Structural Reassignment of Cytosporolides A-C via Biomimetic Synthetic Studies and Reinterpretation of NMR Data

Justin T. J. Spence and Jonathan H. George*

Discipline of Chemistry, School of Chemistry & Physics, University of Adelaide, North Terrace, Adelaide SA 5005, Australia.

Supporting Information

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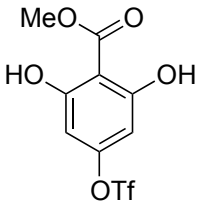
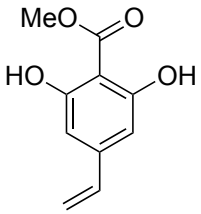
Methyl 2,6-dihydroxy-4-(trifluoromethylsulfonyloxy)benzoate 15[1]



To a solution of methyl 2,4,6-trihydroxybenzoate **14** (2.62 g, 14.2 mmol) and 2,6-lutidine (1.38 mL, 11.9 mmol) in CH_2Cl_2 (100 mL) at 0 °C was added Tf_2O (2.00 mL, 11.9 mmol) in CH_2Cl_2 (30 mL) dropwise over 30 min. The reaction mixture was stirred 0 °C for 1 h, then at room temperature for 3 h. The mixture was then washed with water (100 mL), 1 M HCl solution (100 mL), saturated $NaHCO_3$ solution (100 mL) and brine (100 mL). The organic layer was then dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was then purified by flash chromatography on SiO_2 (hexanes/EtOAc, 10:1 to 1:1 gradient elution) to give **15** (3.84 g, 85%) as a white solid.

Data for **15**: R_f 0.30 (hexanes/EtOAc, 4:1); IR (film): 3371, 1690, 1635, 1595, 1414, 1208, 1170, 1134, 1109, 986 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 4.10 (3H, s), 6.42 (2H, s), 9.93 (2H, br s); ^{13}C NMR (75 MHz, $CDCl_3$): 53.7, 100.3, 102.0, 118.9 (q, J = 319.0 Hz), 154.9, 162.7, 169.5; m.p. 83-84 °C.

Methyl 2,6-dihydroxy-4-vinylbenzoate 16

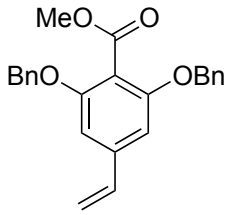


Aryl triflate **15** (2.00 g, 6.32 mmol) was dissolved in DMF (40 mL) at room temperature. Tributylvinyltin (2.22 mL, 7.59 mmol), $Pd(PPh_3)_4$ (364 mg, 0.32 mmol) and LiCl (536 mg, 12.6 mmol) were added sequentially, and the reaction mixture was stirred at 60 °C for 1 h. The resultant black solution was diluted with Et_2O (100 mL) and water (100 mL). The organic layer was separated, and the aqueous phase was extracted with Et_2O (2 x 50 mL). The combined organics were washed with brine (3 x 100 mL), then dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resultant residue was purified by flash chromatography on SiO_2 (neat hexanes to 2:1 hexanes/EtOAc, gradient elution) to give alkene **16** (0.92 g, 75%) as a white solid.

Data for **16**: R_f 0.50 (hexanes/EtOAc, 2:1); IR (film): 3418, 3094, 1637, 1558, 1334, 1280, 1247, 1195, 1148, 1100, 914 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 4.06 (3H, s), 5.39 (1H, d, J = 11.1 Hz), 5.83 (1H, d, J = 17.4 Hz), 6.53 (2H, s), 6.56 (1H, dd, J = 17.4, 10.2 Hz), 9.63 (2H, br s); ^{13}C NMR (75 MHz, $CDCl_3$): 52.8, 99.1, 105.9, 117.8, 135.7, 145.5, 160.8, 169.6; HRMS ($C_{10}H_{10}O_4$, ESI): calculated $[M-H]^-$ 193.0506, found 193.0505; m.p. 58-60 °C.

[1] Bender, C. F.; Yoshimoto, F. K.; Paradise, C. L.; De Brabander, J. K. *J. Am. Chem. Soc.* **2009**, *131*, 11350.

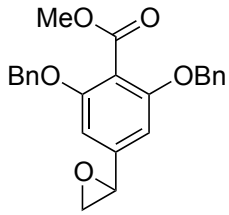
Methyl 2,6-bis(benzyloxy)-4-vinylbenzoate 17



To a solution of **16** (0.92 g, 4.7 mmol) in DMF (30 mL) was added K_2CO_3 (2.62 g, 18.9 mmol) and benzyl bromide (2.25 mL, 18.9 mmol). The reaction mixture was heated to 100 °C and stirred at this temperature for 18 h. The reaction mixture was then cooled to room temperature and diluted with Et_2O (100 mL) and water (100 mL). The organic layer was separated, and the aqueous phase was extracted with Et_2O (2 x 50 mL). The combined organics were washed with brine (3 x 100 mL), then dried over $MgSO_4$, filtered and concentrated under reduced pressure to give **17** (1.60 g, 91%) as a white solid, which was used in the next step without further purification.

Data for **17**: R_f 0.20 (hexanes/EtOAc, 9:1); IR (film): 2924, 1724, 1602, 1574, 1414, 1384, 1317, 1276, 1244, 1086 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 3.89 (3H, s), 5.14 (4H, s), 5.28 (1H, d, J = 10.8 Hz), 5.68 (1H, d, J = 17.4 Hz), 6.61 (1H, dd, J = 17.4, 10.8 Hz), 6.65 (2H, s), 7.30-7.43 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$): 52.3, 70.5, 103.9, 113.7, 115.4, 126.9, 127.8, 128.5, 136.4, 136.7, 140.6, 156.6, 166.6; HRMS ($C_{24}H_{22}O_4$, ESI): calculated $[M+H]^+$ 375.1591, found 375.1587; m.p. 92-93 °C.

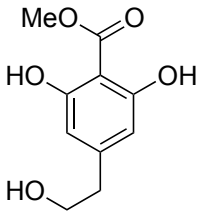
Methyl 2,6-bis(benzyloxy)-4-(oxiran-2-yl)benzoate 18



To a solution of **17** (500 mg, 1.34 mmol) in CH_2Cl_2 (5 mL) at room temperature was added *m*CPBA (approx. 70%, 659 mg, 2.67 mmol). The reaction mixture was then stirred at room temperature for 30 min. The mixture was then loaded directly onto a column of silica gel, and eluted with hexanes/EtOAc (10:1 to 1:1, gradient elution) to give epoxide **18** (288 mg, 55%) as a white solid.

Data for **18**: R_f 0.40 (hexanes/EtOAc, 2:1); IR (film): 2981, 1724, 1583, 1435, 1377, 1242, 1085 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 2.61 (1H, dd, J = 5.4, 2.1 Hz), 3.09 (1H, dd, J = 5.4, 3.6 Hz), 3.79 (1H, dd, J = 3.9, 2.1 Hz), 3.88 (3H, s), 5.12 (4H, s), 6.53 (2H, s), 7.30-7.38 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$): 51.2, 52.2, 52.3, 70.4, 102.6, 113.9, 126.8, 127.8, 128.5, 136.5, 141.5, 156.7, 166.5; HRMS ($C_{24}H_{22}O_5$, ESI): calculated $[M+H]^+$ 391.1540, found 391.1543; m.p. 96-97 °C.

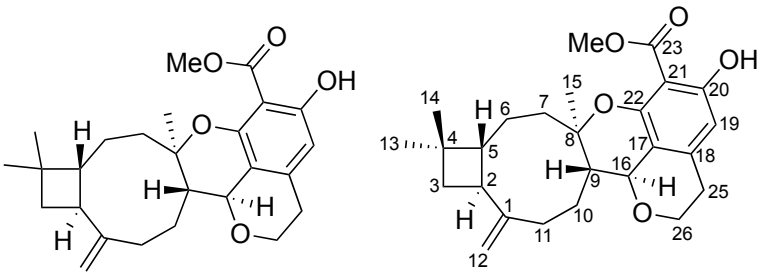
Methyl 2,6-dihydroxy-4-(2-hydroxyethyl)benzoate 19



Epoxide **18** (250 mg, 0.64 mmol) was dissolved in EtOH (10 mL). The flask was purged with N_2, and 10% palladium on carbon (25 mg) was added. The flask was then purged with H_2, and the reaction mixture was stirred under H_2 (balloon pressure) for 12 h. The reaction mixture was filtered through celite (filter pad washed with CH_2Cl_2). The filtrate was then concentrated under reduced pressure, and the residue was purified by flash chromatography on SiO_2 (hexanes/EtOAc, 1:1) to give **19** (116 mg, 86%) as a white solid.

Data for **19**: R_f 0.30 (hexanes/EtOAc, 1:1); IR (film): 3440, 1641, 1566, 1440, 1180, 1035 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 1.63 (1H, br s), 2.76 (2H, t, J = 6.6 Hz), 3.85 (2H, t, J = 6.6 Hz), 4.06 (3H, s), 6.37 (2H, s), 9.63 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$): 39.4, 52.8, 62.7, 98.3, 108.8, 148.8, 160.7, 169.7; HRMS ($C_{10}H_{12}O_5Na$, ESI): calculated $[M+H]^+$ 213.0758, found 213.0758; m.p. 60-61 °C.

Methyl ester 23

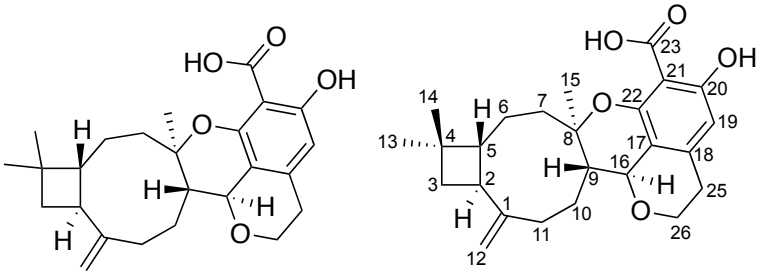


Alcohol **19** (50 mg) and $HC(OEt)_3$ (0.50 mL, 3.01 mmol) were added to a round-bottomed flask at room temperature. TFA (1 drop) was added, followed by β-caryophyllene **22** (0.50 mL, 2.21 mmol). The resultant mixture was heated to 100 °C and was stirred at this temperature for 18 h. The reaction mixture was then loaded directly onto a column of SiO_2 and purified by flash chromatography (hexanes/EtOAc, 50:1 as eluent) to give **23** (52 mg, 53%) as a colourless oil.

Data for **23**: R_f 0.55 (hexanes/EtOAc, 4:1); IR (film): 2926, 1655, 1438, 1378, 1253, 1104 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): 0.95 (3H, s, H-14), 0.98 (3H, s, H-13), 1.28 (3H, s, H-15), 1.36 (1H, m, 1 x H-6), 1.57-1.67 (3H, m, 1 x C-10, 2 x C-3), 1.71-1.79 (3H, m, H-5, 1 x H-6, 1 x H-7), 1.85 (1H, m, H-9), 2.02 (1H, m, 1 x H-10), 2.11 (1H, m, 1 x H-7), 2.22 (1H, m, 1 x H-11), 2.44 (1H, app q, J = 9.6 Hz, H-2), 2.53 (1H, m, 1 x H-11), 2.65 (1H, dd, J = 16.8, 3.6 Hz, 1 x H-25), 2.97 (1H, m, 1 x H-25), 3.83 (1H, dt, J = 10.8, 5.4 Hz, 1 x H-26), 3.88 (3H, s, OMe), 4.05 (1H, d, J = 10.8 Hz, H-16), 4.19 (1H, ddd, J = 11.4, 7.2, 1.8 Hz, 1 x H-26), 4.87 (1H, s, 1 x H-12), 4.90 (1H, s, 1 x H-12), 6.28 (1H, s, H-19), 11.33 (1H, s, OH); ^{13}C NMR (150 MHz, $CDCl_3$): 22.0 (C-13), 22.6 (C-15), 22.7 (C-6), 28.2 (C-10), 28.3 (C-25), 30.0 (C-14), 34.1 (C-4), 36.0 (C-11), 37.0 (C-3), 40.68 (C-7), 40.70 (C-9), 41.6 (C-2), 51.9 (OMe),

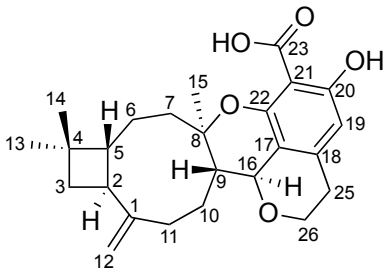
54.3 (C-5), 64.8 (C-26), 74.0 (C-16), 83.7 (C-8), 100.3 (C-21), 107.5 (C-19), 110.7 (C-12), 113.7 (C-17), 140.6 (C-18), 152.4 (C-1), 153.5 (C-22), 161.9 (C-20), 171.8 (C-23); ^{1}H NMR (600 MHz, C_6D_6): 0.80 (3H, s, H-14), 0.91 (3H, s, H-13), 1.16 (3H, s, H-15), 1.31 (1H, m, 1 x H-6), 1.42 (1H, m, 1 x H-10), 1.59 (1H, m, 1 x H-3), 1.67 (1H, m, 1 x H-3), 1.71-1.84 (3H, m, H-5, 1 x H-6, 1 x H-7), 1.96 (1H, m, 1 x H-10), 2.01-2.07 (3H, m, 1 x H-7, H-9, 1 x H-25), 2.15 (1H, m, 1 x H-11), 2.32 (1H, app q, J = 10.2 Hz, H-2), 2.53 (1H, m, 1 x H-25), 2.70 (1H, m, 1 x H-11), 3.40 (1H, dt, J = 10.8, 4.8 Hz, 1 x H-26), 3.46 (3H, s, OMe), 3.83 (1H, ddd, J = 11.4, 7.2, 1.8 Hz, 1 x H-26), 3.94 (1H, d, J = 10.2 Hz, H-16), 5.02 (1H, s, 1 x H-12), 5.06 (1H, s, 1 x H-12), 6.39 (1H, s, H-19), 12.01 (1H, s, OH); ^{13}C NMR (150 MHz, C_6D_6): 22.0 (C-13), 22.7 (C-15), 23.1 (C-6), 28.0 (C-10), 28.4 (C-25), 29.8 (C-14), 34.1 (C-4), 36.7 (C-11), 37.2 (C-3), 40.9 (C-9), 41.3 (C-7), 41.6 (C-2), 51.5 (OMe), 55.2 (C-5), 64.8 (C-26), 74.3 (C-16), 83.7 (C-8), 100.7 (C-21), 108.4 (C-19), 111.2 (C-12), 113.7 (C-17), 140.9 (C-18), 152.1 (C-1), 153.8 (C-22), 163.2 (C-20), 172.2 (C-23); HRMS ($C_{26}H_{34}O_5$, ESI): calculated $[M+H]^+$ 427.2479, found 427.2479.

Carboxylic acid 24



Methyl ester **23** (20 mg, 0.047 mmol) was dissolved in THF (1.5 mL) and MeOH (1 mL). 6M NaOH (1.5 mL) was then added, and the resultant mixture was then heated at reflux for 3 h. The reaction mixture was then acidified with sat. NH_4Cl solution, and the product was extracted with CH_2Cl_2 (2 x 5 mL). The combined organics were then washed with brine (10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (hexanes/EtOAc, 10:1 to 2:1 as eluent, gradient elution) gave the carboxylic acid **24** (11 mg, 57%) as a white solid.

Data for **24**: R_f 0.10 (hexanes/EtOAc, 6:1); IR (film): 2924, 1694, 1635, 1582, 1379, 1281, 1223, 1075 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): 0.96 (3H, s, H-14), 0.98 (3H, s, H-13), 1.41 (3H, s, H-15), 1.48 (1H, m, 1 x H-6), 1.58-1.71 (4H, m, 2 x H-3, 1 x H-6, 1 x H-10), 1.79 (1H, m, H-5), 1.86 (1H, m, 1 x H-7), 1.98 (1H, m, H-9), 2.08 (1H, m, 1 x H-10), 2.22 (2H, m, 1 x H-11, 1 x H-7), 2.45 (1H, app q, J = 9.6 Hz, H-2), 2.55 (1H, m, 1 x H-11), 2.69 (1H, dd, J = 16.8, 3.6 Hz, 1 x H-25), 3.00 (1H, m, 1 x H-25), 3.85 (1H, dt, J = 10.8, 5.4 Hz, 1 x H-26), 4.10 (1H, d, J = 10.8 Hz, H-16) 4.24 (1H, ddd, J = 11.4, 7.2, 1.8 Hz, 1 x H-26), 4.89 (1H, s, 1 x H-12), 4.93 (1H, s, 1 x H-12), 6.42 (1H, s, H-19), 11.40 (1H, br s, CO_2H), 11.83 (1H, s, OH); ^{13}C NMR (150 MHz, $CDCl_3$): 21.9 (C-13), 22.6 (C-6), 22.9 (C-15), 28.1 (C-25), 28.3 (C-10), 29.9 (C-14), 34.3 (C-4), 35.8 (C-11), 37.0 (C-3), 40.6 (C-7), 40.7 (C-9), 41.2 (C-2), 54.1 (C-5), 65.0 (C-26), 73.2 (C-16), 88.6 (C-8), 98.8 (C-21), 109.9 (C-19), 111.3 (C-12), 112.5 (C-17), 141.6 (C-18), 150.7 (C-22), 151.8 (C-1), 162.5 (C-20), 170.8 (C-23); HRMS ($C_{26}H_{34}O_5$, ESI): calculated $[M-H]^-$ 411.2177, found 411.2179; m.p. 122-123 °C.



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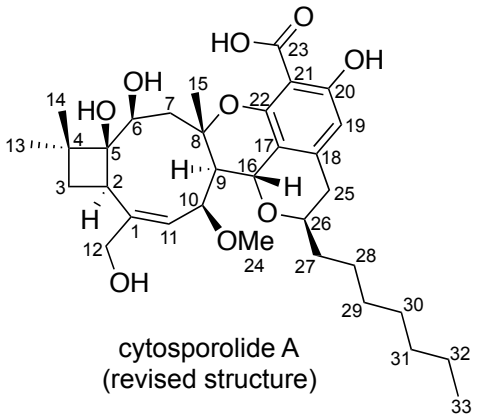
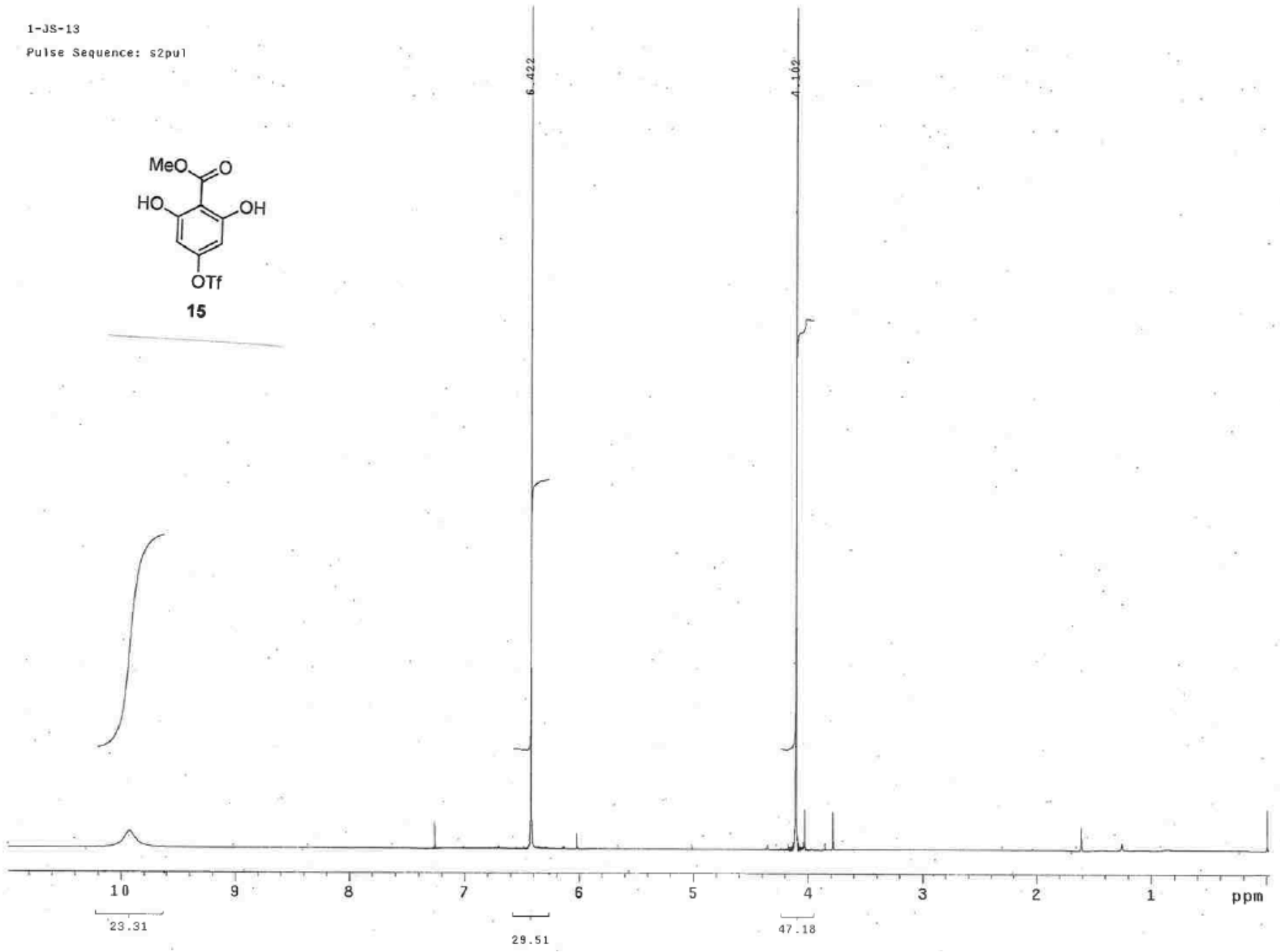


cytosporolide A
(revised structure)

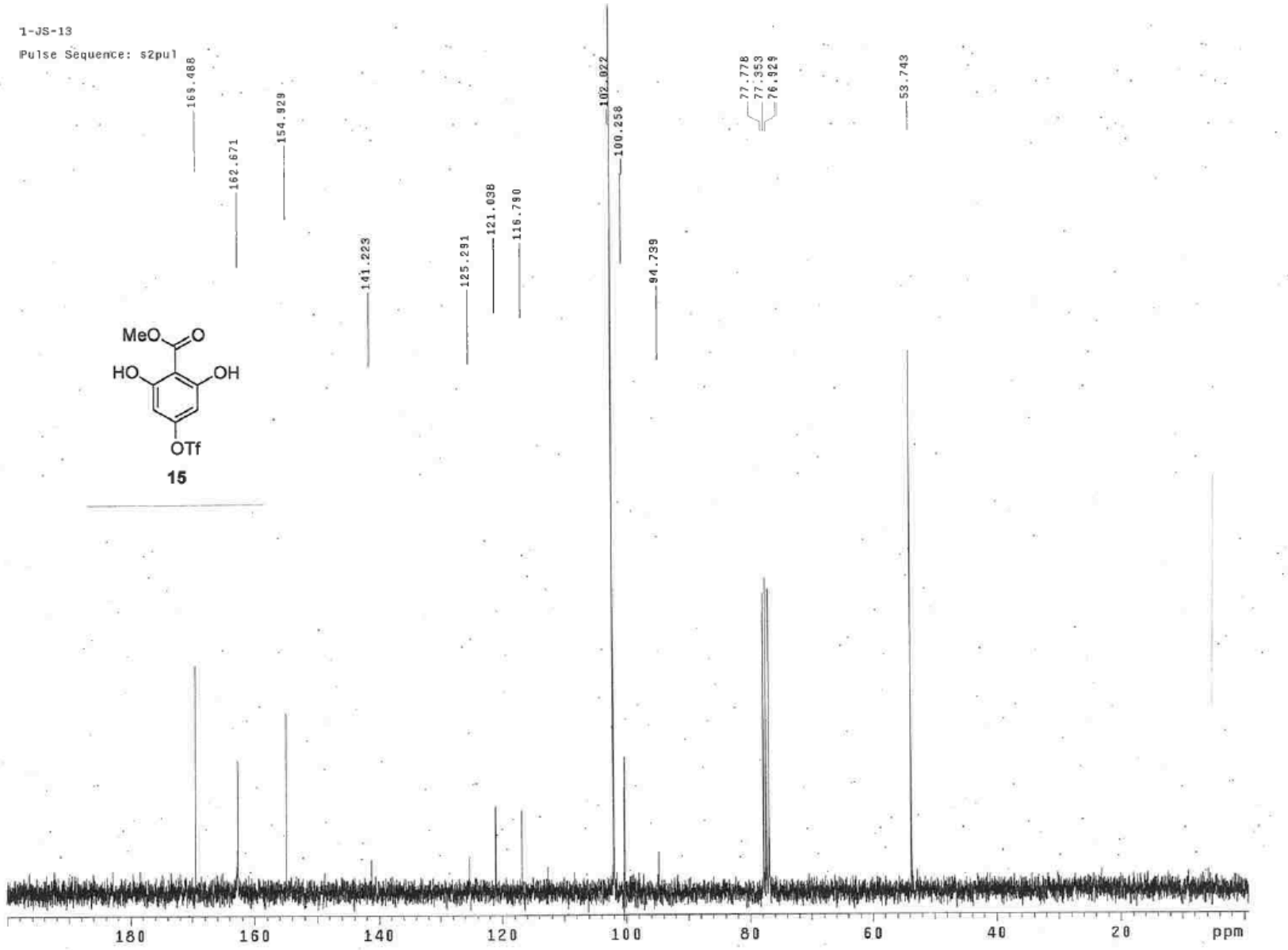
Comparison between selected ^{13}C NMR chemical shifts of **24** and cytosporolide A:

24		Cytosporolide A	
Carbon atom	δ_C ($CDCl_3$)	Carbon atom	δ_C (acetone-d6)
8	88.6	8	87.5
17	112.5	17	113.5
18	141.6	18	145.3
19	109.9	19	109.4
20	162.5	20	163.8
21	98.8	21	99.2
22	150.7	22	151.0
23	170.8	23	171.9

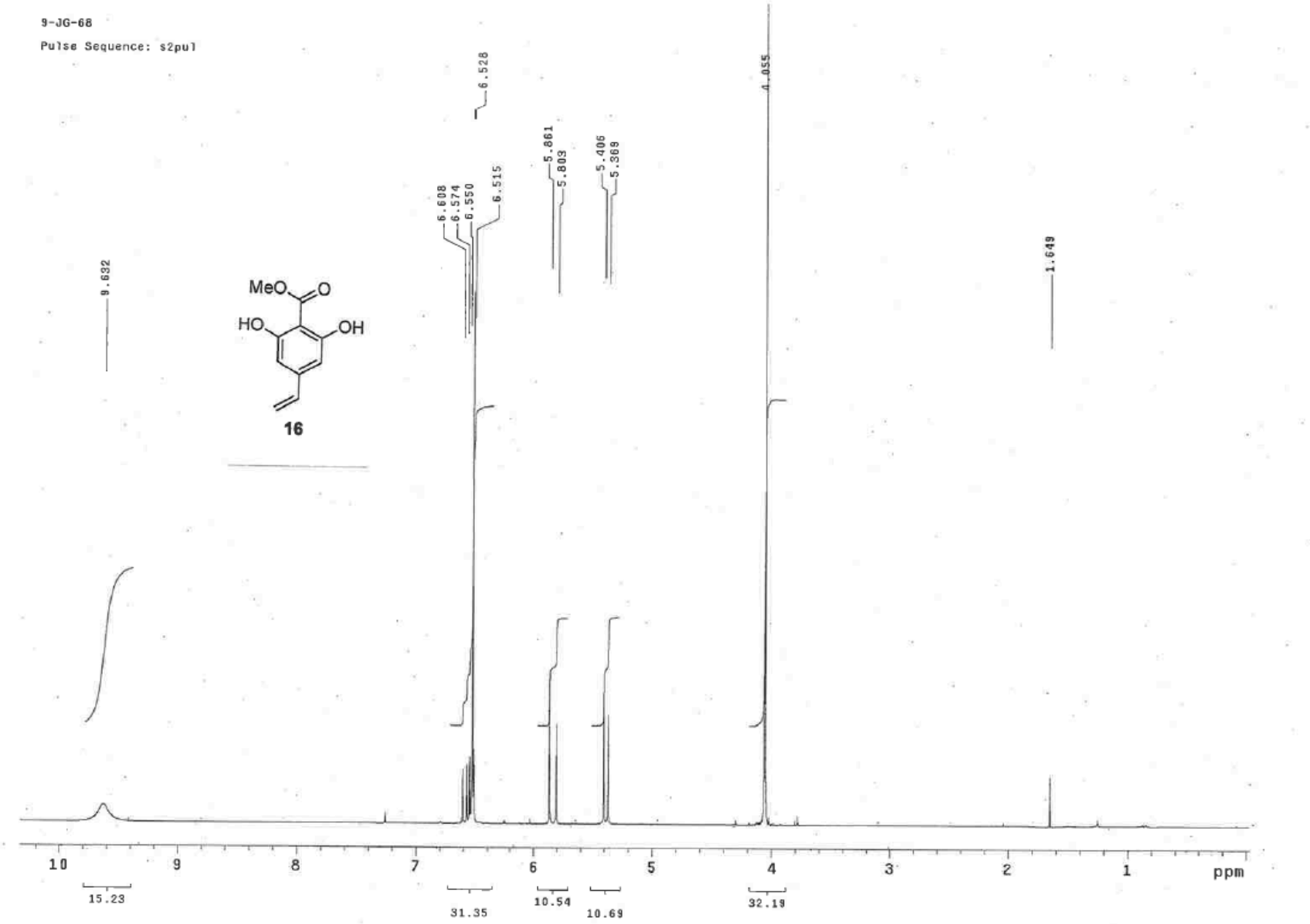
^{1}H NMR, 300 MHz, $CDCl_3$



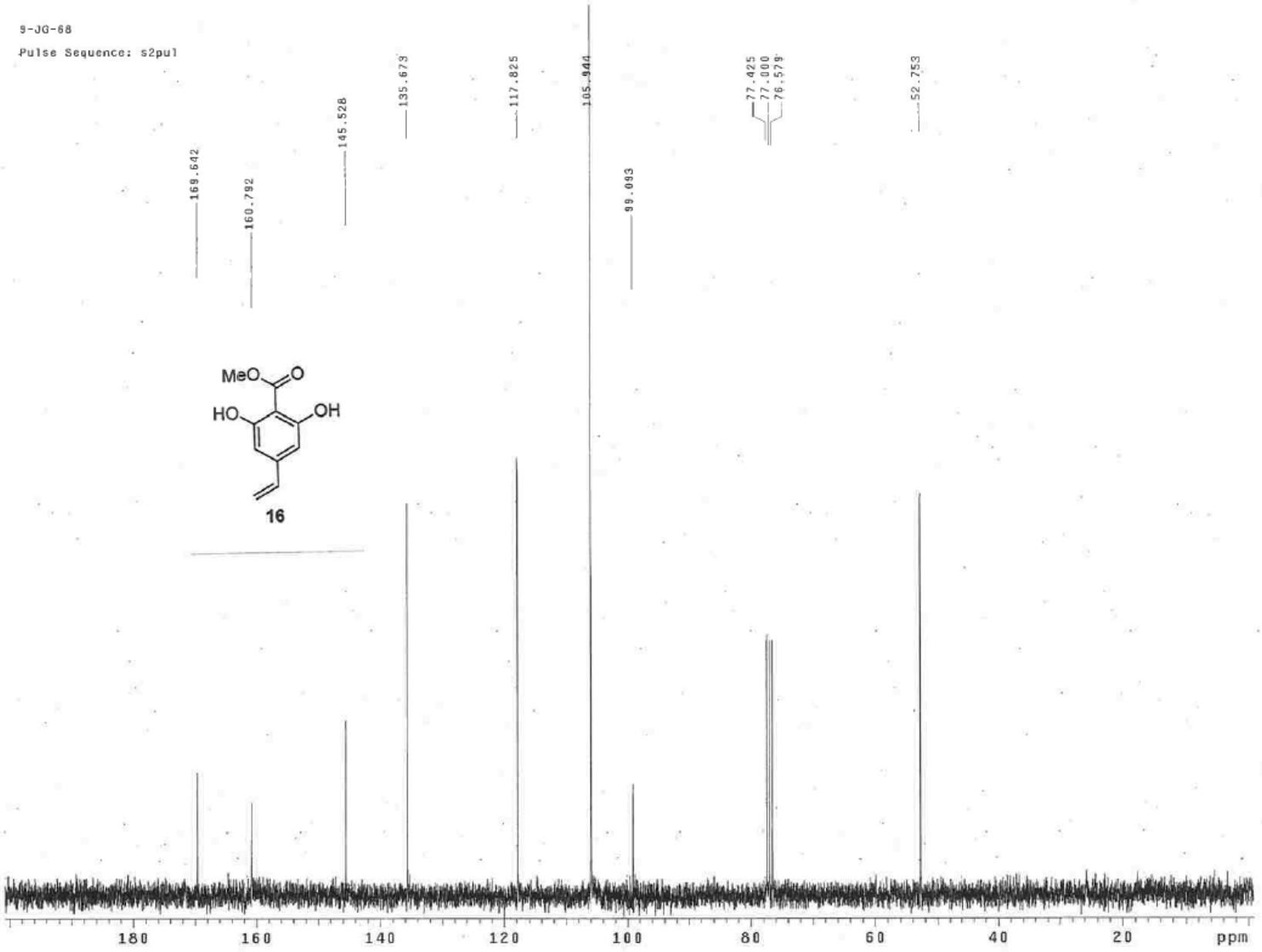
^{13}C NMR, 75 MHz, $CDCl_3$



^{1}H NMR, 300 MHz, $CDCl_3$



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



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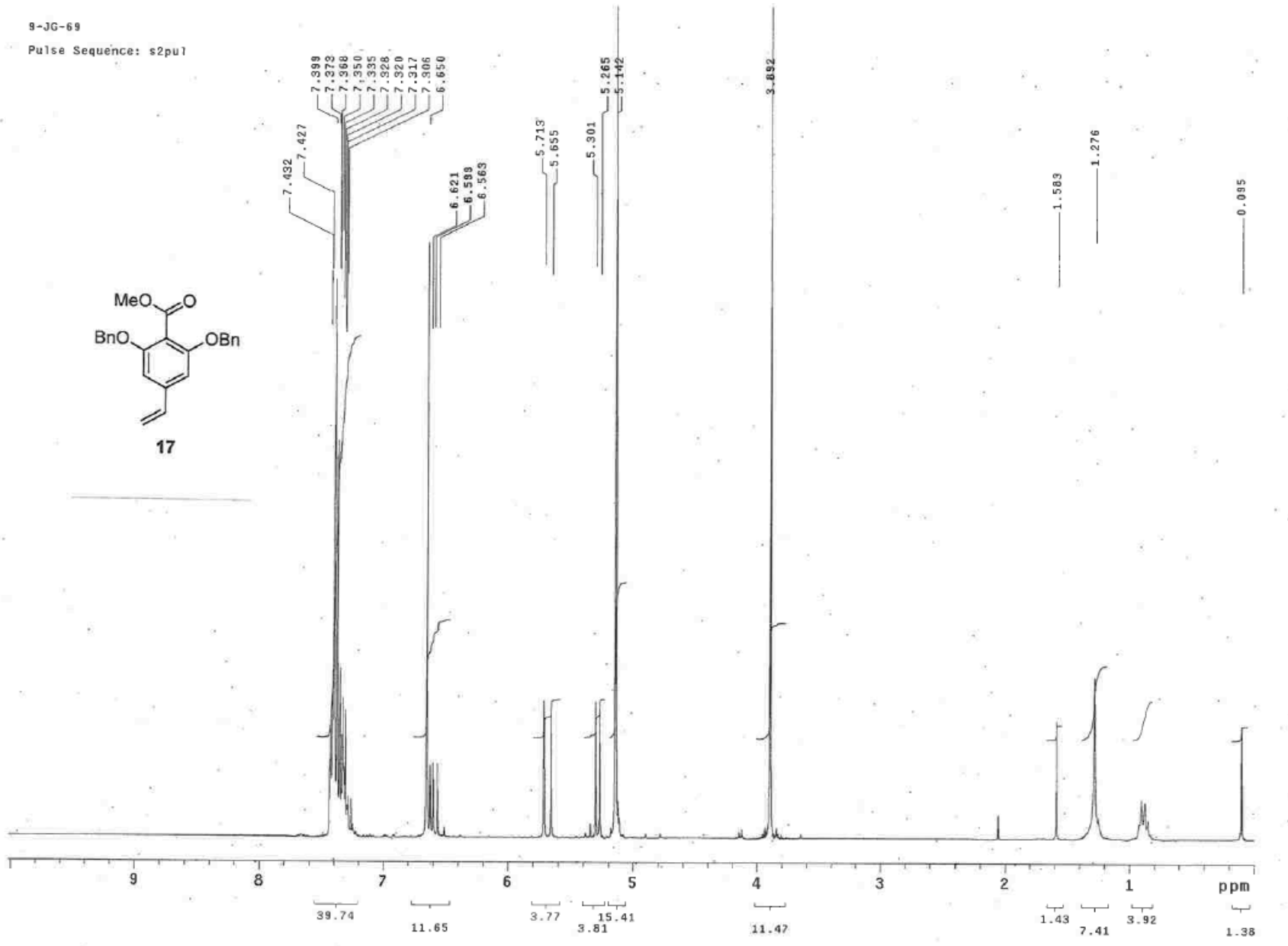
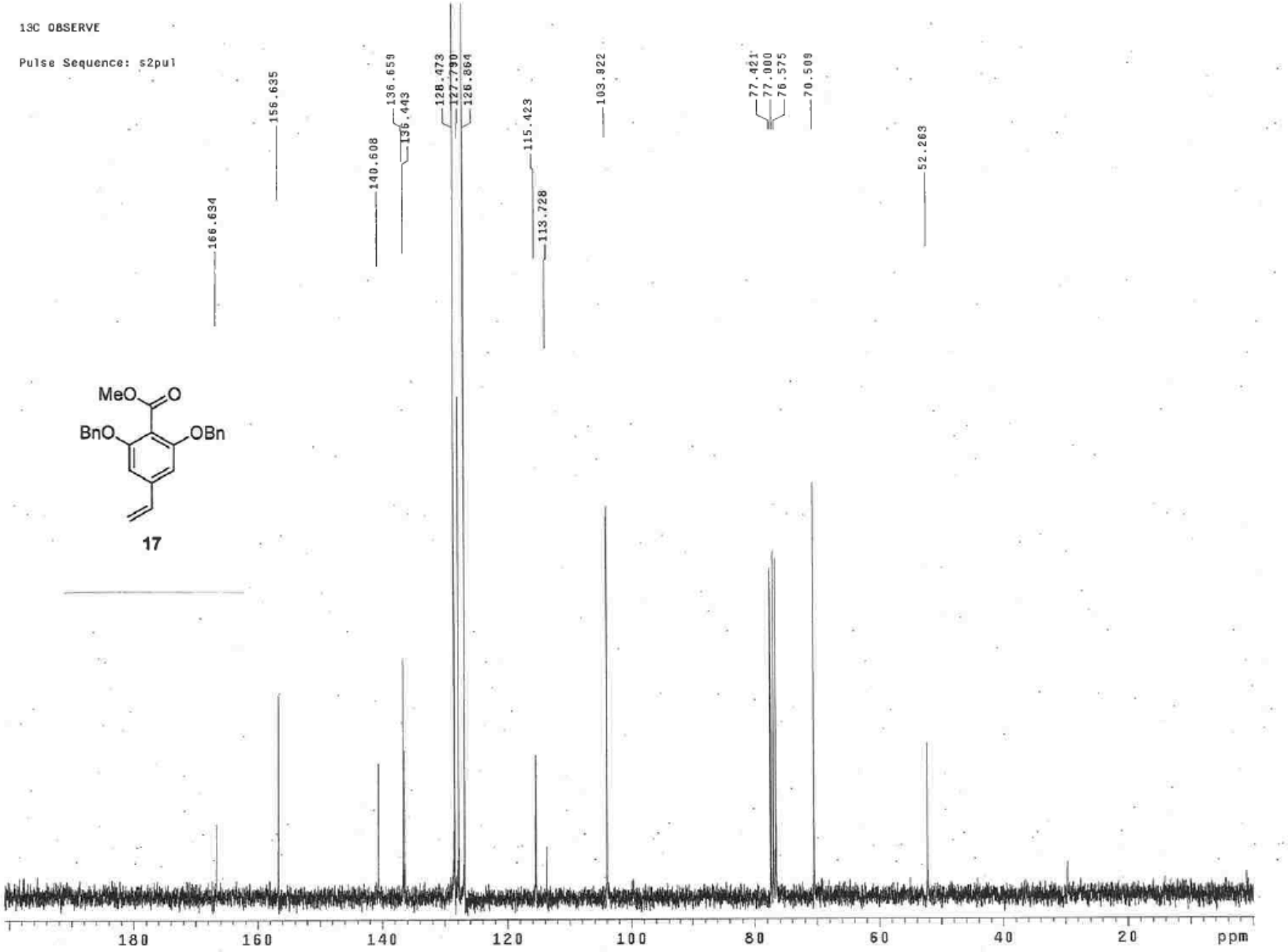
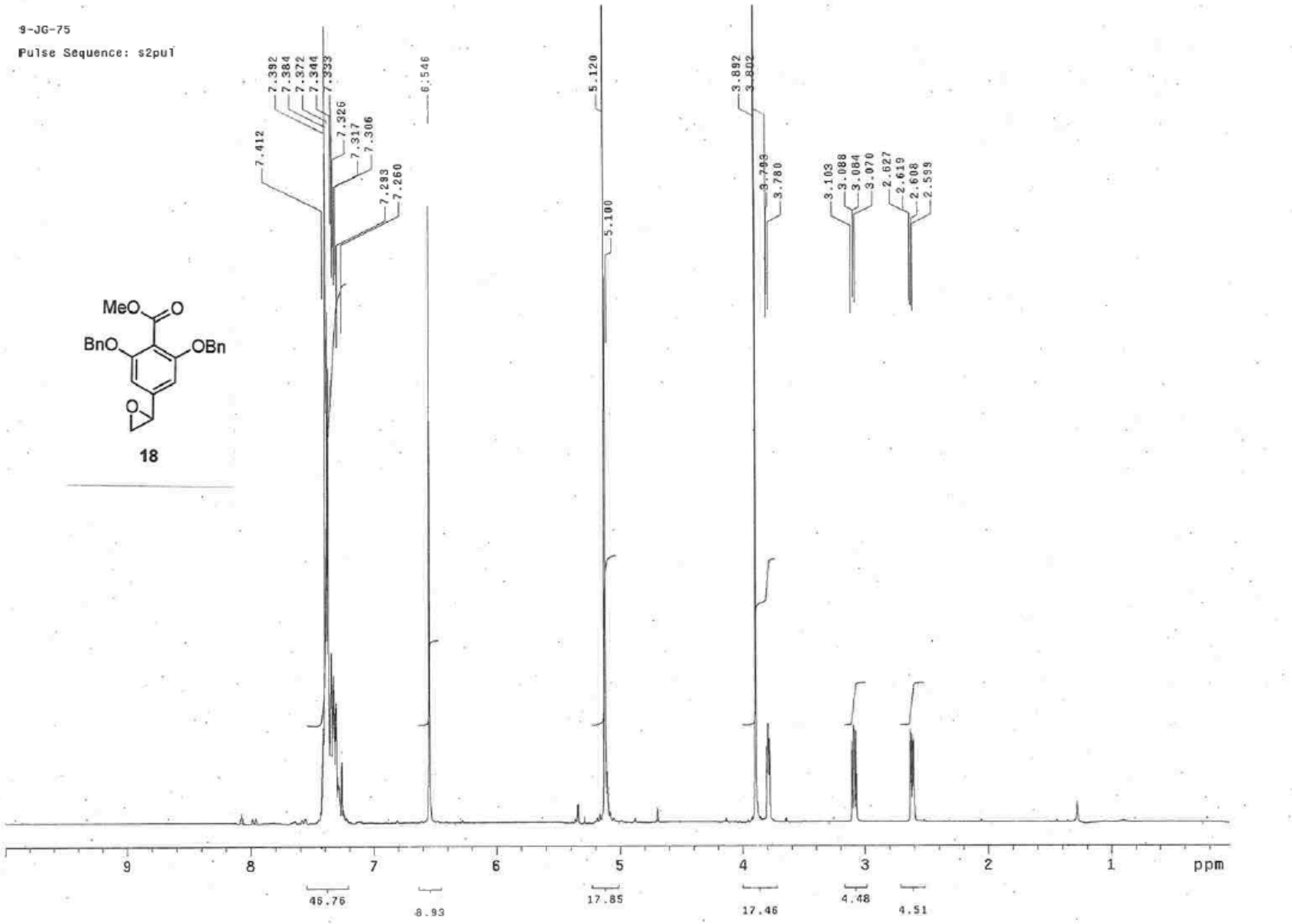


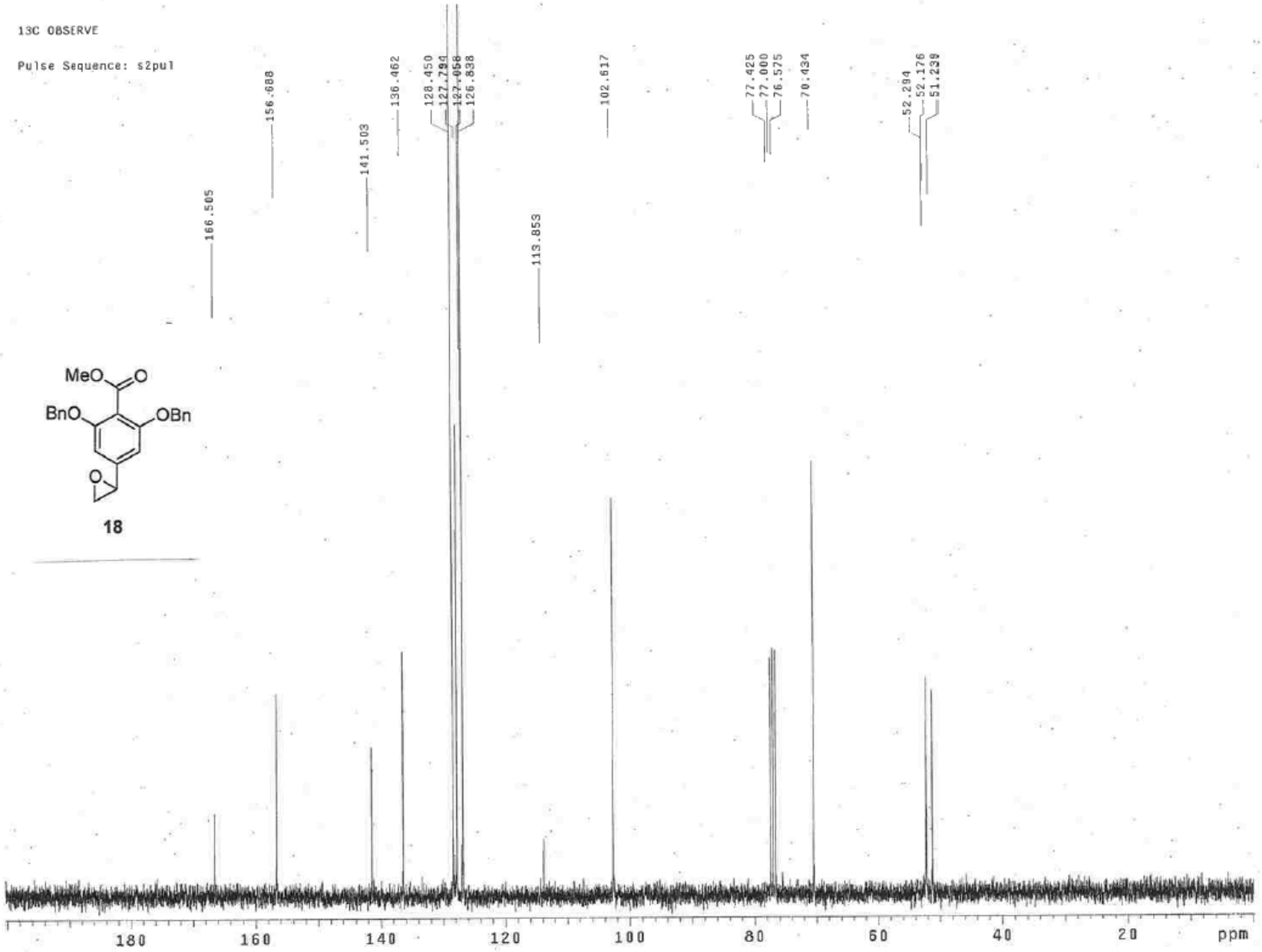
^{13}C NMR, 75 MHz, $CDCl_3$



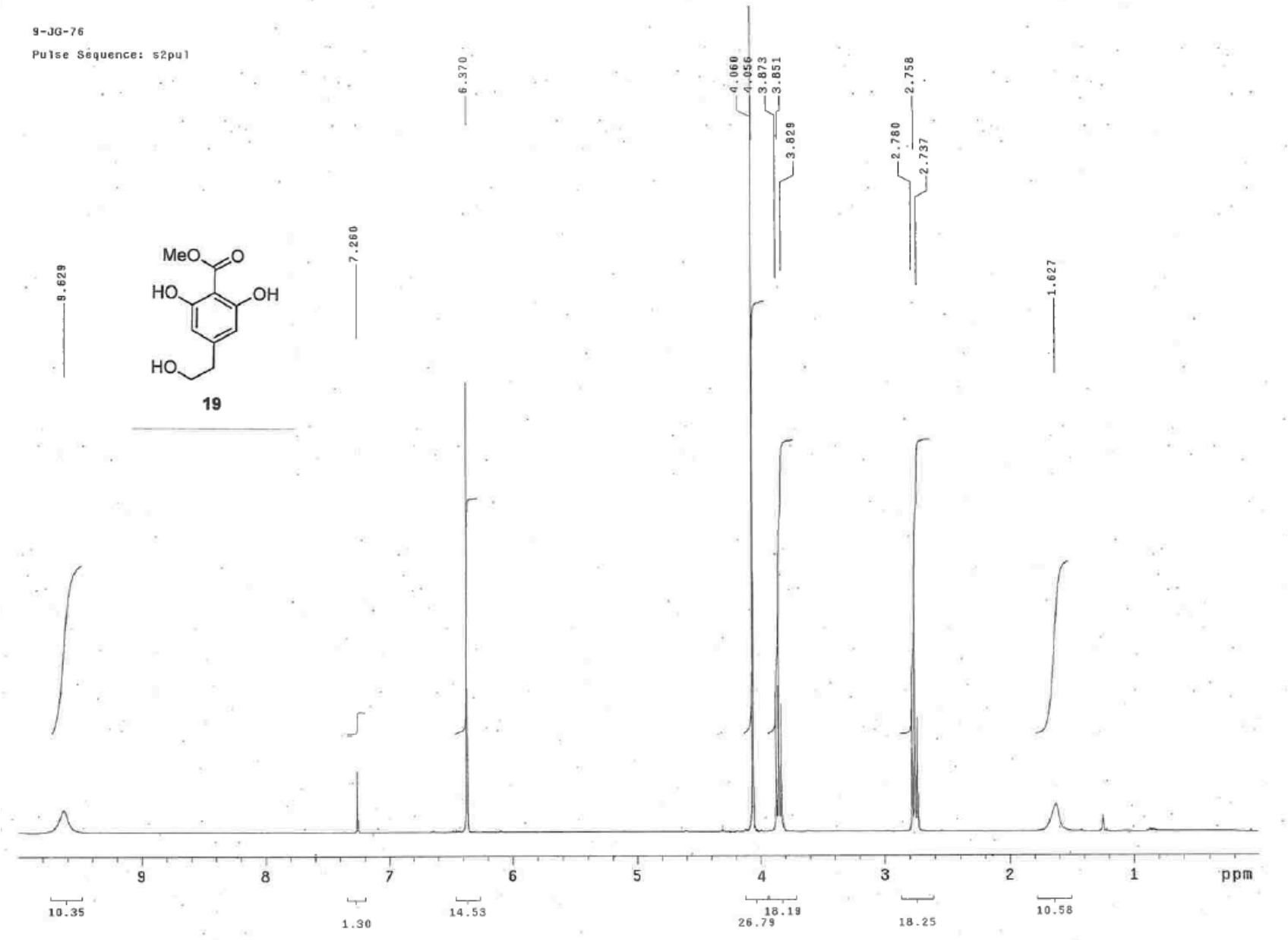
^{1}H NMR, 300 MHz, $CDCl_3$



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



^{1}H NMR, 300 MHz, $CDCl_3$



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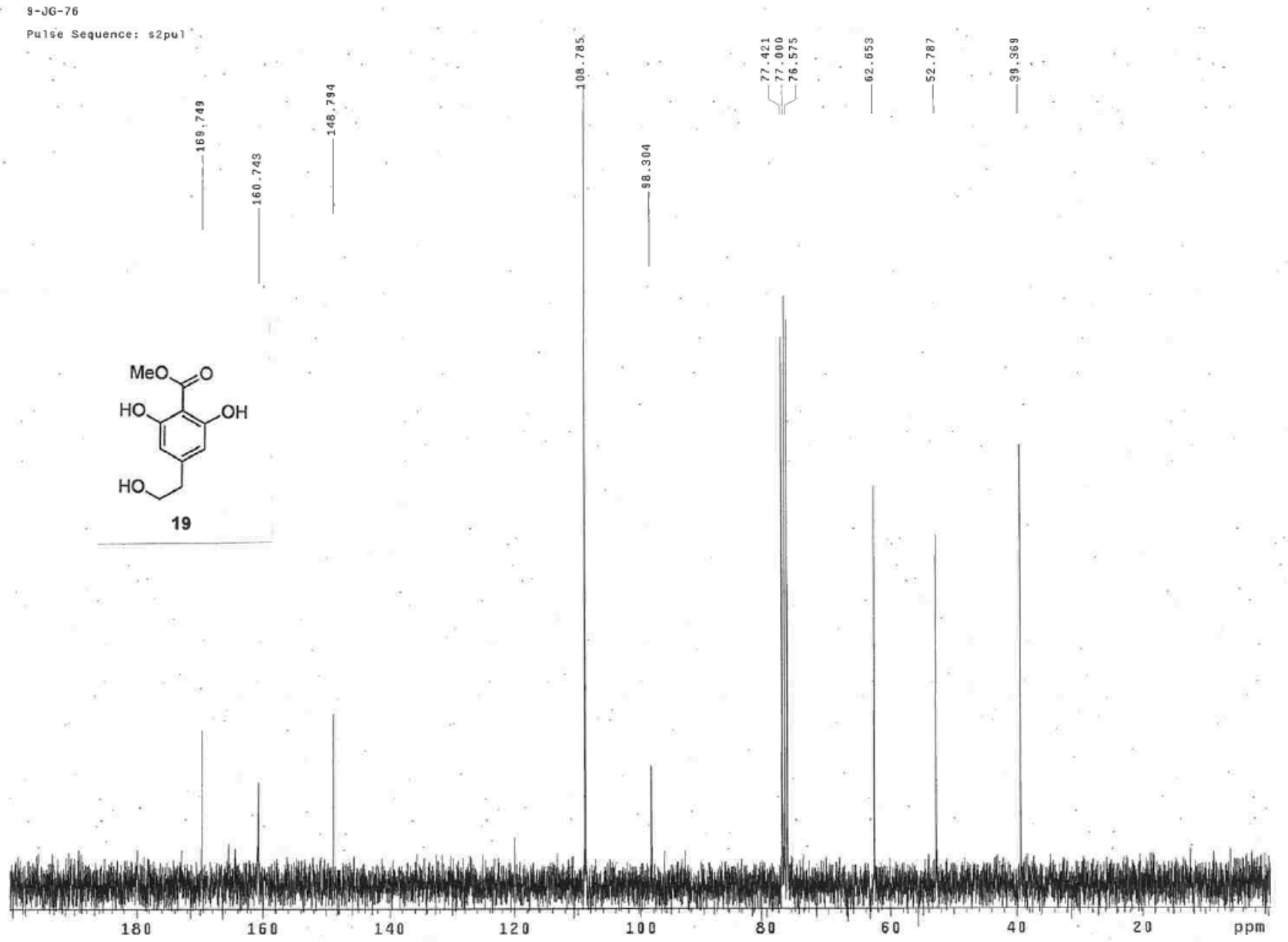

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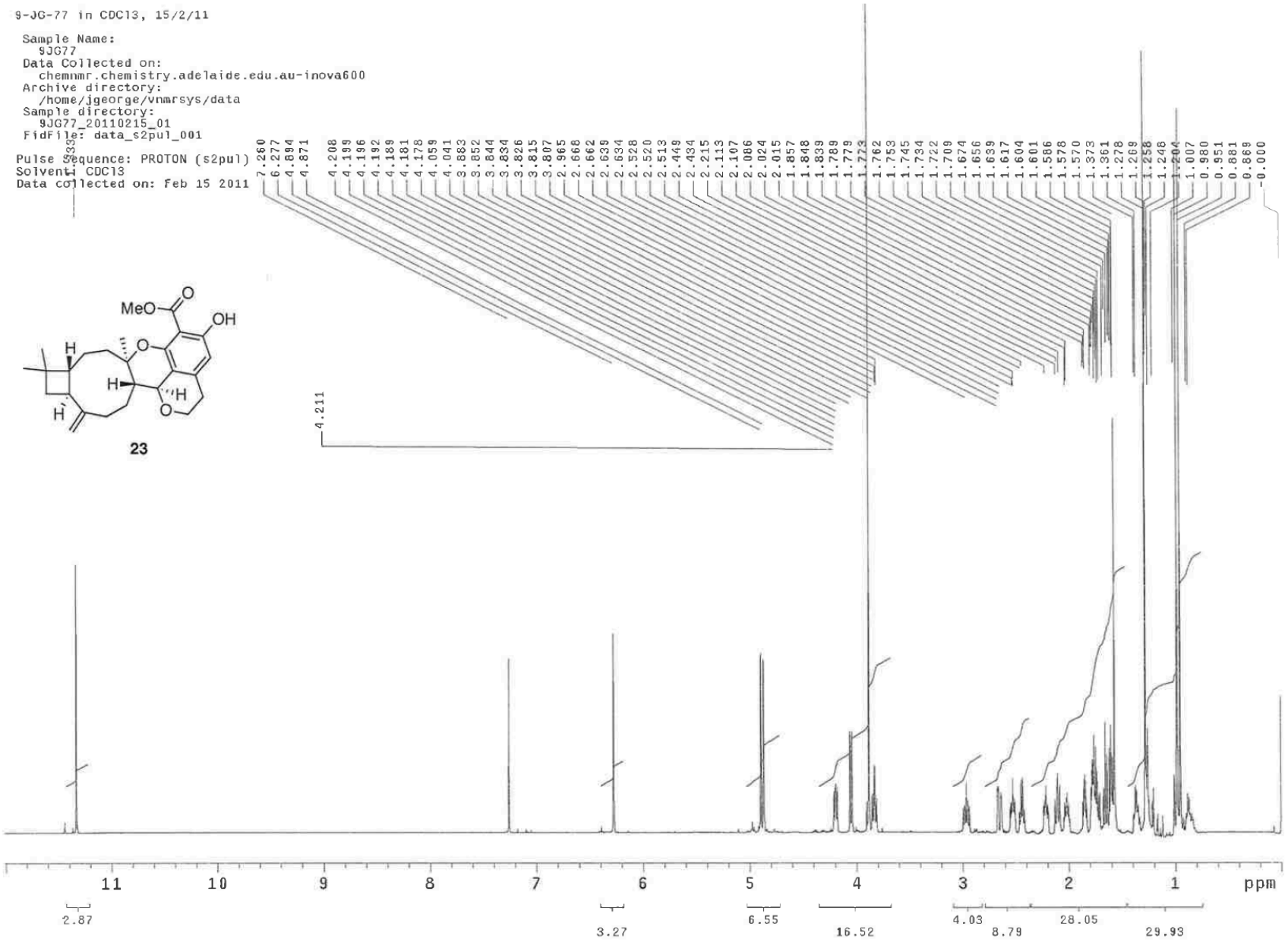
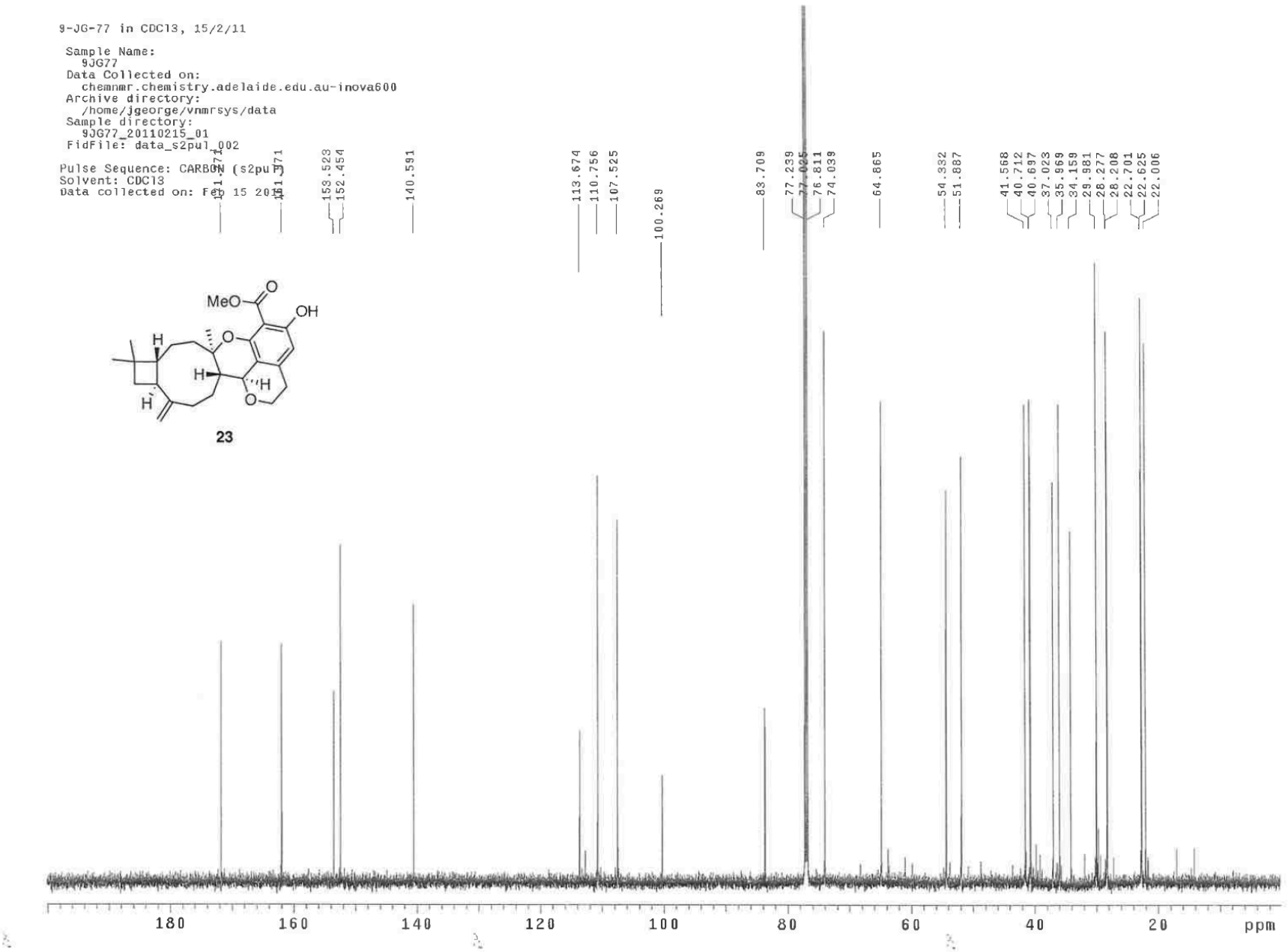


^{13}C NMR, 150 MHz, $CDCl_3$



1-JS-29 in CDCl3, 4/2/11

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Sample directory:
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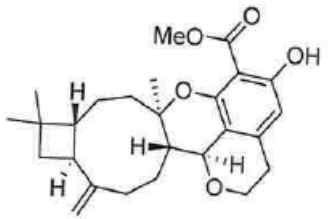
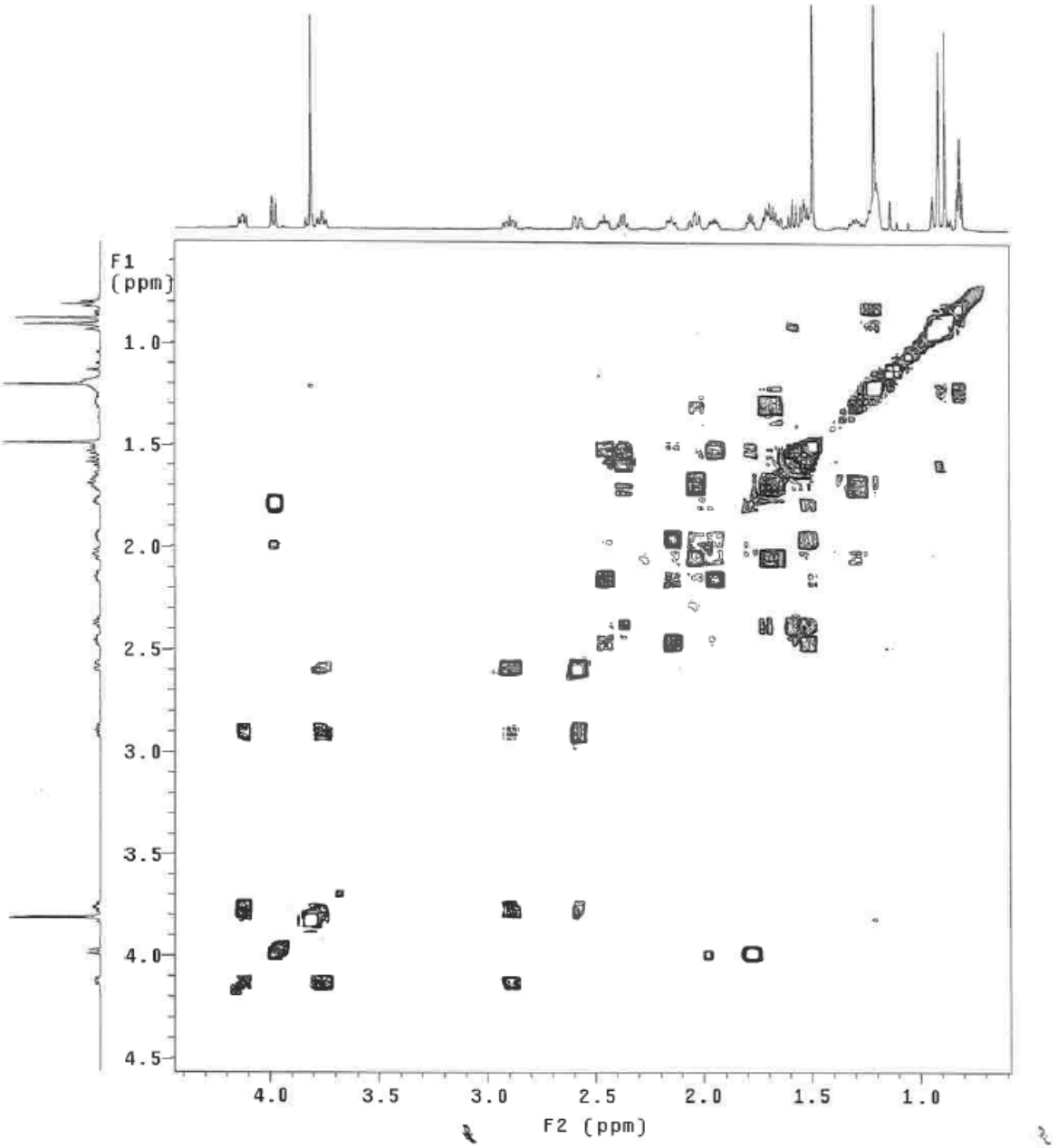
Pulse Sequence: gCOSY
Solvent: CDCl3
Data collected on: Feb 4 2011

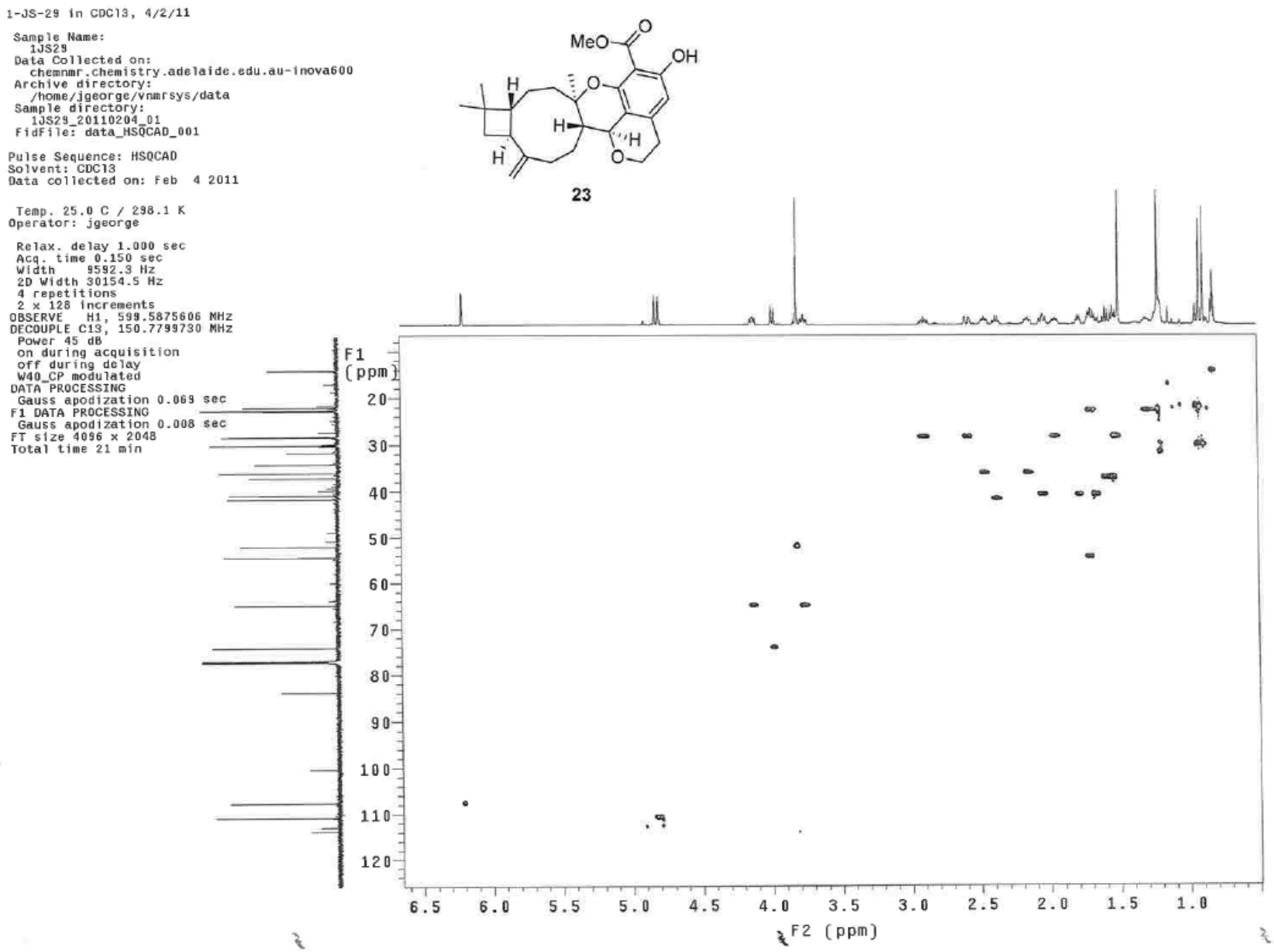
Temp. 25.0 C / 298.1 K
Operator: jgeorge

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 9592.3 Hz
2D Width 9592.3 Hz
2 repetitions
256 increments
OBSERVE H1, 599.5875618 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.027 sec
FT size 4096 x 4096
Total time 10 min



23




1-JS-29 in CDCl3, 4/2/11
Sample Name:
1JS29
Data Collected on:
chemnmr.chemistry.adelaide.edu.au-inova600
Archive directory:
/home/jgeorge/vnmrsys/data
Sample directory:
1JS29_20110204_01
FidFile: data_HSQCAD_001
Pulse Sequence: HSQCAD
Solvent: CDCl3
Data collected on: Feb 4 2011
Temp. 25.0 C / 298.1 K
Operator: jgeorge
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 9592.3 Hz
2D Width 30154.5 Hz
4 repetitions
2 x 128 increments
OBSERVE H1, 599.5875606 MHz
DECOUPLE C13, 150.7799730 MHz
Power 45 dB
on during acquisition
off during delay
W40_CP modulated
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.008 sec
FT size 4096 x 2048
Total time 21 min
MeO
O
OH
H
O
H
H
O
H
23
F1
(ppm)
20
30
40
50
60
70
80
90
100
110
120
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
F2 (ppm)

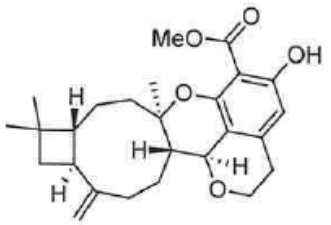
1-JS-29 in CDCl3, 4/2/11

Sample Name:
1JS29
Data Collected on:
chemnmr.chemistry.adelaide.edu.au-inova600
Archive directory:
/home/jgeorge/vnmrsys/data
Sample directory:
1JS29_20110204_01
FidFile: data_gHMBCAD_001

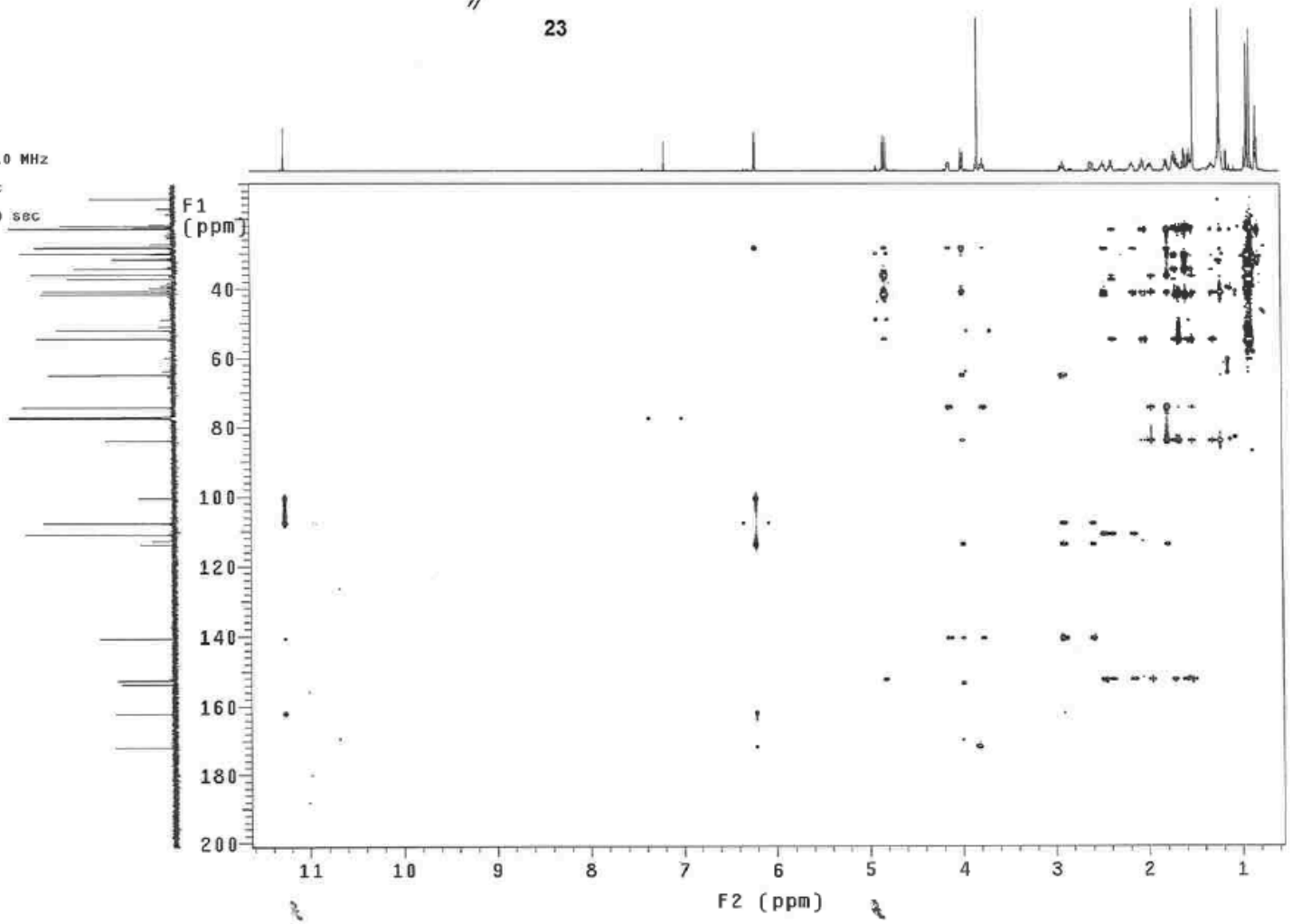
Pulse Sequence: gHMBCAD
Solvent: CDCl3
Data collected on: Feb 4 2011

Temp. 25.0 C / 298.1 K
Operator: jgeorge

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 9592.3 Hz
2D Width 36182.7 Hz
4 repetitions
2 x 200 increments
OBSERVE H1, 599.5875610 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Gauss apodization 0.010 sec
FT size 4096 x 4096
Total time 33 min



23



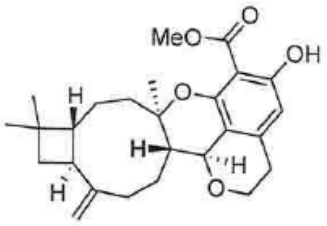
1-JG-29 in CDCl3, 8/2/11

Sample Name:
1JG29
Data Collected on:
chemnmr.chemistry.adelaide.edu.au-inova600
Archive directory:
/home/jgeorge/vnmrsys/data
Sample directory:
1JG29_20110208_01
FidFile: data_NOESY_001

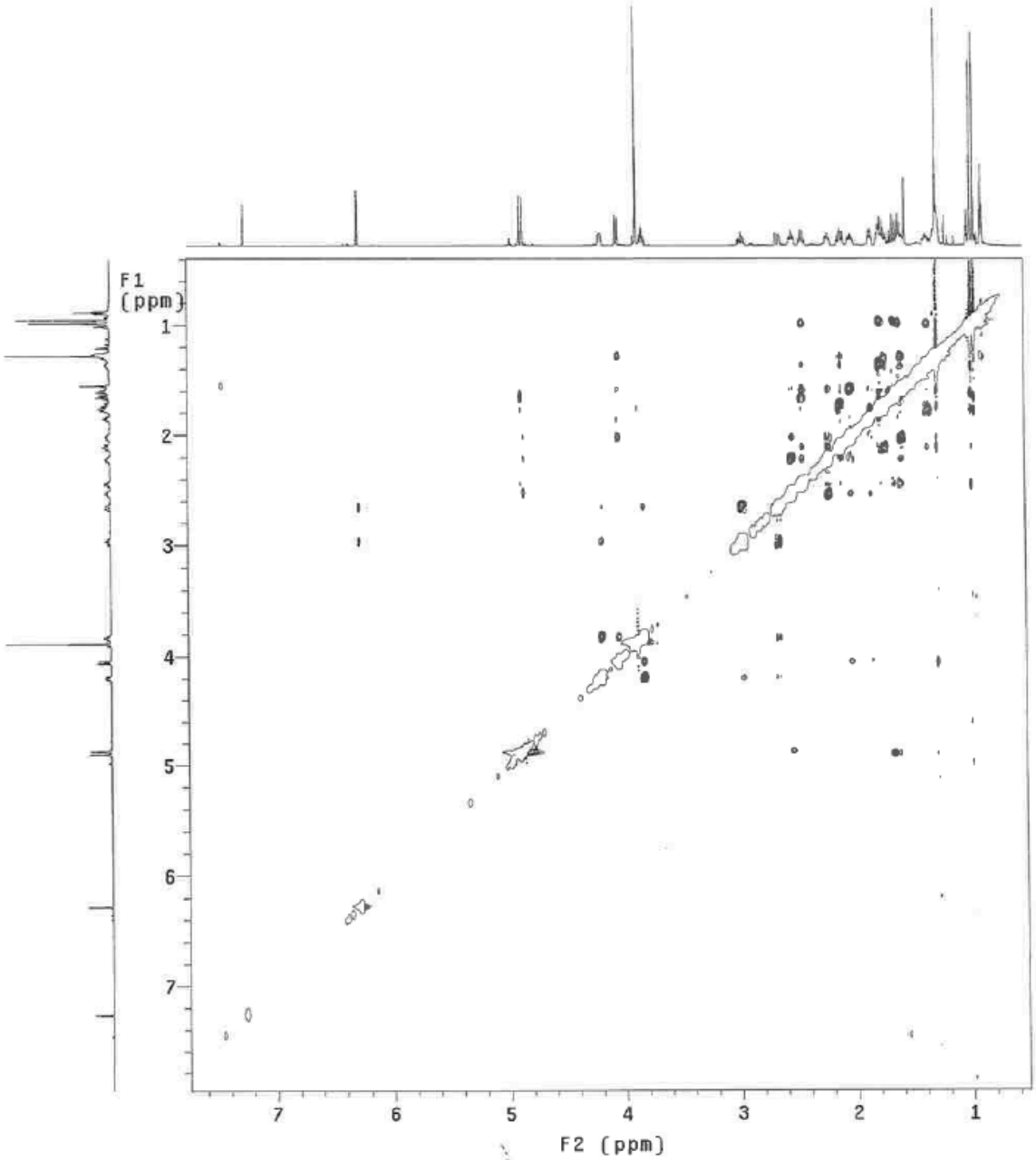
Pulse Sequence: NOESY
Solvent: CDCl3
Data collected on: Feb 8 2011

Temp. 25.0 C / 298.1 K
Operator: jgeorge

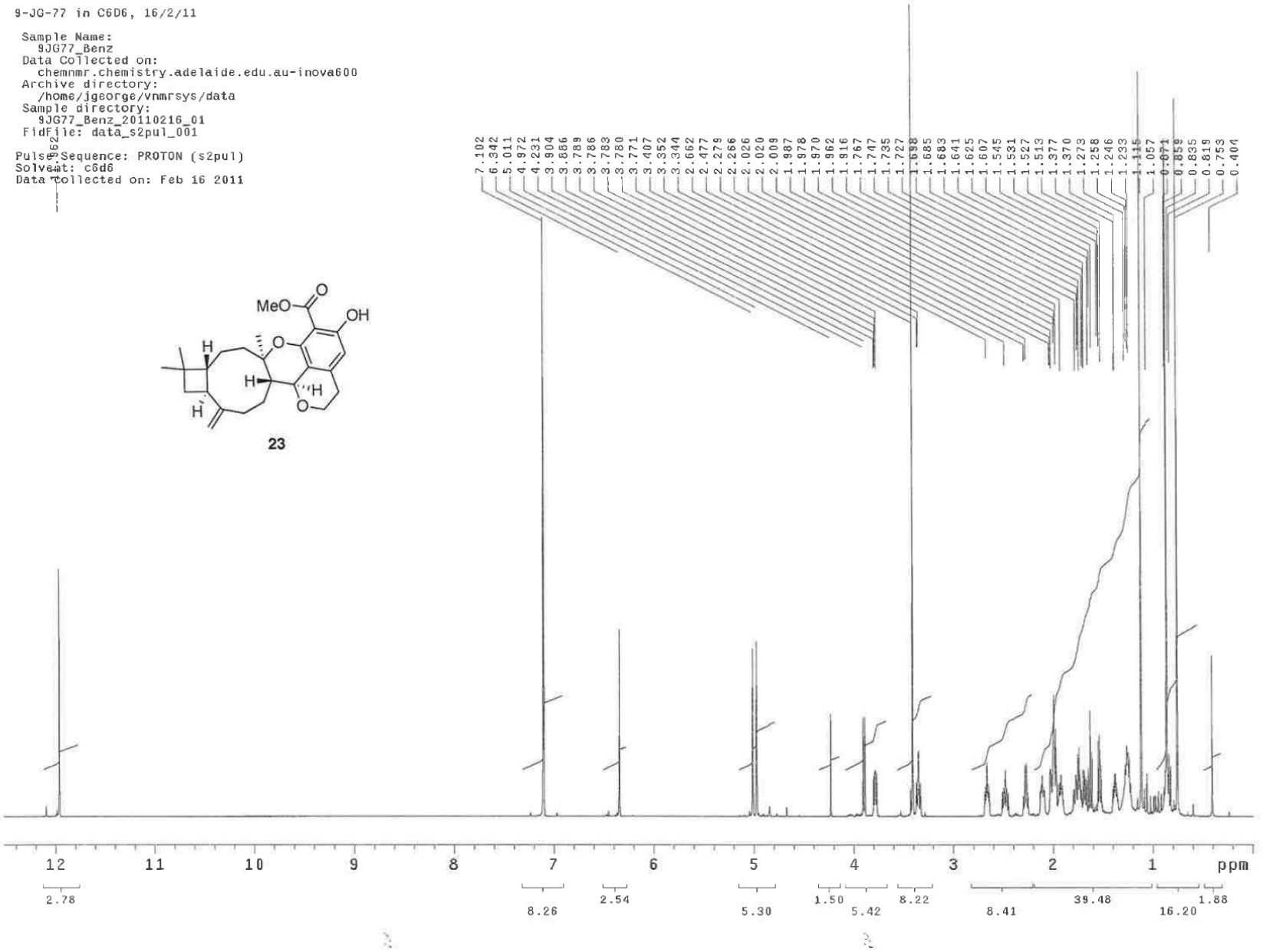
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 9592.3 Hz
2D Width 9592.3 Hz
16 repetitions
2 x 200 increments
OBSERVE H1, 599.5875213 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.019 sec
FT size 4096 x 4096
Total time 2 hr, 38 min



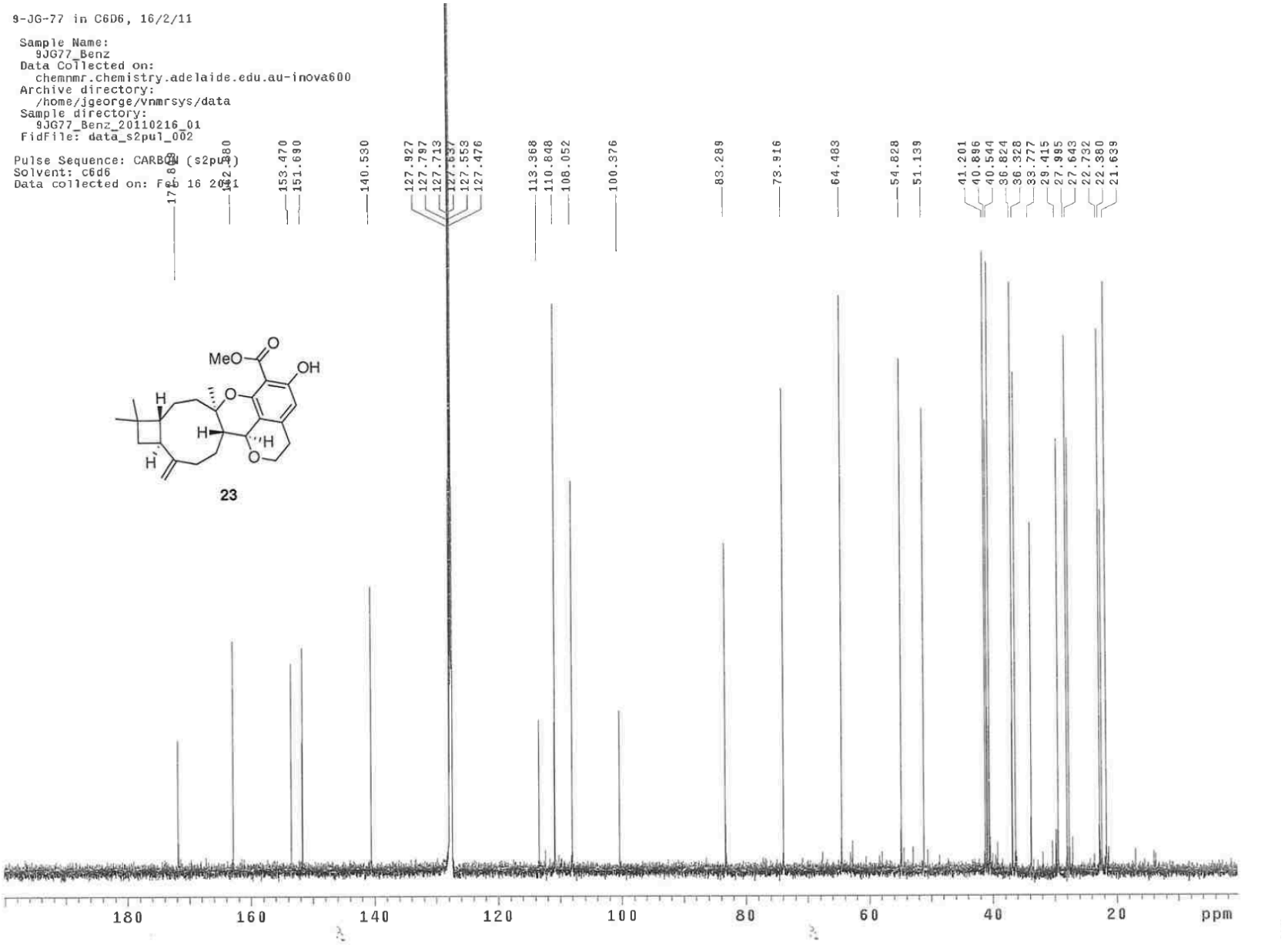
23



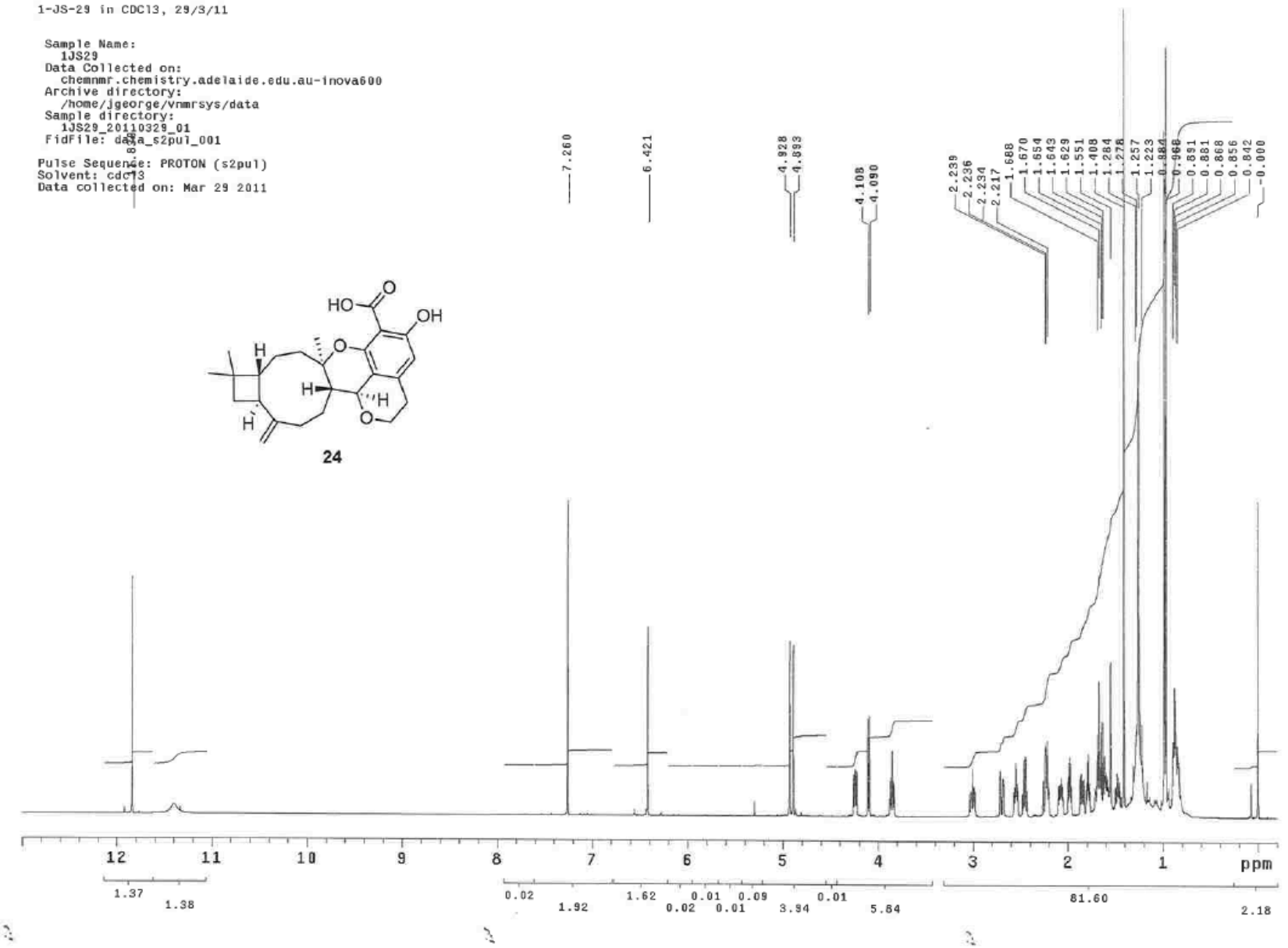
^{1}H NMR, 600 MHz, C_6D_6



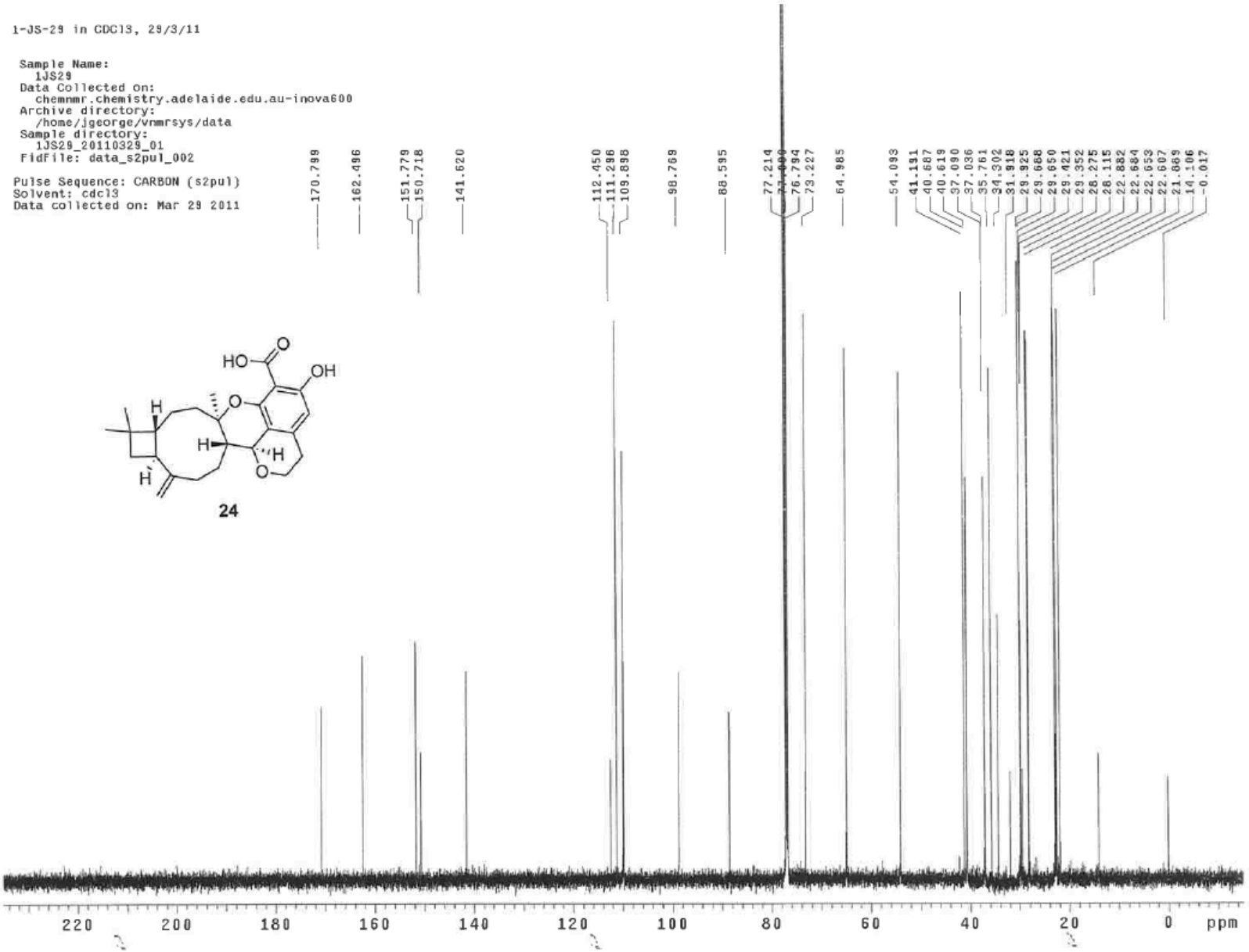
^{13}C NMR, 150 MHz, C_6D_6



^{1}H NMR, 600 MHz, $CDCl_3$



^{13}C NMR, 150 MHz, $CDCl_3$



24

Table 1. Crystal data and structure refinement for **24**.

Identification code	e:_w~1_1	
Empirical formula	C25 H32 O5	
Formula weight	412.51	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 31.984(2) Å	a= 90°.
	b = 12.5310(9) Å	b= 92.744(6)°.
	c = 5.9875(4) Å	g = 90°.
Volume	2397.0(3) $Å^3$	
Z	4	
Density (calculated)	1.143 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	888	
Crystal size	0.61 x 0.49 x 0.15 mm^3	
Theta range for data collection	2.51 to 29.27°.	
Index ranges	-41<=h<=42, -17<=k<=15, -8<=l<=7	
Reflections collected	13925	
Independent reflections	5536 [R(int) = 0.0614]	
Completeness to theta = 26.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.85755	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5536 / 1 / 274	
Goodness-of-fit on F^2	1.111	
Final R indices [I>2sigma(I)]	R1 = 0.0796, wR2 = 0.2195	
R indices (all data)	R1 = 0.1160, wR2 = 0.2589	
Absolute structure parameter	-1(2)	
Largest diff. peak and hole	1.267 and -0.392 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **24**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4444(1)	7158(4)	6574(6)	28(1)
C(2)	4362(1)	6034(4)	5863(7)	26(1)
C(3)	4541(1)	5079(4)	7291(7)	31(1)
C(4)	4144(1)	4425(4)	6621(6)	28(1)
C(5)	3921(1)	5516(3)	6106(6)	24(1)
C(6)	3561(1)	5536(3)	4339(7)	26(1)
C(7)	3201(1)	6331(3)	4682(7)	25(1)
C(8)	3233(1)	7466(3)	3716(6)	22(1)
C(9)	3609(1)	8103(3)	4695(6)	22(1)
C(10)	4000(1)	7933(4)	3353(6)	26(1)
C(11)	4417(1)	7981(4)	4753(7)	27(1)
C(12)	4536(1)	7429(4)	8713(7)	36(1)
C(13)	4210(2)	3753(4)	4530(8)	36(1)
C(14)	3951(2)	3751(4)	8390(7)	36(1)
C(15)	3189(1)	7460(4)	1163(6)	31(1)
C(16)	3500(1)	9290(3)	4858(7)	26(1)
C(17)	3137(1)	9417(3)	6337(6)	24(1)
C(18)	3123(1)	10167(3)	8035(7)	27(1)
C(19)	2780(1)	10212(4)	9384(7)	30(1)
C(20)	2451(1)	9508(3)	9020(7)	28(1)
C(21)	2458(1)	8715(3)	7339(7)	25(1)
C(22)	2811(1)	8702(3)	6022(6)	23(1)
C(23)	2110(1)	7959(4)	7076(7)	31(1)
C(25)	3492(2)	10915(4)	8375(9)	37(1)
C(26)	3750(2)	10924(4)	6337(9)	37(1)
O(27)	2825(1)	7959(2)	4336(4)	27(1)
O(28)	2122(1)	7211(3)	5496(6)	48(1)
O(29)	1810(1)	7974(3)	8279(6)	41(1)
O(30)	2122(1)	9594(3)	10382(5)	39(1)
O(31)	3858(1)	9845(2)	5734(5)	33(1)

Table 3. Bond lengths [Å] and angles [°] for **24**.

C(1)-C(12)	1.344(6)
C(1)-C(2)	1.491(6)
C(1)-C(11)	1.500(6)
C(2)-C(3)	1.565(6)
C(2)-C(5)	1.566(6)
C(2)-H(2)	1.0000
C(3)-C(4)	1.548(6)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(14)	1.510(6)
C(4)-C(13)	1.532(6)
C(4)-C(5)	1.567(6)
C(5)-C(6)	1.526(5)
C(5)-H(5)	1.0000
C(6)-C(7)	1.544(6)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.541(6)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-O(27)	1.507(5)
C(8)-C(15)	1.528(5)
C(8)-C(9)	1.536(5)
C(9)-C(10)	1.532(5)
C(9)-C(16)	1.533(6)
C(9)-H(9)	1.0000
C(10)-C(11)	1.542(6)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9500
C(12)-H(12B)	0.9500
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800

C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-O(31)	1.419(5)
C(16)-C(17)	1.500(5)
C(16)-H(16)	1.0000
C(17)-C(22)	1.382(6)
C(17)-C(18)	1.387(6)
C(18)-C(19)	1.394(6)
C(18)-C(25)	1.513(6)
C(19)-C(20)	1.384(6)
C(19)-H(19)	0.9500
C(20)-O(30)	1.364(5)
C(20)-C(21)	1.415(6)
C(21)-C(22)	1.408(5)
C(21)-C(23)	1.465(6)
C(22)-O(27)	1.375(5)
C(23)-O(29)	1.226(5)
C(23)-O(28)	1.334(6)
C(25)-C(26)	1.506(7)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-O(31)	1.447(5)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
O(28)-H(28A)	0.8400
O(30)-H(30A)	0.8400

C(12)-C(1)-C(2)	122.6(4)
C(12)-C(1)-C(11)	121.4(4)
C(2)-C(1)-C(11)	116.0(3)
C(1)-C(2)-C(3)	120.7(3)
C(1)-C(2)-C(5)	120.8(3)
C(3)-C(2)-C(5)	86.6(3)
C(1)-C(2)-H(2)	108.9

C(3)-C(2)-H(2)	108.9
C(5)-C(2)-H(2)	108.9
C(4)-C(3)-C(2)	89.3(3)
C(4)-C(3)-H(3A)	113.8
C(2)-C(3)-H(3A)	113.8
C(4)-C(3)-H(3B)	113.8
C(2)-C(3)-H(3B)	113.8
H(3A)-C(3)-H(3B)	111.0
C(14)-C(4)-C(13)	110.1(4)
C(14)-C(4)-C(3)	118.2(3)
C(13)-C(4)-C(3)	111.0(3)
C(14)-C(4)-C(5)	115.4(3)
C(13)-C(4)-C(5)	113.5(3)
C(3)-C(4)-C(5)	87.1(3)
C(6)-C(5)-C(2)	125.6(3)
C(6)-C(5)-C(4)	118.2(3)
C(2)-C(5)-C(4)	88.6(3)
C(6)-C(5)-H(5)	107.5
C(2)-C(5)-H(5)	107.5
C(4)-C(5)-H(5)	107.5
C(5)-C(6)-C(7)	117.5(3)
C(5)-C(6)-H(6A)	107.9
C(7)-C(6)-H(6A)	107.9
C(5)-C(6)-H(6B)	107.9
C(7)-C(6)-H(6B)	107.9
H(6A)-C(6)-H(6B)	107.2
C(8)-C(7)-C(6)	118.8(3)
C(8)-C(7)-H(7A)	107.6
C(6)-C(7)-H(7A)	107.6
C(8)-C(7)-H(7B)	107.6
C(6)-C(7)-H(7B)	107.6
H(7A)-C(7)-H(7B)	107.0
O(27)-C(8)-C(15)	102.0(3)
O(27)-C(8)-C(9)	111.4(3)
C(15)-C(8)-C(9)	114.8(3)
O(27)-C(8)-C(7)	102.2(3)
C(15)-C(8)-C(7)	111.4(3)
C(9)-C(8)-C(7)	113.7(3)

C(10)-C(9)-C(16)	111.3(3)
C(10)-C(9)-C(8)	111.8(3)
C(16)-C(9)-C(8)	110.5(3)
C(10)-C(9)-H(9)	107.7
C(16)-C(9)-H(9)	107.7
C(8)-C(9)-H(9)	107.7
C(9)-C(10)-C(11)	114.5(3)
C(9)-C(10)-H(10A)	108.6
C(11)-C(10)-H(10A)	108.6
C(9)-C(10)-H(10B)	108.6
C(11)-C(10)-H(10B)	108.6
H(10A)-C(10)-H(10B)	107.6
C(1)-C(11)-C(10)	112.8(3)
C(1)-C(11)-H(11A)	109.0
C(10)-C(11)-H(11A)	109.0
C(1)-C(11)-H(11B)	109.0
C(10)-C(11)-H(11B)	109.0
H(11A)-C(11)-H(11B)	107.8
C(1)-C(12)-H(12A)	120.0
C(1)-C(12)-H(12B)	120.0
H(12A)-C(12)-H(12B)	120.0
C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(4)-C(14)-H(14A)	109.5
C(4)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(4)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(8)-C(15)-H(15A)	109.5
C(8)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(8)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5

H(15B)-C(15)-H(15C)	109.5
O(31)-C(16)-C(17)	111.3(3)
O(31)-C(16)-C(9)	108.4(3)
C(17)-C(16)-C(9)	109.0(3)
O(31)-C(16)-H(16)	109.4
C(17)-C(16)-H(16)	109.4
C(9)-C(16)-H(16)	109.4
C(22)-C(17)-C(18)	119.3(3)
C(22)-C(17)-C(16)	116.7(3)
C(18)-C(17)-C(16)	123.9(4)
C(17)-C(18)-C(19)	120.4(4)
C(17)-C(18)-C(25)	117.8(4)
C(19)-C(18)-C(25)	121.8(4)
C(20)-C(19)-C(18)	119.9(4)
C(20)-C(19)-H(19)	120.1
C(18)-C(19)-H(19)	120.1
O(30)-C(20)-C(19)	117.3(4)
O(30)-C(20)-C(21)	121.4(4)
C(19)-C(20)-C(21)	121.4(4)
C(22)-C(21)-C(20)	116.6(4)
C(22)-C(21)-C(23)	123.9(4)
C(20)-C(21)-C(23)	119.5(3)
O(27)-C(22)-C(17)	119.2(3)
O(27)-C(22)-C(21)	118.3(3)
C(17)-C(22)-C(21)	122.4(4)
O(29)-C(23)-O(28)	118.5(4)
O(29)-C(23)-C(21)	122.6(4)
O(28)-C(23)-C(21)	118.9(4)
C(26)-C(25)-C(18)	110.4(4)
C(26)-C(25)-H(25A)	109.6
C(18)-C(25)-H(25A)	109.6
C(26)-C(25)-H(25B)	109.6
C(18)-C(25)-H(25B)	109.6
H(25A)-C(25)-H(25B)	108.1
O(31)-C(26)-C(25)	110.0(4)
O(31)-C(26)-H(26A)	109.7
C(25)-C(26)-H(26A)	109.7
O(31)-C(26)-H(26B)	109.7

C(25)-C(26)-H(26B)	109.7
H(26A)-C(26)-H(26B)	108.2
C(22)-O(27)-C(8)	121.2(3)
C(23)-O(28)-H(28A)	109.5
C(20)-O(30)-H(30A)	109.5
C(16)-O(31)-C(26)	110.6(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **24**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	16(2)	39(3)	29(2)	-4(2)	2(2)	2(2)
C(2)	22(2)	36(2)	22(2)	-3(2)	1(2)	5(2)
C(3)	29(2)	33(2)	31(2)	0(2)	-3(2)	3(2)
C(4)	30(2)	30(2)	25(2)	4(2)	3(2)	4(2)
C(5)	25(2)	27(2)	21(2)	-1(2)	1(1)	3(2)
C(6)	24(2)	25(2)	29(2)	-1(2)	-1(2)	2(2)
C(7)	20(2)	28(2)	29(2)	-2(2)	1(2)	-2(2)
C(8)	19(2)	26(2)	23(2)	1(2)	2(1)	3(2)
C(9)	22(2)	25(2)	19(2)	1(2)	3(1)	2(2)
C(10)	22(2)	30(2)	27(2)	0(2)	6(2)	-1(2)
C(11)	19(2)	31(2)	33(2)	-4(2)	6(2)	-2(2)
C(12)	30(2)	48(3)	31(2)	-8(2)	3(2)	-9(2)
C(13)	43(3)	31(2)	36(2)	-1(2)	3(2)	13(2)
C(14)	41(3)	31(2)	34(2)	3(2)	4(2)	0(2)
C(15)	32(2)	36(2)	24(2)	-2(2)	-3(2)	7(2)
C(16)	21(2)	26(2)	30(2)	4(2)	2(2)	-1(2)
C(17)	21(2)	21(2)	28(2)	4(2)	4(2)	4(2)
C(18)	27(2)	22(2)	33(2)	-2(2)	0(2)	4(2)
C(19)	31(2)	27(2)	32(2)	-2(2)	8(2)	5(2)
C(20)	29(2)	27(2)	30(2)	2(2)	8(2)	9(2)
C(21)	19(2)	24(2)	31(2)	9(2)	4(2)	2(2)
C(22)	26(2)	23(2)	20(2)	3(2)	0(1)	1(2)
C(23)	22(2)	27(2)	45(2)	5(2)	2(2)	3(2)
C(25)	31(2)	29(2)	53(3)	-15(2)	4(2)	-1(2)
C(26)	29(2)	22(2)	61(3)	-6(2)	10(2)	-1(2)
O(27)	17(1)	31(2)	31(1)	-7(1)	-2(1)	5(1)
O(28)	27(2)	51(2)	68(2)	-22(2)	13(2)	-10(2)
O(29)	28(2)	41(2)	56(2)	9(2)	16(1)	-4(2)
O(30)	35(2)	40(2)	43(2)	-2(2)	17(1)	5(1)
O(31)	23(2)	24(2)	52(2)	-7(1)	4(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **24**.

	x	y	z	U(eq)
H(2)	4445	5945	4285	32
H(3A)	4802	4775	6732	38
H(3B)	4573	5234	8911	38
H(5)	3809	5782	7536	29
H(6A)	3439	4810	4239	31
H(6B)	3679	5694	2878	31
H(7A)	2940	6007	4034	30
H(7B)	3167	6399	6311	30
H(9)	3674	7835	6247	26
H(10A)	4004	8483	2169	31
H(10B)	3978	7228	2608	31
H(11A)	4651	7873	3754	33
H(11B)	4448	8699	5429	33
H(12A)	4551	6895	9840	44
H(12B)	4587	8155	9098	44
H(13A)	4395	3150	4921	55
H(13B)	4338	4194	3398	55
H(13C)	3940	3483	3933	55
H(14A)	3677	3489	7824	53
H(14B)	3916	4182	9733	53
H(14C)	4134	3143	8761	53
H(15A)	2926	7107	683	46
H(15B)	3425	7072	562	46
H(15C)	3187	8195	606	46
H(16)	3420	9570	3333	31
H(19)	2773	10724	10552	36
H(25A)	3390	11645	8669	45
H(25B)	3668	10682	9691	45
H(26A)	3589	11266	5077	44
H(26B)	4008	11344	6647	44
H(28A)	2343	7275	4808	58
H(30A)	1941	9131	10023	46

Table 6. Torsion angles [°] for **24**.

C(12)-C(1)-C(2)-C(3)	-24.0(6)
C(11)-C(1)-C(2)-C(3)	156.1(4)
C(12)-C(1)-C(2)-C(5)	81.9(5)
C(11)-C(1)-C(2)-C(5)	-98.0(4)
C(1)-C(2)-C(3)-C(4)	145.9(4)
C(5)-C(2)-C(3)-C(4)	21.7(3)
C(2)-C(3)-C(4)-C(14)	-139.0(4)
C(2)-C(3)-C(4)-C(13)	92.4(4)
C(2)-C(3)-C(4)-C(5)	-21.7(3)
C(1)-C(2)-C(5)-C(6)	90.1(5)
C(3)-C(2)-C(5)-C(6)	-145.7(4)
C(1)-C(2)-C(5)-C(4)	-145.5(4)
C(3)-C(2)-C(5)-C(4)	-21.4(3)
C(14)-C(4)-C(5)-C(6)	-88.0(4)
C(13)-C(4)-C(5)-C(6)	40.3(5)
C(3)-C(4)-C(5)-C(6)	152.0(4)
C(14)-C(4)-C(5)-C(2)	141.6(4)
C(13)-C(4)-C(5)-C(2)	-90.1(4)
C(3)-C(4)-C(5)-C(2)	21.6(3)
C(2)-C(5)-C(6)-C(7)	-102.6(5)
C(4)-C(5)-C(6)-C(7)	146.9(4)
C(5)-C(6)-C(7)-C(8)	89.3(5)
C(6)-C(7)-C(8)-O(27)	178.4(3)
C(6)-C(7)-C(8)-C(15)	70.1(4)
C(6)-C(7)-C(8)-C(9)	-61.5(4)
O(27)-C(8)-C(9)-C(10)	-155.8(3)
C(15)-C(8)-C(9)-C(10)	-40.5(5)
C(7)-C(8)-C(9)-C(10)	89.4(4)
O(27)-C(8)-C(9)-C(16)	-31.3(4)
C(15)-C(8)-C(9)-C(16)	84.0(4)
C(7)-C(8)-C(9)-C(16)	-146.1(3)
C(16)-C(9)-C(10)-C(11)	88.1(4)
C(8)-C(9)-C(10)-C(11)	-147.8(4)
C(12)-C(1)-C(11)-C(10)	-126.8(4)
C(2)-C(1)-C(11)-C(10)	53.1(5)
C(9)-C(10)-C(11)-C(1)	59.5(5)

C(10)-C(9)-C(16)-O(31)	-54.2(4)
C(8)-C(9)-C(16)-O(31)	-179.0(3)
C(10)-C(9)-C(16)-C(17)	-175.5(3)
C(8)-C(9)-C(16)-C(17)	59.7(4)
O(31)-C(16)-C(17)-C(22)	-163.1(3)
C(9)-C(16)-C(17)-C(22)	-43.6(5)
O(31)-C(16)-C(17)-C(18)	13.8(6)
C(9)-C(16)-C(17)-C(18)	133.3(4)
C(22)-C(17)-C(18)-C(19)	-1.1(6)
C(16)-C(17)-C(18)-C(19)	-177.9(4)
C(22)-C(17)-C(18)-C(25)	178.2(4)
C(16)-C(17)-C(18)-C(25)	1.3(6)
C(17)-C(18)-C(19)-C(20)	-0.4(6)
C(25)-C(18)-C(19)-C(20)	-179.7(4)
C(18)-C(19)-C(20)-O(30)	-179.5(4)
C(18)-C(19)-C(20)-C(21)	2.0(6)
O(30)-C(20)-C(21)-C(22)	179.7(3)
C(19)-C(20)-C(21)-C(22)	-1.8(6)
O(30)-C(20)-C(21)-C(23)	-1.1(6)
C(19)-C(20)-C(21)-C(23)	177.4(4)
C(18)-C(17)-C(22)-O(27)	179.9(3)
C(16)-C(17)-C(22)-O(27)	-3.0(5)
C(18)-C(17)-C(22)-C(21)	1.1(6)
C(16)-C(17)-C(22)-C(21)	178.2(4)
C(20)-C(21)-C(22)-O(27)	-178.5(3)
C(23)-C(21)-C(22)-O(27)	2.3(6)
C(20)-C(21)-C(22)-C(17)	0.3(6)
C(23)-C(21)-C(22)-C(17)	-178.9(4)
C(22)-C(21)-C(23)-O(29)	178.4(4)
C(20)-C(21)-C(23)-O(29)	-0.8(6)
C(22)-C(21)-C(23)-O(28)	-0.4(6)
C(20)-C(21)-C(23)-O(28)	-179.6(4)
C(17)-C(18)-C(25)-C(26)	17.6(6)
C(19)-C(18)-C(25)-C(26)	-163.2(4)
C(18)-C(25)-C(26)-O(31)	-52.3(5)
C(17)-C(22)-O(27)-C(8)	35.1(5)
C(21)-C(22)-O(27)-C(8)	-146.1(3)
C(15)-C(8)-O(27)-C(22)	-138.3(4)

C(9)-C(8)-O(27)-C(22)	-15.4(5)
C(7)-C(8)-O(27)-C(22)	106.3(4)
C(17)-C(16)-O(31)-C(26)	-48.8(5)
C(9)-C(16)-O(31)-C(26)	-168.7(3)
C(25)-C(26)-O(31)-C(16)	70.9(5)

Symmetry transformations used to generate equivalent atoms: