Supporting Information

Nitric Oxide Inhibitory Sesquiterpenoids and Its Dimers from *Artemisia freyniana*

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Table S1. Crystal data and structure refinement for **8**.

Identification code	artefreynic acid F (**8**)
Empirical formula	$C_{15}H_{20}O_3$
Formula weight	248.31
Temperature/K	293
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	6.83018(8)
b/Å	26.1293(3)
c/Å	7.49108(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1336.92(3)
Z	4
ρ_{calc}g/cm^3	1.234
μ/mm^{-1}	0.680
F(000)	536.0
Crystal size/mm^3	0.78 × 0.47 × 0.29
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/ °	6.766 to 137.248
Index ranges	$-7 \leq h \leq 6$, $-31 \leq k \leq 29$, $-8 \leq l \leq 5$
Reflections collected	10436
Independent reflections	2395 [R_{int} = 0.0269, R_{sigma} = 0.0150]
Data/restraints/parameters	2395/0/166
Goodness-of-fit on F^2	1.148
Final R indexes [I>=2σ (I)]	R_1 = 0.0456, wR_2 = 0.1088
Final R indexes [all data]	R_1 = 0.0523, wR_2 = 0.1169
Largest diff. peak/hole / e Å^{-3}	0.13/-0.15
Flack parameter	0.01(9)

Table S2. Cartesian coordinates of low-energy optimized conformers of compound **1**.

Cartesian coordinate of low-energy optimized conformers of (4*S*,5*R*,7*R*,8*R*,11*S*,2′*S*,4′*S*,6′*S*,7′*S*,10′*S*,11′*S*)-**1** optimized: [method: B3LYP/6-31+G (d)

Total Energy, E(TD-HF/TD-KS) = -1543.26037102 A.U.

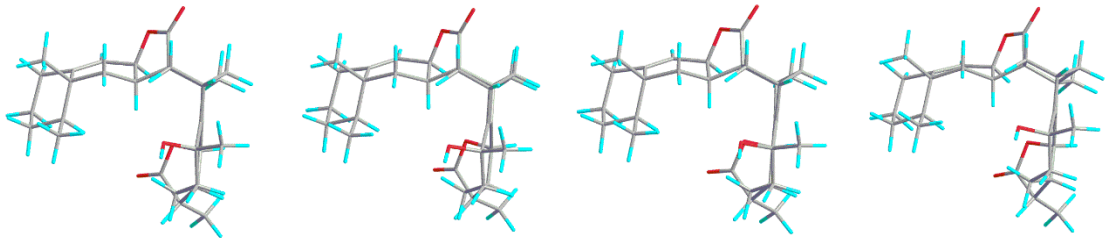
Stoichiometry C30H4005
Framework group C1[X(C30H4005)]
Deg. of freedom 219
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.083378	0.704208	-0.393134
2	6	0	4.728580	2.176746	-0.079405
3	6	0	2.703601	1.386072	1.315454
4	6	0	3.102577	-0.110508	1.020681
5	6	0	3.809545	-0.101598	-0.331076
6	6	0	1.889154	-1.069756	0.977783
7	6	0	0.993179	-0.918938	-0.260855
8	6	0	1.841212	-1.091620	-1.528417
9	6	0	3.253771	-0.611020	-1.441460
10	6	0	1.965165	1.600593	2.646347
11	6	0	4.050132	-0.668411	2.115399
12	8	0	1.776271	-2.537142	-1.821832
13	6	0	-0.072550	-2.039826	-0.411329
14	6	0	-0.676384	-2.638758	0.896103
15	6	0	-2.073688	-0.472389	-0.455105
16	6	0	-2.523541	-0.971510	0.720063
17	6	0	-2.169370	0.882468	-1.101674
18	6	0	-2.953450	2.053423	-0.474246
19	6	0	-2.893090	2.135784	1.054019
20	6	0	-3.731876	1.069951	1.759915
21	6	0	-3.061684	-0.298530	1.975754
22	6	0	-4.059420	-1.203368	2.723906
23	8	0	-1.874270	-0.128789	2.797694
24	6	0	-2.271126	3.270990	-1.140208
25	6	0	-0.849523	2.782697	-1.371442
26	6	0	-2.905213	3.721820	-2.470180
27	8	0	-0.812971	1.428490	-1.311483

28	6	0	0.706537	-3.090198	-1.210549
29	8	0	0.457900	-4.273274	-1.337245
30	8	0	0.147201	3.434328	-1.593688
31	6	0	-2.209809	-2.471826	0.707750
32	6	0	-2.351667	-2.793259	-0.784443
33	6	0	-1.423643	-1.642742	-1.236715
34	6	0	-1.290733	-1.474924	-2.748706
35	6	0	3.936494	2.315778	1.230695
36	1	0	5.822333	0.343223	0.333477
37	1	0	5.541091	0.628453	-1.385992
38	1	0	4.126255	2.569074	-0.910132
39	1	0	5.642378	2.782441	-0.034418
40	1	0	2.020886	1.689522	0.508037
41	1	0	1.301422	-0.936786	1.889043
42	1	0	2.278316	-2.097145	1.013313
43	1	0	0.530834	0.066539	-0.261889
44	1	0	1.366420	-0.601848	-2.384674
45	1	0	3.796745	-0.556990	-2.384469
46	1	0	1.020172	1.049342	2.693930
47	1	0	1.727533	2.663980	2.770636
48	1	0	2.577255	1.300910	3.505104
49	1	0	4.888258	-0.005361	2.341650
50	1	0	3.498618	-0.834899	3.046958
51	1	0	4.464408	-1.633051	1.800337
52	1	0	-0.422743	-3.699895	0.980427
53	1	0	-0.331269	-2.131089	1.795682
54	1	0	-2.561815	0.720928	-2.112930
55	1	0	-4.003123	1.983057	-0.781353
56	1	0	-1.855597	2.083005	1.407304
57	1	0	-3.270155	3.124010	1.344642
58	1	0	-4.001110	1.438446	2.758629
59	1	0	-4.681071	0.925938	1.226073
60	1	0	-4.469937	-0.667093	3.587585
61	1	0	-3.574452	-2.110118	3.092569
62	1	0	-4.897924	-1.491127	2.080182
63	1	0	-2.176241	0.137761	3.683516
64	1	0	-2.232625	4.130433	-0.463140
65	1	0	-2.309859	4.518982	-2.926356
66	1	0	-2.976366	2.897286	-3.188002
67	1	0	-3.914717	4.104112	-2.290170
68	1	0	-2.794715	-3.079005	1.397760
69	1	0	-3.370666	-2.660712	-1.163092
70	1	0	-1.977912	-3.784420	-1.057887
71	1	0	-2.283419	-1.369204	-3.202039

72	1	0	−0. 704333	−0. 596302	−3. 032260
73	1	0	−0. 825223	−2. 356510	−3. 201986
74	1	0	3. 599576	3. 354620	1. 342689
75	1	0	4. 600381	2. 122490	2. 084142



1a 0 kcal/mol **1b** 0.4 kcal/mol **1c** 0.7 kcal/mol **1d** 1.2 kcal/mol

The most Stable Conformers of (4*S*,5*R*,7*R*,8*R*,11*S*,2′*S*,4′*S*,6′*S*,7′*S*,10′*S*,11′*S*)-**1**

Table S3. B3LYP-Calculated relative energies (kcal/mol) and conformational population (%) for the most stable conformers of (4*S*,5*R*,7*R*,8*R*,11*S*,2′*S*,4′*S*,6′*S*,7′*S*,10′*S*,11′*S*)-**1**.

Conf	$\Delta E_{6\text{-}31+G(d)}$[a]	%[b]
1a	0	51.4
1b	0.4	26.1
1c	0.7	15.7
1d	1.2	6.7

[a]Relative to 1a with $E_{6\text{-}31+G(d)}$ = -968410.54 kcal/mol. [b]Calculated using free energy values from Gaussian 03W according to $\Delta G = -RT$ In K.

Table S4. Cartesian coordinates of low-energy optimized conformers of compound **2**.

Cartesian coordinate of low-energy optimized conformers of

(4*S*,5*R*,7*S*,9*R*,10*R*,4'*S*,5'*R*,7'*S*)-**2** optimized: [method: B3LYP/6-31+G (d)

Total Energy, E(TD-HF/TD-KS) = -1619.75490739 A.U.

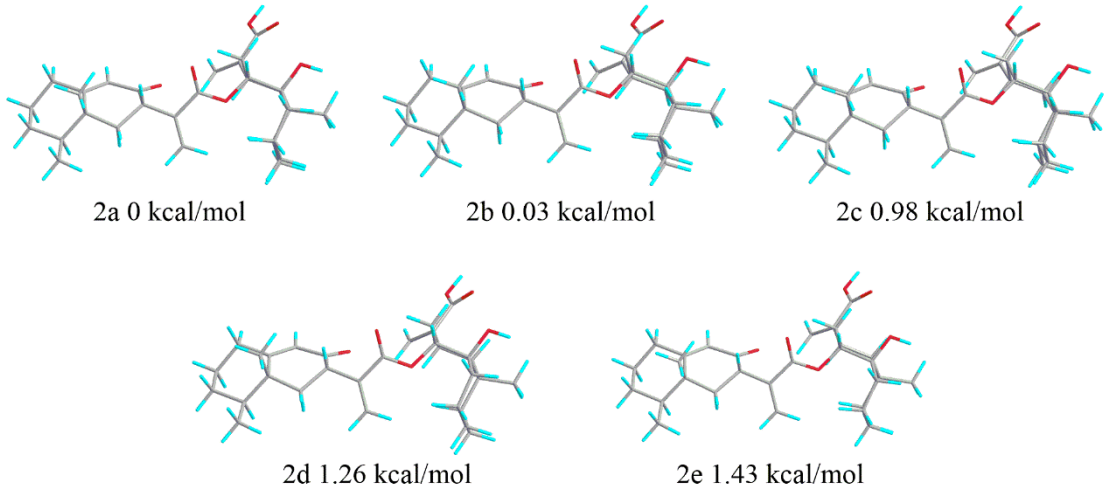
Stoichiometry C30H4206
Framework group C1[X(C30H4206)]
Deg. of freedom 228
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.803731	1.859537	-0.022629
2	6	0	5.001980	1.242794	-0.129167
3	6	0	2.510272	1.175182	-0.086241
4	6	0	2.557587	-0.318691	-0.431551
5	6	0	3.806215	-0.954282	0.196176
6	6	0	5.136708	-0.278741	-0.228240
7	6	0	1.241315	-0.986680	-0.086002
8	6	0	0.125837	-0.655604	-1.029574
9	6	0	1.054583	-1.813601	0.949075
10	8	0	0.314852	-0.225495	-2.155104
11	8	0	-1.101336	-0.888005	-0.515605
12	6	0	-2.240291	-0.462786	-1.320015
13	6	0	-3.483727	-1.357453	-1.040004
14	6	0	-4.157911	-1.103343	0.365582
15	6	0	-4.307366	0.429240	0.585432
16	6	0	-3.016298	1.248119	0.379116
17	6	0	-2.492068	1.021271	-1.052115
18	6	0	-3.194047	-2.854016	-1.285186
19	6	0	-2.463780	-3.583026	-0.148770
20	6	0	-3.096394	-3.295670	1.218574
21	6	0	-3.299374	-1.789302	1.490978
22	8	0	-4.353780	-0.893586	-2.097826
23	6	0	-5.597887	-1.673438	0.368683
24	6	0	-3.841061	-1.594153	2.918416
25	6	0	-3.192217	2.719522	0.720492
26	6	0	-2.492757	3.304086	1.705100
27	6	0	6.269602	2.060116	-0.183728

28	6	0	7.570615	0.058163	0.622939
29	6	0	6.269924	-0.754444	0.759270
30	8	0	1.451149	1.778240	0.080061
31	6	0	6.571506	-2.259537	0.678743
32	6	0	5.474681	-0.643772	-1.698634
33	6	0	-4.167333	3.530158	-0.069481
34	8	0	-4.820101	3.118835	-1.015227
35	8	0	-4.279767	4.811252	0.354892
36	6	0	7.330276	1.557581	0.809665
37	1	0	3.749354	2.942030	0.077028
38	1	0	2.650725	-0.352187	-1.526179
39	1	0	3.727274	-0.894596	1.289581
40	1	0	3.832065	-2.017357	-0.062499
41	1	0	0.085390	-2.250349	1.159248
42	1	0	1.865102	-2.086448	1.617025
43	1	0	-1.974532	-0.612297	-2.367681
44	1	0	-4.704581	0.613942	1.589443
45	1	0	-5.057460	0.800259	-0.118476
46	1	0	-2.251876	0.877773	1.072492
47	1	0	-3.225168	1.382934	-1.776247
48	1	0	-1.559576	1.571959	-1.217123
49	1	0	-2.641657	-2.951365	-2.228431
50	1	0	-4.162774	-3.347725	-1.449212
51	1	0	-1.412224	-3.283705	-0.137473
52	1	0	-2.477280	-4.662113	-0.348765
53	1	0	-2.462029	-3.715785	2.010331
54	1	0	-4.060020	-3.817377	1.299164
55	1	0	-2.306286	-1.327310	1.466617
56	1	0	-5.075268	-1.535712	-2.184747
57	1	0	-5.637942	-2.756614	0.220433
58	1	0	-6.089410	-1.457176	1.322401
59	1	0	-6.205457	-1.202573	-0.410495
60	1	0	-3.940957	-0.538890	3.191236
61	1	0	-4.816718	-2.072745	3.060697
62	1	0	-3.149263	-2.049913	3.636825
63	1	0	-2.612648	4.352053	1.955328
64	1	0	-1.772427	2.737432	2.289118
65	1	0	6.038998	3.117401	-0.015287
66	1	0	6.685188	1.987660	-1.200361
67	1	0	8.288954	-0.302814	1.369939
68	1	0	8.031054	-0.125179	-0.358196
69	1	0	5.881392	-0.552946	1.769601
70	1	0	7.281045	-2.533307	1.468029
71	1	0	7.028634	-2.531386	-0.279399

72	1	0	5.678006	−2.876969	0.814374
73	1	0	6.447238	−0.247729	−2.004433
74	1	0	5.497181	−1.729770	−1.830857
75	1	0	4.726755	−0.238031	−2.387526
76	1	0	−4.929198	5.240476	−0.233675
77	1	0	8.260030	2.121948	0.671670
78	1	0	6.988296	1.751216	1.835541



The most Stable Conformers of (4*S*,5*R*,7*S*,9*R*,10*R*,4'*S*,5'*R*,7'*S*)-**2**

Table S5. B3LYP-Calculated relative energies (kcal/mol) and conformational population (%) for the most stable conformers of (4*S*,5*R*,7*S*,9*R*,10*R*,4'*S*,5'*R*,7'*S*)-**2**.

Conf	$\Delta E_{6\text{-}31+G(d)}$[a]	%[b]
2a	0	42.5
2b	0.03	40.4
2c	0.98	8.1
2d	1.26	5.0
2e	1.43	3.8

[a]Relative to 2a with $E_{6\text{-}31+G(d)}$ = -1016411.59 kcal/mol. [b]Calculated using free energy values from Gaussian 03W according to $\Delta G = -RT \ln K$.

Table S6. Cartesian coordinates of low-energy optimized conformers of compound **3**.

Cartesian coordinate of low-energy optimized conformers of (4*S*,5*R*,7*R*)-**3** optimized: [method: B3LYP/6-31+G (d)

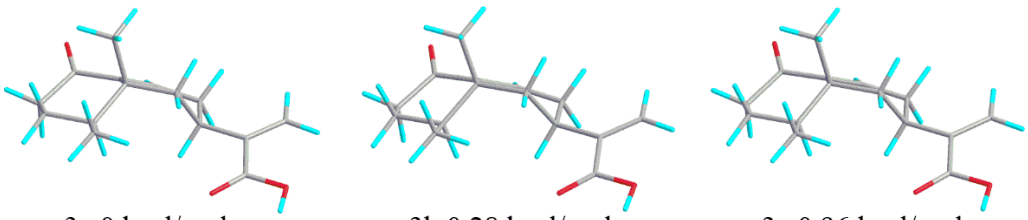
Total Energy, E(TD-HF/TD-KS) = -809.195925627 A.U.

Stoichiometry C15H2003
Framework group C1[X(C15H2003)]
Deg. of freedom 108
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.298586	-0.092744	0.145134
2	6	0	3.416556	-0.533125	-1.156083
3	6	0	3.093521	0.970579	-1.112078
4	6	0	1.622961	1.297990	-0.774062
5	6	0	1.172328	0.573540	0.547720
6	6	0	1.417193	-0.925206	0.363393
7	6	0	-0.322128	0.820482	0.898196
8	6	0	-1.010565	-1.555903	0.557692
9	6	0	0.454448	-1.864085	0.423151
10	6	0	-3.240532	1.000123	1.363400
11	6	0	-2.761172	0.261182	0.349382
12	6	0	2.009594	1.052401	1.764075
13	6	0	1.436500	2.824956	-0.773671
14	6	0	2.784897	-1.358027	-0.048283
15	6	0	-3.698427	-0.274670	-0.683100
16	8	0	-3.343651	-0.866036	-1.692776
17	8	0	3.329305	-2.371225	0.389749
18	8	0	-5.006879	-0.048263	-0.420214
19	1	0	-1.098390	-0.019835	-0.931274
20	1	0	3.009531	-0.960413	-2.086782
21	1	0	4.496047	-0.717595	-1.170310
22	1	0	3.751938	1.463725	-0.386226
23	1	0	3.339387	1.409356	-2.086621
24	1	0	0.997871	0.889149	-1.582197
25	1	0	-0.569907	1.872650	0.727288
26	1	0	-0.447250	0.648615	1.975677
27	1	0	-1.340295	-1.717918	1.596083

28	1	0	−1. 585869	−2. 255679	−0. 059377
29	1	0	0. 736418	−2. 908110	0. 293475
30	1	0	−4. 299749	1. 210019	1. 462767
31	1	0	−2. 586504	1. 420280	2. 120951
32	1	0	3. 087589	0. 939477	1. 609741
33	1	0	1. 810665	2. 107602	1. 983402
34	1	0	1. 742920	0. 470658	2. 653530
35	1	0	2. 037730	3. 308294	0. 005542
36	1	0	0. 393045	3. 123174	−0. 630891
37	1	0	1. 760413	3. 234384	−1. 738250
38	1	0	−5. 525319	−0. 418601	−1. 159779



3a 0 kcal/mol　　3b 0.28 kcal/mol　　3c 0.96 kcal/mol

The most Stable Conformers of (4*S*,5*R*,7*R*)-**3**

Table S7. B3LYP-Calculated relative energies (kcal/mol) and conformational population (%) for the most stable conformers of (4*S*,5*R*,7*R*)-**3**.

Conf	$\Delta E_{6\text{-}31+G(d)}$[a]	%[b]
3a	0	54.9
3b	0.28	34.2
3c	0.96	10.8

[a]Relative to 3a with $E_{6\text{-}31+G(d)}$ = -507778.13 kcal/mol. [b]Calculated using free energy values from Gaussian 03W according to $\Delta G = -RT$ In K.

Table S8. Cartesian coordinates of low-energy optimized conformers of compound **4**.

Cartesian coordinate of low-energy optimized conformers of (4*S*,5*R*,7*S*,9*S*,10*R*)-**4** optimized: [method: B3LYP/6-31+G (d)

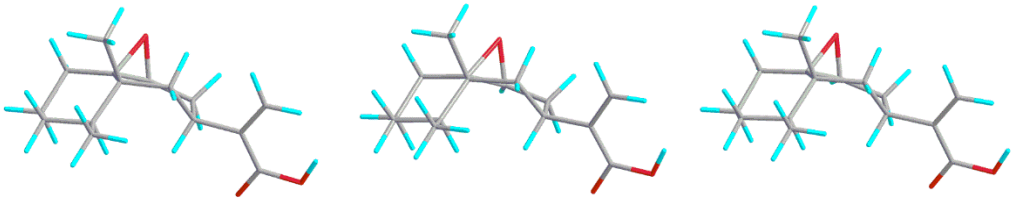
Total Energy, E(TD-HF/TD-KS) = -810.523746691 A.U.

Stoichiometry C15H2203
Framework group C1[X(C15H2203)]
Deg. of freedom 114
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.029054	-1.205533	-0.477102
2	6	0	3.243409	-0.171435	-1.589520
3	6	0	2.973339	1.245325	-1.071191
4	6	0	1.567168	1.397412	-0.452505
5	6	0	1.288523	0.341641	0.679625
6	6	0	1.646579	-1.055943	0.132861
7	6	0	-0.199128	0.353152	1.129252
8	6	0	-1.177664	-0.168966	0.065675
9	6	0	-0.900658	-1.665098	-0.225422
10	6	0	0.578848	-1.990316	-0.289524
11	6	0	-2.639782	0.049843	0.424496
12	6	0	-3.117774	0.054727	1.677393
13	6	0	1.345544	2.855976	-0.018938
14	6	0	2.144054	0.618052	1.938071
15	8	0	1.251210	-2.158221	0.981633
16	6	0	-3.572905	0.161109	-0.745238
17	8	0	-3.317713	-0.293240	-1.844158
18	8	0	-4.754838	0.797430	-0.560003
19	1	0	3.786731	-1.069374	0.306439
20	1	0	3.147250	-2.227071	-0.856296
21	1	0	4.263749	-0.247505	-1.984508
22	1	0	2.564003	-0.391632	-2.425158
23	1	0	3.739111	1.517848	-0.331096
24	1	0	3.073297	1.967791	-1.891471
25	1	0	0.854114	1.188283	-1.263060
26	1	0	-0.478216	1.368877	1.427379
27	1	0	-0.279398	-0.266680	2.029995

28	1	0	−1.002077	0.375317	−0.868850
29	1	0	−1.379518	−1.947145	−1.167585
30	1	0	−1.351394	−2.284089	0.561371
31	1	0	0.853748	−2.757749	−1.016041
32	1	0	−4.177661	0.134895	1.904197
33	1	0	−2.465518	−0.061490	2.536760
34	1	0	1.492999	3.522926	−0.876419
35	1	0	2.056924	3.159811	0.757493
36	1	0	0.335019	3.035037	0.361890
37	1	0	3.206249	0.747910	1.710379
38	1	0	1.801224	1.524106	2.448560
39	1	0	2.051622	−0.215935	2.642106
40	1	0	−4.773178	1.238445	0.306533



4a 0 kcal/mol　　4b 0.50 kcal/mol　　4c 0.70 kcal/mol

The most stable conformers of (4*S*,5*R*,7*S*,9*S*,10*R*)-**4.**

Table S9. B3LYP-Calculated relative energies (kcal/mol) and conformational population (%) for the most stable conformers of (4*S*,5*R*,7*S*,9*S*,10*R*)-**4.**

Conf	$\Delta E_{6\text{-}31+G(d)}$[a]	%[b]
4a	0	57.6
4b	0.50	24.7
4c	0.70	17.6

[a]Relative to 4a with $E_{6\text{-}31+G(d)}$ = -508611.35 kcal/mol. [b]Calculated using free energy values from Gaussian 03W according to $\Delta G = -RT$ In K.

Table S10. Cartesian coordinates of low-energy optimized conformers of (4*S*,5*R*,7*S*)-**5**.

Cartesian coordinate of low-energy optimized conformers of (4*S*,5*R*,7*S*)-**5** optimized:

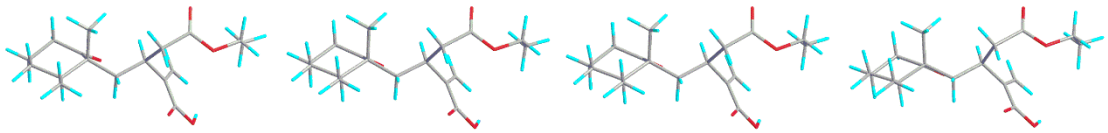
[method: B3LYP/6-31+G (d)

Total Energy, E(TD-HF/TD-KS) = -1039.49282338 A.U.

Stoichiometry C17H2605
Framework group C1[X(C17H2605)]
Deg. of freedom 138
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.750800	-0.875975	0.168498
2	6	0	3.831724	-2.050381	0.508402
3	6	0	1.720747	-0.650775	-0.135908
4	6	0	2.740307	0.435974	-0.522333
5	6	0	0.488580	0.007266	0.541445
6	6	0	-0.492115	0.849963	-0.333508
7	6	0	-1.620761	0.054353	-1.048381
8	8	0	2.481970	1.636918	-0.471754
9	6	0	-1.076200	2.009624	0.479364
10	6	0	-1.945162	1.861647	1.488176
11	6	0	1.573245	-2.858711	1.252506
12	6	0	1.354466	-1.429866	-1.426395
13	6	0	-2.580665	-0.747866	-0.188467
14	8	0	-2.269889	-1.471925	0.742858
15	8	0	-3.846084	-0.597543	-0.620326
16	6	0	-4.877858	-1.376411	0.046229
17	6	0	-4.993466	-2.767613	-0.556026
18	6	0	-0.636677	3.419643	0.178684
19	8	0	-1.346260	4.393367	0.360774
20	8	0	0.606722	3.589034	-0.303006
21	6	0	4.125394	-0.006215	-0.939872
22	6	0	2.410841	-1.612002	0.918254
23	1	0	4.917513	-0.259065	1.061538
24	1	0	5.733616	-1.232824	-0.158841
25	1	0	3.777378	-2.733310	-0.350584
26	1	0	4.262826	-2.632666	1.332005

27	1	0	0.875524	0.658275	1.332535
28	1	0	−0.099397	−0.761642	1.042127
29	1	0	0.072196	1.288344	−1.160947
30	1	0	−2.205138	0.744437	−1.662191
31	1	0	−1.168481	−0.666722	−1.737772
32	1	0	−2.319710	2.729205	2.022003
33	1	0	−2.289809	0.888337	1.820551
34	1	0	0.544715	−2.622314	1.538637
35	1	0	2.034400	−3.392163	2.091288
36	1	0	1.535359	−3.553007	0.405484
37	1	0	0.533991	−2.124831	−1.227130
38	1	0	1.041020	−0.755279	−2.230009
39	1	0	2.197599	−2.014545	−1.803688
40	1	0	−5.789412	−0.795632	−0.107443
41	1	0	−4.651259	−1.417299	1.113631
42	1	0	−5.825521	−3.302312	−0.084759
43	1	0	−4.077680	−3.342389	−0.390002
44	1	0	−5.186209	−2.711876	−1.632191
45	1	0	1.151160	2.763428	−0.290560
46	1	0	4.721368	0.885353	−1.152453
47	1	0	4.053751	−0.595233	−1.863624
48	1	0	2.509327	−1.018999	1.840009



The most stable conformers of (4*S*,5*R*,7*S*)-**5.**

Table S11. B3LYP-Calculated relative energies (kcal/mol) and conformational population (%) for the most stable conformers of (4*S*,5*R*,7*S*)-**5.**

Conf	$\Delta E_{6\text{-}31+G(d)}$[a]	%[b]
5a	0	51.4
5b	0.27	32.2
5c	1.06	8.5
5d	1.11	7.8

[a]Relative to 5a with $E_{6\text{-}31+G(d)}$ = -652291.62 kcal/mol. [b]Calculated using free energy values from Gaussian 03W according to $\Delta G = -RT$ In K.

Table S12. Cartesian coordinates of low-energy optimized conformers of compound (4*S*,5*R*,7*R*)-**5**.

Cartesian coordinate of low-energy optimized conformers of (4*S*,5*R*,7*R*)-**5** optimized: [method: B3LYP/6-31+G (d)

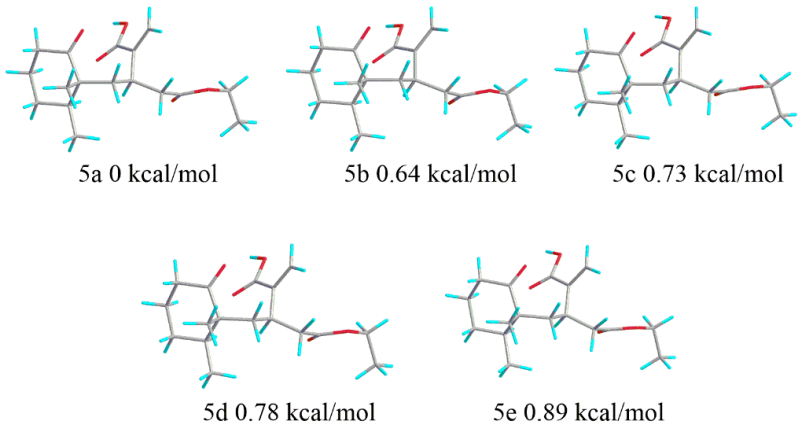
Total Energy, E(TD-HF/TD-KS) = -1039.49478837 A.U.

Stoichiometry C17H2605
Framework group C1[X(C17H2605)]
Deg. of freedom 138
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.980078	-0.282502	-0.882047
2	6	0	4.690253	-0.546104	0.597905
3	6	0	2.123827	-0.327096	0.199016
4	6	0	2.520070	-0.096819	-1.276334
5	6	0	0.920833	0.588323	0.556898
6	6	0	-0.444512	0.253150	-0.120850
7	6	0	-1.347267	-0.612740	0.784668
8	8	0	1.869442	0.623622	-2.020554
9	6	0	-1.171634	1.514621	-0.572310
10	6	0	-1.262567	1.859277	-1.864883
11	6	0	3.193132	-0.185559	2.585601
12	6	0	1.788155	-1.828081	0.388979
13	6	0	-2.490981	-1.266440	0.032063
14	8	0	-2.451494	-1.602309	-1.137554
15	8	0	-3.550417	-1.471481	0.838111
16	6	0	-4.700898	-2.151844	0.267112
17	6	0	-5.645800	-1.166790	-0.402539
18	6	0	-1.705325	2.427343	0.491465
19	8	0	-1.243653	2.493131	1.614879
20	8	0	-2.753783	3.224440	0.169790
21	6	0	3.802647	-0.749809	-1.760207
22	6	0	3.369726	0.089857	1.082336
23	1	0	5.143377	0.791863	-1.042390
24	1	0	5.899051	-0.792280	-1.193372
25	1	0	4.670608	-1.629315	0.780801
26	1	0	5.509390	-0.149930	1.210872

27	1	0	1.203344	1.610992	0.290254
28	1	0	0.778794	0.586371	1.640221
29	1	0	−0.256915	−0.317610	−1.031502
30	1	0	−0.760825	−1.430562	1.219598
31	1	0	−1.739239	−0.037622	1.627194
32	1	0	−1.717414	2.787498	−2.202079
33	1	0	−0.828705	1.234224	−2.638311
34	1	0	2.297399	0.283078	3.003082
35	1	0	4.054828	0.213202	3.133071
36	1	0	3.142142	−1.259923	2.795288
37	1	0	1.424766	−2.013712	1.404350
38	1	0	1.013159	−2.158665	−0.310592
39	1	0	2.659571	−2.469518	0.233183
40	1	0	−5.173412	−2.642386	1.120758
41	1	0	−4.347693	−2.910240	−0.434769
42	1	0	−6.535649	−1.696695	−0.760141
43	1	0	−5.164707	−0.685440	−1.259077
44	1	0	−5.966767	−0.393407	0.302760
45	1	0	−3.114855	2.975969	−0.698445
46	1	0	3.946272	−0.485007	−2.811649
47	1	0	3.711957	−1.841715	−1.694239
48	1	0	3.472335	1.178874	0.956526



The most stable conformers of (4*S*,5*R*,7*R*)-**5.**

Table S13. B3LYP-Calculated relative energies (kcal/mol) and conformational population (%) for the most stable conformers of (4*S*,5*R*,7*R*)-**5.**

Conf	$\Delta E_{6\text{-}31+G(d)}$[a]	%[b]
5a	0	47.1
5b	0.64	16.0
5c	0.73	13.7
5d	0.78	12.6
5e	0.89	10.5

[a]Relative to 5a with $E_{6\text{-}31+G(d)}$ = -652292.85 kcal/mol. [b]Calculated using free energy

values from Gaussian 03W according to $\Delta G = -RT \ln K$.

Table S14. Cartesian coordinates of low-energy optimized conformers of compound **6**.

Cartesian coordinate of low-energy optimized conformers of (1*R*,4*S*,5*R*,7*R*)-**6** optimized: [method: B3LYP/6-31+G (d)

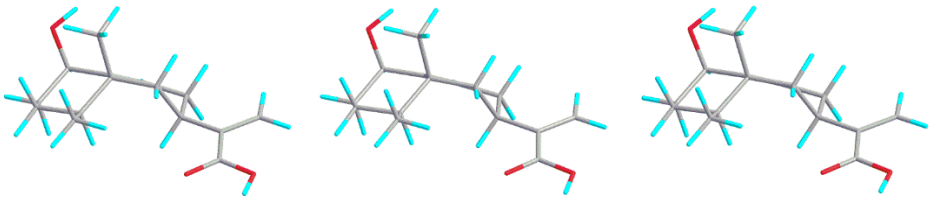
Total Energy, E(TD-HF/TD-KS) = -810.377399089 A.U.

Stoichiometry C15H2203
Framework group C1[X(C15H2203)]
Deg. of freedom 114
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.335489	-0.725525	-0.250268
2	6	0	3.229323	0.250718	-1.368066
3	6	0	2.712548	1.527925	-0.695867
4	6	0	1.226120	1.446703	-0.284039
5	6	0	0.942587	0.191944	0.625760
6	6	0	1.511516	-1.033105	-0.102163
7	6	0	-0.578398	-0.005469	0.884891
8	6	0	-0.748101	-2.135149	-0.389061
9	6	0	0.751678	-2.060533	-0.513846
10	6	0	-3.593729	-1.709799	0.377303
11	6	0	-2.835796	-0.681052	-0.028465
12	6	0	1.594807	0.359751	2.023526
13	6	0	0.784416	2.791585	0.315826
14	6	0	2.971422	-0.998860	-0.518969
15	6	0	-3.471197	0.642498	-0.309375
16	8	0	-2.879054	1.603659	-0.772602
17	8	0	-4.789586	0.698645	-0.010881
18	8	0	3.898935	-0.959894	0.581101
19	1	0	-1.139421	-0.185619	-1.185442
20	1	0	2.723887	0.109566	-2.332377
21	1	0	4.304255	0.327907	-1.574932
22	1	0	3.326686	1.753897	0.184939
23	1	0	2.841653	2.375217	-1.381857
24	1	0	0.645715	1.293821	-1.206713
25	1	0	-1.038543	0.962616	1.098398

26	1	0	−0.702839	−0.610836	1.793505
27	1	0	−1.020191	−2.754830	0.479039
28	1	0	−1.165985	−2.646102	−1.266209
29	1	0	1.234970	−2.891864	−1.028029
30	1	0	−4.662664	−1.602932	0.522760
31	1	0	−3.171773	−2.690240	0.571928
32	1	0	2.651269	0.624230	1.967722
33	1	0	1.068834	1.131938	2.596915
34	1	0	1.516102	−0.577025	2.587541
35	1	0	0.981499	3.597309	−0.401597
36	1	0	1.335943	3.029838	1.232619
37	1	0	−0.285206	2.818506	0.545711
38	1	0	3.180633	−1.892849	−1.126102
39	1	0	−5.090138	1.596248	−0.248191
40	1	0	3.652708	−1.677866	1.186312



6a 0 kcal/mol 6b 0.48 kcal/mol 6c 1.26 kcal/mol

The most stable conformers of (1*R*,4*S*,5*R*,7*R*)-**6.**

Table S15. B3LYP-Calculated relative energies (kcal/mol) and conformational population (%) for the most stable conformers of (1*R*,4*S*,5*R*,7*R*)-**6.**

Conf	$\Delta E_{6\text{-}31+G(d)}$[a]	%[b]
6a	0	63.9
6b	0.48	28.4
6c	1.26	7.6

[a]Relative to 6a with $E_{6\text{-}31+G(d)}$ = -508519.52 kcal/mol. [b]Calculated using free energy values from Gaussian 03W according to $\Delta G = -RT$ In K.

Table S16. Cartesian coordinates of low-energy optimized conformers of compound **7**.

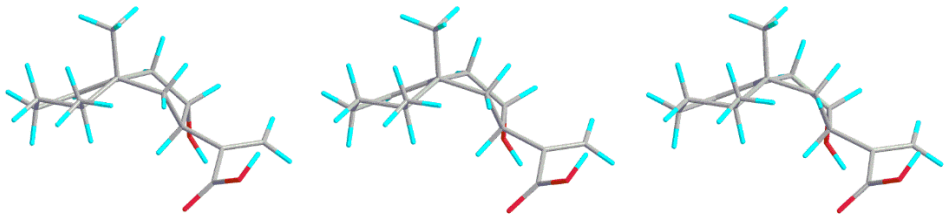
Cartesian coordinate of low-energy optimized conformers of (4*S*,5*R*,7*R*,8*S*)-**7** optimized: [method: B3LYP/6-31+G (d)

Total Energy, E(TD-HF/TD-KS) = -810.379112997

Stoichiometry C15H2203
Framework group C1[X(C15H2203)]
Deg. of freedom 114
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.115644	1.763174	0.604429
2	6	0	3.029842	1.086807	1.588936
3	6	0	3.321861	-0.368699	1.206148
4	6	0	1.541718	-0.373171	-0.635877
5	6	0	1.448999	1.137124	-0.374302
6	8	0	-4.518672	-0.608465	0.779325
7	8	0	-1.686662	2.230762	-0.024911
8	6	0	0.444209	1.855090	-1.241371
9	6	0	2.457162	-0.630071	-1.857868
10	6	0	-2.860674	-1.371552	-1.369298
11	6	0	-3.309943	-0.452272	0.814061
12	6	0	2.084366	-1.093161	0.642289
13	6	0	2.401786	-2.584373	0.446518
14	8	0	-2.672144	-0.104080	1.954352
15	6	0	-1.005088	1.373203	-0.943781
16	6	0	-0.994286	-0.037422	-0.311390
17	6	0	-2.381643	-0.654521	-0.343362
18	6	0	0.101818	-0.883237	-0.986871
19	1	0	1.965734	2.835687	0.736456
20	1	0	3.968069	1.651320	1.686385
21	1	0	2.563409	1.129001	2.586465
22	1	0	4.126423	-0.397596	0.459409
23	1	0	3.698074	-0.915996	2.079632
24	1	0	-1.829633	3.080404	-0.472142

25	1	0	0.494850	2.939591	−1.091476
26	1	0	0.657365	1.672232	−2.303317
27	1	0	2.143341	−0.021485	−2.713189
28	1	0	3.501893	−0.383352	−1.643638
29	1	0	2.411482	−1.679315	−2.171046
30	1	0	−3.871968	−1.764152	−1.347684
31	1	0	−2.262330	−1.587382	−2.248787
32	1	0	1.289383	−1.020501	1.401192
33	1	0	3.275119	−2.729021	−0.200036
34	1	0	1.567252	−3.142557	0.008816
35	1	0	2.631893	−3.045816	1.414030
36	1	0	−3.360259	−0.013481	2.641031
37	1	0	−1.566305	1.329452	−1.888937
38	1	0	−0.712268	0.105869	0.736273
39	1	0	−0.008162	−1.931635	−0.693713
40	1	0	−0.038167	−0.858516	−2.075403



7a 0 kcal/mol　　7b 0.78 kcal/mol　　7c 1.11 kcal/mol

The most stable conformers of (4*S*,5*R*,7*R*,8*S*)-**7.**

Table S17. B3LYP-Calculated relative energies (kcal/mol) and conformational population (%) for the most stable conformers of (4*S*,5*R*,7*R*,8*S*)-**7.**

Conf	$\Delta E_{6\text{-}31+G(d)}$[a]	%[b]
7a	0	70.5
7b	0.78	18.7
7c	1.11	10.8

[a]Relative to 7a with $E_{6\text{-}31+G(d)}$ = -508520.59 kcal/mol. [b]Calculated using free energy values from Gaussian 03W according to $\Delta G = -RT$ In K.

Table S18. Cartesian coordinates of low-energy optimized conformers of **10**.

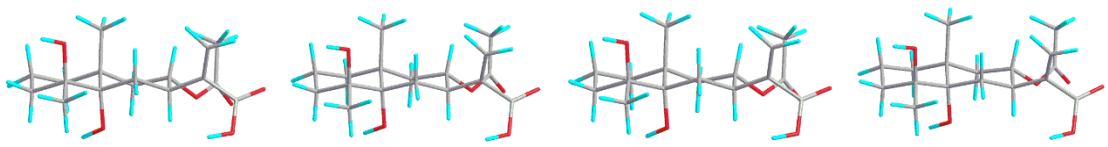
Cartesian coordinate of low-energy optimized conformers of (4*S*,5*S*,7*R*,8*S*,10*R*)-**10** optimized: [method: B3LYP/6-31+G (d)

Total Energy, E(TD-HF/TD-KS) = -1114.69819589

Stoichiometry C17H2606
Framework group C1[X(C17H2606)]
Deg. of freedom 141
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.620439	1.936667	-0.676252
2	6	0	-4.023328	1.427098	-0.314910
3	6	0	-4.164579	-0.077989	-0.574199
4	6	0	-3.072976	-0.947239	0.092785
5	6	0	-1.652308	-0.378256	-0.256791
6	6	0	-1.505221	1.161464	0.064820
7	6	0	-0.504829	-1.170960	0.404853
8	6	0	0.889370	-0.686145	-0.063213
9	6	0	1.046745	0.827404	0.153329
10	6	0	-0.113962	1.629226	-0.445579
11	6	0	2.020902	-1.473060	0.583216
12	6	0	2.195614	-1.574149	1.908100
13	8	0	-3.192275	-0.901932	1.526555
14	6	0	-3.244206	-2.406604	-0.361860
15	6	0	-1.579789	1.504368	1.574891
16	8	0	2.287577	1.213501	-0.504430
17	6	0	2.998856	2.228739	0.032554
18	8	0	2.659602	2.846572	1.023533
19	6	0	4.256624	2.480901	-0.762266
20	8	0	-1.592688	-0.581319	-1.687055
21	6	0	2.960941	-2.157613	-0.353539
22	8	0	2.840574	-2.164889	-1.567130
23	8	0	3.981632	-2.793348	0.264398
24	1	0	-2.532109	3.005673	-0.441473

25	1	0	−2. 471436	1. 836774	−1. 758274
26	1	0	−4. 774010	1. 968706	−0. 904161
27	1	0	−4. 245470	1. 643672	0. 736248
28	1	0	−4. 134931	−0. 265578	−1. 653272
29	1	0	−5. 142951	−0. 432601	−0. 220555
30	1	0	−0. 595301	−2. 228184	0. 140312
31	1	0	−0. 591578	−1. 109135	1. 493116
32	1	0	0. 964206	−0. 867912	−1. 140002
33	1	0	1. 159303	1. 054463	1. 214643
34	1	0	−0. 046692	1. 573934	−1. 541339
35	1	0	0. 020139	2. 687982	−0. 196619
36	1	0	3. 015798	−2. 139795	2. 334928
37	1	0	1. 519388	−1. 092340	2. 609001
38	1	0	−4. 043754	−1. 312457	1. 749860
39	1	0	−2. 581618	−3. 075534	0. 194906
40	1	0	−4. 276788	−2. 725729	−0. 170056
41	1	0	−3. 046631	−2. 522101	−1. 429637
42	1	0	−2. 550540	1. 262841	2. 002694
43	1	0	−0. 831724	0. 974674	2. 170410
44	1	0	−1. 396445	2. 578776	1. 700805
45	1	0	4. 863737	1. 571053	−0. 804415
46	1	0	4. 000168	2. 752266	−1. 791521
47	1	0	4. 828028	3. 286832	−0. 300751
48	1	0	−0. 825966	−0. 108260	−2. 040674
49	1	0	4. 517308	−3. 209810	−0. 436793



10a 0 kcal/mol　10b 0.55 kcal/mol　10c 0.92 kcal/mol　10d 1.27 kcal/mol

The most stable conformers of (4*S*,5*S*,7*R*,8*S*,10*R*)-**10.**

Table S19. B3LYP-Calculated relative energies (kcal/mol) and conformational population (%) for the most stable conformers of (4*S*,5*S*,7*R*,8*S*,10*R*)-**10.**

Conf	$\Delta E_{6\text{-}31+G(d)}$[a]	%[b]
10a	0	58.0
10b	0.55	22.9
10c	0.92	12.2
10d	1.27	6.8

[a]Relative to 10a with $E_{6\text{-}31+G(d)}$ = -699483.71 kcal/mol. [b]Calculated using free energy values from Gaussian 03W according to $\Delta G = -RT$ ln K.

Table S20. Cartesian coordinates of low-energy optimized conformers of **12**.

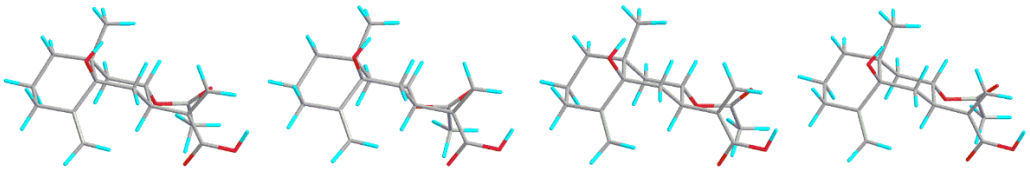
Cartesian coordinate of low-energy optimized conformers of (5*S*,7*R*,8*S*,10*R*)-**12** optimized: [method: B3LYP/6-31+G (d)

Total Energy, E(TD-HF/TD-KS) = -1038.26056489 A.U.

Stoichiometry C17H2405
Framework group C1[X(C17H2405)]
Deg. of freedom 132
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.215755	-1.465804	0.210514
2	6	0	3.687661	-0.981387	-1.163165
3	6	0	3.705620	0.553321	-1.204972
4	6	0	2.354063	1.127926	-0.834827
5	6	0	1.805541	0.666319	0.525247
6	6	0	1.845011	-0.898983	0.666066
7	6	0	0.389055	1.194720	0.844891
8	6	0	-0.760354	0.548880	0.027595
9	6	0	-0.679828	-0.974930	0.140246
10	6	0	0.716217	-1.493693	-0.213185
11	6	0	1.650949	-1.334141	2.136805
12	6	0	1.749528	2.023612	-1.625376
13	8	0	-1.621929	-1.535626	-0.819878
14	6	0	-2.098990	1.142653	0.439613
15	6	0	-2.992183	0.564046	1.254601
16	6	0	-2.431872	-2.538797	-0.421136
17	8	0	-2.445859	-3.000529	0.704816
18	6	0	-3.313664	-2.996435	-1.556909
19	8	0	2.708978	1.179407	1.533120
20	6	0	-2.380301	2.495487	-0.128301
21	8	0	-1.644864	3.079451	-0.908874
22	8	0	-3.541776	3.041341	0.293054
23	1	0	3.159398	-2.562271	0.228889
24	1	0	3.966554	-1.179670	0.957976
25	1	0	4.691112	-1.374489	-1.368226

26	1	0	3.034750	−1.364543	−1.958057
27	1	0	4.456022	0.909785	−0.485475
28	1	0	4.007649	0.916700	−2.193521
29	1	0	0.207763	1.025014	1.910874
30	1	0	0.365068	2.279523	0.701439
31	1	0	−0.608472	0.797281	−1.027494
32	1	0	−0.972690	−1.323629	1.130681
33	1	0	0.898081	−1.271017	−1.270983
34	1	0	0.721706	−2.585922	−0.111587
35	1	0	2.450687	−0.933187	2.764115
36	1	0	0.699245	−1.010657	2.567461
37	1	0	1.683511	−2.428602	2.199587
38	1	0	0.786219	2.471639	−1.406098
39	1	0	2.224237	2.344391	−2.550619
40	1	0	−3.917792	1.062684	1.518507
41	1	0	−2.837072	−0.424624	1.674205
42	1	0	−2.698111	−3.345352	−2.392246
43	1	0	−3.964970	−3.801919	−1.216339
44	1	0	−3.917974	−2.159532	−1.921419
45	1	0	2.772616	2.138245	1.387512
46	1	0	−3.617182	3.911040	−0.143324



12a 0 kcal/mol 12b 0.11 kcal/mol 12c 0.44 kcal/mol 12d 1.40 kcal/mol

The most stable conformers of (5*S*,7*R*,8*S*,10*R*)-**12.**

Table S21. B3LYP-Calculated relative energies (kcal/mol) and conformational population (%) for the most stable conformers of (5*S*,7*R*,8*S*,10*R*)-**12.**

Conf	$\Delta E_{6\text{-}31+G(d)}$[a]	%[b]
12a	0	41.7
12b	0.11	34.4
12c	0.44	19.9
12d	1.40	3.9

[a]Relative to 12a with $E_{6\text{-}31+G(d)}$ = -651518.37 kcal/mol. [b]Calculated using free energy values from Gaussian 03W according to $\Delta G = -RT$ In K.

Table S22. Cartesian coordinates of low-energy optimized conformers of **13**.

Cartesian coordinate of low-energy optimized conformers of (7*R*,8*S*,10*R*)-**13**

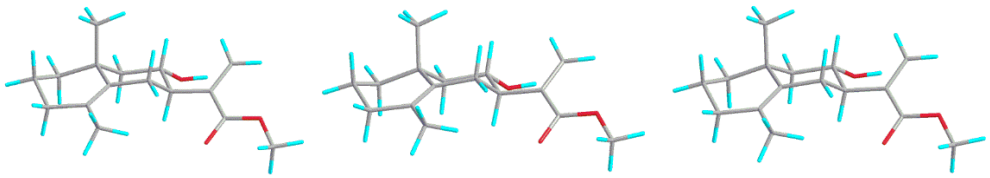
optimized: [method: B3LYP/6-31+G (d)

Total Energy, E(TD-HF/TD-KS) = -849.700174977

Stoichiometry C16H2403
Framework group C1[X(C16H2403)]
Deg. of freedom 123
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.339605	-1.304115	0.087142
2	6	0	-4.326028	-0.328120	-0.551867
3	6	0	-4.050262	1.085489	-0.038479
4	6	0	-2.577246	1.457365	-0.019515
5	6	0	-1.593114	0.541716	-0.144834
6	6	0	-1.870343	-0.968083	-0.259483
7	6	0	-0.119011	0.902459	-0.203663
8	8	0	2.561508	-0.262795	-1.430903
9	8	0	1.260154	-2.037099	1.712820
10	6	0	-0.965358	-1.716257	0.757786
11	6	0	-2.369525	2.947393	0.143709
12	6	0	-1.563823	-1.464918	-1.696590
13	6	0	3.012049	0.221333	-0.403556
14	6	0	2.749155	1.235989	1.819919
15	6	0	5.154211	0.247727	-1.401962
16	8	0	4.320318	0.514949	-0.259785
17	6	0	0.738470	0.125655	0.832361
18	6	0	0.525975	-1.385660	0.665101
19	6	0	2.198241	0.548943	0.808632
20	1	0	-3.468530	-1.263391	1.178146
21	1	0	-3.553987	-2.337636	-0.214971
22	1	0	-4.228880	-0.351446	-1.644885
23	1	0	-5.358595	-0.620480	-0.324532
24	1	0	-4.454275	1.198118	0.981168
25	1	0	-4.594373	1.823763	-0.645304
26	1	0	0.038008	1.970637	-0.043398

27	1	0	0.276287	0.684628	−1.202728
28	1	0	1.139418	−2.993017	1.593078
29	1	0	−1.292366	−1.470448	1.777609
30	1	0	−1.105653	−2.800124	0.631984
31	1	0	−3.012311	3.327704	0.949490
32	1	0	−1.343659	3.238458	0.376165
33	1	0	−2.671050	3.484111	−0.767339
34	1	0	−1.687742	−2.553697	−1.755427
35	1	0	−2.243911	−1.007853	−2.423223
36	1	0	−0.543670	−1.231912	−2.015085
37	1	0	3.782343	1.563439	1.798841
38	1	0	2.166841	1.492678	2.700957
39	1	0	5.130511	−0.815651	−1.652623
40	1	0	6.158754	0.546881	−1.103947
41	1	0	4.821683	0.830322	−2.264715
42	1	0	0.360429	0.381716	1.831478
43	1	0	0.926172	−1.698731	−0.306012



13a 0 kcal/mol 13b 0.07 kcal/mol 13c 1.04 kcal/mol

The most stable conformers of (7*R*,8*S*,10*R*)-**13.**

Table S23. B3LYP-Calculated relative energies (kcal/mol) and conformational population (%) for the most stable conformers of (7*R*,8*S*,10*R*)-**13.**

Conf	$\Delta E_{6\text{-}31+G(d)}$[a]	%[b]
13a	0	48.4
13b	0.07	43.1
13c	1.04	8.4

[a]Relative to 13a with $E_{6\text{-}31+G(d)}$ = -533194.93 kcal/mol. [b]Calculated using free energy values from Gaussian 03W according to $\Delta G = -RT$ In K.

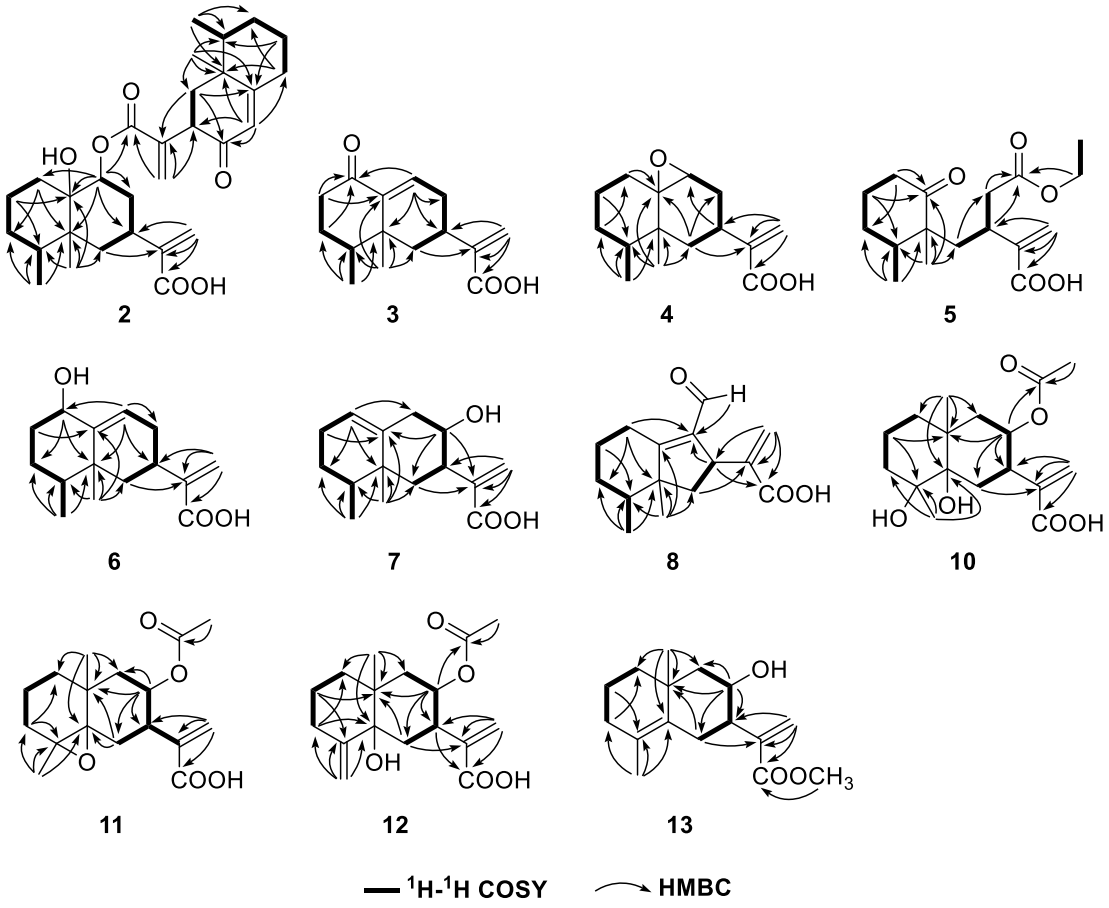


Figure S1. The key HMBC and ^{1}H-^{1}H COSY correlations of **2**–**13**.

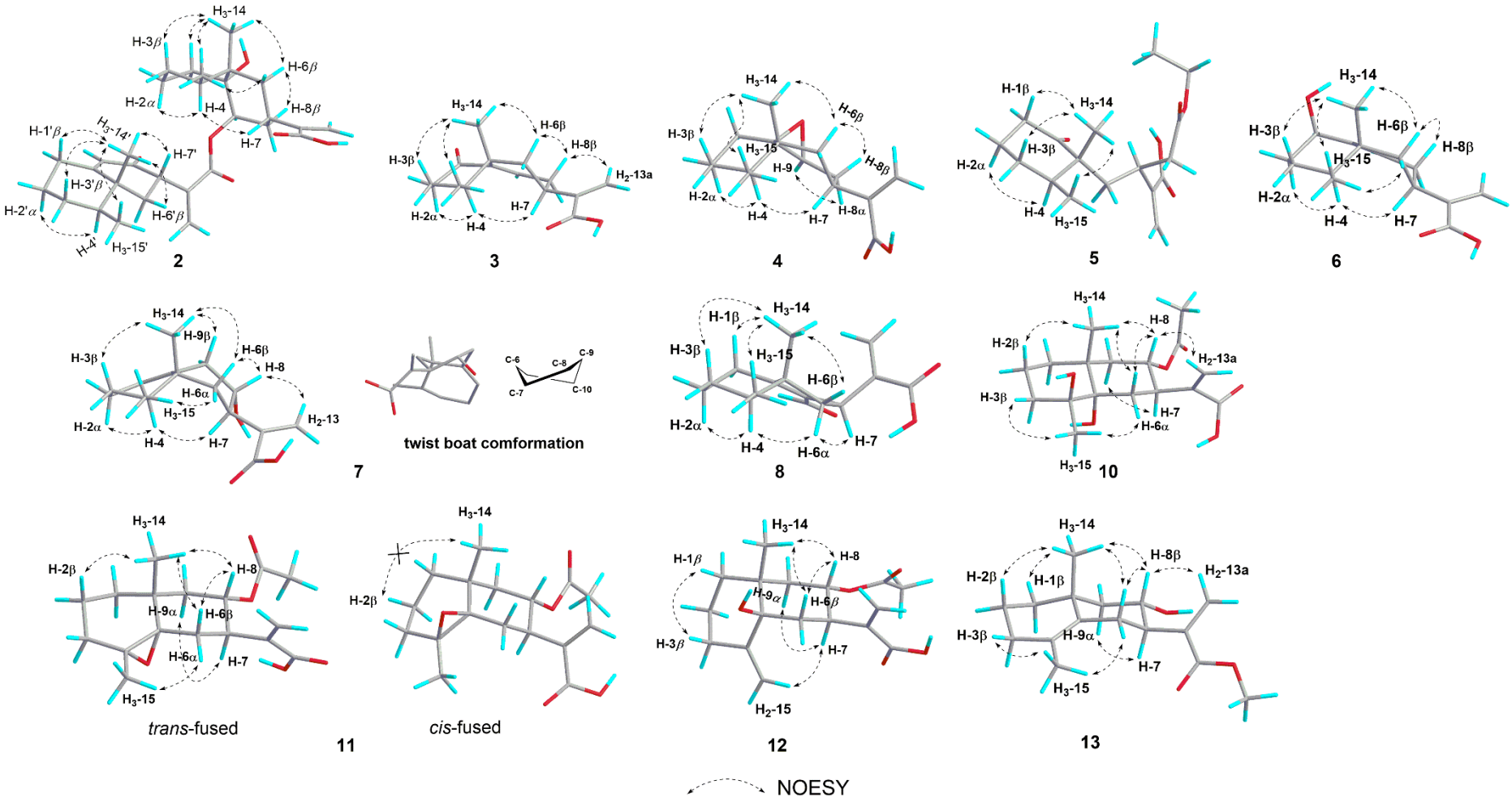


Figure S2. The key NOESY correlations of **2–13**.

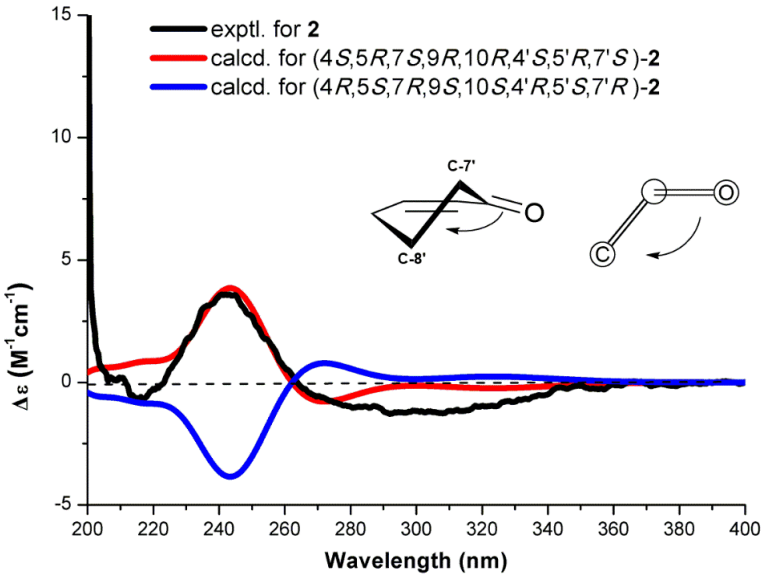


Figure S3. The helicity rule applied for *trans*-ketone in **2** and comparison between calculated ECD spectra [(4*S*,5*R*,7*S*,9*R*,10*R*,4'*S*,5'*R*,7'*S*)-**2** in red line and its enantiomer in blue line] and the experimental spectrum (black line) of **2**.

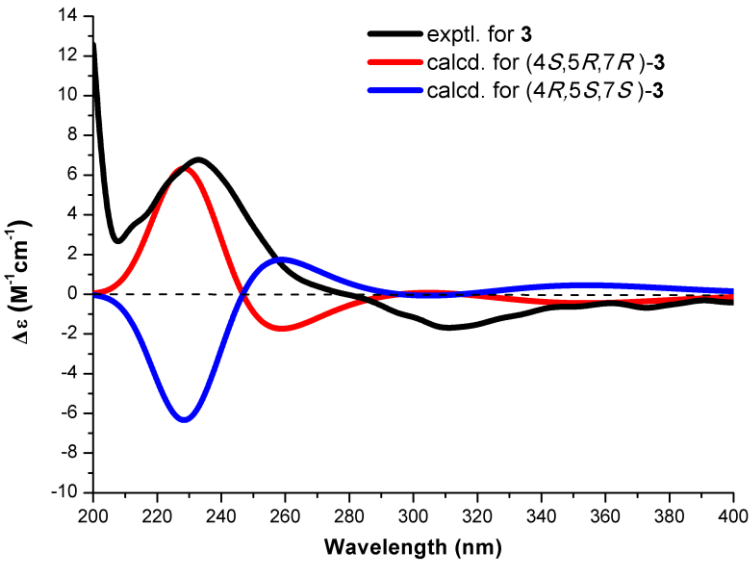


Figure S4. Comparison between calculated ECD spectra [(4*S*,5*R*,7*R*)-**3** in red line and its enantiomer in blue line] and the experimental spectrum (black line) of **3**.

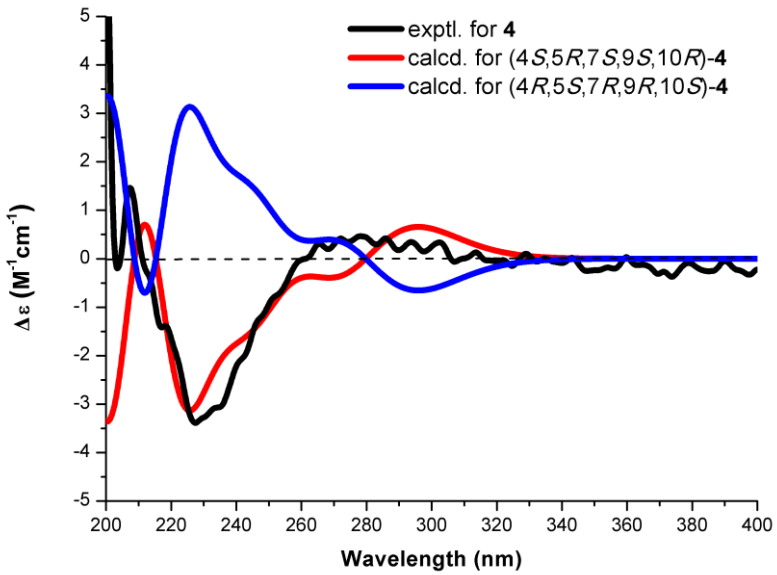


Figure S5. Comparison between calculated ECD spectra [(4*S*,5*R*,7*S*,9*S*,10*R*)-**4** in red line and its enantiomer in blue line] and the experimental spectrum (black line) of **4**.

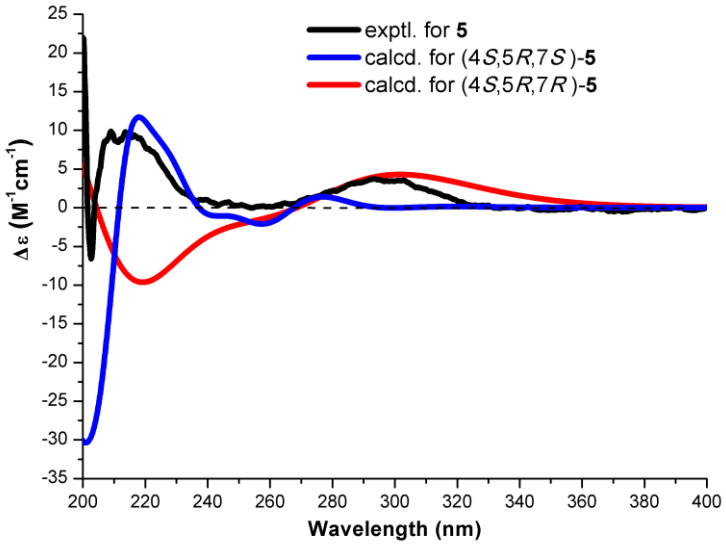


Figure S6. Comparison between calculated ECD spectra [(4*S*,5*R*,7*S*)-**5** in red line and (4*S*,5*R*,7*R*)-**5** in blue line] and the experimental spectrum (black line) of **5**.

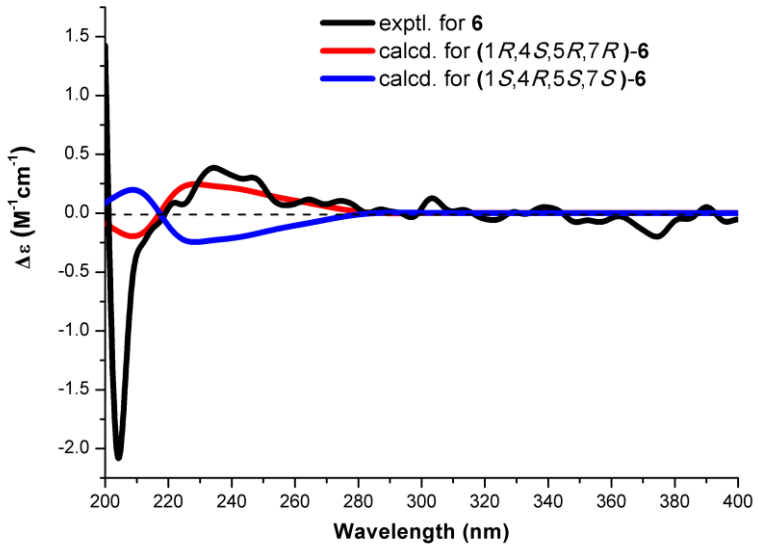


Figure S7. Comparison between calculated ECD spectra [(1*R*,4*S*,5*R*,7*R*)-**6** in red line and its enantiomer in blue line] and the experimental spectrum (black line) of **6**.

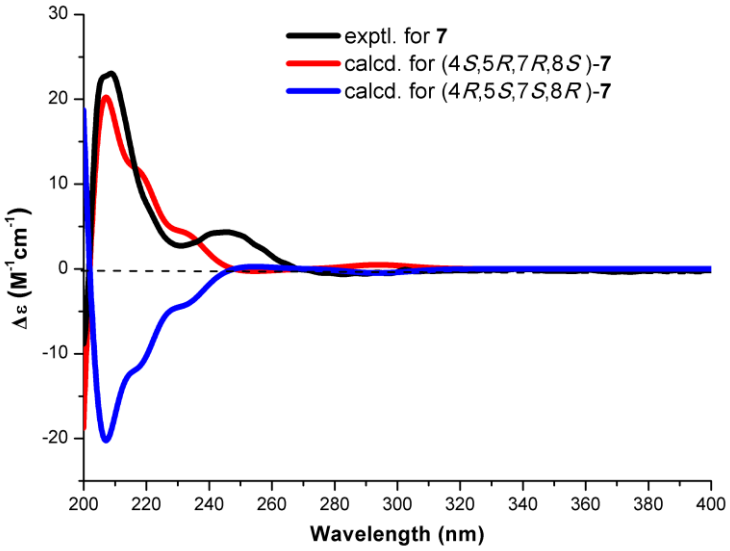


Figure S8. Comparison between calculated ECD spectra [(4*S*,5*R*,7*R*,8*S*)-**7** in red line and its enantiomer in blue line] and the experimental spectrum (black line) of **7**.

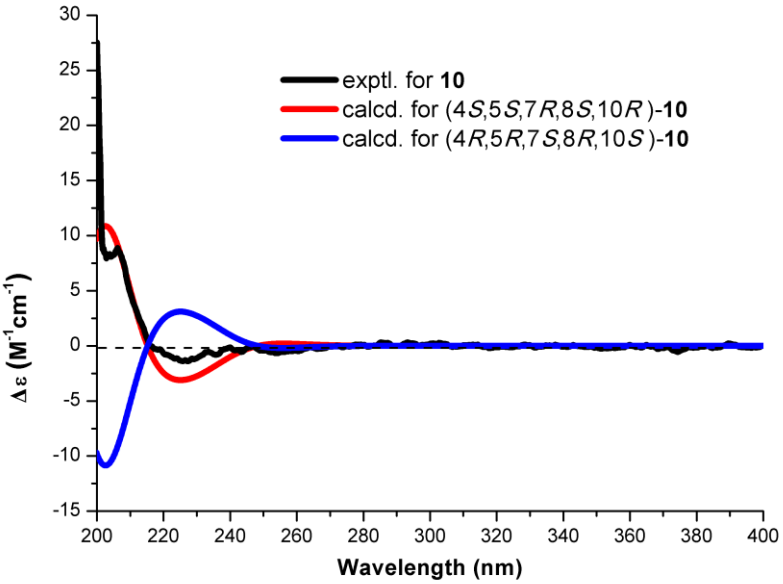


Figure S9. Comparison between calculated ECD spectra [(4*S*,5*S*,7*R*,8*S*,10*R*)-**10** in red line and its enantiomer in blue line] and the experimental spectrum (black line) of **10**.

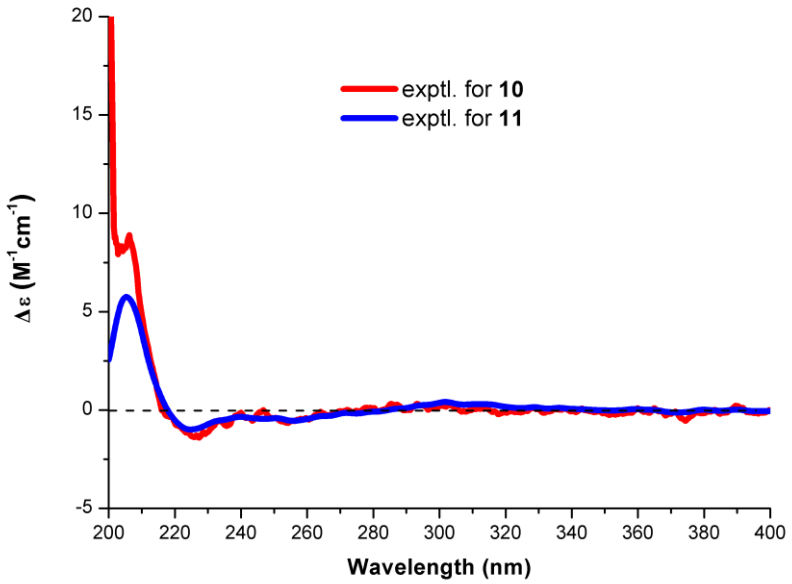


Figure S10. Comparison of experimental ECD spectra between **10** (red line) and **11** (blue line).

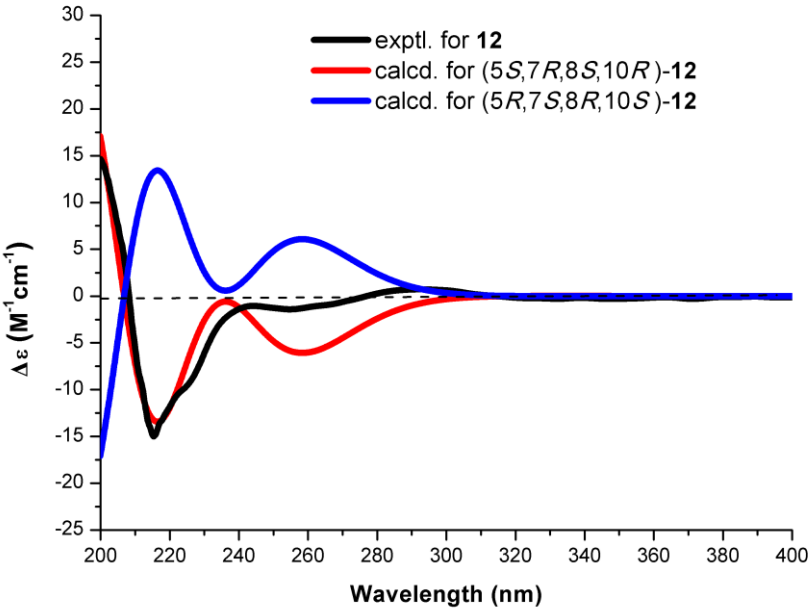


Figure S11. Comparison between calculated ECD spectra [(5*S*,7*R*,8*S*,10*R*)-**12** in red line and its enantiomer in blue line] and the experimental spectrum (black line) of **12**.

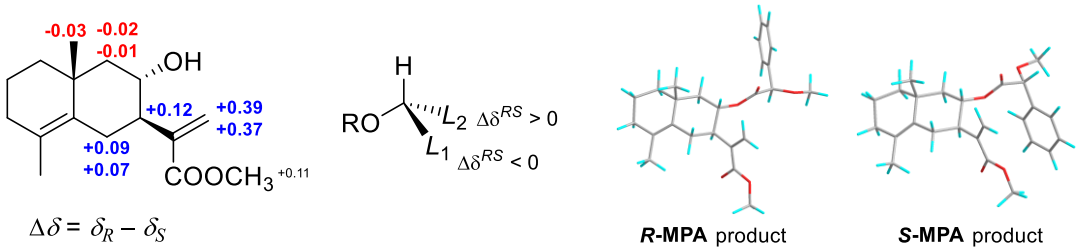


Figure S12. $\Delta\delta$ ($\delta_R - \delta_S$) values obtained from the ^{1}H-NMR spectra of the MPA esters of **13**

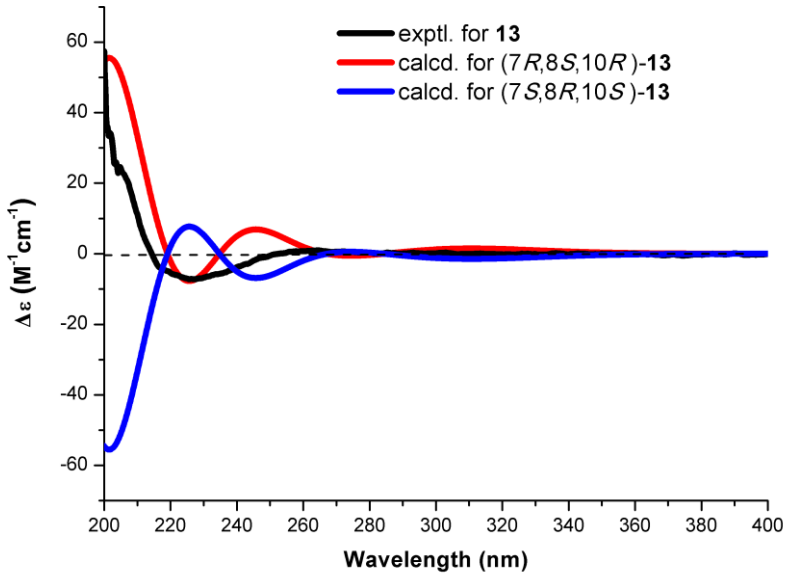


Figure S13. Comparison between calculated ECD spectra [(7*R*,8*S*,10*R*)-**13** in red line and its enantiomer in blue line] and the experimental spectrum (black line) of **13**.

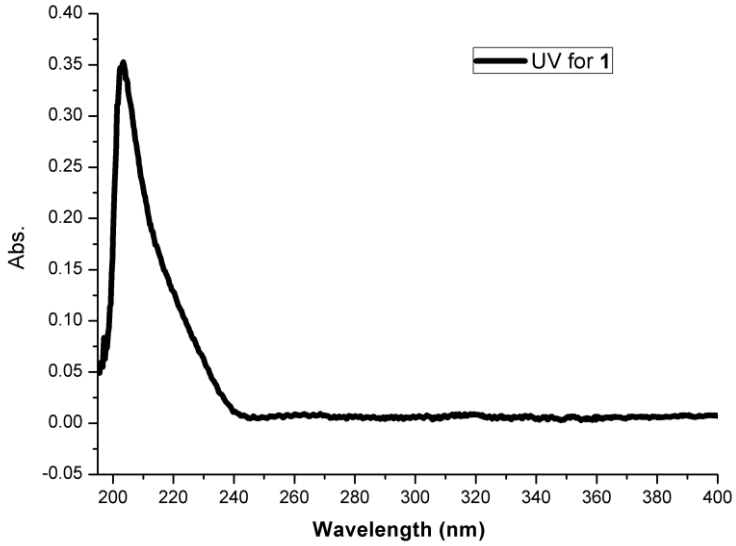


Figure S14. UV spectrum of 1.

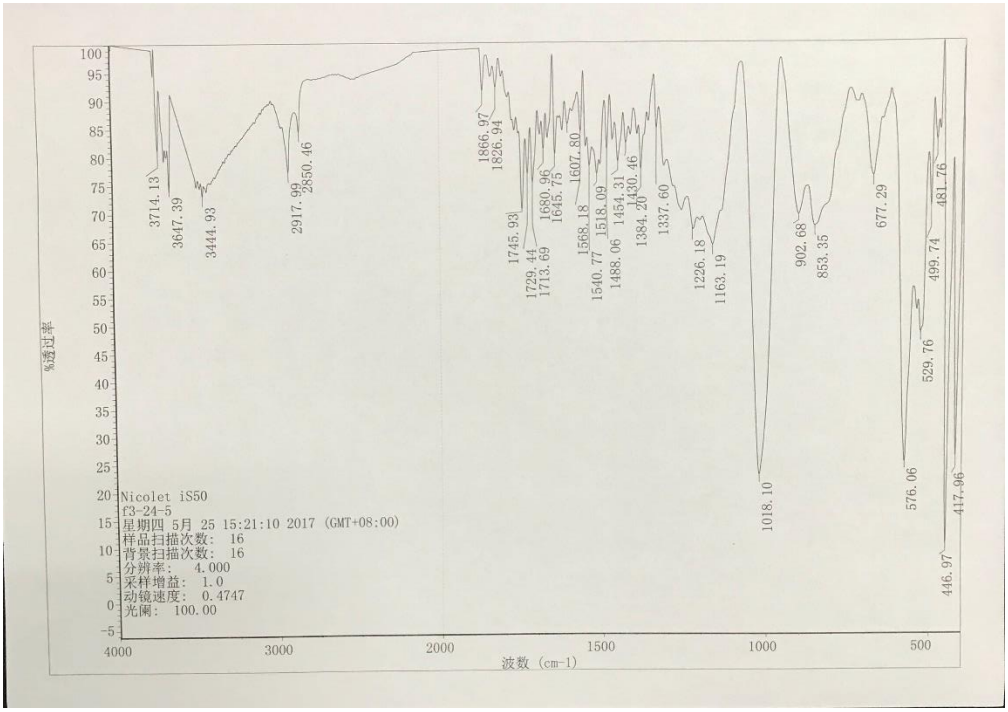


Figure S15. IR spectrum of 1

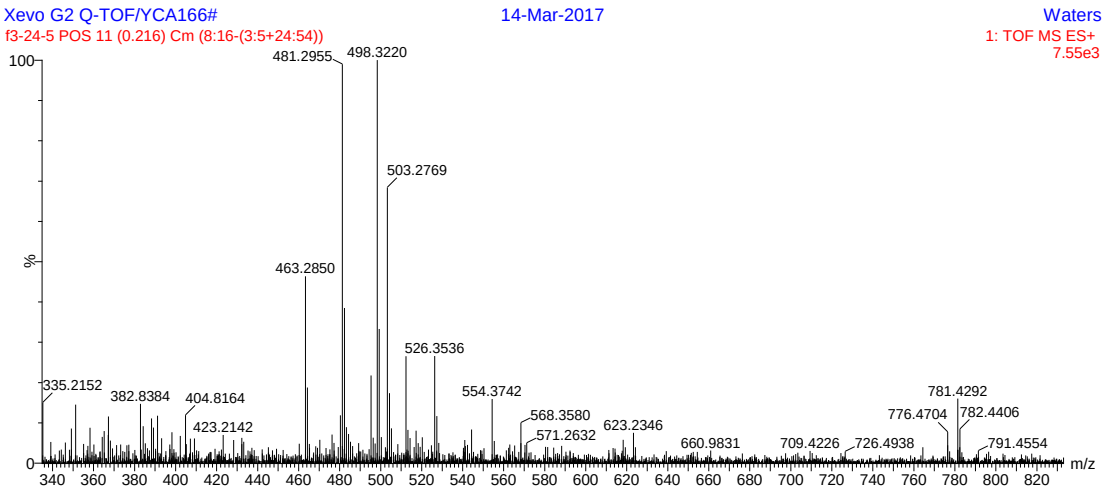


Figure S16. HRMS spectrum of 1

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
222 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-110 H: 0-200 O: 0-50 Na: 0-1

Minimum:						-1.5		
Maximum:				5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
481.2955	481.2954	0.1	0.2	10.5	176.6	n/a	n/a	C30H41O5

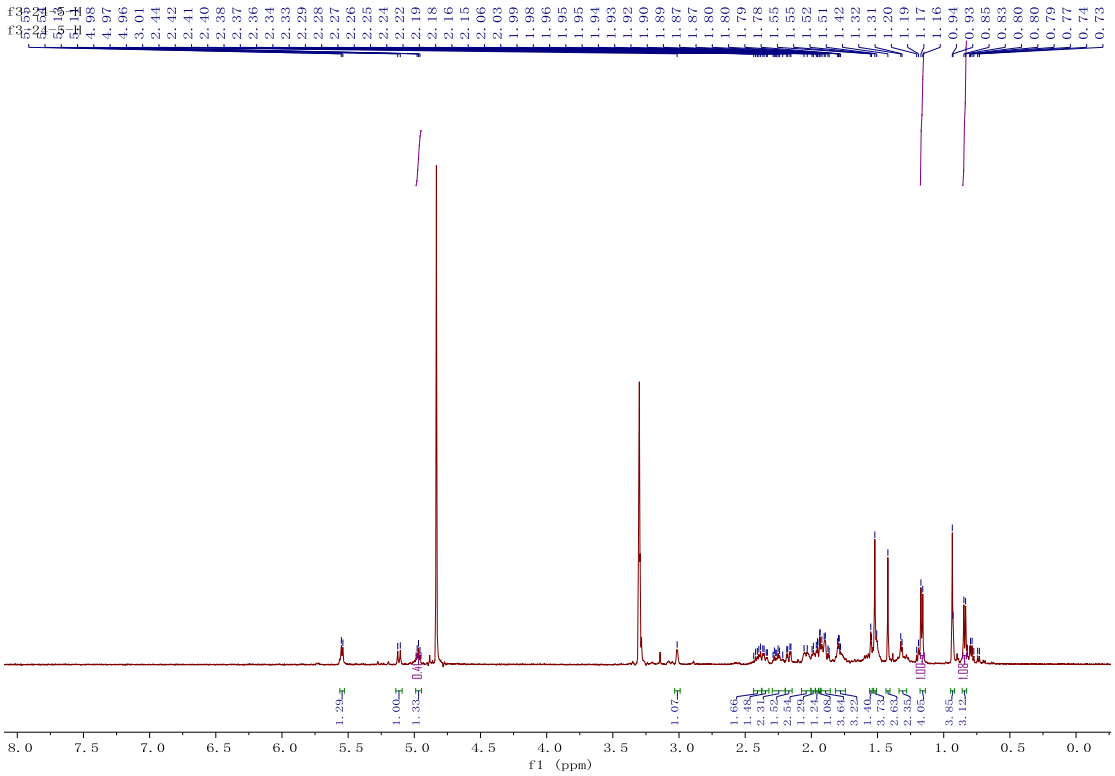


Figure S17. ^{1}H NMR spectrum of 1 in methanol-*d*$_4$

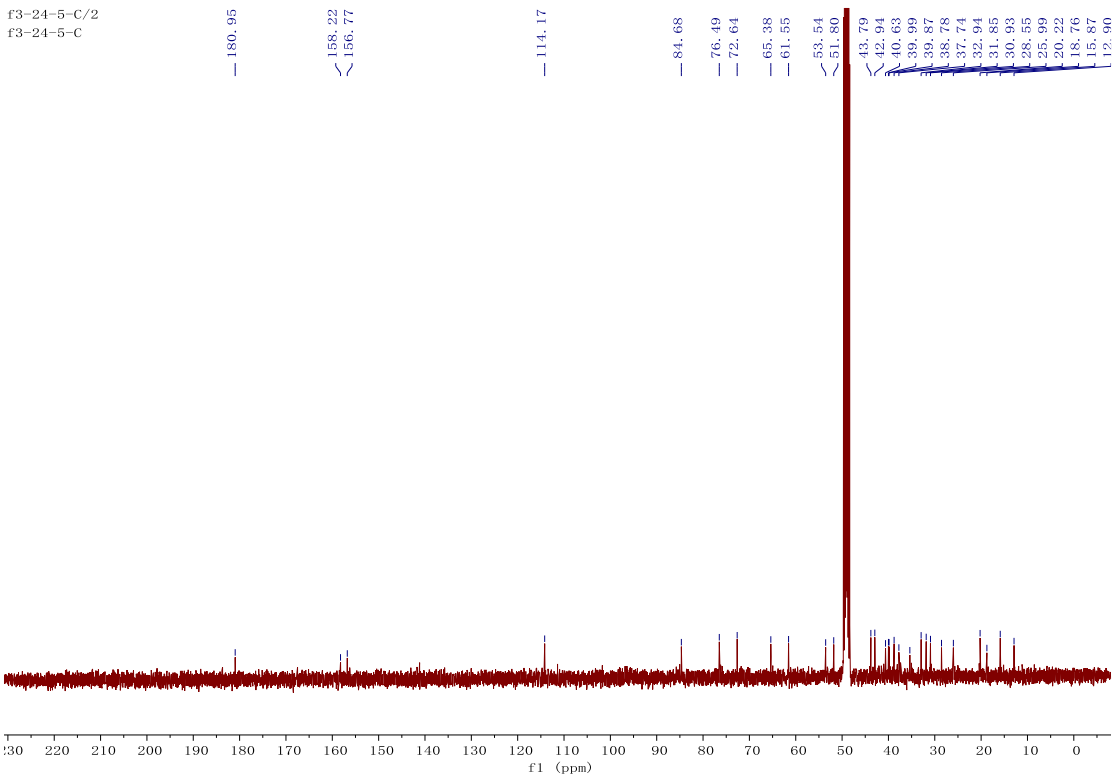


Figure S18. ^{13}C NMR spectrum of 1 in methanol-*d*$_4$

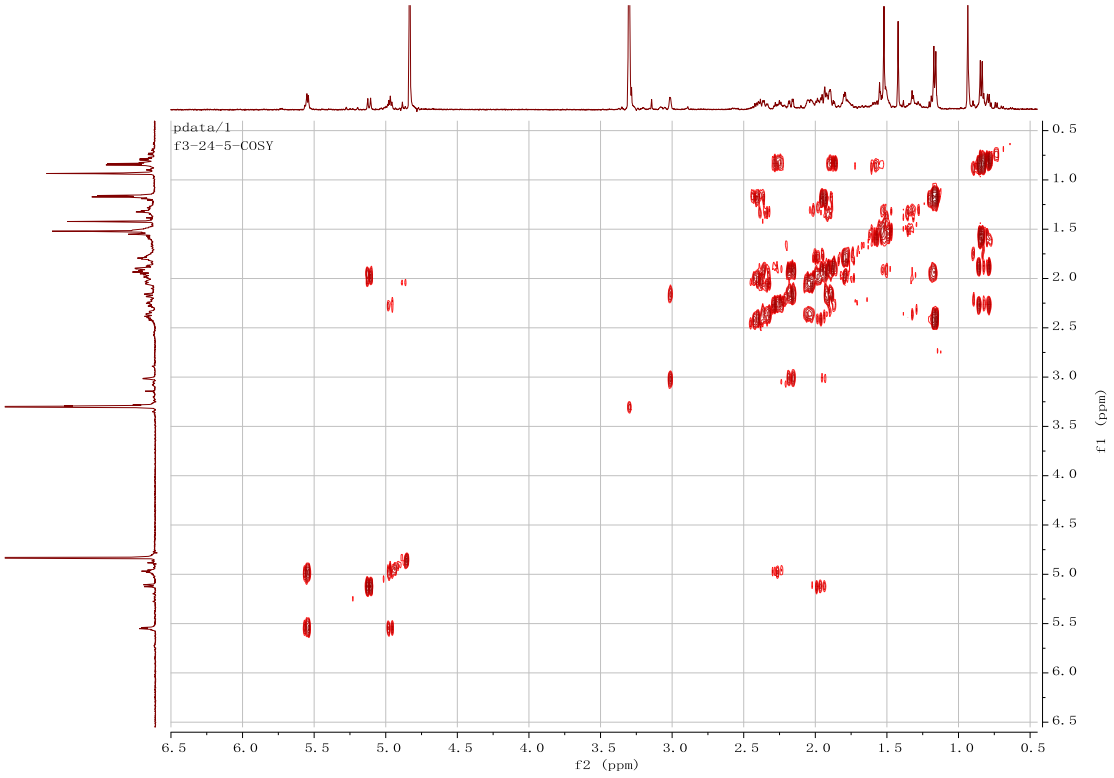


Figure S19. ^{1}H-^{1}H COSY spectrum of 1 in methanol-*d*$_4$

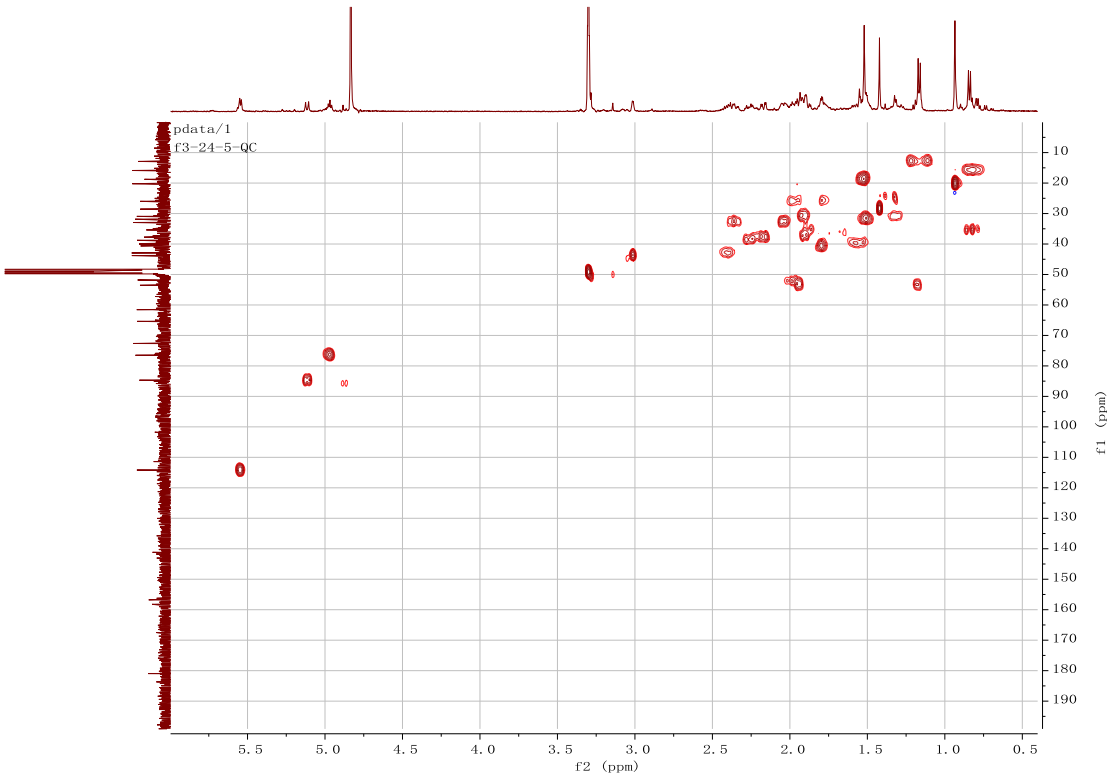


Figure S20. HSQC spectrum of 1 in methanol-*d*$_4$

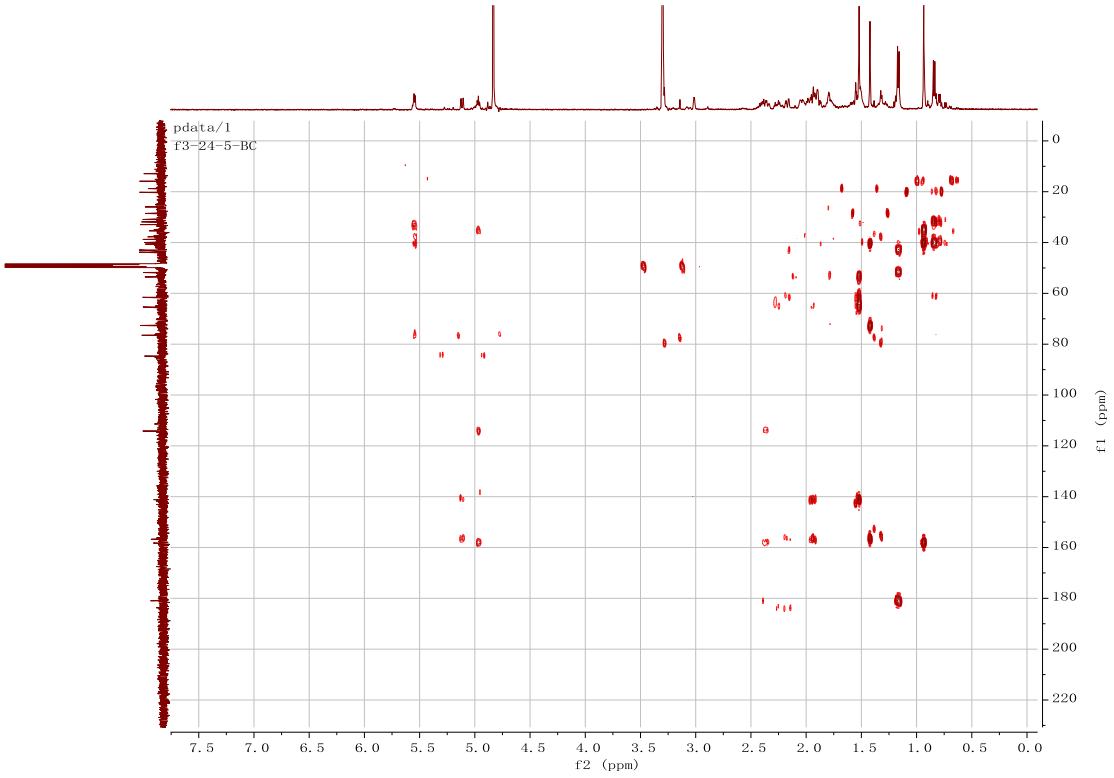


Figure S21. HMBC spectrum of 1 in methanol-*d*$_4$

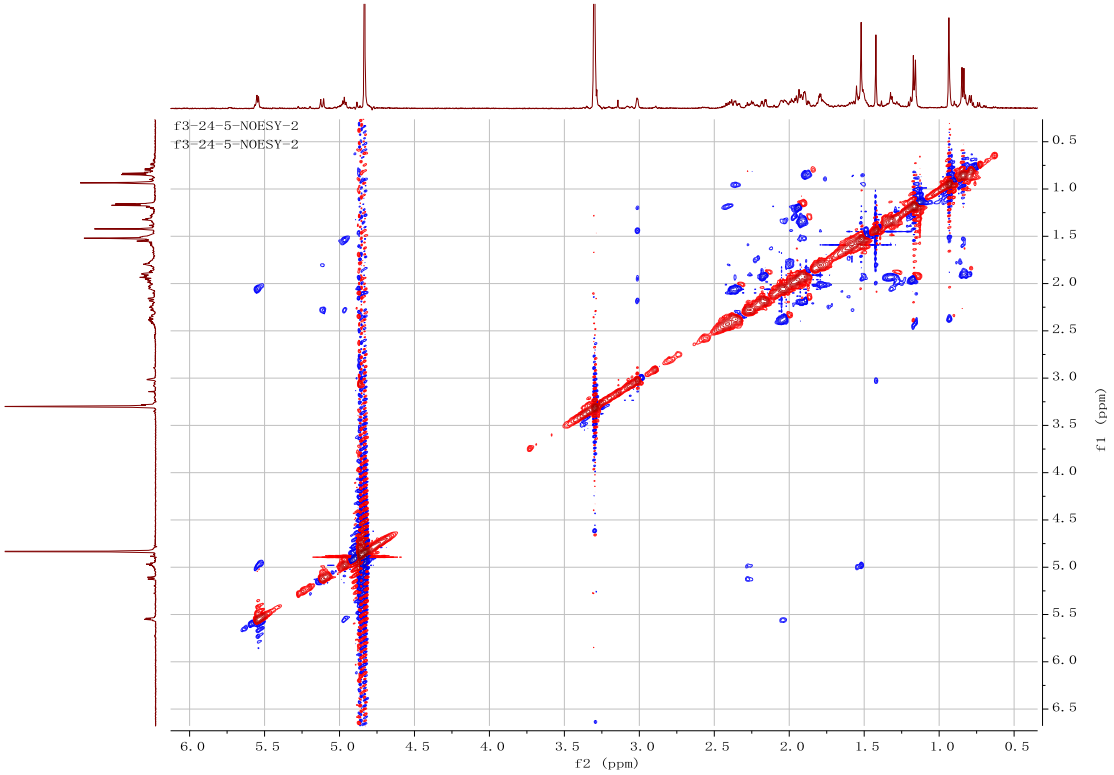


Figure S22. NOESY spectrum of 1 in methanol-*d*$_4$

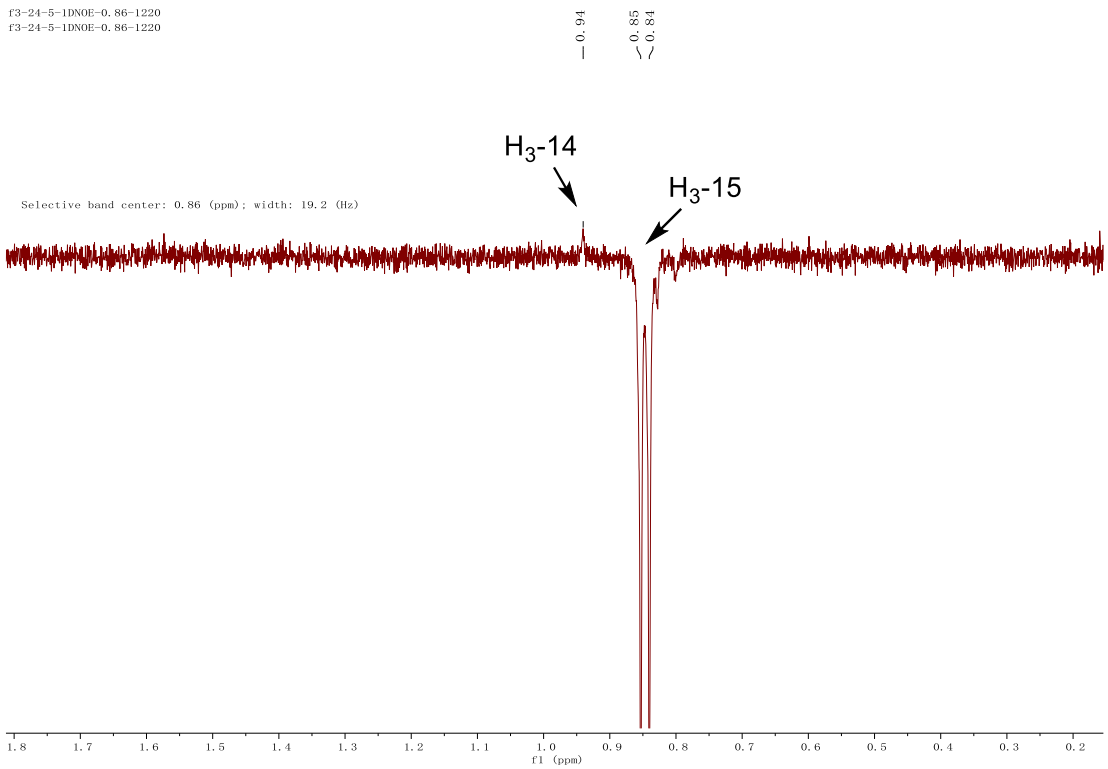


Figure S23. 1D NOE spectrum of 1 in methanol-d_4

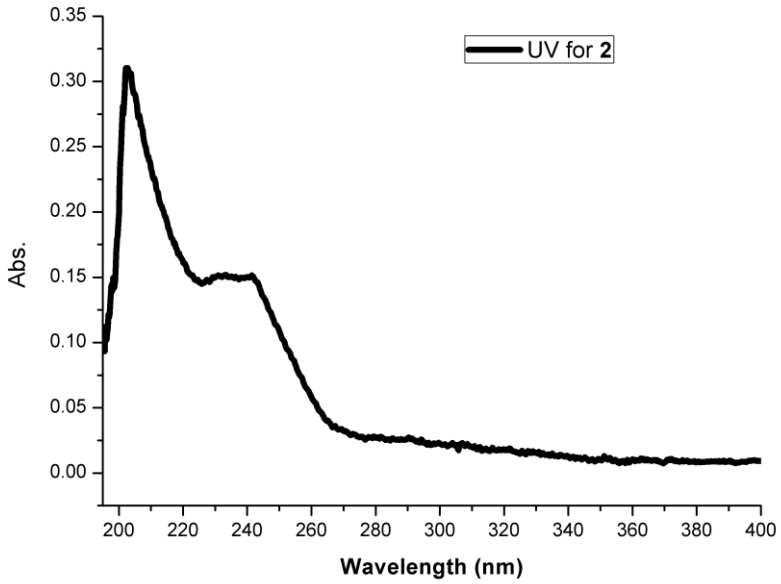


Figure S24. UV spectrum of 2

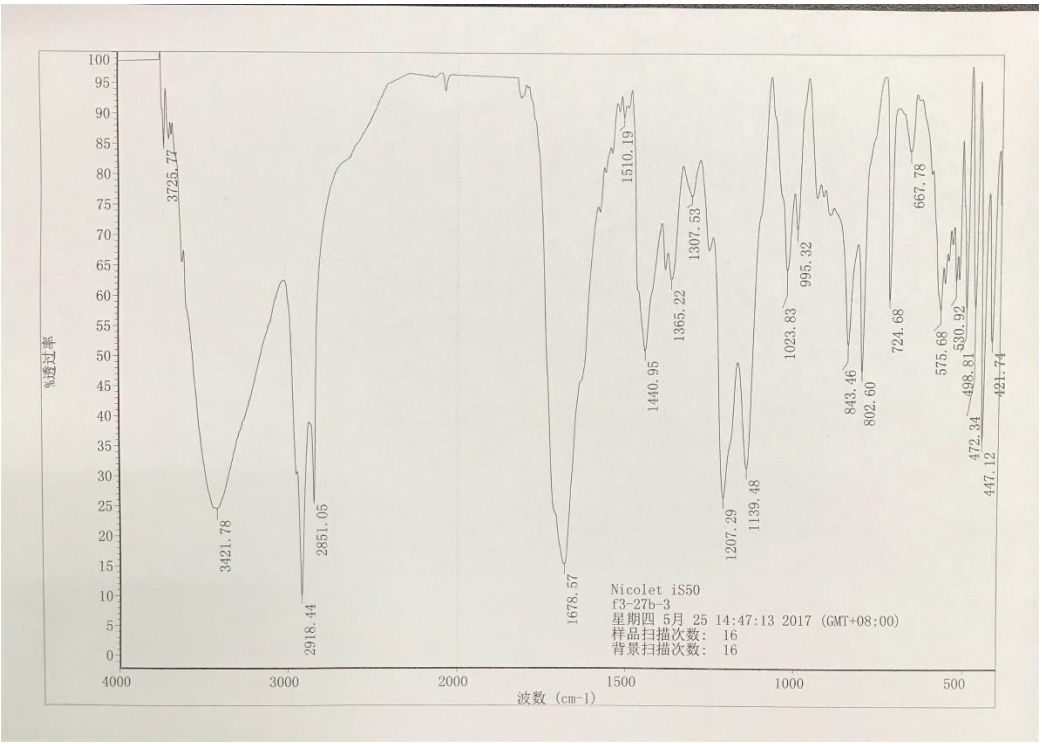


Figure S25. IR spectrum of 2

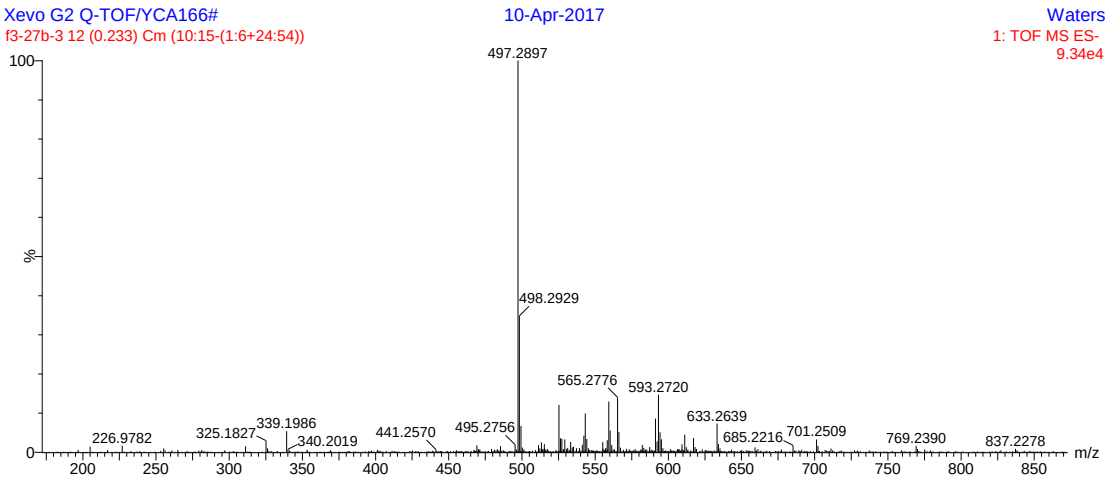


Figure S26. HRMS spectrum of 2

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
705 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-110 H: 0-200 N: 0-5 O: 0-50

Minimum:						-1.5		
Maximum:				5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
497.2897	497.2903	-0.6	-1.2	10.5	148.8	0.972	37.82	C30H41O6

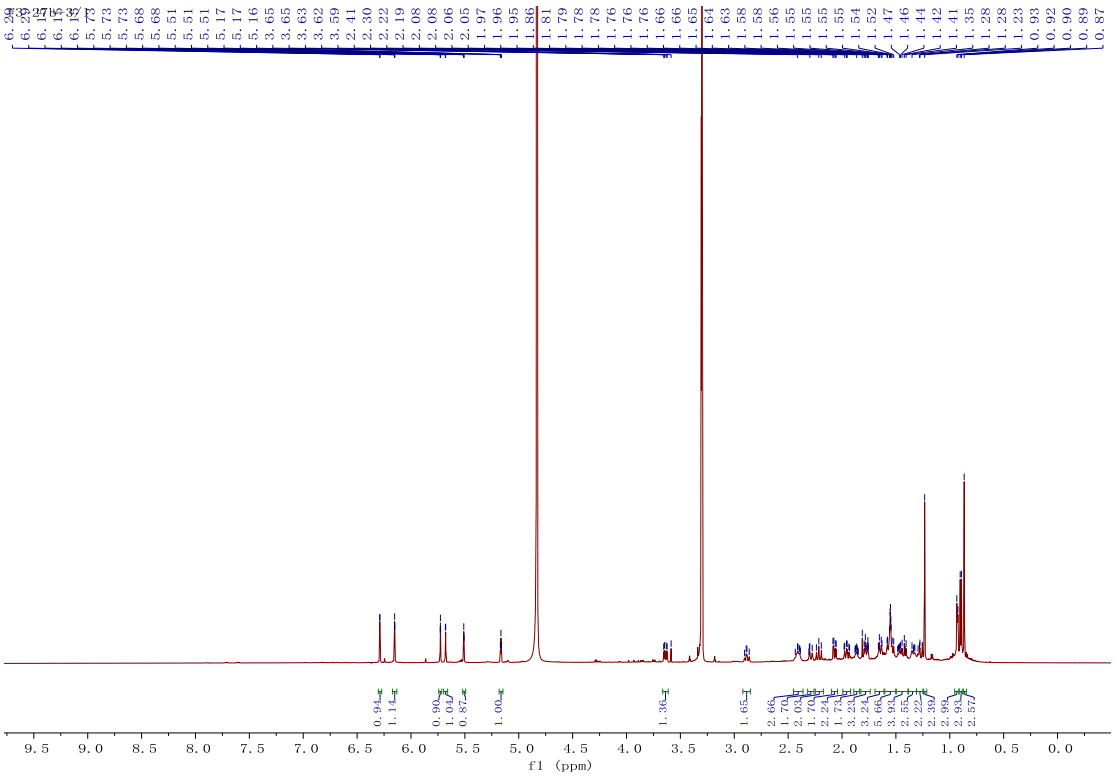


Figure S27. ^{1}H NMR spectrum of 2 in methanol-d_4

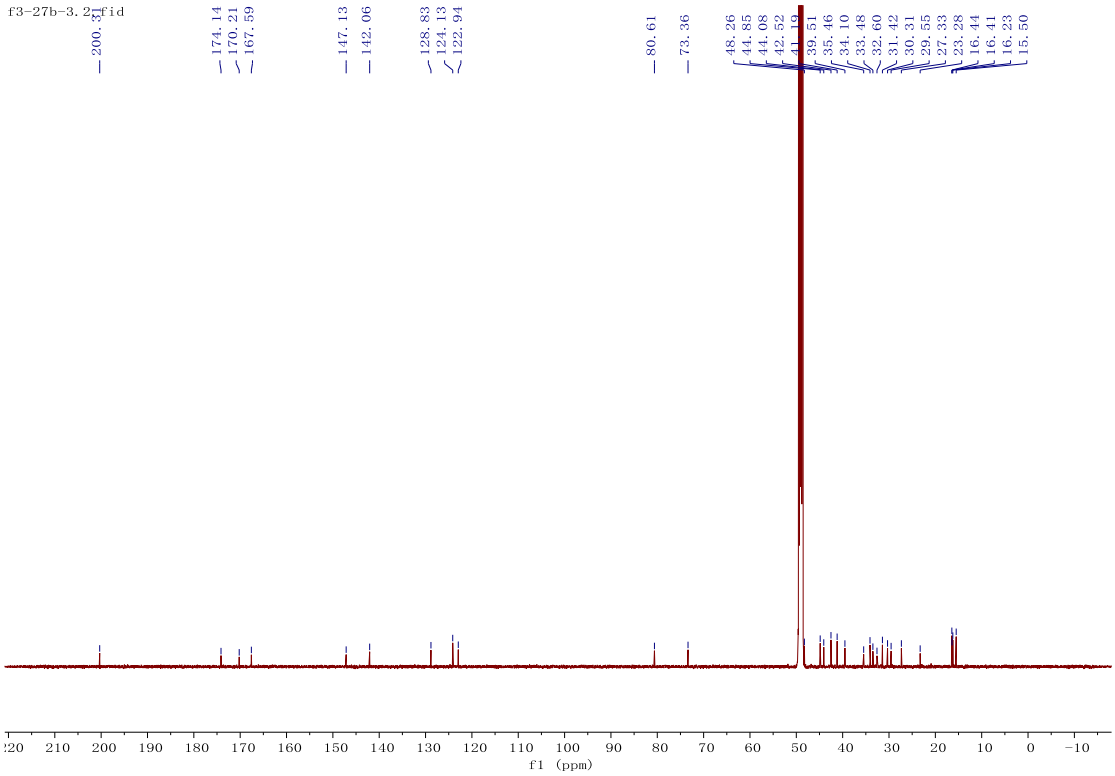


Figure S28. ^{13}C NMR spectrum of 2 in methanol-d_4

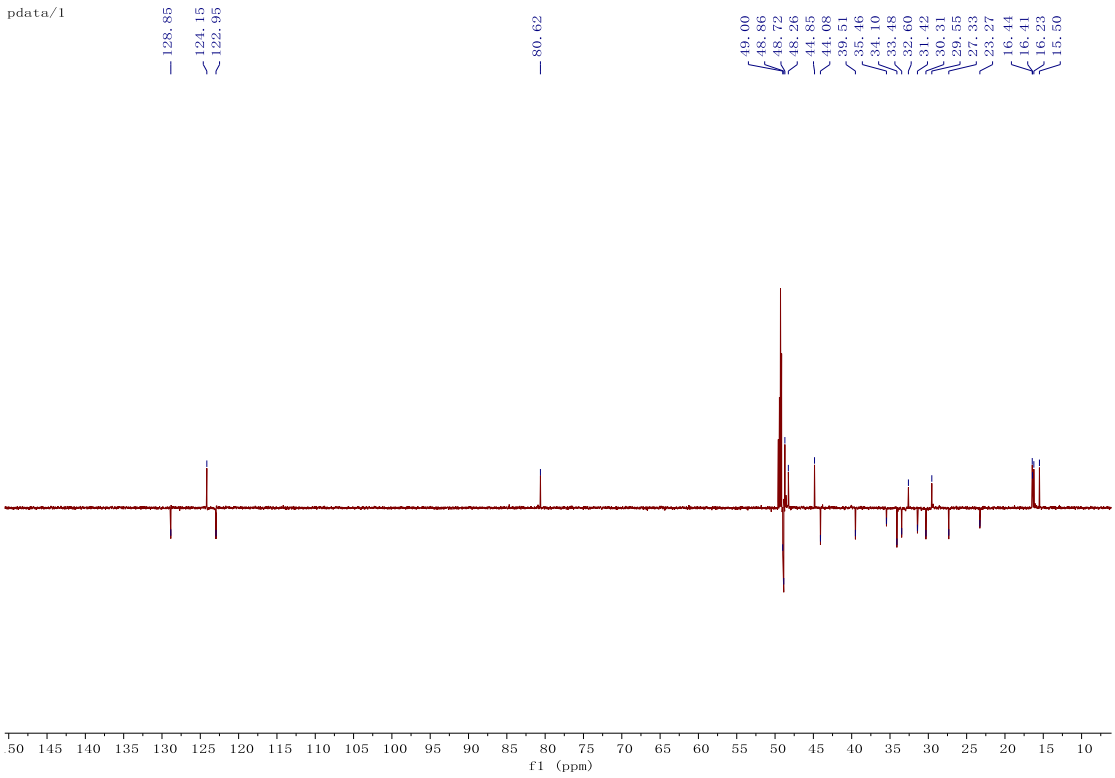


Figure S29. DEPT-135 spectrum of 2 in methanol-d_4

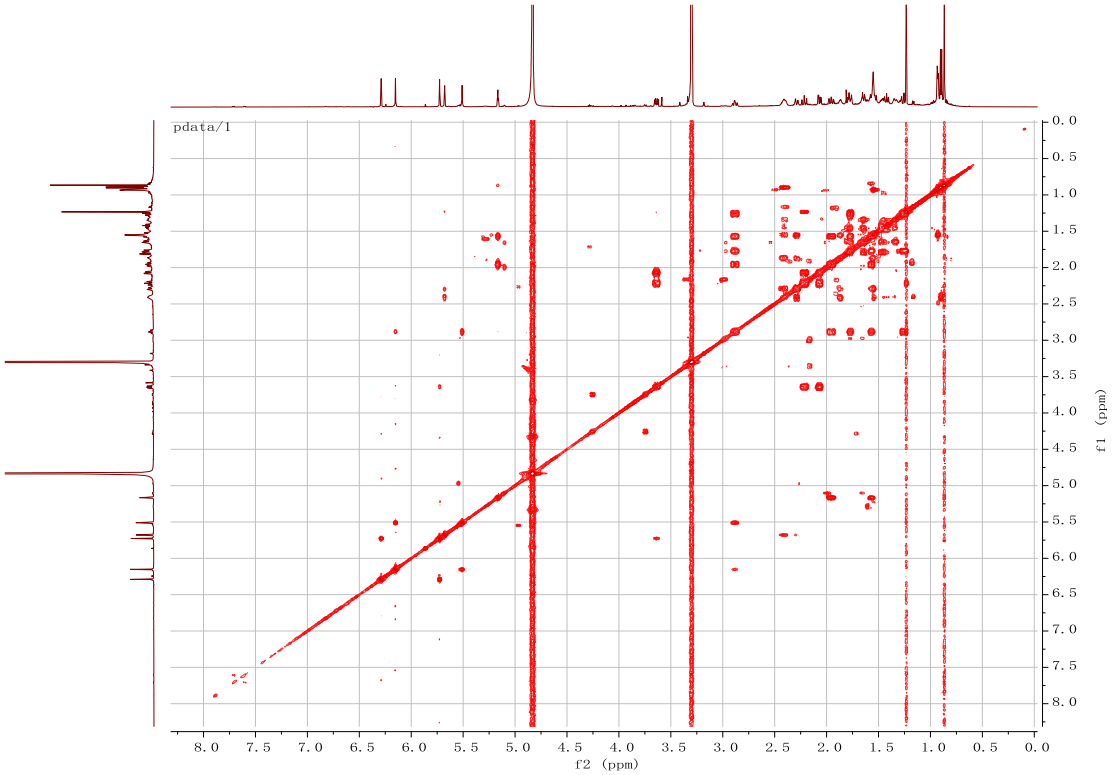


Figure S30. ^{1}H-^{1}H COSY spectrum of 2 in methanol-*d*$_4$

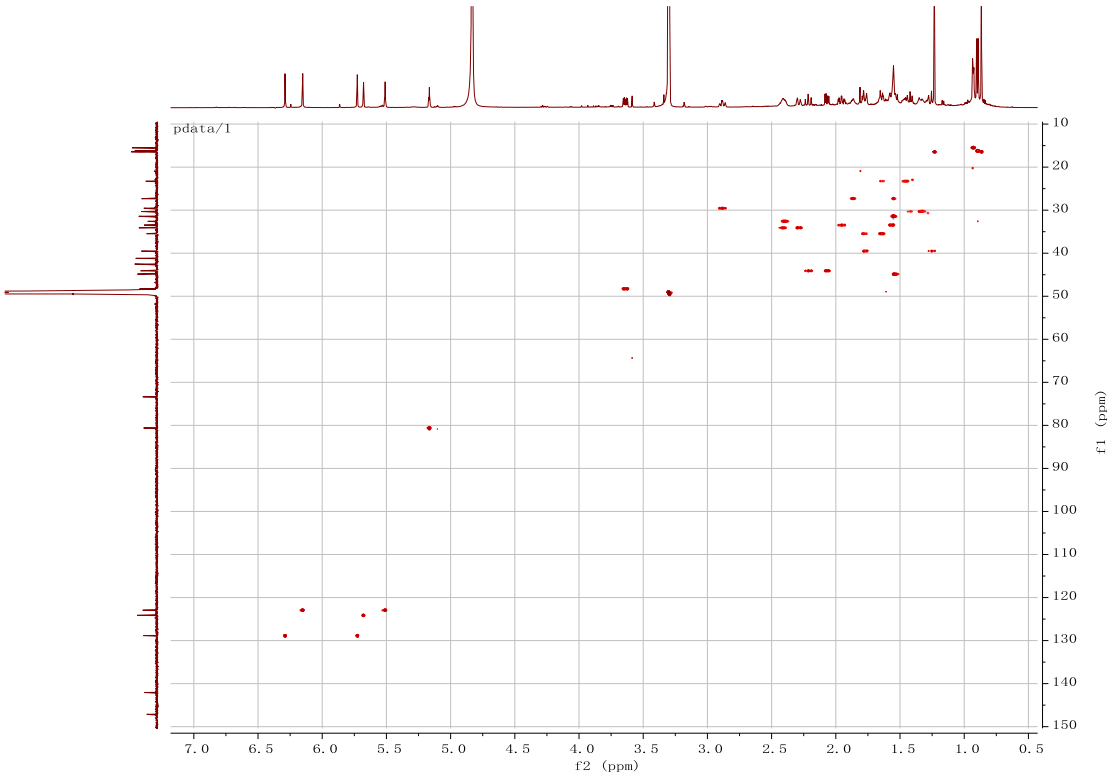
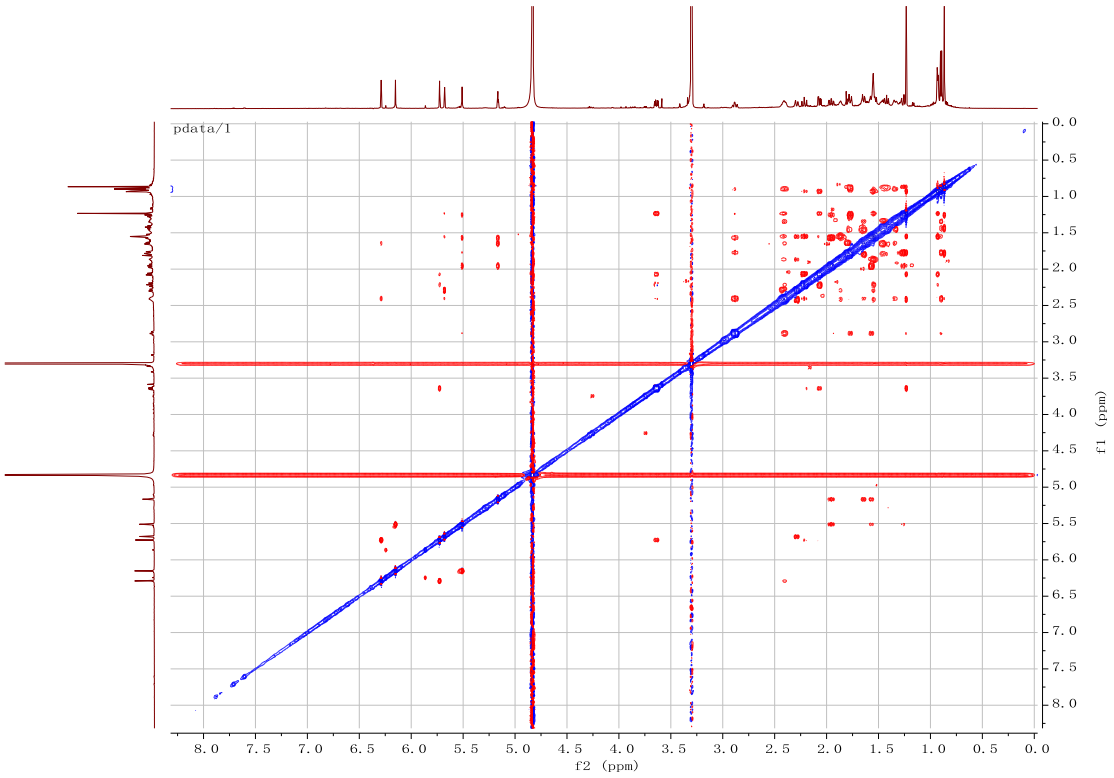


Figure S31. HSQC spectrum of 2 in methanol-*d*$_4$

Figure S32. HMBC spectrum of 2 in methanol-d_4



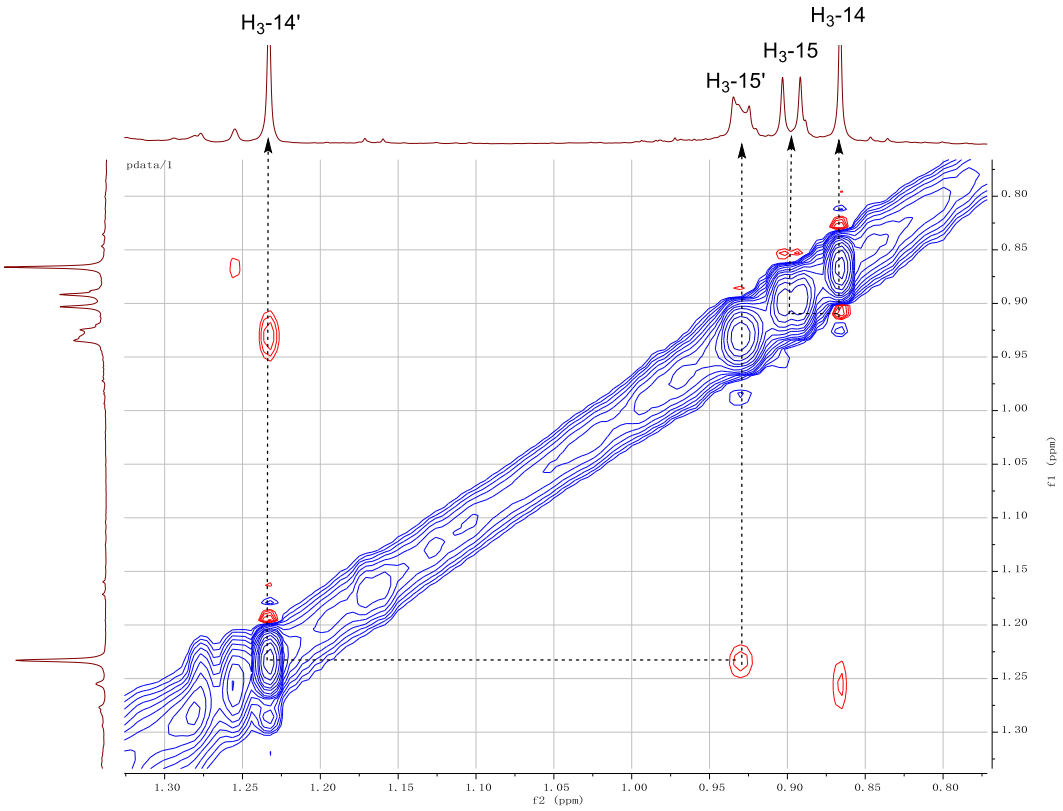


Figure S33. NOESY spectrum of 2 in methanol-d_4

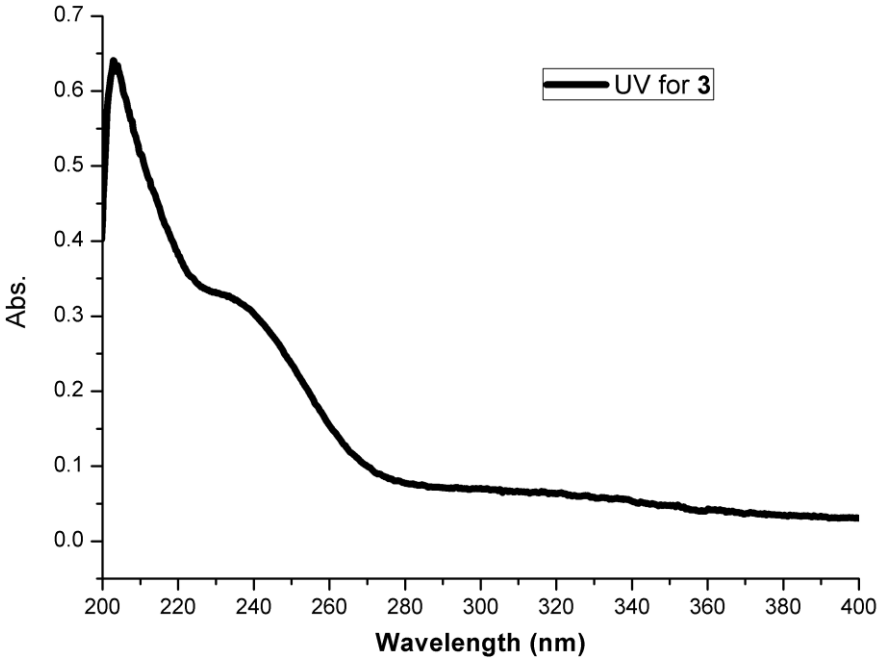


Figure S34. UV spectrum of 3

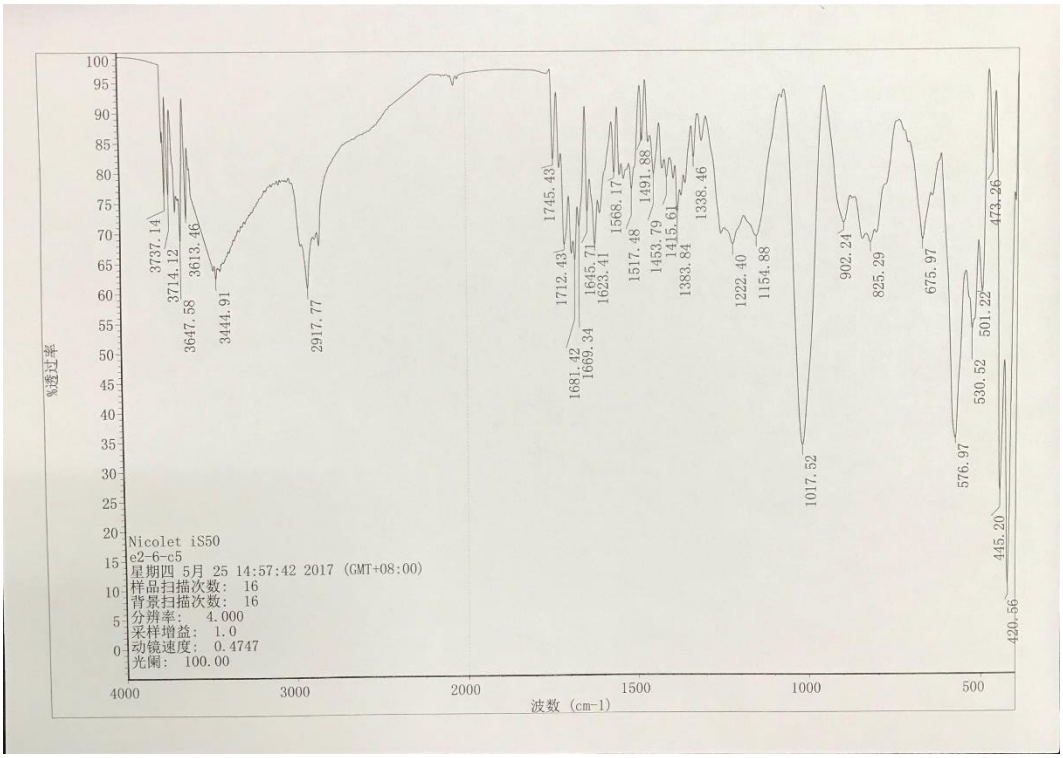


Figure S35. IR spectrum of 3

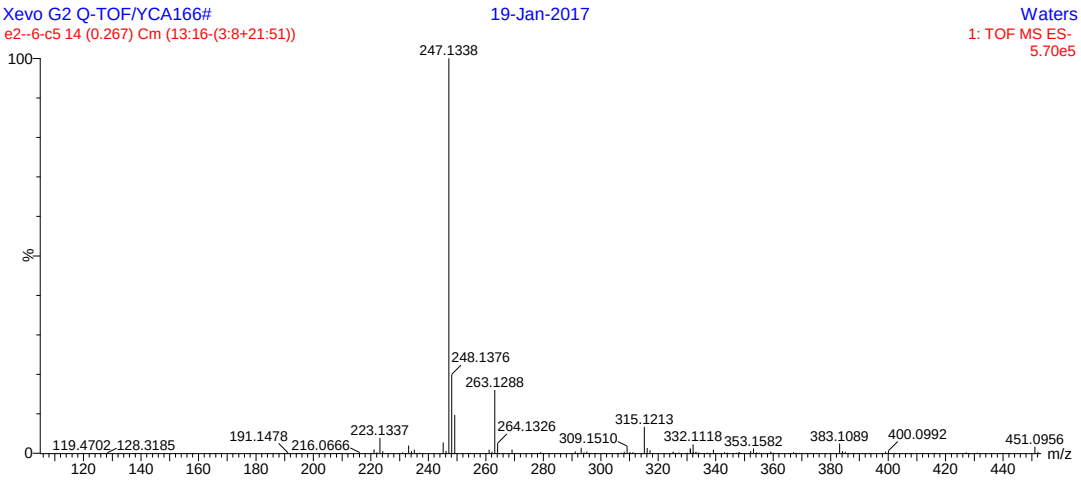


Figure S36. HRMS spectrum of 3

Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
73 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-110 H: 0-200 O: 0-50 Cl: 0-1

Minimum:			-1.5
Maximum:	5.0	10.0	50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
247.1338	247.1334	0.4	1.6	6.5	206.5	n/a	n/a	C15 H19 O3

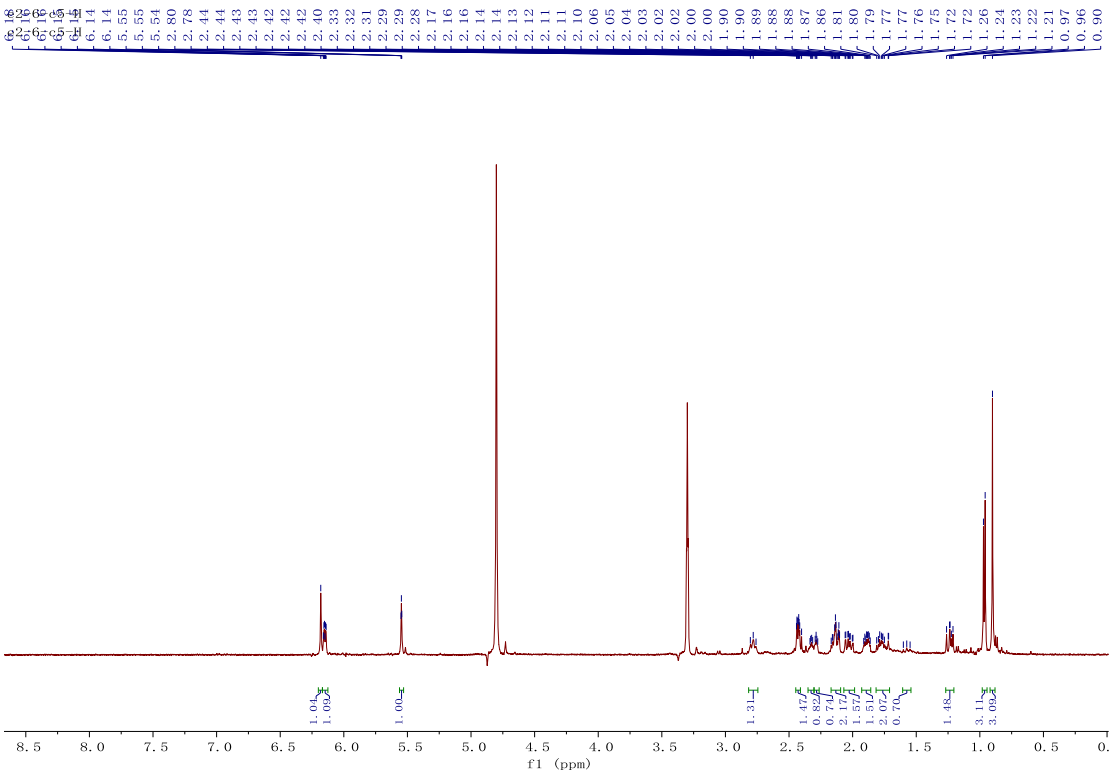


Figure S37. ^{1}H NMR spectrum of 3.

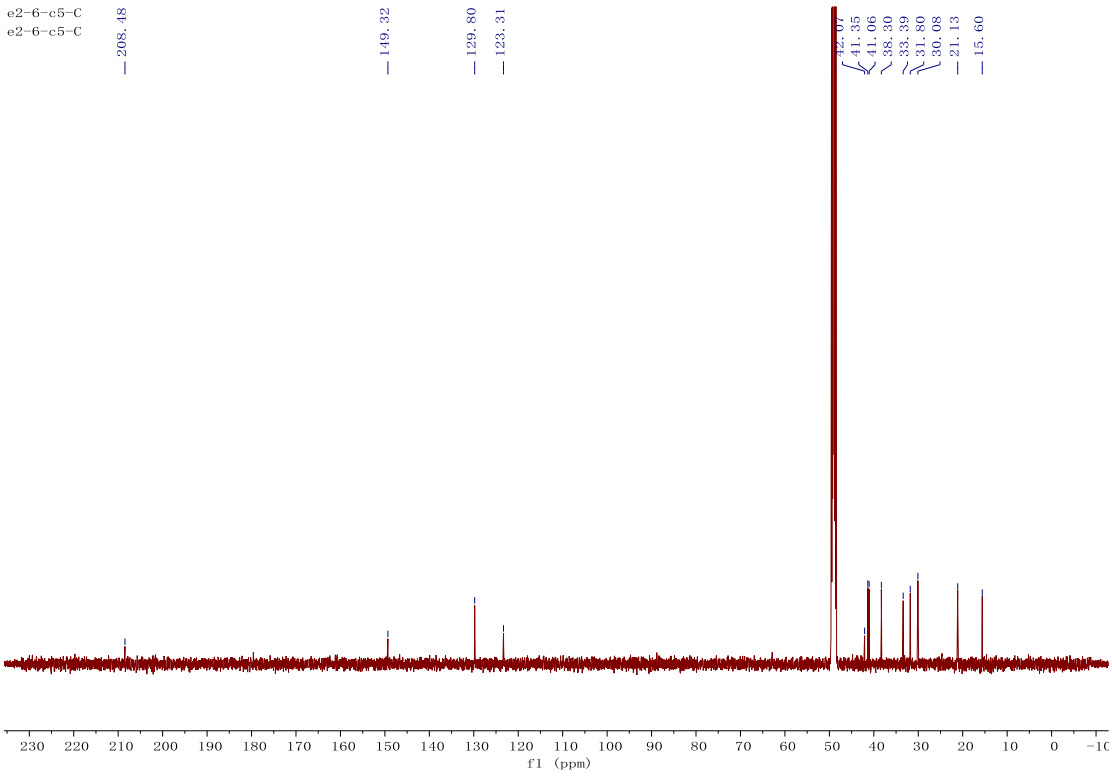


Figure S38. ^{13}C NMR spectrum of 3.

Figure S39. ^{1}H-^{1}H COSY spectrum of 3.

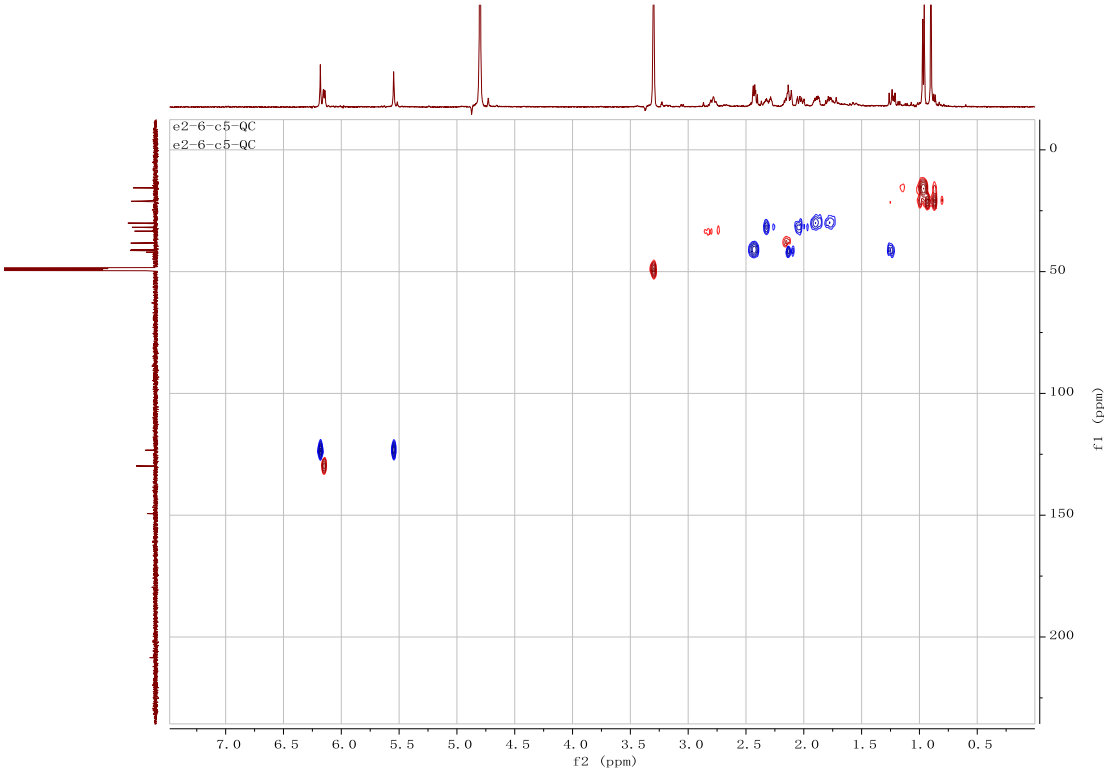


Figure S40. HSQC spectrum of 3.

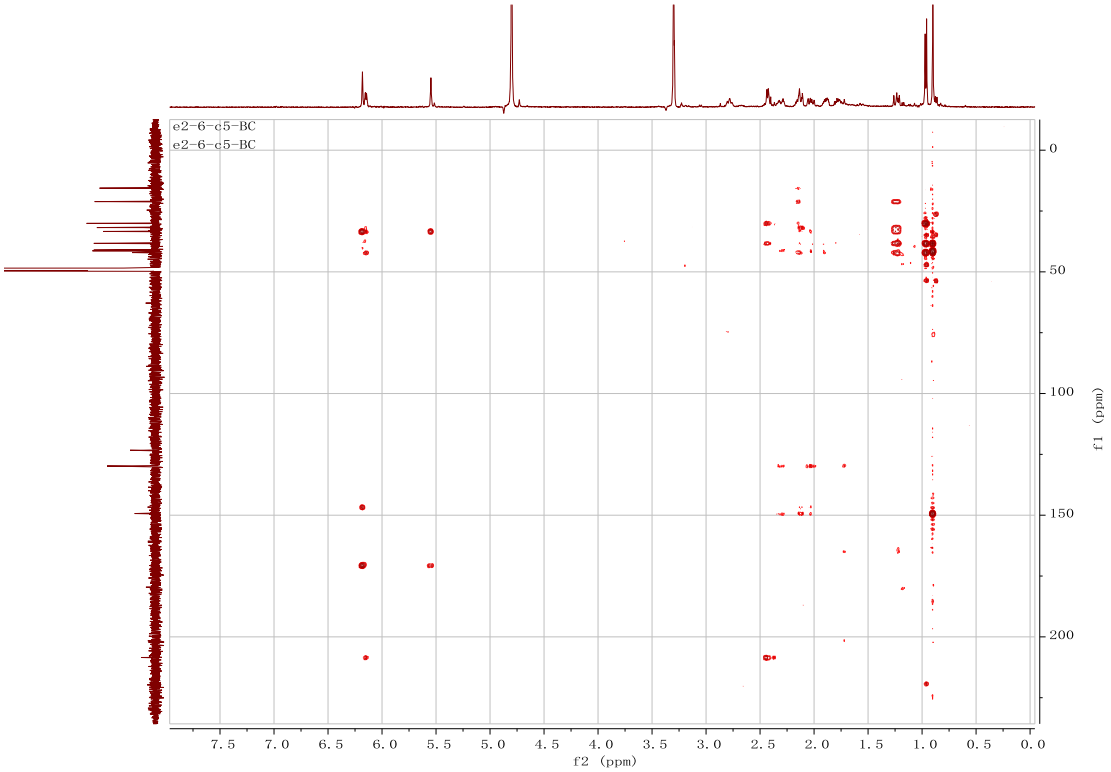


Figure S41. HMBC spectrum of 3

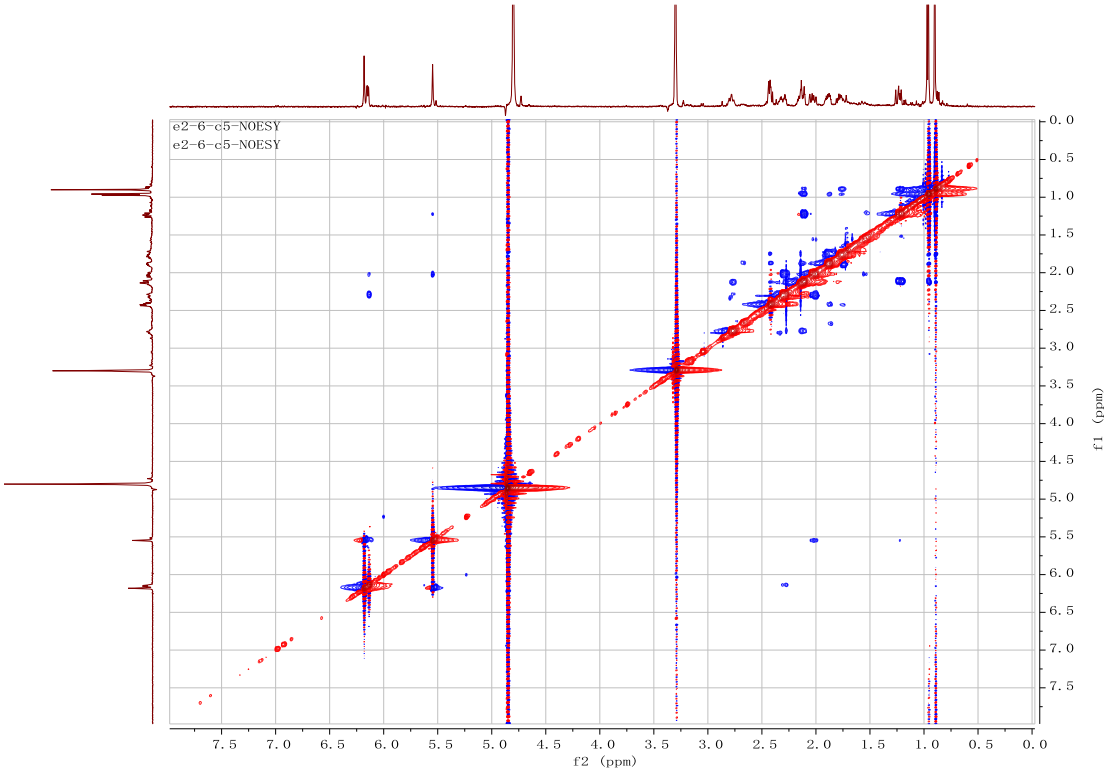


Figure S42. NOESY spectrum of 3

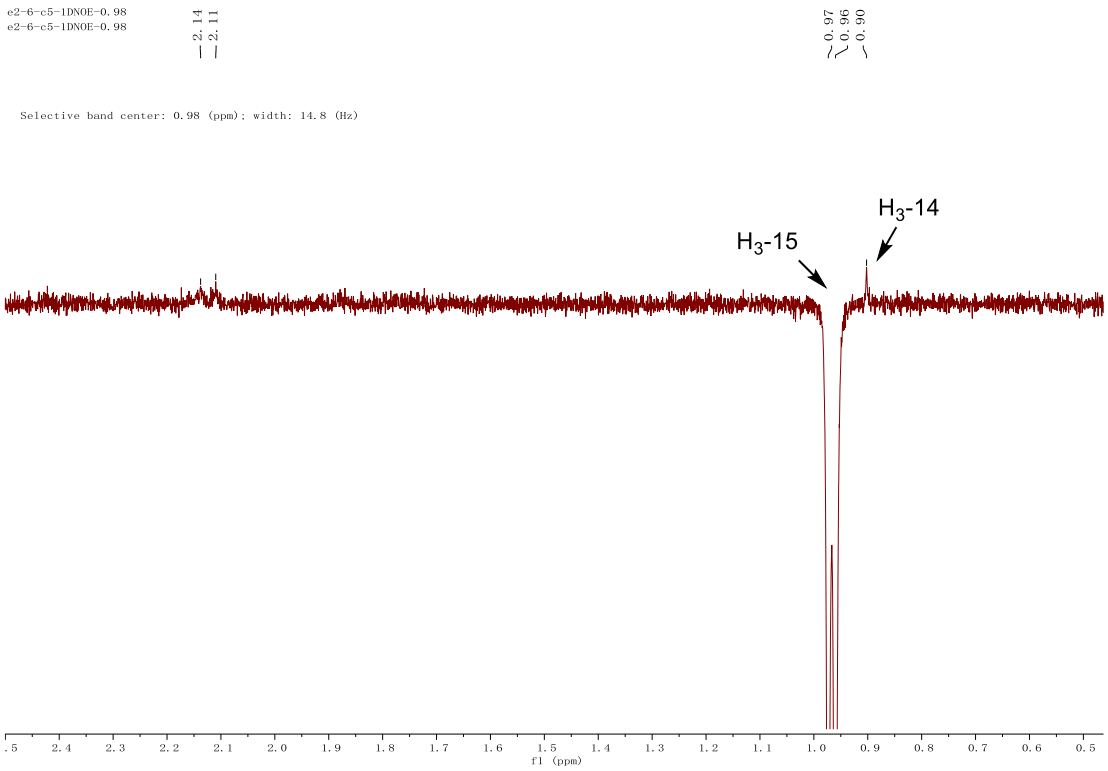


Figure S43. 1D NOE spectrum of 3 in methanol-d_4

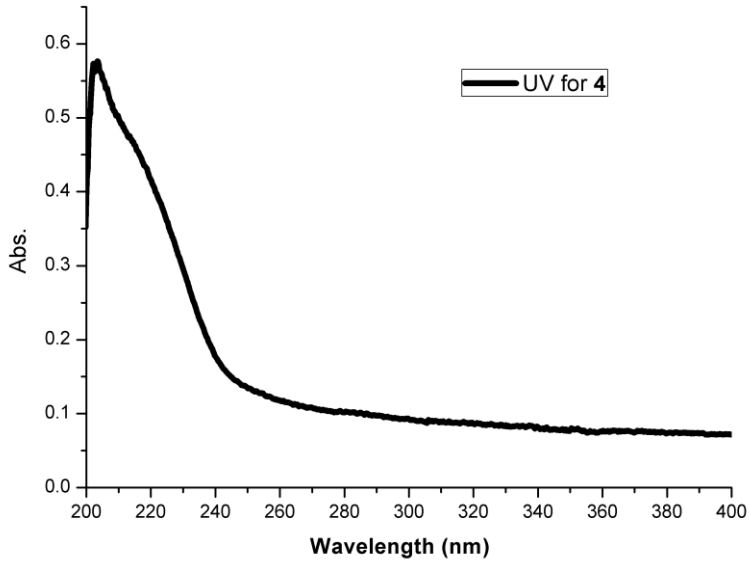


Figure S44. UV spectrum of 4

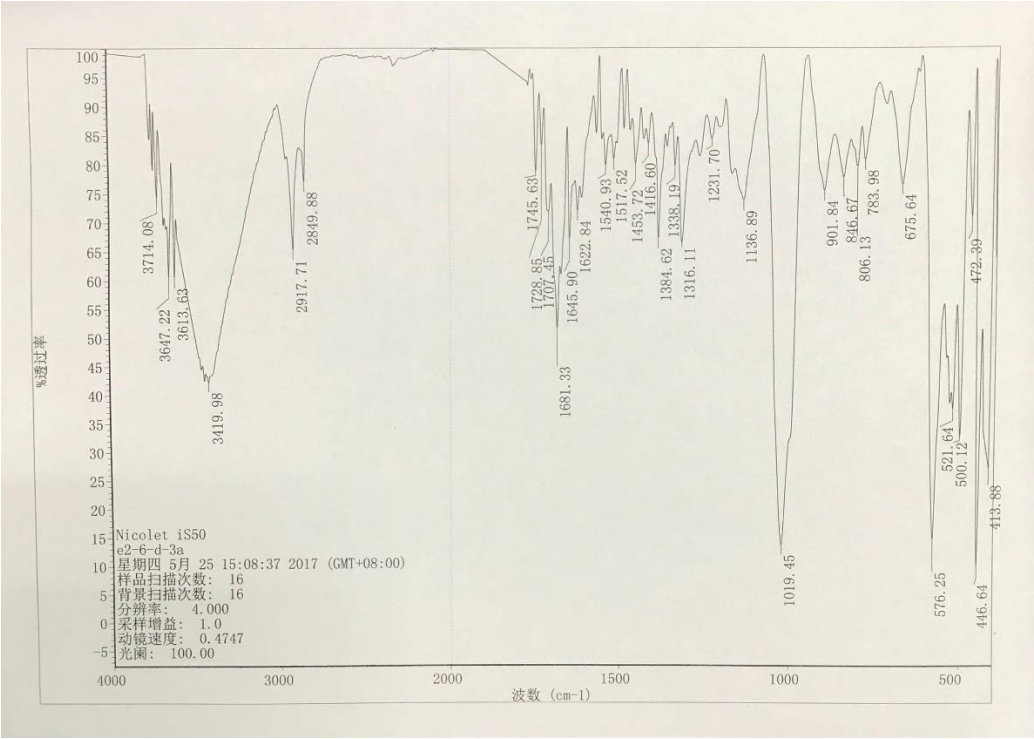


Figure S45. IR spectrum of 4

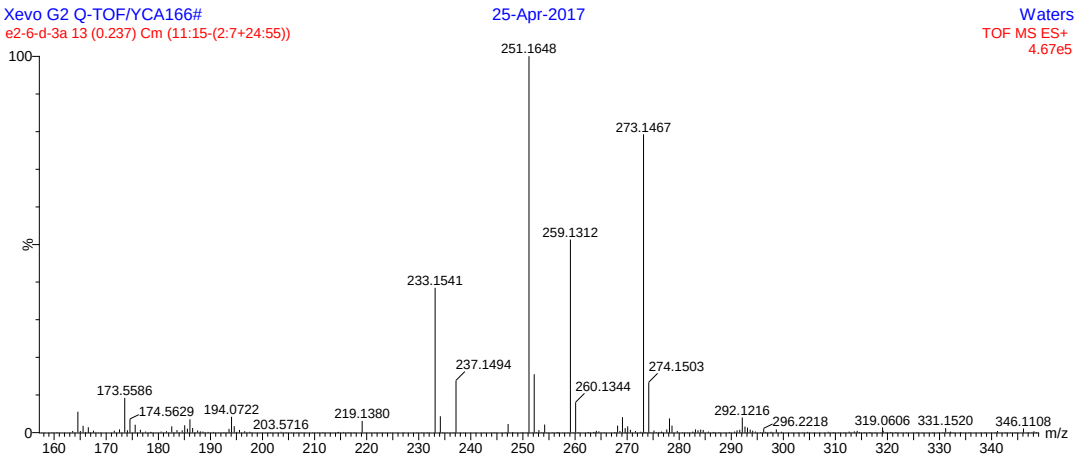


Figure S46. HRMS spectrum of 4

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
381 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-110 H: 0-200 N: 0-5 O: 0-50 Na: 0-1

Minimum:				-1.5				
Maximum:			5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
251.1648	251.1647	0.1	0.4	4.5	108.7	n/a	n/a	C15 H23 O3

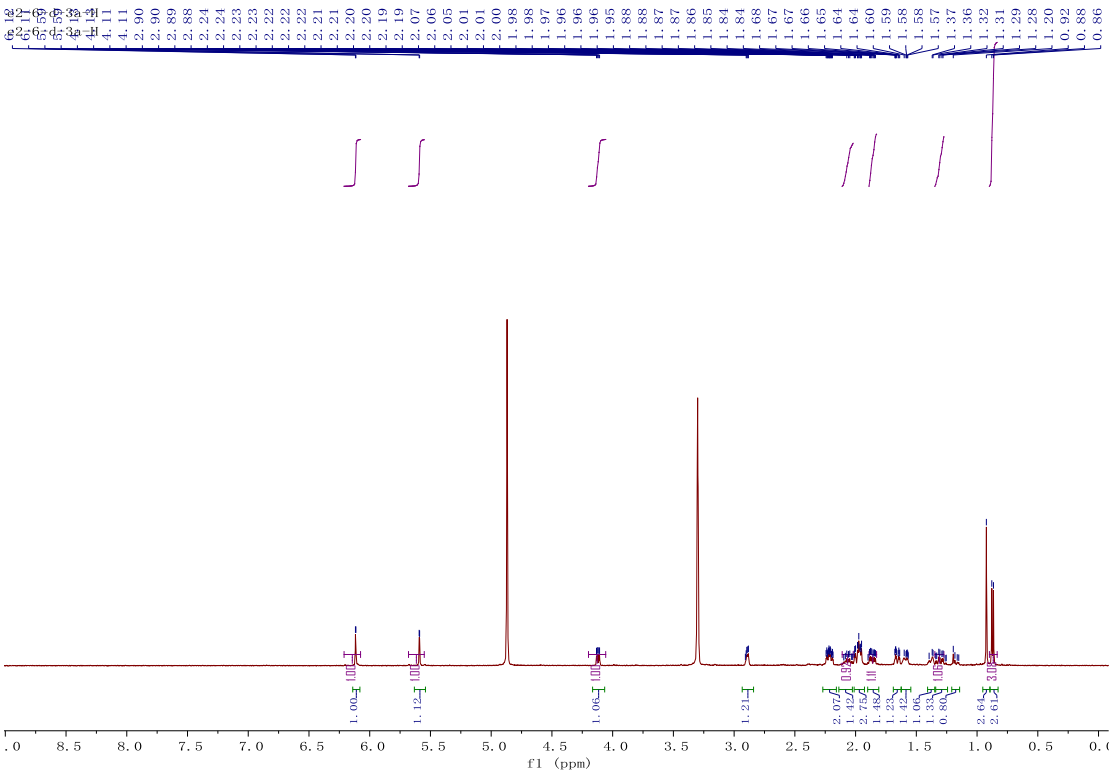


Figure S47. ^{1}H NMR spectrum of 4 in methanol-*d*$_4$

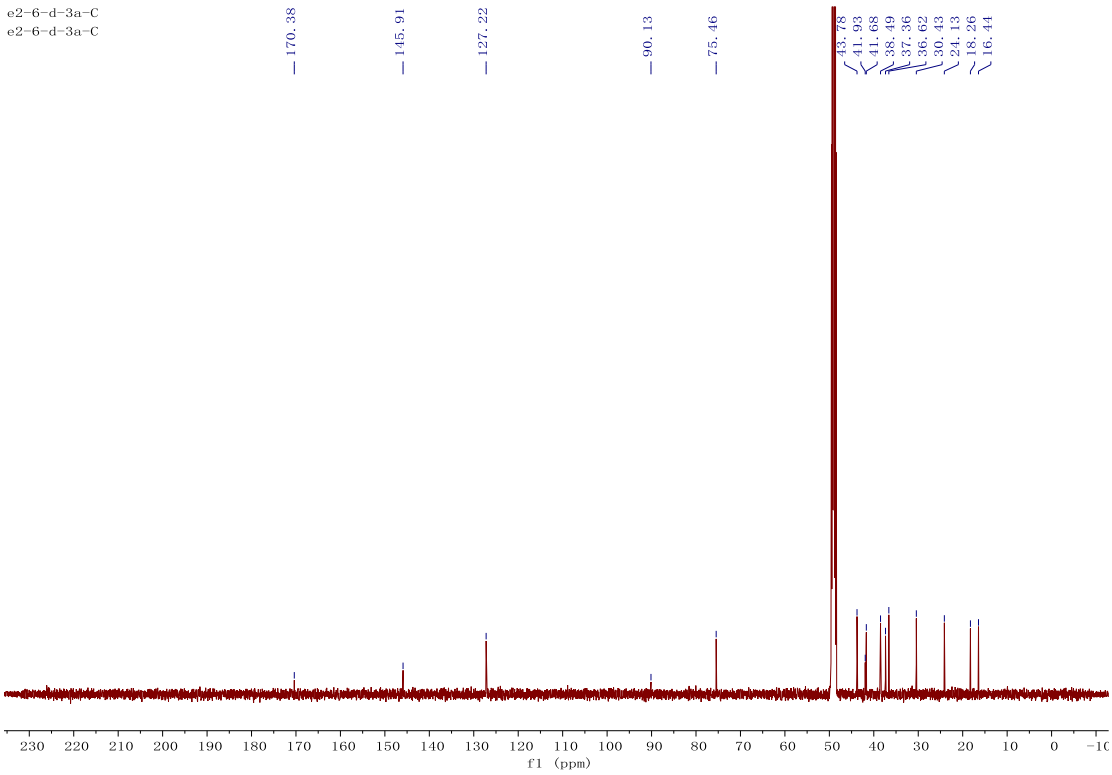


Figure S48. ^{13}C NMR spectrum of 4 in methanol-*d*$_4$

Figure S49. ^{1}H-^{1}H COSY spectrum of 4 in methanol-*d*$_4$

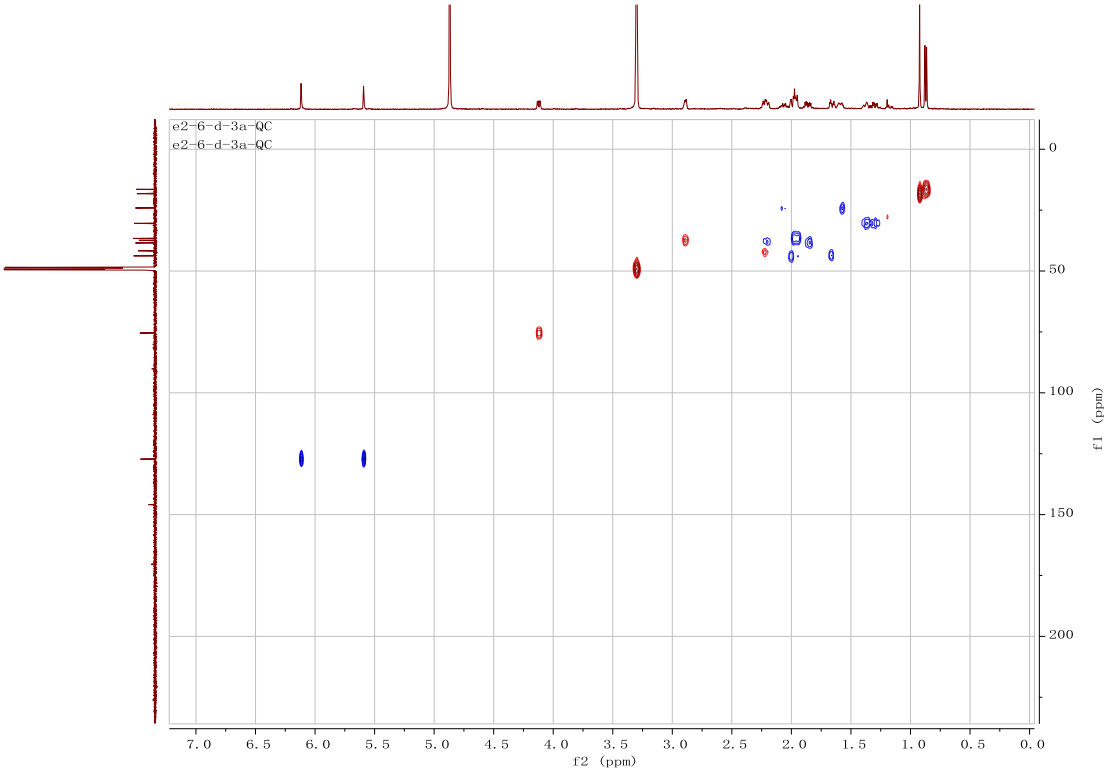


Figure S50. HSQC spectrum of 4 in methanol-*d*$_4$

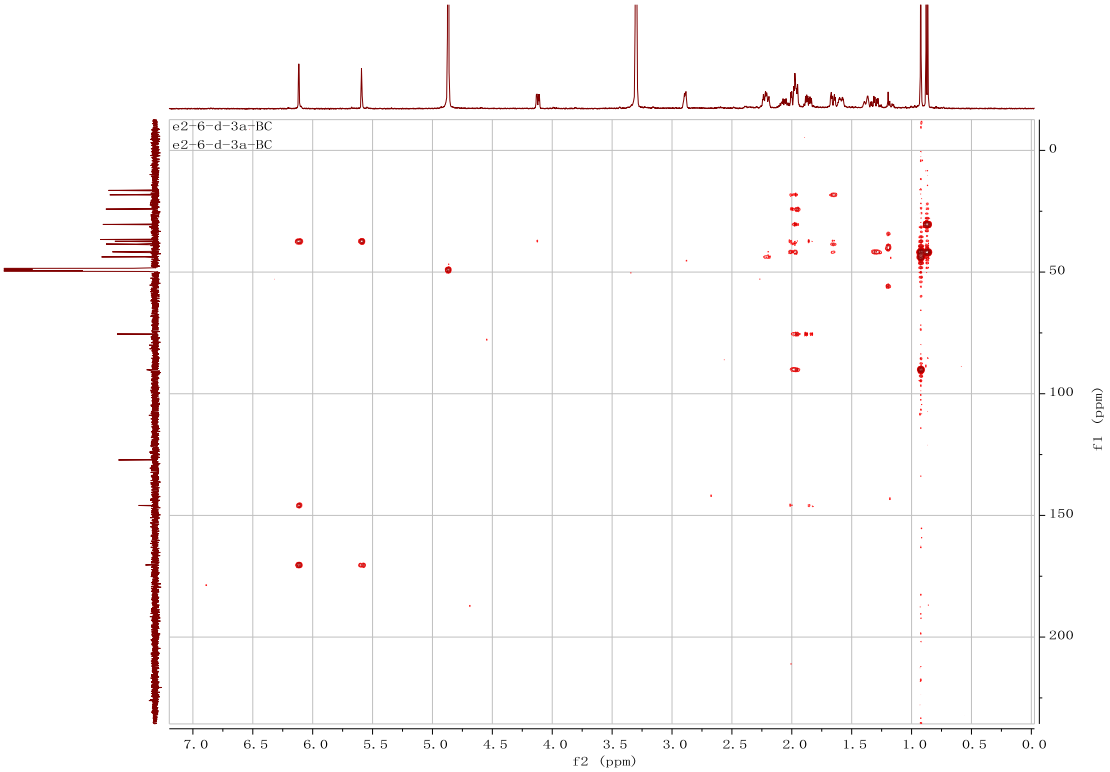


Figure S51. HMBC spectrum of 4 in methanol-*d*4

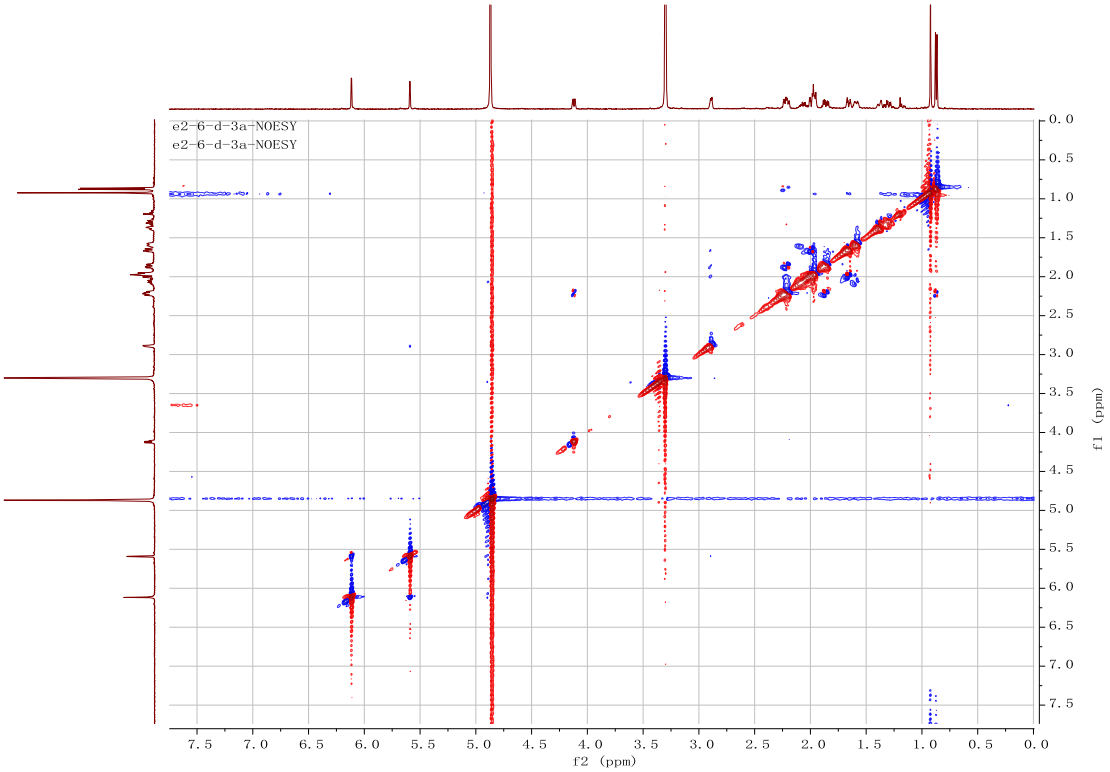


Figure S52. NOESY spectrum of 4 in methanol-*d*4

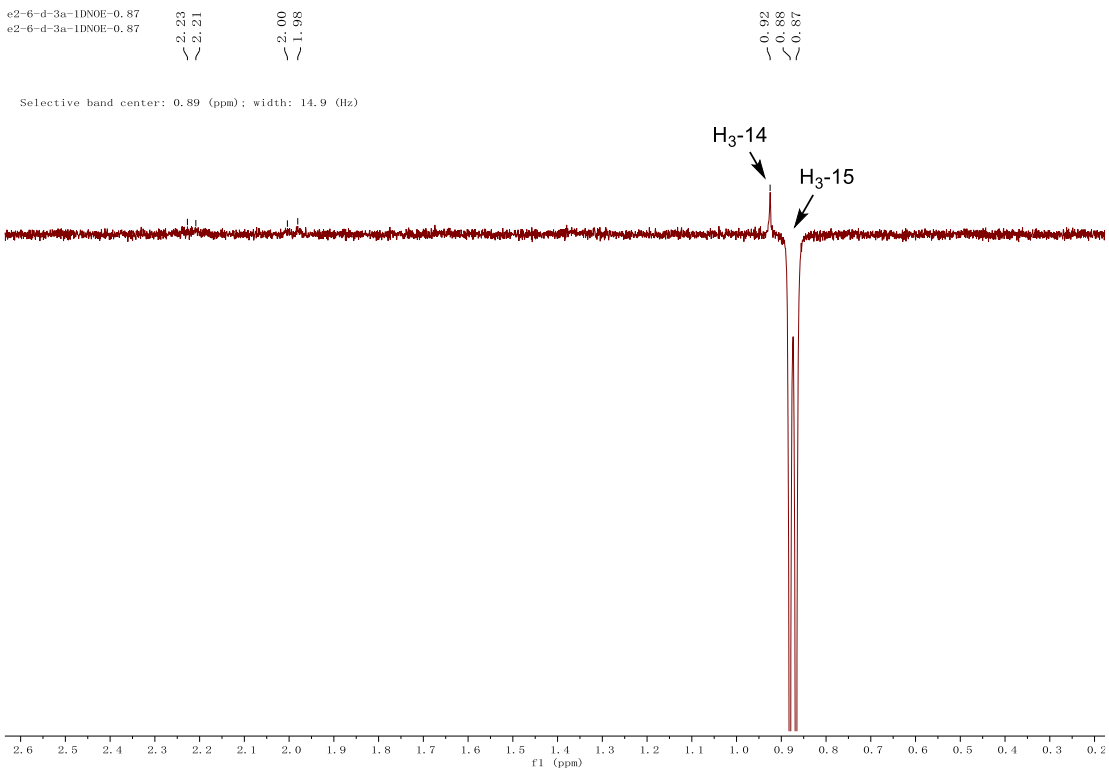


Figure S53. 1D NOE spectrum of 4 in methanol-*d*$_4$

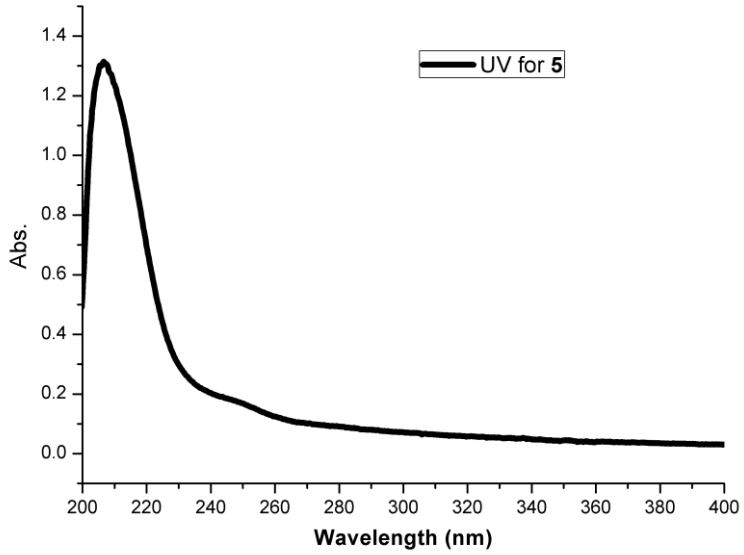


Figure S54. UV spectrum of 5

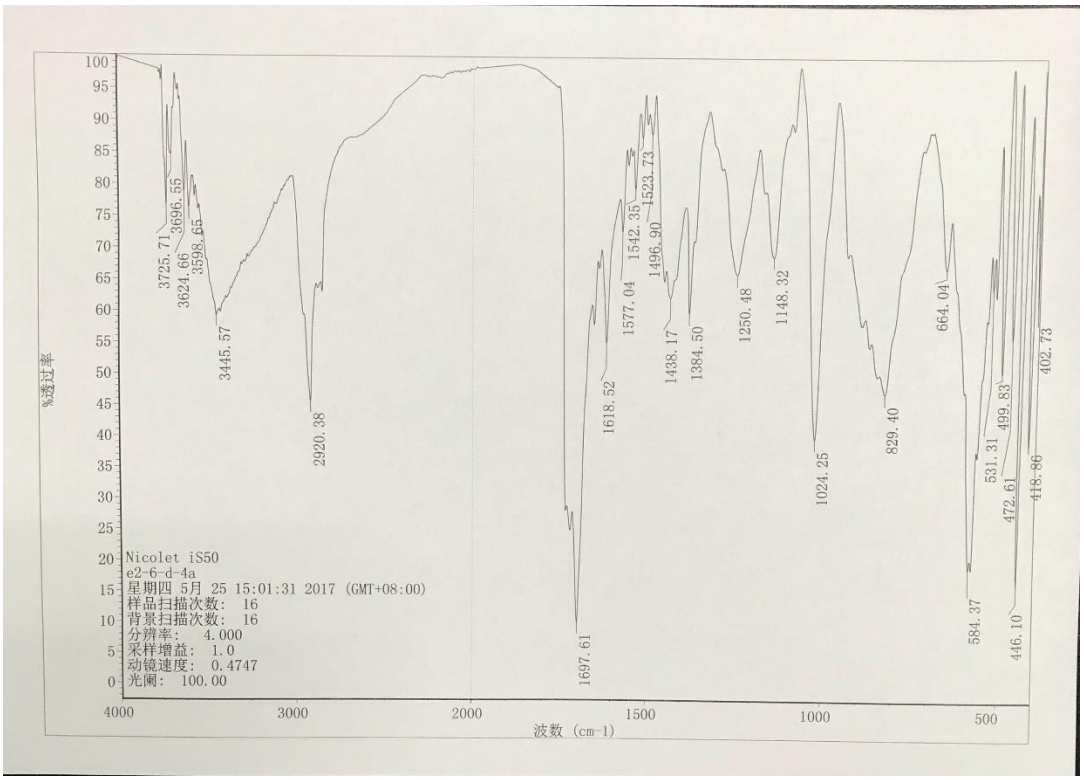


Figure S55. IR spectrum of 5

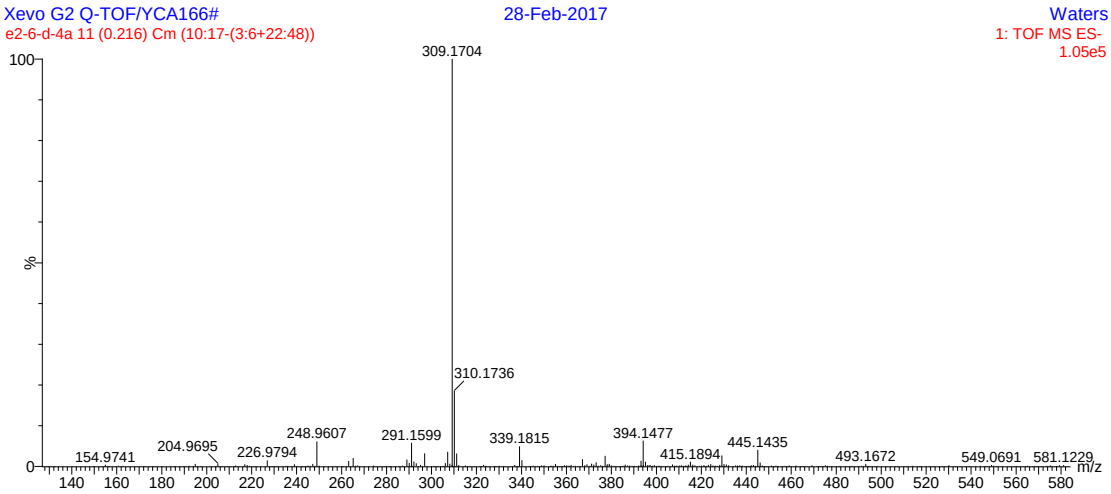


Figure S56. HRMS spectrum of 5

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
483 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-110 H: 0-200 N: 0-10 O: 0-50

Minimum:						-1.5		
Maximum:			5.0	5.0		50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
309.1704	309.1702	0.2	0.6	5.5	89.7	0.005	99.48	C17H25O5
	309.1715	-1.1	-3.6	10.5	94.9	5.257	0.52	C18H21N4O

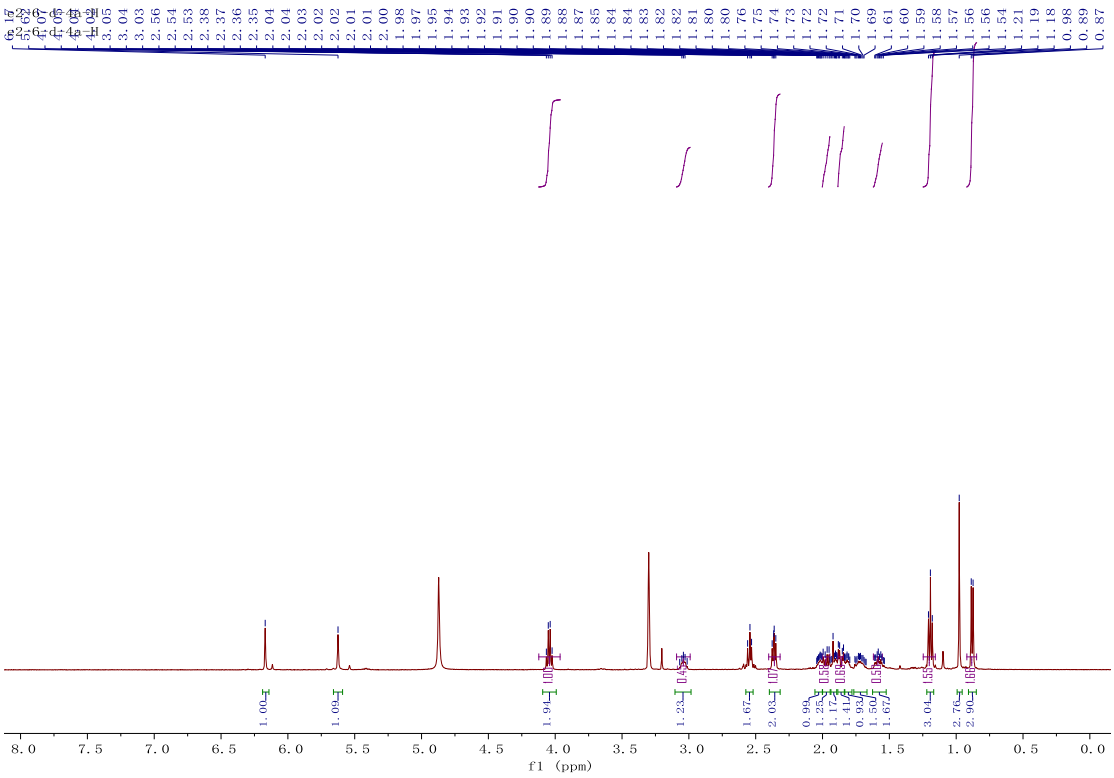


Figure S57. ^{1}H NMR spectrum of 5 in methanol-d_4

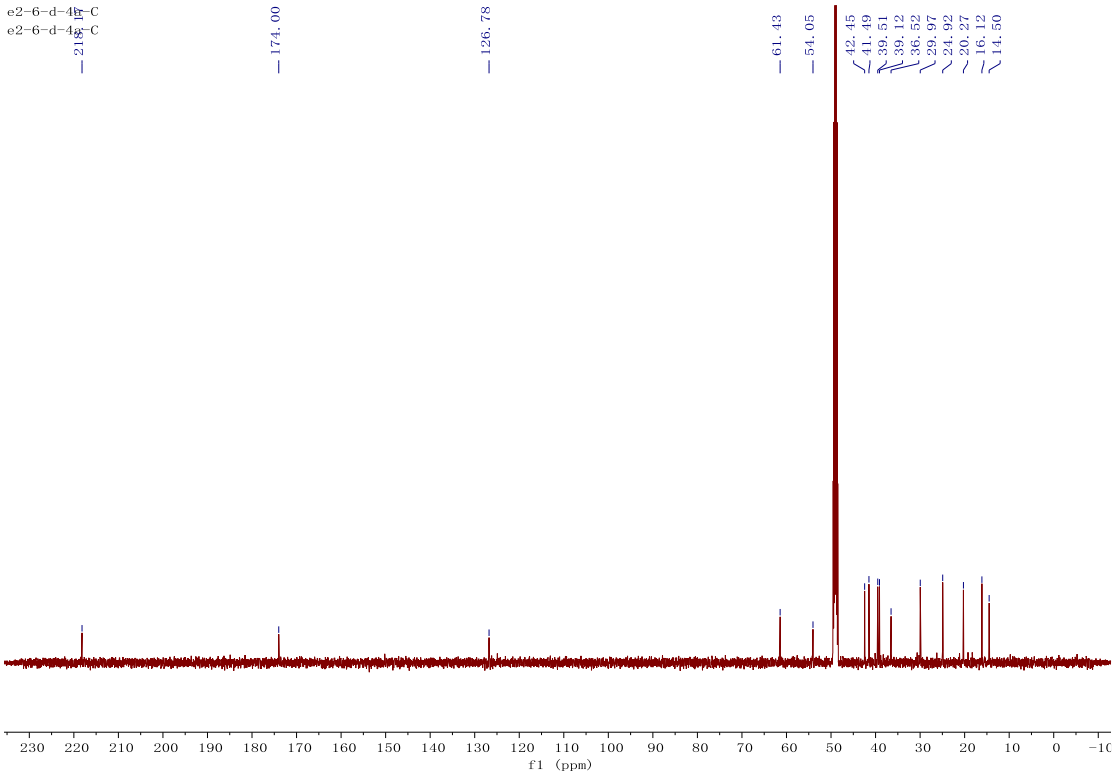


Figure S58. ^{13}C NMR spectrum of 5 in methanol-*d*$_4$

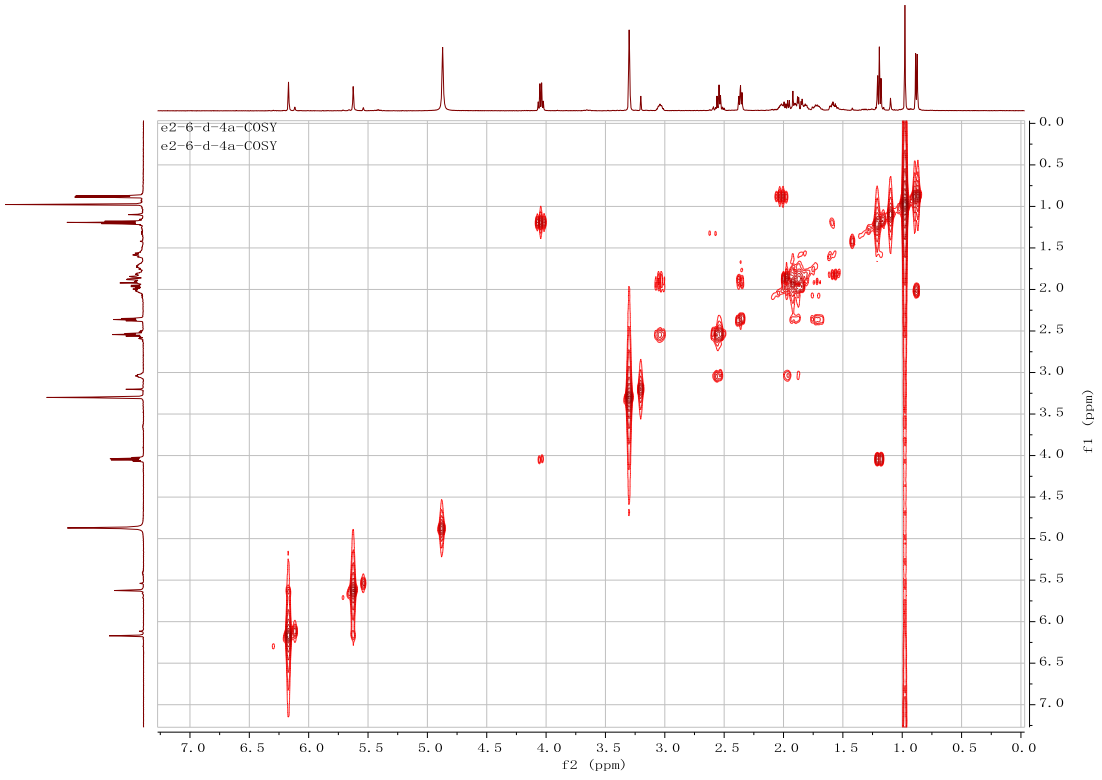


Figure S59. ^{1}H-^{1}H COSY spectrum of 5 in methanol-*d*$_4$

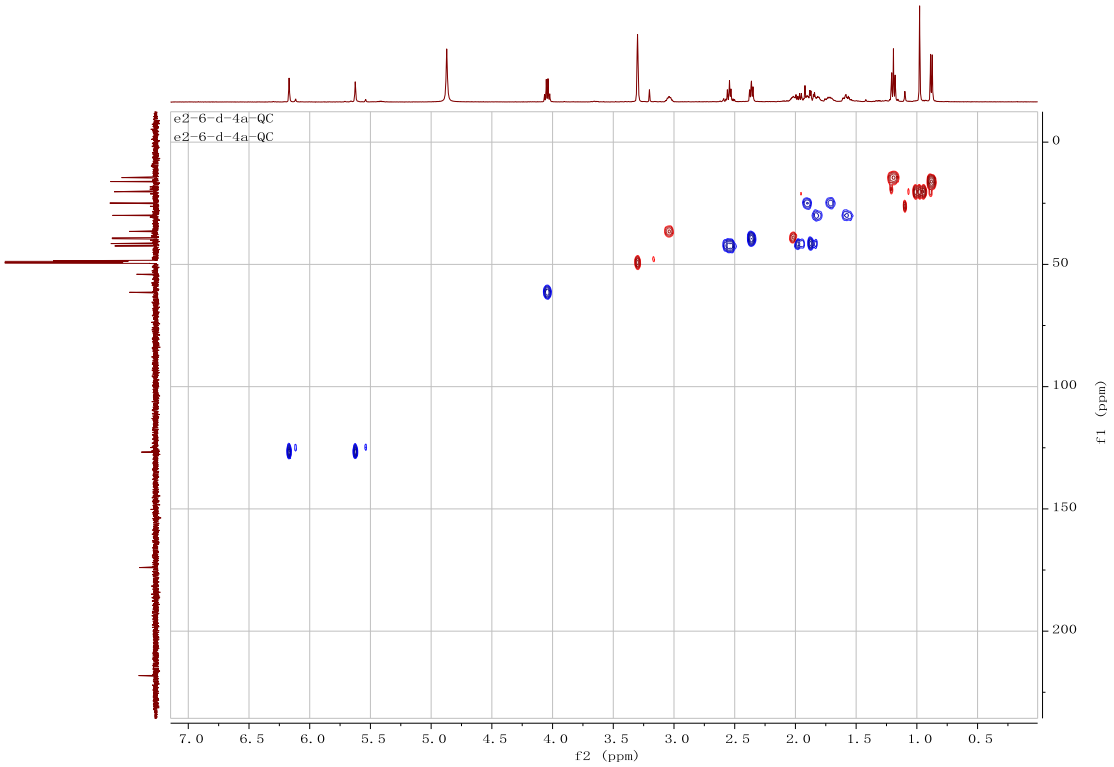


Figure S60. HSQC spectrum of 5 in methanol-*d*4

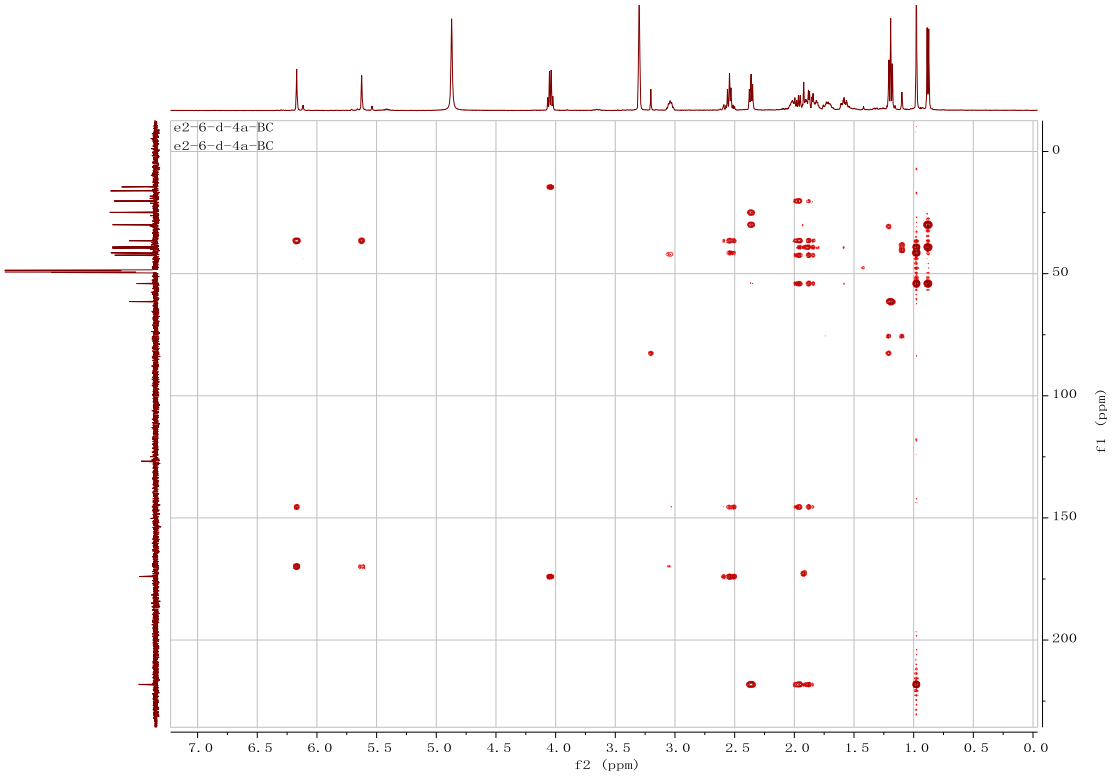


Figure S61. HMBC spectrum of 5 in methanol-*d*4

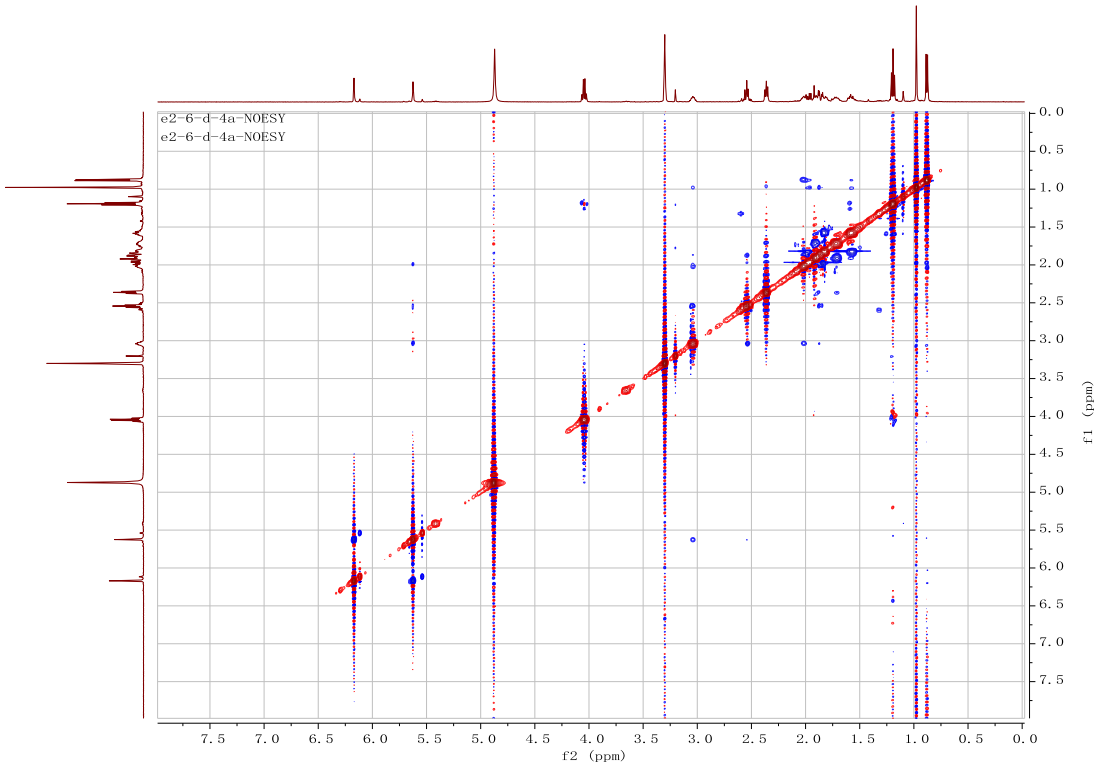


Figure S62. NOESY spectrum of 5 in methanol-d_4

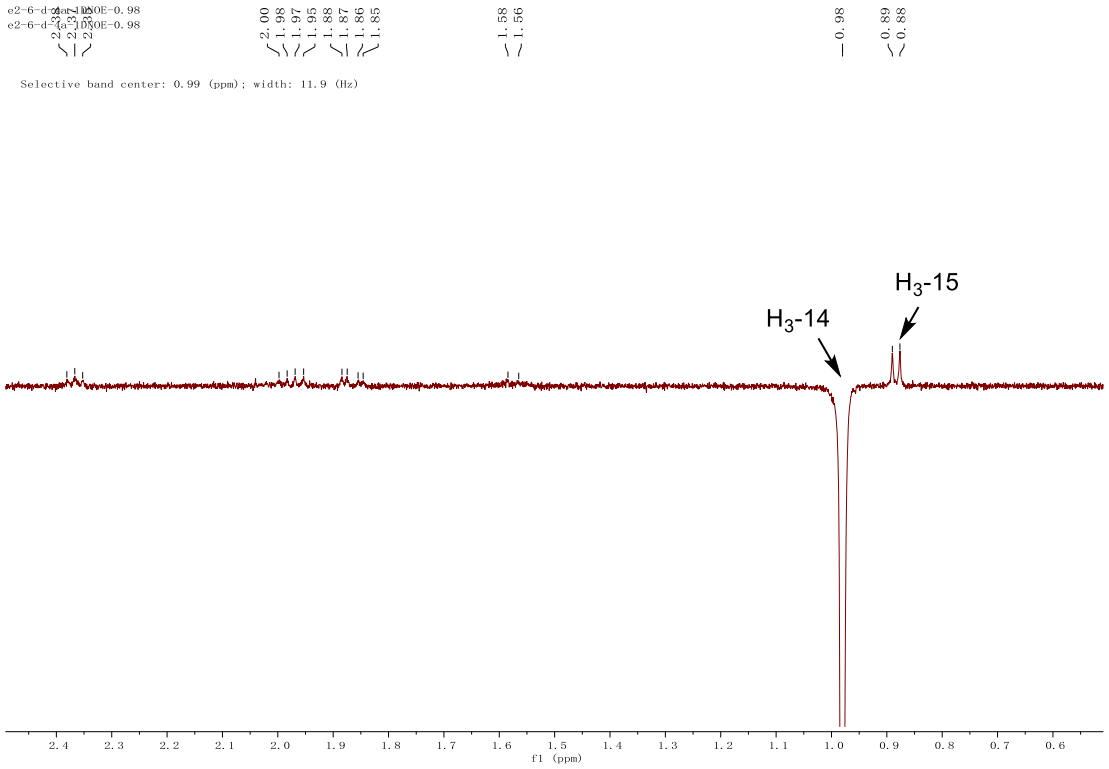


Figure S63. 1D NOE spectrum of 5 in methanol-d_4

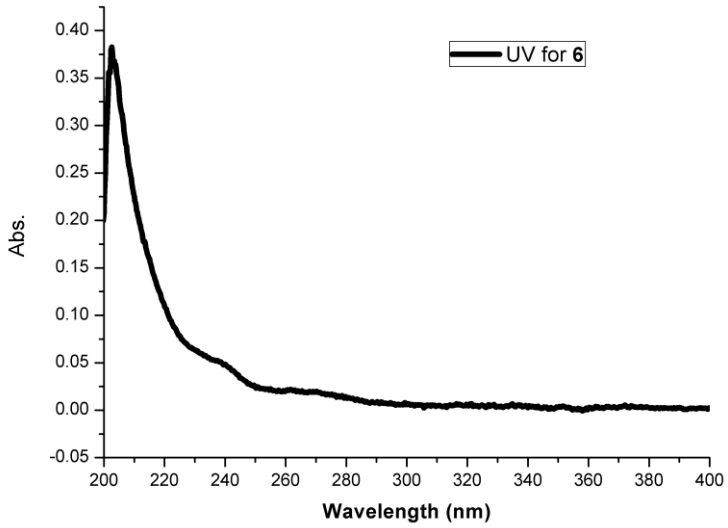


Figure S64. UV spectrum of 6

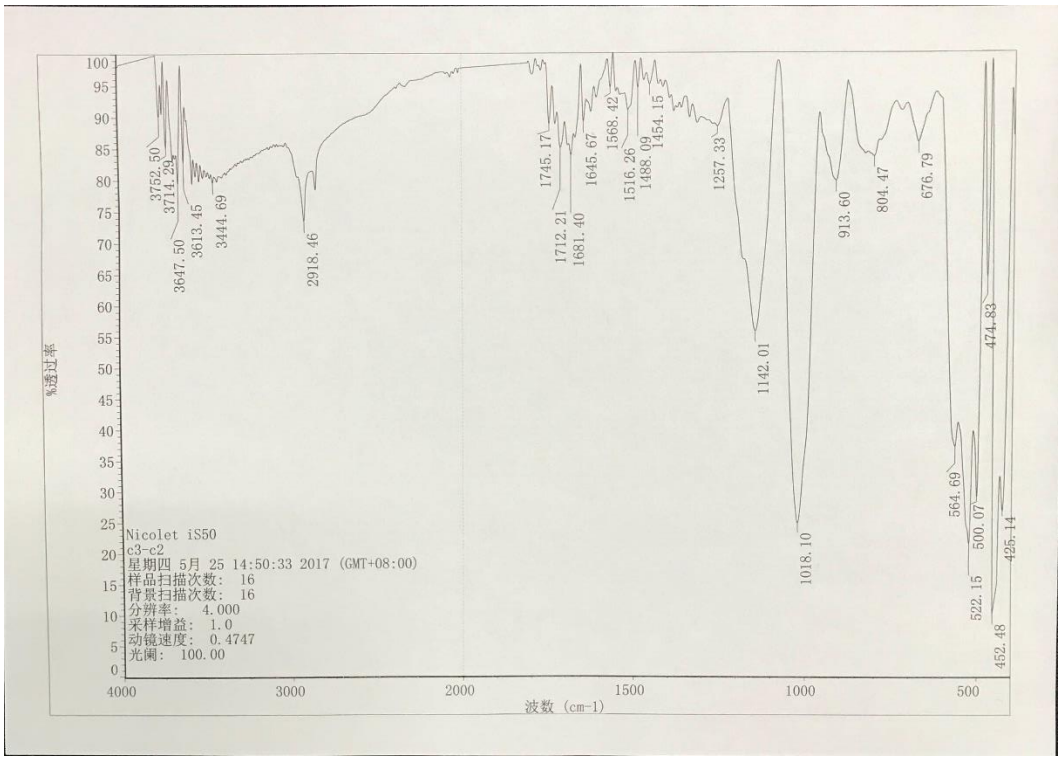


Figure S65. IR spectrum of 6

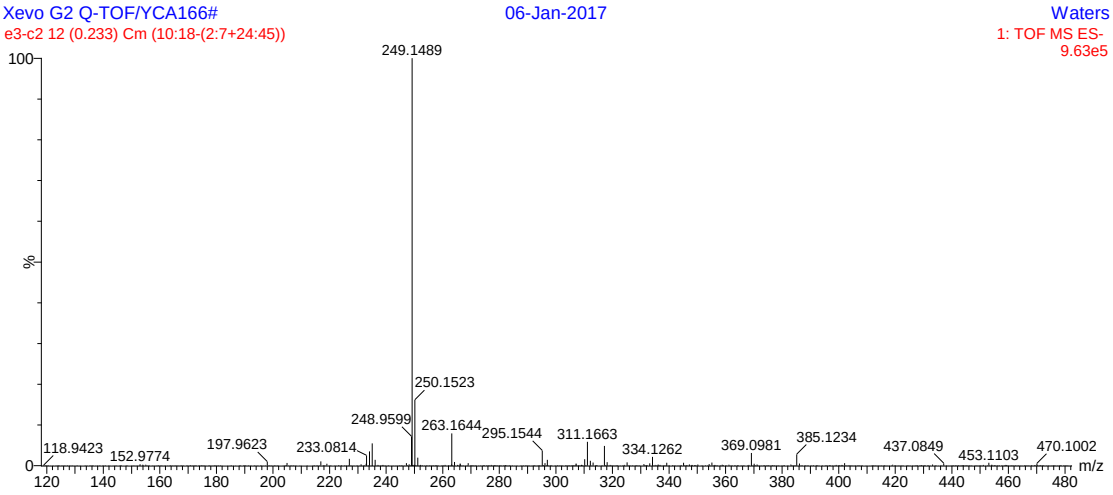


Figure S66. HRMS spectrum of 6

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
566 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-110 H: 0-200 N: 0-10 O: 0-50 Na: 0-1

Minimum:				-1.5				
Maximum:			5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
249.1489	249.1491	-0.2	-0.8	5.5	262.4	n/a	n/a	C15H21O3

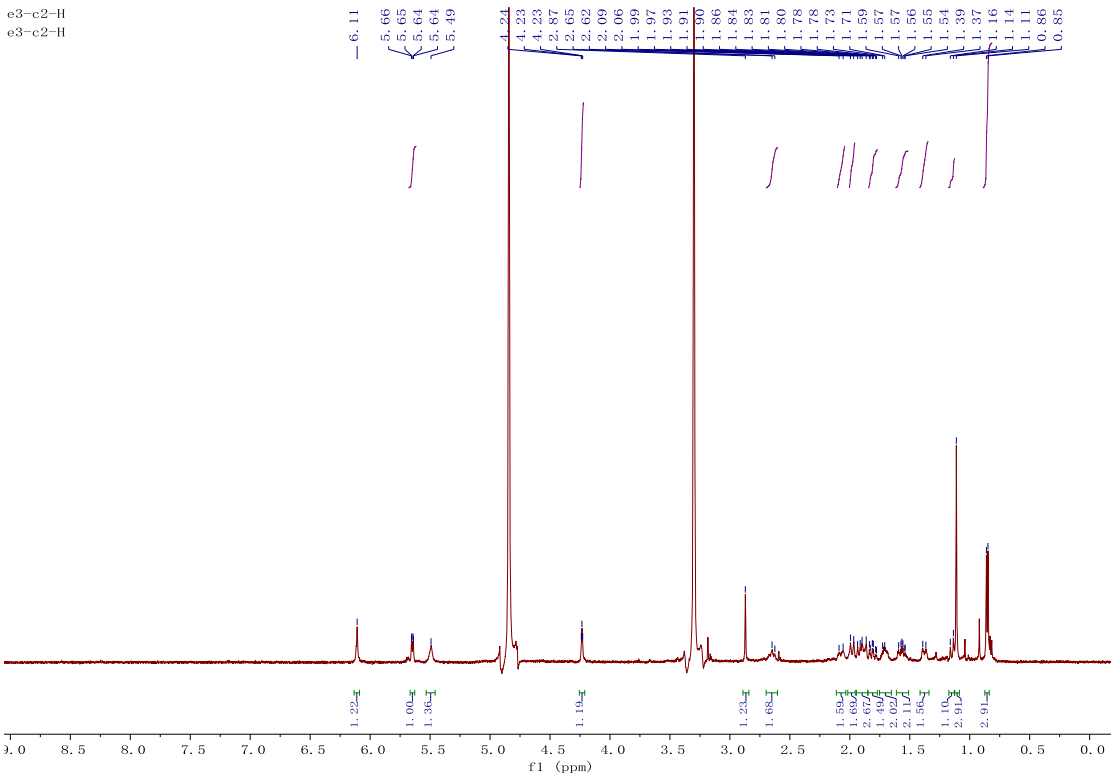


Figure S67. ^{1}H NMR spectrum of 6 in methanol-*d*$_4$

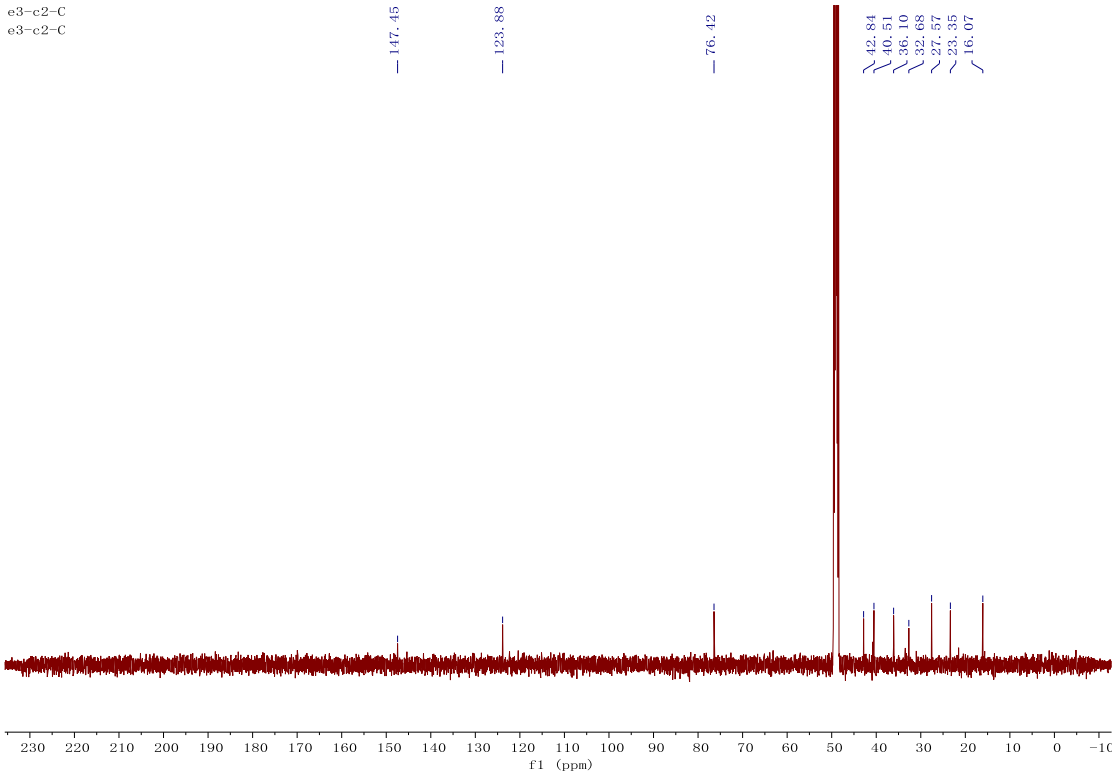


Figure S68. ^{13}C NMR spectrum of 6 in methanol-*d*$_4$

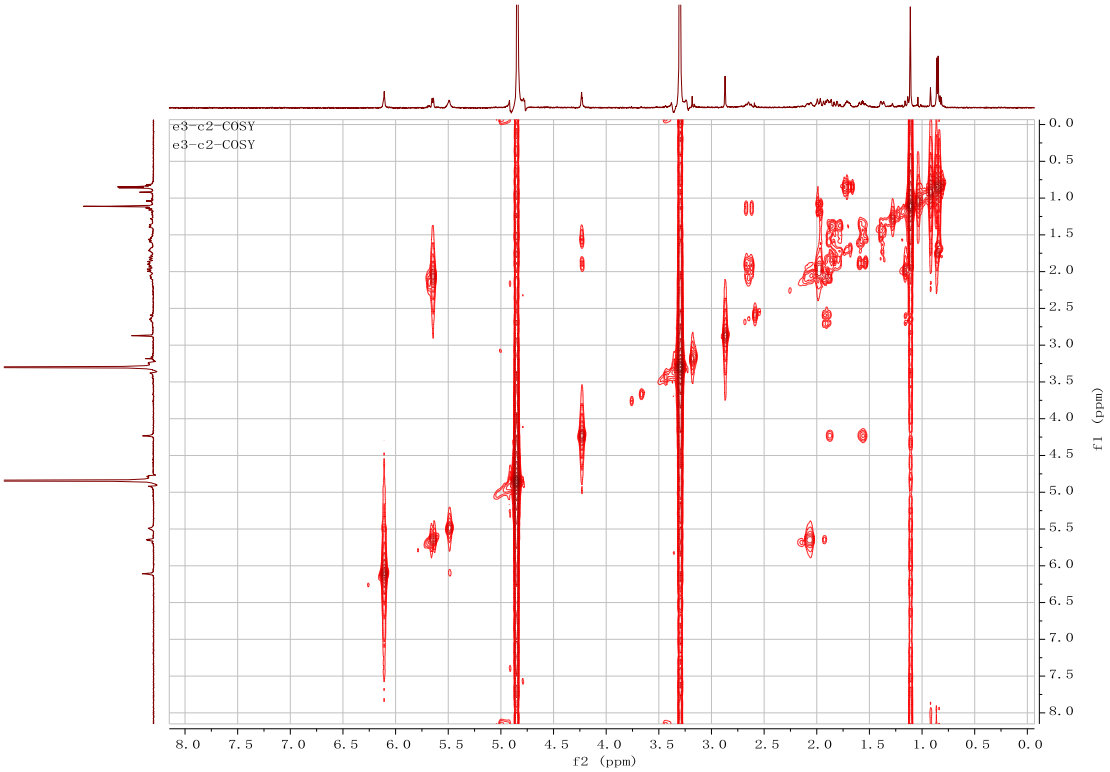


Figure S69. ^{1}H-^{1}H COSY spectrum of 6 in methanol-*d*$_4$

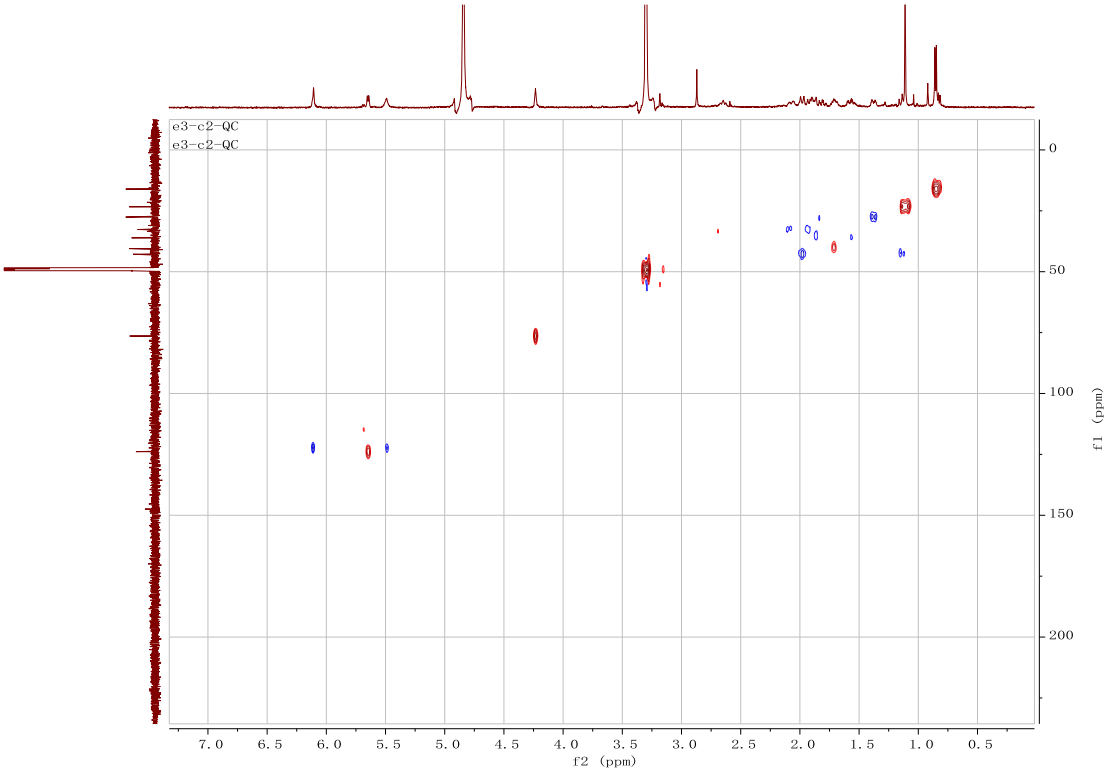


Figure S70. HSQC spectrum of 6 in methanol-*d*$_4$

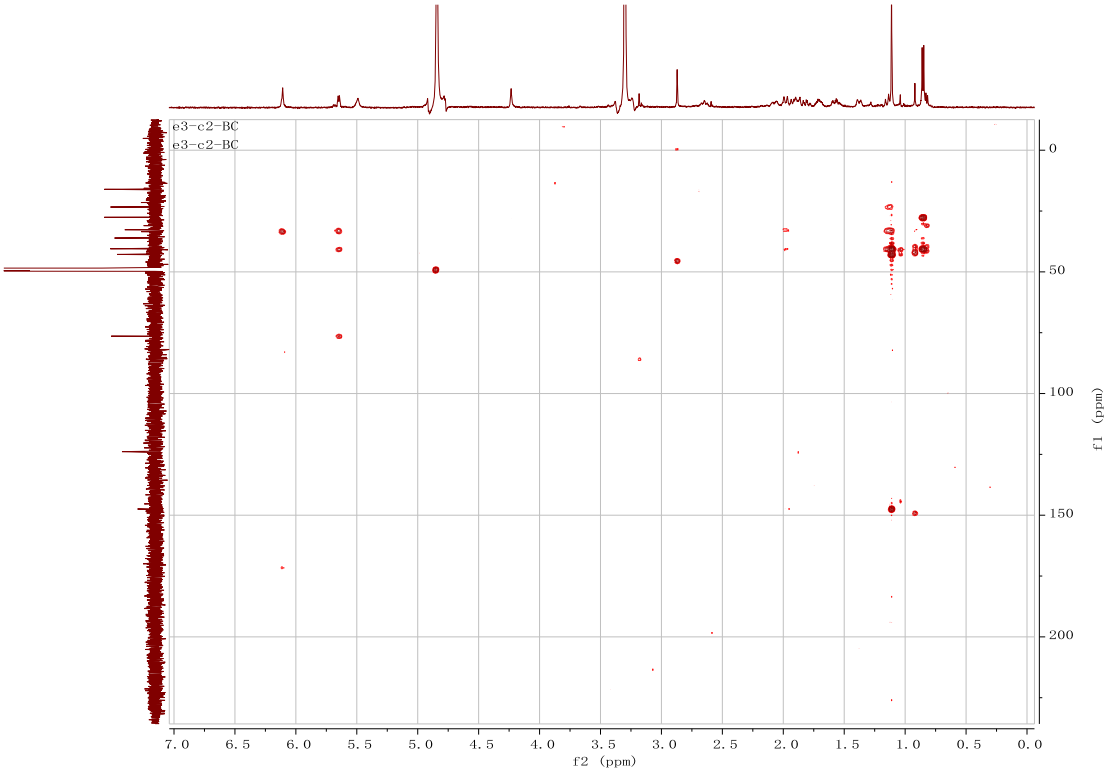
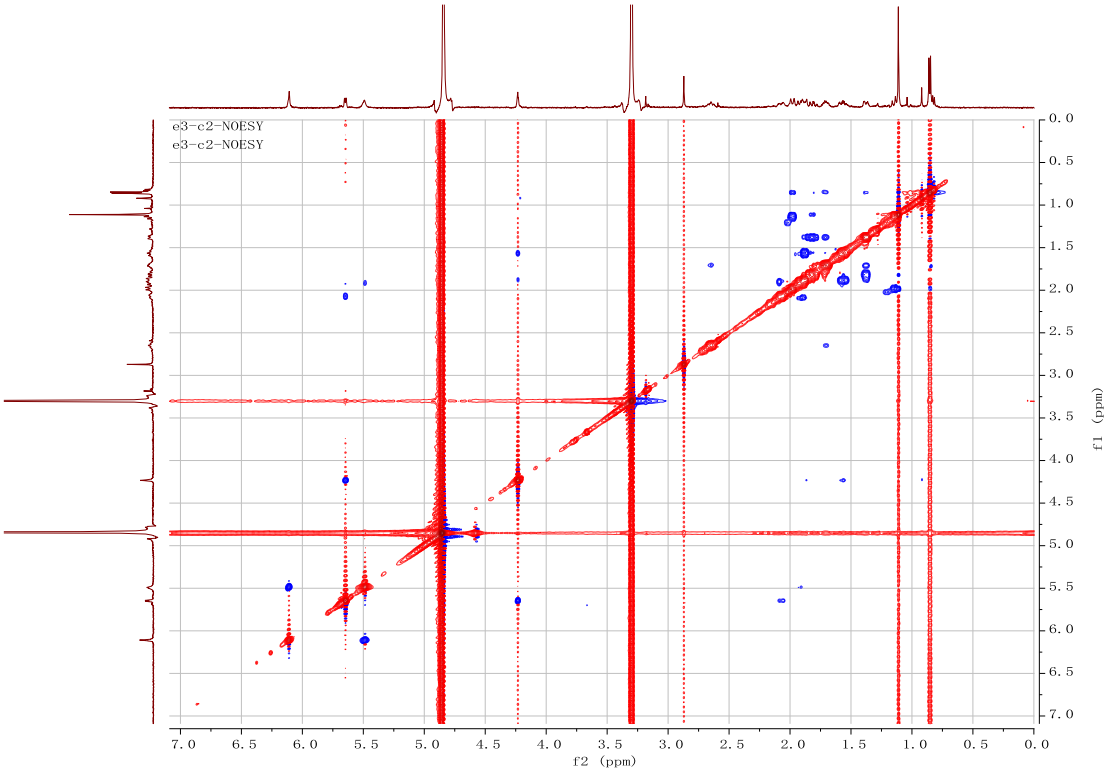


Figure S71. HMBC spectrum of 6 in methanol-*d*4



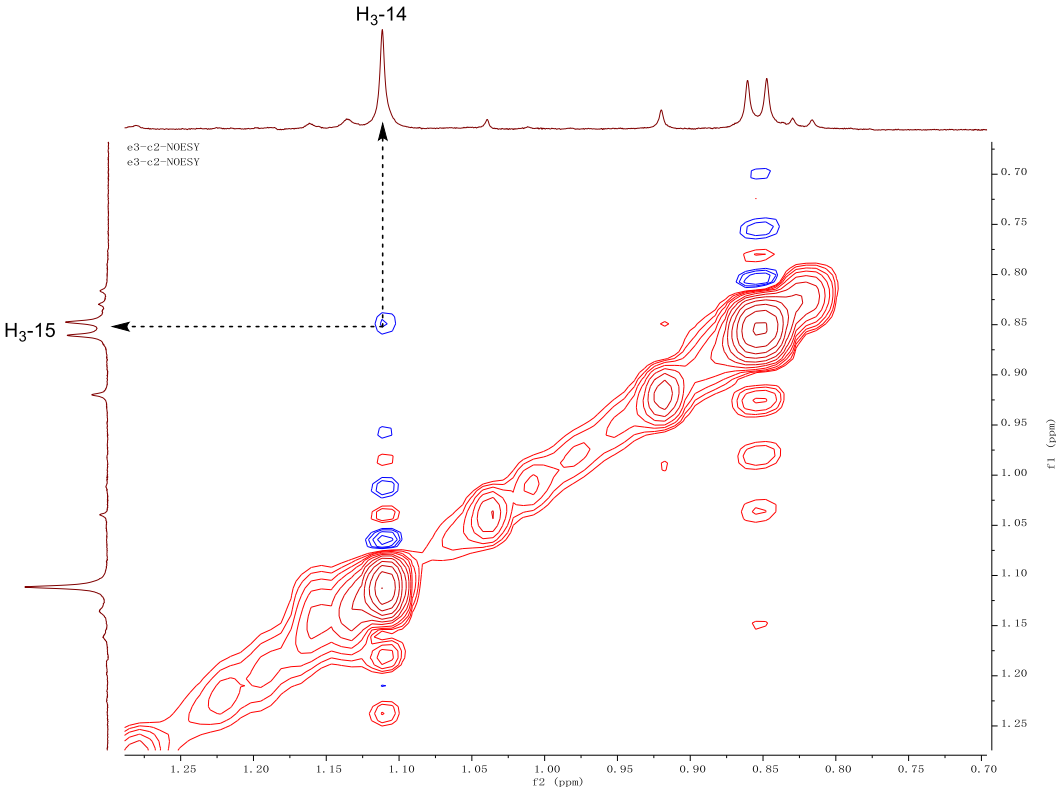


Figure S72. NOESY spectrum of 6 in methanol-d_4

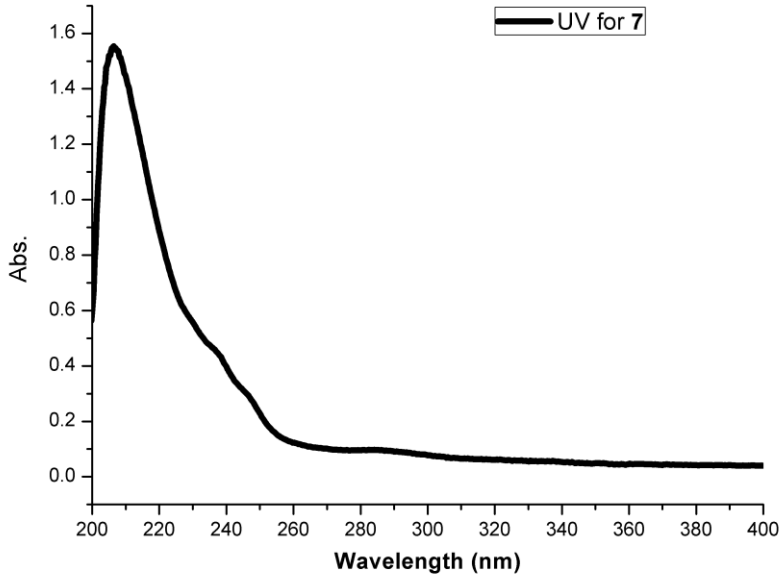


Figure S73. UV spectrum of 7

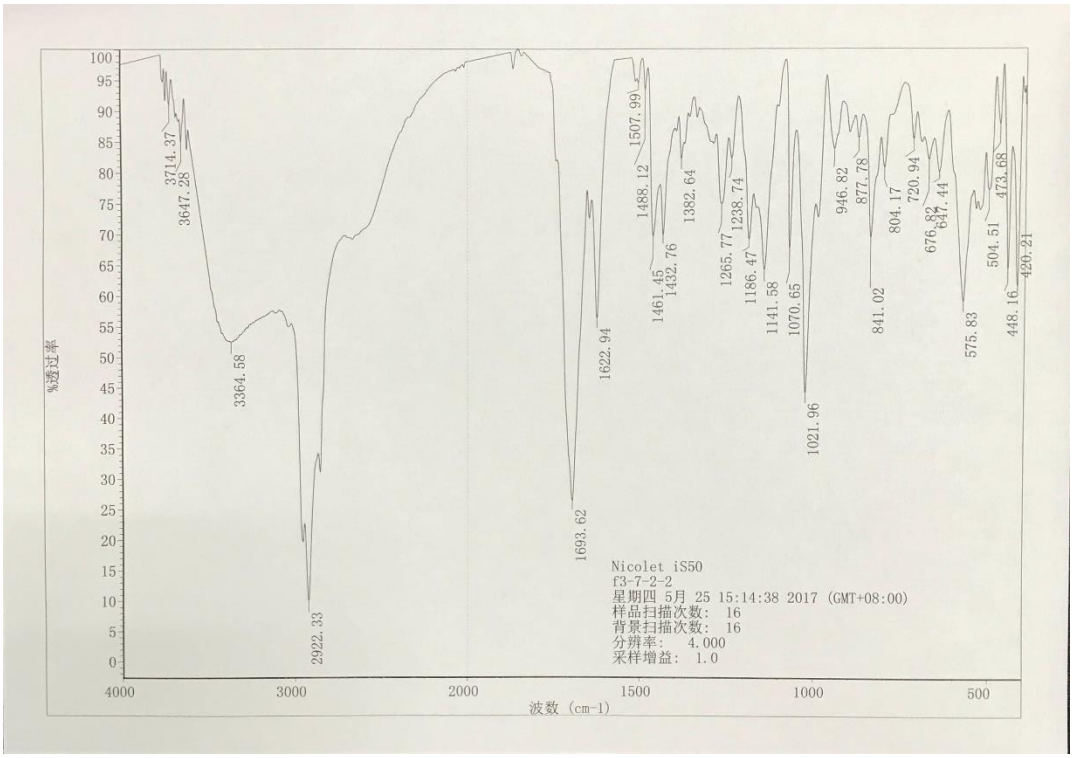


Figure S74. IR spectrum of 7

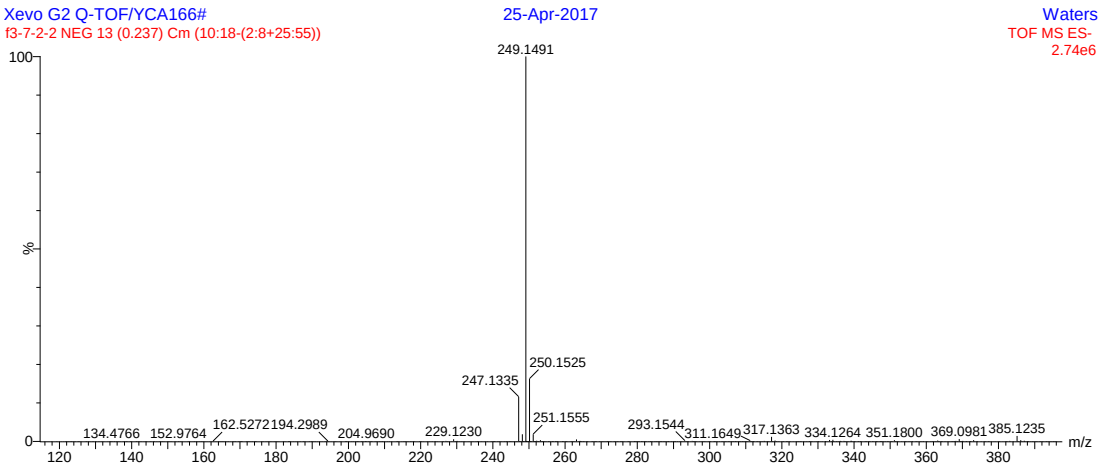


Figure S75. HRMS spectrum of 7

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
377 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-110 H: 0-200 N: 0-5 O: 0-50 Na: 0-1

Minimum:						-1.5		
Maximum:				5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
249.1491	249.1491	0.0	0.0	5.5	412.4	n/a	n/a	C15H21O3

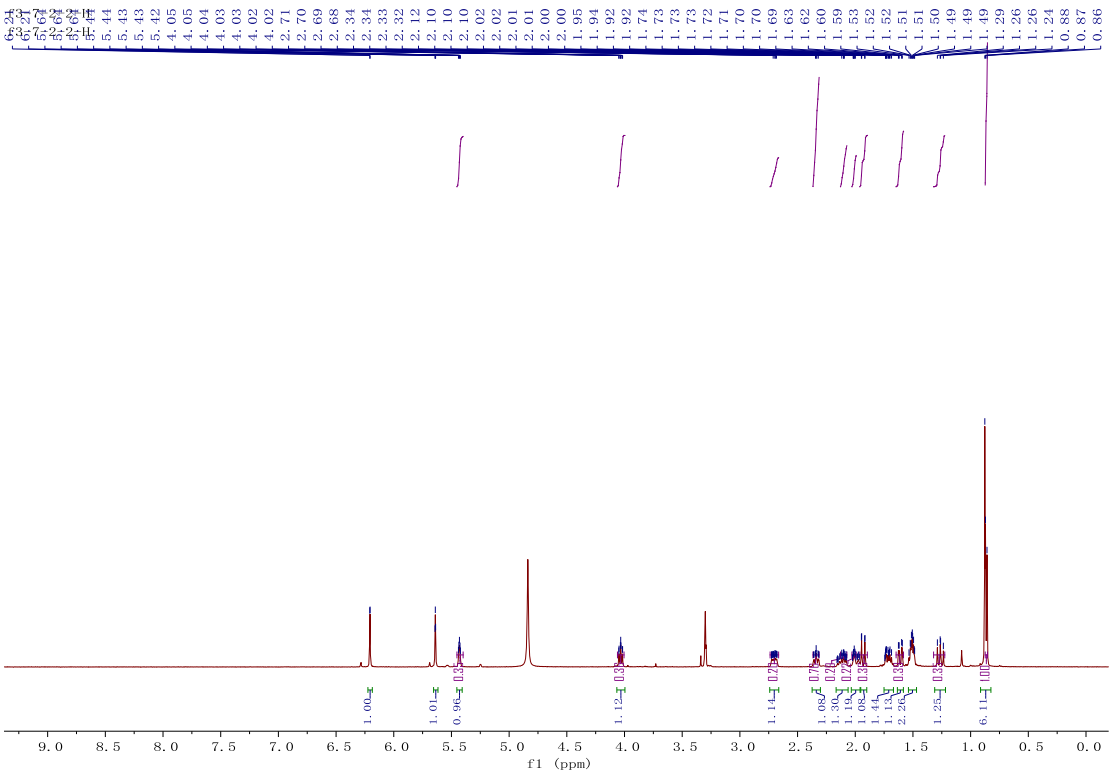


Figure S76. ^{1}H NMR spectrum of 7 in methanol-d_4

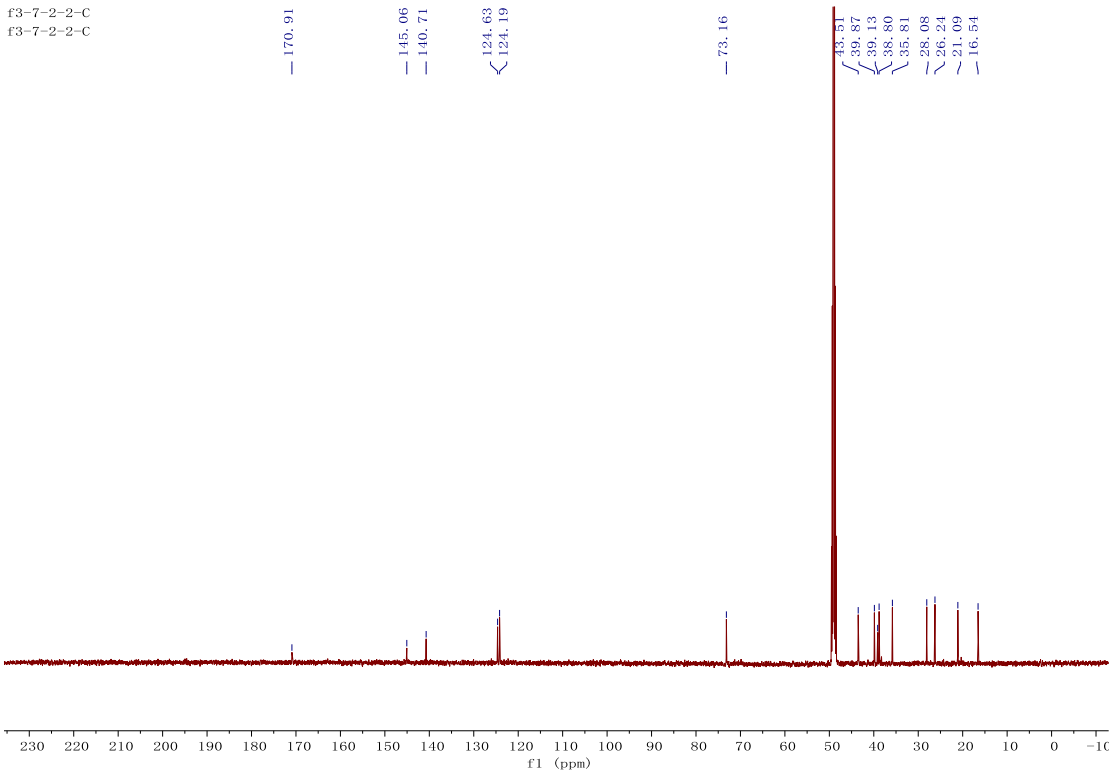


Figure S77. ^{13}C NMR spectrum of 7 in methanol-*d*$_4$

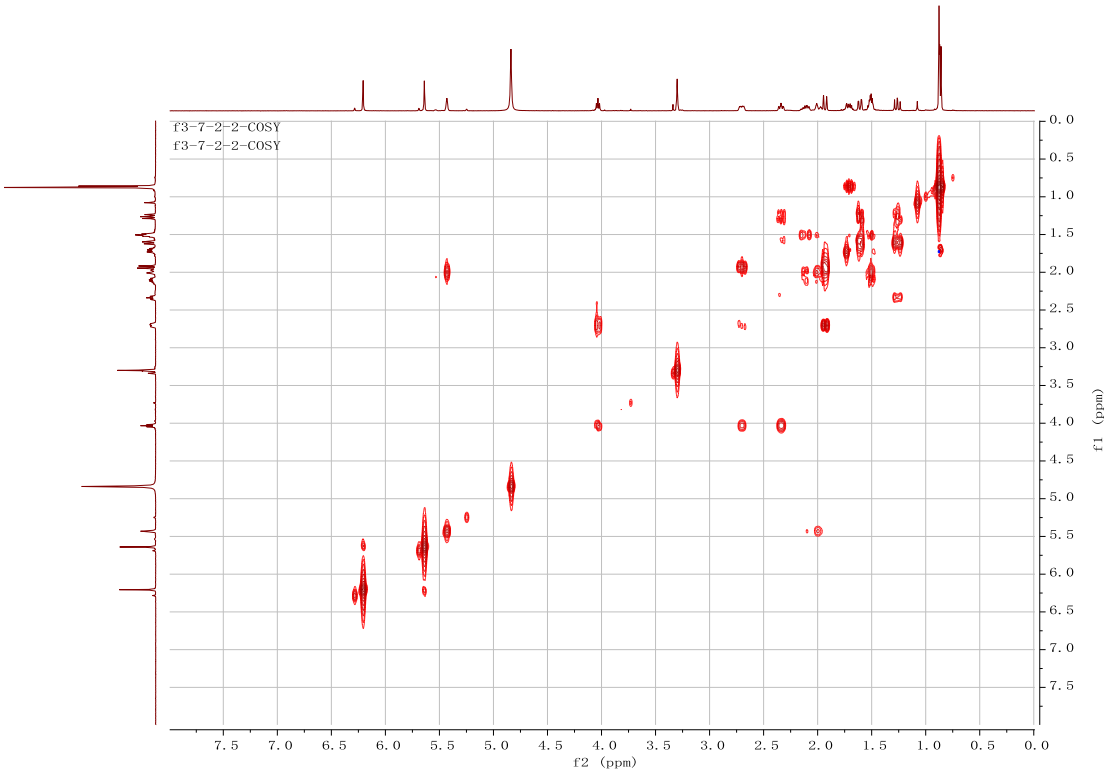


Figure S78. ^{1}H-^{1}H COSY spectrum of 7 in methanol-*d*$_4$

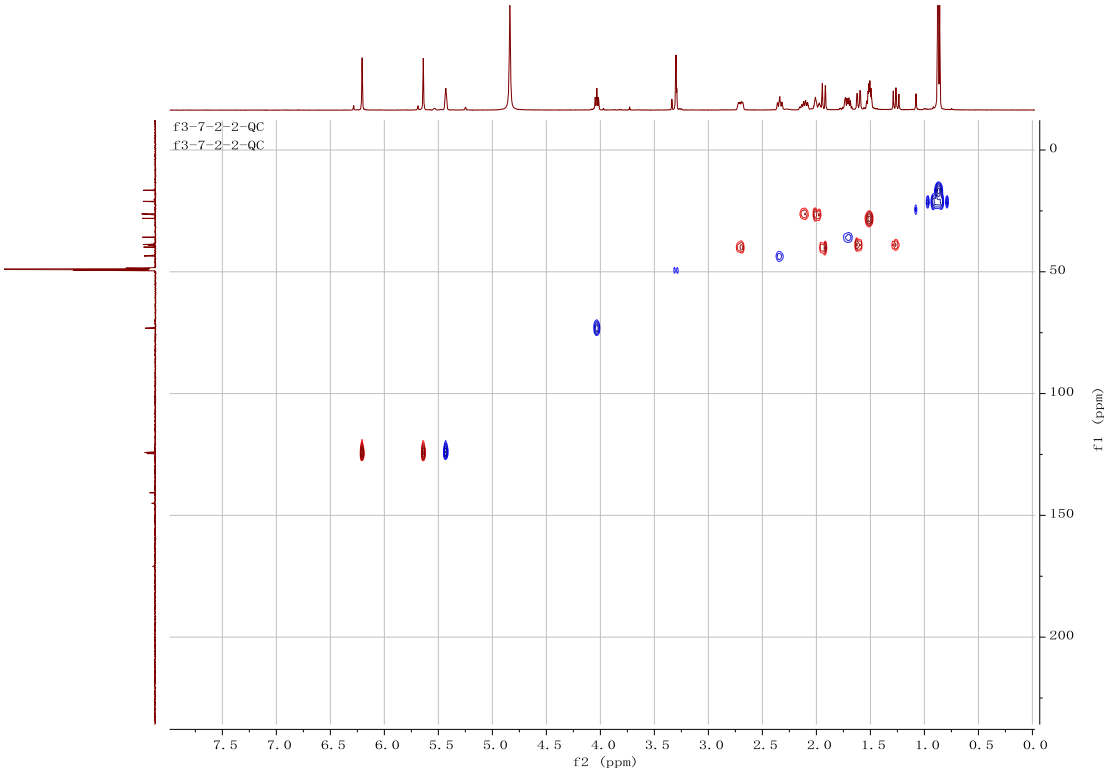


Figure S79. HSQC spectrum of 7 in methanol-d_4

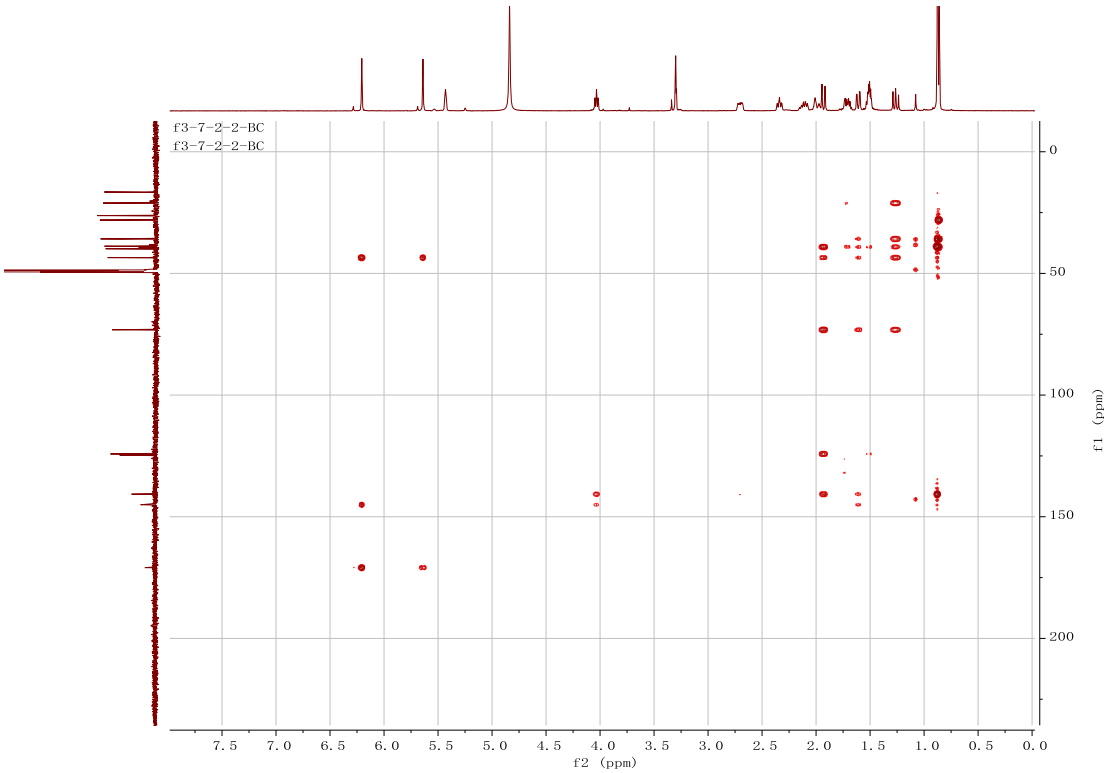


Figure S80. HMBC spectrum of 7 in methanol-d_4

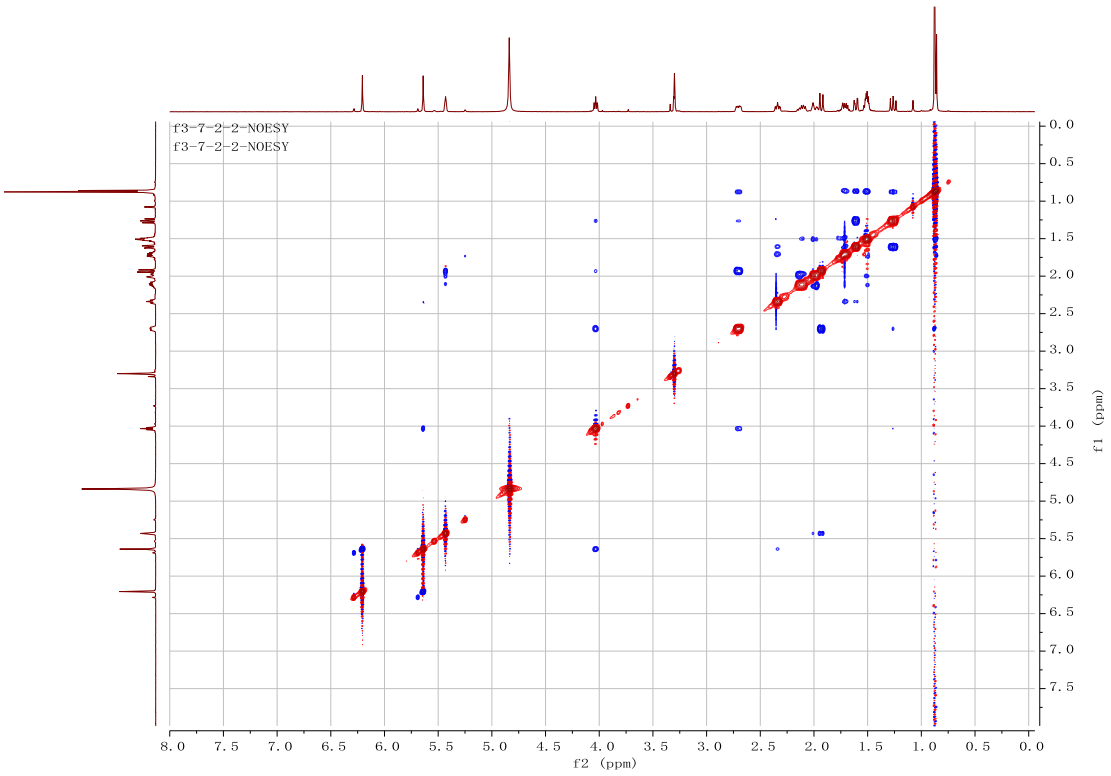


Figure S81. NOESY spectrum of 7 in methanol-d_4

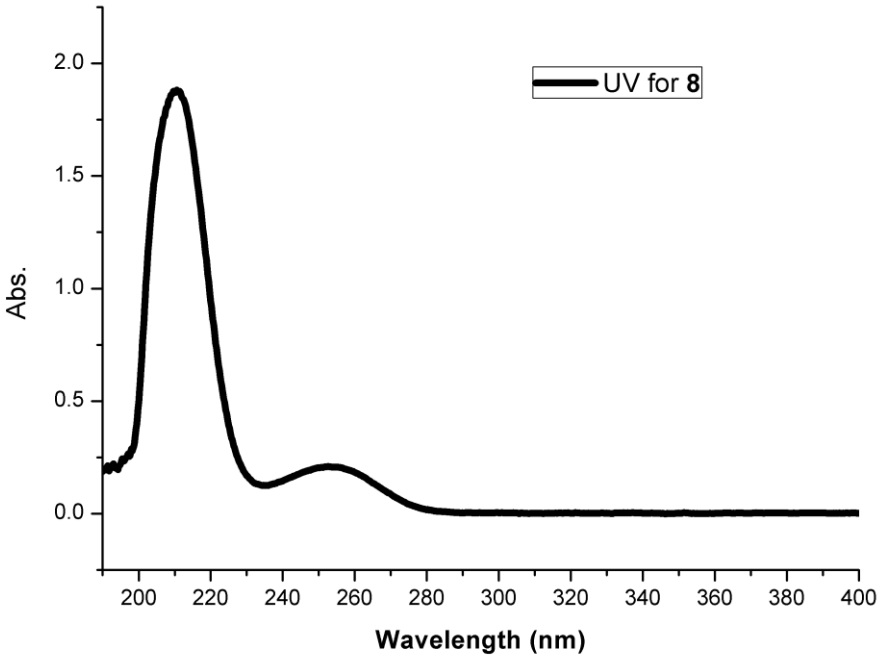


Figure S82. UV spectrum of 8

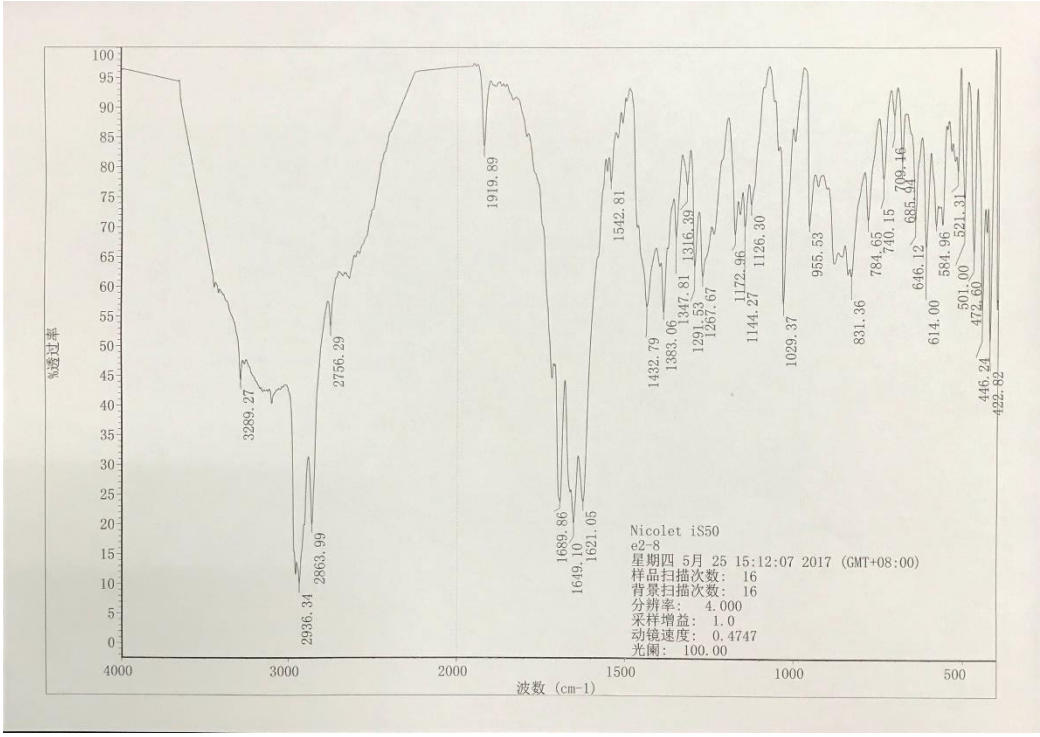


Figure S83. IR spectrum of 8

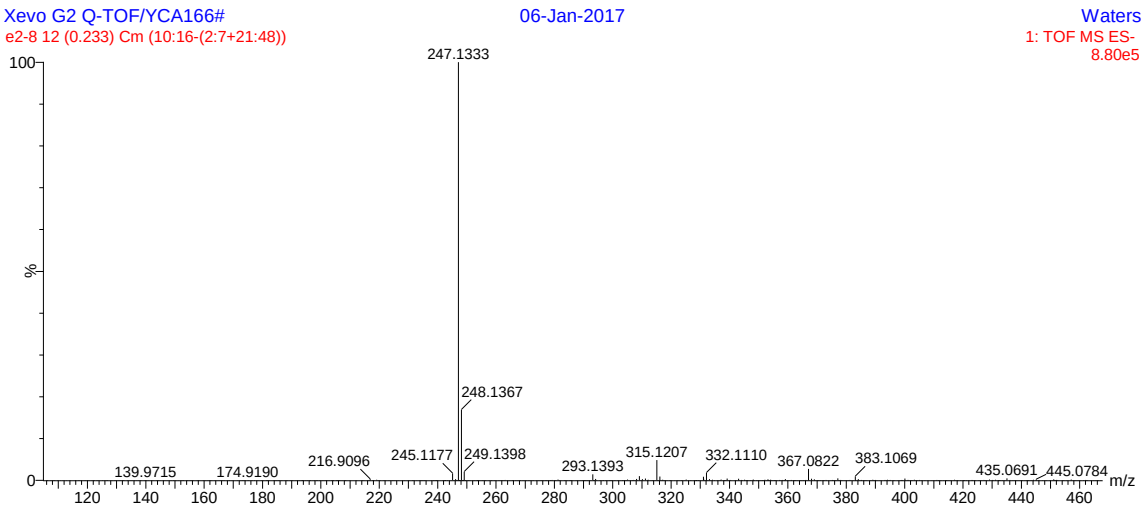


Figure S84. HRMS spectrum of 8

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
561 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-110 H: 0-200 N: 0-10 O: 0-50 Na: 0-1

Minimum:					-1.5			
Maximum:			5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
247.1333	247.1334	-0.1	-0.4	6.5	284.1	n/a	n/a	C15 H19 O3

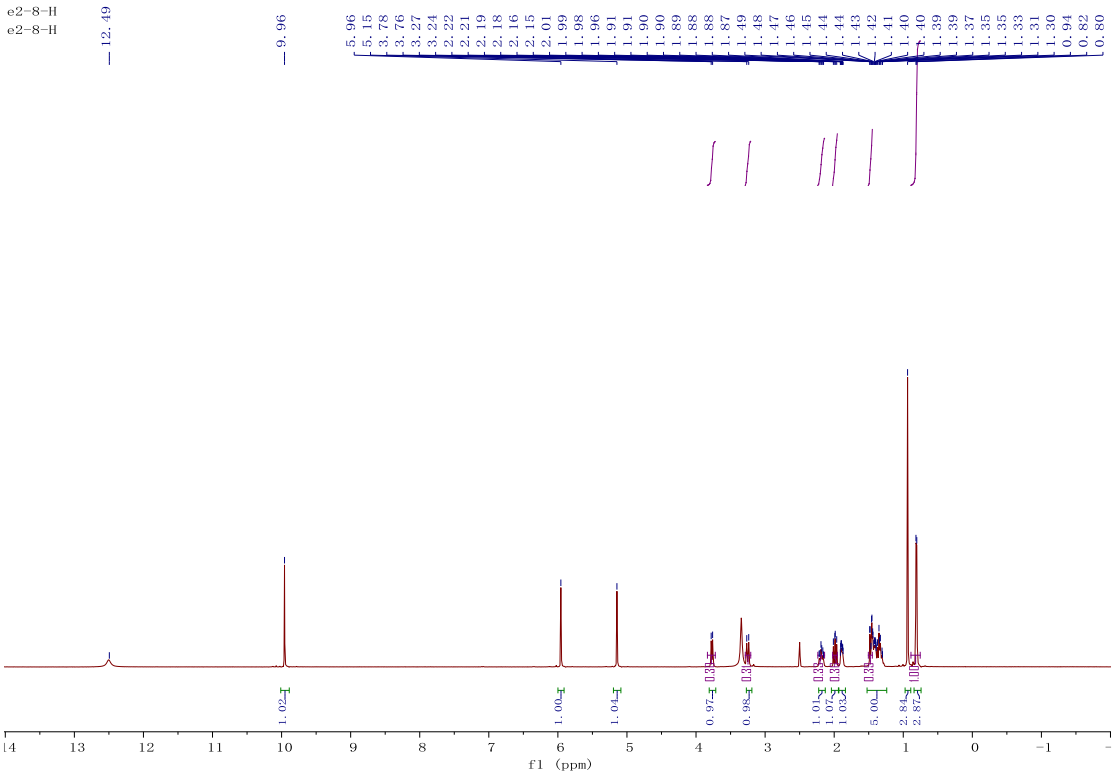


Figure S85. ^{1}H NMR spectrum of 8 in DMSO-d_6

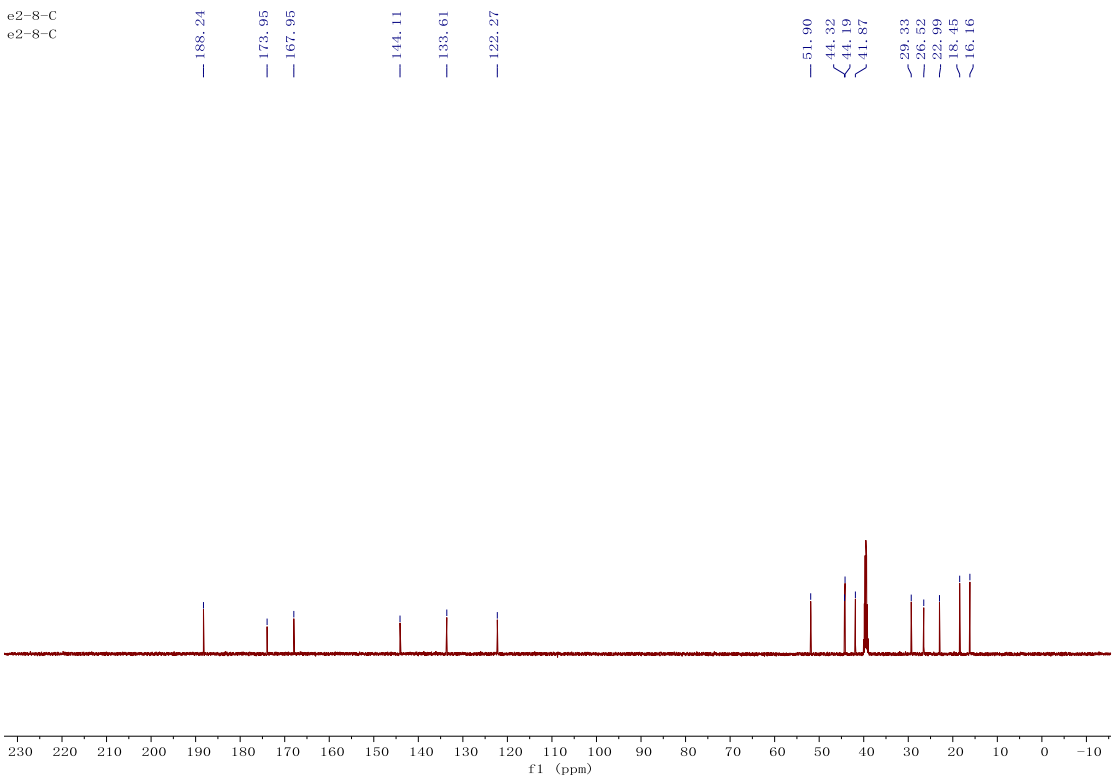


Figure S86. ^{13}C NMR spectrum of 8 in DMSO-*d*$_6$

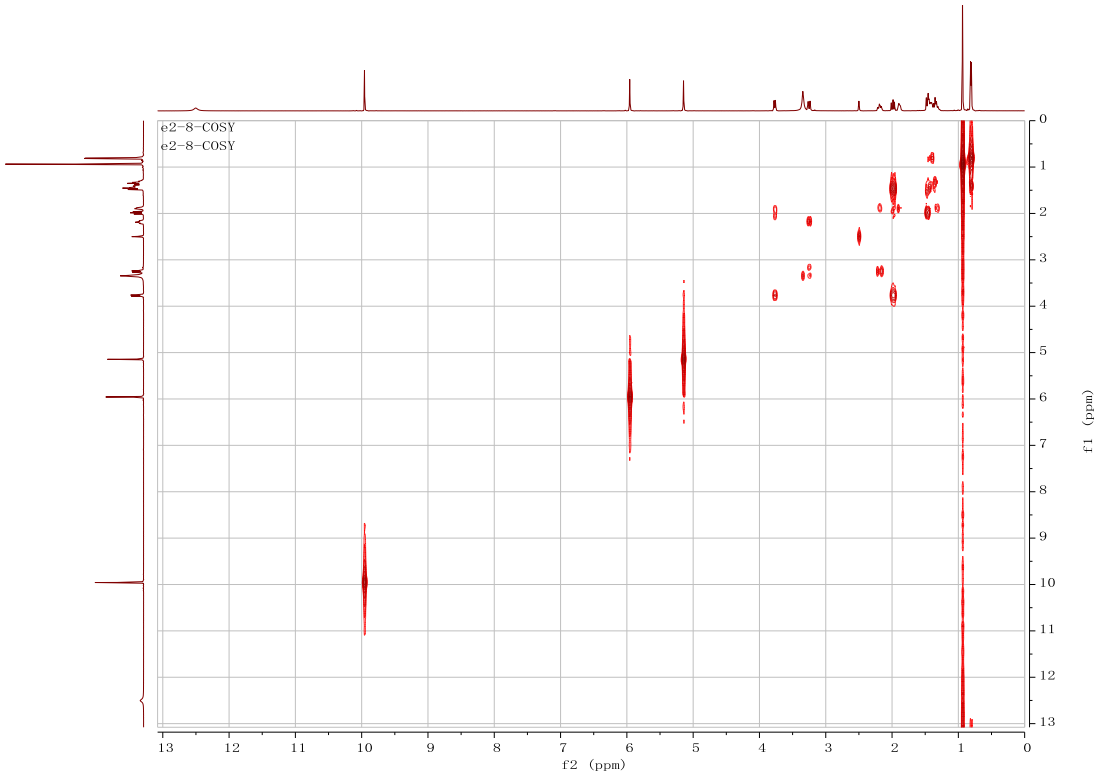


Figure S87. ^{1}H-^{1}H COSY spectrum of 8 in DMSO-*d*$_6$

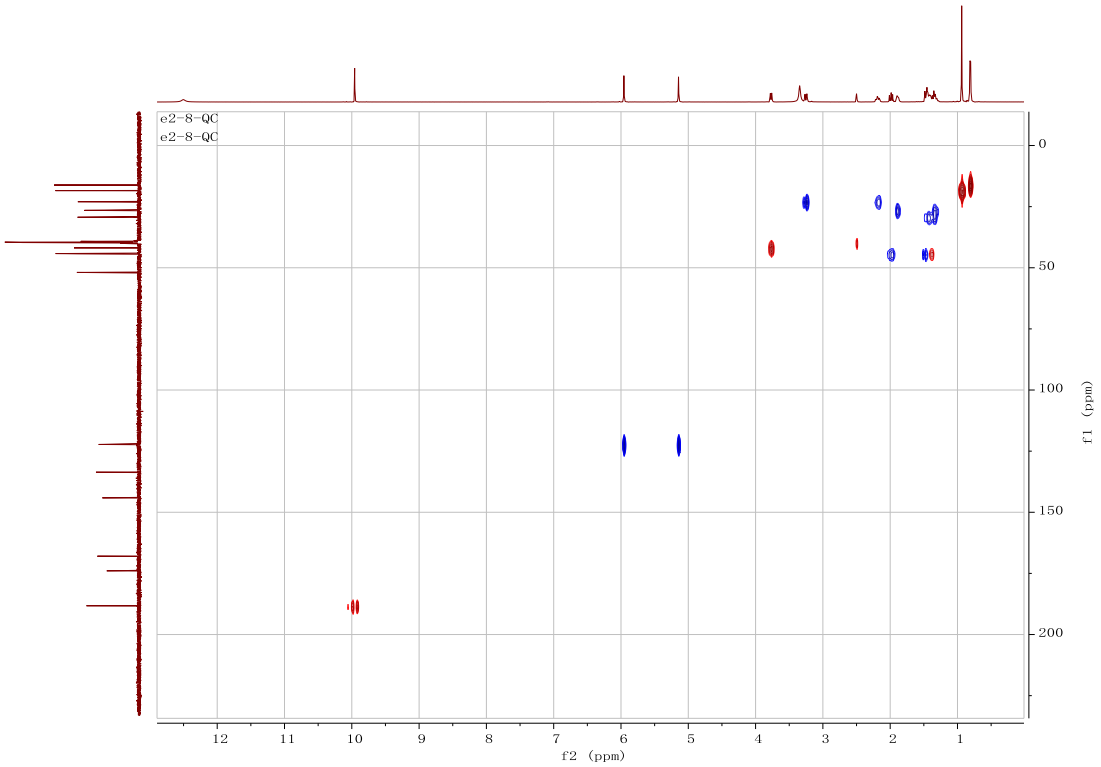


Figure S88. HSQC spectrum of 8 in DMSO-*d*$_6$

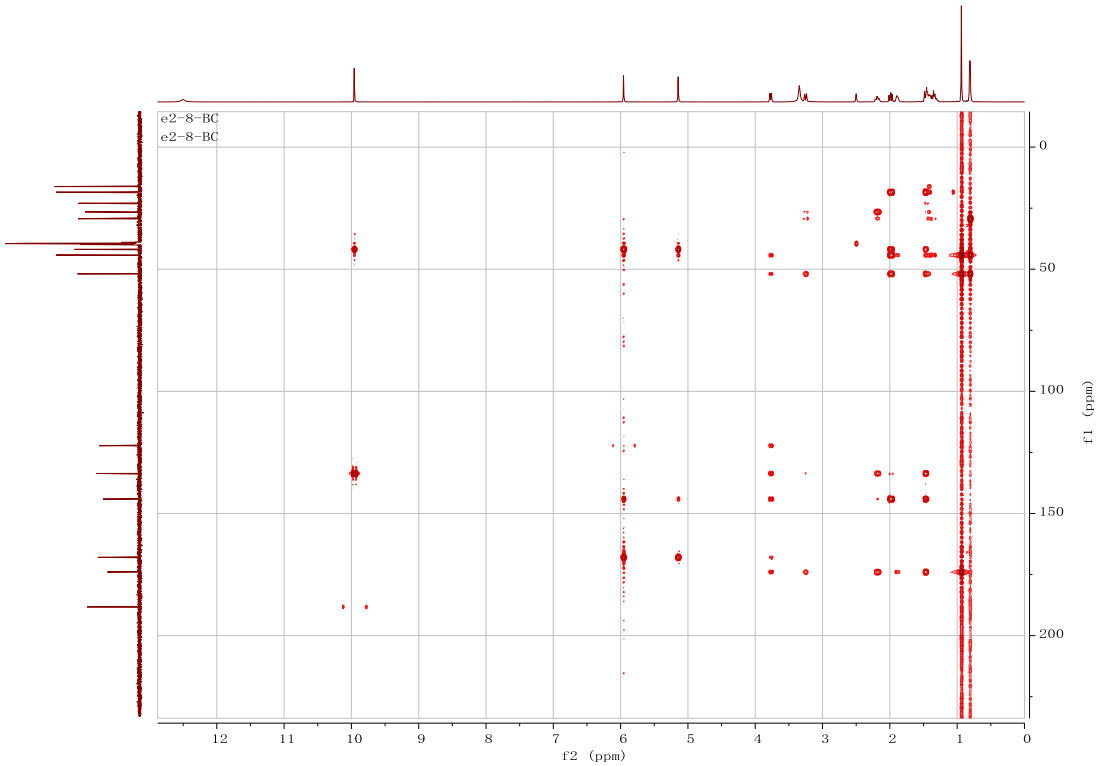


Figure S89. HMBC spectrum of 8 in DMSO-*d*$_6$

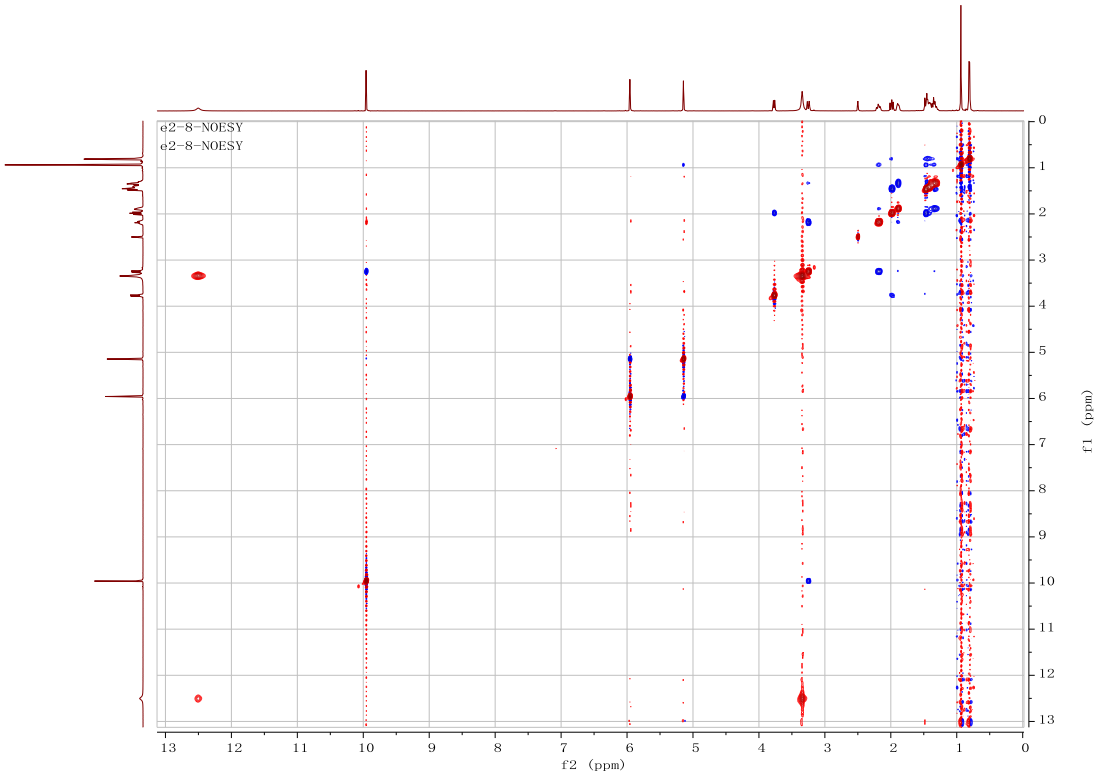


Figure S90. NOESY spectrum of 8 in DMSO-*d*$_6$

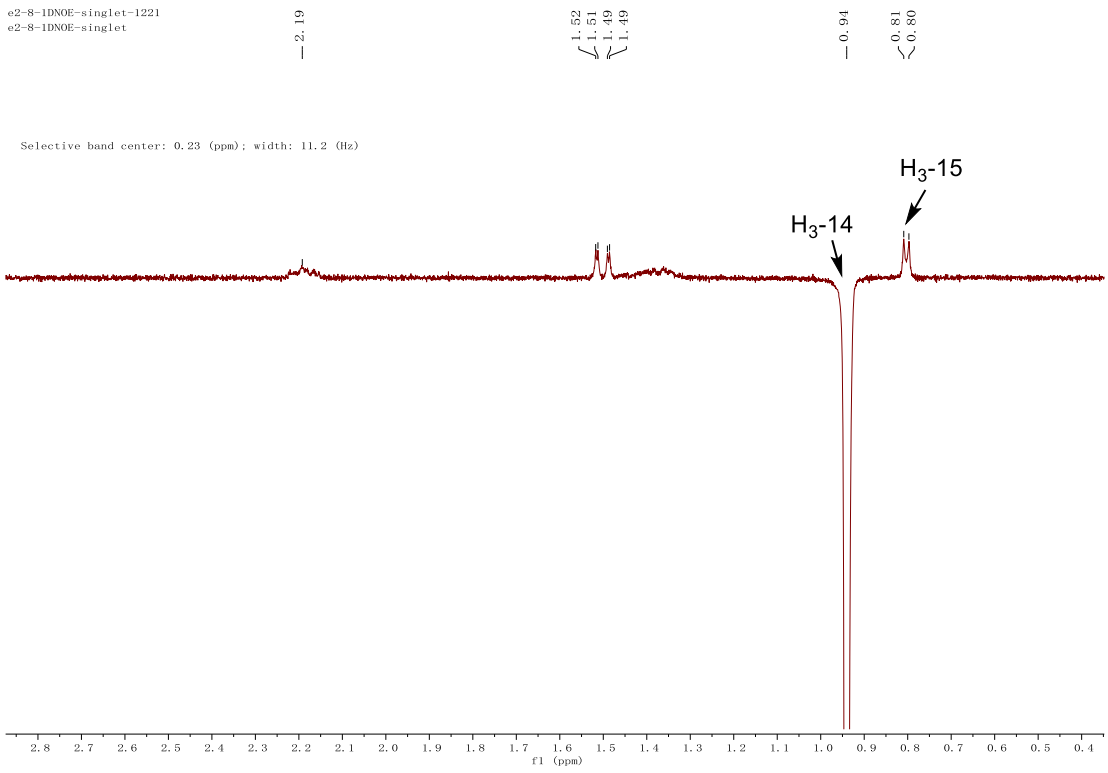


Figure S91. 1D NOE spectrum of 8 in methanol-*d*$_4$

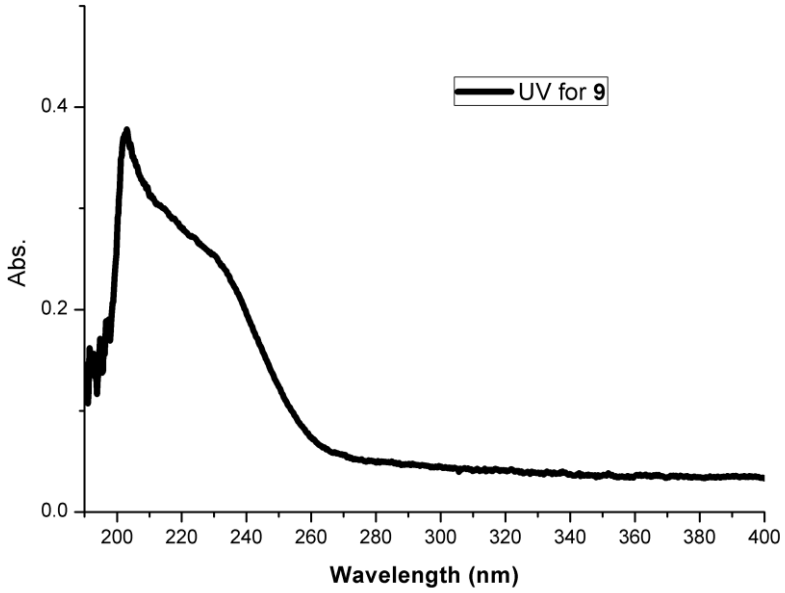


Figure S92. UV spectrum of 9

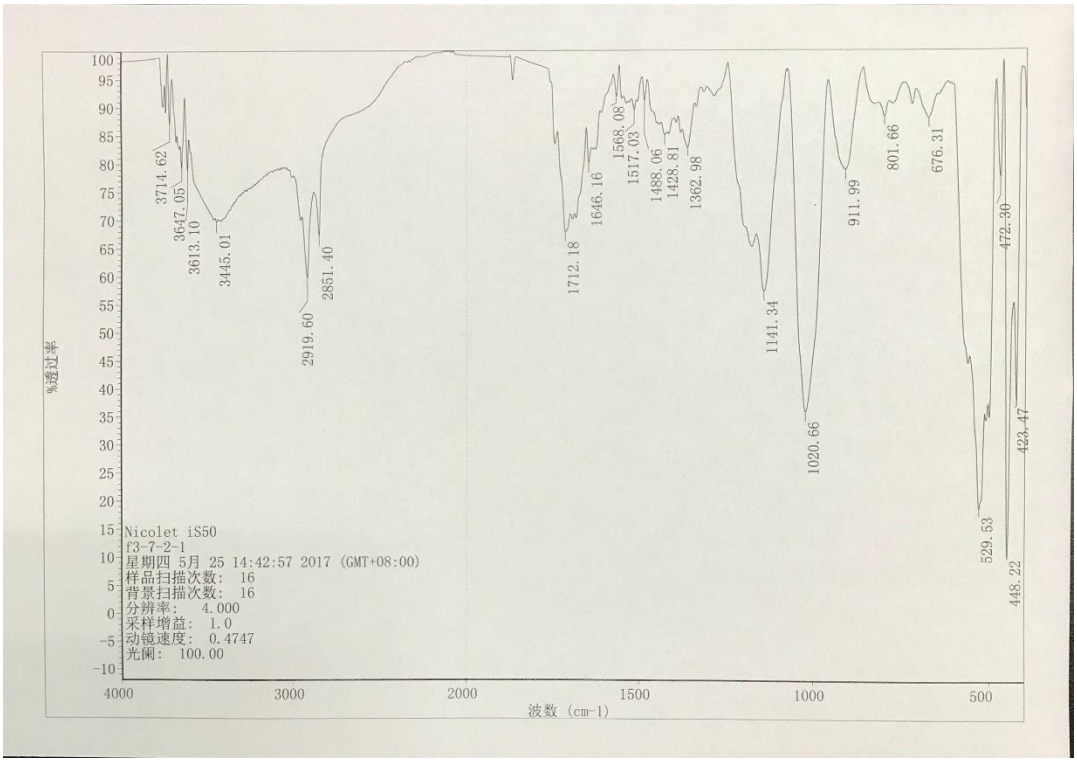


Figure S93. IR spectrum of 9

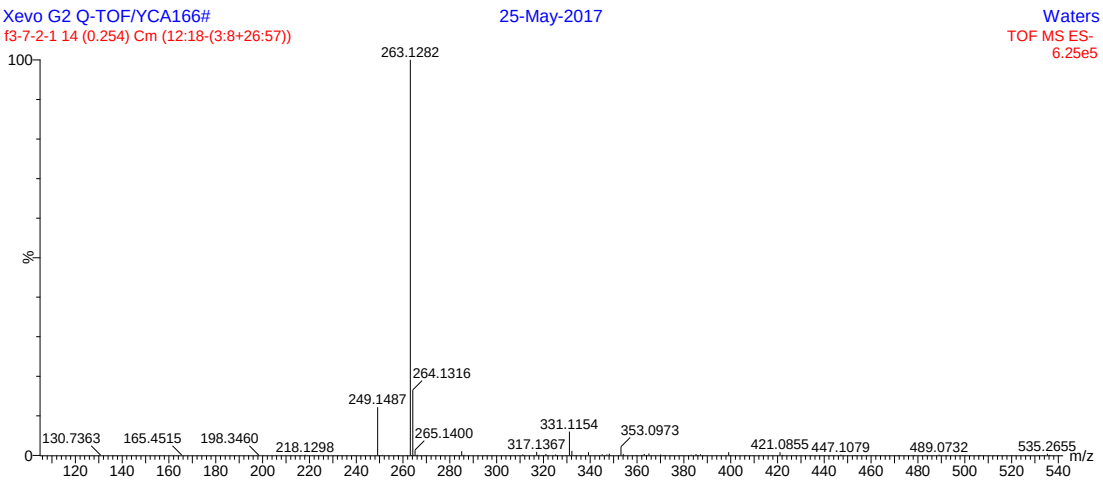


Figure S94. HRMS spectrum of 9

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
355 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-110 H: 0-200 N: 0-10 O: 0-50

Minimum:						-1.5		
Maximum:				5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
263.1282	263.1283	-0.1	-0.4	6.5	110.3	n/a	n/a	C15 H19 O4

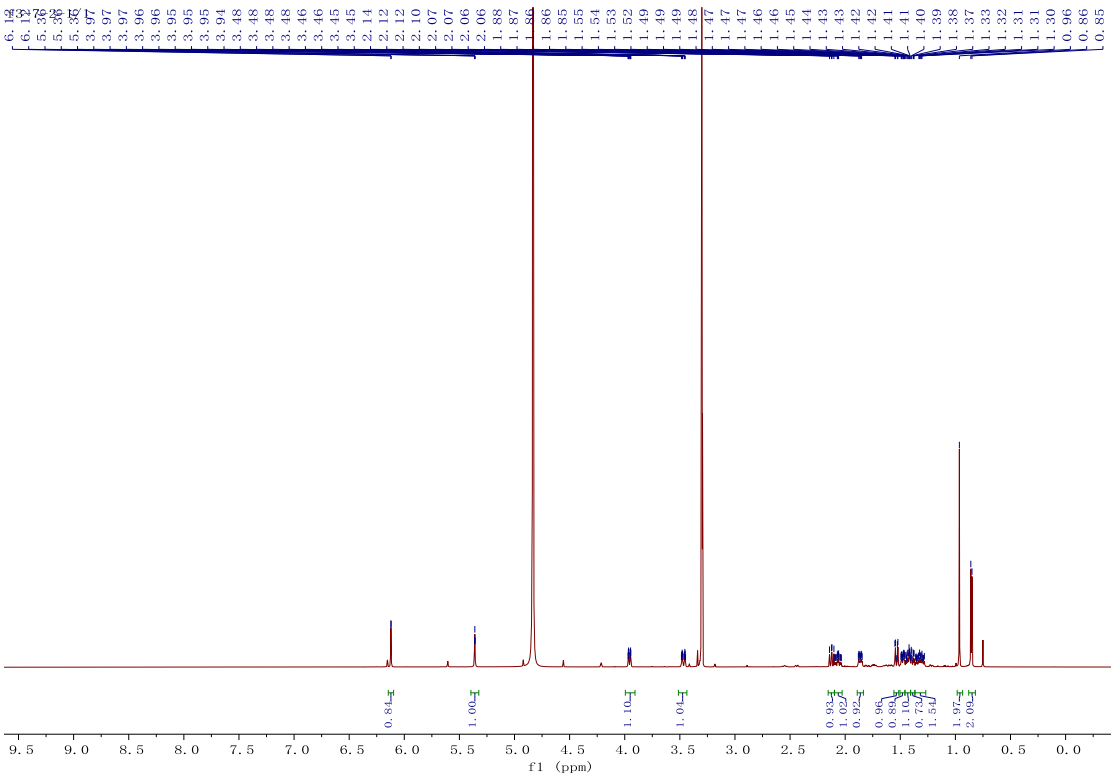


Figure S95. ^{1}H NMR spectrum of 9 in methanol-*d*$_4$

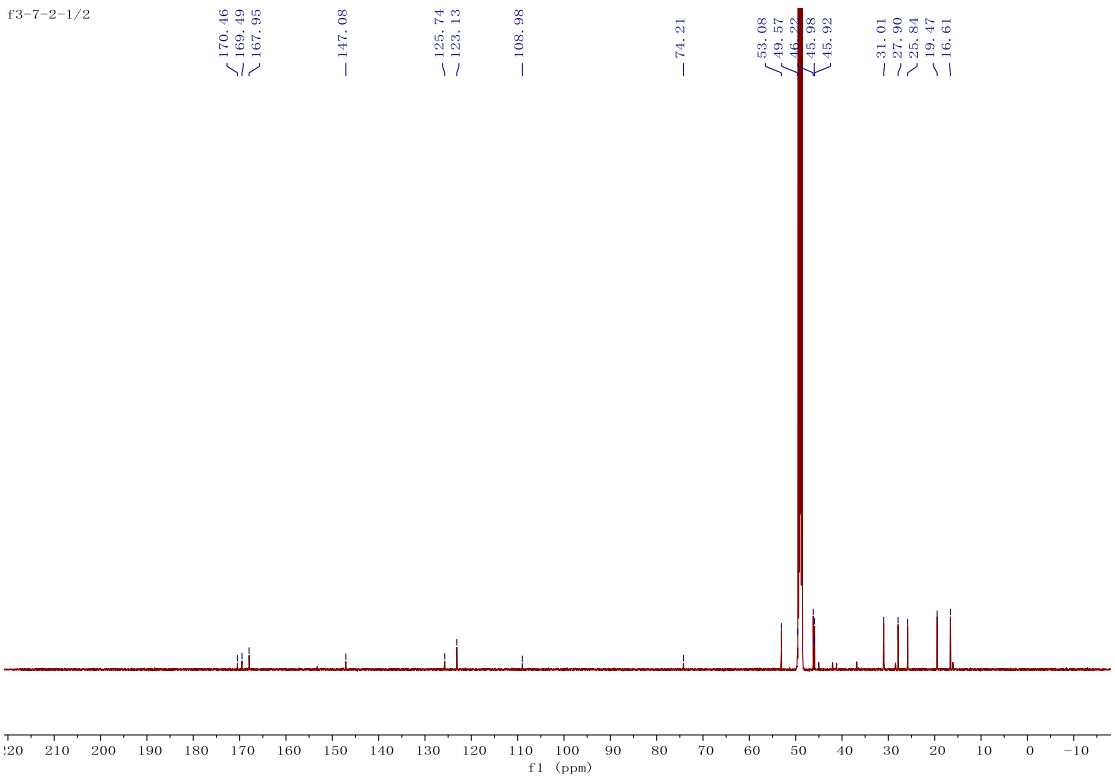


Figure S96. ^{13}C NMR spectrum of 9 in methanol-*d*$_4$

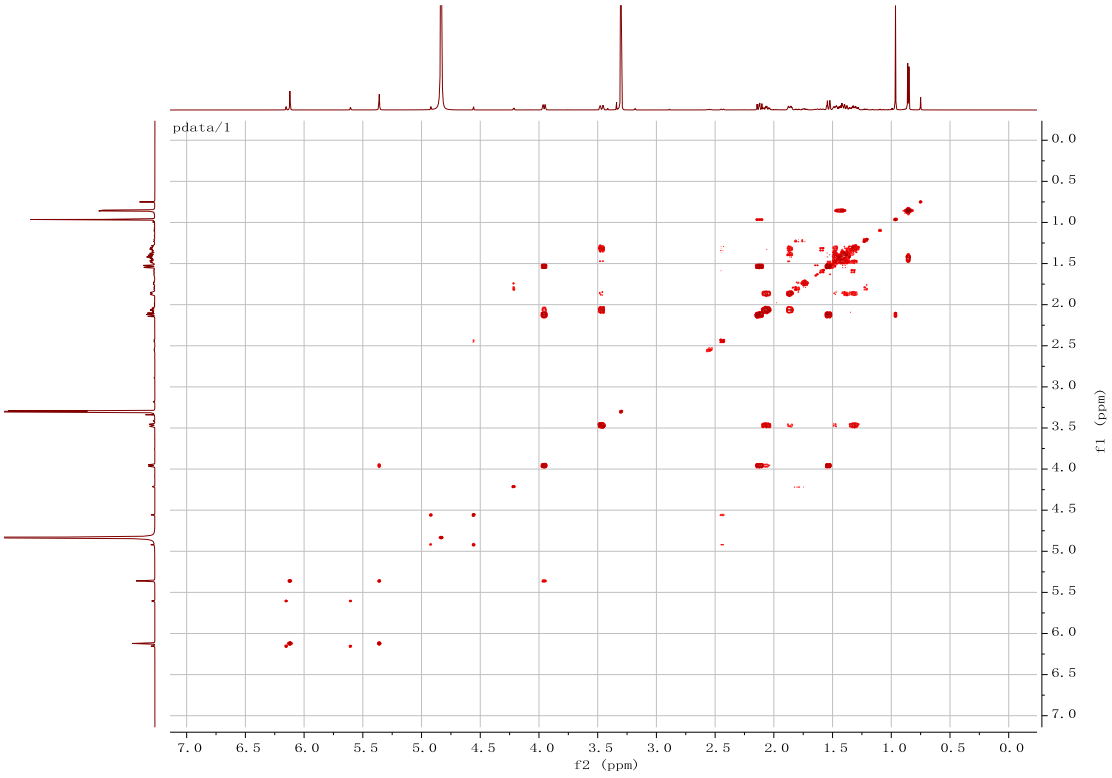


Figure S97. ^{1}H-^{1}H COSY spectrum of 9 in methanol-*d*$_4$

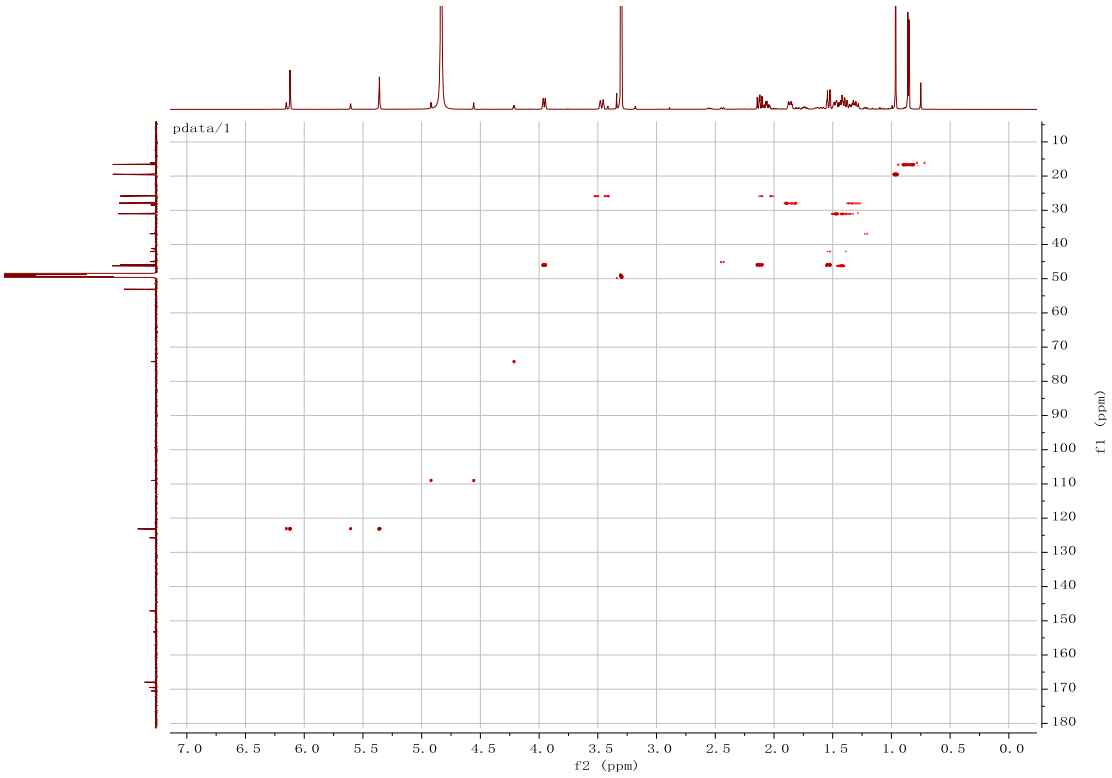


Figure S98. HSQC spectrum of 9 in methanol-*d*$_4$

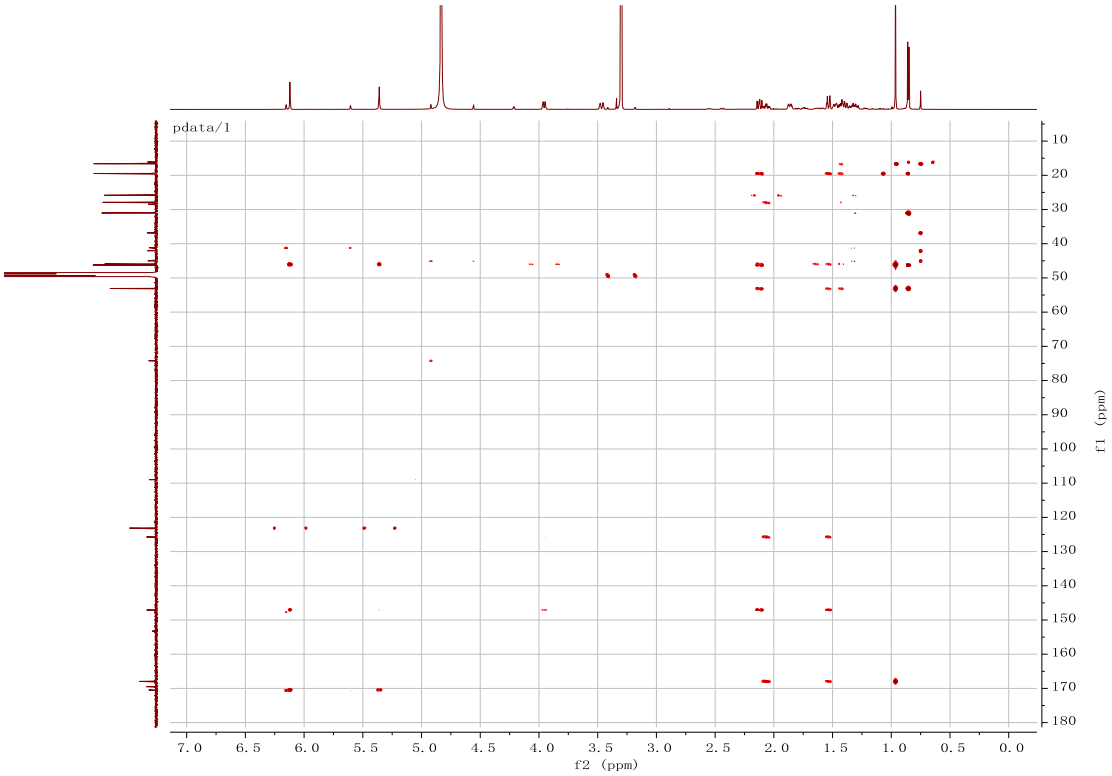
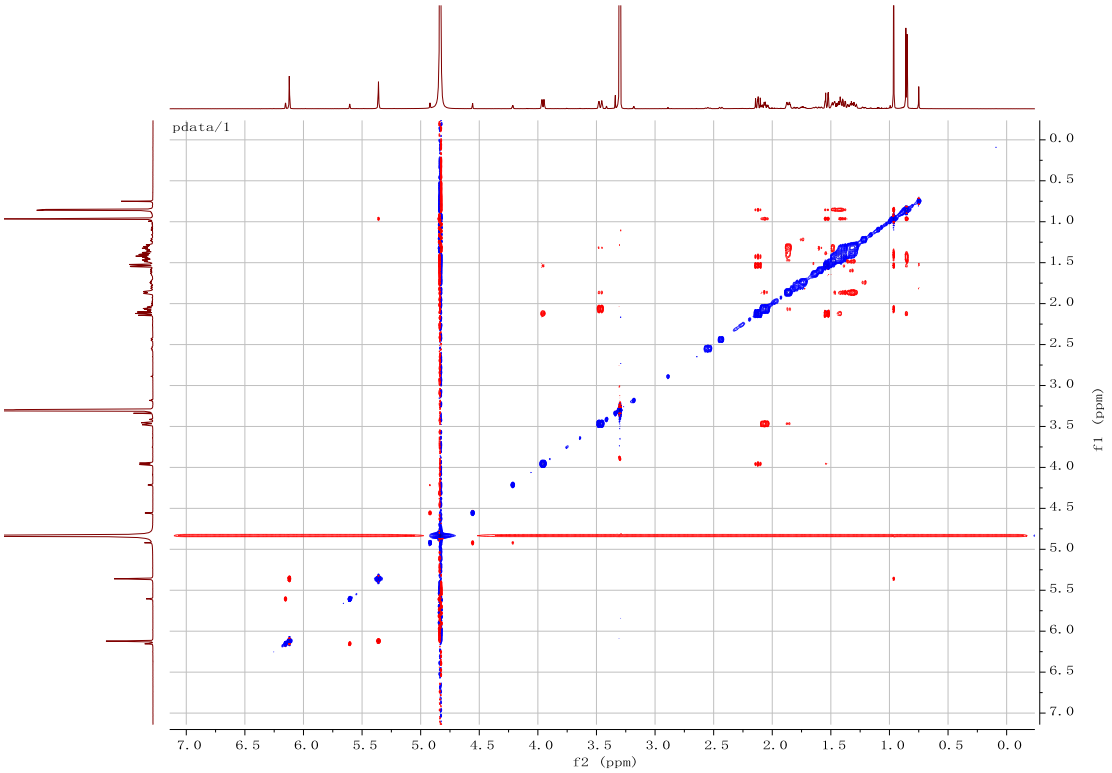


Figure S99. HMBC spectrum of 9 in methanol-d_4



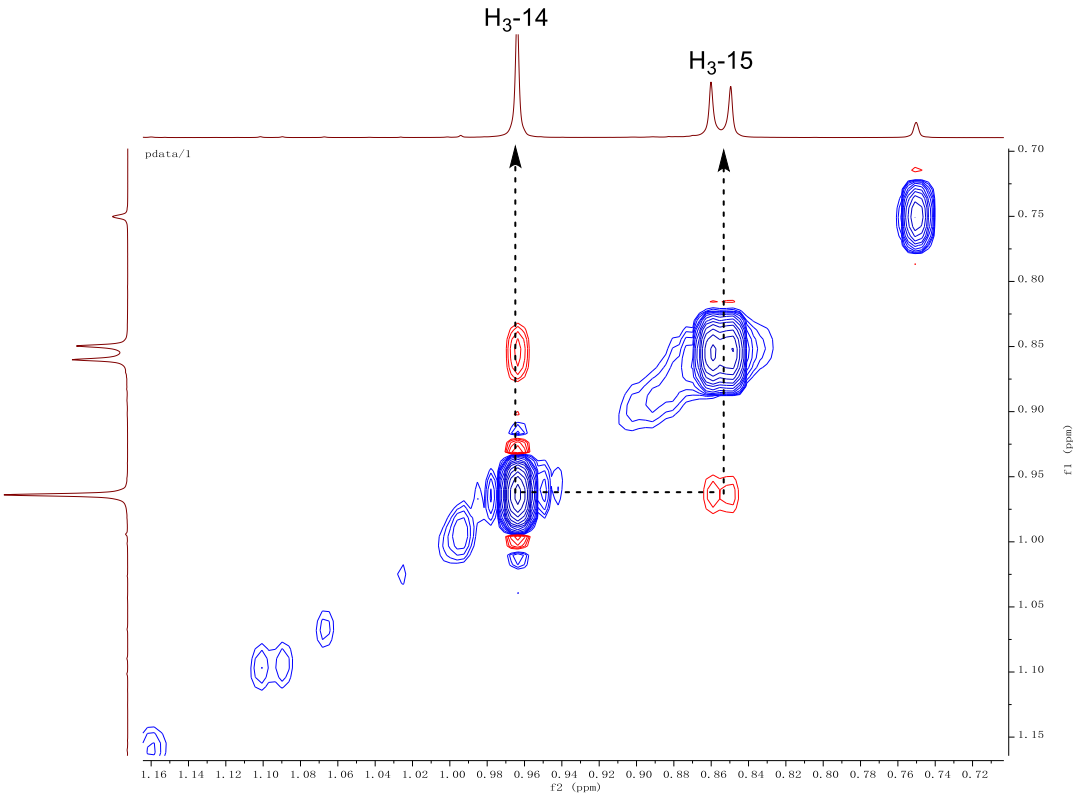


Figure S100. NOESY spectrum of 9 in methanol-d_4

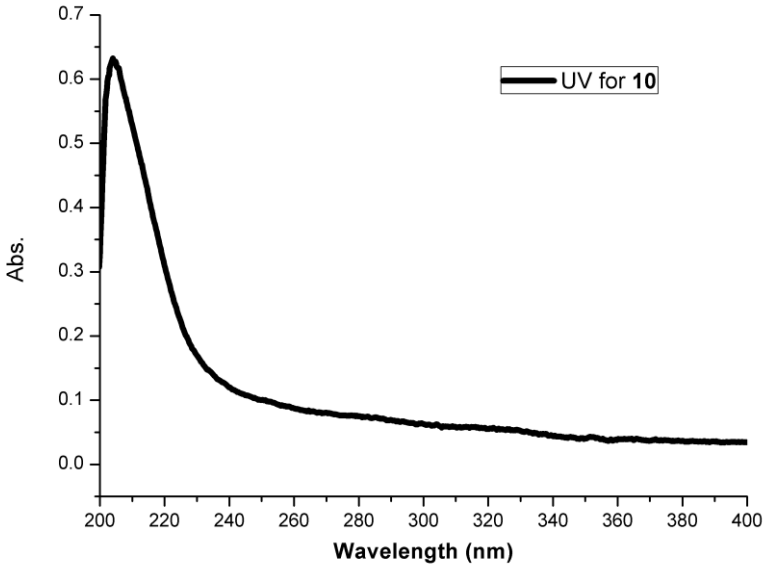


Figure S101. UV spectrum of 10

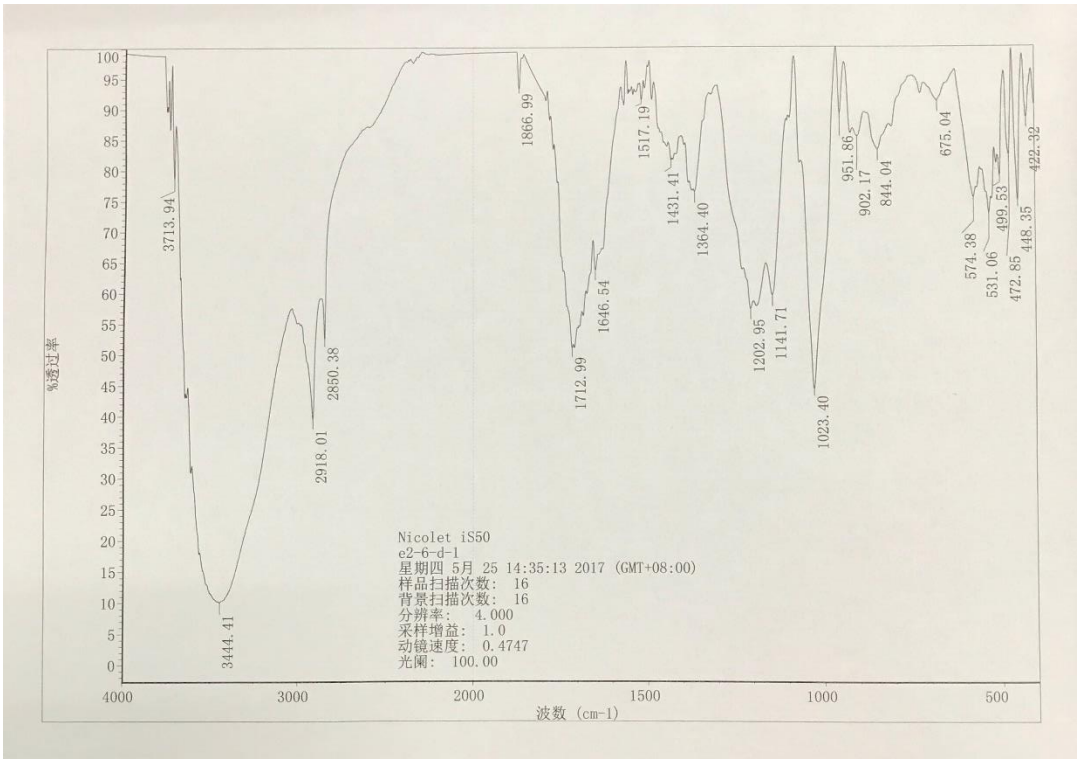


Figure S102. IR spectrum of 10

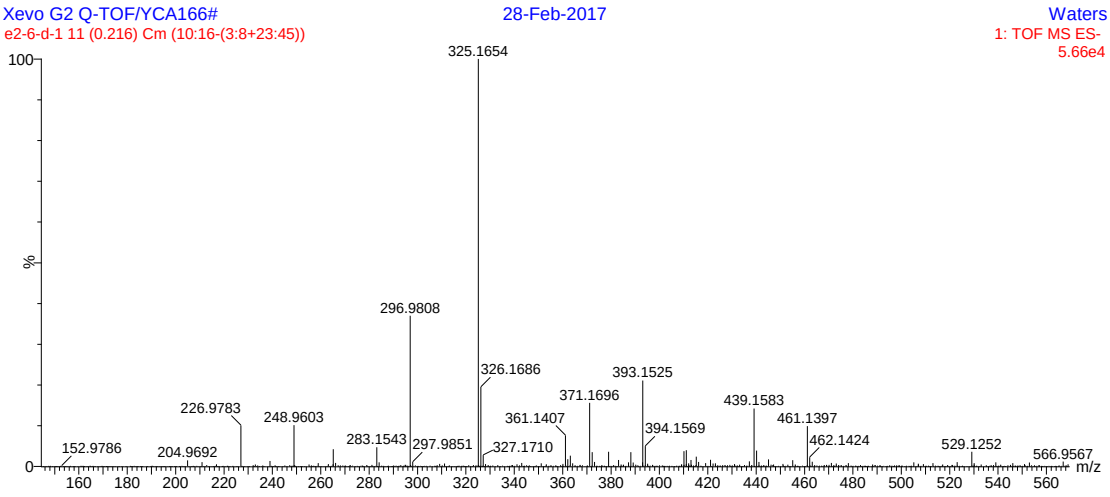


Figure S103. HRMS spectrum of 10

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
532 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-110 H: 0-200 N: 0-10 O: 0-50

Minimum:					-1.5			
Maximum:			5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
325.1654	325.1651	0.3	0.9	5.5	136.0	0.008	99.20	C17H25O6

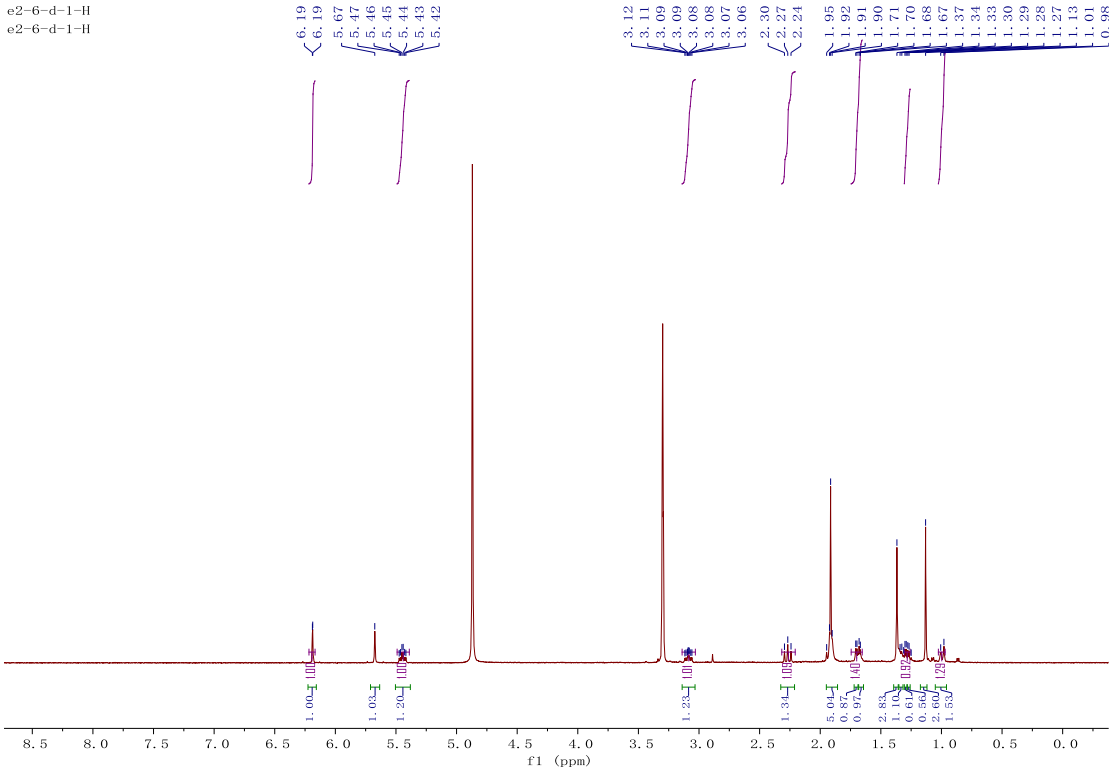


Figure S104. ^{1}H NMR spectrum of 10 in methanol-*d*$_4$

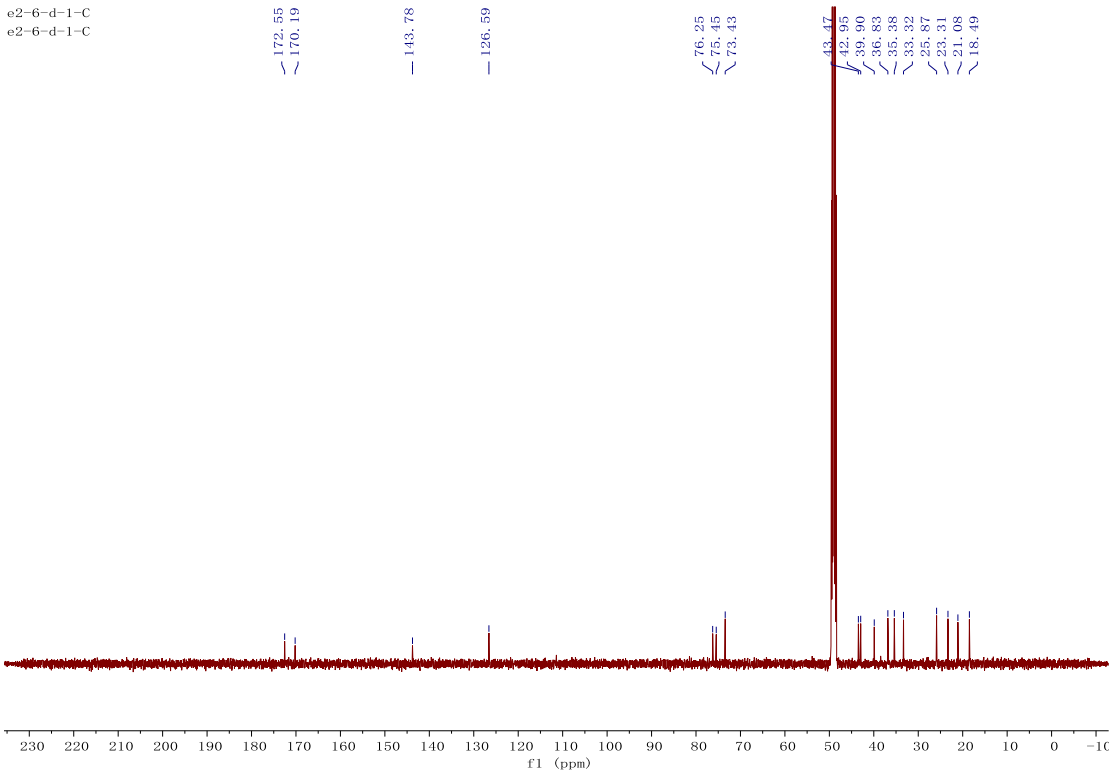


Figure S105. ^{13}C NMR spectrum of 10 in methanol-*d*$_4$

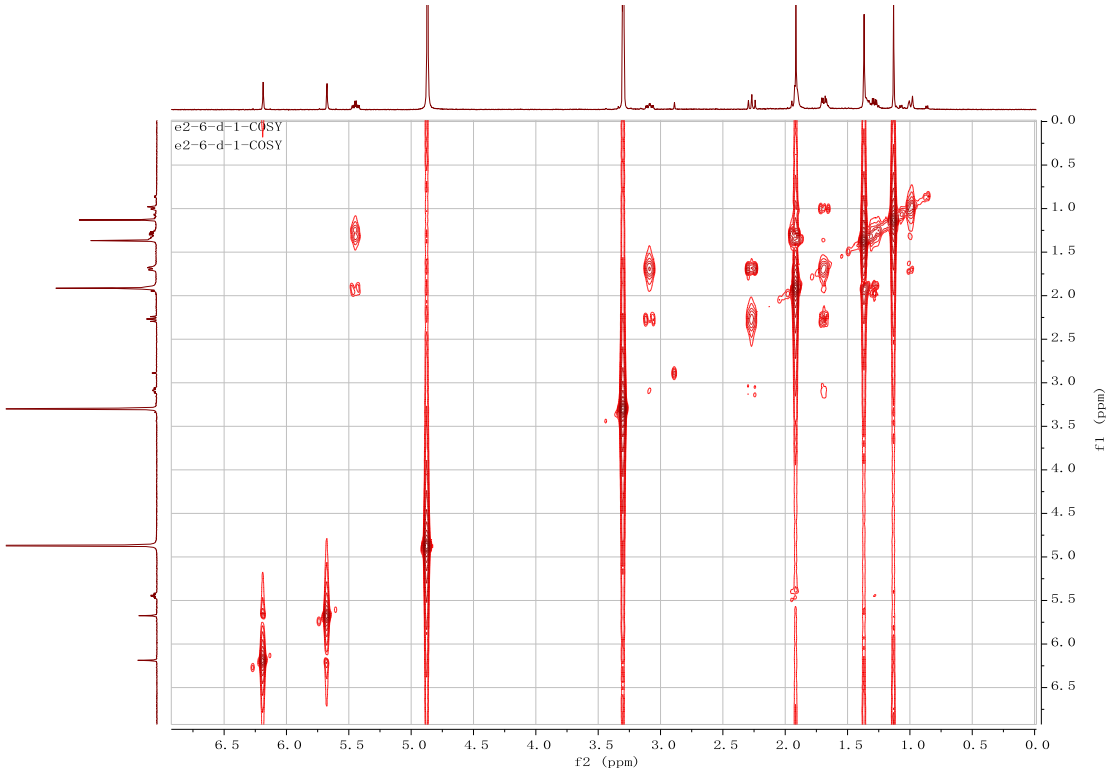


Figure S106. ^{1}H-^{1}H COSY spectrum of 10 in methanol-*d*$_4$

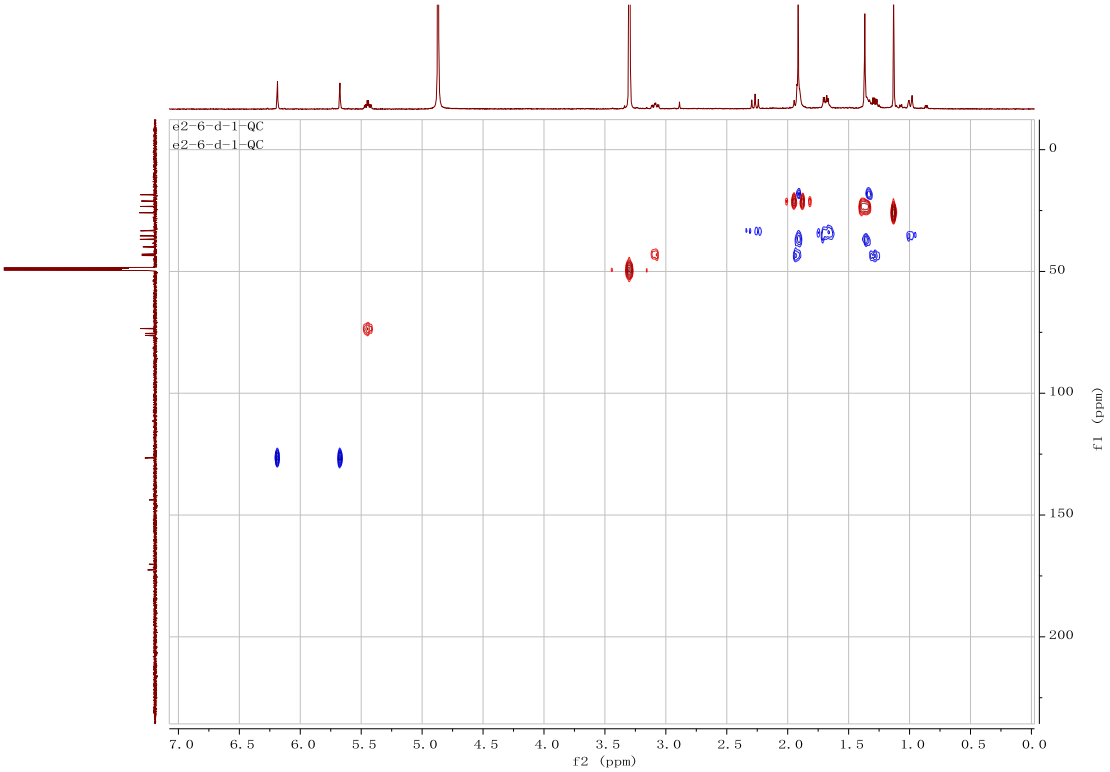


Figure S107. HSQC spectrum of 10 in methanol-d_4

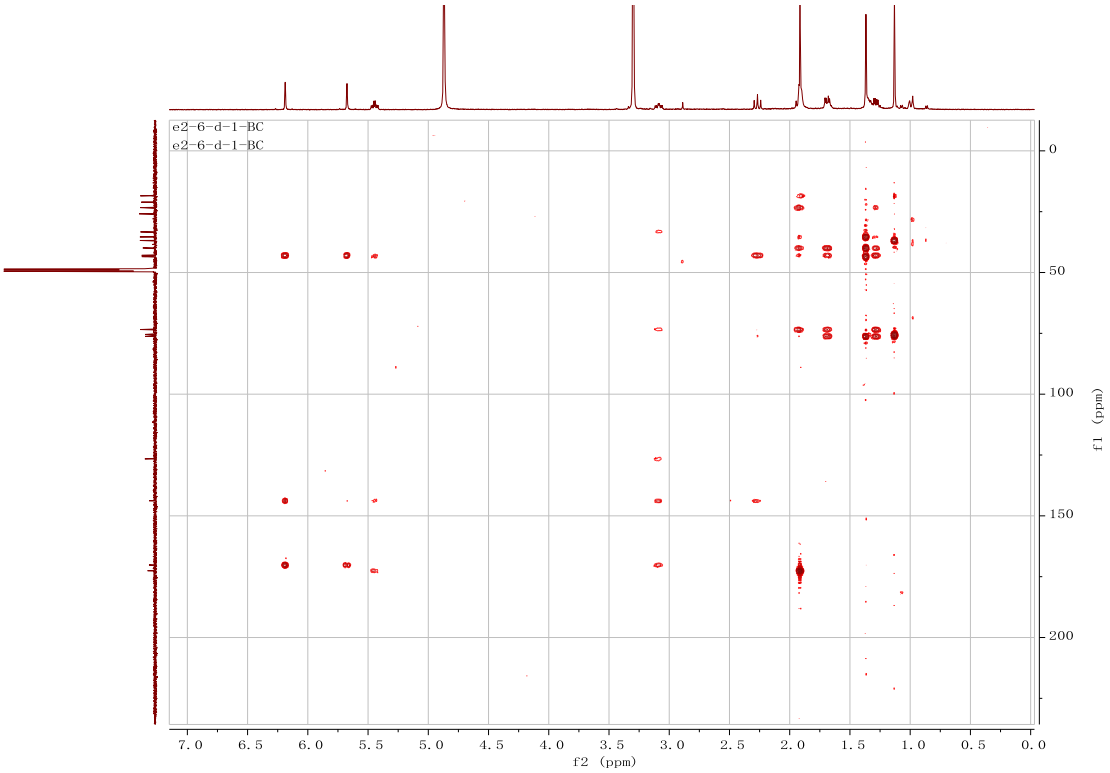


Figure S108. HMBC spectrum of 10 in methanol-d_4

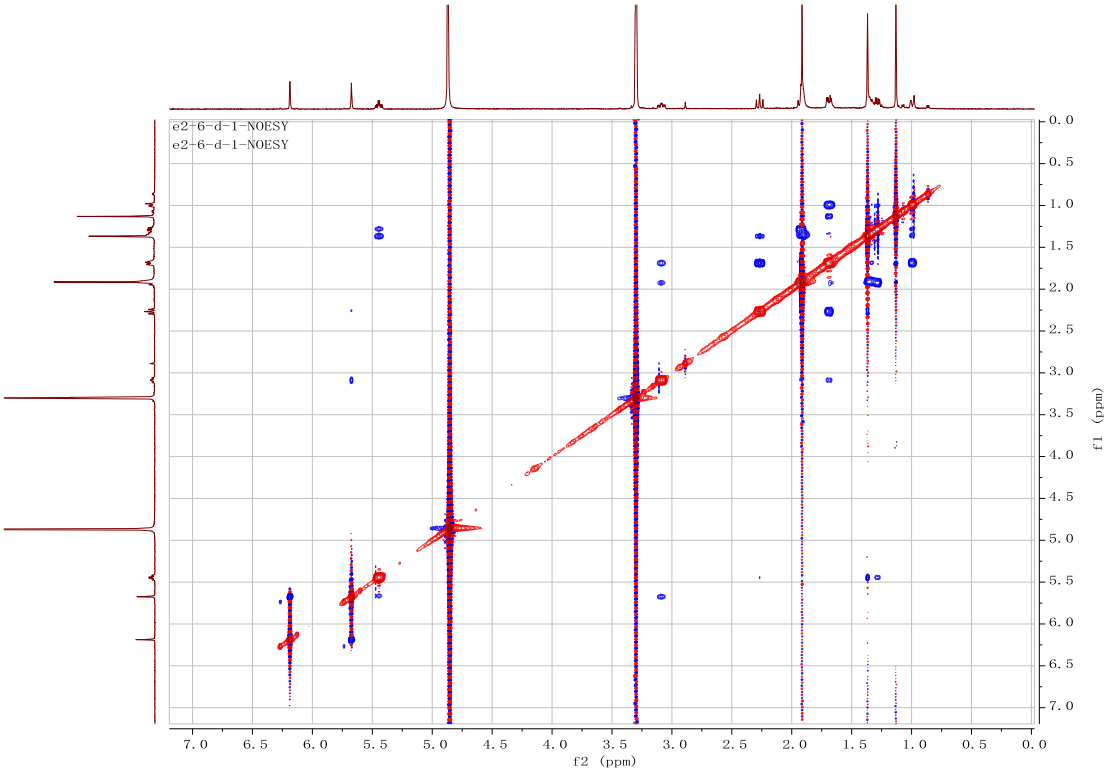


Figure S109. NOESY spectrum of 10 in methanol-d_4

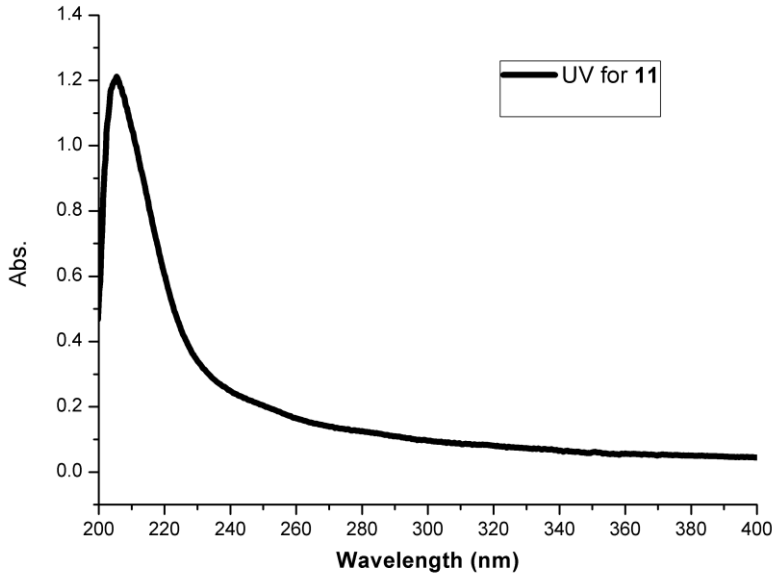


Figure S110. UV spectrum of 11

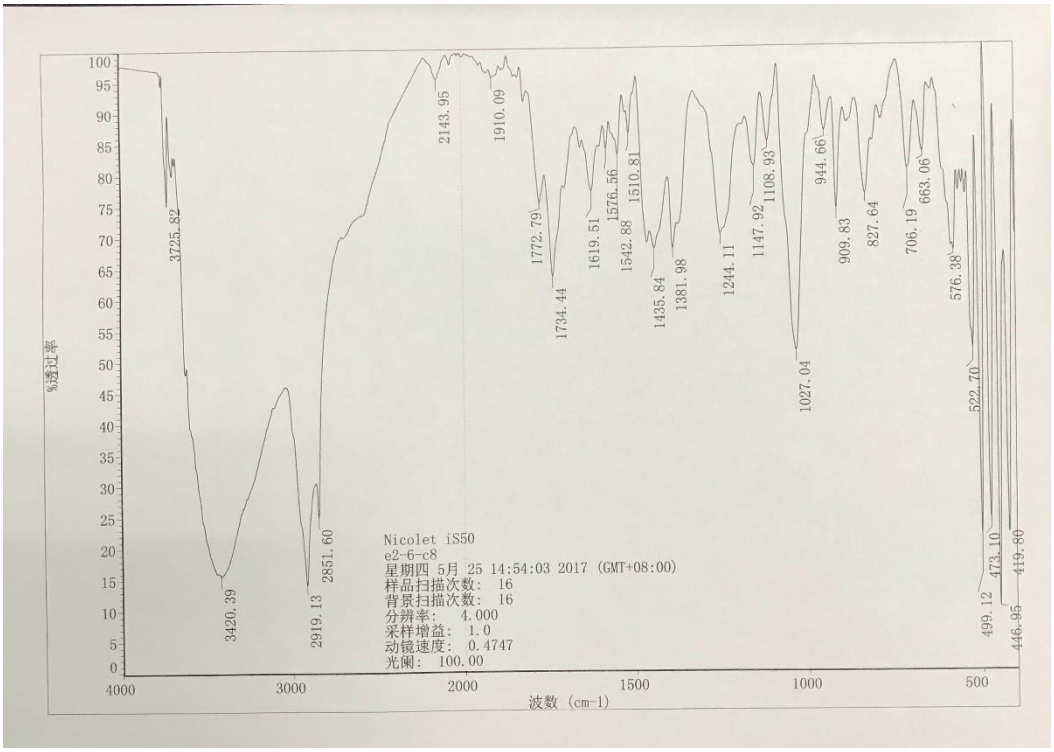


Figure S111. IR spectrum of 11

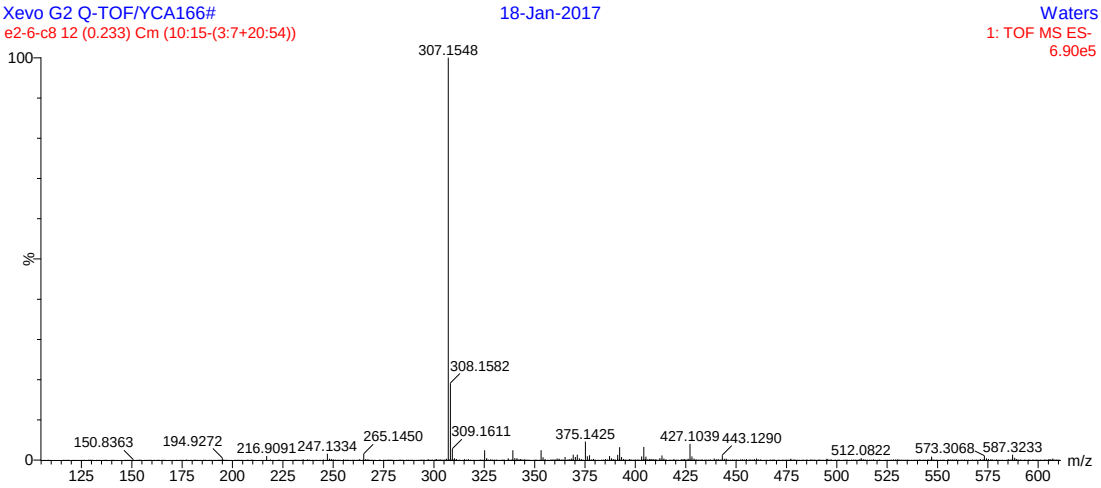


Figure S112. HRMS spectrum of 11

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
305 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-110 H: 0-200 N: 0-5 O: 0-50

Minimum:						-1.5		
Maximum:			5.0	5.0		50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
307.1548	307.1545	0.3	1.0	6.5	226.8	0.000	100.00	C17H23O5

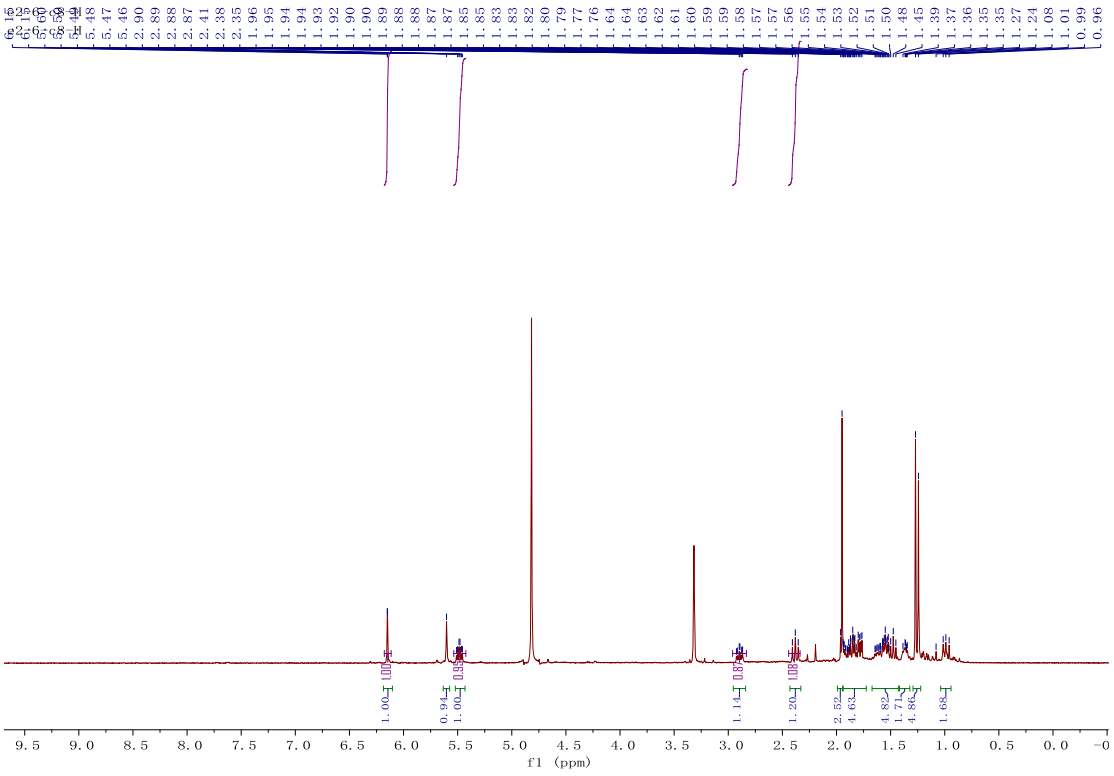


Figure S113. ^{1}H NMR spectrum of 11 in methanol-*d*$_4$

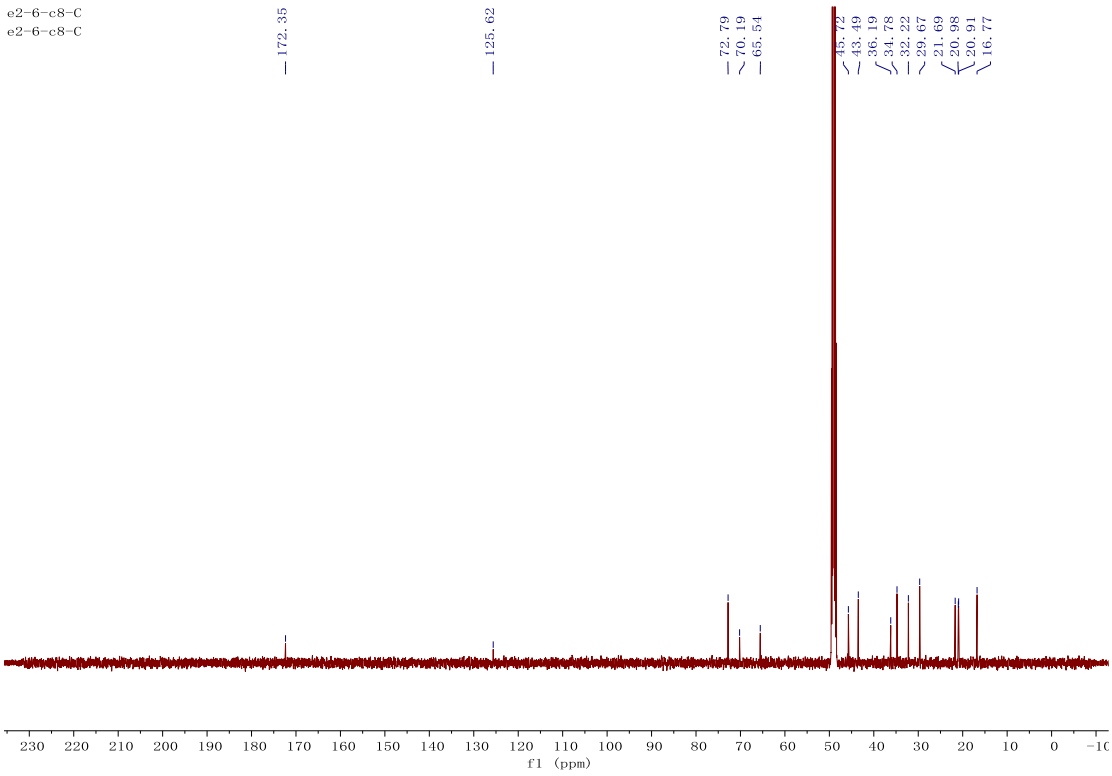


Figure S114. ^{13}C NMR spectrum of 11 in methanol-*d*$_4$

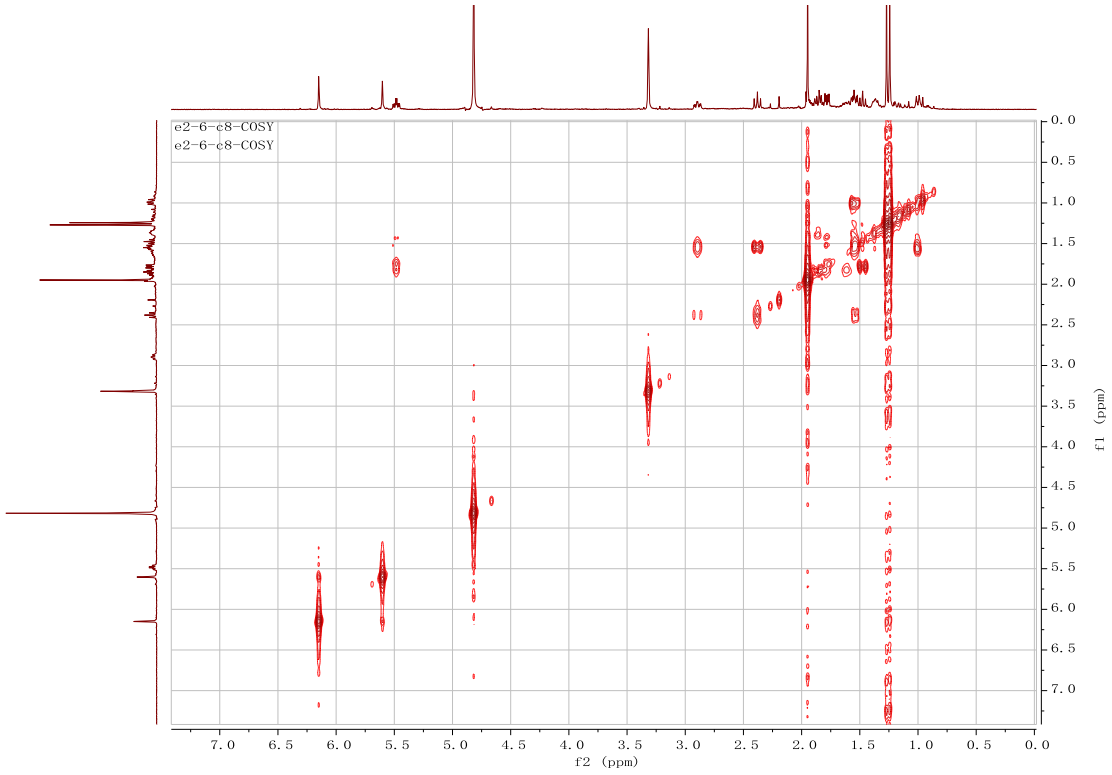


Figure S115. ^{1}H-^{1}H COSY spectrum of 11 in methanol-*d*$_4$

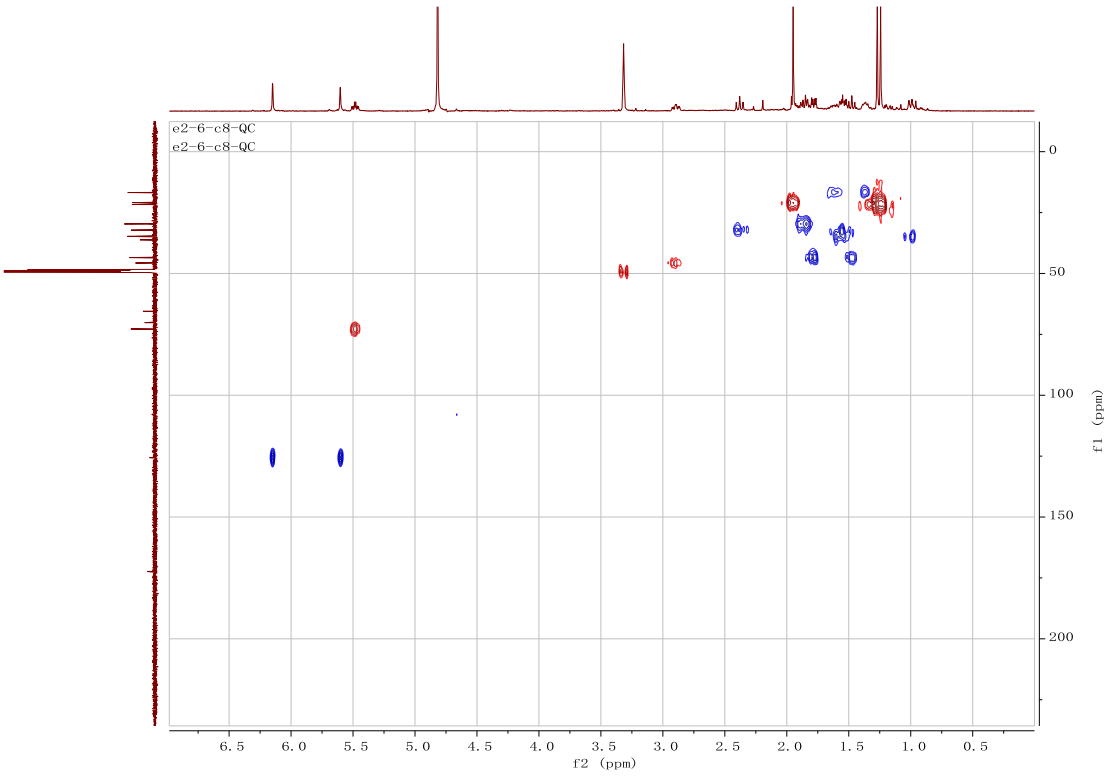


Figure S116. HSQC spectrum of 11 in methanol-d_4

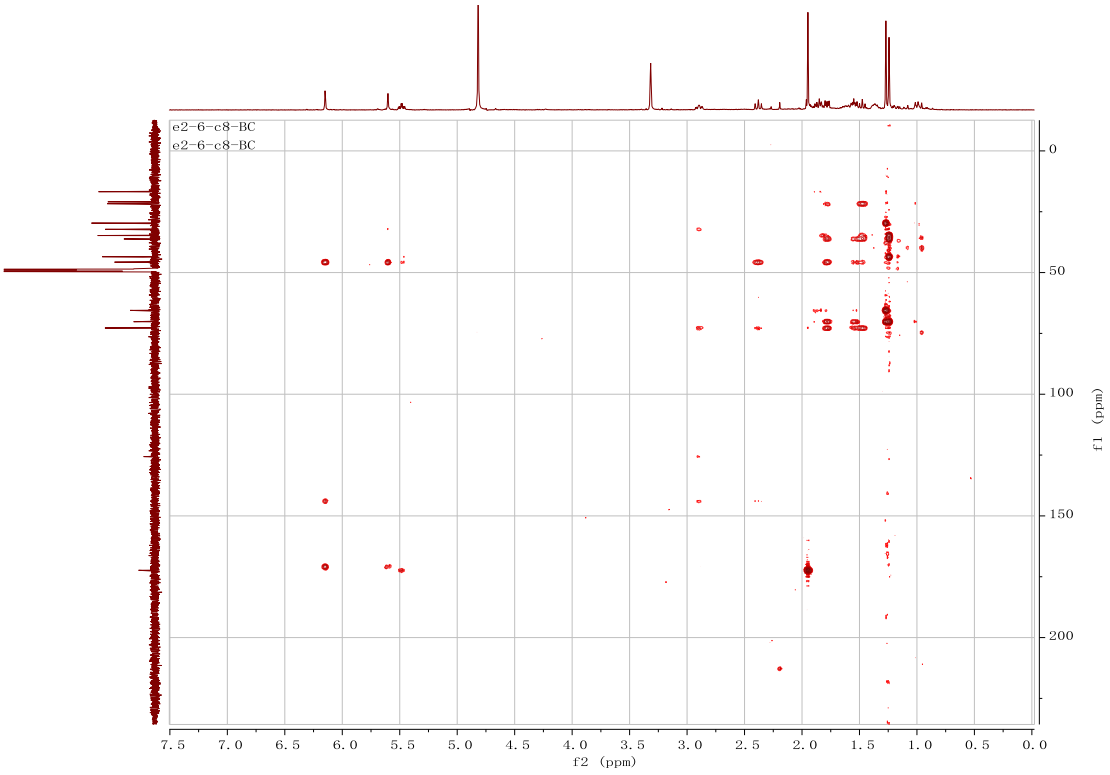


Figure S117. HMBC spectrum of 11 in methanol-d_4

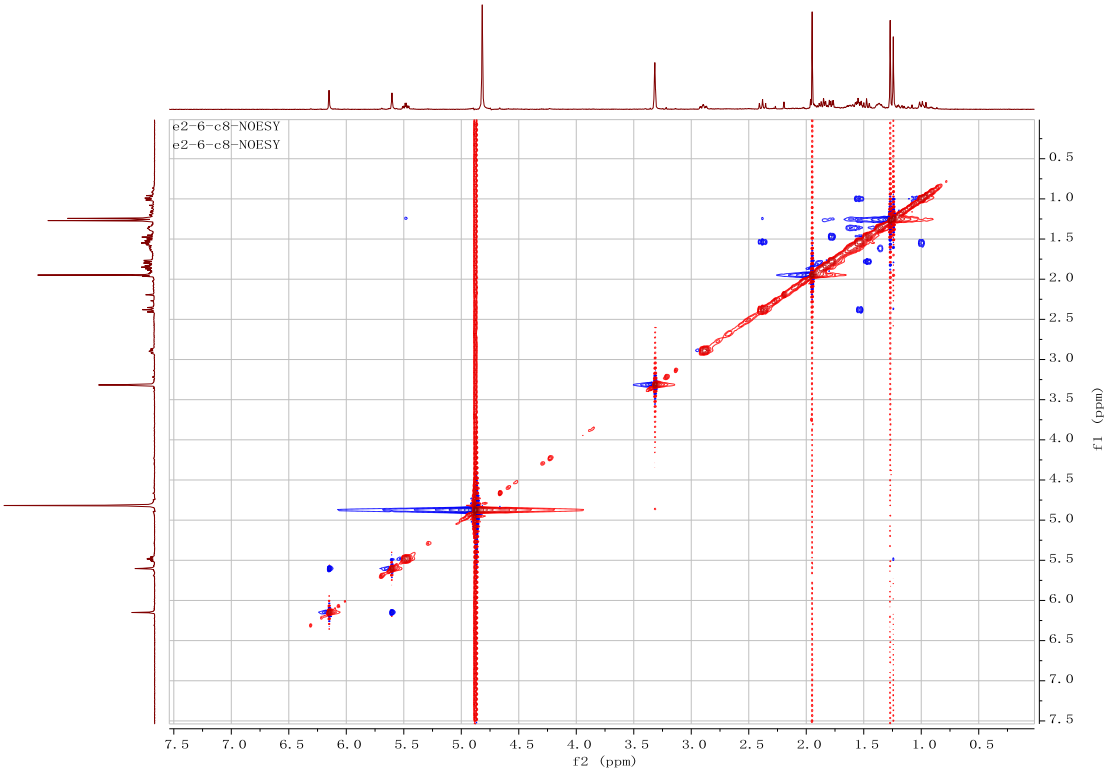


Figure S118. NOESY spectrum of 11 in methanol-d_4

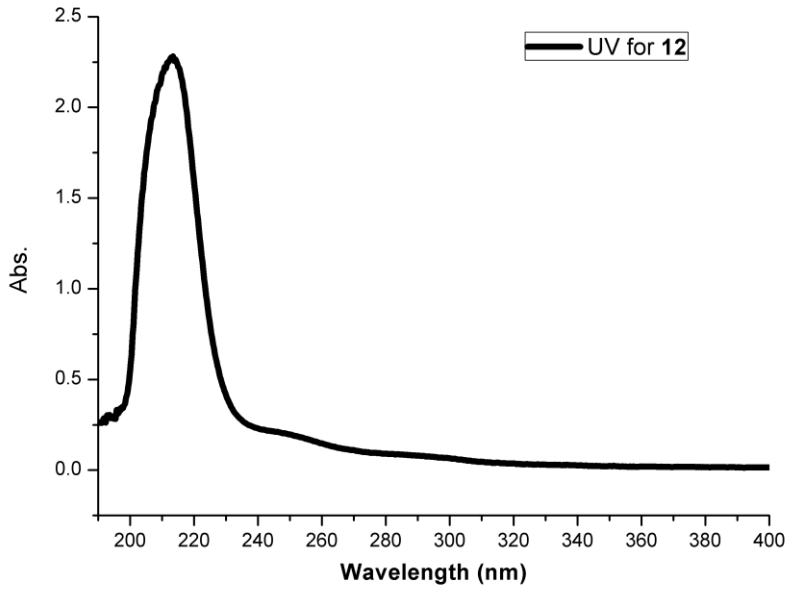


Figure S119. UV spectrum of 12

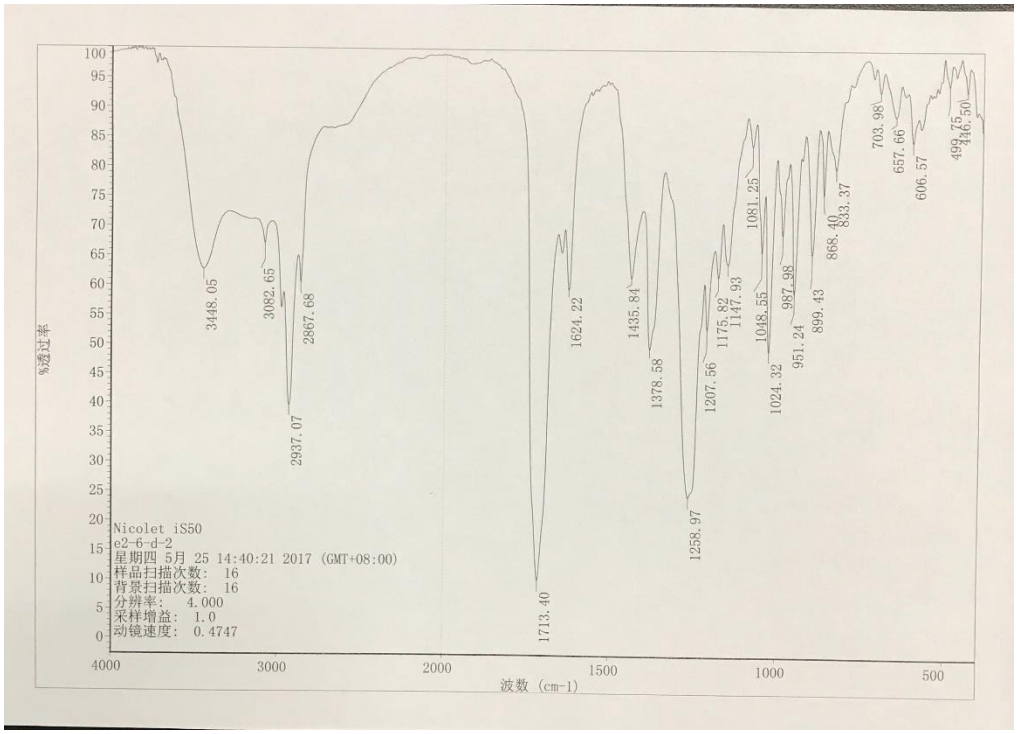


Figure S120. IR spectrum of 12

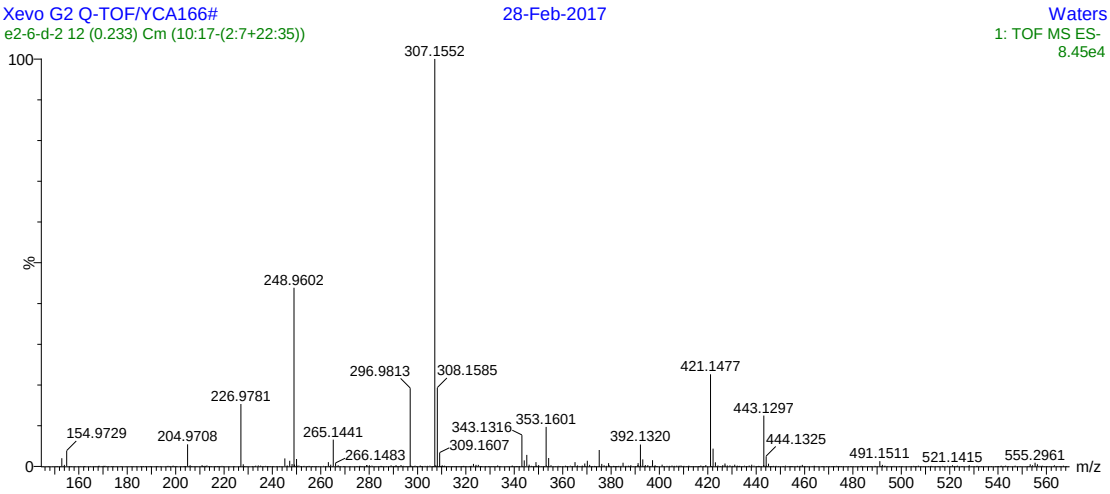


Figure S121. HRMS spectrum of 12

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
480 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-110 H: 0-200 N: 0-10 O: 0-50

Minimum:					-1.5			
Maximum:			5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
307.1552	307.1545	0.7	2.3	6.5	145.3	0.033	96.79	C17H23O5

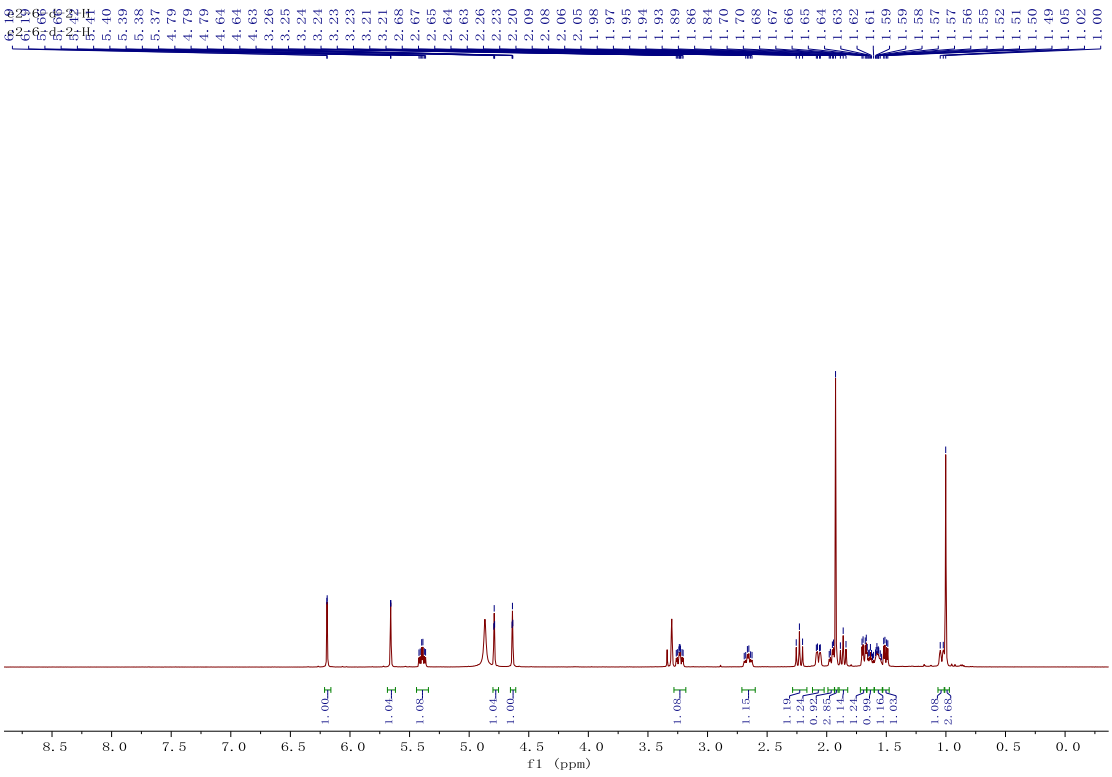


Figure S122. ^{1}H NMR spectrum of 12 in methanol-d_4

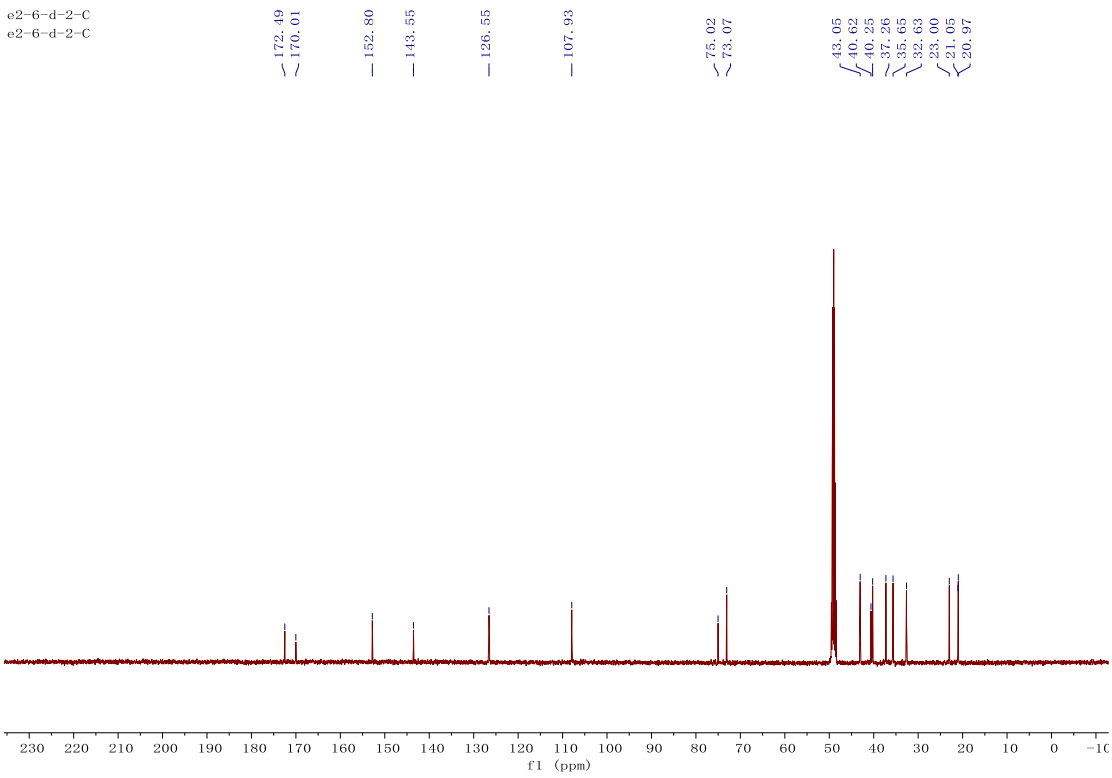


Figure S123. ^{13}C NMR spectrum of 12 in methanol-d_4

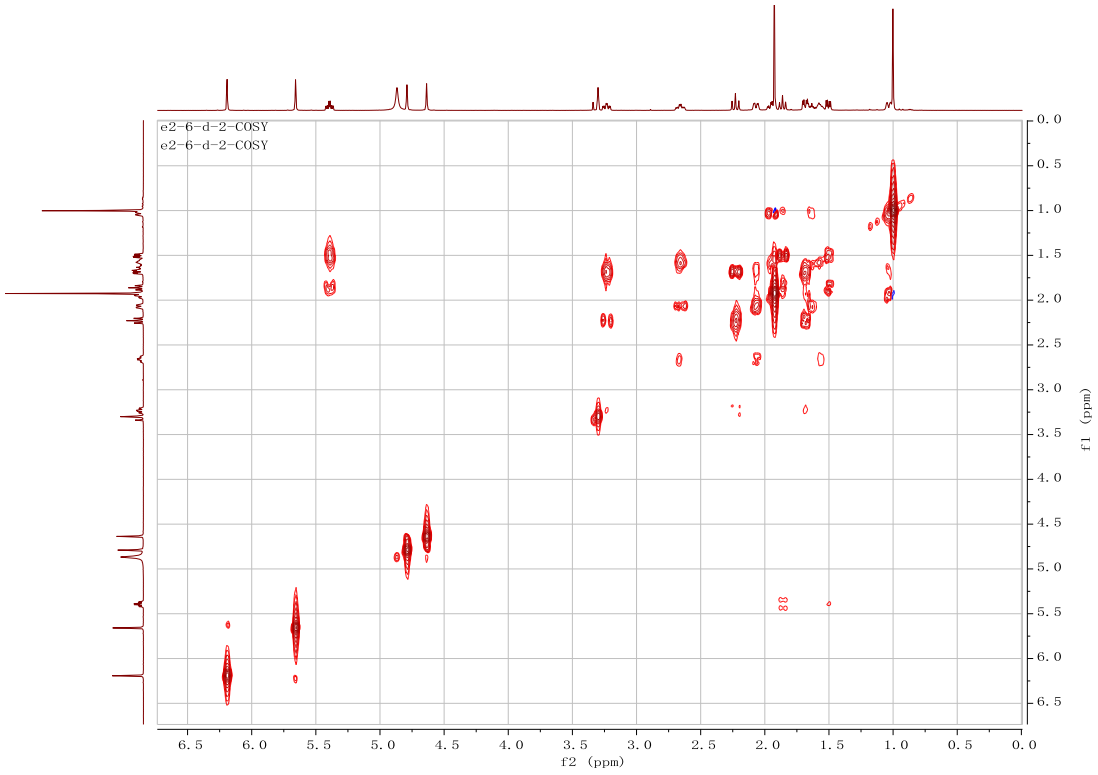


Figure S124. ^{1}H-^{1}H COSY spectrum of 12 in methanol-d_4

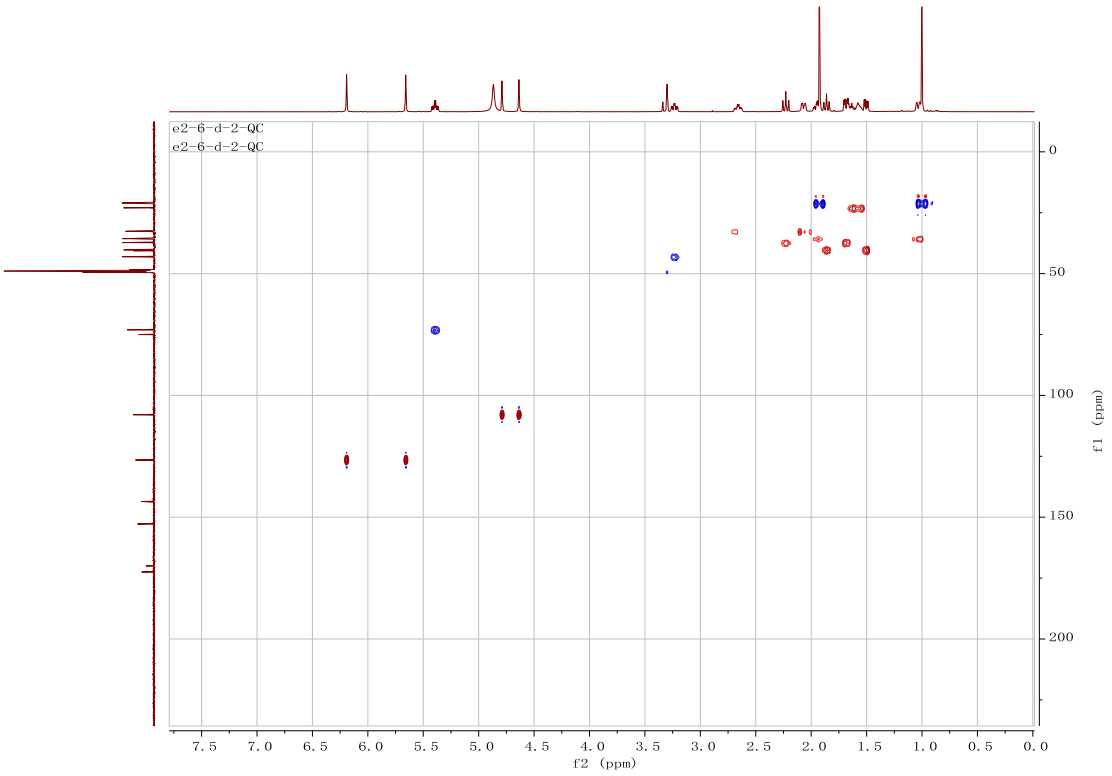


Figure S125. HSQC spectrum of 12 in methanol-d_4

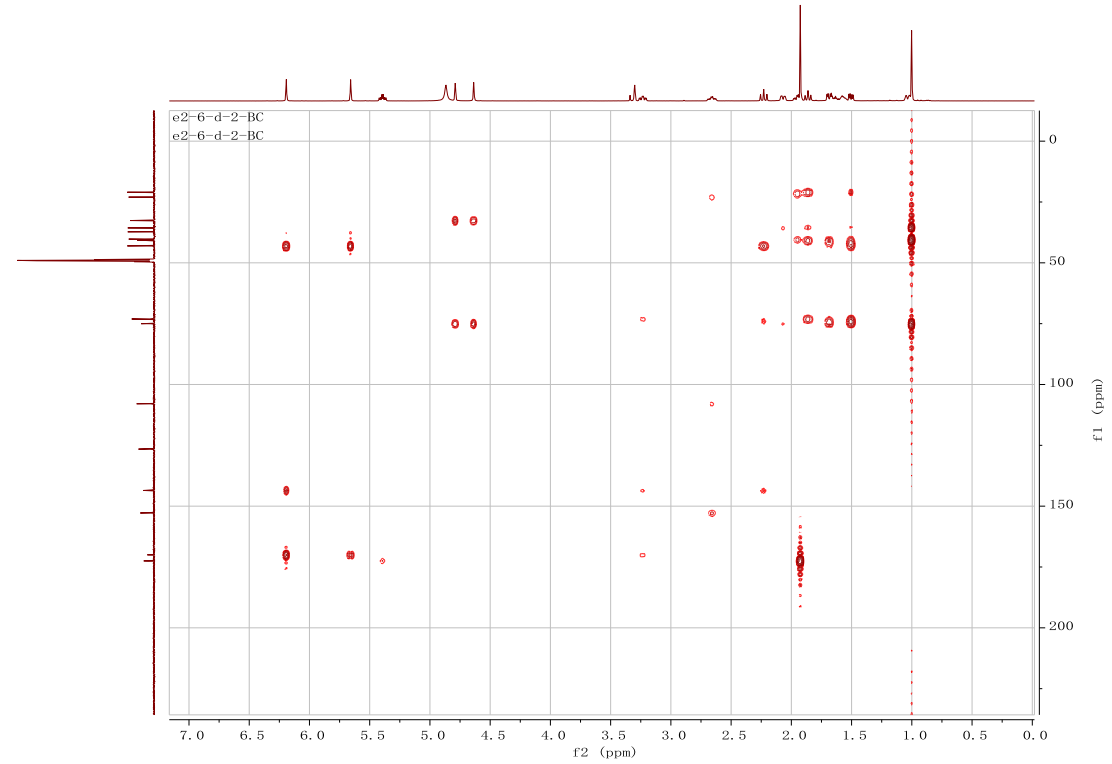


Figure S126. HMBC spectrum of 12 in methanol-d_4

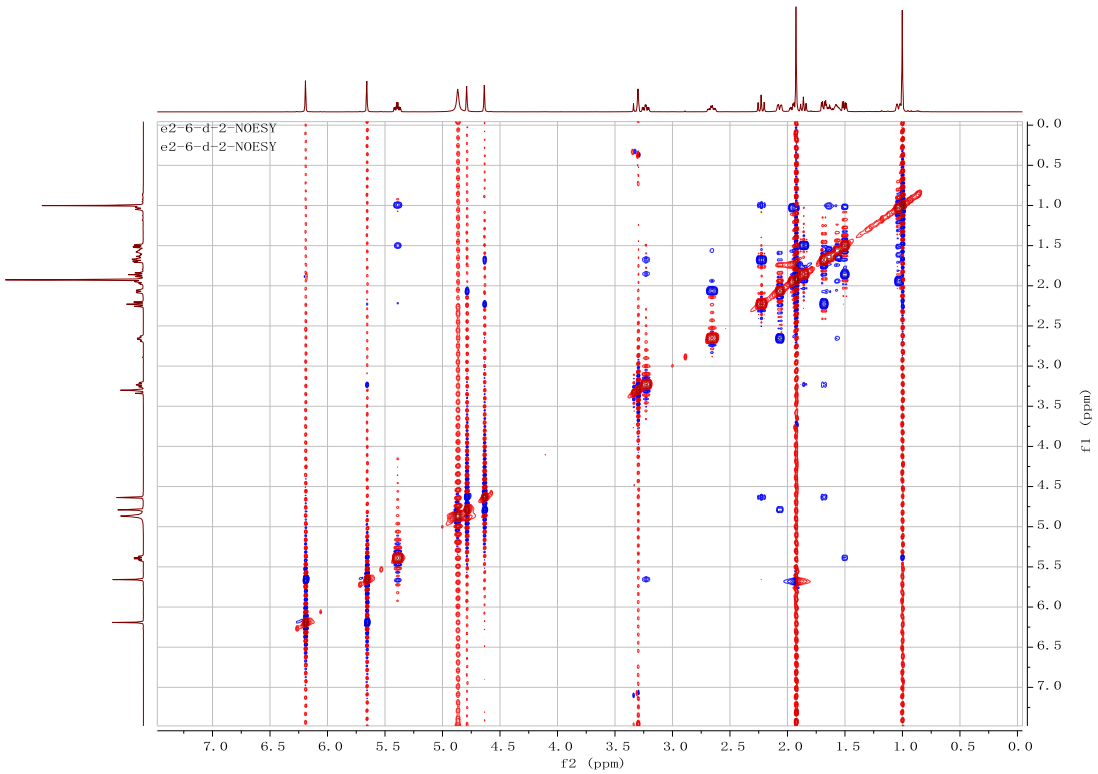


Figure S127. NOESY spectrum of 12 in methanol-d_4

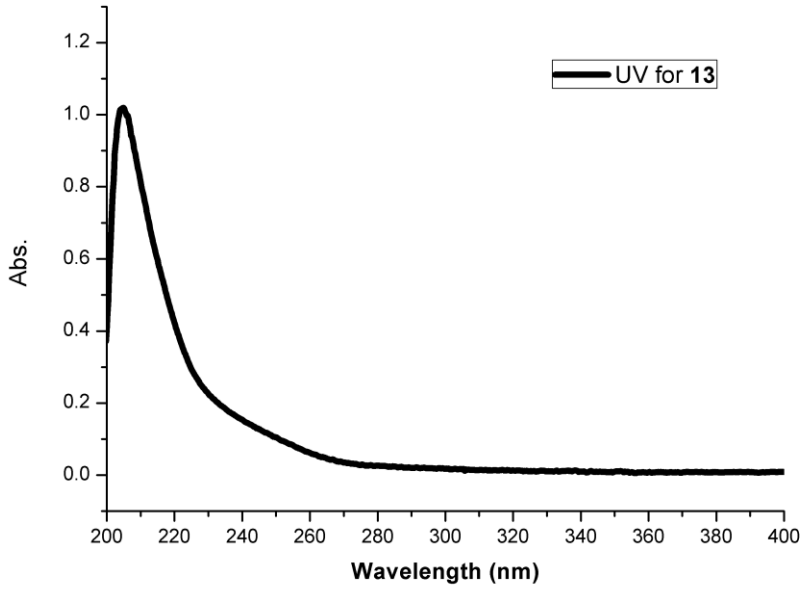


Figure S128. UV spectrum of 13

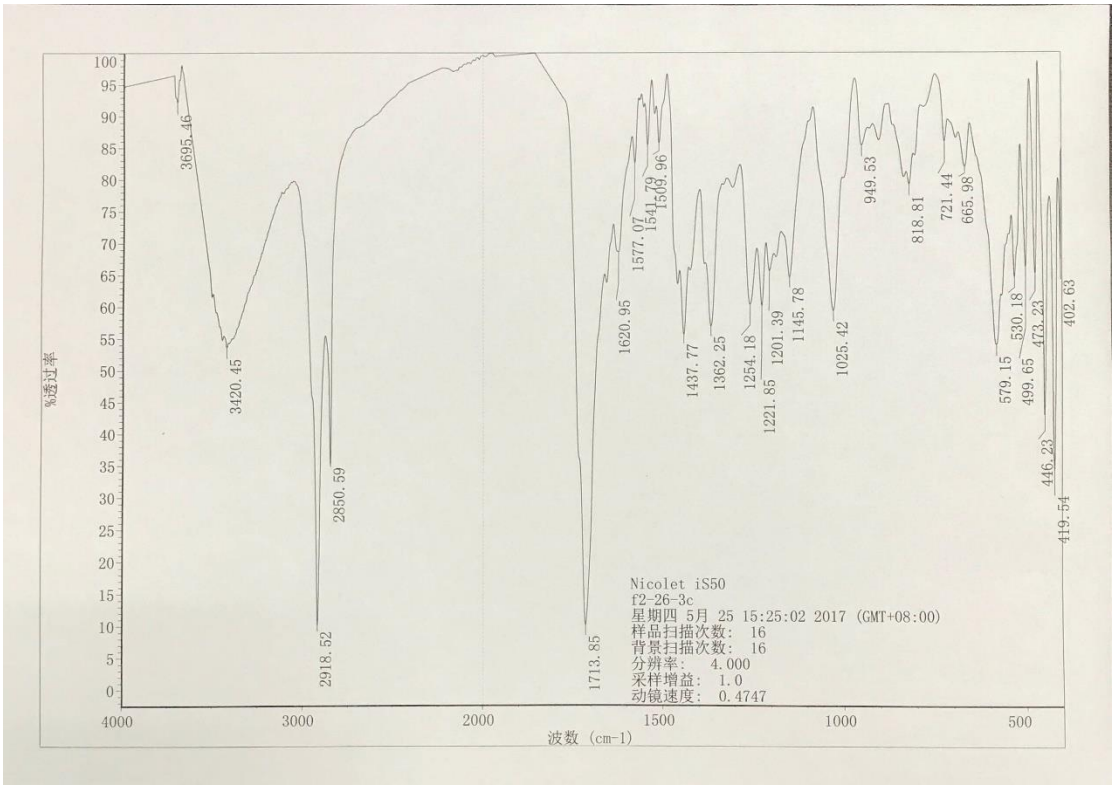


Figure S129. IR spectrum of 13

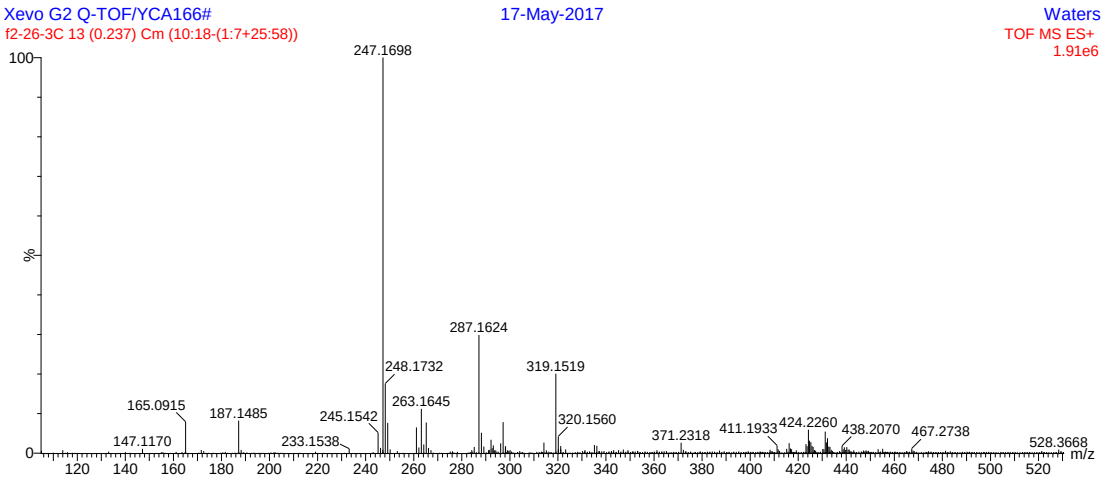


Figure S130. HRMS spectrum of 13

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
759 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-110 H: 0-200 N: 0-10 O: 0-50 Na: 0-1

Minimum:						-1.5		
Maximum:				5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
287.1624	287.1623	0.1	0.3	4.5	212.7	0.339	71.22	C16H24O3 Na

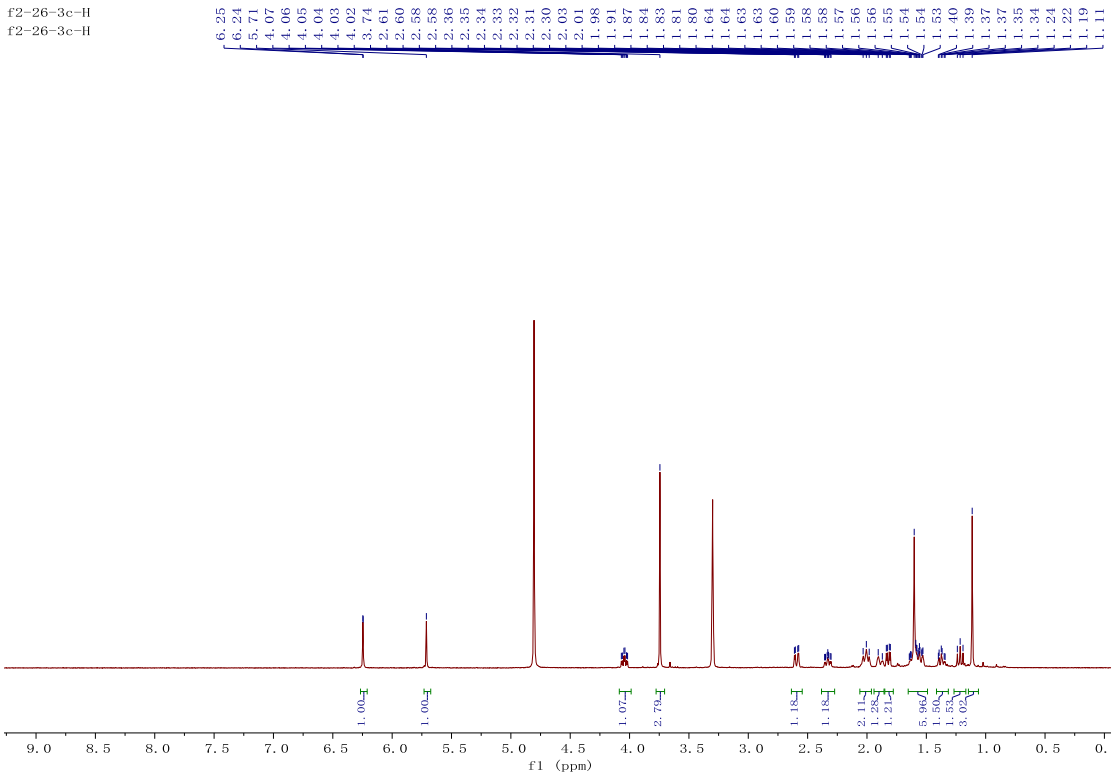


Figure S131. ^{1}H NMR spectrum of 13 in methanol-d_4

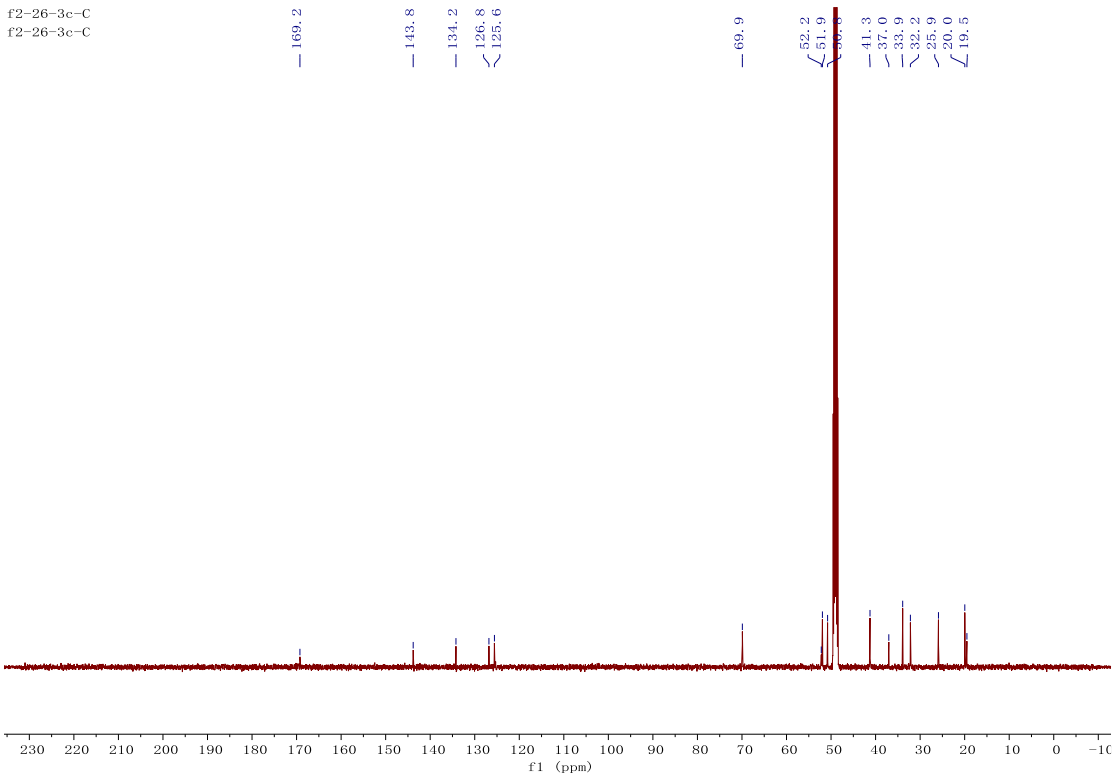


Figure S132. ^{13}C NMR spectrum of 13 in methanol-*d*$_4$

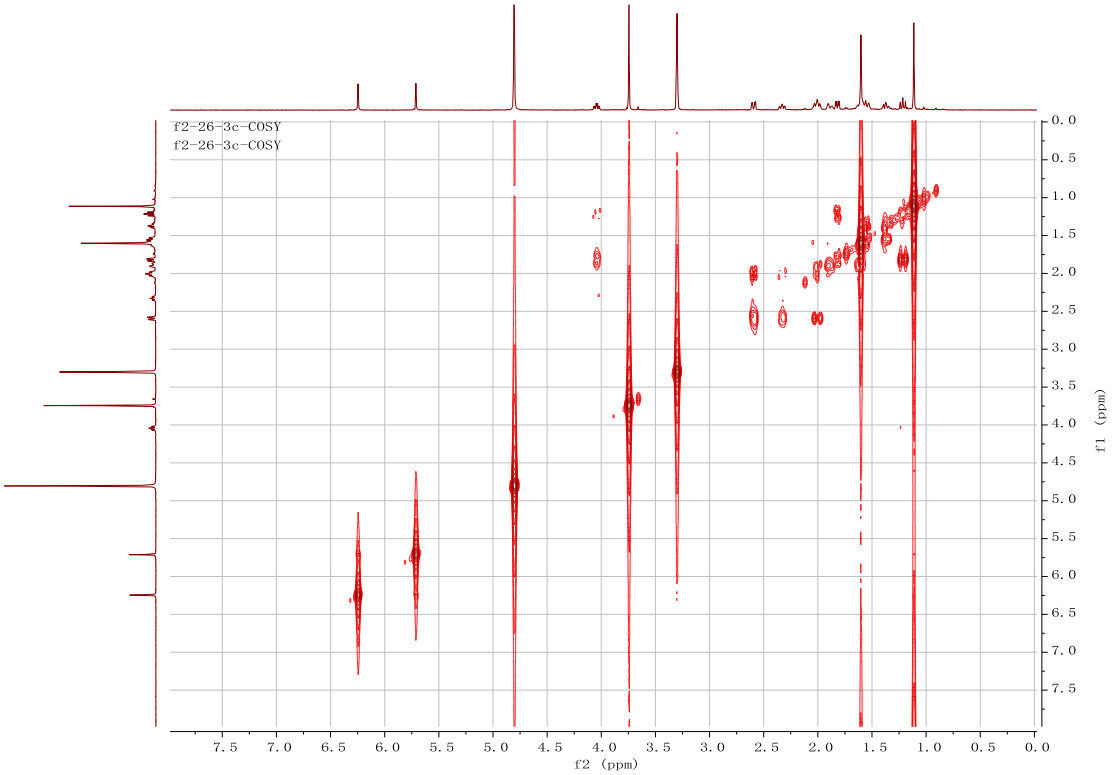


Figure S133. ^{1}H-^{1}H COSY spectrum of 13 in methanol-*d*$_4$

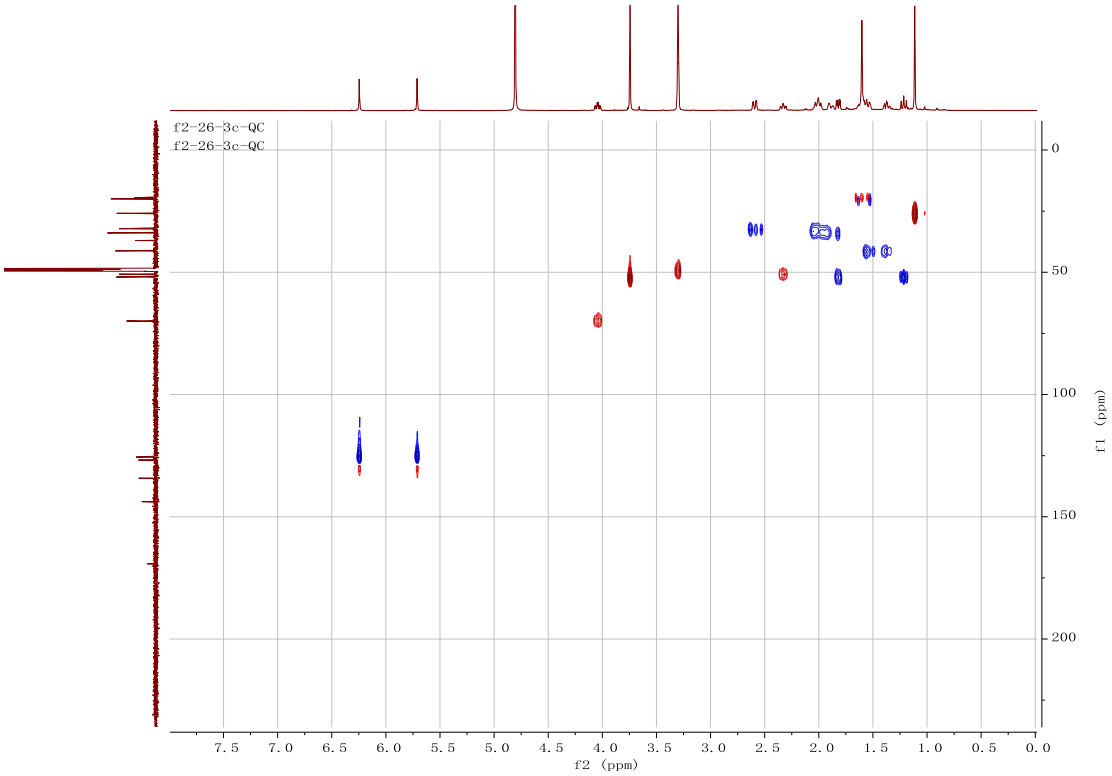


Figure S134. HSQC spectrum of 13 in methanol-d_4

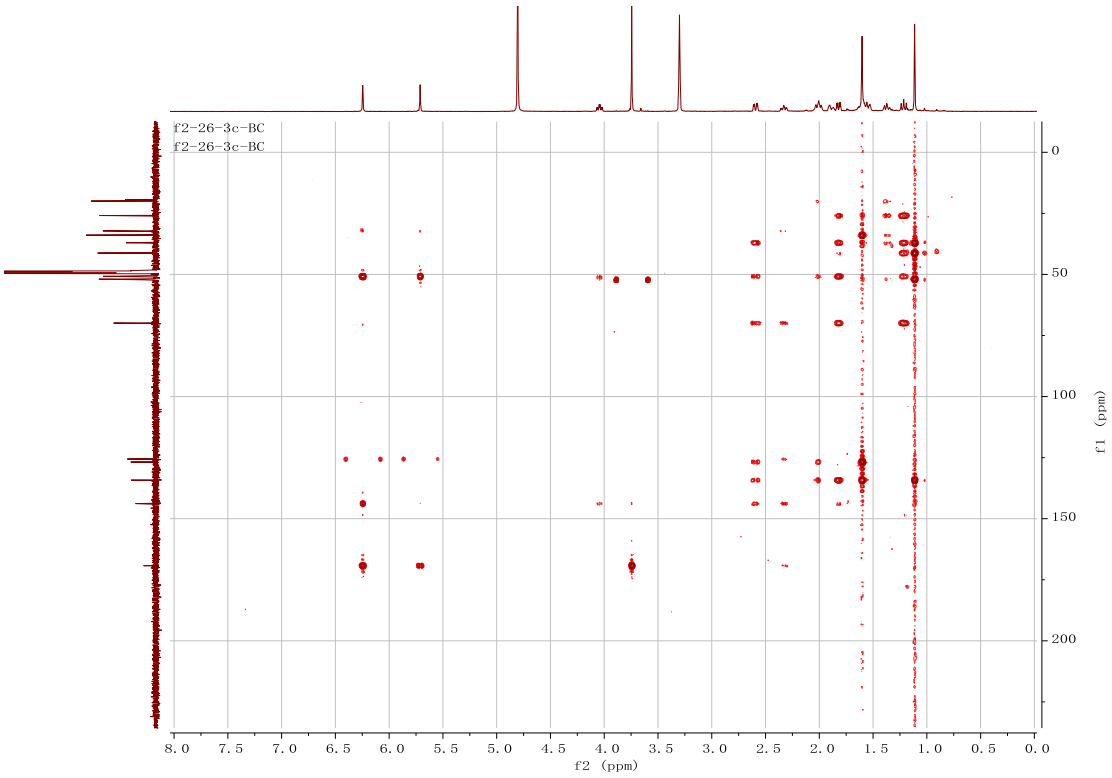


Figure S135. HMBC spectrum of 13 in methanol-d_4

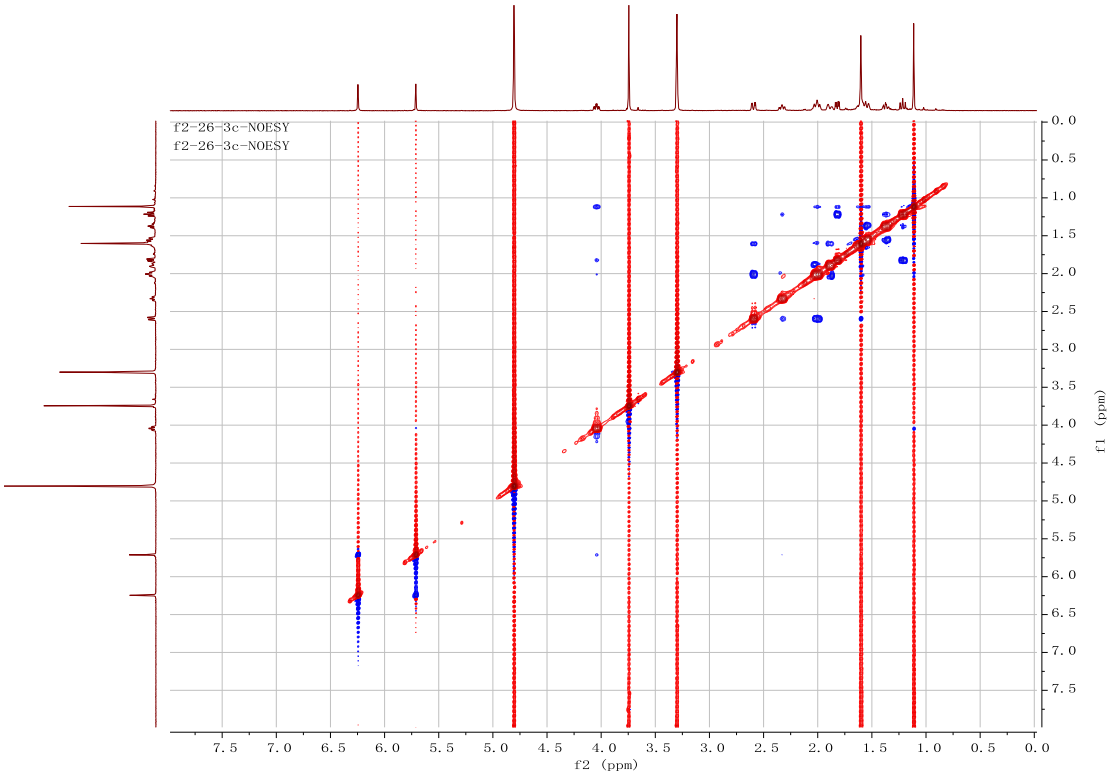
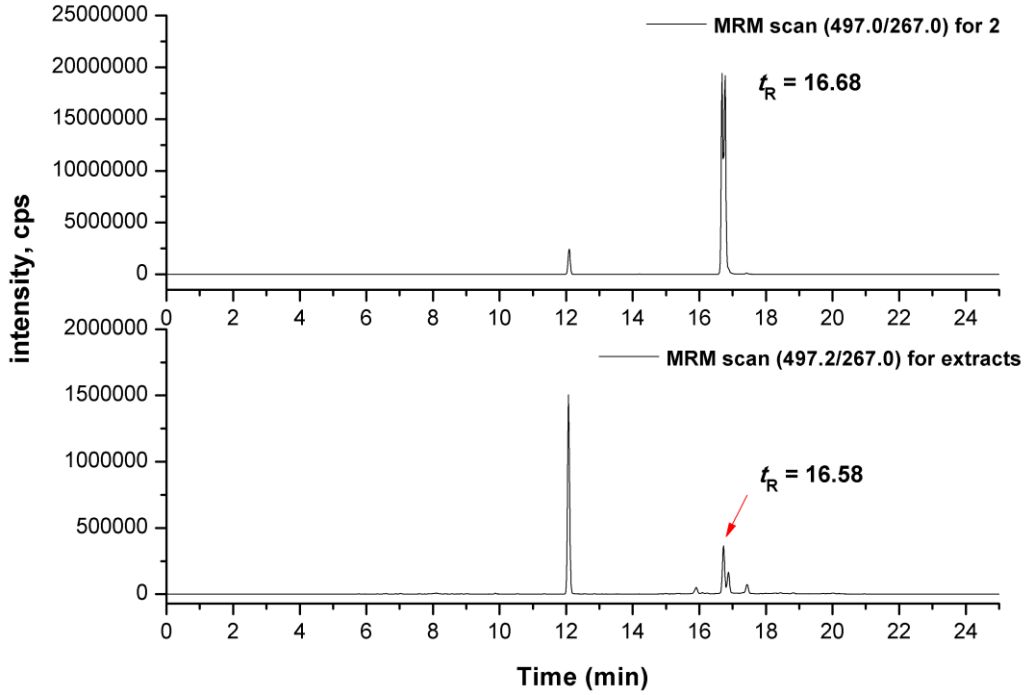
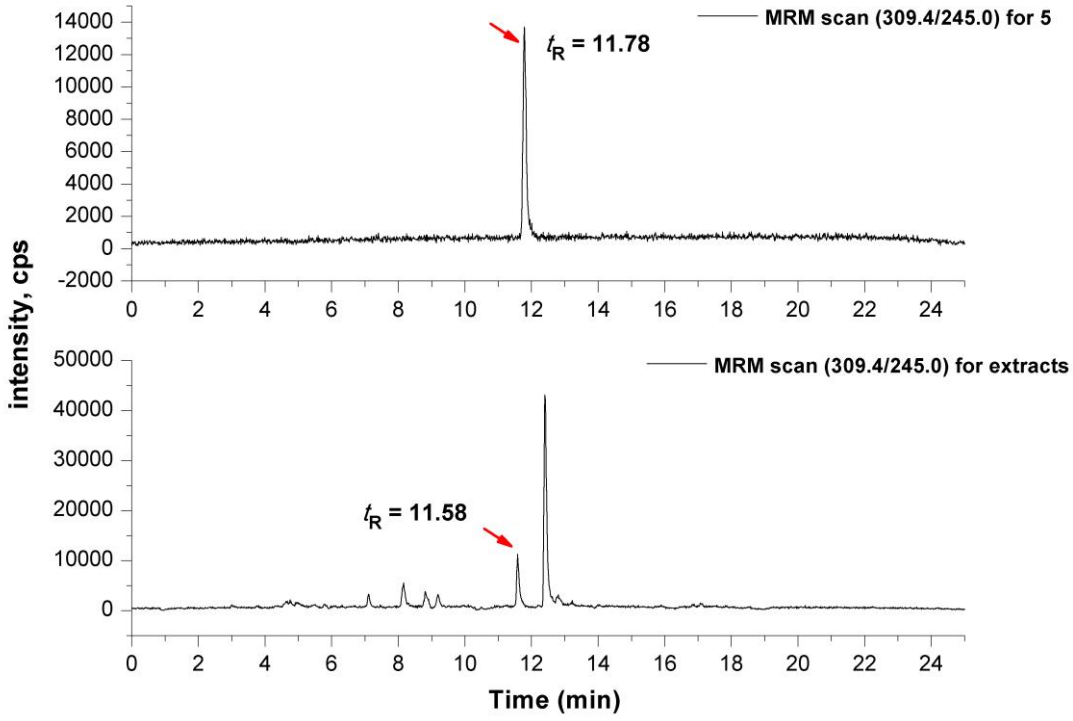


Figure S136. NOESY spectrum of 13 in methanol-d_4


MRM scan (497.0/267.0) for 2
t_R = 16.68
MRM scan (497.2/267.0) for extracts
t_R = 16.58
intensity, cps
Time (min)


MRM scan (309.4/245.0) for 5
t_R = 11.78
MRM scan (309.4/245.0) for extracts
t_R = 11.58
intensity, cps
Time (min)

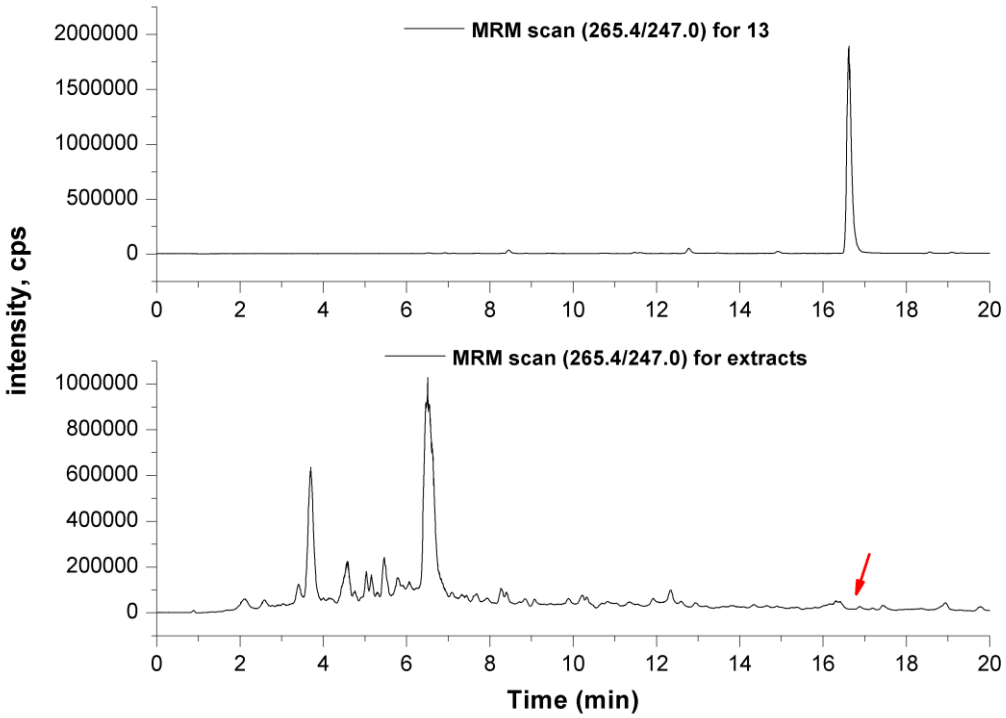


Figure S137. The MRM chromatograms of **2**, **5**, **13**, and methanol percolate extract of *A. freyniana* by LC-MS/MS analysis.