Electronic Supplementary Information

Two Novel Innovanoside Dimers from *Daphne Aurantiaca* and a Concise Total Synthesis of Diinnovanoside A†

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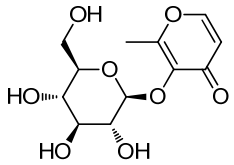
General Experimental Procedures. NMR spectra were recorded on a Avance 400 NMR spectrometer with TMS as interal standard. ESIMS were measured on an Agilent LC/MSD Trap XCT mass spectrometer, whereas HRESIMS were measured using a Q-TOF micro mass spectrometer (Waters, USA). Optical rotations were acquired with Perkin-Elmer 341 polarimeter, whereas IR spectra were recorded on a Bruker Vector 22 spectrometer spectrometer with KBr pellets. Materials for CC were silica gel (100–200 mesh; Huiyou Silical Gel Development Co. Ltd. Yantai, P. R. China), silica gel H (10–40 μm; Yantai), Sephadex LH-20 (40–70 μm; Amersham Pharmacia Biotech AB, Uppsala, Sweden), and YMC-GEL ODS-A (50 μm; YMC, MA, U.S.A.). Prep. TLC (0.4–0.5 mm) was conducted with glass precoated silica gel GF_{254} (Yantai).

Plant Material. The plant material was collected in July 2006 in Lijiang City, Yunnan province, China, and identified as *Daphne aurantiaca* by Prof. Li-Shan Xie of Kunming Institute of Botany. A voucher specimen has been deposited in the Herbarium of the School of Pharmacy, Second Military Medical University, Shanghai (No. 200607-11).

Isolation of compounds 1-3 from *D. aurantiaca.* The air-dried and powdered stem bark of *D. aurantiaca* (7.0 kg) was extracted with MeOH for 3 ×50 L× 2 h. The solvent was evaporated under a vacuum. Then, the extract was suspended in H_2O and partitioned with petroleum ether (5L×3), EtOAc (5L×3), and *n*-butanol (5L×3),

successively. The EtOAc extract (400g) was subjected to column chromatography on silica gel (200–300 mesh, 1000 g), eluted with gradient $CHCl_3$-MeOH (100:0-50:50) and separated into nine fractions (F_1-F_9). Fraction F_2 was rechromatographed on silica gel with $CHCl_3$-MeOH (50:1) and separated into four subfractions ($F_{2\text{-}1}$-$F_{2\text{-}4}$). $F_{2\text{-}2}$ was rechromatographed on ODS (CH_3OH-H_2O, 10:100-100:0) followed by Sephadex LH-20 with MeOH to give **3** (100 mg). Fraction F_5 was rechromatographed on silica gel with gradient mixture of $CHCl_3$-MeOH (10:1) and separated into six subfractions ($F_{5\text{-}1}$-$F_{5\text{-}6}$). $F_{5\text{-}3}$ was rechromatographed on ODS (CH_3OH-H_2O, 10:100-100:0) followed by Sephadex LH-20 with MeOH to give compound **1** (8 mg) and compound **2** (6 mg).

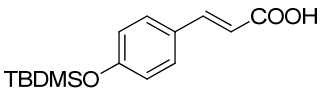
Synthesis of compound 4



The compound was synthesized according to the published protocol.[1] Starting with 2, 3, 4, 6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide and 3-hydroxy-2-methyl-4*H*-pyran-4-one, employed 2 steps in 47.5% yield as yellowish crystals: ^{1}H NMR (600 MHz, DMSO-d_6) δ ppm 8.13 (dd, J = 5.64, 0.41 Hz, 1 H), 6.43 (d, J = 5.64 Hz, 1 H), 5.45 (d, J = 3.16 Hz, 1 H), 5.02 (d, J = 4.95 Hz, 1 H), 4.93 (d, J = 4.81 Hz, 1 H), 4.74 (d, J = 7.70 Hz, 1 H), 4.42 (s, 1 H), 3.64 (ddd, J = 11.76, 5.43, 1.65 Hz, 1 H), 3.37 - 3.49 (m, 1 H), 2.36 (s, 3 H); ^{13}C NMR (150 MHz, DMSO-d_6) δ ppm 174.65, 161.77, 156.13, 142.23, 116.65, 104.08, 77.77, 76.81, 74.38, 70.10, 61.37, 15.69; HR-ESI-MS calcd for $C_{12}H_{16}NaO_8$ $[M+Na]^+$ 311.0737, found 311.0753.

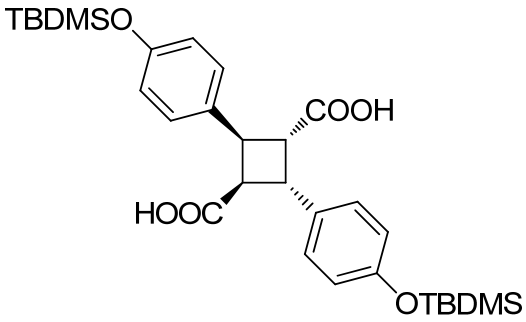
(1) Kröger, L.; Thiem, J. *J. Carbohyd. Chem.* **2003,** *22*, 9-23.

Synthesis of compound 6



p-Coumaric acid (6.56 g, 40 mmol) and TBDMS triflate (31.68 g, 120 mmol) were dissolved in dichloromethane(60 ml), triethylamine (16.16g,160 mmol) was added dropwise to the mixture, stirred and cooled to 0℃ in a flask fitted with dropping funnel. After completion of the addition, stirring was continued at room temperture for 48 h. Then a solution of HCl (1N, 110 mL) was added, and the mixture was stirred overnight at rt. Dichloromethane (60 ml) was added, and the organic phase was washed three times with water, once with brine, dried, and finally concentrated. The residue was purified by fresh column chromatography (Petro Ether/EtOAc 10:1) to afford white crystals (10 g, 36 mmol, 80%): ^{1}H NMR (600 MHz, DMSO-d_6) δ ppm 7.58 (d, J = 8.67 Hz, 1 H), 7.46 - 7.55 (m, 2 H), 6.74 - 6.91 (m, 2 H), 6.24 - 6.43 (m, 1 H), 0.92 - 0.98 (m, 6 H), 0.84 (s, 3 H), 0.26 (s, 3 H), 0.20 (d, J=1.10 Hz, 3 H); ^{13}C NMR (150 MHz, DMSO-d_6) δ ppm 168.35, 160.02, 144.58, 130.49, 130.40, 128.15, 120.72, 120.70, 116.16, 26.23, 18.22, -2.77; HR-ESI-MS calcd for $C_{15}H_{22}NaO_3Si$ $[M+Na]^+$ 301.1230, found 301.1253.

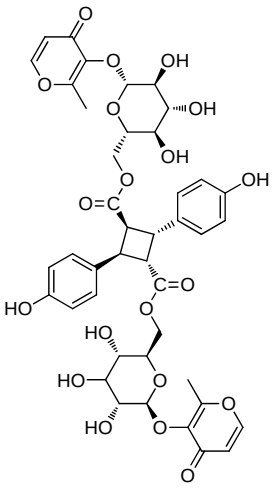
Synthesis of compound 7



A suspension of compound **6** crystals (2.78 g, 10.00 mmol) in hexane contained in a Pyrex reactor was irradiated with a 400 W high-pressure mercury lamp for 60 h. The solvent was evaporated in vacuo, and the residue was purified by chromatography (Petro Ether/EtOAc 15:1) to afford compound **7** (2.23 g, 70%) as a white solid: $[\alpha]_D^{25}$ -4.8 (c 0.17, CH_3COCH_3); ^{1}H NMR (600 MHz, DMSO-d_6) δ ppm 12.03 (br. s., 2 H),

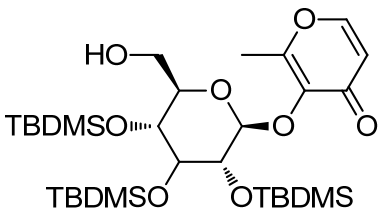
7.21 (d, J = 7.89 Hz, 4 H), 6.78 (d, J = 7.89 Hz, 4 H), 4.17 (t, J = 8.53 Hz, 2 H), 3.64 - 3.75 (m, 2 H), 0.95 (s, 18 H), 0.18 (s, 12 H); ^{13}C NMR (150 MHz, DMSO-d_6) δ ppm 172.96, 153.76, 132.20, 128.78, 119.29, 46.49, 40.28, 25.53, 17.86, -4.54; HR-ESI-MS calcd for $C_{30}H_{44}NaO_6Si_2$ $[M+Na]^+$ 579.2569, found 579.2574.

Synthesis of compound 1



To a solution of compound **8** (300 mg, 0.17 mmol) in THF (20 mL) and AcOH (1 ml) was added tetrabutylammonium fluoride (710 mg, 2.7 mmol). After stirring at room temperature for 96 h, the organic solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate (150 ml), then the organic phase was washed with brine, dried, and finally concentrated. The residue was purified by column chromatography (DCM/MeOH 10:1) to afford compound **1** (103 mg, 0.12 mmol, 70%) as a white solid. ^{1}H and ^{13}C NMR spectroscopic data, see Table 1. $[\alpha]_D^{20}$ -54 (c 0.04, CH_3OH).

Synthesis of compound 5

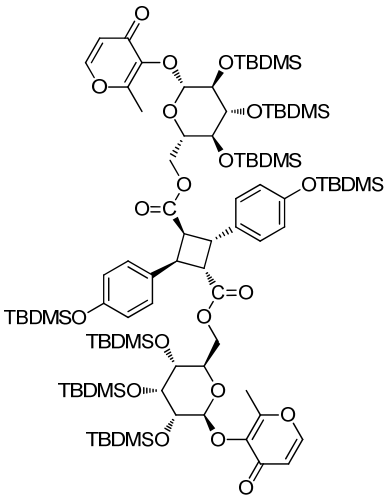


Compound **4** (1.44 g, 5 mmol) and TBDMS triflate (7.92 g, 120 mmol) were dissolved in DMF (50 ml), anhydrous pyridine (30 ml) was added dropwise to the

mixture, stirred and cooled to 0℃ in a flask fitted with dropping funnel. After completion of the addition, stirring was continued at room temperture for 48 h. Ethyl acetate (150 mL) was added, and the organic phase was washed three times with saturated copper sulfate solution (50 ml×3), twice with water, once with brine, dried, and finally concentrated. The residue was no need to further purify and could be used directly in the next reaction.

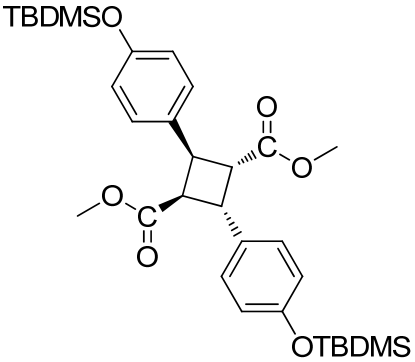
A solution of the residue (3.0 g, 4 mmol), CBr_4 (265.2 mg, 0.8 mmol) and anhydrous MeOH (40 mL) in a Pyrex round flask was irradiated by a TLC lamp (Uvltec Limited, 245 nm, 8 W) for 0.5 h, followed by stirring without irradiation at room temperature. After the reaction was complete (TLC), the organic solvent was removed under reduced pressure. The residue was purified by column chromatography (Petro Ether/EtOAc 6:1) to afford compound **5** (2.3 g, 3.6 mmol, 72%) as a yellow solid: ^{1}H NMR (600 MHz, DMSO-d_6) δ ppm 7.91 - 8.15 (m, 1 H), 6.23 - 6.47 (m, 1 H), 5.60 - 5.79 (m, 1 H), 3.79 - 3.92 (m, 2 H) 4.61 (s, 1 H), 3.74 (s, 1 H), 3.53 - 3.61 (m, 1 H), 3.45 - 3.52 (m, 1 H), 3.41 (d, *J*=5.64 Hz, 1 H), 2.28 (d, *J*=0.69 Hz, 3 H), 0.85 - 0.88 (m, 27 H), 0.05 - 0.11 (m, 18 H); ^{13}C NMR (150 MHz, DMSO-d_6) δ ppm 173.53, 160.03, 155.21, 141.25, 116.96, 100.14, 79.57, 79.07, 76.53, 71.33, 62.02, 26.09, 18.15, 18.10, 18.01, 15.35, -4.07, -4.46, -4.55; HR-ESI-MS calcd for $C_{30}H_{58}NaO_8Si_3$ $[M+Na]^+$ 653.3332, found 653.3329.

Synthesis of compound 8



To a solution of compound **7** (150 mg, o.27 mmol), compound **5** (510 mg, 0.81 mmol), and EDCI (576 mg, 3.0 mmol) in CH_2Cl_2 (30 mL) was added DMAP (122 mg, 1.0 mmol), and the mixture was stirred at room temperature for 24 h. Ethyl acetate (60 mL) was added, and the organic phase was washed three times with water, once with brine, dried, and finally concentrated. The residue was purified by column chromatography (Petro Ether/EtOAc 10:1) to give compound **8** (385 mg, 0.22 mmol, 80%) as a white solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.48 (dd, *J*=13.00, 5.71 Hz, 2 H), 7.05 (t, *J*=7.57 Hz, 4 H), 6.71 (dd, *J*=8.12, 4.68 Hz, 4 H), 6.25 (d, *J*=5.64 Hz, 2 H), 5.67 (d, *J*=3.58 Hz, 1 H), 5.61 (d, *J*=3.58 Hz, 1 H), 4.15 - 4.31 (m, 2 H), 4.00 (dd, *J*=11.28, 7.29 Hz, 1 H), 3.91 (dd, *J*=13.75, 2.48 Hz, 2 H), 3.62 - 3.84 (m, 8 H), 3.57 (dd, *J*=11.49, 4.06 Hz, 1 H), 3.44 (dd, *J*=11.42, 6.19 Hz, 1 H), 2.27 (s, 3 H), 2.15 (s, 3 H), 0.96 (s, 20 H), 0.90 (s, 13 H), 0.85 - 0.88 (m, 29 H), 0.83 (s, 10 H), 0.02 - 0.19 (m, 48 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 175.43, 173.09, 172.96, 161.72, 156.07, 154.55, 143.14, 132.72, 132.54, 129.94, 121.34, 118.65, 102.39, 101.85, 80.00, 79.67, 77.06, 76.97, 76.87, 76.62, 73.31, 73.04, 66.39, 65.98, 48.38, 48.29, 41.97, 27.26, 27.21, 27.09, 19.59, 19.42, 19.31, 19.28, 16.83, 16.67, -2.68, -2.72, -2.72, -2.75, -2.79, -3.01, -3.10, -3.47; HR-ESI-MS calcd for $C_{90}H_{156}NaO_{20}Si_8$ $[M+Na]^+$ 1803.9236, found 1803.9241.

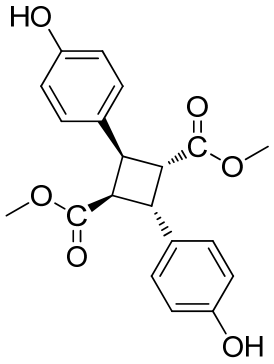
Synthesis of compound 9



To a solution of compound **7** (750 mg, 1.35 mmol) and EDCI (2.8 g, 15.0 mmol) in methanol (30 mL) was added DMAP (610 mg, 5.0 mmol), and the mixture was stirred at room temperature for 12 h. The organic solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate (50 ml), then the organic

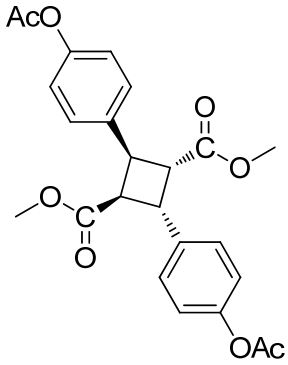
phase was washed with brine, dried, and finally concentrated. The residue was purified by column chromatography (Petro Ether/EtOAc 30:1) to afford compound **9** (755 mg, 1.3 mmol, 96%) as a white solid: $[\alpha]_D^{25}$ -2.2 (*c* 0.22, CH_3COCH_3); ^1H NMR (600 MHz, $CDCl_3$) δ ppm 7.14 (d, *J*=8.39 Hz, 4 H), 6.79 (d, *J*=8.67 Hz, 4 H), 4.31 - 4.40 (m, 2 H), 3.85 - 3.91 (m, 2 H), 3.30 (s, 6 H), 0.97 (s, 18 H), 0.17 (s, 12 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 173.83, 156.14, 132.91, 129.92, 121.41, 52.77, 48.48, 42.14, 27.10, 19.66, -3.01; HR-ESI-MS calcd for $C_{32}H_{48}NaO_6Si_2$ $[M+Na]^+$ 607.2882, found 607.2918.

Synthesis of compound 10



To a solution of compound **9** (584 mg, 1 mmol) in THF (20 mL) and AcOH (1 ml) was added tetrabutylammonium fluoride (710 mg, 2.7 mmol). After stirring at room temperature for 2 h, the organic solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate (150 ml), then the organic phase was washed with brine, dried, and finally concentrated. The residue was purified by column chromatography (Petro Ether/EtOAc 6:1) to afford compound **10** (320 mg, 0.9 mmol, 90%) as a white solid: $[\alpha]_D^{25}$ -2.6 (*c* 0.33, CH_3COCH_3); ^1H NMR (600 MHz, DMSO-d_6) δ ppm 7.07 (d, *J*=8.53 Hz, 4 H), 6.68 (dt, *J*=8.53, 1.65 Hz, 4 H), 4.17 (dd, *J*=10.39, 7.36 Hz, 2 H), 3.68 - 3.88 (m, 2 H), 3.23 (s, 6 H); ^{13}C NMR (150 MHz, DMSO-d_6) δ ppm 173.81, 158.09, 130.68, 130.33, 116.81, 52.96, 48.23, 42.09, 41.96; HR-ESI-MS calcd for $C_{20}H_{20}NaO_6$ $[M+Na]^+$ 379.1152, found 379.1168.

Synthesis of compound 11



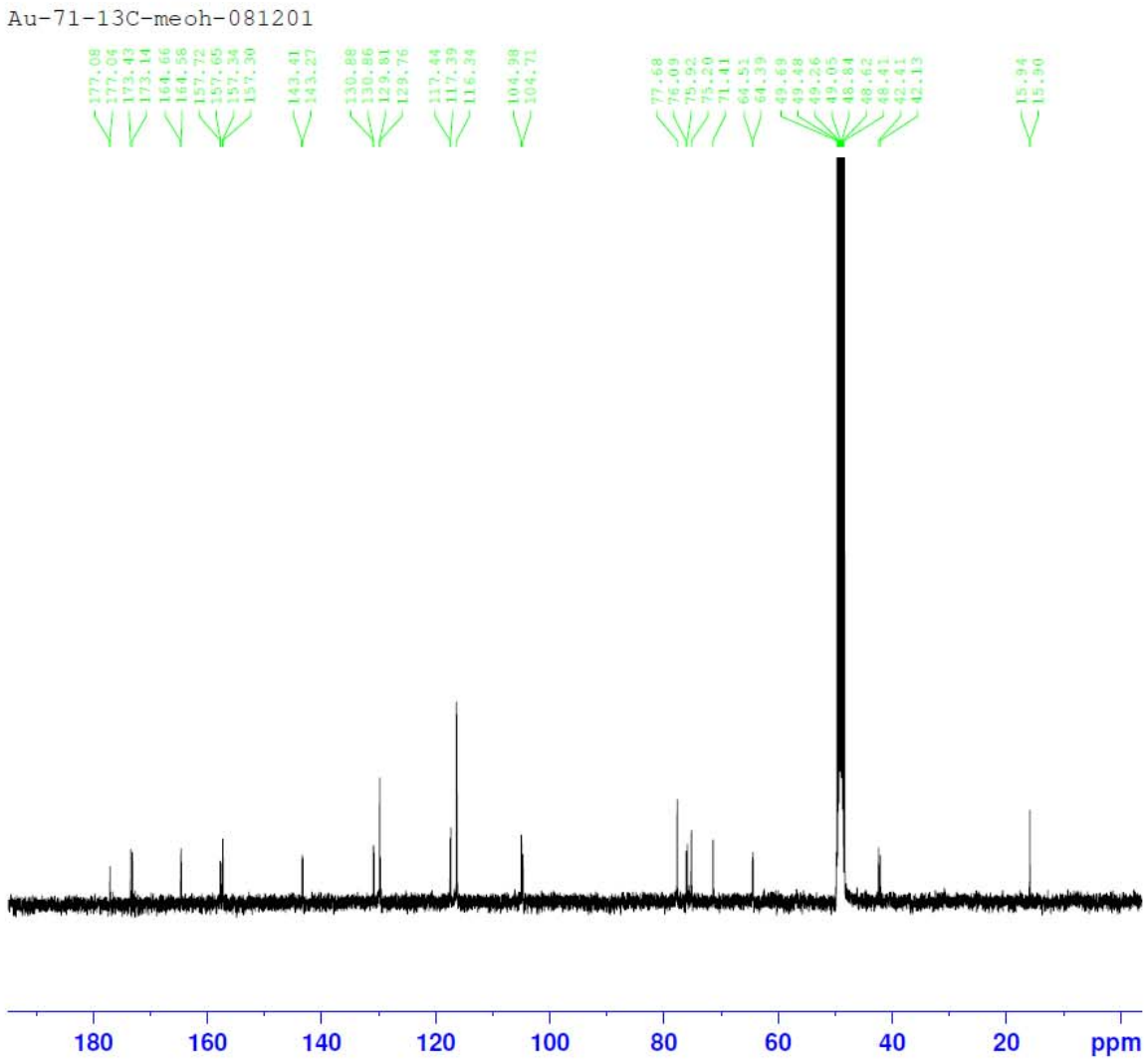
To a solution of compound **10** (178 mg, 0.5 mmol) in anhydrous pyridine (20 mL) was added acetic anhydride (153 mg, 1.5 mmol), and the mixture was stirred at room temperature (overnight). Then ethyl acetate (50 mL) was added, and the organic phase was washed three times with saturated copper sulfate solution (20 ml×3), twice with water, once with brine, dried, and finally concentrated. The residue was purified by column chromatography (Petro Ether/EtOAc 20:1) to afford compound **11** (210mg, 0.48mmol, 95%) as a white solid: $[\alpha]_D^{25}$ -5.6 (*c* 0.20, CH_3COCH_3); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.29 (d, *J*=8.53 Hz, 4 H), 7.05 (d, *J*=8.53 Hz, 4 H), 4.38 - 4.49 (m, 2 H), 3.84 - 3.99 (m, 2 H), 3.32 (s, 6 H), 2.28 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 173.46, 170.75, 151.19, 137.53, 129.88, 122.95, 52.99, 48.21, 42.31, 22.51; HR-ESI-MS calcd for $C_{24}H_{25}O_8$ $[M+H]^+$ 441.1544, found 441.1560.

Crystallographic data of compound 11

Empirical formula	$C_{24}H_{24}O_8$
Formula weight	440.43
Temperature	140(2)K
Wavelength	0.71073Å
Crystal system	Monoclinic
Space group	P 2(1)/c
Unit cell dimensions	a = 14.0632 (14) A, b = 7.2591 (7) A, c = 11.4968 (11) A,
Volume	1093.95 (18) Åˆ 3
Z	2
Calculated density	1.337 Mg/mˆ 3
Absorption coefficient	0.101 mmˆ -1
F(000)	464
Crystal size	0.30 × 0.25 × 0.14 mm
Theta range for data collection	3.11 to 30.67 deg.
Limiting indices	-20 <= h <= 20 -5 <= k <= 10 -15 <= l <= 16
Reflections collected / unique	10346/3382 [R(int) = 0.0178]
Completeness to theta = 30.67	99.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.9860 and 0.9704
Refinement method	Full-matrix least-squares on Fˆ 2
Data / restraints / parameters	3382/0/147
Goodness-of-fit on Fˆ 2	1.022
Final R indices [I>2σ(I)]	R_1 = 0.0400, wR_2 = 0.1109
R indices (all data)	R_1 = 0.0458, wR_2 = 0.1169
Largest diff. peak and hole	0.401 and -0.262 e. Åˆ -3

Colorless prism crystals of **11** were obtained by recrystallization in CH_2Cl_2. Crystal data were obtained on Bruker SMART APEX II CCD area detector with graphite monochromated Mo-Kα radiation (λ =1.54178 Å) at 133(2) and operating in the ϕ-ω scan mode. The structure was solved by direct methods and refined with full-matrix

least-squares calculations of F^2 using SHELX-97. The collected data were reduced by using the program SAINT and empirical absorption correction was made by using the SADABS program. The hydrogen atom positions were geometrically idealized and allowed to ride on their parent atoms. Crystallographic data for **11** have been deposited at the Cambridge Crystallographic Data Centre (deposition no. CCDC 907651). Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK. [fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk].



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PROCNO	1
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TD	65536
SOLVENT	MeOD
NS	2000
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 se
RG	2050
DW	20.800 us
DE	6.00 us
TE	296.6 K
D1	2.00000000 se
d11	0.03000000 se
DELTA	1.89999998 se
TD0	1
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NUC1	13C
P1	9.00 us
PL1	-1.00 dB
SFO1	100.6228298 MH
======== CHANNEL f2 ======	
CPDPRG2	waltz16
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PCPD2	80.00 us
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PL12	15.00 dB
PL13	18.00 dB
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WDW	EM
SSB	0
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GB	0
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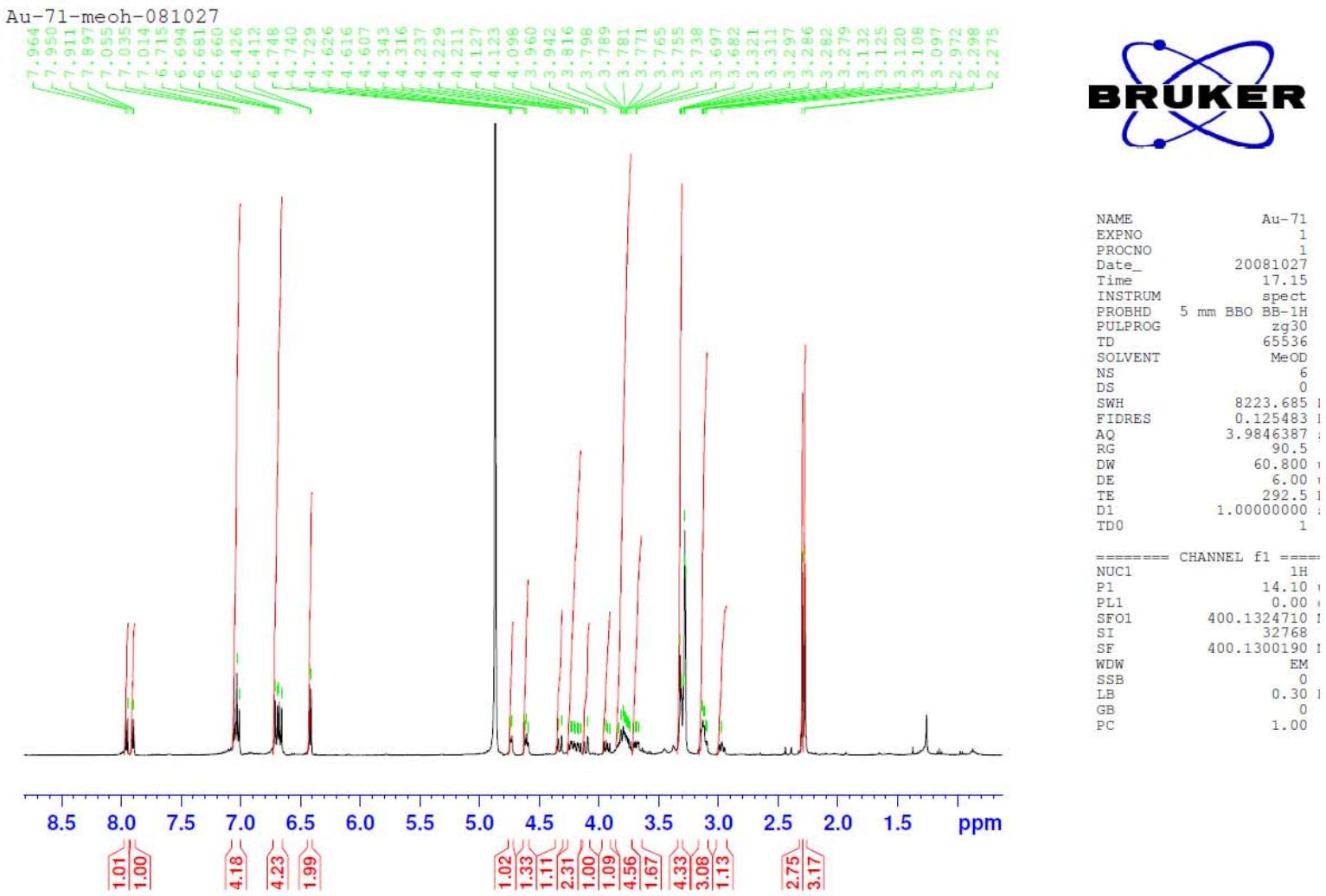
Figure 1. ^{13}C NMR spectrum of compound **1**



BRUKER

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FIDRES	0.125483
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RG	90.5
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Figure 2. ^{1}H NMR spectrum of compound **1**

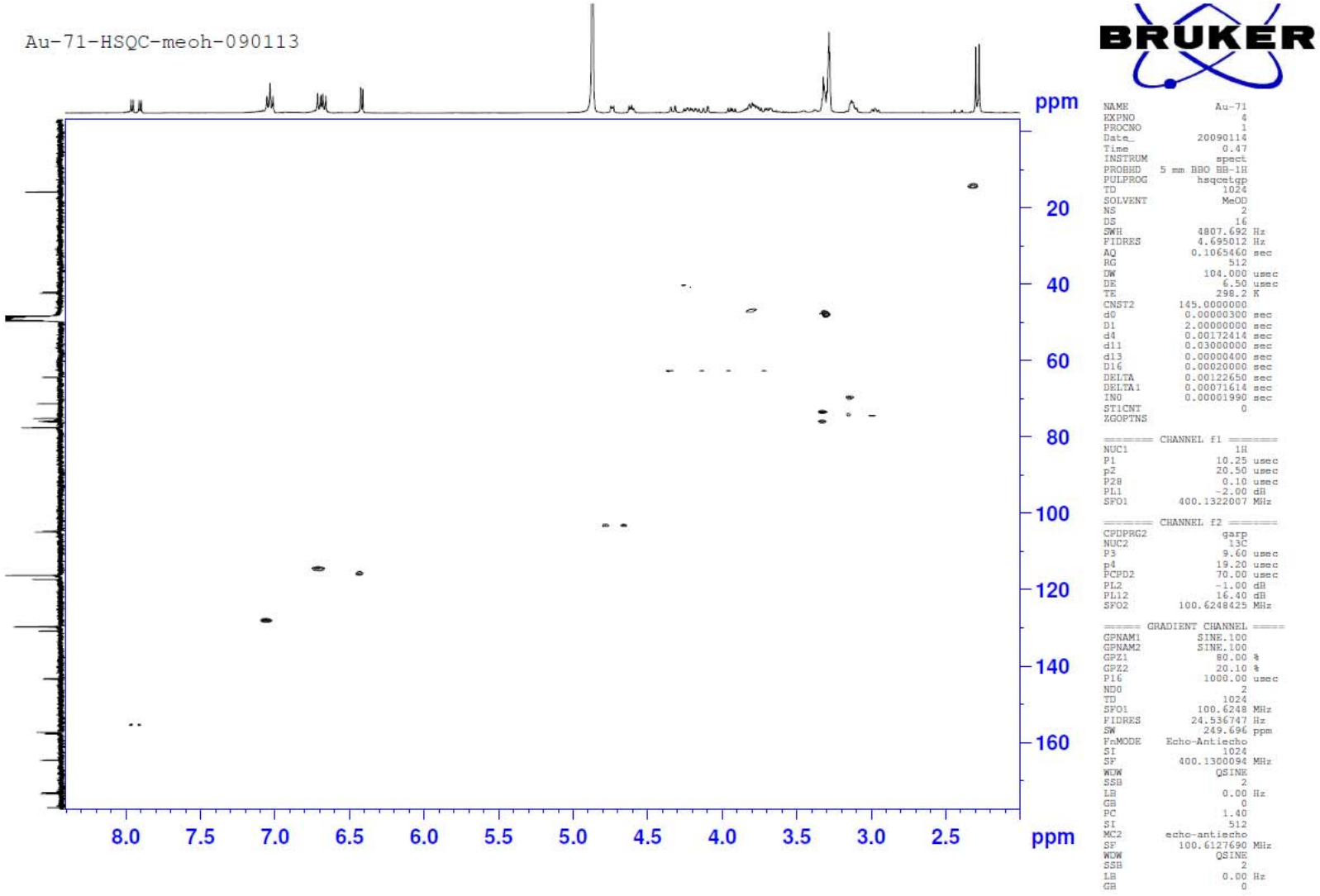


Figure 3. HSQC spectrum of compound **1**

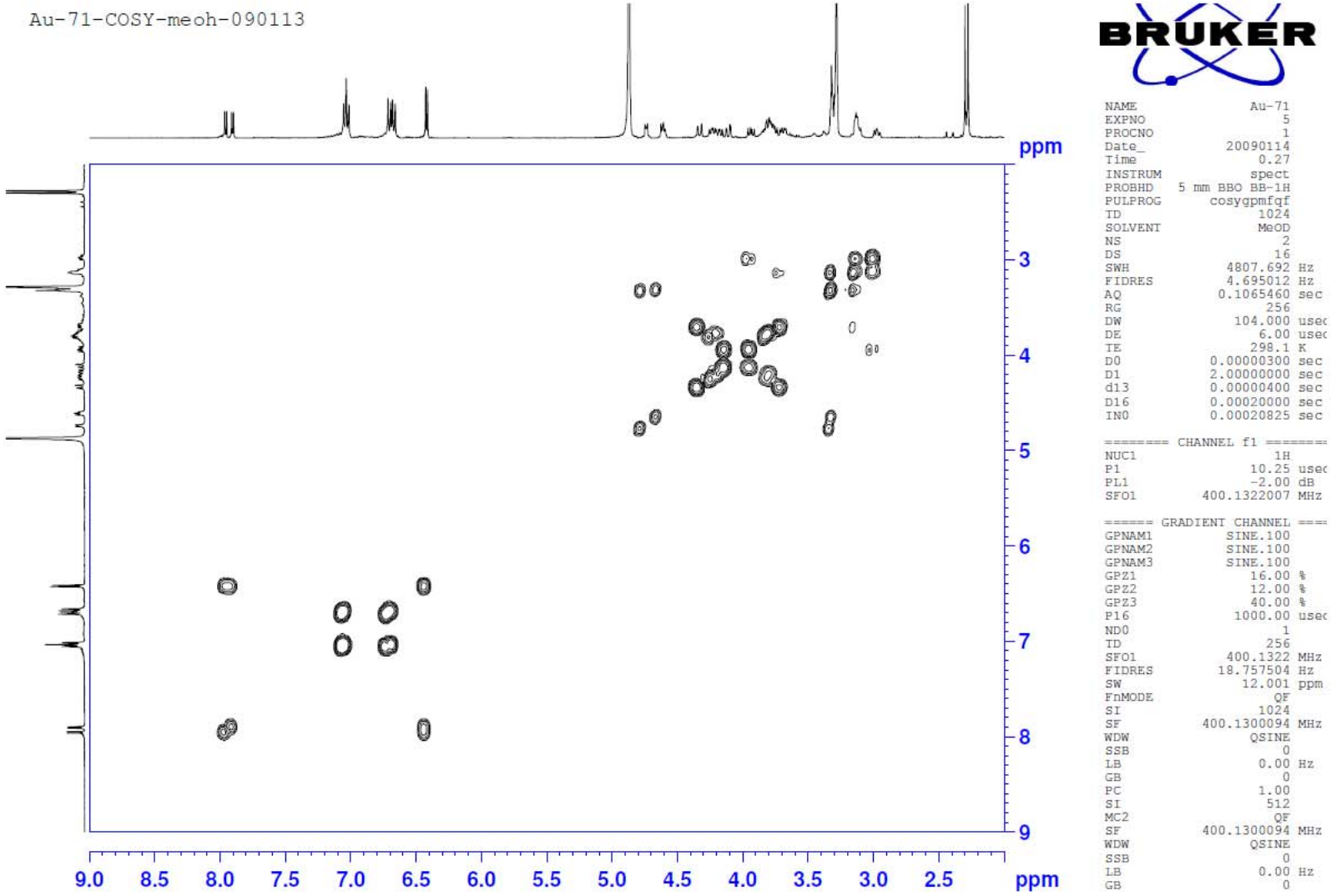


Figure 4. ^{1}H- ^{1}H COSY spectrum of compound **1**

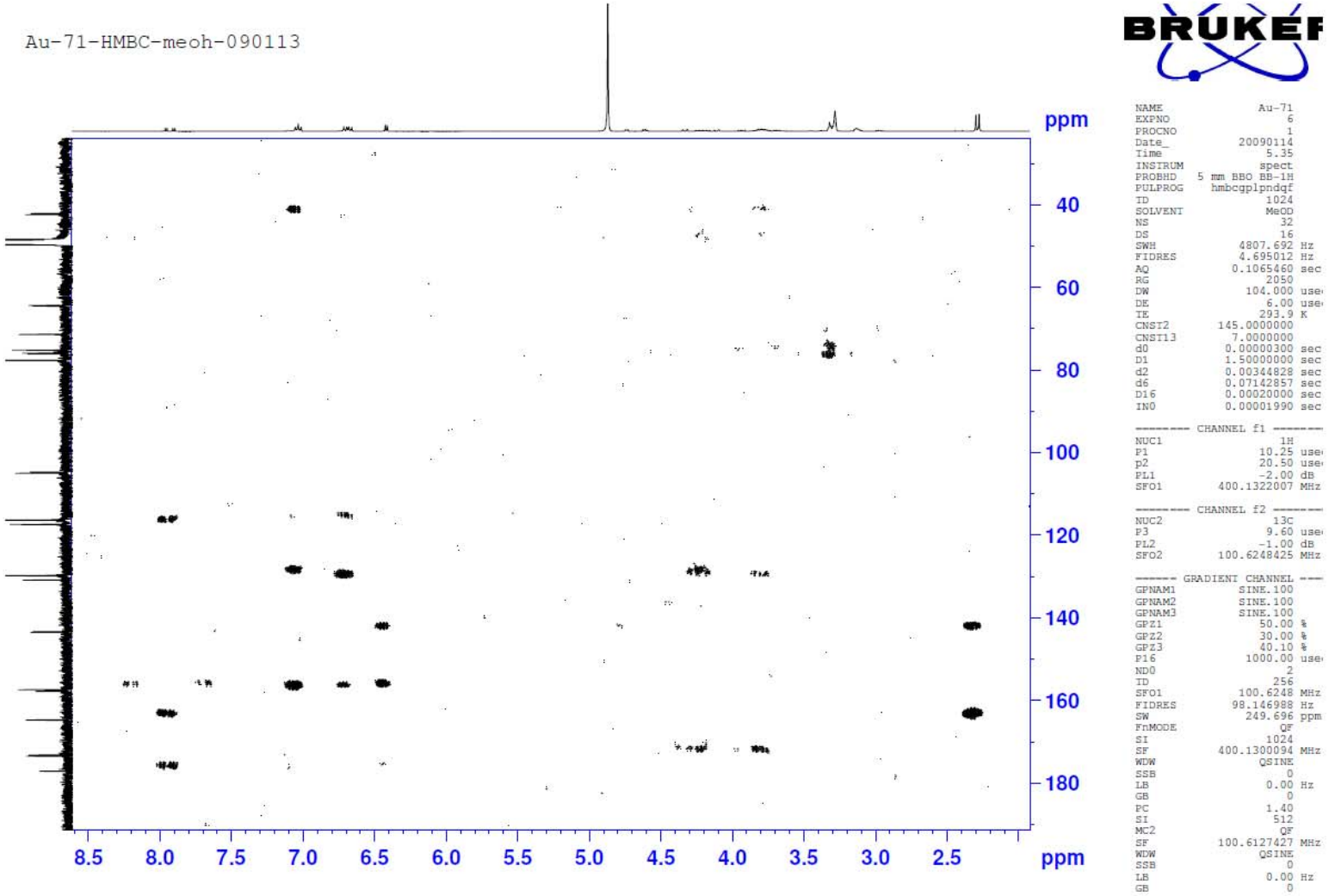


Figure 5. HMBC spectrum of compound **1**

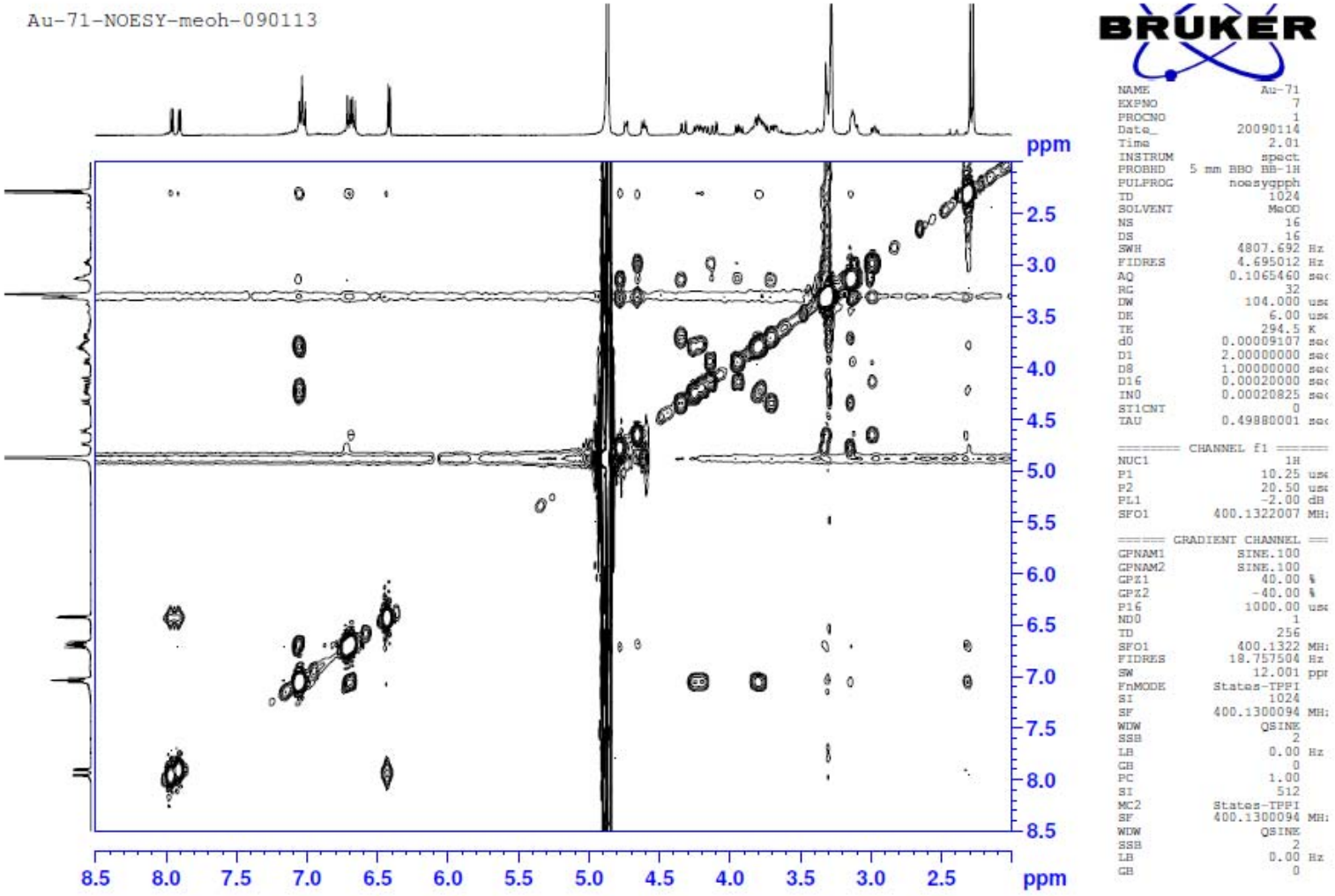


Figure 6. NOESY spectrum of compound **1**

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

319 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 O: 0-50

Minimum:				-1.5				
Maximum:			5.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE		i-FIT	Norm	Conf(%) Formula
867.2354	867.2348	0.6	0.7	21.5	35.6	0.625	53.54	C42 H43 O20
	867.2383	-2.9	-3.3	43.5	37.0	2.006	13.45	C60 H35 O7
	867.2313	4.1	4.7	-0.5	37.0	2.080	12.49	C24 H51 O33
	867.2406	-5.2	-6.0	12.5	36.8	1.809	16.39	C35 H47 O25
	867.2289	6.5	7.5	30.5	38.1	3.188	4.13	C49 H39 O15

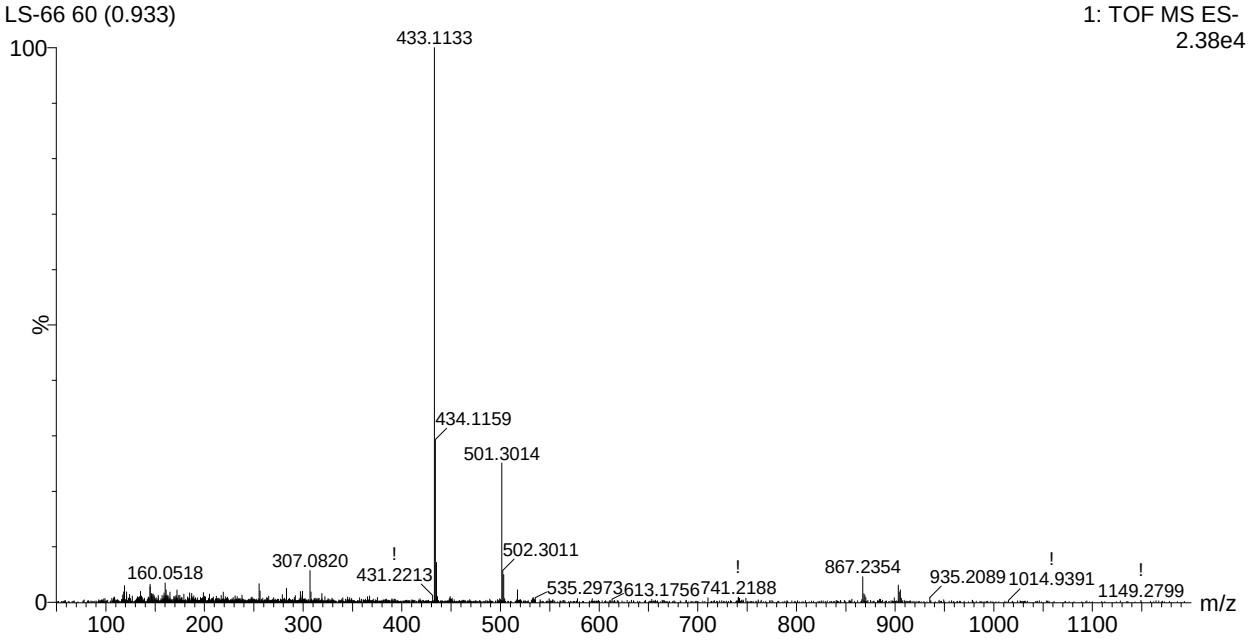
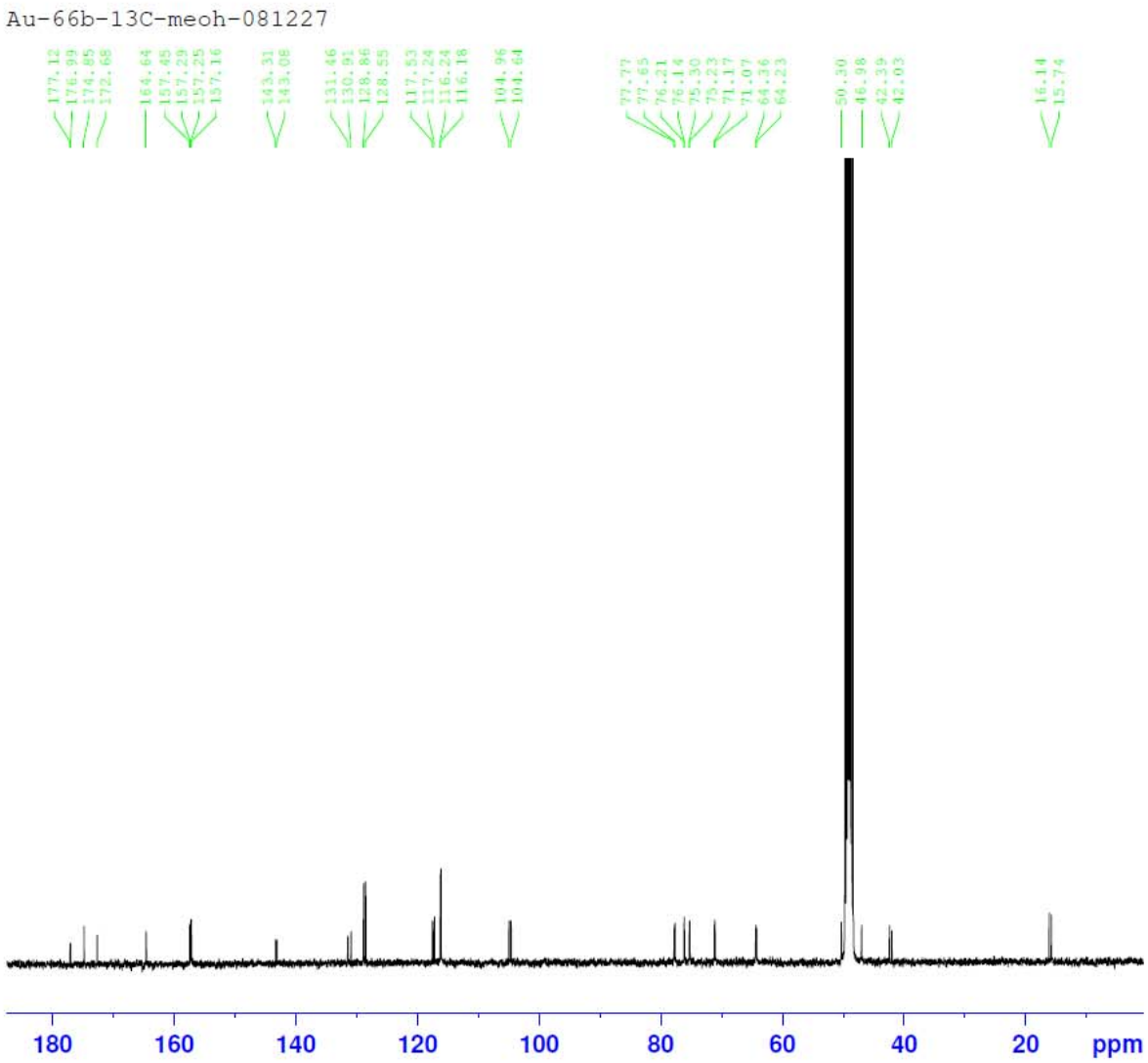


Figure 7. HR-ESI-MS spectrum of compound **1**



NAME	Au-66b
EXPNO	2
PROCNO	1
Date_	20081228
Time	10.35
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	65536
SOLVENT	MeOD
NS	5000
DS	0
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.00 usec
TE	298.2 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	-1.00 dB
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	18.00 dB
SFO2	400.1316005 MHz
SI	32768
SF	100.6126227 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.40

Figure 8. ^{13}C NMR spectrum of compound **2**

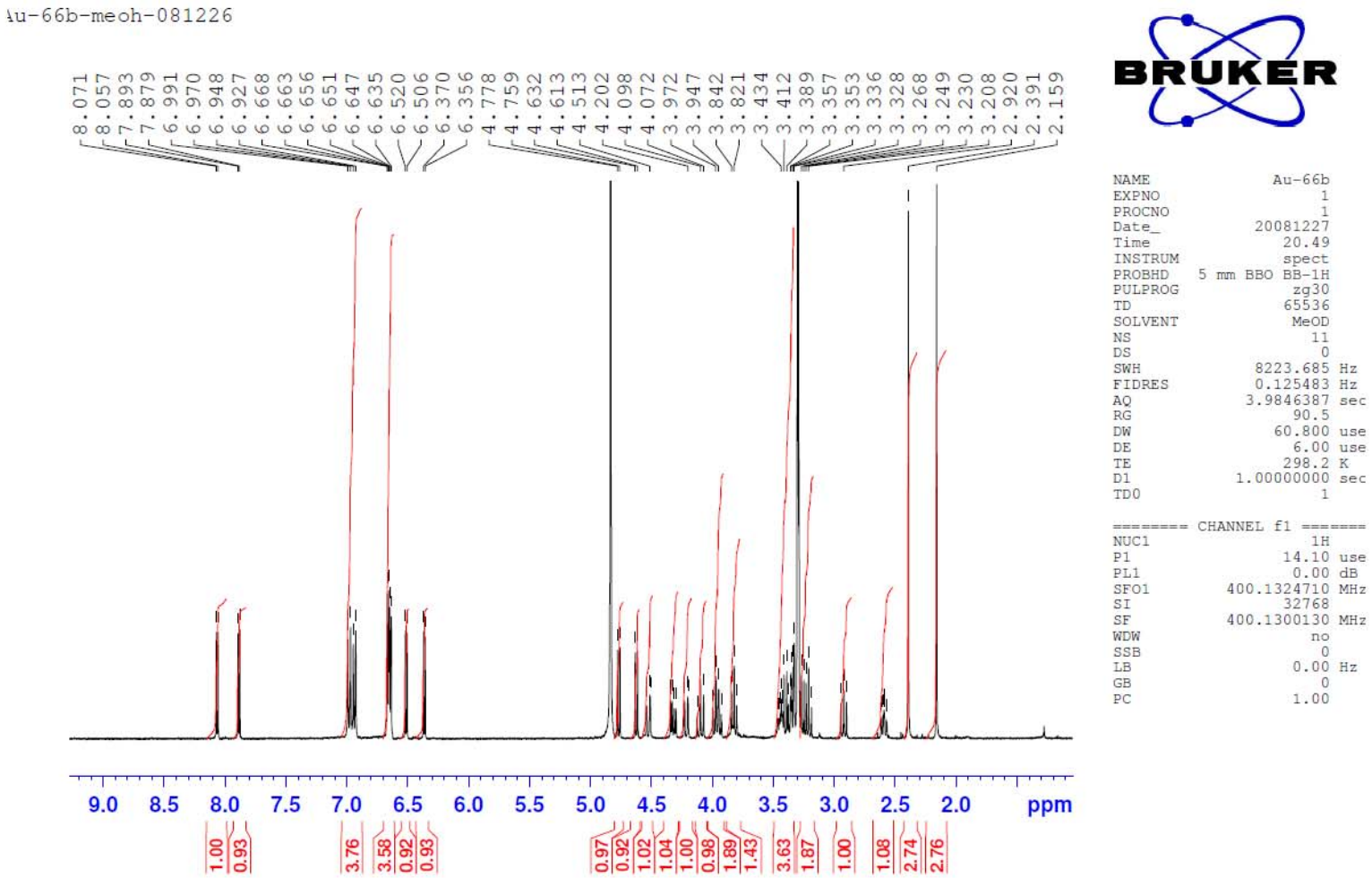


Figure 9. ^{1}H NMR spectrum of compound **2**

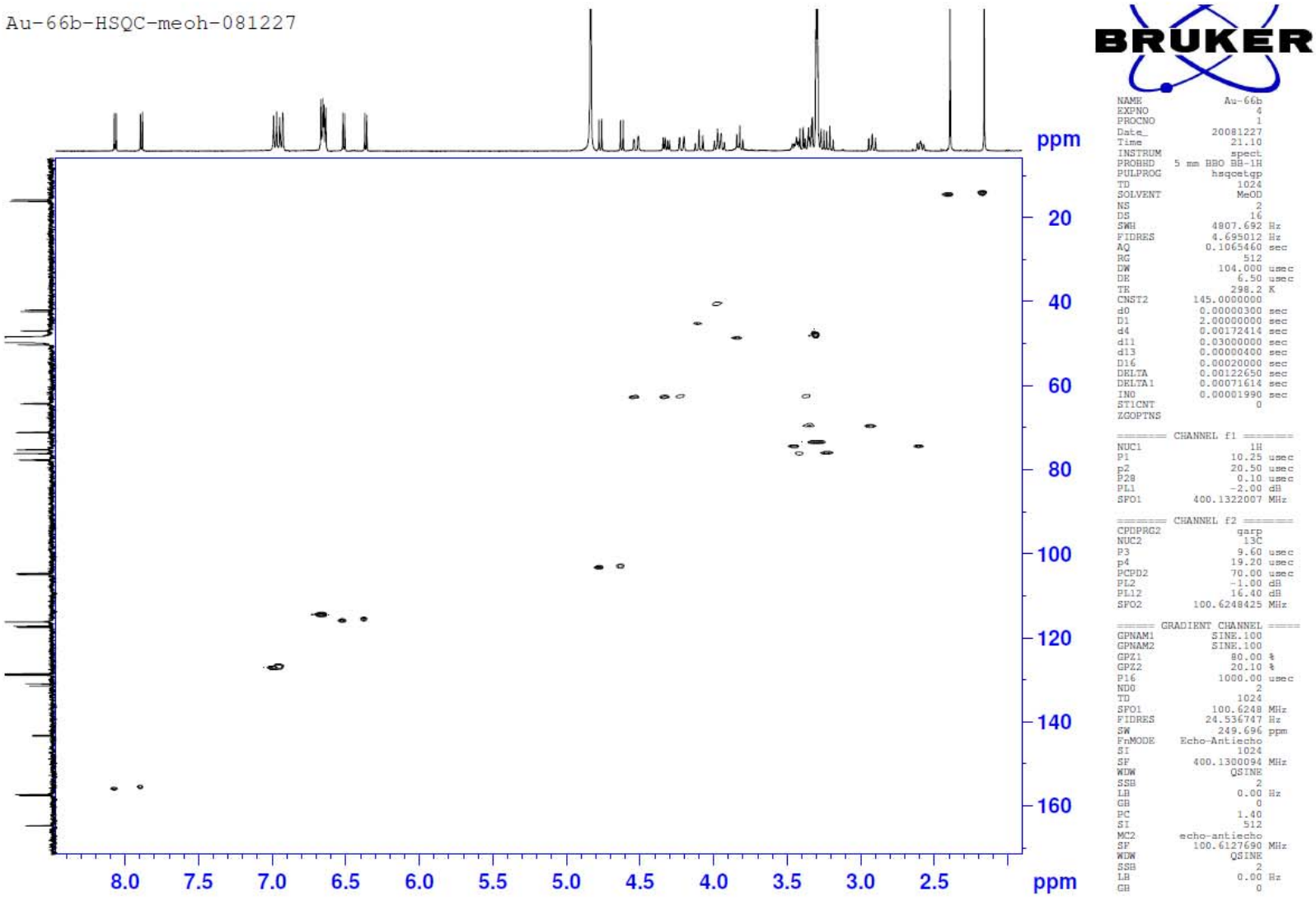


Figure 10. HSQC spectrum of compound **2**

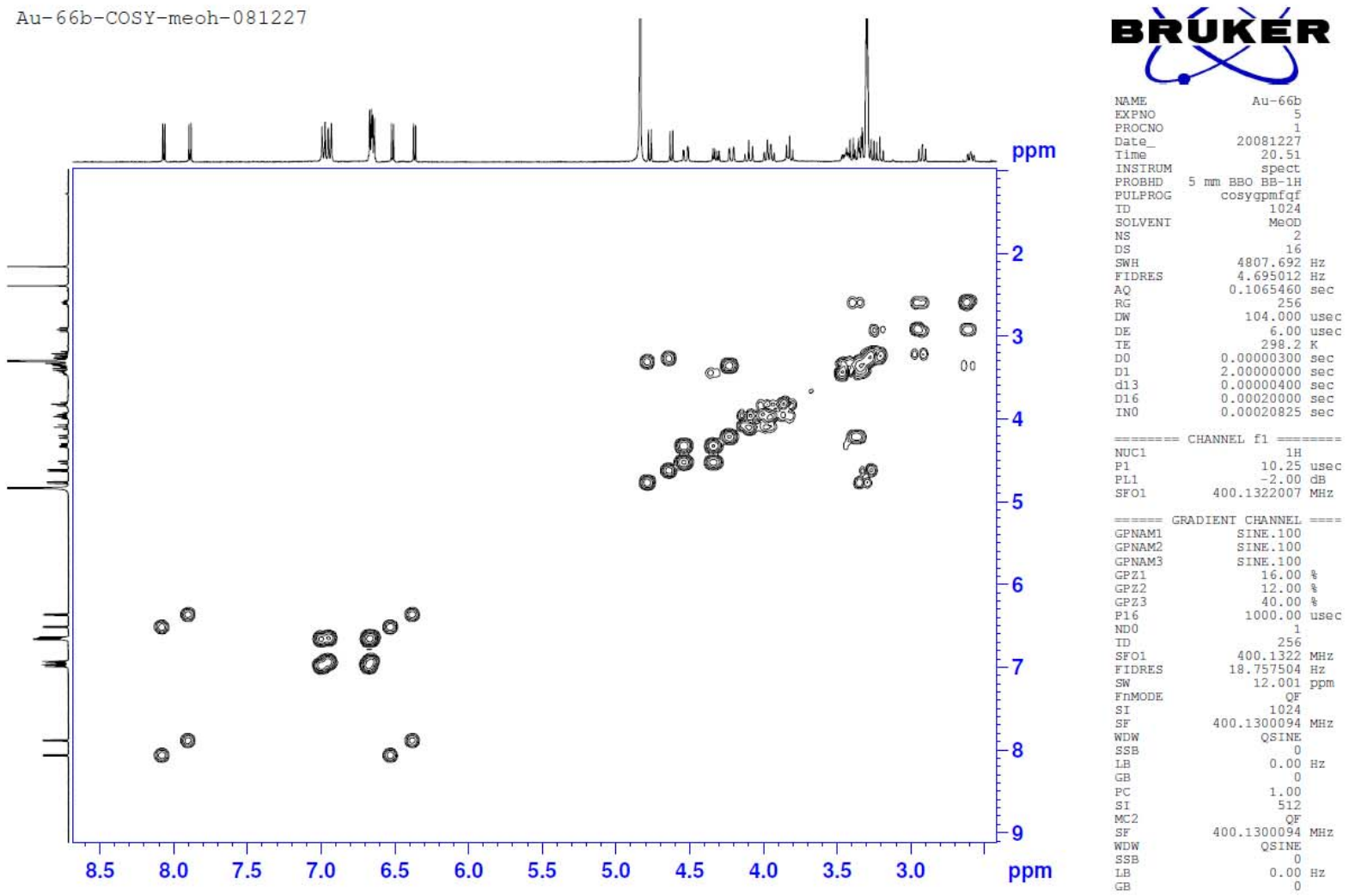


Figure 11. ^{1}H-^{1}H COSY spectrum of compound **2**

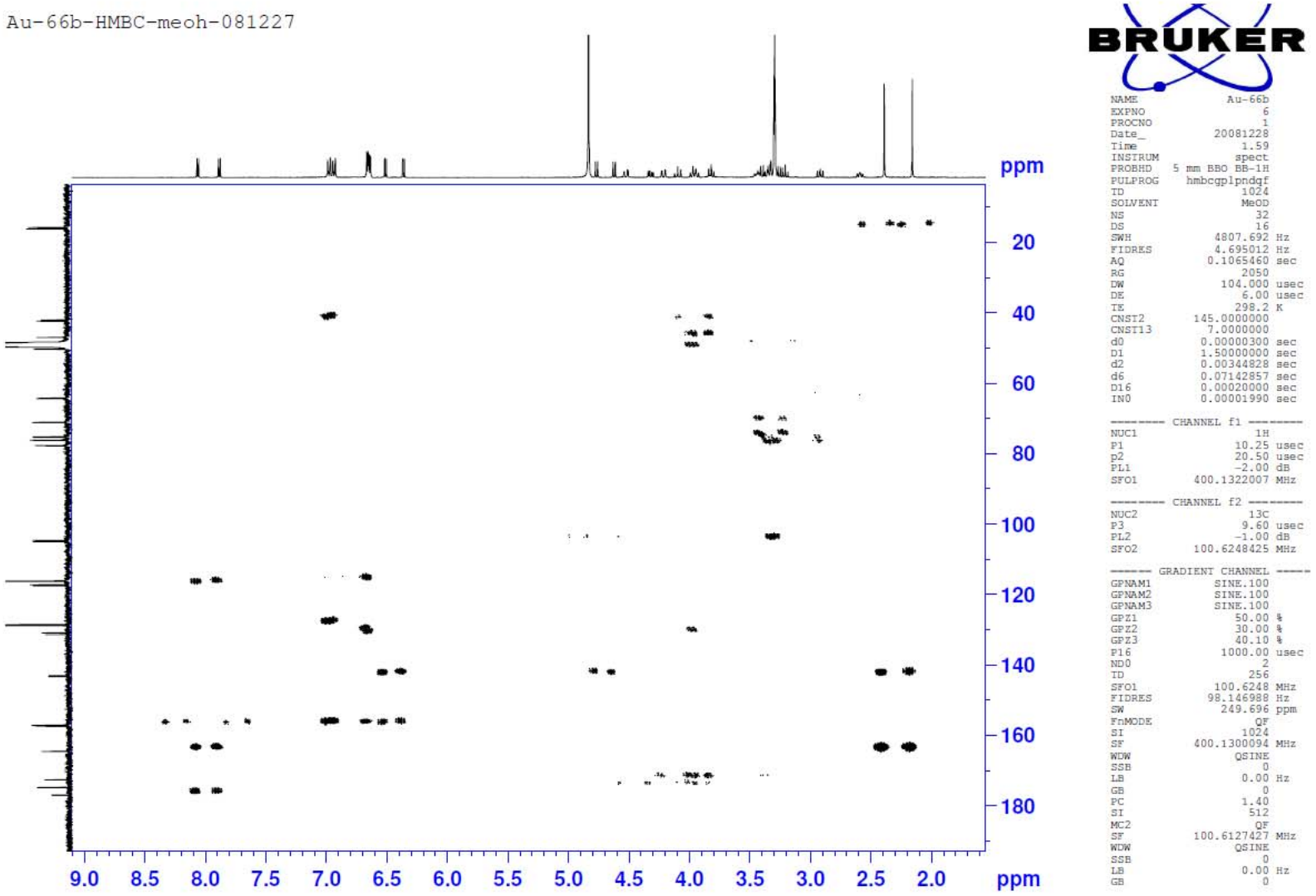


Figure 12. HMBC spectrum of compound **2**

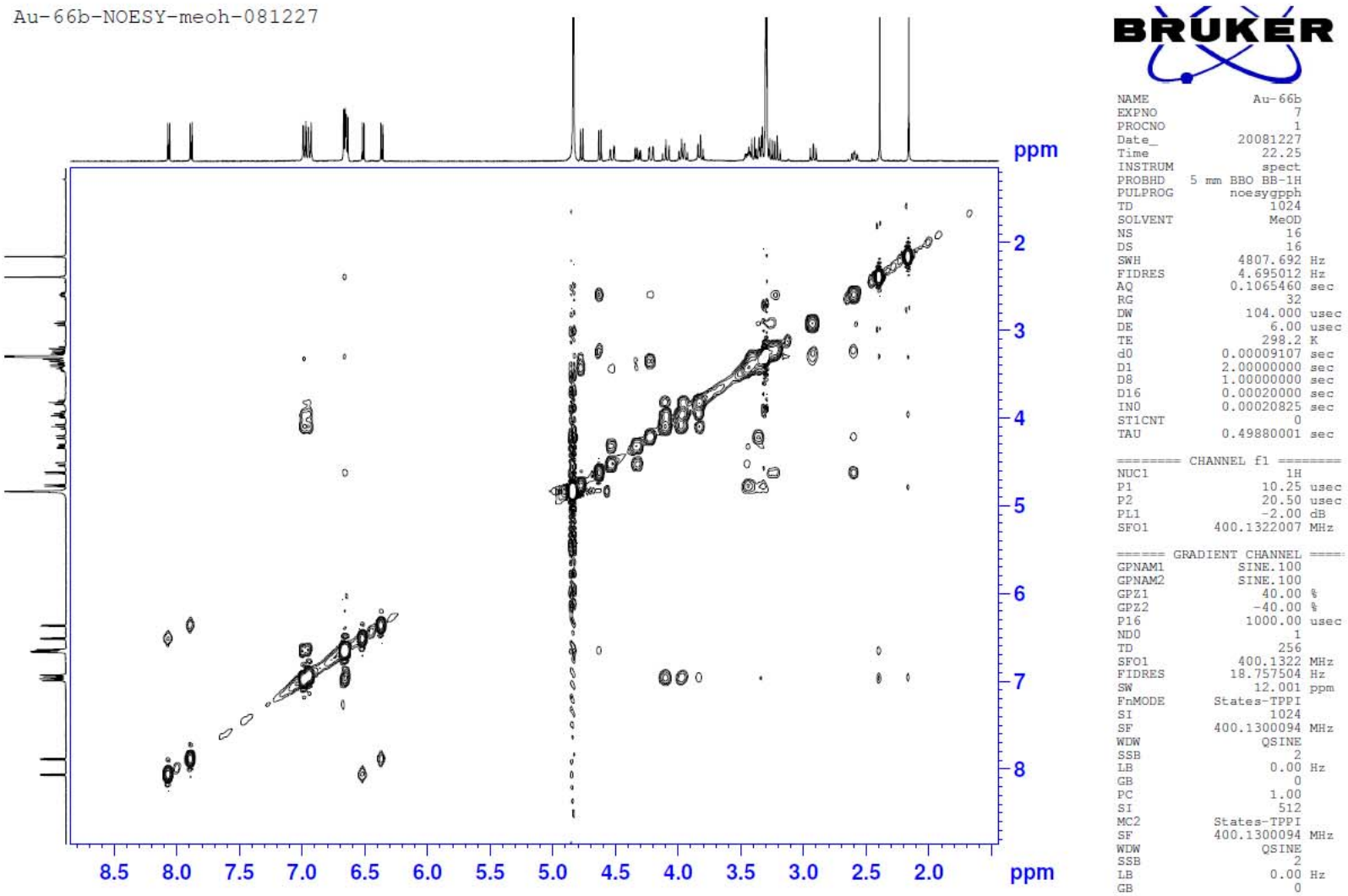


Figure 13. NOESY spectrum of compound **2**

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

319 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 O: 0-50

Minimum:					-1.5			
Maximum:			5.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE		i-FIT	Norm	Conf(%) Formula
867.2354	867.2348	0.6	0.7	21.5	58.7	5.092	0.61	C42 H43 O20
	867.2383	-2.9	-3.3	43.5	53.6	0.027	97.38	C60 H35 O7
	867.2313	4.1	4.7	-0.5	63.0	9.423	0.01	C24 H51 O33
	867.2406	-5.2	-6.0	12.5	60.6	7.056	0.09	C35 H47 O25
	867.2289	6.5	7.5	30.5	57.5	3.960	1.91	C49 H39 O15

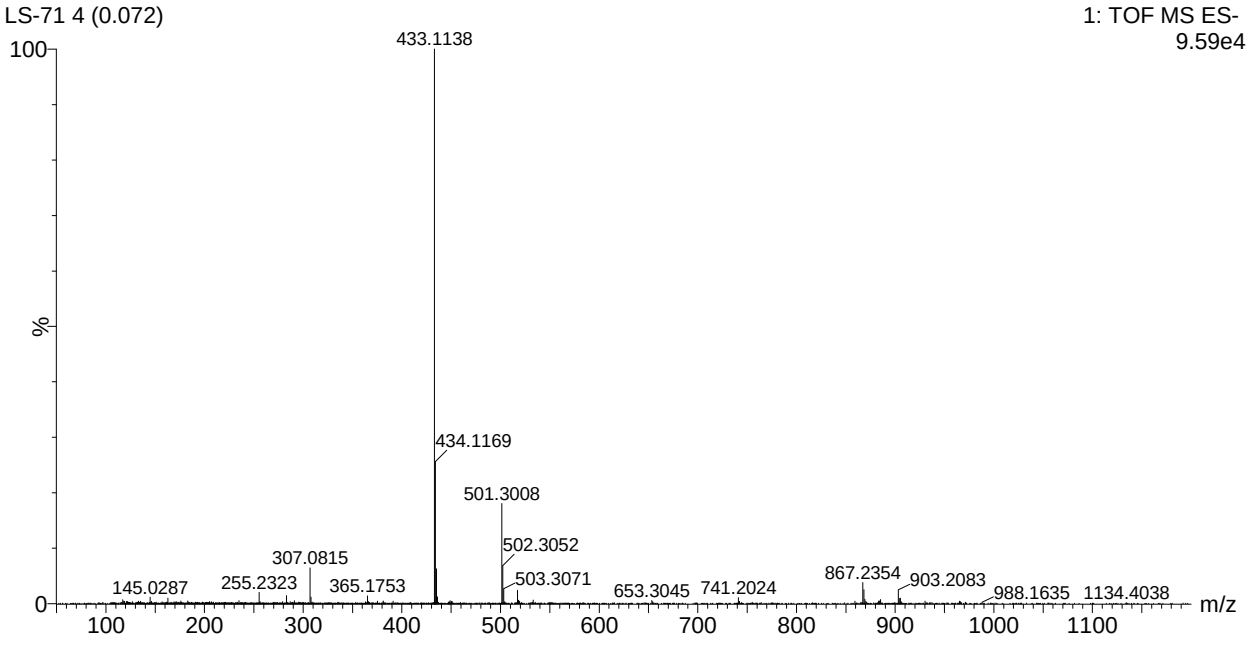


Figure 14. HR-ESI-MS spectrum of compound **2**

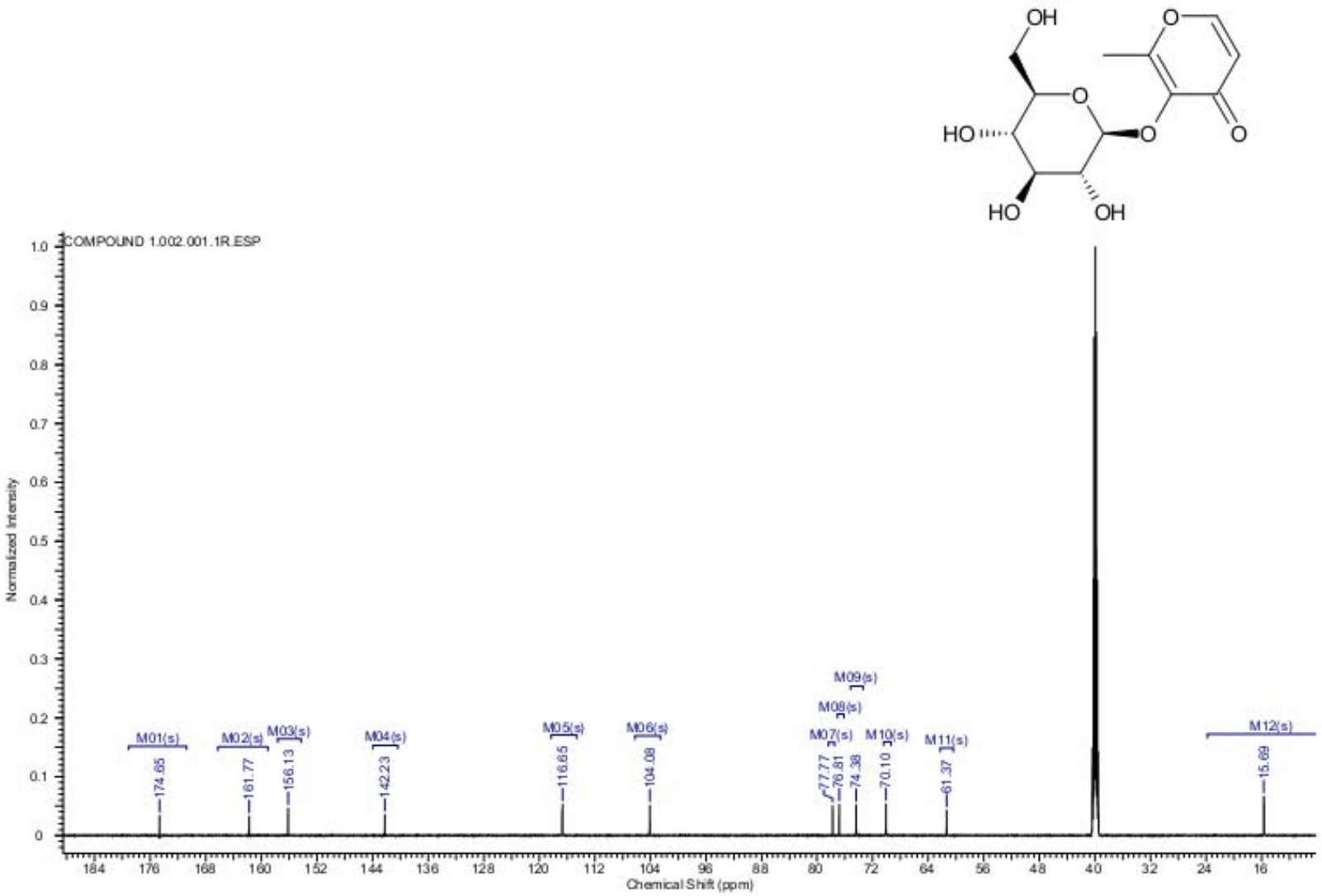


Figure 15. ^{13}C NMR spectrum of compound **4**

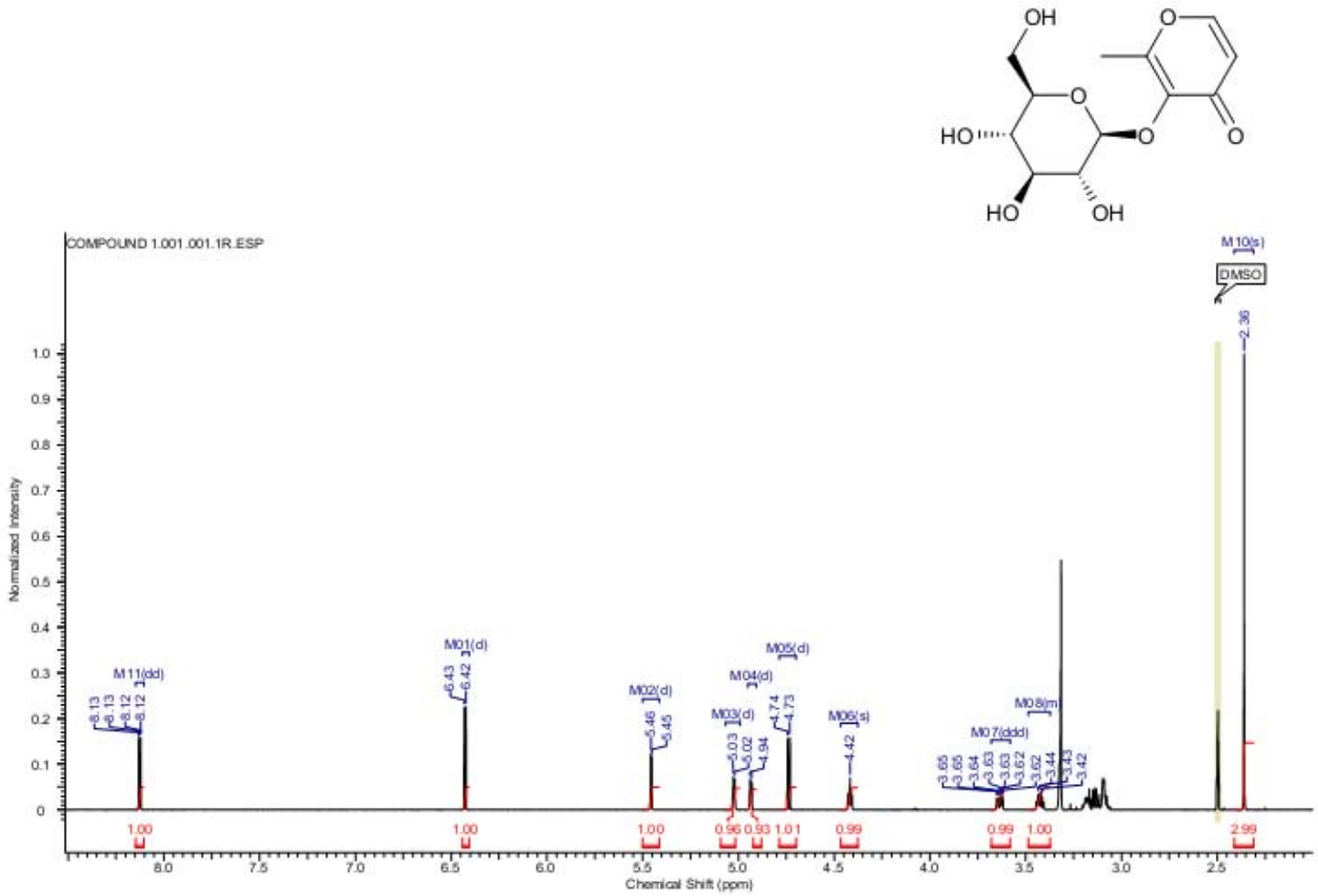


Figure 16. ^{1}H NMR spectrum of compound **4**

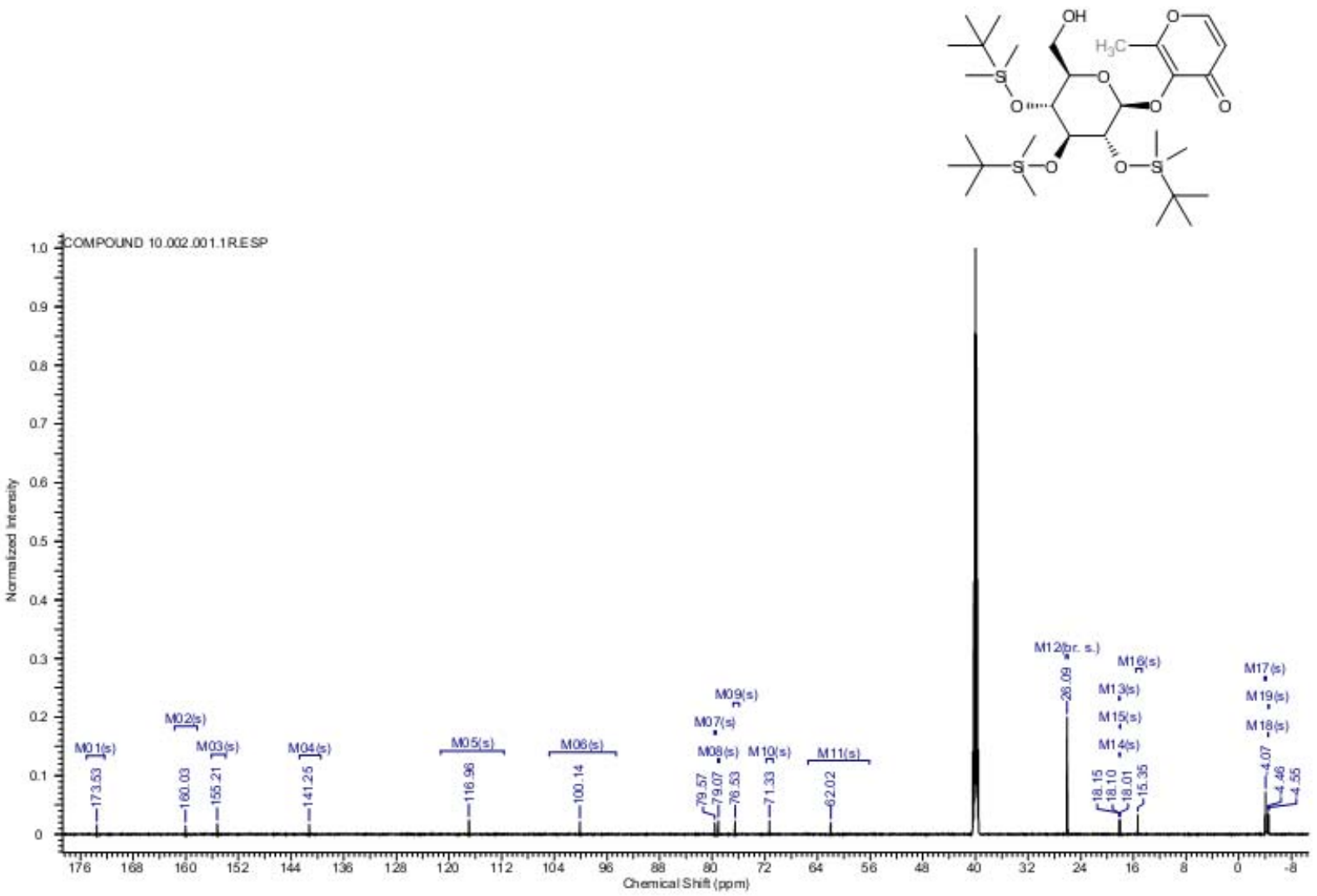


Figure 17. ^{13}C NMR spectrum of compound **5**

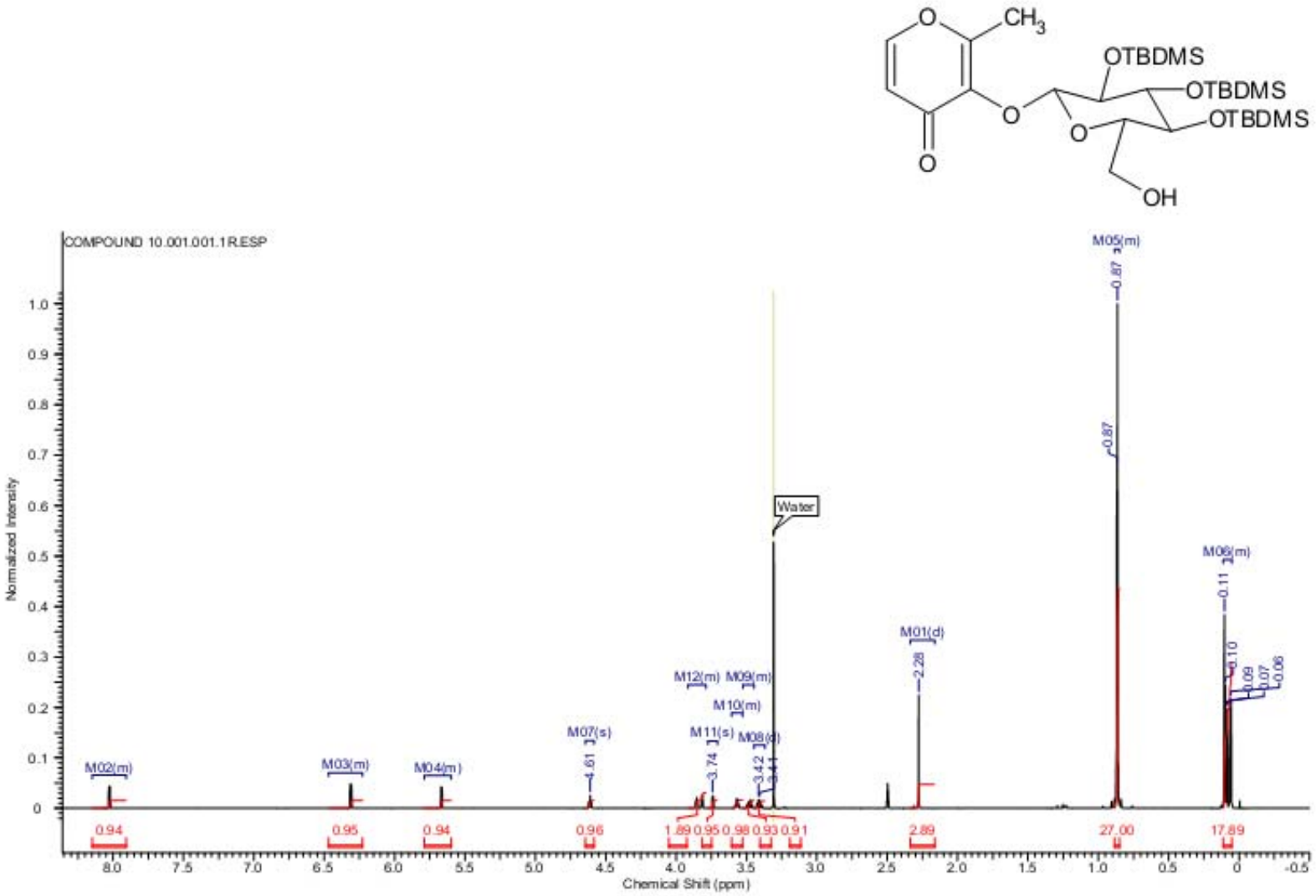


Figure 18. ^{1}H NMR spectrum of compound **5**

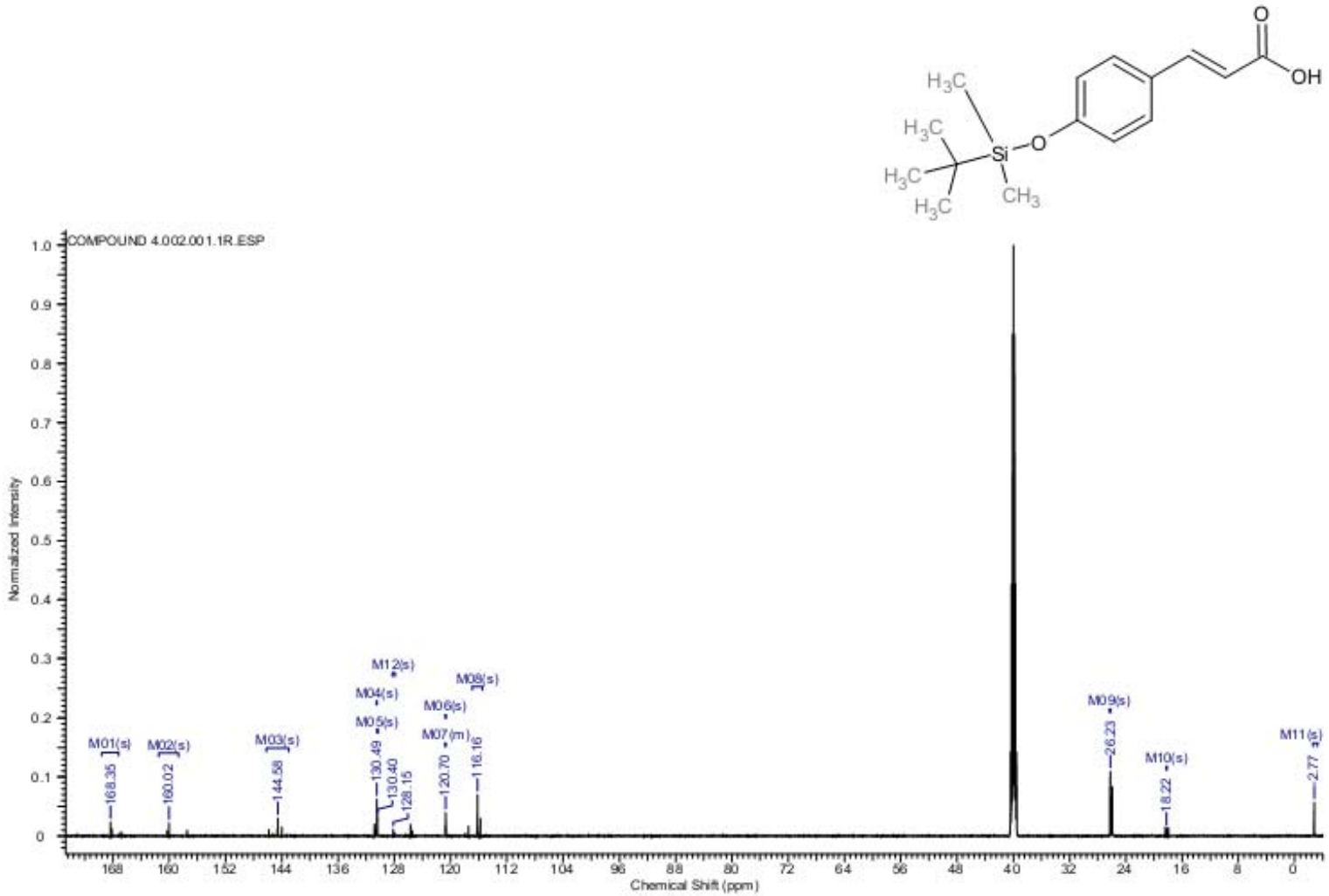


Figure 19. ^{13}C NMR spectrum of compound **6**

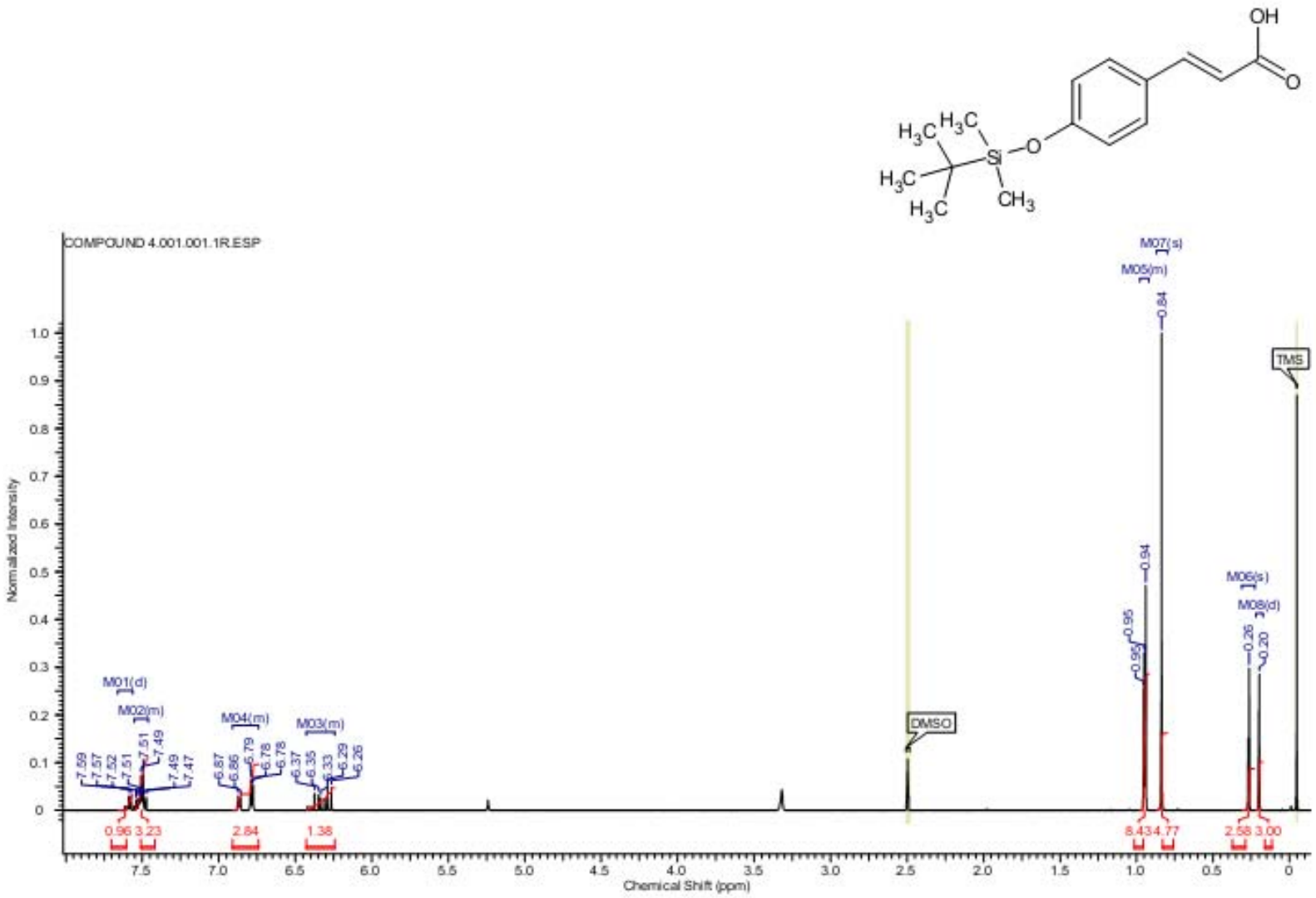


Figure 20. ^{1}H NMR spectrum of compound **6**

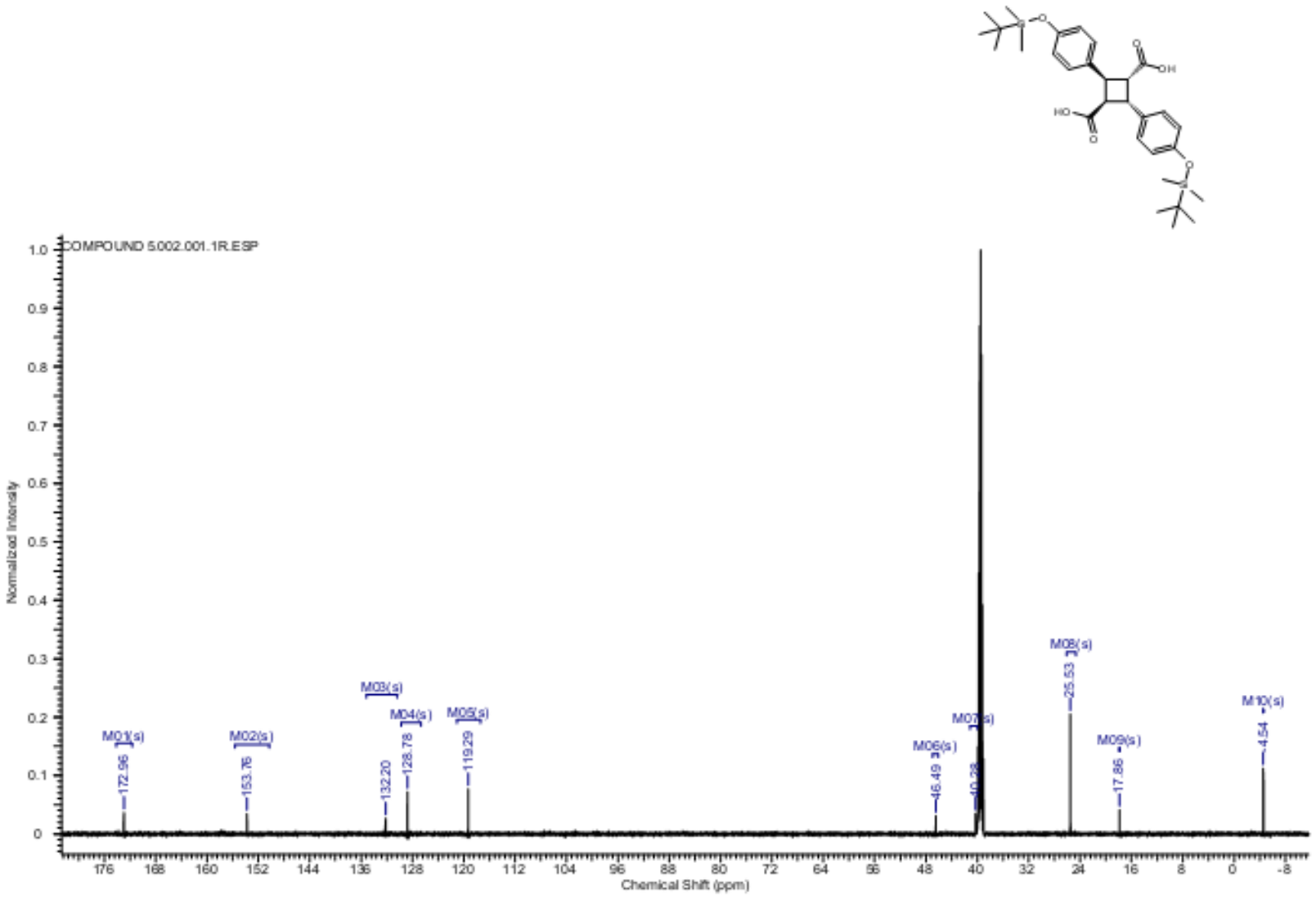


Figure 21. ^{13}C NMR spectrum of compound **7**

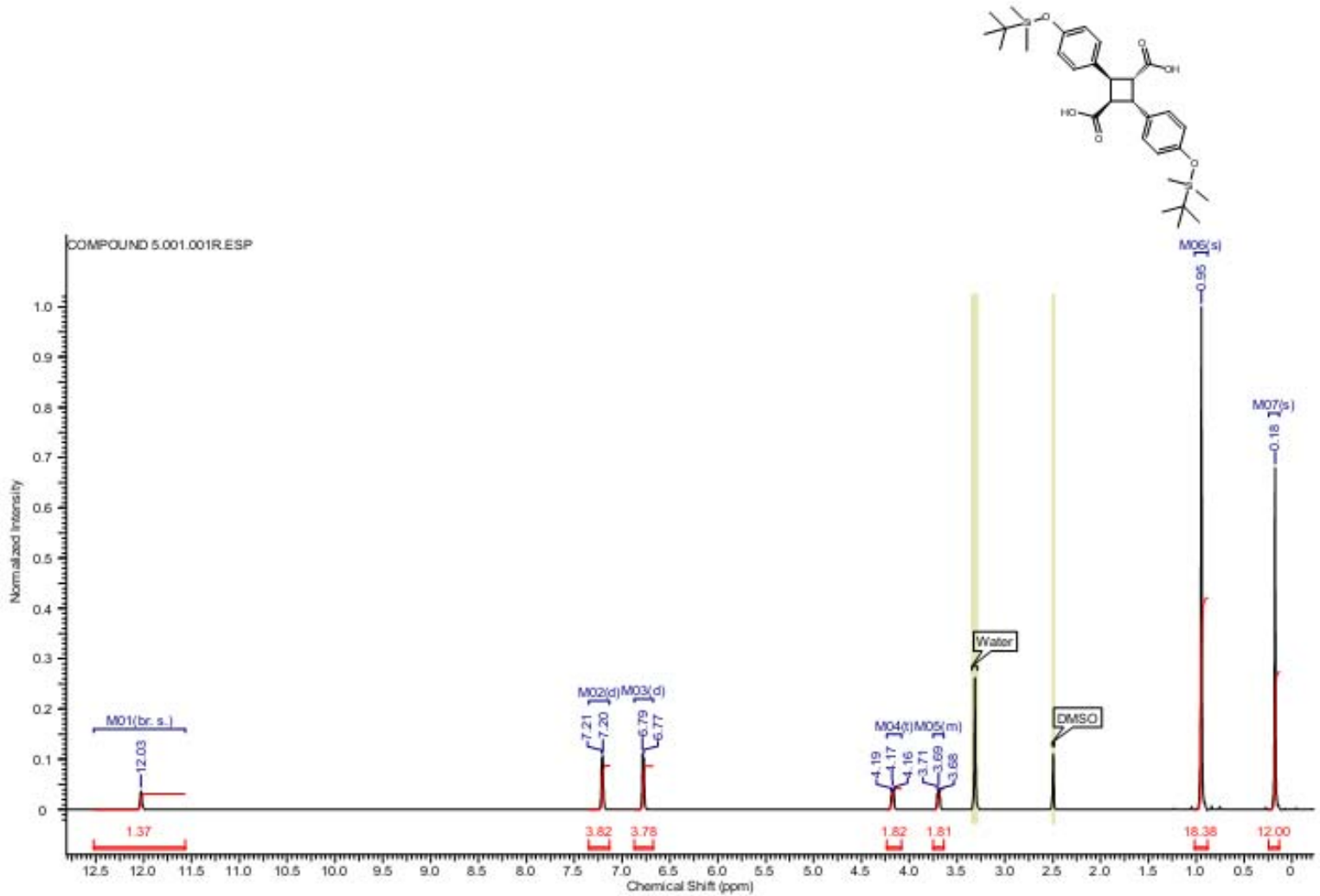


Figure 22. ^{1}H NMR spectrum of compound **7**

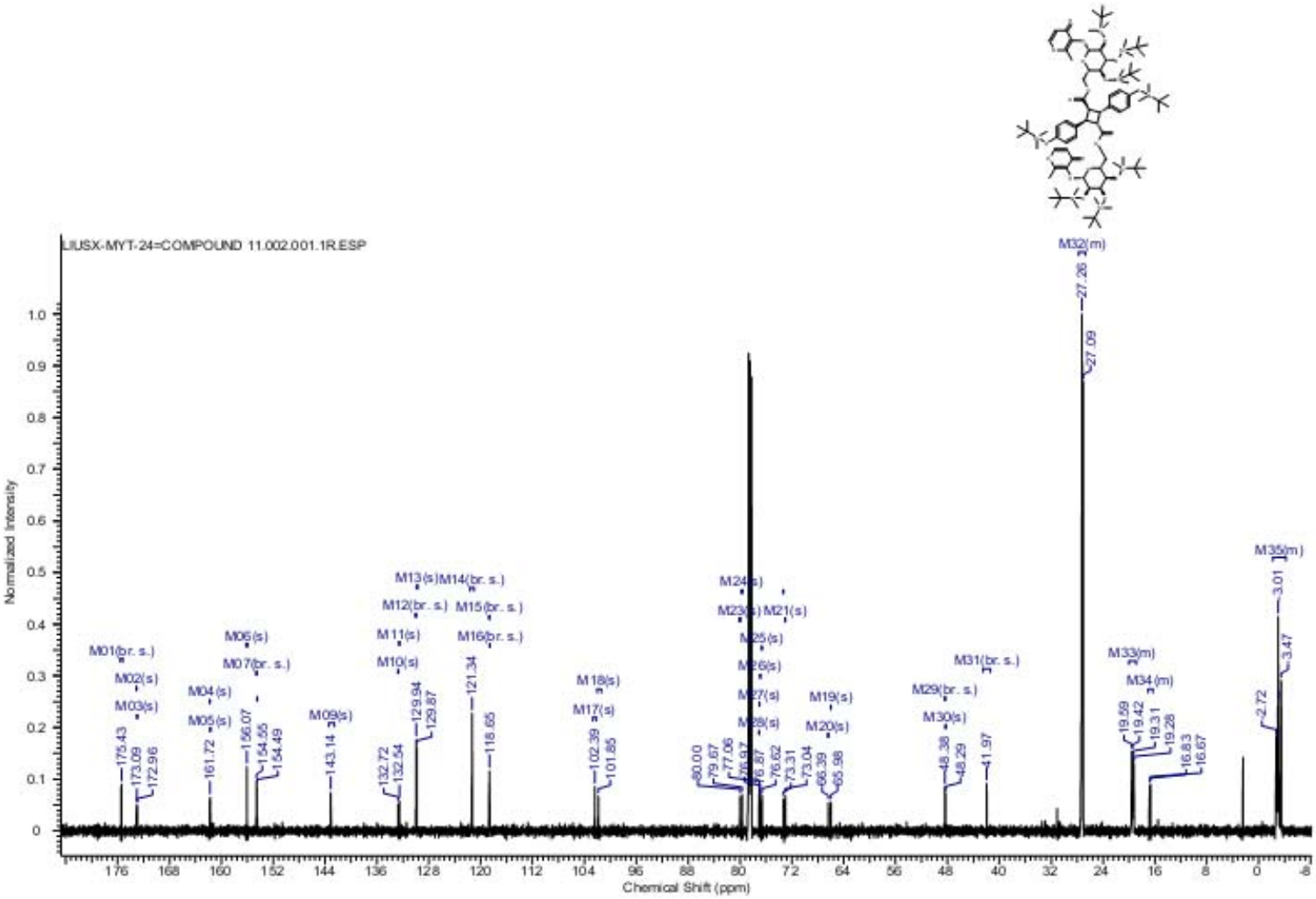


Figure 23. ^{13}C NMR spectrum of compound **8**

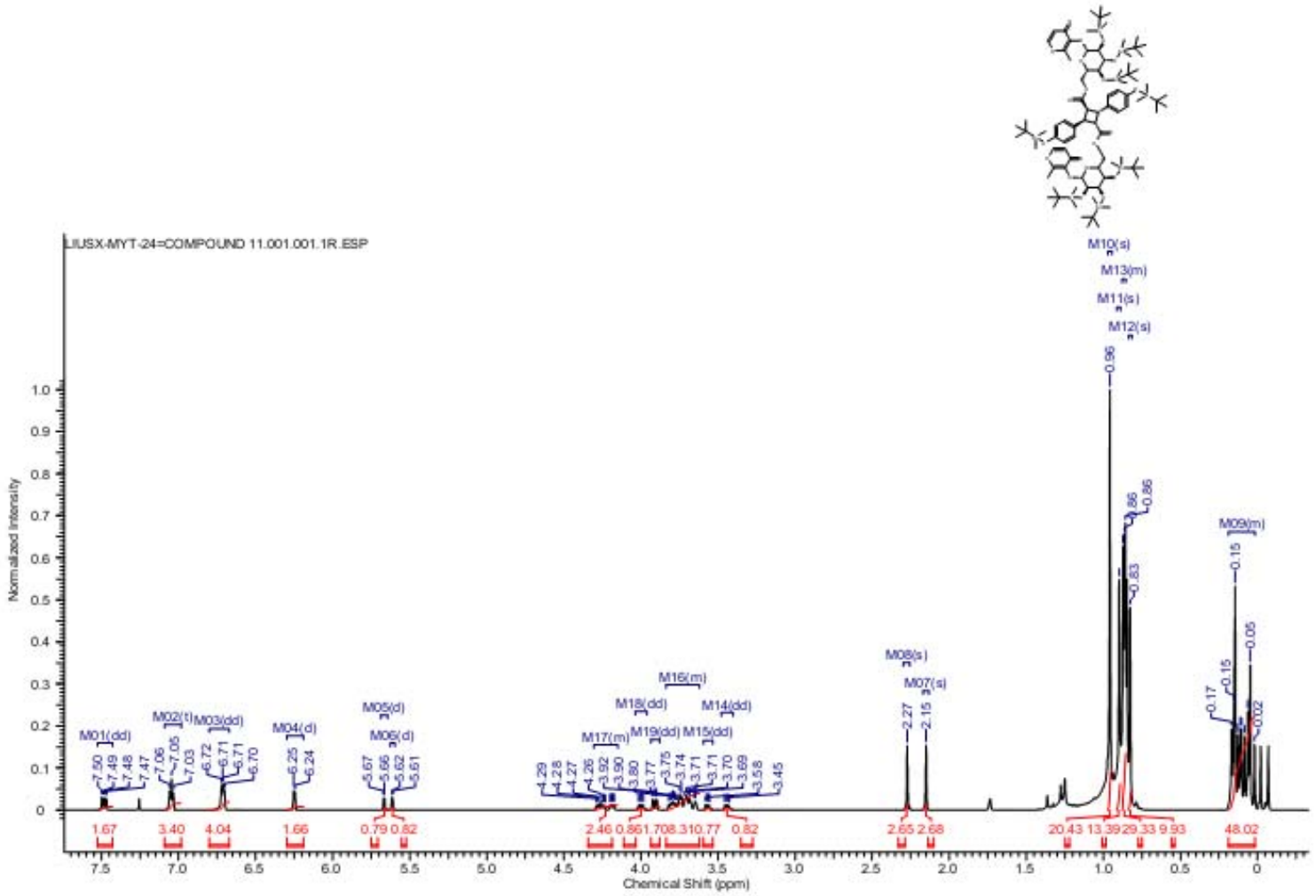


Figure 24. ^{1}H NMR spectrum of compound **8**

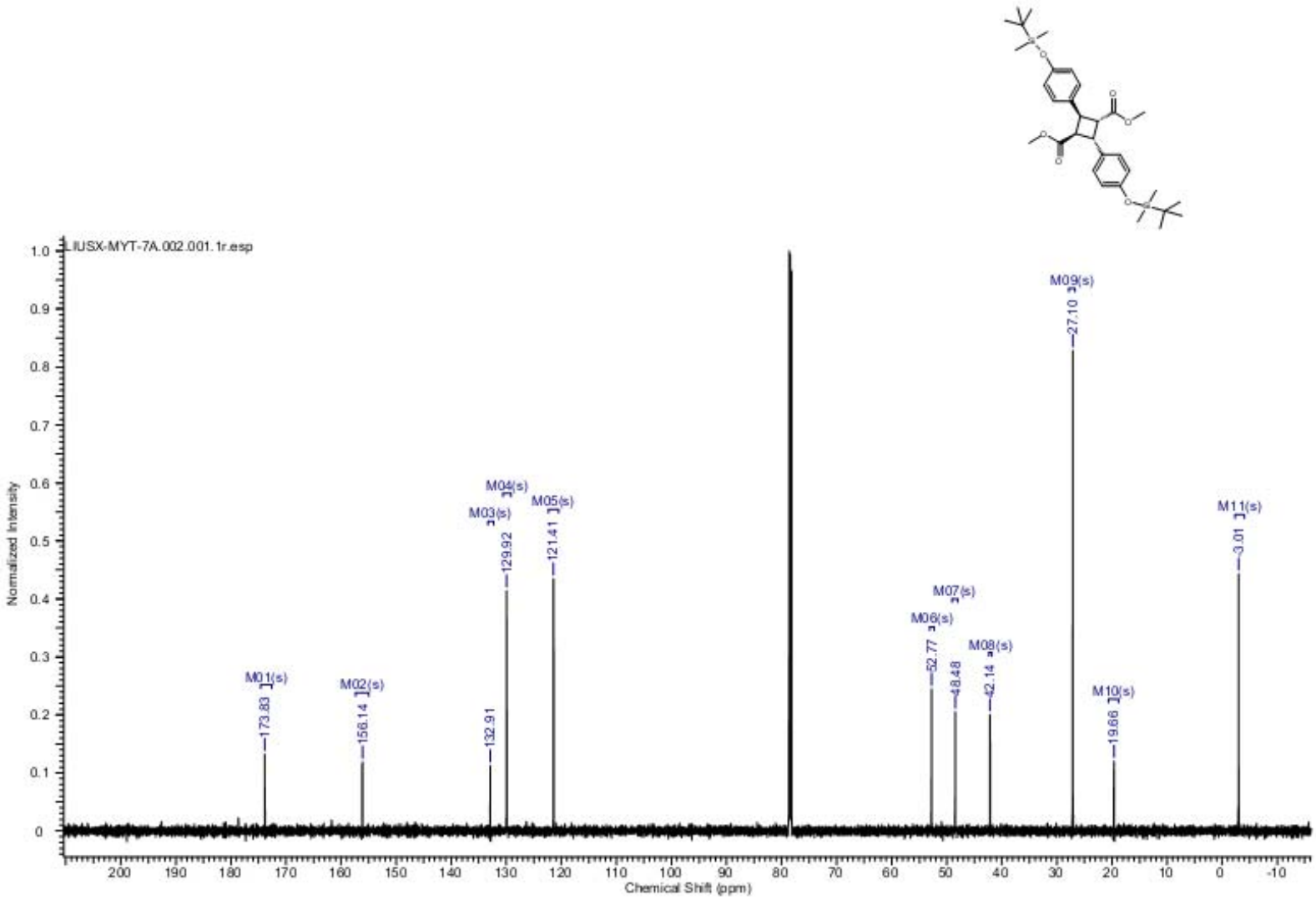


Figure 25. ^{13}C NMR spectrum of compound **9**

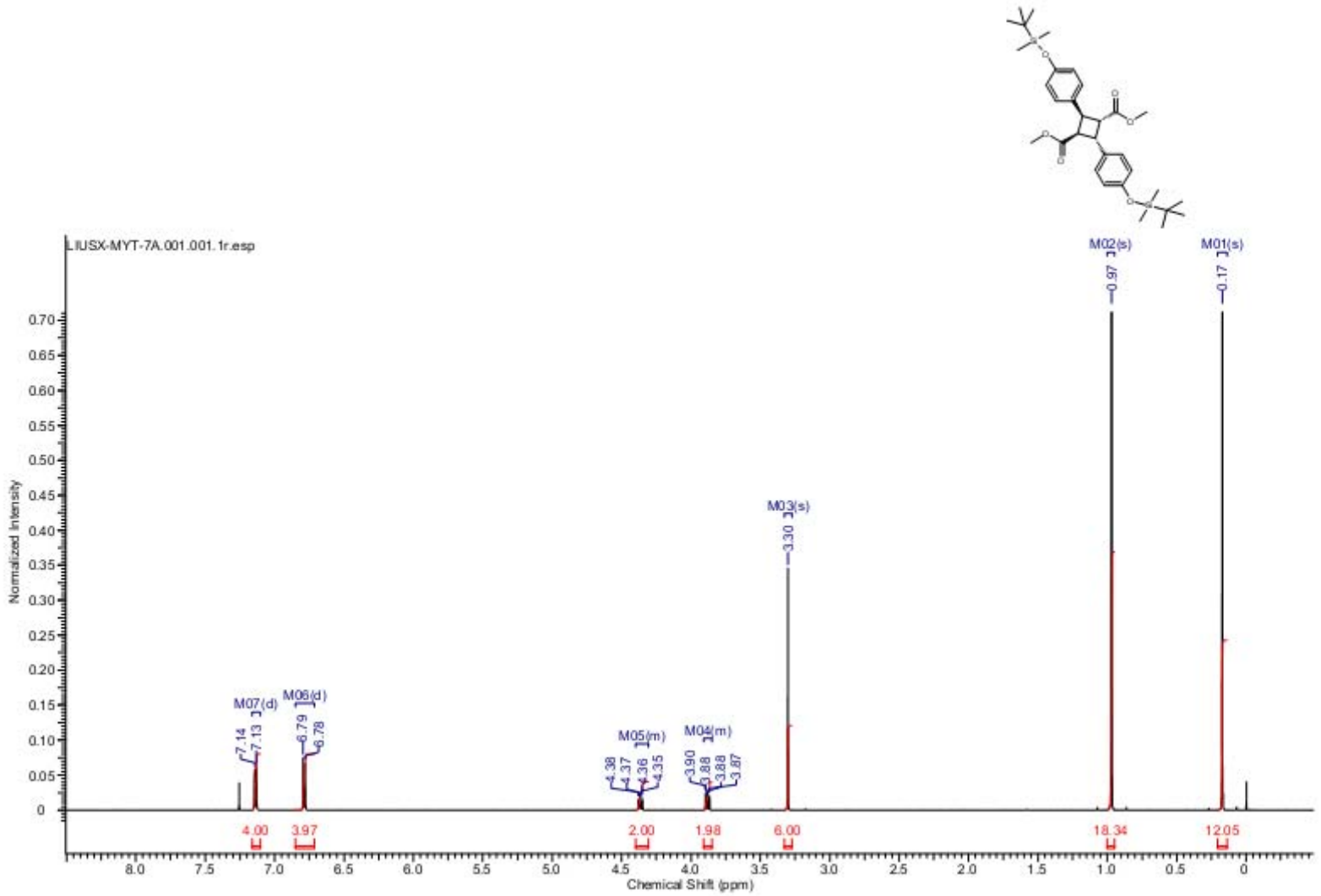


Figure 26. ^{1}H NMR spectrum of compound **9**

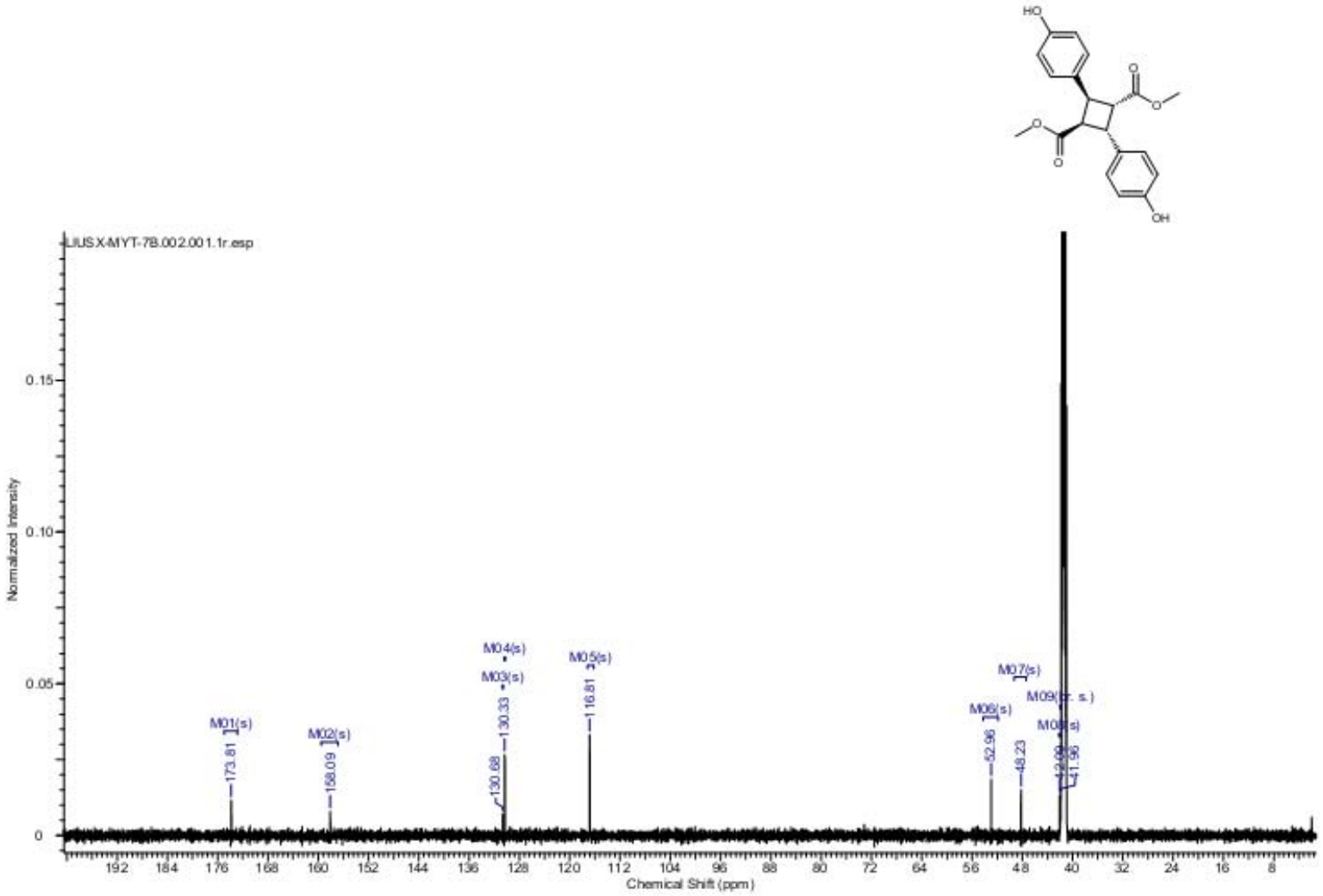


Figure 27. ^{13}C NMR spectrum of compound **10**

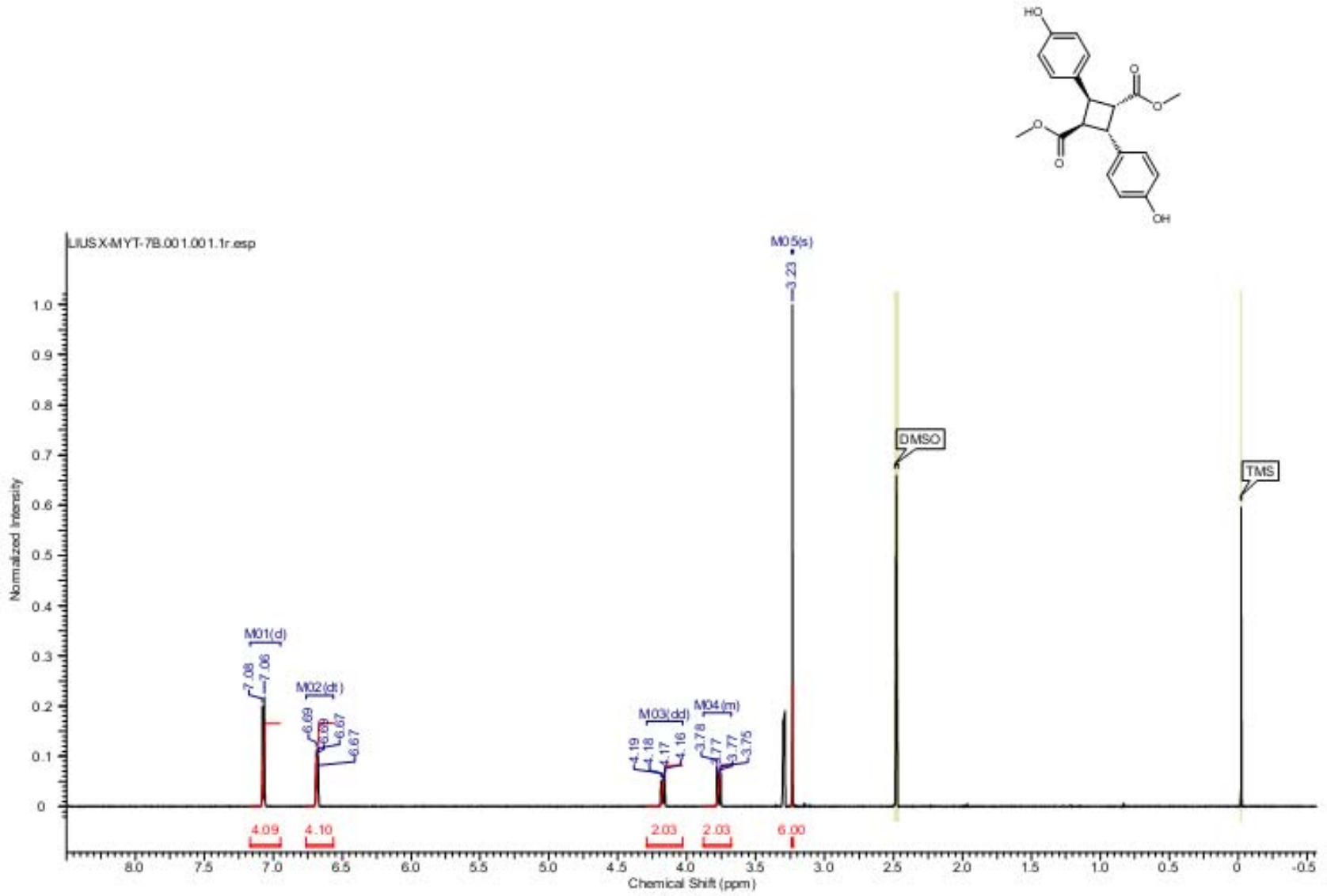


Figure 28. ^{1}H NMR spectrum of compound **10**

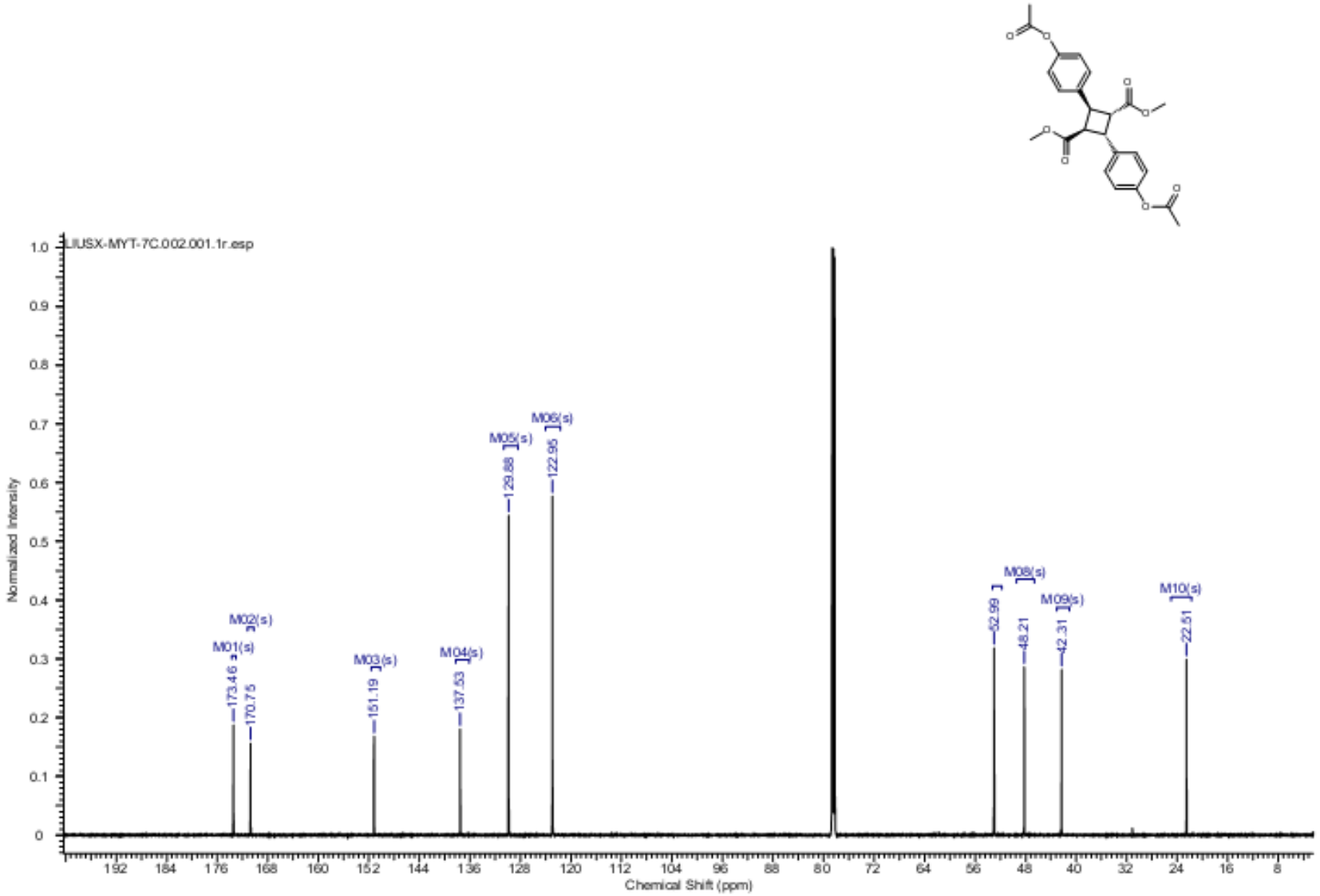


Figure 29. ^{13}C NMR spectrum of compound **11**

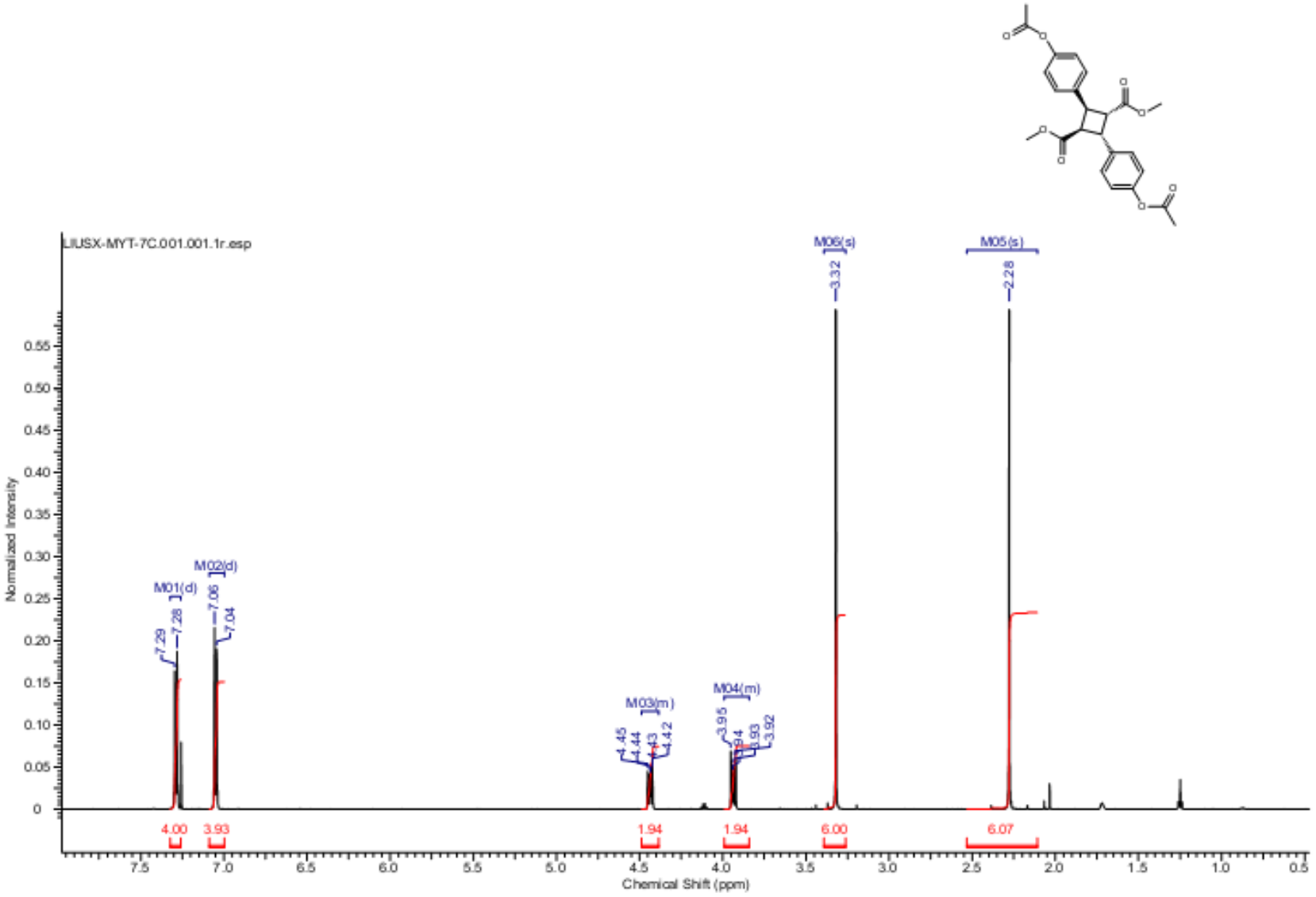


Figure 30. ^{1}H NMR spectrum of compound **11**