Supporting Information

Integrating ReSET with Glycosyl Iodide Glycosylation in Step-Economy Syntheses of Tumor Associated Carbohydrate Antigens and Immunogenic Glycolipids

Hsiao-Wu Hsieh, Matthew W. Schombs, and Jacquelyn Gervay-Hague*

Tel: 1-530-754-9577. Fax: 1-530-754-6915.

jgervayhague@ucdavis.edu

Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, California 95616, United States

Table of Contents

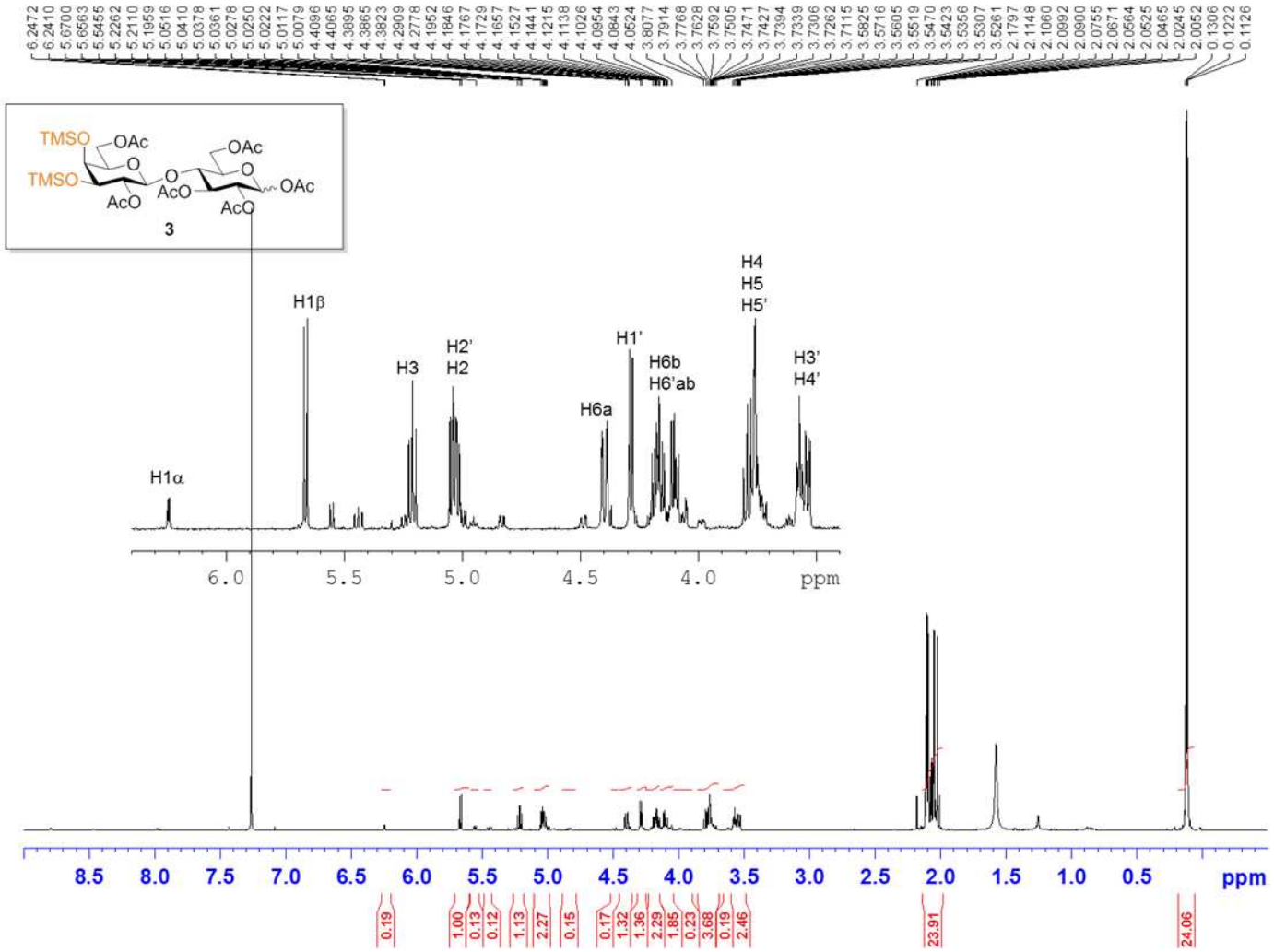
General Information

All reactions were conducted under a dried argon atmosphere. The anhydrous solvents (dichloromethane (DCM) 99.8%, benzene (PhH) 99.8%, Methanol (MeOH) 99.8%, *N*,*N*-dimethylformamide (DMF) 99.8% and pyridine (pyr.) 99.8%) were purchased from commercial sources without further purification. In order to maintain water content of the solvents under 15 ppm, the solvents were dried and stored under 4 Å molecular sieves according to literature procedure.[1] Trimethylsilyl iodide (TMSI, stabilized with copper) was stored at -20 °C under a desiccated Ar atmosphere. TMSI in good condition should be a colorless transparent liquid. All other solvents and reagents were purchased from commercial sources and used without further purification. All glassware utilized was oven-dried or flame-dried before use. Glass-backed TLC plates (Silica Gel 60 with a 254 nm fluorescent indicator) were used without further manipulation and stored with desiccant. TLC plates were visualized using a short-wave UV lamp, stained with an I_2-SiO_2 mixture, and/or by heating TLC plates that were dipped in a solution of ammonium molybdate/cerium (IV) sulfate or anisaldehyde/H_2SO_4/AcOH/EtOH. Flash column

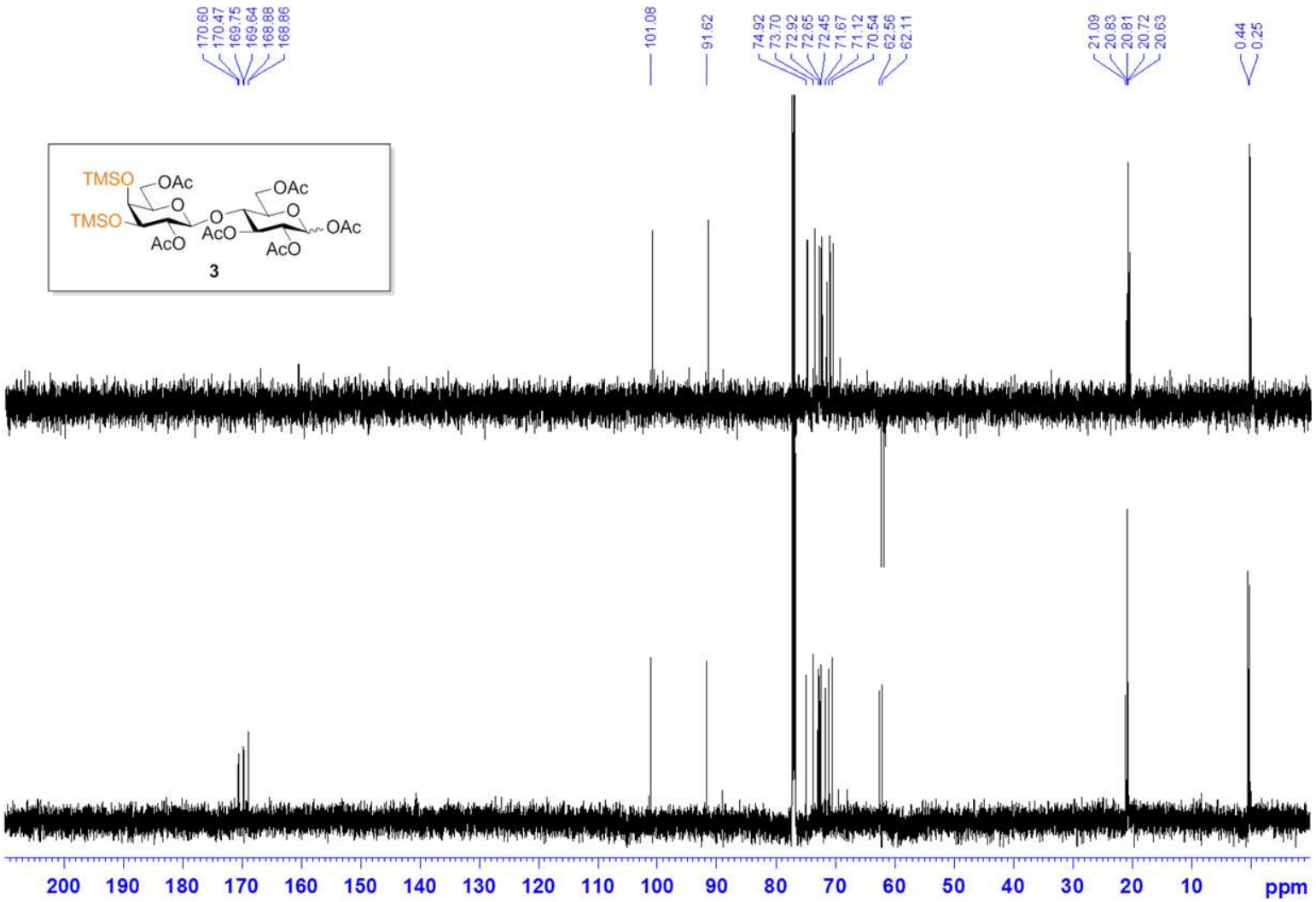
chromatography (FCC) was performed using a silica gel (32-63 μm) stationary phase with a variable mobile phase correlated with TLC mobility. NMR experiments were conducted on either 800 or 600 MHz instruments using C_6D_6 (99.5% D), $CDCl_3$ (99.9% D), methanol-d_4 (99.8% D) or pyridine-d_5 (99.5% D) as the solvent. Chemical shifts were referenced to the appropriate deuterated solvent peak (7.16 ppm for C_6D_6; 7.26 ppm for $CDCl_3$; 3.31 ppm for methanol-d_4; 8.74 ppm for pyridine-d_5) and were reported in parts per million (ppm). Coupling constants of the coupled protons were averaged to match with each other. High resolution mass spectra were recorded using ESI-Orbitrap LC-MS with internal calibration. The microwave-assisted regioselective silyl exchange technology (ReSET) reactions were conducted in sealed 10 mL microwave vessels in a commercial microwave reactor (CEM Discover™) which was operated by the Synergy™ software. The reaction temperatures were monitor by the reactor's built-in infrared (IR) detector.

Reference

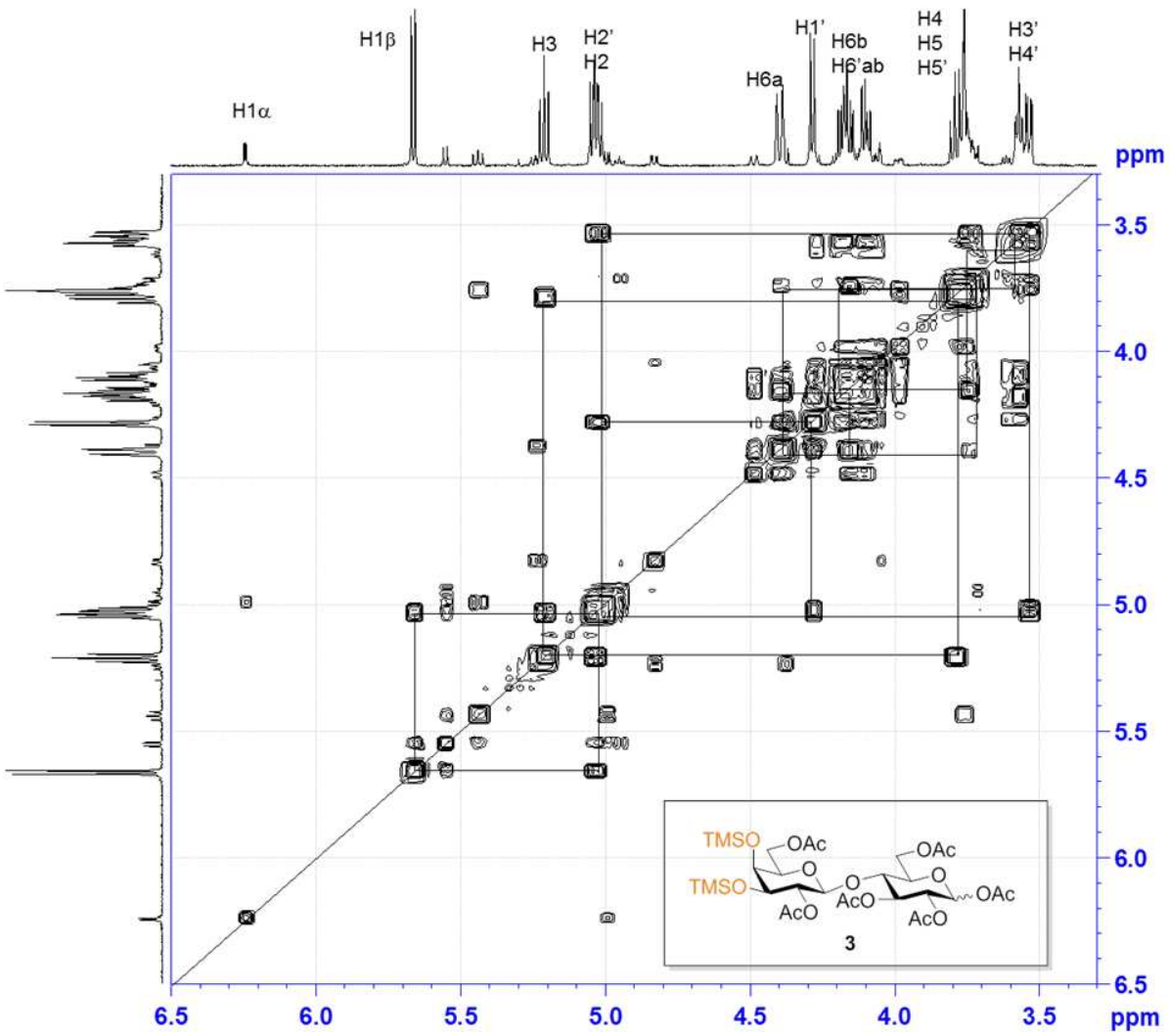
(1) Williams, D. B. G.; Lawton, M. *J. Org. Chem.* **2010**, *75*, 8351-8354.



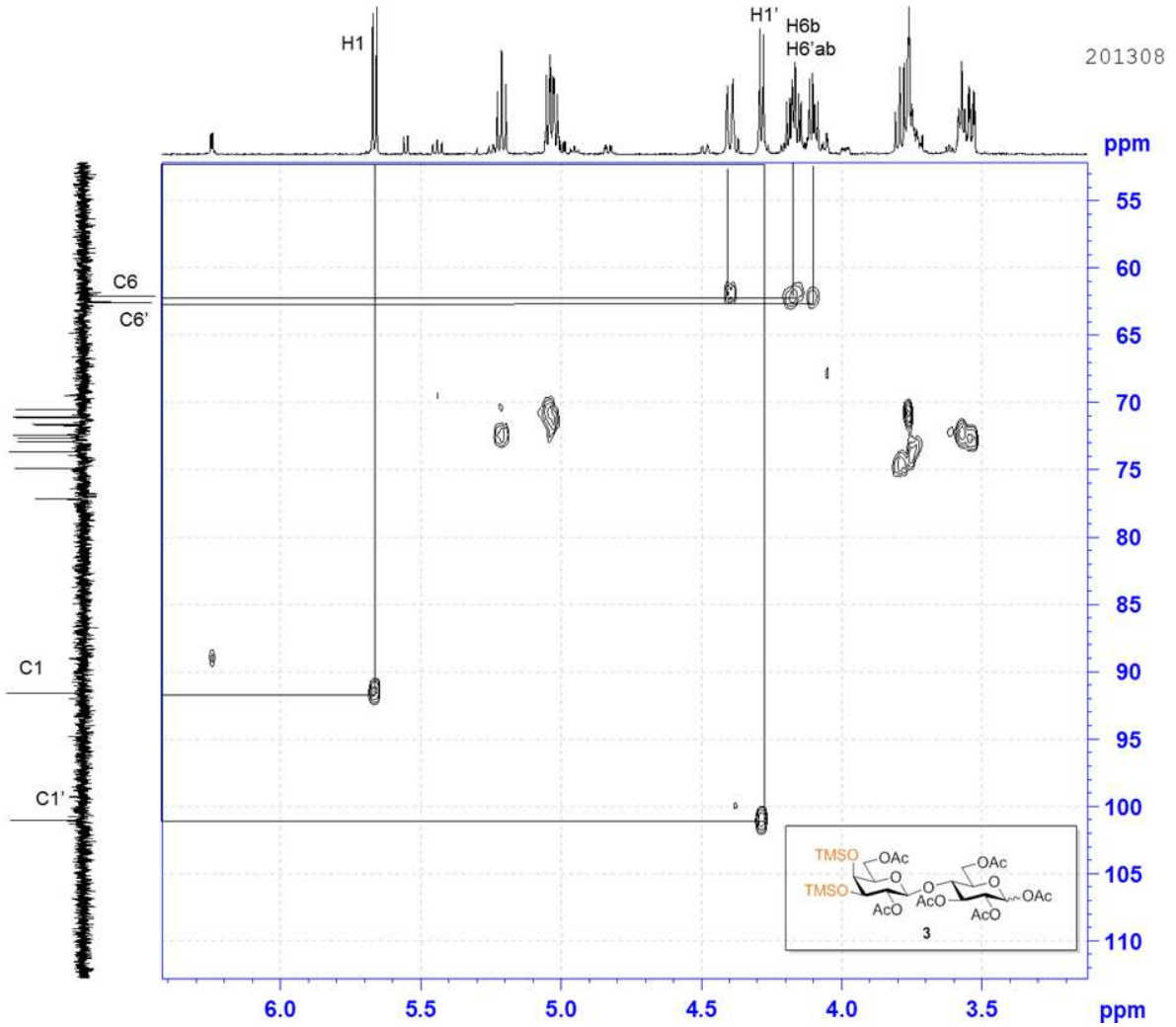
^{1}H NMR spectrum of compound **3** ($CDCl_3$, 800 MHz)



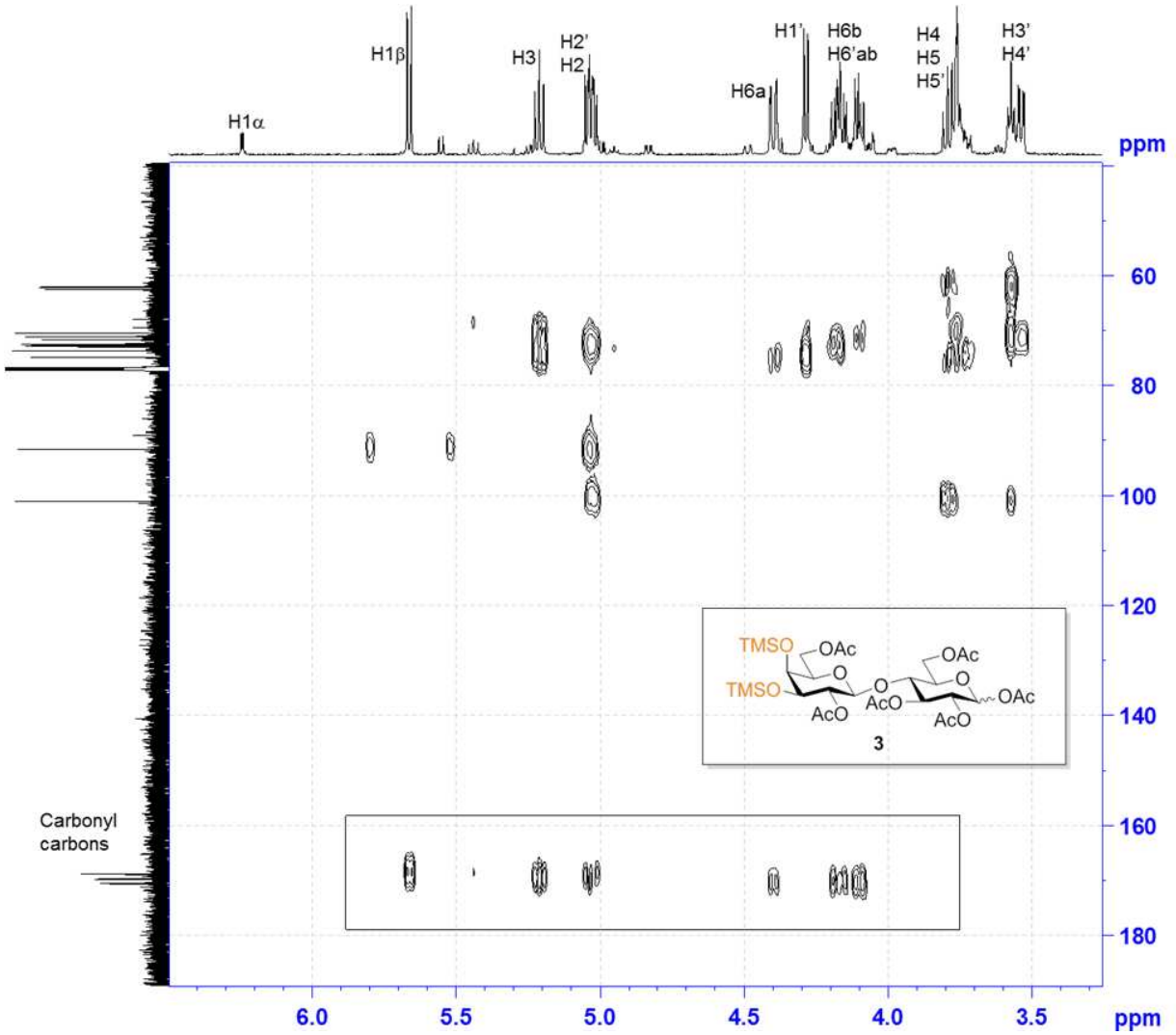
^{13}C and DEPT135 NMR spectrum of compound **3** ($CDCl_3$, 200 MHz)



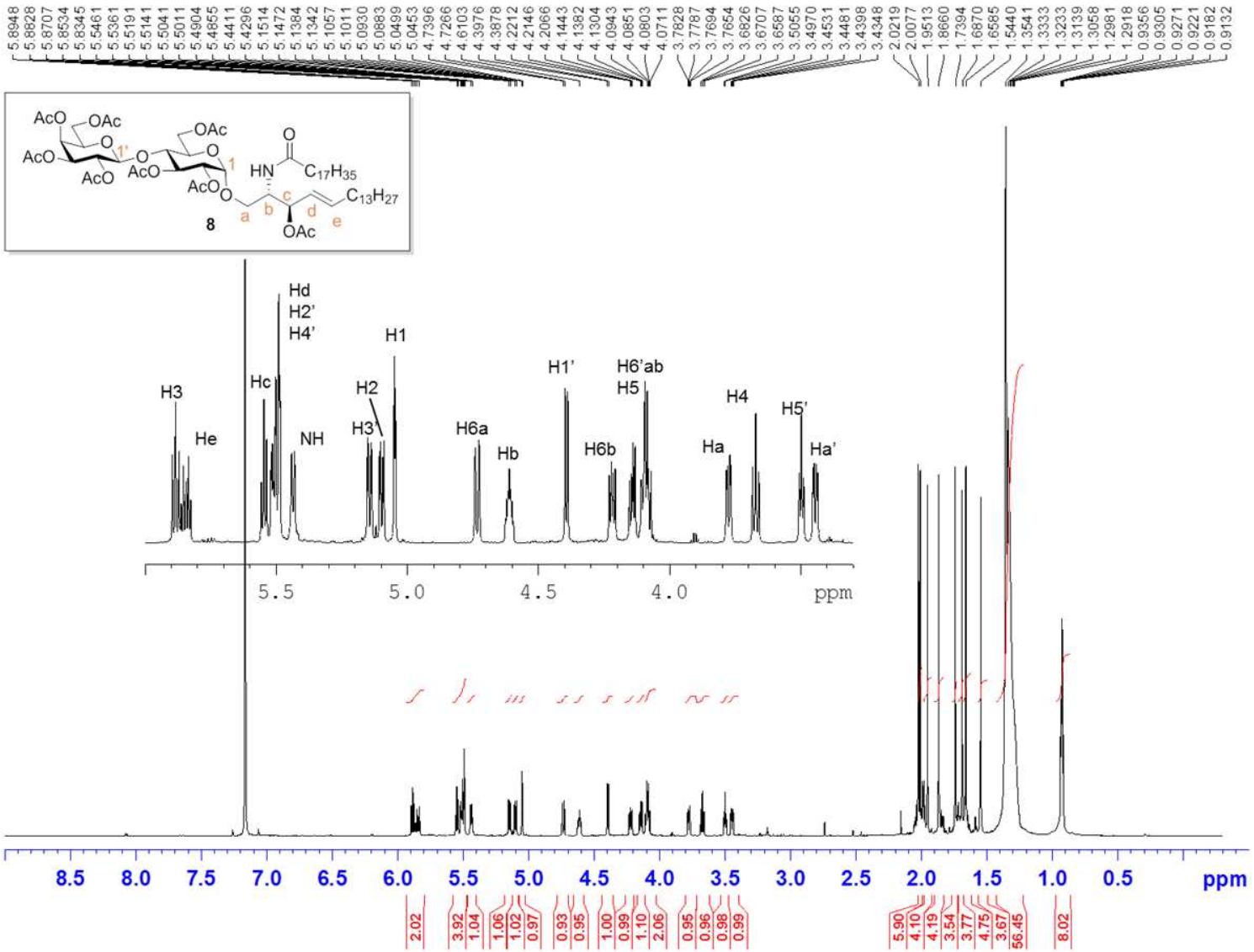
^{1}H-^{1}H COSY spectrum of compound **3** ($CDCl_3$, 800 MHz)



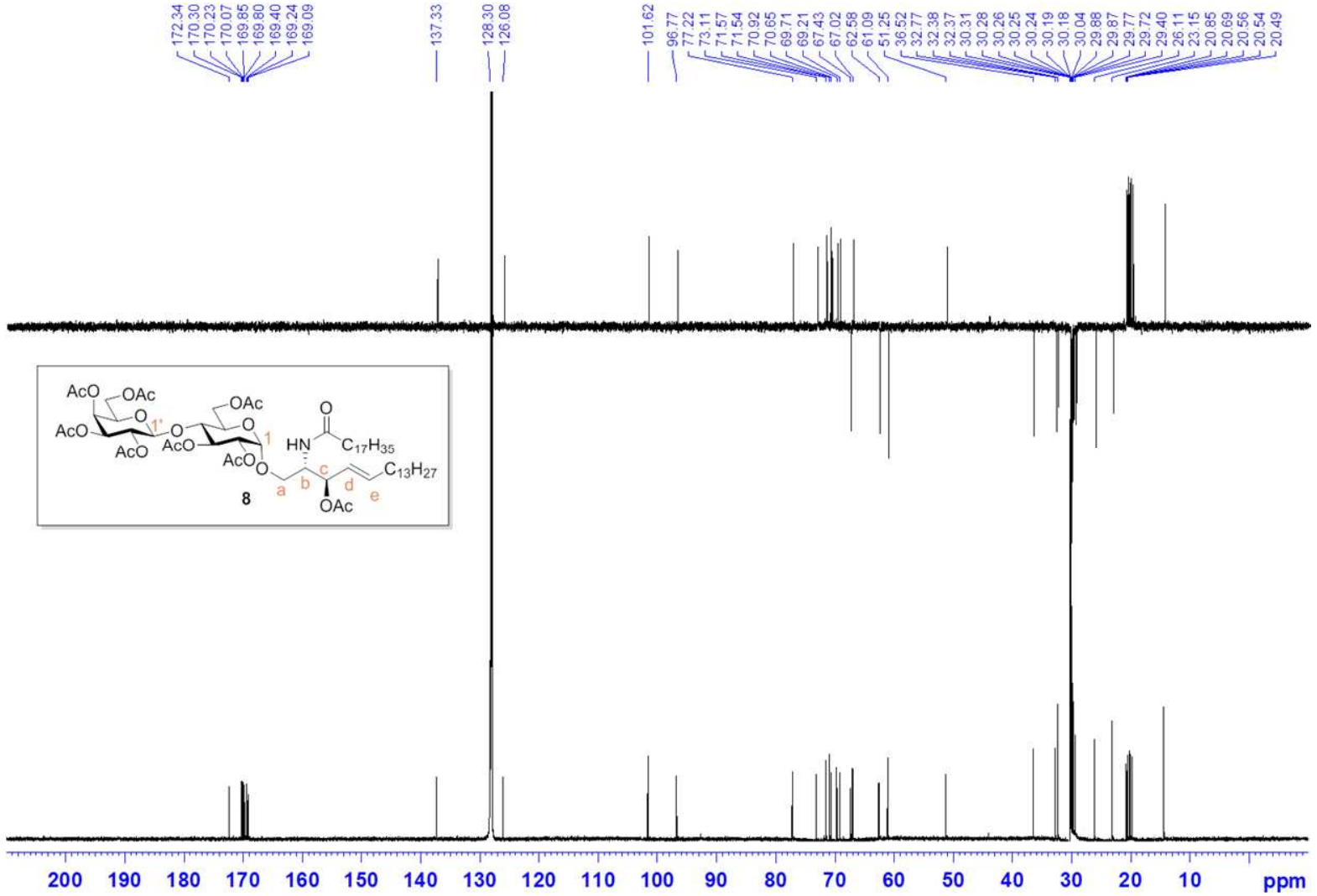
^{1}H-^{13}C HSQC spectrum of compound **3** ($CDCl_3$, 800 MHz)



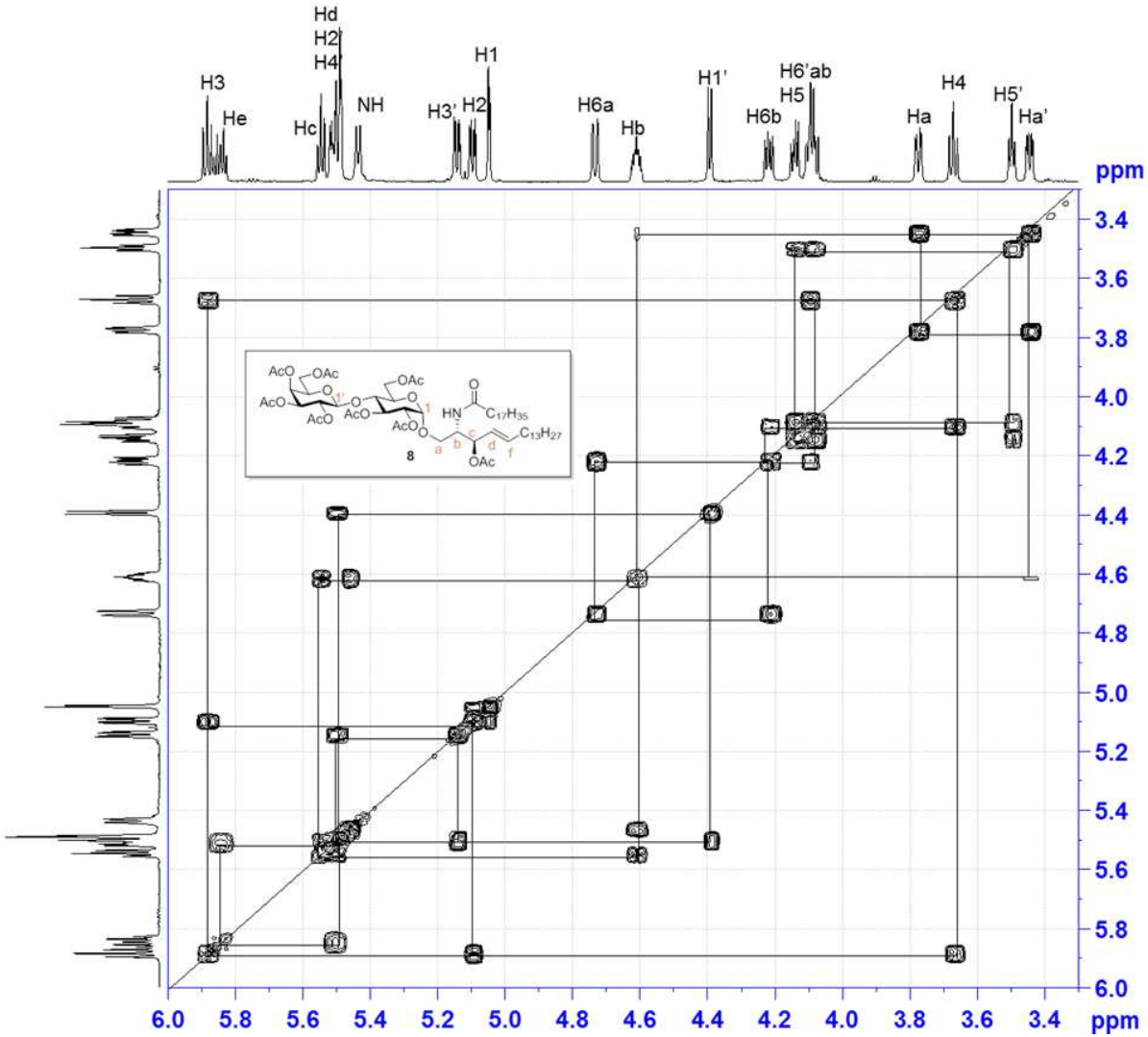
^{1}H-^{13}C HMBC spectrum of compound **3** ($CDCl_3$, 800 MHz)



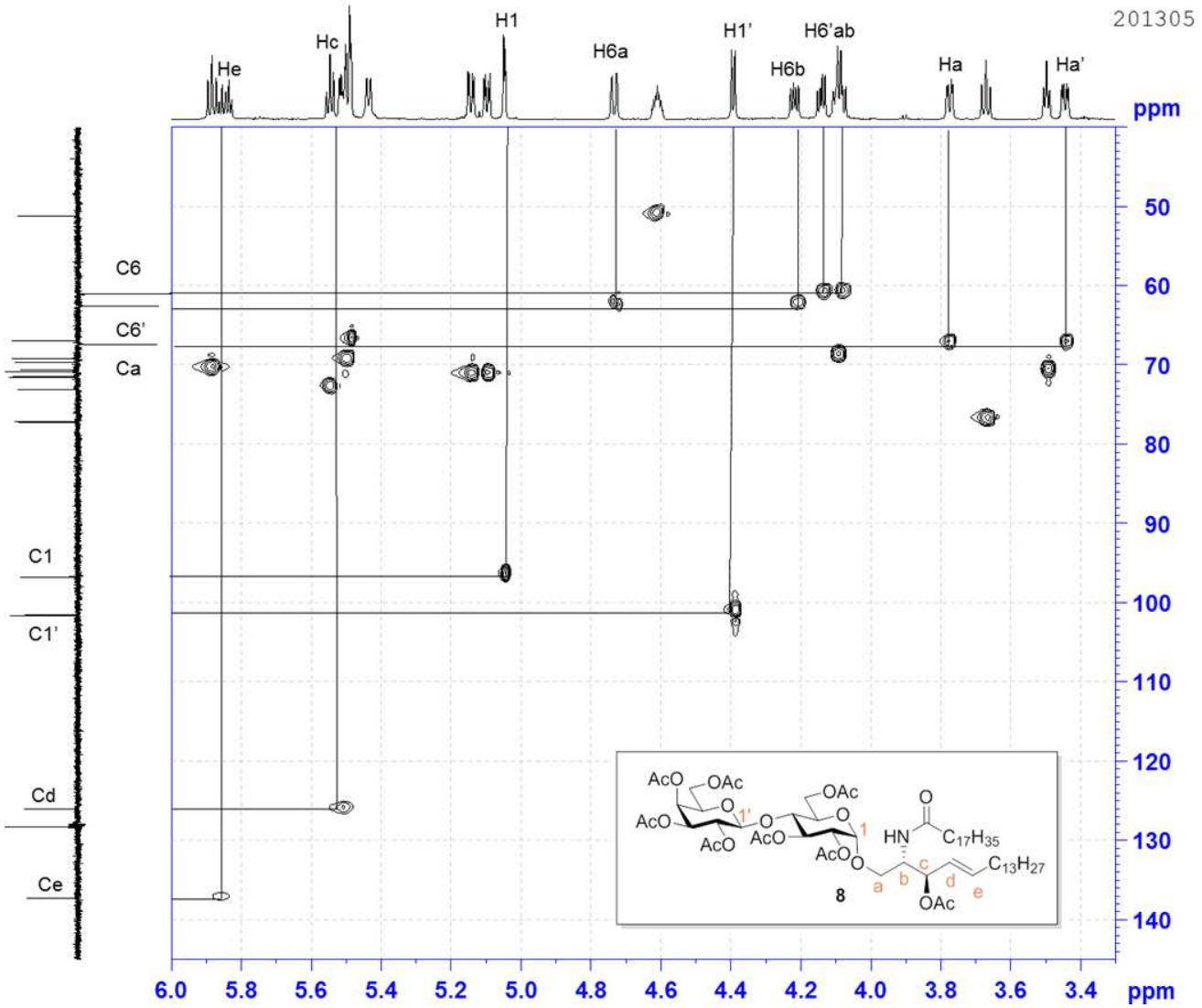
^{1}H NMR spectrum of compound **8** (C_6D_6, 800 MHz)



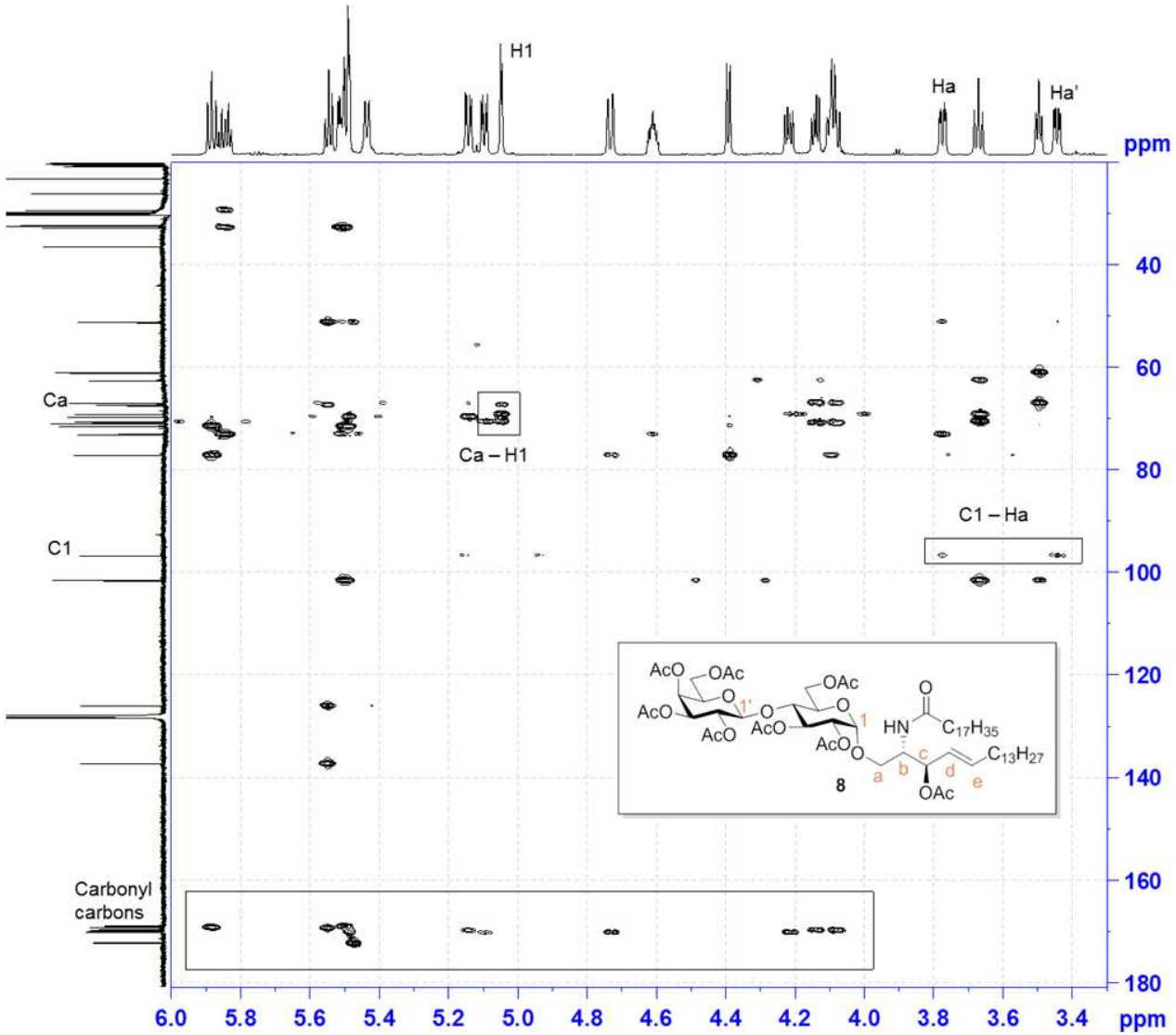
^{13}C and DEPT135 NMR spectrum of compound **8** (C_6D_6, 200 MHz)



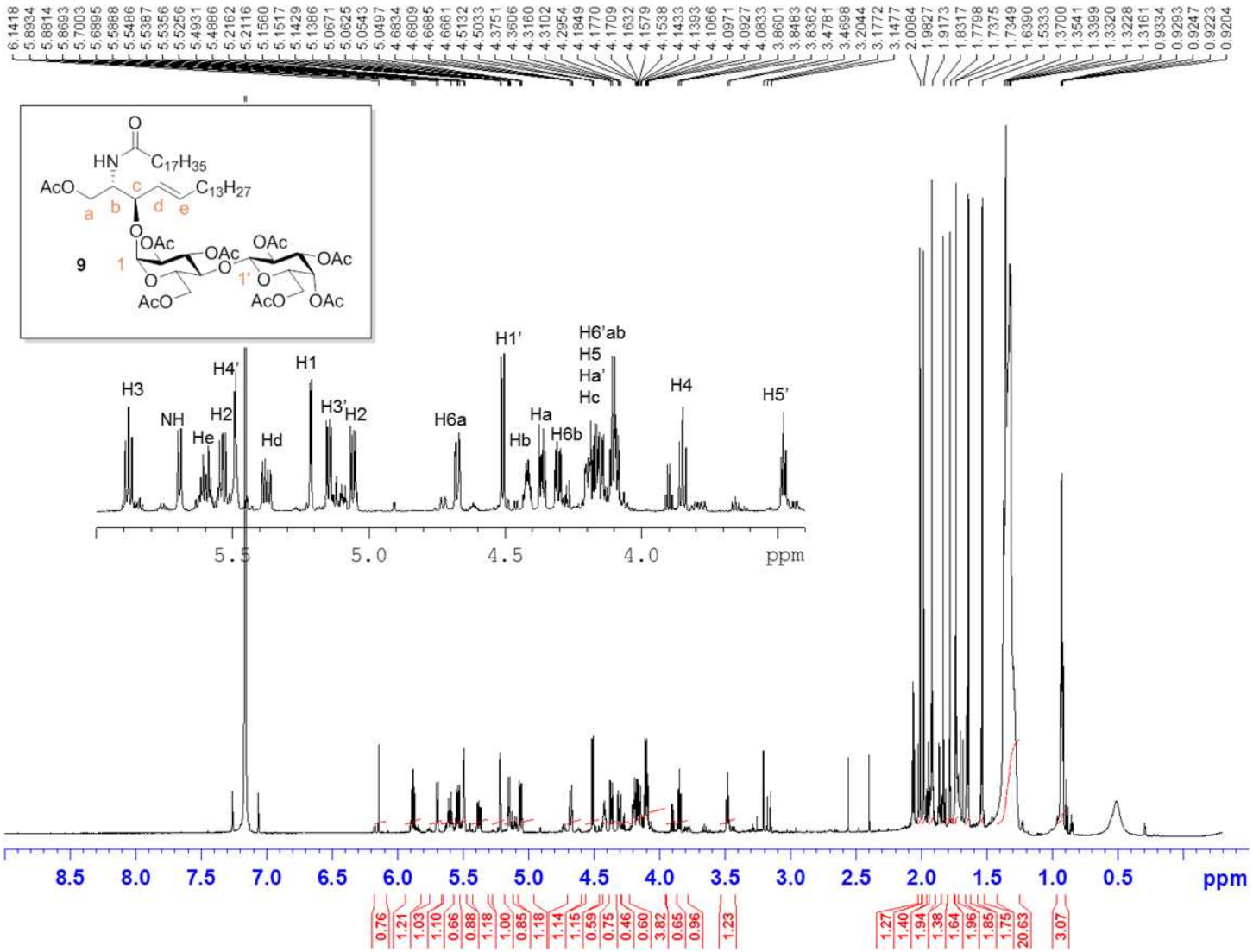
^{1}H-^{1}H COSY spectrum of compound **8** (C_6D_6, 800 MHz)



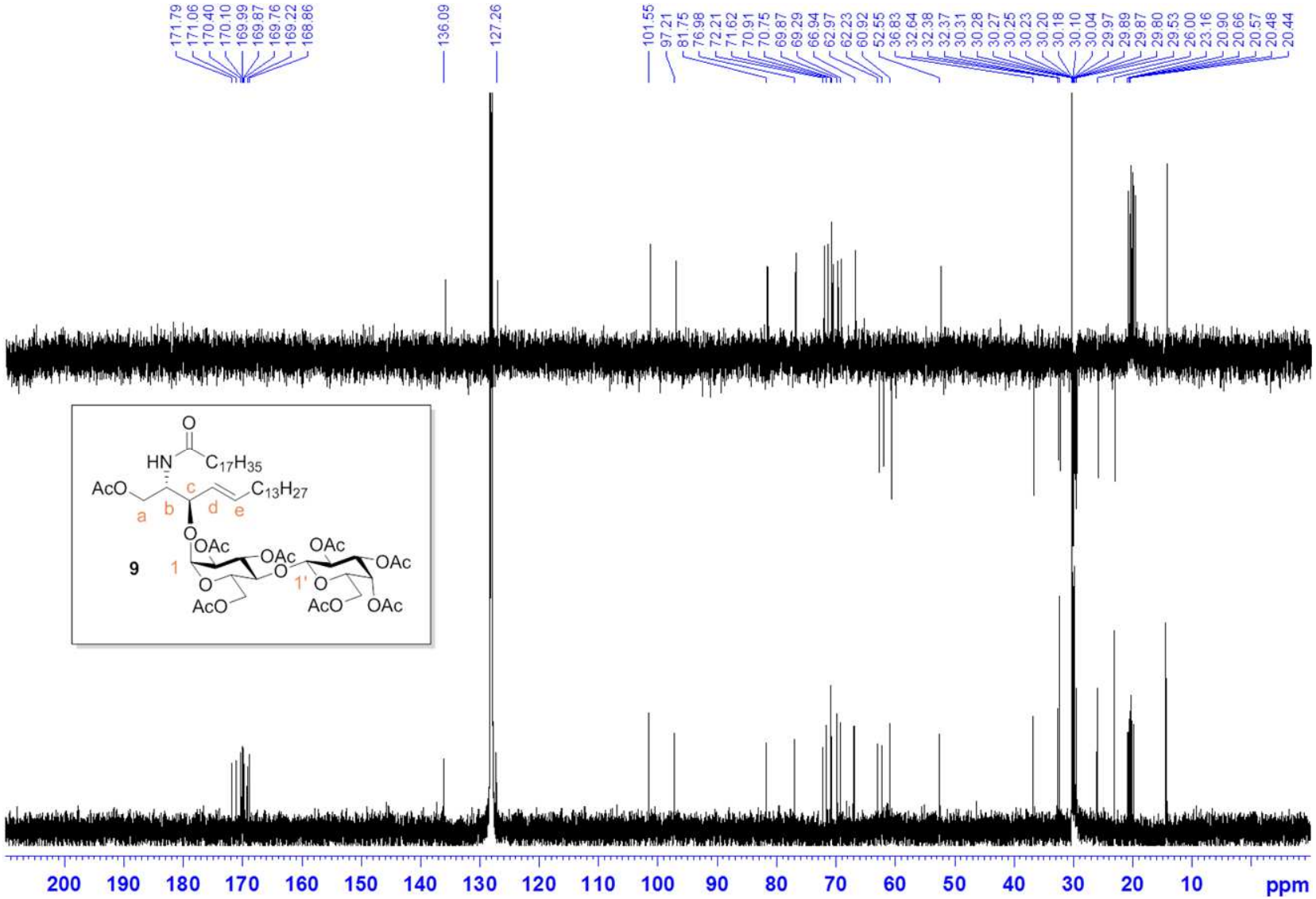
^{1}H-^{13}C HSQC spectrum of compound **8** (C_6D_6, 800 MHz)



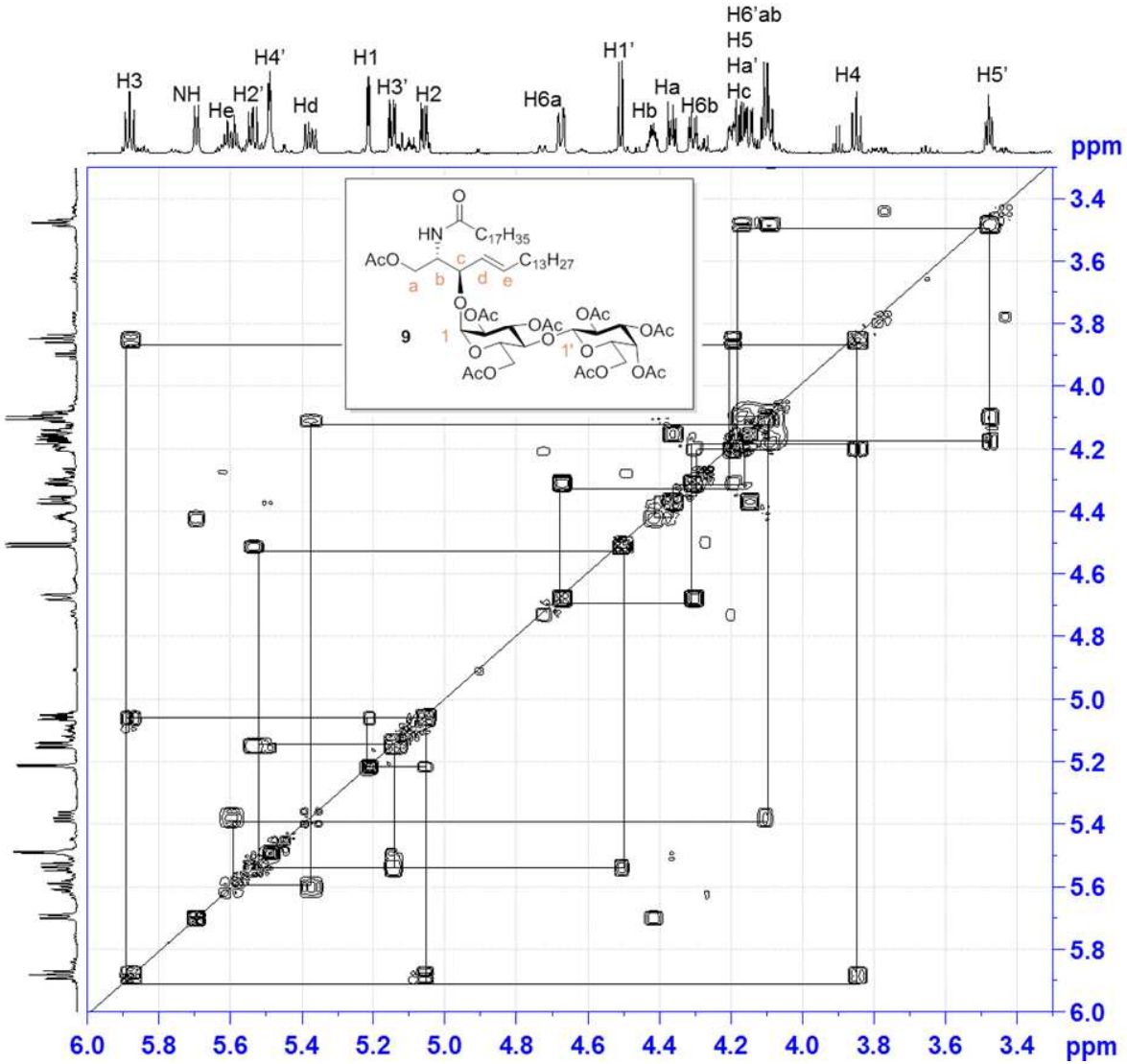
^{1}H-^{13}C HMBC spectrum of compound **8** (C_6D_6, 800 MHz)



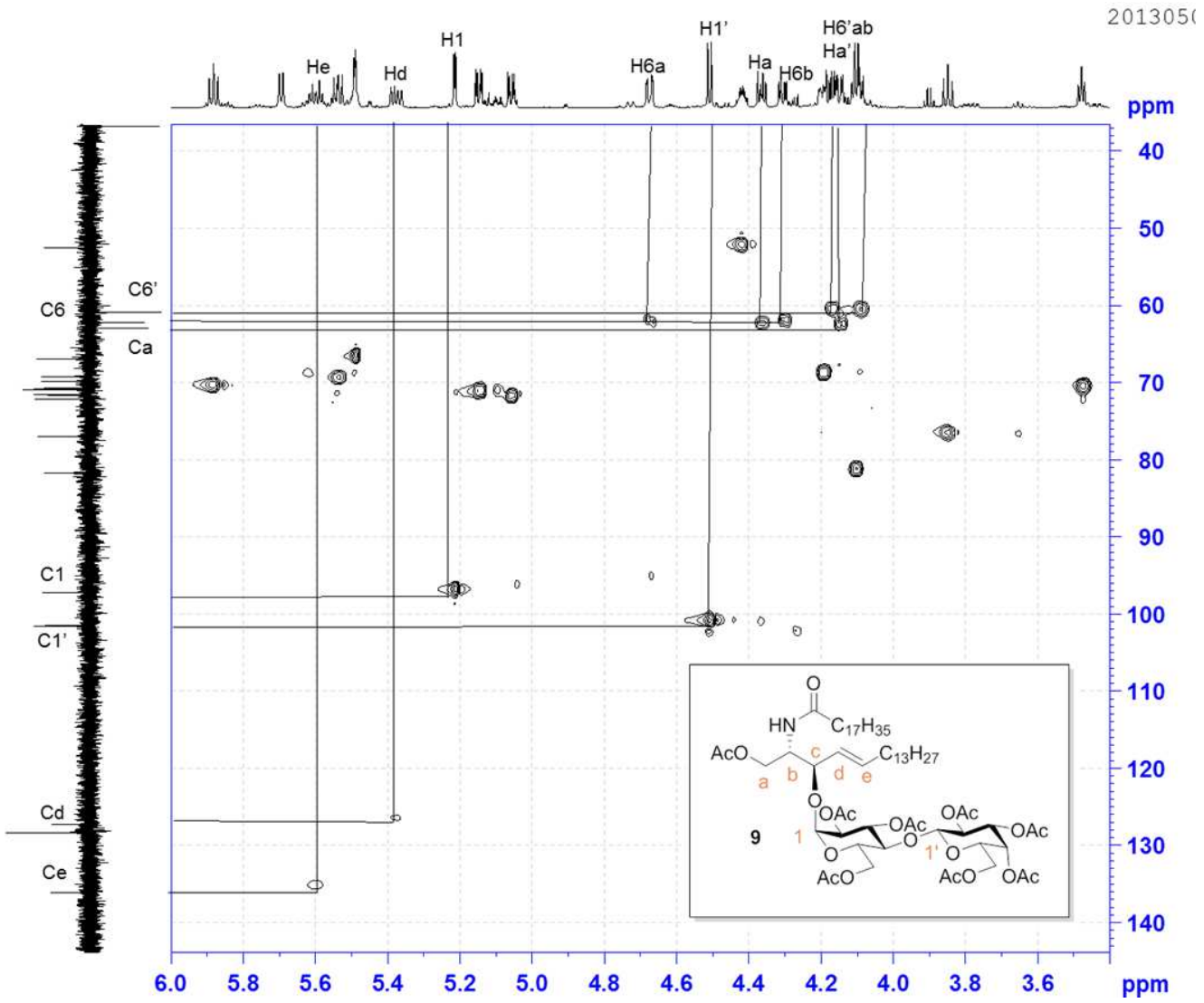
^{1}H NMR spectrum of compound **9** (C_6D_6, 800 MHz)



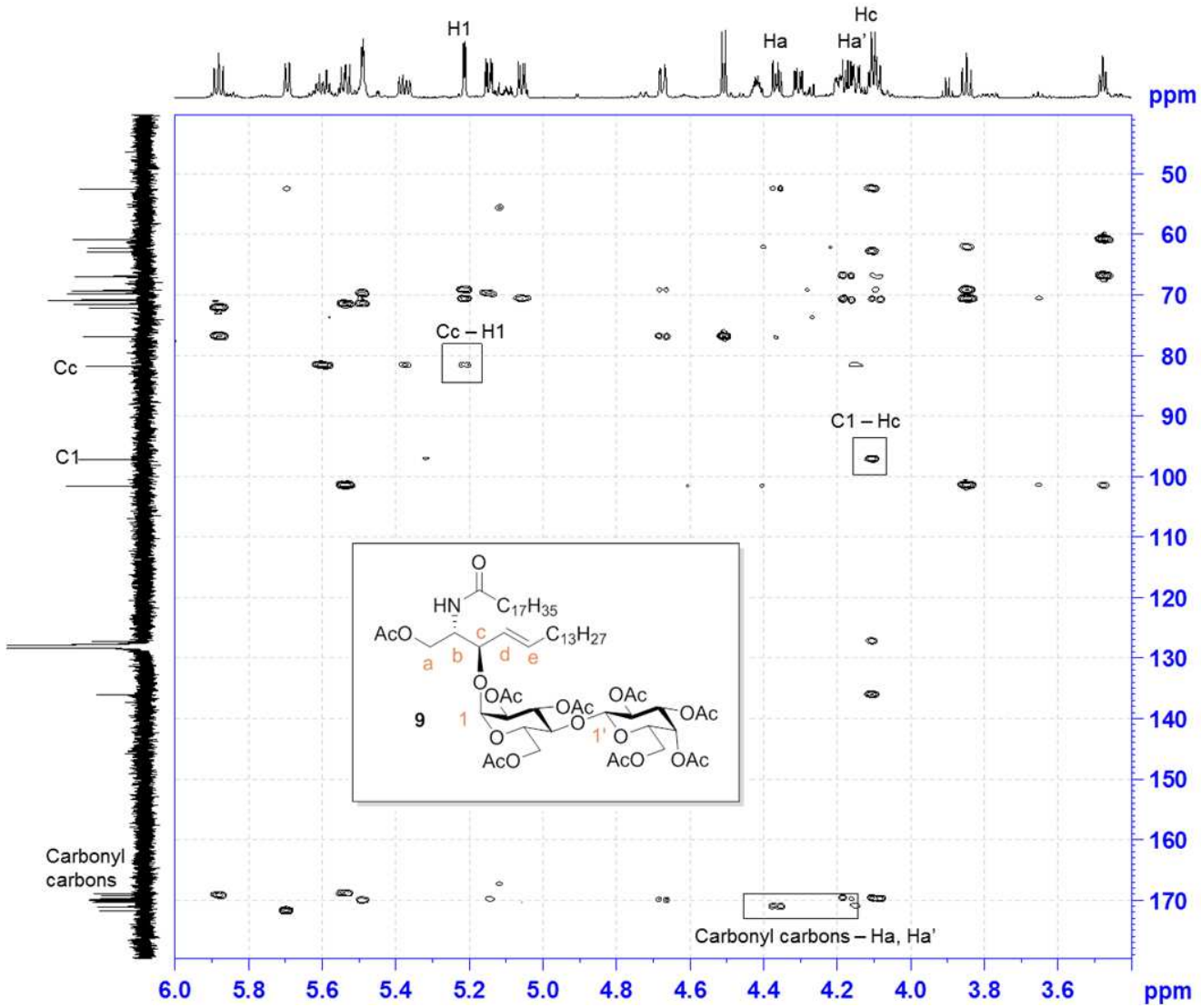
^{13}C and DEPT135 NMR spectrum of compound **9** (C_6D_6, 200 MHz)



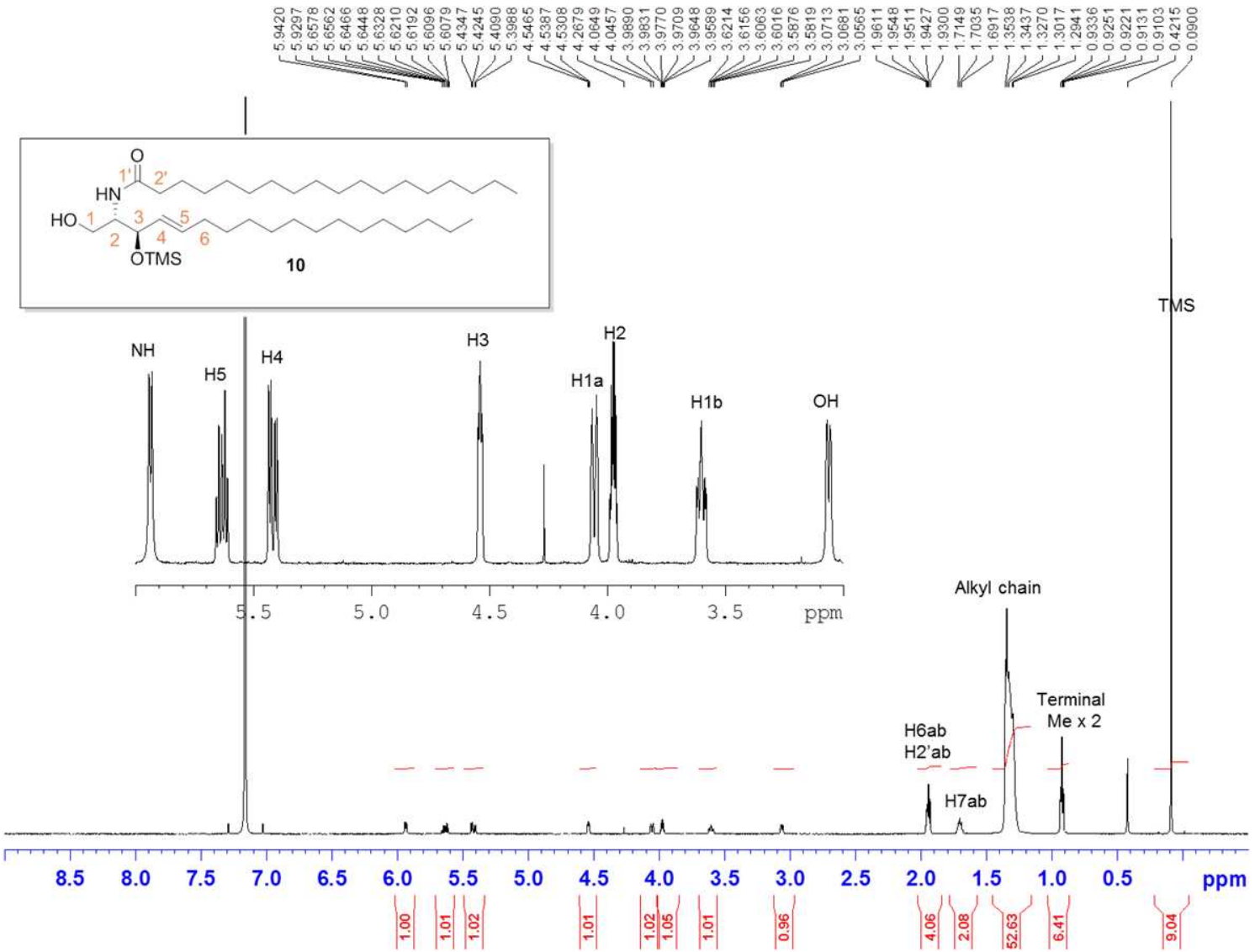
^{1}H-^{1}H COSY spectrum of compound **9** (C_6D_6, 800 MHz)



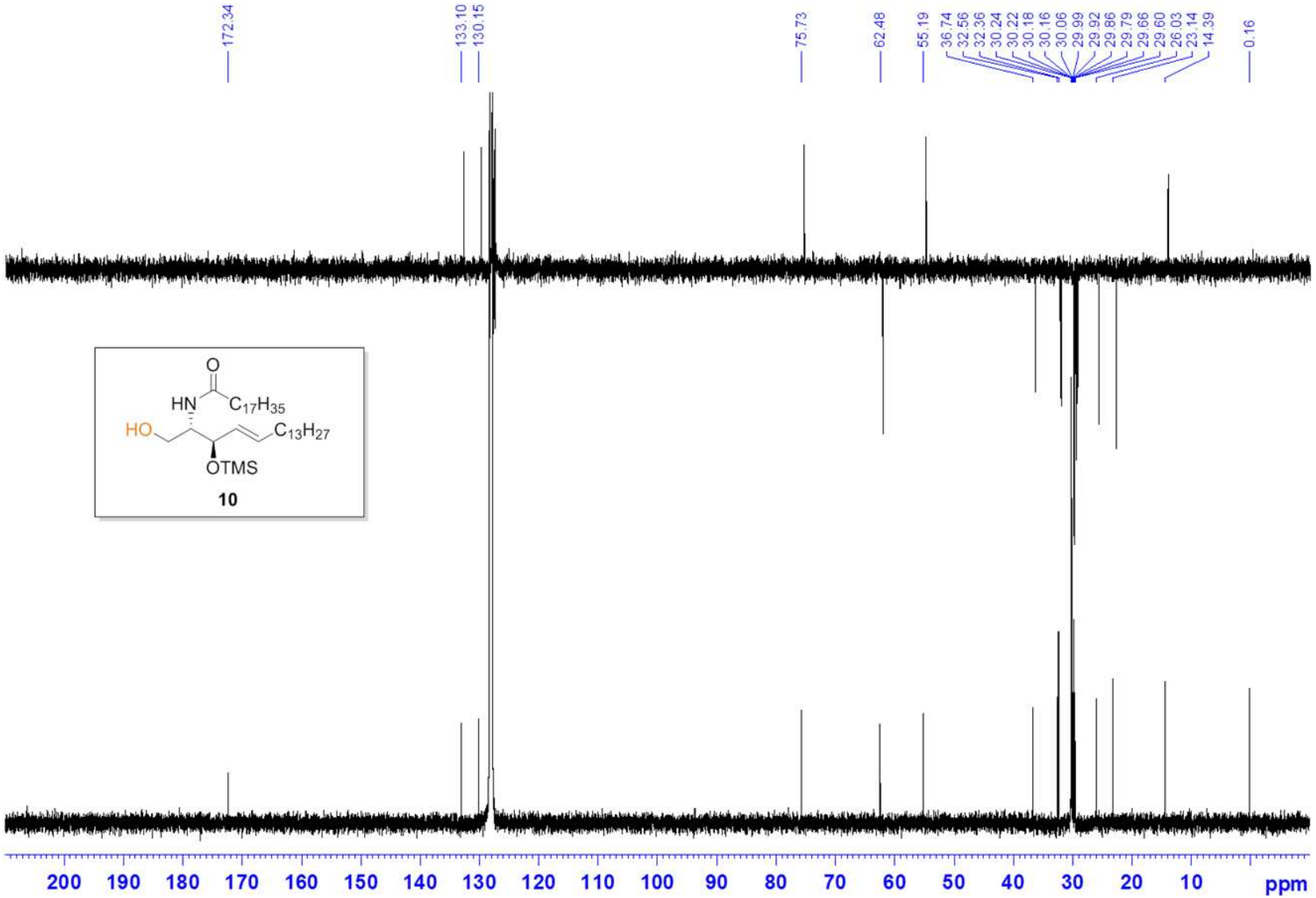
^{1}H-^{13}C HSQC spectrum of compound **9** (C_6D_6, 800 MHz)



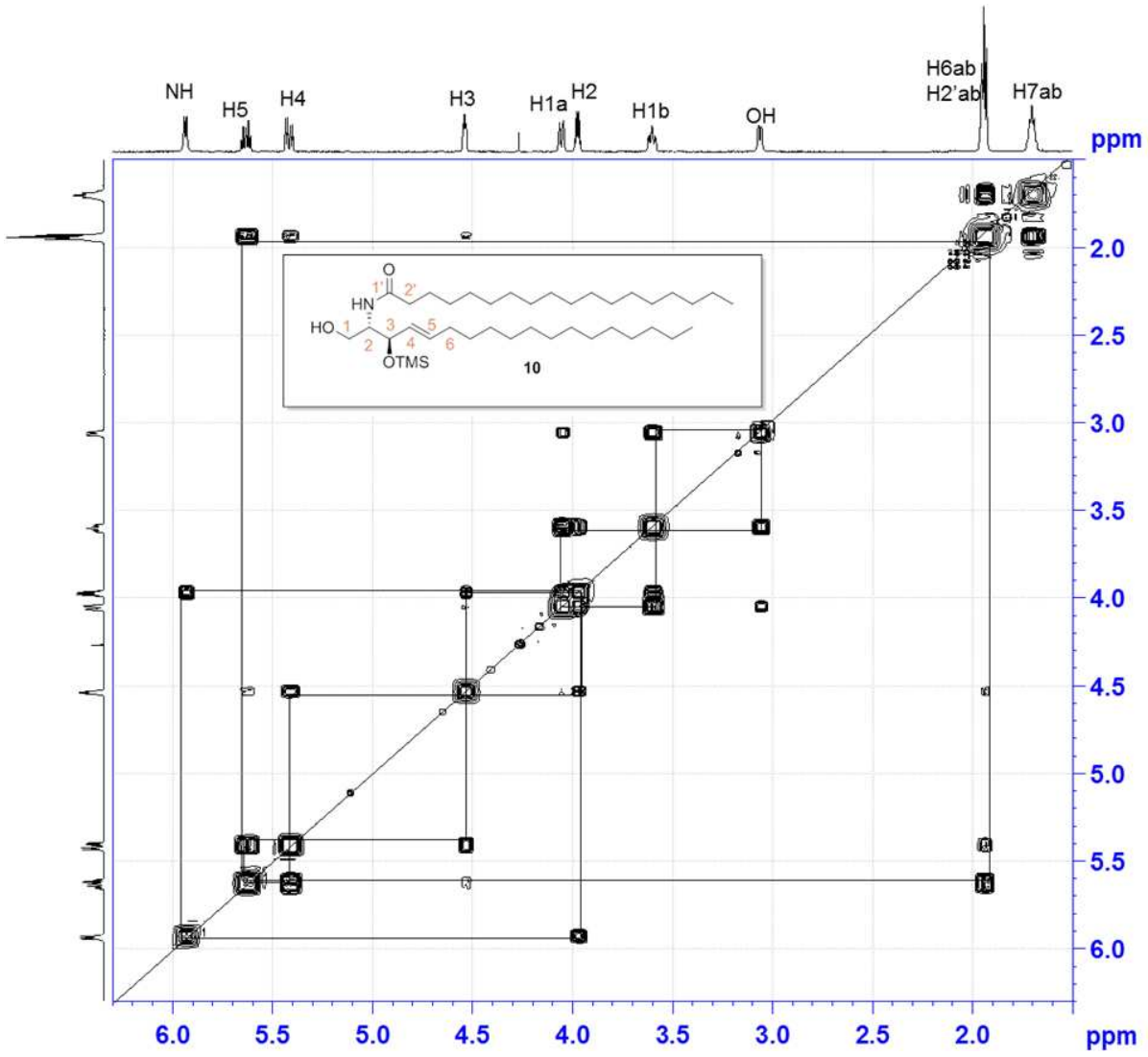
^{1}H-^{13}C HMBC spectrum of compound **9** (C_6D_6, 800 MHz)



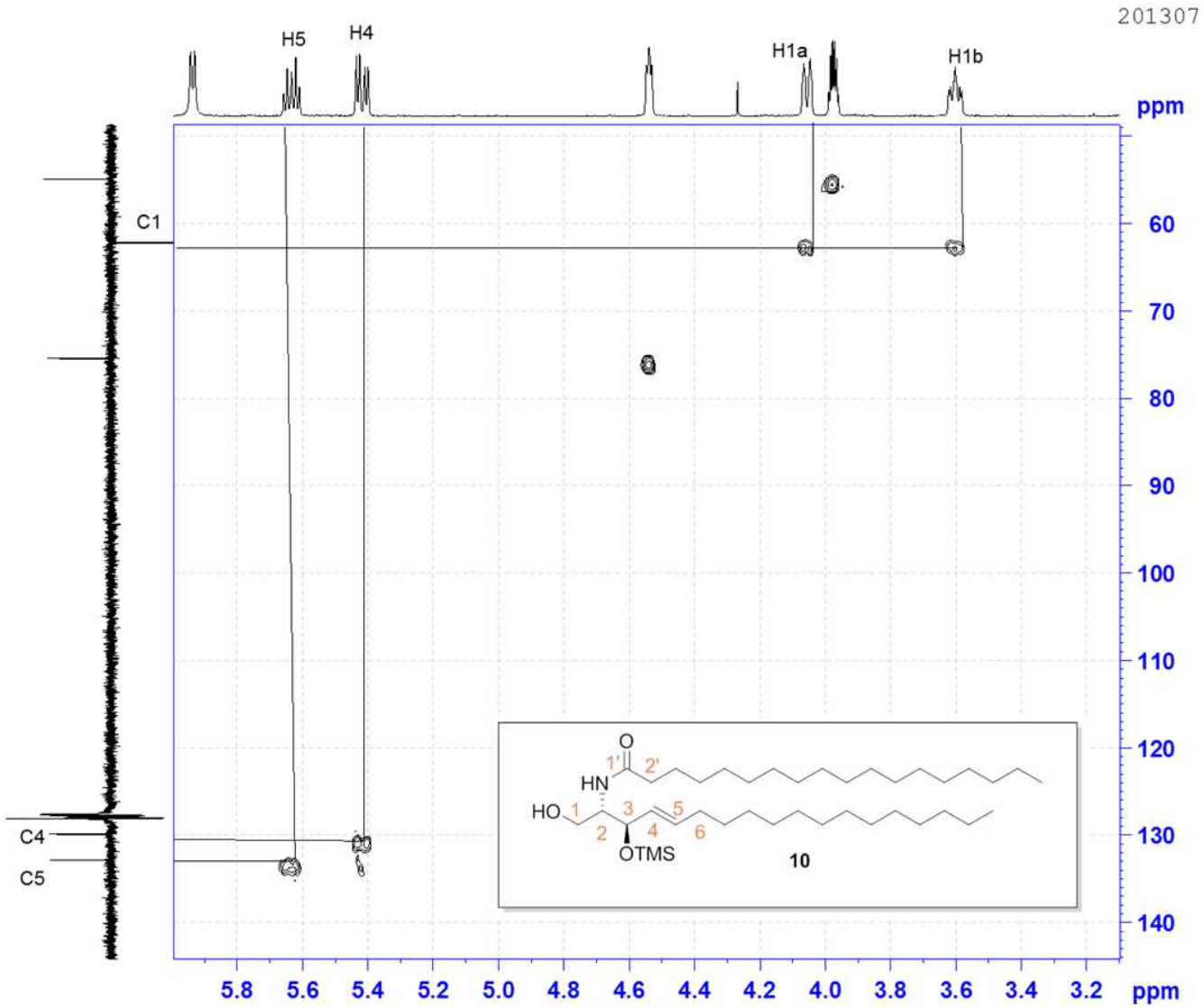
^{1}H NMR spectrum of compound **10** (C_6D_6, 600 MHz)



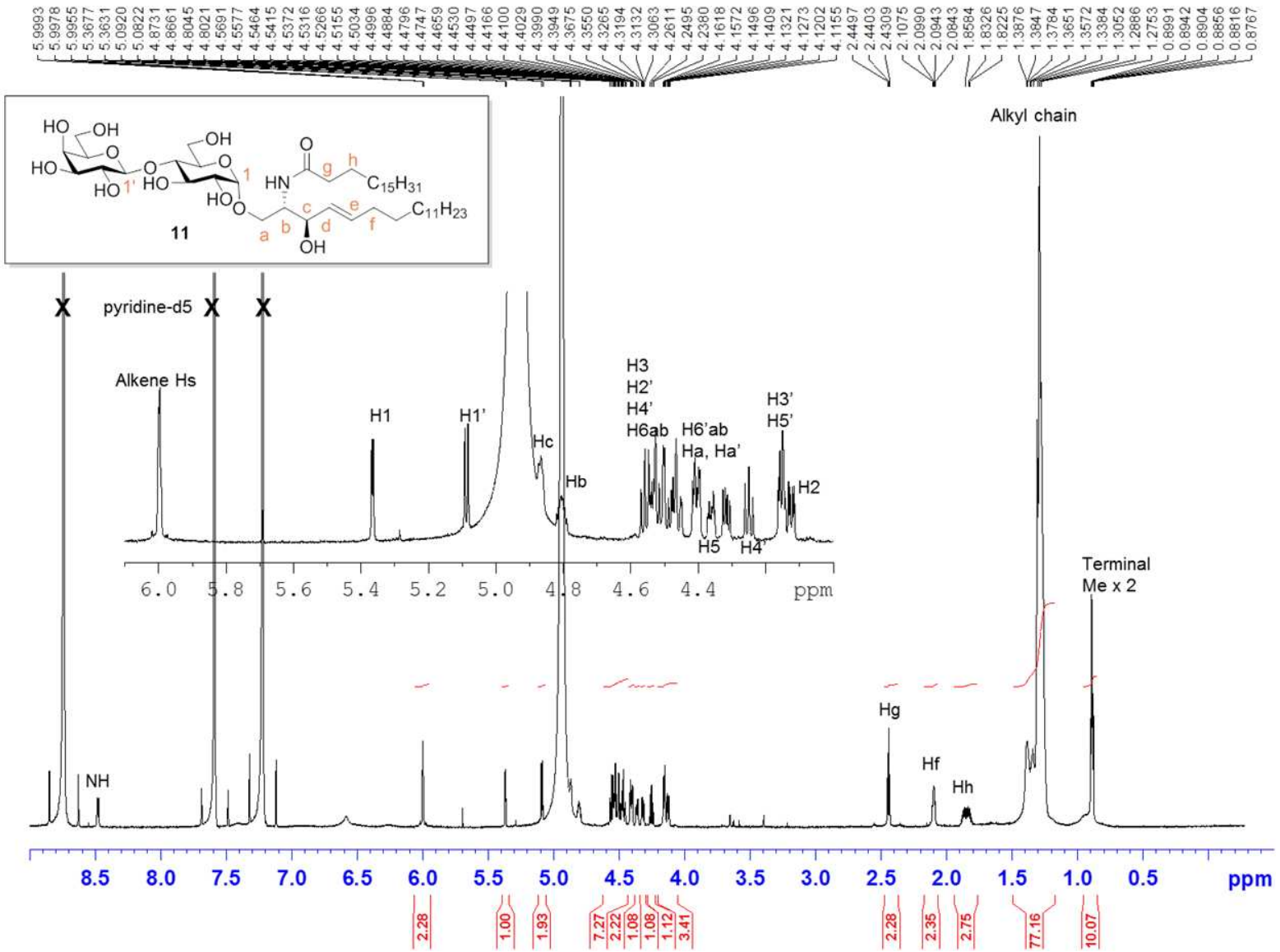
^{13}C and DEPT135 NMR spectrum of compound **10** (C_6D_6, 150 MHz)



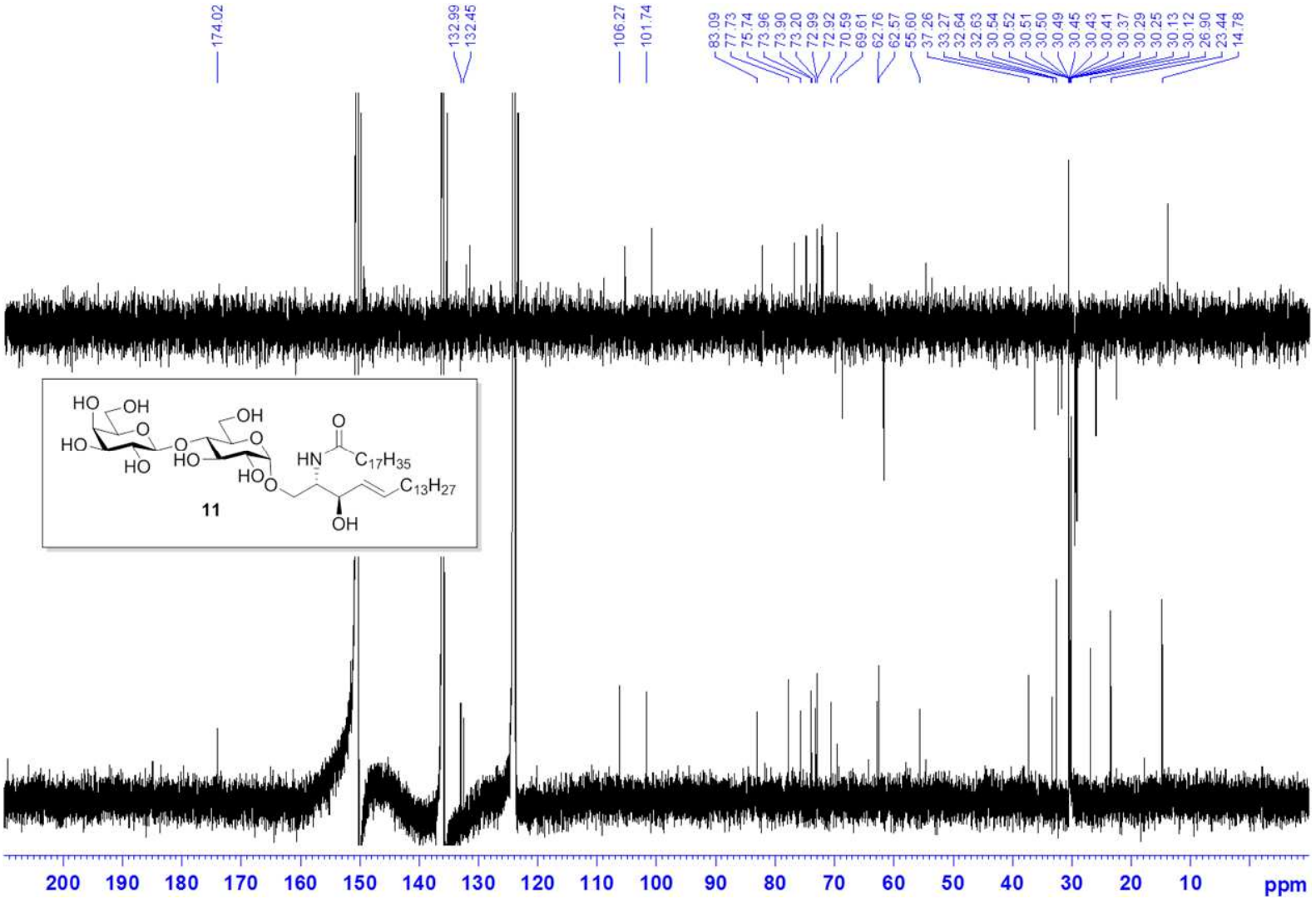
^{1}H-^{1}H COSY spectrum of compound **10** (C_6D_6, 600 MHz)



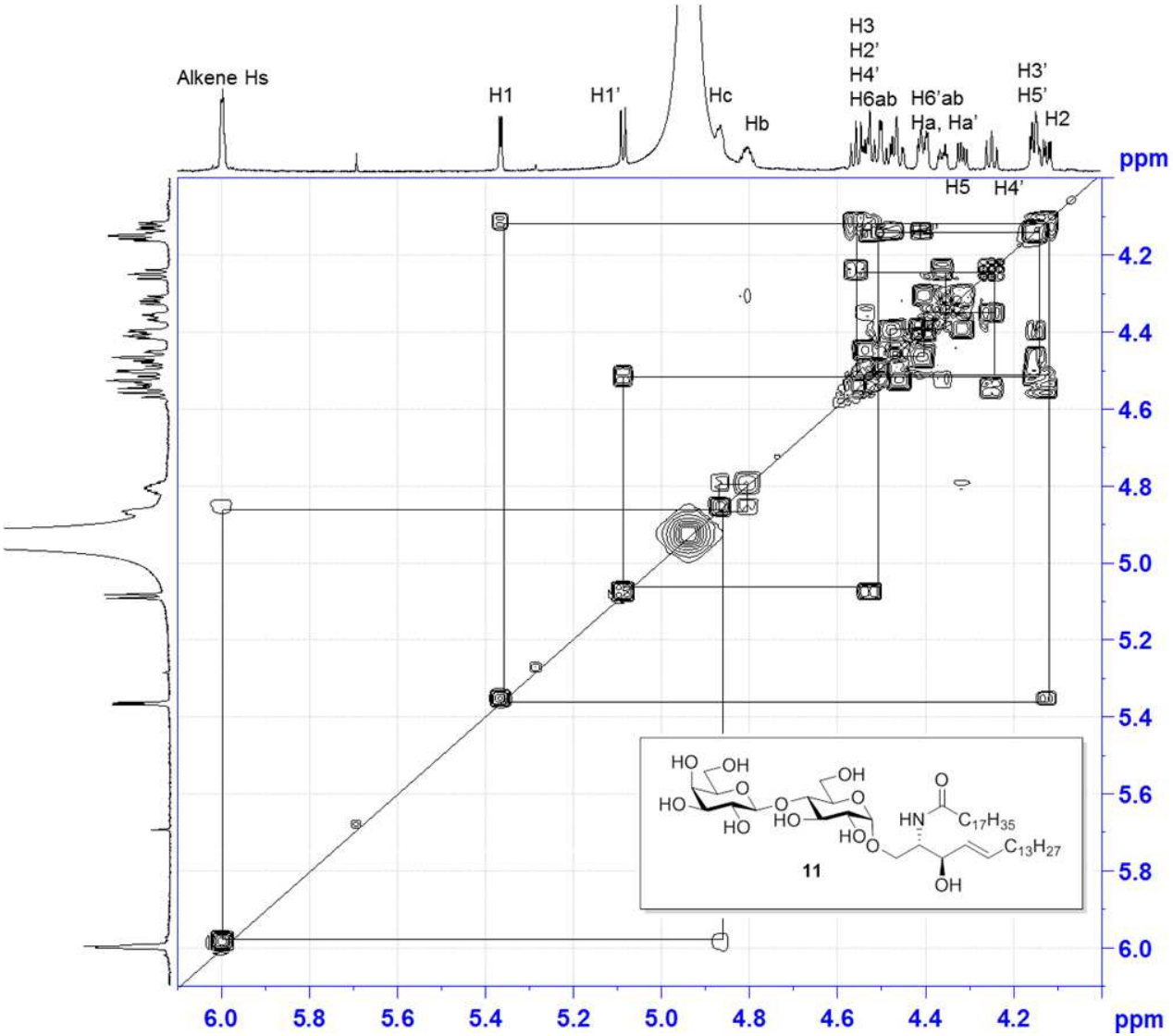
^{1}H-^{13}C HSQC spectrum of compound **10** (C_6D_6, 600 MHz)



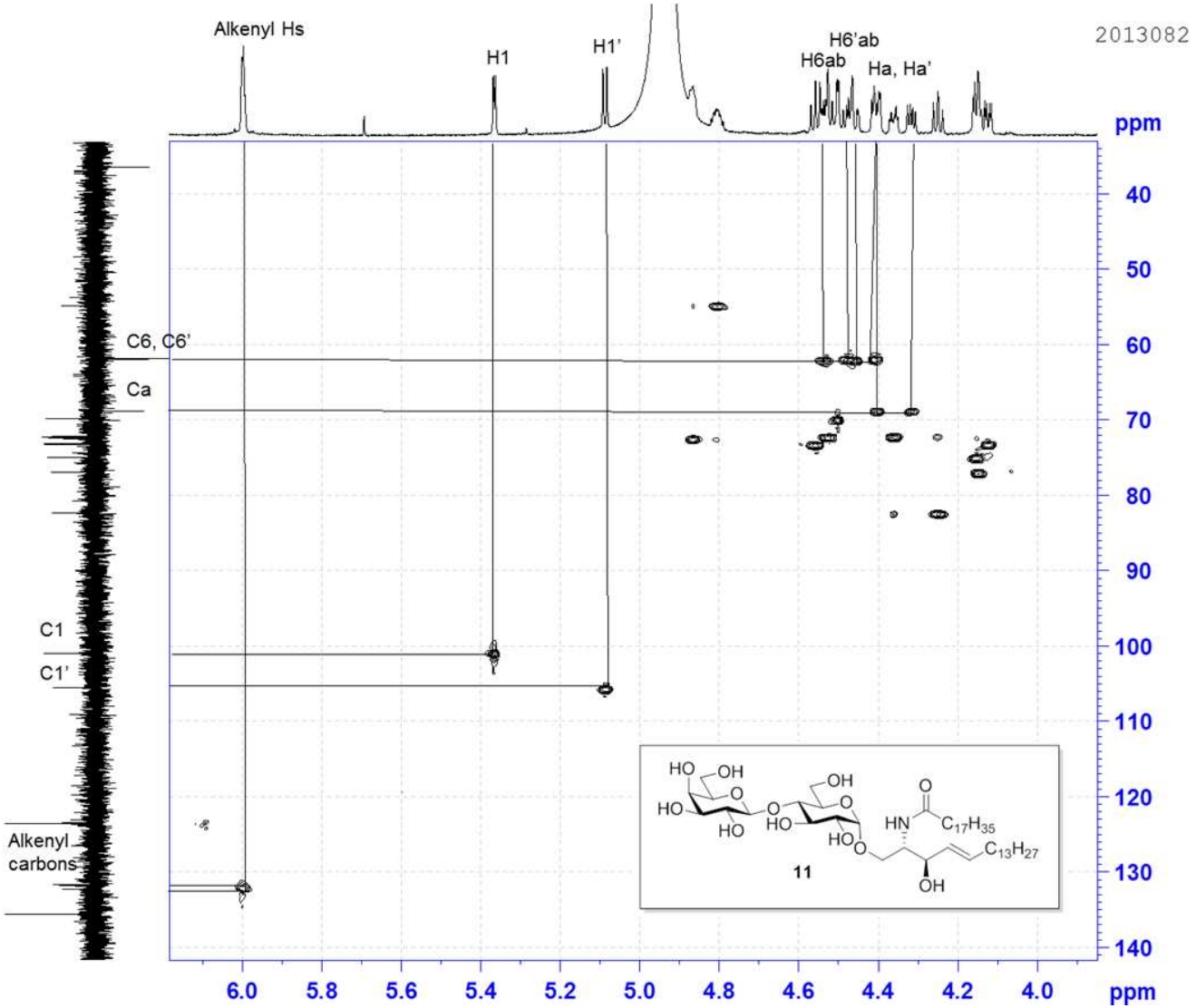
^{1}H NMR spectrum of compound **11** (pyridine-d_5, 800 MHz)



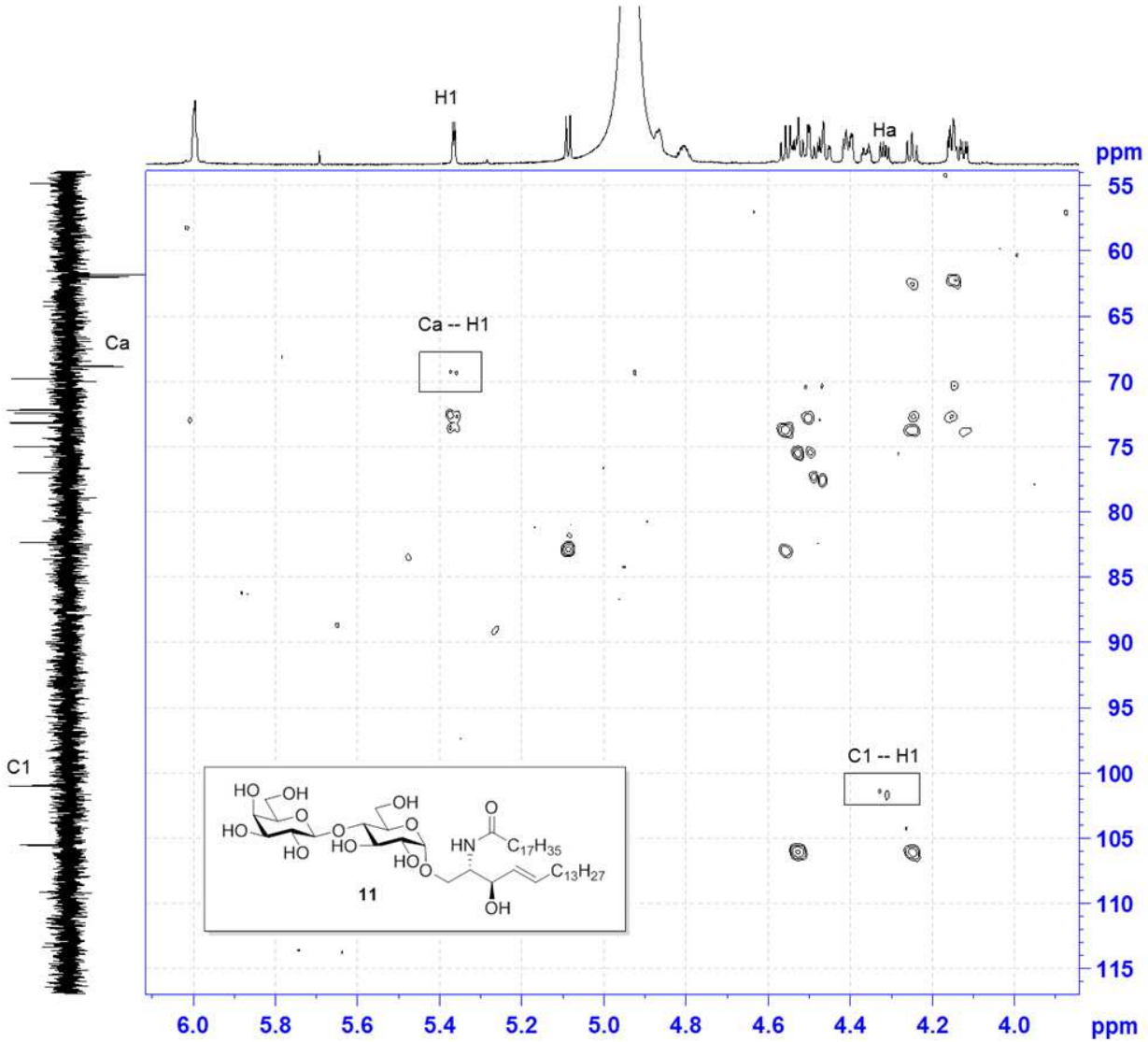
^{13}C and DEPT135 NMR spectrum of compound **11** (pyridine-d_5, 200 MHz)



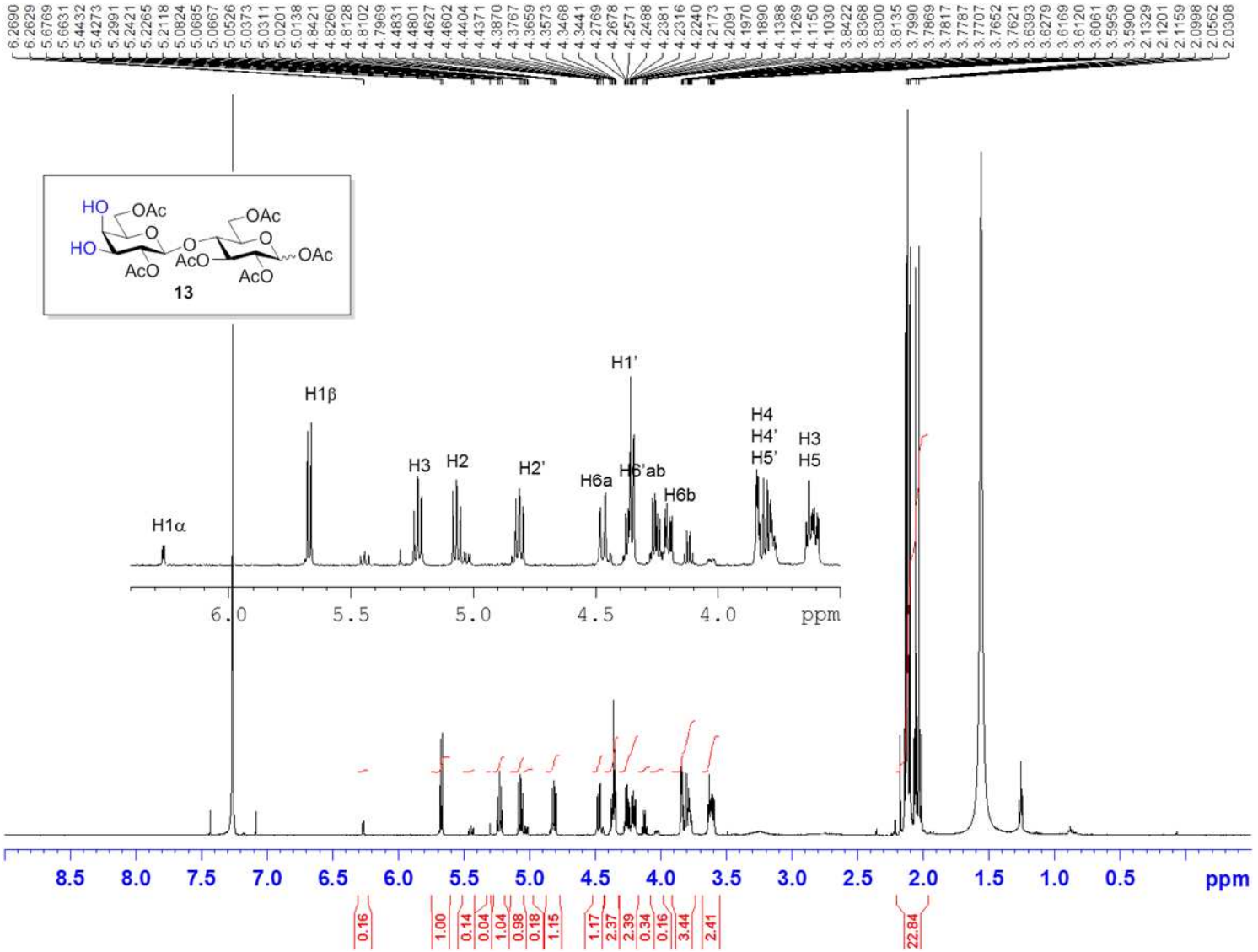
^{1}H-^{1}H COSY spectrum of compound **11** (pyridine-d_5, 800 MHz)



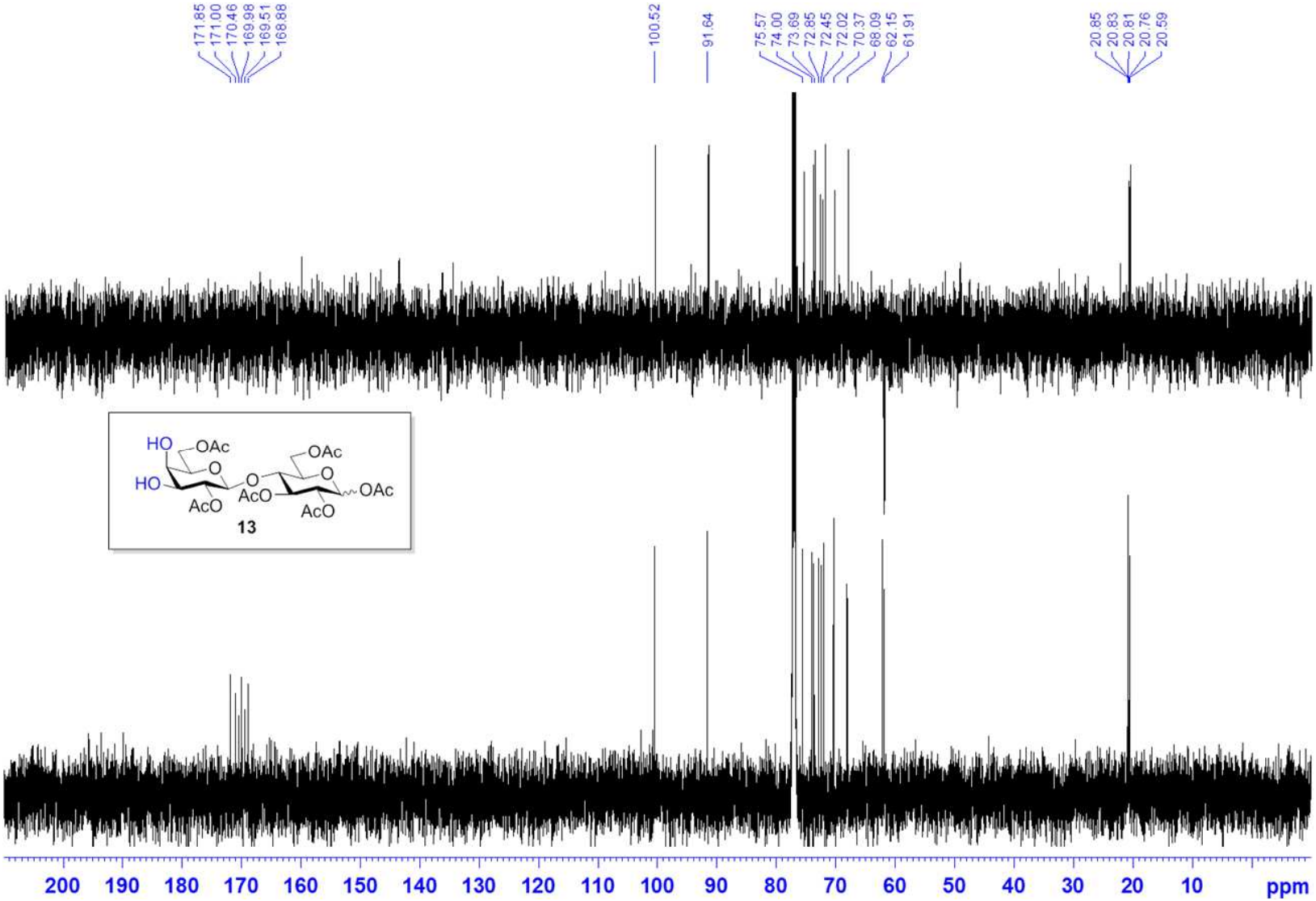
^{1}H-^{13}C HSQC spectrum of compound **11** (pyridine-d_5, 800 MHz)



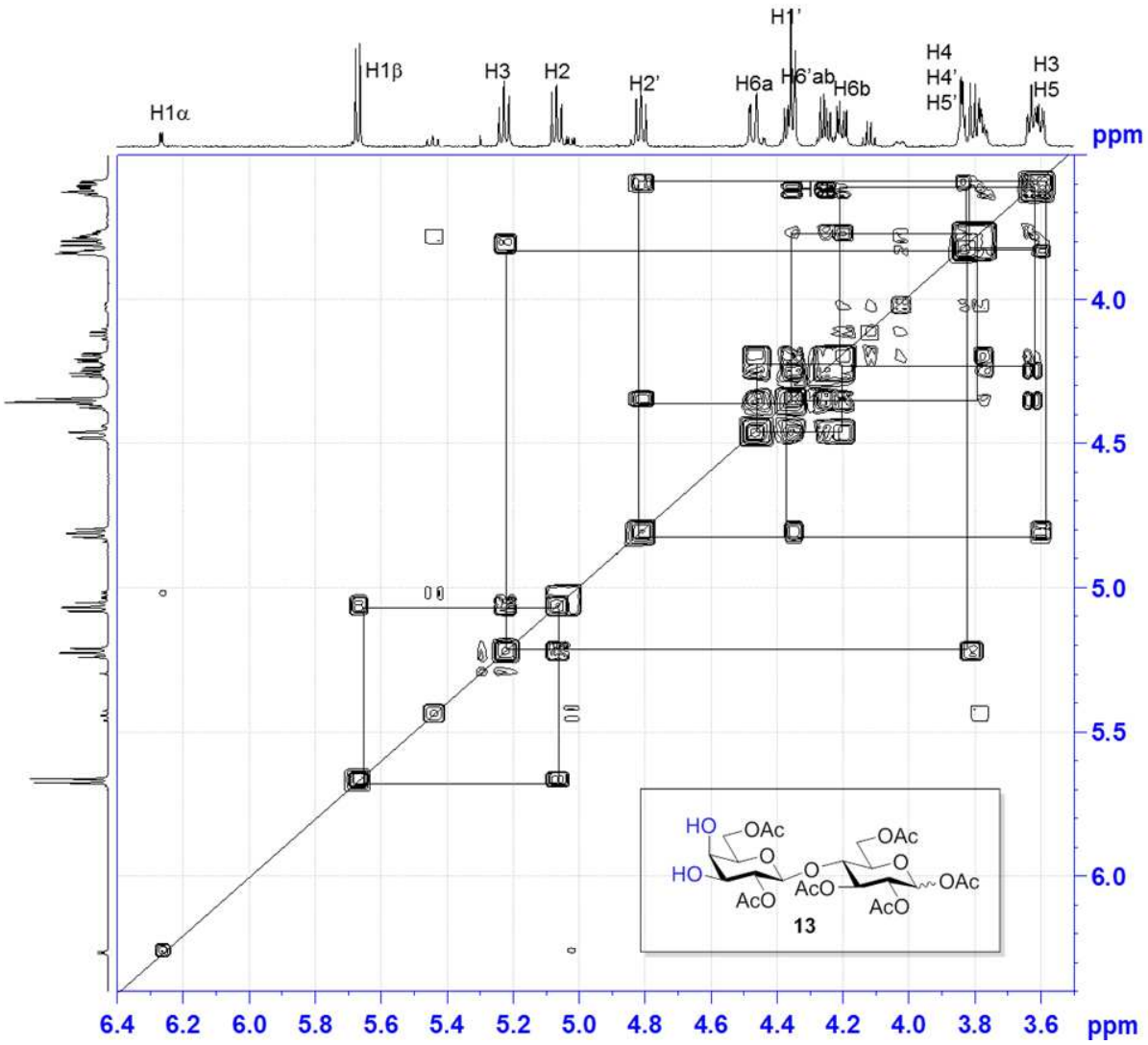
^{1}H-^{13}C HMBC spectrum of compound **11** (pyridine-d_5, 800 MHz)



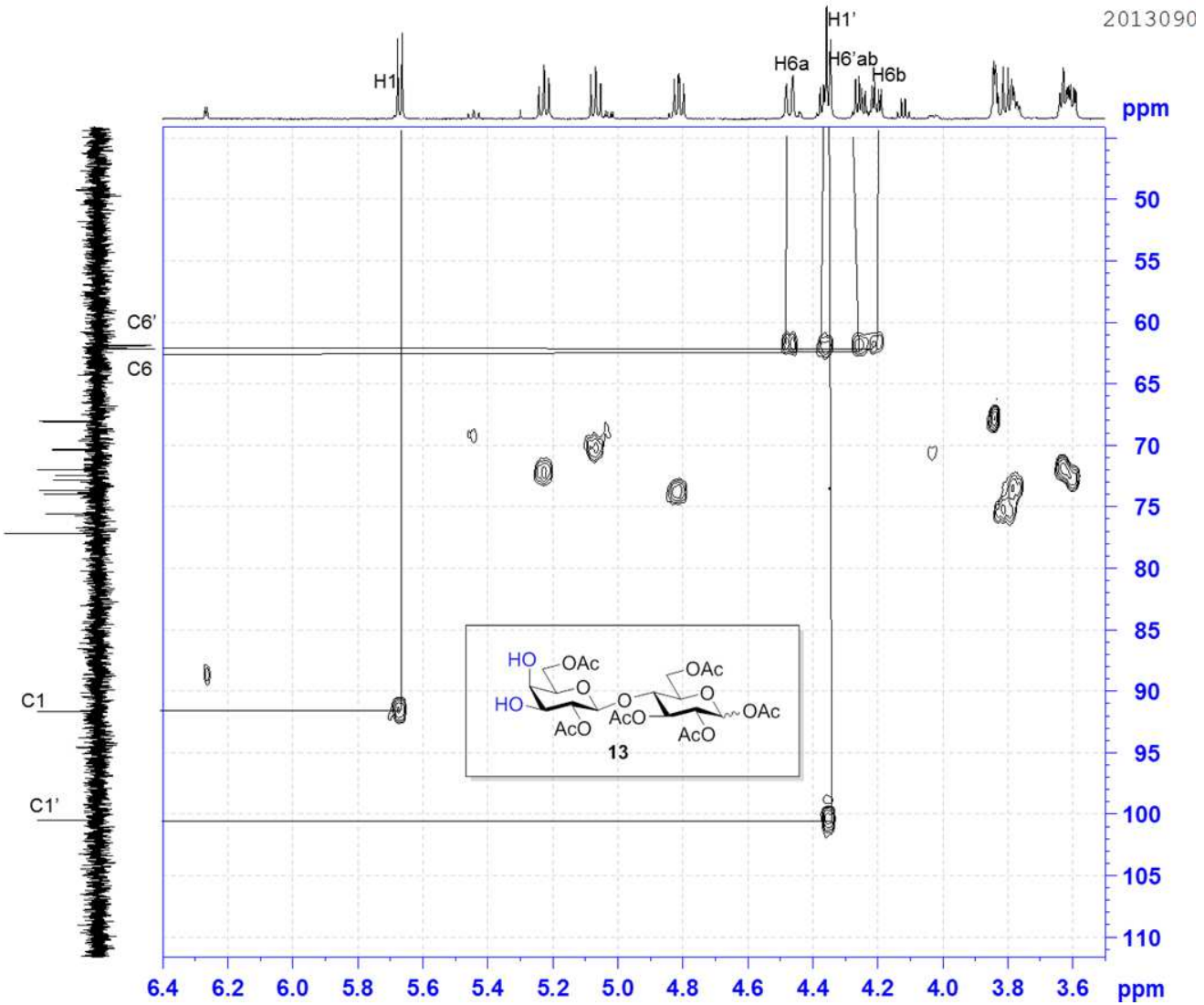
^{1}H NMR spectrum of compound **13** ($CDCl_3$, 600 MHz)



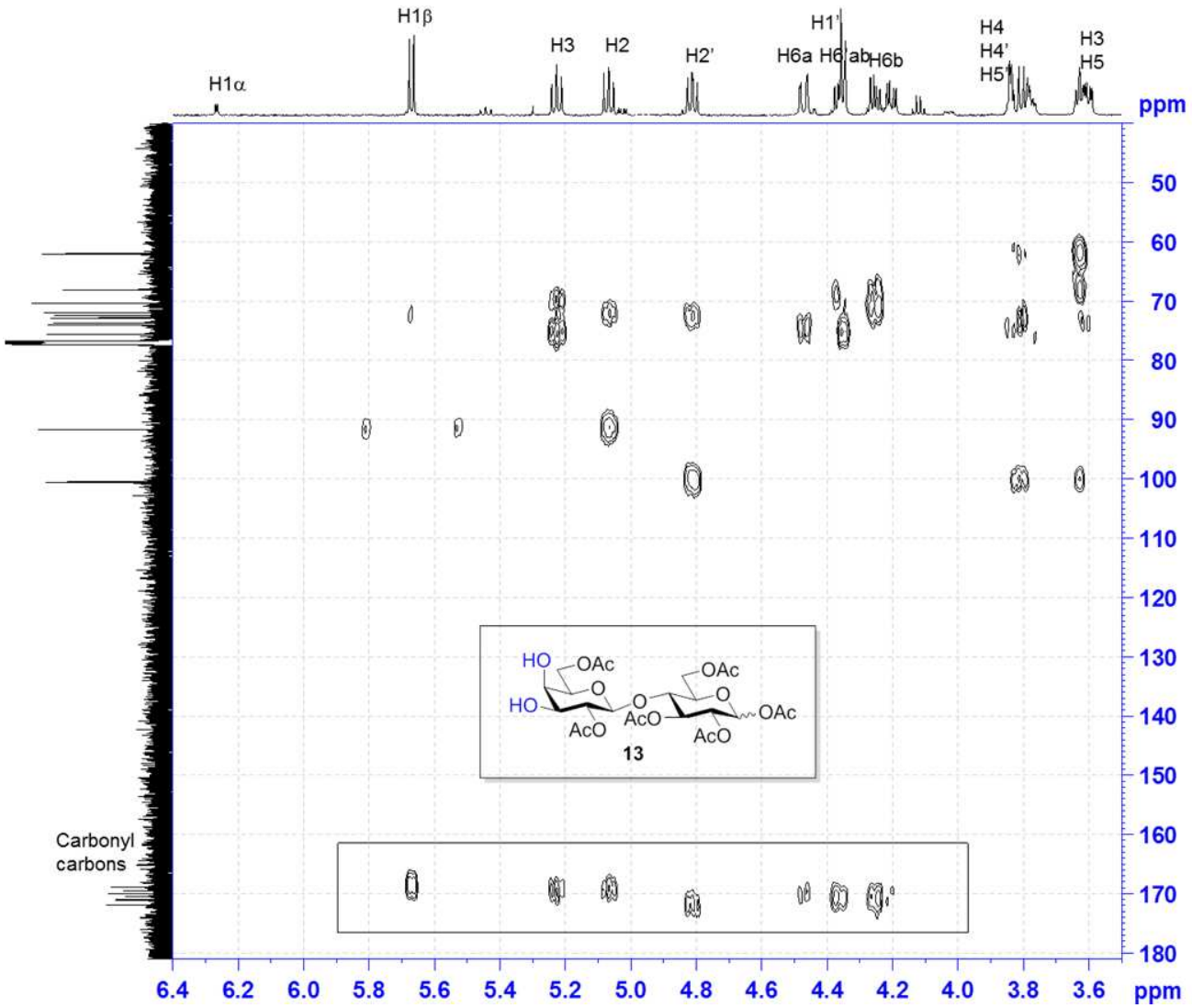
^{13}C and DEPT135 NMR spectrum of compound **13** ($CDCl_3$, 150 MHz)



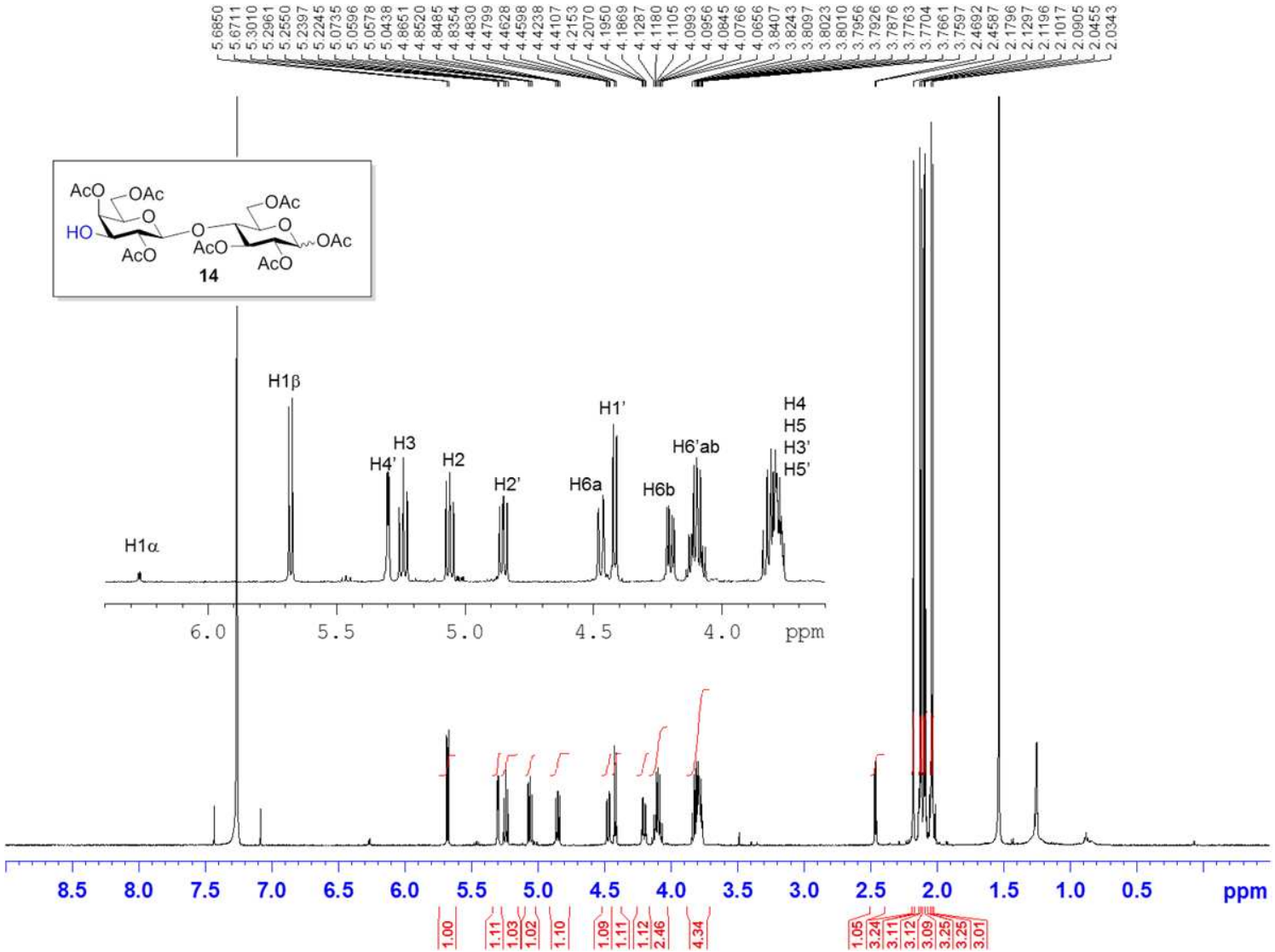
^{1}H-^{1}H COSY spectrum of compound **13** ($CDCl_3$, 600 MHz)



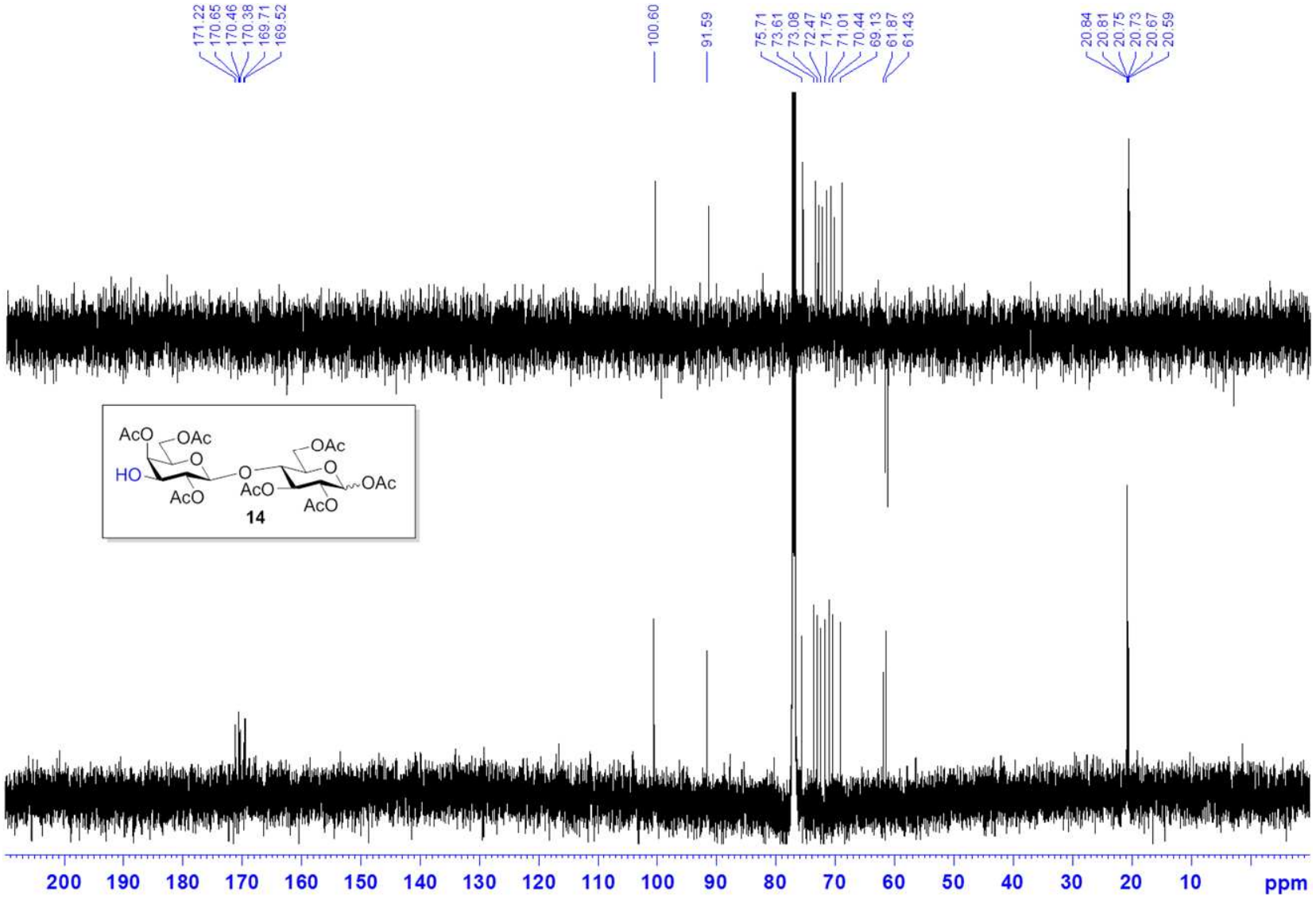
^{1}H-^{13}C HSQC spectrum of compound **13** ($CDCl_3$, 600 MHz)



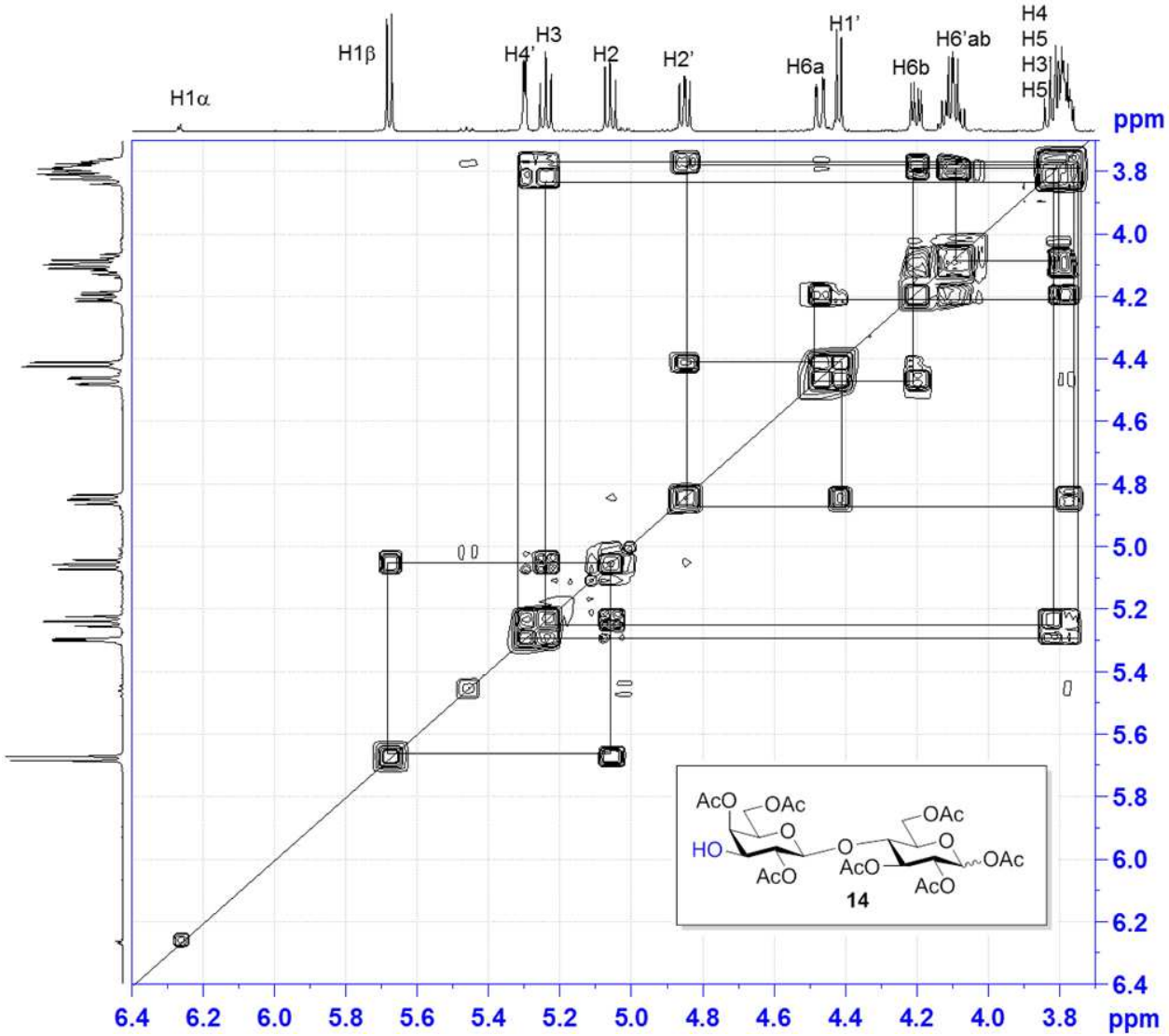
^{1}H-^{13}C HMBC spectrum of compound **13** ($CDCl_3$, 600 MHz)



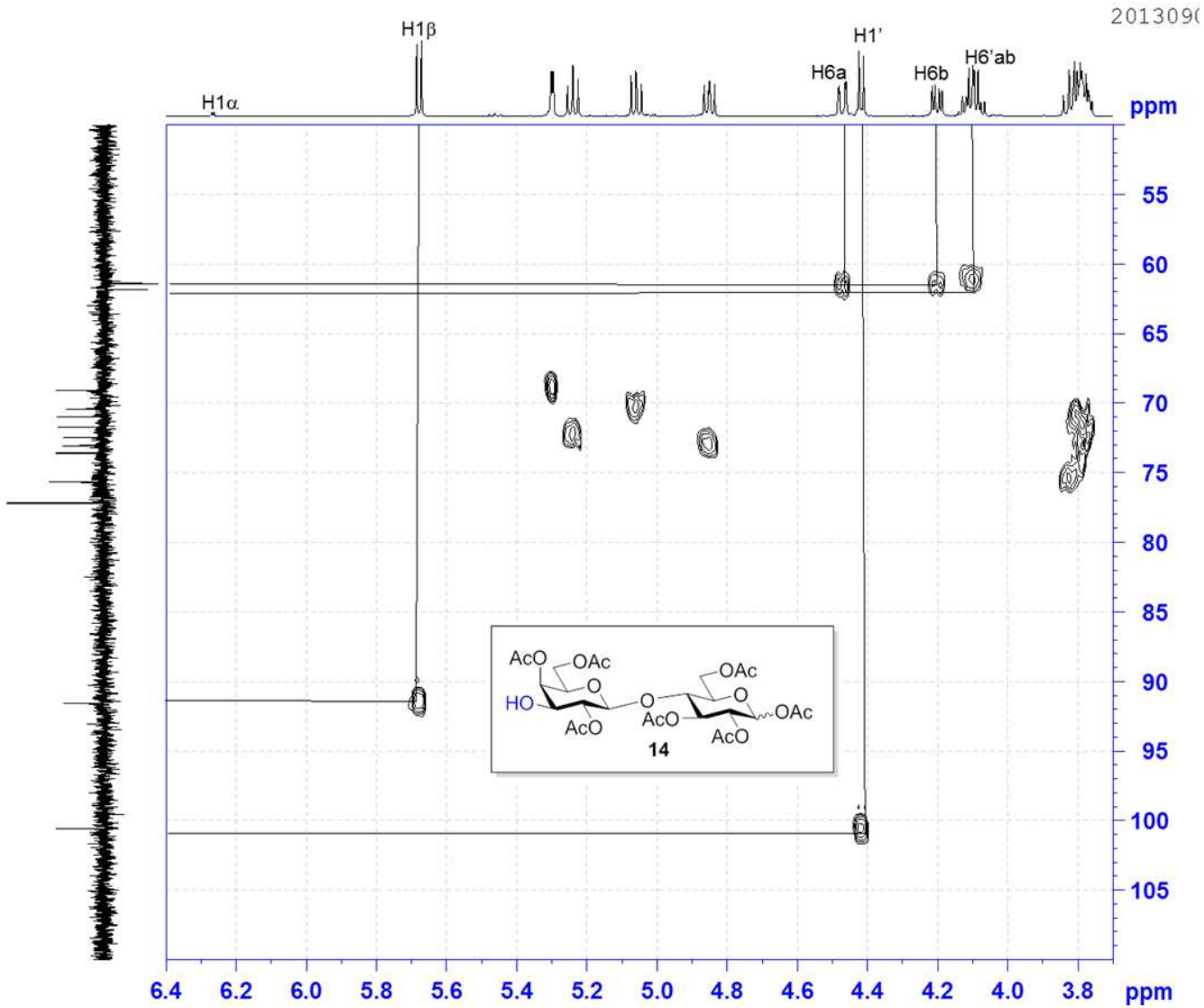
^{1}H NMR spectrum of compound **14** ($CDCl_3$, 600 MHz)



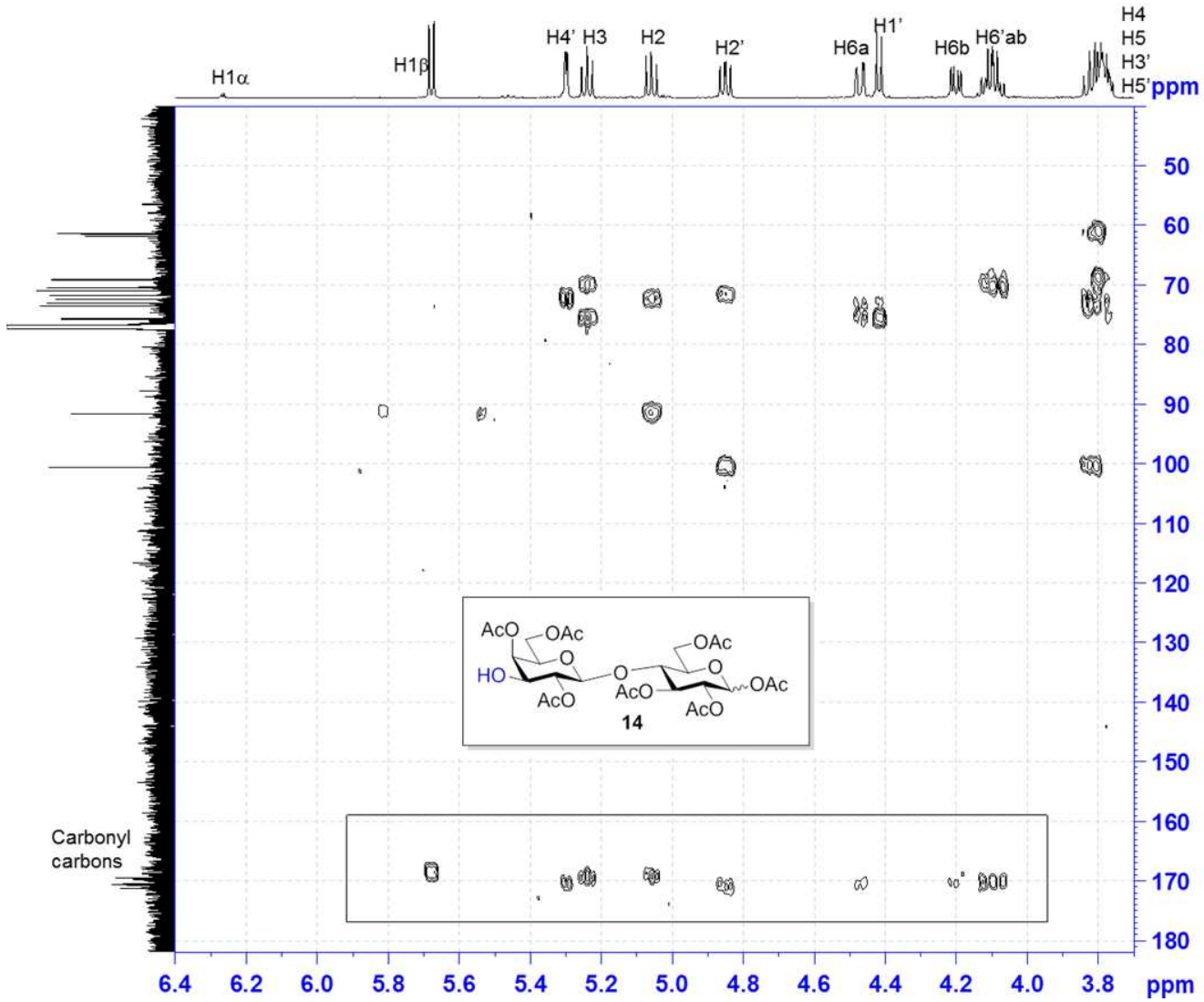
^{13}C and DEPT135 NMR spectrum of compound **14** ($CDCl_3$, 200 MHz)



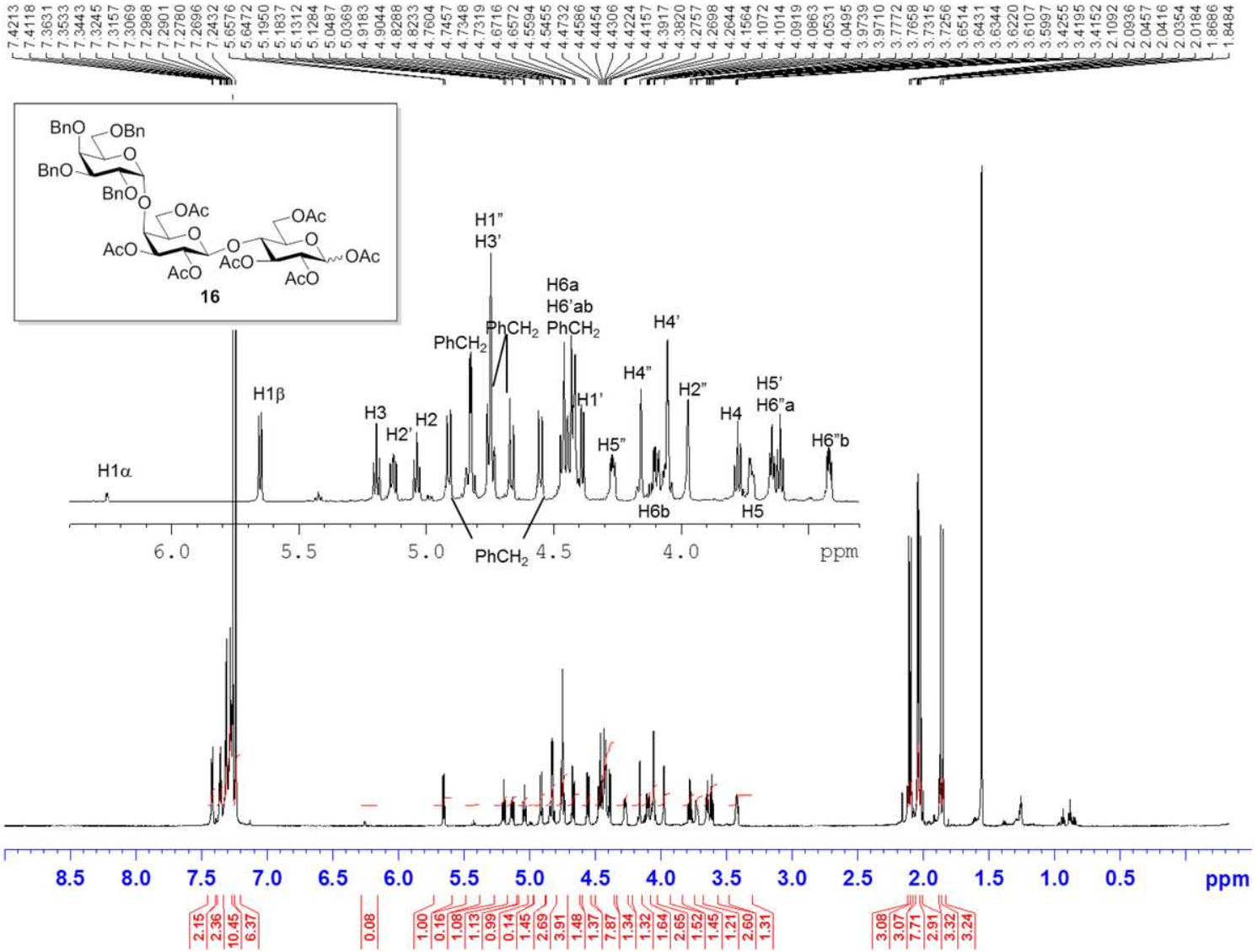
^{1}H-^{1}H COSY spectrum of compound **14** ($CDCl_3$, 800 MHz)



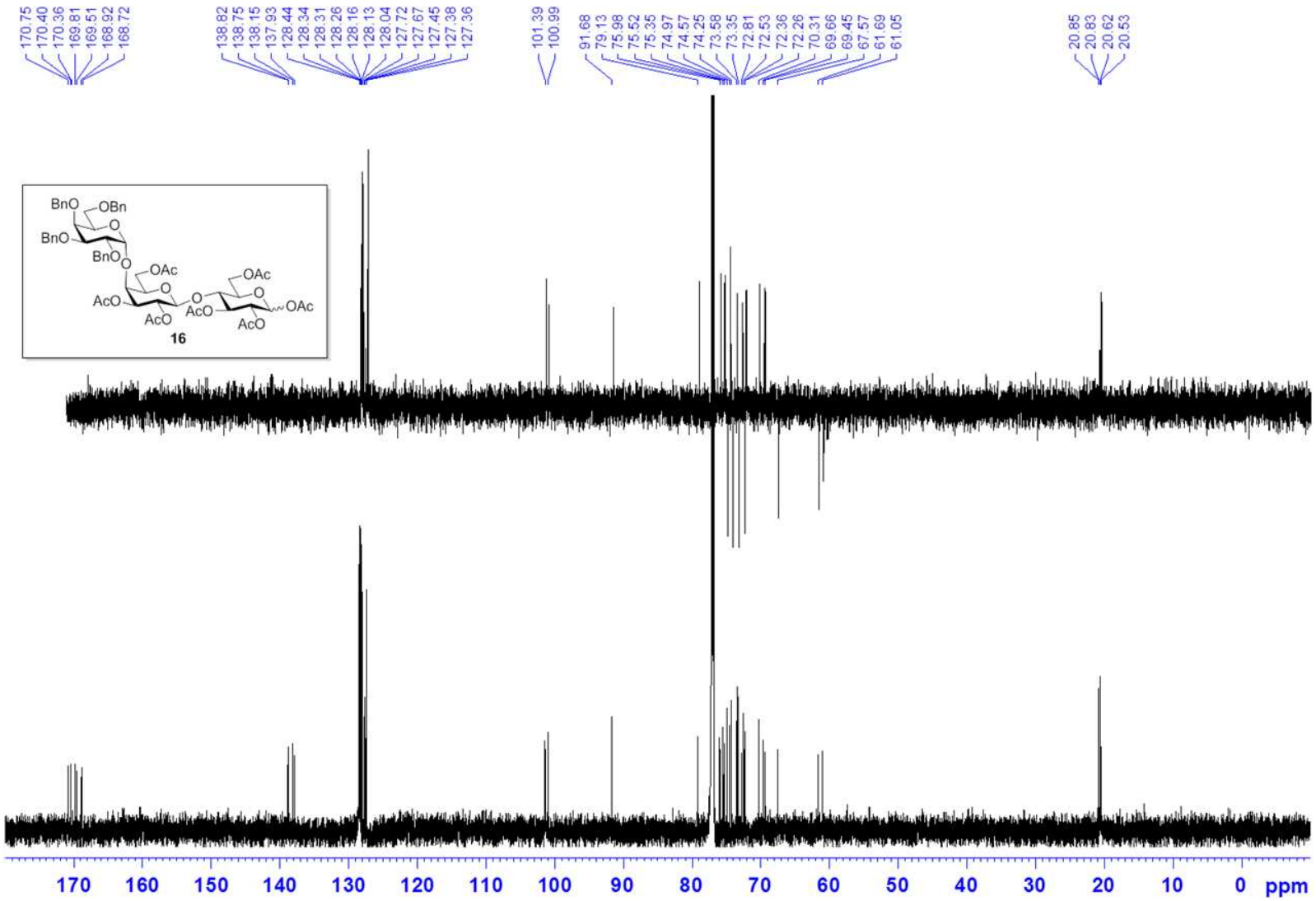
^{1}H-^{13}C HSQC spectrum of compound **14** ($CDCl_3$, 800 MHz)



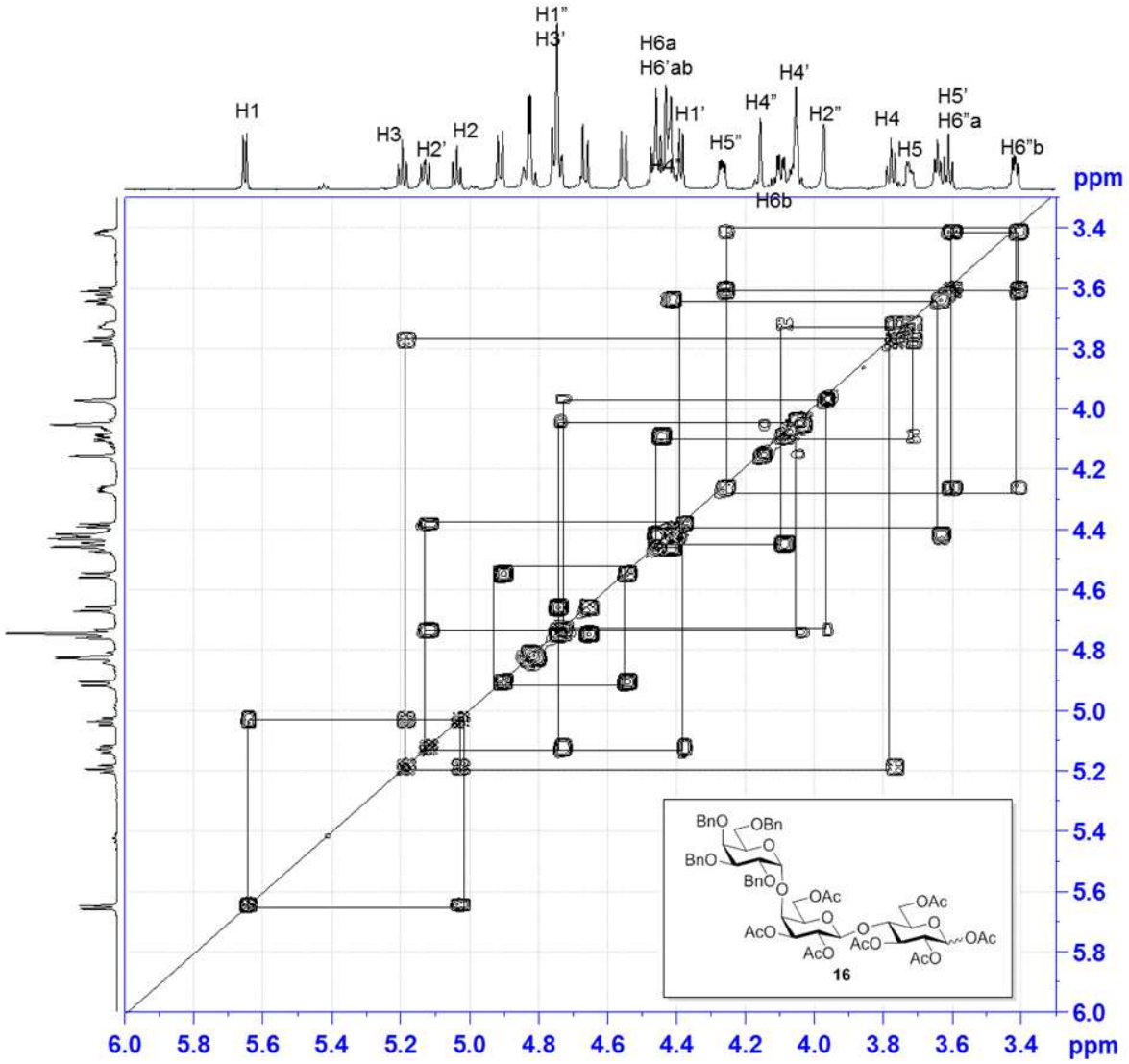
^{1}H-^{13}C HMBC spectrum of compound **14** ($CDCl_3$, 800 MHz)



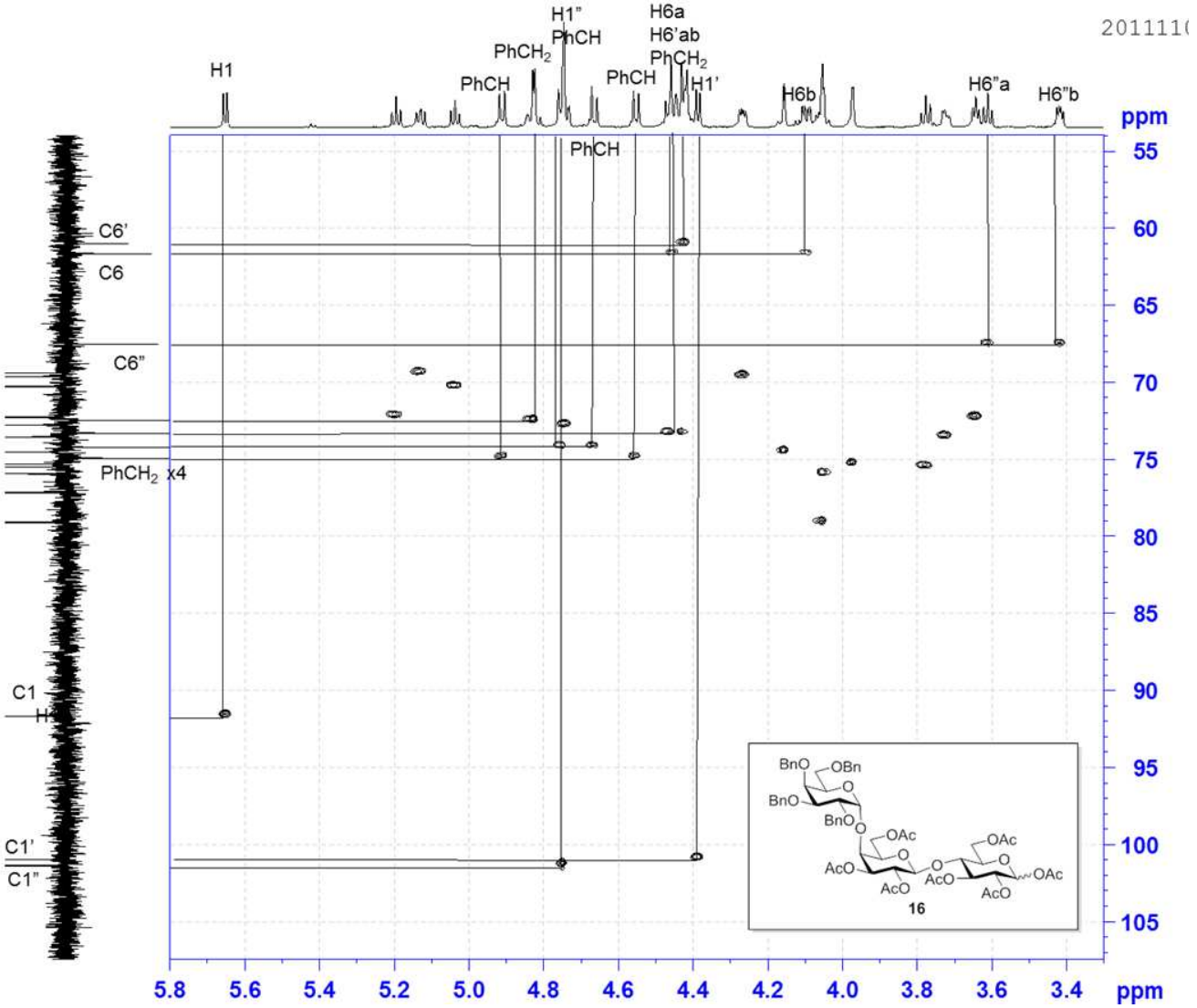
^{1}H NMR spectrum of compound **16** ($CDCl_3$, 800 MHz)



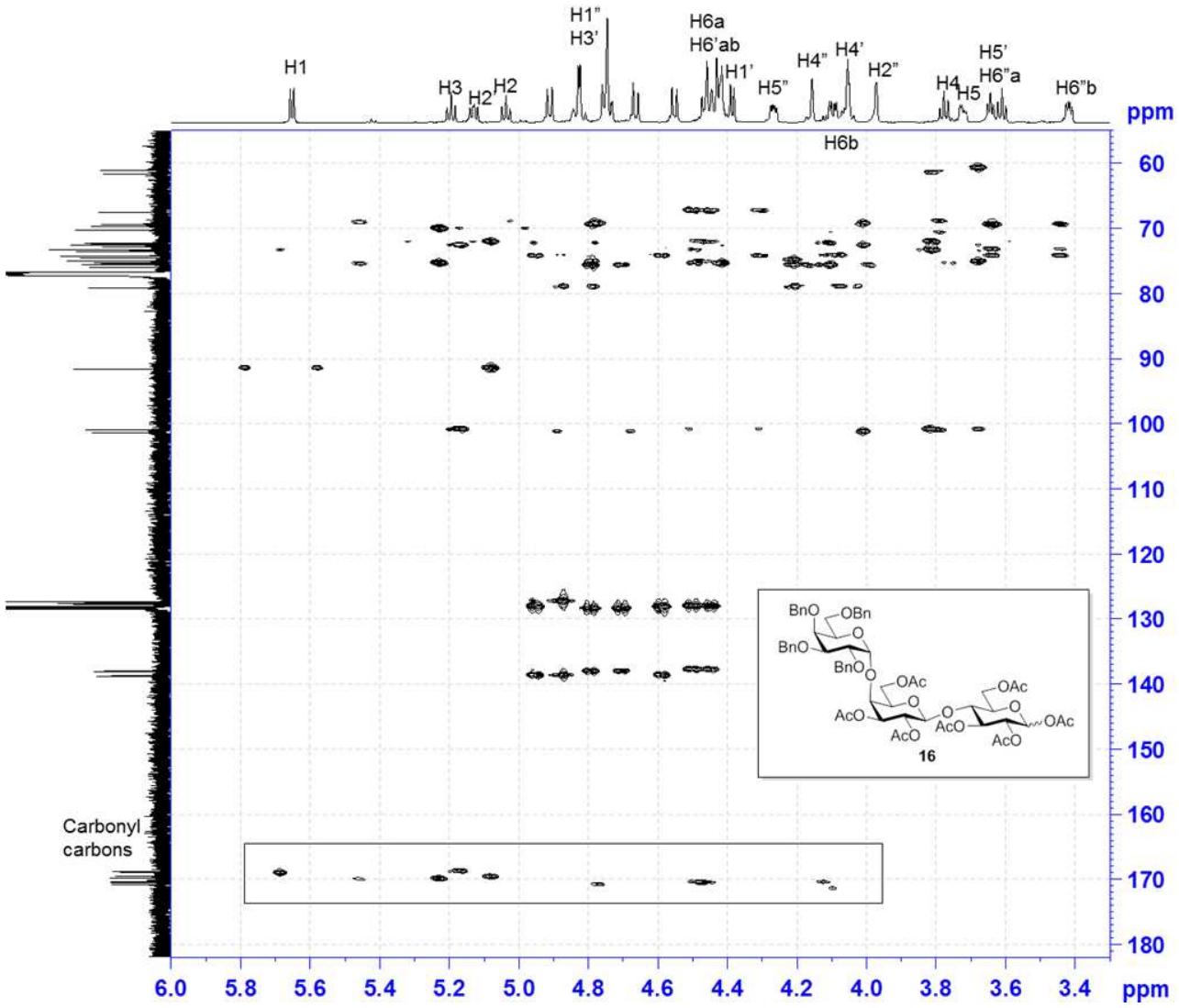
^{13}C and DEPT135 NMR spectrum of compound **16** ($CDCl_3$, 200 MHz)



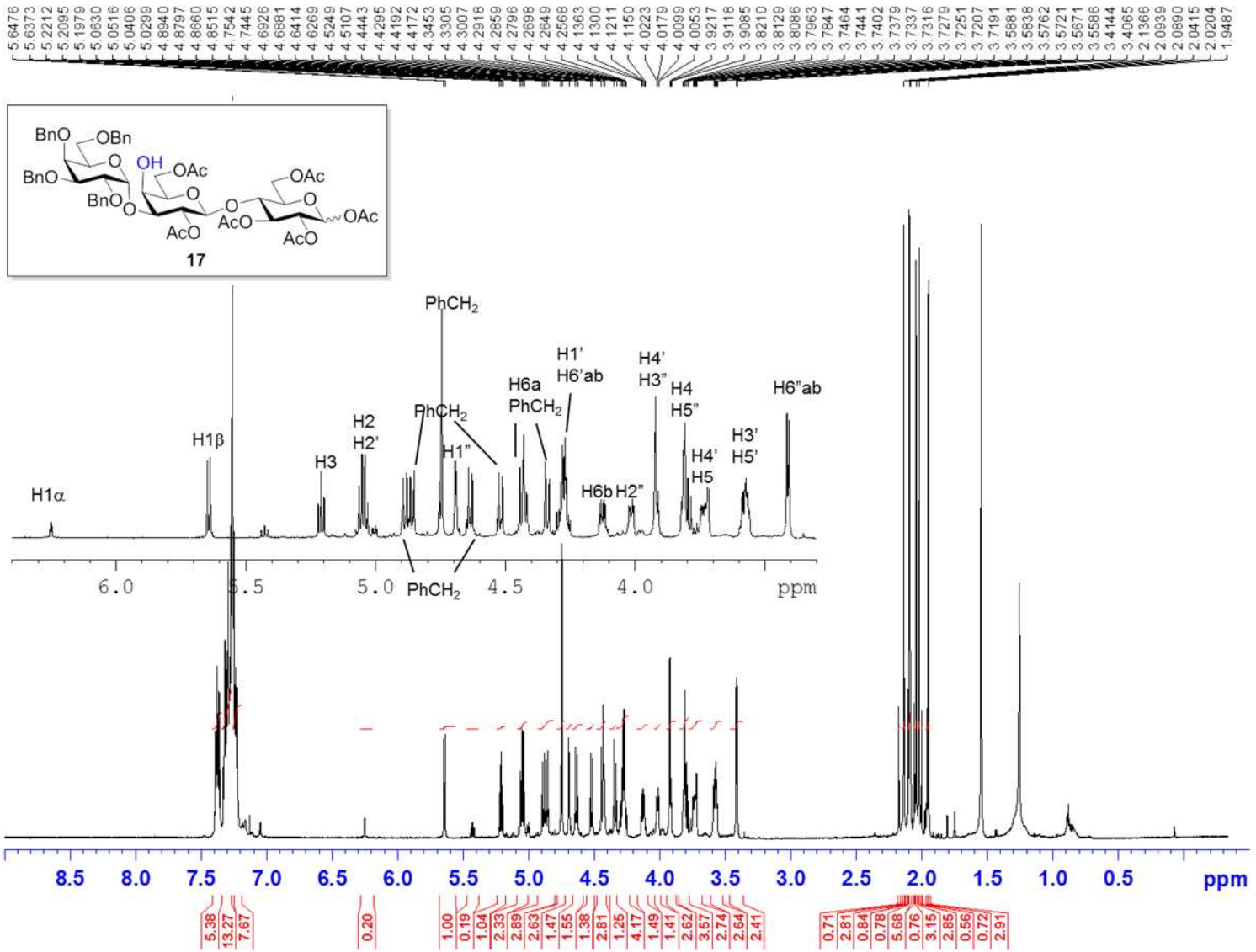
^{1}H-^{1}H COSY spectrum of compound **16** ($CDCl_3$, 800 MHz)



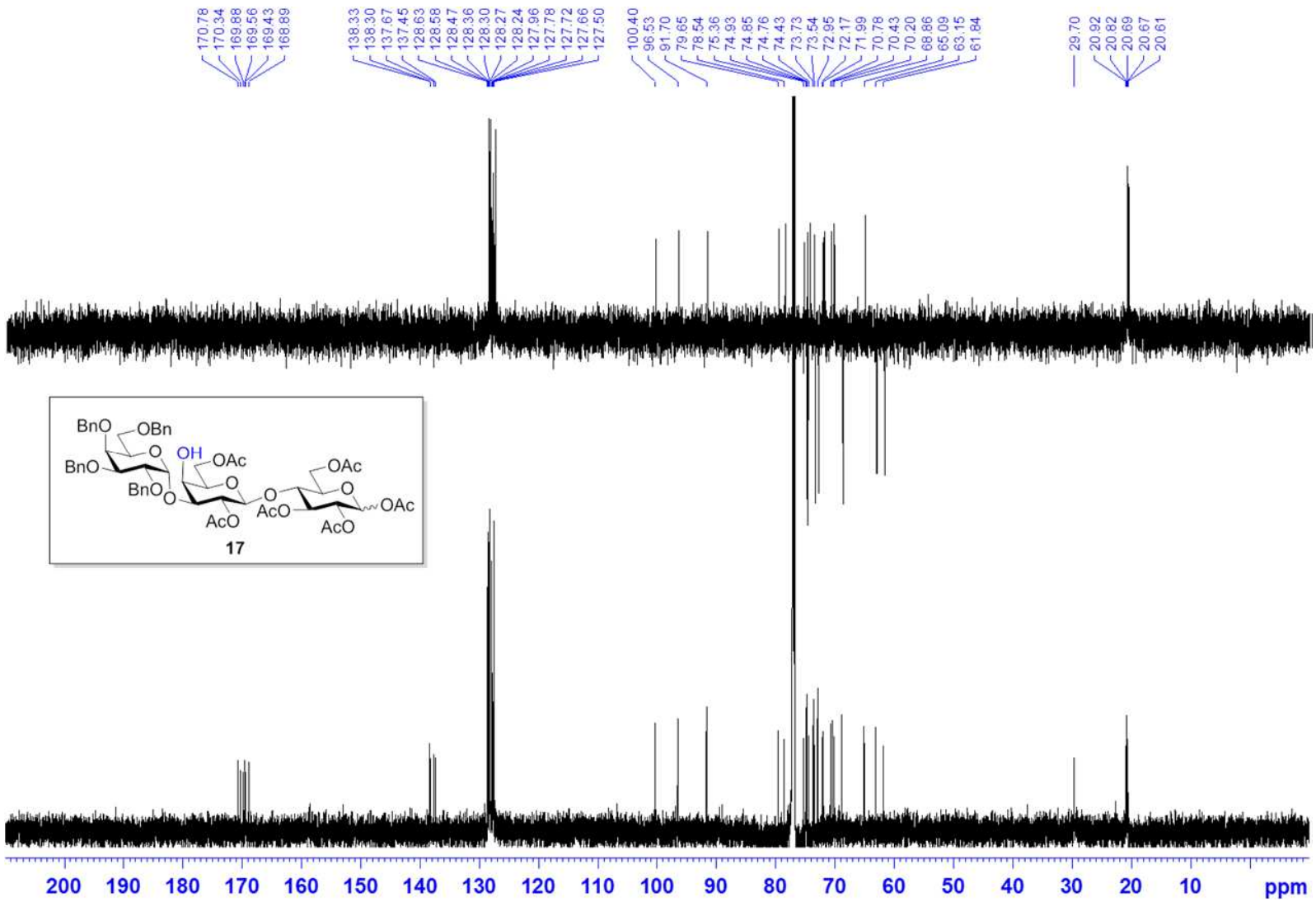
^{1}H-^{13}C HSQC spectrum of compound **16** ($CDCl_3$, 800 MHz)



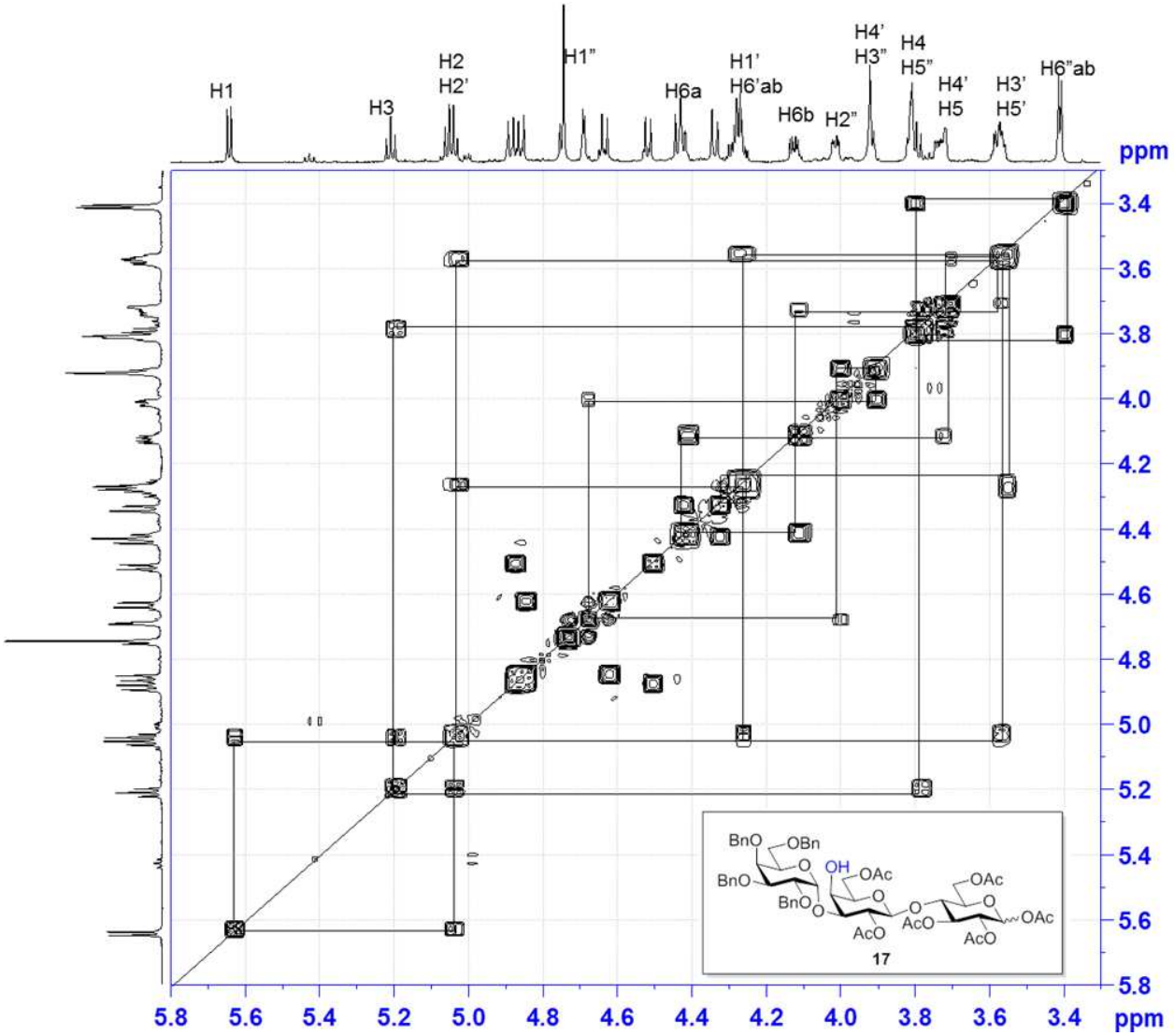
^{1}H-^{13}C HMBC spectrum of compound **16** ($CDCl_3$, 800 MHz)



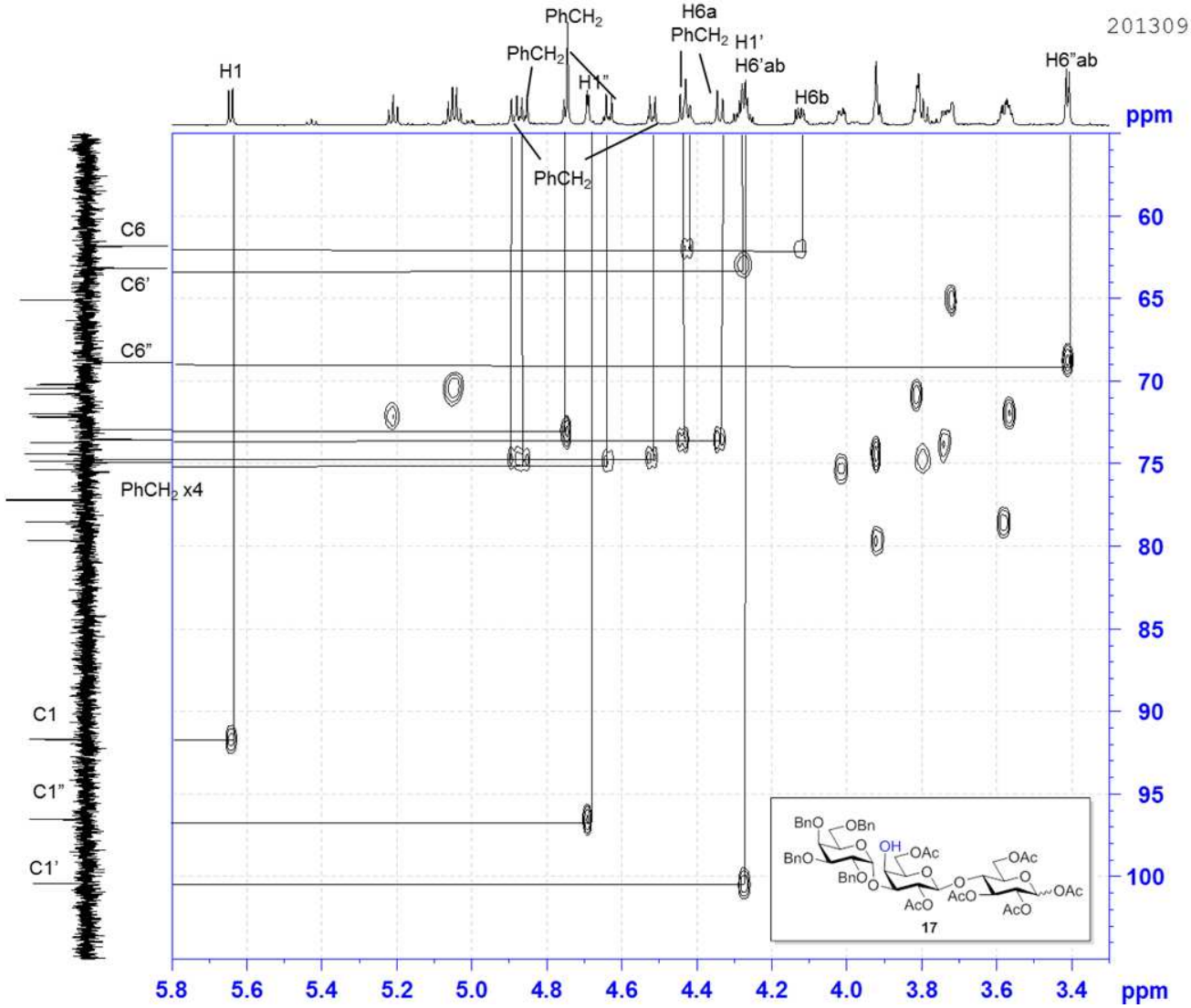
^{1}H NMR spectrum of compound **17** ($CDCl_3$, 800 MHz)



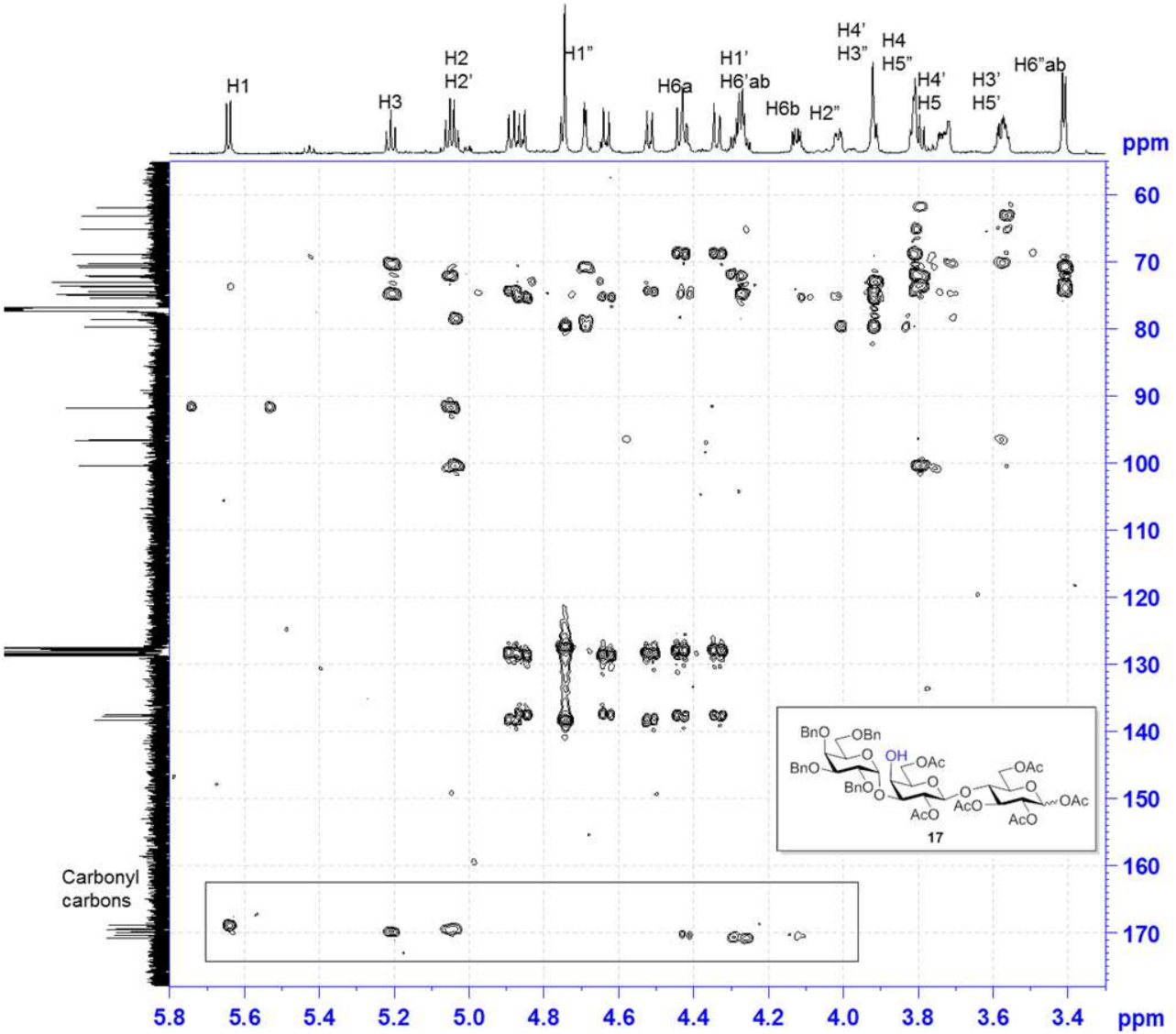
^{13}C and DEPT135 NMR spectrum of compound **17** ($CDCl_3$, 200 MHz)



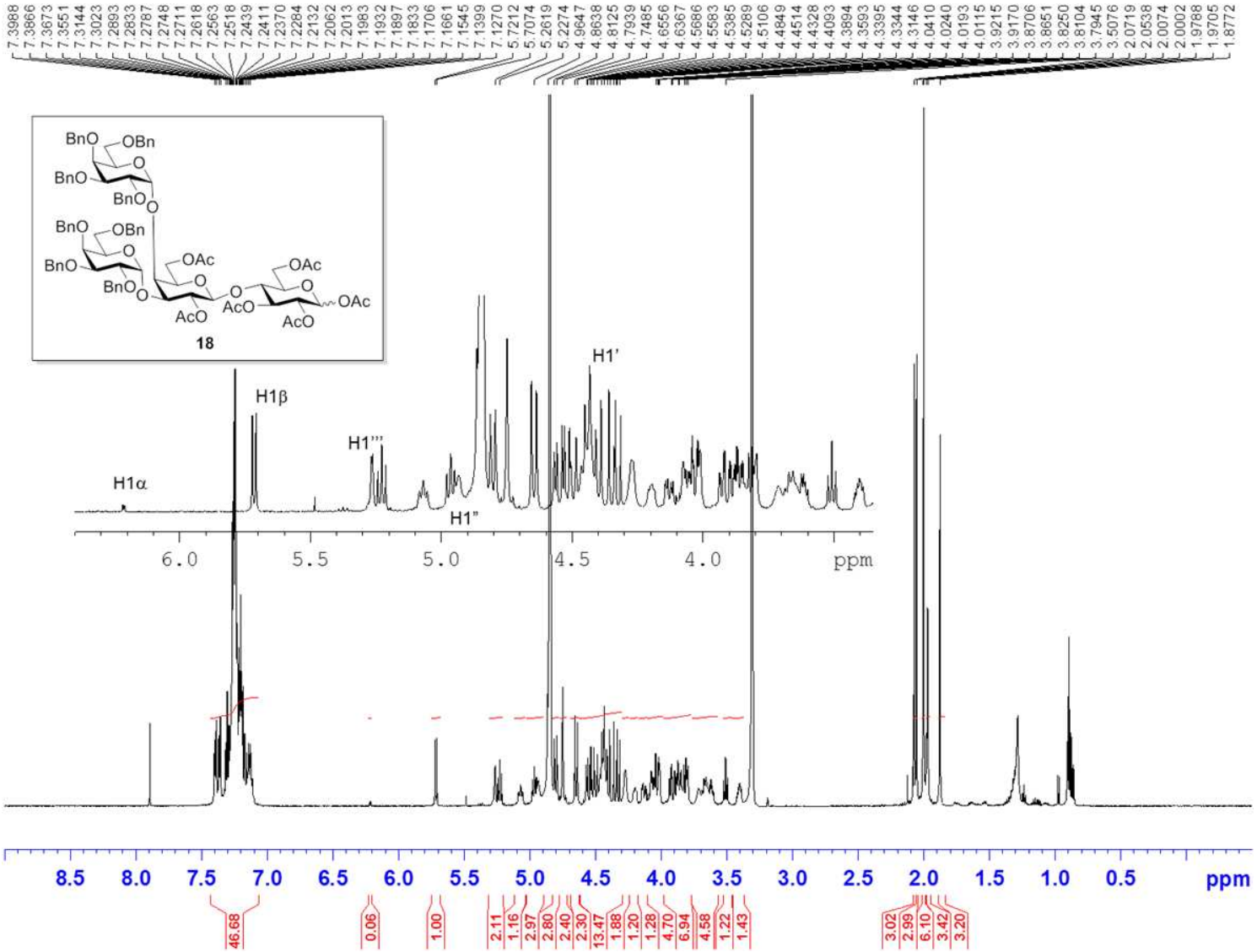
^{1}H-^{1}H COSY spectrum of compound **17** ($CDCl_3$, 800 MHz)



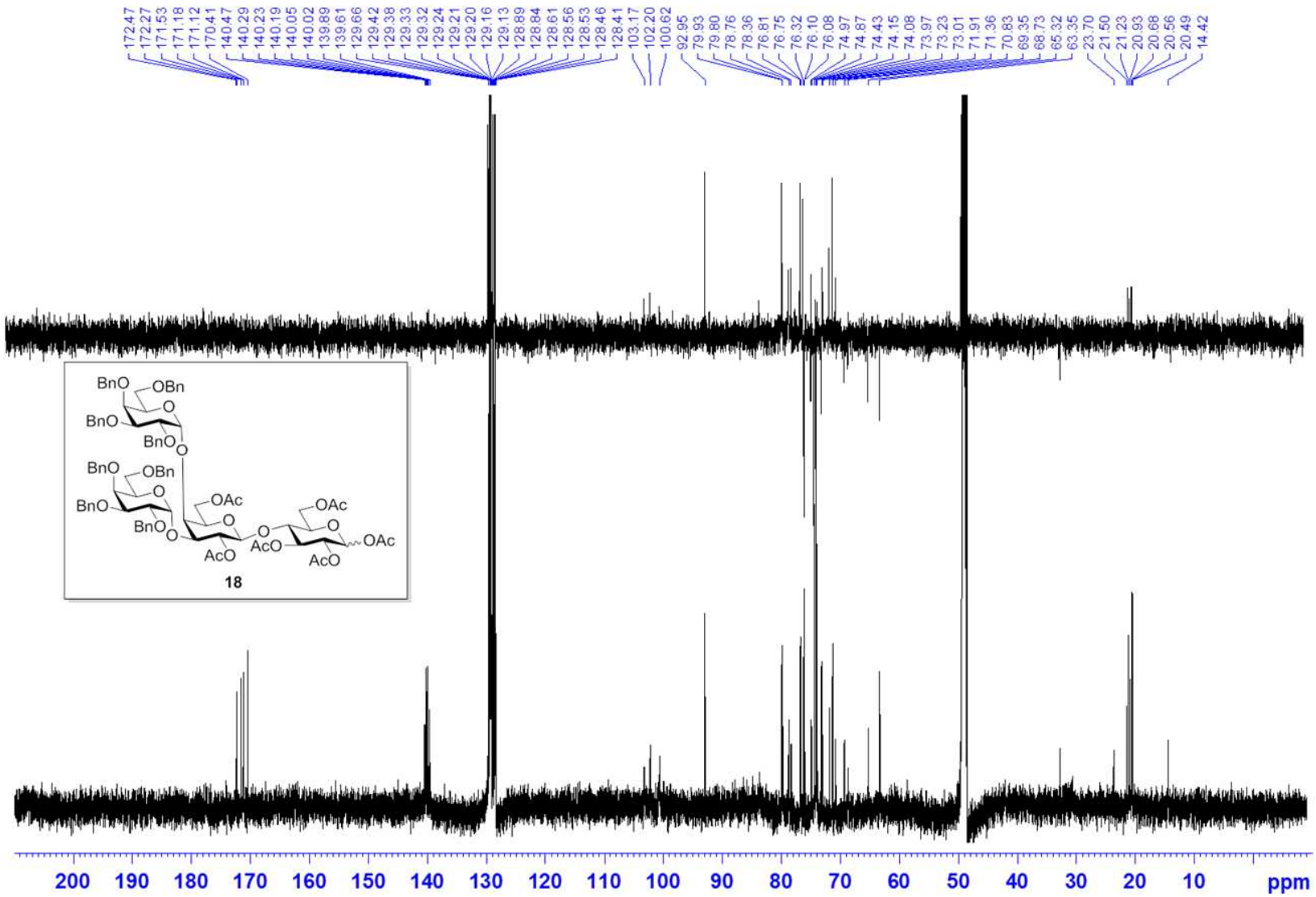
^{1}H-^{13}C HSQC spectrum of compound **17** ($CDCl_3$, 800 MHz)



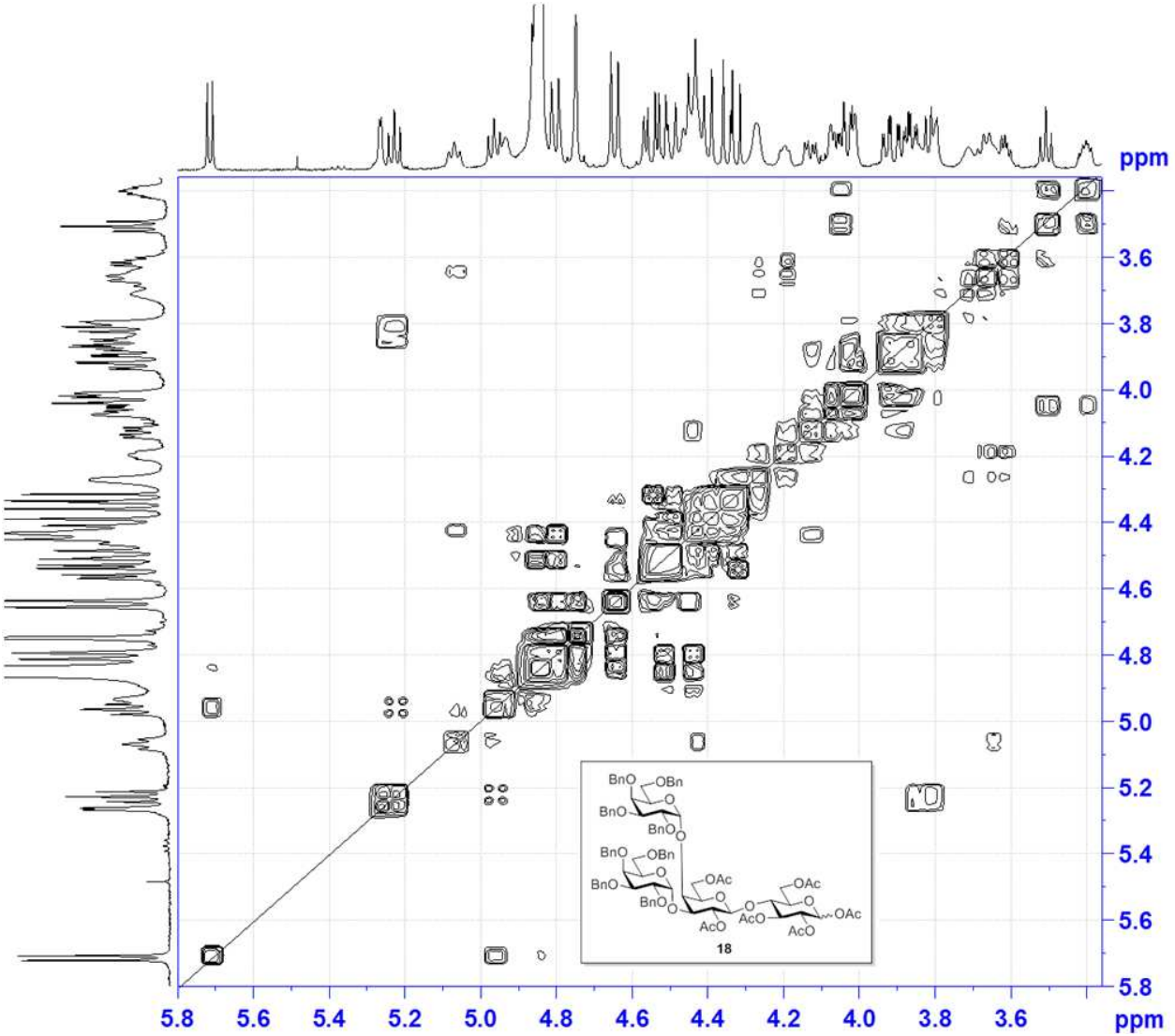
^{1}H-^{13}C HMBC spectrum of compound **17** ($CDCl_3$, 800 MHz)



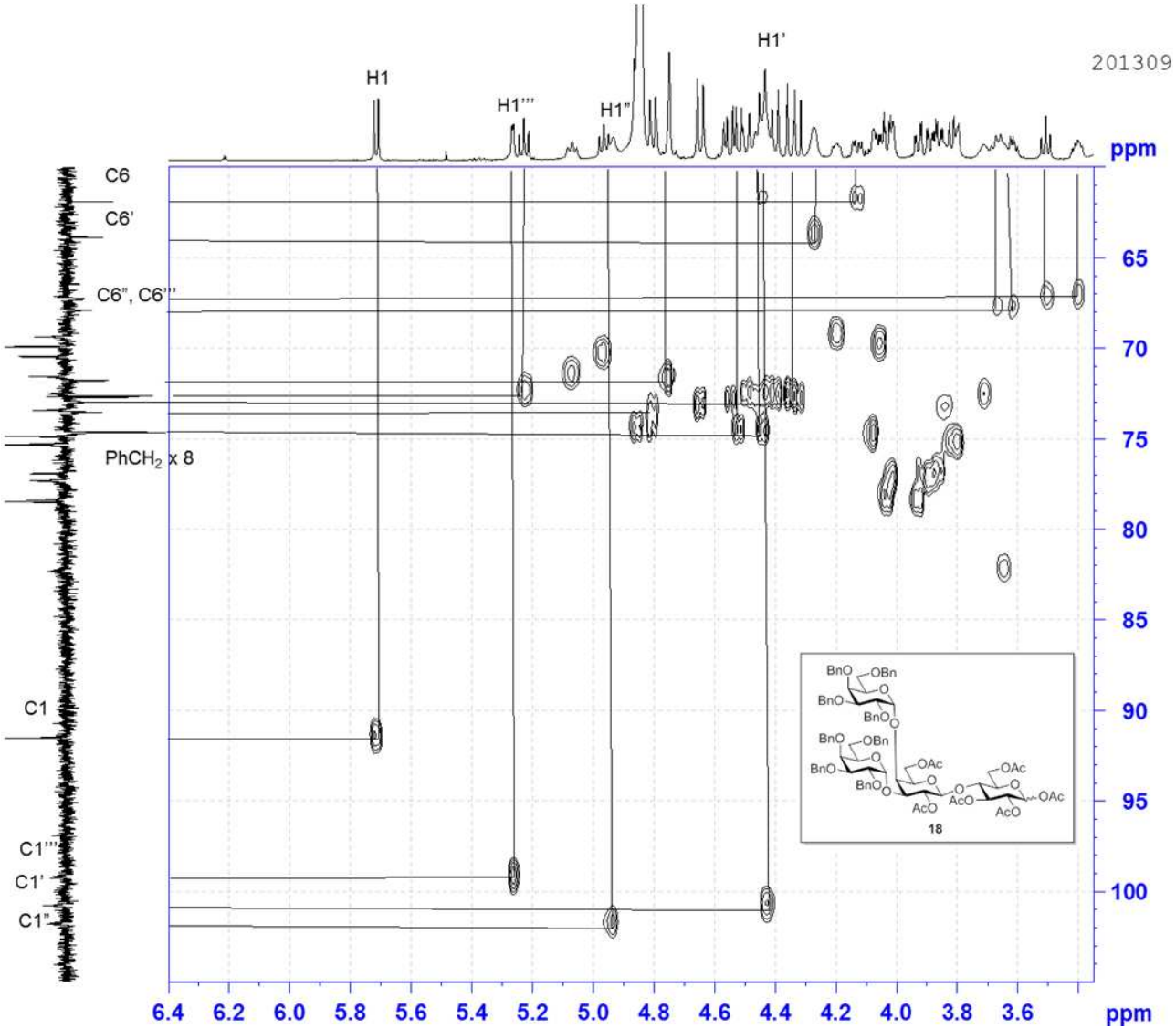
^{1}H NMR spectrum of compound **18** (methanol-d_4, 600 MHz)



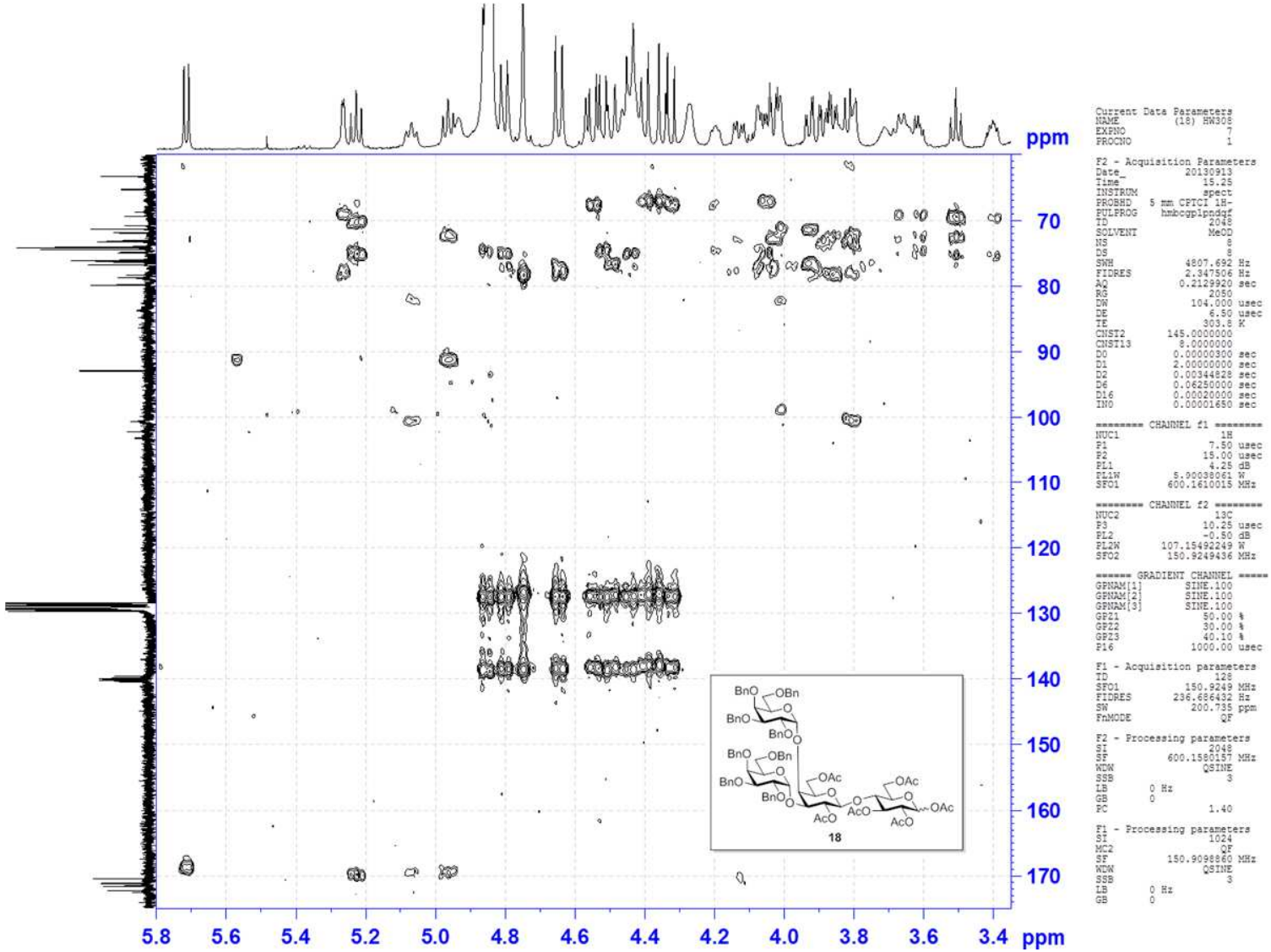
^{13}C and DEPT135 NMR spectrum of compound **18** (methanol-d_4, 150 MHz)



^{1}H-^{1}H COSY spectrum of compound **18** (Methanol-d_4, 600 MHz)

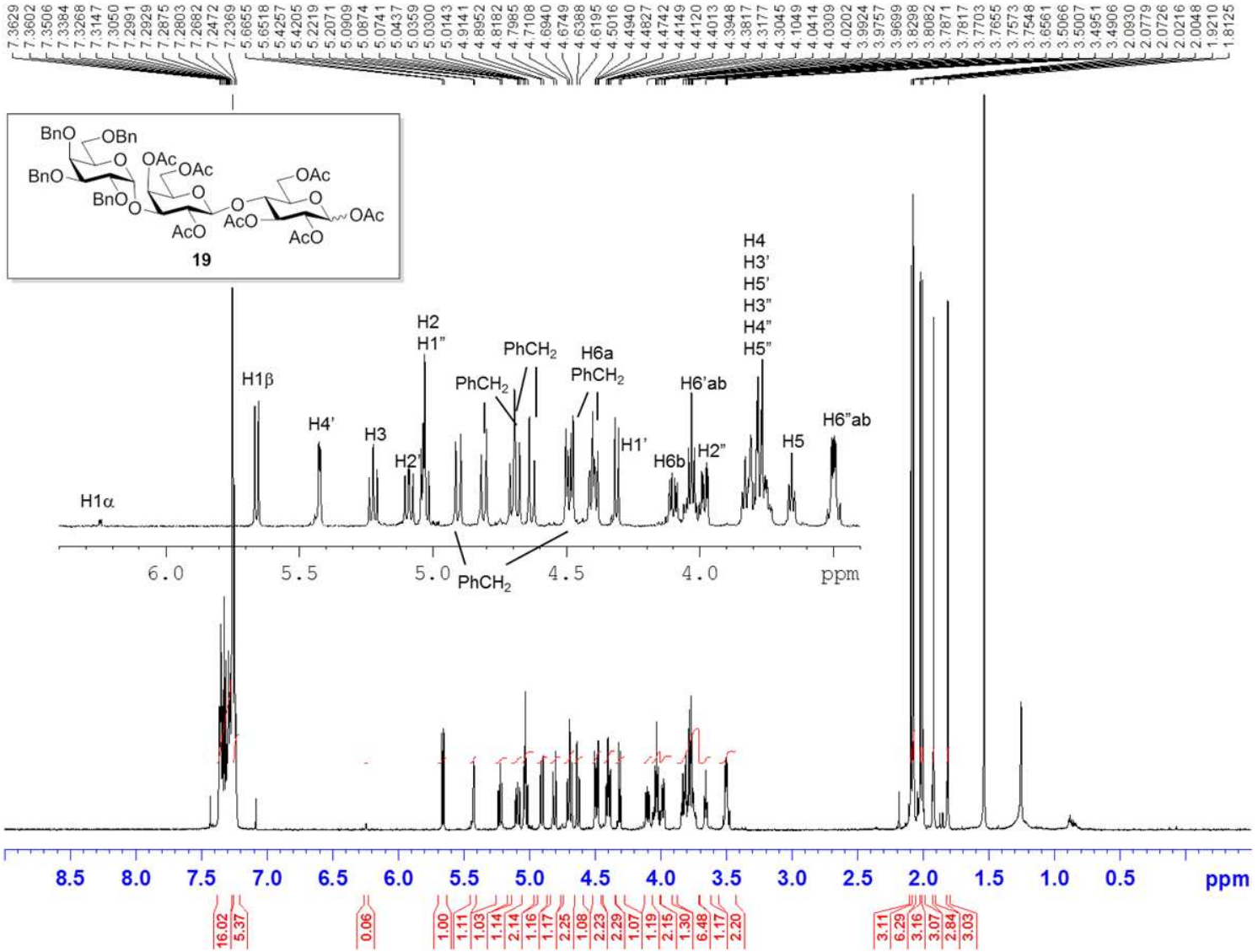


^{1}H-^{13}C HSQC spectrum of compound **18** (Methanol-d_4, 600 MHz)

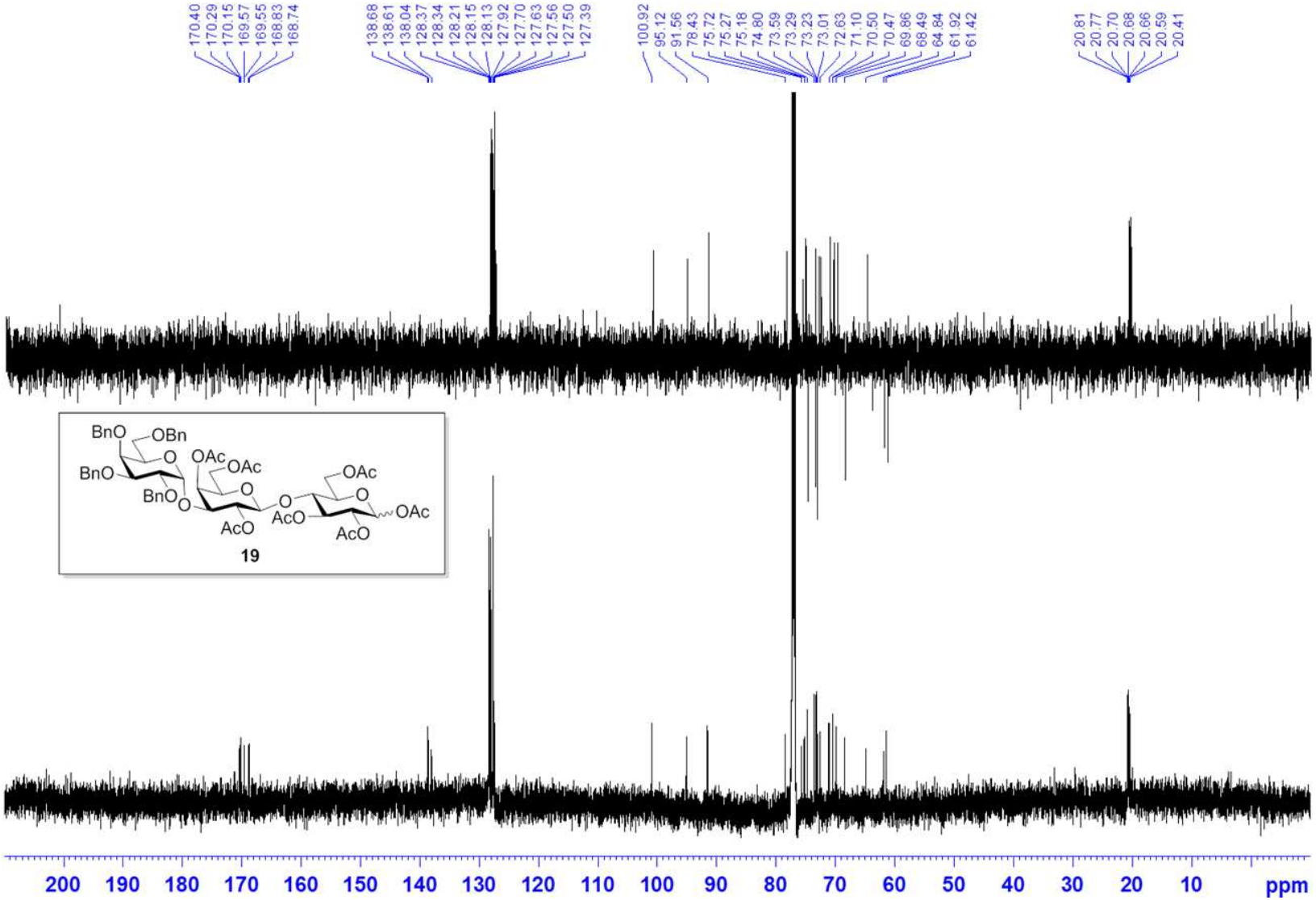



```
Current Data Parameters
NAME                  (18) HW308
EXPNO                        7
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20130913
Time                     15.25
INSTRUM                  spect
PROBHD    5 mm CPTCI 1H-
PULPROG    hmbcgplpndqf
TD                        2048
SOLVENT                   MeOD
NS                           8
DS                           8
SWH                4807.692 Hz
FIDRES             2.347506 Hz
AQ                 0.2129920 sec
RG                        2050
DW                  104.000 usec
DE                    6.50 usec
TE                    303.8 K
CNST2             145.0000000
CNST13              8.0000000
D0                  0.00000300 sec
D1                  2.00000000 sec
D2                  0.00344828 sec
D6                  0.06250000 sec
D16                 0.00020000 sec
IN0                 0.00001650 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      7.50 usec
P2                     15.00 usec
PL1                     4.25 dB
PL1W               5.90038061 W
SFO1             600.1610015 MHz

======== CHANNEL f2 ========
NUC2                      13C
P3                     10.25 usec
PL2                    -0.50 dB
PL2W             107.15492249 W
SFO2              150.9249436 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]              SINE.100
GPNAM[2]              SINE.100
GPNAM[3]              SINE.100
GPZ1                    50.00 %
GPZ2                    30.00 %
GPZ3                    40.10 %
P16                   1000.00 usec

F1 - Acquisition parameters
TD                         128
SFO1              150.9249 MHz
FIDRES           236.686432 Hz
SW                200.735 ppm
FnMODE                     QF

F2 - Processing parameters
SI                        2048
SF             600.1580157 MHz
WDW                    QSINE
SSB                         3
LB          0 Hz
GB          0
PC                      1.40

F1 - Processing parameters
SI                        1024
MC2                       QF
SF             150.9098860 MHz
WDW                    QSINE
SSB                         3
LB          0 Hz
GB          0
```

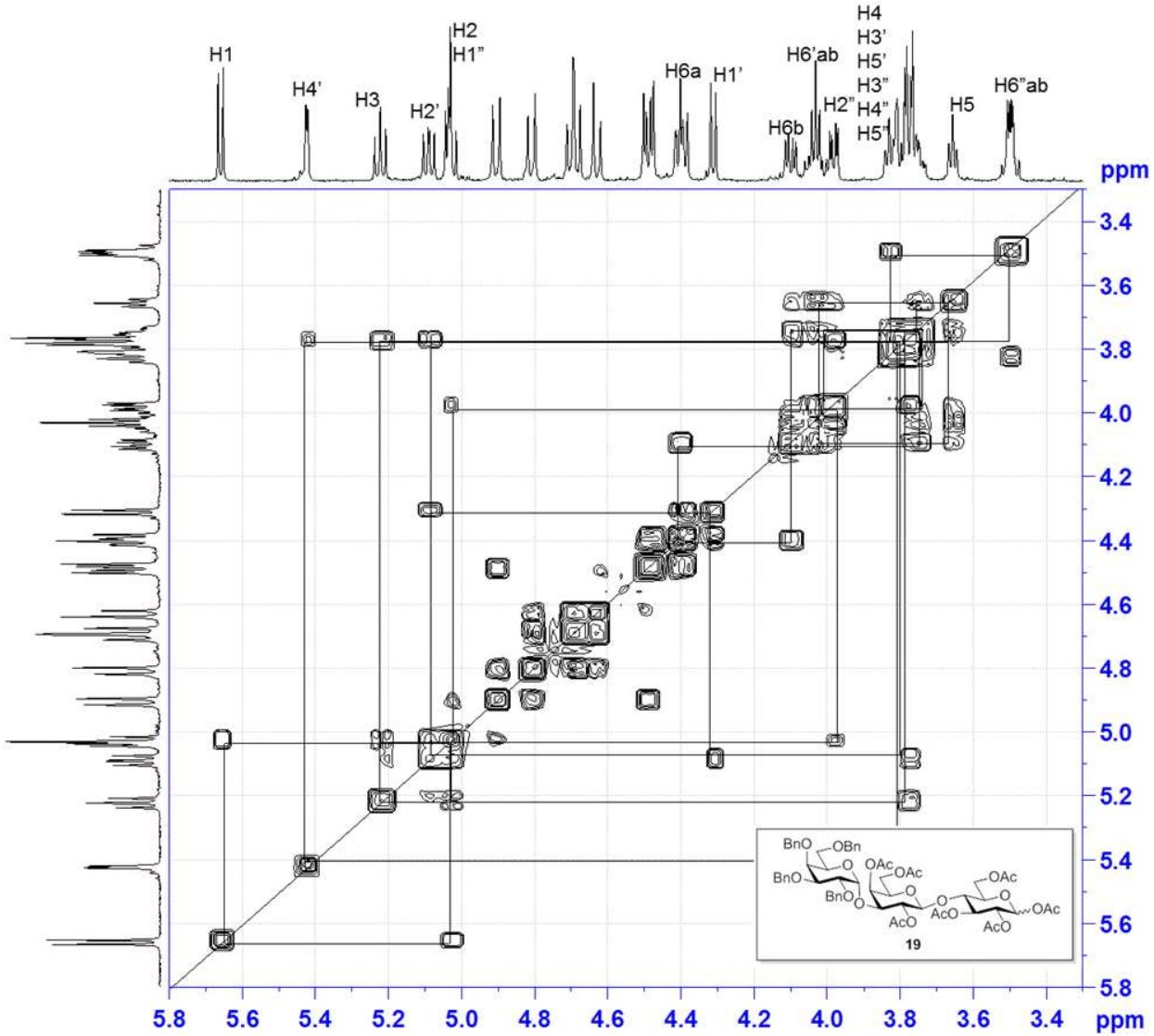
^{1}H-^{13}C HMBC spectrum of compound **18** (Methanol-d_4, 600 MHz)



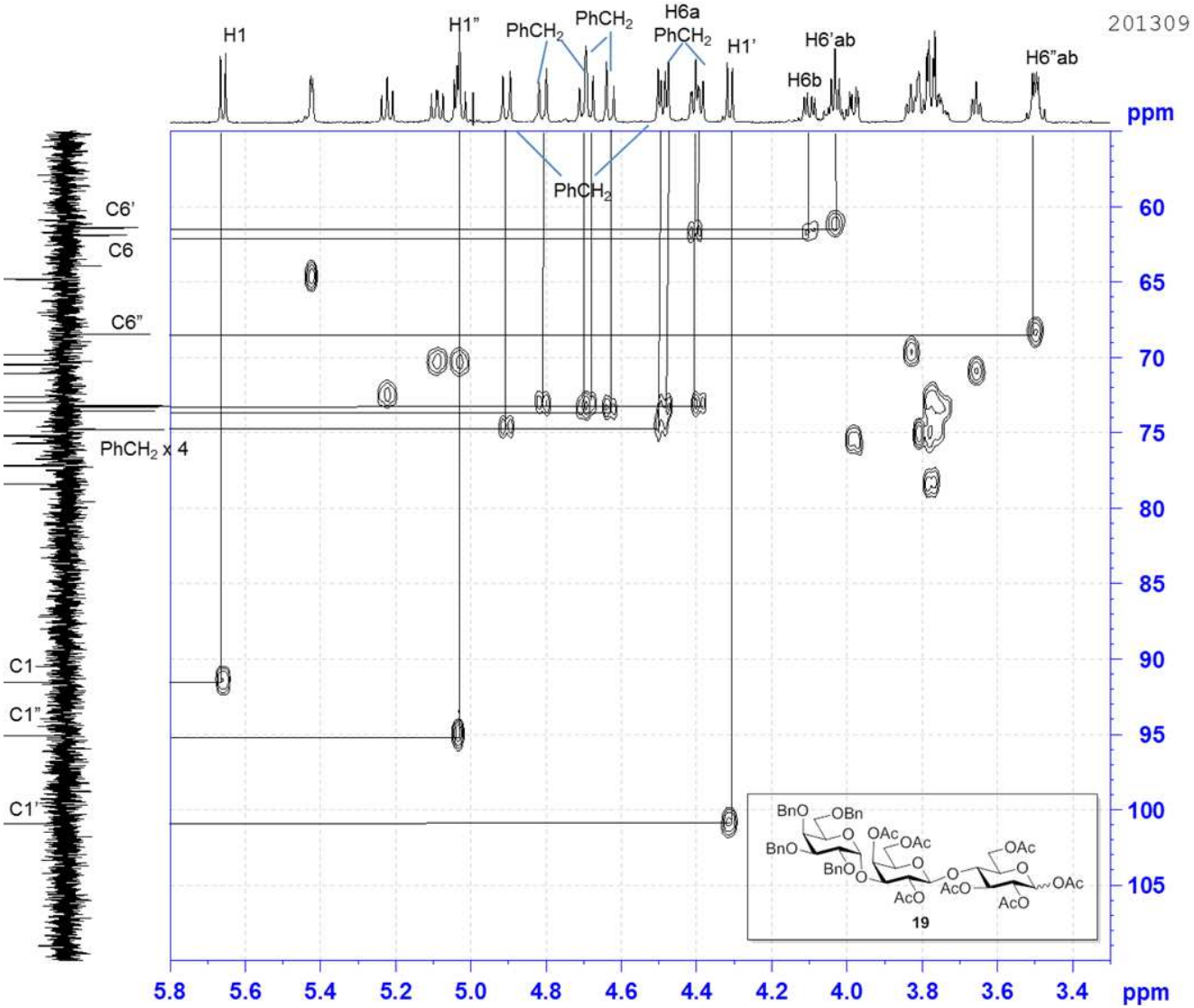
^{1}H NMR spectrum of compound **19** ($CDCl_3$, 600 MHz)



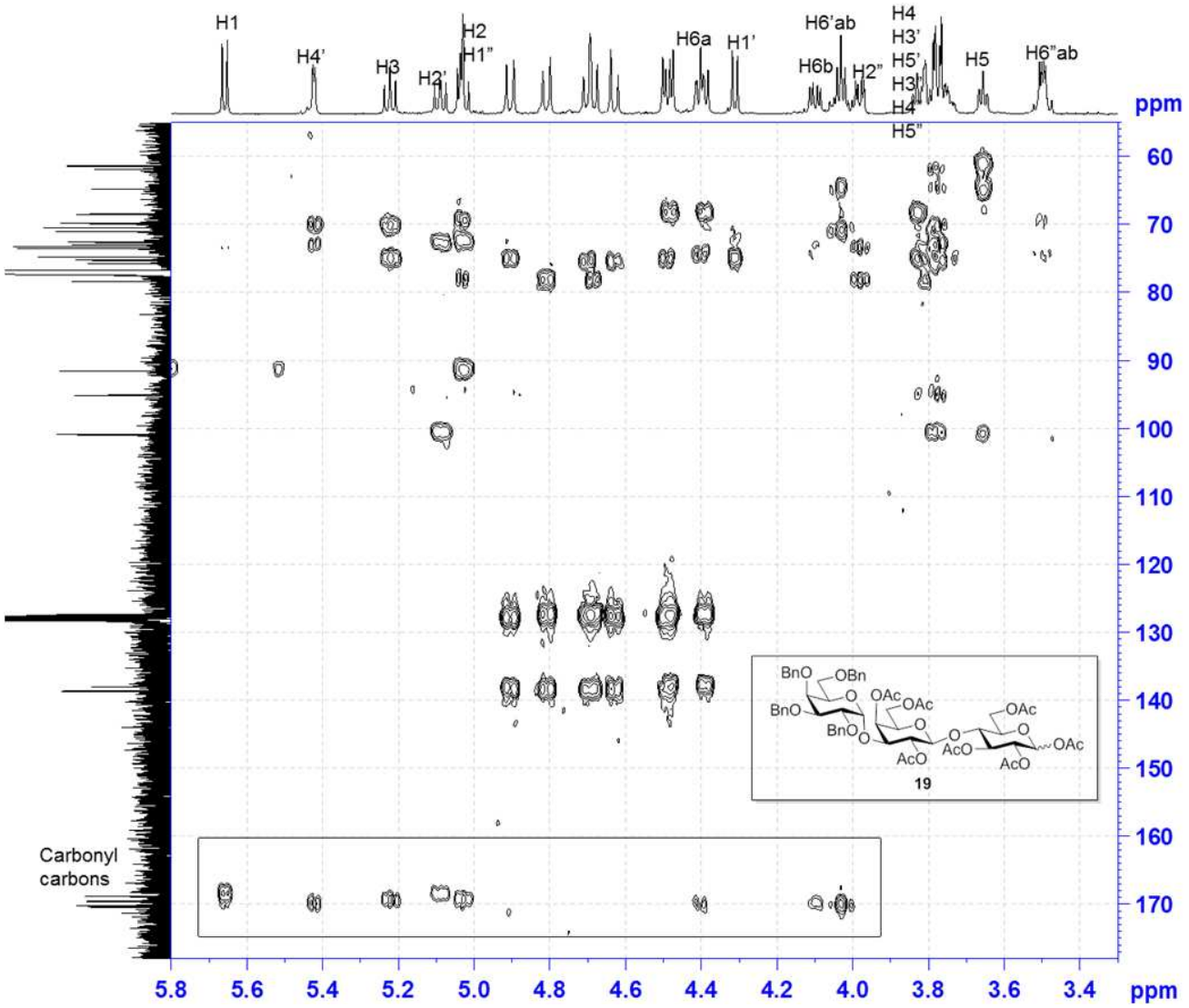
^{13}C and DEPT135 NMR spectrum of compound **19** ($CDCl_3$, 150 MHz)



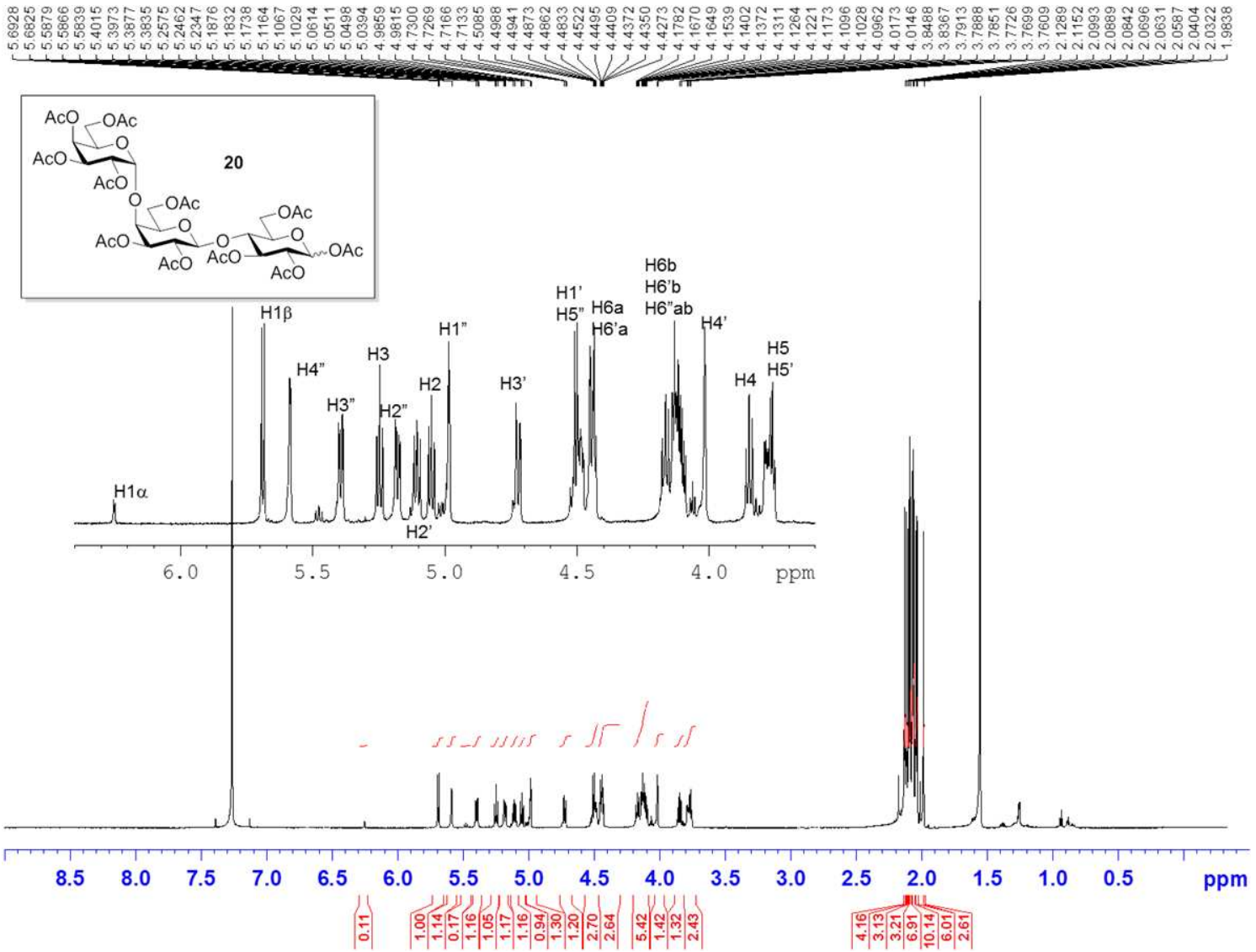
^{1}H-^{1}H COSY spectrum of compound **19** ($CDCl_3$, 600 MHz)



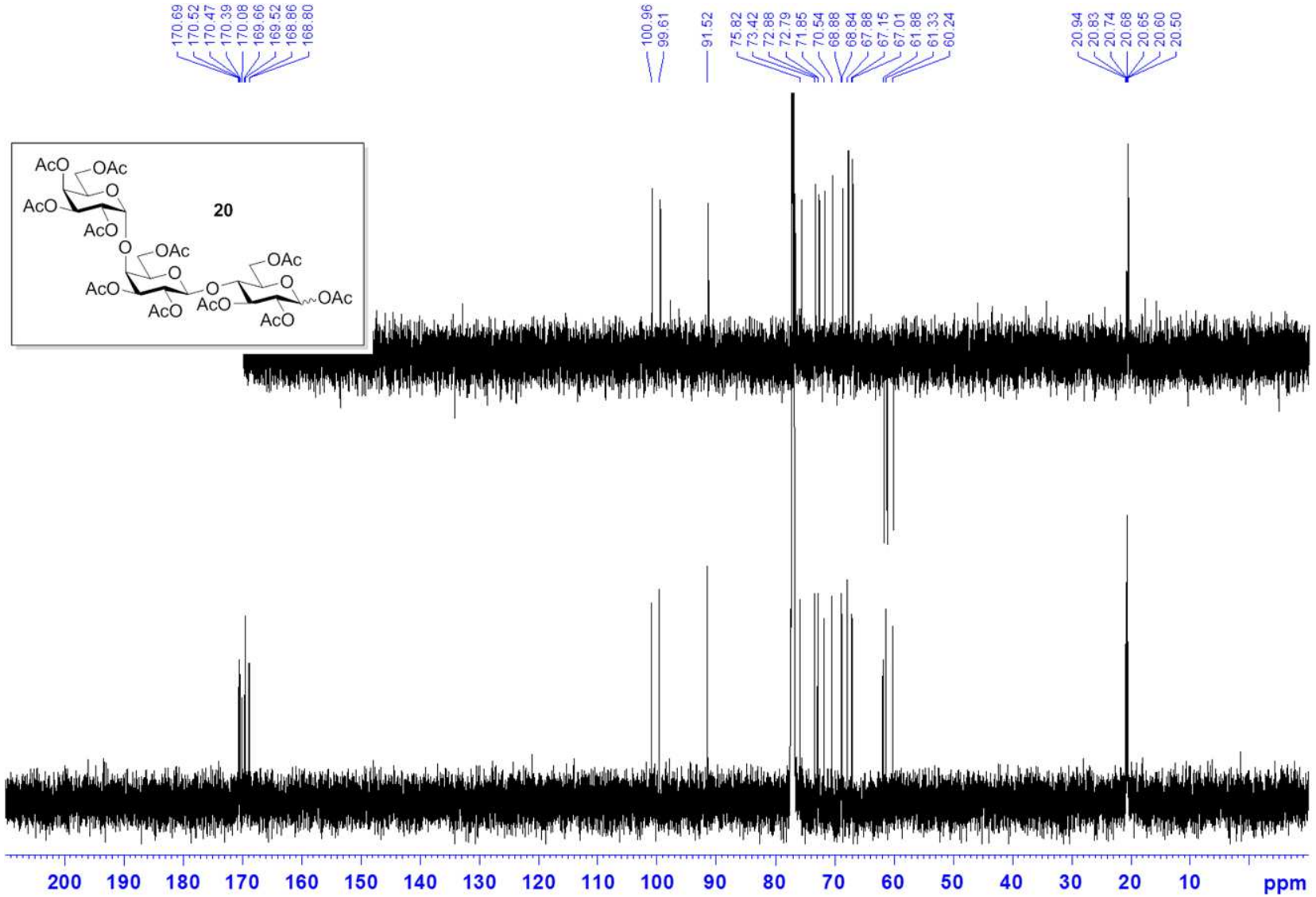
^{1}H-^{13}C HSQC spectrum of compound **19** ($CDCl_3$, 600 MHz)



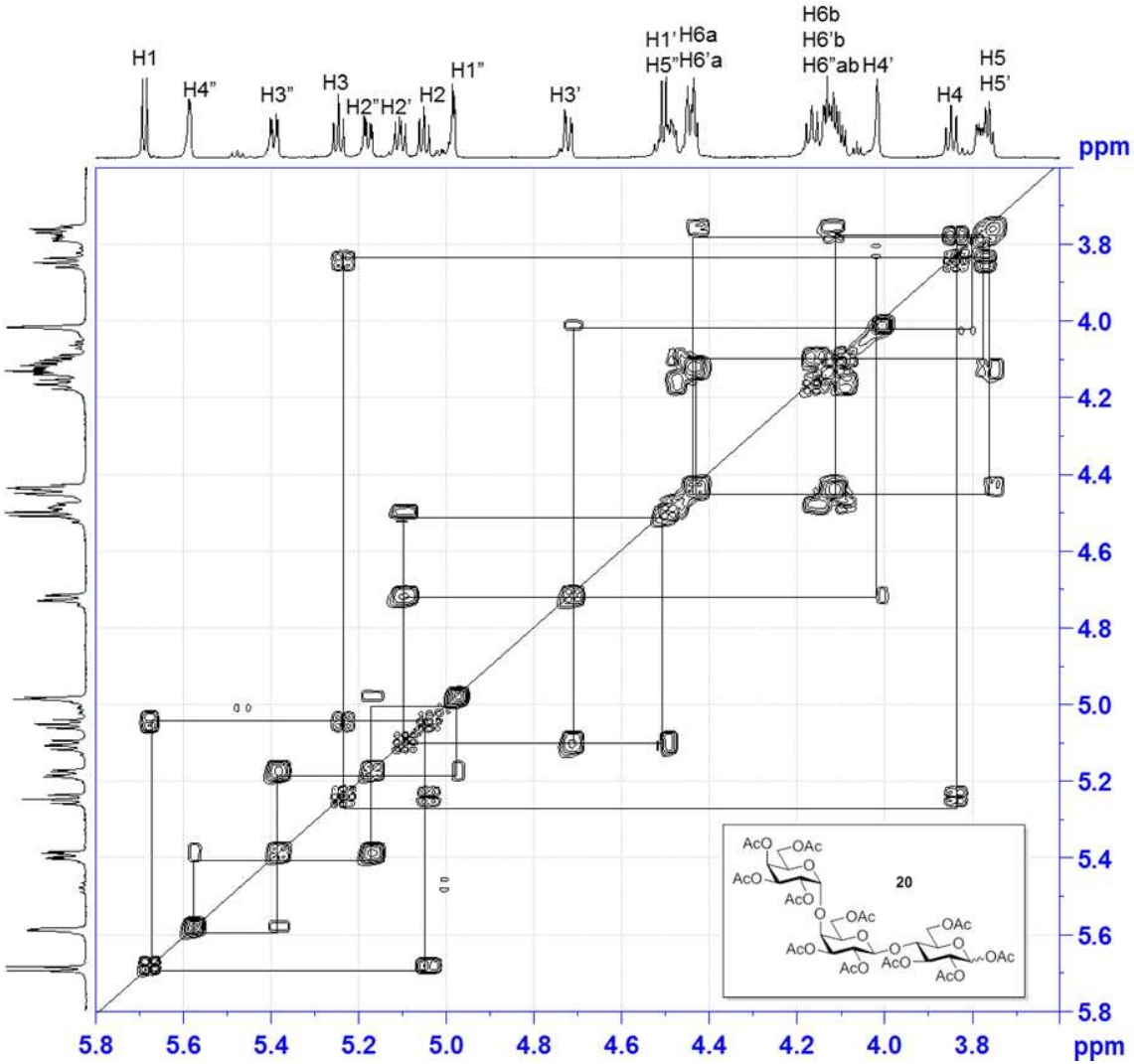
^{1}H-^{13}C HMBC spectrum of compound **19** ($CDCl_3$, 600 MHz)



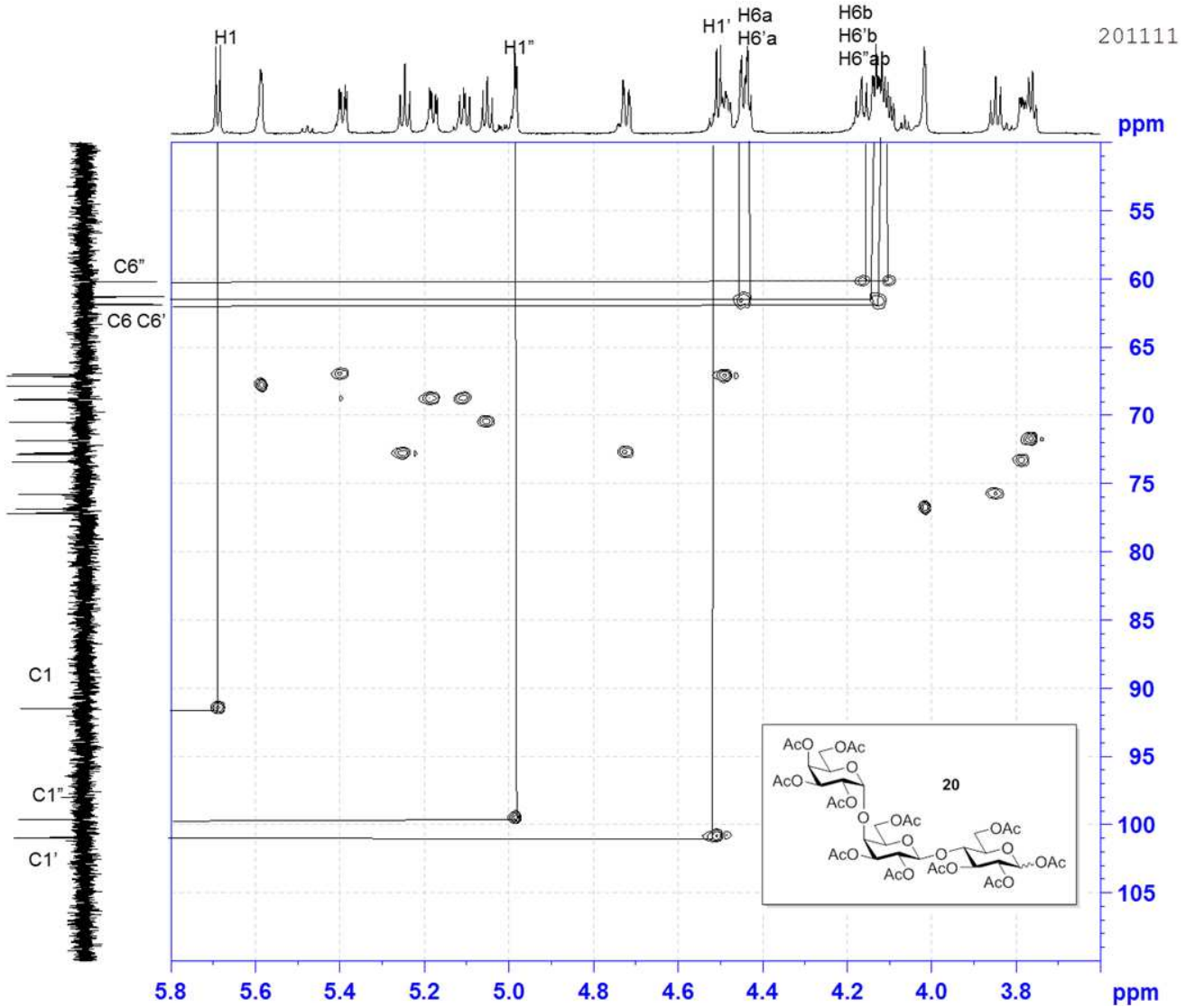
^{1}H NMR spectrum of compound **20** ($CDCl_3$, 800 MHz)



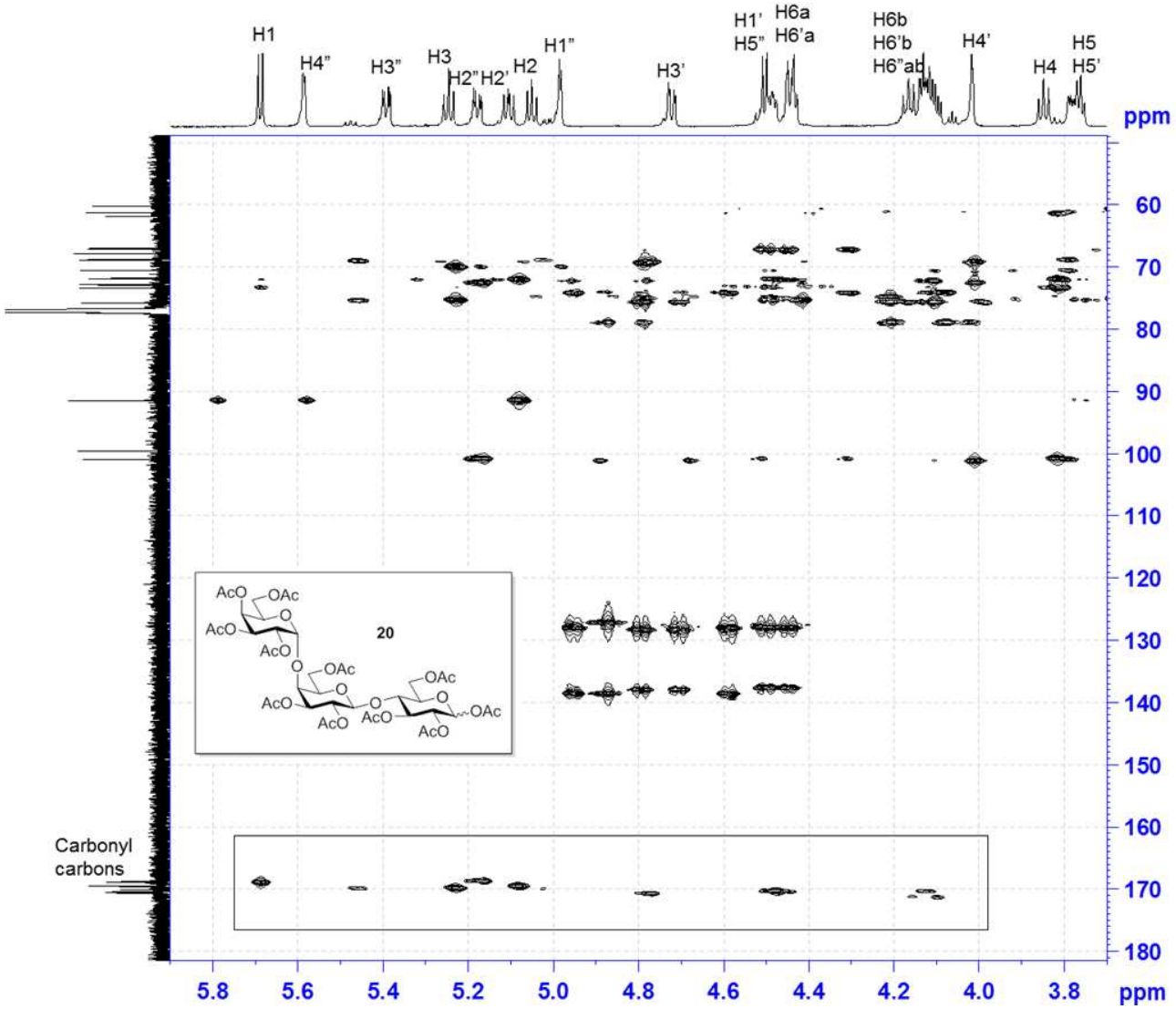
^{13}C and DEPT135 NMR spectrum of compound **20** ($CDCl_3$, 200 MHz)



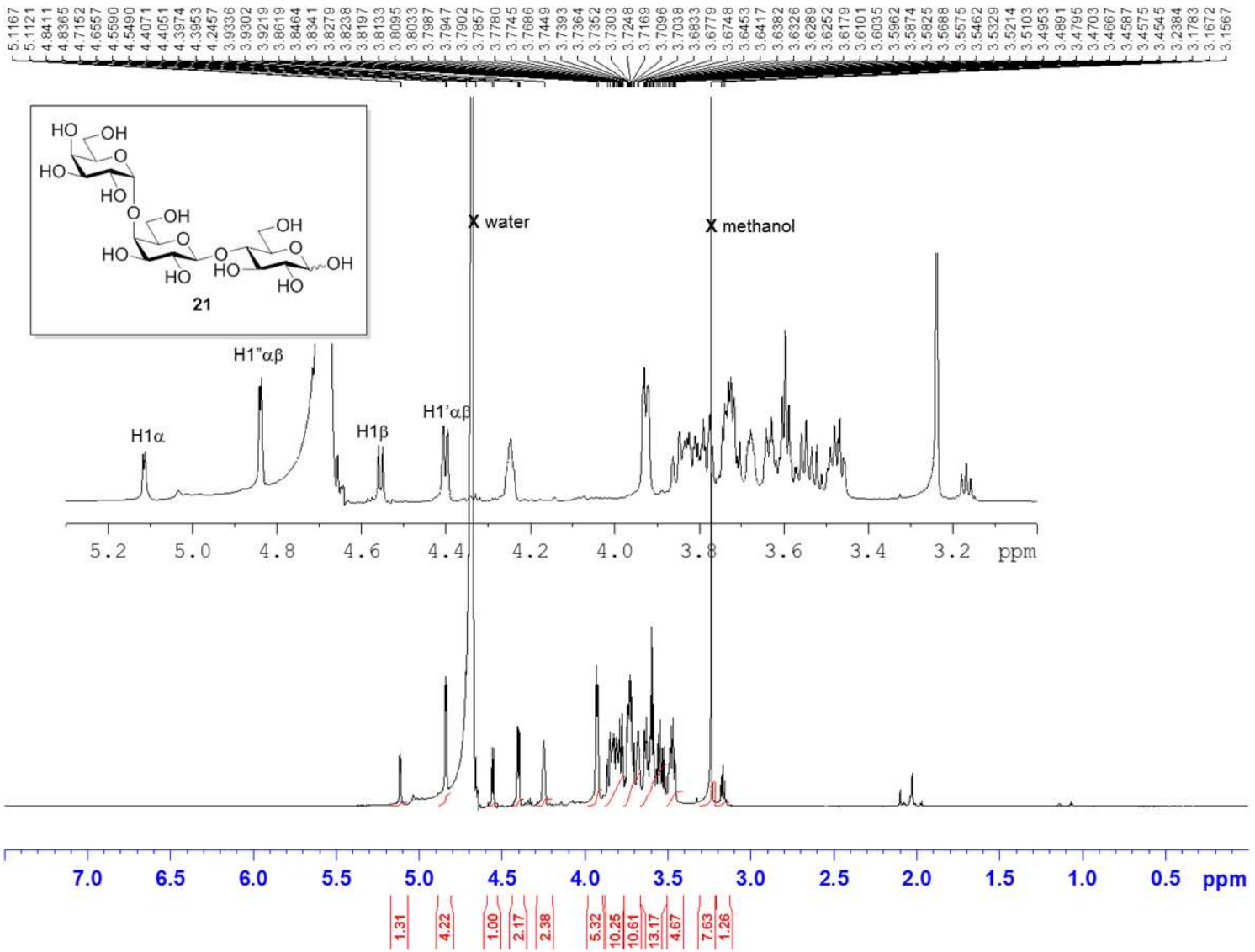
^{1}H-^{1}H COSY spectrum of compound **20** ($CDCl_3$, 800 MHz)



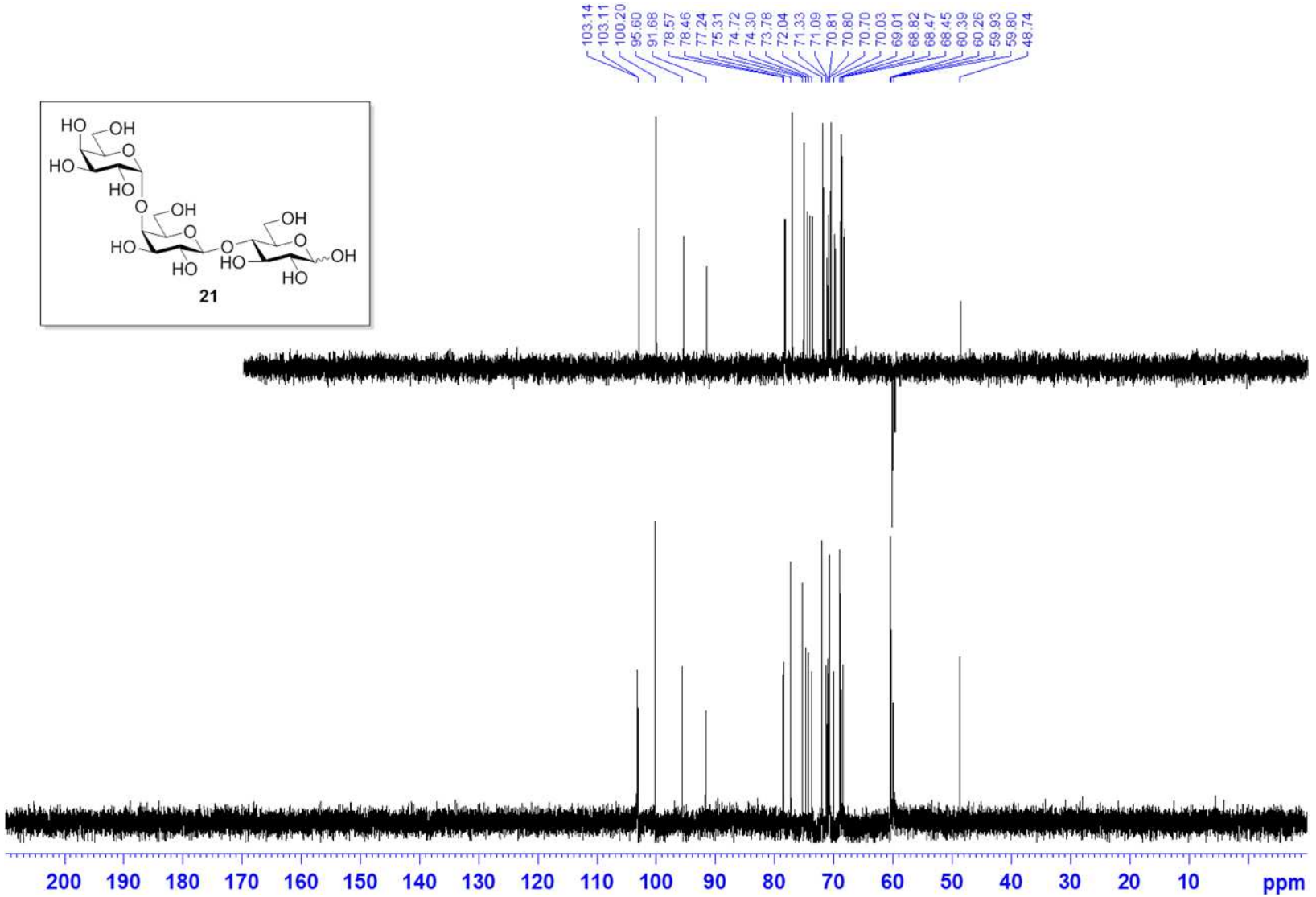
^{1}H-^{13}C HSQC spectrum of compound **20** ($CDCl_3$, 800 MHz)



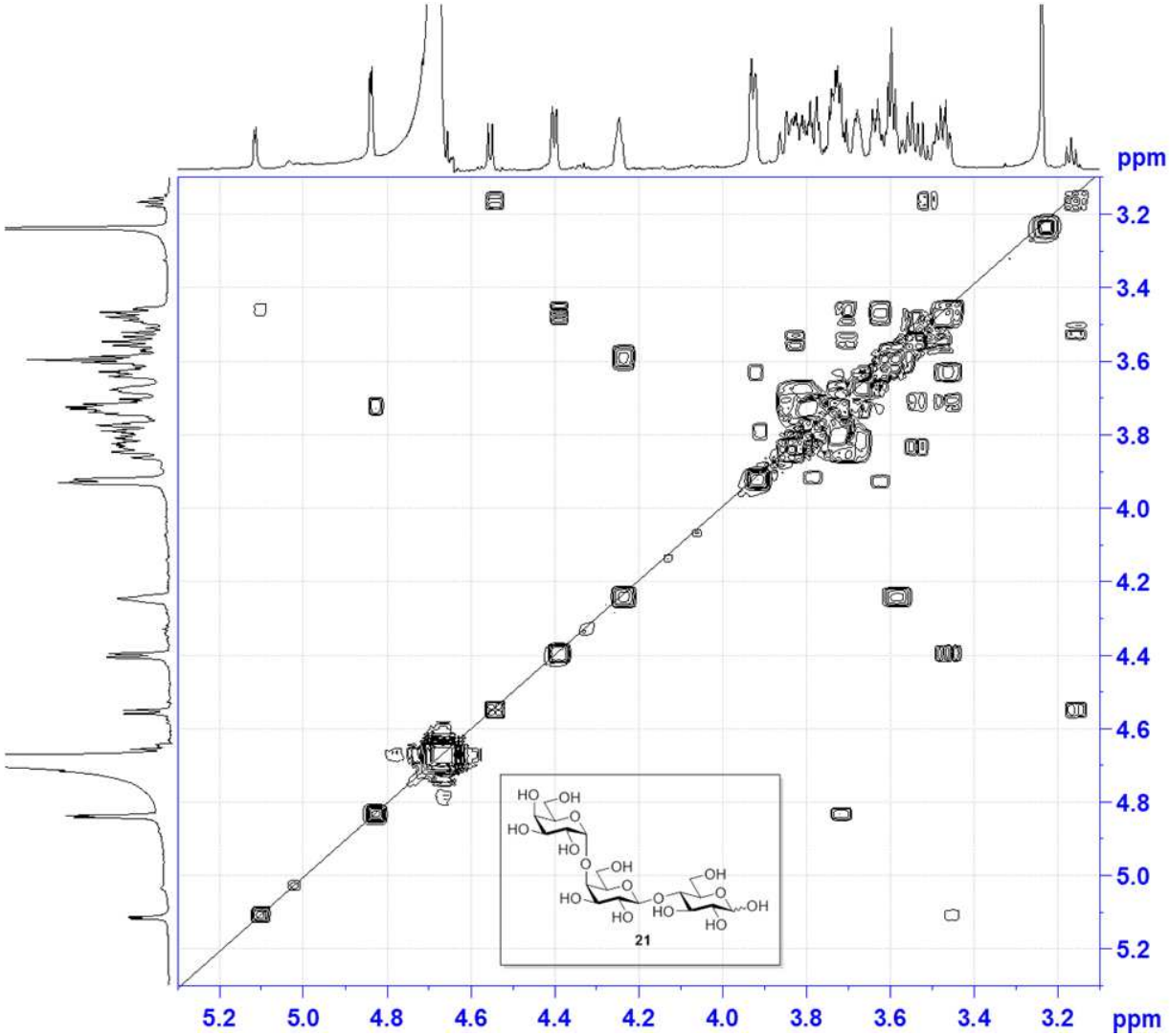
^{1}H-^{13}C HMBC spectrum of compound **20** ($CDCl_3$, 800 MHz)



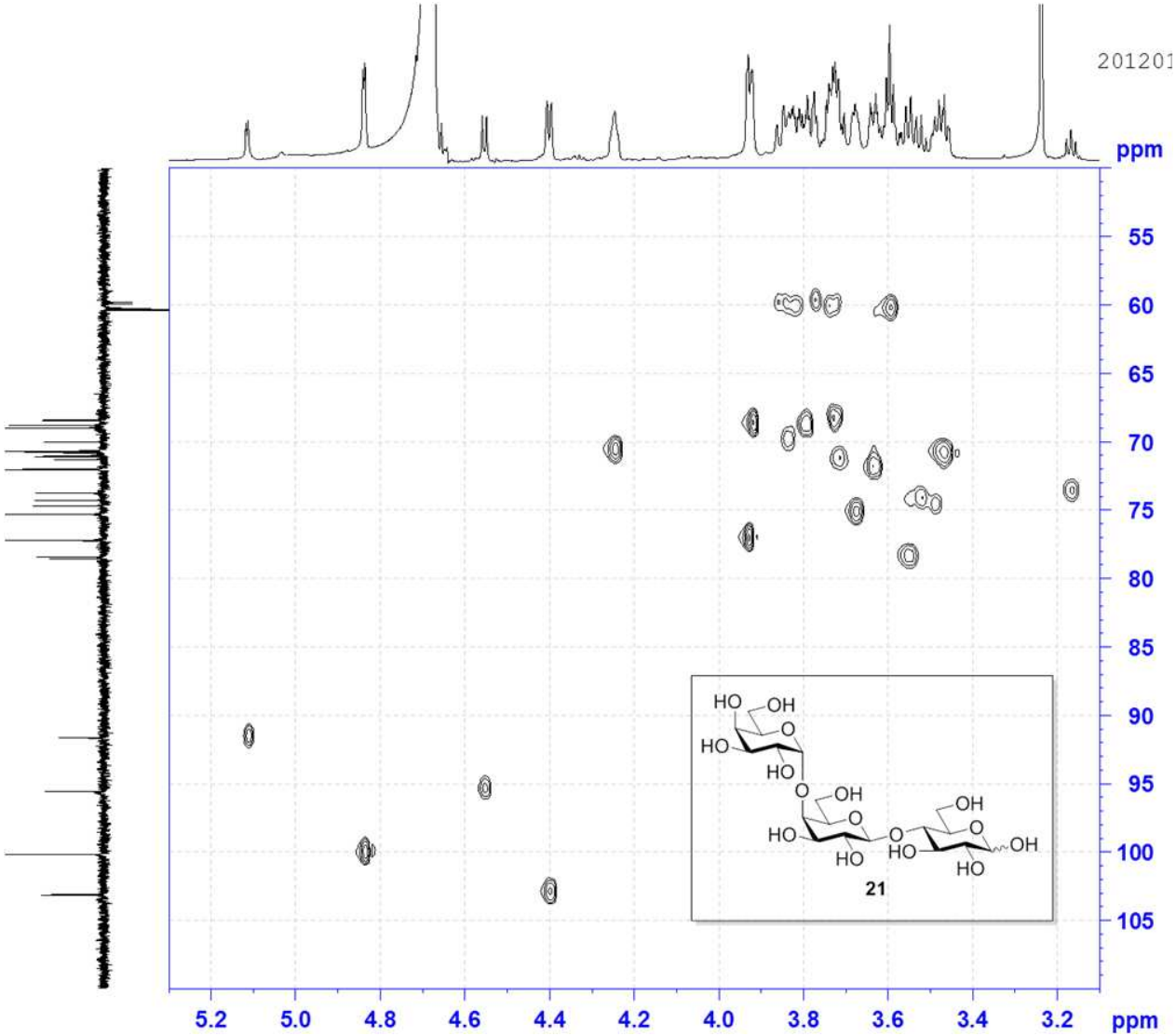
^{1}H NMR spectrum of compound **21** (D_2O, 800 MHz)



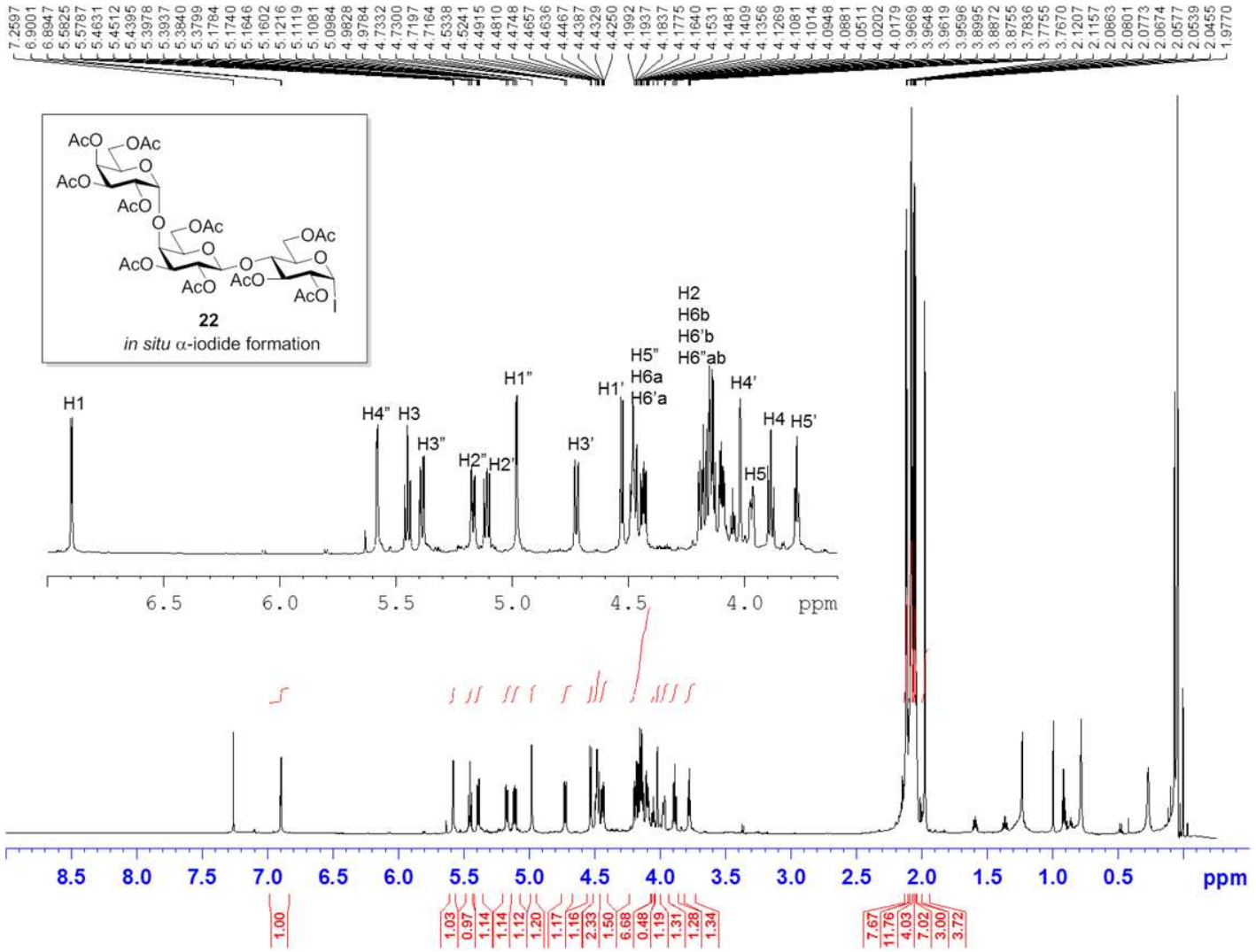
^{13}C and DEPT135 NMR spectrum of compound **21** (D_2O, 200 MHz)



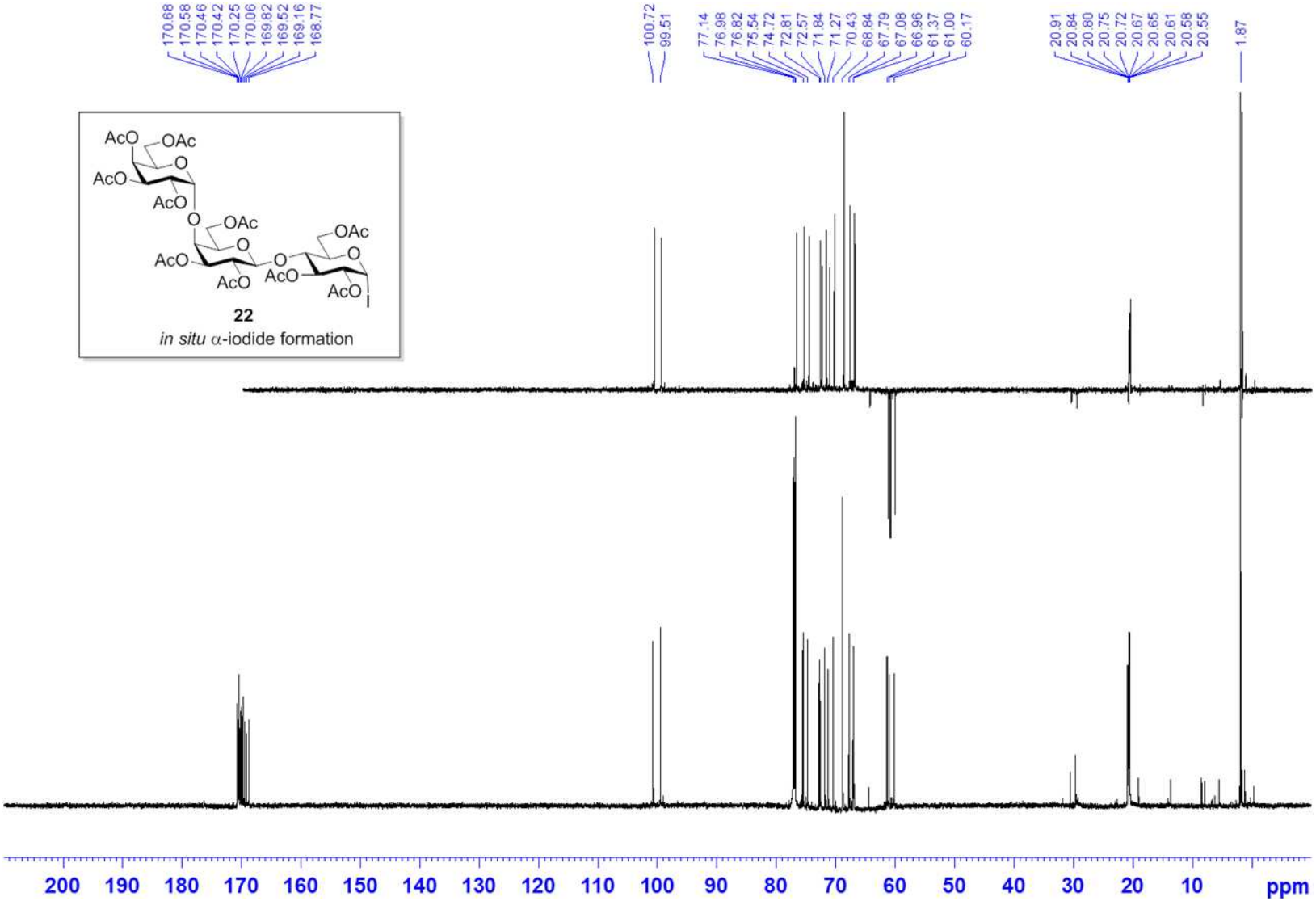
^{1}H-^{1}H COSY spectrum of compound **21** (D_2O, 800 MHz)



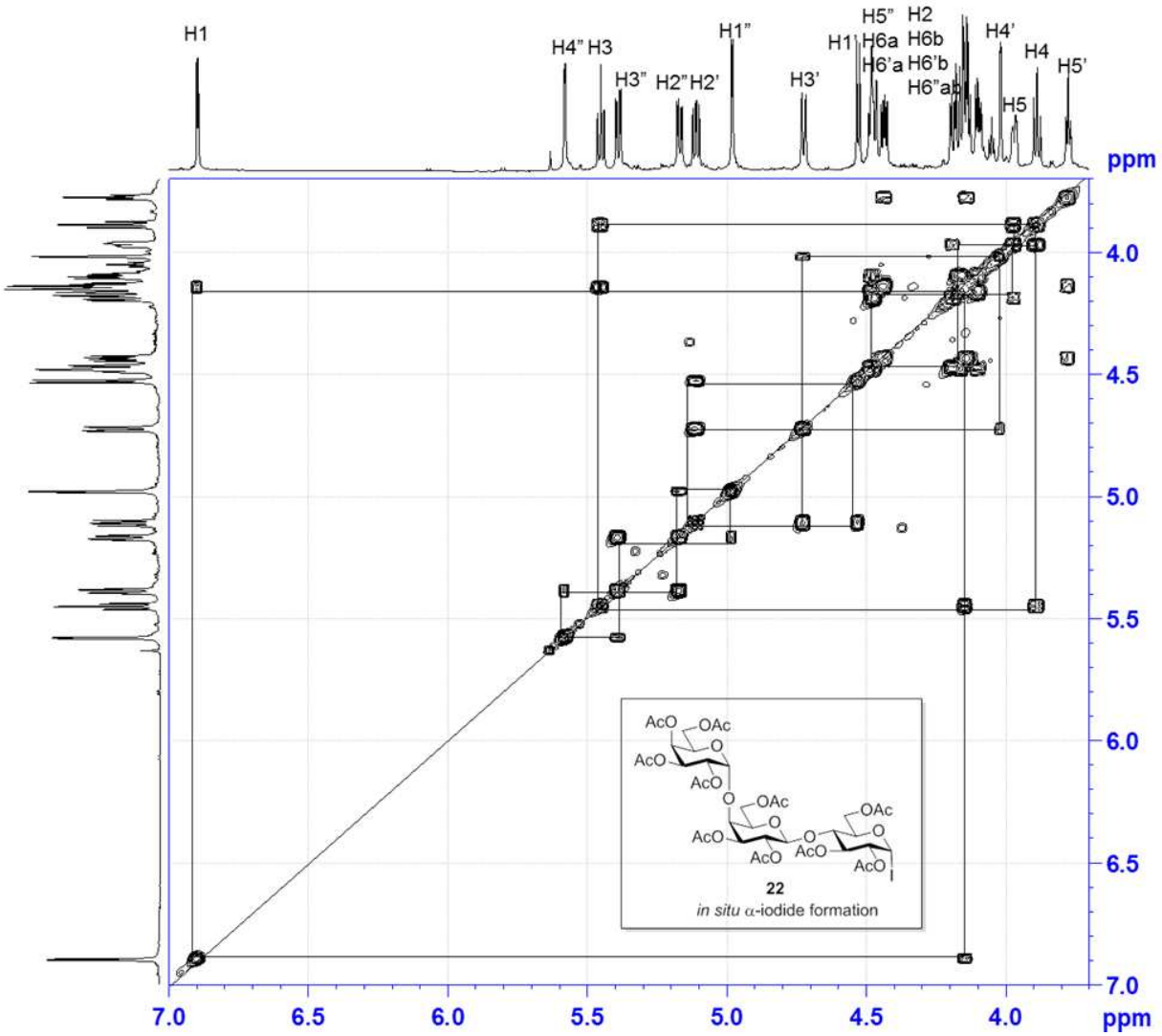
^{1}H-^{13}C HSQC spectrum of compound **21** (D_2O, 800 MHz)



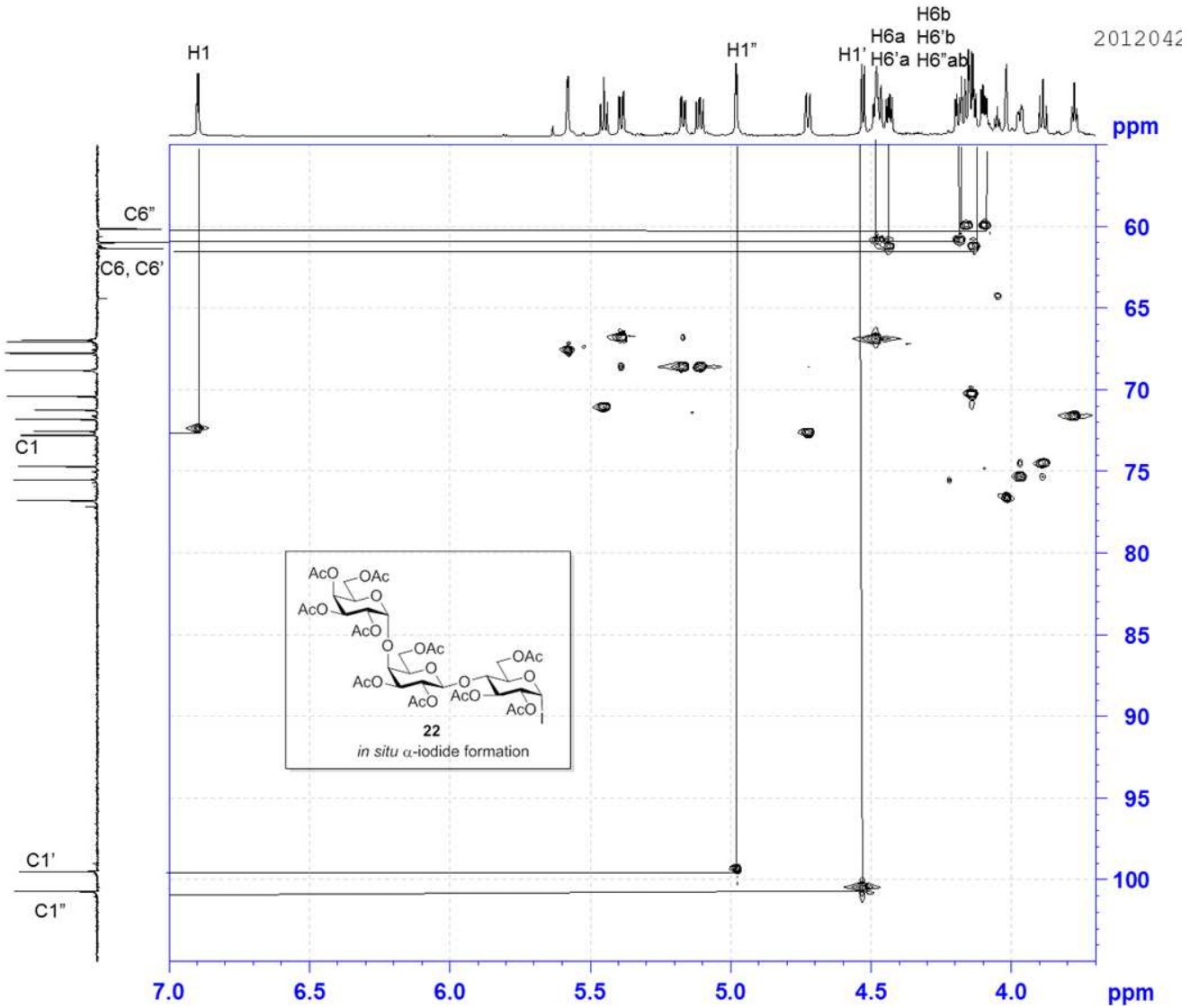
in-situ ^{1}H NMR spectrum of compound **22** ($CDCl_3$, 800 MHz)



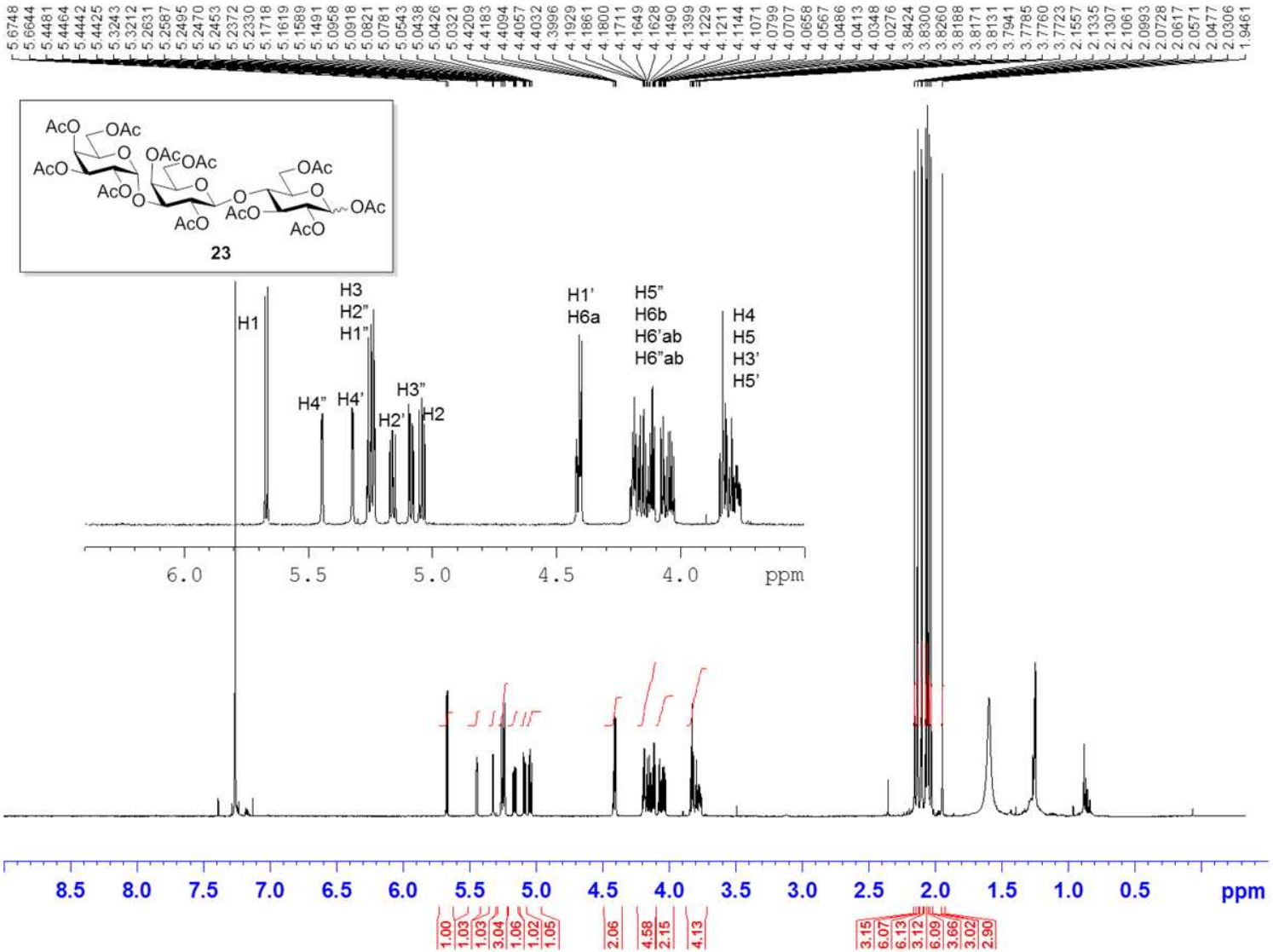
in-situ ^{13}C and DEPT135 NMR spectrum of compound **22** ($CDCl_3$, 200 MHz)



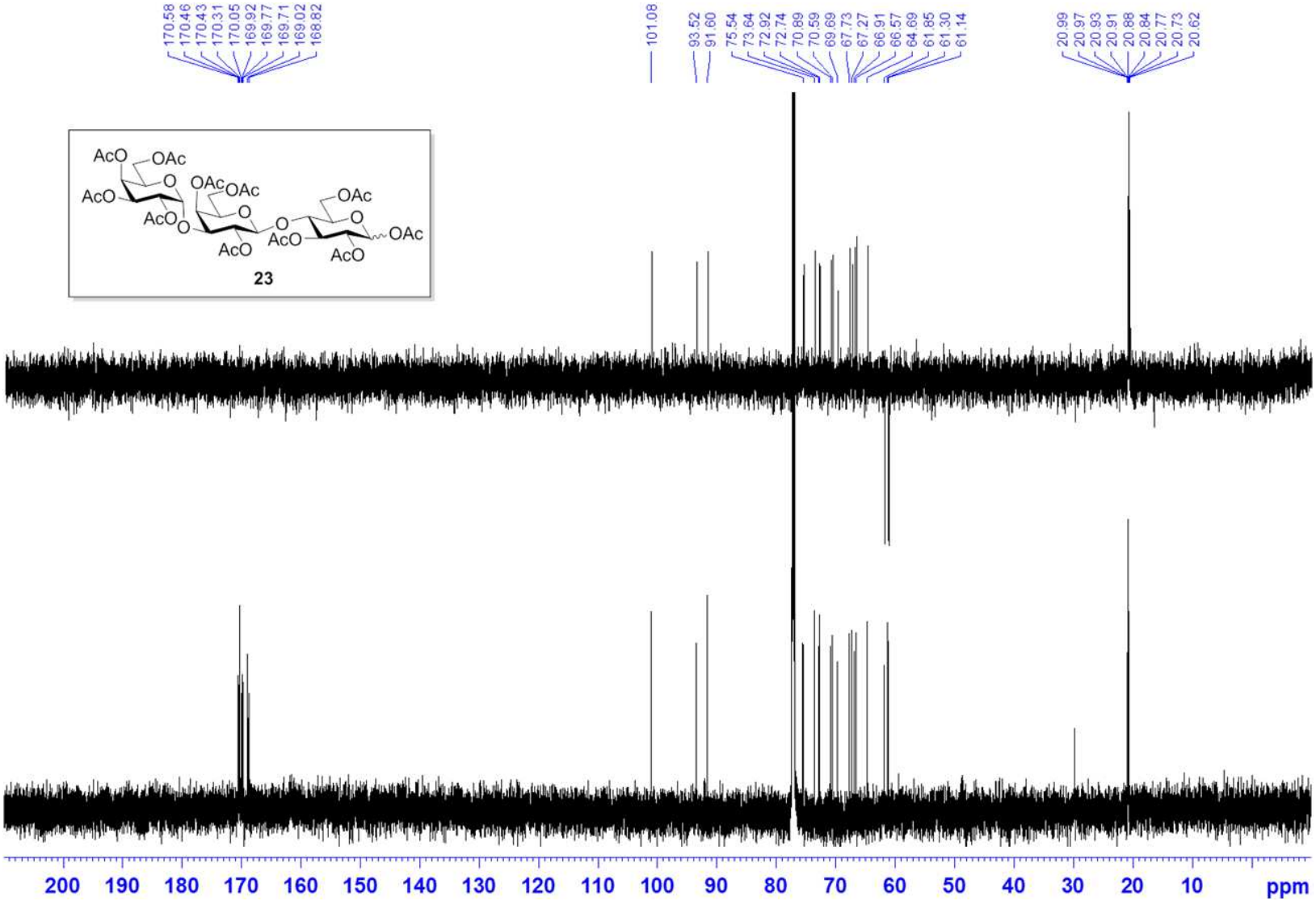
in-situ ^{1}H-^{1}H COSY spectrum of compound **22** ($CDCl_3$, 800 MHz)



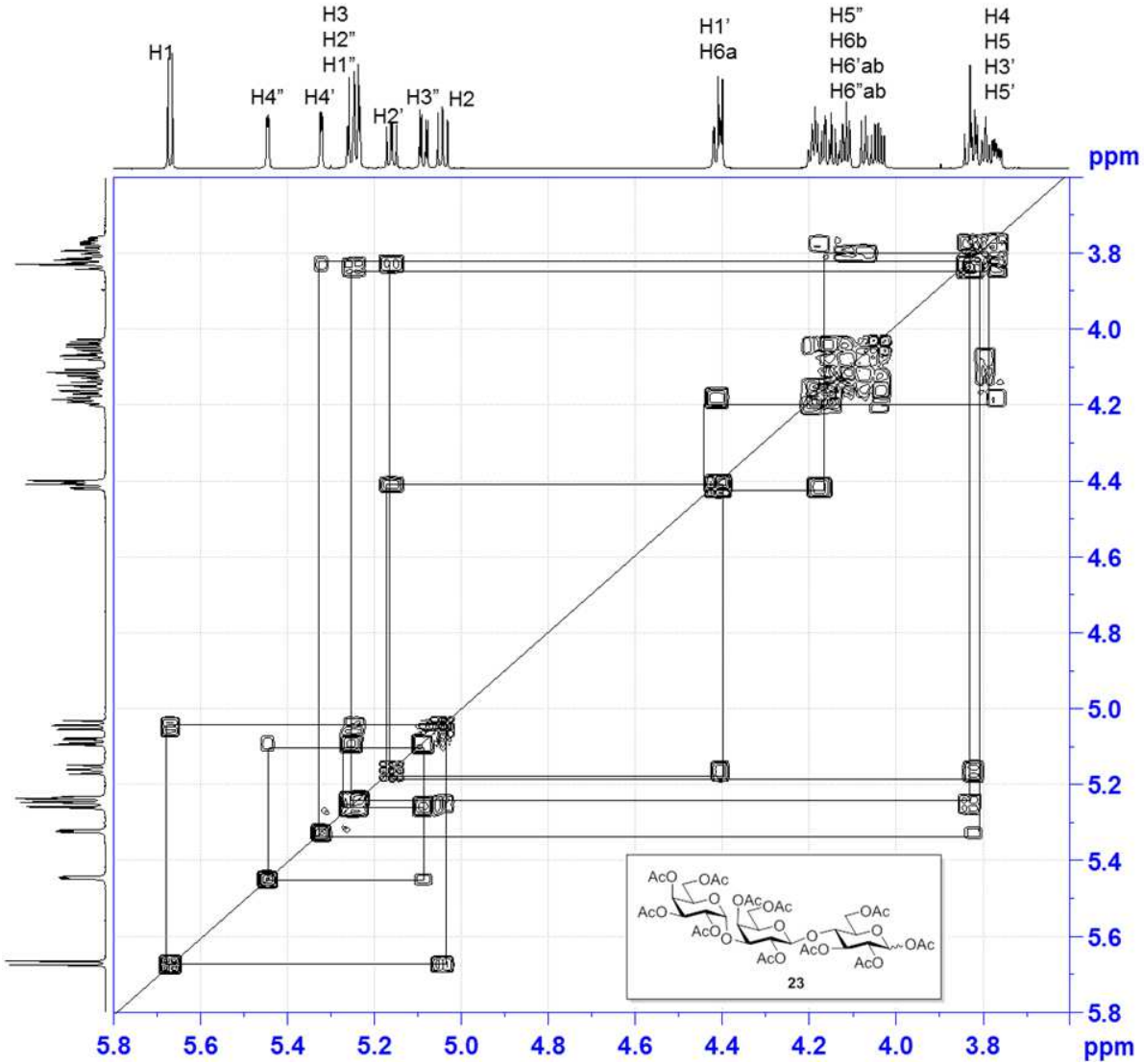
in-situ ^{1}H-^{13}C HSQC spectrum of compound **22** ($CDCl_3$, 800 MHz)



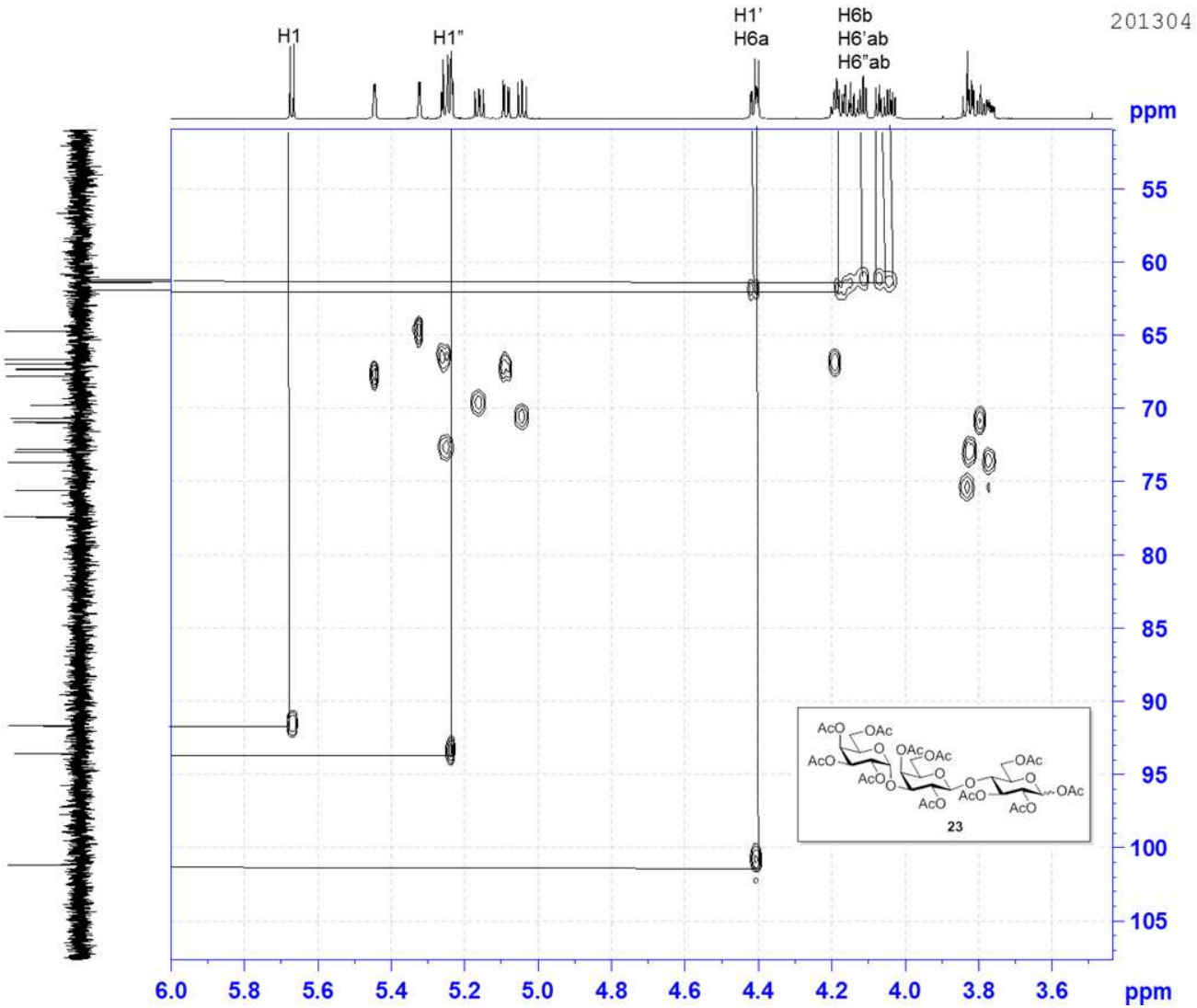
^{1}H NMR spectrum of compound **23** ($CDCl_3$, 800 MHz)



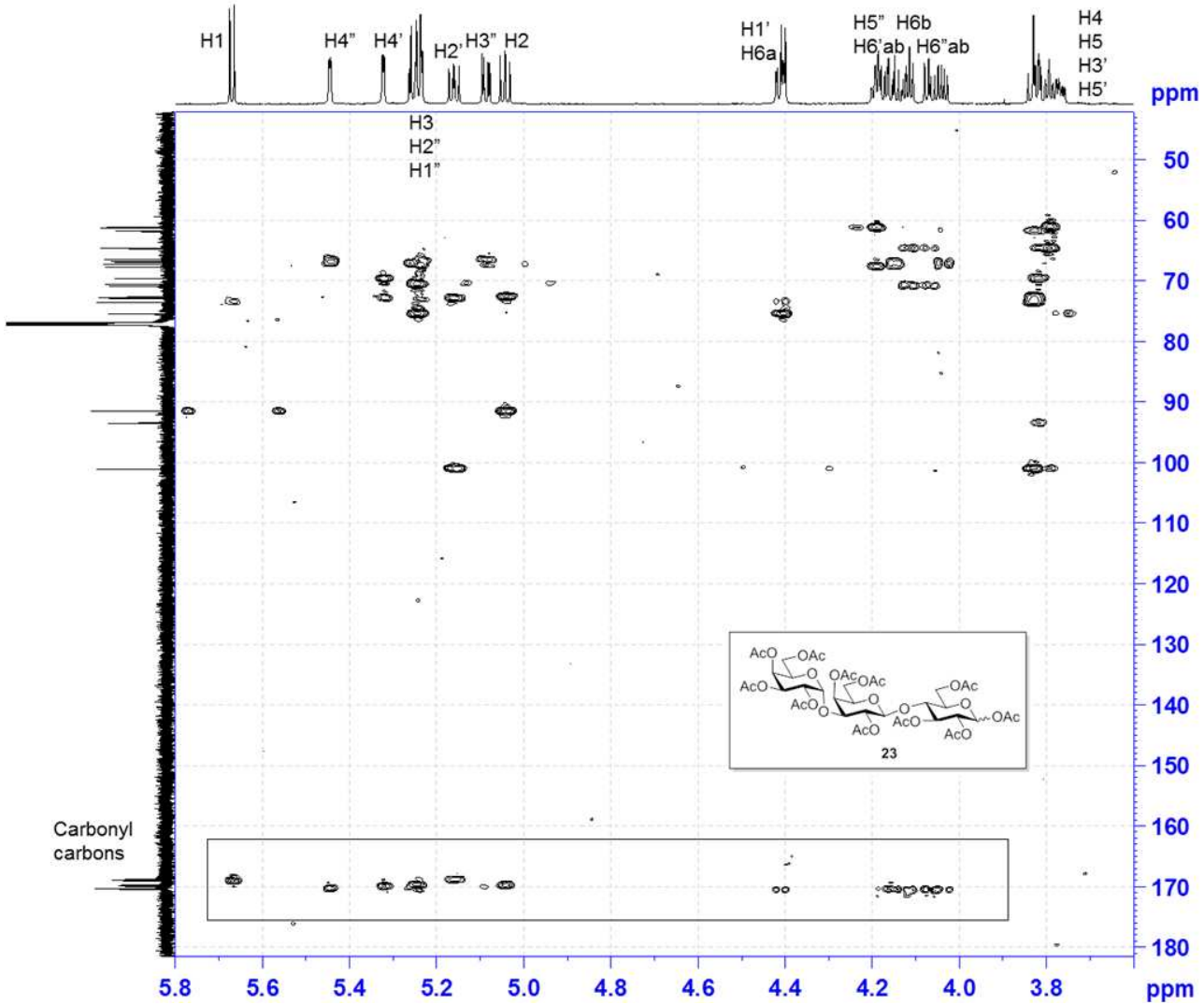
^{13}C and DEPT135 NMR spectrum of compound **23** ($CDCl_3$, 200 MHz)



^{1}H-^{1}H COSY spectrum of compound **23** ($CDCl_3$, 800 MHz)



^{1}H-^{13}C HSQC spectrum of compound **23** ($CDCl_3$, 800 MHz)



^{1}H-^{13}C HMBC spectrum of compound **23** ($CDCl_3$, 800 MHz)