Indole Alkaloid Glucosides from the Roots of *Isatis indigotica*

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Supporting Information

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We dedicate this paper to Prof. Zhong-Jian Jia on the occasion of her 85th birthday.

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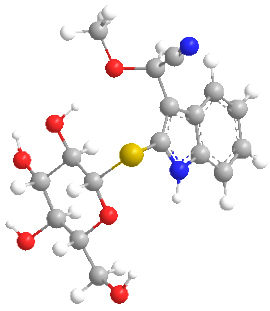
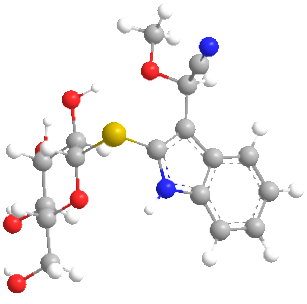
ECD Calculation of 3 and **4.**

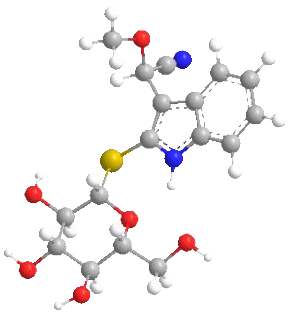
Conformational analysis of **3** was performed on via Monte Carlo searching with the MMFF94 molecular mechanics force field using the Spartan 10 software [S1]. 14 conformers having relative energy within 2 kcal/mol were re-optimized using DFT at the B3LYP/6-31+G(d) level via Gaussian 09 program package [S2], considering the solvent effects through conductor-like polarizable continuum model (CPCM) with the dielectric constant of MeOH (ε = 32.6). The B3LYP/6-31G+(d) harmonic vibrational frequencies were calculated to confirm their stability. The energies, oscillator strengths, and rotational strengths of the first 40 electronic excitations of the conformers were calculated using the TDDFT methodology at the B3LYP/6-311++G (2d,2p) level in gas phase, and yield 6 conformers with relative Gibbs free energies (ΔG) under 2 kcal/mol (Figure S1). The ECD spectra of the 6 conformers were then simulated using the Gaussian function (σ = 0.28 eV), respectively. To gain the final spectrum of **3**, the simulated spectra of the 6 conformers were averaged based on their Gibbs free energies (G). The ECD spectrum of the enantiomeric **3** was depicted by inverting that of **3.** In the 200-400 nm region, compared to the Cotton effects at 213, 229, 270 and 297 nm in the experimental CD spectrum, the calculated ECD spectrum showed four corresponding peaks at 203, 225, 263 and 295 nm, respectively (Figure S2).



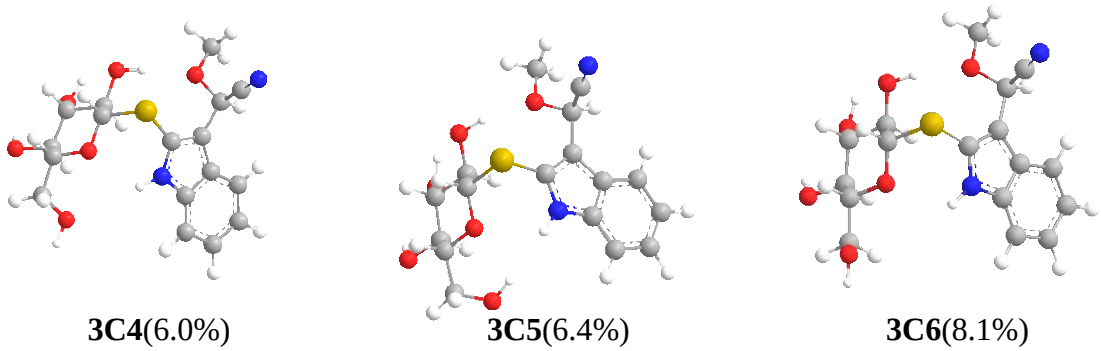
3C1(59.8%)



3C2(11.3%)



3C3(2.6%)



3C4(6.0%) **3C5**(6.4%) **3C6**(8.1%)

Figure S1. The re-optimized conformers of **3** and their equilibrium populations.

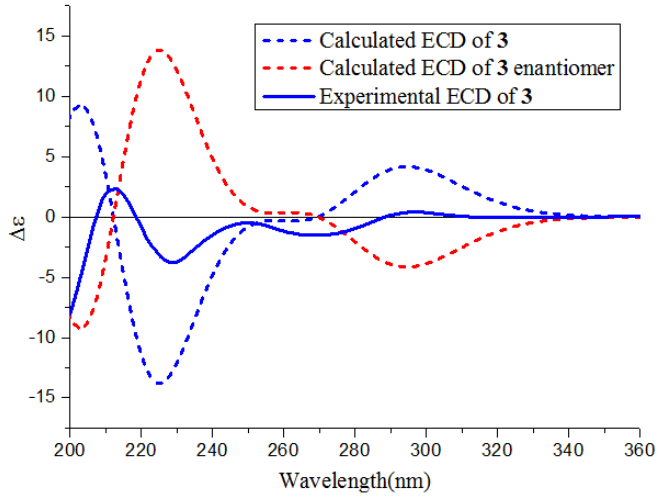


Figure S2. The experimental CD spectra (full line) of **3** (blue) and the calculated ECD spectra (dashed line) of **3** (blue) and its enantiomer (red).

Conformational analysis of **4** and re-optimization were carried out using the same protocol as **3,** and afforded 11 conformers with relative Gibbs free energies (ΔG) under 2 kcal/mol (Figure S3). The ECD spectra of the 11 conformers were simulated using the Gaussian function (σ = 0.28 eV), respectively. Then, the final spectrum of **4** was fitted by averaging the spectra of the lowest energy conformers according to their Gibbs free energies (G). The ECD spectrum of the enantiomeric **4** was depicted by inverting that of **4**. In the 200-400 nm region, compared to the Cotton effects at 218, 232, and 292nm in the experimental CD spectrum of **4**, the calculated ECD spectrum of **4** showed three corresponding peaks at 229, 260, and 292 nm, respectively (Figure S4).

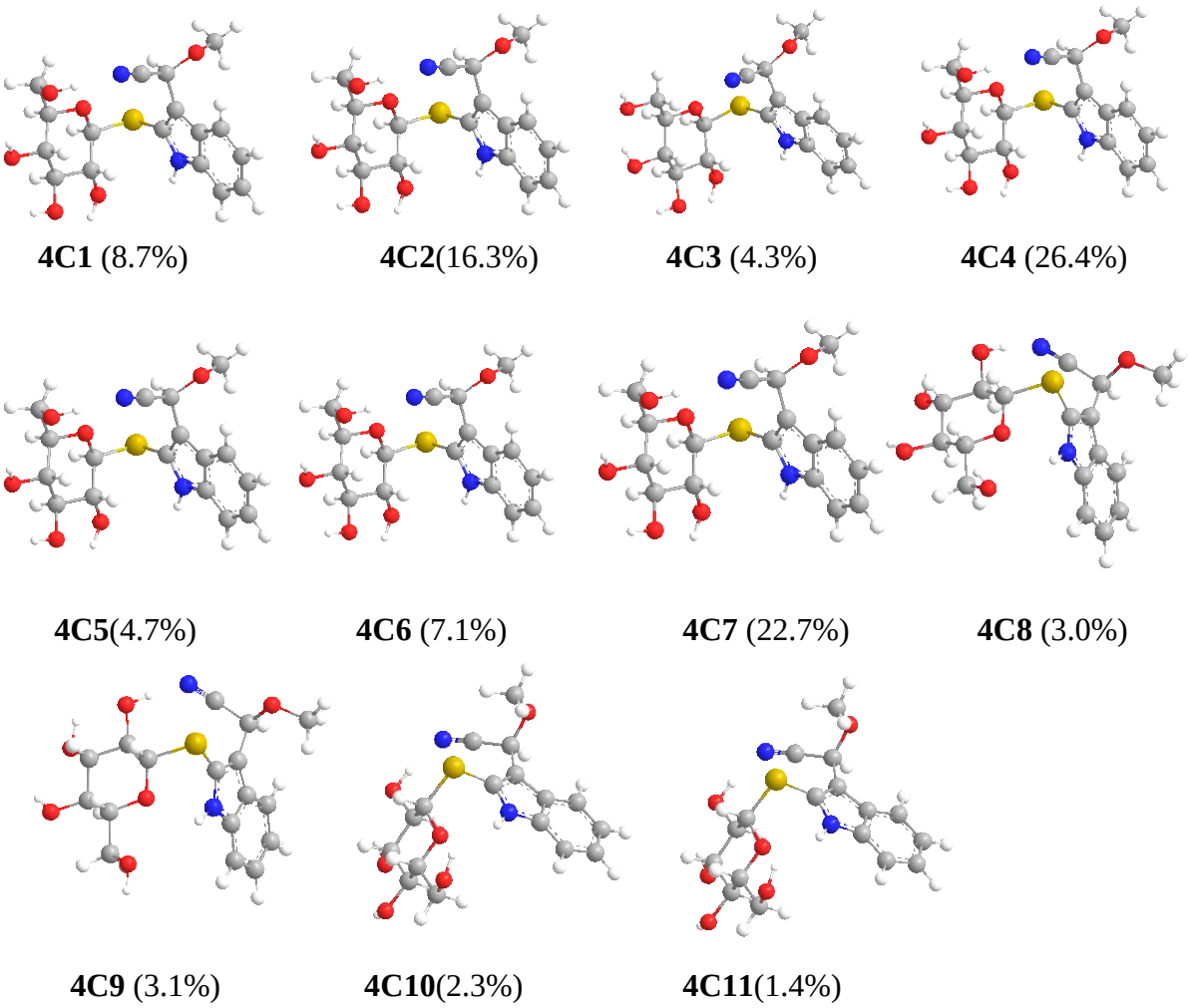


Figure S3. The re-optimized conformers of **4** and their equilibrium populations.

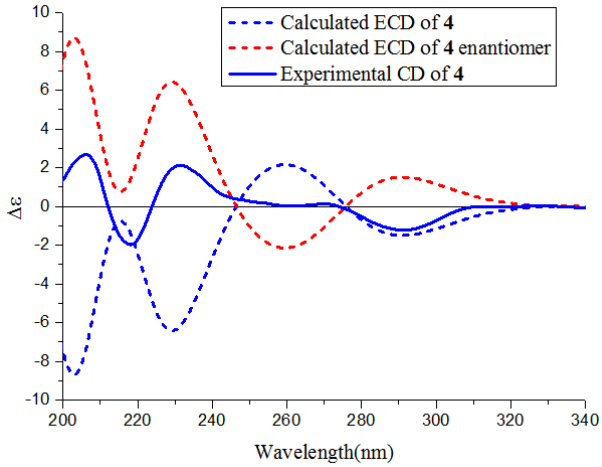
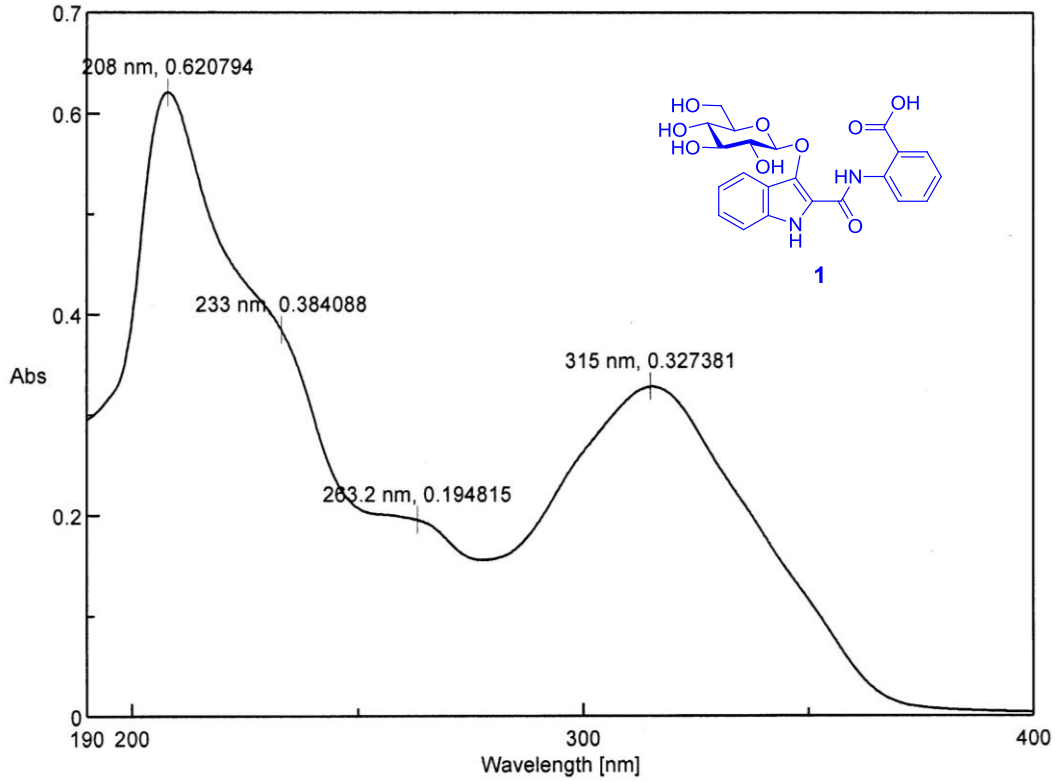


Figure S4. The experimental CD spectrum (full line) of **4** (blue) and the calculated ECD spectra (dashed line) of **4** (blue) and its enantiomer (red).

References

[S1] Spartan 10; Wavefunction, Inc.: Irvine, CA. (2010)

[S2] Gaussian 09, Gaussian, Inc., www.gaussian.com.



BLG-L-119

[Comment]
Sample Name BLG-L-119
Comment 0.02
User
Division UV
Company 324

[Measurement Information]
Instrument Name V-650
Model Name V-650
Serial No. A034461150

Accessory PSC-718
Accessory S/N A001761114
Position 1
Cell Length 10 mm
Temperature 19.93 C
Control Sonsor Holder
Monitor Sensor Holder
Start Mode Start immediately

Photometric Mode Abs
Measurement range 400 - 190 nm
Data pitch 0.2 nm
Band width(UV/Vis) 2.0 nm
Response Medium
Scanning speed 200 nm/min
Source Change 340 nm
Light Source D2/WI
Filter Exchange Step
Correction Baseline

[Data Information]
Creation Date 2014-6-10 9:58

Data array type Linear data array
Horizontal Wavelength [nm]
Vertical Abs
Start 400 nm
End 190 nm
Data pitch 0.2 nm
Data points 1051

Figure S5. The UV spectrum of compound **1** in MeOH.

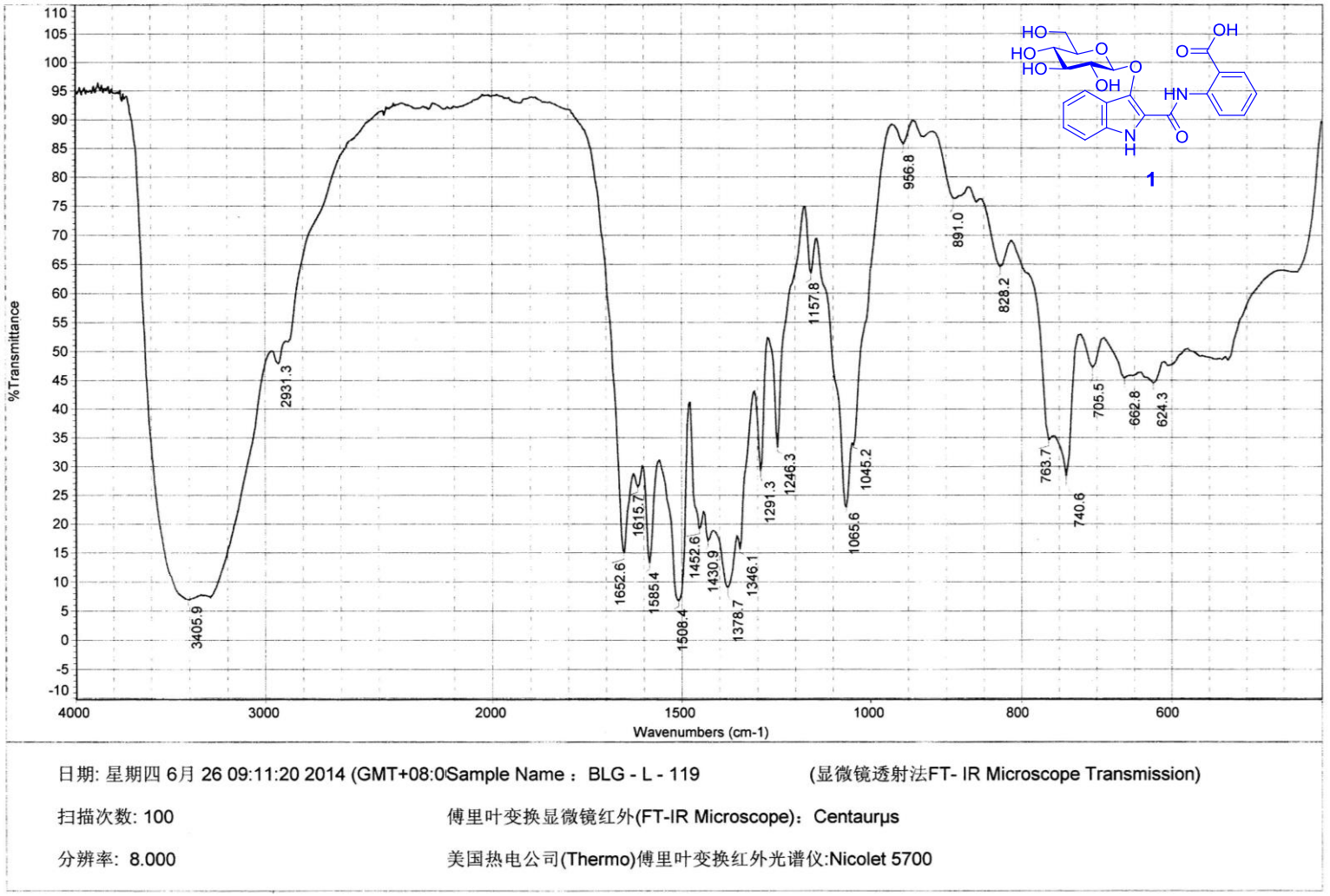


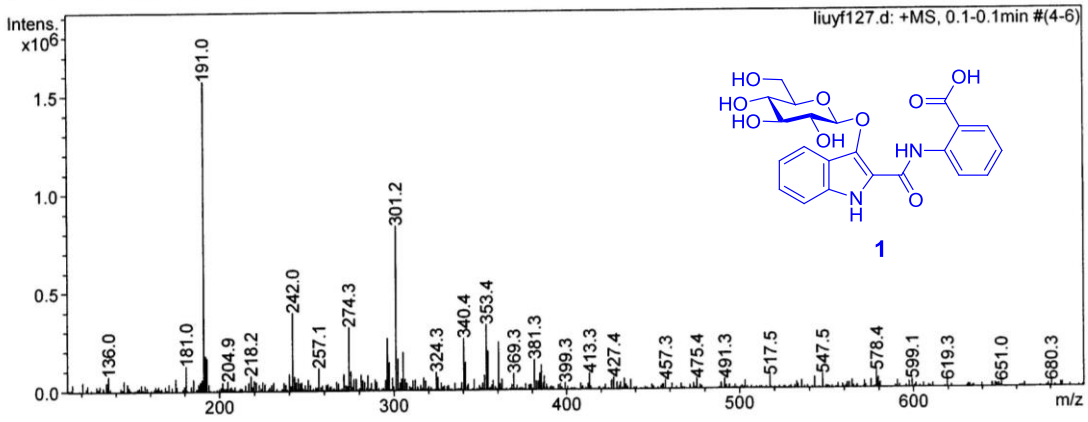
Figure S6. The IR spectrum of compound **1**.

Single Mass Spectrum Deconvolution Report

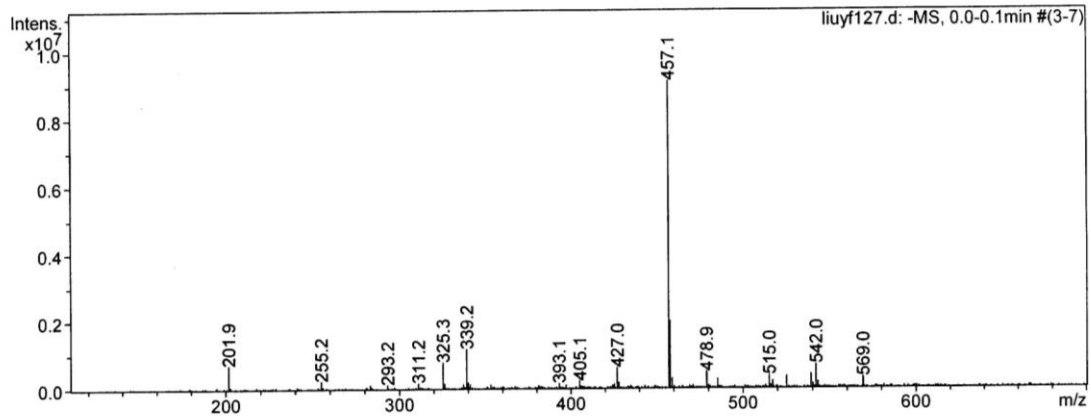
Analysis Name: liuyf127.d **Instrument:** LC-MSD-Trap-SL **Print Date:** 3/25/2014 12:17:52 PM
Method: TEST.MS **Operator:** Operator **Acq. Date:** 3/25/2014 11:35:28 AM
Sample Name: BLG-L-119
Analysis Info:

Acquisition Parameter:

Mass Range Mode	Std/Normal	Trap Drive	41.8	Scan Begin	110 m/z
Ion Polarity	Positive	Octopole RF Amplitude	142.5 Vpp	Scan End	700 m/z
Ion Source Type	ESI	Capillary Exit	-100.4 Volt	Averages	5 Spectra
Dry Temp (Set)	330 °C	Skimmer	-40.0 Volt	Max. Accu Time	200000 µs
Nebulizer (Set)	15.00 psi	Oct 1 DC	-12.00 Volt	ICC Target	20000
Dry Gas (Set)	6.00 l/min	Oct 2 DC	-1.70 Volt	Charge Control	on



Component Molecular Mass Molecule Absolute Abundance Relative Abundance



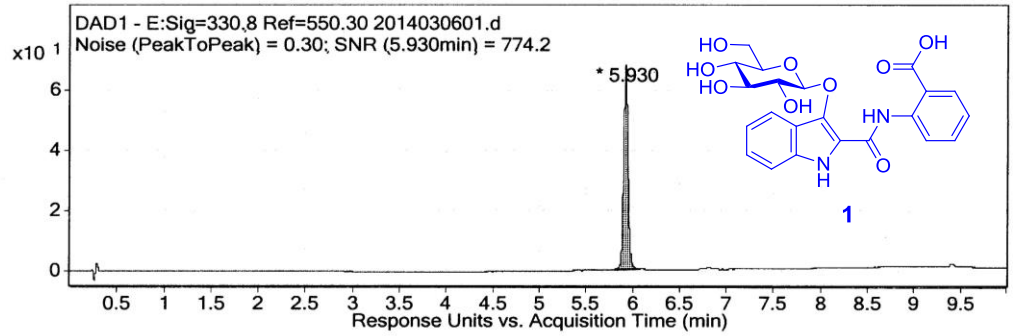
Component Molecular Mass Molecule Absolute Abundance Relative Abundance

Figure S7. The ESI mass spectrum of compound **1**.

Qualitative Analysis Report

Data Filename	2014030601.d	**Sample Name**	BLG-L-119
Sample Type	Sample	**Position**	P1-C1
Instrument Name	Instrument 1	**User Name**	
Acq Method		**IRM Calibration Status**	[redacted]
DA Method	TEST LCMS.m	**Comment**	

User Chromatograms



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.802	5.93	6.09	67.77	229.61	100	774.2

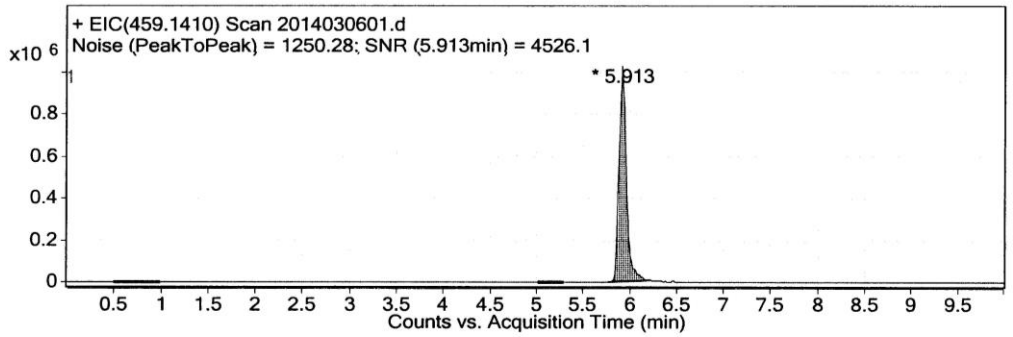
Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	0.296592712

Noise Regions

Start	End
0.5	1
5	5.3
9.99	11

Fragmentor Voltage 135 **Collision Energy** 0 **Ionization Mode** ESI



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.768	5.913	6.219	1025579	5658856	100	4526.1

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	1250.277466

Noise Regions

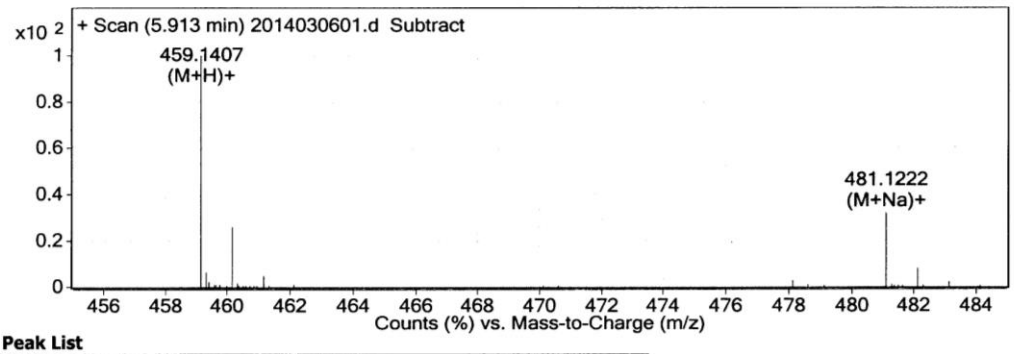
Start	End
0.5	1
5	5.3
9.99	11

User Spectra

Figure S8. The (+)-HRESIMS report of compound **1**, page 1.

Qualitative Analysis Report

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	Esi



Peak List

m/z	z	Abund	Formula	Ion
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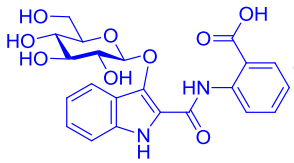
294.1551	1	457844		
297.0875	1	808021		
299.1099		375037		
459.1407	1	1027863	C25 H21 N3 O6	(M+H)+
460.1434	1	267663	C25 H21 N3 O6	(M+H)+
481.1222	1	326710	C25 H20 N3 Na O6	(M+Na)+
575.2313	1	230201		
939.2543	1	353760		
940.2563	1	179292		



1

Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	500
O	0	90
N	0	5
S	0	5
Cl	0	0
Br	0	0
Si	0	0
F	0	0
P	0	0

Formula Calculator Results

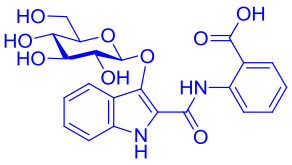
Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C22 H22 N2 O9		458.1334	458.1325	-1.95	C22 H23 N2 O9	99.91
C25 H20 N3 O6	TRUE	458.1334	458.1352	3.9	C25 H21 N3 O6	99.58
C20 H20 N5 O8		458.1334	458.1312	-4.89	C20 H21 N5 O8	99.51
C17 H24 N5 O8 S		458.1334	458.1346	2.46	C17 H25 N5 O8 S	98.6
C29 H20 N3 O S		458.1334	458.1327	-1.57	C29 H21 N3 O S	98.48
C19 H26 N2 O9 S		458.1334	458.1359	5.4	C19 H27 N2 O9 S	98.41
C31 H22 O2 S		458.1334	458.1341	1.37	C31 H23 O2 S	98.13
C16 H28 N O12 S		458.1334	458.1332	-0.44	C16 H29 N O12 S	97.71
C23 H26 N2 O4 S2		458.1334	458.1334	-0.06	C23 H27 N2 O4 S2	97.67
C21 H24 N5 O3 S2		458.1334	458.1321	-3	C21 H25 N5 O3 S2	97.63
C22 H22 N2 O9		458.1329	458.1325	-0.86	C22 H22 N2 Na O9	99.07
C17 H24 N5 O8 S		458.1329	458.1346	3.54	C17 H24 N5 Na O8 S	99.03
C20 H20 N5 O8		458.1329	458.1312	-3.8	C20 H20 N5 Na O8	98.83
C21 H24 N5 O3 S2		458.1329	458.1321	-1.92	C21 H24 N5 Na O3 S2	98.73
C23 H26 N2 O4 S2		458.1329	458.1334	1.02	C23 H26 N2 Na O4 S2	98.62
C29 H20 N3 O S		458.1329	458.1327	-0.48	C29 H20 N3 Na O S	98.45
C25 H20 N3 O6	TRUE	458.1329	458.1352	4.99	C25 H20 N3 Na O6	98.39
C16 H28 N O12 S		458.1329	458.1332	0.64	C16 H28 N Na O12 S	98.36

Figure S9. The (+)-HRESIMS report of compound **1**, page 2.

Qualitative Analysis Report

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C20 H28 N O7 S2		458.1329	458.1307	-4.83	C20 H28 N Na O7 S2	98.02
C31 H22 O2 S		458.1329	458.1341	2.46	C31 H22 Na O2 S	97.98

--- End Of Report ---



1

Figure S10. The (+)-HRESIMS report of compound **1**, page 3.

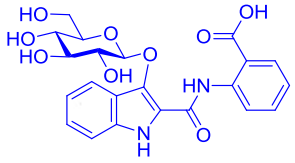
MS Formula Results: + Scan (5.913 min) Sub (2014030601.d)

m/z	Ion	Formula	Abundance
459.1407	(M+H)+	C25 H21 N3 O6	1027863.4

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☐	C22 H22 N2 O9	C22 H23 N2 O9	459.1398	99.91		458.1334	458.1325	-1.95	1.95	99.93	99.95	99.87	459.1407	13
☑	C25 H20 N3 O6	C25 H21 N3 O6	459.1425	99.58		458.1334	458.1352	3.9	3.9	99.41	99.95	99.49	459.1407	17.5
☐	C20 H20 N5 O8	C20 H21 N5 O8	459.1385	99.51		458.1334	458.1312	-4.89	4.89	99.64	99.98	99.2	459.1407	13.5
☐	C17 H24 N5 O8 S	C17 H25 N5 O8 S	459.1418	98.6		458.1334	458.1346	2.46	2.46	95.68	99.73	99.8	459.1407	8.5
☐	C29 H20 N3 O S	C29 H21 N3 O S	459.14	98.48		458.1334	458.1327	-1.57	1.57	94.92	99.87	99.92	459.1407	21.5
☐	C19 H26 N2 O9 S	C19 H27 N2 O9 S	459.1432	98.41		458.1334	458.1359	5.4	5.4	96.25	99.77	99.02	459.1407	8
☐	C31 H22 O2 S	C31 H23 O2 S	459.1413	98.13		458.1334	458.1341	1.37	1.37	93.66	99.88	99.94	459.1407	21
☐	C16 H28 N O12 S	C16 H29 N O12 S	459.1405	97.71		458.1334	458.1332	-0.44	0.44	92.21	99.74	99.99	459.1407	3.5
☐	C23 H26 N2 O4 S2	C23 H27 N2 O4 S2	459.1407	97.67		458.1334	458.1334	-0.06	0.06	92.17	99.59	100	459.1407	12
☐	C21 H24 N5 O3 S2	C21 H25 N5 O3 S2	459.1393	97.63		458.1334	458.1321	-3	3	92.59	99.54	99.7	459.1407	12.5
☐	C14 H26 N4 O11 S	C14 H27 N4 O11 S	459.1392	97.14		458.1334	458.1319	-3.39	3.39	90.89	99.71	99.61	459.1407	4
☐	C26 H24 N3 O S2	C26 H25 N3 O S2	459.1434	97.05		458.1334	458.1361	5.79	5.79	91.86	99.63	98.88	459.1407	16.5
☐	C34 H18 O2	C34 H19 O2	459.138	97.01		458.1334	458.1307	-5.98	5.98	91.65	99.87	98.8	459.1407	26

m/z	Ion	Formula	Abundance
481.1222	(M+Na)+	C25 H20 N3 Na O6	326710.4

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☐	C22 H22 N2 O9	C22 H22 N2 Na O9	481.1218	99.07		458.1329	458.1325	-0.86	0.86	99.35	96.92	99.98	481.1222	13
☐	C17 H24 N5 O8 S	C17 H24 N5 Na O8 S	481.1238	99.03		458.1329	458.1346	3.54	3.54	97.87	99.25	99.61	481.1222	8.5
☐	C20 H20 N5 O8	C20 H20 N5 Na O8	481.1204	98.83		458.1329	458.1312	-3.8	3.8	99.01	97.17	99.55	481.1222	13.5
☐	C21 H24 N5 O3 S2	C21 H24 N5 Na O3 S2	481.1213	98.73		458.1329	458.1321	-1.92	1.92	96.1	99.56	99.89	481.1222	12.5
☐	C23 H26 N2 O4 S2	C23 H26 N2 Na O4 S2	481.1226	98.62		458.1329	458.1334	1.02	1.02	95.69	99.44	99.97	481.1222	12
☐	C29 H20 N3 O S	C29 H20 N3 Na O S	481.1219	98.45		458.1329	458.1327	-0.48	0.48	95.64	98.73	99.99	481.1222	21.5
☑	C25 H20 N3 O6	C25 H20 N3 Na O6	481.1244	98.39		458.1329	458.1352	4.99	4.99	98.3	96.83	99.23	481.1222	17.5
☐	C16 H28 N O12 S	C16 H28 N Na O12 S	481.1224	98.36		458.1329	458.1332	0.64	0.64	95.02	99.11	99.99	481.1222	3.5
☐	C20 H28 N O7 S2	C20 H28 N Na O7 S2	481.1199	98.02		458.1329	458.1307	-4.83	4.83	94.71	99.48	99.28	481.1222	7.5
☐	C31 H22 O2 S	C31 H22 Na O2 S	481.1233	97.98		458.1329	458.1341	2.46	2.46	94.45	98.53	99.81	481.1222	21
☐	C14 H26 N4 O11 S	C14 H26 N4 Na O11 S	481.1211	97.94		458.1329	458.1319	-2.31	2.31	93.68	99.28	99.84	481.1222	4



1

page 1

Figure S11. The (+)-HRESIMS report of compound **1**, page 4.

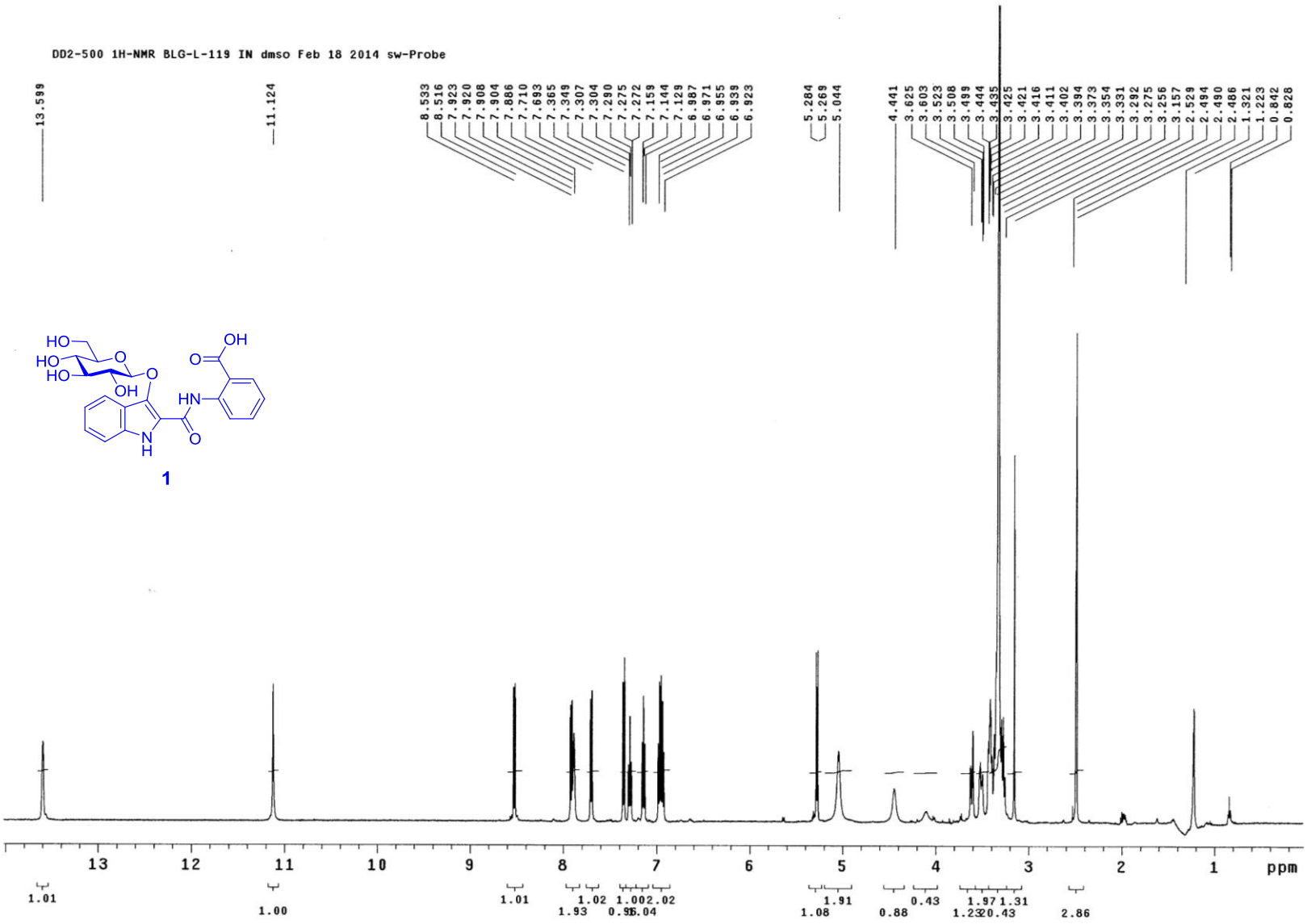


Figure S12. The ^{1}H NMR spectrum of compound **1** in DMSO-d_6 (500 MHz).

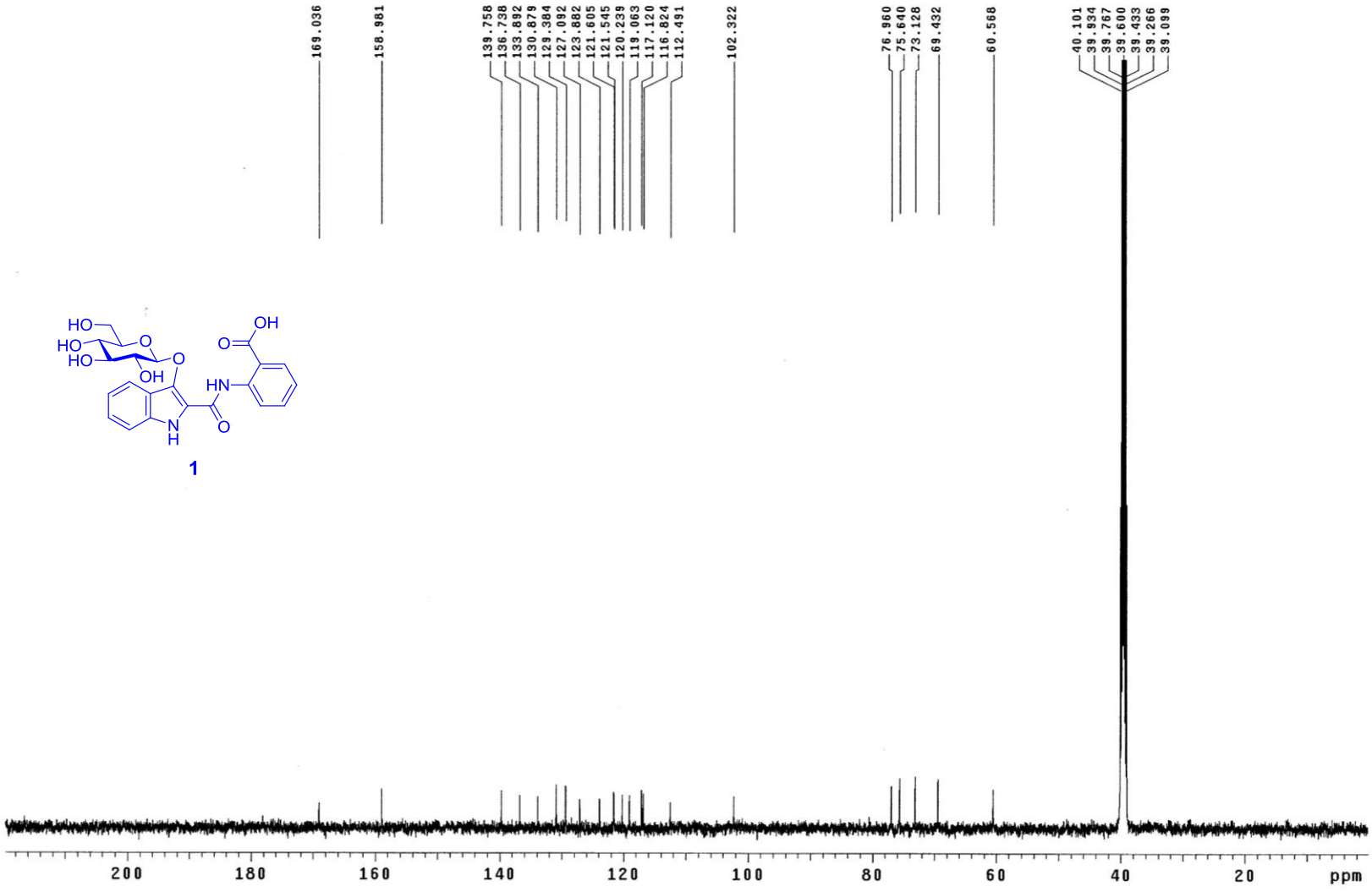


Figure S13. The ^{13}C NMR spectrum of compound **1** in DMSO-d_6 (125 MHz).

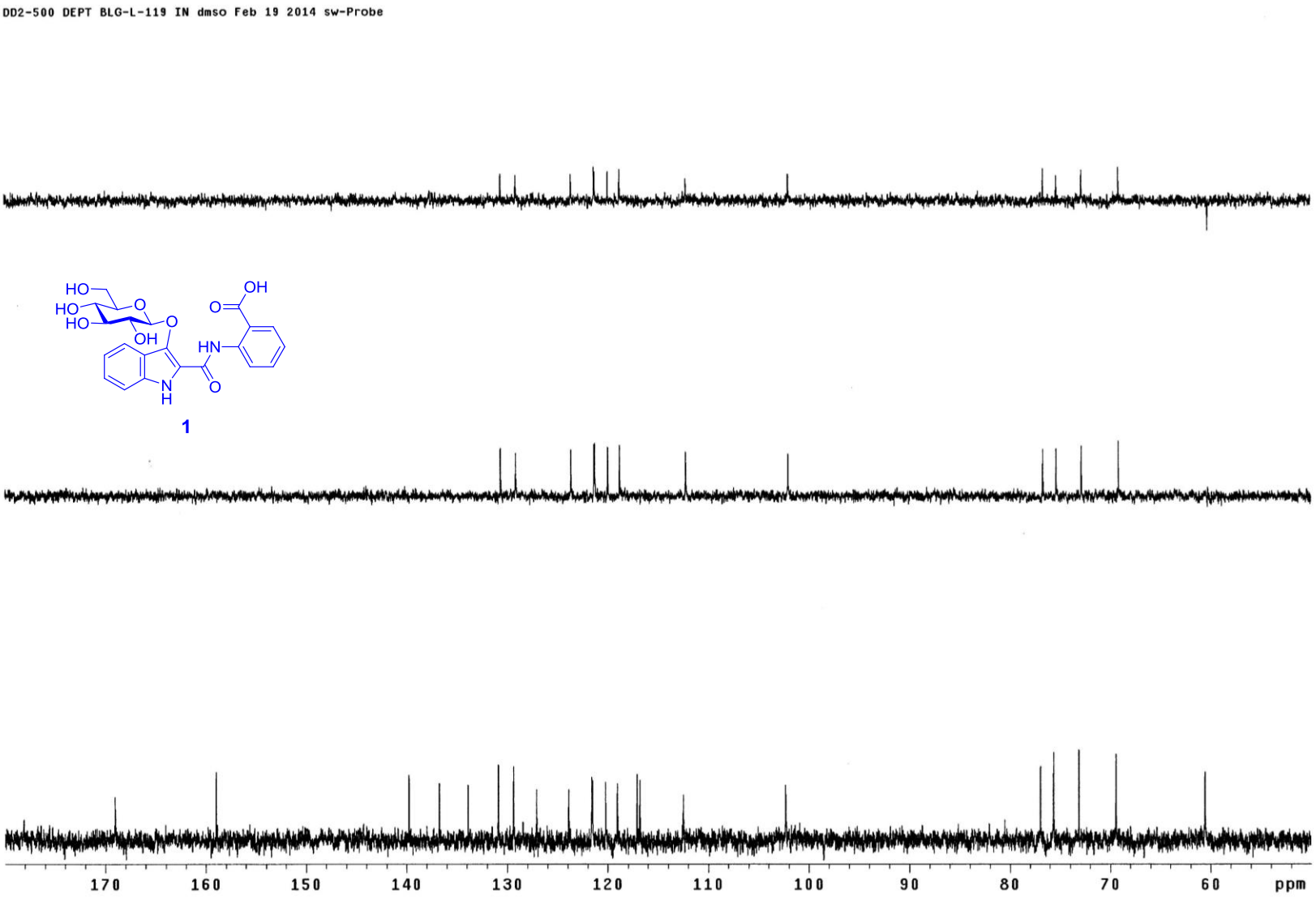


Figure S14. The DEPT spectrum of compound **1** in DMSO-d_6 (125 MHz).

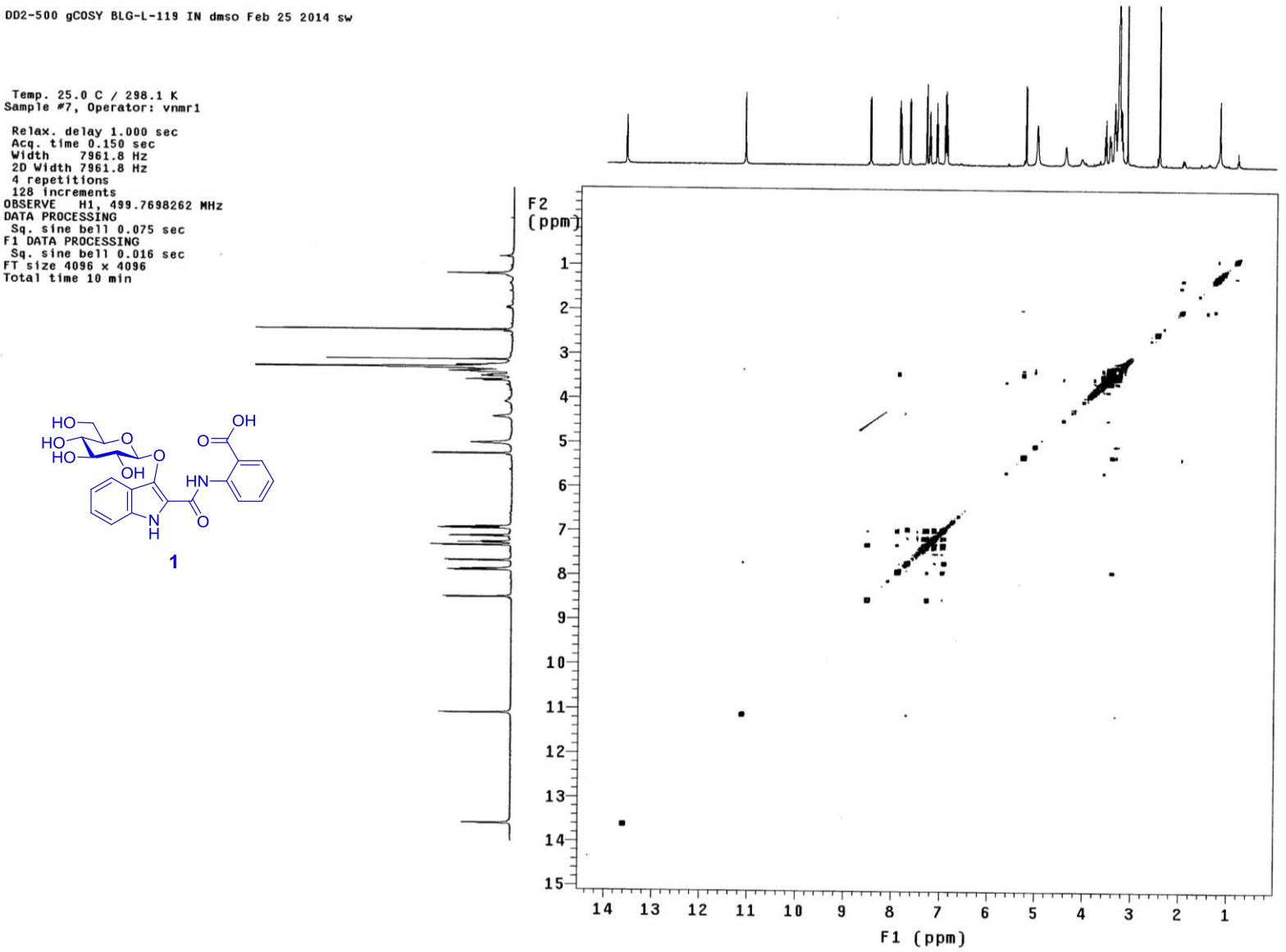


Figure S15.The ^{1}H-^{1}H COSY spectrum of compound **1** in DMSO-d_6 (500 MHz).

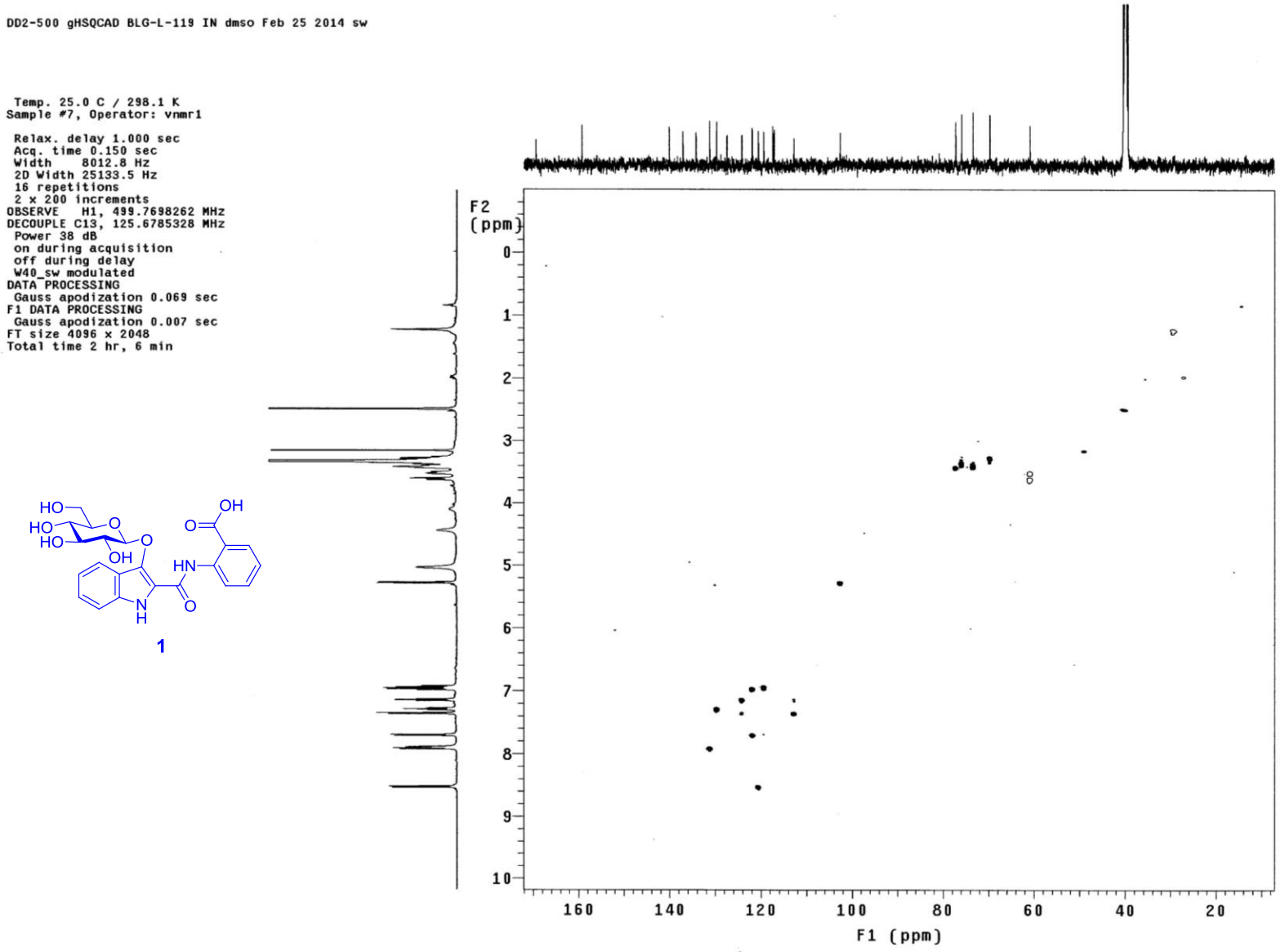


Figure S16. The HSQC spectrum of compound **1** in DMSO-d_6 (500 MHz for ^{1}H).

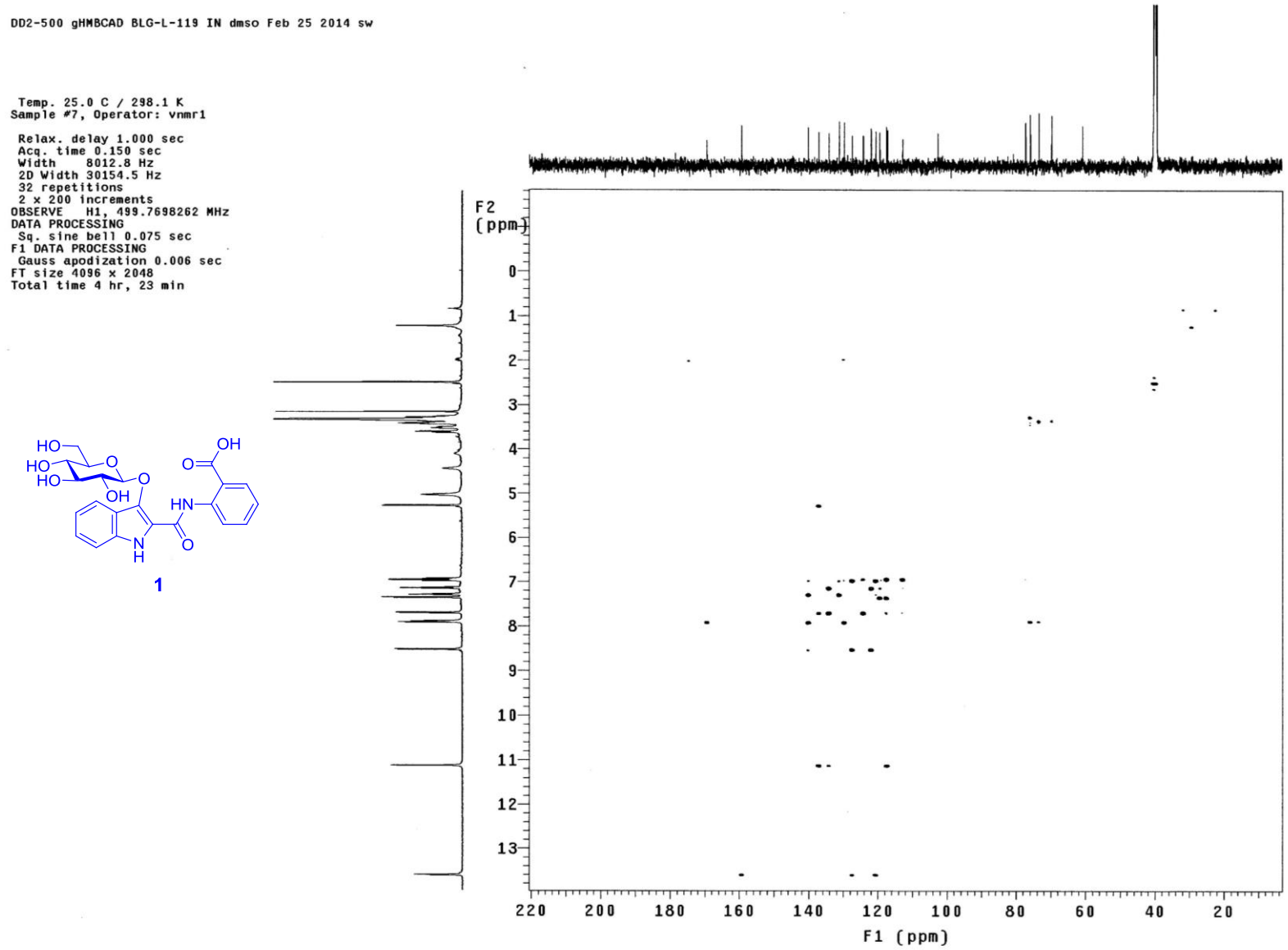


Figure S17. The HMBC spectrum of compound **1** in DMSO-d_6 (500 MHz for ^{1}H).

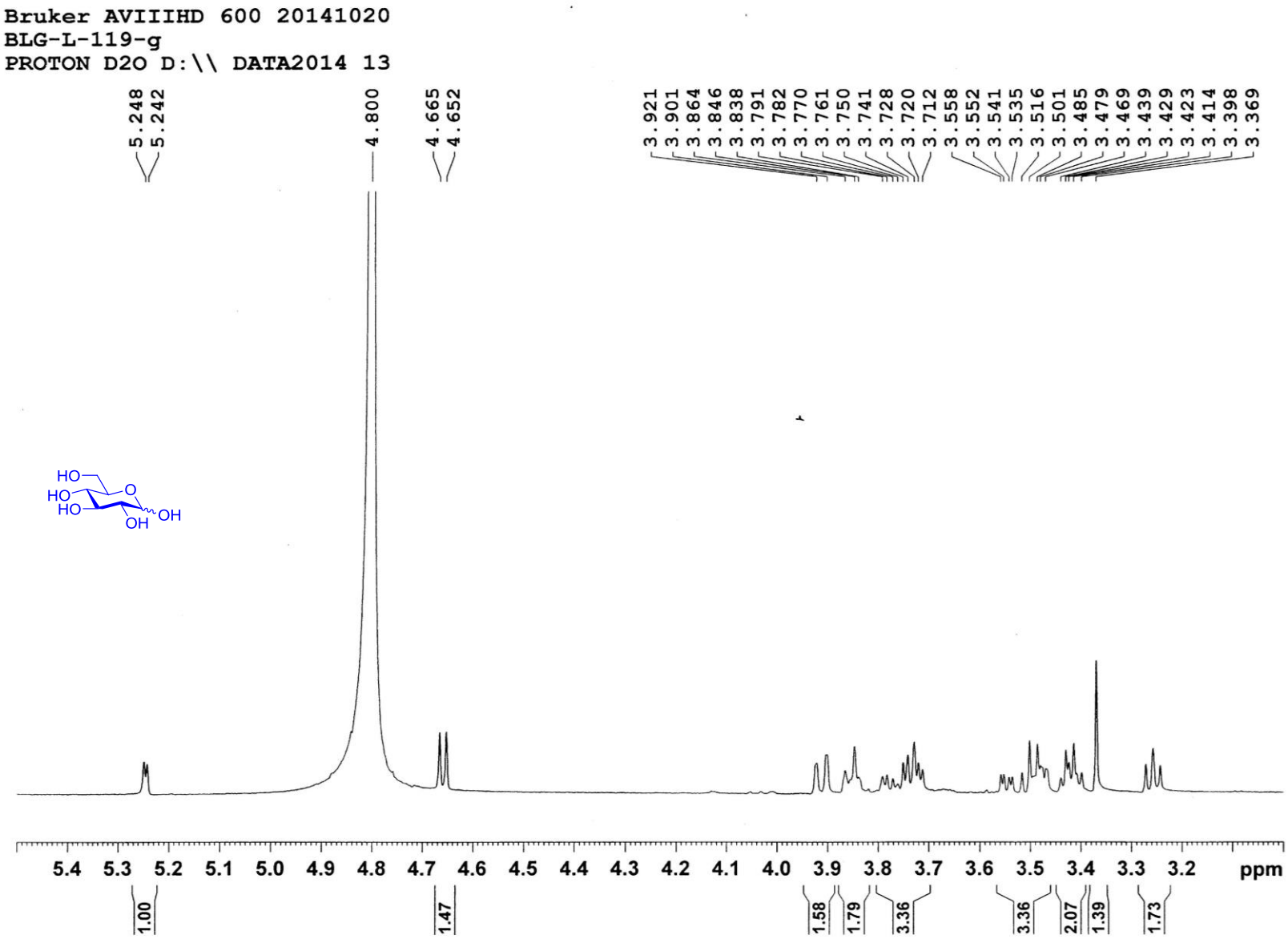
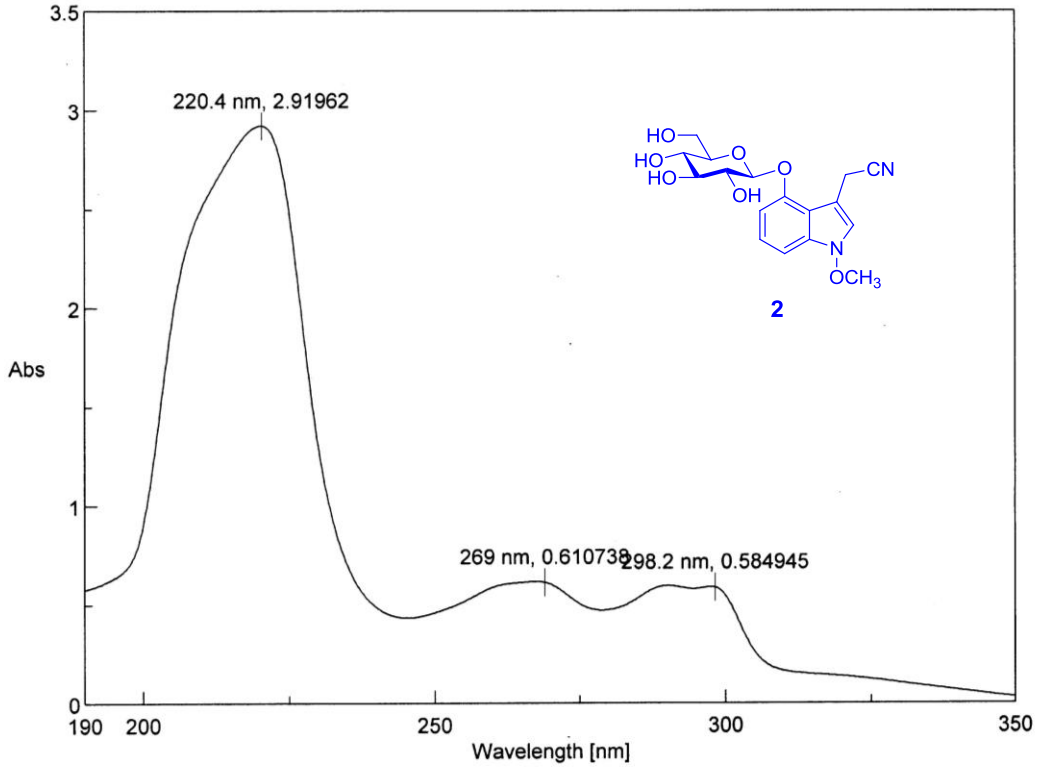


Figure S18. The ^{1}H NMR spectrum of D-glucose in D_2O (600 MHz), isolated from hydrolysate of compound **1**.



Memory-21

[Comment]
Sample Name BLG-L-47
Comment 0.02
User
Division UV
Company 324

[Measurement Information]
Instrument Name V-650
Model Name V-650
Serial No. A034461150

Accessory PSC-718
Accessory S/N A001761114
Position 1
Cell Length 10 mm
Temperature 19.96 C
Control Sonsor Holder
Monitor Sensor Holder
Start Mode Start immediately

Photometric Mode Abs
Measurement range 400 - 190 nm
Data pitch 0.2 nm
Band width(UV/Vis) 2.0 nm
Response Medium
Scanning speed 200 nm/min
Source Change 340 nm
Light Source D2/WI
Filter Exchange Step
Correction Baseline

[Data Information]
Creation Date 2014-1-1 14:10

Data array type Linear data array
Horizontal Wavelength [nm]
Vertical Abs
Start 400 nm
End 190 nm
Data pitch 0.2 nm
Data points 1051

Figure S19. The UV spectrum of compound **2** in MeOH.

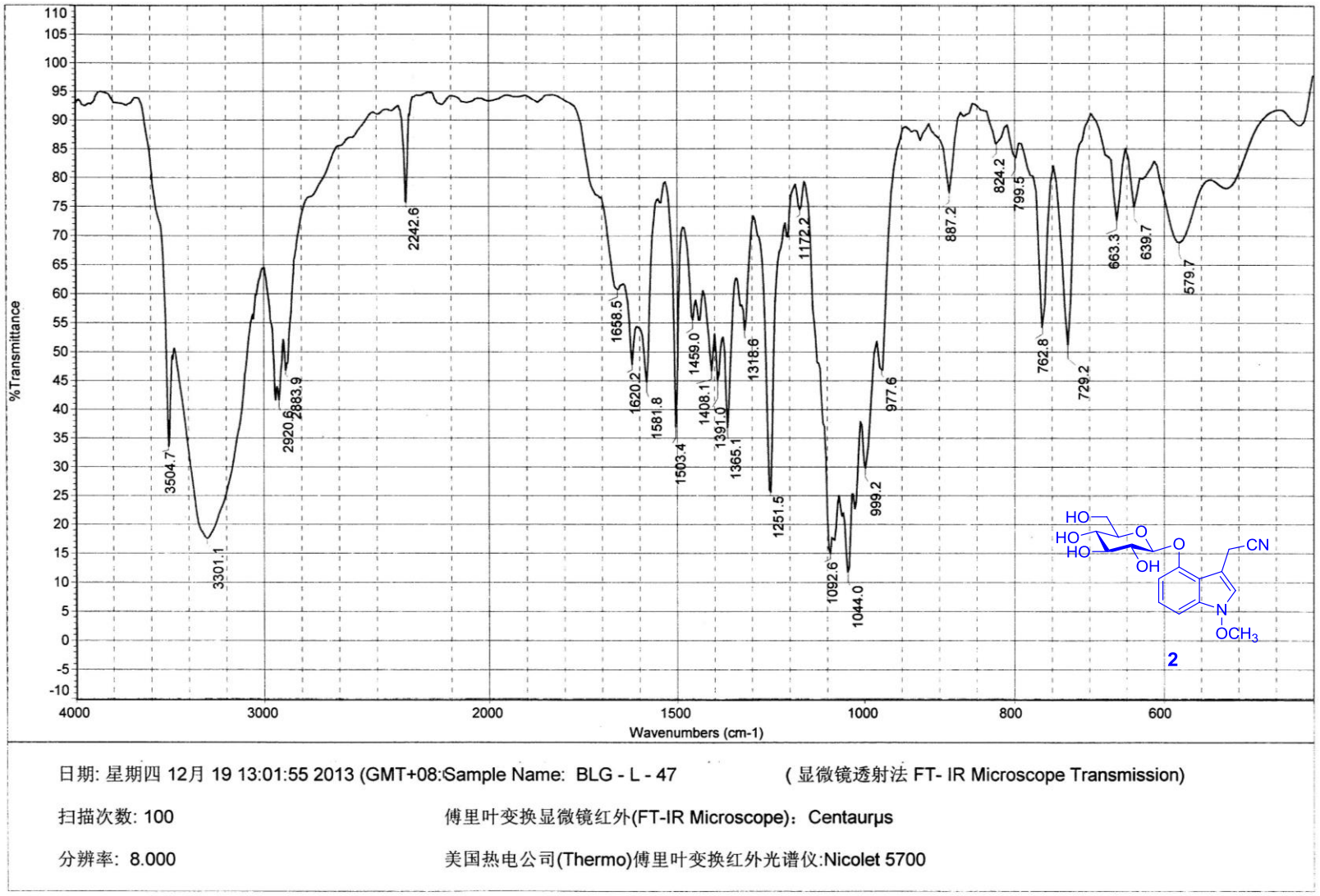


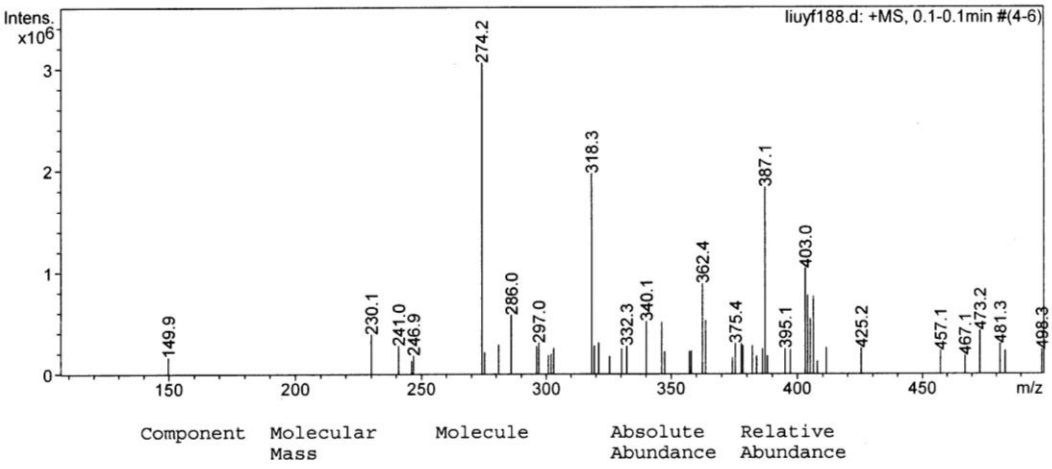
Figure S20. The IR spectrum of compound **2**.

Single Mass Spectrum Deconvolution Report

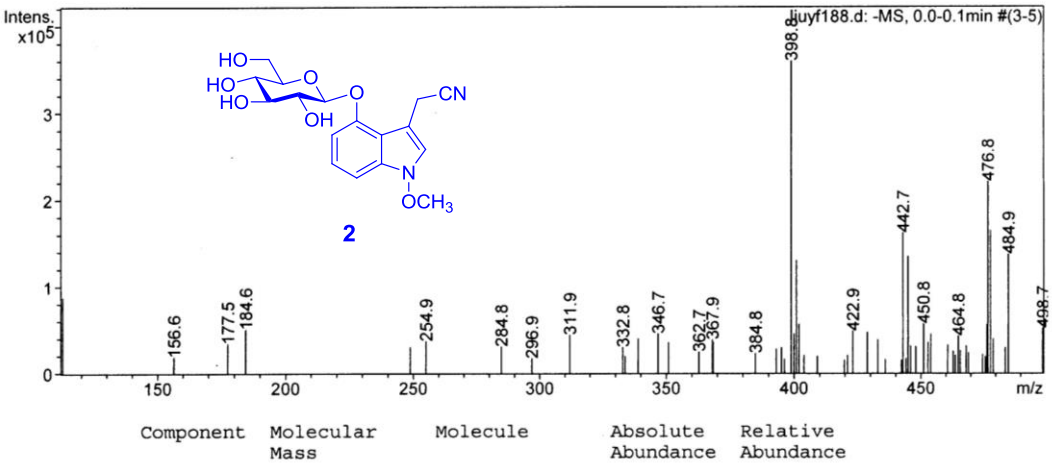
Analysis Name: liuyf188.d **Instrument:** LC-MSD-Trap-SL **Print Date:** 8/22/2013 11:00:22 AM
Method: TEST.MS **Operator:** Operator **Acq. Date:** 8/22/2013 10:52:42 AM
Sample Name: BLG-L-47
Analysis Info:

Acquisition Parameter:

Mass Range Mode	Std/Normal	Trap Drive	53.0	Scan Begin	100 m/z
Ion Polarity	Positive	Octopole RF Amplitude	171.0 Vpp	Scan End	500 m/z
Ion Source Type	ESI	Capillary Exit	-121.0 Volt	Averages	5 Spectra
Dry Temp (Set)	330 °C	Skimmer	-40.0 Volt	Max. Accu Time	200000 µs
Nebulizer (Set)	15.00 psi	Oct 1 DC	-12.00 Volt	ICC Target	348
Dry Gas (Set)	6.00 l/min	Oct 2 DC	-1.70 Volt	Charge Control	on



Component	Molecular Mass	Molecule	Absolute Abundance	Relative Abundance



Component	Molecular Mass	Molecule	Absolute Abundance	Relative Abundance

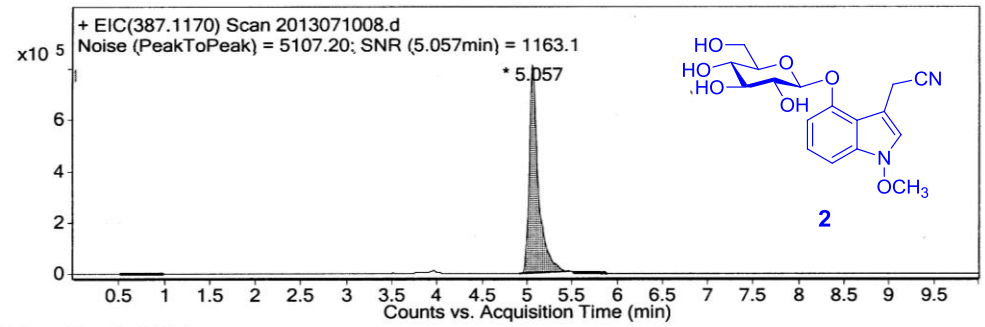
Figure S21. The ESI mass spectrum of compound **2**.

Qualitative Analysis Report

Data Filename	2013071008.d	**Sample Name**	BLG-L-47
Sample Type	Sample	**Position**	P1-C8
Instrument Name	Instrument 1	**User Name**	
Acq Method		**IRM Calibration Status**	[redacted]
DA Method	TEST LCMS.m	**Comment**	

User Chromatograms

Fragmentor Voltage 135 **Collision Energy** 0 **Ionization Mode** ESI



Integration Peak List

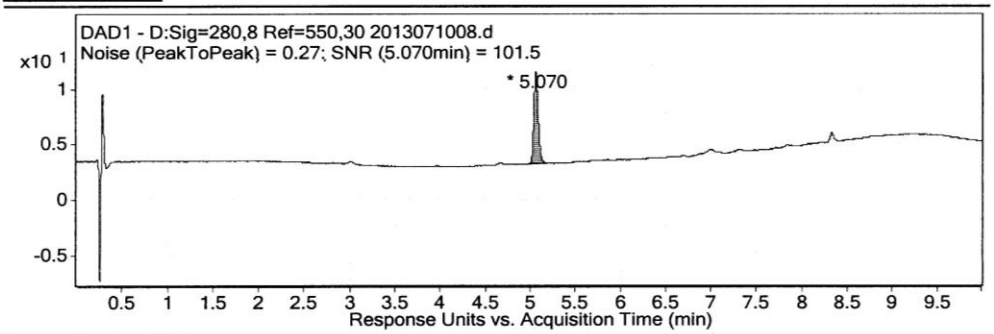
Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	4.912	5.057	5.475	812989	5940443	100	1163.1

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	5107.203125

Noise Regions

Start	End
0.5	1
5.5	5.9
9.99	11



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	4.976	5.07	5.193	8.28	27.49	100	101.5

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	0.270843506

Noise Regions

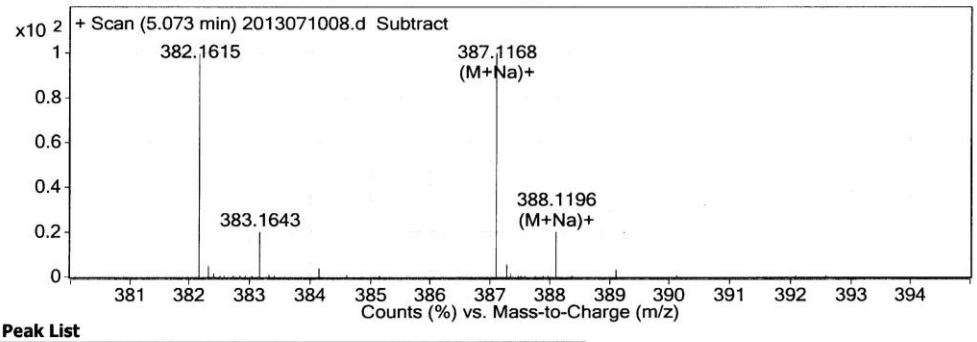
Start	End
0.5	1
5.5	5.9
9.99	11

User Spectra

Figure S22.The (+)-HRESIMS report of compound **2**, page 1.

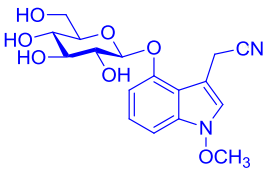
Qualitative Analysis Report

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	Esi



Peak List

m/z	z	Abund	Formula	Ion
203.0815	1	488406		
204.0842	1	63975		
382.1615	1	789822		
383.1643	1	156850		
387.1168	1	793402	C17 H20 N2 Na O7	(M+Na)+
388.1196	1	159952	C17 H20 N2 Na O7	(M+Na)+
396.1763		53934		
751.2435	1	464328		
752.2464	1	178017		
753.2474	1	48170		



2

Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	500
O	0	90
N	0	5
S	0	5
Cl	0	2
Br	0	0
Si	0	0
F	0	0
P	0	0

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C17 H20 N2 O7	TRUE	364.1276	364.1271	-1.47	C17 H20 N2 Na O7	99.96
C22 H20 O5		364.1276	364.1311	9.59	C22 H20 Na O5	98.25
C21 H20 N2 O2 S		364.1276	364.1245	-8.34	C21 H20 N2 Na O2 S	97.99
C14 H24 N2 O7 S		364.1276	364.1304	7.79	C14 H24 N2 Na O7 S	97.96
C26 H20 S		364.1276	364.1286	2.71	C26 H20 Na S	97.55
C18 H24 N2 O2 S2		364.1276	364.1279	0.91	C18 H24 N2 Na O2 S2	97.45
C9 H24 N4 O9 S		364.1276	364.1264	-3.27	C9 H24 N4 Na O9 S	96.82
C29 H16		364.1276	364.1252	-6.54	C29 H16 Na	96.23

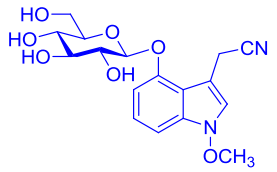
--- End Of Report ---

Figure S23.The (+)-HRESIMS report of compound **2**, page 2.

MS Formula Results: + Scan (5.073 min) Sub (2013071008.d)

m/z	Ion	Formula	Abundance
387.1168	(M+Na)+	C17 H20 N2 Na O7	793401.9

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☑	C17 H20 N2 O7	C17 H20 N2 Na O7	387.1163	99.96		364.1276	364.1271	-1.47	1.47	99.97	99.98	99.94	387.1168	9
☐	C22 H20 O5	C22 H20 Na O5	387.1203	98.25		364.1276	364.1311	9.59	9.59	98.32	99.93	97.36	387.1168	13
☐	C21 H20 N2 O2 S	C21 H20 N2 Na O2 S	387.1138	97.99		364.1276	364.1245	-8.34	8.34	96.51	99.77	98	387.1168	13
☐	C14 H24 N2 O7 S	C14 H24 N2 Na O7 S	387.1196	97.96		364.1276	364.1304	7.79	7.79	96	99.71	98.25	387.1168	4
☐	C26 H20 S	C26 H20 Na S	387.1178	97.55		364.1276	364.1286	2.71	2.71	91.92	99.82	99.79	387.1168	17
☐	C18 H24 N2 O2 S2	C18 H24 N2 Na O2 S2	387.1171	97.45		364.1276	364.1279	0.91	0.91	91.46	99.57	99.98	387.1168	8
☐	C9 H24 N4 O9 S	C9 H24 N4 Na O9 S	387.1156	96.82		364.1276	364.1264	-3.27	3.27	89.69	99.65	99.69	387.1168	0
☐	C29 H16	C29 H16 Na	387.1144	96.23		364.1276	364.1252	-6.54	6.54	88.94	99.92	98.76	387.1168	22



2

page 1

Figure S24.The (+)-HRESIMS report of compound **2**, page 3.

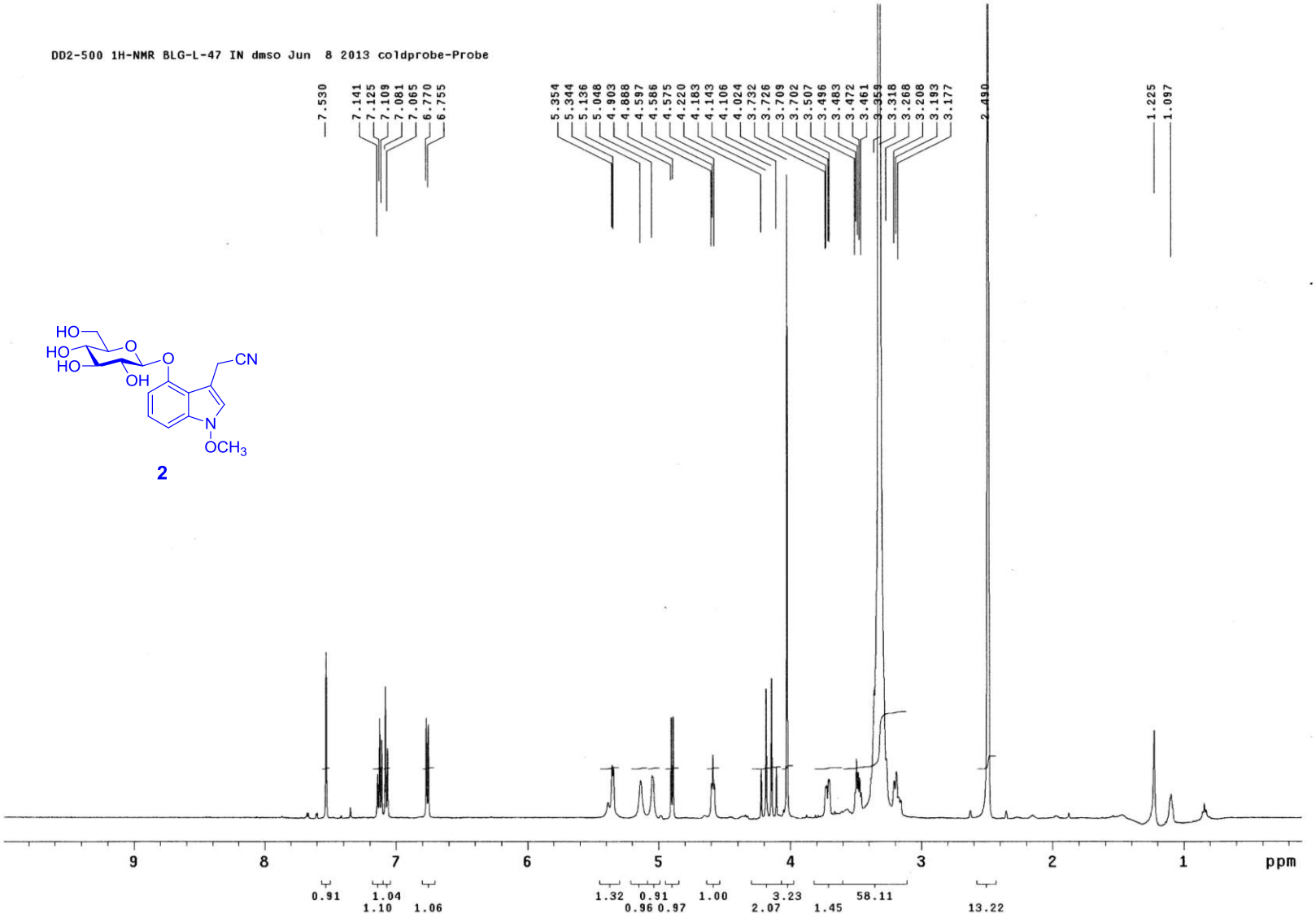


Figure S25.The ^{1}H NMR spectrum of compound **2** in DMSO-d_6 (500 MHz).

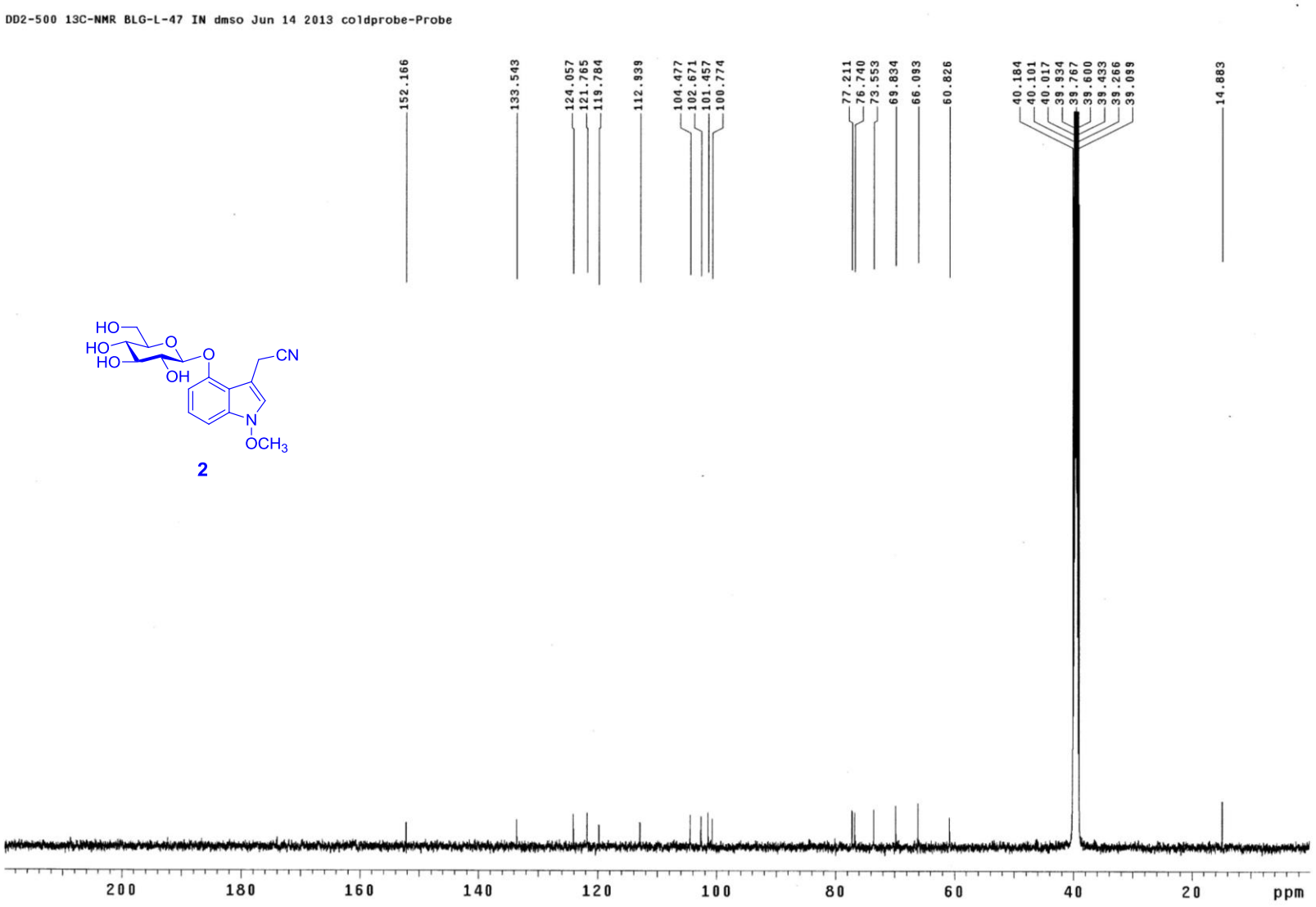


Figure S26. ^{13}C NMR spectrum of compound **2** in DMSO-d_6 (125 MHz).

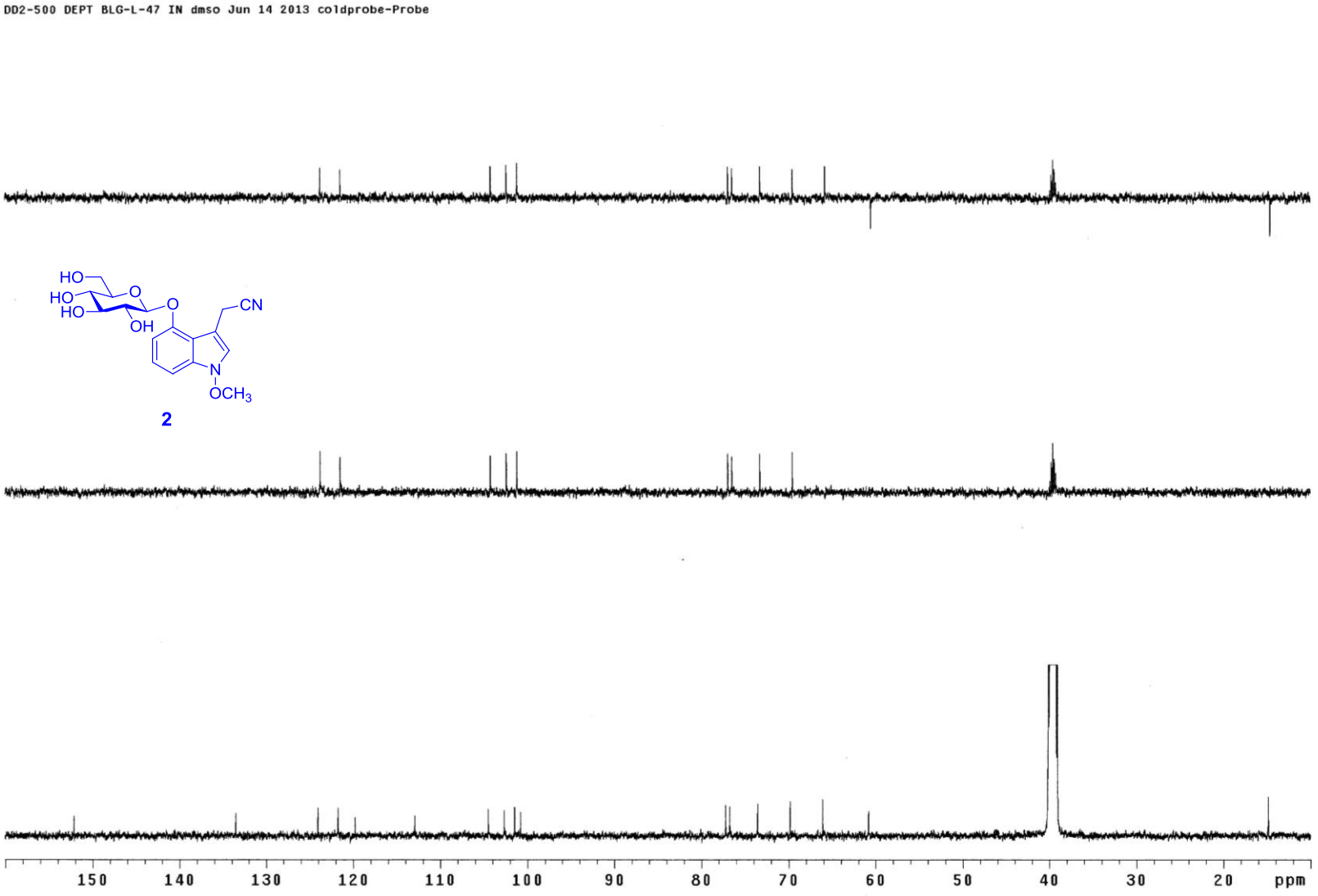


Figure S27. DEPT spectrum of compound **2** in DMSO-d_6 (125 MHz).

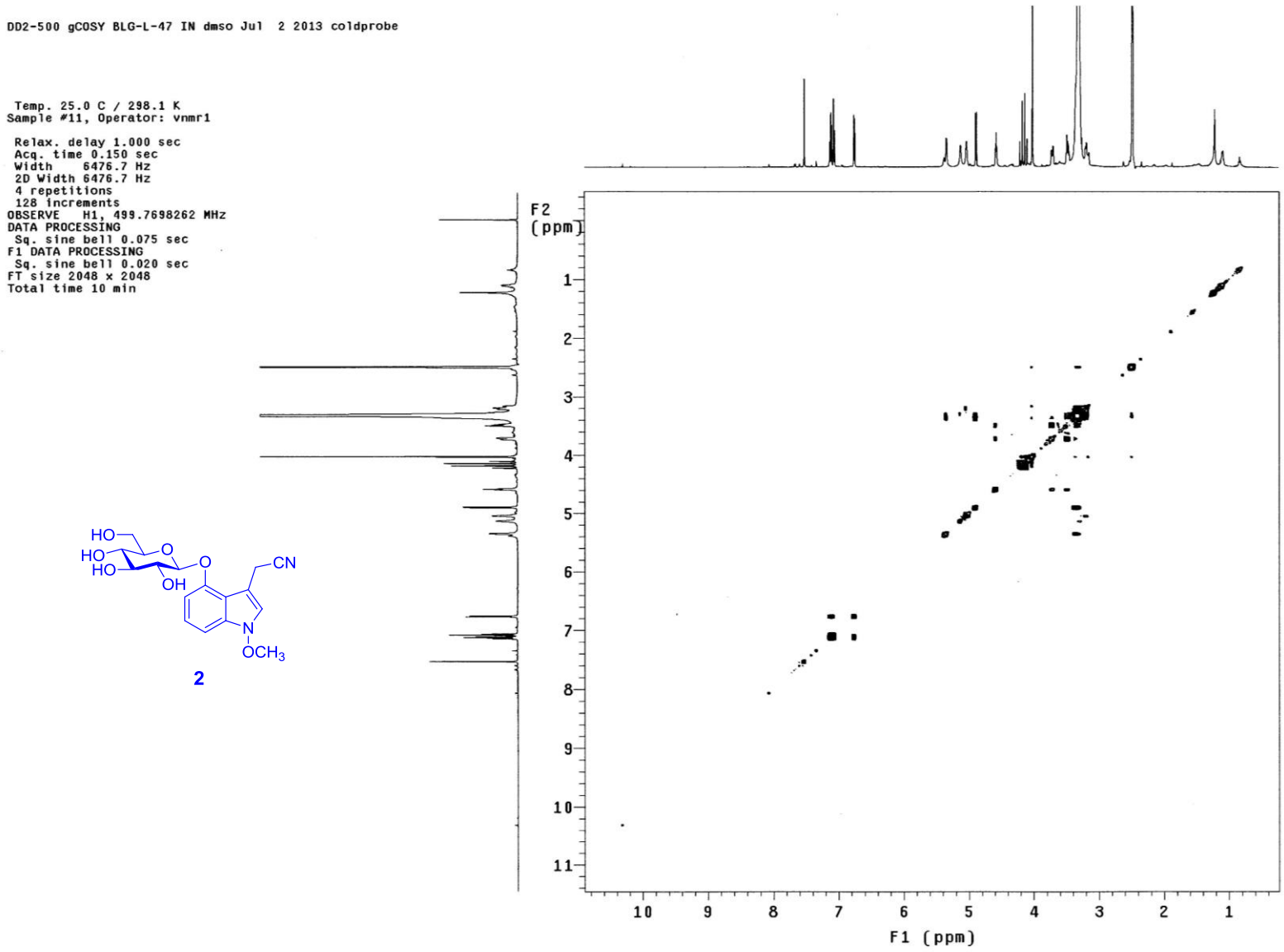


Figure S28. The ^{1}H-^{1}H COSY spectrum of compound **2** in DMSO-d_6 (500 MHz).

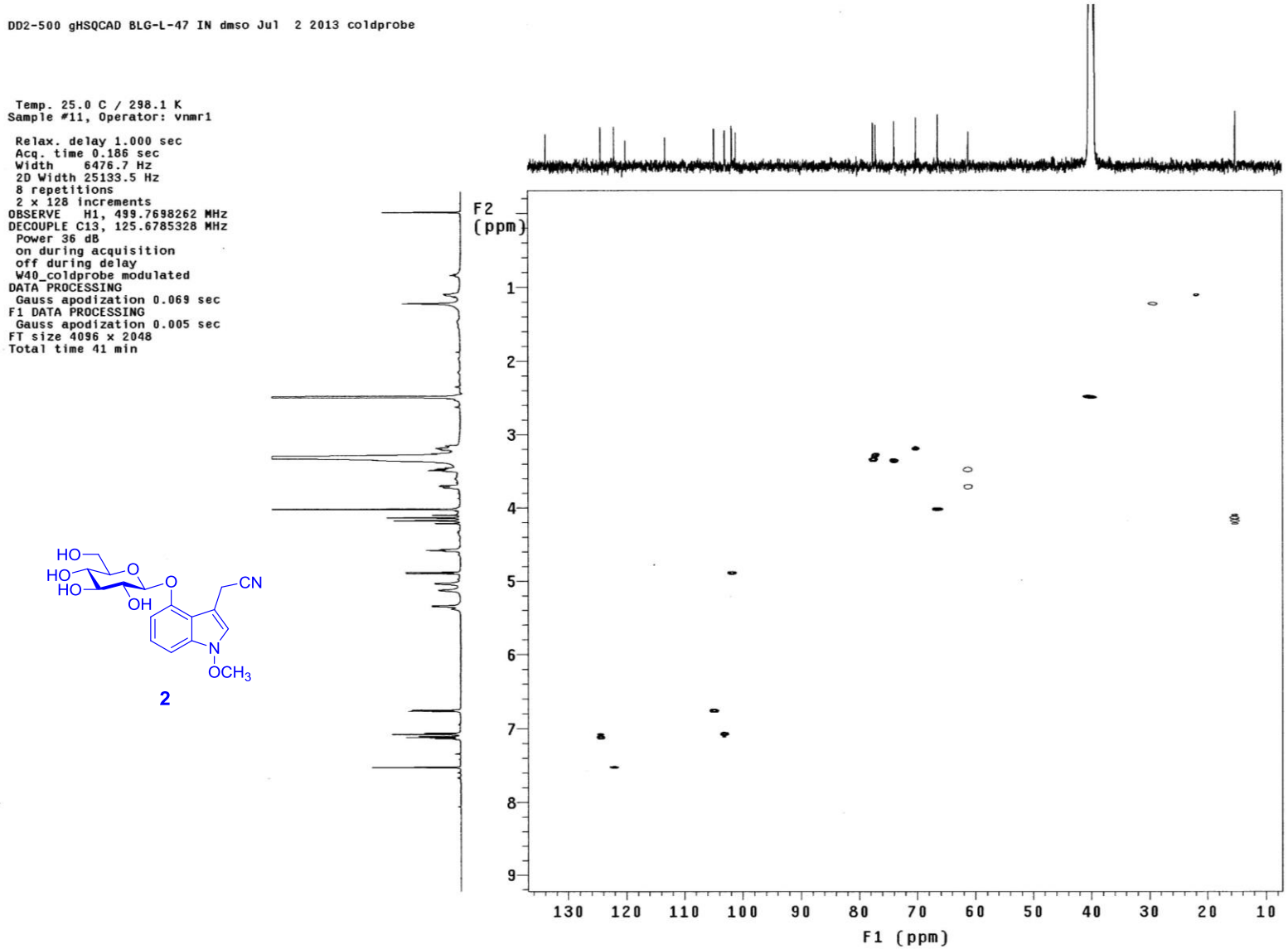


Figure S29. The HSQC spectrum of compound **2** in DMSO-d_6 (500 MHz for ^{1}H).

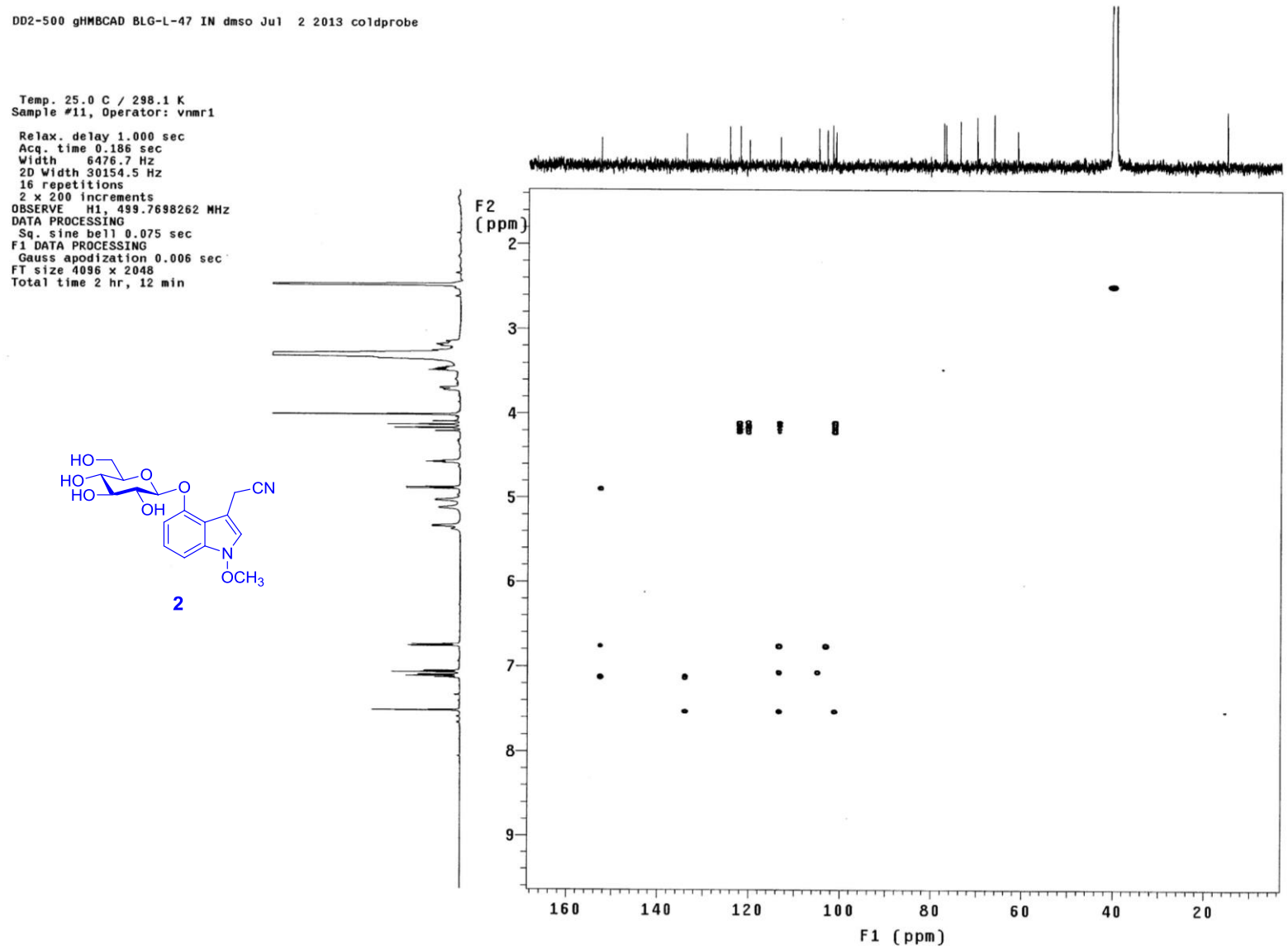


Figure S30.The HMBC spectrum of compound **2** in DMSO-d_6 (500 MHz for ^{1}H).

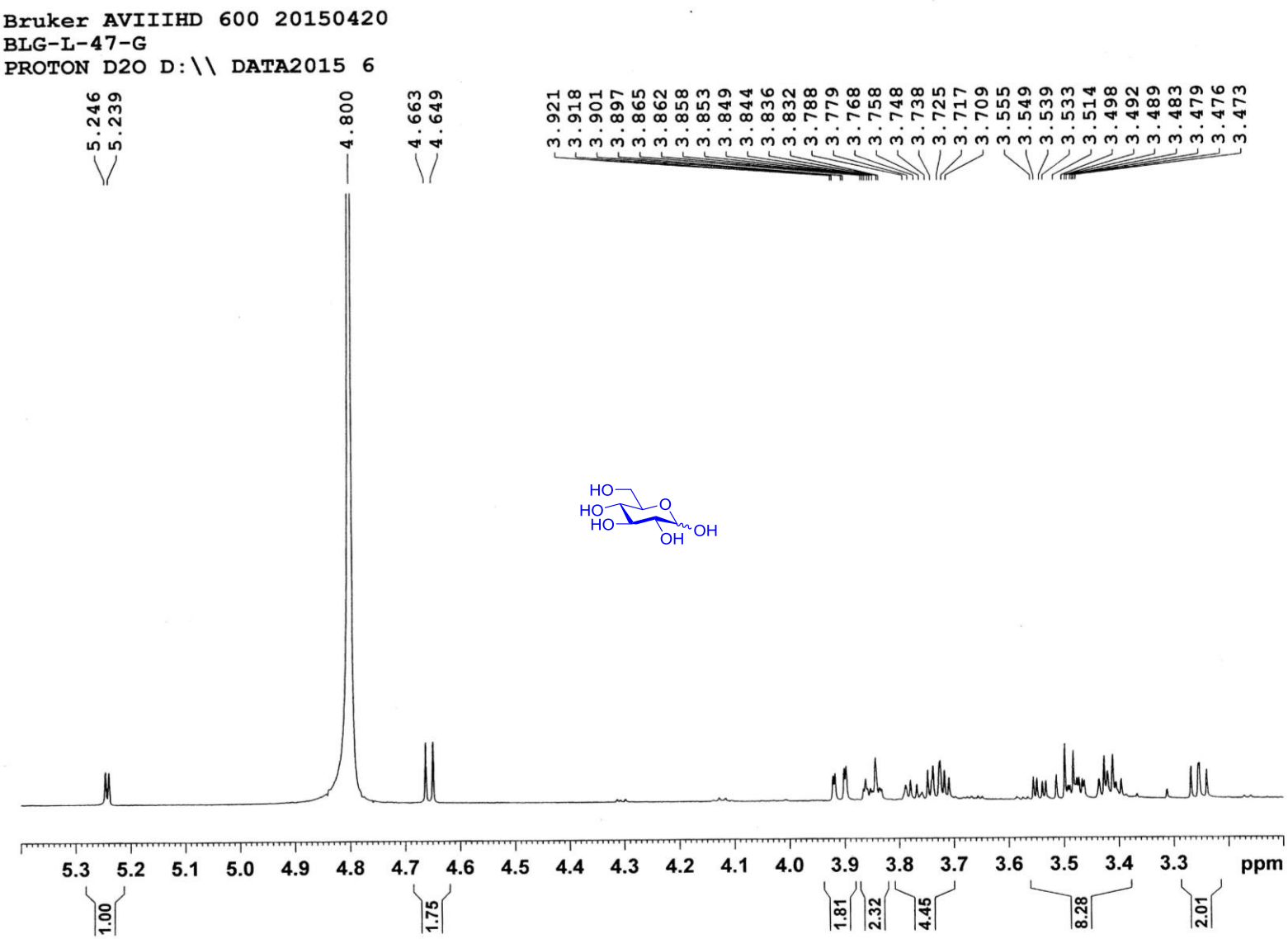
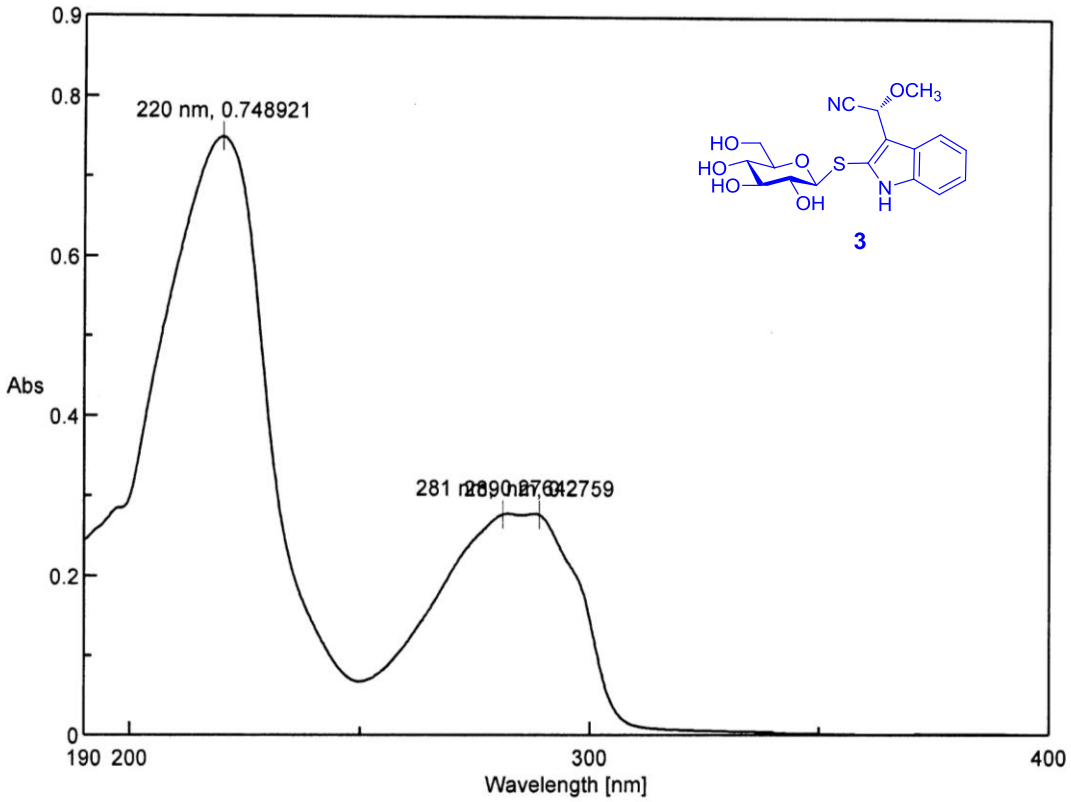


Figure S31. The[1]H NMR spectrum of D-glucose in D_2O (600 MHz), isolated from hydrolysate of compound **2**



bIg-I-20a-1-2

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Sample Name bIg-I-20a-1
Comment 0.02
User
Division UV
Company 324

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Model Name V-650
Serial No. A034461150

Accessory PSC-718
Accessory S/N A001761114
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Temperature 19.94 C
Control Sonsor Holder
Monitor Sensor Holder
Start Mode Start immediately

Photometric Mode Abs
Measurement range 400 - 190 nm
Data pitch 0.2 nm
Band width(UV/Vis) 2.0 nm
Response Medium
Scanning speed 200 nm/min
Source Change 340 nm
Light Source D2/WI
Filter Exchange Step
Correction Baseline

[Data Information]
Creation Date 2015-7-22 12:20

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Vertical Abs
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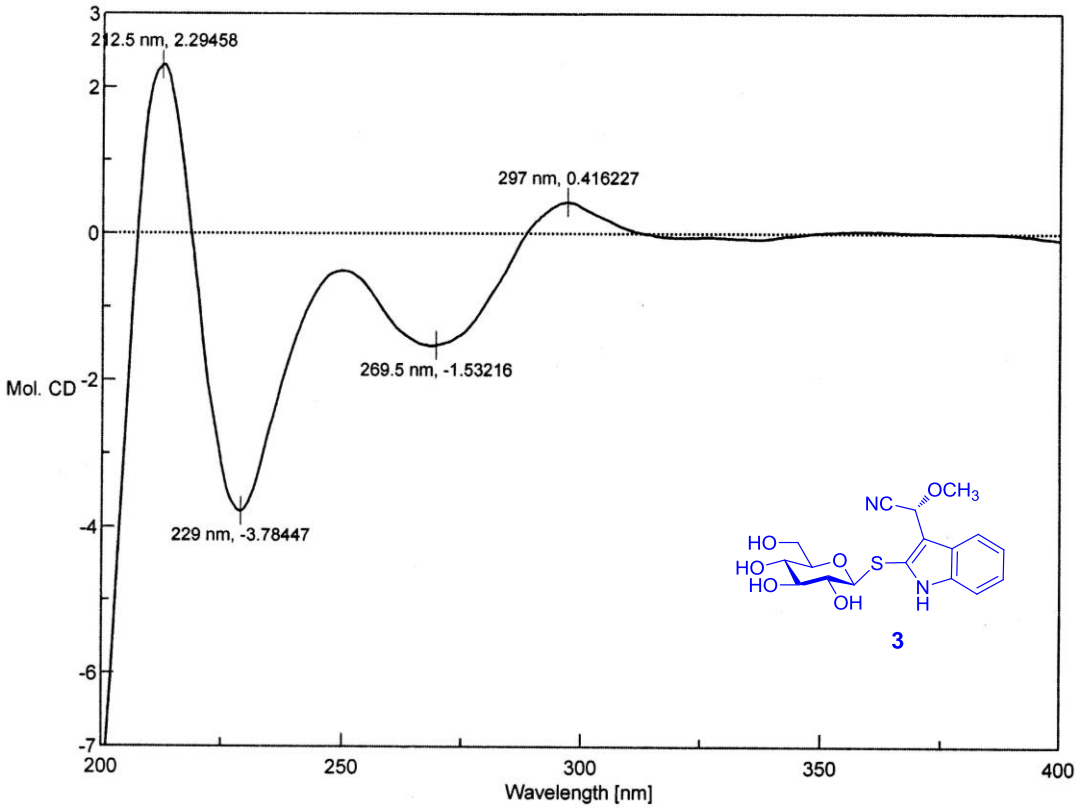
Data pitch 0.2 nm
Data points 1051

Figure S32. The UV spectrum of compound **3** in MeOH.



[Comments]

Sample name	BLG-L-20a-1
Comment	
User	
Division	
Company	dell

[Measurement Information]

Instrument Name	J-815
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	1 mm
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Band width	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
PMT Voltage	Auto
Accumulations	3
Solvent	MEOH
Concentration	0.1358 (w/v)%

[Detailed Information]

Creation date	2014-1-6 15:53
Data array type	Linear data array * 3
Horizontal axis	Wavelength [nm]
Vertical axis(1)	Mol. CD
Vertical axis(2)	HT [V]
Vertical axis(3)	Abs
Start	400 nm
End	200 nm
Data interval	0.5 nm
Data points	401

Figure S33. The CD spectrum of compound **3** in MeOH.

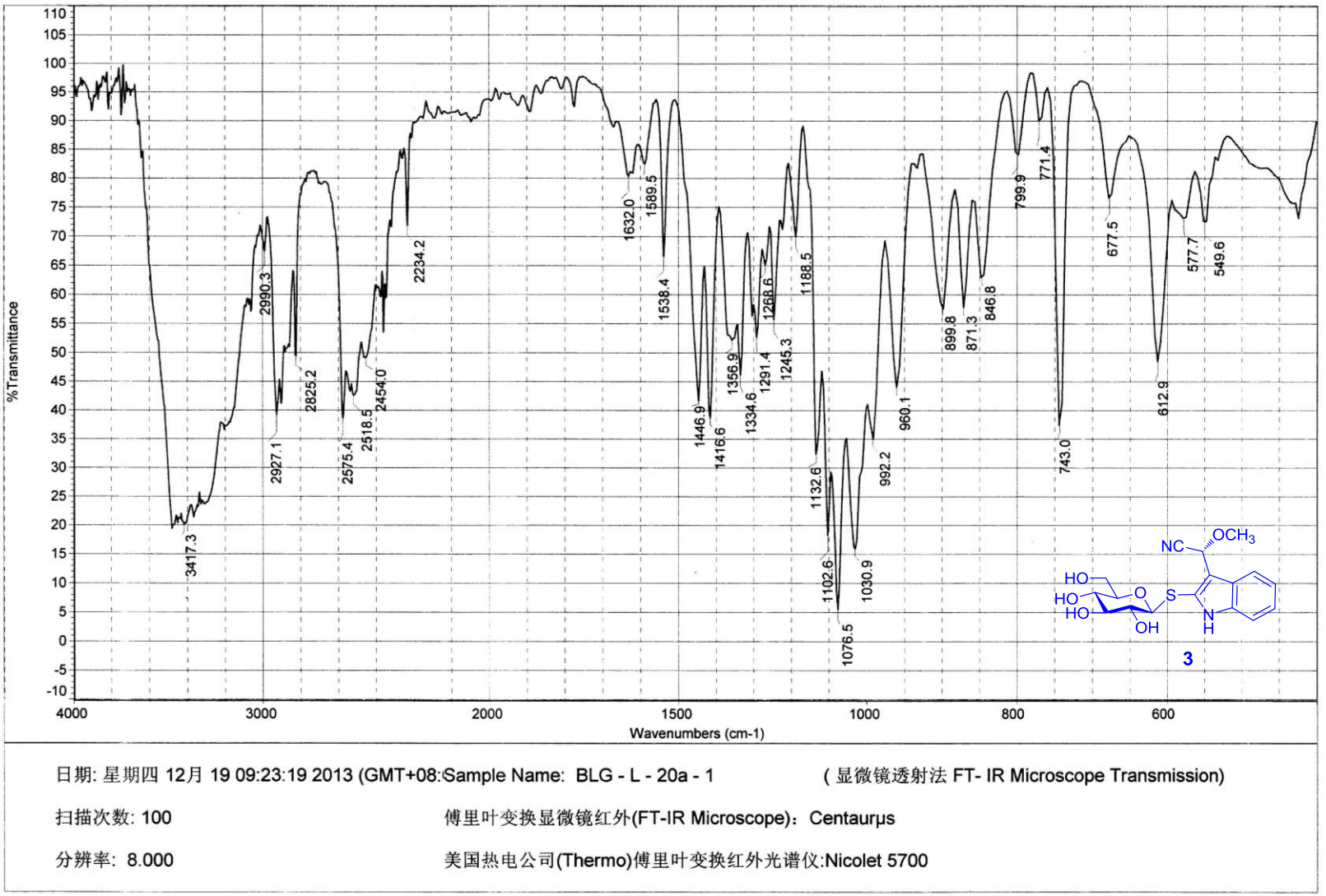


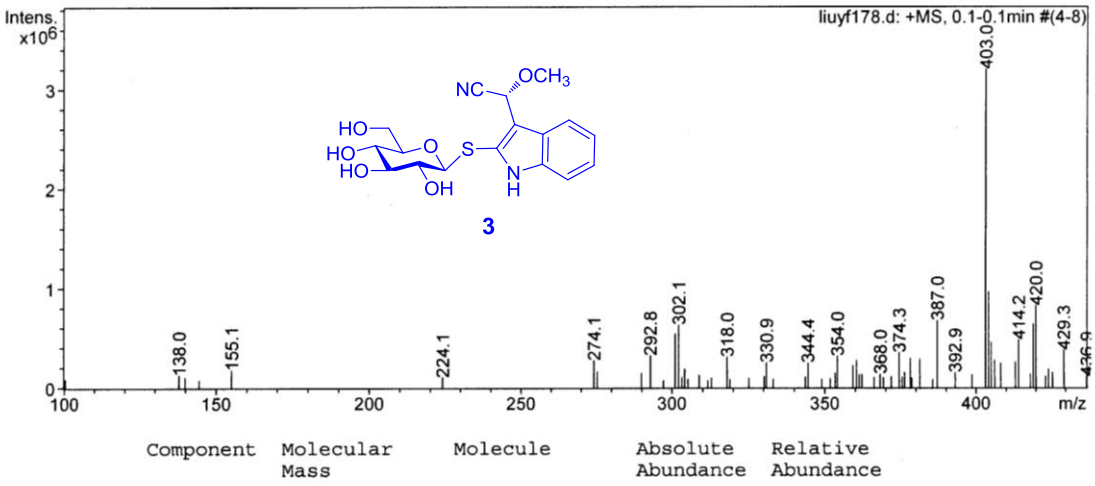
Figure S34. The IR spectrum of compound **3**.

Single Mass Spectrum Deconvolution Report

Analysis Name: liuyf178.d **Instrument:** LC-MSD-Trap-SL **Print Date:** 8/22/2013 10:43:11 AM
Method: TEST.MS **Operator:** Operator **Acq. Date:** 8/22/2013 10:32:39 AM
Sample Name: BLG-L-20a-1
Analysis Info:

Acquisition Parameter:

Mass Range Mode	Std/Normal	Trap Drive	53.0	Scan Begin	100 m/z
Ion Polarity	Positive	Octopole RF Amplitude	171.0 Vpp	Scan End	450 m/z
Ion Source Type	ESI	Capillary Exit	-121.0 Volt	Averages	5 Spectra
Dry Temp (Set)	330 °C	Skimmer	-40.0 Volt	Max. Accu Time	200000 µs
Nebulizer (Set)	15.00 psi	Oct 1 DC	-12.00 Volt	ICC Target	204
Dry Gas (Set)	6.00 l/min	Oct 2 DC	-1.70 Volt	Charge Control	on



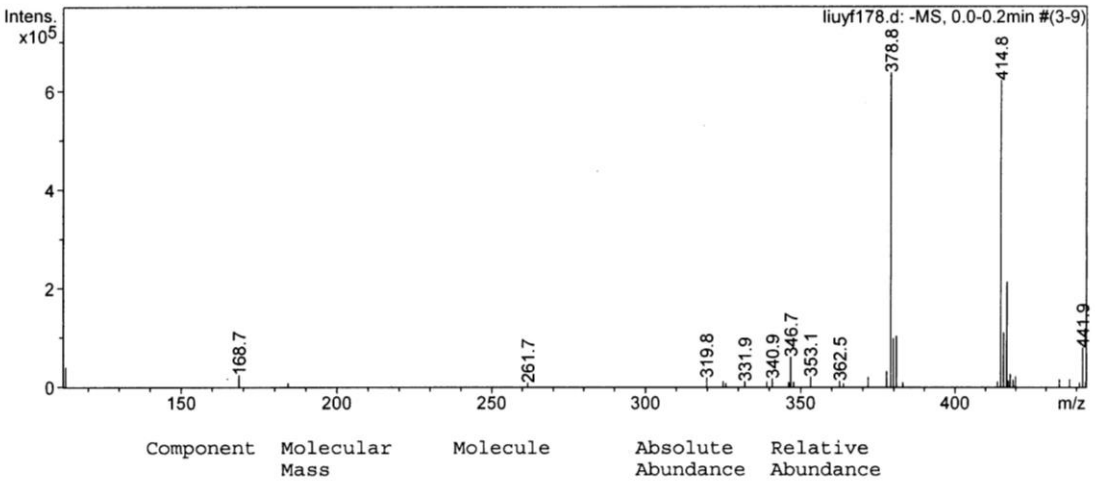


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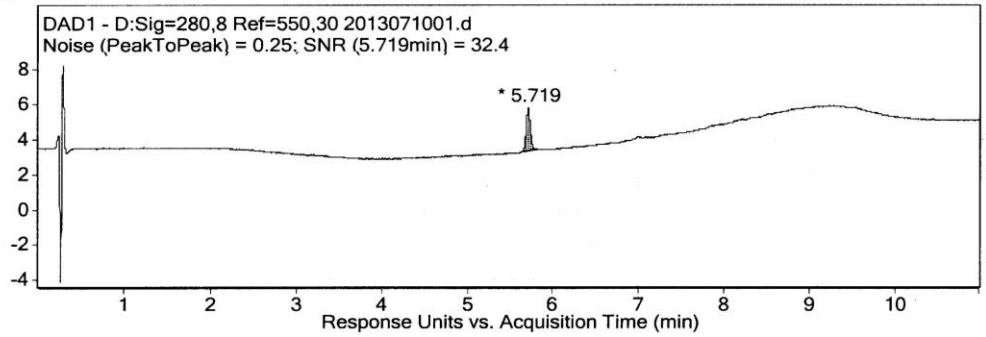
Figure S35. The ESI mass spectrum of compound **3**.

Qualitative Analysis Report

Data Filename	2013071001.d	**Sample Name**	BLG-L-20a1
Sample Type	Sample	**Position**	P1-C1
Instrument Name	Instrument 1	**User Name**	
Acq Method		**IRM Calibration Status**	[redacted]
DA Method	TEST LCMS.m	**Comment**	

User Chromatograms



Integration Peak List

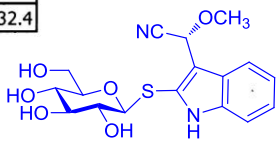
Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.643	5.719	5.831	2.45	8.24	100	32.4

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	0.254154205

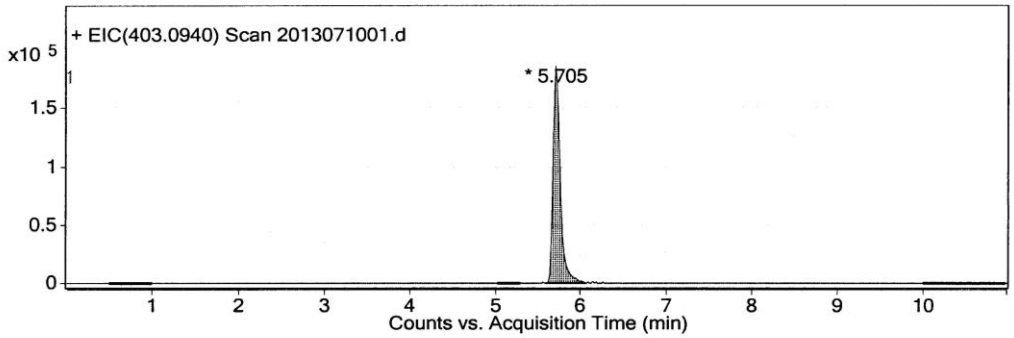
Noise Regions

Start	End
0.5	1
5	5.3
9.99	11



3

Fragmentor Voltage 135 **Collision Energy** 0 **Ionization Mode** ESI



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.593	5.705	6.06	186017	1120294	100	Infinity

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	0

Noise Regions

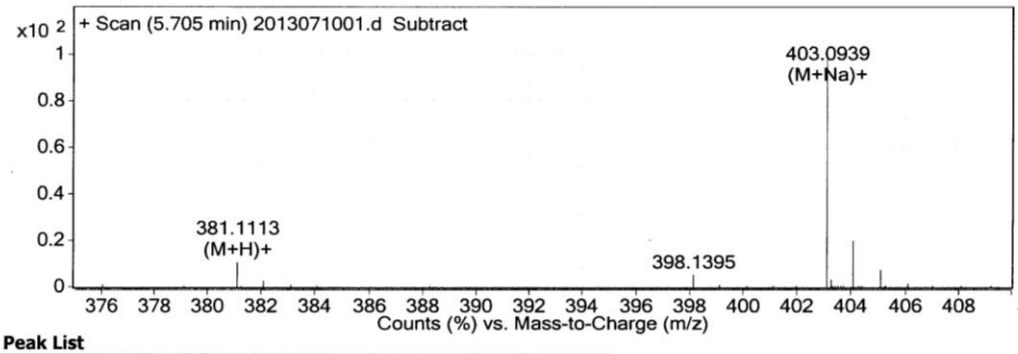
Start	End
0.5	1
5	5.3
9.99	11

User Spectra

Figure S36. The (+)-HRESIMS report of compound **3**, page 1.

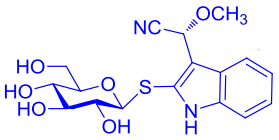
Qualitative Analysis Report

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	Esi



Peak List

m/z	z	Abund	Formula	Ion
116.9859		21301		
163.0399		16874		
187.0325		38520		
211.0959		15483		
217.0497		14690		
349.0856	1	61543		
354.1012		18085		
381.1113		20224	C25 H17 O4	(M+H)+
403.0939	1	185989	C25 H16 Na O4	(M+Na)+
404.0973	1	37427	C25 H16 Na O4	(M+Na)+



3

Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	500
O	0	90
N	0	5
S	0	5
Cl	0	2
Br	0	0
Si	0	0
F	0	0
P	0	0

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C17 H20 N2 O6 S		380.104	380.1042	0.53	C17 H21 N2 O6 S	98.42
C25 H16 O4	TRUE	380.104	380.1049	2.27	C25 H17 O4	98.4
C17 H20 N2 O6 S		380.1047	380.1042	-1.36	C17 H20 N2 Na O6 S	99.94
C13 H20 N2 O11		380.1047	380.1067	5.24	C13 H20 N2 Na O11	98.34
C22 H20 O4 S		380.1047	380.1082	9.23	C22 H20 Na O4 S	98.2
C14 H24 N2 O6 S2		380.1047	380.1076	7.51	C14 H24 N2 Na O6 S2	98.13
C21 H20 N2 O S2		380.1047	380.1017	-7.94	C21 H20 N2 Na O S2	97.99
C18 H24 N2 O S3		380.1047	380.1051	0.92	C18 H24 N2 Na O S3	97.62
C25 H16 O4	TRUE	380.1047	380.1049	0.37	C25 H16 Na O4	97.52
C9 H24 N4 O8 S2		380.1047	380.1036	-3.09	C9 H24 N4 Na O8 S2	97.22
C26 H12 N4		380.1047	380.1062	3.89	C26 H12 N4 Na	96.18
C13 H24 N4 O3 S3		380.1047	380.1011	-9.67	C13 H24 N4 Na O3 S3	95.92

--- End Of Report ---

Figure S37. The (+)-HRESIMS report of compound **3**, page 2.

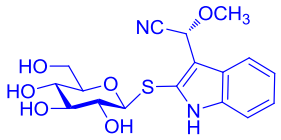
MS Formula Results: + Scan (5.705 min) Sub (2013071001.d)

m/z	Ion	Formula	Abundance
381.1113	(M+H)+	C25 H17 O4	20223.9

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☐	C17 H20 N2 O6 S	C17 H21 N2 O6 S	381.1115	98.42		380.104	380.1042	0.53	0.53	98.47	95.2	99.99	381.1113	9
☑	C25 H16 O4	C25 H17 O4	381.1121	98.4		380.104	380.1049	2.27	2.27	95.02	99.61	99.83	381.1113	18

m/z	Ion	Formula	Abundance
403.0939	(M+Na)+	C25 H16 Na O4	185989

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☐	C17 H20 N2 O6 S	C17 H20 N2 Na O6 S	403.0934	99.94		380.1047	380.1042	-1.36	1.36	99.95	99.91	99.95	403.0939	9
☐	C13 H20 N2 O11	C13 H20 N2 Na O11	403.0959	98.34		380.1047	380.1067	5.24	5.24	96.05	99.4	99.2	403.0939	5
☐	C22 H20 O4 S	C22 H20 Na O4 S	403.0975	98.2		380.1047	380.1082	9.23	9.23	97.84	99.99	97.52	403.0939	13
☐	C14 H24 N2 O6 S2	C14 H24 N2 Na O6 S2	403.0968	98.13		380.1047	380.1076	7.51	7.51	96.55	99.56	98.36	403.0939	4
☐	C21 H20 N2 O S2	C21 H20 N2 Na O S2	403.0909	97.99		380.1047	380.1017	-7.94	7.94	96.28	99.7	98.16	403.0939	13
☐	C18 H24 N2 O S3	C18 H24 N2 Na O S3	403.0943	97.62		380.1047	380.1051	0.92	0.92	92.22	99.41	99.97	403.0939	8
☑	C25 H16 O4	C25 H16 Na O4	403.0941	97.52		380.1047	380.1049	0.37	0.37	92.23	98.91	100	403.0939	18
☐	C9 H24 N4 O8 S2	C9 H24 N4 Na O8 S2	403.0928	97.22		380.1047	380.1036	-3.09	3.09	91.28	99.33	99.72	403.0939	0
☐	C26 H12 N4	C26 H12 N4 Na	403.0954	96.18		380.1047	380.1062	3.89	3.89	88.24	98.97	99.56	403.0939	23
☐	C13 H24 N4 O3 S3	C13 H24 N4 Na O3 S3	403.0903	95.92		380.1047	380.1011	-9.67	9.67	90.93	99.19	97.28	403.0939	4
☐	C15 H28 N2 O S4	C15 H28 N2 Na O S4	403.0977	93.88		380.1047	380.1084	9.78	9.78	83.89	99.17	97.22	403.0939	3



3

page 1

Figure S38. The (+)-HRESIMS report of compound **3**, page 3.

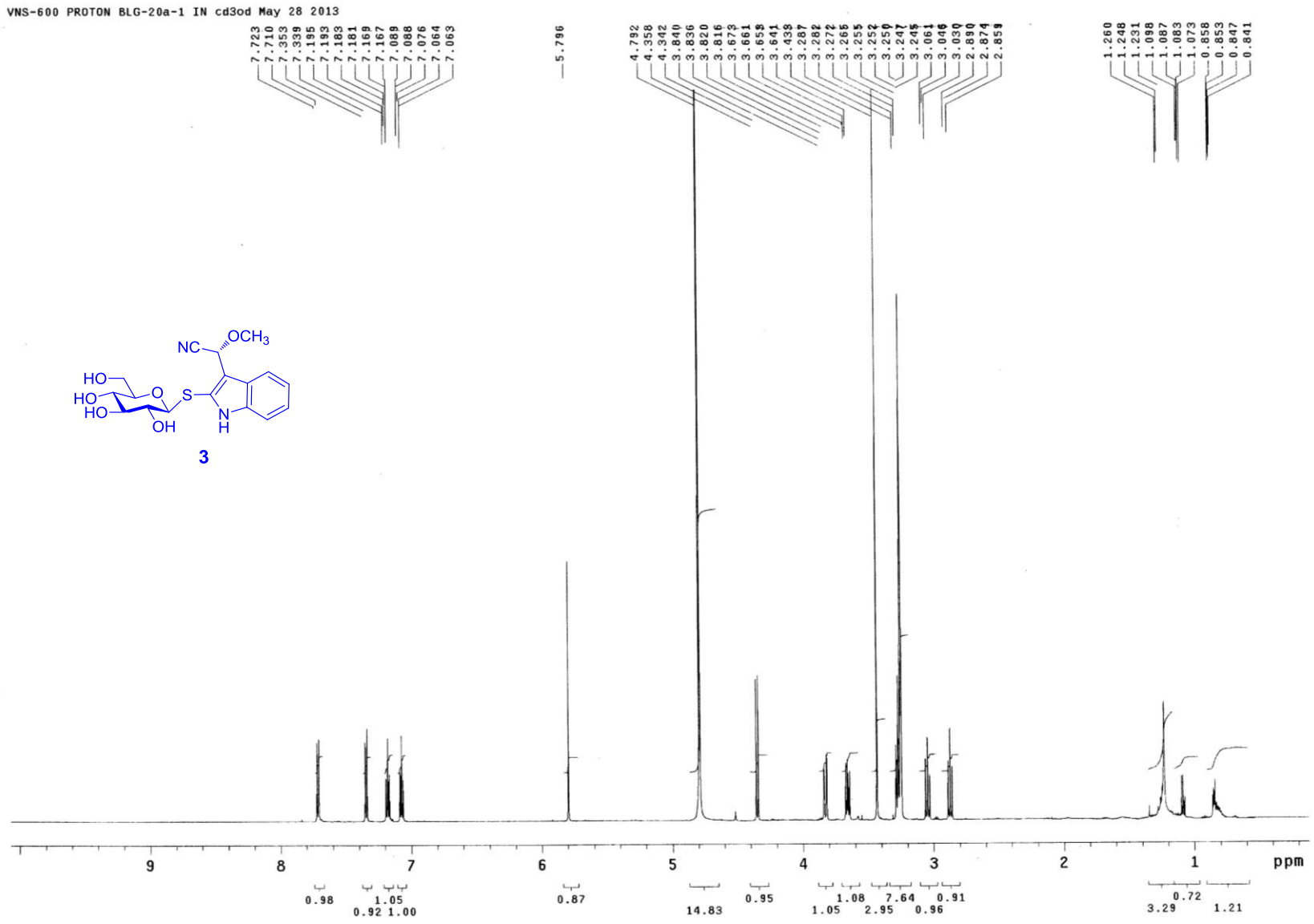


Figure S39. The ^{1}H NMR spectrum of compound **3** in CD_3OD (600 MHz).

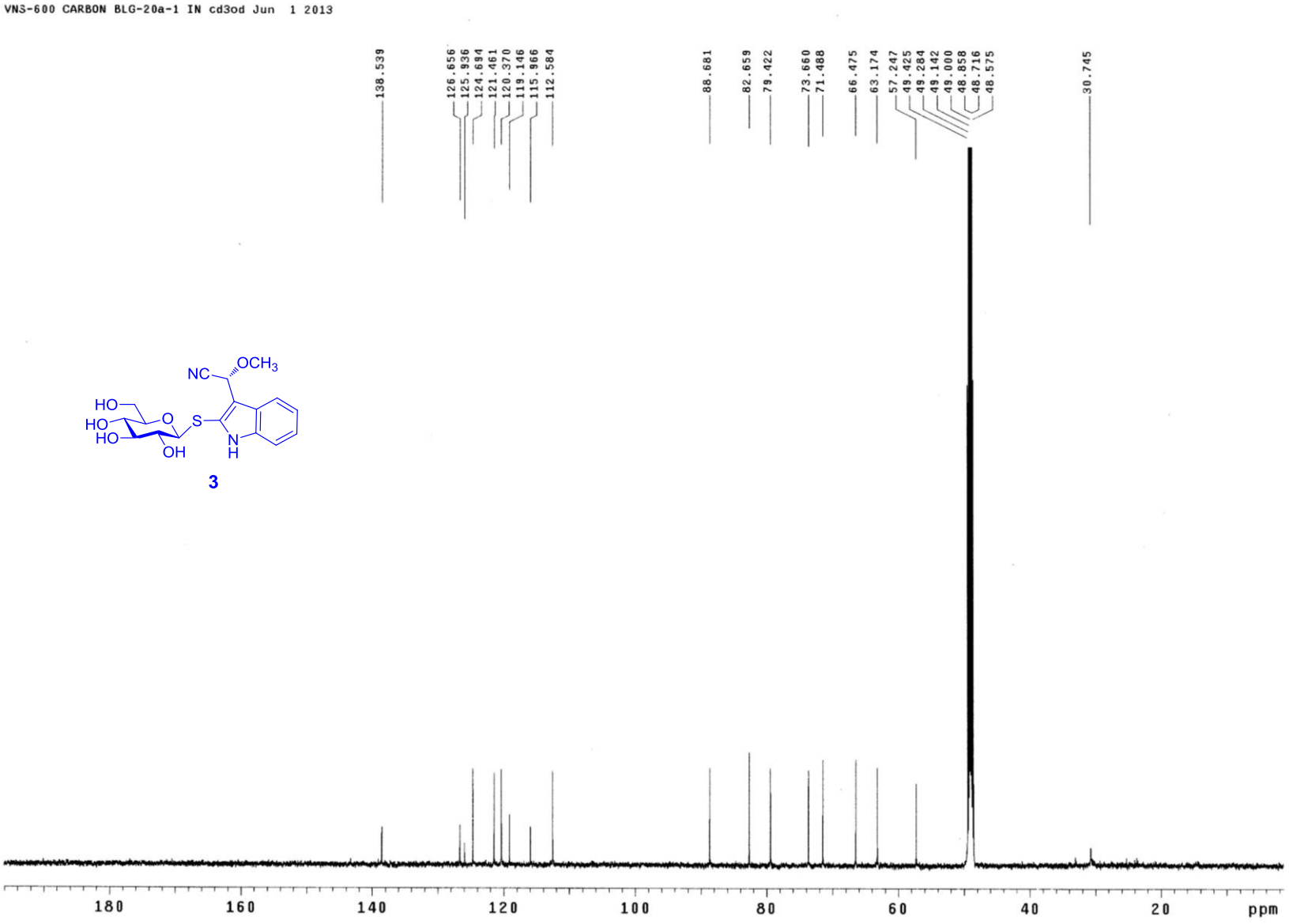


Figure S40. The ^{13}C NMR spectrum of compound **3** in CD_3OD (150 MHz).

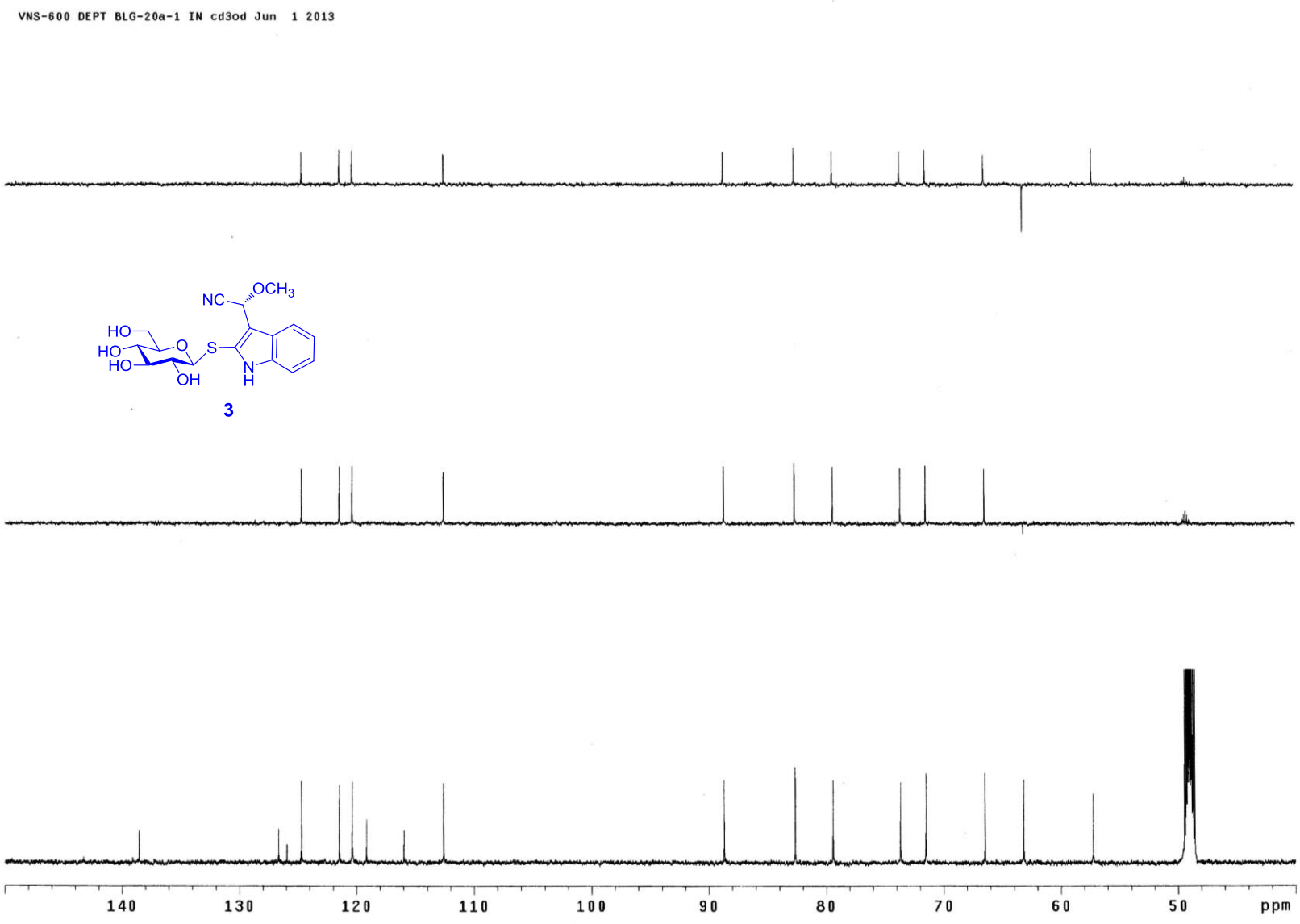


Figure S41. The DEPT spectrum of compound **3** in CD_3OD (150 MHz).

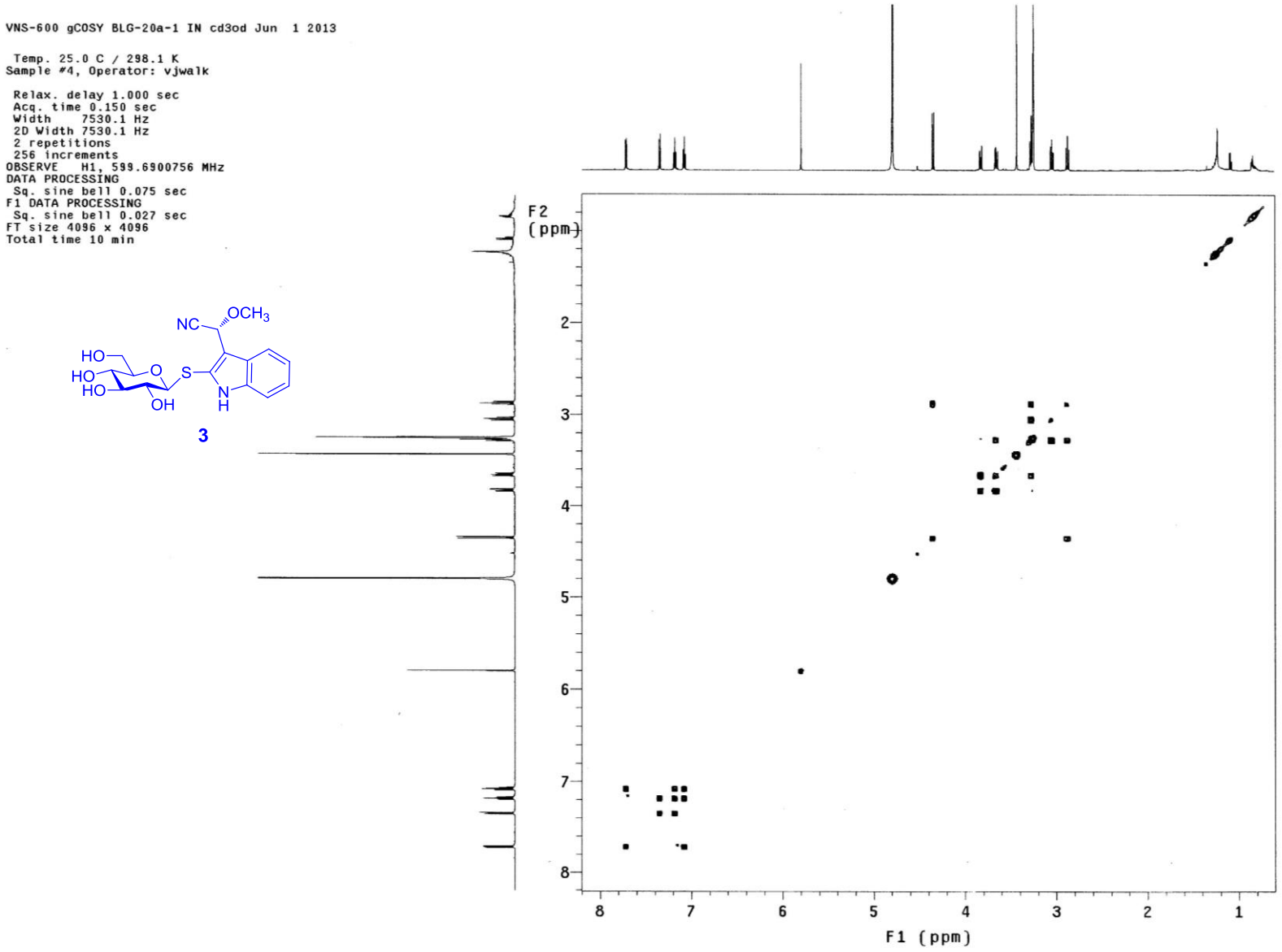


Figure S42. The ^{1}H-^{1}H COSY spectrum of compound **3** in CD_3OD (600 MHz).

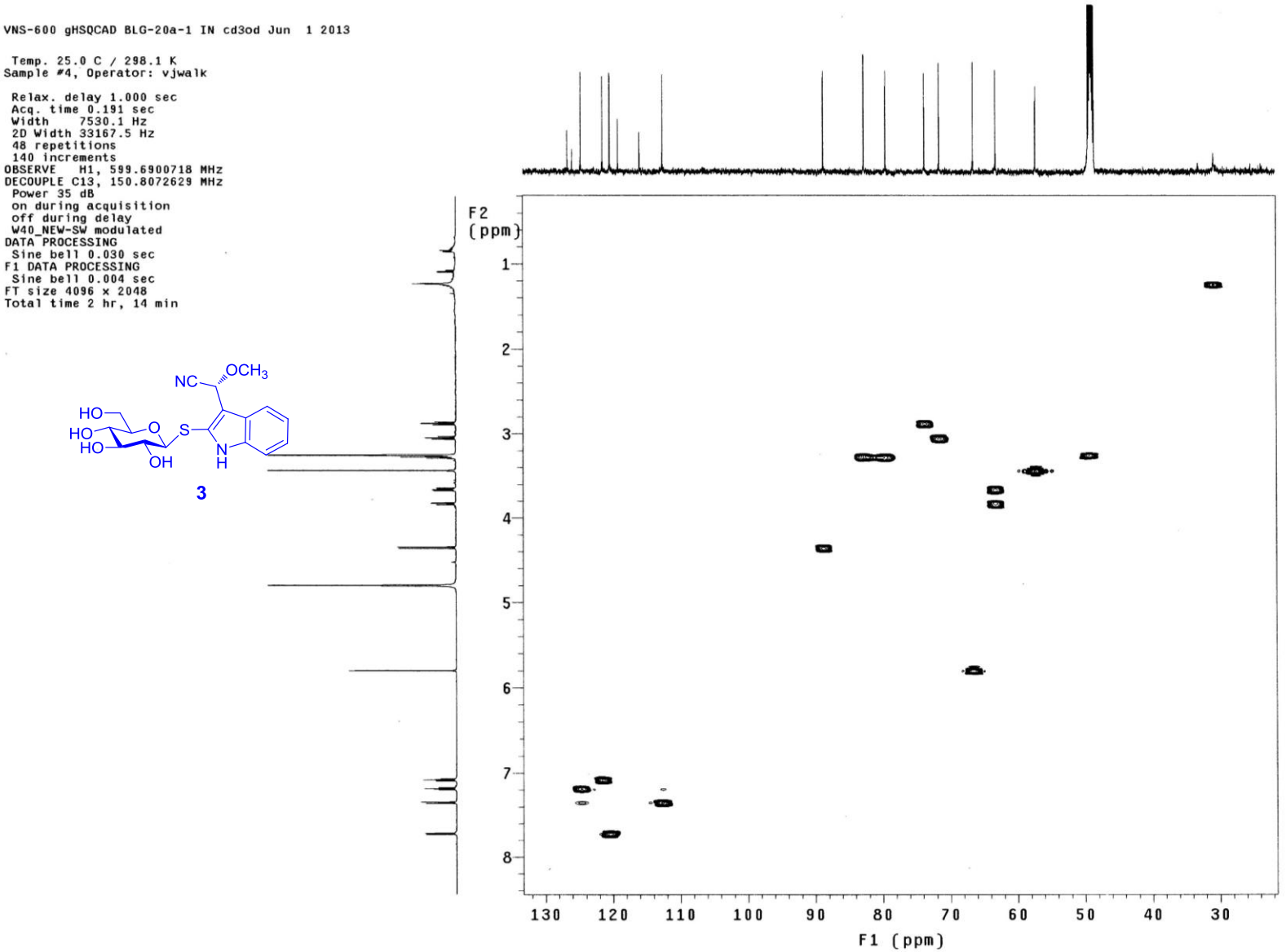


Figure S43.The HSQC spectrum of compound **3** in CD_3OD (600 MHz for ^1H).

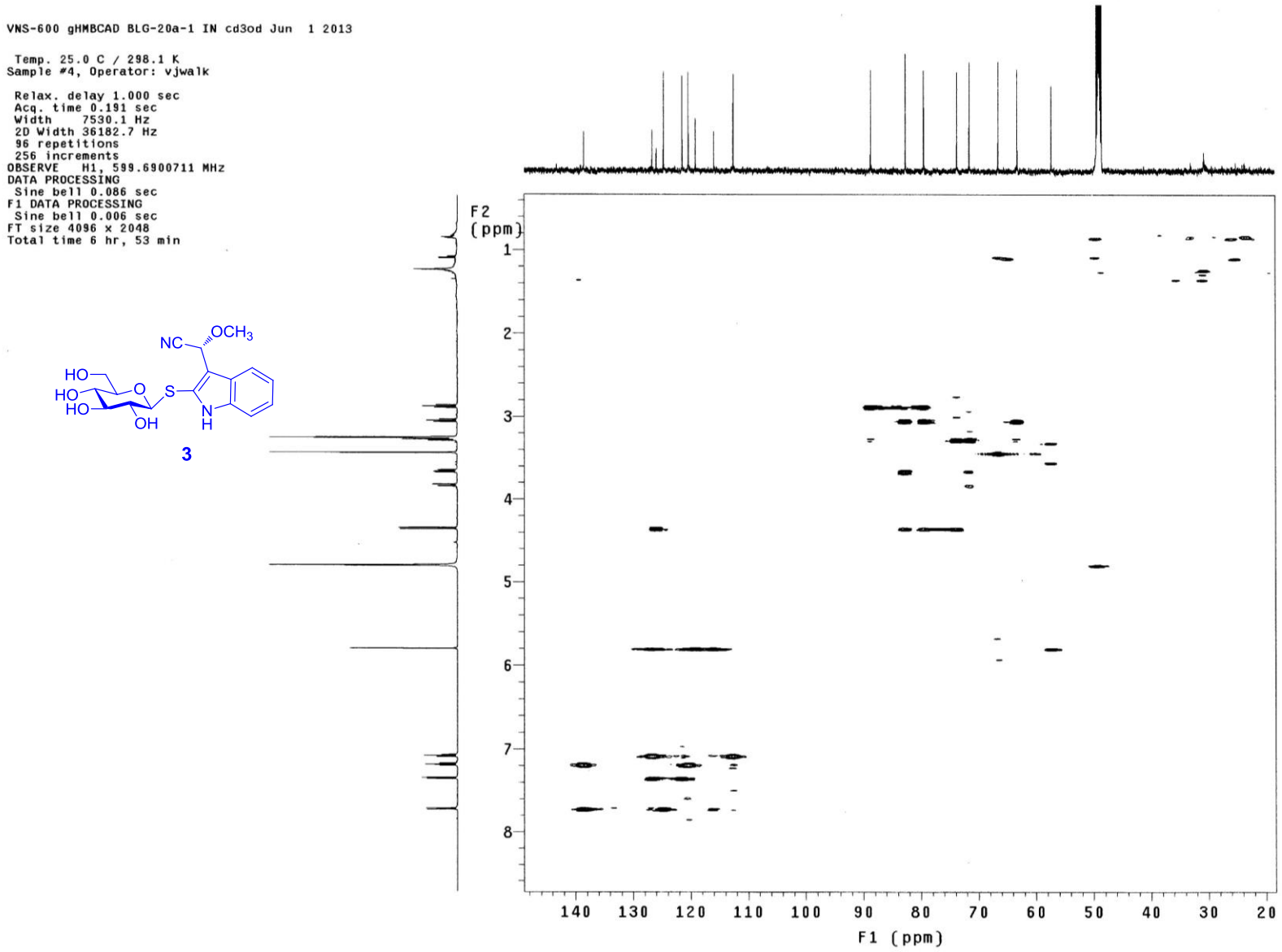


Figure S44. The HMBC spectrum of compound **3** in CD_3OD (600 MHz for ^1H).

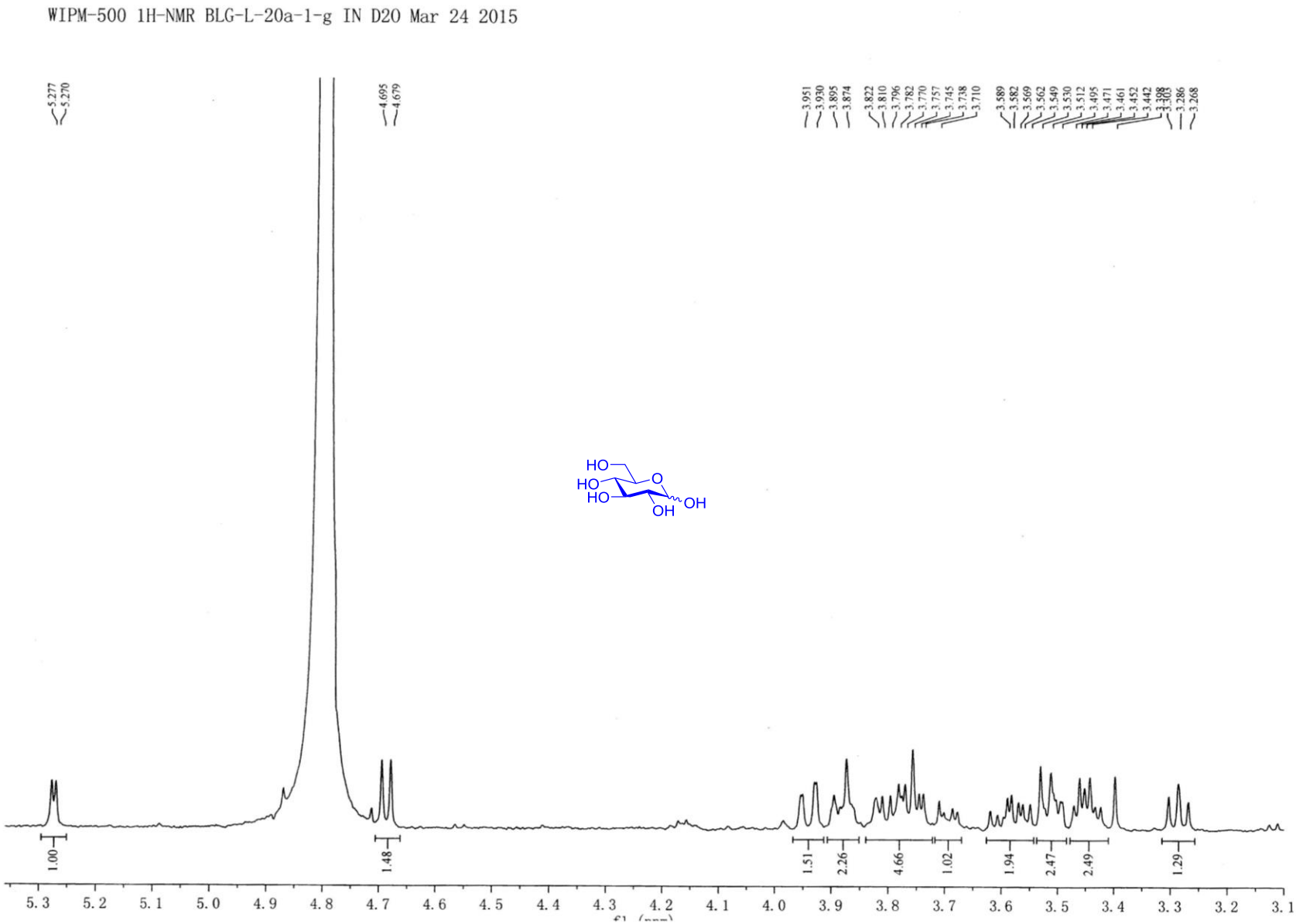
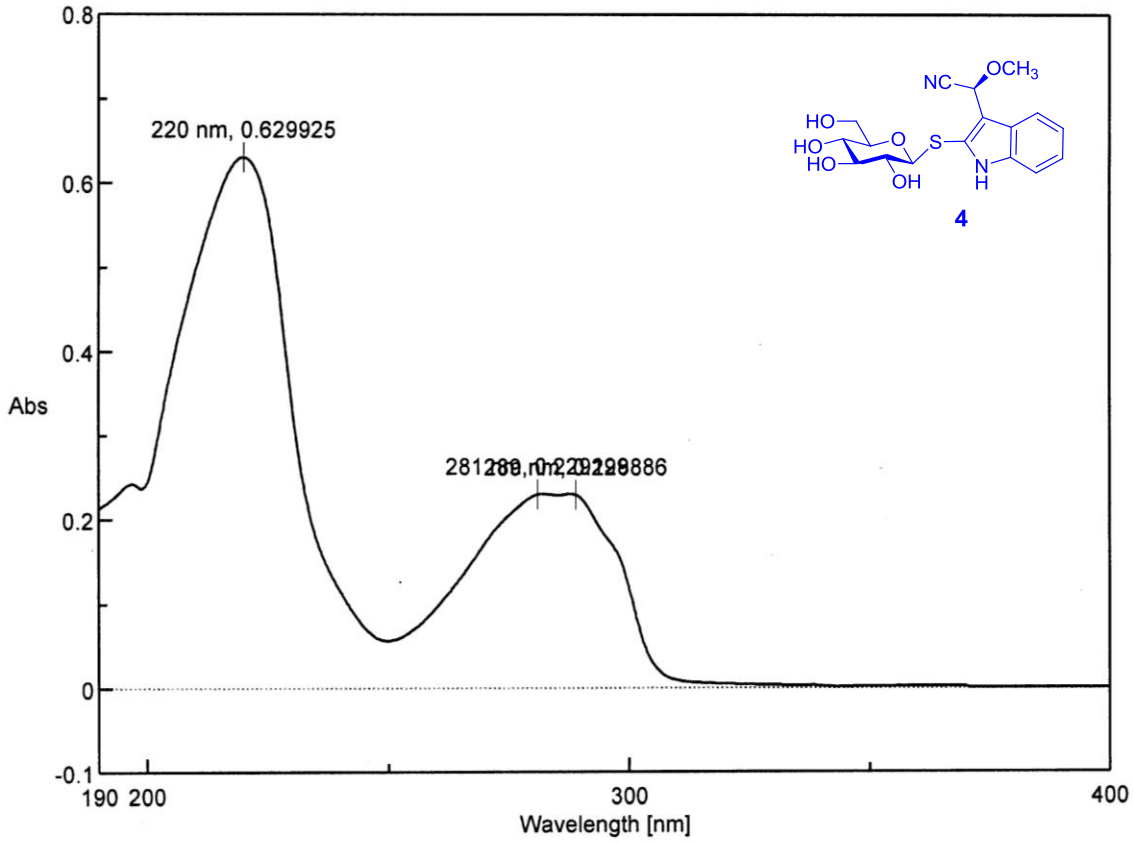


Figure S45. The ^{1}H NMR spectrum of D-glucose in D_2O (500 MHz), isolated from hydrolysate of compound **3**



[Comment]
Sample Name blg-20a-2
Comment 0.02
User
Division UV
Company 324

[Measurement Information]
Instrument Name V-650
Model Name V-650
Serial No. A034461150

Accessory PSC-718
Accessory S/N A001761114
Position 1
Cell Length 10 mm
Temperature 19.97 C
Control Sonsor Holder
Monitor Sensor Holder
Start Mode Start immediately

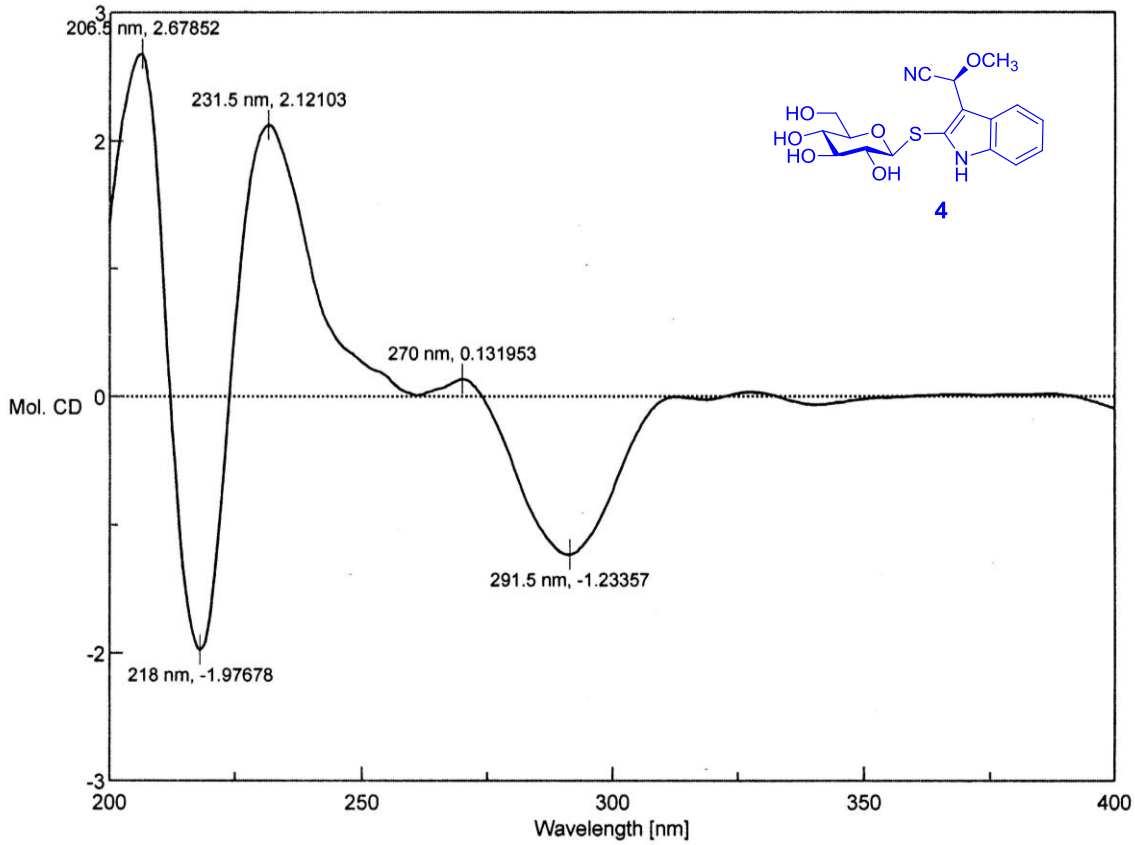
Photometric Mode Abs
Measurement range 400 - 190 nm
Data pitch 0.2 nm
Band width(UV/Vis) 2.0 nm
Response Medium
Scanning speed 200 nm/min
Source Change 340 nm
Light Source D2/WI
Filter Exchange Step
Correction Baseline

blg-l-20a-2-1

[Data Information]
Creation Date 2015-7-22 12:30

Data array type Linear data array
Horizontal Wavelength [nm]
Vertical Abs
Start 400 nm
End 190 nm
Data pitch 0.2 nm
Data points 1051

Figure S46. The UV spectrum of compound **4** in MeOH.



[Comments]

Sample name	BLG-L-20a-2
Comment	
User	
Division	
Company	dell

[Measurement Information]

Instrument Name	J-815
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	1 mm
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Band width	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
PMT Voltage	Auto
Accumulations	3
Solvent	MEOH
Concentration	0.1344 (w/v)%

[Detailed Information]

Creation date	2014-1-6 15:45
Data array type	Linear data array * 3
Horizontal axis	Wavelength [nm]
Vertical axis(1)	Mol. CD
Vertical axis(2)	HT [V]
Vertical axis(3)	Abs
Start	400 nm
End	200 nm
Data interval	0.5 nm
Data points	401

Figure S47. The CD spectrum of compound **4** in MeOH.

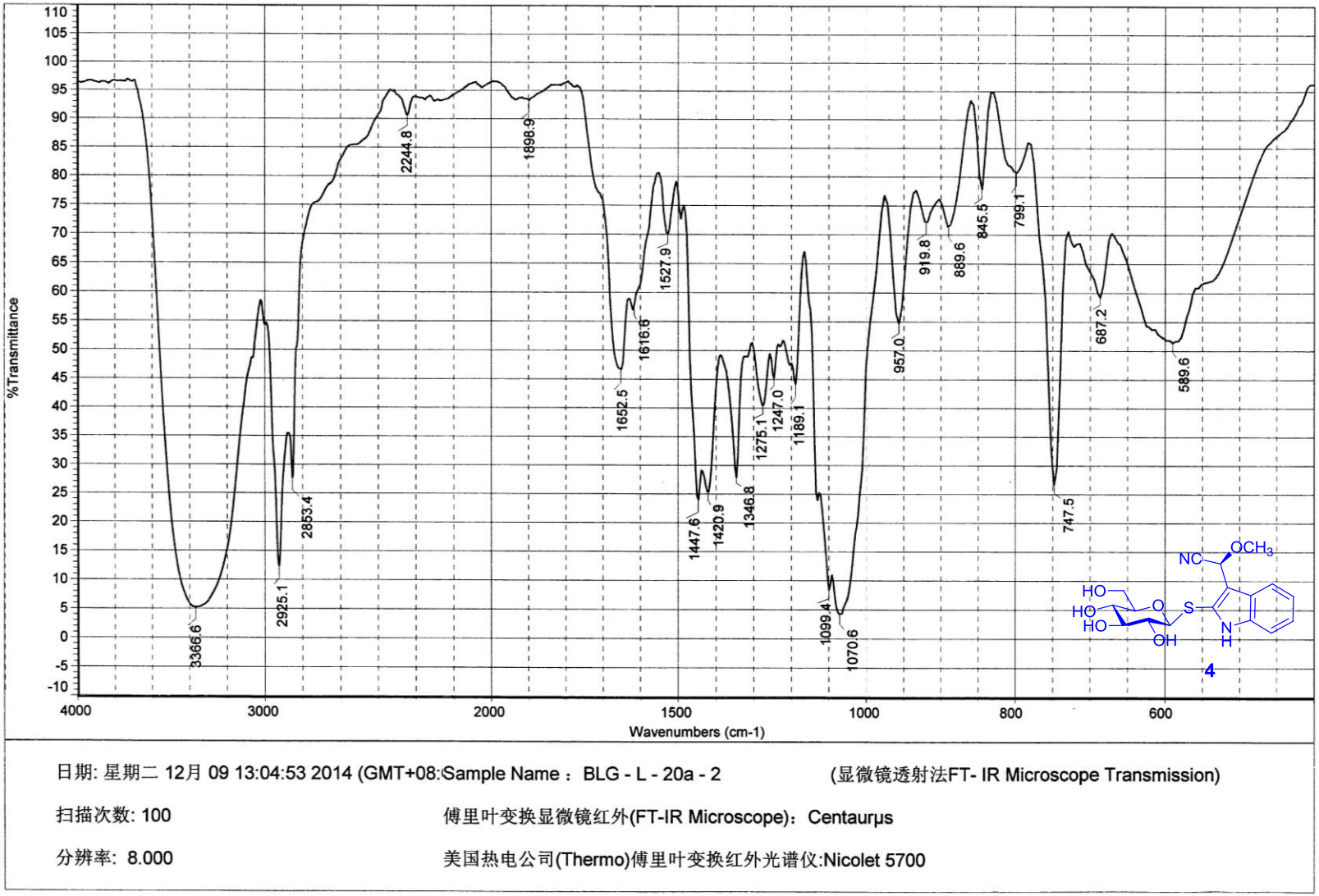


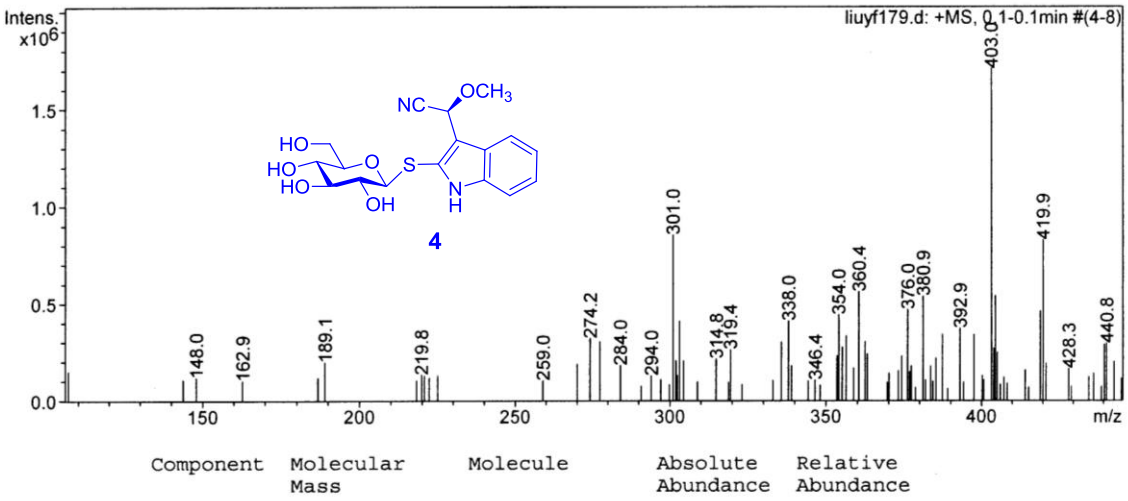
Figure S48. The IR spectrum of compound **4.**

Single Mass Spectrum Deconvolution Report

Analysis Name: liuyf179.d **Instrument:** LC-MSD-Trap-SL **Print Date:** 8/22/2013 10:43:42 AM
Method: TEST.MS **Operator:** Operator **Acq. Date:** 8/22/2013 10:34:22 AM
Sample Name: BLG-L-20a-2
Analysis Info:

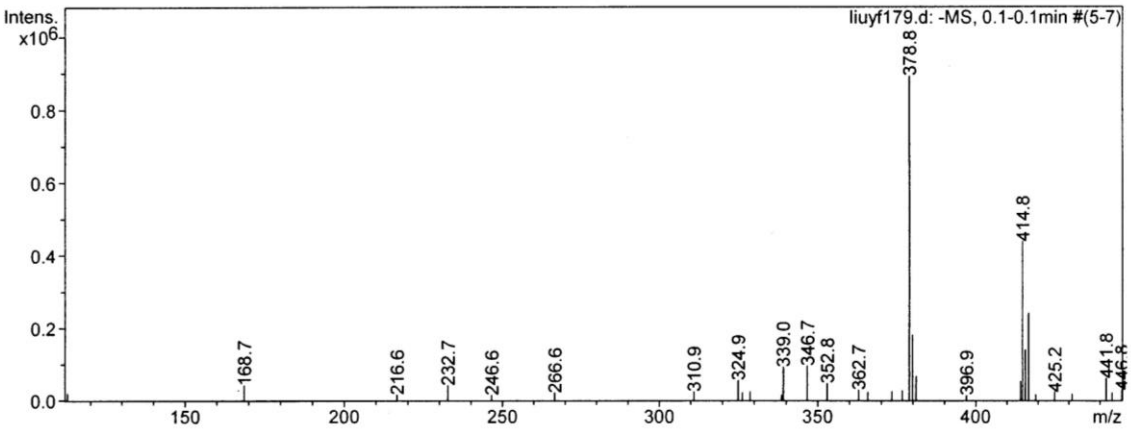
Acquisition Parameter:

Mass Range Mode	Std/Normal	Trap Drive	53.0	Scan Begin	100 m/z
Ion Polarity	Positive	Octopole RF Amplitude	171.0 Vpp	Scan End	450 m/z
Ion Source Type	ESI	Capillary Exit	-121.0 Volt	Averages	5 Spectra
Dry Temp (Set)	330 °C	Skimmer	-40.0 Volt	Max. Accu Time	200000 µs
Nebulizer (Set)	15.00 psi	Oct 1 DC	-12.00 Volt	ICC Target	380
Dry Gas (Set)	6.00 l/min	Oct 2 DC	-1.70 Volt	Charge Control	on



4

Component	Molecular Mass	Molecule	Absolute Abundance	Relative Abundance



Component	Molecular Mass	Molecule	Absolute Abundance	Relative Abundance

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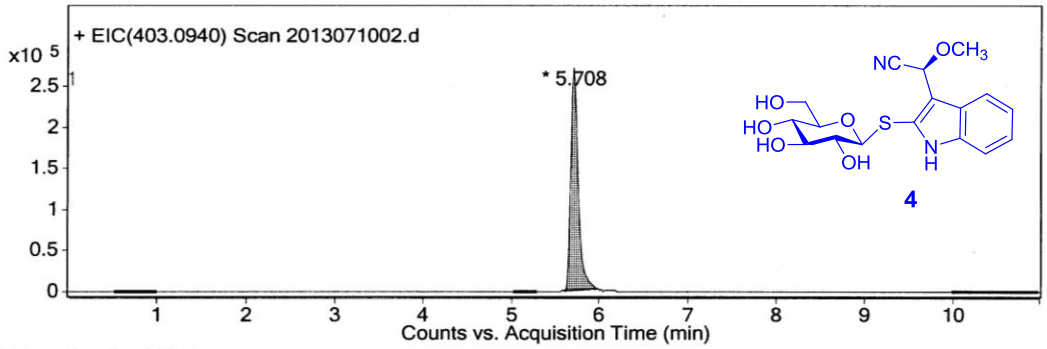
Figure S49. The ESI mass spectrum of compound **4**.

Qualitative Analysis Report

Data Filename	2013071002.d	**Sample Name**	BLG-L-20a2
Sample Type	Sample	**Position**	P1-C2
Instrument Name	Instrument 1	**User Name**	
Acq Method		**IRM Calibration Status**	[redacted]
DA Method	TEST LCMS.m	**Comment**	

User Chromatograms

Fragmentor Voltage 135 **Collision Energy** 0 **Ionization Mode** ESI



Integration Peak List

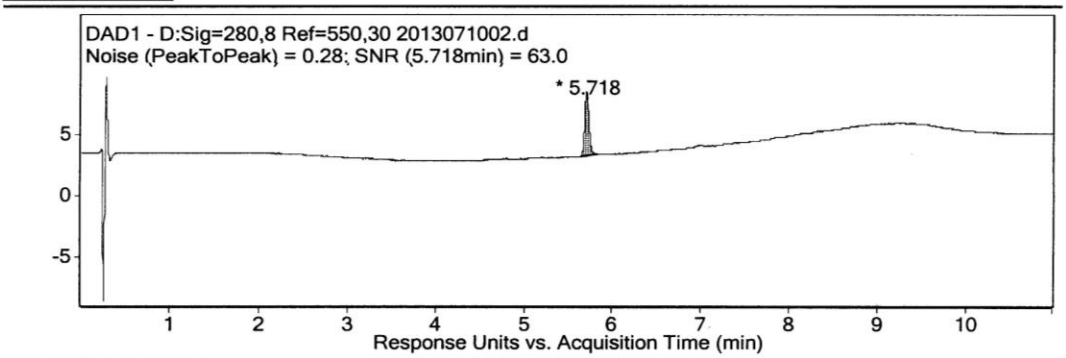
Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.595	5.708	5.998	270678	1624200	100	Infinity

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	0

Noise Regions

Start	End
0.5	1
5	5.3
9.99	11



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.645	5.718	5.847	5.23	17.67	100	63

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	0.280380249

Noise Regions

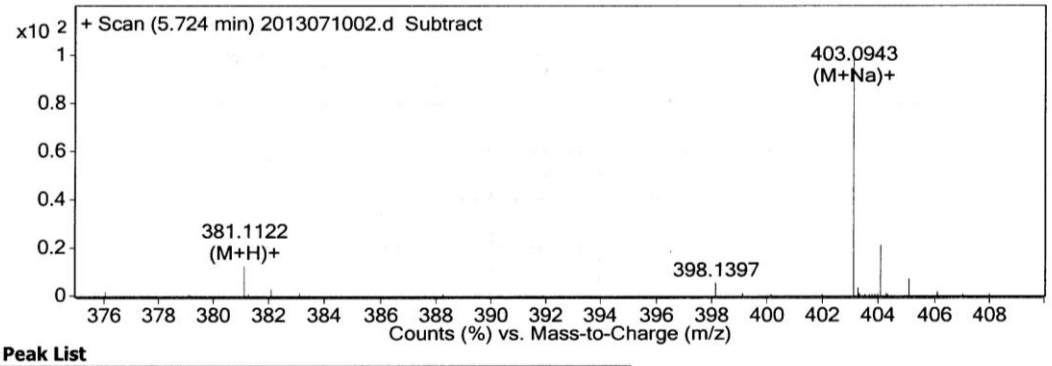
Start	End
0.5	1
5	5.3
9.99	11

User Spectra

Figure S50. The (+)-HRESIMS report of compound **4**, page 1.

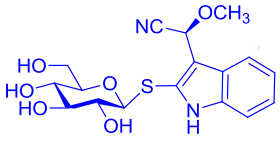
Qualitative Analysis Report

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	Esi



Peak List

m/z	z	Abund	Formula	Ion
187.0327		78374		
211.0957		22705		
349.0856	1	105173		
350.0881	1	20237		
354.1014		38946		
381.1122		30989	C25 H17 O4	(M+H)+
403.0943	1	248433	C25 H16 Na O4	(M+Na)+
404.0963	1	52472	C25 H16 Na O4	(M+Na)+
405.0944	1	17986	C25 H16 Na O4	(M+Na)+
783.1982		24246		



4

Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	500
O	0	90
N	0	5
S	0	5
Cl	0	2
Br	0	0
Si	0	0
F	0	0
P	0	0

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C17 H20 N2 O6 S		380.1051	380.1042	-2.23	C17 H20 N2 Na O6 S	99.86
C22 H20 O4 S		380.1051	380.1082	8.36	C22 H20 Na O4 S	98.59
C13 H20 N2 O11		380.1051	380.1067	4.36	C13 H20 N2 Na O11	98.14
C14 H24 N2 O6 S2		380.1051	380.1076	6.63	C14 H24 N2 Na O6 S2	98.06
C21 H20 N2 O S2		380.1051	380.1017	-8.82	C21 H20 N2 Na O S2	97.93
C25 H16 O4	TRUE	380.105	380.1049	-0.5	C25 H16 Na O4	97.84
C18 H24 N2 O S3		380.1051	380.1051	0.05	C18 H24 N2 Na O S3	97.58
C17 H20 N2 O6 S		380.105	380.1042	-1.96	C17 H21 N2 O6 S	98.87
C13 H20 N2 O11		380.1049	380.1067	4.63	C13 H21 N2 O11	98
C25 H16 O4	TRUE	380.1049	380.1049	-0.23	C25 H17 O4	97.48
C22 H20 O4 S		380.105	380.1082	8.63	C22 H21 O4 S	97.39
C14 H24 N2 O6 S2		380.105	380.1076	6.9	C14 H25 N2 O6 S2	97.05

--- End Of Report ---

Figure S51.The (+)-HRESIMS report of compound **4**, page 2.

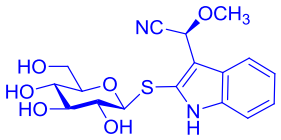
MS Formula Results: + Scan (5.724 min) Sub (2013071002.d)

m/z	Ion	Formula	Abundance
381.1122	(M+H)+	C25 H17 O4	30988.5

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☐	C17 H20 N2 O6 S	C17 H21 N2 O6 S	381.1115	98.87		380.105	380.1042	-1.96	1.96	99.88	95.63	99.87	381.1122	9
☐	C13 H20 N2 O11	C13 H21 N2 O11	381.114	98		380.1049	380.1067	4.63	4.63	94.87	99.14	99.3	381.1122	5
☑	C25 H16 O4	C25 H17 O4	381.1121	97.48		380.1049	380.1049	-0.23	0.23	91.47	99.65	100	381.1122	18
☐	C22 H20 O4 S	C22 H21 O4 S	381.1155	97.39		380.105	380.1082	8.63	8.63	97.93	96.29	97.6	381.1122	13
☐	C14 H24 N2 O6 S2	C14 H25 N2 O6 S2	381.1149	97.05		380.105	380.1076	6.9	6.9	97.41	93.81	98.46	381.1122	4

m/z	Ion	Formula	Abundance
403.0943	(M+Na)+	C25 H16 Na O4	248433.3

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☐	C17 H20 N2 O6 S	C17 H20 N2 Na O6 S	403.0934	99.86		380.1051	380.1042	-2.23	2.23	99.88	99.83	99.85	403.0943	9
☐	C22 H20 O4 S	C22 H20 Na O4 S	403.0975	98.59		380.1051	380.1082	8.36	8.36	98.68	99.74	97.96	403.0943	13
☐	C13 H20 N2 O11	C13 H20 N2 Na O11	403.0959	98.14		380.1051	380.1067	4.36	4.36	95.31	98.92	99.44	403.0943	5
☐	C14 H24 N2 O6 S2	C14 H24 N2 Na O6 S2	403.0968	98.06		380.1051	380.1076	6.63	6.63	95.58	99.71	98.71	403.0943	4
☐	C21 H20 N2 O S2	C21 H20 N2 Na O S2	403.0909	97.93		380.1051	380.1017	-8.82	8.82	96.74	99.75	97.74	403.0943	13
☑	C25 H16 O4	C25 H16 Na O4	403.0941	97.84		380.105	380.1049	-0.5	0.5	93.92	98.24	99.99	403.0943	18
☐	C18 H24 N2 O S3	C18 H24 N2 Na O S3	403.0943	97.58		380.1051	380.1051	0.05	0.05	91.83	99.62	100	403.0943	8



4

page 1

Figure S52. The (+)-HRESIMS report of compound **4**, page 3.

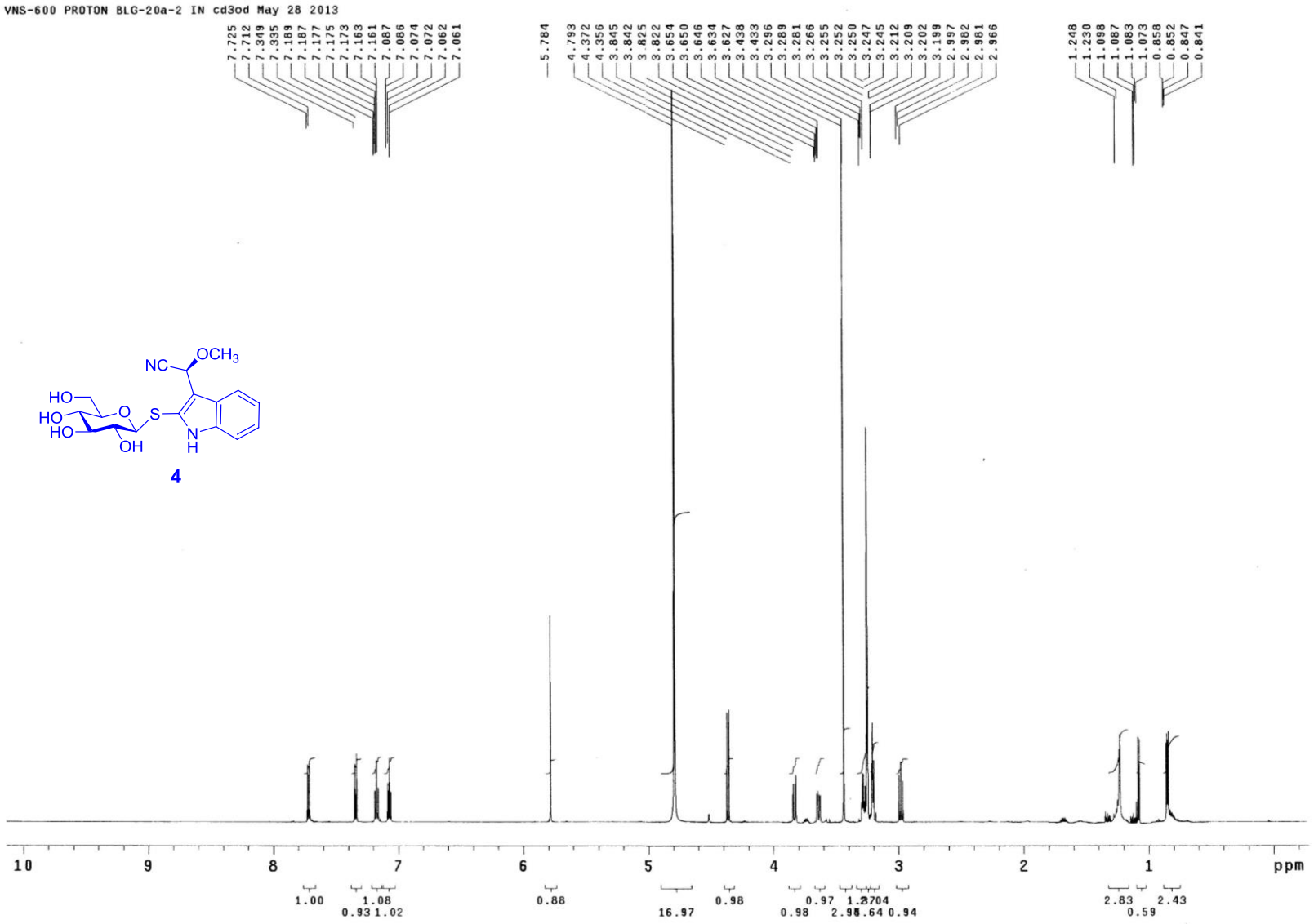


Figure S53.The ^{1}H NMR spectrum of compound **4** in CD_3OD (600 MHz).

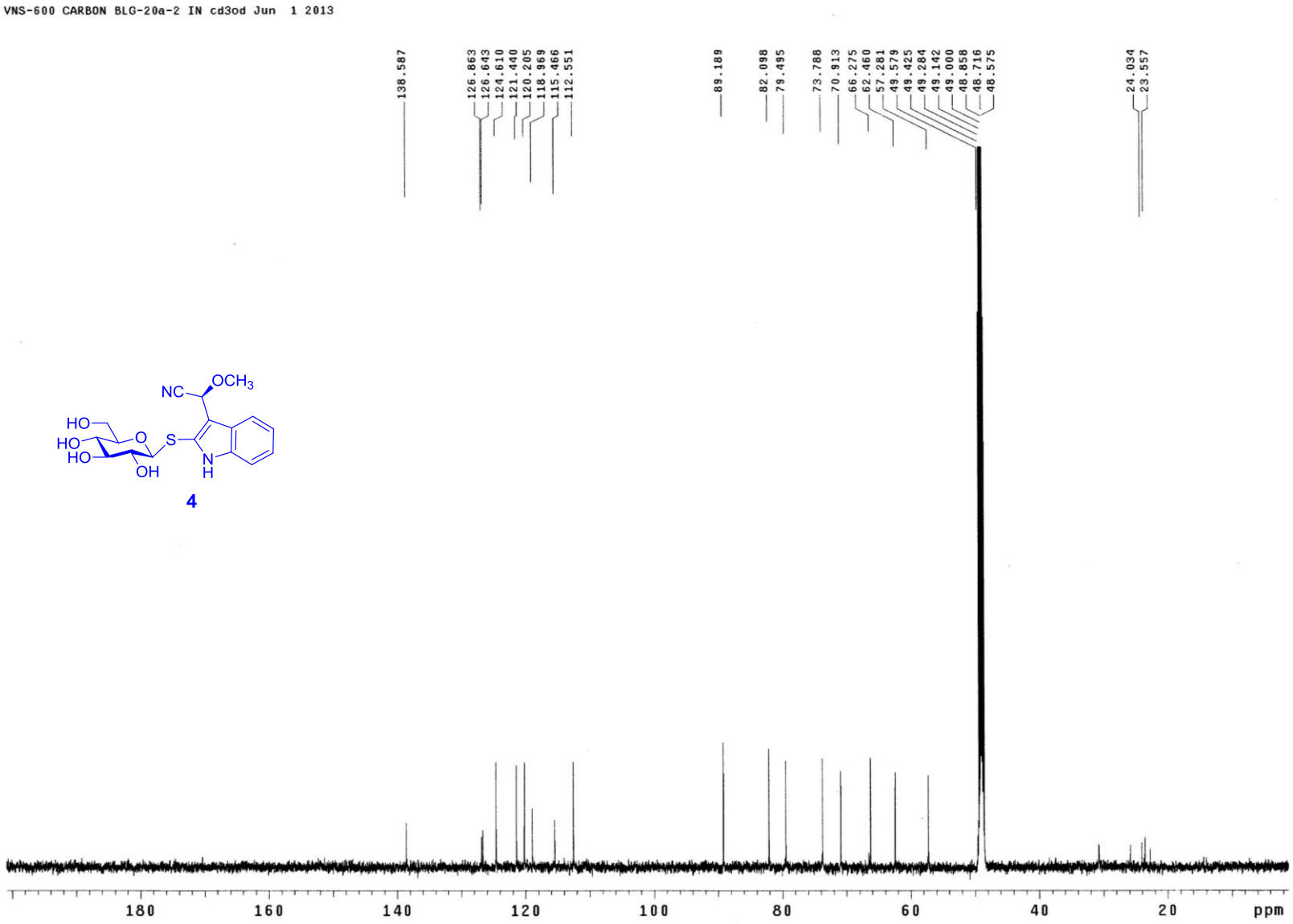


Figure S54. The ^{13}C NMR spectrum of compound **4** in CD_3OD (150 MHz).

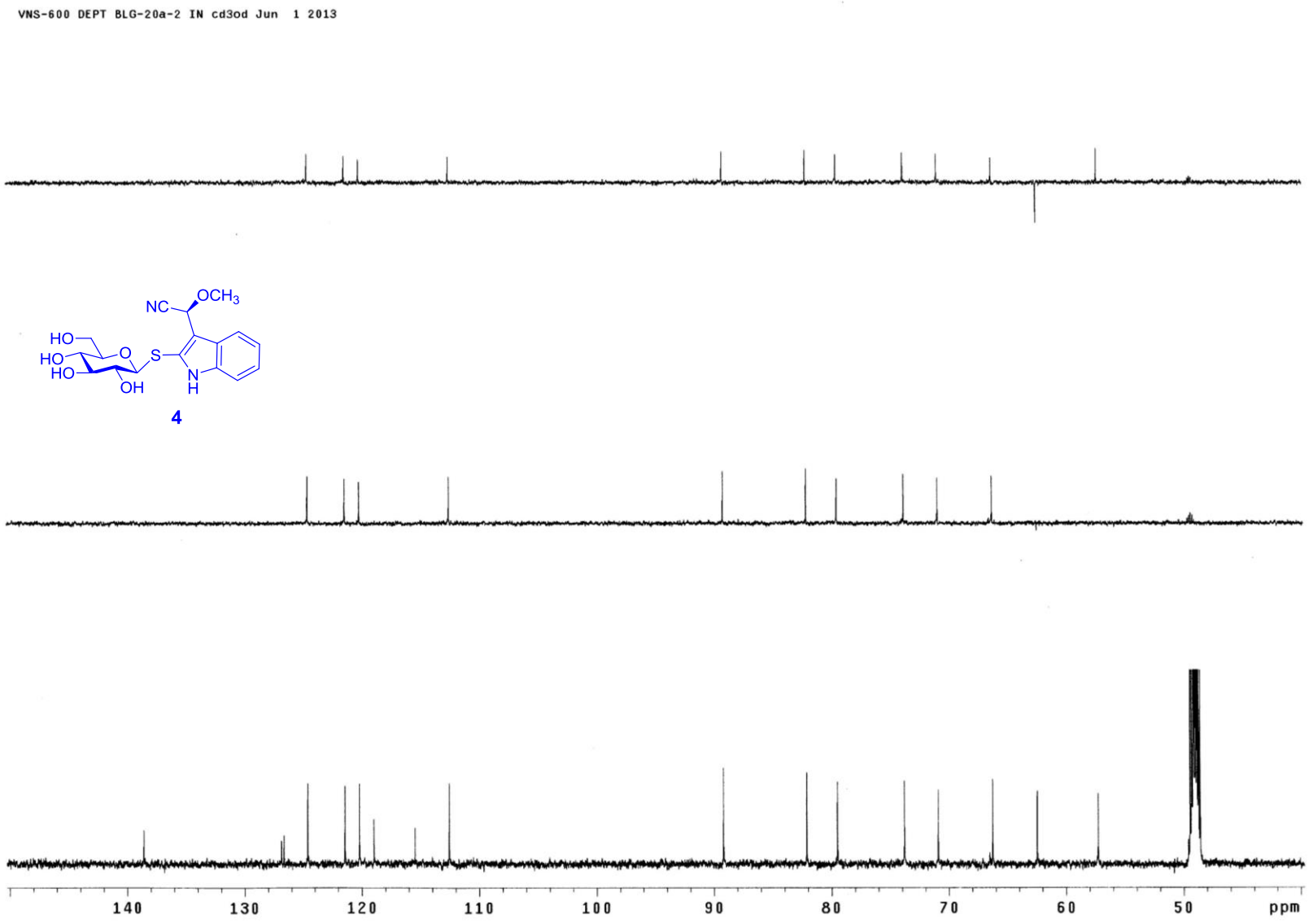


Figure S55. The DEPT spectrum of compound **4** in CD_3OD (150 MHz).

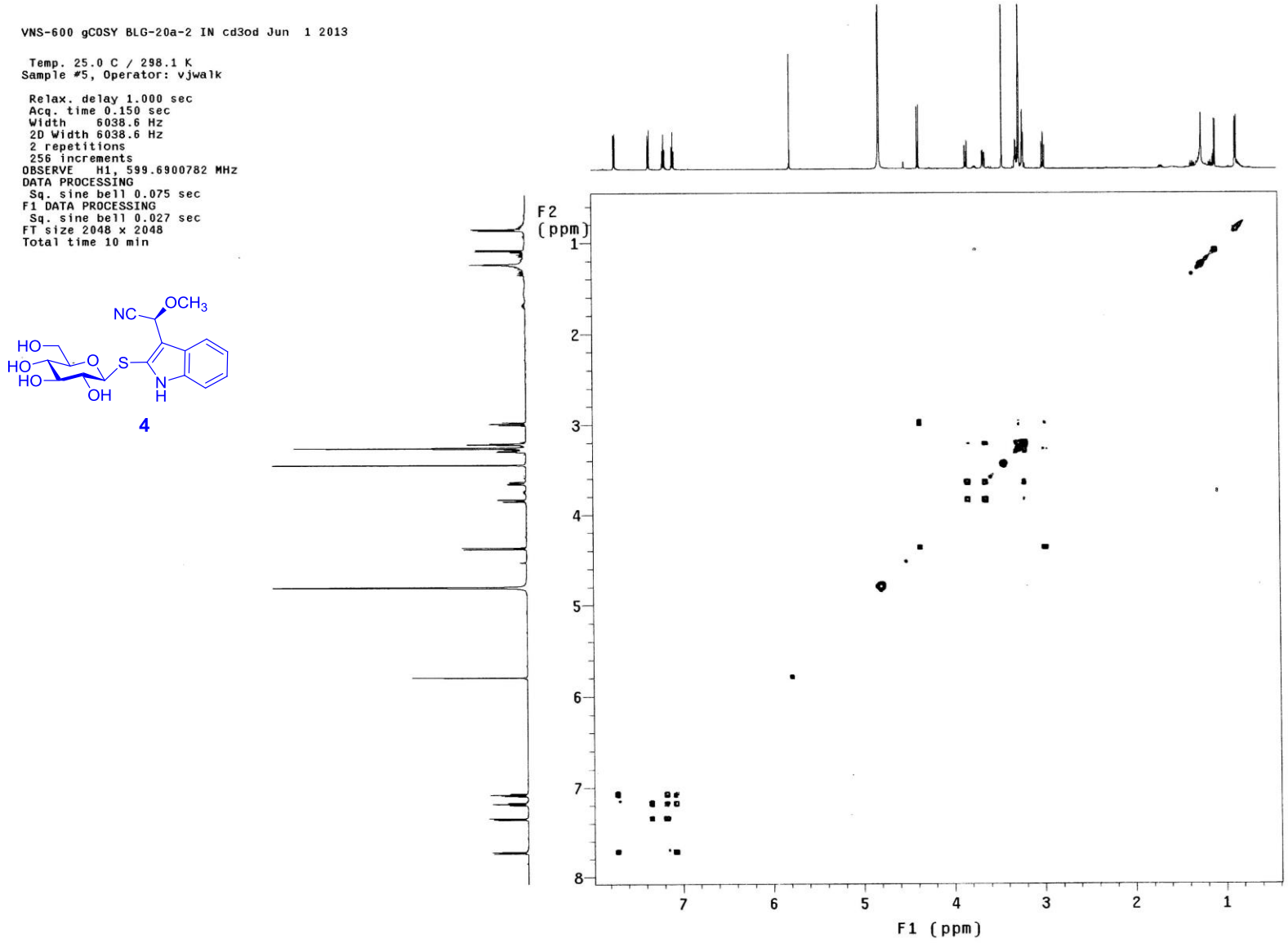


Figure S56. The ^{1}H-^{1}H COSY spectrum of compound **4** in CD_3OD (600 MHz).

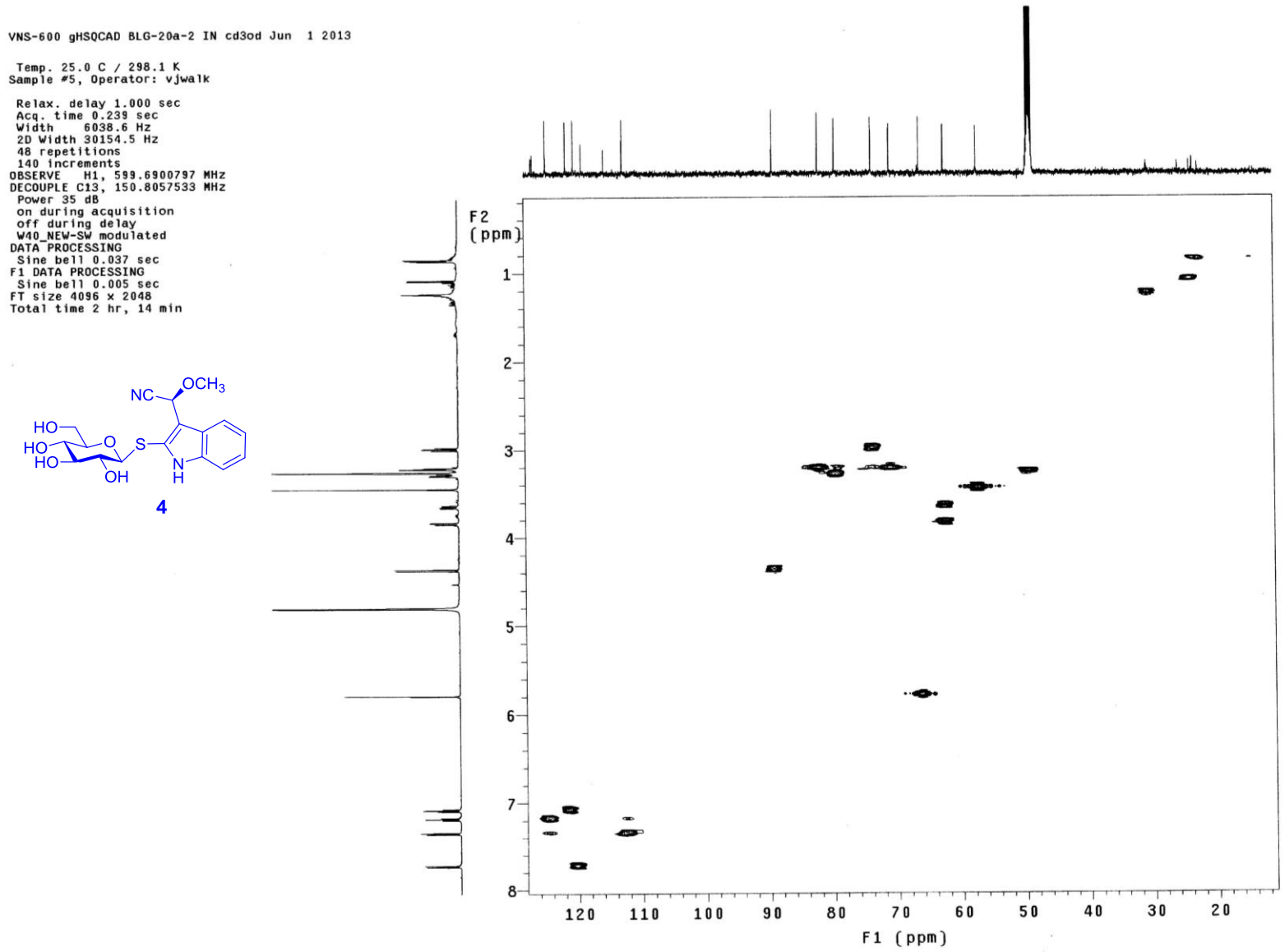


Figure S57. The HSQC spectrum of compound **4** in CD_3OD (600 MHz for ^1H).

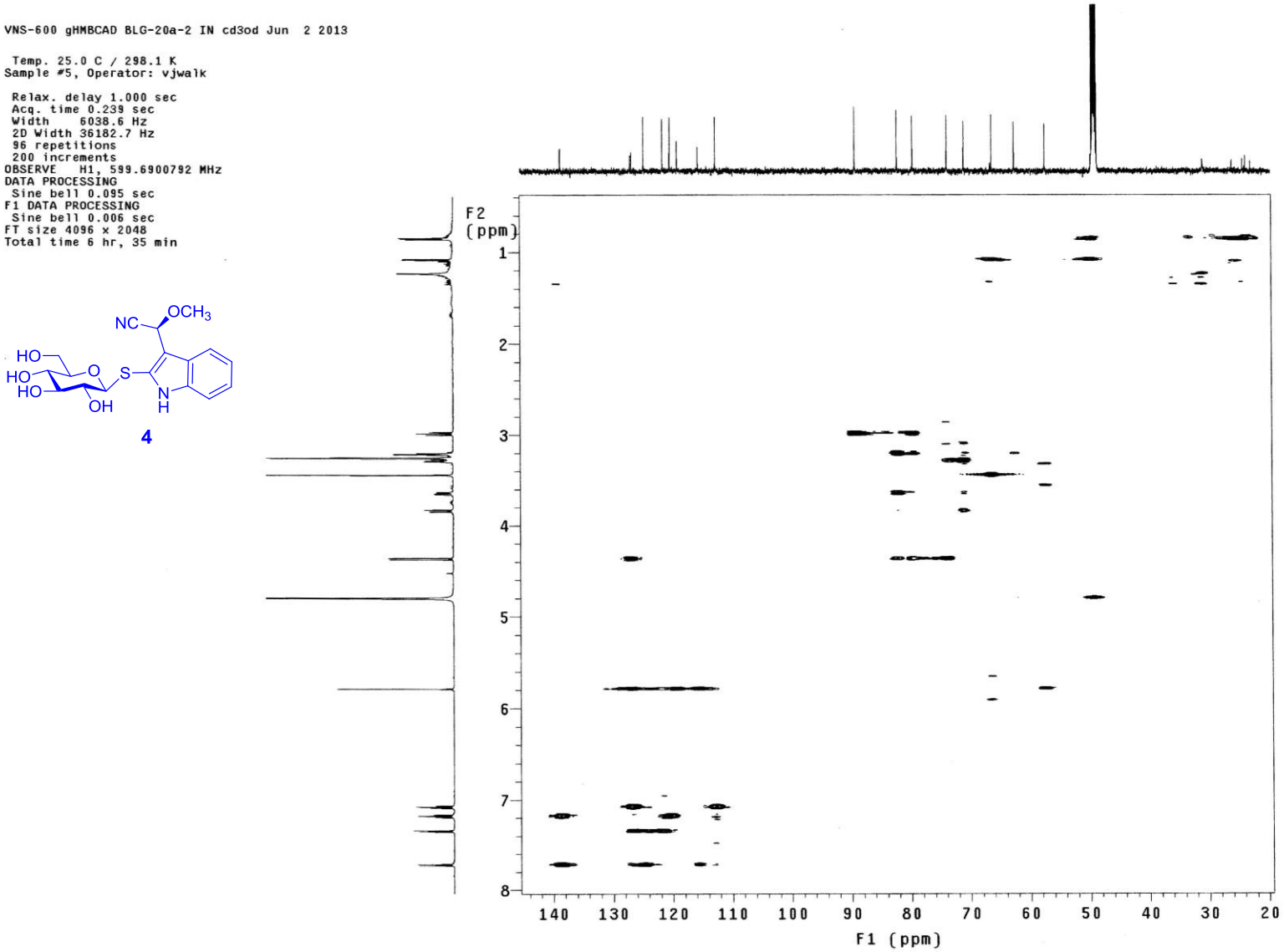


Figure S58. The HMBC spectrum of compound **4** in CD_3OD (600 MHz for ^1H).

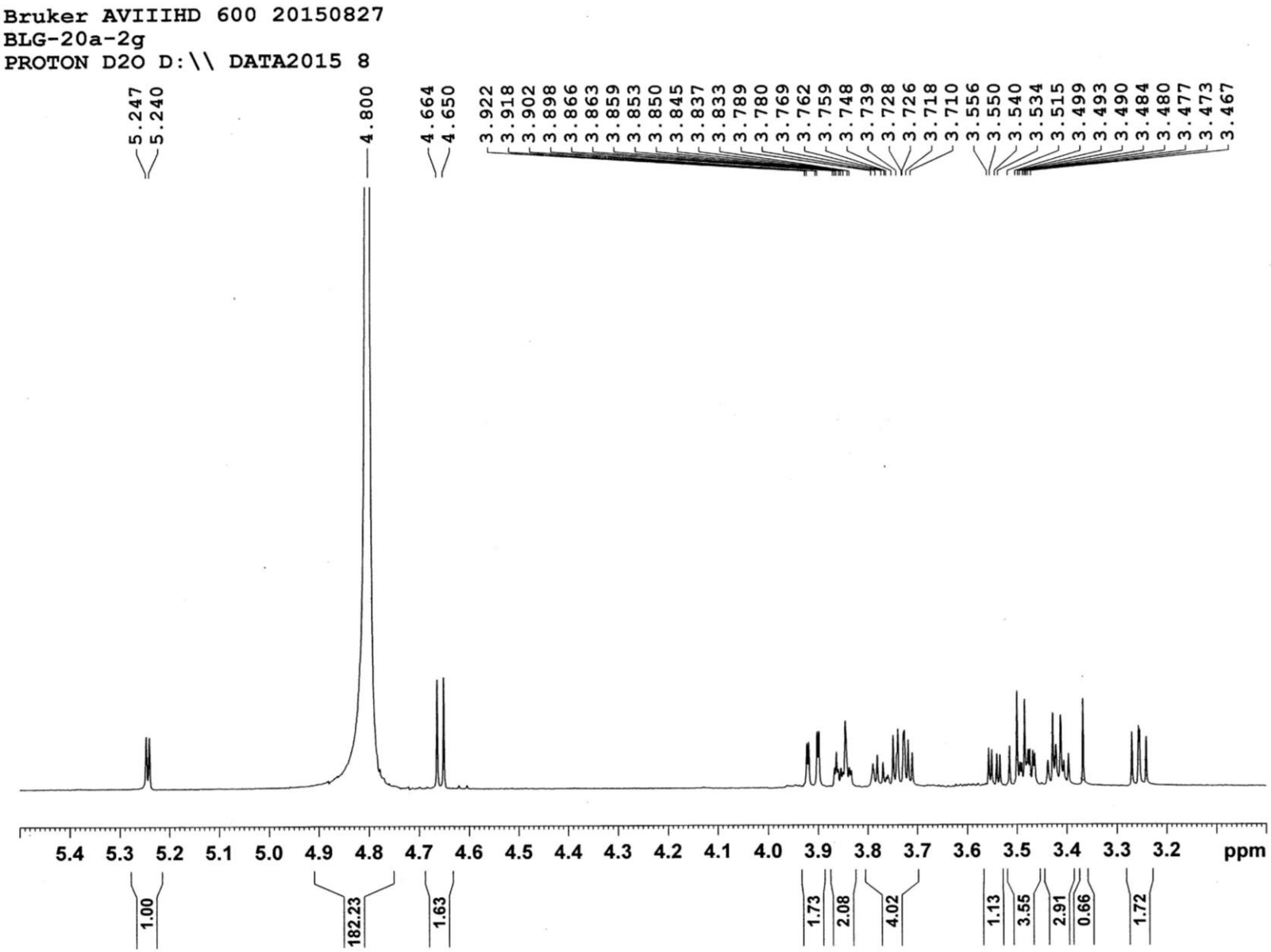
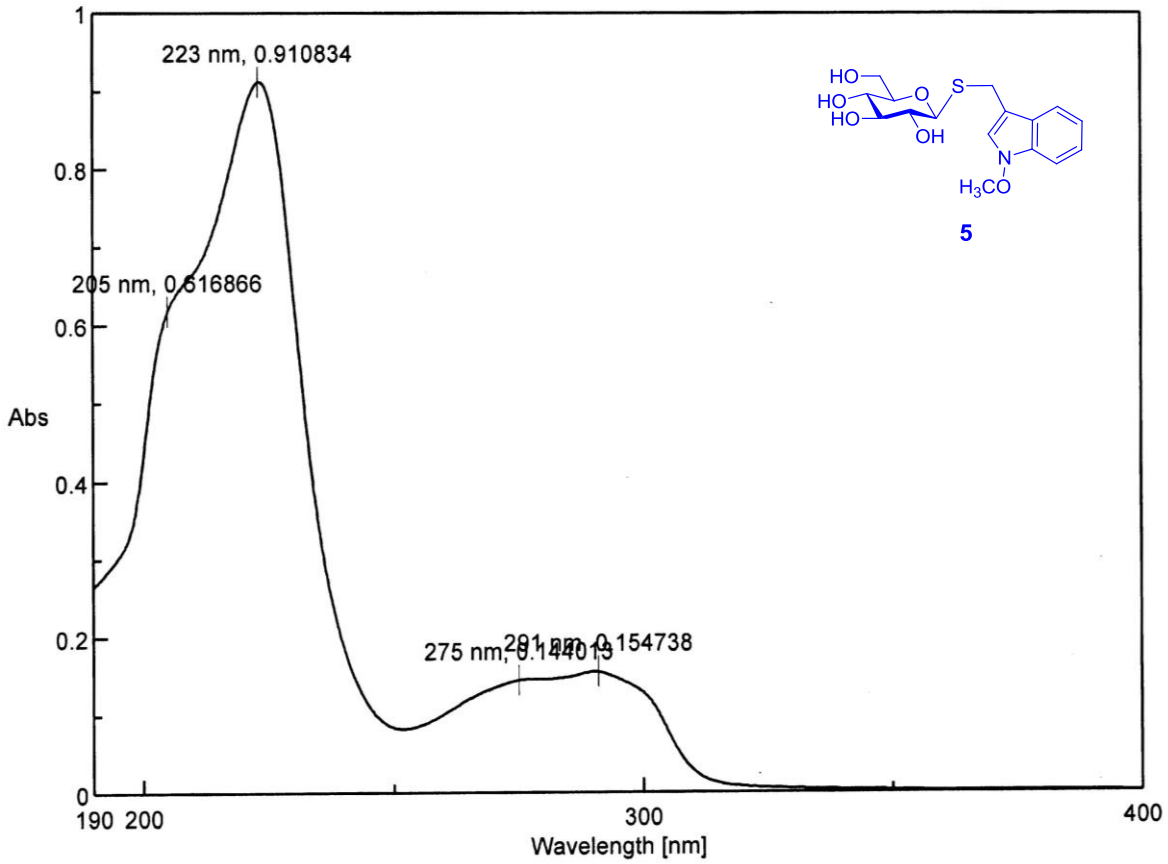


Figure S59. The ^{1}H NMR spectrum of D-glucose in D_2O (600 MHz), isolated from hydrolysate of compound **4**.



blg-I-48

[Comment]	
Sample Name	blg-I-48
Comment	0.02
User	
Division	UV
Company	324

[Measurement Information]	
Instrument Name	V-650
Model Name	V-650
Serial No.	A034461150
Accessory	PSC-718
Accessory S/N	A001761114
Position	1
Cell Length	10 mm
Temperature	19.98 C
Control Sonsor	Holder
Monitor Sensor	Holder
Start Mode	Start immediately
Photometric Mode	Abs
Measurement range	400 - 190 nm
Data pitch	0.2 nm
Band width(UV/Vis)	2.0 nm
Response	Medium
Scanning speed	200 nm/min
Source Change	340 nm
Light Source	D2/WI
Filter Exchange	Step
Correction	Baseline

[Data Information]	
Creation Date	2015-7-22 12:55
Data array type	Linear data array
Horizontal	Wavelength [nm]
Vertical	Abs
Start	400 nm
End	190 nm
Data pitch	0.2 nm
Data points	1051

Figure S60. The UV spectrum of compound **5** in MeOH.

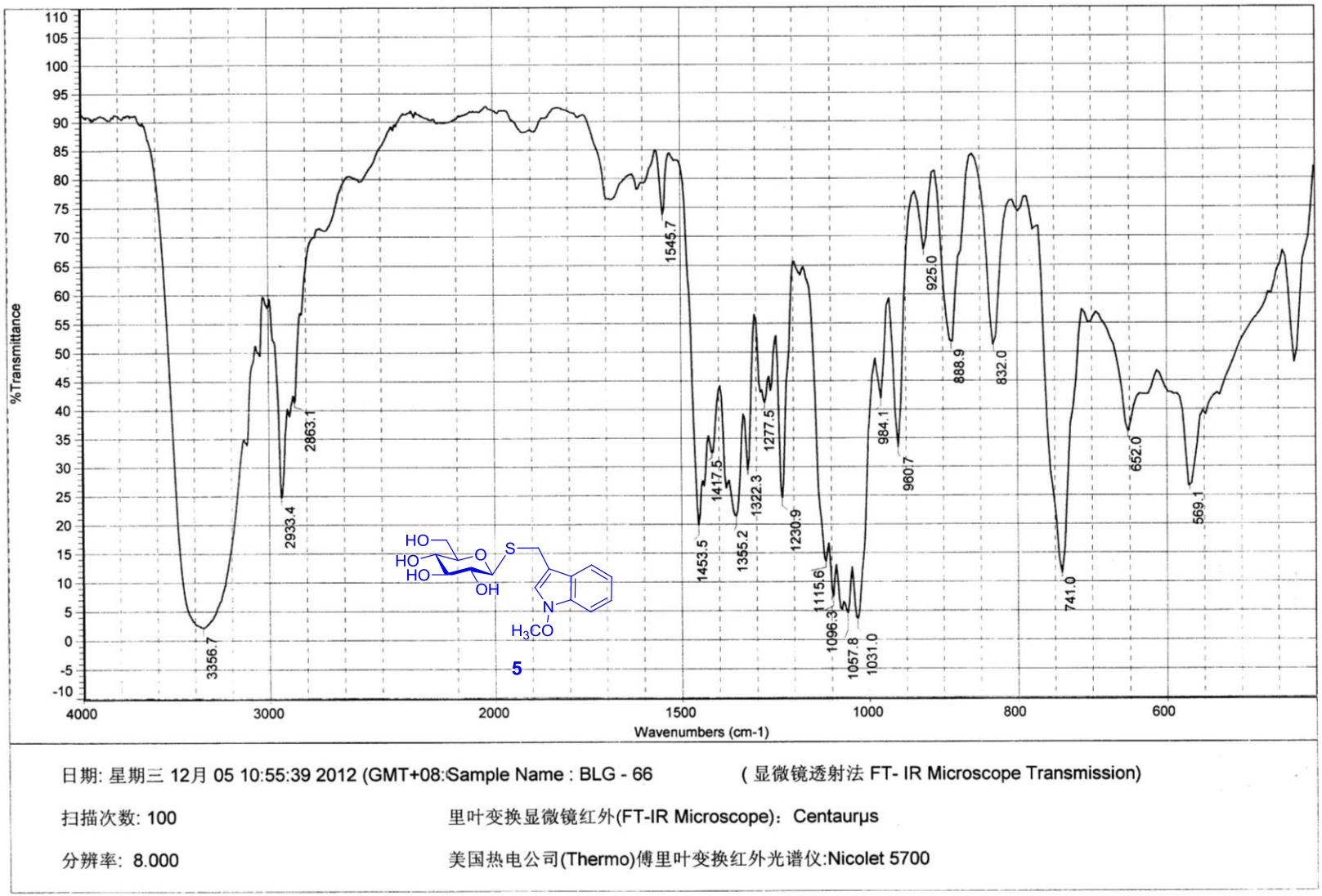


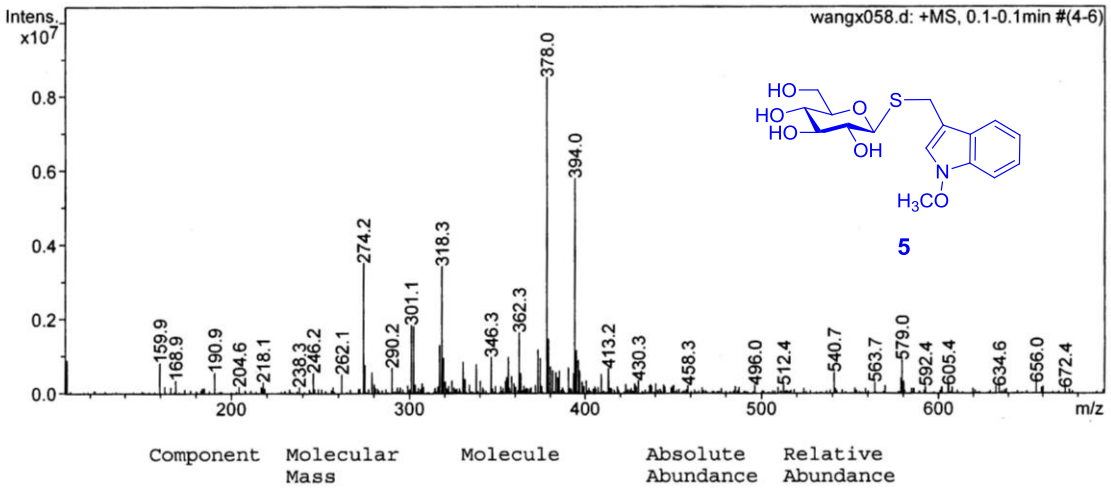
Figure S61. The IR spectrum of compound **5**.

Single Mass Spectrum Deconvolution Report

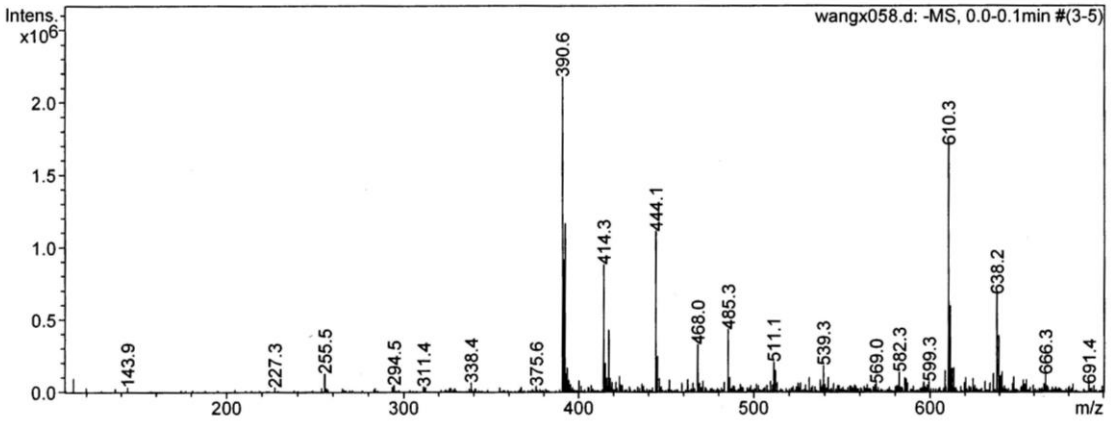
Analysis Name: wangx058.d **Instrument:** LC-MSD-Trap-SL **Print Date:** 7/3/2012 12:29:22 PM
Method: TEST.MS **Operator:** Operator **Acq. Date:** 7/3/2012 12:24:42 PM
Sample Name: BLG-66
Analysis Info:

Acquisition Parameter:

Mass Range Mode	Std/Normal	Trap Drive	49.1	Scan Begin	100 m/z
Ion Polarity	Positive	Octopole RF Amplitude	161.9 Vpp	Scan End	700 m/z
Ion Source Type	ESI	Capillary Exit	-104.1 Volt	Averages	5 Spectra
Dry Temp (Set)	330 °C	Skimmer	-40.0 Volt	Max. Accu Time	200000 µs
Nebulizer (Set)	15.00 psi	Oct 1 DC	-12.00 Volt	ICC Target	20000
Dry Gas (Set)	5.00 l/min	Oct 2 DC	-1.70 Volt	Charge Control	on



Component	Molecular Mass	Molecule	Absolute Abundance	Relative Abundance



Component	Molecular Mass	Molecule	Absolute Abundance	Relative Abundance

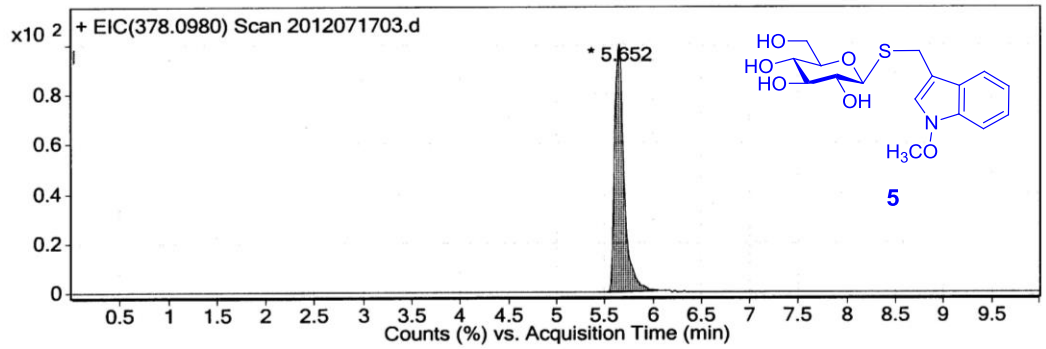
Figure S62. The ESI mass spectrum of compound **5**.

Qualitative Analysis Report

Data Filename	2012071703.d	**Sample Name**	BLG-66
Sample Type	Sample	**Position**	P1-D9
Instrument Name	Instrument 1	**User Name**	
Acq Method		**IRM Calibration Status**	[redacted]
DA Method	TEST LCMS.m	**Comment**	

User Chromatograms

Fragmentor Voltage 135 **Collision Energy** 0 **Ionization Mode** ESI

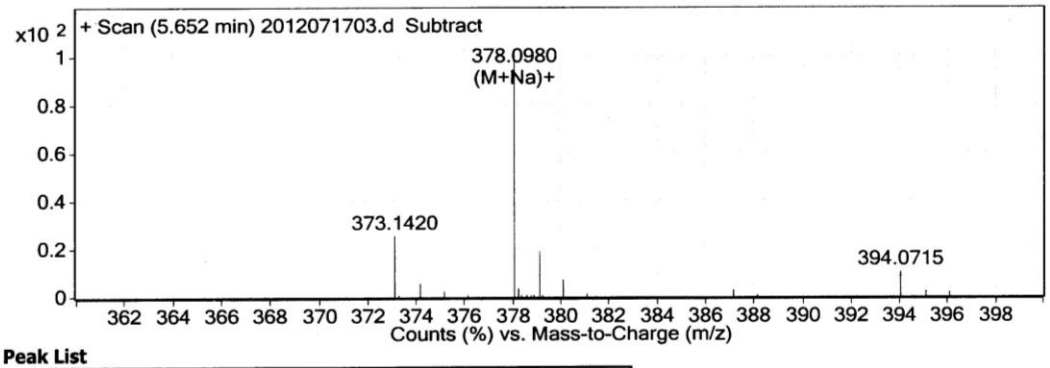


Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	5.523	5.652	6.054	405840	2701582	100

User Spectra

Fragmentor Voltage 135 **Collision Energy** 0 **Ionization Mode** Esi



Peak List

m/z	z	Abund	Formula	Ion
125.9861		31349		
160.0751		46814		
217.0475		22471		
373.142	1	102863		
374.1448	1	21284		
378.098	1	406273	C16 H21 N Na O6 S	(M+Na)+
379.1007	1	76116	C16 H21 N Na O6 S	(M+Na)+
380.0976	1	28060	C16 H21 N Na O6 S	(M+Na)+
394.0715		42511		

Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	500
O	0	90
N	0	5

Figure S63. The (+)-HRESIMS report of compound **5**, page 1.

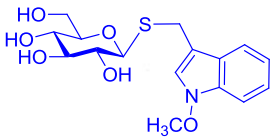
Qualitative Analysis Report

Element	Min	Max
S	0	2
Cl	0	0
Br	0	0
Si	0	0

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C16 H21 N O6 S	TRUE	355.1088	355.109	0.47	C16 H21 N Na O6 S	99.98
C17 H17 N5 O2 S		355.1088	355.1103	4.23	C17 H17 N5 Na O2 S	99.56
C20 H21 N O S2		355.1088	355.1065	-6.58	C20 H21 N Na O S2	98.23
C12 H21 N O11		355.1088	355.1115	7.52	C12 H21 N Na O11	97.83
C19 H17 N O6		355.1088	355.1056	-9.02	C19 H17 N Na O6	97.64
C20 H13 N5 O2		355.1088	355.1069	-5.26	C20 H13 N5 Na O2	97.62
C13 H25 N O6 S2		355.1088	355.1123	9.95	C13 H25 N Na O6 S2	97.51
C25 H13 N3		355.1088	355.1109	6.08	C25 H13 N3 Na	95.74

--- End Of Report ---



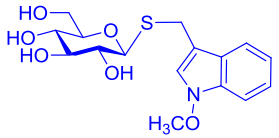
5

Figure S64 The (+)-HRESIMS report of compound **5**, page 2.

MS Formula Results: + Scan (5.652 min) Sub (2012071703.d)

m/z	Ion	Formula	Abundance
378.098	(M+Na)+	C16 H21 N Na O6 S	406273.2

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☑	C16 H21 N O6 S	C16 H21 N Na O6 S	378.0982	99.98		355.1088	355.109	0.47	0.47	99.96	99.97	99.99	378.098	7
☐	C17 H17 N5 O2 S	C17 H17 N5 Na O2 S	378.0995	99.56		355.1088	355.1103	4.23	4.23	99.33	99.99	99.49	378.098	12
☐	C20 H21 N O S2	C20 H21 N Na O S2	378.0957	98.23		355.1088	355.1065	-6.58	6.58	95.94	99.91	98.76	378.098	11
☐	C12 H21 N O11	C12 H21 N Na O11	378.1007	97.83		355.1088	355.1115	7.52	7.52	96.07	98.85	98.38	378.098	3
☐	C19 H17 N O6	C19 H17 N Na O6	378.0948	97.64		355.1088	355.1056	-9.02	9.02	96.85	98.49	97.68	378.098	12
☐	C20 H13 N5 O2	C20 H13 N5 Na O2	378.0961	97.62		355.1088	355.1069	-5.26	5.26	94.13	98.62	99.21	378.098	17
☐	C13 H25 N O6 S2	C13 H25 N Na O6 S2	378.1016	97.51		355.1088	355.1123	9.95	9.95	96.08	99.87	97.18	378.098	2
☐	C25 H13 N3	C25 H13 N3 Na	378.1002	95.74		355.1088	355.1109	6.08	6.08	88.29	98.26	98.94	378.098	21



5

page 1

Figure S65. The (+)-HRESIMS report of compound **5**, page 3.

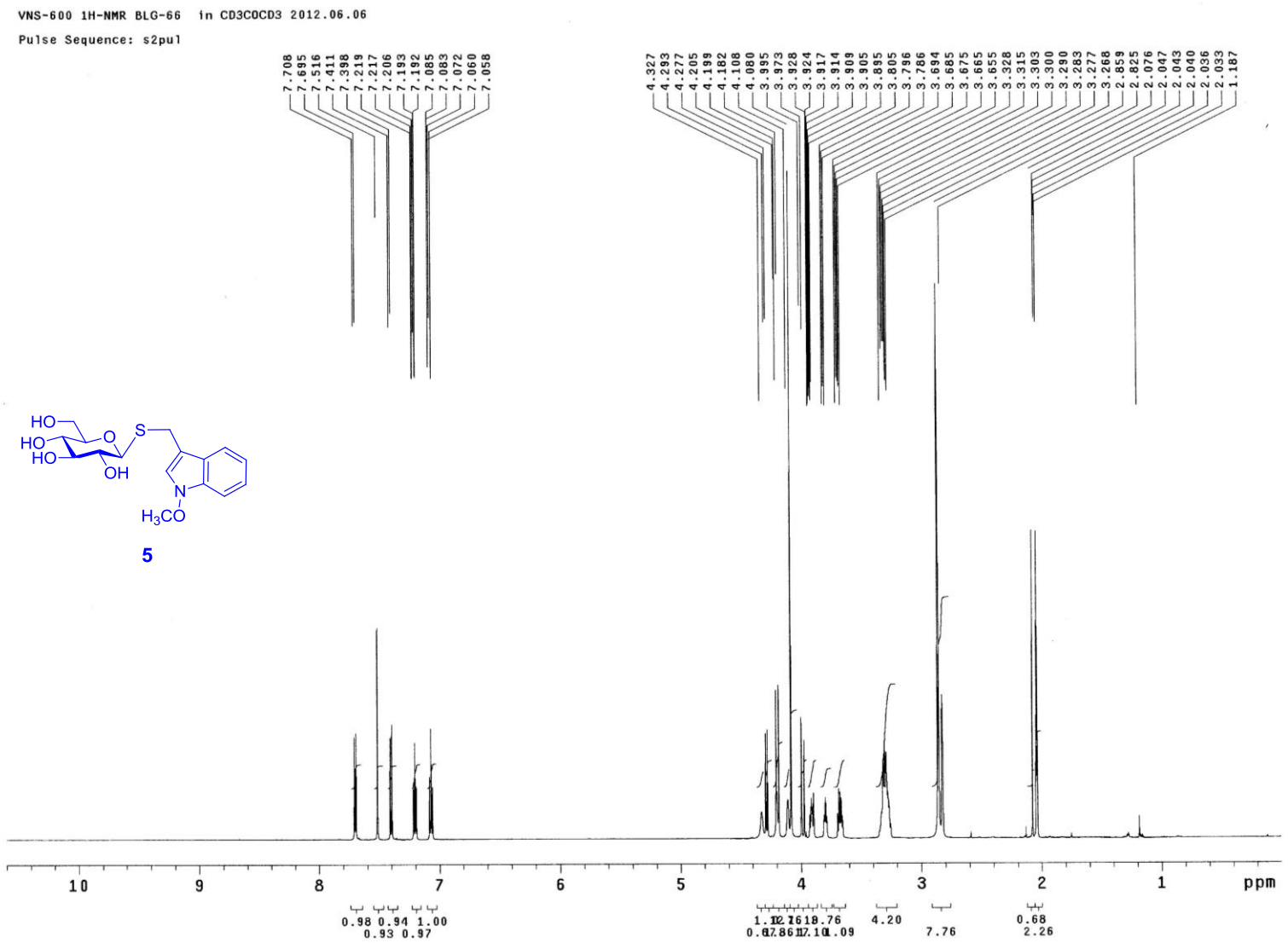


Figure S66. The ^{1}H NMR spectrum of compound **5** in acetone-d_6 (600 MHz).

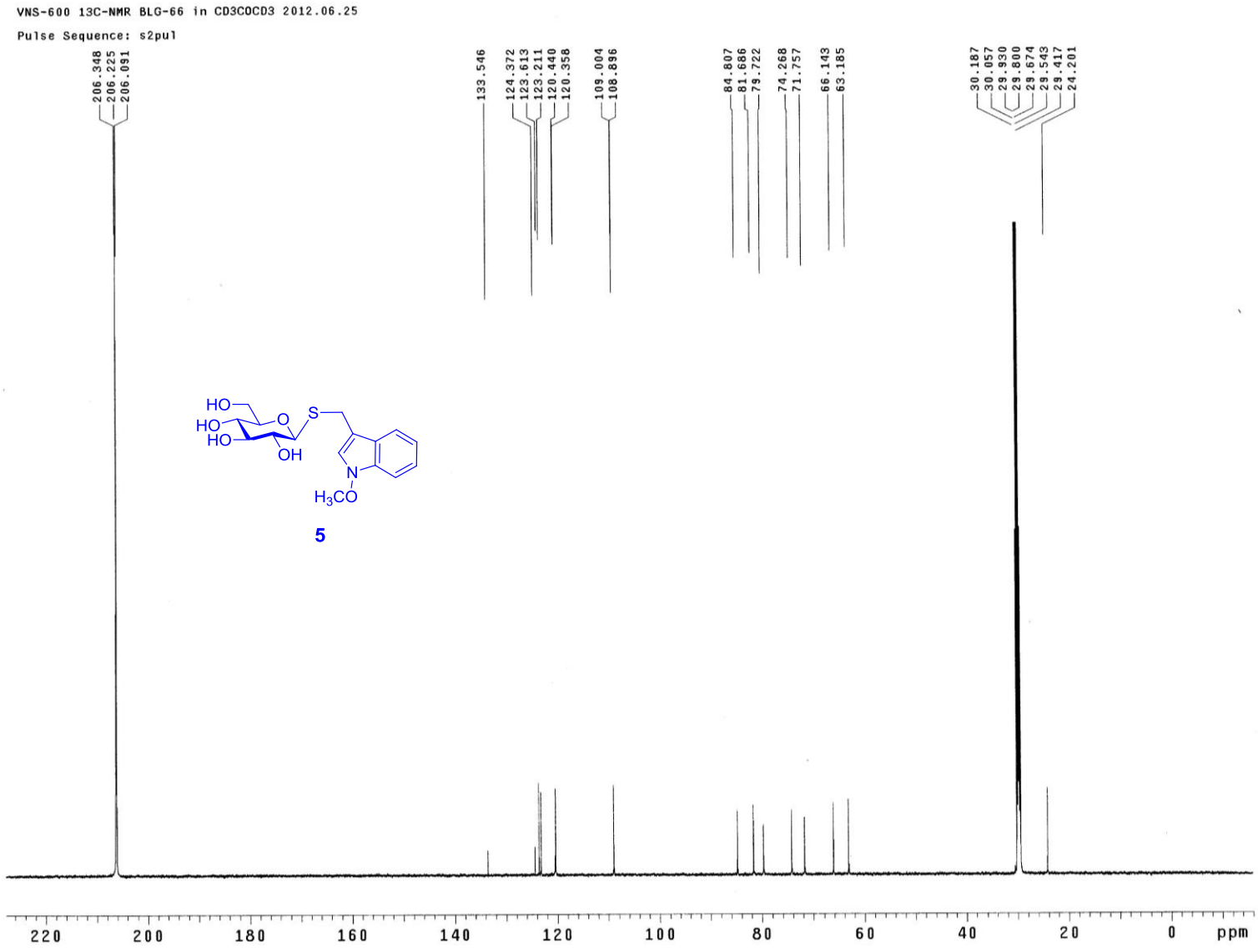


Figure S67. The ^{13}C NMR spectrum of compound **5** in acetone-d_6 (150 MHz)..

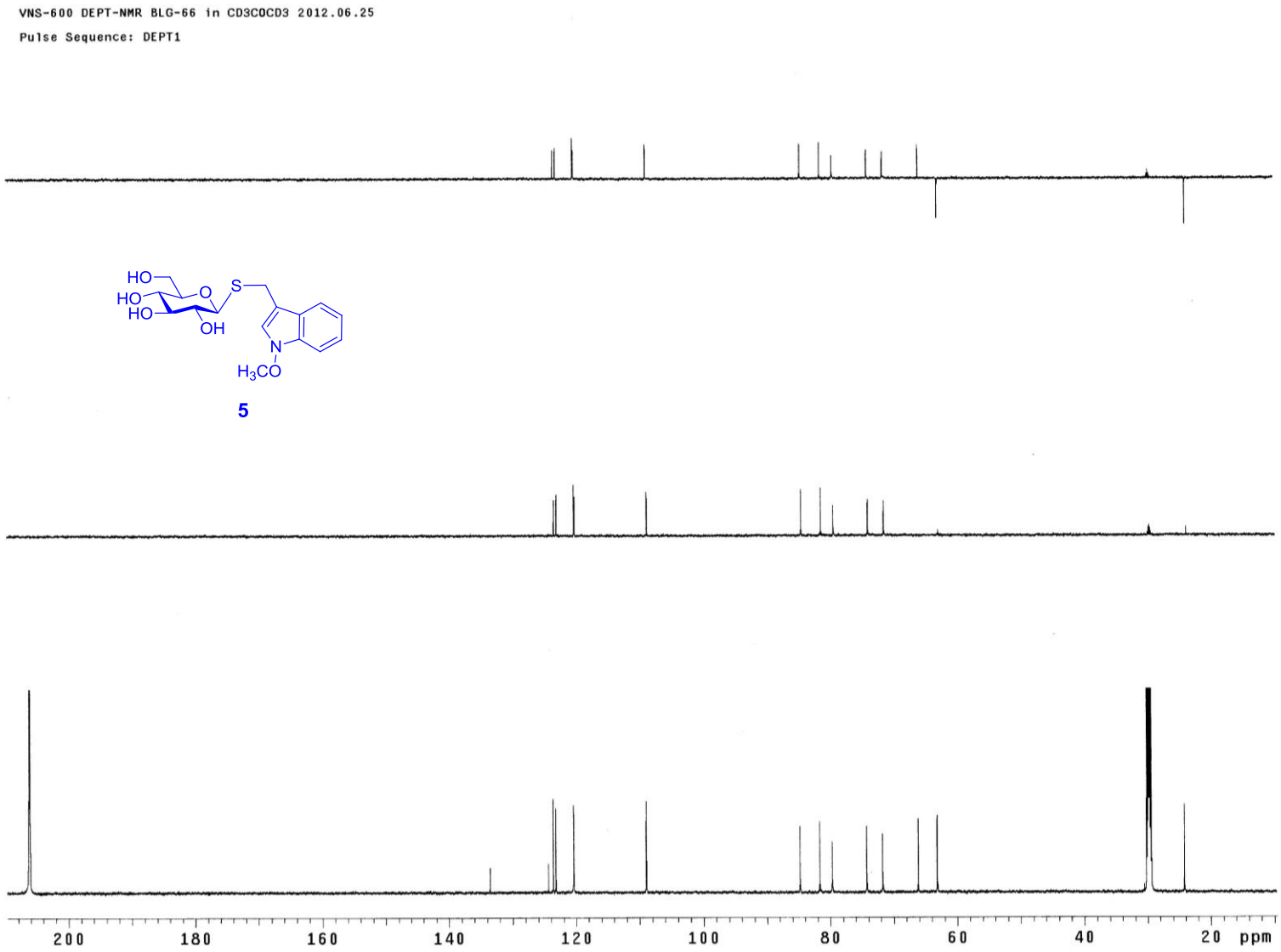


Figure S68. The DEPT spectrum of compound **5** in acetone-d_6 (150 MHz).

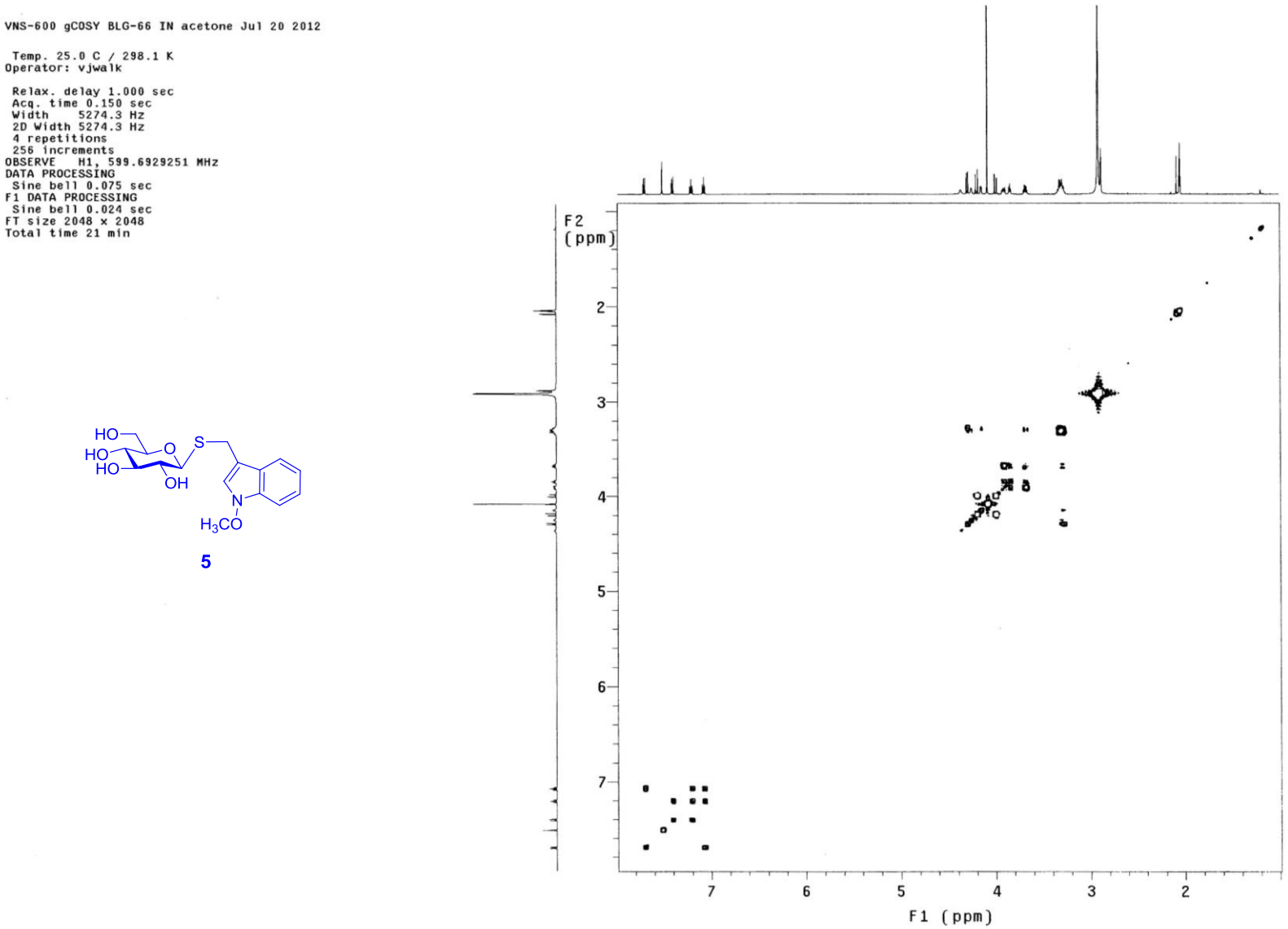


Figure S69. The ^{1}H-^{1}H COSY spectrum of compound **5** in acetone-d_6 (600 MHz).

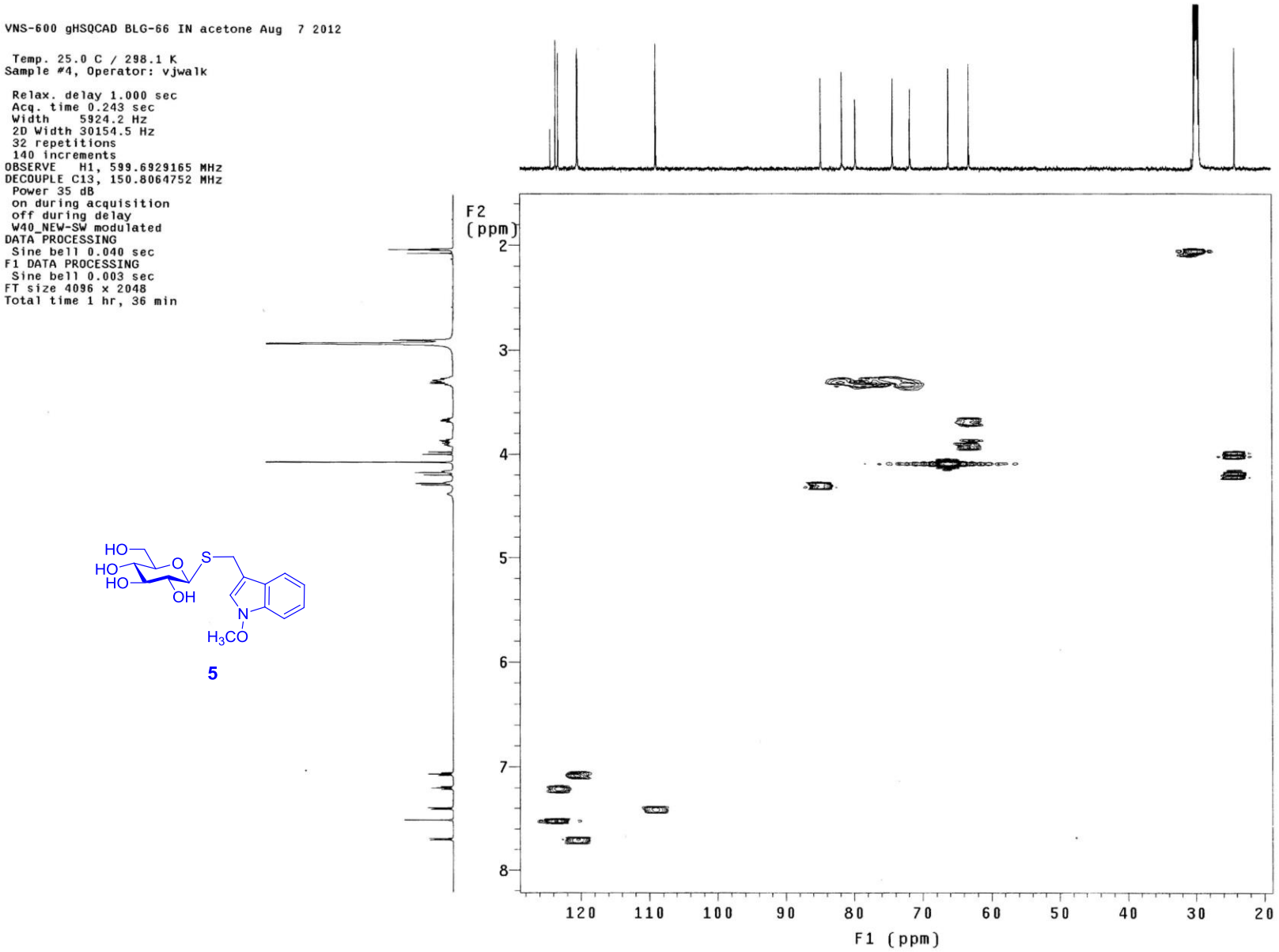


Figure S70. The HSQC spectrum of compound **5** in acetone-d_6 (600 MHz for ^{1}H).

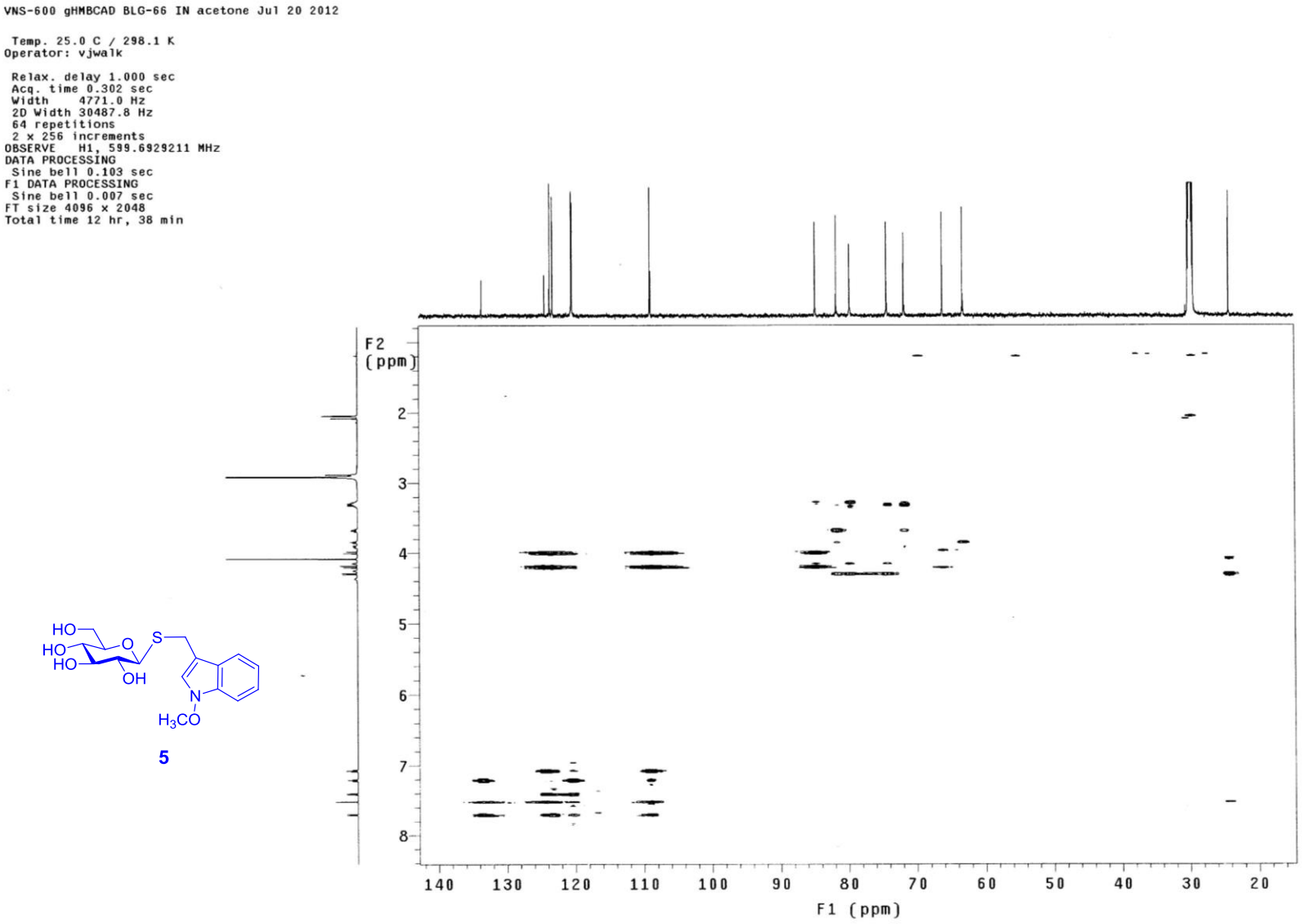


Figure S71. The HMBC spectrum of compound **5** in acetone-d_6 (600 MHz for ^{1}H).

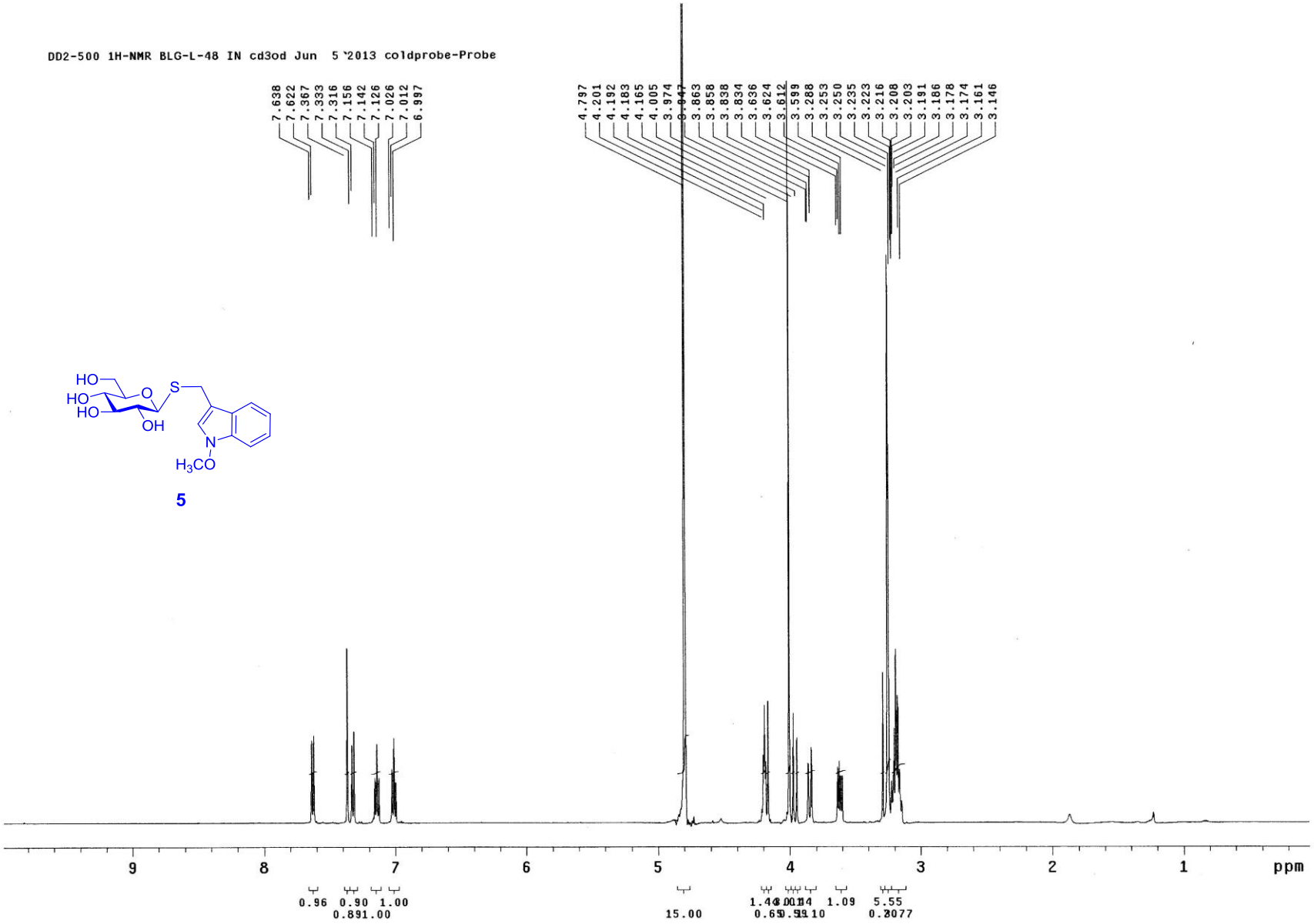


Figure S72.The ^{1}H NMR spectrum of compound **5** in CD_3OD (500 MHz).

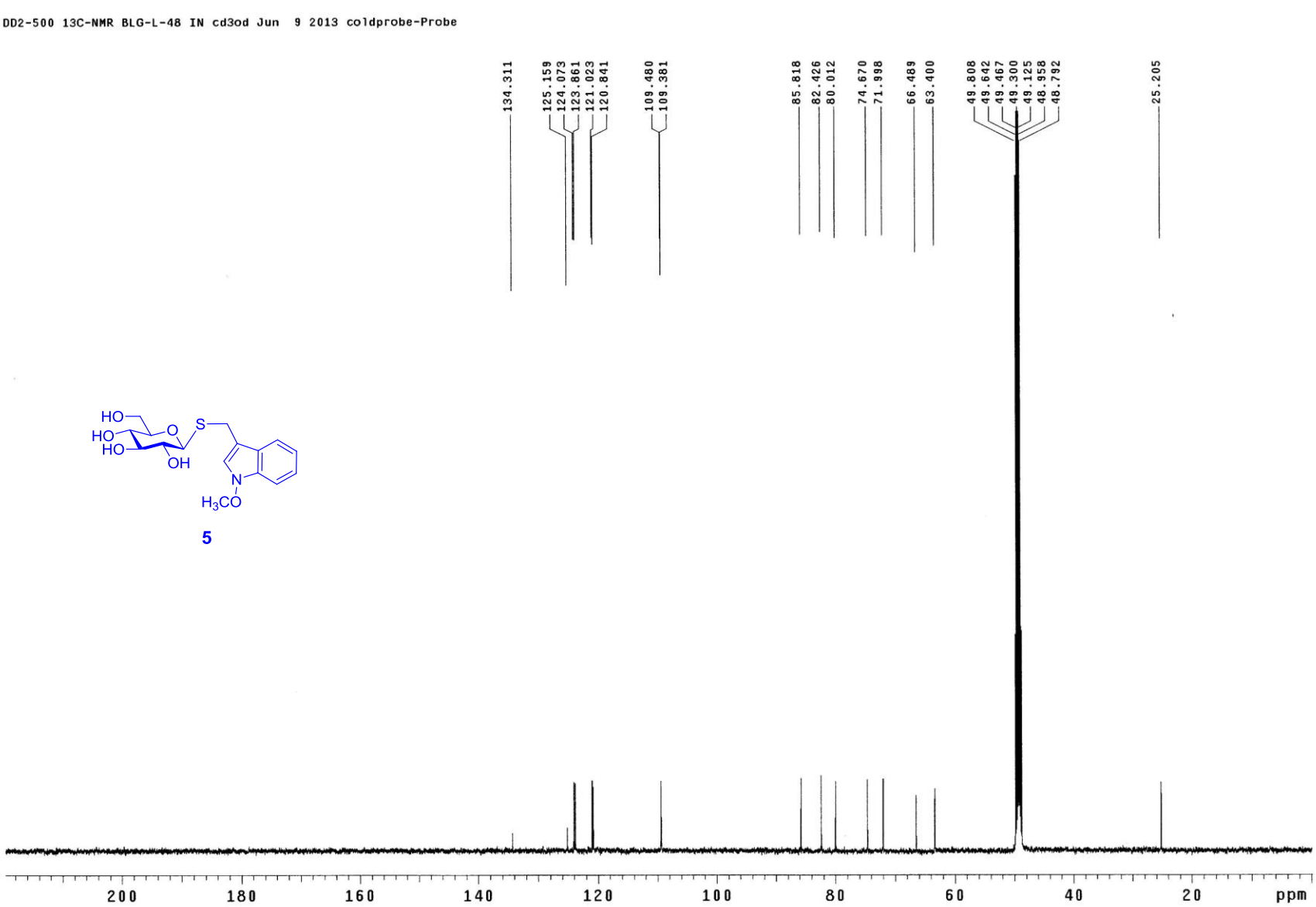


Figure S73.The ^{13}C NMR spectrum of compound **5** in CD_3OD (125 MHz).

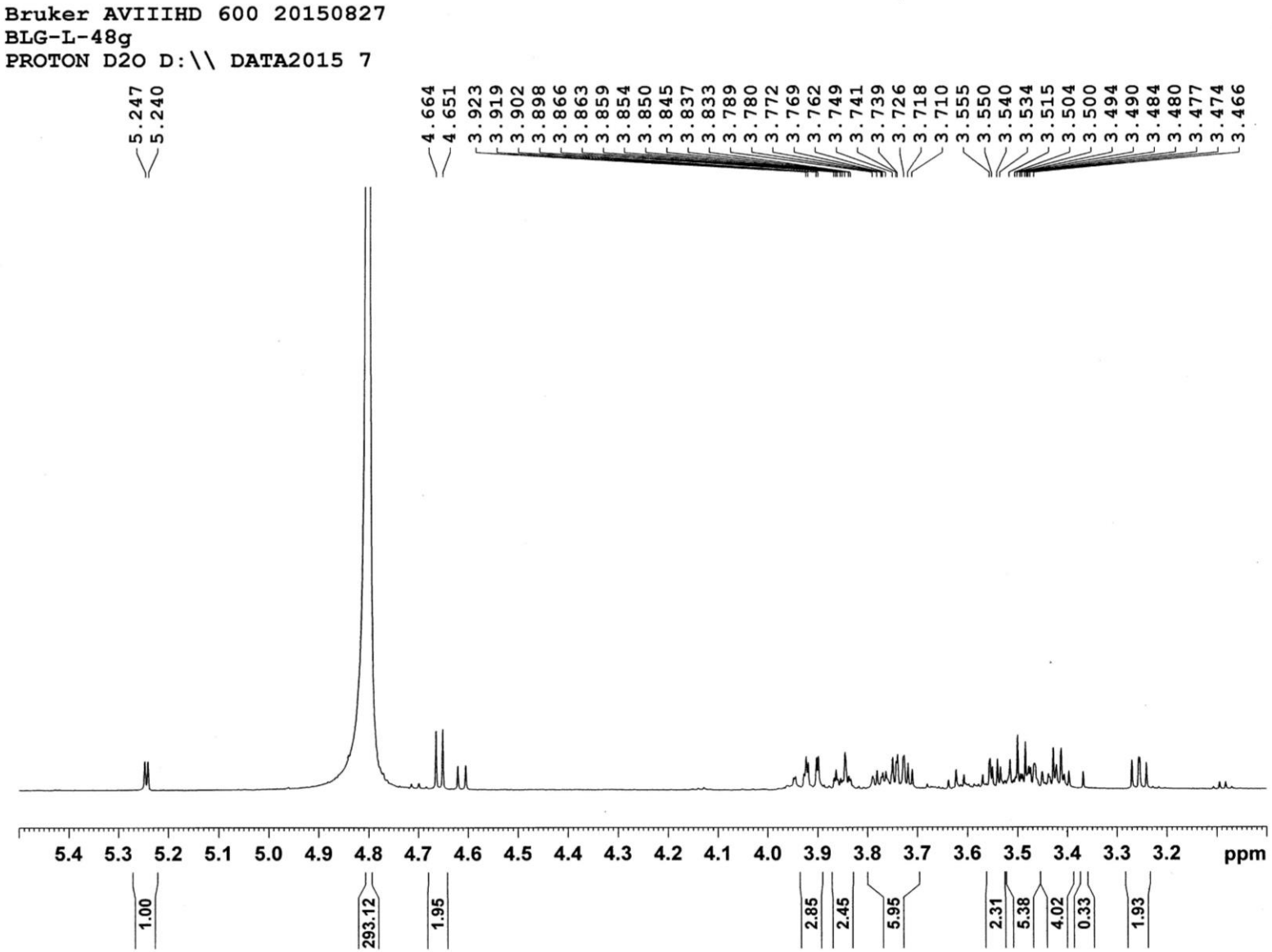


Figure S74. The ^{1}H NMR spectrum of D-glucose in D_2O (600 MHz), isolated from hydrolysate of compound **5**.

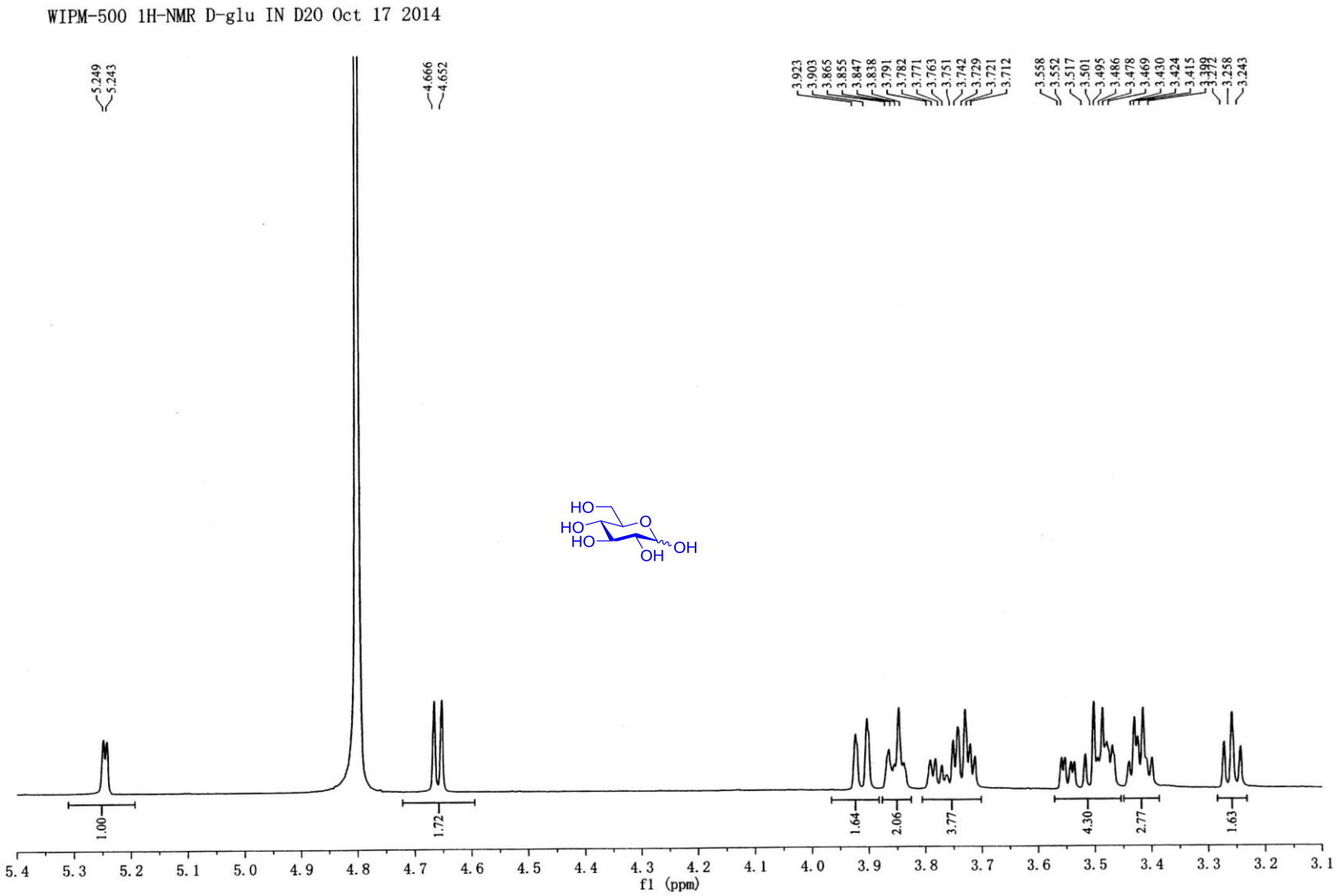


Figure S75 The ^{1}H NMR spectrum of an authentic D-glucose in D_2O (500 MHz)

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