**Supporting Information I**

**for**

# Peloruside B, a Potent Antitumor Macrolide from the New Zealand Marine Sponge *Mycale hentscheli*: Isolation, Structure, Total Synthesis and Bioactivity

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**General Synthetic Experimental Methods:**

All anhydrous solvents were obtained according to the following procedures: diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone under argon; toluene, methanol, and dichloromethane from calcium hydride and benzene from sodium. Other solvents were used without purification. All moisture-sensitive reactions were carried out in flame-dried flasks under argon atmosphere. Reactions were monitored by thin layer chromatography (TLC) using silica gel precoated plates. Flash column chromatography was performed using 230-400 mesh silica gel. All reactions are carried out under argon and yields refer to chromatographically and spectroscopically pure compounds. 600 MHz NMR spectra for *synthetic* peloruside B (**2**) were obtained using a spectrometer equipped with a triple resonance HCN cryogenic probe, operating at 600 MHz or 150 MHz for $^{1}H$ and $^{13}C$ nuclei respectively. Chemical shifts δ (ppm) were referenced to the residual solvent peak ($\delta_H$ 7.26 ppm, $\delta_C$ 77.16 ppm for $CDCl_3$). Catalytic amounts (1-2 μL) of $d_5$-pyridine were added to each NMR sample performed in $CDCl_3$ to prevent compound degradation due to trace acidity associated with the solvent.

**Synthesis of alkene 9:** To a solution of diethyl D-tartrate (32.2 g, 0.16 mol) and dimethoxymethane (152 mL, 1.69 mol) in $CH_2Cl_2$ (680 mL) was added phosphorous pentoxide (110 g, 0.388 mol) in portions at 0 °C. The mixture was stirred at 0 °C for 10 h, and the reaction was then poured into ice-cold saturated $NaHCO_3$ solution. The aqueous layer was extracted with $CH_2Cl_2$ (3 × 600 mL). The combined extracts were washed with brine and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum, and the crude product was used for the next reaction without purification.

A solution of the crude product from above dissolved in anhydrous ethyl ether (90 mL) was added to a suspension of LAH (11.86 g, 314 mmol) in ethyl ether (360 mL) dropwise at 0 °C over 30 min. The mixture was continuously stirred for 1 h at 0 °C and quenched with $H_2O$ (12 mL), 15% NaOH solution (12 mL) and $H_2O$ (36 mL). The suspension was stirred for 1 h, and the white precipitate was filtered out and washed with ethyl ether. The filtrate was concentrated under vacuum to afford the crude diol.

To a solution of the above diol (26.4 g, 0.13 mol) dissolved in THF (220 mL) and DMF (170 mL) was added sodium hydride (5.52 g, 60% suspension, 0.14 mol) in portions at 0 °C. The mixture was stirred at 0 °C for 0.5 h and *p*-methoxylbenzyl chloride (18 mL, 0.13 mol) was added dropwise. Then the mixture was allowed to warm to 23 °C for 10 h. The reaction was quenched with saturated ammonium chloride solution, and the aqueous layer was extracted with ethyl acetate (3 × 300 mL). The combined extracts were washed with brine and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum, and the crude product was purified by flash chromatography on silica gel (hexanes/ethyl acetate: 8/2 to 7/3 to 65/35) to afford the alcohol (34.4 g, 83% yield over three steps) as a colorless oil with ethyl ether. To a solution of the mono-PMB protected alcohol (34.4 g, 0.1 mol) in THF (230 mL) was added imidazole (14.2 g, 0.21 mol), $Ph_3P$ (32.7 g, 0.125 mol) and iodine (31.7 g, 0.12 mol) at 0 °C successively. The resulting mixture was warmed to 23 °C over 2 h, stirred overnight and then quenched with 10% aqueous $Na_2S_2O_3$. The aqueous layer was extracted with ether and the organic extracts were washed with water and brine. The resulting mixture was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The residue was passed through a short column to afford the crude iodide as a colorless oil.

To a solution of the resulting iodide from above (35 g, 79.5 mmol) in THF (94 mL) was added HMPA (55 mL) and CuI (3.0 g, 15.8 mmol) at 23 °C. The resulting mixture was cooled to -30 °C and vinylmagnesium bromide (155 mL, 1M in THF, 155 mmol) was added dropwise at this temperature over 1 h. The resulting mixture was stirred at -30 °C for 1 h and then warmed to 10 °C and then quenched with saturated aqueous $NH_4Cl$. The organic layer was separated and the aqueous layer was extracted with $Et_2O$; the combined organic layer was washed with brine, dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo*. Column chromatography on silica gel (hexanes/ethyl acetate: 95/5) provided product **9** (17 g, 63%).

$^1$H NMR (400 MHz, $CDCl_3$) δ 2.28 (m, 1H), 2.44 (m, 1H), 3.35 (s, 3H), 3.38 (s, 3H), 3.56 (dd, *J* = 10.0, 5.8 Hz, 1H), 3.62 (dd, *J* = 10.0, 4.7 Hz, 1H), 3.79 (s, 3H), 3.79 (m, 1H), 4.45 (dd, *J* = 15.8, 11.6 Hz, 2H), 4.67 (s, 2H), 4.68 (m, 1H), 4.70 (d, *J* = 6.8 Hz, 1H), 4.78 (d, *J* = 6.8 Hz, 1H), 5.07 (m, 2H), 5.83 (m, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 35.3, 55.2, 55.7, 69.4, 71.8, 72.9, 77.3, 81.0, 96.7, 97.0, 113.6,

117.3, 129.3, 130.1, 134.7, 159.1; FT-IR (film, NaCl) 1035.1, 1102.6, 1248.6, 1513.4, 1612.2 $cm^{-1}$; $[\alpha]_D^{20}$ +0.5 (*c* 5.5, $CHCl_3$); *m/z* (EI/CI), 339 $[M-H]^+$; HRMS (EI/CI) $[M-CH_2OCH_3]^+$ calcd for $C_{16}H_{28}O_5$ 295.1546, found 295.1544.

**TBS ether 10:** To a solution of the MOM ether **9** (17 g, 50 mmol) in acetone/$H_2O$ (150 mL / 20 mL) was added NMO (7.1 g, 60 mmol) and $OsO_4$ (2.5 w% in *t*-BuOH, 6.25 mL, 0.5 mmol). The resulting mixture was stirred at 23 °C for 3 h and quenched with saturated aqueous $NaHSO_3$ (42 mL). The solid was removed by filtration, and the filtrate was extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo*. To a solution of the crude diol from above in THF/$H_2O$ (120 mL/30 mL) was added $NaIO_4$ (12.6 g, 60 mmol) at 23 °C, and the reaction was stirred for 2 h. The solid was removed by filtration, and the filtrate was extracted with $Et_2O$. The combined organic layer was washed with a buffer solution (pH 7), water and brine, dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo*. The aldehyde was used without further purification. To a solution of (+)-$Ipc_2BOMe$ (21.5 g, 68 mmol) in $Et_2O$ (75 mL) was added allylmagnesium bromide (1 M in $Et_2O$, 62 mL, 62 mmol) dropwise at 0 °C. The resulting mixture was warmed to 23 °C over 1 h. The solid was removed by filtration. The filtrate was added to the resulting crude aldehyde in $Et_2O$ (75 mL) via cannula at -78 °C over 15 min, and the mixture was stirred for 2 h at -78 °C, then the reaction was quenched with aqueous NaOH (4 M, 37 mL) and $H_2O_2$ (30%, 20 mL) and slowly warmed to 23 °C overnight. The resulting mixture was extracted with $Et_2O$, and the combined organic layers were washed with water and brine, dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo*. The crude material was passed through a short column to give the crude diastereomers (14.2 g, 95:5), which were separated during the next step. $^1H$ NMR (400 MHz, $CDCl_3$) δ 1.62 (m, 1H), 1.85 (m, 1H), 2.26 (m, 2H), 2.93 (s, 1H), 3.49 (s, 6H), 3.58 (dd, *J* = 6.6, 10 Hz, 1H), 3.67 (dd, *J* = 3.8, 10 Hz, 1H), 3.82 (s, 3H), 3.90 (m, 2H), 3.98 (m, 1H), 4.48 (s, 2H), 4.68 (d, *J* = 6.8 Hz, 2H), 4.73 (d, *J* = 6.8 Hz, 1H), 4.83 (d, *J* = 6.8 Hz, 1H), 5.11 (m, 2H), 5.85 (m, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 37.0, 42.1, 55.2, 55.8, 56.0, 69.4, 69.5, 73.1, 77.4, 77.8, 97.0, 97.1, 113.7, 117.7, 129.3, 130.1, 134.7, 159.2.

To a solution of the crude diastereomeric mixture (14.5 g, 36.8 mmol) in DMF (73 mL) was added imidazole (3.74 g, 55.2 mmol), DMAP (450 mg, 3.68 mmol) and TBSCl (6.09 g, 40.5 mmol) at 23 °C. The mixture was stirred overnight. To the resulting mixture was added water and EtOAc, and the organic layer was washed with water and brine, dried over anhydrous $Na_2SO_4$, and concentrated *in vacuo*. Column chromatography on silica gel (hexanes/ethyl acetate: 90/10) provided the pure diastereomeric isomer **10** (13.3 g, 53% over 4 steps, *dr* 95:5):

$^1$H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 3H), 0.05 (s, 3H), 0.90 (s, 9H), 1.65 (m, 1H), 1.83 (m, 1H), 2.21 (m, 1H), 2.30 (m, 1H), 3.35 (s, 3H), 3.37 (s, 3H), 3.60 (m, 1H), 3.79 (s, 3H), 3.80-3.89 (m, 2H), 4.45 (s, 2H), 4.64 (s, 2H), 4.67 (d, *J* = 6.8 Hz, 1H), 4.80 (d, *J* = 6.8 Hz, 1H), 5.05 (m, 2H), 5.77-5.86 (m, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ -4.6, -4.4, 17.9, 25.8, 37.6, 41.6, 55.1, 55.7, 55.8, 68.7, 69.9, 72.9, 74.7, 77.2, 96.5, 96.8, 113.6, 117.0, 129.1, 130.2, 134.8, 159.1; FT-IR (film, NaCl) 1036.0, 1102.0, 1249.9, 1514.8, 1652.6 cm$^{-1}$; $[\alpha]_D^{20}$ -62.4 (*c* 1.17, $CHCl_3$); HRMS (ESI) $[M+Na]^+$ calcd for $C_{26}H_{46}O_7SiNa$ 521.2911, found 521.2907.

**Alkene 11**: To a solution of silyl ether **10** (13 g, 26.1 mmol) in acetone/water (120 mL/ 15 mL) was added $OsO_4$ (2.5w % in $^t$BuOH, 3.2 mL, 0.26 mmol) and NMO (3.67 g, 31.3 mmol) at 23 °C, and the reaction mixture was stirred at that temperature for 5 h. The solid was removed and the filtrate was extracted with EtOAc. The combined organic layer was washed with water and brine, dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo*. To a solution of the crude diol in THF/$H_2O$ (100 mL/ 25 mL) was added $NaIO_4$ (6.69 g, 31.3 mmol), and the reaction mixture was stirred at 23 °C for 3 h. The solid was removed by filtration, and the filtrate was extracted with EtOAc. The combined organic layer was washed with water and brine, dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo*. The crude aldehyde was used without further purification.

To a solution of (*o*-cresol)$_2$P(O)$CH_2CO_2Et$ (10.3 g, 32.6 mmol) in THF (210 mL) was added NaI (3.8 g, 191 mmol) and NaH (60% in mineral oil, 1.2 g, 30 mmol) at 0 °C. The solution was stirred at 0 °C for 10 min and cooled to -78 °C. The aldehyde in THF (50 mL) was added dropwise to the resulting anion at -78 °C. The reaction mixture was stirred at -78

°C for 2 h and warmed up to -50 °C and then quenched with saturated aqueous $NH_4Cl$ and extracted with EtOAc. The combined organic layer was washed with water and brine, dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo*. Column chromatography on silica gel (hexanes/ethyl acetate: 85/15) provided the *Z* isomer **11** (12 g, 81%) and *E* isomer (1.6 g, 11%). *Z* isomer: $^1$H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 6H), 0.86 (s, 9H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.68 (m, 1H), 1.77 (m, 1H), 2.82 (m, 1H), 2.97 (m, 1H), 3.34 (s, 3H), 3.36 (s, 3H), 3.79 (s, 3H), 3.81 (m, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 4.44 (s, 2H), 4.64 (s, 2H), 4.65 (d, *J* = 6.8 Hz, 1H), 4.79 (d, *J* = 6.8 Hz, 1H), 5.84 (d, *J* = 11.6 Hz, 1H), 6.35 (m, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ -4.6, -4.5, 14.2, 17.9, 25.8, 35.9, 37.9, 55.1, 55.7, 55.8, 59.7, 68.3, 69.8, 72.9, 74.9, 77.1, 96.7, 113.6, 121.1, 129.2, 130.2, 146.0, 159.1, 166.1; FT-IR (film, NaCl) 1035.4, 1101.3, 1250.2, 1513.8, 1717.5 cm$^{-1}$; $[\alpha]_D^{20}$ -13.7 (*c* 12.1, $CHCl_3$); HRMS (ESI) $[M+Na]^+$ calcd for $C_{29}H_{50}O_9SiNa$ 593.3122, found 593.3118.

**Acetonide 12:** The olefin **10** (10.9 g, 19.1 mmol) was dissolved in *t*-butanol (96 mL) and $H_2O$ (96 mL). The solution was cooled to 0 $^o$C followed by addition of AD-mix-α (26.8 g) and methanesulfonamide (1.81 g). The mixture was stirred at 0 $^o$C for 5 days. A saturated sodium thiosulfate solution was added to quench the reaction. The aqueous layer was extracted with ethyl acetate (3 × 100 mL). The combined extracts were washed with 15% KOH solution, brine and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under vacuum, and the residue was passed through a short column of silica gel (hexanes/ethyl acetate: 1/1) to afford the crude product.

To the crude diol from above dissolved in $CH_2Cl_2$ (80 mL) was added 2-methoxypropene (2.93 mL, 30.6 mmol) and PPTS (276 mg) at 23 $^o$C. The mixture was stirred at 23 $^o$C for 1 h and quenched with a saturated $NaHCO_3$ solution. The aqueous layer was extracted with $CH_2Cl_2$, and the combined extracts were washed with brine and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum, and the crude product was purified by flash chromatography on silica gel (hexanes/ethyl acetate: 85/15) to afford the major isomer **12** (5.95 g, 77% yield over 2 steps) as a colorless oil along with minor isomer (1 g, 13% yield).

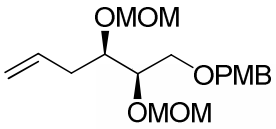
$^1$H NMR (500 MHz, $CDCl_3$) δ 0.06 (s, 6H), 0.88 (s, 9H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.35 (s,

3H), 1.57 (s, 3H), 1.61 (m, 2H), 1.72 (t, *J* = 6.4 Hz, 2H), 3.35 (s, 3H), 3.36 (s, 3H), 3.53 (dd, *J* = 10.0, 6.6 Hz, 1H), 3.63 (dd, *J* = 10.0, 3.8 Hz, 1H), 3.74 (m, 1H), 3.79 (s, 3H), 3.79 (m, 1H), 4.04 (m, 1H), 4.16 (m, 2H), 4.45 (s, 2H), 4.52 (m, 2H), 4.60 (d, *J* = 6.8 Hz, 1H), 4.65 (d, *J* = 7.4 Hz, 2H), 4.76 (d, *J* = 6.8 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ -4.8, -4.2, 14.1, 17.9, 25.7, 25.8, 26.8, 37.1, 39.2, 55.1, 55.6, 55.9, 60.8, 66.3, 69.6, 72.9, 73.9, 74.2, 77.3, 77.5, 96.6, 96.7, 110.5, 113.6, 129.2, 130.1, 159.1, 170.5; FT-IR (film, NaCl) 1039.1, 1097.6, 1249.2, 1513.6, 1729.6, 1756.5; $[\alpha]_D^{20}$ +21.2 (*c* 1.0, $CHCl_3$); HRMS (ESI) $[M+Na]^+$ calcd for $C_{32}H_{56}O_{11}SiNa$ 667.3490, found 667.3496.

**Enone 5:** To a solution of ester **12** (5.95 g, 9.23 mmol) in $CH_2Cl_2$ (110 mL) was added DIBAL-H (1M in $CH_2Cl_2$, 9.69 mL, 9.69 mmol) dropwise at -78 °C. The resulting mixture was stirred at that temperature for 1 h and quenched with saturated potassium sodium tartrate solution. The solid was removed by filtration, and the filtrate was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo*. The crude material was passed through a short silica gel pad to provide the crude aldehyde, which was then dissolved in THF (100 mL). To the solution was added isopropenylmagnesium bromide (0.5 M in THF, 92 mL, 46 mmol) dropwise at 0 °C and the solution was stirred at 0 °C for 15 min before quenched with saturated aqueous $NH_4Cl$. The resulting mixture was extracted with EtOAc, and the combined organic layer was washed with water and brine, dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo*. Column chromatography provided a diastereomeric mixture of the corresponding alcohol (5.37 g).

To a solution of the above alcohol mixture (5.37 g, 9.23 mmol) in $CH_2Cl_2$ (33 mL) was added Dess-Martin periodinane (4.7 g, 11.1 mmol) and $NaHCO_3$ (2.7 g, 32.1 mmol) at 23 °C. The reaction mixture was stirred for 30 min and then quenched with saturated aqueous $Na_2S_2O_3$ (15 mL) and saturated aqueous $NaHCO_3$ (20 mL). The aqueous layer was extracted with $Et_2O$ and the combined organic layer was washed with water and brine, dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo*. Column chromatography over silica gel provided enone **5** (4.54 g, 76% for three steps).

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 0.09 (s, 3H), 0.10 (s, 3H), 0.91 (s, 9H), 1.34 (m, 1H), 1.40 (s, 3H), 1.49 (m, 1H), 1.62 (s, 3H), 1.70 (m, 2H), 1.91 (s, 3H), 3.37 (s, 3H), 3.38 (s, 3H), 3.55 (dd, *J* = 10.1, 6.8 Hz, 1H), 3.65 (dd, *J* = 10.1, 3.7 Hz, 1H), 3.71 (m, 1H), 3.82 (m, 1H), 3.83 (s, 3H), 4.02 (m, 1H), 4.48 (s, 2H), 4.62 (m, 1H), 4.63 (s, 2H), 4.67 (d, *J* = 6.8 Hz, 1H), 4.79 (d, *J* = 6.8 Hz, 1H), 5.31 (d, *J* = 7.3 Hz, 1H), 5.88 (d, *J* = 1.4 Hz, 1H), 5.92 (s, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ -4.8, -4.2, 17.8, 18.0, 25.5, 25.8, 27.2, 38.1, 39.3, 55.2, 55.7, 56.0, 66.3, 69.7, 73.0, 74.4, 74.6, 77.5, 78.6, 96.8, 109.7, 113.7, 125.4, 129.2, 130.2, 144.1, 159.1, 197.2; FT-IR (film, NaCl) 1040.6, 1103.5, 1249.5, 1378.5, 1462.7, 1513.8, 1612.4, 1692.3 $cm^{-1}$; $[\alpha]_D^{20}$ +22.4 (*c* 1.09, $CHCl_3$); HRMS (ESI) $[M+Na]^+$ calcd for $C_{33}H_{56}O_{10}SiNa$ 663.3540, found 663.3547.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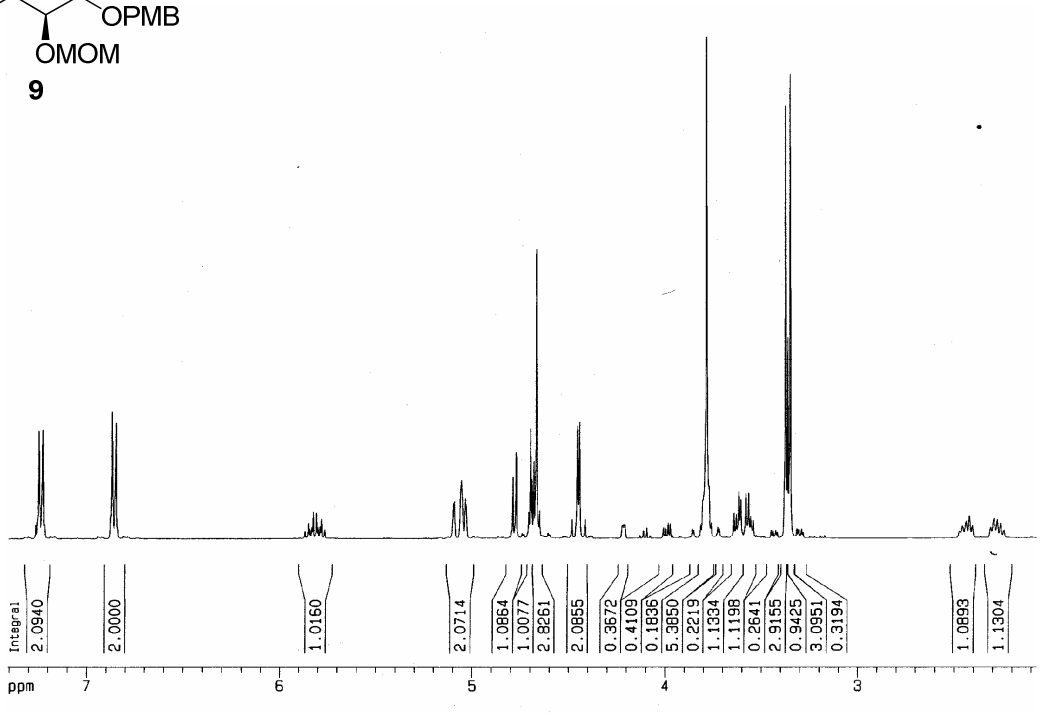
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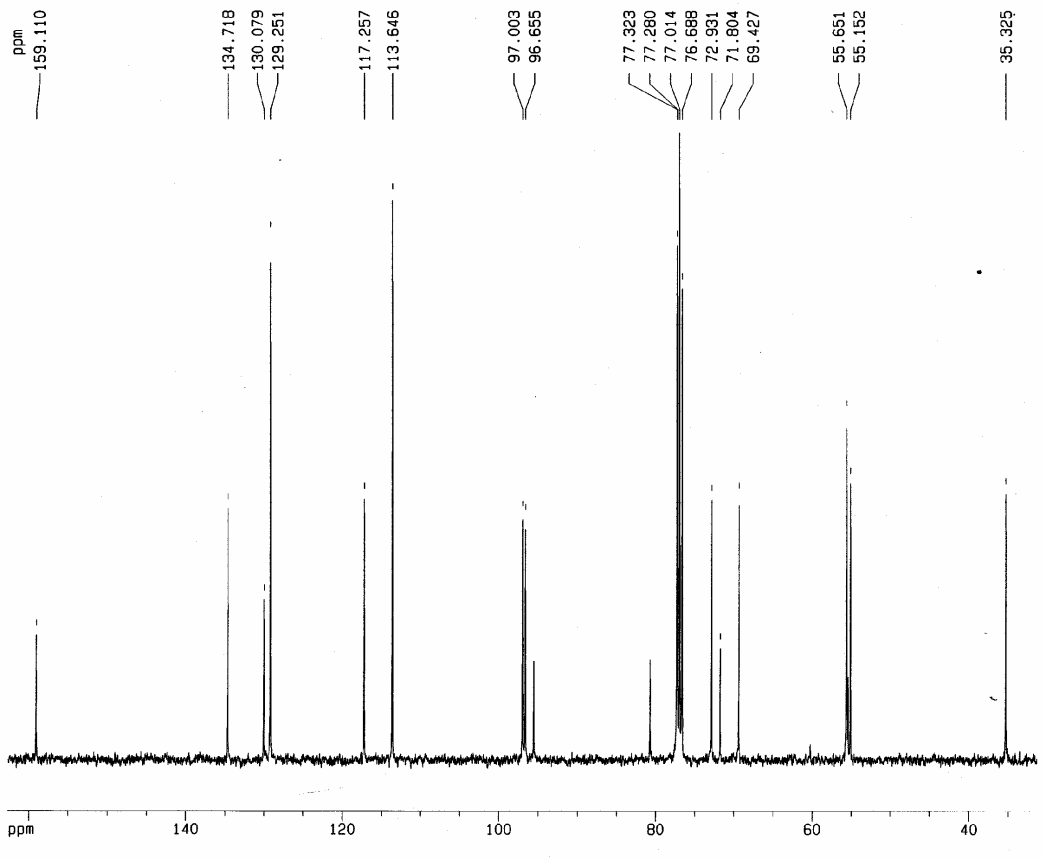
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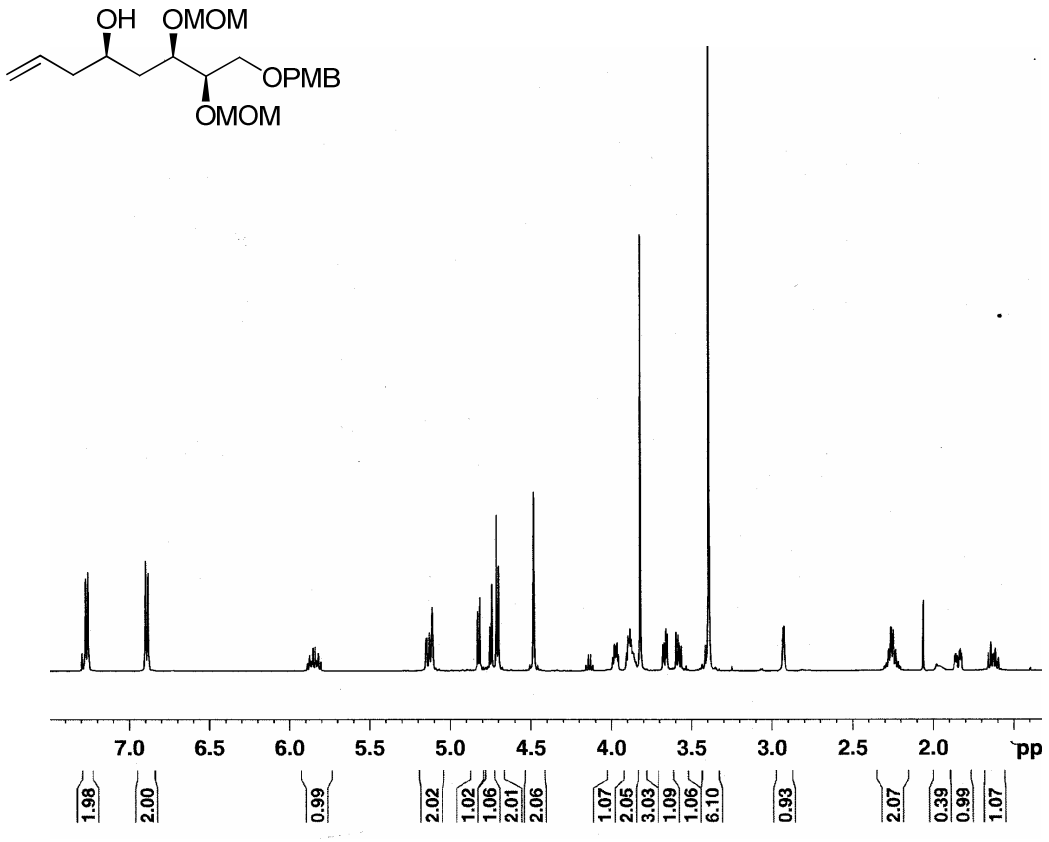
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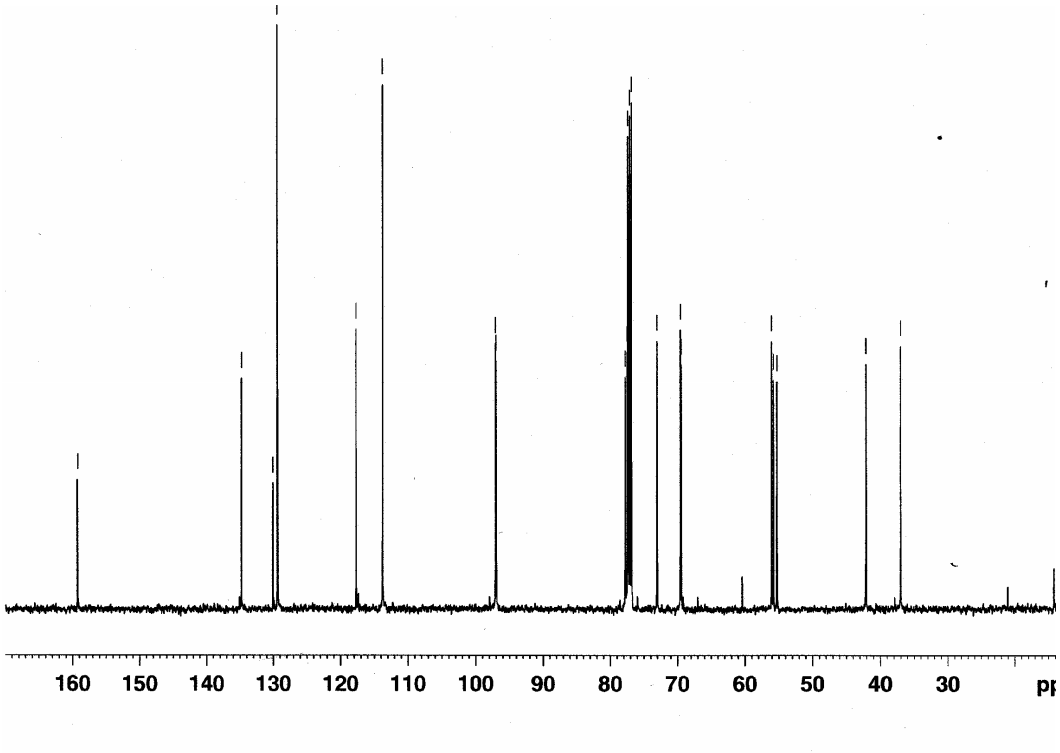
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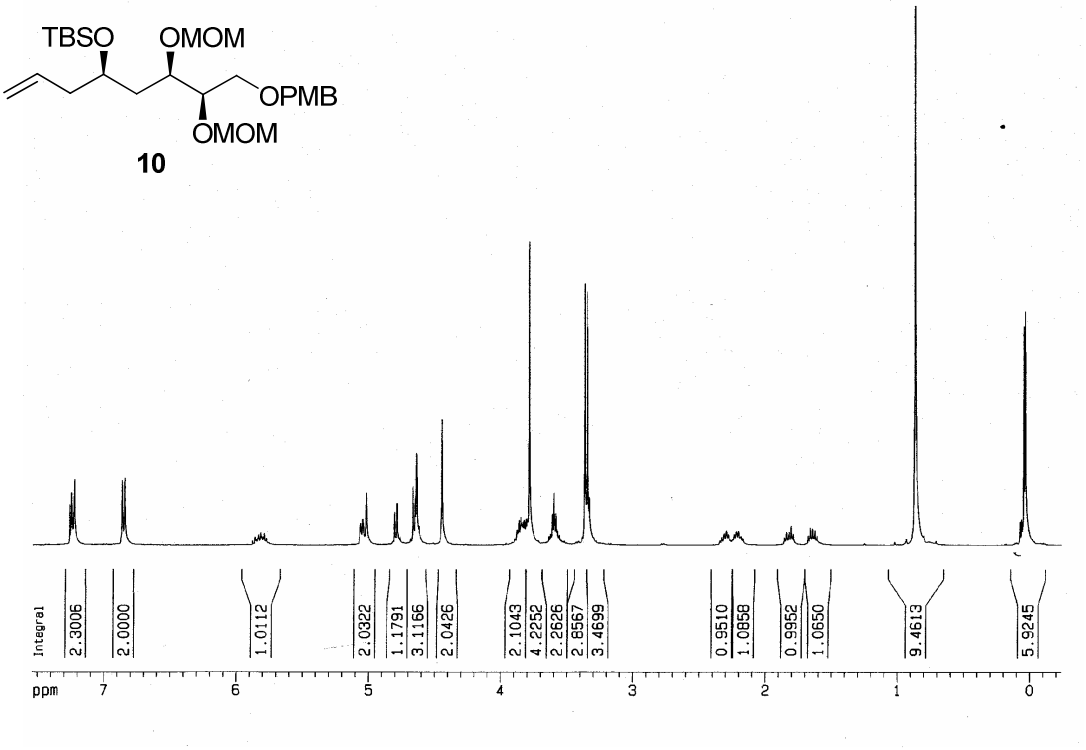
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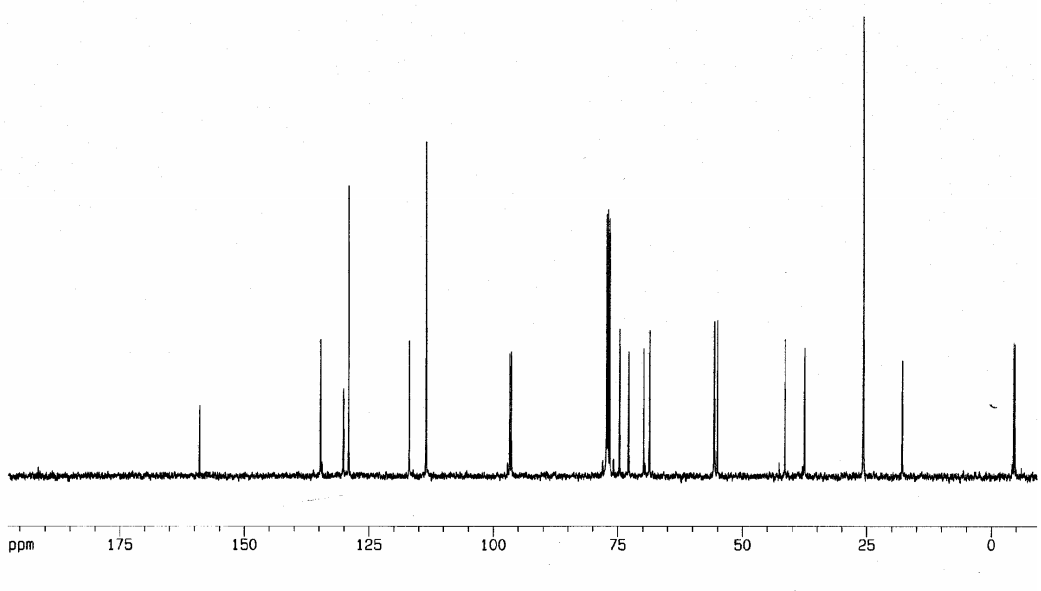
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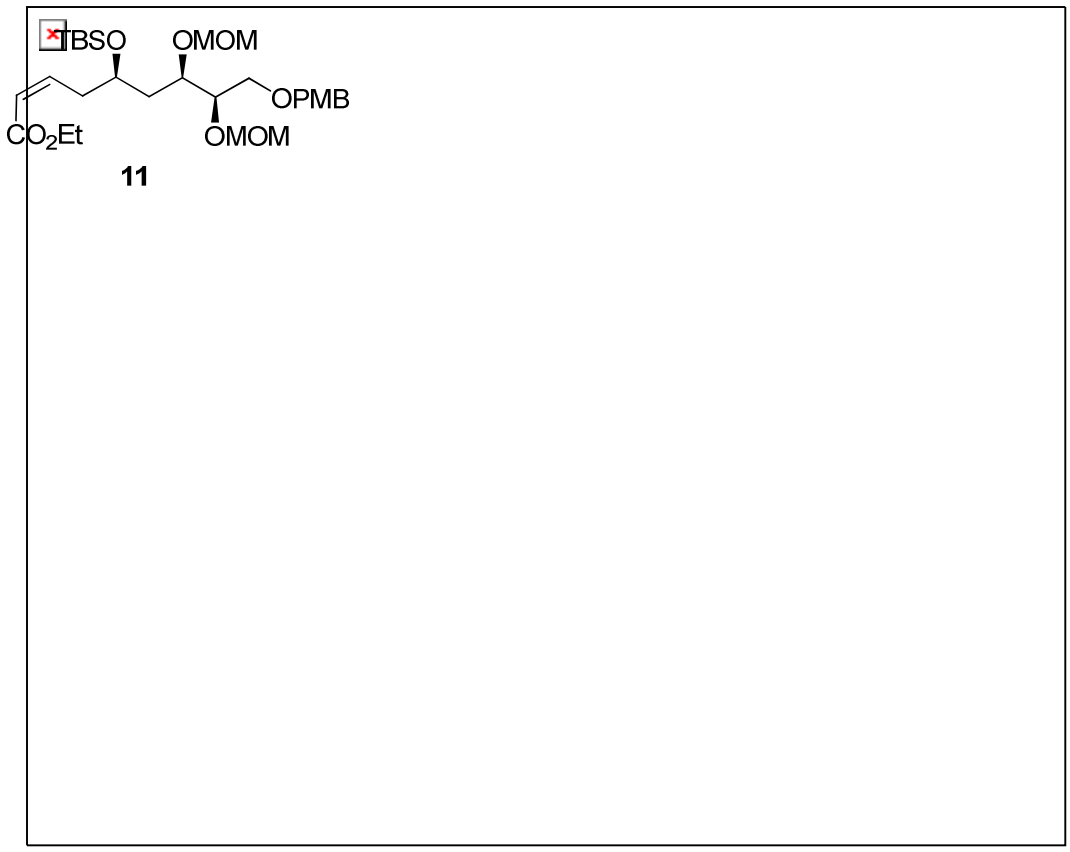
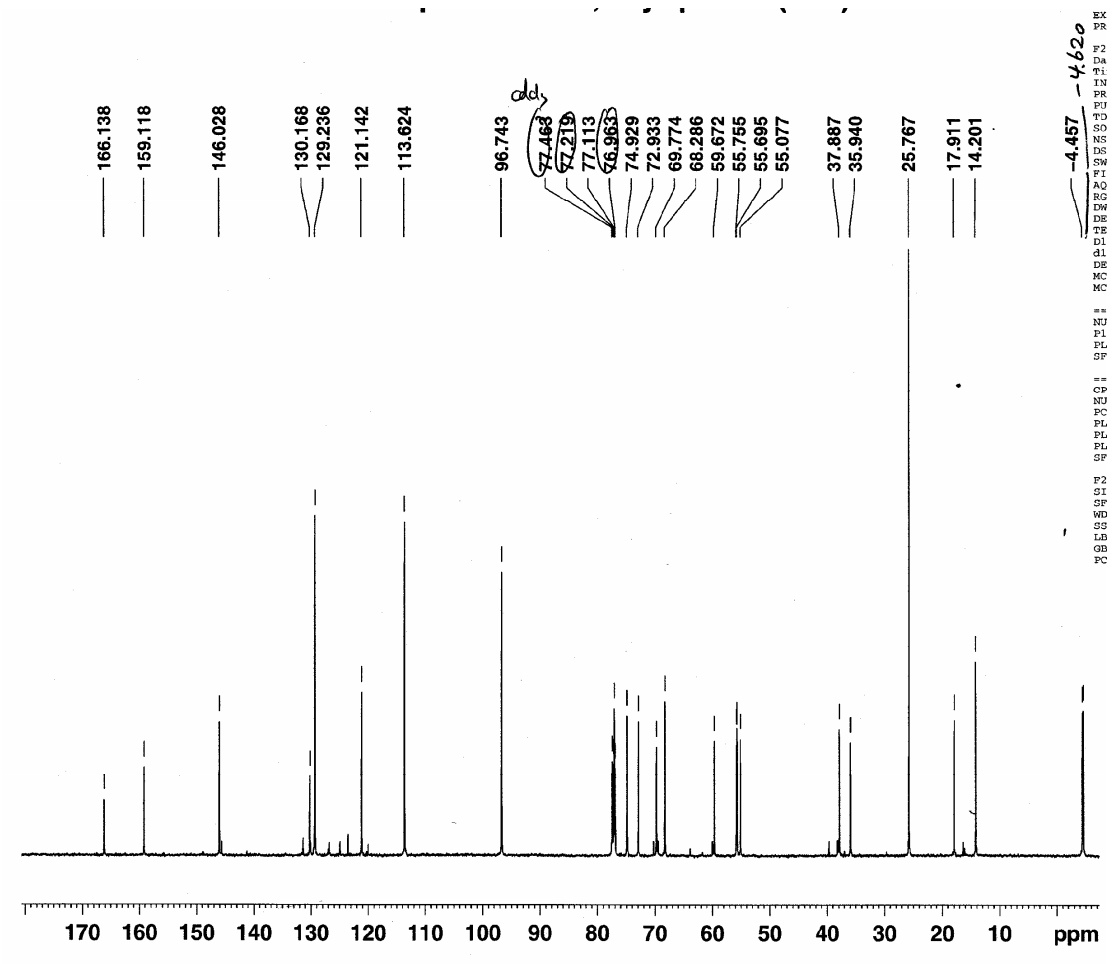
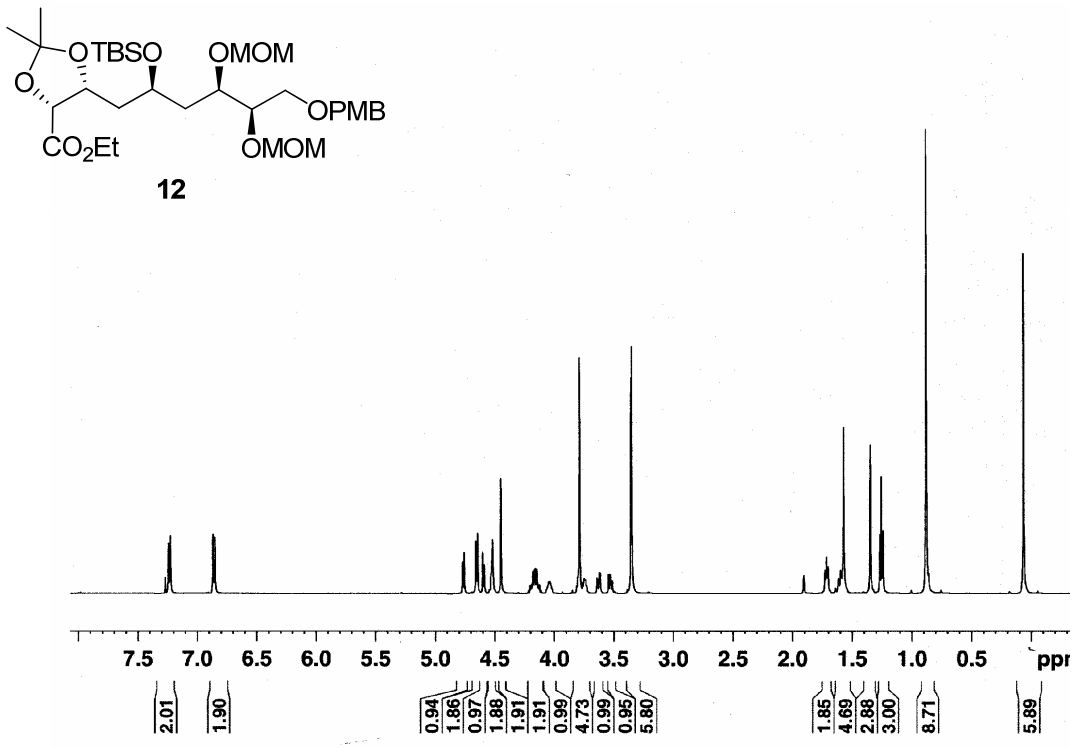
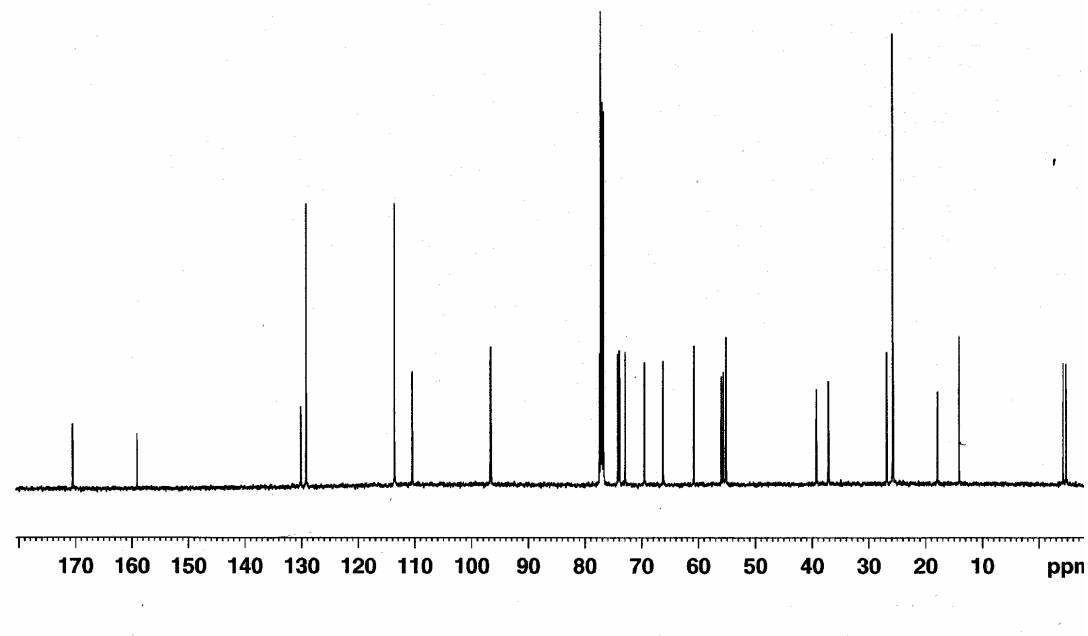
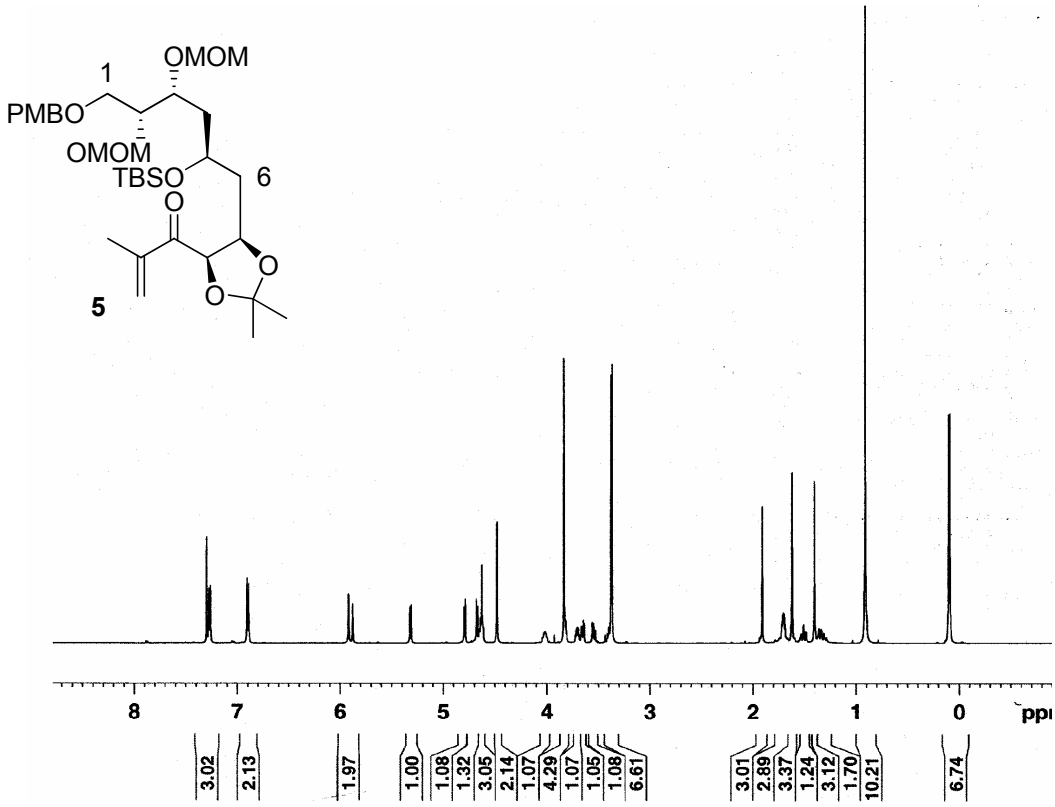
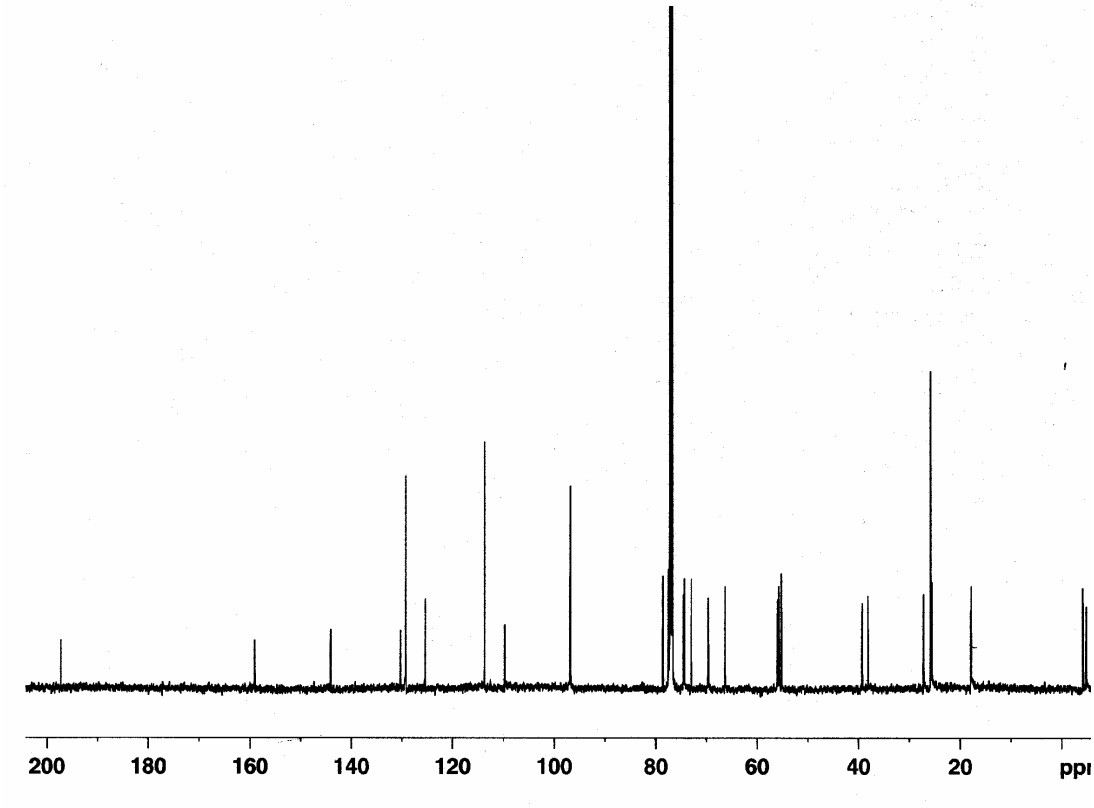

TBSO
OMOM
OPMB
CO2Et
OMOM
11

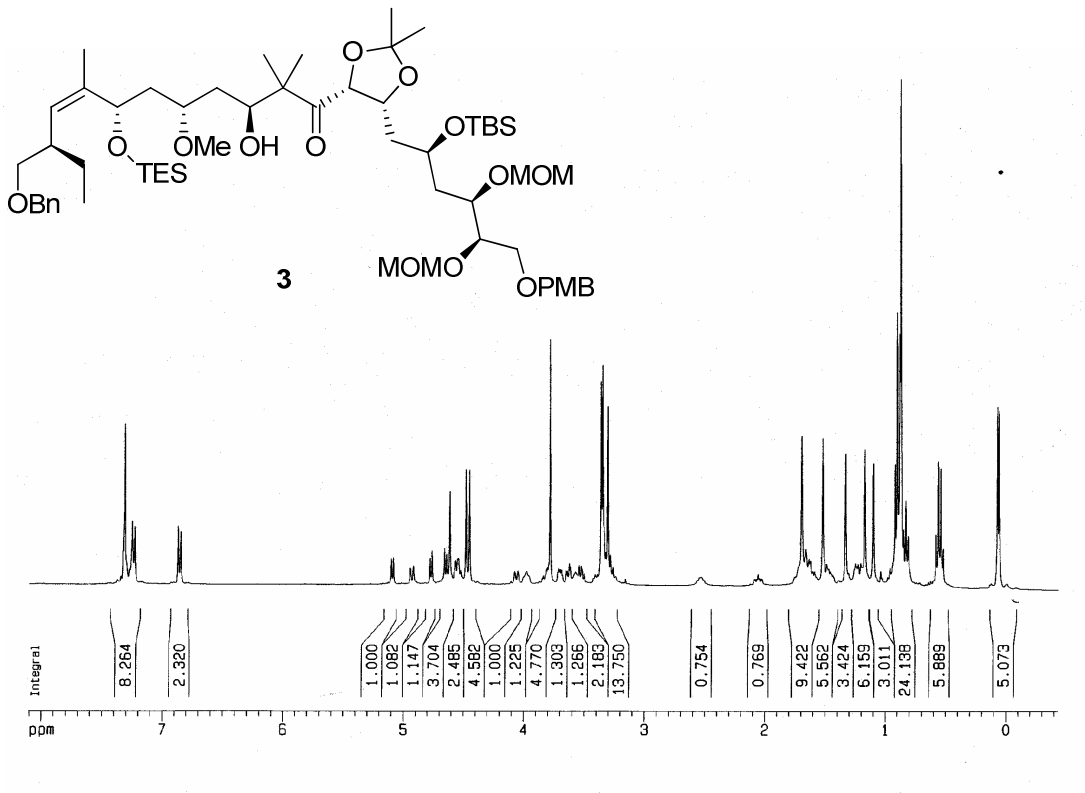

166.138
159.118
146.028
130.168
129.236
121.142
113.624
96.743
77.463
77.219
77.113
76.963
74.929
72.933
69.774
68.286
59.672
55.755
55.695
55.077
37.887
35.940
25.767
17.911
14.201
-4.457
-4.620
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

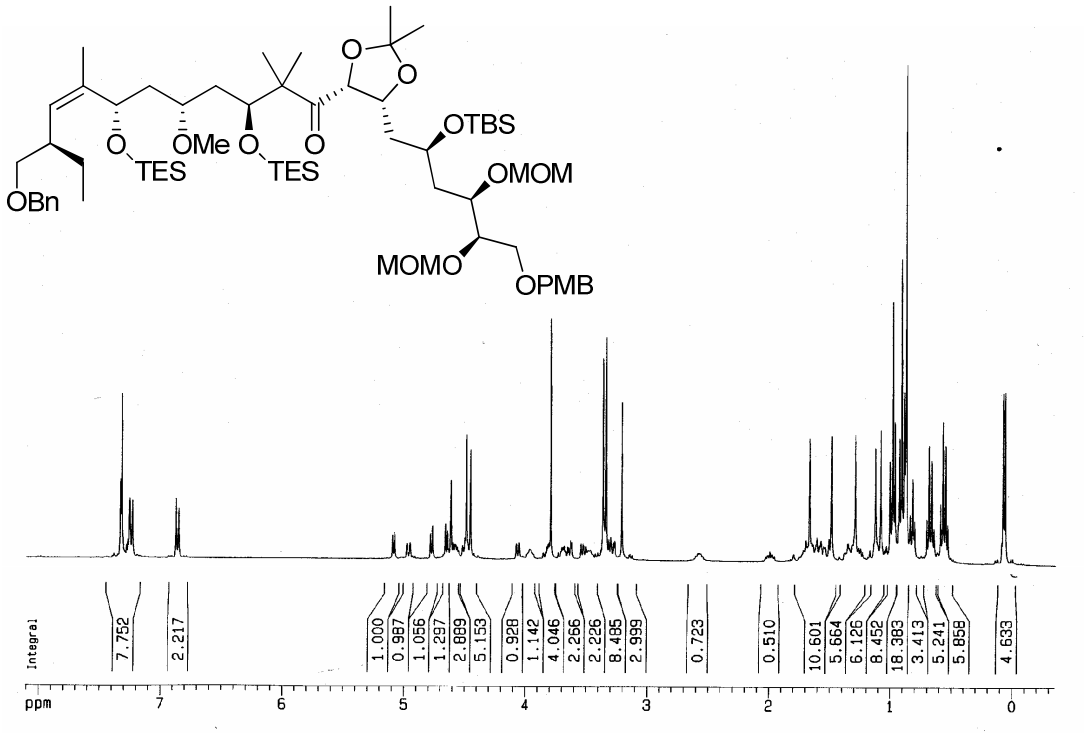

OTBSO
OMOM
O
OPMB
CO2Et
OMOM
12
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppr
2.01 1.90 0.94 1.86 0.97 1.88 1.91 1.91 0.99 4.73 0.99 0.95 5.80 1.85 4.69 2.88 3.00 8.71 5.89

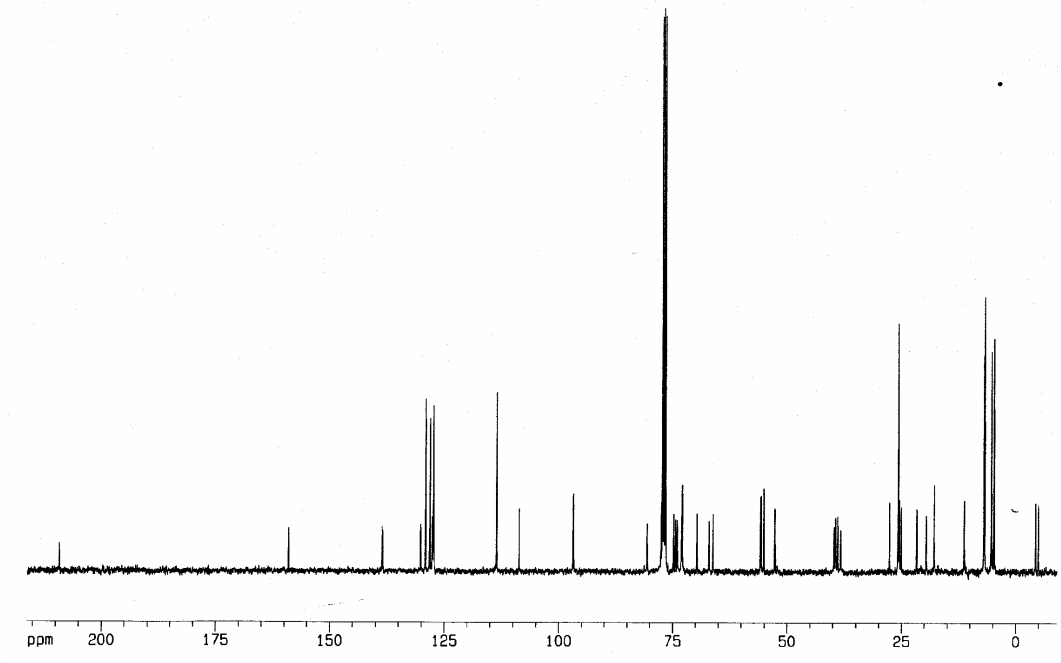

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppn

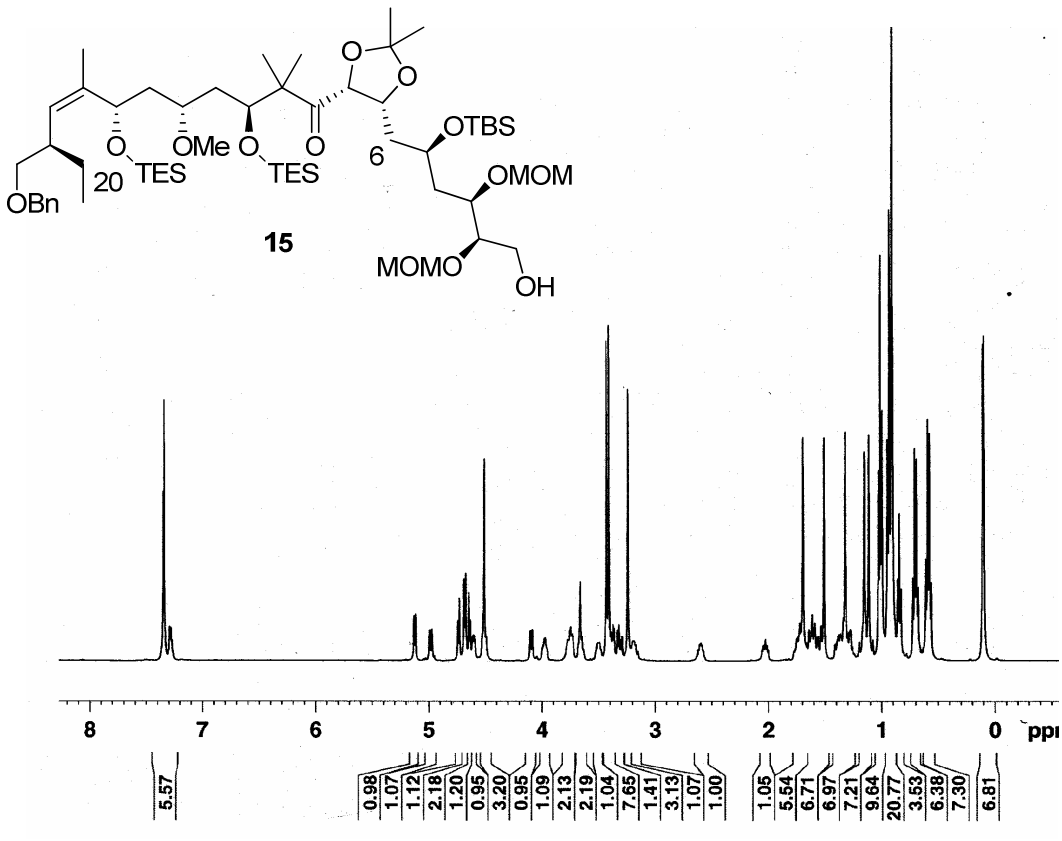

OMOM
1
PMBO
OMOM
TBSO
6
O
O
O
5
8
7
6
5
4
3
2
1
0
ppm
3.02
2.13
1.97
1.00
1.08
1.32
3.05
2.14
1.07
4.29
1.07
1.05
1.08
6.61
3.01
2.89
3.37
1.24
3.12
1.70
10.21
6.74

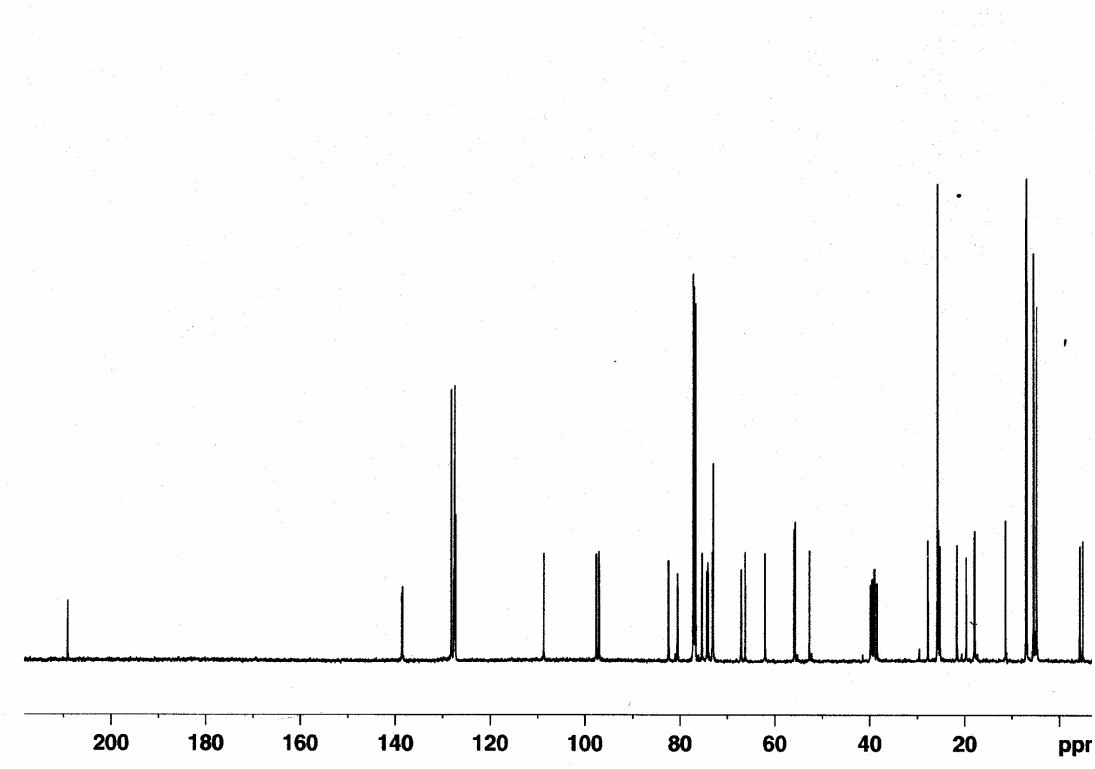

200
180
160
140
120
100
80
60
40
20
ppm

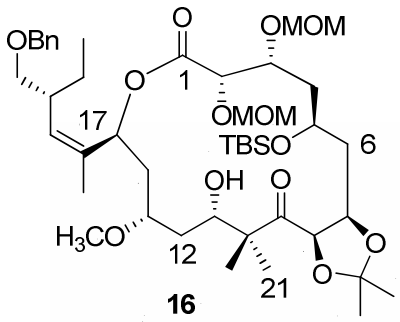

OBn
O
TES
OMe
OH
O
O
O
OTBS
OMOM
MOMO
OPMB
3
Integral
8.264
2.320
1.000
1.082
1.147
3.704
2.485
4.582
1.000
1.225
4.770
1.303
1.266
2.183
13.750
0.754
0.769
9.422
5.562
3.424
6.159
3.011
24.138
5.889
5.073
ppm
7
6
5
4
3
2
1
0


OBn
OTES
OMe
OTES
O
O
O
OTBS
OMOM
MOMO
OPMB
Integral
7.752
2.217
1.000
0.987
1.056
1.237
2.889
5.153
0.928
1.142
4.046
2.286
2.226
8.485
2.999
0.723
0.510
10.601
5.664
6.126
8.452
18.383
3.413
5.241
5.858
4.633
ppm
7
6
5
4
3
2
1
0


ppm
200
175
150
125
100
75
50
25
0

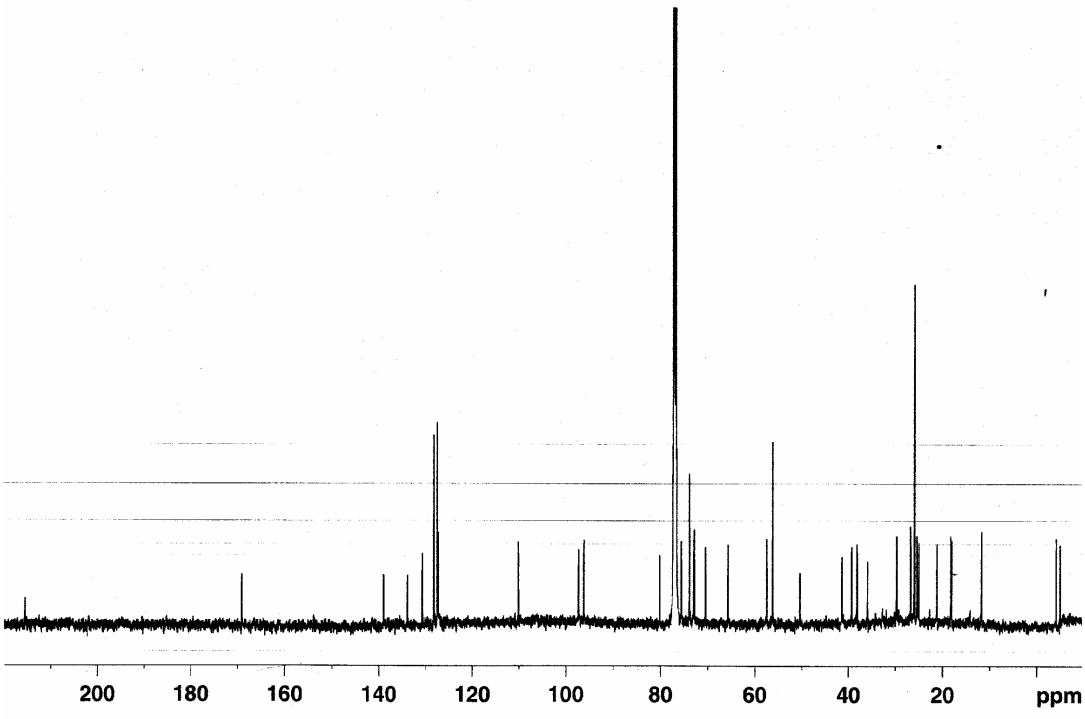

OBn
20
TES
OMe
O
TES
O
6
OTBS
OMOM
MOMO
OH
15
8
7
6
5
4
3
2
1
0
ppı
5.57
0.98
1.07
1.12
2.18
1.20
0.95
3.20
0.95
1.09
2.13
2.19
1.04
7.65
1.41
3.13
1.07
1.00
1.05
5.54
6.71
6.97
7.21
9.64
20.77
3.53
6.38
7.30
6.81

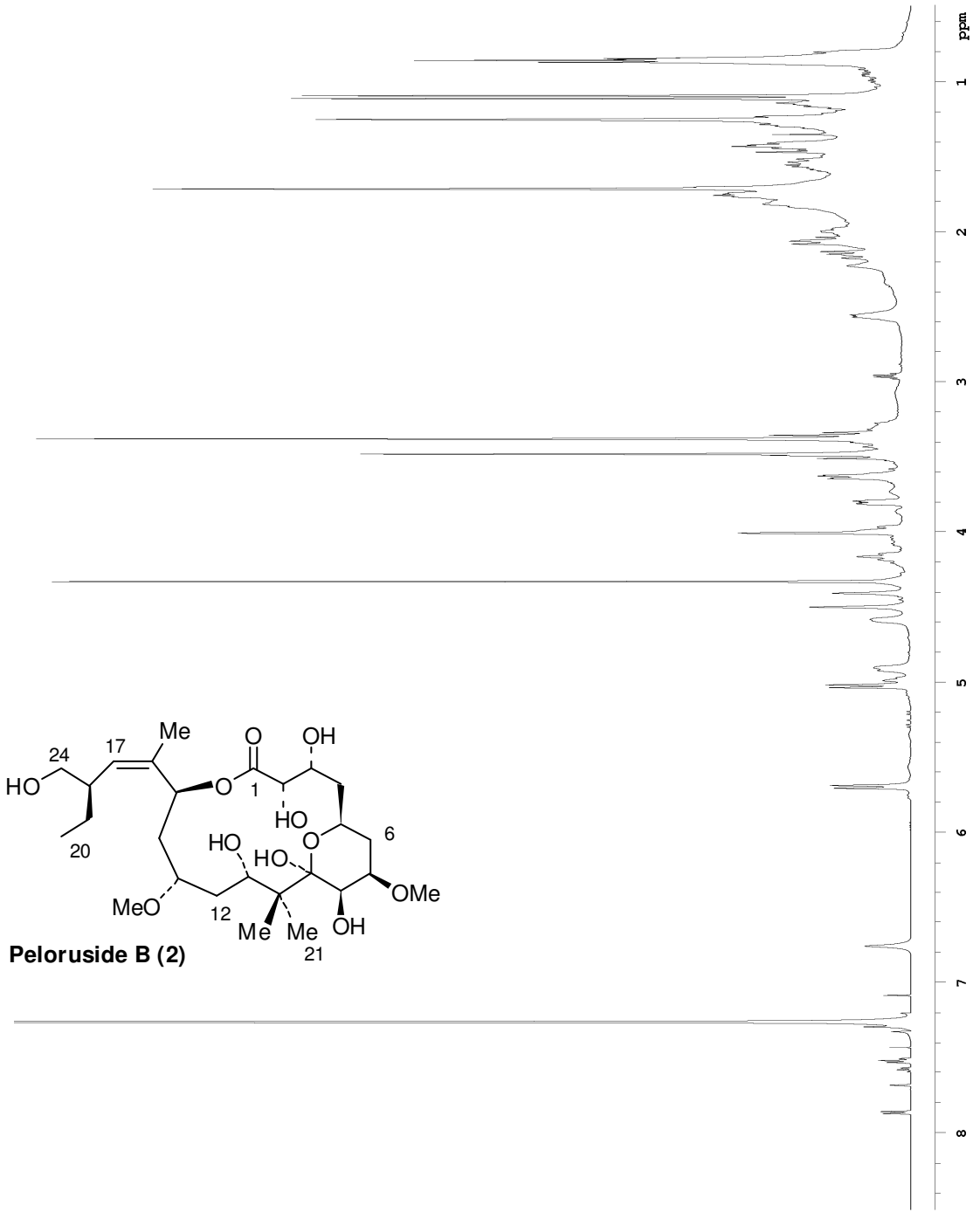

200
180
160
140
120
100
80
60
40
20
ppr


OBn
O
OMOM
1
O
17
OMOM
TBSO
6
OH
O
H3CO
12
21
O
O

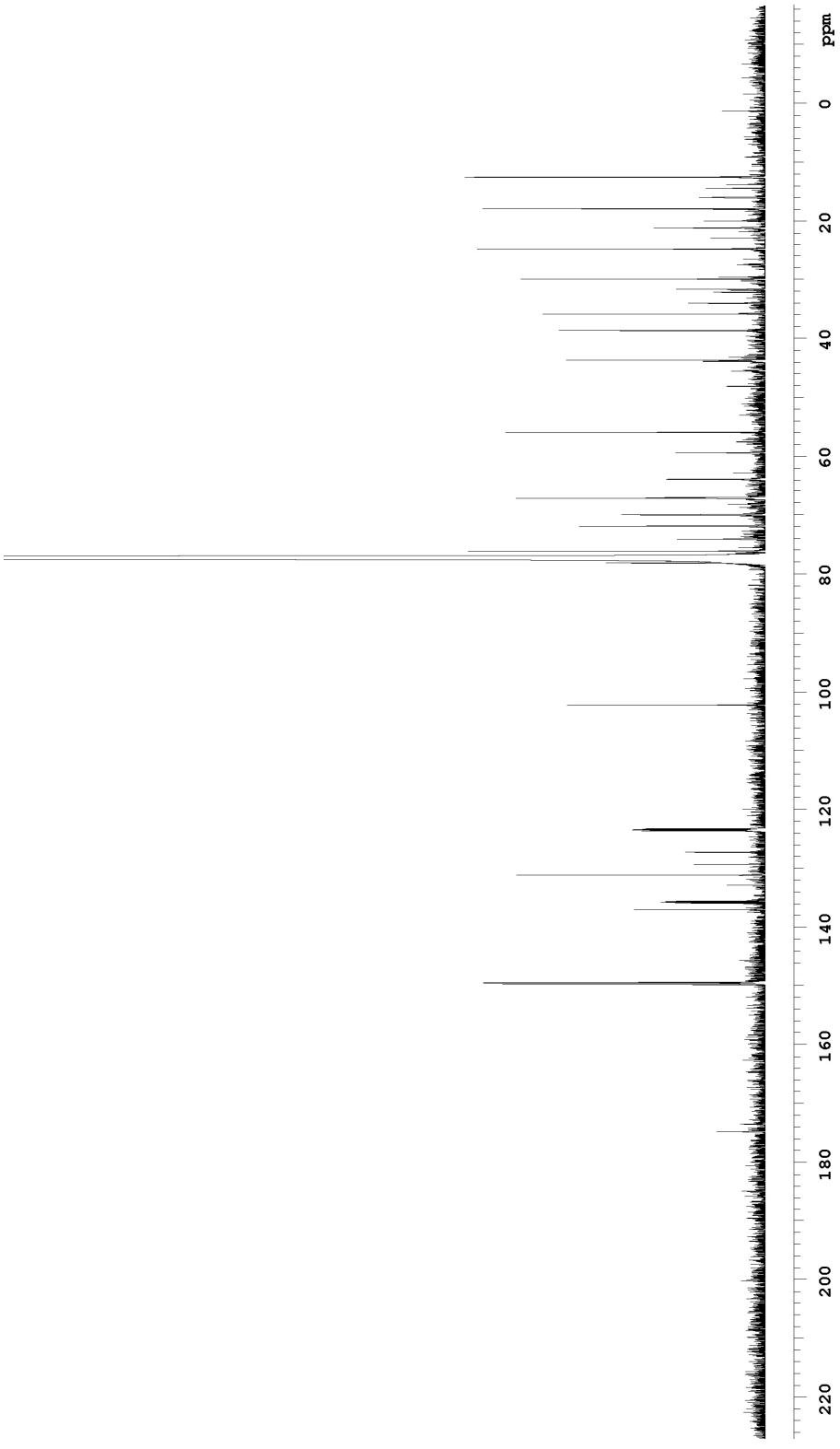
**16**


8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.15 3.19 0.96 1.00 0.99 0.98 3.84 1.99 1.03 0.91 1.81 0.86 10.60 1.05 0.86 2.45 1.11 4.16 8.78 2.86 3.33 7.18 3.47 9.69 4.17 6.16


200 180 160 140 120 100 80 60 40 20 ppm

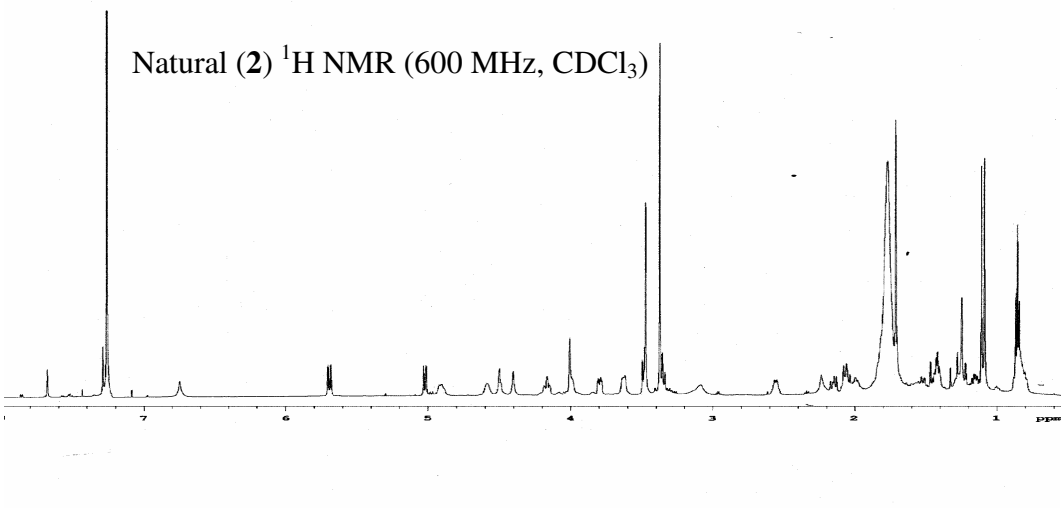



$^1$H NMR spectrum of synthetic peloruside B (**2**) in $CDCl_3$ (600 MHz). $d_5$-Pyridine (1 μL) was added to prevent the decomposition and $MeNO_2$ (3 μL, $\delta_H$ 4.33) was added to determine the quantity of peloruside B (**2**).

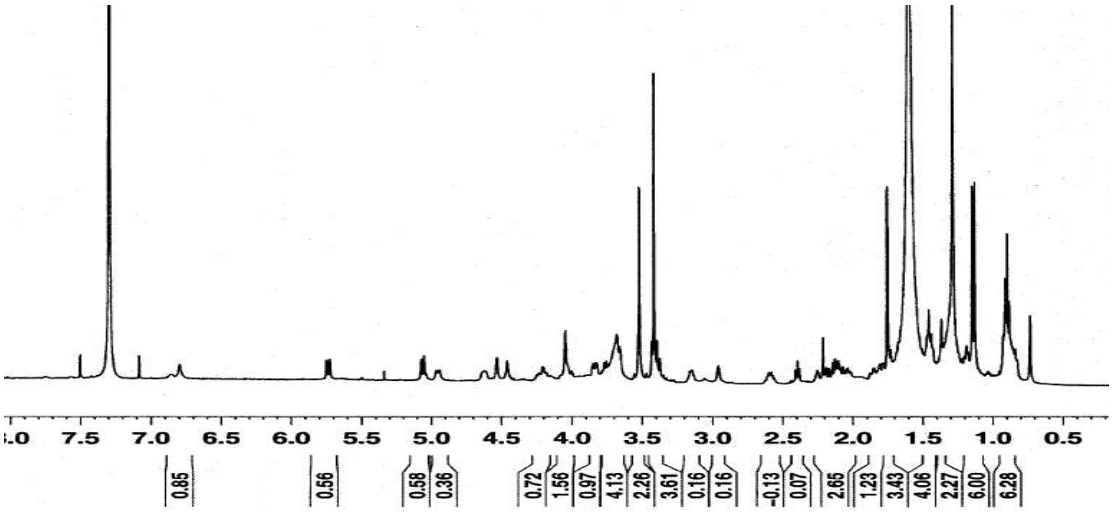



$^{13}$C NMR spectrum of synthetic peloruside B (**2**) in $CDCl_3$ (150 MHz). $d_5$-Pyridine (1 μL) ($\delta_C$ 123.3, 135.6, 149.6) was added to prevent the decomposition and $MeNO_2$ ($\delta_C$ 62.7) was added to determine the quantity of peloruside B (**2**).

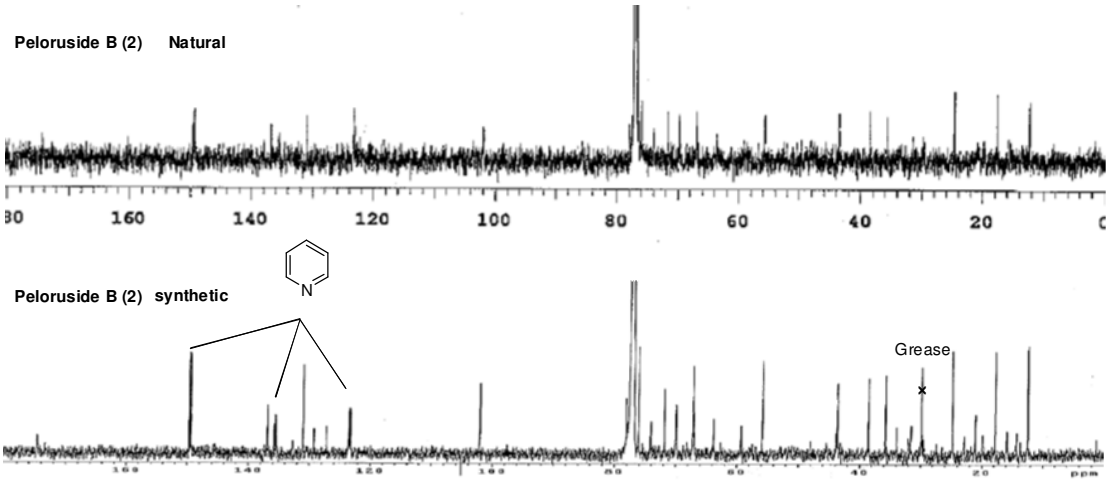
Natural (**2**) $^1$H NMR (600 MHz, $CDCl_3$)



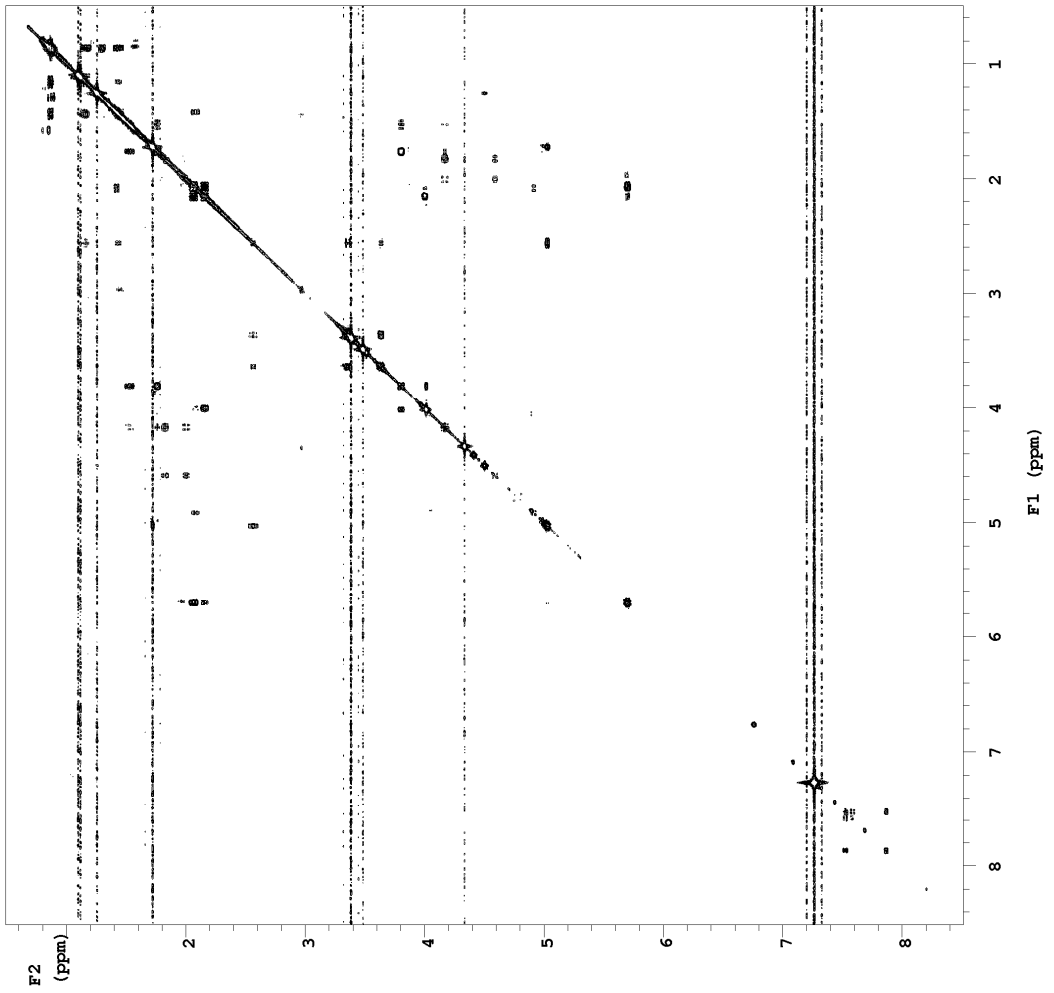
Synthetic (**2**) $^1$H NMR (500 MHz, $CDCl_3$)



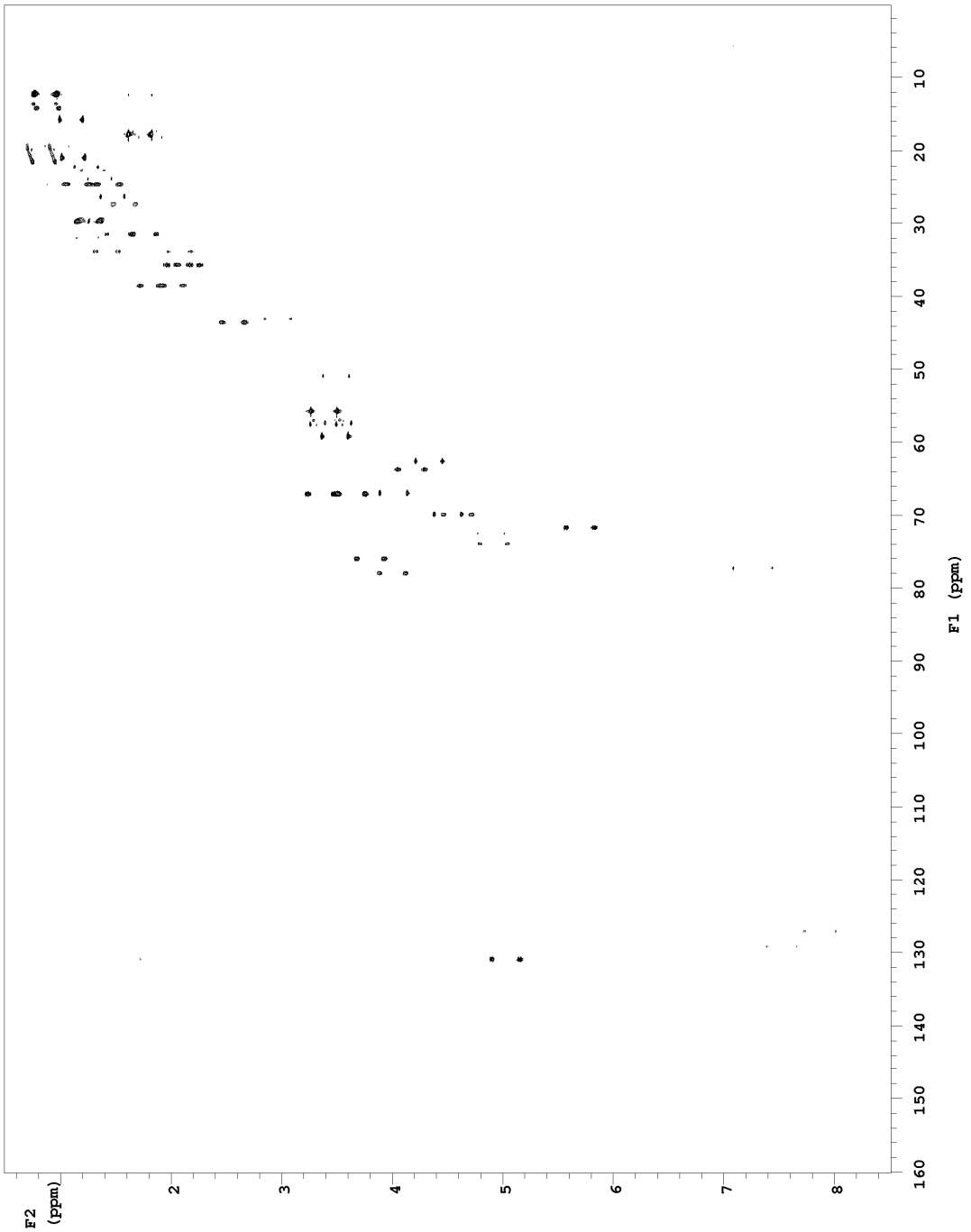

$^1$H NMR spectra of natural peloruside B (**2**) and synthetic peloruside B (**2**) in $CDCl_3$. $d_5$-Pyridine (1 μL) was added to natural peloruside B (**2**) to prevent decomposition.



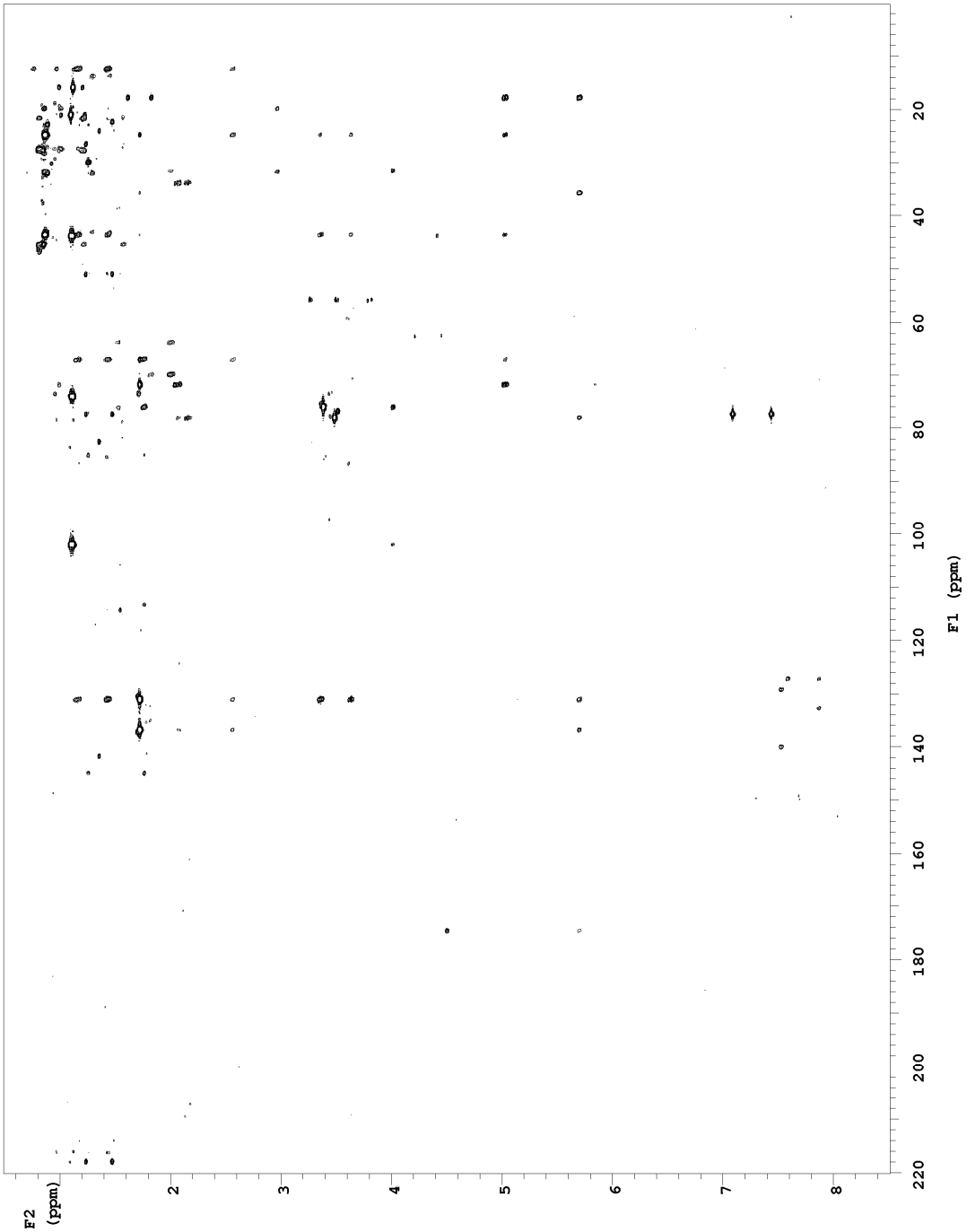

$^{13}$C NMR (150 MHz) spectra of natural peloruside B (**2**) and synthetic peloruside B (**2**) in $CDCl_3$ (150 MHz). $d_5$-Pyridine (1 μL) ($\delta_C$, 123.3, 135.6, 149.6) was added to prevent decomposition.



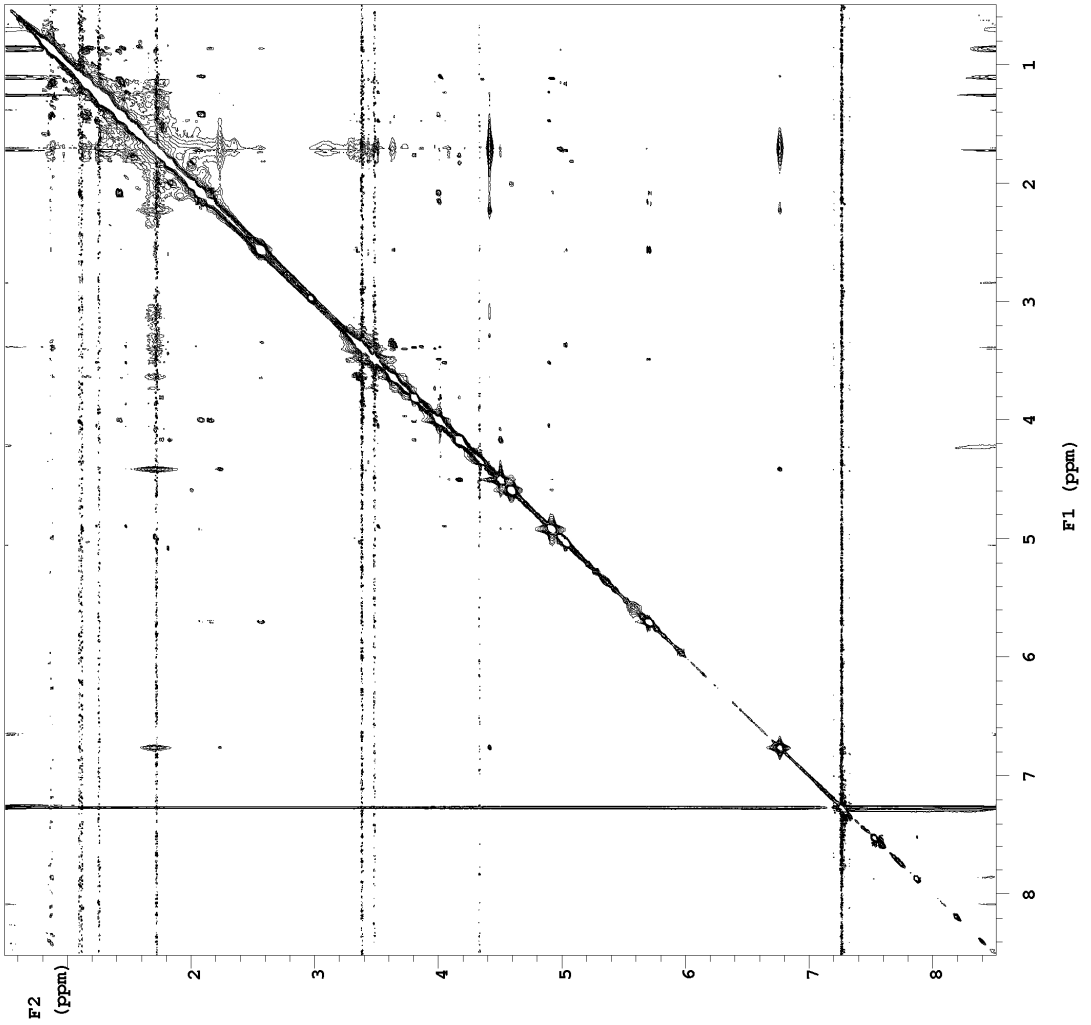

COSY NMR spectrum of *synthetic* peloruside B (**2**) in $CDCl_3$ (600 MHz).




Fully-coupled $HSQC_{ad}$ NMR spectrum of *synthetic* peloruside B (**2**) in $CDCl_3$ (600 MHz).




HMBC NMR spectrum of *synthetic* peloruside B (**2**) in $CDCl_3$ (600 MHz).




NOESY NMR spectrum of *synthetic* peloruside B (**2**) in $CDCl_3$ (600 MHz).