Supporting Information

Total Synthesis of (–)-Bitungolide F

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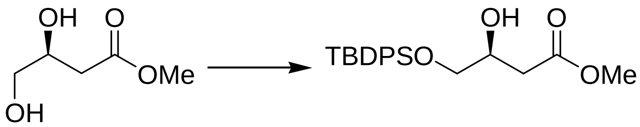
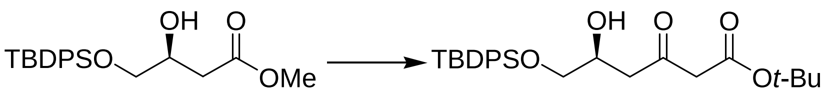
1. Experimental procedures and data for the compounds

General Experimental Details. Oxygen- and moisture-sensitive reactions were carried out under argon atmosphere. Solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. Column chromatography was performed on silica gel (200-300 mesh). Optical rotations were measured on a precision automated polarimeter. Infrared spectra were recorded on a FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 300 MHz and a 400 MHz spectrometers. Chemical shifts are reported as δ values relative to internal chloroform (δ 7.26 for ^{1}H NMR and 77.0 for ^{13}C NMR) and internal acetone (δ 2.05 for ^{1}H NMR and 29.9 for ^{13}C NMR).



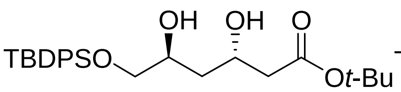
16 **17**

TBDPS Ether 17. To a solution of diol **16** (402 mg, 3 mmol) in CH_2Cl_2 (15 mL) at 0 ºC was added Et_3N (333 mg, 3.3 mmol), N,N-4-dimethylaminopyridine (37 mg, 0.1 mmol) and TBDPSCl (908 mg, 3.3 mmol). The mixture was stirred at 0 ºC for 15 min and then at rt for 3 h. Water (30 mL) was added and the mixture was stirred for additional 15 min. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexane:EtOAc, 8:1) to afford TBDPS ether **17** (1.004 g, 90%) as a colorless oil: $[\alpha]^{20}_{D}$ = -10 (c = 2.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (s, 9 H), 2.58 (m, 2 H), 2.96 (d, J = 4.5 Hz, 1 H), 3.67 (m, 2 H), 3.69 (s, 3 H), 4.18 (m, 1 H), 7.45 (m, 6 H), 7.68 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 26.8, 37.8, 51.7, 66.8, 68.6, 127.7, 129.8, 132.9, 133.0, 135.5, 172.4; IR (KBr) ν_{max} 3472, 3070, 2932, 1737, 1431, 1111, 704 cm^{-1}; HRMS (ESIMS) caled for $C_{21}H_{28}O_4SiNa$ $[M + Na]^+$ 395.1649, found 395.1656.



17 **14**

Ester 14. A solution of diisopropylamine (1.8 mL, 12.9 mmol) in THF (20 mL) was cooled to - 40 ºC. *n*-Butyllithium (1.55 M in hexanes, 8 mL, 12.5 mmol) was added dropwise via a syringe. The mixture was stirred for 10 min at -40 ºC and at 0 ºC for 30 min. After recooling to -40 ºC, *t*-BuOAc (1.61 mL, 12 mmol) was added dropwise and the mixture was stirred for 30 min at -40 ºC followed by addition of TBDPS ether **17** (1.116 g, 3 mmol) in THF (6 mL), The mixture was stirred for 15 min and for 2 h after warming to 0 ºC. The reaction mixture was quenched with water (40 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic extracts was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexane:EtOAc, 8:1) to afford δ-hydroxyl-β-keto ester **14** (1.162 g, 85%) as a colorless oil: $[\alpha]^{20}_{D}$ = -14 (c = 2.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (s, 9 H), 1.48 (s, 9 H), 2.75 (d, J = 6.4 Hz, 2 H), 3.41 (s, 2 H), 3.66 (s, 3 H), 4.23 (m, 1 H), 7.45 (m, 6 H), 7.67(m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 26.8, 27.9, 28.3, 45.9, 51.2, 67.0, 68.1, 82.0, 127.8, 129.8, 133.0 (2), 135.5 (2), 166.2, 202.8; IR (KBr) ν_{max} 3464, 3071, 2932, 1734, 1714, 1255, 1148, 1111, 705 cm^{-1}; HRMS (ESIMS) caled for $C_{26}H_{36}O_5SiNa$ $[M + Na]^+$ 479.2224, found 479.2228.



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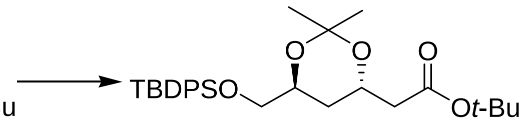
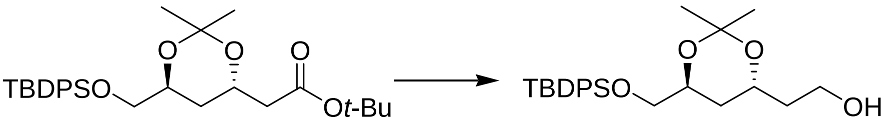


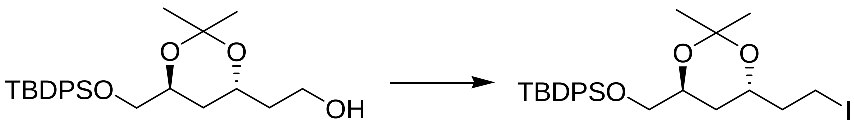
19

Acetonide Ester 19. To a solution of diol **18** (870 mg, 1.9 mmol) in CH_2Cl_2 (20 mL) was added 2,2-dimethoxypropane (2.3 mL, 19 mmol) and PPTS (48 mg, 0.2 mmol) in ambient atmosphere. After stirring for 10 h at rt, saturated $NaHCO_3$ (aq.) was added and the mixture was stirred for additional 10 min. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexane:EtOAc, 30:1) to give acetonide ester **19** (888 mg, 94%) as colorless liquid: $[\alpha]^{20}_{D}$ = -18.5 (c = 7.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.07 (s, 9 H), 1.35 (s, 3 H), 1.37 (s, 3 H), 1.46 (s, 9 H), 1.59 (m, 1 H), 1.73 (m, 1 H), 2.39 (m, 2 H), 3.63 (dd, J = 10.5 Hz, J = 4.5 Hz, 1 H), 3.73 (dd, J = 10.5 Hz, J = 6.0 Hz, 1 H), 3.95 (m, 1 H), 4.21 (m, 1 H), 7.41 (m, 6 H), 7.69 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3, 24.7, 24.9, 26.8, 28.1, 33.9, 42.3, 63.8, 66.6, 67.5, 80.5, 100.4, 127.6 (2), 129.6, 133.7 (2), 135.6, 135.7, 170.2; IR (KBr) ν_{max} 2933, 1732, 1368, 1224, 1148, 1112, 704 cm^{-1}; HRMS (ESIMS) caled for $C_{29}H_{42}O_5SiNa$ $[M + Na]^+$ 521.2694, found 521.2699.



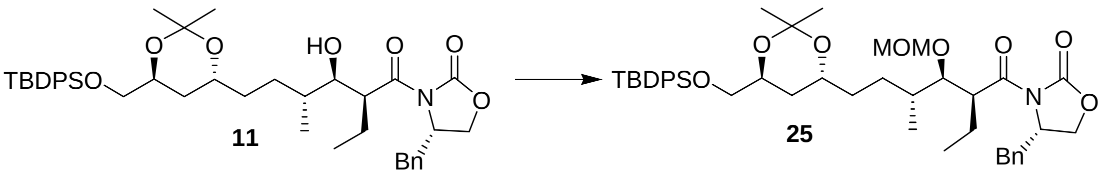
19 **20**

Alcohol 20. To a suspension of $LiAlH_4$ (195 mg, 5.2 mmol) in THF (10 mL) at 0 °C was added dropwise a solution of ester **19** (640 mg, 1.3 mmol) in THF (8 mL). After 30 min of being stirred at 0 °C, the mixture was treated dropwise with saturated $NaHCO_3$ (aq.). Then the mixture was filtered through celite and washed with EtOAc (3 × 20 mL). The filtrate was dried over Na_2SO_4, filtered and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography (Hexane:EtOAc, 4:1) to give alcohol **20** (528 mg, 96%): $[\alpha]^{20}_{D}$ = -13 (*c* = 3.70, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.07 (s, 9 H), 1.37 (s, 3 H), 1.38 (s, 3 H), 1.65 (m, 2 H), 1.74 (m, 2 H), 3.63 (dd, J = 10.8 Hz, J = 4.8 Hz, 1 H), 3.71 (dd, J = 10.8 Hz, J = 6.0 Hz, 1 H), 3.76 (m, 2 H), 3.99 (m, 1 H), 4.01 (m, 1 H), 7.41 (m, 6 H), 7.71 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3, 24.8, 25.1, 26.8, 34.2, 37.6, 61.2, 66.6, 67.0, 67.6, 100.3, 127.6, 129.6, 133.6, 133.7, 135.6, 135.7; IR (KBr) ν_{max} 3517, 2958, 2931, 1784, 1693, 1460, 1381, 1225, 1136, 1101, 702 cm^{-1}; HRMS (ESIMS) caled for $C_{25}H_{36}O_4SiNa$ $[M + Na]^+$ 451.2275, found 451.2269.

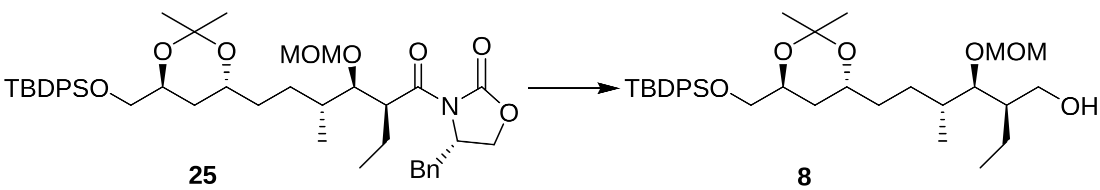


20 **13**

Iodide 13. To a solution of the alcohol **20** (2.582 g, 6.03 mmol), imidazole (615 mg, 9.0 mmol) and PPh_3 (1.897 g, 7.2 mmol) in CH_2Cl_2 (60 mL) at 0 ºC was slowly added iodine (1.839 g, 7.2 mmol). The solution was stirred for 5 min at 0 ºC and then for 3 h at rt. The reaction was quenched by the addition of an aqueous $Na_2S_2O_3$ (30 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers was washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexanes:EtOAc, 30:1) to yield iodide **13** (3.141 g, 97%) as a colorless oil: $[\alpha]^{20}_{D}$ = -3 (*c* = 2.80, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.06 (s, 9 H), 1.34 (s, 3 H), 1.37 (s, 3 H), 1.60 (m, 2 H), 1.95 (m, 2 H), 3.22 (m, 2 H), 3.62 (dd, J = 10.5 Hz, J = 4.8 Hz, 1 H), 3.72 (dd, J = 10.5 Hz, J = 6.0 Hz, 1 H), 3.91 (m, 1 H), 3.94 (m, 1 H), 7.39 (m, 6 H), 7.69 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 2.4, 19.3, 24.7, 25.1, 26.8, 33.9, 39.1, 66.3, 66.6, 67.6, 100.4, 127.6 (2), 129.6, 133.6, 133.7, 135.6, 135.7; IR (KBr) ν_{max} 2932, 1225, 1110, 703 cm^{-1}; HRMS (ESIMS) calcd for $C_{25}H_{35}IO_3SiNa$ [M + Na]$^+$ 561.1292, found 561.1288.

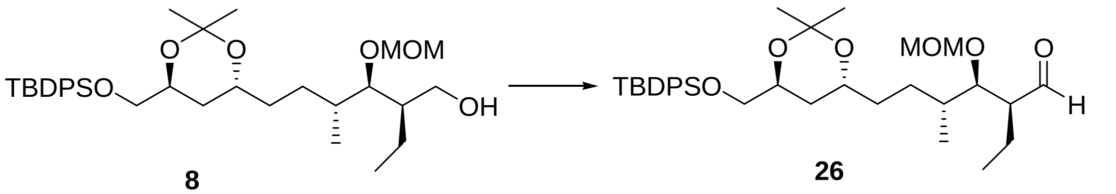


MOM Ether 25. To a solution of imide alcohol **11** (1.877 g, 2.63 mmol) in CH_2Cl_2 (20 mL) at 0 ºC was added diisopropylethylamine (7.4 mL, 52.5 mmol,), chloromethylmethyl ether (2 mL, 26.3 mmol,) and tetrabutylammonium iodide (100 mg, 0.26 mmol). The reaction mixture was immediately allowed to warm to rt. After 18 h of being stirred, saturated $NaHCO_3$ (aq.) was added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers was washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexanes:EtOAc, 10:1) to provid MOM ether **25** (1.90g, 92%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (m, 6 H), 1.05 (s, 9 H), 1.28 (m, 1 H), 1.31 (s, 6 H), 1.52 (m, 2 H), 1.65 (m, 4 H), 1.91 (m, 1 H), 2.73 (dd, J = 12.9 Hz, J = 9.9 Hz, 1 H), 3.35 (s, 3 H), 3.39 (m, 1 H), 3.60 (m, 2 H), 3.68 (m, 2 H), 3.74 (m, 2 H), 3.95 (m, 2 H), 4.13 (d, J = 4.8 Hz, 2 H), 4.60 (m, 3 H), 7.24 (m, 2 H), 7.37 (m, 9 H), 7.68 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.0, 15.9, 19.2, 19.9, 24.7, 24.8, 26.7, 27.7, 33.7, 34.6, 37.0, 37.8, 47.4, 56.1, 56.4, 65.9, 66.7, 66.8, 67.7, 84.7, 98.5, 100.0, 127.3, 127.5 (2), 128.9, 129.4, 129.5, 133.6, 135.5, 135.6, 135.7, 153.1, 174.6; IR (KBr) ν_{max} 3517, 3069, 2960, 2933, 1783, 1737, 1695, 1458, 1383, 1224, 1110, 704 cm^{-1}; HRMS (ESIMS) calcd for $C_{44}H_{61}NO_8SiNa$ [M + Na]$^+$ 782.4059, found 782.4065.



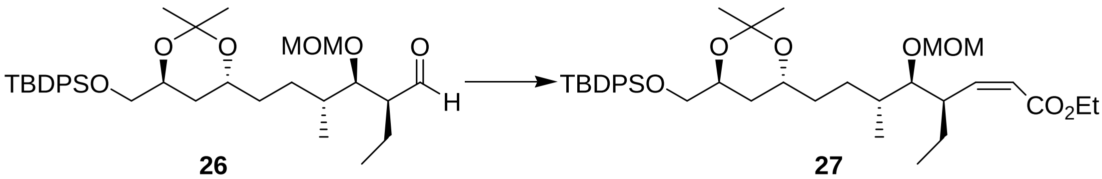
Alcohol 8. To a solution of **25** (1.80 g, 2.37 mmol) in THF (7.5 mL) was added a solution of $NaBH_4$ (450 mg, 11.86 mmol) in H_2O (2.5 mL) at 0 ºC. The mixture was stirred at 0 °C for 5 min, warmed to rt and stirred overnight. The reaction was quenched by addition of saturated NH_4Cl (aq.) followed by stirring for additional 30min. The organic layer was separated and the aqueous

layer was extracted with EtOAc (3 × 15 mL). The combined organic layers was washed with saturated $NaHCO_3$ (10 mL), H_2O (10 mL), brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexanes:EtOAc, 5:1) to give the alcohol **8** (1.20g, 90%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86 (d, J = 6.6 Hz, 3 H), 0.92 (t, J = 7.5 Hz, 3 H), 1.06 (s, 9 H), 1.21 (m, 3 H), 1.34 (s, 3 H), 1.35 (s, 3 H), 1.60 (m, 7 H), 3.01 (m, 1 H), 3.42 (s, 3 H), 3.47 (dd, J = 8.7 Hz, 2.4 Hz, 1 H), 3.61 (m, 1 H), 3.62 (dd, J = 10.5 Hz, J = 4.5 Hz, 1 H), 3.70 (m, 2 H), 3.71 (dd, J = 10.5 Hz, J = 6.0 Hz 1 H), 3.94 (m, 1 H), 4.67 (s, 2 H), 7.40 (m, 6 H), 7.70 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 12.4, 15.9, 18.1, 19.2, 24.8 (2), 26.7, 28.3, 33.2, 34.7, 35.6, 43.4, 56.1, 62.7, 66.7, 66.8, 67.6, 84.4, 98.9, 100.1, 127.5 (2), 129.6, 133.6, 133.7, 135.6 (2); IR (KBr) ν_{max} 3386, 2933, 1738, 1619, 1376, 1225, 1111, 704 cm^{-1}; HRMS (ESIMS) caled for $C_{34}H_{54}O_6SiNa$ [M + Na]$^+$ 609.3582, found 609.3586.



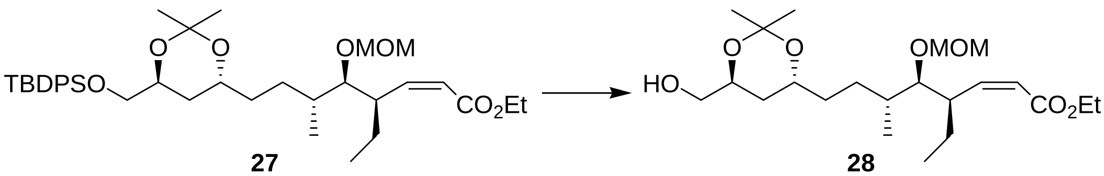
8 26

Aldehyde 26. To a solution of alcohol **8** (1.149 g, 1.96 mmol) in EtOAc (50 mL) was added IBX (1.647 g, 58.82 mmol). The resulting suspension was heated to reflux in ambient atmosphere. After refluxing for 3 h, the reaction was cooled to rt and filtered through a medium glass frit. The filter cake was washed with Et_2O (3 × 20 mL) and the combined filtrate was concentrated to dryness. The residue was purified by flash column chromatography (Hexane:EtOAc, 20:1) to give aldehyde **26** (972 mg, 85%) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.93 (d, J = 6.9 Hz, 3 H), 0.97 (t, J = 7.8 Hz, 3 H), 1.06 (s, 9 H), 1.24 (m, 2 H), 1.34 (s, 3 H), 1.35 (s, 3 H), 1.63 (m, 7 H), 2.36 (m, 1 H), 3.32 (s, 3 H), 3.62 (dd, J = 10.5 Hz, J = 4.5 Hz, 1 H), 3.72 (m, 3 H), 3.95 (m, 1 H), 4.61 (m, 2 H), 7.40 (m, 6 H), 7.69 (m, 4 H), 9.72 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 12.7, 16.1, 17.3, 19.2, 24.8 (2), 26.7, 27.7, 33.4, 34.7, 36.2, 55.9, 56.2, 66.6, 66.7, 67.6, 82.0, 97.7, 100.1, 127.5 (2), 129.5, 133.6, 133.7, 135.5, 135.6 (2), 204.2; HRMS (ESIMS) caled for $C_{34}H_{52}O_6SiNa$ [M + Na]$^+$ 607.3425, found 607.3426.



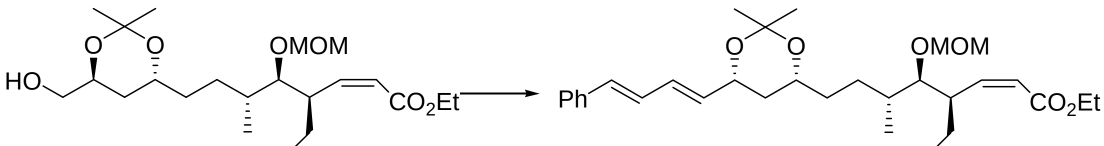
26 **27**

Enoate 27. To a suspension of sodium hydride (50% dispersion in mineral oil, 83 mg, 1.73 mmol) in THF (10 mL) was added ethyl (di-*o*-tolylphosphono)acetate (189mg, 0.54 mmol) at 0 ºC. After stirring for 10 min, the mixture was cooled to -78 ºC followed by addition of aldehyde **26** (215mg, 0.47 mmol) in THF (5 mL). After the mixture was warmed to -10 ºC, the resulting mixture was stirred for additional 1 h. The mixture was quenched with saturated NH_4Cl (20 mL) and diluted with EtOAc (10 mL). The organic layer was separated and the aqueous layer was separated and extracted with EtOAc (3 × 10 mL). The combined organic extracted was washed with saturated $NaHCO_3$ (2 × 10 mL) and brine (15 mL), dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexane:EtOAc, 20:1) to afford enoate **27** (715 mg, 70%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.84 (t, J = 6.9 Hz, 3 H), 0.97 (d, J = 6.9 Hz, 3 H), 1.06 (s, 9 H), 1.26 (m, 6 H), 1.34 (s, 6 H), 1.51 (m, 2 H), 1.62 (m, 3 H)1.78 (m, 1 H), 3.24 (m, 1 H), 3.39 (s, 3 H), 3.61 (dd, J = 10.5 Hz, J = 4.8 Hz, 1 H), 3.71 (dd, J = 10.5 Hz, J = 6.3 Hz, 1 H), 3.72 (m, 2 H), 3.94 (m, 1 H), 4.15 (q, J = 6.9 Hz, 2 H), 4.63 (s, 2 H), 5.84 (d, J = 11.7 Hz, 1 H), 6.03 (m, 1 H), 7.39 (m, 6 H), 7.70 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 11.7, 14.2, 16.5, 19.2, 22.4, 24.8, 26.7, 27.4, 33.8, 34.7, 36.4, 42.0, 56.0, 59.7, 66.7, 66.9, 67.6, 86.9, 98.3, 100.0, 120.5, 127.5 (2), 129.5, 133.6, 133.8, 135.6 (2), 152.0, 166.1; HRMS (ESIMS) caled for $C_{38}H_{58}O_7SiNa$ $[M + Na]^+$ 677.3844, found 609.3848.

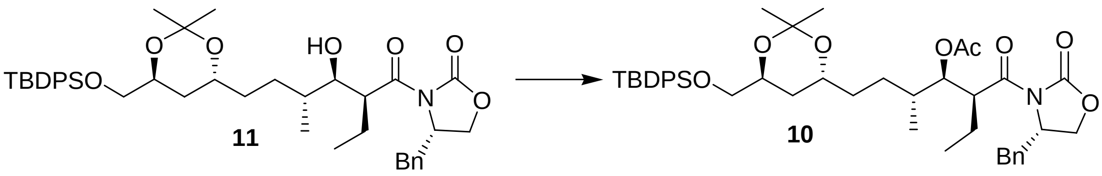


27 **28**

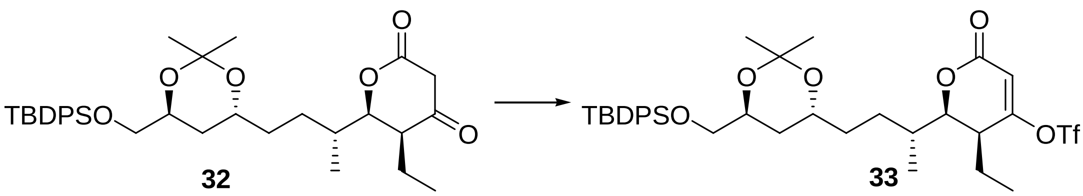
Enoate Alcohol 28. To a solution of enoate **27** (661 mg, 1.01 mmol) in THF (10 mL) was added TBAF (638 mg, 2.02 mmol) and the mixture was stirred for 12 h. Water (10 mL) was added and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexanes:EtOAc, 4:1) to provide enoate alcohol **28** (378 mg, 90%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.80 (t, J = 7.5 Hz, 3 H), 0.93 (d, J = 6.9 Hz, 3 H), 1.22 (m, 3 H), 1.25 (t, J = 7.2 Hz, 3 H), 1.32 (s, 3 H), 1.33 (s, 3 H), 1.45 (m, 2 H), 1.59 (m, 3 H), 1.74 (m, 1 H), 2.19 (brs, 1 H), 3.20 (dd, J = 10.5 Hz, 5.4 Hz, 1 H), 3.36 (s, 3 H), 3.49 (m, 1 H), 3.55 (m, 1 H), 3.68 (m, 2 H), 3.90 (m, 1 H), 4.12 (q, J = 7.2 Hz, 2 H), 4.60 (s, 2 H), 5.81 (d, J = 11.7 Hz, 1 H), 5.98 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 11.6, 14.2, 16.6, 22.5, 24.7, 24.8, 27.1, 33.8 (2), 36.4, 42.0, 56.0, 59.8, 65.4, 66.9, 67.5, 87.0, 98.4, 100.3, 120.5, 151.8, 166.2; HRMS (ESIMS) caled for $C_{22}H_{40}O_7Na$ [M + Na]$^+$ 439.2666, found 439.2657.



Enoate 30. To a solution of enoate alcohol **28** (40 mg, 0.096 mmol) in CH_2Cl_2 (5 mL) was added Dess–Martin periodinane (122 mg, 0.288 mmol). The reaction mixture was stirred at rt for 4 h followed by addition of saturated $NaHCO_3$ (2 mL) and $Na_2S_2O_3$ (2 mL). After the solids was dissolved, the mixture was extracted with Et_2O (3 × 10 mL). The combined organic layers was washed with water (5 mL), brine (5 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was directly used for further transformation without purification. Compound **29** (49 mg, 0.192 mmol), LiOH (7 mg, 0.291 mmol), 4 Å molecular sieves (127 mg) and crude aldehyde was mixed in THF (5 mL). The mixture was refluxed for 10 h and then filtered through silica gel. The filtrate was concentrated to dryness and the residue was purified by flash column chromatography (Hexane:EtOAc, 30:1) to give enoate **30** (20 mg, 40% for two steps) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (t, J = 7.2 Hz, 3 H), 0.97 (d, J = 6.8 Hz, 3 H), 1.28 (m, 7 H), 1.43 (s, 3 H), 1.48 (s, 3 H), 1.62 (m, 4 H), 1.79 (m, 1 H), 3.24 (m, 1 H), 3.40 (s, 3 H), 3.72 (m, 1 H), 3.82 (m, 1 H), 4.15 (q, J = 7.2 Hz, 2 H), 4.44 (m, 1 H), 4.64 (s, 2 H), 5.76 (dd, J = 15.2 Hz, J = 6.0 Hz, 1 H), 5.85 (d, J = 12.0 Hz, 1 H), 6.00 (t, J = 11.2 Hz, 1 H), 6.41 (dd, J = 15.2 Hz, J = 10.8 Hz, 1 H), 6.54 (d, J = 15.2 Hz, 1 H), 6.74 (dd, J = 16.0 Hz, J = 10.8 Hz, 1 H), 7.22 (t, J = 7.6 Hz, 1 H), 7.31 (t, J = 8.0 Hz, 2 H), 7.40 (d, J = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 14.3, 16.8, 19.8, 22.8, 26.7, 30.3, 34.4, 36.5, 37.1, 42.2, 56.1, 59.8, 69.1, 39.8, 87.0, 98.5, 98.6, 120.6, 126.3, 127.5, 128.4, 128.6, 130.8, 132.7, 134.2, 137.2, 151.7, 166.2; HRMS (ESIMS) caled for $C_{31}H_{46}O_6Na$ [M + Na]$^+$ 537.3187, found 537.3185.

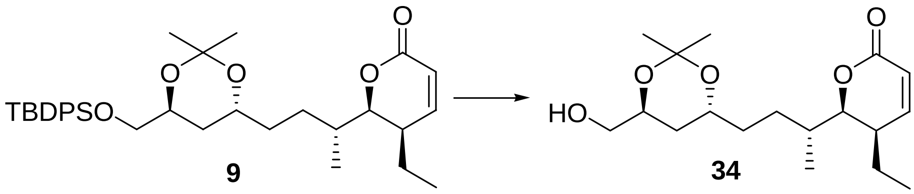


Imide Acetate 10. To a solution of imide alcohol **11** (1.282 g, 1.79 mmol) in CH_2Cl_2 (45 mL) was added Et_3N (1 mL, 7.16 mmol), Ac_2O (0.34 mL, 3.58 mmol) and N,N-4-dimethylaminopyridine (22 mg, 0.18 mmol). The mixture was stirred at rt for 4 h followed by addition of saturated $NaHCO_3$ (aq.). The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers was washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexanes:EtOAc, 6:1) to provide imide acetate **10** (1.292g, 95%) as a viscous colorless oil: $[\alpha]^{20}_{D}$ = +17.8 (c = 3.30, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (d, J = 6.9 Hz, 3 H), 0.97 (t, J = 7.8 Hz, 3 H), 1.06 (s, 9 H), 1.30 (m, 2 H), 1.32 (s, 3 H), 1.33 (s, 3 H), 1.56 (m, 5 H), 1.79 (m, 1 H), 1.93 (m, 1 H), 2.03 (s, 3 H), 2.79 (dd, J = 12.9 Hz, J = 9.9 Hz, 1 H), 3.27 (dd, J = 12.9 Hz, J = 3.0 Hz, 1 H), 3.61 (dd, J = 10.5 Hz, J = 4.8 Hz, 1 H), 3.71 (dd, J = 10.5 Hz, J = 5.7 Hz, 1 H), 3.72 (m, 1 H), 3.92 (m, 1 H), 4.08 (m, 1 H), 4.13 (m, 1 H), 4.25 (m, 1 H), 4.55 (m, 1 H), 4.95 (dd, J = 9.3 Hz, J = 2.4 Hz, 1 H), 7.26 (m, 2 H), 7.40 (m, 9 H), 7.69 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.1, 15.0, 17.1, 19.2, 20.7, 24.9, 26.8, 28.2, 32.8, 34.3, 34.5, 38.1, 46.4, 55.8, 66.3, 66.4, 66.7, 67.6, 100.0, 127.2, 127.5, 128.8, 129.4, 129.5, 133.6, 133.7, 135.4, 135.6 (2), 153.6, 171.0, 173.4; IR(KBr) ν_{max} 2934, 1780, 1736, 1699, 1382, 1230, 1110, 1020, 703 cm^{-1}; HRMS (ESIMS) caled for $C_{44}H_{59}NO_8SiNa$ $[M + Na]^+$ 780.3902, found 780.3907.



Triflate 33. To a solution of β-keto lactone **32** (918 mg, 1.58 mmol) in CH_2Cl_2 (50 mL) was added Et_3N (0.7 mL, 4.75mmol) at -78 ºC and the mixture was stirred for 10 min. Triflic anhydride (0.3 mL, 1.74 mmol) was added within 0.5 min followed by stirring for additional 30 min. The reaction was quenched with saturated $NaHCO_3$ (20 mL) and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexanes:EtOAc,

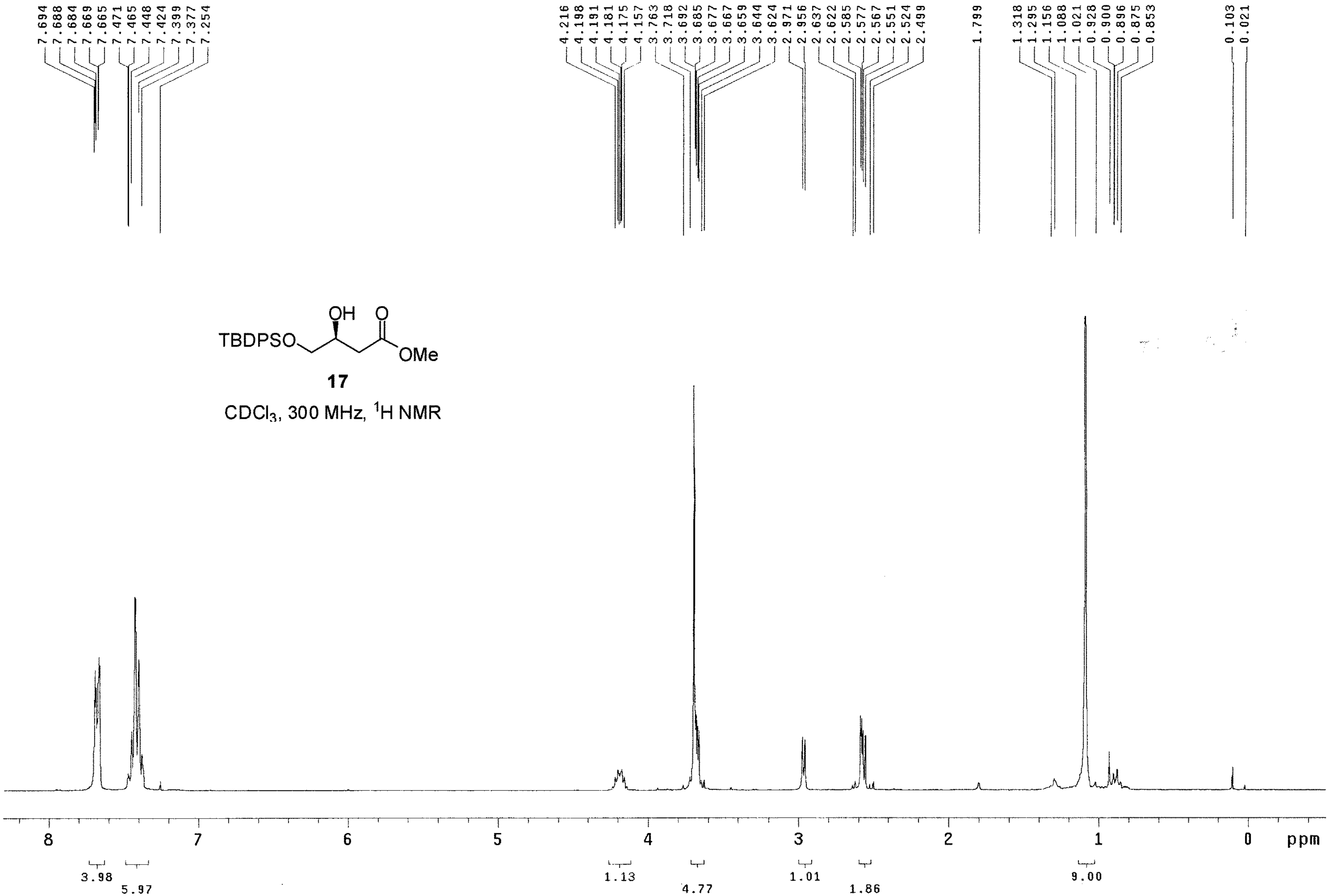
10:1) to provide triflate **32** (1.043 g, 93%) as a colorless oil: $[\alpha]^{20}_{D}$ -63.3 (c = 4.10, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 0.95 (d, J = 6.8 Hz, 3 H), 1.04 (t, J = 7.6 Hz, 3 H), 1.09 (s, 9 H), 1.29 (m, 1 H), 1.36 (s, 3 H), 1.37 (s, 3 H), 1.43 (m, 1 H), 1.55 (m, 1 H), 1.72 (m, 4 H), 1.90 (m, 2 H), 2.57 (m, 1 H), 3.65 (dd, J = 10.8 Hz, J = 4.8 Hz, 1 H), 3.74 (dd, J = 10.8 Hz, J = 6.4 Hz,1 H), 3.77 (m, 1 H), 3.97 (m, 1 H), 4.13 (dd, J = 10.4Hz, J = 2.8 Hz, 1 H), 6.11 (s, 1 H), 7.43 (m, 6 H), 7.72 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.7, 14.5, 19.2 (2), 24.8, 24.9, 26.8, 28.2, 32.7, 33.3, 34.7, 40.7, 66.6, 66.7, 67.6, 83.7, 100.1, 109.1, 118.3 (q, J = 319 Hz, C-F), 127.5 (2), 129.5 (2), 133.7, 133.8, 135.6 (2), 163.1, 167.0; IR(KBr) ν_{max} 2930, 2858, 1736, 1655, 1562, 1428, 1221, 1137, 1110, 704 cm^{-1}; HRMS (ESIMS) caled for $C_{35}H_{47}F_3O_8SSiNa$ $[M + Na]^+$ 735.2605, found 735.2607.

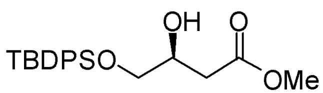


9 **34**

Alcohol 34. To a solution of δ-lactone **9** (108 mg, 0.191 mmol) in CH_3CN (5 mL) was added Et_3N (0.8 mL, 5.73 mmol) and $Et_3N{\cdot}3HF$ (0.62 mL, 3.82 mmol). This mixture was heated at 45 °C for 4 h followed by addition of Et_3N (2 mL). The mixture was concentrated to dryness. The residue was diluted with EtOAc (10 mL), Et_3N (2 mL), saturated $NaHCO_3$ (10 mL). After stirring for 5 min, the organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic extracts was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexane:EtOAc, 1.5:1) to afford alcohol **34** (61 mg, 97%) as a colorless oil: $[\alpha]^{20}_{D}$ -78 (c = 1.40, $CHCl_3$); ^1H NMR (400 MHz, $(CD_3)_2CO$): δ 0.93 (d, J = 6.8 Hz, 3 H), 0.94 (t, J = 7.2 Hz, 3 H), 1.25 (m, 1 H), 1.28 (s, 6 H) 1.43 (m, 2 H), 1.52 (m, 1 H), 1.63 (m, 1 H), 1.68 (m, 2 H), 1.86 (m, 2 H), 2.47 (m, 1 H), 3.47 (m, 2 H), 3.53 (m, 1 H), 3.77 (m, 1 H), 3.87 (m, 1 H), 4.03 (dd, J = 10.0 Hz, J = 2.8 Hz, 1 H), 5.96 (d, J = 9.6 Hz, 1 H), 7.21 (dd, J = 9.6 Hz, J = 6.4 Hz, 1 H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 11.2, 15.0, 20.9, 25.4 (2), 29.1, 33.7, 34.5, 35.3, 37.3, 65.9, 67.5, 68.8, 85.0, 100.6, 121.4, 152.3, 164.7; IR(KBr) ν_{max} 3452, 2964, 2935, 2876, 1723, 1625, 1462, 1381, 1252, 1225, 1061, 1019 cm^{-1}; HRMS (ESIMS) caled for $C_{18}H_{30}O_5Na$ $[M + Na]^+$ 349.1985, found 349.1992.

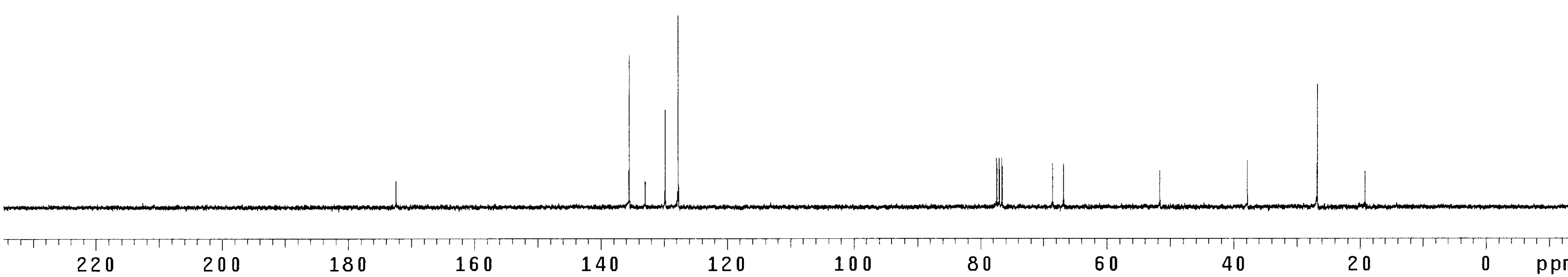
2. Spectra (^{1}H and ^{13}C NMR) of compounds

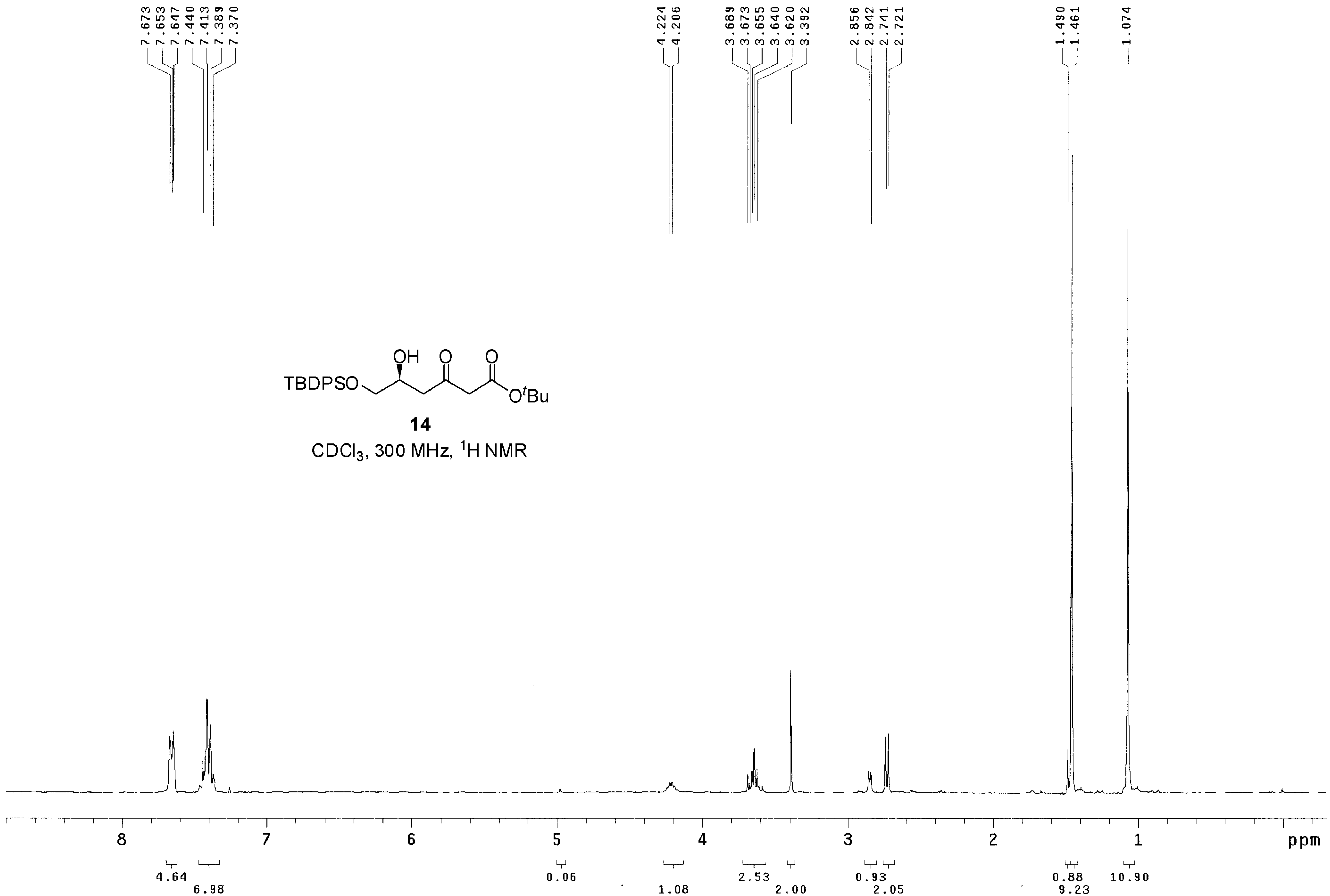


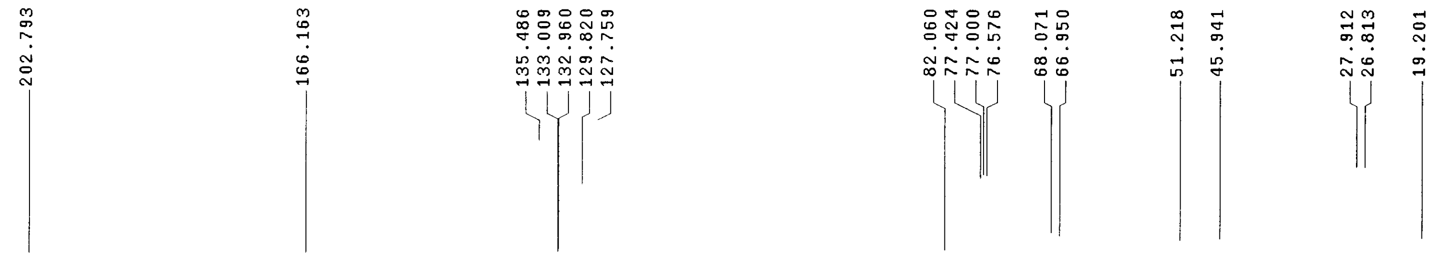


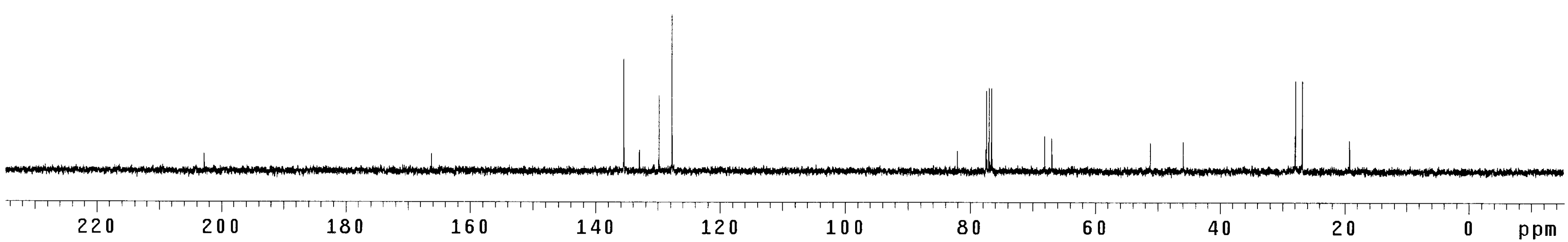
17

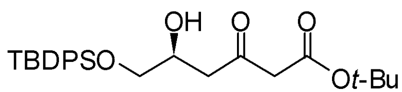
$CDCl_3$, 75 MHz, ^{13}C NMR




7.673
7.653
7.647
7.440
7.413
7.389
7.370
4.224
4.206
3.689
3.673
3.655
3.640
3.620
3.392
2.856
2.842
2.741
2.721
1.490
1.461
1.074
TBDPSO
OH
O
O
O^{t}Bu
14
CDCl$_3$, 300 MHz, ^{1}H NMR
8
7
6
5
4
3
2
1
ppm
4.64
6.98
0.06
1.08
2.53
2.00
0.93
2.05
0.88
9.23
10.90

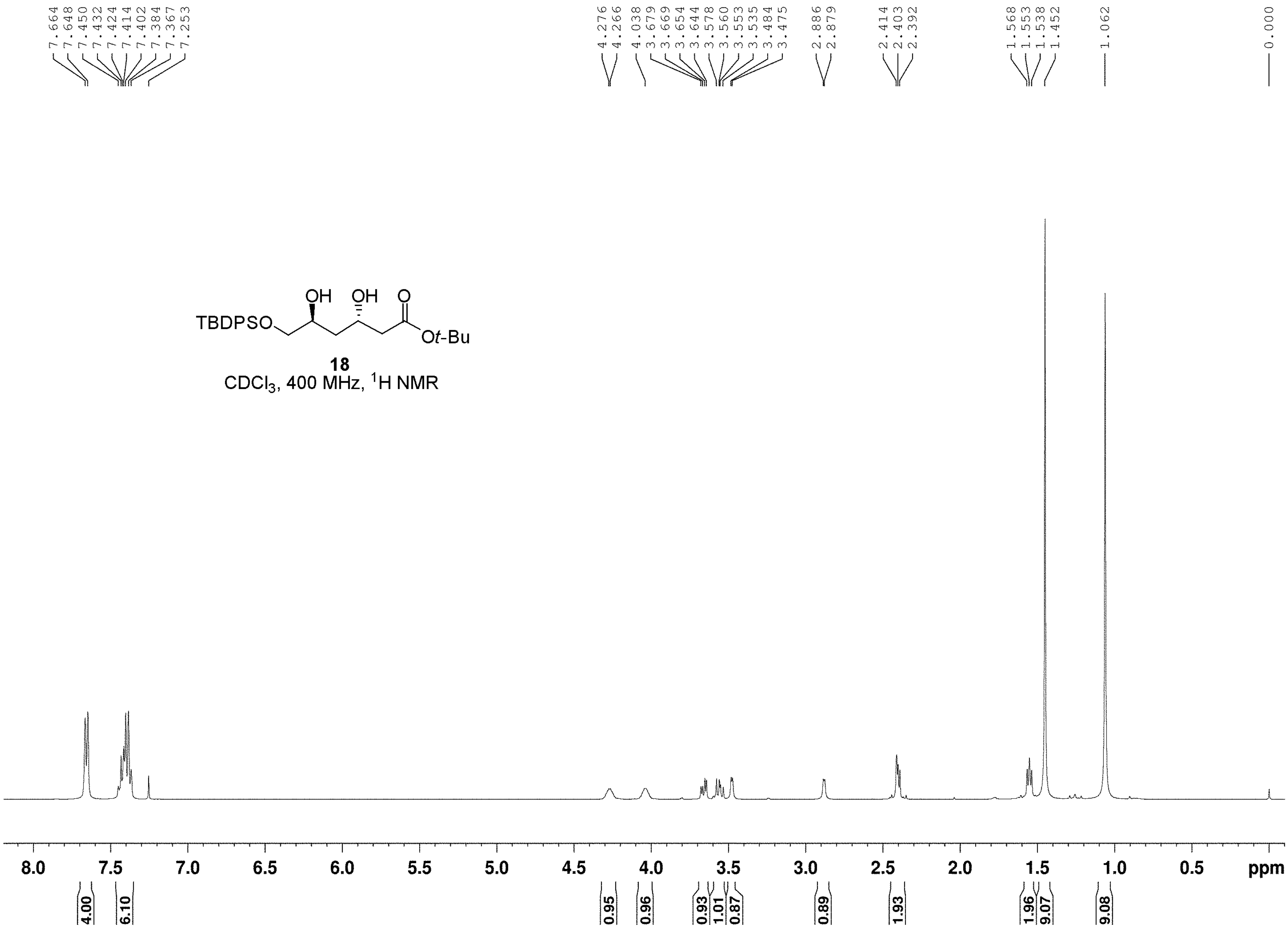


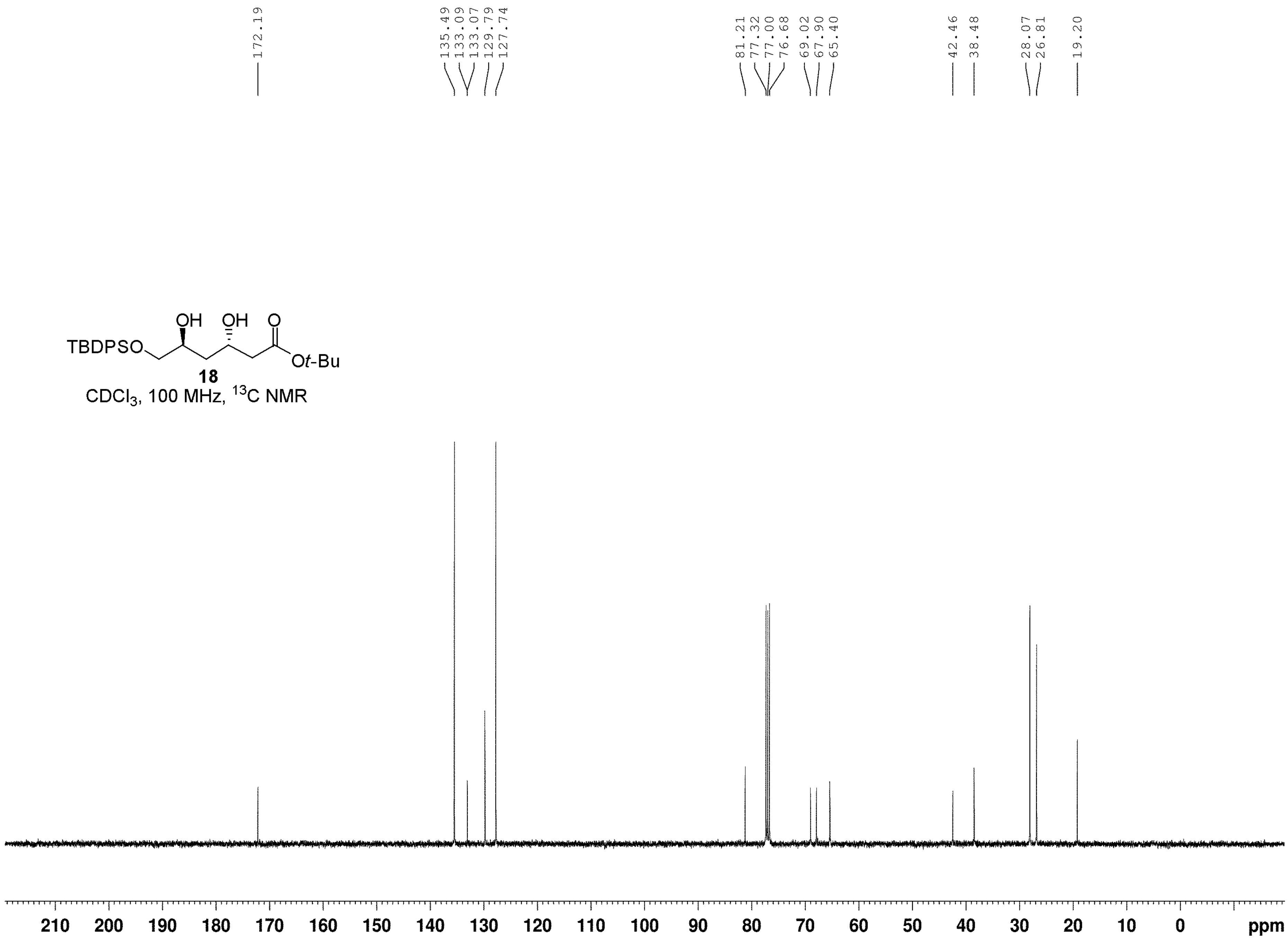


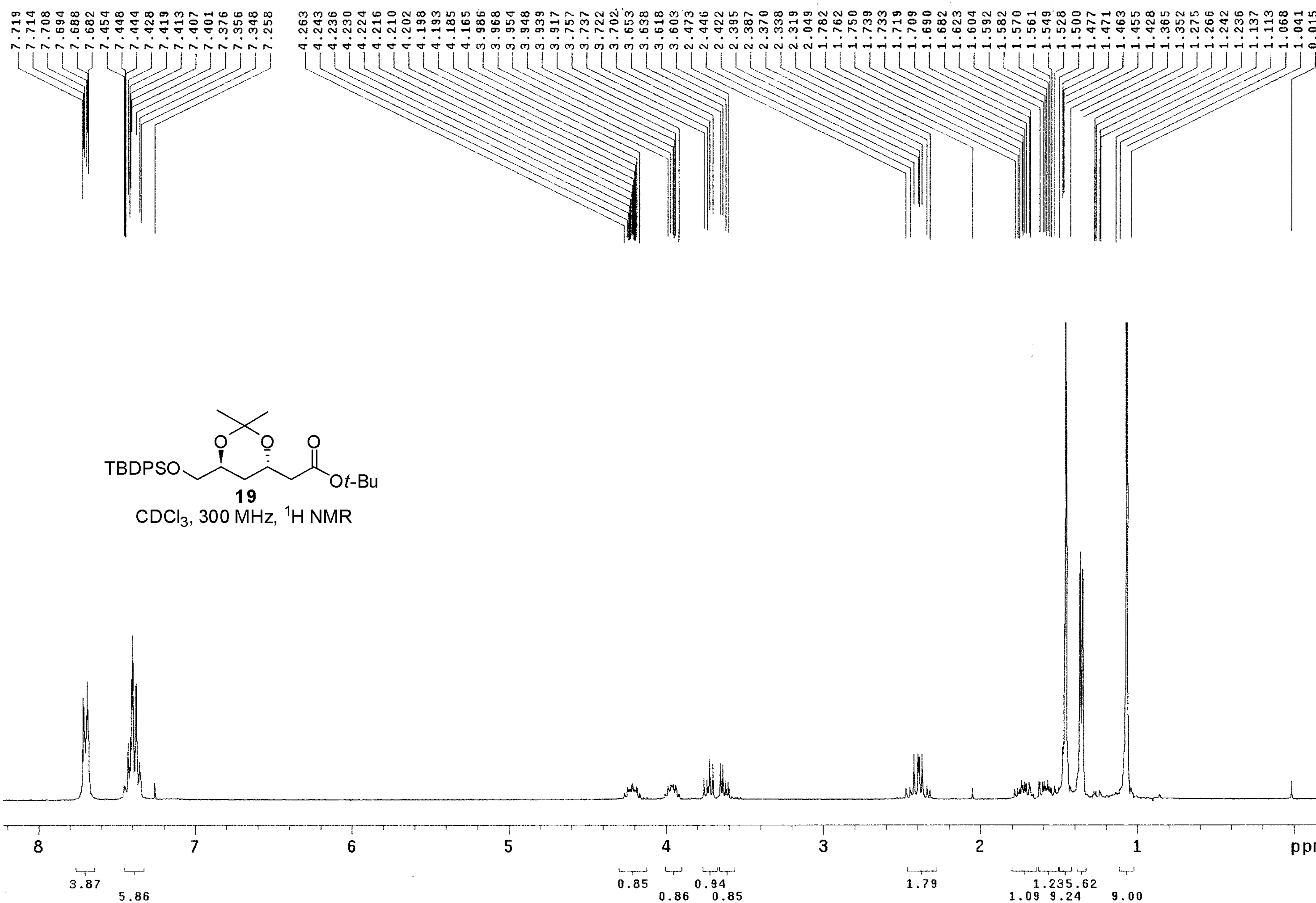


14

$CDCl_3$, 75 MHz, ^{13}C NMR

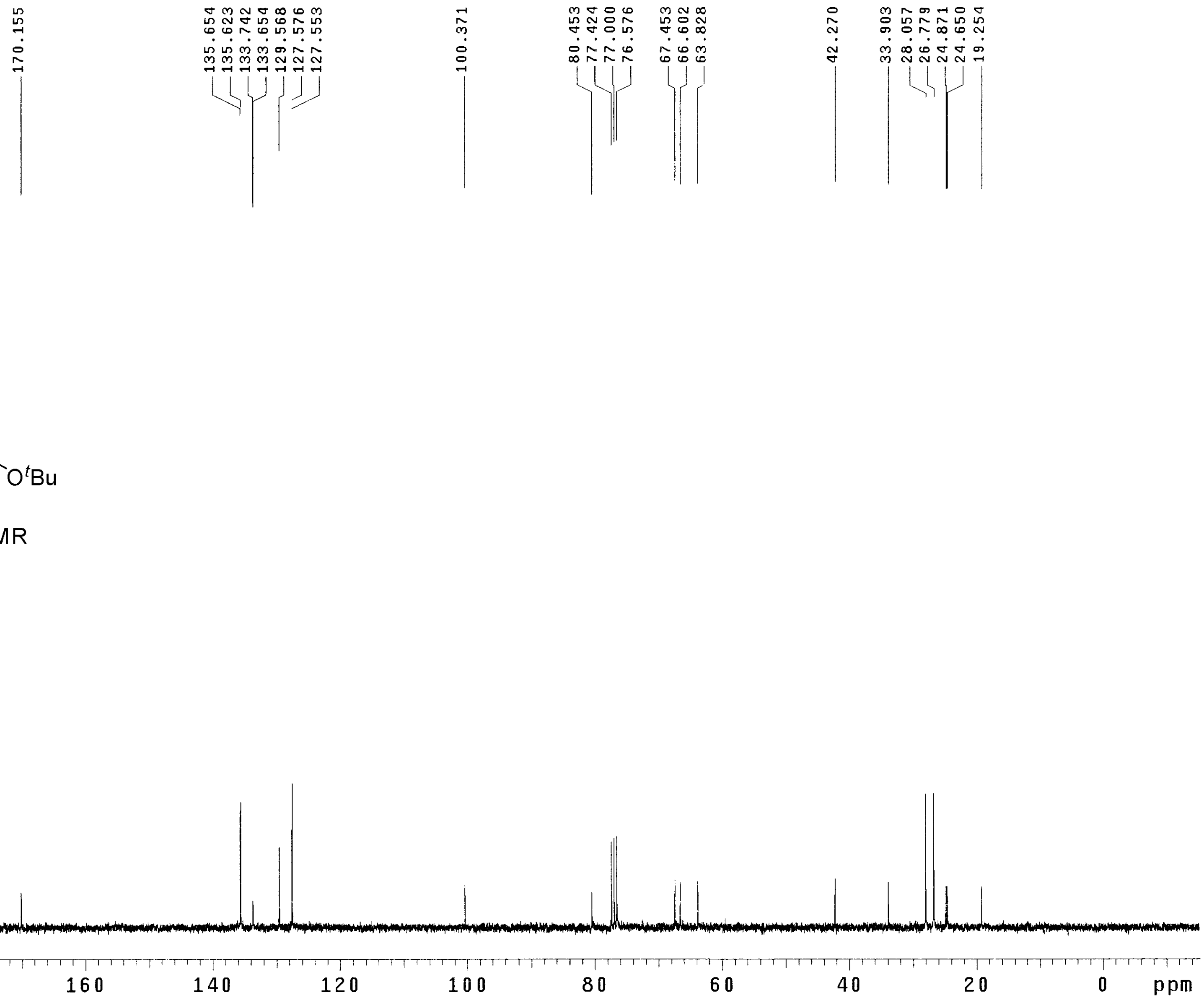

7.664 7.648 7.450 7.432 7.424 7.414 7.402 7.384 7.367 7.253
4.276 4.266 4.038 3.679 3.669 3.654 3.644 3.578 3.560 3.553 3.535 3.484 3.475
2.886 2.879
2.414 2.403 2.392
1.568 1.553 1.538 1.452
1.062
0.000
TBDPSO
OH
OH
O
Ot-Bu
18
CDCl3, 400 MHz, 1H NMR
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.00 6.10 0.95 0.96 0.93 1.01 0.87 0.89 1.93 1.96 9.07 9.08

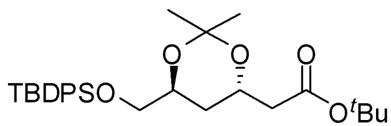

172.19
135.49
133.09
133.07
129.79
127.74
81.21
77.32
77.00
76.68
69.02
67.90
65.40
42.46
38.48
28.07
26.81
19.20
TBDPSO
OH
OH
O
Ot-Bu
18
CDCl3, 100 MHz, 13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



7.719 7.714 7.708 7.694 7.688 7.682 7.454 7.448 7.444 7.428 7.419 7.413 7.407 7.401 7.376 7.356 7.348 7.258
4.263 4.243 4.236 4.230 4.224 4.216 4.210 4.202 4.198 4.193 4.185 4.165 3.986 3.968 3.954 3.948 3.939 3.917 3.757 3.737 3.722 3.702 3.653 3.638 3.618 3.603 2.473 2.446 2.422 2.395 2.387 2.370 2.338 2.319 2.049 1.782 1.762 1.750 1.739 1.733 1.719 1.709 1.690 1.682 1.623 1.604 1.592 1.582 1.570 1.561 1.549 1.528 1.500 1.477 1.471 1.463 1.455 1.428 1.365 1.352 1.275 1.266 1.242 1.236 1.137 1.113 1.068 1.041 0.015
TBDPSO
O
O
O
Ot-Bu
19
CDCl3, 300 MHz, 1H NMR
8
7
6
5
4
3
2
1
ppm
3.87
5.86
0.85
0.86
0.94
0.85
1.79
1.09
1.23
9.24
5.62
9.00

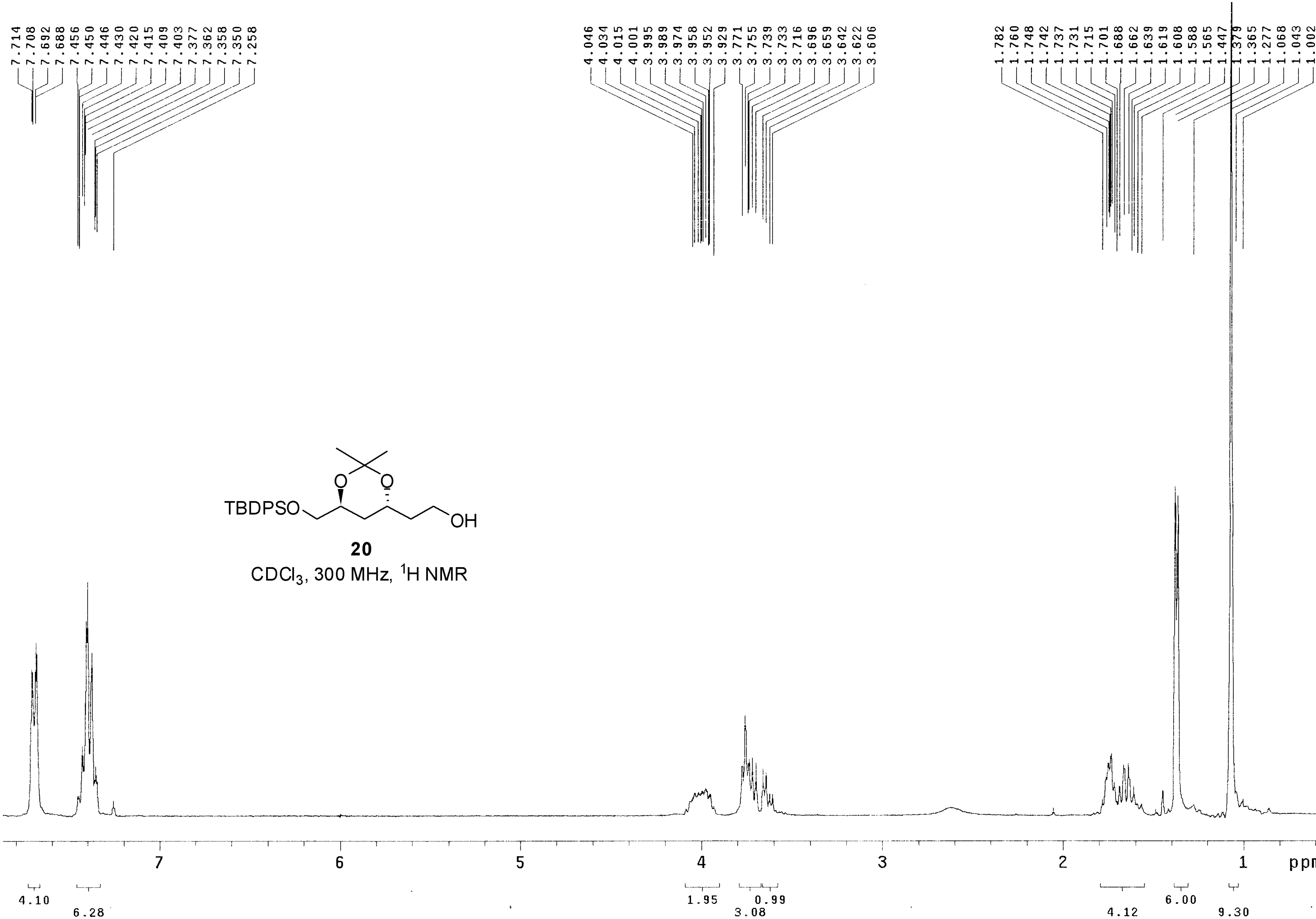
••••••





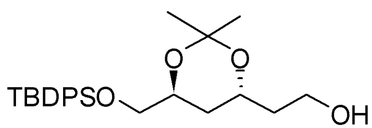
19

$CDCl_3$, 75 MHz, ^{13}C NMR



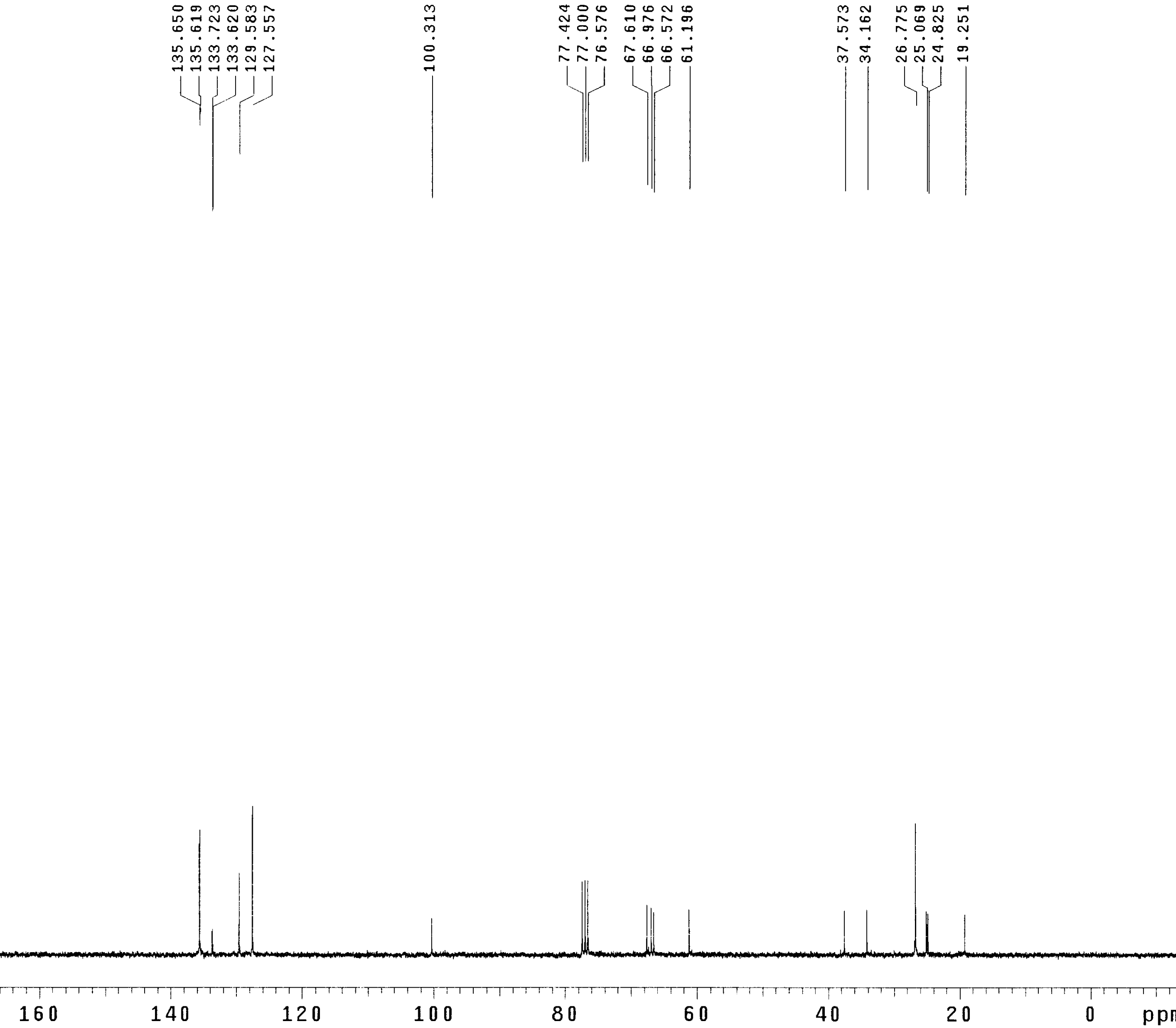
20

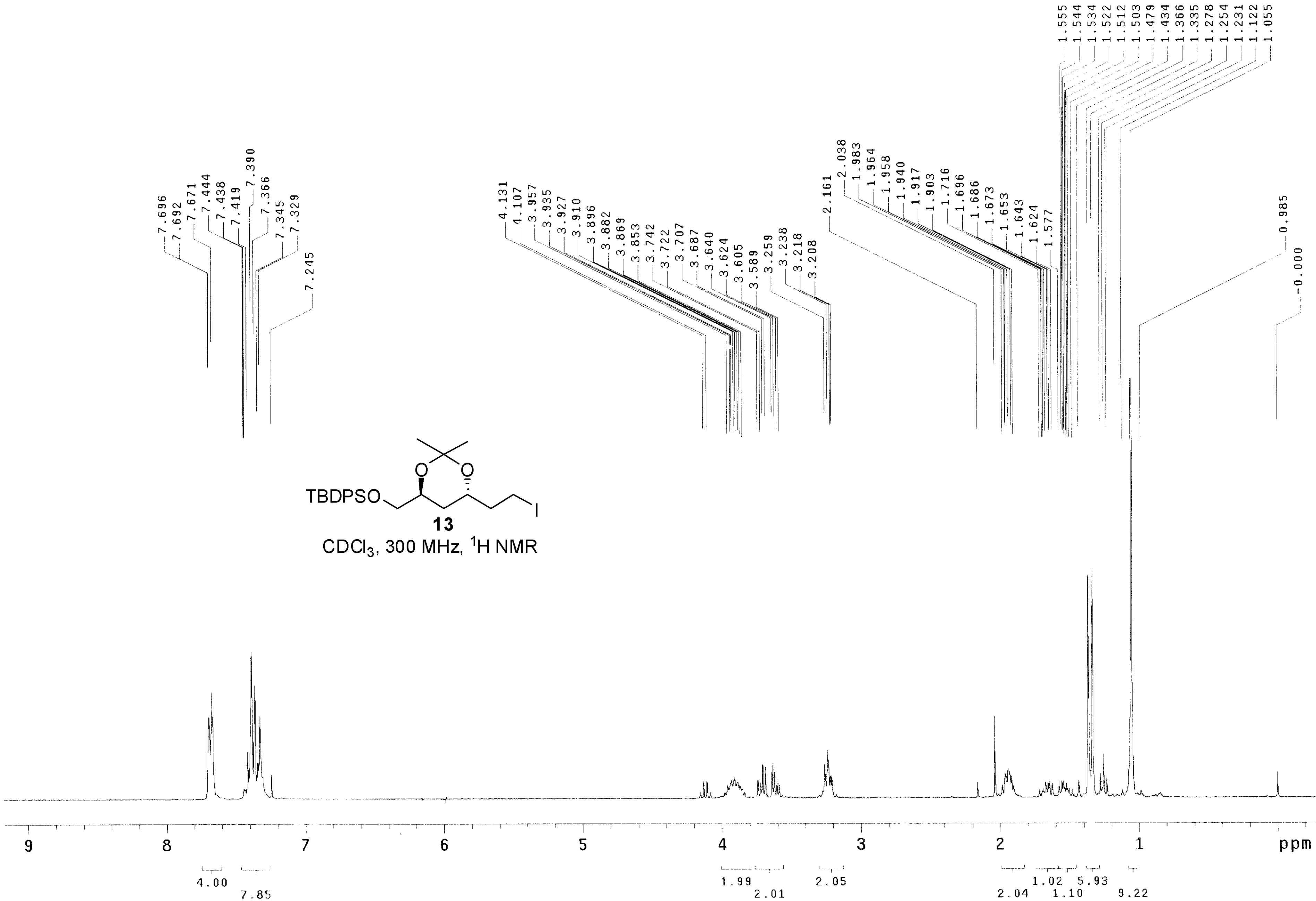
$CDCl_3$, 300 MHz, ^1H NMR



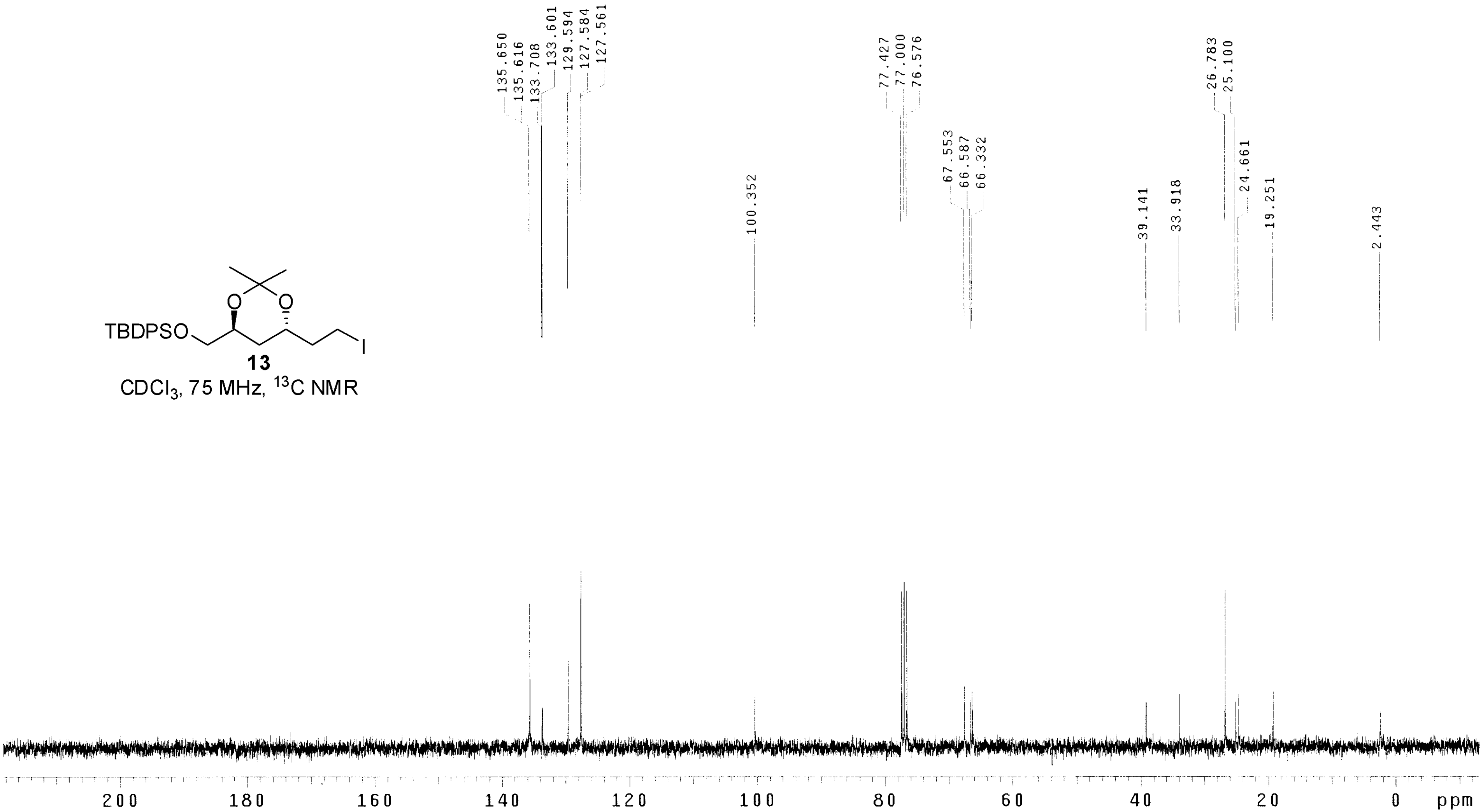
20

$CDCl_3$, 75 MHz, ^{13}C NMR



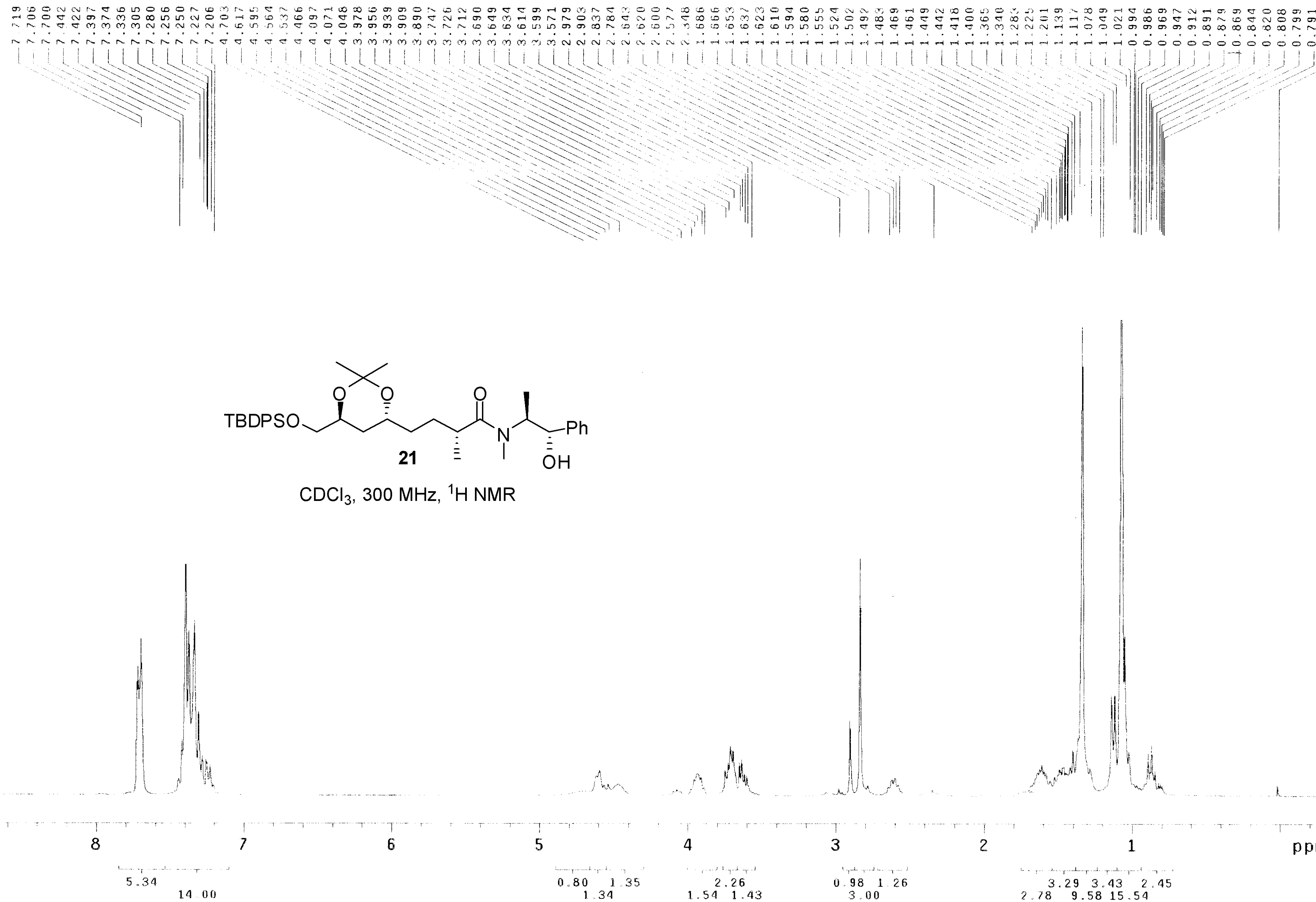


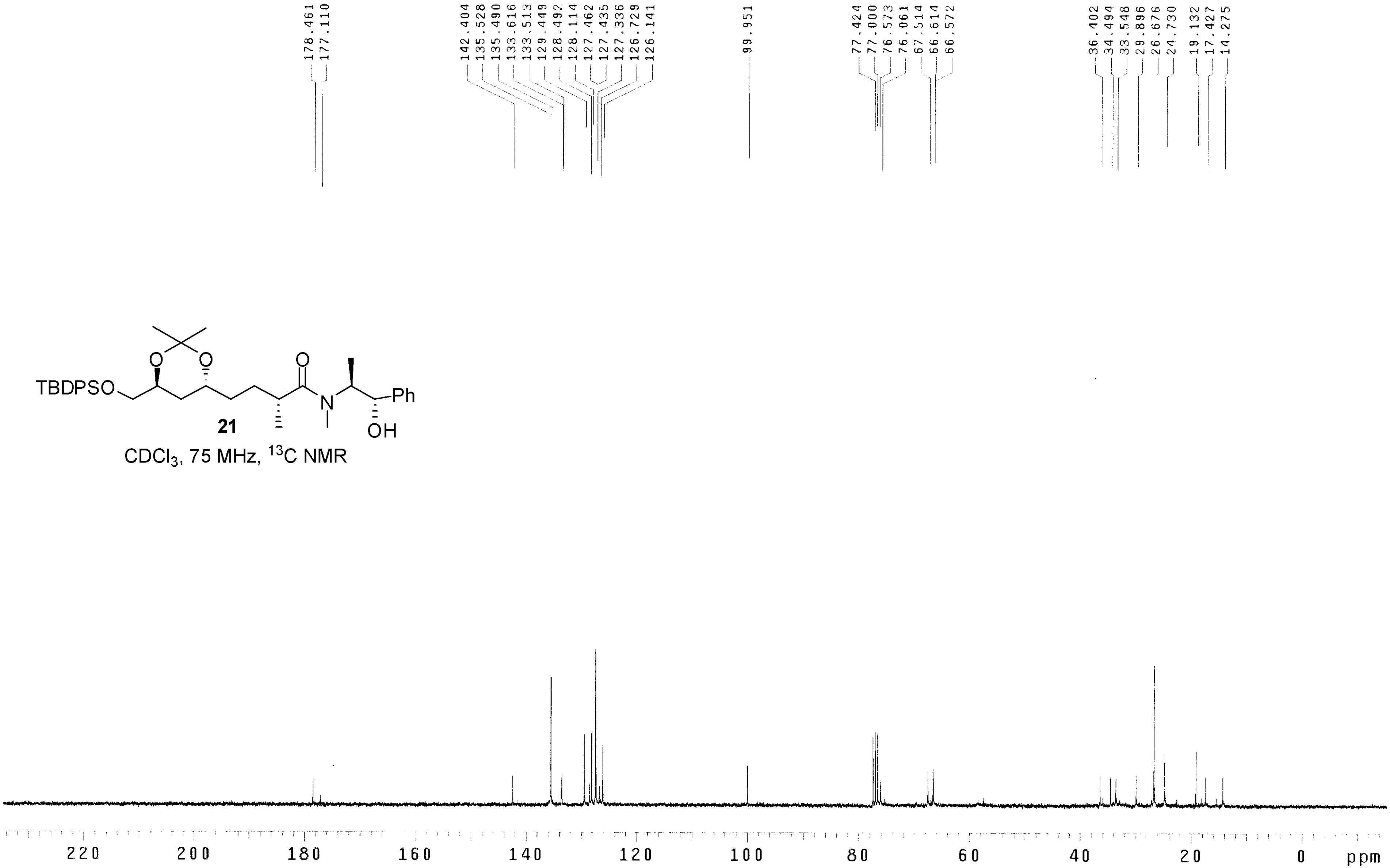
TBDPSO
O
O
I
13
CDCl3, 300 MHz, 1H NMR
ppm
4.00
7.85
1.99
2.01
2.05
2.04
1.02
1.10
5.93
9.22



13

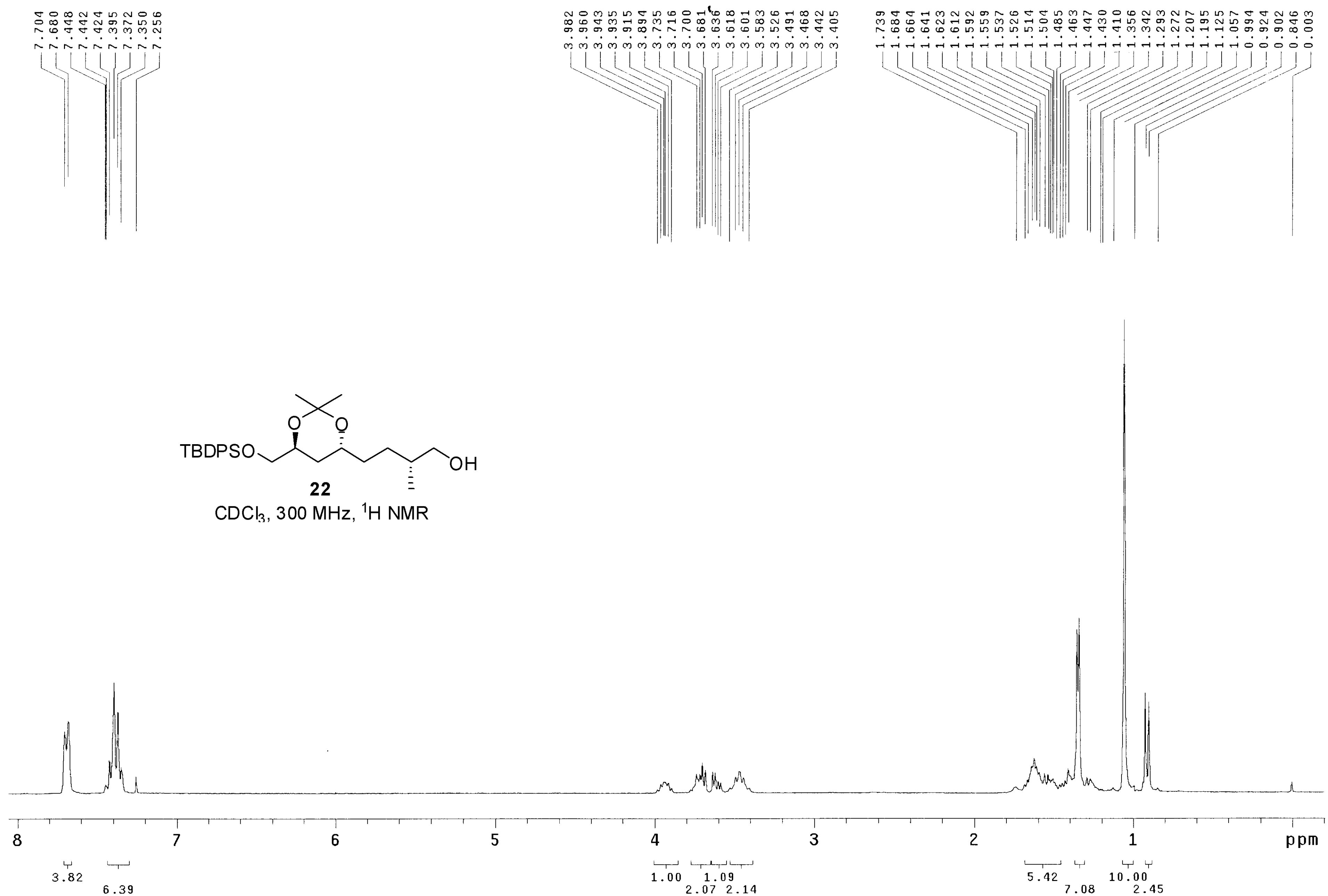
$CDCl_3$, 75 MHz, ^{13}C NMR


7.719 7.706 7.700 7.442 7.422 7.397 7.374 7.336 7.305 7.280 7.256 7.250 7.227 7.206 4.703 4.617 4.595 4.564 4.537 4.466 4.097 4.071 4.048 3.978 3.956 3.939 3.909 3.890 3.747 3.726 3.712 3.690 3.649 3.634 3.614 3.599 3.571 2.979 2.903 2.837 2.784 2.643 2.620 2.600 2.577 2.348 1.686 1.666 1.653 1.637 1.623 1.610 1.594 1.580 1.555 1.524 1.502 1.492 1.483 1.469 1.461 1.449 1.442 1.418 1.400 1.365 1.340 1.283 1.225 1.201 1.139 1.117 1.078 1.049 1.021 0.994 0.986 0.969 0.947 0.912 0.891 0.879 0.869 0.844 0.820 0.808 0.799 0.791 0.017
TBDPSO
O
O
O
N
Ph
OH
21
CDCl3, 300 MHz, 1H NMR
8
7
6
5
4
3
2
1
ppm
5.34
14.00
0.80 1.35
1.34
2.26
1.54 1.43
0.98 1.26
3.00
3.29 3.43 2.45
2.78 9.58 15.54



21

$CDCl_3$, 75 MHz, ^{13}C NMR


7.704
7.680
7.448
7.442
7.424
7.395
7.372
7.350
7.256
3.982
3.960
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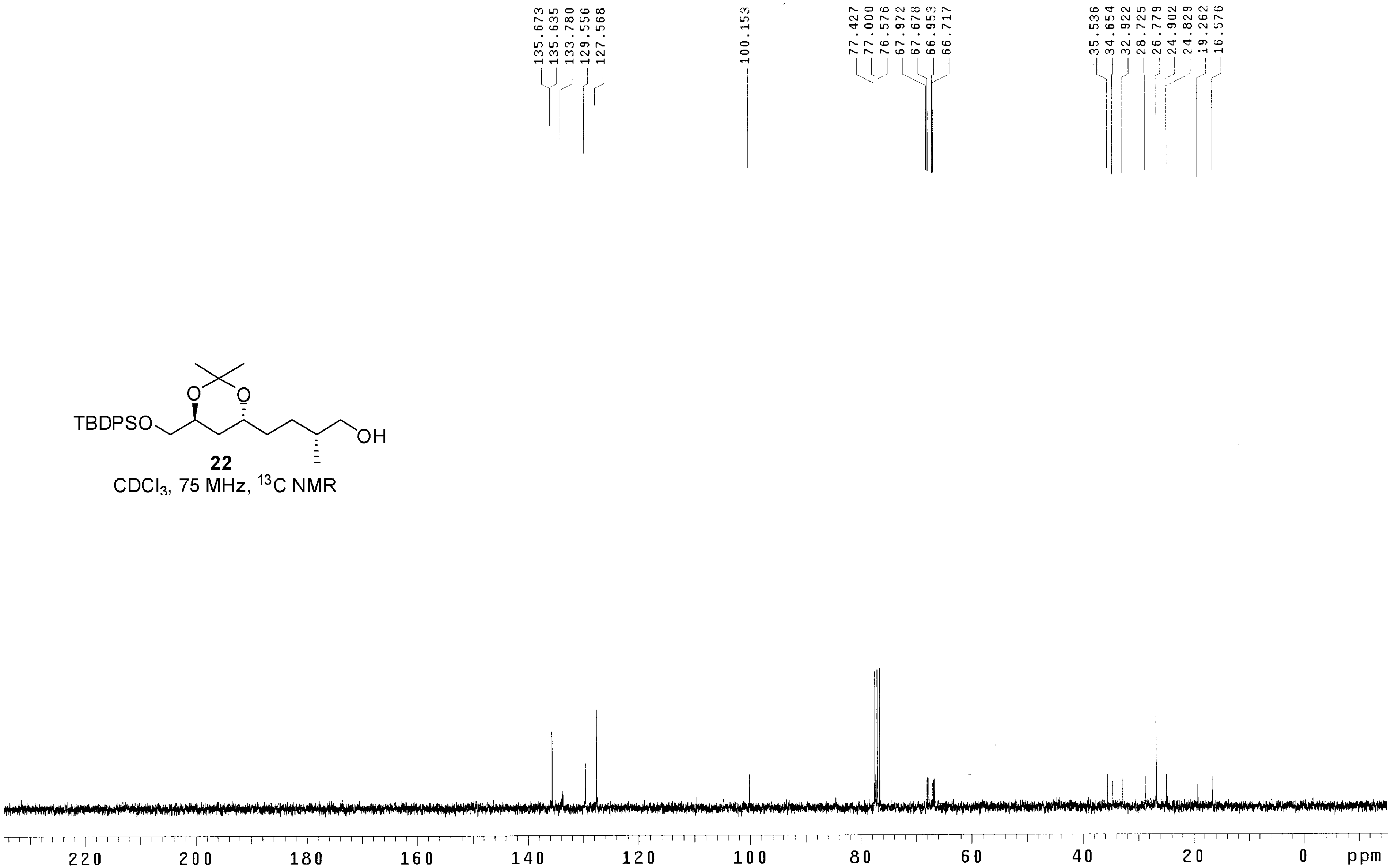
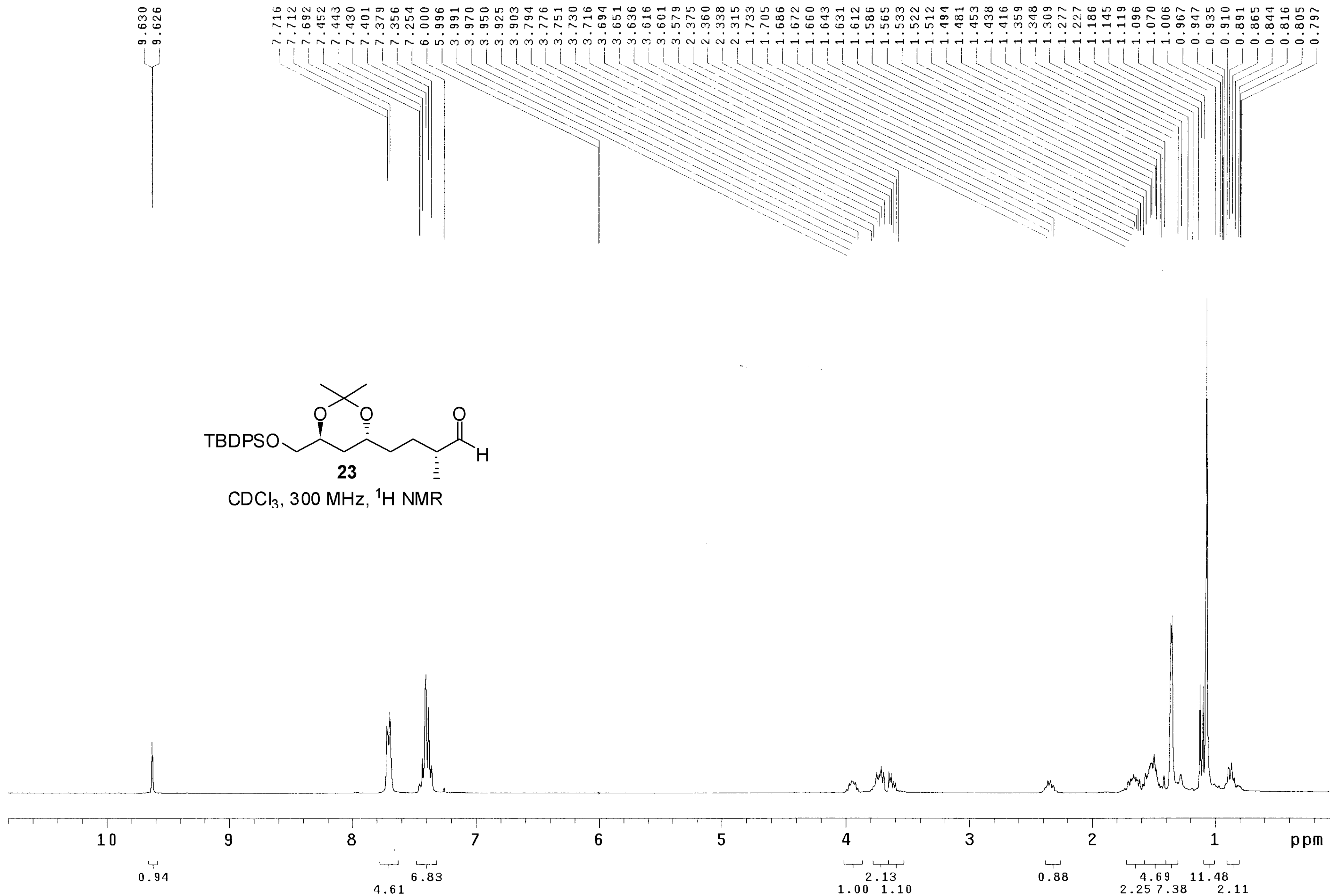
3.915
3.894
3.735
3.716
3.700
3.681
3.636
3.618
3.601
3.583
3.526
3.491
3.468
3.442
3.405
1.739
1.684
1.664
1.641
1.623
1.612
1.592
1.559
1.537
1.526
1.514
1.504
1.485
1.463
1.447
1.430
1.410
1.356
1.342
1.293
1.272
1.207
1.195
1.125
1.057
0.994
0.924
0.902
0.846
0.003
TBDPSO
O
O
OH
22
CDCl3, 300 MHz, 1H NMR
8
7
6
5
4
3
2
1
ppm
3.82
6.39
1.00
2.07
1.09
2.14
5.42
7.08
10.00
2.45



22

$CDCl_3$, 75 MHz, ^{13}C NMR


9.630
9.626
7.716 7.712 7.692 7.452 7.443 7.430 7.401 7.379 7.356 7.254 6.000 5.996 3.991 3.970 3.950 3.925 3.903 3.794 3.776 3.751 3.730 3.716 3.694 3.651 3.636 3.616 3.601 3.579 2.375 2.360 2.338 2.315 1.733 1.705 1.686 1.672 1.660 1.643 1.631 1.612 1.586 1.565 1.533 1.522 1.512 1.494 1.481 1.453 1.438 1.416 1.359 1.348 1.309 1.277 1.227 1.186 1.145 1.119 1.096 1.070 1.006 0.967 0.947 0.935 0.910 0.891 0.865 0.844 0.816 0.805 0.797
TBDPSO
O
O
O
H
23
CDCl3, 300 MHz, 1H NMR
10
9
8
7
6
5
4
3
2
1
ppm
0.94
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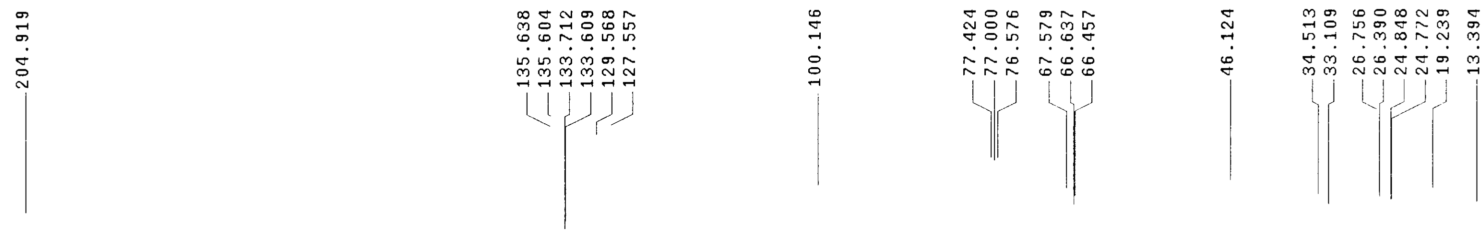
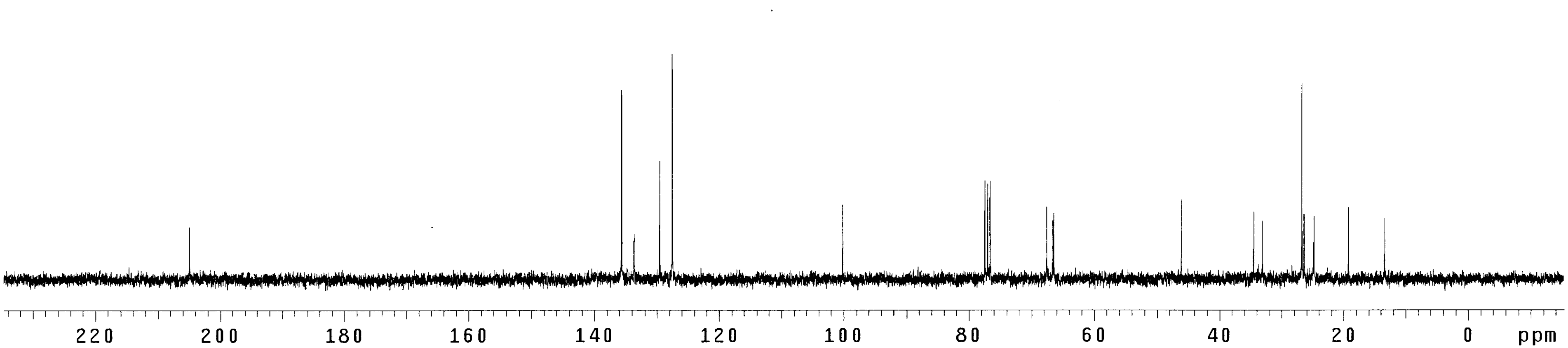
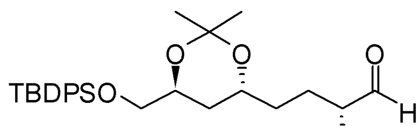
6.83
1.00
2.13
1.10
0.88
2.25
4.69
7.38
11.48
2.11

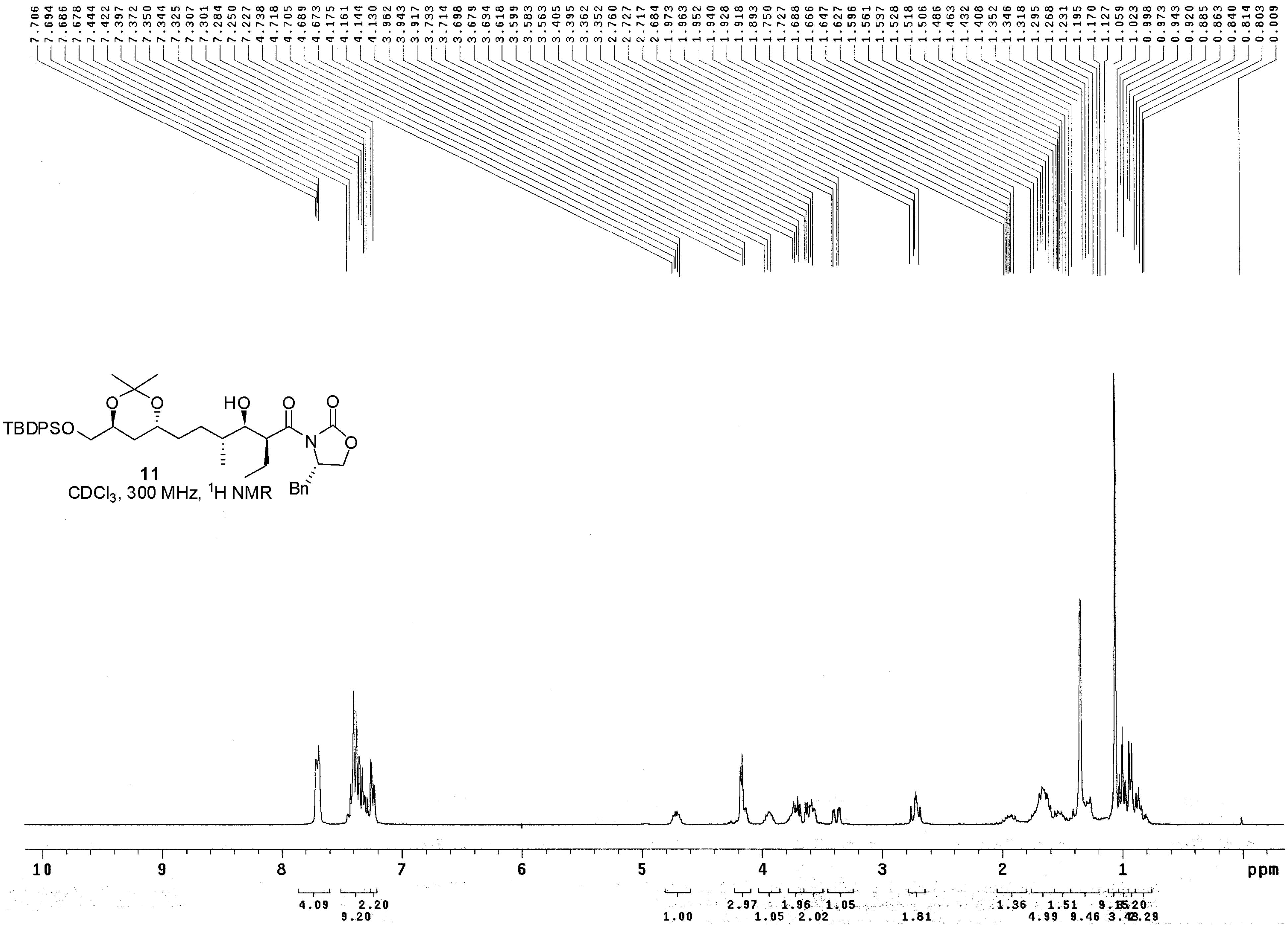


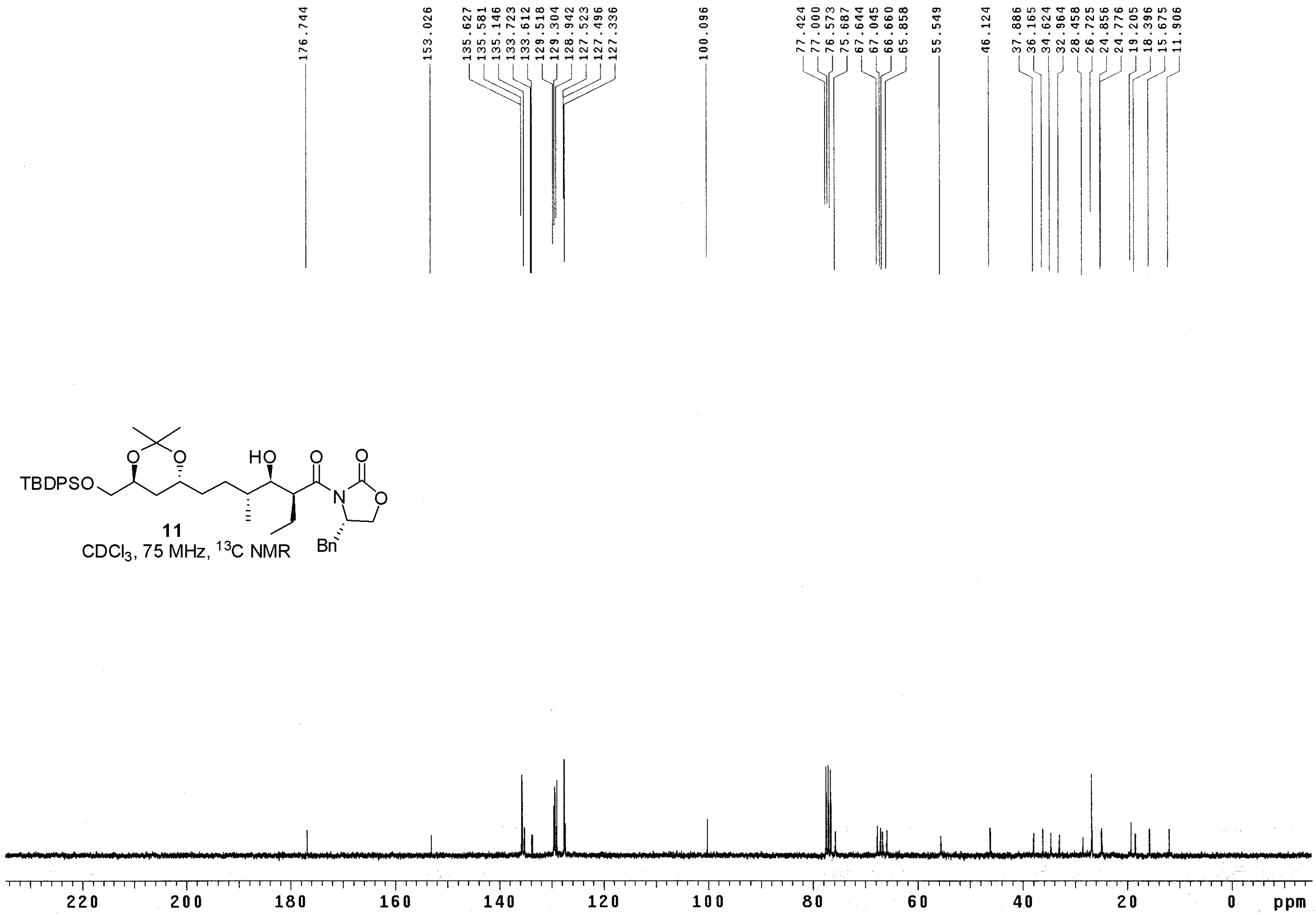


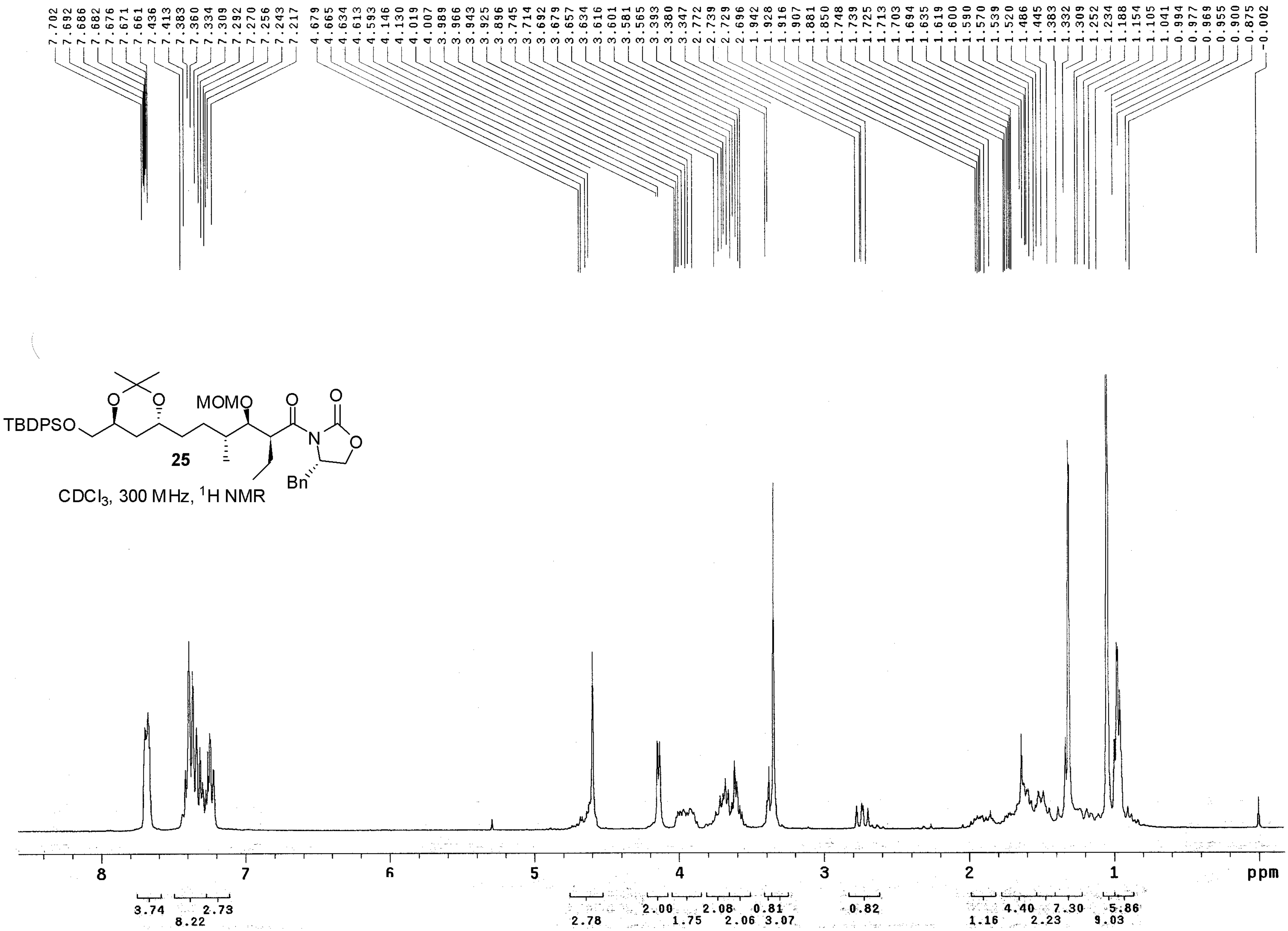


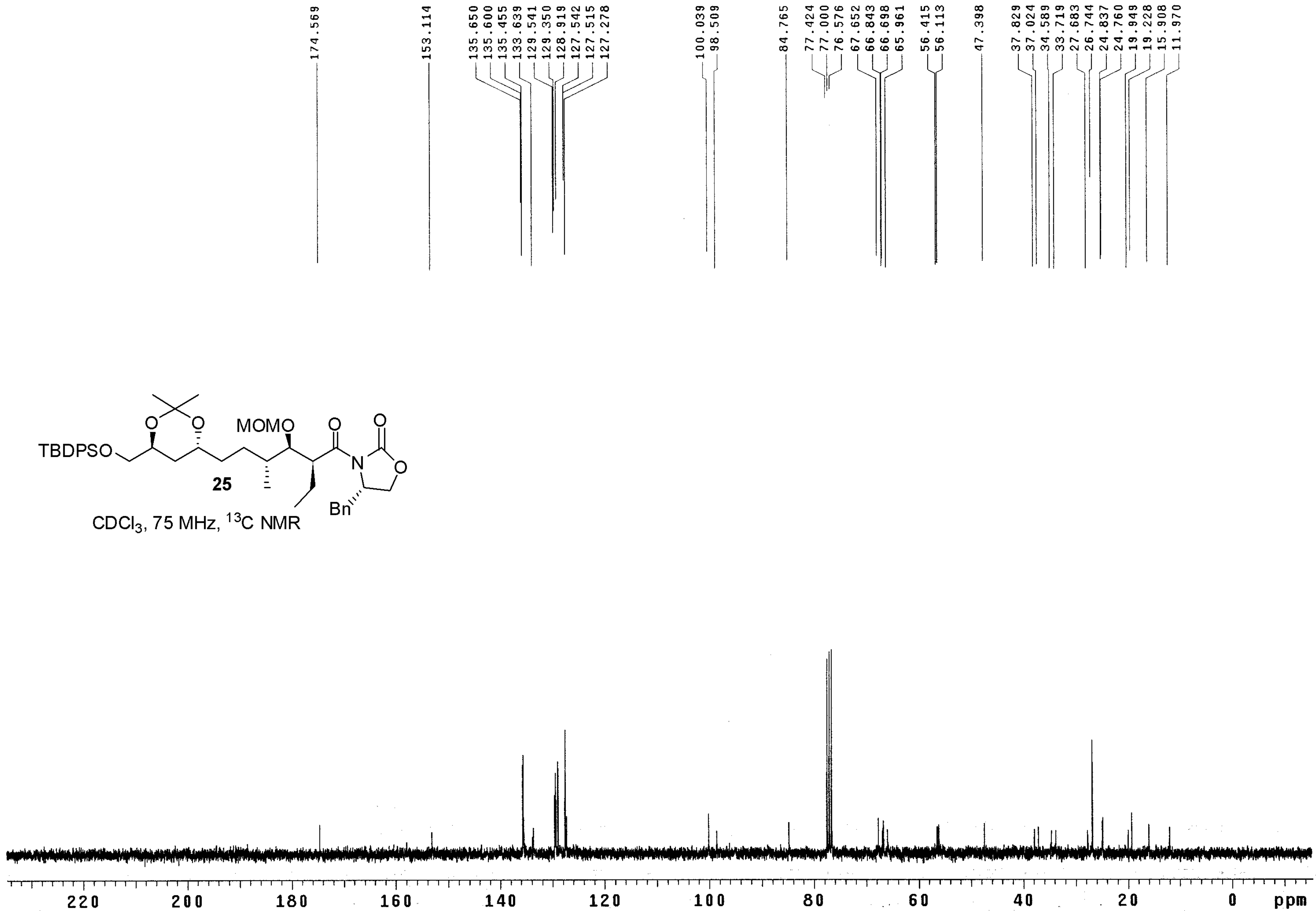
23

$CDCl_3$, 75 MHz, ^{13}C NMR

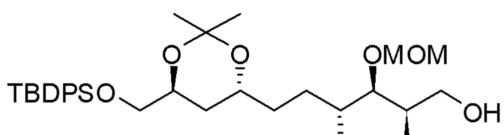

7.706 7.694 7.686 7.678 7.444 7.422 7.397 7.372 7.350 7.344 7.325 7.307 7.301 7.284 7.250 7.227 4.738 4.718 4.705 4.689 4.673 4.175 4.161 4.144 4.130 3.962 3.943 3.917 3.733 3.714 3.698 3.679 3.634 3.618 3.599 3.583 3.563 3.405 3.395 3.362 3.352 2.760 2.727 2.717 2.684 1.973 1.963 1.952 1.940 1.928 1.918 1.893 1.750 1.727 1.688 1.666 1.647 1.627 1.596 1.561 1.537 1.528 1.518 1.506 1.486 1.463 1.432 1.408 1.352 1.346 1.318 1.295 1.268 1.231 1.195 1.170 1.127 1.059 1.023 0.998 0.973 0.943 0.920 0.885 0.863 0.840 0.814 0.803 0.009
TBDPSO
O
O
HO
O
O
N
O
Bn
11
CDCl3, 300 MHz, 1H NMR
10
9
8
7
6
5
4
3
2
1
ppm
4.09
2.20
9.20
1.00
2.97
1.05
1.96
2.02
1.05
1.81
1.36
4.99
1.51
9.46
9.15
5.20
3.42
3.29


176.744
153.026
135.627
135.581
135.146
133.723
133.612
129.518
129.304
128.942
127.523
127.496
127.336
100.096
77.424
77.000
76.573
75.687
67.644
67.045
66.660
65.858
55.549
46.124
37.886
36.165
34.624
32.964
28.458
26.725
24.856
24.776
19.205
18.396
15.675
11.906
TBDPSO
HO
O
N
Bn
11
CDCl3, 75 MHz, 13C NMR
220
200
180
160
140
120
100
80
60
40
20
0
ppm


TBDPSO
MOMO
25
Bn
CDCl3, 300 MHz, 1H NMR
ppm

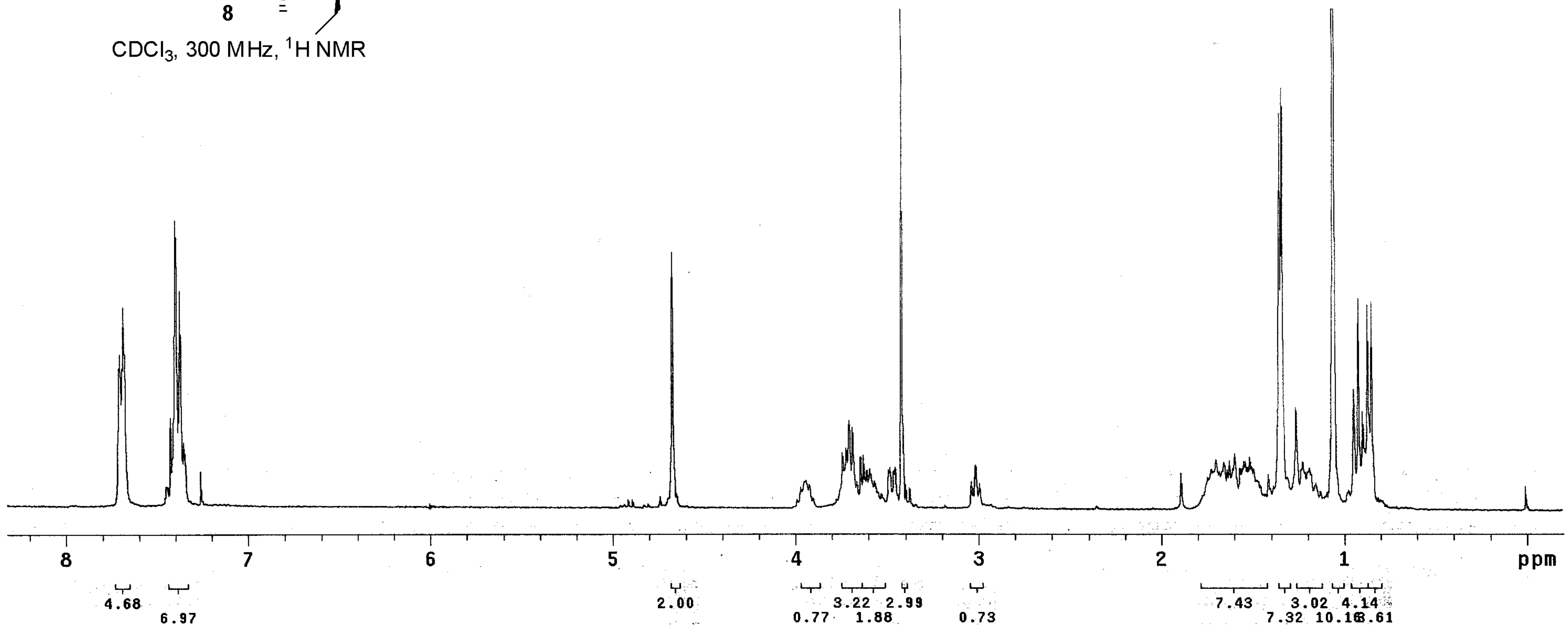


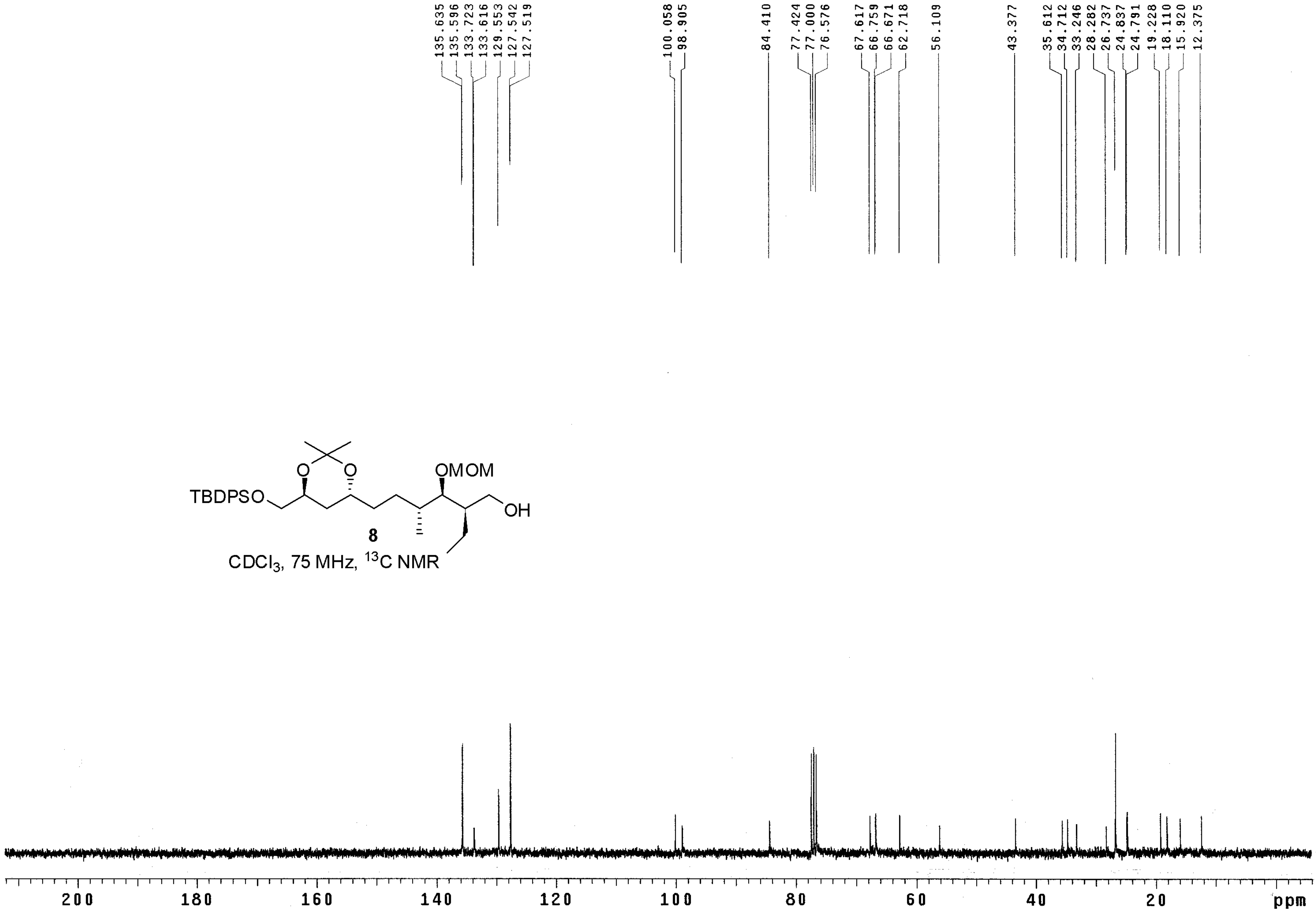
174.569
153.114
135.650
135.600
135.455
133.639
129.541
129.350
128.919
127.542
127.515
127.278
100.039
98.509
84.765
77.424
77.000
76.576
67.652
66.843
66.698
65.961
56.415
56.113
47.398
37.829
37.024
34.589
33.719
27.683
26.744
24.837
24.760
19.949
19.228
15.908
11.970
TBDPSO
MOMO
O
N
Bn
25
CDCl3, 75 MHz, 13C NMR
220
200
180
160
140
120
100
80
60
40
20
0
ppm

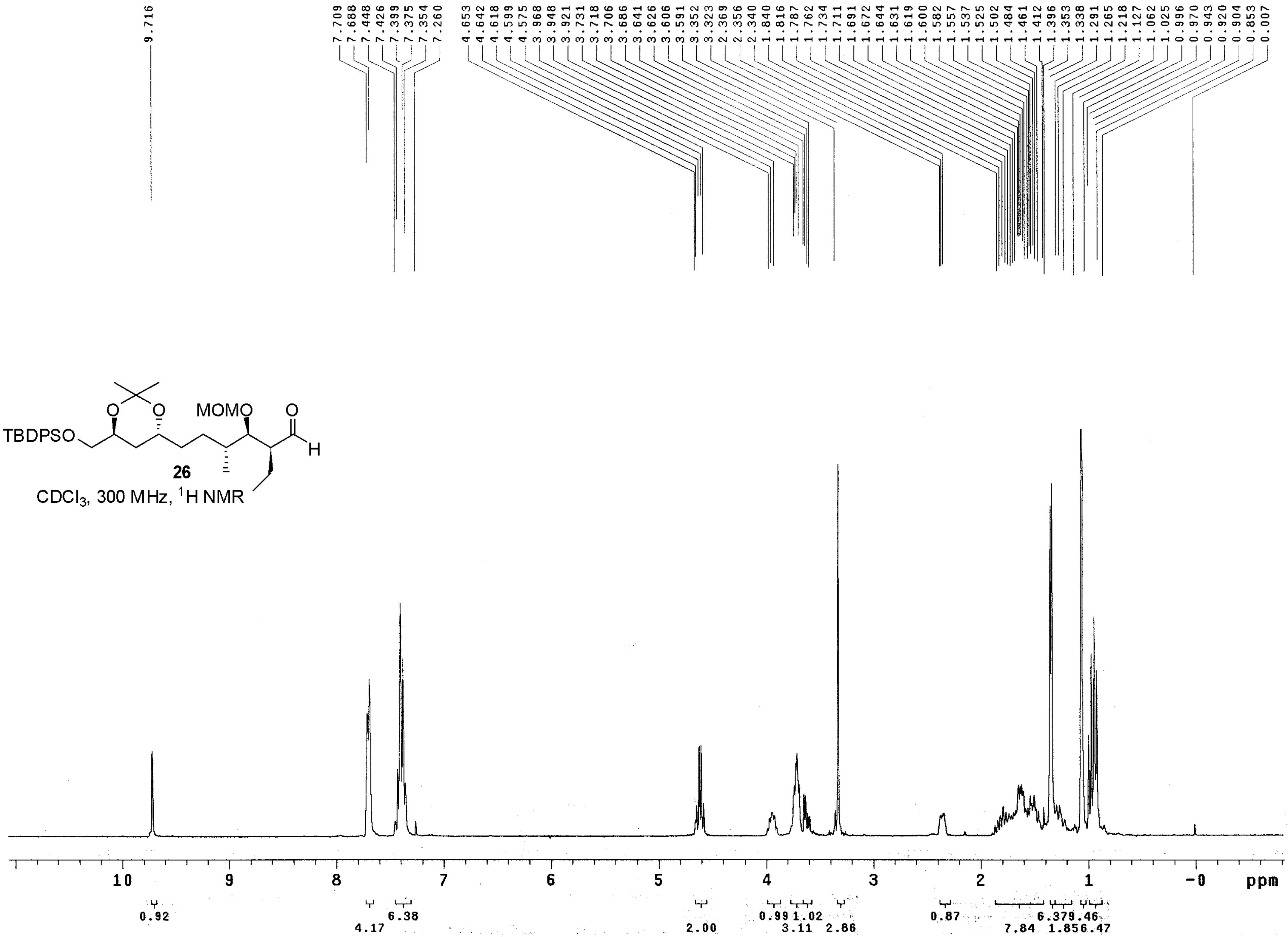


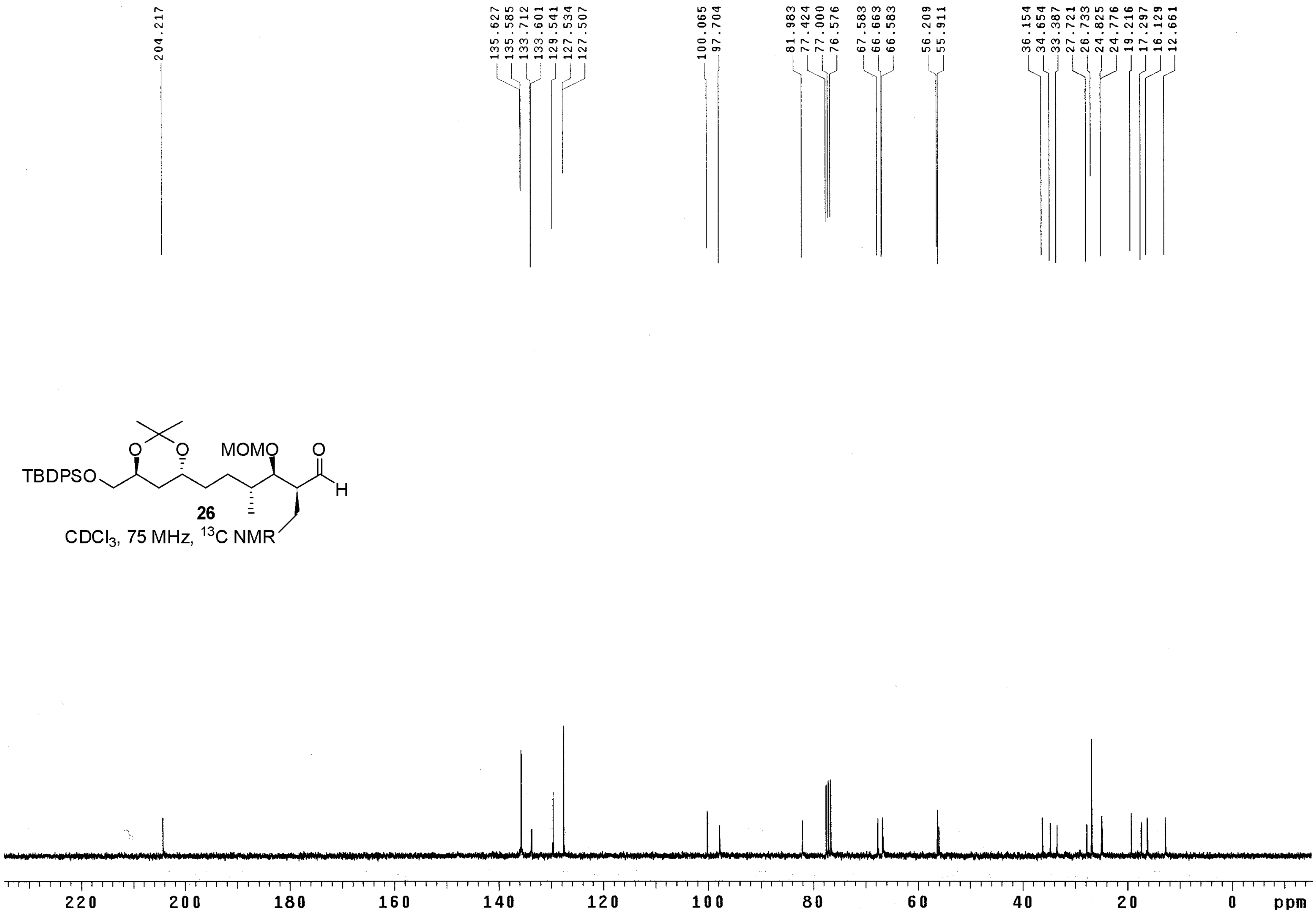
8

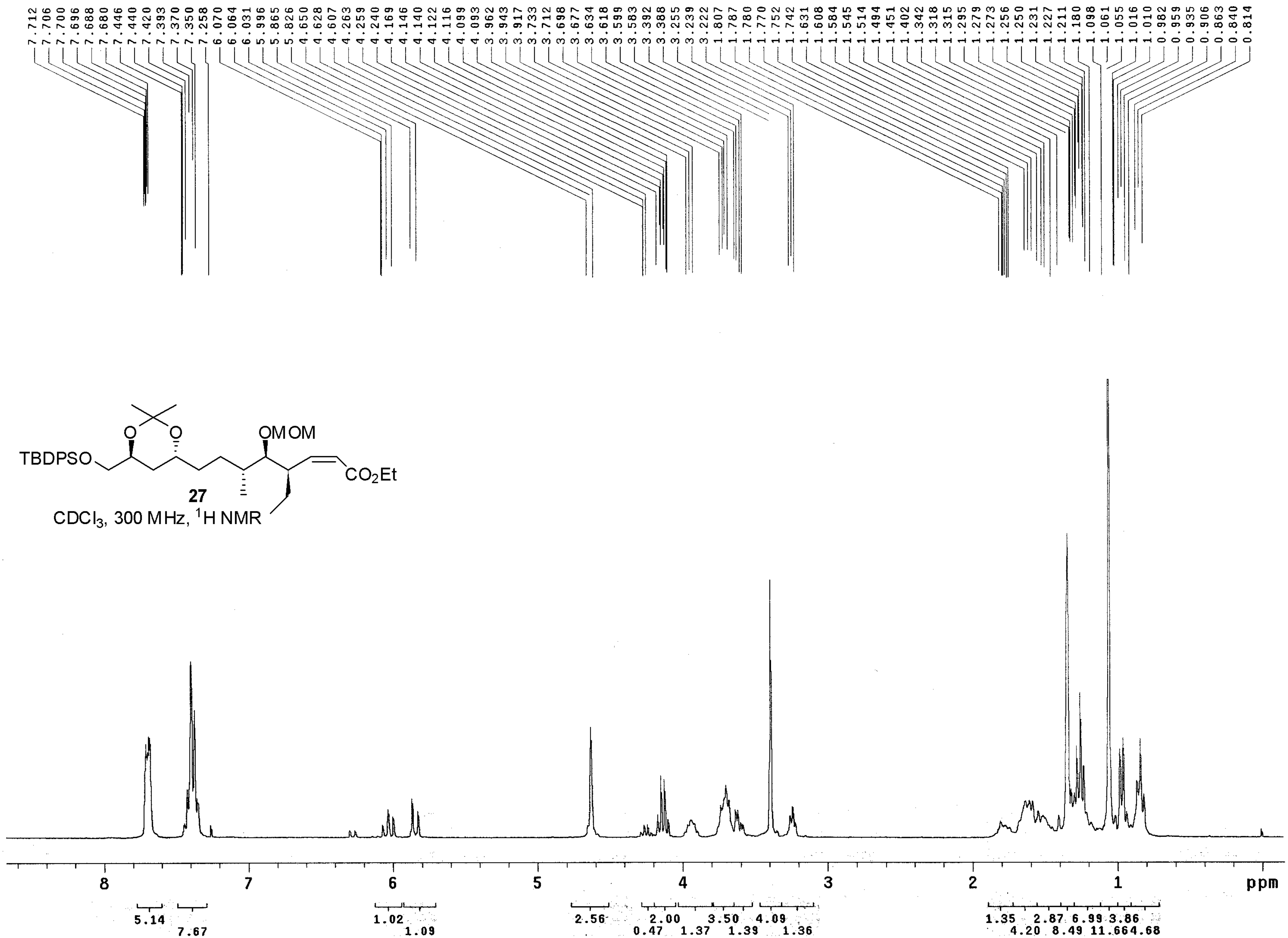
CDCl$_3$, 300 MHz, ^{1}H NMR

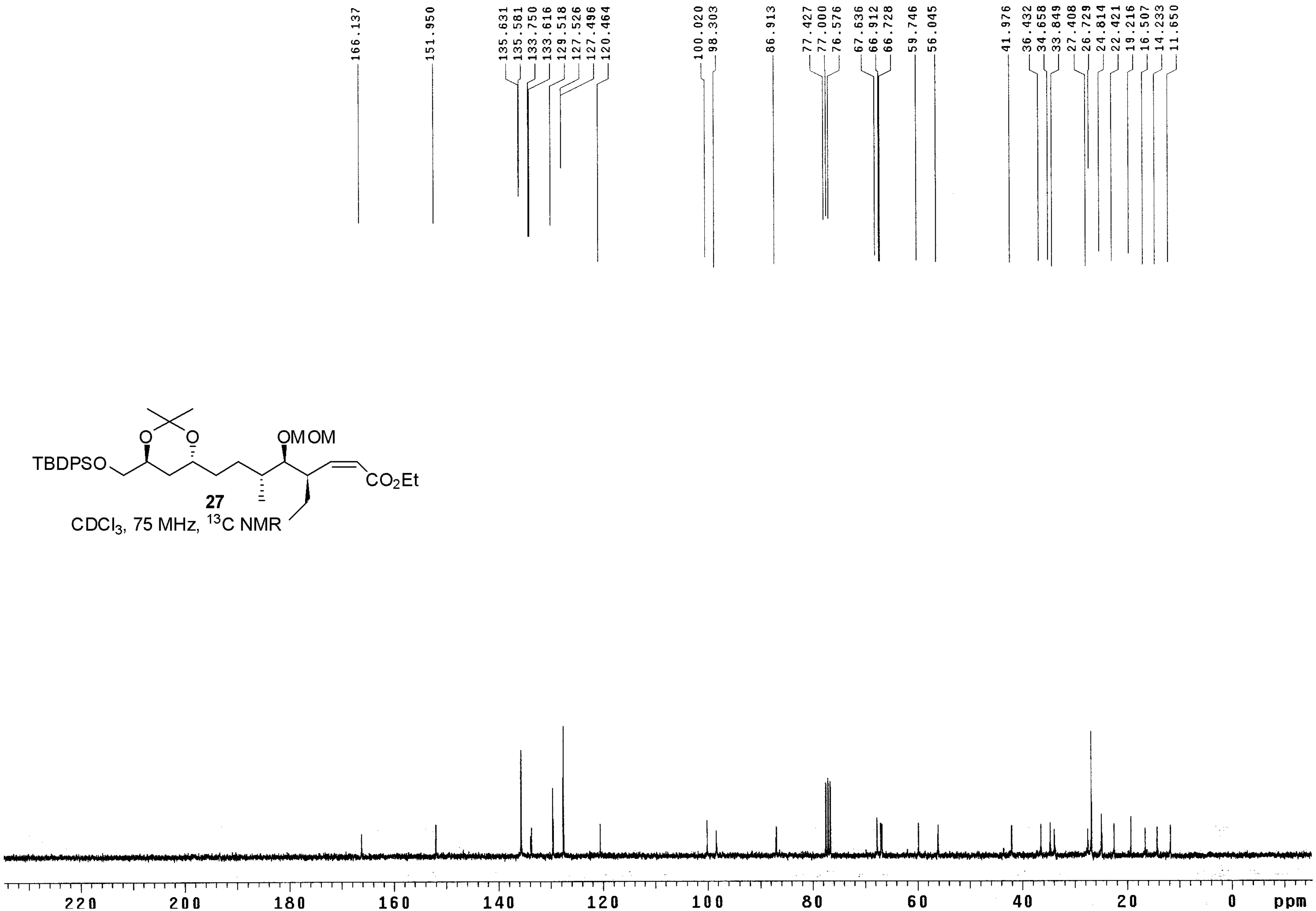


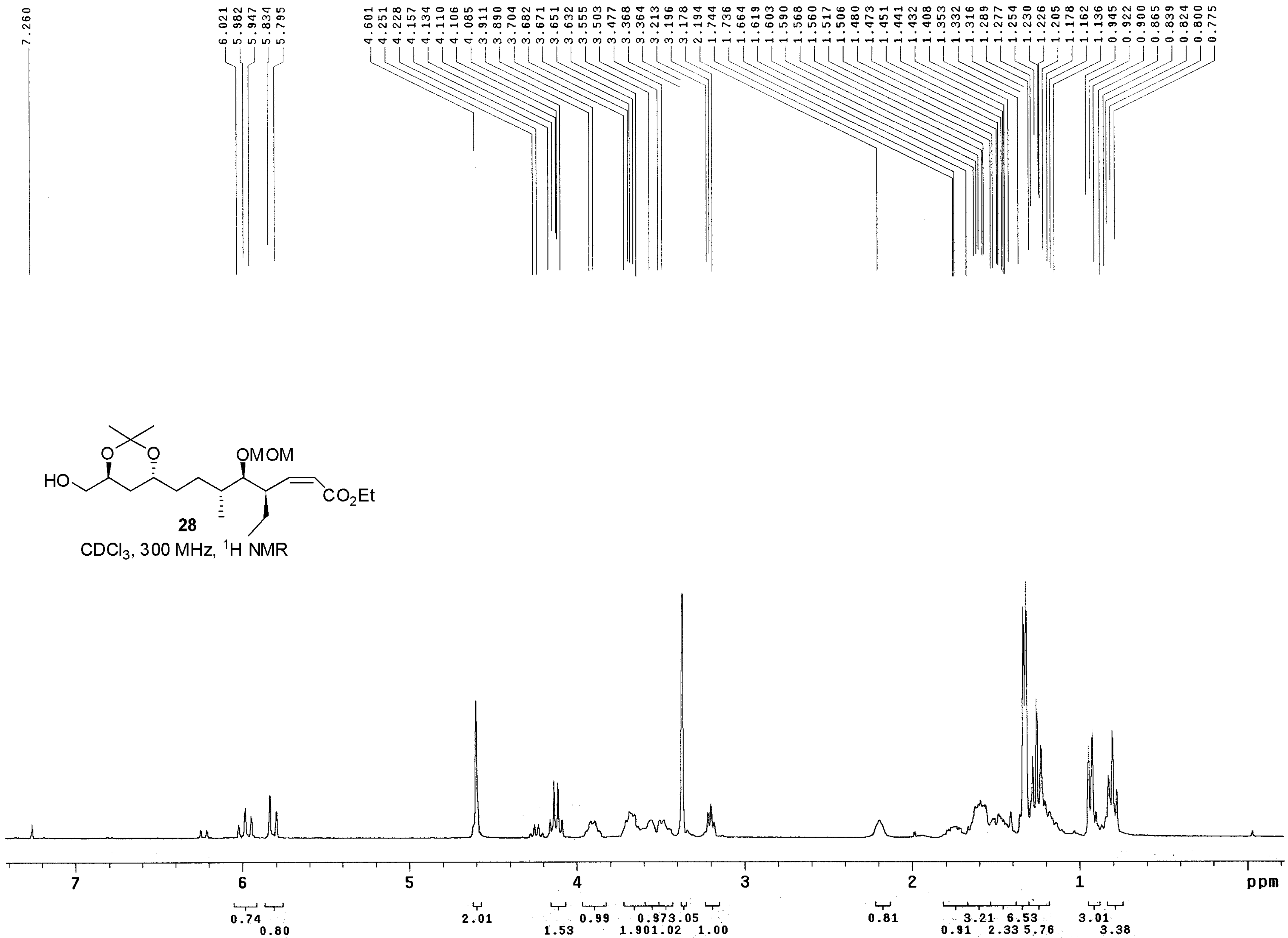

135.635
135.596
133.723
133.616
129.553
127.542
127.519
100.058
98.905
84.410
77.424
77.000
76.576
67.617
66.759
66.671
62.718
56.109
43.377
35.612
34.712
33.246
28.282
26.737
24.837
24.791
19.228
18.110
15.920
12.375
O
O
OMOM
TBDPSO
OH
8
CDCl3, 75 MHz, 13C NMR
200
180
160
140
120
100
80
60
40
20
ppm

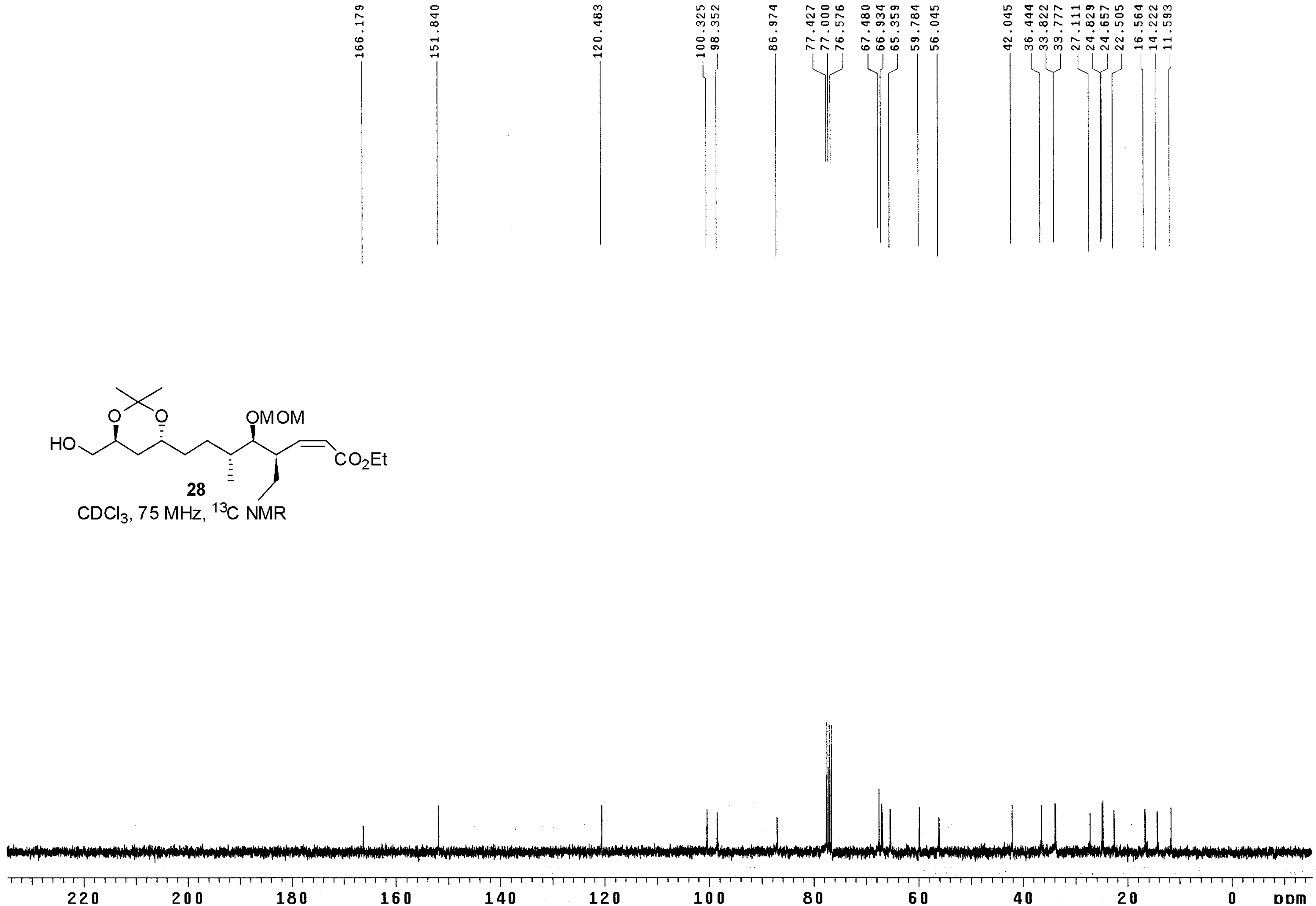

9.716
7.709 7.688 7.448 7.426 7.399 7.375 7.354 7.260
4.653 4.642 4.618 4.599 4.575 3.968 3.948 3.921 3.731 3.718 3.706 3.686 3.641 3.626 3.606 3.591 3.352 3.323 2.369 2.356 2.340 1.840 1.816 1.787 1.762 1.734 1.711 1.691 1.672 1.644 1.631 1.619 1.600 1.582 1.557 1.537 1.525 1.502 1.484 1.461 1.412 1.396 1.353 1.338 1.291 1.265 1.218 1.127 1.062 1.025 0.996 0.970 0.943 0.920 0.904 0.853 0.007
TBDPSO
O
O
MOMO
O
H
26
CDCl3, 300 MHz, 1H NMR
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.92
4.17
6.38
2.00
0.99
3.11
1.02
2.86
0.87
7.84
6.37
1.85
9.46
6.47

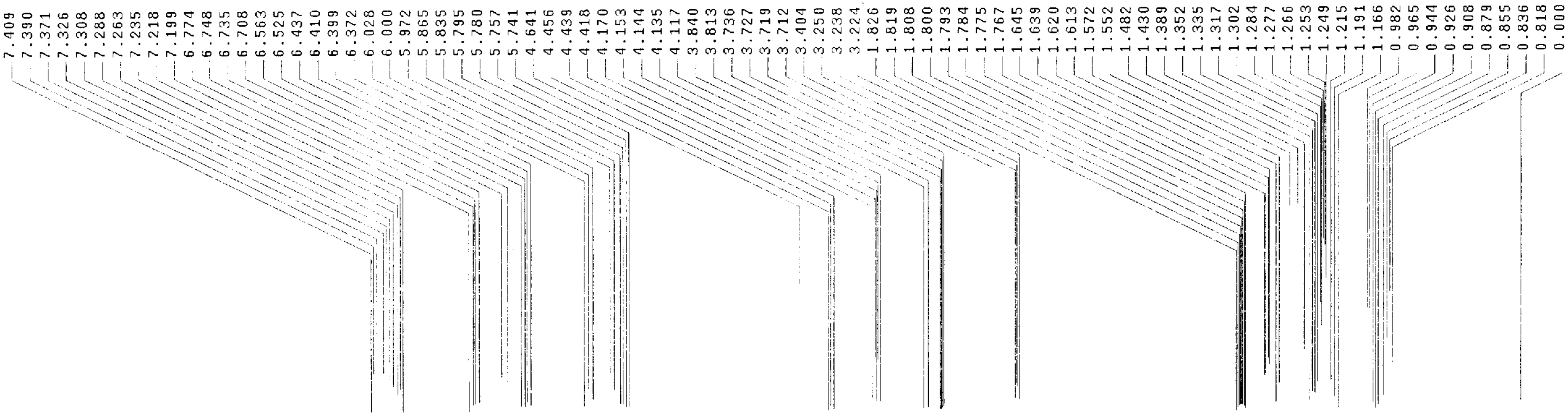

204.217
135.627
135.585
133.712
133.601
129.541
127.534
127.507
100.065
97.704
81.983
77.424
77.000
76.576
67.583
66.663
66.583
56.209
55.911
36.154
34.654
33.387
27.721
26.733
24.825
24.776
19.216
17.297
16.129
12.661
TBDPSO
O
O
MOMO
O
H
26
CDCl3, 75 MHz, 13C NMR
220
200
180
160
140
120
100
80
60
40
20
0
ppm

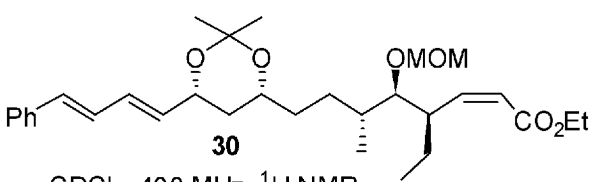

7.712 7.706 7.700 7.696 7.688 7.680 7.446 7.440 7.420 7.393 7.370 7.350 7.258 6.070 6.064 6.031 5.996 5.865 5.826 4.650 4.628 4.607 4.263 4.259 4.240 4.169 4.146 4.140 4.122 4.116 4.099 4.093 3.962 3.943 3.917 3.733 3.712 3.698 3.677 3.634 3.618 3.599 3.583 3.392 3.388 3.255 3.239 3.222 1.807 1.787 1.780 1.770 1.752 1.742 1.631 1.608 1.584 1.545 1.514 1.494 1.451 1.402 1.342 1.318 1.315 1.295 1.279 1.273 1.256 1.250 1.231 1.227 1.211 1.180 1.098 1.061 1.055 1.016 1.010 0.982 0.959 0.935 0.906 0.863 0.840 0.814
TBDPSO
OMOM
CO2Et
27
CDCl3, 300 MHz, 1H NMR
8 7 6 5 4 3 2 1 ppm
5.14 7.67 1.02 1.09 2.56 2.00 0.47 1.37 3.50 1.39 4.09 1.36 1.35 4.20 2.87 8.49 6.99 11.66 3.86 4.68


166.137
151.950
135.631
135.581
133.750
133.616
129.518
127.526
127.496
120.464
100.020
98.303
86.913
77.427
77.000
76.576
67.636
66.912
66.728
59.746
56.045
41.976
36.432
34.658
33.849
27.408
26.729
24.814
22.421
19.216
16.507
14.233
11.650
TBDPSO
O
O
OMOM
CO2Et
27
CDCl3, 75 MHz, 13C NMR
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.260
6.021 5.982 5.947 5.834 5.795
4.601 4.251 4.228 4.157 4.134 4.110 4.106 4.085 3.911 3.890 3.704 3.682 3.671 3.651 3.632 3.555 3.503 3.477 3.368 3.364 3.213 3.196 3.178 2.194 1.744 1.736 1.664 1.619 1.603 1.590 1.568 1.560 1.517 1.506 1.480 1.473 1.451 1.441 1.432 1.408 1.353 1.332 1.316 1.289 1.277 1.254 1.230 1.226 1.205 1.178 1.162 1.136 0.945 0.922 0.900 0.865 0.839 0.824 0.800 0.775
HO
OMOM
CO2Et
28
CDCl3, 300 MHz, 1H NMR
7 6 5 4 3 2 1 ppm
0.74 0.80 2.01 1.53 0.99 1.90 0.97 1.02 3.05 1.00 0.81 0.91 3.21 2.33 6.53 5.76 3.01 3.38

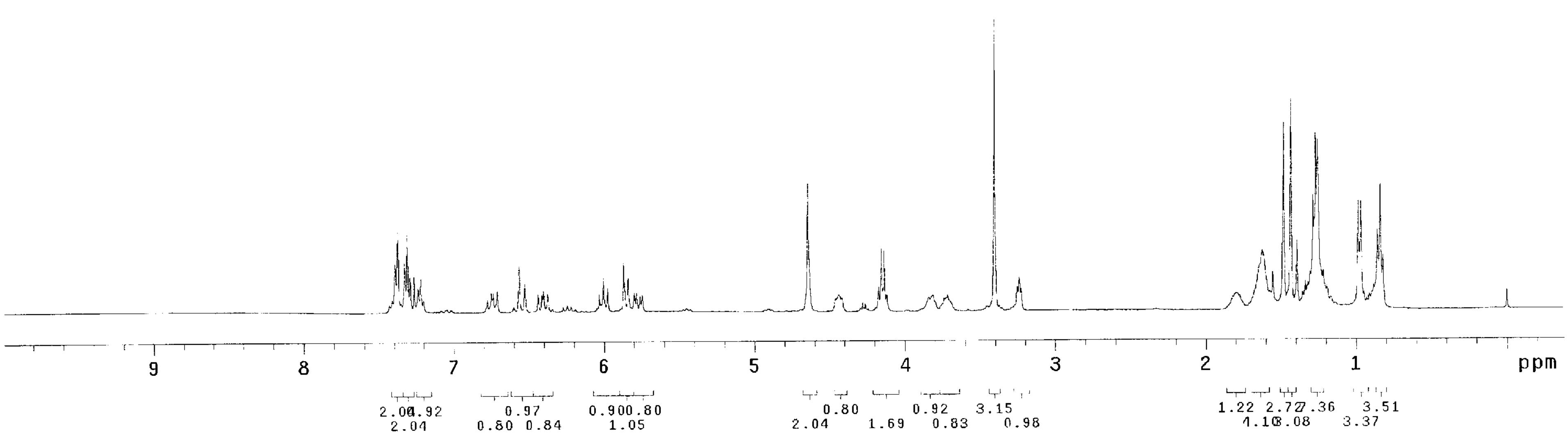

166.179
151.840
120.483
100.325
98.352
86.974
77.427
77.000
76.576
67.480
66.934
65.359
59.784
56.045
42.045
36.444
33.822
33.777
27.111
24.829
24.657
22.505
16.564
14.222
11.593
HO
O
O
OMOM
CO_2Et
28
$CDCl_3$, 75 MHz, ^{13}C NMR
220
200
180
160
140
120
100
80
60
40
20
0
ppm

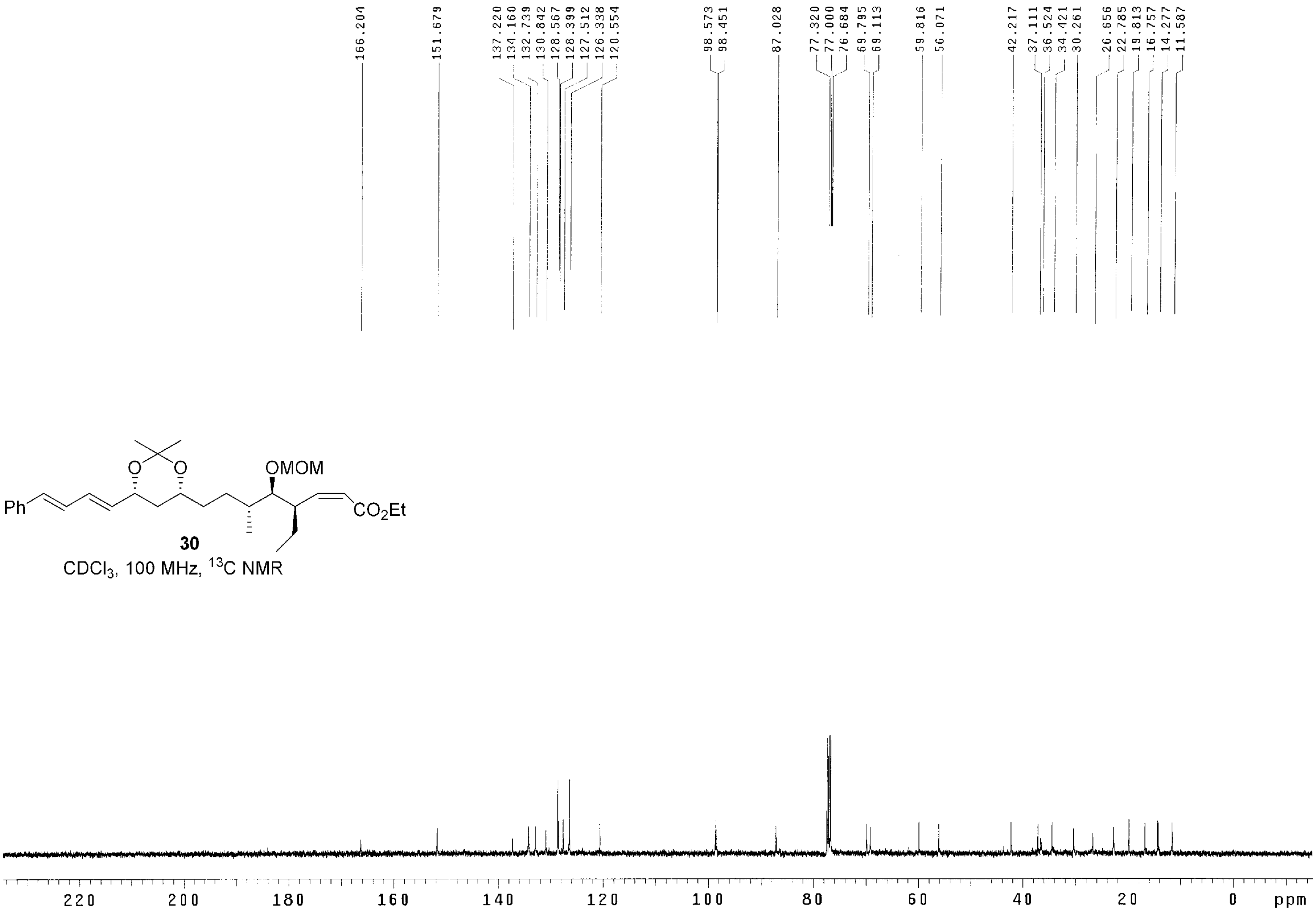




30

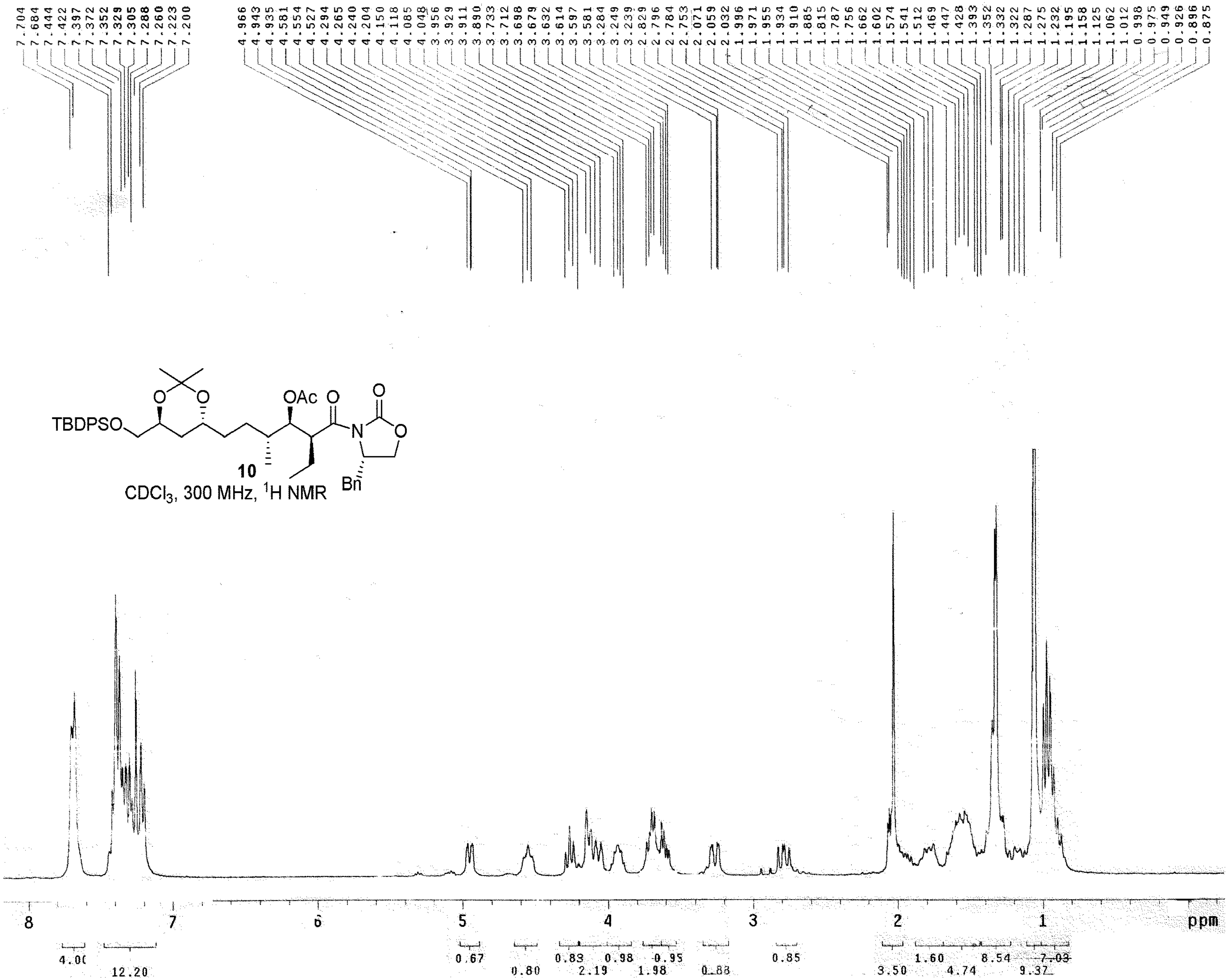
$CDCl_3$, 400 MHz, ^1H NMR

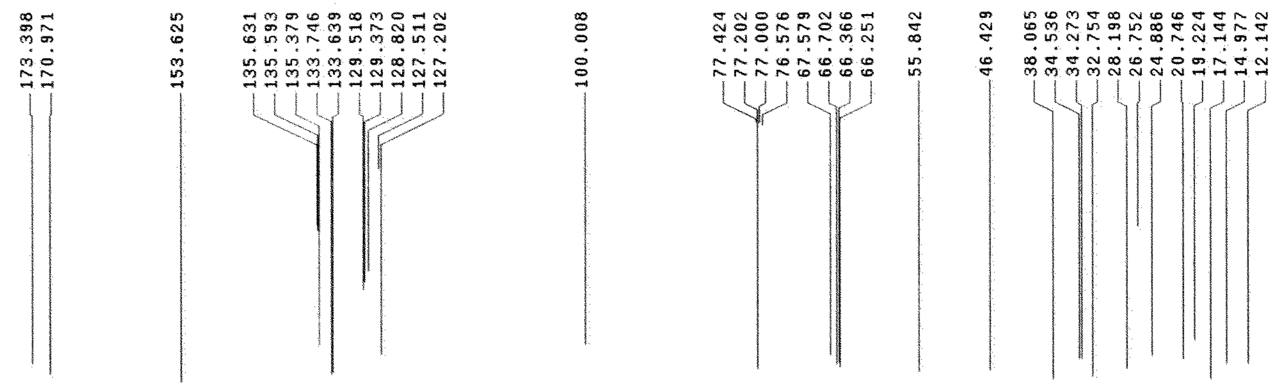


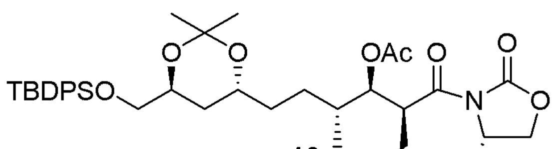


30

$CDCl_3$, 100 MHz, ^{13}C NMR

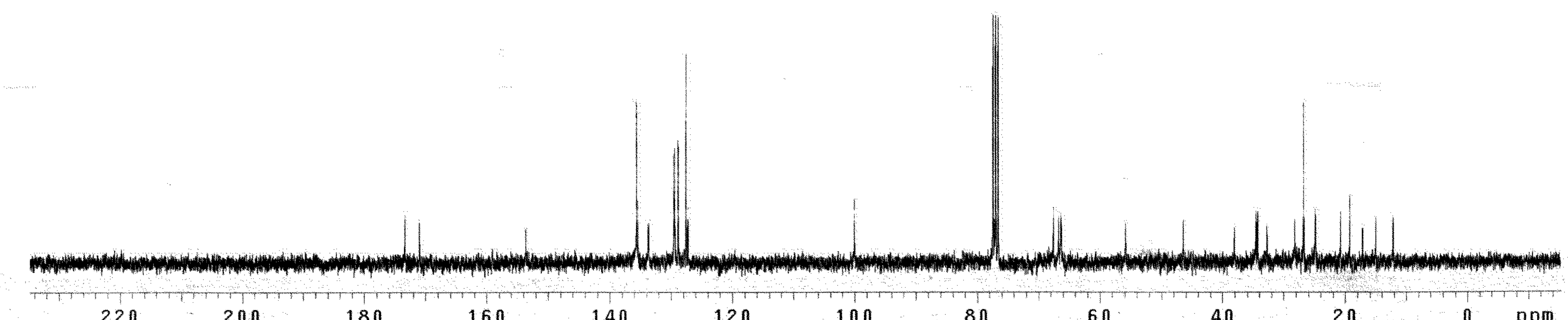

7.704
7.684
7.444
7.422
7.397
7.372
7.352
7.329
7.305
7.288
7.260
7.223
7.200
4.966
4.943
4.935
4.581
4.554
4.527
4.294
4.265
4.240
4.204
4.150
4.118
4.085
4.048
3.956
3.929
3.911
3.890
3.733
3.712
3.698
3.679
3.632
3.614
3.597
3.581
3.284
3.249
3.239
2.829
2.796
2.784
2.753
2.071
2.059
2.032
1.996
1.971
1.955
1.934
1.910
1.885
1.815
1.787
1.756
1.662
1.602
1.574
1.541
1.512
1.469
1.447
1.428
1.393
1.352
1.332
1.322
1.287
1.275
1.232
1.195
1.158
1.125
1.062
1.012
0.998
0.975
0.949
0.926
0.896
0.875
TBDPSO
OAc
O
N
Bn
10
CDCl3, 300 MHz, 1H NMR
8
7
6
5
4
3
2
1
ppm
4.00
12.20
0.67
0.80
0.83
2.19
0.98
1.98
0.95
0.88
0.85
3.50
1.60
4.74
8.54
9.37
7.03

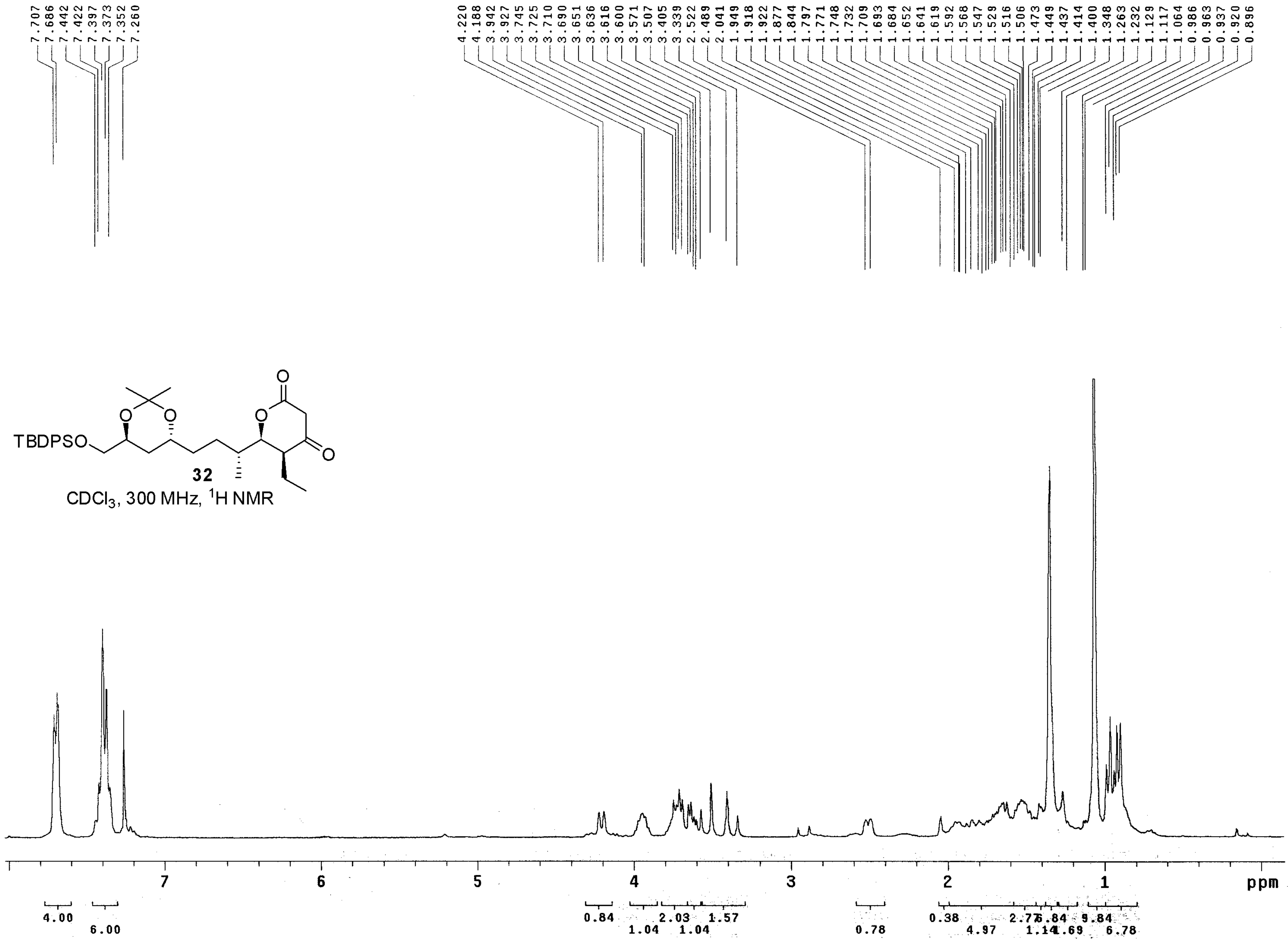




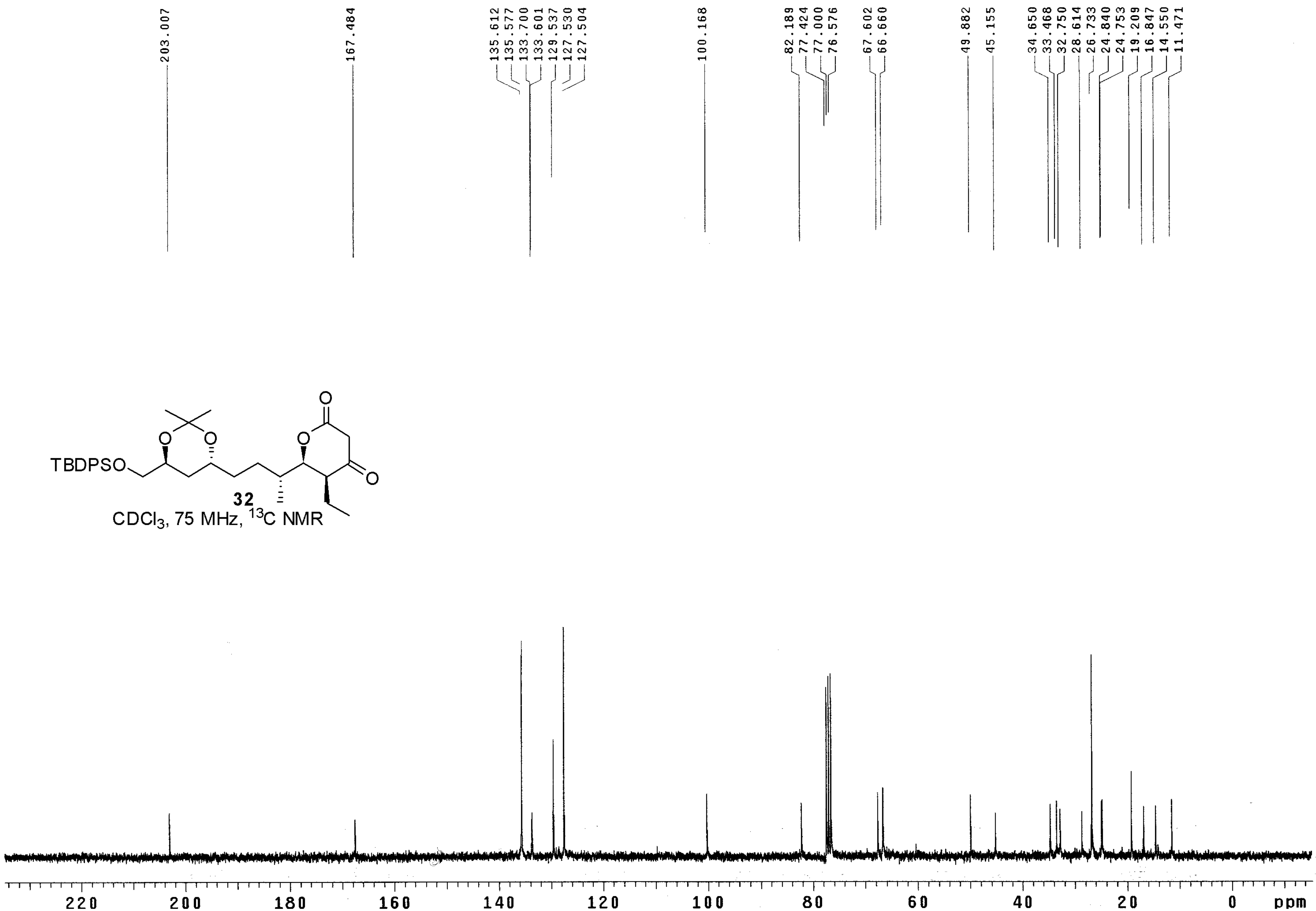
10

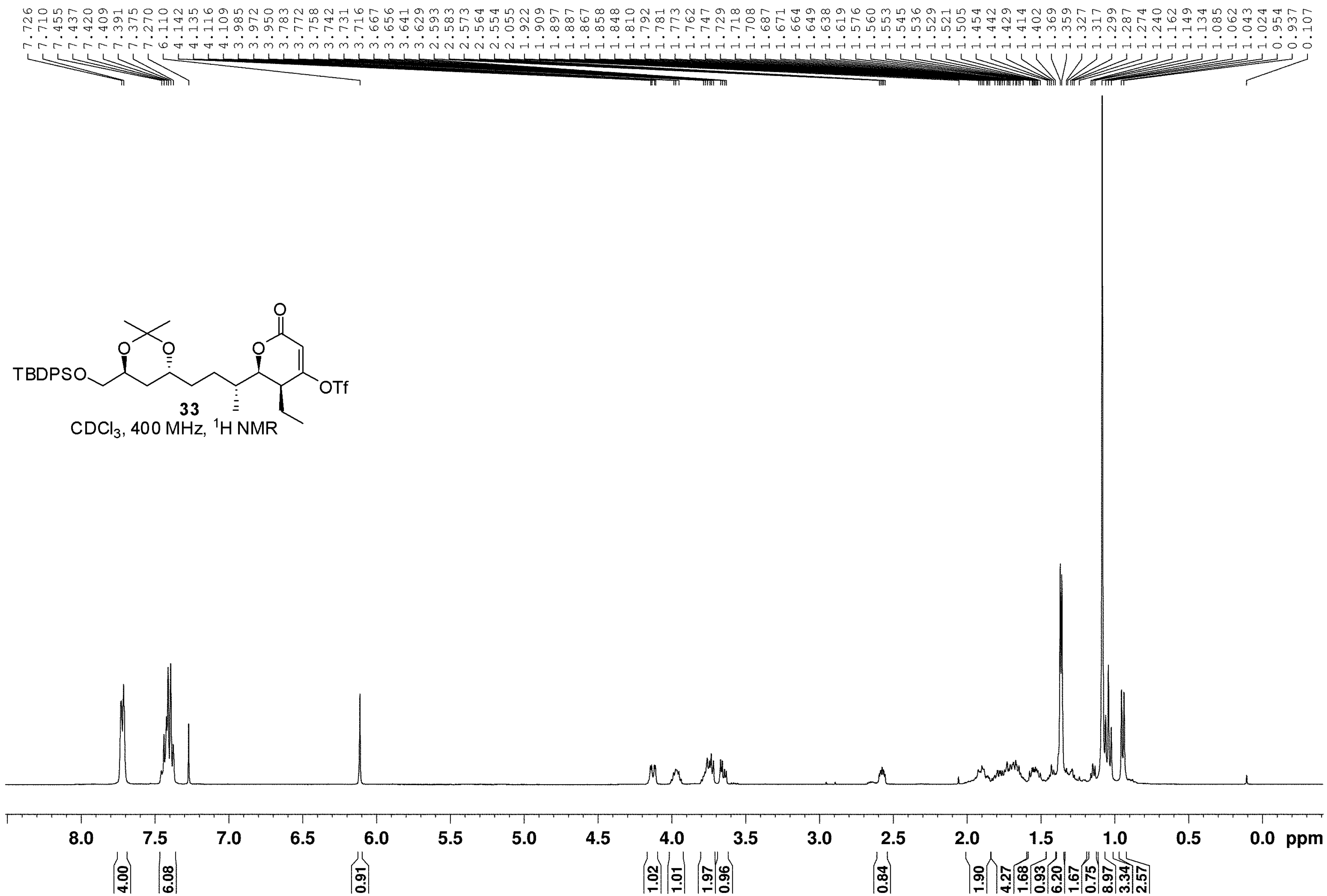
$CDCl_3$, 75 MHz, ^{13}C NMR

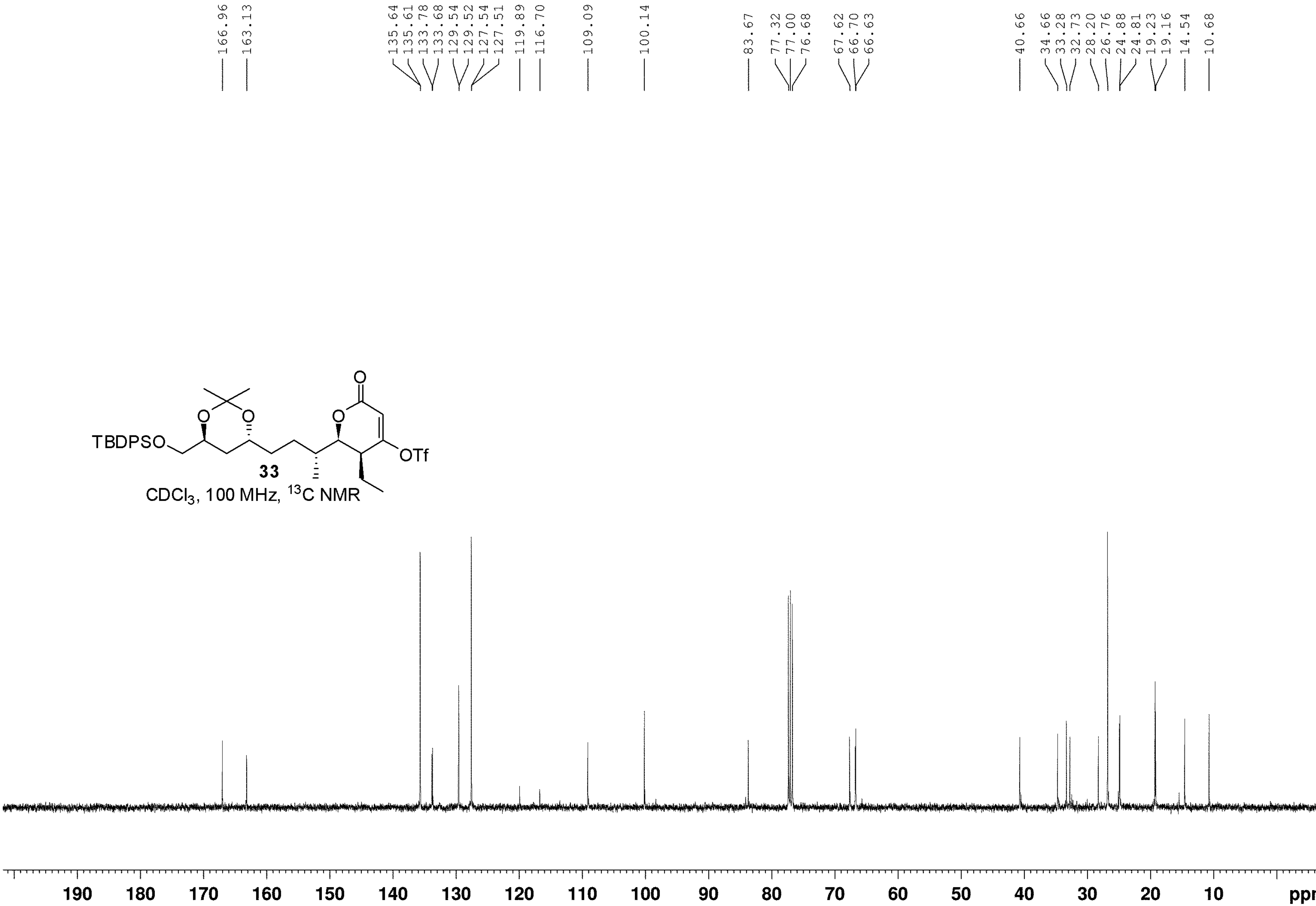


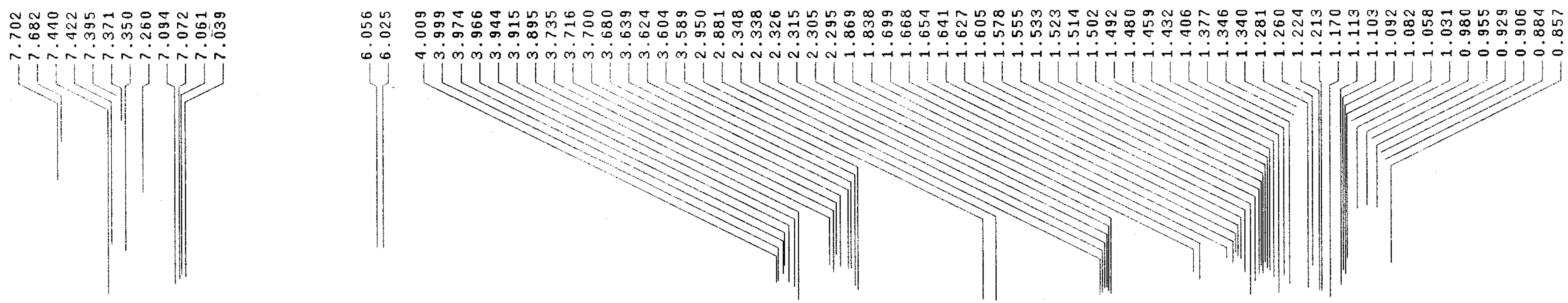


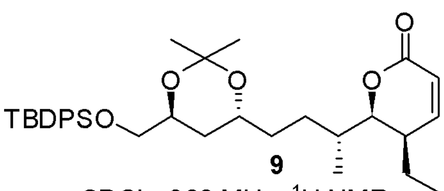
7.707
7.686
7.442
7.422
7.397
7.373
7.352
7.260
4.220
4.188
3.942
3.927
3.745
3.725
3.710
3.690
3.651
3.636
3.616
3.600
3.571
3.507
3.405
3.339
2.522
2.489
2.041
1.949
1.918
1.922
1.877
1.844
1.797
1.771
1.748
1.732
1.709
1.693
1.684
1.652
1.641
1.619
1.592
1.568
1.547
1.529
1.516
1.506
1.473
1.449
1.437
1.414
1.400
1.348
1.263
1.232
1.129
1.117
1.064
0.986
0.963
0.937
0.920
0.896
TBDPSO
O
O
O
O
O
32
CDCl3, 300 MHz, 1H NMR
7
6
5
4
3
2
1
ppm
4.00
6.00
0.84
1.04
2.03
1.04
1.57
0.78
0.38
4.97
2.77
6.84
1.14
1.69
9.84
6.78


203.007
167.484
135.612
135.577
133.700
133.601
129.537
127.530
127.504
100.168
82.189
77.424
77.000
76.576
67.602
66.660
49.882
45.155
34.650
33.468
32.750
28.614
26.733
24.840
24.753
19.209
16.847
14.550
11.471
TBDPSO
32
CDCl3, 75 MHz, 13C NMR
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.726 7.710 7.455 7.437 7.420 7.409 7.391 7.375 7.270 6.110 4.142 4.135 4.116 4.109 3.985 3.972 3.950 3.783 3.772 3.758 3.742 3.731 3.716 3.667 3.656 3.641 3.629 2.593 2.583 2.573 2.564 2.554 2.055 1.922 1.909 1.897 1.887 1.867 1.858 1.848 1.810 1.792 1.781 1.773 1.762 1.747 1.729 1.718 1.708 1.687 1.671 1.664 1.649 1.638 1.619 1.576 1.560 1.553 1.545 1.536 1.529 1.521 1.505 1.454 1.442 1.429 1.414 1.402 1.369 1.359 1.327 1.317 1.299 1.287 1.274 1.240 1.162 1.149 1.134 1.085 1.062 1.043 1.024 0.954 0.937 0.107
TBDPSO
O
O
O
O
OTf
33
CDCl3, 400 MHz, 1H NMR
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 0.0 ppm
4.00 6.08 0.91 1.02 1.01 1.97 0.96 0.84 1.90 4.27 1.68 0.93 6.20 1.67 0.75 8.97 3.34 2.57

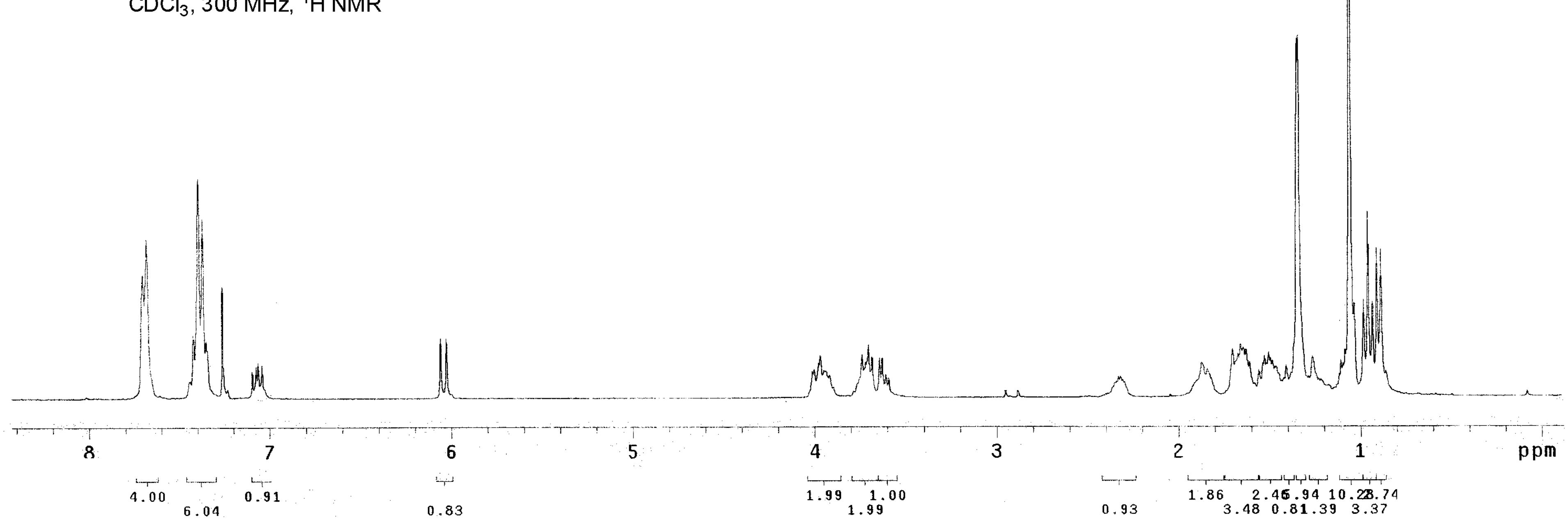

166.96
163.13
135.64
135.61
133.78
133.68
129.54
129.52
127.54
127.51
119.89
116.70
109.09
100.14
83.67
77.32
77.00
76.68
67.62
66.70
66.63
40.66
34.66
33.28
32.73
28.20
26.76
24.88
24.81
19.23
19.16
14.54
10.68
TBDPSO
O
O
O
O
OTf
33
CDCl3, 100 MHz, 13C NMR
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

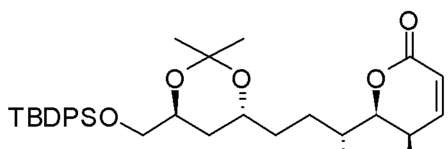




9

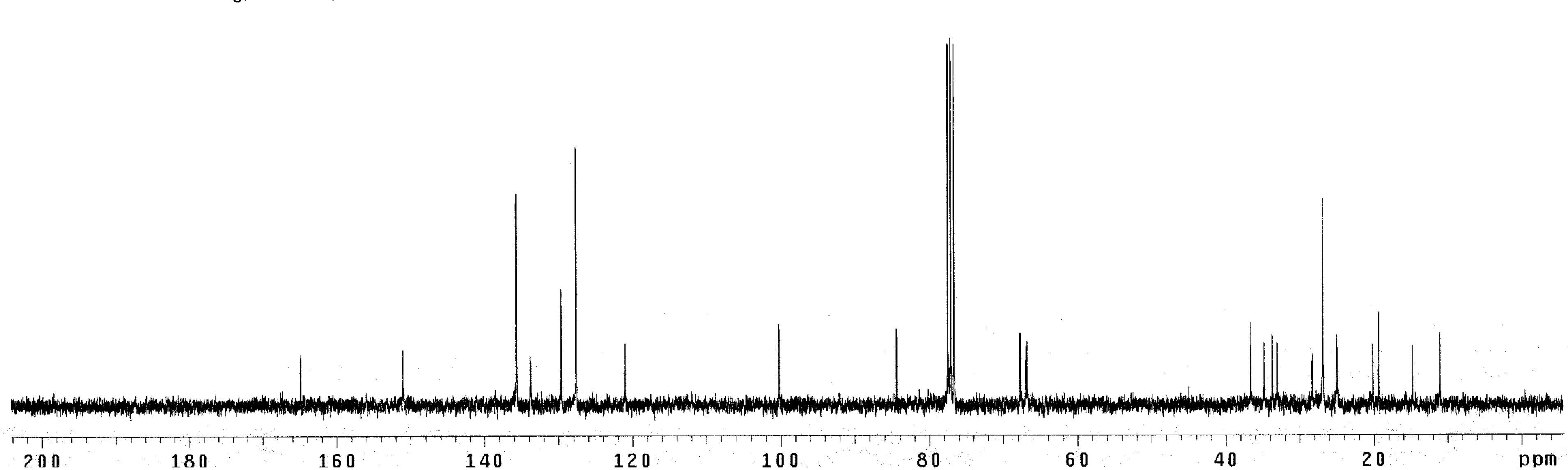
CDCl$_3$, 300 MHz, ^{1}H NMR

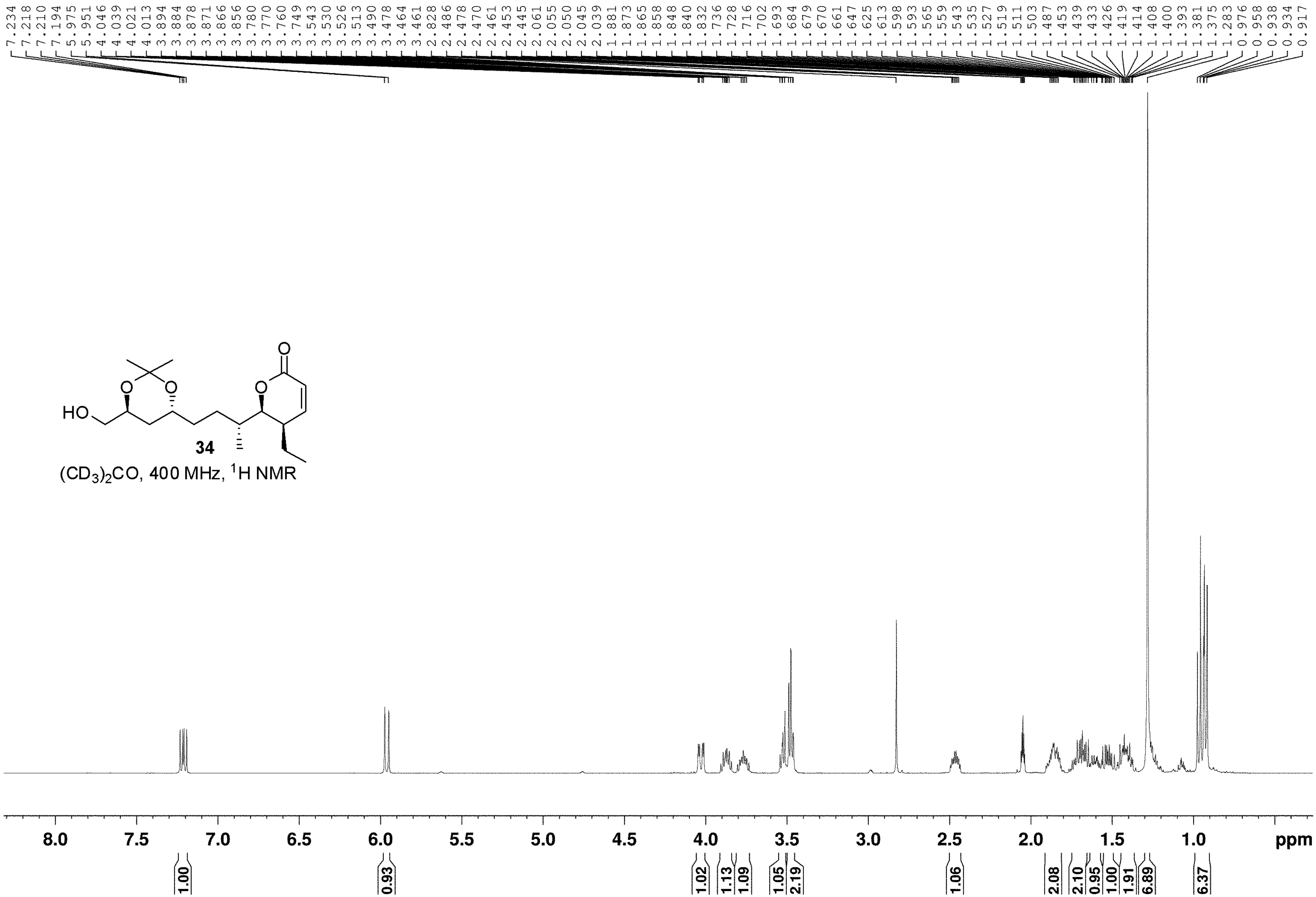


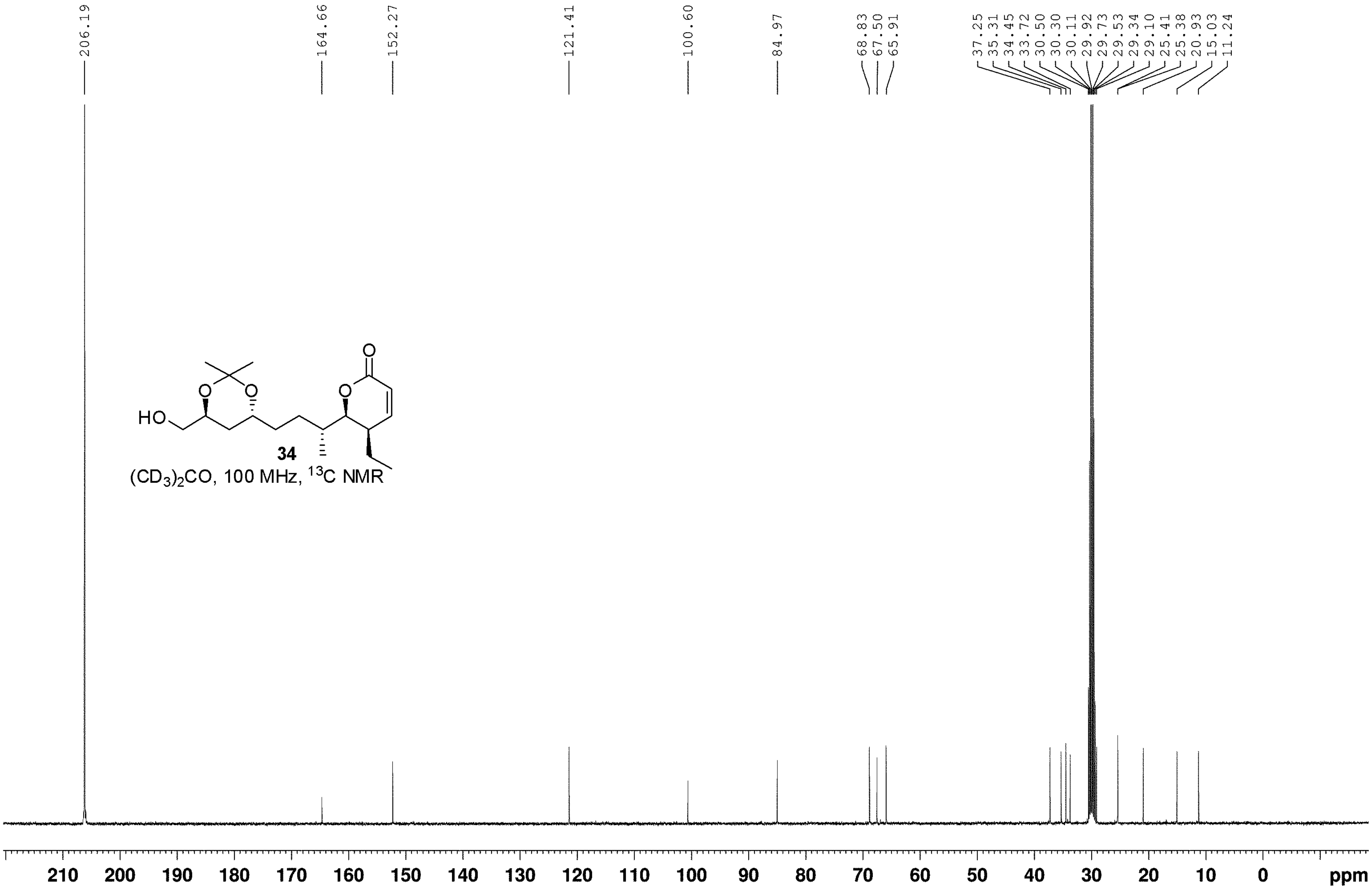


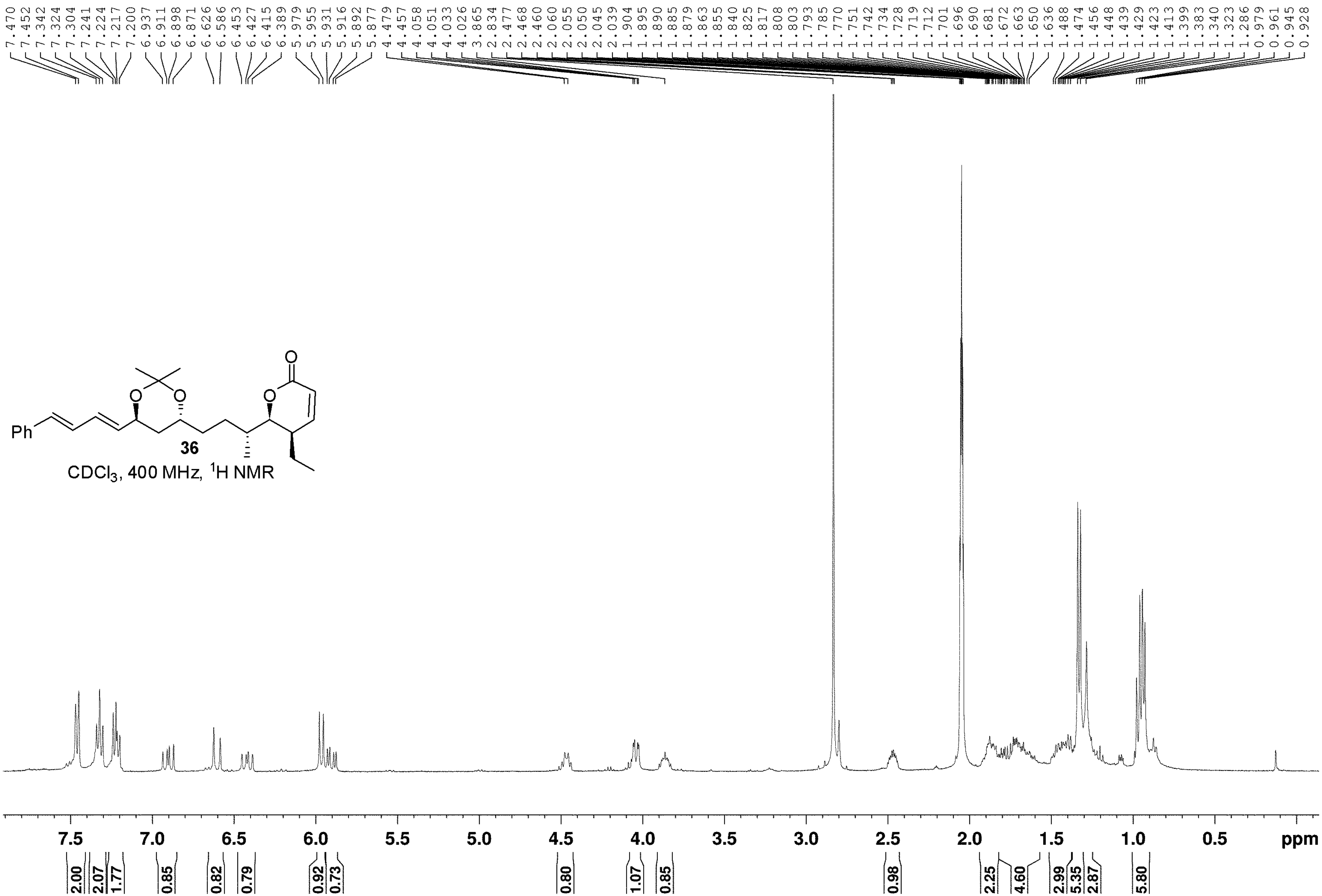
9

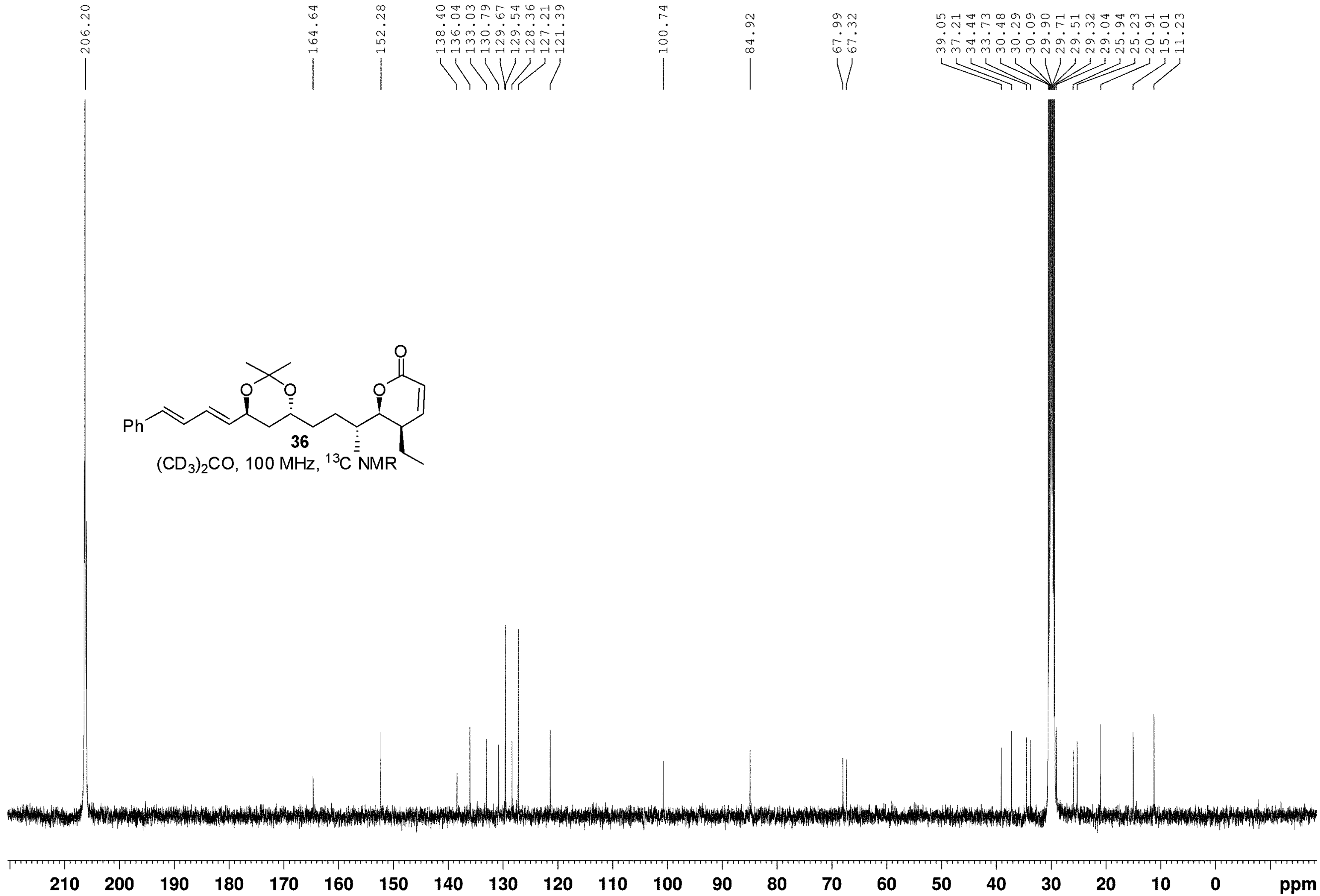
CDCl$_3$, 75 MHz, ^{13}C NMR

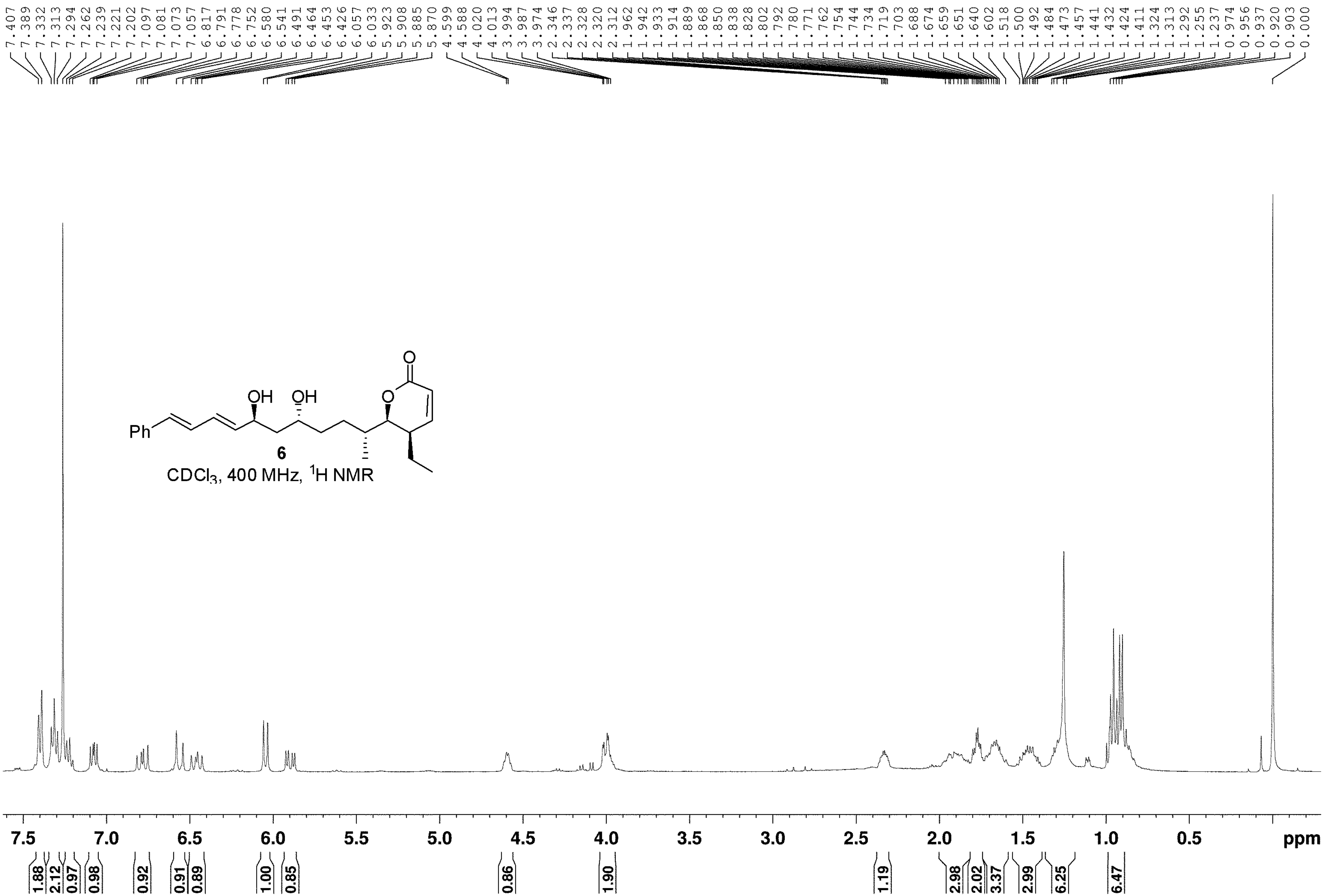


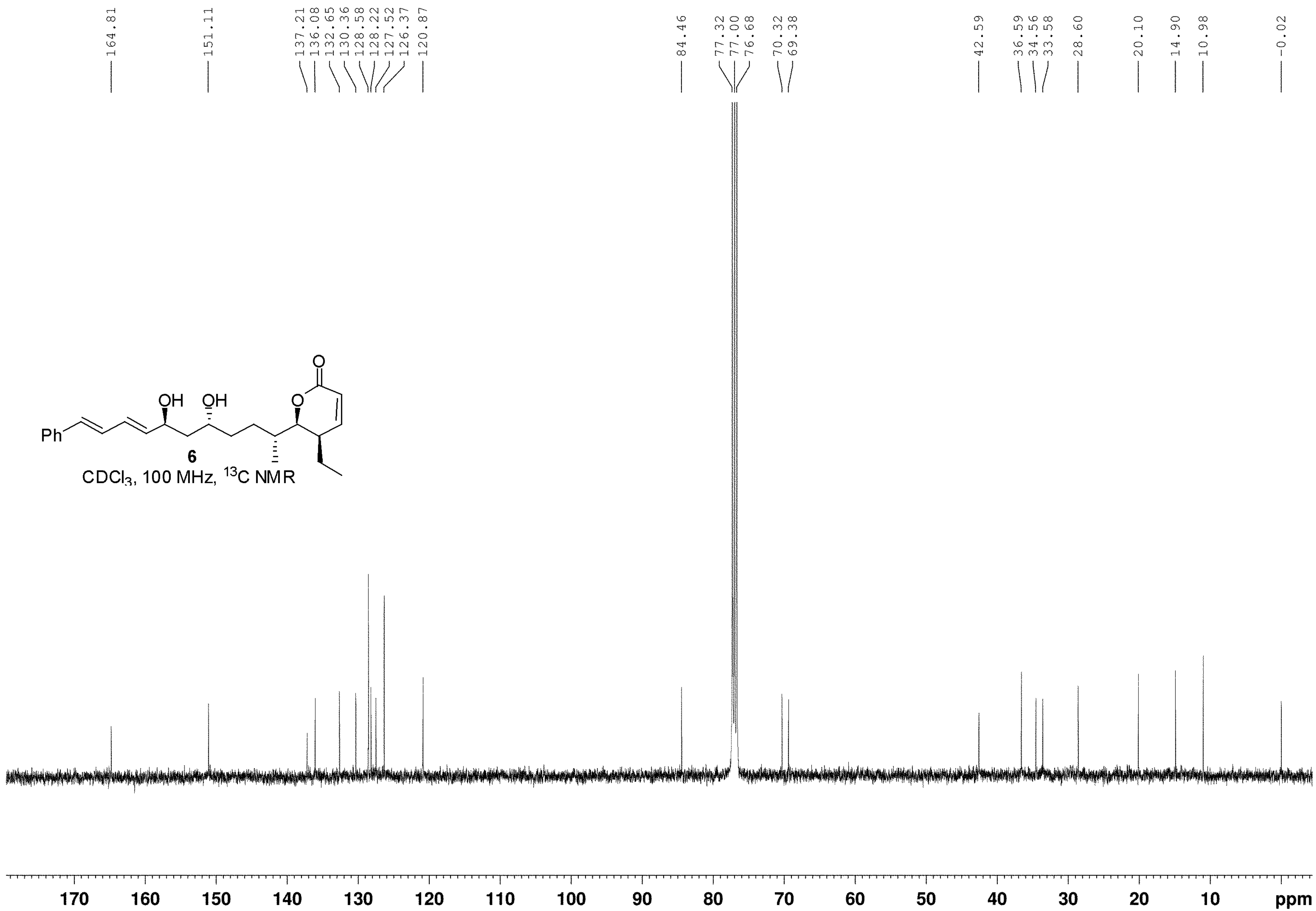

7.234 7.218 7.210 7.194 5.975 5.951 4.046 4.039 4.021 4.013 3.894 3.884 3.878 3.871 3.866 3.856 3.780 3.770 3.760 3.749 3.543 3.530 3.526 3.513 3.490 3.478 3.464 3.461 2.828 2.486 2.478 2.470 2.461 2.453 2.445 2.061 2.055 2.050 2.045 2.039 1.881 1.873 1.865 1.858 1.848 1.840 1.832 1.736 1.728 1.716 1.702 1.693 1.684 1.679 1.670 1.661 1.647 1.625 1.613 1.598 1.593 1.565 1.559 1.543 1.535 1.527 1.519 1.511 1.503 1.487 1.453 1.439 1.433 1.426 1.419 1.414 1.408 1.400 1.393 1.381 1.375 1.283 0.976 0.958 0.938 0.934 0.917
HO
O
O
O
O
34
(CD3)2CO, 400 MHz, 1H NMR
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 ppm
1.00 0.93 1.02 1.13 1.09 1.05 2.19 1.06 2.08 2.10 0.95 1.00 1.91 6.89 6.37


206.19
164.66
152.27
121.41
100.60
84.97
68.83
67.50
65.91
37.25
35.31
34.45
33.72
30.50
30.30
30.11
29.92
29.73
29.53
29.34
29.10
25.41
25.38
20.93
15.03
11.24
HO
O
34
(CD3)2CO, 100 MHz, 13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.470 7.452 7.342 7.324 7.304 7.241 7.224 7.217 7.200 6.937 6.911 6.898 6.871 6.626 6.586 6.453 6.427 6.415 6.389 5.979 5.955 5.931 5.916 5.892 5.877 4.479 4.457 4.058 4.051 4.033 4.026 3.865 2.834 2.477 2.468 2.460 2.060 2.055 2.050 2.045 2.039 1.904 1.895 1.890 1.885 1.879 1.863 1.855 1.840 1.825 1.817 1.808 1.803 1.793 1.785 1.770 1.751 1.742 1.734 1.728 1.719 1.712 1.701 1.696 1.690 1.681 1.672 1.663 1.650 1.636 1.488 1.474 1.456 1.448 1.439 1.429 1.423 1.413 1.399 1.383 1.340 1.323 1.286 0.979 0.961 0.945 0.928
Ph
O
36
CDCl3, 400 MHz, 1H NMR
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
2.00 2.07 1.77 0.85 0.82 0.79 0.92 0.73 0.80 1.07 0.85 0.98 2.25 4.60 2.99 5.35 2.87 5.80


206.20
164.64
152.28
138.40
136.04
133.03
130.79
129.67
129.54
128.36
127.21
121.39
100.74
84.92
67.99
67.32
39.05
37.21
34.44
33.73
30.48
30.29
30.09
29.90
29.71
29.51
29.32
29.04
25.94
25.23
20.91
15.01
11.23
Ph
O
36
(CD3)2CO, 100 MHz, 13C NMR
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.407
7.389
7.332
7.313
7.294
7.262
7.239
7.221
7.202
7.097
7.081
7.073
7.057
6.817
6.791
6.778
6.752
6.580
6.541
6.491
6.464
6.453
6.426
6.057
6.033
5.923
5.908
5.885
5.870
4.599
4.588
4.020
4.013
3.994
3.987
3.974
2.346
2.337
2.328
2.320
2.312
1.962
1.942
1.933
1.914
1.889
1.868
1.850
1.838
1.828
1.802
1.792
1.780
1.771
1.762
1.754
1.744
1.734
1.719
1.703
1.688
1.674
1.659
1.651
1.640
1.602
1.518
1.500
1.492
1.484
1.473
1.457
1.441
1.432
1.424
1.411
1.324
1.313
1.292
1.255
1.237
0.974
0.956
0.937
0.920
0.903
0.000
O
OH
OH
O
Ph
6
CDCl3, 400 MHz, 1H NMR
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
1.88
2.12
0.97
0.98
0.92
0.91
0.89
1.00
0.85
0.86
1.90
1.19
2.98
2.02
3.37
2.99
6.25
6.47


164.81
151.11
137.21
136.08
132.65
130.36
128.58
128.22
127.52
126.37
120.87
84.46
77.32
77.00
76.68
70.32
69.38
42.59
36.59
34.56
33.58
28.60
20.10
14.90
10.98
-0.02
OH
OH
O
O
Ph
6
CDCl3, 100 MHz, 13C NMR
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm