Applying Molecular Networking for Targeted Isolation of Depsipeptides

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Supporting Information List

Table S1. HRESIMS data of the compounds 1-10

Compounds	formula	det. *m/z*	calc. *m/z*	Δ Error (ppm)
Neoantimycin L (1)	$H^+C_{37}H_{46}N_2O_{12}$	711.3106	711.3129	3.23
Unantimycin B1 (2)	$H^+C_{35}H_{43}NO_{11}$	654.2924	654.2914	1.53
Unantimycin B2 (3)	$H^+C_{35}H_{43}NO_{11}$	654.2925	654.2914	1.68
Unantimycin D1 (4)	$H^+C_{34}H_{41}NO_{11}$	640.2747	640.2758	1.72
Unantimycin D2 (5)	$H^+C_{34}H_{41}NO_{11}$	640.2743	640.2758	2.34
Neoantimycin G (6)	$H^+C_{37}H_{48}N_2O_{12}$	713.3262	713.3286	3.36
Unantimycin C1 (7)	$H^+C_{35}H_{45}NO_{11}$	656.3067	656.3071	0.63
Unantimycin C2 (8)	$H^+C_{35}H_{45}NO_{11}$	656.3069	656.3071	0.24
Unantimycin E1 (9)	$H^+C_{34}H_{43}NO_{11}$	642.2906	642.2914	1.25
Unantimycin E2 (10)	$H^+C_{34}H_{43}NO_{11}$	642.2905	642.2914	1.40

Table S2. NMR (600 MHz, DMSO-d_6) data for Neoantimycin L (1)

	δ_C	δ_H	HMBC	COSY	ROESY
1	202.6				
2	76.7	5.67, dd (7.6, 5.6)	1, 3, 12, 13	12a, 12b	14/18, 33
3	167.0				
4	75.4	5.10, d (5.2)	3, 5, 19, 20, 21	19	20, 21
5	168.0				
6	55.4	5.04, br s			29
7	70.8	5.59, m	5, 8	6, 29	
8	167.7				
9	75.6	4.83, d (7.6)	8, 10, 30, 31, 32	30	31, 32
10	170.9				
11	54.1				
12	37.1	3.16, dd (14.2, 5.6) 3.07, dd (14.2, 7.7)	1, 2, 13, 14/18	2	14/18
13	135.4				
14/18	129.6	7.20, overlapped	12, 16	15/17	2, 12, 34
15/17	128.3	7.30, t (7.5)	13	14/18, 16	
16	126.9	7.25, overlapped		15/17	
19	36.4	1.79, m	3, 4, 20, 21	4, 20, 21	
20	14.2	0.77, overlapped	4, 19, 21	19	4
21	23.7	1.03, m	19, 20	19, 35	4
22	169.6				
23	114.8				
24	n.o.[a]				
25	128.3				
26	n.o.[a]	8.14, m	28	27	
27	n.o.[a]	6.57, br s		26, 28	
28	123.6	7.69, br s		27	
29	15.7	1.23, d (6.6)	6, 7	7	6, 36
30	35.7	1.88, m		9, 31, 32	
31	14.1	0.86, d (7.8)	9, 30, 32	30	
32	24.0	1.43, m 1.14, m	9, 30	30, 36	
33	21.3	1.34, s	1, 10, 11, 34		2
34	21.2	1.21, s	1, 10, 11, 33		
35	11.1	0.77 overlapped	19, 21	21	
36	10.5	0.84, t (7.6)	30, 32	32	29
25-NH		9.70 br s		CHO	
CHO	159.8	8.31, d (2.0)		25-NH	

[a] Carbon resonances are not observed due to signal broadening

Table S3. NMR (600 MHz, DMSO-d_6) data for Unantimycin B1 (2)

	δ_C	δ_H	HMBC	COSY	ROESY
1	202.4				
2	76.4	5.40, dd (10.0, 2.6)	3, 12, 13	12a, 12b	14/18, 33
3	168.09				
4	75.5	5.02, d (3.0)	3, 5, 19, 20, 21	19	20, 21
5	168.5				
6	55.4	5.16, dd (9.2, 2.9)	5, 7, 22	7, 6-NH	29
7	70.3	5.67, qd (6.4, 3.0)	5, 8, 29	6, 29	6-NH
8	167.7				
9	75.5	5.21, d (8.2)	8, 10, 30, 31, 32	30	31, 32
10	170.8				
11	55.0				
12	36.6	3.16, m 2.92, m	1, 2, 13, 14/18	2	33, 14/18 14/18
13	136.2				
14/18	129.2	7.28, overlapped	12, 16	15/17	2, 12
15/17	128.5	7.33, overlapped	13	14/18, 16	
16	126.9	7.25, m	14/18	15/17	
19	29.7	2.24, m	3, 4, 20, 21	4, 20, 21	
20	16.1	0.79, d (6.9)	4, 19, 21	19	
21	18.3	0.91, d (6.9)	4, 19, 20	19	
22	167.9				
23	135.2				
24	114.8	7.28, overlapped	26, 28		
25	157.2				
26	118.5	6.94, dd (8.1, 2.4)	24, 28	27	
27	129.2	7.28, overlapped	23, 25	26, 28	
28	118.5	7.35, overlapped	22, 24, 26	27	
29	16.1	1.21, d (6.5)	6, 7	7	35
30	36.7	1.81, m	8, 9, 31, 32	31, 32	
31	13.8	0.87, d (6.8)	9, 30, 32	30	
32	24.0	1.45, m 1.06, m	9, 30, 31	30	
33	21.3	1.41, s	1, 10, 11, 34		2, 12a
34	20.7	1.32, s	1, 10, 11, 33		
35	10.6	0.87, t (6.8)	30, 32		
6-NH		8.72, d (9.2)	5, 7, 22	6	
25-OH		9.66, s			

Table S4. NMR (600 MHz, DMSO-d_6) data for Unantimycin B2 (3)

	δ_C	δ_H	HMBC	COSY	ROESY
1	202.6				
2	76.4	5.68, dd (7.7, 5.6)	1, 3, 12, 13	12	14/18, 33
3	167.2				
4	75.9	5.05, d (5.4)	3, 19, 20, 21	19	20, 21
5	168.2				
6	55.9	4.95, dd (8.4, 3.1)	5	7, 6-NH	29
7	70.6	5.55, m	5, 8	6, 29	
8	167.7				
9	75.6	4.86, d (7.7)	10, 30, 31, 32	30	31, 32
10	171.0				
11	54.2				
12	37.1	3.16, dd (14.1, 7.8) 3.06, dd (14.1, 7.8)	1, 2, 13, 14/18	2	33, 34 34
13	135.4				
14/18	129.6	7.20, overlapped	12, 16	15/17	2, 12
15/17	128.4	7.28, overlapped	13	14/18, 16	
16	127.0	7.25, m	14/18	15/17	
19	30.0	2.01, m	3, 4, 20, 21	4, 20, 21	
20	16.8	0.69, d (6.8)	4, 19, 21	19	4
21	17.9	0.83, overlapped	4, 19, 20	19	4
22	167.8				
23	135.0				
24	114.7	7.28, overlapped	26, 28		
25	157.2				
26	118.5	6.95, dd (7.6, 1.8)	24, 28	27	
27	129.2	7.28, overlapped	23, 25	26, 28	
28	118.5	7.34, br d (7.8)	22, 24, 26	27	
29	15.6	1.23, d (6.3)	6, 7	7	6, 31
30	35.7	1.88, qd (7.6, 3.6)		9, 31	
31	14.0	0.86, d (6.9)	9, 30, 32	30	
32	24.0	1.43, m 1.13, m	9, 30, 31, 35	30, 35	
33	21.1	1.34, s	1, 10, 11, 34		
34	21.3	1.20, s	1, 10, 11, 33		
35	10.4	0.83, overlapped	32, 30	32	
6-NH		8.67, d (8.3)	22	6	
25-OH		9.68, s			

Table S5. NMR (600 MHz, DMSO-d_6) data for Unantimycin D1 (4)

	δ_C	δ_H	HMBC	COSY	ROESY
1	202.5				
2	76.4	5.37, dd (10.0, 2.6)	1, 3, 12, 13	12a, 12b	14/18, 33
3	168.1				
4	75.5	5.01, d (2.9)	3, 5, 19, 20, 21	19	20, 21
5	168.6				
6	55.4	5.15, overlapped	5, 7, 22, 29	7, 6-NH	29
7	70.2	5.66, qd (6.4, 4.0)	5, 8, 29	6, 29	6-NH
8	167.7				
9	76.8	5.15, overlapped	8, 10, 30, 31, 32	30	31, 32
10	170.9				
11	55.2				
12	36.6	3.15, dd (14.9, 2.7) 2.91, dd (14.9, 2.7)	1, 2, 13, 14/18	2	33, 14/18 14/18
13	136.3				
14/18	129.3	7.28, overlapped	12, 16	15/17	2, 12
15/17	128.6	7.34, overlapped	13	14/18, 16	
16	127.0	7.25, m	14/18	15/17	
19	29.7	2.25, m	3, 4, 20, 21	4, 20, 21	
20	16.1	0.80, d (6.9)	4, 19, 21	19	
21	18.3[a]	0.92, d (6.9)	4, 19, 20	19	
22	168.0				
23	135.2				
24	114.8	7.28, overlapped	25, 26, 28		
25	157.2				
26	118.5	6.94, ddd (8.0, 2.5, 1.1)	24, 25, 28	27	
27	129.3	7.28, overlapped	23, 25	26, 28	
28	118.5	7.35, overlapped	22, 24, 26	27	
29	16.2	1.21, d (6.4)	6, 7	7	
30	30.7	1.99, m	8, 9, 31, 32	9, 31, 32	
31	17.6[a]	0.88, d (8.4)	9, 30, 32	30	
32	18.0[a]	0.90, d (8.4)	9, 30, 31	30	
33	21.3	1.43, s	1, 10, 11, 34		2, 12a
34	20.6	1.33, s	1, 10, 11, 33		
6-NH		8.70, d (9.2)	5, 7, 22	6	
25-OH		9.70, s			

[a] values are interchangeable

Table S6. NMR (600 MHz, DMSO-d_6) data for Unantimycin D2 (5)

	δ_C	δ_H	HMBC	COSY	ROESY
1	202.6				
2	76.4	5.69, dd (7.8, 5.6)	1, 3, 12, 13	12a, 12b	14/18, 33
3	167.2				
4	76.0	5.05, d (5.3)	3, 5, 19, 20, 21	19	20, 21
5	168.3				
6	55.9	4.94, dd (8.3, 3.1)	5, 7, 22	7, 6-NH	29
7	70.6	5.54, qd (6.4, 3.0)	5, 8	6, 29	6-NH
8	167.8				
9	76.7	4.80, d (7.2)	8, 10, 30, 31, 32	30	31, 32
10	171.0				
11	54.2				
12	37.2	3.15, dd (14.1, 5.6) 3.06, dd (14.0, 7.8)	1, 2, 13, 14/18	2	14/18 14/18
13	135.4				
14/18	129.6	7.20, m	12, 16	15/17	2, 12
15/17	128.4	7.28, overlapped	13	14/18, 16	
16	127.0	7.25, m	14/18	15/17	
19	30.0	2.03, overlapped	3, 4, 20, 21	4, 20, 21	
20	16.8	0.69, d (6.8)	4, 19, 21	19	
21	17.6[a]	0.82, d (6.9)	4, 19, 20	19	
22	167.6				
23	135.0				
24	114.8	7.28, overlapped	26, 28		
25	157.3				
26	118.6	6.95, ddd (8.0, 2.6, 1.1)	24, 28	27	
27	129.3	7.28, overlapped	23, 25	26, 28	
28	118.5	7.34, m	22, 24, 26	27	
29	15.7	1.23, d (6.5)	6, 7	7	
30	29.8	2.03, overlapped	8, 9, 31, 32	9, 31, 32	
31	17.7[a]	0.88, dd (6.8, 2.6)	9, 30, 32	30	
32	17.9[a]	0.88, dd (6.8, 2.6)	9, 30, 31	30	
33	21.3	1.34, s	1, 10, 11, 34		2
34	21.2	1.21, s	1, 10, 11, 33		12
6-NH		8.65, d (8.3)	5, 7, 22	6	
25-OH		9.76, br s			

Table S7a. NMR (600 MHz, DMSO-d_6) data for NAT-G (6)

	δ_C	δ_H	HMBC	COSY	ROESY
1	77.8	3.29, d (10.5)	10, 11, 12, 33	1-OH	2, 12b, 33, 34
2	71.6	5.45, dd (10.2, 4.6)	1, 3, 12, 13	12	12b, 14/18, 34
3	167.6				
4	75.7	5.34, d (3.7)	3, 5, 19, 20, 21	19	20, 21
5	167.6				
6	55.3	5.14, dd (8.7, 3.3)		7	29
7	70.7	5.56, m	5, 22	6, 29	
8	168.1				
9	74.6	4.57, d (8.3)	8, 10, 30, 31, 32	30	31, 32
10	174.8				
11	45.4				
12	39.2	3.04, dd (14.2, 10.2) 2.97, dd (14.2, 4.6)	1, 2, 13, 14/18	2	14/18 1, 14/18
13	137.5				
14/18	129.0	7.22, overlapped	12, 16	15/17	2, 12
15/17	128.3	7.28, m	13	14/18, 16	
16	126.4	7.20, overlapped	14/18	15/17	
19	36.6	1.50, m	3, 4, 20, 21	4, 20, 21	
20	14.4	0.60, overlapped	4, 19, 21	19	
21	22.9	0.8, m	19, 20	19, 35	
22	170.0				
23	114.7				
24	n.o.[a]				
25	127.4				
26	n.o.[a]	8.19, d (7.8)	24, 28	27	
27	n.o.[a]	6.81, br s		26, 28	
28	123.6	7.87, d (7.2)		27	
29	15.6	1.21, d (6.4)	6, 7	7	6, 36
30	35.4	1.85, m		9, 31, 32	
31	14.0	0.87, d (7.1)	9, 30, 32	30	
32	24.3	1.50, m 1.17, m	9, 31	30, 36	
33	26.2	1.31, s	1, 10, 11, 34		1-OH
34	22.0	1.25, s	1, 10, 11, 33		1, 2
35	11.1	0.60 overlapped	19, 21	21	
36	10.3	0.84, d (7.6)	30, 32	32	29
CHO	159.8	8.32, d (1.7)		25-NH	
1-OH		4.39, d (10.4)		1	

	δ_C	δ_H	HMBC	COSY	ROESY
24-OH		12.7, s			
25-NH		9.78 br s		CHO	

[a] Carbon resonances are not observed due to signal broadening

Table S7b. NMR (600 MHz, DMSO-d_6) data for NAT-G (6)

	Experimental δ_C (125 MHz)	Literature[a] δ_C (100 MHz)	Experimental δ_H (600 MHz)	Literature[a] δ_H (400 MHz)
1	77.8	77.9	3.29, d (10.5)	3.28, d (10.4)
2	71.6	71.6	5.45, dd (10.2, 4.6)	5.44, dd (10.2 , 4.5)
3	167.6	167.6		
4	75.7	75.8	5.34, d (3.7)	5.33, d (3.6)
5	167.6	167.5		
6	55.3	55.3	5.14, dd (8.7, 3.3)	5.15, dd (8.7, 3.1)
7	70.7	70.6	5.56, m	5.55, qd (6.5, 3.1)
8	168.1	168.1		
9	74.6	74.6	4.57, d (8.3)	4.56, d (8.3)
10	174.8	174.8		
11	45.4	45.4		
12	39.2	39.2	3.04, dd (14.2, 10.2) 2.97, dd (14.2, 4.6)	3.03, dd (14.2, 10.2) 2.95, dd (14.2, 4.5)
13	137.5	137.6		
14/18	129.0	129.0	7.22, overlapped	7.22, d (7.5)
15/17	128.3	128.3	7.28, m	7.27, dd (7.3, 7.5)
16	126.4	126.4	7.20, overlapped	7.19, t (7.3)
19	36.6	36.6	1.50, m	1.50, m
20	14.4	14.3	0.60, overlapped	0.58, d (6.8)
21	22.9	22.9	0.8, m	0.80, m
22	170.0	170.2		
23	114.7	114.5		
24	n.o.[b]	150.7		
25	127.4	127.1		
26	n.o.[b]	125.0	8.19, d (7.8)	8.20, d (7.7)
27	n.o.[b]	n.o.[b]	6.81, br s	6.90, br s
28	123.6	123.6	7.87, d (7.2)	7.92, br s
29	15.6	15.5	1.21, d (6.4)	1.20, d (6.5)
30	35.4	35.4	1.85, m	1.84, dqd (8.3, 7.0, 3.6)
31	14.0	14.0	0.87, d (7.1)	0.86, d (7.0)
32	24.3	24.3	1.50, m 1.17, m	1.49, m 1.17, m
33	26.2	26.2	1.31, s	1.30, s
34	22.0	22.0	1.25, s	1.25, s
35	11.1	11.1	0.60 overlapped	0.59, t (6.8)
36	10.3	10.2	0.84, d (7.6)	0.84, dd (7.5, 7.5)
CHO	159.8	160.4	8.32, d (1.7)	8.31, d (1.8)

1-OH	4.39, d (10.4)	4.39, d (10.4)
24-OH	12.7, s	12.8, br s
25-NH	9.78 br s	9.81, br s

[a] Salim, A. A. *et al. Org. Lett.* **2014**, *16* (19), 5036–5039.

Table S8. NMR (600 MHz, DMSO-d_6) data for Unantimycin C1 (7)

	δ_C	δ_H	HMBC	COSY	ROESY
1	75.8	3.48, overlapped	10, 11, 12, 33, 34	1-OH	33, 34
2	76.7	5.42, t (7.0)	3, 12, 13	12a, 12b	14/18, 33, 34
3	168.4[a]				
4	76.9	5.17, d (4.6)	3, 5, 19, 20, 21	19	20, 21
5	168.5 [a]				
6	55.9	5.15, dd (9.0, 3.1)	5, 7, 22	7, 6-NH	29
7	70.7	5.80, qd (6.4, 2.9)	8	6, 29	6-NH
8	170.4				
9	74.9	5.01, d (7.9)	8, 10, 30, 31, 32	30	31, 32
10	174.2				
11	45.4				
12	37.3	3.04, dd (13.6, 5.7) 2.90, dd (13.7, 8.3)	1, 2, 13, 14/18	2	33, 14/18
13	137.4				
14/18	129.3	7.29, overlapped	12, 16	15/17	2, 12
15/17	128.4	7.29, overlapped	13	14/18, 16	
16	126.4	7.20, overlapped	14/18	15/17	
19	31.5	1.99, overlapped		4, 20, 21	
20	17.0	0.67, d (7.0)	4, 19, 21	19	
21	18.2	0.67, d (7.0)	4, 19, 20	19	
22	167.6				
23	135.1				
24	114.7	7.29, overlapped	22, 26, 28		
25	157.3				
26	118.4[a]	6.96, dd (8.1, 2.4)	24, 28	27	
27	128.0	7.29, overlapped	23, 25	26, 28	
28	118.6[a]	7.36, d (7.7)	22, 24, 26	27	
29	15.9	1.28, d (6.4)	6, 7	7	35, 6-NH
30	35.8	1.93, overlapped	31, 32, 35	31, 32	
31	14.7	0.92, d (6.9)	9, 30, 32	30	
32	24.1	1.49, m 1.19, m	30, 31, 35	35 30, 35	
33	23.7	1.10, s	1, 10, 11, 34		2
34	22.6	1.32, s	1, 10, 11, 33		2, 12
35	10.9	0.88, t (7.3)	30, 32	32	
1-OH		4.85, br d (10.3)	1	1	
6-NH		8.77, d (8.9)	22	6	28, 29

[a] values are interchangeable

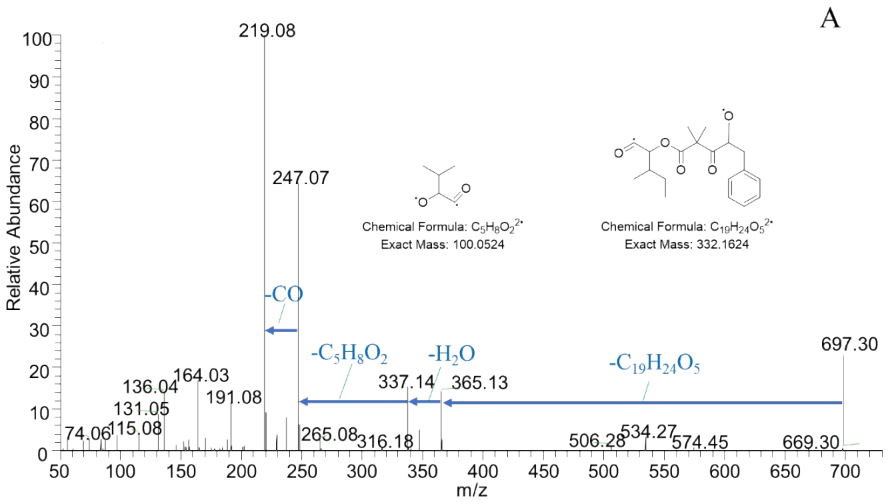
Table S9. NMR (600 MHz, DMSO-d_6) data for Unantimycin C2 (8)

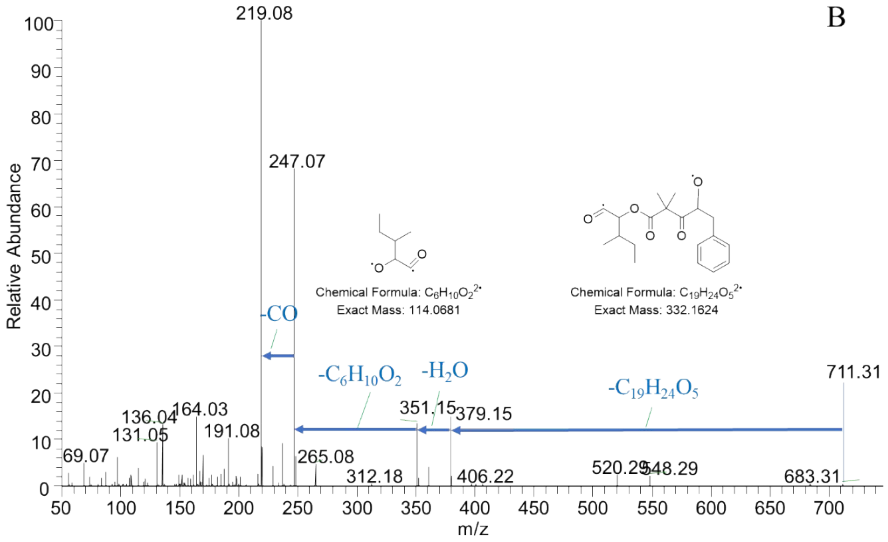
	δ_C	δ_H	HMBC	COSY	ROESY
1	77.9	3.29, d (10.6)	10, 11, 12, 33, 34	1-OH	12b, 34
2	71.8	5.38, dd (10.4, 4.4)	3, 12	12	14/18, 34
3	168.1				
4	75.4	5.29, d (3.4)	3, 5, 19, 20, 21	19	20, 21
5	167.8				
6	55.5	5.05, dd (9.1, 3.4)	5, 7, 22	7, 6-NH	29
7	71.0	5.50, qd (6.4, 3.4)	8	6, 29	
8	168.1				
9	74.4	4.57, d (8.6)	8, 10, 30, 31, 32	30	31, 32
10	174.9				
11	45.3				
12	39.2	3.04, dd (14.0, 10.4) 2.95, dd (14.0, 4.4)	1, 2, 13, 14/18	2	33, 14/18
13	137.6				
14/18	129.1	7.23, overlapped	12, 16	15/17	2, 12
15/17	128.3	7.28, overlapped	13	14/18, 16	
16	126.4	7.20, overlapped	14/18	15/17	
19	30.3	1.70, m		20, 21	
20	15.9	0.30, d (6.9)	4, 19, 21	19	
21	18.4	0.67, d (6.9)	4, 19, 20	19	
22	167.8				
23	135.2				
24	114.8	7.28, overlapped	22, 26, 28		
25	157.2				
26	118.5	6.94, ddd (8.0, 2.5, 1.0)	24, 25, 28	27	
27	129.2	7.28, overlapped	25	26, 28	
28	118.5	7.34, br d (7.7)	22, 24, 26	27	
29	15.4	1.20, d (6.4)	6, 7	7	35, 6-NH
30	35.4	1.84, m	9, 31	9, 31, 32	
31	13.9	0.86, d (6.9)	9, 30, 32	30	
32	24.2	1.49, m 1.16, m	31	30, 35	
33	26.3	1.30, s	1, 10, 11, 34		1, 1-OH
34	21.9	1.26, s	1, 10, 11, 33		1, 2
35	10.2	0.83, t (7.5)	30, 32	32	29, 32

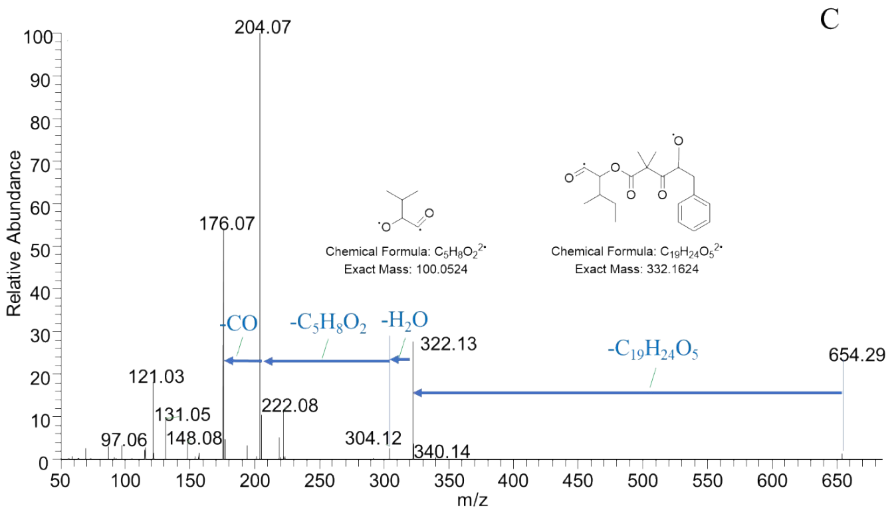
	δ_C	δ_H	HMBC	COSY	ROESY
1-OH		4.38, d (10.5)	1	1	33
6-NH		8.65, d (9.1)	5, 22	6	28, 29
25-OH		9.67 br, s			

Table S10. ^{1}H NMR (600 MHz $CDCl_3$) Data for the MTPA Esters of Bhdo

	S-MTPA ester δ_H (multiplicity, *J* = Hz)	*R*-MTPA ester δ_H (multiplicity, *J* = Hz)	$\Delta\delta$ (δ_S - δ_R) values
2-Me	1.34, s	1.33, s	+0.01
	1.12, s	1.06, s	+0.06
3	5.47, d (3.8)	5.51, d (3.7)	-0.04
4	4.83, dt (9.4, 3.8)	4.89, dt (9.4, 3.8)	-0.06
5	2.78, dd (14.7, 9.4)	2.82, dd (14.7, 9.4)	-0.04
	2.69, dd (14.9, 4.0)	2.76, dd (14.7, 3.8)	-0.07
7/11	7.13, d (6.8)	7.18, d (7.4)	-0.05
8/10	7.48, m	7.48, m	
9	7.53, m	7.53, m	


A
Relative Abundance
m/z
219.08
247.07
697.30
-CO
-C5H8O2
-H2O
-C19H24O5
Chemical Formula: C5H8O2 2+
Exact Mass: 100.0524
Chemical Formula: C19H24O5 2+
Exact Mass: 332.1624
136.04
164.03
131.05
191.08
115.08
74.06
265.08
316.18
337.14
365.13
506.28
534.27
574.45
669.30


B
Relative Abundance
m/z
219.08
247.07
711.31
-CO
-C6H10O2
-H2O
-C19H24O5
Chemical Formula: C6H10O2 2+
Exact Mass: 114.0681
Chemical Formula: C19H24O5 2+
Exact Mass: 332.1624
136.04
164.03
131.05
191.08
69.07
265.08
312.18
351.15
379.15
406.22
520.29
548.29
683.31


C
Relative Abundance
m/z
204.07
176.07
-CO
-C5H8O2
-H2O
-C19H24O5
Chemical Formula: C5H8O2 2+
Exact Mass: 100.0524
Chemical Formula: C19H24O5 2+
Exact Mass: 332.1624
121.03
131.05
97.06
148.08
222.08
304.12
322.13
340.14
654.29

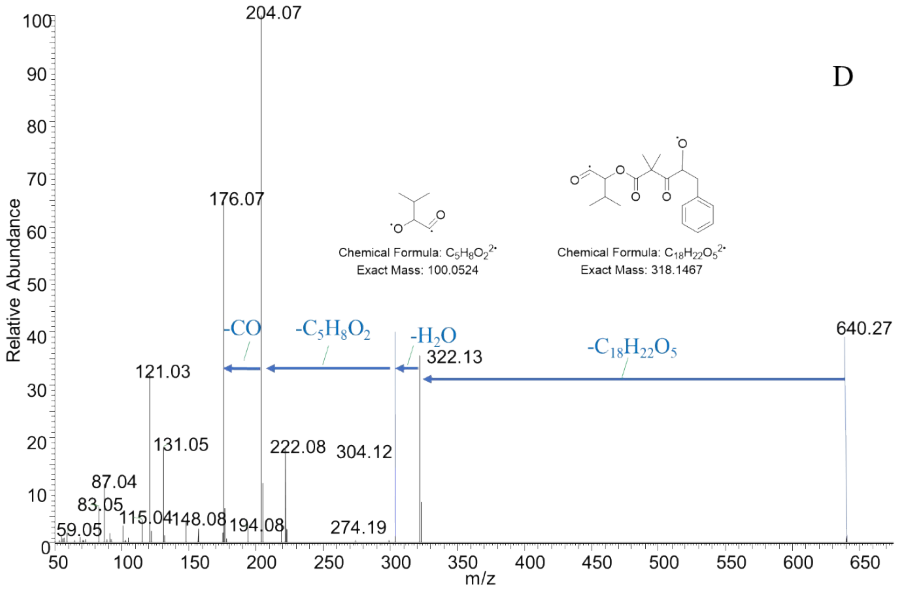


Figure S1 MS/MS spectrum of NAT-H (A), NAT-L (B), UAT-B1&B2 (C), and UAT-D1&D2 (D)

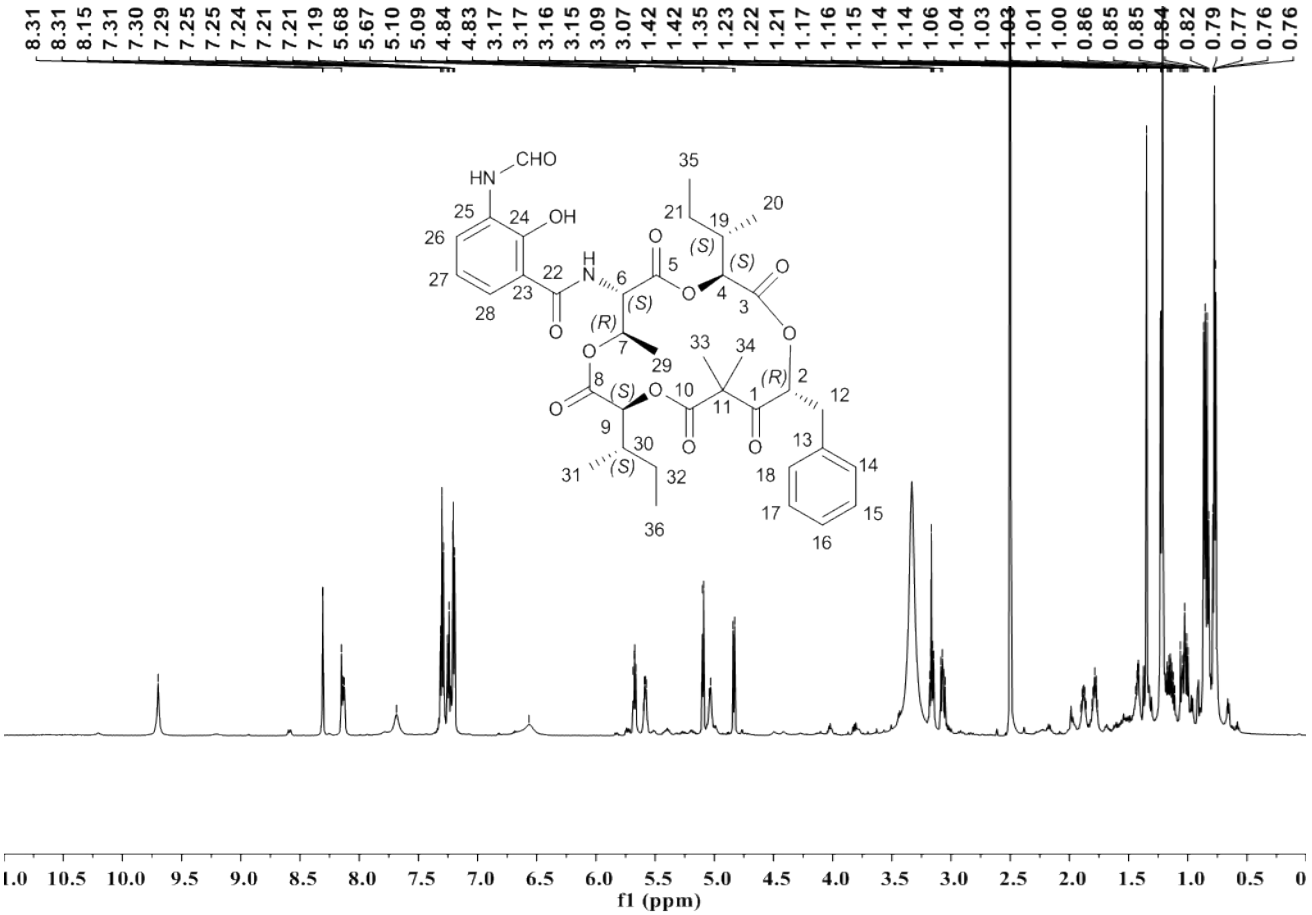


Figure S2a ^{1}H NMR spectrum of 1 in DMSO-d_6

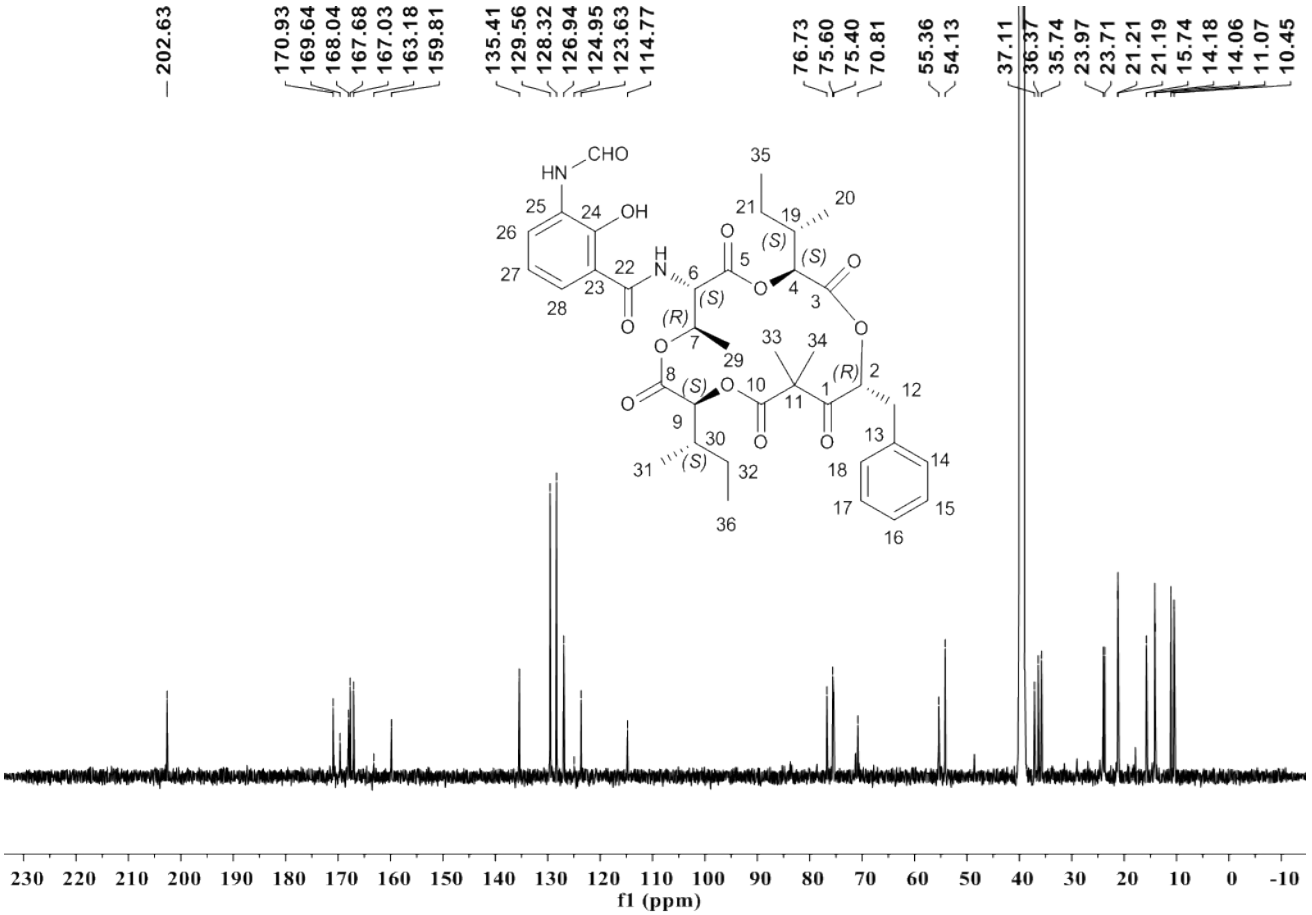


Figure S2b ^{13}C NMR spectrum of 1 in DMSO-d_6

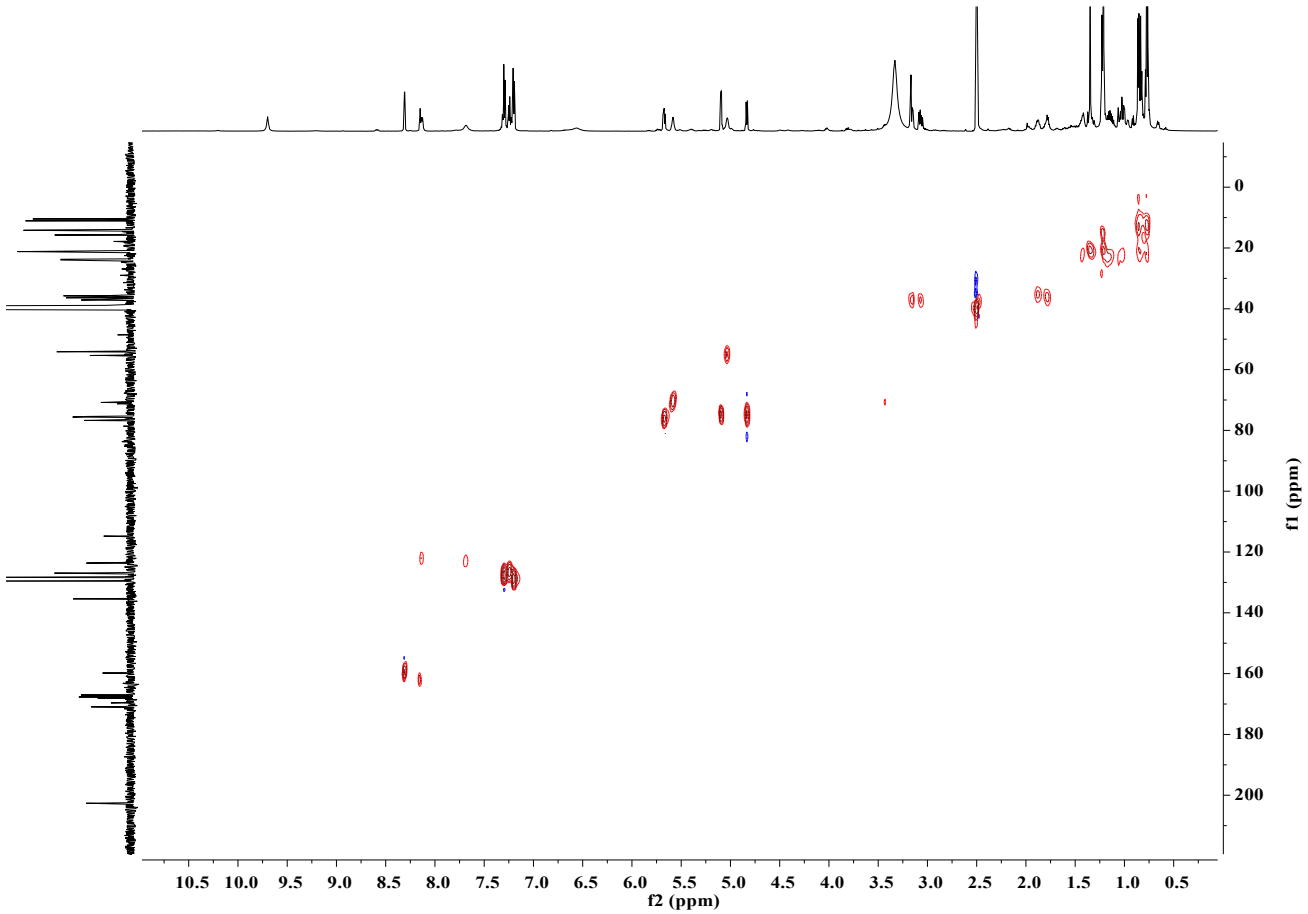


Figure S2c HSQC spectrum of 1 in DMSO-d_6

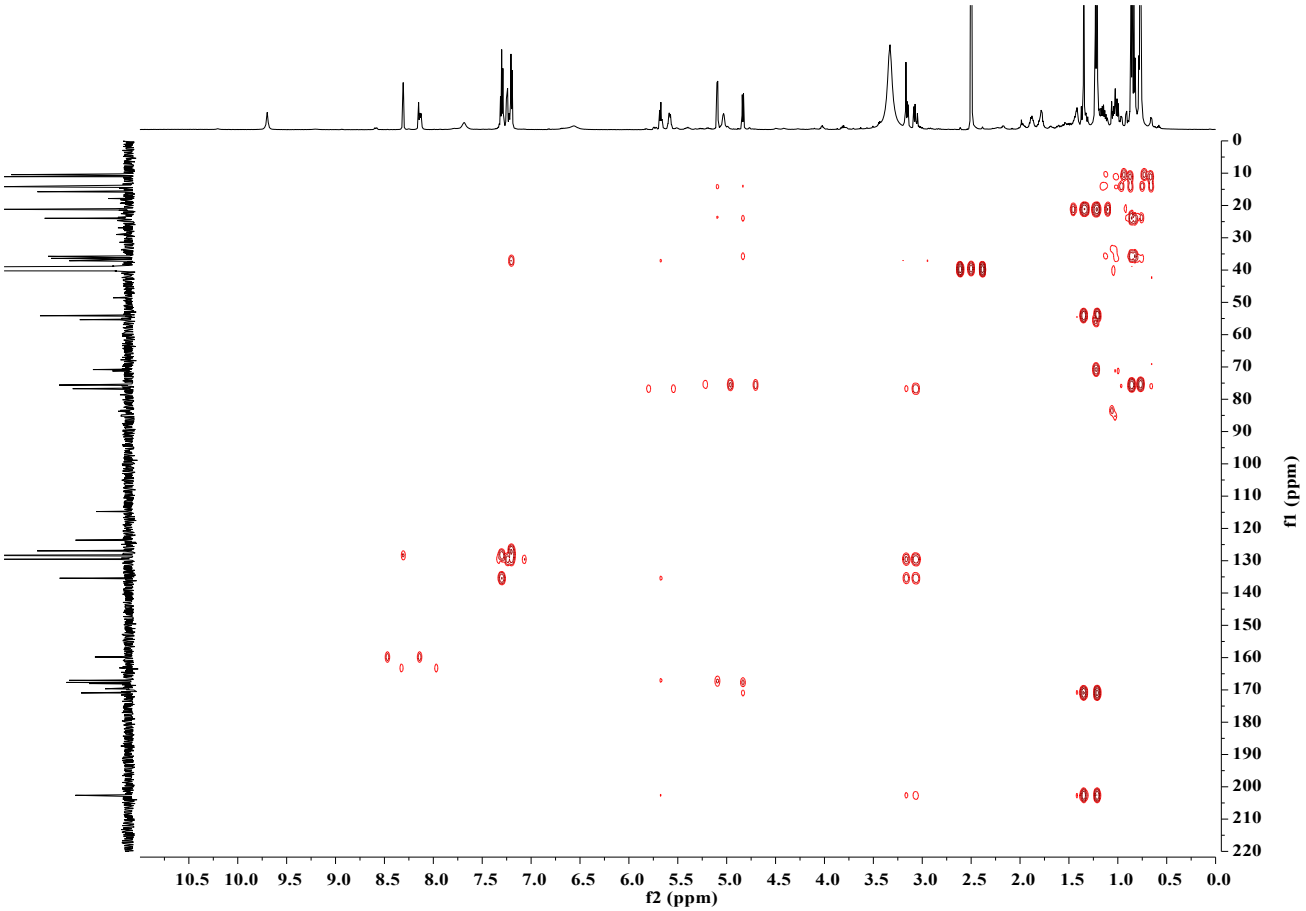


Figure S2d HMBC spectrum of 1 in DMSO-d_6

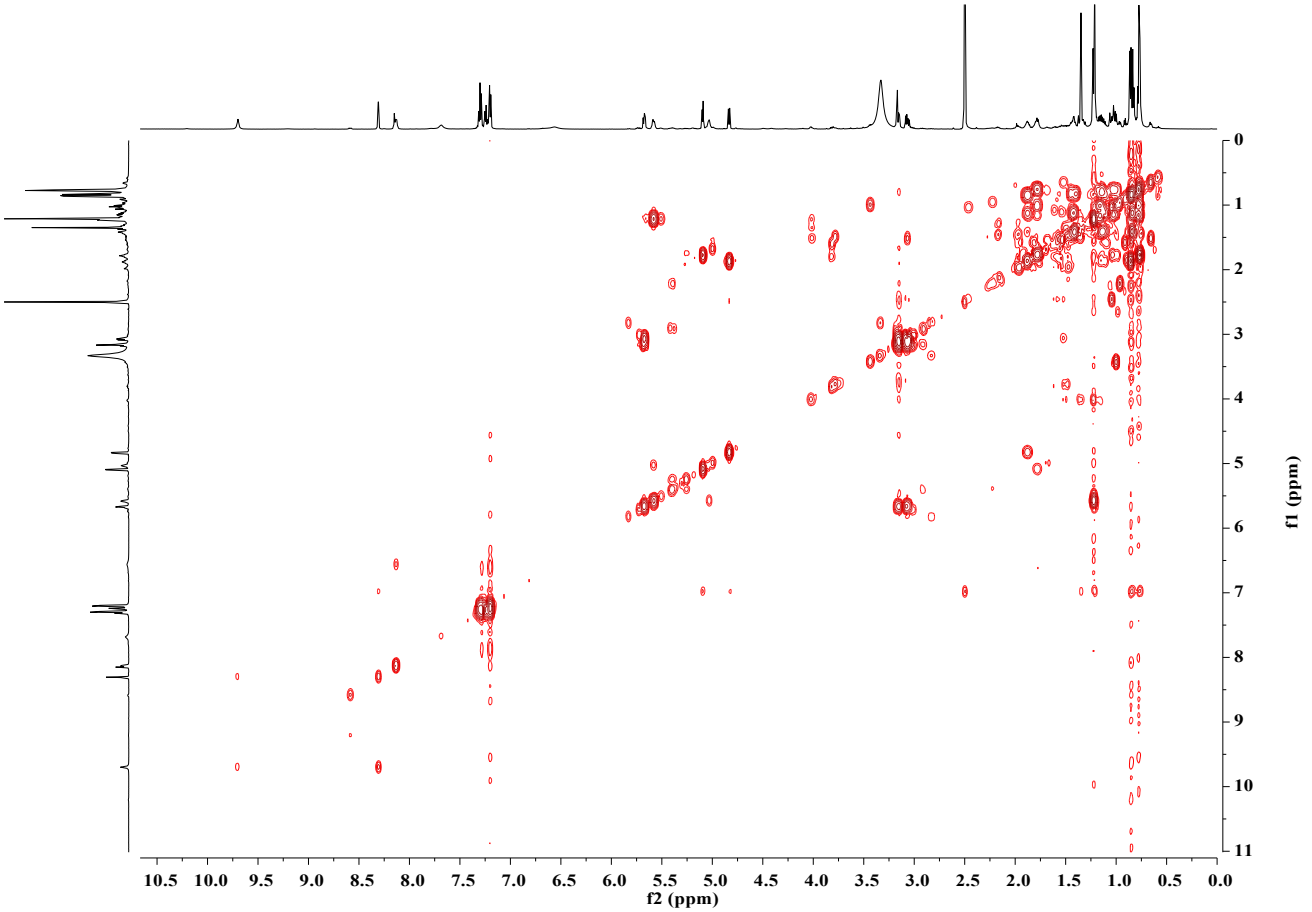


Figure S2e ^{1}H-^{1}H COSY spectrum of 1 in DMSO-d_6

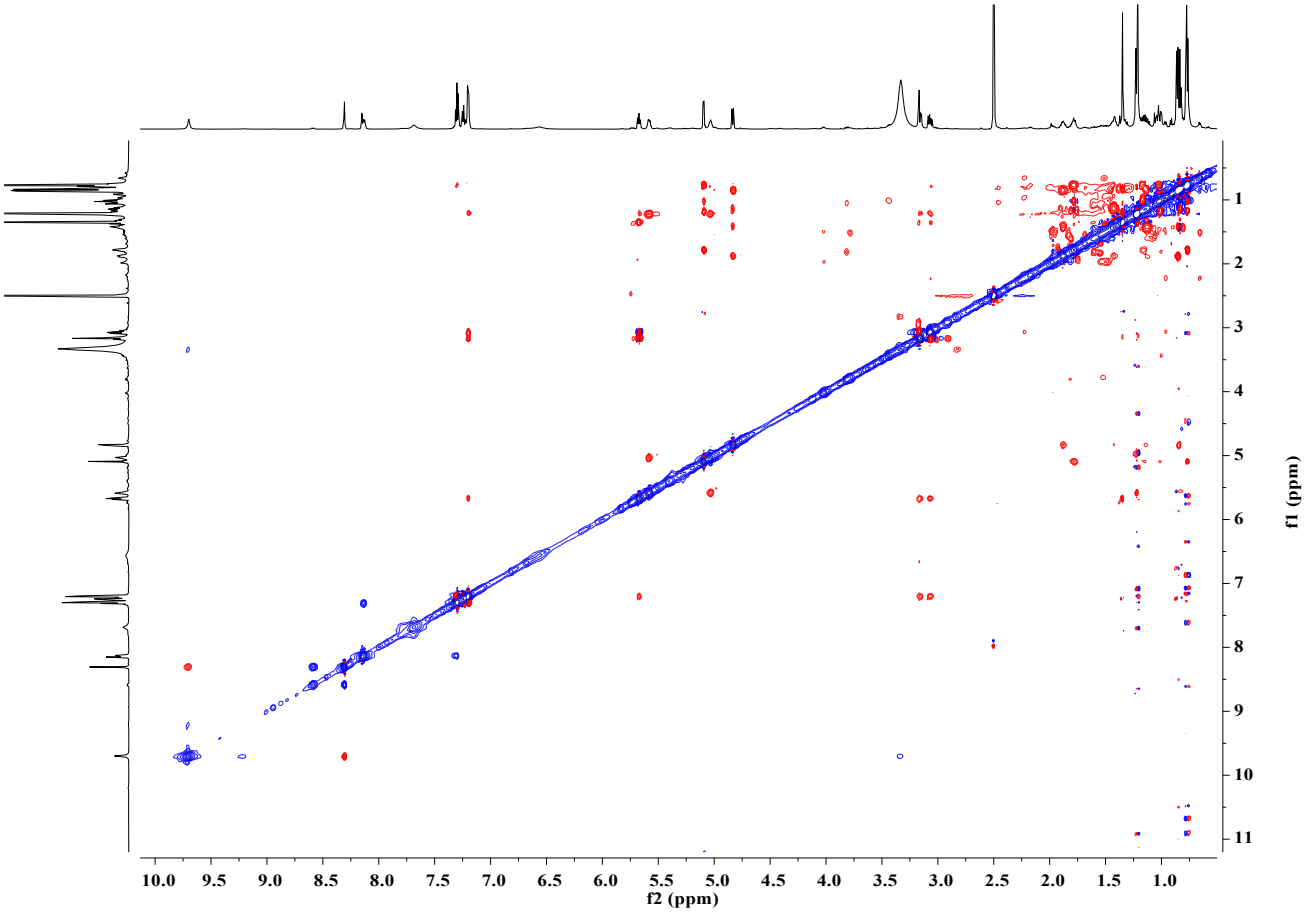


Figure S2f ROESY spectrum of 1 in DMSO-d_6

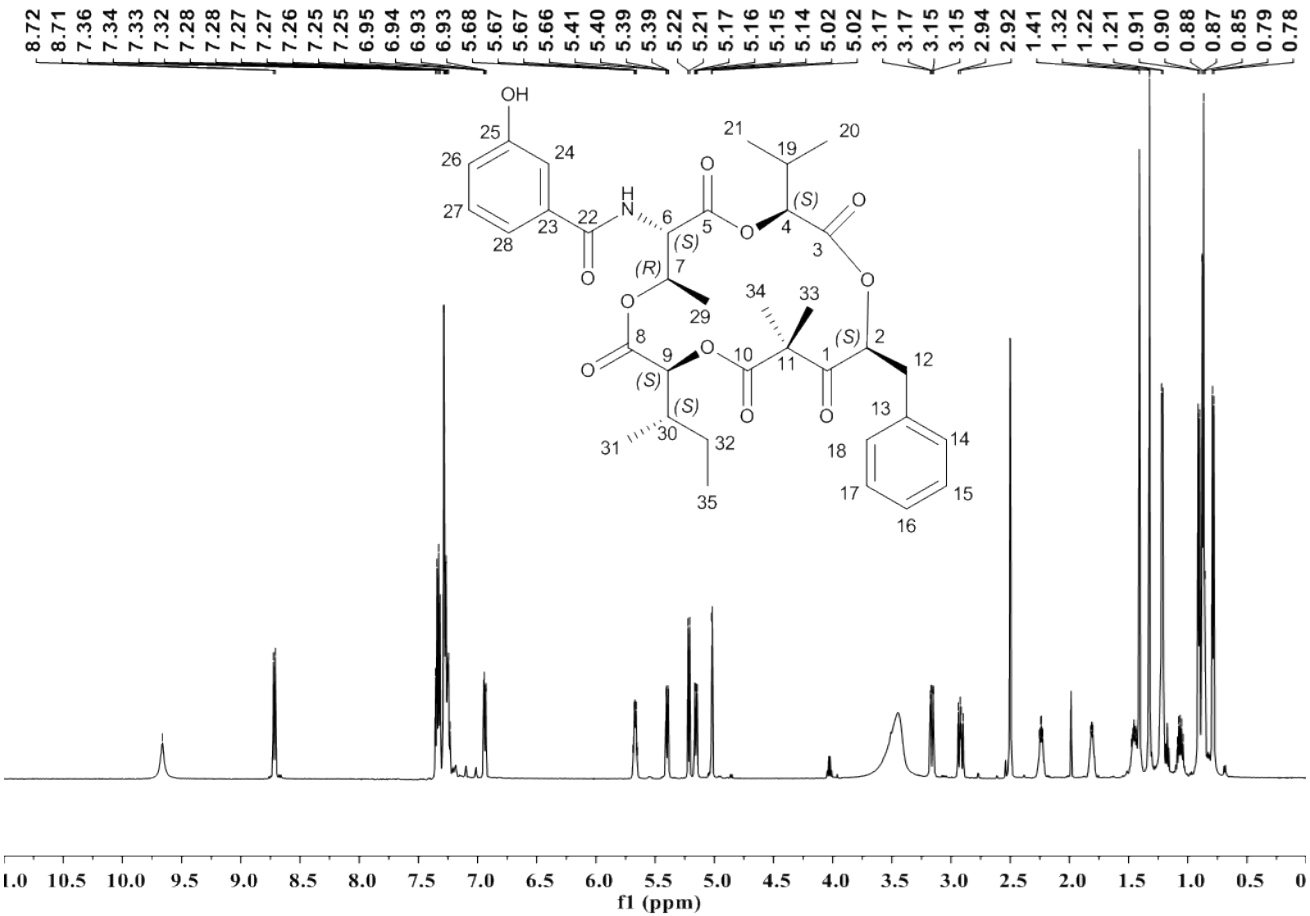


Figure S3a ^{1}H NMR spectrum of 2 in DMSO-d_6

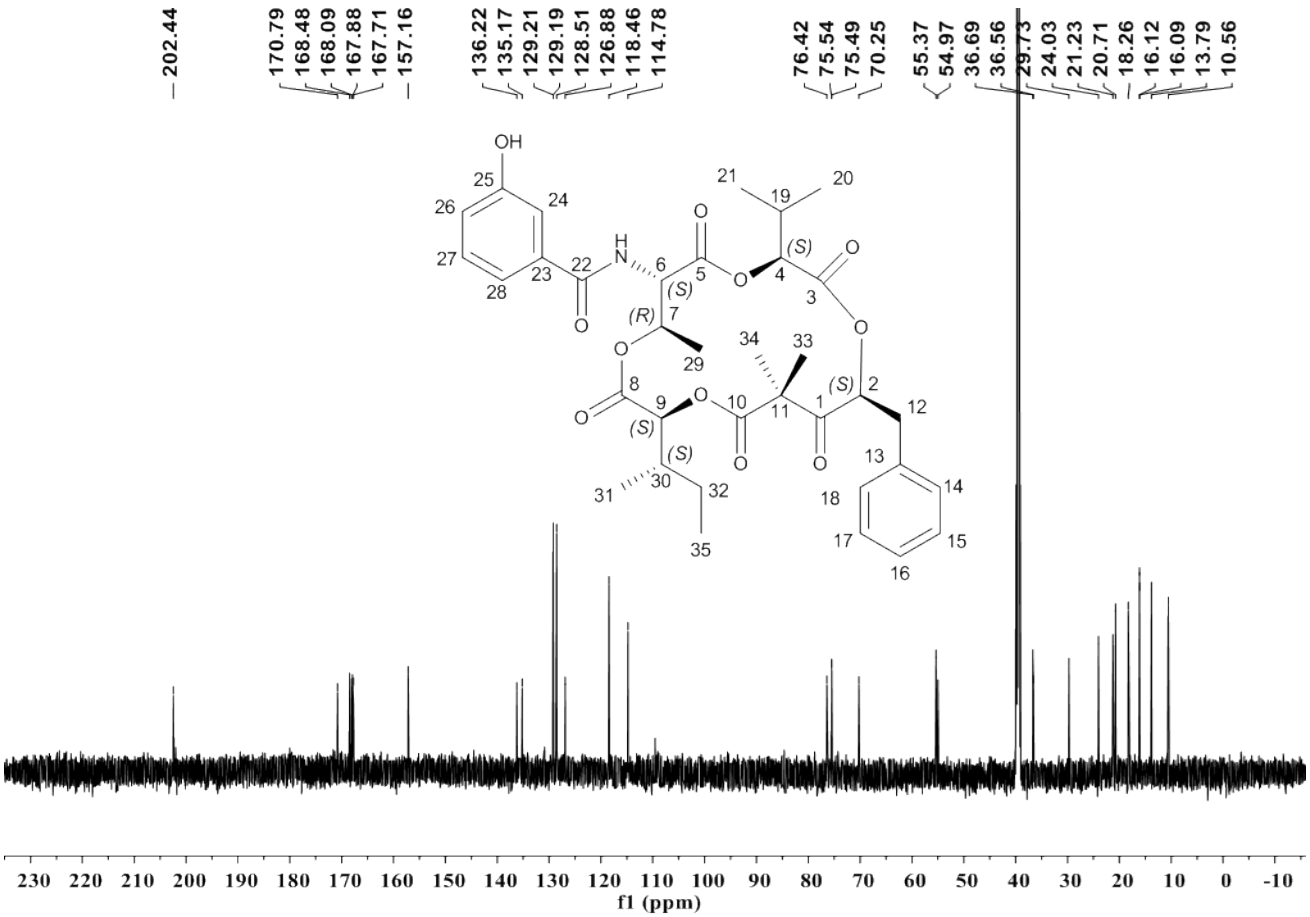


Figure S3b ^{13}C NMR spectrum of 2 in DMSO-d_6

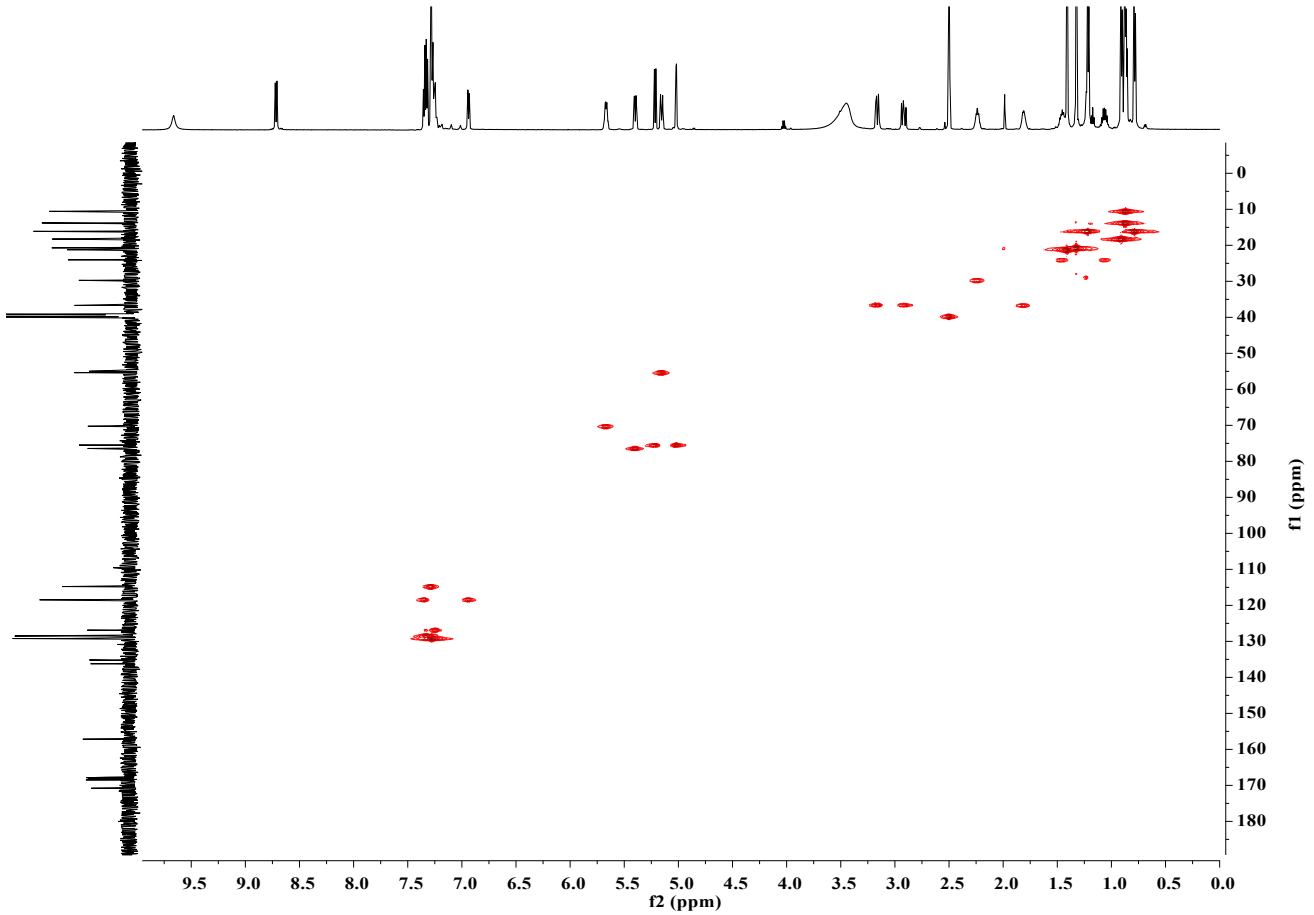


Figure S3c HSQC spectrum of 2 in DMSO-d_6

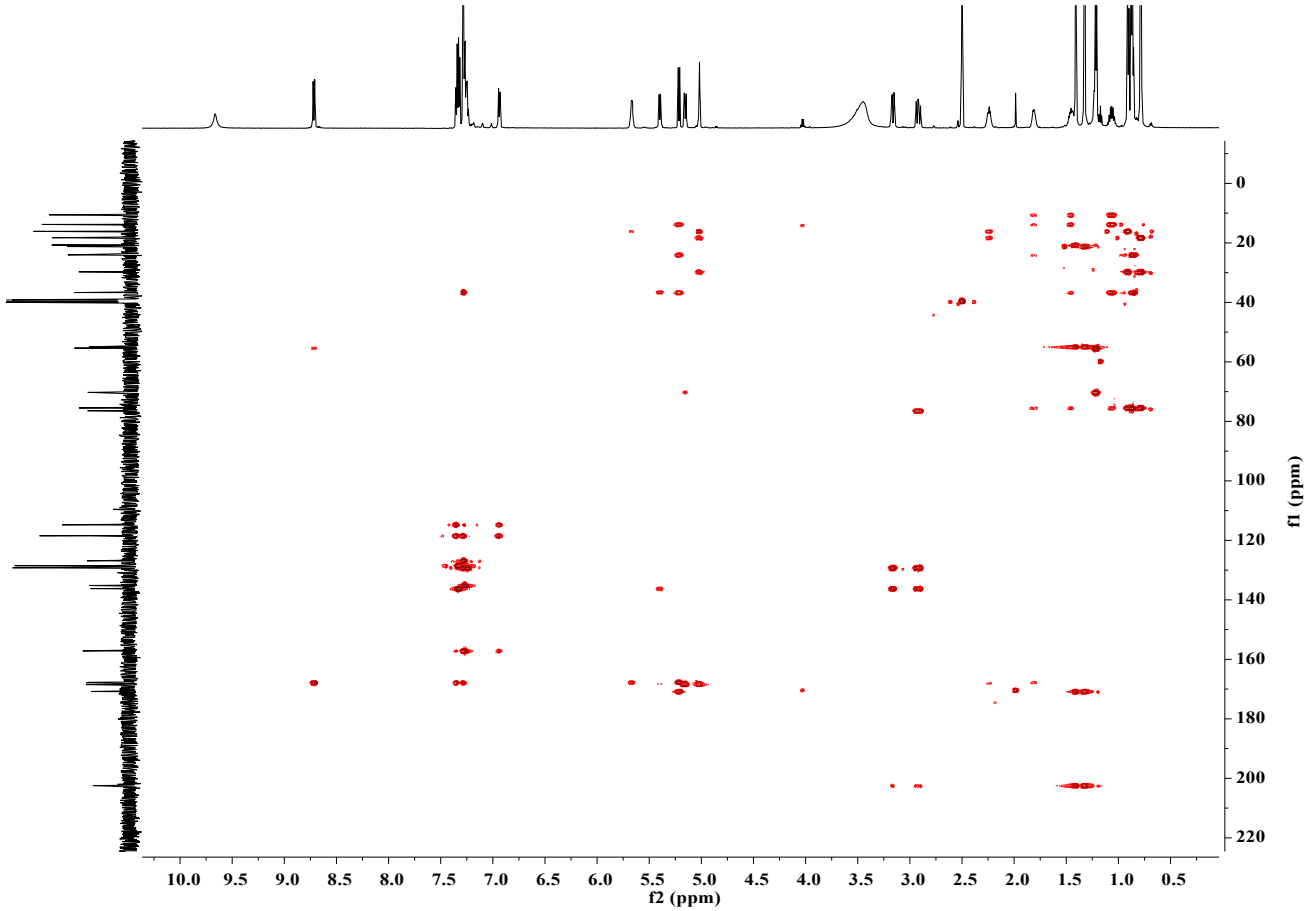


Figure S3d HMBC spectrum of 2 in DMSO-d_6

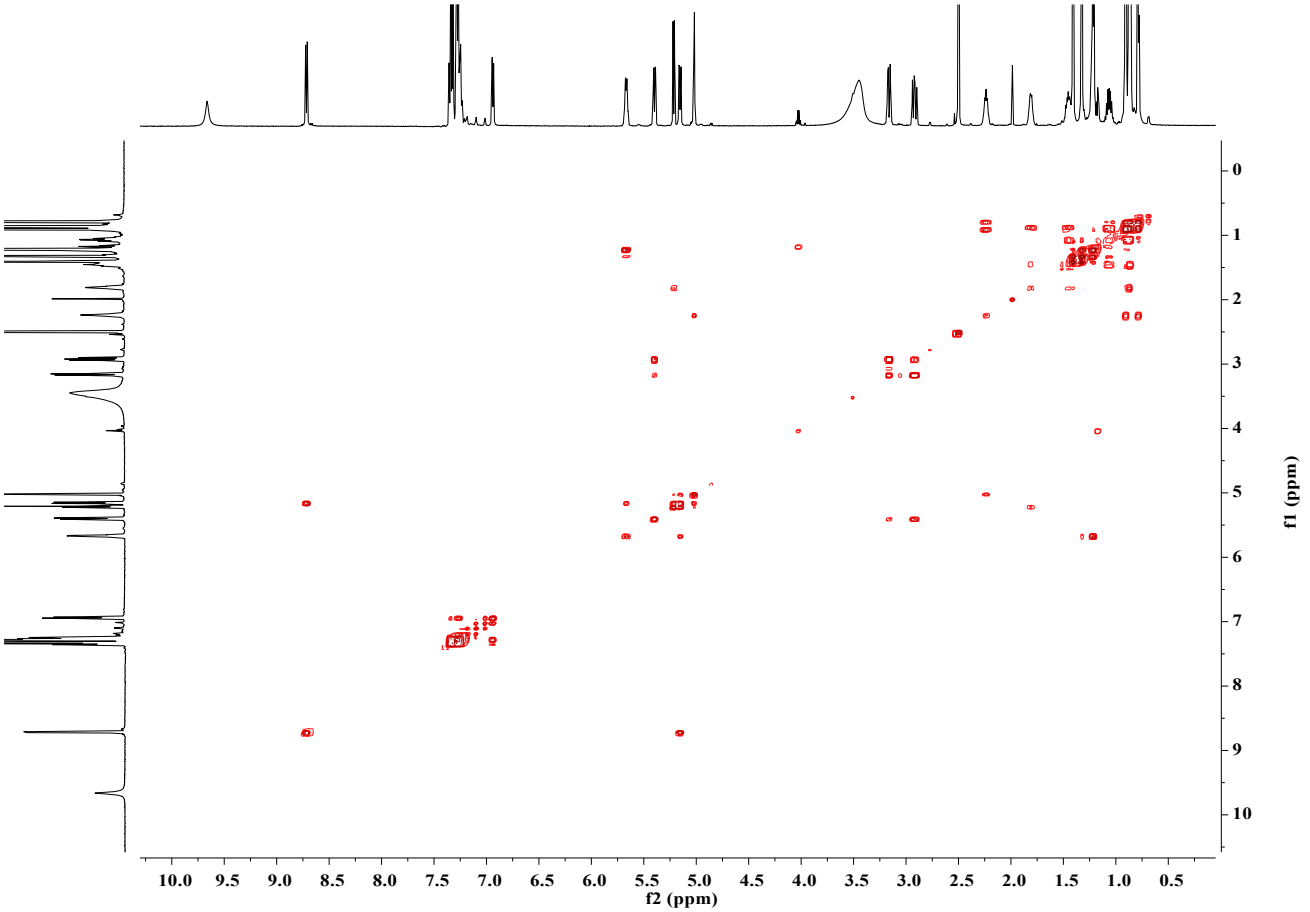


Figure S3e ^{1}H-^{1}H COSY spectrum of 2 in DMSO-d_6

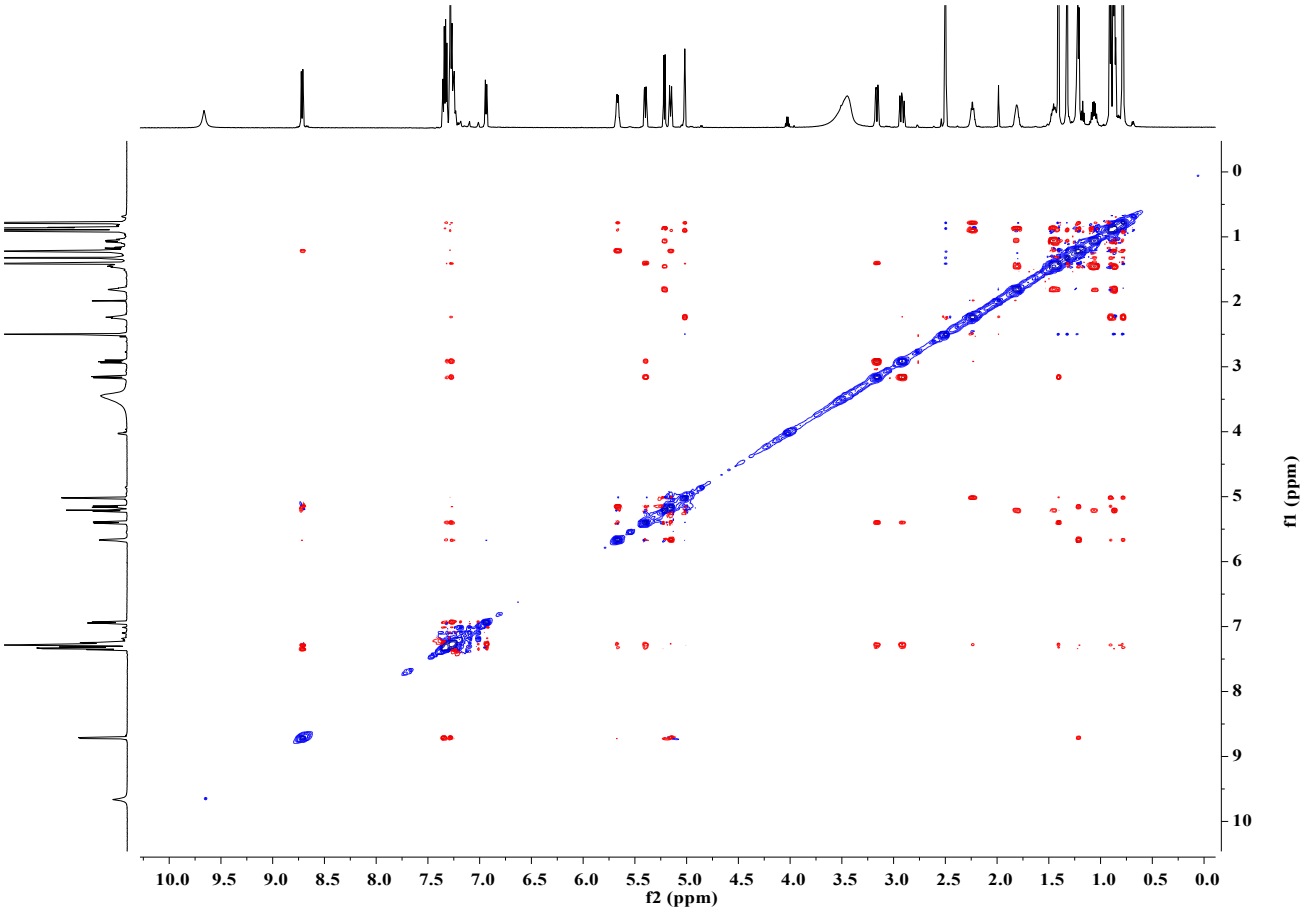


Figure S3f ROESY spectrum of 2 in DMSO-d_6

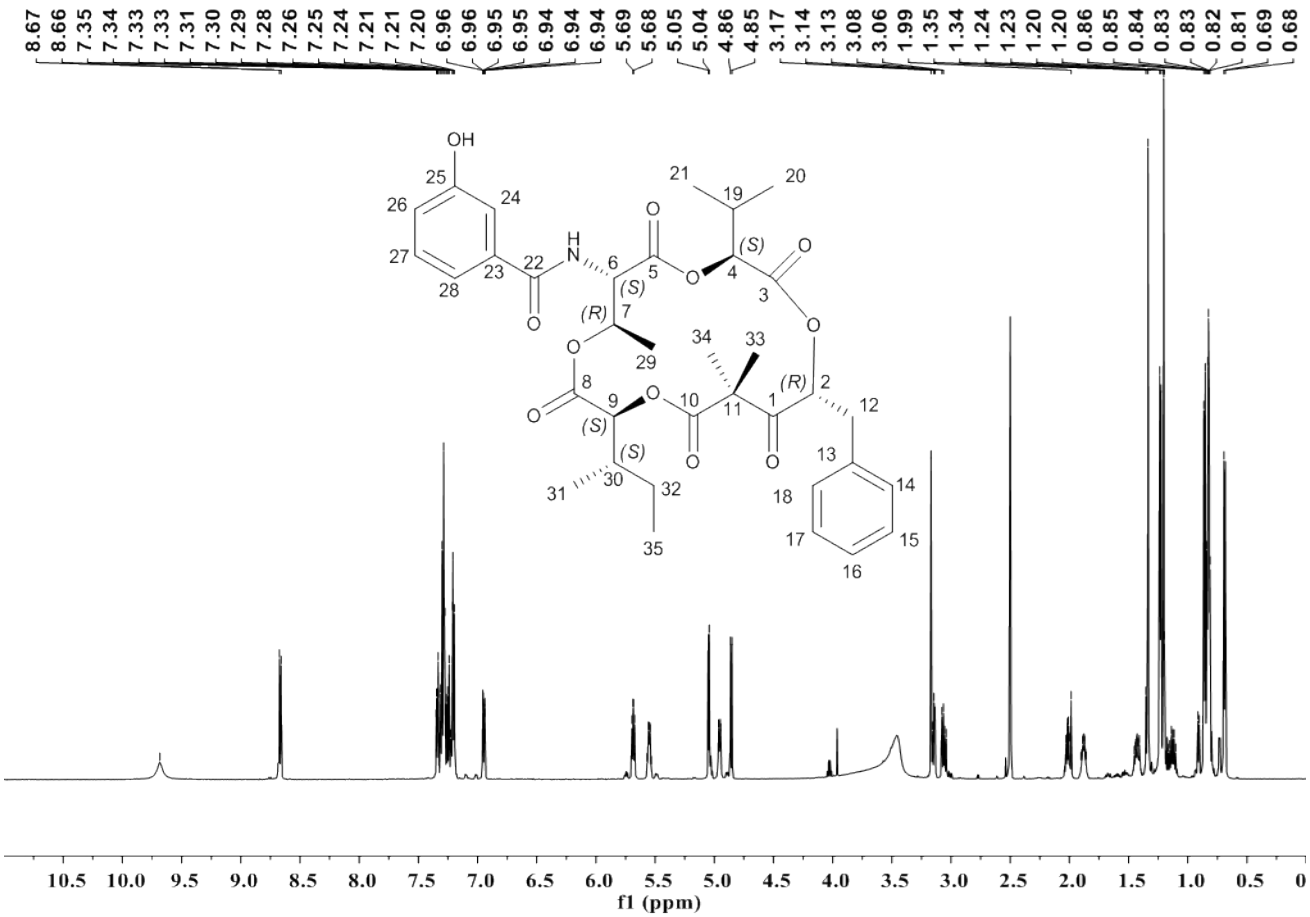


Figure S4a ^{1}H NMR spectrum of 3 in DMSO-d_6

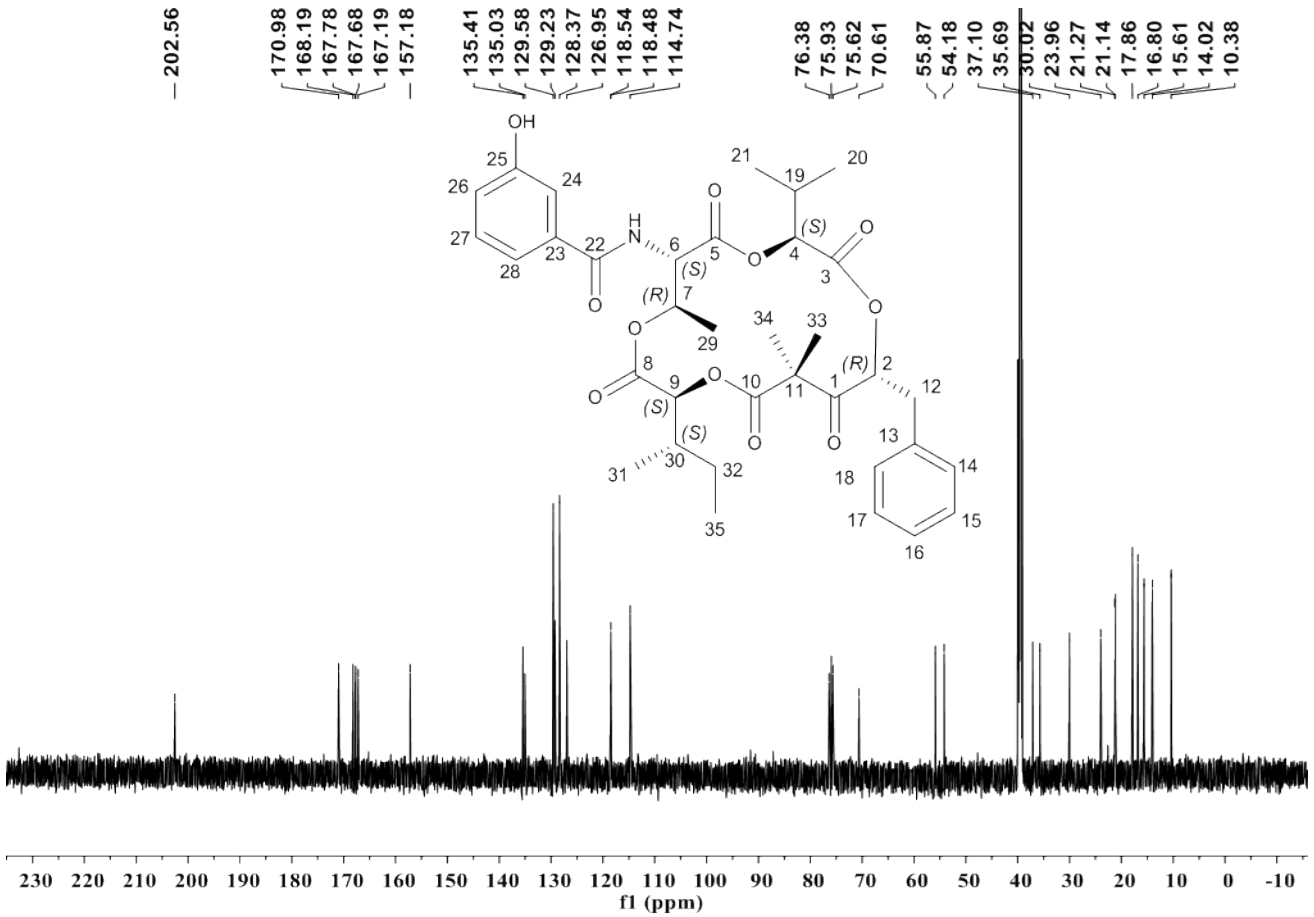


Figure S4b ^{13}C NMR spectrum of 3 in DMSO-d_6

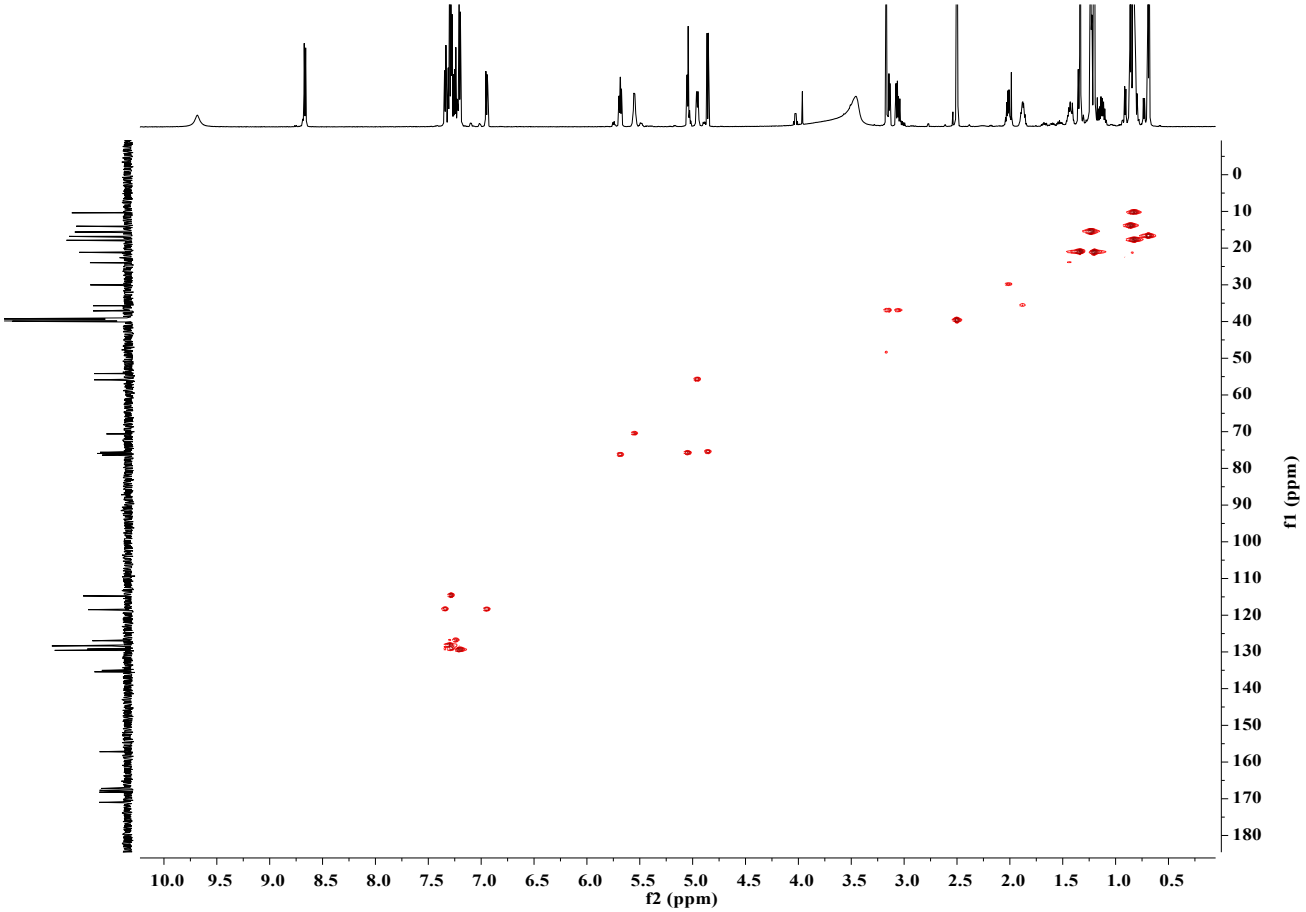


Figure S4c HSQC spectrum of 3 in DMSO-d_6

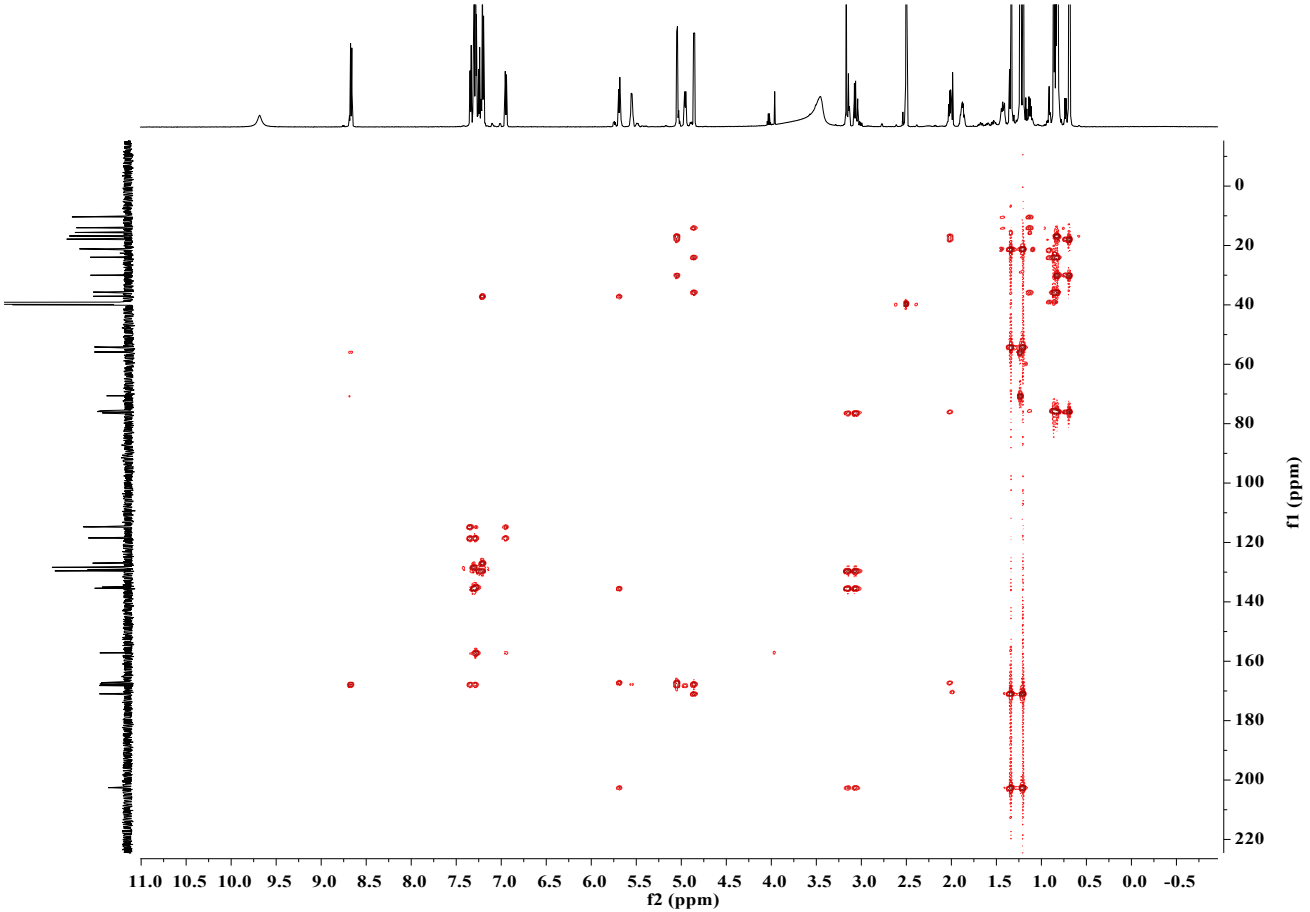


Figure S4d HMBC spectrum of 3 in DMSO-d_6

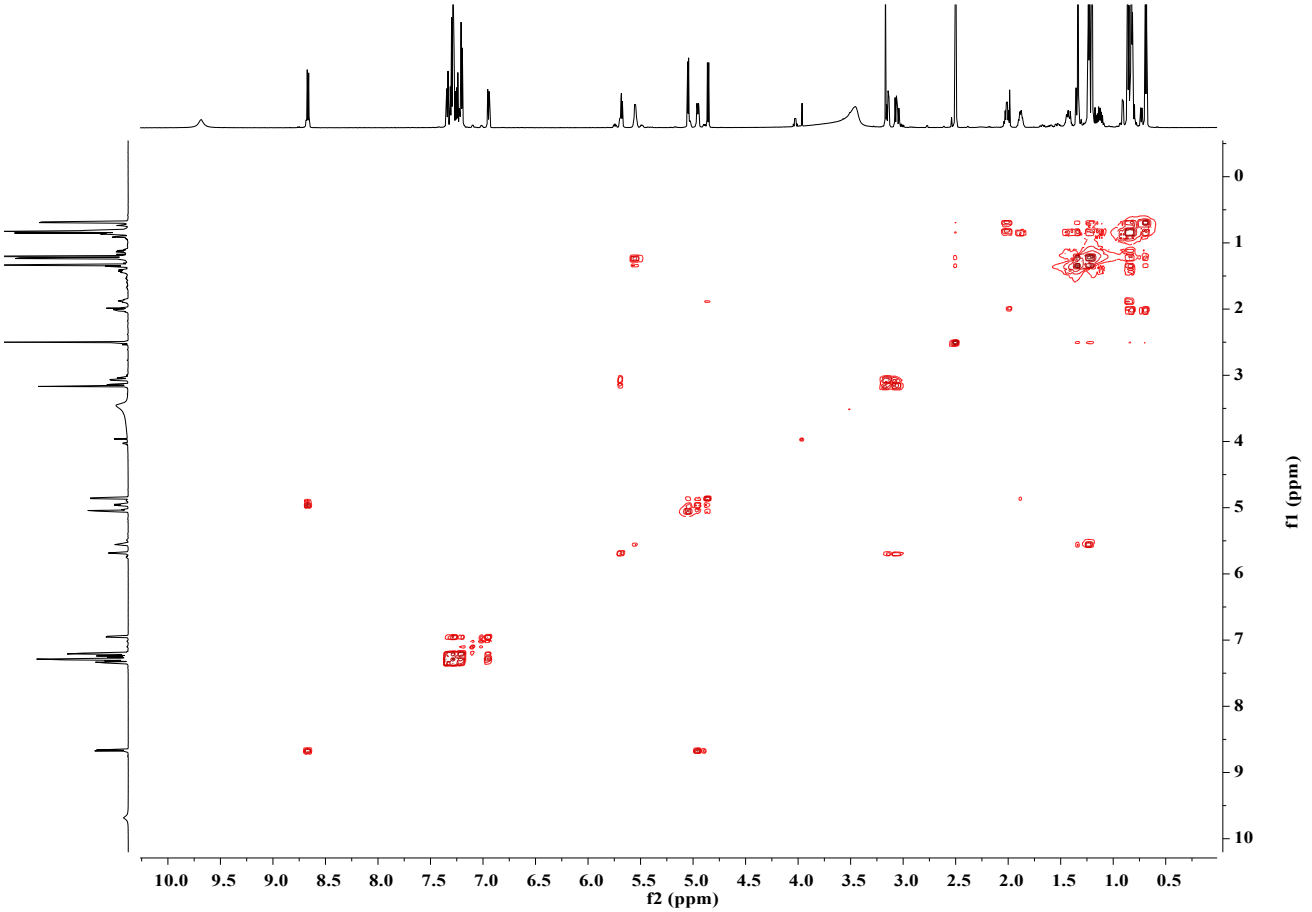


Figure S4e ^{1}H-^{1}H COSY spectrum of 3 in DMSO-d_6

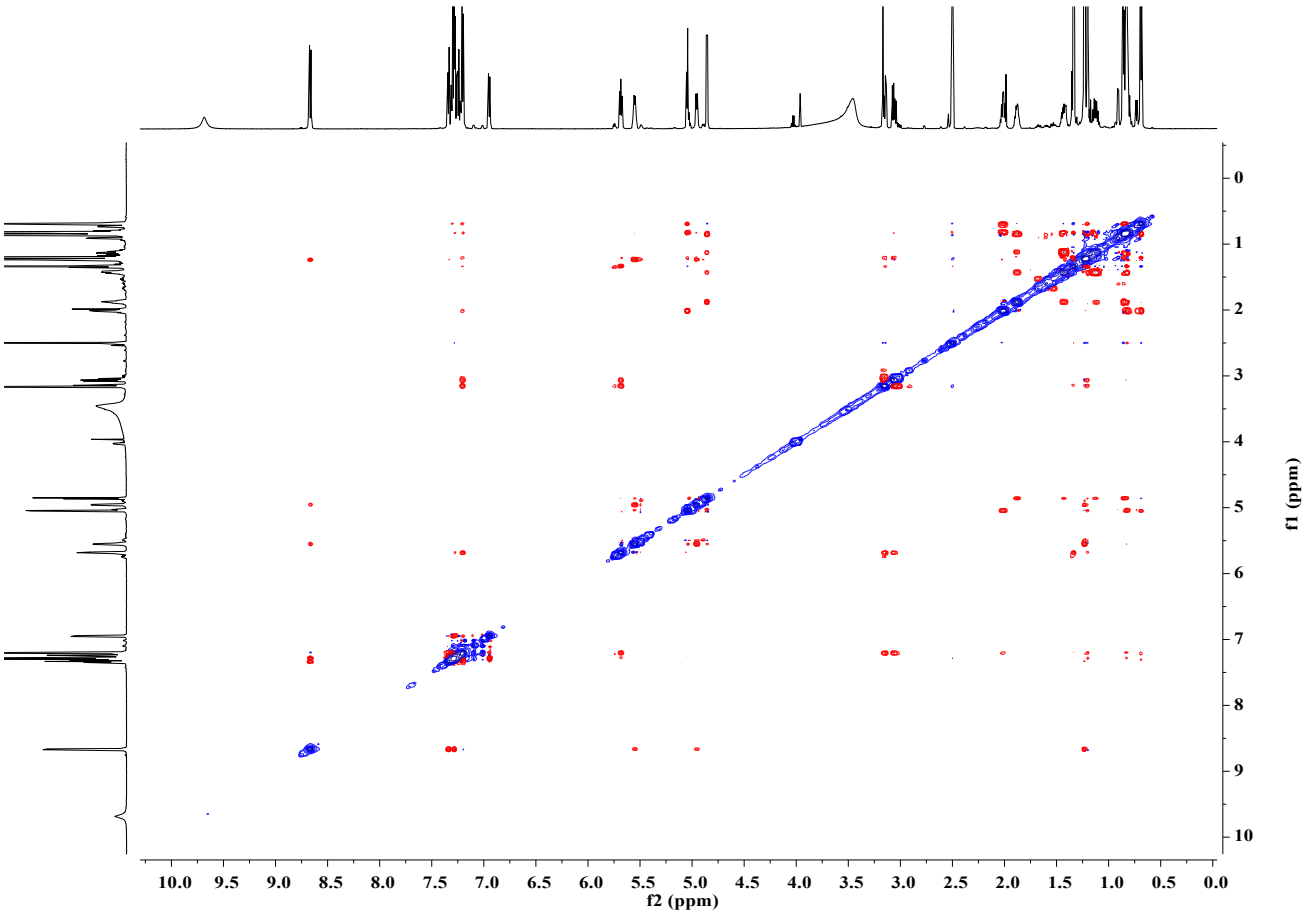


Figure S4f ROESY spectrum of 3 in DMSO-d_6

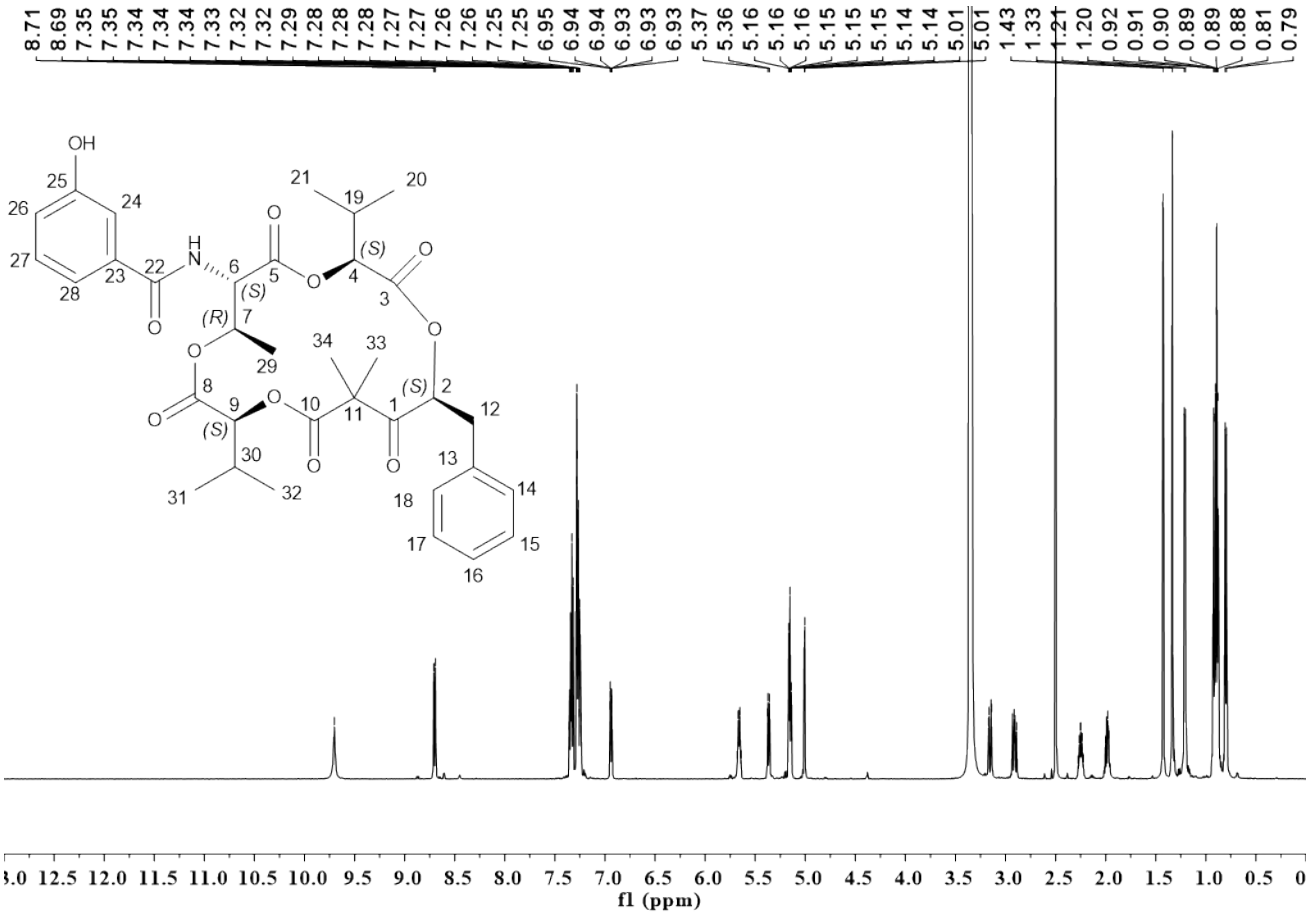


Figure S5a ^{1}H NMR spectrum of 4 in DMSO-d_6

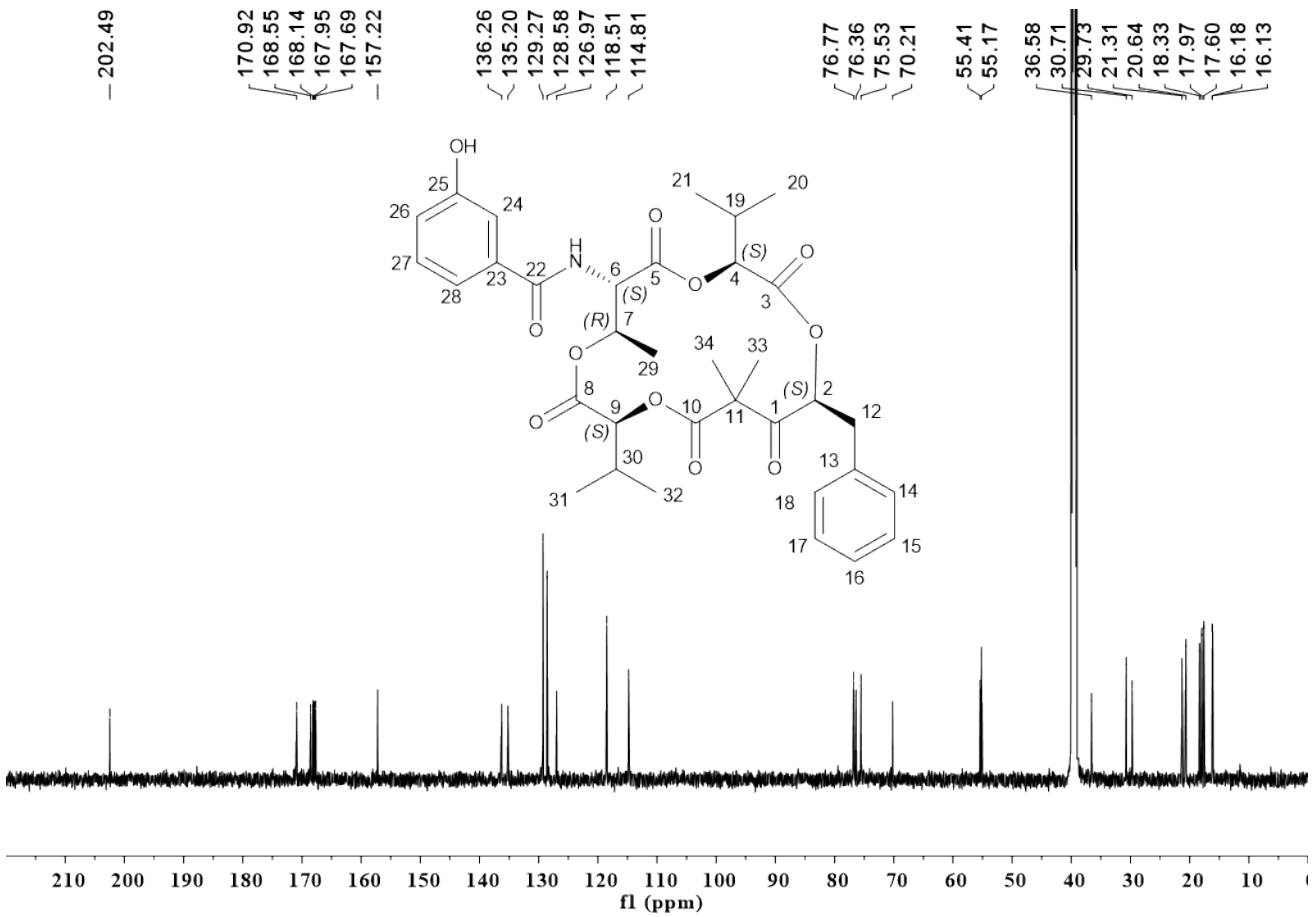


Figure S5b ^{13}C NMR spectrum of 4 in DMSO-d_6

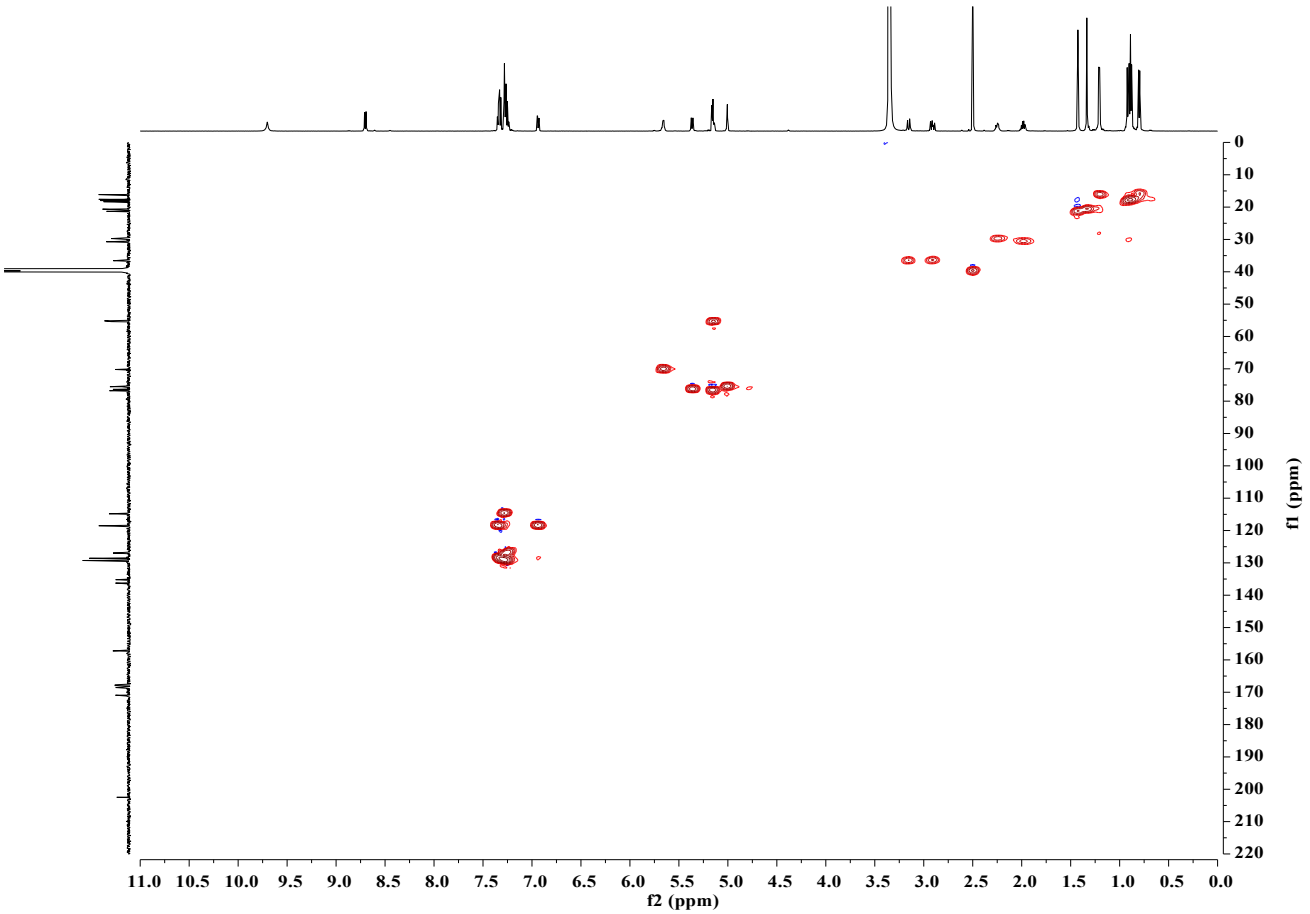


Figure S5c HSQC spectrum of 4 in DMSO-d_6

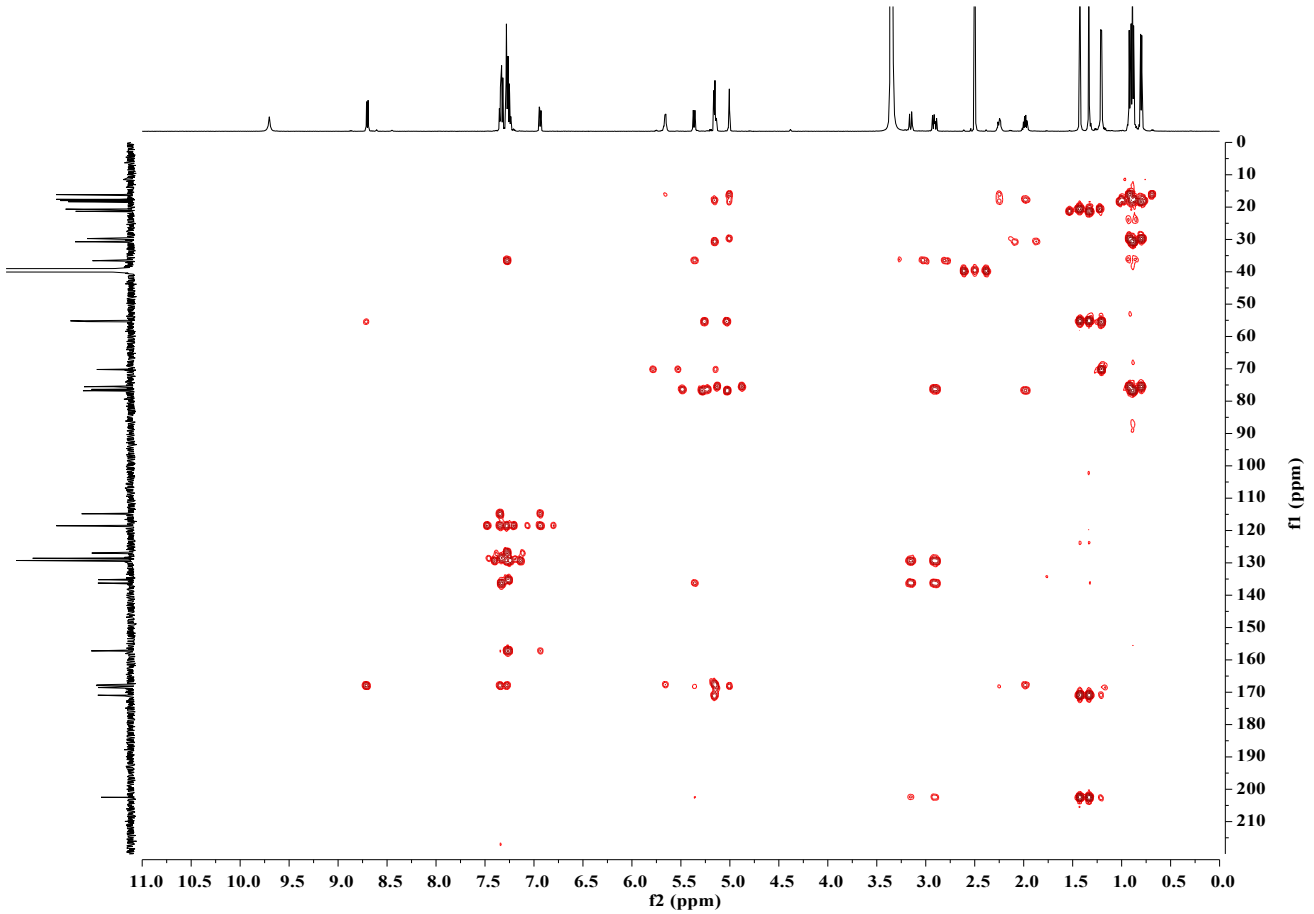


Figure S5d HMBC spectrum of 4 in DMSO-d_6

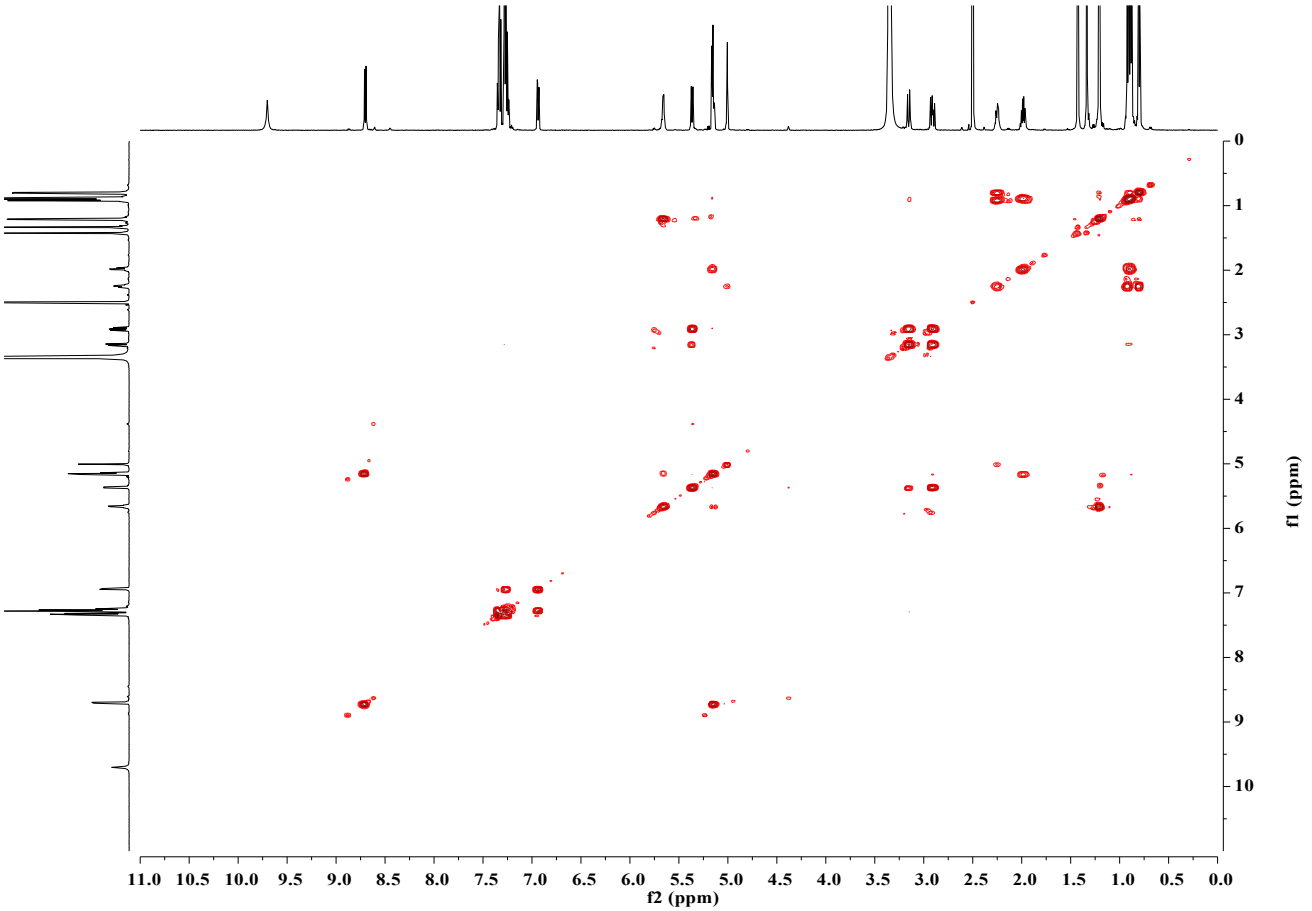


Figure S5e ^{1}H-^{1}H COSY spectrum of 4 in DMSO-d_6

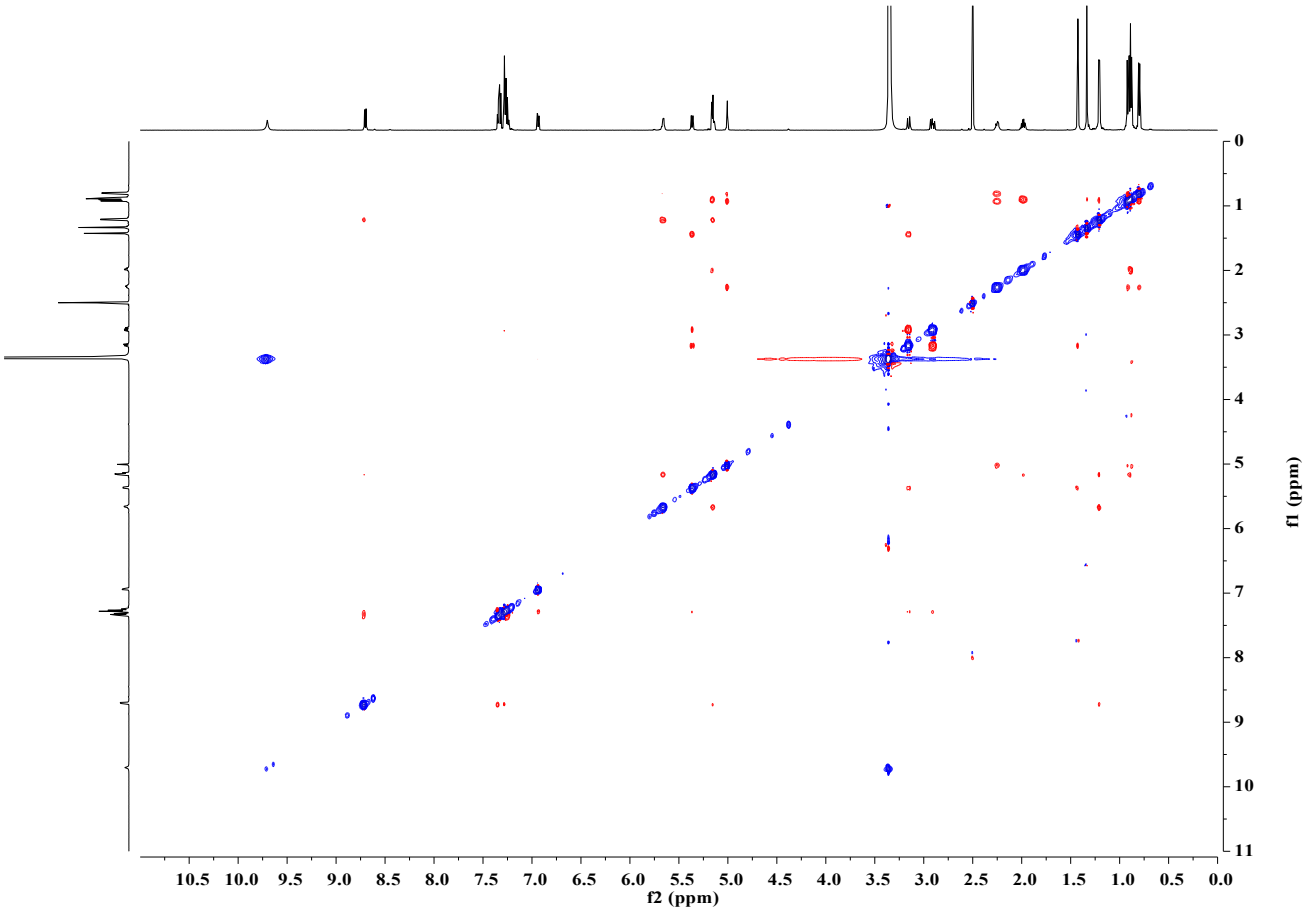


Figure S5f ROESY spectrum of 4 in DMSO-d_6

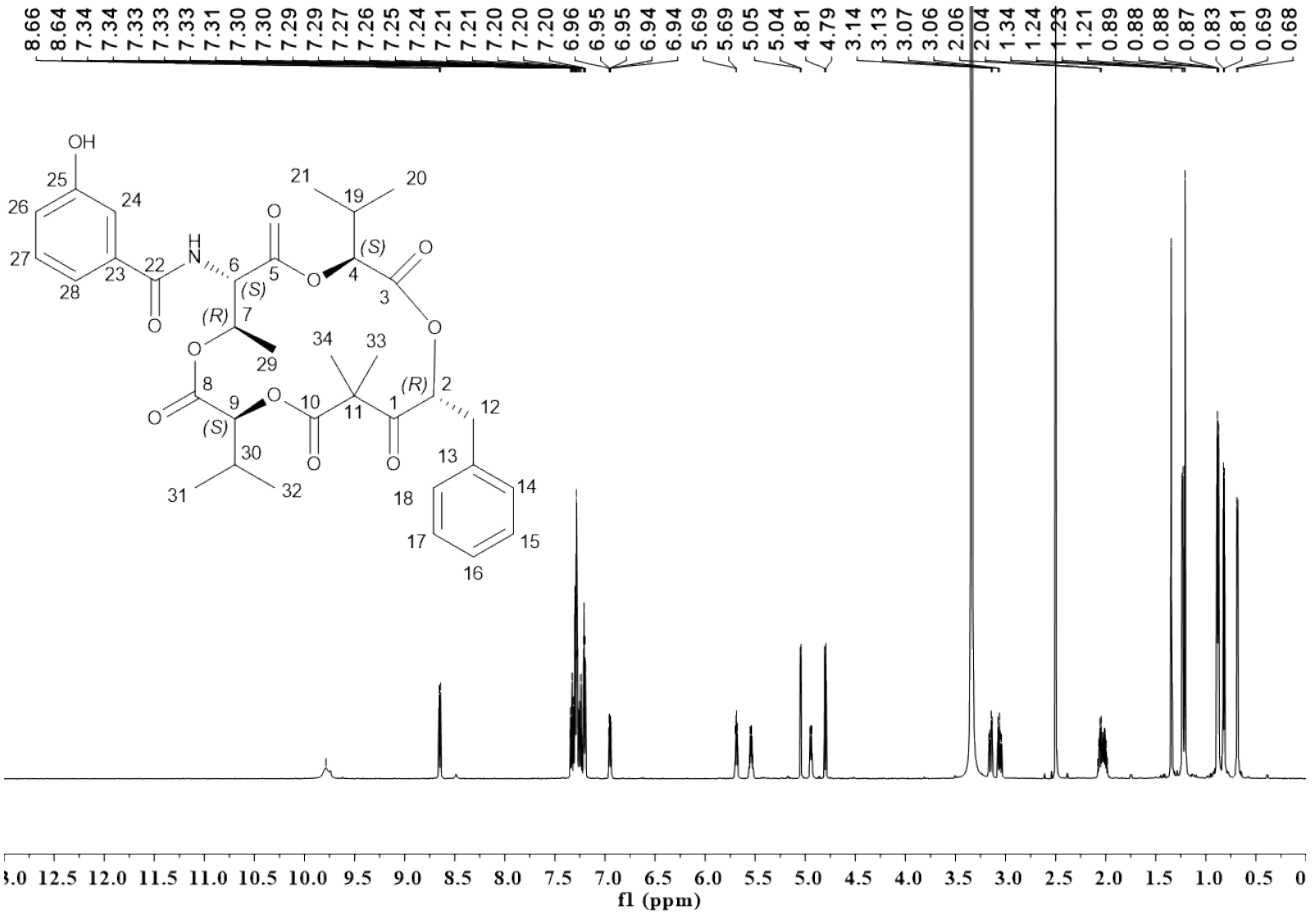


Figure S6a ^{1}H NMR spectrum of 5 in DMSO-d_6

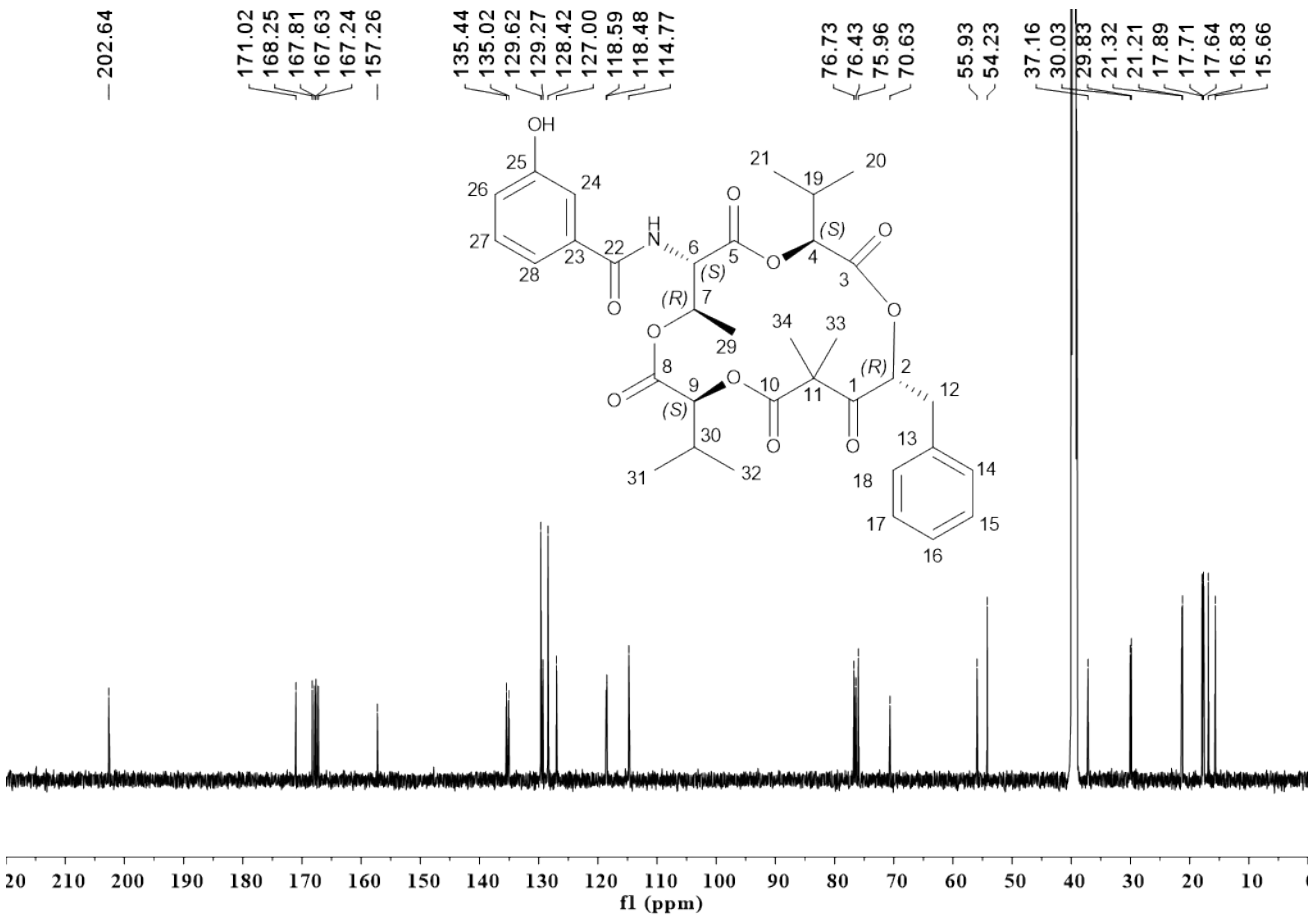


Figure S6b ^{13}C NMR spectrum of 5 in DMSO-d_6

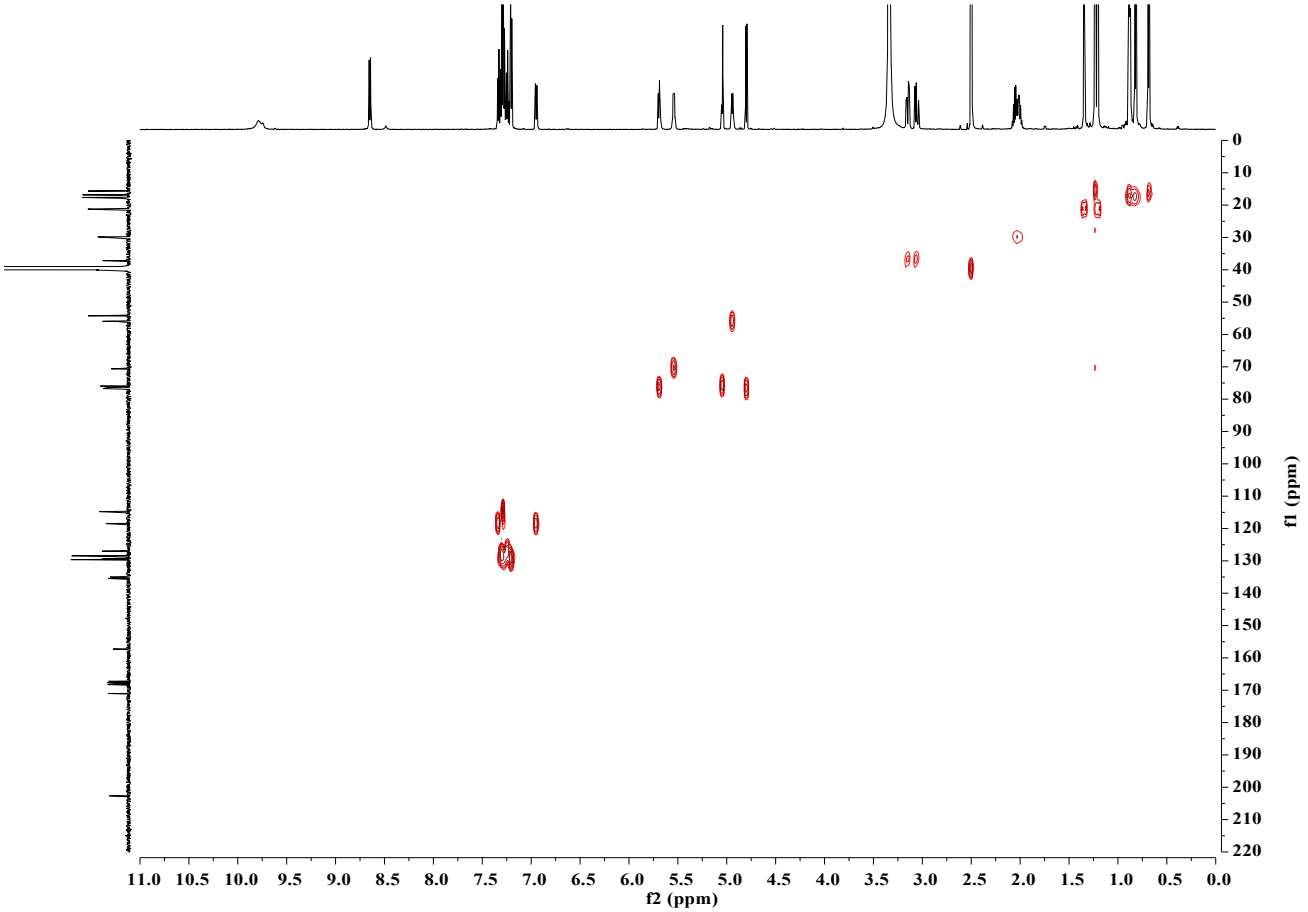


Figure S6c HSQC spectrum of 5 in DMSO-d_6

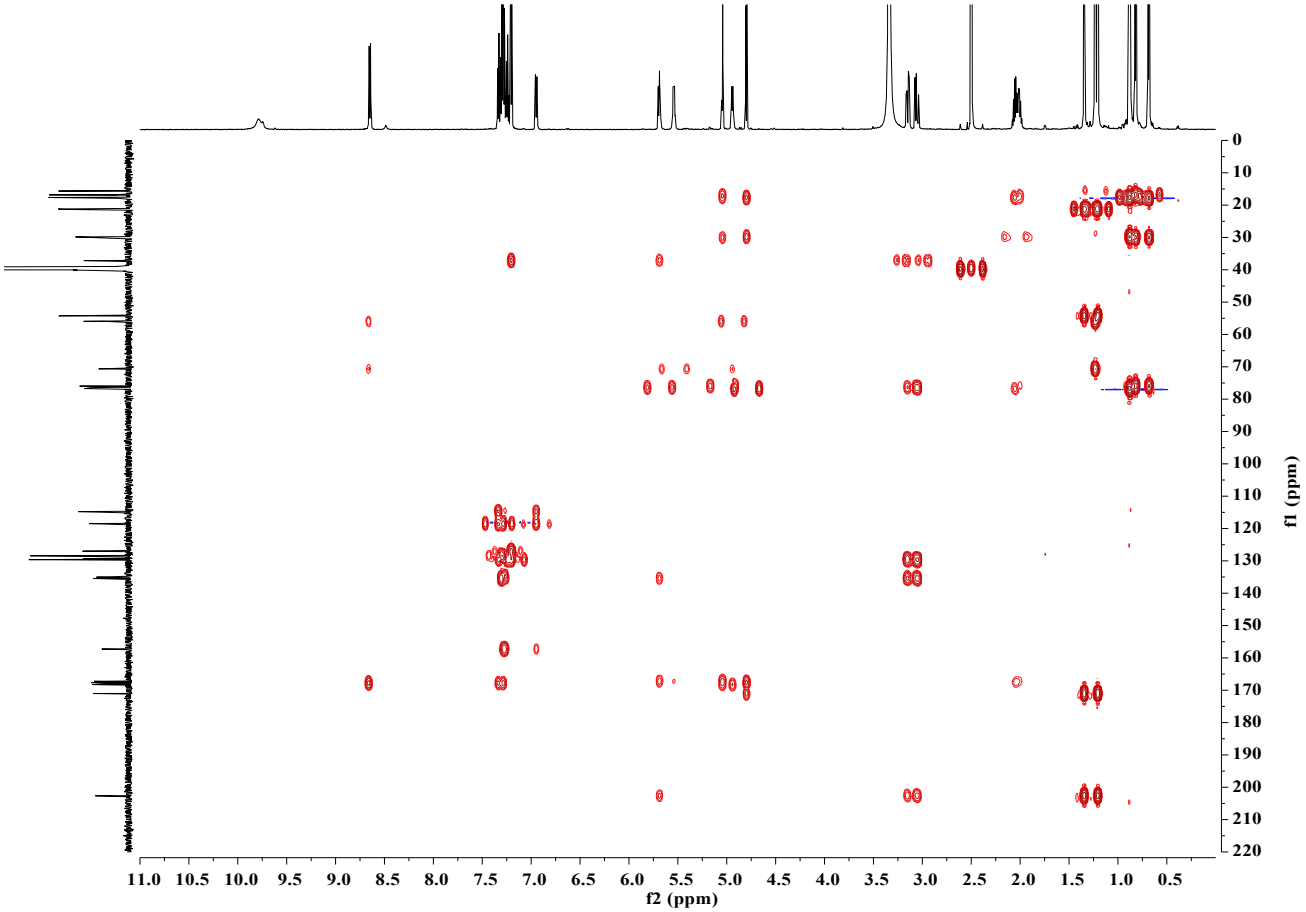


Figure S6d HMBC spectrum of 5 in DMSO-d_6

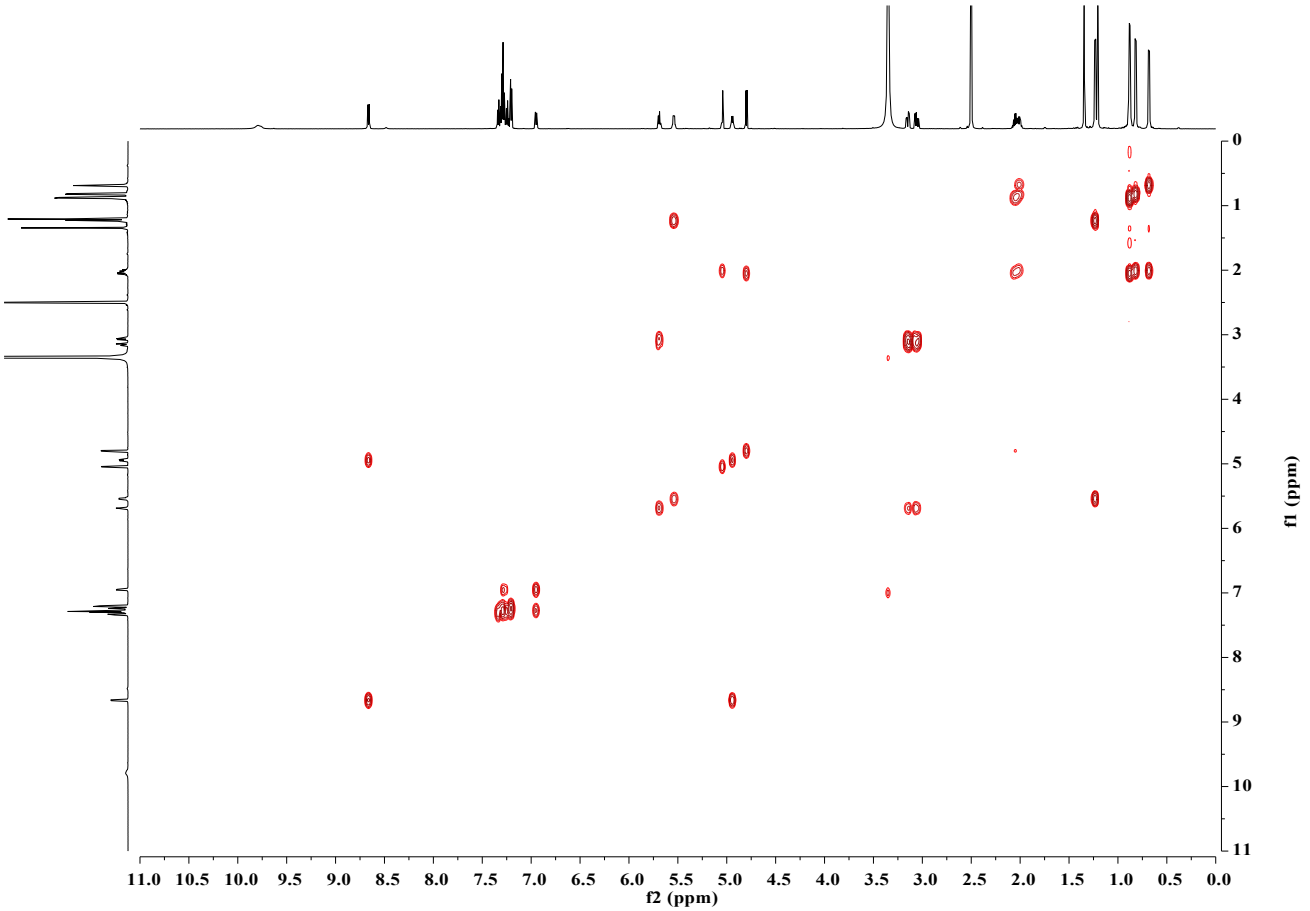


Figure S6e ^{1}H-^{1}H COSY spectrum of 5 in DMSO-d_6

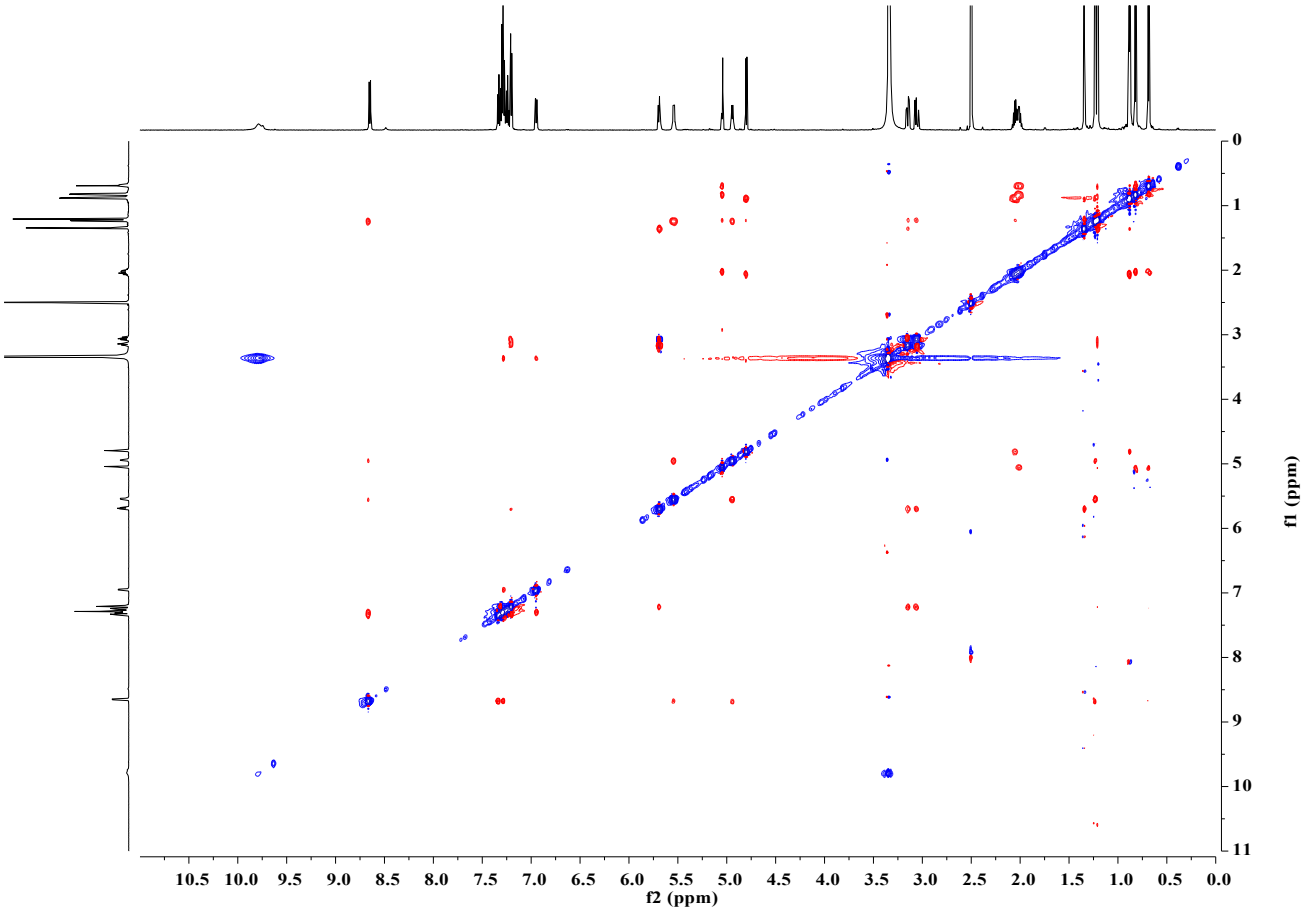


Figure S6f ROESY spectrum of 5 in DMSO-d_6

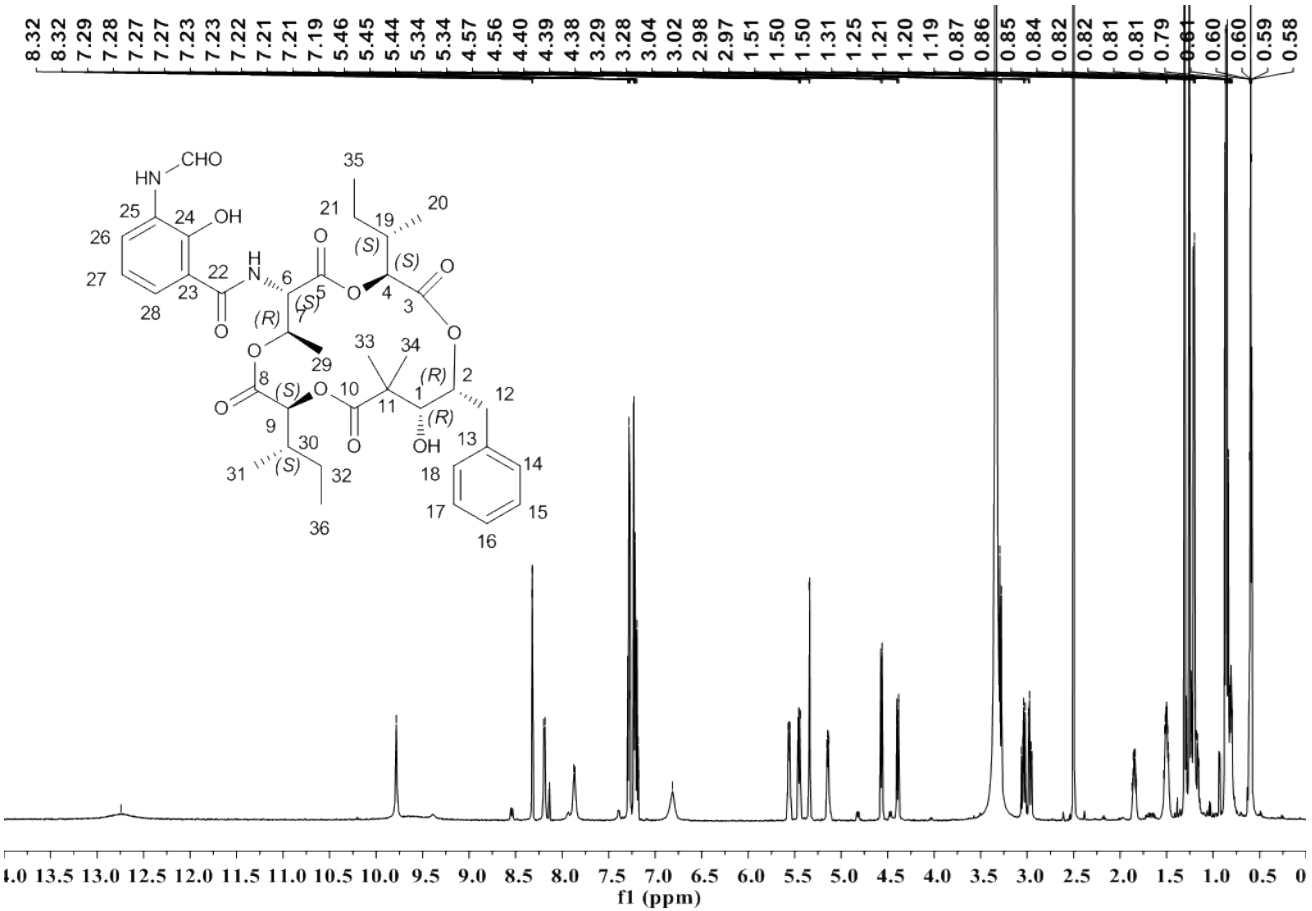


Figure S7a ^{1}H NMR spectrum of 6 in DMSO-d_6

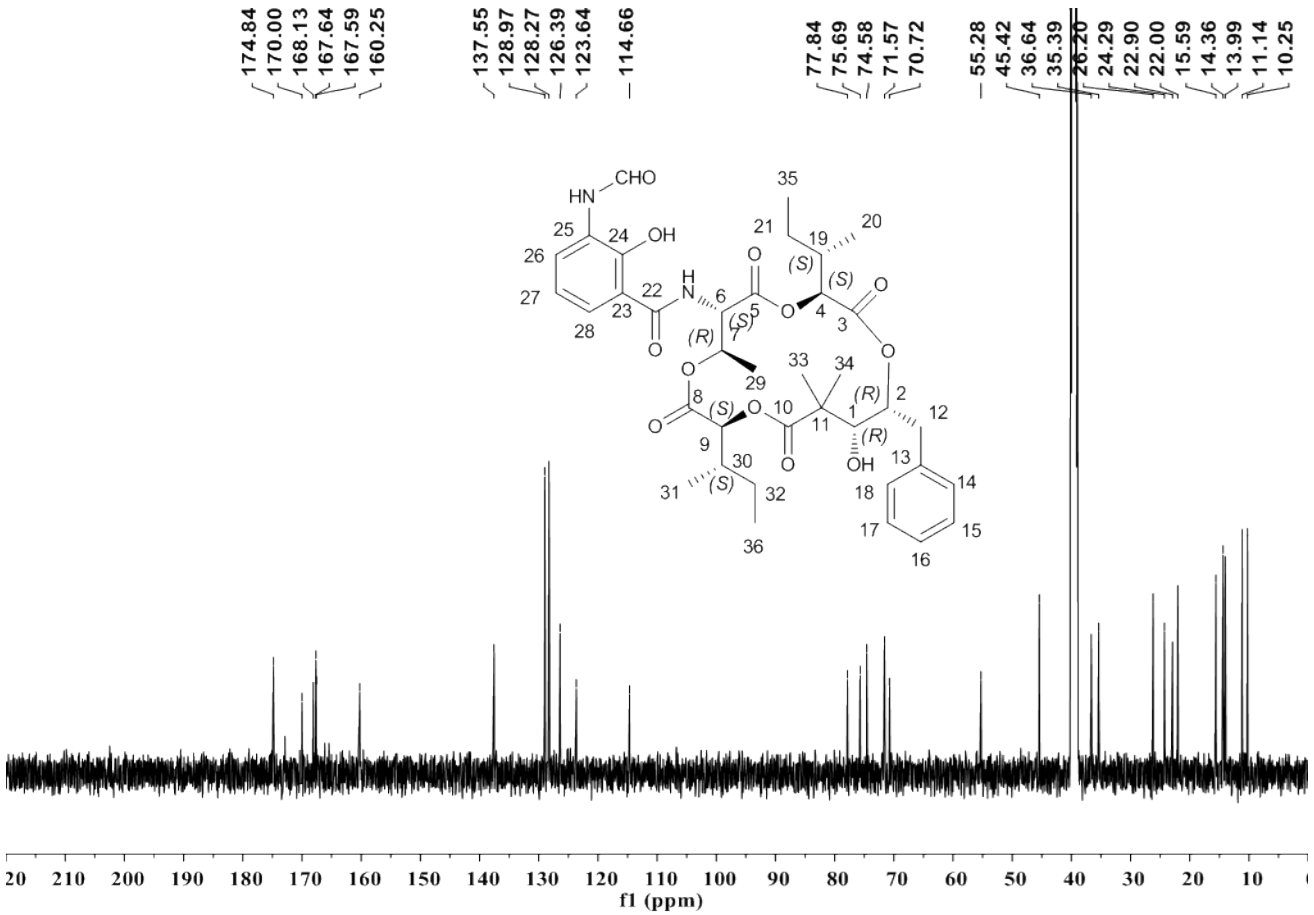


Figure S7b ^{13}C NMR spectrum of 6 in DMSO-*d*

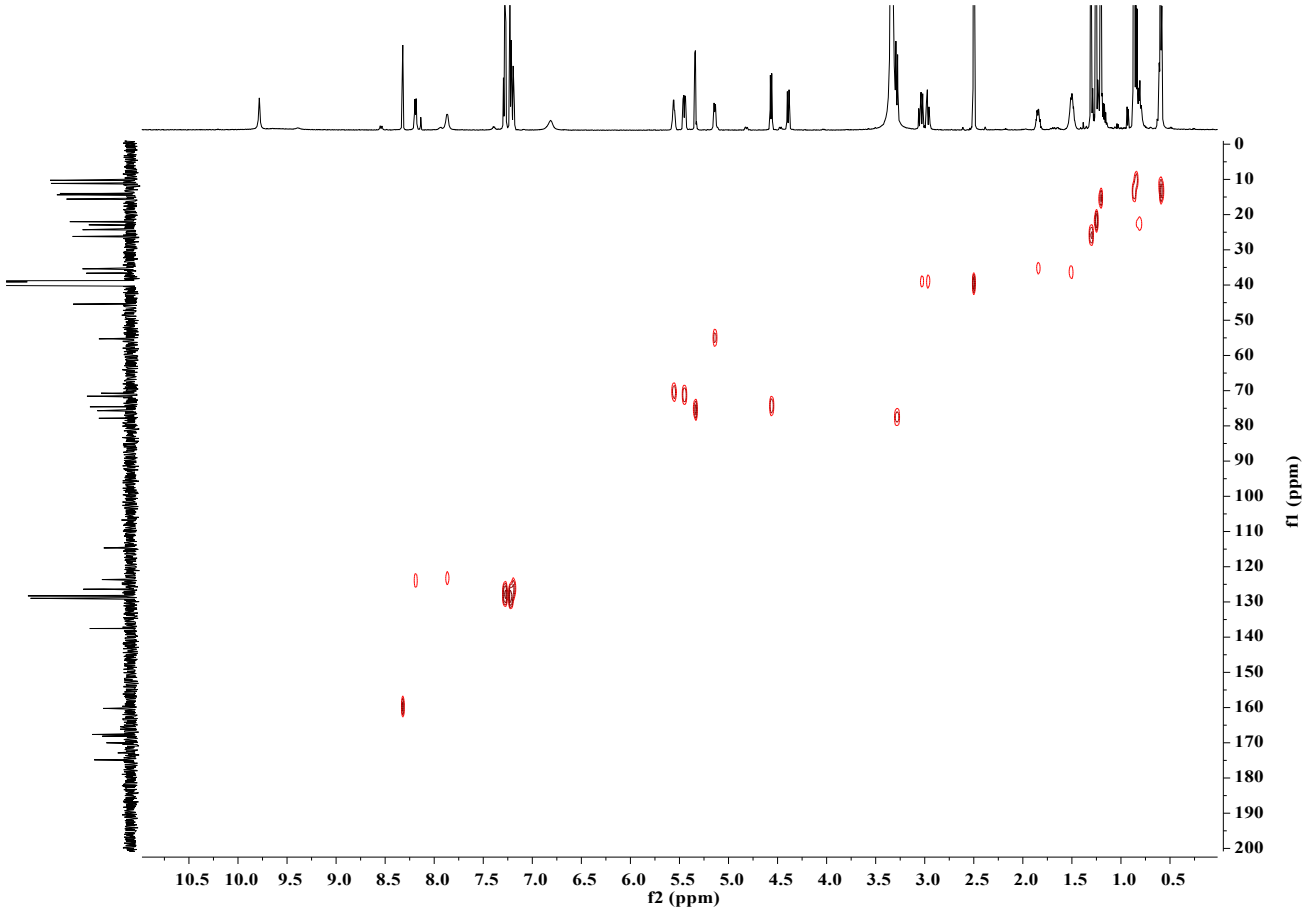


Figure S7c HSQC spectrum of 6 in DMSO-d_6

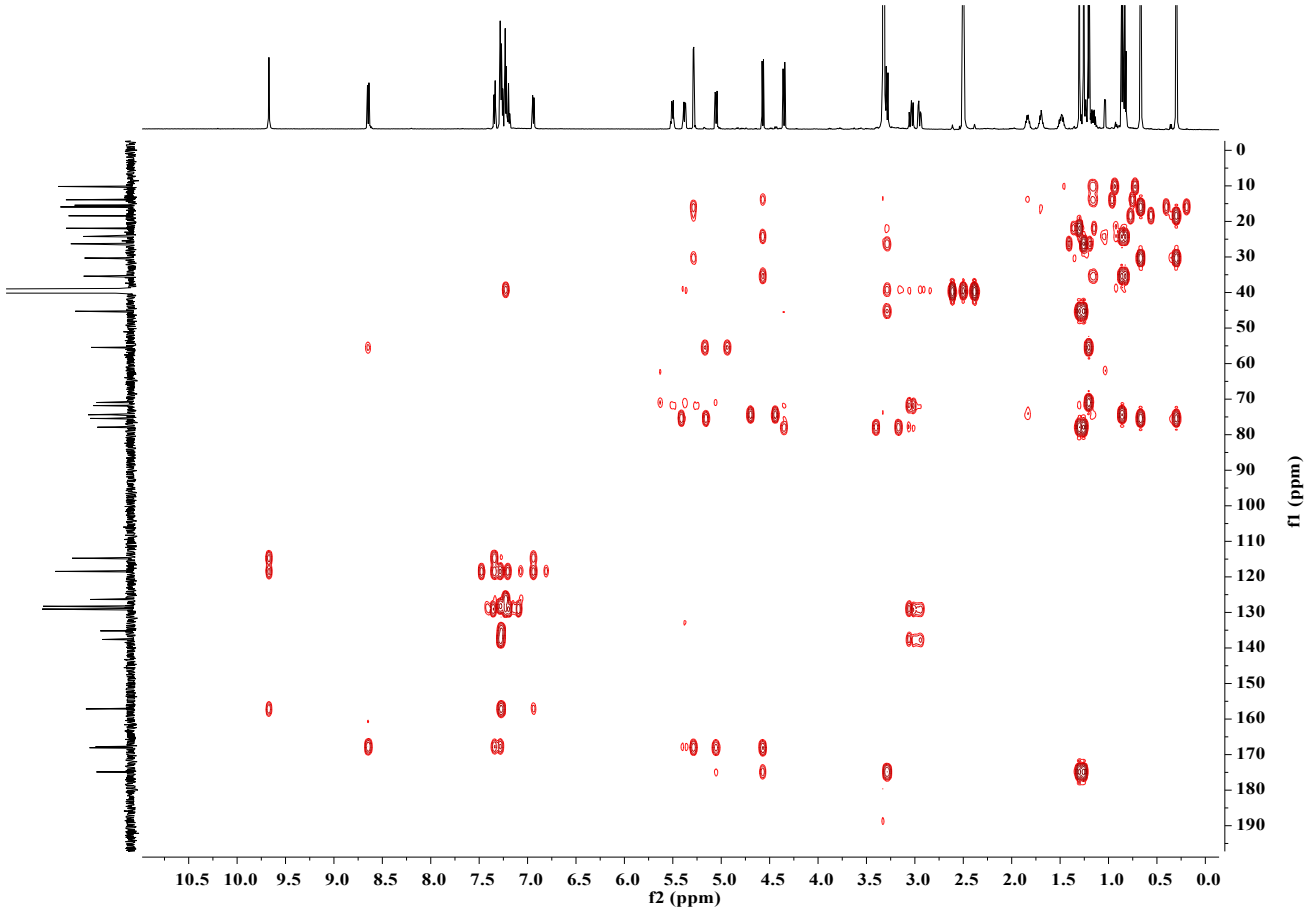


Figure S7d HMBC spectrum of 6 in DMSO-d_6

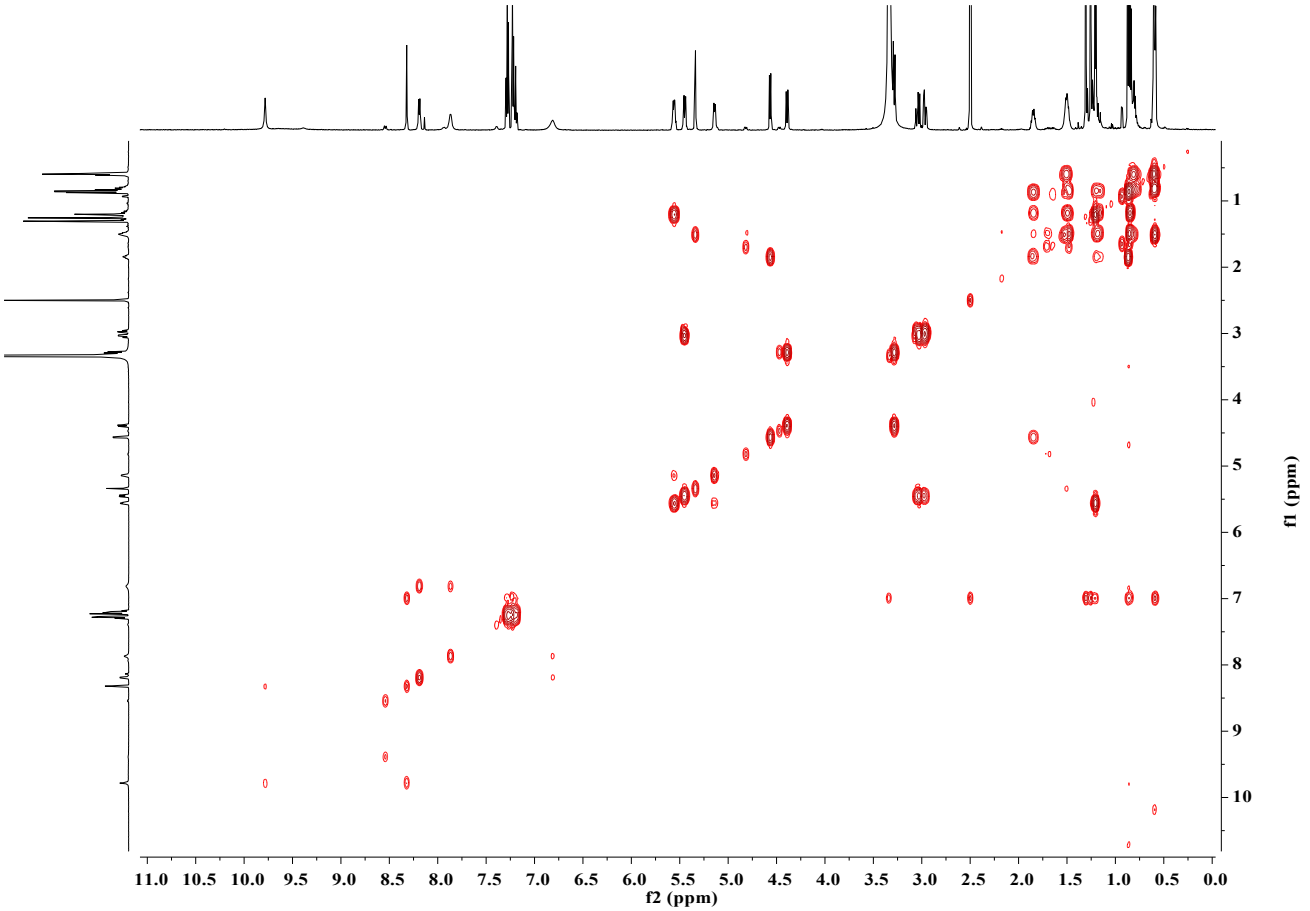


Figure S7e ^{1}H-^{1}H COSY spectrum of 6 in DMSO-d_6

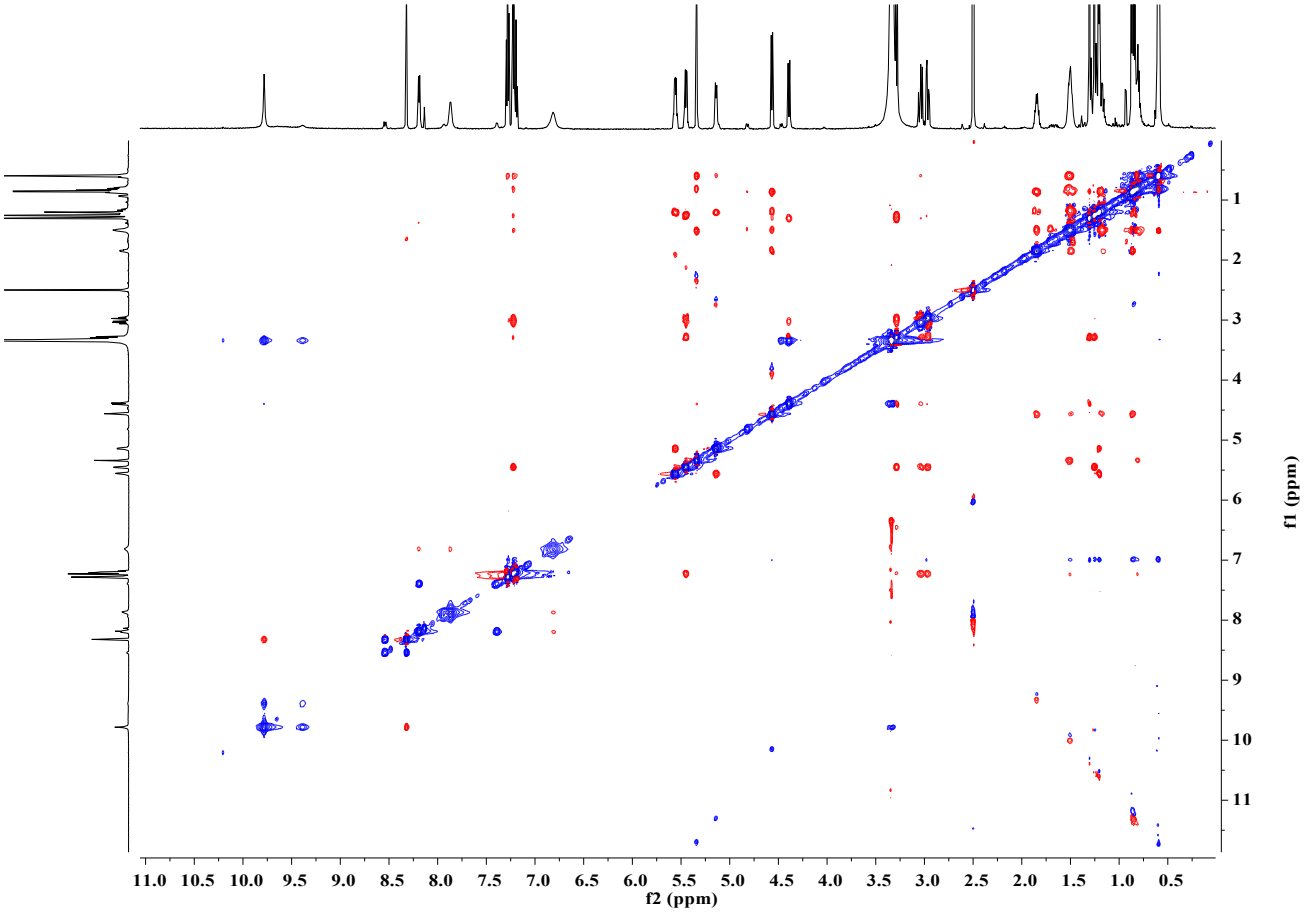


Figure S7f ROESY spectrum of 6 in DMSO-d_6

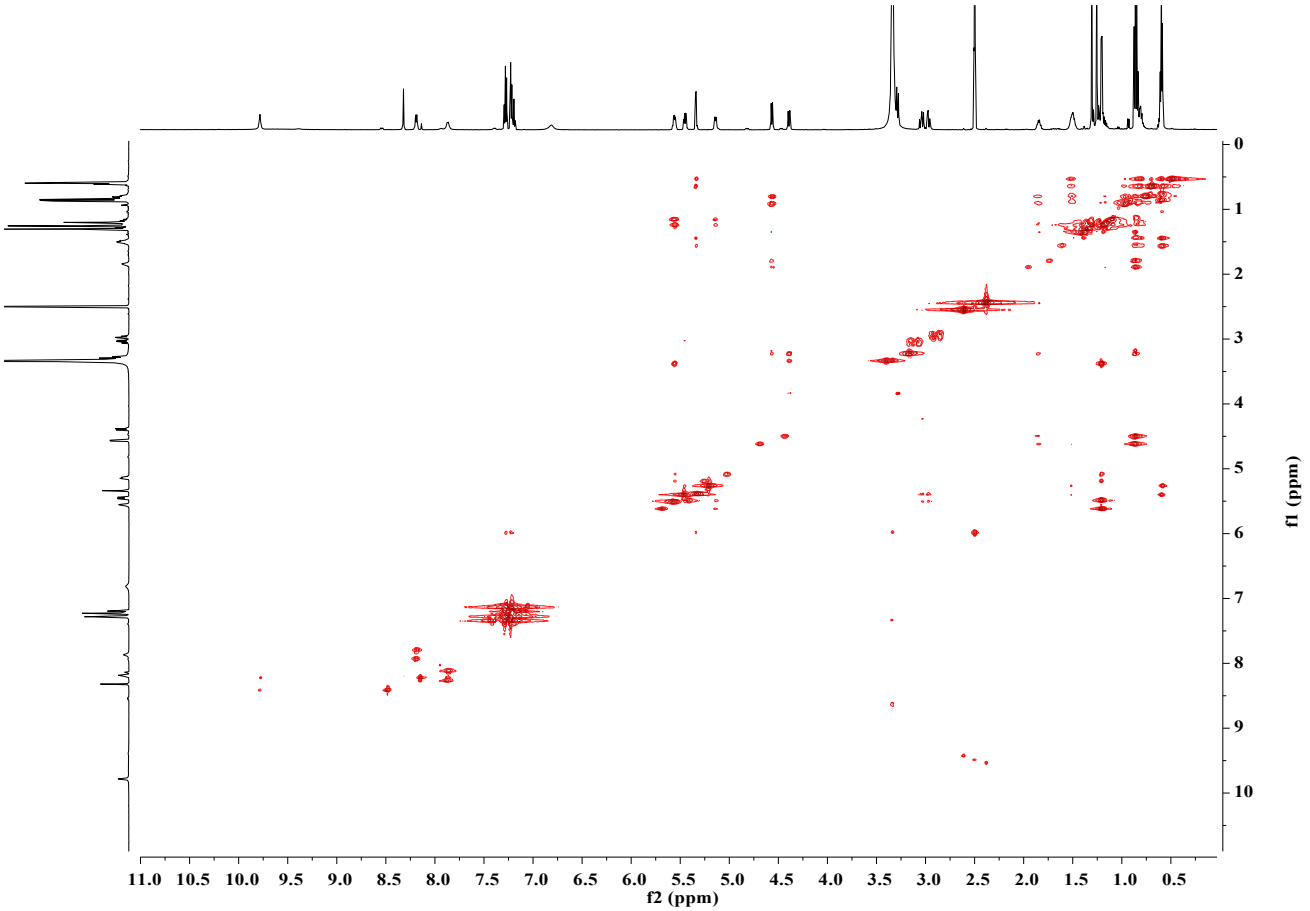


Figure S7g HETLOC spectrum of 6 in DMSO-d_6

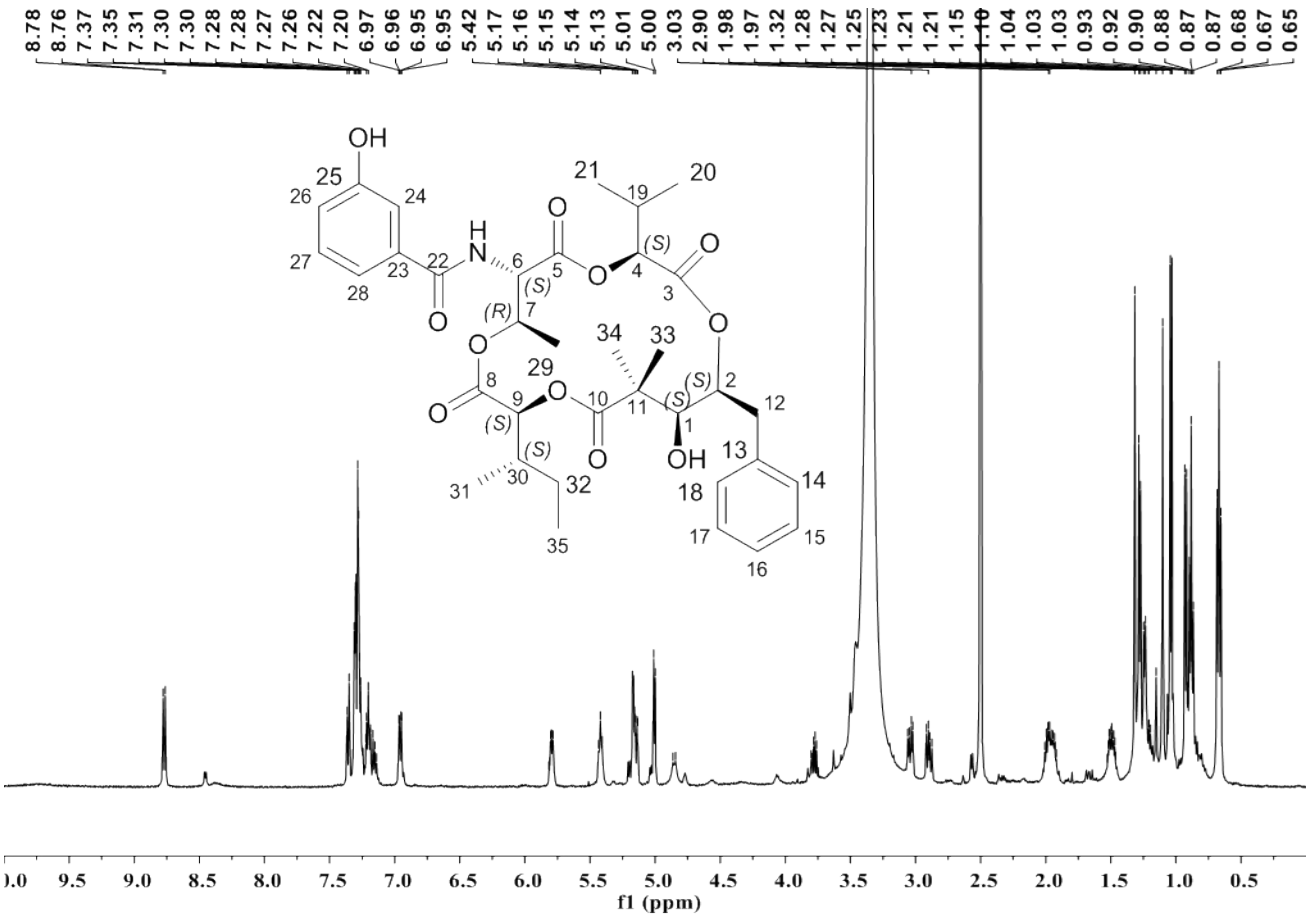


Figure S8a ^{1}H NMR spectrum of 7 in DMSO-d_6

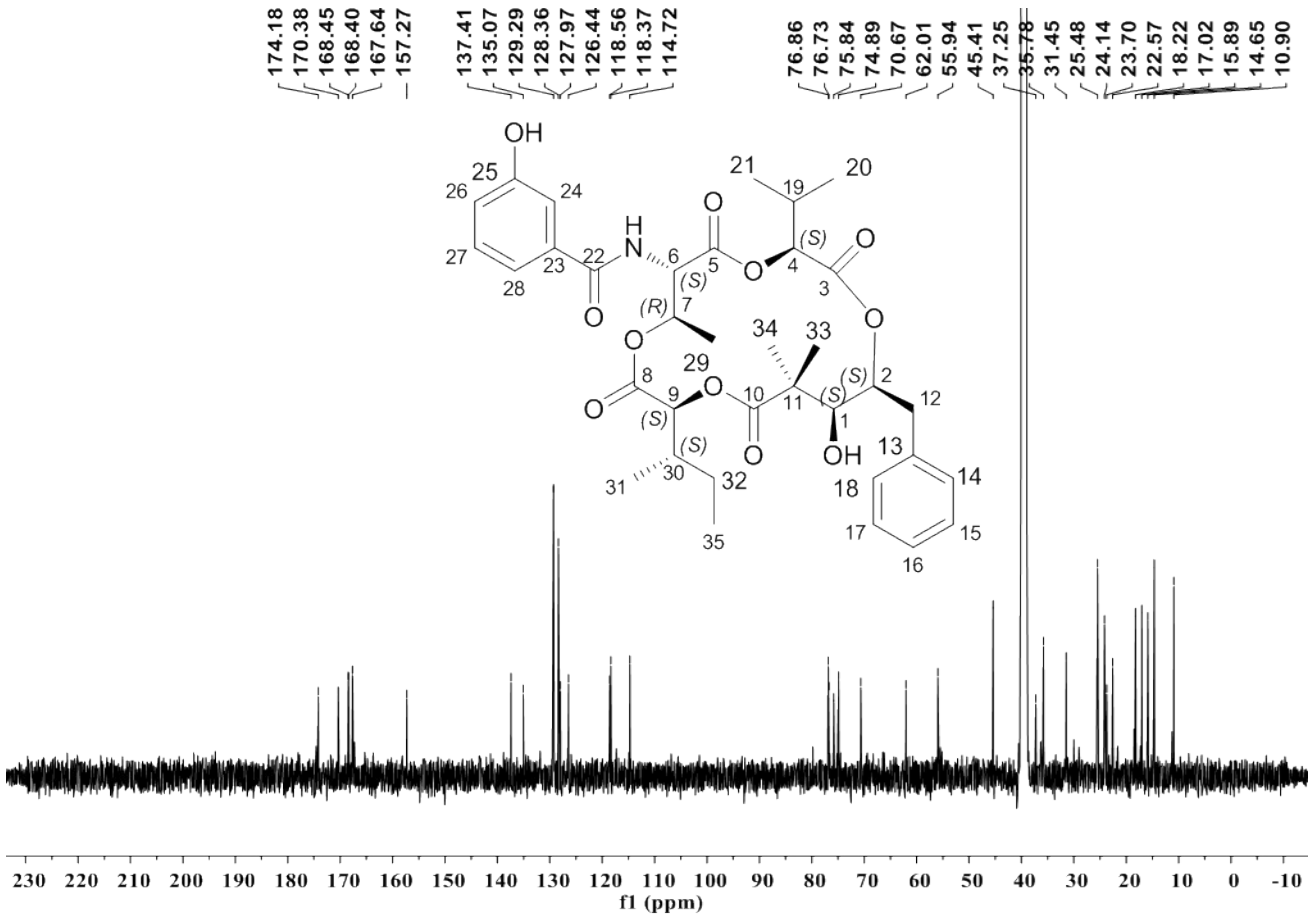


Figure S8b ^{13}C NMR spectrum of 7 in DMSO-d_6

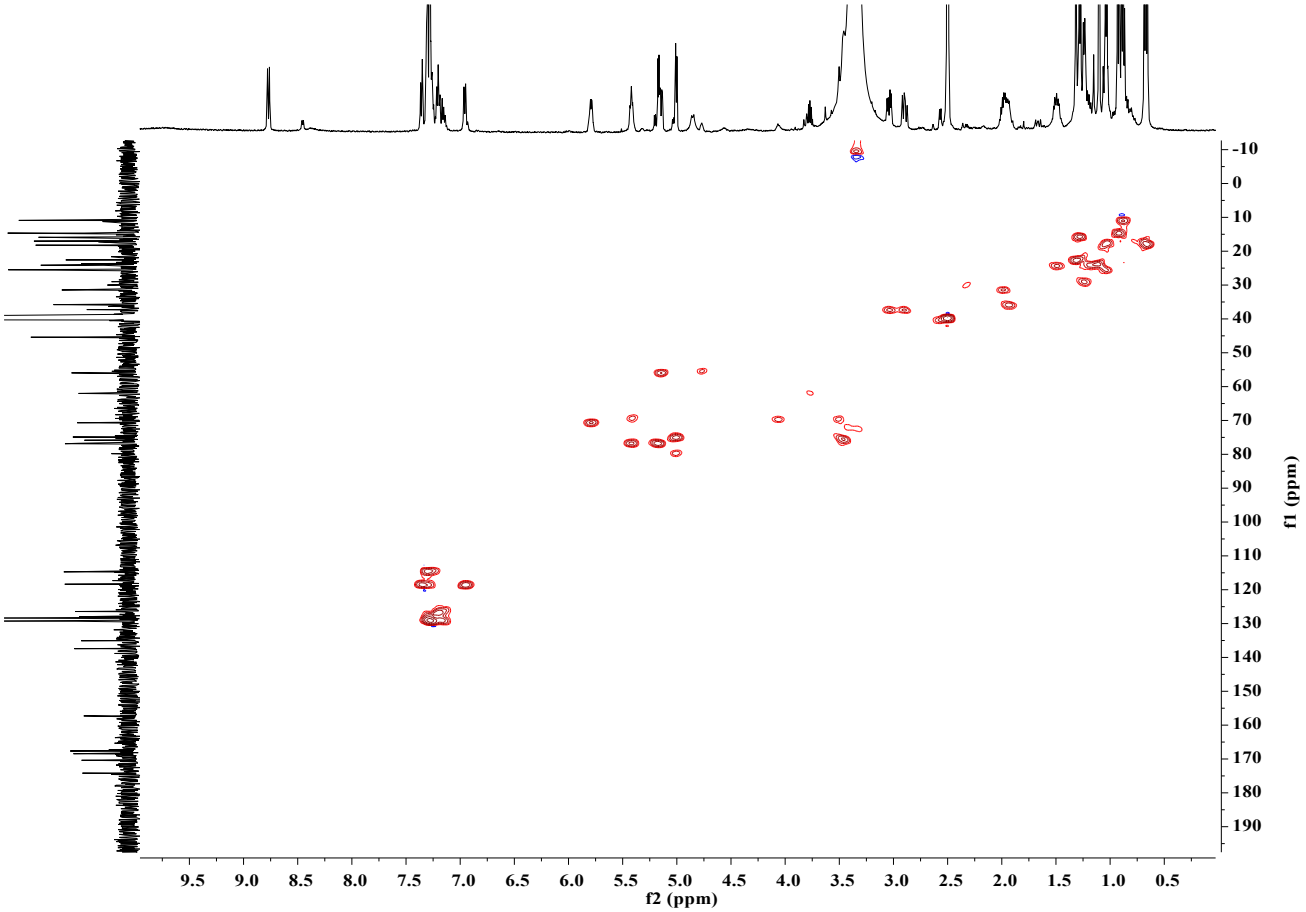


Figure S8c HSQC spectrum of 7 in DMSO-d_6

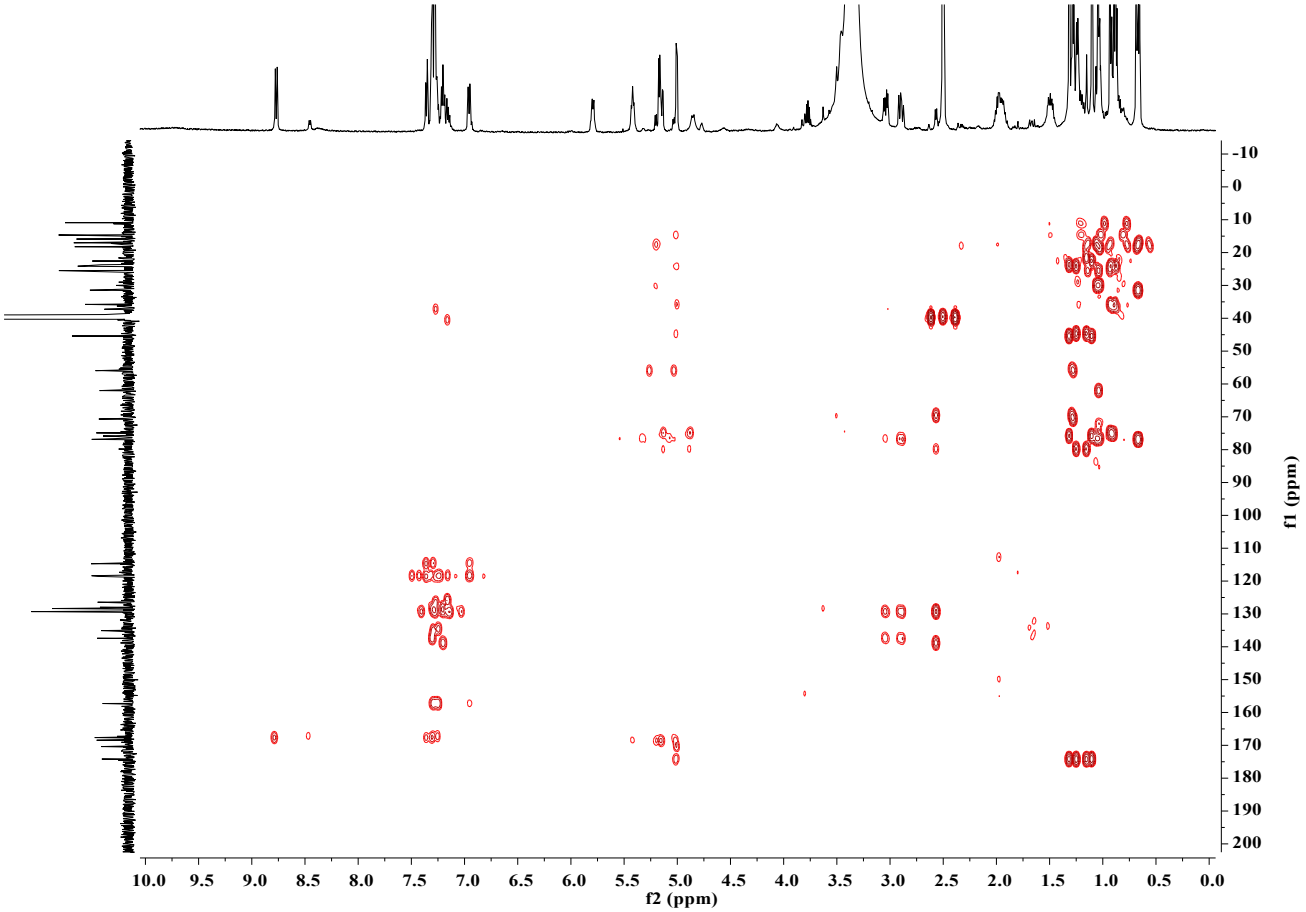


Figure S8d HMBC spectrum of 7 in DMSO-d_6

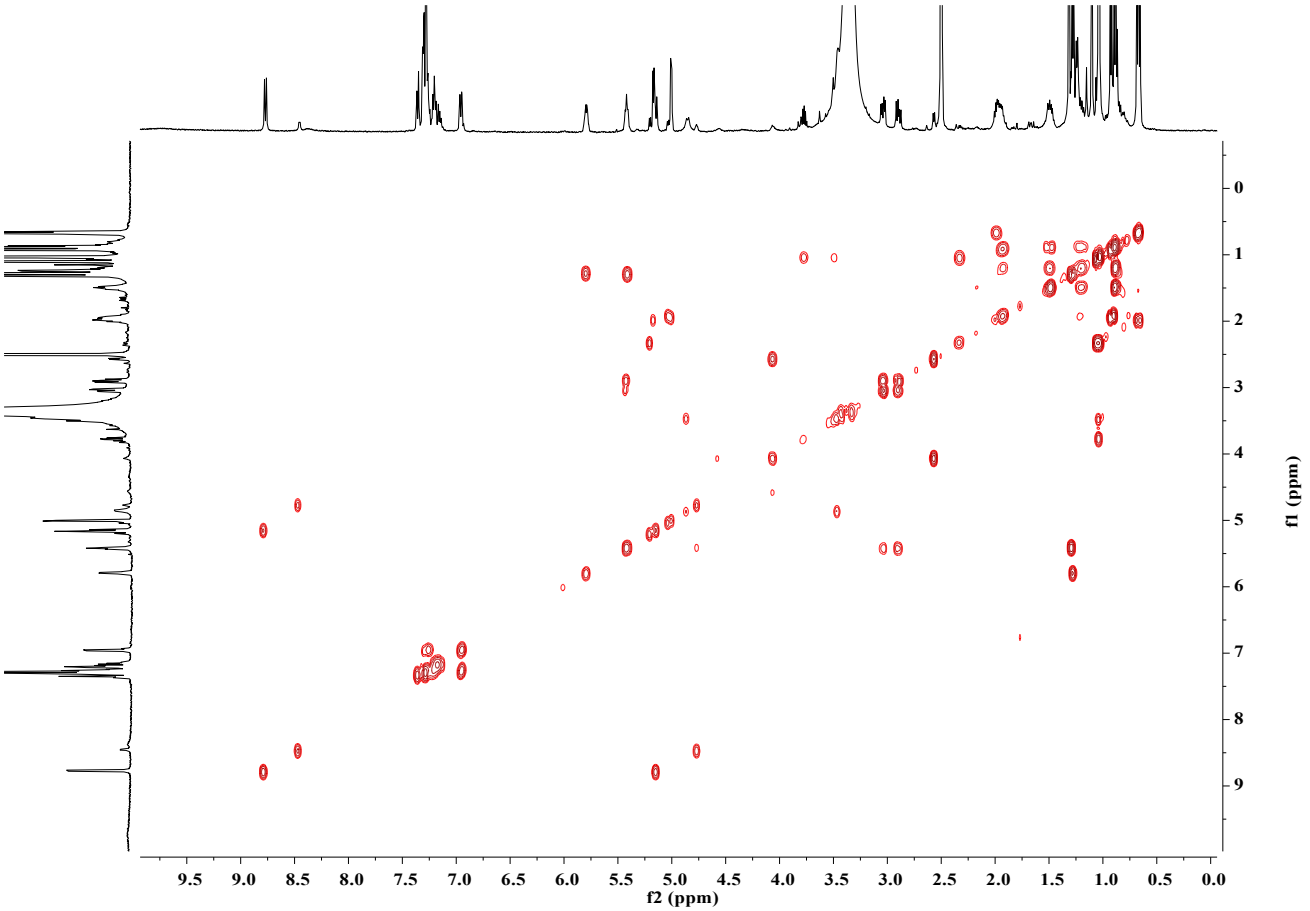


Figure S8e ^{1}H-^{1}H COSY spectrum of 7 in DMSO-d_6

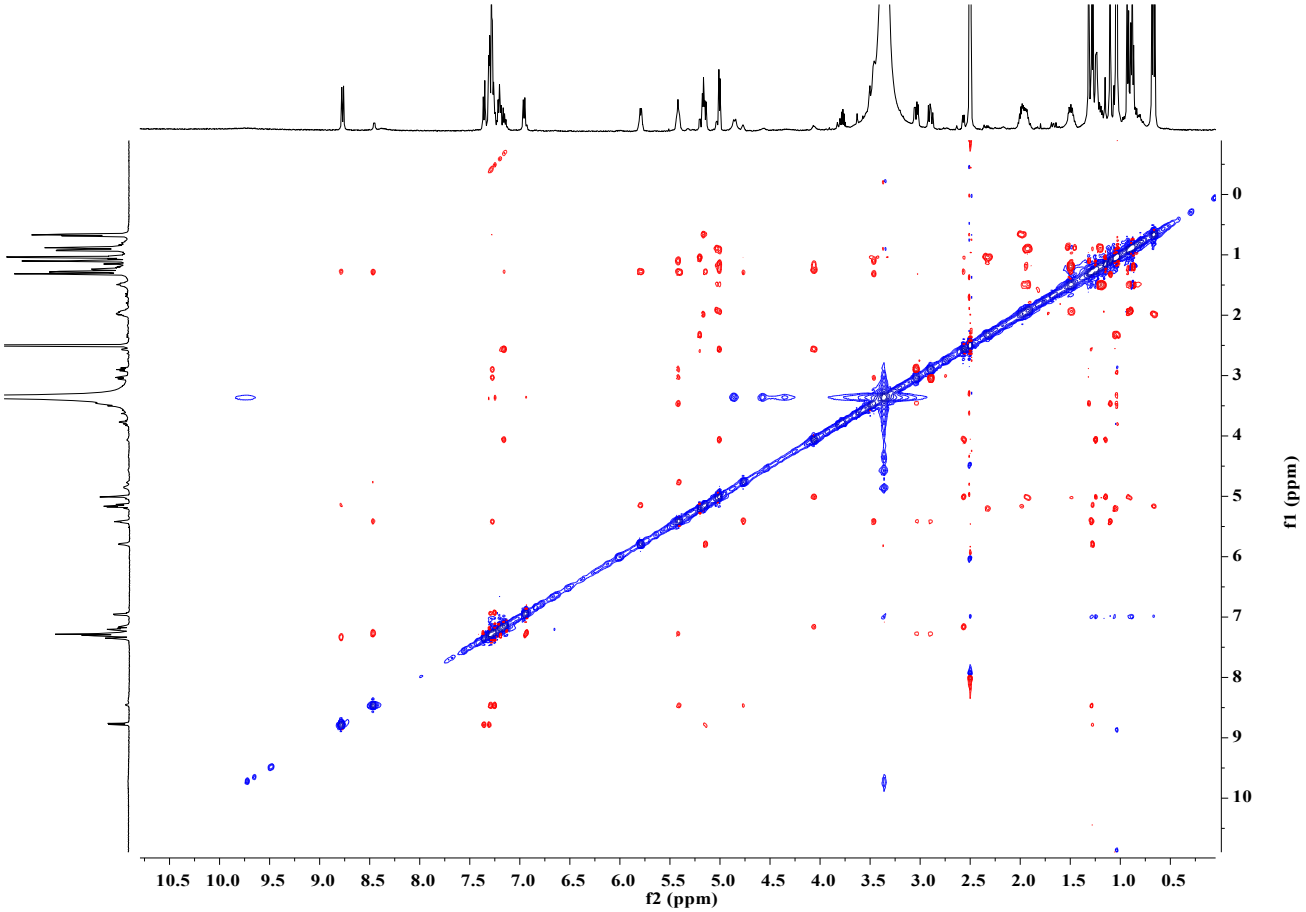


Figure S8f ROESY spectrum of 7 in DMSO-d_6

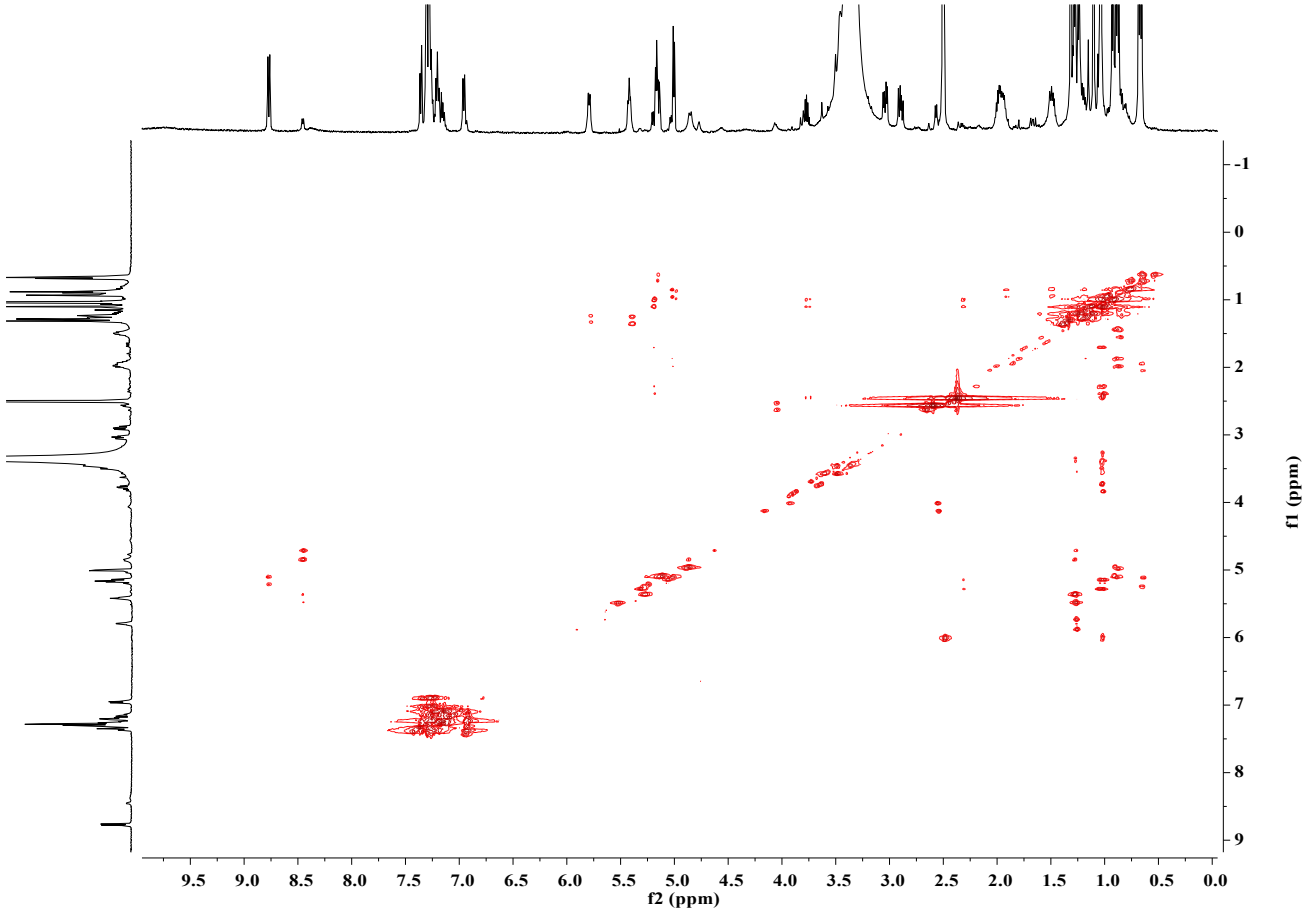


Figure S8g HETLOC spectrum of 7 in DMSO-d_6

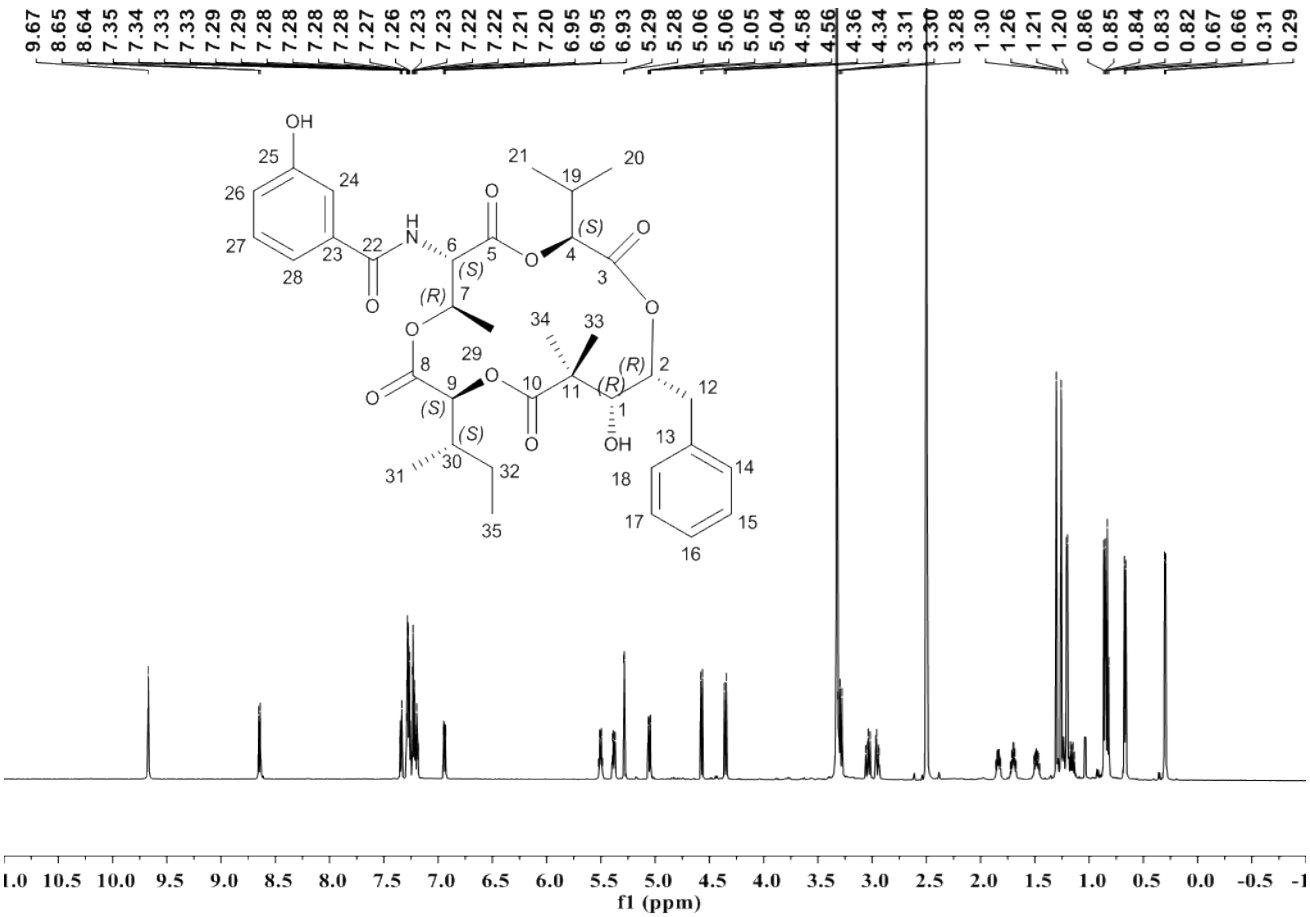


Figure S9a ^{1}H NMR spectrum of 8 in DMSO-d_6

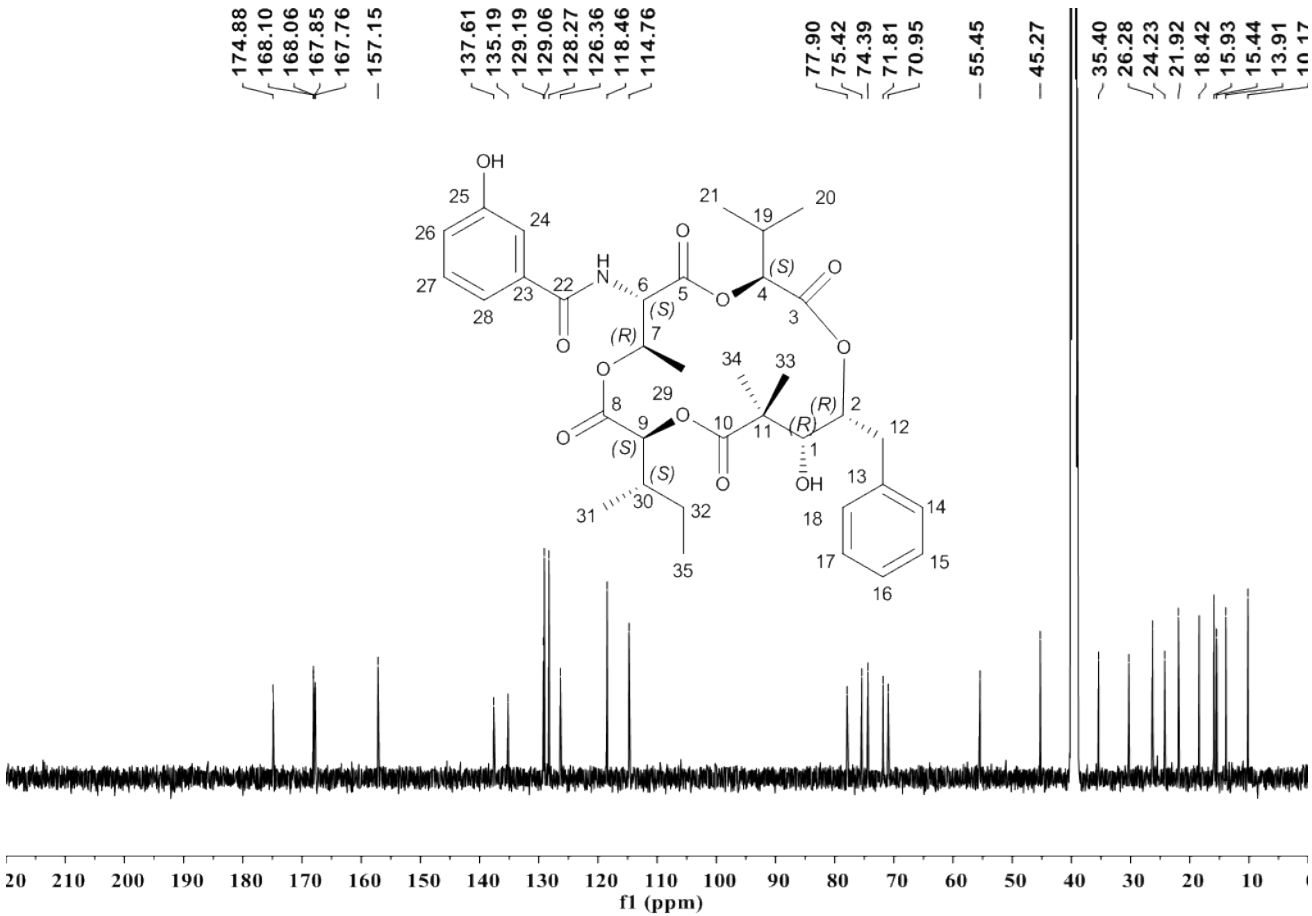


Figure S9b ^{13}C NMR spectrum of 8 in DMSO-d_6

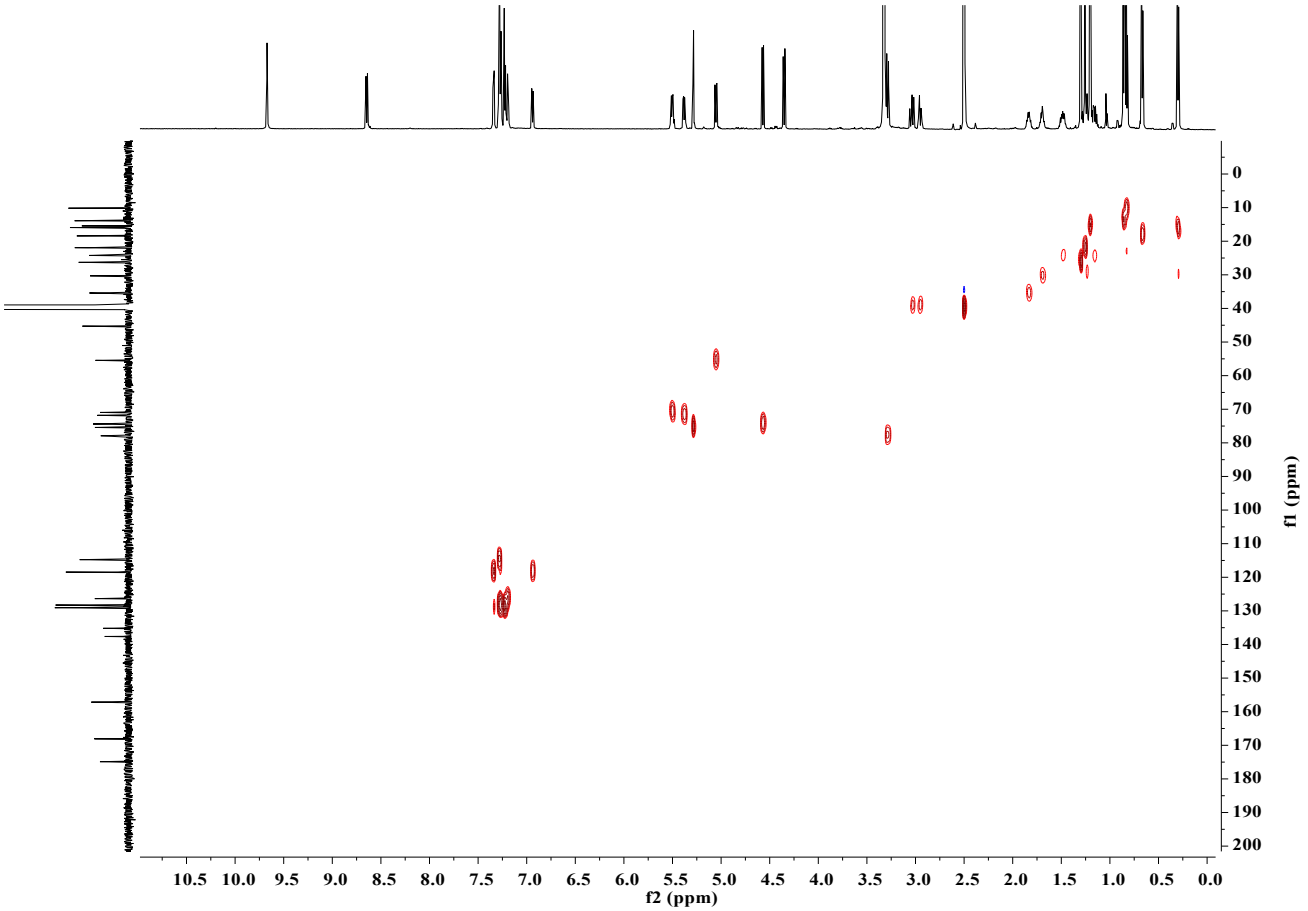


Figure S9c HSQC spectrum of 8 in DMSO-d_6

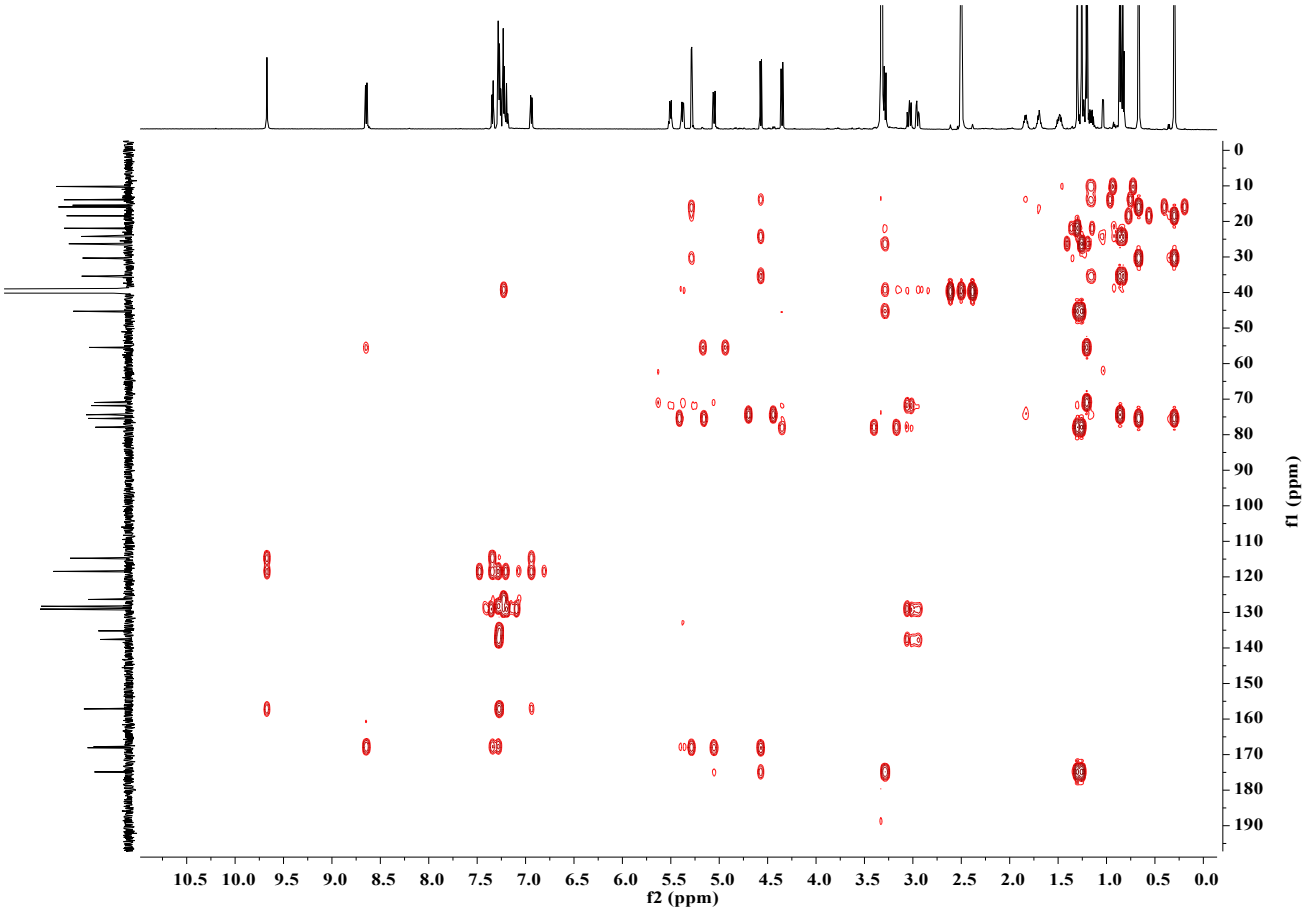


Figure S9d HMBC spectrum of 8 in DMSO-d_6

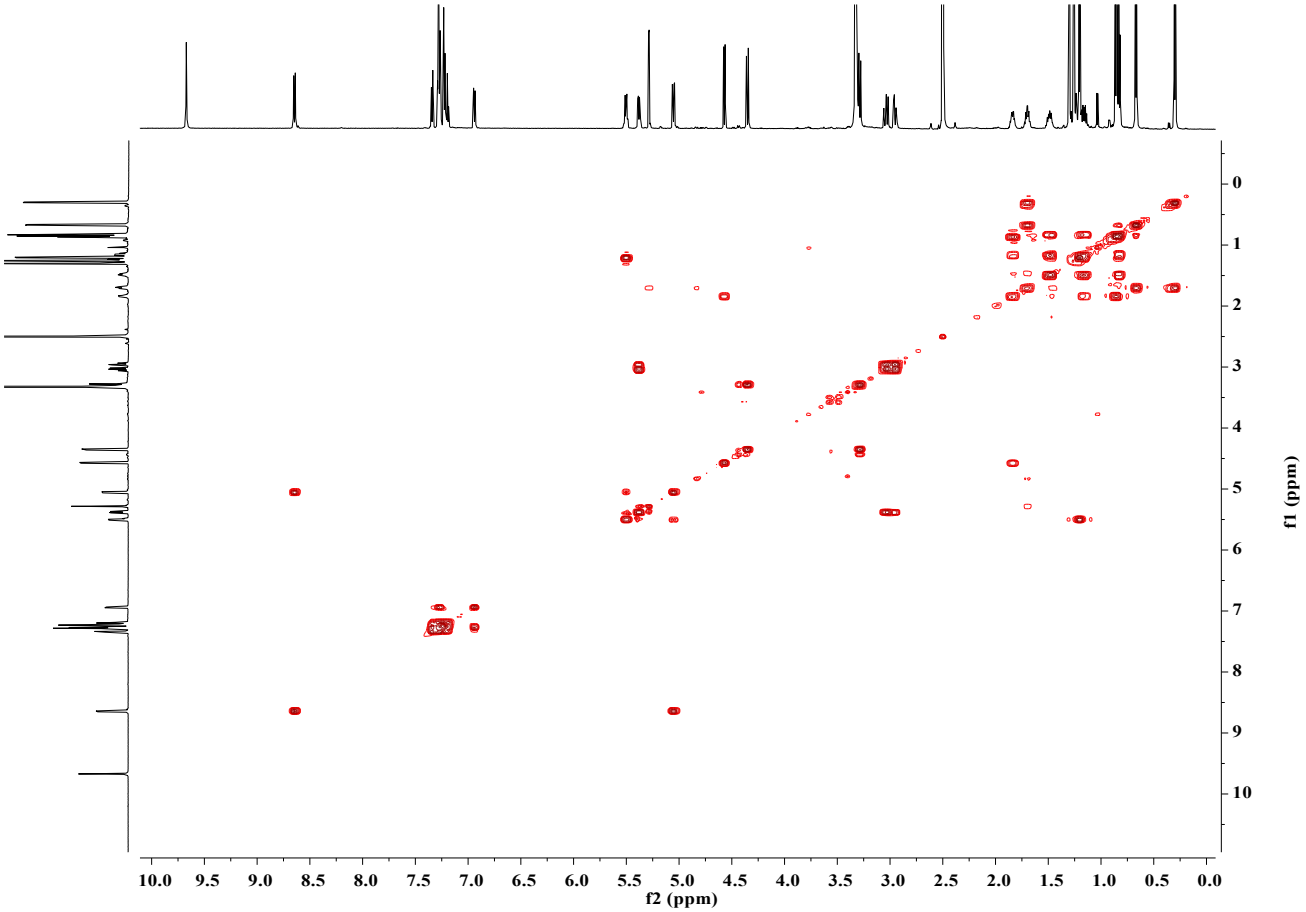


Figure S9e ^{1}H-^{1}H COSY spectrum of 8 in DMSO-d_6

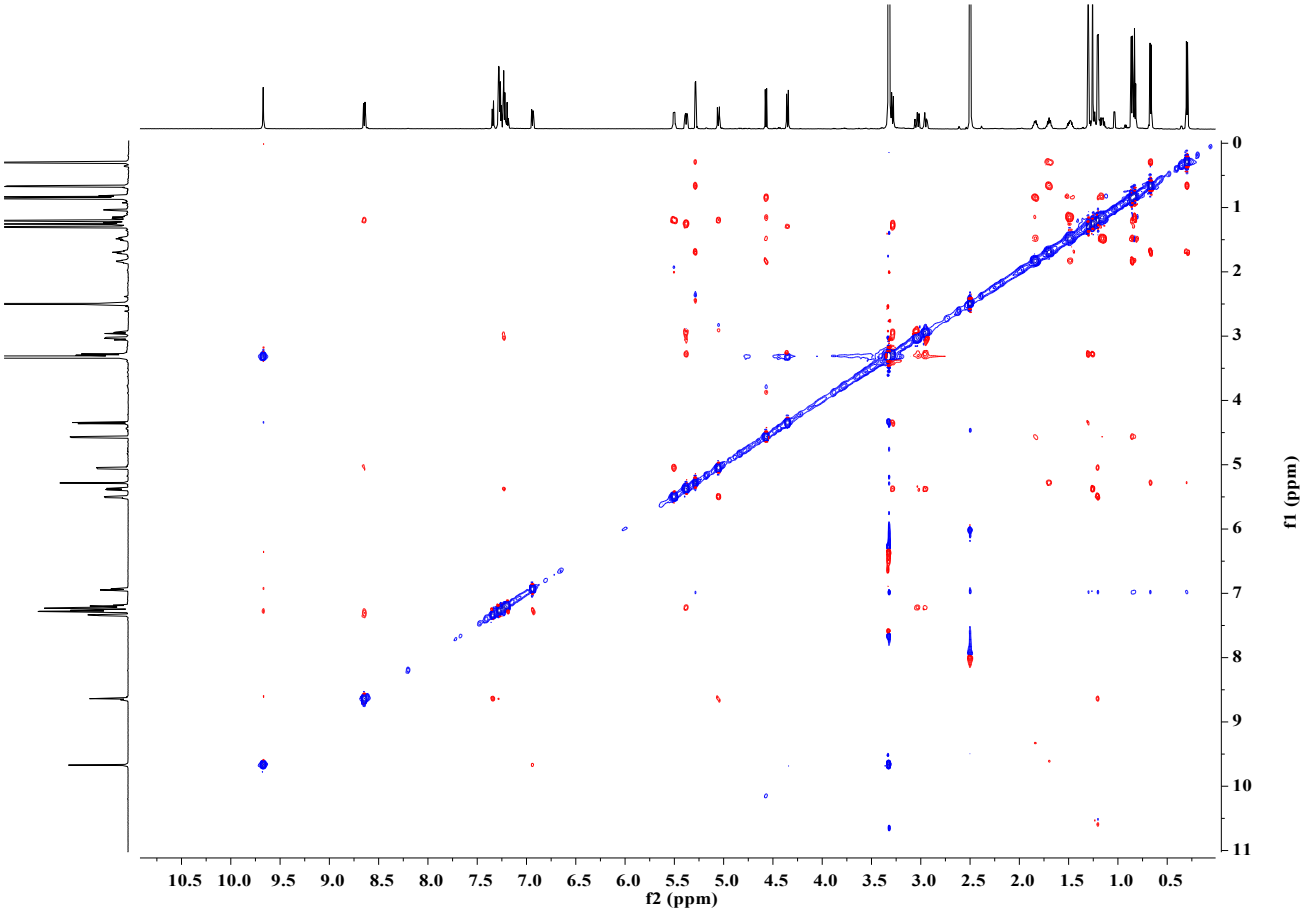


Figure S9f ROESY spectrum of 8 in DMSO-d_6

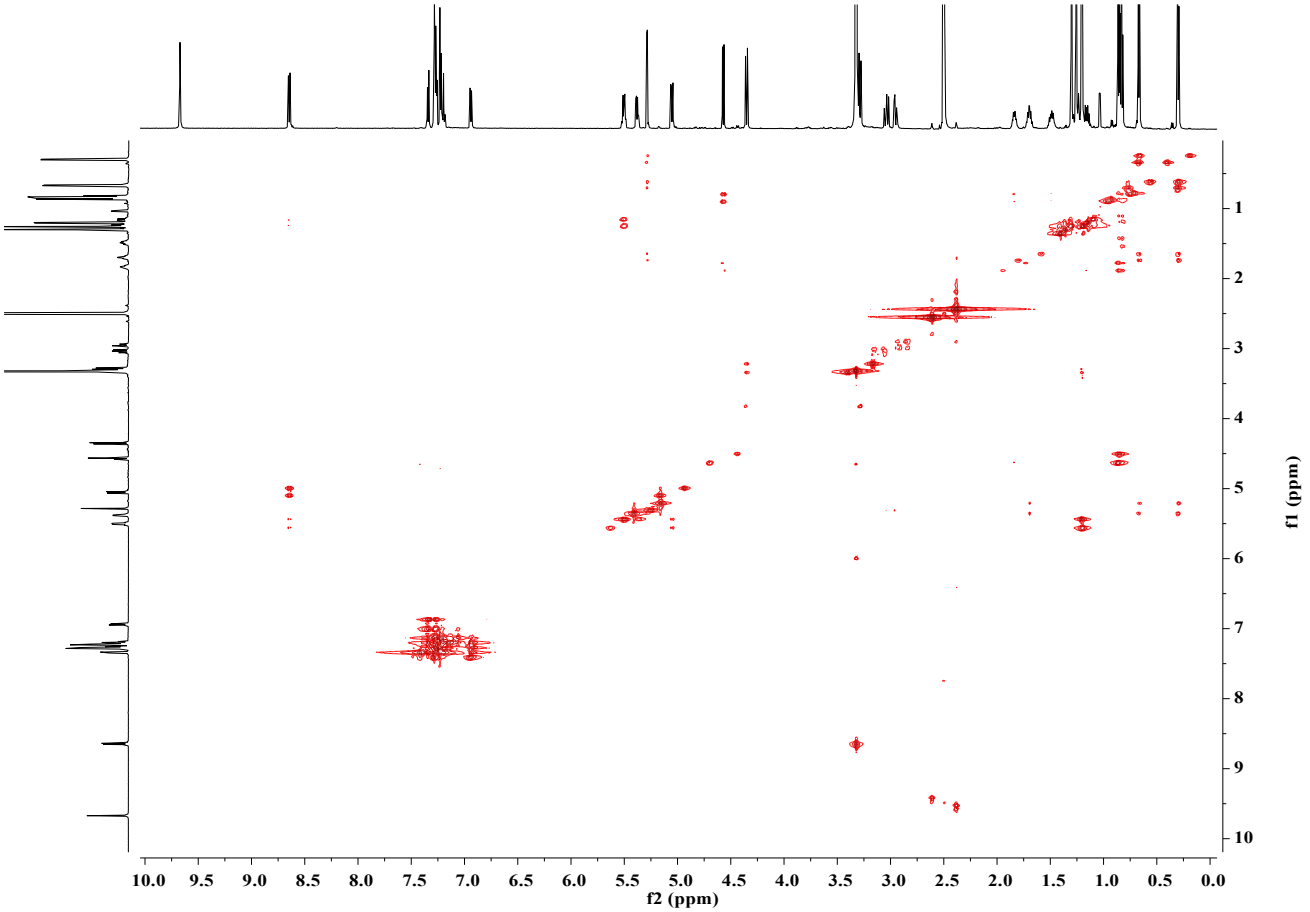


Figure S9g HETLOC spectrum of 8 in DMSO-d_6

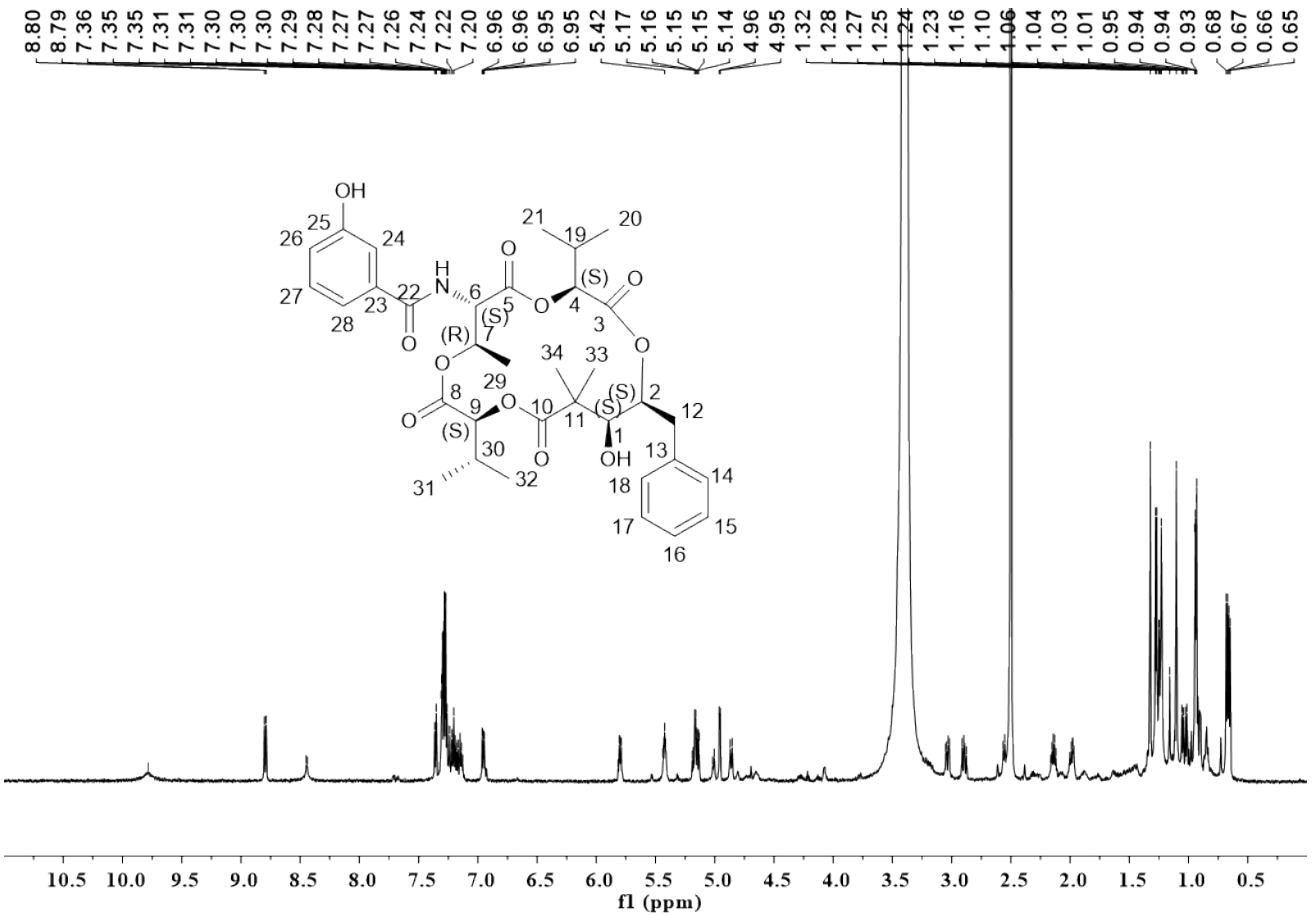


Figure S10 ^{1}H NMR spectrum of 9 in DMSO-d_6

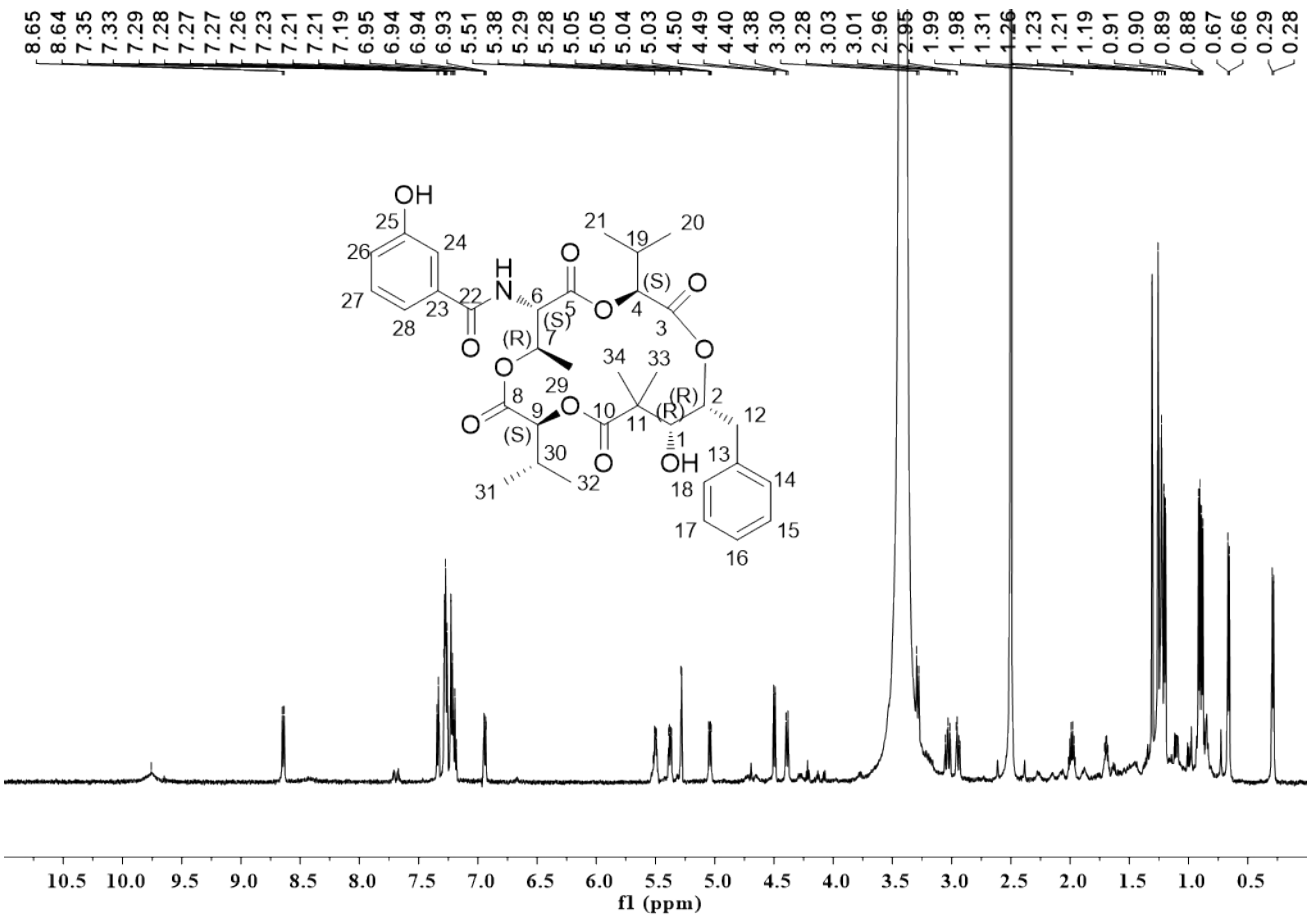


Figure S11 ^{1}H NMR spectrum of 10 in DMSO-d_6

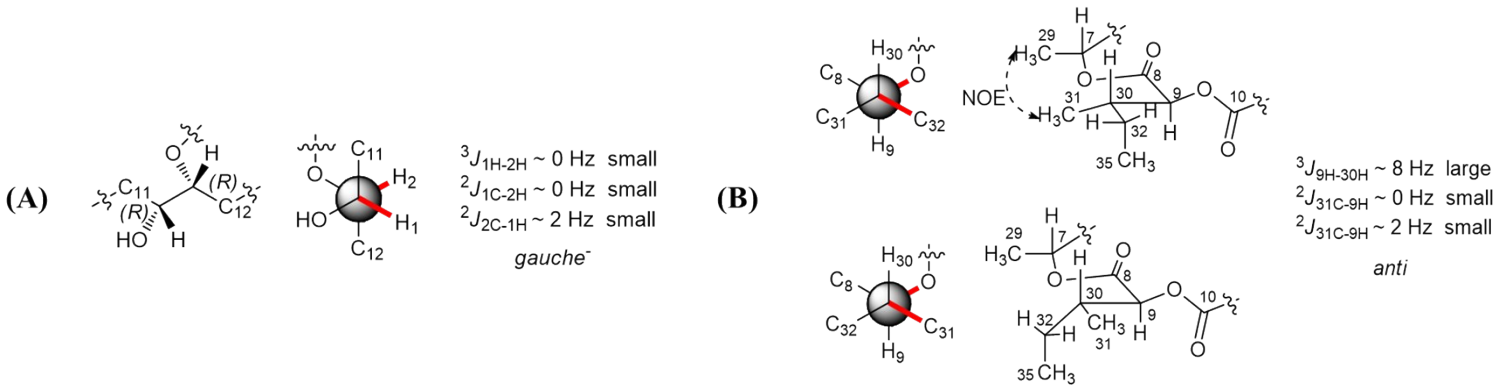
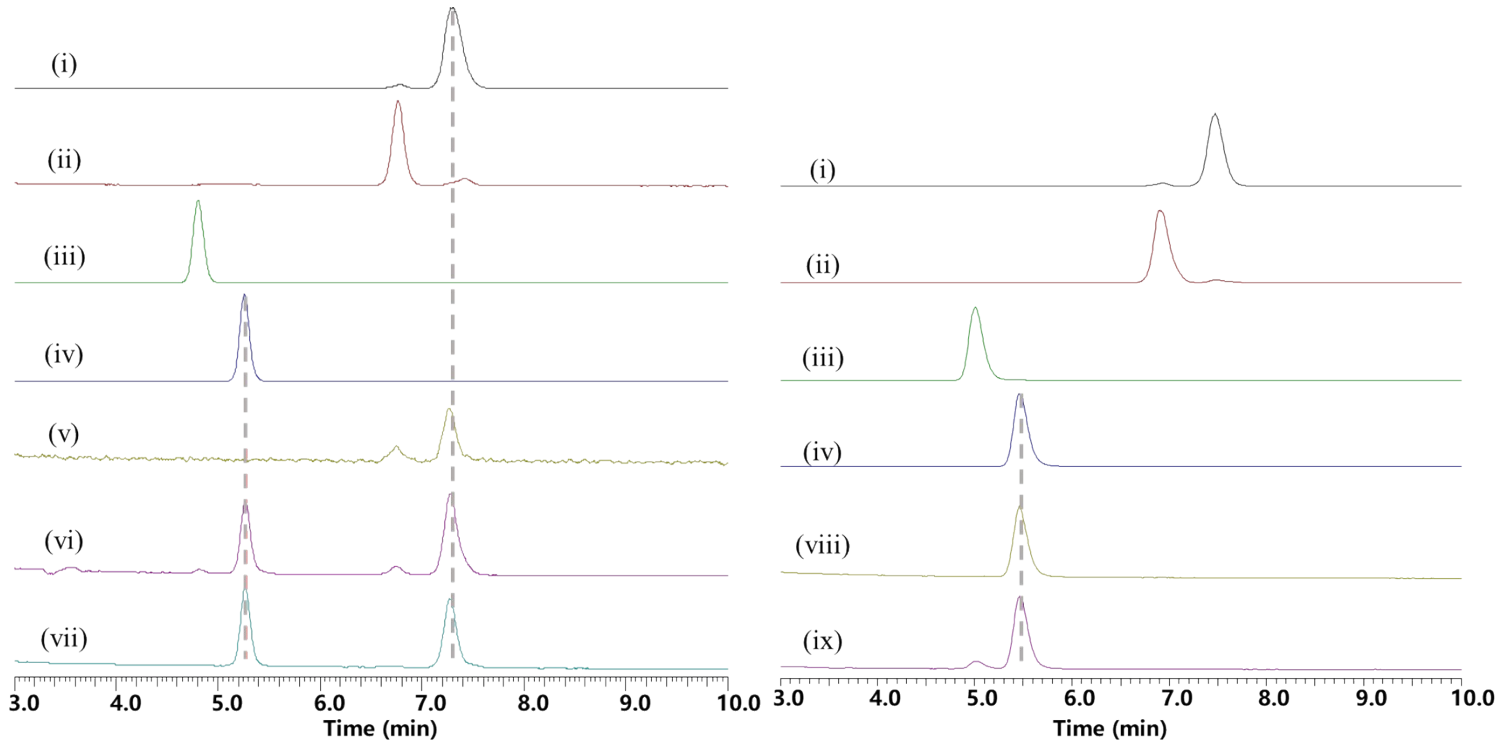


Figure S12 Relative Stereochemical Analysis of NATs

(A) The Relative stereochemistry of C-1 and C-2; (B) The Relative stereochemistry of C-9 and C-30



c

Figure S13 LC-MS chromatogram of extracted ion at 333 $[M - H]^-$ and 347 $[M - H]^-$ from Mosher's esterification reaction of 6-10

(i) *L*-Ila reacted with *R*-MTPA-Cl, (ii) *D*-Ila reacted with *R*-MTPA-Cl, (iii) (2*R*)-Hia reacted with *R*-MTPA-Cl, (iv) (2*S*)-Hia reacted with *R*-MTPA-Cl, (v) Hydrolysate of **6** reacted with *R*-MTPA-Cl, (vi) Hydrolysate of **7** reacted with *R*-MTPA-Cl, (vii) Hydrolysate of **8** reacted with *R*-MTPA-Cl, (viii) Hydrolysate of **9** reacted with *R*-MTPA-Cl, (ix) Hydrolysate of **10** reacted with *R*-MTPA-Cl

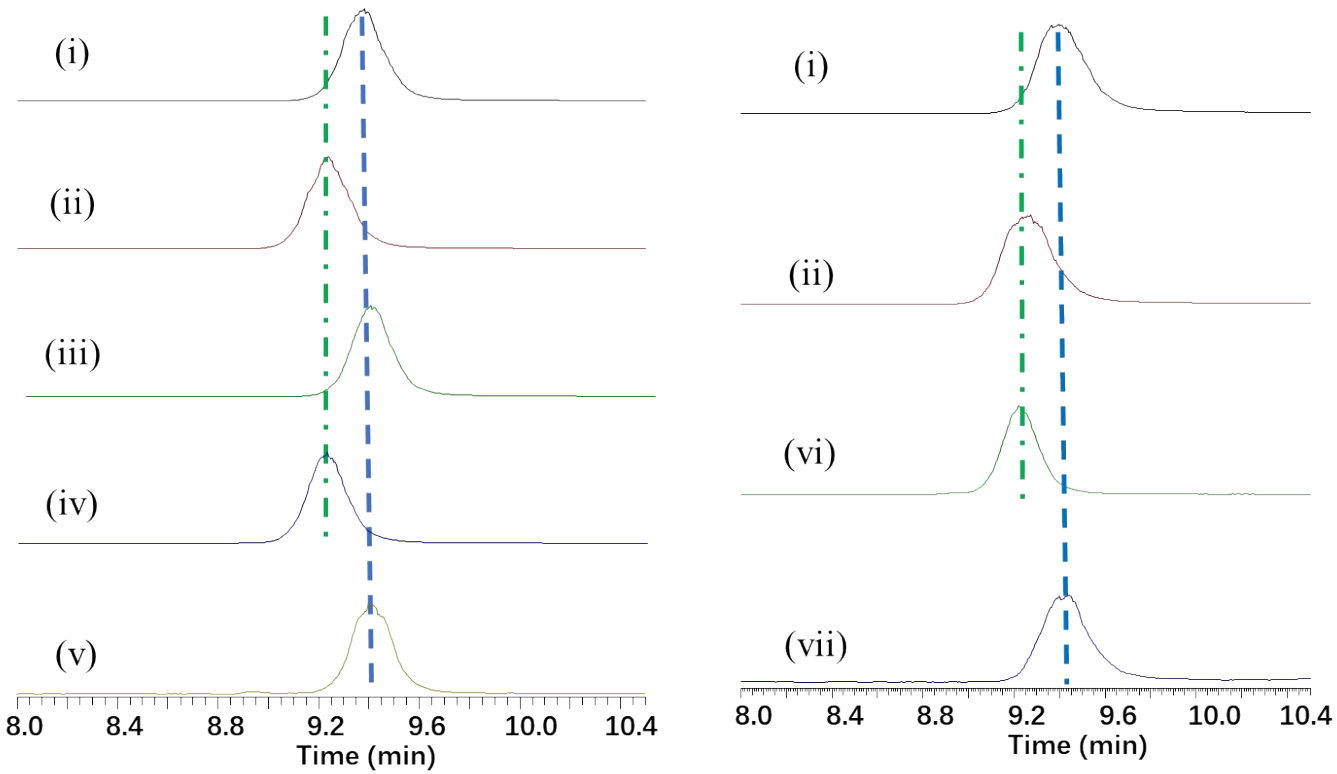


Figure S14 LC-MS chromatogram of extracted ion at 437 [M + H]+from Mosher's esterification reaction of 6-10

(i) (4*R*, 5*R*)-Bhdo reacted with *R*-MTPA-Cl, (ii) (4*R*, 5*R*)-Bhdo reacted with *S*-MTPA-Cl, (iii) Hydrolysed sample of **6** reacted with *R*-MTPA-Cl, (iv) Hydrolysed sample of **7** reacted with *R*-MTPA-Cl, (v) Hydrolysed sample of **8** reacted with *R*-MTPA-Cl, (vi) Hydrolysed sample of **9** reacted with *R*-MTPA-Cl, (vii) Hydrolysed sample of **10** reacted with *R*-MTPA-Cl

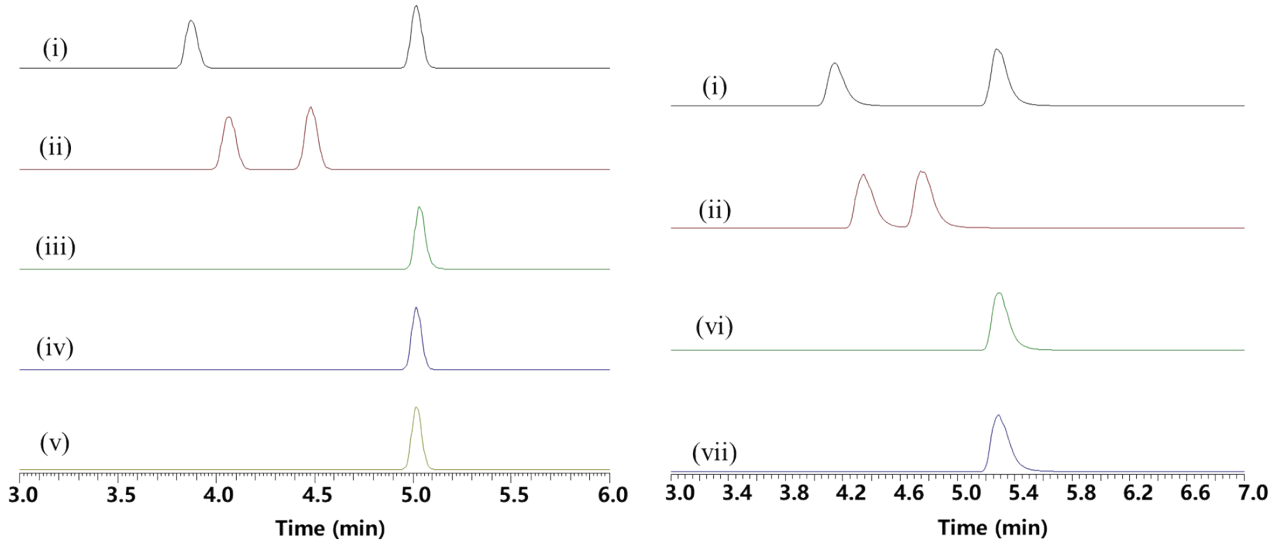


Figure S15 LC-MS chromatogram of extracted ion at 412 $[M - H]^-$ from FDLA 6-10

(i) Standard *L*-threonine reacted with *L*-FDLA or *D*-FDLA to give (a) *L*-FDAA-*L*-Thr, (b) *D*-FDAA- *L*-Thr

(ii) Standard *L-allo*-Thr reacted with *L*-FDLA or *D*-FDLA to give (a) *L*-FDAA-*L-allo*-Thr, (b) *D*-FDAA- *L-allo*-Thr

(iii) Hydrolysate of **6** reacted with *D*-FDLA

(iv) Hydrolysate of **7** reacted with *D*-FDLA

(v) Hydrolysate of **8** reacted with *D*-FDLA

(vi) Hydrolysate of **9** reacted with *D*-FDLA

(vii) Hydrolysate of **10** reacted with *D*-FDLA