Supplementary Material (ESI) for Chemical Communications
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A Highly Stereocontrolled Total Synthesis of Dysiherbaine

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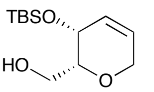
Supporting Information

General Procedure. Where appropriate, reactions performed in flame dried glassware under argon atmosphere. All extracts were dried over $MgSO_4$ and concentrated by rotary evaporation below 30 °C at 25 Toor. Commercial reagents and solvents were used as supplied with following exceptions. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et_2O) was purchased from Kanto Chemical Co., Inc. Dichloromethane (CH_2Cl_2) triethylamine, dimethyl sulfoxide (DMSO), *N, N*-dimethylformamide (DMF), N, N-dimethylacetoamide (DMA), *N,N,N,N',N',N'*-hexamethylphosphoramide (HMPA), benzene, acetonitrile (MeCN) were distilled from CaH_2. Methanol (MeOH) was distilled from sodium. Analytical thin-layer chromatography was performed with Merck F-254 TLC plates. Column chromatography was performed using Kanto Chemical Co., Inc. silica gel 60N (spherical, neutral). Infrared spectra were measured on a JASCO FTIR-230 spectrometer. Optical rotations were recorded on a JASCO DIP-370 polarimeter at ambient temperature. ^{1}H and ^{13}C NMR spectra were measured on a Varian Gemini 300, JEOL JNM-AL 400, or Varian Unity plus 500 spectrometer. For ^{1}H spectra, Chemical shifts are reported as δ values in ppm and are calibrated according to internal $CHCl_3$ (7.26 ppm) or PhH (7.14 ppm). For ^{13}C spectra, chemical shifts are reported as δ values in ppm relative to chloroform or methanol. EI and FAB Mass spectra were measured on a JEOL JMS-700N.

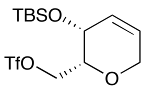


((2*R*,3*R*)-3-(*tert*-Butyldimethylsilyl)oxy-3,6-dihydro-2*H*-pyran-2-yl)methanol (10). To a stirred solution of tri-*O*-acetyl-D-galactal (**9**) (30 g, 110 mmol) in CH_2Cl_2 (550 ml) at 0 °C were added triethylsilane (25.6 g, 522 mmol) and $BF_3 \cdot OEt_2$ (28.1 g, 198 mmol). After stirring at 0 °C for 2 h, the reaction was quenched with saturated $NaHCO_3$. The reaction mixture was extracted with CH_2Cl_2, washed with brine and concentrated to give the corresponding diacetate (28 g) as a colorless oil, which was used for the next reaction without purification.

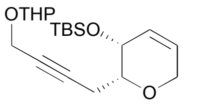
Crude diacetate (28 g) was dissolved into MeOH (360 ml) and NaOMe (1.19 g, 22.0 mmol) was added. After being stirred at room temperature for 2 h, the reaction mixture was neutralized with Dowex 50, filtrated, and evaporated to give the corresponding diol (14 g) as a colorless solid, which was used for the next reaction without purification.

Crude diol (14 g) was dissolved into DMF (368 ml) and cooled to 0 °C. Imidazole (22.5 g, 275 mmol) and *tert*-butyldimethylsilyl chloride (41.5 g, 330 mmol) were added and the mixture was stirred at room temperature for 12 h. Saturated NH_4Cl (200 ml) was added and the mixture was stirred at room temperature for 10 min. The reaction mixture was extracted with Et_2O, washed with water and brine, and concentrated to give (2*R*,3*R*)-3-(*tert*-butyldimethylsilyl)oxy-2-(*tert*-butyldimethylsilyl)oxymethyl-3,6-dihydro-2*H*-pyran (38.7 g) as a pale yellow oil, which was used for the next reaction without purification. A sample for the characterization data was obtained by column chromatography (hexane/AcOEt = 15/1): $[\alpha]^{22}_D$ –90.6° (*c* 1.10, $CHCl_3$); FTIR (neat) 1471, 1254, 1103 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.89 (m, 2H), 4.26 (dd, *J* = 1.8, 16.2 Hz, 1H), 4.10 (m, 1H), 4.04 (m, 1H), 3.82 (dd, *J* = 5.7, 10.8 Hz, 1H), 3.74 (dd, *J* = 6.3, 10.8 Hz, 1H), 3.49 (dt, *J* = 2.6, 6.3 Hz, 1H), 0.90 (s, 18H), 0.08 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.3, 126.6, 79.0, 65.5, 63.2, 62.8, 26.0, 25.7, 18.5, 18.3, –3.5, –3.9, –4.5, –5.1; MS (EI) m/z 117, 147, 301 (100), 343 [(M-Me)$^+$]; HRMS (EI) calcd for $C_{17}H_{35}O_3Si_2$ [(M-Me)$^+$] 343.2125, found 343.2125.

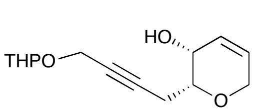
Crude di-TBS ether (38.7 g) was dissolved into MeOH (360 ml), and NH_4F (12 g, 324 mmol) was added. After being stirred at 0 °C for 7 days, most of the MeOH was evaporated in vacuo. The residue was extracted with AcOEt, washed with saturated $NaHCO_3$, dried, concentrated, and chromatographed (SiO_2 800 g, hexane/AcOEt = 5/1) to give **10** (23.1 g, 88 %) as a colorless solid: $[\alpha]^{22}_D$ –159.1° (*c* 1.07, $CHCl_3$); FTIR (neat) 3433, 3037, 1471, 1389, 1257 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (m, 1H), 5.86 (m, 1H), 4.30 (m, 1H), 4.11 (m, 2H), 3.90 (ddd, *J* = 2.9, 7.3, 11.2 Hz, 1H), 3.73 (ddd, *J* = 3.9, 9.3, 11.7 Hz, 1H), 3.59 (quint, *J* = 3.4 Hz, 1H), 2.19 (dd, *J* = 2.9, 9.3 Hz, 1H), 0.90 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.3, 126.1, 78.2, 65.1, 64.1, 62.8, 25.7, 18.1, –4.1, –4.7; MS (EI) m/z 75 (100), 105, 157, 243 [(M-H)$^+$]; HRMS (EI) calcd for $C_{12}H_{23}O_3Si$ [(M-H)$^+$] 243.1417, found 243.1411.



((2*R*,3*R*)-3-(*tert*-Butyldimethylsilyl)oxy-3,6-dihydro-2*H*-pyran-2-yl)methyl trifluoromethanesulfonate. To a stirred solution of **10** (3.06 g, 15.0 mmol) in CH_2Cl_2 (125 ml) at –78 °C were added 2,6-lutidine (2.01 g, 18.8 mmol) and trifluoromethanesulfonic anhydride (4.2 g, 15.0 mmol). After being stirred at –78 °C for 90 min, the mixture was diluted with CH_2Cl_2 (200 ml), washed with water, 1M HCl, saturated $NaHCO_3$ and brine, dried, and concentrated. The residue was purified by column chromatography (SiO_2 90 g, hexane/AcOEt = 20/1) to give the corresponding triflate (4.6 g, 98 %) as a yellow oil: $[\alpha]^{24}_D$ –116.4° (*c* 1.05, $CHCl_3$); FTIR (neat) 1417, 1248, 1217, 1151, 1007 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (m, 1H), 5.87 (m, 1H), 4.65 (m, 2H), 4.29 (m, 1H), 4.14 (m, 1H), 4.11 (m, 1H), 3.86 (dt, *J* = 3.7, 7.5 Hz, 1H), 0.89 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.6, 125.5, 118.6 (q, $^1J_{C,F}$ = 317.6 Hz), 75.8, 75.1, 64.8, 63.12, 25.7, 18.0, –4.0, –4.8; MS (EI) m/z 43 (100), 95, 289, 319, 377 (M)$^+$; HRMS (EI) calcd for $C_{13}H_{23}F_3O_5SSi$ (M)$^+$] 376.0988, found 376.0900.

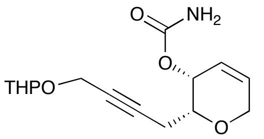


(2*R*,3*R*)-3-(*tert*-Butyldimethylsilyl)oxy-3,6-dihydro-2-(4-(tetrahydro-2*H*-pyran-2-yl)oxybut-2-ynyl)-2*H*-pyran (11). To a stirred solution of propargyl tetrahydropyranyl ether (55 g, 393 mmol) in THF (220 ml) at –65 °C was added *n*-butyllithium (1.6 M in hexane, 227 ml, 364 mmol), and the mixture was stirred for 1 h. A solution of the triflate (29.1g, 77.3 mmol) in THF (20 ml) and DMPU (60 ml) was added, and the mixture was stirred at –65 °C for 5 days. The reaction was quenched with saturated $NaHCO_3$ and the reaction mixture was extracted with AcOEt, washed with brine, dried, concentrated, and chromatographed (SiO_2 700g, hexane/AcOEt = 15/1-8/1) to give **11** (23.6 g, 83 %) as a colorless oil: FTIR (neat) 1471, 1360, 1254, 1184, 1119, 1082, 1024 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (m, 2H), 4.80 (br, 1H), 4.30 (dt, *J* = 2.4, 15.3 Hz, 1H), 4.25 (m, 1H), 4.20 (dt, *J* = 15.0, 2.1 Hz, 1H), 4.11 (m, 1H), 4.07 (m, 1H), 3.84 (m, 1H), 3.63 (dt, *J* = 2.3, 7.5 Hz, 1H), 3.53 (m, 1H), 2.58 (m, 2H), 1.68-1.40 (m, 6H), 0.90 (s, 9H), 0.10 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.0, 126.4, 96.5, 96.4, 83.1, 76.9, 76.5, 65.4, 63.4, 61.7, 54.43, 54.39, 30.1, 25.8, 25.3, 25.2, 20.8, 18.9, 18.1, –4.1, –4.8; MS (EI) m/z 85, 159 (100), 184, 225, 309, 366 (M$^+$); HRMS (EI) calcd for $C_{20}H_{34}O_4Si$ (M$^+$) 366.2227, found 366.2222.



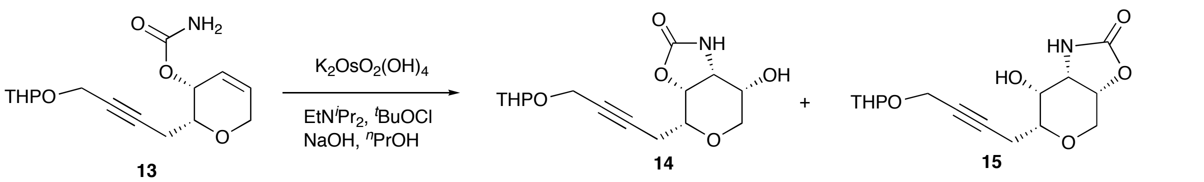
(2*R*,3*R*)-3,6-dihydro-2-(4-(tetrahydro-2*H*-pyran-2-yloxy)but-2-ynyl)-2*H*-pyran-3-ol (12): To a stirred solution of **11** (293 mg, 0.799

mmol) in THF (8 ml) was added TBAF (1M in THF, 0.8 ml, 0.8 mmol) at room temperature. After being stirred at room temperature for 13 h, saturated NH_4Cl was added and the reaction mixture was extracted with AcOEt. The extract was washed with $NaHCO_3$ and brine, dried, and concentrated to give **12** (217 mg) as a yellow oil, which was used for the next reaction without purification. A sample for the characterization data was obtained by column chromatography (hexane/AcOEt = 2/1): $[\alpha]^{19}_D$ –88.6° (*c* 0.99, $CHCl_3$); FTIR (neat) 3654, 3438, 2225, 1354, 1265, 1084, 1024 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.06 (m, 1H), 5.96 (m, 1H), 4.80 (t, *J* = 3.2 Hz, 1H), 4.35-4.10 (m, 2H), 4.21 (m, 2H), 3.96 (br, 1H), 3.84 (m, 1H), 3.63 (dt, *J* = 1.4, 7.8 Hz, 1H), 3.53 (m, 1H), 2.69-2.56 (m, 2H), 1.82-1.53 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.7, 126.5, 96.4, 82.3, 77.1, 76.5, 66.1, 62.5, 61.6, 54.4, 30.0, 25.1, 21.1, 18.8; MS (EI) m/z 85 (100), 150, 183, 198, 228, 251 [$(M-H)^+$]; HRMS (EI) calcd for $C_{14}H_{20}O_4$ (M^+) 252.1361, found 252.1355.



(2*R*,3*R*)-3,6-Dihydro-2-(4-(tetrahydro-2*H*-pyran-2-yl)oxybut-2-ynyl)-2*H*-pyran-3-yl Carbamate (13): To an ice-cooled solution of crude **12** (217 mg) in CH_2Cl_2 (4 ml) was added trichloroacetylisocyanate (240 mg, 1.28 mmol), and the mixture was stirred at 0 °C for 3 h. Most of the CH_2Cl_2 was removed in vacuo and the residue was dissolved into MeOH (4 ml). 2 M K_2CO_3 (1.2 ml) was added at 0 °C, and the mixture was stirred at room temperature overnight. The reaction mixture was extracted with CH_2Cl_2, washed with brine, dried, concentrated, and chromatographed (SiO_2 5 g, hexane/AcOEt = 1/1) to give **13** (237 mg, 100%) as a colorless solid: $[\alpha]^{22}_D$ –227.7° (*c* 0.92, $CHCl_3$); FTIR (neat) 3456, 3352, 1716, 1604, 1377, 1309, 1084 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.07 (m, 2H), 5.05 (m, 1H), 4.81 (m, 3H), 4.33-4.19 (m, 4H), 3.86-3.77 (m, 2H), 3.54 (m, 1H), 2.59 (brd, *J* = 6.8 Hz, 2H), 1.81-1.54 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 131.8, 122.9, 96.6, 81.7, 74.8, 66.1, 65.3, 61.9, 54.4, 30.2, 25.3, 21.3, 19.0; MS (EI) m/z 85 (100), 105, 133, 183, 294 [$(M-H)^+$]; HRMS (EI) calcd for $C_{15}H_{20}NO_5$ [$(M-H)^+$] 294.1341, found 294.1344.

Aminohydroxylation of 13

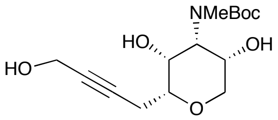


To a stirred solution of **13** (237 mg, 0.828 mmol) in *n*-propanol (9 ml) was added 0.08 M NaOH (9 ml) at room temperature. After stirring at room temperature for 5 min, *tert*-butyl hypochlorite (96 mg, 0.882 mmol) was added, and stirring was continued at room temperature for 25 min. *N*,*N*-diisopropylethylamine (5.16 mg, 0.04 mmol) was added and, 5 min later, $K_2OsO_2(OH)_4$ (30 mg, 0.08 mmol) was added with a few drops of 0.08 M NaOH. After stirring at room temperature for 80 min, the reaction was quenched with Na_2SO_3 (150 mg). Most of the *n*-propanol was evaporated in vacuo and the residue was extracted with AcOEt. The extract was washed with brine, dried over Na_2SO_4, concentrated, and chromatographed (SiO_2 19 g, AcOEt) to give **14** (142 mg, 57 %) and **15** (20.0 mg, 8%) each as a colorless amorphous solid together with recovered **13** (21.0 mg, 9%).

Compound 14: $[\alpha]^{20}_D$ –96.8° (*c* 1.24, $CHCl_3$); FTIR (neat) 3392, 1751, 1392, 1265, 1219, 1115, 1018 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.63 (s, 1H), 4.78 (d, *J* = 3.4 Hz, 1H), 4.60 (m, 1H), 4.29 (dt, *J* = 15.1, 2.0 Hz, 1H), 4.19 (d, *J* = 15.1 Hz, 1H), 4.07 (dd, *J* = 2.4, 12.2 Hz, 1H), 3.83 (m, 3H), 3.71 (dt, *J* = 2.0, 7.3 Hz, 1H), 3.53 (m, 1H), 3.48 (d, *J* = 12.7 Hz, 1H), 2.70

(d, *J* = 7.2 Hz, 2H), 1.69-1.50 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 96.8, 81.1, 78.1, 74.2, 74.1, 68.9, 63.7, 62.1, 62.0, 54.5, 53.3, 30.2, 25.3, 21.6, 19.1, 19.0; MS (EI) m/z 85 (100), 158, 211, 256, 284, 311 (M^+); HRMS (EI) calcd for $C_{15}H_{21}NO_6$ (M^+) 311.1369, found 311.1346.

Compound 15: $[\alpha]^{19}_D$ –72.5° (*c* 1.10, $CHCl_3$); FTIR (neat) 3354, 2243, 1751, 1356, 1215, 1126, 1024 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (brd, *J* = 13.6 Hz, 1H), 4.79 (t, *J* = 3.18 Hz, 1H), 4.47 (dd, *J* = 2.4, 6.3 Hz, 1H), 4.39 (d, *J* = 14.2 Hz, 1H), 4.28 (dt, *J* = 15.6, 2.0 Hz, 1H), 4.19 (d, *J* = 15.6 Hz, 1H), 3.92-3.75 (m, 4H), 3.53(m, 1H), 3.37 (t, *J* = 7.0 Hz, 1H), 2.65 (m, 2H), 2.00 (br, 1H), 1.81-1.54 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 96.8, 96.7, 81.9, 77.4, 75.6, 73.3, 66.5, 65.01, 65.0, 62.0, 54.5, 53.9, 30.2, 30.1, 25.3, 21.6, 19.0; MS (EI) m/z 85 (100), 158, 210, 280, 311 (M^+); HRMS (EI) calcd for $C_{15}H_{21}NO_6$ (M^+) 311.1369, found 311.1348.



***tert*-Butyl (2*R*,3*R*,4*R*,5*S*)-Tetrahydro-3,5-dihydroxy-2-(4-hydroxybut-2-ynyl)-2*H*-pyran-4-ylmethylcarbamate (16):** A mixture of **14** and **15** (1.71 g, 5.49 mmol) was dissolved in 4:1 DMF-acetone (34 ml). 2-Methoxypropene (1.2 g, 16.5 mmol) and PPTS (97 mg, 0.38 mmol) were added to this solution at room temperature, and the mixture was stirred at room temperature overnight. The reaction mixture was diluted with AcOEt, washed with saturated $NaHCO_3$ and brine, dried, concentrated, and chromatographed (SiO_2 100 g, hexane/AcOEt = 4/1-2/1) to give a mixture of the corresponding acetonides (1.58 g, 82 %), which was used for the next reaction without separation.

Major acetonide: FTIR (neat) 2239, 1759, 1385, 1271, 1234, 1122, 1028 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.79 (s, 1H), 4.69 (m, 1H), 4.56 (t, *J* = 7.8 Hz, 1H), 4.26-4.15 (m, 3H), 4.05 (dd, *J* = 4.0, 8.1 Hz, 1H), 3.85 (m, 1H) 3.67 (dd, *J* = 13.5, 4.0 Hz, 1H), 3.50 (m, 1H), 3.41 (dt, *J* = 8.1, 2.0 Hz, 1H), 2.67 (d, *J* = 7.2 Hz, 2H), 1.90-1.40 (m, 6H), 1.81 (s, 3H), 1.40 (s, 3H); MS (EI) m/z 85, 192, 251 (100), 336, 351 (M^+); HRMS (EI) calcd for $C_{18}H_{25}NO_6$ (M^+) 351.1682, found 351.1682.

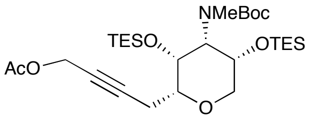
Minor acetonide: FTIR (neat) 2235, 1757, 1683, 1378, 1239, 1117, 1028 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.81（t、*J* = 3.0 Hz, 1H）, 4.56 (d, *J* = 4.5 Hz, 2H), 4.35-4.10(m, 3H), 4.12 (m, 1H), 3.84 (m, 1H), 3.60-3.51 (m, 3H), 2.64 (d, *J* = 7.2 Hz, 2H), 1.90 –1.50 (m, 6H), 1.79 (s, 3H), 1.40 (s, 3H); MS (EI) m/z 85 (100),252, 267, 336, 351 (M^+); HRMS (EI) calcd for $C_{18}H_{25}NO_6$ (M^+) 351.1682, found 351.1675.

The mixture of acetonides (1.58 g) was dissolved into THF (45 ml) and cooled to 0 °C. $LiAlH_4$ (513 mg, 13.5 mmol) was added, and the mixture was stirred overnight. 3 M NaOH (10 ml) was added, and the reaction mixture was filtered through Celite, concentrated, and chromatographed (SiO_2 100 g, hexane/AcOEt = 1/1) to give a mixture of the corresponding methyl amines (1.25 g, 80%).

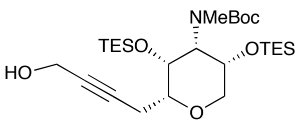
The mixture was dissolved into methanol (47 ml). 35% HCl (4.8 ml) was added to the solution. The mixture was refluxed for 23 h and then cooled to 0 °C. NaOH (3 N, 17 ml) and Boc_2O (3.1g, 14.2 mmol) were added to the mixture and further stirred for 19 h. Saturated NH_4Cl (20 ml) was added to the mixture which was extracted with CH_2Cl_2 (100 ml). Organic layer was washed by brine (40 ml) dried and concentrated. The residue (263 mg) was purified by column chromatography (SiO_2 125 g, hexane/AcOEt = 2/1-1/2) to give **16** (1.19 g, 3.77 mmol, 80%) as white amorphous.

$[\alpha]^{25}_D$ –21.4° (*c* 1.02, $CHCl_3$); FTIR (neat) 3392, 2974, 2927, 1668, 1446, 1363, 1153, 1099, 1014 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (brd, *J* = 6.8 Hz, 1H), 4.45 (br, 1H), 4.21 (s, 2H), 4.13 (d, *J* = 8.0 Hz, 1H), 4.07 (br, 1H), 4.02 (d, *J* = 12.4 Hz, 1H), 3.87 (s, 1H), 3.65 (d, *J* = 12.0 Hz, 1H), 3.55 (t, *J* = 7.2 Hz, 1H), 3.22 (s, 3H), 2.70-2.58 (m, 2H), 1.48 (s, 9H); ^{13}C

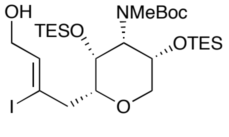
NMR (100 MHz, $CDCl_3$) δ 156.6, 81.6, 80.5, 79.2, 77.2, 73.4, 70.6, 70.0, 57.9, 51.0, 33.7, 28.4, 21.5; MS (EI) m/z 57 (100), 104, 172, 228, 315 (M^+); HRMS (EI) calcd for $C_{15}H_{25}NO_6$ (M^+) 315.1681, found 315.1668.



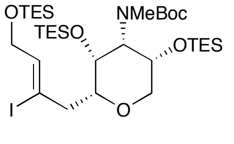
***tert*-Butyl (2*R*,3*R*,4*R*,5*S*)-2-(4-Acetoxybut-2-ynyl)-3,5-bis(triethylsilyloxy)-tetrahydro-2*H*-pyran-4-ylmethylcarbamate:** To an ice-cooled solution of **16** (1.18 g, 3.74 mmol) in pyridine (37 ml) was added Ac_2O (573 mg, 5.61 mmol), and the mixture was stirred at room temperature overnight. The reaction was quenched with MeOH (1 ml) and the reaction mixture was extracted with CH_2Cl_2. The extract was washed with brine, dried, and concentrated. The residue (1.81 g) was dissolved into CH_2Cl_2 (20 ml) and cooled to –78 °C. 2,6-Lutidine (1.52 g, 14.2 mmol) and TESOTf (3.21 g, 12.17 mmol) were added, and the mixture was stirred at –78 °C for 4 h. The reaction was quenched with aaturated NH_4Cl, and the reaction mixture was extracted with AcOEt. The extract was washed with brine, dried, concentrated, and chromatograped (SiO_2 60 g, hexane/AcOEt = 20/1) to give the acetate (1.74 g, 80 %) as a colorless oil: $[\alpha]^{24}_D$ –21.7° (*c* 1.15, $CHCl_3$); FTIR (neat) 2239, 1232, 1147, 1011 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.66 (s, 2H), 4.10 (s, 2H), 4.00 (s, 1H), 3.93 (d, *J* = 12.2 Hz, 1H), 3.56 (d, *J* = 11.2 Hz, 1H), 3.46 (t, *J* = 6.6 Hz, 1H), 3.16 (s, 3H), 2.51 (br, 2H), 2.08 (s, 3H), 1.48 (s, 9H), 0.99-0.94 (m, 18H), 0.69-0.58 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 156.5, 84.0, 79.6, 77.2, 76.0, 74.0, 71.1, 69.7, 55.9, 52.6, 33.8, 28.3, 21.9, 20.6, 7.0, 6.7, 5.4, 5.1, 5.0; MS (EI) m/z 145, 246, 356, 456, 500 (100), 585 $(M)^+$; HRMS (EI) calcd for $C_{29}H_{55}NO_7Si_2$ (M^+) 585.3517, found 585.3514.



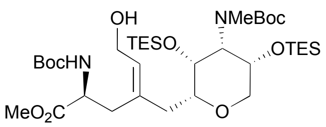
***tert*-Butyl (2*R*,3*R*,4*R*,5*S*)-Tetrahydro-3,5-bis(triethylsilyloxy)-2-(4-hyroxybut-2-ynyl)-2*H*-pyran-4-ylmethylcarbamate (17):** To an iced-cooled solution of the acetate (1.74 g, 2.97 mmol) in MeOH (30 ml) was added K_2CO_3 (410 mg, 2.97 mmol), and the mixture was stirred at room temperature for 3 h. NH_4Cl (20 ml) was added and the reaction mixture was extracted with AcOEt. The extract was washed with brine, dried, concentrated, and chromatographed (SiO_2 70 g, hexane/AcOEt = 3/1) to give **17** (1.72 g, 100%) as a colorless oil: $[\alpha]^{24}_D$ –20.5° (*c* 1.02, $CHCl_3$); FTIR (neat) 3442, 1684, 1456, 1366, 1307, 1241, 1150, 1006 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.24 (br, 2H), 4.10 (d, *J* = 1.8 Hz, 1H), 4.08 (d, *J* = 2.4 Hz, 1H), 4.01 (s, 1H), 3.94 (d, *J* = 12.0 Hz, 1H), 3.56 (d, *J* = 12.6 Hz, 1H), 3.46 (t, *J* = 7.1 Hz, 1H), 3.16 (s, 3H), 2.48 (m, 2H), 1.48 (s, 9H), 0.96 (m, 18H), 0.62 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 82.5, 80.7, 79.8, 77.2, 74.1, 71.2, 69.7, 56.1, 51.1, 33.7, 28.4, 21.9, 7.0, 6.8, 5.1, 5.0; MS (EI) m/z 246, 319, 349, 414, 458 (100), 543 (M^+); HRMS (EI) calcd for $C_{27}H_{53}NO_6Si_2$ (M^+) 543.3411, found 543.3406.



***tert*-Butyl (2*R*,3*R*,4*R*,5*S*)-3,5-Bis(triethylsilyloxy)-tetrahydro-2-((*Z*)-4-hydroxy-2-iodobut-2-enyl)-2*H*-pyran-4-ylmethylcarbamate:** To an ice-cooled solution of **17** (1.35 g, 2.48 mmol) in Et_2O, was added $NaH_2Al(OCH_2CH_2OMe)_2$ (Red-Al) (65% in toluene, 5.2 ml, 17.38 mmol). After stirring at 0° C for 2 h, additional Red-Al (65% in toluene, 1.5 ml, 4.96 mmol) was added, and the mixture was stirred at room temperature for 18 h. The reaction mixture was cooled to 0 °C and AcOEt (1.7 ml, 17.4 mmol) was added. After being stirred at 0 °C for 10 min, the mixture was cooled to –40 °C and solid I_2 (945 mg, 3.72 mmol) was added. The reaction mixture was allowed to warm up to room temperature and stirred at room temperature for 2 h. The reaction was quenched with saturated $Na_2S_2O_3$ (5 ml) at 0 °C, and the reaction mixture was diluted with AcOEt, filtrated through Celite, washed with brine, dried, and concentrated. Purification of the residue by column chromatography (SiO_2 90 g, hexane/AcOEt = 10/1) gave the title alkenyl iodide (965 mg, 58 %) as colorless oil: $[\alpha]^{24}_{D}$ +3.5° (*c* 0.93, $CHCl_3$); FTIR (neat) 3436, 1685, 1456, 1364, 1241, 1147, 1009 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (t, *J* = 5.4 Hz, 1H), 4.22 (br, 2H), 4.10 (s, 1H), 4.02 (s, 1H), 3.97 (s, 1H), 3.93 (d, *J* = 12.0 Hz, 1H), 3.63 (d, *J* = 9.6 Hz, 1H), 3.51 (d, *J* = 12.0 Hz, 1H), 3.15 (s, 3H), 2.92 (dd, *J* = 10.4, 14.8 Hz, 1H), 2.36 (d, *J* = 14.8 Hz, 1H), 1.48 (s, 9H), 0.97 (m, 18H), 0.61 (q, *J* = 7.7 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 136.1, 105.9, 79.6, 78.9, 73.9, 72.7, 69.6, 67.3, 56.5, 48.0, 33.7, 28.4, 7.0, 6.8, 5.3, 5.1; MS (EI) m/z 227, 246, 586 (100), 642, 671 (M^+); HRMS (EI) calcd for $C_{27}H_{54}INO_6Si_2$ (M^+) 671.2535, found 671.2529.



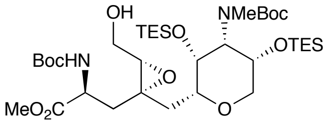
***tert*-Butyl (2*R*,3*R*,4*R*,5*S*)-Tetrahydro-2-((*Z*)-4-triethylsilyloxy-2-iodobut-2-enyl)-3,5-bis(triethylsilyloxy)-2*H*-pyran-4-ylmethylcarbamate (18):** To an ice-cooled solution of the alkenyl iodide (104 mg, 0.155 mmol) in CH_2Cl_2 (1.5 ml) were added Et_3N (20 mg, 0.197 mmol), DMAP (2 mg, 0.0155 mmol), and TESCl (28 mg, 0.186 mol). After being stirred at room temperature for 11 h, the reaction mixture was diluted with hexane, washed with water and brine, dried, and concentrated. Purification of the residue by column chromatography (SiO_2 18 g, hexane/AcOEt = 20/1) gave **18** (122.7 mg, 100%) as a colorless oil: $[\alpha]^{25}_{D}$ +3.6° (*c* 1.04, $CHCl_3$); FTIR (neat) 1686, 1457, 1345, 1240, 1148 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (t, *J* = 5.4 Hz, 1H), 4.22 (d, *J* = 4.9 Hz, 2H), 4.09 (s, 1H), 4.01 (s, 1H), 3.96 (s, 1H), 3.91 (d, *J* = 12.7 Hz, 1H), 3.60 (d, *J* = 10.2 Hz, 1H), 3.49 (d, *J* = 12.2 Hz, 1H), 3.15 (s, 3H), 2.89 (dd, *J* = 10.2, 14.6 Hz, 1H), 2.33 (d, *J* = 14.2 Hz, 1H), 1.48 (s, 9H), 0.97 (t, *J* = 7.8 Hz, 27H), 0.62 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 136.9, 103.2, 79.6, 78.9, 73.8, 72.7, 69.7, 68.2, 56.6, 48.0, 33.6, 28.4, 7.0, 6.8, 6.7, 6.5, 5.8, 5.3, 5.2, 4.4; MS (FAB) m/z 154 (100), 307, 686, 786 $[(M+H)^+]$; HRMS (FAB) calcd for $C_{33}H_{69}INO_6Si_3$ $[(M+H)^+]$ 786.3478, found 786.3447.



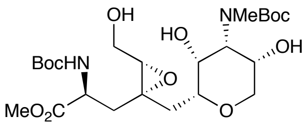
Compound 19: A mixture of (*R*)-*N*-Boc-3-iodoalanine methyl ester (1.4 g, 4.26 mmol) and Zn-Cu (2.29 g) in benzene (14 ml) and *N, N'*-dimethylacetamide (DMA) (1.4 ml) was sonicated at 45 °C until the starting material disappeared on TLC. This mixture of the organozinc reagent was added to a degassed mixture of **18** (1.11 g, 1.41 mmol) and $(PPh_3)_4Pd$ (326 mg, 0.282 mmol) in benzene (14 ml) and HMPA (1.4 ml), and the mixture was heated at 80 °C for 2 h. After cooling, the reaction mixture was diluted with AcOEt, filtered through Celite, washed with saturated $NaHCO_3$ and brine, dried, concentrated, and chromatographed (SiO_2 96 g, hexane/AcOEt = 12/1) to give the coupling product accompanied by some decomposed products as a yellow oil (1.59 g).

To a solution of the coupling product (1.59 g) in THF (16 ml) were added AcOH (102 mg, 1.69 mmol) and TBAF (1.0 M in THF 1.27 ml, 1.27 mmol), and the mixture was stirred at room temperature for 1h. The reaction mixture was diluted with AcOEt, washed with saturated $NaHCO_3$ and brine, dried, and concentrated. The residue was chromatographed (SiO_2 64g, hexane/AcOEt = 4/1-2/1) to give **19** (959 mg, 91%) as a colorless oil: $[\alpha]^{23}_{D}$ +5.9° (*c* 0.97, $CHCl_3$); FTIR (neat) 3357, 1687, 1455, 1365, 1240, 1148, 1049, 1006 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67 (t, *J* = 7.5 Hz, 1H), 5.39 (brd, *J* = 7.5 Hz, 1H), 4.41 (br, 1H), 4.12 (d, *J* = 7.5 Hz, 2H), 4.02 (d, *J* = 12.5 Hz, 2H), 3.92 (d, *J* = 12.5 Hz, 2H), 3.73 (s, 3H), 3.46 (d, *J* = 12.0 Hz, 1H), 3.39 (d, *J* = 10.5 Hz, 1H), 3.15 (s, 3H), 2.67 (br, 1H), 2.48 (m, 2H), 1.95 (d, *J* = 14.0 Hz, 1H), 1.47 (s, 9H), 1.42 (s, 9H), 0.98 (m, 18H), 0.61 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 156.4, 155.4, 137.1, 129.1, 80.7, 79.9, 79.5, 73.3, 69.5, 58.3, 56.5, 52.3, 52.1, 40.0, 33.5, 33.3, 28.4, 28.2, 7.0, 6.8, 5.3, 5.1; MS (FAB) m/z 57 (100), 218, 591, 648, 748 $[(M+H)^+]$; HRMS (FAB) calcd for $C_{36}H_{71}N_2O_{10}Si_2$ $[(M+H)^+]$ 747.4648, found

747.4655.

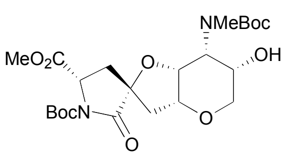


Compound 20: To a suspention of powdered 4 A molecular sieves (930 mg) in CH_2Cl_2 were added (+)-diisopropyl L-tartrate (DIPT) (29 mg, 0.126 mmol) and Ti(O-*i*-Pr)$_4$ (32 mg, 0.113 mmol) at –35 °C, and the mixture was stirred at –35 °C for 50 min. *ter*t-Butyl hydroperoxide (TBHP) (2.86 M in CH_2Cl_2, 0.88 ml, 2.51 mmol) was added, and then 70 min later, a solution of **19** (938 mg, 1.26 mmol) in CH_2Cl_2 (10 ml) was added. After stirring at –35 °C for 15 h, 17% aqueous acetone (20 ml) was added, and the mixture was stirred at room temperature for 30 min. The reaction mixture was filtered through Celite and concentrated. The residue was dissolved into toluene, evaporated to remove the remaining TBHP by azeotropic distillation, and chromatographed (SiO_2 30 g, Hexane/AcOEt = 2/1-1/1) to give **20** (755 mg, 79%) as a colorless amorphous solid. $[\alpha]^{23}_{D}$ +3.1° (*c* 1.17, $CHCl_3$); FTIR (neat) 3442, 1721, 1456, 1366, 1241, 1153, 1050 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.29 (brd, *J* = 6.9 Hz, 1H), 4.50 (br, 1H), 4.00 (br, 2H), 3.88 (m, 3H), 3.72 (m, 5H), 3.47 (d, *J* = 12.0 Hz, 1H), 3.31 (d, *J* = 9.9 Hz, 1H), 3.13 (s, 3H), 3.01 (t, *J* = 5.7 Hz, 1H), 2.30 (m, 3H), 1.79 (m, 1H), 1.45 (s, 9H), 1.43 (s, 9H), 0.96 (m, 18H), 0.60 (q, *J* = 8.1 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 156.5, 155.3, 79.9, 79.6, 77.8, 73.6, 73.4, 69.5, 60.9, 60.6, 60.4, 56.4, 52.3, 51.3, 37.4, 34.0, 33.6, 28.4, 28.2, 7.0, 6.8, 5.3, 5.1; MS (FAB) m/z 87, 607 (100), 764 $[(M+H)^+]$; HRMS (FAB) calcd for $C_{36}H_{71}N_2O_{11}Si_2$ $[(M+H)^+]$ 763.4596, found 763.4598.



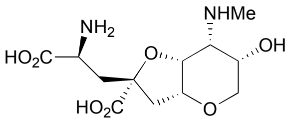
Compound 21: To a stirred solution of **20** (33 mg, 0.043 mmol) in THF (0.6 ml) were added AcOH (6.5 mg, 0.108 mmol) and TBAF (1.0 M in THF, 87 μl, 0.087 mmol) at 0 °C and the mixture was stirred at room temperature for 12 h. Additional AcOH (3.3 mg, 0.054 mmol) and TBAF (1.0 M in THF, 43 μl, 0.043 mmol) were added at 0 °C and stirring was continued at room temperature for 11 h. The reaction mixture was concentrated and chromatographed (SiO_2 4 g, AcOEt) to give **21** (25 mg, 100%) as a colorless oil: FTIR (neat) 3432, 1693, 1367, 1166, 1098 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.44 (brd, *J* = 7.2 Hz, 1H), 4.55 (br, 1H), 4.39 (br, 2H), 4.04-4.00 (m, 2H), 3.89 (s, 1H), 3.80 –3.60 (m, 3H), 3.76 (s, 3H), 3.59 (d, *J* = 12.0 Hz, 1H), 3.43 (m, 1H), 3.18 (s, 3H), 3.12 (t, *J* = 5.8 Hz, 1H), 2.30-2.15 (m, 2H), 1.81 (m, 2H), 1.49 (s, 9H), 1.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 156.0, 155.3, 79.9, 79.7, 76.4, 72.8, 72.4, 69.7, 60.7, 59.8, 59.4, 56.4, 52.1, 50.8, 35.8, 33.2, 32.8, 27.9; MS (FAB) m/z 154, 379 (100), 435, 535 $[(M+H)^+]$; HRMS (FAB) calcd for $C_{24}H_{43}N_2O_{11}$ $[(M+H)^+]$ 535.2867, found 535.2861.

Compound 23: To a stirred solution of **21** (450 mg, 0.842 mmol) in CH_2Cl_2 (8 ml) was added PPTS (212 mg, 0,842 mmol), and the mixture was stirred at room temperature for 9 h. The reaction was quenched with saturated $NaHCO_3$, and the reaction mixture was extracted with AcOEt. The extract was washed with brine, dried, and concentrated to give **22** (391 mg) as a yellow oil, which was used for the next reaction without purification.



To a solution of crude **26** (391 mg) in 20% aqueous THF (4.5 ml) was added $NaIO_4$ (386 mg, 1.85 mmol) at 0 °C. After stirring at room temperature for 10 h, the reaction was quenched with saturated $Na_2S_2O_3$ (3 ml), and the reaction mixture was extracted with AcOEt. The extract was washed with saturated $NaHCO_3$ and brine, dried, concentrated, and chromatographed (SiO_2 9 g, hexane/AcOEt = 1/4) to give the corresponding aminal (291 mg) as a yellow oil, which was used for next reaction without further purification.

To a solution of crude aminal (291 mg) in MeCN (10 ml) were added 4 A molecular sieves (300 mg), *N*-methylmorpholine *N*-oxide (NMO) (136 mg, 1.16 mmol) tetra–*n*-propylammonium perruthenate (TPAP) (41 mg, 0.116 mmol) at room temperature, and stirring was continued for 90 minutes. The reaction mixture was filtered through Celite, concentrated, and chromatographed (SiO_2 17 g, hexane/AcOEt = 1/2 ~ 0/1) to give **23** (134 mg, 32%) as a colorless soild: $[\alpha]^{22}_D$ +29.6° (*c* 0.78, $CHCl_3$); FTIR (neat) 3429, 1793, 1754, 1680, 1454, 1368, 1291, 1150 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.64 (brd, *J* = 12.4 Hz, 1H), 4.45 (m, 2H), 4.20 (m, 2H), 4.00 (dd, *J* = 2.1, 11.9 Hz, 1H), 3.86 (d, *J* = 12.6 Hz, 1H), 3.77 (s, 3H), 3.58 (d, *J* = 13.3 Hz, 1H), 3.18 (s, 3H), 2.48 (d, *J* = 14.2 Hz, 1H), 2.34 (dd, *J* = 7.1, 12.8 Hz, 1H), 2.30 (dd, *J* = 8.5, 12.8 Hz, 1H), 2.08 (dd, *J* = 4.3, 14.2 Hz, 1H), 1.51 (s, 9H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 170.4, 149.1, 85.0, 84.6, 82.7, 79.8, 78.5, 72.5, 68.9, 55.0, 52.6, 42.8, 37.2, 28.4, 27.8; MS (FAB) m/z 154, 301 (100), 501 $[(M+H)^+]$, 523 $[(M+Na)^+]$; HRMS (FAB) calcd for $C_{23}H_{37}N_2O_{10}$ $[(M+H)^+]$ 501.2448, found 501.2459.

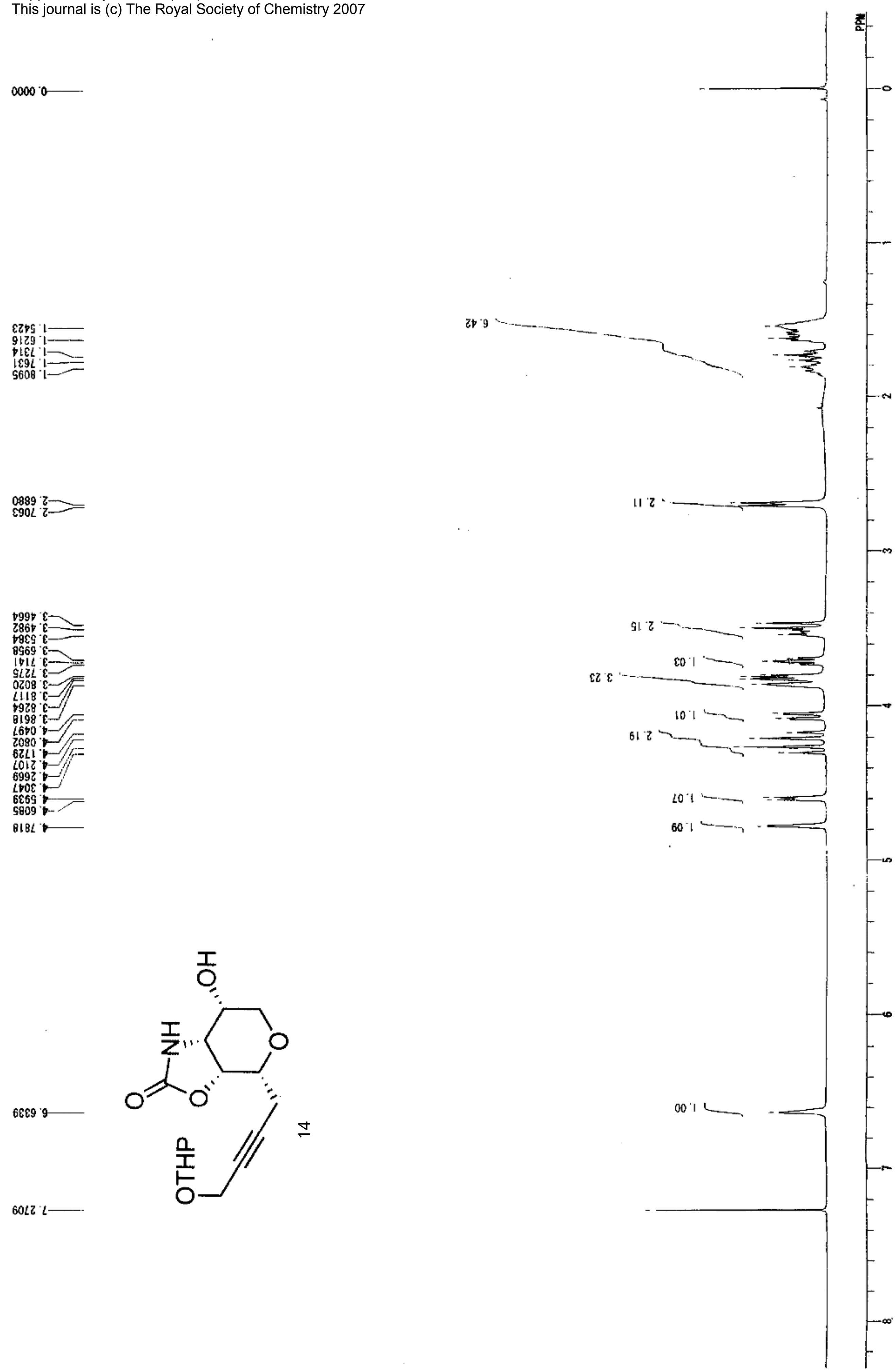


Dysiherbaine: A solution of **23** (28 mg, 0.056 mmol) in 6 M HCl (2.8 ml) was heated at 80 °C for 13 h. The reaction mixture was concentrated to give dysiherbaine hydrochloride (21 mg) as a pale yellow solid: $[\alpha]^{23}_D$ +7.0° (*c* 0.53 H_2O); ^1H NMR (500 MHz, D_2O) δ 4.39 (brt, *J* = 1.9 Hz, 1H), 4.22 (brs, 1H), 3.93 (br, 1H), 3.88 (dd, *J* = 2.8, 5.6 Hz, 1H), 3.86 (t, *J* = 3.0 Hz, 1H), 3.62 (t, *J* = 3.8 Hz, 1H), 3.56 (d, *J* = 13.0 Hz, 1H), 2.75 (dd, *J* = 3.4, 15.4 Hz, 1H), 2.73 (s, 3H), 2.62 (d, *J* = 14.0 Hz, 1H), 2.29 (dd, *J* = 3.5, 14.5 Hz, 1H), 2.12 (dd, *J* = 10.5, 15.4 Hz, 1H); ^{13}C NMR (100 MHz, D_2O) δ 178.3, 171.9, 87.1, 76.9, 76.5, 69.6, 62.9, 56.8, 52.1, 45.4, 38.9, 30.5. These spectral data were identical with those reported for natural dysiherbaine hydrochloride.[1]

Dysiherbaine hydrochloride (21 mg) was treated with 10 M NaOH and subjected to ion-exchange chromatography using IRC-50 to give dysiherbaine (18 mg, 100%) as a colorless solid: HPLC (YMC-Pack ODS-AM, 1x25cm, eluent: distilled water, flow: 2.0 ml/min. detect: UV 210 nm, retention time: 8.7 min); $[\alpha]^{23}_D$ –7.5° (*c* 0.52, H_2O) (lit.[2] $[\alpha]^{26}_D$ –3.5° (c 0.4, H_2O)); ^1H NMR (500 MHz, D_2O) δ 4.24 (brs, 1H), 4.08 (brs, 1H), 3.80 (dd, *J* = 2.0, 13.0 Hz, 1H), 3.78 (m, 1H), 3.47-3.44 (m, 2H), 3.43 (dd, *J* = 2.0, 11.8 Hz, 1H), 2.66 (s, 3H), 2.52 (dd, *J* = 2.0, 15.3 Hz, 1H), 2.50 (d, *J* = 14.0 Hz, 1H), 2.08 (dd, *J* = 3.5, 14.0 Hz, 1H), 1.85 (dd, *J* = 15.3, 11.8 Hz, 1H); ^{13}C NMR (100 MHz, D_2O) δ 179.8, 173.4, 88.5, 76.9, 75.9, 69.5, 62.9, 57.1, 53.5, 45.2, 39.5, 30.5; MS (FAB) m/z 115 (100), 154, 305 $[(M+H)^+]$; HRMS (FAB) calcd for $C_{12}H_{21}N_2O_7$ $[(M+H)^+]$ 305.1344, found 305.1351.

Reference

(1) H. Masaki, J. Maeyama, K. Kameda, T. Esumi, Y. Iwabuchi and S. Hatakeyama, *J. Am. Chem., Soc*. 2000, **122**, 5216.
(2) R. Sakai, H. Kamiya, M. Murata and K. Shimamoto, *J. Am. Chem. Soc*., 1997, **119**, 4112.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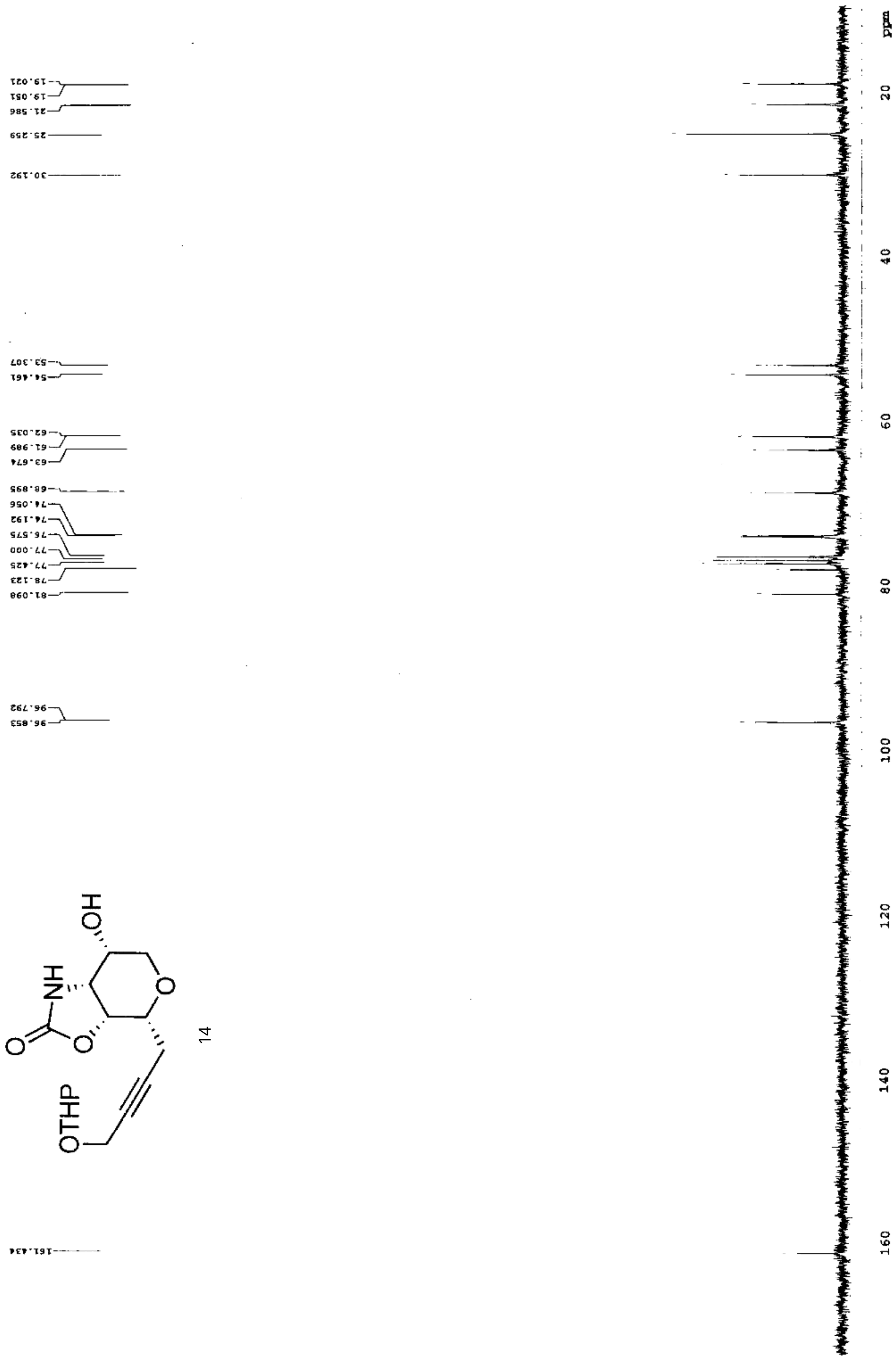
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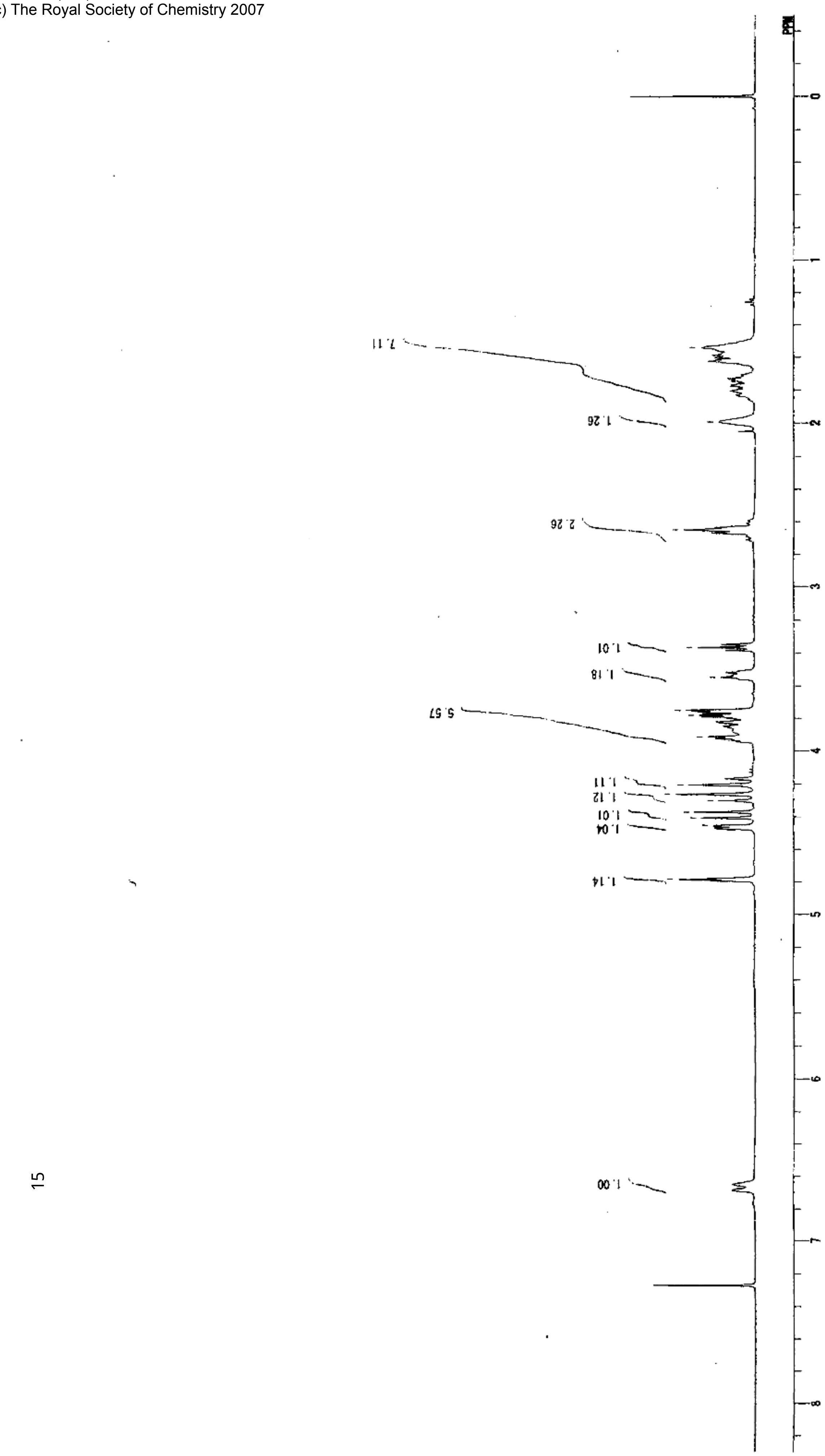
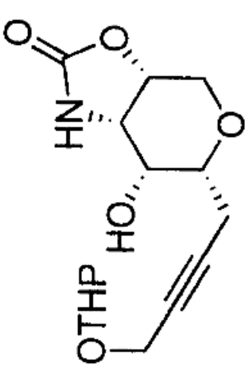
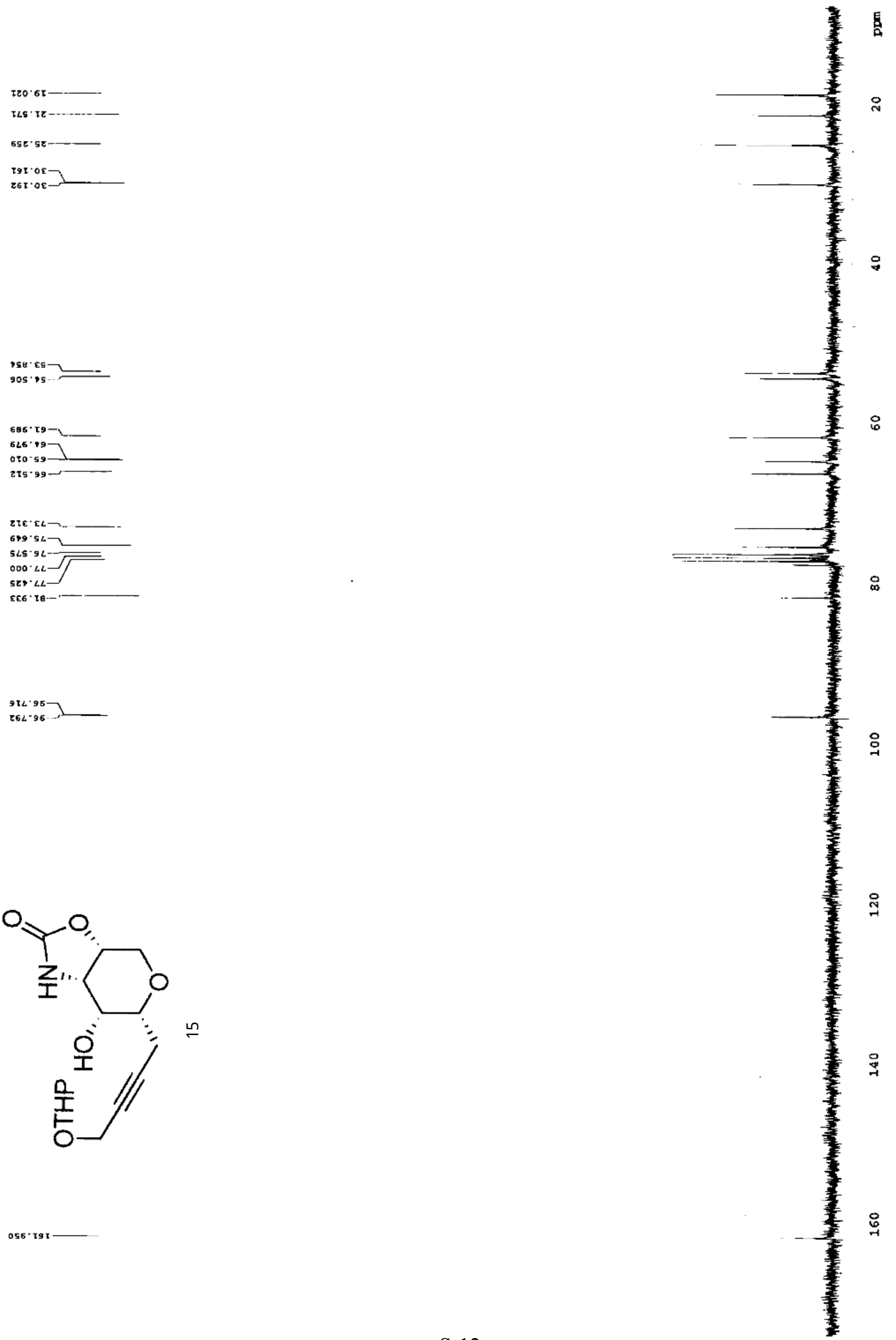
63.674
68.895
74.056
74.192
76.575
77.000
77.425
78.123
81.098
96.792
96.853
161.434
ppm
20
40
60
80
100
120
140
160
OH
NH
O
O
O
OTHP
14

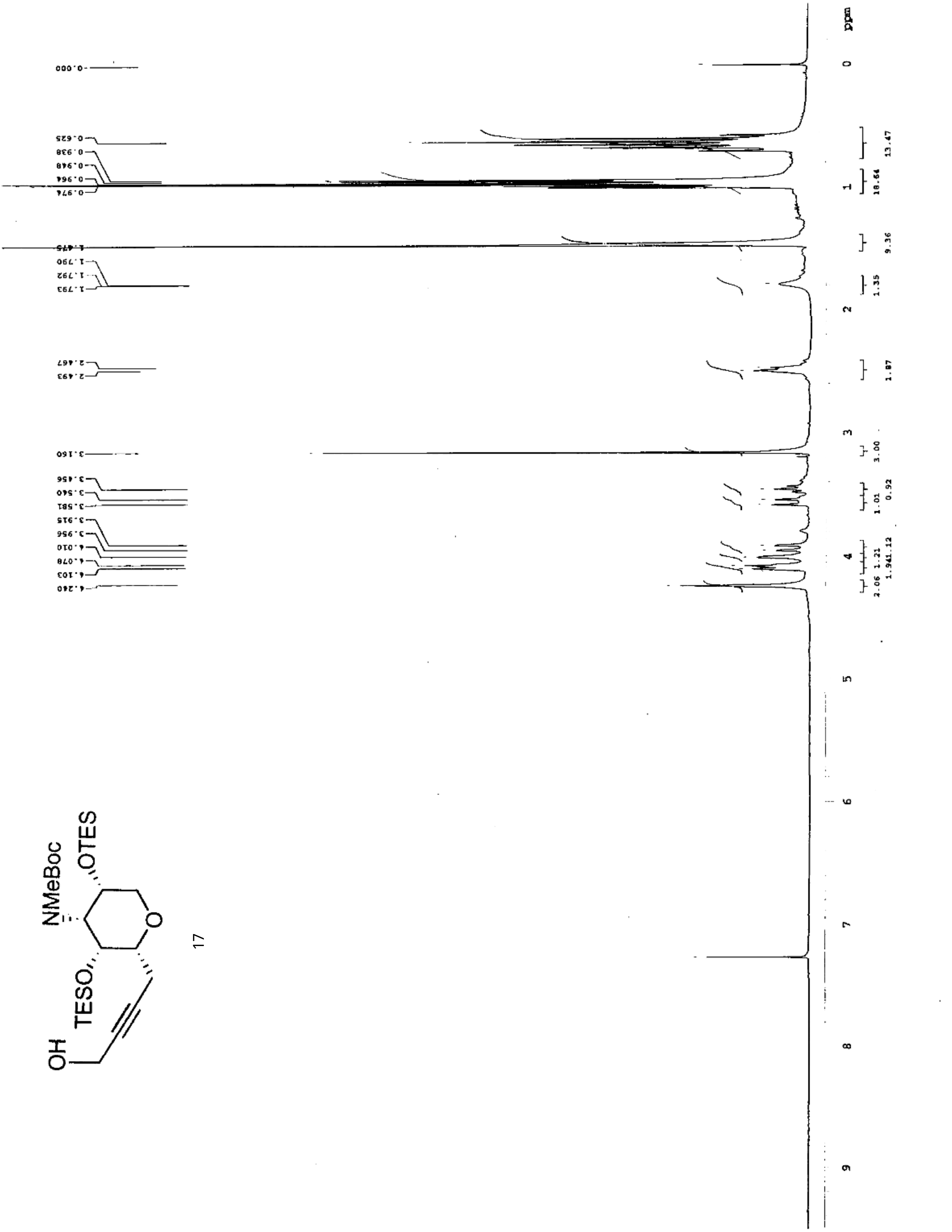

1.5410
1.9925
2.6502
3.3688
3.5482
3.7495
3.7837
3.9142
4.2083
4.2644
4.3035
4.3730
4.4084
4.4548
4.7866
7.11
1.26
2.26
1.01
1.18
5.57
1.11
1.12
1.01
1.04
1.14
1.00
PPM


OTHP
HO
HN
O

15


19.021
21.571
25.259
30.161
30.192
53.854
54.506
61.989
64.979
65.010
66.512
73.312
75.649
76.575
77.000
77.425
81.933
96.716
96.792
161.950
ppm
20
40
60
80
100
120
140
160
OTHP
HO
HN
O

15



17

Supplementary Material (ESI) for Chemical Communications
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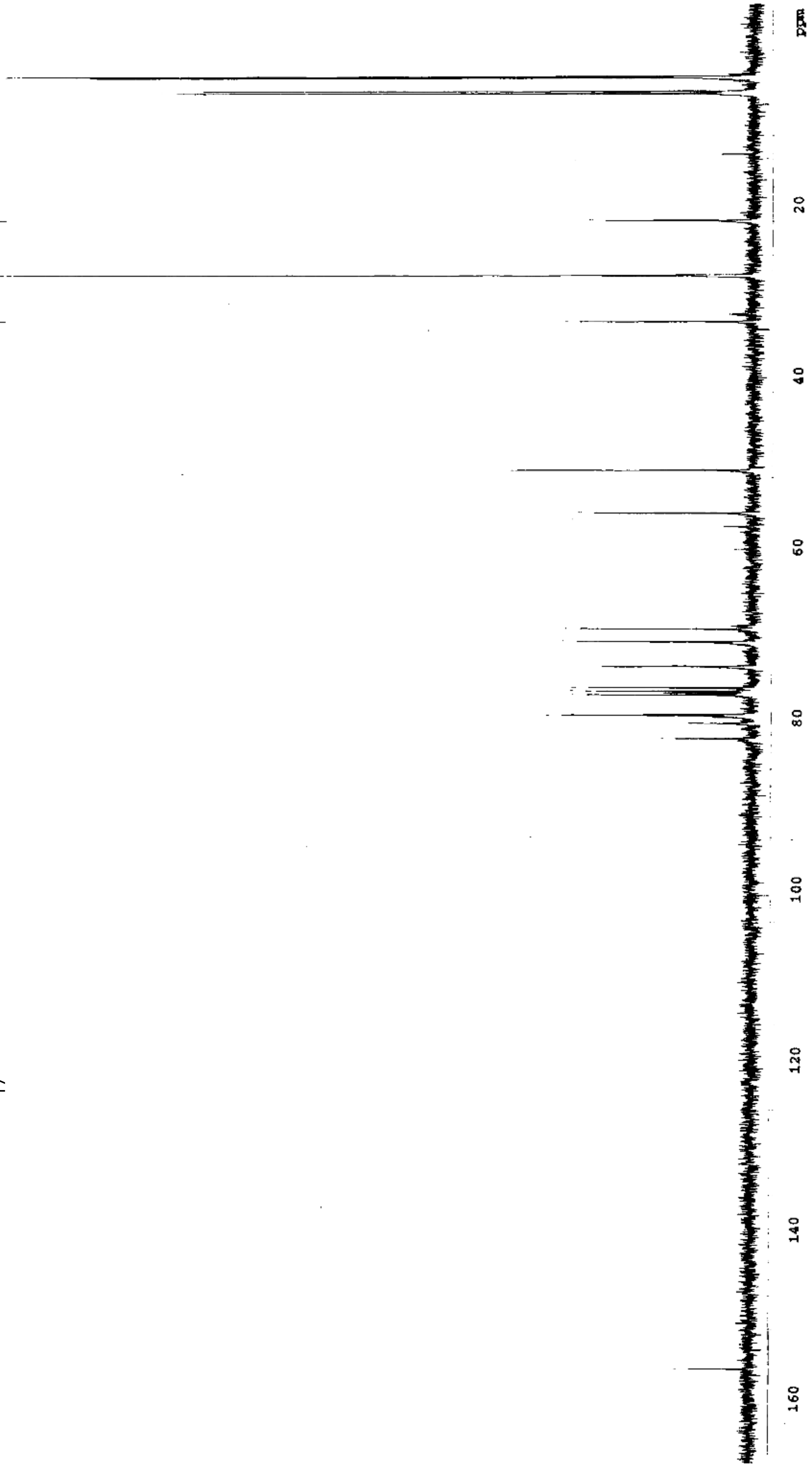
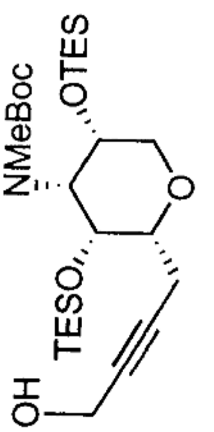
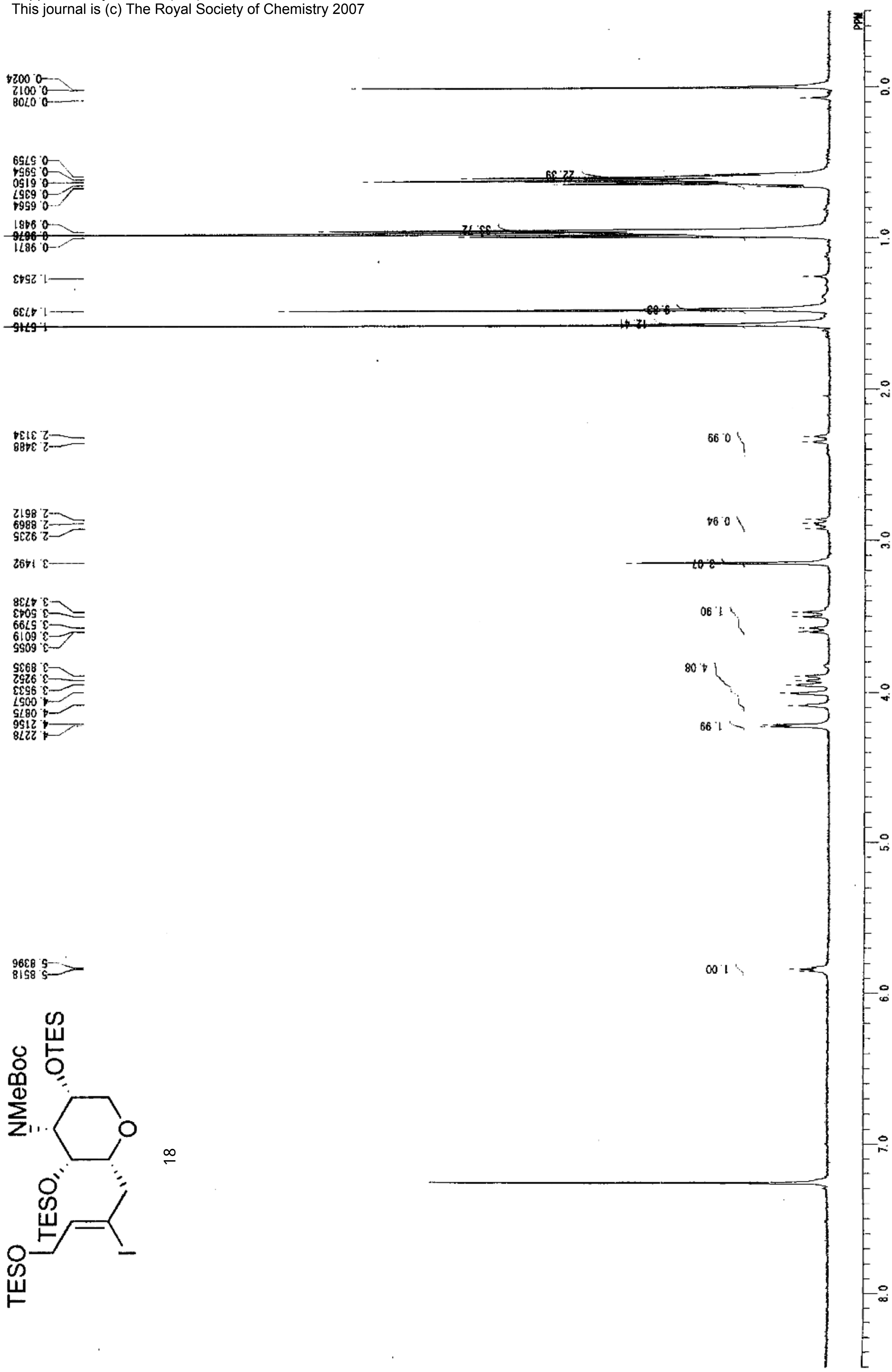
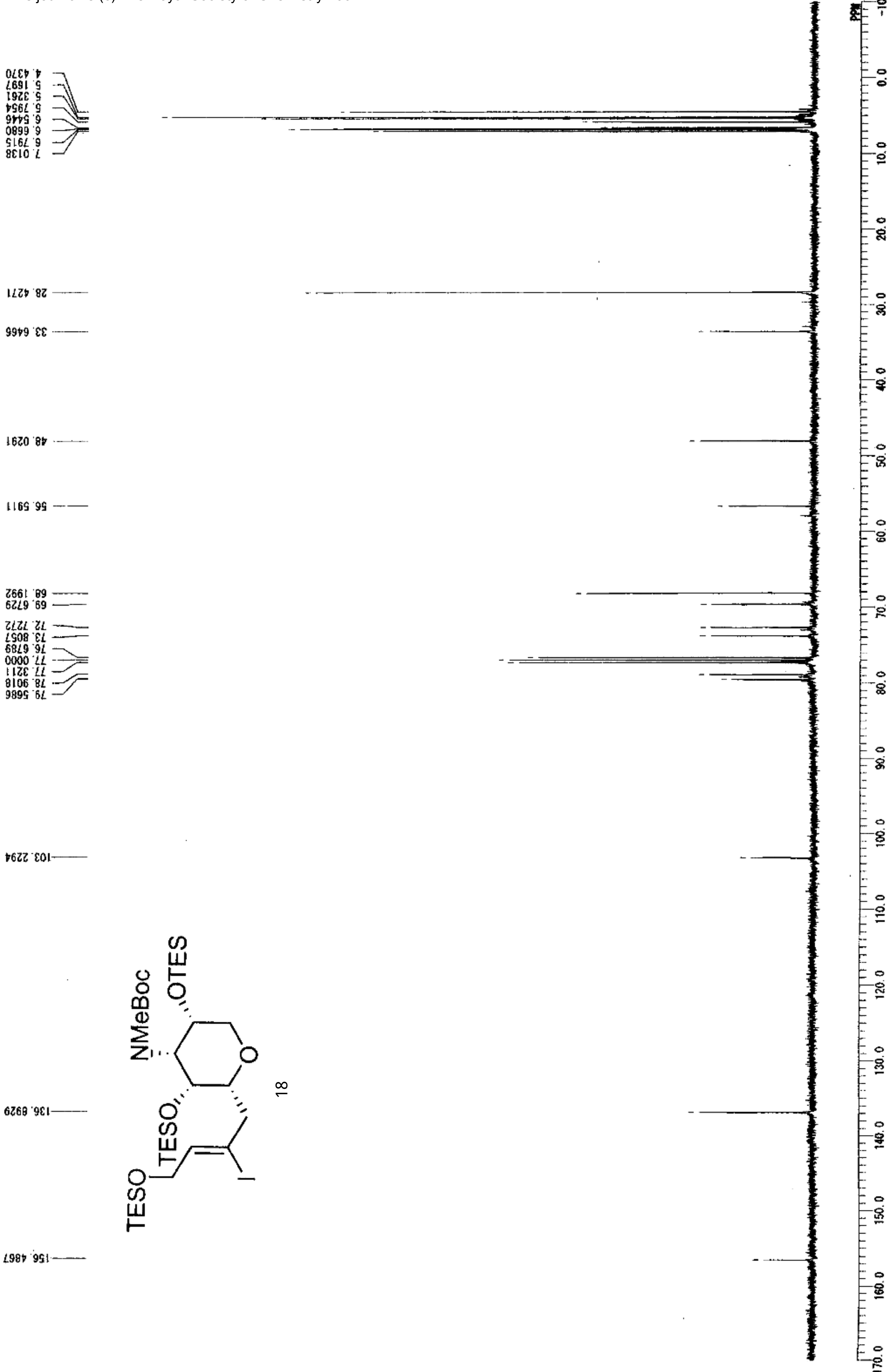




17



18


4.4370
5.1697
5.3261
5.7954
6.5446
6.6680
6.7915
7.0138
28.4271
33.6466
48.0291
56.6911
68.1992
69.6729
72.7272
73.8057
76.6789
77.0000
77.3211
78.9018
79.5686
103.2294
136.8929
156.4867
NMeBoc
OTES
TESO
TESO
O
I
18
PPM

Supplementary Material (ESI) for Chemical Communications
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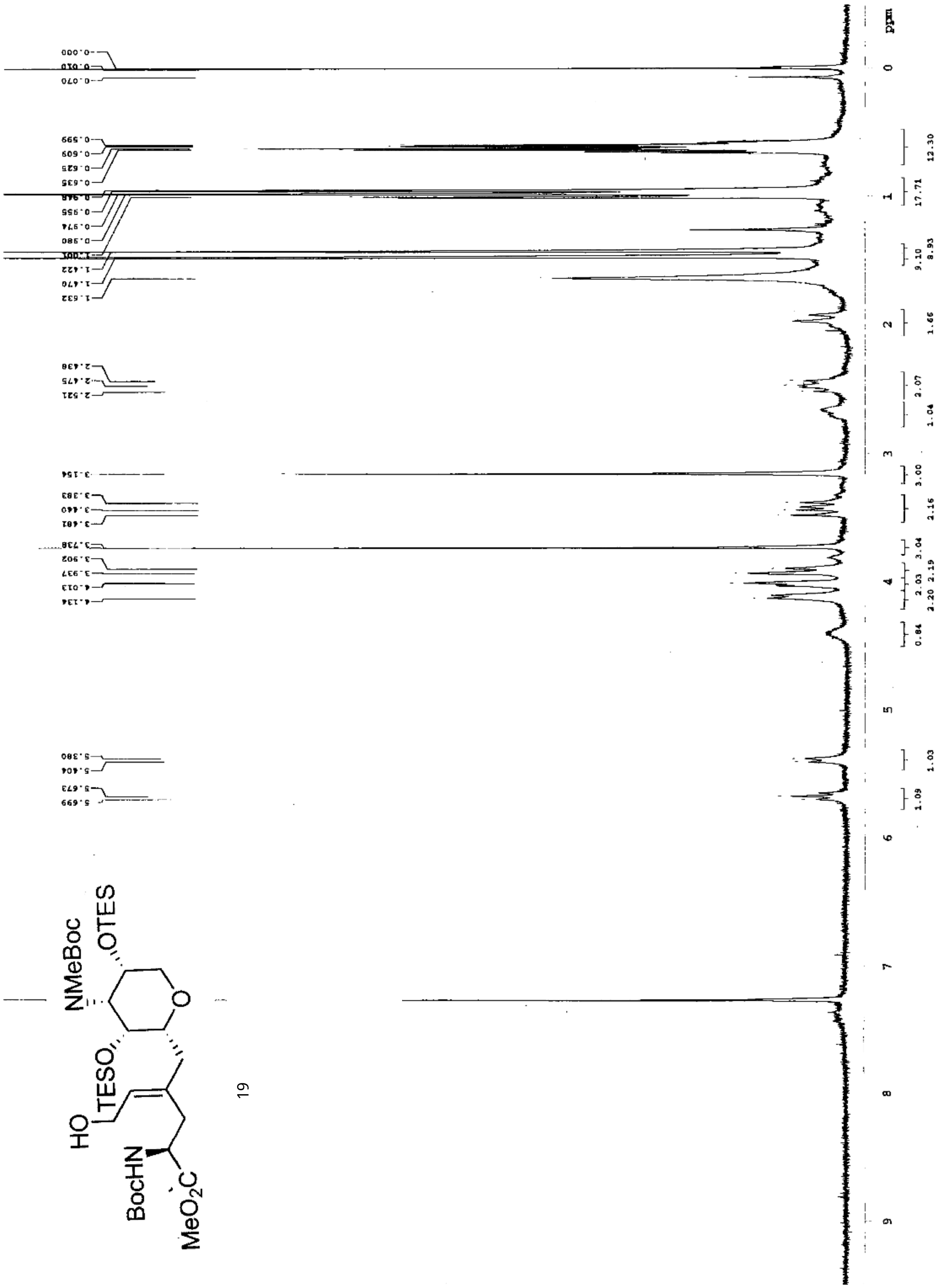

19

Supplementary Material (ESI) for Chemical Communications
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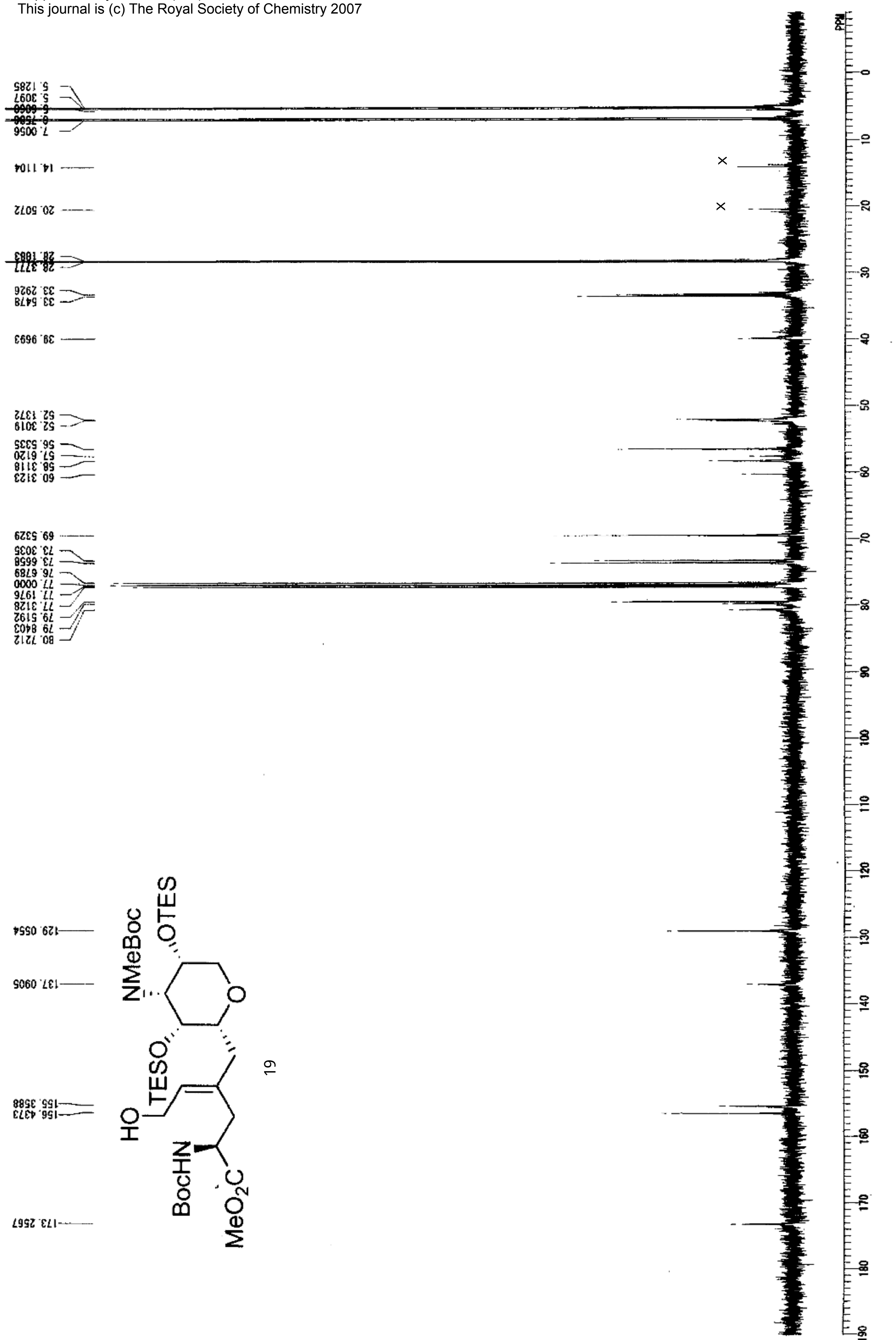
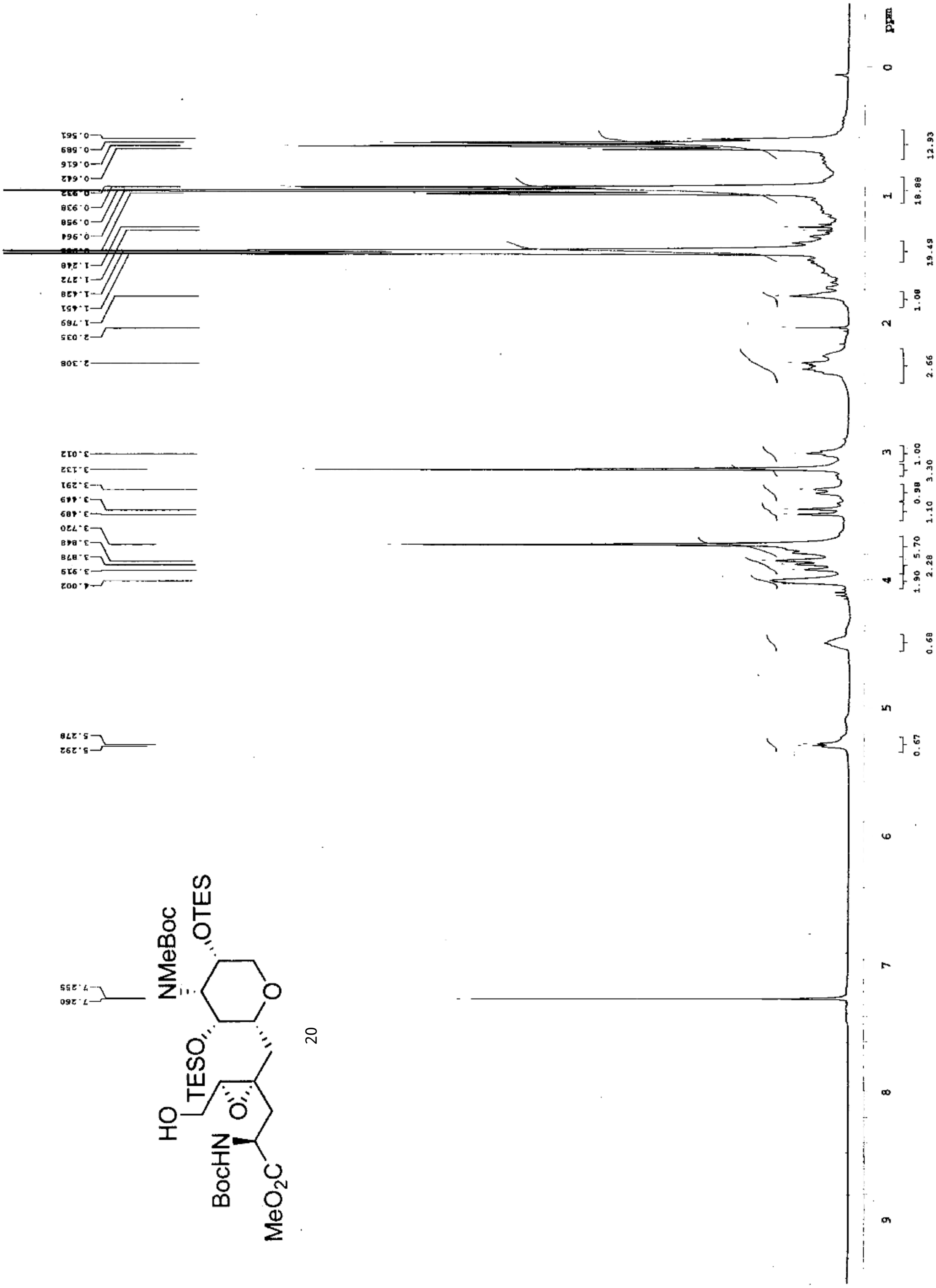
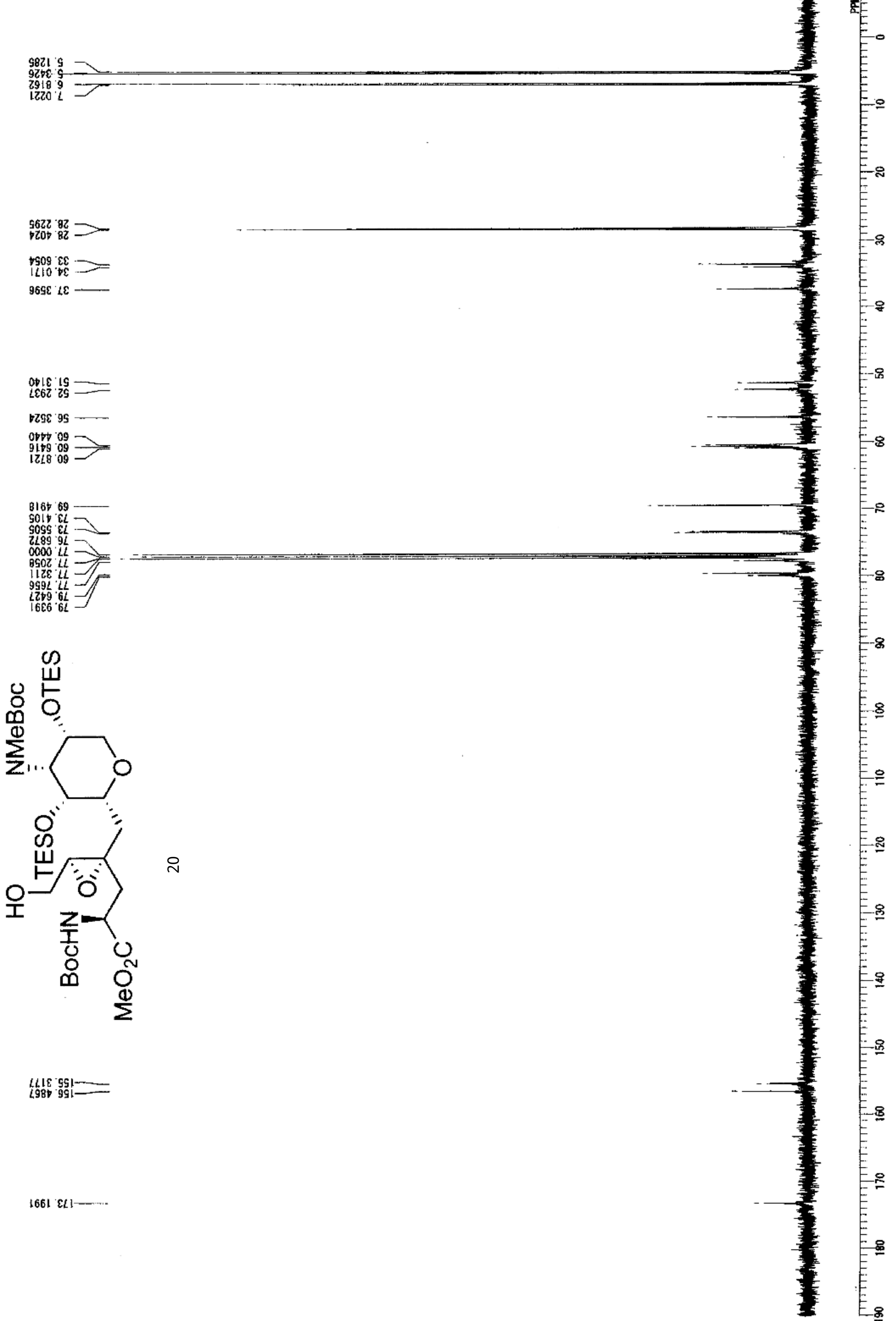


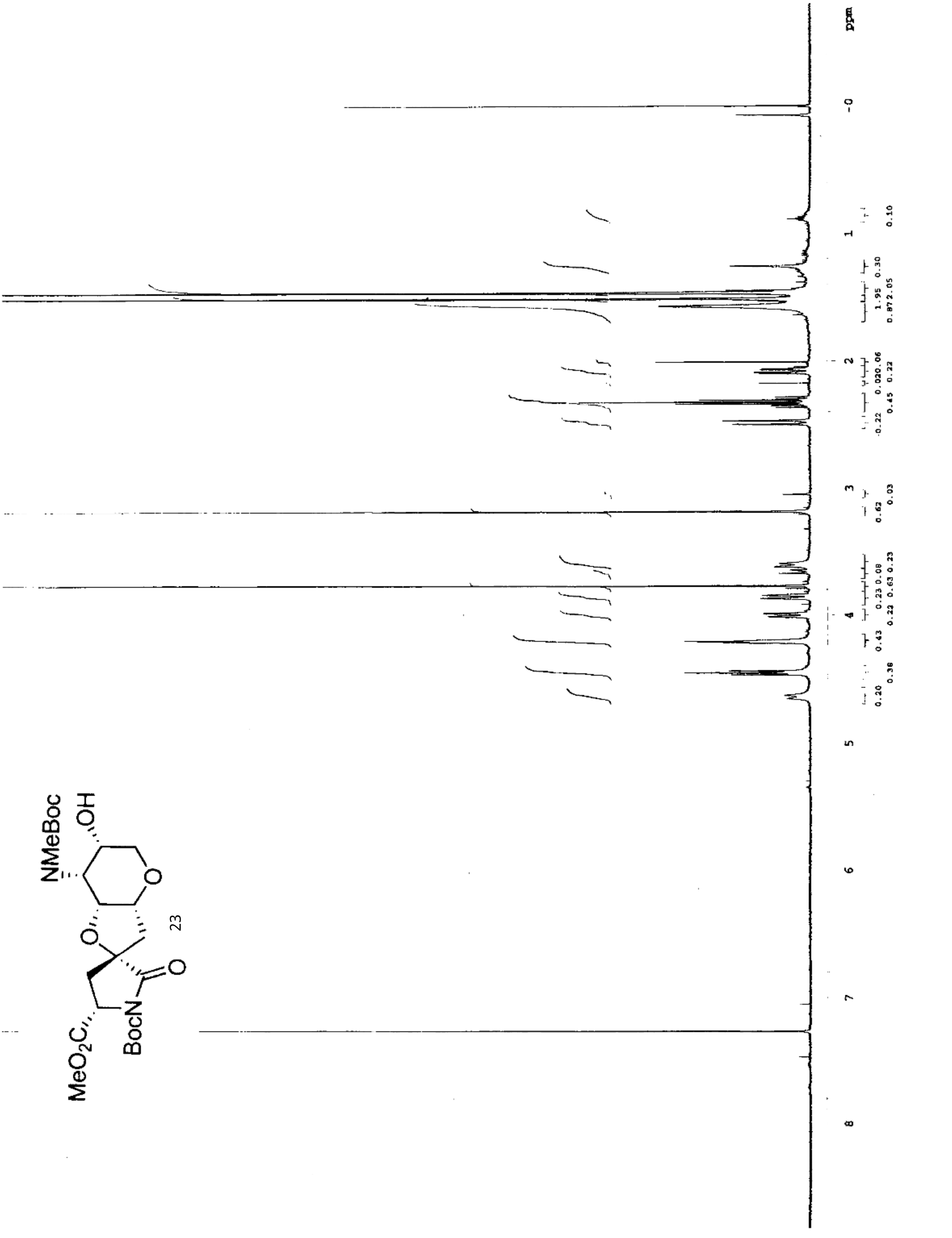
19



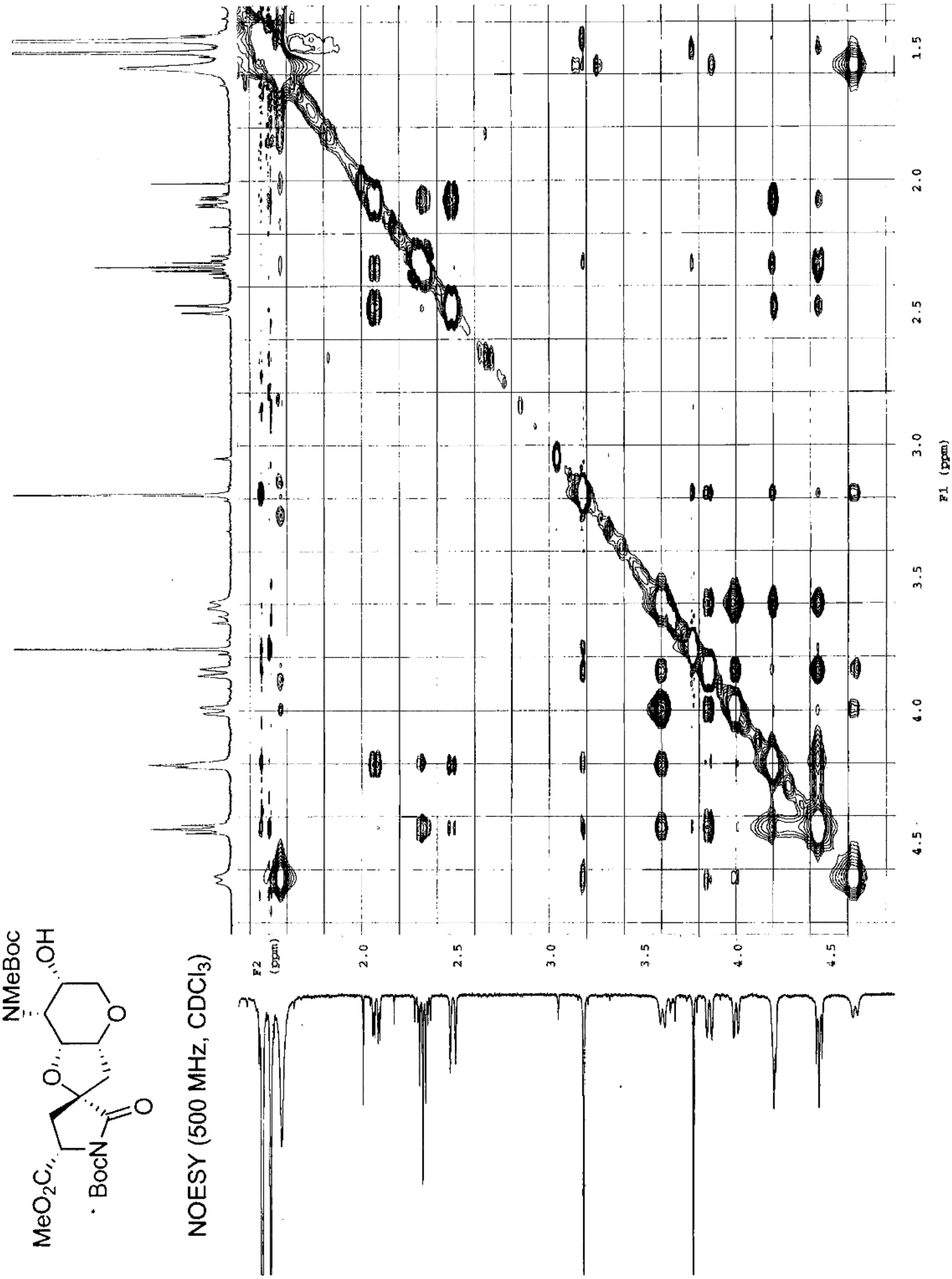
20


5.1285
5.3426
6.8162
7.0221
28.2295
28.4024
33.6054
34.0171
37.3596
51.3140
52.2937
56.3524
60.4440
60.6416
60.8721
69.4918
73.4105
73.5506
76.6872
77.0000
77.2058
77.3211
77.7656
79.6427
79.9391
155.3177
156.4867
173.1991
NMeBoc
OTES
TESO
HO
O
BocHN
MeO2C
PPM

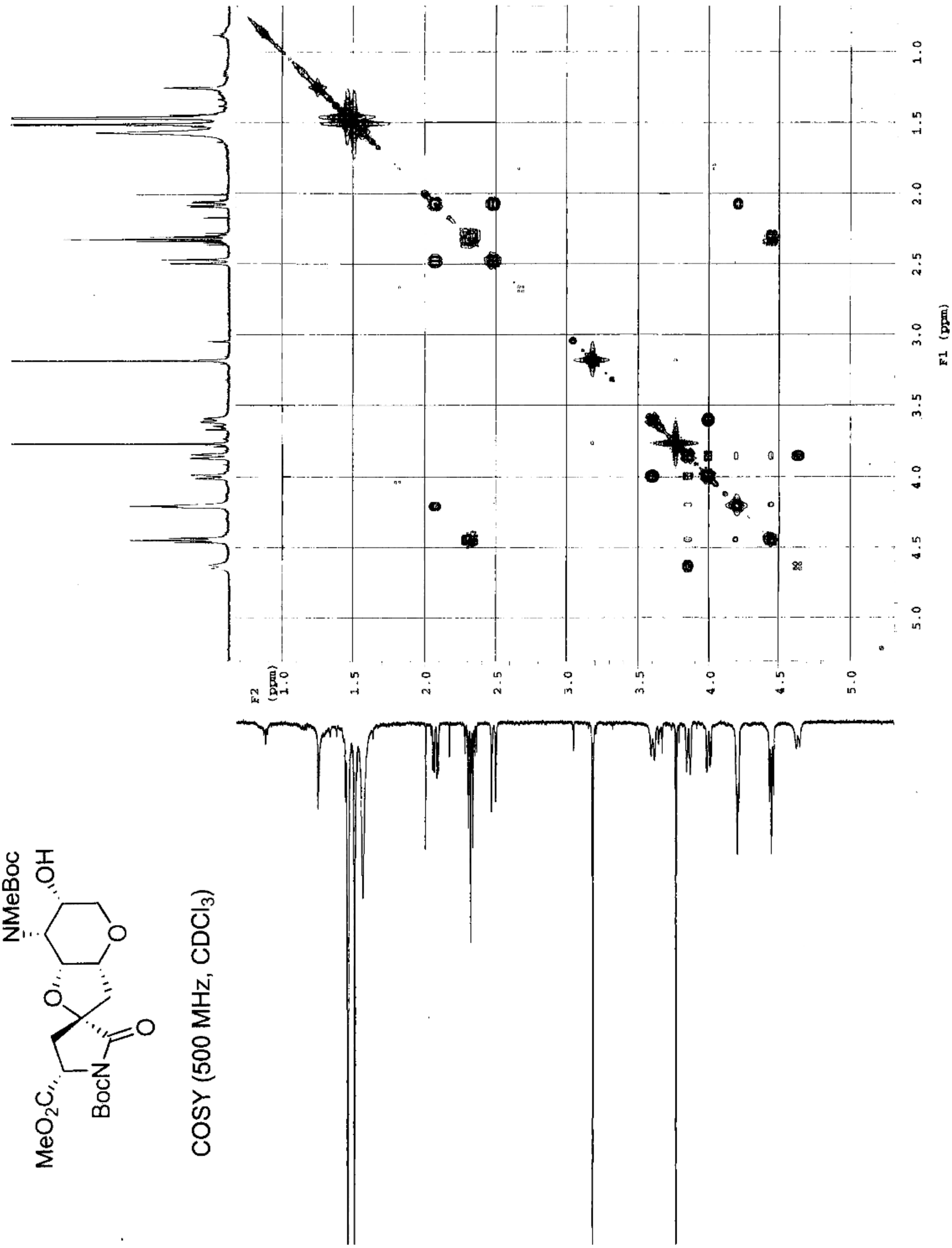
20

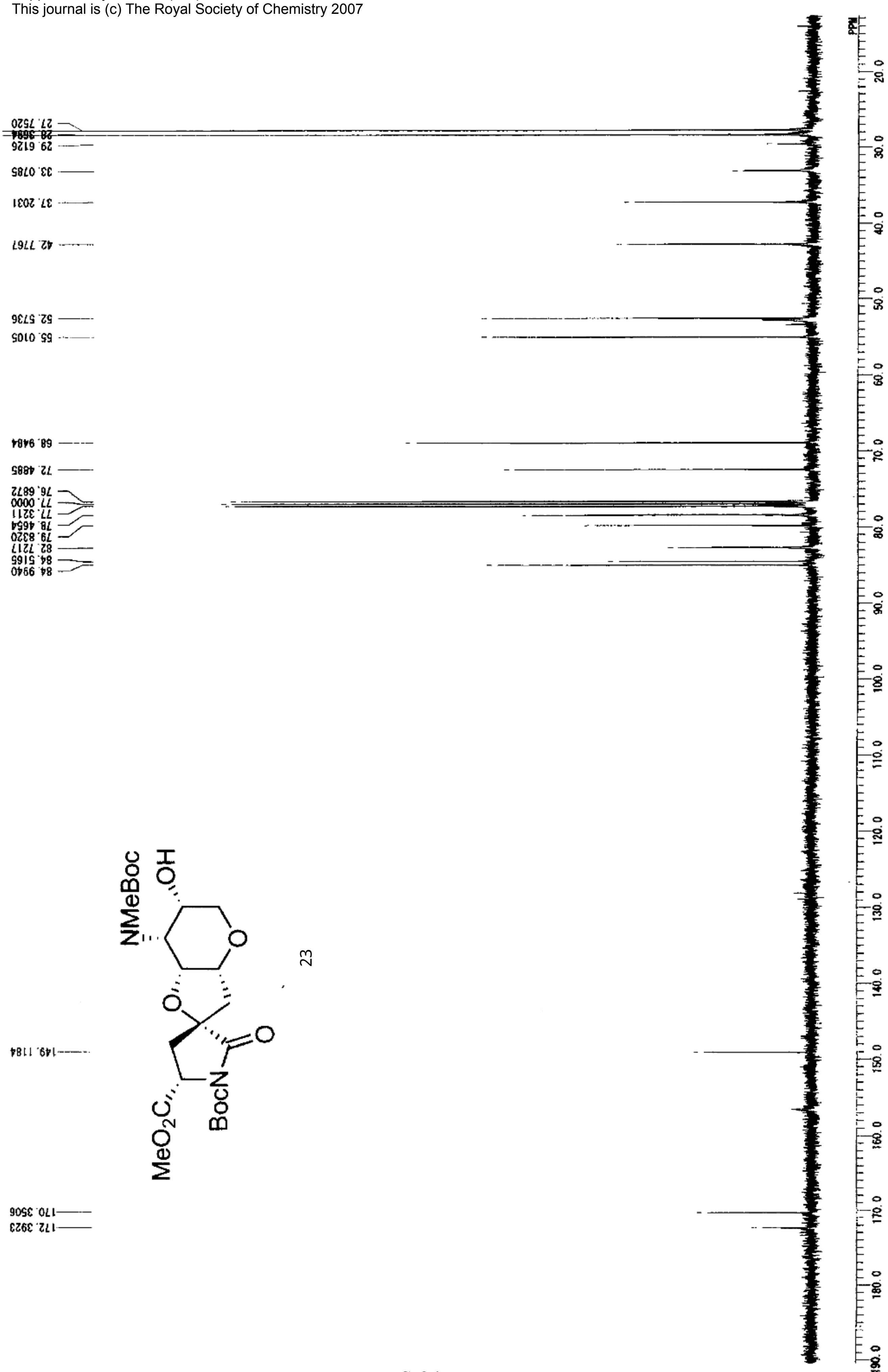


23



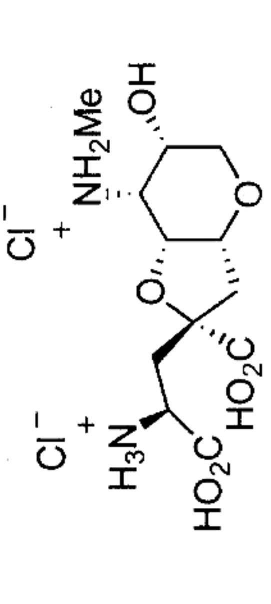
NOESY (500 MHz, $CDCl_3$)


NMeBoc
OH
MeO2C
BocN
O
COSY (500 MHz, CDCl3)
F2 (ppm)
F1 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0

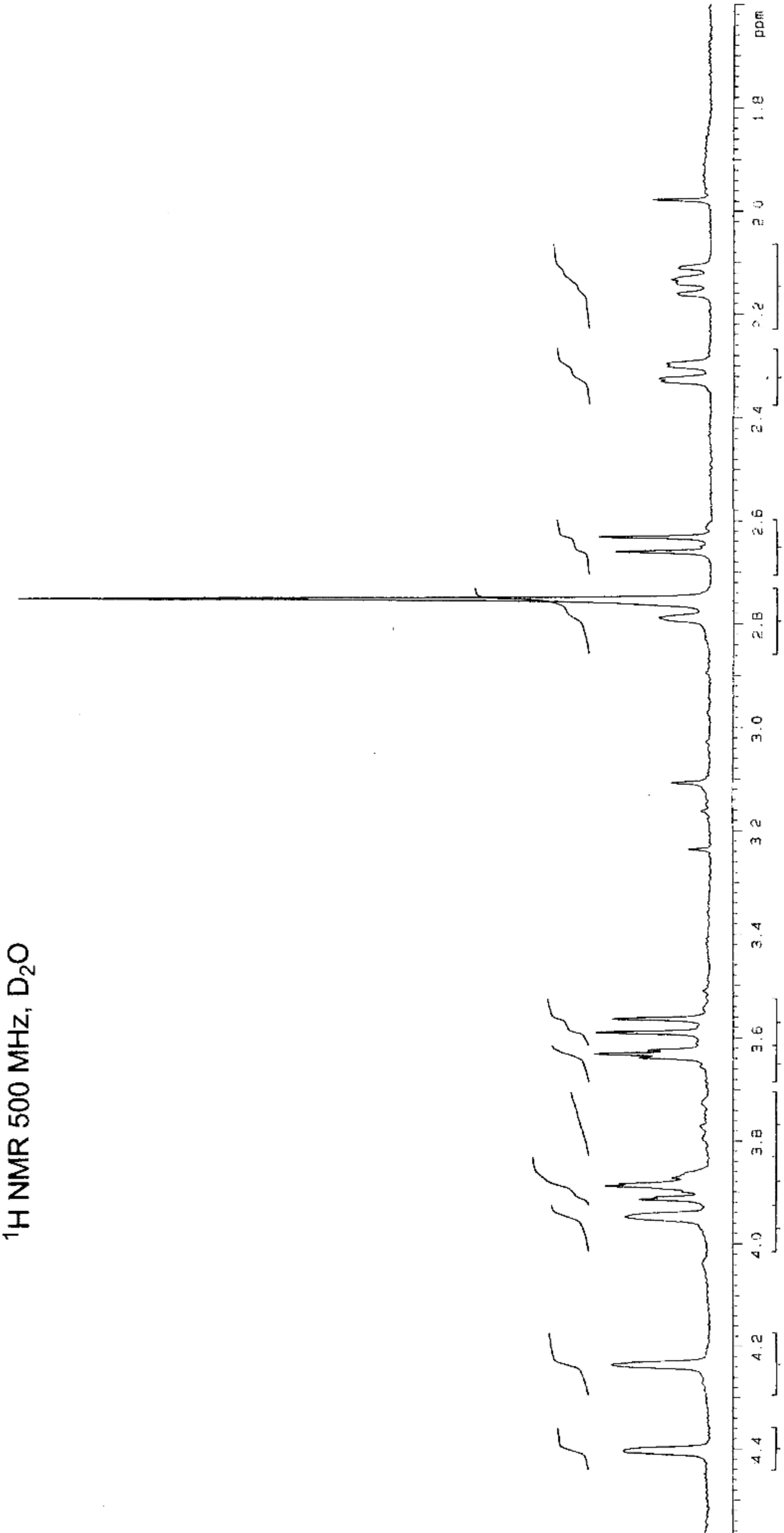

27.7520
28.3684
29.6126
33.0785
37.2031
42.7767
52.5736
55.0105
68.9484
72.4885
76.6872
77.0000
77.3211
78.4654
79.8320
82.7217
84.5165
84.9940
149.1184
170.3506
172.3923
NMeBoc
OH
O
O
O
MeO2C
BocN
PPM

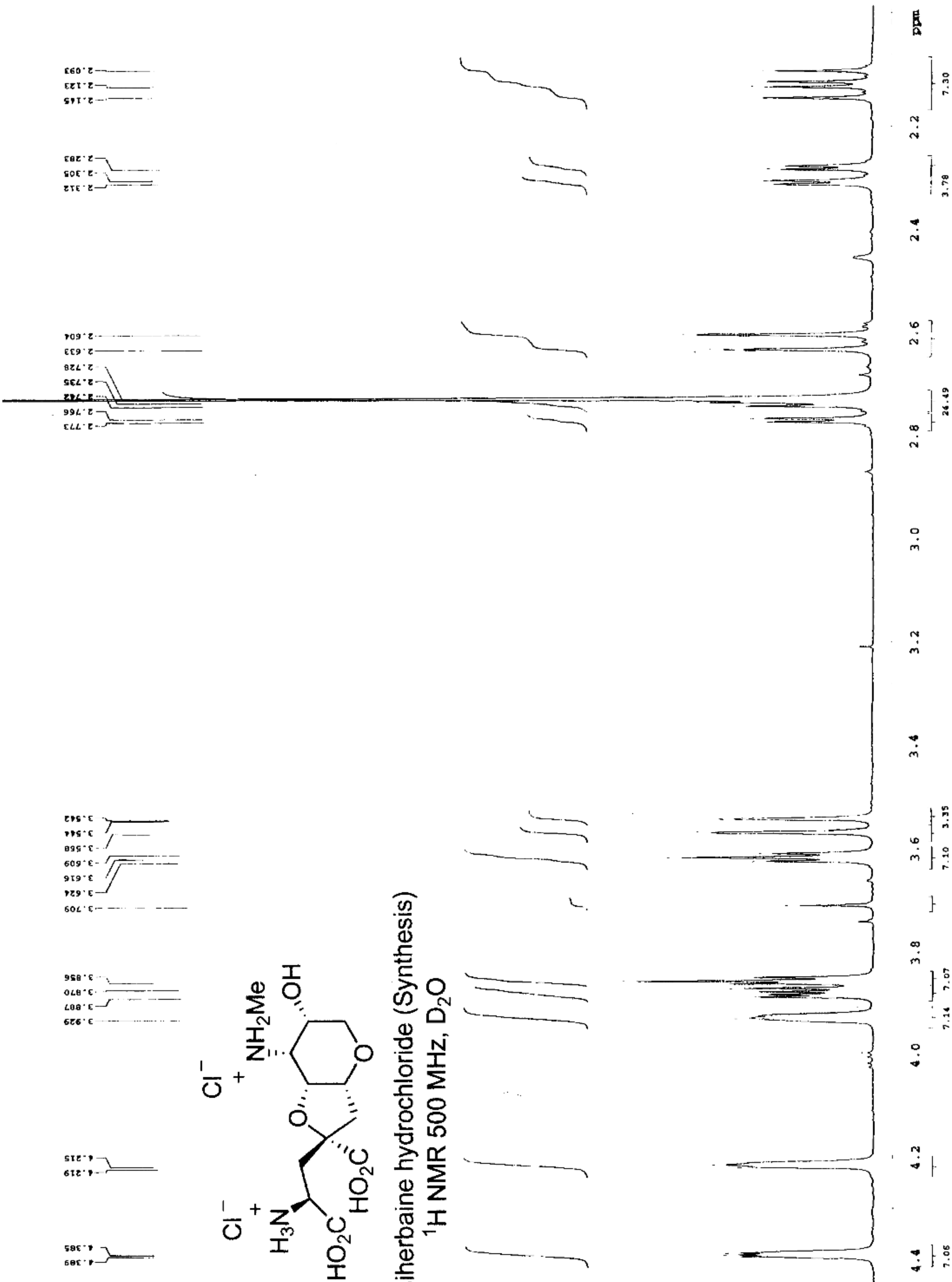
23

Supplementary Material (ESI) for Chemical Communications

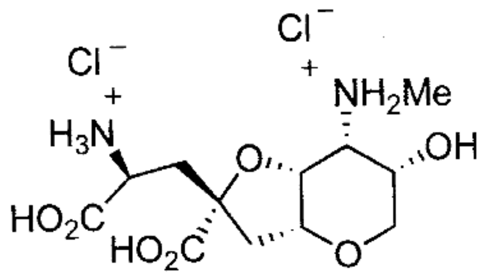


Dysiherbaine hydrochloride (Natural)
^{1}H NMR 500 MHz, D_2O

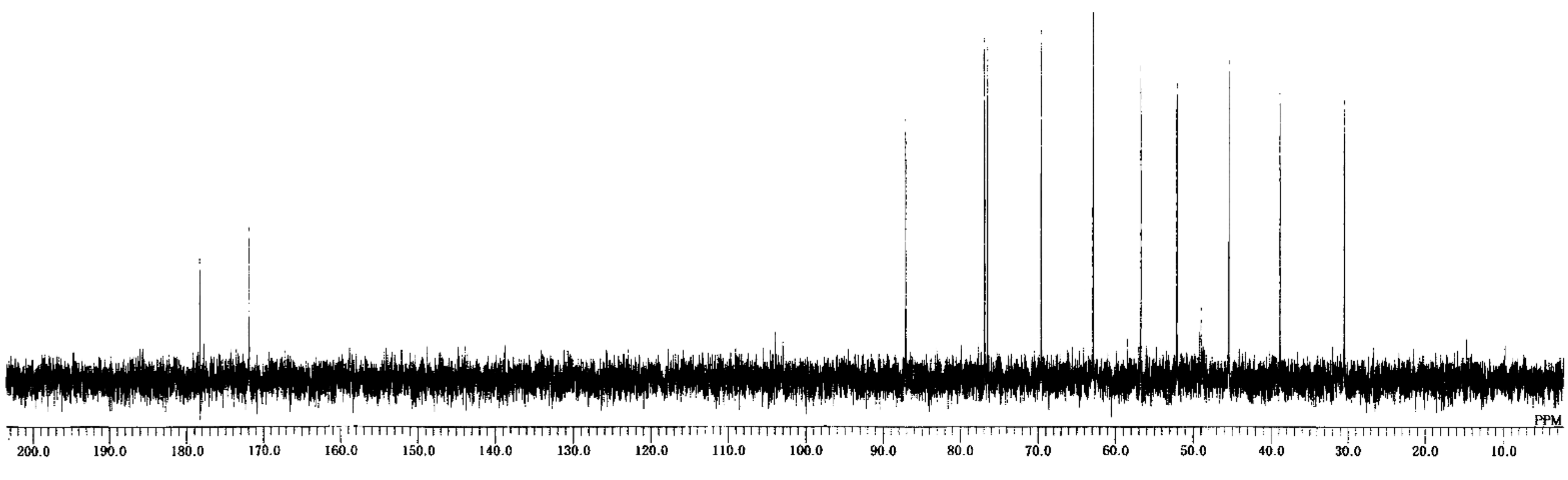


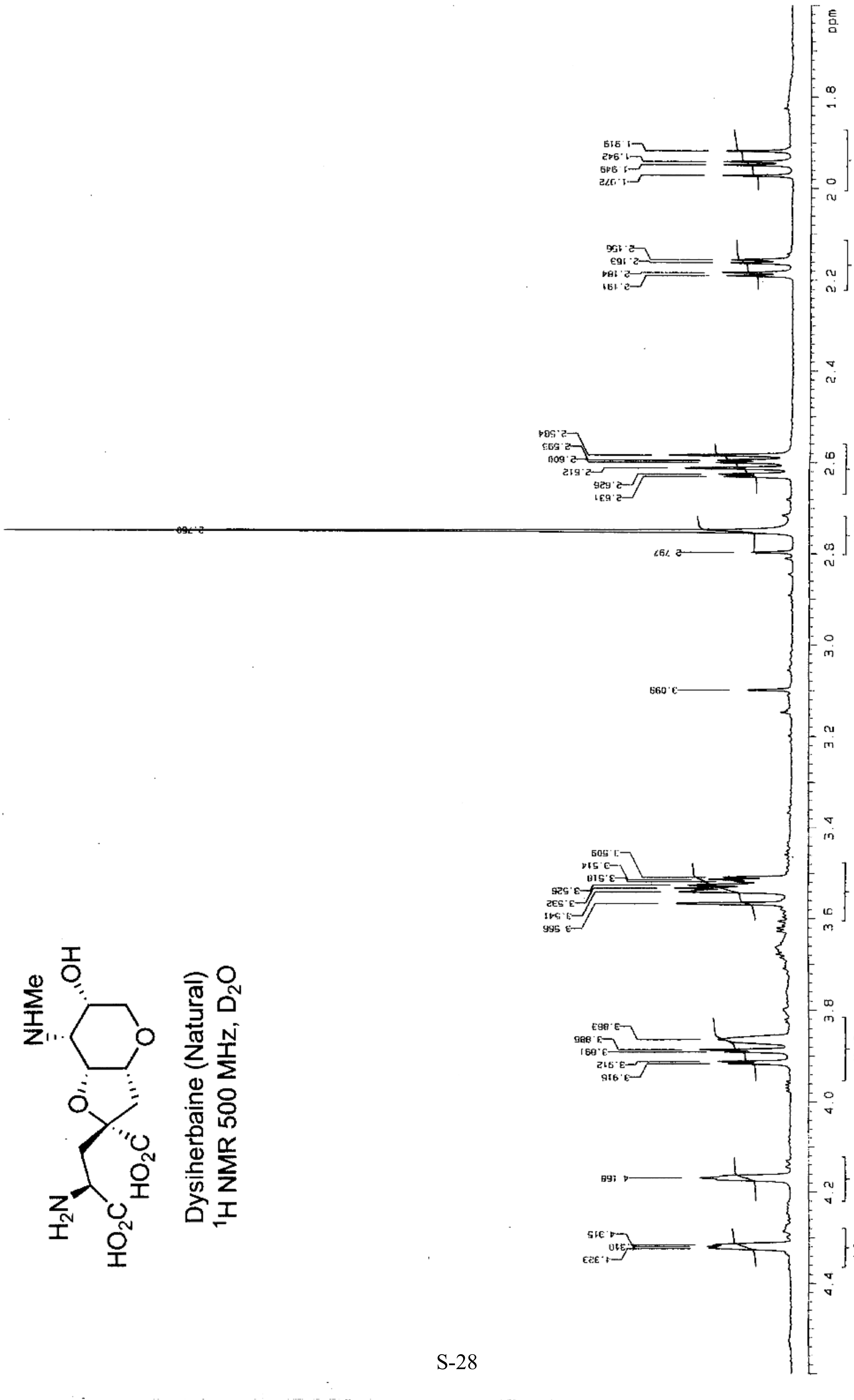


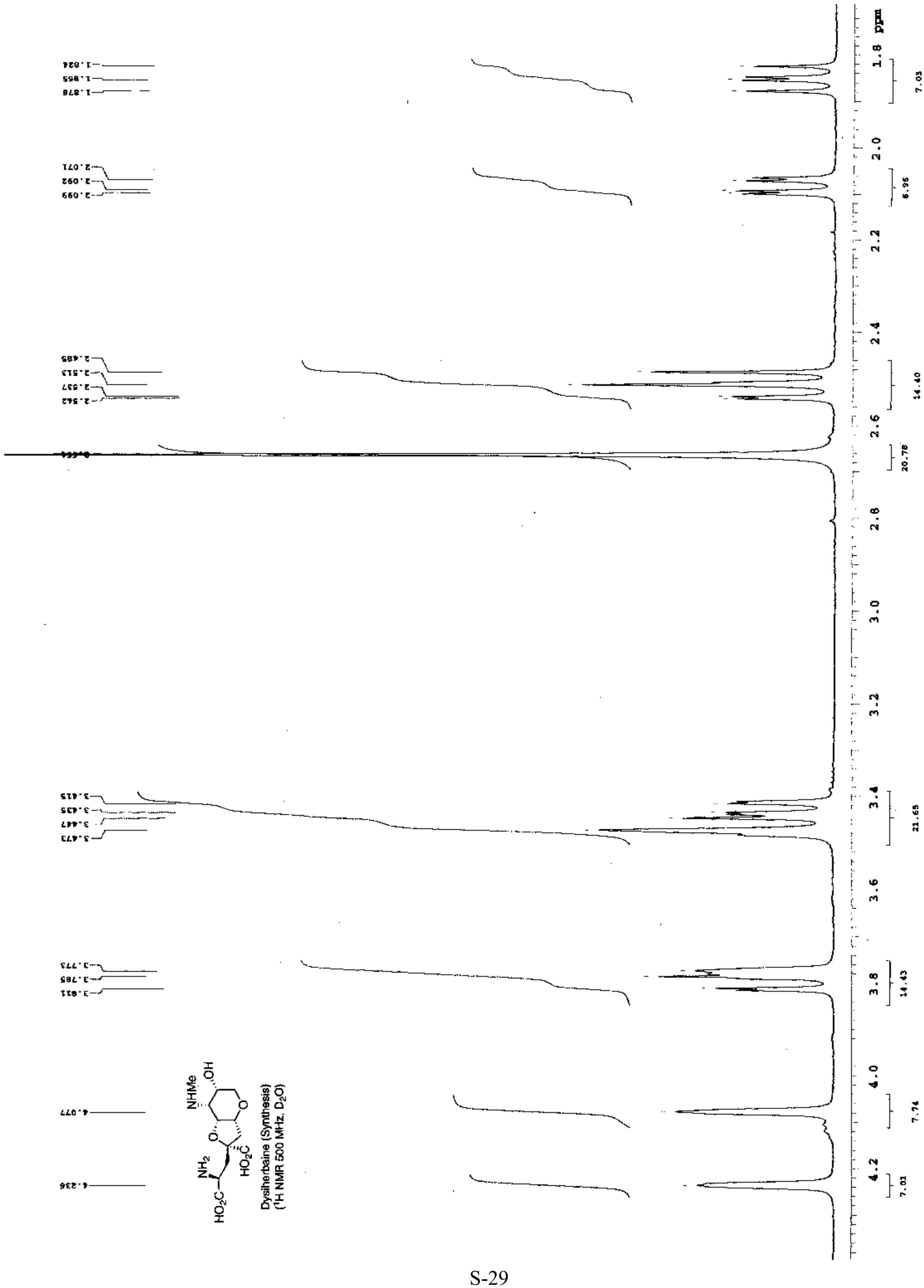
Dysiherbaine hydrochloride (Synthesis)
^1H NMR 500 MHz, D_2O

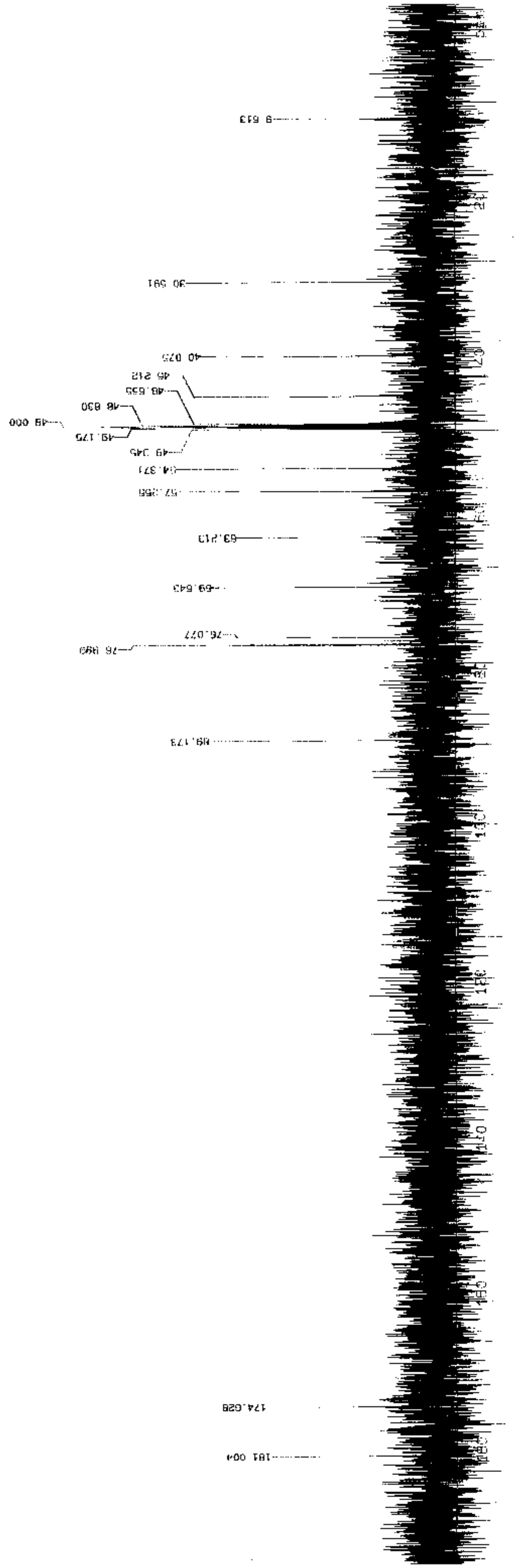


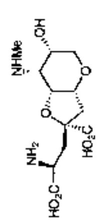
Dysiherbaine hydrochloride (Synthesis)
^{13}C NMR 100 MHz, D_2O



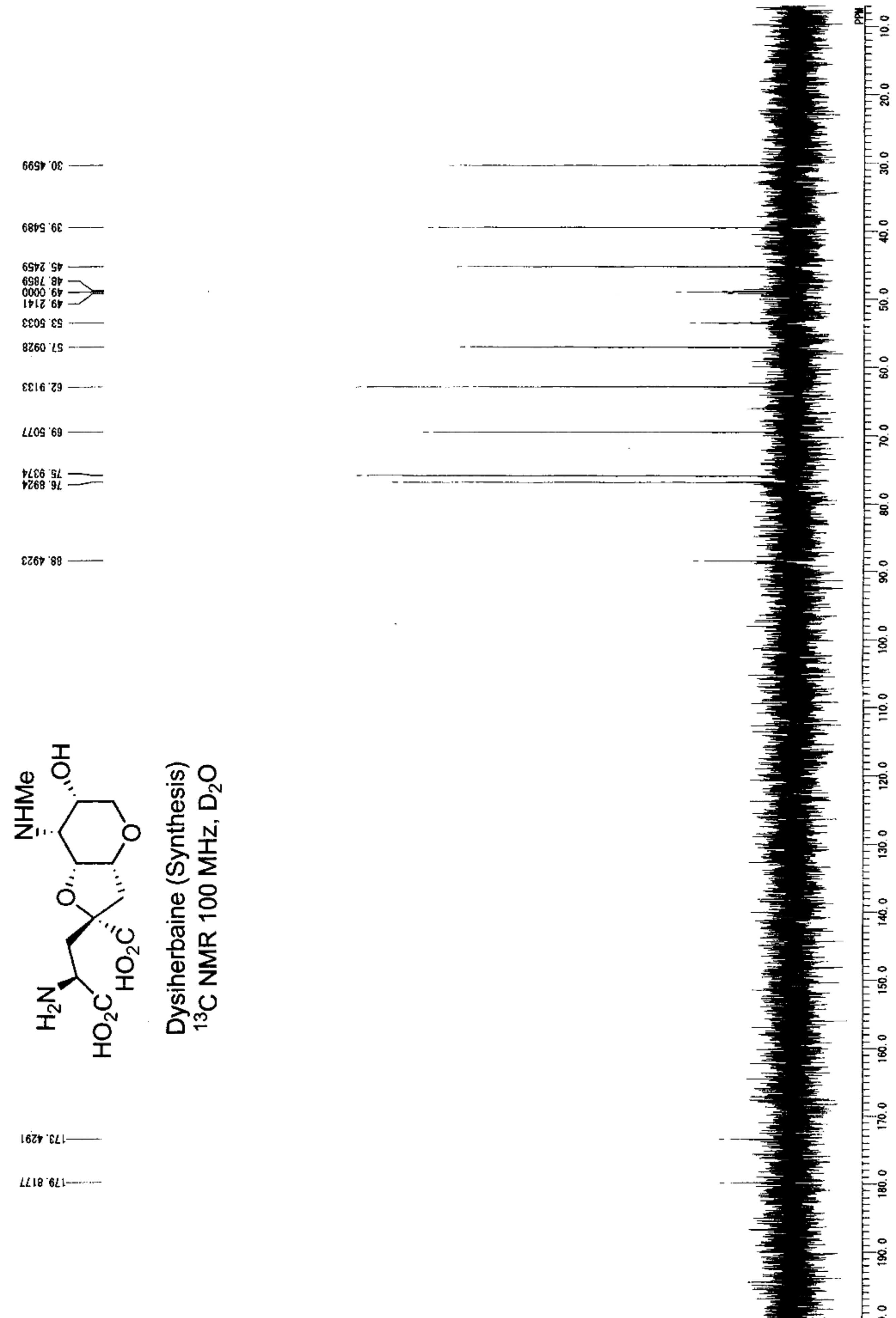

NHMe
OH
O
O
H$_2$N
HO$_2$C
HO$_2$C
Dysiherbaine (Natural)
^{1}H NMR 500 MHz, D$_2$O
ppm


1.824
1.865
1.878
2.071
2.092
2.099
2.485
2.513
2.537
2.542
3.415
3.435
3.447
3.473
3.773
3.785
3.811
4.077
4.236
NHMe
OH
NH2
HO2C
HO2C
Dysiherbaine (Synthesis)
(1H NMR 500 MHz, D2O)
ppm
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
7.03
6.96
14.40
20.78
21.65
14.43
7.74
7.01





Dysiherbaine (Natural)
^{13}C NMR 125 MHz, D_2O



Dysiherbaine (Synthesis)
^{13}C NMR 100 MHz, D_2O