SUPPORTING INFORMATION

Total Synthesis of (+)-Sorangicin A

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Experimental procedures and high field ^{1}H NMR and ^{13}C NMR spectra for all compounds.

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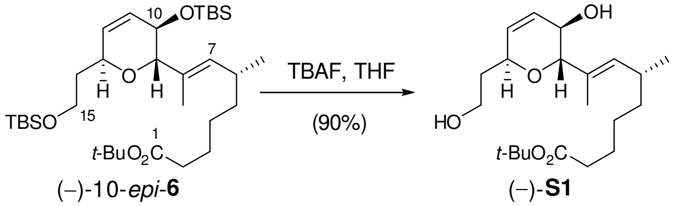
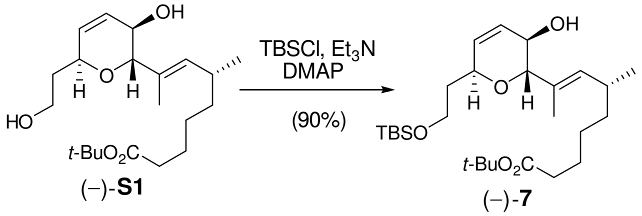
Experimental Section

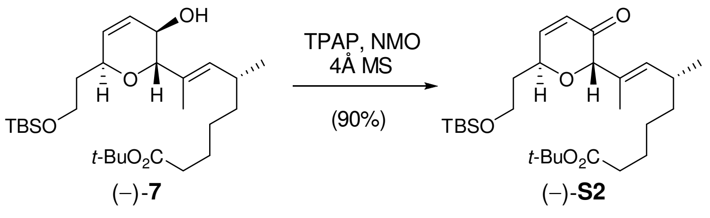
Materials and Methods: All solvents were reagent grade. Anhydrous dichloromethane (CH_2Cl_2), diethyl ether (Et_2O) and tetrahydrofuran (THF) were obtained from the Pure Solve^{TM} PS-400 under an argon atmosphere. All reagents were purchased from Aldrich or Acros and used as received. Reactions were magnetically stirred under an argon atmosphere and monitored by thin layer chromatography (TLC) with 0.25 mm E. Merck pre-coated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040 – 0.062 mm) supplied by Silicycle and Sorbent Technologies. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. Infrared spectra were recorded on a Jasco Model FT/IR-480 Plus spectrometer. Proton and carbon-13 NMR spectra were recorded on a Bruker AMX-500 spectrometer or a Bruker Avance III 500 spectrometer equipped with a 5 mm DCH CryoProbe at University of Pennsylvania. Chemical shifts are reported relative to either chloroform (δ 7.26) or benzene (δ 7.16) for ^{1}H NMR and either chloroform (δ 77.2) or benzene (δ 128.4) for ^{13}C NMR. Optical rotations were measured on a Perkin-Elmer model 241 polarimeter. High resolution mass spectra were measured at the University of Pennsylvania Mass Spectrometry Service Center on either a VG Micromass 70/70H or VG ZAB-E spectrometer.



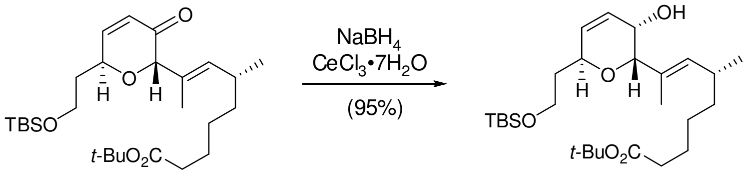
Diol (–)-**S1.** To a solution of (–)-10-*epi*-**6** (72 mg, 0.12 mmol) in THF (3.4 mL) was added tetrabutylammonium fluoride (TBAF, 1 M in THF, 0.36 mL, 0.36 mmol). After being stirred overnight, the reaction mixture was diluted with water (5 mL) and EtOAc (5 mL). The aqueous phase was then washed with EtOAc (3x5 mL), and the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (20% to 70%, EtOAc/hexanes) afforded diol (–)-**S1** (40 mg, 90%) as a pale yellow oil: $[\alpha]_D^{29}$ –39.4 (*c* 1.06, $CHCl_3$); IR (neat, cm^{-1}) 3426 (br), 1728, 1454, 1391, 1367, 1156, 1061; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 (ddd, *J* = 10.3, 2.3, 2.3 Hz, 1H), 5.72, (ddd, *J* = 10.3, 2.3, 2.3 Hz, 1H), 5.23 (d, *J* = 9.6 Hz, 1H), 4.34-4.31 (m, 1H), 4.12-4.11 (m, 1H), 3.84-3.76 (m, 3H), 2.56 (br s, 1H), 2.45-2.39 (m, 1H), 2.21-2.13 (m, 3H), 1.98 (dddd, *J* = 14.6, 10.2, 7.9, 4.3 Hz, 1H), 1.67 (s, 3H), 1.56-1.48 (m, 2H), 1.43 (s, 9H), 1.36-1.16 (m, 4H), 0.94 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 137.6, 130.8, 130.2, 128.5, 80.3, 79.9, 72.6, 63.6, 61.8, 37.1, 35.6, 34.9, 32.2, 28.3 (3C), 27.2, 25.0, 21.0, 12.4; HRMS (ES) m/z $(M+Na)^+$ calcd for $C_{21}H_{36}O_5Na^+$ 391.2460, obsd 391.2460.



Allylic alcohol (–)-**7.** To a solution of diol (–)-**S1** (40 mg, 0.109 mmol) in CH_2Cl_2 (1.2 mL) was added DMAP (1.8 mg, 0.015 mmol) and Et_3N (25 μL, 0.18 mmol) followed by the addition of TBSCl (26.5 mg, 0.18 mmol) in CH_2Cl_2 (1.2 mL). After 22 h the reaction mixture was quenched with saturated NH_4Cl solution (6 mL), and extracted with Et_2O (3×10 mL). The combined organic layers were dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash chromatography (2% to 30% EtOAc/hexanes) to afford allylic alcohol (–)-**7** (47 mg, 90%) as a pale yellow oil, along with (–)-10-*epi*-**6** (4 mg, 6%). $[\alpha]^{23}_{D}$ –38.8 (c 0.74, $CHCl_3$); IR (neat, cm^{-1}) 3440 (br), 1730, 1461, 1367, 1253, 1099, 837; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (ddd, J = 10.3, 2.1, 2.1 Hz, 1H), 5.77 (ddd, J = 10.3, 2.1, 2.1 Hz, 1H), 5.19 (d, J = 9.5 Hz, 1H), 4.30-4.27 (m, 1H), 4.09 (br s, 1H), 3.78-3.70 (m, 2H), 3.69 (d, J = 7.1 Hz, 1H), 2.46-2.40 (m, 1H), 2.18 (dt, J = 7.4, 2.5 Hz, 2H), 2.01 (br d, J = 4.3 Hz, 1H), 1.89-1.82 (m, 1H), 1.75-1.68 (m, 1H), 1.67 (d, J = 1.0 Hz, 3H), 1.57-1.50 (m, 2H), 1.43 (s, 9H), 1.36-1.18 (m, 4H), 0.95 (d, J = 6.7 Hz, 3H), 0.88 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5, 136.5, 131.6, 131.0, 128.0, 80.2, 79.6, 69.4, 64.0, 60.2, 37.2, 36.3, 35.6, 32.1, 28.3 (3C), 27.2, 26.1 (3C), 25.1, 21.0, 18.5, 12.3, -5.2 (2C); HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{27}H_{50}O_5SiNa^+$ 505.3325, obsd 505.3307.



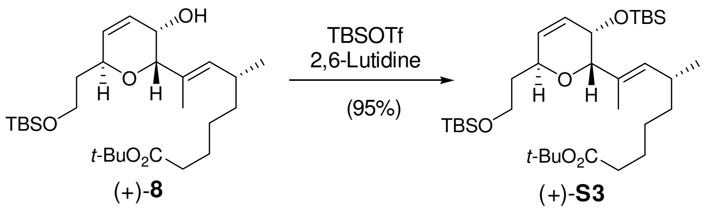
Enone (–)-S2. A stirred solution of allylic alcohol (–)-**7** (52 mg, 0.108 mmol) and *N*-methylmorpholine *N*-oxide monohydrate (19 mg, 0.16 mmol) in CH_2Cl_2 (2 mL) was treated with 4 Å molecular sieves (54 mg). After 5 min, TPAP (3.8 mg, 0.011 mmol) was added, and the reaction mixture was stirred for a further 1 h before being passed through a pad of silica gel which was rinsed with ethyl acetate (20 mL). The solvent was evaporated under reduced pressure to yield enone (–)-**S2** (47 mg, 90%) as a yellow oil. $[\alpha]^{29}_{D}$ –43.9 (*c* 0.54, C_6H_6); IR (neat, cm^{-1}) 1730, 1693, 1462, 1254, 1155, 1093, 838; ^1H NMR (500 MHz, $CDCl_3$) δ 6.93 (dd, *J* = 10.3, 2.0 Hz, 1H), 6.04 (dd, *J* = 10.3, 2.4 Hz, 1H), 4.93 (d, *J* = 9.4 Hz, 1H), 4.44 (s, 1H), 4.39 (ddd, *J* = 6.5, 2.0, 2.0 Hz, 1H), 3.81-3.72 (m, 2H), 2.41-2.34 (m, 1H), 2.14 (t, *J* = 7.5 Hz, 2H), 1.86 (dd, *J* = 12.1, 6.2 Hz, 2H), 1.70 (d, *J* = 0.7 Hz, 3H), 1.54-1.48 (m, 2H), 1.42 (s, 9H), 1.29-1.11 (m, 4H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.87 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.1, 173.2, 151.9, 136.4, 128.1, 126.3, 82.6, 80.1, 66.3, 58.9, 37.04, 37.00, 35.6, 32.6, 28.2 (3C), 27.2, 26.0 (3C), 25.3, 20.5, 18.4, 14.4, -5.3 (2C)**;** HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{27}H_{48}O_5SiNa^+$ 503.3169, obsd 503.3175.



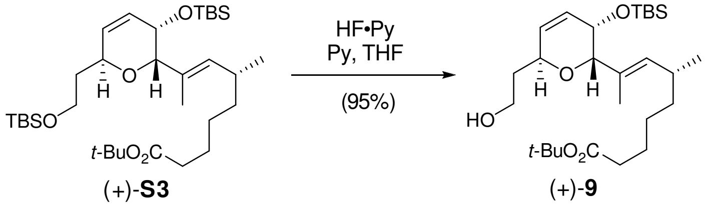
(–)-**S2**

(+)-**8**

Allylic Alcohol (+)-**8.** To a solution of enone (–)-**S2** (36 mg, 0.075 mmol) in MeOH (3 mL) was added $CeCl_3$•$7H_2O$ (279 mg, 0.75 mmol) at rt. After 5 min, $NaBH_4$ (5.7 mg, 0.15 mmol) was added at 0 °C. After 15 min, the reaction mixture was quenched with saturated NH_4Cl solution (15 mL)$_3$, and extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated to leave a crude residue, which was purified by flash chromatography (5% to 30% EtOAc/hexanes) to afford allylic alcohol (+)-**8** (34.2 mg, 95%) as a pale yellow oil. $[\alpha]^{30}_{D}$ +85.2 (*c* 0.54, $CHCl_3$); IR (neat, cm^{-1}) 3448, 1731, 1461, 1254, 1155, 1095, 837; ^1H NMR (500 MHz, $CDCl_3$) δ 6.05 (ddd, *J* = 10.1, 5.6, 2.0 Hz, 1H), 5.91 (dd, *J* = 10.1, 3.2 Hz, 1H), 5.43 (d, *J* = 9.6 Hz, 1H), 4.53-4.50 (m, 1H), 4.01 (s, 1H), 3.87 (t, *J* = 5.4 Hz, 1H), 3.78-3.73 (m, 1H), 3.71-3.67 (m, 1H), 2.48-2.41 (m, 1H), 2.19 (dt, *J* = 7.5, 1.5 Hz, 2H), 1.87-1.80 (m, 1H), 1.72 (d, *J* = 7.4 Hz, 1H), 1.65 (d, *J* = 0.5 Hz, 3H), 1.68-1.53 (m, 3H), 1.44 (s, 9H), 1.36-1.25 (m, 4H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 133.7, 132.8, 129.9, 126.3, 80.0, 73.7, 70.3, 62.5, 59.8, 37.4, 35.8, 34.4, 31.9, 28.3 (3C), 27.2, 26.1 (3C), 25.4, 21.4, 18.5, 14.2, -5.2 (2C); HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{27}H_{50}O_5SiNa^+$ 505.3325, obsd 505.3327.

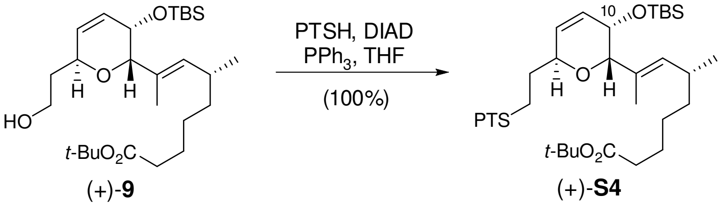


Bis-TBS Ether (+)-S3. A stirred solution of (+)-**8** (45 mg, 0.093 mmol) in anhydrous CH_2Cl_2 (2.2 mL) was cooled to **–**78 ºC and treated with 2,6-lutidine (43 μL, 0.373 mmol) and TBS triflate (43 μL, 0.187 mmol). After 1 h, the reaction mixture was quenched with saturated NH_4Cl solution (10 mL) and extracted with Et_2O (3x10 mL). The combined organic extracts were washed with brine (10 mL), dried, and concentrated *in vacuo* to yield the crude product, which was purified by flash chromatography (2-10% EtOAc/hexanes) to yield (+)-**S3** (53 mg, 95%) as a pale yellow oil. $[\alpha]_D^{29}$ +59.0 (*c* 0.60, $CHCl_3$); IR (neat, cm^{-1}) 1733, 1463, 1365, 1253, 1100, 836; ^1H NMR (500 MHz, $CDCl_3$) δ 5.85 (ddd, *J* = 10.2, 4.6, 2.0 Hz, 1H), 5.78 (dd, *J* = 10.2, 1.7 Hz, 1H), 5.34 (d, *J* = 9.4 Hz, 1H), 4.38-4.36 (m, 1H), 4.09 (t, *J* = 3.7 Hz, 1H), 3.96 (s, 1H), 3.76-3.66 (m, 2H), 2.41-2.35 (m, 1H), 2.18 (t, *J* = 7.6 Hz, 2H), 1.83-1.76 (m, 1H), 1.65 (d, *J* = 0.8 Hz, 3H), 1.66-1.52 (m, 3H), 1.44 (s, 9H), 1.31-1.22 (m, 4H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.88 (s, 9H), 0.86 (s, 9H), 0.05 (s, 6H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 132.9, 132.4, 130.3, 127.2, 80.0, 76.1, 69.3, 65.4, 60.1, 37.4, 35.8, 35.4, 32.0, 28.3 (3C), 27.2, 26.11 (3C), 26.08 (3C), 25.5, 21.0, 18.5, 18.4, 14.3, -3.9, -4.3, -5.19, -5.24; HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{33}H_{64}O_5Si_2Na^+$ 619.4190, obsd 619.4211.

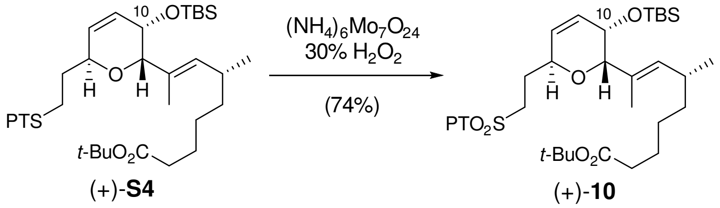


Alcohol (+)-9. To a solution of bis-TBS ether (+)-**S3** (53 mg, 0.089 mmol) and THF (3.6 mL) in a nalgene container was added a stock solution of HF•pyridine (0.54 mL). The stock solution was prepared by adding pyridine (3.1 mL) portion wise to a solution of HF•pyridine (1.3 g) and THF (10 mL) in a nalgene container. After 18 h, additional HF•pyridine stock solution (0.2 mL) was added. After being stirred for an additional 8 h, the reaction was carefully diluted with saturated $NaHCO_3$ solution (10 mL) and diethyl ether (25 mL). The aqueous layer was then washed with diethyl ether (3x5 mL), and the combined organic layers were washed with saturated NH_4Cl solution (10 mL), saturated $NaHCO_3$ solution (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography

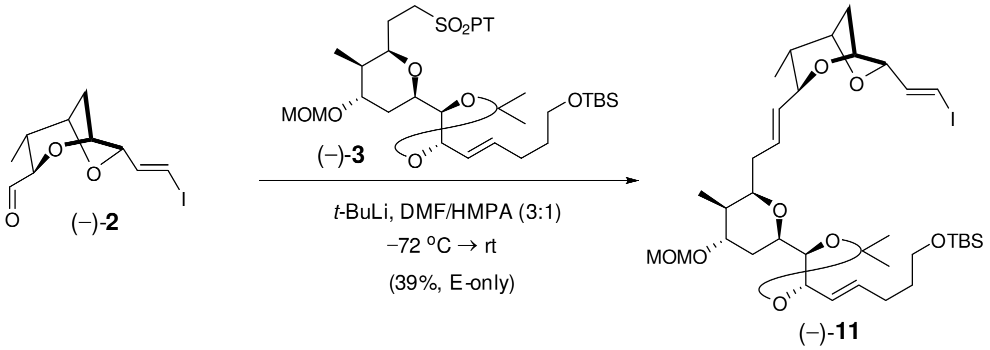
(5% to 30% EtOAc/hexanes) afforded alcohol (+)-**9** (41 mg, 95%) as a pale yellow oil. $[\alpha]_D^{29}$ +84.6 (*c* 0.36, $CHCl_3$); IR (neat, cm^{-1}) 3450, 1730, 1460, 1366, 1252, 1114, 838; ^1H NMR (500 MHz, $CDCl_3$) δ 5.90 (ddd, *J* = 10.2, 4.8, 2.2 Hz, 1H), 5.73 (dd, *J* = 10.2, 2.4 Hz, 1H), 5.36 (d, *J* = 9.5 Hz, 1H), 4.46 (dd, *J* = 10.6, 2.5 Hz, 1H), 4.14-4.12 (m, 1H), 4.05 (s, 1H), 3.86-3.81 (m, 1H), 3.78-3.73 (m, 1H), 2.85 (dd, *J* = 8.3, 1.9 Hz, 1H), 2.41-2.36 (m, 1H), 2.18 (t, *J* = 7.6 Hz, 2H), 1.99-1.91 (m ,1H), 1.65 (d, *J* = 0.9 Hz, 3H), 1.61-1.51 (m, 3H), 1.43 (s, 9H), 1.32-1.21 (m, 4H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.85 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5, 133.3, 131.2, 129.6, 127.7, 80.0, 75.9, 73.5, 64.6, 62.1, 37.4, 35.8, 33.6, 32.0, 28.3 (3C), 27.1, 26.0 (3C), 25.4, 21.0, 18.3, 14.4, -3.9, -4.4; HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{27}H_{50}O_5SiNa^+$ 505.3325, obsd 505.3310.



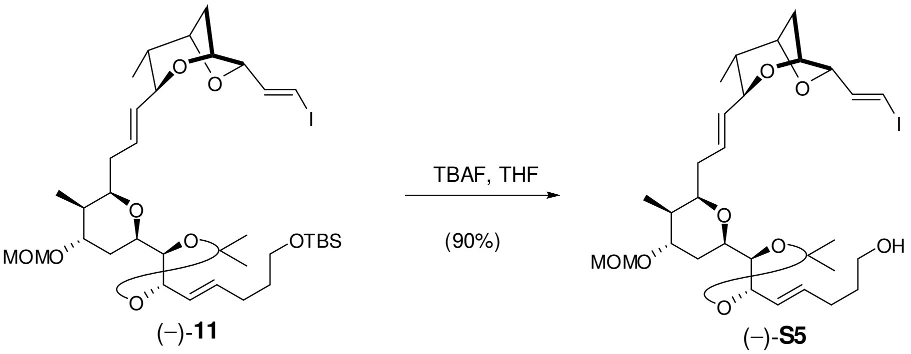
PTS Ether (+)-S4. To a solution of alcohol (+)-**9** (20 mg, 0.041 mmol), triphenylphosphine (22 mg, 0.083 mmol) and 1-phenyl-1H-tetrazole-5-thiol (30 mg, 0.166 mmol) in THF (0.83 mL) was added diisopropylazodicarboxylate (DIAD, 33 μL, 0.166 mmol). After being stirred overnight, the reaction mixture was concentrated *in vacuo* and purified by flash chromatography (2% to 15% EtOAc/hexanes) to furnish (+)-**S4** (26.6 mg, 100%) as a pale yellow oil. $[\alpha]_D^{28}$ +62.2 (*c* 0.86, $CHCl_3$); IR (neat, cm^{-1}) 1728, 1597, 1499, 1388, 1366, 1250, 1154, 1110, 838; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58-7.51 (m, 5H), 5.89 (ddd, *J* = 10.2, 4.6, 2.2 Hz, 1H0, 5.73 (dd, *J* = 10.2, 2.8 Hz, 1H), 5.35 (d, *J* = 9.4 Hz, 1H), 4.38-4.36 (m, 1H), 4.12 (t, *J* = 3.6 Hz, 1H), 4.01 (s, 1H0, 3.53 (ddd, v 13.4, 7.8, 4.9 Hz, 1H), 3.40 (ddd, *J* = 13.4, 7.7, 7.7 Hz, 1H), 2.40-2.34 (m, 1H), 2.15 (t, *J* = 7.6 Hz, 2H), 2.12-2.01 (m, 2H), 1.66 (s, 3H), 1.55-1.50 (m, 2H), 1.42 (s, 9H), 1.31-1.20 (m, 4H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.85 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 154.5, 133.9, 133.4, 130.6, 130.2, 129.9 (2C), 129.7, 128.4, 124.0 (2C), 80.0, 76.3, 70.7, 65.3, 37.3, 35.7, 32.0, 31.8, 30.0, 28.3 (3C), 27.1, 26.0 (3C), 25.4, 20.9, 18.3, 14.4, -4.0, -4.4; HRMS (ES) *m/z* $(M+H)^+$ calcd for $C_{34}H_{55}N_4O_4SiS^+$ 643.3713, obsd 643.3740.



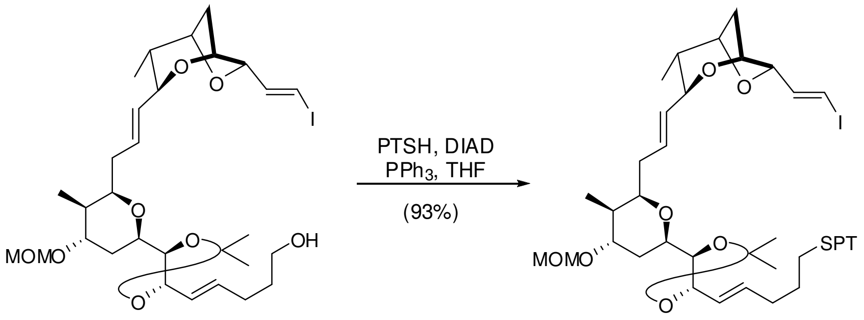
Sulfone (+)-10. To a 0 °C solution of PTS-ether (+)-**S4** (26 mg, 0.040 mmol) in absolute EtOH (4 mL) was added a pre-mixed solution of $(NH_4)_6Mo_7O_{24}{\bullet}4H_2O$ (12.5 mg, 0.01 mmol) in H_2O_2 (30% aq., 0.06 mL, 0.60 mmol) via a glass pipette. The resulting yellow solution was then removed from the ice bath and allowed to warm to room temperature. After 18 h, the reaction mixture was diluted with diethyl ether (10 mL), saturated $NaHCO_3$ solution (5 mL) and water (10 mL). The aqueous layer was then extracted with diethyl ether (3x5 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (2% to 15% EtOAc/hexanes) furnished sulfone (+)-**10** (20 mg, 74%) as a pale yellow oil. $[\alpha]_D^{28}$ +78.5 (*c* 1.2, $CHCl_3$); IR (neat, cm^{-1}) 1728, 1460, 1342, 1154, 1111, 838; ^1H NMR (500 MHz, $CDCl_3$) δ 7.70-7.68 (m, 2H), 7.62-7.59 (m, 3H), 5.94 (ddd, *J* = 10.2, 4.3, 2.1 Hz, 1H), 5.70 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.39 (d, *J* = 9.5 Hz, 1H), 4.32-4.30 (m, 1H), 4.17(t, *J* = 3.8 Hz, 1H), 4.04 (d, *J* = 2.9 Hz, 1H), 3.91 (ddd, *J* = 15.1, 11.1, 4.5 Hz, 1H), 3.79 (ddd, *J* = 15.1, 11.0, 5.1 Hz, 1H), 2.42-2.36 (m, 1H), 2.28-2.20 (m, 1H), 2.17-2.08 (m, 3H), 1.68 (d, *J* = 0.8 Hz, 3H), 1.56-1.50 (m, 2H), 1.43 (s, 9H), 1.32-1.22 (m, 4H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.86 (s, 9H), 0.06 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 153.5, 134.3, 133.2, 131.6, 130.0 (2C), 129.8, 129.2, 129.0, 125.2 (2C), 80.0, 76.7, 69.7, 65.2, 53.4, 37.3, 35.7, 32.1, 28.3 (3C), 27.2, 26.0 (3C), 25.7, 25.4, 20.9, 18.3, 14.4, -4.1, -4.4; HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{34}H_{54}N_4O_6SiSNa^+$ 697.3431, obsd 697.3405.



Triene (–)-11. At –72 °C, *t*-BuLi (1.7 M in pentane, 250 μL, 420 μmol) was added via syringe to a solution of sulfone (–)-**3** (292 mg, 420 μmol) in 3:1 DMF/HMPA (5.3 mL). After 2 min, a solution of aldehyde (–)-**2** (96 mg, 312 μmol) in 3:1 DMF/HMPA (3.9 mL) was rapidly added via cannula, and the resulting mixture was allowed to warm to rt over 2.5 h in the dark. A solution of saturated NH_4Cl solution (5 mL) was added to the reaction mixture, followed by H_2O (10 mL). The aqueous phase was extracted with Et_2O (3x10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting crude oil was purified by preparatory TLC (SiO_2, 1 mm) eluting with hexanes/Et_2O (1:2) to afford triene (–)-**11** (94 mg, 39%) as a pale yellow oil, along with recovered (–)-**2** (12 mg, 13%) and (–)-**3** (113 mg, 39%). $[\alpha]_D^{20}$ –32.3 (*c* 0.55, C_6H_6); IR (neat, cm^{-1}) 1602, 1461, 1379, 1250, 1216, 1144, 1099, 1067, 1038; ^1H NMR (500 MHz, C_6D_6) δ 6.82 (dd, *J* = 14.5, 4.8 Hz, 1H), 6.43 (dd, *J* = 14.5, 1.5 Hz, 1H), 5.93 (ddd, *J* = 15.2, 6.7, 6.7 Hz, 1H), 5.82 (dd, *J* = 15.2, 6.3 Hz, 1H), 5.68 (m, 1H), 5.45 (dd, *J* = 15.2, 7.1 Hz, 1H), 4.76 (dd, *J* = 5.9, 5.9 Hz, 1H), 4.52 (d, J_{AB} = 6.7 Hz, 1H), 4.50 (d, J_{AB} = 6.7 Hz, 1H), 4.05 (m, 2H), 3.98 (m, 2H), 3.91 (d, *J* = 6.3 Hz, 1H), 3.88 (ddd, *J* = 2.6, 2.6, 2.6 Hz, 1H), 3.83 (ddd, *J* = 4.8, 2.2, 2.2 Hz, 1H), 3.66 (ddd, *J* = 2.9, 2.9, 2.9 Hz, 1H), 3.61 (app t, *J* = 6.3 Hz, 2H), 3.19 (s, 3H), 2.34 (ddd, *J* = 13.4, 6.7, 6.7 Hz, 1H), 2.22 (m, 2H), 2.05 (m, 1H), 2.02 (d, *J* = 14.5 Hz, 1H), 1.76-1.62 (m, 4H), 1.51 (s, 3H), 1.44 (d, *J* = 11.5 Hz, 1H), 1.40 (ddd, *J* = 11.5, 5.9, 2.6 Hz, 1H), 1.31 (s, 3H), 1.08 (dq, *J* = 9.3, 6.7 Hz, 1H), 1.00 (s, 9H), 0.81 (d, *J* = 7.1 Hz, 3H), 0.80 (d, *J* = 6.7 Hz, 3H), 0.09 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 142.0, 132.7, 132.55, 129.2, 127.5, 108.3, 95.2, 83.5, 80.6, 79.4, 79.1, 78.9, 78.6, 75.8, 75.5, 73.9, 72.0, 62.7, 55.2, 41.8, 38.7, 36.3, 35.6, 323.0, 29.6, 29.1, 28.2, 26.2, 25.7, 18.5, 15.2, 10.8, -5.0; HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{36}H_{61}IO_8SiNa^+$ 799.3078, obsd 799.3081.

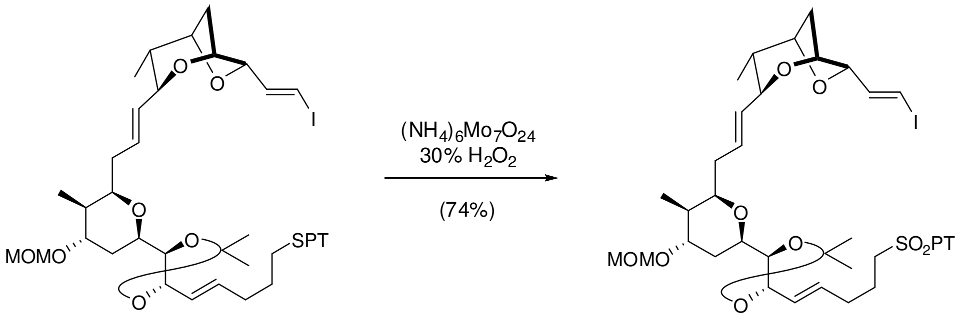


Alcohol (–)-S5. To a –20 °C solution of TBS ether (–)-**11** (11.1 mg, 14.2 µmol) in THF (500 µL) was added tetrabutylammonium fluoride (TBAF, 1 M in THF, 21 µL, 21 µmol). The solution was then allowed to warm to room temperature. After 2 h, additional TBAF (21 µL) was added. After another 1.5 h, additional TBAF (21 µL) was again added. After 1 h, the reaction mixture was diluted with saturated $NaHCO_3$ solution (3 mL), water (10 mL) and EtOAc (15 mL). The aqueous phase was then extracted with EtOAc (3x5 mL), and the combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (50% to 70% EtOAc/hexanes) afforded alcohol (–)-**S5** (8.5 mg, 90%) as a pale yellow oil. $[\alpha]^{20}_{D}$ –26.2 (*c* 0.42, C_6H_6); IR (neat, cm^{-1}) 3480, 1670, 1602, 1455, 1379, 1247, 1216, 1144, 1097, 1066, 1037; ^1H NMR (500 MHz, C_6D_6) δ 6.82 (dd, *J* = 14.6, 4.9 Hz, 1H), 6.43 (dd, *J* = 14.6, 1.7 Hz, 1H), 5.89 (ddd, *J* = 15.3, 6.6, 6.6 Hz, 1H), 5.80 (ddd, *J* = 15.3, 6.2, 0.8 Hz, 1H), 5.70 (ddd, *J* = 15.3, 6.7, 6.7 Hz, 1H), 5.45 (dd, *J* = 15.3, 7.2 Hz, 1H), 4.76 (dd, *J* = 5.8, 5.8 Hz, 1H), 4.50 (br s, 2H), 4.06 (m, 2H), 4.00 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.95 (ddd, *J* = 7.1, 7.1, 1.7 Hz, 1H), 3.89 (m, 2H), 3.81 (ddd, *J* = 4.5, 2.0, 2.0 Hz, 1H), 3.64 (ddd, *J* = 2.7, 2.7, 2.7 Hz, 1H), 3.47 (app t, *J* = 6.4 Hz, 2H), 3.19 (s, 3H), 2.31 (ddd, *J* = 14.1, 7.0, 7.0 Hz, 1H), 2.14 (ddd, *J* = 7.0, 7.0, 7.0 Hz, 2H), 2.02 (m, 2H), 1.73 (m, 1H), 1.68 (m, 1H), 1.58 (m, 2H), 1.50 (s, 3H), 1.44 (dd, *J* = 11.4, 1.4 Hz, 1H), 1.38 (ddd, *J* = 11.4, 6.2, 2.7 Hz, 1H), 1.31 (s, 3H), 1.07 (dq, *J* = 9.3, 6.8 Hz, 1H), 0.80 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 141.94, 132.53, 132.40, 129.63, 127.66, 108.35, 95.29, 83.54, 80.55, 79.41, 79.08, 78.65, 76.03, 75.51, 74.13, 71.99, 62.07, 55.25, 41.74, 38.72, 36.37, 35.76, 32.82, 29.62, 29.13, 28.13, 25.62, 15.17, 10.85; HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{30}H_{47}IO_8Na^+$ 685.2213, obsd 685.2204.



(–)-**S5** (–)-**S6**

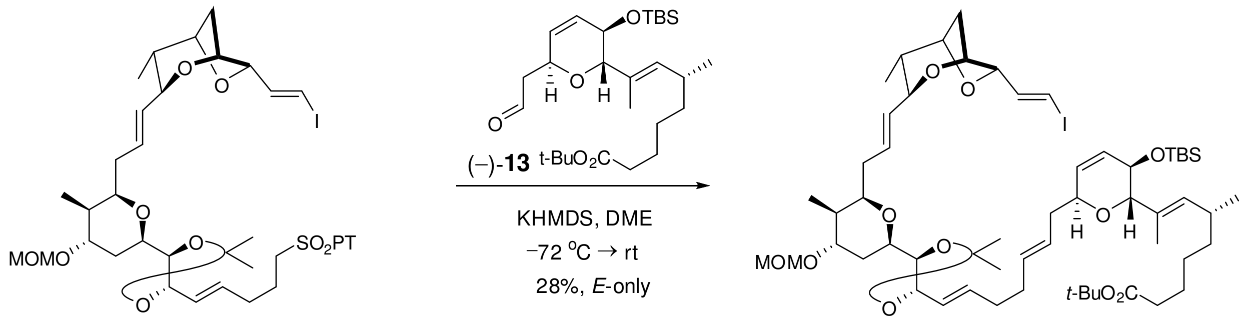
PTS Ether (–)-S6. To a solution of alcohol (–)-**S5** (6.9 mg, 10.4 μmol), triphenylphosphine (4.4 mg, 16.6 μmol) and 1-phenyl-1H-tetrazole-5-thiol (5.0 mg, 28.1 μmol) in THF (1.3 mL) was added one drop of diisopropylazodicarboxylate (DIAD, ~5 μL, ~25 μmol). The resulting pale yellow solution gradually become colorless, and after 45 min, was concentrated *in vacuo* and purified via Preparative-TLC (1:1, hexanes/EtOAc on ½ of a 500 mM plate) to furnish of PTS ether (–)-**S6** (7.9 mg, 93%) as a colorless oil. $[\alpha]^{20}_{D}$ –12.1 (*c* 0.45, C_6H_6); IR (neat, cm^{-1}) 1597, 1499, 1456, 1380, 1244, 1216, 1145, 1096, 1066, 1037; ^1H NMR (500 MHz, C_6D_6) δ 7.23 (m, 2H), 6.90-6.99 (m, 3H), 6.82 (dd, *J* = 14.5, 4.9 Hz, 1H), 6.43 (dd, *J* = 14.5, 1.7 Hz, 1H), 5.81 (m, 2H), 5.71 (ddd, *J* = 15.3, 7.0, 7.0 Hz, 1H), 5.45 (dd, *J* = 15.3, 6.9 Hz, 1H), 4.74 (m, 1H), 4.51 (br s, 2H), 4.02 (m, 3H), 3.95 (m, 1H), 3.90 (m, 2H), 3.86 (m, 1H), 3.65 (ddd, *J* = 2.6, 2.6, 2.6 Hz, 1H), 3.23 (m, 2H), 3.18 (s, 3H), 2.29 (ddd, *J* = 14.1, 7.0, 7.0 Hz, 1H), 2.12 (m, 2H), 2.00 (m, 2H), 1.84 (m, 2H), 1.72 (m, 1H), 1.64 (m, 1H), 1.50 (s, 3H), 1.43 (m, 2H), 1.30 (s, 3H), 1.09 (dq, *J* = 9.7, 6.7 Hz, 1H), 0.81 (d, *J* = 7.1 Hz, 3H), 0.80 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 154.27, 142.03, 134.37, 132.58, 130.91, 129.56, 129.27, 128.71, 124.00, 108.40, 95.19, 83.61, 80.54, 79.40, 79.06, 78.84, 78.49, 75.75, 75.57, 73.96, 71.94, 55.22, 41.82, 38.73, 36.44, 35.80, 32.94, 31.49, 30.16, 29.68, 29.10, 28.11, 25.56, 15.23, 10.84; HRMS (ES) *m/z* (M+Na)$^+$ calcd for $C_{37}H_{51}IN_4O_7SNa^+$ 845.2421, obsd 845.2408.



(–)-**S6**

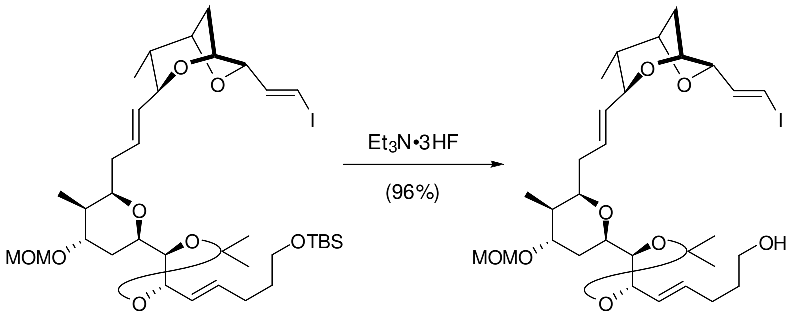
(–)-**12**

Sulfone (–)-12. To a 0 °C solution of PTS ether (–)-**S6** (10.1 mg, 12.2 μmol) in absolute EtOH (1 mL), not under argon, was added a pre-mixed solution of $(NH_4)_6Mo_7O_{24}$•$4H_2O$ (5.6 mg, 4.9 μmol) in H_2O_2 (30% aq., 40 μL) via a glass pipette, followed by 2x100 μL absolute EtOH rinses. The resulting yellow solution was then removed from the ice bath and allowed to warm to room temperature. After 8 h, the reaction mixture was diluted with diethyl ether (10 mL), saturated $NaHCO_3$ solution (5 mL) and water (10 mL). The aqueous layer was then extracted with diethyl ether (3x5 mL), and the combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purificaton via preparative-TLC (2:1, hexanes/EtOAc, 500 μM plate) furnished sulfone (–)-**12** (7.7 mg, 74%) as a colorless oil. $[\alpha]_{D}^{20}$ –20.3 (*c* 0.32, C_6H_6); IR (neat, cm^{-1}) 1598, 1498, 1479, 1461, 1343, 1247, 1216, 1153, 1097, 1066, 1037; ^{1}H NMR (500 MHz, C_6D_6) δ 7.36 (m, 2H), 6.90 (m, 3H), 6.82 (dd, *J* = 14.5, 5.0 Hz, 1H), 6.42 (dd, *J* = 14.5, 1.7 Hz, 1H), 5.79 (dd, *J* = 15.4, 5.9 Hz, 1H), 5.68-5.76 (m, 2H), 5.47 (dd, *J* = 15.3, 6.9 Hz, 1H), 4.71 (dd, *J* = 5.7, 5.7 Hz, 1H), 4.55 (br s, 2H), 4.01 (m, 3H), 3.96 (m, 1H), 3.89 (m, 2H), 3.84 (ddd, *J* = 5.0, 1.8, 1.8 Hz, 1H), 3.65 (ddd, *J* = 2.6, 2.6, 2.6 Hz, 1H), 3.53-3.43 (m, 2H), 3.21 (s, 3H), 2.29 (ddd, *J* = 14.1, 7.1, 7.1, 1H), 2.04-1.92 (m, 6H), 1.74 (m, 1H), 1.64 (m, 1H), 1.51 (s, 3H), 1.42 (m, 2H), 1.30 (s, 3H), 1.09 (dq, *J* = 9.3, 6.7 Hz, 1H), 0.81 (br d, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 154.17, 141.99, 133.60, 132.65, 130.89, 129.86, 129.58, 129.45, 129.35, 108.48, 95.21, 83.65, 80.48, 79.38, 79.20, 78.67, 78.48, 75.72, 75.58, 73.96, 71.89, 55.74, 55.24, 41.87, 38.72, 36.44, 35.84, 30.86, 29.68, 28.10, 25.54, 22.21, 15.22, 10.83; HRMS (ES) *m/z* (M+Na)$^+$ calcd for $C_{37}H_{51}IN_4O_9SNa^+$ 877.2319, obsd 877.2283.



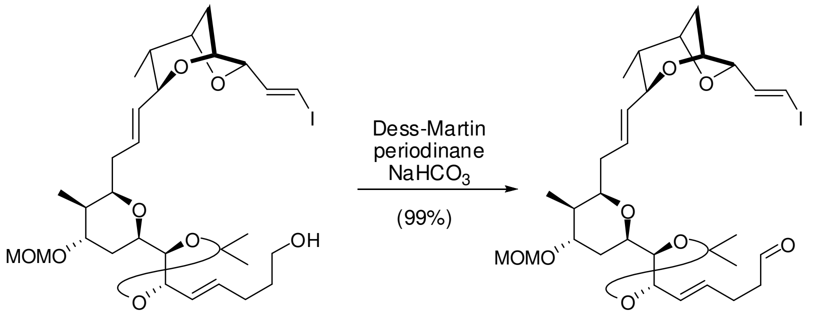
(–)-12 (–)-14

TBS Ether (–)-14. At –72 °C, KHMDS (0.5 M in PhMe, 23 μL, 11.5 μmol) was added via syringe to a solution of (–)-**12** (8 mg, 9.35 μmol) in DME (0.12 mL). After 10 min, the bright yellow mixture was treated via cannula with a solution of (–)-**13** (6 mg, 12.2 μmol) in DME (0.12 mL) and the mixture was allowed to warm to rt over 2 h. The reaction mixture was quenched with saturated NH_4Cl solution (2 mL). The aqueous phase was extracted with Et_2O (3x1 mL) and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude mixture was purified by flash chromatography (SiO_2) eluting with 3:1 hexanes/EtOAc to afford TBS ether (–)-**14** (2.9 mg, 28%) as a pale yellow oil, along with recovered sulfone (–)-**12** (4 mg, 50%) and aldehyde (–)-**13** (2.4 mg, 40%). $[\alpha]_D^{24}$ –34.9 (*c* 0.59, C_6H_6); IR (neat, cm^{-1}) 1730, 1459, 1368, 1251, 1150, 1066, 1038, 971, 837, 775; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84-6.79 (dd, *J* = 14.5, 4.5 Hz, 1H), 6.56-6.52 (dd, *J* = 14.6, 1.7 Hz, 1H), 5.80-5.69 (m, 3H), 5.60-5.46 (m, 3H), 5.44-5.35 (m, 1H), 5.25-5.22 (d, *J* = 9.0 Hz, 1H), 4.67-4.59 (m, 3H), 4.35-4.33 (m, 1H), 4.31-4.28 (m, 1H), 4.24-4.22 (d, *J* = 6.4 Hz, 1H), 4.14-4.08 (m, 2H), 3.93-3.90 (m, 1H), 3.87-3.84 (t, *J* = 8.0 Hz, 1H), 3.77-3.69 (m, 3 H), 3.67-3.65 (d, *J* = 7.8 Hz, 1H), 3.34 (s, 3H), 2.44-2.35 (m, 2H), 2.29-2.21 (m, 2H), 2.19-2.02 (m, 7H), 1.98-1.86 (m, 1H), 1.86-1.83 (m, 1H), 1.78-1.73 (m, 1H), 1.71-1.65 (m, 1H), 1.63-1.59 (m, 4H), 1.58-1.49 (m, 6H), 1.42 (s, 9H), 1.38-1.15 (m, 11H), 0.94-0.77 (m, 15H), 0.05-0.01 (d, *J* = 21.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 141.0, 136.6, 133.7, 132.4, 131.7, 131.1, 130.3, 130.1, 129.73, 129.66, 126.5, 125.9, 108.2, 94.9, 83.5, 79.9, 79.8, 79.4, 79.3, 78.9, 78.7, 77.8, 75.6, 75.3, 73.6, 73.2, 71.6, 65.8, 55.4, 41.3, 37.1, 37.0, 36.9, 35.8, 35.6, 35.1, 32.4, 32.3, 31.9, 29.7, 28.6, 28.1, 27.7, 26.8, 25.9, 25.4, 25.3, 22.7, 20.3, 18.1, 15.1, 14.1, 12.8, 10.6, -4.2, -4.5; HRMS (ES) *m/z* (M+Na)$^+$ calcd for $C_{57}H_{93}IO_{11}SiNa^+$ 1131.5429, obsd 1131.5425.



(–)-**11** (–)-**S5**

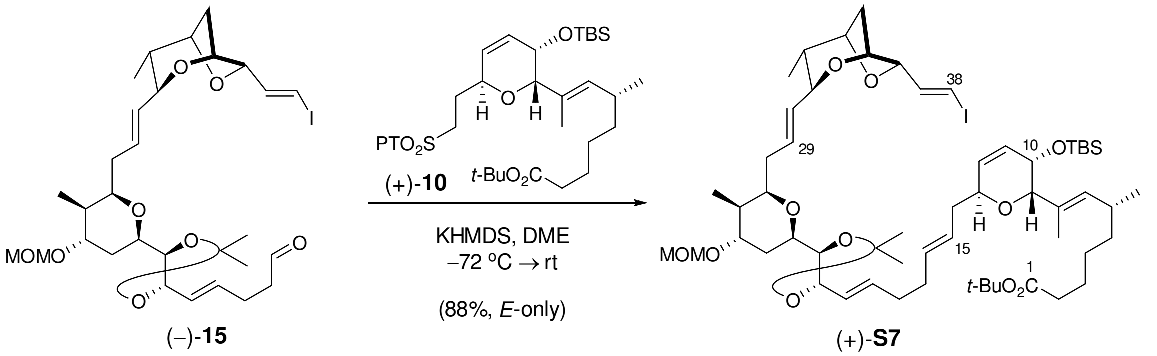
Alcohol (–)-S5: TBS ether **(–)-11** (44 mg, 57 μmol) was dissolved in THF (1.1 mL) in a polyethylene vial. Neat $Et_3N{\cdot}3HF$ (65 μL, 0.39 mmol) was added via autopipetter and the resulting solution was stirred in the dark for 17 h. The reaction mixture was concentrated *in vacuo* and directly purified by flash chromatography (SiO_2) eluting with 2:3 hexanes/EtOAc to afford **(–)-S5** (36 mg, 96%) as a pale yellow oil. All characterization data are same as above.



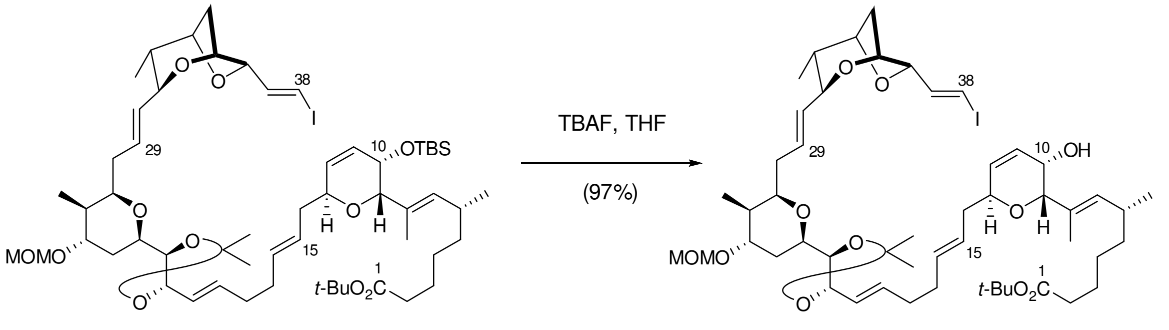
(–)-**S5** (–)-**15**

Aldehyde (–)-15: At room temperature, solid Dess-Martin periodinane (35 mg, 82 μmol) was added in one portion to a slurry of (–)-**S5** (18 mg, 27 μmol) and $NaHCO_3$ (27 mg, 0.33 mmol) in CH_2Cl_2 (1.4 mL). The mixture was stirred in the dark for 2 h and then diluted with Et_2O (1.5 mL), whereupon a 1:1:1 solution of saturated $NaHCO_3$/brine/$Na_2S_2O_3$ (3 mL) was added and stirring was continued until the aqueous layer became homogenous (20 min). The layers were separated and the aqueous phase was extracted with Et_2O (2x1 mL). The combined organic extracts were dried (Na_2SO_4), filtered through a pad of SiO_2 (5 g) with an Et_2O rinse (10 mL) and concentrated *in vacuo*. The crude residue was purified by flash chromatography (SiO_2) eluting with 1:1 hexanes/EtOAc to afford (–)-**15** (17.7 mg, 99%) as a pale yellow oil. $[\alpha]^{24}_{D}$ –31.9 (*c* 1.0, C_6H_6); IR (neat, cm^{-1}) 1724, 1457, 1378, 1216, 1144, 1101, 1066, 1036, 970, 941, 877, 799, 676; ^1H NMR (500 MHz, C_6D_6) δ 9.39-9.38 (m, 1H), 6.83-6.79 (dd, *J* = 14.5, 4.5 Hz, 1H), 6.46-6.42 (dd, *J* = 15.0, 2.0 Hz, 1H), 5.84-5.67 (m, 3H), 5.49-5.44 (dd, *J* = 15.5, 7.0 Hz, 1H), 4.73-4.70 (t, *J* = 6.0 Hz, 1H), 4.53 (s, 2H), 4.05-3.94 (m, 4H), 3.92-3.90 (d, *J* = 5.5 Hz, 1H), 3.98-

3.87 (m, 1H), 3.85-3.82 (m, 1H), 3.67-3.65 (m, 1H), 3.21 (s, 3H), 2.33-2.20 (m, 2H), 2.08-1.97 (m, 4H), 1.77-1.71 (m, 1H), 1.68-1.62 (m, 1H), 1.51 (s, 3H), 1.43-1.27 (m, 6H), 1.11-1.05 (m, 1H), 0.87-0.75 (m, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 200.6, 142.4, 133.0, 131.1, 129.6, 108.8, 95.6, 84.0, 80.9, 79.8, 79.3, 79.2, 78.8, 76.2, 75.9, 74.4, 72.3, 55.6, 43.6, 42.2, 39.1, 36.8, 36.2, 30.5, 30.1, 28.5, 26.0, 25.6, 21.6, 15.6, 11.2; HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{30}H_{45}IO_8Na^+$ 683.2057, obsd 683.2081.

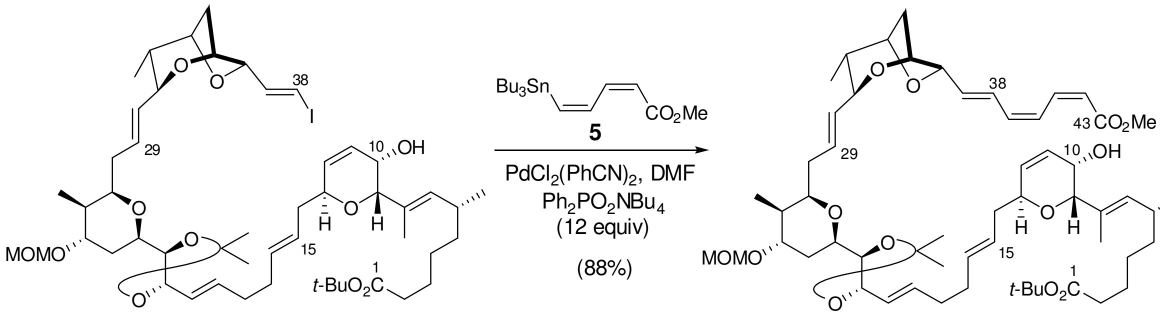


TBS Ether (+)-S7. At –72 °C, KHMDS (0.5 M in PhMe, 30 μL, 15 μmol) was added via syringe to a solution of (+)-**10** (10.2 mg, 15 μmol) in DME (0.16 mL). After 10 min, the bright yellow mixture was treated via cannula with a solution of (–)-**15** (5 mg, 7.6 μmol) in DME (0.16 mL) and the mixture was allowed to warm to rt over 2 h. The reaction mixture was quenched with saturated NH_4Cl solution (5 mL). The aqueous phase was extracted with Et_2O (3x5 mL) and the combined organic layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude mixture was purified by flash chromatography (SiO_2, 5% to 30% EtOAc/hexanes, silica gel was pretreated with 0.5% Et_3N) to afford TBS ether (+)-**S7** (7.4 mg, 88%) as a pale yellow oil, along with recovered sulfone (+)-**10** (5.2 mg, 51%). $[\alpha]_D^{29}$ +26.0 (*c* 0.54, C_6H_6); IR (neat, cm^{-1}) 1730, 1457, 1367, 1251, 1099, 1066, 1038, 837, 775; ^{1}H NMR (500 MHz, C_6D_6) δ 6.84 (dd, *J* = 14.6, 4.8 Hz, 1H), 6.46 (dd, *J* = 14.6, 1.8 Hz, 1H), 5.96 (ddd, *J* = 15.2, 6.8, 6.8 Hz, 1H), 5.88 (ddd, *J* = 10.2, 4.7, 2.1 Hz, 1H), 5.83 (dd, *J* = 15.2, 6.4 Hz, 1H), 5.76 (dd, *J* = 10.2, 2.5 Hz, 1H), 5.71 (ddd, *J* = 15.2, 7.8, 7.8 Hz, 1H), 5.57-5.53 (m, 3H), 5.46 (dd, *J* = 15.2, 7.1 Hz, 1H), 4.79 (dd, *J* = 5.5, 5.5 Hz, 1H), 4.54 (ABq, *J* = 6.9 Hz, Δν = 10.1 Hz, 2H), 4.29-4.26 (m, 1H), 4.12 (s, 1H), 4.08-4.06 (m, 3H), 4.04-3.96 (m, 2H), 3.93 (d, *J* = 6.0 Hz, 1H), 3.91 (s, 1H), 3.87-3.85 (m, 1H), 3.69-3.67 (m, 1H), 3.21 (s, 3H), 2.45-2.40 (m, 2H), 2.37-2.31 (m, 1H), 2.27-2.18 (m, 7H), 2.06-2.00 (m, 2H), 1.84 (s, 3H), 1.74-1.62 (m, 4H), 1.54 (s, 3H), 1.48-1.40 (m, 2H), 1.42 (s, 9H), 1.34 (s, 3H), 1.31-1.27 (m, 4H), 1.12-1.06 (m, 1H), 1.04 (d, *J* = 6.6 Hz, 3H), 1.00 (s, 9H), 0.83 (d, *J* = 7.1 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 3H), 0.12 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 172.6, 142.1, 133.2, 132.65, 132.54, 132.47, 132.1, 131.3, 129.5, 127.64, 127.62, 127.0, 108.4, 95.2, 83.6, 80.7, 79.5, 79.4, 79.14, 79.05, 78.6, 76.8, 75.8, 75.5, 74.0, 72.8, 72.0, 66.1, 55.3, 41.8, 38.8, 37.8, 37.0, 36.5, 35.9, 35.8, 33.0, 32.9, 32.3, 29.7, 28.2 (4C), 27.5, 26.2 (3C), 25.8, 25.7, 21.3, 18.5, 15.3, 14.6, 10.9, -3.6, -4.1; HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{57}H_{93}IO_{11}SiNa^+$ 1131.5429, obsd 1131.5415.



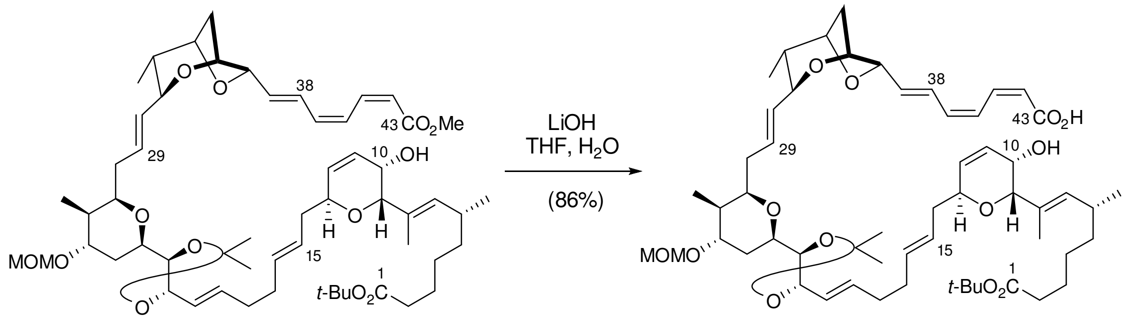
(+)-**S7** (+)-**16**

Vinyl Iodide (-)-16. Solid TBAF•3H_2O (33 mg, 0.126 mmol) was added to a solution of (+)-**S7** (7 mg, 6.3 μmol) in THF (0.15 mL) at rt. The reaction mixture was stirred in the dark for 20 h, and then diluted with Et_2O (2 mL) and saturated NH_4Cl solution (2 mL). The aqueous phase was extracted with Et_2O (4×2 mL). The combined organic extracts were dried (Na_2SO_4), filtered through a short plug of SiO_2, washed with additional Et_2O (25 mL), and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography (SiO_2, 0.5% to 1.5% MeOH/CH_2Cl_2, silica gel was pretreated with 0.5% Et_3N) to afford vinyl iodide (+)-**16** (6.1 mg, 97%) as a pale yellow oil. $[\alpha]_D^{29}$ +26.9 (*c* 0.32, C_6H_6); IR (neat, cm^{-1}) 3436, 1729, 1456, 1367, 1217, 1149, 1066, 1038, 970; ^1H NMR (500 MHz, C_6D_6) δ 6.85 (dd, *J* = 14.6, 4.9 Hz, 1H), 6.46 (dd, *J* = 14.6, 1.8 Hz, 1H), 6.00 (ddd, *J* = 10.2, 5.6, 1.9 Hz, 1H), 5.96 (ddd, *J* = 15.2, 6.6, 6.6 Hz, 1H), 5.84 (dd, *J* = 15.2, 6.4 Hz, 1H), 5.75 (dd, *J* = 10.2, 3.3 Hz, 1H), 5.71 (ddd, *J* = 15.2, 8.5, 6.7 Hz, 1H), 5.60 (ddd, *J* = 9.7, 1.3, 1.3 Hz, 1H), 5.57-5.47 (m, 2H), 5.46 (dd, *J* = 15.2, 7.1 Hz, 1H), 4.80 (dd, *J* = 5.8, 5.8 Hz, 1H), 4.54 (ABq, *J* = 6.8 Hz, Δν = 9.7 Hz, 2H), 4.31-4.27 (m, 1H), 4.08-3.97 (m, 5H), 3.93 (d, *J* = 6.0 Hz, 1H), 3.91-3.90 (m, 1H), 3.86-3.84 (m, 1H), 3.78-3.77 (m, 1H), 3.69-3.67 (m, 1H), 3.21 (s, 3H), 2.45-2.32 (m, 3H), 2.23-2.15 (m, 7H), 2.07-2.01 (m, 2H), 1.72 (d, *J* = 0.8 Hz, 3H), 1.70-1.57 (m, 4H), 1.54 (s, 3H), 1.47-1.40 (m, 2H), 1.41 (s, 9H), 1.33 (s, 3H), 1.31-1.24 (m, 4H), 1.12-1.06 (m, 1H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.83 (d, *J* = 7.1 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 172.7, 142.1, 132.8, 132.6, 132.5, 132.4, 132.3, 131.3, 129.5, 127.7, 127.6, 126.9, 108.4, 95.2, 83.6, 80.7, 79.44, 79.36, 79.12, 79.08, 78.7, 76.8, 75.8, 75.5, 75.0, 74.1, 74.0, 72.0, 63.3, 55.3, 41.8, 38.8, 37.8, 36.5, 36.3, 35.84, 35.77, 33.0, 32.9, 32.2, 29.7, 28.2 (4C), 27.5, 25.72, 25.68, 21.6, 15.3, 14.3, 10.9; HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{51}H_{79}IO_{11}Na^+$ 1017.4565, obsd 1017.4566.



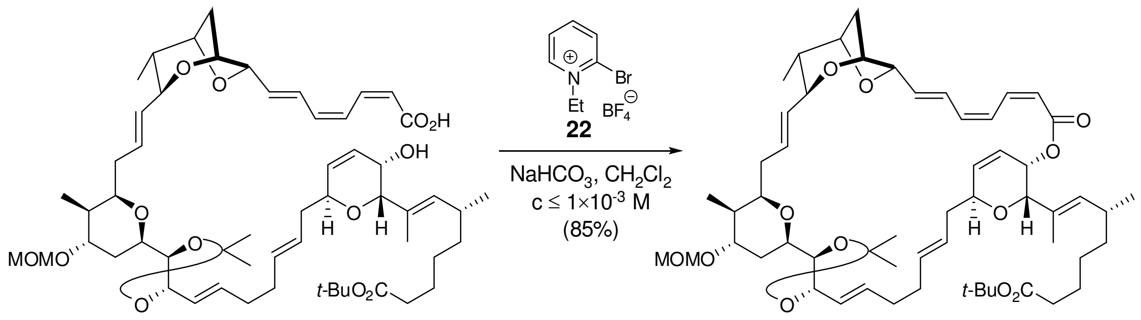
(+)-**16** (+)-**17**

Trienoate (+)-17. A 15 mL round bottom flask was charged with stannane **5** (16 mg, 40 μmol), vinyl iodide (+)-**16** (10 mg, 10 μmol), $Ph_2PO_2NBu_4$ (55 mg, 120 μmol), and dissolved in degassed DMF (1.1 mL). To this was added $PdCl_2(PhCN)_2$ (0.2 mg, 0.5 μmol), and the reaction mixture was purged with argon for 5 min, and stirred at rt in the dark overnight. The reaction mixture was diluted with Et_2O/hexanes (1:1, 4 mL), filtered through a Celite plug into brine (5 mL), and rinsed with Et_2O/hexanes (1:1, 20 mL). The mixture was extracted using Et_2O/hexanes (1:1, 3×10 mL), and the combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo* to give a crude residue, which was purified by flash chromatography (SiO_2, 0.2% to 1.5% MeOH/CH_2Cl_2, silica gel was pretreated with 0.5% Et_3N) to afford trienoate (+)-**17** (8.6 mg, 88%) as a yellow oil. $[\alpha]_D^{29}$ +49.0 (*c* 0.26, C_6H_6); IR (neat, cm^{-1}) 3417, 1720, 1650, 1612, 1454, 1368, 1246, 1218, 1149, 1097, 1067, 1038, 974, 876; ^1H NMR (500 MHz, C_6D_6) δ 7.75 (dd, *J* = 11.5, 11.5 Hz, 1H), 7.05-7.00 (m, 1H), 6.88 (dd, *J* = 11.5, 11.5 Hz, 1H), 6.26 (dd, *J* = 11.5, 11.5 Hz, 1H), 6.10 (dd, *J* = 15.3, 4.9 Hz, 1H), 6.01 (ddd, *J* = 10.2, 5.6, 2.0 Hz, 1H), 5.93 (ddd, *J* = 15.4, 6.4, 6.4 Hz, 1H), 5.82 (dd, *J* = 15.4, 6.3 Hz, 1H), 5.74 (dd, *J* = 10.2, 3.2 Hz, 1H), 5.71 (ddd, *J* = 15.2, 7.6, 7.6 Hz, 1H), 5.64 (d, *J* = 11.5 Hz, 1H), 5.59 (d, *J* = 9.5 Hz, 1H), 5.54-5.43 (m, 3H), 4.78 (dd, *J* = 5.8, 5.8 Hz, 1H), 4.51 (ABq, *J* = 6.8 Hz, Δν = 11.0 Hz, 2H), 4.30-4.26 (m, 1H), 4.24-4.23 (m, 1H), 4.11-4.04 (m, 6H), 4.00-3.96 (m, 1H), 3.80-3.78 (m, 1H), 3.67-3.65 (m, 1H), 3.38 (s, 3H), 3.19 (s, 3H), 2.46-2.33 (m, 3H), 2.19-2.13 (m, 7H), 2.08-2.02 (m, 2H), 1.79-1.47 (m, 6H), 1.73 (s, 3H), 1.53 (s, 3H), 1.41 (s, 9H), 1.33 (s, 3H), 1.31-1.23 (m, 4H), 1.20-1.14 (m, 1H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 172.7, 166.5, 138.7, 136.9, 134.6, 132.8, 132.7, 132.5, 132.3 (2C), 131.4, 129.1, 127.7, 127.6, 126.9, 126.8, 125.0, 118.0, 108.4, 95.2, 82.0, 80.7, 79.5, 79.4, 79.1, 78.7, 76.4, 75.9, 75.0, 74.1, 74.0, 72.0, 63.4, 55.2, 50.8, 42.0, 39.3, 37.8, 36.5, 36.3, 35.83, 35.77, 33.0, 32.8, 32.2, 29.7, 28.2 (4C), 27.5, 25.7 (2C), 21.6, 15.4, 14.3, 10.9; HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{57}H_{86}O_{13}Na^+$ 1001.5966, obsd 1001.5975.



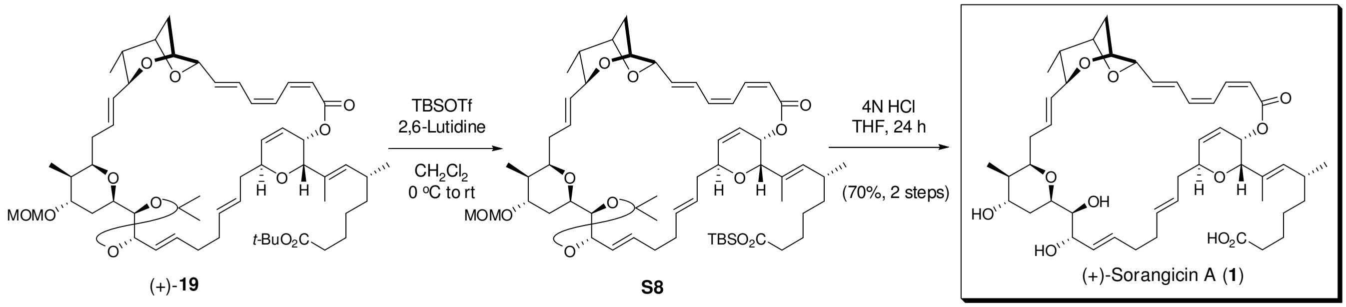
(+)-**17** **18**

Seco Acid 18. A solution of trienoate (+)-**17** (6.6 mg, 6.7 μmol) in THF (1.6 mL) and H_2O (0.4 mL) was treated with 1 M LiOH solution (0.4 mL). The yellow reaction mixture was stirred for 1.5 days at rt in the dark. Brine (1 mL) was added and the pH value of the reaction mixture was adjusted to ca. 3 with 1 M $NaHSO_4$. The aqueous layer was extracted with EtOAc (4×2 mL), and the combined organic layers were washed with brine (2 mL), dried (Na_2SO_4) and concentrated *in vacuo* to give a crude residue, which was purified by flash chromatography (SiO_2, 0.5% to 5% MeOH/CH_2Cl_2) to afford seco acid **18** (5.6 mg, 86%) as a yellow oil. Seco acid **18** proved very unstable, and was carried on to the next step immediately after the ^{1}H NMR spectrum was taken. ^{1}H NMR (500 MHz, C_6D_6) δ 7.64 (dd, *J* = 11.5, 11.5 Hz, 1H), 7.03-6.97 (m, 1H), 6.89 (dd, *J* = 11.5, 11.5 Hz, 1H), 6.27 (dd, *J* = 11.5, 11.5 Hz, 1H), 6.08 (dd, *J* = 15.0, 4.7 Hz, 1H), 6.02 (ddd, *J* = 10.1, 5.8, 2.0 Hz, 1H), 5.93 (ddd, *J* = 15.4, 6.3, 6.3 Hz, 1H), 5.81 (dd, *J* = 15.4, 6.3 Hz, 1H), 5.74 (dd, *J* = 10.1, 3.1 Hz, 1H), 5.67-5.58 (m, 3H), 5.52-5.41 (m, 3H), 4.78 (dd, *J* = 5.5, 5.5 Hz, 1H), 4.53 (ABq, *J* = 6.9 Hz, Δν = 9.8 Hz, 2H), 4.33-4.28 (m, 1H), 4.24-4.23 (m, 1H), 4.09-4.04 (m, 6H), 3.98-3.95 (m, 1H), 3.82 (dd, *J* = 5.6, 2.0 Hz, 1H), 3.68-3.67 (m, 1H), 3.20 (s, 3H), 2.47-2.34 (m, 3H), 2.19-2.12 (m, 7H), 2.11-2.01 (m, 2H), 1.74 (d, *J* = 0.7 Hz, 3H), 1.72-1.47 (m, 6H), 1.53 (s, 3H), 1.41 (s, 9H), 1.33 (s, 3H), 1.31-1.24 (m, 4H), 1.18-1.12 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.83 (d, *J* = 7.1 Hz, 3H).



18 (+)-**19**

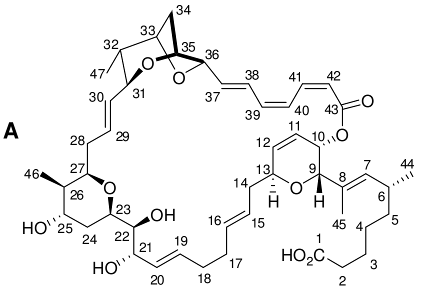
Macrolide (+)-19. A slurry of seco acid **18** (5.4 mg, 5.6 μmol) and $NaHCO_3$ (120 mg, 1.4 mmol) in CH_2Cl_2 (12 mL) was treated with solid 2-bromo-1-ethylpyridinium tetrafluoroborate **22** (31 mg, 0.11 mmol) in one portion. The reaction mixture was vigorously stirred in the dark overnight, then transferred directly onto a silica gel column and purified by flash chromatography (0.2% to 1.6% $MeOH/CH_2Cl_2$) to afford macrolide (+)-**19** (4.5 mg, 85%) as a pale yellow foam. $[\alpha]^{28}_{D}$ +41.6 (*c* 0.36, MeOH); IR (neat, cm^{-1}) 1722, 1698, 1610, 1452, 1367, 1250, 1211, 1148, 1095, 1066, 1037, 971, 916, 871; ^1H NMR (500 MHz, CD_3OD) δ 7.16-7.06 (m, 2H), 7.04-6.99 (m, 1H), 6.44 (dd, *J* = 10.6, 10.6 Hz, 1H), 6.26 (dd, *J* = 15.4, 3.3 Hz, 1H), 6.14 (dd, *J* = 10.1, 3.1 Hz, 1H), 6.02 (ddd, *J* = 10.1, 5.9, 2.1 Hz, 1H), 5.73 (ddd, *J* = 15.1, 6.7, 6.7 Hz, 1H), 5.61 (d, *J* = 10.5 Hz, 1H), 5.56-5.52 (m, 3H), 5.38-5.34 (m, 3H), 5.26 (d, *J* = 10.1 Hz, 1H), 4.64 (ABq, *J* = 7.1 Hz, Δν = 17.6 Hz, 2H), 4.61-4.57 (m, 2H), 4.41-4.39 (m, 2H), 4.31 (d, *J* = 6.3 Hz, 1H), 4.21 (s, 1H), 3.94 (dd, *J* = 8.4, 6.3 Hz, 1H), 3.84 (dd, *J* = 9.6, 7.5 Hz, 1H), 3.77-3.68 (m, 3H), 3.32 (s, 3H), 2.42-2.33 (m, 2H), 2.23-2.01 (m, 9H), 1.92 (d, *J* = 10.5 Hz, 1H), 1.75 (d, *J* = 13.8 Hz, 1H), 1.69-1.62 (m, 2H), 1.61 (d, *J* = 0.8 Hz, 3H), 1.60-1.50 (m, 2H), 1.44 (s, 9H), 1.42 (s, 3H), 1.41-1.36 (m, 1H), 1.32 (s, 3H), 1.27-1.15 (m, 4H), 0.90 (d, *J* = 7.2 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 174.9, 167.8, 138.9, 137.7, 137.1, 135.7, 134.2, 133.9, 133.6 (2C), 131.24, 131.17, 128.0, 127.9, 127.6, 126.8, 123.7, 119.8, 109.8, 96.0, 81.9, 81.22 (2C), 81.18, 81.09, 80.1, 77.7, 76.6, 74.9, 74.4, 73.8, 73.3, 66.6, 55.8, 41.8, 39.6, 38.9, 36.7 (2C), 35.6, 35.1, 34.1, 33.1, 32.9, 30.8, 30.4, 28.5 (3C), 28.3, 28.2, 26.3, 25.7, 22.3, 15.3, 14.5, 10.8; HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{56}H_{82}O_{12}Na^+$ 969.5704, obsd 969.5670.



(+)-Sorangicin A (1). To a stirred solution of macrolide (+)-**19** (3.5 mg, 3.7 μmol) and 2,6-lutidine (13 μL, 111 μmol) in CH_2Cl_2 (200 μL) was added TBSOTf (9 μL, 37 μmol) at 0 °C. After 30 min at 0 °C, the reaction mixture was warmed to rt and stirred for 3 h before being quenched with 0.2N HCl (1 mL). The aqueous layer was extracted with Et_2O (4×2 mL), and the combined organic layers were washed with brine (2 mL), dried (Na_2SO_4) and evaporated to give the crude TBS ester **S8**.

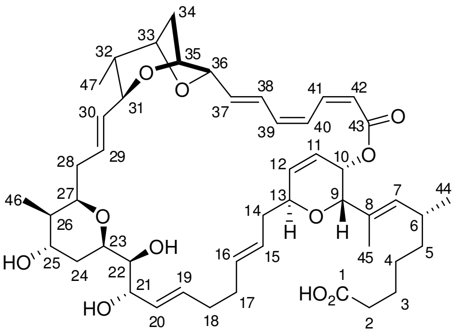
Without further purification, TBS ester **S8** was dissolved in THF (200 μL) and treated with 4N HCl (200 μL) at 0 °C. The reaction mixture was warmed to rt and stirred for 24 h before being cooled to 0 °C and carefully neutralized with saturated $NaHCO_3$ solution (2 mL), and then acidified with HCOOH (0.5 mL, pH~3). The aqueous phase was extracted with CH_2Cl_2 (4×3 mL), and the combined organic layers were concentrated *in vacuo* to give a crude residue, which was purified by flash chromatography (SiO_2, 1% to 5% MeOH/CH_2Cl_2) to furnish (+)-sorangicin A (**1**) (2.1 mg, 70%, 2 steps) as an off-white solid. $[\alpha]_D^{20}$ +56 (*c* 0.06, MeOH); ^{1}H NMR (500 MHz, CD_3OD) δ 7.22-7.12 (m, 2H, 40-H, 41-H), 6.99 (dd, *J* = 15.0, 11.0 Hz, 1H, 38-H), 6.44 (dd, *J* = 10.5, 10.5 Hz, 1H, 39-H), 6.22 (dd, *J* = 15.5, 4.5 Hz, 1H, 37-H), 6.13 (dd, *J* = 9.9, 3.0 Hz, 1H, 12-H), 6.01 (ddd, *J* = 9.9, 5.7, 2.0 Hz, 1H, 11-H), 5.75 (ddd, *J* = 15.4, 6.2, 6.2 Hz, 1H, 19-H), 5.62 (d, *J* = 10.6 Hz, 1H, 42-H), 5.60 (dd, *J* = 15.4, 7.4 Hz, 1H, 20-H), 5.55-5.53 (m, 2H, 15-H, 16-H), 5.52-5.48 (m, 1H, 29-H), 5.38 (ddd, *J* = 15.0, 8.4, 1.0 Hz, 1H, 30-H), 5.32-5.30 (m, 2H, 7-H, 10-H), 4.57 (br s, 1H, 36-H), 4.40-4.38 (m, 2H, 35-H, 13-H), 4.28 (d, *J* = 6.2 Hz, 1H, 33-H), 4.23 (s, 1H, 9-H), 4.15 (dd, *J* = 7.4, 4.5 Hz, 1H, 21-H), 3.88-3.82 (m, 3H, 27-H, 25-H, 31-H), 3.71 (ddd, *J* = 11.0, 7.3, 2.7 Hz, 1H, 23-H), 3.48 (dd, *J* = 7.3, 4.5 Hz, 1H, 22-H), 2.42-2.36 (m, 2H, 14-H_a, 6-H), 2.28-2.22 (m, 1H, 28-H_a), 2.23 (t, *J* = 7.5 Hz, 2H, 2-H), 2.19-2.09 (m, 6H, 17-H, 14-H_b, 28-H_b, 18-H), 2.05 (ddd, *J* = 11.5, 6.5, 2.6 Hz, 1H, 34-H_a), 1.93 (dd, *J* = 11.5, 1.5 Hz, 1H, 34-H_b), 1.74 (ddd, *J* = 14.0, 2.5, 2.5 Hz, 1H, 24-H_a), 1.66 (ddd, *J* = 14.0, 11.5, 2.6 Hz, 1H, 24-H_b), 1.63 (d, *J* = 0.7 Hz, 3H, 45-H), 1.61-1.53 (m, 3H, 3-H, 26-H), 1.42 (m, 1H, 32-H), 1.37-1.16 (m, 4H, 5-H, 4-H), 0.88 (d, *J* = 7.2 Hz, 3H, 46-H), 0.87 (d, *J* = 6.6 Hz, 3H, 44-H), 0.82 (d, *J* = 6.8 Hz, 3H, 47-H); ^{13}C NMR (125 MHz, CD_3OD) δ 179.18 (C-1), 167.66 (C-43), 139.16 (C-41), 137.77 (C-39), 136.95 (C-12), 134.94 (C-37), 134.61 (C-19), 134.10 (C-7), 133.69 (C-16), 132.98 (C-29), 132.79 (C-30), 131.09 (C-8), 129.96 (C-20), 128.25 (C-15), 127.74 (C-38), 126.96 (C-40), 123.71 (C-11), 119.55 (C-42), 82.08 (C-36), 81.20 (C-31), 80.98 (C-33), 77.76 (C-22), 77.49 (C-35), 75.23 (C-13), 74.85 (C-23), 74.67 (C-27), 74.37 (C-21), 74.17 (C-9), 71.01 (C-25), 66.68 (C-10), 42.06 (C-32), 39.80 (C-34), 38.69 (C-5), 38.28 (C-26), 37.14 (C-28), 36.23 (C-2), 35.34 (C-14), 34.20 (C-18), 33.51 (C-17), 32.96 (C-6), 30.89 (C-24), 28.40 (C-4), 26.64 (C-3), 21.85 (C-44), 15.39 (C-47), 14.39 (C-45), 10.85 (C-46); HRMS (ES) *m/z* $(M+Na)^+$ calcd for $C_{47}H_{66}O_{11}Na^+$ 829.4503, obsd 829.4507.

^{1}H NMR Chemical Shifts of (+)-Sorangicin A
δ (ppm in CD$_3$OD)



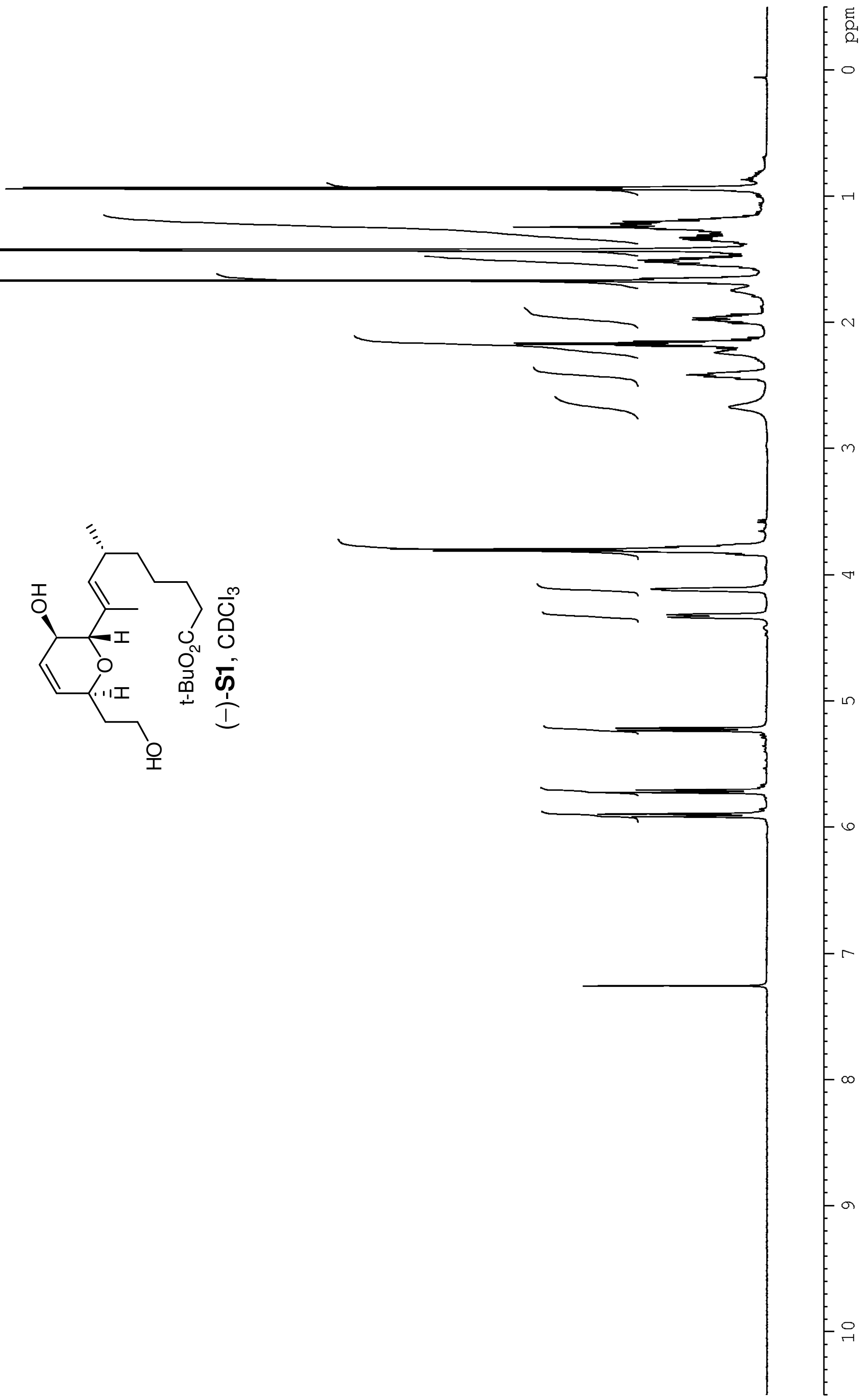
Proton Number	Synthetic (+)-Sorangicin A	Natural (+)-Sorangicin A
40-H, 41-H	7.22-7.12 (m, 2H)	7.22-7.12 (m, 2H)
38-H	6.99 (dd, J = 15.0, 11.0 Hz, 1H)	6.99 (dd, J = 14.9, 11.1 Hz, 1H)
39-H	6.44 (dd, J = 10.5, 10.5 Hz, 1H)	6.44 (dd, J = 10.6, 10.6 Hz, 1H)
37-H	6.22 (dd, J = 15.5, 4.5 Hz, 1H)	6.22 (dd, J = 15.4, 4.7 Hz, 1H)
12-H	6.13 (dd, J = 9.9, 3.0 Hz, 1H)	6.13 (dd, J = 10.0, 3.1 Hz, 1H)
11-H	6.01 (ddd, J = 9.9, 5.7, 2.0 Hz, 1H)	6.01 (ddd, J = 10.0, 5.8, 2.1 Hz, 1H)
19-H	5.75 (ddd, J = 15.4, 6.2, 6.2 Hz, 1H)	5.75 (ddd, J = 15.4, 6.2, 6.2 Hz, 1H)
42-H	5.62 (d, J = 10.6 Hz, 1H)	5.62 (d, J = 10.5 Hz, 1H)
20-H	5.60 (dd, J = 15.4, 7.4 Hz, 1H)	5.60 (dd, J = 15.5, 7.5 Hz, 1H)
15-H, 16-H	5.55-5.53 (m, 2H)	5.55-5.53 (m, 2H)
29-H	5.52-5.48 (m, 1H)	5.52-5.48 (m, 1H)
30-H	5.38 (ddd, J = 15.0, 8.4, 1.0 Hz, 1H)	5.38 (ddd, J = 15.0, 8.5, 1.0 Hz, 1H)
7-H, 10-H	5.32-5.30 (m, 2H)	5.32-5.30 (m, 2H)
36-H	4.57 (br s, 1H)	4.57 (br s, 1H)
35-H, 13-H	4.40-4.38 (m, 2H)	4.40-4.38 (m, 2H)
33-H	4.28 (d, J = 6.2 Hz, 1H)	4.28 (d, J = 6.4 Hz, 1H)
9-H	4.23 (s, 1H)	4.23 (s, 1H)
21-H	4.15 (dd, J = 7.4, 4.5 Hz, 1H)	4.15 (dd, J = 7.4, 4.6 Hz, 1H)
27-H, 25-H, 31-H	3.88-3.82 (m, 3H)	3.88-3.82 (m, 3H)
23-H	3.71 (ddd, J = 11.0, 7.3, 2.7 Hz, 1H)	3.71 (ddd, J = 11.0, 7.3, 2.7 Hz, 1H)
22-H	3.48 (dd, J = 7.3, 4.5 Hz, 1H)	3.48 (dd, J = 7.2, 4.6 Hz, 1H)
14-H$_a$, 6-H	2.42-2.36 (m, 2H)	2.42-2.36 (m, 2H)
28-H$_a$	2.28-2.22 (m, 1H)	2.28-2.23 (m, 1H)
2-H	2.23 (t, J = 7.5 Hz, 2H)	2.24 (t, J = 7.6 Hz, 2H)
17-H,14-H$_b$,28-H$_b$,18-H	2.19-2.09 (m, 6H)	2.19-2.09 (m, 6H)
34-H$_a$	2.05 (ddd, J = 11.5, 6.5, 2.6 Hz, 1H)	2.05 (ddd, J = 11.6, 6.5, 2.8 Hz, 1H)
34-H$_b$	1.93 (dd, J = 11.5, 1.5 Hz, 1H)	1.93 (dd, J = 11.6, 1.4 Hz, 1H)
24-H$_a$	1.74 (ddd, J = 14.0, 2.5, 2.5 Hz, 1H)	1.73 (ddd, J = 14.0, 2.5, 2.5 Hz, 1H)
24-H$_b$	1.66 (ddd, J = 14.0, 11.5, 2.6 Hz, 1H)	1.66 (ddd, J = 14.0, 11.6, 2.6 Hz, 1H)
45-H	1.63 (d, J = 0.7 Hz, 3H)	1.63 (d, J = 0.6 Hz, 3H)
3-H, 26-H	1.61-1.53 (m, 3H)	1.60-1.53 (m, 3H)
32-H	1.42 (m, 1H)	1.42 (m, 1H)
5-H, 4-H	1.37-1.16 (m, 4H)	1.38-1.16 (m, 4H)
46-H	0.88 (d, J = 7.2 Hz, 3H)	0.88 (d, J = 7.4 Hz, 3H)
44-H	0.87 (d, J = 6.6 Hz, 3H)	0.87 (d, J = 6.5 Hz, 3H)
47-H	0.82 (d, J = 6.8 Hz, 3H)	0.82 (d, J = 6.5 Hz, 3H)

^{13}C NMR Chemical Shifts of (+)-Sorangicin A
δ (ppm in CD_3OD)

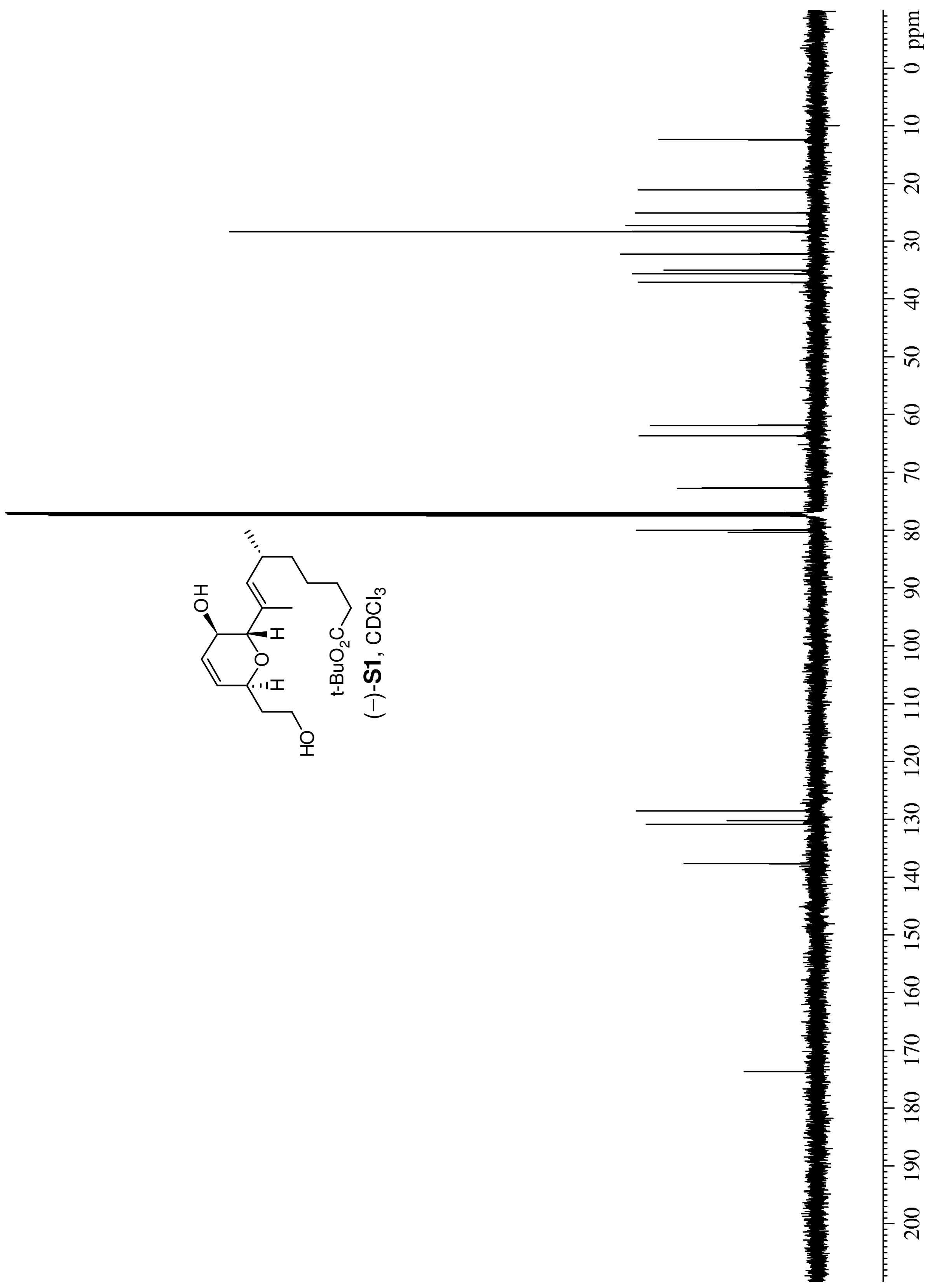


Carbon Number	Synthetic (+)-Sorangicin A	Natural (+)-Sorangicin A
C-1	179.18	178.61
C-43	167.66	167.66
C-41	139.16	139.19
C-39	137.77	137.78
C-12	136.95	136.96
C-37	134.94	134.93
C-19	134.61	134.63
C-7	134.10	134.10
C-16	133.69	133.70
C-29	132.98	132.97
C-30	132.79	132.80
C-8	131.09	131.17
C-20	129.96	129.95
C-15	128.25	128.25
C-38	127.74	127.74
C-40	126.96	126.96
C-11	123.71	123.70
C-42	119.55	119.55
C-36	82.08	82.09
C-31	81.20	81.21
C-33	80.98	80.99
C-22	77.76	77.76
C-35	77.49	77.49
C-13	75.23	75.22
C-23	74.85	74.85
C-27	74.67	74.67
C-21	74.37	74.36
C-9	74.17	74.19
C-25	71.01	71.01
C-10	66.68	66.73
C-32	42.06	42.05
C-34	39.80	39.81
C-5	38.69	38.64
C-26	38.28	38.30
C-28	37.14	37.14

Carbon Number	Synthetic (+)-Sorangicin A	Natural (+)-Sorangicin A
C-2	36.23	35.78
C-14	35.34	35.34
C-18	34.20	34.20
C-17	33.51	33.51
C-6	32.96	32.95
C-24	30.89	30.88
C-4	28.40	28.33
C-3	26.64	26.46
C-44	21.85	21.84
C-47	15.39	15.39
C-45	14.39	14.38
C-46	10.85	10.85



(−)-**S1**, $CDCl_3$


OH
HO
H
H
O
t-BuO$_2$C
ppm
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10
20
30
40
50
60
70
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90
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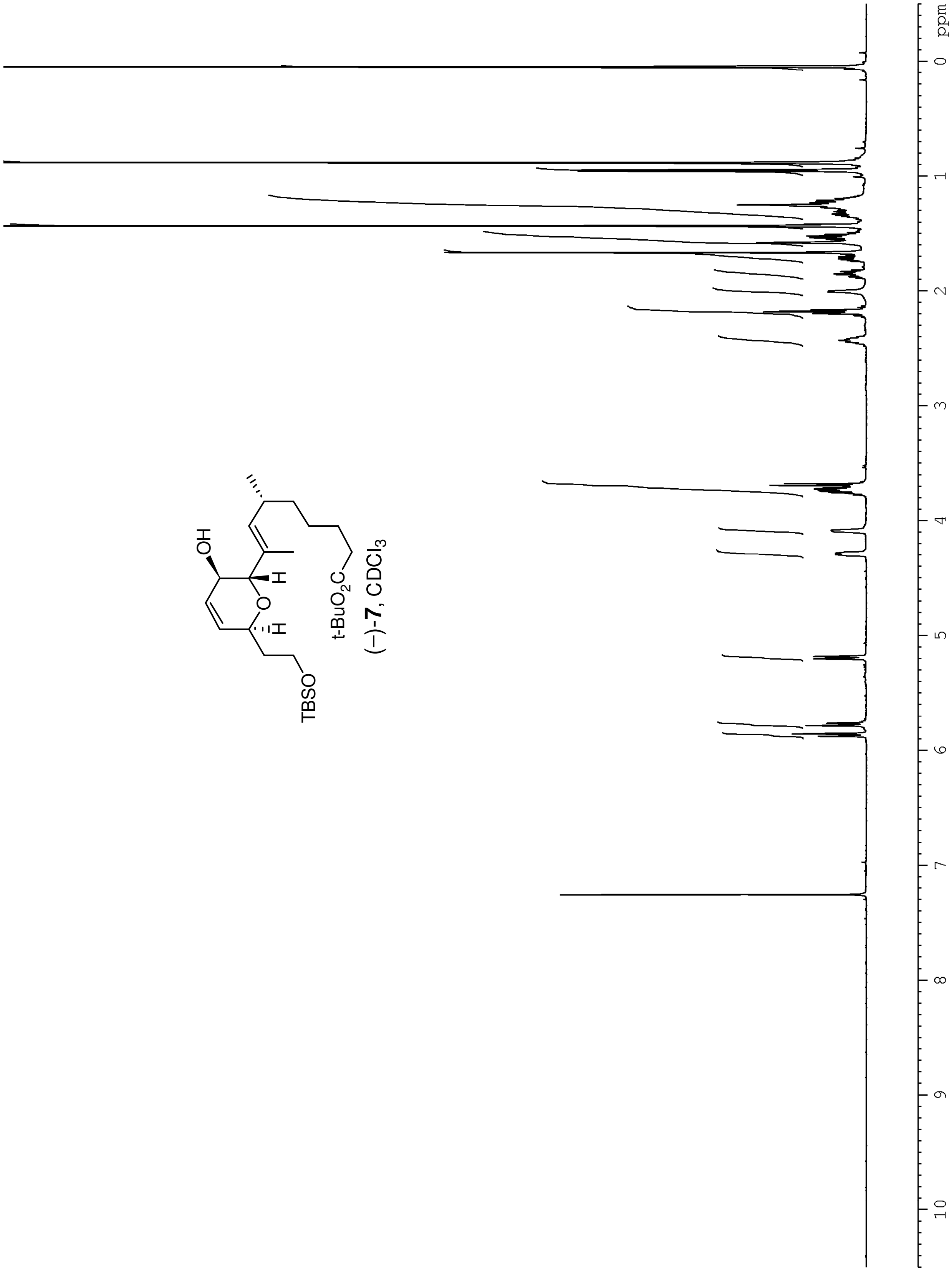
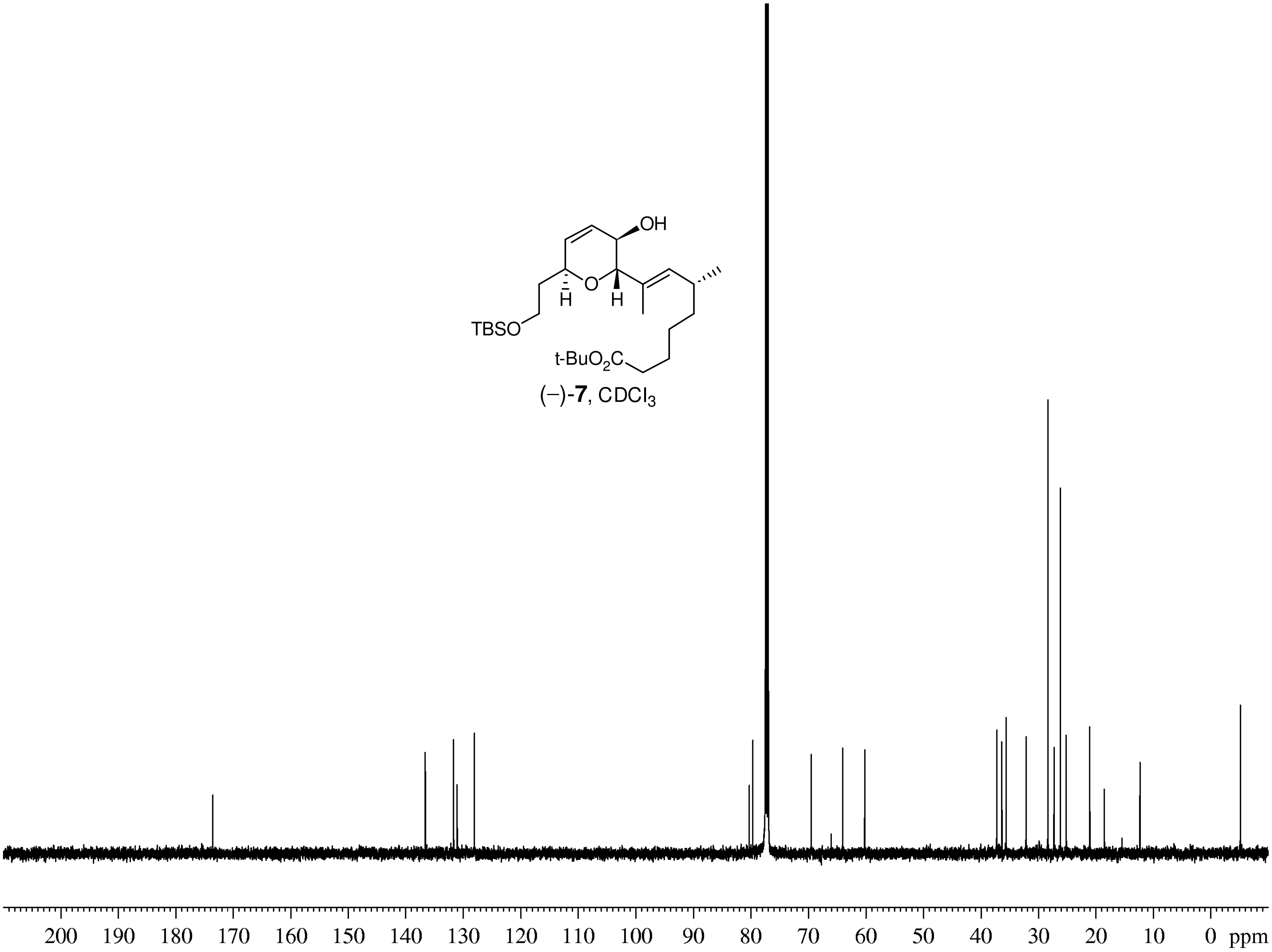
190
200

(−)-**S1**, CDCl$_3$



(−)-**7**, CDCl$_3$


OH
H
H
TBSO
t-BuO$_2$C
(−)-**7**, CDCl$_3$
200
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180
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150
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120
110
100
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80
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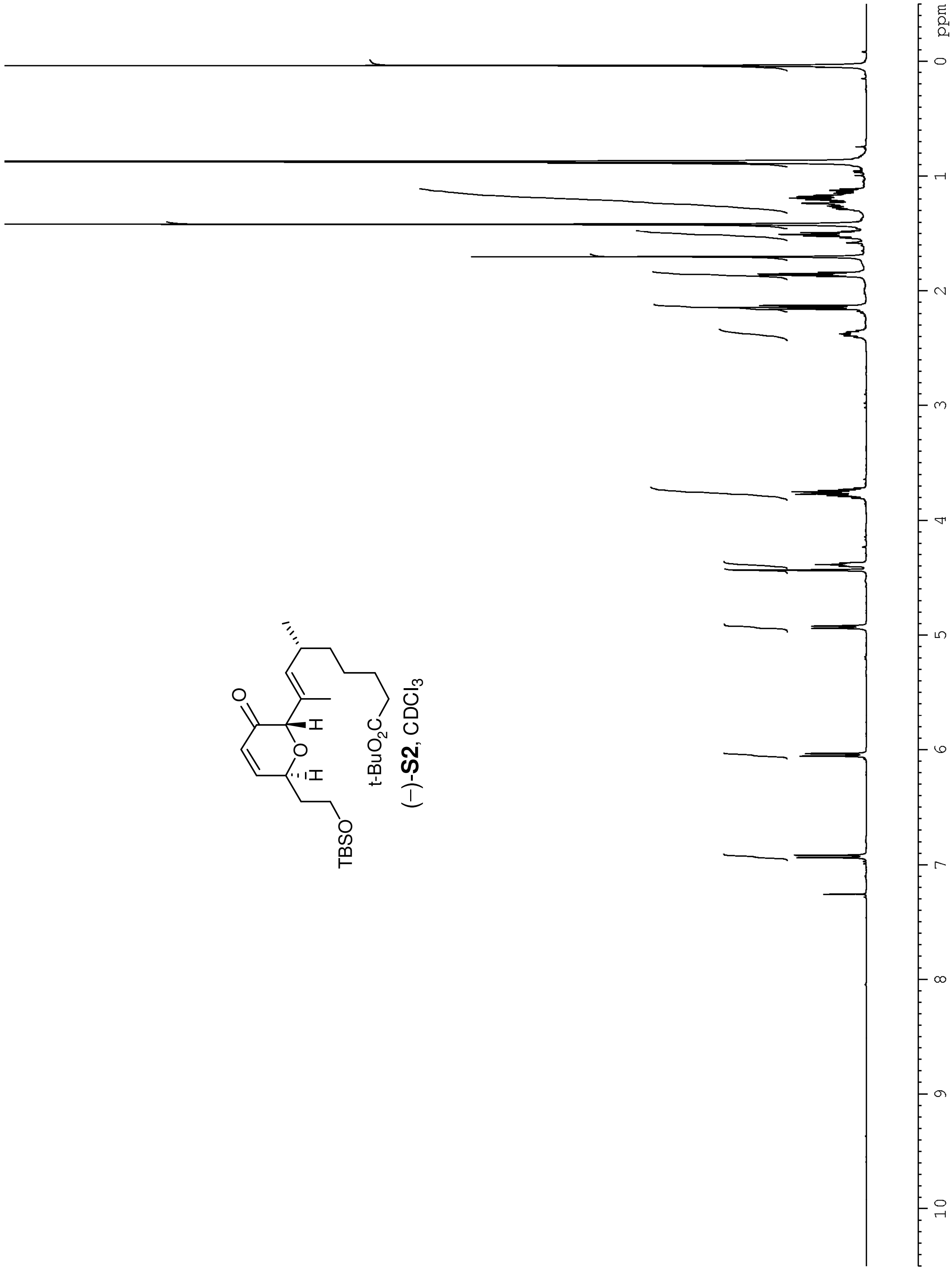
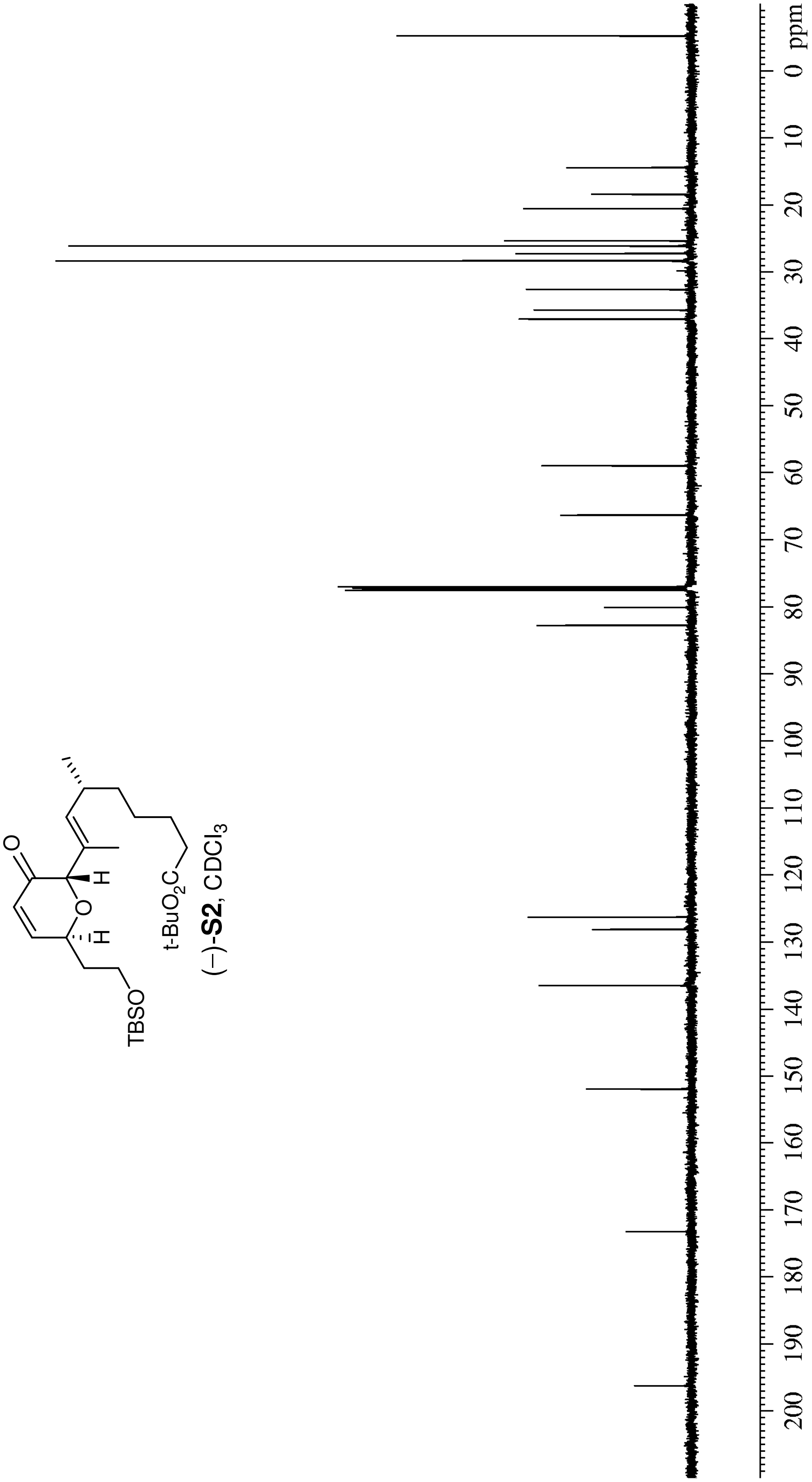
60
50
40
30
20
10
0
ppm



(−)-**S2**, CDCl$_3$


(−)-**S2**, $CDCl_3$
TBSO
O
H
t-BuO2C
ppm
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20
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60
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150
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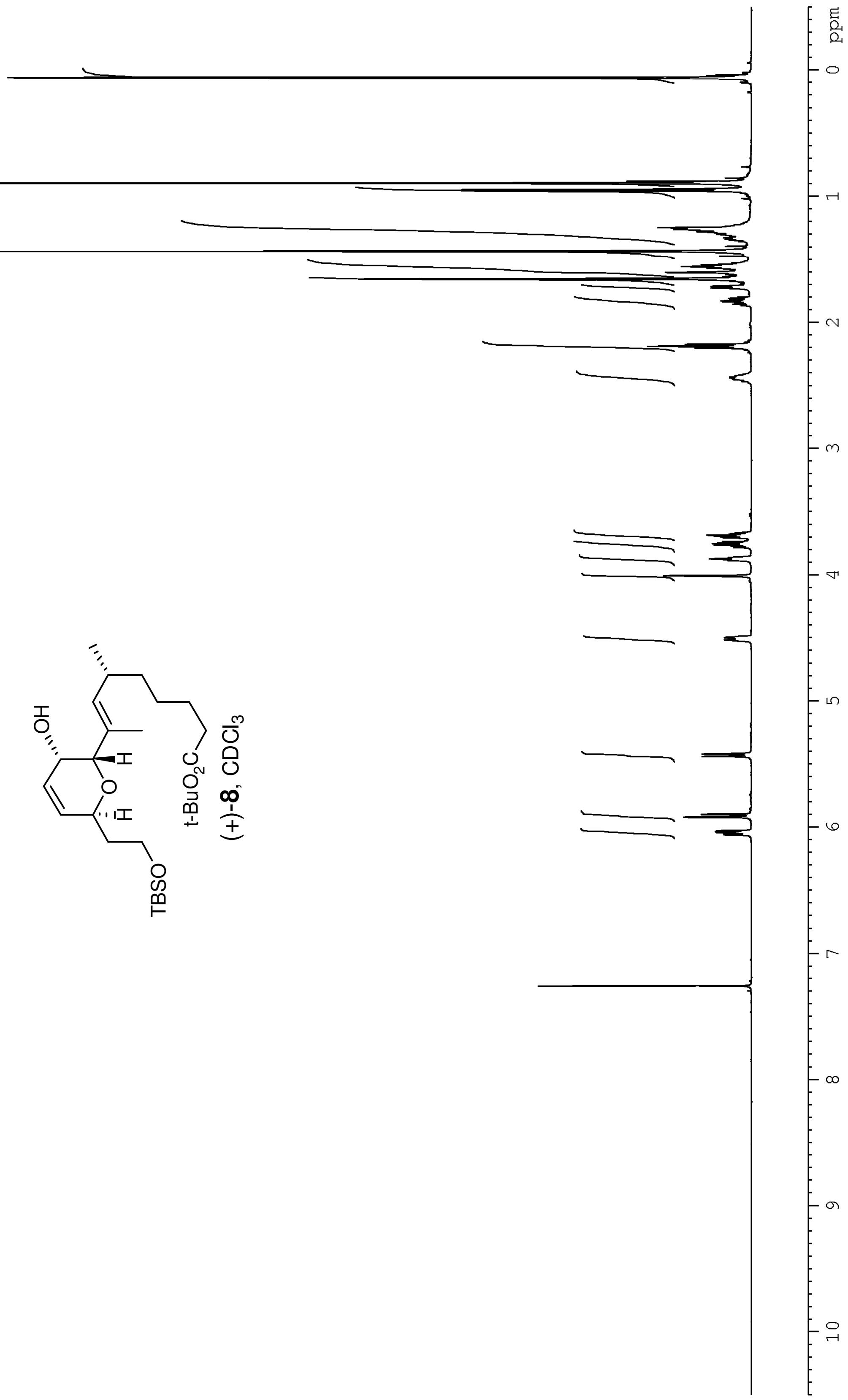
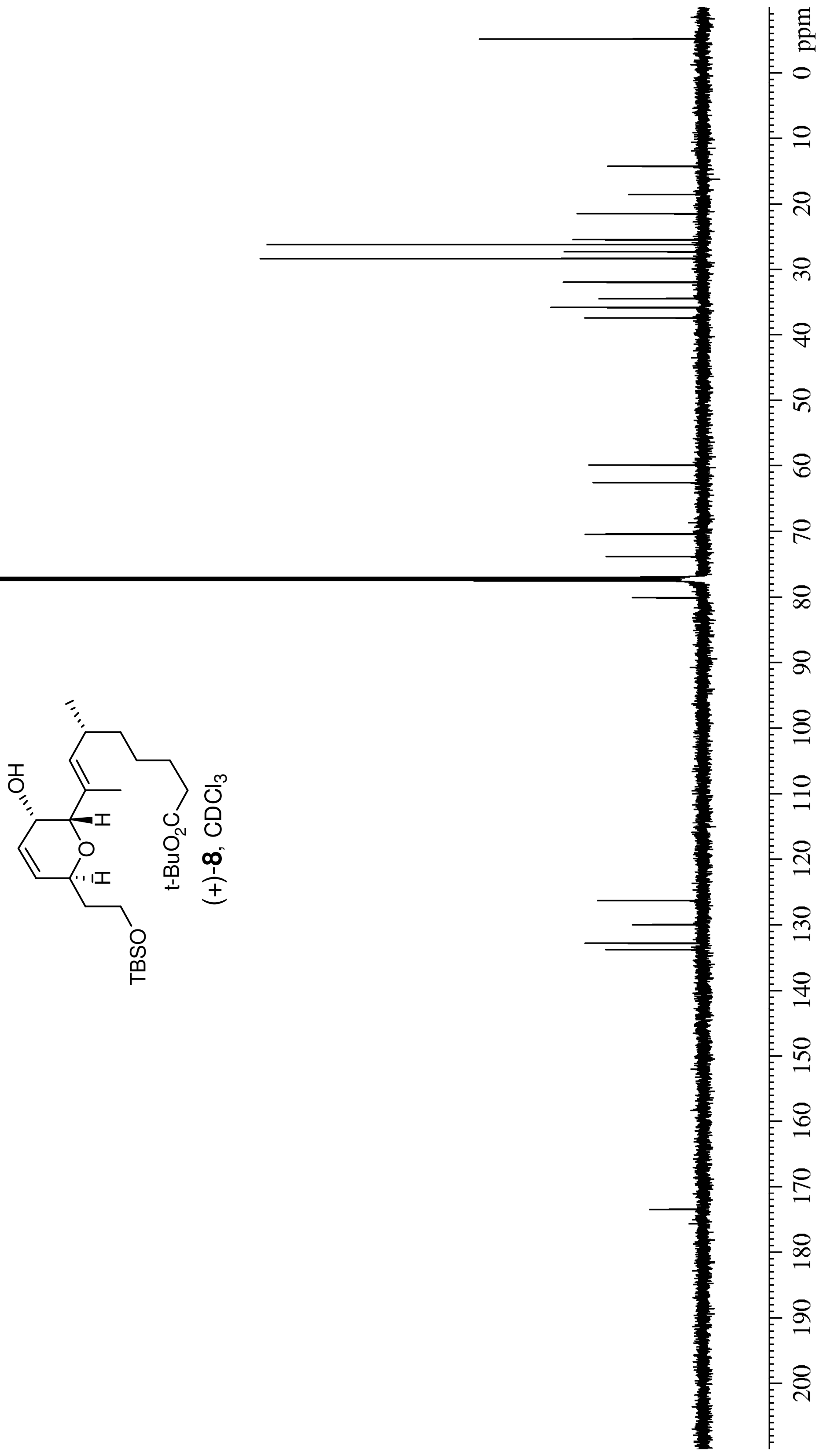
170
180
190
200



(+)-**8**, $CDCl_3$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OH
O
H
H
t-BuO$_2$C
200
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180
170
160
150
140
130
120
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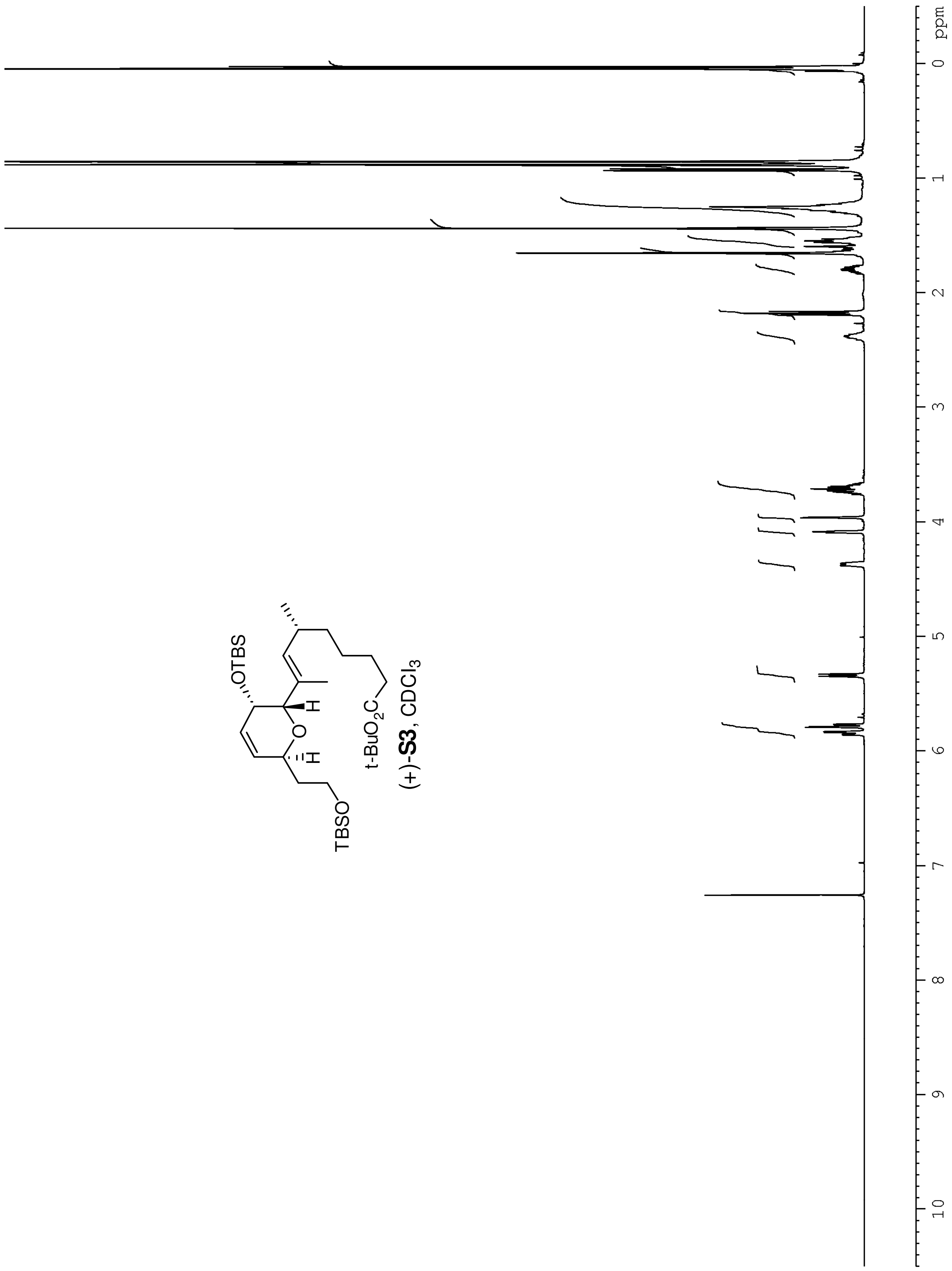
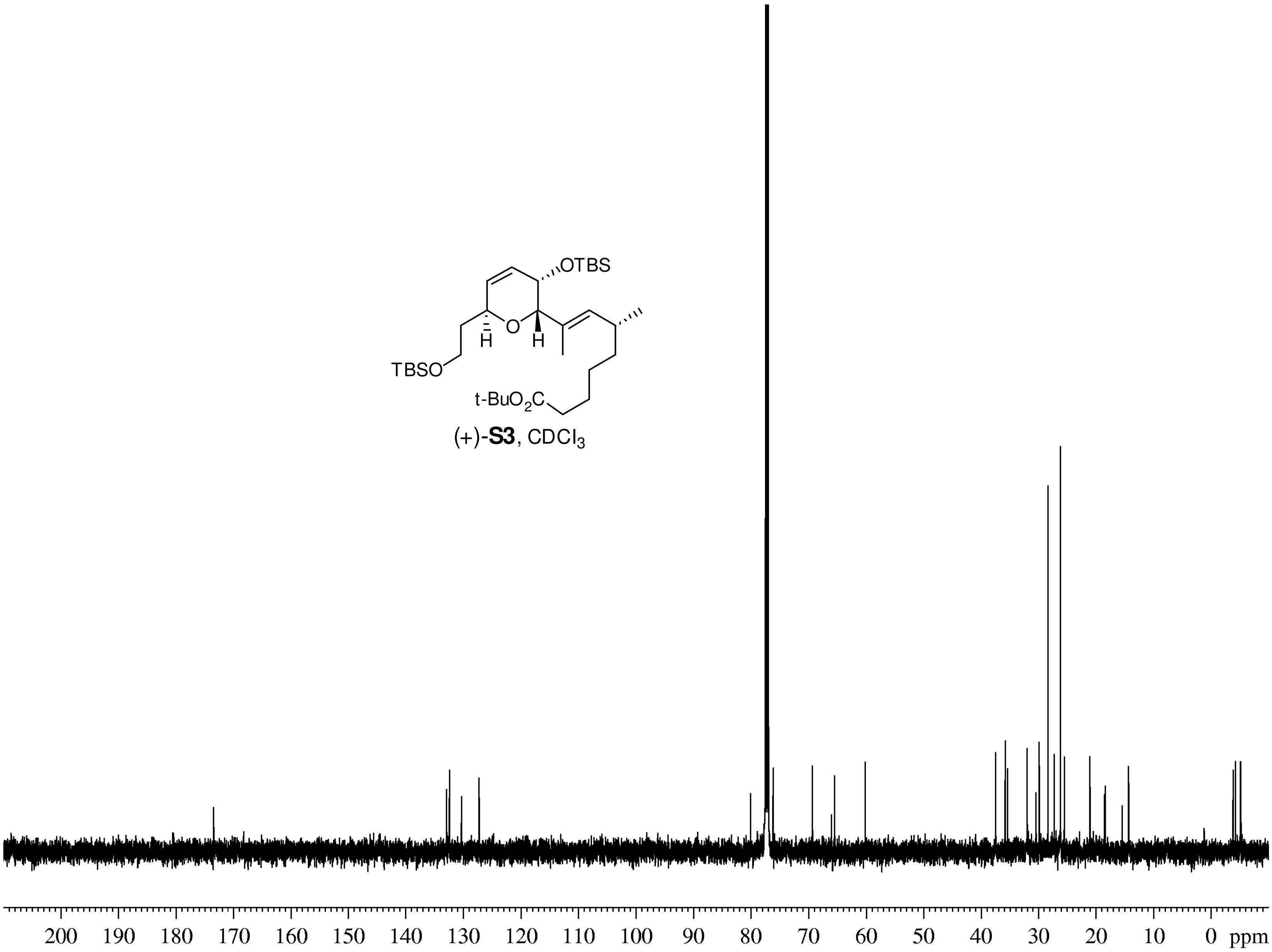
100
90
80
70
60
50
40
30
20
10
0
ppm

(+)-**8**, $CDCl_3$



(+)-**S3**, CDCl$_3$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TBSO
O
H
H
t-BuO$_2$C
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180
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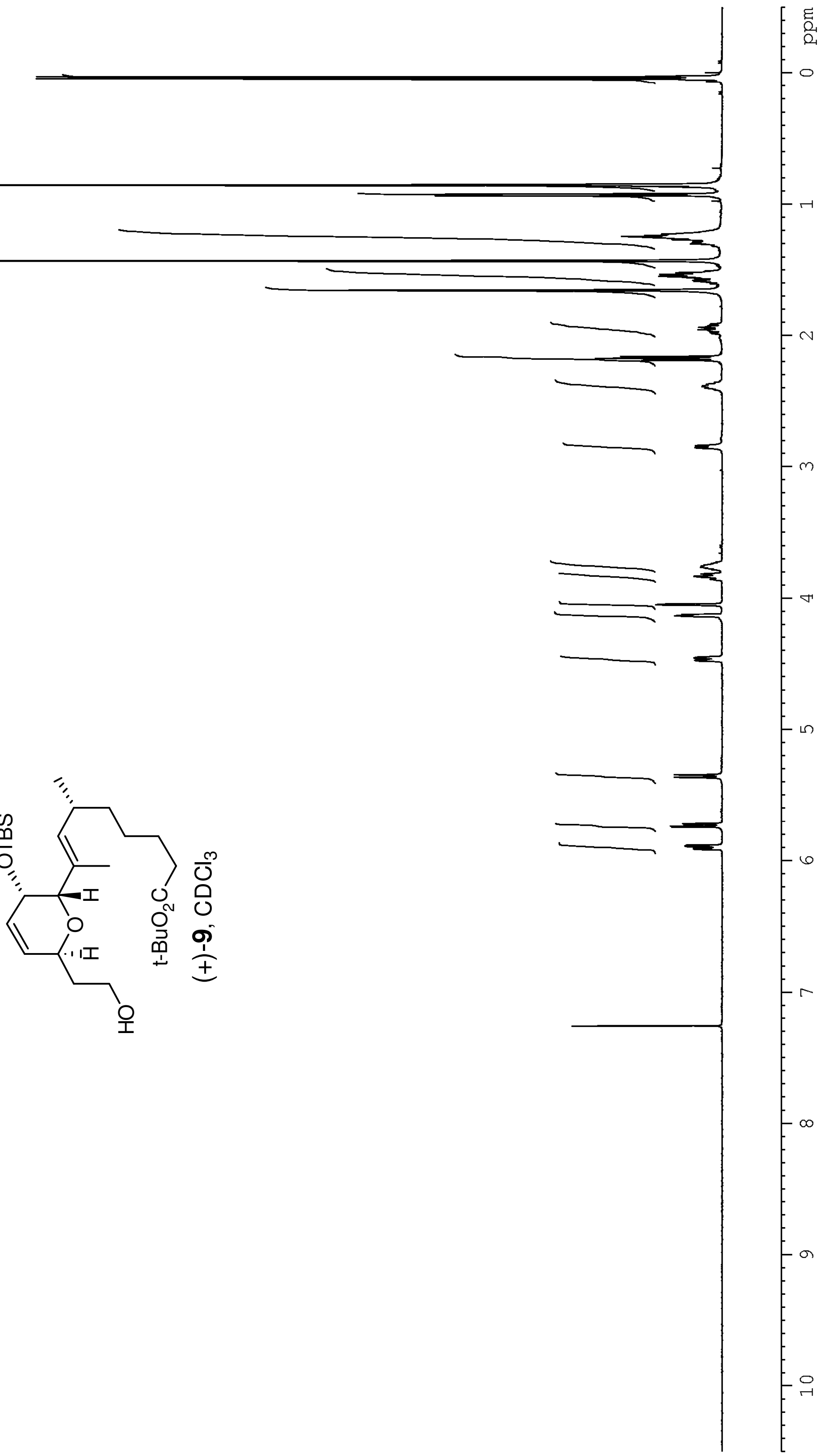
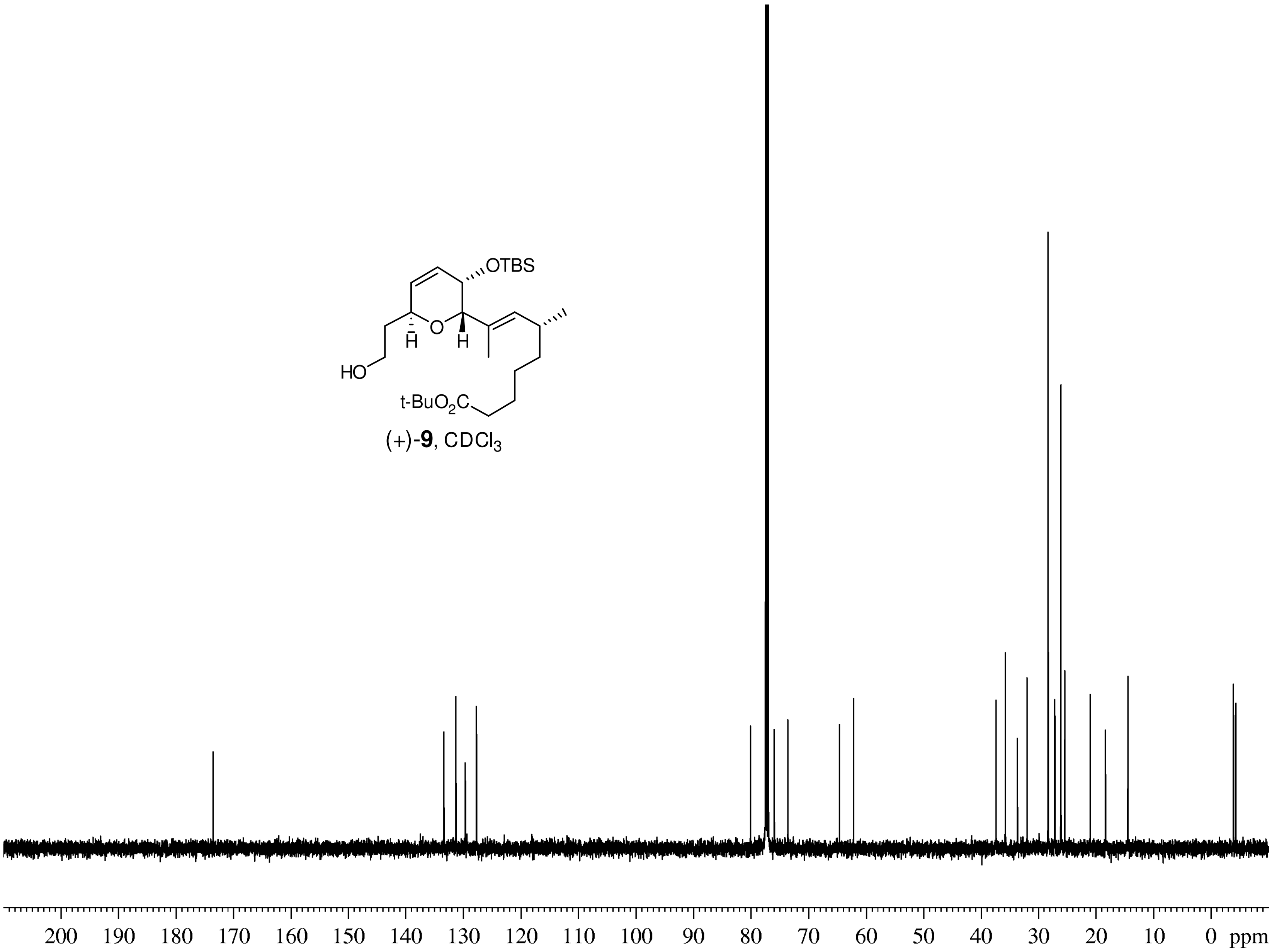
20
10
0
ppm

(+)-**S3**, $CDCl_3$



(+)-**9**, $CDCl_3$


OTBS
HO
O
H
H
t-BuO$_2$C
200
190
180
170
160
150
140
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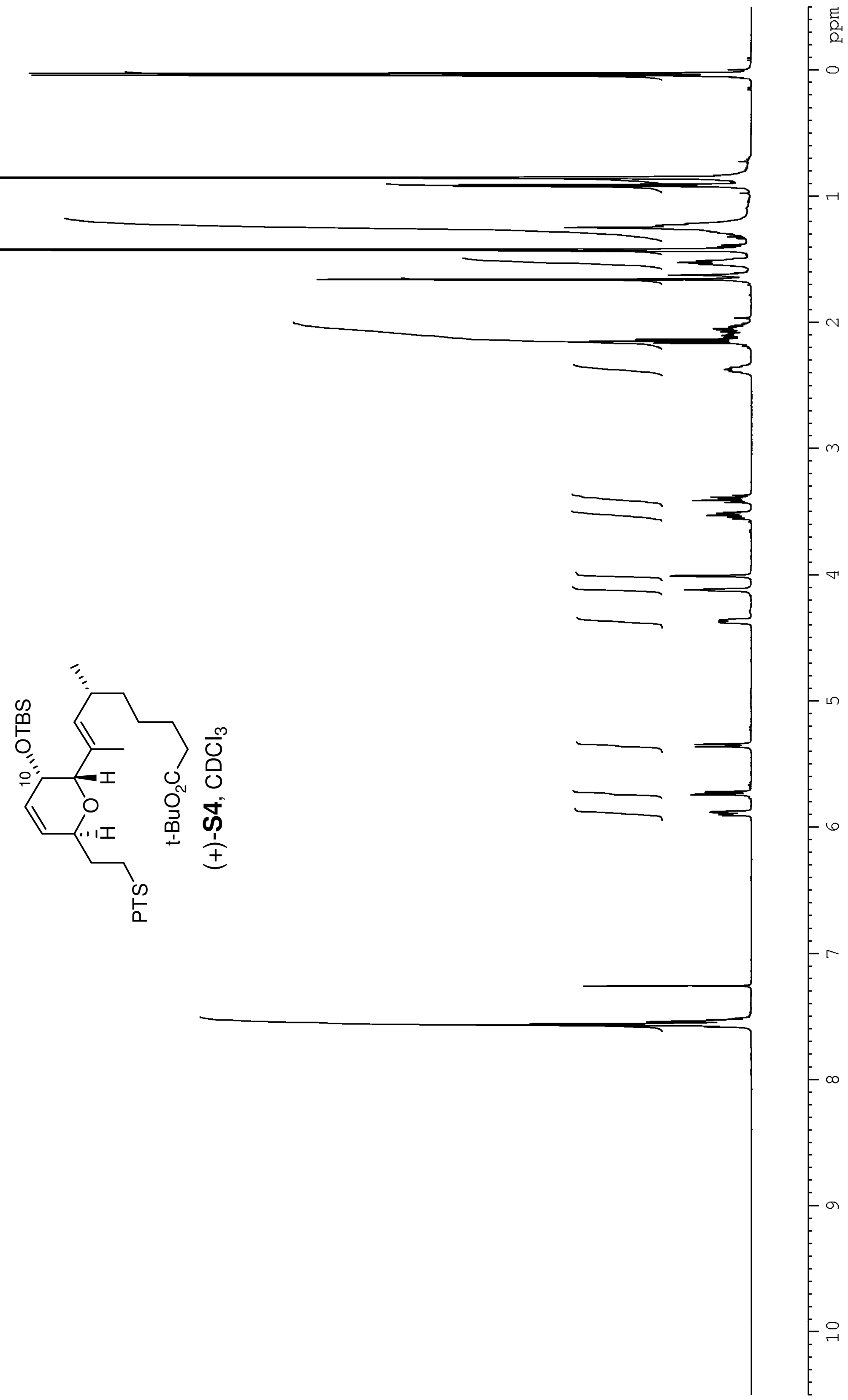
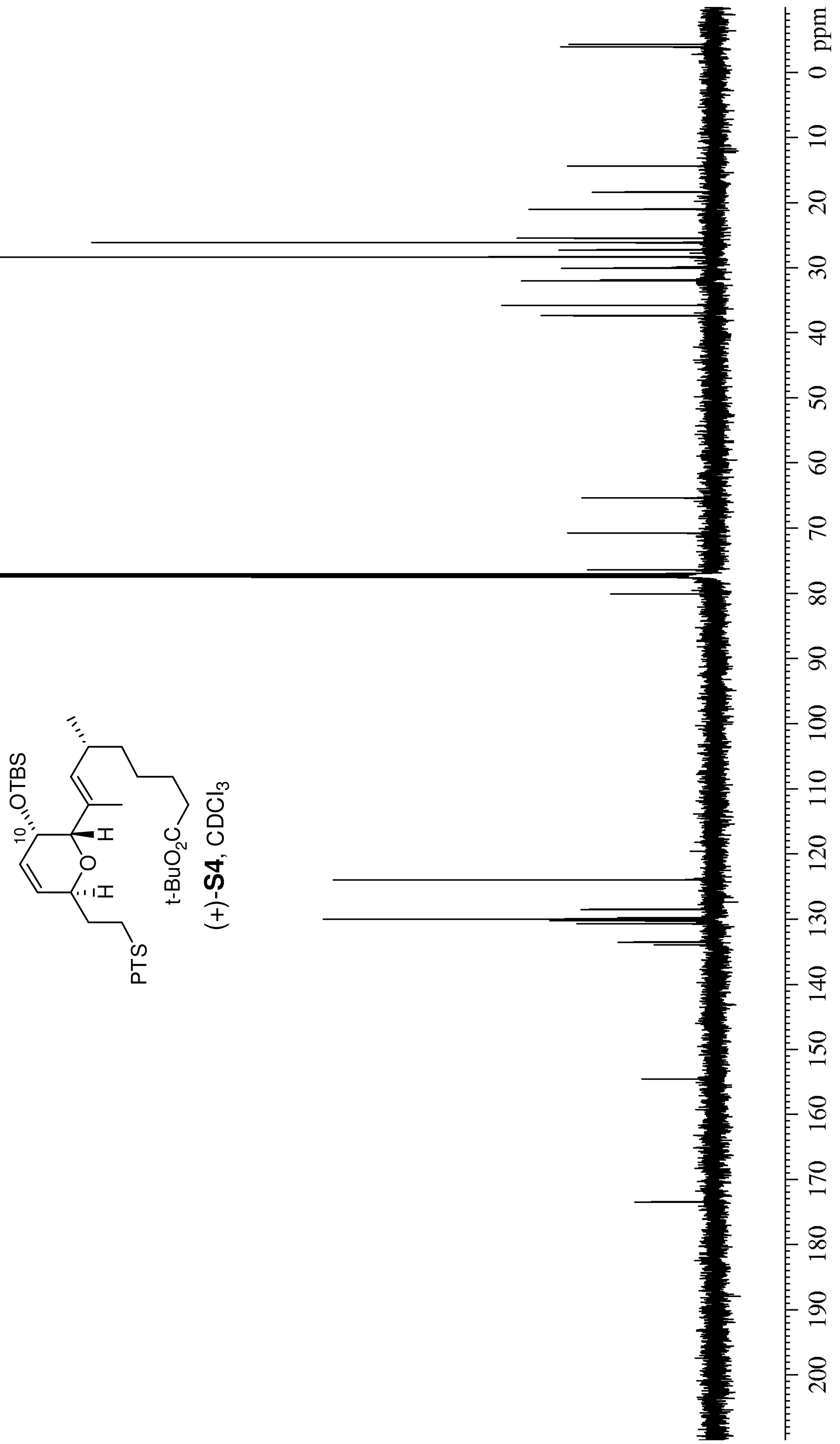
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

(+)-**9**, $CDCl_3$



(+)-**S4**, $CDCl_3$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PTS
O
H
H
t-BuO$_2$C
ppm
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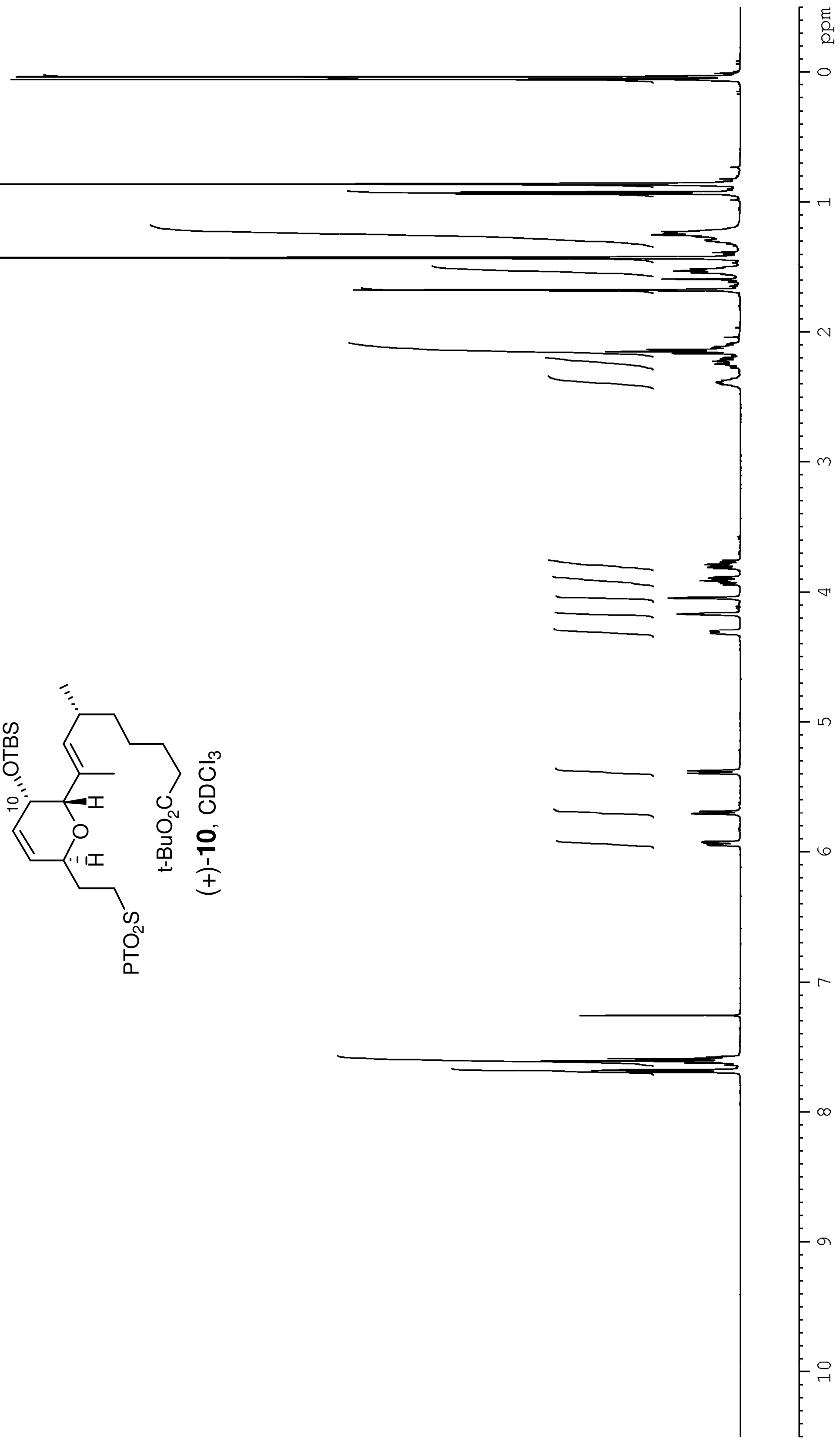
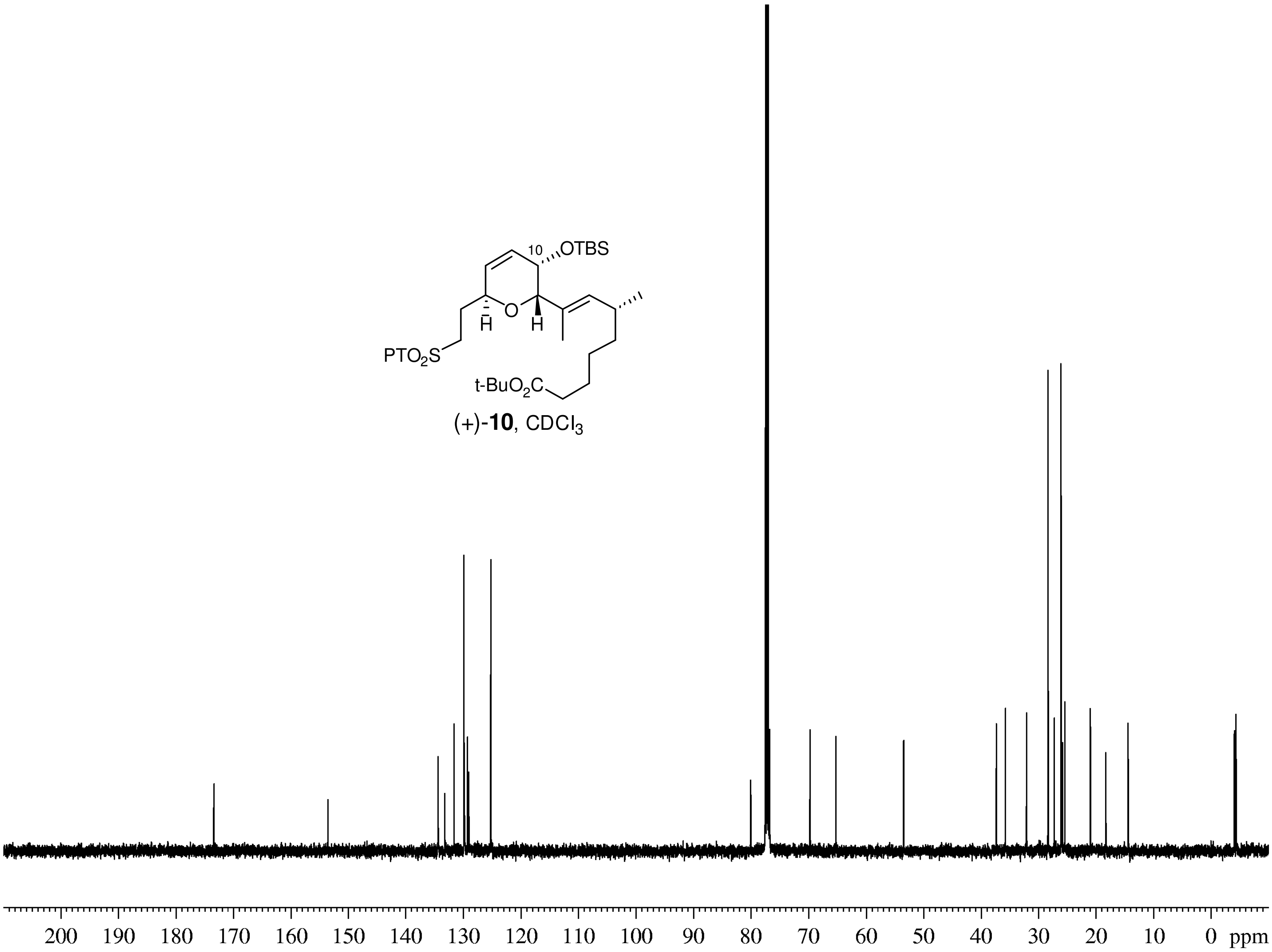
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

(+)-**S4**, $CDCl_3$



(+)-**10**, CDCl$_3$


PTO$_2$S
10
OTBS
H
O
H
t-BuO$_2$C
200
190
180
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20
10
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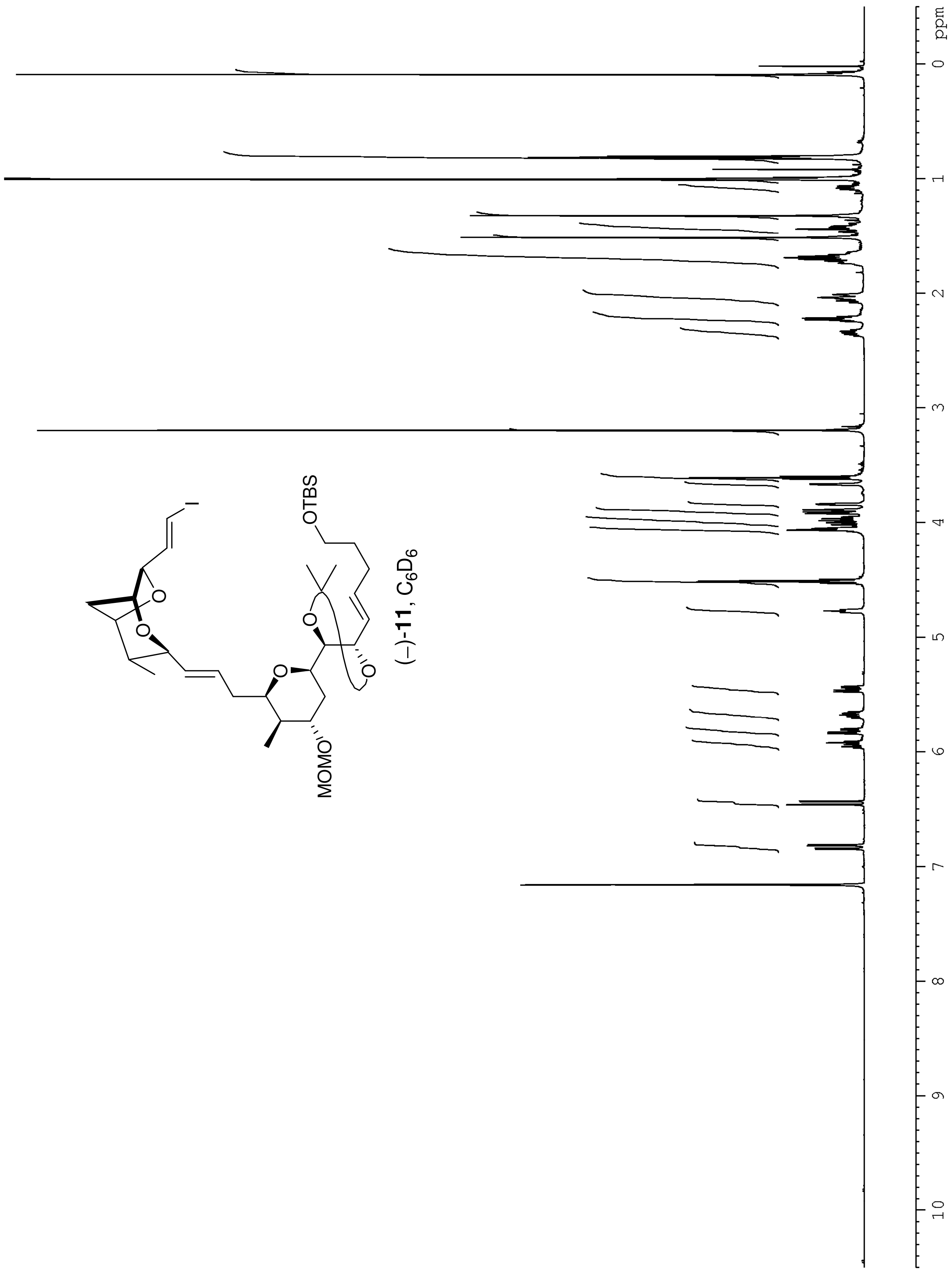
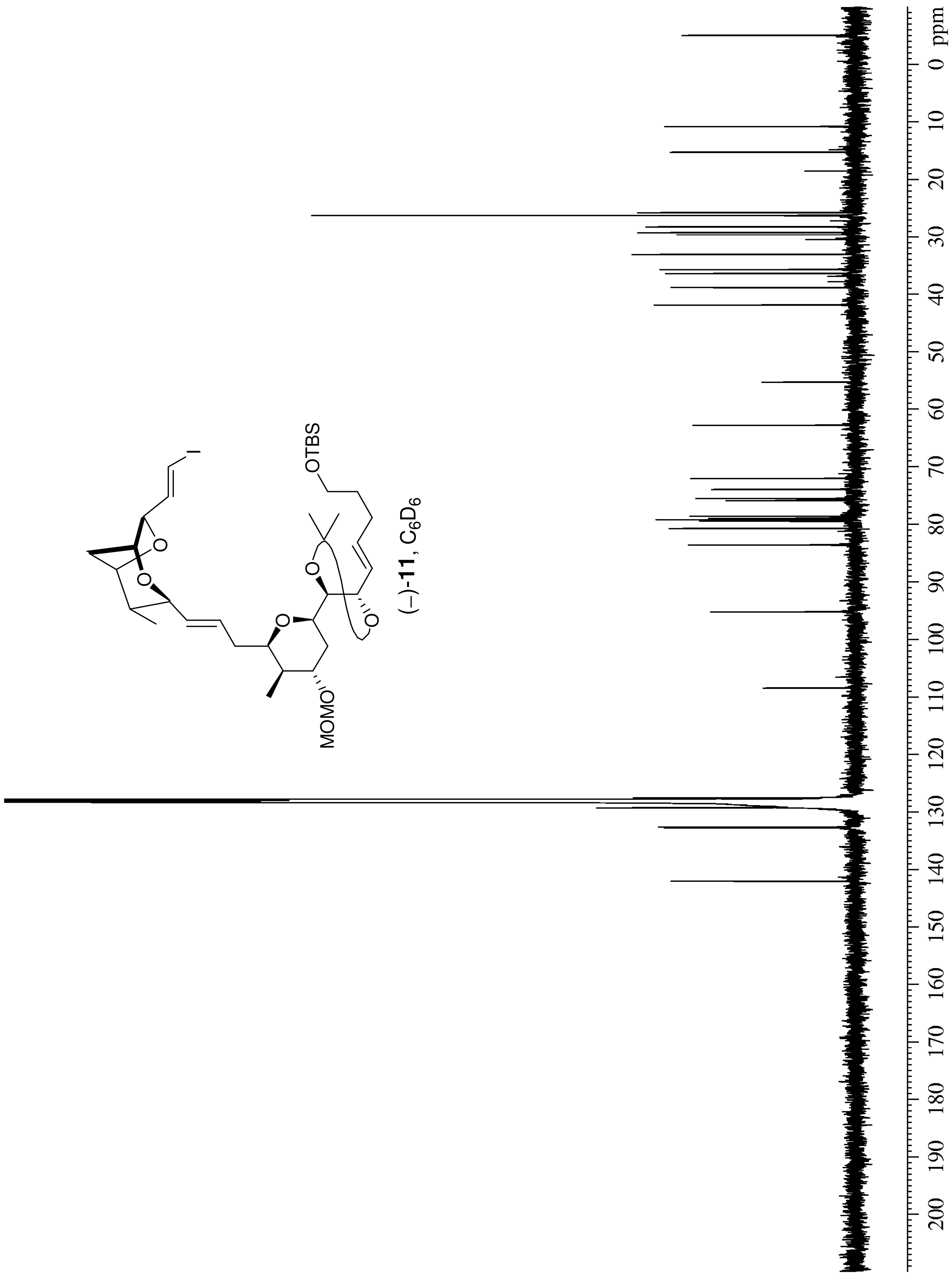
ppm

(+)-**10**, CDCl$_3$



(–)-**11**, C_6D_6


(–)-**11**, C_6D_6

OTBS
MOMO
O
I
ppm
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20
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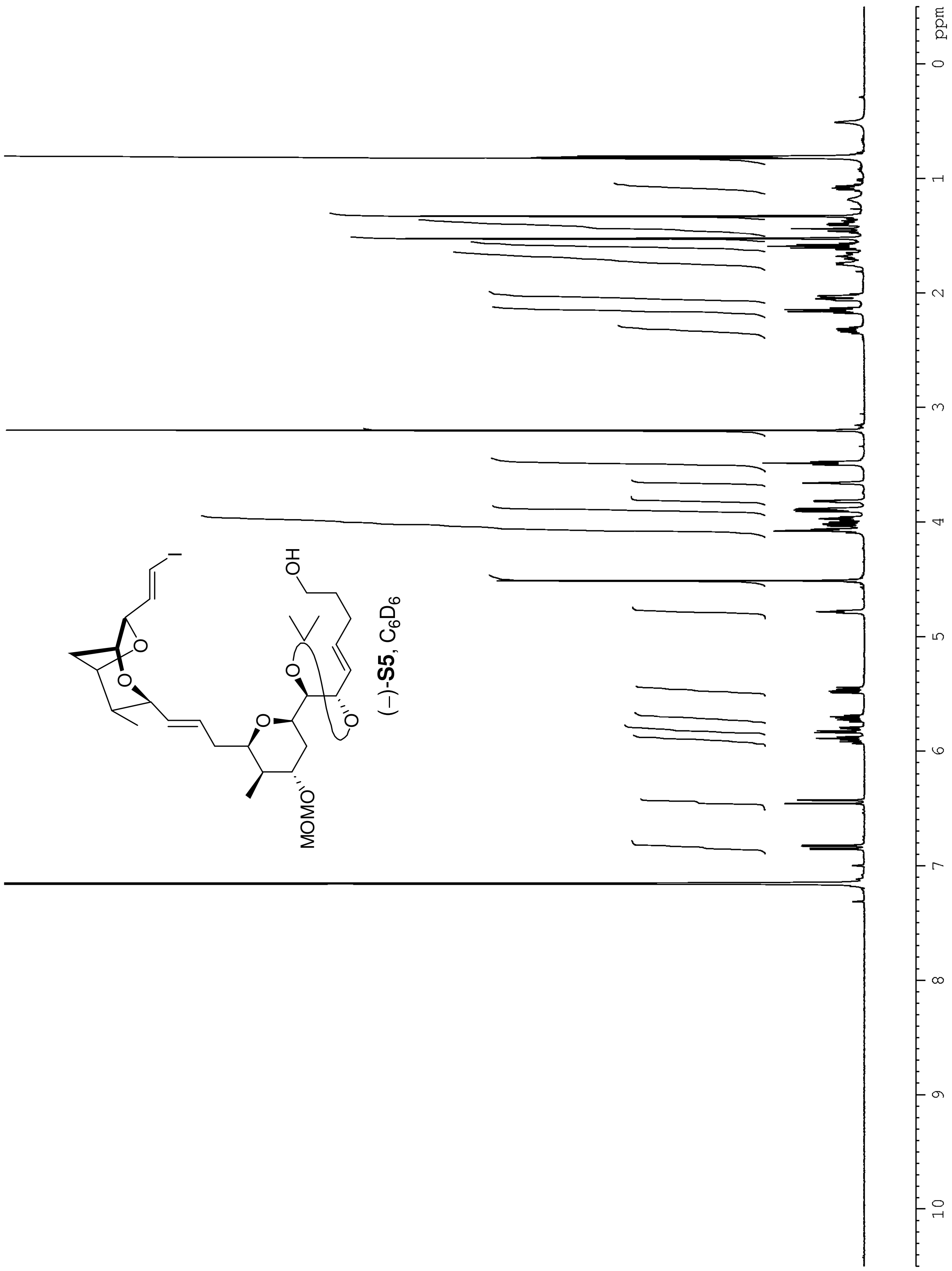
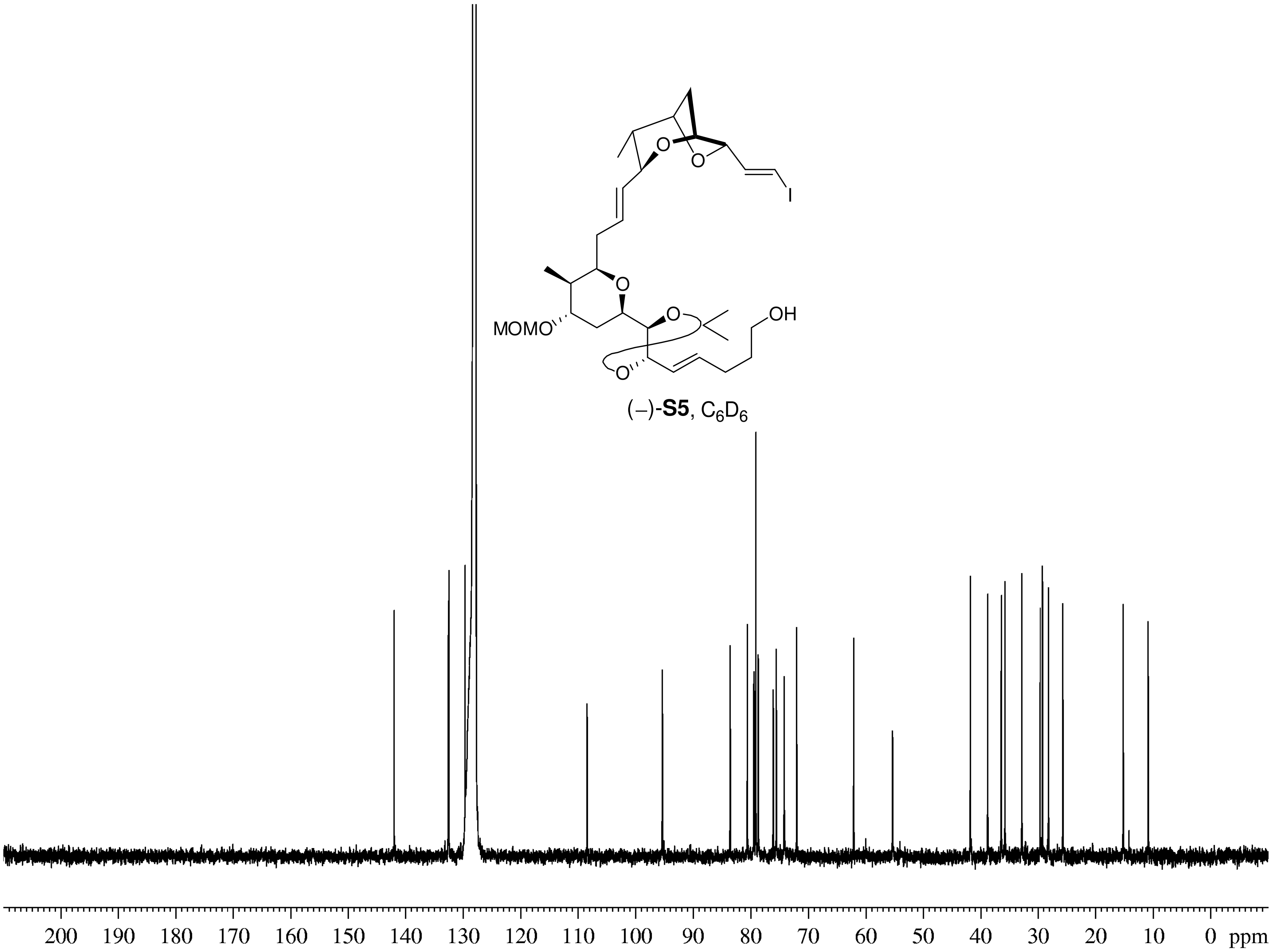
180
190
200

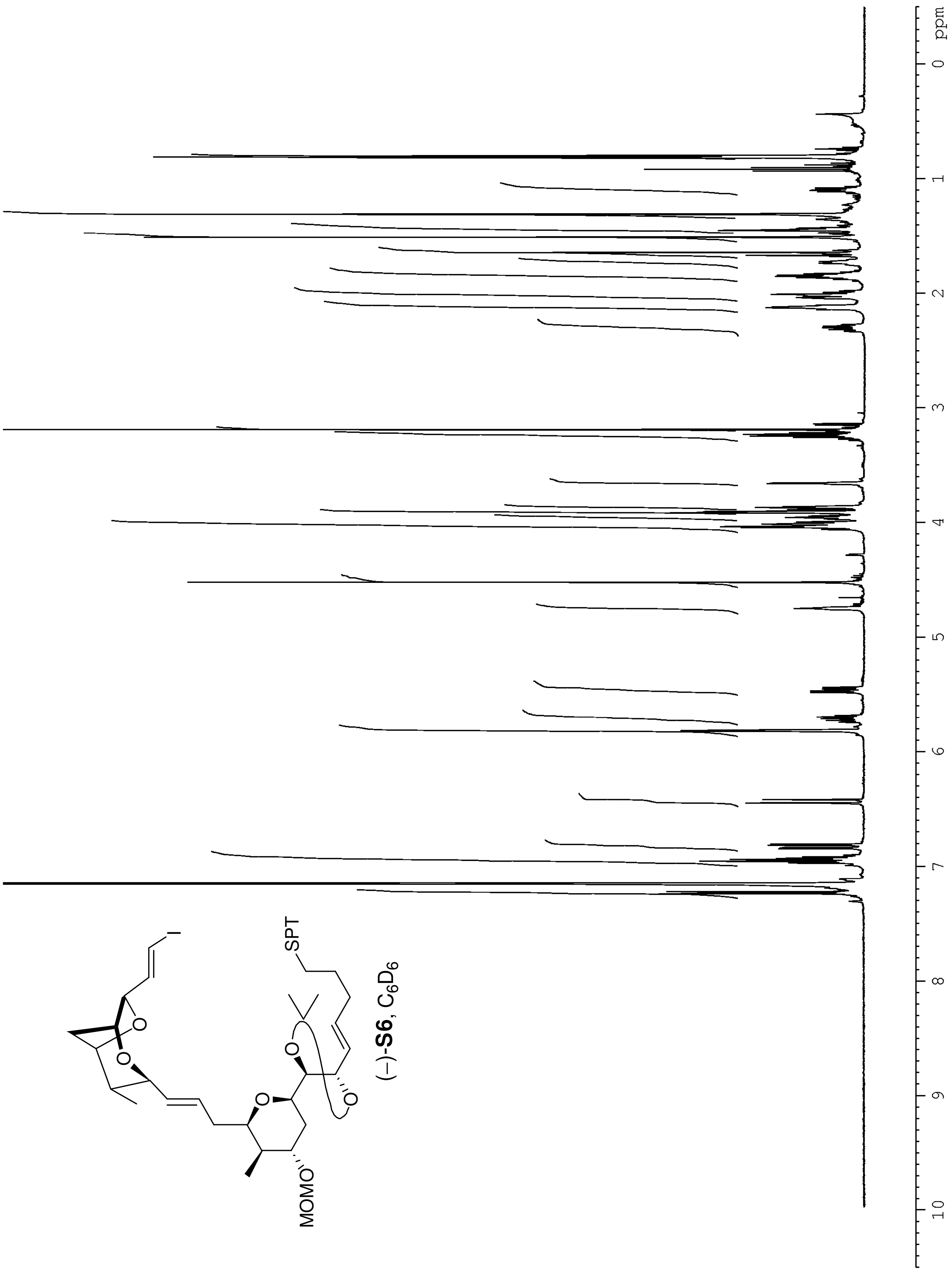


(−)-**S5**, C_6D_6

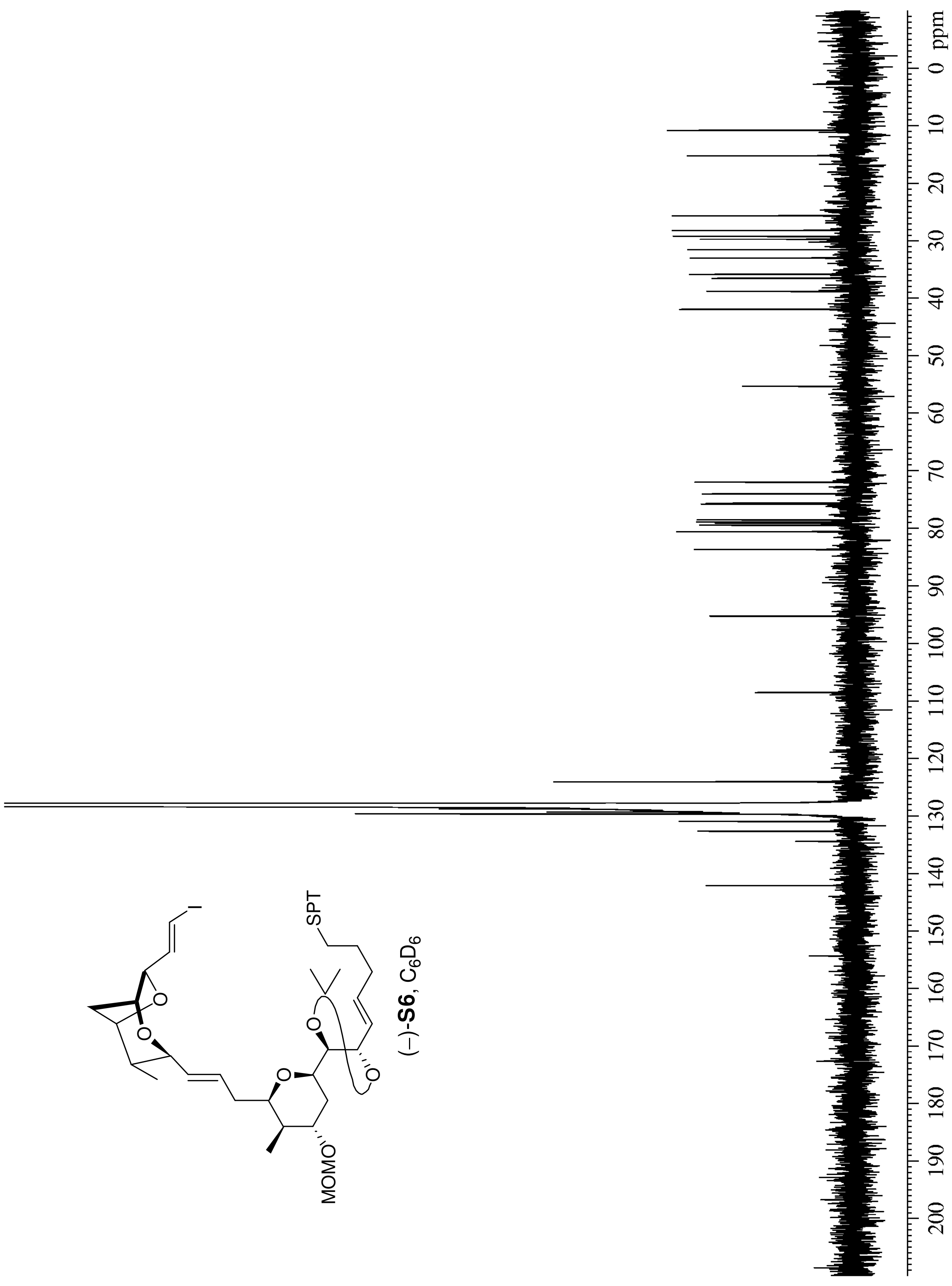


(−)-**S5**, C_6D_6

MOMO
O
OH
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



(–)-**S6**, C_6D_6


MOMO
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O
O
O
O
SPT
I
ppm
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10
20
30
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70
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90
100
110
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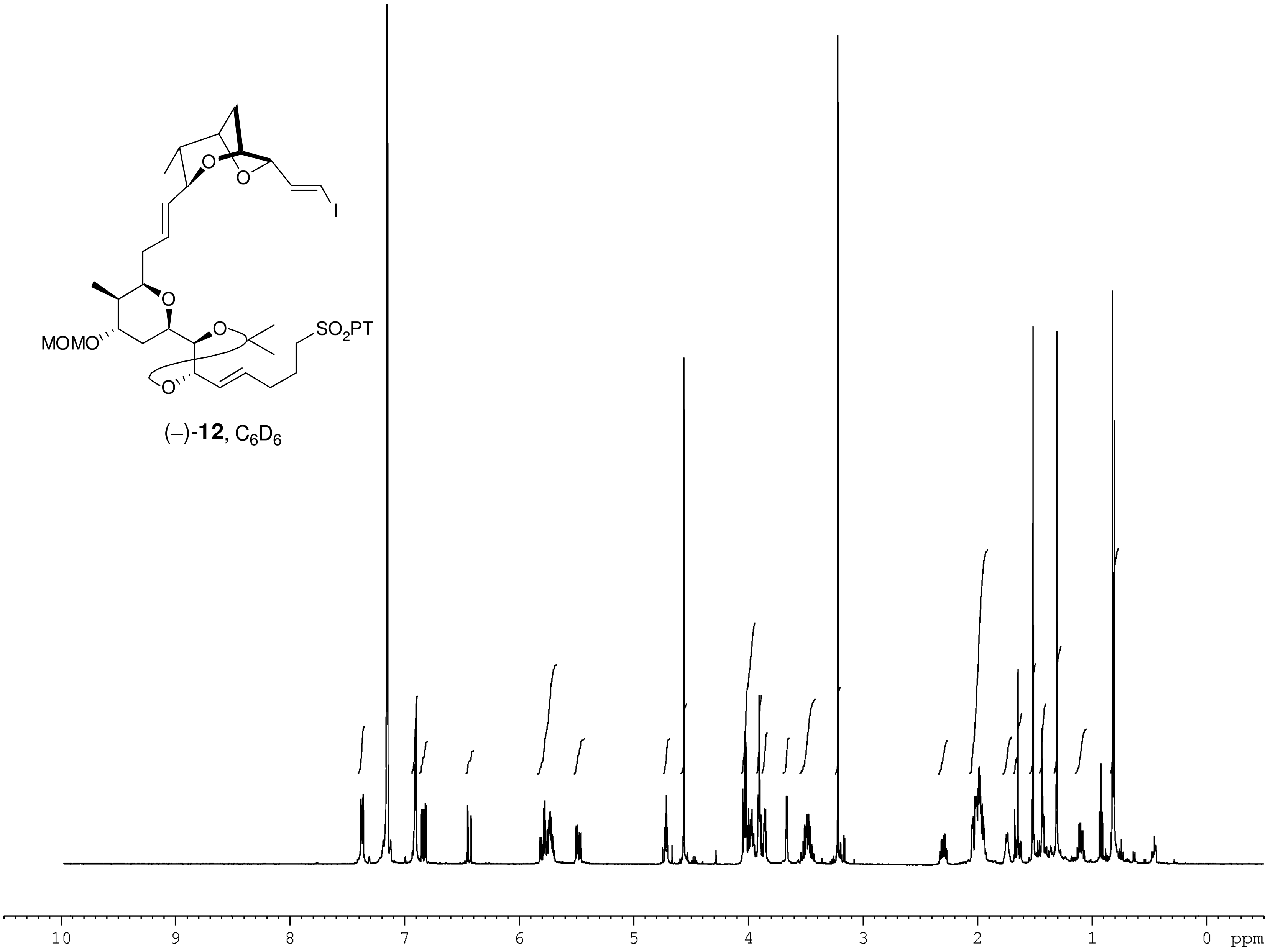
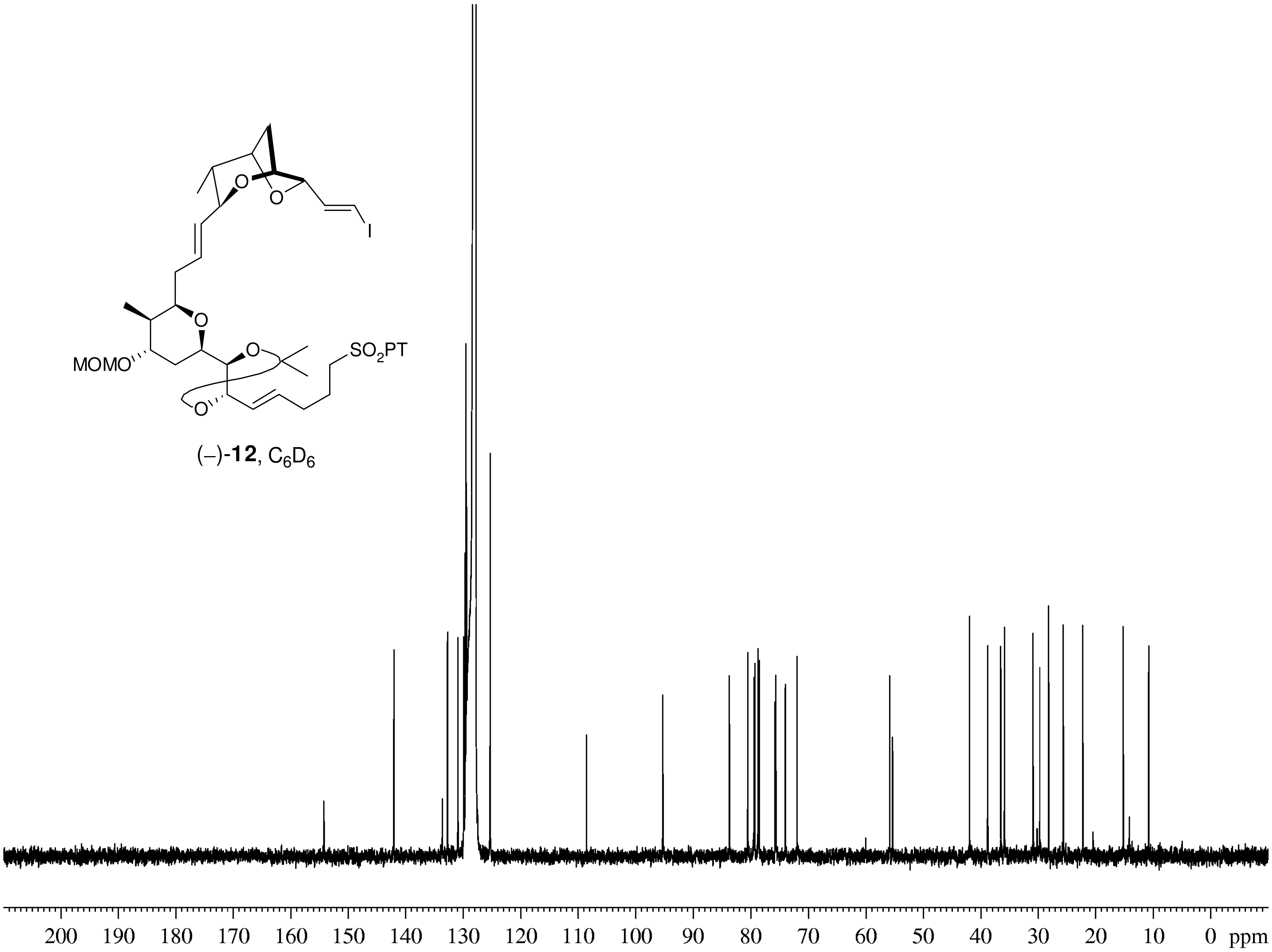
130
140
150
160
170
180
190
200

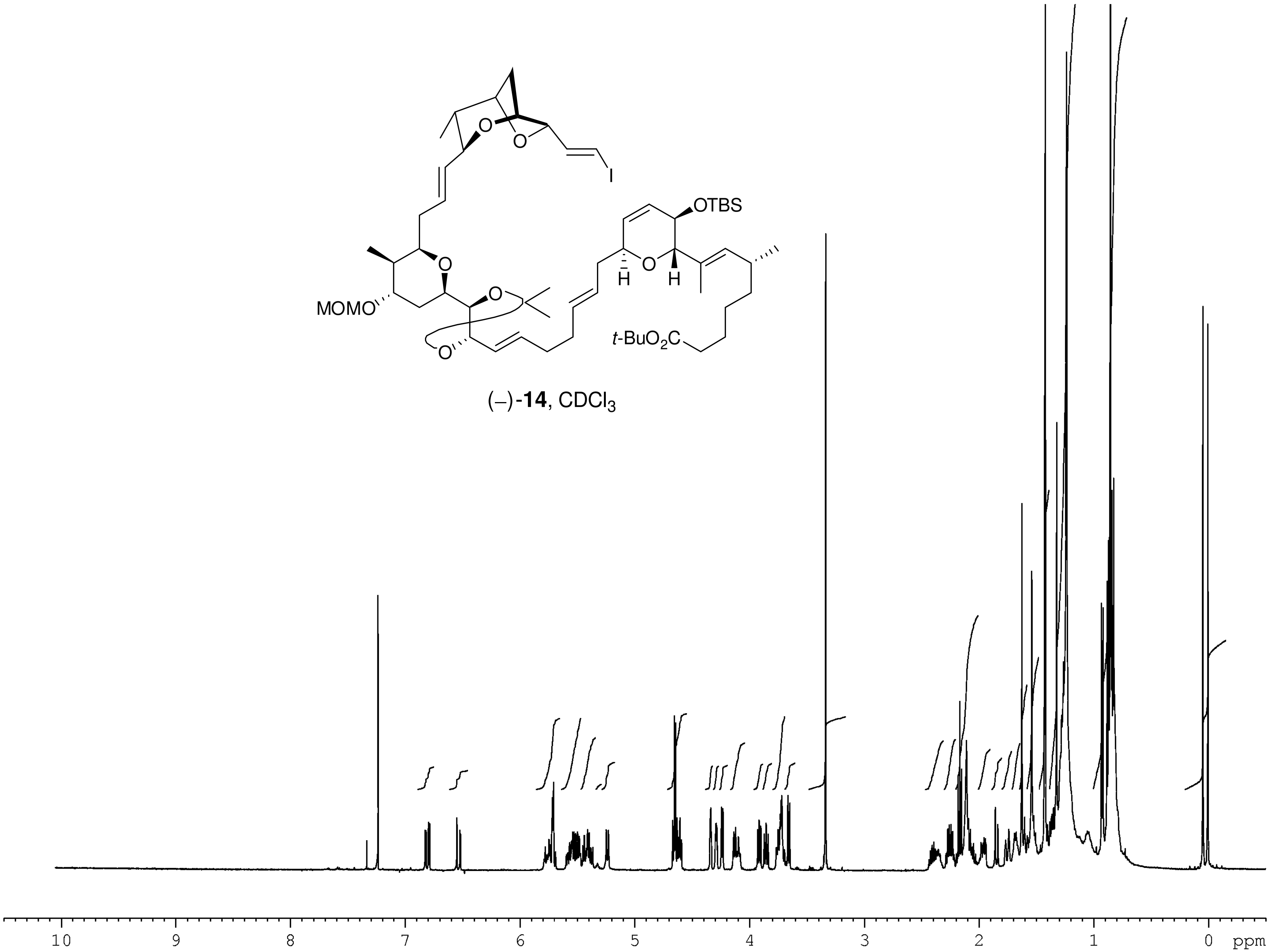
(–)-**S6**, C_6D_6



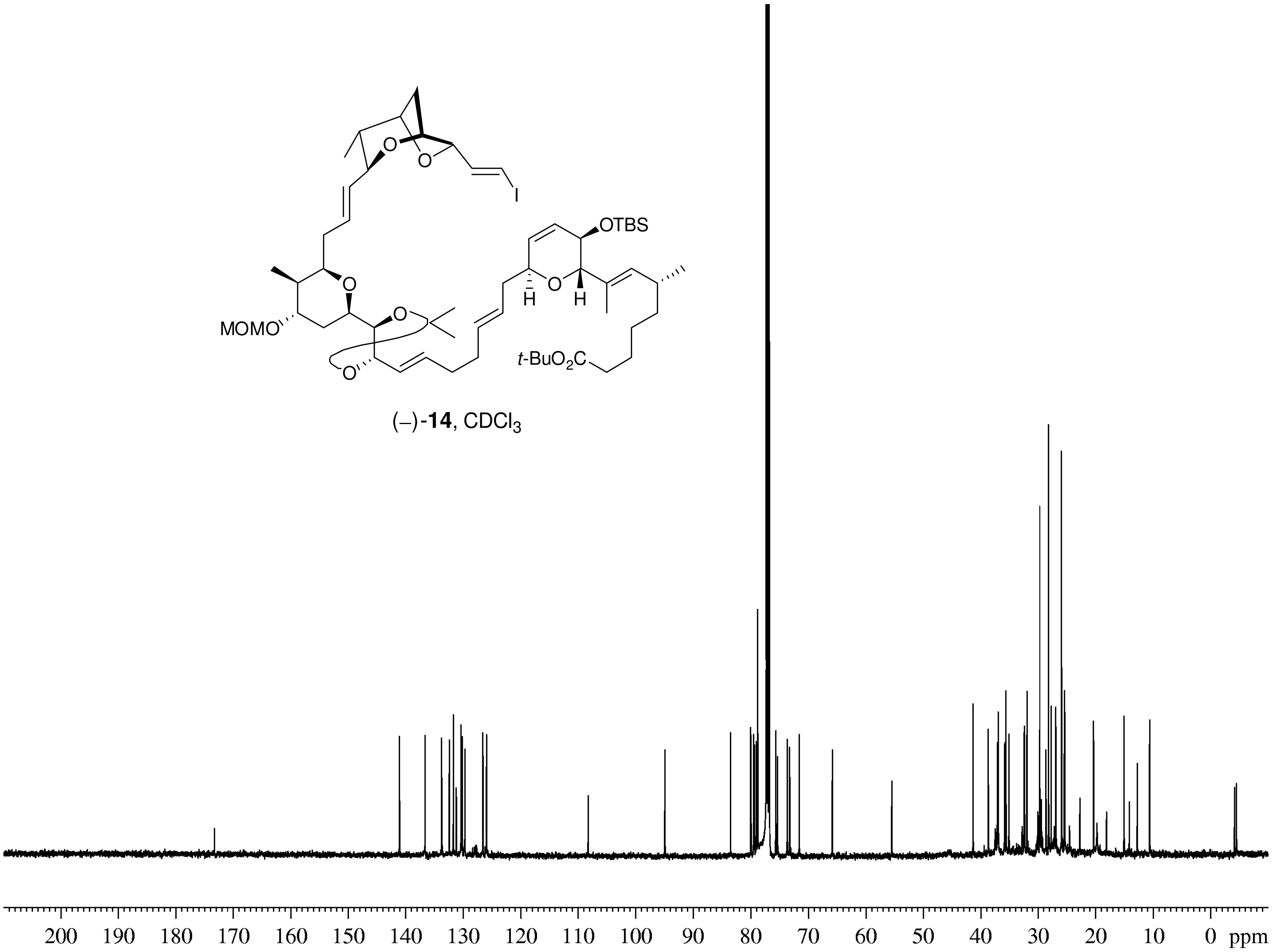
(–)-**12**, C_6D_6


MOMO
O
O
O
O
O
I
SO2PT
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

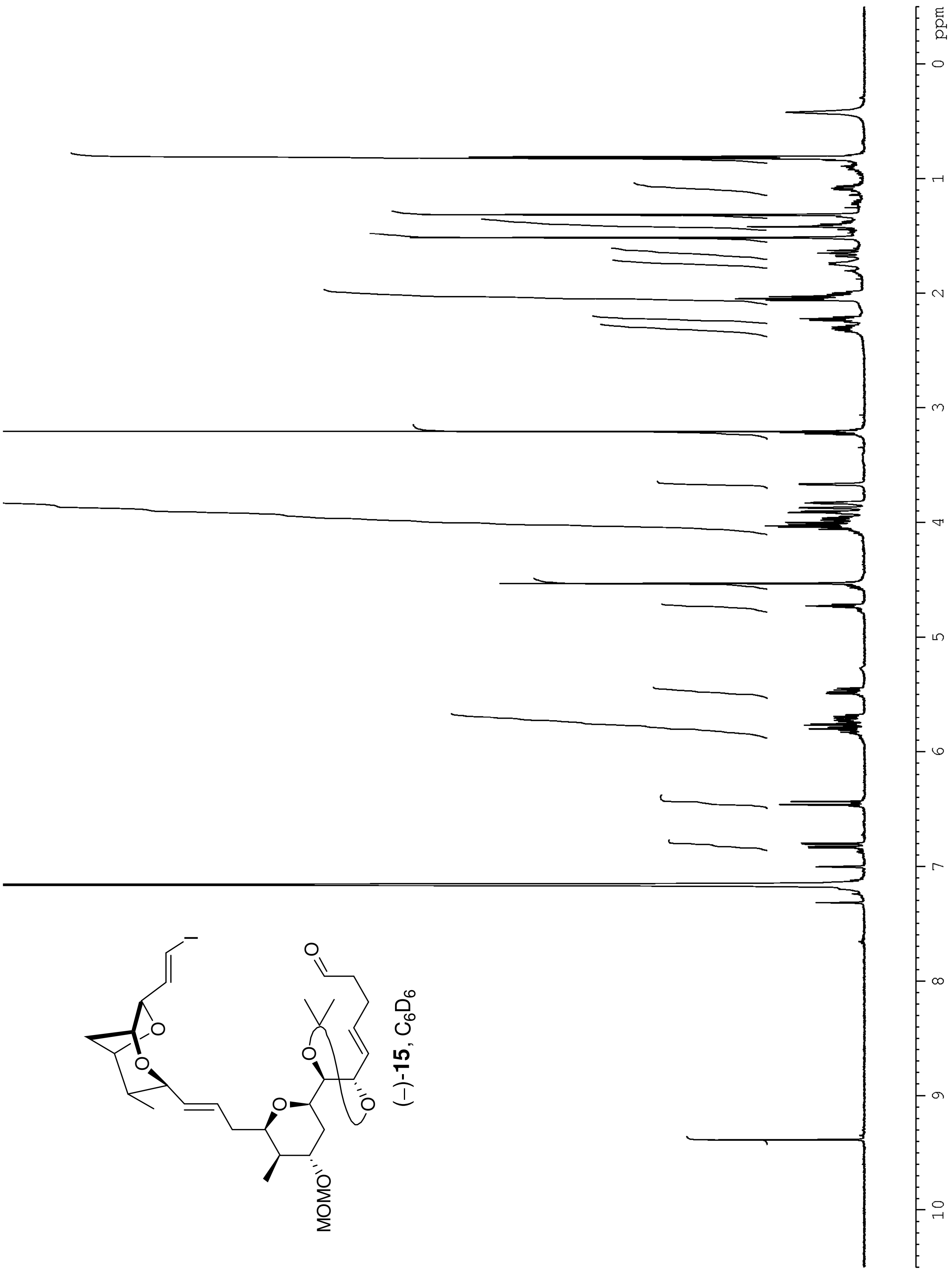
(–)-**12**, C_6D_6



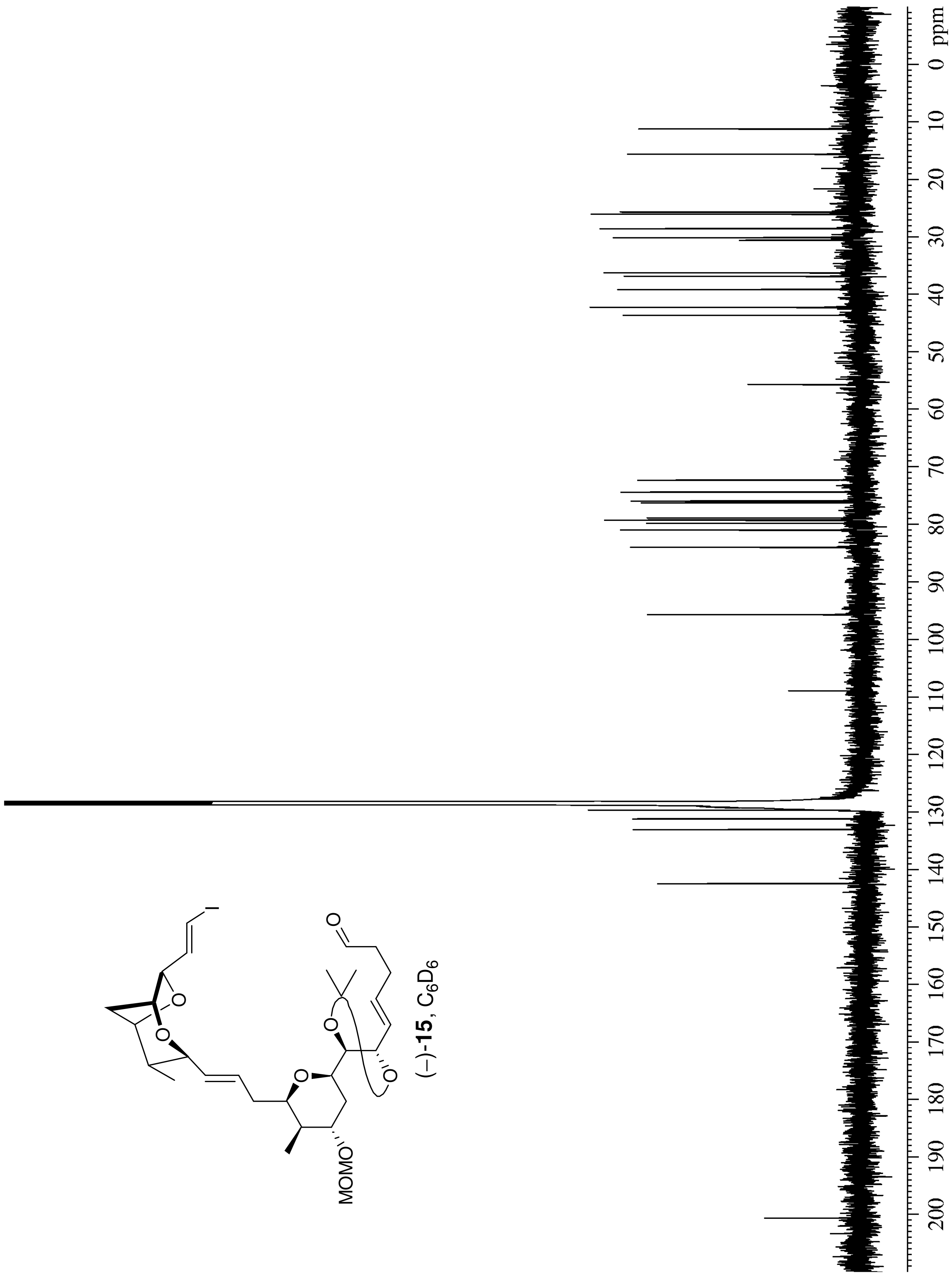
(−)-**14**, CDCl$_3$


MOMO
O
O
O
O
I
OTBS
O
H
H
t-BuO2C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

(–)-**14**, $CDCl_3$

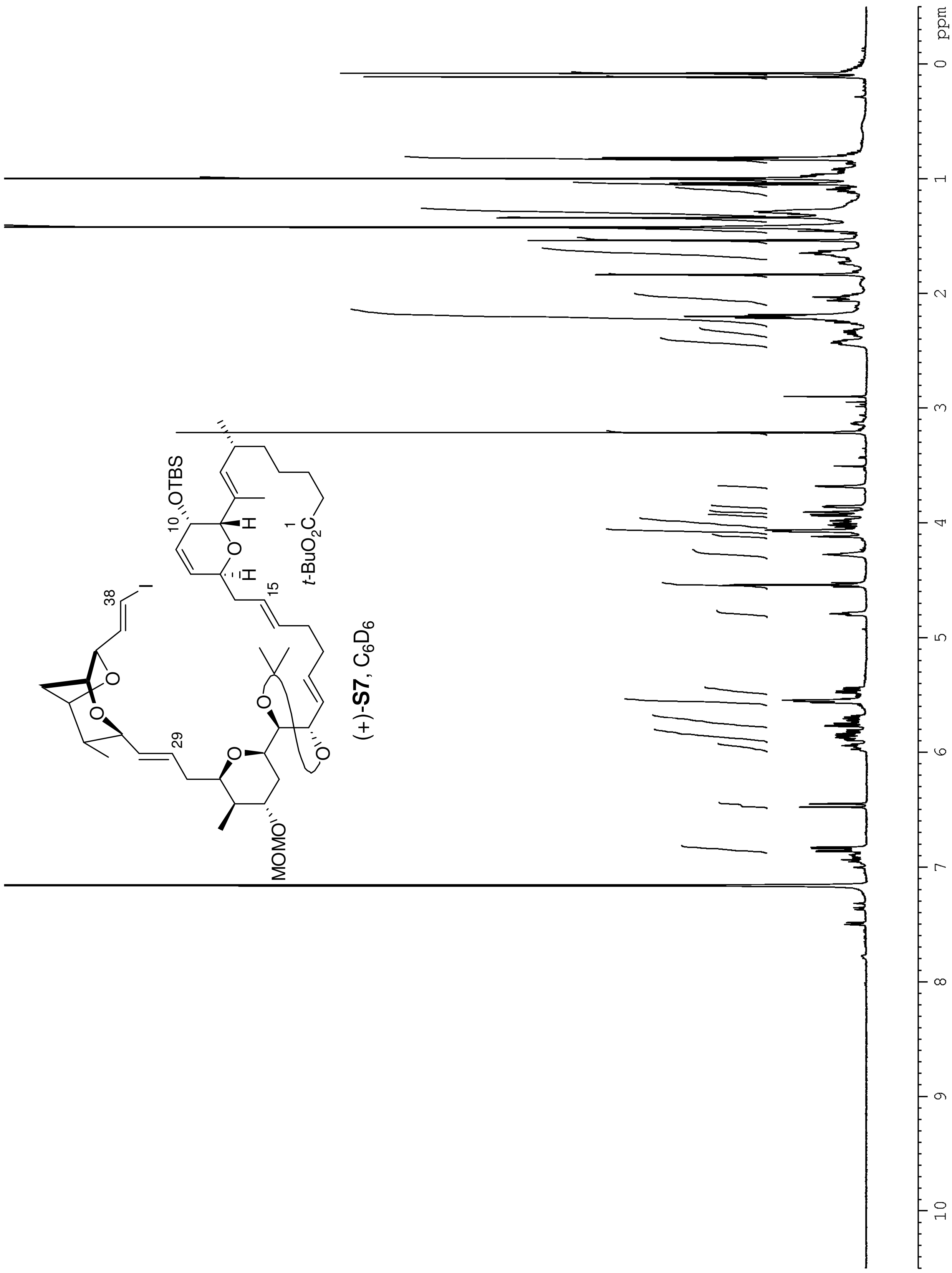


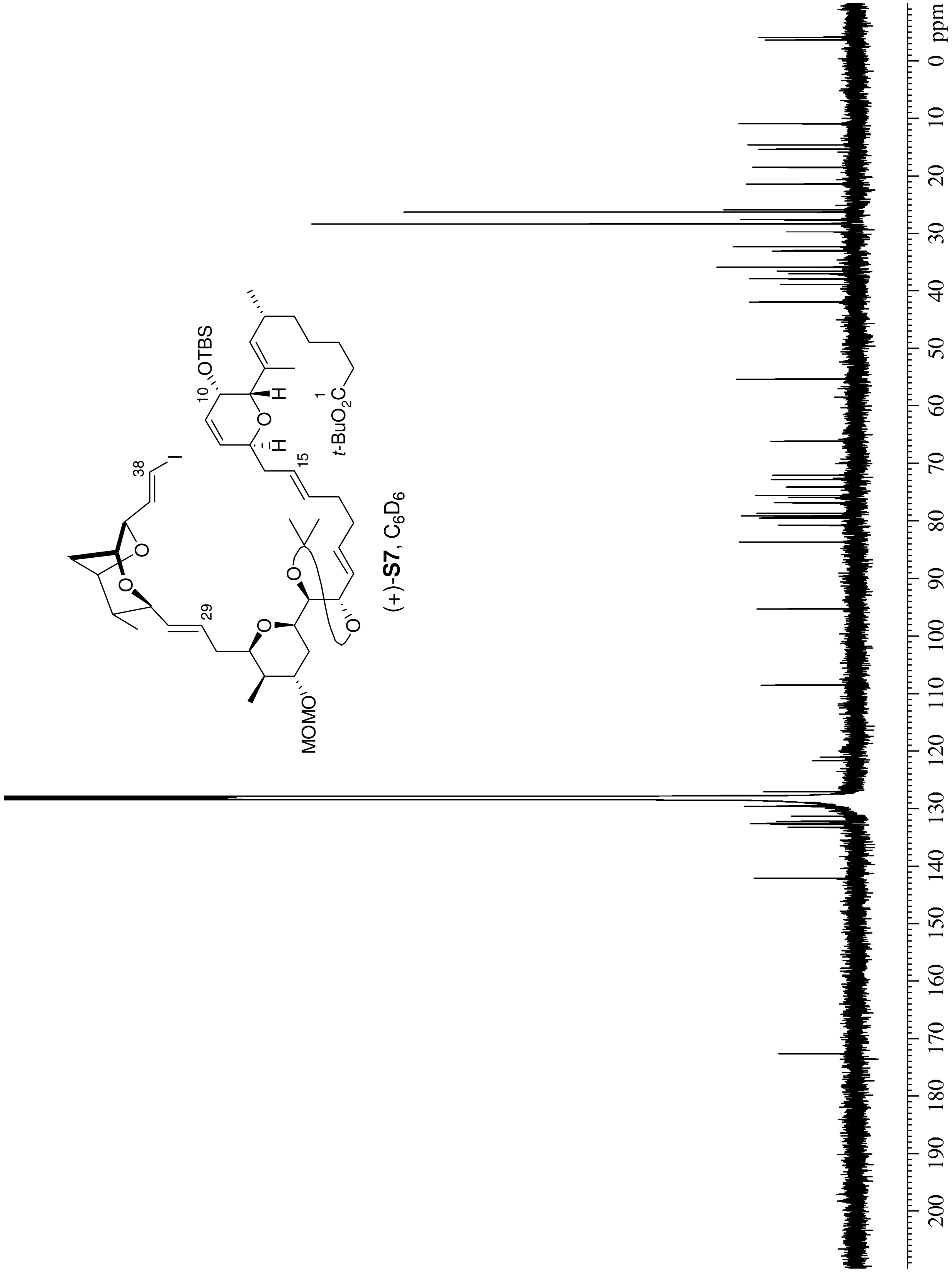
(–)-**15**, C_6D_6



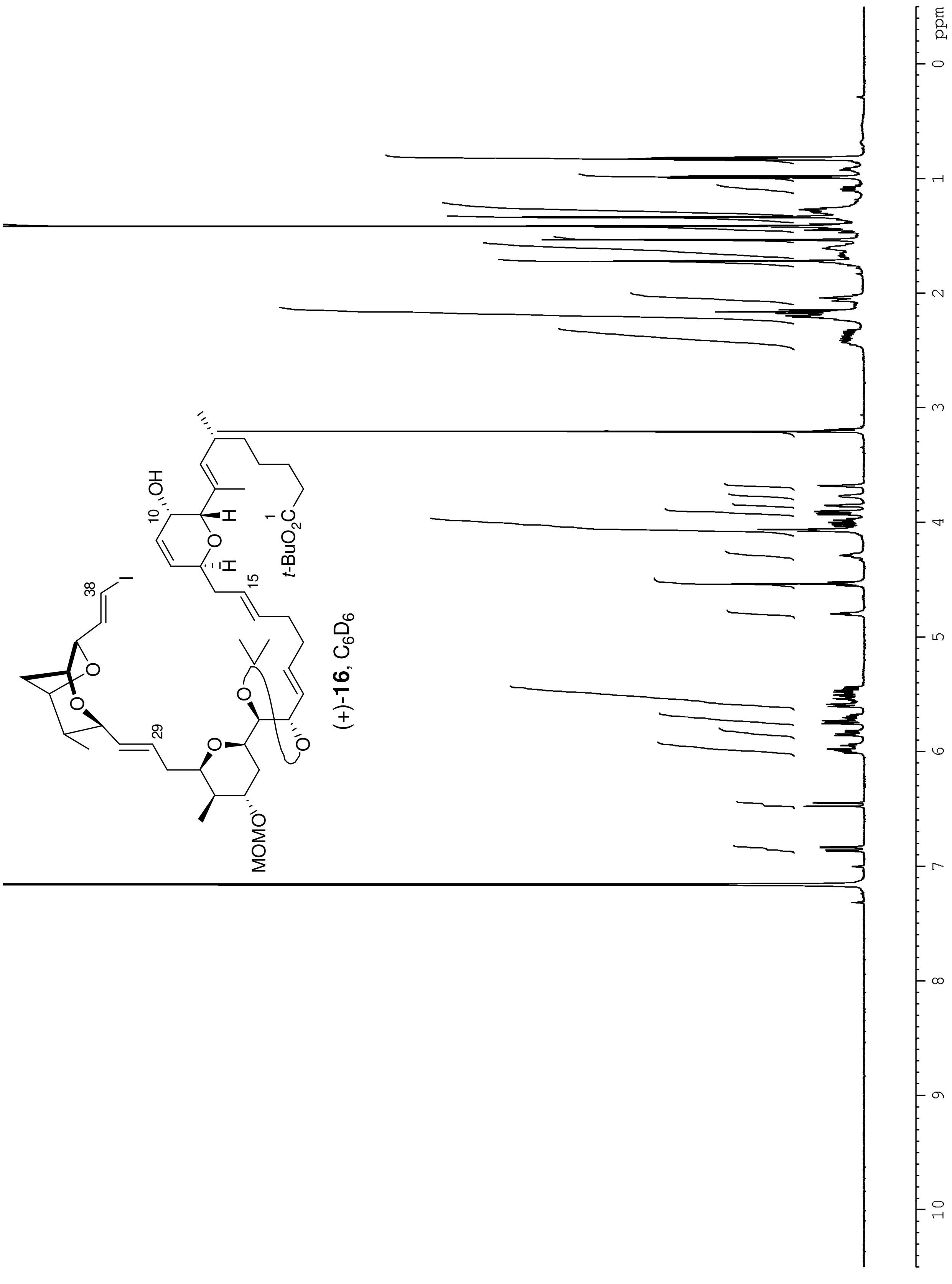
(−)-**15**, C_6D_6

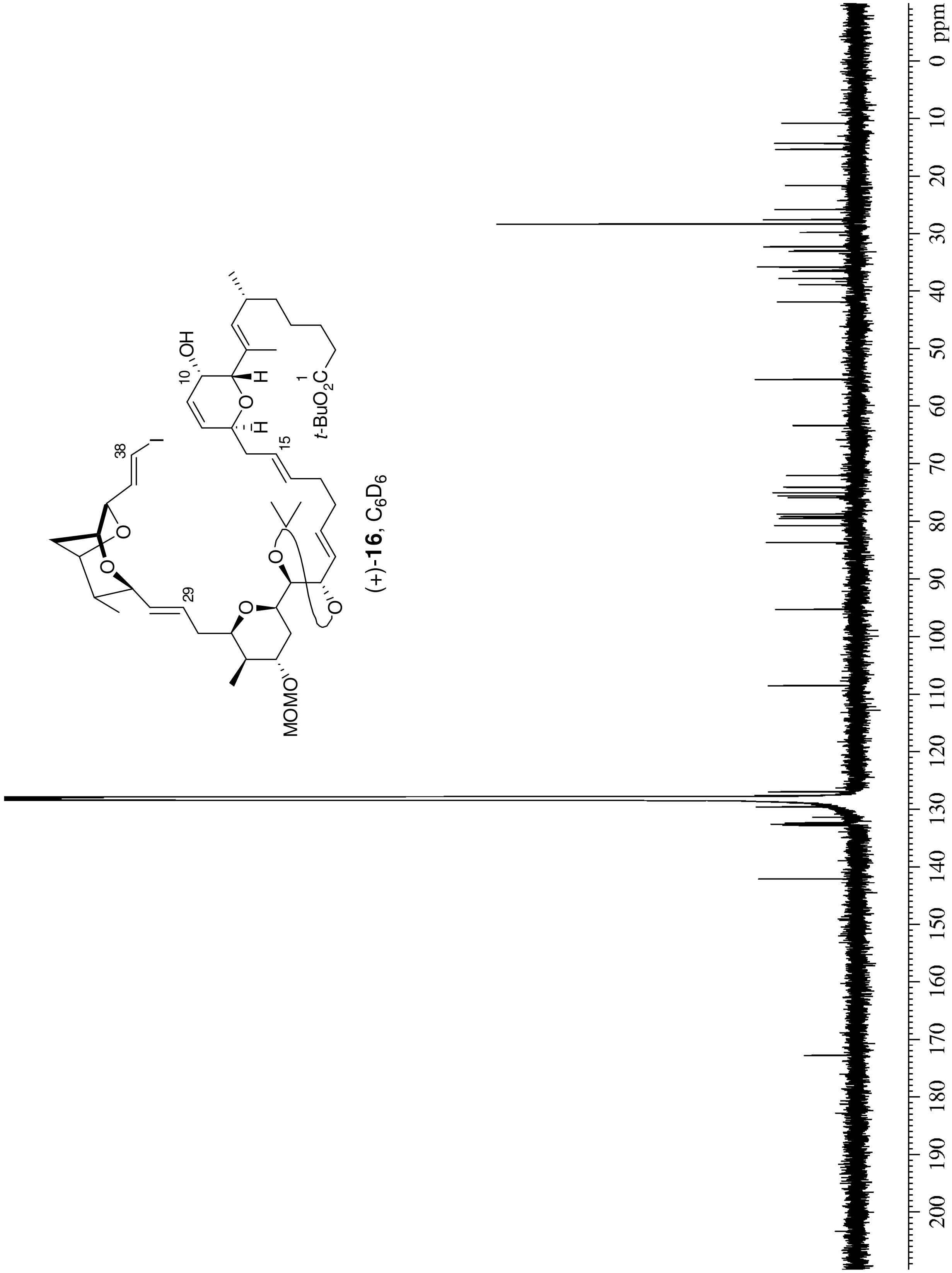
MOMO
O
O
O
O
O
O
I
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200


(+)-**S7**, C_6D_6

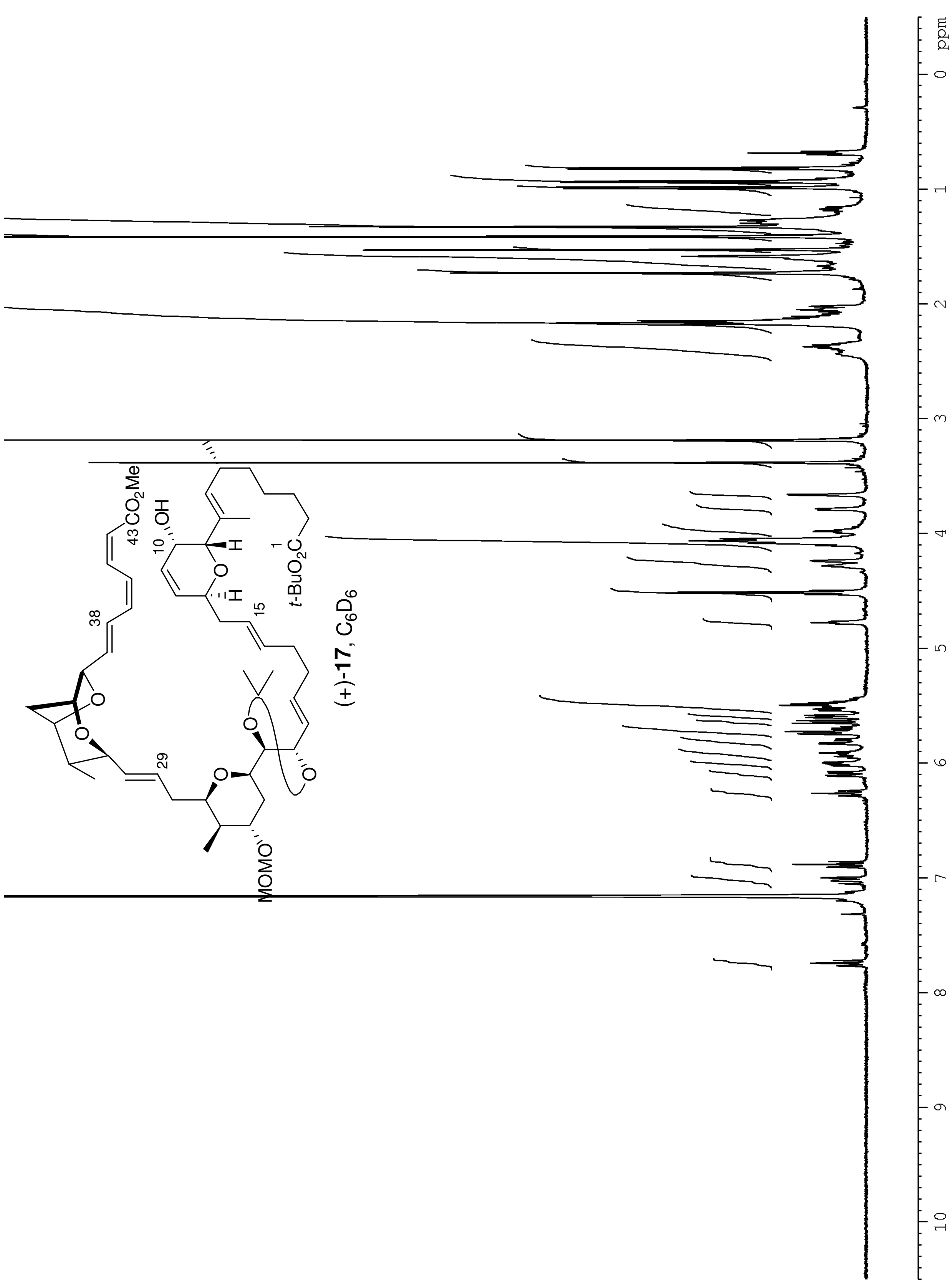

38
I
O
O
29
O
O
O
MOMO
OTBS
10
O
H
H
15
1
t-BuO2C
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

(+)-**S7**, C_6D_6

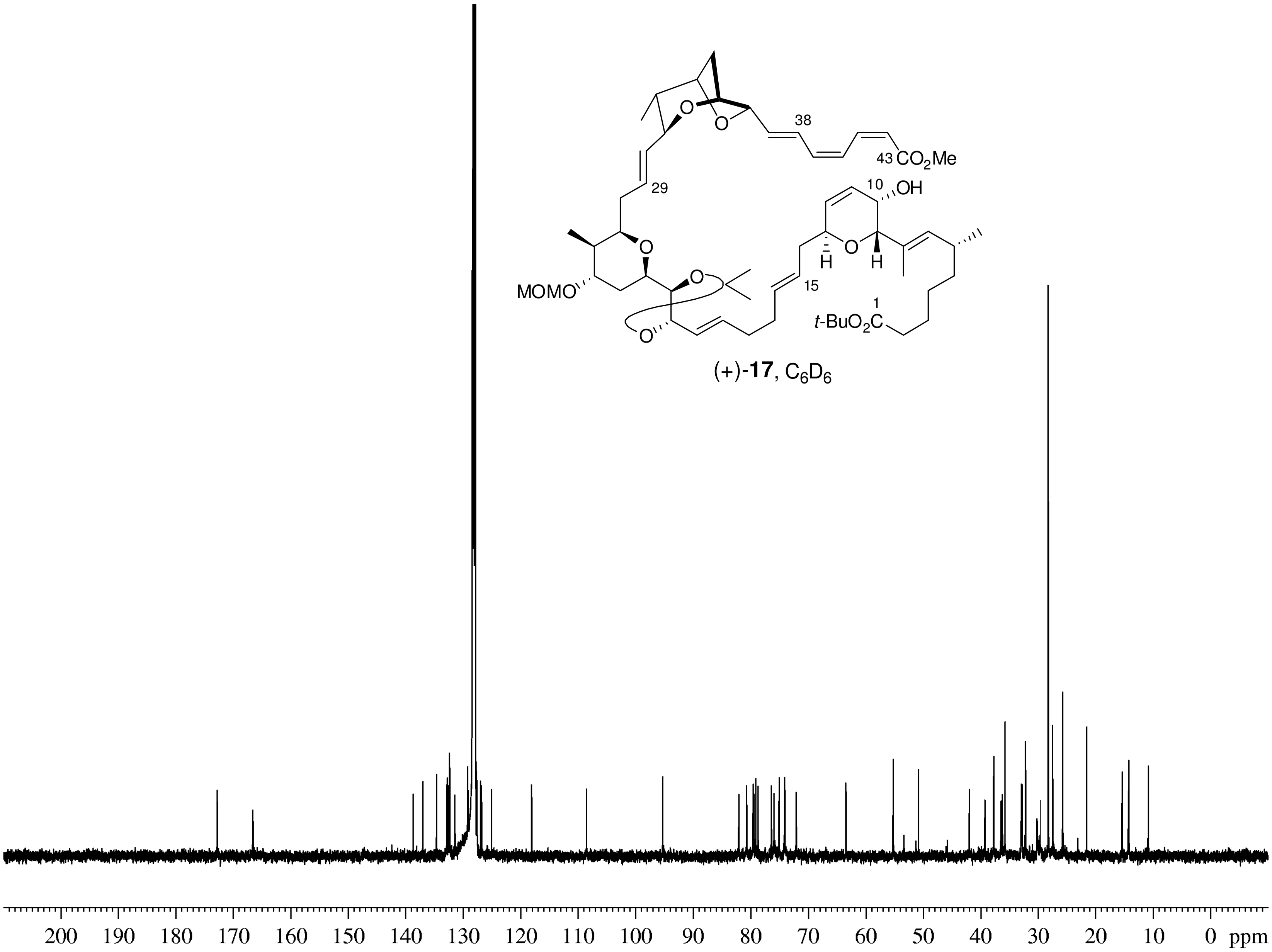

(+)-**16**, C_6D_6

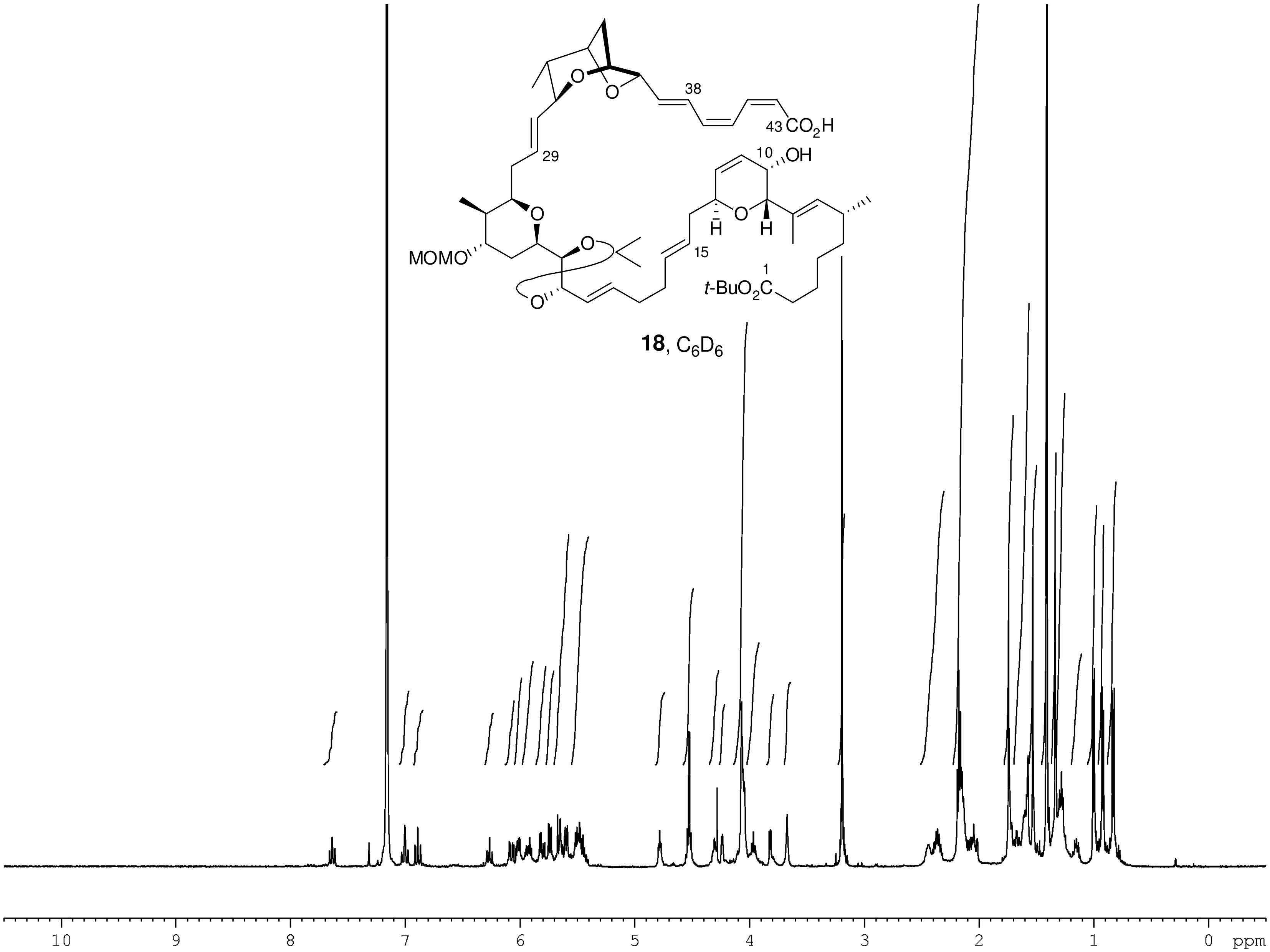

(+)-**16**, C_6D_6

MOMO
29
38
I
10
OH
H
H
15
1
t-BuO2C
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

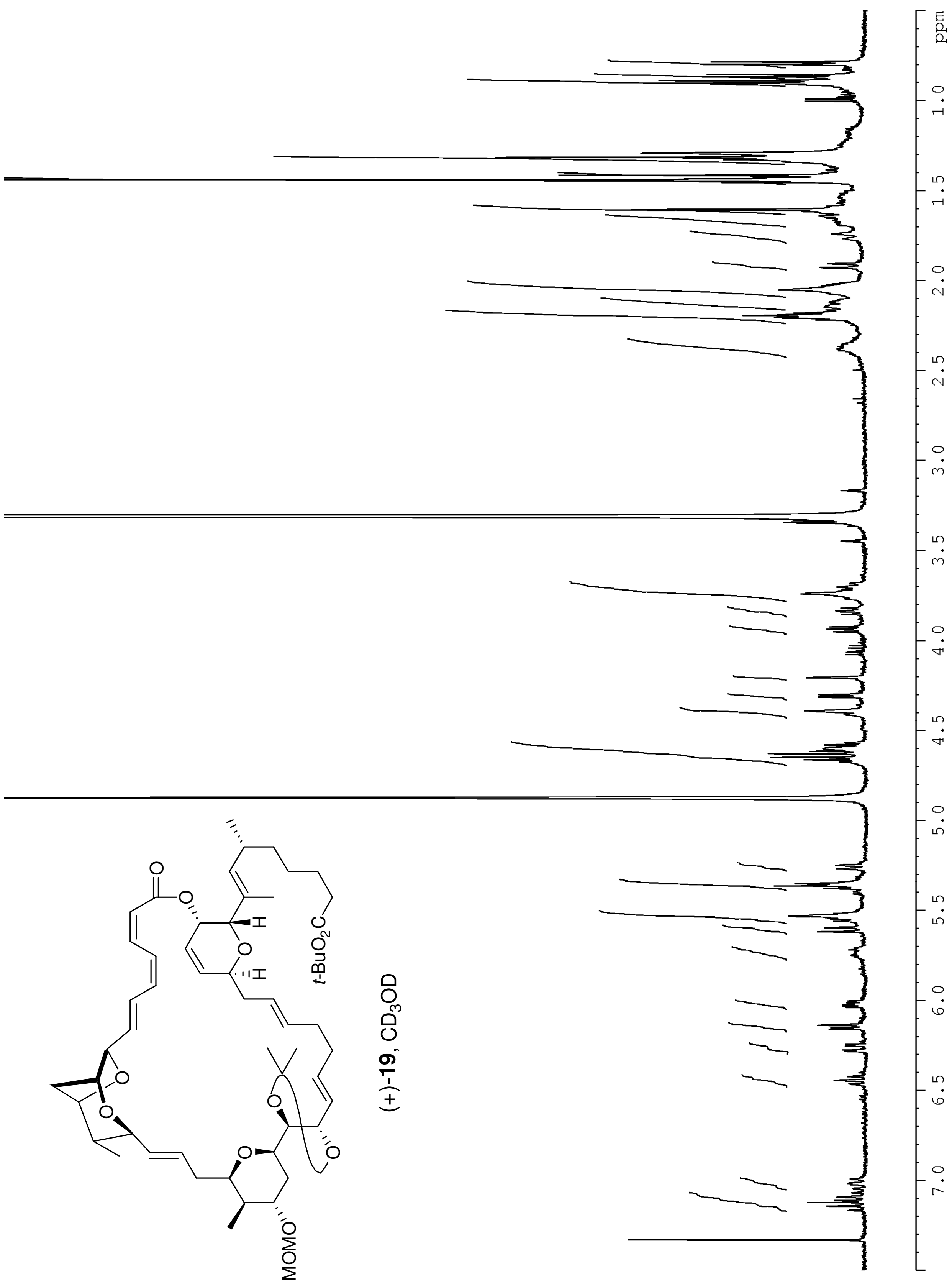


(+)-**17**, C_6D_6

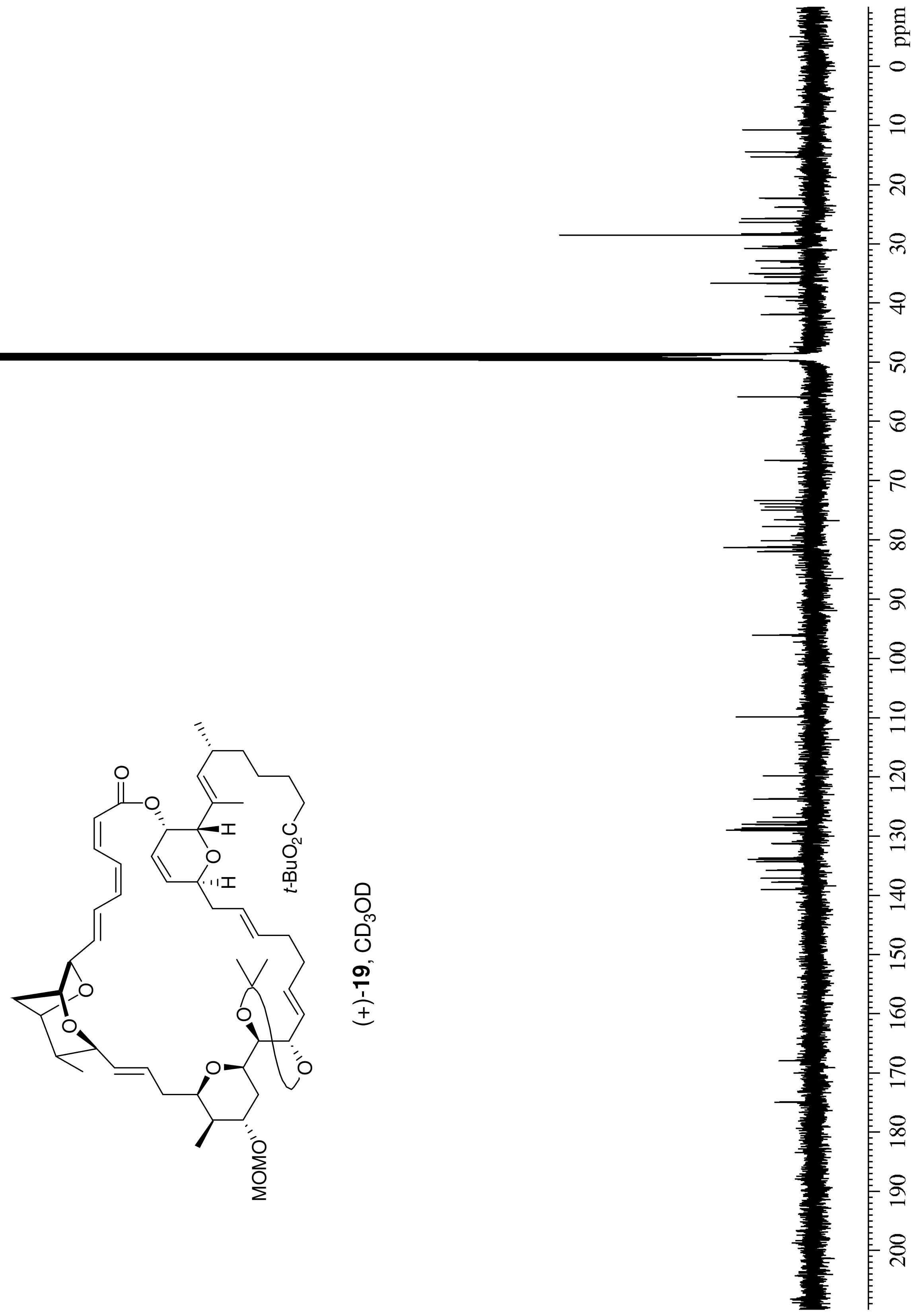

MOMO
29
38
43 CO$_2$Me
10 OH
15
1
t-BuO$_2$C
(+)-**17**, C$_6$D$_6$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm



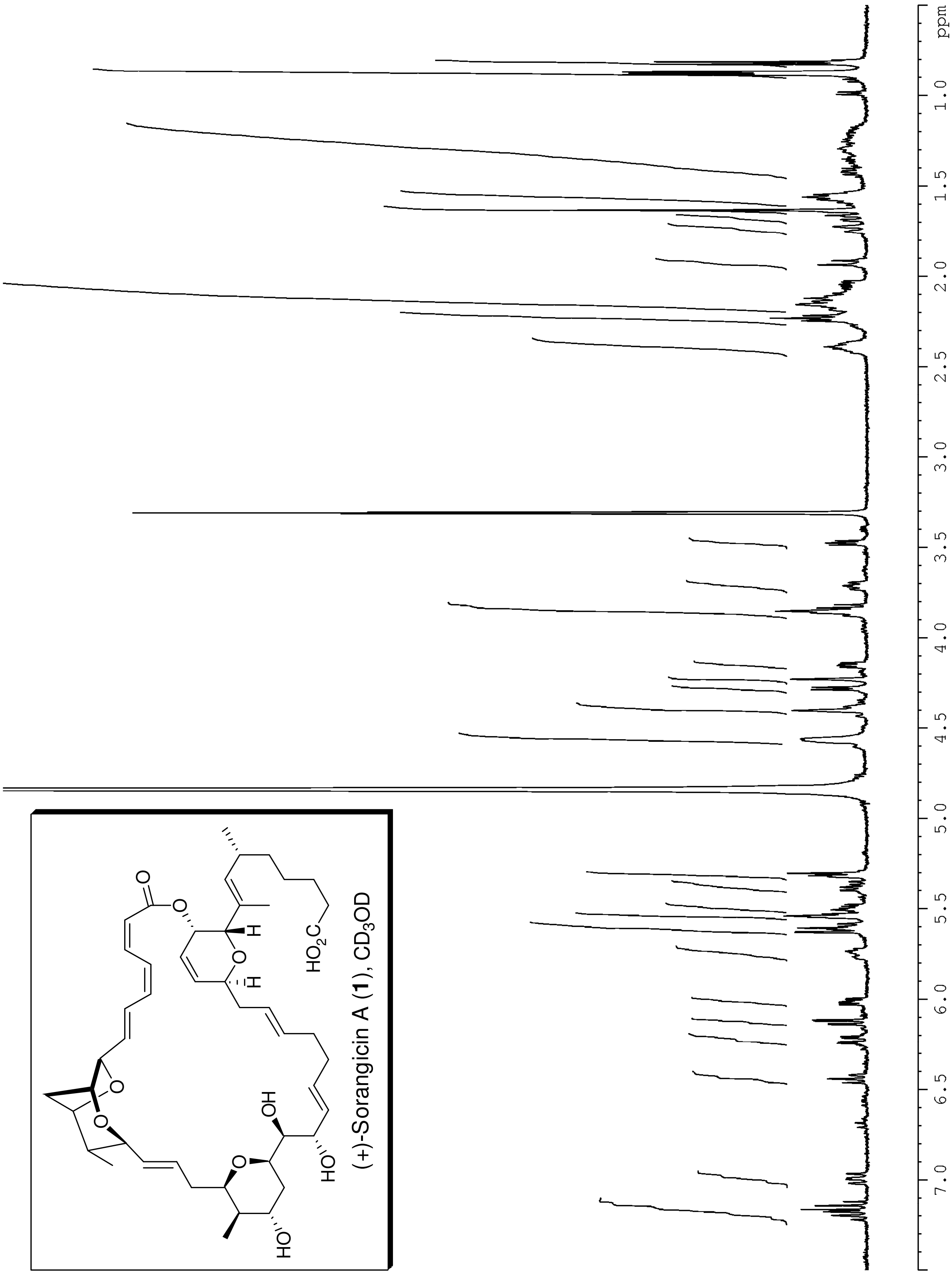
18, C_6D_6

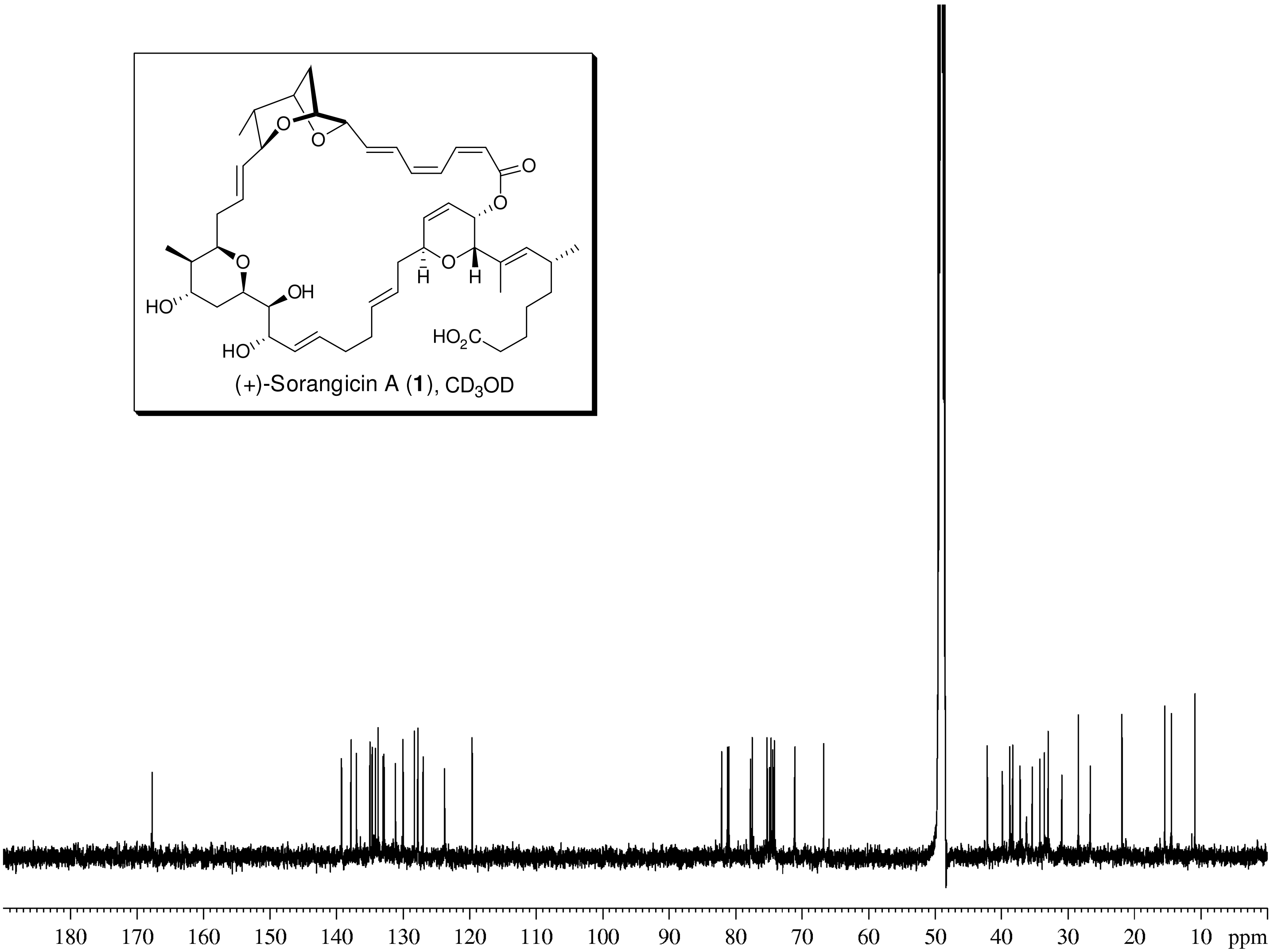


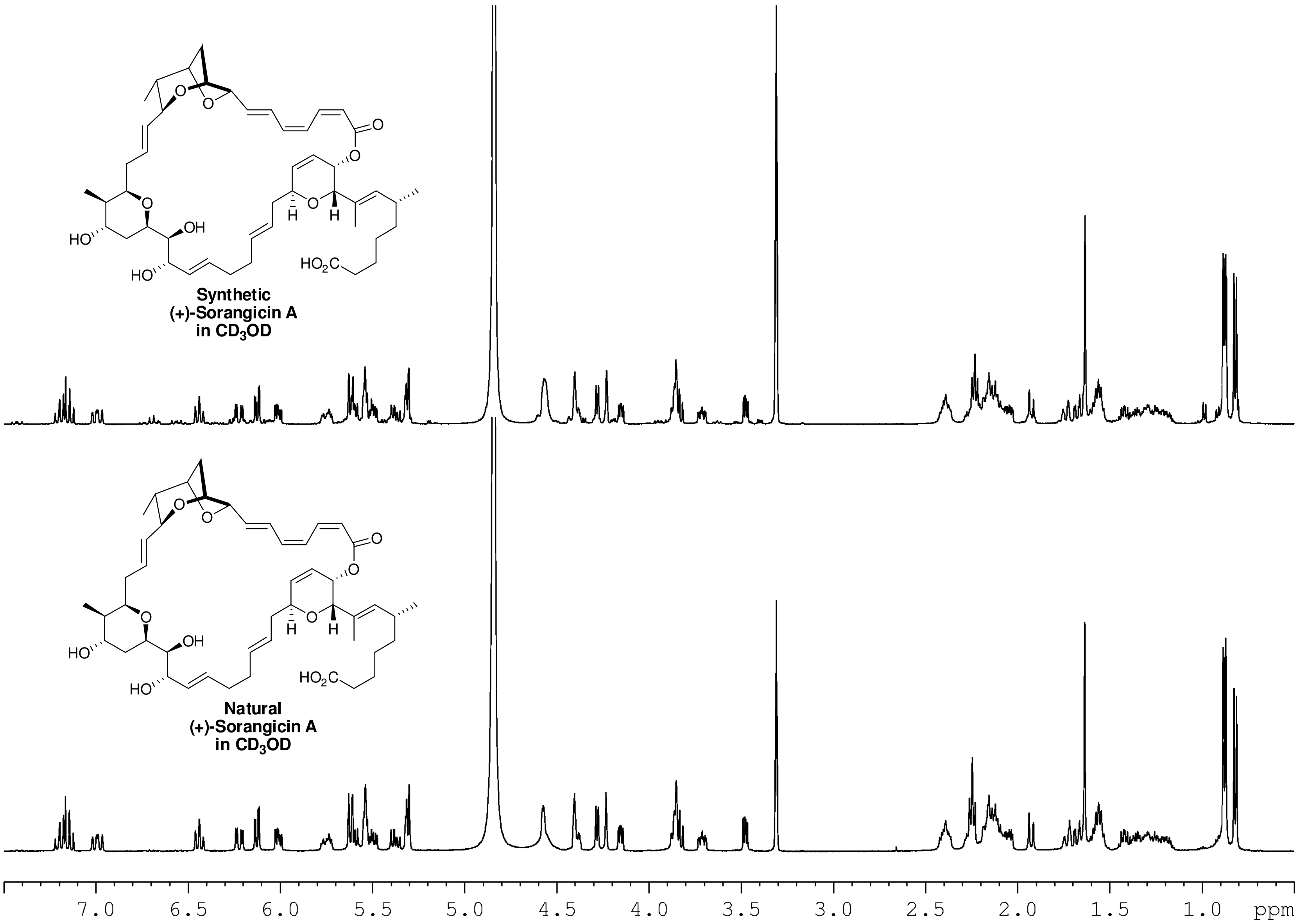
(+)-**19**, CD_3OD

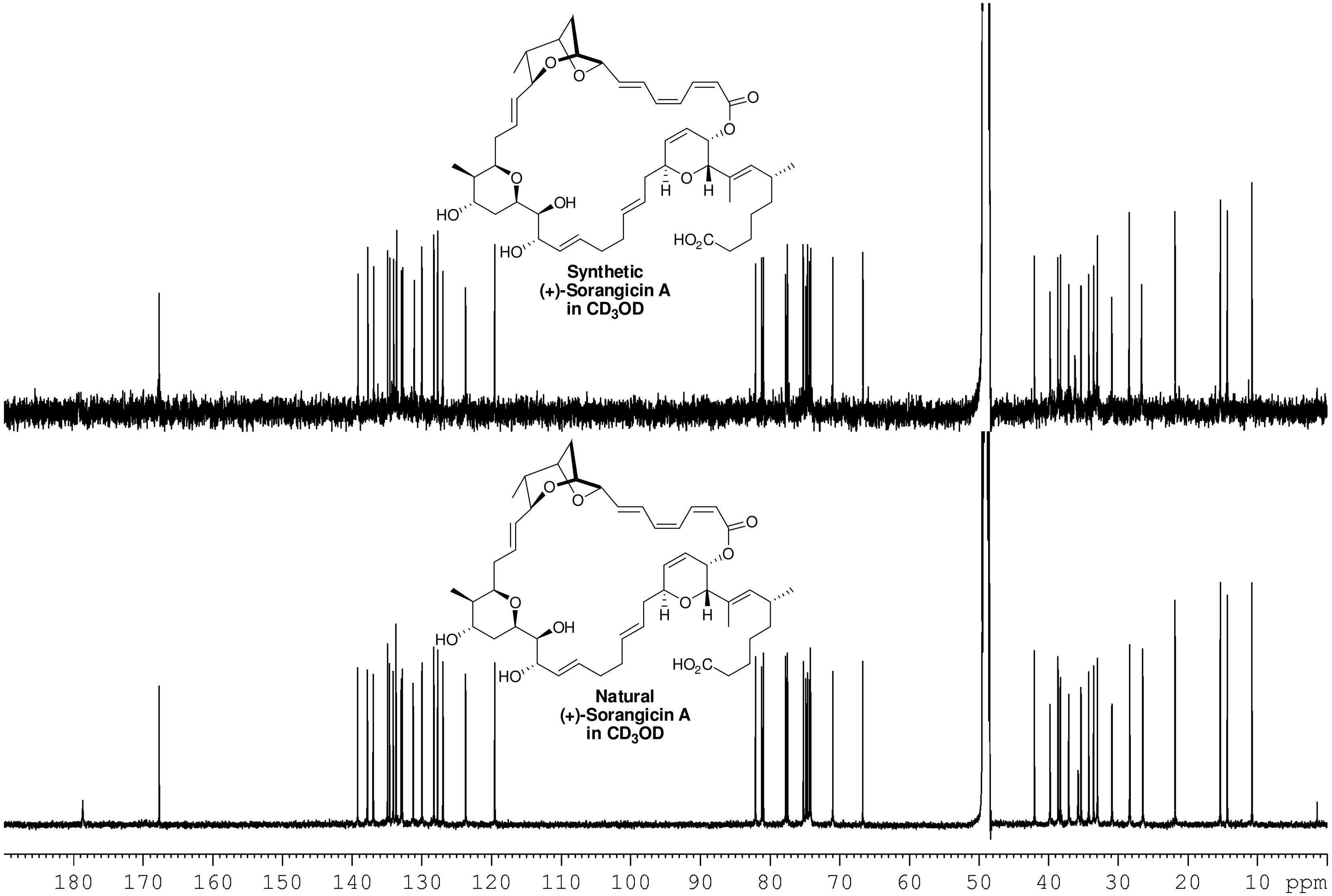

MOMO
O
O
O
O
O
O
H
H
t-BuO$_2$C
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

(+)-**19**, CD_3OD


(+)-Sorangicin A (**1**), CD_3OD


(+)-Sorangicin A (**1**), CD_3OD


Synthetic
(+)-Sorangicin A
in CD_3OD
Natural
(+)-Sorangicin A
in CD_3OD
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


Synthetic
(+)-Sorangicin A
in CD$_3$OD
Natural
(+)-Sorangicin A
in CD$_3$OD
HO
OH
HO
HO$_2$C
H
H
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm