Supporting Information

Structural diversification of hapalindole and fischerindole natural products via cascade biocatalysis

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Table S1: Protein amino acid sequence
Protein sequences

FamD2
MNDVNRIRTDIINVAKTFGAEYSEKVLDEVFQVFGEQFADNSFMIRTSNKQPDKLGCYFRYHEE
DESQLGLAWDIARKSGLLSDQGRPVDQLIPEICETFPIMADGVDFDVKHGLAKIWQSIKGVVPV
QDAFKLSLPASVTTHSDFLKNHHLDALYAFGIDYHHSSVNLYFDTYHPKHHTSEYYKNLLQDLQ
FQPPSDELLELLTNNGEIALTFNFASPRIERLCFYLPFLNREAVPQNLLNPLLKKYINEAPALVDN
PGFILGWSFGPQGGKGTYTKVDVDYHGRTVPLFMKVHSQPLPKAADFALAQ

FamC1
MKRKLIVAVVFLIFICLGINTPAHATSAVSIPINNAGFENPFMDVVDDYTIDTPPGWTTYDPNNLV
PEKRTTWTSNNGVGYVGPGTQFYNQLAPEGRNIGYIYLSQNPGSGVAGFEQILDATLEPDTKY
TLTVDVGNLAGTFKGLSFAGFPGYRVELLAGDTVLAADHNNLFIKEGEFKTSTVTYTSTAKDLHL
GQKLGIRLVNLLQDKFSGLDFDNVRLTTEPTET

FimC5
MKRNFIIAAIVLLVYIFSGINVFANAASAVCIPIKNAGFEEPILQIEDDYTIDTPPGWITYDPGGLVP
AKRTRITSNNGVGYTGSNSEFYNHKAPEGRNVAFVYLAQEIGSGIAGLEQTLDAVLKPNTKYTL
TVDIGNSGGSFQGKTLDGFPGYRIELLAGDTVLAADHNTLYIKEKDFKSTTVTFTATPESPYLGQ
HLGIRLINPLQGKFSGVDFDNVRLTAEPAET

HpiC1
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VPEKRTTWTSNNGVGYVGPGTQFYNQLAPEGRNIGYIYLAQKPGSGVAGFEQILDATLEPDTK
YTLKVDVGNFGGEFQKISLAGFPGYRVELLAGDTVLAADHNNLYIKDGEFKTSTVTFTATPDNP
YLDQKLGIRLINLLQGTFSGLDFDNVRLTVEPAQT

HpiC1_Y101F
MGSSHHHHHHSSGLVPRGSHMASTSVVSIPINNAGFEDPFIEVVDDYTVDTPPGWTTYNPNNL
VPEKRTTWTSNNGVGYVGPGTQFYNQLAPEGRNIGFIYLAQKPGSGVAGFEQILDATLEPDTK
YTLKVDVGNFGGEFQKISLAGFPGYRVELLAGDTVLAADHNNLYIKDGEFKTSTVTFTATPDNP
YLDQKLGIRLINLLQGTFSGLDFDNVRLTVEPAQT

HpiC1_F138S
MGSSHHHHHHSSGLVPRGSHMASTSVVSIPINNAGFEDPFIEVVDDYTVDTPPGWTTYNPNNL
VPEKRTTWTSNNGVGYVGPGTQFYNQLAPEGRNIGYIYLAQKPGSGVAGFEQILDATLEPDTK
YTLKVDVGNSGGEFQKISLAGFPGYRVELLAGDTVLAADHNNLYIKDGEFKTSTVTFTATPDNP
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VPEKRTTWTSNNGVGYVGPGTQFYNQLAPEGRNIGFIYLAQKPGSGVAGFEQILDATLEPDTK
YTLKVDVGNSGGEFQKISLAGFPGYRVELLAGDTVLAADHNNLYIKDGEFKTSTVTFTATPDNP
YLDQKLGIRLINLLQGTFSGLDFDNVRLTVEPAQT

HpiC1_L147F
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VPEKRTTWTSNNGVGYVGPGTQFYNQLAPEGRNIGYIYLAQKPGSGVAGFEQILDATLEPDTK

YTLKVDVGNFGGEFQKISFAGFPGYRVELLAGDTVLAADHNNLYIKDGEFKTSTVTFTATPDNP
YLDQKLGIRLINLLQGTFSGLDFDNVRLTVEPAQT

HpiC1_F138L

MGSSHHHHHHSSGLVPRGSHMASTSVVSIPINNAGFEDPFIEVVDDYTVDTPPGWTTYNPNNL
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YTLKVDVGNLGGEFQKISLAGFPGYRVELLAGDTVLAADHNNLYIKDGEFKTSTVTFTATPDNP
YLDQKLGIRLINLLQGTFSGLDFDNVRLTVEPAQT

HpiC1_V51I

MGSSHHHHHHSSGLVPRGSHMASTSVVSIPINNAGFEDPFIEVVDDYTIDTPPGWTTYNPNNL
VPEKRTTWTSNNGVGYVGPGTQFYNQLAPEGRNIGYIYLAQKPGSGVAGFEQILDATLEPDTK
YTLKVDVGNFGGEFQKISLAGFPGYRVELLAGDTVLAADHNNLYIKDGEFKTSTVTFTATPDNP
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YTLKVDVGNLGGEFQKISFAGFPGYRVELLAGDTVLAADHNNLYIKDGEFKTSTVTFTATPDNP
YLDQKLGIRLINLLQGTFSGLDFDNVRLTVEPAQT

Table S2: Mutagenic primers (5'→3')

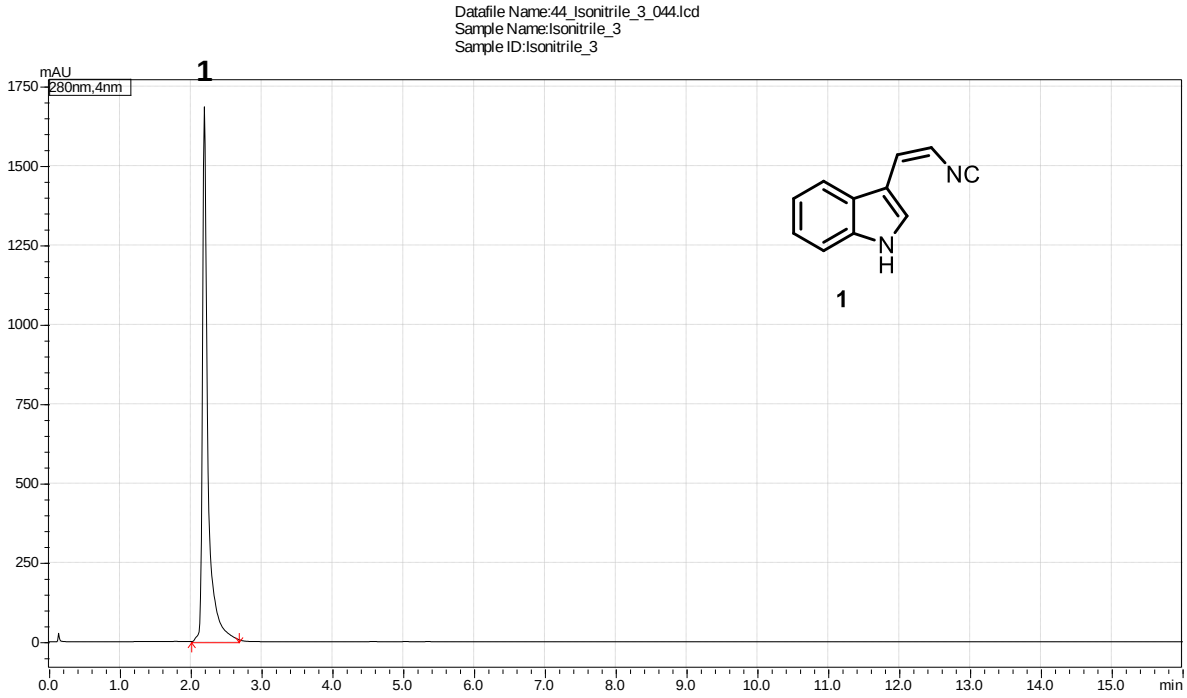
SN_HpiC1_F138S	CCCTGAAAGTGGACGTTGGTAACtctGGTGGCGAGTTTCAGAAAATTAGCC
SN_HpiC1_Y101F	CGCCGGAAGGTCGTAACATCGGCttcATTTATCTGGCGCAGAACCGGG
RMH_HpiC1_F138L	CACCCTGAAAGTGGACGTTGGTAACctgGGTGGCGAGTTTCAG
RMH_HpiC1_L147F	GGTGGCGAGTTTCAGAAAATTAGCtttGCGGGTTTTCCGGGCTACCG
RMH_HpiC1_V51I	CGAAGTGGTTGACGATTACACCattGATACCCCGCCGGGTTGGAC

Tables S3-S15: FamD2 TTN calculations (Compound #'s given)

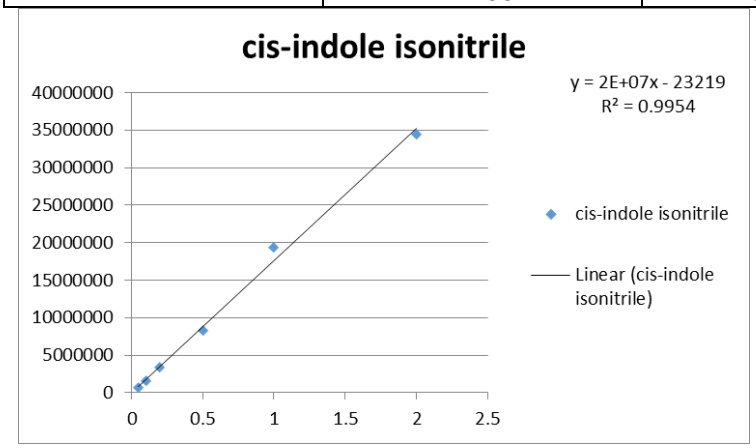
All TTN values were calculated by using (#mol substrate consumed/#mol of enzyme). Each starting concentration was 2 mM substrate and 1 µM FamD2 (1:2000 ratio) for 1 hour

Note: Molarity absorptivity of 3-GC and 2-GC intermediates is much lower than starting material at 280 nm.

Table S3: FamD2 TTN calculations for **1**

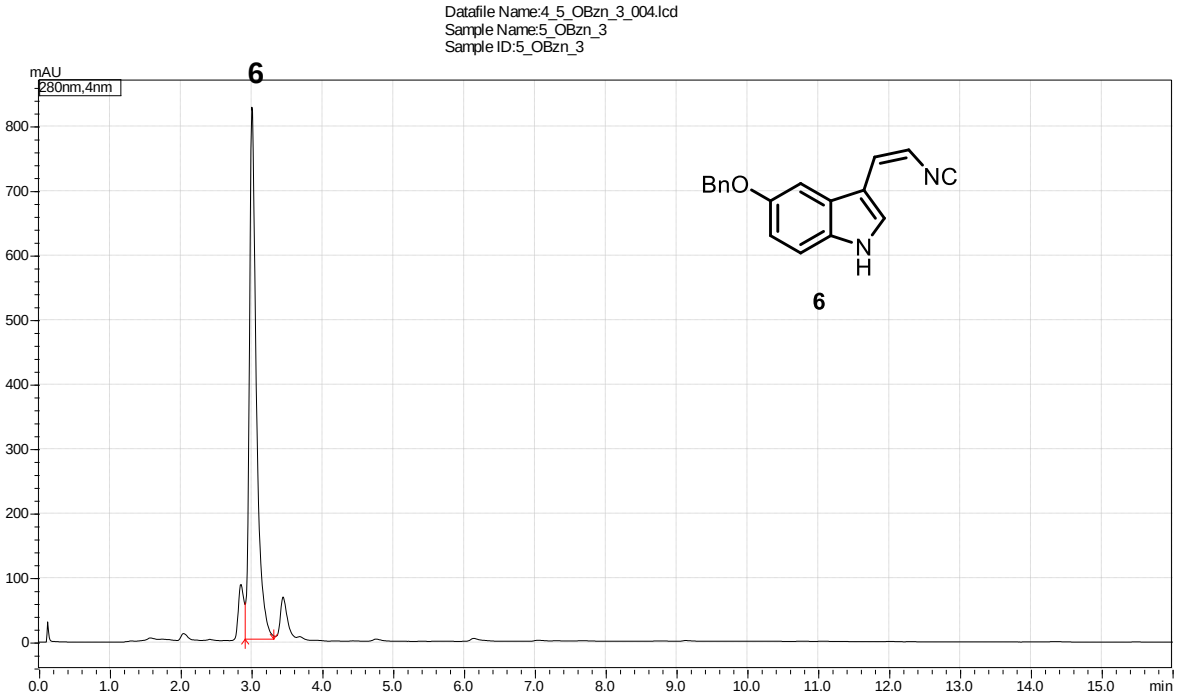


Peak#	Ret. Time (min)	Area	Height
1	2.199	8894557	1685057

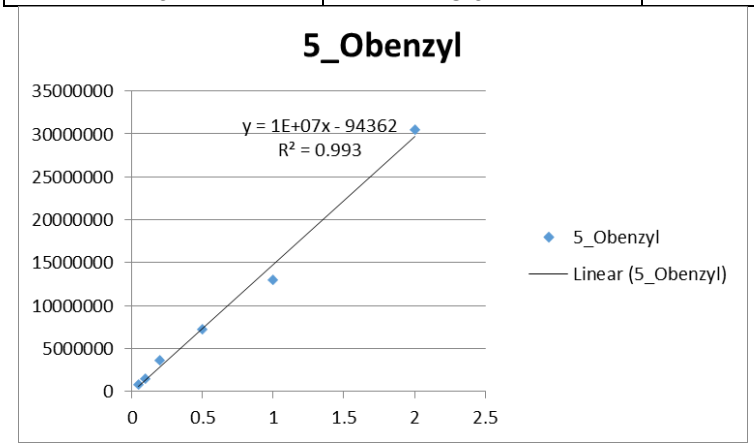


Concentration (mM)	Peak Area
0.05	653893
0.1	1554188
0.2	3331471
0.5	8326797
1	19411897
2	34535180
Eq: Area=17650000C-23219 TTN=(2-(8894557+23219)/17650000))*1000 TTN=1495	

Table S4: FamD2 TTN calculations for **6**

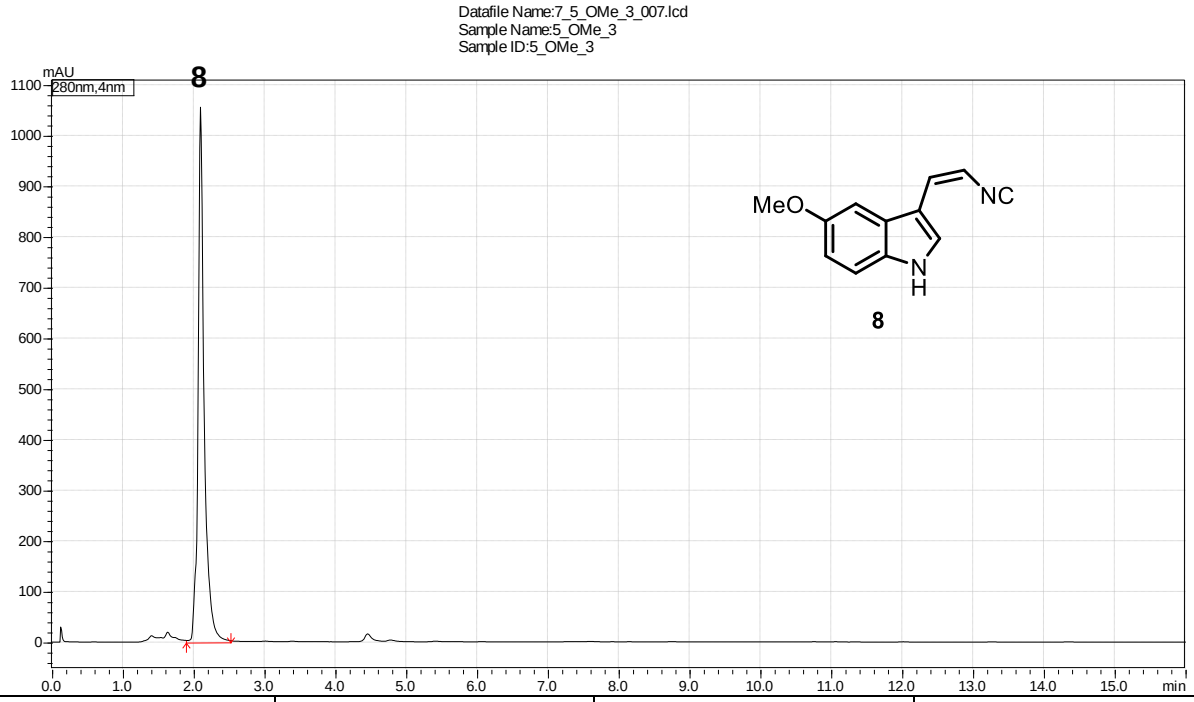


Peak#	Ret. Time (min)	Area	Height
6	3.012	5643864	823270

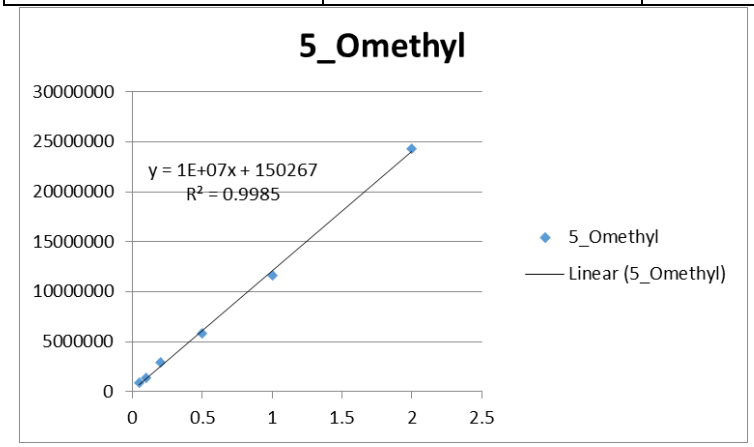


Concentration (mM)	Peak Area
0.05	845526
0.1	1552167
0.2	3612819
0.5	7210308
1	13033420
2	30538409
Eq: Area=14898000C-94361 TTN=(2-(5643864+94361)/14898000))*1000 TTN=1615	

Table S5: FamD2 TTN calculations for **8**

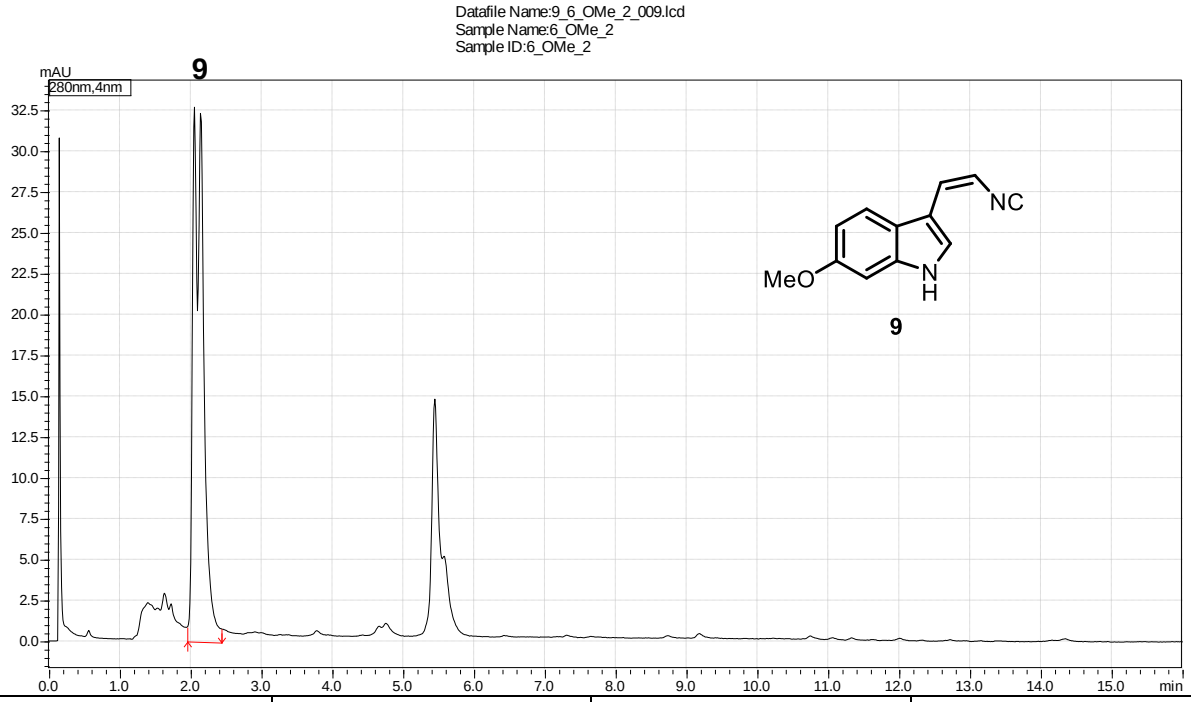


Peak#	Ret. Time (min)	Area	Height
8	2.103	6345503	1055592

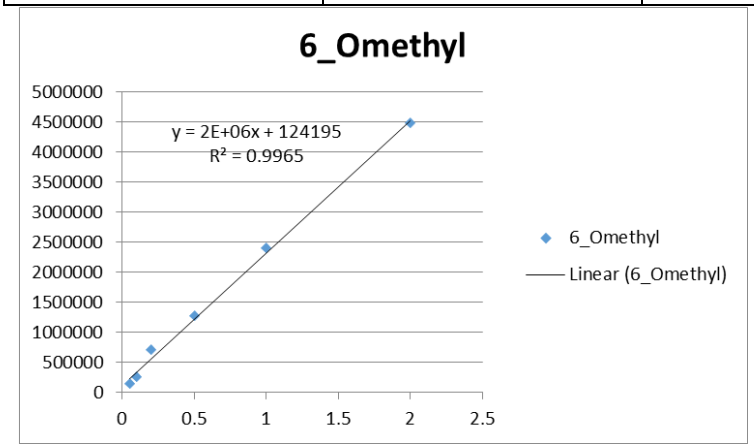


Concentration (mM)	Peak Area
0.05	880751
0.1	1350825
0.2	2934652
0.5	5795652
1	11602799
2	24324966
Eq: Area=11945000C+150267 TTN=(2-(6345503-150267)/11945000))*1000 TTN=1481	

Table S6: FamD2 TTN calculations for **9**

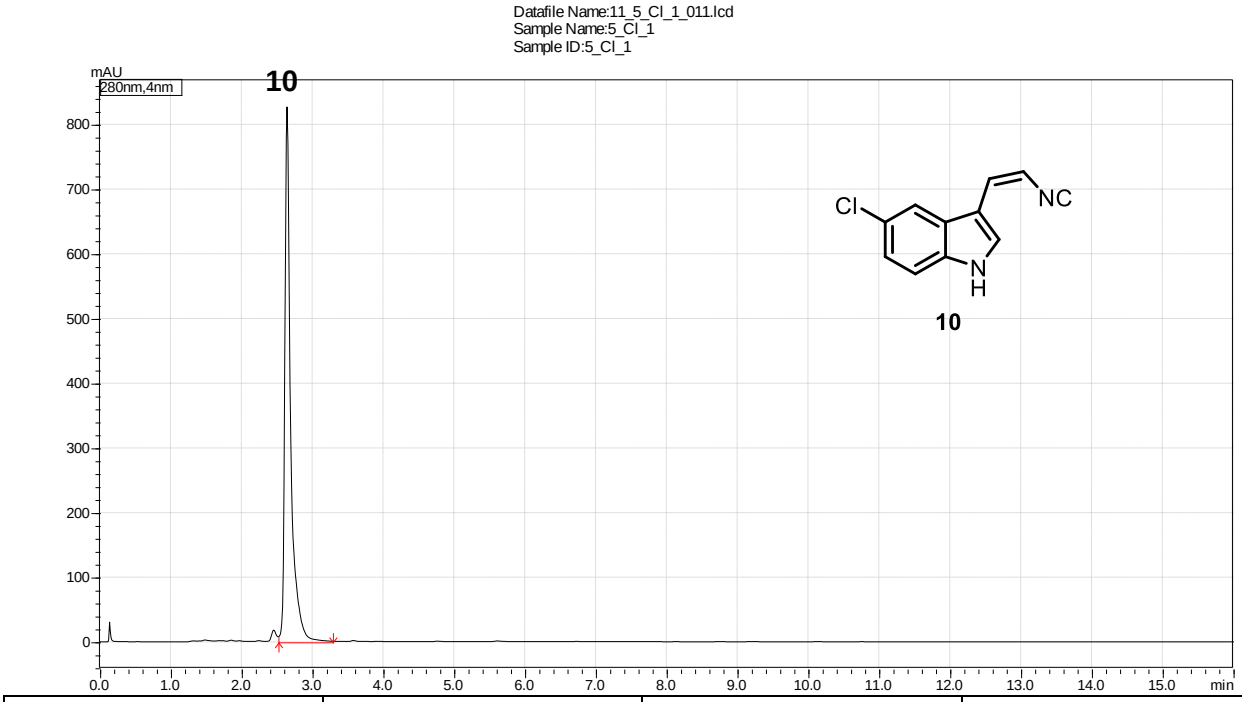


Peak#	Ret. Time (min)	Area	Height
9	2.057	339537	32684

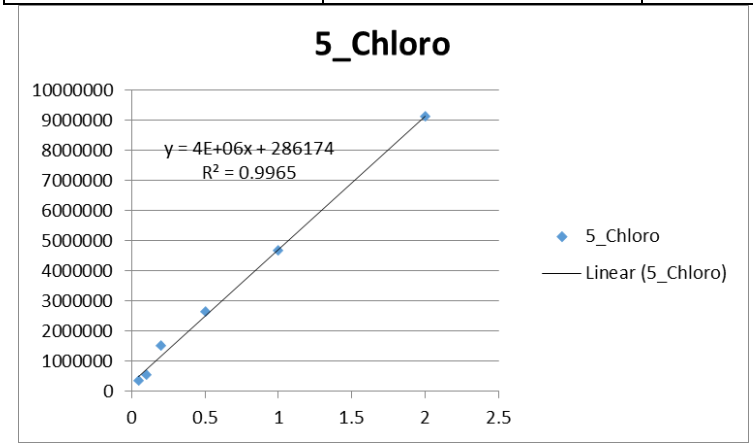


Concentration (mM)	Peak Area
0.05	126960
0.1	250899
0.2	702230
0.5	1269780
1	2384291
2	4465861
Eq: Area=2196100C+124195 TTN=(2-(339537-124196)/2196100))*1000 TTN=1902	

Table S7: FamD2 TTN calculations for **10**

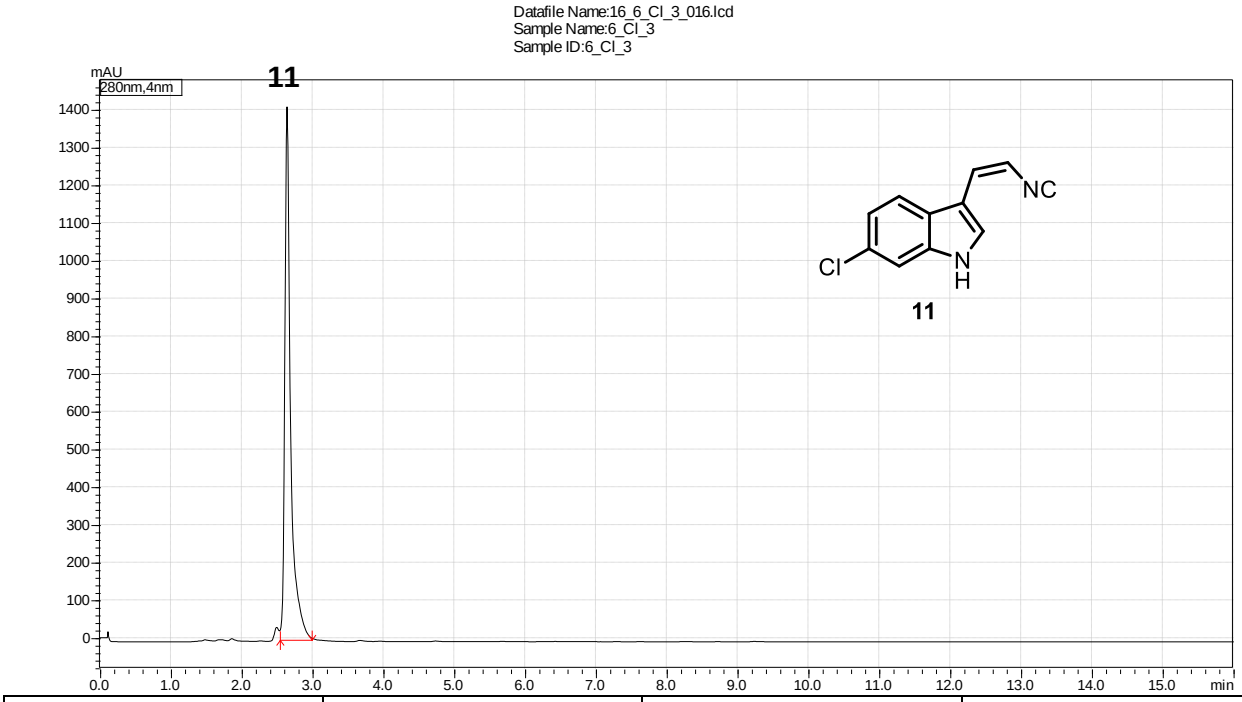


Peak#	Ret. Time (min)	Area	Height
10	2.645	4768339	827062

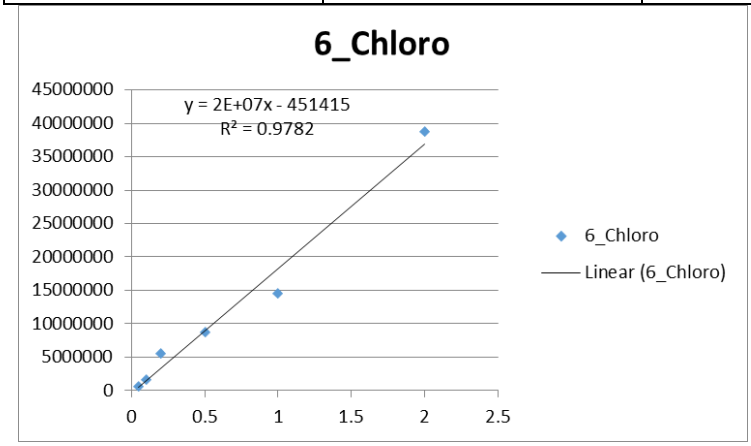


Concentration (mM)	Peak Area
0.05	338062
0.1	521558
0.2	1488020
0.5	2633172
1	4663983
2	9110272
Eq: Area=4254600C+286174 TTN=(2-(4768339-286175)/4254600))*1000 TTN=947	

Table S8: FamD2 TTN calculations for **11**

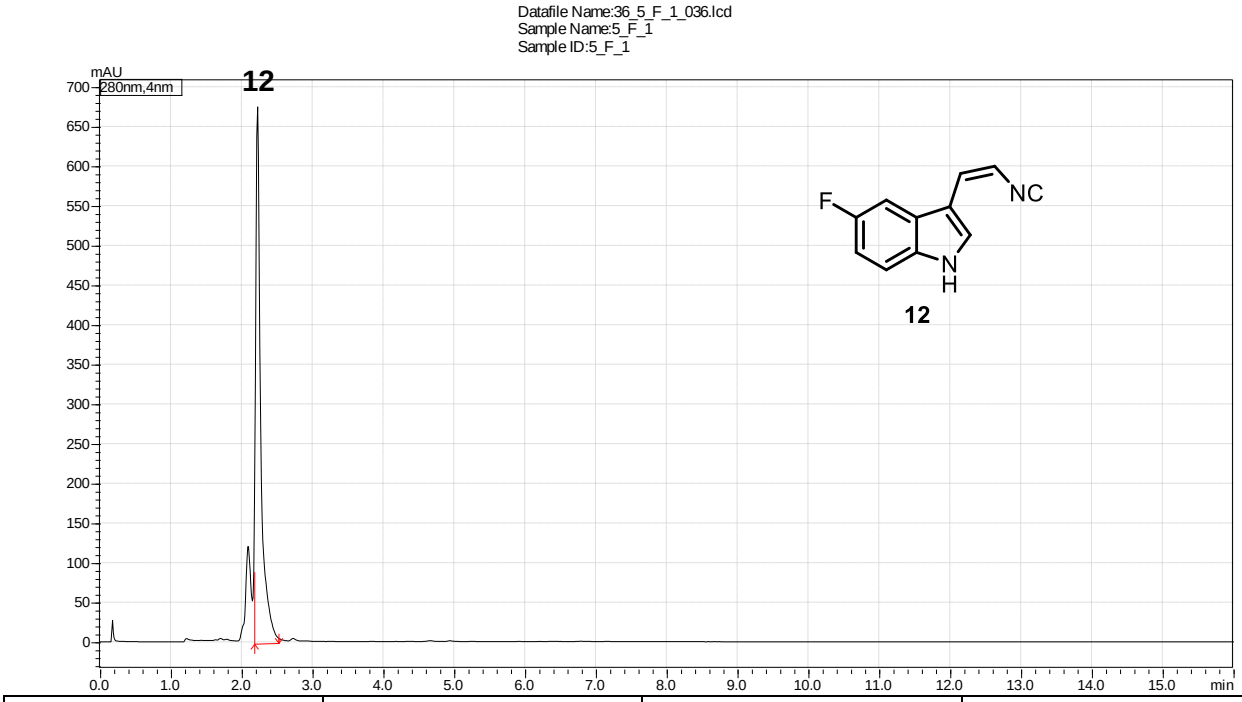


Peak#	Ret. Time (min)	Area	Height
11	2.645	8018316	1411263

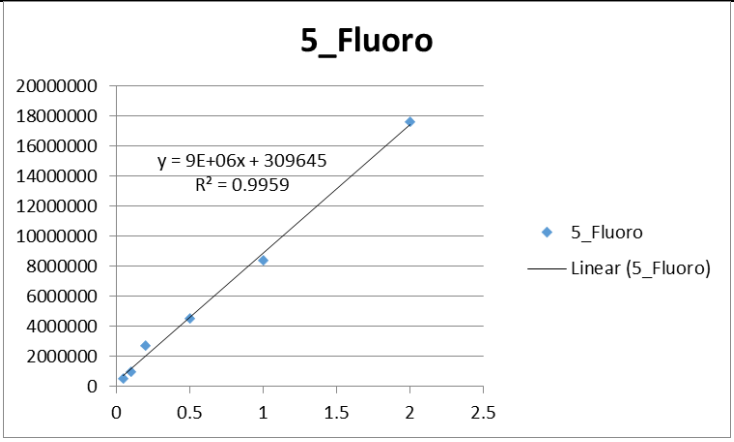


Concentration (mM)	Peak Area
0.05	550712
0.1	1523935
0.2	5421020
0.5	8628390
1	14447101
2	38655405
Eq: Area=18684000C-451415 TTN=(2-(8018316+451415)/18684000))*1000 TTN=1547	

Table S9: FamD2 TTN calculations for **12**

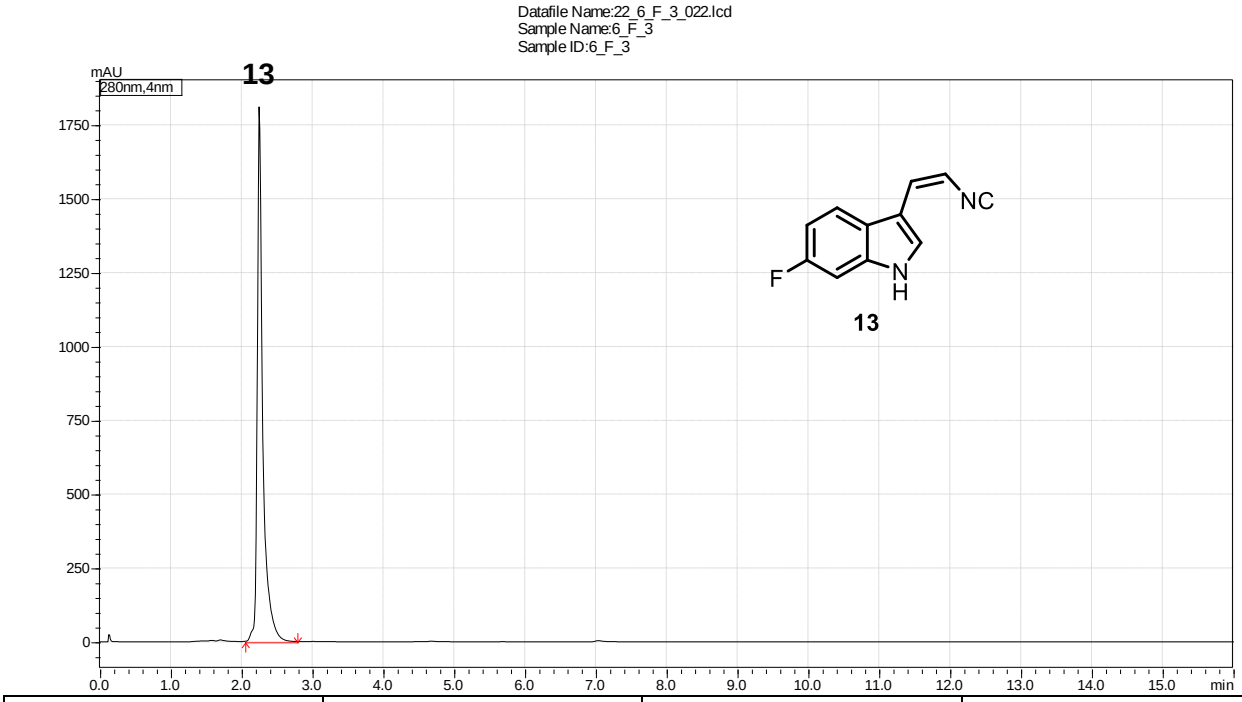


Peak#	Ret. Time (min)	Area	Height
12	2.228	3450687	676146

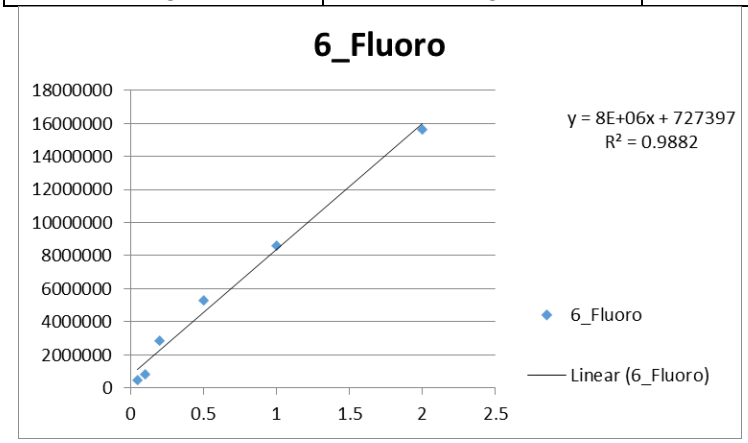


Concentration (mM)	Peak Area
0.05	524363
0.1	998106
0.2	2736403
0.5	4522171
1	8384625
2	17593782
Eq: Area=8372900C+309645 TTN=(2-(3450687-309645)/8372900))*1000 TTN=1625	

Table S10: FamD2 TTN calculations for **13**

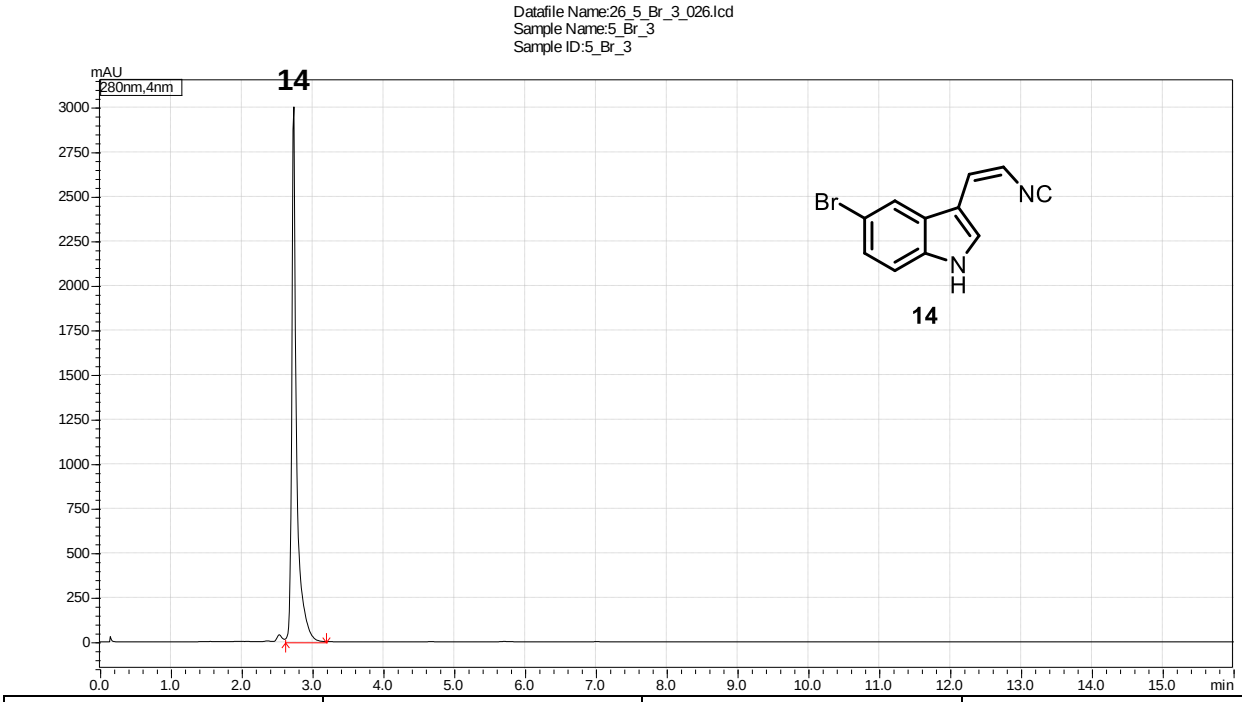


Peak#	Ret. Time (min)	Area	Height
13	2.254	9844920	1810594

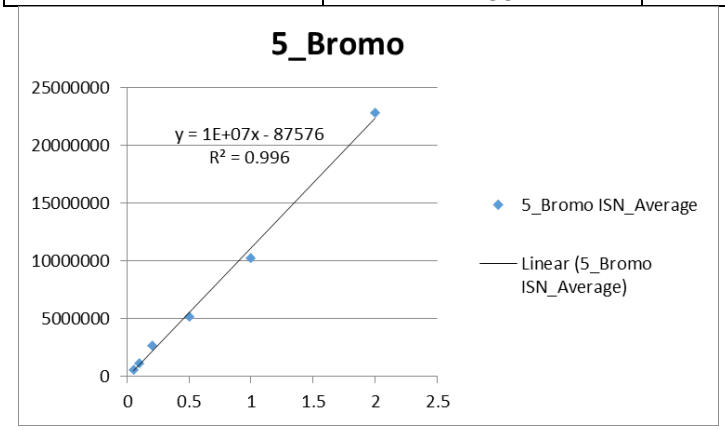


Concentration (mM)	Peak Area
0.05	463672
0.1	833895
0.2	2879462
0.5	5292420
1	8583214
2	15642615
Eq: Area=7618400C+727397 TTN=(2-(98944920-727397)/7618400))*1000 TTN=803	

Table S11: FamD2 TTN calculations for **14**

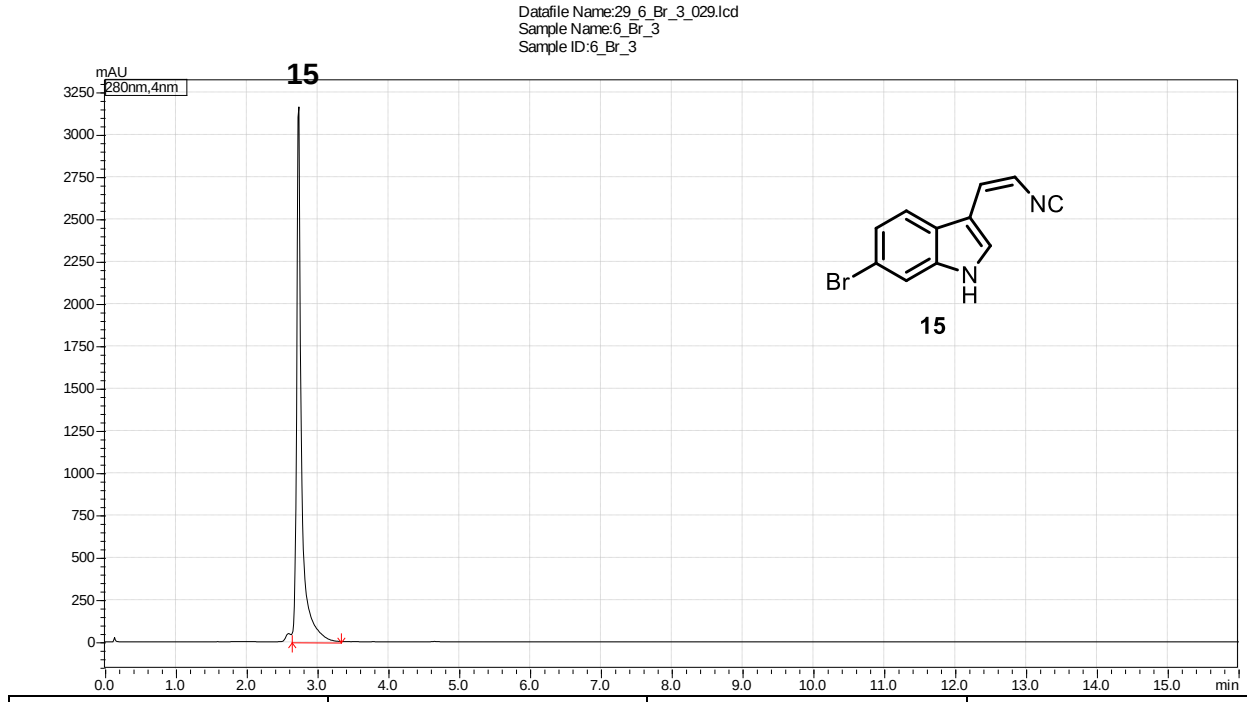


Peak#	Ret. Time (min)	Area	Height
14	2.738	13892693	3002168

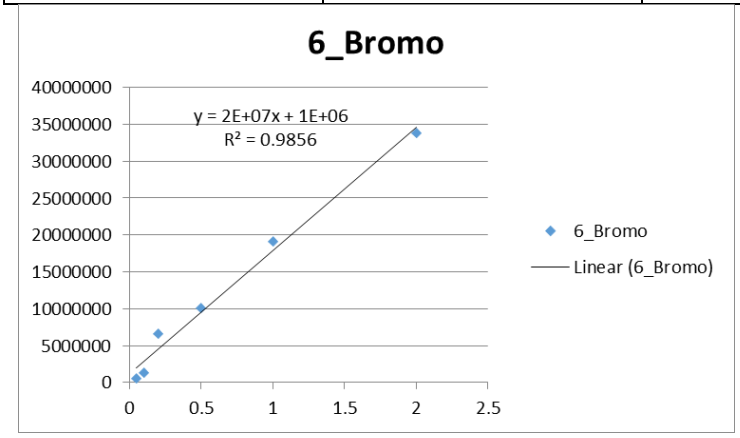


Concentration (mM)	Peak Area
0.05	574234
0.1	1172302
0.2	2680616
0.5	5195618
1	10238688
2	22839230
Eq: Area=11228000C-97576 TTN=(2-(13892693+97576)/11228000))*1000 TTN=755	

Table S12: FamD2 TTN calculations for **15**

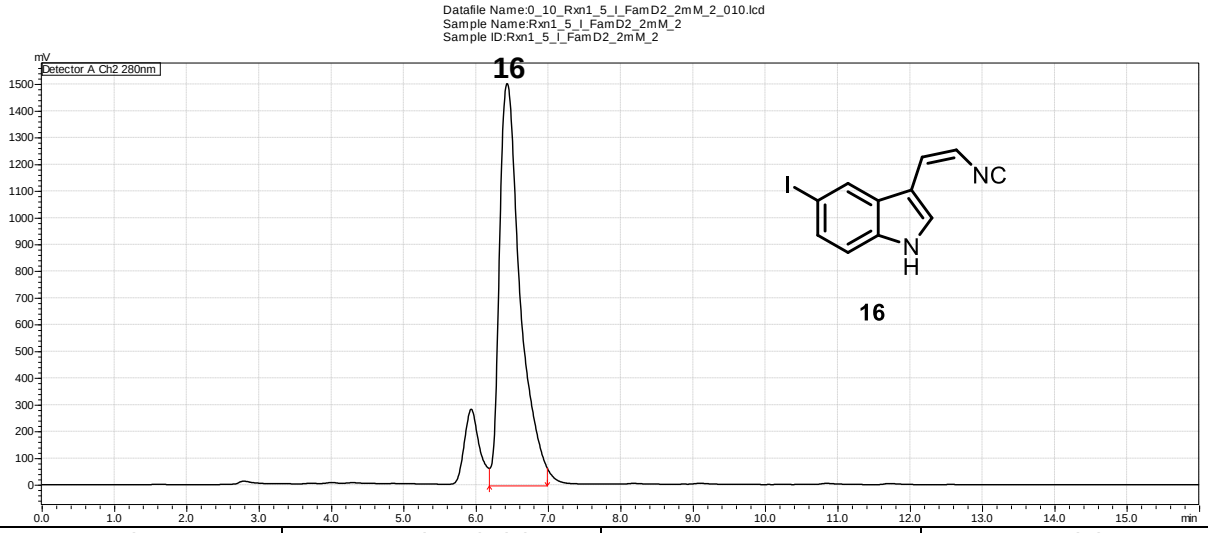


Peak#	Ret. Time (min)	Area	Height
15	2.737	14992583	3162897

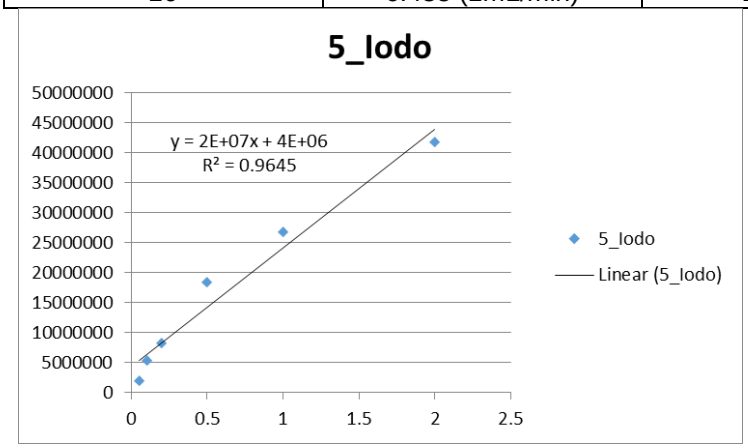


Concentration (mM)	Peak Area
0.05	523053
0.1	1281699
0.2	6598523
0.5	10125820
1	19156883
2	33784053
Eq: Area=16737000C+1171800 TTN=(2-(14992583-1171800)/16737000))*1000 TTN=1174	

Table S13: FamD2 TTN calculations for **16**

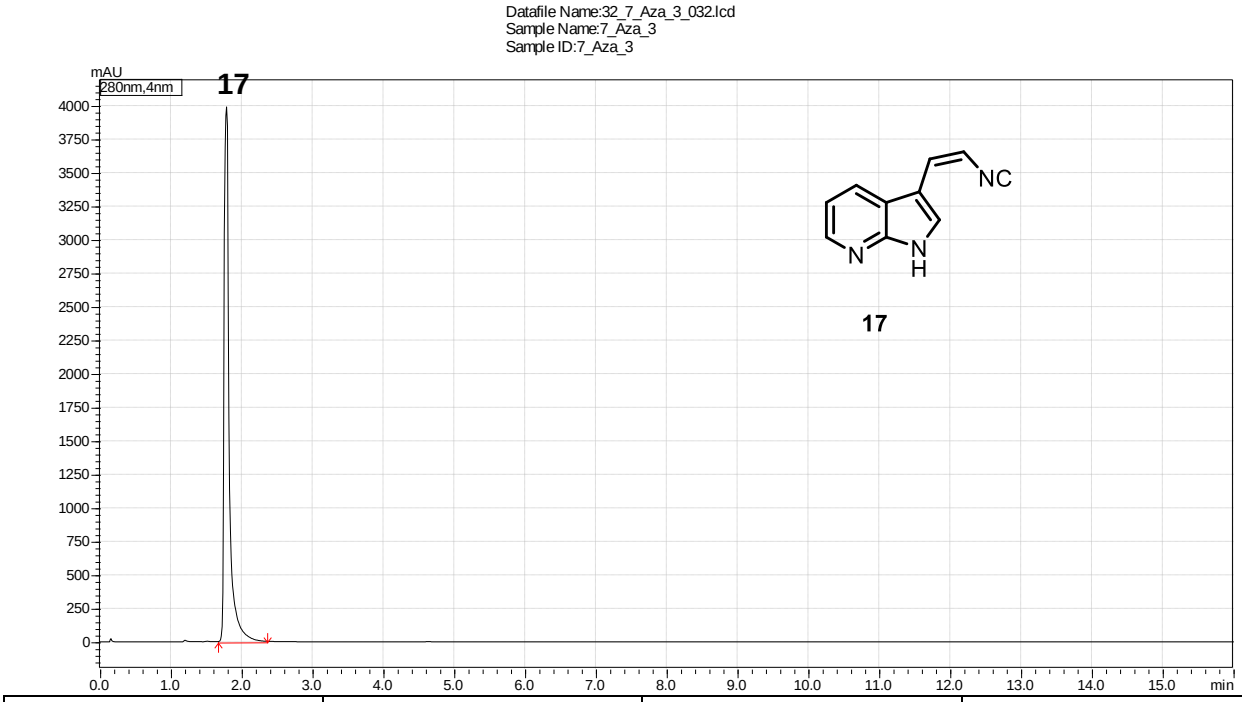


Peak#	Ret. Time (min)	Area	Height
16	6.435 (1mL/min)	29908556	1519361

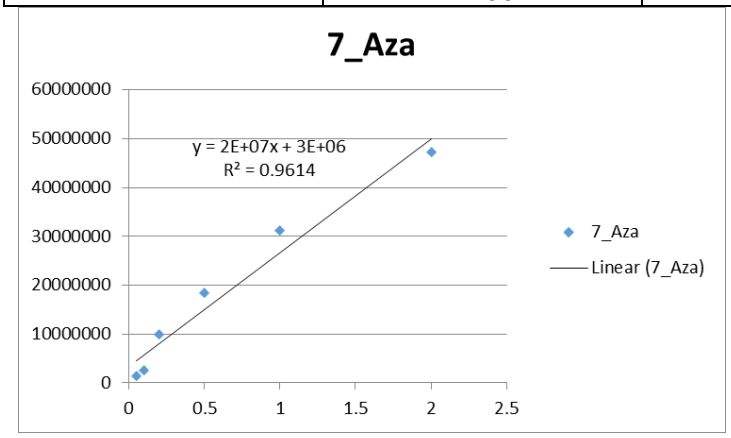


Concentration (mM)	Peak Area
0.05	2021327
0.1	5413201
0.2	8326473
0.5	18357085
1	26803087
2	41734933
Eq: Area=19734000C+4446700 TTN=(2-(29908566-4446700)/19734000))*1000 TTN=710	

Table S14: FamD2 TTN calculations for **17**

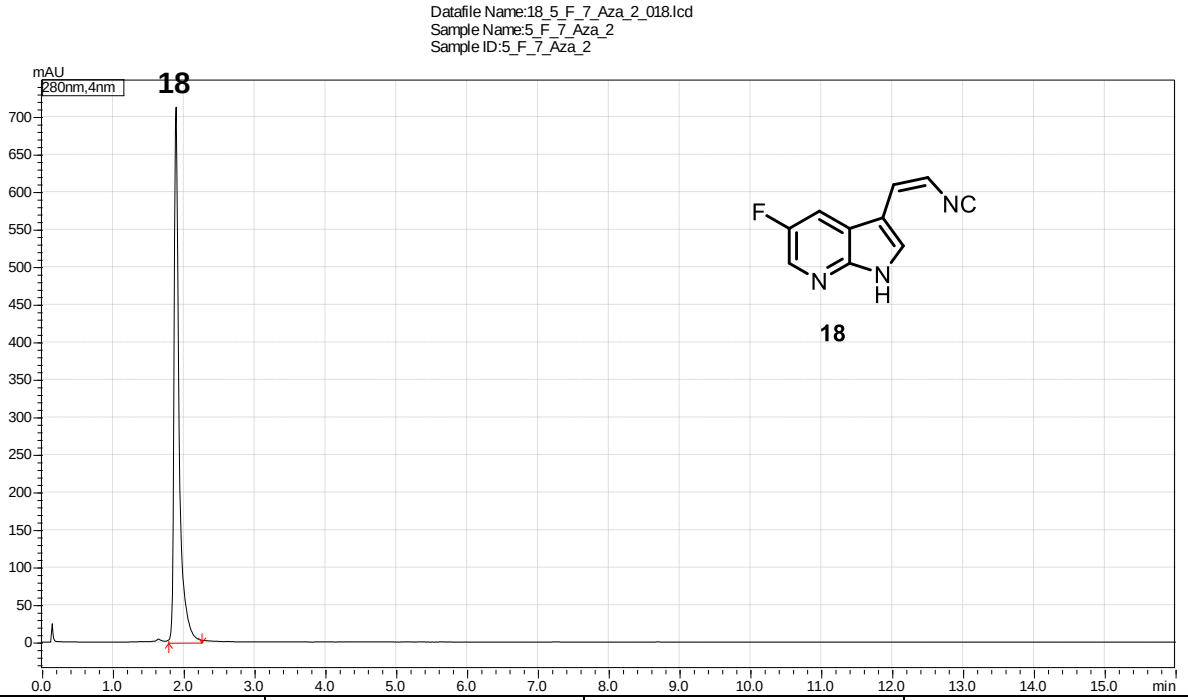


Peak#	Ret. Time (min)	Area	Height
17	1.790	20093276	3989928

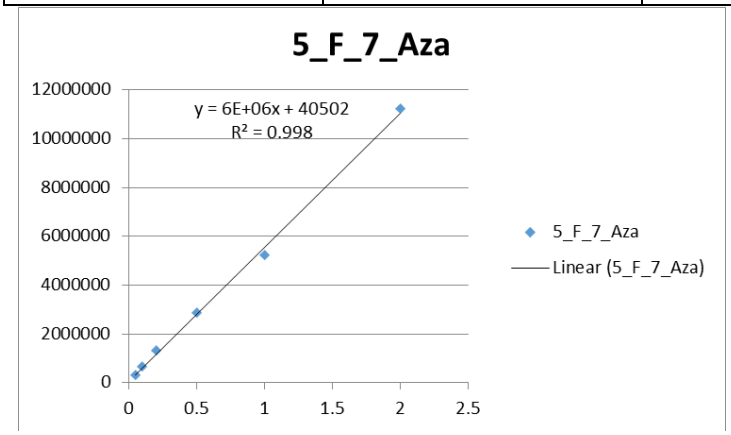


Concentration (mM)	Peak Area
0.05	1258424
0.1	2439309
0.2	9730293
0.5	18168987
1	31076307
2	47068189
Eq: Area=23351000C+3306500 TTN=(2-(20093276-3306500)/23351000))*1000 TTN=1281	

Table S15: FamD2 TTN calculations for **18**

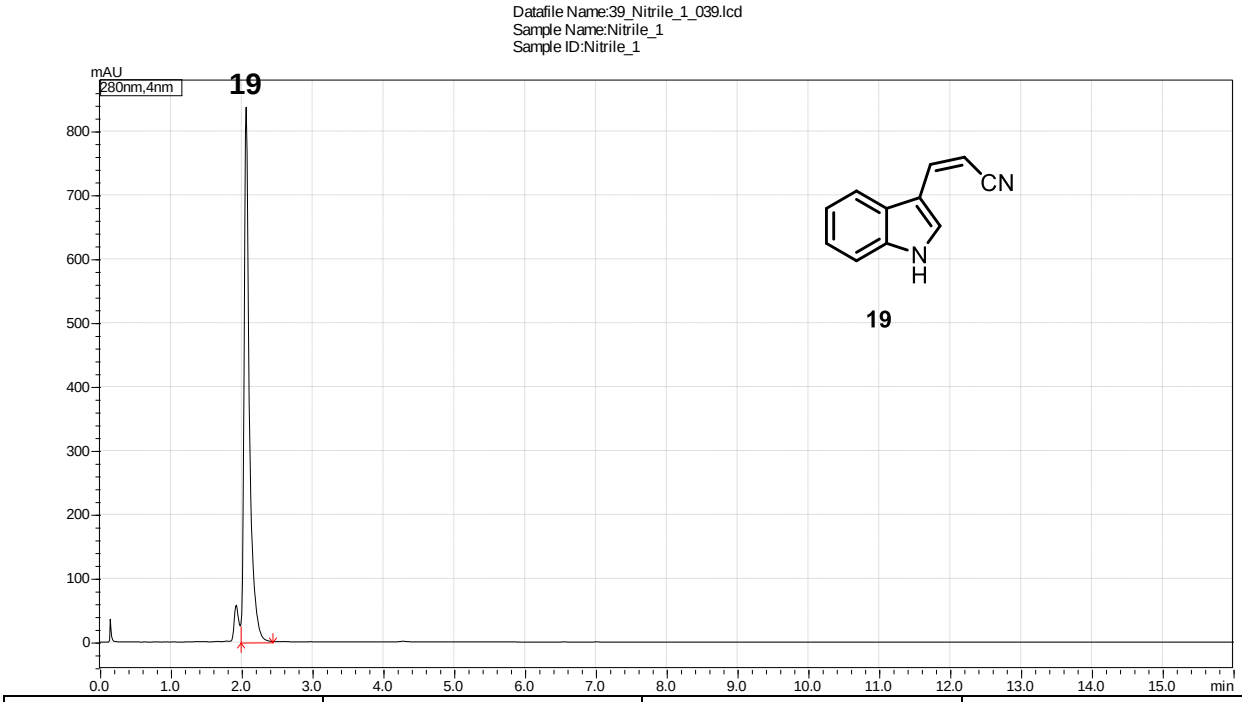


Peak#	Ret. Time (min)	Area	Height
18	1.896	3530558	712821

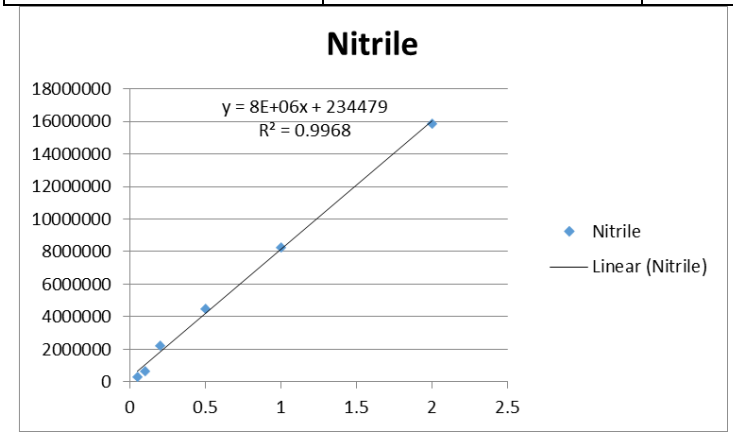


Concentration (mM)	Peak Area
0.05	283081
0.1	645116
0.2	1286867
0.5	2826221
1	5191694
2	11199120
Eq: Area=5503700C+40502 TTN=(2-(3530558-40502)/5503700))*1000 TTN=1366	

Table S16: FamD2 TTN calculations for **19**



Peak#	Ret. Time (min)	Area	Height
19	2.068	4373769	837043



Concentration (mM)	Peak Area
0.05	326968
0.1	628233
0.2	2231327
0.5	4492460
1	8254223
2	15871448
Eq: Area=7579000C+234479 TTN=(2-(4373769-234479)/7579000))*1000 TTN=1454	

Characterization Tables (Tables S17-S35)

12-*epi*-Hapalindole U Derivatives

Table S17: 5-Fluoro-12-*epi*-Hapalindole U (22)
Full characterization data[1]

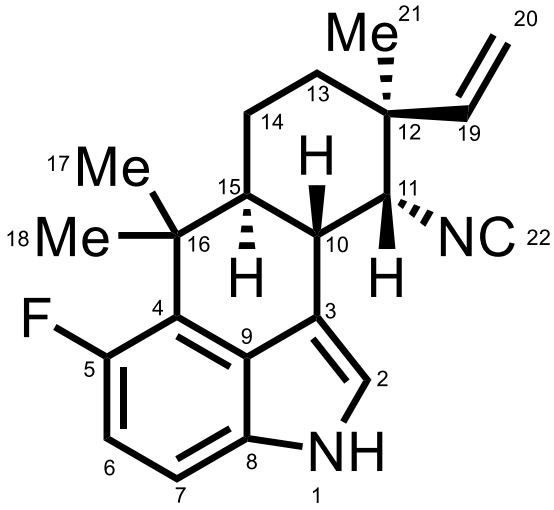


Table S18: 6-Fluoro-12-*epi*-Hapalindole U (23)
Full characterization data[1]

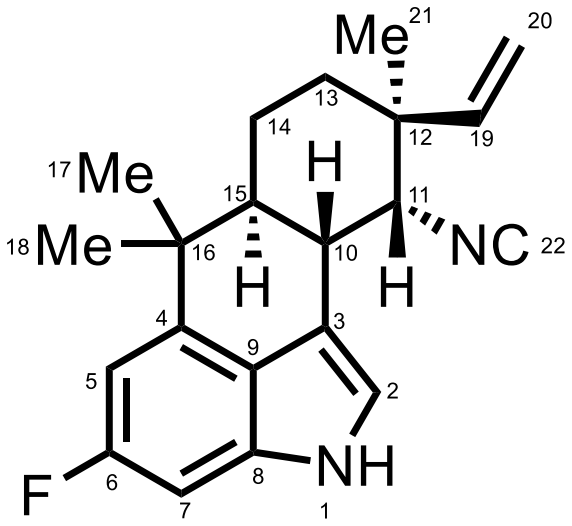
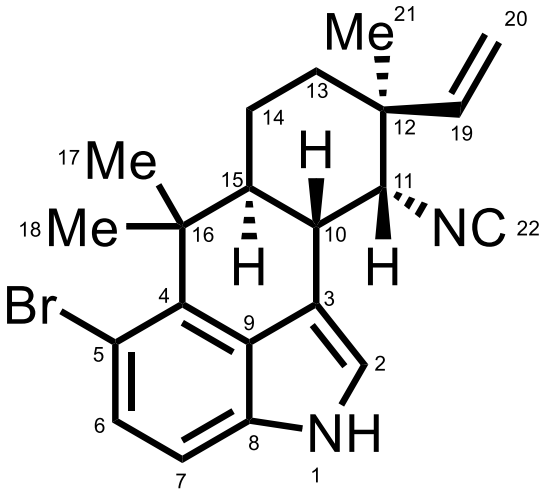
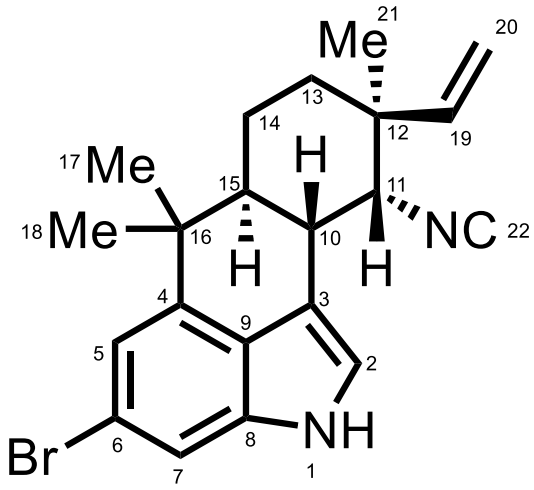


Table S19: 5-Bromo-12-*epi*-Hapalindole U (26)
$[\alpha]_D^{25}$=+10.5 (c=0.15, CH_2Cl_2)



Position	^{13}C shift (ppm)	^{1}H shift (ppm), multi (J)	COSY	HMBC
1		6.53, bs		
2	117.00	6.26, t, (2.0)	10	3,8,9
3	113.74			
4	137.84			
5	110.12			
6	130.05	7.52, d, (8.5)	7	4,5,8
7	110.62	6.59, d, (8.5)	6	5,9
8	133.68			
9	127.61			
10	34.00	2.83, d, (11.8)	11,15	3,15
11	63.18	3.88, s	10,14	3,10,12,14,15,16,19,22
12	39.66			
13	22.10	1.48, dd, (13.1, 3,6) & 1.29, td, (13.0, 3.5)	14	15,17,21
14	31.49	1.65, td, (13.9, 3.9) & 1.42, d, (14.2)	13	13,16,19
15	44.64	1.96, td, (12.0, 3.3)	10,14	10,16,17
16	39.51			
17	21.09	1.22, s		4,15,16,18
18	24.50	1.77, s		4,15,16,17
19	142.51	5.37, dd, (17.7, 11.1)	20	11,12,14
20	114.50	Cis 4.90, d, (11.0) Trans 4.83, d, (17.6)	19	12,19
21	28.21	1.17, s		11,12,15,19
22	160.92			

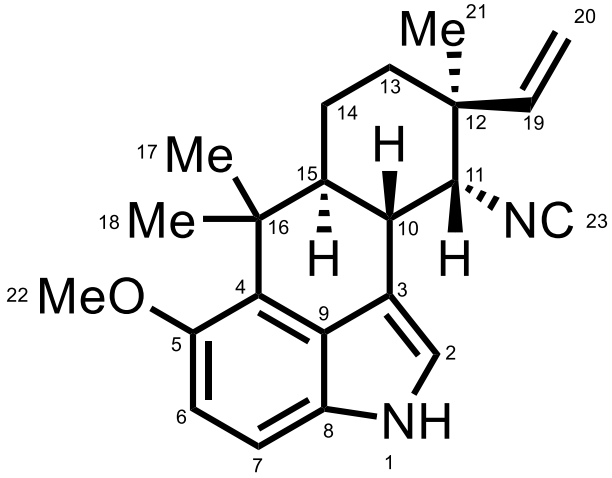
Table S20: 6-Bromo-12-*epi*-Hapalindole U (27)
$[\alpha]_D^{25}$=+6.1 (c=0.08, CH_2Cl_2)



Position	^{13}C shift (ppm)	^{1}H shift (ppm), multi (J)	COSY	HMBC
1		6.46, bs		
2	117.06	6.24, t, (1.9)		3,8,9
3	113.22			
4	142.74			
5	117.33	7.31, d, (1.9)		6,7,9,16
6	117.42			
7	111.94	7.16 (in solvent)		
8	135.10			
9	124.75			
10	34.81	2.92, d, (10.3)	11,15	3,15
11	63.43	3.85, d, (3.1)	10	3,10,12,13,15,19,22
12	39.78			
13	31.07	1.64, td, (13.8,3.9) & 1.42, dt, (14.3,3.7)	14	
14	21.58	1.39, dd, (13.0,3.5) & 1.26, qd, (13.0,3.7)	13,15	
15	43.49	1.88, td, (12.0,3.5)	10,14	10,14,16,18
16	37.41			
17	24.07	1.10, s		4,15,16,18
18	24.94	0.85, s		4,15,16,17
19	142.49	5.39, dd, (17.7,11.0)	20	11,12,13
20	114.51	(cis) 4.91, d, (11.0) (trans) 4.84, d, (17.7)	19	12,19,21
21	28.23	1.16, s		11,12,13,19
22	160.89			

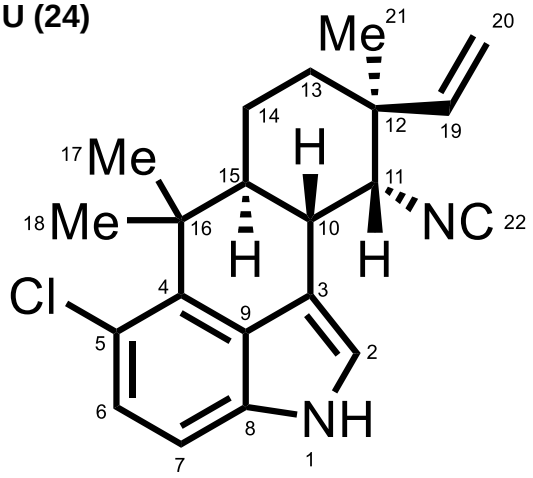
Table S21: 5-Methoxy-12-*epi*-Hapalindole U (28)

$[\alpha]_D^{25}$=+7.4 (c=0.06, CH_2Cl_2)



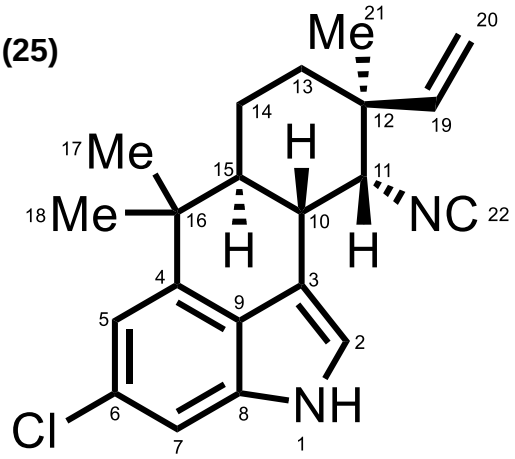
Position	^{13}C shift (ppm)	^{1}H shift (ppm), multi (J)	COSY	HMBC
1		6.57, bs	2	
2	117.40	6.40, t, (1.90)	1	3,4,9
3	113.53			
4	130.57			
5	150.60			
6	111.74	6.88, m	7	5,8,9
7	109.12	6.88, m	6	5,9
8	126.52			
9	127.46			
10	34.57	2.96, d, (11.6)	11, 15	3,15
11	63.47	3.96, s	10, 13, 15	3,10,12,15,13,19,21,23
12	39.77			
13	31.54	1.72 & 1.49, m	14	11,14,15,17
14	21.61	1.63 & 1.40, m	13	13,18
15	44.59	2.06, td, (12.0, 3.4)	10, 11, 14	10,16,17
16	37.84			
17	22.53	1.25, s	18	4,15,16,18
18	25.09	1.75, s	17	4,15,16,17
19	142.74	5.43, dd, (17.7, 10.9)	20	11,12,13,21,
20	114.36	4.92 (cis), d, (10.9) 4.87 (trans), d, (17.7)	19	12,19,21
21	28.32	1.20, s		11,12,13,14,19
22	57.12	3.59, s		5
23	160.72			

Table S22: 5-Chloro-12- *epi*-Hapalindole U (24)
$[\alpha]_D^{25}$=+3.2 (c=0.08, CH_2Cl_2)



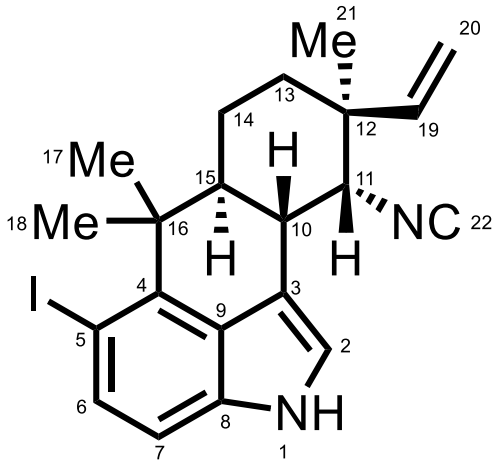
Position	^{13}C shift (ppm)	^{1}H shift (ppm), multi (J)	COSY	HMBC
1		6.52, bs		
2	117.27	6.29, d, (2.0)		3,8,9
3	113.76			
4	136.16			
5	121.85			
6	126.70	7.30, d, (8.4)	7	4,8,5
7	110.24	6.66, d, (8.4)	6	5,9
8	133.26			
9	127.69			
10	34.13	2.85, d, (11.7)	15	3
11	63.22	3.89, s	10,13	10,13,15,22
12	39.67			
13	31.48	1.66, td, (13.8,3.8) & 1.43, m	14	
14	21.87	1.50, dt, (13.3,3.5) & 1.30, m	10,13	
15	44.86	1.97, td, (11.9,3.2)	10,14	
16	39.10			
17	21.23	1.20, s		4,15,16,18
18	24.52	1.74, s		4,15,16,17
19	142.49	5.38, dd, (17.7,11.0)	20	11,12,13,
20	114.48	Cis 4.90, d, (11.0) Trans 4.83, d, (17.7)	19	12,19
21	28.21	1.18, s		11,12,13,19
22	160.90			

Table S23: 6-Chloro-12-*epi*-Hapalindole U (25)
$[\alpha]_D^{25}$=+2.6 (c=0.15, CH_2Cl_2)



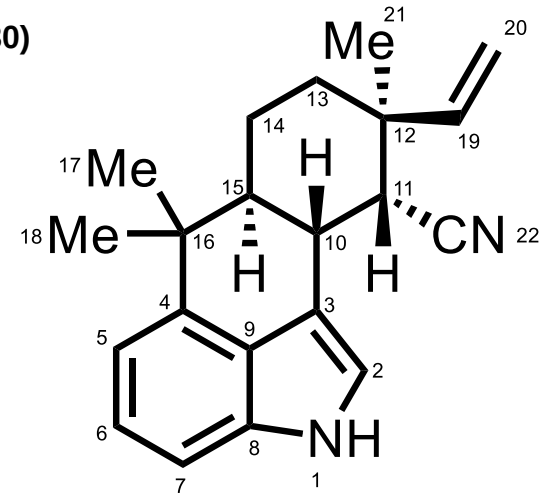
Position	^{13}C shift (ppm)	^{1}H shift (ppm), multi (J)	COSY	HMBC
1		6.48, bs		
2	116.70	6.26, s	1,10	3,4,9
3	112.76			
4	141.93			
5	108.58	7.02, s	7	4,7
6	124.07			
7	114.38	7.22, s	5	5
8	129.09			
9	134.19			
10	34.40	2.92, d, (11.5)	11, 15	
11	63.07	3.85, s	14,15	15
12	39.36			
13	21.17	1.39 & 1.25, m	14	
14	30.63	1.64, t, (13.0) & 1.41, m	13,15	13,19
15	43.09	1.89, t, (12.0)	10,11,14	
16	37.00			
17	23.67	1.12, s		4,15,16,18
18	24.52	0.86, s		4,15,16,17
19	142.07	5.38, dd, (17.7, 11.0)	20	11,12,14
20	114.10	Cis 4.92, d, (11.0) Trans 4.84, d, (17.7)	19	12,19
21	27.83	1.16, s		11,12,13,19
22	160.44			

Table S24: 5-Iodo-12-*epi*-Hapalindole U (29)
$[\alpha]_D^{25}$=+13.7 (c=0.10, CH_2Cl_2)



Position	^{13}C shift (ppm)	^{1}H shift (ppm), multi (J)	COSY	HMBC
1		6.54, bs	2	
2	116.47	6.21, s	1,10	3,8,9
3	113.46			
4	140.95			
5	81.03			
6	137.30	7.88, d, (8.5)	7	4,8
7	111.10	6.45, d, (8.4)	6	5,9
8	134.38			
9	127.61			
10	33.82	2.83, d, (11.8)	11,15	3,15
11	63.18	3.87, s	10,14	10,12,13,15,22
12	39.64			
13	31.50	1.63, td, (13.7, 3.6) & 1.39, m	14	12,14,19
14	22.43	1.44, m & 1.30, m	11,13,15	11,12,15
15	45.25	1.93, td, (12.0, 3.4)	10,14	10,16,17
16	39.37			
17	21.08	1.22, s	18	4,15,16,18
18	24.44	1.77, s	17	4,15,16,17
19	142.50	5.37, dd, (17.7, 11.0)	20	11,12,13
20	114.50	(cis) 4.89, d, (11.0) (trans) 4.82, d, (17.7)	19	12,19
21	28.20	1.17, s		11,12,13,19
22	161.00			

Table S25: 12-*epi*-hapalindole U Nitrile (30)
$[\alpha]_D^{25}$=+3.4 (c=0.13, CH_2Cl_2)



Position	^{13}C shift (ppm)	^{1}H shift (ppm), multi (J)	COSY	HMBC
1		6.66, bs		
2	116.64	6.38, d, (1.9)		3,8,9
3	114.20			
4	141.10			
5	113.48	7.08, d, (7.3)	6	7,9
6	123.54	7.29, t, (7.7)	5,7	4,8
7	108.76	6.97, d, (8.1)	6	5,9
8	134.60			
9	125.62			
10	33.34	3.04, ddd, (11.5, 4.4, 1.6)	11,15	3,13,15,22
11	44.16	3.09, dd, (4.3, 2.0)	10	3,10,12,13,15,22
12	38.98			
13	33.46	1.69, m & 1.53, m	14	15,19
14	22.01	1.53, m & 1.33, m	10,13	15
15	46.15	1.97, m	10,14	13,14,16,17
16	37.48			
17	25.31	1.00, s		4,15,16,18
18	24.43	1.30, s		4,15,16,17
19	143.71	5.44, dd, (17.7, 11.0)	20	10,11,12,13
20	114.08	Cis 4.93, d, (11.0) Trans 4.85, d, (17.7)	19	12,19
21	29.68	1.23, s		11,12,13,19
22	119.28			

12-*epi*-Fischerindole U Derivatives

Table S26: 5-Fluoro-12-*epi*-Fischerindole U (33)
Full characterization data[1]

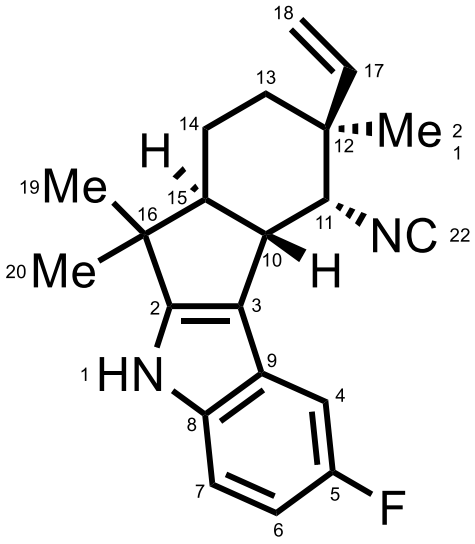


Table S27: 6-Fluoro-12-*epi*-Fischerindole U (37)
Full characterization data[1]

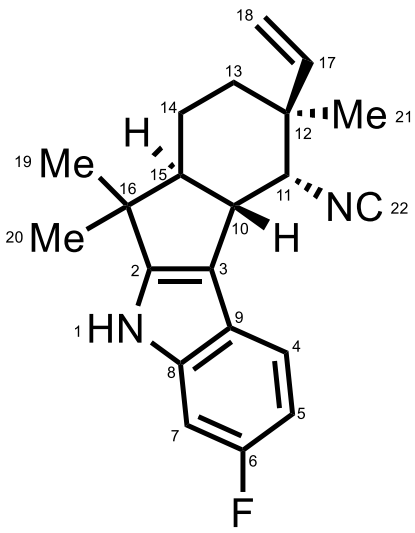
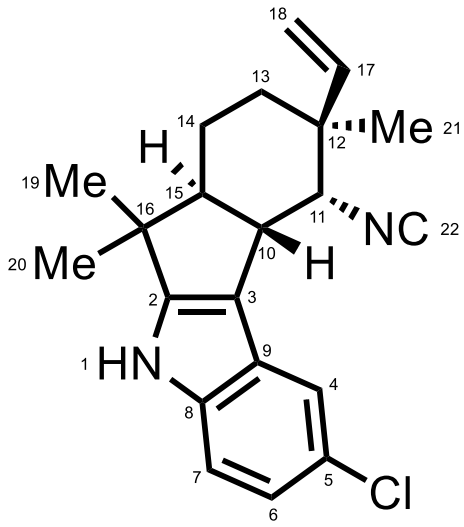
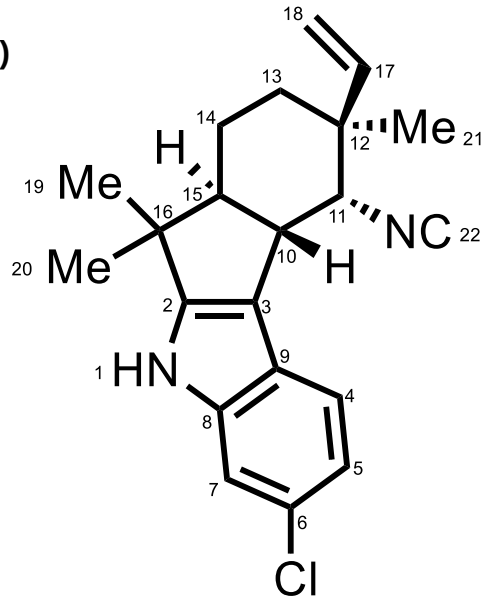


Table S28: 5-Chloro-12-*epi*-Fischerindole U (34)
$[\alpha]_D^{25}$=+9.8 (c=0.08, CH_2Cl_2)



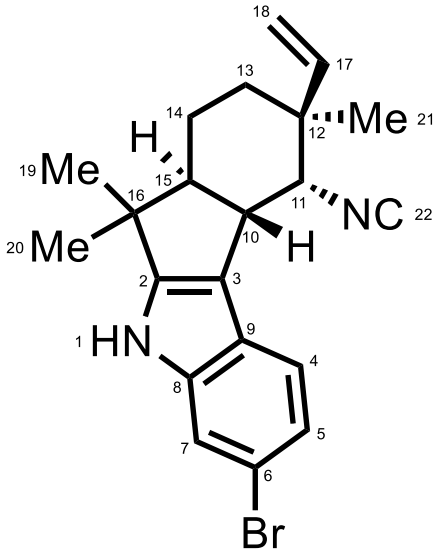
Position	^{13}C shift (ppm), C6D6	^{1}H shift (ppm), multi (J) C6D6	COSY	HMBC
1		6.48, bs		
2	153.58			
3	114.76			
4	118.24	7.68, d, (2.0)		3,5,6,8
5	125.40			
6	121.31	7.23, dd, (8.6,2.0)	6	4,8,9
7	113.07	6.81, d, (8.6)	7	4,5
8	138.40			
9	126.18			
10	42.37	2.86, dd,(10.8,4.3)	11	3,15
11	62.22	3.89, d,(2.9)	10,15	12,13,15
12	41.06			
13	31.81	1.54, m	15	11,12,14,15,17
14	20.82	1.33, m & 1.22, m	13,15	
15	55.16	2.35, ddd, (13.3,10.7,3.1)	11,14	16,19,20
16	40.16			
17	143.02	5.31, dd,(17.6,11.0)	18	11,12,13
18	114.19	(cis) 4.88, d, (10.9) (trans) 4.83, d, (17.6)	17	12,17
19	24.90	1.00, s		2,16,15,20
20	20.73	0.72, s		2,16,15,19
21	28.13	1.12, s		11,12,13,17
22	161.37			

Table S29: 6-Chloro-12-*epi*-Fischerindole U (38)
$[\alpha]_D^{25}$=+20.3 (c=0.05, CH_2Cl_2)



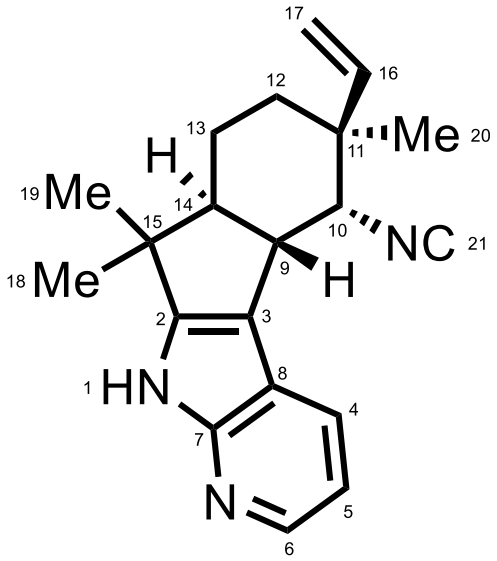
Position	^{13}C shift (ppm), C6D6	^{1}H shift (ppm), multi (J) C6D6	COSY	HMBC
1		6.39, bs		
2	152.70			
3	115.00			
4	112.25	7.16, in solvent peak	5	3
5	120.96	7.23, dd, (8.4, 1.9)	4	4,9
6	126.93			
7	119.44	7.17, s		
8	140.37			
9	122.93			
10	42.39	2.86, m	11,15	
11	62.34	4.00, d, (3.0)	10	12,13,15
12	41.02			
13	31.84	1.55, dd, (9.0, 3.8)	14	12,15
14	20.64	1.32, m & 1.22, m	10,13	13,15
15	55.30	2.34, ddd, (13.5, 10.7, 3.2)	10,14	
16	40.22			
17	143.03	5.32, dd, (17.6, 11.0)	18	11,12,13
18	114.20	4.87, m	17	12,17
19	24.92	0.99, s		2,15,16,20
20	20.79	0.72, s		2,15,16,19
21	28.15	1.15, s		11,12,13,17
22	161.38			

Table S30: 6-Bromo-12-*epi*-Fischerindole U (39)
$[\alpha]_D^{25}$=+14.8 (c=0.07, CH_2Cl_2)



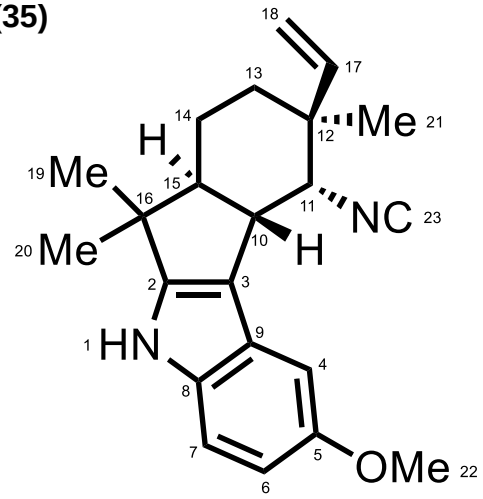
Position	^{13}C shift (ppm), C6D6	^{1}H shift (ppm), multi (J) C6D6	COSY	HMBC
1		6.41, bs		
2	152.65			
3	115.03			
4	119.82	7.12, d, (8.4)	5	6,8
5	123.55	7.35, dd, (8.3,1.8)	4	3,7,9
6	114.49			
7	115.22	7.29, d, (1.8)		5,6
8	140.78			
9	123.18			
10	42.38	2.86, dd, (11.1,4.1)	11,15	3
11	62.33	4.00, d, (3.0)	10	10,13,15,22
12	41.02			
13	31.83	1.55, m		11,12,15,17
14	20.61	1.22, m & 1.34, m	15	
15	55.31	2.33, ddd, (13.4,10.6,3.1)	10,14	16,19,20
16	40.20			
17	143.01	5.33, dd, (17.6,11.0)	18	11,12,13
18	114.20	(cis) 4.88, d, (11.6) (trans) 4.86, d, (18.1)	17	12,17
19	24.89	0.99, s		2,15,16,20
20	20.79	0.72, s		2,15,16,19
21	28.15	1.14, s		11,12,13,17
22	161.35			

Table S31: 7-Aza-12-*epi*-Fischerindole U (36)
$[\alpha]_D^{25}$=+17.2 (c=0.17, CH_2Cl_2)



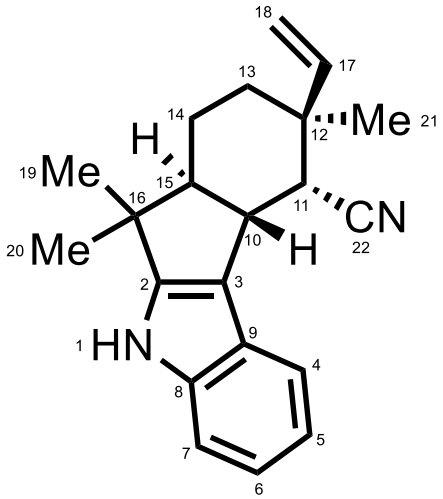
Position	^{13}C shift (ppm), C6D6	^{1}H shift (ppm), multi (J) C6D6	COSY	HMBC
1		10.42, bs		
2	153.16			
3	112.46			
4	126.02	7.55, dd, (7.7, 1.6)	5	3,6,7,8
5	116.25	6.89, dd, (7.7, 4.7)	4,6	6,8
6	141.04	8.35, dd, (4.7,1.6)	5	4,5,7
7	152.56			
8	117.63			
9	42.91	2.96, dd, (10.5,3.6)	10,14	3,14
10	62.47	4.06, d, (3.0)	9	9,12,14,16,21
11	41.03			
12	31.89	1.56, dd, (11.3,4.0)	13	14,16
13	20.75	1.35, dq, (17.8,6.3) & 1.24, dt, (12.7,3.7)	12,14	14
14	54.82	2.37, ddd, (13.4, 10.7,3.1)	9,13	13,15
15	40.63			
16	143.07	5.37, dd, (17.6,11.0)	17	10,11,12
17	114.22	(cis) 4.90, d, (11.2) (trans) 4.88, d, (17.9)	16	11,16,20
18	20.62	0.80, s		2,14,15,19
19	24.94	1.14, s		2,14,15,18
20	28.15	1.16, s		10,11,12,16
21	161.50			

Table S32: 5-Methoxy-12-*epi*-Fischerindole U (35)
$[\alpha]_D^{25}$=+36.6 (c=0.03, CH_2Cl_2)



Position	^{13}C shift (ppm), C6D6	^{1}H shift (ppm), multi (J) C6D6	COSY	HMBC
1		6.47, bs		
2	152.81			
3	114.78			
4	101.45	7.20, d, (2.4)		3,6,9
5	155.28			
6	110.76	7.05, dd, (8.8,2.4)		4,9
7	112.69	6.99, d, (8.8)		4,8,5
8	125.00			
9	135.34			
10	42.64	3.01, dd, (11.0,4.2)	11,15	3,15
11	62.66	4.18, d, (3.0)	10	10,12,13,15
12	41.07			
13	31.86	1.59, m	14	12,15,17
14	20.91	1.40, m & 1.27, dt, (12.3,3.6)	13	
15	55.25	2.42, ddd, (13.4,10.7,3.5)	10,14	16,19
16	40.11			
17	143.12	5.34, dd, (17.5,11.0)	18	12,13
18	114.10	(cis) 4.89, d, (1.5) (trans) 4.87, d, (8.4)	17	12,17
19	25.07	1.06, s		2,15,16,20
20	20.86	0.81, s		2,15,16,19
21	28.12	1.12, s		11,12,13,17
22	55.59	3.58, s		5
23	161.34			

Table S33: 12-*epi*-Fischerindole U Nitrile (40)
$[\alpha]_D^{25}$=+66.5 (c=0.03, CH_2Cl_2)

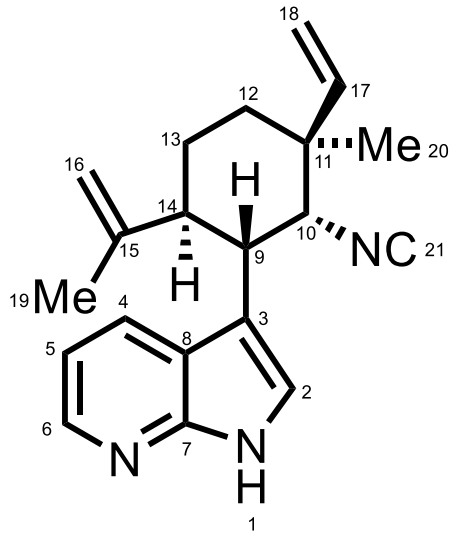


Position	^{13}C shift (ppm), C6D6	^{1}H shift (ppm), multi (J) C6D6	COSY	HMBC	NOESY
1		6.54, bs			
2	151.63				
3	115.55				
4	118.77	7.52, dd, (6.2,2.9)	5	5,8	
5	120.40	7.24, dd, (6.0,3.1)		4,7,8	
6	121.13	7.24, dd, (6.0,3.1)		4,7,8	
7	112.19	7.11, m	6	6,9	
8	140.23				
9	124.61				
10	40.93	2.98, dd, (10.6,4.0)	11,15	3,14,15,22	14a,20
11	43.04	3.25, d, (3.9)	10,13	12,13,15,17,22	21
12	40.40				
13	33.76	1.61, m	14	12,14,15,17	14,21
14	21.03	1.38 (a), m & 1.28 (b), m	13,15	12,21	
15	58.49	2.39, ddd, (13.3,10.5,3.1)	10,14	10,14,19	14b,19
16	40.32				
17	113.94	5.34, dd, (17.6,10.9)	18	12,18	18
18	144.19	Cis 4.88, d, (10.9) Trans 4.85, d, (17.6)	17	11,12,13	17
19	25.03	1.03, s		2,15,16,20	14b,20,21
20	20.72	0.76, s		2,15,16,19	14a,19
21	29.68	1.19, s		11,12,13,14,17	
22	118.91				

12-*epi*-Hapalindole C Derivatives

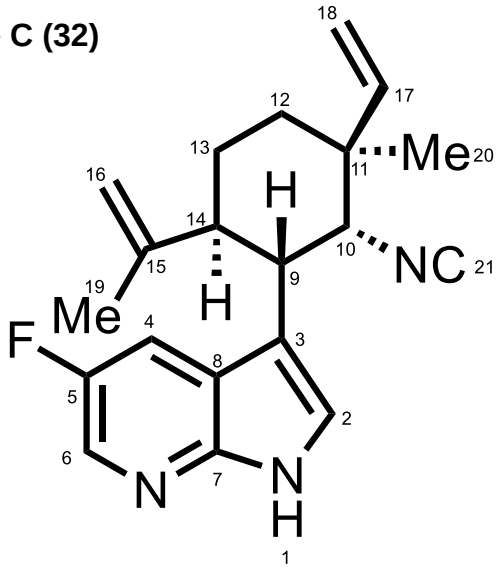
Table S34: 7-Aza-12-*epi*-Hapalindole C (31)

$[\alpha]_D^{25}$=+2.5 (c=0.27, CH_2Cl_2)



Position	^{13}C shift (ppm)	^{1}H shift (ppm), multi (J)	COSY	HMBC
1		7.72, bs		
2	124.20	6.88, s		3,7,8
3	112.65			
4	125.65	7.55, d, (7.9)	5	3,6,7,8
5	115.82	6.82, t (11.9, 6.9)	4,6	4,6,8
6	143.71	8.42, d, (3.9)	5	4,5,7
7	148.86			
8	119.24			
9	36.58	3.23, d, (12.2)		2,3,8,10,14
10	66.36	3.35, s		3,9,11,12,14,21
11	40.42			
12	30.81	1.77, td, (13.9, 3.5) & 1.37, m	13,20	11,13,14,17
13	28.69	1.56, m	12	9,12,14,15
14	43.79	2.87, td, (12.8, 3.5)	13	3,9,10,13,15,19
15	147.72			
16	112.68	4.72, s & 4.60, s	19	14,15,19
17	142.84	5.48, dd, (17.7, 10.9)	18	10,11,12
18	114.73	(cis) 5.01, d, (11.1) (trans) 4.84, d, (17.7)	17	11,17
19	18.82	1.32, s	16	14, 15,16
20	28.43	1.02, s		11,12,13,17
21	161.25			

Table S35: 5-Fluoro-7-Aza-12-*epi*-Hapalindole C (32)
$[\alpha]_D^{25}$=+17.3 (c=0.05, CH_2Cl_2)



Position	^{13}C shift (ppm) (Fluorine coupling, J)	^{1}H shift (ppm), multi (J)	COSY	HMBC
1		7.64, bs	2	
2	126.46	6.89, d, (2.6)	1	3,7,8
3	112.74			
4	111.38, d, (21)	7.31, dd, (9.1, 3.0)	6	3,5,7
5	156.21, d, (242)			
6	132.19, d, (29)	8.29, t, (2.1)	4	4,7
7	145.27			
8	119.07			
9	36.50	3.08, dq, (10.9, 3.4)	10,14	2,3,8,14
10	66.16	3.27, s	9,12	9,11,12,14
11	40.29			
12	30.72	1.73, td, (13.7, 4.5) & 1.37, m	10,13,20	11,17,20
13	28.54	1.52, m & 1.46, m	12,14,20	12,14,17
14	43.64	2.80, td, (12.0, 4.2)	9,13,20	3,9,13,15,16,19
15	147.05			
16	112.77	4.67, s & 4.58, s	19	15,19
17	142.54	5.39, dd, (17.7, 11.0)	18	10,11,12
18	114.91	(cis) 4.95, d, (11.0) (trans) 4.78, d, (17.7)	17	11,17
19	18.79	1.28, s	16	14,15,16
20	28.40	1.00, s	10,13,14	10,11,12,17
21	161.34			

Table S36: HpiC1→FamC1 mutagenesis percent conversions

Substrate	WT HpiC1	WT FamC1	V51I	F138L	L147F	F138LL147F
12	>99%	>99%	70%	92%	33%	56%
13	>99%	>99%	76%	31%	19%	>99%
10	>99%	20%	60%	26%	>99%	42%
11	77%	30%	13%	39%	81%	73%
14	85%	10%	67%	31%	18%	13%
15	90%	12%	11%	52%	27%	47%
8	14% tri, 52% tet	<1% tri, 19% tet	4% tri, 63% tet	<1% tri, 36% tet	<1% tri, 47% tet	<1% tri, 17% tet
9	N/A	N/A	N/A	N/A	N/A	N/A
16	30%	N/A	30%	8%	10%	N/A
19	>99%	60%	30%	40%	54%	35%
6	N/A	N/A	N/A	N/A	N/A	N/A
17	93%	70%	8%	9%	5%	5%
18	45%	N/A	3%	2%	<1%	N/A

Table S37: HpiC1→FimC5 mutagenesis percent conversions and hapalindole/fischerindole product ratio

Substrate	WT HpiC1	WT FimC5	Y101F	F138S	Y101FF138S
12	>99% 22	>99% 33	60% 22	9% 33, 29% 22	37% 33, 22% 22
13	>99% 23	>99% 37	57% 23	14% 37, 18% 23	27% 37, 5% 23
10	>99% 24	20% 34	36% 24	N/A	1% 34
11	77% 25	58% 38	59% 25	10% 38, 59% 25	12% 38, 10% 25
14	85% 26	N/A	18% 26	N/A	N/A
15	90% 27	>99% 39	34% 27	22% 39, 4% 27	50% 39, 20% 27
8	14% tri, 52% 28	>99% 35	2% tri, 18% 28	20% 35	30% 35
9	N/A	N/A	N/A	N/A	N/A
16	30% 29	N/A	17% 29	N/A	N/A
19	>99% 30	77% 40	18% 30	6% 40, 14% 30	10% 40, 3% 30
6	N/A	N/A	N/A	N/A	N/A
17	93% 31	59% 36 , 39% 31	13% 31	10% 36, 10% 31	13% 36, 6% 31
18	45% 32	14% 32	73% 32	24% 32	24% 32

Figures S1-S11: HpiC1→FimC5 mutagenesis HPLC traces
Note: HPLC traces do not represent best possible conversion

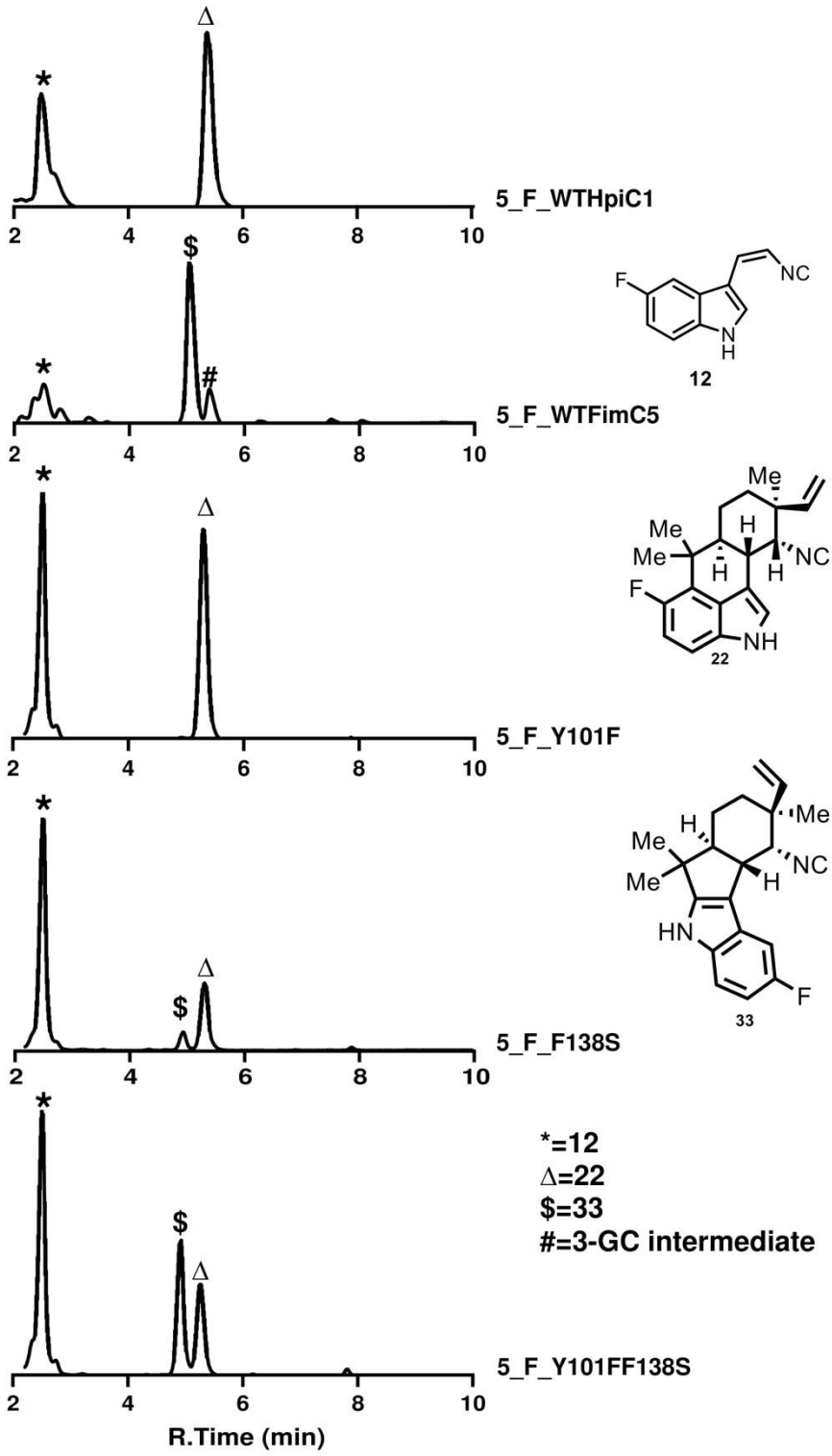


Figure S1: HpiC1→FimC5 mutagenesis results for substrate **12**

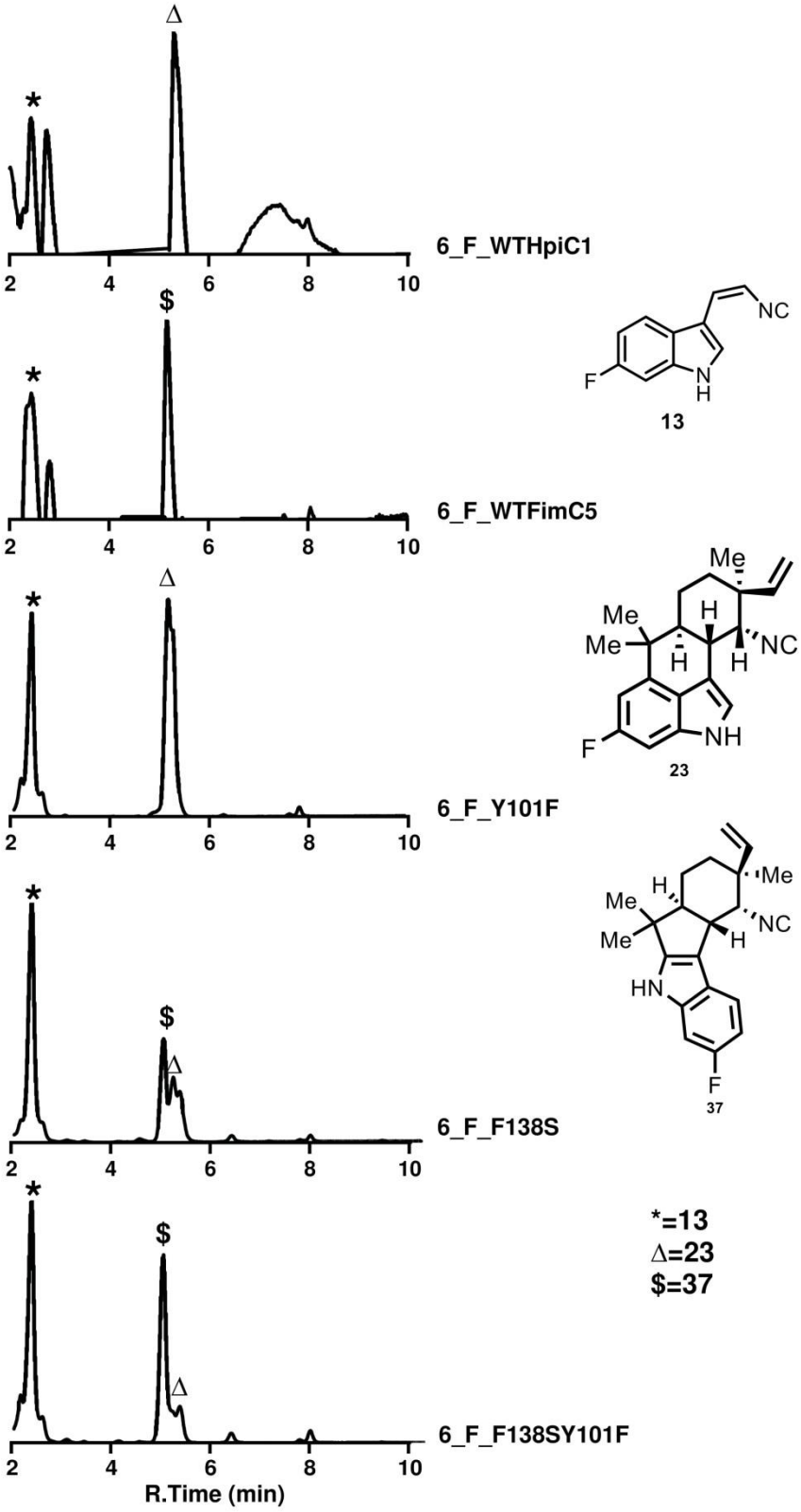


Figure S2: HpiC1→FimC5 mutagenesis results for substrate **13**

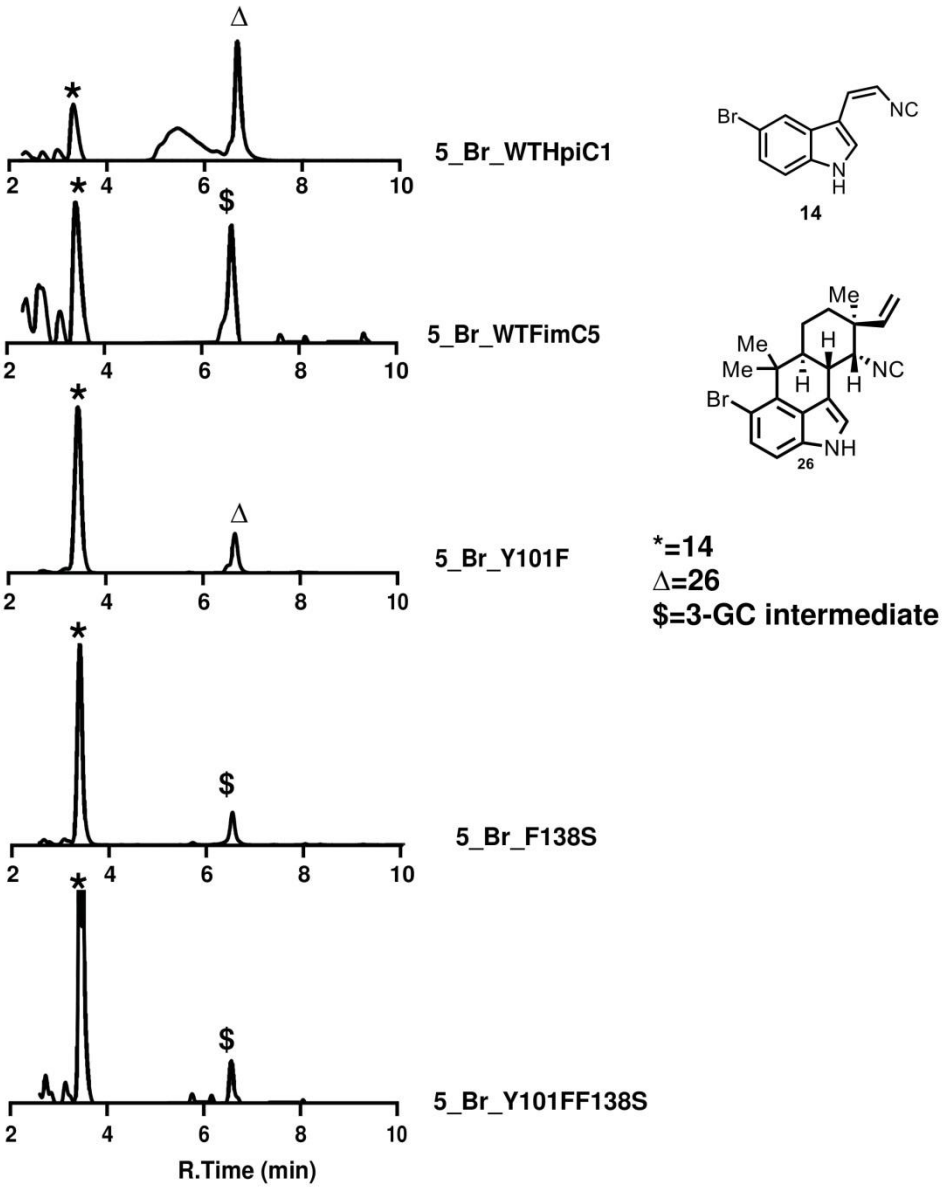


Figure S3: HpiC1→FimC5 mutagenesis results for substrate **14**

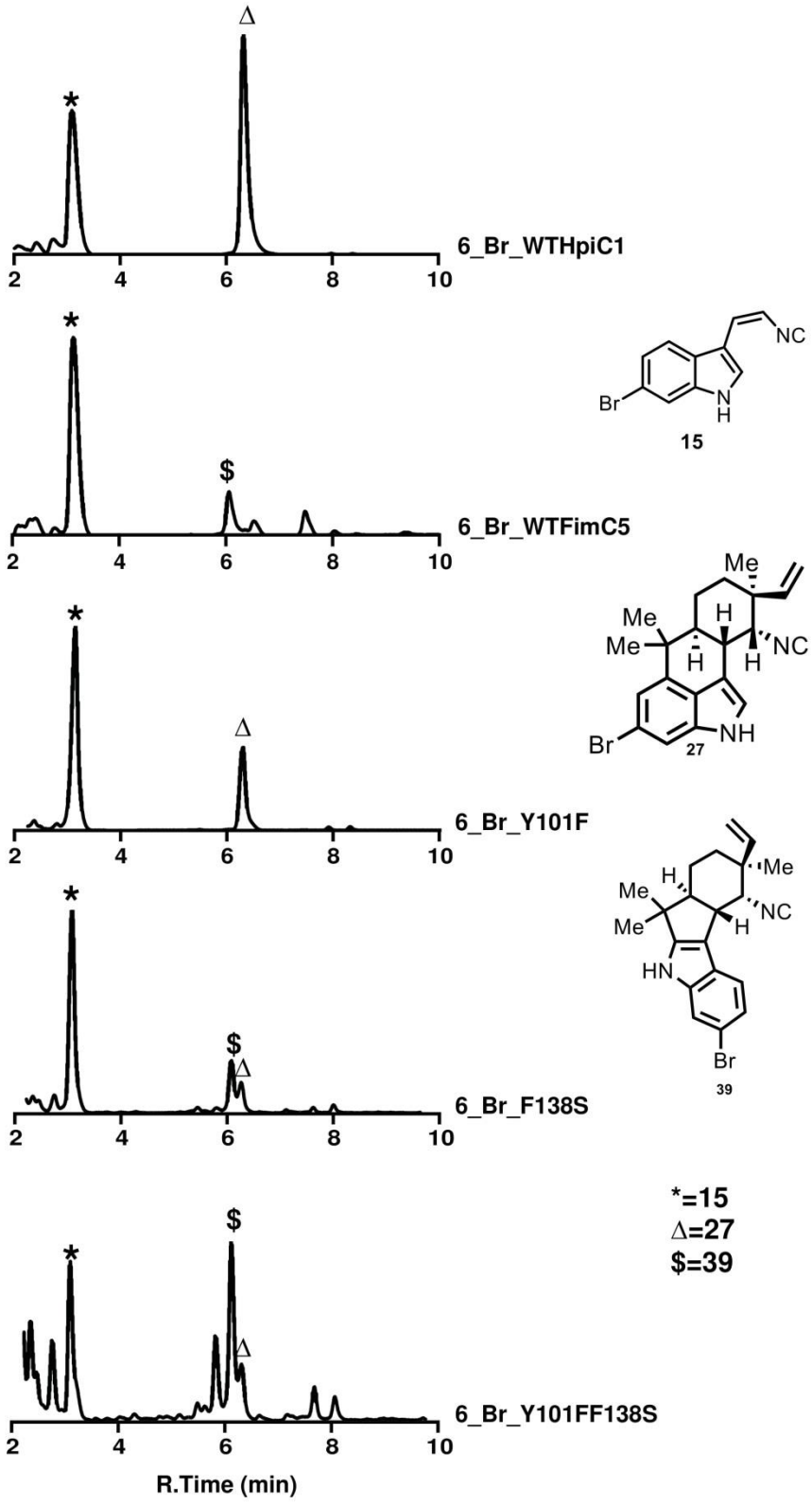


Figure S4: HpiC1→FimC5 mutagenesis results for substrate **15**

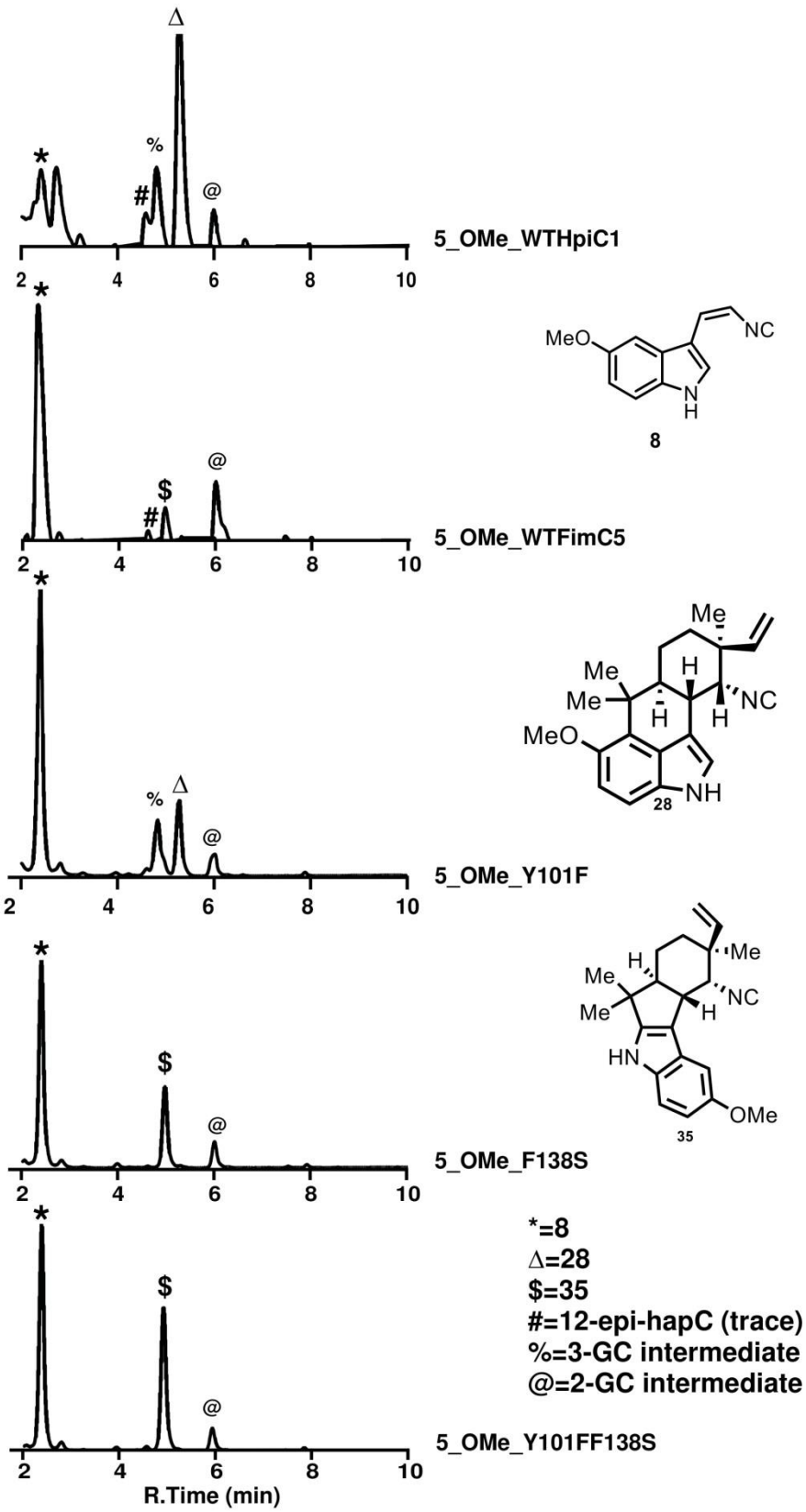


Figure S5: HpiC1→FimC5 mutagenesis results for substrate **8**

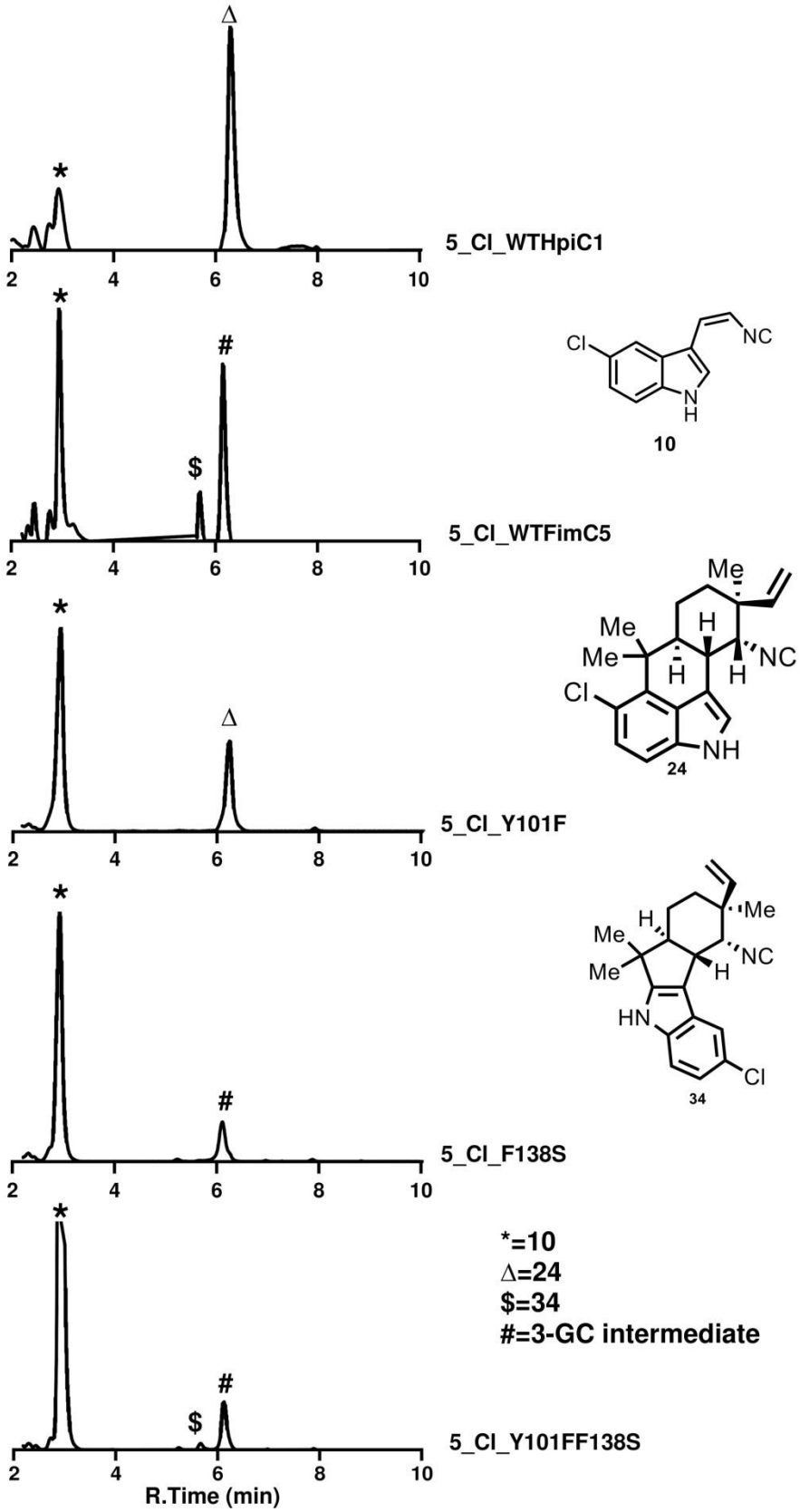


Figure S6: HpiC1→FimC5 mutagenesis results for substrate **10**

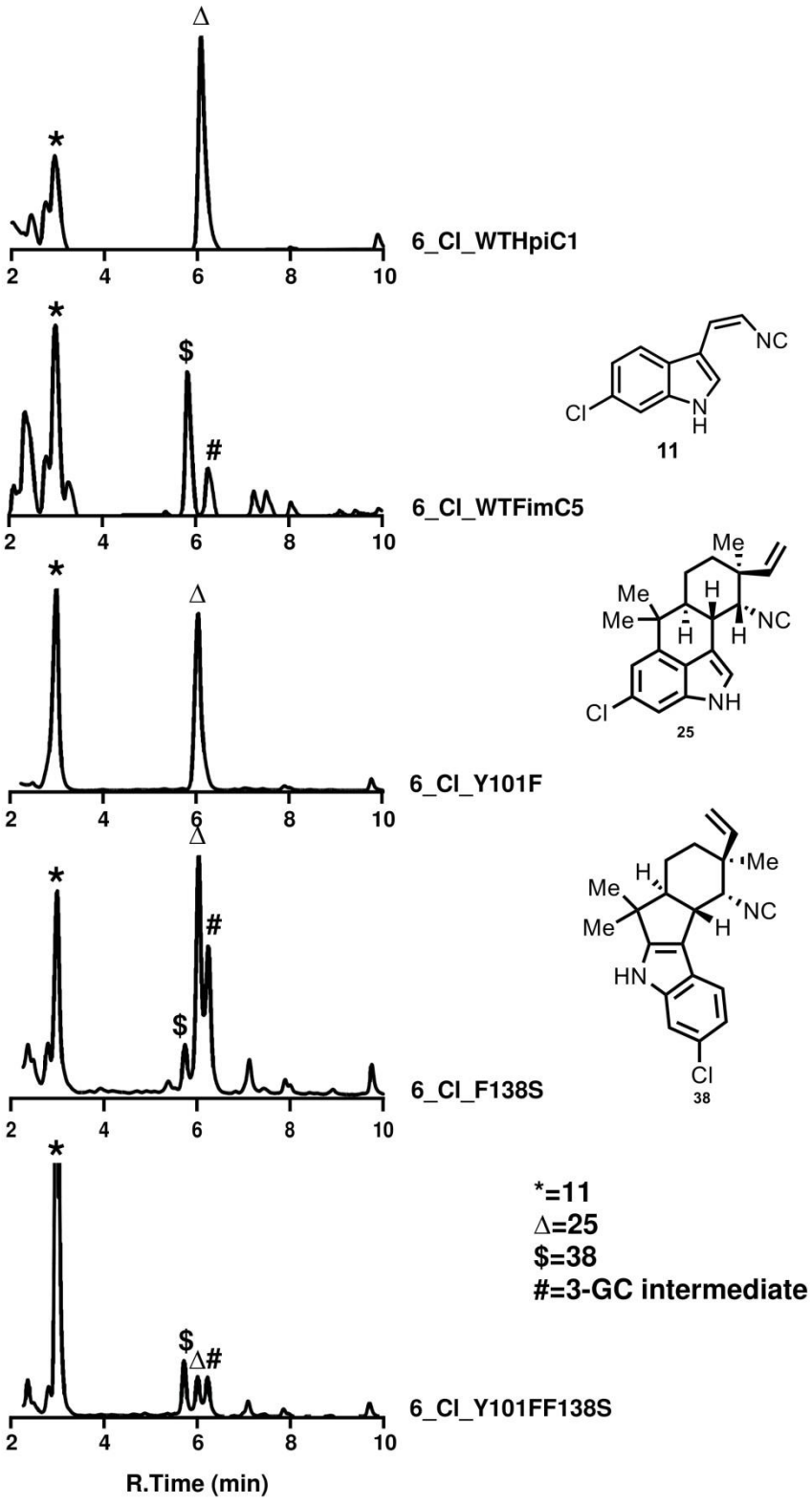


Figure S7: HpiC1→FimC5 mutagenesis results for substrate **11**

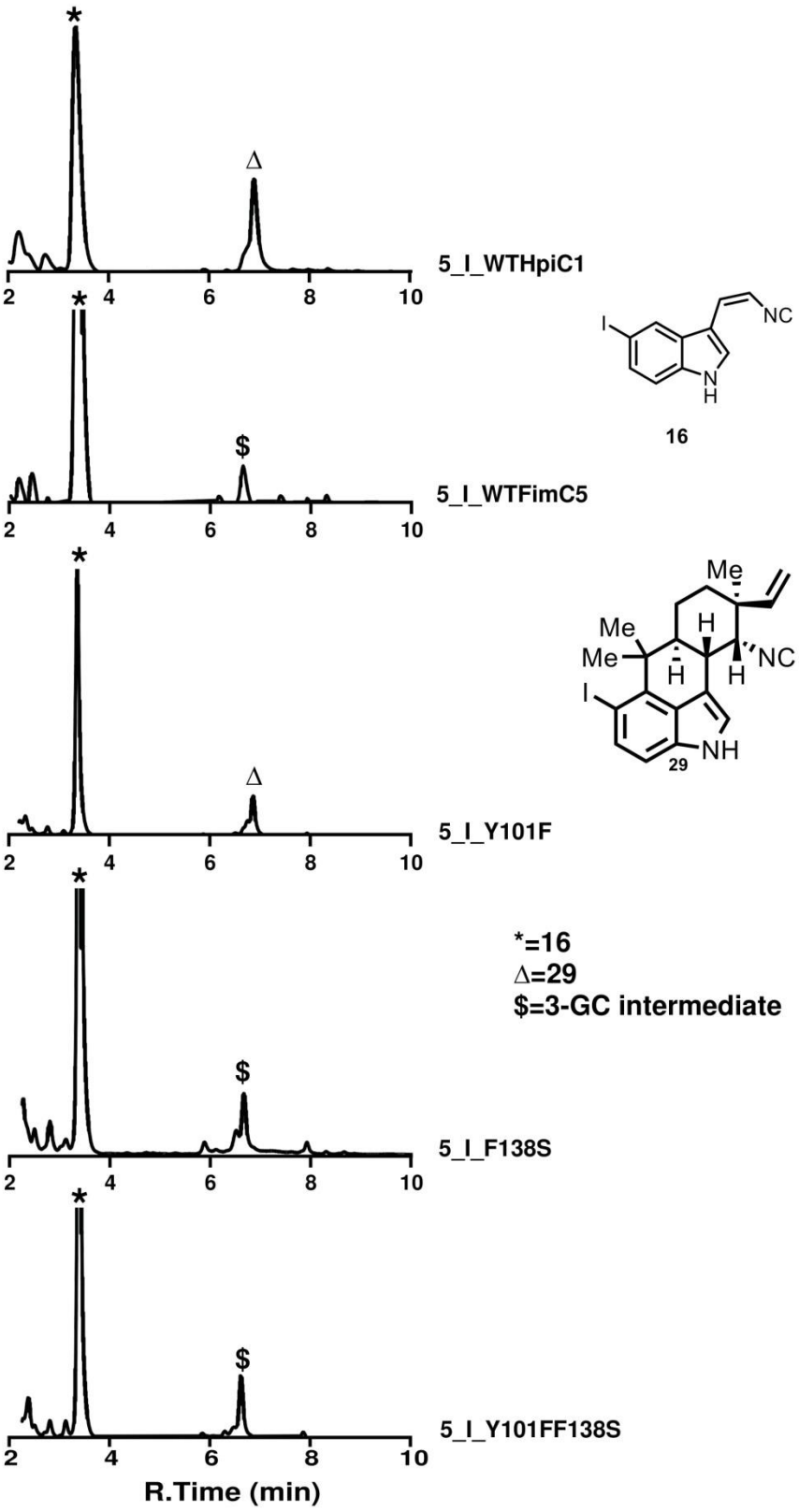


Figure S8: HpiC1→FimC5 mutagenesis results for substrate **16**

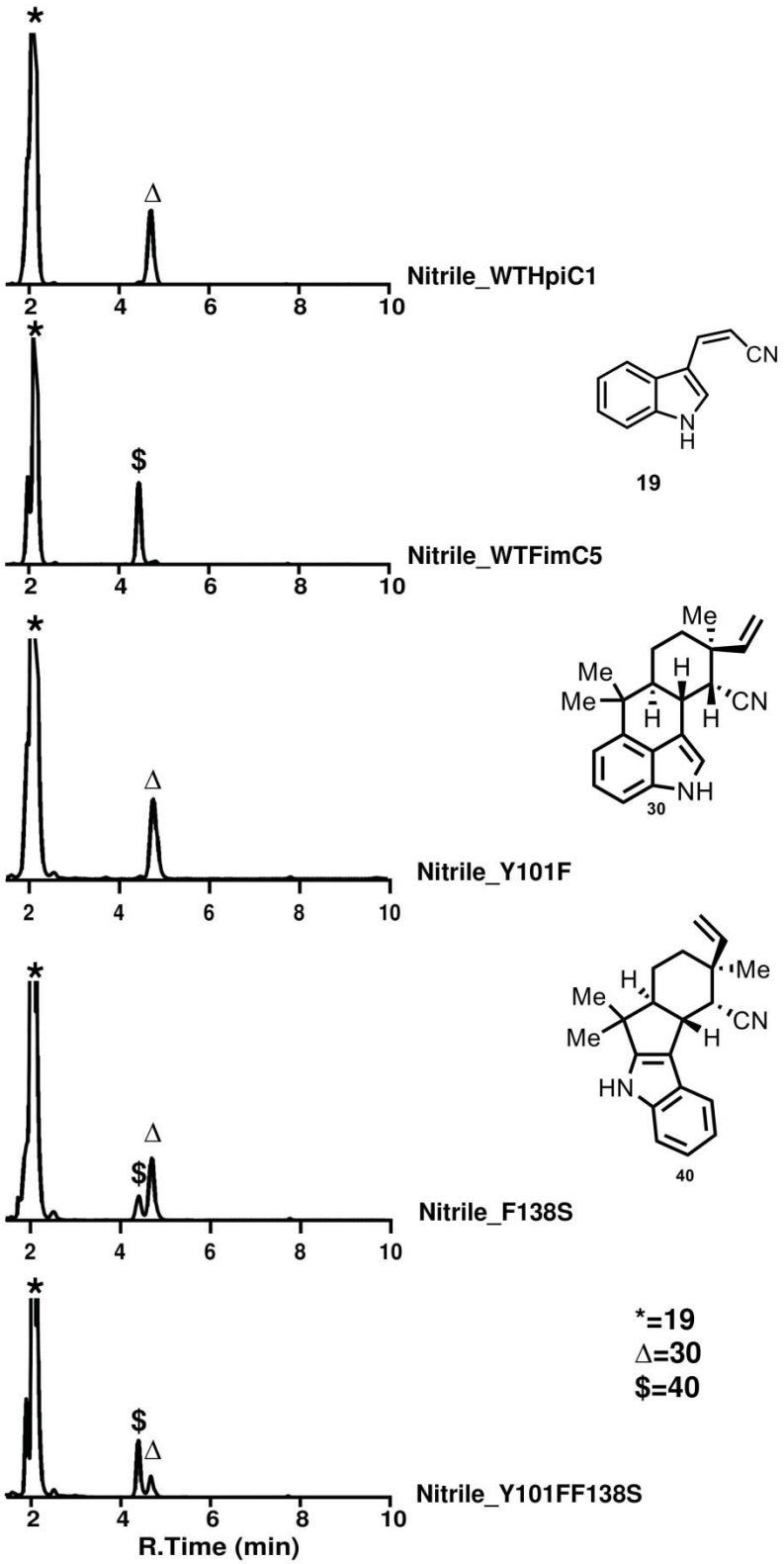


Figure S9: HpiC1→FimC5 mutagenesis results for substrate **19**

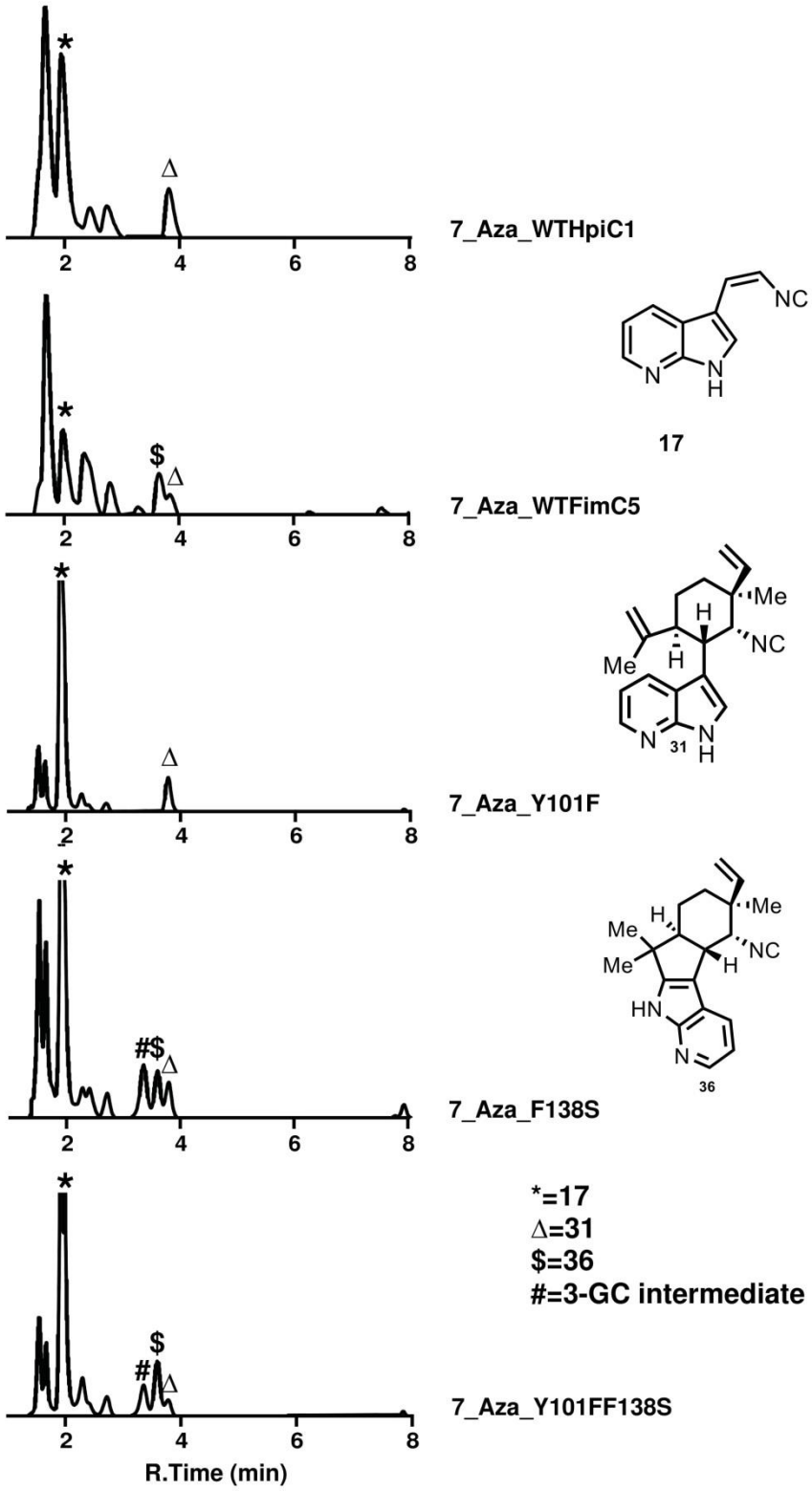


Figure S10: HpiC1→FimC5 mutagenesis results for substrate **17**

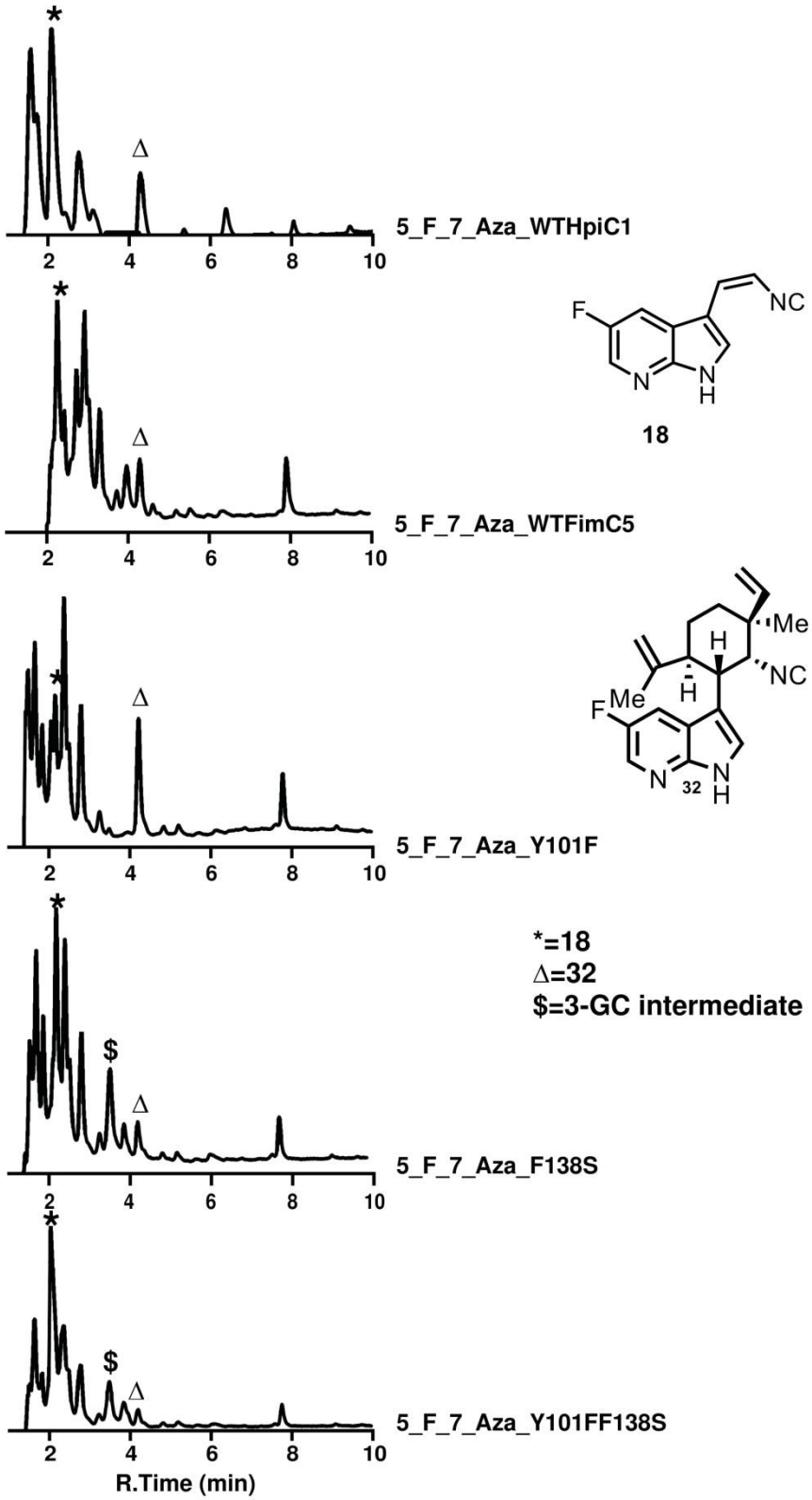


Figure S11: HpiC1→FimC5 mutagenesis results for substrate **18**

Figures S12-S22: HpiC1→FamC1 mutagenesis HPLC traces
Note: HPLC traces do not represent best possible conversion

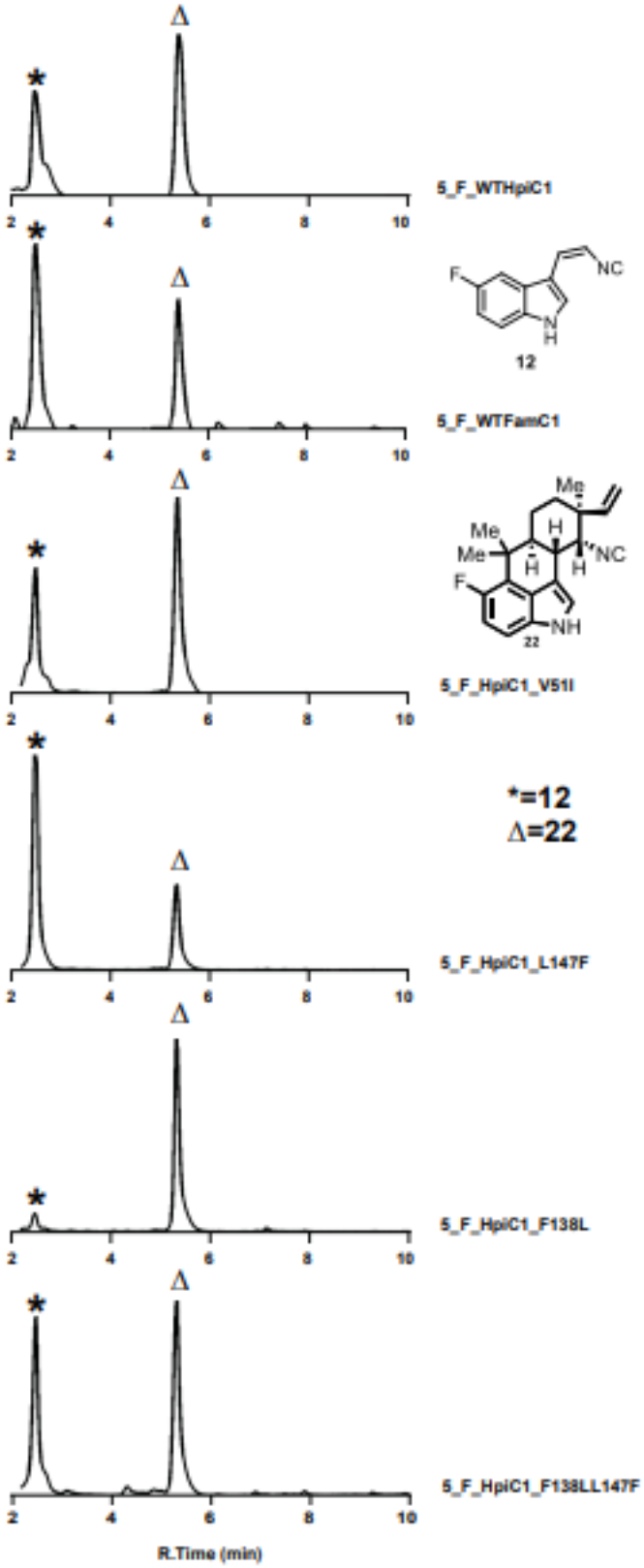


Figure S12: HpiC1→FamC1 mutagenesis results for substrate **12**

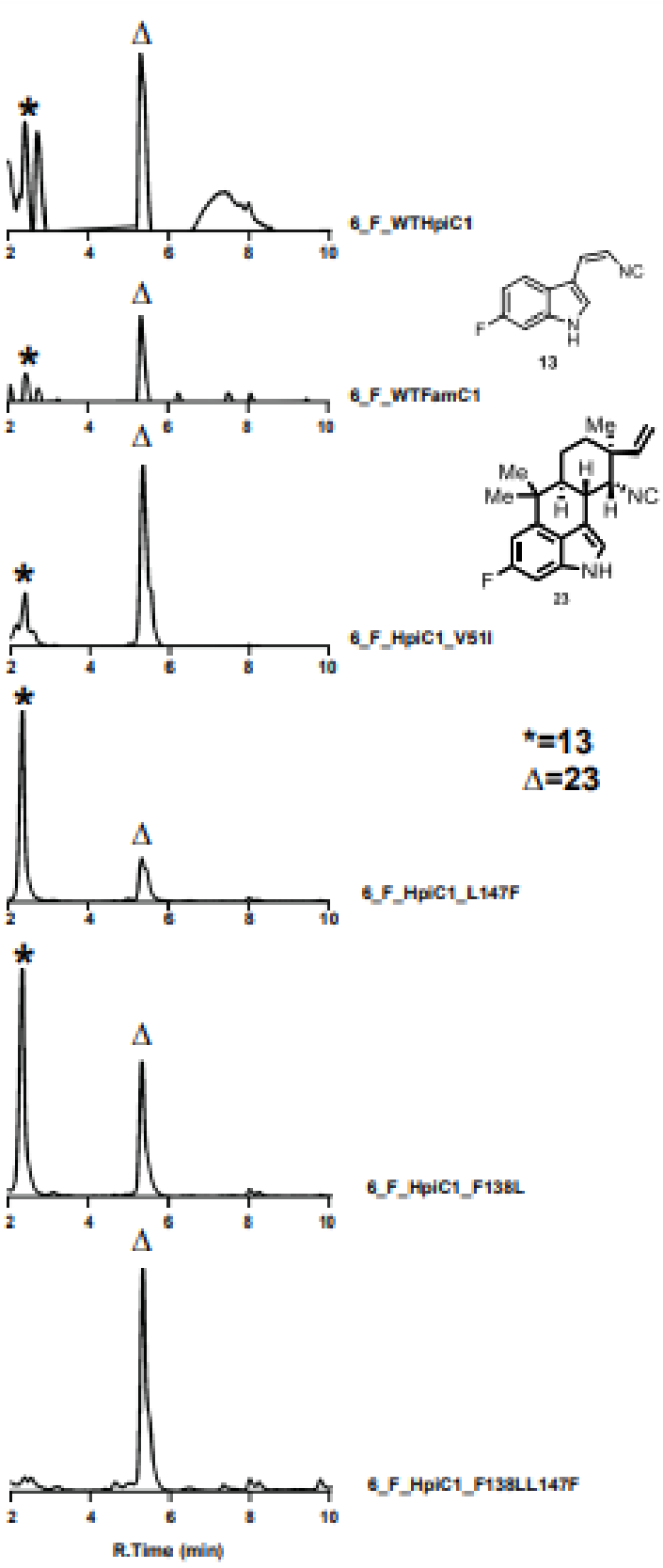


Figure S13: HpiC1→FamC1 mutagenesis results for substrate **13**

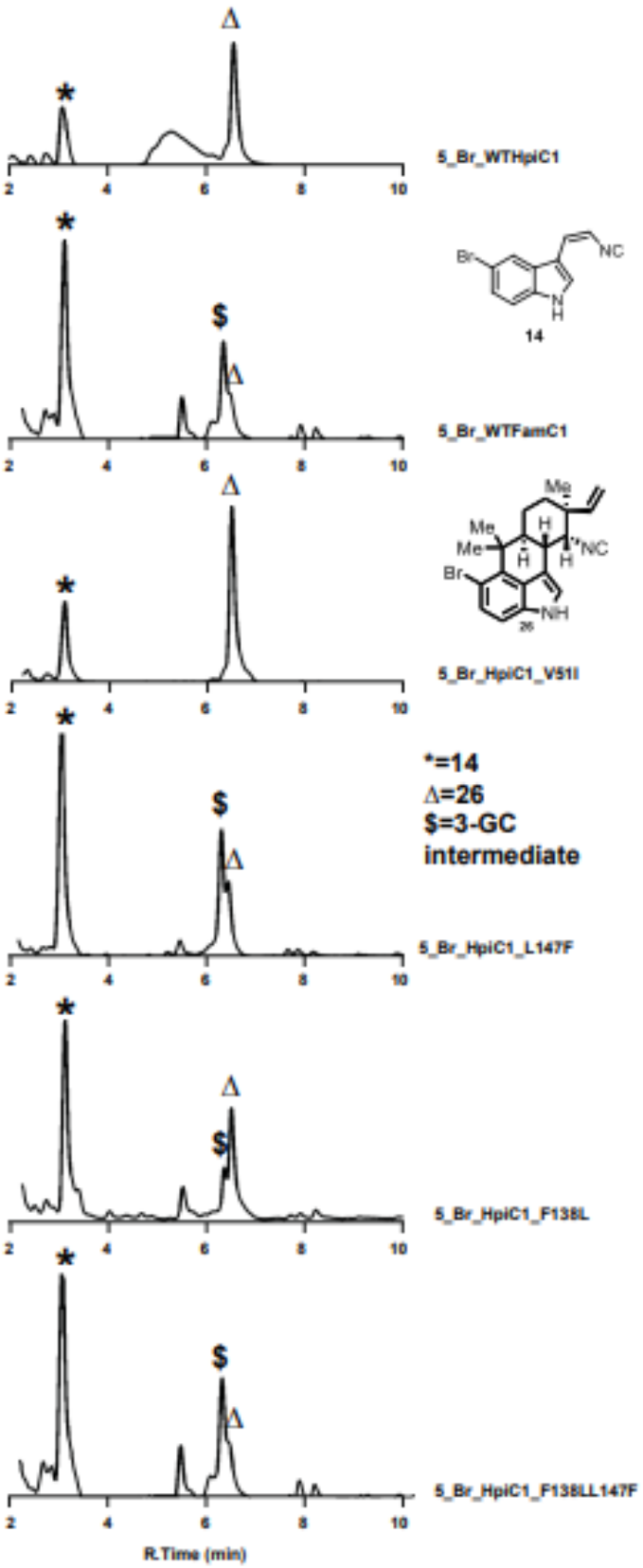


Figure S14: HpiC1→FamC1 mutagenesis results for substrate **14**

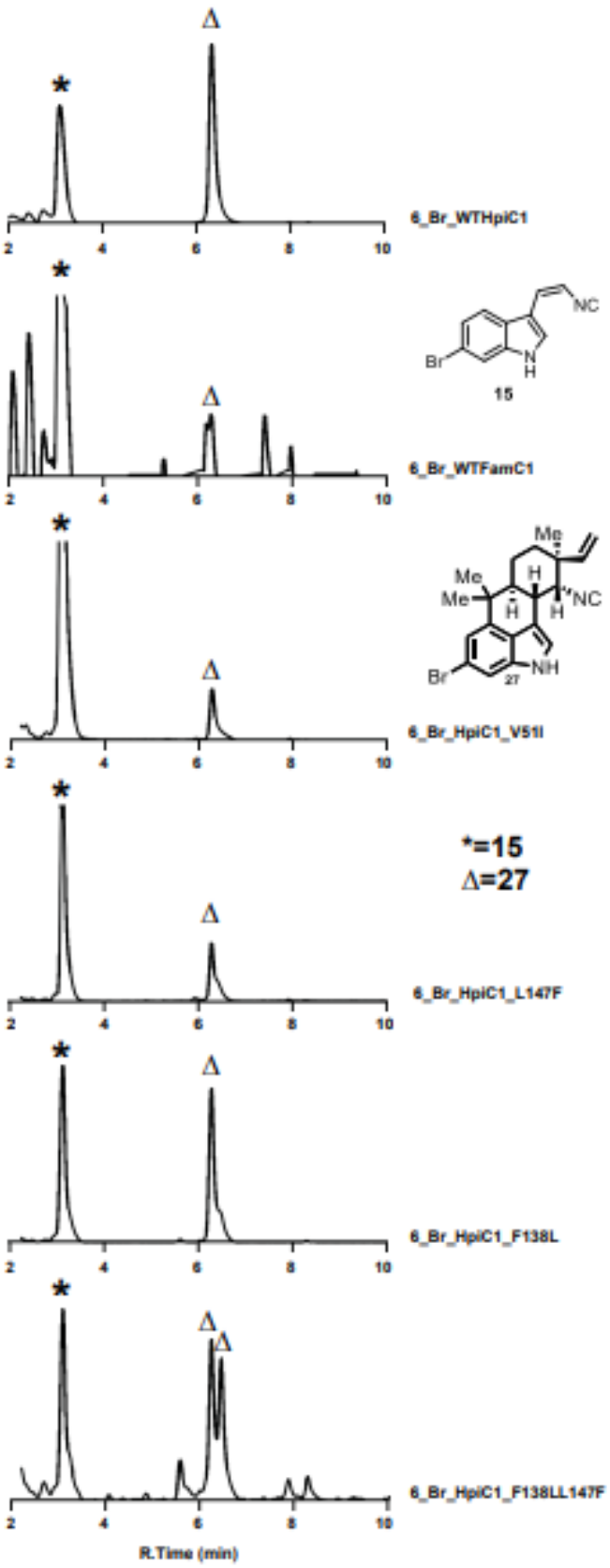


Figure S15: HpiC1→FamC1 mutagenesis results for substrate **15**

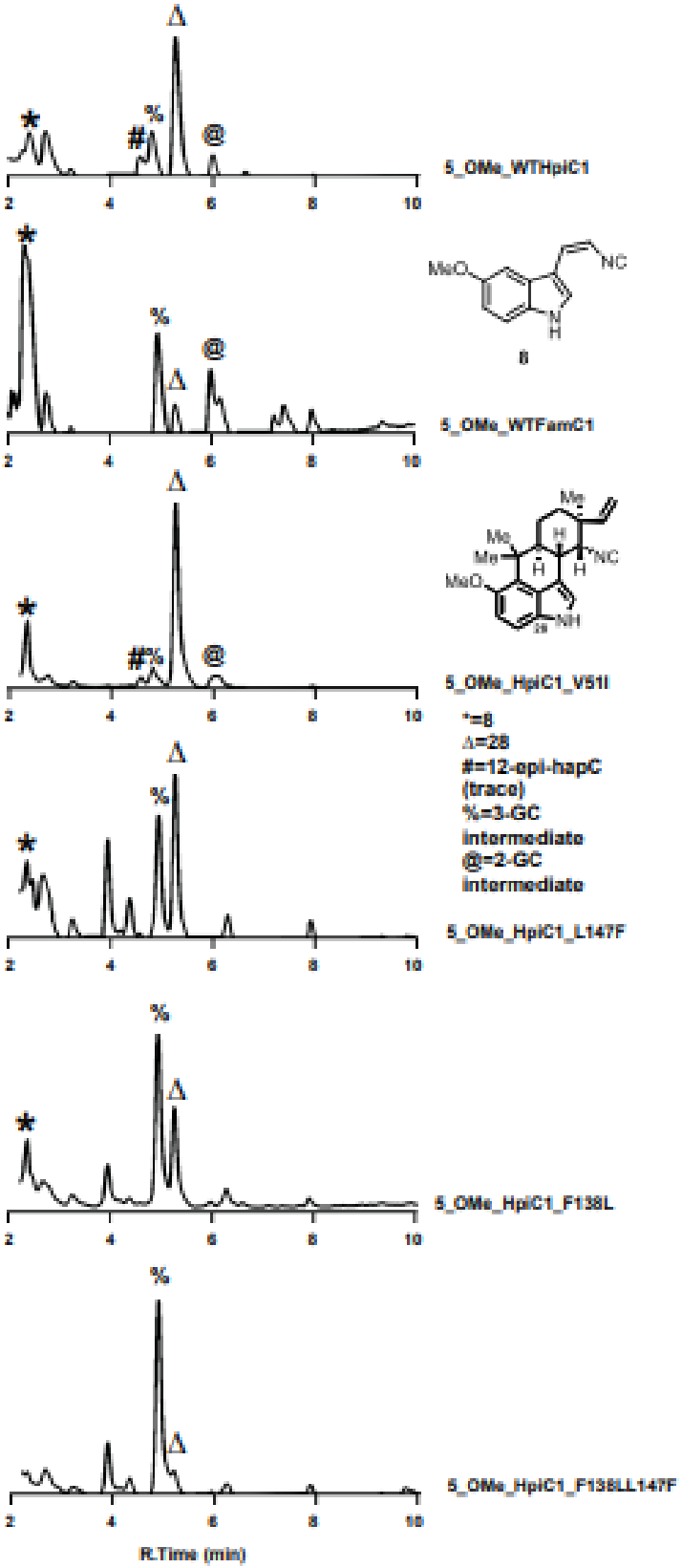


Figure S16: HpiC1→FamC1 mutagenesis results for substrate **8**

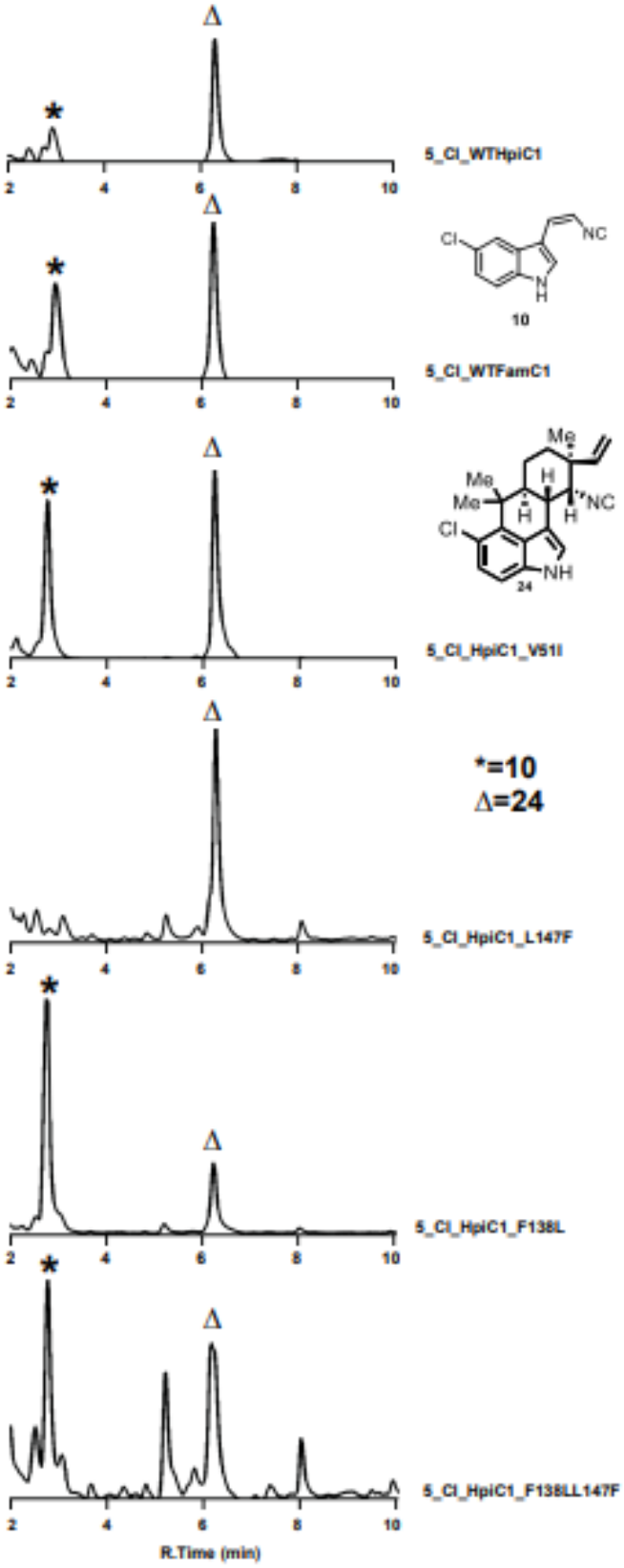


Figure S17: HpiC1→FamC1 mutagenesis results for substrate **10**

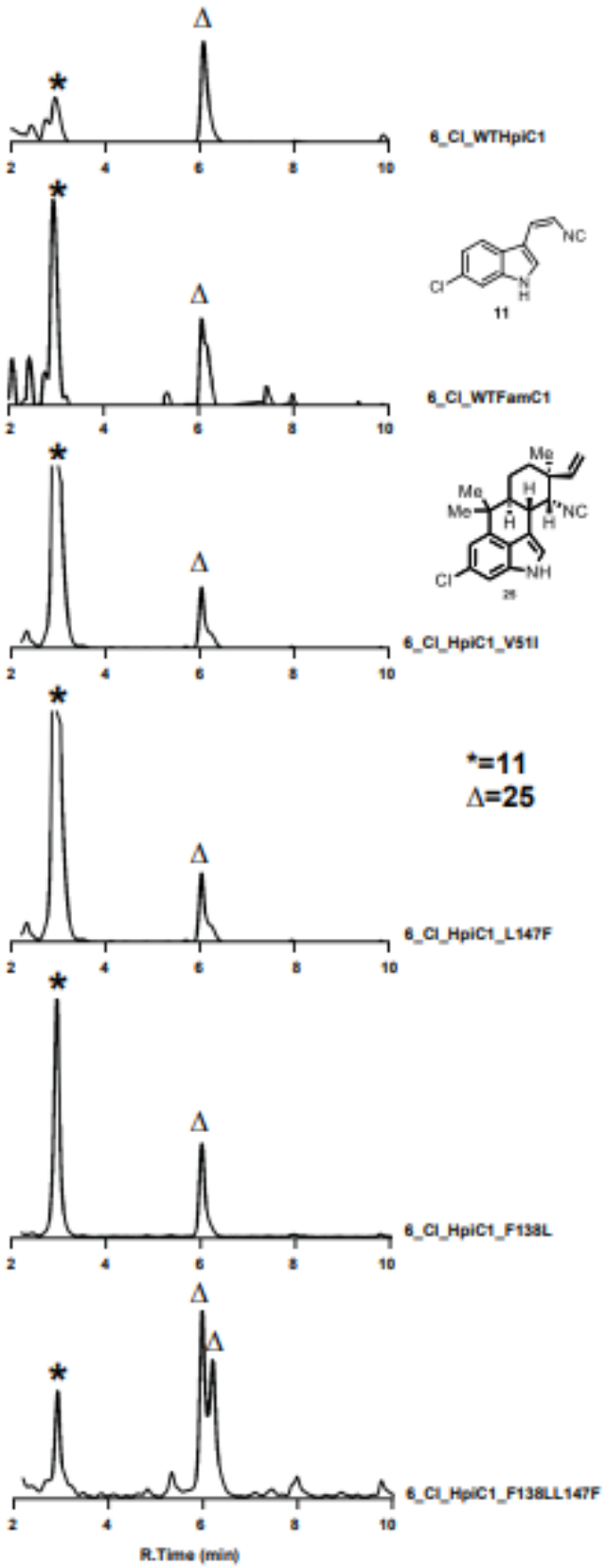


Figure S18: HpiC1→FamC1 mutagenesis results for substrate **11**

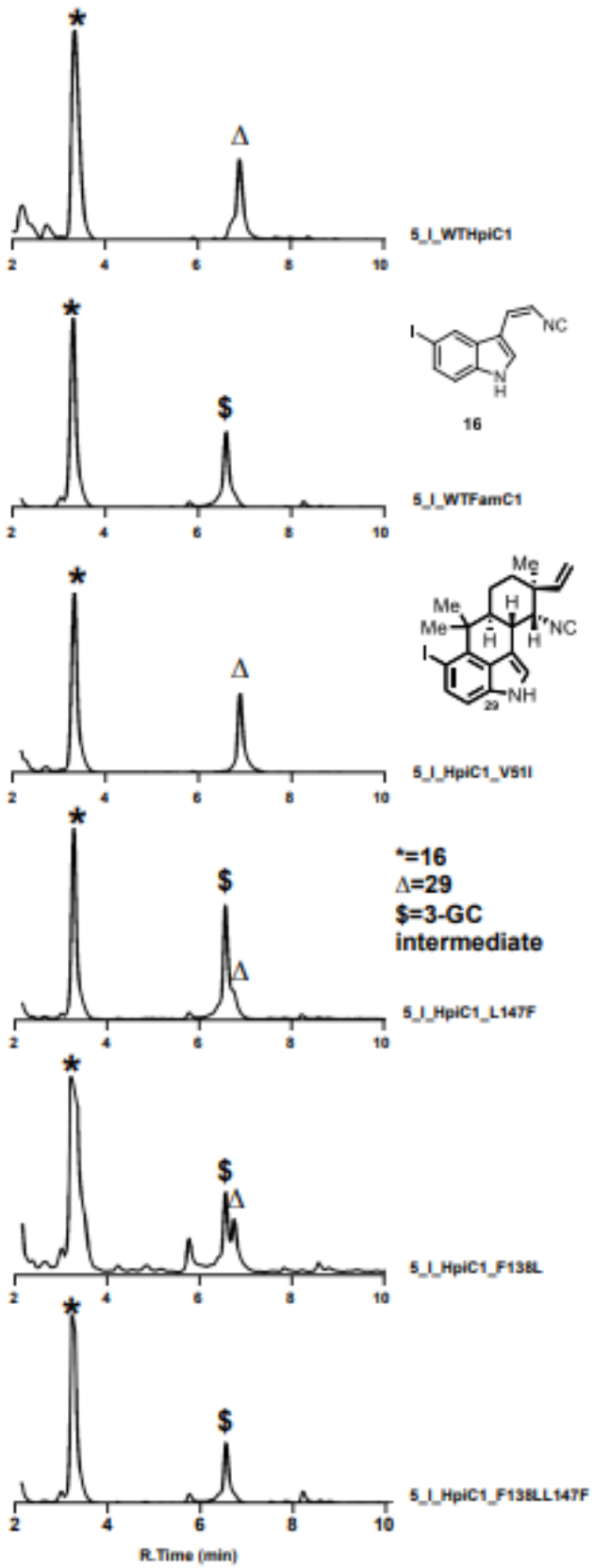


Figure S19: HpiC1→FamC1 mutagenesis results for substrate **16**

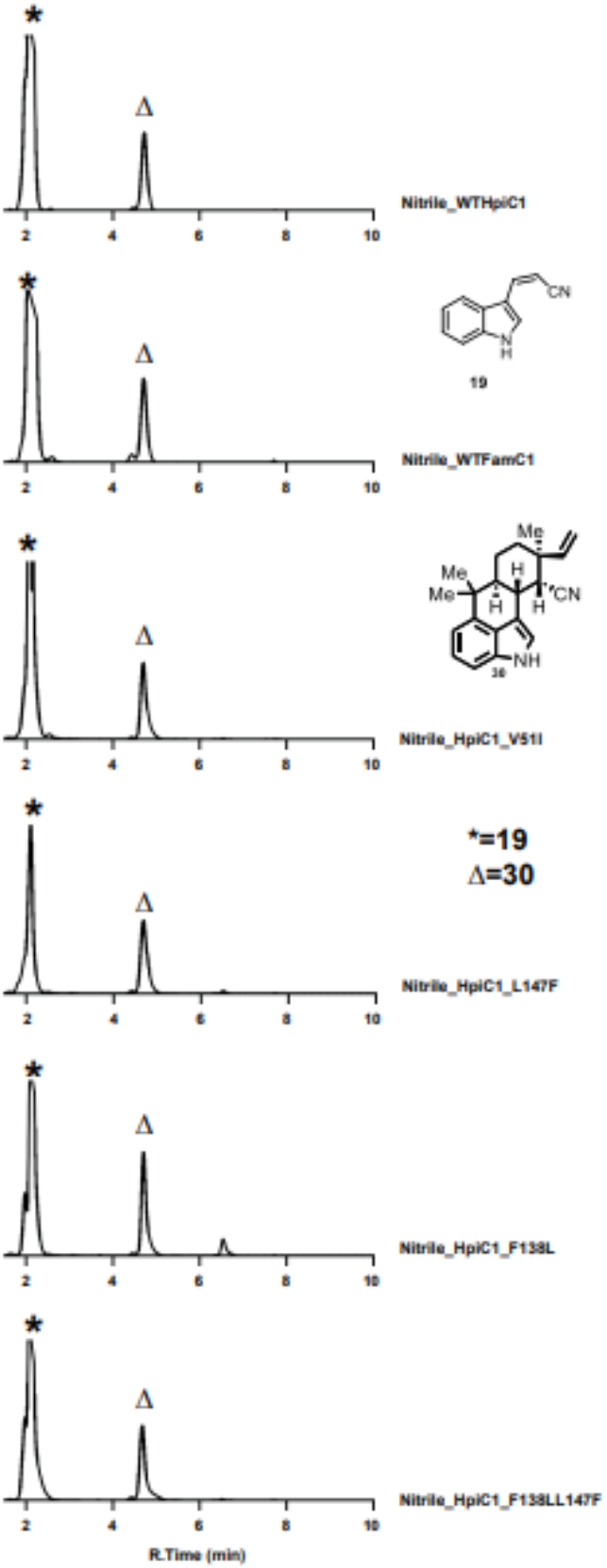


Figure S20: HpiC1→FamC1 mutagenesis results for substrate **19**

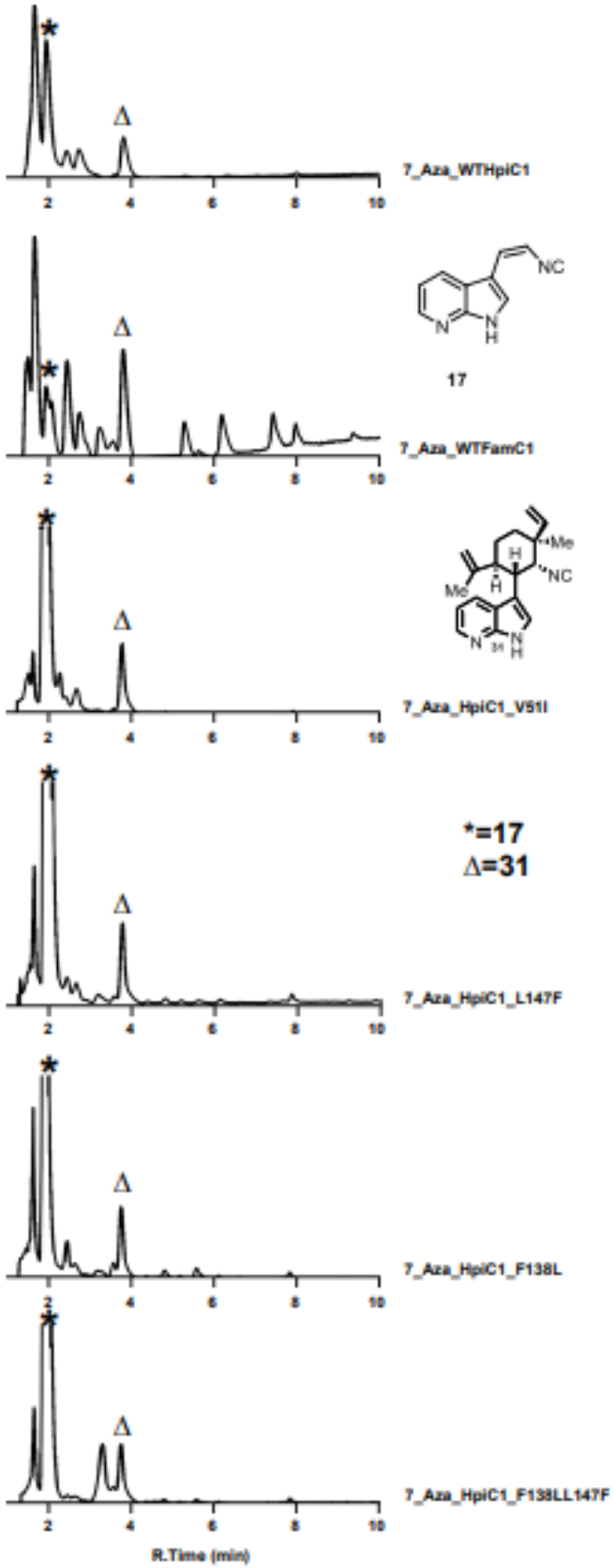


Figure S21: HpiC1→FamC1 mutagenesis results for substrate **17**

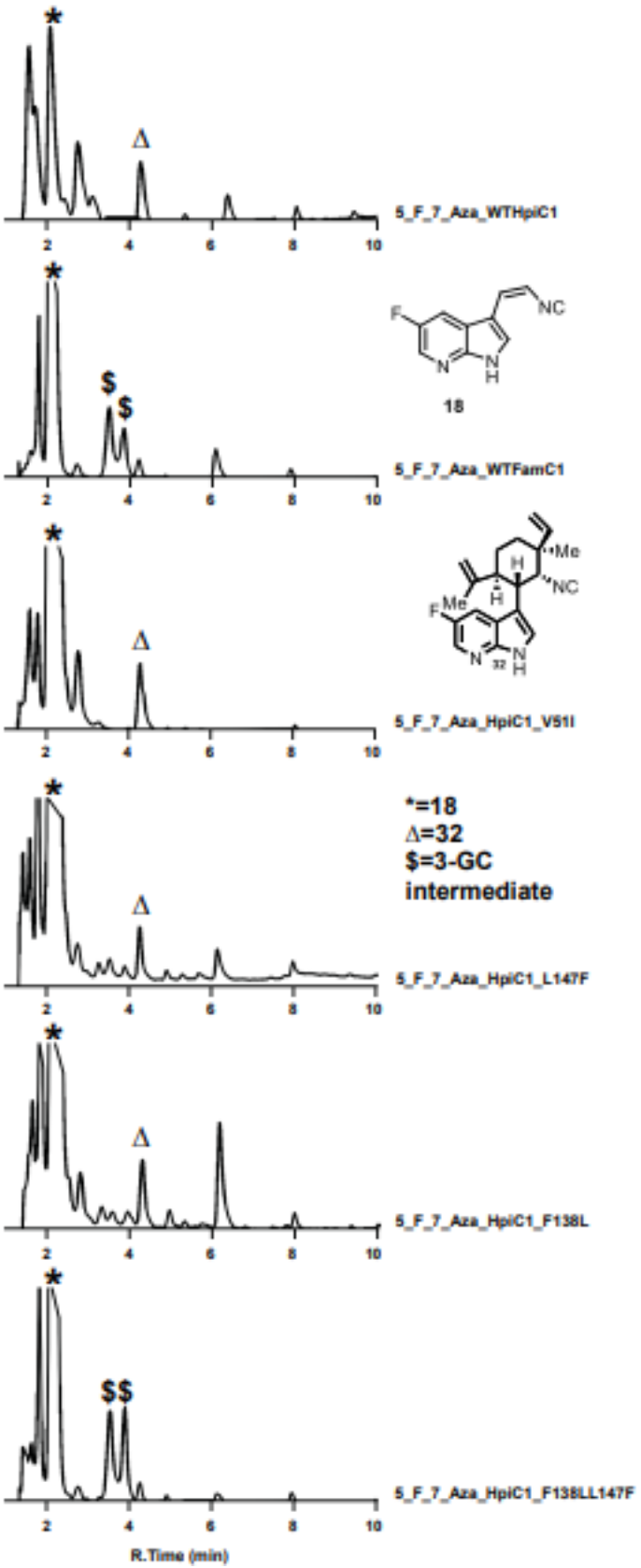


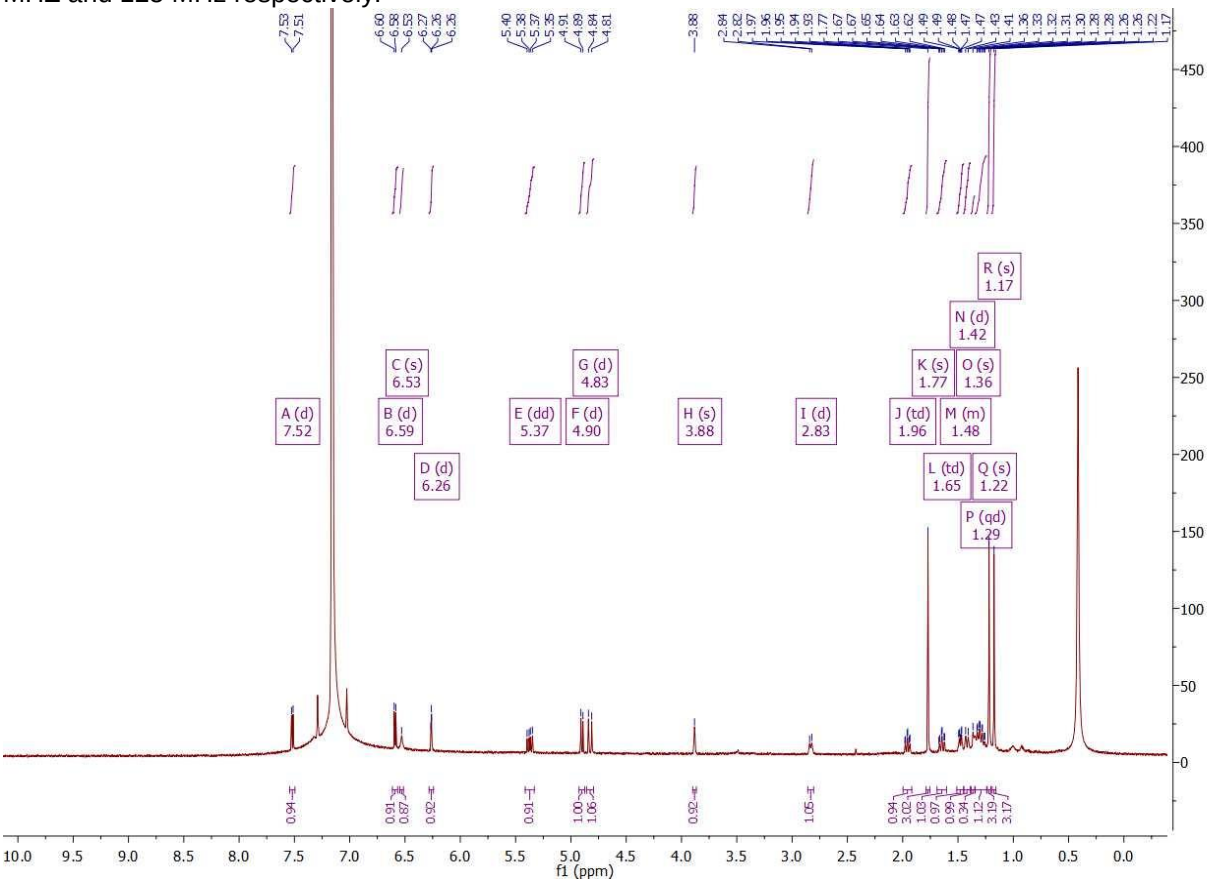
Figure S22: HpiC1→FamC1 mutagenesis results for substrate **18**

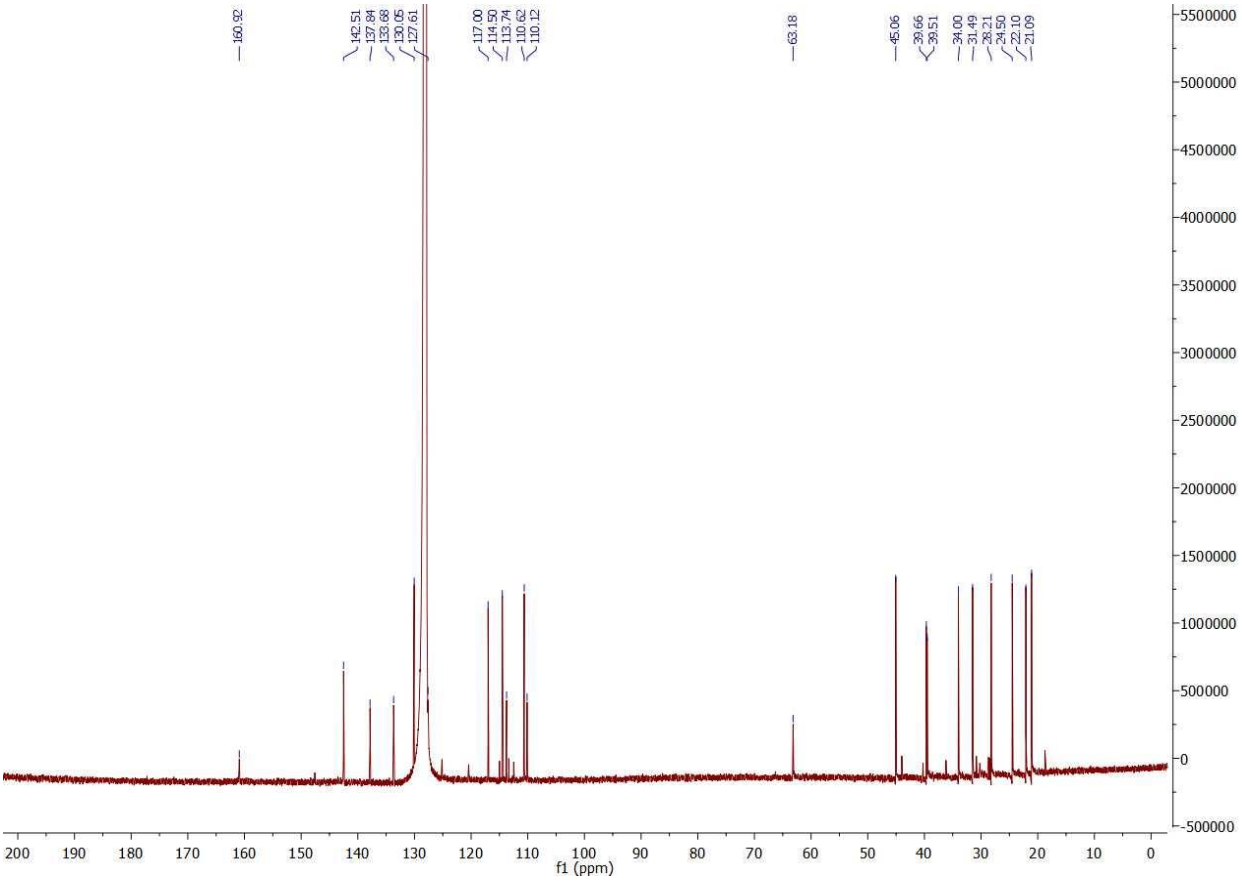
Spectra Section

^{1}H and ^{13}CNMR spectra and HRMS of 5-F-12-*epi*-Hapalindole U (**22**)
Full characterization data[1]

^{1}H and ^{13}CNMR spectra and HRMS of 6-F-12-*epi*-Hapalindole U (**23**)
Full characterization data[1]

^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 5-Br-12-*epi*-Hapalindole U (**26**) in C_6D_6 at 600 MHZ and 125 MHz respectively.

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117.00
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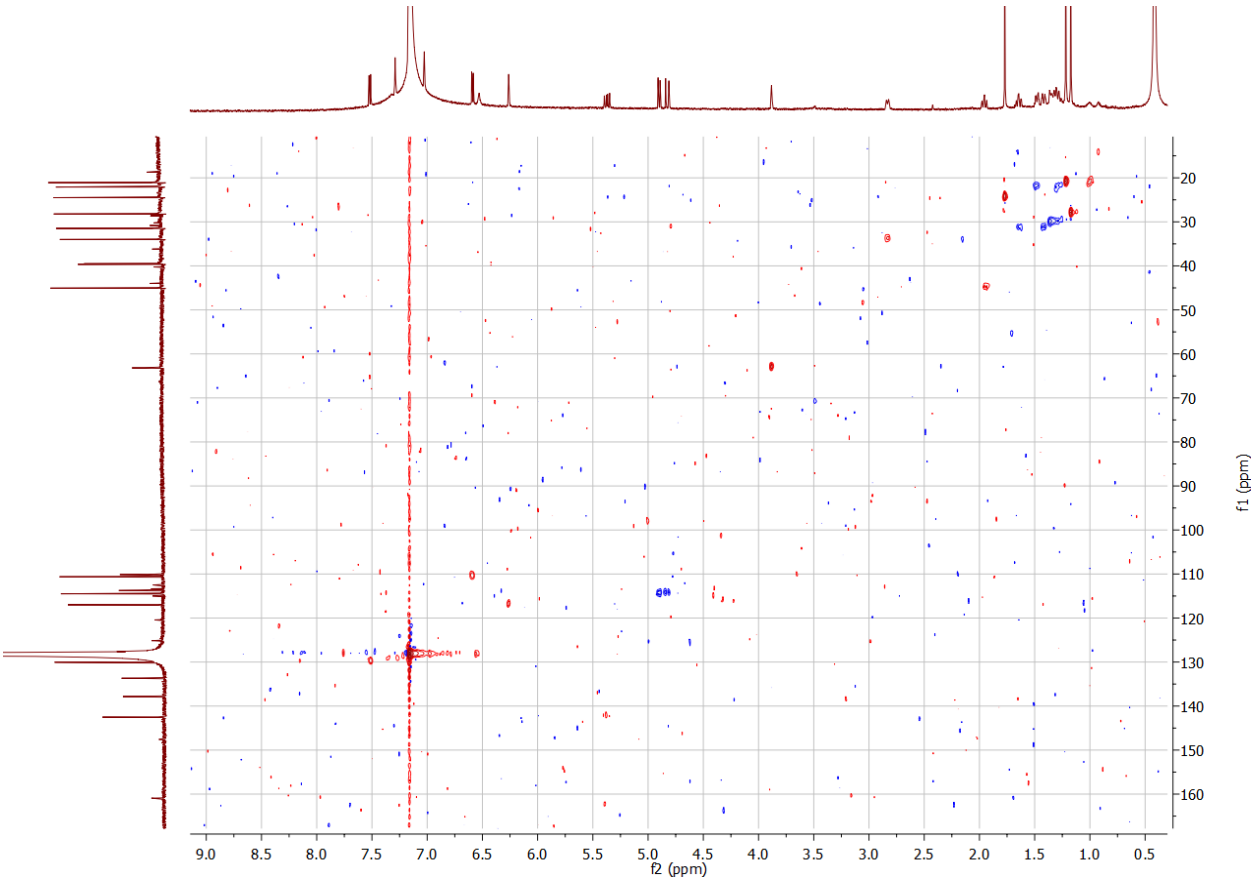
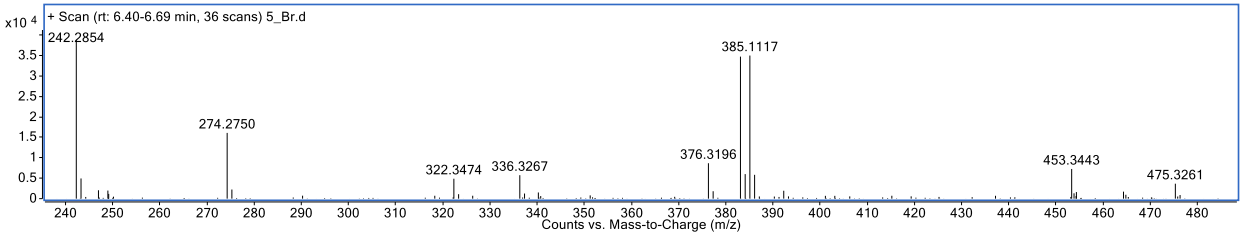
110.62
110.12
63.18
45.06
39.66
39.51
34.00
31.49
28.21
24.50
22.10
21.09
f1 (ppm)

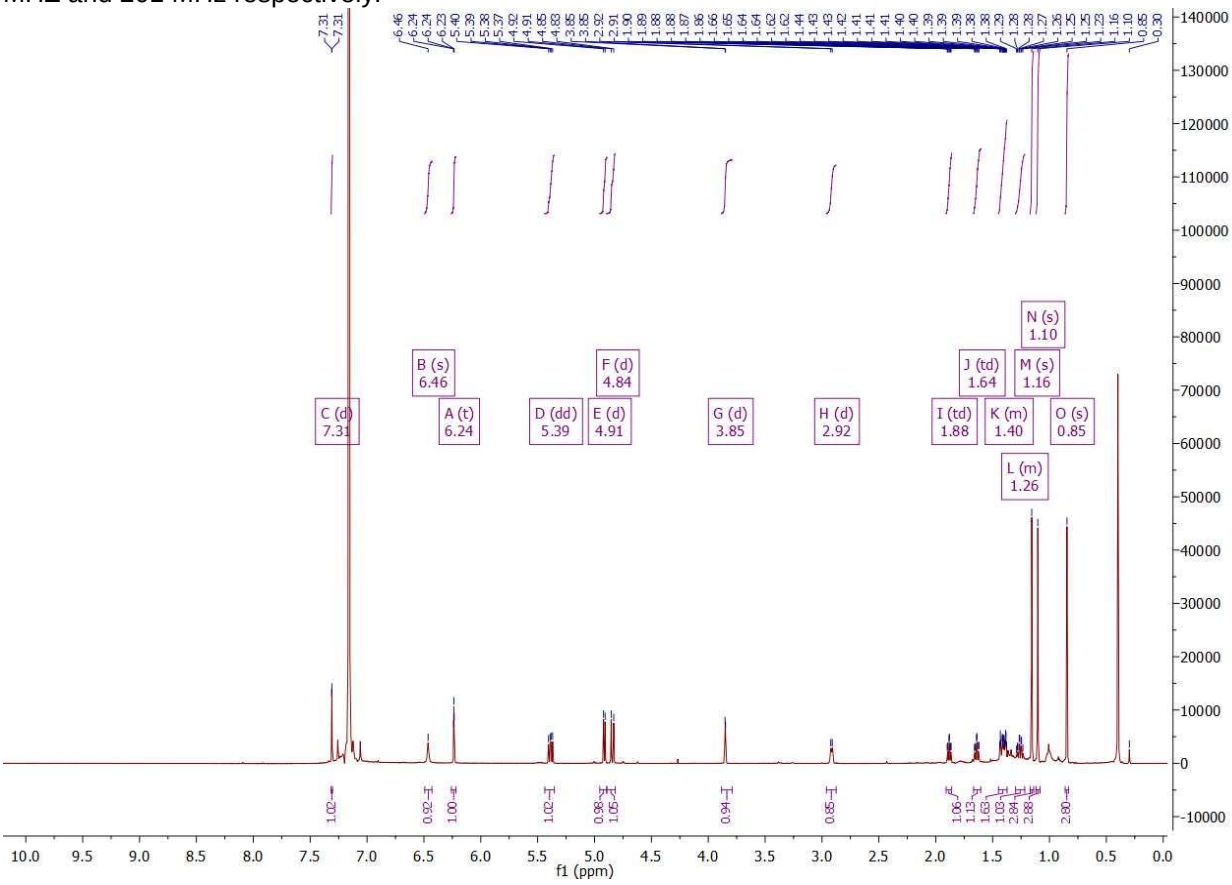

f2 (ppm)
f1 (ppm)

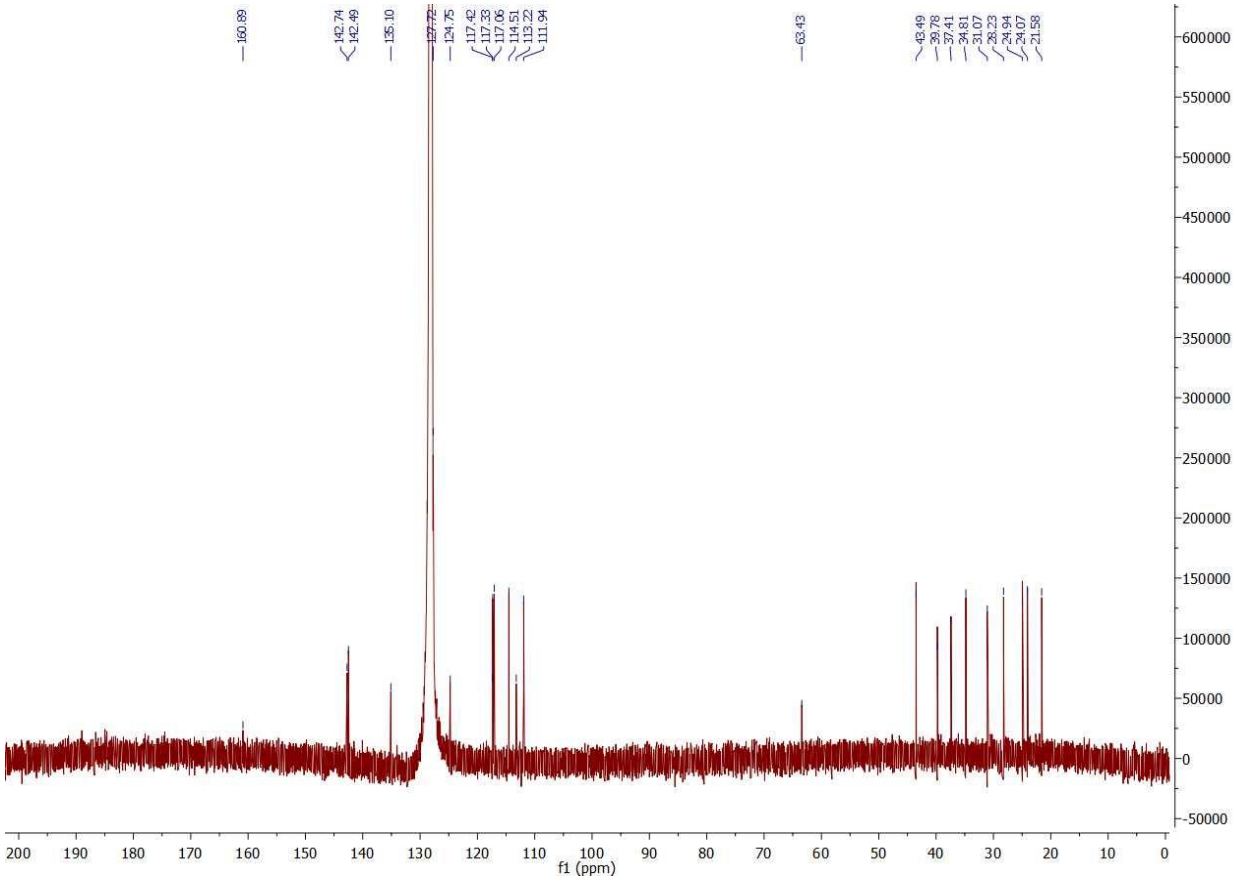

f2 (ppm)
f1 (ppm)



Calc. $[M+H]^+$ 383.1117 Obsv. 383.1117

^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 6-Br-12-*epi*-Hapalindole U (**27**) in C_6D_6 at 800 MHZ and 201 MHz respectively.

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24.94
24.07
21.58
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300000
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200000
150000
100000
50000
0
-50000
200
190
180
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110
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90
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50
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30
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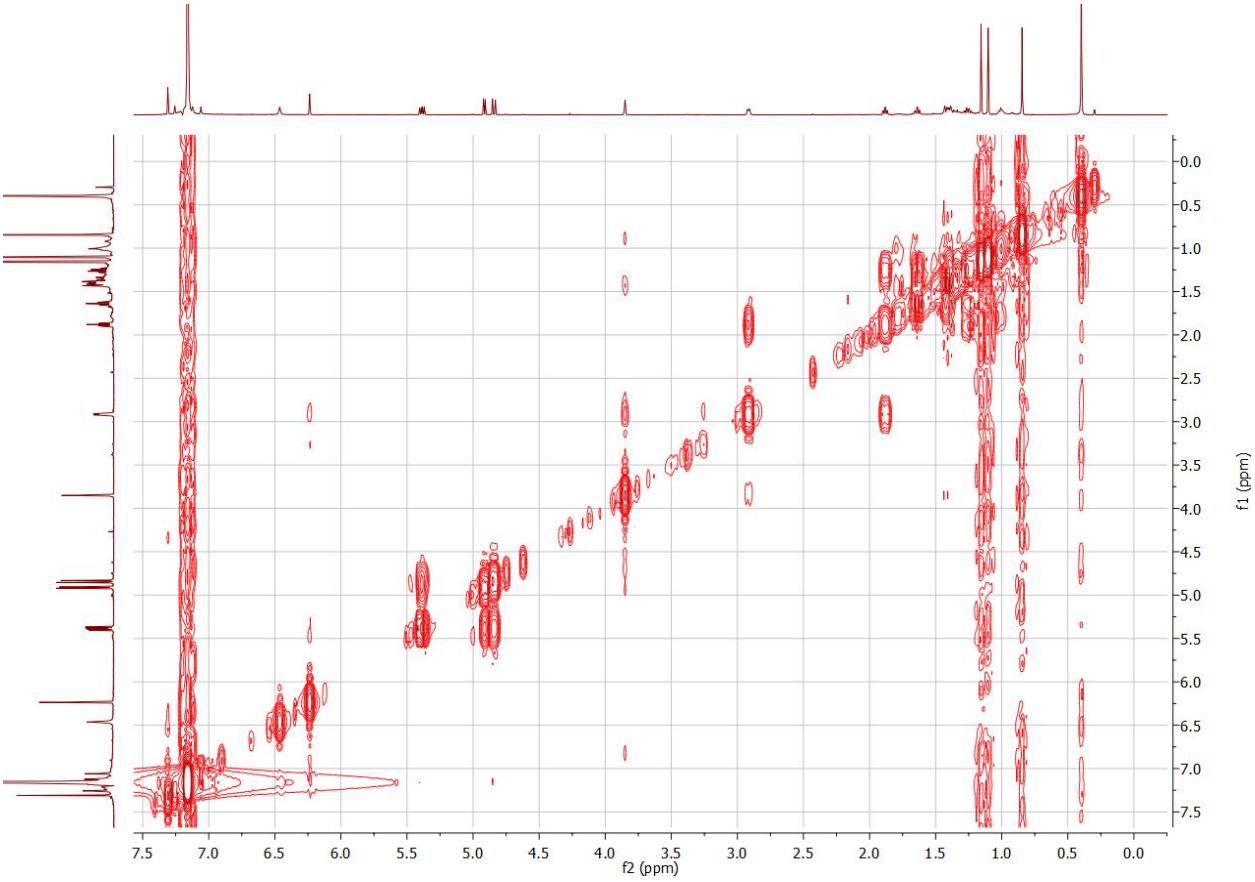
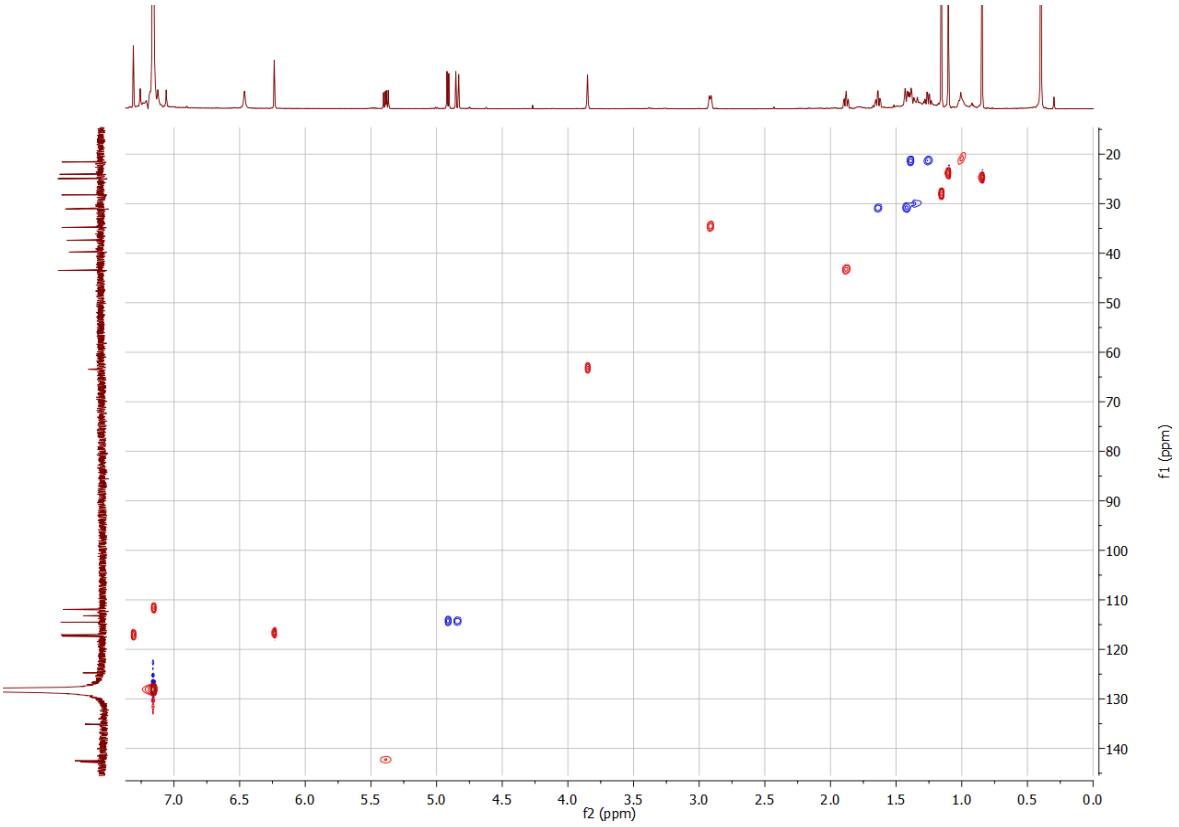
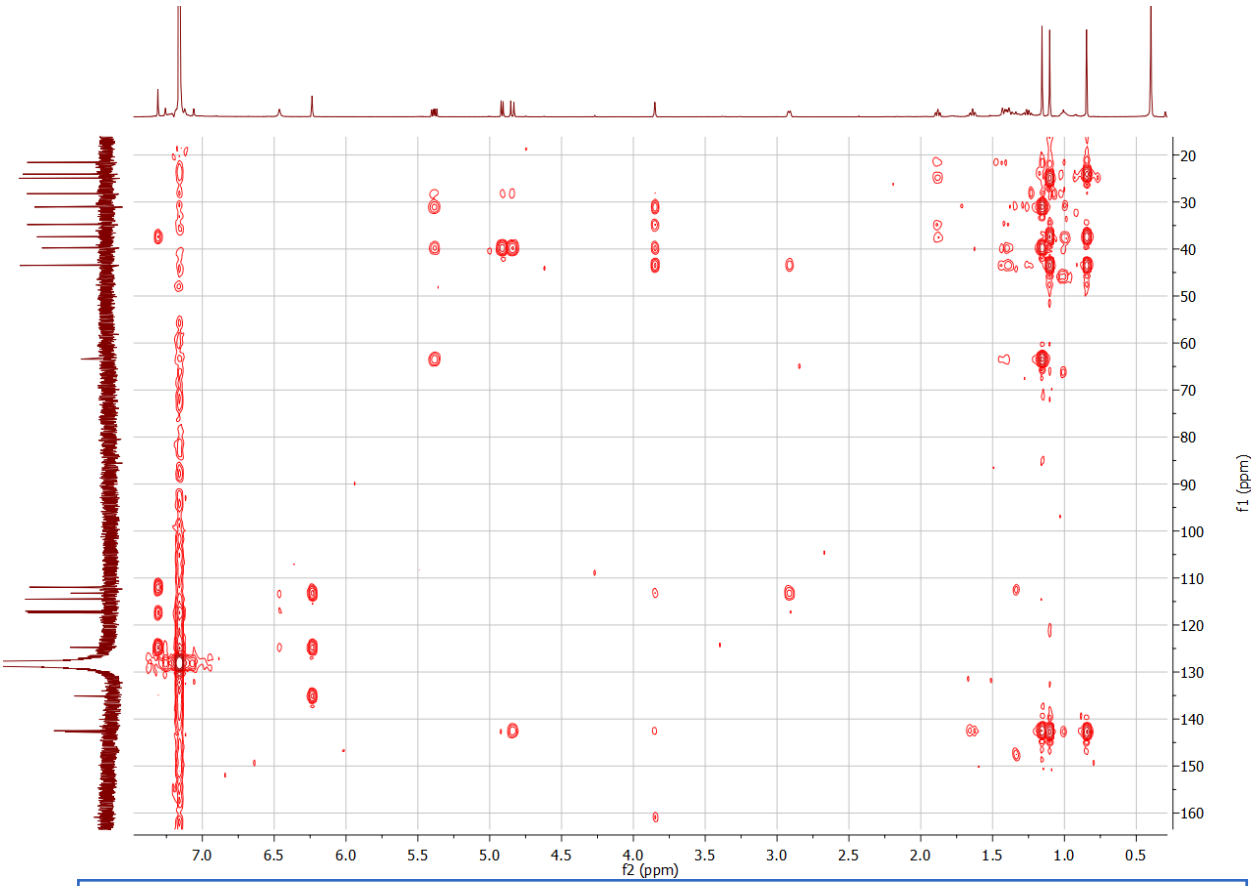
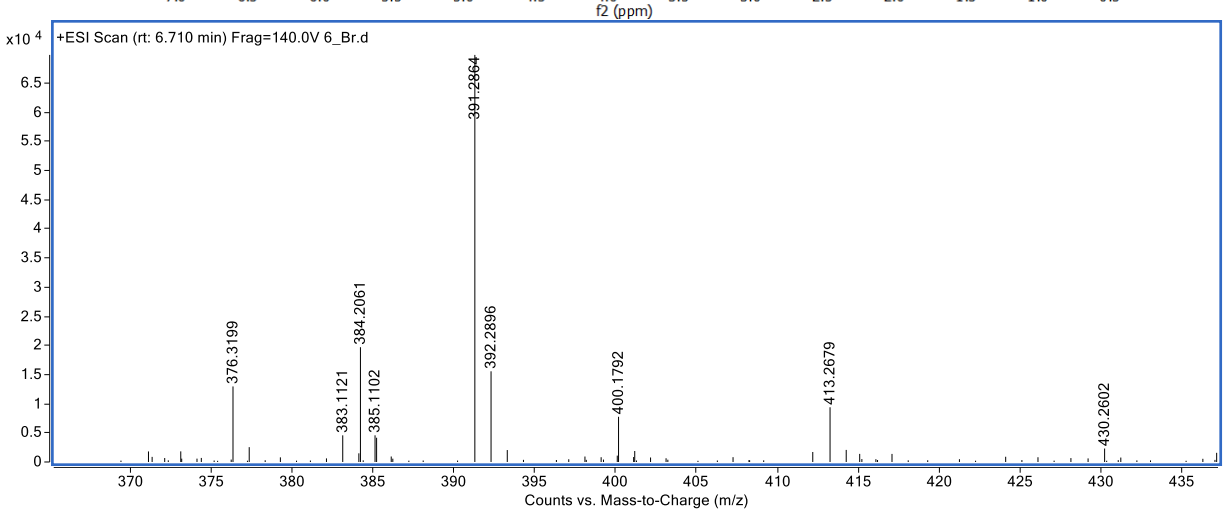
10
0
f1 (ppm)


7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5
f1 (ppm)

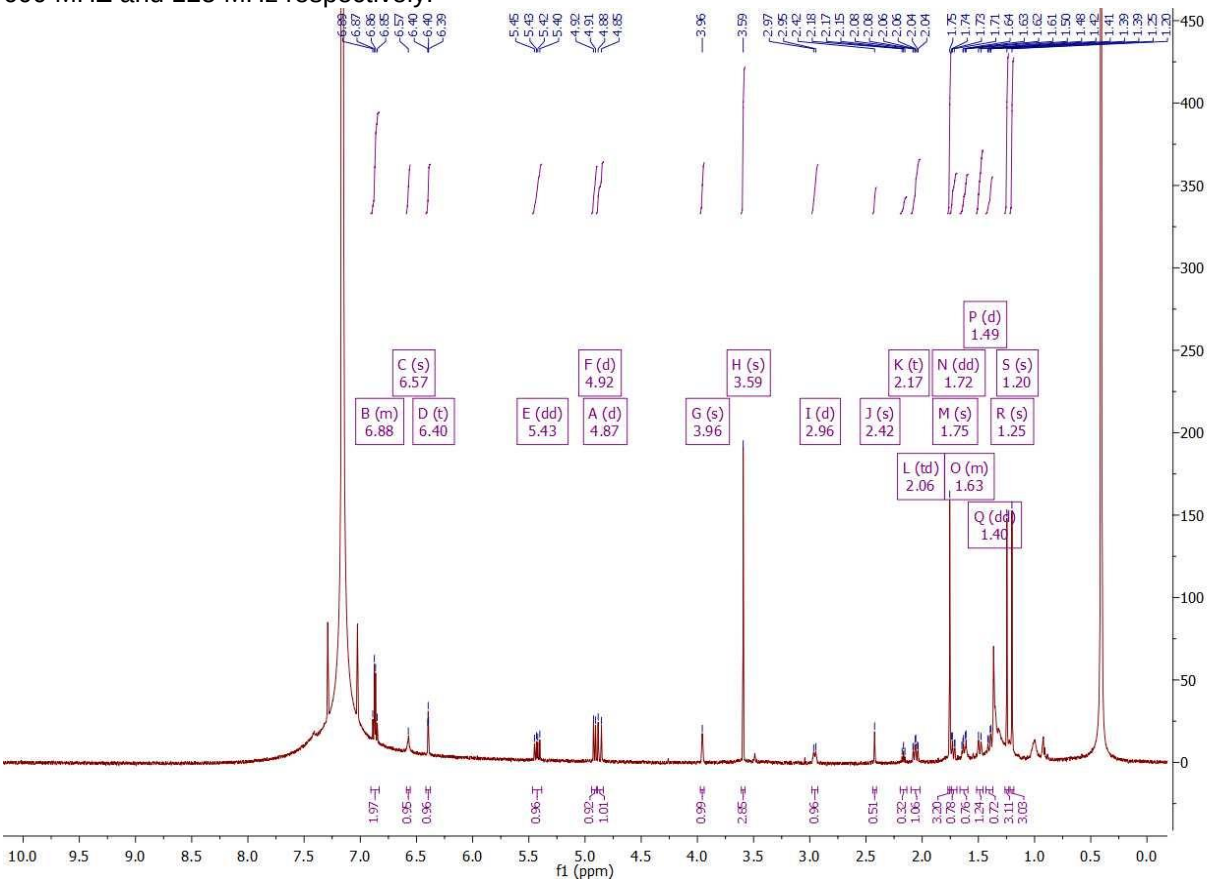

7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
20 30 40 50 60 70 80 90 100 110 120 130 140
f1 (ppm)

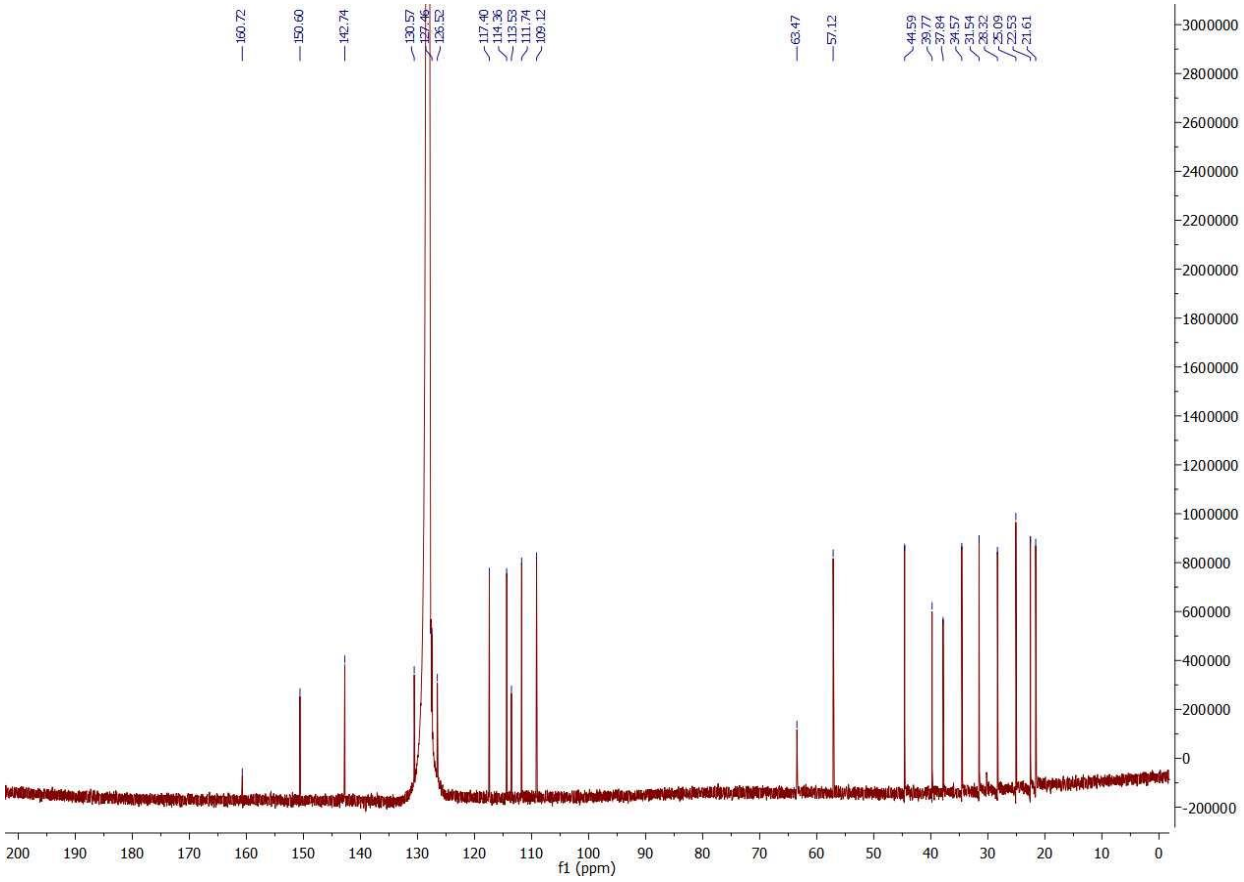


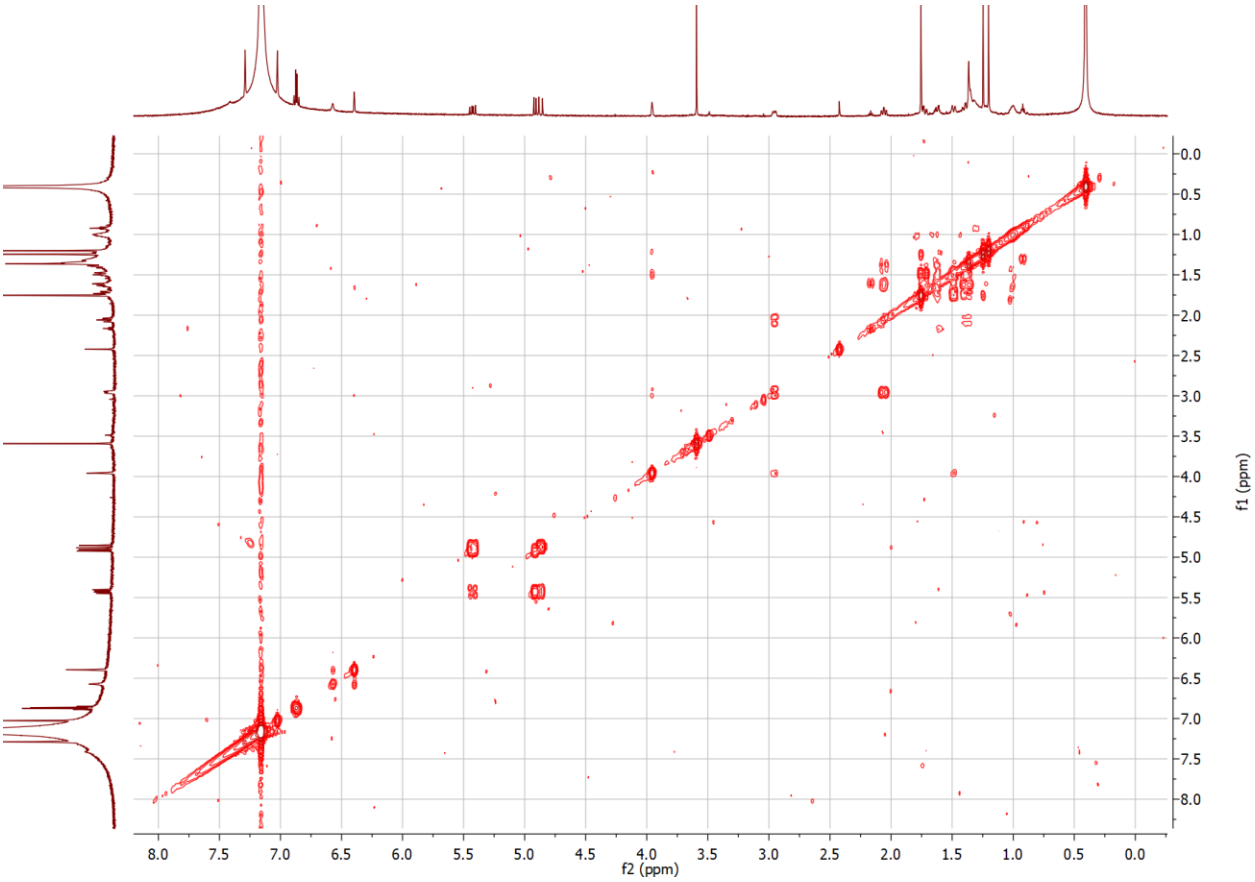


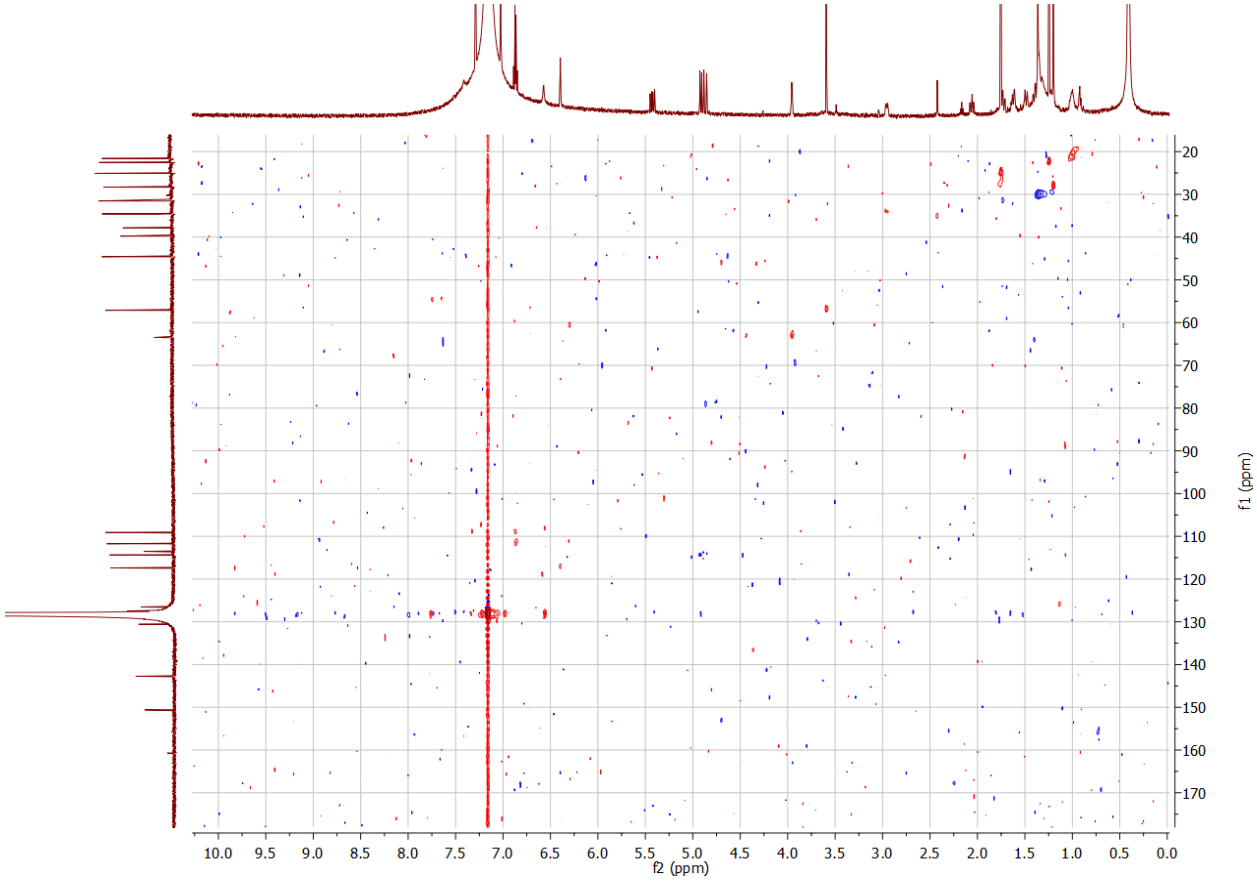
Calc. $[M+H]^+$ 383.1117 Obsv. 383.1121

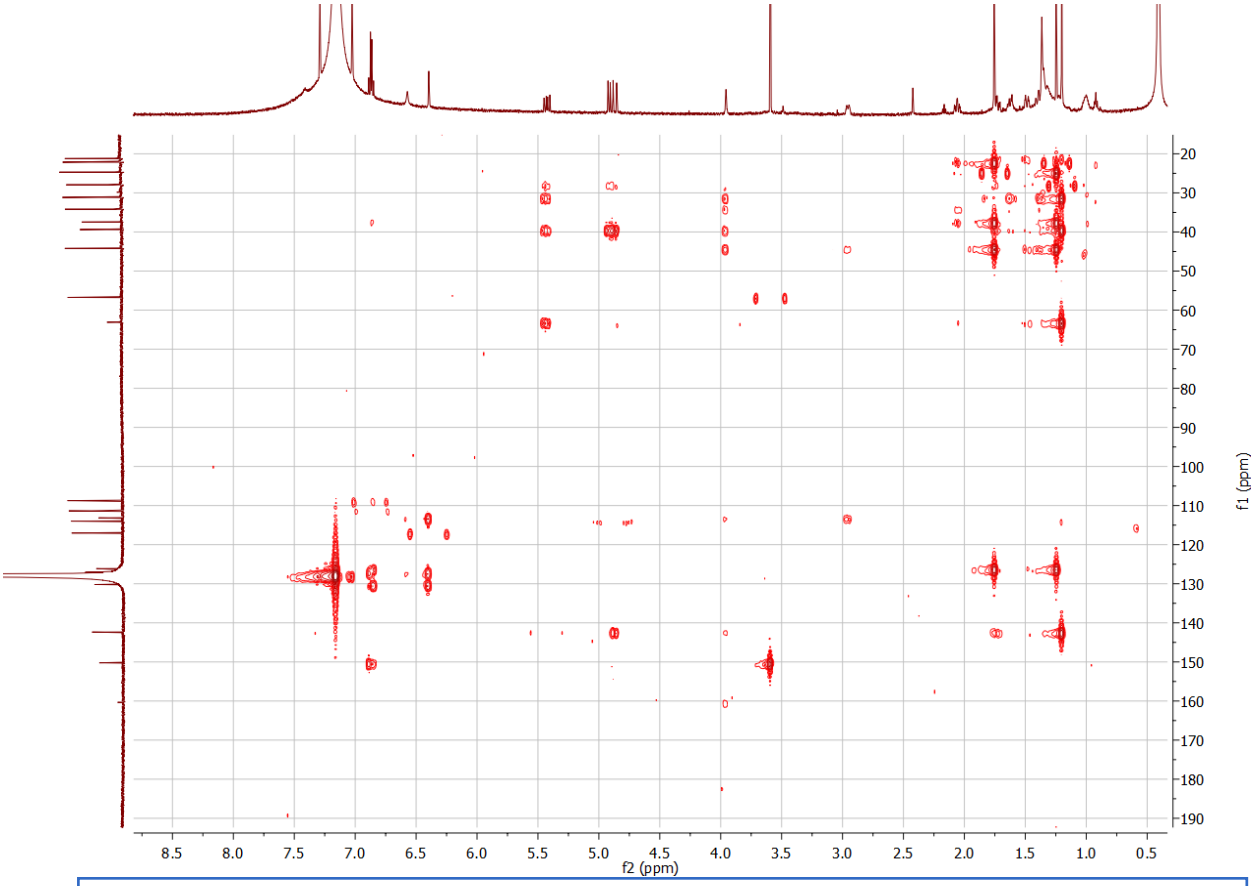
^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 5-OMe-12-*epi*-Hapalindole U (**28**) in C_6D_6 at 600 MHZ and 125 MHz respectively.

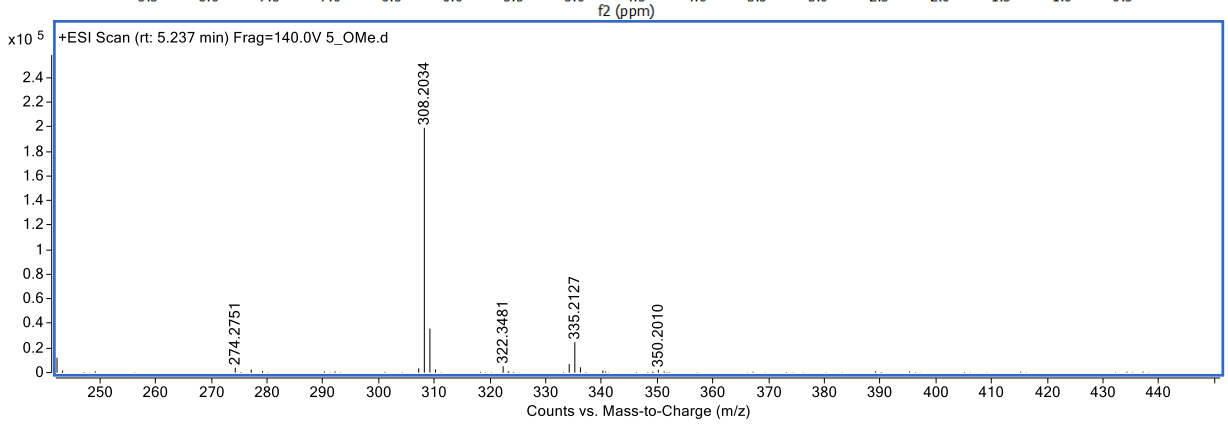



160.72
150.60
142.74
130.57
127.46
126.52
117.40
114.36
113.53
111.74
109.12
63.47
57.12
44.59
39.77
37.84
34.57
31.54
28.32
25.09
22.53
21.61
f1 (ppm)


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
f1 (ppm)

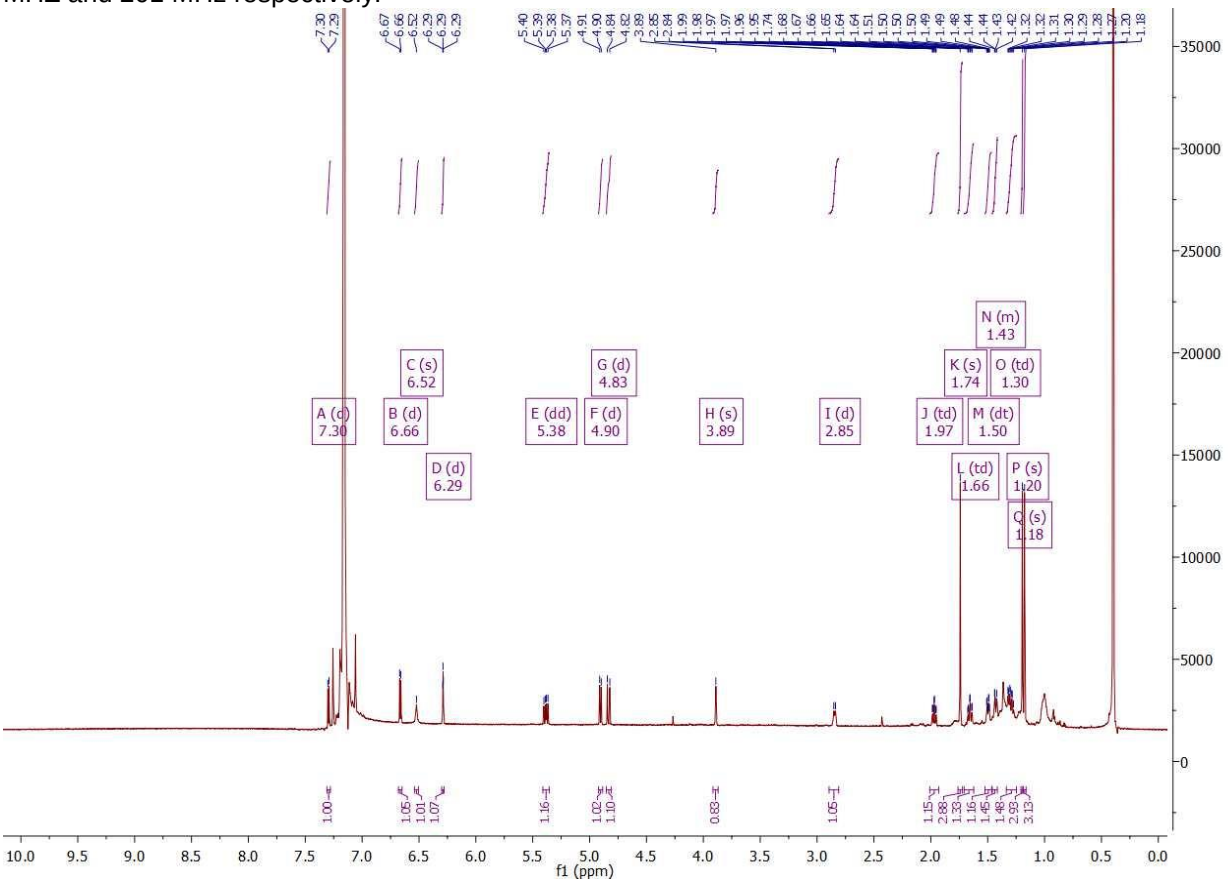

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)

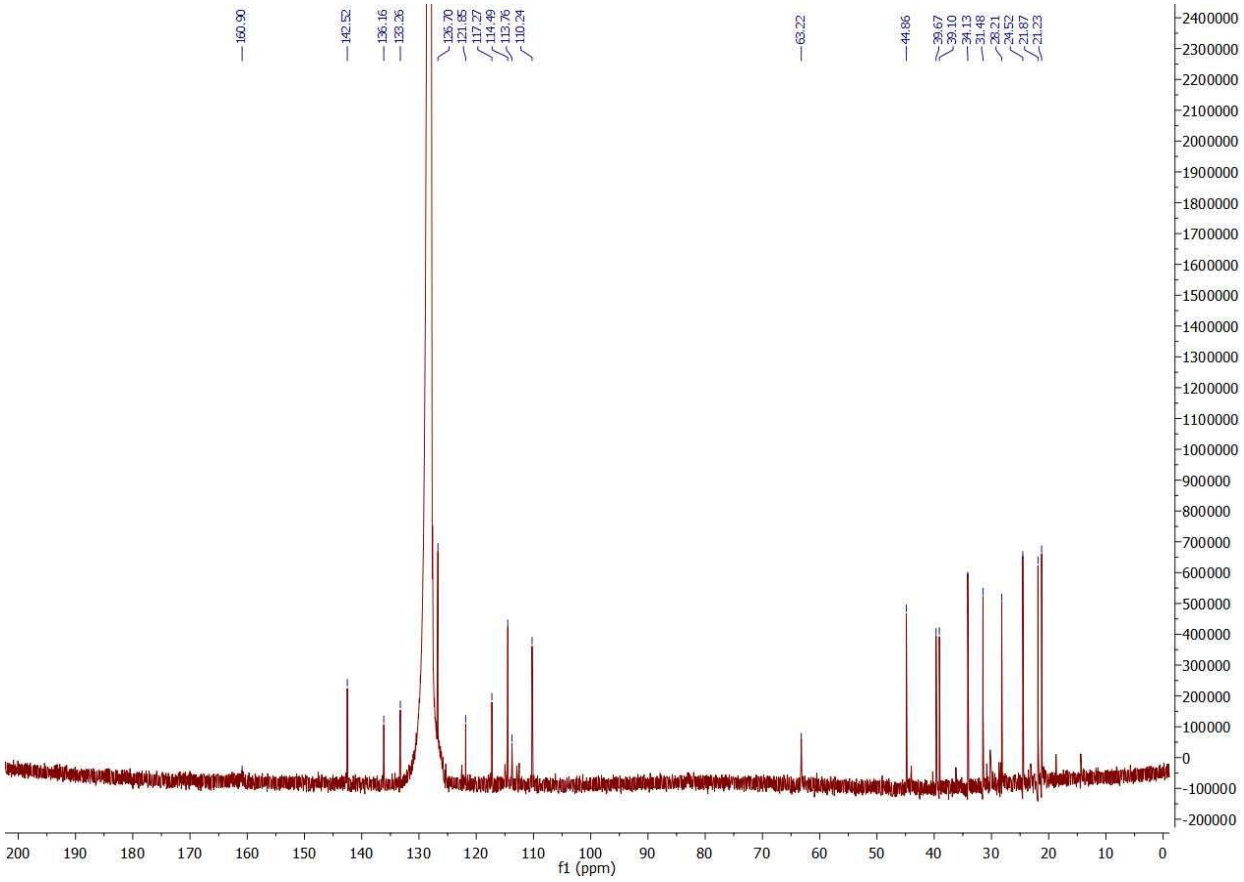




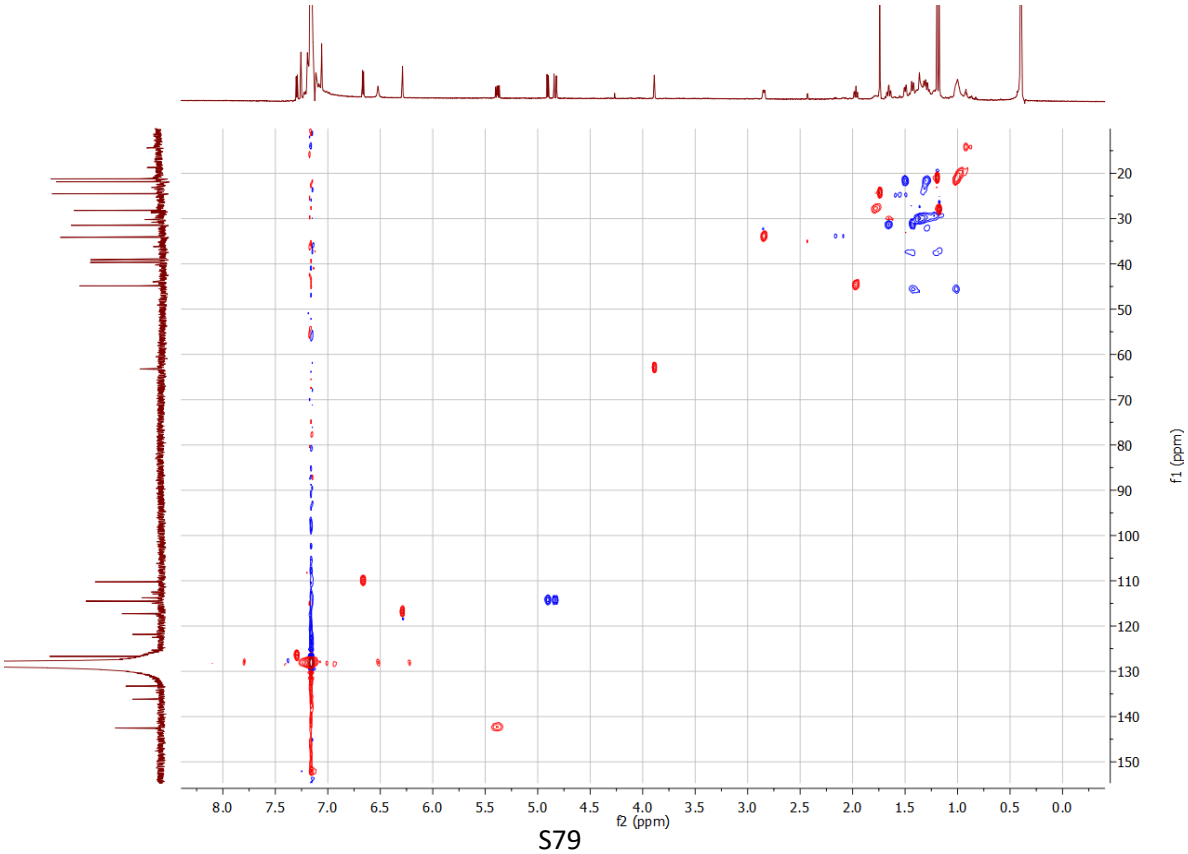
Calc. $[M+H]^+$ 335.2118 Obsv. 335.2127

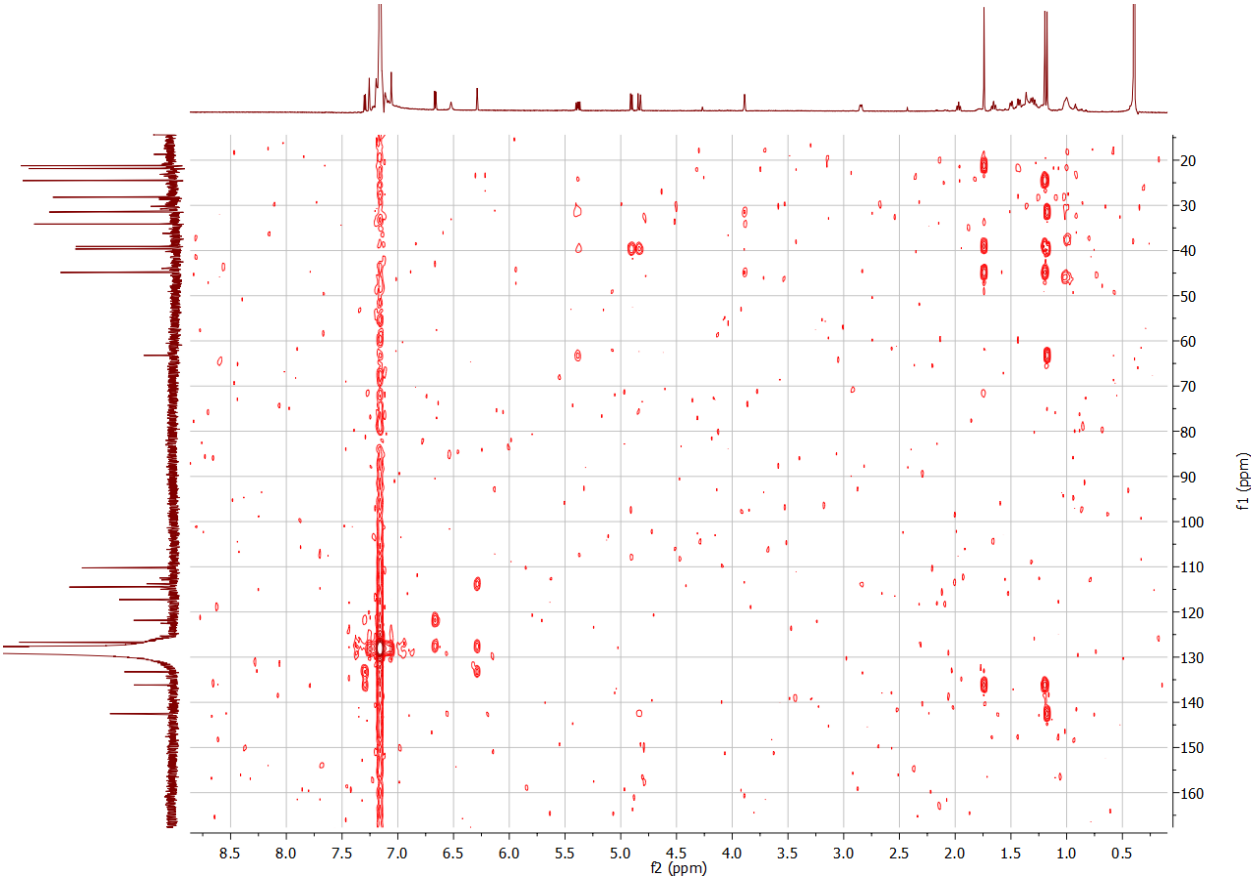
^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 5-Cl-12-*epi*-Hapalindole U (**24**) in C_6D_6 at 800 MHZ and 201 MHz respectively.

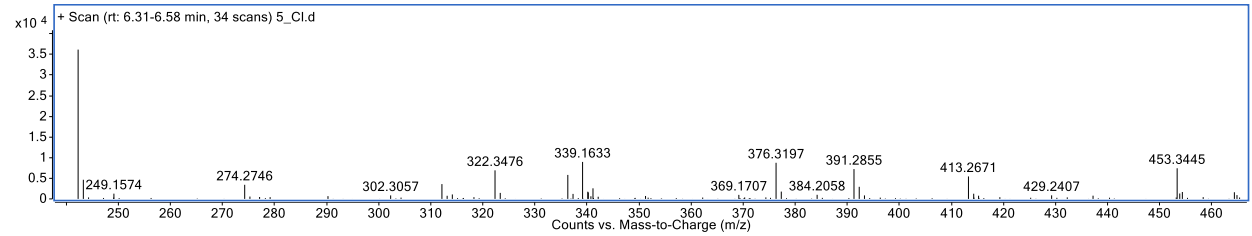



160.90
142.52
136.16
133.26
126.70
121.85
117.27
114.49
113.76
110.24
63.22
44.86
39.67
39.10
34.13
31.48
28.21
24.52
21.87
21.23
f1 (ppm)


f2 (ppm)
f1 (ppm)

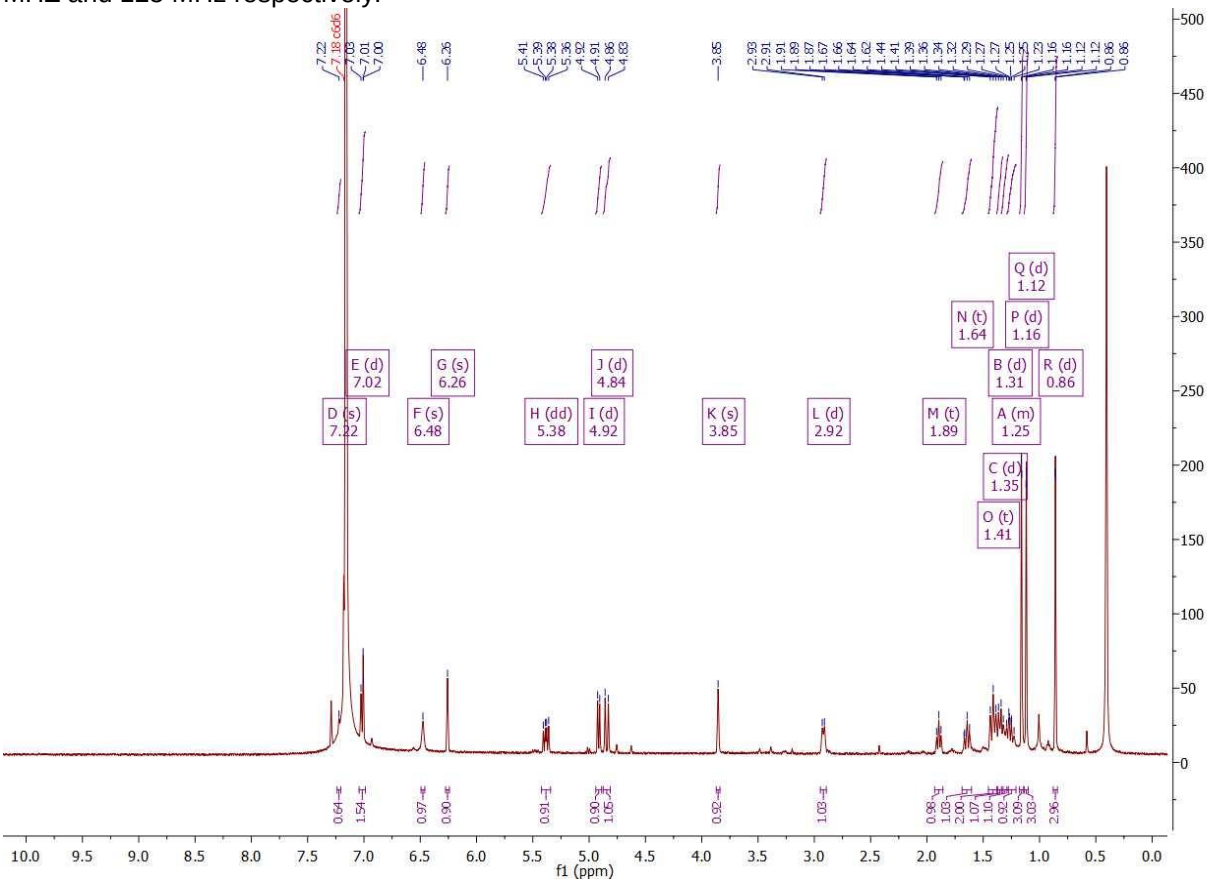

f2 (ppm)
f1 (ppm)

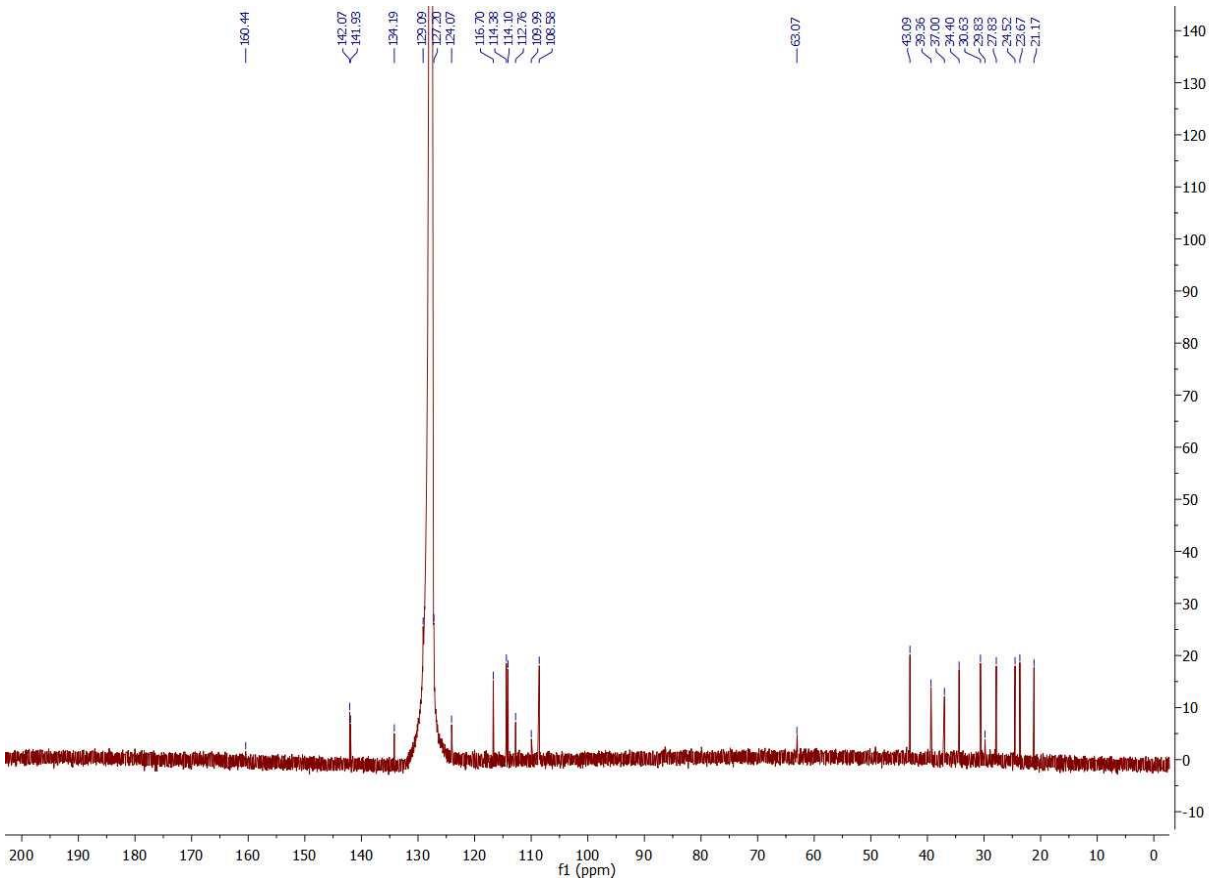


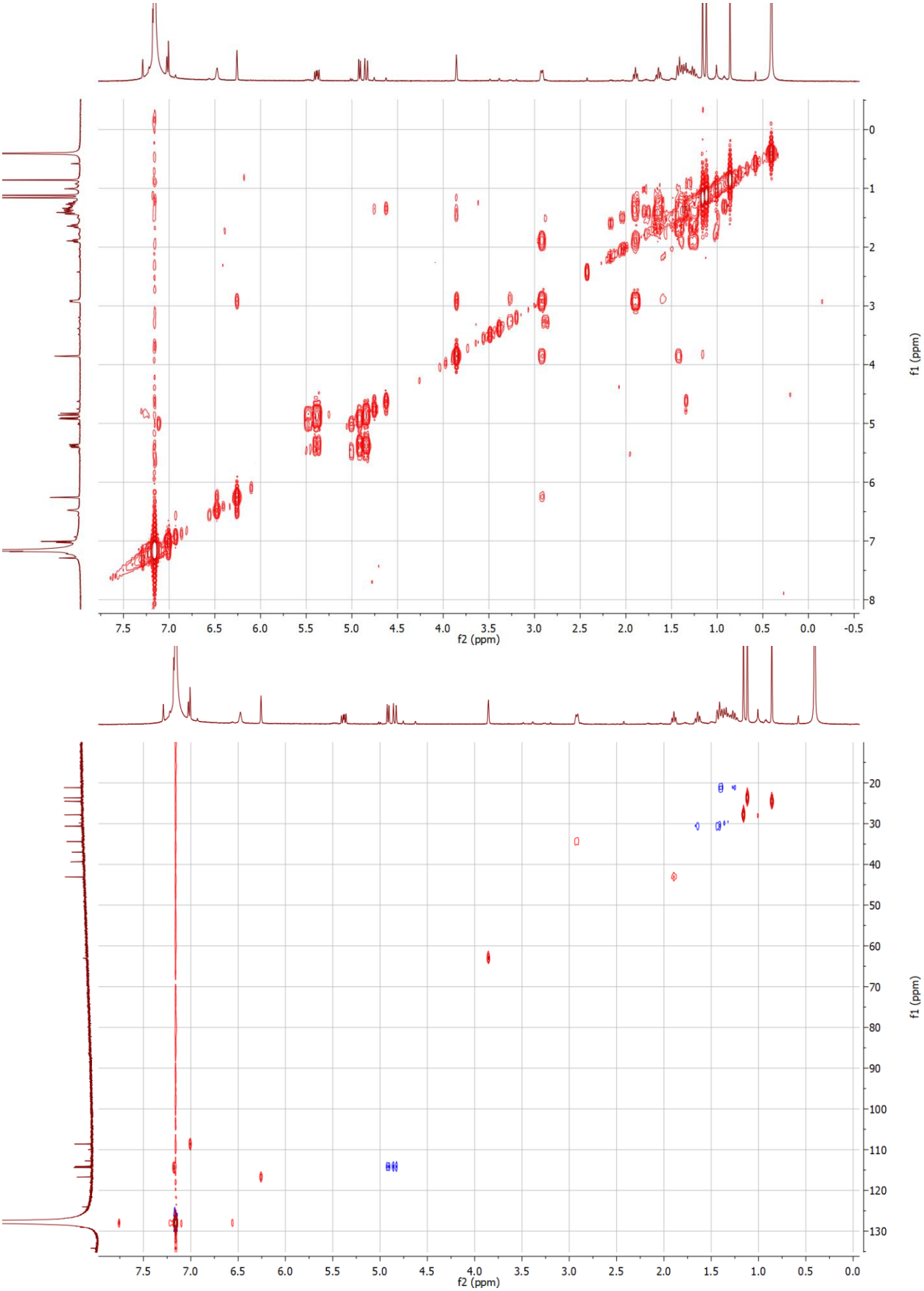


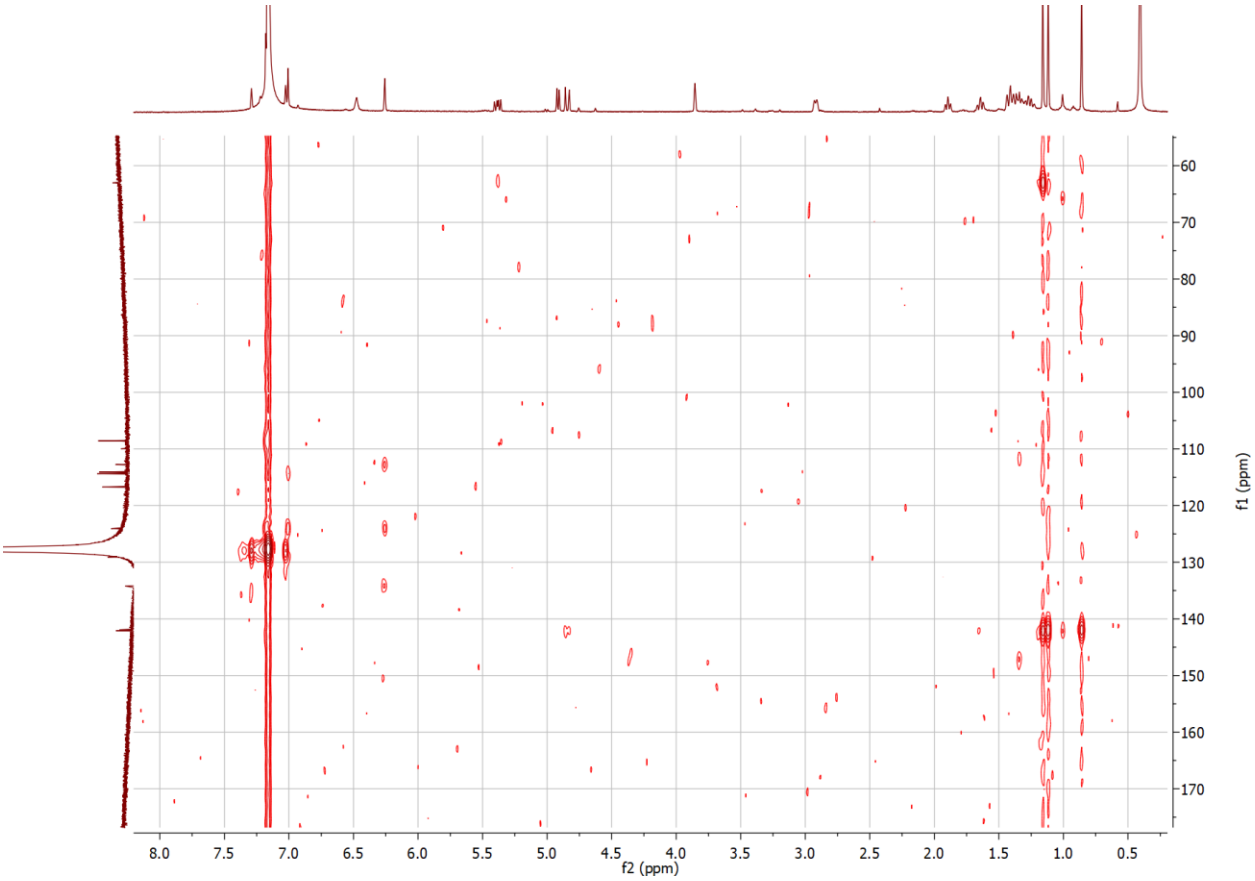
Calc. $[M+H]^+$ 339.1623 Obsv. 339.1633

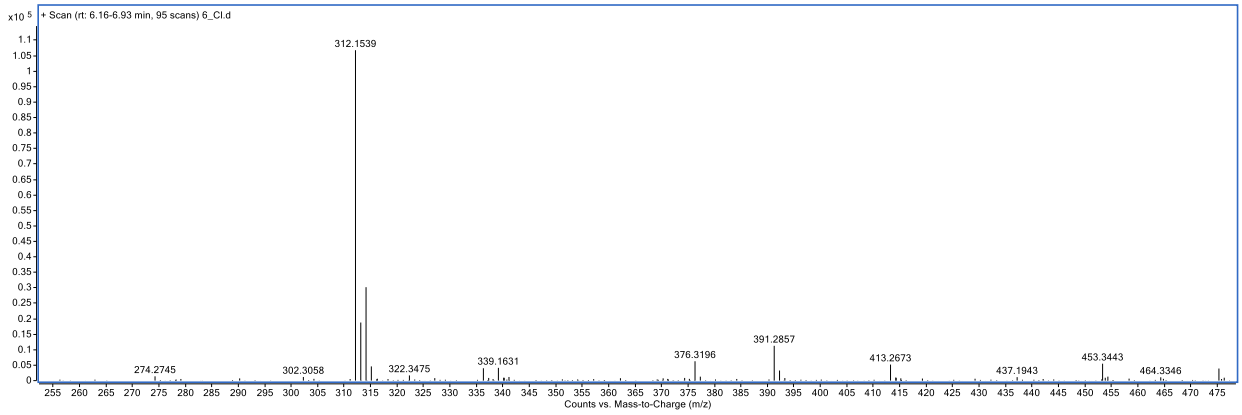
^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 6-Cl-12-*epi*-Hapalindole U (**25**) in C_6D_6 at 600 MHZ and 125 MHz respectively.




160.44
142.07
141.93
134.19
129.09
127.20
124.07
116.70
114.38
114.10
112.76
109.99
108.58
63.07
43.09
39.36
37.00
34.40
30.63
29.83
27.83
24.52
23.67
21.17
f1 (ppm)

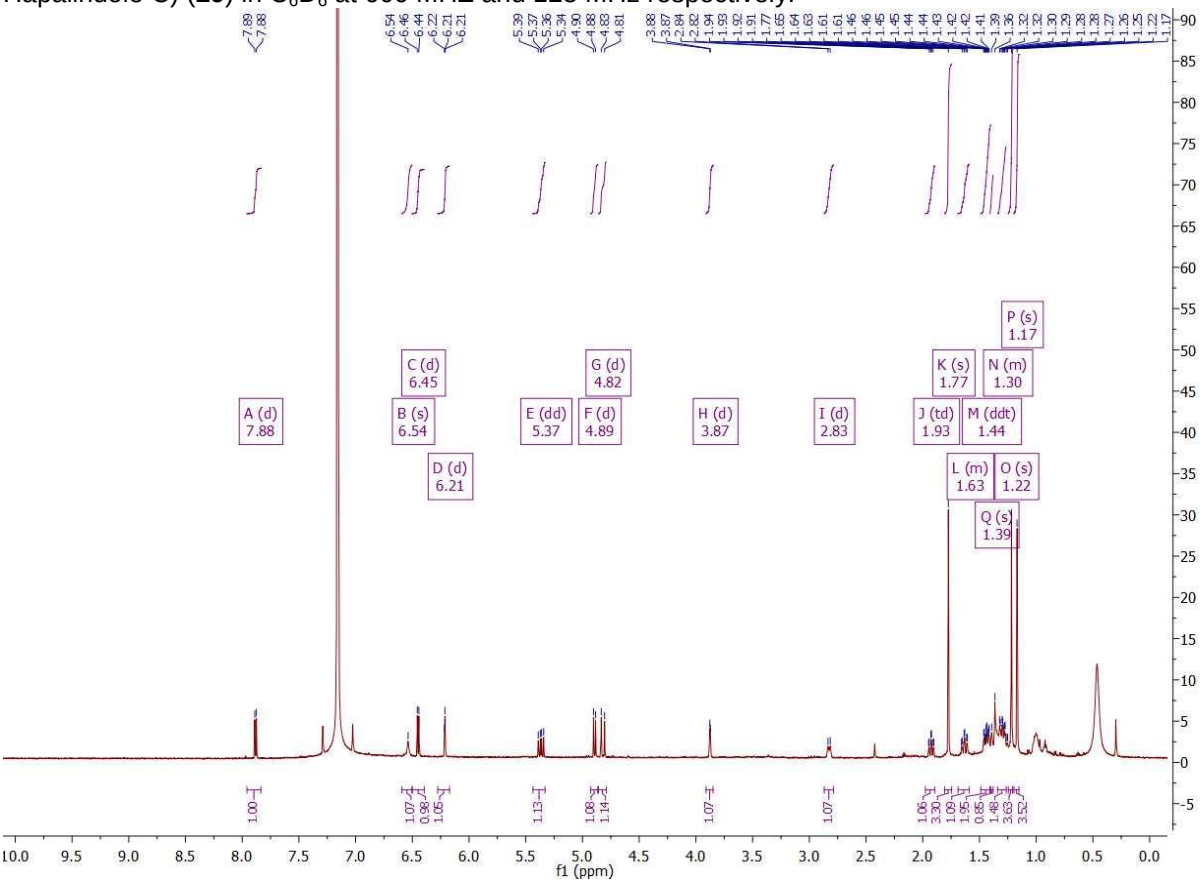

f2 (ppm)
f1 (ppm)
f2 (ppm)
f1 (ppm)

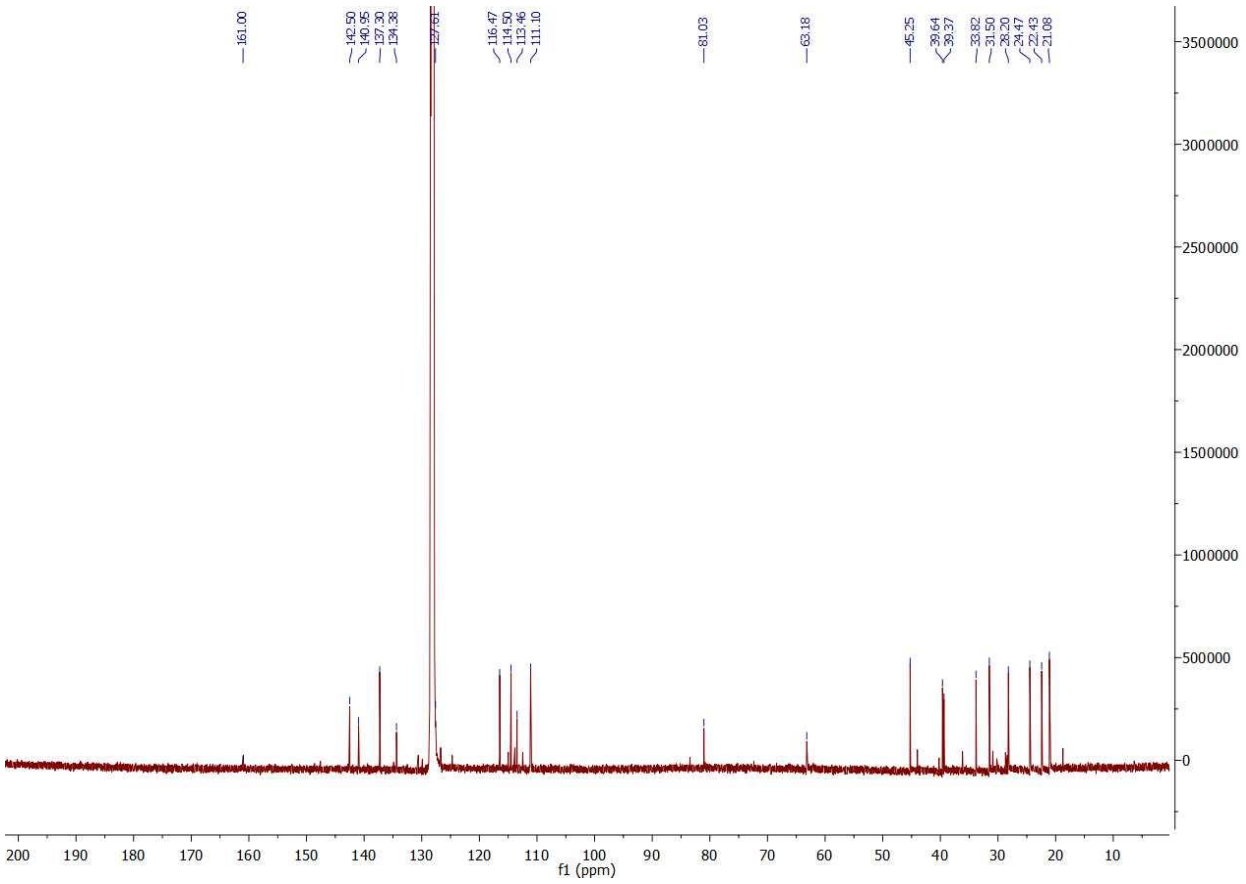


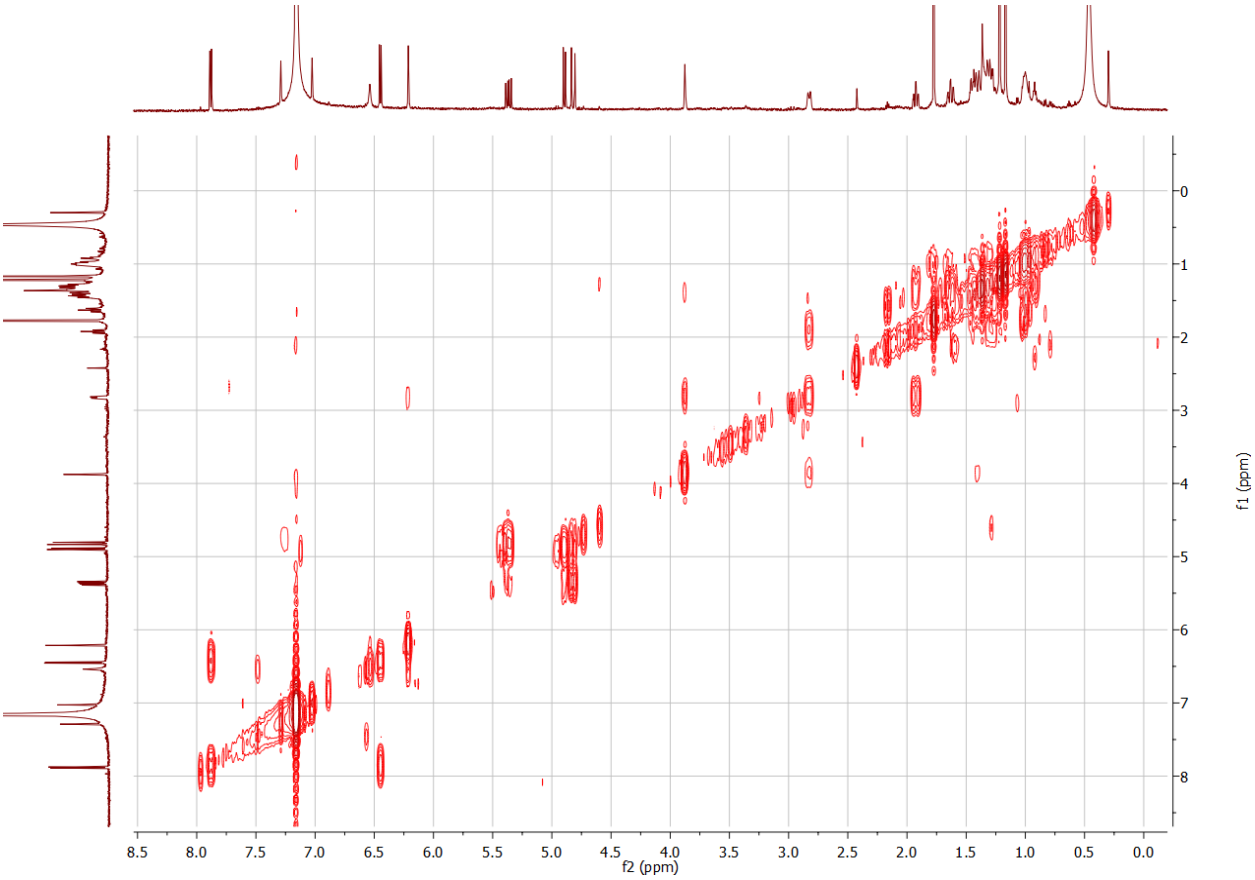


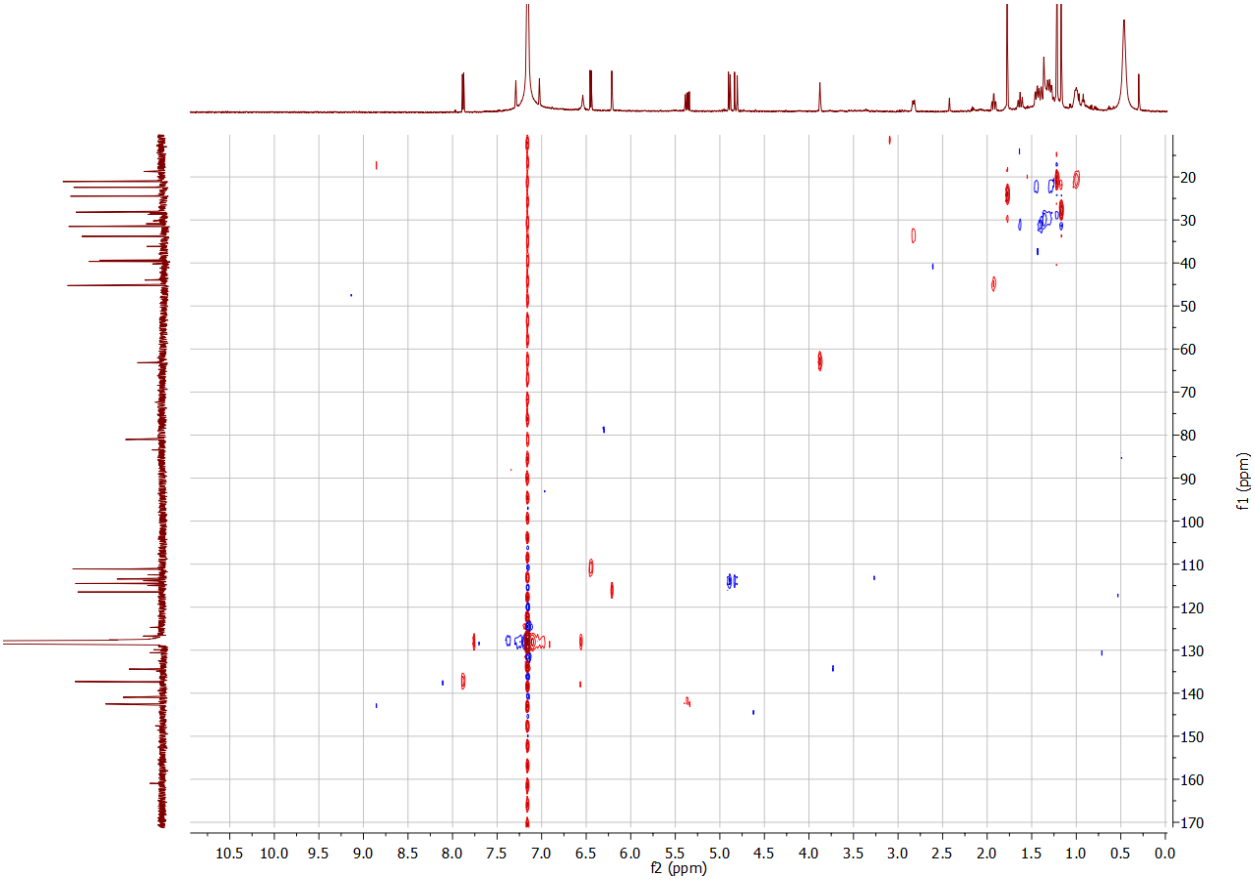
Calc. $[M+H]^+$ 339.1623 Obsv. 339.1631

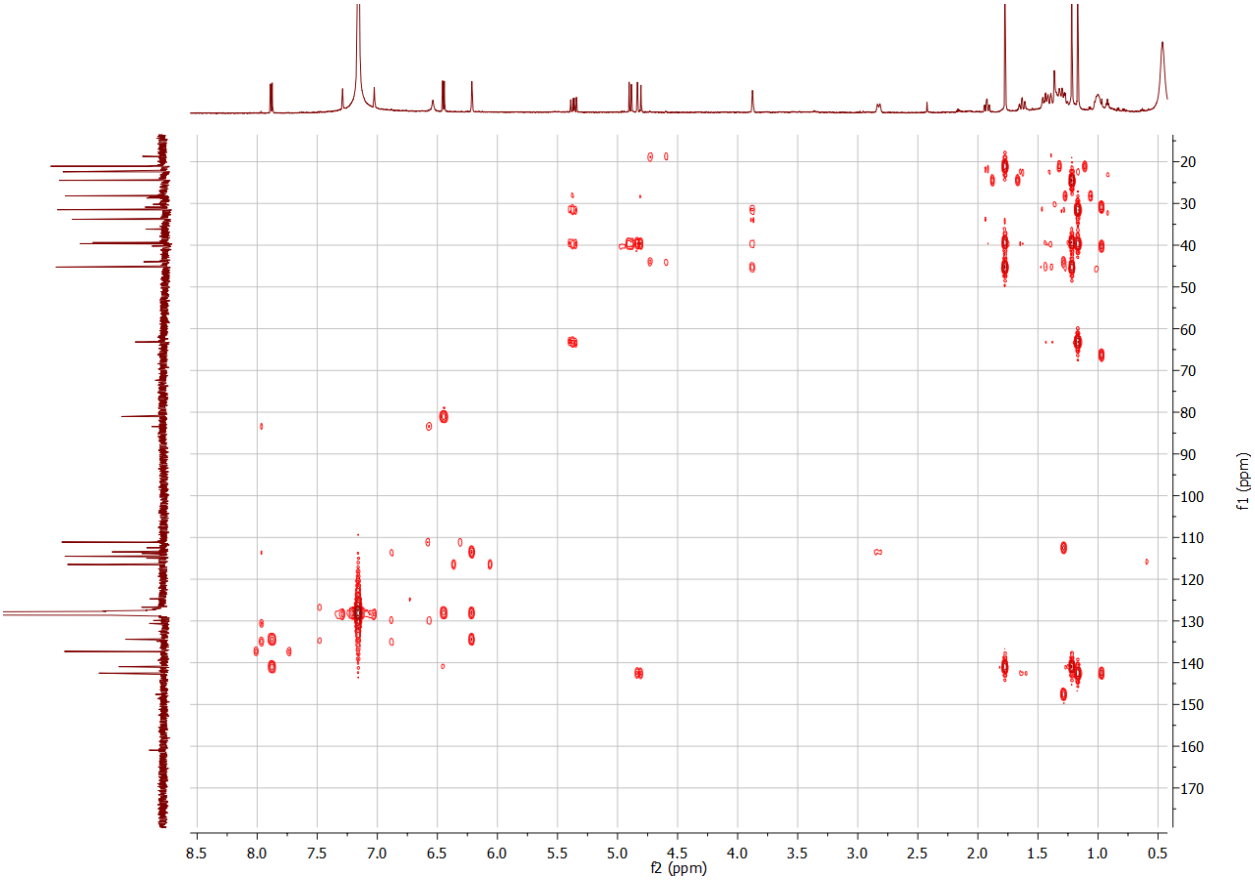
^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 5-I-12-*epi*-Hapalindole U (with trace 5-I-12-*epi*-Hapalindole C) (**29**) in C_6D_6 at 600 MHZ and 125 MHz respectively.

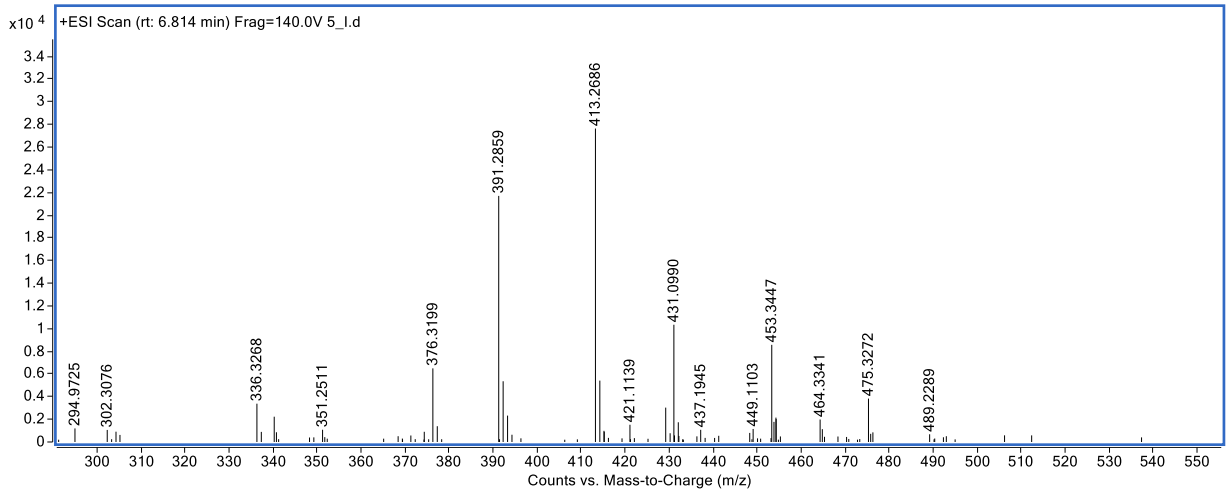



161.00
142.50
140.95
137.30
134.38
129.61
116.47
114.50
113.46
111.10
81.03
63.18
45.25
39.64
39.37
33.82
31.50
28.20
24.47
22.43
21.08
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

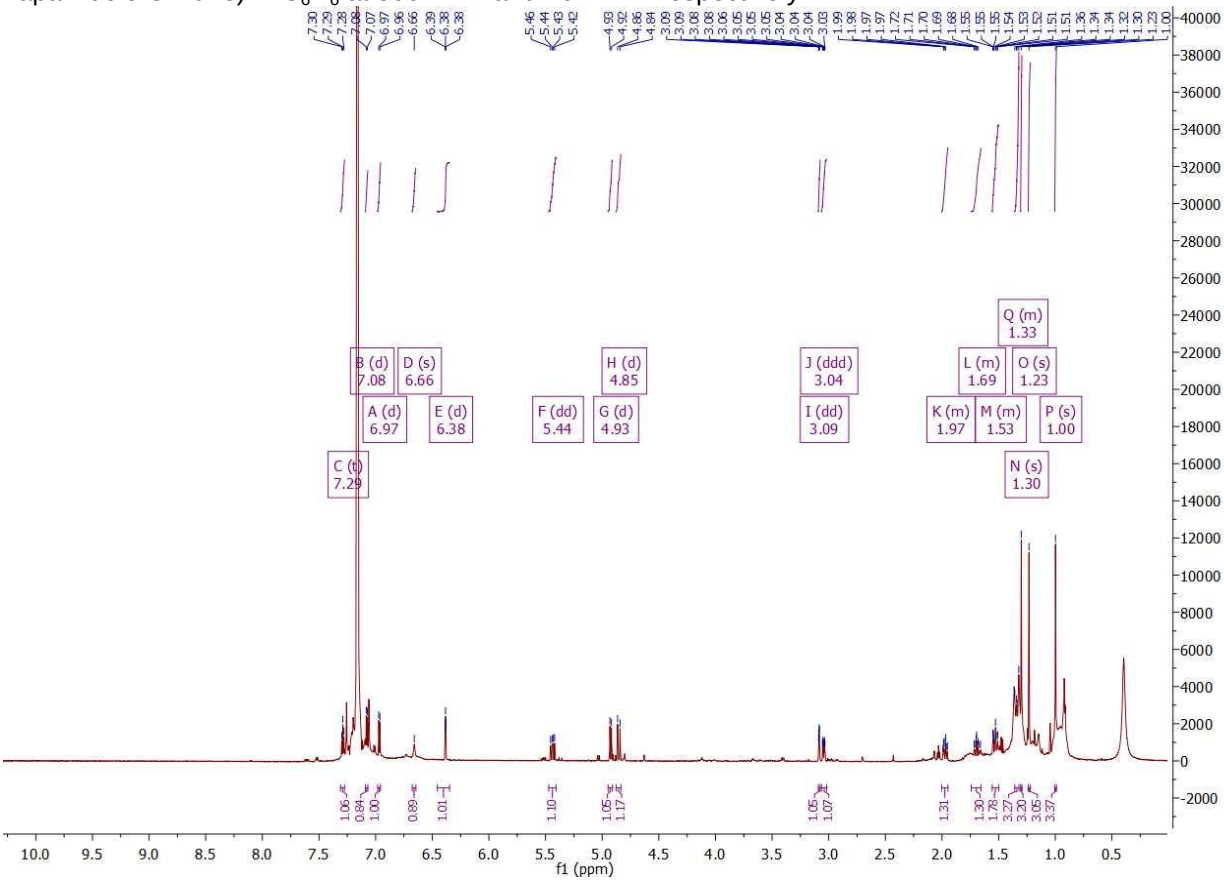

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170
f1 (ppm)

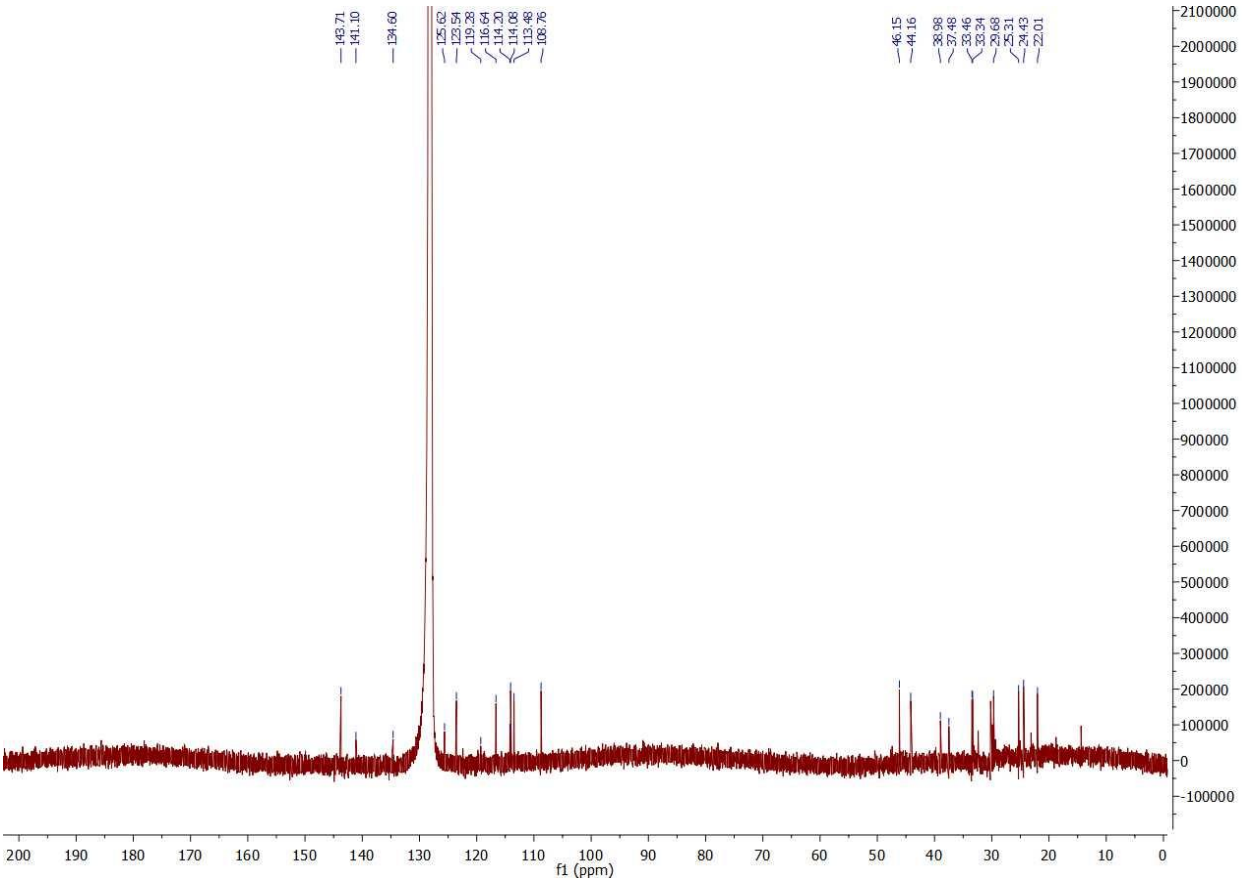


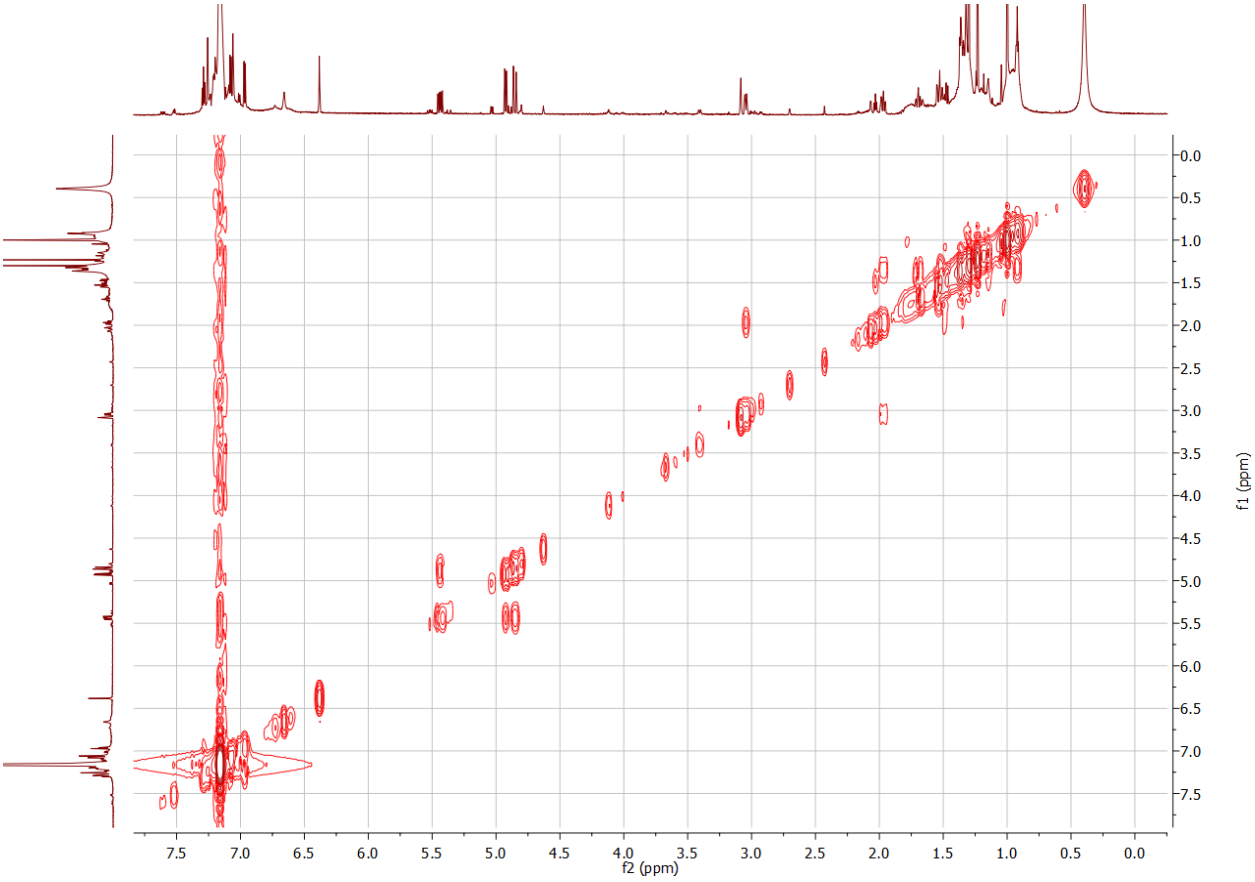


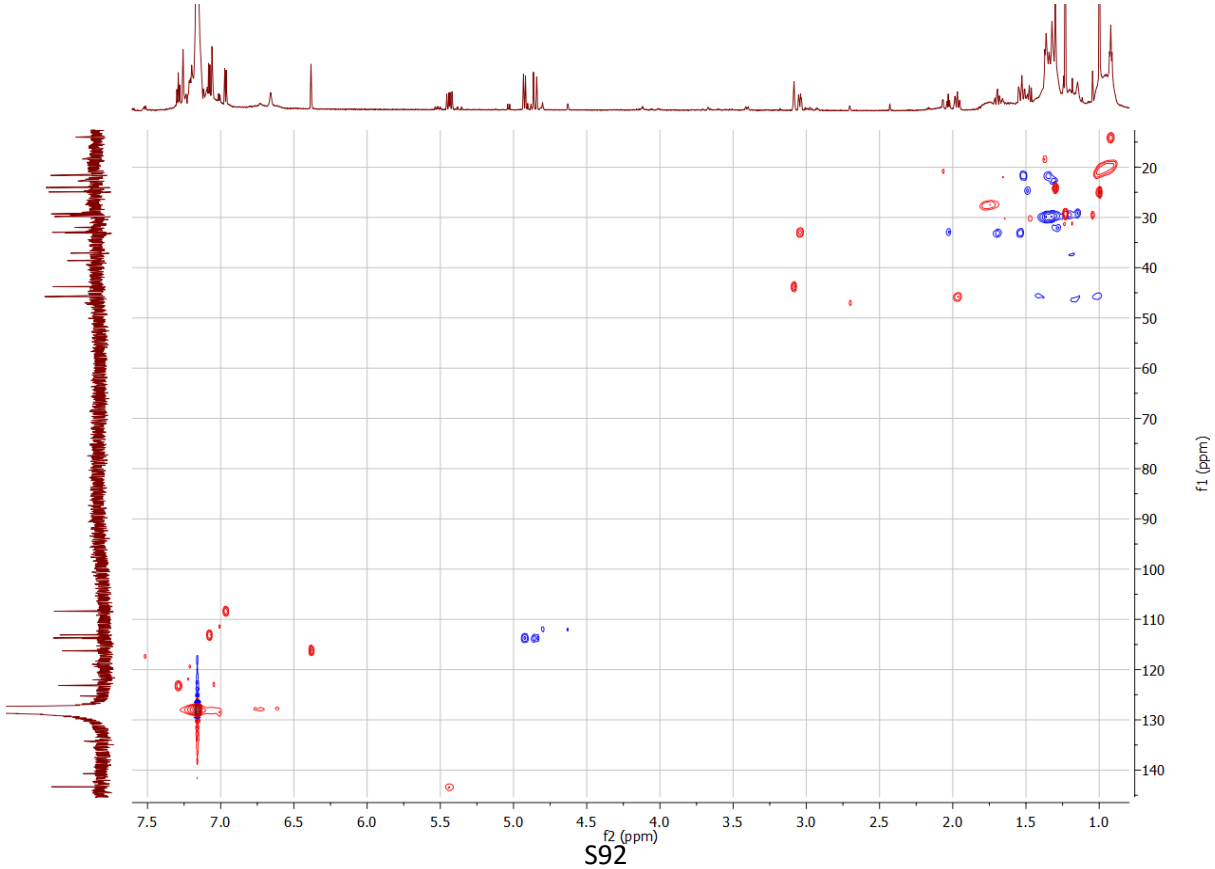
Calc. $[M+H]^+$431.0979 Obsv. 431.0990

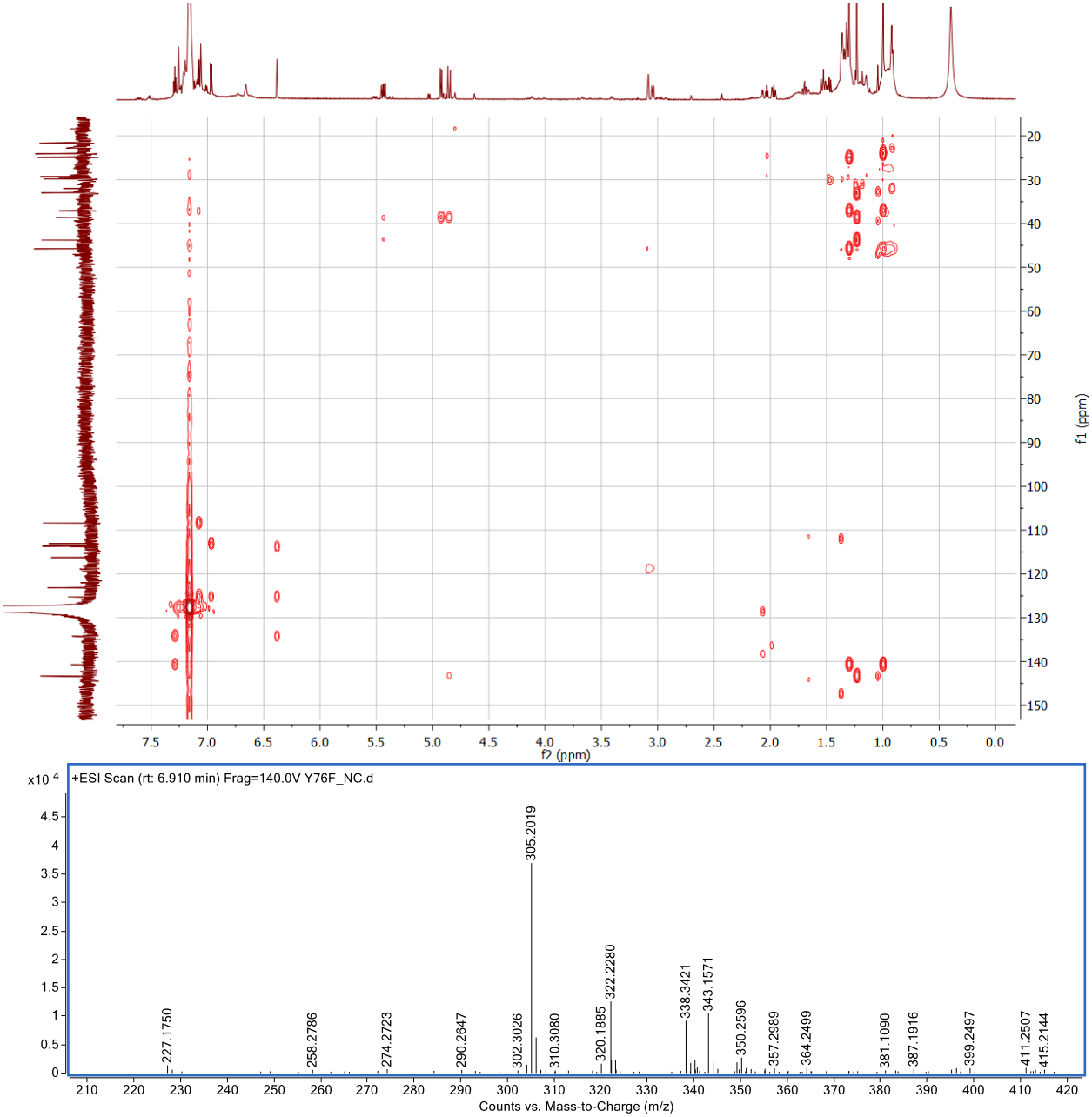
^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 12-epi-hapalindole nitrile (**30**) (w/trace 12-*epi*-hapalindole C nitrile) in C_6D_6 at 800 MHZ and 201 MHz respectively.




143.71
141.10
134.60
125.62
123.54
119.28
116.64
114.20
114.00
113.48
108.76
46.15
44.16
38.98
37.48
33.46
33.34
29.68
25.31
24.43
22.01
f1 (ppm)


f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)

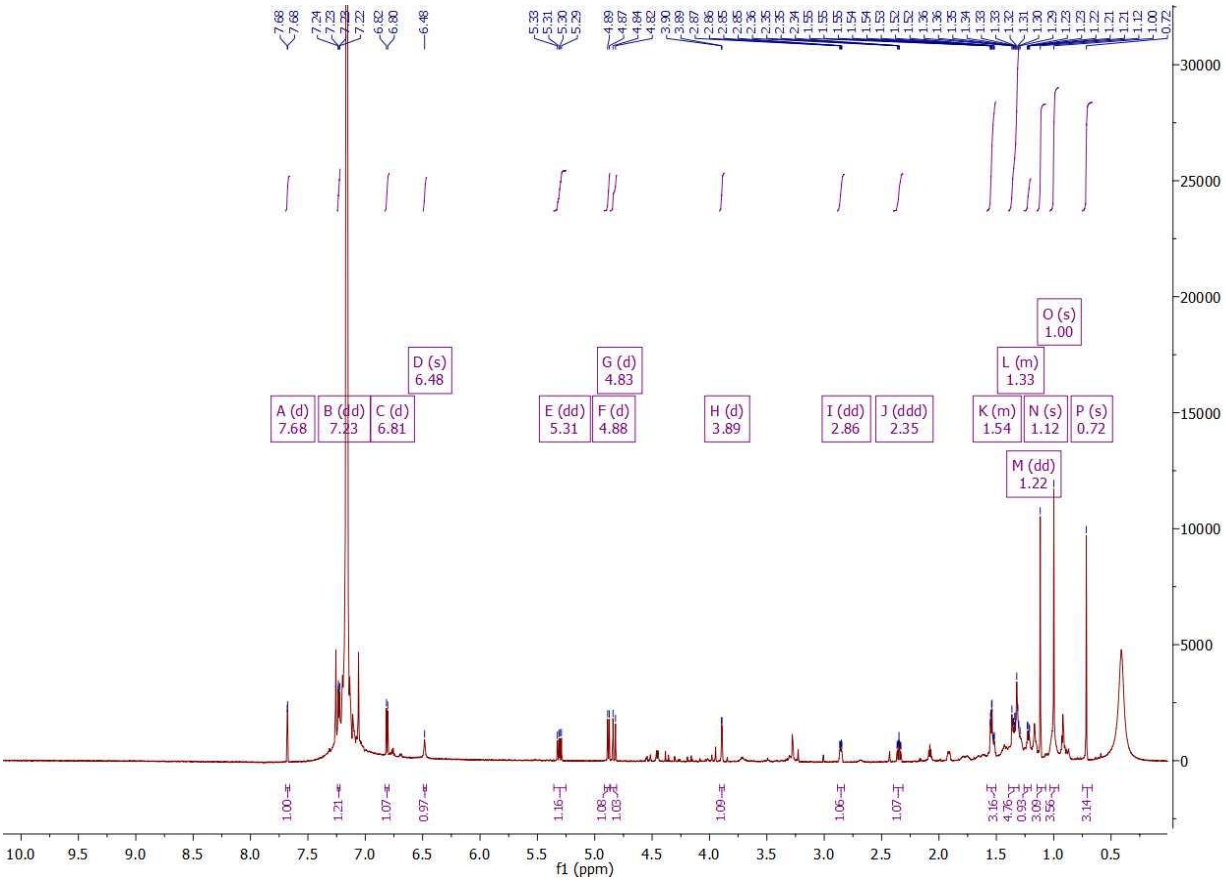


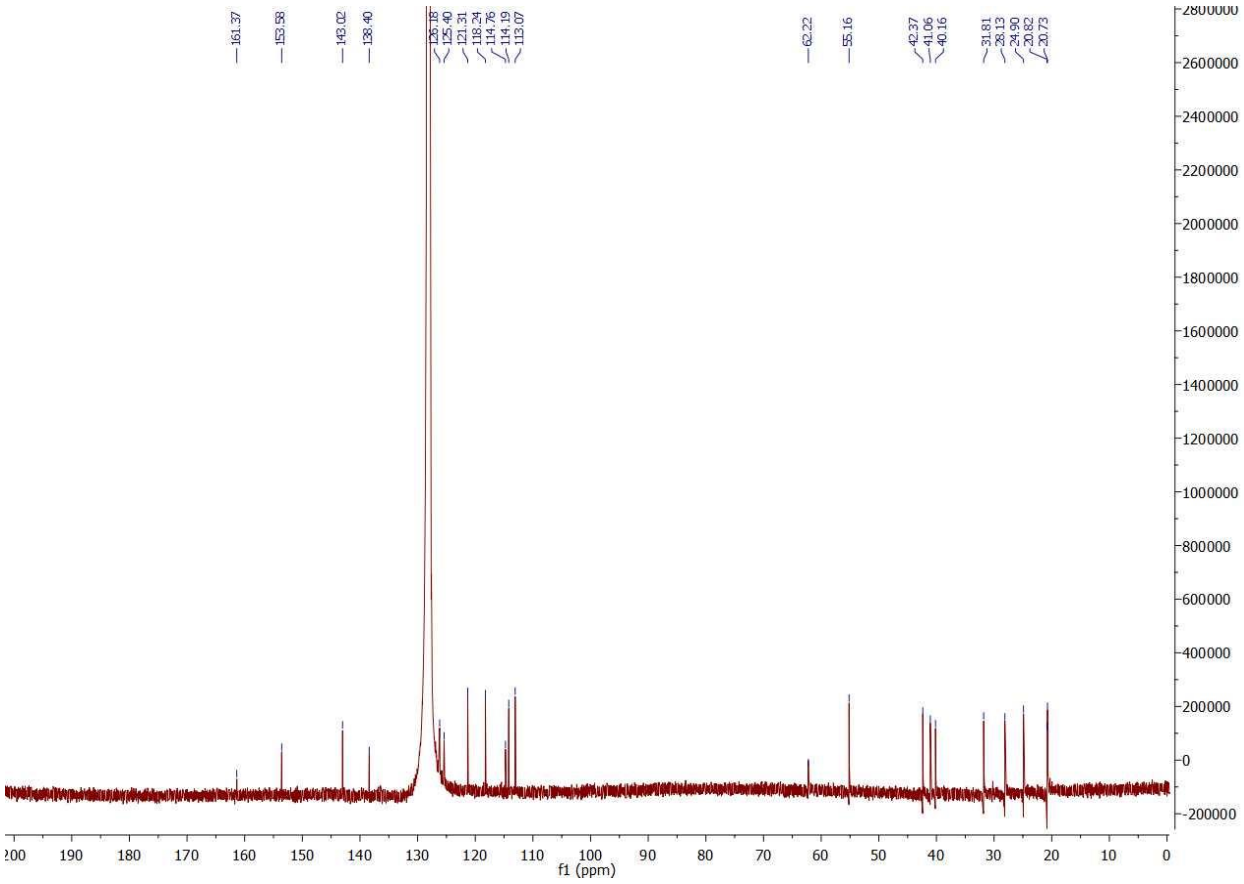
Calc. $[M+H]^+$ 305.2012 Obsv. 305.2019

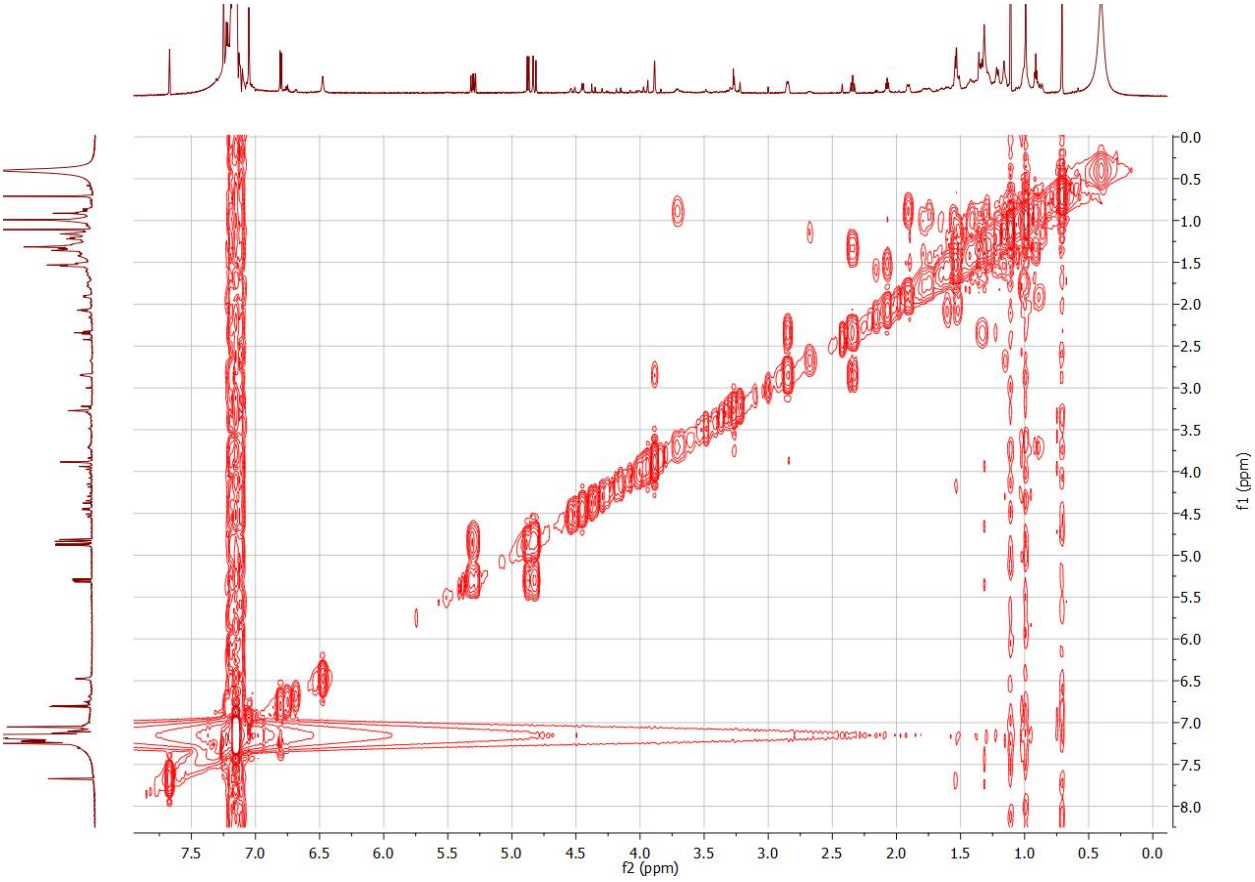
^{1}H and ^{13}Cspectra and HRMS of 5-F-12-*epi*-Fischerindole U (**33**)
Full characterizationn data[1]

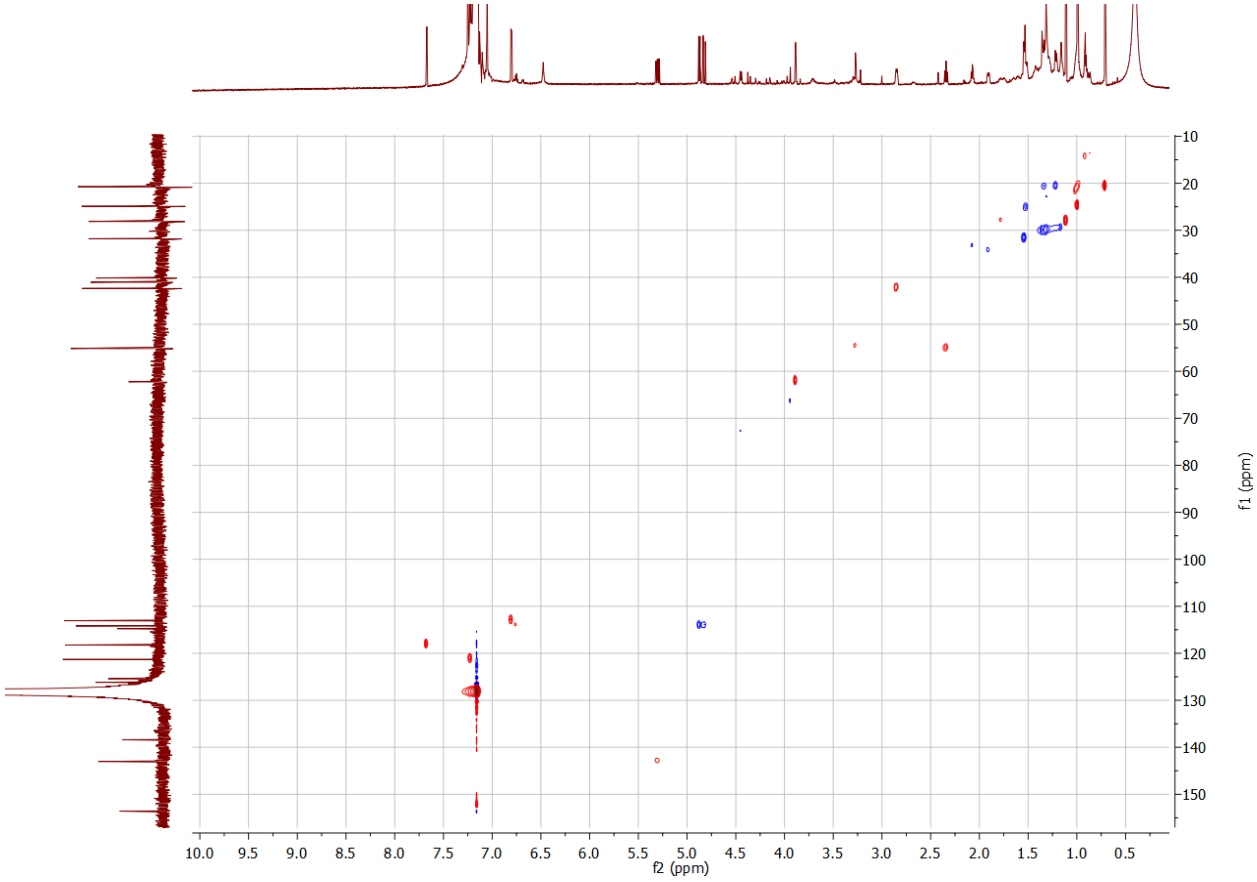
^{1}H and ^{13}CNMR spectra and HRMS of 6-F-12-*epi*-Fischerindole U (**37**)
Full characterization data[1]

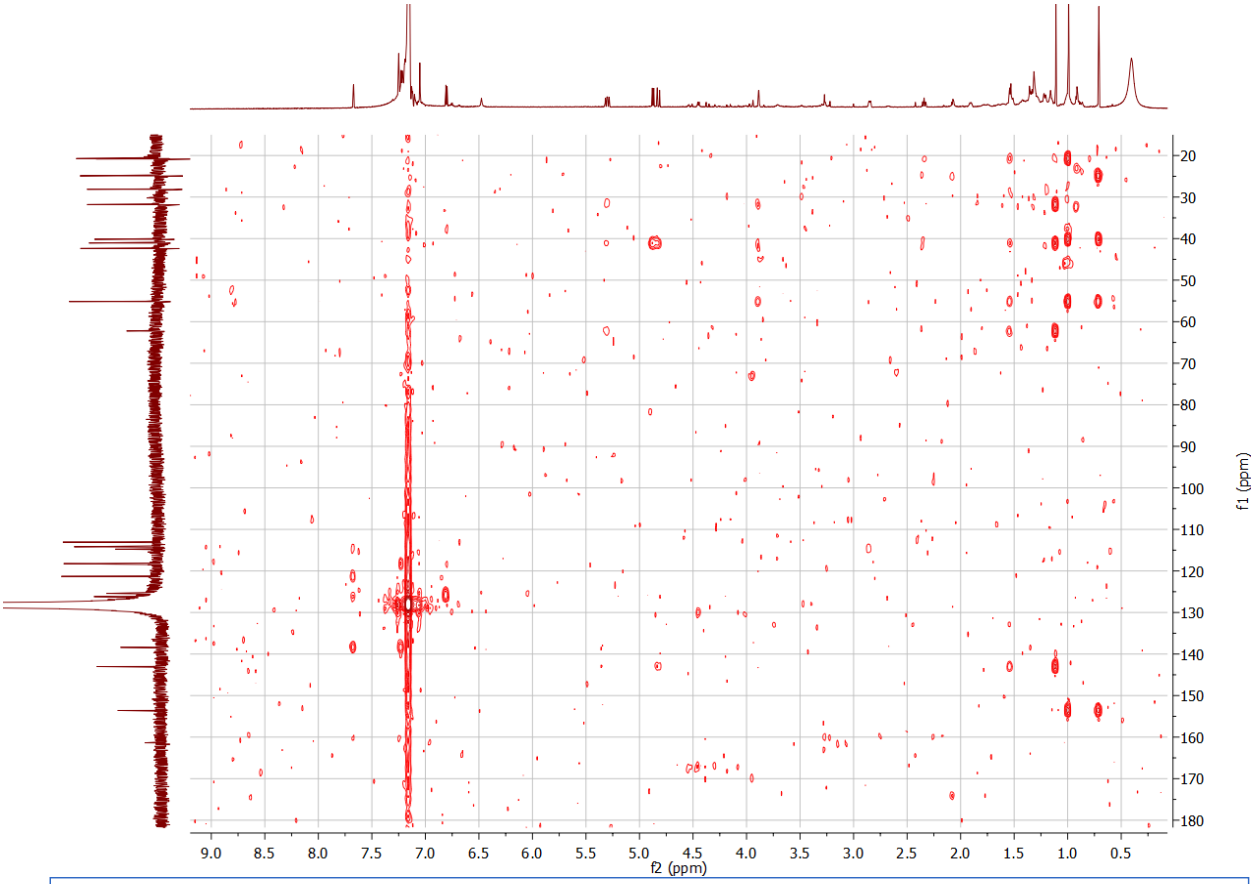
^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 5-Cl-12-*epi*-Fischerindole U (**34**) in C_6D_6 at 800 MHZ and 201 MHz respectively.

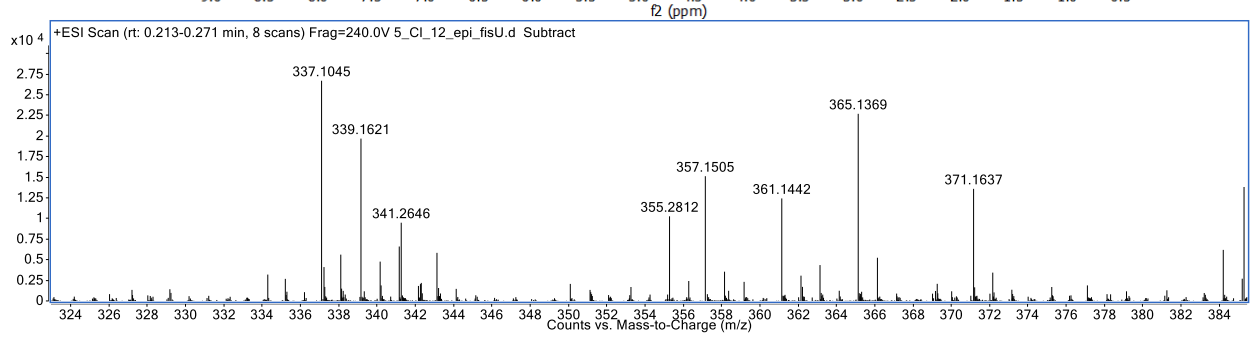



161.37
153.58
143.02
138.40
126.18
125.40
121.31
118.24
114.76
114.19
113.07
62.22
55.16
42.37
41.06
40.16
31.81
28.13
24.90
20.82
20.73
f1 (ppm)


f2 (ppm)
f1 (ppm)

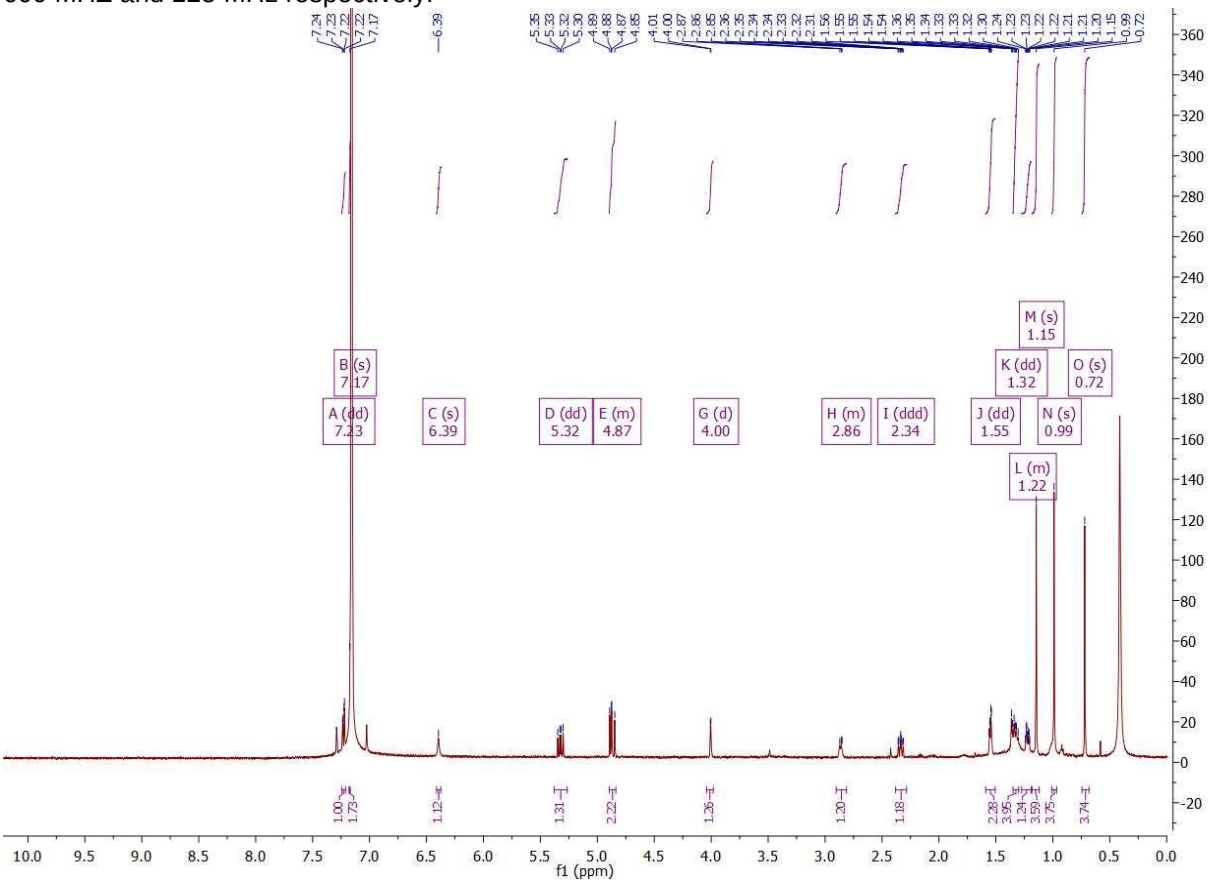

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

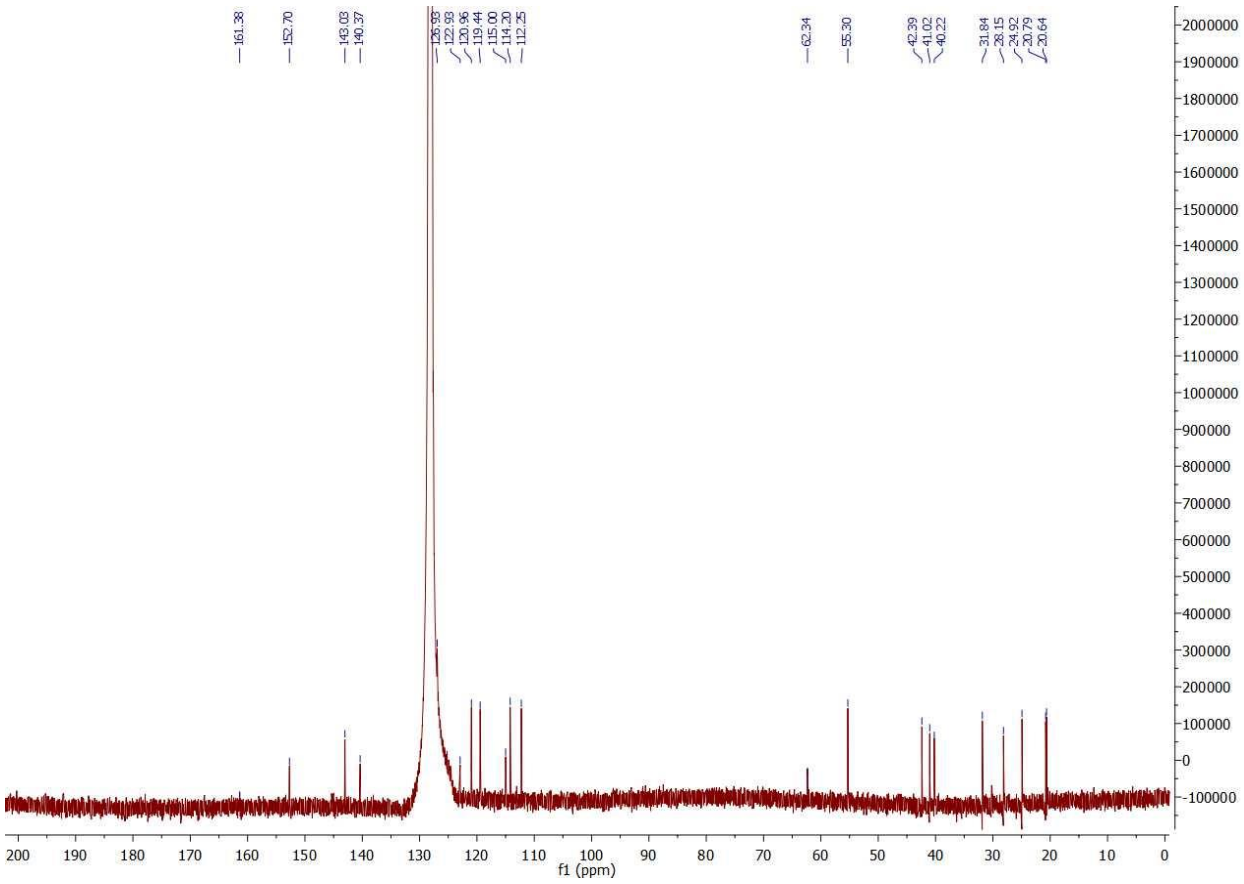


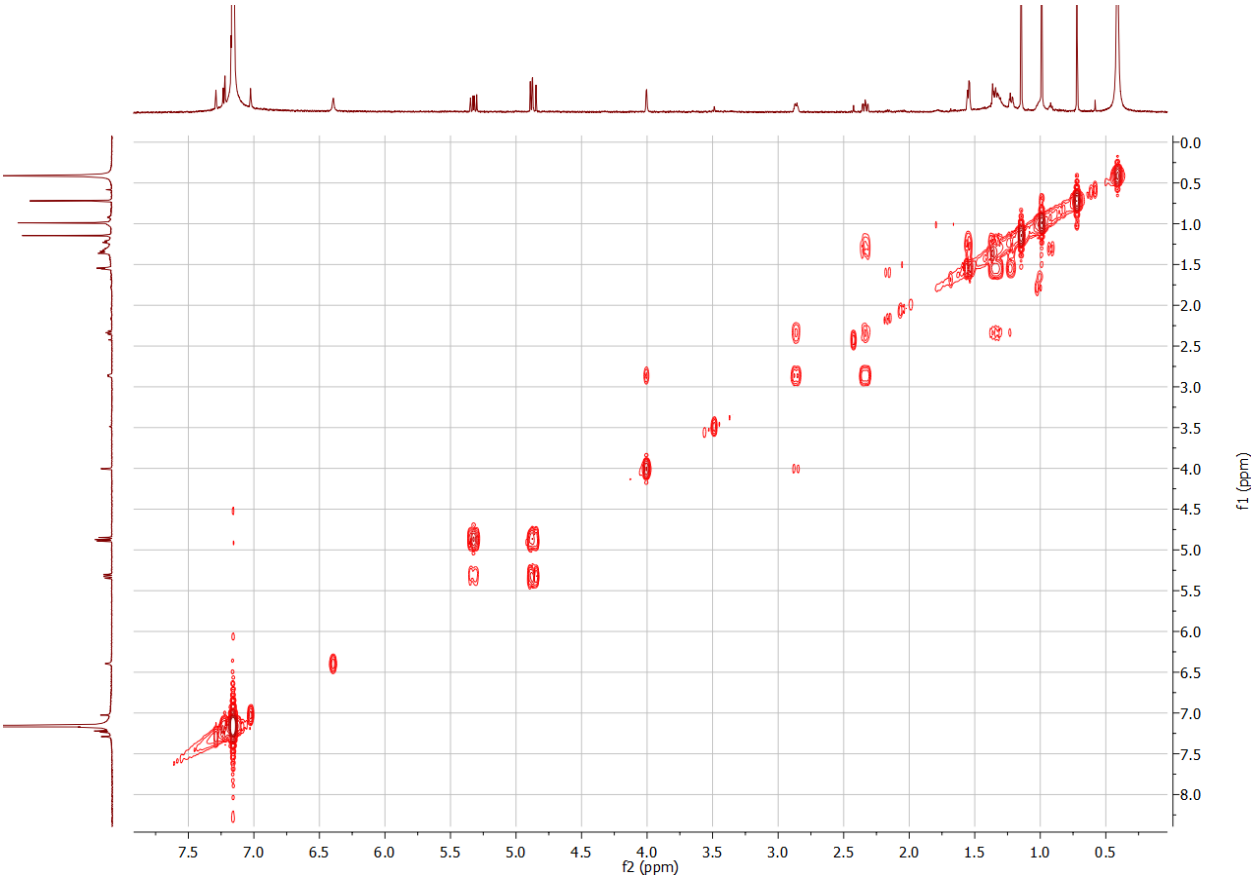


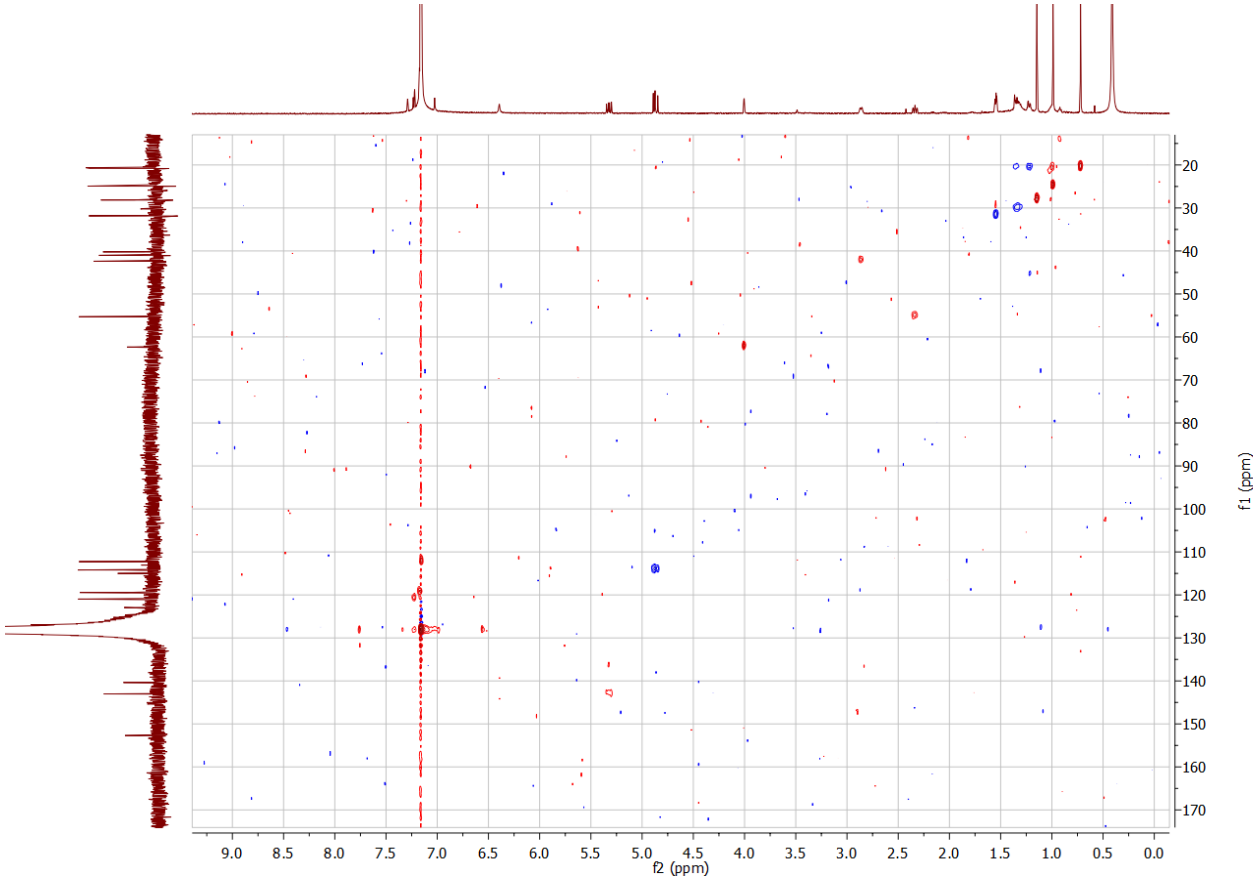
Calc. $[M+H]^+$ 339.1623 Obsv. 339.1621

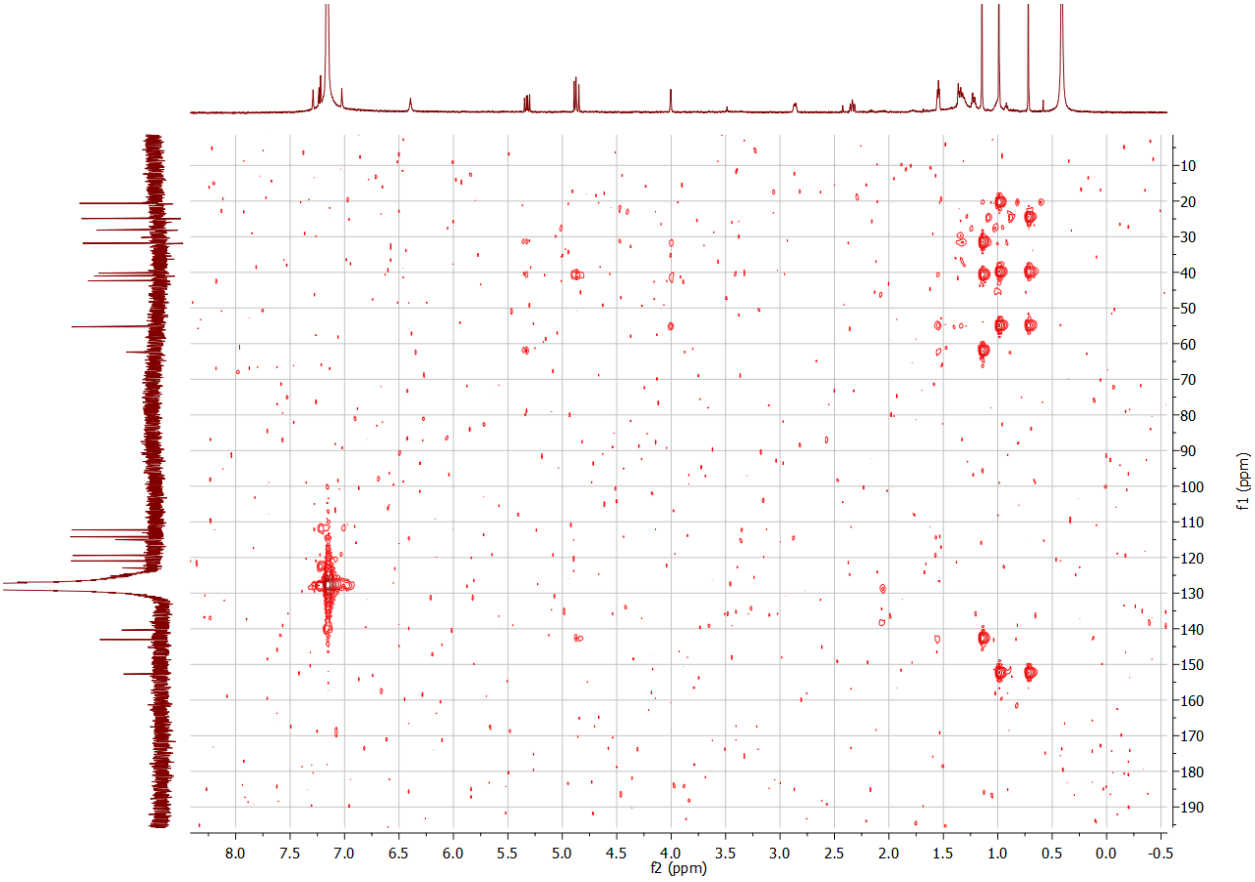
^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 6-Cl-12-*epi*-Fischerindole U (**38**) in C_6D_6 at 600 MHZ and 125 MHz respectively.

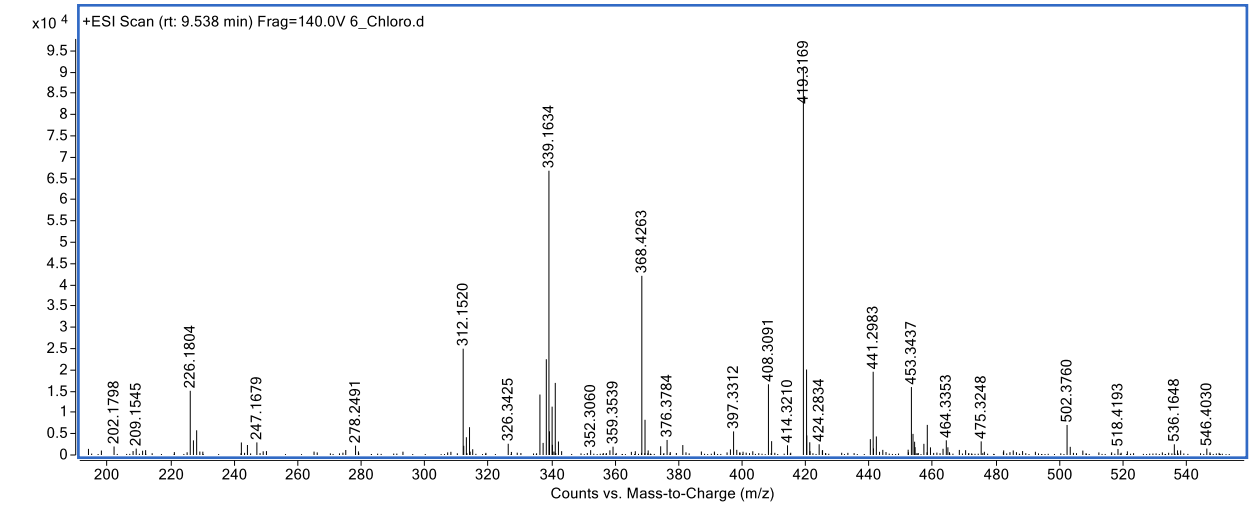



161.38
152.70
143.03
140.37
126.93
122.93
120.96
119.44
115.00
114.20
112.25
62.34
55.30
42.39
41.02
40.22
31.84
28.15
24.92
20.79
20.64
f1 (ppm)


f2 (ppm)
f1 (ppm)

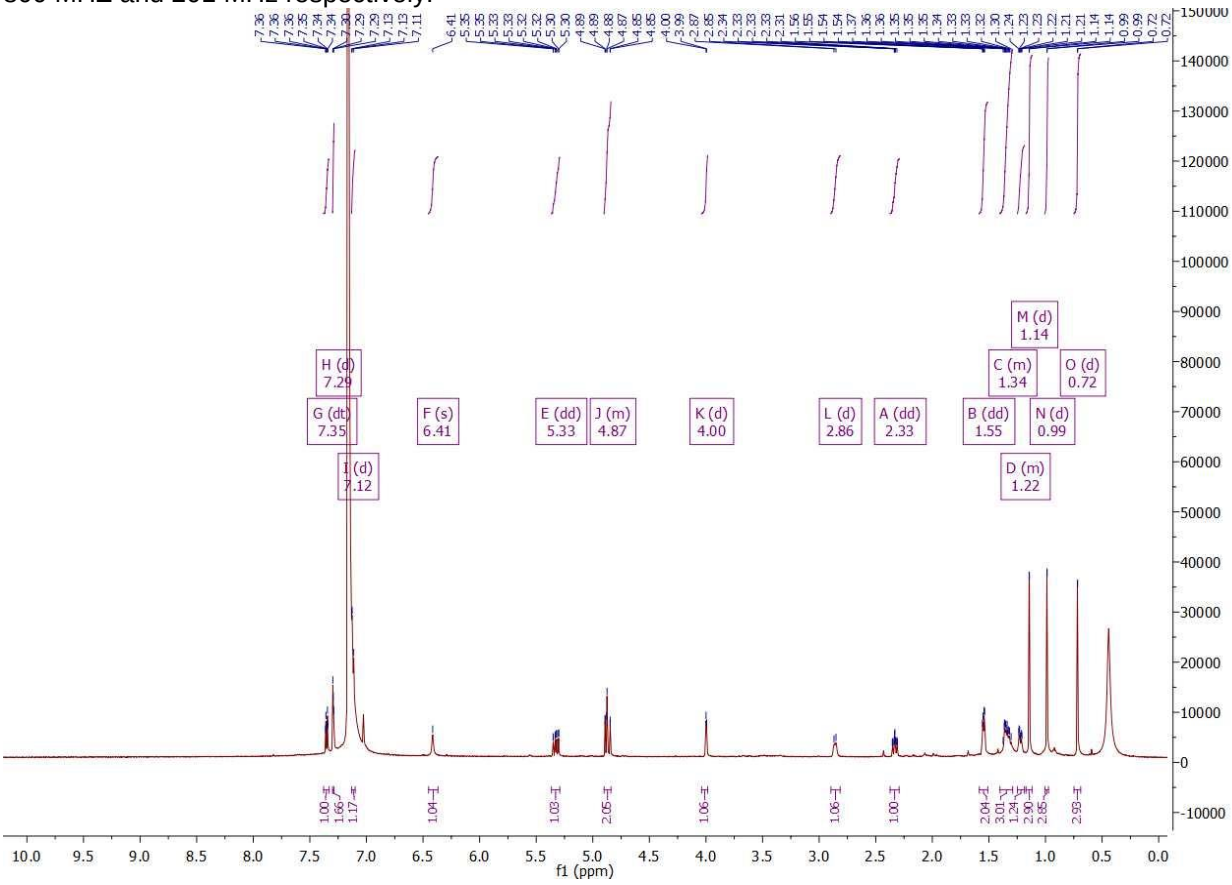

f2 (ppm)
f1 (ppm)

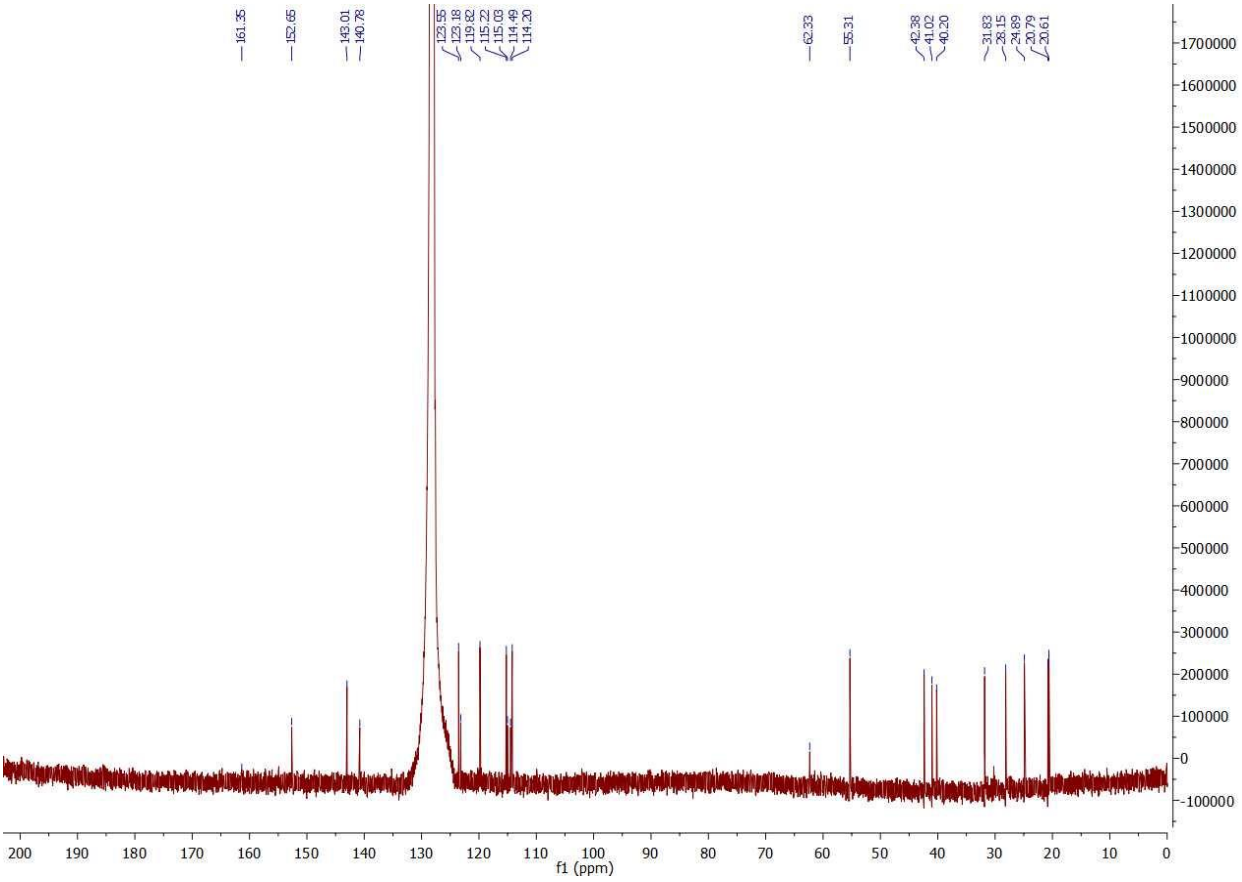


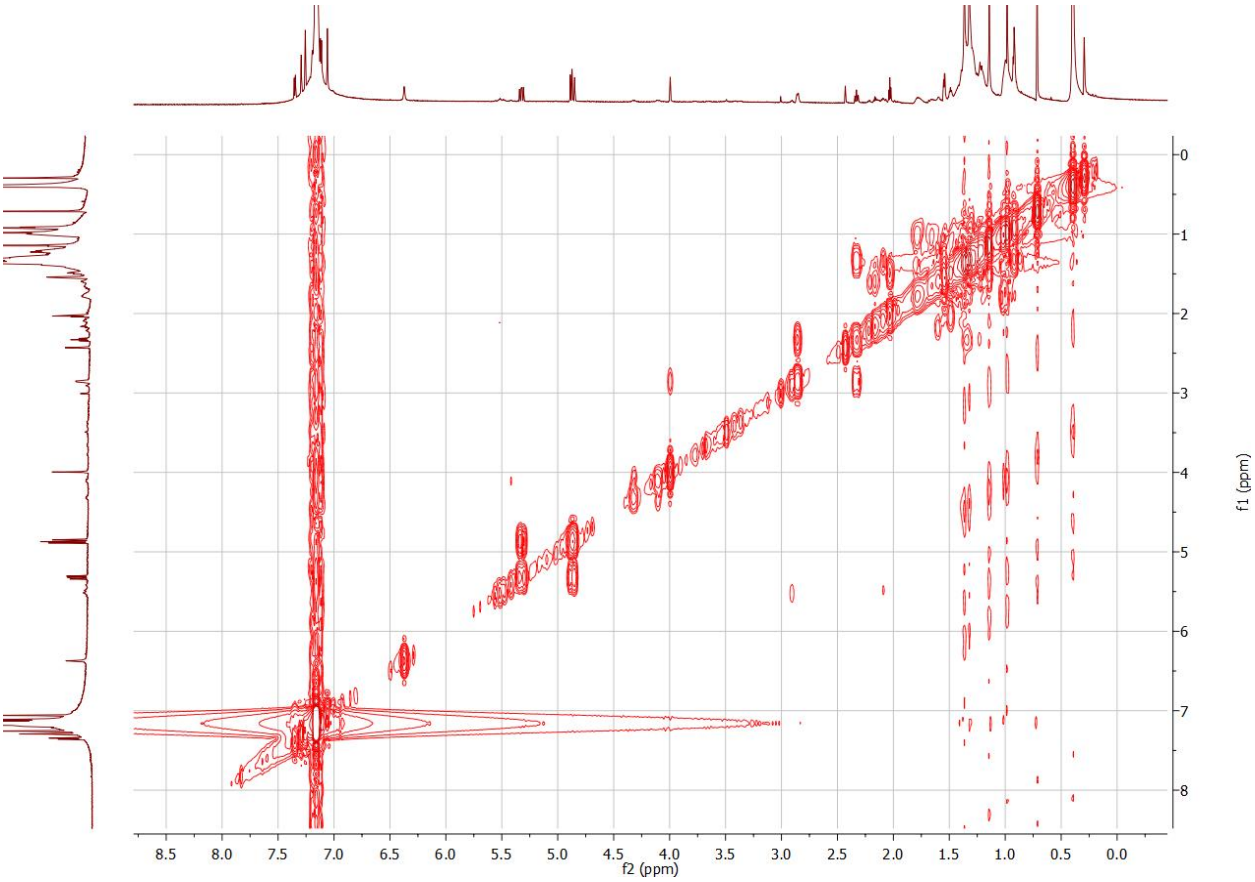


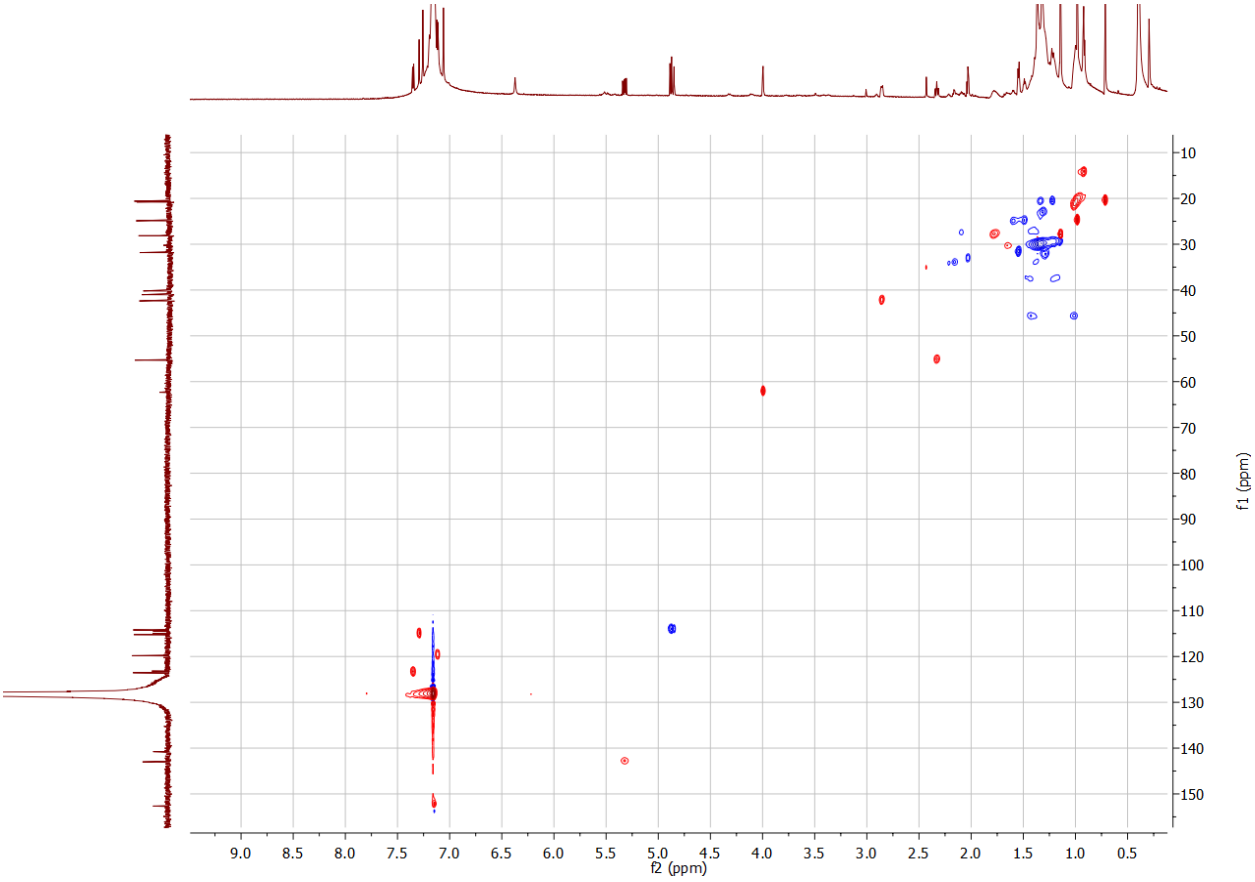
Calc. $[M+H]^+$ 339.1623 Obsv. 339.1634

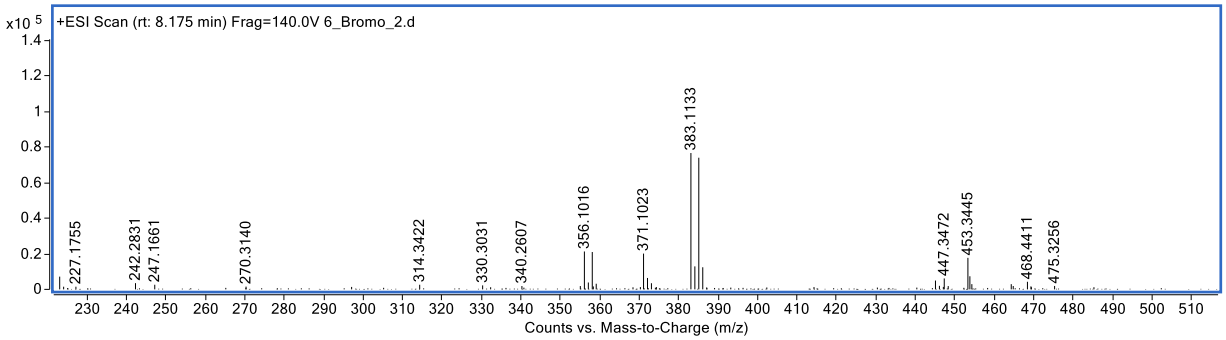
^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 6-Br-12-*epi*-Fischerindole U (**39**) in C_6D_6 at 800 MHZ and 201 MHz respectively.




161.35
152.65
143.01
140.78
129.55
123.18
119.82
115.22
115.03
114.49
114.30
62.33
55.31
42.38
41.02
40.20
31.83
28.15
24.89
20.79
20.61
f1 (ppm)

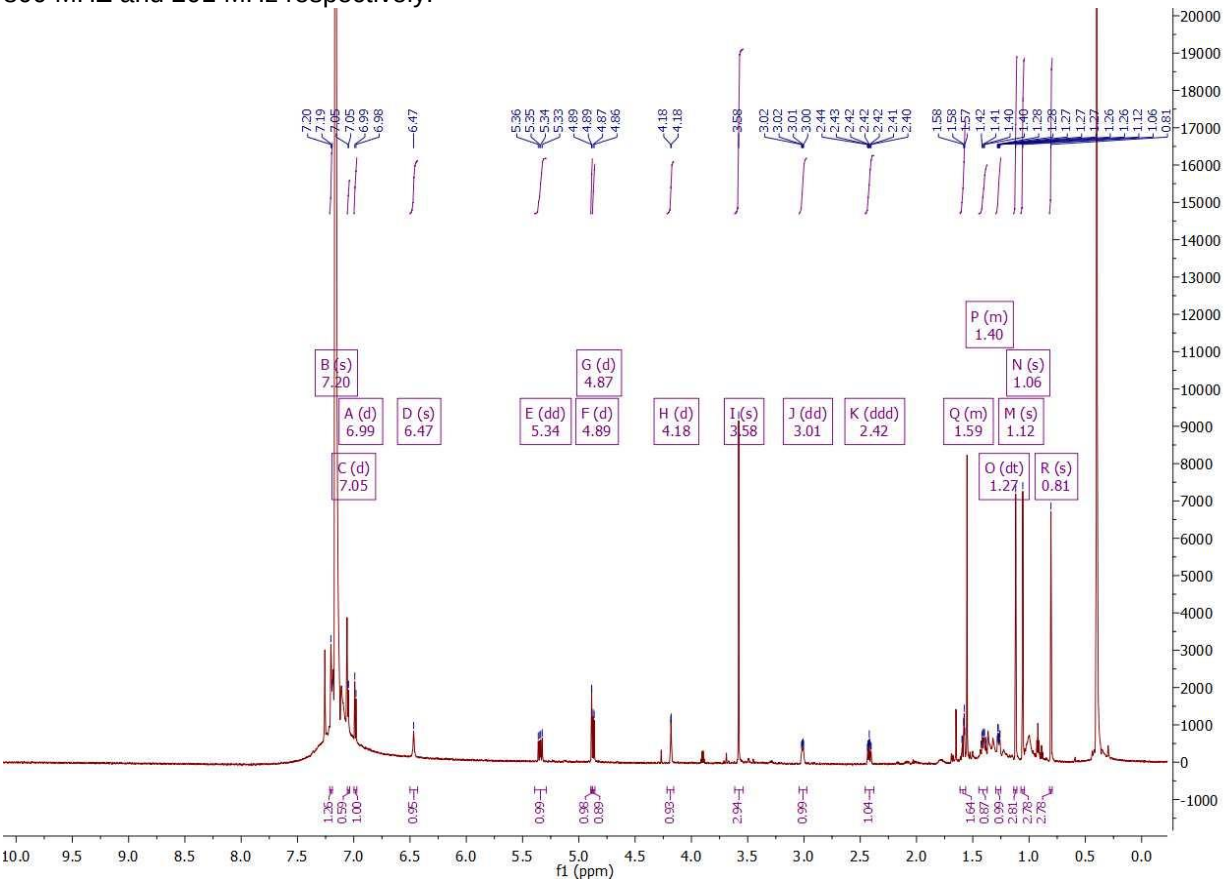

f2 (ppm)
f1 (ppm)

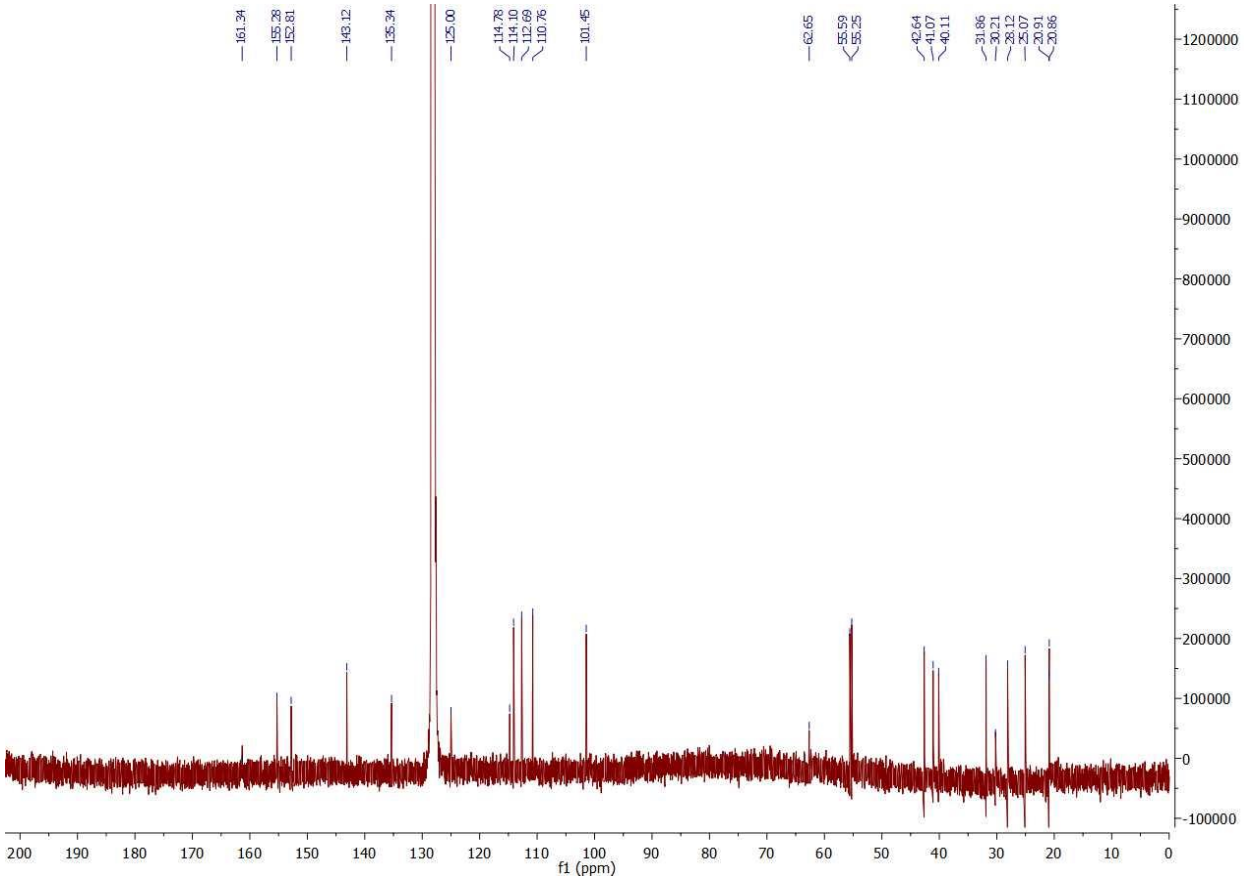

f2 (ppm)
f1 (ppm)

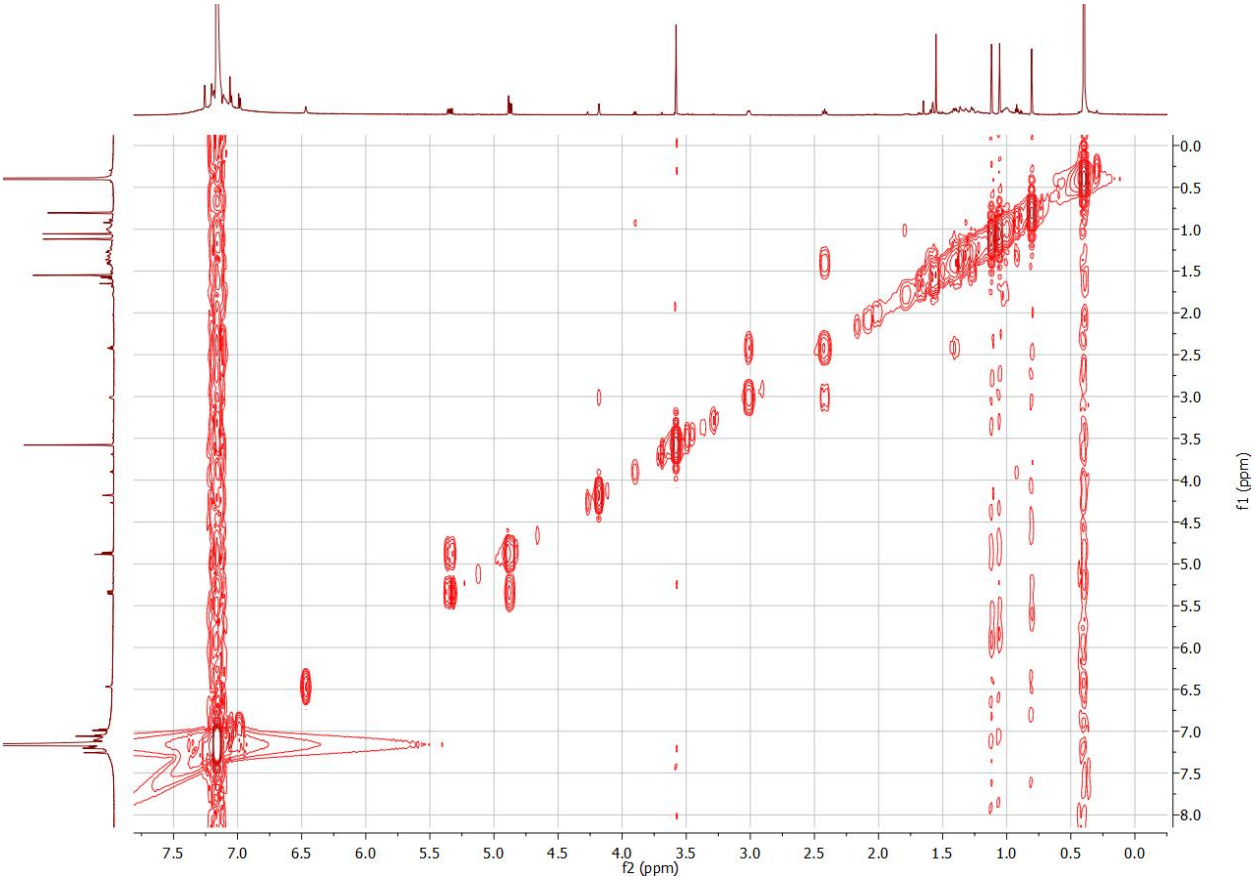


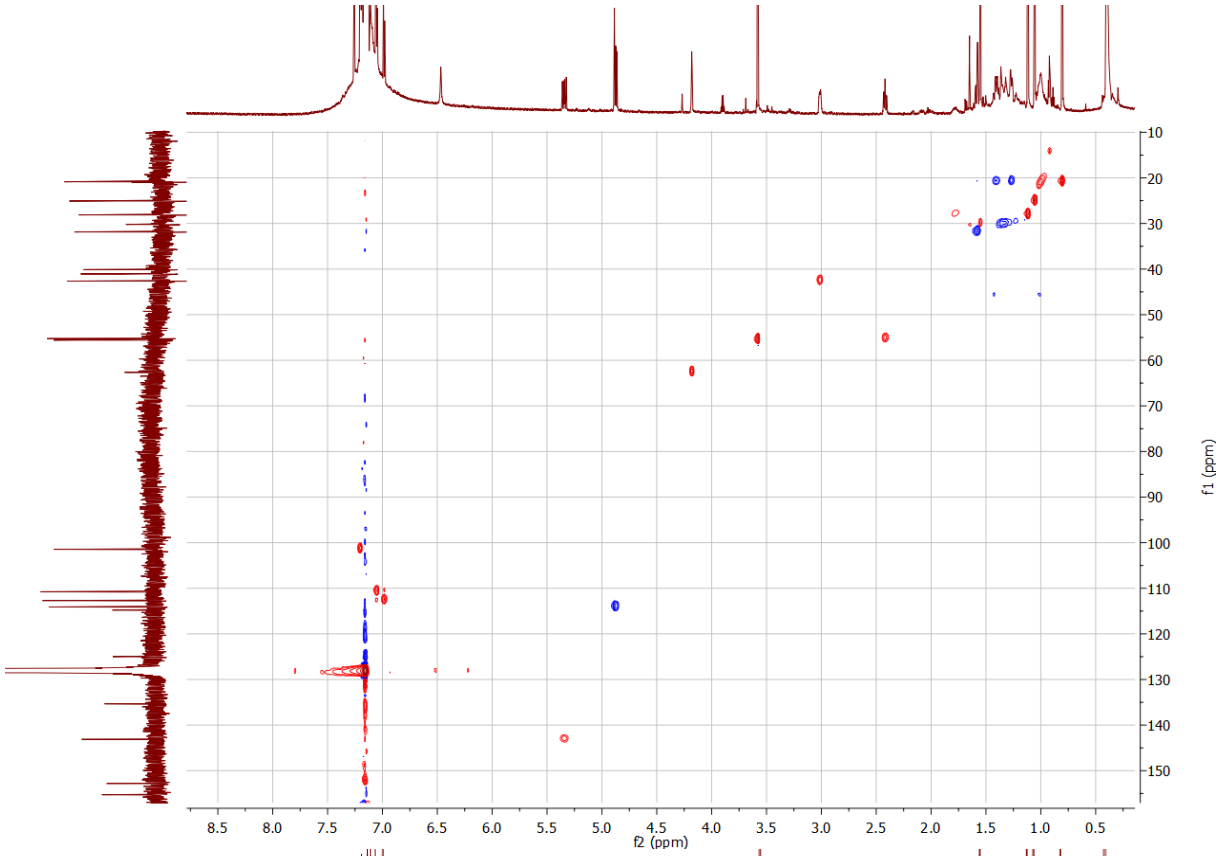
Calc. $[M+H]^+$ 383.1117 Obsv. 383.1133

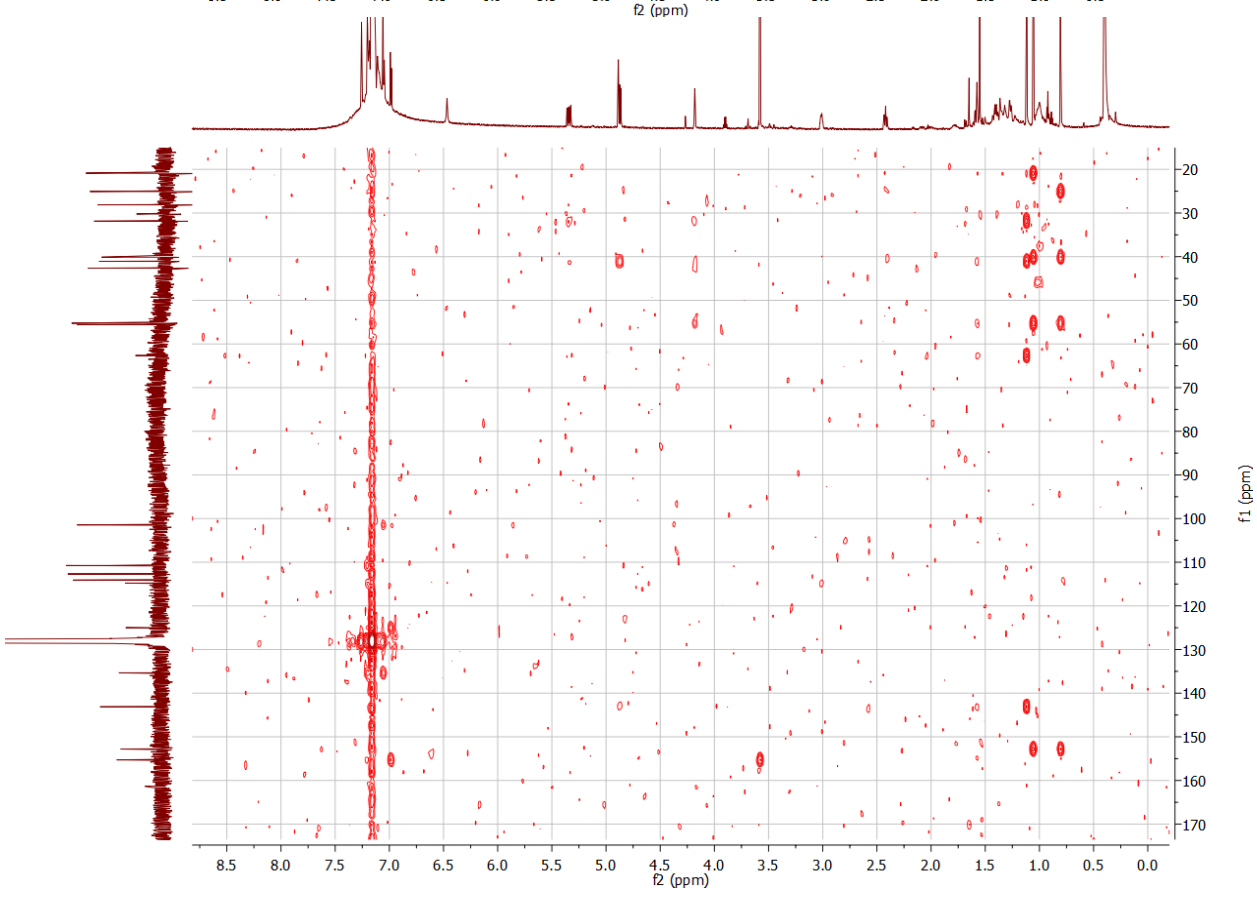
^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 5-OMe-12-*epi*-Fischerindole U (**35**) in C_6D_6 at 800 MHZ and 201 MHz respectively.

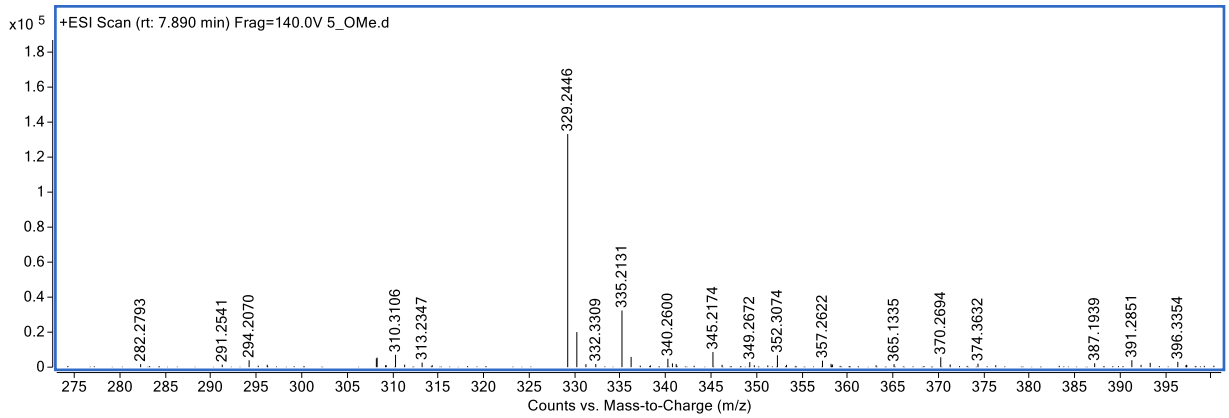



161.34
155.28
152.81
143.12
135.34
125.00
114.78
114.10
112.69
110.76
101.45
62.65
55.59
55.25
42.64
41.07
40.11
31.86
30.21
28.12
25.07
20.91
20.86
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)

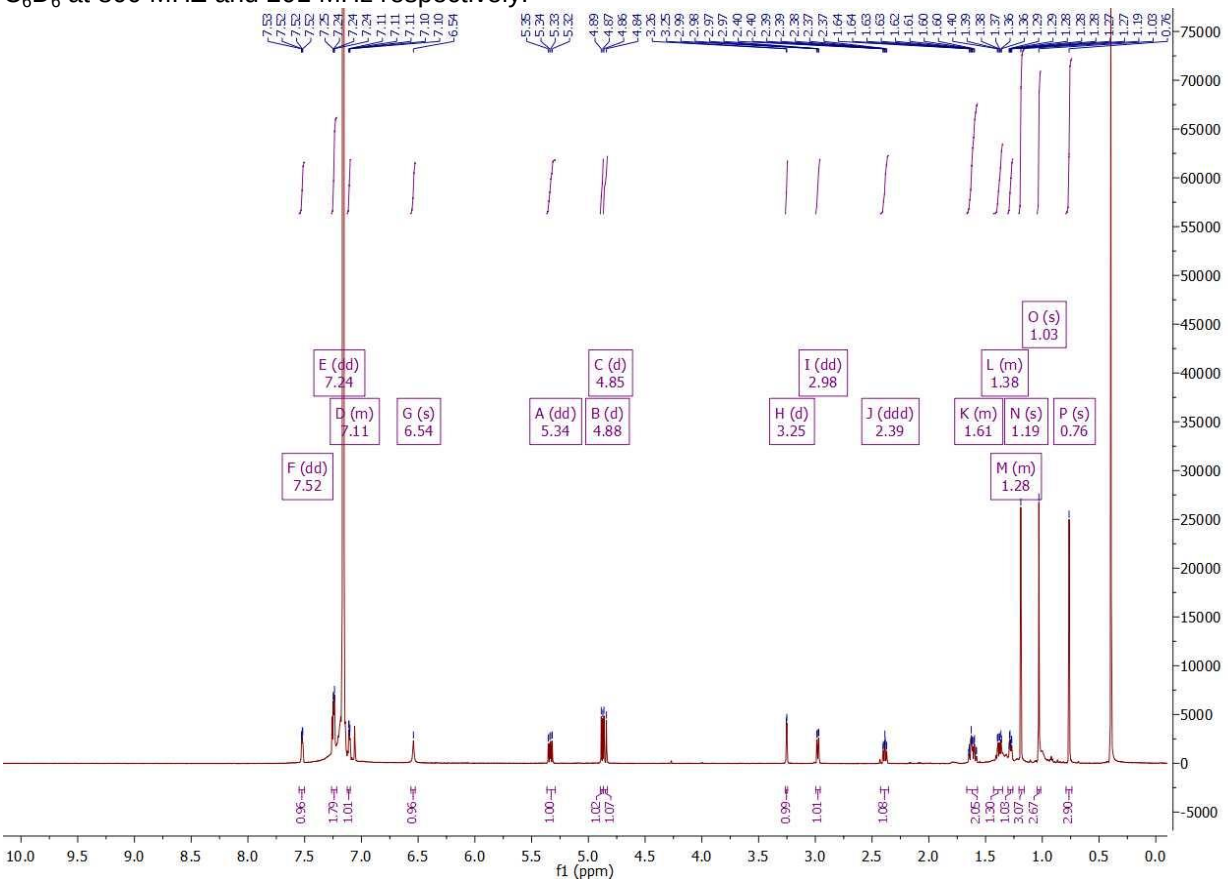

f2 (ppm)
f1 (ppm)

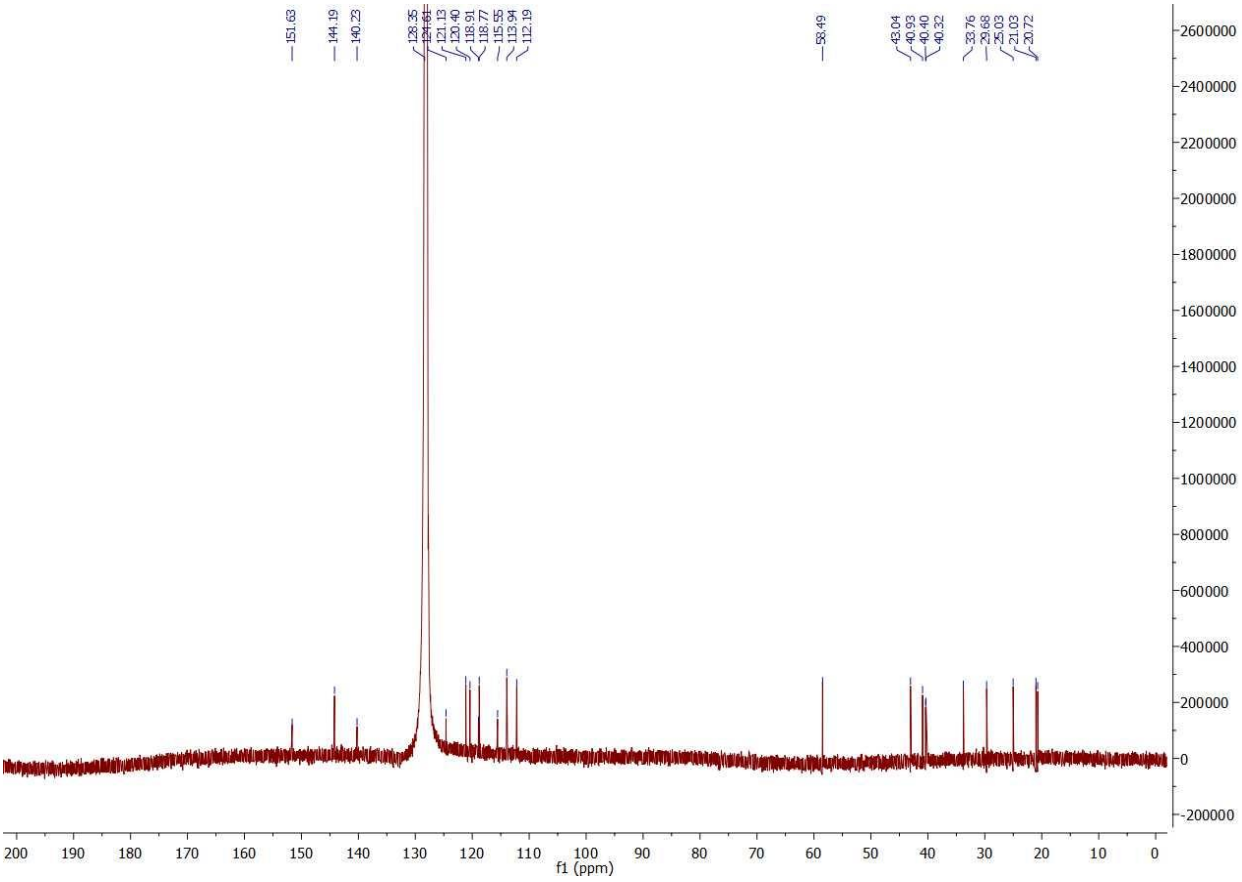

f2 (ppm)
f1 (ppm)

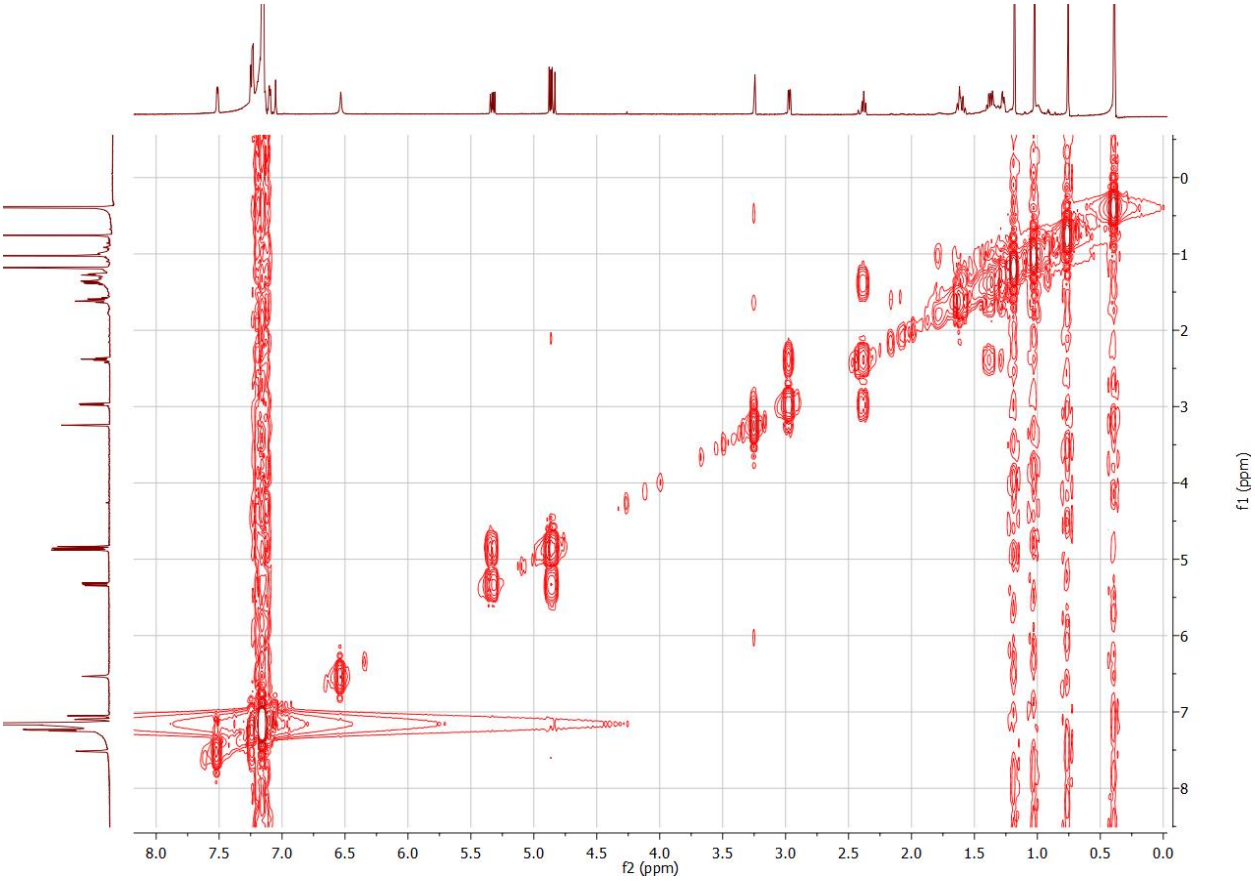


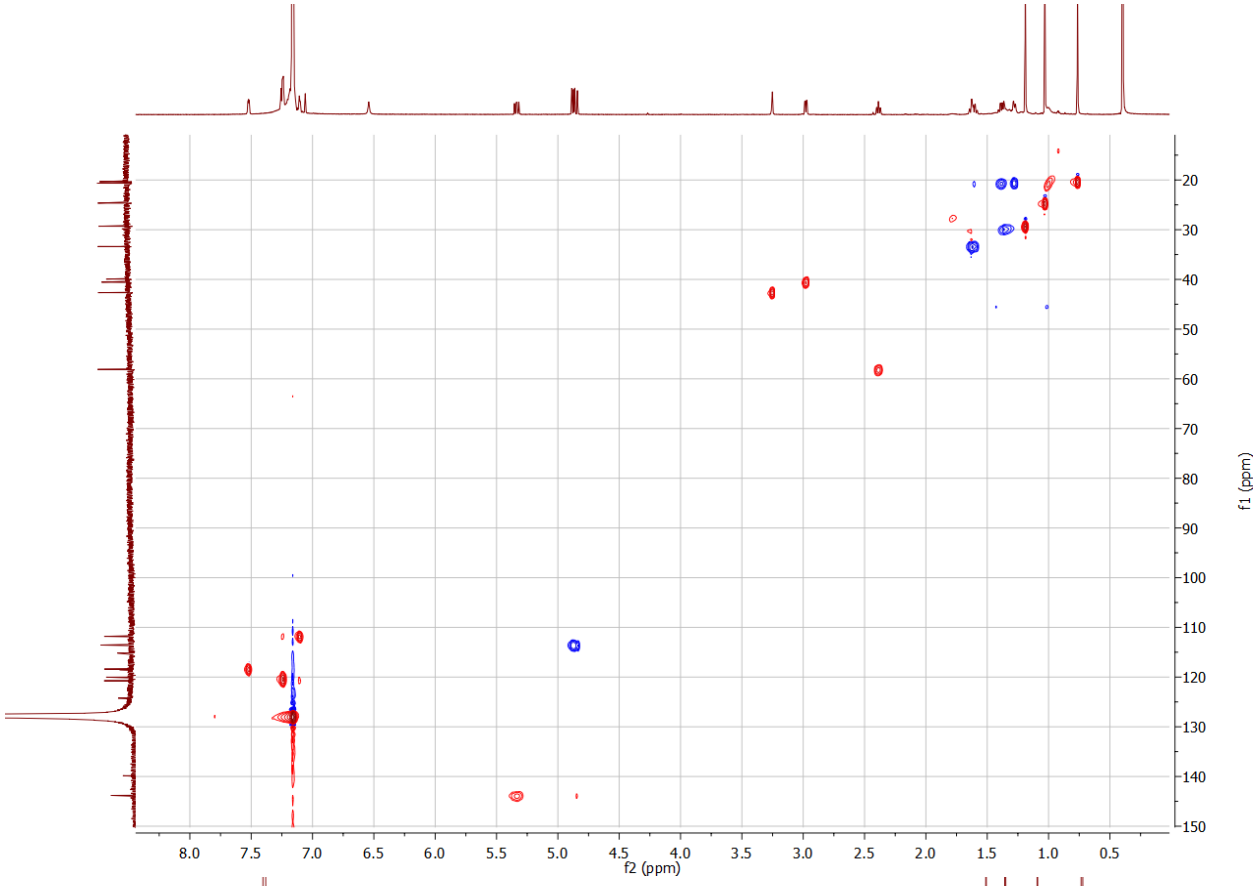
Calc. $[M+H]^+$ 335.2118 Obsv. 335.2131

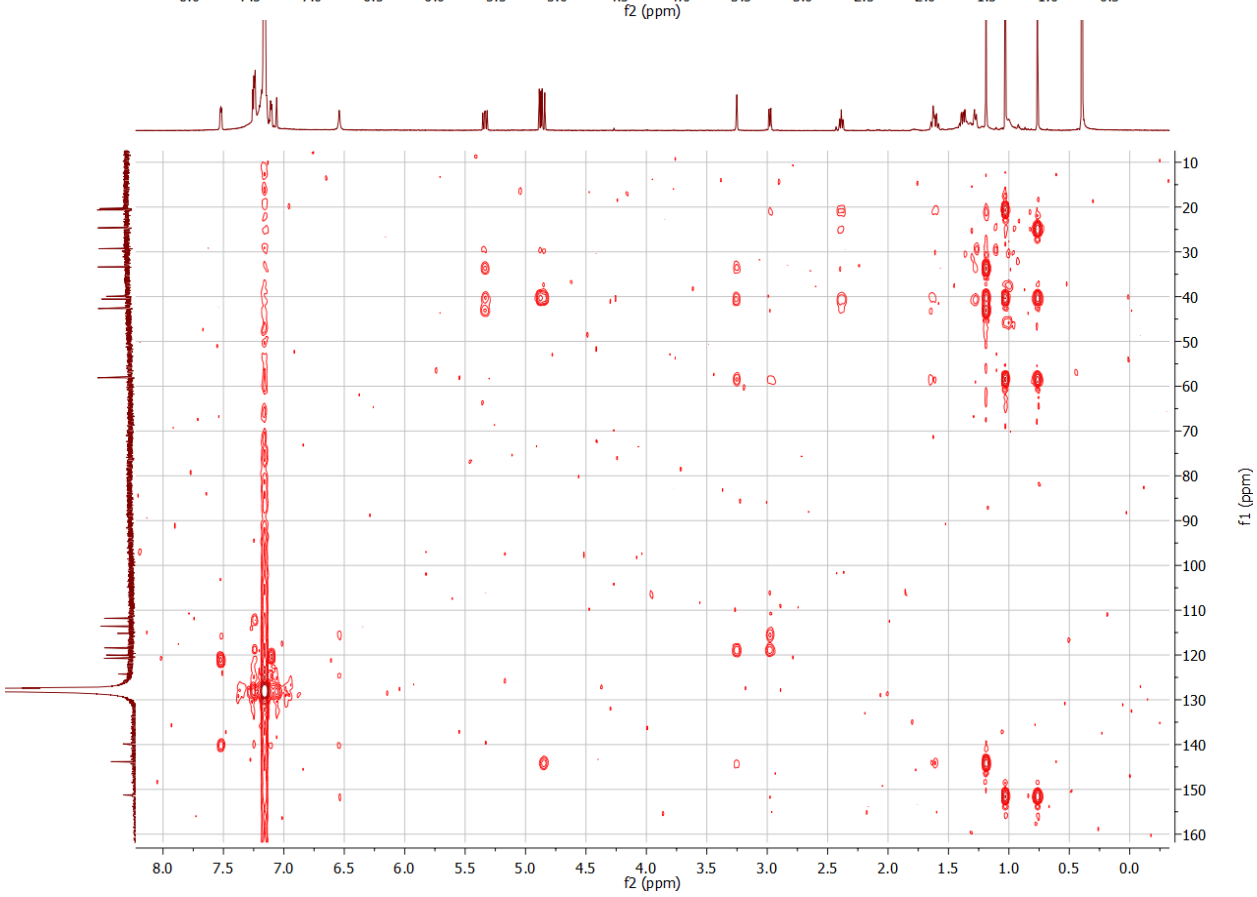
^{1}H, ^{13}C, COSY, HSQC, HMBC, NOESY NMR spectra and HRMS of 12-epi-Fischerindole U Nitrile (**40**) in C_6D_6 at 800 MHZ and 201 MHz respectively.

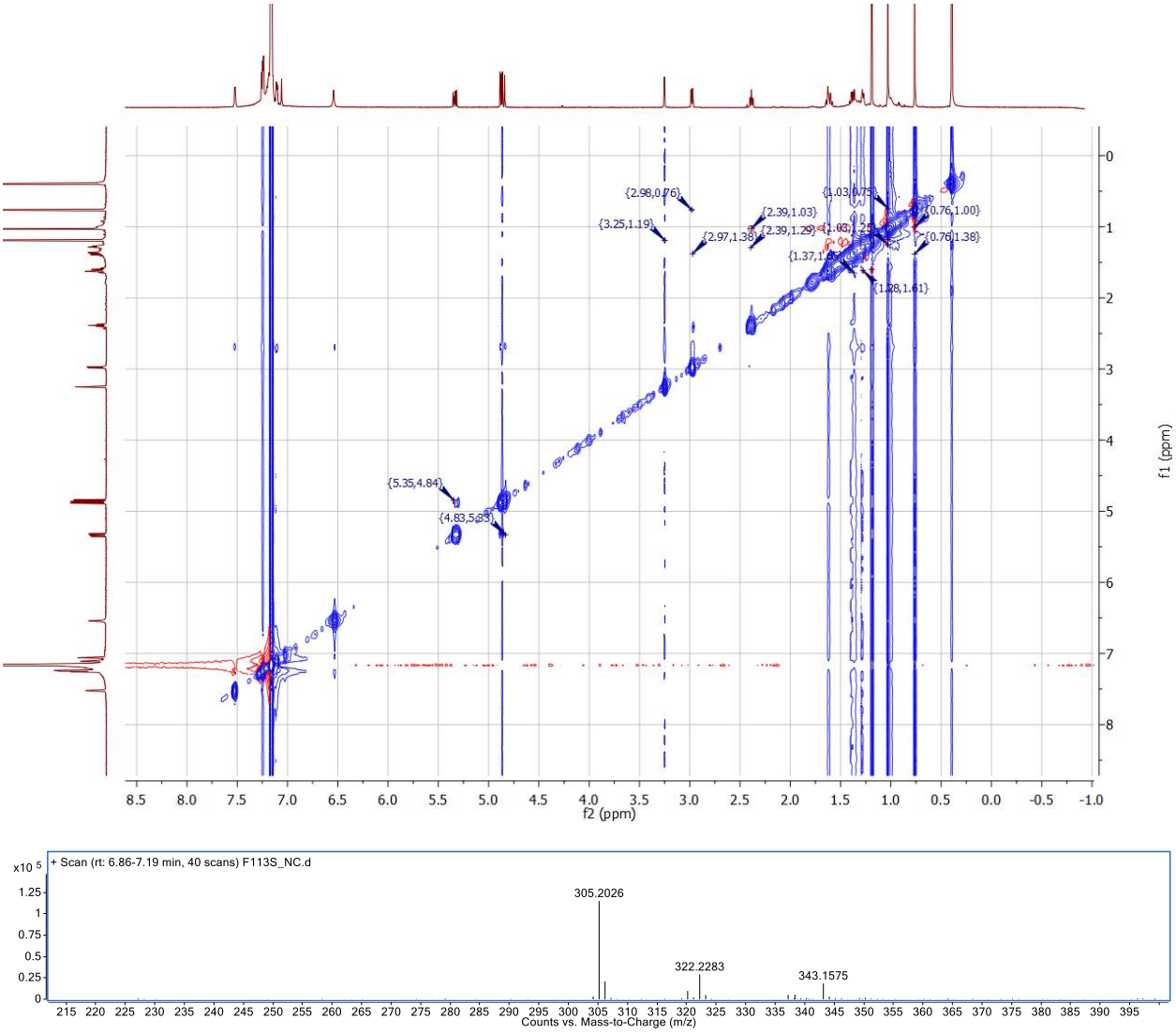



151.63
144.19
140.23
128.35
124.61
121.13
120.40
118.91
118.77
115.55
113.94
112.19
58.49
43.04
40.93
40.40
40.32
33.76
29.68
25.03
21.03
20.72
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

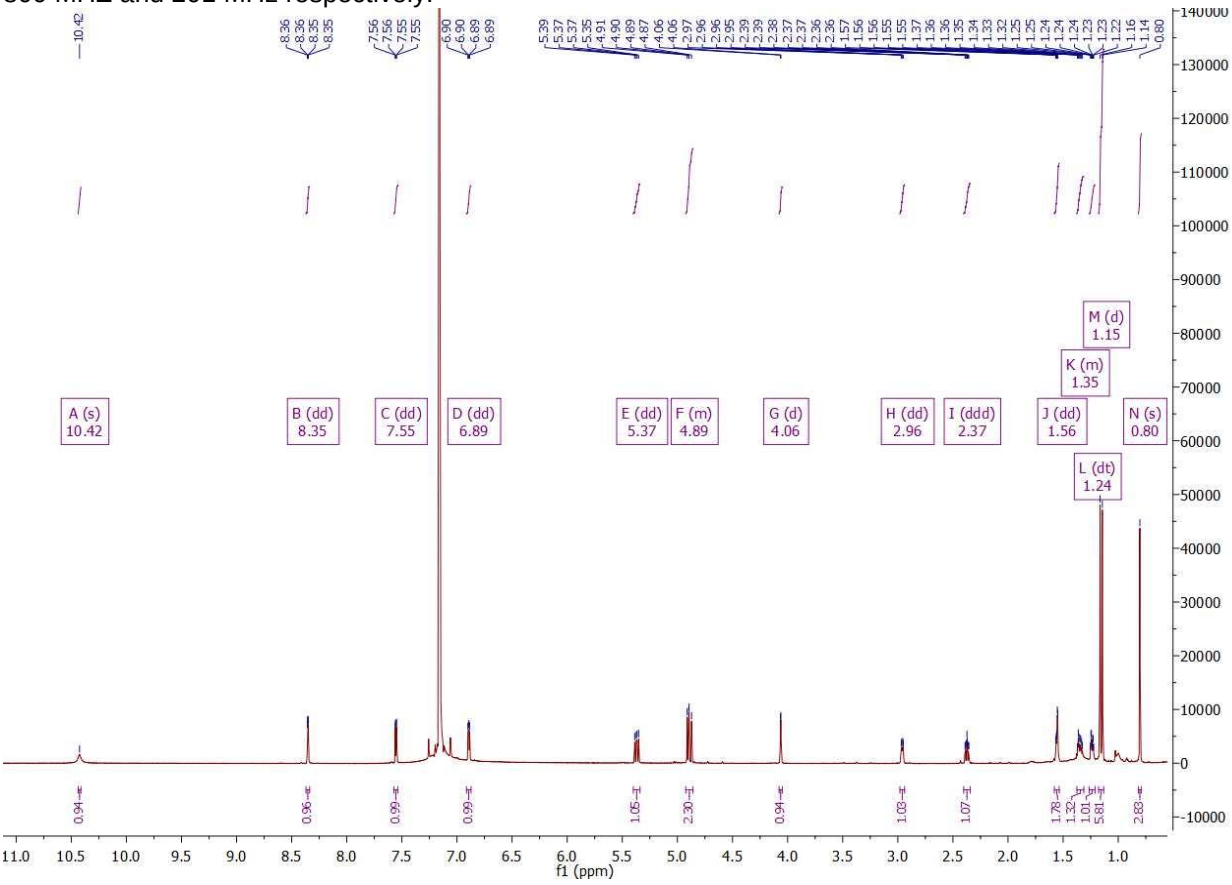

f2 (ppm)
f1 (ppm)

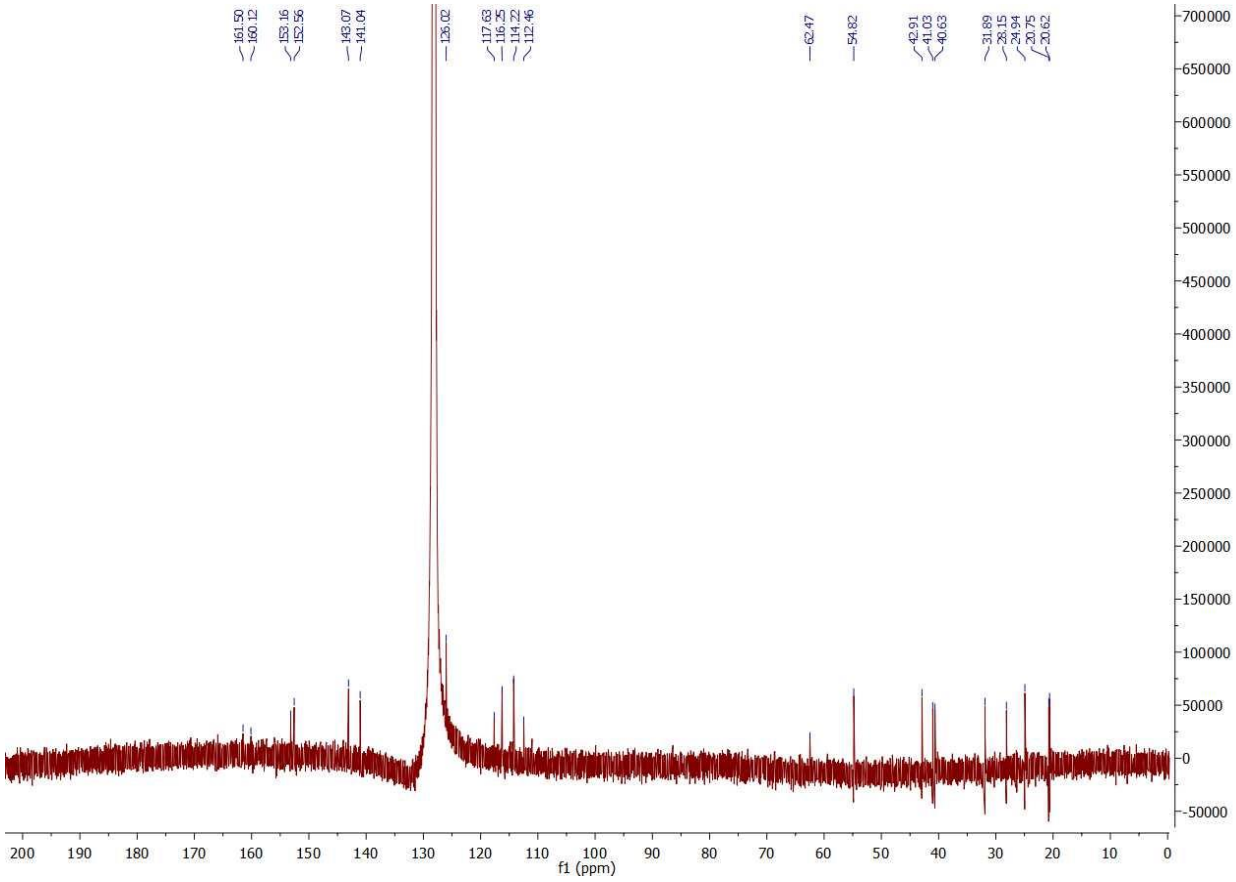

f2 (ppm)
f1 (ppm)

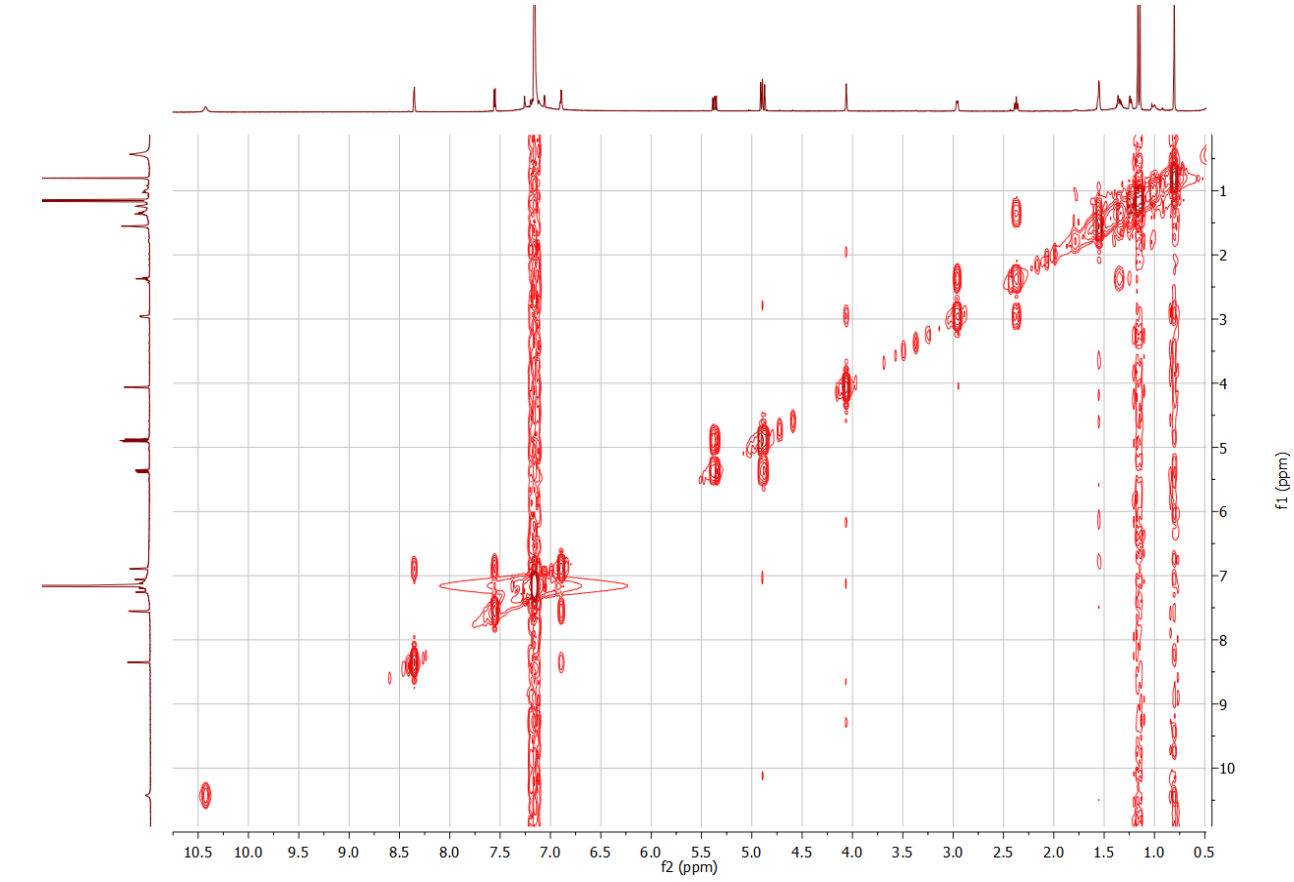


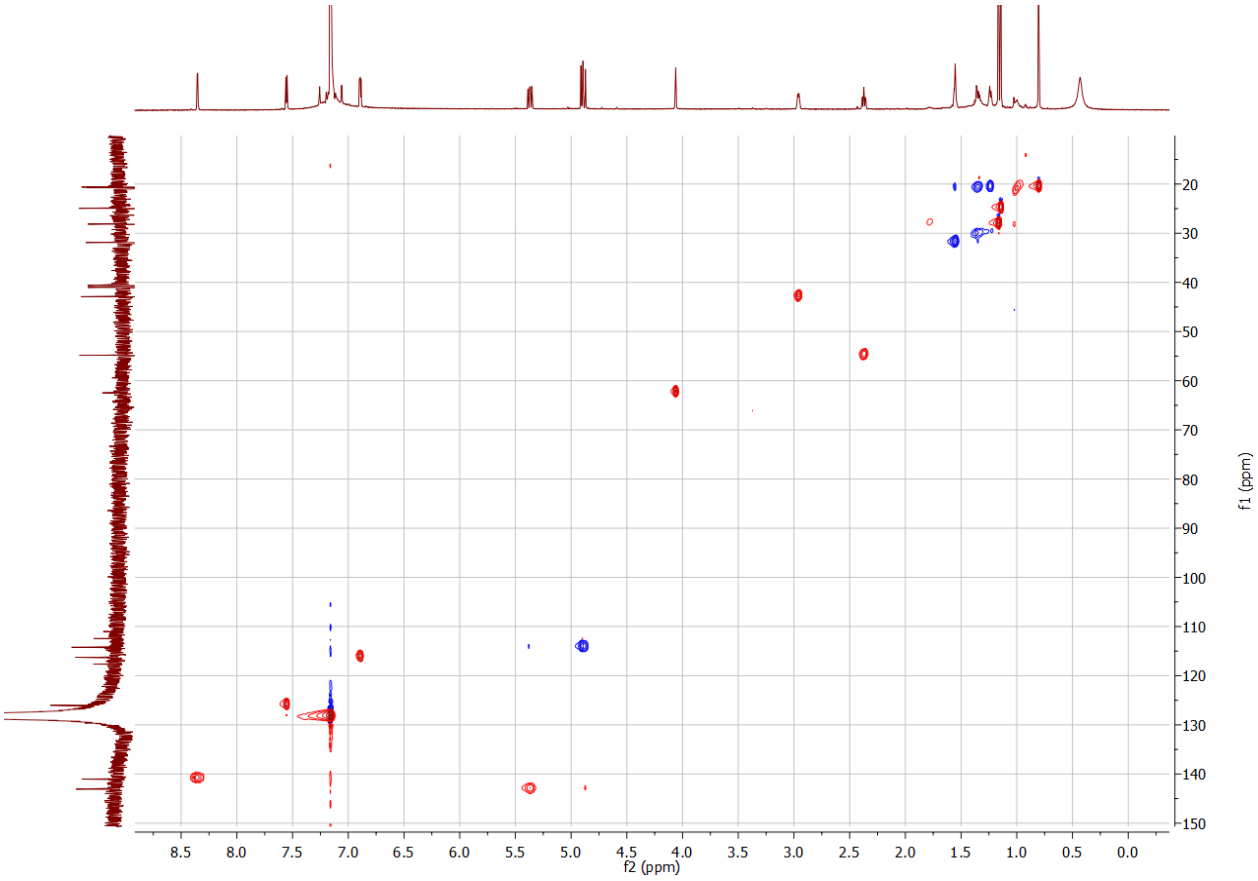
Calc. $[M+H]^+$ 305.2012 Obsv. 305.2026

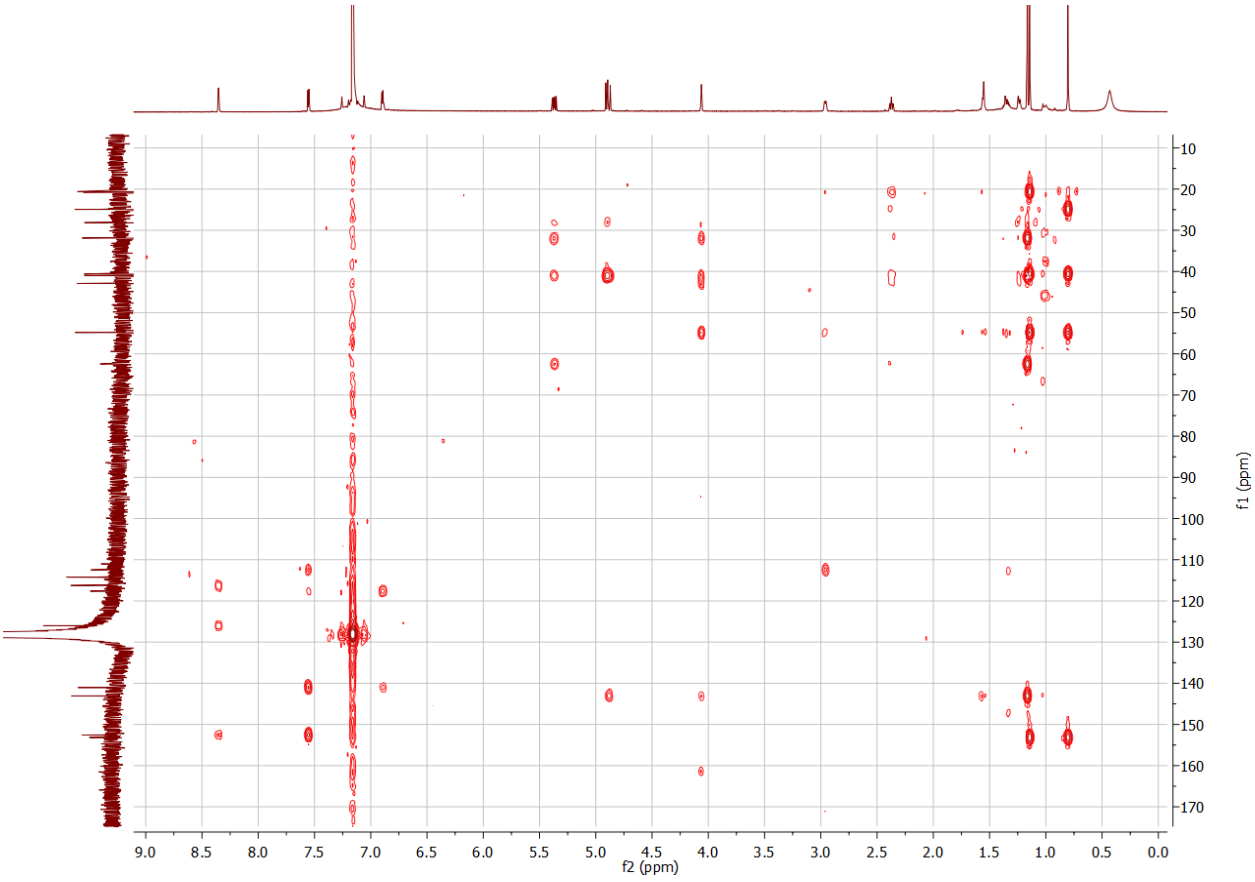
^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 7-Aza-12-*epi*-Fischerindole U (**36**) in C_6D_6 at 800 MHZ and 201 MHz respectively.

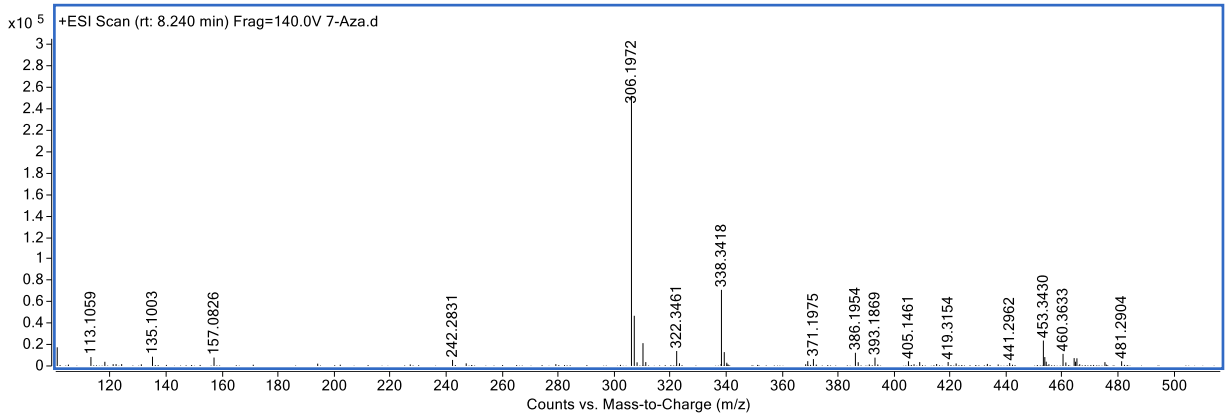



161.50
160.12
153.16
152.56
143.07
141.04
126.02
117.63
116.25
114.22
112.46
62.47
54.82
42.91
41.03
40.63
31.89
28.15
24.94
20.75
20.62
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


f2 (ppm)
f1 (ppm)

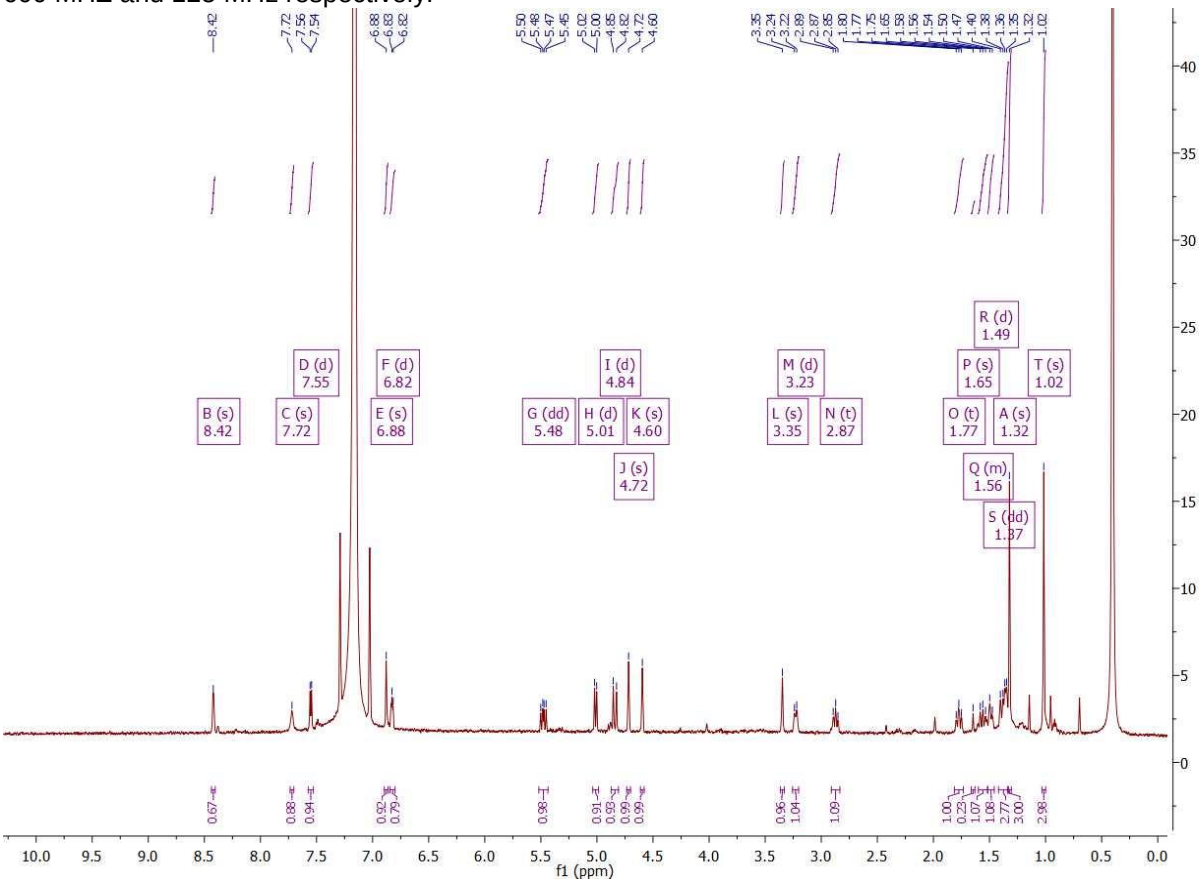

f2 (ppm)
f1 (ppm)

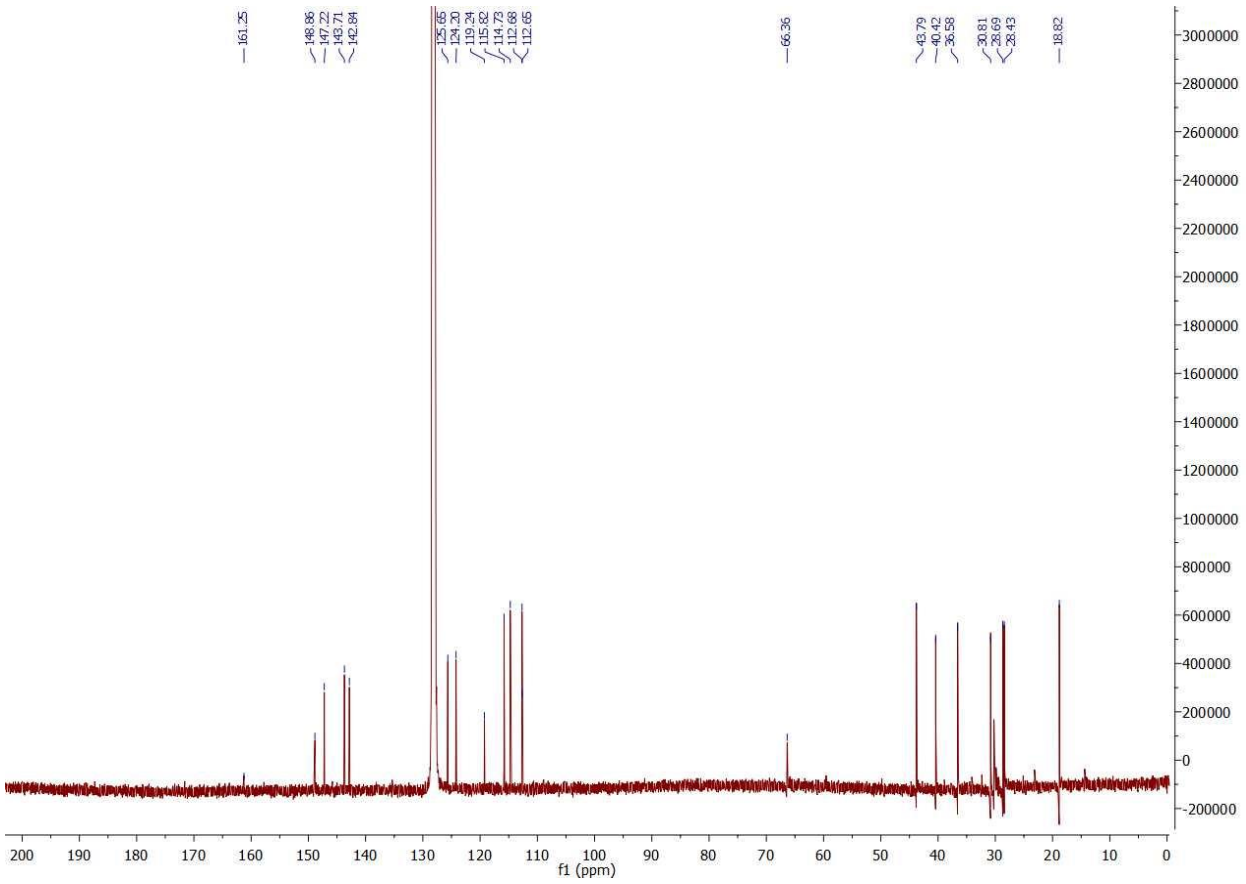


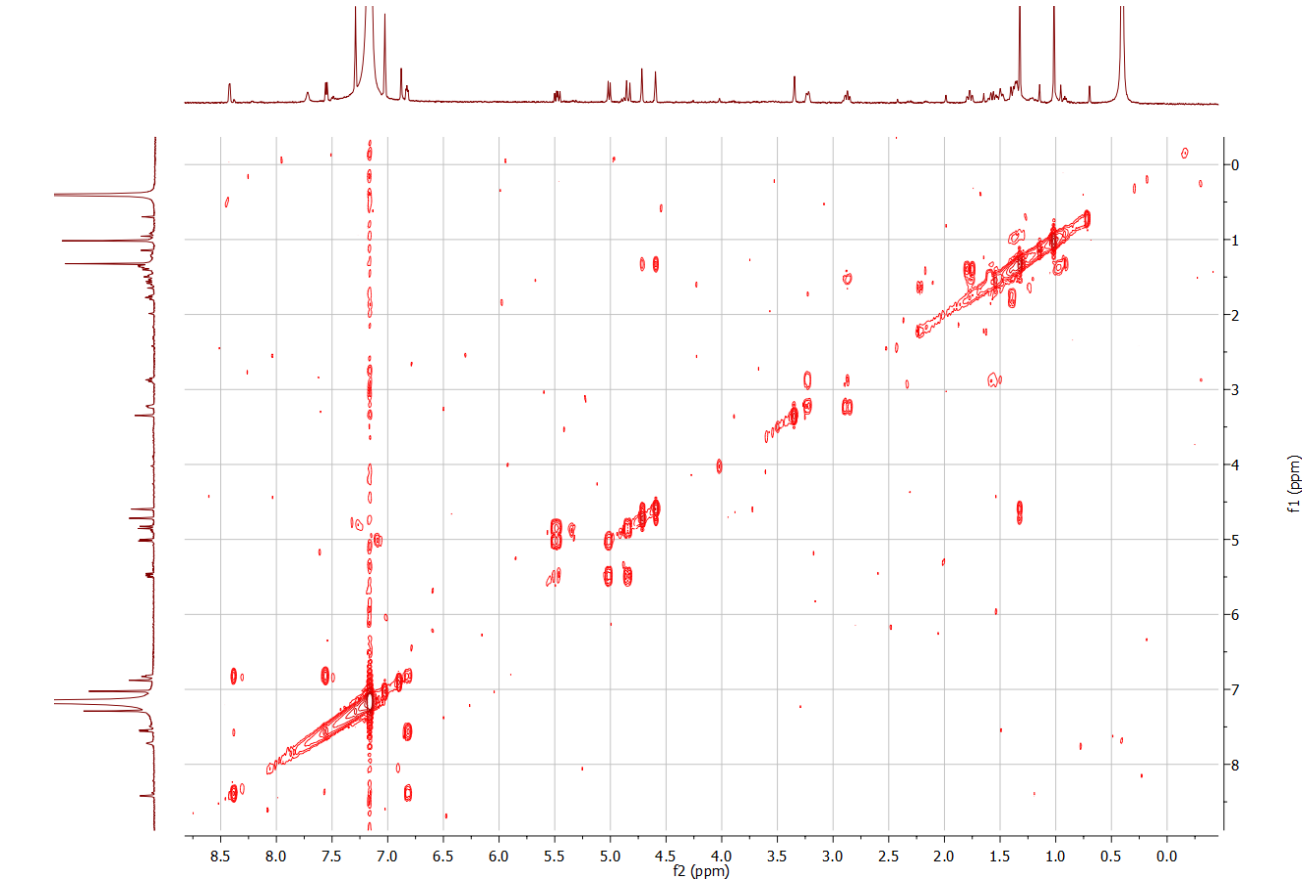


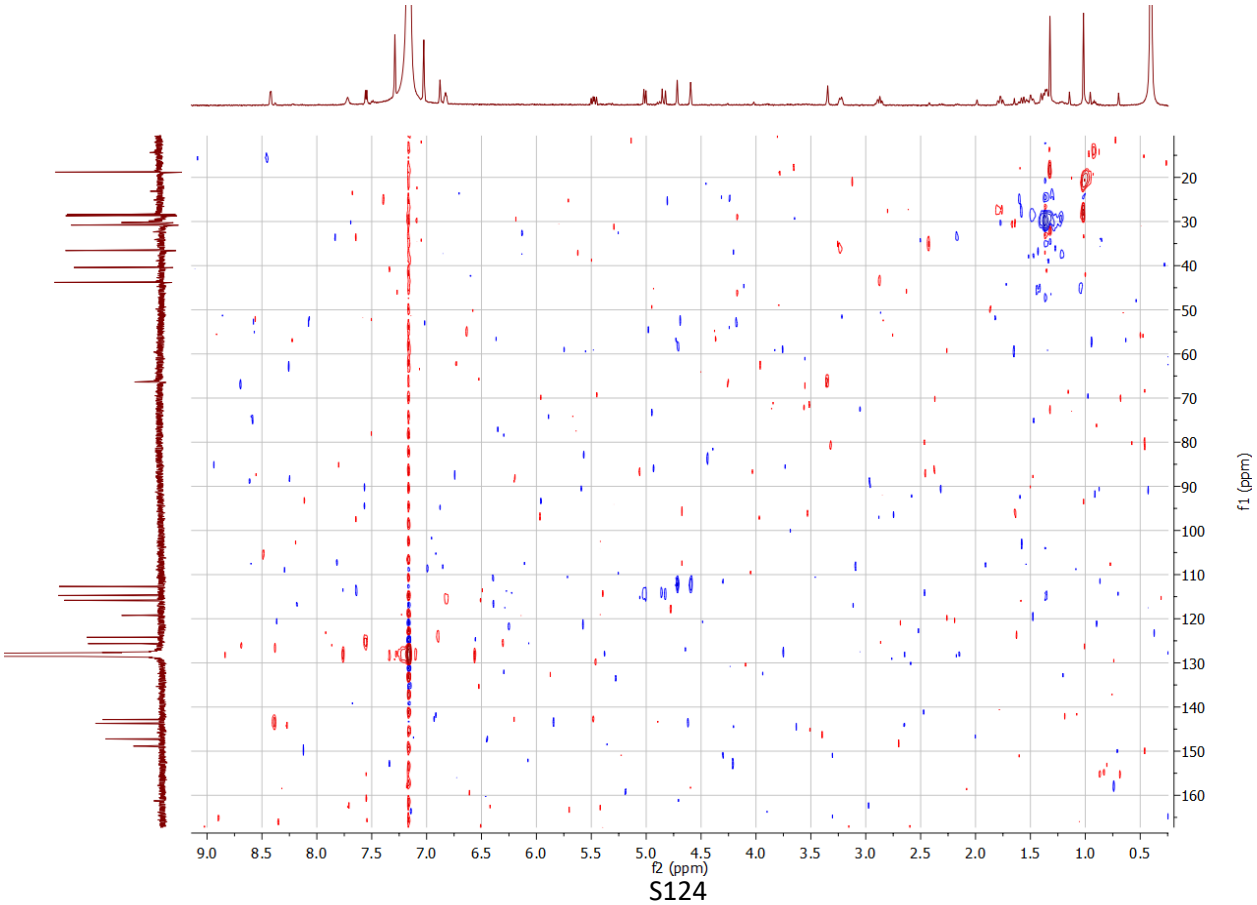
Calc. $[M+H]^+$ 306.1965 Obsv. 306.1972

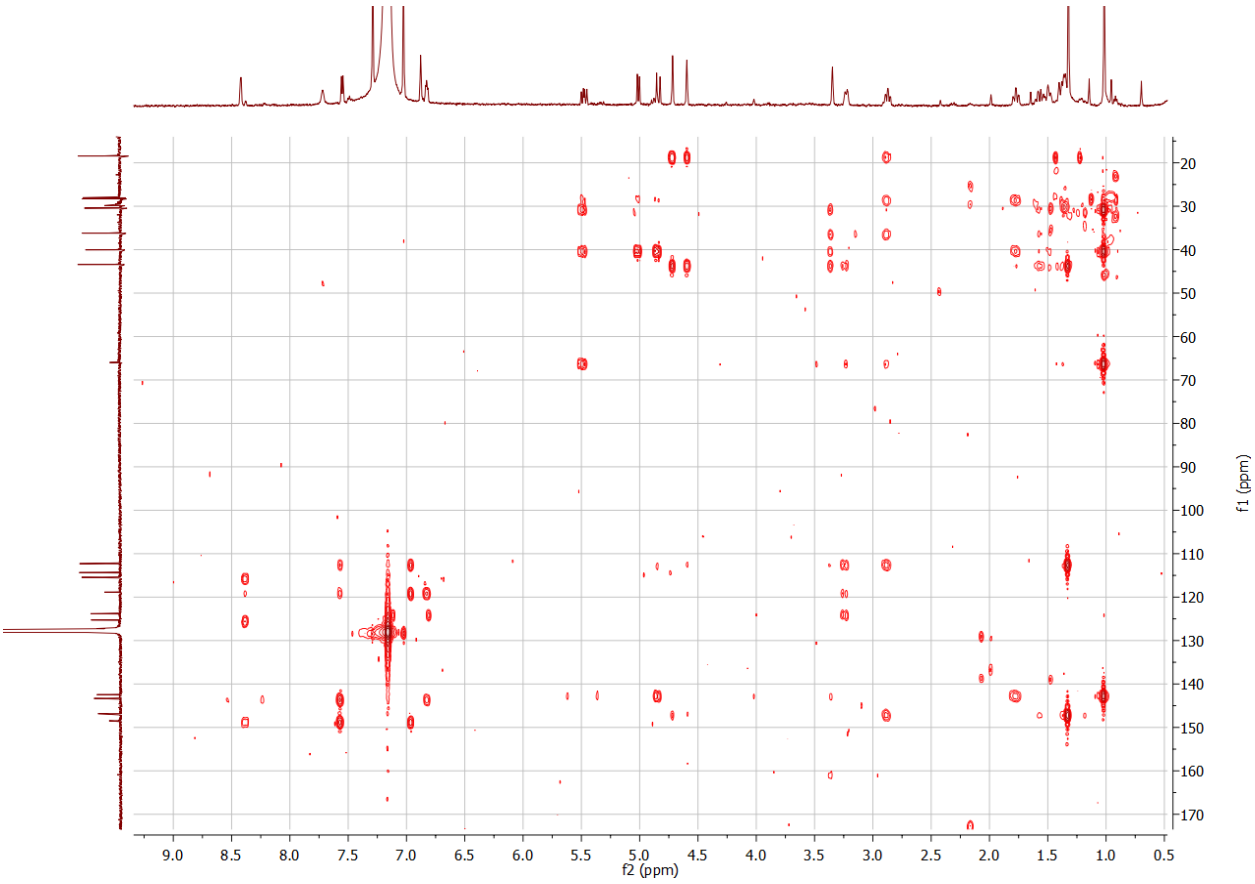
^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 7-Aza-12-*epi*-Hapalindole C (**31**) in C_6D_6 at 600 MHZ and 125 MHz respectively.

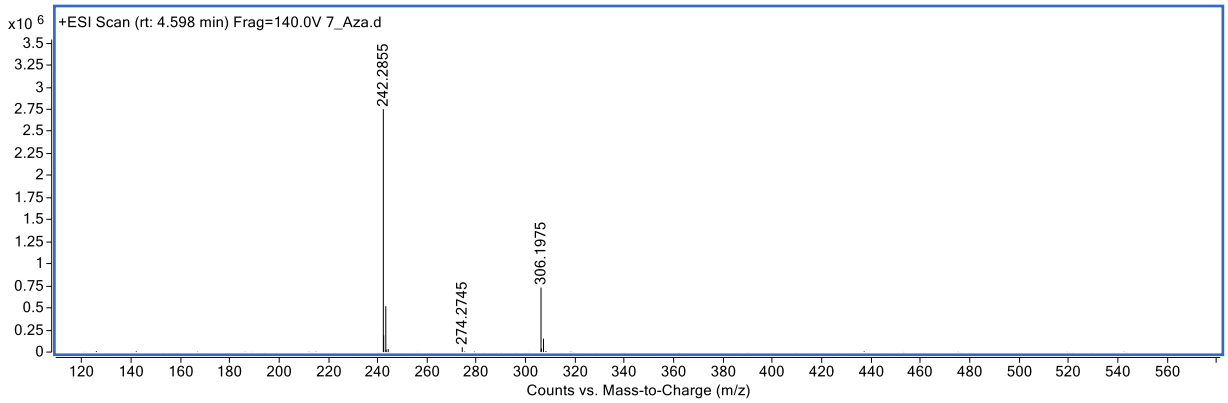



161.25
148.86
147.22
143.71
142.84
125.65
124.20
119.24
115.82
114.73
112.68
112.65
66.36
43.79
40.42
36.58
30.81
28.69
28.43
18.82
f1 (ppm)


f2 (ppm)
f1 (ppm)

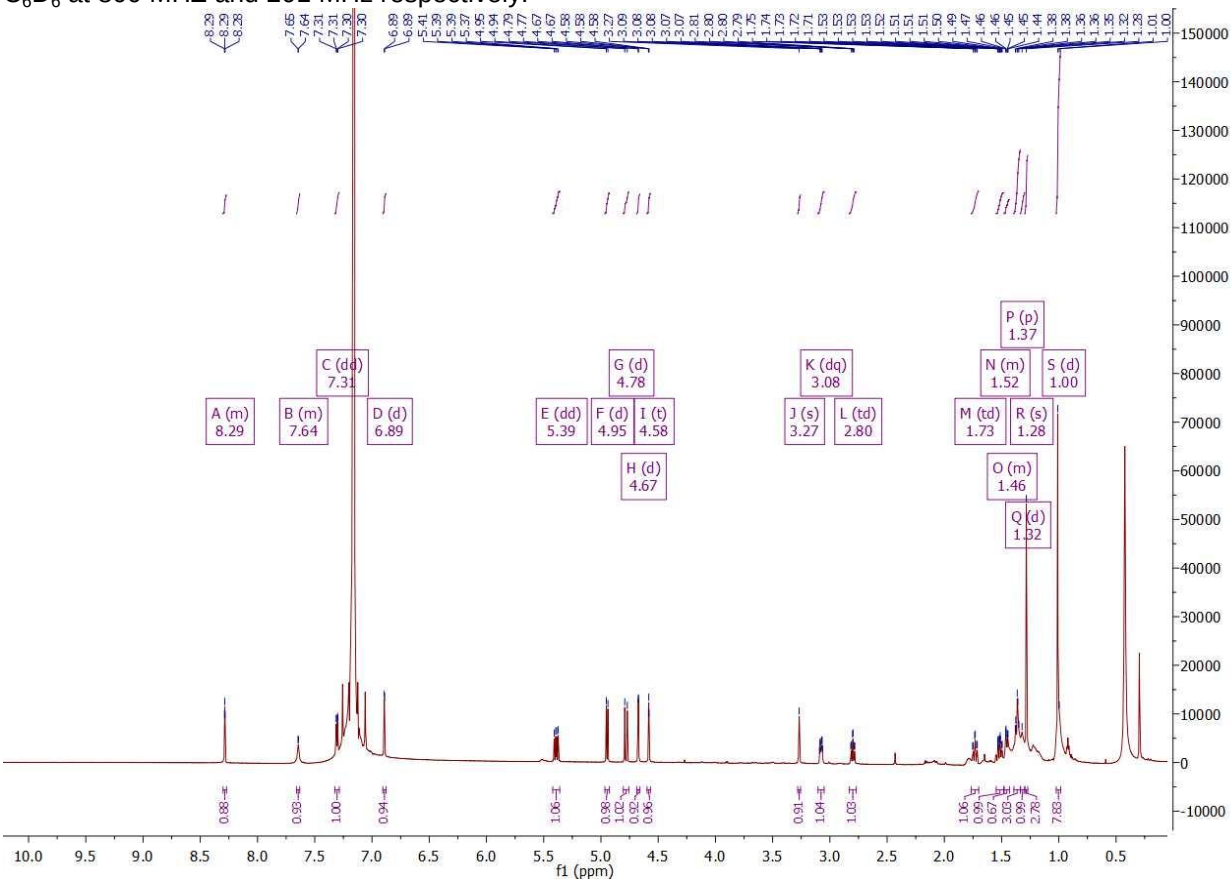

f2 (ppm)
f1 (ppm)

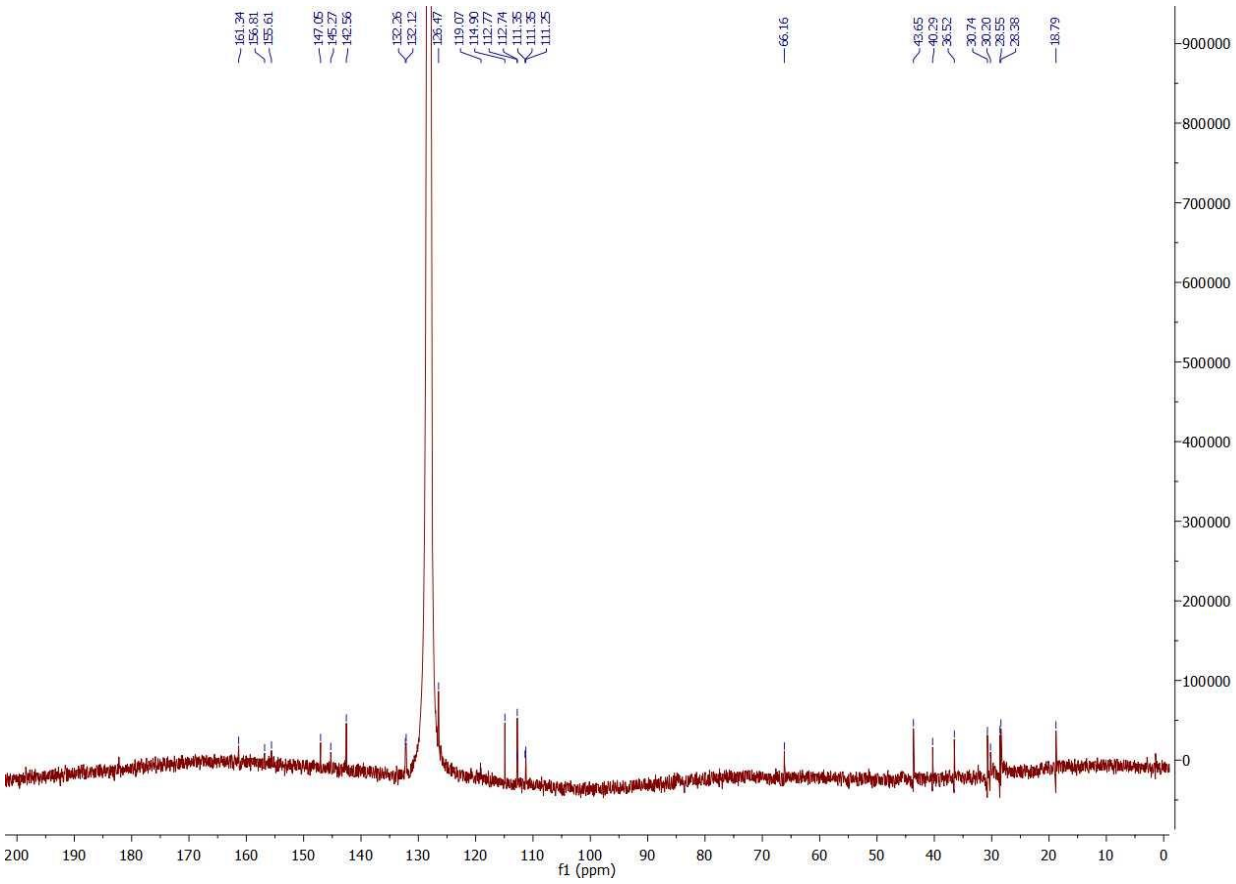


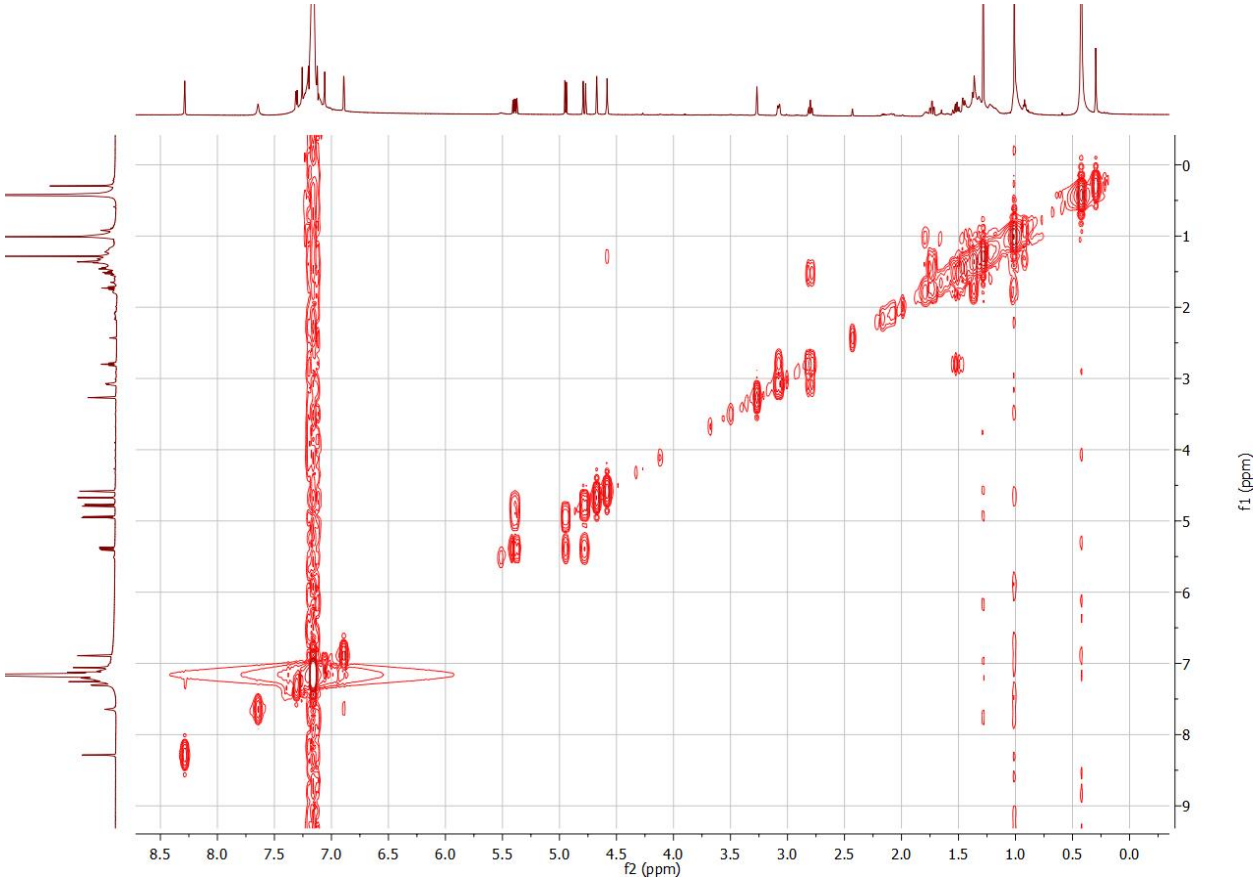


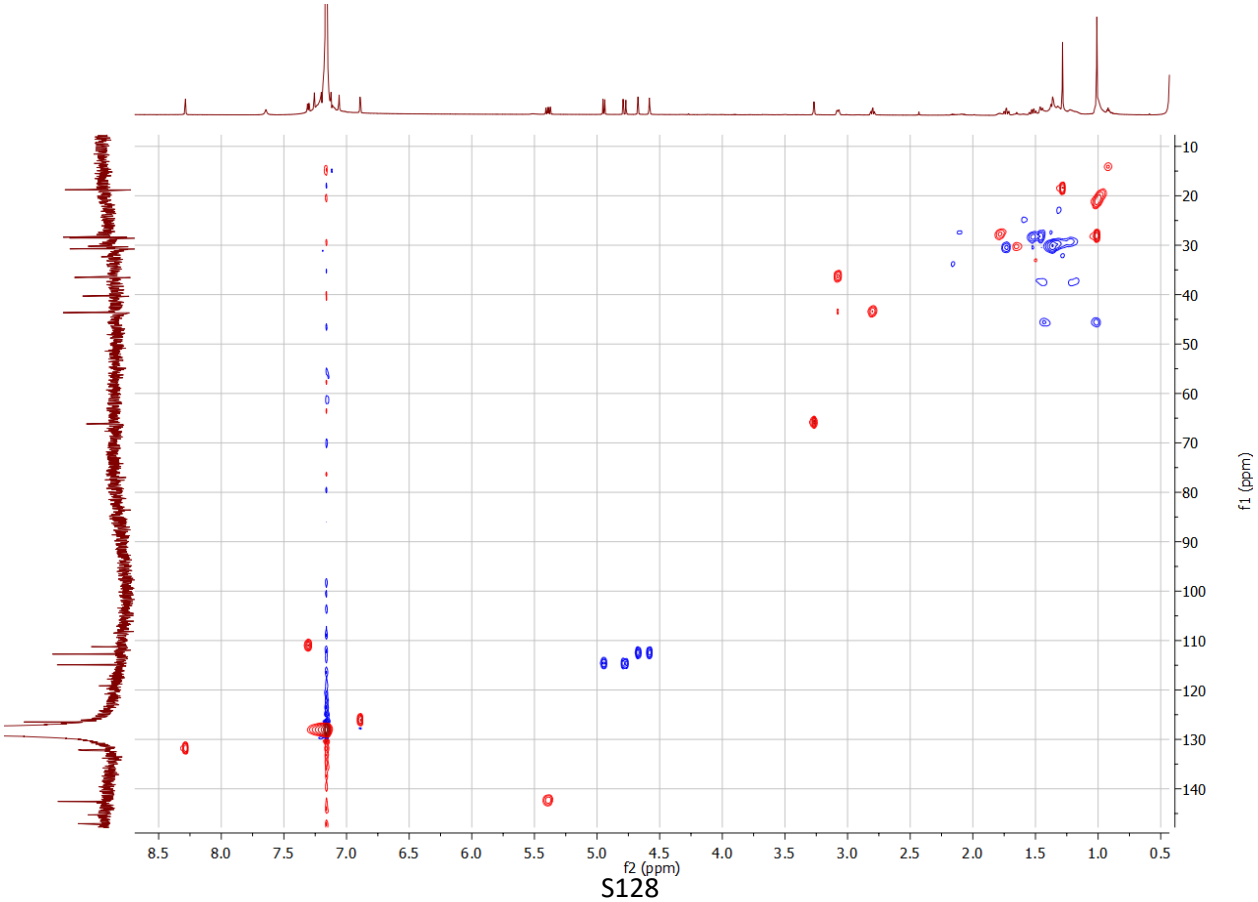
Calc. $[M+H]^+$ 306.1965 Obsv. 306.1975

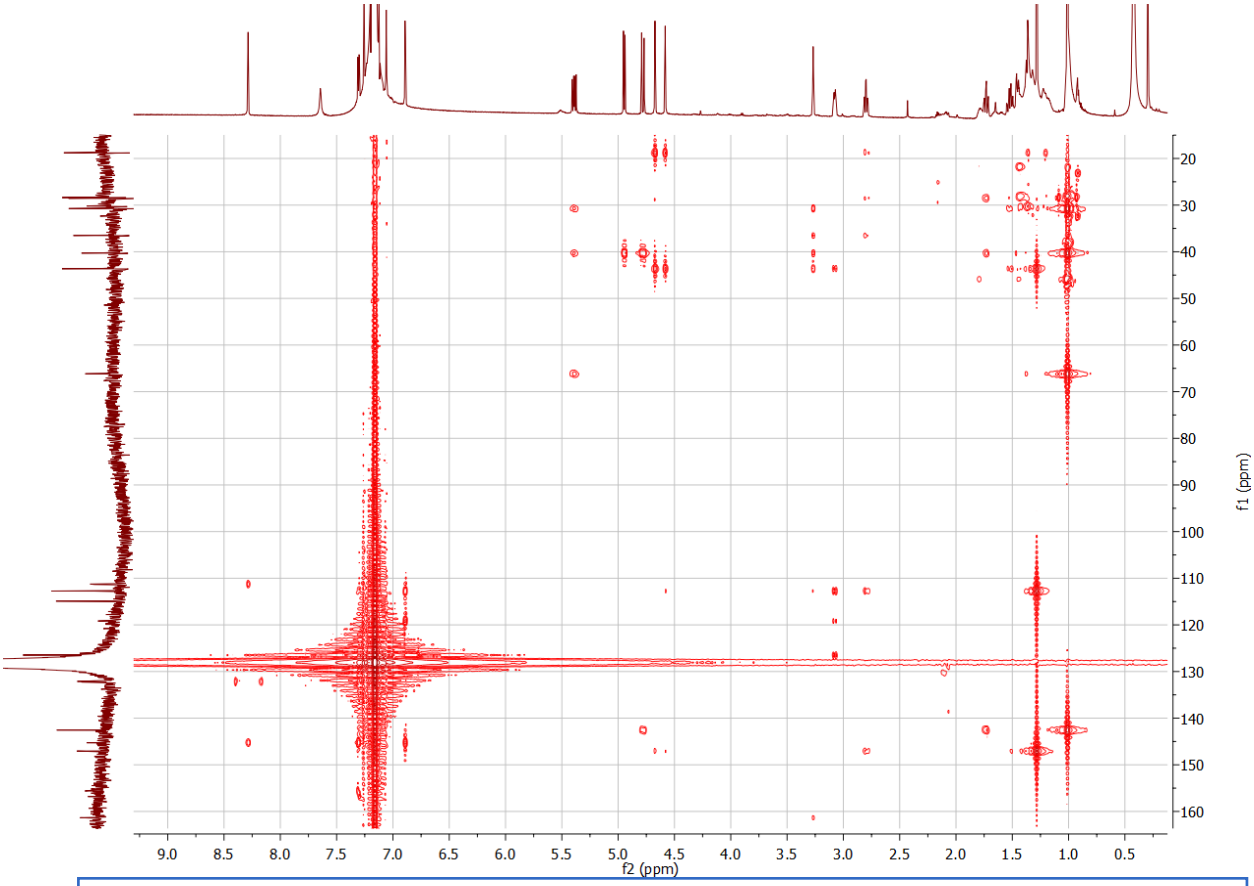
^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectra and HRMS of 5-Fluoro-7-Aza-12-*epi*-Hapalindole C (**32**) in C_6D_6 at 800 MHZ and 201 MHz respectively.

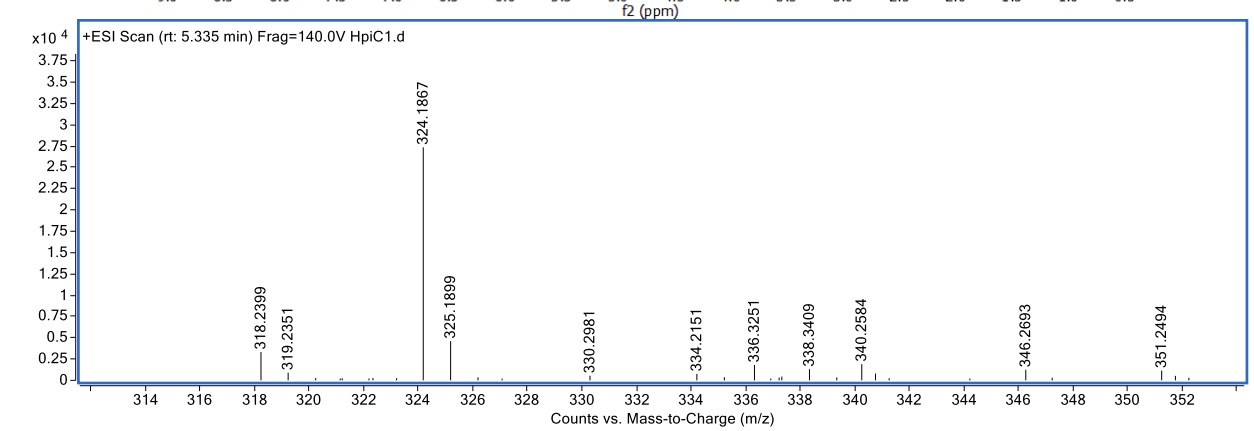



161.34
156.81
155.61
147.05
145.27
142.56
132.26
132.12
126.47
119.07
114.90
112.77
112.74
111.35
111.35
111.25
66.16
43.65
40.29
36.52
30.74
30.20
28.55
28.38
18.79
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)





Calc. $[M+H]^+$ 324.1871 Obsv. 324.1867

Table S38. Crystal data and structure refinement for **36**.

Identification code	rh7a2a
Empirical formula	C44 H56 N6 O
Formula weight	684.94
Temperature	85(2) K
Wavelength	1.54184 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 11.3688(9) A alpha = 90 deg. b = 15.8213(4) A beta = 90 deg. c = 22.0726(9) A gamma = 90 deg.
Volume	3970.2(4) A^3
Z, Calculated density	4, 1.146 Mg/m^3
Absorption coefficient	0.537 mm^-1
F(000)	1480
Crystal size	0.060 x 0.040 x 0.020 mm
Theta range for data collection	3.437 to 69.917 deg.
Limiting indices	-13<=h<=13, -18<=k<=19, -26<=l<=26
Reflections collected / unique	61153 / 7384 [R(int) = 0.1104]
Completeness to theta = 67.684	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.54753
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7384 / 29 / 495
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0874, wR2 = 0.2313
R indices (all data)	R1 = 0.1088, wR2 = 0.2539
Absolute structure parameter	0.3(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.374 and -0.266 e.A^-3

Table S39. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **36**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	4102(6)	7390(3)	7568(2)	83(2)
N(1)	5670(5)	4905(3)	5658(2)	54(1)
N(2)	6763(5)	5834(3)	5014(2)	56(1)
N(3)	8434(6)	8076(3)	6437(3)	65(2)
N(4)	7024(5)	4592(3)	4055(2)	60(1)
N(5)	5636(6)	3749(3)	4608(2)	57(1)
N(6)	6323(6)	933(3)	3706(3)	60(1)
C(1)	5120(7)	4865(3)	6193(3)	63(2)
C(2)	5051(7)	5531(3)	6609(3)	61(2)
C(3)	5608(7)	6300(3)	6478(3)	60(2)
C(4)	6178(6)	6376(3)	5930(3)	55(2)
C(5)	6825(6)	7002(3)	5599(3)	55(2)
C(6)	7085(6)	7949(3)	5570(3)	59(2)
C(7)	7449(7)	8459(4)	6128(3)	62(2)
C(9)	8578(8)	9406(3)	5398(3)	71(2)
C(10)	8217(8)	8867(3)	4845(3)	68(2)
C(11)	8043(6)	7965(3)	5072(3)	55(2)
C(12)	7709(7)	7254(3)	4615(3)	58(2)
C(13)	7155(6)	6658(3)	5062(3)	55(2)
C(14)	9205(9)	7787(4)	6720(3)	76(2)
C(8)	7736(7)	9394(4)	5941(4)	71(2)
C(15)	6652(13)	9854(9)	5679(8)	65(4)
C(16)	5671(13)	9969(8)	5963(7)	75(4)
C(8A)	7736(7)	9394(4)	5941(4)	71(2)
C(15A)	6505(18)	9759(15)	5953(9)	63(5)
C(16A)	6080(20)	10192(10)	5502(8)	75(6)
C(17)	8299(9)	9862(4)	6468(4)	87(3)
C(18)	6769(8)	7550(4)	4158(3)	72(2)
C(19)	8766(8)	6884(4)	4297(3)	72(2)
C(20)	6194(6)	5651(3)	5543(3)	52(2)
C(21)	7627(8)	4631(4)	3528(3)	72(2)
C(22)	7551(8)	4033(4)	3069(3)	67(2)
C(23)	6817(7)	3346(3)	3133(3)	64(2)
C(24)	6187(7)	3271(3)	3664(3)	58(2)
C(25)	5383(6)	2684(3)	3934(3)	57(2)
C(26)	4687(7)	1889(3)	3819(3)	60(2)
C(27)	5225(6)	1156(3)	3466(3)	61(2)
C(29)	4019(8)	166(4)	4129(4)	76(2)
C(30)	3509(7)	908(4)	4485(4)	72(2)
C(31)	4404(7)	1621(3)	4472(3)	59(2)
C(32)	4189(6)	2464(3)	4833(3)	59(2)
C(33)	5072(6)	2994(3)	4496(3)	56(2)
C(34)	6317(7)	3924(3)	4106(3)	57(2)
C(35)	7220(8)	793(4)	3913(4)	71(2)
C(28)	4368(7)	388(4)	3468(4)	70(2)

C(36)	3257(10)	584(5)	3120(5)	96(3)
C(37)	3121(12)	1071(5)	2657(5)	105(3)
C(38)	4952(9)	-382(4)	3173(4)	83(2)
C(39)	2944(7)	2797(4)	4747(3)	68(2)
C(40)	4439(7)	2375(3)	5508(3)	66(2)
C(41)	5789(12)	8274(7)	7637(5)	116(4)
C(42)	4933(9)	7740(5)	7973(4)	87(2)
C(43)	3224(9)	6912(4)	7877(4)	81(2)
C(44)	2329(11)	6633(5)	7444(4)	99(3)

Table S40. Bond lengths [A] and angles [deg] for **36**.

O(1)-C(42)	1.413(11)
O(1)-C(43)	1.426(10)
N(1)-C(1)	1.337(8)
N(1)-C(20)	1.347(7)
N(2)-C(20)	1.366(8)
N(2)-C(13)	1.382(6)
N(2)-H(2N)	0.91(3)
N(3)-C(14)	1.171(10)
N(3)-C(7)	1.444(10)
N(4)-C(34)	1.332(8)
N(4)-C(21)	1.352(9)
N(5)-C(33)	1.378(7)
N(5)-C(34)	1.381(8)
N(5)-H(5N)	0.90(3)
N(6)-C(35)	1.139(10)
N(6)-C(27)	1.402(10)
C(1)-C(2)	1.399(8)
C(1)-H(1)	0.9500
C(2)-C(3)	1.401(8)
C(2)-H(2)	0.9500
C(3)-C(4)	1.377(9)
C(3)-H(3)	0.9500
C(4)-C(20)	1.431(8)
C(4)-C(5)	1.433(8)
C(5)-C(13)	1.358(8)
C(5)-C(6)	1.529(7)
C(6)-C(7)	1.528(9)
C(6)-C(11)	1.547(9)
C(6)-H(6)	1.0000
C(7)-C(8A)	1.569(8)
C(7)-C(8)	1.569(8)
C(7)-H(7)	1.0000
C(9)-C(8A)	1.535(11)
C(9)-C(8)	1.535(11)
C(9)-C(10)	1.543(9)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.525(7)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.559(8)
C(11)-H(11)	1.0000

C(12)-C(13)	1.503(8)
C(12)-C(19)	1.510(11)
C(12)-C(18)	1.542(10)
C(8)-C(17)	1.519(11)
C(8)-C(15)	1.544(15)
C(15)-C(16)	1.293(16)
C(15)-H(15)	0.9500
C(16)-H(16A)	0.9500
C(16)-H(16B)	0.9500
C(8A)-C(15A)	1.515(19)
C(8A)-C(17)	1.519(11)
C(15A)-C(16A)	1.302(19)
C(15A)-H(15A)	0.9500
C(16A)-H(16C)	0.9500
C(16A)-H(16D)	0.9500
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(21)-C(22)	1.389(9)
C(21)-H(21)	0.9500
C(22)-C(23)	1.377(9)
C(22)-H(22)	0.9500
C(23)-C(24)	1.379(9)
C(23)-H(23)	0.9500
C(24)-C(34)	1.428(7)
C(24)-C(25)	1.434(9)
C(25)-C(33)	1.381(8)
C(25)-C(26)	1.507(8)
C(26)-C(27)	1.524(8)
C(26)-C(31)	1.538(9)
C(26)-H(26)	1.0000
C(27)-C(28)	1.557(9)
C(27)-H(27)	1.0000
C(29)-C(30)	1.526(9)
C(29)-C(28)	1.552(11)
C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900
C(30)-C(31)	1.519(9)
C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900
C(31)-C(32)	1.572(7)
C(31)-H(31)	1.0000
C(32)-C(33)	1.505(9)
C(32)-C(39)	1.523(10)
C(32)-C(40)	1.523(10)
C(28)-C(36)	1.511(12)
C(28)-C(38)	1.533(9)
C(36)-C(37)	1.289(13)
C(36)-H(36)	0.9500
C(37)-H(37A)	0.9500

C(37)-H(37B)	0.9500
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-C(42)	1.488(14)
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800
C(41)-H(41C)	0.9800
C(42)-H(42A)	0.9900
C(42)-H(42B)	0.9900
C(43)-C(44)	1.464(13)
C(43)-H(43A)	0.9900
C(43)-H(43B)	0.9900
C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800
C(44)-H(44C)	0.9800

C(42)-O(1)-C(43)	111.9(6)
C(1)-N(1)-C(20)	114.5(5)
C(20)-N(2)-C(13)	106.6(5)
C(20)-N(2)-H(2N)	128(7)
C(13)-N(2)-H(2N)	126(7)
C(14)-N(3)-C(7)	175.8(7)
C(34)-N(4)-C(21)	114.5(5)
C(33)-N(5)-C(34)	106.9(5)
C(33)-N(5)-H(5N)	118(4)
C(34)-N(5)-H(5N)	135(4)
C(35)-N(6)-C(27)	176.4(6)
N(1)-C(1)-C(2)	124.8(6)
N(1)-C(1)-H(1)	117.6
C(2)-C(1)-H(1)	117.6
C(1)-C(2)-C(3)	119.6(6)
C(1)-C(2)-H(2)	120.2
C(3)-C(2)-H(2)	120.2
C(4)-C(3)-C(2)	118.0(5)
C(4)-C(3)-H(3)	121.0
C(2)-C(3)-H(3)	121.0
C(3)-C(4)-C(20)	117.4(5)
C(3)-C(4)-C(5)	138.5(5)
C(20)-C(4)-C(5)	104.1(5)
C(13)-C(5)-C(4)	108.1(4)
C(13)-C(5)-C(6)	107.6(5)
C(4)-C(5)-C(6)	142.9(6)
C(5)-C(6)-C(7)	122.4(5)
C(5)-C(6)-C(11)	100.5(5)
C(7)-C(6)-C(11)	111.9(5)
C(5)-C(6)-H(6)	107.0
C(7)-C(6)-H(6)	107.0
C(11)-C(6)-H(6)	107.0
N(3)-C(7)-C(6)	111.6(5)

N(3)-C(7)-C(8A)	111.0(6)
C(6)-C(7)-C(8A)	110.1(6)
N(3)-C(7)-C(8)	111.0(6)
C(6)-C(7)-C(8)	110.1(6)
N(3)-C(7)-H(7)	108.0
C(6)-C(7)-H(7)	108.0
C(8)-C(7)-H(7)	108.0
C(8A)-C(9)-C(10)	116.4(6)
C(8)-C(9)-C(10)	116.4(6)
C(8)-C(9)-H(9A)	108.2
C(10)-C(9)-H(9A)	108.2
C(8)-C(9)-H(9B)	108.2
C(10)-C(9)-H(9B)	108.2
H(9A)-C(9)-H(9B)	107.3
C(11)-C(10)-C(9)	107.0(5)
C(11)-C(10)-H(10A)	110.3
C(9)-C(10)-H(10A)	110.3
C(11)-C(10)-H(10B)	110.3
C(9)-C(10)-H(10B)	110.3
H(10A)-C(10)-H(10B)	108.6
C(10)-C(11)-C(6)	109.9(5)
C(10)-C(11)-C(12)	119.6(5)
C(6)-C(11)-C(12)	106.1(5)
C(10)-C(11)-H(11)	106.9
C(6)-C(11)-H(11)	106.9
C(12)-C(11)-H(11)	106.9
C(13)-C(12)-C(19)	113.3(5)
C(13)-C(12)-C(18)	109.3(6)
C(19)-C(12)-C(18)	111.4(6)
C(13)-C(12)-C(11)	97.4(5)
C(19)-C(12)-C(11)	112.7(6)
C(18)-C(12)-C(11)	111.9(5)
C(5)-C(13)-N(2)	110.9(5)
C(5)-C(13)-C(12)	116.0(4)
N(2)-C(13)-C(12)	132.5(5)
C(17)-C(8)-C(9)	109.2(7)
C(17)-C(8)-C(15)	113.1(7)
C(9)-C(8)-C(15)	101.5(8)
C(17)-C(8)-C(7)	110.3(6)
C(9)-C(8)-C(7)	110.3(5)
C(15)-C(8)-C(7)	112.1(8)
C(16)-C(15)-C(8)	124.9(15)
C(16)-C(15)-H(15)	117.5
C(8)-C(15)-H(15)	117.5
C(15)-C(16)-H(16A)	120.0
C(15)-C(16)-H(16B)	120.0
H(16A)-C(16)-H(16B)	120.0
C(15A)-C(8A)-C(17)	101.0(11)
C(15A)-C(8A)-C(9)	125.8(10)
C(17)-C(8A)-C(9)	109.2(7)
C(15A)-C(8A)-C(7)	99.4(11)
C(17)-C(8A)-C(7)	110.3(6)
C(9)-C(8A)-C(7)	110.3(5)
C(16A)-C(15A)-C(8A)	122.3(19)
C(16A)-C(15A)-H(15A)	118.9
C(8A)-C(15A)-H(15A)	118.9

C(15A)-C(16A)-H(16C) 120.0
C(15A)-C(16A)-H(16D) 120.0
H(16C)-C(16A)-H(16D) 120.0
C(8)-C(17)-H(17A) 109.5
C(8)-C(17)-H(17B) 109.5
H(17A)-C(17)-H(17B) 109.5
C(8)-C(17)-H(17C) 109.5
H(17A)-C(17)-H(17C) 109.5
H(17B)-C(17)-H(17C) 109.5
C(12)-C(18)-H(18A) 109.5
C(12)-C(18)-H(18B) 109.5
H(18A)-C(18)-H(18B) 109.5
C(12)-C(18)-H(18C) 109.5
H(18A)-C(18)-H(18C) 109.5
H(18B)-C(18)-H(18C) 109.5
C(12)-C(19)-H(19A) 109.5
C(12)-C(19)-H(19B) 109.5
H(19A)-C(19)-H(19B) 109.5
C(12)-C(19)-H(19C) 109.5
H(19A)-C(19)-H(19C) 109.5
H(19B)-C(19)-H(19C) 109.5
N(1)-C(20)-N(2) 123.8(5)
N(1)-C(20)-C(4) 125.8(6)
N(2)-C(20)-C(4) 110.3(5)
N(4)-C(21)-C(22) 124.4(6)
N(4)-C(21)-H(21) 117.8
C(22)-C(21)-H(21) 117.8
C(23)-C(22)-C(21) 120.1(6)
C(23)-C(22)-H(22) 120.0
C(21)-C(22)-H(22) 120.0
C(22)-C(23)-C(24) 118.0(5)
C(22)-C(23)-H(23) 121.0
C(24)-C(23)-H(23) 121.0
C(23)-C(24)-C(34) 117.7(6)
C(23)-C(24)-C(25) 137.8(5)
C(34)-C(24)-C(25) 104.5(5)
C(33)-C(25)-C(24) 107.8(5)
C(33)-C(25)-C(26) 108.3(5)
C(24)-C(25)-C(26) 143.7(5)
C(25)-C(26)-C(27) 120.7(6)
C(25)-C(26)-C(31) 100.5(5)
C(27)-C(26)-C(31) 110.7(5)
C(25)-C(26)-H(26) 108.1
C(27)-C(26)-H(26) 108.1
C(31)-C(26)-H(26) 108.1
N(6)-C(27)-C(26) 110.8(5)
N(6)-C(27)-C(28) 111.1(5)
C(26)-C(27)-C(28) 109.9(5)
N(6)-C(27)-H(27) 108.3
C(26)-C(27)-H(27) 108.3
C(28)-C(27)-H(27) 108.3
C(30)-C(29)-C(28) 114.0(6)
C(30)-C(29)-H(29A) 108.7
C(28)-C(29)-H(29A) 108.7
C(30)-C(29)-H(29B) 108.7
C(28)-C(29)-H(29B) 108.7

H(29A)-C(29)-H(29B)	107.6
C(31)-C(30)-C(29)	107.9(6)
C(31)-C(30)-H(30A)	110.1
C(29)-C(30)-H(30A)	110.1
C(31)-C(30)-H(30B)	110.1
C(29)-C(30)-H(30B)	110.1
H(30A)-C(30)-H(30B)	108.4
C(30)-C(31)-C(26)	111.3(5)
C(30)-C(31)-C(32)	121.1(6)
C(26)-C(31)-C(32)	105.9(4)
C(30)-C(31)-H(31)	105.9
C(26)-C(31)-H(31)	105.9
C(32)-C(31)-H(31)	105.9
C(33)-C(32)-C(39)	111.4(5)
C(33)-C(32)-C(40)	114.3(6)
C(39)-C(32)-C(40)	109.1(6)
C(33)-C(32)-C(31)	96.9(5)
C(39)-C(32)-C(31)	112.0(5)
C(40)-C(32)-C(31)	112.8(5)
N(5)-C(33)-C(25)	110.5(5)
N(5)-C(33)-C(32)	134.8(5)
C(25)-C(33)-C(32)	114.6(5)
N(4)-C(34)-N(5)	124.4(5)
N(4)-C(34)-C(24)	125.4(6)
N(5)-C(34)-C(24)	110.2(5)
C(36)-C(28)-C(38)	107.9(6)
C(36)-C(28)-C(29)	108.1(7)
C(38)-C(28)-C(29)	109.4(6)
C(36)-C(28)-C(27)	111.1(6)
C(38)-C(28)-C(27)	110.3(6)
C(29)-C(28)-C(27)	109.9(5)
C(37)-C(36)-C(28)	128.8(11)
C(37)-C(36)-H(36)	115.6
C(28)-C(36)-H(36)	115.6
C(36)-C(37)-H(37A)	120.0
C(36)-C(37)-H(37B)	120.0
H(37A)-C(37)-H(37B)	120.0
C(28)-C(38)-H(38A)	109.5
C(28)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(28)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(32)-C(39)-H(39A)	109.5
C(32)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(32)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(32)-C(40)-H(40A)	109.5
C(32)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(32)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(42)-C(41)-H(41A)	109.5

C(42)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(42)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
O(1)-C(42)-C(41)	110.2(8)
O(1)-C(42)-H(42A)	109.6
C(41)-C(42)-H(42A)	109.6
O(1)-C(42)-H(42B)	109.6
C(41)-C(42)-H(42B)	109.6
H(42A)-C(42)-H(42B)	108.1
O(1)-C(43)-C(44)	109.6(7)
O(1)-C(43)-H(43A)	109.8
C(44)-C(43)-H(43A)	109.8
O(1)-C(43)-H(43B)	109.8
C(44)-C(43)-H(43B)	109.8
H(43A)-C(43)-H(43B)	108.2
C(43)-C(44)-H(44A)	109.5
C(43)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
C(43)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S41. Anisotropic displacement parameters (A^2 x 10^3) for **36**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	142(5)	42(2)	64(3)	-12(2)	4(3)	-4(3)
N(1)	92(4)	20(2)	50(3)	1(2)	-1(2)	-5(2)
N(2)	97(4)	19(2)	51(3)	0(2)	0(3)	-5(2)
N(3)	103(5)	31(2)	60(3)	-9(2)	3(3)	-9(3)
N(4)	102(4)	23(2)	55(3)	0(2)	3(3)	-3(2)
N(5)	99(4)	22(2)	49(3)	-4(2)	-1(3)	0(2)
N(6)	59(4)	30(2)	90(4)	-22(2)	11(3)	-2(2)
C(1)	117(6)	25(2)	47(3)	2(2)	-2(3)	0(3)
C(2)	106(5)	27(2)	50(3)	2(2)	4(3)	-4(3)
C(3)	100(5)	26(2)	54(3)	-5(2)	-3(3)	0(3)
C(4)	84(4)	26(2)	54(3)	-1(2)	-2(3)	1(3)
C(5)	92(5)	17(2)	55(3)	-3(2)	-1(3)	-6(2)
C(6)	87(5)	21(2)	70(4)	-3(2)	0(3)	-8(3)
C(7)	80(5)	28(3)	76(4)	-12(3)	2(4)	-4(3)
C(9)	110(6)	23(2)	78(4)	-1(3)	-17(4)	-9(3)
C(10)	110(6)	21(2)	73(4)	2(2)	-3(4)	-9(3)
C(11)	80(4)	22(2)	62(3)	1(2)	1(3)	-7(2)
C(12)	93(5)	24(2)	57(3)	3(2)	2(3)	-8(3)
C(13)	93(5)	19(2)	54(3)	1(2)	-1(3)	-7(2)
C(14)	132(7)	41(3)	57(4)	-3(3)	-2(4)	-10(4)

C(8)	101(5)	26(3)	87(5)	-9(3)	-4(4)	-4(3)
C(15)	99(8)	27(6)	70(10)	-6(7)	-6(7)	9(6)
C(16)	99(9)	45(6)	82(9)	10(5)	-4(7)	9(6)
C(8A)	101(5)	26(3)	87(5)	-9(3)	-4(4)	-4(3)
C(15A)	91(12)	50(11)	49(11)	-7(9)	11(9)	-1(9)
C(16A)	123(16)	30(8)	74(11)	-1(7)	10(10)	8(9)
C(17)	138(7)	31(3)	93(5)	-21(3)	1(5)	-13(4)
C(18)	115(6)	35(3)	65(4)	9(3)	-14(4)	-12(3)
C(19)	112(6)	34(3)	70(4)	-10(3)	12(4)	-11(3)
C(20)	85(4)	21(2)	51(3)	3(2)	-5(3)	-1(2)
C(21)	144(7)	28(2)	44(3)	0(2)	6(4)	-6(3)
C(22)	117(6)	32(3)	53(3)	4(2)	6(4)	-5(3)
C(23)	121(6)	29(3)	43(3)	0(2)	1(3)	1(3)
C(24)	101(5)	23(2)	50(3)	-4(2)	-5(3)	1(3)
C(25)	93(5)	26(2)	52(3)	-3(2)	-1(3)	-6(3)
C(26)	92(5)	28(2)	61(3)	-14(2)	0(3)	0(3)
C(27)	81(5)	31(3)	71(4)	-19(3)	10(3)	-4(3)
C(29)	108(6)	36(3)	85(5)	-16(3)	14(4)	-16(3)
C(30)	100(6)	35(3)	82(5)	-17(3)	15(4)	-10(3)
C(31)	80(4)	25(2)	72(4)	-12(2)	4(3)	-8(3)
C(32)	84(5)	32(2)	60(4)	-11(2)	5(3)	-4(3)
C(33)	92(5)	18(2)	58(3)	-4(2)	-2(3)	-5(2)
C(34)	105(5)	21(2)	45(3)	-2(2)	-3(3)	2(3)
C(35)	63(5)	39(3)	111(6)	-23(3)	15(4)	-3(3)
C(28)	88(5)	31(3)	90(5)	-25(3)	5(4)	-4(3)
C(36)	130(8)	53(4)	104(7)	-37(5)	-6(6)	-6(5)
C(37)	148(9)	54(4)	113(7)	-28(5)	-7(7)	4(5)
C(38)	132(7)	34(3)	82(5)	-21(3)	24(5)	-9(4)
C(39)	96(5)	42(3)	65(4)	-15(3)	1(4)	-3(3)
C(40)	107(6)	28(2)	65(4)	-6(2)	7(4)	-4(3)
C(41)	168(10)	87(6)	93(6)	-44(5)	32(7)	-28(7)
C(42)	129(7)	60(4)	72(5)	-23(4)	10(5)	-3(5)
C(43)	134(7)	41(3)	69(4)	5(3)	7(4)	-2(4)
C(44)	162(9)	57(4)	78(5)	5(4)	-7(6)	-14(5)

Table S42. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **36**.

	x	y	z	U(eq)
H(2N)	6860(90)	5490(60)	4690(30)	120(30)
H(5N)	5520(50)	4000(40)	4971(17)	51(16)
H(1)	4749	4348	6298	76
H(2)	4630	5462	6977	73
H(3)	5594	6755	6759	72
H(6)	6372	8229	5397	71
H(7)	6768	8471	6414	74
H(9A)	9360	9211	5537	85
H(9B)	8667	9999	5262	85
H(10A)	7479	9085	4667	82
H(10B)	8840	8883	4532	82
H(11)	8797	7790	5269	66
H(15)	6711	10070	5278	78

H(16A)	5579	9763	6365	90
H(16B)	5042	10260	5771	90
H(15A)	6029	9669	6301	76
H(16C)	6540	10289	5151	90
H(16D)	5300	10412	5525	90
H(17A)	9077	9621	6550	131
H(17B)	7802	9805	6828	131
H(17C)	8382	10461	6364	131
H(18A)	6528	7072	3904	107
H(18B)	7096	7997	3902	107
H(18C)	6084	7768	4378	107
H(19A)	9310	6650	4598	108
H(19B)	9165	7328	4065	108
H(19C)	8511	6434	4022	108
H(21)	8138	5099	3468	86
H(22)	8006	4098	2711	81
H(23)	6747	2937	2820	77
H(26)	3933	2051	3616	72
H(27)	5341	1341	3037	73
H(29A)	3431	-296	4121	92
H(29B)	4722	-47	4345	92
H(30A)	2761	1096	4300	87
H(30B)	3350	736	4909	87
H(31)	5148	1377	4638	71
H(36)	2565	311	3260	115
H(37A)	3777	1364	2493	126
H(37B)	2364	1138	2480	126
H(38A)	4424	-870	3201	124
H(38B)	5691	-509	3382	124
H(38C)	5114	-259	2746	124
H(39A)	2866	3344	4951	101
H(39B)	2382	2395	4921	101
H(39C)	2783	2866	4314	101
H(40A)	5250	2181	5566	100
H(40B)	3894	1963	5685	100
H(40C)	4334	2924	5706	100
H(41A)	6183	7933	7327	174
H(41B)	6375	8499	7919	174
H(41C)	5372	8744	7442	174
H(42A)	5356	7279	8185	104
H(42B)	4522	8086	8281	104
H(43A)	2854	7264	8195	97
H(43B)	3589	6415	8074	97
H(44A)	1935	7127	7269	148
H(44B)	1749	6279	7653	148
H(44C)	2703	6305	7120	148

Table S43. Torsion angles [deg] for **36**.

C(20)-N(1)-C(1)-C(2)	1.1(10)
N(1)-C(1)-C(2)-C(3)	-1.4(12)
C(1)-C(2)-C(3)-C(4)	1.9(11)
C(2)-C(3)-C(4)-C(20)	-2.2(10)
C(2)-C(3)-C(4)-C(5)	178.7(8)

C(3)-C(4)-C(5)-C(13)	-179.6(8)
C(20)-C(4)-C(5)-C(13)	1.2(8)
C(3)-C(4)-C(5)-C(6)	-16.0(17)
C(20)-C(4)-C(5)-C(6)	164.8(9)
C(13)-C(5)-C(6)-C(7)	-147.4(7)
C(4)-C(5)-C(6)-C(7)	48.9(13)
C(13)-C(5)-C(6)-C(11)	-22.9(7)
C(4)-C(5)-C(6)-C(11)	173.5(9)
C(5)-C(6)-C(7)-N(3)	52.4(9)
C(11)-C(6)-C(7)-N(3)	-66.8(7)
C(5)-C(6)-C(7)-C(8A)	176.1(6)
C(11)-C(6)-C(7)-C(8A)	56.9(7)
C(5)-C(6)-C(7)-C(8)	176.1(6)
C(11)-C(6)-C(7)-C(8)	56.9(7)
C(8A)-C(9)-C(10)-C(11)	-55.9(8)
C(8)-C(9)-C(10)-C(11)	-55.9(8)
C(9)-C(10)-C(11)-C(6)	58.9(8)
C(9)-C(10)-C(11)-C(12)	-178.1(6)
C(5)-C(6)-C(11)-C(10)	165.2(6)
C(7)-C(6)-C(11)-C(10)	-63.3(7)
C(5)-C(6)-C(11)-C(12)	34.6(6)
C(7)-C(6)-C(11)-C(12)	166.1(5)
C(10)-C(11)-C(12)-C(13)	-156.9(7)
C(6)-C(11)-C(12)-C(13)	-32.1(6)
C(10)-C(11)-C(12)-C(19)	83.9(8)
C(6)-C(11)-C(12)-C(19)	-151.2(5)
C(10)-C(11)-C(12)-C(18)	-42.7(9)
C(6)-C(11)-C(12)-C(18)	82.2(6)
C(4)-C(5)-C(13)-N(2)	0.1(8)
C(6)-C(5)-C(13)-N(2)	-169.7(6)
C(4)-C(5)-C(13)-C(12)	172.2(6)
C(6)-C(5)-C(13)-C(12)	2.5(9)
C(20)-N(2)-C(13)-C(5)	-1.4(8)
C(20)-N(2)-C(13)-C(12)	-171.8(7)
C(19)-C(12)-C(13)-C(5)	137.4(7)
C(18)-C(12)-C(13)-C(5)	-97.7(7)
C(11)-C(12)-C(13)-C(5)	18.7(8)
C(19)-C(12)-C(13)-N(2)	-52.5(10)
C(18)-C(12)-C(13)-N(2)	72.4(9)
C(11)-C(12)-C(13)-N(2)	-171.2(7)
C(10)-C(9)-C(8)-C(17)	172.8(6)
C(10)-C(9)-C(8)-C(15)	-67.5(8)
C(10)-C(9)-C(8)-C(7)	51.5(8)
N(3)-C(7)-C(8)-C(17)	-46.1(8)
C(6)-C(7)-C(8)-C(17)	-170.1(7)
N(3)-C(7)-C(8)-C(9)	74.6(7)
C(6)-C(7)-C(8)-C(9)	-49.4(8)
N(3)-C(7)-C(8)-C(15)	-173.1(8)
C(6)-C(7)-C(8)-C(15)	62.8(10)
C(17)-C(8)-C(15)-C(16)	-66.5(16)
C(9)-C(8)-C(15)-C(16)	176.7(13)
C(7)-C(8)-C(15)-C(16)	59.0(15)
C(10)-C(9)-C(8A)-C(15A)	-67.2(14)
C(10)-C(9)-C(8A)-C(17)	172.8(6)
C(10)-C(9)-C(8A)-C(7)	51.5(8)
N(3)-C(7)-C(8A)-C(15A)	-151.6(10)

C(6)-C(7)-C(8A)-C(15A)	84.4(10)
N(3)-C(7)-C(8A)-C(17)	-46.1(8)
C(6)-C(7)-C(8A)-C(17)	-170.1(7)
N(3)-C(7)-C(8A)-C(9)	74.6(7)
C(6)-C(7)-C(8A)-C(9)	-49.4(8)
C(17)-C(8A)-C(15A)-C(16A)	118(2)
C(9)-C(8A)-C(15A)-C(16A)	-6(3)
C(7)-C(8A)-C(15A)-C(16A)	-130(2)
C(1)-N(1)-C(20)-N(2)	-177.4(6)
C(1)-N(1)-C(20)-C(4)	-1.5(10)
C(13)-N(2)-C(20)-N(1)	178.7(6)
C(13)-N(2)-C(20)-C(4)	2.2(7)
C(3)-C(4)-C(20)-N(1)	2.1(10)
C(5)-C(4)-C(20)-N(1)	-178.5(6)
C(3)-C(4)-C(20)-N(2)	178.5(6)
C(5)-C(4)-C(20)-N(2)	-2.1(7)
C(34)-N(4)-C(21)-C(22)	-0.6(11)
N(4)-C(21)-C(22)-C(23)	0.5(12)
C(21)-C(22)-C(23)-C(24)	-1.0(11)
C(22)-C(23)-C(24)-C(34)	1.6(10)
C(22)-C(23)-C(24)-C(25)	-177.5(8)
C(23)-C(24)-C(25)-C(33)	179.6(8)
C(34)-C(24)-C(25)-C(33)	0.4(7)
C(23)-C(24)-C(25)-C(26)	-6.6(17)
C(34)-C(24)-C(25)-C(26)	174.3(9)
C(33)-C(25)-C(26)-C(27)	-145.4(6)
C(24)-C(25)-C(26)-C(27)	40.7(13)
C(33)-C(25)-C(26)-C(31)	-23.6(7)
C(24)-C(25)-C(26)-C(31)	162.6(9)
C(25)-C(26)-C(27)-N(6)	51.3(8)
C(31)-C(26)-C(27)-N(6)	-65.4(7)
C(25)-C(26)-C(27)-C(28)	174.5(6)
C(31)-C(26)-C(27)-C(28)	57.7(8)
C(28)-C(29)-C(30)-C(31)	-56.3(9)
C(29)-C(30)-C(31)-C(26)	58.6(8)
C(29)-C(30)-C(31)-C(32)	-176.1(7)
C(25)-C(26)-C(31)-C(30)	169.8(6)
C(27)-C(26)-C(31)-C(30)	-61.6(8)
C(25)-C(26)-C(31)-C(32)	36.4(7)
C(27)-C(26)-C(31)-C(32)	165.0(6)
C(30)-C(31)-C(32)-C(33)	-161.9(7)
C(26)-C(31)-C(32)-C(33)	-34.2(7)
C(30)-C(31)-C(32)-C(39)	-45.5(9)
C(26)-C(31)-C(32)-C(39)	82.3(7)
C(30)-C(31)-C(32)-C(40)	78.1(9)
C(26)-C(31)-C(32)-C(40)	-154.2(6)
C(34)-N(5)-C(33)-C(25)	0.2(7)
C(34)-N(5)-C(33)-C(32)	-177.6(7)
C(24)-C(25)-C(33)-N(5)	-0.4(8)
C(26)-C(25)-C(33)-N(5)	-176.6(6)
C(24)-C(25)-C(33)-C(32)	177.9(6)
C(26)-C(25)-C(33)-C(32)	1.7(8)
C(39)-C(32)-C(33)-N(5)	81.1(9)
C(40)-C(32)-C(33)-N(5)	-43.1(10)
C(31)-C(32)-C(33)-N(5)	-162.0(7)
C(39)-C(32)-C(33)-C(25)	-96.6(6)

C(40)-C(32)-C(33)-C(25)	139.2(6)
C(31)-C(32)-C(33)-C(25)	20.3(7)
C(21)-N(4)-C(34)-N(5)	178.8(7)
C(21)-N(4)-C(34)-C(24)	1.4(10)
C(33)-N(5)-C(34)-N(4)	-177.7(6)
C(33)-N(5)-C(34)-C(24)	0.1(7)
C(23)-C(24)-C(34)-N(4)	-1.9(10)
C(25)-C(24)-C(34)-N(4)	177.4(6)
C(23)-C(24)-C(34)-N(5)	-179.6(6)
C(25)-C(24)-C(34)-N(5)	-0.3(7)
C(30)-C(29)-C(28)-C(36)	-67.0(8)
C(30)-C(29)-C(28)-C(38)	175.7(7)
C(30)-C(29)-C(28)-C(27)	54.5(9)
N(6)-C(27)-C(28)-C(36)	-170.8(6)
C(26)-C(27)-C(28)-C(36)	66.2(8)
N(6)-C(27)-C(28)-C(38)	-51.1(8)
C(26)-C(27)-C(28)-C(38)	-174.1(6)
N(6)-C(27)-C(28)-C(29)	69.6(7)
C(26)-C(27)-C(28)-C(29)	-53.4(8)
C(38)-C(28)-C(36)-C(37)	-89.8(9)
C(29)-C(28)-C(36)-C(37)	152.0(8)
C(27)-C(28)-C(36)-C(37)	31.3(11)
C(43)-O(1)-C(42)-C(41)	-176.6(7)
C(42)-O(1)-C(43)-C(44)	174.7(7)

Symmetry transformations used to generate equivalent atoms:

Table S44. Hydrogen bonds for **36** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2N)...N(4)	0.91(3)	2.00(3)	2.903(7)	171(11)
N(5)-H(5N)...N(1)	0.90(3)	2.09(3)	2.952(6)	159(6)

Symmetry transformations used to generate equivalent atoms:

Computational Methods

Conformational searches of all hapalindole and fischerindole products were performed using the Schrödinger MacroModel[2] software package, and the lowest energy conformation was used for all reported quantum mechanical computations. All quantum mechanical calculations were performed using the Gaussian 09[3] software package on an ultrafine grid. Structures were optimized at the B3LYP[4,5]/6-31G(d) level of theory; frequency calculations were used to confirm the presence of local minima (no imaginary frequencies) and transition states (one imaginary frequency). Thermochemistry corrections to obtain enthalpies and free energies were computed at 25 °C and 1 M. To obtain more accurate energetics, single-point energy calculations were performed on the optimized structures at the B3LYP[4,5]/6-311++G(d,p) level of theory using Grimme's D3(BJ) dispersion correction[6,7] and the CPCM[8–10] solvent model for diethyl ether, which is intended to mimic the hydrophobic nature of the enzyme active sites.

Table S45: Optimized Quantum Mechanical Energies and Geometries

Structure	**Single-Point Energy** (Hartree) B3LYP/6-311++G(d,p) CPCM diethyl ether solvent	**Enthalpy Correction** (Hartree) B3LYP/6-31G(d)	**Gibbs Free Energy Correction** (Hartree) B3LYP/6-31G(d)
2-T	-924.869068910	0.436100	0.362161
TS from **2-T** to **2-H**	-924.861768738	0.435517	0.366601
2-H	-924.879360164	0.437886	0.369401
TS from **2-T** to **2-F**	-924.869011094	0.435240	0.364728
2-F	-924.890827959	0.437475	0.367863
17-T	-940.910995530	0.424076	0.350630
TS from **17-T** to **17-H**	-940.891628344	0.423525	0.354648
17-H	-940.901120546	0.425162	0.356731
TS from **17-T** to **17-F**	-940.910547946	0.423316	0.353193
17-F	-940.930000542	0.425439	0.356083
18-T	-1040.17431066	0.416424	0.340667
TS from **18-T** to **18-H**	-1040.15655568	0.416097	0.345202
18-H	-1040.16622917	0.418282	0.348253
TS from **18-T** to **18-F**	-1040.17270403	0.415794	0.343746
18-F	-1040.19039875	0.417846	0.346430

Table S46: Optimized Quantum Mechanical Geometries

2-T

```
1 1
 C   -3.514752    2.323036   -0.919023
 C   -4.631133    1.713579   -0.311448
 C   -4.504197    0.564819    0.467282
 H   -3.659192    3.217824   -1.515951
 H   -5.615288    2.149323   -0.453066
 H   -5.369711    0.100061    0.929423
 C   -1.433591   -1.197740    1.195781
 C   -0.942157   -0.160015    0.385836
 C   -2.078233    0.643549    0.027683
 C   -3.219971    0.049236    0.626963
 N   -2.780798   -1.070067    1.329387
 H   -0.891712   -1.936683    1.767641
 C   -0.084588   -2.100048   -1.004059
 C    1.037414   -1.371321   -0.317839
 C    0.494153    0.034567   -0.023712
 C    2.393314   -1.287859   -1.059636
 C    3.369572   -0.470167   -0.183700
 C    2.866841    0.923831    0.273527
 C    1.444972    0.790383    0.938180
 C   -0.344288   -3.528584   -0.674624
 C   -0.655823   -1.607631   -2.286482
 N    1.493421    0.103507    2.189513
 C    1.488677   -0.525809    3.186743
 C    2.731266    1.933572   -0.858078
 C    3.225260    1.855084   -2.094727
 C    3.862648    1.514792    1.298492
 H    1.221820   -1.878256    0.636685
 H    0.509261    0.614199   -0.953091
 H    2.250639   -0.814869   -2.036832
 H    2.808478   -2.287334   -1.231248
 H    4.316783   -0.350099   -0.720164
 H    3.604272   -1.056112    0.713288
 H    1.051521    1.795054    1.133462
 H   -1.382066   -3.820765   -0.862422
 H    0.272295   -4.131116   -1.366555
 H   -0.047052   -3.802094    0.339572
 H   -1.711347   -1.879690   -2.389199
 H   -0.534561   -0.537050   -2.451251
 H   -0.124839   -2.133115   -3.099733
 H    2.221494    2.855383   -0.568868
 H    3.119614    2.682902   -2.789872
 H    3.775381    0.993315   -2.462571
 H    3.962809    0.868124    2.175394
 H    4.847142    1.629519    0.835593
 H    3.537775    2.503971    1.640214
 C   -2.239207    1.797936   -0.762509
 H   -1.384477    2.279525   -1.229412
 H   -3.364462   -1.667346    1.898760
```

TS from **2-T** to **2-H**

```
1 1
 C   -3.497926   -1.417648   -0.871284
 C   -4.537352   -0.518690   -0.654609
 C   -4.303382    0.863331   -0.466489
 H   -3.729712   -2.459322   -1.072533
 H   -5.562340   -0.875281   -0.657043
 H   -5.136515    1.541698   -0.306173
 C   -1.046114    2.397105   -0.185033
 C   -0.700614    1.080820   -0.471471
 C   -1.916076    0.397641   -0.684607
 C   -2.989734    1.302462   -0.475862
 N   -2.408805    2.535596   -0.216978
 H   -0.420239    3.243097    0.061572
 C   -0.858496   -1.536921    1.001761
 C    0.451268   -0.784217    0.814919
 C    0.551985    0.283472   -0.376954
 C    1.690113   -1.708135    0.724982
 C    3.001977   -0.907186    0.783177
 C    3.133760    0.193381   -0.289551
 C    1.858171    1.099572   -0.230848
 C   -1.756621   -1.011268    2.079257
 C   -0.907431   -3.020408    0.782549
 N    1.811358    1.875834    0.971755
 C    1.749900    2.490689    1.976393
 C    3.242404   -0.334335   -1.714129
 C    3.560782   -1.568183   -2.108064
 C    4.395733    1.044405   -0.019309
 H    0.541760   -0.164624    1.717397
 H    0.668719   -0.303333   -1.296678
 H    1.649026   -2.294359   -0.198699
 H    1.683955   -2.420411    1.557619
 H    3.848263   -1.598259    0.706124
 H    3.088735   -0.436036    1.770139
 H    1.903812    1.809354   -1.066313
 H   -2.763513   -1.431778    2.037182
 H   -1.310057   -1.315066    3.041246
 H   -1.801331    0.080759    2.088587
 H   -1.931385   -3.398467    0.800394
 H   -0.407150   -3.346812   -0.131641
 H   -0.374037   -3.495752    1.621849
 H    3.109829    0.429987   -2.483100
 H    3.680530   -1.802804   -3.161732
 H    3.742572   -2.385107   -1.414882
 H    4.361517    1.508398    0.970998
 H    5.285414    0.410518   -0.075482
 H    4.506309    1.839403   -0.765620
 C   -2.147595   -0.981751   -0.884714
 H   -1.397534   -1.599707   -1.367308
 H   -2.903022    3.399073   -0.040020
```

2-H

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1 1
 C    3.540333    1.337070   -0.254846
 C    4.532774    0.403160   -0.156895
 C    4.265518   -1.008142   -0.222102
 H    3.800615    2.391056   -0.222185
 H    5.562577    0.718123   -0.024331
 H    5.087058   -1.712359   -0.117865
 C    1.014722   -2.506372   -0.502058
 C    0.700799   -1.132706   -0.552073
 C    1.913340   -0.476196   -0.493308
 C    2.968201   -1.421243   -0.397567
 N    2.359611   -2.673677   -0.427149
 H    0.359488   -3.366955   -0.491658
 C    0.977074    1.732813    0.371196
 C   -0.330513    0.835930    0.538516
 C   -0.557347   -0.313418   -0.506214
 C   -1.611024    1.687772    0.659288
 C   -2.862705    0.844606    0.949314
 C   -3.113848   -0.281277   -0.074965
 C   -1.819371   -1.152284   -0.172001
 C    1.521277    2.007885    1.788932
 C    0.714174    3.071815   -0.344948
 N   -1.588546   -1.896238    1.032064
 C   -1.356232   -2.498592    2.018944
 C   -3.432575    0.207394   -1.481821
 C   -3.857847    1.416269   -1.850825
 C   -4.301566   -1.159737    0.381859
 H   -0.196953    0.308635    1.492157
 H   -0.741890    0.130266   -1.494974
 H   -1.762027    2.255959   -0.262726
 H   -1.489411    2.420075    1.465945
 H   -3.741010    1.497751    0.996128
 H   -2.773853    0.387843    1.942931
 H   -1.965559   -1.890778   -0.971881
 H    2.349054    2.724737    1.774645
 H    0.733382    2.435241    2.417922
 H    1.868994    1.088755    2.273664
 H    1.655225    3.611616   -0.504257
 H    0.242809    2.931257   -1.324637
 H    0.070821    3.725326    0.248996
 H   -3.371740   -0.569153   -2.248091
 H   -4.128715    1.621015   -2.882555
 H   -3.978947    2.240363   -1.153229
 H   -4.121038   -1.594438    1.369620
 H   -5.209014   -0.551038    0.431135
 H   -4.488151   -1.977976   -0.323524
 C    2.110587    0.974910   -0.489108
 H    1.919563    1.314490   -1.527713
 H    2.826637   -3.568340   -0.353829
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TS from **2-T** to **2-F**

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1 1
 C    2.225726   -1.887033   -0.679098
 C    3.500951   -2.400374   -0.848392
 C    4.629799   -1.731302   -0.325125
 C    4.515084   -0.534300    0.375567
 H    1.361741   -2.409164   -1.080319
 H    3.641377   -3.330404   -1.389645
 H    5.615136   -2.161421   -0.476138
 H    5.390254   -0.025180    0.767163
 N    2.800950    1.135216    1.181209
 C    3.228308   -0.026459    0.552428
 C    2.073596   -0.684287    0.043401
 C    0.942421    0.115792    0.393141
 C    0.095351    2.154689   -0.878075
 C    0.710377    1.724332   -2.165537
 C    0.260017    3.595719   -0.528749
 C   -1.023093    1.371221   -0.242724
 C   -2.377222    1.336258   -0.990717
 C   -3.362195    0.480343   -0.161696
 C   -2.870082   -0.937711    0.227396
 C   -1.448112   -0.848303    0.899887
 C   -0.491444   -0.053309   -0.024546
 H   -2.234746    0.915920   -1.991809
 H   -2.786183    2.345894   -1.109679
 H   -4.307717    0.392805   -0.707305
 H   -3.597321    1.021795    0.762712
 C   -3.871362   -1.570783    1.221549
 C   -2.739973   -1.892143   -0.951710
 N   -1.491858   -0.223048    2.183028
 H   -1.064301   -1.864844    1.046114
 H   -1.214349    1.819760    0.739714
 H   -0.510927   -0.586741   -0.981813
 C   -3.226572   -1.747934   -2.185363
 C   -1.486897    0.356452    3.210198
 H    0.624550    0.657200   -2.369921
 H    0.191020    2.266047   -2.974606
 H    1.761589    2.025416   -2.227137
 H    1.277436    3.957155   -0.705920
 H   -0.392734    4.166747   -1.213040
 H   -0.057027    3.834979    0.488645
 H   -3.554458   -2.578090    1.514309
 H   -3.967300   -0.967314    2.129140
 H   -4.856248   -1.654931    0.752979
 H   -2.241761   -2.832672   -0.705640
 H   -3.125822   -2.541771   -2.919753
 H   -3.765333   -0.863209   -2.513293
 C    1.440601    1.230232    1.094656
 H    0.906405    1.958814    1.685901
 H    3.391388    1.761421    1.710727
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2-F

1 1

C	2.315459	-2.174391	-0.368852
C	3.607146	-2.586507	-0.547989
C	4.701422	-1.676347	-0.371737
C	4.531633	-0.352854	-0.028639
H	1.482053	-2.858421	-0.490617
H	3.823106	-3.613266	-0.823202
H	5.709569	-2.051819	-0.522450
H	5.377817	0.315976	0.088689
N	2.758418	1.339002	0.425423
C	3.206584	0.097693	0.152253
C	2.081220	-0.815438	0.012012
C	0.942180	-0.076838	0.256024
C	0.288479	2.215211	-0.162126
C	0.629111	2.304407	-1.657574
C	0.188012	3.618441	0.446919
C	-0.970004	1.334416	0.147959
C	-2.309306	1.562037	-0.548066
C	-3.333733	0.552154	0.024862
C	-2.911811	-0.942666	0.002971
C	-1.473401	-1.124482	0.626832
C	-0.512264	-0.131752	-0.070319
H	-2.202497	1.441988	-1.631770
H	-2.678548	2.578689	-0.370369
H	-4.289428	0.651358	-0.500220
H	-3.536233	0.824925	1.068131
C	-3.928183	-1.773853	0.819787
C	-2.850979	-1.546685	-1.393005
N	-1.443904	-0.910761	2.037519
H	-1.150121	-2.157446	0.450481
H	-1.147909	1.450811	1.227213
H	-0.583042	-0.380072	-1.140925
C	-3.308684	-1.030294	-2.535110
C	-1.392461	-0.695620	3.196458
H	0.716600	1.324796	-2.139699
H	-0.150116	2.864260	-2.183794
H	1.573565	2.836298	-1.811875
H	1.118887	4.181676	0.312911
H	-0.606019	4.189412	-0.045529
H	-0.040583	3.581381	1.518353
H	-3.665342	-2.837950	0.819224
H	-3.975575	-1.435137	1.858978
H	-4.923748	-1.676811	0.377201
H	-2.436414	-2.557301	-1.420354
H	-3.264601	-1.598900	-3.459510
H	-3.765807	-0.047395	-2.601859
C	1.323430	1.312279	0.623650
H	1.112943	1.463218	1.697238
H	3.356744	2.098579	0.725303

17-T

1 1

C	3.592236	-2.264871	-0.973712
C	4.646266	-1.588917	-0.323248
H	3.815696	-3.139145	-1.575573
H	5.666594	-1.948178	-0.430005
C	1.466943	1.134215	1.188469
C	0.954153	0.114974	0.367423
C	2.078568	-0.680412	-0.029274
C	3.232624	-0.098549	0.561886
N	2.819523	1.004675	1.293339
H	0.936912	1.852494	1.796270
C	0.032874	2.193531	-0.878003
C	-1.041650	1.385276	-0.213329
C	-0.486726	-0.038192	-0.041344
C	-2.416406	1.350114	-0.932154
C	-3.371659	0.461357	-0.104709
C	-2.854264	-0.960722	0.229299
C	-1.421569	-0.868511	0.876168
C	0.252931	3.603924	-0.460734
C	0.603285	1.797273	-2.192342
N	-1.450895	-0.277426	2.175554
C	-1.435349	0.276632	3.216627
C	-2.734173	-1.876077	-0.981429
C	-3.252861	-1.703970	-2.198369
C	-3.826708	-1.638389	1.222702
H	-1.210589	1.814721	0.780986
H	-0.517802	-0.544116	-1.012838
H	-2.290900	0.956615	-1.946116
H	-2.837733	2.358086	-1.015540
H	-4.327735	0.380498	-0.632813
H	-3.591516	0.973167	0.839953
H	-1.020340	-1.882838	0.988117
H	1.267947	3.953209	-0.672708
H	-0.419333	4.223320	-1.082943
H	-0.011324	3.796317	0.580904
H	1.658376	2.079485	-2.273778
H	0.482235	0.741967	-2.435169
H	0.075141	2.384082	-2.964424
H	-2.213555	-2.814125	-0.775792
H	-3.156004	-2.473463	-2.958723
H	-3.816437	-0.820660	-2.486211
H	-3.913804	-1.064061	2.149863
H	-4.819136	-1.723573	0.770568
H	-3.489326	-2.649029	1.478584
C	2.286801	-1.812151	-0.838028
H	1.464161	-2.324621	-1.329349
H	3.436376	1.569836	1.862301
N	4.488543	-0.501420	0.440972

TS from **17-T** to **17-H**

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1 1
 C   -3.517498   -1.354274   -0.756432
 C   -4.490703   -0.391342   -0.529681
 H   -3.823756   -2.383216   -0.916432
 H   -5.538605   -0.669999   -0.479554
 C   -1.061656    2.419579   -0.255310
 C   -0.690345    1.096765   -0.531408
 C   -1.885922    0.397441   -0.694271
 C   -2.979892    1.282778   -0.458825
 N   -2.421999    2.538489   -0.249929
 H   -0.441003    3.278518   -0.040188
 C   -0.926604   -1.575722    0.829088
 C    0.397381   -0.786344    0.724312
 C    0.563830    0.296426   -0.434847
 C    1.645373   -1.703901    0.702914
 C    2.949241   -0.899227    0.837573
 C    3.137379    0.205580   -0.221999
 C    1.861241    1.111784   -0.222955
 C   -1.773157   -1.183578    2.014762
 C   -0.907661   -3.061583    0.555836
 N    1.751628    1.882439    0.979759
 C    1.633605    2.495896    1.980318
 C    3.317316   -0.314667   -1.642159
 C    3.656191   -1.546318   -2.025706
 C    4.383875    1.055119    0.116392
 H    0.431233   -0.187135    1.642768
 H    0.706797   -0.258692   -1.370962
 H    1.659674   -2.288298   -0.222368
 H    1.595485   -2.417363    1.532755
 H    3.800131   -1.588202    0.804499
 H    2.980334   -0.431780    1.829581
 H    1.949811    1.826447   -1.051019
 H   -2.752754   -1.666040    2.014099
 H   -1.238076   -1.518122    2.917225
 H   -1.892388   -0.100657    2.104878
 H   -1.917509   -3.477589    0.537863
 H   -0.386410   -3.332756   -0.364899
 H   -0.376672   -3.550951    1.385185
 H    3.224309    0.453775   -2.412898
 H    3.829804   -1.775393   -3.073070
 H    3.803601   -2.366481   -1.328229
 H    4.300111    1.512811    1.106688
 H    5.275266    0.421436    0.100956
 H    4.531710    1.854629   -0.618548
 C   -2.133684   -0.989263   -0.829186
 H   -1.470793   -1.604090   -1.431704
 H   -2.945212    3.382177   -0.052912
 N   -4.240338    0.944225   -0.381862
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17-H

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1 1
 C    3.568439    1.282990   -0.209904
 C    4.501404    0.286329   -0.104118
 H    3.899904    2.315189   -0.152072
 H    5.548044    0.515732    0.063190
 C    1.052823   -2.489651   -0.519278
 C    0.708716   -1.107570   -0.591433
 C    1.900337   -0.437421   -0.532124
 C    2.977337   -1.367552   -0.397183
 N    2.389551   -2.640552   -0.428286
 H    0.404241   -3.355979   -0.506413
 C    0.968531    1.762502    0.344059
 C   -0.323561    0.845326    0.518618
 C   -0.558778   -0.304500   -0.530495
 C   -1.612265    1.682318    0.658180
 C   -2.847846    0.823830    0.971349
 C   -3.107493   -0.302126   -0.050559
 C   -1.806003   -1.158094   -0.179295
 C    1.501989    2.073714    1.758122
 C    0.689759    3.081100   -0.402051
 N   -1.538129   -1.909642    1.012729
 C   -1.270242   -2.518755    1.986708
 C   -3.460649    0.186731   -1.449341
 C   -3.903638    1.392881   -1.806289
 C   -4.274233   -1.196435    0.428997
 H   -0.171975    0.313976    1.467349
 H   -0.758959    0.141175   -1.514890
 H   -1.784505    2.245912   -0.262866
 H   -1.485961    2.417868    1.460906
 H   -3.732151    1.466975    1.037175
 H   -2.733927    0.366654    1.962247
 H   -1.960516   -1.891604   -0.982155
 H    2.321669    2.798953    1.730220
 H    0.706123    2.507853    2.372090
 H    1.856813    1.170221    2.266172
 H    1.624376    3.630728   -0.565133
 H    0.226906    2.913008   -1.381581
 H    0.032007    3.735962    0.174355
 H   -3.410937   -0.587857   -2.218349
 H   -4.198824    1.597087   -2.831392
 H   -4.017005    2.214676   -1.104692
 H   -4.068062   -1.630920    1.411865
 H   -5.187662   -0.598916    0.498736
 H   -4.465798   -2.015195   -0.274339
 C    2.128568    1.001422   -0.494436
 H    1.982481    1.376138   -1.528447
 H    2.887964   -3.517896   -0.330671
 N    4.218090   -1.071518   -0.182795
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TS from **17-T** to **17-F**

1 1

C	2.268557	-1.941666	-0.682178
C	3.576013	-2.374584	-0.829729
C	4.639631	-1.610925	-0.294426
H	1.438681	-2.517110	-1.082624
H	3.799818	-3.299123	-1.350761
H	5.662928	-1.960081	-0.407933
N	2.823184	1.099524	1.116292
C	3.228234	-0.066948	0.497190
C	2.064280	-0.739358	0.024986
C	0.941862	0.059216	0.389729
C	0.113932	2.177386	-0.786378
C	0.733858	1.797394	-2.088200
C	0.260234	3.609792	-0.393350
C	-1.006522	1.369086	-0.184496
C	-2.361742	1.384250	-0.931863
C	-3.358118	0.507551	-0.138751
C	-2.885846	-0.932043	0.189991
C	-1.461821	-0.890542	0.863376
C	-0.494974	-0.072283	-0.030282
H	-2.225541	1.005810	-1.950371
H	-2.756957	2.403470	-1.006440
H	-4.304497	0.456328	-0.687407
H	-3.585879	1.012992	0.807558
C	-3.894263	-1.591539	1.159551
C	-2.770422	-1.838667	-1.027649
N	-1.493850	-0.317585	2.170577
H	-1.093455	-1.918046	0.966752
H	-1.193628	1.774157	0.817471
H	-0.525089	-0.564777	-1.009374
C	-3.252705	-1.635273	-2.254678
C	-1.482472	0.219062	3.220959
H	0.635419	0.741831	-2.341035
H	0.230228	2.383048	-2.875680
H	1.789522	2.087299	-2.127006
H	1.270376	3.992478	-0.566734
H	-0.407219	4.189964	-1.055000
H	-0.052905	3.812961	0.633174
H	-3.590975	-2.614272	1.410125
H	-3.980628	-1.024501	2.091228
H	-4.880813	-1.642844	0.689828
H	-2.289309	-2.797262	-0.820201
H	-3.164940	-2.399847	-3.021075
H	-3.776274	-0.728924	-2.546081
C	1.457045	1.187368	1.063295
H	0.935944	1.898941	1.685868
H	3.446615	1.716657	1.620351
N	4.489239	-0.455198	0.359243

17-F

1 1

C	2.350018	-2.200262	-0.385221
C	3.665097	-2.532372	-0.570828
C	4.689396	-1.549206	-0.356706
H	1.552952	-2.924980	-0.517246
H	3.959253	-3.534707	-0.861659
H	5.729511	-1.844833	-0.480801
N	2.774153	1.286791	0.433979
C	3.200200	0.046657	0.151412
C	2.069459	-0.858280	0.015767
C	0.936755	-0.110565	0.260906
C	0.315796	2.194458	-0.150718
C	0.658033	2.284759	-1.645748
C	0.236731	3.596198	0.464707
C	-0.953776	1.329613	0.157283
C	-2.289143	1.578678	-0.539192
C	-3.328121	0.578791	0.024938
C	-2.926434	-0.921363	-0.005884
C	-1.492559	-1.126596	0.621346
C	-0.516897	-0.141620	-0.067806
H	-2.181694	1.464839	-1.623447
H	-2.644918	2.598890	-0.355137
H	-4.280945	0.694344	-0.501922
H	-3.529765	0.847464	1.069397
C	-3.955922	-1.744379	0.802851
C	-2.868340	-1.517235	-1.405356
N	-1.463041	-0.921717	2.032922
H	-1.182466	-2.162553	0.438603
H	-1.130342	1.443988	1.236953
H	-0.588959	-0.382886	-1.140326
C	-3.311285	-0.985930	-2.546612
C	-1.413258	-0.715225	3.193674
H	0.728677	1.306408	-2.133423
H	-0.112149	2.859923	-2.168636
H	1.610785	2.802054	-1.798142
H	1.175833	4.145852	0.333082
H	-0.548683	4.180499	-0.025847
H	0.007367	3.558001	1.535876
H	-3.707068	-2.811793	0.796473
H	-4.002248	-1.411333	1.843891
H	-4.948682	-1.631532	0.357813
H	-2.471274	-2.534757	-1.437041
H	-3.272252	-1.549504	-3.474308
H	-3.752090	0.004634	-2.609406
C	1.340513	1.275105	0.632059
H	1.131612	1.426386	1.706037
H	3.405384	2.033407	0.701245
N	4.490969	-0.288668	-0.009368

18-T

```
1 1
 C    3.699222   -1.696206   -0.369834
 C    4.630212   -0.810195    0.207259
 H    5.685673   -1.068129    0.199486
 C    1.031869    1.666507    1.085804
 C    0.706467    0.478806    0.409821
 C    1.947559   -0.215508    0.210682
 C    2.974498    0.596699    0.759305
 N    2.375680    1.734975    1.281971
 H    0.375357    2.406471    1.519906
 C   -0.423981    2.080403   -1.312766
 C   -1.410676    1.294147   -0.506775
 C   -0.673880    0.039591   -0.006316
 C   -2.722080    0.898878   -1.239765
 C   -3.593136    0.077095   -0.264180
 C   -2.904373   -1.148022    0.387982
 C   -1.542217   -0.705406    1.041074
 C   -0.376231    3.558510   -1.180365
 C    0.249106    1.495879   -2.499914
 N   -1.735252    0.138994    2.176199
 C   -1.860809    0.899777    3.068608
 C   -2.582354   -2.270395   -0.589221
 C   -3.046339   -2.441334   -1.828243
 C   -3.832001   -1.737489    1.475902
 H   -1.694275    1.902274    0.359687
 H   -0.574691   -0.659904   -0.843617
 H   -2.480647    0.318628   -2.136129
 H   -3.272492    1.791333   -1.557459
 H   -4.494917   -0.254679   -0.789851
 H   -3.938561    0.740457    0.537809
 H   -1.010037   -1.599946    1.386215
 H    0.598246    3.976560   -1.449981
 H   -1.095118    3.958973   -1.919855
 H   -0.696028    3.918859   -0.200968
 H    1.262946    1.890676   -2.624041
 H    0.267124    0.406537   -2.516399
 H   -0.314811    1.836028   -3.386896
 H   -1.947090   -3.053288   -0.168884
 H   -2.795652   -3.330922   -2.398673
 H   -3.712131   -1.735713   -2.317763
 H   -4.056050   -0.999289    2.251770
 H   -4.772709   -2.064759    1.023643
 H   -3.372899   -2.608466    1.956781
 C    2.342064   -1.423858   -0.389493
 H    1.648948   -2.129491   -0.836501
 H    2.875624    2.462210    1.776806
 N    4.275884    0.346694    0.770884
 F    4.158055   -2.830703   -0.913983
```

TS from **18-T** to **18-H**

```
1 1
 C   -3.457807   -0.912159   -0.577348
 C   -4.348823    0.137622   -0.371103
 H   -5.410401   -0.067117   -0.274102
 C   -0.642764    2.595261   -0.327166
 C   -0.410646    1.230549   -0.548965
 C   -1.676010    0.649295   -0.658326
 C   -2.667098    1.644260   -0.439808
 N   -1.984099    2.845633   -0.299370
 H    0.063358    3.397316   -0.163807
 C   -0.831468   -1.347903    0.994099
 C    0.536851   -0.674838    0.804974
 C    0.762613    0.318387   -0.429283
 C    1.700268   -1.700632    0.811901
 C    3.073485   -1.010988    0.862512
 C    3.325213    0.001180   -0.273221
 C    2.136439    1.018785   -0.298232
 C   -1.626994   -0.818265    2.156199
 C   -0.972398   -2.829670    0.762350
 N    2.135135    1.864206    0.858075
 C    2.108949    2.539840    1.824675
 C    3.409903   -0.622817   -1.660059
 C    3.627516   -1.901736   -1.969856
 C    4.653580    0.752513   -0.026277
 H    0.646550   -0.021729    1.679662
 H    0.826779   -0.306606   -1.329058
 H    1.635171   -2.337502   -0.075408
 H    1.609527   -2.355721    1.685472
 H    3.857068   -1.776309    0.853579
 H    3.177356   -0.486332    1.820253
 H    2.263328    1.672226   -1.170616
 H   -2.635154   -1.235074    2.208905
 H   -1.095679   -1.124578    3.071568
 H   -1.668862    0.274174    2.172612
 H   -2.021245   -3.132432    0.725813
 H   -0.461158   -3.184358   -0.134970
 H   -0.518216   -3.345980    1.621856
 H    3.357450    0.099914   -2.477402
 H    3.744492   -2.212097   -3.004040
 H    3.727770   -2.685315   -1.223582
 H    4.644483    1.278347    0.933190
 H    5.483238    0.039767   -0.023817
 H    4.848258    1.486241   -0.816778
 C   -2.057331   -0.712063   -0.717925
 H   -1.489735   -1.442093   -1.285187
 H   -2.417793    3.745291   -0.135479
 N   -3.956853    1.432917   -0.308552
 F   -3.931859   -2.157673   -0.658286
```

18-H

```
1 1
 C   -3.472545   -0.805093   -0.207157
 C   -4.321594    0.270726   -0.084723
 H   -5.380053    0.110245    0.089489
 C   -0.605843    2.677296   -0.520961
 C   -0.402696    1.266810   -0.597509
 C   -1.656669    0.720744   -0.538935
 C   -2.629728    1.748396   -0.392228
 N   -1.920898    2.955628   -0.420486
 H    0.124700    3.475309   -0.512078
 C   -0.945575   -1.550362    0.385377
 C    0.432681   -0.762523    0.538579
 C    0.777041    0.340531   -0.530933
 C    1.630564   -1.724462    0.686795
 C    2.949888   -0.991260    0.976527
 C    3.314961    0.084921   -0.066459
 C    2.106963    1.067627   -0.199208
 C   -1.518155   -1.758018    1.802383
 C   -0.803133   -2.912902   -0.320654
 N    1.926644    1.857171    0.984616
 C    1.732022    2.500806    1.953793
 C    3.602980   -0.460170   -1.459327
 C    3.915772   -1.711345   -1.798772
 C    4.571602    0.862104    0.389379
 H    0.341434   -0.203438    1.478680
 H    0.924716   -0.138929   -1.508679
 H    1.737087   -2.319633   -0.224155
 H    1.435697   -2.427760    1.504527
 H    3.763729   -1.720999    1.047763
 H    2.891953   -0.508472    1.960051
 H    2.328537    1.771040   -1.013130
 H   -2.415545   -2.383271    1.788332
 H   -0.778275   -2.264767    2.430306
 H   -1.761972   -0.804793    2.285207
 H   -1.788747   -3.367288   -0.462096
 H   -0.329599   -2.820933   -1.305282
 H   -0.208028   -3.608101    0.275874
 H    3.626567    0.302962   -2.240922
 H    4.179094   -1.961745   -2.822301
 H    3.950202   -2.528825   -1.083910
 H    4.420122    1.331214    1.366262
 H    5.419412    0.175020    0.462487
 H    4.839795    1.645368   -0.329145
 C   -2.013858   -0.697620   -0.495189
 H   -1.902211   -1.108276   -1.516711
 H   -2.331309    3.877225   -0.320476
 N   -3.897247    1.574376   -0.162677
 F   -3.981652   -2.025402   -0.142770
```

TS from **18-T** to **18-F**

```
1 1
 C    2.336138   -1.549912   -0.257633
 C    3.695698   -1.773875   -0.310799
 C    4.632371   -0.793310    0.095680
 H    1.636959   -2.318847   -0.569441
 H    5.693111   -1.024566    0.041200
 N    2.379105    1.799527    1.010547
 C    2.971523    0.621988    0.605288
 C    1.939155   -0.291953    0.243480
 C    0.700268    0.372288    0.457105
 C   -0.334813    2.195753   -0.998964
 C    0.403918    1.754284   -2.218622
 C   -0.435227    3.674334   -0.807652
 C   -1.370514    1.311533   -0.347491
 C   -2.669327    1.043939   -1.143227
 C   -3.583382    0.142589   -0.280919
 C   -2.943015   -1.163466    0.256156
 C   -1.576253   -0.840013    0.971235
 C   -0.680790   -0.014981    0.011838
 H   -2.426029    0.564218   -2.097094
 H   -3.193083    1.980044   -1.366673
 H   -4.480883   -0.110438   -0.855054
 H   -3.931513    0.726885    0.579474
 C   -3.907259   -1.826691    1.267229
 C   -2.640389   -2.193929   -0.823027
 N   -1.753977   -0.115880    2.188517
 H   -1.081751   -1.785481    1.223486
 H   -1.668661    1.803383    0.586583
 H   -0.593159   -0.626430   -0.894306
 C   -3.071075   -2.215626   -2.085429
 C   -1.870664    0.545732    3.158185
 H    0.475463    0.672620   -2.332814
 H   -0.136923    2.152172   -3.093233
 H    1.406286    2.194233   -2.258672
 H    0.511281    4.188531   -0.998501
 H   -1.147179    4.044488   -1.565932
 H   -0.832260    3.959741    0.169255
 H   -3.485772   -2.757113    1.663938
 H   -4.119494   -1.162617    2.110429
 H   -4.850784   -2.073650    0.771967
 H   -2.053386   -3.044517   -0.468937
 H   -2.840240   -3.052733   -2.737792
 H   -3.688669   -1.433176   -2.517652
 C    1.015469    1.667225    0.931192
 H    0.376847    2.362569    1.455149
 H    2.884930    2.571483    1.425194
 N    4.282532    0.409914    0.543327
 F    4.168923   -2.942352   -0.756563
```

18-F

```
1 1
 C    2.455762   -1.675270   -0.154093
 C    3.810081   -1.780138   -0.287215
 C    4.676843   -0.645182   -0.126317
 H    1.809672   -2.540520   -0.252763
 H    5.749549   -0.808692   -0.214454
 N    2.306073    1.885053    0.425455
 C    2.929248    0.713033    0.239956
 C    1.964201   -0.369795    0.147402
 C    0.719334    0.202507    0.316568
 C   -0.245247    2.344289   -0.276003
 C    0.126885    2.385296   -1.765989
 C   -0.564604    3.753923    0.234306
 C   -1.370122    1.309346    0.068095
 C   -2.705881    1.293114   -0.670821
 C   -3.590021    0.180100   -0.056468
 C   -2.954448   -1.234560    0.029912
 C   -1.527095   -1.163276    0.699835
 C   -0.698438   -0.084609   -0.040521
 H   -2.548610    1.124575   -1.741759
 H   -3.224485    2.253130   -0.567535
 H   -4.531917    0.104883   -0.609578
 H   -3.864747    0.483866    0.961353
 C   -3.865190   -2.155066    0.875284
 C   -2.757499   -1.907800   -1.320953
 N   -1.574888   -0.857959    2.092513
 H   -1.051203   -2.146300    0.600306
 H   -1.596195    1.467293    1.132924
 H   -0.697550   -0.408625   -1.093641
 C   -3.242350   -1.533834   -2.506788
 C   -1.594183   -0.563969    3.235198
 H    0.368425    1.399960   -2.179140
 H   -0.708246    2.790717   -2.345219
 H    0.988630    3.038714   -1.936356
 H    0.279987    4.436224    0.084327
 H   -1.414952    4.170507   -0.315434
 H   -0.821690    3.752777    1.299816
 H   -3.449526   -3.166320    0.951859
 H   -3.997263   -1.763090    1.888078
 H   -4.848458   -2.234415    0.402823
 H   -2.203348   -2.848191   -1.270368
 H   -3.084687   -2.146053   -3.390003
 H   -3.832775   -0.633696   -2.650499
 C    0.887083    1.656270    0.593819
 H    0.624079    1.849089    1.649004
 H    2.802816    2.738861    0.653357
 N    4.265151    0.579692    0.127557
 F    4.394667   -2.945386   -0.554114
```

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