Supporting Information

Spiro Meroterpenoids from *Ganoderma applanatum*

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Contents

1. ECD and ^{13}C NMR chemical shift calculated methods

1.1. ECD calculations of 1–9.

Computational methods

Molecular Merck force field (MMFF) and DFT/TDDFT calculations were performed with Spartan'14 software package (Wavefunction Inc., Irvine, CA, USA) and Gaussian09 program package,[1] respectively, using default grids and convergence criteria. MMFF conformational search generated low-energy conformers within a 10 kcal/mol energy window were subjected to geometry optimization using DFT method at the B3LYP/6-31G (d) level. Frequency calculations were run at the same level to estimate their relative thermal free energies (ΔG) at 298.15K. Energies of the low-energy conformers in MeOH were re-calculated at the B3LYP/def2-TZVP level. Solvent effects were taken into account by using polarizable continuum model (PCM). The TDDFT calculations were performed using the hybrid M06[2] and BMK[3] and the long-range corrected hybrid CAM-B3LYP[4] functionals, and the Ahlrichs' basis set TZVP (triple zeta valence plus polarization).[5] The number of excited states per each molecule was 40. The CD spectra were generated by the program SpecDis [6] using a Gaussian band shape with 0.24 or 0.28 eV exponential half-width from dipole-length dipolar and rotational strengths. The equilibrium population of each conformer at 298.15K was calculated from its relative free energies using Boltzmann statistics. The calculated spectra of compounds were generated from the low-energy conformers according to the Boltzmann weighting of each conformer in MeOH solution. (2'*S*,3'*S*)-**1** and (2'*R*,3'*S*)-**2** were subjected to MMFF, DFT, and TDDFT calculations. The calculated ECD spectra of (2'*S*,3'*R*)-**1** and (2'*R*,3'*R*)-**2** were the mirror images of calculated spectra of (2'*R*,3'*S*)-**2** and (2'*S*,3'*S*)-**1**, respectively.

References

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.;

Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision C.01. Gaussian, Inc.: Wallingford CT, 2010.

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(3) Boese, A. D.; Martin, M. L. *J. Chem. Phys.* 2004, *121*, 3405–3416.

(4) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* 2004, *393*, 51–57.

(5) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* 1994, *100*, 5829–5835.

(6) Bruhn, T.; Schaumlöffel, A.; Hemberger, Y.; Bringmann, G. *Chirality* 2013, *25*, 243–249.

Table S1. Relative and free energies[a] and equilibrium populations[b] of low-energy conformers of (2'*S*,3'*S*)-**1** and (2'*R*,3'*S*)-**2** in MeOH.

Conformer	*ΔE*	*ΔG*	P (%)
(2'*S*,3'*S*)-**1**			
SS-1a	0.0	0.0	60.6
SS-1b	1.01	0.87	13.9
SS-1c	1.34	1.21	7.9
SS-1d	1.41	1.34	6.3
SS-1e	0.87	1.45	5.2
SS-1f	2.11	1.56	4.3
SS-1g[c]	2.33	2.11	1.7
(2'*R*,3'*S*)-**2**			
RS-2a	0.0	0.0	66.7
RS-2b	0.91	0.72	19.7
RS-2c	0.68	1.19	9.0
RS-2d	1.41	1.91	2.7
RS-2e[c]	2.03	2.53	0.9
RS-2f[c]	2.11	2.77	0.6
RS-2g[c]	2.74	3.02	0.4

[a]At the B3LYP/def2-TZVP level, in kcal/mol. [b]From Δ*G* values at 298.15 K. [c]Conformer not applied to ECD/TDDFT calculations.

1.2. ECD calculations of 10, 14, and 18.

Computational Methods

Molecular Merck force field (MMFF) and DFT/TDDFT calculations were performed with Spartan'14 software package (Wavefunction Inc., Irvine, CA, USA) and Gaussian09 program package, Conflex conformational search generated low-energy conformers within a 10 kcal/mol energy was finished by software CONFLEX 7. The predominant conformers of (2′*R*,3′*R*,7′*S*)-**10** (90%), (2′*S*,3′*R*,7′*S*)-**10** (90%), (2′*S*,3′*R*,6′*R*)-**14** (90%), (2′*S*,3′*S*,6′*S*)-**14** (90%), (2'*R*,3'*S*,6'*R*,7'*S*)-**18** (90%) and (2'*S*,3'*S*,6'*R*,7'*S*)-**18** (90%) were optimized by DFT calculation at B3LYP/6-311G (d, p) level with the PCM in MeOH. ECD calculations further were conducted at the B3LYP SCRF(PCM)/6-311G (d, p) level with the PCM in MeOH. For comparisions of the calculated curves and experimental CD spectra, the program SpecD is was used.

1.3. ECD and ^{13}C NMR chemical shift calculated methods of 12, 15, and 20

Computational Methods

The CONFLEX 7 searches based on molecular mechanics with MMFF94S force fields were performed for model compounds of (2′*R*,3′*R*,6′*S*)-**12**, (2′*S*,3′*R*,6′*S*)-**12**, (2′*R*,3′*S*,6′*R*)-**15**, (2′*R*,3′*R*,6′*S*)-**15**, (2′*R*,3′*S*,6′*R*)-**20** and (2′*R*,3′*R*,6′*S*)-**20**, respectively. All of the predominant conformers (90%) were optimized by DFT calculation at B3LYP/6-311G (d, p) level with the PCM in MeOH. All the above calculations were carried out with the Gaussian 09 package of programs. Under the circumstances, the calculations of their ^{13}C NMR chemical shifts at MPW1PW91-SCRF/6-311+G (2d, p) level with the PCM in MeOH were performed. Boltzmann averaging over all accessible conformers according to

$$\overline{\sigma}^{x} = \frac{\sum_{\text{confSi}} \sigma_i^x g_i \exp(-E_i/RT)}{\sum_{\text{confSi}} g_i \exp(-E_i/RT)}$$

Where $\overline{\sigma}^{x}$ is the Boltzmann-averaged calculated shielding constant for portion *x*, σ_i^x is the shielding constant for portion *x* in conformer *i*, and *Ei* is the potential energy of conformer *i* (relative to the global minimum) kJ mol^{-1}, obtained from a single-point solvent calculation on the pas-phase structures as discussed previously. *R* is the molar

gas constant (8.3145 J K^{-1} mol^{-1}), g_i is the degeneracy of conformer i, and the temperature T was taken as 298 K.

Chemical shifts were then calculated according to

$$\delta^x_{\text{calc}} = \frac{\sigma_{\text{ref}} - \overline{\sigma}^x}{1 - 10^{-6}\sigma_{\text{ref}}}$$

Where $\delta^x{}_{calc}$ is the calculated chemical shift for portion x (in ppm), $\overline{\sigma}^x$ is the shielding constant for carbon x as calculated above (again in ppm) and σ_{ref} is the shielding constant for the carbon in tetramethylsilane (TMS). This last value was obtained by minimizing TMS in MeOH at the MPW1PW91-SCRF/6-311+G (2d, p) level and calculating the shielding constant for this structure again at the MPW1PW91-SCRF/6-311+G (2d, p) level; the value obtained was σ_{ref} = 188.0549 ppm.

The parameters a and b of the linear regression $\delta_{calcd} = a\delta_{exptl} + b$; the correlation coefficient, R^2; the mean absolute error (MAE) defined as $\Sigma n\ |\delta_{calcd} - \delta_{exptl}|/n$; the corrected mean absolute error (CMAE), defined as $\Sigma n\ |\delta_{corr} - \delta_{exptl}|/n$, where $\delta_{corr} = (\delta_{calcd} - b)/a$ and therefore corrects for systematic errors were presented.

Table S2. The ^{13}C NMR experimental values and calculated chemical shifts of (2′*R*,3′*R*,6′*S*)-**12** and (2′*S*,3′*R*,6′*S*)-**12** are compared.

	12	(2′*R*,3′*R*,6′*S*)-**12**		(2′*S*,3′*R*,6′*S*)-**12**	
No.	δ_{exptl}	δ_{corr}	$\Delta\delta_C{}^a$	δ_{corr}	$\Delta\delta_C{}^a$
1	167.11	165.77	1.34	166.43	0.68
2	123.32	121.81	1.51	121.81	1.51
3	107.88	107.12	0.76	107.72	0.16
4	153.68	152.71	0.97	150.97	2.71
5	128.16	127.54	0.62	127.90	0.26
6	114.62	113.22	1.40	113.30	1.32
1′	205.22	204.63	0.59	203.83	1.39
2′	98.83	98.87	0.04	102.08	3.25
3′	58.09	56.13	1.96	52.96	5.13
4′	28.37	31.05	2.68	29.75	1.38
5′	30.67	27.61	3.06	26.81	3.86
6′	53.87	53.19	0.68	57.58	3.71
7′	146.21	150.33	4.12	152.71	6.50
8′	113.14	117.64	4.50	116.64	3.50
9′	65.42	67.39	1.97	65.94	0.52
10′	174.3	173.87	0.43	172.46	1.84
CMAE			1.66		2.36

[a] $\Delta\delta_C = |\delta_{corr} - \delta_{exptl}|$

Table S3. The ^{13}C NMR experimental values and calculated chemical shifts of (2′*R*,3′*S*,6′*R*)-**15** and (2′*R*,3′*R*,6′*S*)-**15** are compared.

	15	(2′*R*,3′*S*,6′*R*)-**15**		(2′*R*,3′*R*,6′*S*)-**15**	
No.	δ_{exptl}	δ_{corr}	$\Delta\delta_C$[a]	δ_{corr}	$\Delta\delta_C$[a]
1	166.6	167.35	0.75	166.34	0.26
2	123.17	122.13	1.04	121.89	1.28
3	108.11	108.14	0.03	108.04	0.07
4	153.71	152.44	1.27	152.22	1.49
5	127.86	127.78	0.08	127.70	0.16
6	114.3	113.69	0.61	113.79	0.51
1′	204.62	202.69	1.93	204.54	0.08
2′	96.16	100.96	4.80	97.74	1.58
3′	56.07	53.95	2.12	55.35	0.72
4′	27.98	26.68	1.30	28.12	0.14
5′	29.97	31.00	1.03	31.22	1.25
6′	47.27	47.47	0.20	46.81	0.46
7′	147.91	147.91	0	147.91	0
8′	138.09	138.09	0	138.09	0
9′	195.17	197.77	2.60	197.19	2.02
10′	174.32	173.28	1.04	174.37	0.05
CMAE			1.18		0.63

[a] $\Delta\delta_C = |\delta_{corr} - \delta_{exptl}|$.

Table S4. The ^{13}C NMR experimental data (δ in ppm) and calculated chemical shifts of (2′*R*,3′*S*,6′*R*)-**20** and (2′*R*,3′*R*,6′*S*)-**20** are compared.

	20	(2′*R*,3′*S*,6′*R*)-**20**		(2′*R*,3′*R*,6′*S*)-**20**	
No.	δ_{exptl}	δ_{corr}	$\Delta\delta_C$[a]	δ_{corr}	$\Delta\delta_C$[a]
1	167.99	167.54	0.45	167.46	0.53
2	123.81	122.79	1.02	121.91	1.90
3	107.75	107.59	0.16	107.63	0.12
4	153.8	151.76	2.04	152.46	1.34
5	128.21	127.61	0.60	127.82	0.39
6	114.67	113.65	1.02	113.53	1.14
1′	203.47	202.95	0.52	203.29	0.18
2′	97.48	99.70	2.22	98.74	1.26
3′	49.96	50.82	0.86	50.24	0.28
4′	22.24	22.62	0.38	23.28	1.04
5′	32.1	29.74	2.36	32.16	0.06
6′	79.19	80.17	0.98	78.77	0.42
7′	171.77	174.85	3.08	175.58	3.81
OCH_3	52	52.65	0.65	51.58	0.42
CMAE			1.17		0.92

[a] $\Delta\delta_C = |\delta_{corr} - \delta_{exptl}|$

2. Supplementary Figures

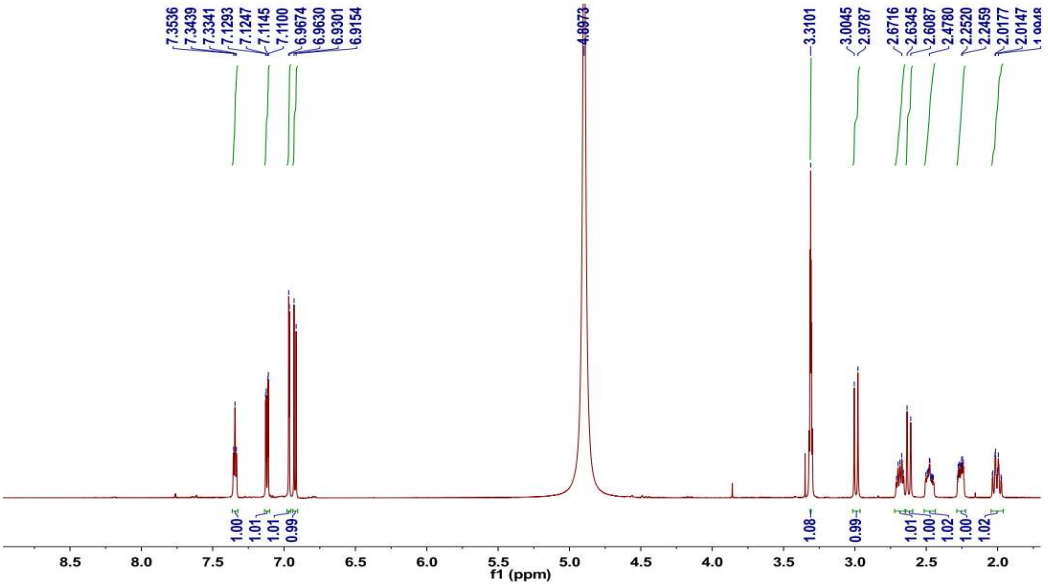

Figure S1. ^{1}H NMR spectrum of **1** in methanol-d_4

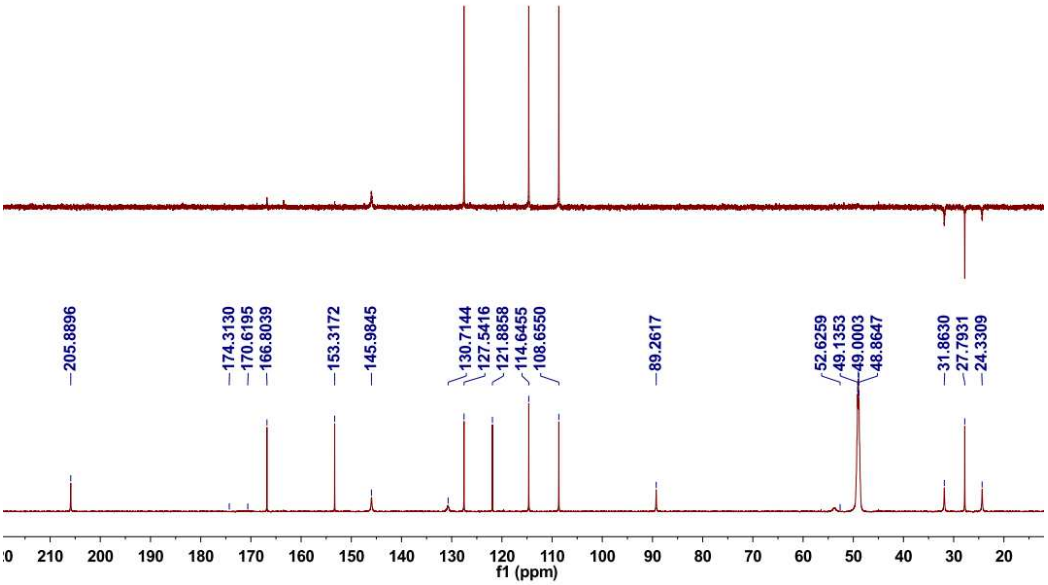

Figure S2. ^{13}C NMR spectrum of **1** in methanol-d_4

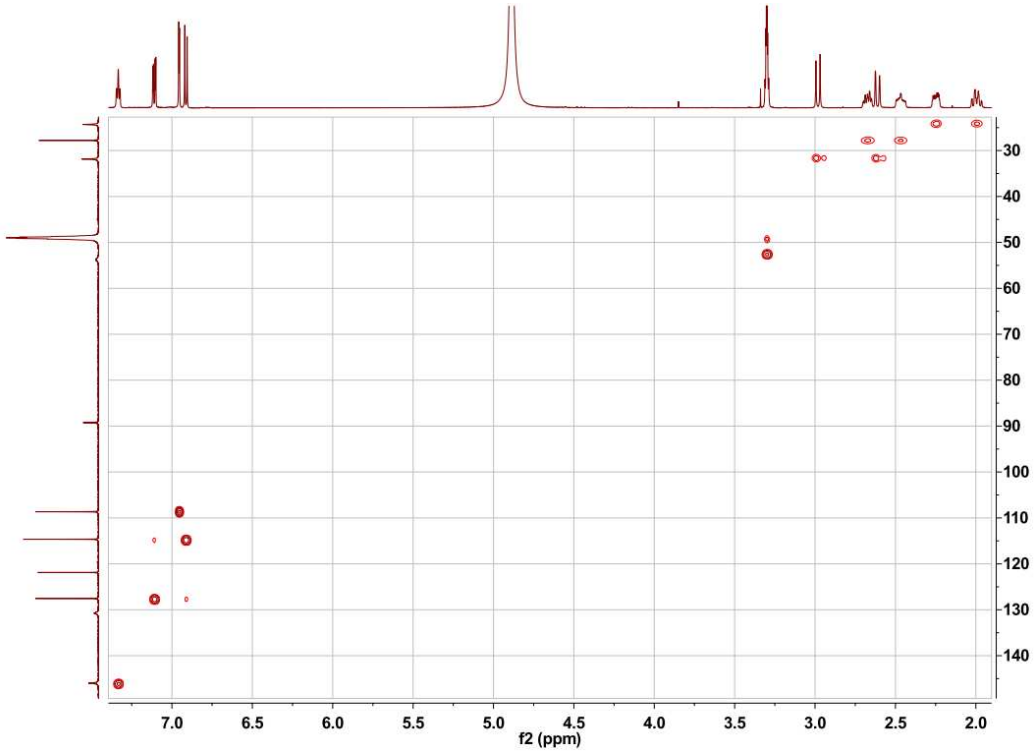

Figure S3. HSQC spectrum of **1** in methanol-d_4

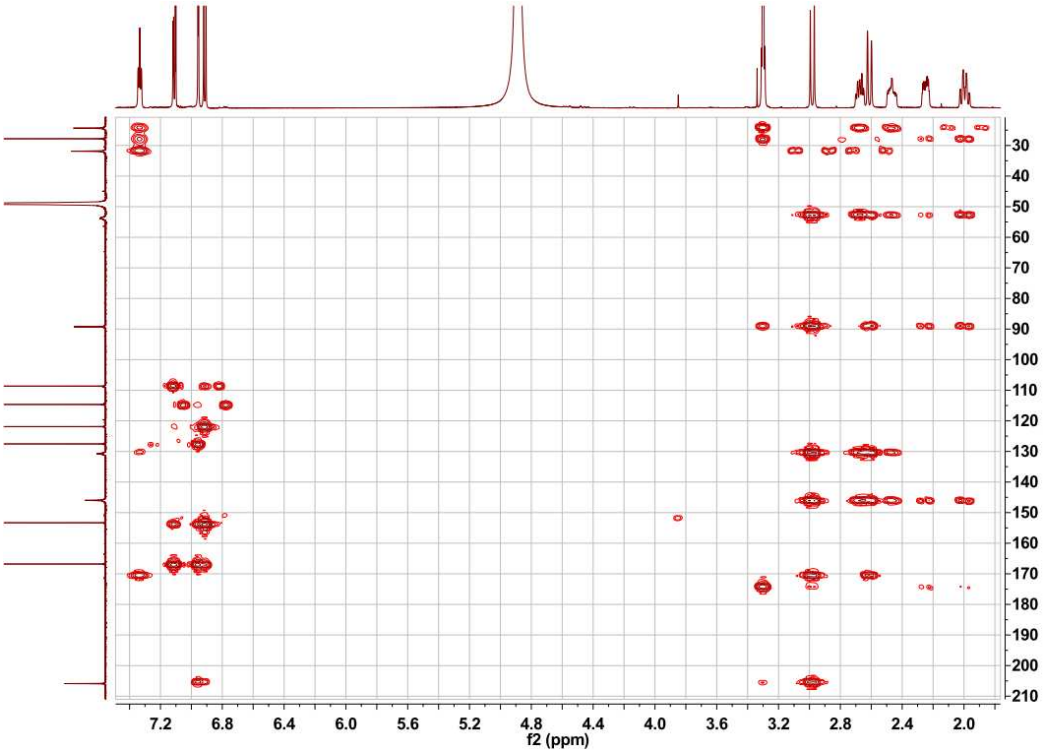

Figure S4. HMBC spectrum of **1** in methanol-d_4

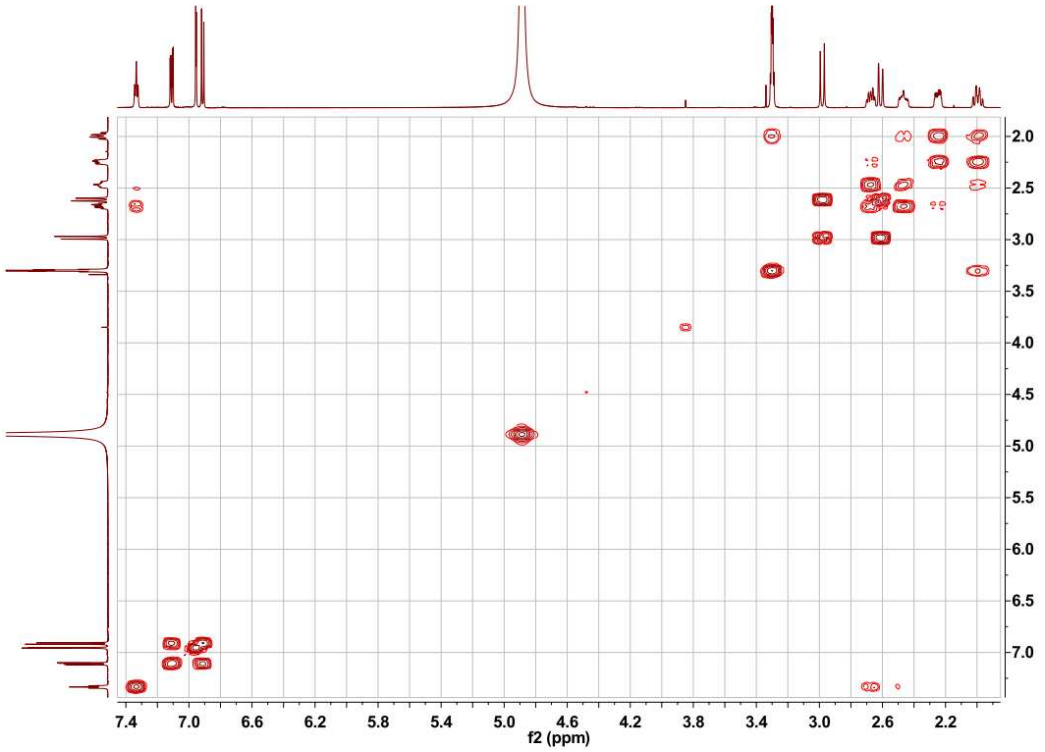

Figure S5. ^{1}H-^{1}H COSY spectrum of **1** in methanol-d_4

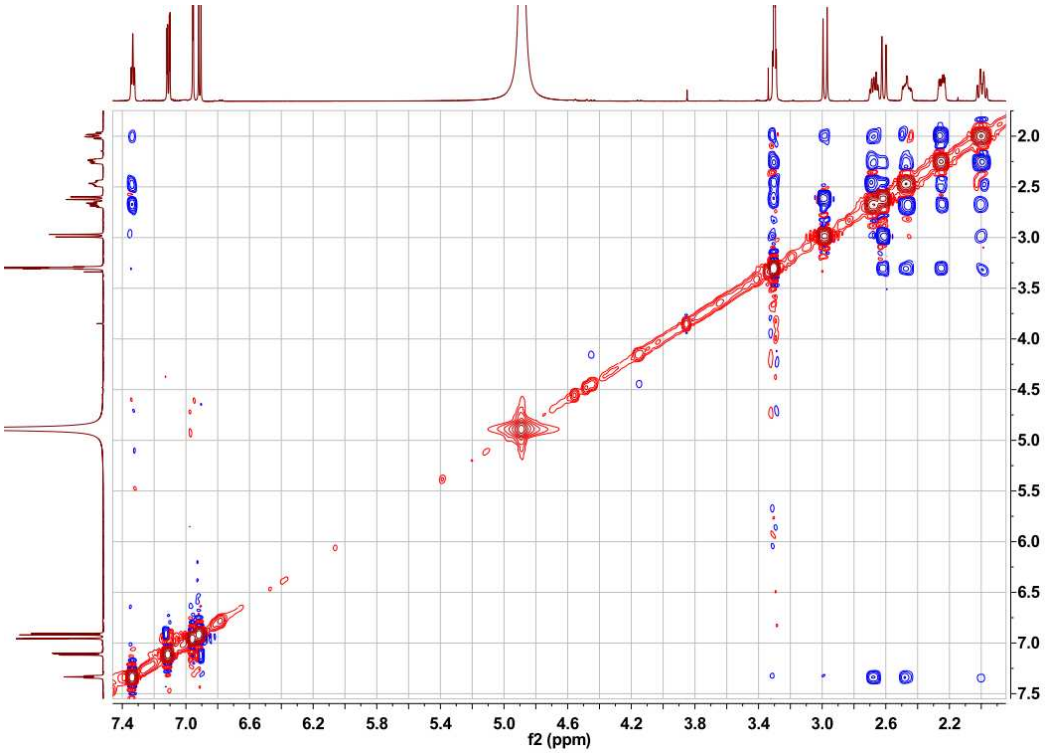

Figure S6. ROESY spectrum of **1** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
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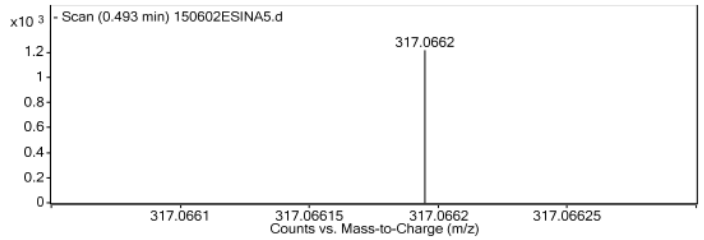


Peak List

m/z	z	Abund
112.9856		7800.05
154.9734		2495.44
174.9674	1	4335.37
229.0869	1	6273.56
248.9603		1873.57
268.9543	1	12128.6
362.9406	1	2475.2
1033.9881	1	79942.13
1034.9892	1	6892.25
1933.9278	1	2946.28

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	11

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C16 H13 O7	317.0661	317.0667	317.0662	0.5	1.5	10.5000

Figure S7. HRESIMS spectrum of **1**

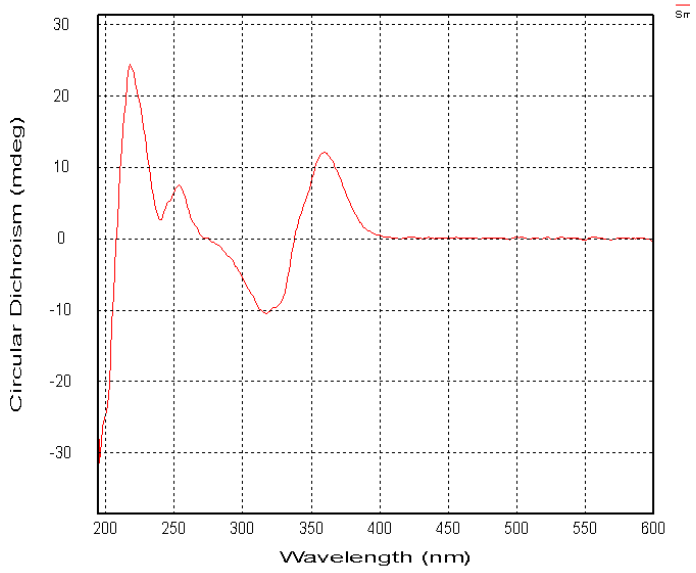


Figure S8. CD spectrum of **1** in methanol

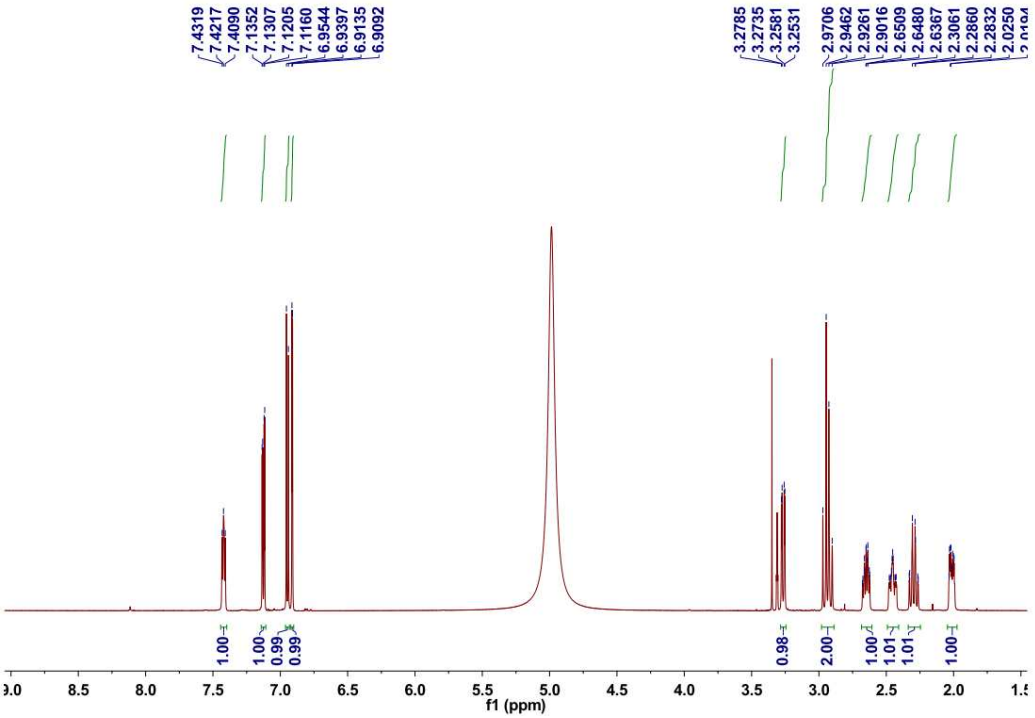


Figure S9. ^{1}H NMR spectrum of **2** in methanol-d_4

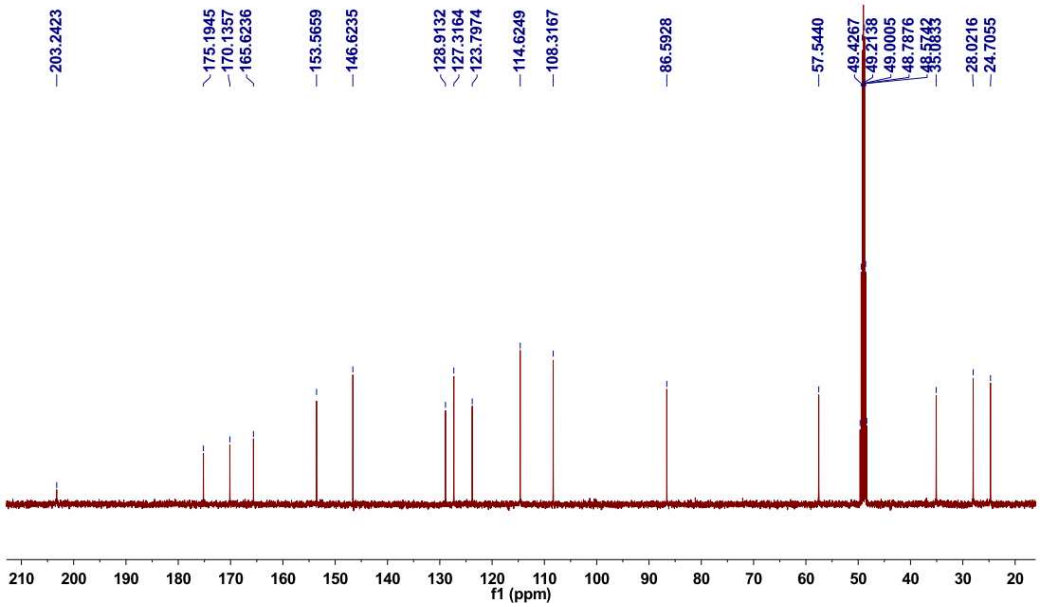


Figure S10. ^{13}C NMR spectrum of **2** in methanol-d_4

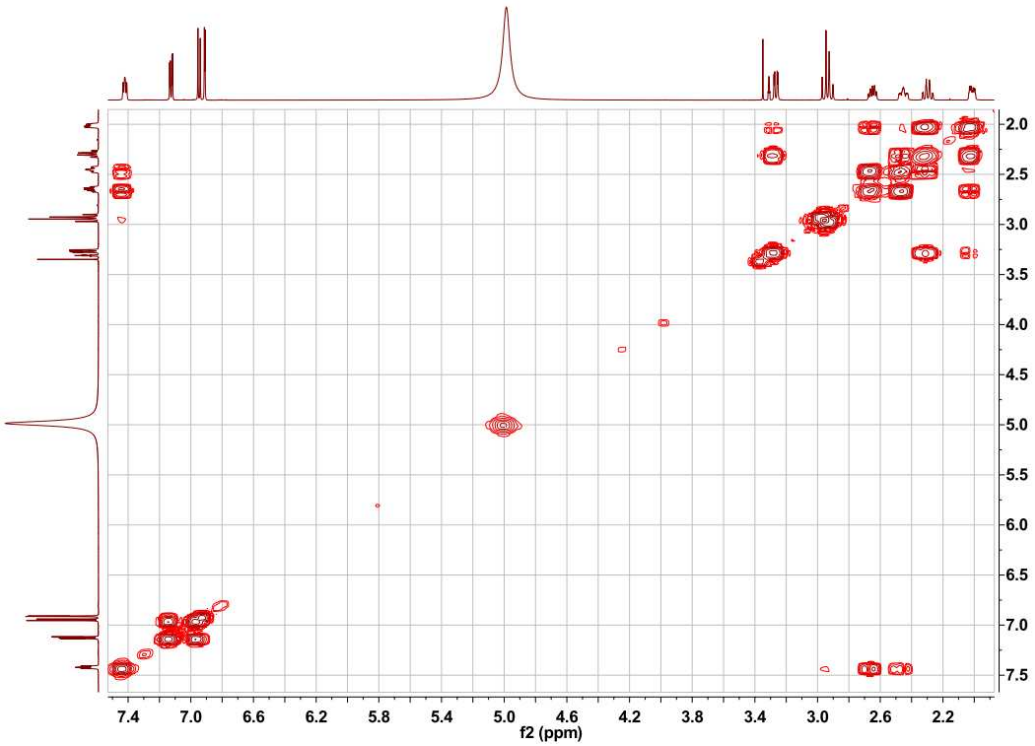


Figure S11. HSQC spectrum of **2** in methanol-d_4

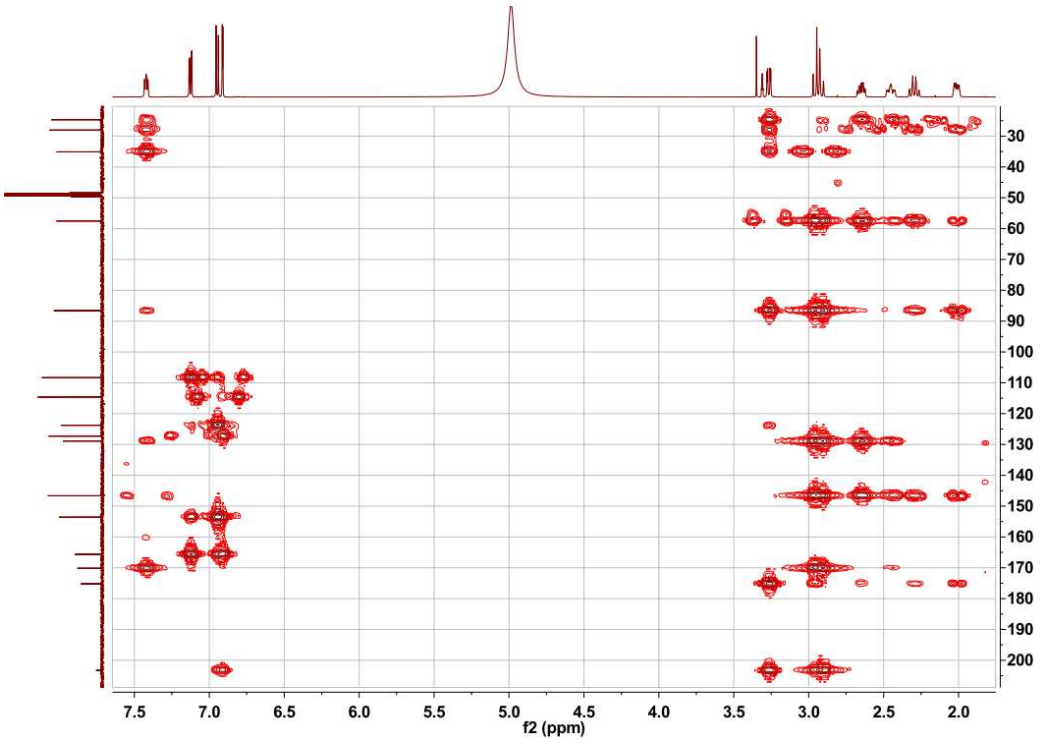


Figure S12. HMBC spectrum of **2** in methanol-d_4

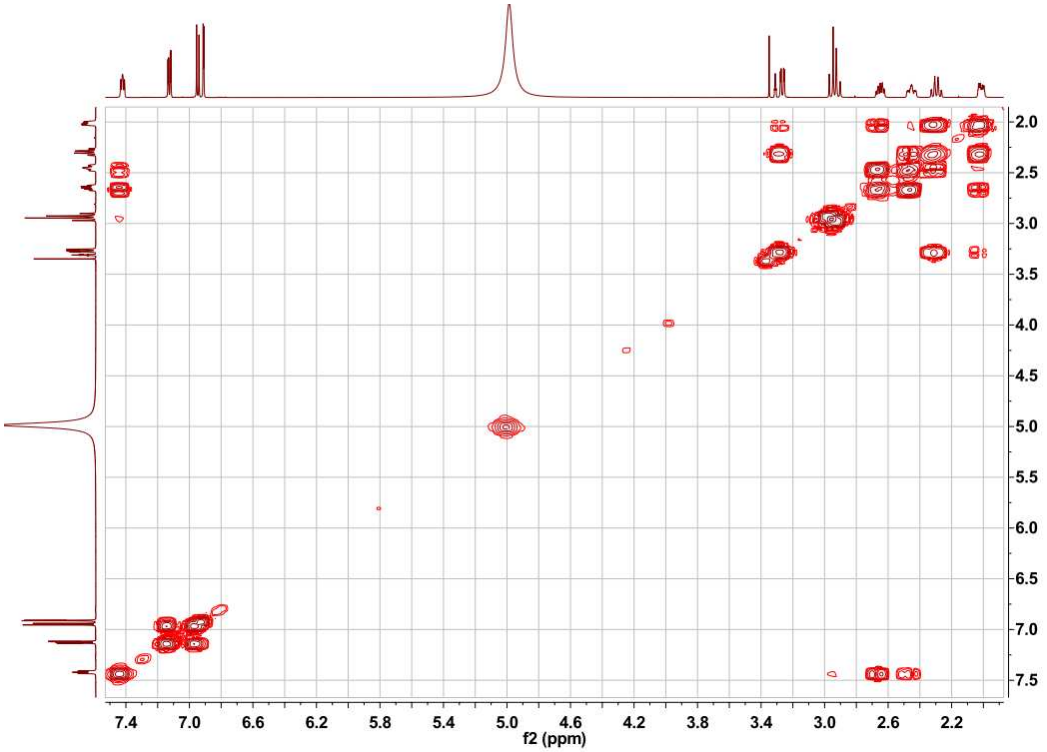


Figure S13. ^{1}H-^{1}H COSY spectrum of **2** in methanol-d_4

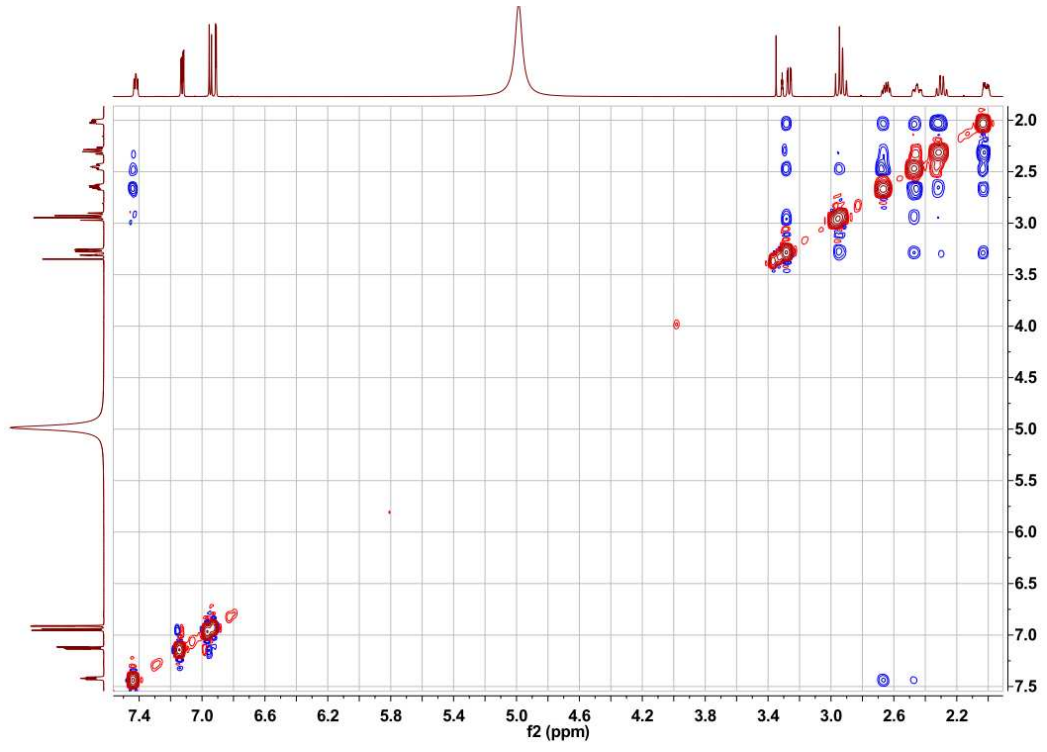
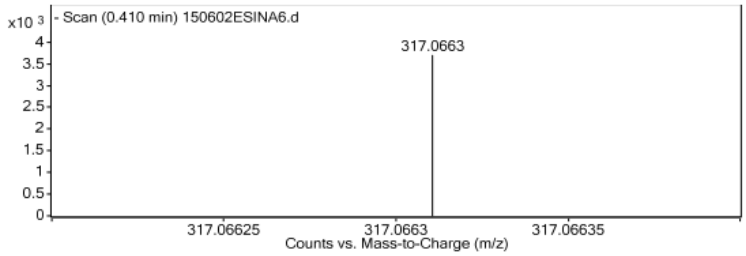


Figure S14. ROESY spectrum of **2** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
112.9856		2349.79		
229.087	1	13584.07		
230.0901	1	994.78		
273.0758		1281.41		
317.0663	1	3683.15	C16 H13 O7	M-
1033.9881	1	177718.09		
1034.9895	1	22103.53		
1035.9901	1	1000.92		
1933.9291	1	24470.54		
1934.93	1	4055.48		

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	11

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C16 H13 O7	317.0661	317.0667	317.0663	0.4	1.3	10.5000

Figure S15. HRESIMS spectrum of **2**

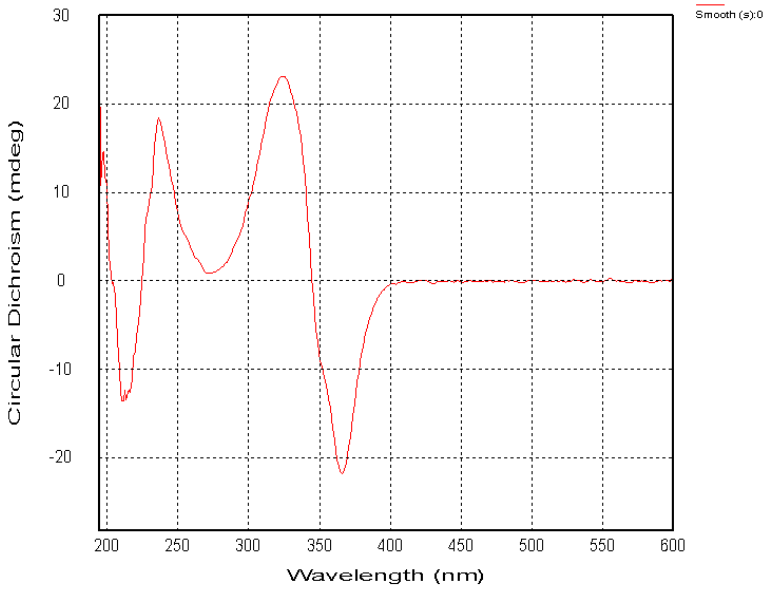


Figure S16. CD spectrum of **2** in methanol

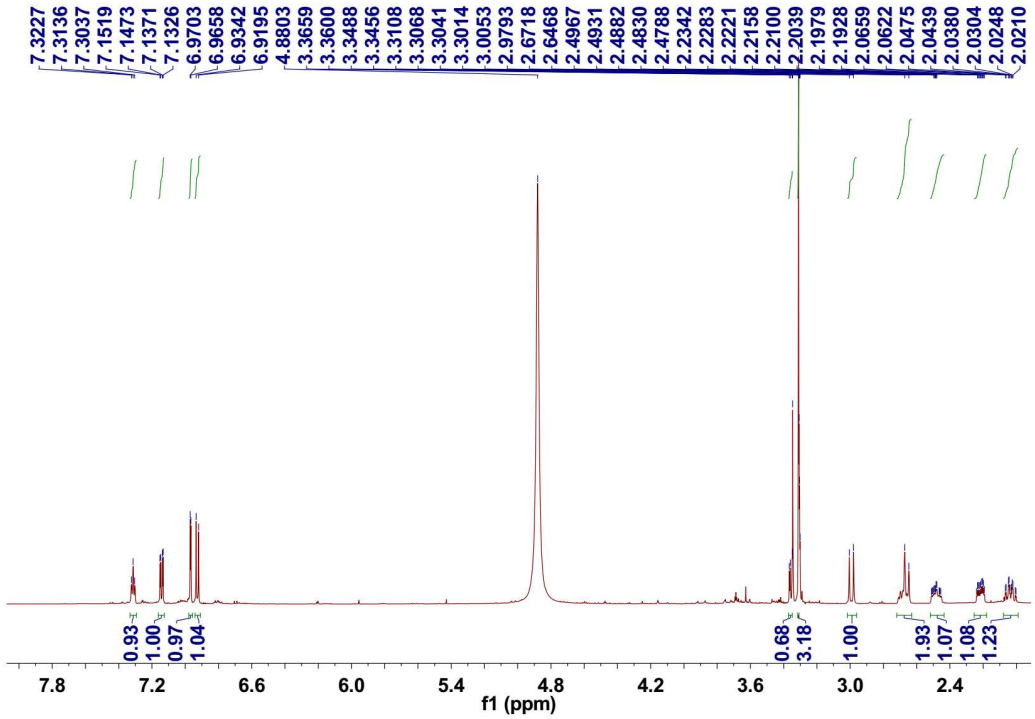


Figure S17. ^{1}H NMR spectrum of **3** in methanol-d_4

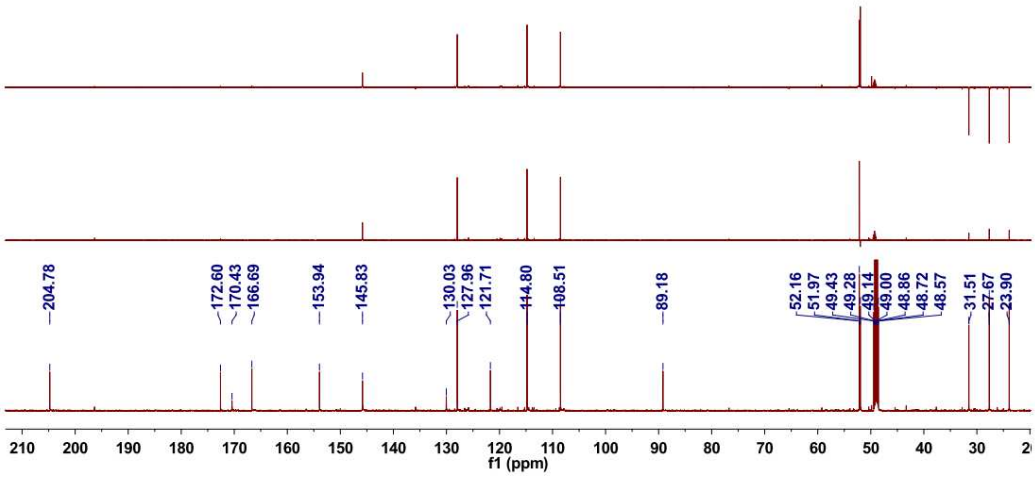


Figure S18. ^{13}C NMR and DEPT spectra of **3** in methanol-d_4

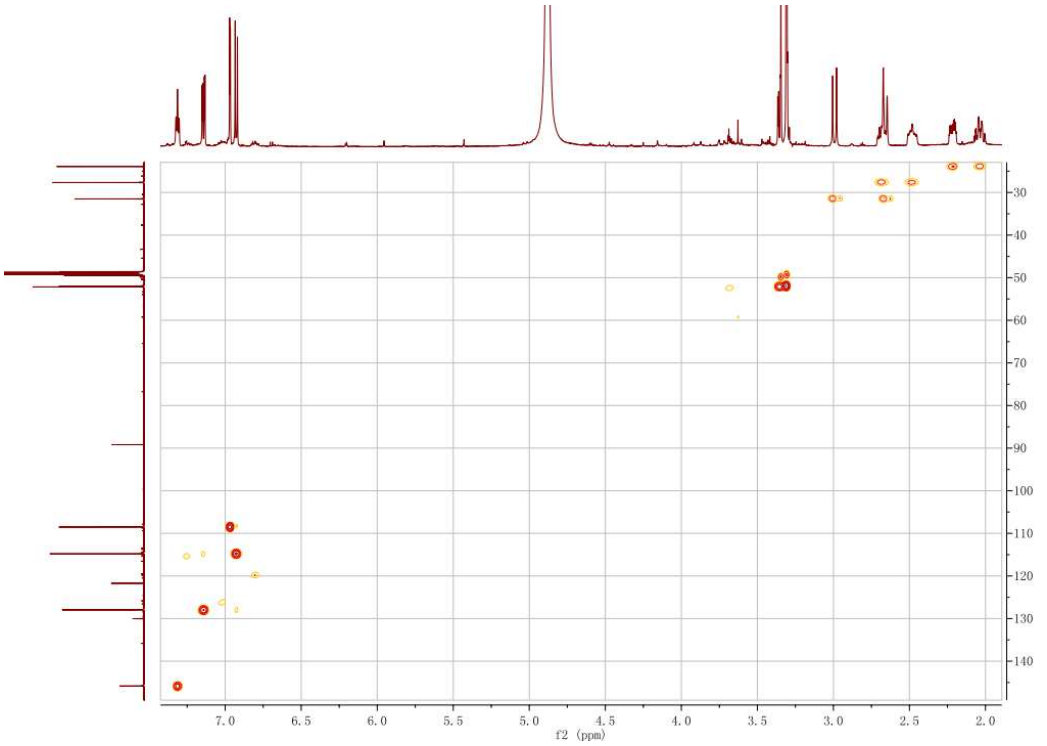


Figure S19. HSQC spectrum of **3** in methanol-d_4

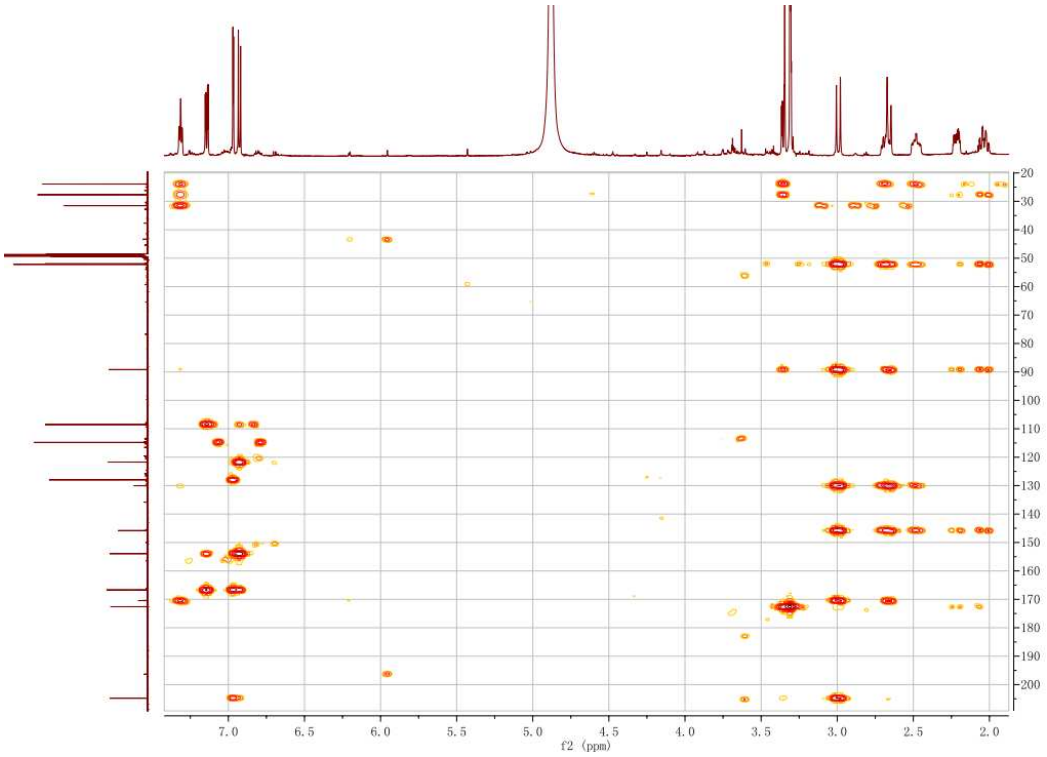


Figure S20. HMBC spectrum of **3** in methanol-d_4

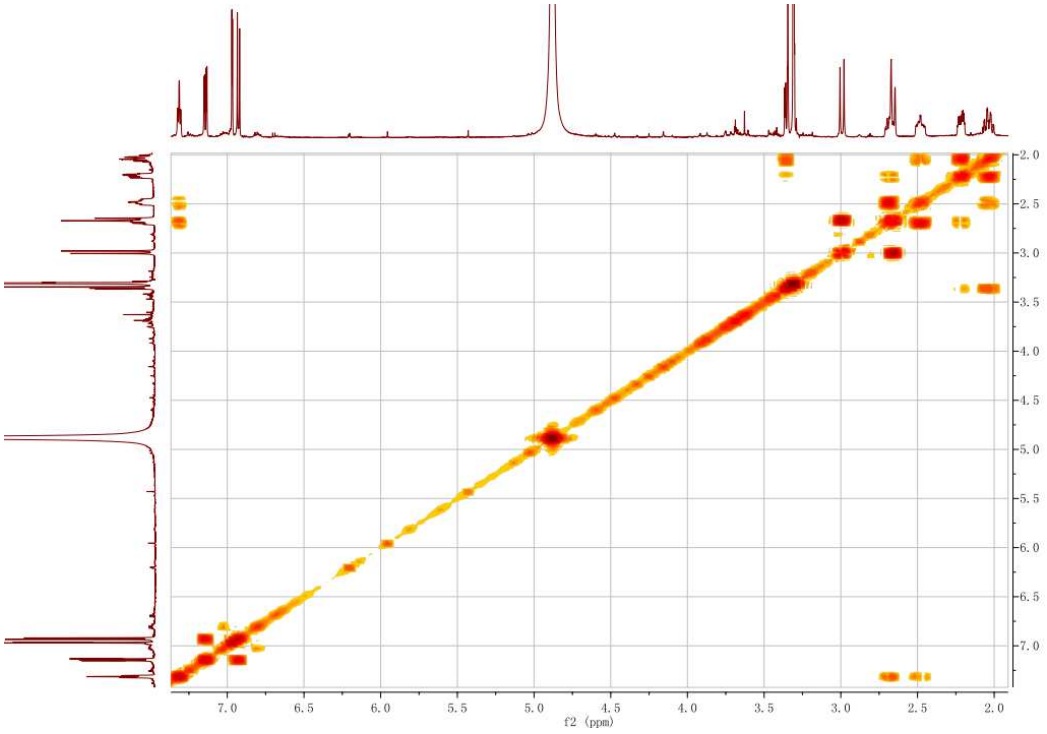


Figure S21. ^{1}H-^{1}H COSY spectrum of **3** in methanol-d_4

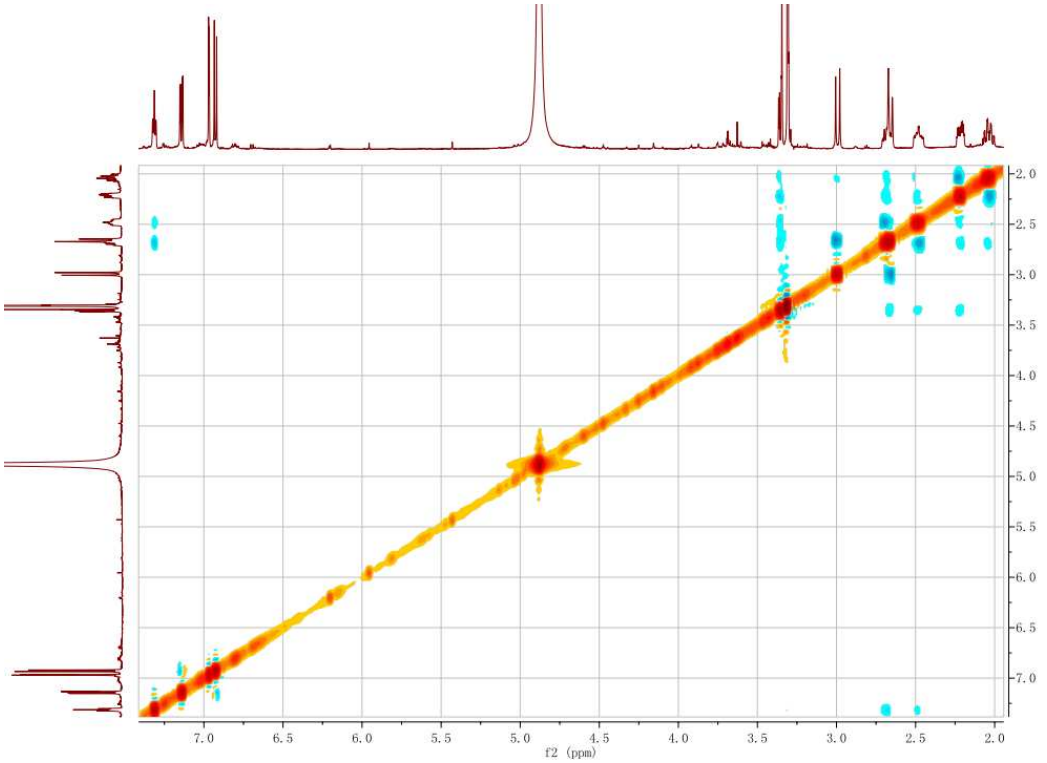


Figure S22. ROESY spectrum of **3** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI

Peak List

m/z	z	Abund	Formula	Ion
112.9856		15003.93		
255.0664	1	7578.97		
255.2323	1	4288.79		
268.9541	1	6941.25		
287.0925	1	6157.01		
303.0875	1	11826.12		
331.0826	1	17852.56	C17 H15 O7	M-
335.1069	1	4688.38		
663.1706	1	4780.52		
1033.9881	1	45939.58		

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	11

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C17 H15 O7	331.0818	331.0823	331.0826	-0.7	-2.1	10.5000

--- End Of Report ---

Figure S23. HRESIMS spectrum of **3**

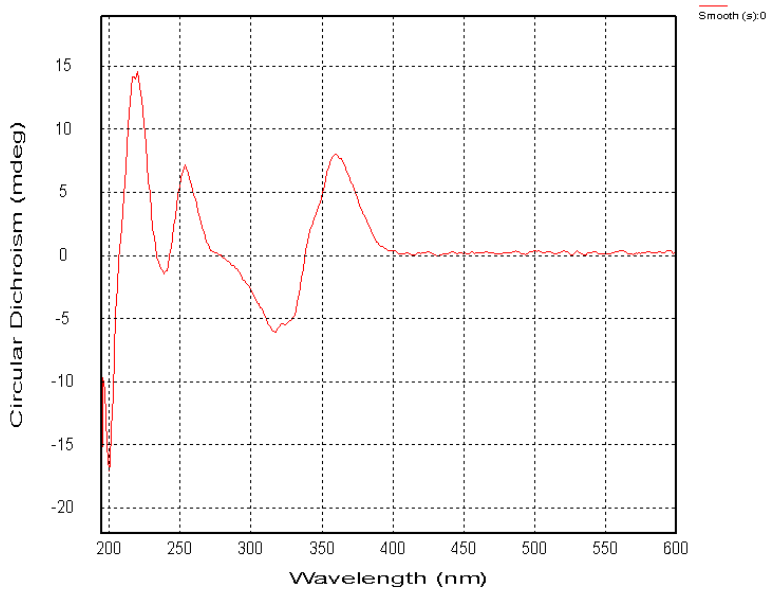


Figure S24. CD spectrum of **3** in methanol

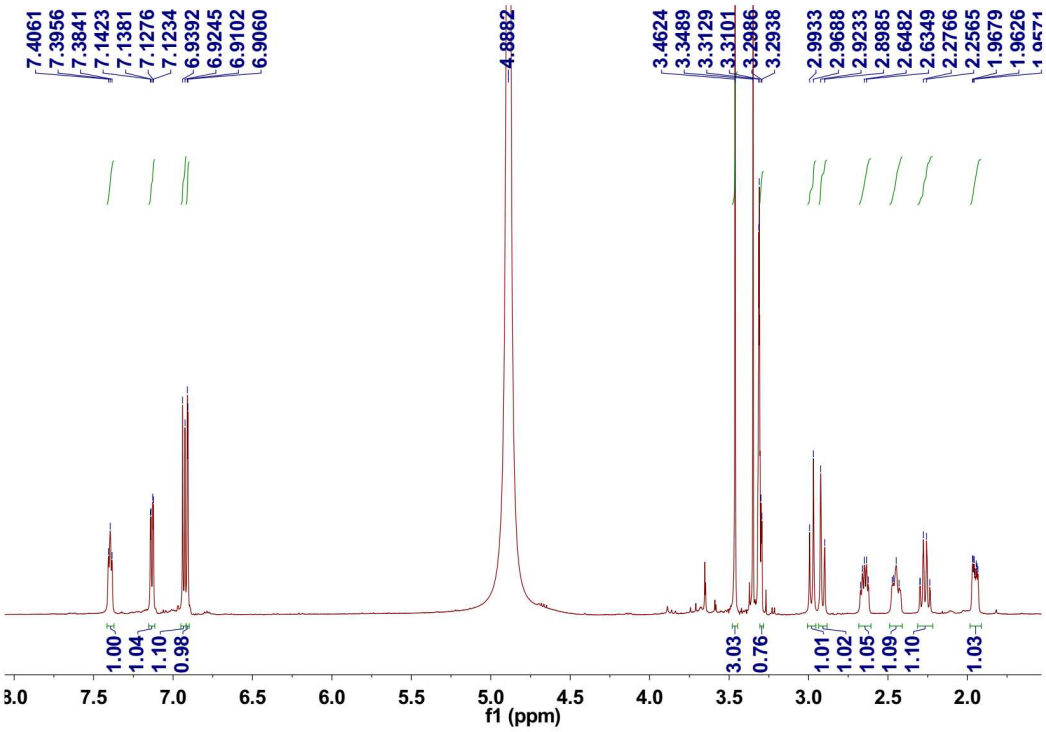


Figure S25. ^{1}H NMR spectrum of **4** in methanol-d_4

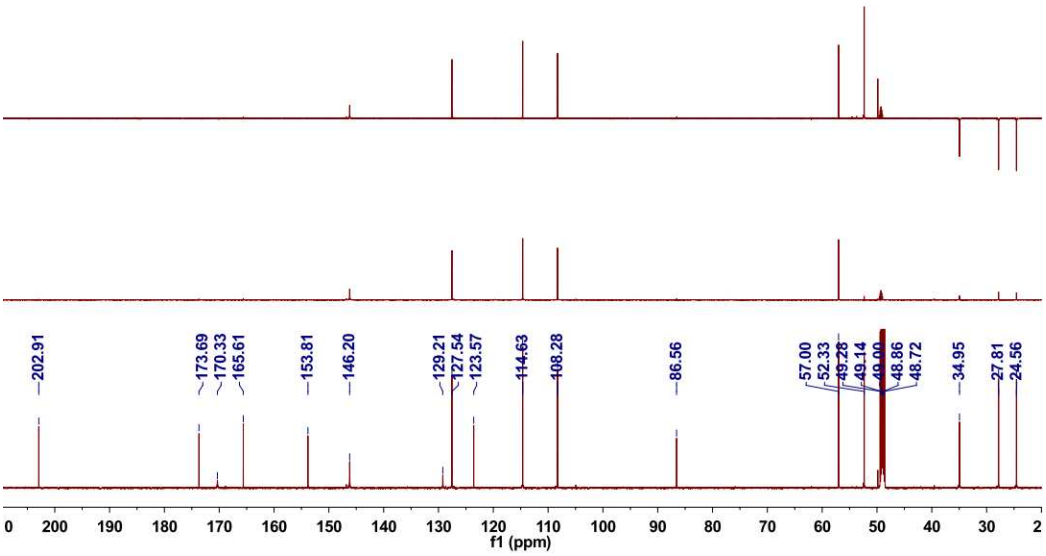


Figure S26. ^{13}C NMR and DEPT spectra of **4** in methanol-d_4

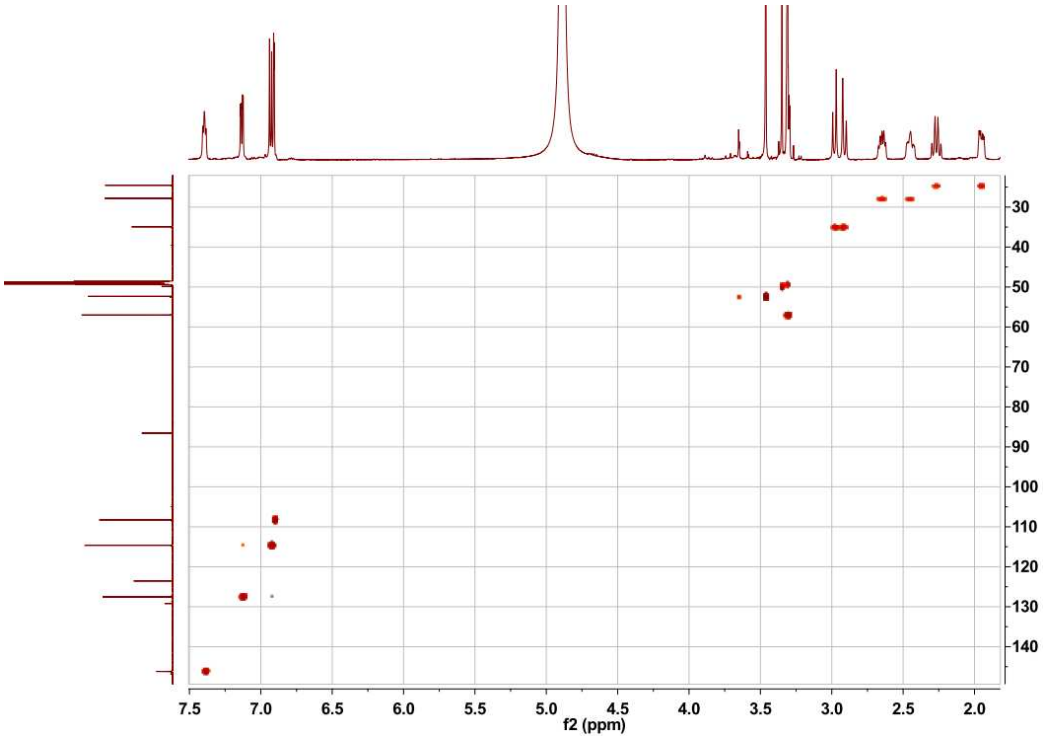


Figure S27. HSQC spectrum of **4** in methanol-d_4

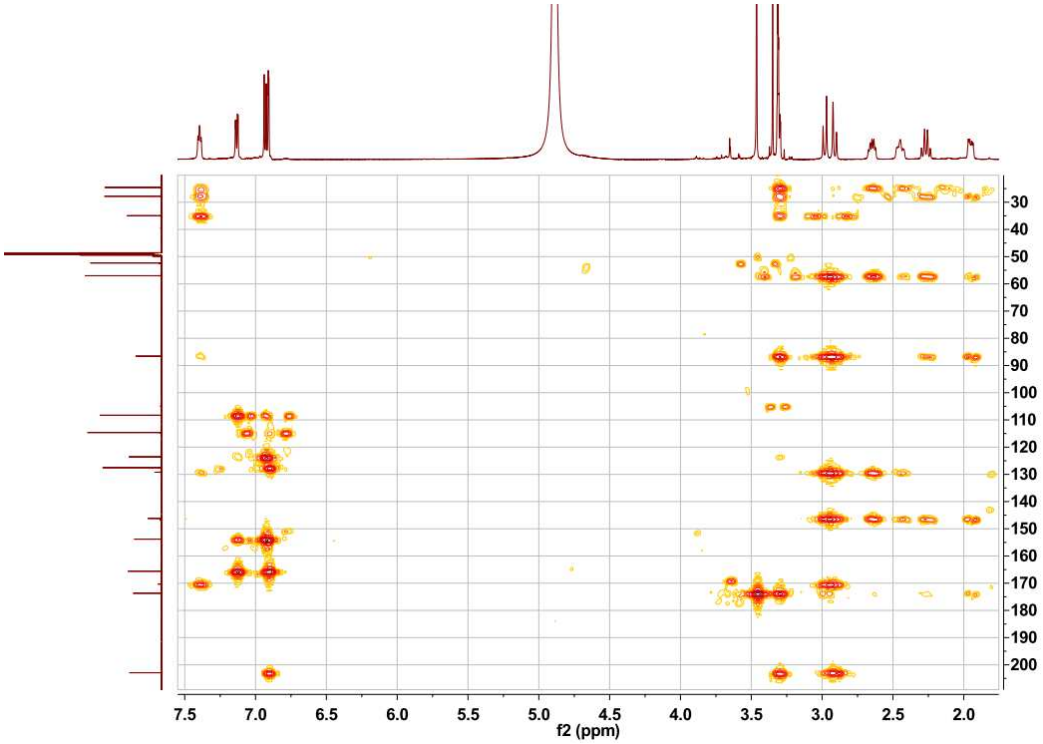


Figure S28. HMBC spectrum of **4** in methanol-d_4

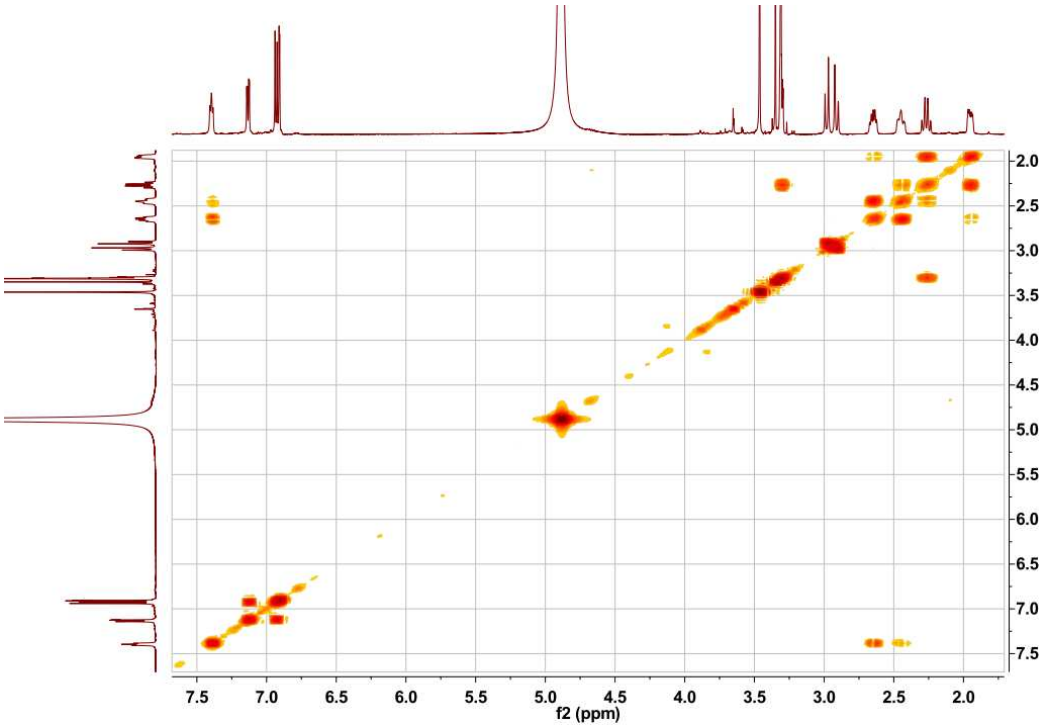
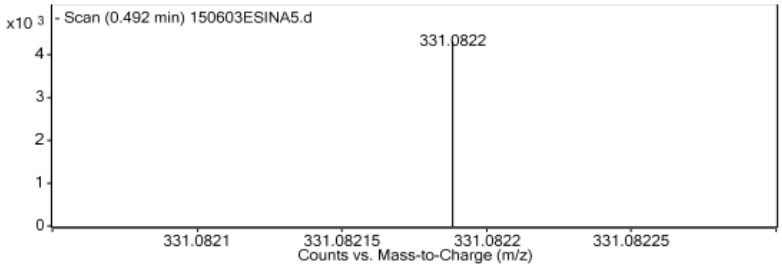


Figure S29. ^{1}H-^{1}H COSY spectrum of **4** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
112.9856		2706.72		
211.0758		968		
255.066	1	2986.16		
287.0921	1	2870.33		
331.0822	1	4295.06	C17 H15 O7	M-
1033.9881	1	181524.47		
1034.9891	1	22190.38		
1035.9901	1	997.91		
1933.9292	1	26058.9		
1934.9312	1	4353.46		

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	11

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C17 H15 O7	331.0818	331.0823	331.0822	0.2	0.5	10.5000

Figure S30. HRESIMS spectrum of **4**

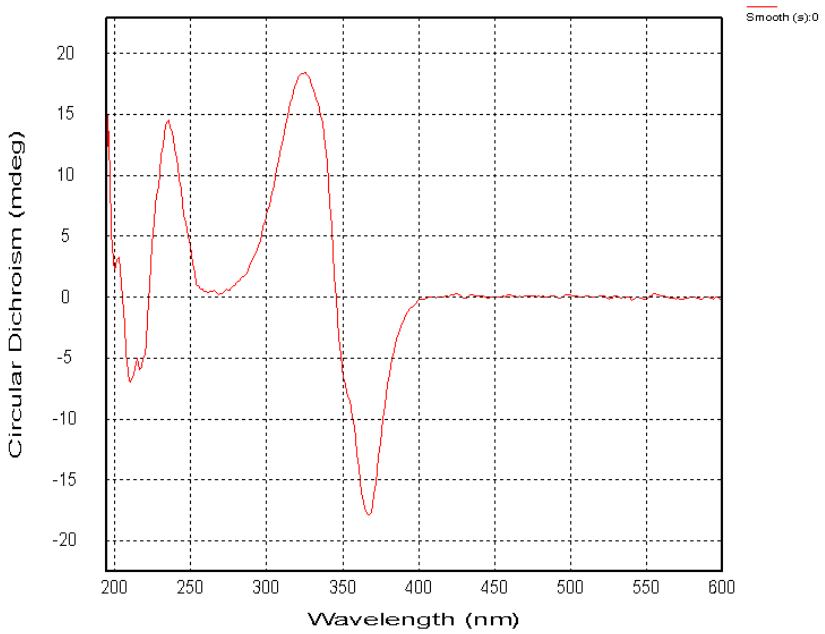


Figure S31. CD spectrum of **4** in methanol

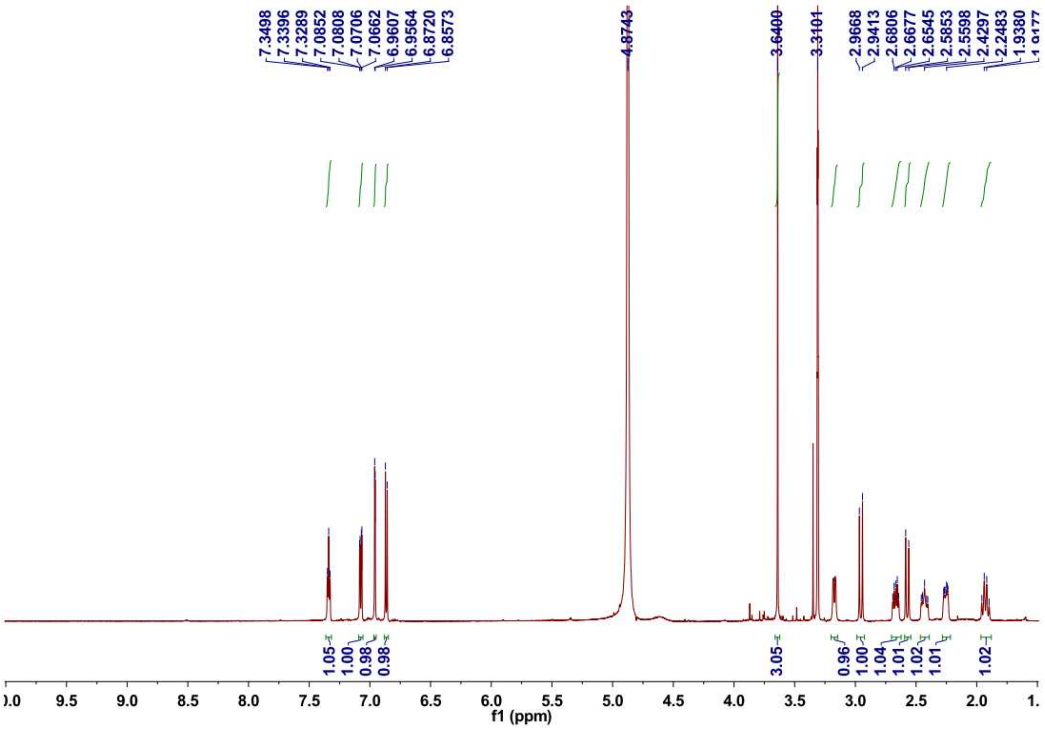


Figure S32. ^{1}H NMR spectrum of **5** in methanol-d_4

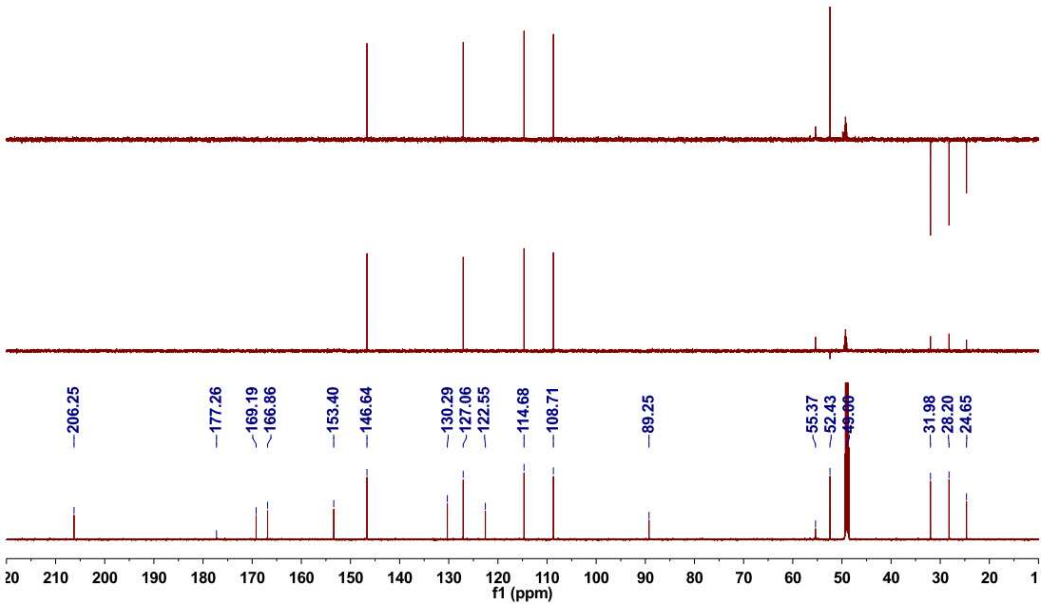


Figure S33. ^{13}C NMR and DEPT spectra of **5** in methanol-d_4

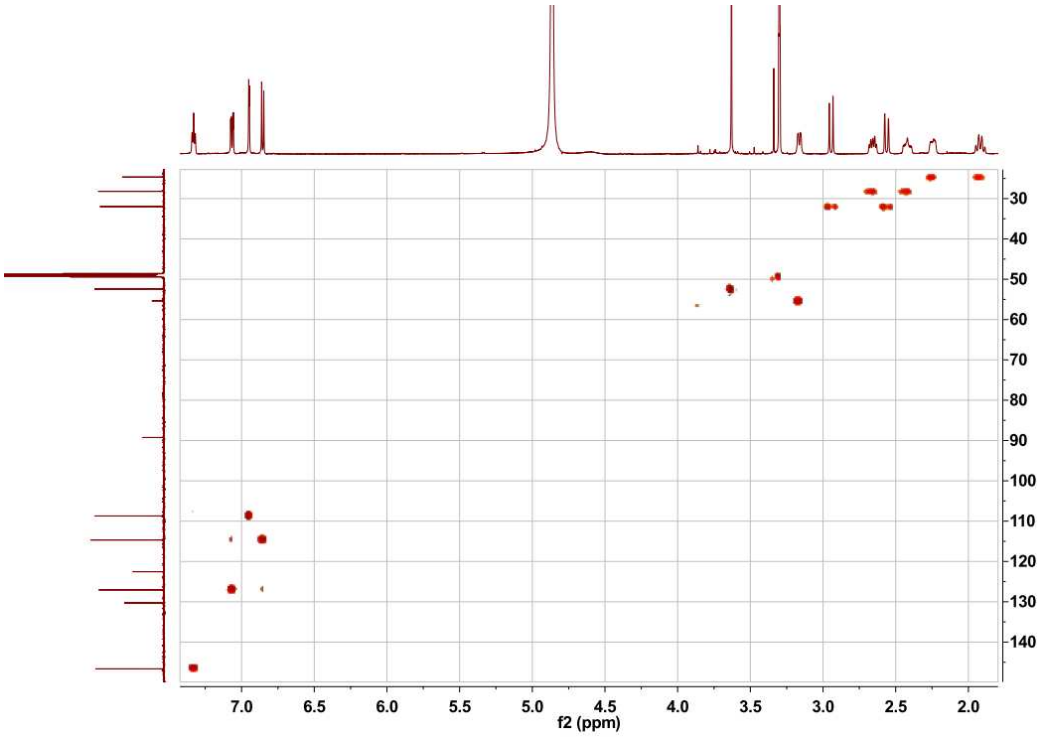


Figure S34. HSQC spectrum of **5** in methanol-d_4

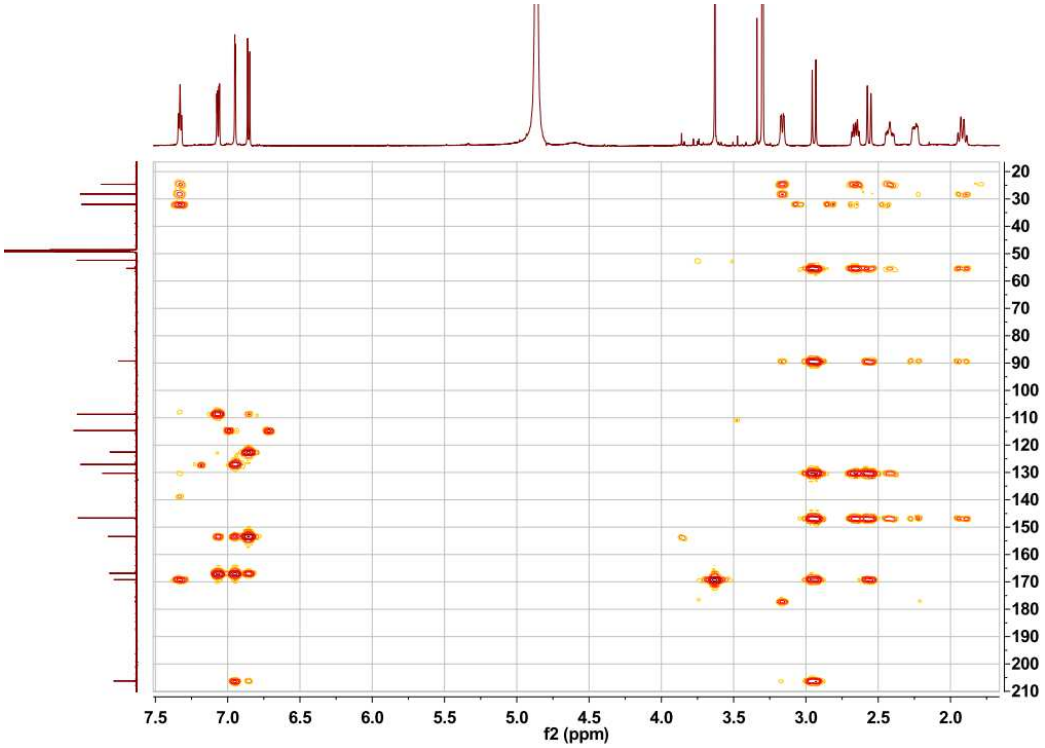


Figure S35. HMBC spectrum of **5** in methanol-d_4

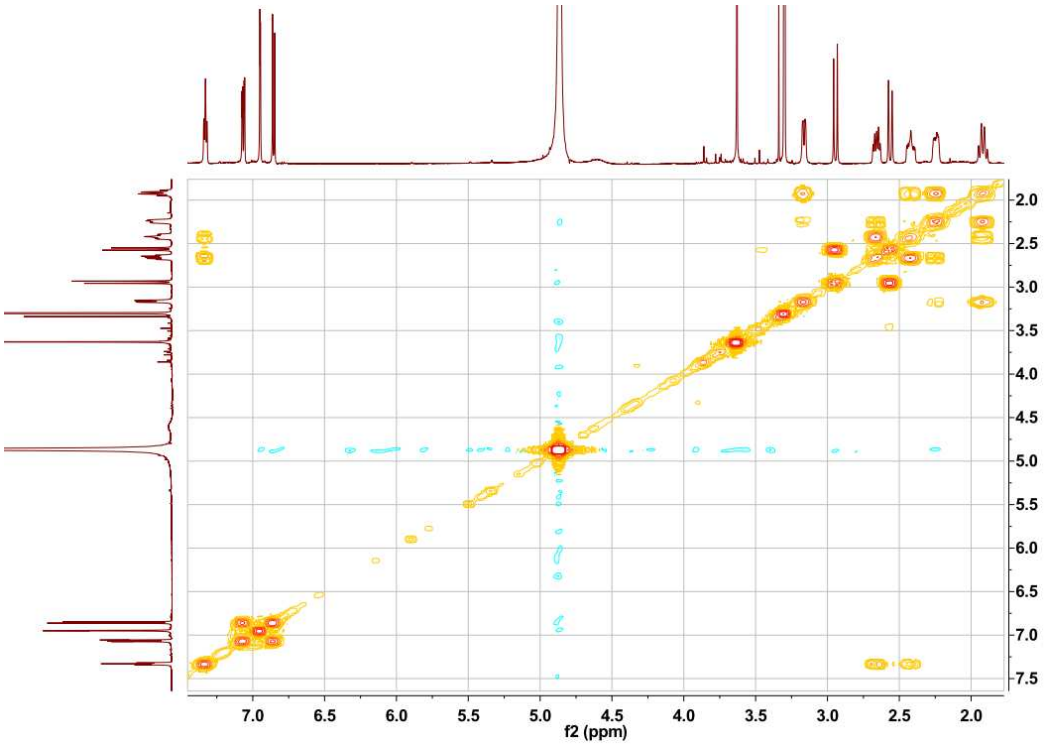
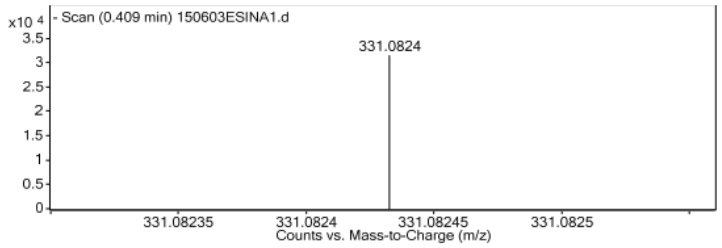


Figure S36. ^{1}H-^{1}H COSY spectrum of **5** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
255.0663	1	16119.53		
255.2327	1	18700.15		
283.2641	1	15648.53		
287.0929	1	71779.91		
288.0958	1	5963.84		
331.0824	1	31426.8	C17 H15 O7	M-
685.1528	1	11897.68		
1033.9881	1	121984.91		
1034.9896	1	13150.03		
1933.9296	1	15800.22		

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	11

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C17 H15 O7	331.0818	331.0823	331.0824	-0.1	-0.2	10.5000

Figure S37. HRESIMS spectrum of **5**

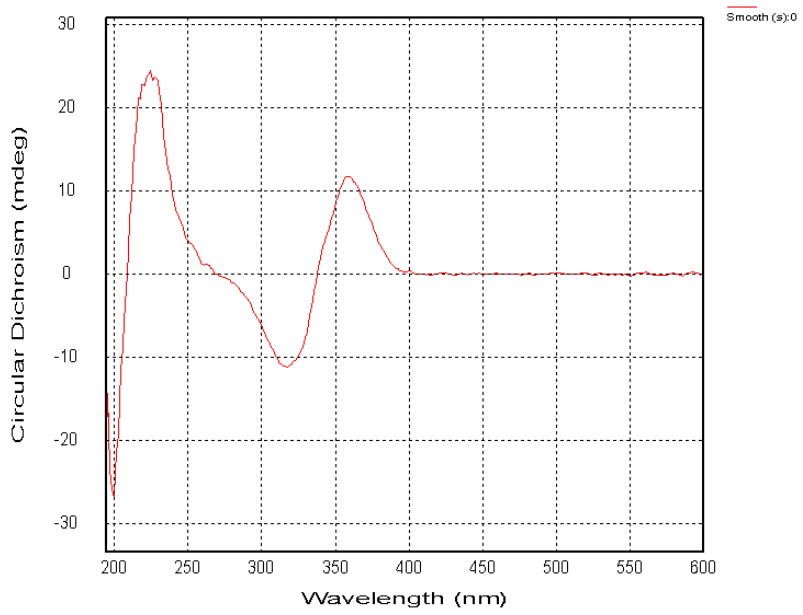


Figure S38. CD spectrum of **5** in methanol

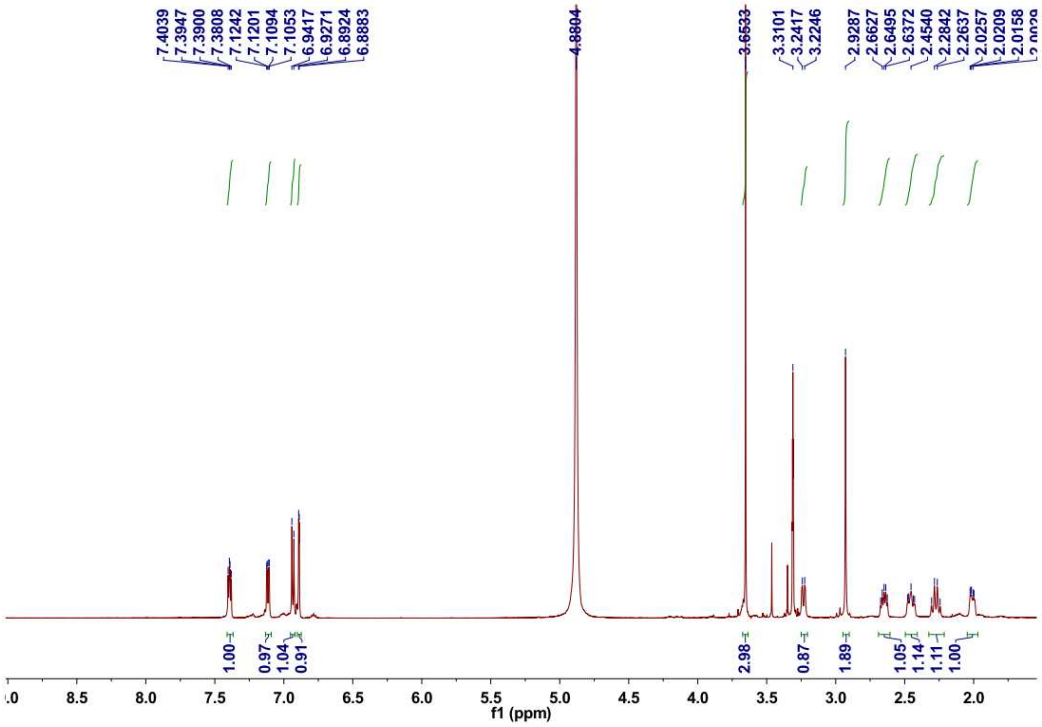


Figure S39. ^{1}H NMR spectrum of **6** in methanol-d_4

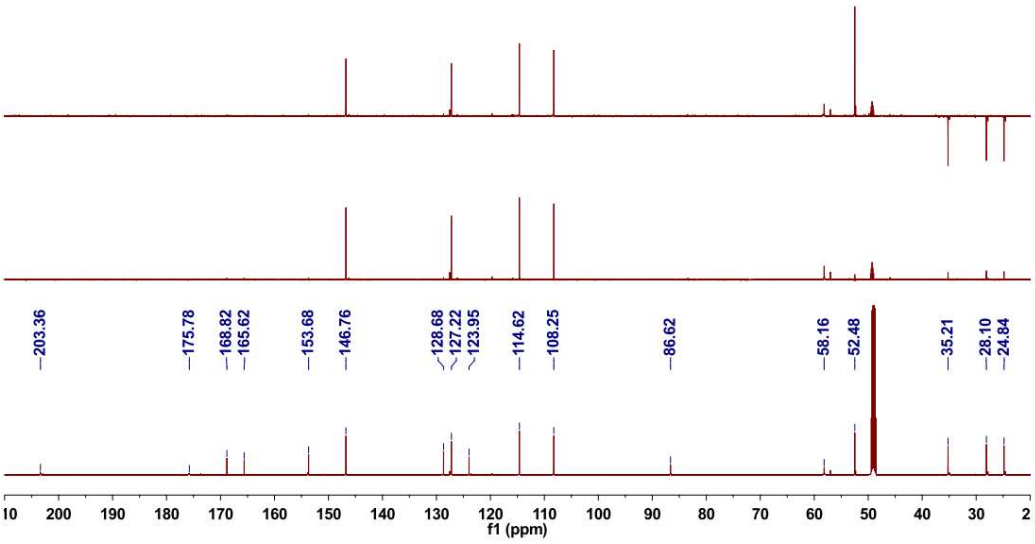


Figure S40. ^{13}C NMR and DEPT spectra of **6** in methanol-d_4

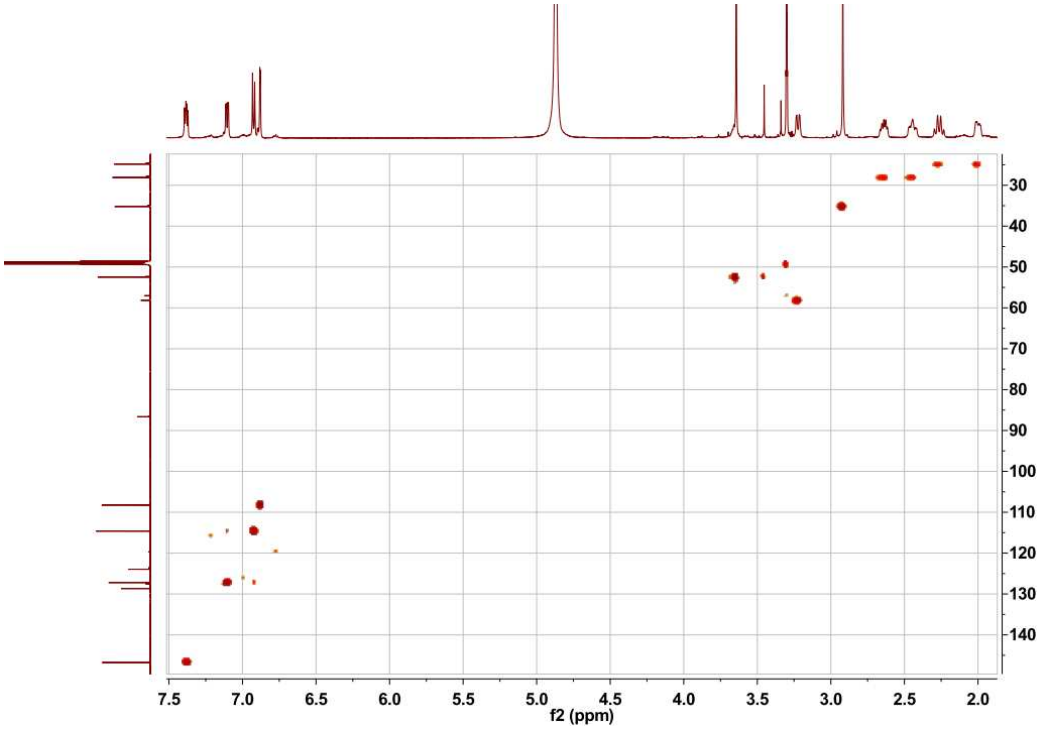


Figure S41. HSQC spectrum of **6** in methanol-d_4

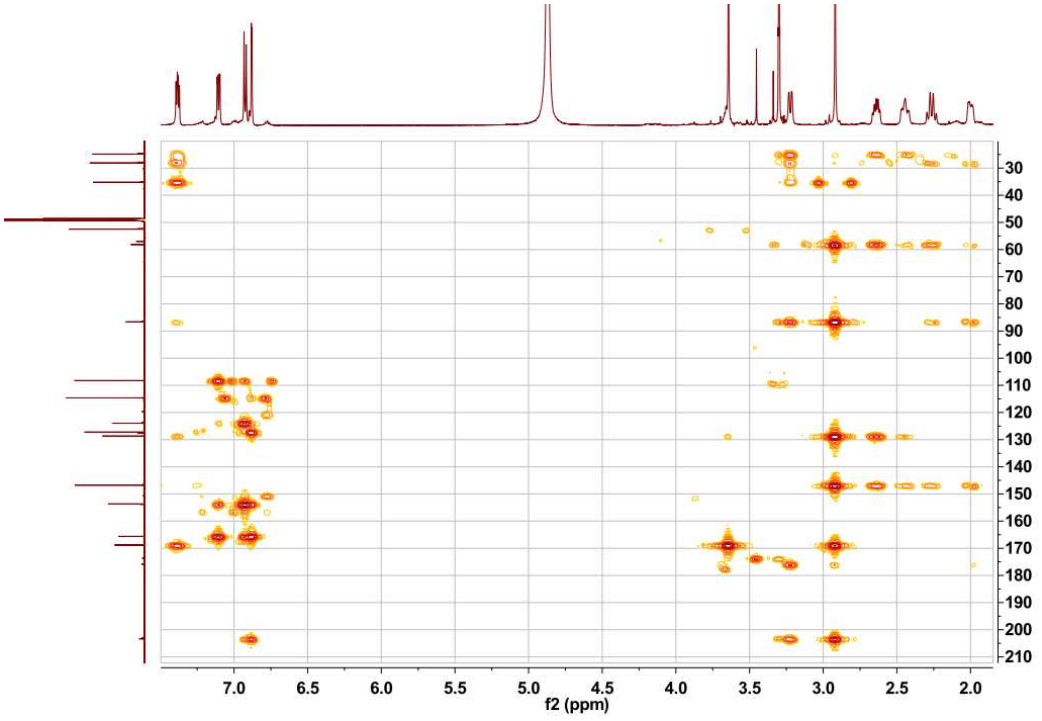


Figure S42. HMBC spectrum of **6** in methanol-d_4

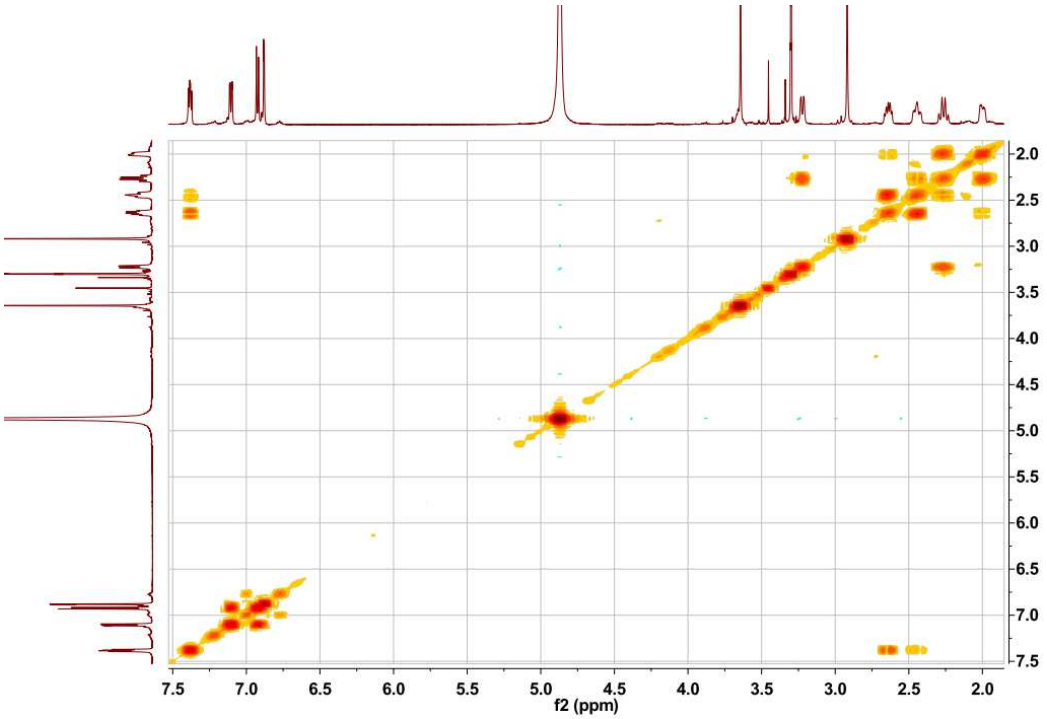
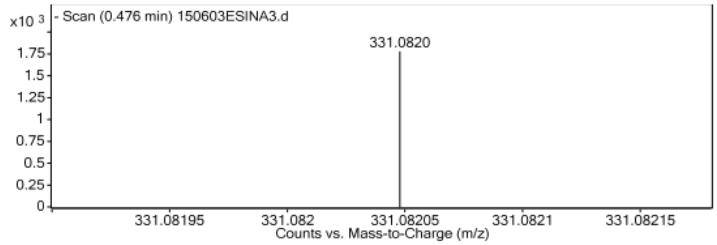


Figure S43. ^{1}H-^{1}H COSY spectrum of **6** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
112.9856		2504.42		
255.0663		1120.88		
287.0927	1	8213.56		
288.0962	1	715.75		
331.082	1	1773.35	C17 H15 O7	M-
1033.9881	1	179238.39		
1034.9892	1	22458.5		
1035.9906	1	1008.46		
1933.9285	1	25315.72		
1934.9309	1	4274.44		

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	11

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C17 H15 O7	331.0818	331.0823	331.0820	0.2	0.7	10.5000

Figure S44. HRESIMS spectrum of **6**

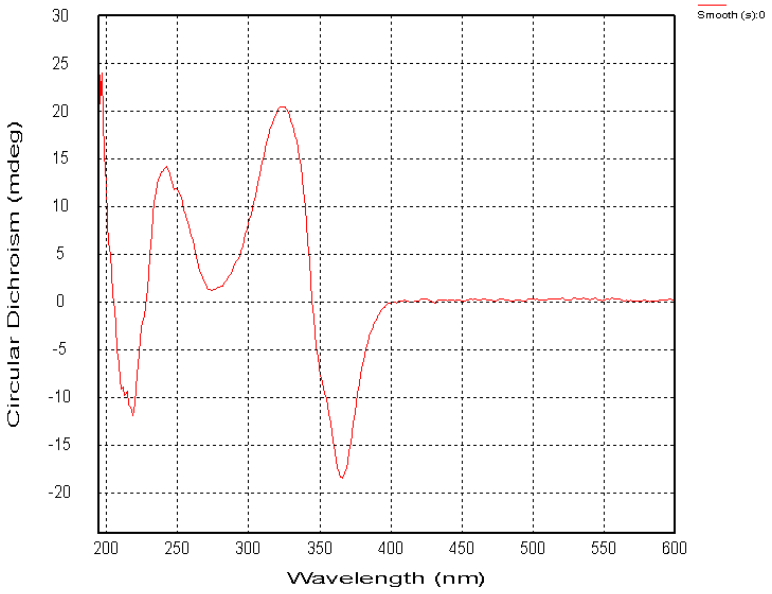


Figure S45. CD spectrum of **6** in methanol

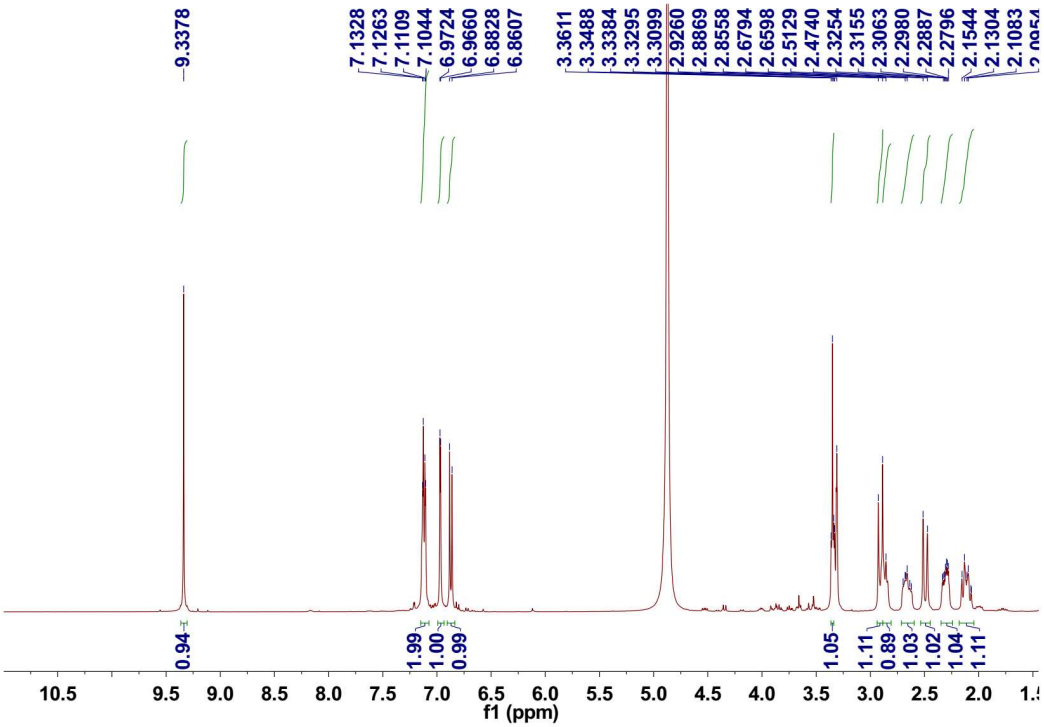


Figure S46. ^{1}H NMR spectrum of **7** in methanol-d_4

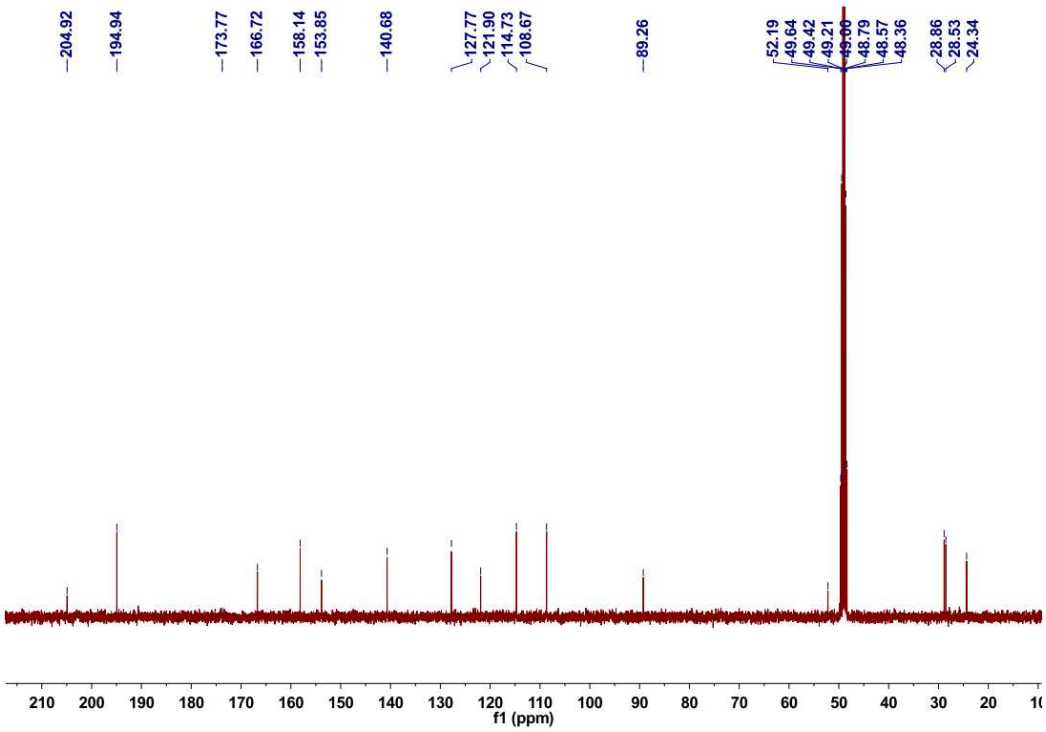


Figure S47. ^{13}C NMR spectrum of **7** in methanol-d_4

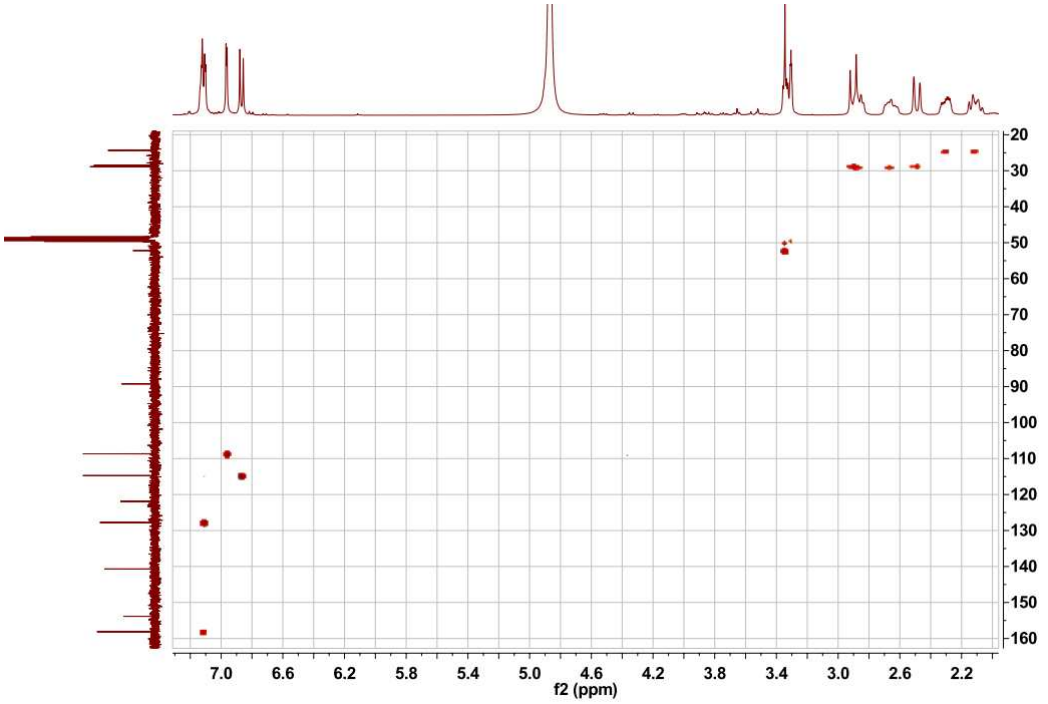


Figure S48. HSQC spectrum of **7** in methanol-d_4

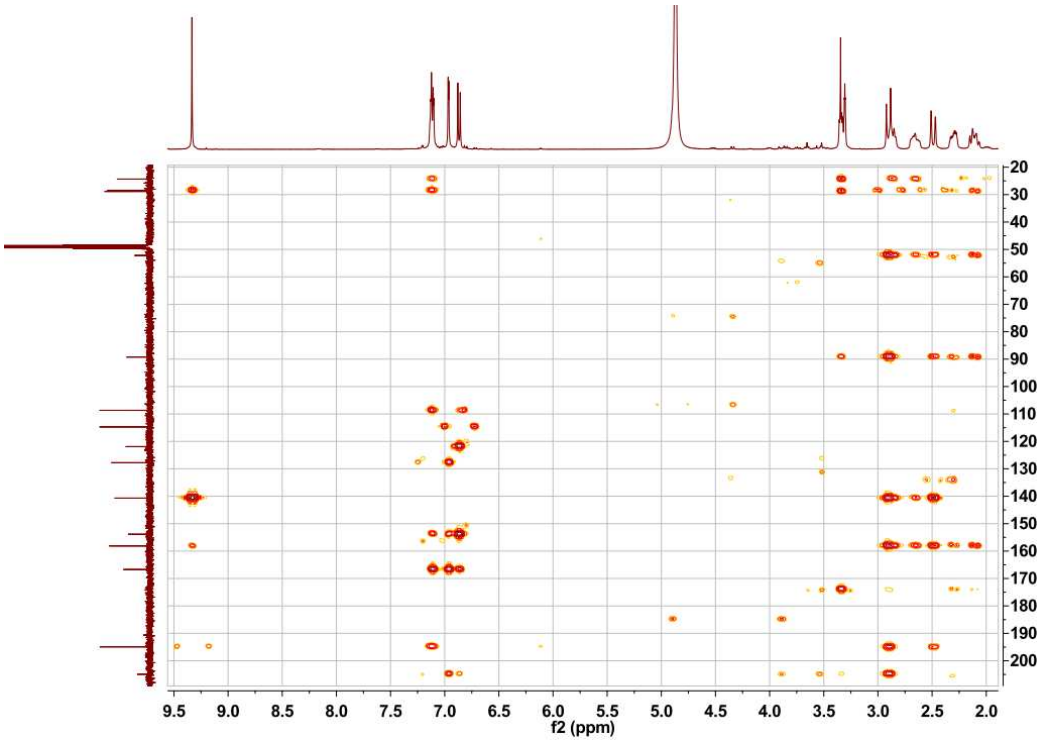


Figure S49. HMBC spectrum of **7** in methanol-d_4

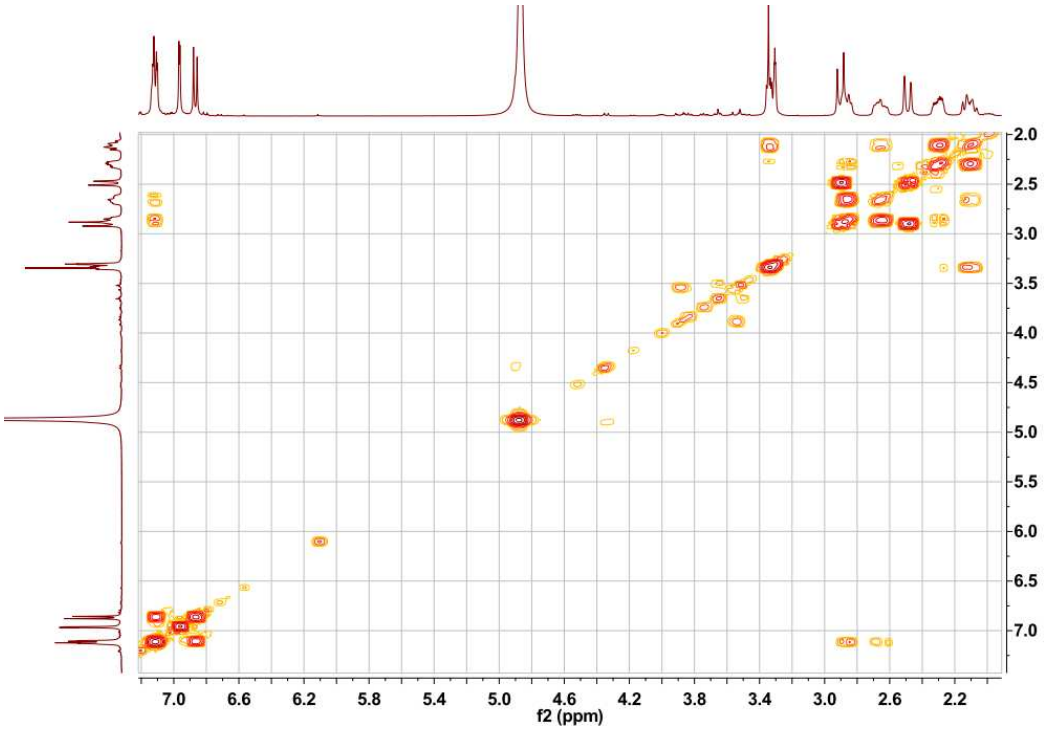
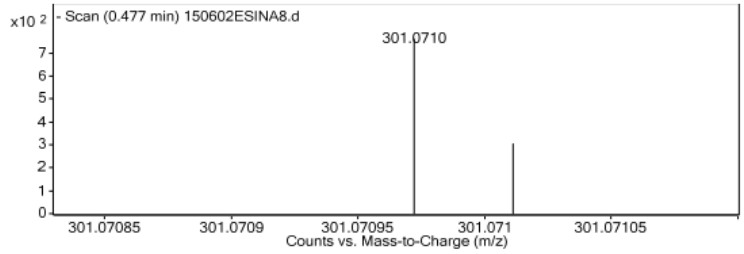


Figure S50. ^{1}H-^{1}H COSY spectrum of **7** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund
112.9856		2502.12
121.0659		3063.45
239.0716		1976.23
257.0822	1	12782.9
625.1315	1	3118.52
1033.9881	1	175692.36
1034.989	1	20841.21
1035.9905	1	1038.42
1933.9286	1	24443.91
1934.9309	1	4062.54

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	11

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C16 H13 O6	301.0712	301.0718	301.0710	0.8	2.6	10.5000

Figure S51. HRESIMS spectrum of **7**

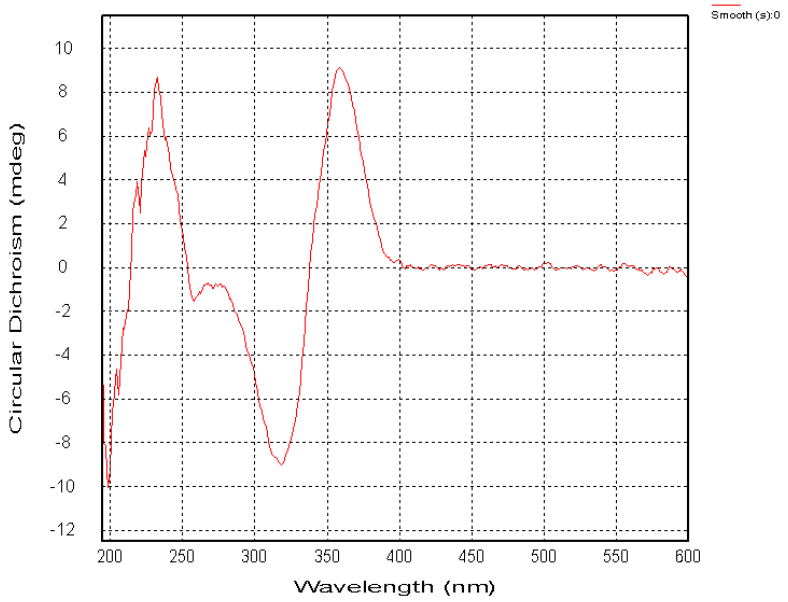


Figure S52. CD spectrum of **7** in methanol

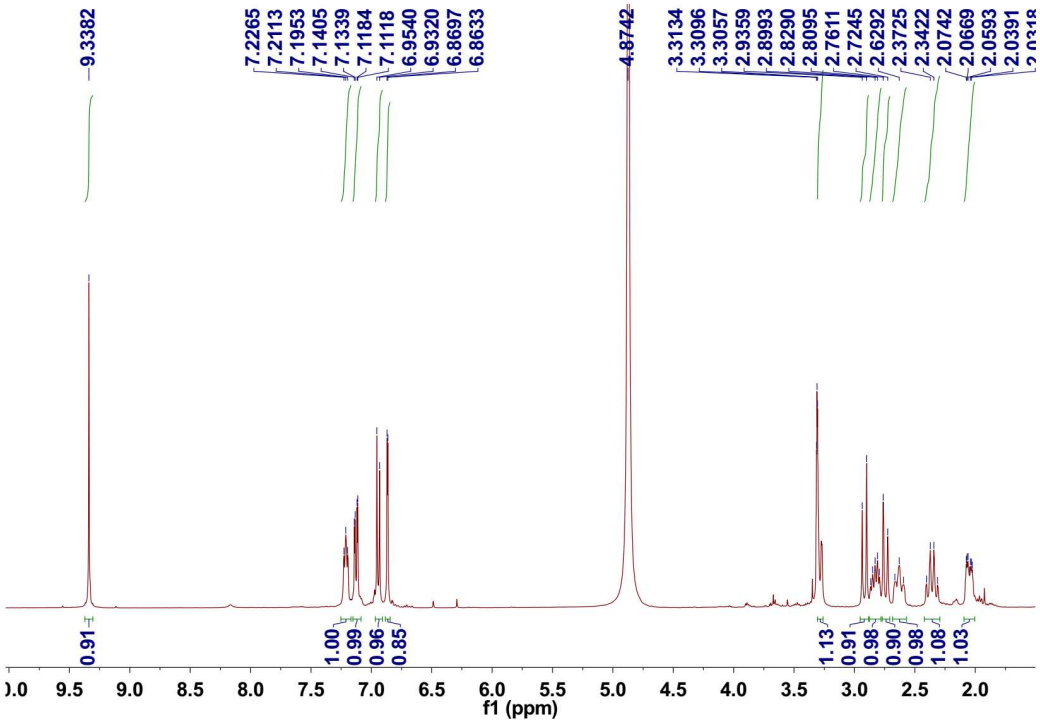


Figure S53. ^{1}H NMR spectrum of **8** in methanol-d_4

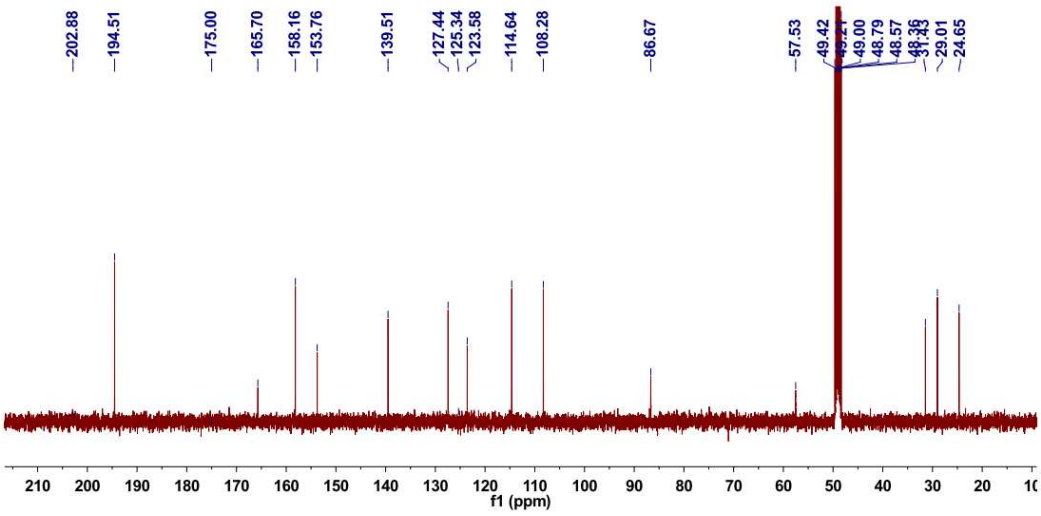


Figure S54. ^{13}C NMR spectrum of **8** in methanol-d_4

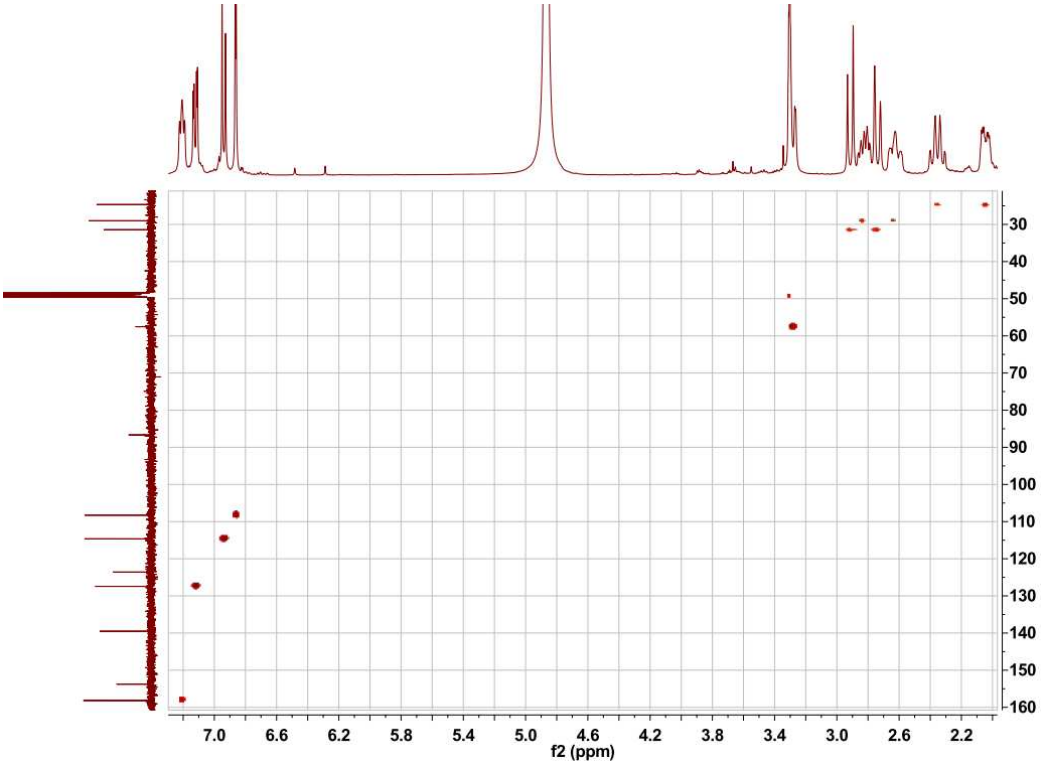


Figure S55. HSQC spectrum of **8** in methanol-d_4

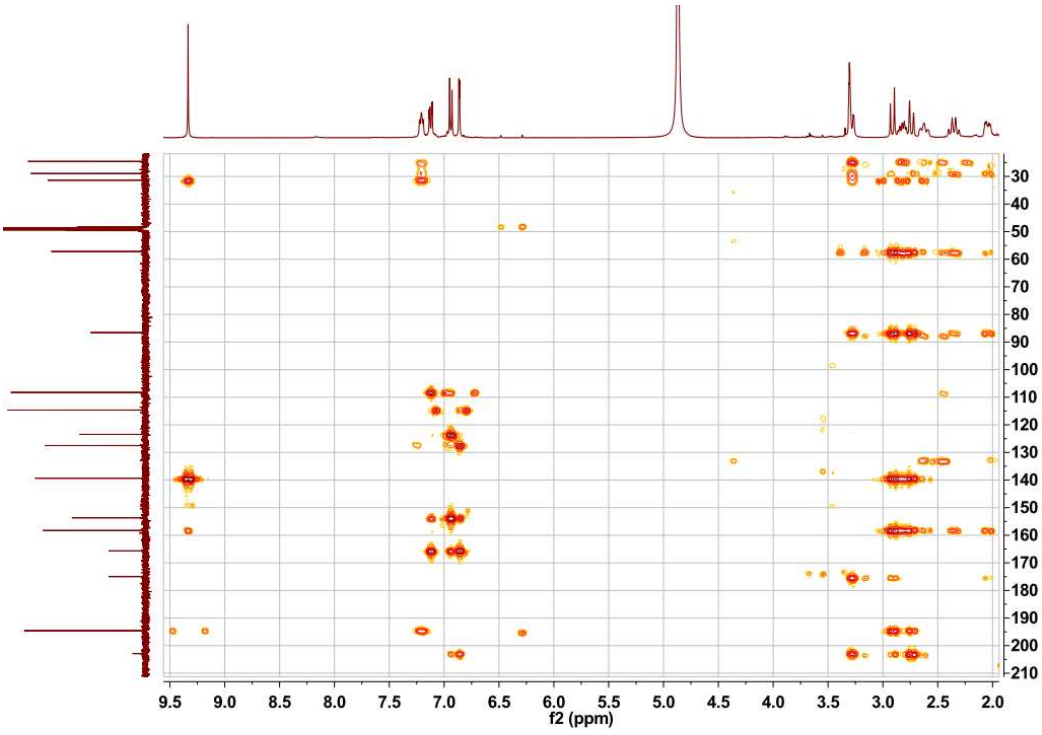


Figure S56. HMBC spectrum of **8** in methanol-d_4

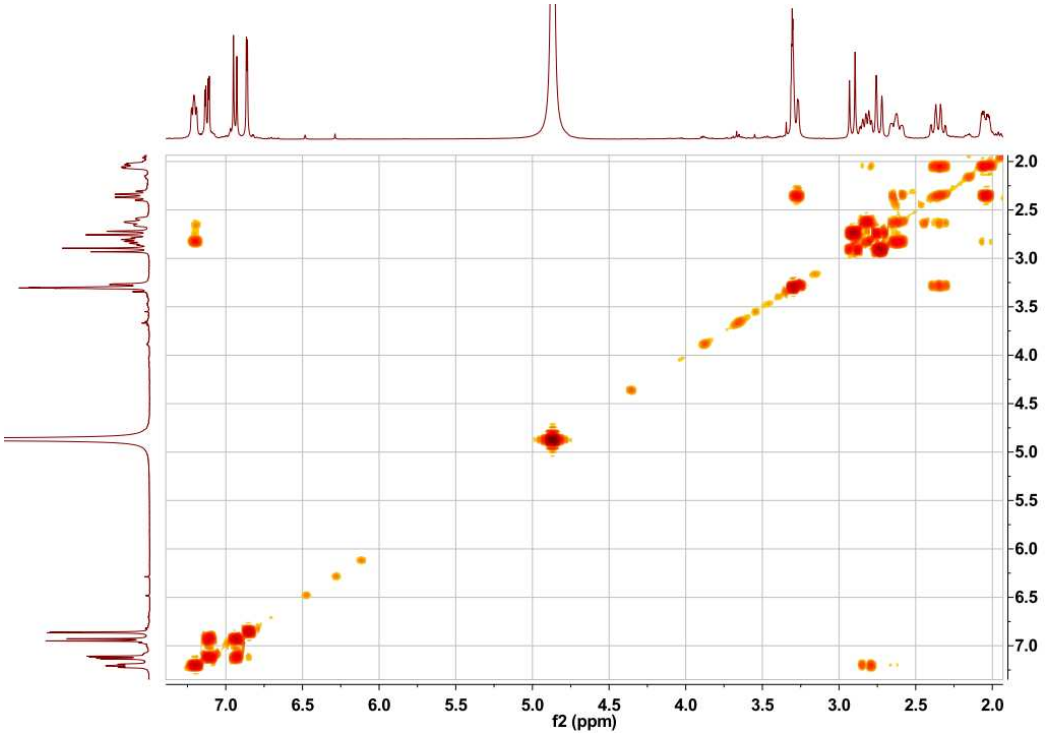
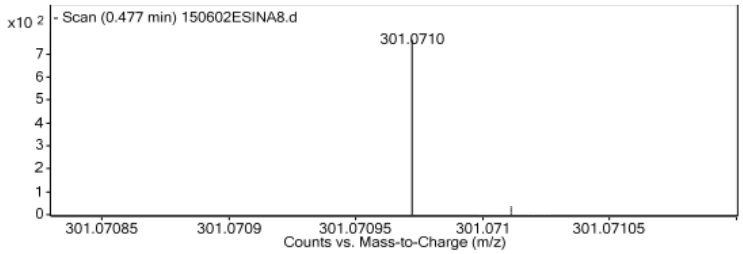


Figure S57. ^{1}H-^{1}H COSY spectrum of **8** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund
112.9856		2502.12
121.0659		3063.45
239.0716		1976.23
257.0822	1	12782.9
625.1315	1	3118.52
1033.9881	1	175692.36
1034.989	1	20841.21
1035.9905	1	1038.42
1933.9286	1	24443.91
1934.9309	1	4062.54

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	11

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C16 H13 O6	301.0712	301.0718	301.0710	0.8	2.6	10.5000

Figure S58. HRESIMS spectrum of **8**

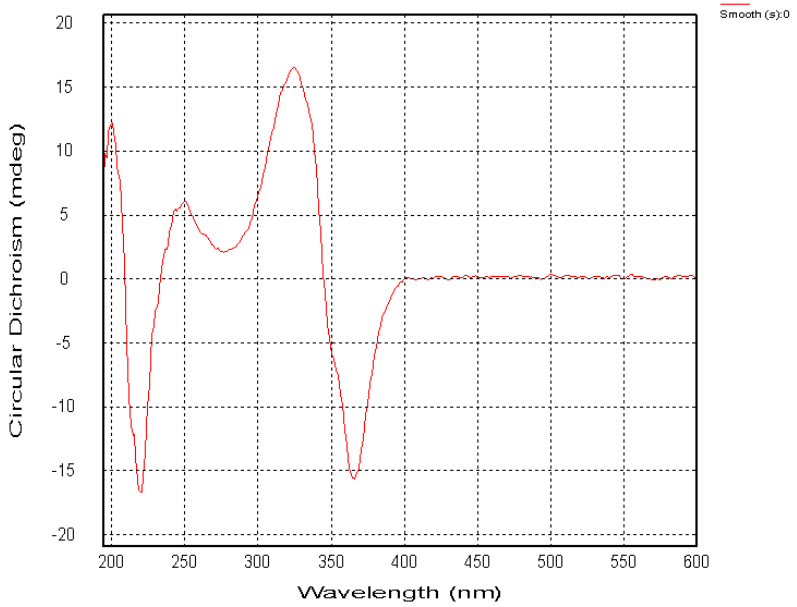


Figure S59. CD spectrum of **8** in methanol

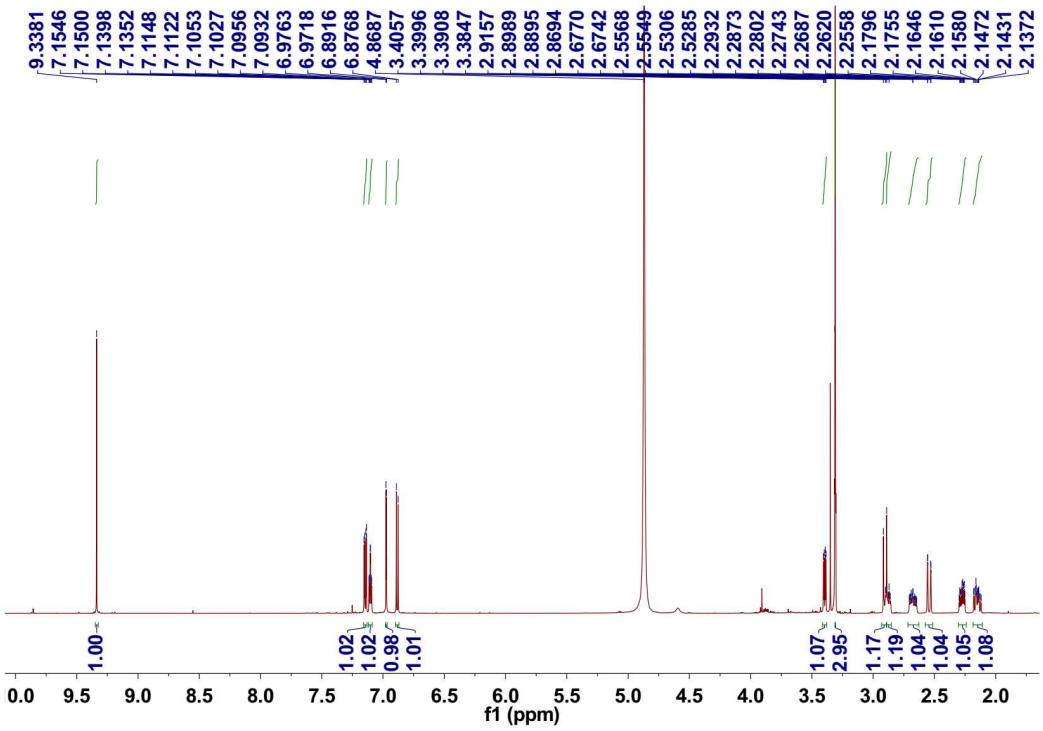


Figure S60. ^{1}H NMR spectrum of **9** in methanol-d_4

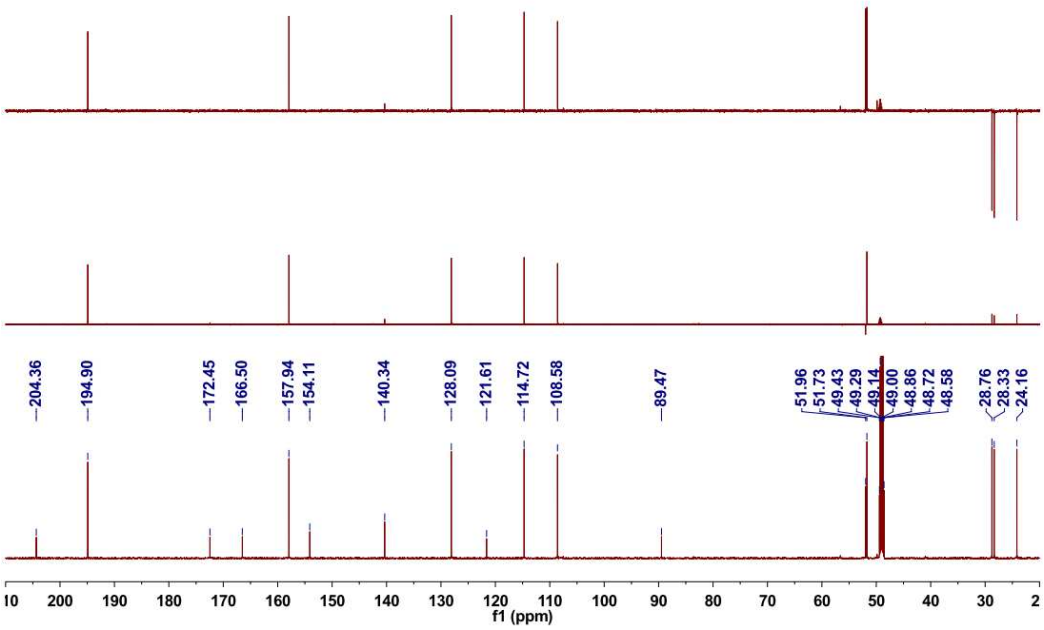


Figure S61. ^{13}C NMR and DEPT spectrum of **9** in methanol-d_4

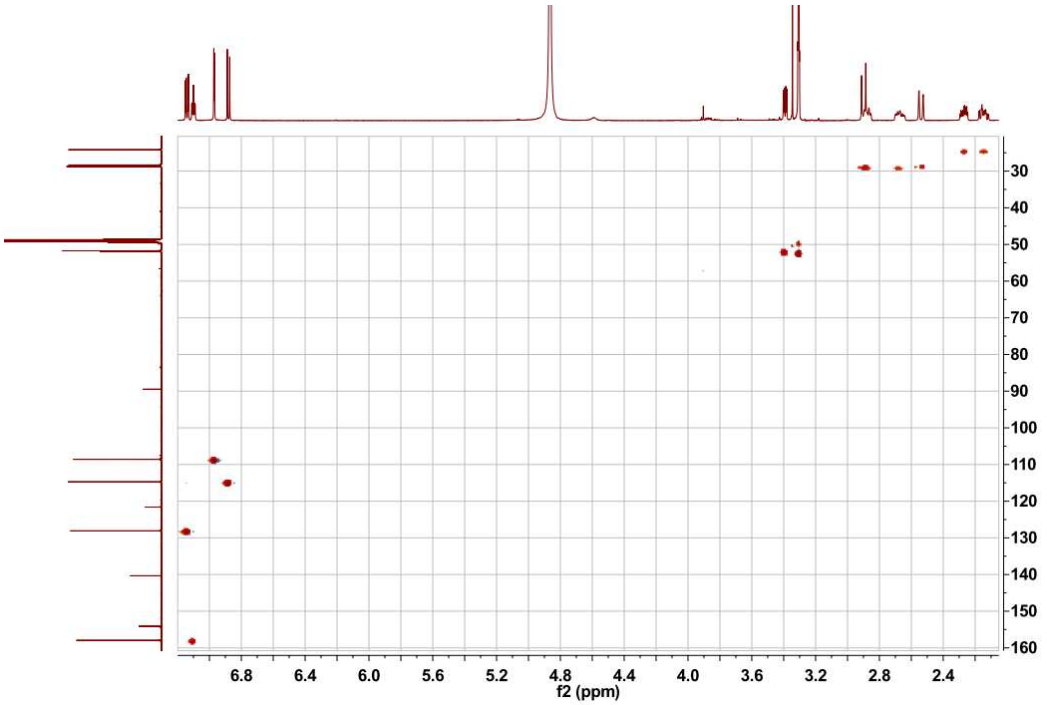


Figure S62. HSQC spectrum of **9** in methanol-d_4

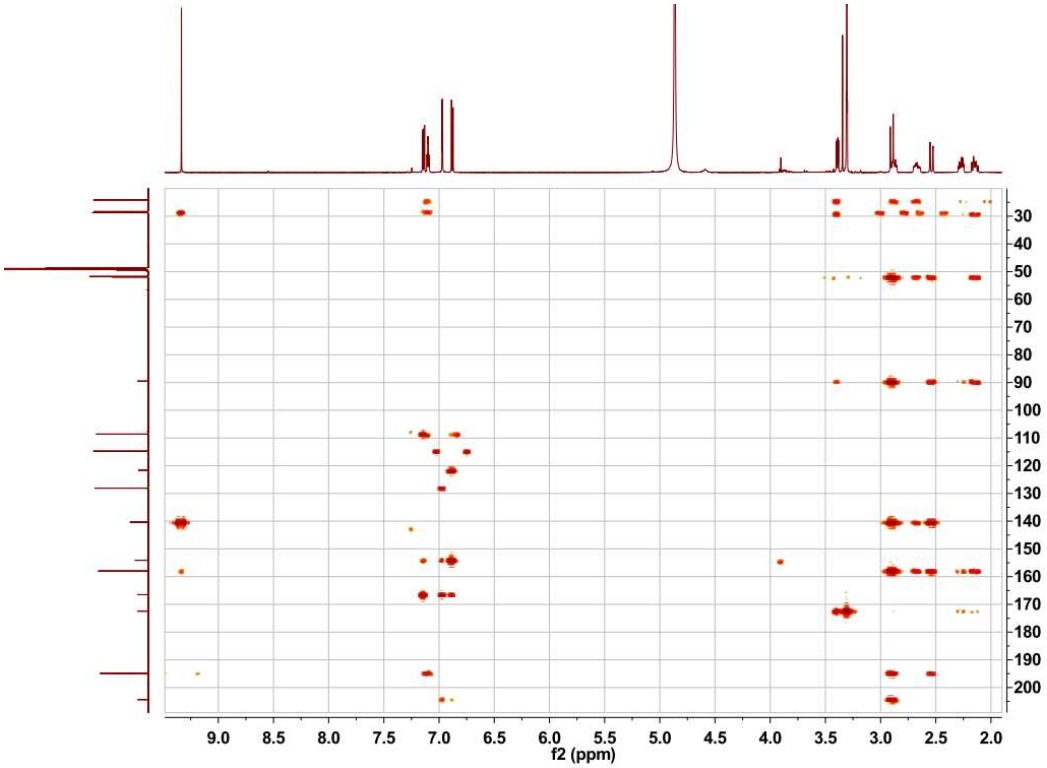


Figure S63. HMBC spectrum of **9** in methanol-d_4

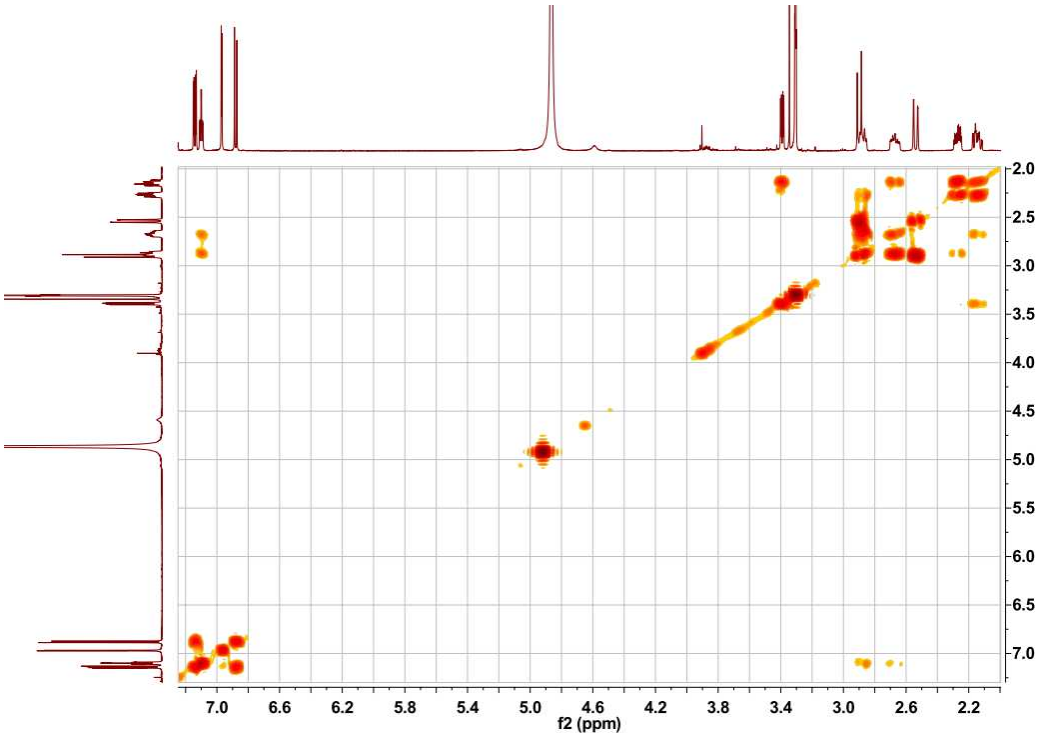
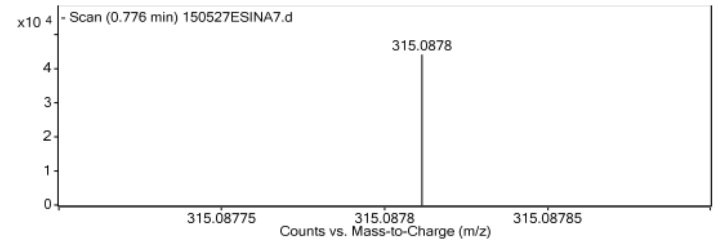


Figure S64. ^{1}H-^{1}H COSY spectrum of **9** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
112.9856	1	27747.77		
255.2332	1	18145.16		
268.9539	1	7823.53		
283.2641	1	14536.58		
311.1687	1	8554.13		
315.0878	1	44000.31	C17 H15 O6	M-
325.1841	1	9001.95		
485.2832	1	77648.08		
486.2857	1	14994.52		
1033.9881	1	36560.03		

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	12

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C17 H15 O6	315.0869	315.0874	315.0878	-0.4	-1.4	10.5000

Figure S65. HRESIMS spectrum of **9**

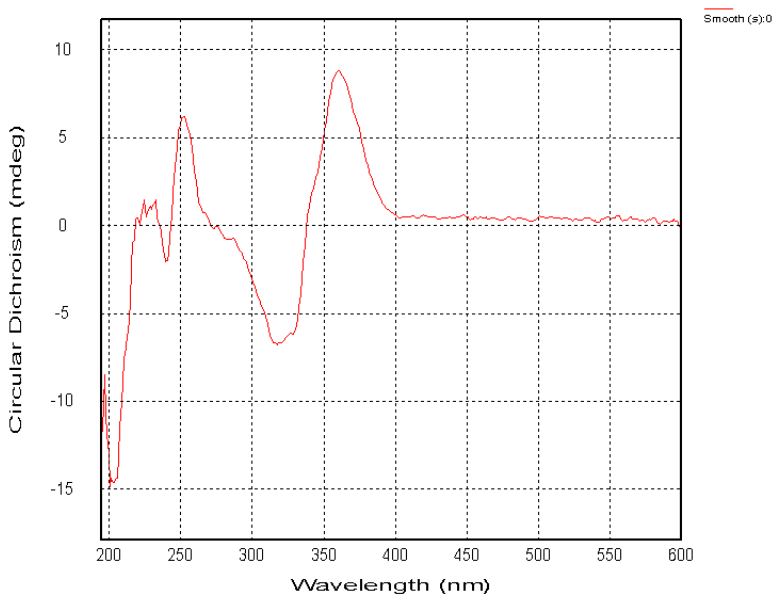


Figure S66. CD spectrum of **9** in methanol

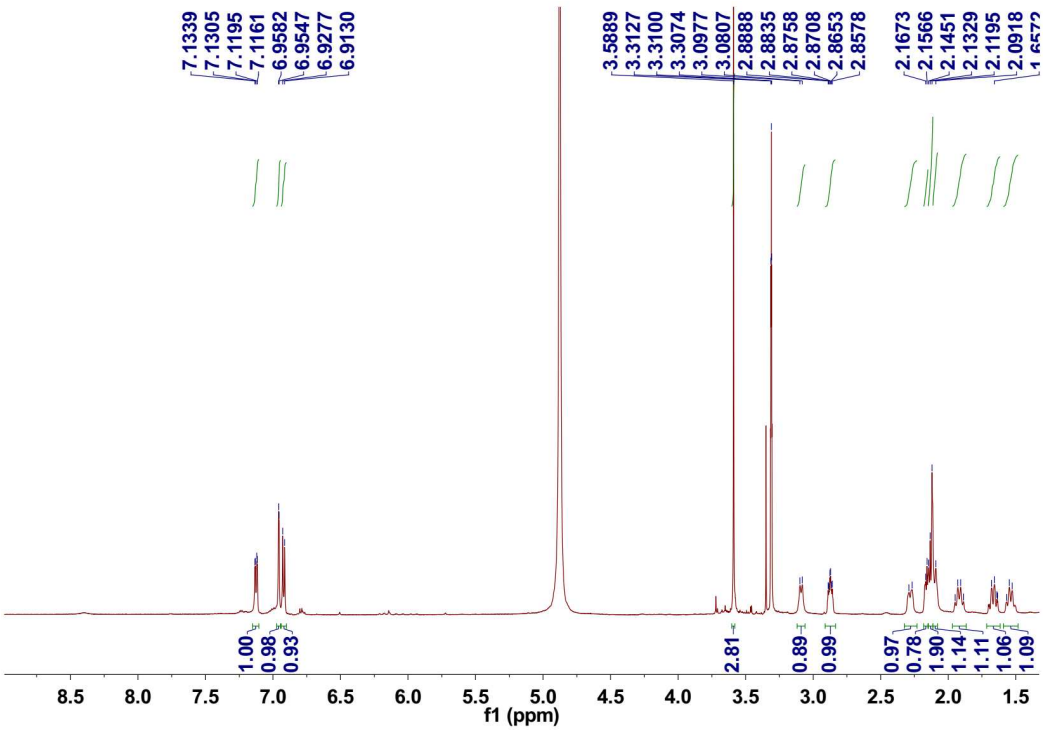


Figure S67. ^{1}H NMR spectrum of **10** in methanol-d_4

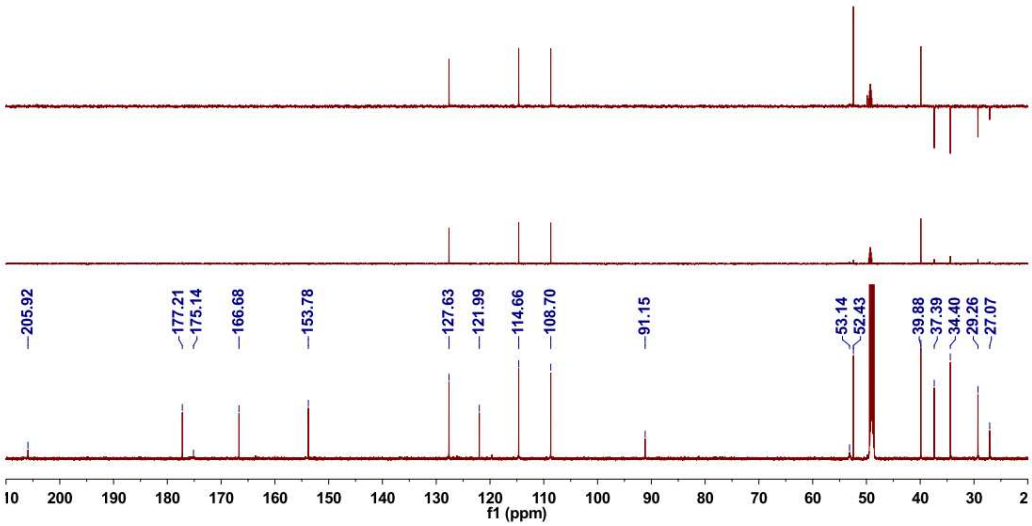


Figure S68. ^{13}C NMR and DEPT spectra of **10** in methanol-d_4

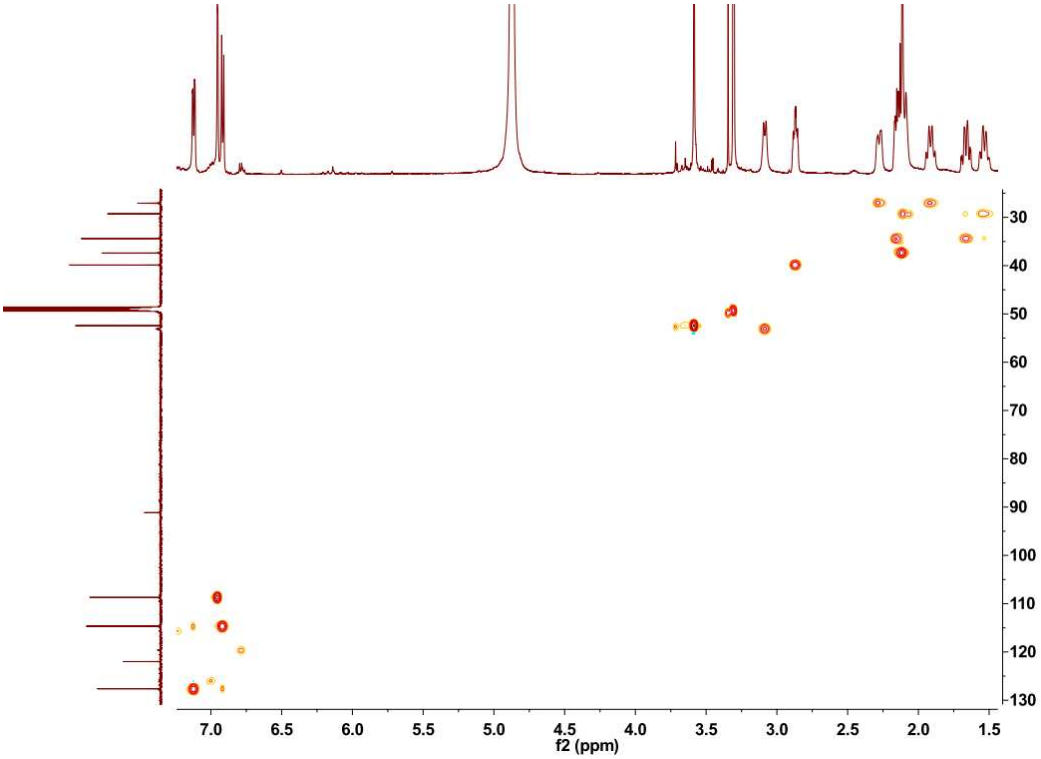


Figure S69. HSQC spectrum of **10** in methanol-d_4

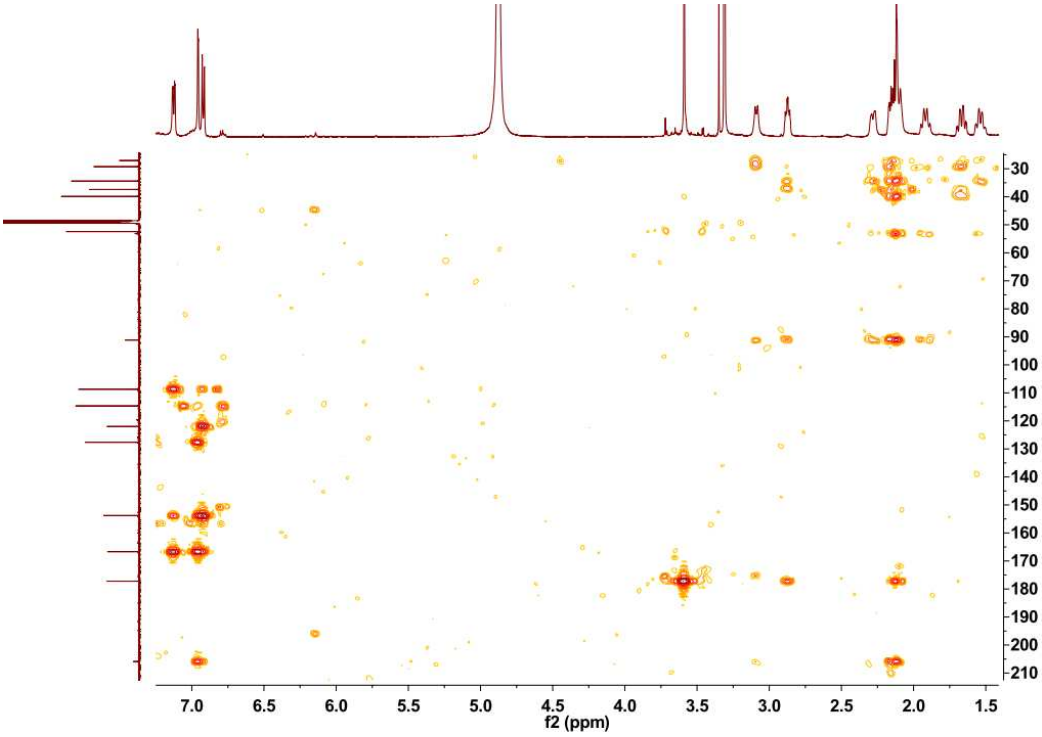


Figure S70. HMBC spectrum of **10** in methanol-d_4

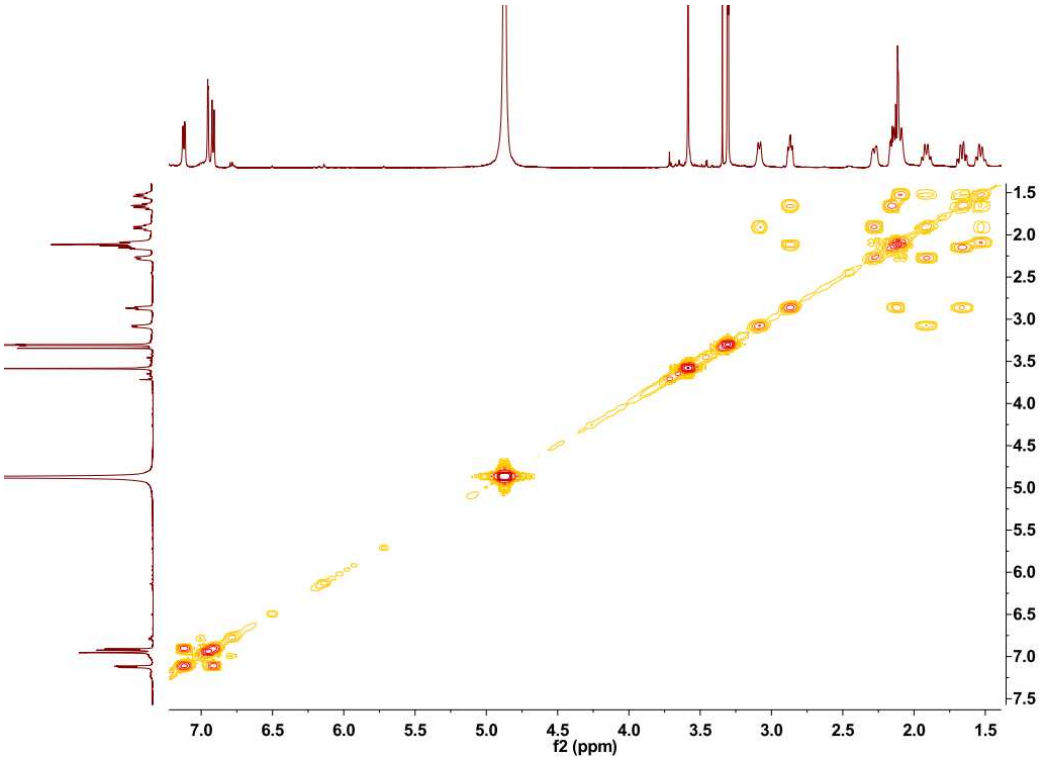


Figure S71. ^{1}H-^{1}H COSY spectrum of **10** in methanol-d_4

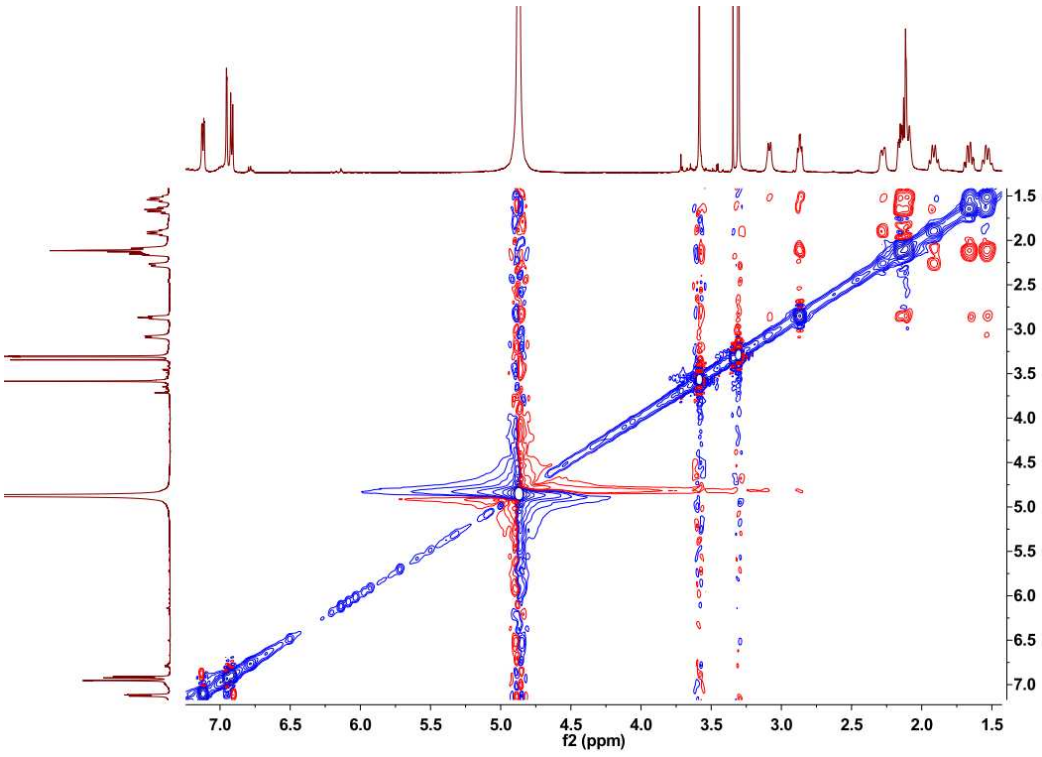
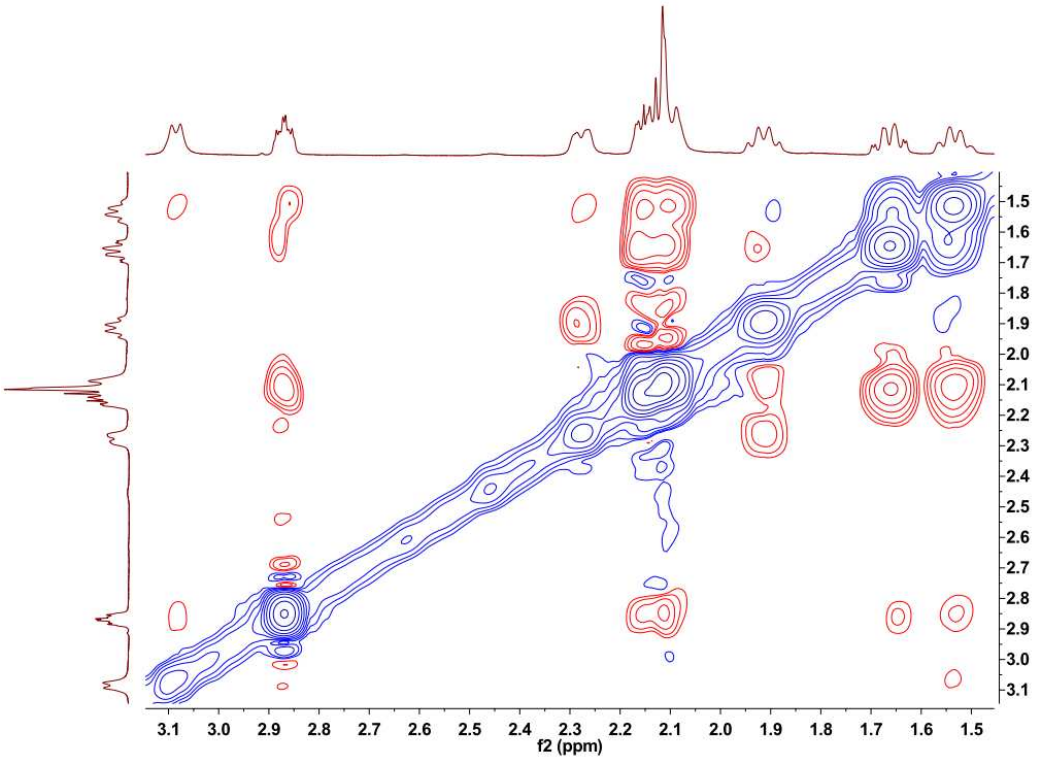


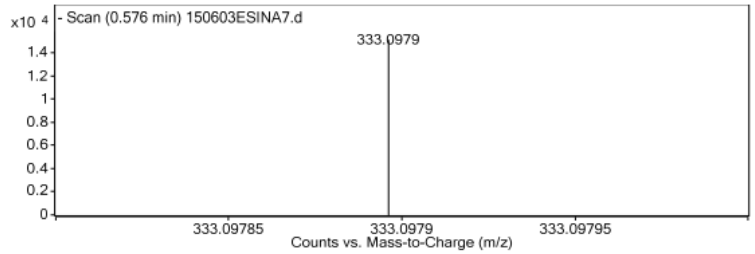
Figure S72. ROESY spectrum of **10** in methanol-d_4



Enlarged ROESY spectrum of **10** (up-field region) in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
112.9856		13750.75		
154.9735		7532.63		
174.9672	1	5836.2		
248.9603		5964.73		
257.0818	1	6290.03		
268.9543	1	18205.96		
289.1082	1	31471.48		
333.0979	1	15060.72	C17 H17 O7	M-
362.9405	1	5475.06		
1033.9881	1	55807.36		

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	11

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C17 H17 O7	333.0974	333.0980	333.0979	0.0	0.0	9.5000

Figure S73. HRESIMS spectrum of **10**

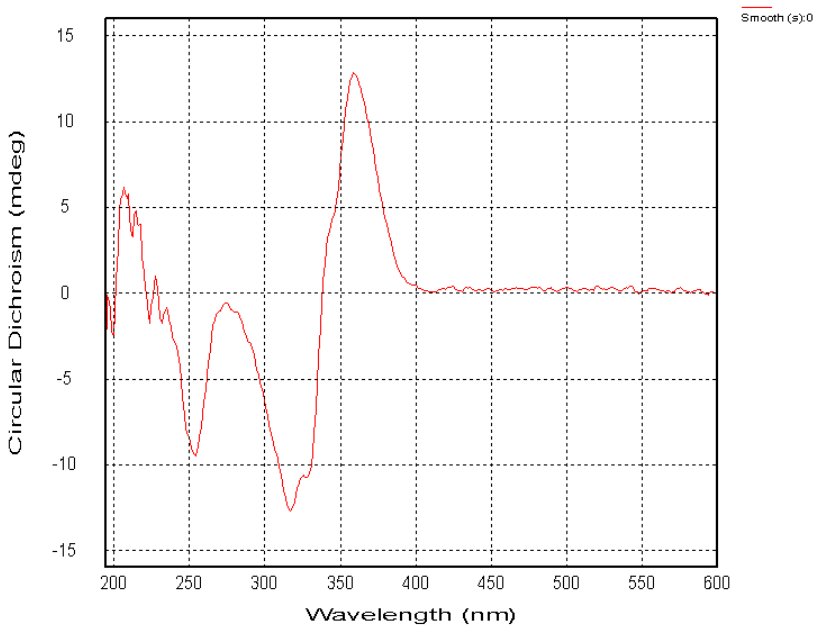


Figure S74. CD spectrum of **10** in methanol

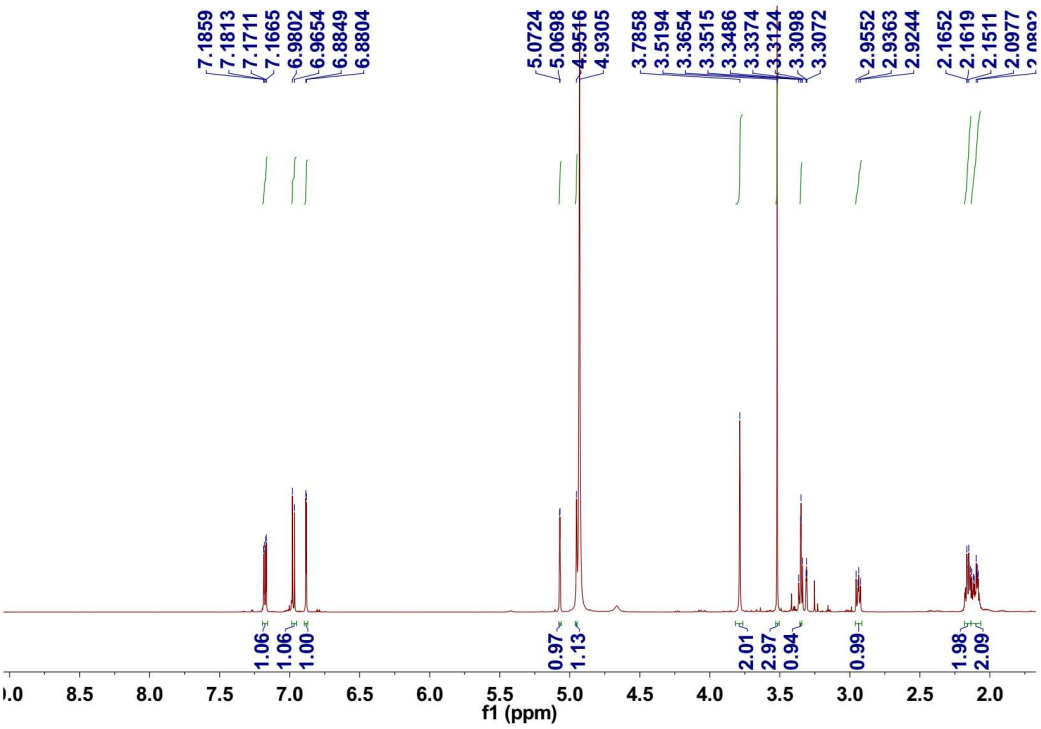


Figure S75. ^{1}H NMR spectrum of **11** in methanol-d_4

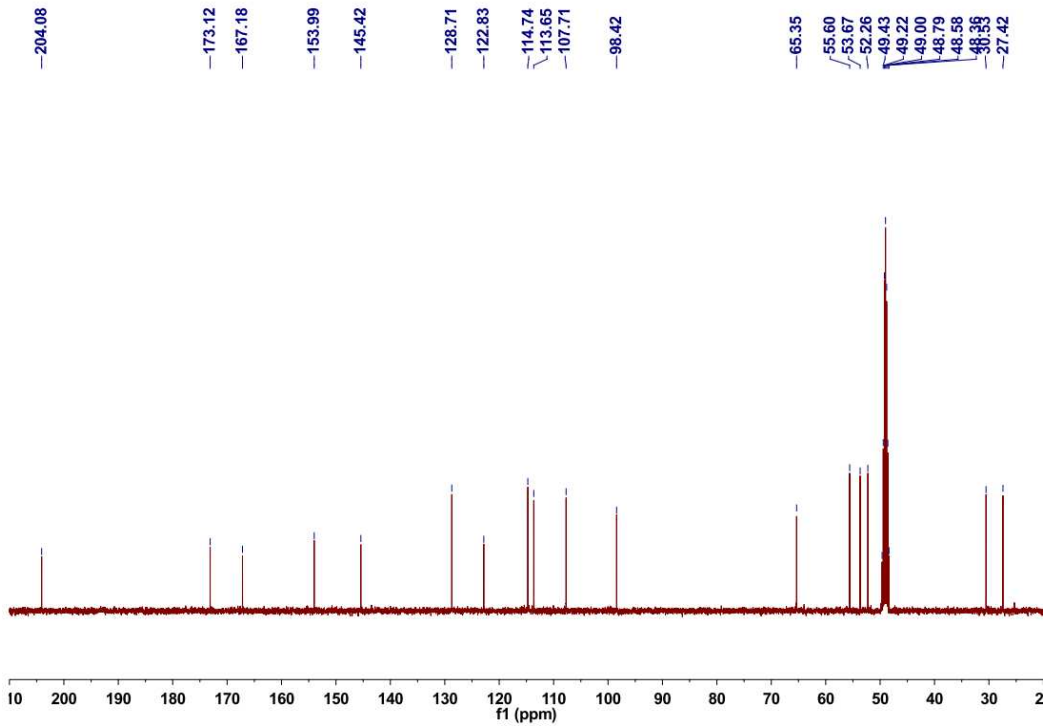


Figure S76. ^{13}C NMR spectrum of **11** in methanol-d_4

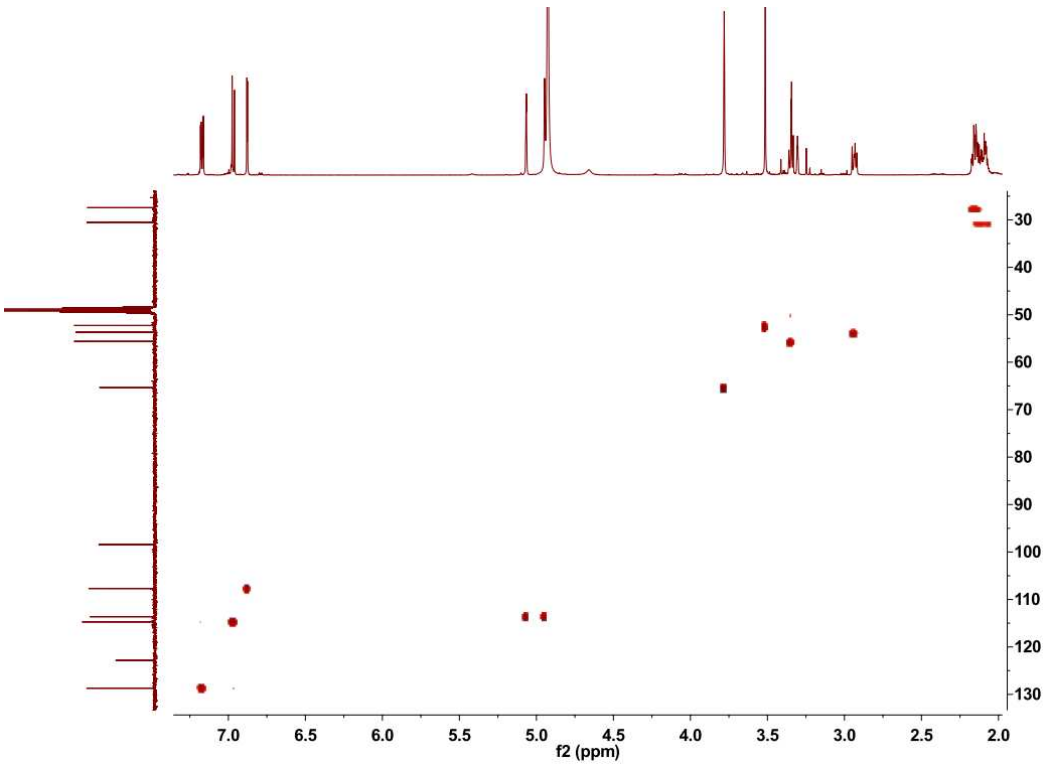


Figure S77. HSQC spectrum of **11** in methanol-d_4

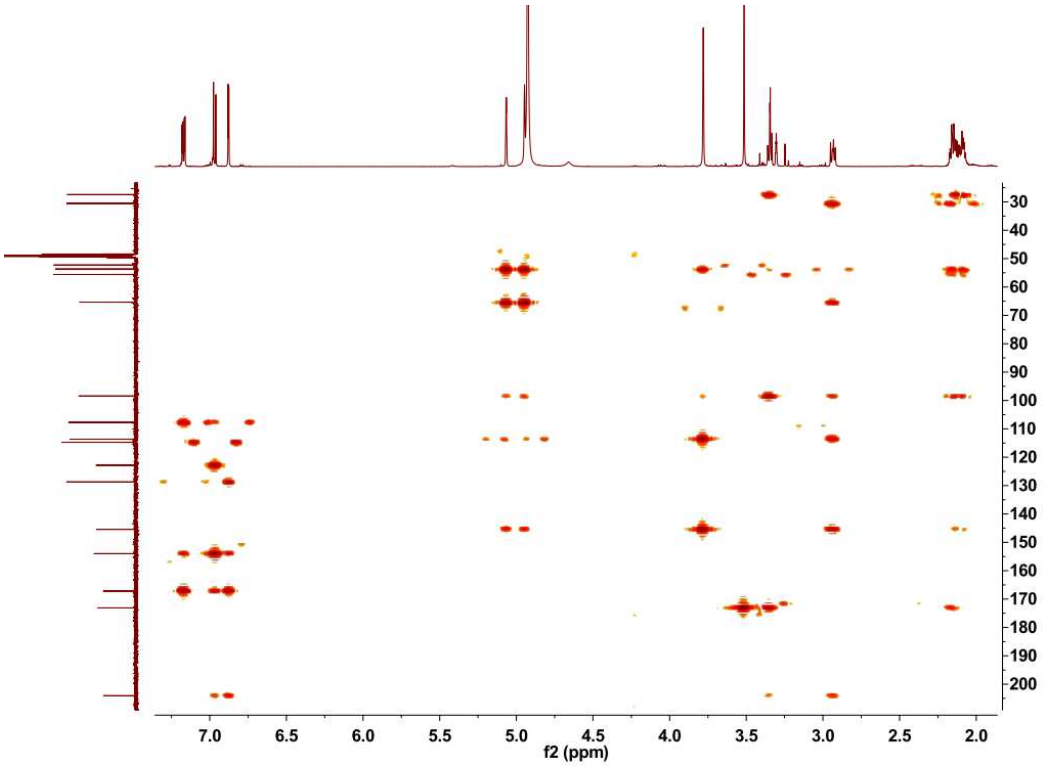


Figure S78. HMBC spectrum of **11** in methanol-d_4

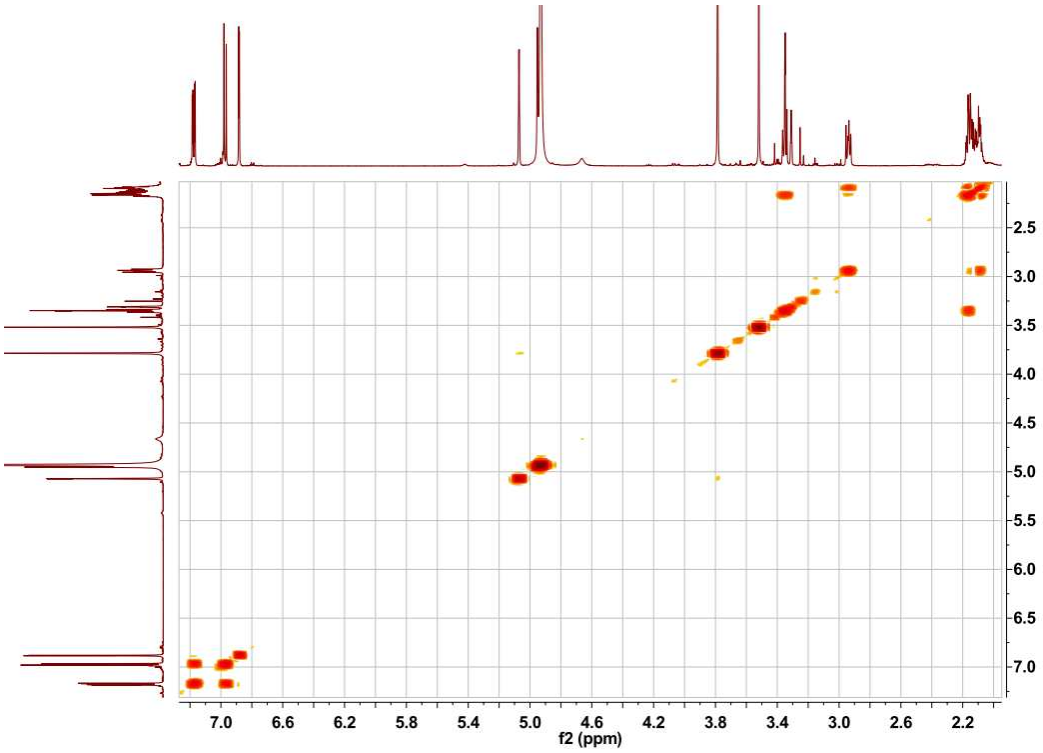


Figure S79. ^{1}H-^{1}H COSY spectrum of **11** in methanol-d_4

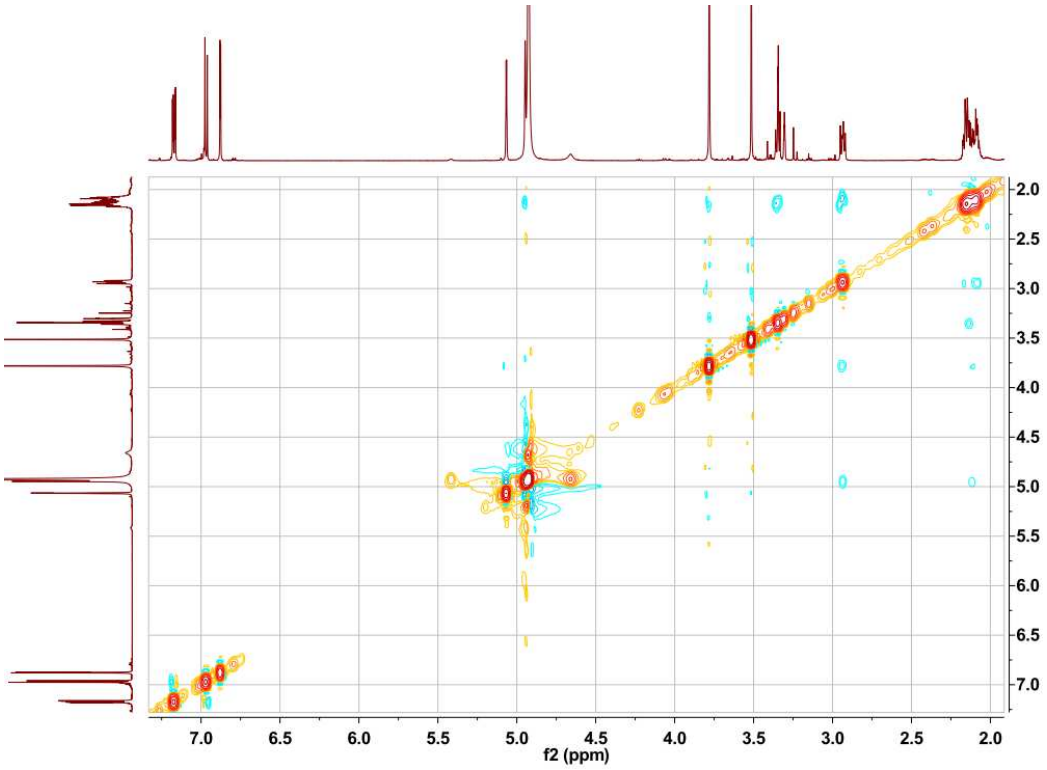
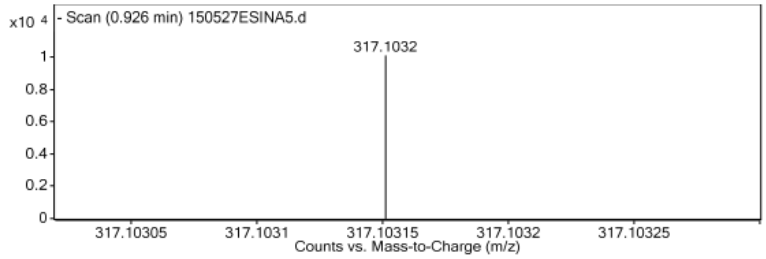


Figure S80. ROESY spectrum of **11** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
112.9856		11192.93		
154.9734		5660.44		
174.9671	1	7027		
248.9601		4691.56		
268.9542	1	20825.78		
269.9556	1	1452.13		
317.1032	1	10076.08	C17 H17 O6	M-
362.9405	1	4556.04		
1033.9881	1	96189.16		
1034.9891	1	8964.7		

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	12

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C17 H17 O6	317.1025	317.1031	317.1032	0.0	-0.1	9.5000

Figure S81. HRESIMS spectrum of **11**

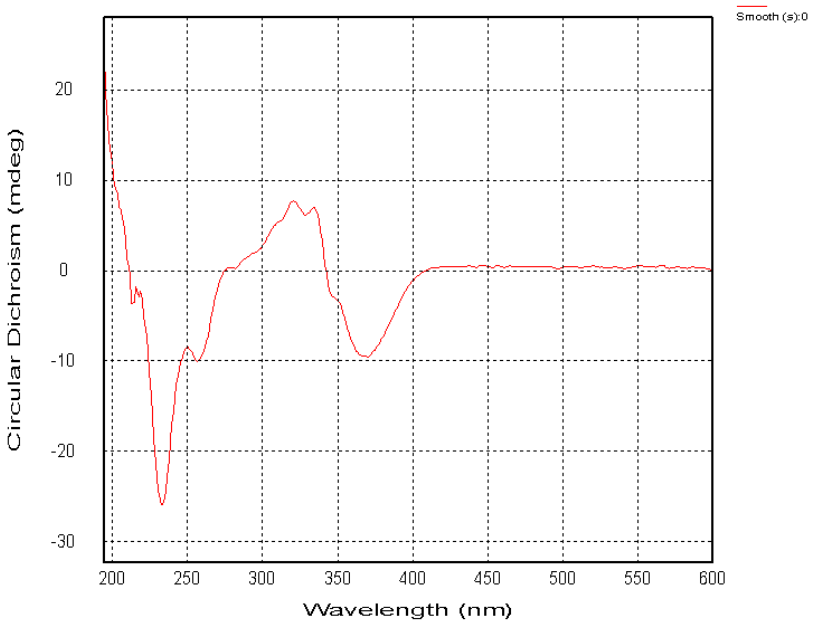


Figure S82. CD spectrum of **11** in methanol

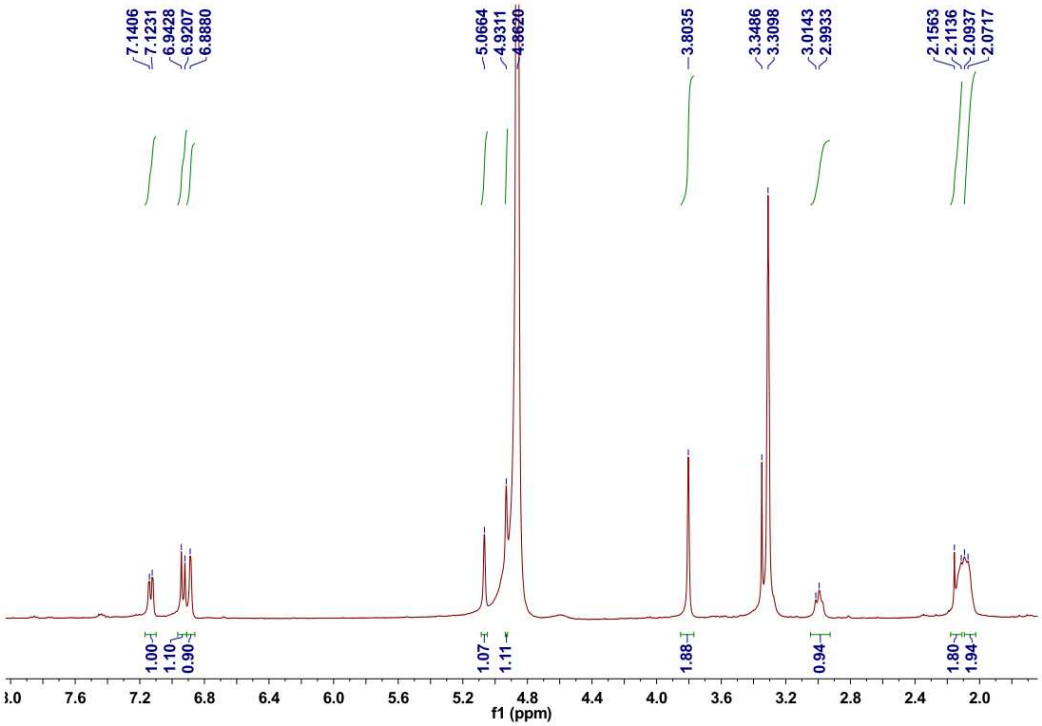


Figure S83. ^{1}H NMR spectrum of **12** in methanol-d_4

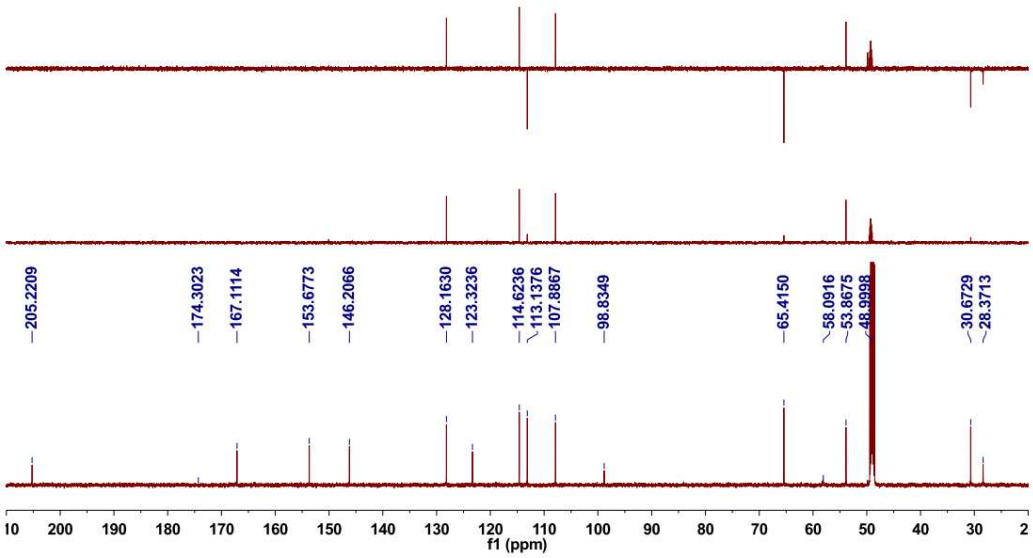


Figure S84. ^{13}C NMR and DEPT spectra of **12** in methanol-d_4

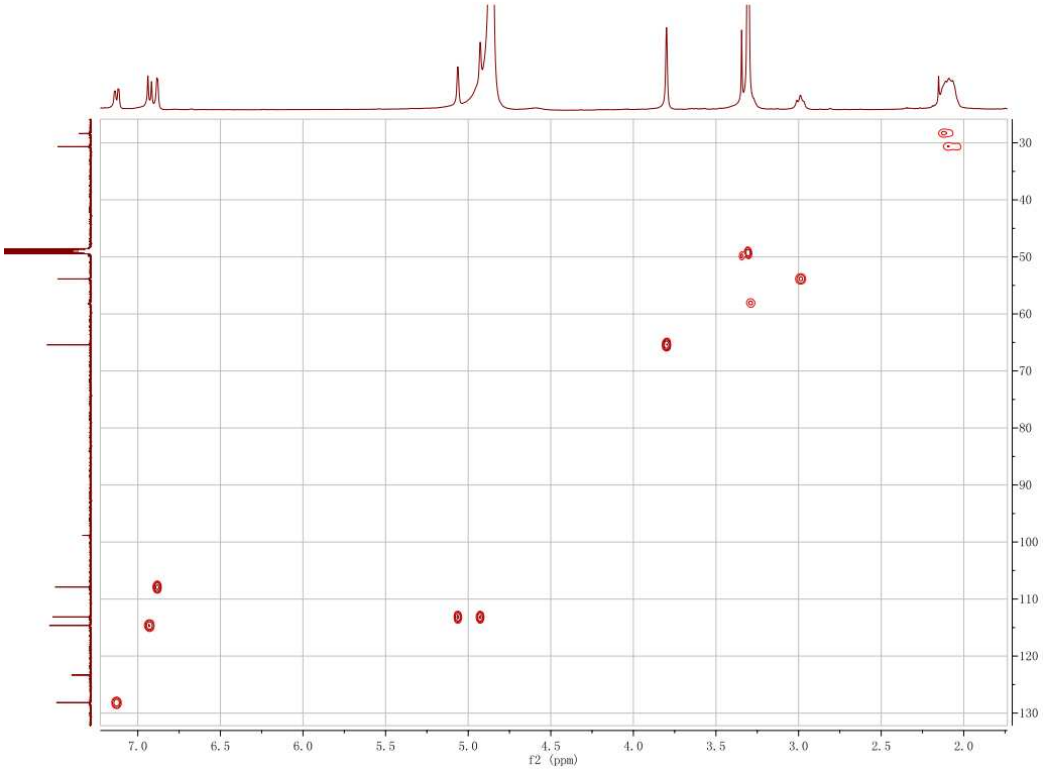


Figure S85. HSQC spectrum of **12** in methanol-d_4

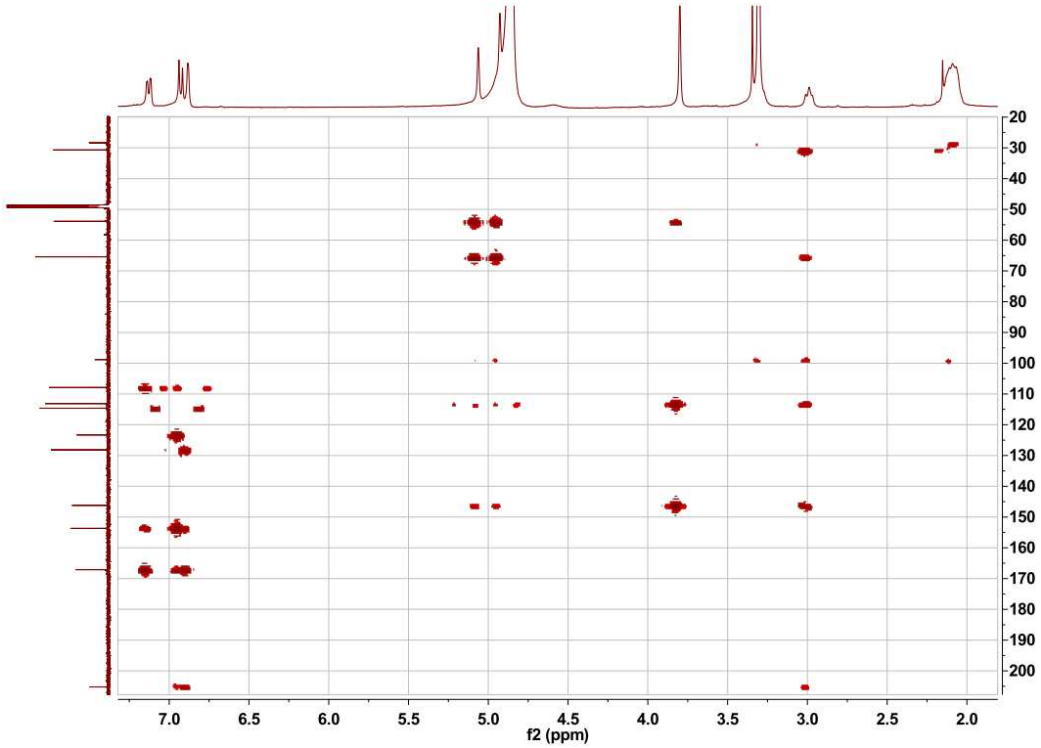


Figure S86. HMBC spectrum of **12** in methanol-d_4

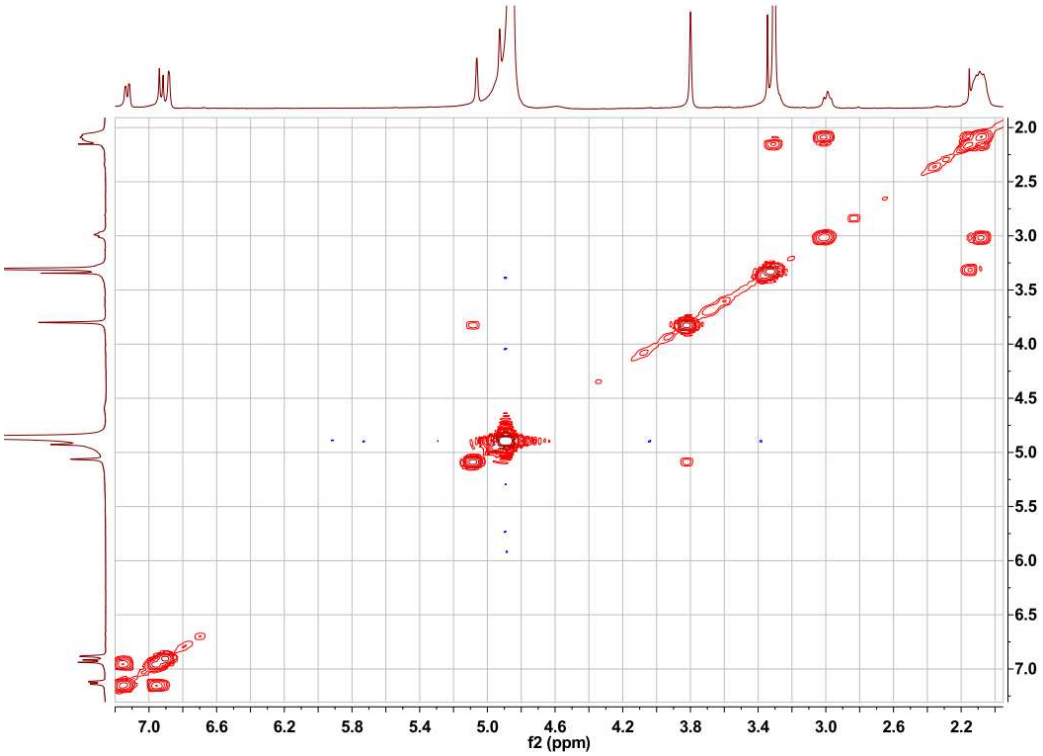


Figure S87. ^{1}H-^{1}H COSY spectrum of **12** in methanol-d_4

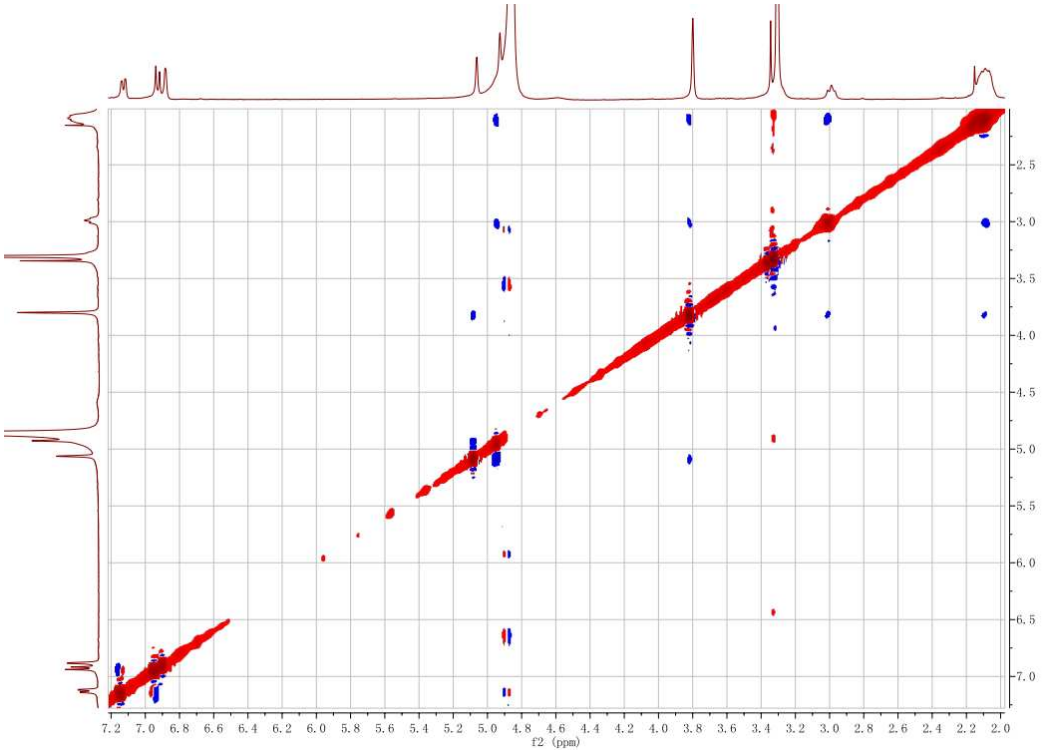
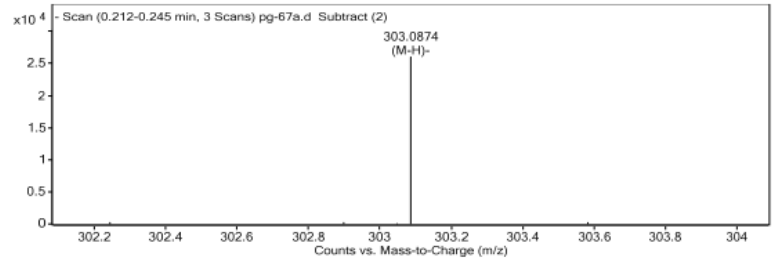


Figure S88. ROESY spectrum of **12** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
241.0868	1	3165.54		
259.0974	1	19603.11		
260.1012	1	3508.16		
303.0874	1	26041.33	C16 H16 O6	(M-H)-
304.0907	1	4511.85	C16 H16 O6	(M-H)-
371.0748	1	5769.04		
439.062		1847.77		
439.2333	1	1884.3		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C16 H16 O6	304.0947	303.0874	303.0874	-0.3	-1.0	9.0000

Figure S89. HREIMS spectrum of **12**

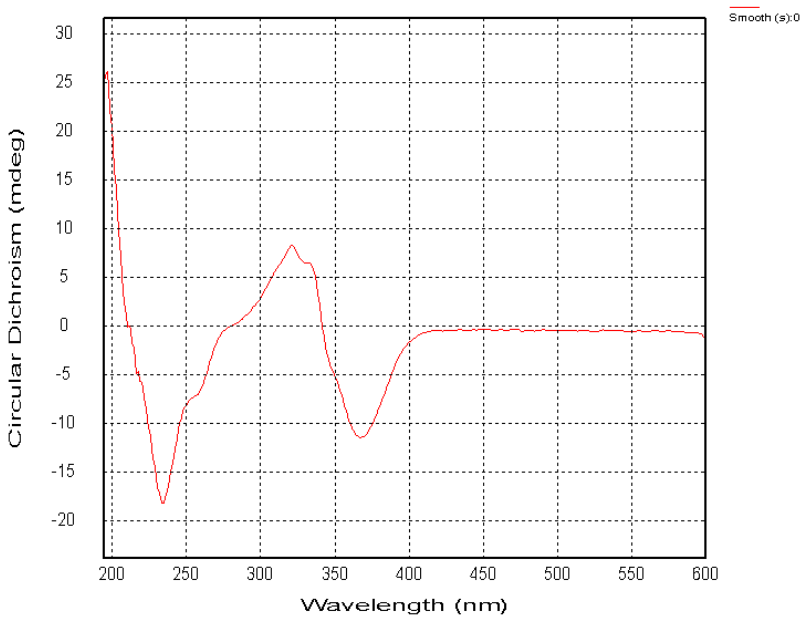


Figure S90. CD spectrum of **12** in methanol

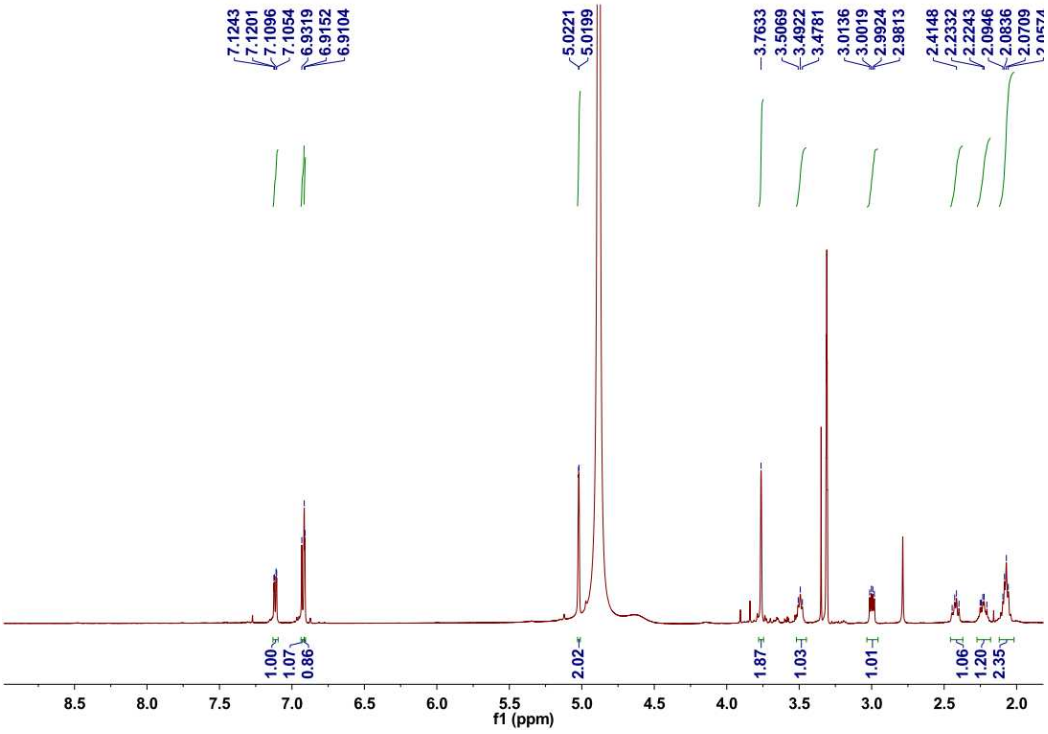


Figure S91. ^{1}H NMR spectrum of **14** in methanol-d_4

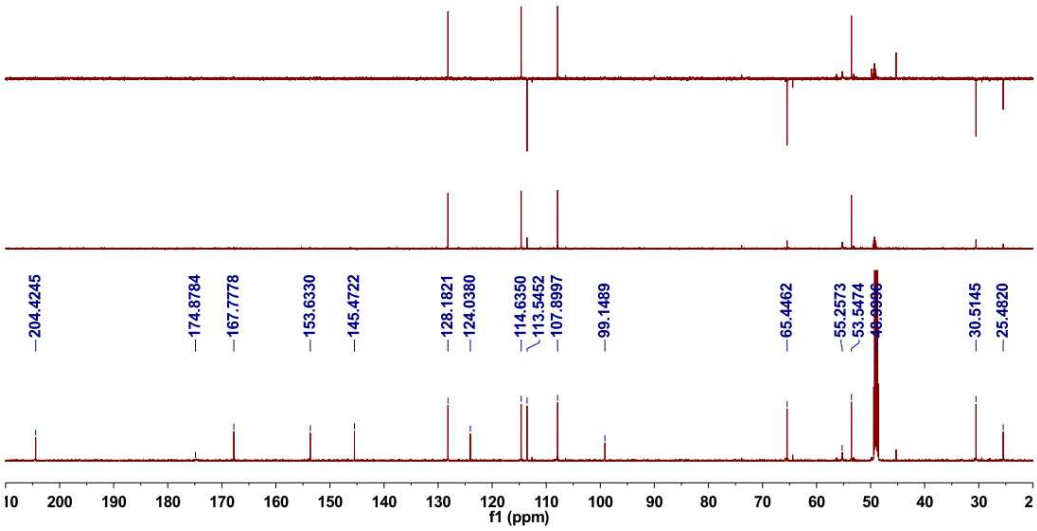


Figure S92. ^{13}C NMR and DEPT spectra of **14** in methanol-d_4

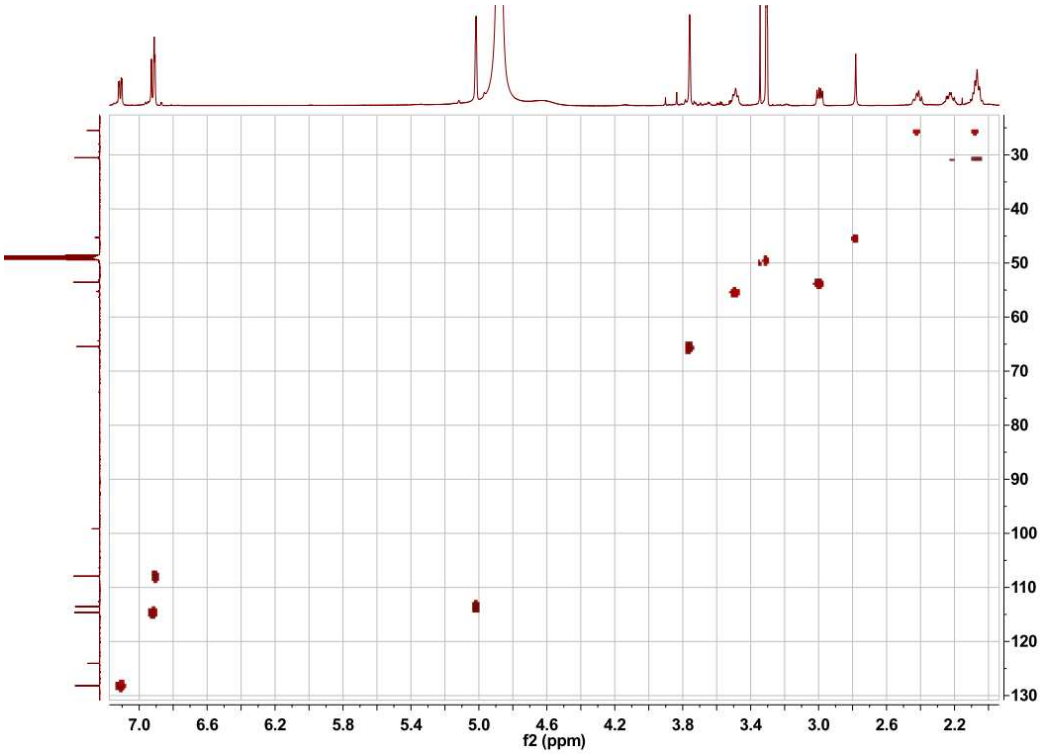


Figure S93. HSQC spectrum of **14** in methanol-d_4

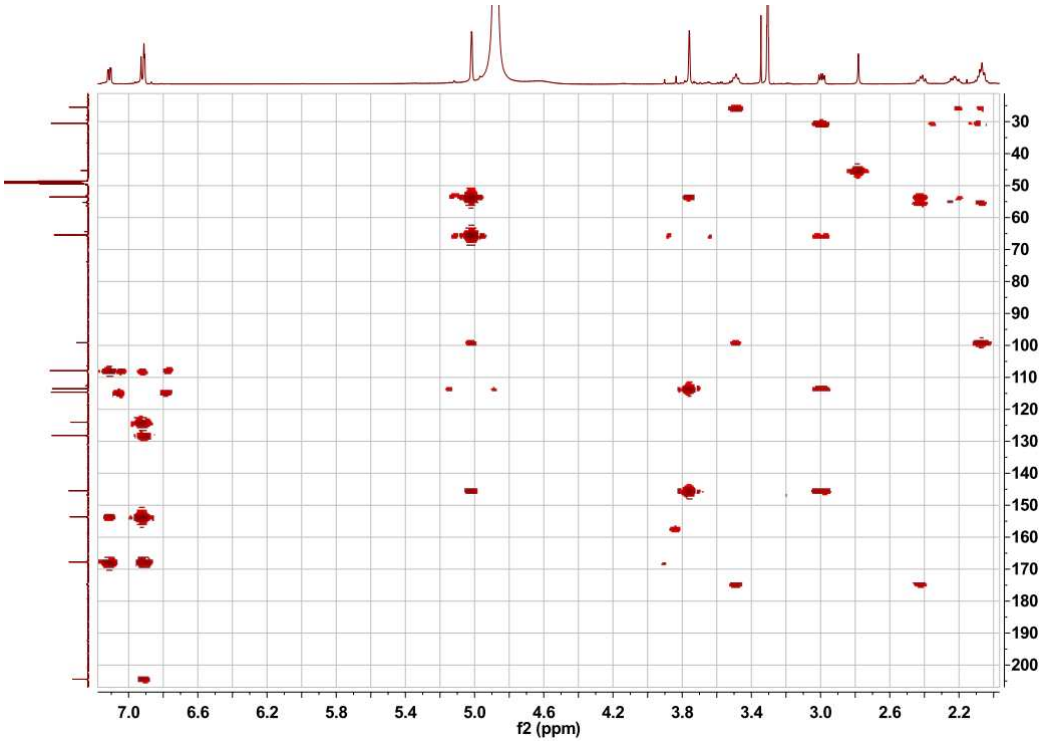


Figure S94. HMBC spectrum of **14** in methanol-d_4

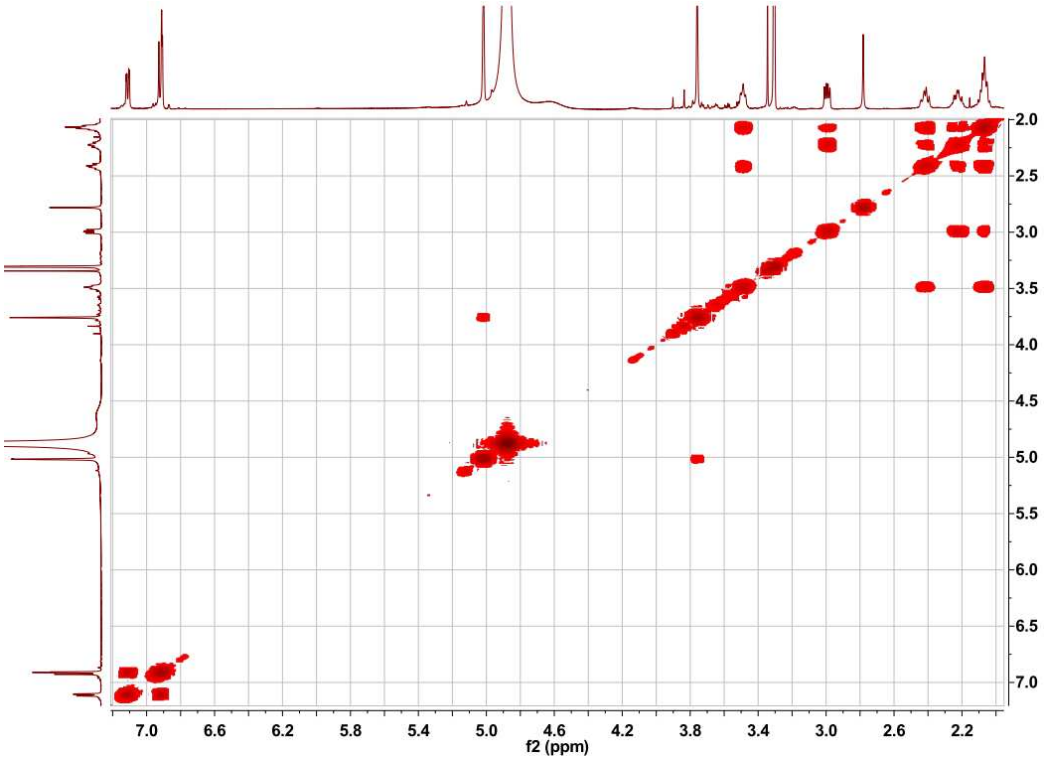


Figure S95. ^{1}H-^{1}H COSY spectrum of **14** in methanol-d_4

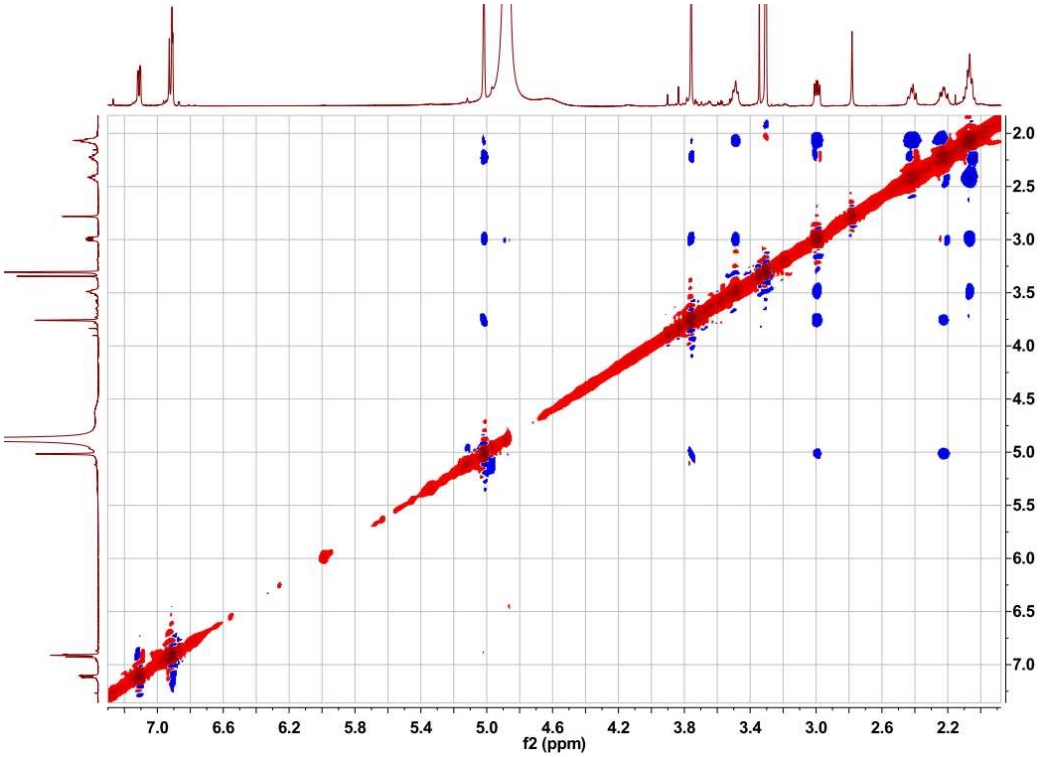
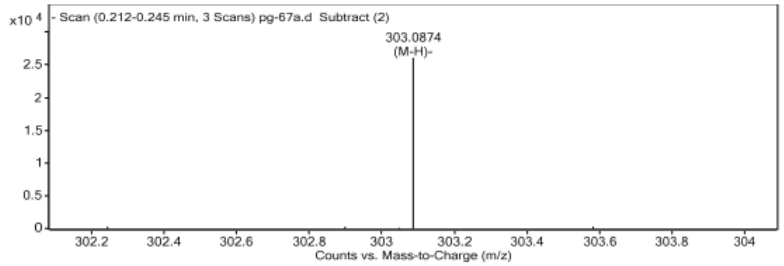


Figure S96. ROESY spectrum of **14** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
241.0868	1	3165.54		
259.0974	1	19603.11		
260.1012	1	3508.16		
303.0874	1	26041.33	C16 H16 O6	(M-H)-
304.0907	1	4511.85	C16 H16 O6	(M-H)-
371.0748	1	5769.04		
439.062		1847.77		
439.2333	1	1884.3		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C16 H16 O6	304.0947	303.0874	303.0874	-0.3	-1.0	9.0000

Figure S97. HRESIMS spectrum of **14**

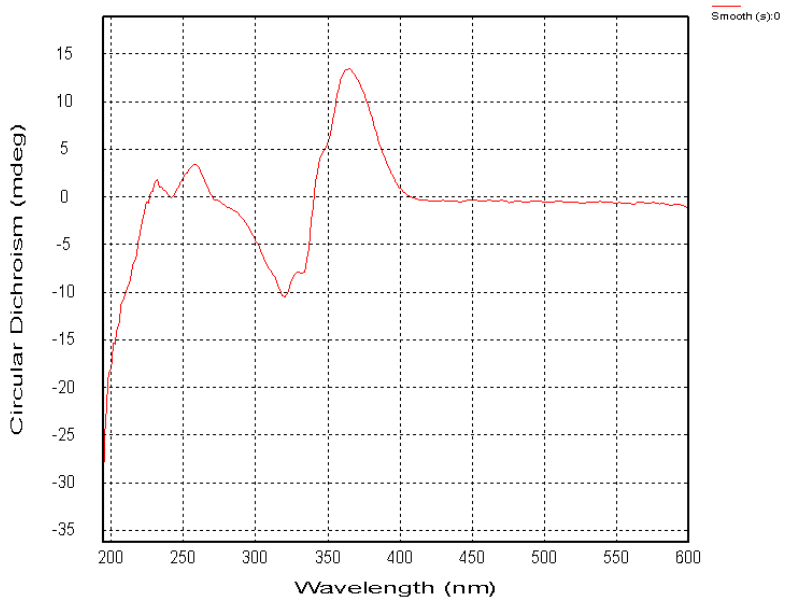


Figure S98. CD spectrum of **14** in methanol

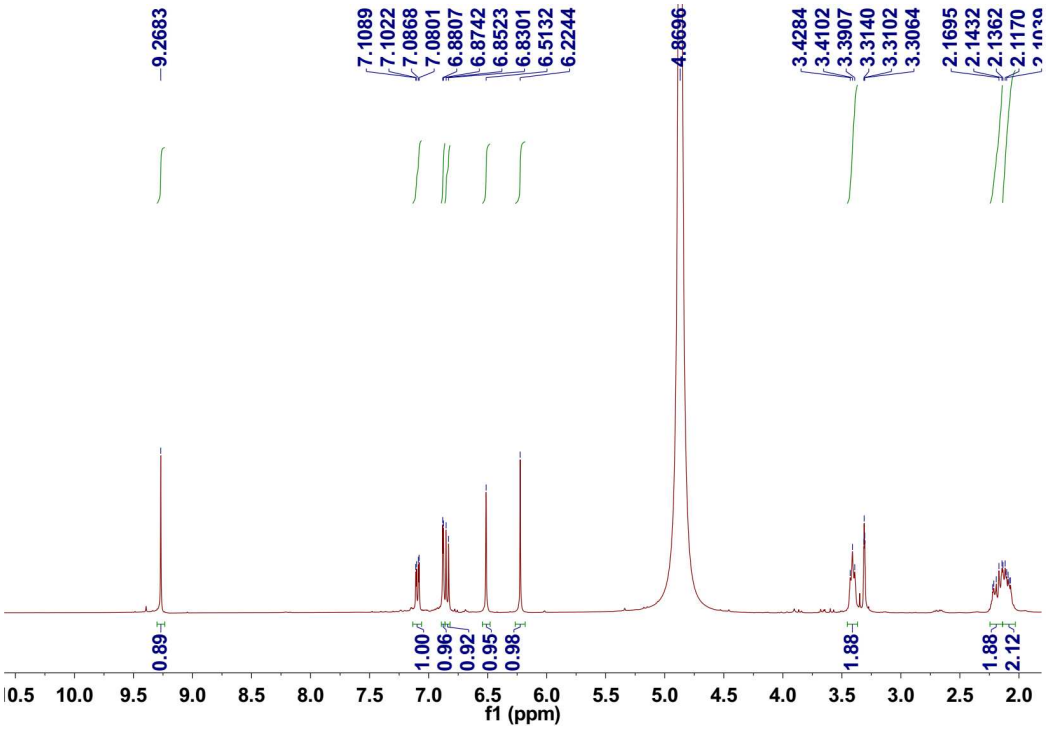


Figure S99. ^{1}H NMR spectrum of **15** in methanol-d_4

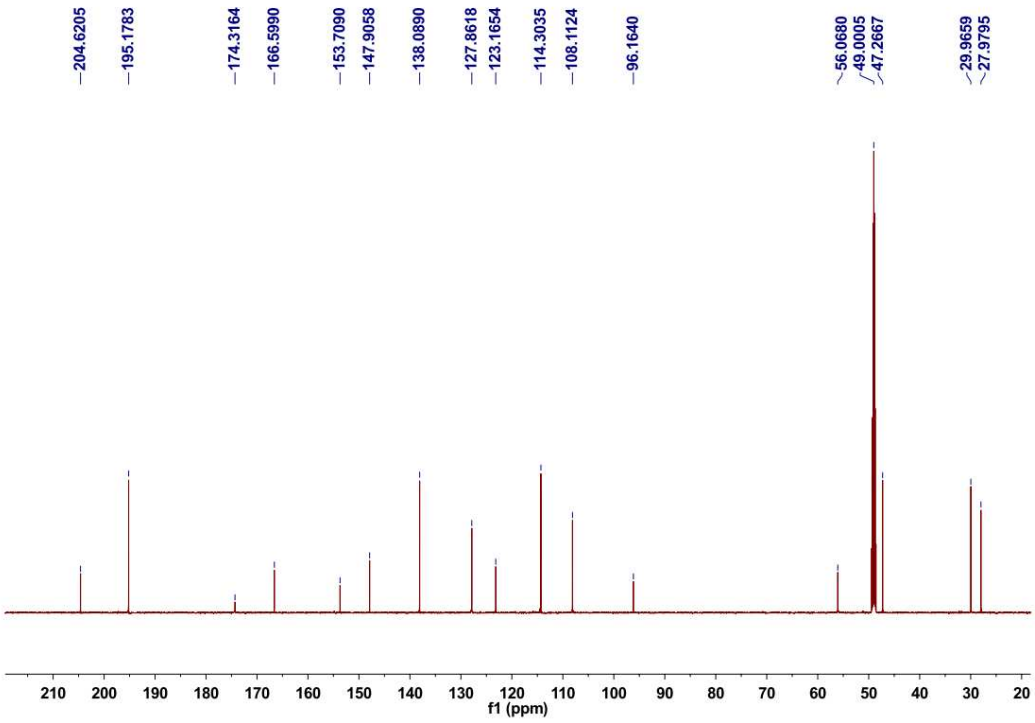


Figure S100. ^{13}C NMR spectrum of **15** in methanol-d_4

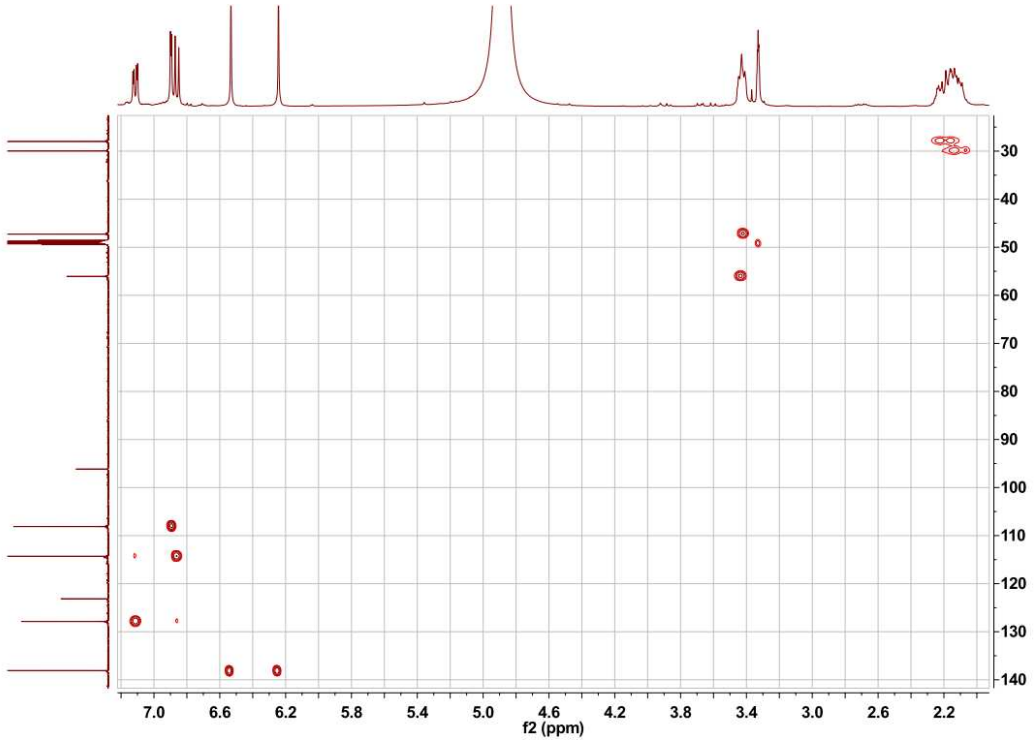


Figure S101. HSQC spectrum of **15** in methanol-d_4

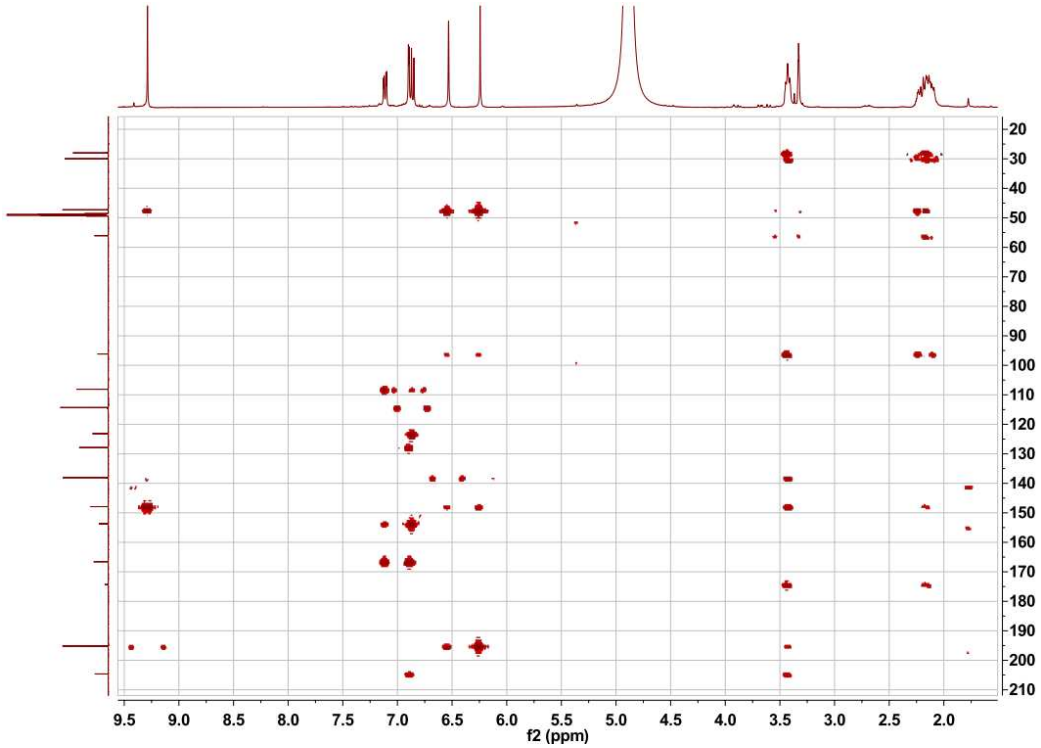


Figure S102. HMBC spectrum of **15** in methanol-d_4

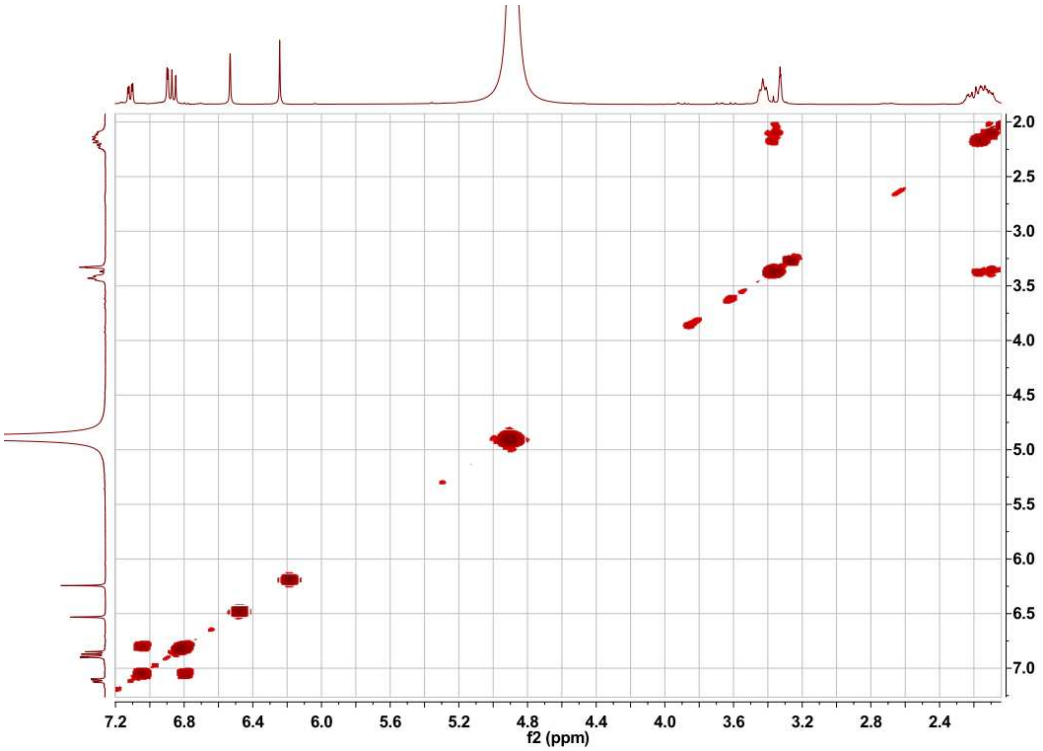


Figure S103. ^{1}H-^{1}H COSY spectrum of **15** in methanol-d_4

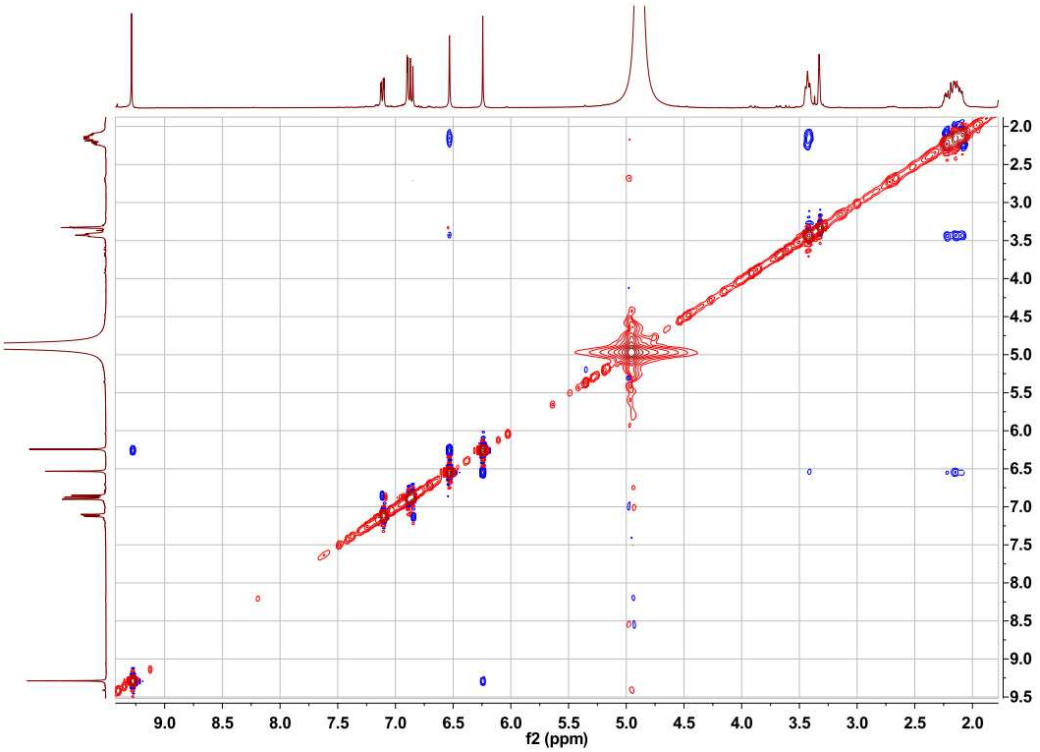
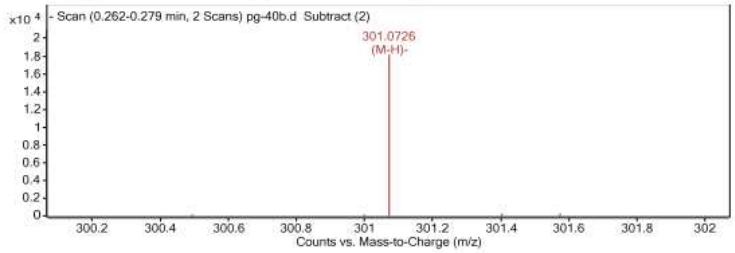


Figure S104. ROESY spectrum of **15** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
213.0926	1	4453.49		
257.0823	2	23796.84		
258.086	2	3628.75		
301.0726	1	18106.98	C16 H14 O6	(M-H)-
365.1249	1	3437.55		
369.0606	1	5771.54		
603.1533	1	12400.1		
604.1571	1	4434.56		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30
N	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C16 H14 O6	302.0790	301.0718	301.0726	-0.9	-2.9	10.0000

Figure S105. HRESIMS spectrum of **15**

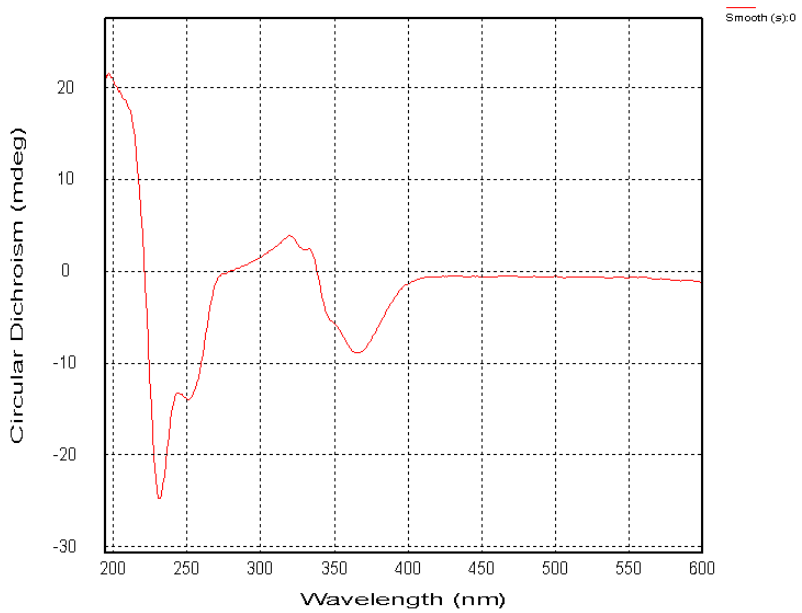


Figure S106. CD spectrum of **15a** in methanol

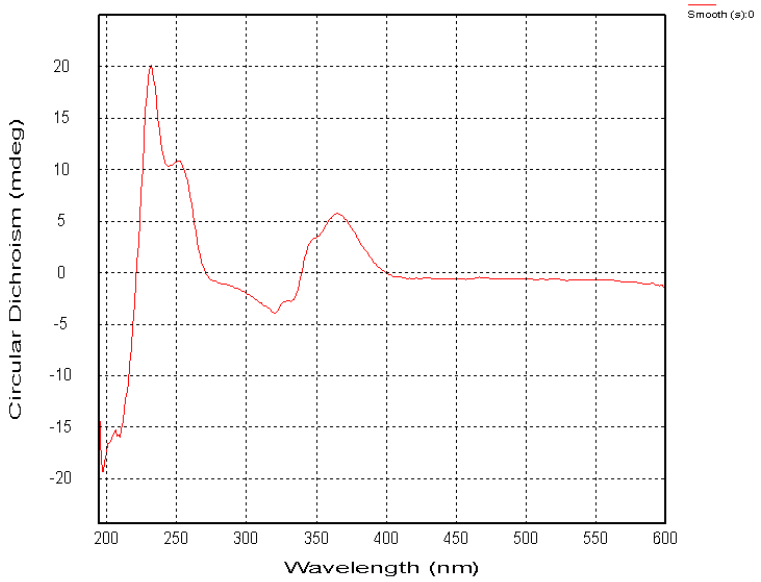


Figure S107. CD spectrum of **15b** in methanol

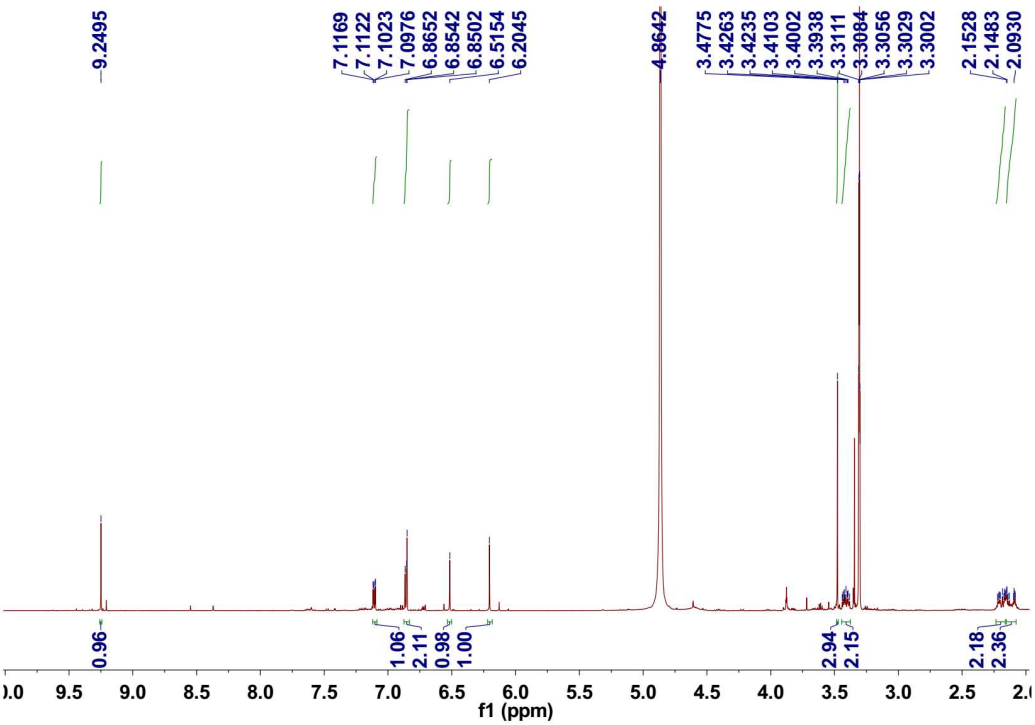


Figure S108. ^{1}H NMR spectrum of **16** in methanol-d_4

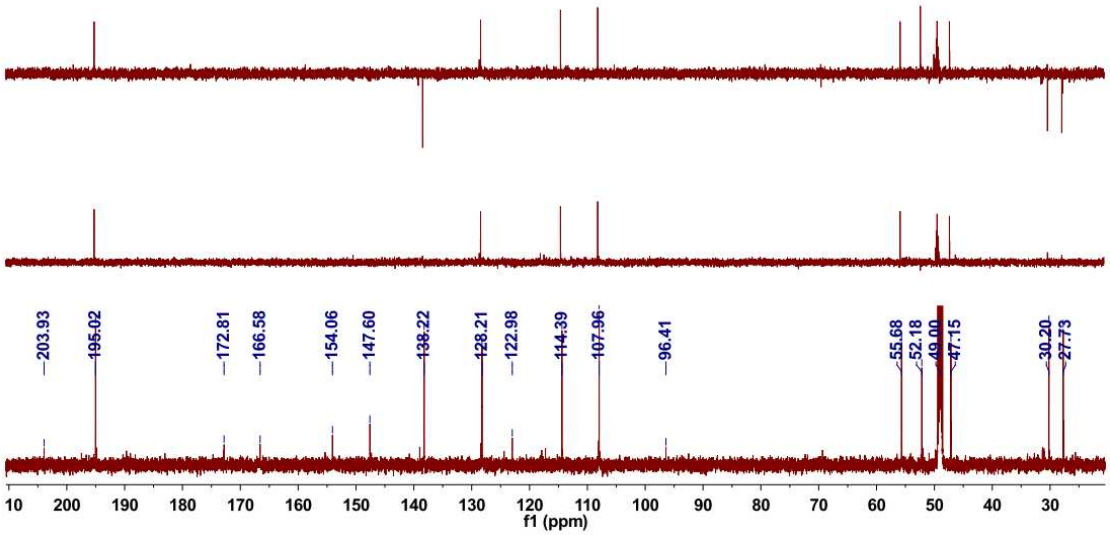


Figure S109. ^{13}C NMR and EDPT spectra of **16** in methanol-d_4

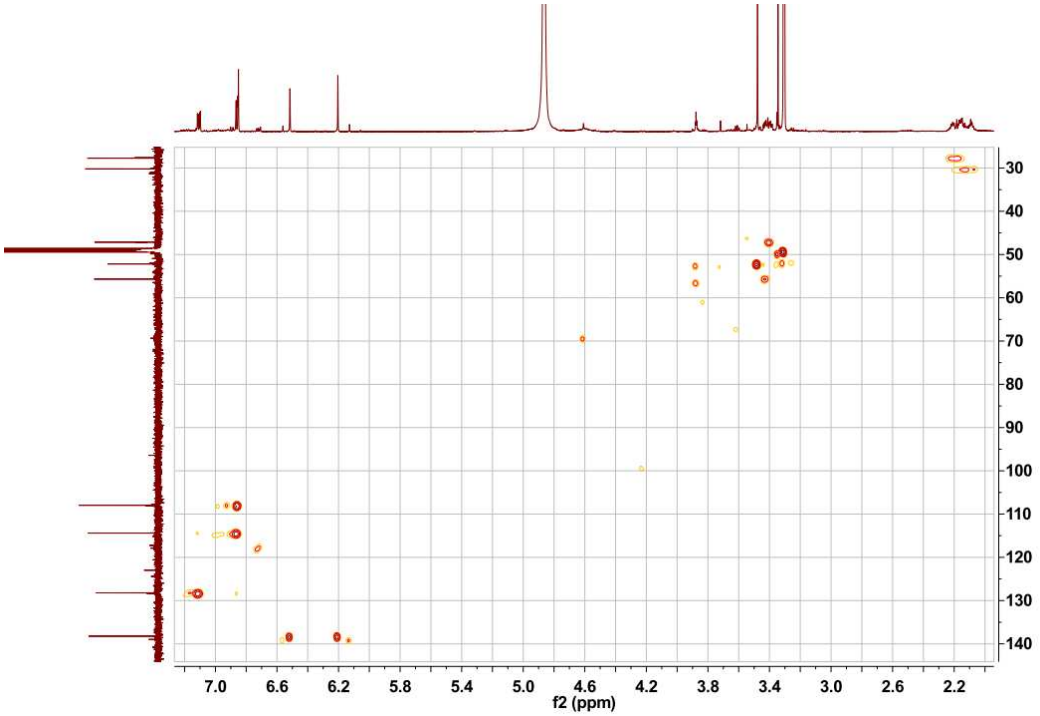


Figure S110. HSQC spectrum of **16** in methanol-d_4

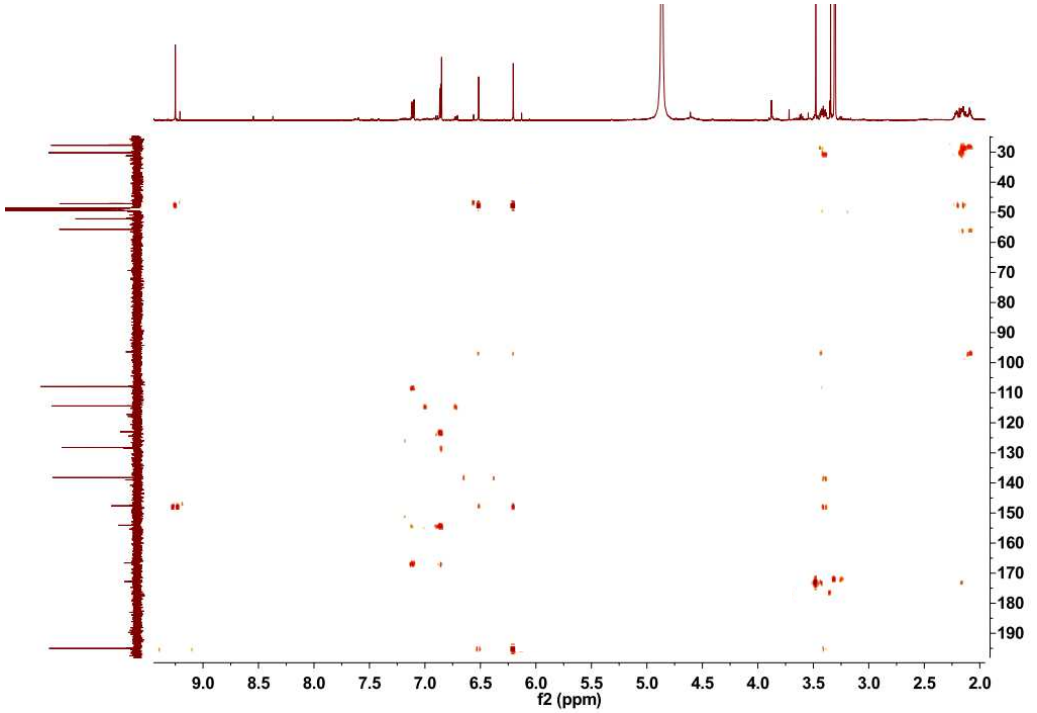


Figure S111. HMBC spectrum of **16** in methanol-d_4

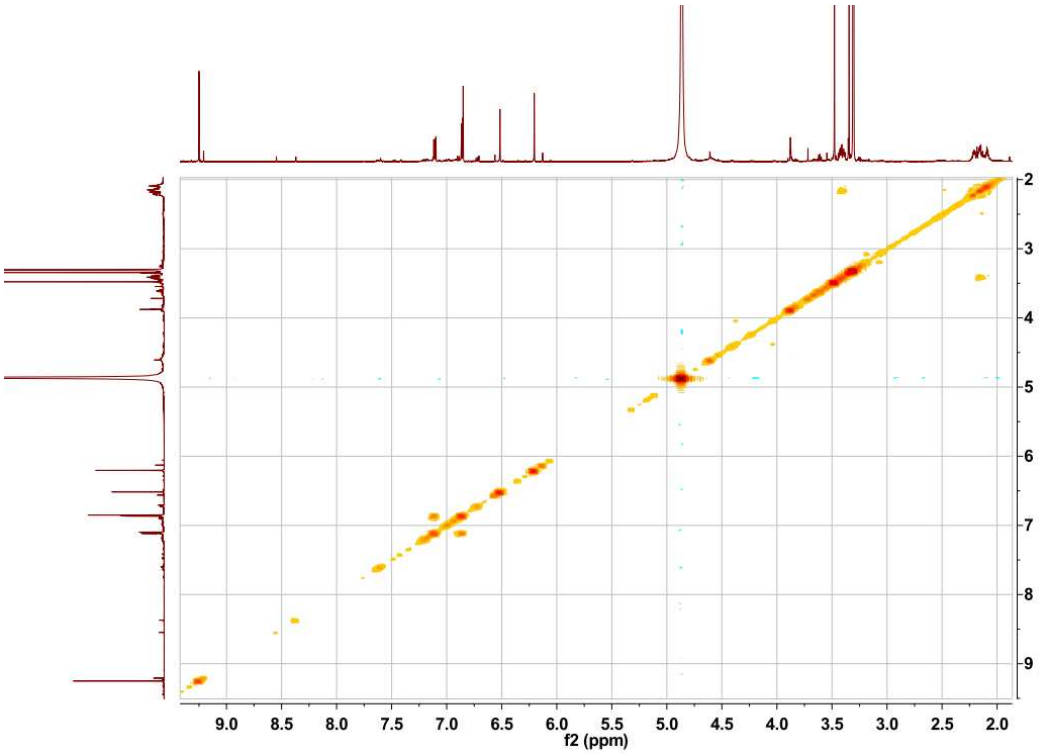
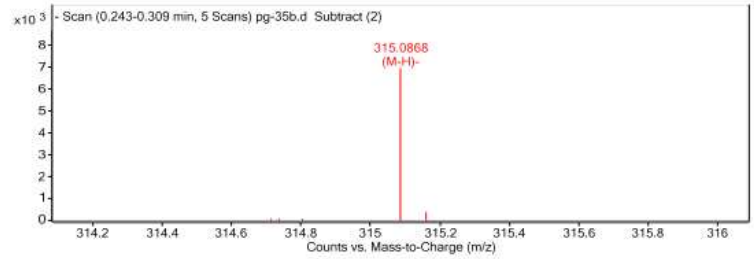


Figure S112. ^{1}H-^{1}H COSY spectrum of **16** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
89.0247		4671.55		
259.0615	1	1336.83		
315.0868		6922.04	C17 H16 O6	(M-H)-
316.0931	1	7511.63		
317.0953	1	1495.17		
325.1837		947.66		
439.2365		1041.89		
632.1869	1	920.27		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C17 H16 O6	316.0947	315.0874	315.0868	0.7	2.1	10.0000

Figure S113. HRESIMS spectrum of **16**

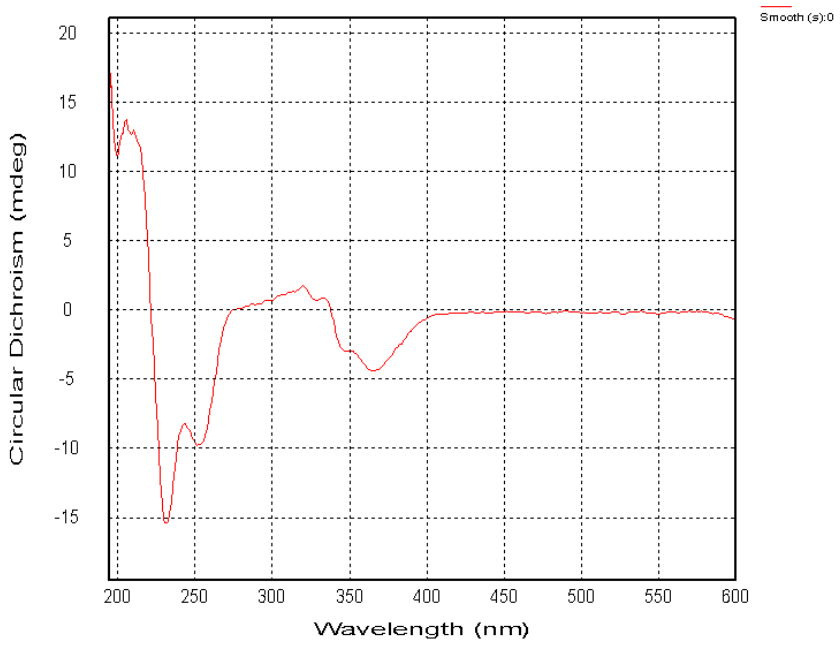


Figure S114. CD spectrum of **16** in methanol

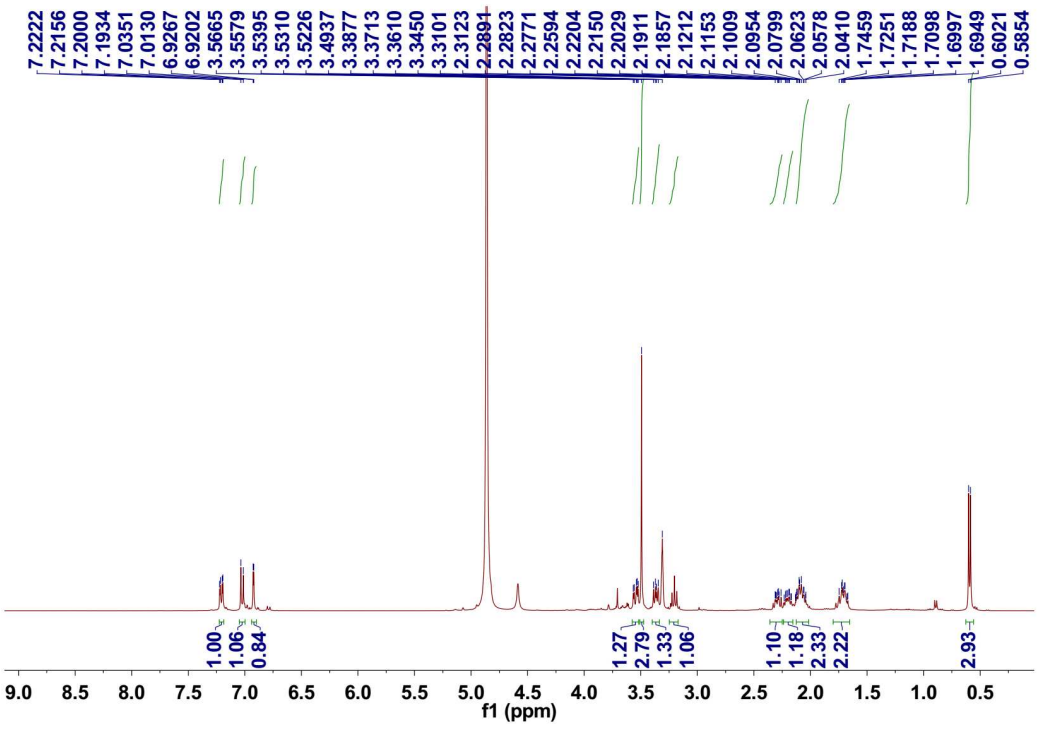


Figure S115. ^{1}H NMR spectrum of **18** in methanol-d_4

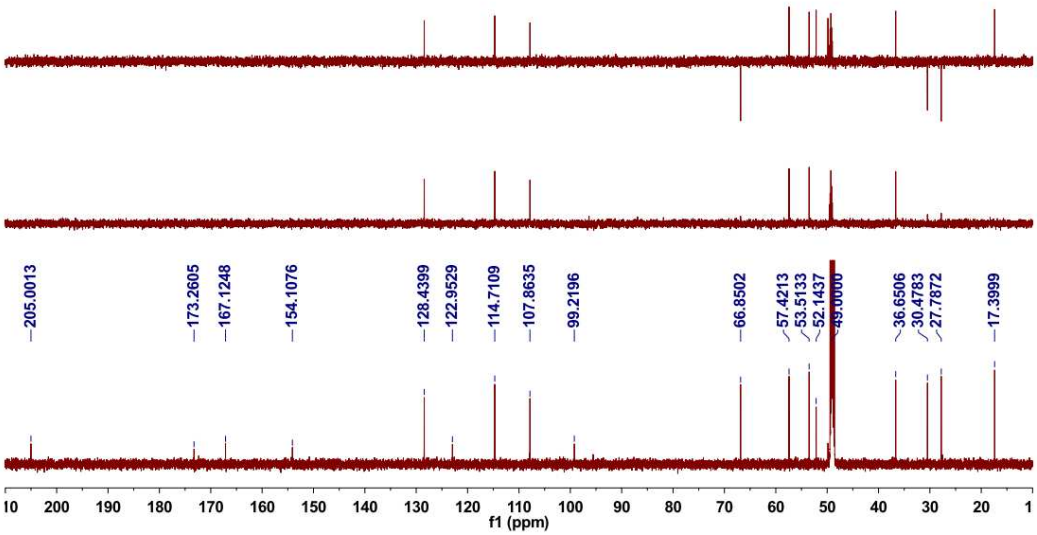


Figure S116. ^{13}C NMR and DEPT spectra of **18** in methanol-d_4

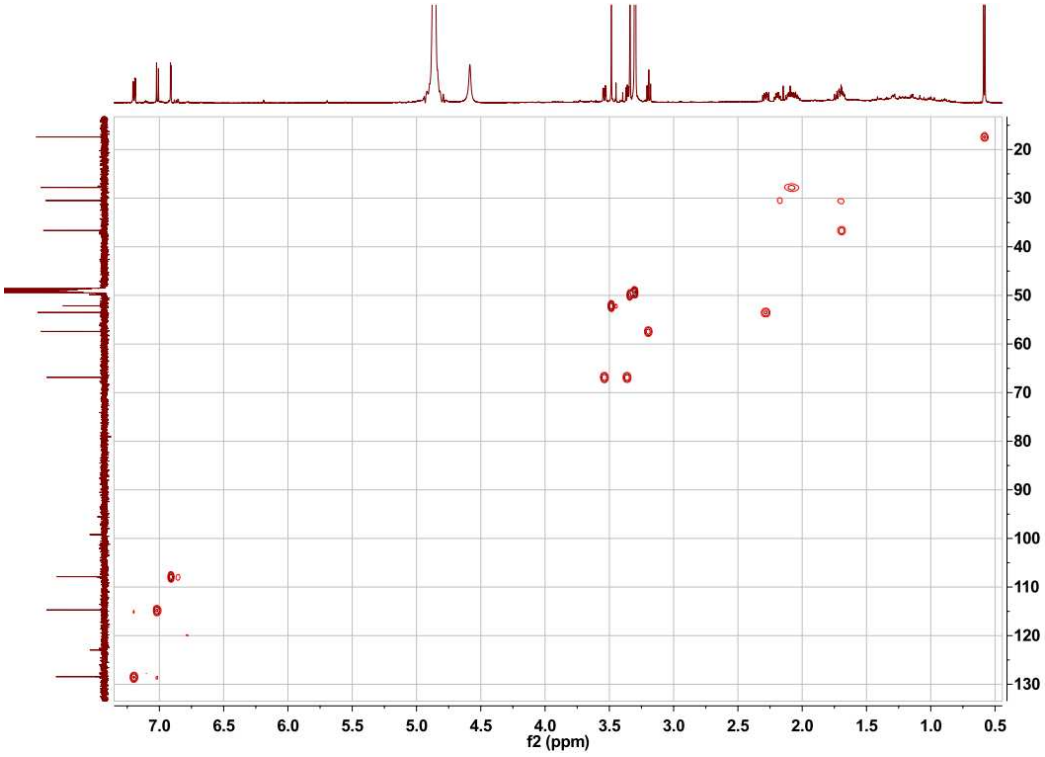


Figure S117. HSQC spectrum of **18** in methanol-d_4

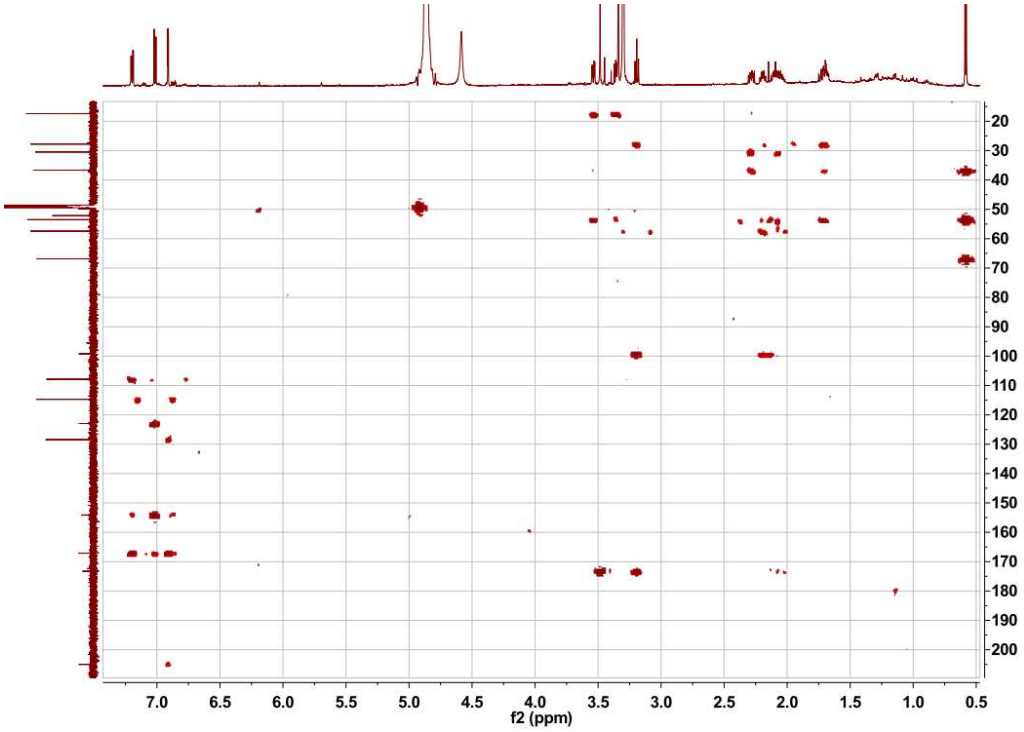


Figure S118. HMBC spectrum of **18** in methanol-d_4

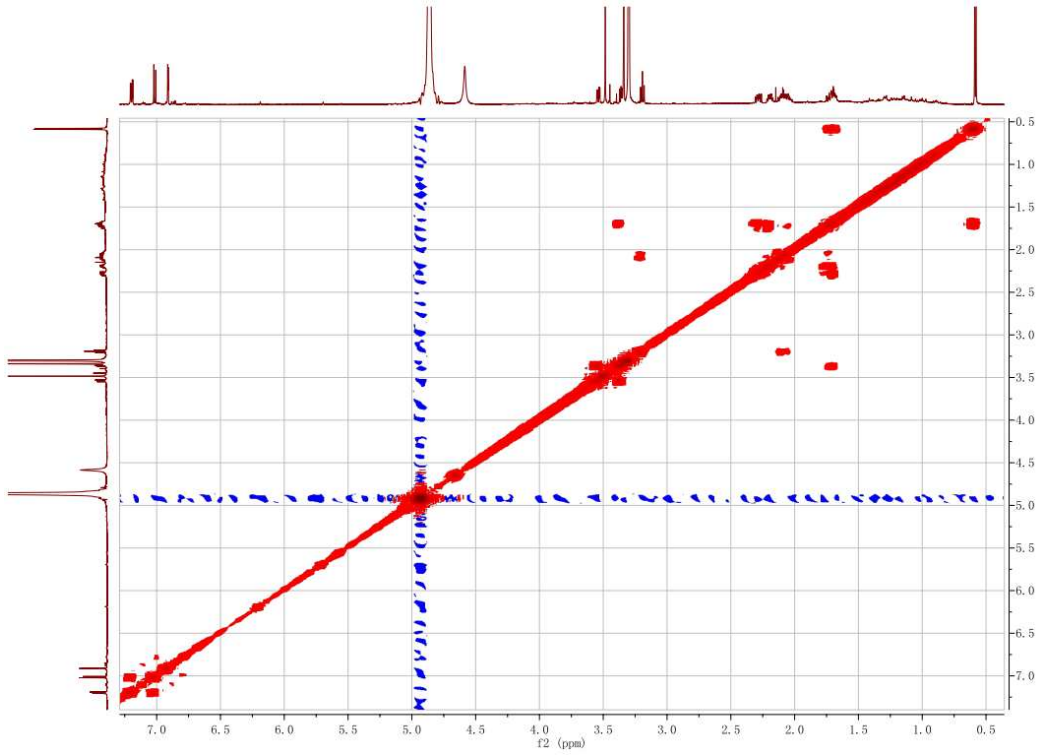


Figure S119. ^{1}H-^{1}H COSY spectrum of **18** in methanol-d_4

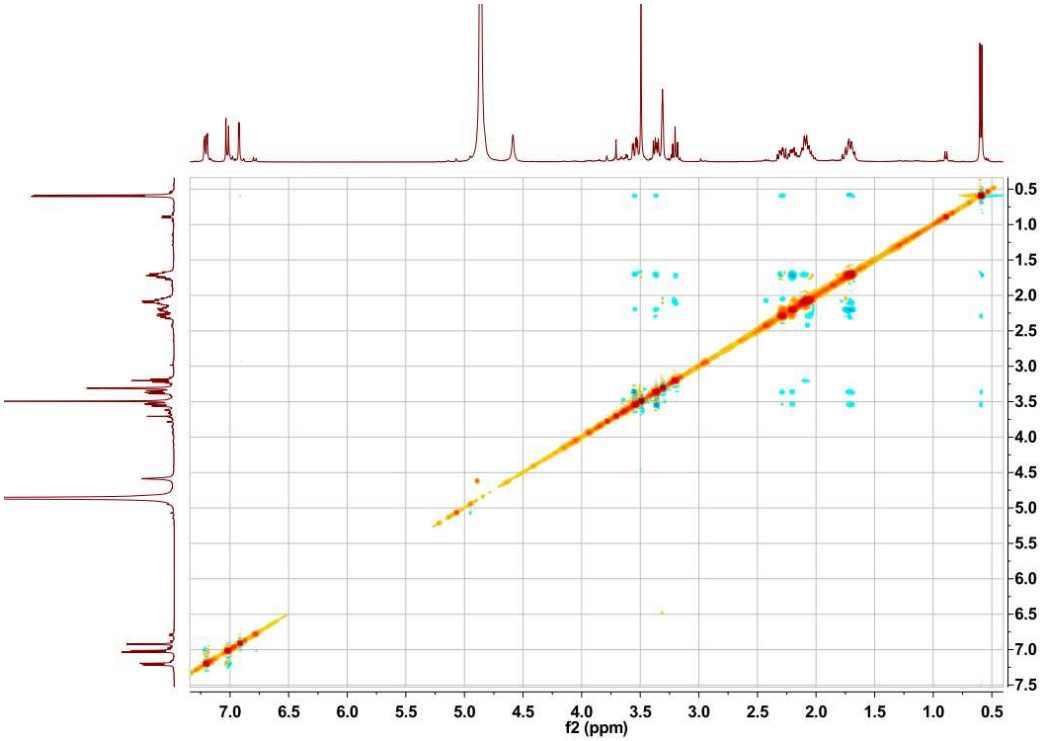
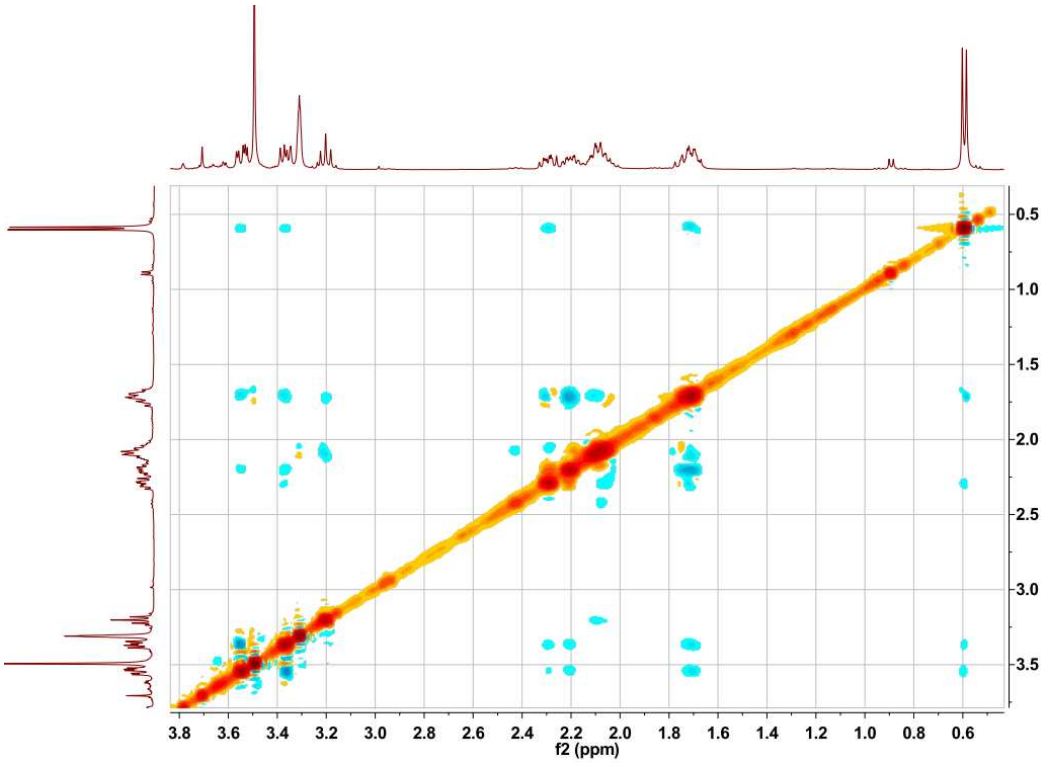


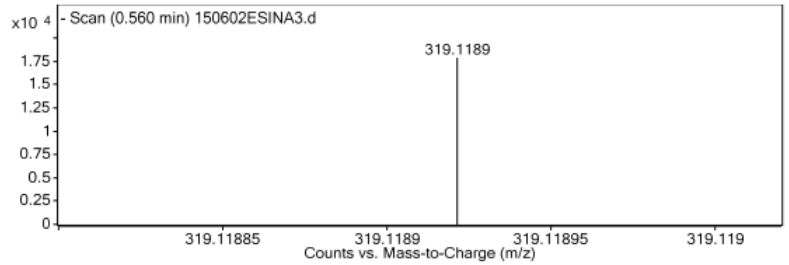
Figure S120. ROESY spectrum of **18** in methanol-d_4



Enlarged ROESY spectrum of **18** (up-field region) in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
112.9856		15347.11		
255.233	1	21388.95		
268.954	1	2129.99		
281.2487	1	2029.56		
283.2641	1	9797.1		
319.1189	1	17735.6	C17 H19 O6	M-
325.1835	1	3309.07		
339.1996	1	2120.37		
1033.9881	1	24998.41		
1034.9881	1	1760.23		

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	11

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C17 H19 O6	319.1182	319.1187	319.1189	-0.3	-0.9	8.5000

Figure S121. HRESIMS spectrum of **18**

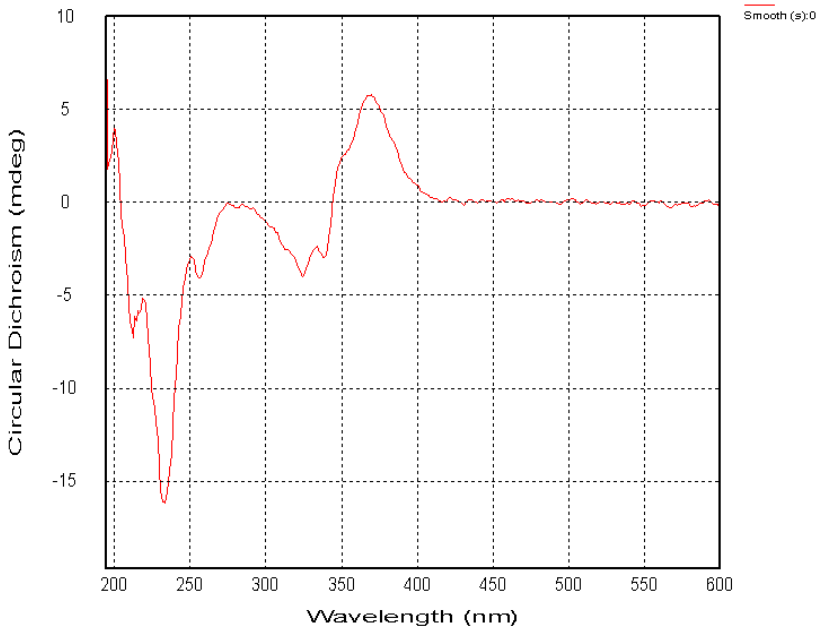


Figure S122. CD spectrum of **18** in methanol

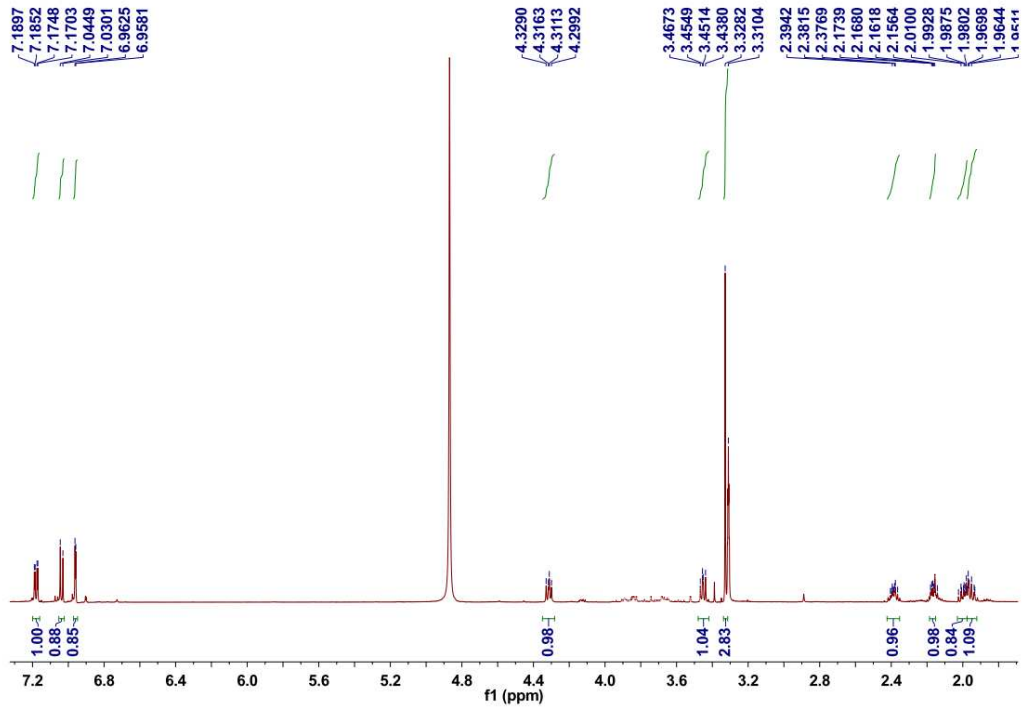


Figure S123. ^{1}H NMR spectrum of **20** in methanol-d_4

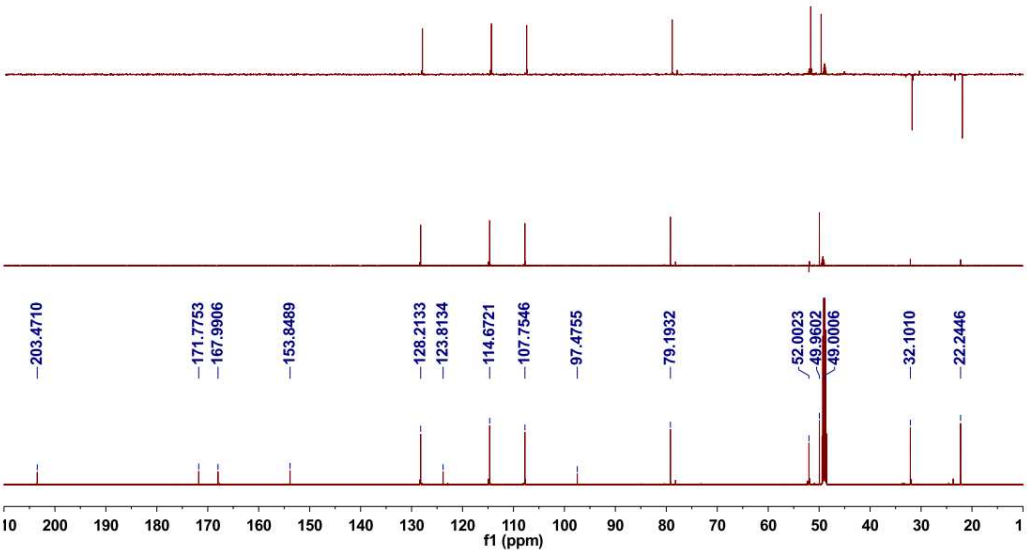


Figure S124. ^{13}C NMR and DEPT spectra of **20** in methanol-d_4

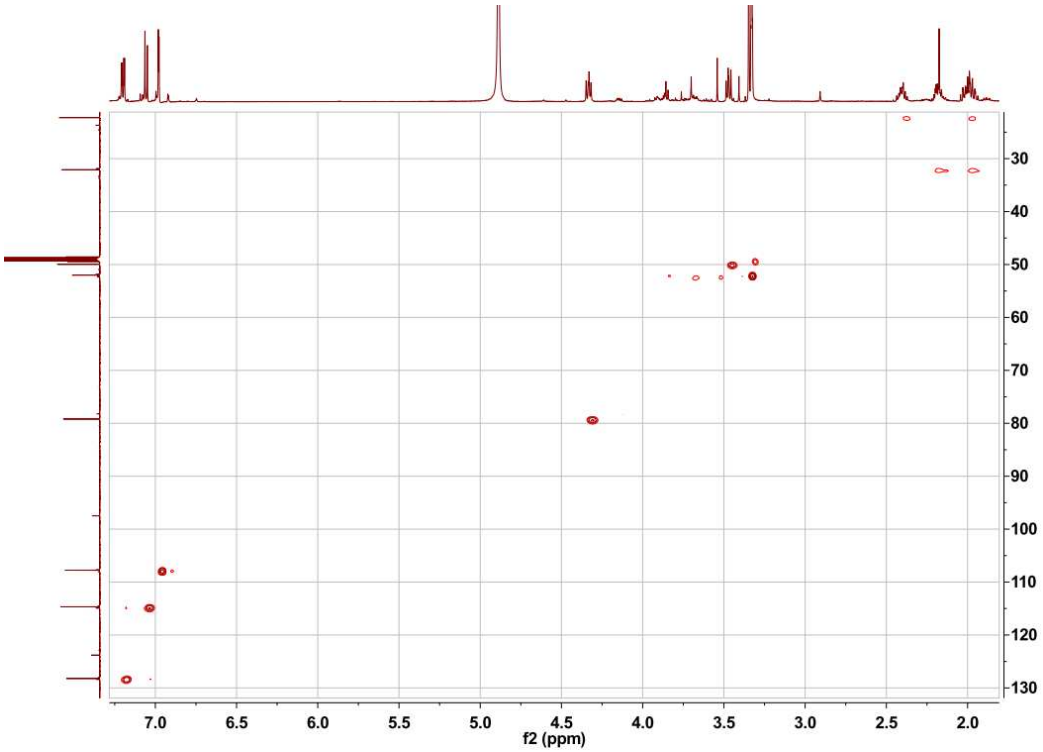


Figure S125. HSQC spectrum of **20** in methanol-d_4

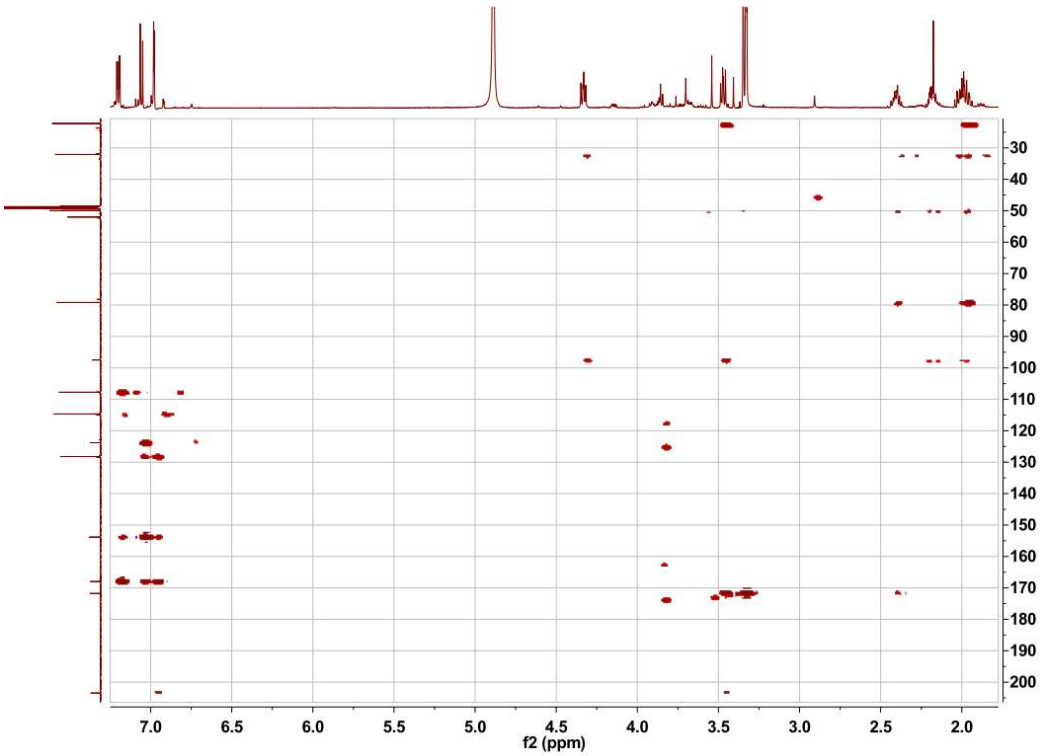


Figure S126. HMBC spectrum of **20** in methanol-d_4

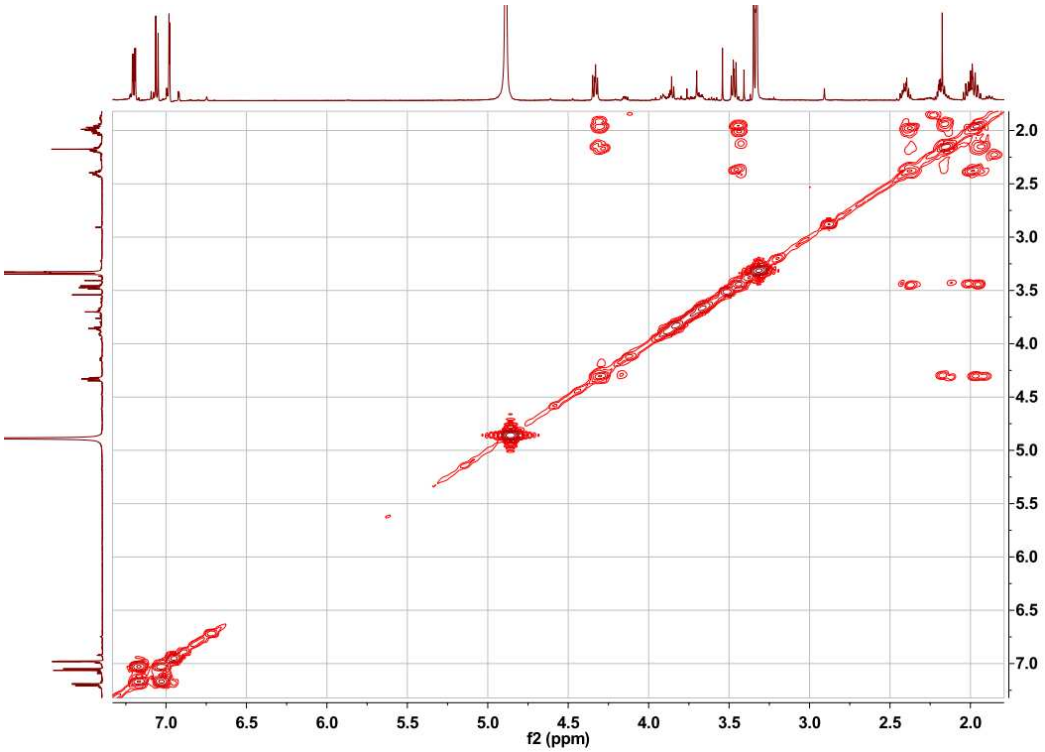


Figure S127. ^{1}H-^{1}H COSY spectrum of **20** in methanol-d_4

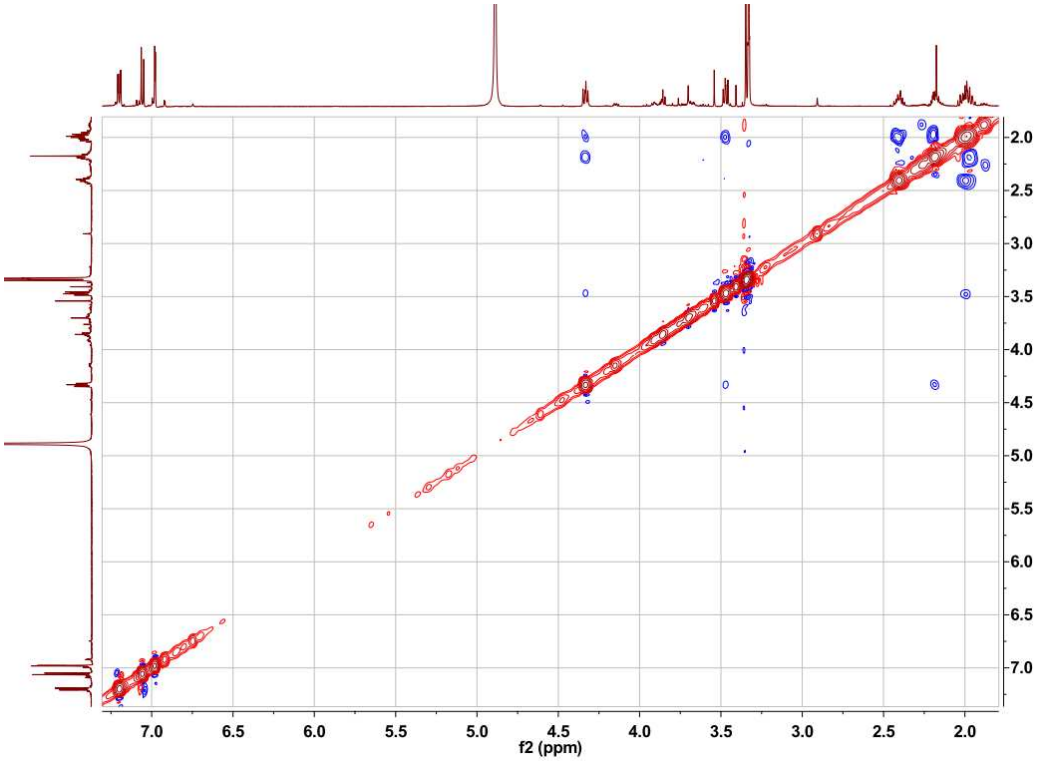
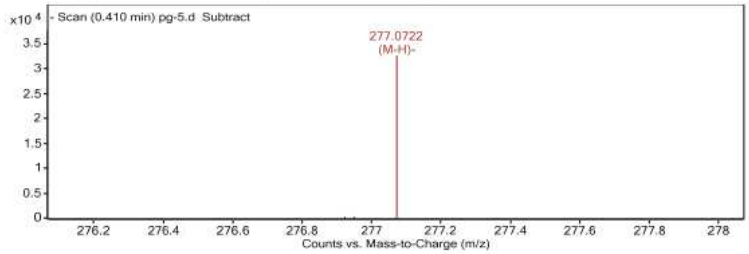


Figure S128. ROESY spectrum of **20** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
112.9855		8925.3		
277.0722	1	32555.65	C14 H14 O6	(M-H)-
278.0749	1	5100.3	C14 H14 O6	(M-H)-
325.185	1	1734.88		
955.9747		1788.94		
982.9933	1	4184.04		
1033.9907	1	7148.6		
1034.9932	1	1840.23		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C14 H14 O6	278.0790	277.0718	277.0722	-0.4	-1.3	8.0000

Figure S129. HRESIMS spectrum of **20**

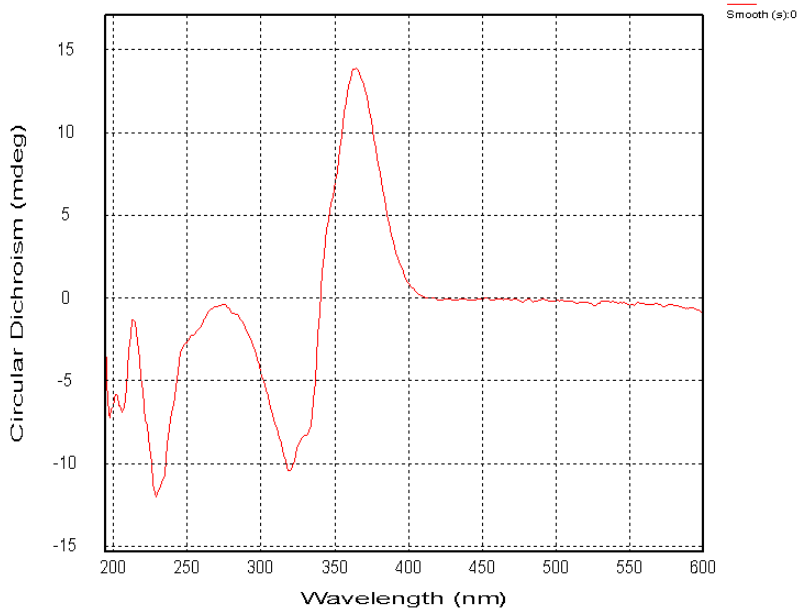


Figure S130. CD spectrum of **20** in methanol