

*Supporting Information for*

## **Stereoselective Synthesis of the C1-C16 Fragment of Purported Structure of Formosalide B**

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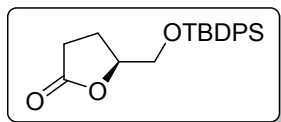
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## 1. Experimental procedures and analytical data:

**1.1 General Information:** Experiments which required an inert atmosphere were carried out under argon in flame-dried glassware. THF freshly distilled over sodium/benzophenone and transferred via syringe. Dichloromethane was freshly distilled from  $\text{CaH}_2$ . Tertiary amines were freshly distilled over KOH. Commercially available reagents were used as received. Unless detailed otherwise, “workup” means pouring the reaction mixture into brine, followed by extraction with the solvent indicated in parentheses. If the reaction medium was acidic (basic), an additional washing with saturated aqueous  $\text{NaHCO}_3$  solution (saturated aqueous  $\text{NH}_4\text{Cl}$  solutions) was performed. Washing with brine, drying over anhydrous  $\text{Na}_2\text{SO}_4$ , and evaporation of the solvent under reduced pressure followed by chromatography on a silica gel column (60–120 mesh) with the indicated eluent furnished the corresponding products. Where solutions were filtered through a Celite pad, the pad was additionally washed with the same solvent used, and the washings were incorporated to the main organic layer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts ( $\delta$ ) are reported in ppm, and coupling constants ( $J$ ) are reported in hertz (Hz). High resolution mass spectra were run by the electron impact mode (ESIMS, 70 eV) or by the FAB mode (*m*-nitrobenzyl alcohol matrix) using an orbitrap mass analyzer. IR data were measured with oily films on NaCl plates (oils) or KBr pellets (solids). Specific optical rotations  $[\alpha]_D$  are given in  $10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$  and were measured at 25 °C or otherwise mentioned. The following abbreviations are used to designate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad.

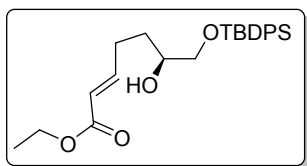
## 2. EXPERIMENTAL SECTION

**(*S*)-5-(((*tert*-Butyldiphenylsilyl)oxy)methyl)dihydrofuran-2(3*H*)-one (8):**



To a stirred solution of (*S*)-5-(hydroxymethyl)dihydrofuran-2(3*H*)-one (2.0 g, 17.24 mmol) in  $\text{CH}_2\text{Cl}_2$  (60 mL) under nitrogen atmosphere, was added imidazole (2.3 g, 34.48 mmol) followed by *tert*-butyldiphenylchlorosilane (5.6 g, 20.68 mmol) at 0 °C and allowed to stir for 30 min. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with water (50 mL) and diluted with  $\text{CH}_2\text{Cl}_2$  (100 mL), the organic layer was separated. The organic layer was washed with brine ( $2 \times 50$  mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated under reduced pressure to obtain the crude product which on purification by silica gel column chromatography purification (ethyl acetate: hexane produced = 1:19) furnished the desired lactone **8** (5.42 g, 89%).  $[\alpha]_{\text{D}}^{25} +28.7$  (*c* 0.9,  $\text{CHCl}_3$ ); lit.<sup>7d</sup>  $[\alpha]_{\text{D}} +28.95$  (*c* 2.0,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  2952, 2858, 1772, 1110, 702  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.70 – 7.63 (m, 4 H), 7.47 – 7.65 (m, 6H), 4.62 – 4.57 (m, 1H), 3.88 (dd, *J* = 11.44, 3.35 Hz, 1H), 3.69 (dd, *J* = 11.44, 3.35 Hz, 1H), 2.71 – 2.63 (m, 1H), 2.55 – 2.47 (m, 1H), 2.33 – 2.18 (m, 2H), 1.06 (s, 9H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  77.4, 135.6, 135.5, 129.9, 127.8, 79.9, 65.5, 28.5, 26.7, 23.6, 19.2 ppm; HRMS (ESI): *m/z* calcd for  $\text{C}_{21}\text{H}_{26}\text{O}_3\text{Si}$  [*M* + *Na*]<sup>+</sup> 377.1549, found 377.1568.

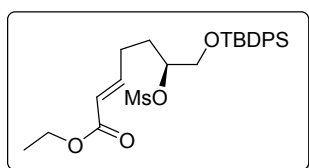
**(*S,E*)-Ethyl-7-((*tert*-butyldiphenylsilyl)oxy)-6-hydroxyhept-2-enoate (**10**):**



To a stirred solution of lactone **8** (4.5 g, 12.71 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) at  $-78$  °C under nitrogen atmosphere, DIBAL-*H* (9.98 mL, 1.4 *M* in toluene, 13.98 mmol) was slowly added over a period of 15 min. After 30 min of stirring at the same temperature (TLC), the reaction was

quenched by slow addition of saturated sodium potassium tartrate solution (50 mL), diluted with  $\text{CH}_2\text{Cl}_2$  (50 mL) and allowed to stir at room temperature for another 2 h to get a clear two separated layers. The organic layer was separated and the aqueous layer extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 80$  mL). The combined organic layer was washed with brine ( $2 \times 50$  mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated under reduced pressure to provide crude lactol which was directly used for the next reaction without purification. The corresponding lactol was dissolved in benzene (100 mL) and was added ethoxycarbonylmethylenetriphenyl phosphorane (8.84 g, 25.42 mmol) at room temperature. After stirring for 4 h at  $100^\circ\text{C}$ , the reaction mixture was concentrated under reduced pressure and purified by silica gel column chromatography (ethyl acetate/hexane = 1:19) to give **9** (4.43 g, 82% over two steps).  $[\alpha]_{\text{D}}^{25} -6.07$  ( $c$  1.8,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  3427, 2978, 1716, 1445, 1151, 1039, 922  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.67 – 7.63 (m, 4H), 7.45 – 7.36 (m, 6H), 6.94 (dt,  $J = 13.8, 7.0$  Hz, 1H), 5.81 (dt,  $J = 17.2, 3.2$  Hz, 1H), 4.18 (q,  $J = 14.3, 7.2$  Hz, 2H), 3.75 – 3.68 (m, 1H), 3.65 (dd,  $J = 10.2, 3.6$  Hz, 1H), 3.49 (dd,  $J = 10.2, 7.2$  Hz, 1H), 2.49 (d,  $J = 3.7$  Hz, 1H), 2.40 – 2.19 (m, 2H), 1.66 – 1.46 (m, 2H), 1.28 (t,  $J = 14.3, 7.1$  Hz, 3H), 1.07 (s, 9H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.6, 148.5, 135.5, 133.0, 130.0, 127.8, 121.6, 71.0, 67.8, 60.2, 31.1, 28.2, 26.8, 19.2, 14.2 ppm; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{25}\text{H}_{34}\text{O}_4\text{Si}$   $[\text{M} + \text{Na}]^+$ : 449.2119, found 449.2134.

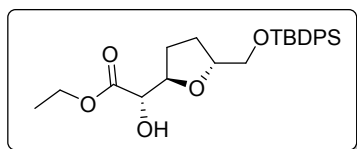
**(*S,E*)-Ethyl-7-((*tert*-butyldiphenylsilyl)oxy)-6-((methanesulfonyl)oxy)hept-2-enoate (**11**):**



To the mixture of **9** (4.1 g, 9.61 mmol) and triethylamine (2.7 mL, 19.23 mmol) in  $\text{CH}_2\text{Cl}_2$  (60 mL), methanesulphonylchloride (1.1 mL, 14.42 mmol) was added dropwise at  $0^\circ\text{C}$ . After stirring for 3 h at same temperature, the reaction was quenched with saturated aqueous  $\text{NaHCO}_3$

(30 mL). The organic layer was separated and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 50$  mL). The combined organic layer was washed with brine (70 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated under reduced pressure to obtain the crude product which was passed through short plug silica gel to get the mesylated product **10** (4.59 g, 95%) as a colorless oil.  $[\alpha]_{\text{D}}^{25} -4.49$  ( $c$  1.95,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  2939, 2861, 1715, 1353, 1173, 701  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.74 – 7.62 (m, 4H), 7.49 – 7.35 (m, 6H), 6.90 (dt,  $J = 15.65$ , 13.69, 6.84 Hz, 1H), 5.83 (dt,  $J = 15.65$  Hz, 1H), 4.76 – 4.69 (m, 1H), 4.18 (q,  $J = 14.18$ , 7.09 Hz, 2H), 3.85 – 3.71 (m, 2H), 2.96 (s, 3 H), 2.38 – 2.21 (m, 2H), 1.93 – 1.79 (m, 2H), 1.28 (t,  $J = 14.30$ , 7.09 Hz, 2H), 1.07 (s, 9H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.3, 146.9, 135.5, 135.4, 134.7, 132.6, 132.5, 130.0, 130.0, 127.9, 122.2, 82.3, 65.1, 60.2, 38.6, 29.7, 27.4, 26.8, 19.2, 14.2 ppm; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{26}\text{H}_{36}\text{O}_6\text{SSi}$   $[\text{M} + \text{Na}]^+$ : 527.1894, found 527.1902.

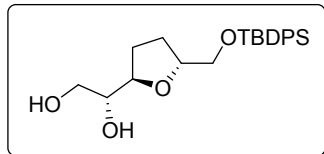
**(S)-Ethyl-2-((2R,5R)-5-(((tert-butyldiphenylsilyl)oxy)methyl)tetrahydrofuran-2-yl)-2-hydroxyacetate (**11**):**



A mixture of  $\text{K}_2\text{OsO}_2(\text{OH})_2$  (16.6 mg, 0.045 mmol, 0.006 equiv),  $(\text{DHQD})_2\text{PHAL}$  (88 mg, 0.11 mmol, 0.015 equiv.),  $\text{K}_3\text{Fe}(\text{CN})_6$  (7.44 g, 22.6 mmol, 3.0 equiv),  $\text{K}_2\text{CO}_3$  (3.12 g, 22.6 mmol, 3.0 equiv) and  $\text{MeSO}_2\text{NH}_2$  (716 mg, 7.53 mmol, 1.0 equiv) in 1:1  $t$ -BuOH/ $\text{H}_2\text{O}$  (100 mL) was stirred for 30 minutes at room temperature. This mixture was slowly poured into 4 °C solution of **10** (3.8 g, 7.53 mmol, 1.0 equiv) in  $t$ -BuOH/ $\text{H}_2\text{O}$  (500 mL). The reaction was stirred at 4 °C for 24 h. After completion of the reaction, solid  $\text{Na}_2\text{S}_2\text{O}_3$  (10 g) was added and the mixture was stirred for 1.5 h while warming to room temperature (color change from orange to dark green). After phase separation, the aqueous layer was extracted with ethyl acetate ( $5 \times 20$  mL). The combined

organic layers were dried over  $\text{Na}_2\text{SO}_4$ , concentrated under reduced pressure to give crude product which was purified by silica gel column chromatography (ethyl acetate/hexane = 4:1) to give **11** (2.93 g, 88%).  $[\alpha]_{\text{D}}^{25} -8.3$  ( $c$  1.6,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  3477, 2931, 2858, 1739, 1110, 704  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.73 – 7.60 (m, 4 H), 7.46 – 7.34 (m, 6H), 4.37 (dt,  $J$  = 2.20, 7.09, 13.93 Hz, 1H), 4.43 – 4.16 (m, 3H), 4.07 (dd,  $J$  = 1.95, 8.06 Hz, 1H), 3.63 (dq,  $J$  = 4.64, 10.63, 25.30, 2H), 2.94 (d,  $J$  = 8.18, 1H), 2.13 – 2.20 (m, 3H), 1.98 – 1.86 (m, 1H), 1.27 (t,  $J$  = 7.21, 14.30 Hz, 3 H), 1.04 (s, 9H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  173.0, 135.6, 135.5, 134.8, 133.6, 133.5, 129.6, 129.5, 127.6, 127.6, 80.8, 80.0, 72.5, 66.2, 61.6, 28.1, 27.8, 26.7, 19.2, 14.1 ppm; HRMS (ESI) :  $m/z$  calcd. for  $\text{C}_{25}\text{H}_{34}\text{O}_5\text{Si}$   $[\text{M} + \text{Na}]^+$ : 465.2068, found 465.2085.

**(*R*)-1-((2*R*,5*R*)-5-(((*tert*-Butyldiphenylsilyl)oxy)methyl)tetrahydrofuran-2-yl)ethane-1,2-diol (**12**):**

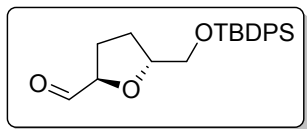


To a solution of ester **11** (2.5 g, 5.65 mmol) in diethyl ether (50 mL),  $\text{LiBH}_4$  (184 mg, 8.48 mmol) was added at 0  $^\circ\text{C}$  in a single portion. MeOH (5 mL) was added to the above reaction mixture at same temperature. The above reaction mixture was stirred for additional 2 h at room temperature. After completion of reaction (TLC), it was quenched with aqueous  $\text{NaHCO}_3$  solution (20 mL) and extracted with ethyl acetate ( $3 \times 50$  mL), the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , evaporated under reduced pressure to crude product which was purified by silica gel column chromatography (ethyl acetate/hexane = 1:1) to furnish diol **12** (1.96 g, 87%) as a colorless viscous liquid  $[\alpha]_{\text{D}}^{25} -4.0$  ( $c$  1.3,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  3421, 2931, 2858, 1427, 1110, 703  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.70 – 7.66 (m, 4H), 7.45 – 7.35 (m, 6H), 4.18 – 4.09 (m, 1H), 4.03, 3.97 (m, 1H), 3.72 – 3.60 (m, 4H), 3.53 (q,  $J$  = 4.40, 8.68 Hz, 1H), 2.72 (br s,



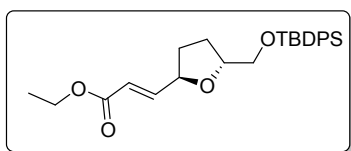
1H), 2.58 (br, 1H), 2.03 – 1.76(m, 4H), 1.05 (s, 9H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  135.6, 133.6, 133.5, 129.6, 127.6, 80.7, 80.2, 72.8, 66.3, 64.9, 28.1, 27.9, 26.8, 19.2 ppm; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{23}\text{H}_{32}\text{O}_4\text{Si}$   $[\text{M} + \text{Na}]^+$ : 423.1962, found 423.1970.

**(2*R*,5*R*)-5-(((*tert*-Butyldiphenylsilyl)oxy)methyl)tetrahydrofuran-2-carbaldehyde (13):**



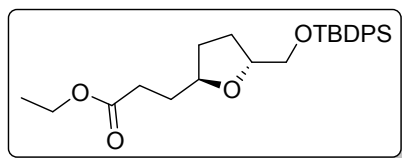
To the solution of **12** (1.4 g, 3.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (80 mL),  $\text{NaIO}_4$ -silica (35 g) was added at 0 °C. The reaction was stirred for 30 min at room temperature. After completion of reaction (TLC), the reaction mixture was filtered and washed with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 30$  mL). The resulting solution was concentrated under reduced pressure to provide the crude product which upon silica-gel column chromatography purification (ethyl acetate/hexane = 1:5) afforded **13** (0.828 g, 90%) as a colorless viscous liquid.  $[\alpha]_{\text{D}}^{25} + 3.41$  ( $c$  3.45,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  2931, 2858, 1733, 1427, 1110, 704  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.66 (d,  $J = 1.67$  Hz, 1 H), 7.70 – 7.66 (m, 4H), 7.44 – 7.35 (m, 6H), 4.36 – 4.32 (m, 1H), 4.29 – 4.22 (m, 1H), 3.71 (dq,  $J = 25.63, 10.83, 4.42$  Hz, 2H), 2.24 – 2.16 (m, 1H), 2.01 – 1.90 (m, 3H), 1.06 (s, 9H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.8, 135.5, 133.3, 133.3, 129.7, 127.6, 83.3, 81.0, 65.9, 27.3, 27.2, 26.8, 19.2 ppm; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{28}\text{O}_3\text{Si}$   $[\text{M} + \text{NH}_4]^+$ : 386.2146, found 386.2155.

**(*E*)-Ethyl-3-((2*R*,5*R*)-5-(((*tert*-butyldiphenylsilyl)oxy)methyl)tetrahydrofuran-2-yl)acrylate (14):**



To a stirred suspension of ethyl 2-(triphenylphosphoranylidene)acetate (1.5 g, 4.34 mmol) in toluene (50 mL) was added a solution of **13** (800 mg, 2.17 mmol) was added at reflux and maintained for 5h. Cool the reaction mass to room temperature and poured into water carefully. The mixture was extracted with ethyl acetate ( $2 \times 40$  mL) and the organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated under reduced pressure. The resulting syrup was purified by silica gel column chromatography (EtOAc/hexane = 1:9) to give compound **15** (846 mg, 89%) as a colorless liquid.  $[\alpha]_{\text{D}}^{25} +6.2$  ( $c$  2.2,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  2932, 2859, 1721, 1187, 1110, 704  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.73 – 7.57 (m, 4H), 7.45 – 7.32 (m, 6H), 6.91 (dd,  $J$  = 15.65, 4.86 Hz, 1H), 6.02 (dd,  $J$  = 15.65, 1.58 Hz, 1H), 4.63 – 4.57 (m, 1H), 4.30 – 4.09 (m, 1H), 4.20 (q,  $J$  = 14.30, 7.21 Hz, 2H), 3.67 (d,  $J$  = 4.64 Hz, 2H), 2.23 – 1.58 (m, 3H), 1.29 (t,  $J$  = 14.30, 7.21 Hz, 3H), 1.36 – 1.20 (m, 2H), 1.06 (s, 9H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.6, 148.5, 135.6, 133.5, 129.6, 127.8, 127.6, 120.1, 79.8, 78.0, 66.3, 60.3, 31.8, 27.6, 26.8, 19.2, 14.2 ppm; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{26}\text{H}_{34}\text{O}_4\text{Si}$   $[\text{M} + \text{NH}_4]^+$ : 456.2564 found 456.2564.

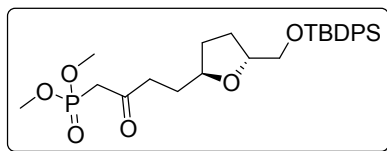
**Ethyl-3-((2*R*,5*R*)-5-(((*tert*-butyldiphenylsilyl)oxy)methyl)tetrahydrofuran-2-yl)propanoate (**15**):**



To a solution of  $\alpha,\beta$ -unsaturated ester **14** (800 mg, 1.82 mmol) in ethyl acetate (15 mL), was added Pd/C (0.2 g, 0.18 mmol) under hydrogen atmosphere at room temperature and stirring continued for 2 h. After completion of the reaction (monitored by TLC), the reaction mass was passed through a small Celite pad and washed with ethyl acetate ( $2 \times 25$  mL). The filtrate was concentrated under reduced pressure to provide crude product which was purified by silica gel column chromatography (ethyl acetate/hexane = 1:19) to furnish **15** (794 mg, 99%) as a colorless

viscous liquid.  $[\alpha]_D^{25} -3.9$  ( $c$  2.2,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  2930, 2858, 1732, 1108, 701  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.71 – 7.66 (m, 4H), 7.43 – 7.35 (m, 6H), 4.14 – 4.08 (m, 3H), 3.99 – 3.93 (m, 1H), 3.63 (dd,  $J = 4.57, 1.52$  Hz, 2 H), 2.49 – 2.42 (m, 1H), 2.40 – 2.33 (m, 1H), 2.06 – 1.96 (m, 2H), 1.88 – 1.78 (m, 3H), 1.56 – 1.47 (m, 1H), 1.64 (br s, 1H), 1.24 (t,  $J = 14.19, 7.17$  Hz, 3H), 1.05 (s, 9H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  173.6, 135.6, 133.7, 129.5, 127.6, 78.9, 78.5, 66.5, 60.3, 31.7, 31.2, 30.8, 29.7, 28, 26.8, 19.2, 14.2 ppm; HRMS (ESI):  $m/z$  calcd for  $m/z$  calcd. for  $\text{C}_{26}\text{H}_{36}\text{O}_4\text{Si}[\text{M} + \text{Na}]^+$  463.2281, found 463.2267.

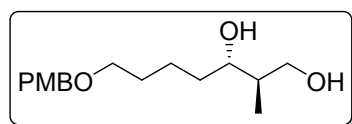
**Dimethyl-4-((2*R*,5*R*)-5-((*tert*-butyldiphenylsilyloxy)methyl)tetrahydrofuran-2-yl)-2-oxobutylphosphonate (5):**



To a stirred solution of the dimethylmethylphosphonate (570 mg, 4.60 mmol) in THF (30 mL),  $n\text{-BuLi}$  (1.7 mL, 4.29 mmol, 2.5  $M$  in hexane) was slowly added at  $-78$   $^{\circ}\text{C}$  under Argon atmosphere and allowed to slowly warm to  $0$   $^{\circ}\text{C}$ . After 1 h, the reaction mixture was again cooled to  $-78$   $^{\circ}\text{C}$  and the solution of ester **15** (450 mg, 1.02 mmol) in THF (30 mL) was slowly added and stirred at the same temperature for 1 h. After complete consumption of the starting material (monitored by TLC), the reaction mixture was quenched with saturated  $\text{NH}_4\text{Cl}$  (20 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate ( $2 \times 40$  mL). The combined organic layers were washed with brine (50 mL) and dried over  $\text{Na}_2\text{SO}_4$ . The organic layer was concentrated under reduced pressure to obtain the crude mass which on purification by silica gel column chromatography (ethyl acetate/hexane = 1:1) afforded the desired **6** (428 mg, 90%) as a colorless liquid.  $[\alpha]_D^{25} -4.0$  ( $c$  1.0,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  2933, 2859, 1716, 1109, 1034, 702  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ ) :  $\delta$  7.70 – 7.65 (m, 4H), 7.44 –

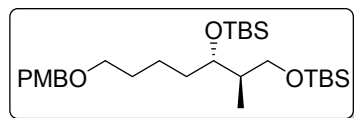
7.35 (m, 6H), 4.12 – 4.05 (m, 1H), 3.96 – 3.89 (m, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.65 – 3.58 (m, 2H), 3.16 – 3.04 (m, 2H), 2.80 – 2.61 (m, 2H), 2.05 – 1.95 (m, 2H), 1.85 – 1.70 (m, 3H), 1.55 – 1.46 (m, 1H), 1.05 (s, 9H) ppm;  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  201.7, 201.7, 135.6, 133.7, 129.5, 127.6, 78.9, 78.3, 66.5, 53.0, 52.9, 41.8, 40.9, 40.7, 31.7, 29.5, 28, 26.8, 19.2 ppm; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{27}\text{H}_{39}\text{O}_6\text{Psi}$   $[\text{M} + \text{NH}_4]^+$ : 536.2591 found 536.2598.

**(2*R*,3*S*)-7-((4-Methoxybenzyl)oxy)-2-methylheptane-1,3-diol (17):**



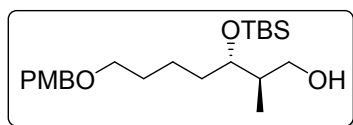
To a solution of chiral epoxide **16** (1.8 g, 6.76 mmol) in dry THF (40 mL), CuI (0.128 g, 0.676 mmol) was added and the mixture was stirred at 25 °C for 30 min. It was cooled to –5 °C and methyl magnesium bromide (20.28 mL, 1M in THF, 20.28 mmol) was slowly added at the same temperature. It was allowed to stir for another 12 h at same temperature. After completion of the reaction (TLC), it was quenched with saturated  $\text{NH}_4\text{Cl}$  (30 mL) and diluted with ethyl acetate (50 mL). The two layers were separated and the aqueous layer was extracted with ethyl acetate (2 × 50 mL). The combined organic layers were washed with brine (100 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure to obtain the crude product which was then purified by column chromatography over silica gel (ethyl acetate/hexane = 1:1) to afford the product **17** (1.43 g, 75%).  $[\alpha]_{\text{D}}^{25}$  –8.0 ( $c$  0.51,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  3385, 2936, 2863, 1512, 1247, 1032, 770  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.25 (d,  $J$  = 8.54 Hz, 2H), 6.87 (d,  $J$  = 8.69 Hz, 2H), 4.42 (s, 2H), 3.79 (s, 3H), 3.71 (dd,  $J$  = 10.83, 3.66 Hz, 1H), 3.59 – 3.49 (m, 2H), 3.49 – 3.42 (m, 2H), 1.73 – 1.36 (m, 7H), 0.85 (d,  $J$  = 7.01 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.1, 132.0, 129.3, 113.7, 76.8, 72.5, 70.0, 67.5, 55.2, 39.7, 34.8, 29.5, 21.8, 13.8 ppm; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{26}\text{O}_4$   $[\text{M} + \text{Na}]^+$ : 305.1723, found 305.1739.

**(5*S*,6*R*)-5-(4-((4-Methoxybenzyl)oxy)butyl)-2,2,3,3,6,9,9,10,10-nonamethyl-4,8-dioxa-3,9-disilaundecane (18):**



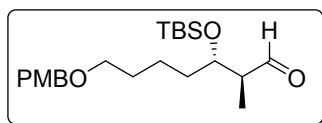
To a stirred solution of **17** (1.2 g, 4.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) under nitrogen atmosphere, was added DIPEA (2.67 mL, 14.88 mmol) followed by *tert*-butyldimethylsilyl trifluoromethanesulfonate (2.81 g, 10.63 mmol) at 0 °C and was stirred for 6 h. After completion of the reaction (monitored by TLC), it was quenched with water (20 mL). The organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 40 mL). The combined organic layer was washed with brine (70 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure to obtain the crude product which on purification by silica gel column chromatography (ethyl acetate/hexane = 1:19) furnished **18** (1.97 g, 91%). [ $\alpha$ ]<sub>D</sub><sup>25</sup> -6.9 (*c* 1.6, CHCl<sub>3</sub>); IR (KBr):  $\nu_{max}$  2934, 2857, 1515, 1250, 1094, 837, 772 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.26 (d, *J* = 8.68 Hz, 2 H), 6.87 (d, *J* = 8.80 Hz, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.69 (q, *J* = 9.53, 4.64 Hz, 1H), 3.55 (dd, *J* = 10.02, 6.48 Hz, 1H), 3.46 – 3.37 (m, 3H), 1.88 – 1.75 (m, 1H), 1.64 – 1.24 (m, 6H), 0.89 (s, 9H), 0.88 (s, 9H), 0.83 (d, *J* = 6.96 Hz, 3H), 0.03 (s, 12H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  159.0, 130.8, 129.2, 113.7, 73.1, 72.5, 70.2, 65.2, 55.3, 40.9, 32.4, 30.0, 25.9, 21.8, 18.3, 18.1, 12.2, -4.4, -4.6, -5.4, -5.5 ppm; HRMS (ESI) : *m/z* calcd. for C<sub>28</sub>H<sub>54</sub>O<sub>4</sub>Si<sub>2</sub>[M + NH<sub>4</sub>]<sup>+</sup>: 528.3898, found 528.3902.

**(2*R*,3*S*)-3-((*tert*-Butyldimethylsilyl)oxy)-7-((4-methoxybenzyl)oxy)-2-methylheptan-1-ol (19):**



To a stirred solution of **18** (1.6 g, 3.13 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL) and MeOH (40 mL), pyridinium *p*-toluenesulfonate (78 mg, 0.31 mmol) was added at 0 °C. The reaction was stirred for 6 h at same temperature. Triethylamine (3 mL) was added to the reaction mixture and concentrated under reduced pressure to get the crude product which was purified by silica gel chromatography (ethyl acetate/hexane = 1:9) to furnish **19** (1.1 g, 90%) as a colorless liquid.  $[\alpha]_{\text{D}}^{25} +5.3$  (*c* 0.51  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  3447, 2932, 2857, 1513, 1249, 772  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.25 (d,  $J = 8.69$  Hz, 2H), 6.87 (d,  $J = 8.69$  Hz, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.77 (dd,  $J = 10.83, 3.81$  Hz, 1H), 3.69 (dd,  $J = 11.13, 5.18$  Hz, 1H), 3.52 (dd,  $J = 10.83, 5.18$  Hz, 1H), 3.44 (dt,  $J = 12.97, 6.40, 1.67$  Hz, 2H), 1.76 (m, 1H), 1.63 – 1.50 (m, 4H), 1.37 (q,  $J = 15.71, 7.93$  Hz, 2H), 0.99 (d,  $J = 7.01$  Hz, 3H), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.1, 130.6, 129.2, 113.7, 77.2, 72.6, 69.9, 65.3, 55.2, 37.7, 34.6, 29.9, 25.8, 21.6, 18.0, 14.6,  $-4.3, -4.8$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{40}\text{O}_4\text{Si}$   $[\text{M} + \text{Na}]^+$ : 419.2594, found 419.2581.

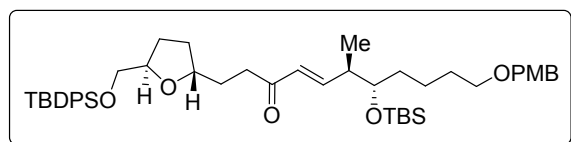
**(2*S*,3*S*)-3-(*tert*-Butyldimethylsilyloxy)-7-(4-methoxybenzyloxy)-2-methylheptanal (**6**):**



To a solution of alcohol **20** (0.9 g, 2.27 mmol) in  $\text{CH}_2\text{Cl}_2$  (25 mL),  $\text{NaHCO}_3$  (0.381 g, 4.54 mL) and Dess-Martin periodinane (1.92 g, 4.54 mmol) were added at 0 °C under nitrogen atmosphere and was stirred for 2 h at room temperature. After complete conversion of the starting material (monitored by TLC), the reaction was quenched with water (20 mL) and diluted with  $\text{CH}_2\text{Cl}_2$  (25 mL). The two layers were separated and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 30$

mL). The combined organic layer was washed with brine (50 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure to get the crude product which was passed through silica gel (ethyl acetate/hexane = 1:5) to afford the aldehyde **7** (0.797 g, 89%) as a colorless liquid.  $[\alpha]_{\text{D}}^{25} +8.0$  ( $c$  1.5,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  2930, 2856, 1724, 1512, 1250, 773  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.81 (d,  $J$  = 2.59 Hz, 1H), 5.90 (dd,  $J$  = 10.83, 17.39 Hz, 1H), 5.20 (dd,  $J$  = 1.52, 17.24 Hz, 1H), 5.00 (dd,  $J$  = 1.52, 10.68 Hz, 1H), 4.17 (ddd,  $J$  = 6.10, 8.24, 14.34 Hz, 1H), 2.54 – 2.47 (m, 1H), 1.97 – 1.88 (m, 2H), 1.83 – 1.75 (m, 2H), 1.31 (s, 3H), 1.05 (d,  $J$  = 7.01 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  204.6, 144.2, 111.8, 79.6, 78.6, 51.9, 37.4, 32.2, 26.4, 23.4 ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{38}\text{O}_4\text{Si}[\text{M} + \text{Na}]^+$ : 417.2437, found 417.2426.

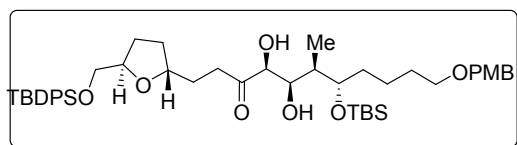
**(6*R*,7*S*,*E*)-7-((*tert*-Butyldimethylsilyl)oxy)-1-((2*R*,5*R*)-5-(((*tert*-butyldiphenylsilyl)oxy)methyl)tetrahydrofuran-2-yl)-11-((4-methoxybenzyl)oxy)-6-methylundec-4-en-3-one (4):**



To a stirred solution of the keto phosphonate **5** (0.157 g, 0.303 mmol) in MeCN (15 mL), was added DIPEA (39 mg, 0.303 mmol) at 0 °C under nitrogen atmosphere. LiCl (13 mg, 0.303 mmol) followed by aldehyde **6** (120 mg, 0.303 mmol) were slowly added to the reaction mixture and stirred at the same temperature for 1 h. The reaction was allowed to warm to room temperature and the stirring was then continued for 8 h. After complete consumption of the starting material (monitored by TLC), the reaction mixture was quenched with saturated  $\text{NH}_4\text{Cl}$  (15 mL), diluted with ethyl acetate (30 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate ( $2 \times 30$  mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and was concentrated under reduced pressure

to get the crude product which on purification by silica gel column chromatography (ethyl acetate/hexane = 1:8) furnished the desired ketone **5** (0.216 g, 91%) as a colorless liquid.  $[\alpha]_D^{25} +4.6$  ( $c$  1.0,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\max}$  2931, 2857, 1669, 1249, 1106, 701  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.71 – 7.65 (m, 4H), 7.44 – 7.33 (m, 6H), 7.25 (d,  $J$  = 8.55 Hz, 2H), 6.87 (d,  $J$  = 8.68 Hz, 2H), 6.82 (dd,  $J$  = 16.01, 7.82 Hz, 1H), 6.07 (dd,  $J$  = 16.01, 0.85 Hz, 1H), 4.41 (s, 2H), 4.15 – 4.08 (m, 1H), 3.99 – 3.91 (m, 1H), 3.79 (s, 3H), 3.68 – 3.57 (m, 3H), 3.45 – 3.37 (m, 2H), 2.78 – 2.68 (m, 1H), 2.64 – 2.54 (m, 1H), 2.49 – 2.40 (m, 1H), 2.06 – 1.96 (m, 2H), 1.88 – 1.70 (m, 3H), 1.60 – 1.48 (m, 3H), 1.48 – 1.24 (m, 4H), 1.05 (s, 9 H), 1.04 (d,  $J$  = 0.9 Hz, 3H), 0.88 (s, 9H), 0.03 (s, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.3, 159.1, 149.1, 135.6, 133.7, 130.7, 130.2, 129.5, 129.2, 127.6, 113.7, 78.9, 78.7, 75.3, 72.5, 69.9, 66.5, 52.2, 41.9, 36.7, 34.1, 31.8, 29.9, 29.9, 28.1, 26.8, 25.9, 22.1, 19.2, 18.1, 15.4, –4.3, –4.5 ppm; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{47}\text{H}_{70}\text{O}_6\text{Si}_2$   $[\text{M} + \text{NH}_4]^+$ : 804.5049, found 804.5066.

**(4*S*,5*R*,6*R*,7*S*)-7-((*tert*-Butyldimethylsilyl)oxy)-1-((2*R*,5*R*)-5-(((*tert*-butyldiphenylsilyl)oxy)methyl)tetrahydrofuran-2-yl)-4,5-dihydroxy-11-((4-methoxybenzyl)oxy)-6-methylundecan-3-one (4):**

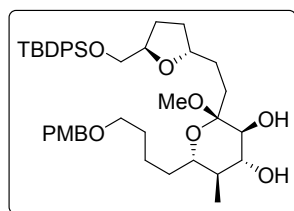


A mixture of  $\text{K}_2\text{OSO}_2(\text{OH})_2$  (0.33 mg, 0.0009 mmol, 0.006 equiv),  $(\text{DHQD})_2\text{PHAL}$  (1.78 mg, 0.002 mmol, 0.015 equiv),  $\text{K}_3\text{Fe}(\text{CN})_6$  (150 mg, 0.45 mmol, 3.0 equiv.),  $\text{K}_2\text{CO}_3$  (63 mg, 0.45 mmol, 3.0 equiv) and  $\text{MeSO}_2\text{NH}_2$  (14.5 mg, 0.152 mmol, 1.0 equiv) in 1:1  $t$ -BuOH/ $\text{H}_2\text{O}$  (50 mL) was stirred for 30 min at room temperature. The mixture was slowly poured into a 4 °C solution of **5** (120 mg, 0.152 mmol, 1.0 equiv) in  $t$ -BuOH/ $\text{H}_2\text{O}$  (30 mL). Then, the reaction was stirred at 4 °C for 36 h. After completion of reaction (TLC), solid  $\text{Na}_2\text{S}_2\text{O}_3$  (0.5 g) was added and the



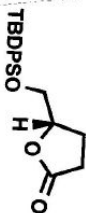
mixture stirred for 1.5 h while warming to room temperature (color changed from orange to dark green). After phase separation, the aqueous layer was extracted with ethyl acetate ( $3 \times 20$  mL). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , concentrated under reduced pressure to provide crude product which was purified by silica gel column chromatography (ethyl acetate/hexane = 3:7) to furnish **20** (100 mg, 80%).  $[\alpha]_{\text{D}}^{25} +15.25$  ( $c$  0.8,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  3468, 2931, 2857, 1714, 1471, 1112, 704  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.70 – 7.64 (m, 4H), 7.44 – 7.34 (m, 6H), 7.25 (d,  $J = 8.7$  Hz, 1H), 6.87 (d,  $J = 8.7$  Hz, 2H), 4.42 (s, 2H), 4.20 – 4.04 (m, 3H), 3.99 – 3.90 (m, 1H), 3.88 – 3.81 (m, 1H), 3.79 (s, 3H), 3.77 – 3.71 (m, 1H), 3.69 – 3.56 (m, 3H), 3.45 – 3.69 (m, 2H), 3.1 – 3.0 (m, 1H), 2.74 – 2.64 (m, 1H), 2.08 – 1.94 (m, 2H), 1.93 – 1.72 (m, 4H), 1.68 – 1.44 (m, 7H), 1.43 – 1.30 (m, 1H), 1.05 (s, 9H), 1.03 (d,  $J = 7.2$  Hz, 3H), 0.88 (s, 9H), 0.08 – 0.06 (m, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.6, 159.0, 135.6, 133.6, 130.7, 130.6, 129.6, 129.2, 127.6, 113.7, 78.9, 78.6, 76.3, 72.6, 71.5, 70.1, 69.9, 66.4, 55.2, 40.3, 39.5, 35.3, 33.8, 31.7, 29.8, 29.5, 28.0, 26.8, 25.9, 22.0, 21.6, 19.2, 18.0, 12.0, –4.4, –4.4, –4.6, –4.7 ppm; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{47}\text{H}_{72}\text{O}_8\text{Si}_2[\text{M} + \text{Na}]^+$ : 843.4658, found 843.4656.

**(2R,3S,4R,5R,6S)-2-(2-((2R,5R)-5-((tert-Butyldiphenylsilyloxy)methyl)tetrahydrofuran-2-yl)ethyl)-2-methoxy-6-(3-(4-methoxybenzyloxy)propyl)-5-methyltetrahydro-2H-pyran-3,4-diol (3):**

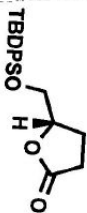


To the solution of keto diol **20** (60 mg, 0.073 mmol) in MeOH (20 mL), pyridinium *p*-toluenesulfonate (1.8 mg, 0.0073 mmol) was added at 0 °C. The resulting solution was stirred for

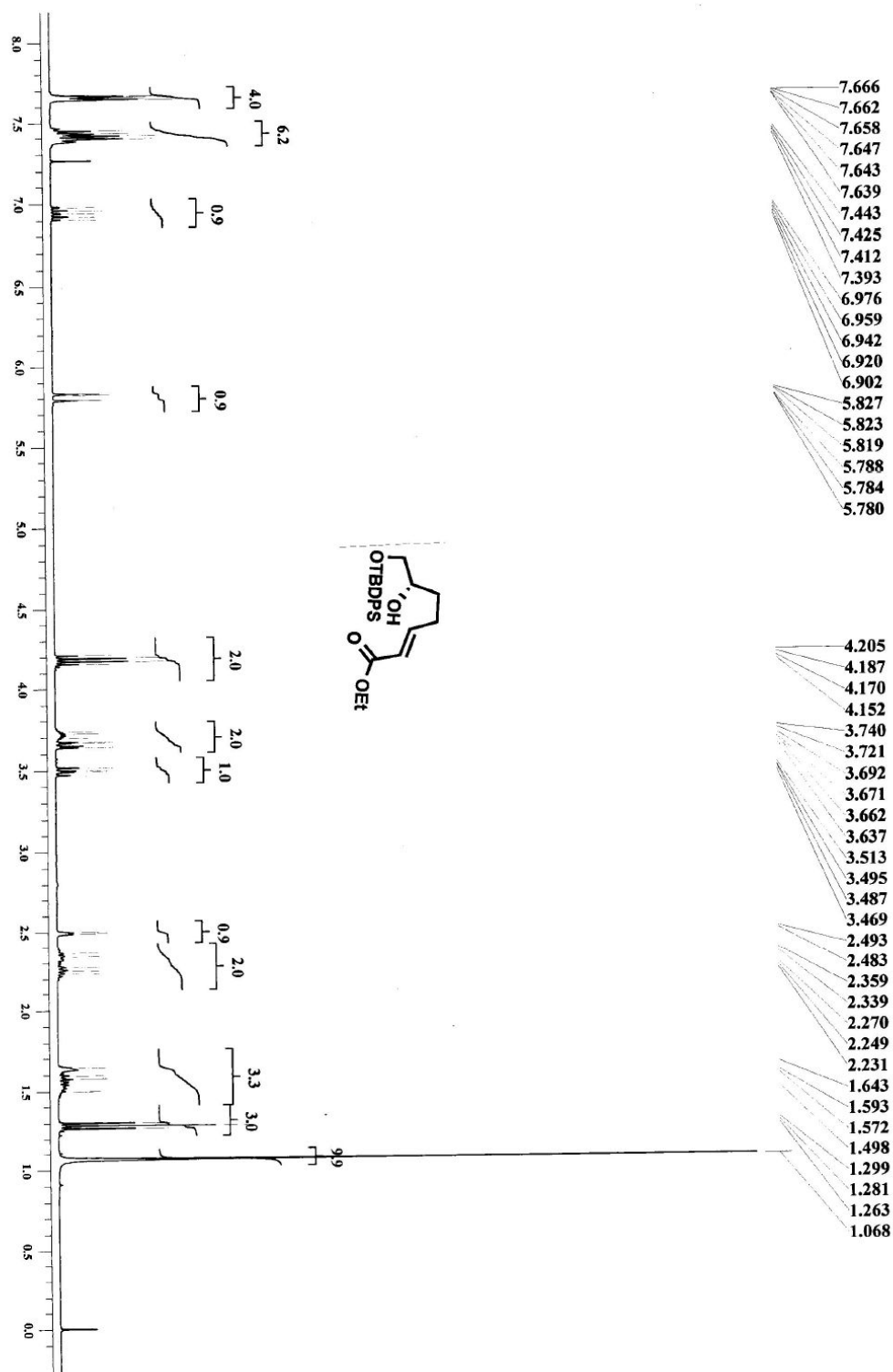
12 h at room temperature. After completion of the reaction (TLC), triethylamine (0.5 mL) was added and concentrated under reduced pressure to give crude residue which was purified by silica gel chromatography (ethyl acetate/hexane = 3:7) to furnish C1-C16 fragment of formosalide **3** (42 mg, 82%) as a colorless liquid.  $[\alpha]_{\text{D}}^{25} -31.2$  ( $c$  1.0,  $\text{CHCl}_3$ ); IR (KBr):  $\nu_{\text{max}}$  3424, 2933, 2859, 1513, 1428, 1112, 705  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.71 – 7.65 (m, 4H), 7.44 – 7.34 (m, 6H), 7.25 (d,  $J$  = 7.5 Hz, 2H), 6.87 (d,  $J$  = 8.7 Hz, 2H), 4.43 (s, 2H), 4.19 – 4.09 (m, 1H), 3.95 – 3.88 (m, 1H), 3.79 (s, 3H), 3.64 (dd,  $J$  = 4.8, 0.9 Hz, 2H), 3.46 – 3.27 (m, 4H), 3.18 (s, 3H), 2.58 (d,  $J$  = 8.8 Hz, 1H), 2.40 (br s, 1H), 2.05 – 1.94 (m, 2H), 1.87 – 1.73 (m, 4H), 1.64 – 1.33 (m, 8H), 1.05 (s, 9H), 0.95 (d,  $J$  = 6.6 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.1, 135.6, 133.7, 129.5, 129.2, 127.6, 113.7, 100.5, 79.8, 79.1, 75.8, 74.8, 73.4, 72.5, 70.0, 66.5, 55.2, 47.4, 41.2, 32.1, 31.9, 29.9, 29.9, 29.7, 29.4, 28.0, 26.8, 21.9, 19.2, 12.9 ppm; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{42}\text{H}_{60}\text{O}_8\text{Si}$   $[\text{M} + \text{Na}]^+$ : 743.3955, found 743.3945.



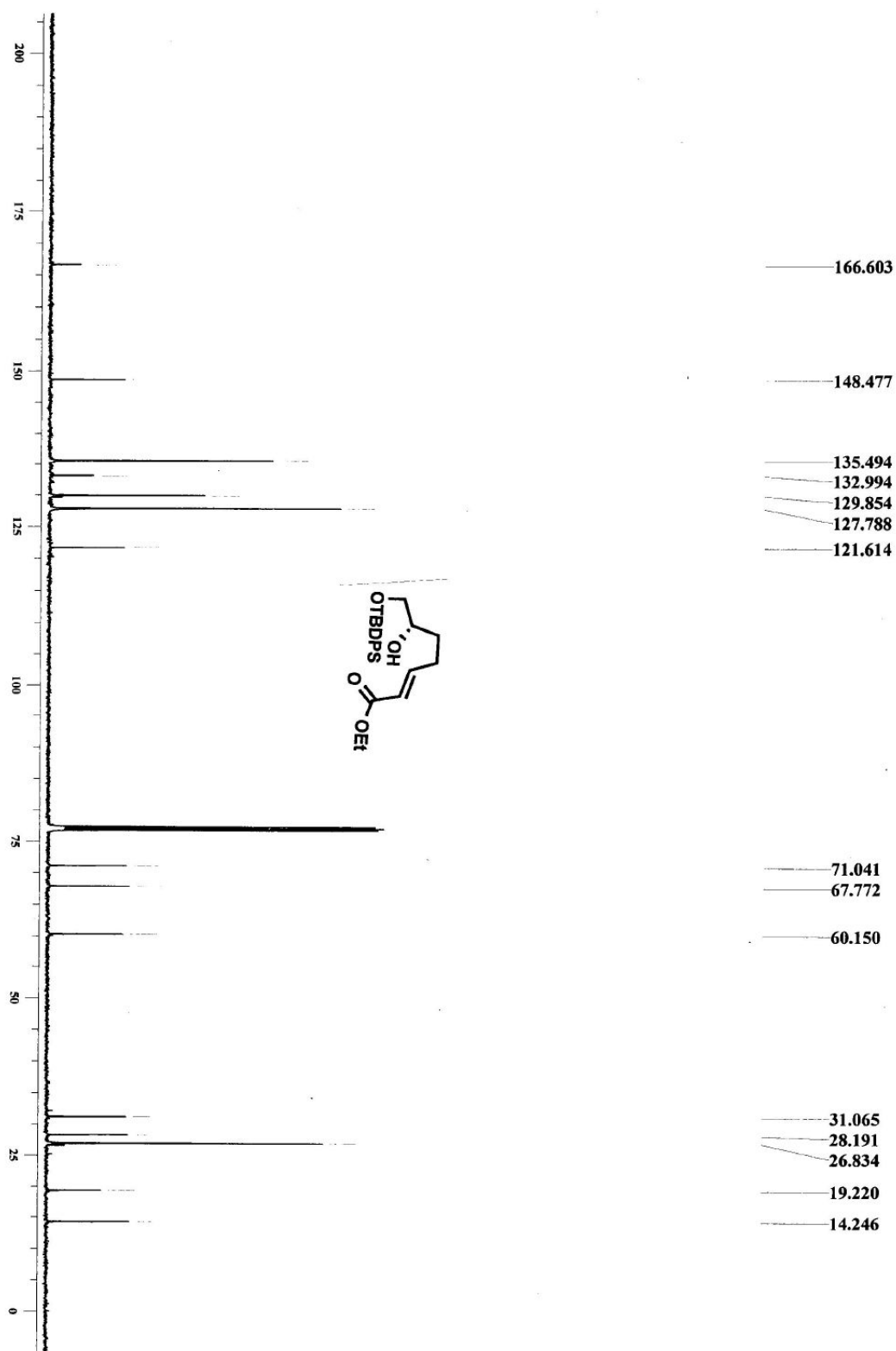
<sup>1</sup>H NMR spectrum of **7** (500 MHz, CDCl<sub>3</sub>)



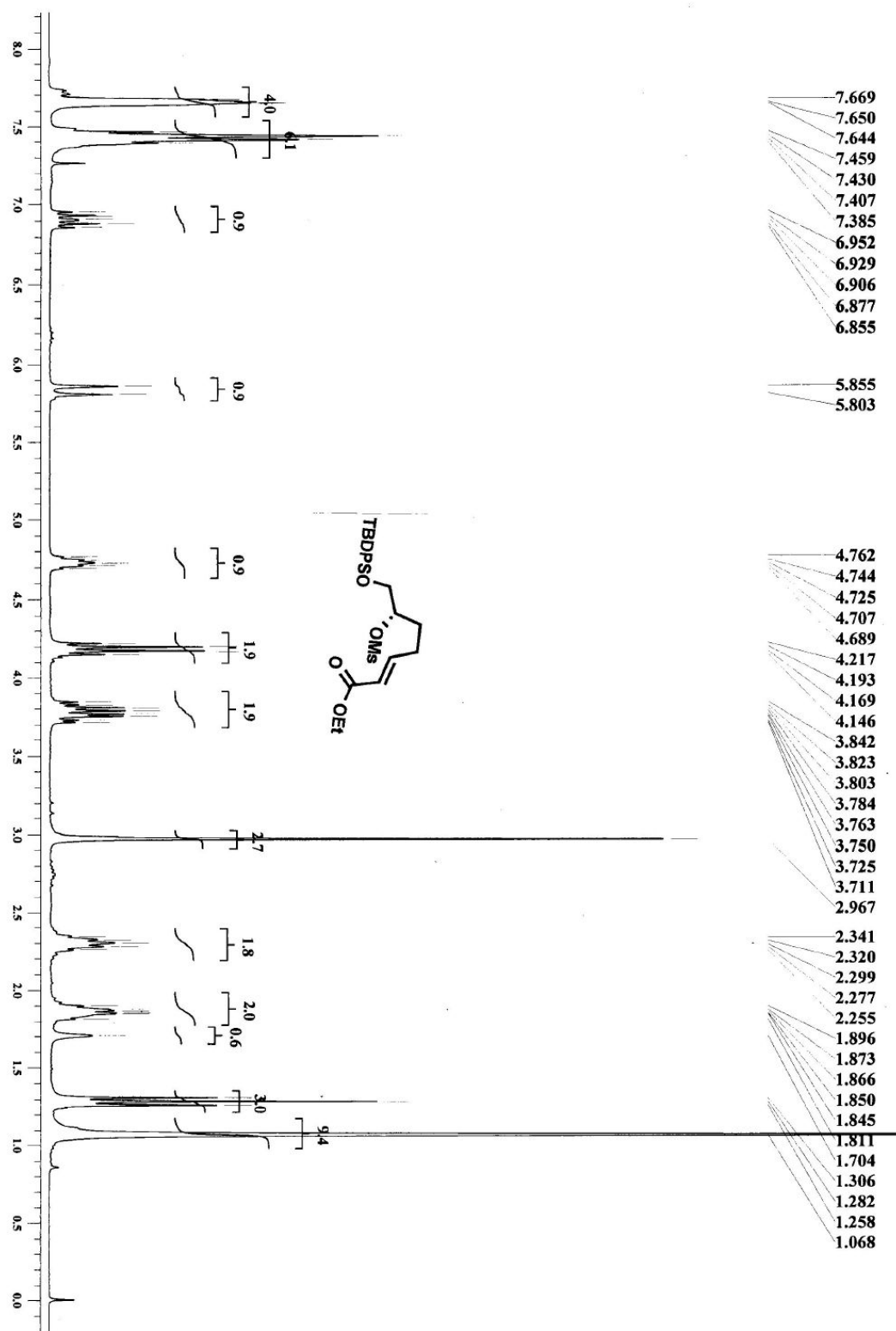
<sup>13</sup>C NMR spectrum of **7** (75 MHz, CDCl<sub>3</sub>)

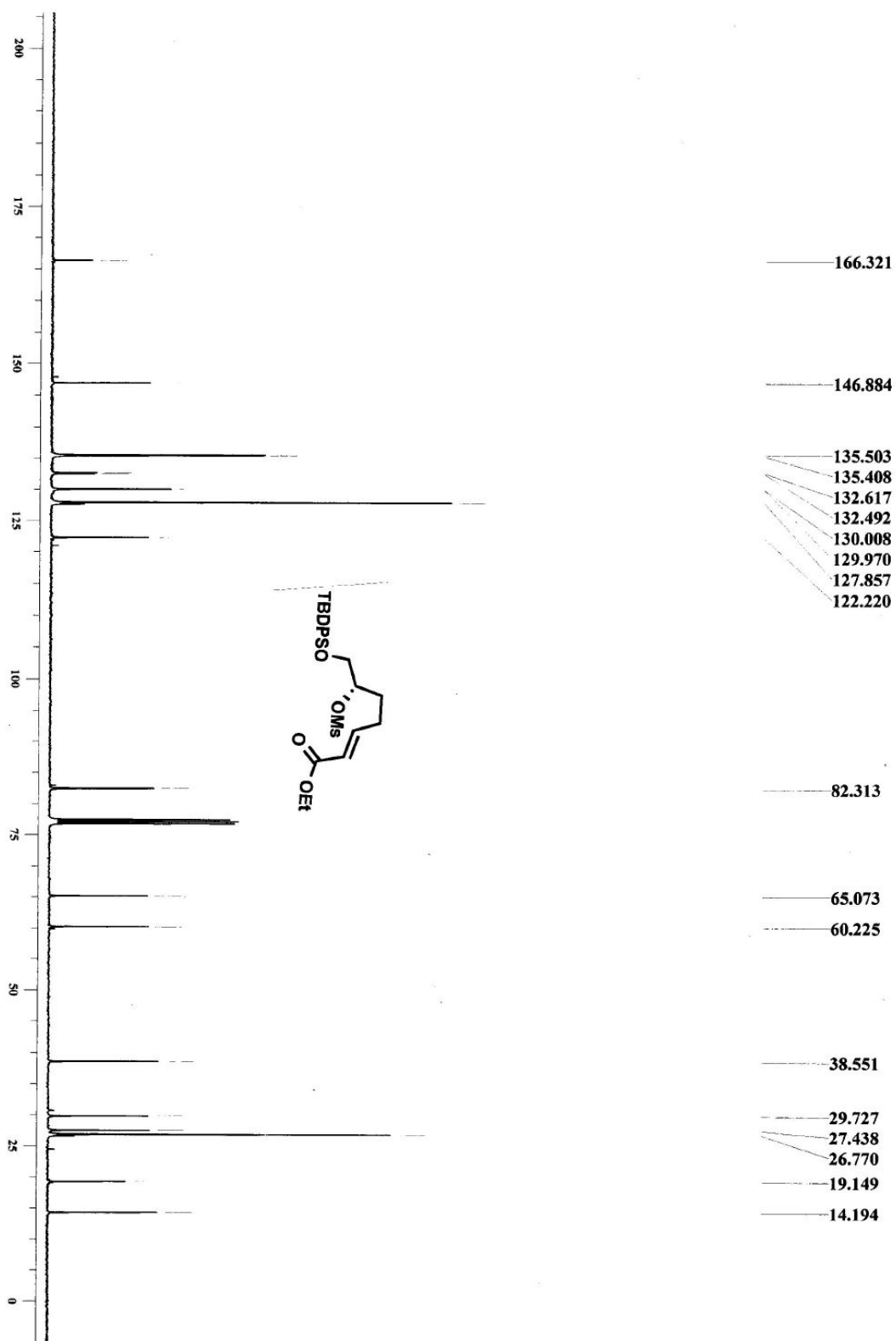


<sup>1</sup>H NMR spectrum of 9 (400 MHz, CDCl<sub>3</sub>)

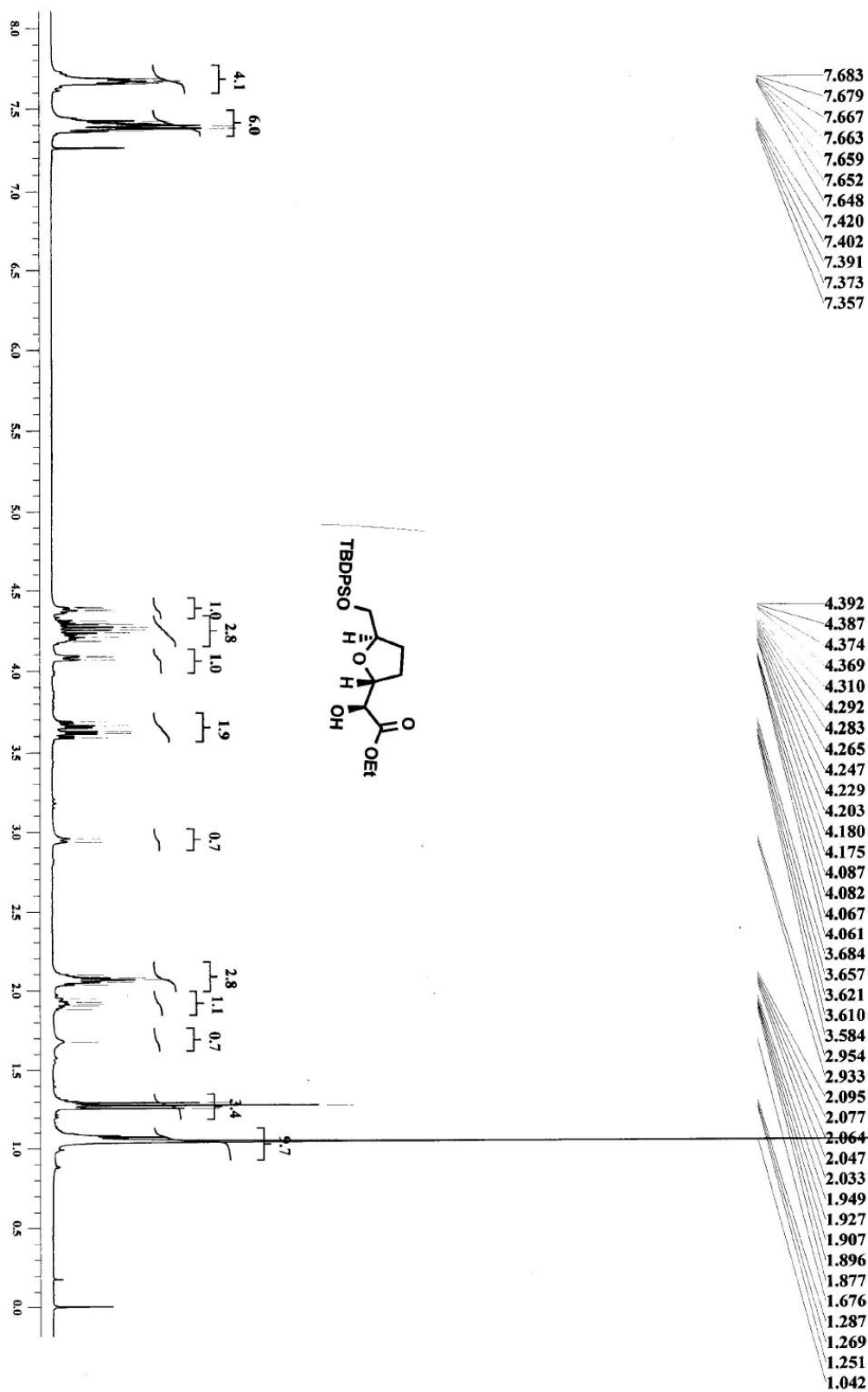


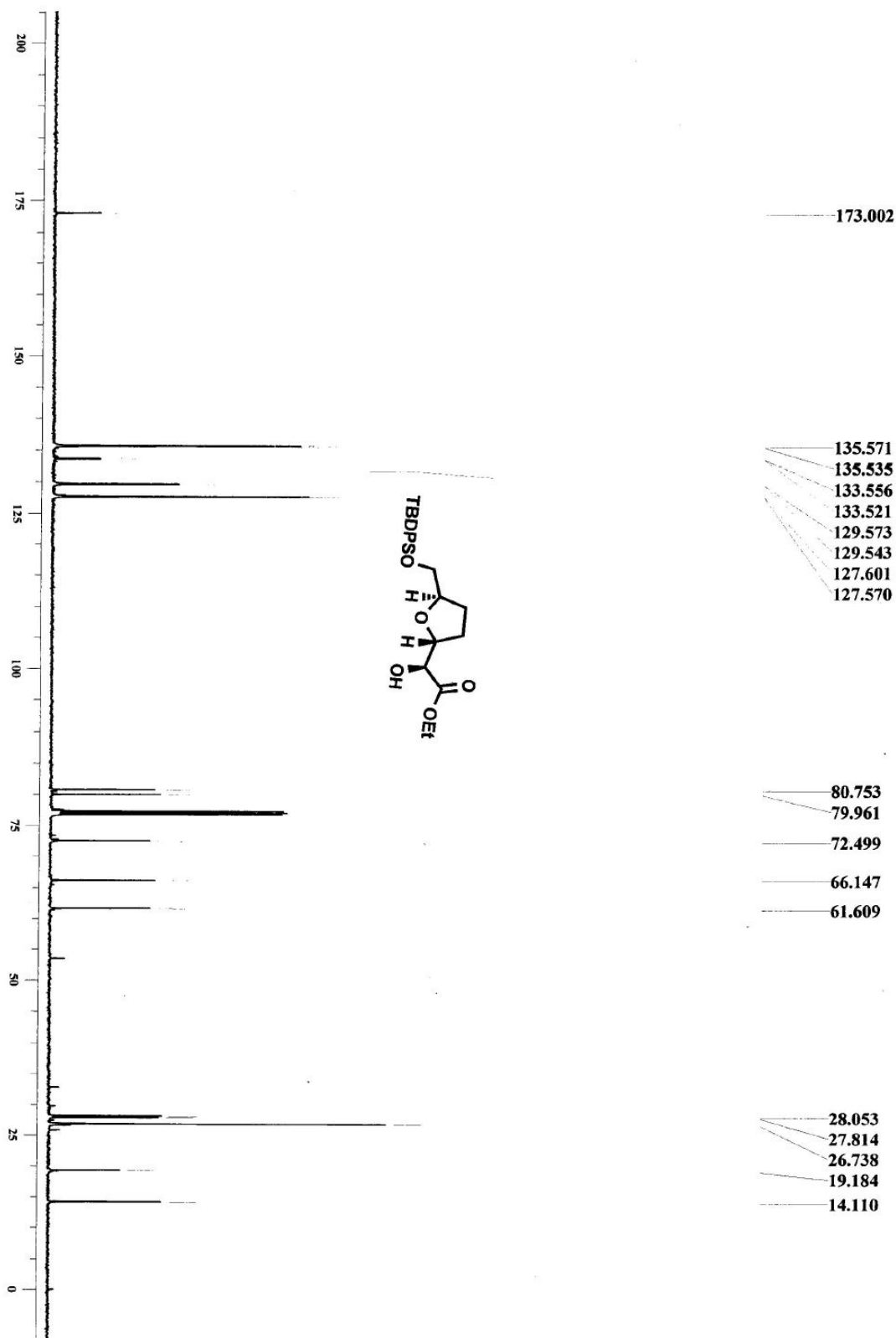
<sup>13</sup>C NMR spectrum of **9** (125 MHz, CDCl<sub>3</sub>)

 $^1\text{H}$  NMR spectrum of **10** (400 MHz,  $\text{CDCl}_3$ )

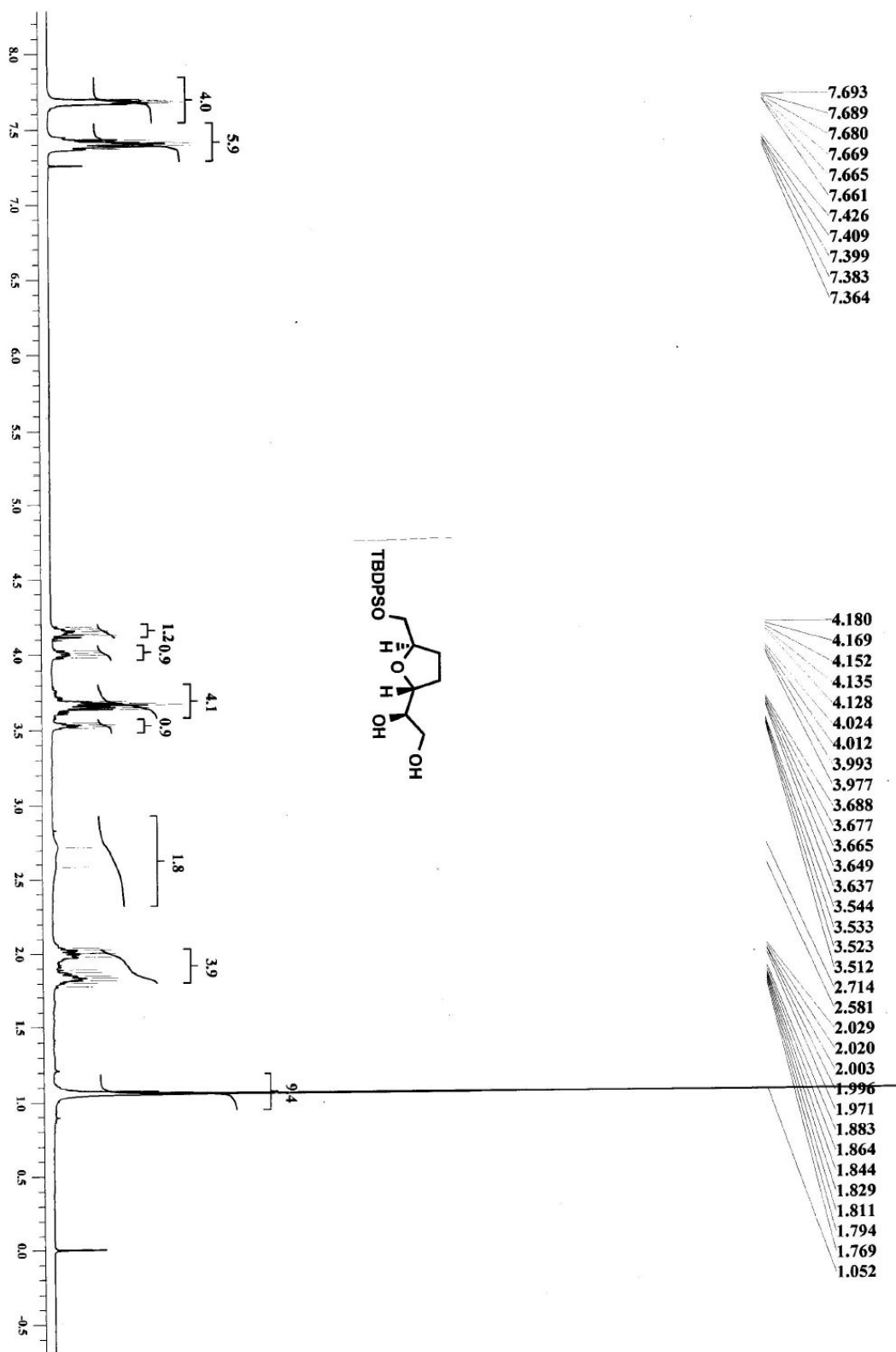
 $^{13}\text{C}$  NMR spectrum of **10** (100 MHz,  $\text{CDCl}_3$ )



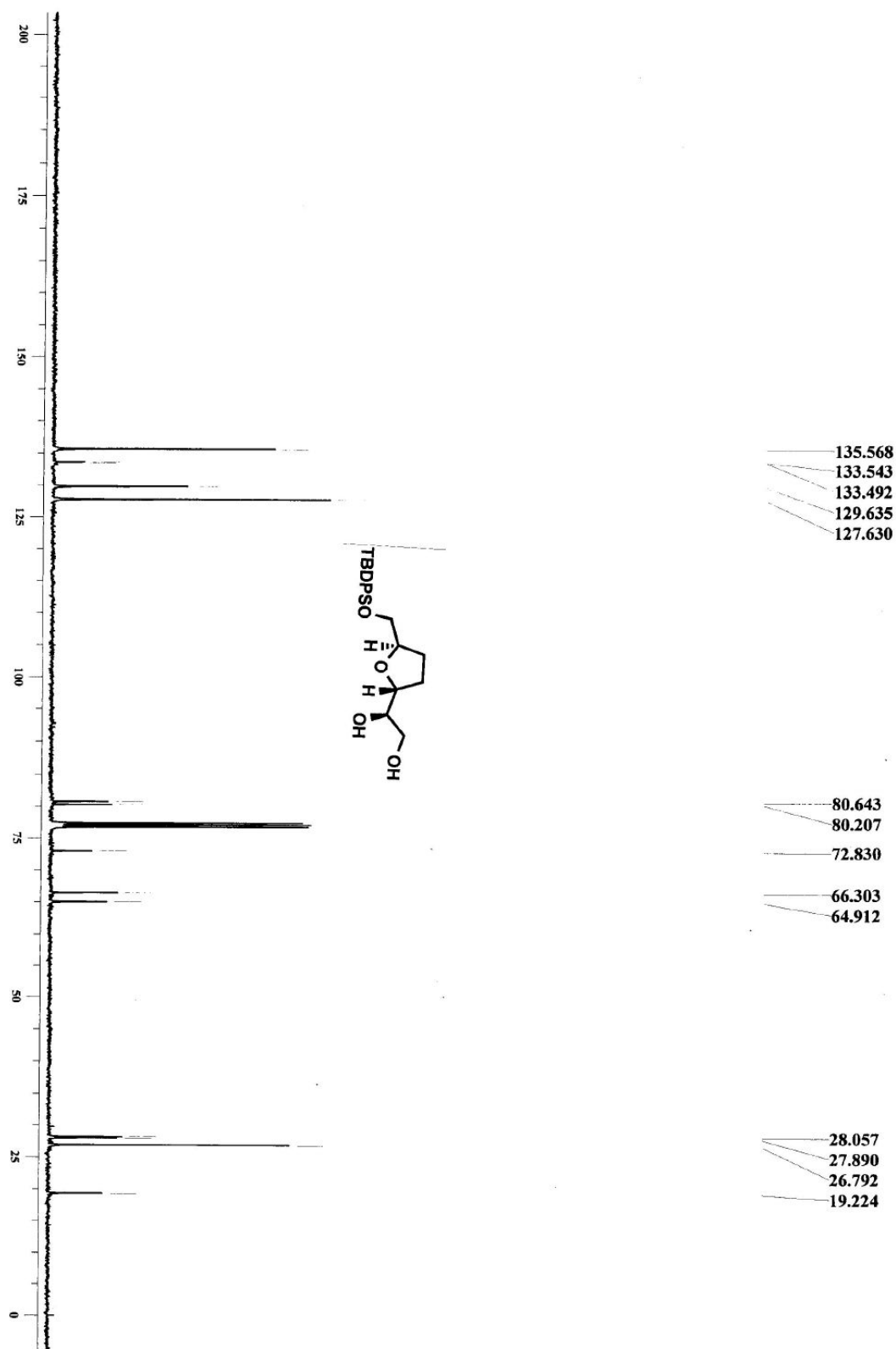
 $^1\text{H}$  NMR spectrum of **11** (400 MHz,  $\text{CDCl}_3$ )



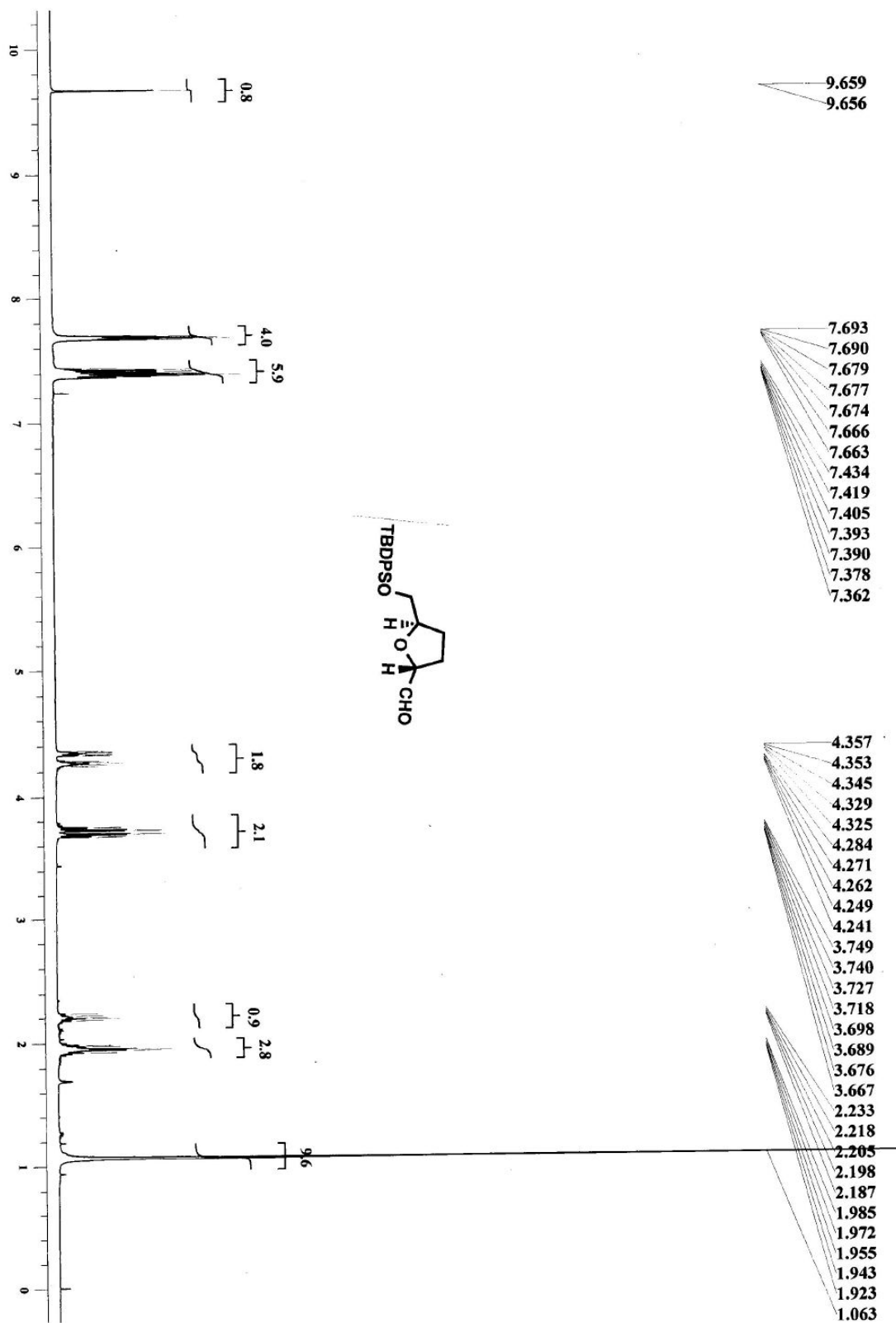
<sup>13</sup>C NMR spectrum of **11** (125 MHz, CDCl<sub>3</sub>)



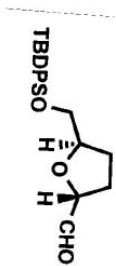
$^1\text{H}$  NMR spectrum of **12** (400 MHz,  $\text{CDCl}_3$ )



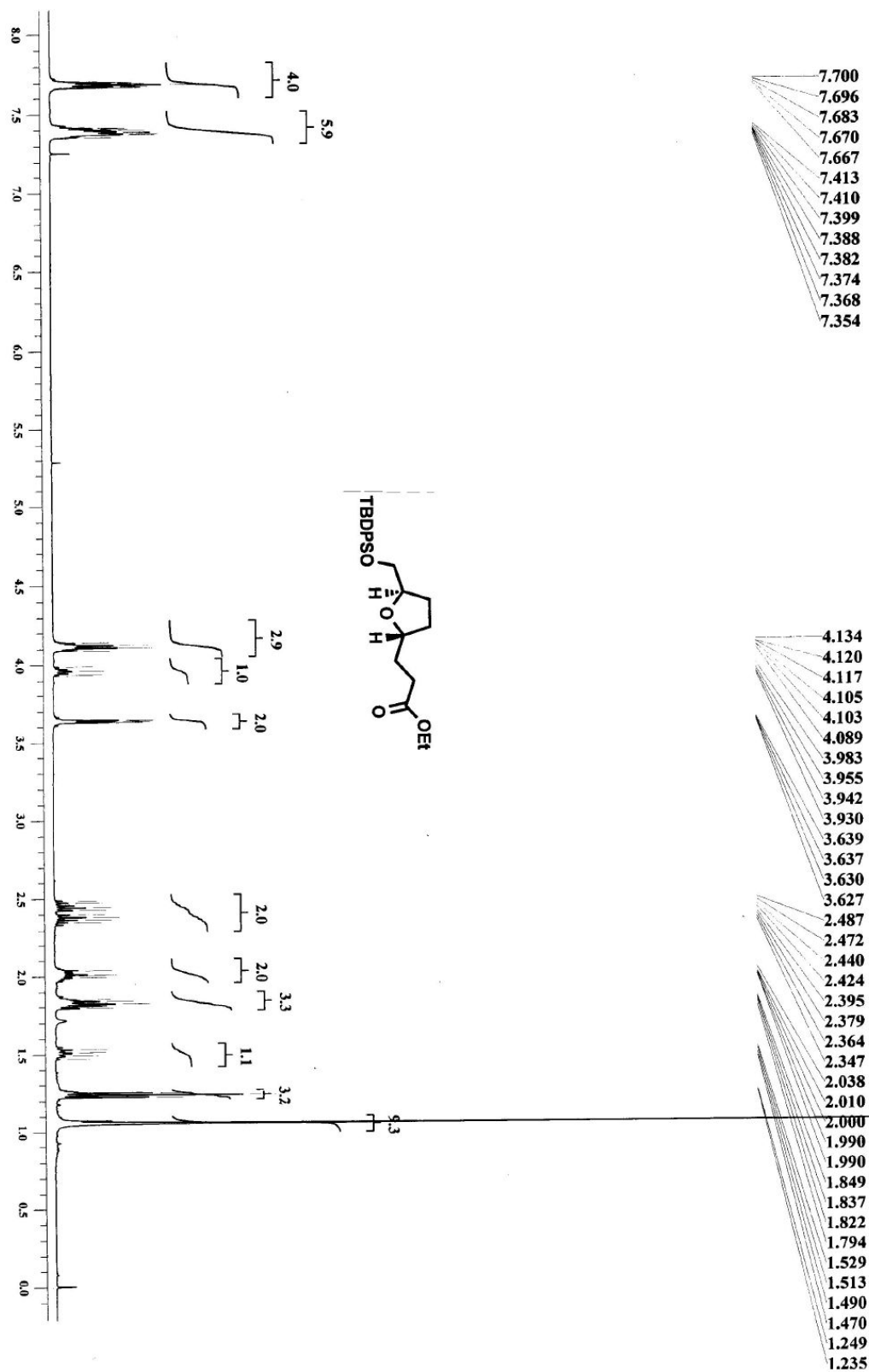
<sup>13</sup>C NMR spectrum of **12** (100 MHz, CDCl<sub>3</sub>)

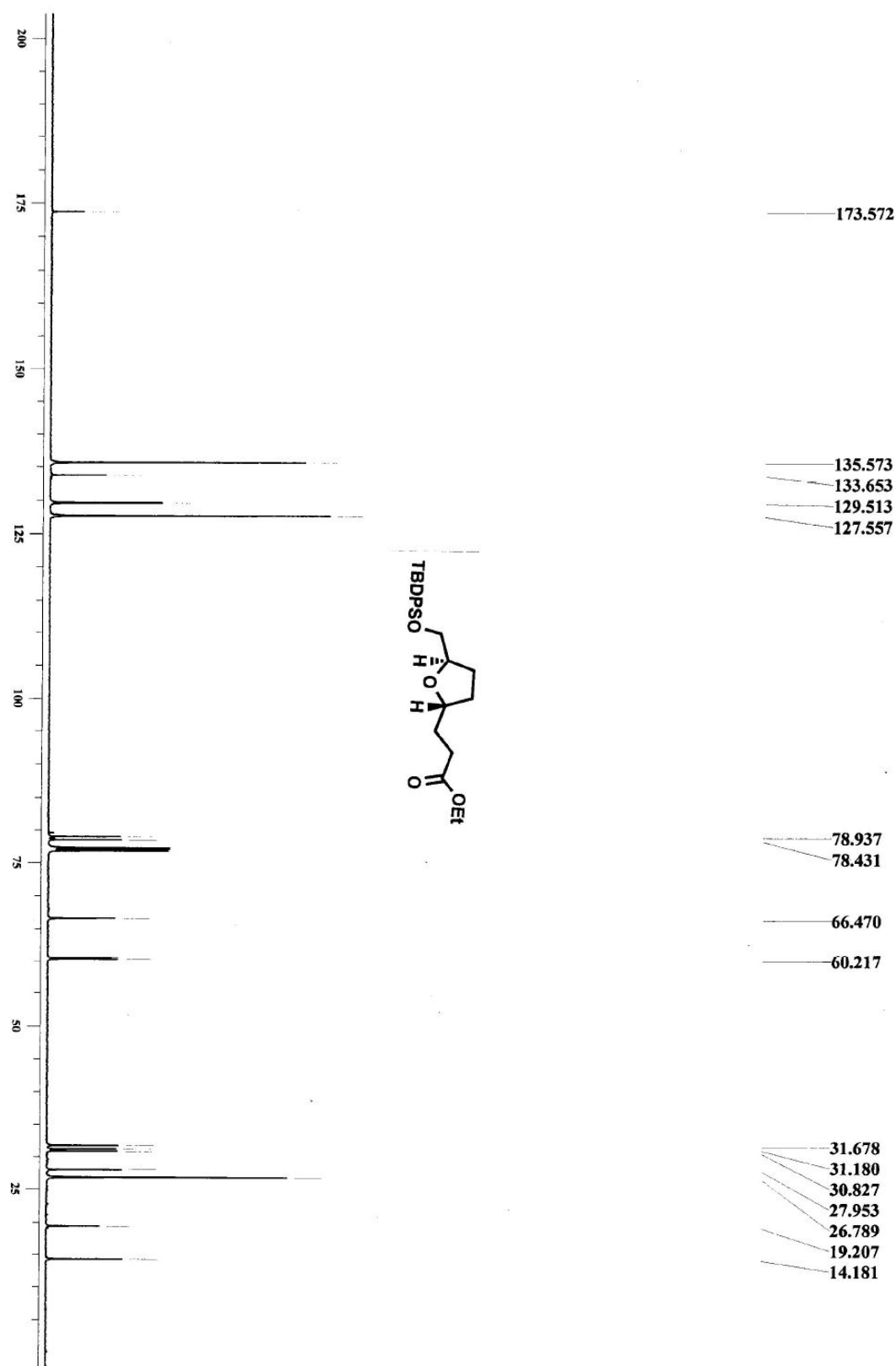


$^1\text{H}$  NMR spectrum of **13** (500 MHz,  $\text{CDCl}_3$ )



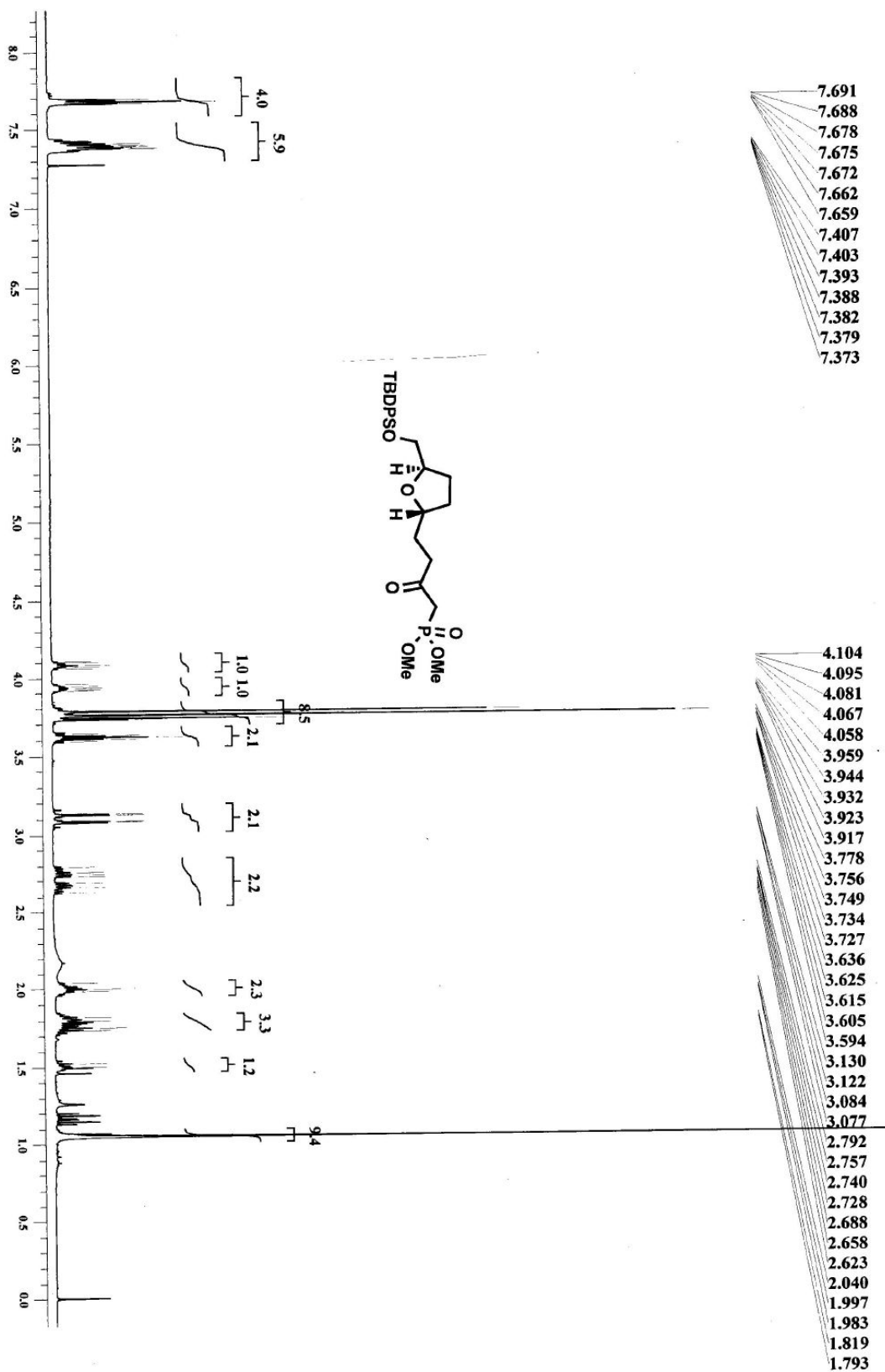
<sup>13</sup>C NMR spectrum of **13** (125 MHz, CDCl<sub>3</sub>)

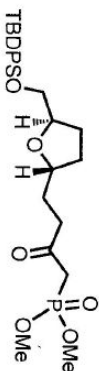
<sup>1</sup>H NMR spectrum of **15** (500 MHz, CDCl<sub>3</sub>)



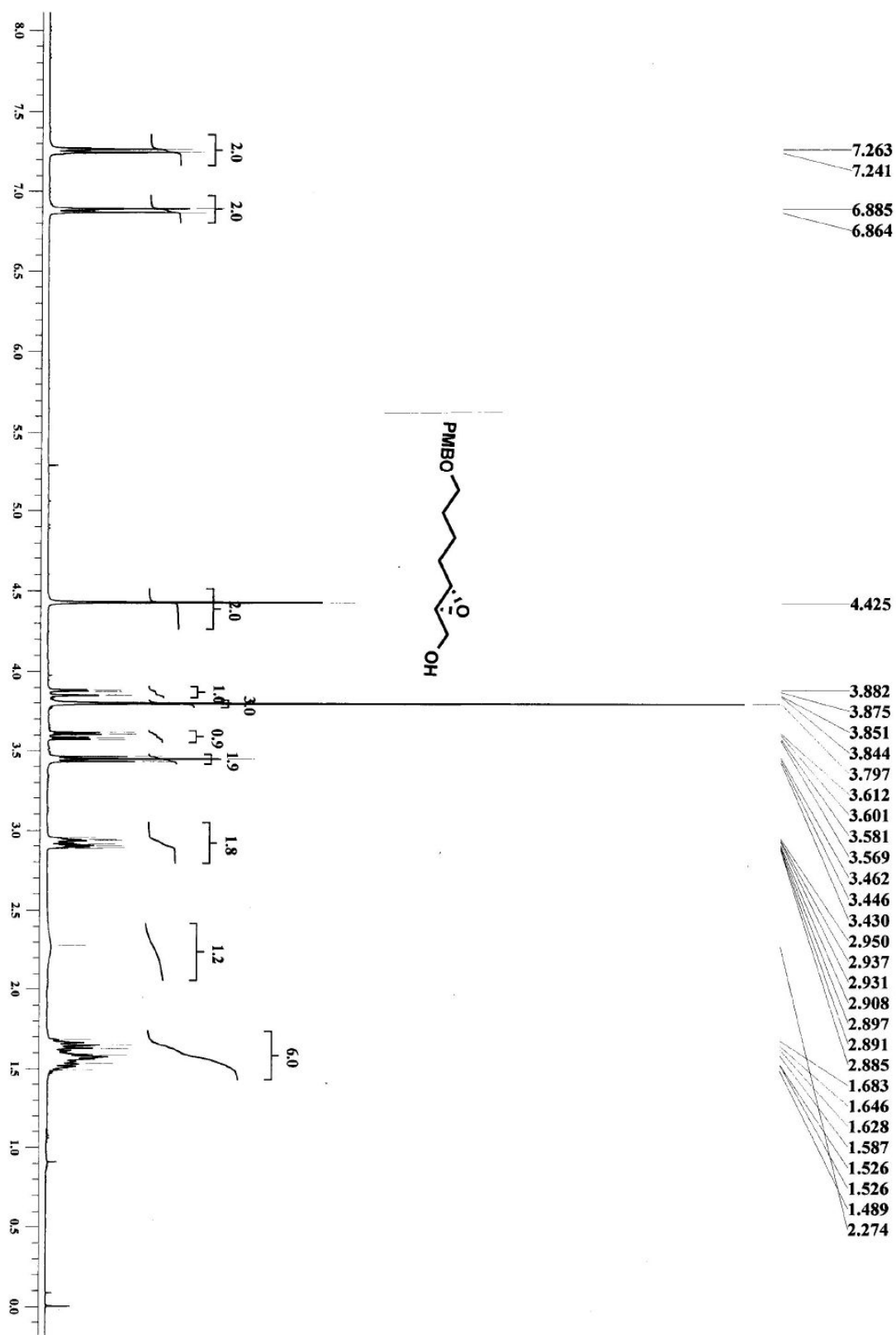
$^{13}\text{C}$  NMR spectrum of **15** (100 MHz,  $\text{CDCl}_3$ )



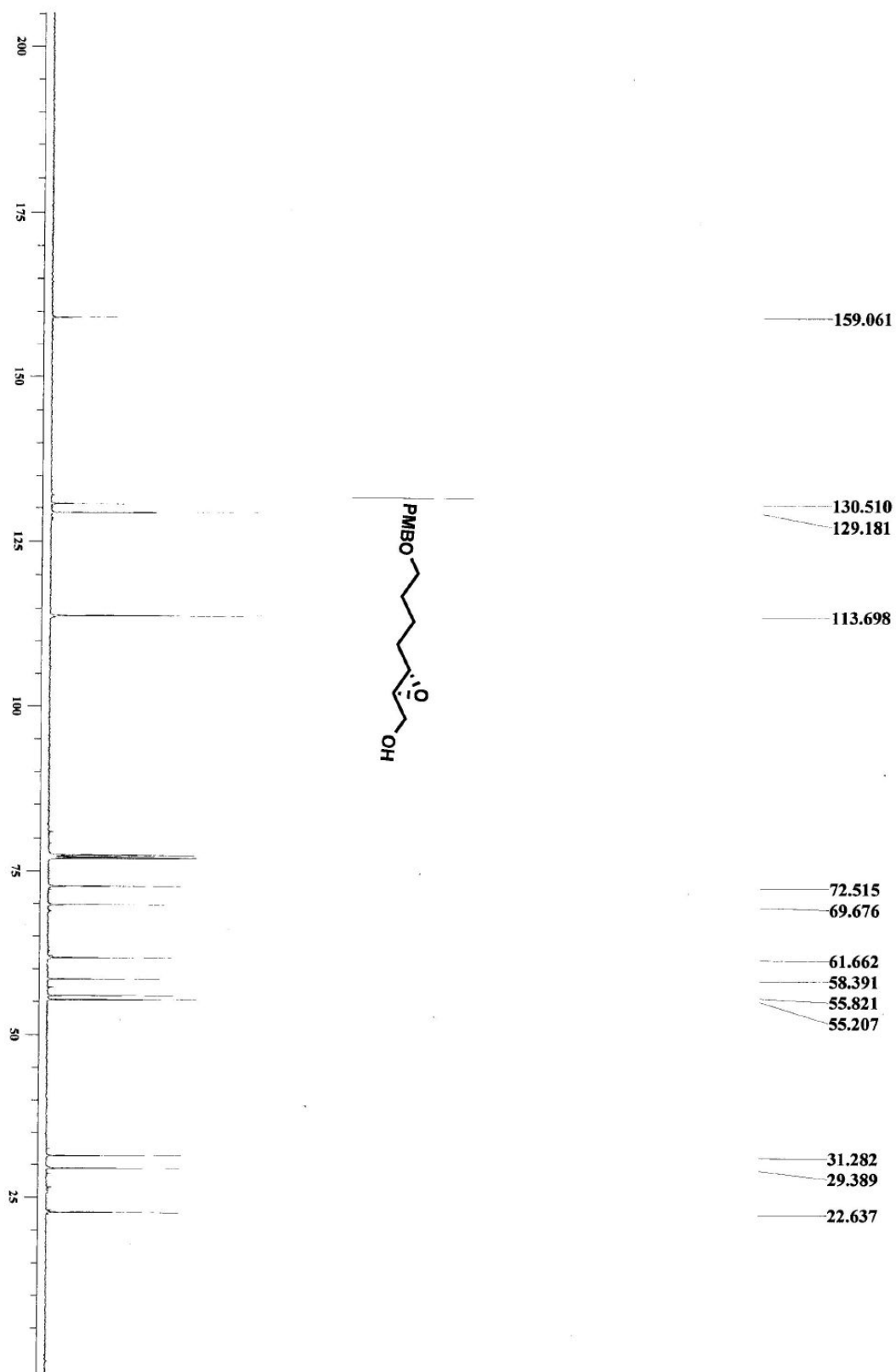
<sup>1</sup>H NMR spectrum of **5** (500 MHz, CDCl<sub>3</sub>)



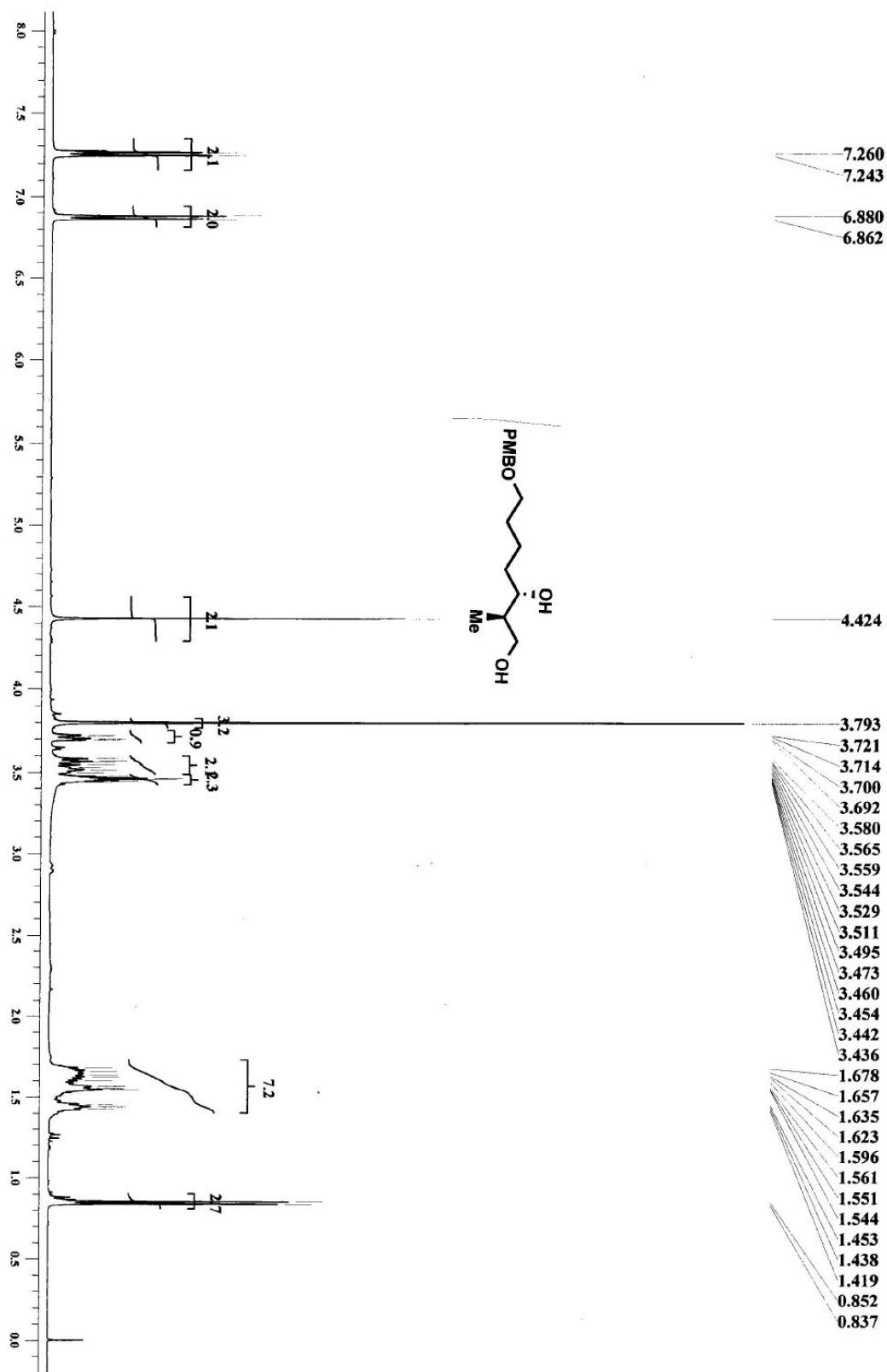
<sup>13</sup>C NMR spectrum of **5** (100 MHz, CDCl<sub>3</sub>)



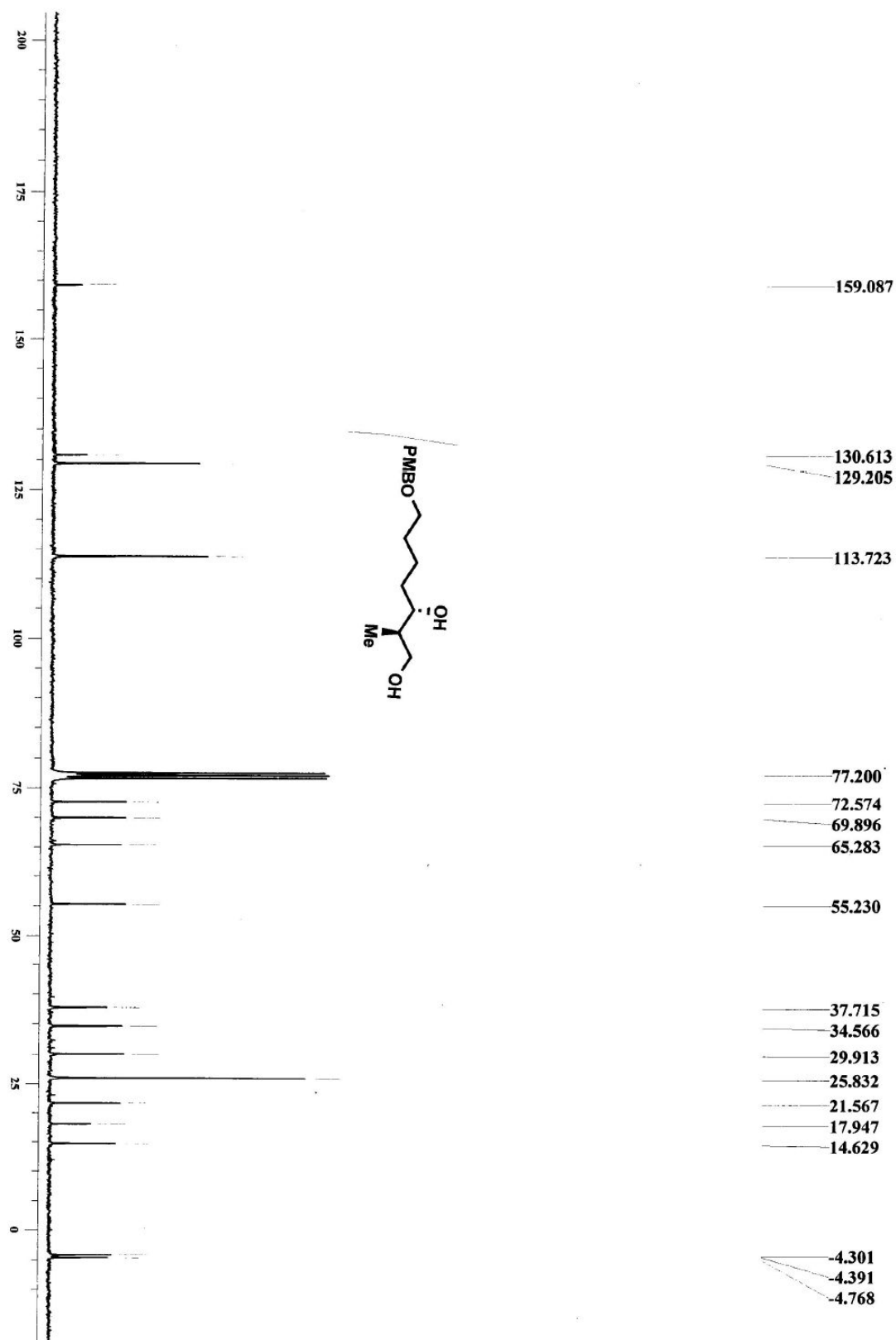
<sup>1</sup>H NMR spectrum of **16** (500 MHz, CDCl<sub>3</sub>)



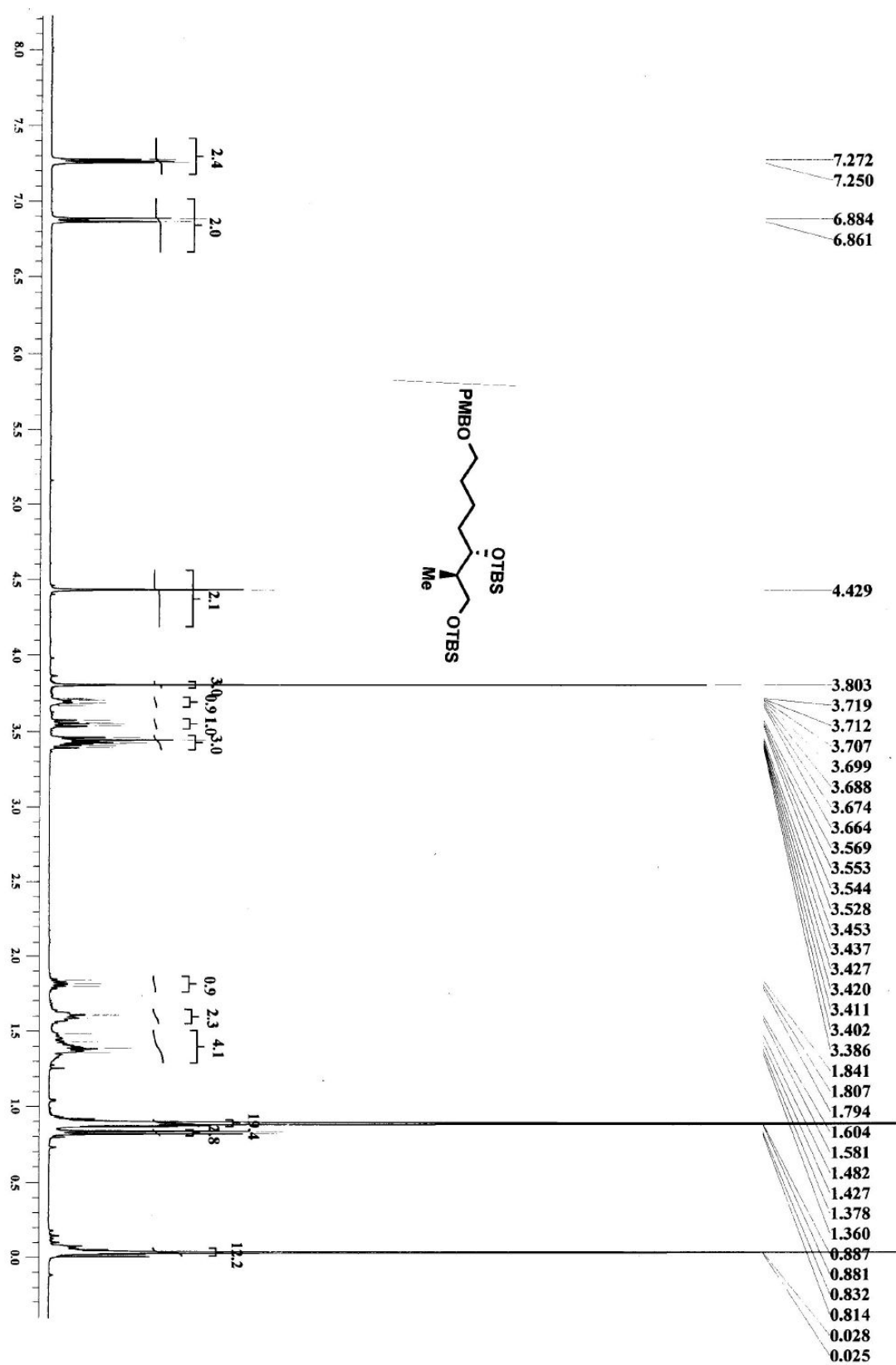
<sup>13</sup>C NMR spectrum of **16** (100 MHz, CDCl<sub>3</sub>)

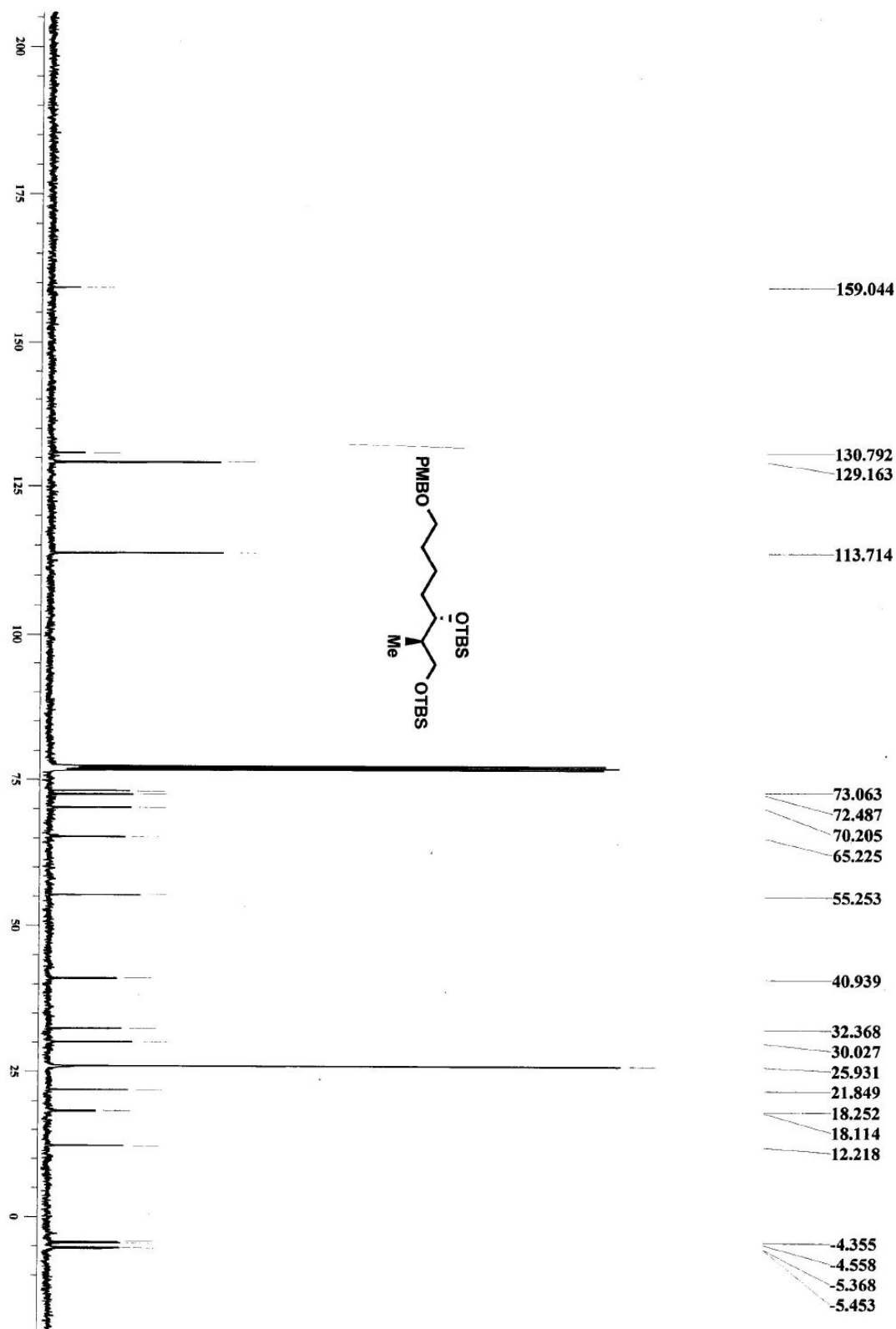


<sup>1</sup>H NMR spectrum of **17** (500 MHz, CDCl<sub>3</sub>)

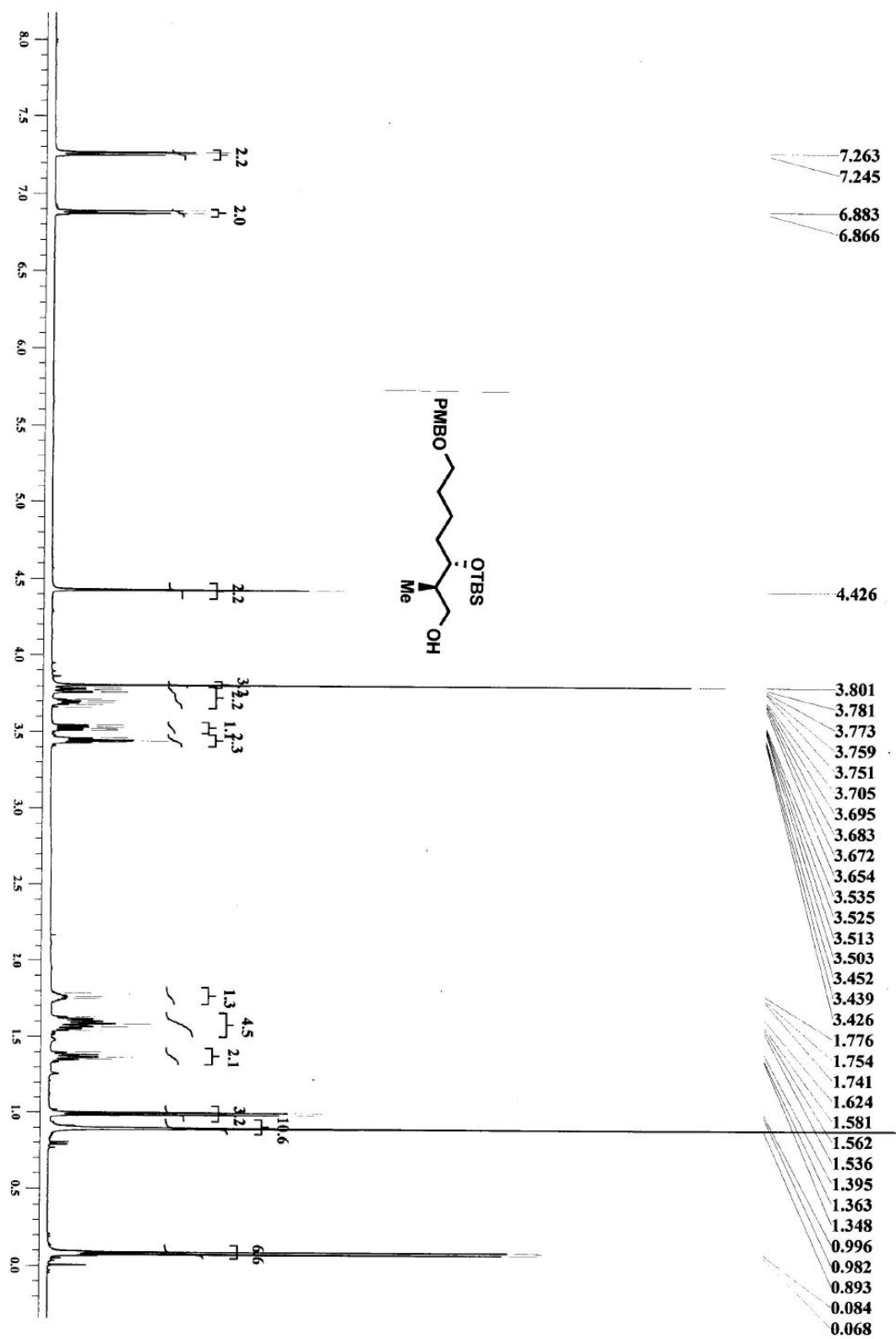


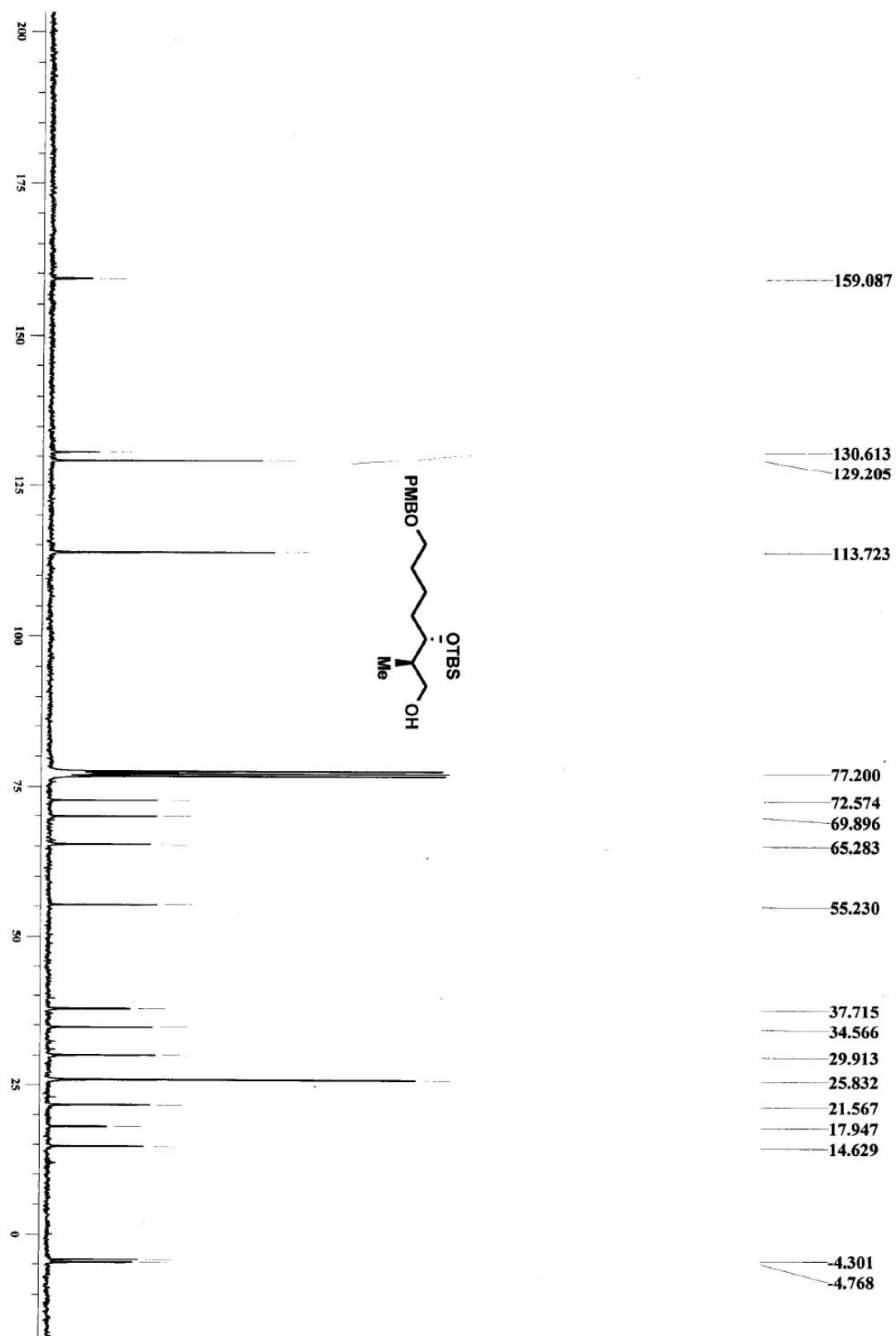
$^{13}\text{C}$  NMR spectrum of **17** (125 MHz,  $\text{CDCl}_3$ )

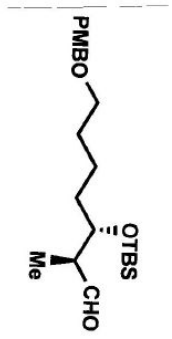
<sup>1</sup>H NMR spectrum of **18** (500 MHz, CDCl<sub>3</sub>)

 $^{13}\text{C}$  NMR spectrum of **18** (125 MHz,  $\text{CDCl}_3$ )

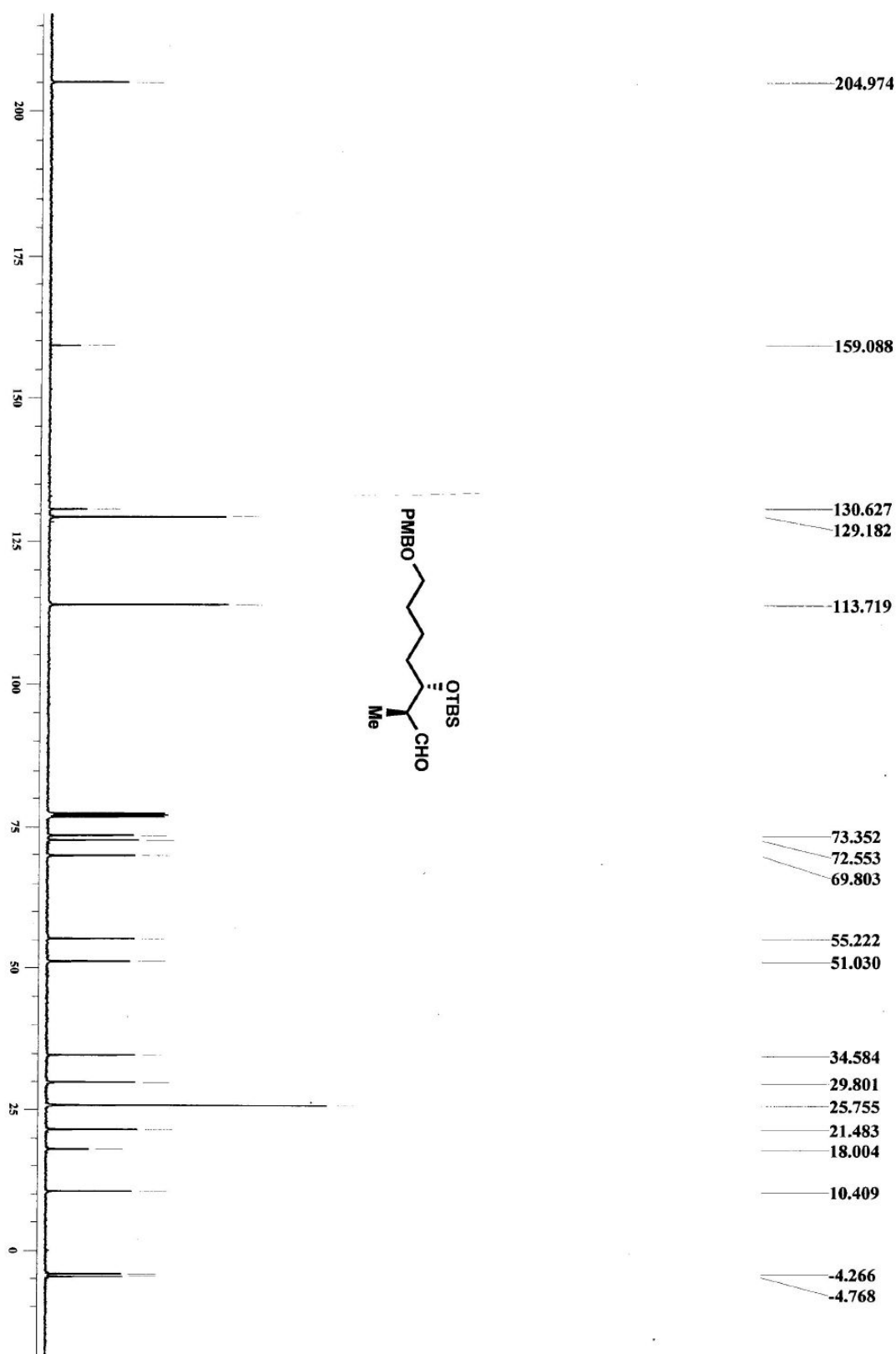


<sup>1</sup>H NMR spectrum of **19** (500 MHz, CDCl<sub>3</sub>)

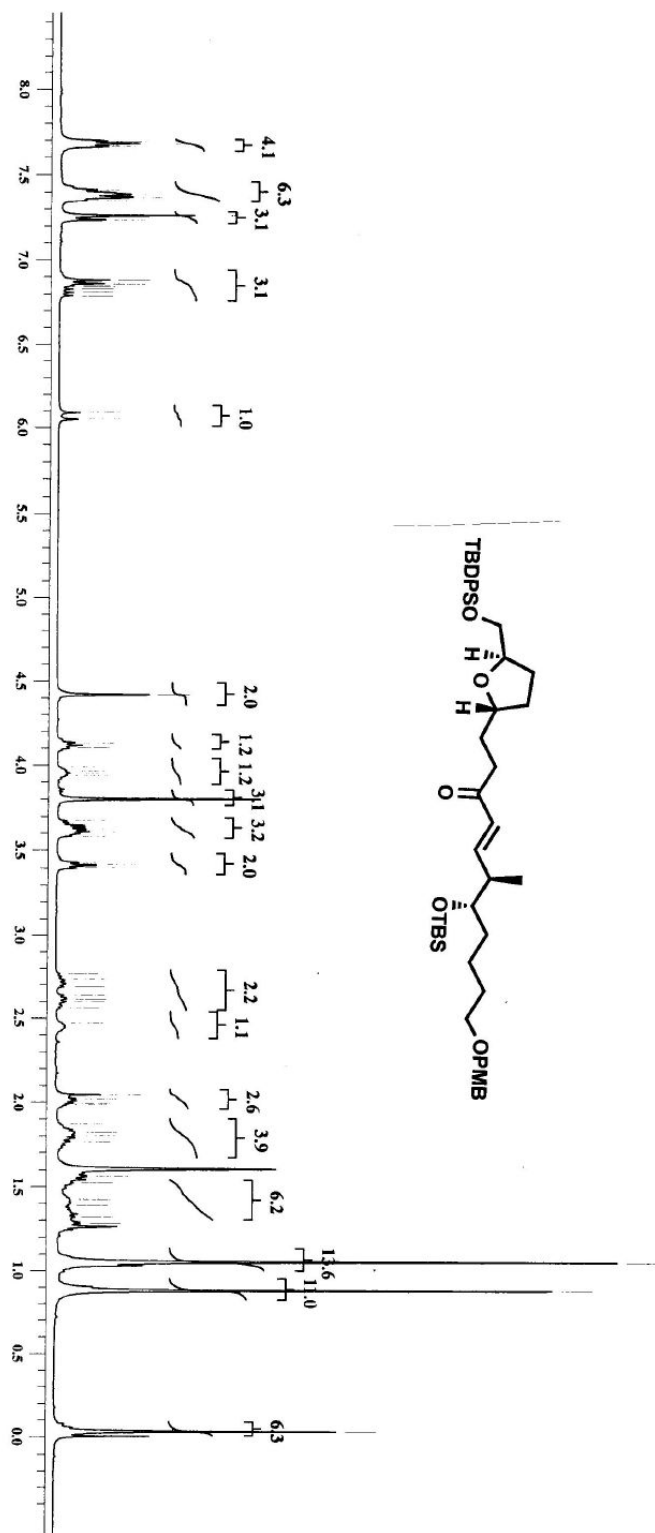
 $^{13}\text{C}$  NMR spectrum of **19** (75 MHz,  $\text{CDCl}_3$ )



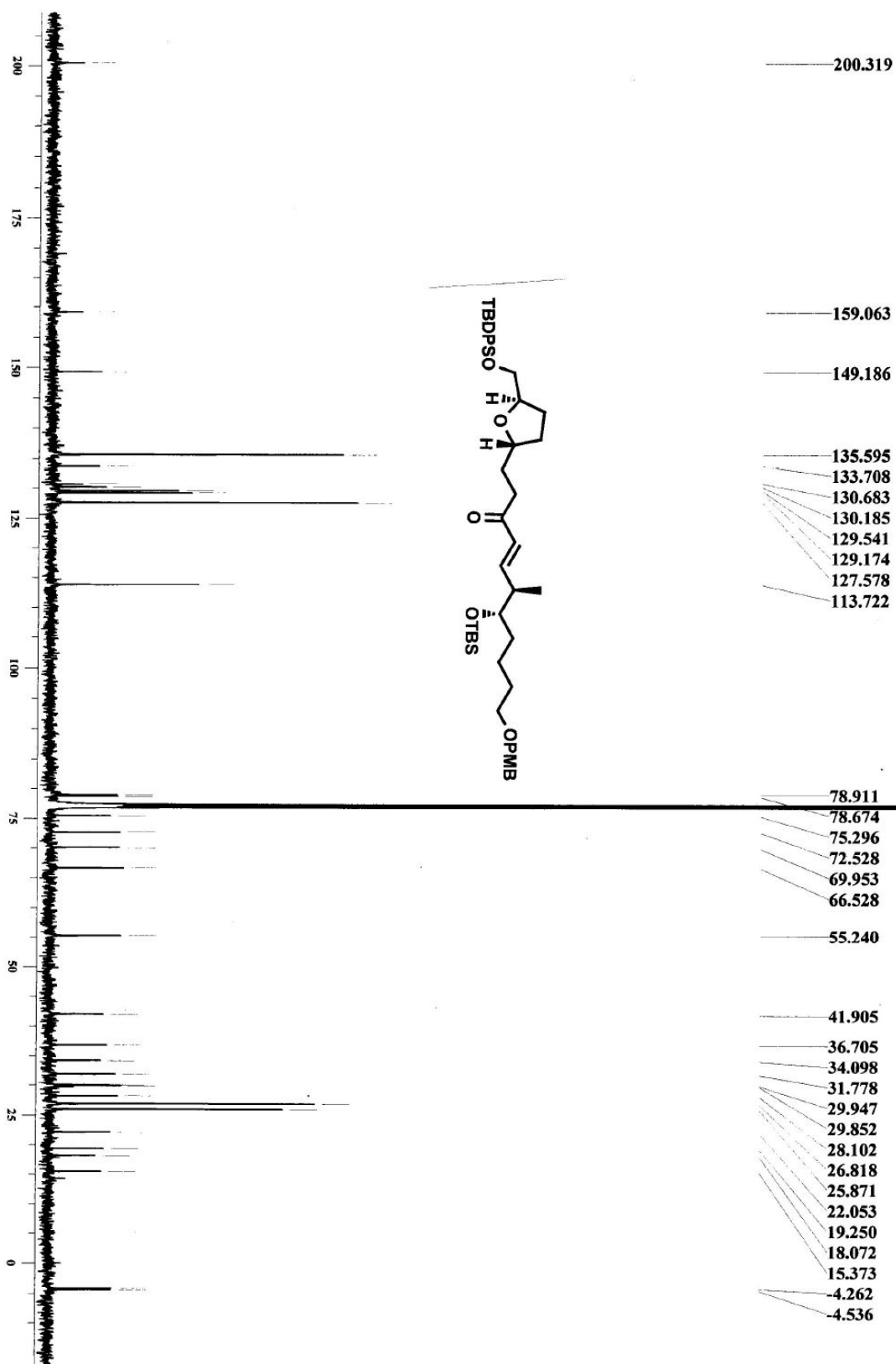
<sup>1</sup>H NMR spectrum of **6** (500 MHz, CDCl<sub>3</sub>)



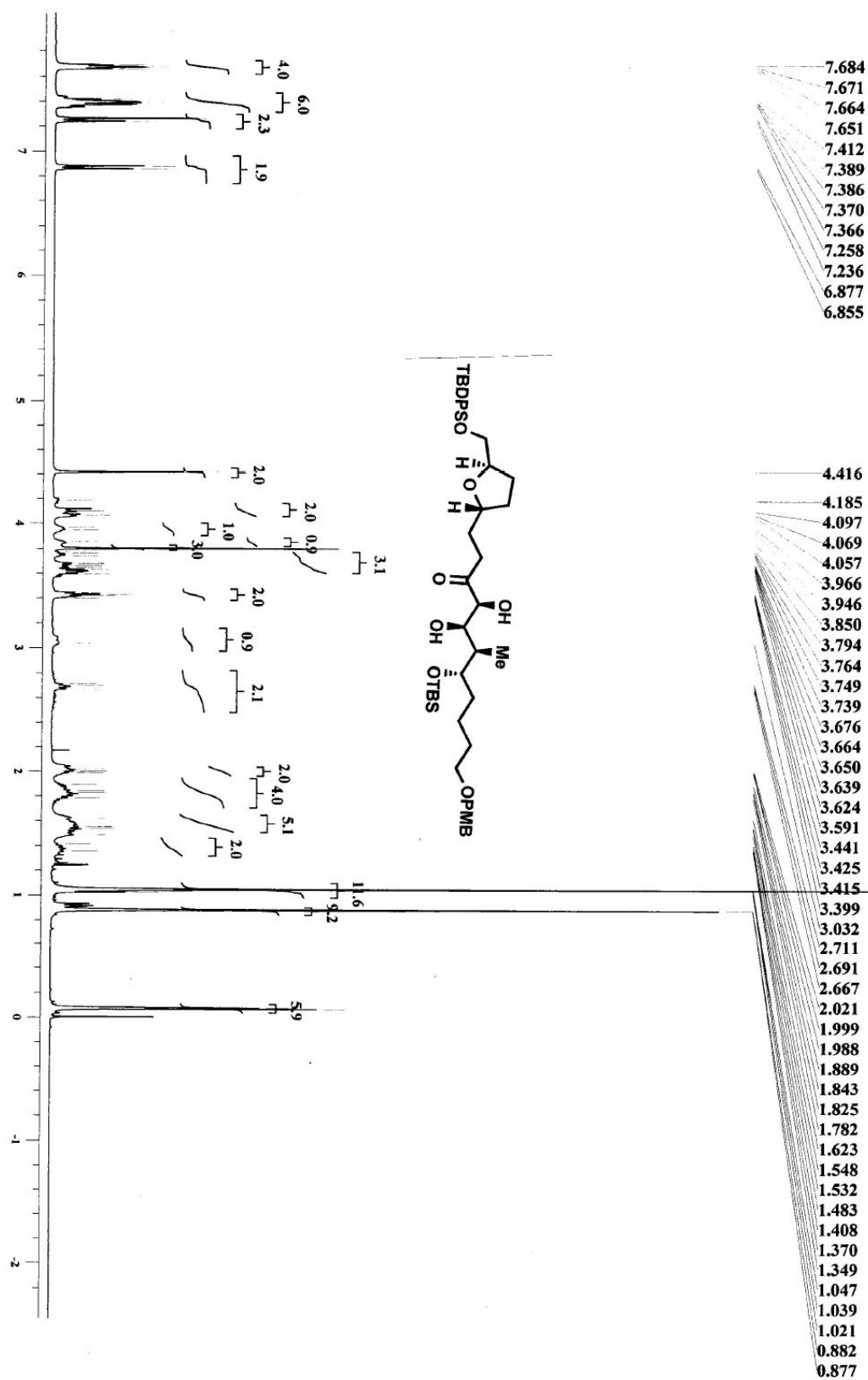
<sup>13</sup>C NMR spectrum of **6** (125 MHz, CDCl<sub>3</sub>)

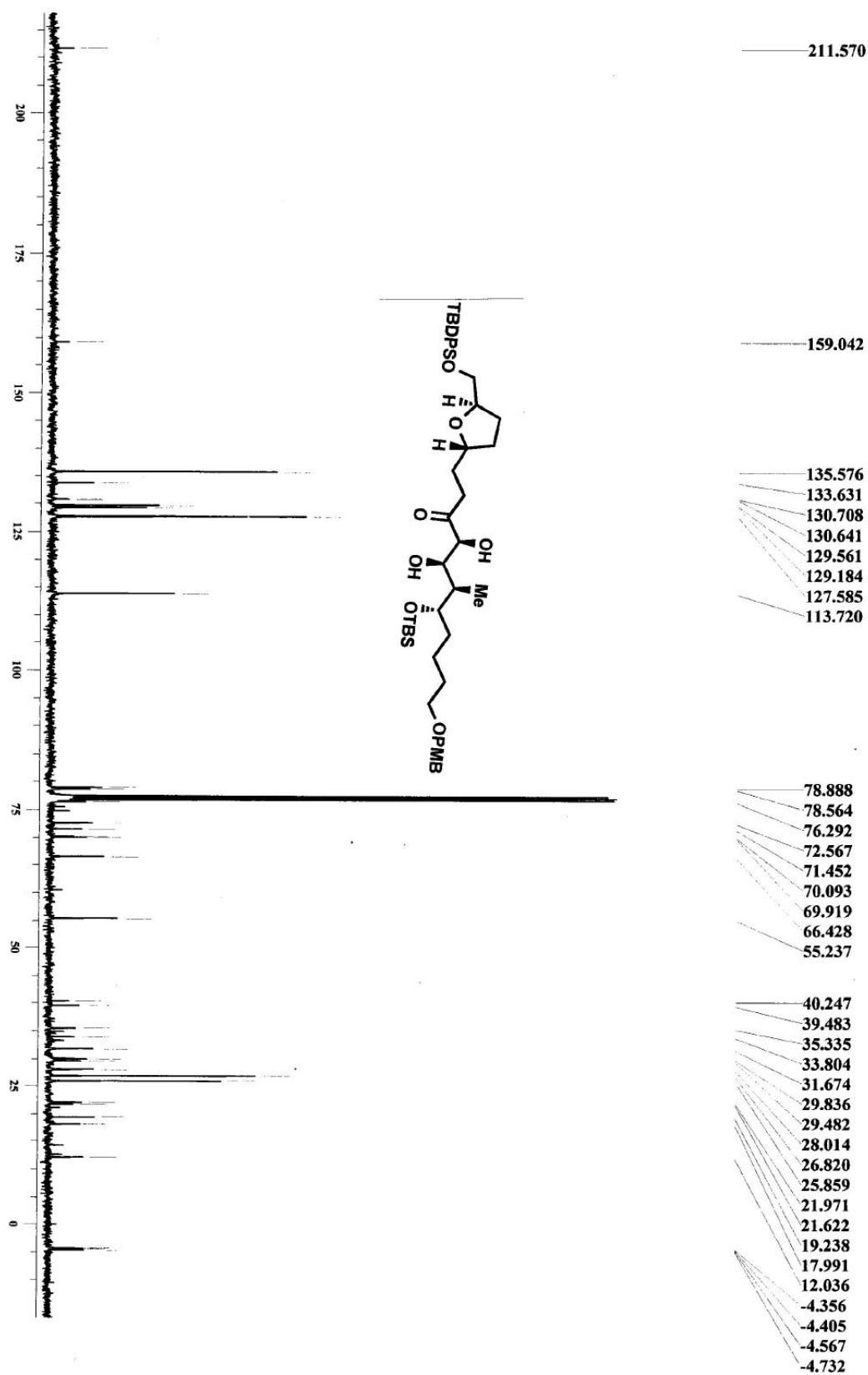


<sup>1</sup>H NMR spectrum of **4** (400 MHz, CDCl<sub>3</sub>)



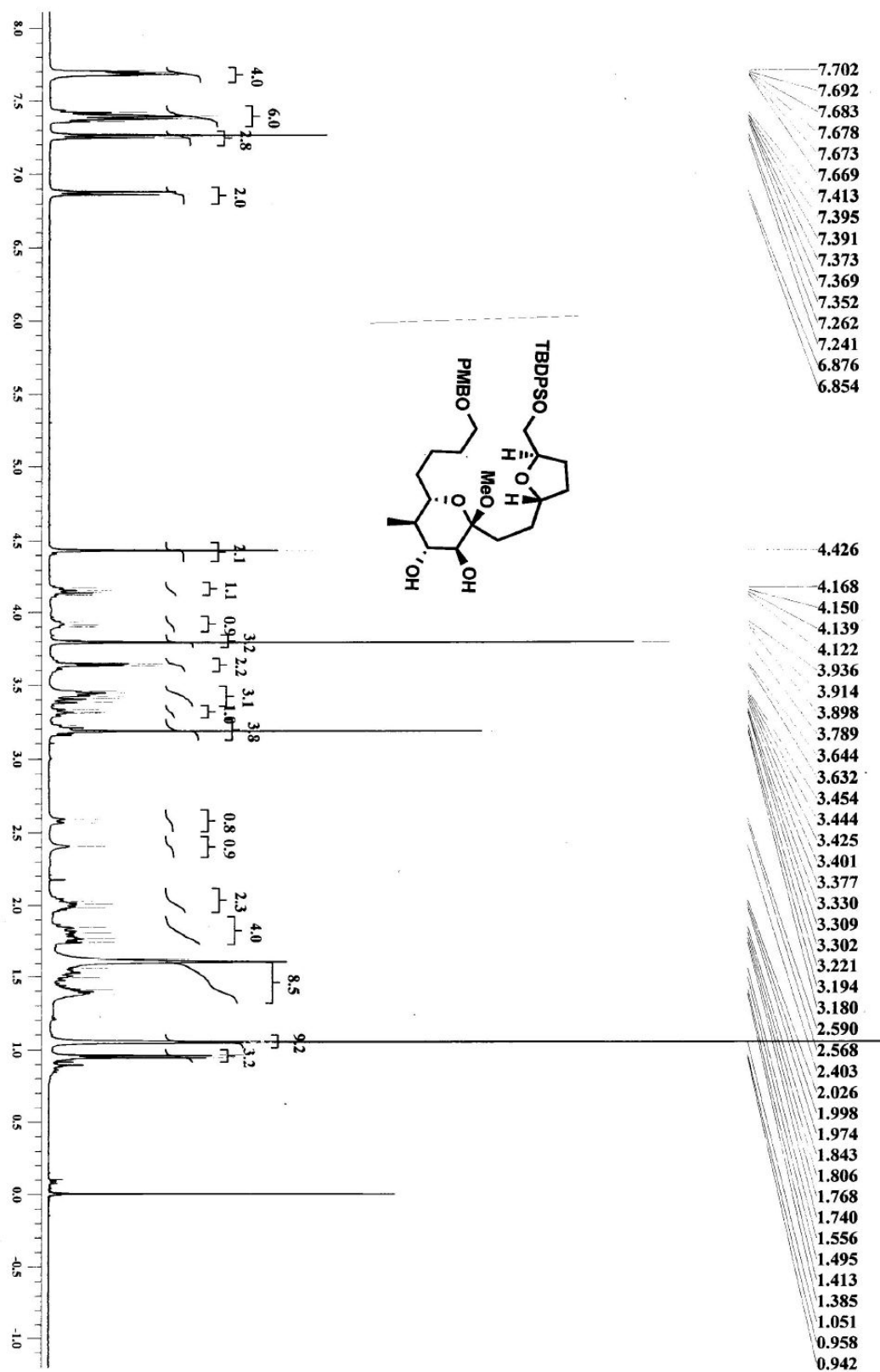
<sup>13</sup>C NMR spectrum of 4 (100 MHz, CDCl<sub>3</sub>)

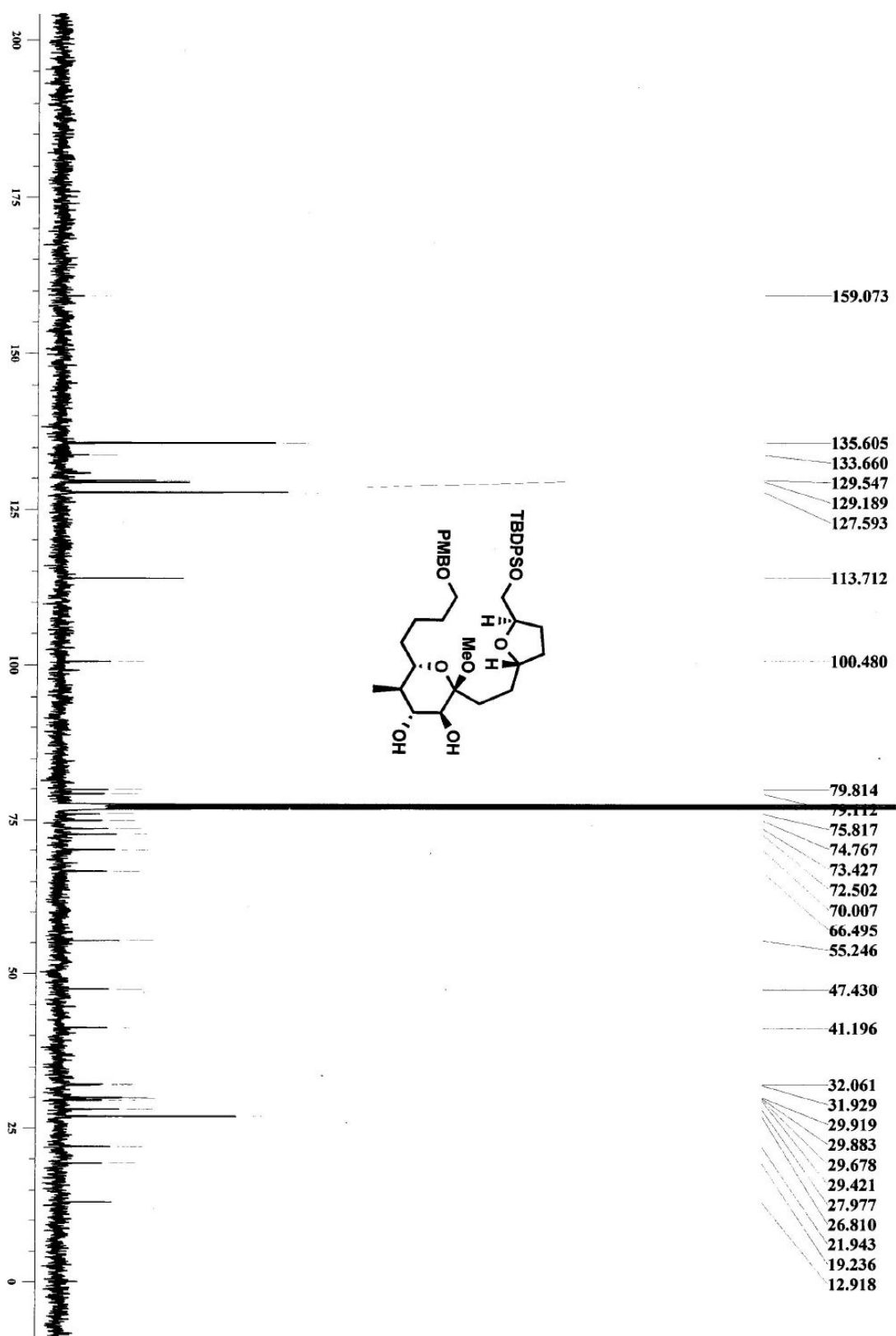
 $^1\text{H}$  NMR spectrum of **20** (400 MHz,  $\text{CDCl}_3$ )



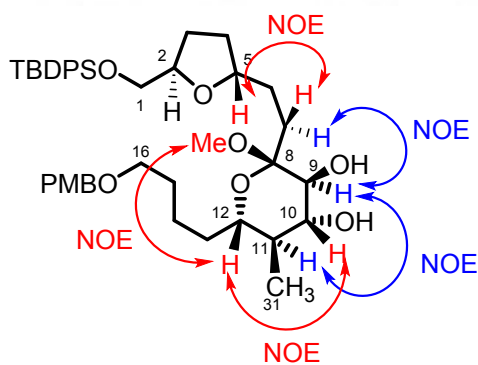
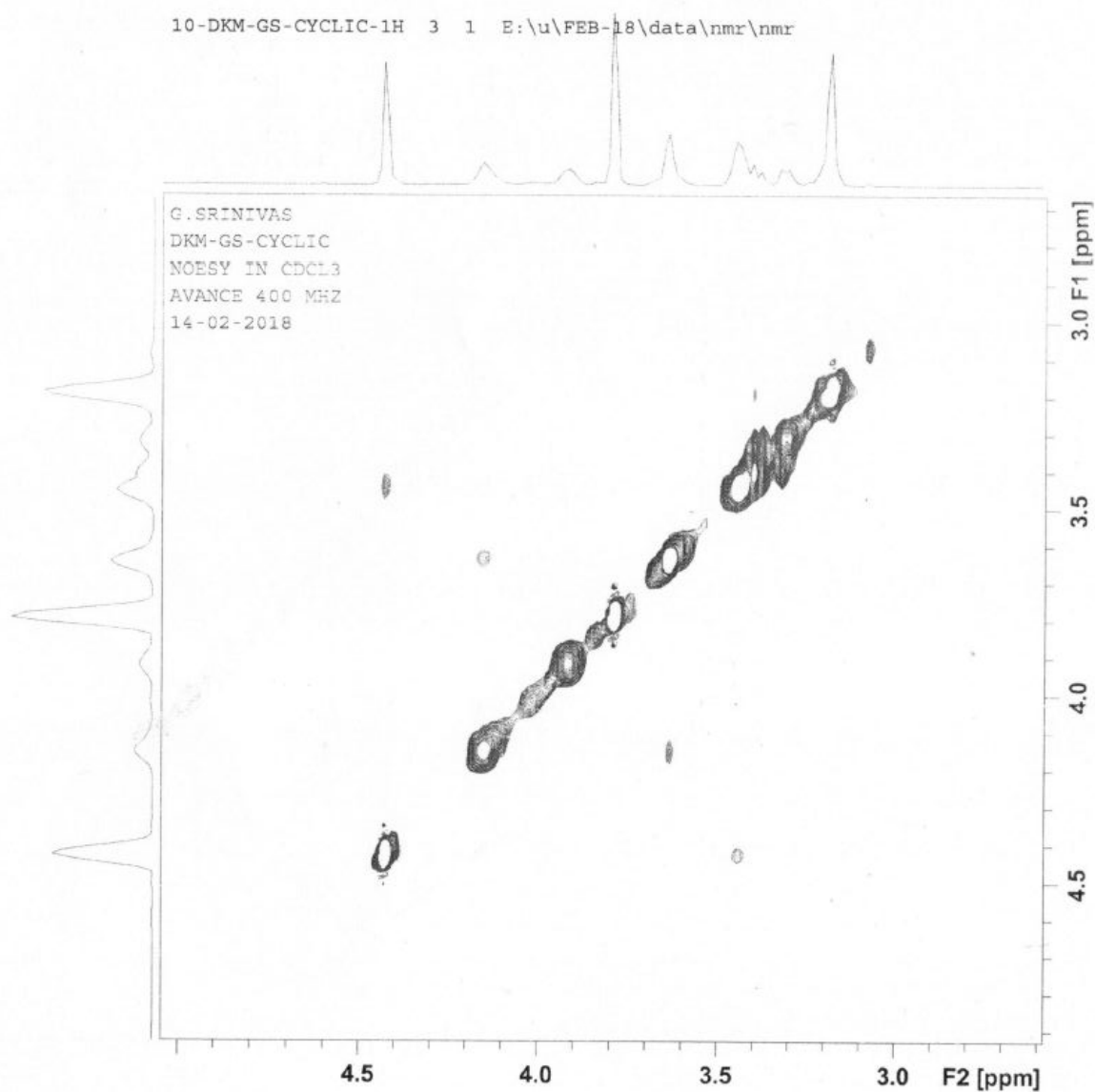
<sup>13</sup>C NMR spectrum of **20** (125 MHz, CDCl<sub>3</sub>)



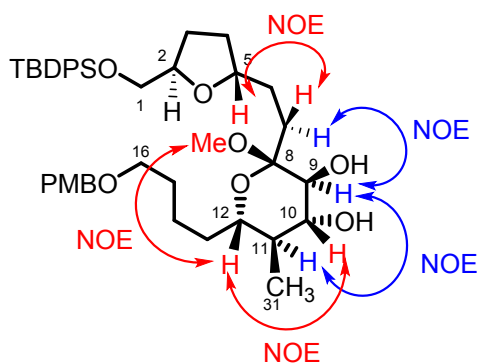
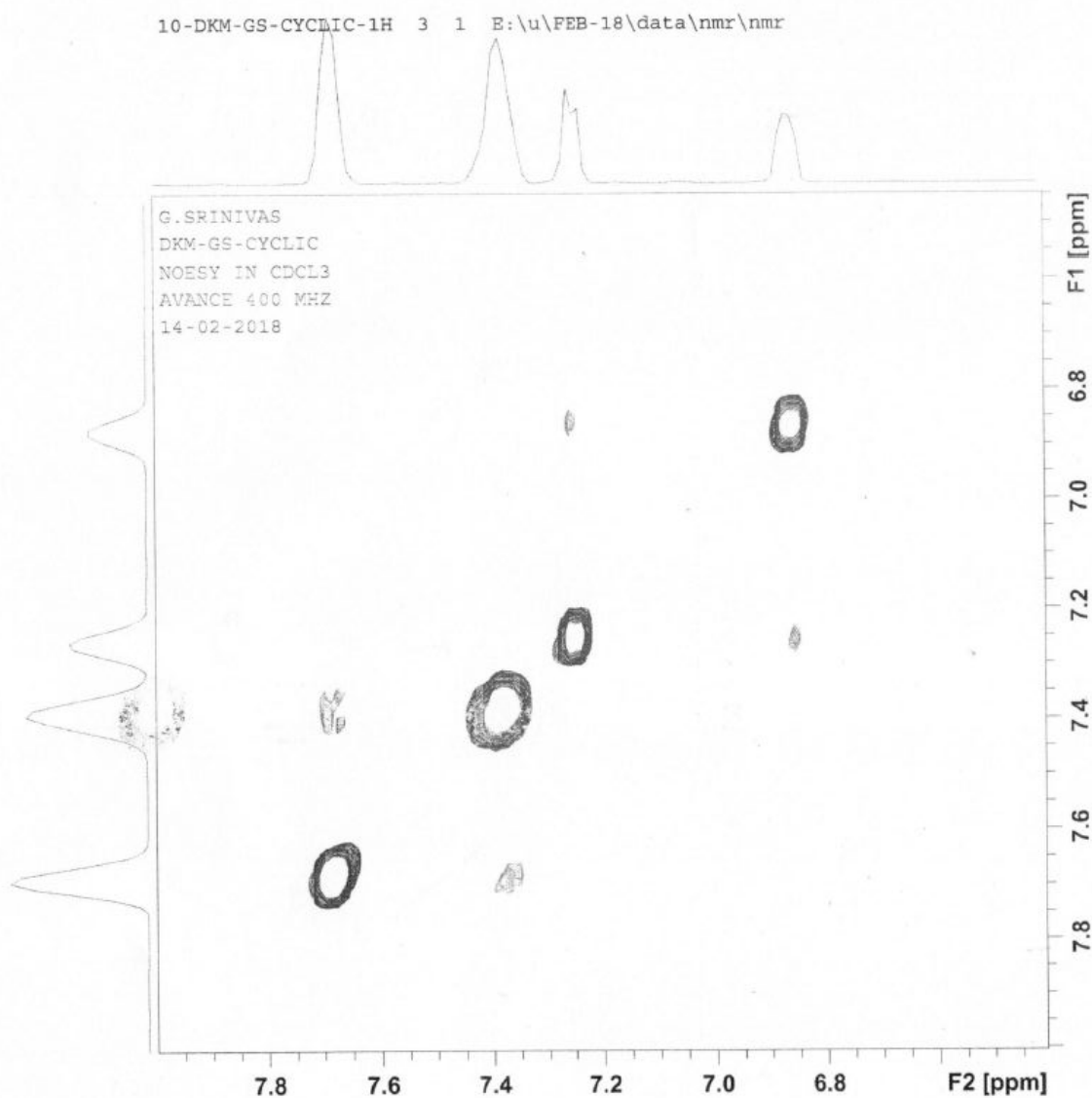
<sup>1</sup>H NMR spectrum of **3** (500 MHz, CDCl<sub>3</sub>)



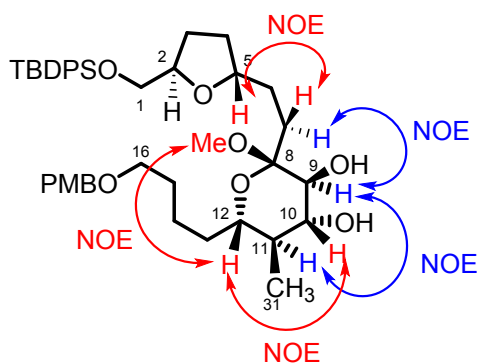
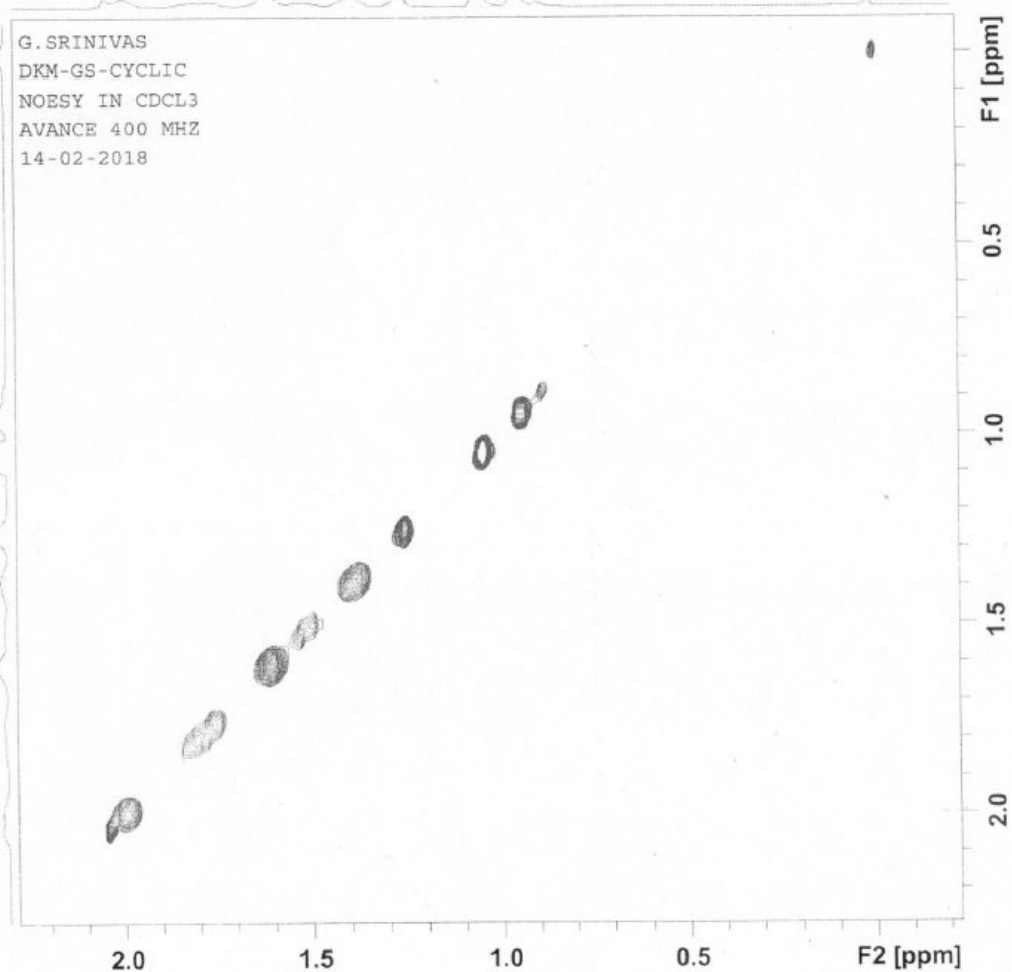
$^{13}\text{C}$  NMR spectrum of **5** (125 MHz,  $\text{CDCl}_3$ )



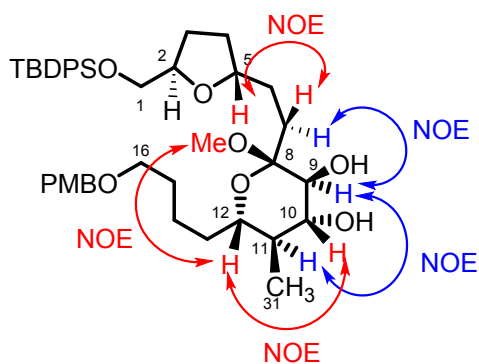
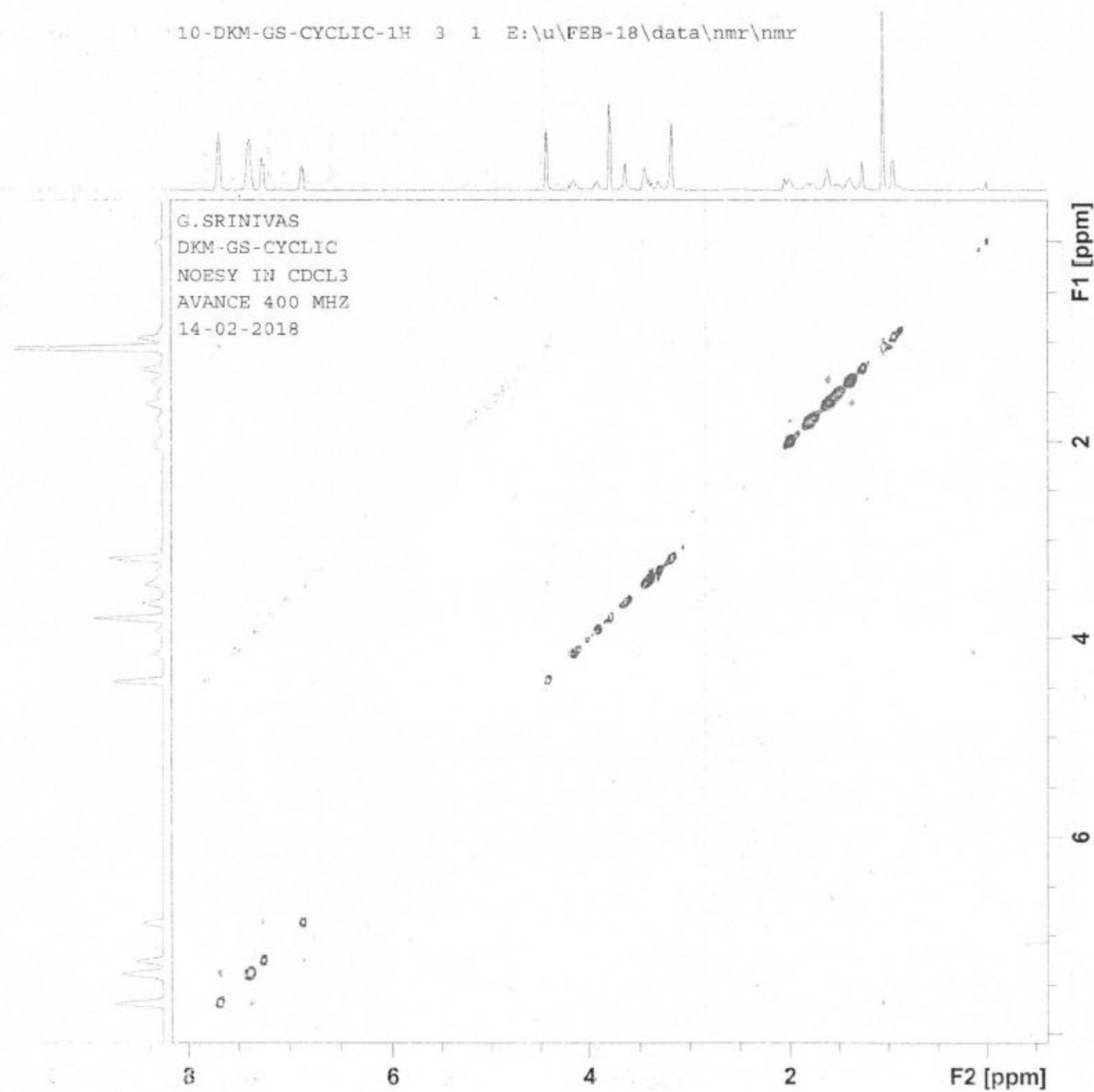
NOESY Spectrum of compound **3** (400 MHz, CDCl<sub>3</sub>) (2.5 to 5.0 ppm)



NOESY Spectrum of compound **3** (400 MHz, CDCl<sub>3</sub>) (6.0 to 8.0 ppm)



NOESY Spectrum of compound **3** (400 MHz, CDCl<sub>3</sub>) (-0.2 to 2.2 ppm)



NOESY Spectrum of compound **3** (400 MHz, CDCl<sub>3</sub>) (Full Spectrum)