si_4 + Na]^+$: 679.4036, Found: 679.4037.

(*E*,4*R*,5*R*,7*R*)-ethyl-4,5-bistriethylsilyl-7-tert-butyldimethylsilyl-4-methyl-9-non-2-en-8-ynoate (23)



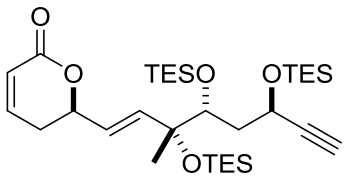
(23)

To a solution of compound **5p** (315 mg, 0.48 mmol) in 5 mL of EtOH was added K_2CO_3 (199 mg, 1.48 mmol) at room temperature. The reaction was stirred at room temperature for 24 h, then diluted with EtOAc and quenched by 1 M $NaHSO_4$. The reaction mixture was extracted with Et_2O, and the combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the silyl ether **23** (258 mg, 92% yield) as a colorless oil. R_f = 0.44 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2989, 1752; $[\alpha]^{25}_{D}$ +17° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 7.01 (d, *J* = 15.8 Hz, 1H), 5.96 (d, *J* = 15.8 Hz, 1H), 4.48 (ddd, *J* = 8.2, 6.2, 2.0 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.74 (dd, *J* = 6.4, 5.7 Hz, 1H), 2.39 (d, *J* = 2.2 Hz, 1H), 1.99 (ddd, *J* = 13.9, 8.2, 5.4 Hz, 1H), 1.60-1.51 (m, 1H), 1.39 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.9 Hz, 18H), 0.89 (s, 9H), 0.64 (q, *J* = 7.9 Hz, 12H), 0.14 (s, 3H), 0.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.6, 152.0, 120.1, 86.1, 78.5, 76.0, 72.8, 60.3, 60.1, 43.6, 25.8 (3C), 25.3, 18.2, 14.3, 7.2 (3C), 7.0 (3C), 6.9

(3C), 5.4 (3C), –4.10, –4.48; HRMS (CI) calcd for $[C_{30}H_{60}O_5Si_3 + Na]^+$: 607.3641, Found: 607.3643.

Compounds in Scheme 6:

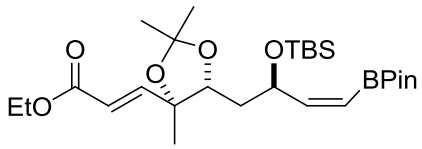
(*R*)-5,6-dihydro-6-((*E*, 3*R*, 4*R*, 6*R*)-3,4,6-tritriethylsilyl-3-methyloct-1-en-7-ynyl) pyran-2-one (33)



(33)

To a solution of triol **4** (79 mg, 0.30 mmol) in 3.0 mL of CH_2Cl_2 was added 2,6-lutidine (317 mg, 2.96 mmol) at –78 °C. After stirring for 10 min at –78 °C, TESOTf (309 mg, 1.17 mmol) was added to the reaction mixture and kept stirring for 30 min. The reaction mixture was diluted with CH_2Cl_2, quenched by saturated aqueous solution of $NaHCO_3$, and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 1:4 (v/v) hexane/EtOAc) to afford the TES protected compound **33** (143 mg, 78% yield) as a colorless oil. R_f = 0.35 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2956, 1736; $[\alpha]^{25}{}_D$ +51° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 6.86 (ddd, *J* = 8.4, 5.4, 3.0 Hz, 1H), 6.04 (ddd, *J* = 10.2, 1.8, 1.8 Hz, 1H), 5.91 (dd, *J* = 16.2, 1.2 Hz, 1H), 5.79 (dd, *J* = 15.6, 6.6 Hz, 1H), 4.97 (ddd, *J* = 9.6, 6.6, 1.2 Hz, 1H), 4.50 (ddd, *J* = 7.8, 6.0, 1.8 Hz, 1H), 3.68 (dd, *J* = 6.6, 5.4 Hz, 1H), 2.47-2.42 (m, 2H), 2.39 (d, *J* = 1.8 Hz, 1H), 2.05-1.97 (m, 1H), 1.46-1.51 (m, 1H), 0.97 (t, *J* = 7.8 Hz, 27H), 0.71-0.59 (m, 18H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 164.1, 144.5, 138.1, 125.7, 86.0, 78.0, 77.9, 75.9, 72.7, 59.8, 43.3, 30.0, 26.0, 7.2 (3C), 7.0 (3C), 6.9 (3C), 6.8 (3C), 5.4 (3C), 5.2 (3C). HRMS (CI) calcd for $[C_{32}H_{60}O_5Si_3 + Na]^+$: 631.3592, Found: 631.3565.

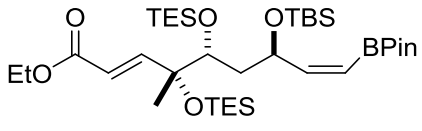
(2*E*,4*S*,5*R*,7*R*,8*Z*)-ethyl-7-*tert*-butyldimethylsiloxy-4-methyl-2,2,4-trimethyl-1,3-dioxolan-4-yl)-9-(3,3,4,4-tetramethylborolan-1-yl)nona-2,8-dienoate (34)



(34)

To a solution of $[Rh(COD)Cl]_2$ (8 mg, 0.017 mmol, 1.5 mol %) in 1 mL of cyclohexane was added P*i*-Pr_3 (11 mg, 0.068 mmol, 6.0 mol %), Et_3N (38 mg, 0.37 mmol) and catecholborane (39 mg, 0.32 mmol) at room temperature. After stirring at room temperature for 30 minutes, alkyne **32** (132 mg, 0.034 mmol) in 1 mL of cyclohexane was added, and the reaction was stirred for 6 h. Then pinacol (60 mg, 0.51 mmol) in 1 mL of cyclohexane was added dropwise and the reaction mixture was stirred for another 12 h at room temperature. The reaction was quenched by saturated aqueous solution of NH_4Cl and extracted with Et_2O. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford compound **34** (119 mg, 70% yield) as a colorless oil. R_f = 0.24 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2986, 1758; $[\alpha]^{25}{}_D$ –0.03° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 6.86 (d, *J* = 15.6 Hz, 1H), 6.30 (dd, *J* = 13.6, 8.4 Hz, 1H), 6.05 (d, *J* = 15.6 Hz, 1H), 5.32 (dd, *J* = 13.6, 0.75 Hz, 1H), 5.02 (ddd, *J* = 8.6, 8.6, 3.9 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.00 (dd, *J* = 8.9, 3.2 Hz, 1H), 1.52 (ddd, *J* = 8.4, 4.2, 4.2 Hz, 2H), 1.43 (s, 3H), 1.33 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.25 (s, 12H), 1.15 (s, 3H), 0.83 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.4, 157.2, 149.7, 120.0, 107.8, 83.1, 81.4, 77.7, 69.3, 60.4, 37.7, 28.4, 26.4, 25.8 (3C), 24.8 (2C), 24.7 (2C), 21.1, 20.0, 18.1, 14.2, –4.4, –5.0; HRMS (CI) calcd for $[C_{27}H_{49}BO_7Si + Na]^+$: 547.3233, Found: 547.3234.

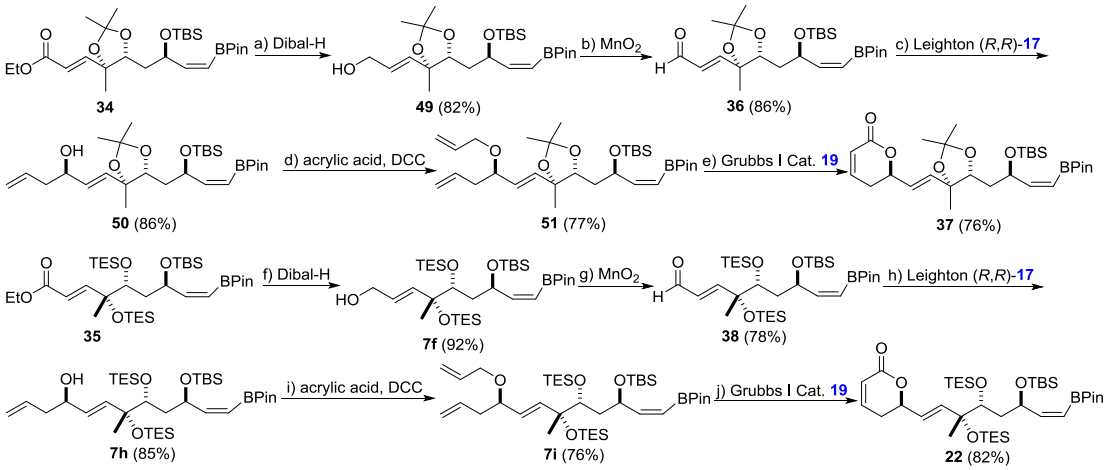
(2*E*,4*S*,5*R*,7*R*,8*Z*)-ethyl-4,5-bistriethylsilyl-7-*tert*-butyldimethylsilyl-4-methyl-9-(4,4,5,5-tetra-methyl-1,3,2-dioxaborolan-2-yl)nona-2,8-dienoateate (35)



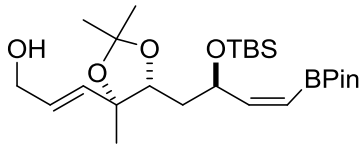
(35)

To a solution of $[Rh(COD)Cl]_2$ (20 mg, 0.04 mmol, 1.5 mol %) in 3 mL of cyclohexane was added P*i*-Pr_3 (26 mg, 0.16 mmol, 6.0 mol %), Et_3N (84 mg, 0.83 mmol) and catecholborane (86 mg, 0.71 mmol) at room temperature. After stirring at room temperature for 30 minutes, alkyne **23** (438 mg, 0.72 mmol) in 1 mL of cyclohexane was added, and the reaction was stirred for 6 h. Then pinacol (133 mg, 1.13 mmol) in 1 mL of cyclohexane was added dropwise and the reaction mixture was stirred for another 12 h at room temperature. The reaction was quenched by saturated aqueous solution of NH_4Cl and extracted with Et_2O. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford compound **35** (407 mg, 79% yield) as a colorless oil. R_f = 0.35 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2986, 1758; $[\alpha]^{25}{}_D$ +24° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 7.03 (d, *J* = 15.8 Hz, 1H), 6.19 (dd, *J* = 13.9, 8.9 Hz, 1H), 5.91 (d, *J* = 15.6 Hz, 1H), 5.30 (d, *J* = 13.6 Hz, 1H), 4.78 (td, *J* = 9.4, 3.7 Hz, 1H), 4.21-4.14 (m, 2H), 3.76 (dd, *J* = 8.1, 1.7 Hz, 1H), 2.14-2.05 (m, 1H), 1.87-1.79 (m, 1H), 1.36 (s, 3H), 1.26 (s, 12 H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.96 (dt, *J* = 8.2, 7.7 Hz, 18H), 0.86 (s, 9H), 0.73-0.56 (m, 12H), 0.06 (s, 3H), 0.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.9, 157.7, 153.0, 119.7, 83.2, 78.2, 75.4, 69.0, 60.2, 42.0, 26.9 (3C), 25.9 (2C), 24.9 (2C), 24.6, 24.2, 21.2, 17.9, 14.2, 7.2 (3C), 7.1 (3C), 6.74 (3C), 5.60 (3C), –3.0, –4.0; HRMS (CI) calcd for $[C_{36}H_{73}BO_7Si_3 + Na]^+$: 735.4649, Found: 735.4648.

Intermediates related to Scheme 7:



(2*E*,4*S*,5*R*,7*R*,8*Z*)-4-methyl-9-(3,3,4,4-tetramethylborolan-1-yl)nona-2,8-diene-1,3-dioxolan-7-*tert*-butyldimethylsiloxyol (49)

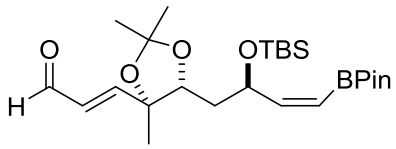


(49)

To a solution of ester **34** (65 mg, 0.12 mmol) in CH_2Cl_2 (2 mL) was dropwise added diisobutylaluminum hydride $(i\text{-Bu})_2AlH$ (1.0 M in CH_2Cl_2, 0.31 mL, 0.31 mmol) at –78 °C under an argon atmosphere. After stirring for 30 min at –78 °C, the reaction mixture was allowed warming up to 0 °C and kept stirring for 30 min. Then the reaction mixture was diluted with Et_2O and was quenched with saturated aqueous solution of potassium sodium tartrate (Rochelle's salt, 5 mL). The biphasic mixture was stirred until two layers separated once stopped stirring. The aqueous layer was extracted with Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the primary alcohol **49** (49 mg, 82% yield) as a colorless oil. R_f = 0.32 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3427, 2982; $[\alpha]^{25}_D$ –7° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 6.30 (dd, *J* = 13.2, 7.8 Hz, 1H), 5.9 (ddd, *J* = 15.6, 5.4, 5.4 Hz, 1H), 5.71 (ddd, *J* = 16.2, 1.8, 1.2 Hz, 1H), 5.32 (dd, *J* = 13.8, 0.6 Hz, 1H), 5.21-5.02 (m, 2H), 4.14 (dd, *J* = 5.4, 4.8 Hz, 1H), 3.98 (dd, *J* = 10.2, 2.4 Hz, 1H), 1.56-1.44 (m, 2H), 1.42 (s, 3H), 1.34 (s, 3H), 1.26 (s, 12H), 1.41 (s, 3H), 0.86 (s, 9H), 0.08 (s, 3H), 0.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 157.3, 134.4, 129.2, 107.2, 83.2, 81.4, 78.5, 69.5, 63.3, 37.7, 28.5, 26.8, 25.9 (3C), 24.9 (2C), 24.8(2C), 21.0,

18.2, –4.3, –4.9; HRMS (CI) calcd for $[C_{25}H_{47}BO_6Si + Na]^+$: 505.3127, Found: 505.2984.

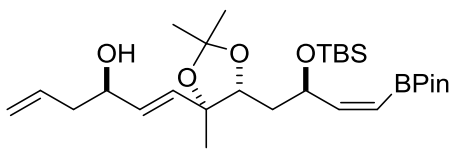
(2*E*,4*S*,5*R*,7*R*,8*Z*)-1,3-dioxolan-7-*tert*-butyldimethylsiloxy-4-methyl-9-(3,3,4,4-tetramethyl-borolan-1-yl)nona-2,8-dienal (36)



(36)

To a solution of primary alcohol **49** (28 mg, 0.058 mmol) in 1 mL of CH_2Cl_2 was added MnO_2 (51 mg, 0.58 mmol) at room temperature. The reaction mixture was stirred at room temperature for 4 h and then filtered through a pad of celite and washed with Et_2O. The filtrate was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the enal **36** (24 mg, 86% yield) as a colorless oil. R_f = 0.60 (7:3 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3427, 2982, 1680; $[\alpha]^{25}{}_D$ –15° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 9.57 (d, *J* = 7.7 Hz, 1H), 6.74 (d, *J* = 15.6 Hz, 1H), 6.36 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.30 (dd, *J* = 13.8, 5.9 Hz, 1H), 5.36 (d, *J* = 13.8 Hz, 1H), 5.04 (td, *J* = 9.2, 3.0 Hz, 1H), 4.06 (dd, *J* = 10.2, 2.0 Hz, 1H), 1.61-1.54 (m, 2H), 1.46 (s, 3H), 1.36 (s, 12H), 1.26 (s, 12H), 1.22 (s, 3H), 0.85 (s, 9H), 0.05 (s, 3H), 0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 194.3, 158.6, 157.2, 130.7, 108.2, 83.2, 81.7, 69.3, 37.9, 28.6, 26.4, 25.8 (3C), 24.9 (2C), 24.8 (2C), 21.1, 20.7, –4.3, –4.9; HRMS (CI) calcd for $[C_{25}H_{45}BO_6Si + Na]^+$: 503.2970, Found: 503.2972.

(1*Z*,3*R*,5*R*,6*S*,7*E*,9*R*)-6-methyl-1-(3,3,4,4-tetramethylborolan-1-yl)dodeca-1,7,11-triene-3-*tert*-butyldimethylsiloxy-1,3-dioxolan-9-ol (50)

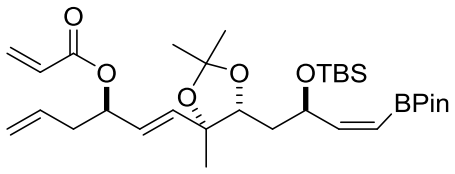


(50)

To a solution of Leighton allylsilane reagent (*R*,*R*)-**17** (72 mg, 0.13 mmol) in 0.3 mL of CH_2Cl_2 was dropwise added enal **36** (21 mg, 0.044 mmol) in 0.4 mL of CH_2Cl_2 at –10

^{o}C. The reaction was stirred –10 ^{o}C at for 36 h, then diluted with EtOAc and quenched by adding 1 N $NaHSO_4$. The reaction mixture was vigorously stirred at room temperature for 1 h, then filtered through a pad of celite, and the filtrate was extracted with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the allylic alcohol **50** (38 mg, 86% yield) as a light yellow oil. R_f = 0.30 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3450, 2981, 1755; $[\alpha]^{25}{}_{D}$ +9^{o} (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.19 (dd, *J* = 13.2, 8.4 Hz, 1H), 5.83-5.76 (m, 2H), 5.70 (dd, *J* = 15.6 Hz, 1H), 5.33 (d, *J* = 13.8 Hz, 1H), 5.14 (d, *J* = 8.4 Hz, 1H), 5.11 (s, 1H), 5.03 (td, *J* = 10.2, 2.4 Hz, 1H), 4.18 (d, *J* = 5.4 Hz, 1H), 3.98 (d, *J* = 9.6 Hz, 1H), 2.34 (ddd, *J* = 13.8, 6.6, 6.0 Hz, 1H), 2.27 (ddd, *J* = 14.4, 7.8, 7.2 Hz, 1H), 1.53-1.46 (m, 1H), 1.43 (s, 3H), 1.35 (s, 3H), 1.27 (s, 12H), 1.13 (s, 3H), 0.87 (s, 9H), 0.07 (s, 3H), 0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 157.3, 134.1, 133.9, 131.9, 118.2, 107.2, 83.1, 81.4, 78.5, 71.2, 69.5, 41.9, 37.8, 28.5, 26.7, 25.9 (3C), 24.9 (2C), 24.7 (2C), 21.2, 18.2, –4.3, –4.9; HRMS (CI) calcd for $[C_{28}H_{51}BO_6Si + Na]^+$: 545.3440, Found: 545.3443.

(4*R*,5*E*,7*S*,8*R*,10*R*,11*Z*)-1,3-dioxolan-10-*tert*-butyldimethylsiloxy-7-methyl-12-(3,3,4,4-tetramethyl-borolan-1-yl)dodeca-1,5,11-trien-4-yl acrylate (51)

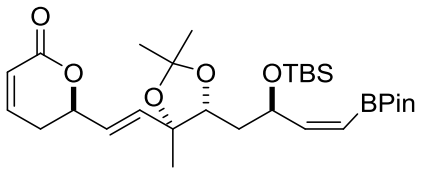


(51)

To a solution of allylic alcohol **50** (30 mg, 0.043 mmol) in 1.5 mL of CH_2Cl_2 was added acrylic acid (15 mg, 0.21 mmol), DCC (43 mg, 0.21 mmol) and catalytic amount of DMAP (2 mg, 0.016 mmol). The reaction was stirred at room temperature for 3 h, then diluted with Et_2O and filtered through a pad of celite. The filtrate was extracted with Et_2O, and the combined organic phases were washed with saturated aqueous solution of $NaHSO_4$, saturated aqueous solution of $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography

(silica gel, 9:1 (v/v) hexane/EtOAc) to afford the ester **51** (25 mg, 77% yield) as a colorless oil. R_f = 0.50 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2987, 1736; $[\alpha]^{25}{}_D$ +12° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 6.38 (dd, *J* = 17.4, 1.2 Hz, 1H), 6.32 (dd, *J* = 13.8, 8.4 Hz, 1H), 6.10 (dd, *J* = 16.8, 10.2 Hz, 1H), 5.80 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.76-5.70 (m, 3H), 5.40 (dd, *J* = 6.0, 6.0 Hz, 1H), 5.33 (d, *J* = 13.8 Hz, 1H), 5.10-5.03 (m, 3H), 3.97 (dd, *J* = 10.8, 2.4 Hz, 1H), 2.41 (dd, *J* = 6.6, 6.6 Hz, 2H), 1.49 (ddd, *J* = 21.6, 10.2, 3.0 Hz, 2H), 1.43 (s, 3H), 1.34 (s, 3H), 1.27 (s, 12H), 1.12 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 187.4, 136.3, 133.0, 130.5, 128.8, 127.0, 118.1, 107.3, 83.2, 81.4, 78.4, 73.2, 69.4, 39.1, 37.9, 29.7, 28.5, 26.5, 25.9 (3C), 24.9 (2C), 24.8 (2C), 21.4, 18.1, –4.3, –4.9; HRMS (CI) calcd for $[C_{31}H_{53}BO_7Si + Na]^+$: 599.3546, Found: 599.3573.

(*R*)-5,6-dihydro-6-((1*E*,3*S*,4*R*,6*R*,7*Z*)-1,3-dioxolan-6-*tert*-butyldimethylsiloxy-3-methyl-8-(3,3,4,4-tetramethylborolan-1-yl)octa-1,7-dienyl)pyran-2-one (37)

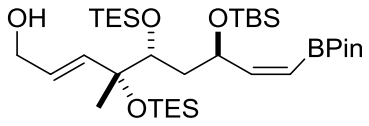


(37)

To a solution of ester **51** (14 mg, 0.024 mmol) in 2.5 mL of CH_2Cl_2 was added Grubbs catalyst **29** (4 mg, 0.005 mmol, 20 mol %). The reaction was refluxed for 3 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the lactone **37** (10 mg, 76% yield) as a colorless oil. R_f = 0.25 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2930, 1731; $[\alpha]^{25}{}_D$ +32° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 6.86 (ddd, *J* = 9.0, 5.4, 3.0 Hz, 1 H), 6.32 (dd, *J* = 13.8, 8.4 Hz, 1H), 6.05 (ddd, *J* = 9.6, 1.2, 1.2 Hz, 1H), 5.88 (dd, *J* = 15.6, 4.8 Hz, 1H), 5.84 (d, *J* = 16.2 Hz, 1H), 5.34 (d, *J* = 13.8 Hz, 1H), 5.03 (ddd, *J* = 9.6, 3.6, 3.0 Hz, 1H), 4.94 (ddd, *J* = 9.6, 4.8, 4.8 Hz, 1H), 3.98 (dd, *J* = 10.2, 2.4 Hz, 1H), 2.45-2.41 (m, 2H), 1.52-1.46 (m, 2H), 1.44 (s, 3H), 1.35 (s, 3H), 1.28 (s, 12H), 1.15 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 163.8, 157.3, 144.4, 136.5, 126.4, 121.7, 107.3, 83.2, 81.3, 78.4, 77.3, 69.4, 39.1, 37.7,

29.8, 28.5, 26.6, 25.9 (3C), 24.9 (2C), 24.8 (2C), 21.1, 18.1, –4.3, –5.0; HRMS (CI) calcd for $[C_{29}H_{49}BO_7Si + Na]^+$: 571.3233, Found: 571.3205.

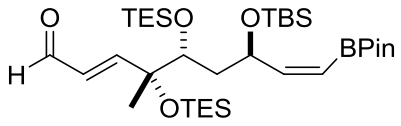
(2*E*,4*R*,5*R*,7*R*,8*Z*)-4,5-bistriethylsilyl-7-*tert*-butyldimethylsilyl-4-methyl-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-2,8-dien-1-ol (7f)



(7f)

To a solution of ester **35** (140 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) was dropwise added diisobutylaluminum hydride (*i*-Bu)$_2$AlH (1.0 M in CH_2Cl_2, 0.45 mL, 0.45 mmol) at –78 °C under an argon atmosphere. After stirring for 30 min at –78 °C, the reaction mixture was allowed warming up to 0 °C and kept stirring for 30 min. Then the reaction mixture was diluted with Et_2O and was quenched with saturated aqueous solution of potassium sodium tartrate (Rochelle's salt, 10 mL). The biphasic mixture was stirred until two layers separated once stopped stirring. The aqueous layer was extracted with Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the primary alcohol **7f** (123 mg, 92% yield) as a colorless oil. R_f = 0.33 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3427, 2982; $[\alpha]^{25}_D$ +4^o (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz): δ 6.19 (dd, *J* = 13.9, 8.9 Hz, 1H), 5.77-5.74 (m, 2H), 5.31 (d, *J* = 13.9 Hz, 1H), 4.76 (td, *J* = 9.4, 4.2 Hz, 1H), 4.15 (bs, 2H), 3.76 (dd, *J* = 7.4, 2.0 Hz, 1H), 1.82 (ddd, *J* = 14.1, 9.4, 2.2 Hz, 1H), 1.30 (s, 3H), 1.27 (s, 6 H), 1.26 (s, 6 H), 0.96 (dt, *J* = 8.2, 7.7 Hz, 18H), 0.86 (s, 9H), 0.72-0.53 (m, 12H), 0.07 (s, 3H), 0.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 157.8, 137.1, 128.1, 83.3 (3C), 77.9, 75.8, 69.4, 63.8, 42.4, 26.1 (3C), 25.0 (2C), 24.7 (2C), 23.4, 18.3, 7.3 (3C), 7.2 (3C), 6.9 (3C), 5.7 (3C), –2.9, –3.9; HRMS (CI) calcd for $[C_{34}H_{71}BO_6Si_3 + Na]^+$: 693.4544, Found: 693.4549.

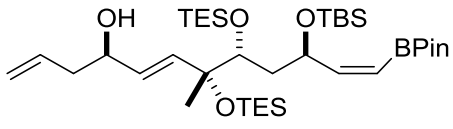
(2*E*,4*R*,5*R*,7*R*,8*Z*)-4,5-bistriethylsilyl-7-*tert*-butyldimethylsilyl-4-methyl-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-2,8-dienal (38)



(38)

To a solution of primary alcohol **7f** (30 mg, 0.045 mmol) in 1 mL of CH_2Cl_2 was added MnO_2 (39 mg, 0.45 mmol) at room temperature. The reaction mixture was stirred at room temperature for 4 h and then filtered through a pad of celite and washed with Et_2O. The filtrate was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the enal **38** (25 mg, 78% yield) as a colorless oil. R_f = 0.45 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3427, 2982, 1680; $[\alpha]^{25}{}_D$ +43º (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 9.56 (d, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 15.6 Hz, 1H), 6.25 (dd, *J* = 15.6, 7.9 Hz, 1H), 6.18 (dd, *J* = 13.9, 9.2 Hz, 1H), 5.31 (d, *J* = 13.9 Hz, 1H), 4.76 (td, *J* = 9.6, 3.7 Hz, 1H), 3.83 (dd, *J* = 8.4, 1.5 Hz, 1H), 1.88 (ddd, *J* = 14.3, 10.2, 2.4 Hz, 1H), 1.42 (s, 3H), 1.26 (s, 12H), 0.98 (t, *J* = 8.2 Hz, 9H), 0.95 (t, *J* = 7.4 Hz, 9H), 0.87 (s, 9H), 0.76-0.56 (m, 12H), 0.07 (s, 3H), 0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 194.0, 162.7, 157.5, 130.7, 83.2, 78.3, 75.5, 68.8, 41.8, 26.1 (3C), 24.9, 24.6, 18.2, 7.2 (3C), 7.1 (3C), 6.8 (3C), 5.6 (3C), –2.9, –3.9; HRMS (CI) calcd for $[C_{34}H_{69}BO_6Si_3 + Na]^+$: 691.4387, Found: 691.4393.

(1*Z*,3*R*,5*R*,6*R*,7*E*,9*R*)-4,5-bistriethylsilyl-7-*tert*-butyldimethylsilyl-6-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodeca-1,7,11-trien-1-ol (7h)

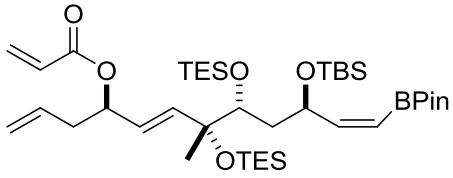


(7c)

To a solution of To a solution of Leighton allylsilane reagent (*R*,*R*)-**17** (102 mg, 0.19 mmol) in 0.3 mL of CH_2Cl_2 was dropwise added enal **38** (42 mg, 0.063 mmol) in 0.4 mL of CH_2Cl_2 at –10 ºC. The reaction was stirred –10 ºC at for 36 h, then diluted with EtOAc and quenched by adding 1 N $NaHSO_4$. The reaction mixture was vigorously stirred at room temperature for 1 h, then filtered through a pad of celite, and the filtrate was extracted with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by

column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the allylic alcohol **7h** (38 mg, 85% yield) as a light yellow oil. R_f = 0.30 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3450, 2981, 1755; $[\alpha]^{25}{}_D$ +9° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz): δ 6.19 (dd, *J* = 13.8, 9.2 Hz, 1H), 5.87-5.73 (m, 2H), 5.60 (dd, *J* = 15.8, 6.2 Hz, 1H), 5.30 (d, *J* = 13.9 Hz, 1H), 5.16-5.09 (m, 2H), 4.76 (td, *J* = 9.4, 3.7 Hz, 1H), 4.18 (dd, *J* = 6.2, 5.9 Hz, 1H), 3.71 (dd, *J* = 7.7, 1.5 Hz, 1H), 2.37-2.25 (M, 2H), 1.83 (ddd, *J* = 14.1, 9.6, 1.7 Hz, 1H), 1.10-1.21 (m, 1H), 1.30 (s, 3H), 1.26 (s, 6H), 1.25 (s, 6H), 0.97 (t, *J* = 8.2 Hz, 9H), 0.95 (t, *J* = 7.4 Hz, 9H), 0.87 (s, 9H), 0.69 (q, *J* = 8.2 Hz, 6H), 0.58 (q, *J* = 7.9 Hz, 6H), 0.08 (s, 3H), 0.01 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 157.8, 135.9, 134.3, 131.1, 118.0, 83.1, 77.8, 75.7, 71.6, 69.3, 42.3, 41.7 (3C), 26.0 (3C), 24.9 (2C), 24.6 (2C), 23.5, 18.2, 7.3 (3C), 7.2 (3C), 6.8 (3C), 5.6 (3C), –2.9, –4.1; HRMS (CI) calcd for $[C_{37}H_{75}BO_6Si_3 + Na]^+$: 733.4857, Found: 733.4855.

(4*R*,5*E*,7*R*,8*R*,10*R*,11*Z*)-7,8-bistriethylsilyl-10-*tert*-butyldimethylsilyl-7-methyl-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodeca-1,5,11-trien-4-ylacrylate (7i)

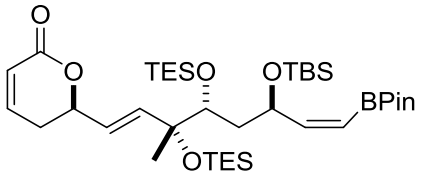


(7d)

To a solution of allylic alcohol **7h** (30 mg, 0.043 mmol) in 1.5 mL of CH_2Cl_2 was added acrylic acid (15 mg, 0.21 mmol), DCC (43 mg, 0.21 mmol) and catalytic amount of DMAP (2 mg, 0.016 mmol). The reaction was stirred at room temperature for 3 h, then diluted with Et_2O and filtered through a pad of celite. The filtrate was extracted with Et_2O, and the combined organic phases were washed with saturated aqueous solution of $NaHSO_4$, saturated aqueous solution of $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the ester **7i** (25 mg, 76% yield) as a colorless oil. R_f = 0.50 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2987, 1736; $[\alpha]^{25}{}_D$ +10° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 6.37 (dd, *J* = 17.4, 1.2 Hz, 1H),

6.18 (dd, *J* = 13.8, 9.0 Hz, 1H), 6.09 (dd, *J* = 17.4, 10.2 Hz, 1H), 5.80 (dd, *J* = 15.6, 10.8 Hz, 2H), 5.76-5.70 (m, 1H), 5.59 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.41 (dd, *J* = 6.6, 6.0 Hz, 1H), 5.29 (d, *J* = 13.8 Hz, 1H), 5.08-5.03 (m, 2H), 3.96 (dt, *J* = 9.6, 3.6 Hz, 1H), 3.70 (dd, *J* = 7.8, 1.2 Hz, 1H), 3.21-3.17 (m, 1H), 2.42 (dd, J = 6.6, 6.6 Hz, 1H), 1.92-1.90 (m, 1H), 1.75-1.73 (m, 1H), 1.29 (s, 3H), 1.26 (s, 6H), 1.25 (s, 6H), 0.96 (t, *J* = 7.8 Hz, 9H), 0.92 (t, *J* = 8.4 Hz, 9H), 0.87 (s, 9H), 0.67 (qd, *J* = 7.8, 2.4 Hz,24 6H), 0.56 (q, *J* = 7.8 Hz, 6H), 0.07 (s, 3H), 0.01 (s, 3H);^{13}C NMR ($CDCl_3$, 150 MHz): δ165.2, 157.9, 137.8, 133.2, 130.2, 128.8, 126.6, 117.9, 83.1, 77.8, 75.7, 73.4, 69.1, 55.7, 42.2, 39.1, 34.9 (3C), 26.1, 25.5 (3C), 24.9 (2C), 24.7 (2C), 24.6, 18.2, 7.2 (3C), 7.1 (3C), 6.8 (3C), 5.7 (3C), –2.9, –4.1; HRMS (CI) calcd for $[C_{40}H_{77}BO_7Si_3 + Na]^+$: 787.4962, Found: 787.4961.

(*R*)-5,6-dihydro-6-((1*E*,3*R*,4*R*,6*R*,7*Z*)-3,4-bistriethylsilyl-6-*tert*-butyldimethylsilyl-3-methyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-1,7-dienyl)pyran-2-one (22)



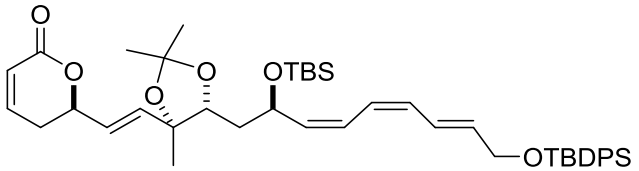
(22)

To a solution of ester **7d** (25 mg, 0.032 mmol) in 3.5 mL of CH_2Cl_2 was added Grubbs catalyst **29** (6 mg, 0.007 mmol, 20 mol %). The reaction was refluxed for 3 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the lactone **22** (20 mg, 82% yield) as a colorless oil. R_f = 0.35 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2930, 1731; $[\alpha]^{25}_D$ +32^o (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.86 (ddd, *J* = 8.4, 3.6, 1.2 Hz, 1 H), 6.20 (dd, *J* = 13.8, 9.6 Hz, 1H), 6.04 (ddd, *J* = 9.6, 1.8, 1.8 Hz, 1H), 5.91 (dd, *J* = 15.6, 1.2 Hz, 1H), 5.72 (dd, *J* = 15.6, 6.0 Hz, 1H), 5.30 (dd, *J* = 13.8, 1.2 Hz, 1H), 4.92 (ddd, *J* = 6.6, 6.0, 1.2 Hz, 1H), 4.79 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.72 (dd, *J* = 9.6, 1.8 Hz, 1H), 2.43-2.41 (m, 2H), 1.84 (ddd, *J* = 14.4, 10.2, 1.8 Hz, 1H), 1.33 (s, 3H), 1.27 (s, 6H), 1.26 (s, 6H), 1.05 (m, 1H), 0.97 (dd, *J* = 8.4, 7.8 Hz, 9H), 0.92 (dd, *J* = 8.4,

7.8 Hz, 9H), 0.87 (s, 9H), 0.67 (qd, *J* = 8.4, 4.2 Hz, 6H), 0.59 (q, *J* = 7.8 Hz, 6H), 0.08 (s, 3H), 0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 164.0, 157.8, 144.4, 138.9, 125.5, 121.7, 83.2, 77.9, 77.7, 75.6, 69.1, 42.1, 29.8 (3C), 26.1 (3C), 24.9 (2C), 24.6 (2C), 24.4, 18.2, 7.3 (3C), 7.2 (3C), 6.9 (3C), 5.7 (3C), –2.9, –4.0; HRMS (CI) calcd for $[C_{38}H_{73}BO_7Si_3 + Na]^+$: 759.4649, Found: 759.4648.

Compounds in Scheme 8:

(*R*)-5,6-dihydro-6-((1*E*,3*R*,4*R*,6*R*,7*Z*,9*Z*,11*E*)-1,3-dioxolan-6-*tert*-butyldimethylsiloxy-13-*tert*-butyldiphenylsiloxy-3-methyltrideca-1,7,9,11-tetraenyl)pyran-2-one (39)

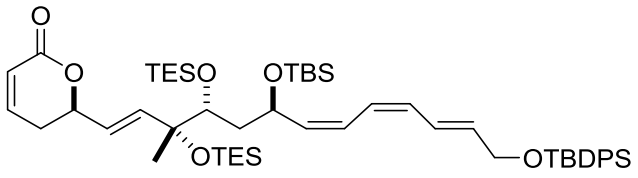


(39)

To a suspension of Ag_2O aqueous (8 mg, 0.030 mmol) in 1 mL of THF was added *Z*-vinylboronate **37** (8 mg, 0.015 mmol) in 0.5 mL of THF at room temperature. In 2 min, a solution of iodide **20b** (20 mg, 0.045 mmol) and $Pd(PPh_3)_4$ (4 mg, 0.003 mmol) in 0.5 mL of THF was added. The mixture was stirred at 65 °C for 1.5 h, then cooled down to room temperature, diluted with Et_2O, and filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, 1:4 (v/v) hexane/EtOAc) to afford the triene **39** (8 mg, 77% yield) as a colorless oil. R_f = 0.30 (1:4 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3407, 2981, 1742; $[\alpha]^{25}_D$ +19° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.69-7.68 (m, 4H), 7.44-7.36 (m, 6H), 6.87 (ddd, *J* = 9.0, 8.4, 3.0 Hz, 1H), 6.77 (dd, *J* = 13.8, 12.0 Hz, 1H), 6.35 (dd, *J* = 12.0, 11.4 Hz, 1H), 6.24 (dd, *J* = 10.8, 12.0 Hz, 1H), 6.09 (d, *J* = 10.8 Hz, 1H), 6.06-6.04 (m, 1H), 5.88 (dd, *J* = 15.6, 5.4 Hz, 1H), 5.86-5.82 (m, 2H), 5.45 (dd, *J* = 10.2, 9.6 Hz, 1H), 4.95 (ddd, *J* = 10.2, 4.8, 4.8 Hz, 1H), 4.78 (td, *J* = 9.0, 4.8 Hz, 1H), 4.30 (d, *J* = 3.6 Hz, 1H), 4.03 (dd, *J* = 9.0, 3.0 Hz, 1H), 2.46-2.36 (m, 4H), 1.54-1.51 (m, 1H), 1.47 (s, 3H), 1.36 (s, 3H), 1.15 (s, 3H), 1.08 (s, 9H), 0.88 (s, 9H), 0.06 (s, 3H), 0.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 163.0, 144.4, 136.3, 135.9, 135.5 (2C), 134.3,

133.6, 130.1, 129.7 (2C), 128.3, 127.7 (2C), 126.6, 124.5, 123.4, 122.4, 121.7, 107.7, 81.2, 78.4, 77.3, 65.7, 64.2, 60.4, 37.7, 31.6, 29.8, 28.5, 26.8 (3C), 26.7, 25.9, 22.6, 21.0, 20.9, 19.3, 18.1, 14.2, 14.1, –4.2, –5.0; HRMS (CI) calcd for $[C_{44}H_{62}O_6Si_2 + Na]^+$: 765.3977, Found: 765.3981.

(*R*)-5,6-dihydro-6-((1*E*,3*R*,4*R*,6*R*,7*Z*,9*Z*,11*E*)-3,4-bistriethylsilyl-6-*tert*-butyldimethylsilyl-13-*tert*-butyldiphenylsilyl-3-methyltrideca-1,7,9-11-tetraenyl)pyran-2-one (40)

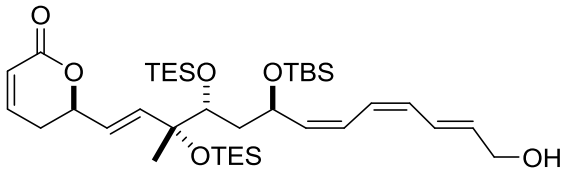


(40)

To a solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (2 mg, 0.0019 mmol) in 0.5 mL of THF was added PPh_3 (4mg, 0.015 mmol) at room temperature. The color changed from dark red to light yellow, then the solution was added to a flask containing iodide **20b** (13 mg, 0.029 mmol). After stirring for 2 min, the solution was added into the mixture of Z-vinylboronate **22** (7 mg, 0.0092 mmol) and Ag_2O (7 mg, 0.029 mmol) in 0.5 mL THF at room temperature. The reaction mixture was heated at 65 ^oC for 1.5 h, then cooled down to room temperature, diluted with Et_2O, and filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the triene **40** (8 mg, 80% yield) as a colorless oil. R_f = 0.15 (9:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 2981, 1703; $[\alpha]^{25}{}_D$ +22^o (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.69-7.60 (m, 4H), 7.44-7.36 (m, 6H), 6.85 (ddd, *J* = 9.6, 4.8, 3.6 Hz, 1H), 6.75 (dd, *J* = 15.6, 11.4 Hz, 1H), 6.30 (dd, *J* = 11.4, 11.4 Hz, 1H), 6.20 (dd, *J* = 11.4, 11.4 Hz, 1H), 6.06 (d, *J* = 11.4 Hz, 1H), 6.04 (ddd, *J* = 9.6, 1.8, 1.8 Hz, 1H), 5.87 (dd, *J* = 15.6, 1.2 Hz, 1H), 5.83 (ddd, *J* = 15.0, 5.4, 5.4 Hz, 1H), 5.75 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.42 (dd, *J* = 11.4, 9.0 Hz, 1H), 4.93 (ddd, *J* = 15.6, 6.6, 1.2 Hz, 1H), 4.69 (td, *J* = 9.0, 9.0, 3.0 Hz, 1H), 4.29 (d, *J* = 3.6 Hz, 1H), 3.70 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.43-2.41 (m, 3H), 1.90 (ddd, *J* = 14.4, 9.6, 1.8 Hz, 2H), 1.33 (s, 3H), 1.08 (s, 9H), 1.00 (t, *J* = 8.4 Hz, 9H),

0.96 (t, *J* = 8.4 Hz, 9H), 0.88 (s, 9H), 0.68 (qd, *J* = 7.8, 2.4 Hz, 6H), 0.68 (qd, *J* = 7.8, 1.2 Hz, 6H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 164.1, 144.5, 138.5, 136.6, 135.5 (4C), 134.8, 134.1, 133.6, 129.7, 129.6, 128.4, 127.7 (4C), 125.9, 124.6, 123.6, 122.4, 121.7, 78.0, 77.6, 76.2, 66.0, 64.2, 42.5, 29.8, 26.8 (3C), 26.0 (3C), 24.7, 19.3, 18.1, 7.2 (3C), 7.2 (3C), 6.9 (3C), 5. 8 (3C), –3.1, –4.1; HRMS (CI) calcd for $[C_{53}H_{86}O_6Si_4 + Na]^+$: 953.5392, Found: 953.5395.

(*R*)-5,6-dihydro-6-((1*E*,3*R*,4*R*,6*R*,7*Z*,9*Z*,11*E*)-3,4-bistriethylsilyl-6-*tert*-butyldimethylsilyl-13-hydroxy-3-methyltrideca-1,7,9-11-tetraenyl)pyran-2-one (41a)

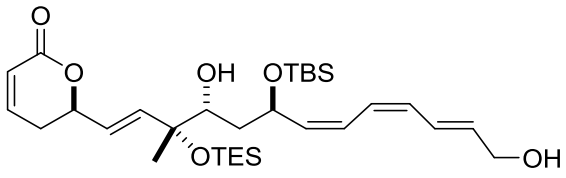


(41a)

To a 5 mL solution of CH_3CN/H_2O/Pyridine: 9/1/2, silyl ether **40** (10 mg, 0.011 mmol) was added, then dropwise addition of HF·pyridine complex (15 μL) at room temperature. After stirring for 48 h, the reaction was diluted with Et_2O and quenched by saturated aqueous solution of $NaHCO_3$. The aqueous solution was extracted with Et_2O, and the combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 7:3 (v/v) hexane/EtOAc) to afford the alcohol **41a** (3 mg, 40% yield) and the diol **41b** (3 mg, 45% yield). Both of these two compounds appeared as colorless oil. R_f = 0.52 (1:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3425, 2987, 1720; $[\alpha]^{25}{}_D$ +45° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.86 (ddd, *J* = 9.0, 4.8, 3.6 Hz, 1H), 6.73 (ddd, *J* = 15.0, 11.4, 1.2 Hz, 1H), 6.37 (dd, *J* = 11.4, 11.4 Hz, 1H), 6.24 (dd, *J* = 11.4, 11.4 Hz, 1H), 6.06 (d, *J* = 11.4 Hz, 1H), 6.04 (ddd, *J* = 9.6, 1.8, 1.8 Hz, 1H), 5.91 (dd, *J* = 15.6, 6.0, 5.4 Hz, 1H), 5.86 (dd, *J* = 15.6, 1.2 Hz, 1H), 5.74 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.45 (dd, *J* = 10.2, 9.6 Hz, 1H), 4.93 (ddd, *J* = 15.6, 6.0, 1.2 Hz, 1H), 4.68 (td, *J* = 9.6, 9.6, 2.4 Hz, 1H), 4.25 (d, *J* = 4.8 Hz, 1H), 3.70 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.43-2.41 (m, 2H), 1.89 (ddd, *J* = 14.4, 10.2, 1.8 Hz, 2H), 1.33 (s, 3H), 1.08 (ddd, *J* = 11.4, 8.4,3.0 Hz, 2H), 0.98 (t, *J* = 8.4 Hz, 9H), 0.95 (t, *J* = 8.4 Hz, 9H), 0.87 (s, 9H), 0.67 (qd, *J* = 7.8, 2.4 Hz,

6H), 0.61 (qd, *J* = 7.8, 1.2 Hz, 6H), 0.04 (s, 3H), 0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 164.0, 144.5, 138.4, 137.1, 133.8, 129.4, 126.0, 125.9, 124.5, 122.2, 121.7, 77.9, 77.6, 76.2, 66.0, 63.4, 42.5, 29.7 (3C), 26.0 (3C), 24.7, 18.1, 13.3, 7.2 (3C), 7.2 (3C), 6.9 (3C), 5.8 (3C), –3.05, –4.10; HRMS (CI) calcd for $[C_{37}H_{68}O_6Si_3 + Na]^+$: 715.4192, Found: 715.4215.

(*R*)-5,6-dihydro-6-((1*E*,3*R*,4*R*,6*R*,7*Z*,9*Z*,11*E*)-3-triethylsilyl-6-*tert*-butyldimethylsilyl-4,13-hydroxy-3-methyltrideca-1,7,9-11-tetraenyl)pyran-2-one (41b)

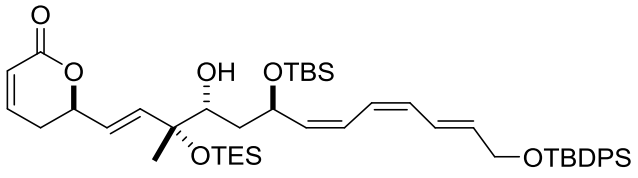


(41b)

To a 0.6 mL solution of CH_3CN/H_2O/Pyridine: 9/1/2, silyl ether **41a** (6 mg, 0.008 mmol) was added, then dropwise addition of HF·pyridine complex (12 μL) at room temperature. After stirring for 24 h, the reaction was diluted with Et_2O and quenched by saturated aqueous solution of $NaHCO_3$. The aqueous solution was extracted with Et_2O, and the combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 7:3 (v/v) hexane/EtOAc) to afford the diol **41b** (4 mg, 82% yield) as a colorless oil. R_f = 0.24 (1:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3420, 2980, 1715; $[\alpha]^{25}{}_D$ –11° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.88 (ddd, *J* = 9.0, 5.4, 3.6 Hz, 1H), 6.73 (ddd, *J* = 15.0, 11.4, 1.2 Hz, 1H), 6.38 (dd, *J* = 11.4, 11.4 Hz, 1H), 6.20 (dd, *J* = 11.4, 11.4 Hz, 1H), 6.06 (d, *J* = 10.8 Hz, 1H), 6.04 (ddd, *J* = 9.6, 1.8, 1.8 Hz, 1H), 5.91 (dd, *J* = 15.0, 6.0, 5.4 Hz, 1H), 5.88 (dd, *J* = 16.2, 1.2 Hz, 1H), 5.79 (dd, *J* = 15.6, 6.0 Hz, 1H), 5.55 (dd, *J* = 10.2, 9.6 Hz, 1H), 4.96 (ddd, *J* = 10.2, 6.0, 1.2 Hz, 1H), 4.91 (td, *J* = 7.8, 7.8, 2.4 Hz, 1H), 4.24 (dd, *J* = 4.8, 4.8 Hz, 1H), 3.67 (dd, *J* = 11.4, 2.4 Hz, 1H), 2.95 (d, *J* = 2.4 Hz, 1H), 2.46-2.42 (m, 2H), 1.64 (dd, *J* = 13.8, 7.8 Hz, 2H), 1.31 (s, 3H), 0.92 (t, *J* = 8.4 Hz, 9H), 0.87 (s, 9H), 0.77 (q, *J* = 7.8 Hz, 6H), 0.06 (s, 3H), 0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 164.1, 144.6, 138.1, 136.3, 134.1, 129.8, 127.1, 126.2, 124.3, 122.3, 122.0, 77.8, 77.1, 75.1, 67.1, 63.6, 39.2, 29.8, 26.0 (3C),

22.3, 18.3, 7.3 (3C), 6.9 (3C), –4.1, –4.9; HRMS (CI) calcd for $[C_{31}H_{54}O_6Si_2 + Na]^+$: 601.3392, Found: 601.3350.

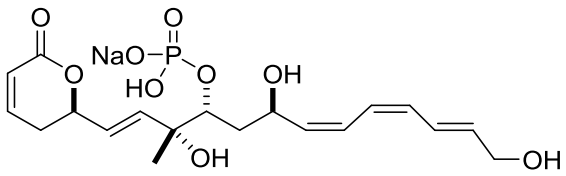
(*R*)-5,6-dihydro-6-((1*E*,3*R*,4*R*,6*R*,7*Z*,9*Z*,11*E*)-3-bistriethylsilyl-4-hydroxy-6-*tert*-butyldimethylsilyl-13-*tert*-butyldiphenylsilyl-3-methyltrideca-1,7,9-11-tetraenyl)pyran-2-one (21)



(21)

To a solution of diol **41b** (5 mg, 0.0083 mmol) in 0.2 mL of CH_2Cl_2 was added imidazole (2 mg, 0.027 mmol) and TBDPSCl (3 mg, 0.012 mmol) at 0 ^oC. After stirring for 15 min at 0 ^oC, the reaction mixture was purified by chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) without workup provided compound **21** (5 mg, 78% yield) as a yellow oil. R_f = 0.46 (4:1 (v/v) hexane/EtOAc); IR (neat, cm^{-1}): 3412, 2981, 1728; $[\alpha]^{25}{}_D$ –18^o (*c* 0.4, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.69-7.67 (m, 4H), 7.44-7.33 (m, 6H), 6.88 (ddd, *J* = 8.4, 5.4, 3.6 Hz, 1H), 6.75 (dd, *J* = 15.6, 11.4 Hz, 1H), 6.33 (dd, *J* = 11.4, 11.4 Hz, 1H), 6.15 (dd, *J* = 11.4, 11.4 Hz, 1H), 6.07-6.03 (m, 2H), 5.89 (dd, *J* = 15.6, 1.2 Hz, 1H), 5.83 (ddd, *J* = 15.6, 5.4, 5.4 Hz, 1H), 5.80 (dd, *J* = 15.6, 6.0 Hz, 1H), 5.53 (dd, *J* = 10.2, 9.6 Hz, 1H), 4.98-4.91 (m, 2H), 4.29 (d, *J* = 4.2 Hz, 2H), 3.68 (d, *J* = 10.8 Hz, 1H), 2.99 (d, *J* = 2.4 Hz, 1H), 2.46-2.43 (m, 2H), 1.64 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.33-1.37 (m, 1H), 1.32 (s, 3H), 1.08 (s, 9H), 0.93 (t, *J* = 7.8 Hz, 9H), 0.88 (s, 9H), 0.57 (q, *J* = 7.8 Hz, 6H), 0.07 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 163.9, 144.3, 137.9, 135.5 (4C), 134.3, 133.6, 133.6, 130.1, 129.7 (2C), 127.7 (4C), 126.8, 124.5, 123.2, 122.3, 121.8, 77.6, 75.0, 67.0, 64.2, 39.0, 29.6 (3C), 26.8 (3C), 25.8 (3C), 22.2, 19.3, 18.1, 7.1 (3C), 6.7 (3C), –4.33, –5.07; HRMS (CI) calcd for $[C_{47}H_{72}O_6Si_3 + Na]^+$: 839.4492, Found: 839.4528.

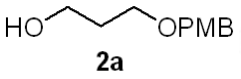
Fosriecin (1)



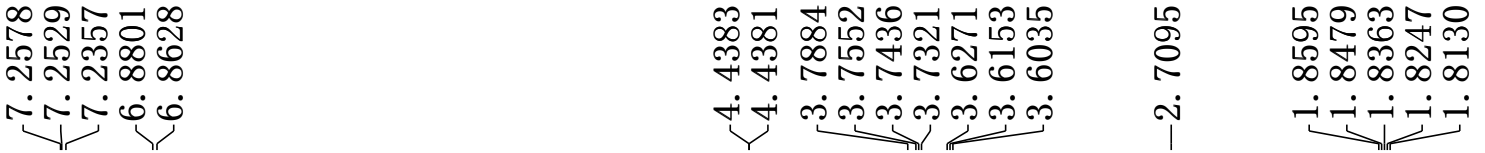
(1)

To a solution of alcohol **21** (5 mg, 0.006 mmol) in 0.4 mL of pyridine was added PCl_3 (4.1 mg, 0.03 mmol) at 0 ^oC and stirred for 15 min. 4-Methoxybenyl alcohol (20.7 mg, 0.15 mmol) was added into the reaction mixture, and the reaction was gradually warmed to room temperature. After stirring at room temperature for 1 h, the reaction was diluted with 1.2 mL of CH_2Cl_2, then *tert*-Butyl hydroperoxide (5.5 M in decane, 55 µL, 0.35 mmol) was added and stirred at room temperature for 1.5 h. The reaction was quenched by saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was treated with 48% HF-acetonitrile (1: 19, 0.3 mL) at room temperature for 15 min. After ice cooling, pyridine (95 µL) was added to the reaction mixture, and the mixture was stirred at room temperature for another 23 h. The reaction mixture was basified with saturated aqueous solution of $NaHCO_3$, extraced with Et_2O, and the combined organic solution was concentrated under reduced pressure. The residue was purified by 18-reversed phase column chromatography (silica gel, 9:1 (v/v) H_2O/acetonitrile) to afford the fostriecin **1** (0.5 mg, 31% yield) as a white solid. $[\alpha]^{25}{}_D$ –325^o (*c* 0.1, D_2O); ^1H NMR (D_2O, 600 MHz): δ 7.03 (ddd, *J* = 10, 6, 3 Hz, 1H), 6.70 (dd, *J* = 15, 12 Hz, 1H), 6.49 (t, *J* = 11 Hz, 1H), 6.29 (t, *J* = 12 Hz, 1H), 6.09 (t, *J* = 11 Hz, 1H), 5.96 (dd, *J* = 10, 2 Hz, 1H), 5.92-5.84 (m, 3H), 5.50 (t, *J* = 10 Hz, 1H), 5.06 (m, 1H), 4.88 (t, *J* = 9 Hz, 1H), 4.12 (d, *J* = 6 Hz, 2H), 4.10-4.06 (m, 1H), 2.56 (td, *J* = 19, 6 Hz, 1H), 2.44-2.50 (m, 1H), 1.58 (t, *J* = 12 Hz, 1H), 1.46 (m, 1H), 1.24 (s, 3H); ^{13}C NMR: Data was not available due to lack of sample; HRMS (CI) calcd for $[C_{19}H_{26}NaO_9P + Na]^+$: 475.1104, Found: 475.1114.

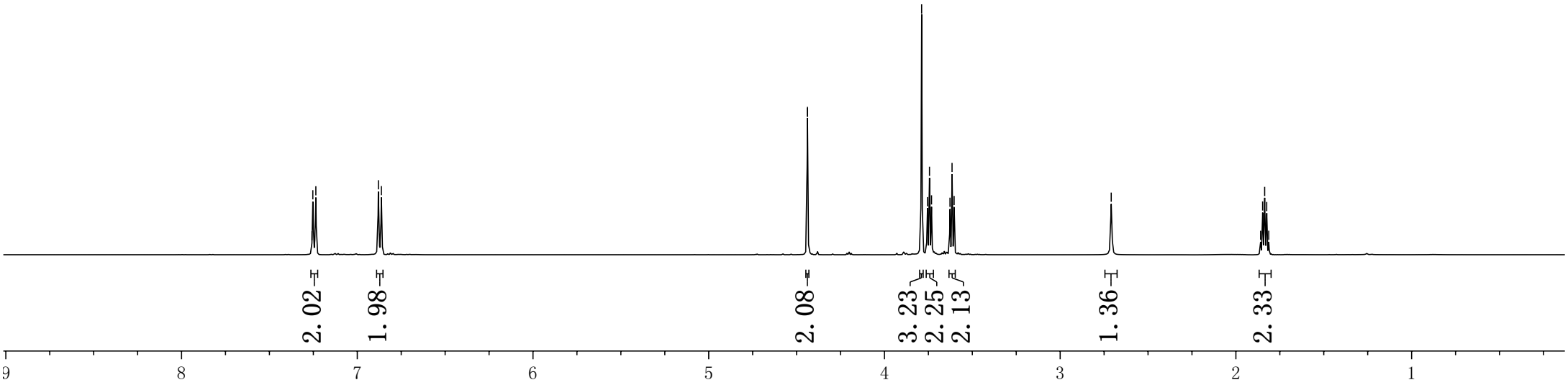
^{1}H and ^{13}C NMR Spectra



2a

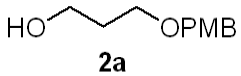


^{1}H NMR spectrum of **2a** ($CDCl_3$, 500 Hz)



CARBON_01

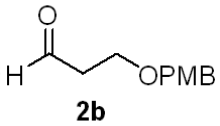
158.8373
130.0130
128.9333
113.4291
77.4117
77.1600
76.9083
72.3504
67.8306
60.1201
54.5268
32.2560



2a

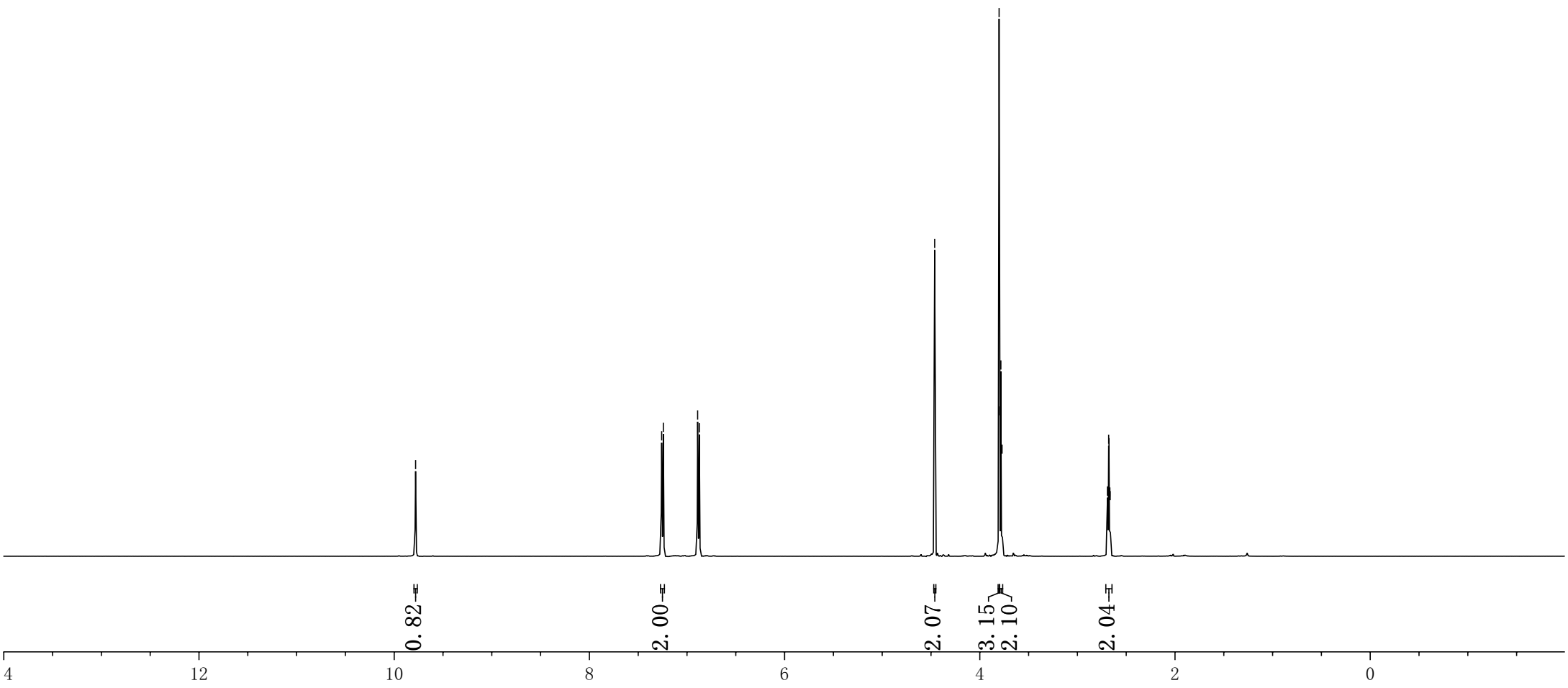
^{13}C NMR spectrum of **2a** ($CDCl_3$, 500 Hz)

PROTON_01



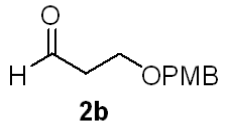
2b

^{1}H NMR spectrum of **2b** ($CDCl_3$, 500 Hz)



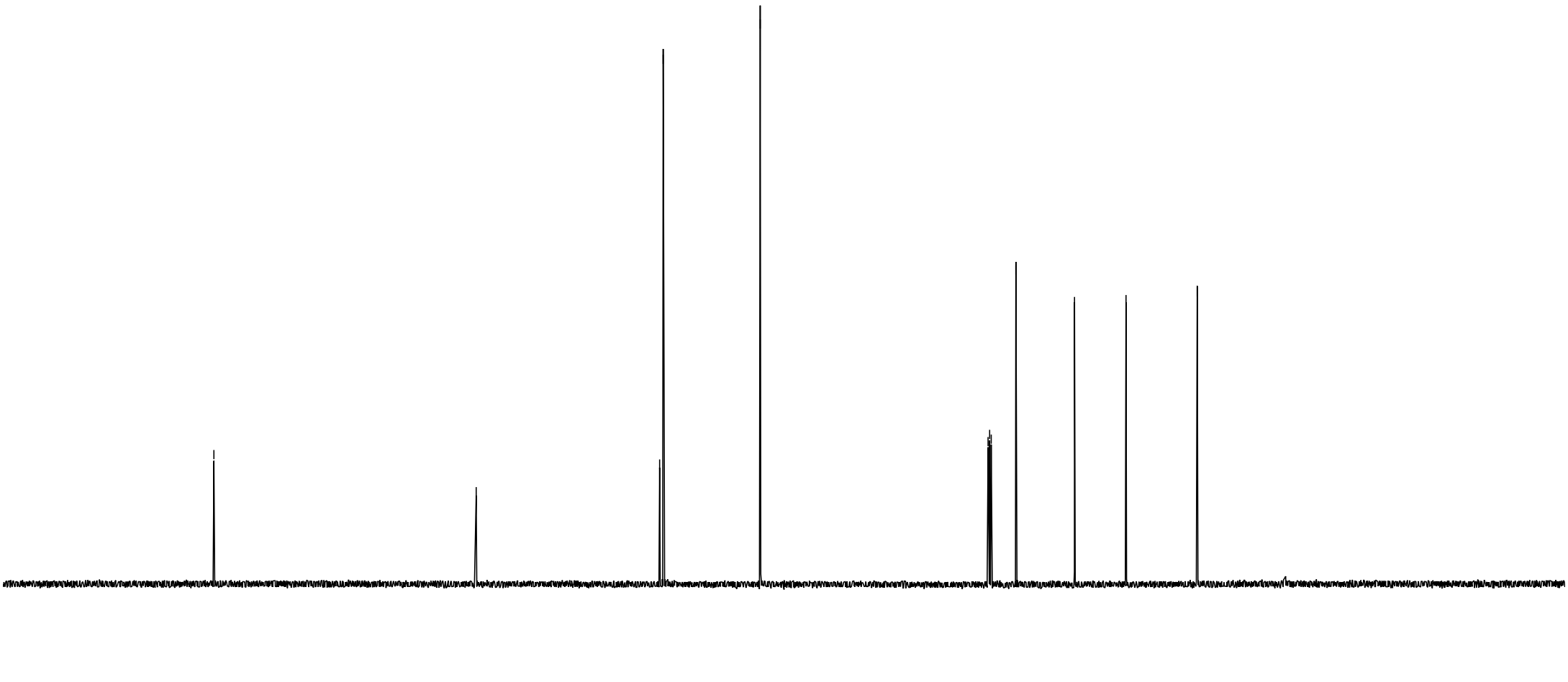
CARBON_01

201.3356
159.3480
129.9847
129.4204
113.8860
77.4147
77.1596
76.9057
72.9582
63.5740
55.3283
43.9303

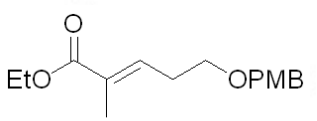


2b

^{13}C NMR spectrum of **2b** ($CDCl_3$, 500 Hz)



PROTON_01

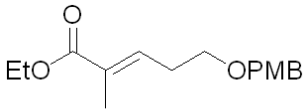


11a

^{1}H NMR spectrum of **11a** ($CDCl_3$, 500 Hz)

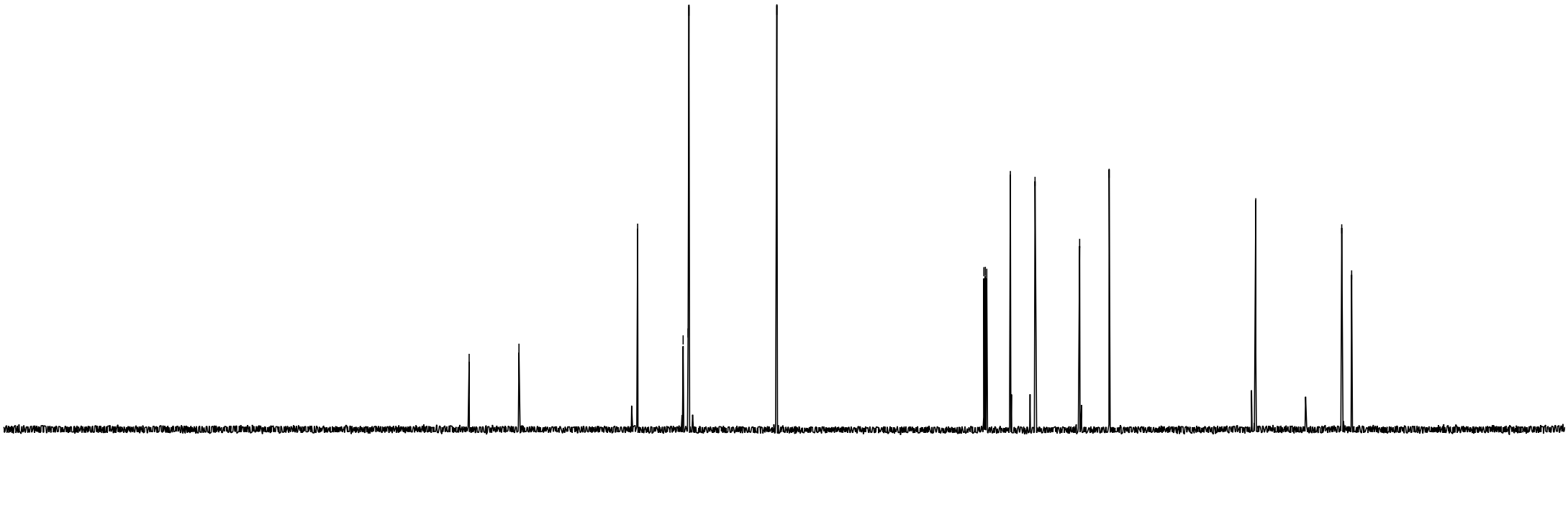
CARBON_01

168.0654
159.2914
138.3912
130.3789
129.5045
129.3565
113.8782
77.4142
77.1596
76.9053
72.7524
68.4049
60.5485
55.3534
29.5280
14.3896
12.6466



11a

^{13}C NMR spectrum of **11a** ($CDCl_3$, 500 Hz)



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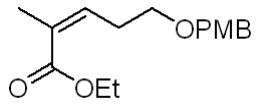
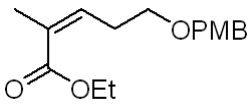


11b

^{1}H NMR spectrum of **11b** ($CDCl_3$, 500 Hz)

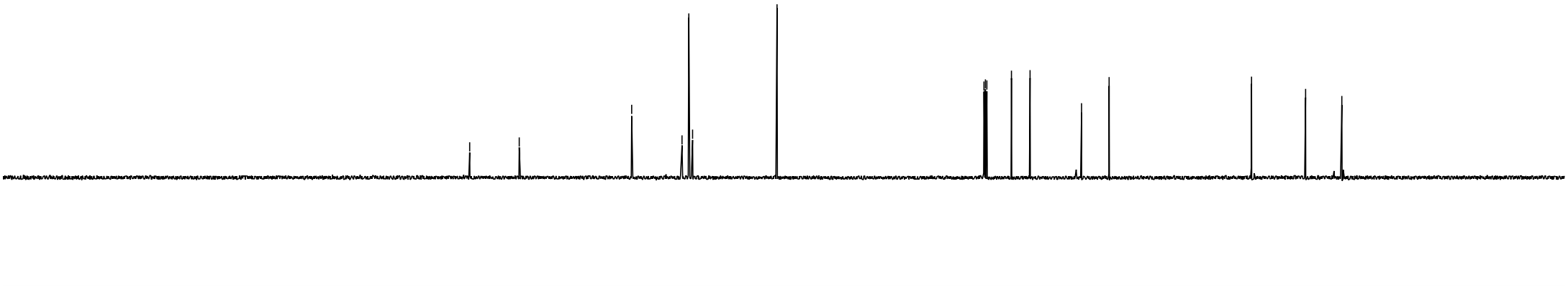
CARBON_01



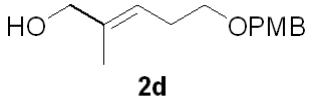
11b

167.9889
159.2603
139.4569
130.5950
129.3948
128.7327
113.8618
77.4147
77.1604
76.9059
72.5754
69.2980
60.2305
55.3738
30.2914
20.7702
14.3896

^{13}C NMR spectrum of **11b** ($CDCl_3$, 500 Hz)



PROTON_01

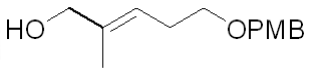


2d

^{1}H NMR spectrum of **2d** ($CDCl_3$, 500 Hz)

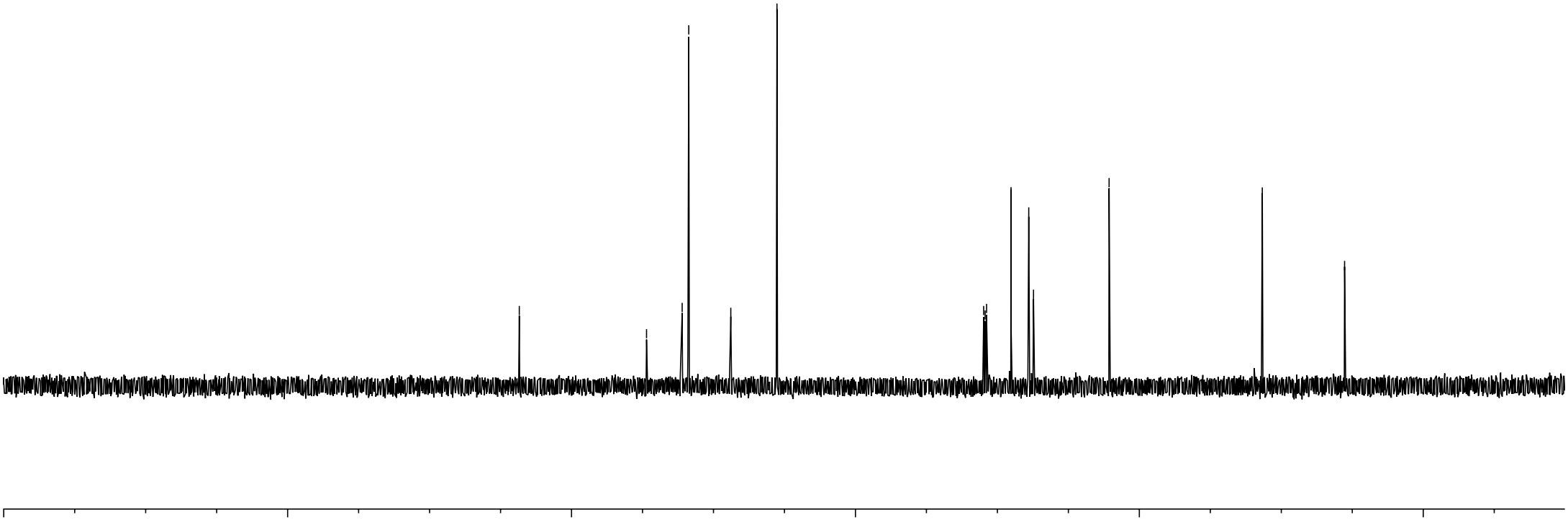
CARBON_01

159.1999
136.7885
130.5177
129.3556
121.9510
113.8204
77.4167
77.1596
76.9043
72.5985
69.4772
68.6374
55.3272
28.3450
13.8537



2d

^{13}C NMR spectrum of **2d** ($CDCl_3$, 500 Hz)



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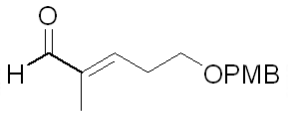
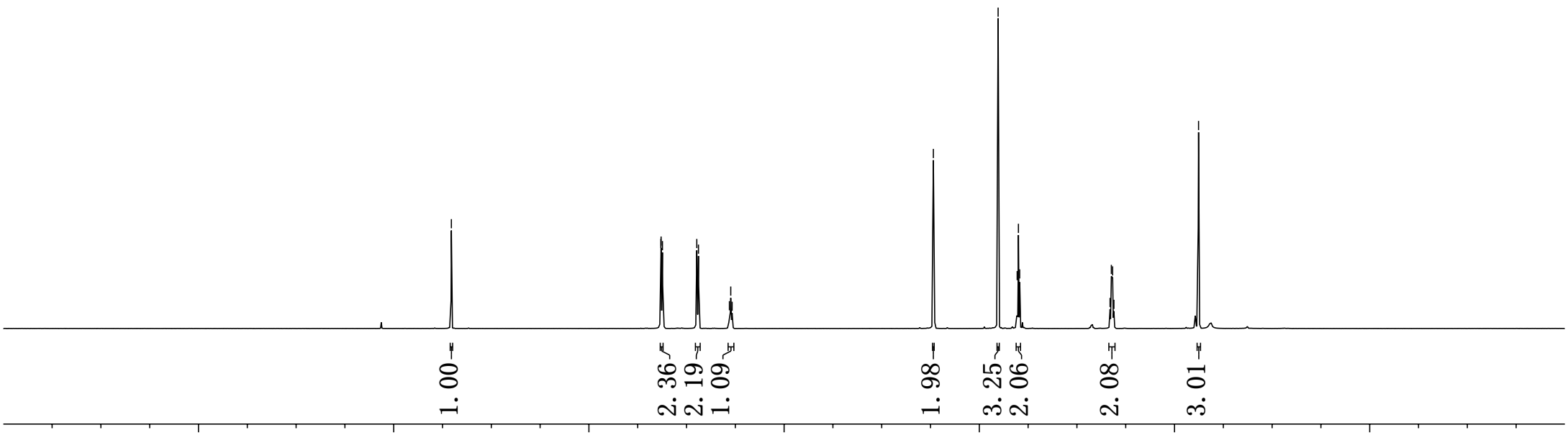
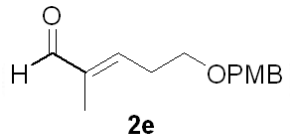


2e

9.4092
7.2627
7.2603
7.2465
6.8946
6.8775
6.5604
6.5467
6.5327
4.4707
3.8074
3.6121
3.5993
3.5865
2.6603
2.6472
2.6341
2.6209
1.7536

^{1}H NMR spectrum of **2e** ($CDCl_3$, 500 Hz)

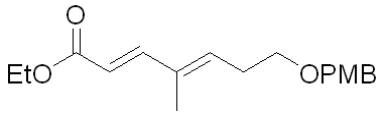




2e

^{13}C NMR spectrum of **2e** ($CDCl_3$, 500 Hz)

PROTON_01

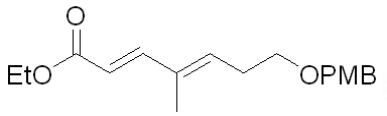


8a

^{1}H NMR spectrum of **8a** ($CDCl_3$, 500 Hz)

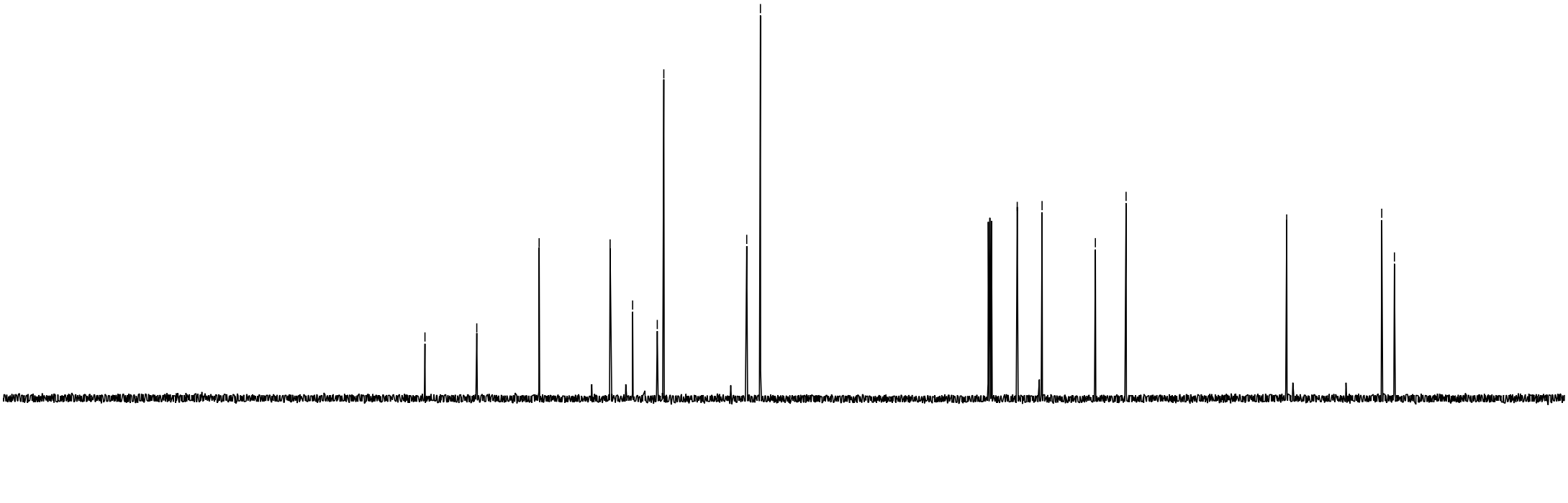
CARBON_01

167.4783
159.1836
149.2019
137.8406
134.2348
130.2908
129.2451
115.9715
113.7795
72.6715
68.6963
60.1640
55.2476
29.5374
14.3217
12.2926

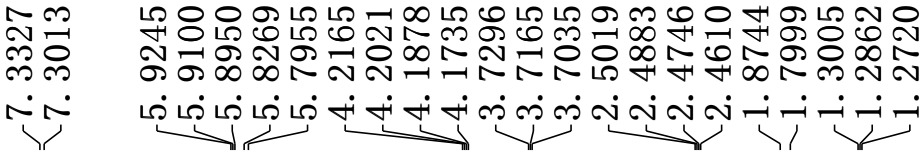


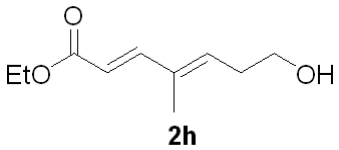
8a

^{13}C NMR spectrum of **8a** ($CDCl_3$, 500 Hz)

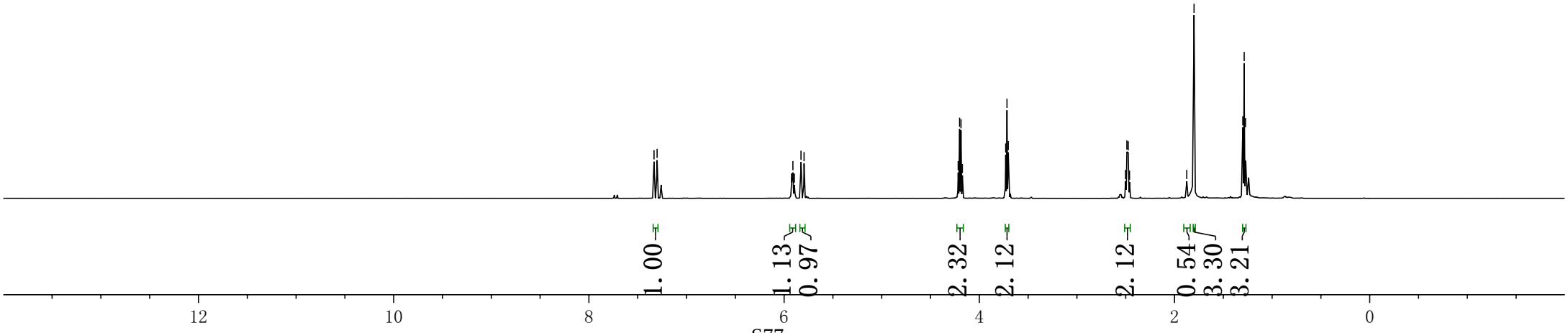


PROTON_01



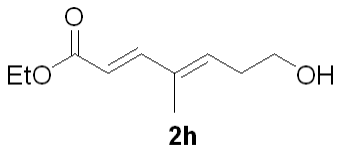


^{1}H NMR spectrum of **2h** ($CDCl_3$, 500 Hz)



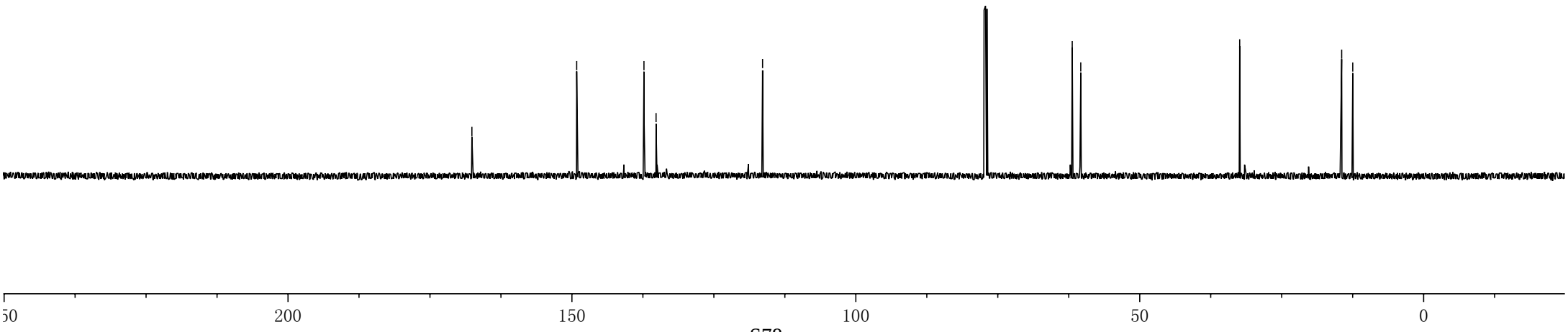
CARBON_01

167.6166
149.1603
137.3139
135.1822
116.4242
61.8889
60.3855
32.3964
14.4350
12.4842

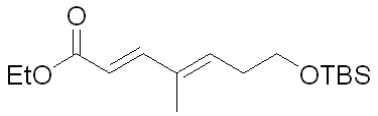


2h

^{13}C NMR spectrum of **2h** ($CDCl_3$, 500 Hz)



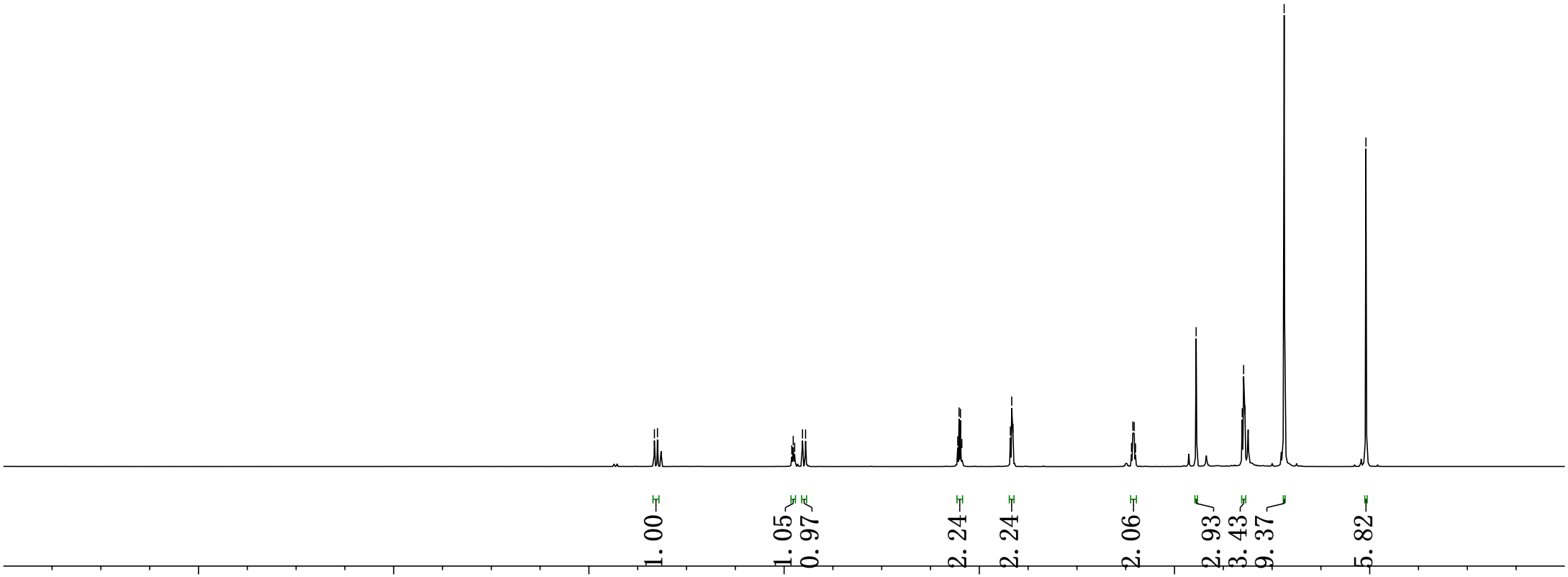
PROTON_02



8b

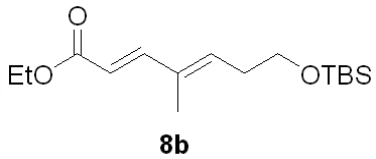
7.3288
7.2974
5.9212
5.9066
5.8919
5.8116
5.7803
4.2213
4.2076
4.1934
4.1791
3.6814
3.6681
3.6547
2.4406
2.4269
2.4131
2.3995
1.7784
1.3061
1.2918
1.2775
0.8767
0.0391

^{1}H NMR spectrum of **8b** ($CDCl_3$, 500 Hz)



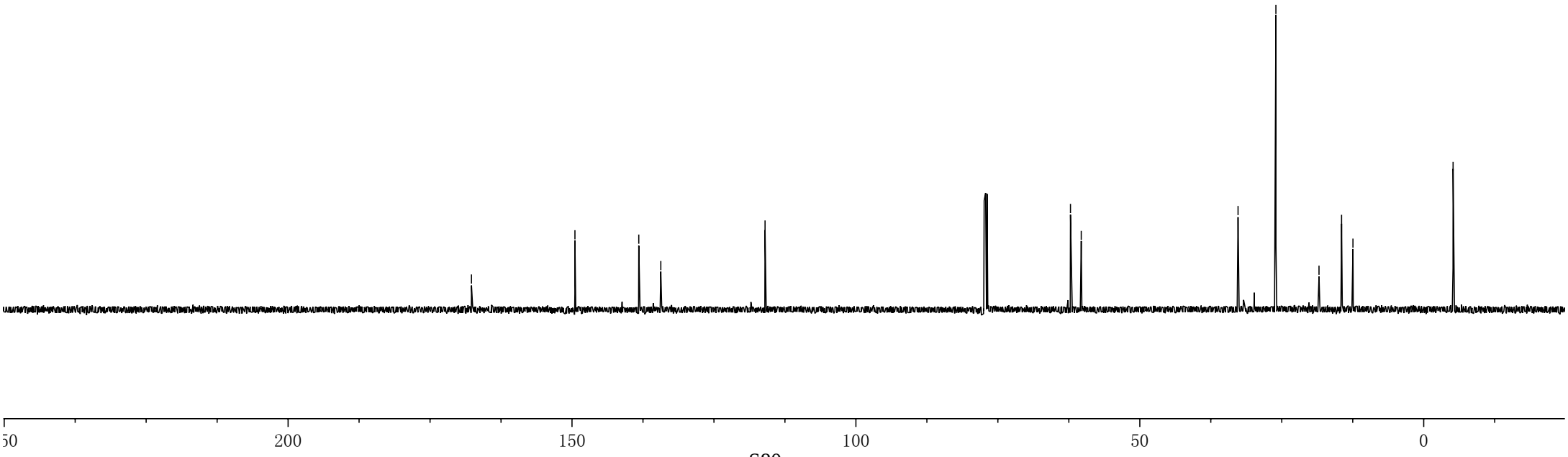
CARBON_01

167.7071
149.4831
138.2393
134.3592
116.0009
62.2125
60.3146
32.6995
26.0334
18.4418
14.4673
12.4629
-5.1724



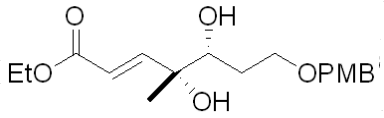
8b

^{13}C NMR spectrum of **8b** ($CDCl_3$, 500 Hz)



dg486.3

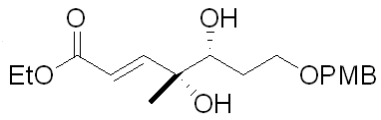
^{1}H NMR spectrum of **2i-1** ($CDCl_3$, 270 Hz)



2i-1

dg486c13.3

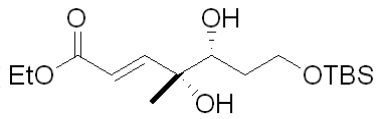
^{13}C NMR spectrum of **2i-1** ($CDCl_3$, 67.5 Hz)



2i-1

dg264–1.3

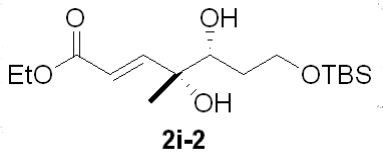
^{1}H NMR spectrum of **2i-2** ($CDCl_3$, 270 Hz)



2i-2

dg264–1c13.3

^{13}C NMR spectrum of **2i-2** ($CDCl_3$, 67.5 Hz)



2i-2

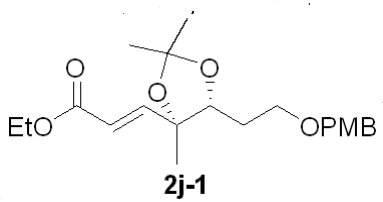
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0

166.6335
152.3401
120.1706
77.4739
77.2448
77.0003
76.5343
74.5786
62.6153
60.3387
32.1188
25.7704
22.8216
18.0470
14.1891
−5.6428

X : parts per Million : 13C

dg485.3

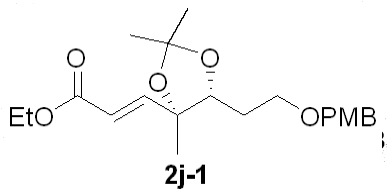
^{1}H NMR spectrum of **2j-1** ($CDCl_3$, 150 Hz)



2j-1

dg485C13.3

^{13}C NMR spectrum of **2j-1** ($CDCl_3$, 67.5 Hz)



2j-1

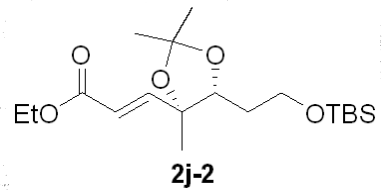
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0

166.4017
159.1061
149.3811
130.2368
129.2360
120.3208
113.7051
107.9832
81.5585
78.8083
77.4637
76.9977
76.5241
72.7197
66.9901
60.4584
55.1872
29.5188
28.2812
26.2873
20.8022
14.1789

X : parts per Million : 13C

dg271–1.3

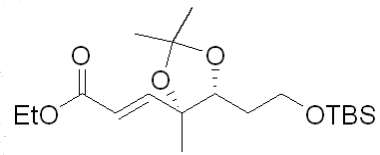
^{1}H NMR spectrum of **2j-2** ($CDCl_3$, 270 Hz)



2j-2

dg272c13.3

^{13}C NMR spectrum of **2j-2** ($CDCl_3$, 67.5 Hz)



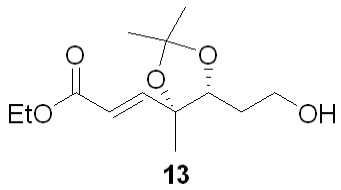
2j-2

166.4493
149.4593
120.2691
107.9391
78.3287
77.4655
76.9995
76.5258
60.4525
60.0858
32.2478
28.3288
26.2891
25.8613
20.9338
18.2677
14.2035
−5.3916
−5.4450

X : parts per Million : 13C

dg271–3.3

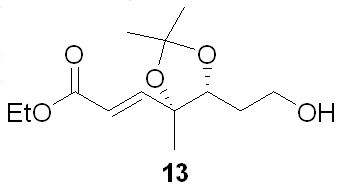
^{1}H NMR spectrum of **13** ($CDCl_3$, 270 Hz)



13

dg271–3c13.3

^{13}C NMR spectrum of **13** ($CDCl_3$, 67.5 Hz)



13

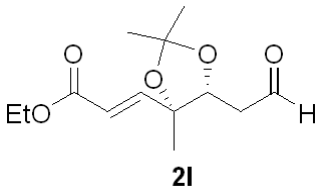
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0

166.6693
149.0528
120.5120
108.5181
80.5350
77.4716
76.9979
76.5319
60.9170
60.5808
31.3906
28.2814
26.4098
20.9247
14.1791

X : parts per Million : 13C

dg274.3

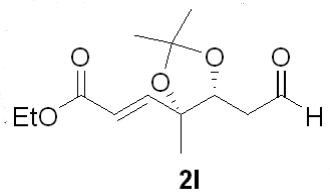
^{1}H NMR spectrum of **2l** ($CDCl_3$, 270 Hz)



2l

dg274c13.3

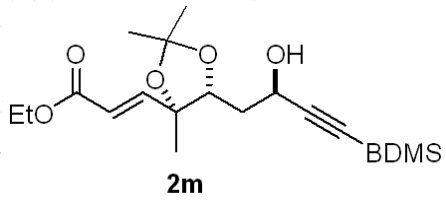
^{13}C NMR spectrum of **2l** ($CDCl_3$, 67.5 Hz)



2l

dg288–1.3

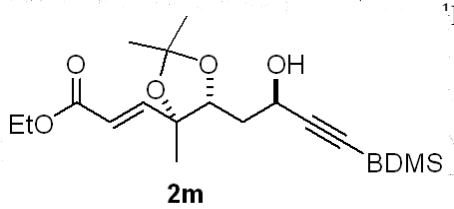
^{1}H NMR spectrum of **2m** ($CDCl_3$, 150 Hz)



2m

dg288–1c13.3

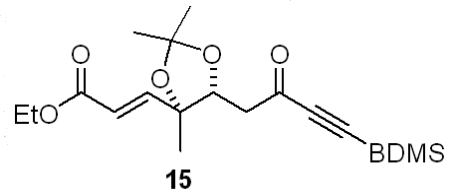
^{1}H NMR spectrum of **2m** ($CDCl_3$, 270 Hz)



2m

dgketone.3

^{1}H NMR spectrum of **15** ($CDCl_3$, 270 Hz)



15

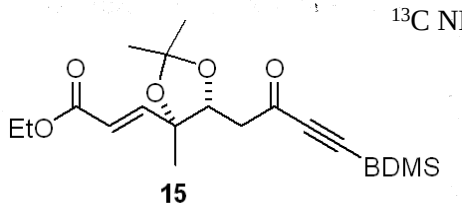
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 −1.0 −2.0

7.2371 7.2096 7.0731 7.0685 6.9192 6.8615 6.1450 6.1111 6.0873 4.3878 4.2467 4.2201 4.1936 4.1679 2.8596 2.8257 2.6782 2.6635 2.6159 2.2595 2.0378 1.6640 1.4633 1.3800 1.3213 1.2948 1.2691 1.2233 0.2622 0.2503 0.2054 0.2027 0.1660

X : parts per Million : 1H

dgketonec13.3

^{13}C NMR spectrum of **15** ($CDCl_3$, 67.5 Hz)



15

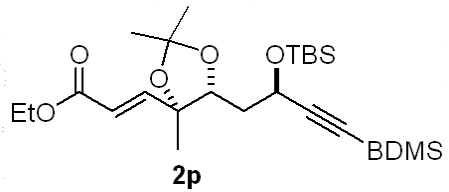
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0

183.0949 166.2348 148.6106 137.6710 128.3662 128.2592 124.7833 120.8643 108.7100 102.4457 98.1141 77.4648 76.9988 76.7773 76.5252 60.6046 44.7452 28.1524 26.2120 25.1807 21.1089 14.1876 −2.8177

X : parts per Million : 13C

dg291.3

^{1}H NMR spectrum of **2p** ($CDCl_3$, 270 Hz)



2p

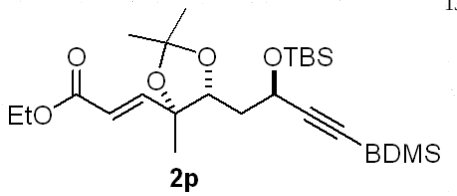
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 −1.0 −2.0

7.2160
7.0804
7.0758
6.9054
6.8477
6.1111
6.0534
4.5408
4.4913
4.2146
4.1880
4.0359
2.1880
1.8417
1.8252
1.6282
1.4596
1.3415
1.3195
1.2938
1.2672
1.2214
0.8889
0.1248
0.1147
0.1101
0.0991
0.0707

X : parts per Million : 1H

dg291c13.3

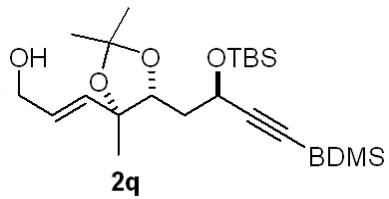
^{13}C NMR spectrum of **2p** ($CDCl_3$, 67.5 Hz)



2p

dg292fast.3

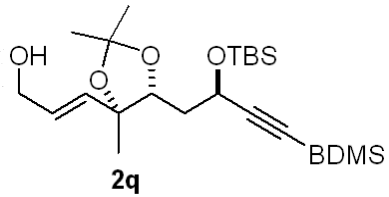
^{1}H NMR spectrum of **2q** ($CDCl_3$, 270 Hz)



2q

dg292fastc13.3

^{13}C NMR spectrum of **2q** ($CDCl_3$, 67.5 Hz)



2q

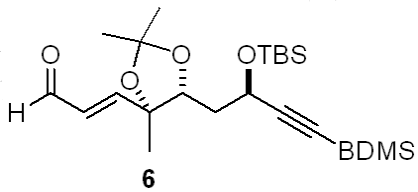
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0

138.8402
133.7447
129.6576
128.3284
128.1374
124.3253
108.7027
107.5568
81.2543
77.4652
76.9992
76.5256
63.0802
60.2154
38.0076
28.4355
26.6708
26.0443
25.7540
20.8648
18.2063
−2.2826
−2.2826
−2.2826

X : parts per Million : 13C

dg305.3

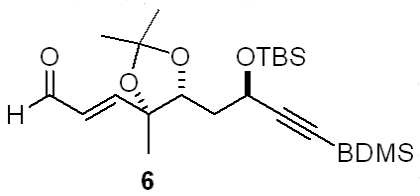
^{1}H NMR spectrum of **6** ($CDCl_3$, 270 Hz)



6

dg305c13.3

^{13}C NMR spectrum of **6** ($CDCl_3$, 67.5 Hz)

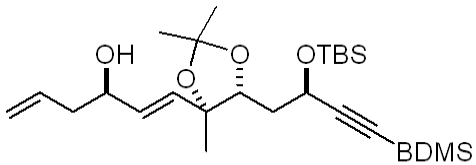


6

193.2250
157.7399
138.6872
130.7193
128.2594
128.0990
124.3099
108.4428
108.2365
87.3122
81.3000
77.4726
77.0601
76.9990
76.5254
59.9555
38.1526
28.2290
26.2428
25.9372
25.6469
20.8188
18.1068
−2.3133
−4.6128
−5.2010

X : parts per Million : 13C

^{1}H NMR spectrum of **2s** ($CDCl_3$, 600 Hz)



2s

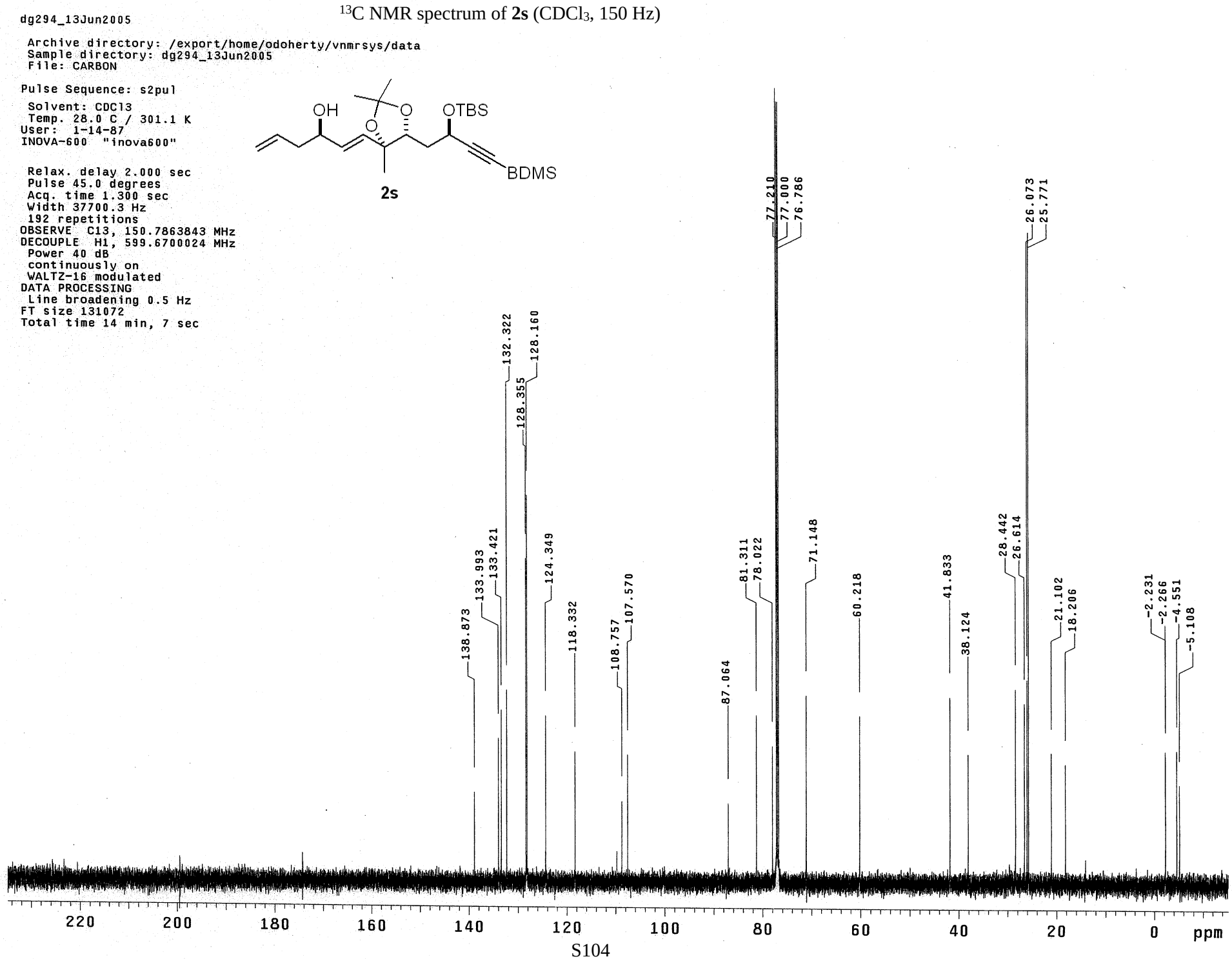
```
STANDARD PROTON PARAMETERS

 Archive directory: /export/home/vnmr1/vnmrsys/data
 Sample directory:
 File: PROTON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
INOVA-600  "inova600"

 Pulse 30.3 degrees
 Acq. time 1.892 sec
 Width 9594.6 Hz
 16 repetitions
OBSERVE   H1, 599.6669942 MHz
DATA PROCESSING
 Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 30 sec
```

^{13}C NMR spectrum of **2s** ($CDCl_3$, 150 Hz)



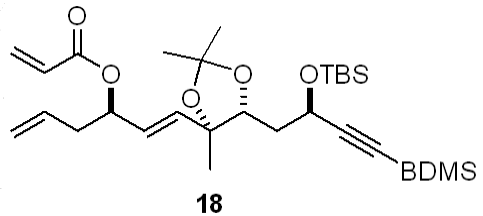
dg296_15Jun2005

^{1}H NMR spectrum of **18** ($CDCl_3$, 600 Hz)

Archive directory: /export/home/odoherty/vnmrsys/data
Sample directory: dg296_15Jun2005

Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 28.0 C / 301.1 K
File: PROTON
INOVA-600 "inova600"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 9594.6 Hz
32 repetitions
OBSERVE H1, 599.6670558 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 2 min, 4 sec



18

^{13}C NMR spectrum of **18** ($CDCl_3$, 150 Hz)

```
dg296_15Jun2005

 Archive directory: /export/home/odoherty/vnmrsys/data
 Sample directory: dg296_15Jun2005

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
User:  1-14-87
File: CARBON
INOVA-600  "inova600"

 Relax. delay 2.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 37700.3 Hz
 256 repetitions
OBSERVE  C13, 150.7863837 MHz
DECOUPLE  H1, 599.6700024 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 131072
Total time 14 min, 7 sec
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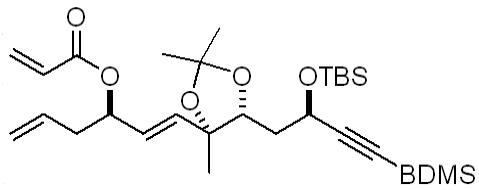
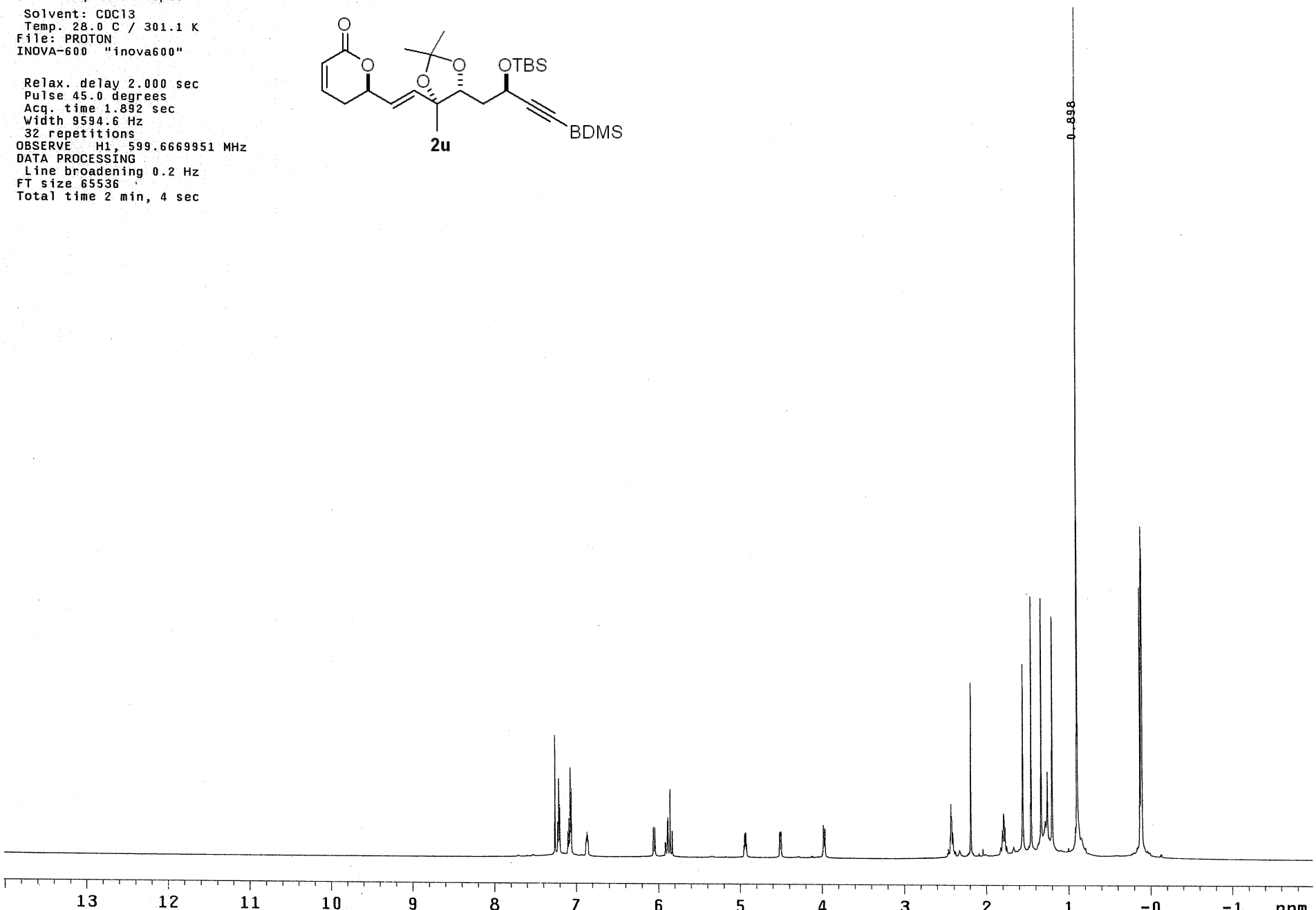
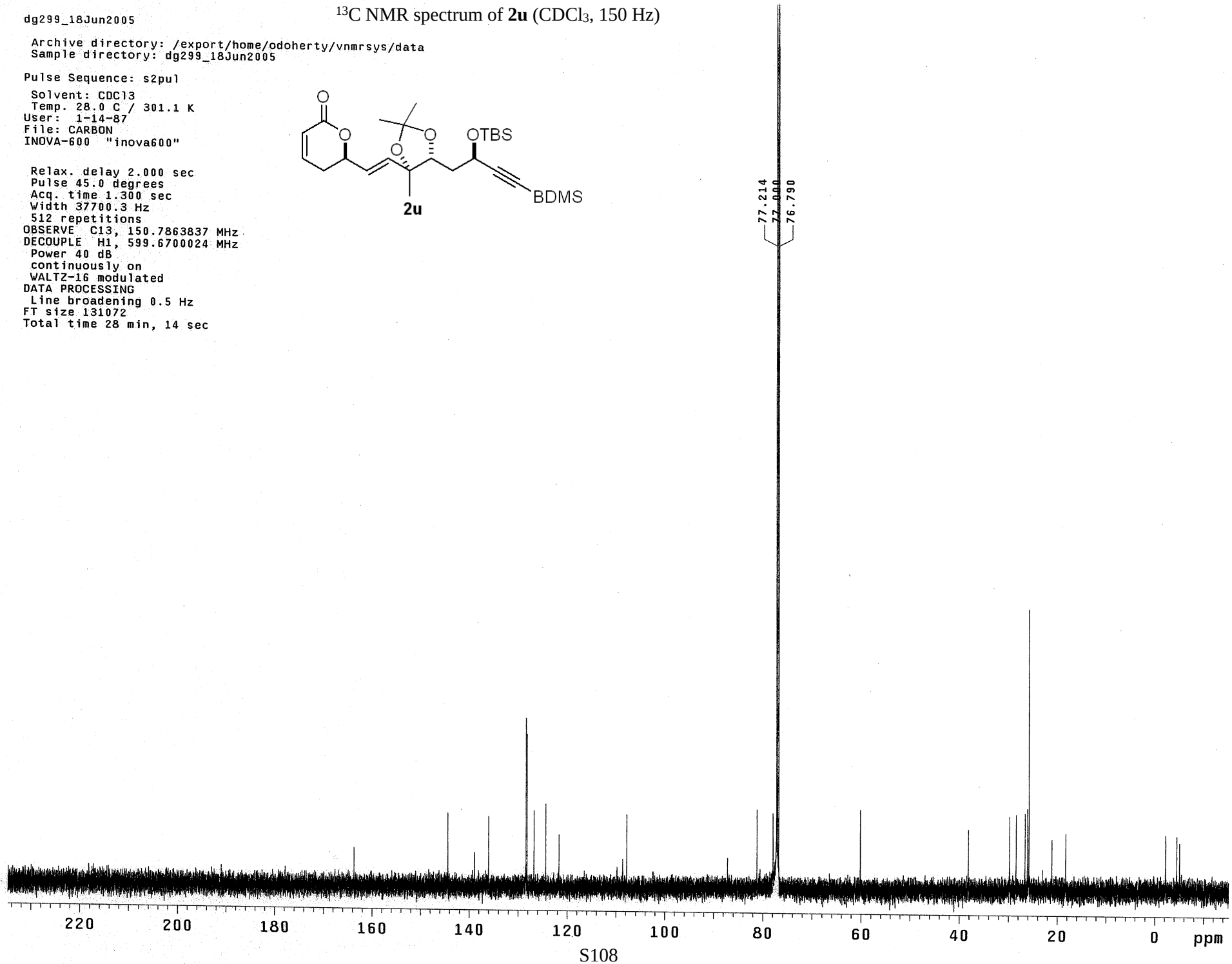


18

^{1}H NMR spectrum of **2u** ($CDCl_3$, 600 Hz)

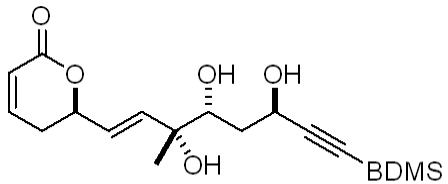


^{13}C NMR spectrum of **2u** ($CDCl_3$, 150 Hz)



dg314.3

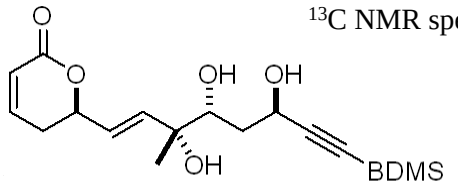
^{1}H NMR spectrum of **5** ($CDCl_3$, 600 Hz)



5

dg314.4

^{13}C NMR spectrum of **5** ($CDCl_3$, 150 Hz)



5

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0

164.1354
144.9758
137.9170
128.3448
128.1614
126.6030
124.3876
121.3624
107.4816
88.2608
77.4740
77.2677
77.0003
76.5343
74.5175
74.0209
60.7818
37.0538
29.7811
26.0455
22.4473
−2.1440

X : parts per Million : 13C

^{1}H NMR spectrum of **3a** ($CDCl_3$, 600 Hz)

```
STANDARD PROTON PARAMETERS

 Archive directory: /export/home/vnmr1/vnmrsys/data
 Sample directory:
 File: PROTON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
INOVA-600  "inova600"

 Relax. delay 1.000 sec
 Pulse 26.9 degrees
 Acq. time 1.892 sec
 Width 9594.6 Hz
 16 repetitions
OBSERVE   H1, 599.6669954 MHz
DATA PROCESSING
 Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 46 sec
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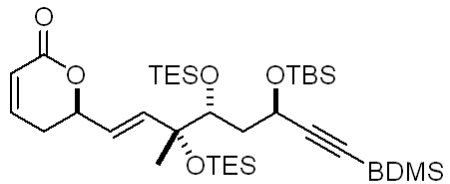

3a

^{13}C NMR spectrum of **3a** ($CDCl_3$, 150 Hz)

```
dg366-1_03Nov2005

 Archive directory: /export/home/odoherty/vnmrsys/data
 Sample directory: dg366-1_03Nov2005

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
User:  1-14-87
File: CARBON
INOVA-600  "inova600"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 37700.3 Hz
 256 repetitions
OBSERVE  C13, 150.7857285 MHz
DECOUPLE  H1, 599.6700024 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 131072
Total time 9 min, 51 sec
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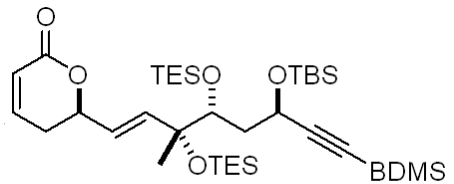
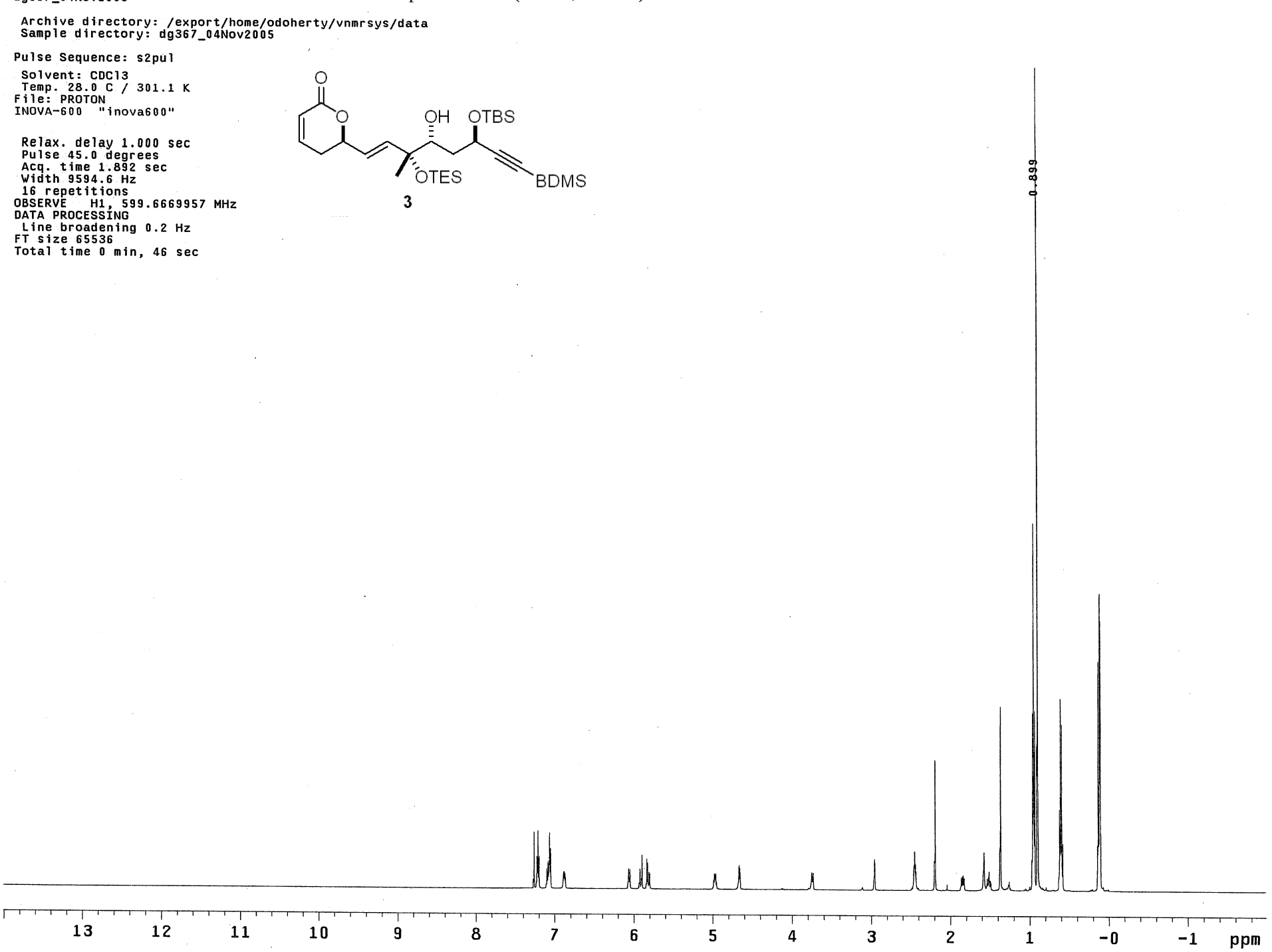
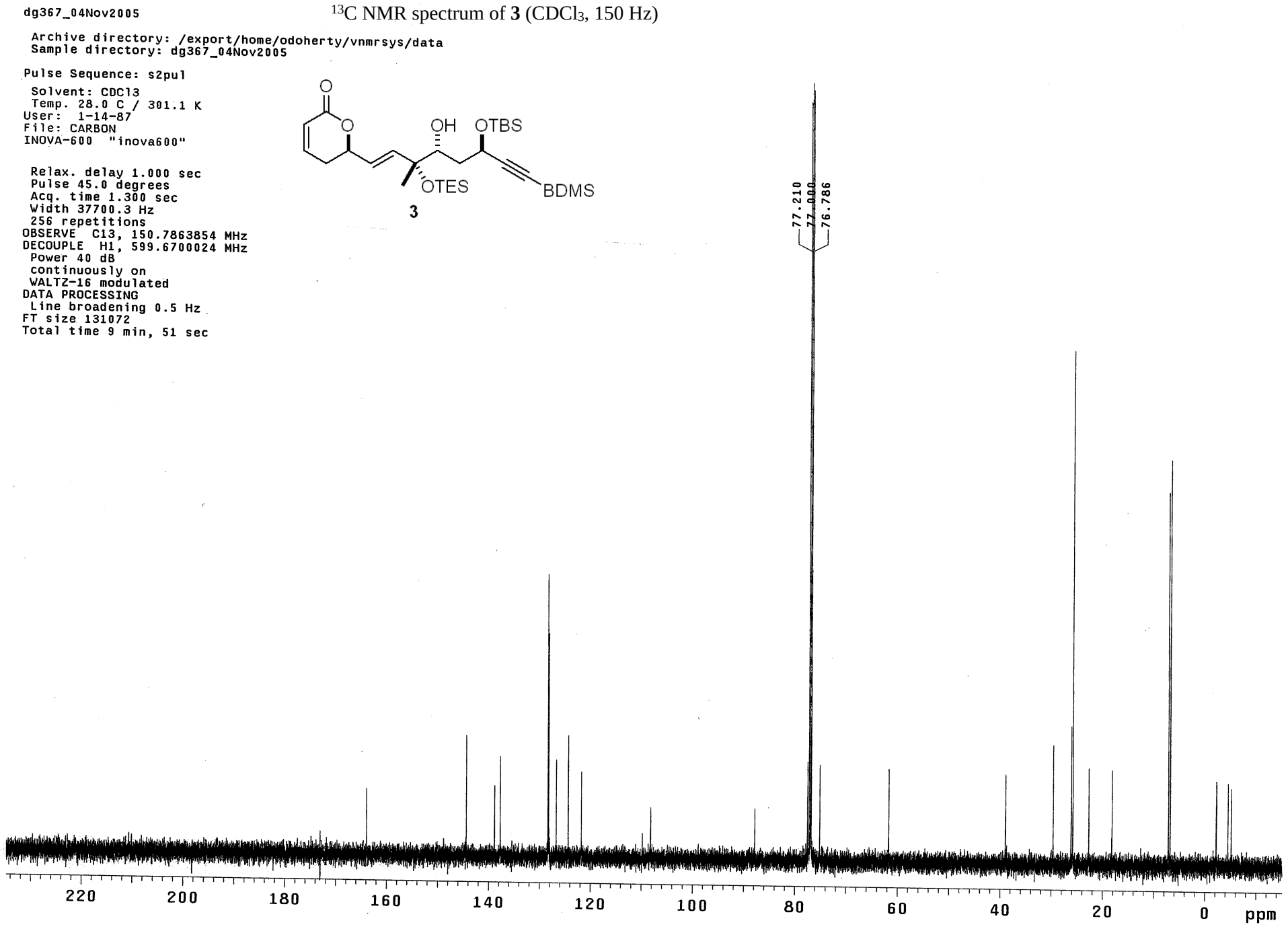


3a

^{1}H NMR spectrum of **3** ($CDCl_3$, 600 Hz)

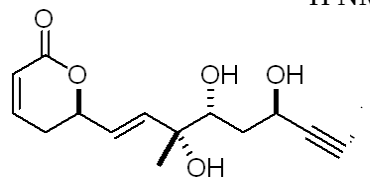


^{13}C NMR spectrum of **3** ($CDCl_3$, 150 Hz)



dg354.3

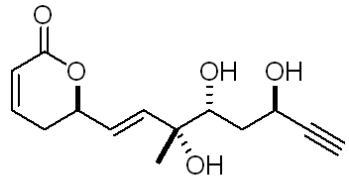
^{1}H NMR spectrum of **4** ($CDCl_3$, 600 Hz)



4

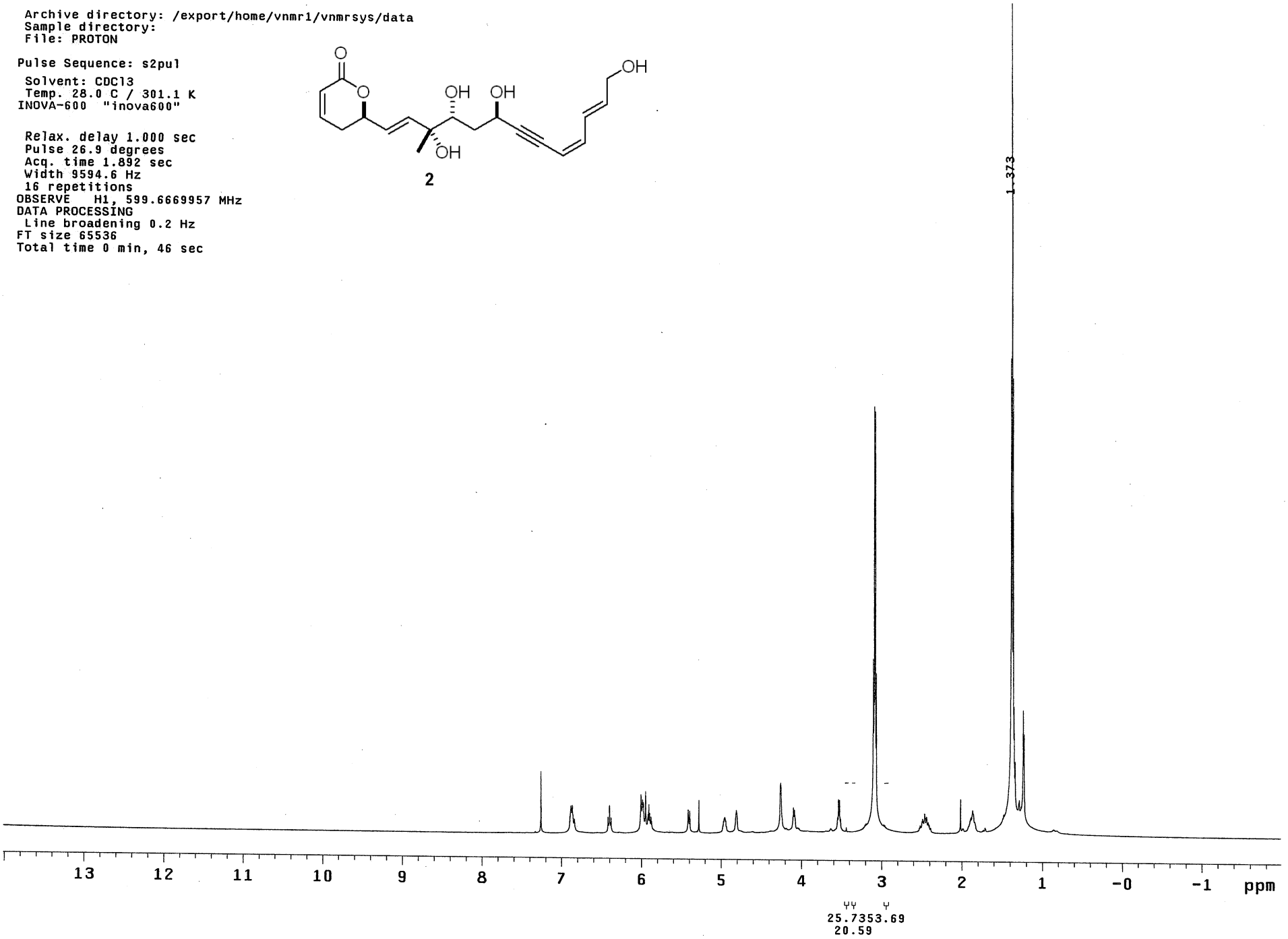
dg354c13.3

^{13}C NMR spectrum of **4** ($CDCl_3$, 150 Hz)

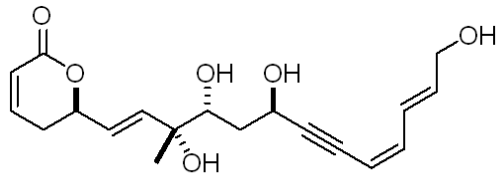


4

^{1}H NMR spectrum of **2** ($CDCl_3$, 600 Hz)



^{13}C NMR spectrum of **2** ($CDCl_3$, 150 Hz)



2

```
STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
User:  1-14-87
INOVA-600  "inova600"

 Relax. delay 1.000 sec
 Pulse 36.5 degrees
 Acq. time 1.300 sec
 Width 36003.6 Hz
 1000 repetitions
OBSERVE  C13, 150.7863852 MH
DECOUPLE  H1, 599.6700024 MH
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 131072
Total time 38 min, 29 sec
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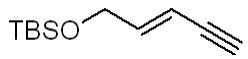
dg210.3

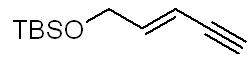
^{1}H NMR spectrum of **42** ($CDCl_3$, 270 Hz)



42

dg210c13.3

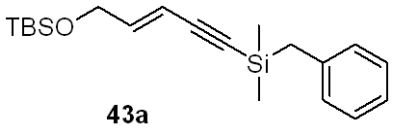
^{13}C NMR spectrum of **42** ($CDCl_3$, 270 Hz)



42

dg223.3

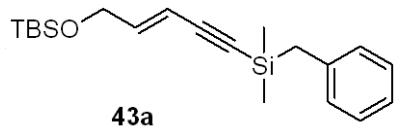
^{1}H NMR spectrum of **43a** ($CDCl_3$, 270 Hz)



43a

dg223c13.3

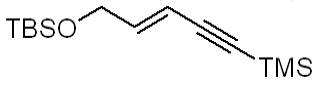
^{13}C NMR spectrum of **43a** ($CDCl_3$, 67.5 Hz)



43a

dg405.3

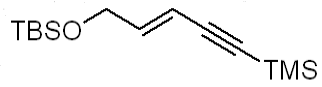
^{1}H NMR spectrum of **43b** ($CDCl_3$, 270 Hz)



43b

dg409c13.3

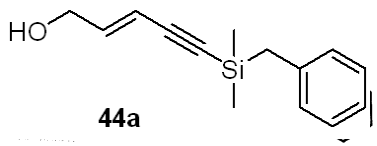
^{13}C NMR spectrum of **43b** ($CDCl_3$, 67.5 Hz)



43b

dg224.3

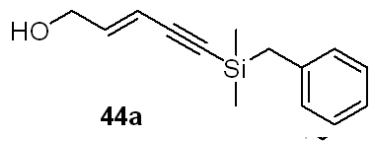
^{1}H NMR spectrum of **44a** ($CDCl_3$, 270 Hz)



44a

dg224c13.3

^{13}C NMR spectrum of **44a** ($CDCl_3$, 67.5 Hz)



44a

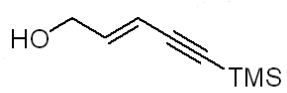
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0

176.7697
143.0265
138.8095
128.2671
128.0762
124.2794
110.0471
104.2259
93.5460
77.4651
76.9991
76.5254
62.4918
26.0977
20.7119
−2.2675

X : parts per Million : 13C

dg406.3

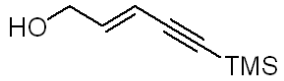
^{1}H NMR spectrum of **44b** ($CDCl_3$, 270 Hz)



44b

dg406.4

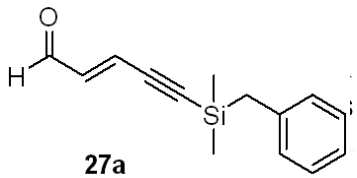
^{13}C NMR spectrum of **44b** ($CDCl_3$, 67.5 Hz)



44b

dg225.3

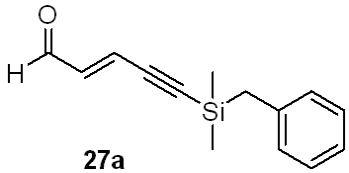
^{1}H NMR spectrum of **27a** ($CDCl_3$, 270 Hz)



27a

dg225c13.3

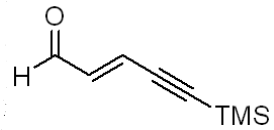
^{13}C NMR spectrum of **27a** ($CDCl_3$, 67.5 Hz)



27a

dg406.6

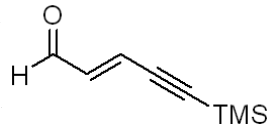
^{1}H NMR spectrum of **27b** ($CDCl_3$, 270 Hz)



27b

dg406.7

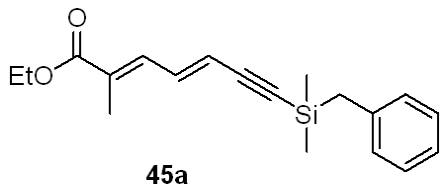
^{13}C NMR spectrum of **27b** ($CDCl_3$, 67.5 Hz)



27b

dg227.3

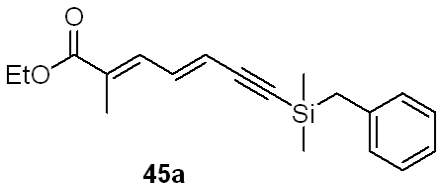
^{1}H NMR spectrum of **45a** ($CDCl_3$, 270 Hz)



45a

dg227C13.3

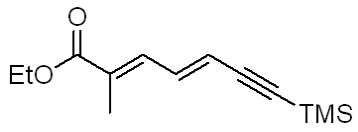
^{13}C NMR spectrum of **45a** ($CDCl_3$, 67.5 Hz)



45a

dg409.3

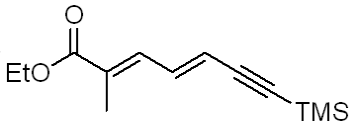
^{1}H NMR spectrum of **45b** ($CDCl_3$, 270 Hz)



45b

dg409.4

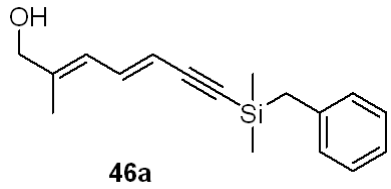
^{13}C NMR spectrum of **45b** ($CDCl_3$, 67.5 Hz)



45b

dg330.3

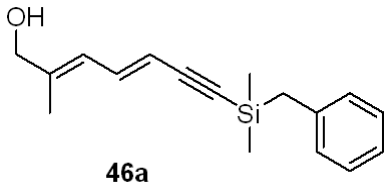
^{1}H NMR spectrum of **46a** ($CDCl_3$, 270 Hz)



46a

dg330c13.3

^{13}C NMR spectrum of **46a** ($CDCl_3$, 67.5 Hz)



46a

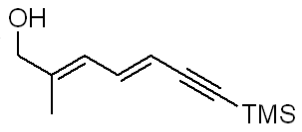
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0

141.2237
138.6798
128.3666
128.1298
124.3177
123.4697
110.3911
77.4729
76.9992
76.5332
67.8167
26.2735
14.3866
−2.1374

X : parts per Million : 13C

dg410.3

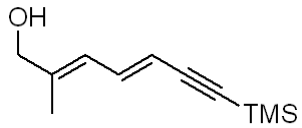
^{1}H NMR spectrum of **46b** ($CDCl_3$, 270 Hz)



46b

dg410C13.3

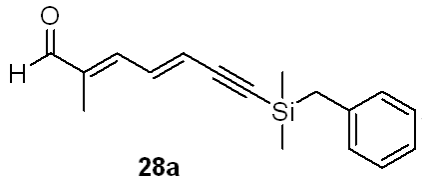
^{13}C NMR spectrum of **46b** ($CDCl_3$, 67.5 Hz)



46b

dg334.3

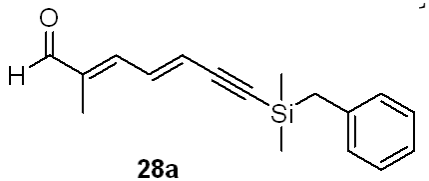
^{1}H NMR spectrum of **28a** ($CDCl_3$, 270 Hz)



28a

dg334c13.3

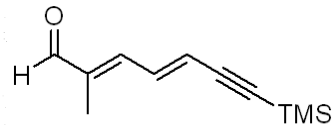
^{13}C NMR spectrum of **28a** ($CDCl_3$, 67.5 Hz)



28a

dg411crude.3

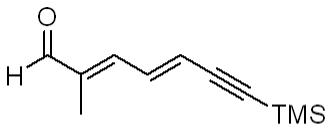
^{1}H NMR spectrum of **28b** ($CDCl_3$, 270 Hz)



28b

dg411.3

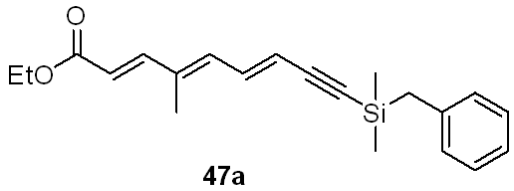
^{13}C NMR spectrum of **28b** ($CDCl_3$, 67.5 Hz)



28b

dg236.3

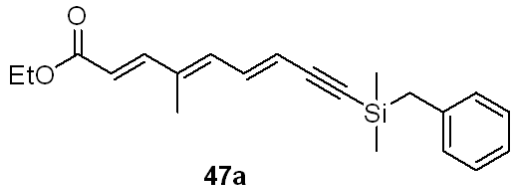
^{1}H NMR spectrum of **47a** ($CDCl_3$, 270 Hz)



47a

dg236c13.3

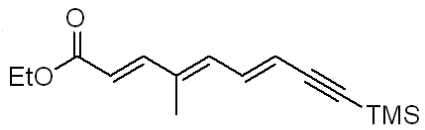
^{13}C NMR spectrum of **47a** ($CDCl_3$, 67.5 Hz)



47a

dg412.3

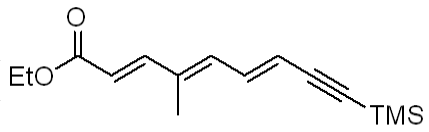
^{1}H NMR spectrum of **47b** ($CDCl_3$, 270 Hz)



47b

dg412c13.3

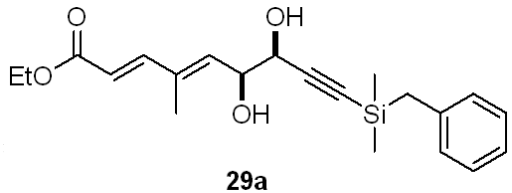
^{13}C NMR spectrum of **47b** ($CDCl_3$, 67.5 Hz)



47b

dg237–2.4

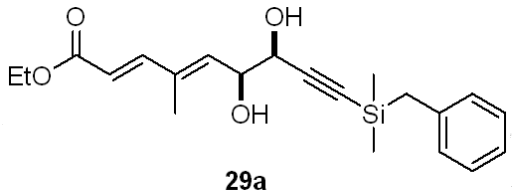
^{1}H NMR spectrum of **29a** ($CDCl_3$, 270 Hz)



29a

dg237–2c13.3

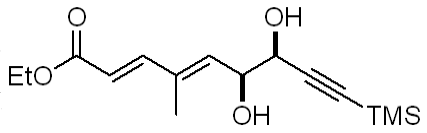
^{13}C NMR spectrum of **29a** ($CDCl_3$, 67.5 Hz)



29a

dg413.4

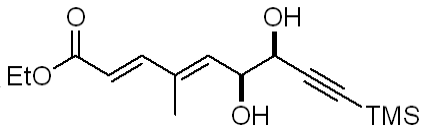
^{1}H NMR spectrum of **29b** ($CDCl_3$, 270 Hz)



29b

dg413c13.3

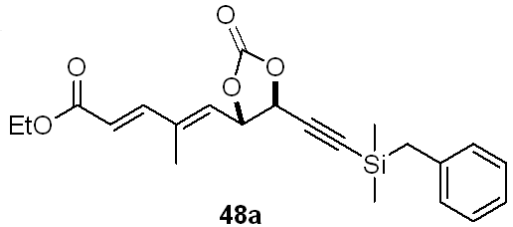
^{13}C NMR spectrum of **29b** ($CDCl_3$, 67.5 Hz)



29b

dg238.4

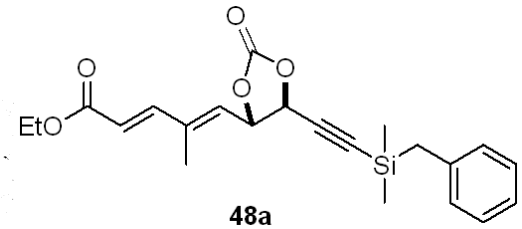
^{1}H NMR spectrum of **48a** ($CDCl_3$, 270 Hz)



48a

dg238c13.4

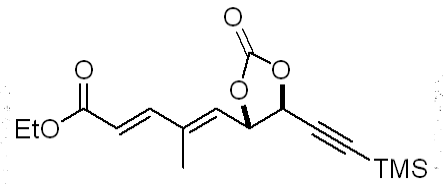
^{13}C NMR spectrum of **48a** ($CDCl_3$, 67.5 Hz)



48a

dg415.3

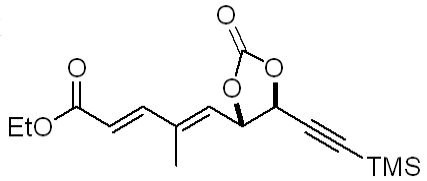
^{1}H NMR spectrum of **48b** ($CDCl_3$, 270 Hz)



48b

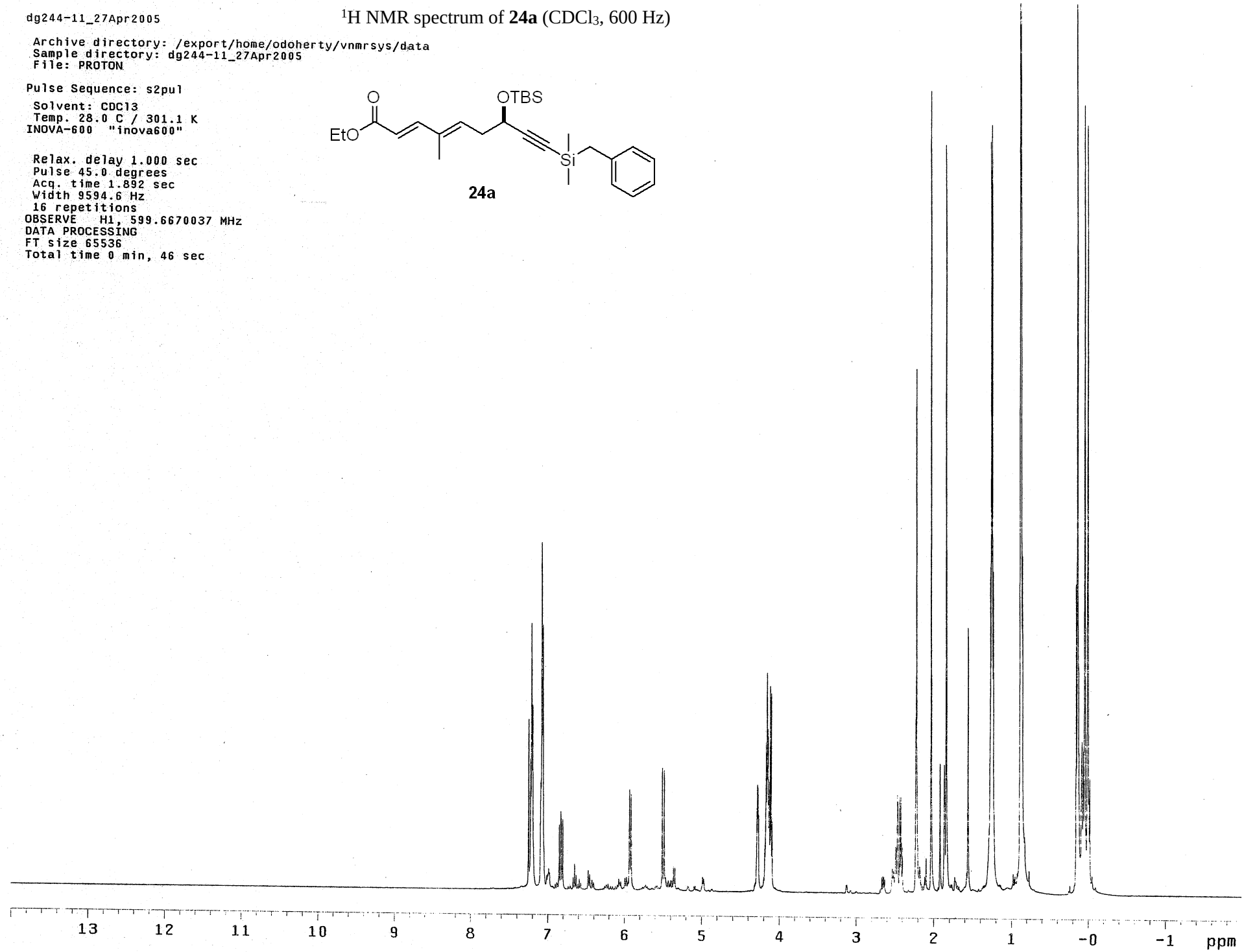
dg415c13.3

^{13}C NMR spectrum of **48b** ($CDCl_3$, 67.5 Hz)

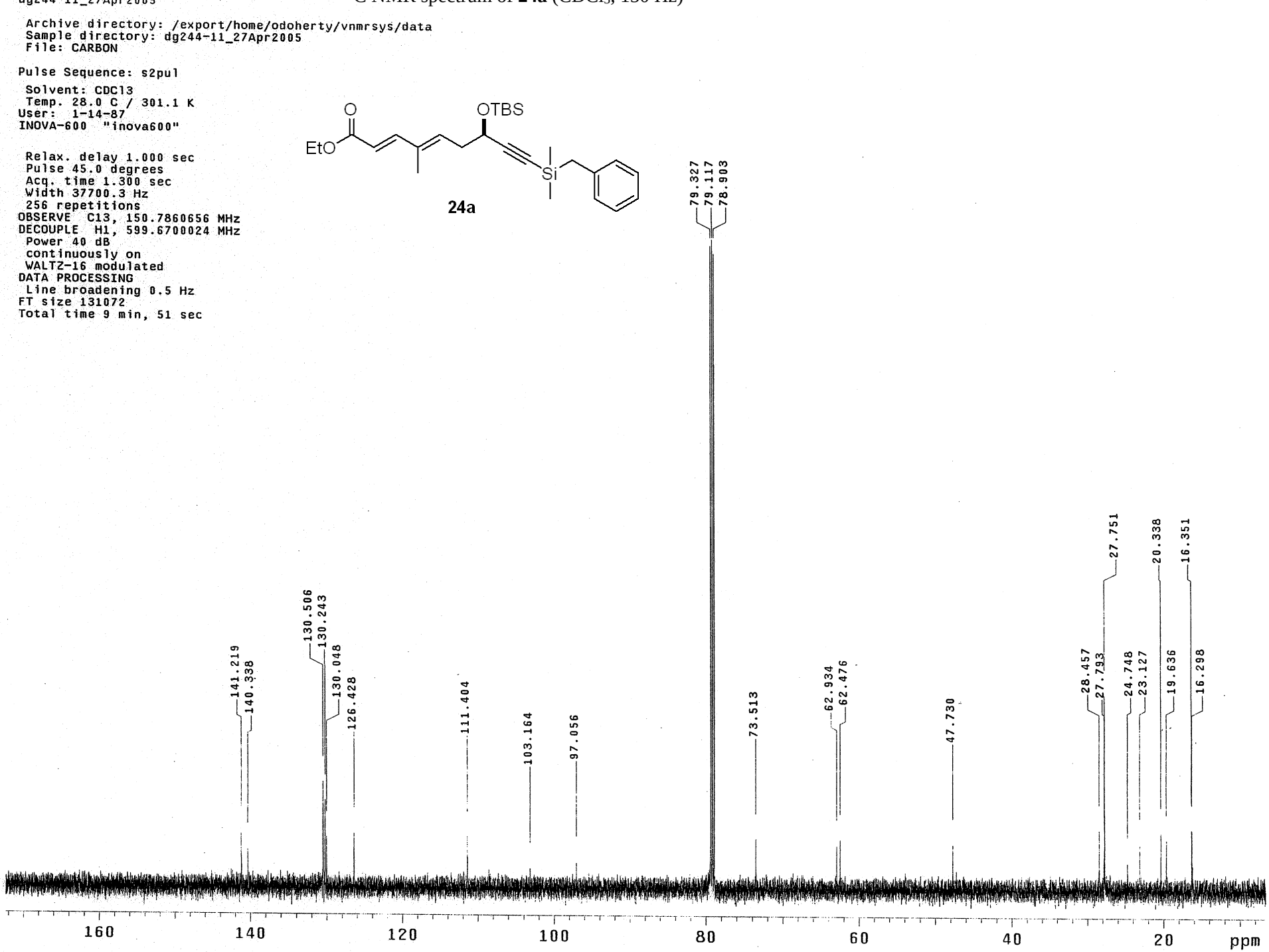


48b

^{1}H NMR spectrum of **24a** ($CDCl_3$, 600 Hz)

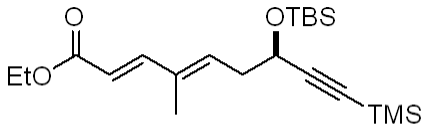


^{13}C NMR spectrum of **24a** ($CDCl_3$, 150 Hz)



dg417b.3

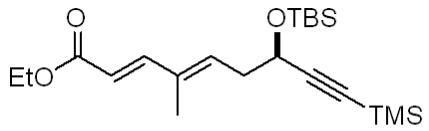
^{1}H NMR spectrum of **24b** ($CDCl_3$, 270 Hz)



24b

dg417b.4

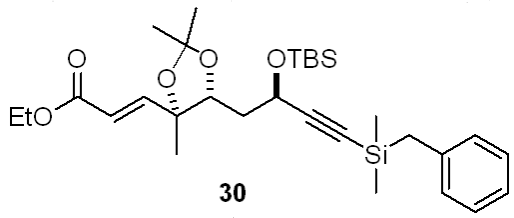
^{13}C NMR spectrum of **24b** ($CDCl_3$, 67.5 Hz)



24b

dg291.3

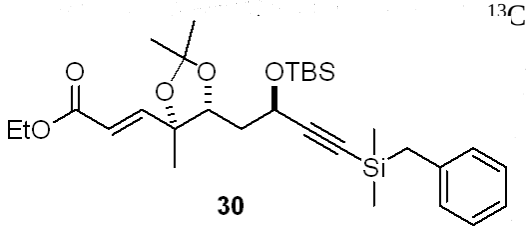
^{1}H NMR spectrum of **30** ($CDCl_3$, 270 Hz)



30

dg291c13.3

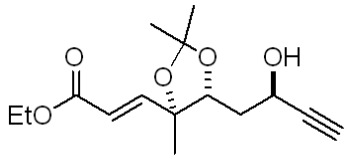
^{13}C NMR spectrum of **30** ($CDCl_3$, 67.5 Hz)



30

dg398.4

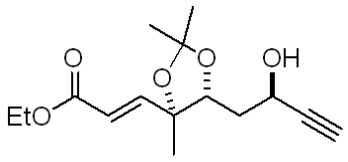
^{1}H NMR spectrum of **31** ($CDCl_3$, 270 Hz)



31

dg398C13.3

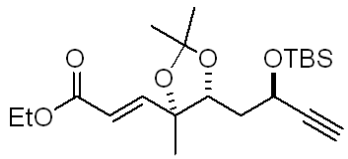
^{13}C NMR spectrum of **31** ($CDCl_3$, 67.5 Hz)



31

dg399.3

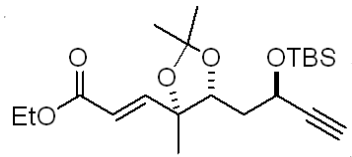
^{1}H NMR spectrum of **32** ($CDCl_3$, 270 Hz)



32

dg399c13.3

^{13}C NMR spectrum of **32** ($CDCl_3$, 67.5 Hz)



32

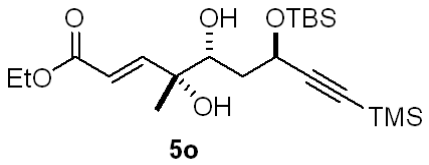
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0

166.2506
149.0085
120.3225
108.1376
85.1659
81.2240
77.4731
77.0758
76.9994
76.5334
72.2248
60.4143
59.4441
38.3058
28.2829
26.3425
25.6473
21.0178
18.0767
14.1653
1.0790
−3.0081
−3.1151
−4.6811
−5.2770

X : parts per Million : 13C

dgTBSDIOL.3

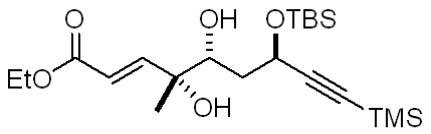
^{1}H NMR spectrum of **5o** ($CDCl_3$, 270 Hz)



5o

dgtbsdiolc13.3

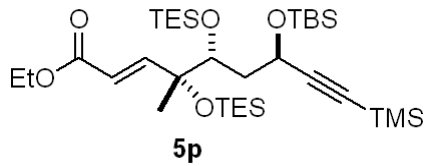
^{13}C NMR spectrum of **5o** ($CDCl_3$, 67.5 Hz)



5o

dg457.3

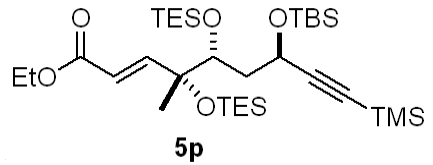
^{1}H NMR spectrum of **5p** ($CDCl_3$, 270 Hz)



5p

dg458c13.3

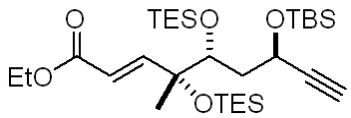
^{13}C NMR spectrum of **5p** ($CDCl_3$, 67.5 Hz)



5p

dg460.3

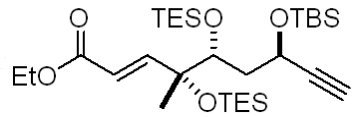
^{1}H NMR spectrum of **23** ($CDCl_3$, 270 Hz)



23

dg460C13.4

^{13}C NMR spectrum of **23** ($CDCl_3$, 67.5 Hz)



23

^{1}H NMR spectrum of **33** ($CDCl_3$, 600 Hz)

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dg376_21Nov2005

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 Sample directory: dg376_21Nov2005
 File: PROTON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
INOVA-600  "inova600"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.892 sec
 Width 9594.6 Hz
 16 repetitions
OBSERVE   H1, 599.6670039 MHz
DATA PROCESSING
 Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 46 sec
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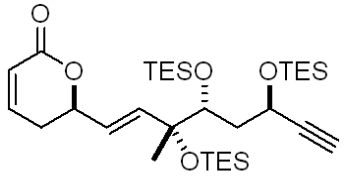
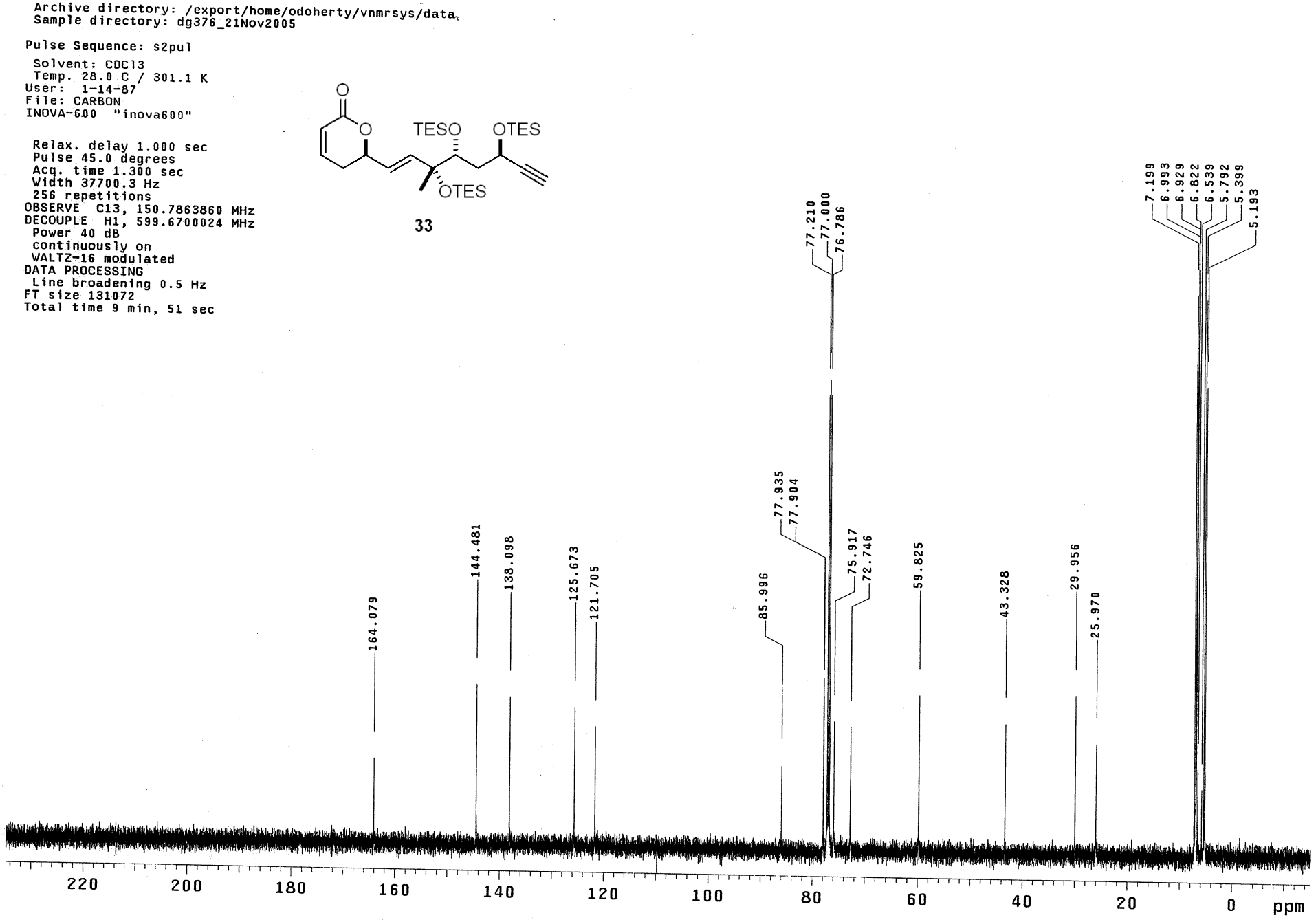


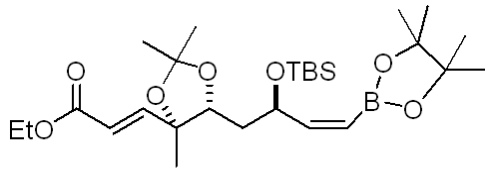
33

^{13}C NMR spectrum of **33** ($CDCl_3$, 150 Hz)



dg401.5

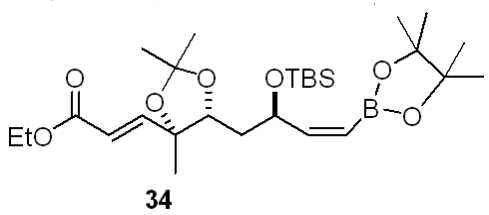
^{1}H NMR spectrum of **34** ($CDCl_3$, 270 Hz)



34

dg401c13.4

^{13}C NMR spectrum of **34** ($CDCl_3$, 67.5 Hz)



34

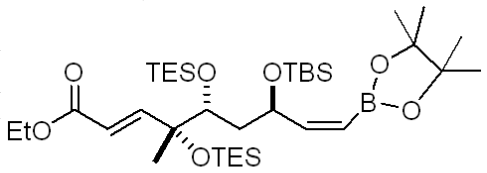
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0

166.4338
157.1595
149.6806
119.9785
107.7631
83.1031
81.3995
77.6715
77.4729
76.9992
76.5332
69.3140
60.3759
37.7097
28.3820
26.3958
25.8304
24.8297
24.7151
21.1093
20.0245
18.0994
14.1880
−4.3987
−4.9487

X : parts per Million : 13C

dg461.4

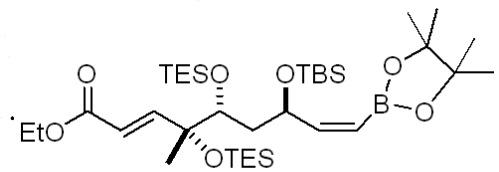
^{1}H NMR spectrum of **35** ($CDCl_3$, 270 Hz)



35

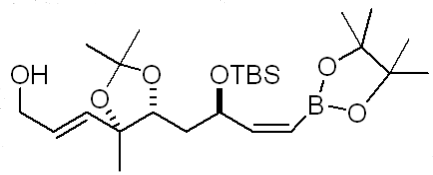
dg461c13.4

^{13}C NMR spectrum of **35** ($CDCl_3$, 67.5 Hz)



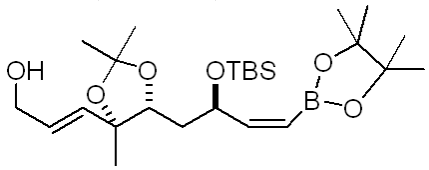
35

^{1}H NMR spectrum of **49** ($CDCl_3$, 600 Hz)



49

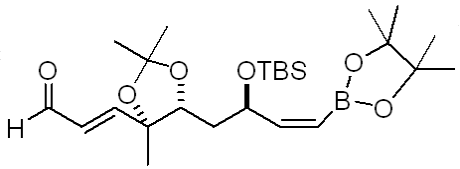
^{13}C NMR spectrum of **49** ($CDCl_3$, 150 Hz)



49

dg420.4

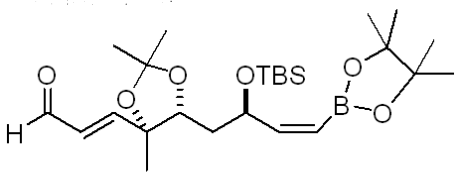
^{1}H NMR spectrum of **36** ($CDCl_3$, 270 Hz)



36

dg420c13.4

^{13}C NMR spectrum of **36** ($CDCl_3$, 67.5 Hz)



36

^{1}H NMR spectrum of **50** ($CDCl_3$, 600 Hz)

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STANDARD PROTON PARAMETERS

 Archive directory: /export/home/vnmr1/vnmrsys/data
 Sample directory:
 File: PROTON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
INOVA-600  "inova600"

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 4.000 sec
 Width 9594.6 Hz
 16 repetitions
OBSERVE   H1, 599.6669958 MHz
DATA PROCESSING
 Line broadening 0.2 Hz
FT size 131072
Total time 1 min, 20 sec
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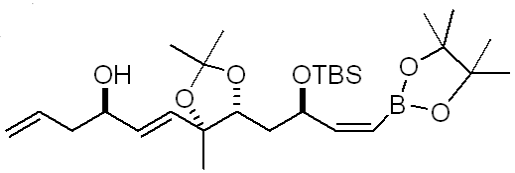
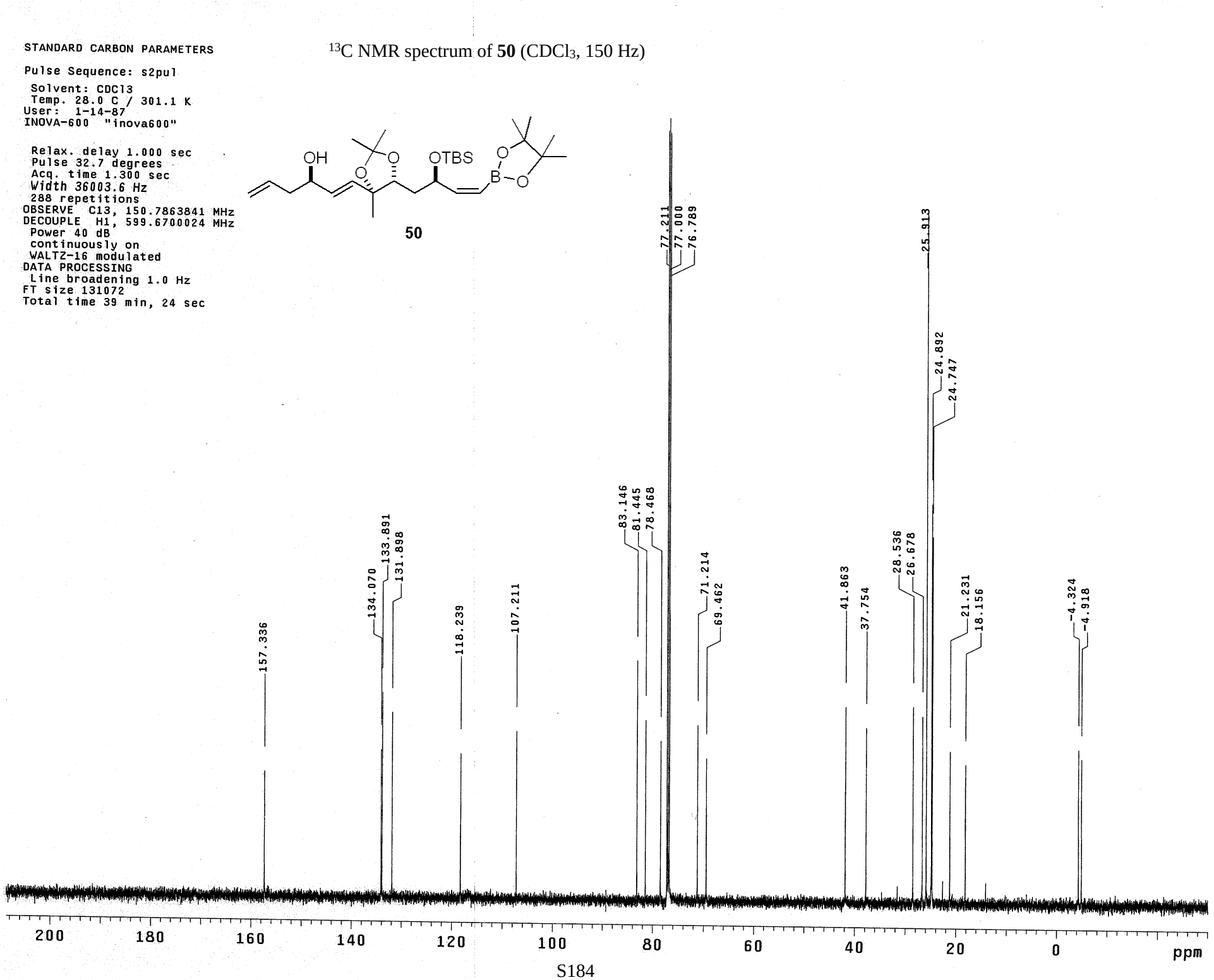
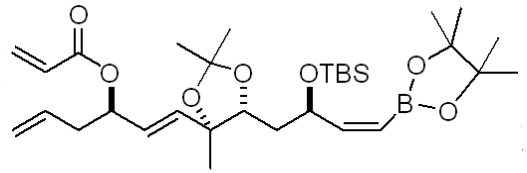


50

^{13}C NMR spectrum of **50** ($CDCl_3$, 150 Hz)

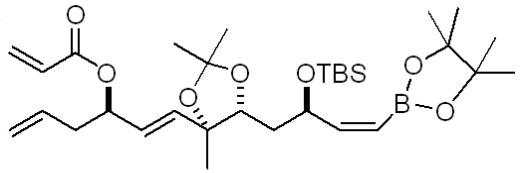


^{1}H NMR spectrum of **51** ($CDCl_3$, 600 Hz)



51

^{13}C NMR spectrum of **51** ($CDCl_3$, 150 Hz)



51

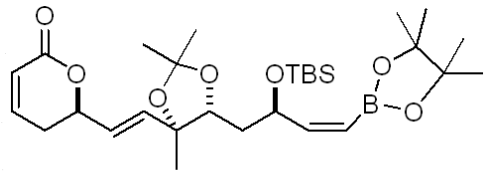
^{1}H NMR spectrum of **36** ($CDCl_3$, 600 Hz)

STANDARD PROTON PARAMETERS

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

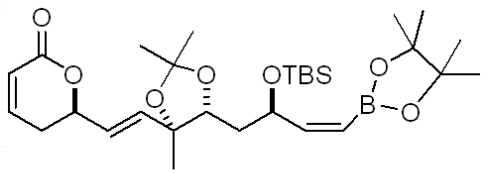
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 28.0 C / 301.1 K
INOVA-600 "inova600"

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 4.000 sec
Width 9594.6 Hz
4 repetitions
OBSERVE H1, 599.6669945 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 131072
Total time 0 min, 20 sec



37

^{13}C NMR spectrum of **37** ($CDCl_3$, 150 Hz)



37

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STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul
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User:  1-14-87
INOVA-600  "inova600"

 Relax. delay 1.000 sec
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 Acq. time 1.300 sec
 Width 36003.6 Hz
 1688 repetitions
OBSERVE  C13, 150.7863835 MHz
DECOUPLE  H1, 599.6700024 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 641495 hr, 49 min, 7 sec
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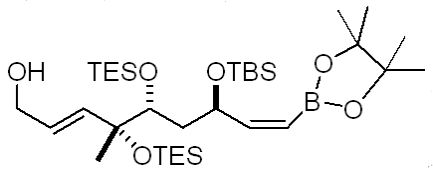
dg462.3

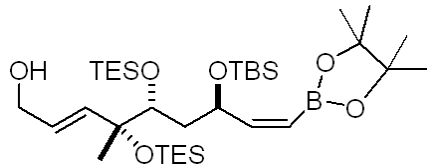
^{1}H NMR spectrum of **7f** ($CDCl_3$, 270 Hz)



7f

dg462–c13.3

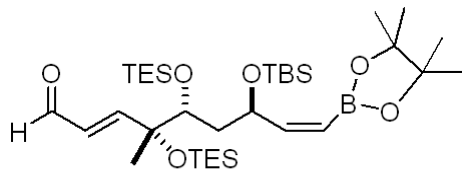
^{13}C NMR spectrum of **7f** ($CDCl_3$, 67.5 Hz)



7f

dg463.3

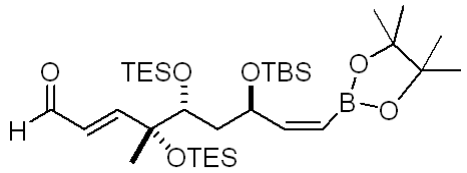
^{1}H NMR spectrum of **38** ($CDCl_3$, 270 Hz)



38

dg463C13.3

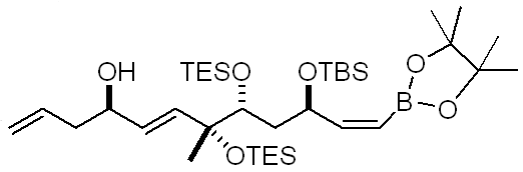
^{13}C NMR spectrum of **38** ($CDCl_3$, 67.5 Hz)



38

dg464.3

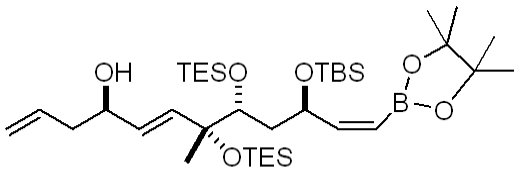
^{1}H NMR spectrum of **7h** ($CDCl_3$, 270 Hz)



7h

dg464c13.3

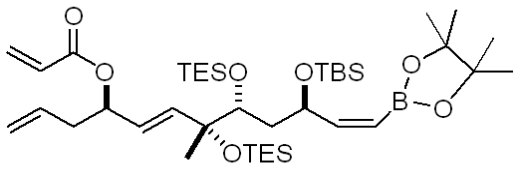
^{13}C NMR spectrum of **7h** ($CDCl_3$, 67.5 Hz)



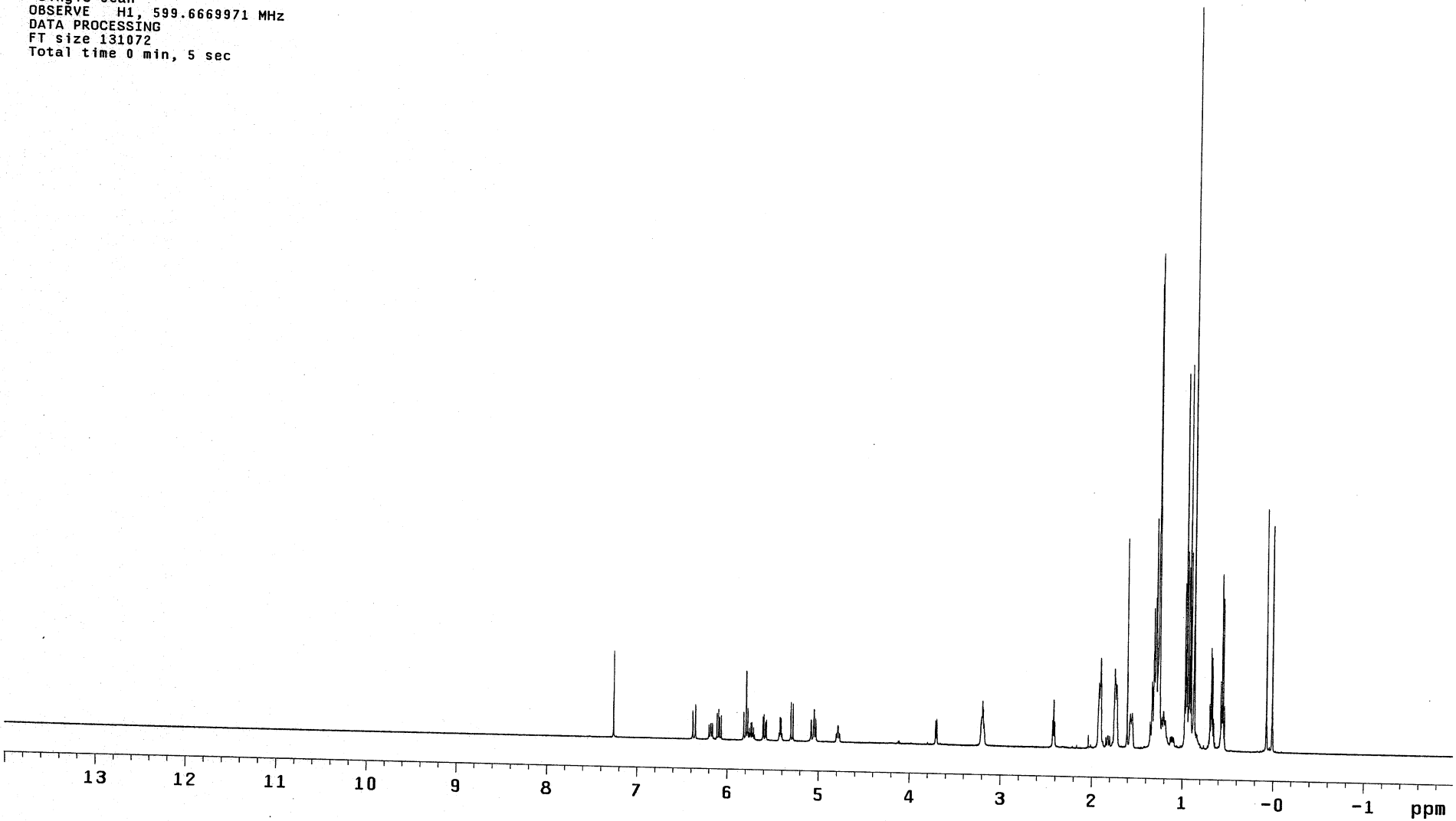
7h

^{1}H NMR spectrum of **7i** ($CDCl_3$, 600 Hz)

```
STANDARD PROTON PARAMETERS

 Archive directory: /export/home/vnmr1/vnmrsys/data
 Sample directory:
 File: PROTON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
INOVA-600  "inova600"

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 4.000 sec
 Width 9594.6 Hz
 Single scan
OBSERVE   H1, 599.6669971 MHz
DATA PROCESSING
FT size 131072
Total time 0 min, 5 sec
```

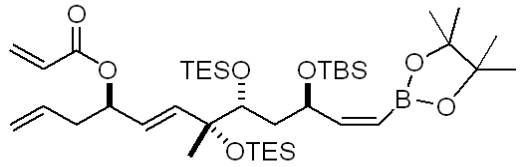


7i

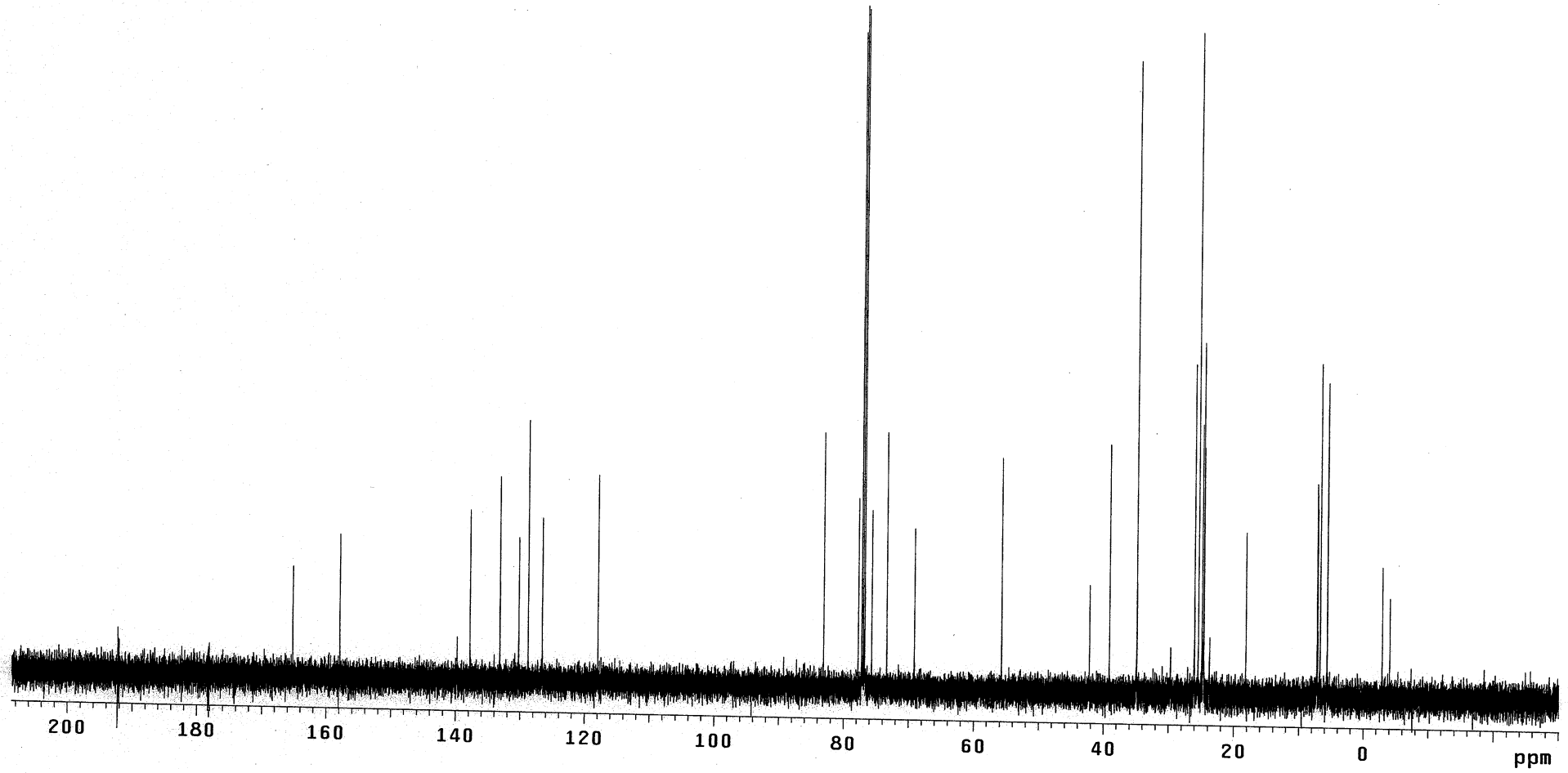


^{13}C NMR spectrum of **7i** ($CDCl_3$, 150 Hz)

```
STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
User:  1-14-87
INOVA-600  "inova600"

 Relax. delay 0.500 sec
 Pulse 29.9 degrees
 Acq. time 1.400 sec
 Width 36003.6 Hz
 416 repetitions
OBSERVE  C13, 150.7863846 MHz
DECOUPLE  H1, 599.6700024 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
FT size 131072
Total time 32 min, 34 sec
```

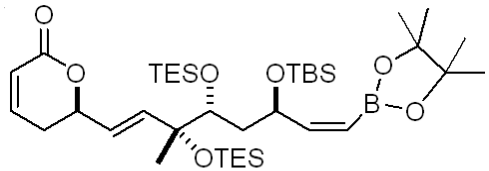


7i



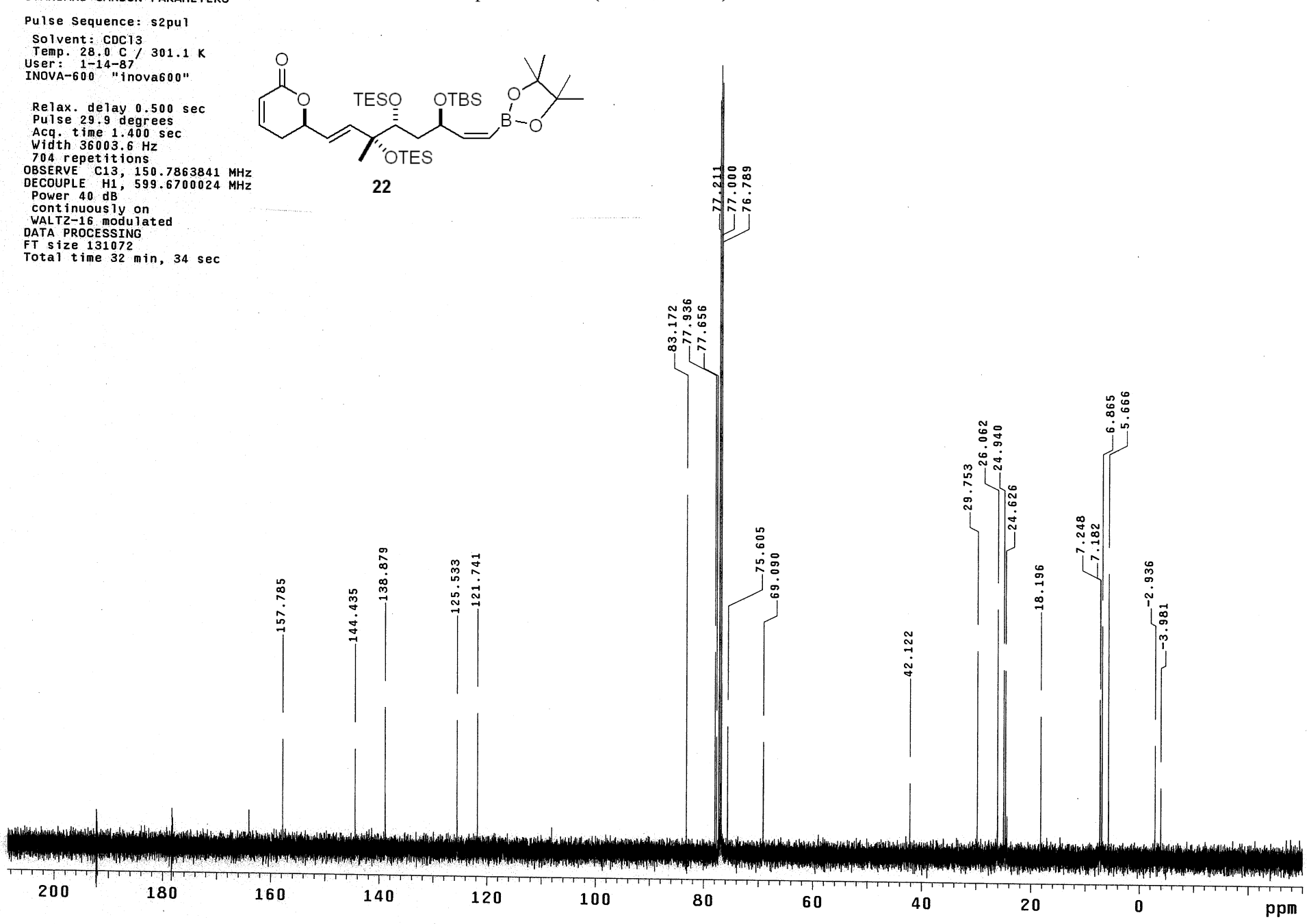
^{1}H NMR spectrum of **22** ($CDCl_3$, 600 Hz)

```
STANDARD PROTON PARAMETERS

 Archive directory: /export/home/vnmr1/vnmrsys/data
 Sample directory:
 File: PROTON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
INOVA-600  "inova600"

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 4.000 sec
 Width 9594.6 Hz
 16 repetitions
OBSERVE   H1, 599.6669967 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 20 sec
```



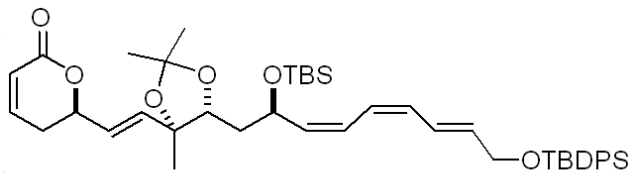
22

^{13}C NMR spectrum of **22** ($CDCl_3$, 150 Hz)



^{1}H NMR spectrum of **39** ($CDCl_3$, 600 Hz)

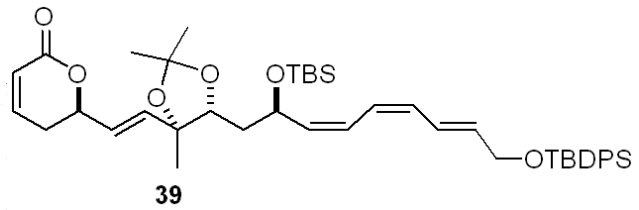
```
STANDARD PROTON PARAMETERS

 Archive directory: /export/home/vnmr1/vnmrsys/data
 Sample directory:
 File: PROTON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
INOVA-600  "inova600"

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 4.000 sec
 Width 9594.6 Hz
 Single scan
OBSERVE   H1, 599.6669951 MHz
DATA PROCESSING
 Line broadening 0.2 Hz
FT size 131072
Total time 0 min, 5 sec
```



39

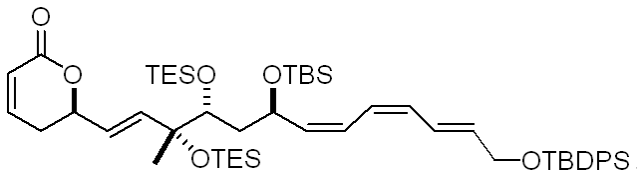
^{13}C NMR spectrum of **39** ($CDCl_3$, 150 Hz)

```
STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
User:  1-14-87
INOVA-600  "inova600"

 Relax. delay 1.000 sec
 Pulse 29.9 degrees
 Acq. time 1.300 sec
 Width 36003.6 Hz
 288 repetitions
OBSERVE  C13, 150.7969390 M
DECOUPLE  H1, 599.6700024 M
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 39 min, 24 sec
```



39

^{1}H NMR spectrum of **40** ($CDCl_3$, 600 Hz)

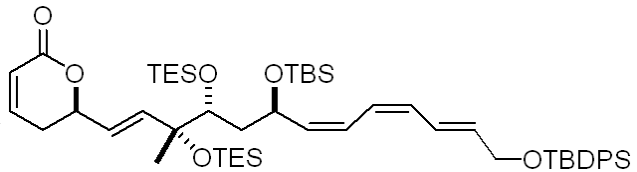


40

```
STANDARD PROTON PARAMETERS

 Archive directory: /export/home/vnmr1/v
 Sample directory:
 File: PROTON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
INOVA-600  "inova600"

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 4.000 sec
 Width 9594.6 Hz
 20 repetitions
OBSERVE   H1, 599.6669957 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 40 sec
```

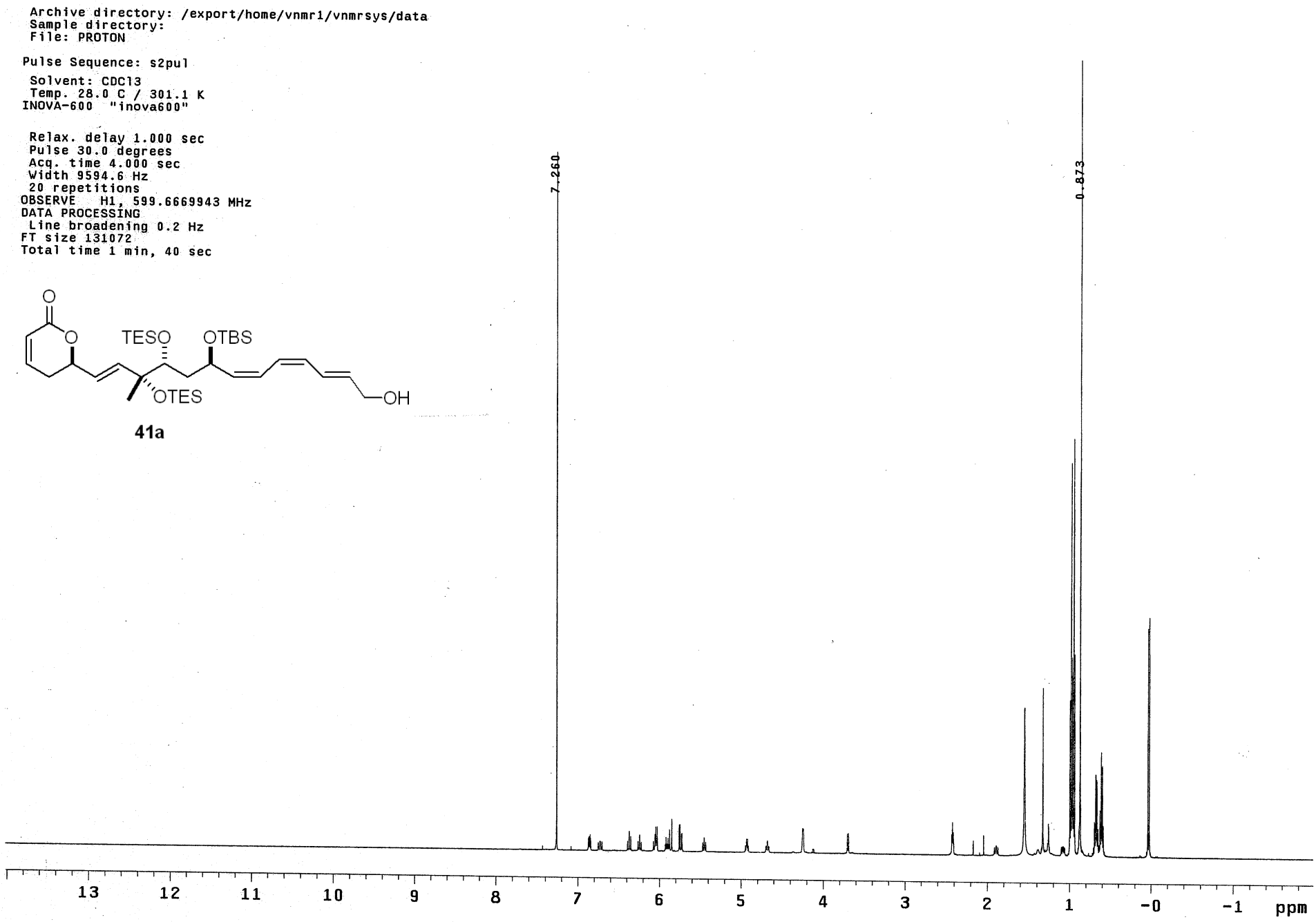
^{13}C NMR spectrum of **40** ($CDCl_3$, 150 Hz)

```
STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
User:  1-14-87
INOVA-600  "inova600"

 Relax. delay 0.500 sec
 Pulse 29.9 degrees
 Acq. time 1.400 sec
 Width 36003.6 Hz
 2896 repetitions
OBSERVE  C13, 150.7863841 MH
DECOUPLE  H1, 599.6700024 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
FT size 131072
Total time 5 hr, 18 min, 9 sec
```

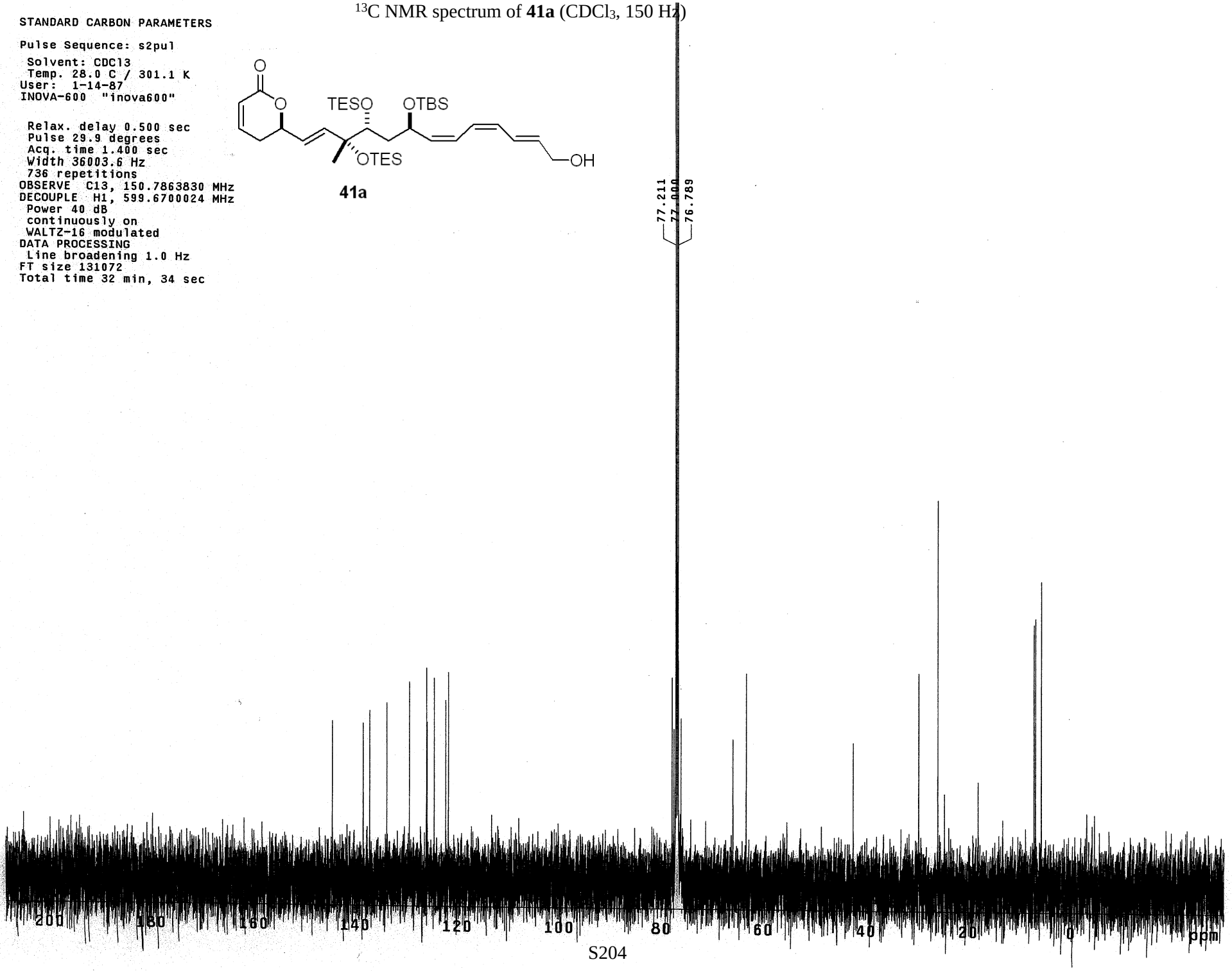


40

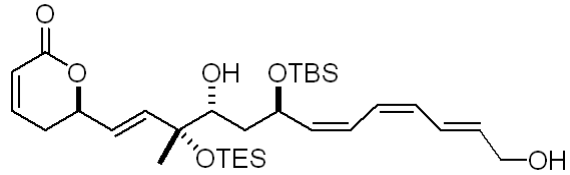
^{1}H NMR spectrum of **41a** ($CDCl_3$, 600 Hz)



^{13}C NMR spectrum of **41a** ($CDCl_3$, 150 Hz)



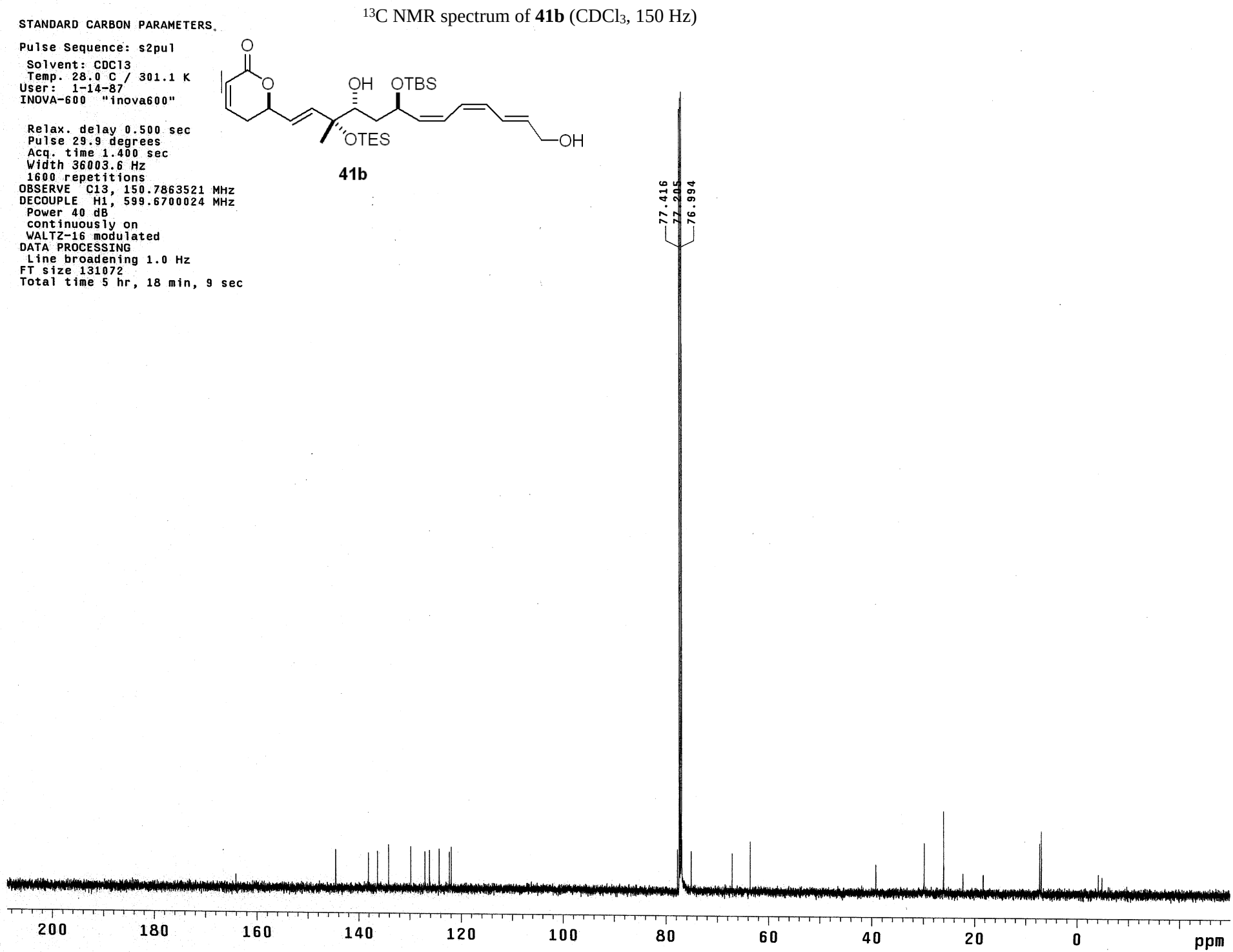
^{1}H NMR spectrum of **41b** ($CDCl_3$, 600 Hz)



41b

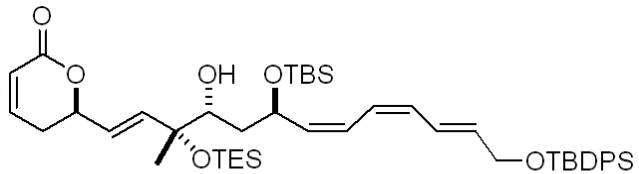
```
STANDARD PROTON PARAMETERS

 Archive directory: /export/home/vnmr1/vnmrsys/data
 Sample directory:
 File: PROTON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
INOVA-600  "inova600"

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 4.000 sec
 Width 9594.6 Hz
 16 repetitions
OBSERVE   H1, 599.6669942 MHz
DATA PROCESSING
 Line broadening 0.2 Hz
FT size 131072
Total time 1 min, 20 sec
```

^{13}C NMR spectrum of **41b** ($CDCl_3$, 150 Hz)



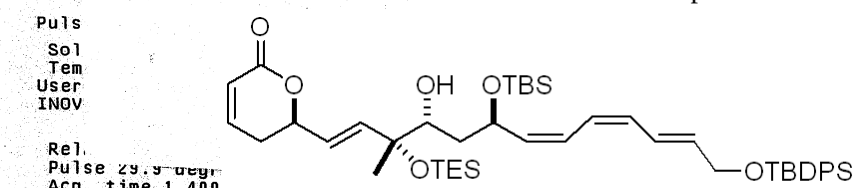
^{1}H NMR spectrum of **21** ($CDCl_3$, 600 Hz)

```
STANDARD PROTON PARAMETERS

 Archive directory: /export/home/vnmr1/vnmrsys/data
 Sample directory:
 File: PROTON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 28.0 C / 301.1 K
INOVA-600  "inova600"

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 4.000 sec
 Width 9594.6 Hz
 20 repetitions
OBSERVE   H1, 599.6669945 MHz
DATA PROCESSING
 Line broadening 0.2 Hz
FT size 131072
Total time 1 min, 40 sec
```



21

^{13}C NMR spectrum of **21** ($CDCl_3$, 150 Hz)



21

STANDARD CARBON PARAMETERS
Puls
Sol
Tem
User
INOV
Rel.
Pulse 29.9 degr
Acq. time 1.400
Width 36003.6 H
4256 repetition
OBSERVE C13, 150.7863830 MHz
DECOUPLE H1, 599.6700024 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 10 hr, 36 min, 18 sec

^{1}H NMR spectrum of Fostriecin **1** ($CDCl_3$, 600 Hz)