Supplementary Information

Bioactive Ascochlorin Analogues from the Marine-Derived Fungus *Stilbella fimetaria*

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Table S1. ^{1}H and ^{13}C NMR data for known ascochlorin analogues (**1**, **3**, **5**, **8**-**9**).

	Ascochlorin **(1)**		Ilicicolin F **(3)**		Ilicicolin C **(5)**		LL-Z1272ε **(8)**		Ilicicolin E **(9)**	
Pos.	δC	δH, mult. (J in Hz)	δC	δH, mult. (J in Hz)	δC	δH, mult. (J in Hz)	δC	δH, mult. (J in Hz)	δC	δH, mult. (J in Hz)
1CHO		10.14, s		10.15, s		10.14, s		10.08, s		10.14, s
2OH		12.70, s		12.71, s		12.69, s		12.74, s		12.70, s
4OH		6.42, s		6.38, s		6.43, s		6.15, br s		6.40, s
5							110.6	6.21, s		
6CH₃	14.4	2.60, s	14.4	2.61, s	14.4	2.60, s	18.0	2.50, s	14.4	2.60,s
1'	22.1	3.53, d (7.4)	22.2	3.54, d (7.5)	22.0	3.39, d (7.2)	21.2	3.39, d (7.2)	22.1	3.54, d (7.5)
2'	127.4	5.52, t (7.5)	128.2	5.55, t (7.4)	120.8	5.24, t (5.2)	121.1	5.28, t (7.2)	128.0	5.54, t (7.4)
3'CH₃	12.5	1.92, s	12.6	1.92, s	16.3	1.80, s	16.5	1.84, s	12.5	1.93, s
4'a	133.1	5.89, d (16.0)	134.1	5.92, d (16.0)	32.5	1.98, m	32.6	2.05, td(13.2, 4.8)	128.1	5.98,dd(10.1, 3.2)
4'b					32.5	1.84, m	32.6	1.90, td(13.1, 4.6)		
5'a	135.6	5.37, d (16.0)	134.1	5.32, d (16.0)	35.5	1.42, qd(14.6, 4.6)	35.6	1.44, dd(14.4, 4.5)	134.3	5.42, d(16.0)
5'b					35.5	1.35, qd(14.5, 4.4)	35.6	1.38, m		
6'CH₃	10.3	0.69, s	11.3	0.73, s	15.3	0.56, s	15.2	0.57, s	9.9	0.79, s
7'	40.7	1.93, m	45.3	1.99, m	36.0	1.97, m	36.1	1.98, m	41.9	2.63, m
7'CH₃	16.2	0.80, d (6.6)	12.4	0.86, d (6.8)	15.0	0.87, d (6.8)	15.1	0.88, d (6.7)	15.1	0.98, d (7.5)
8'a	31.0	1.92, m	73.6	4.89, td (11.1,5.6)	30.9	1.83, m	30.8	1.85, m	152.1	6.55, dd(10.1,2.0)
8'b	31.0	1.61, qd (13.8, 4.9)			30.9	1.60, m	30.8	1.62, m		
8'OCH₃			21	2.06, s						
9'a	41.5	2.43, ddd(13.7,6.9,1.0)	47.1	2.87, dd(13.3,5.7)	41.5	2.31, m	41.5	2.33, m	134.1	5.98, d (15.8)
9'b	41.5	2.36, ddd(13.6,5.1,1.8)	47.1	2.42, m						
11'	53.5	2.40, m	53.8	2.41, m	50.4	2.45, q (6.7)	50.4	2.46, q (6.7)	51.8	2.45, q (6.7)
11'CH₃	8.8	0.83, d (6.7)	8.8	0.86, d (6.8)	7.5	0.90, d (6.7)	7.5	0.91, d (6.8)	50.4	2.46, q (6.7)

Table S2. ^{1}H and ^{13}C NMR data for ascofuranol (**10**) and ascofuranone (**11**).

	Ascofuranol (**10**)		Ascofuranone (**11**).	
Pos.	δC	δH, mult. (J in Hz)	δC	δH, mult. (J in Hz)
1CHO	10.13, s			10.11, s
2OH	12.69, s			12.66, s
4OH	7.01, brs			6.56, brs
6CH_3	14.3	2.59, s	14.3	2.58, s
1'			21.9	3.37, d (7.1)
2'	121.5	5.15, t (6.9)	121.2	5.19, td (7.2, 1.2)
3'CH_3	15.9	1.76, s	16.0	1.77, s
4'a	39.1	2.05, t (7.4)	38.8	2.02, m
5'a	25.5	2.17, m	25.8	2.14, m
5'b	25.5	2.10, m		
6'	124.5	5.49, t (7.2)	128.4	5.49, t (7.1)
7'CH_3	12.3	1.59, s	11.1	1.61,s
8'a	79.7	4.30, t (7.2)	77.7	4.50, dd (10.3, 6.1)
9'a	39.0	2.39, m	39.8	2.40, dd (18.2, 16.2)
9'b	39.0	1.78, m	39.8	2.34, dd (18.2, 10.3)
10'	78.4	3.94, dd (6.1, 3.9)		
11'	21.8	3.37, qd (15.0, 7.2)		
11'CH_3a	22.3	1.28, s	21.8	1.20, s
11'CH_3b	25.9	1.20, s	24.1	1.26, s

Table S3. ^{1}H and ^{13}C NMR data for 4'5'-dihydro-4'-hydroxyascochlorin (**6**) in CD_3OD and $CDCl_3$.

	6 in CD_3OD		**6** in $CDCl_3$	
Pos.	δC	δH, mult. (J in Hz)	δC	δH, mult. (J in Hz)
1	114.6	-	113.5	
1CHO	195.6	10.12 s		10.11, s
2	162.8	-	162.0	
2OH				12.67, s
3	115.1	-	113.5	
4	159.4	-	156.0	
4OH				6.50, brs
5	115	-	113.5	
6	140.1	-	137.8	
6CH_3	14.7	2.57 s	14.4	2.58, s
1'a	22.5	3.54 dd(13.8,8.9)	21.4	3.39, d (7.4)
1'b		3.29 m		
2'	125	5.60 t(7.3)	122.8	5.48, t (7.1)
3'	140.3	-	139.1	
3'CH_3	11.4	1.83 s	11.3	1.81, s
4'	75.4	4.23 dd(7.2,5.1)	74.6	4.21, dd (7.4, 4.2)
4'CHO				
5'a	42.1	1.59 dd(15.6,7.2)	41.2	1.66, dd (15.4, 7.3)
5'b		1.52 dd(15.6, 5.1)	41.2	1.46, dd (15.4, 4.2)
6'	45	-	44.1	
6'CH_3	16.4	0.49 s	15.5	0.54, s
7'	37.5	2.20 m	36.6	2.30, m
7'CH_3	16	0.96 d(6.6)	15.7	0.96, d (6.7)
8'a	32.2	1.48 dq(13.1,4.9)	31.1	1.80, m
8'b		1.75 m	31.1	1.54, qd (13.3, 5.1)
9'a	42.6	2.07 m	41.5	2.27, ddd (13.8, 5.0, 2.1)
9'b		1.99 m	41.5	2.21, td (13.6, 6.9)
10'	216.6	-	215.8	
11'	51.5	2.50 q(6.6)	50.3	2.56. q (6.7)
11'CH_3	8.8	0.68 d(6.6)	8.0	0.80, d (6.8)

Figure S1: MS/HRMS spectra (10, 20 and 40eV) for ascochlorin N-acetylglucosamine (**19**).

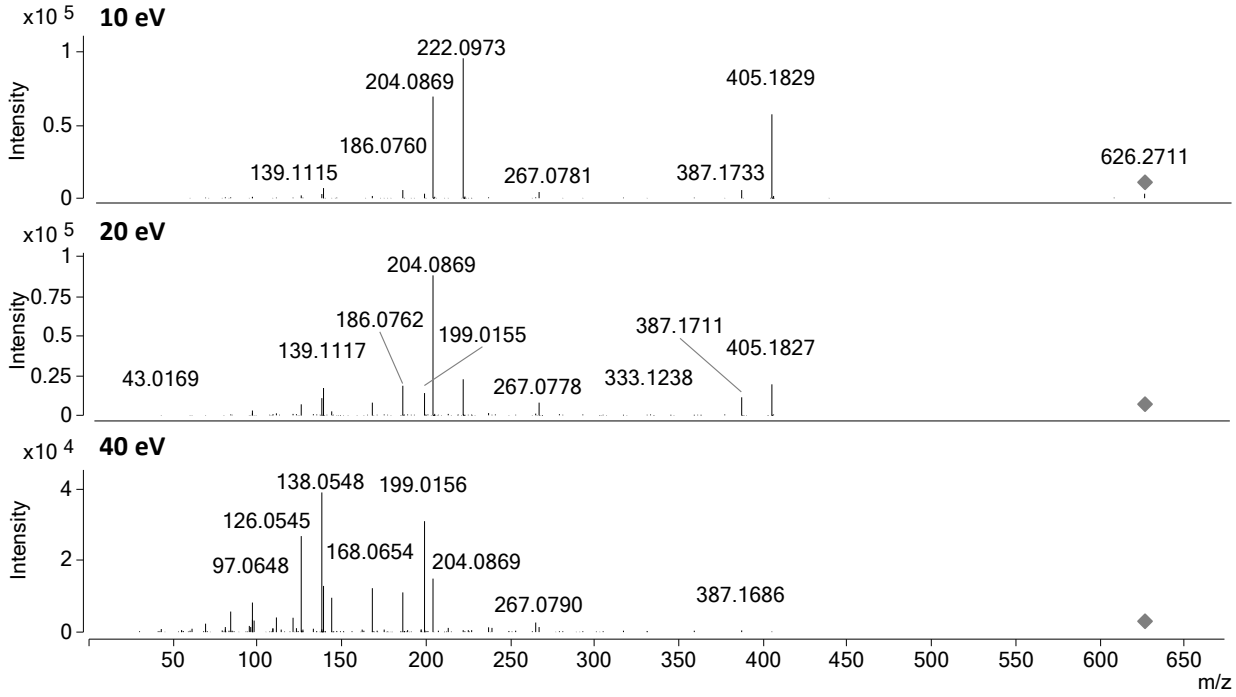


Figure S2: MS/HRMS spectra (10, 20 and 40eV) for 4'-ketoascochlorin (**20**).

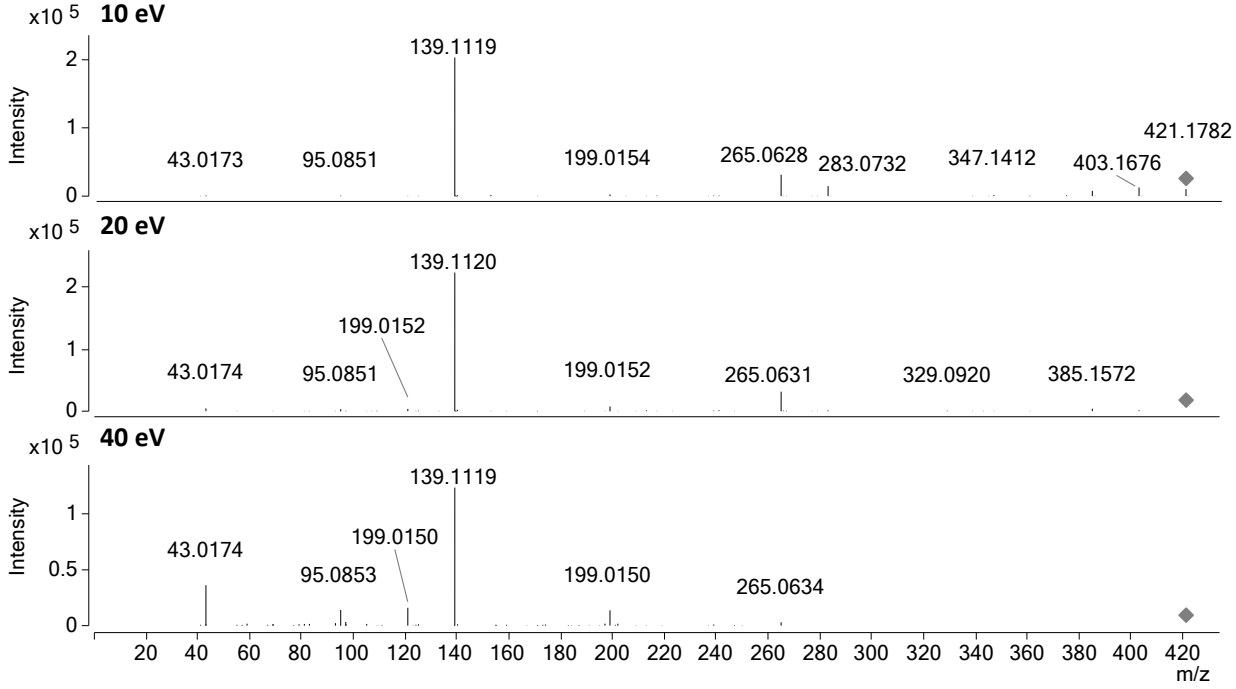


Figure S3: MS/HRMS spectra (10, 20 and 40eV) of $[M\text{-}CH_2O_2+H]^+$ for 4',5'- dihydro-4'-formylascochlorin (**21**). $[M+H]^+$ adduct was not observed.

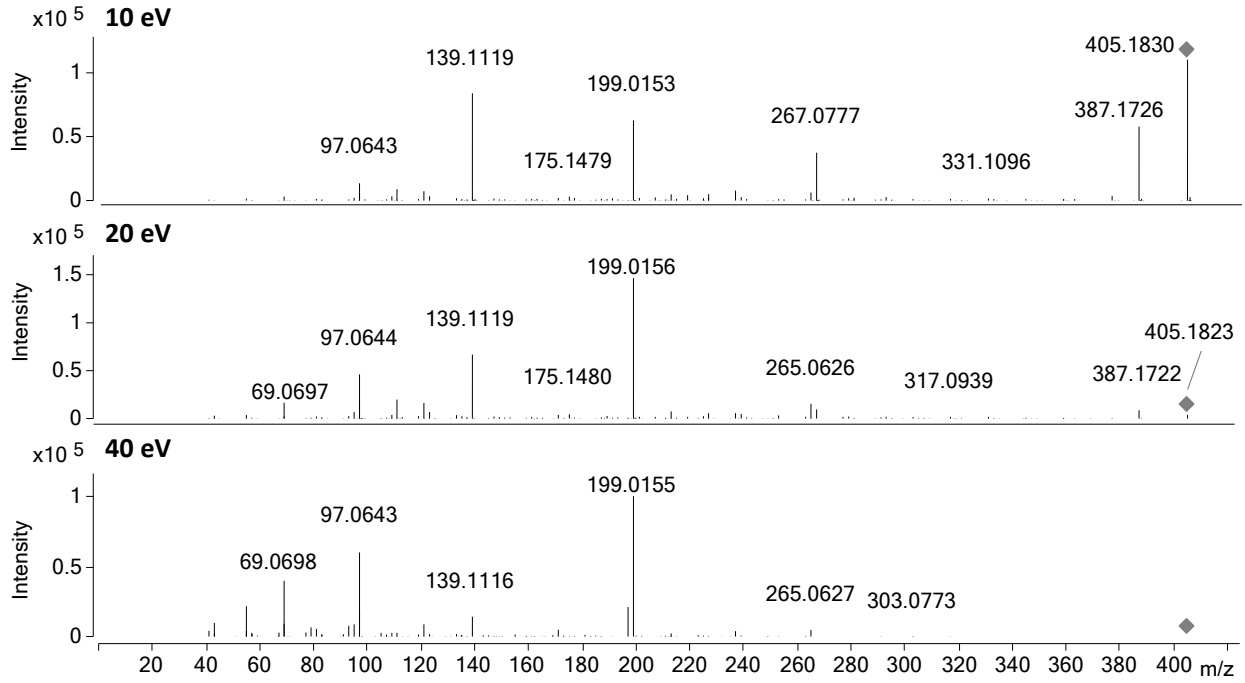


Figure S4: MS/HRMS spectra (10, 20 and 40eV) for fimetarin A (**22**).

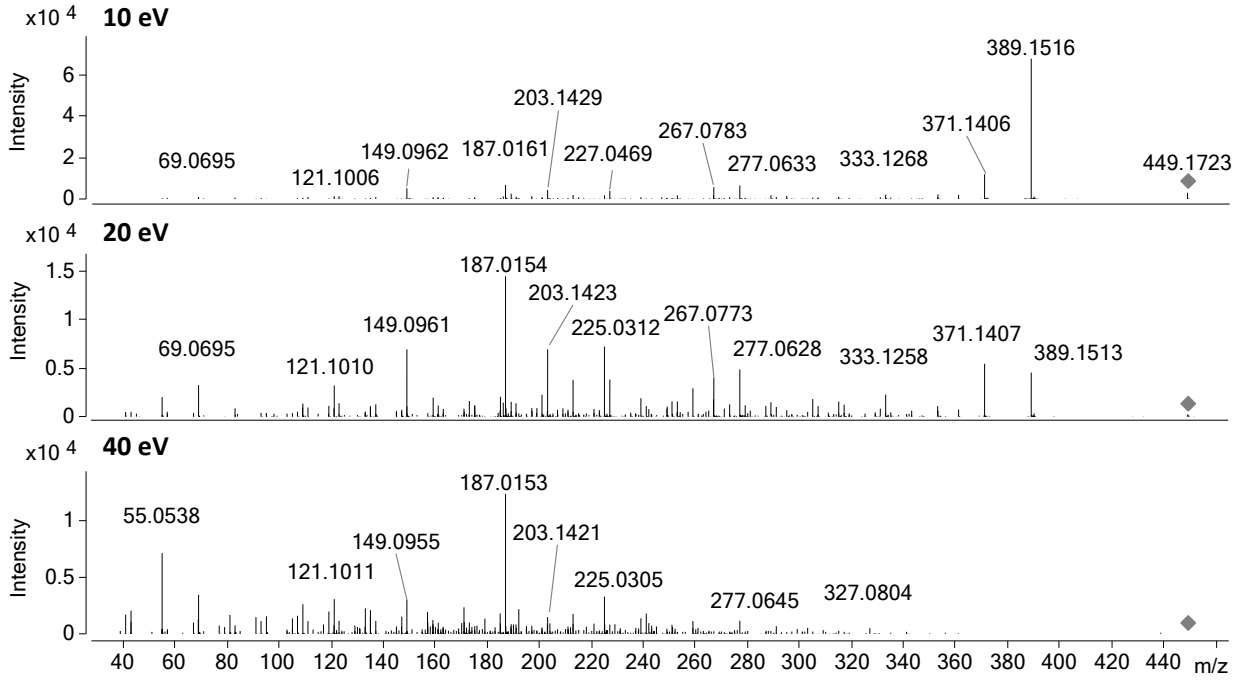


Figure S5: MS/HRMS spectra (10, 20 and 40eV) for fimetarin B (**23**).

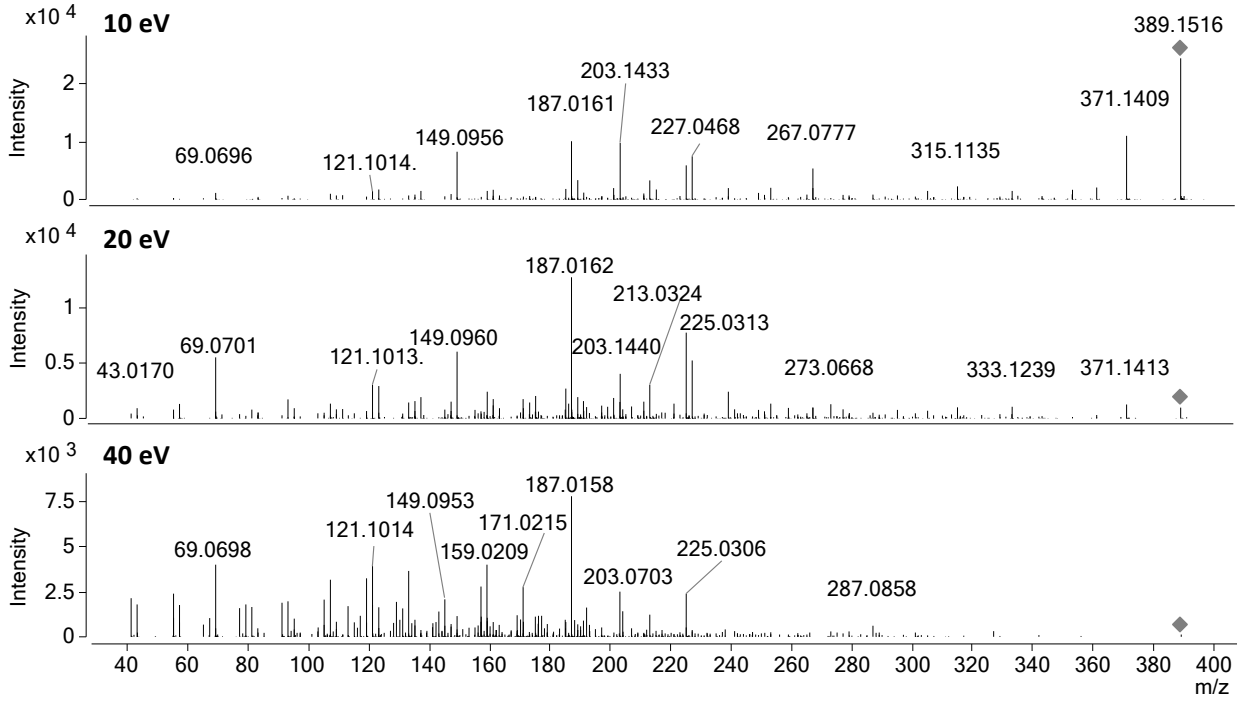


Figure S6: MS/HRMS spectra (10, 20 and 40eV) for fimetarin C (**24**).

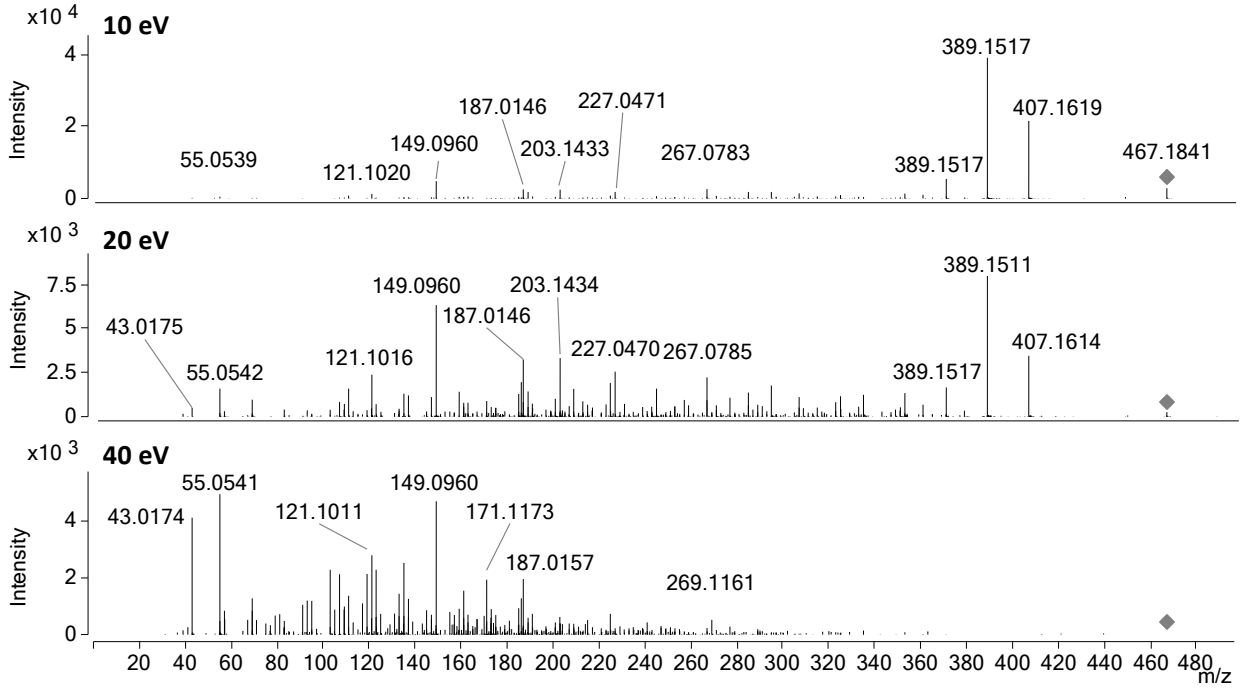


Figure S7: MS/HRMS spectra (10, 20 and 40eV) for fimetarin D (**25**).

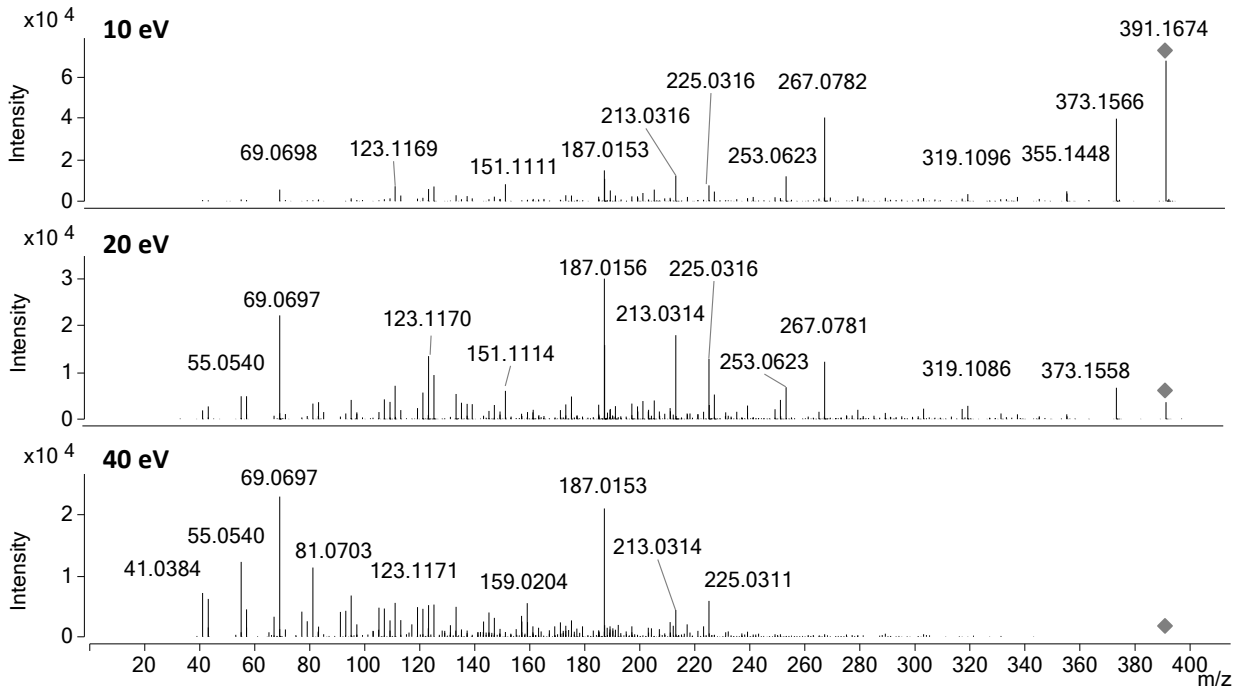


Figure S8. Proposed fragmentation patterns for fimetarins A-D (**22-25**) based on key fragments observed in 10 eV MS/HRMS spectra (Figures S4-S7). To the left, fragmentation patterns for fimetarins A-C (**22-24**), to the right – for fimetarin D (**25**). Fragments highlighted in green are observed in all four compounds, in blue – observed only in fimetarins A-C, in red – observed only in fimetarin D.

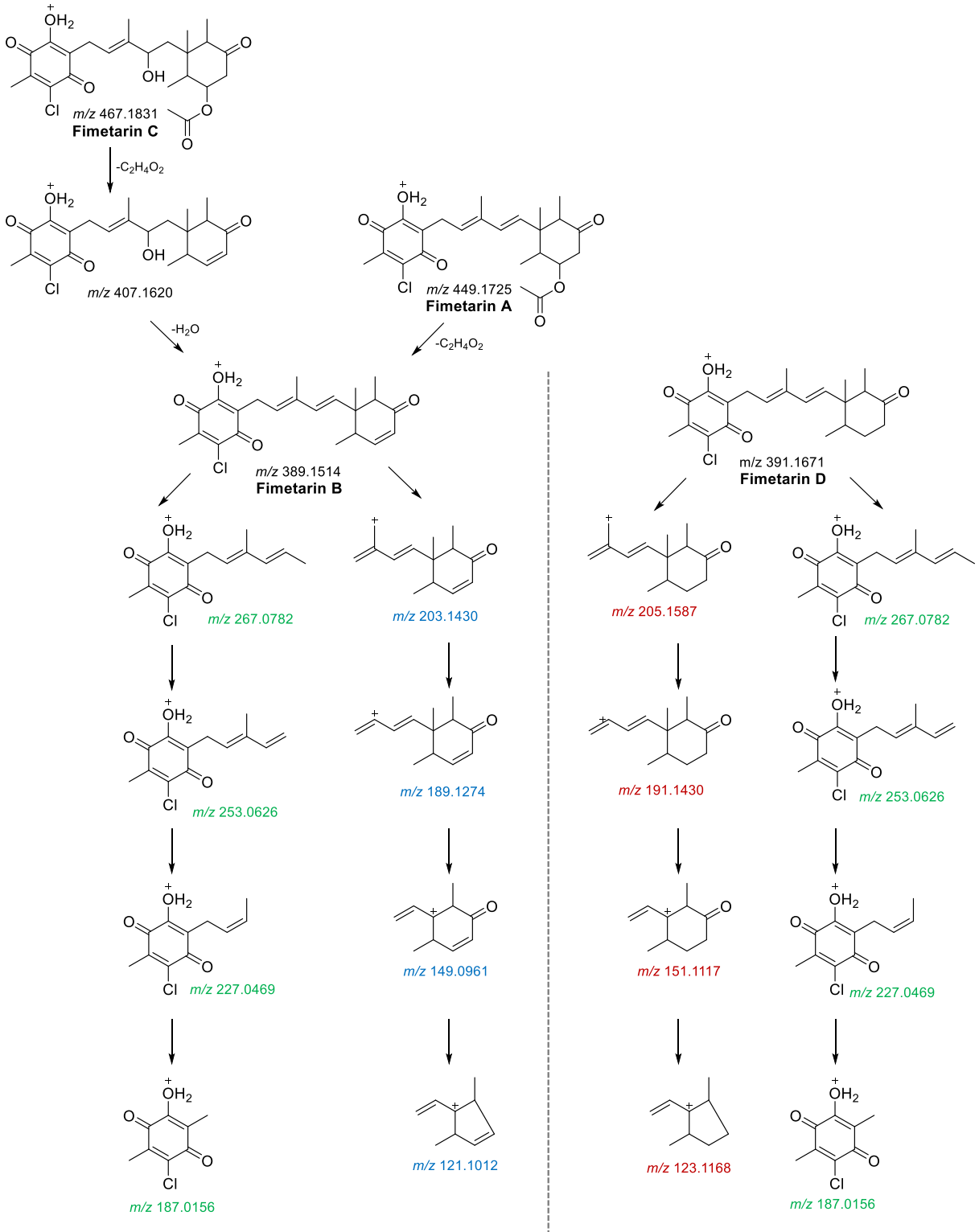
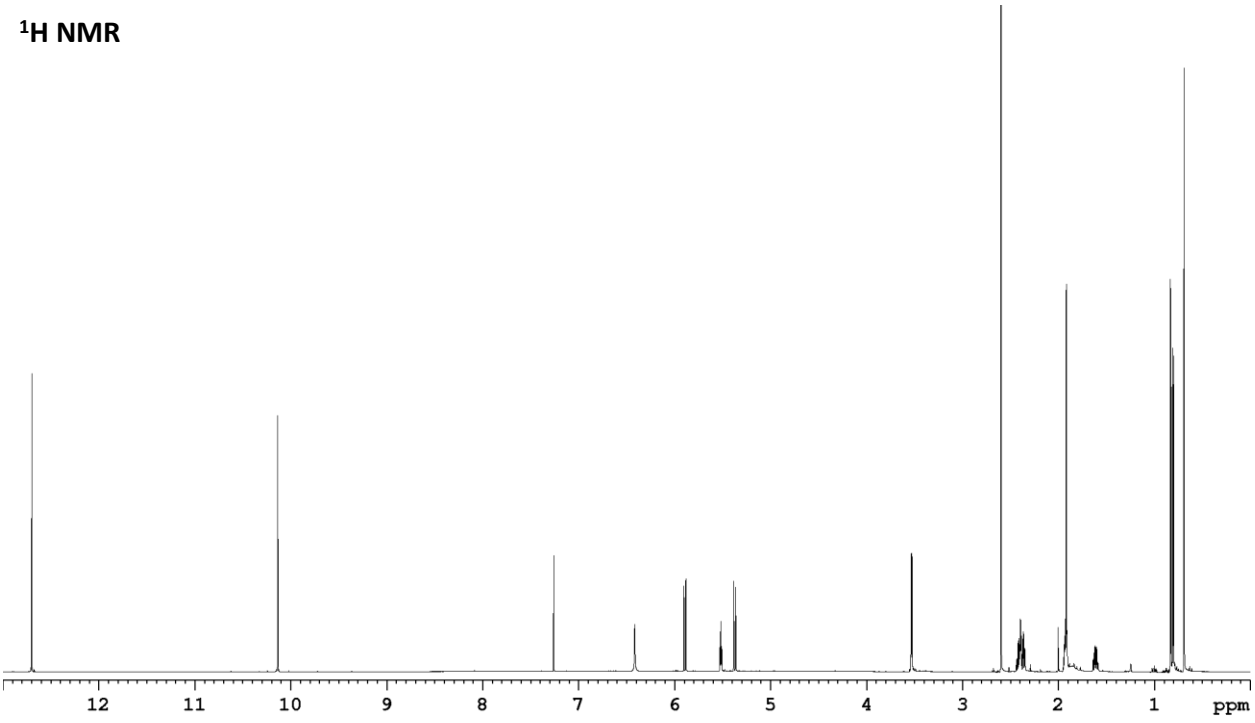


Figure S9. ^{1}H and HSQC spectra for ilicicolin D (**1**) in $CDCl_3$.



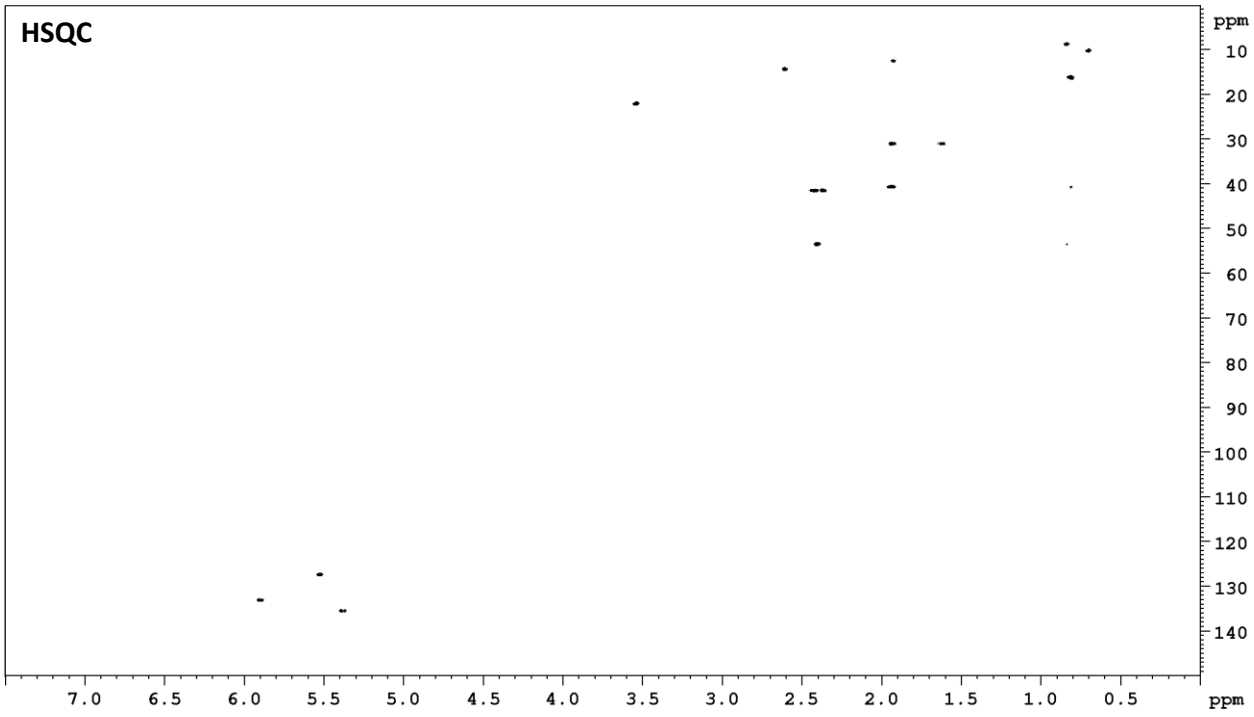
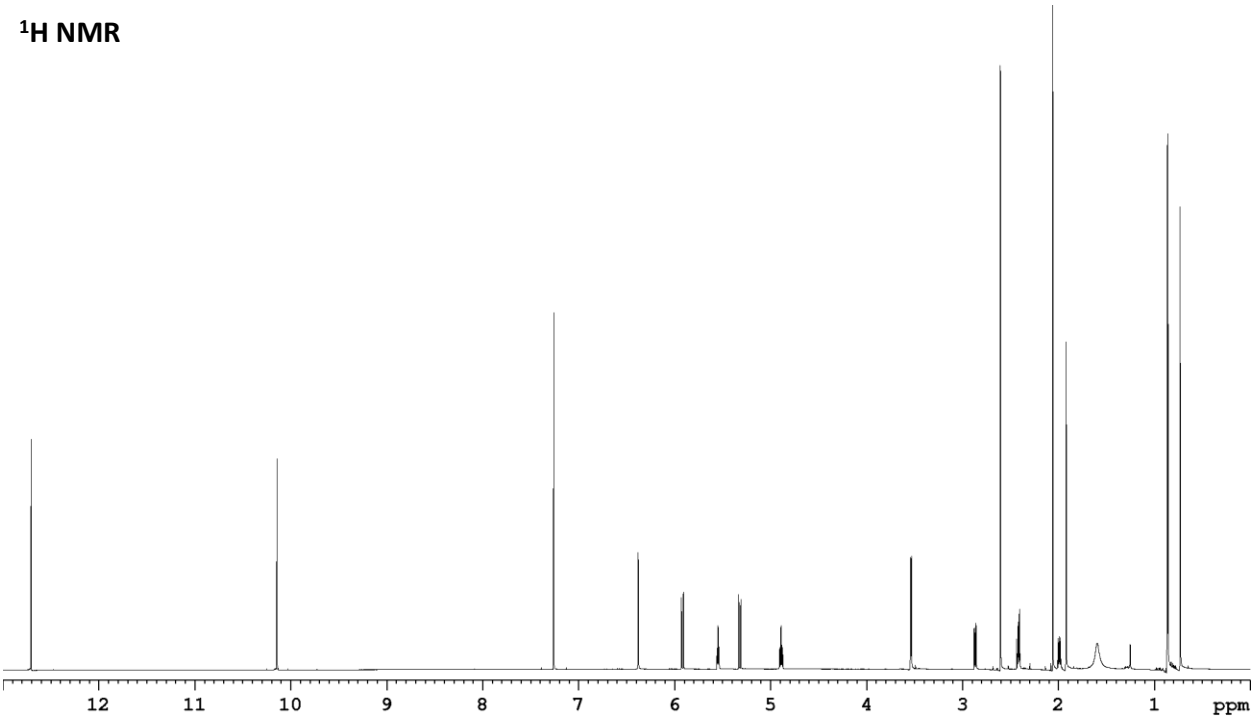


Figure S10. ^{1}H and HSQC spectra for ilicicolin F (**3**) in $CDCl_3$.



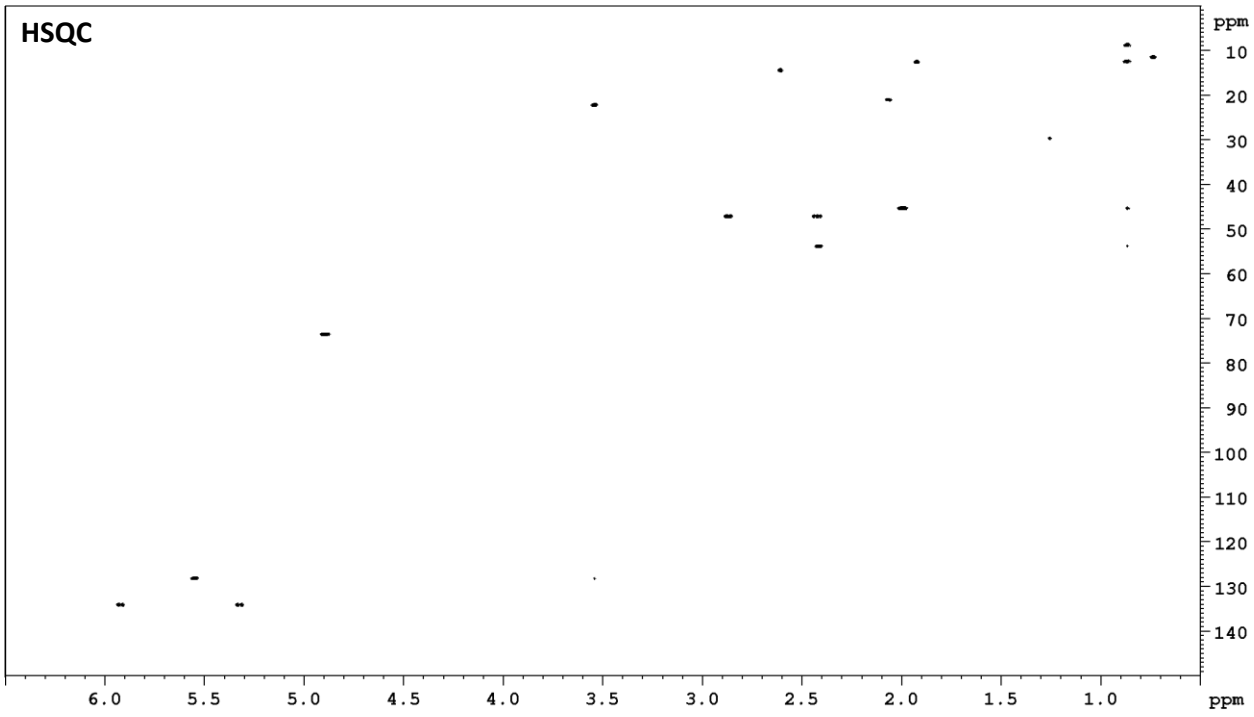


Figure S11. ^{1}H and HSQC spectra for ilicicolin C (**5**) in $CDCl_3$.

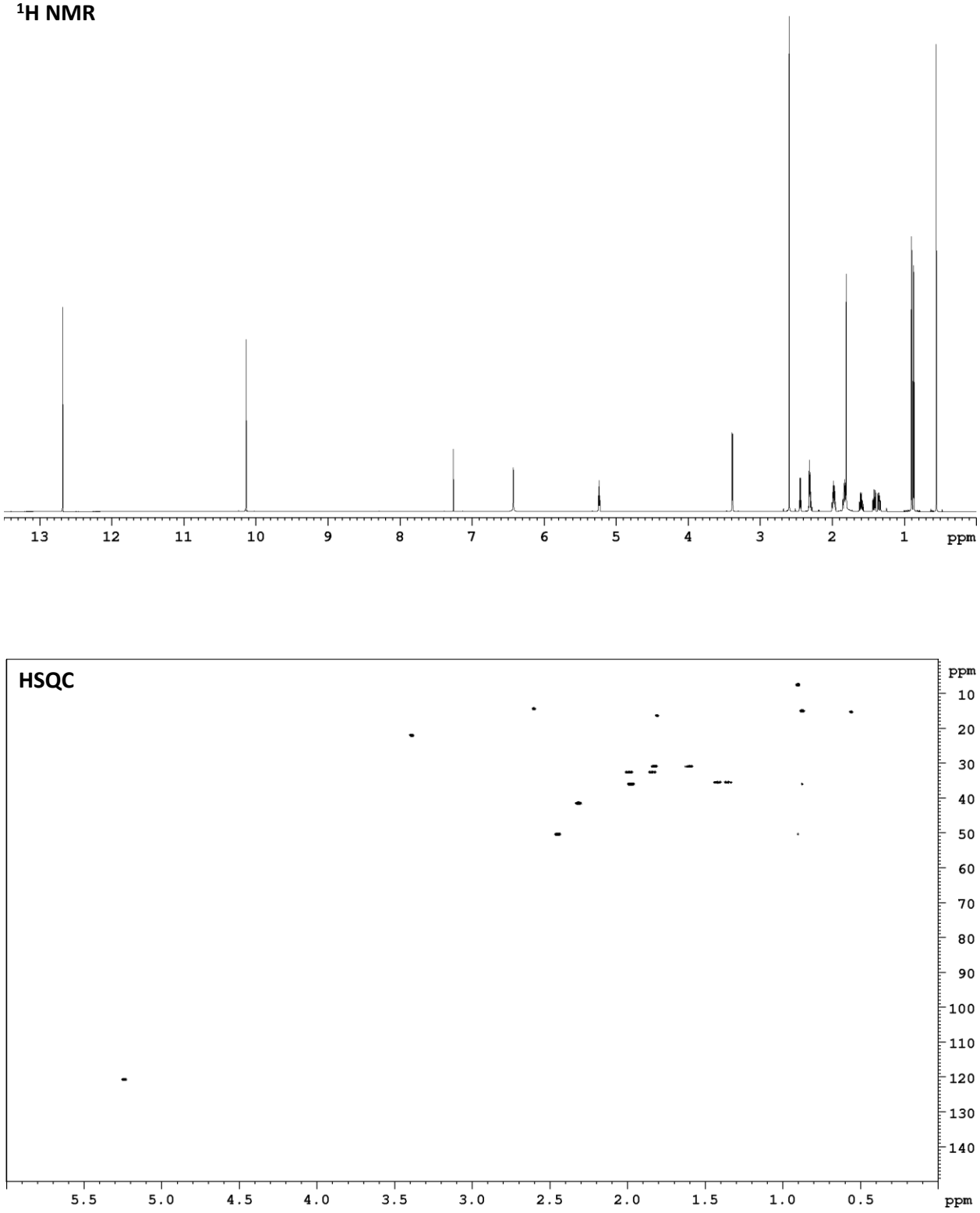
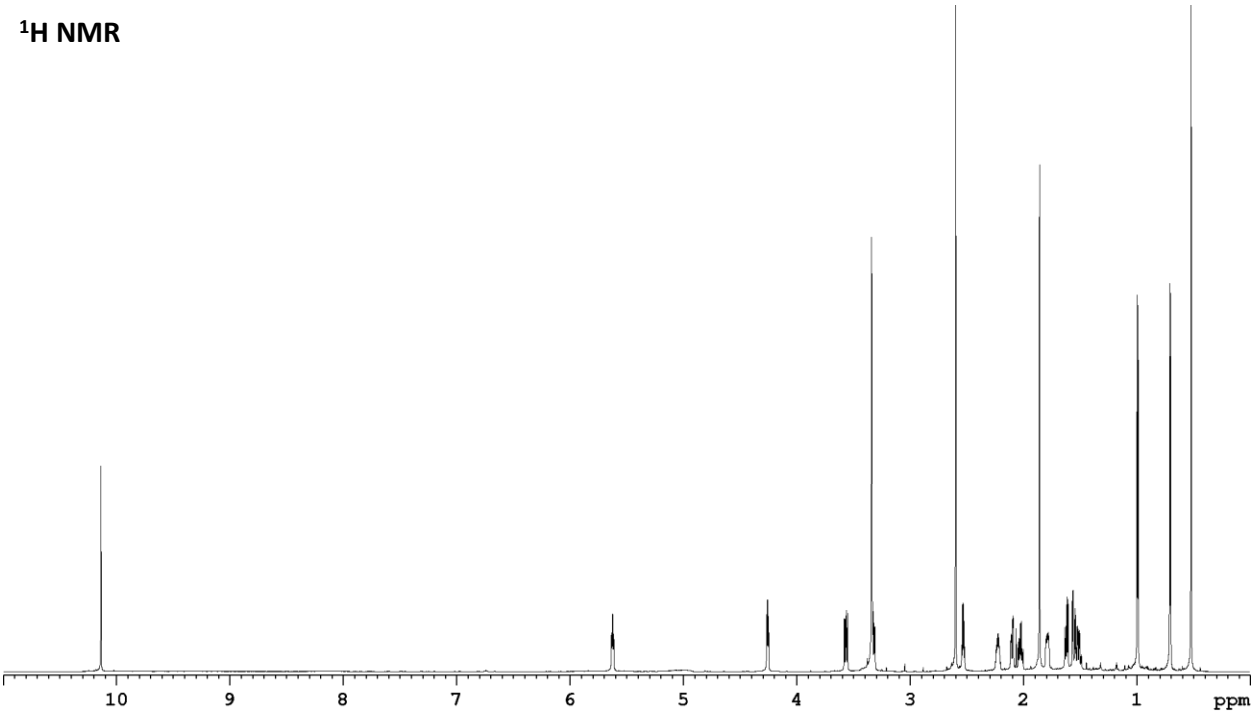
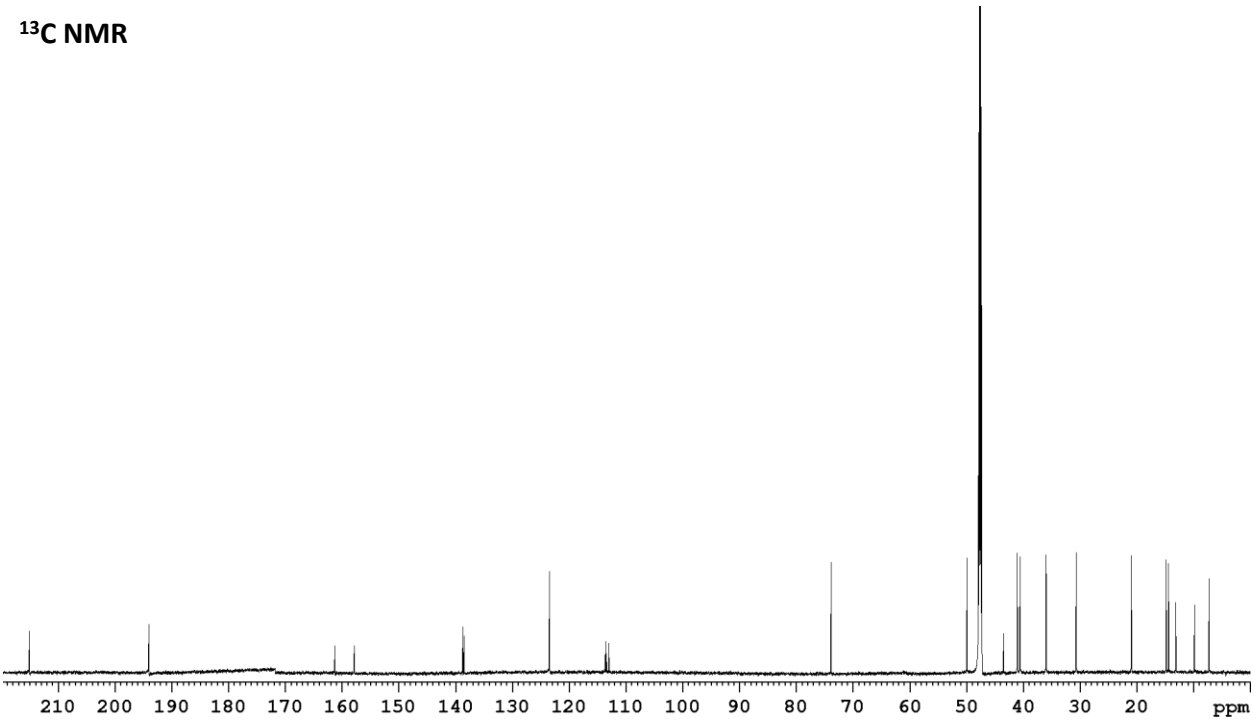


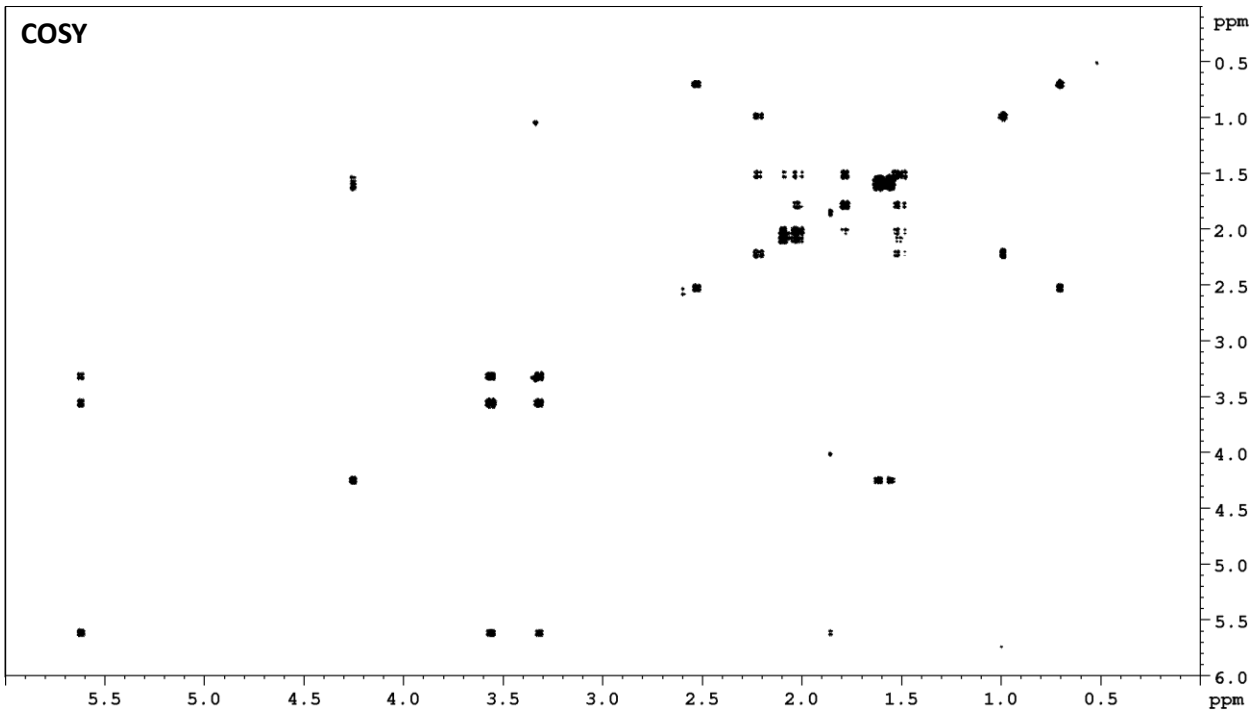
Figure S12. 1D and 2D NMR spectra for 4’5’-dihydro-4’-hydroxyascochlorin (**6**) in CD_3OD.

^{1}H NMR



^{13}C NMR

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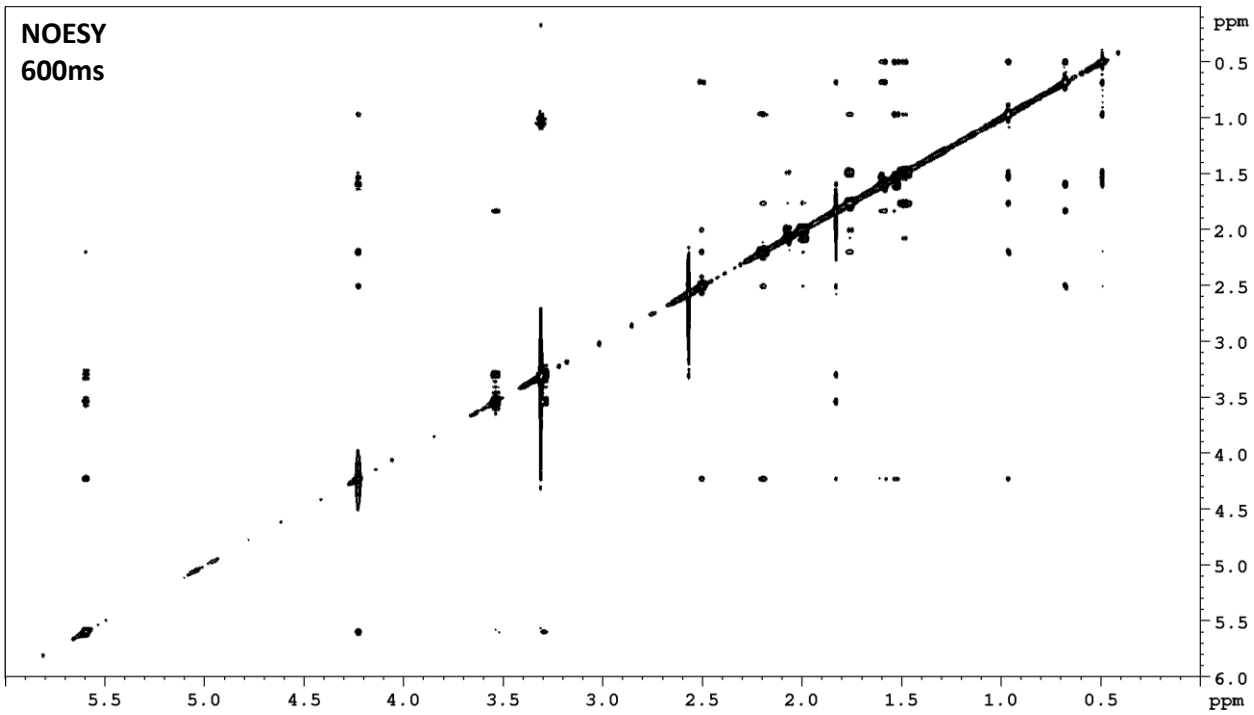
ppm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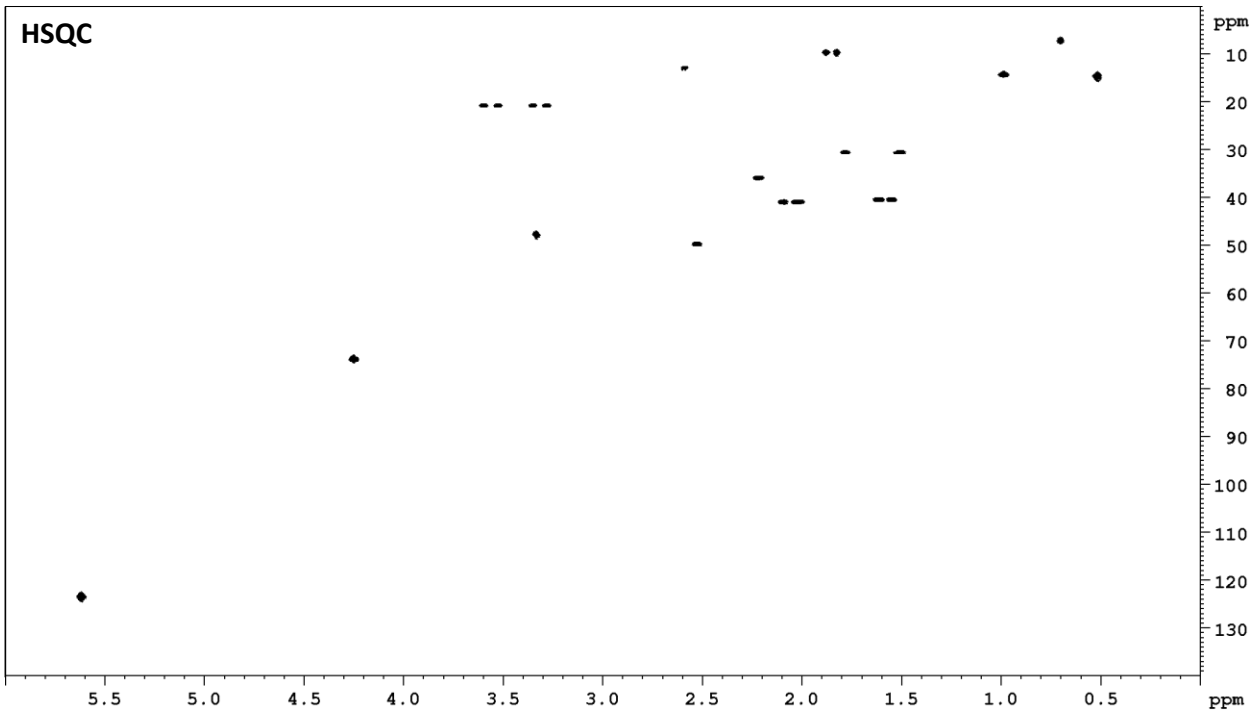
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ppm

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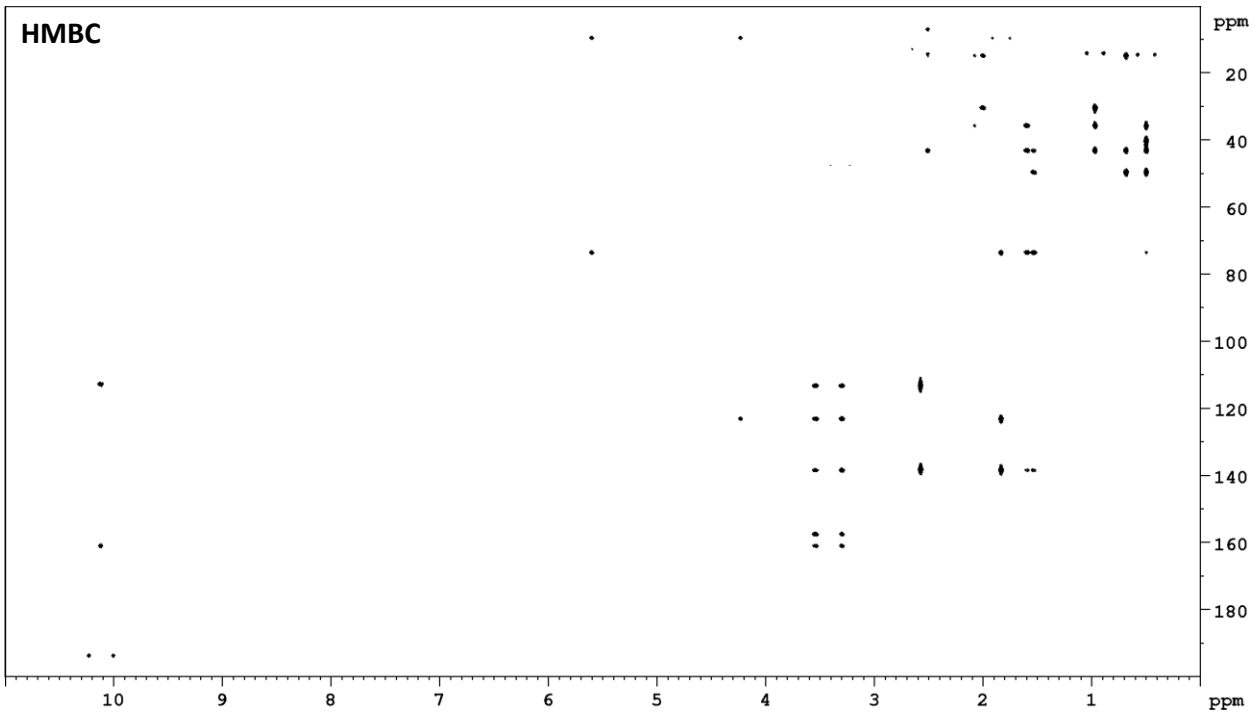
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4
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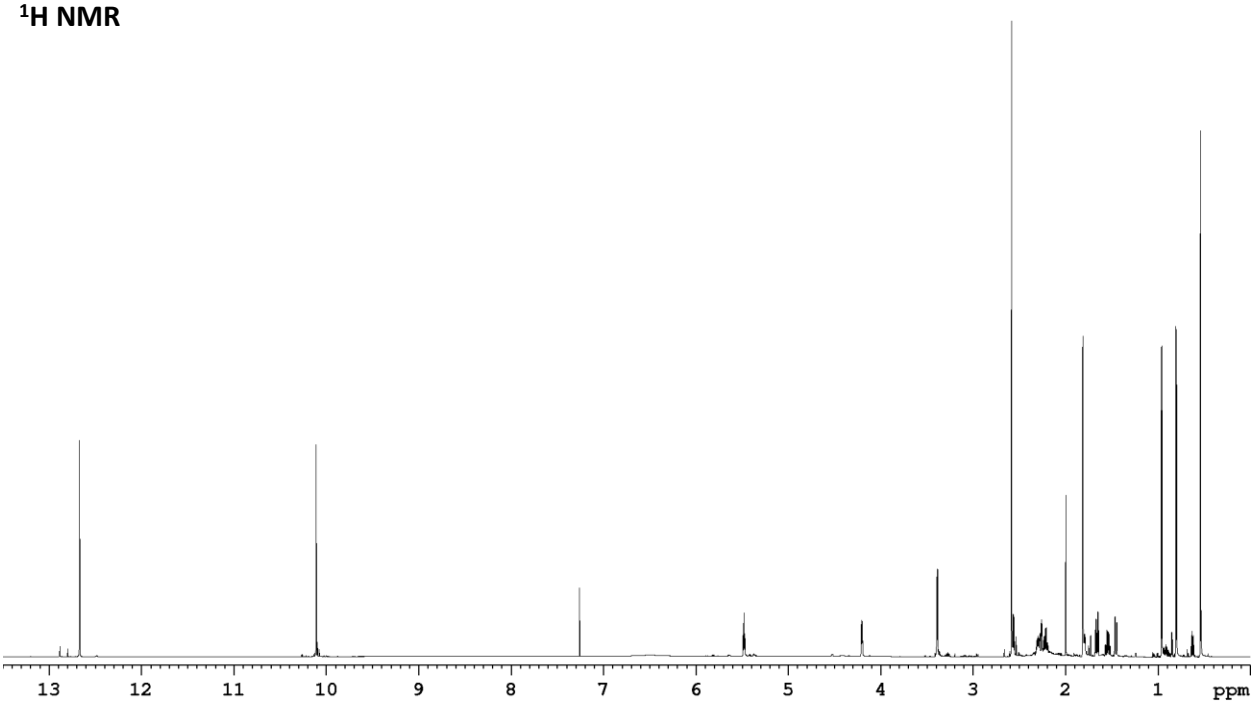
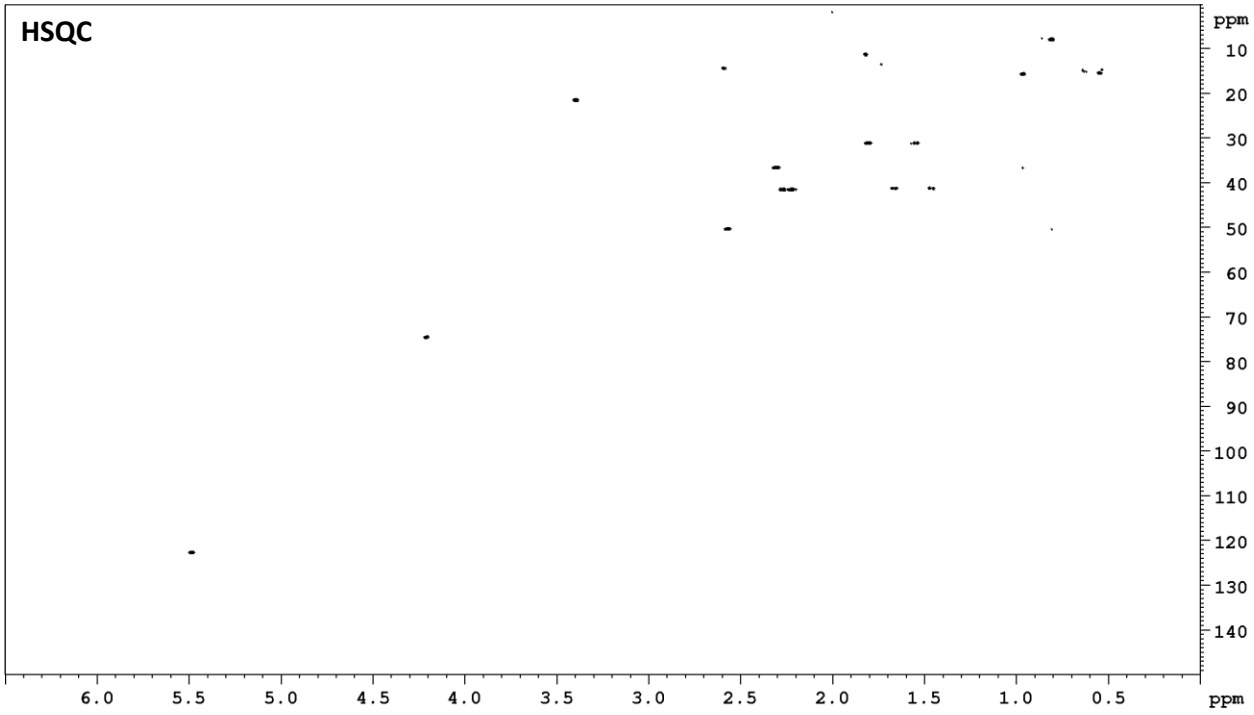
ppm

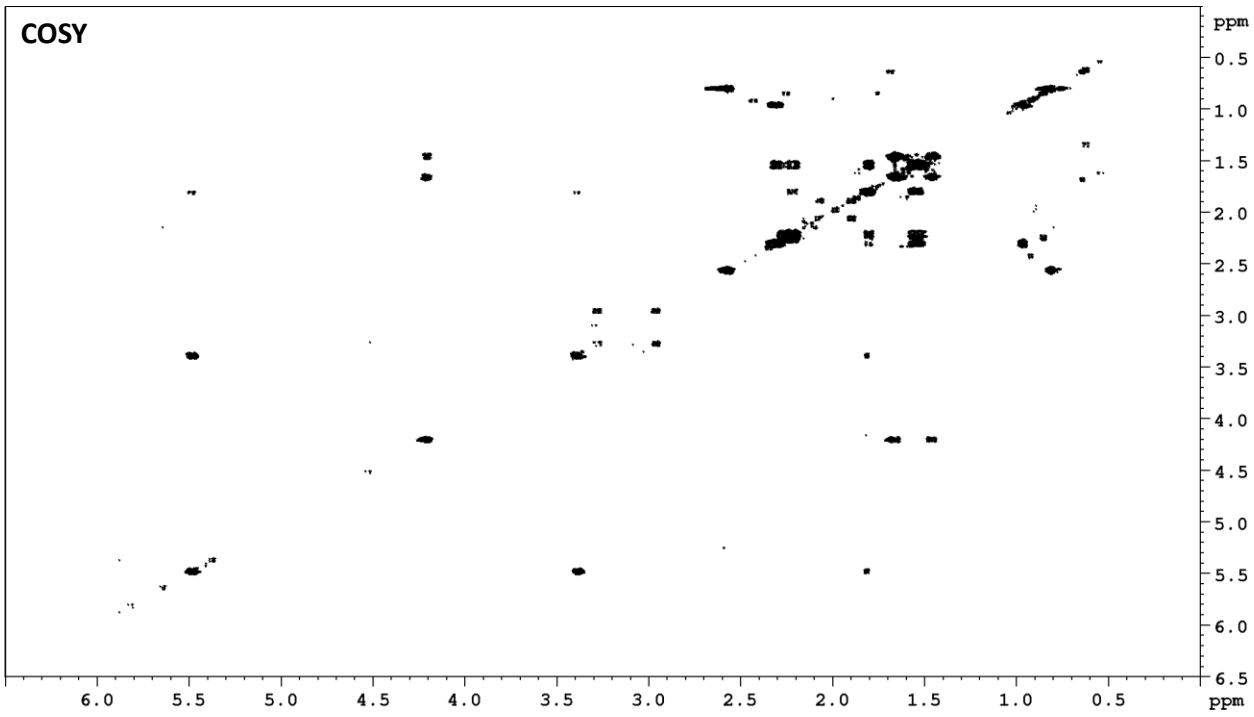
Figure S13. 1D and 2D NMR spectra for 4’5’-dihydro-4’-hydroxyascochlorin (**6**) in $CDCl_3$.

^{1}H NMR



HSQC

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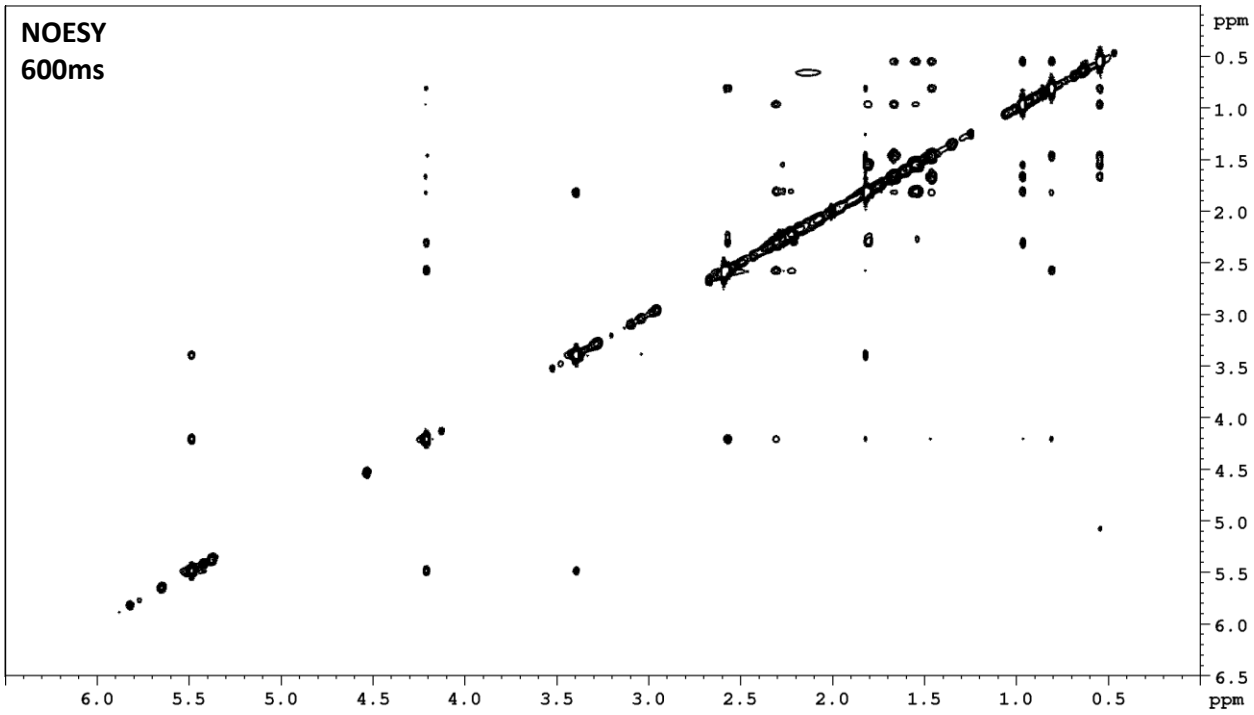
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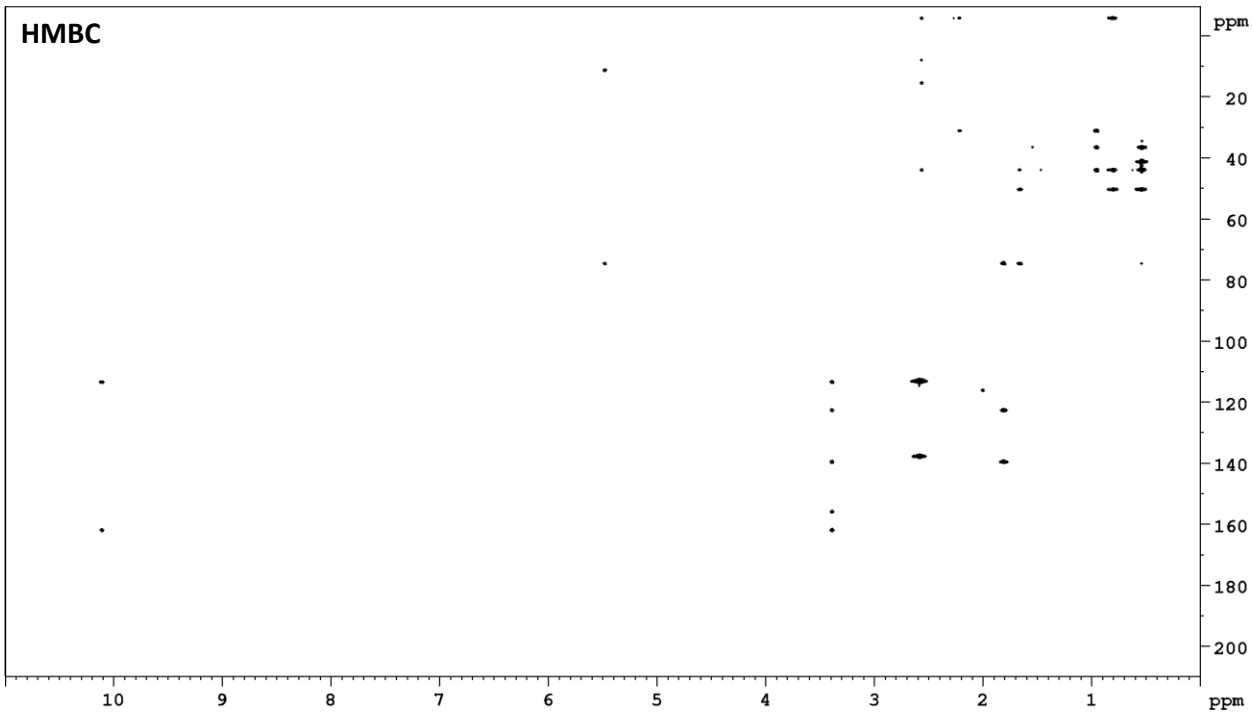
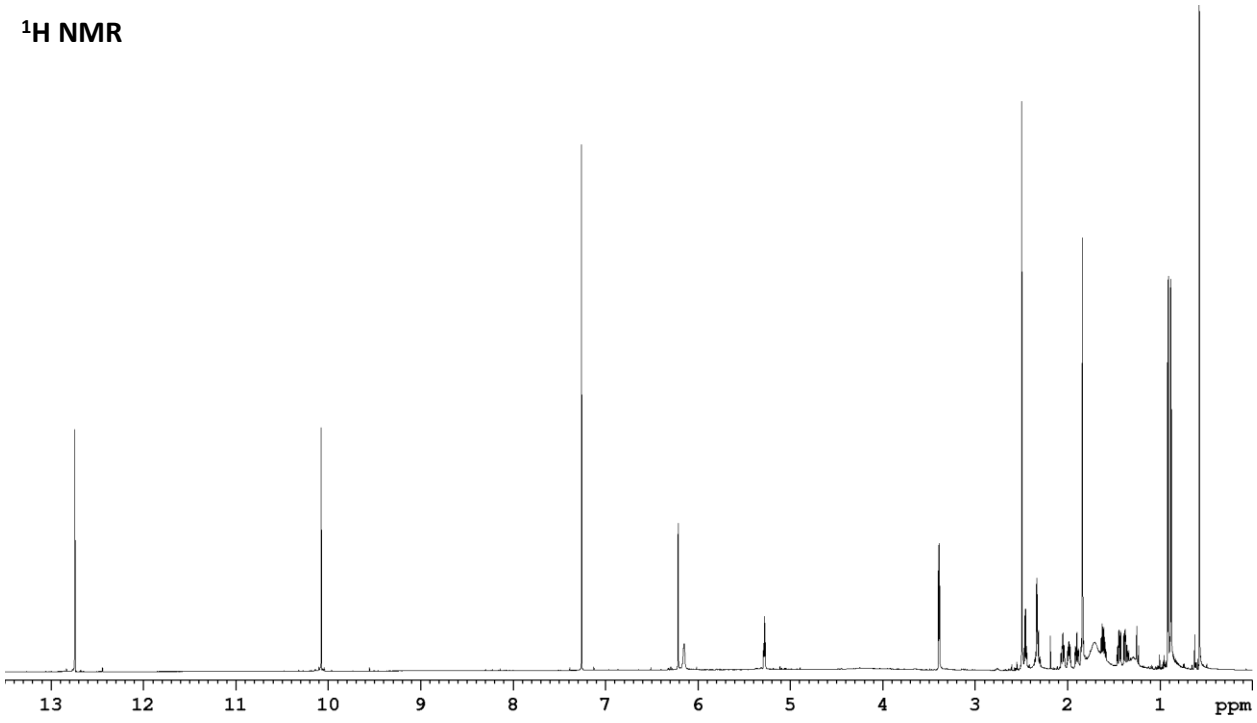


*The ketone group at C-10’ is observed at the wrong ^{13}C chemical shift (δ_C -5.8ppm) due to ^{13}C SW set to 220ppm.

Figure S14. ^{1}H and HSQC spectra for LL-Z1272ε (**8**) in $CDCl_3$.



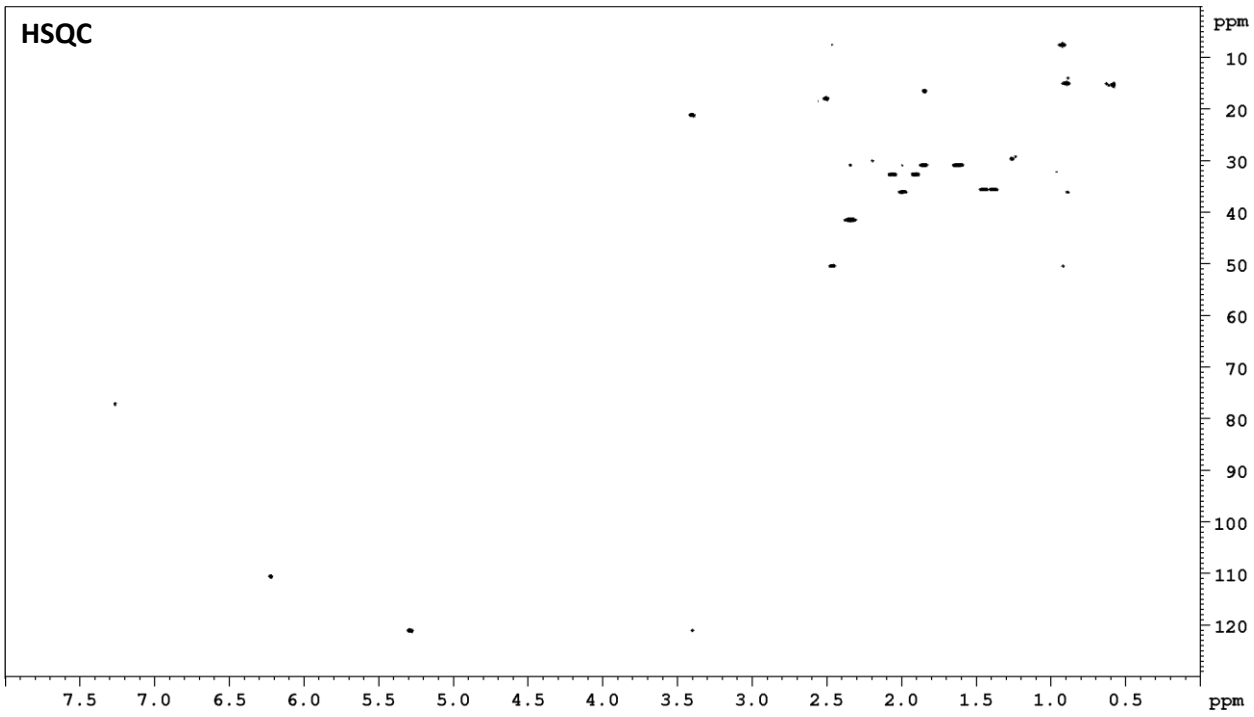
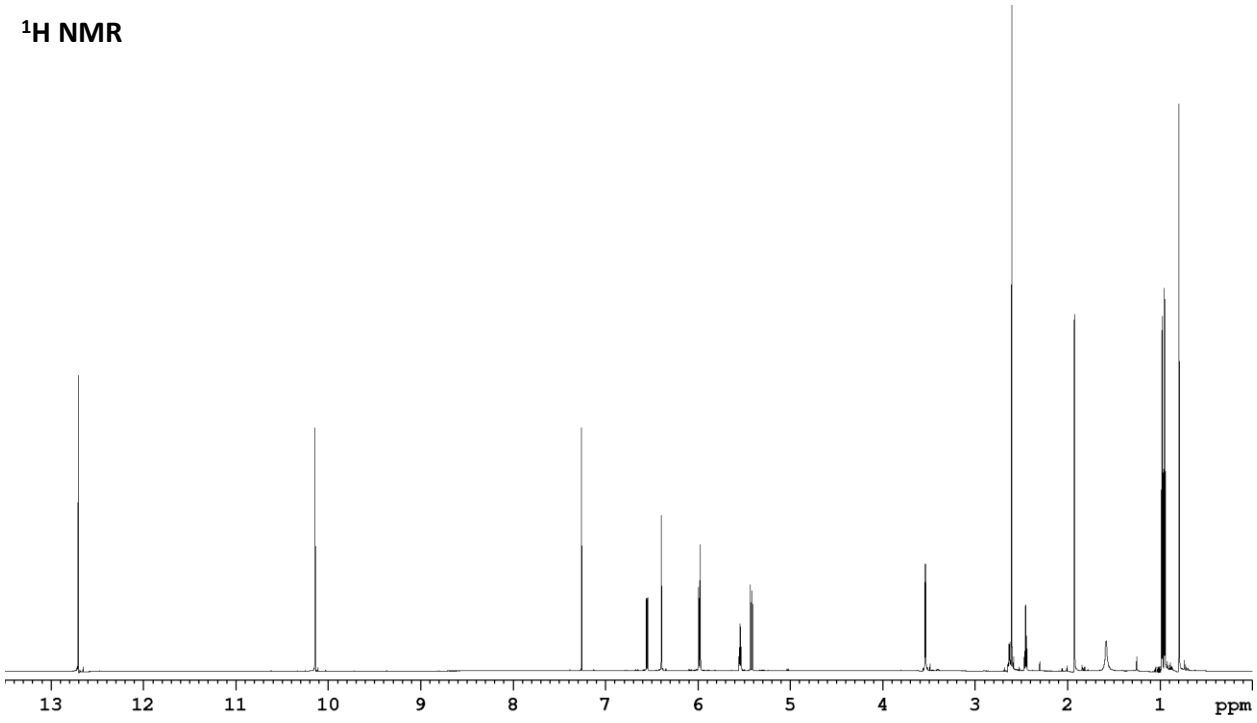


Figure S15. ^{1}H and HSQC spectra for ilicicolin E (**9**) in $CDCl_3$.



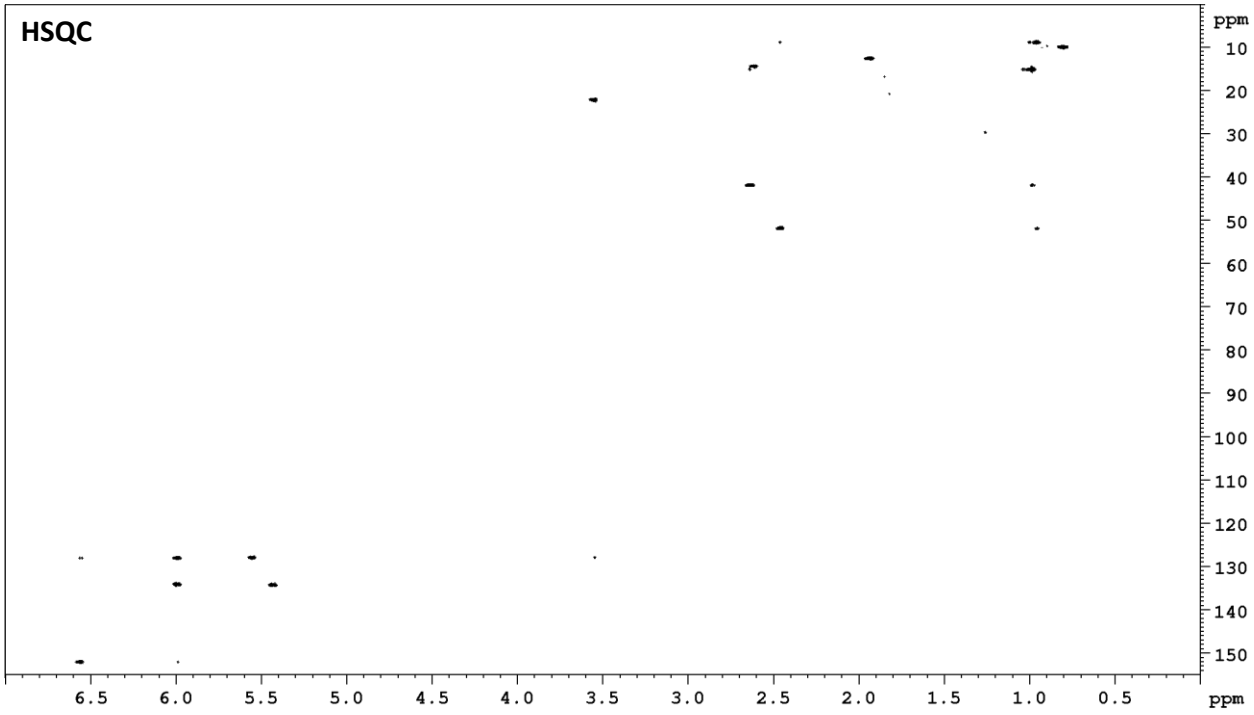
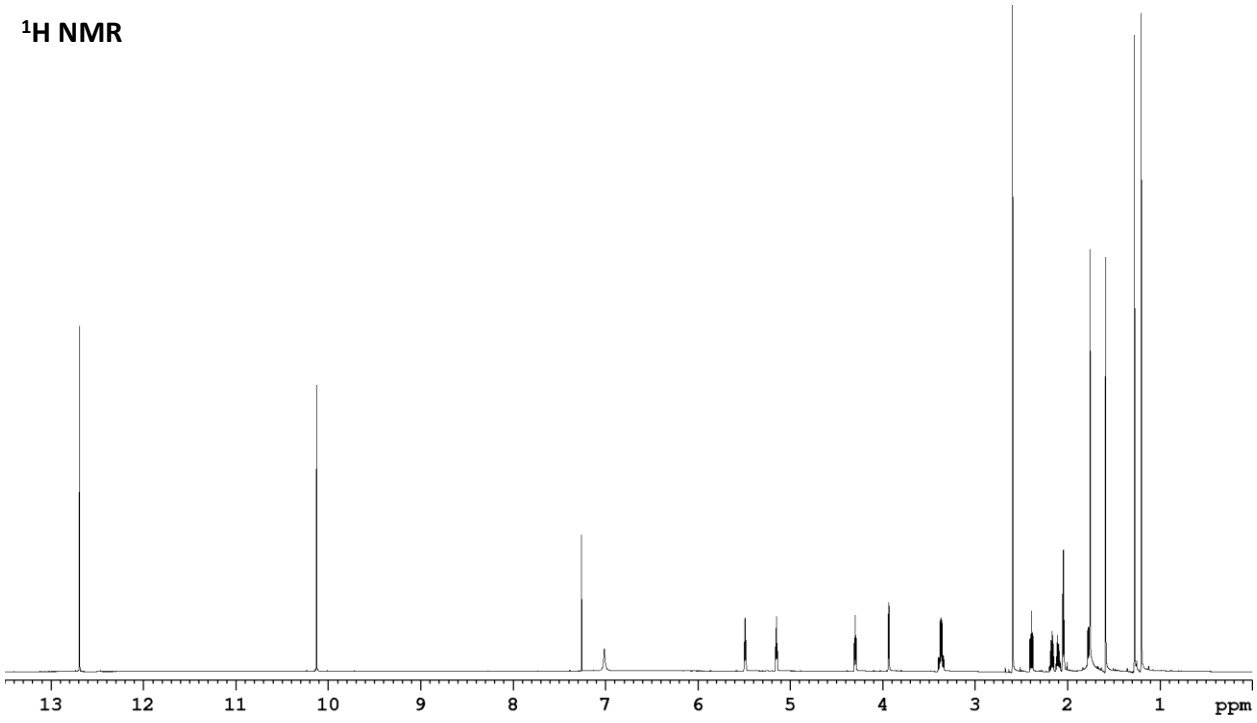


Figure S16. ^{1}H and HSQC spectra for ascofuranol (**10**) in $CDCl_3$.



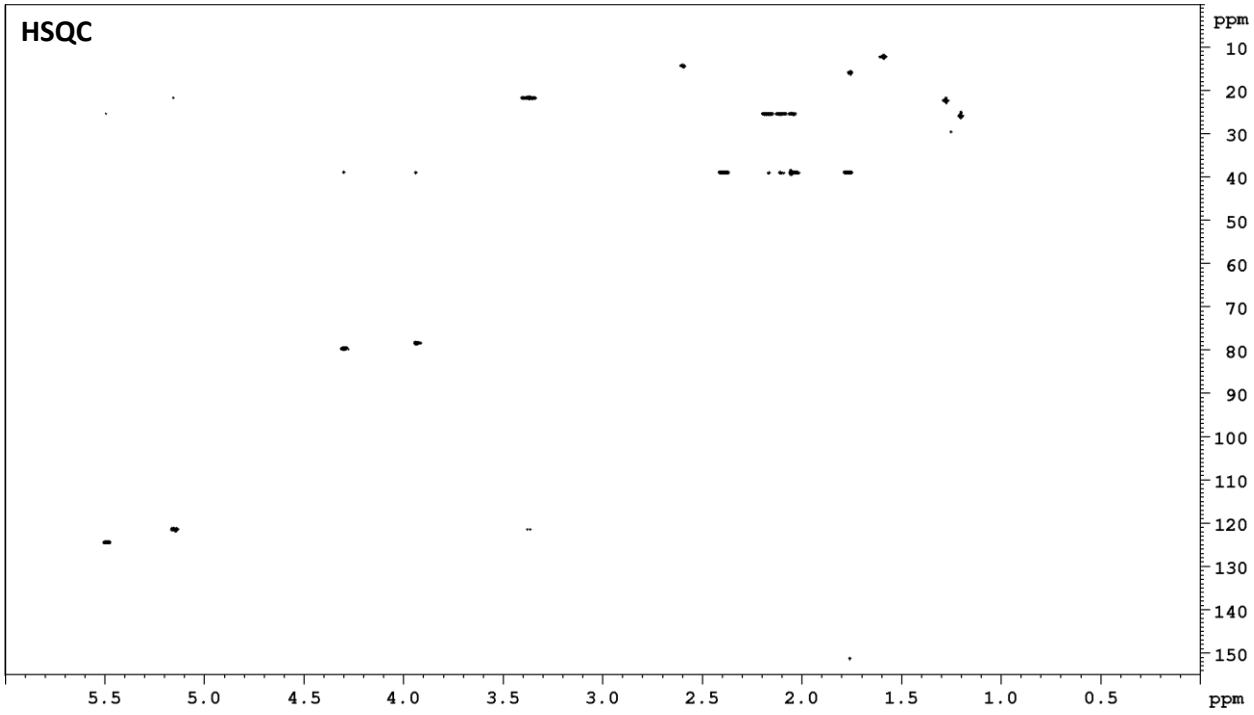
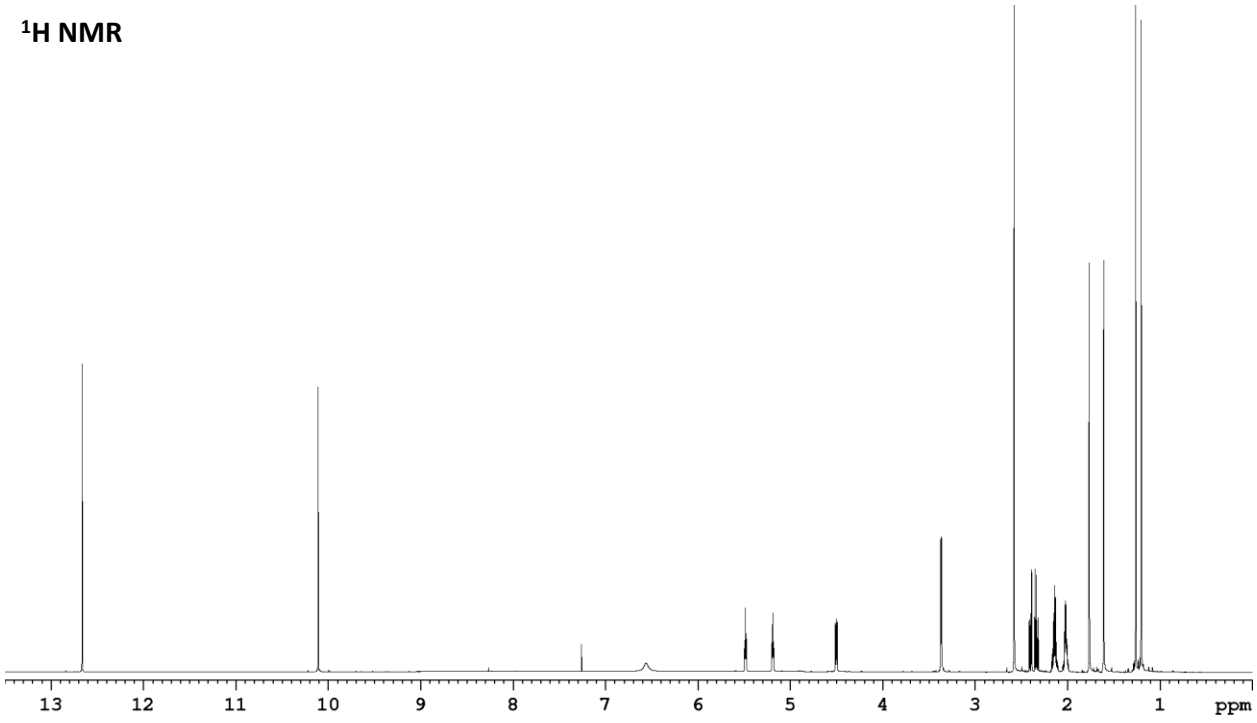


Figure S17. ^{1}H and HSQC spectra for ascofuranone (**11**) in $CDCl_3$.



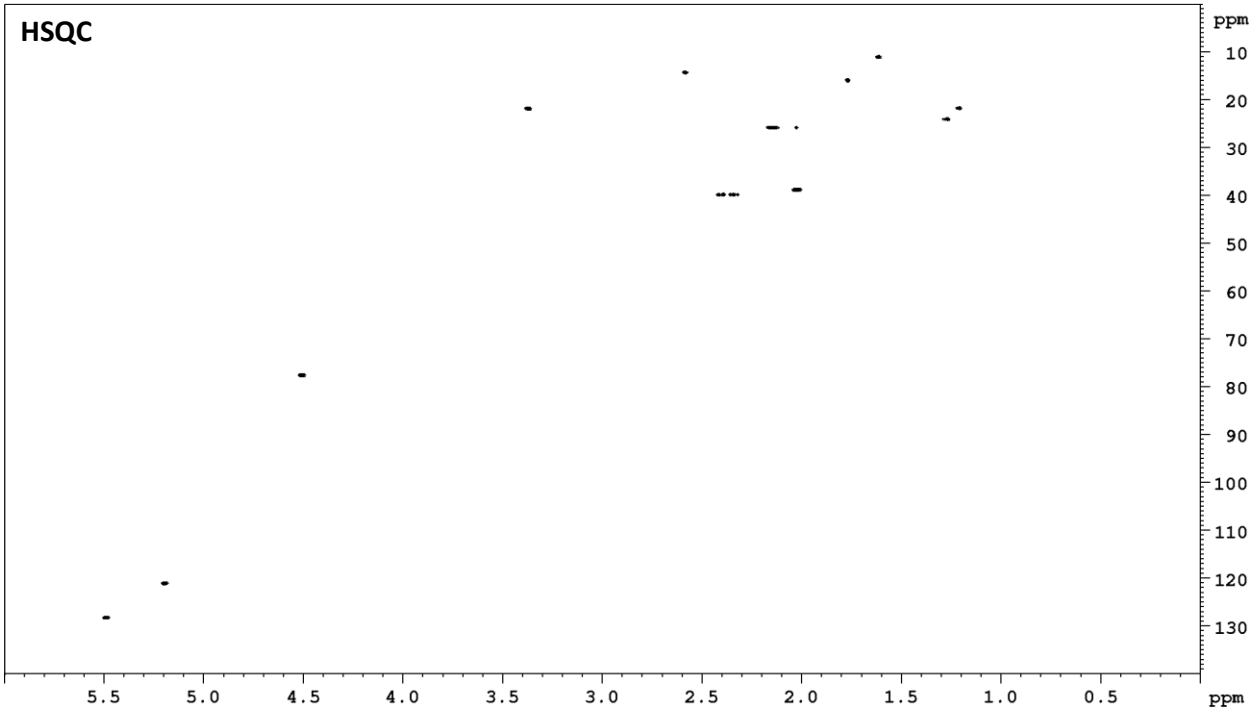
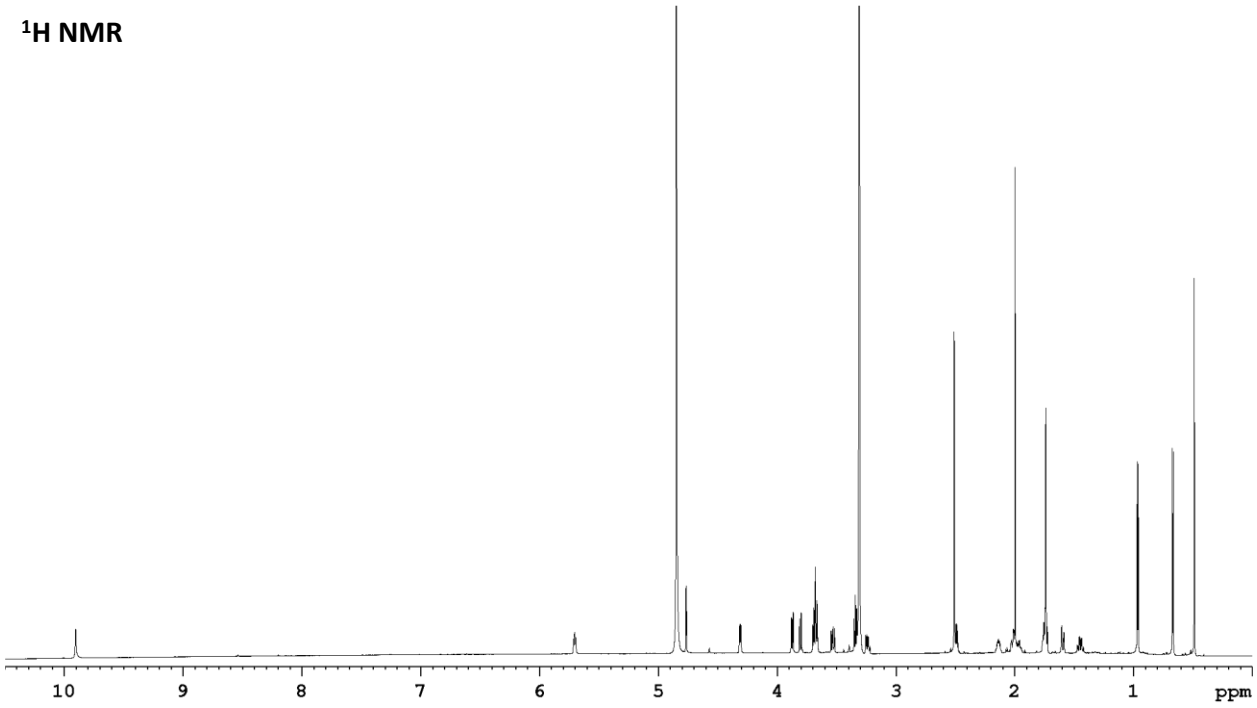
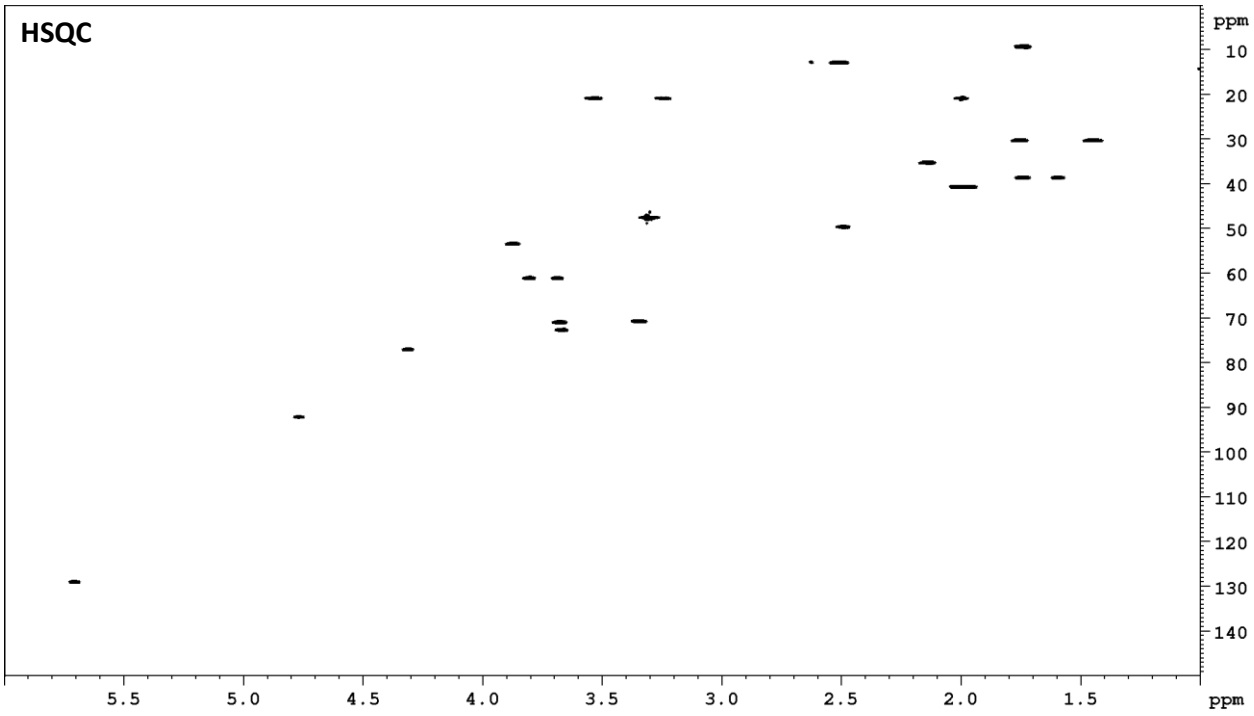
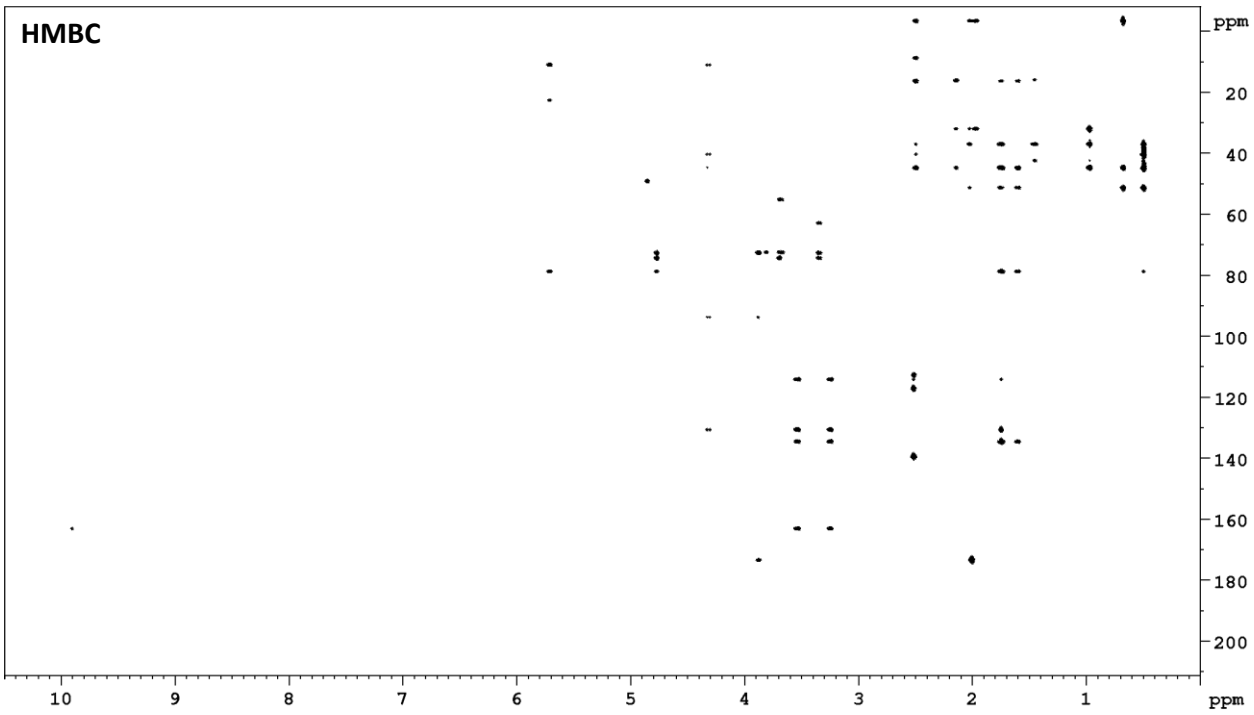


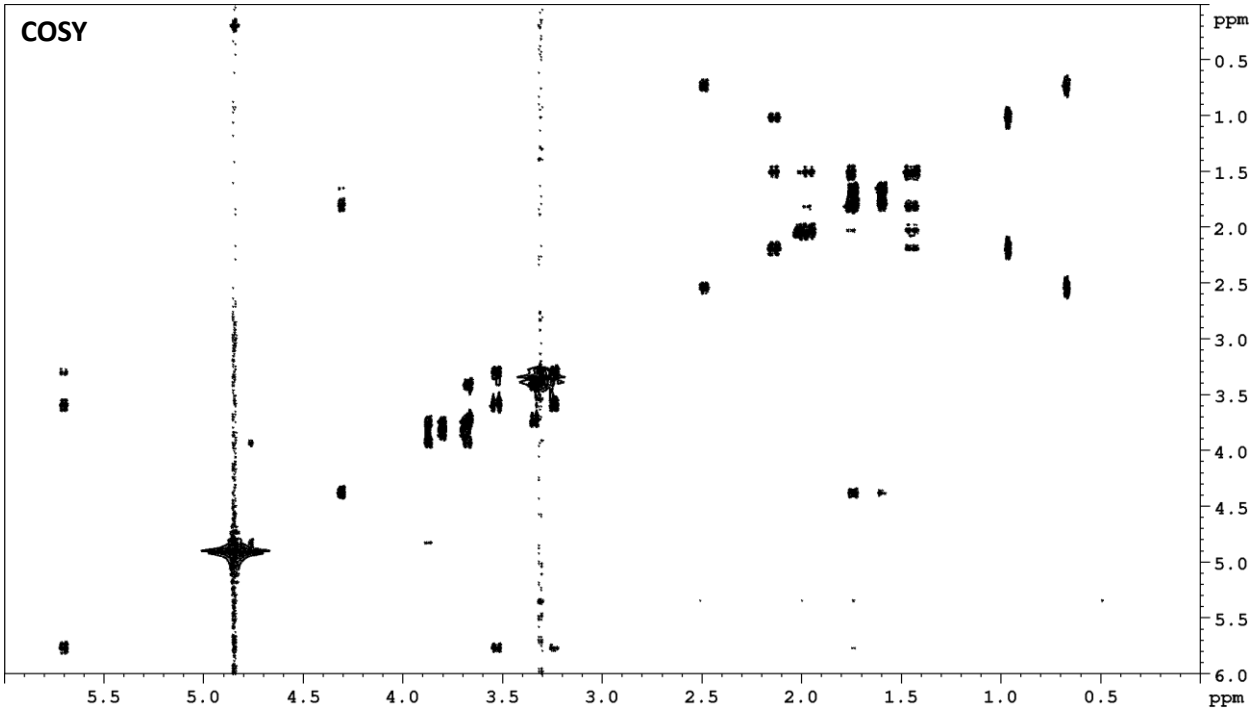
Figure S18. 1D and 2D NMR spectra for ascochlorin N-acetylglucosamine (**19**) in CD_3OD.

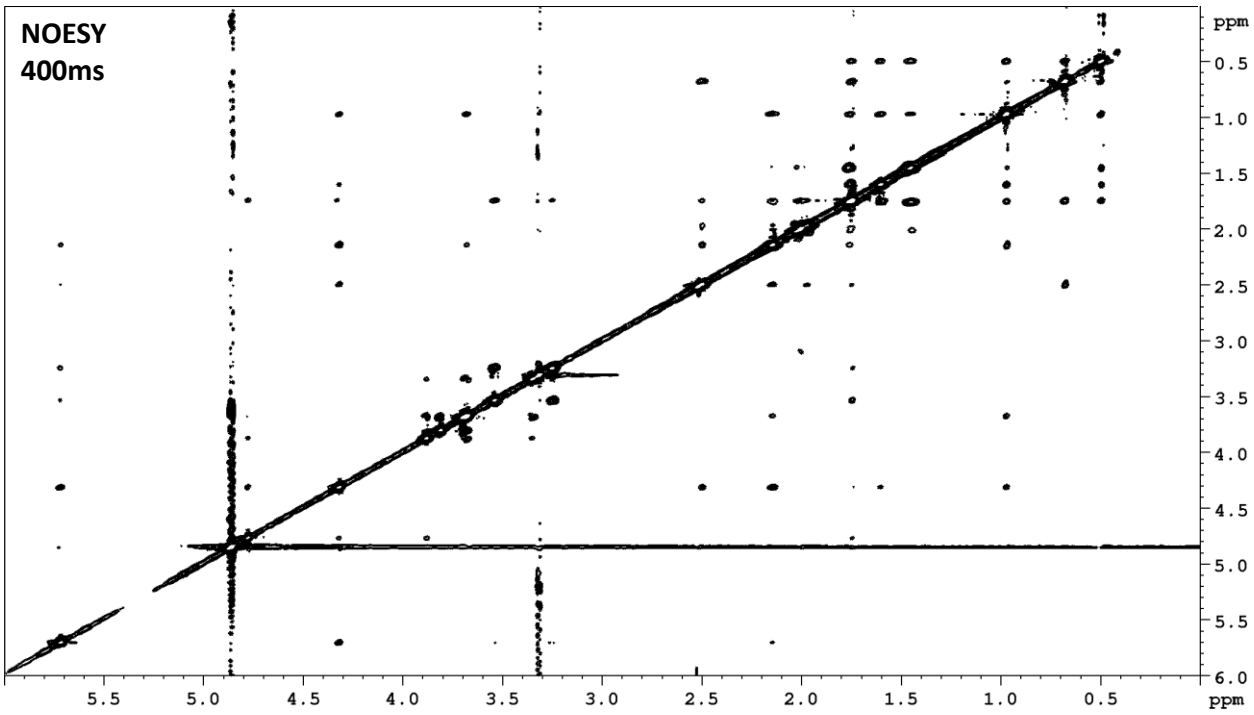






*The ketone group at C-10' is observed at the wrong ^{13}C chemical shift (δ_C -3.3ppm) due to ^{13}C SW set to 220ppm.

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6.0
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5.0
4.5
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3.5
3.0
2.5
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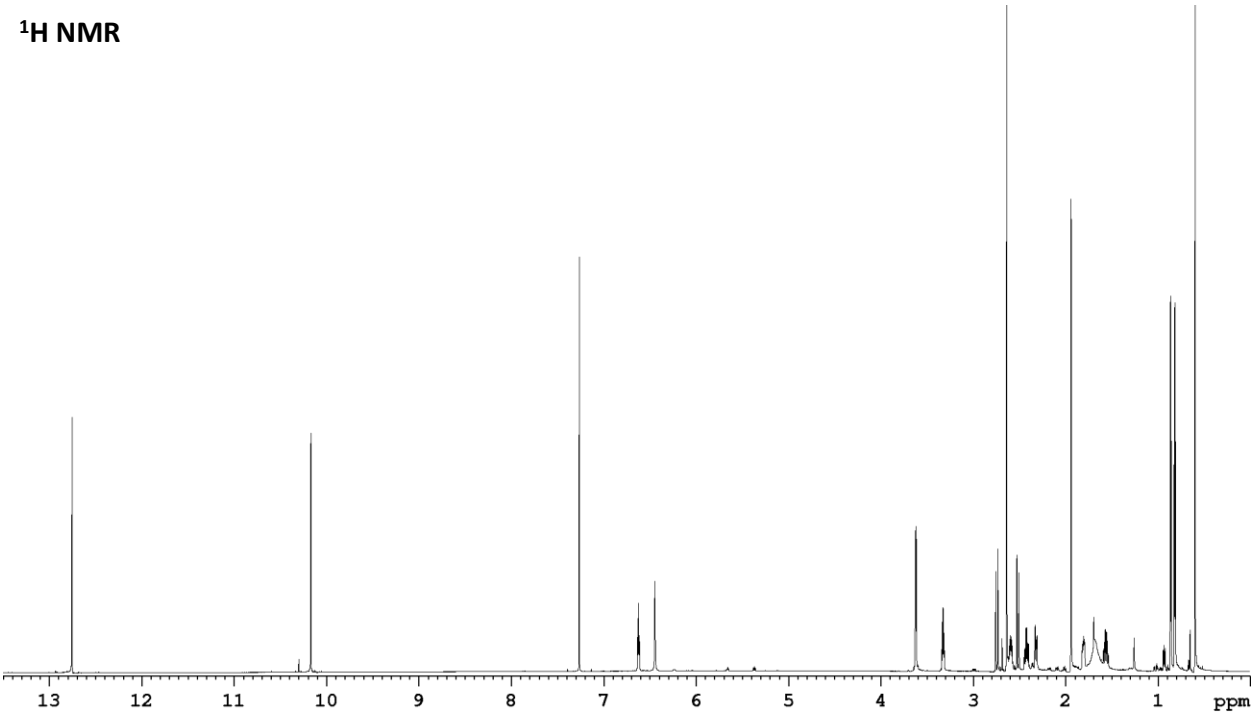
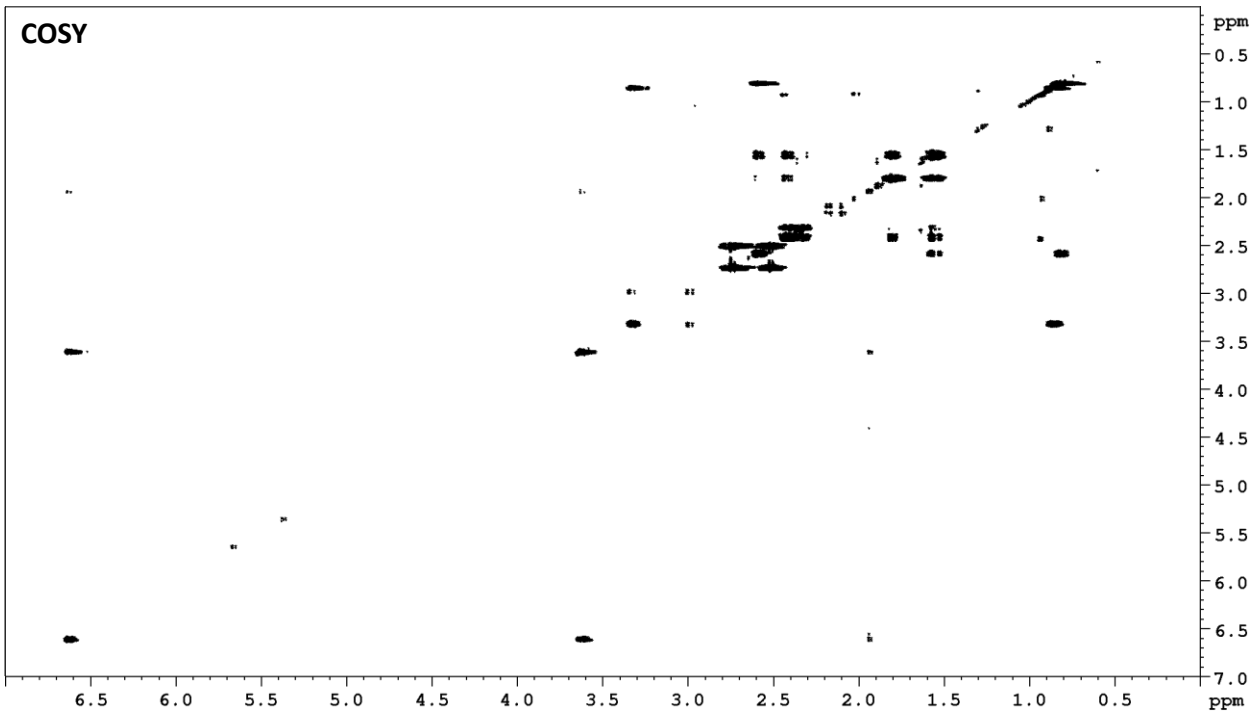
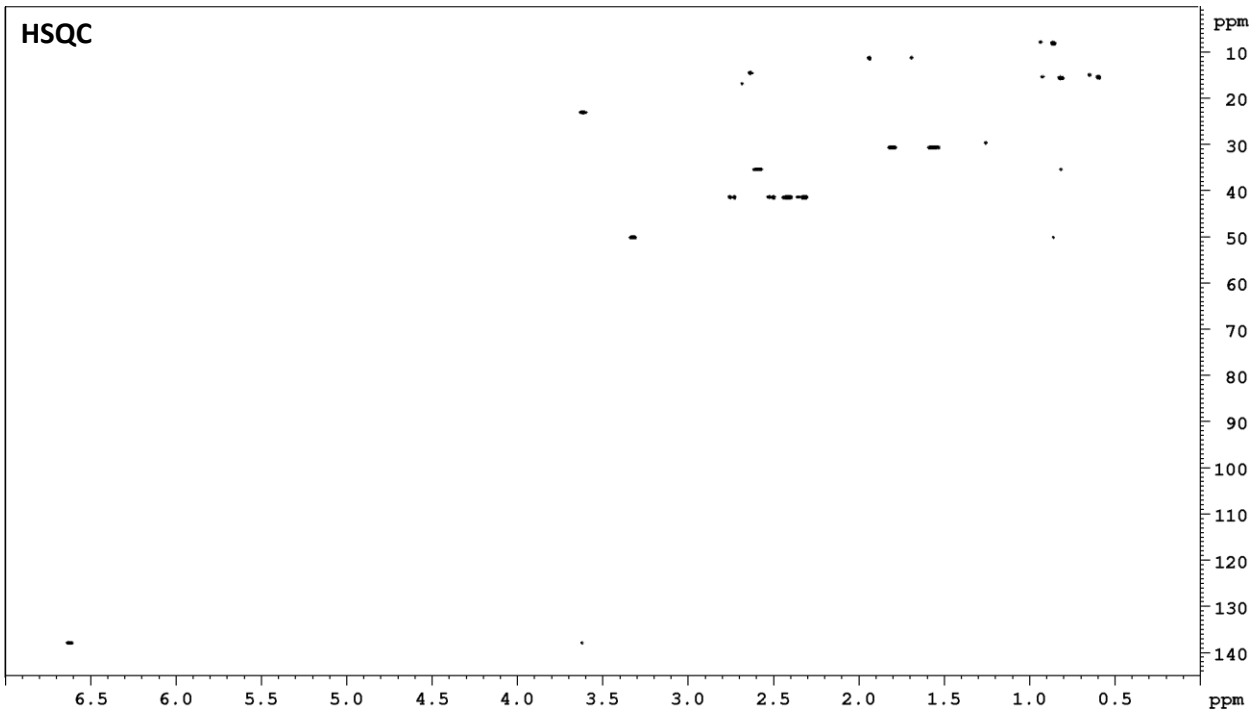
1.5
1.0
0.5
ppm

Figure S19. 1D and 2D NMR spectra for 4'-ketoascochlorin (**20**) in $CDCl_3$.

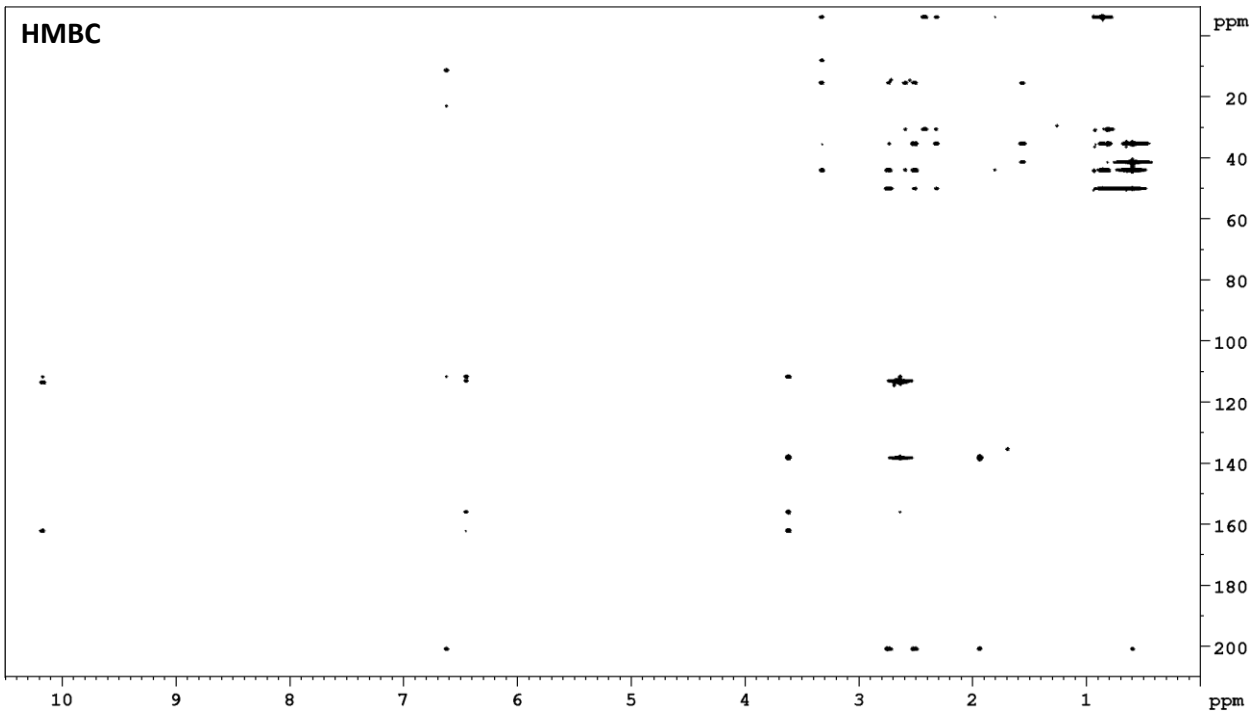




HSQC

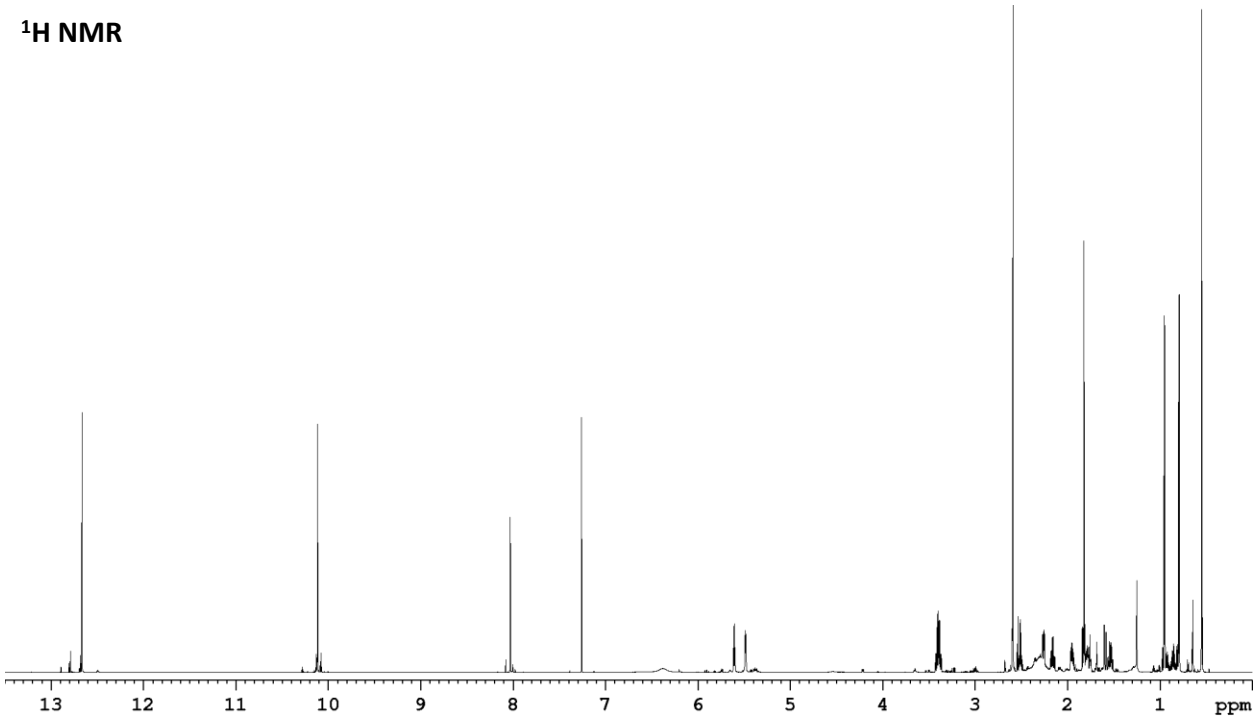


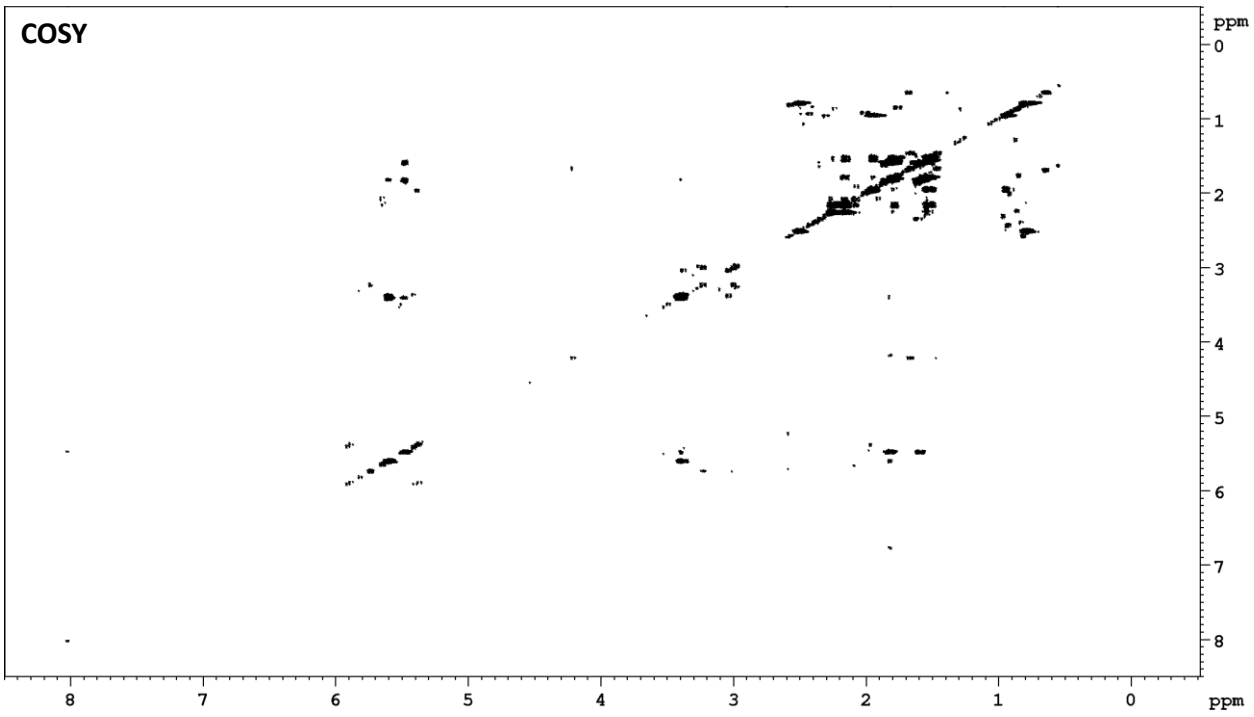
HMBC



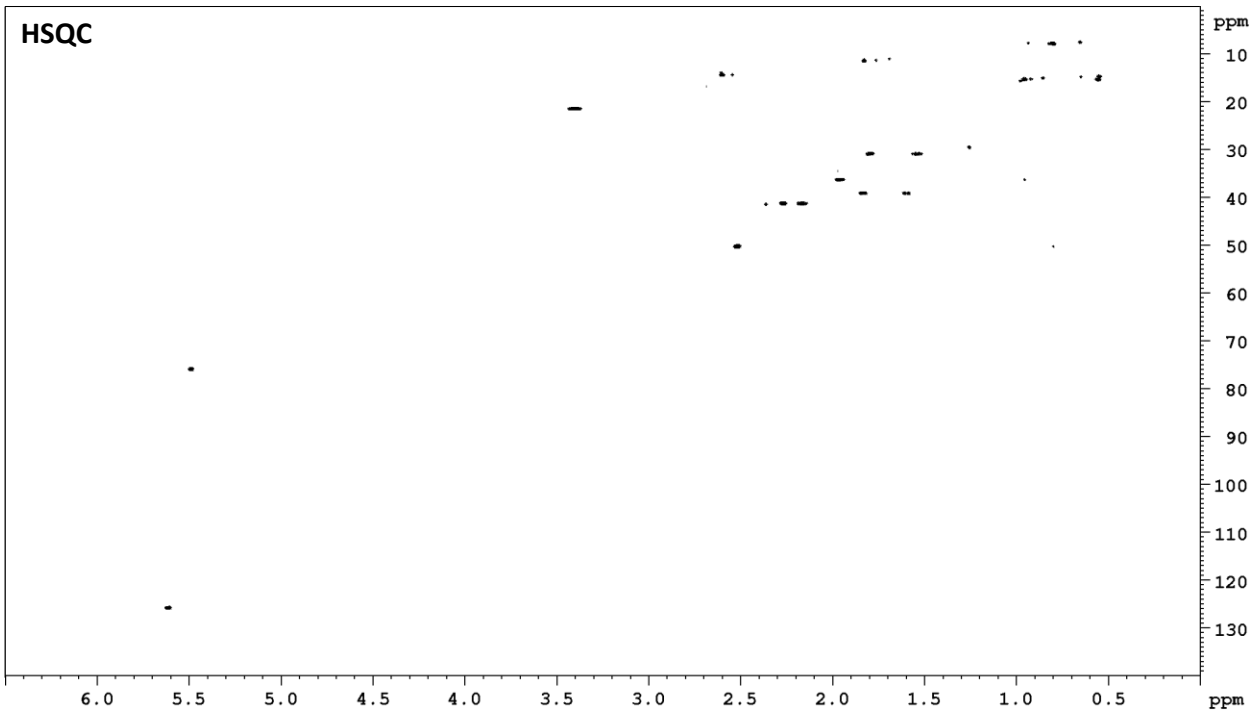
*The ketone group at C-10' is observed at the wrong ^{13}C chemical shift (δ_C -6.1ppm) due to ^{13}C SW set to 220ppm.

Figure S20. 1D and 2D NMR spectra for 4',5'- dehydro-4'-formylascochlorin (**21**) in $CDCl_3$.

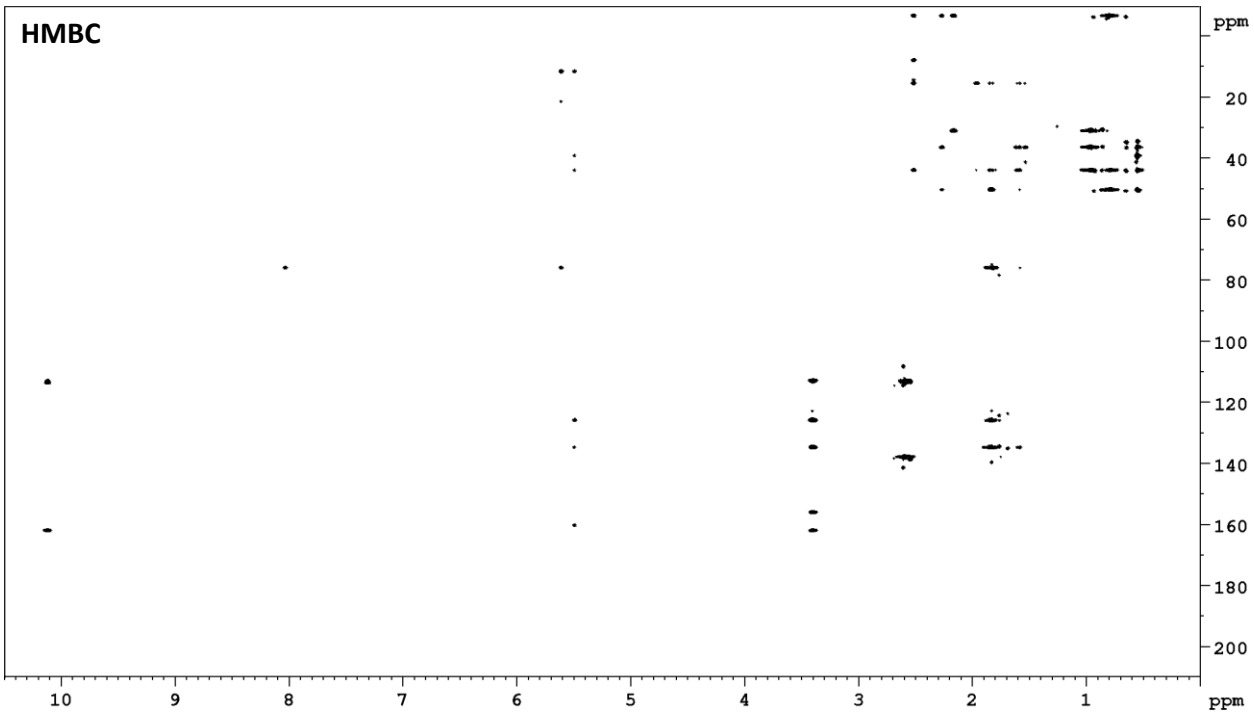




HSQC



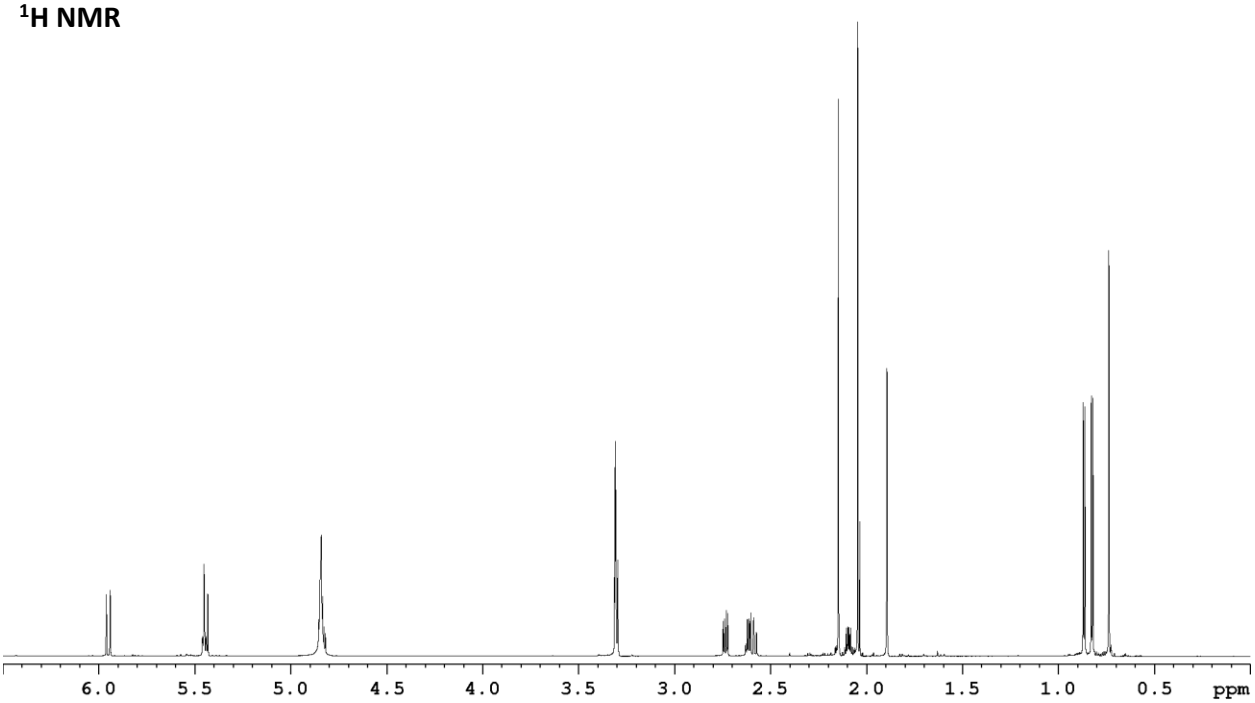
HMBC



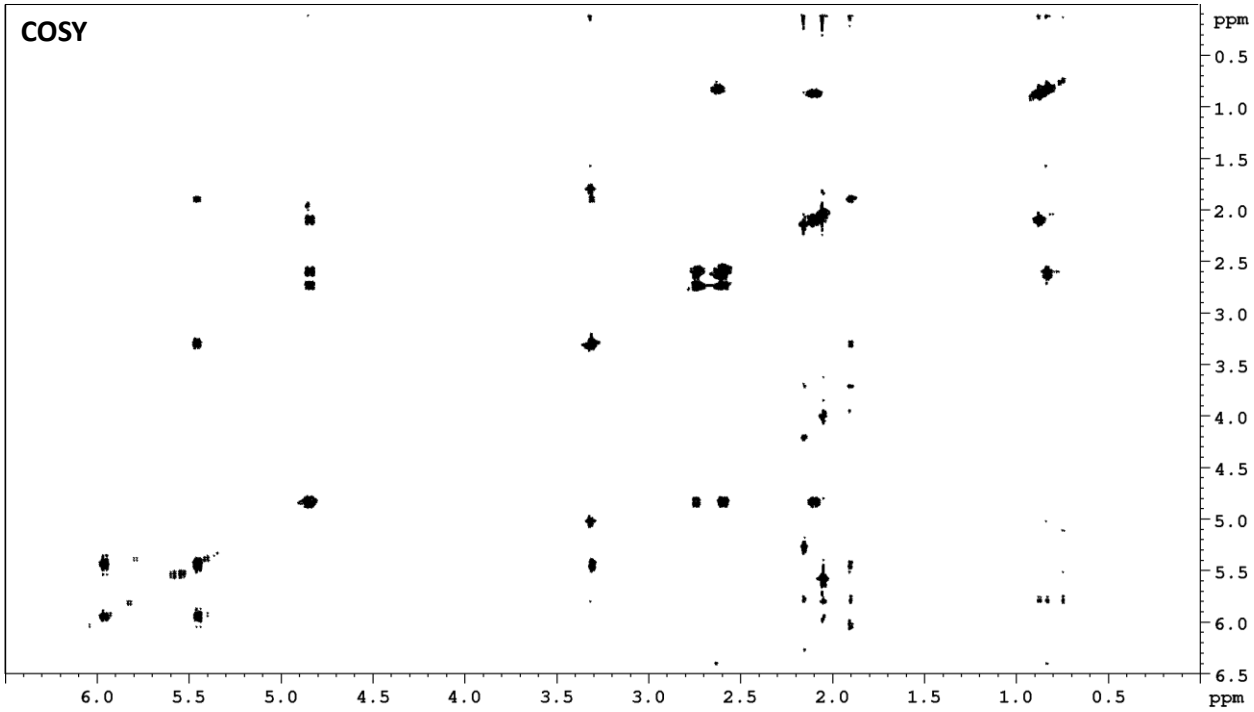
*The ketone group at C-10' is observed at the wrong ^{13}C chemical shift (δ_C -6.7ppm) due to ^{13}C SW set to 220ppm.

Figure S21. 1D and 2D NMR spectra for fimetarin A (**22**) in CD_3OD.

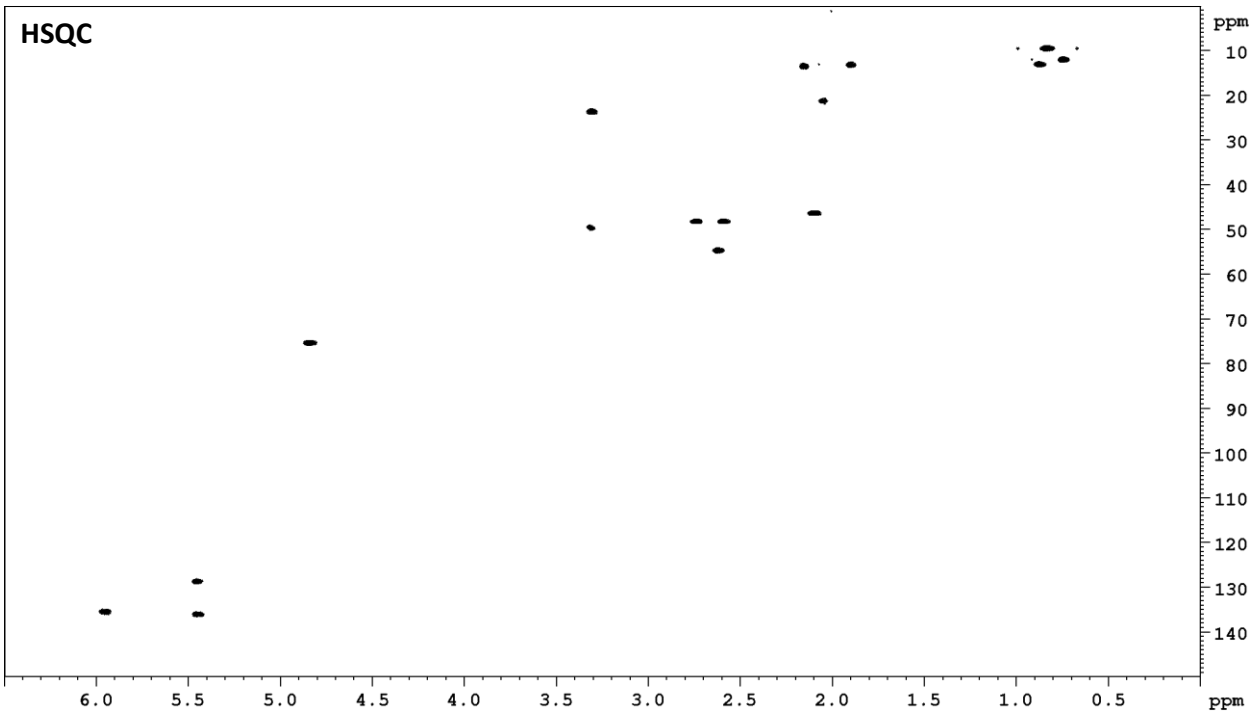
^{1}H NMR



COSY



HSQC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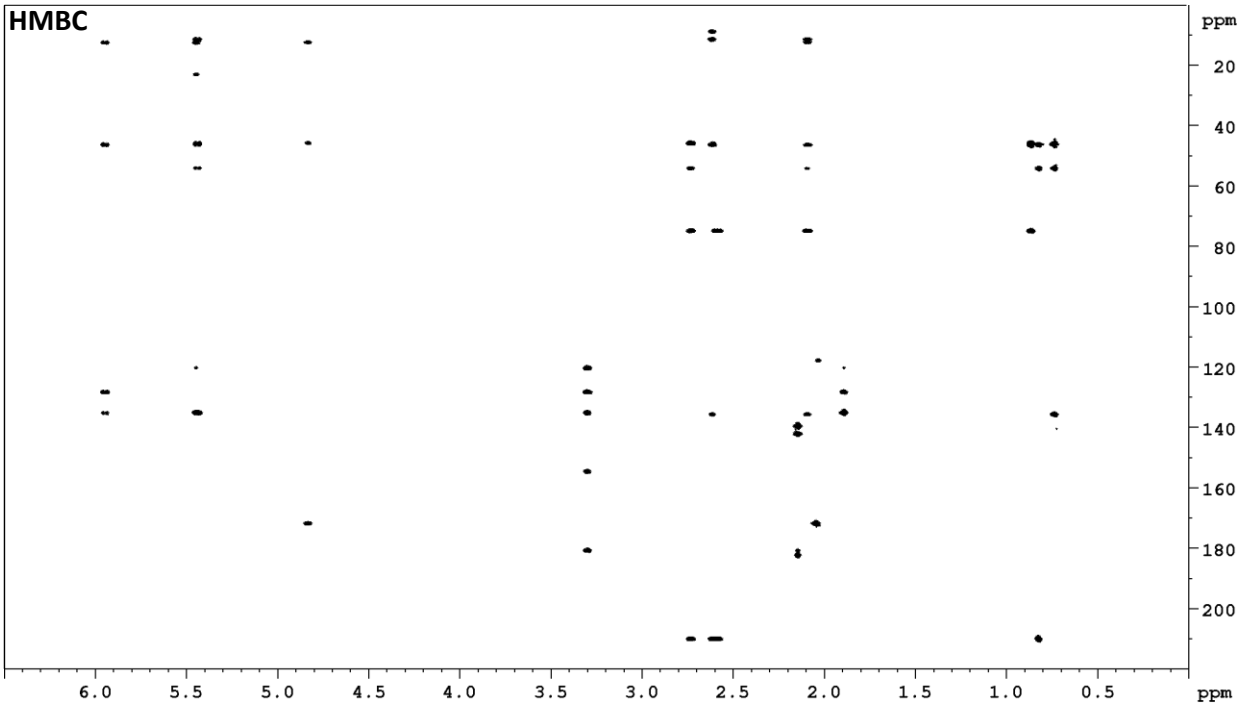
0.5
ppm

HMBC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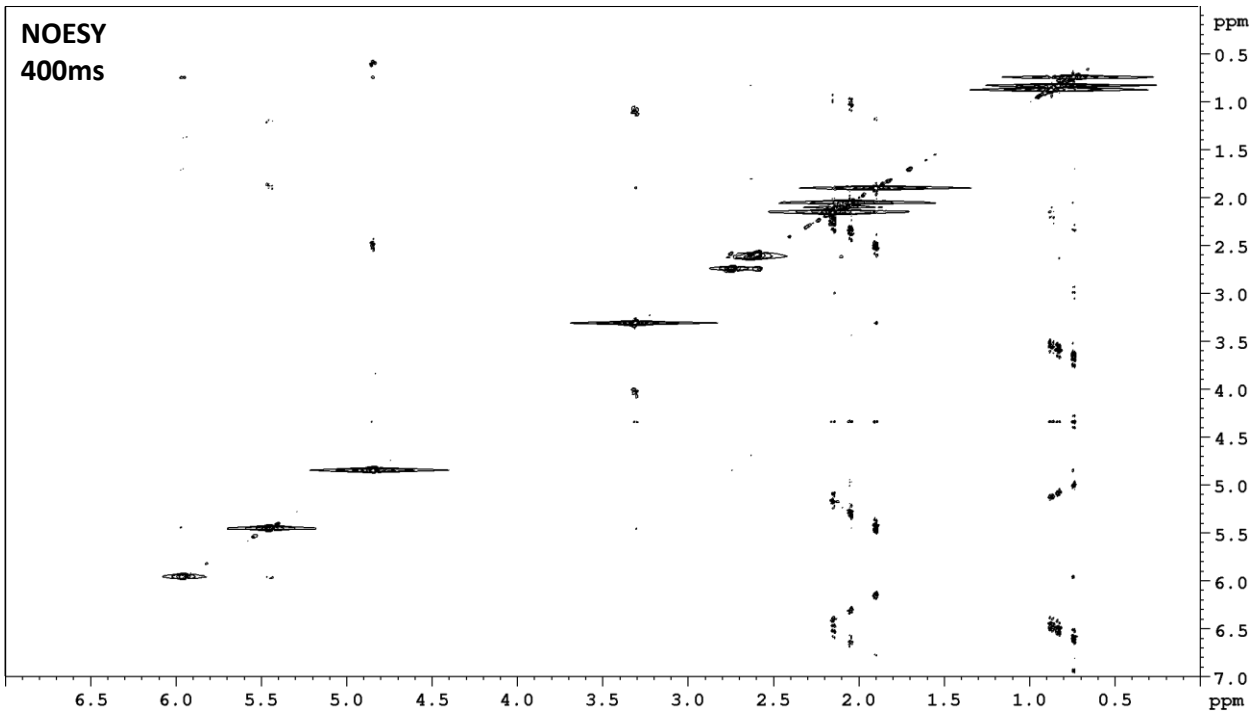
ppm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ppm