Supplementary Material

Lobocalines A–I, Antibacterial Diterpenes and Steroids from the South China Sea soft coral *Lobophytum catalai*

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1. X-ray crystallographic analyses

Table S1. X-ray crystallographic data for **1**.

Empirical formula	$C_{44}H_{68}O_6$
Formula weight	692.98
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.6135(3)
b/Å	16.2226(5)
c/Å	11.8888(4)
α/°	90
β/°	92.695(2)
γ/°	90
Volume/Å^3	2044.73(11)
Z	2
ρ_{calc}g/cm^3	1.126
μ/mm^{-1}	0.570
F(000)	760.0
Crystal size/mm^3	0.11 × 0.05 × 0.04
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.228 to 149.386
Index ranges	-12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -14 ≤ l ≤ 14
Reflections collected	15315
Independent reflections	7619 [R_{int} = 0.0385, R_{sigma} = 0.0475]
Data/restraints/parameters	7619/1/461
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0479, wR_2 = 0.1174
Final R indexes [all data]	R_1 = 0.0523, wR_2 = 0.1215
Largest diff. peak/hole / e Å^{-3}	0.89/-0.27
Flack parameter	0.00(10)

Table S2. X-ray crystallographic data for **15a**.

Empirical formula	$C_{20}H_{36}O_4$
Formula weight	340.49
Temperature/K	100.0
Crystal system	tetragonal
Space group	I4
a/Å	14.6887(3)
b/Å	14.6887(3)
c/Å	37.2232(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	8031.2(4)
Z	16
ρ_{calc}g/cm^3	1.126
μ/mm^{-1}	0.605
F(000)	3008.0
Crystal size/mm^3	0.15 × 0.08 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.748 to 149.44
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -46 ≤ l ≤ 46
Reflections collected	57940
Independent reflections	8240 [R_{int} = 0.0620, R_{sigma} = 0.0327]
Data/restraints/parameters	8240/15/462
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0399, wR_2 = 0.1022
Final R indexes [all data]	R_1 = 0.0431, wR_2 = 0.1051
Largest diff. peak/hole / e Å^{-3}	0.23/-0.47
Flack parameter	0.12(7)

2. Spectra of compound 1

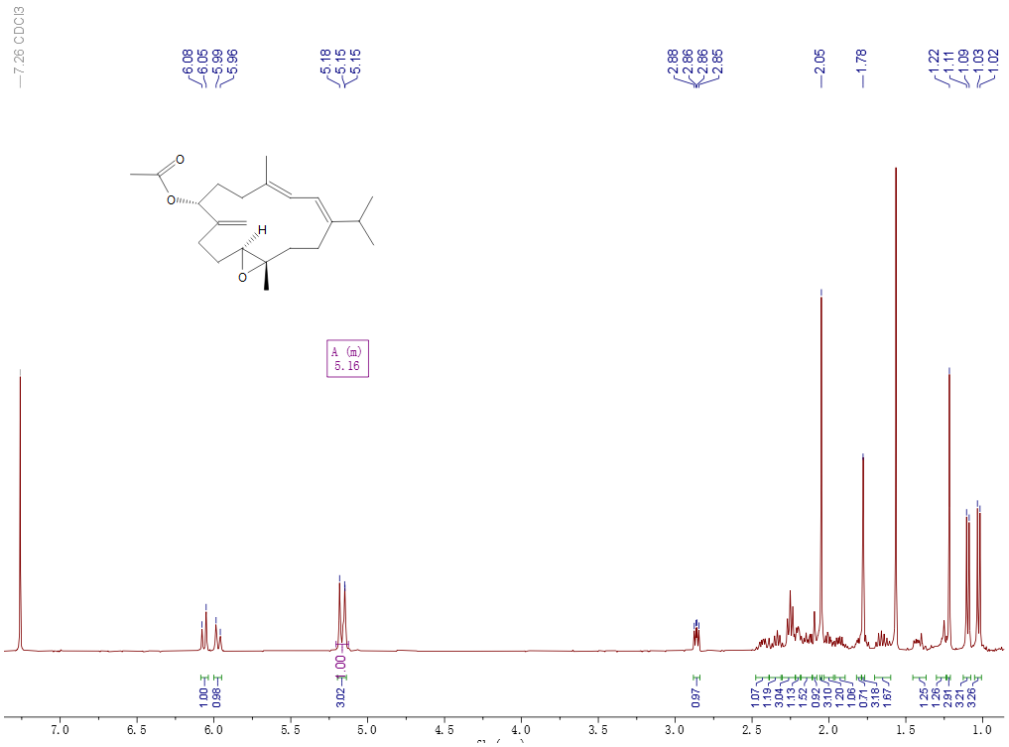


Figure S1.1. ^{1}H NMR spectrum (600 MHz) of compound **1** in $CDCl_3$.

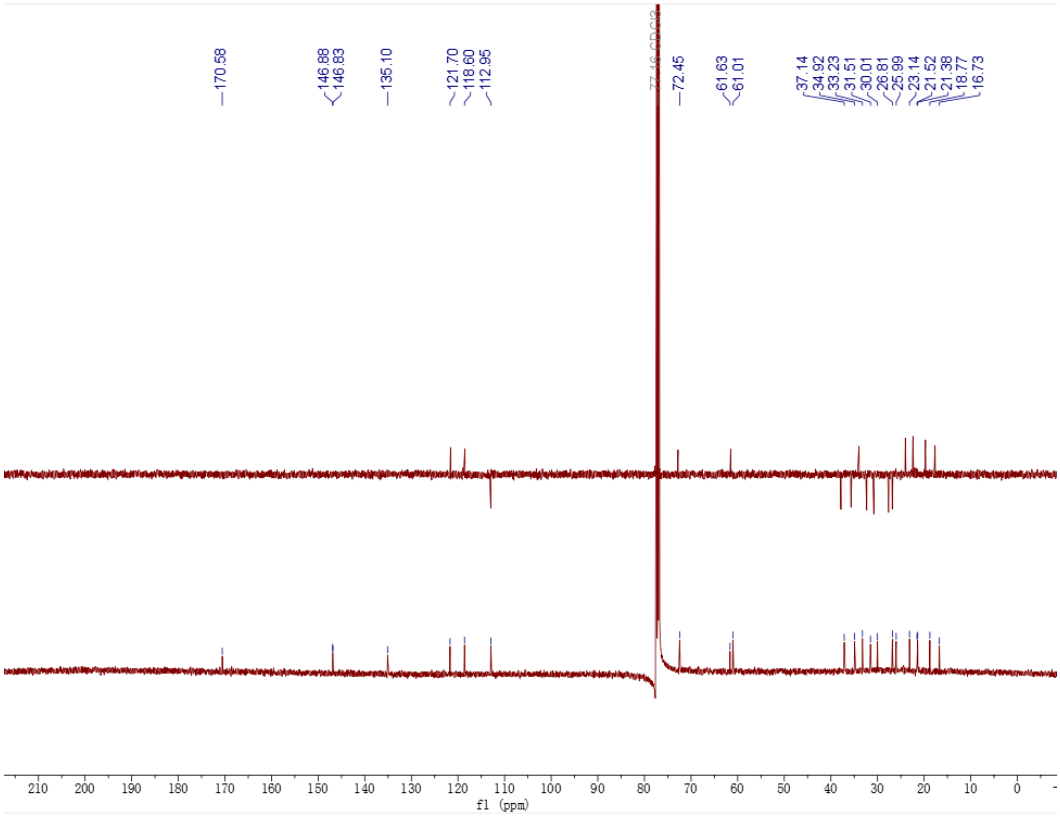


Figure S1.2. ^{13}C NMR spectrum (150 MHz) of compound **1** in $CDCl_3$.

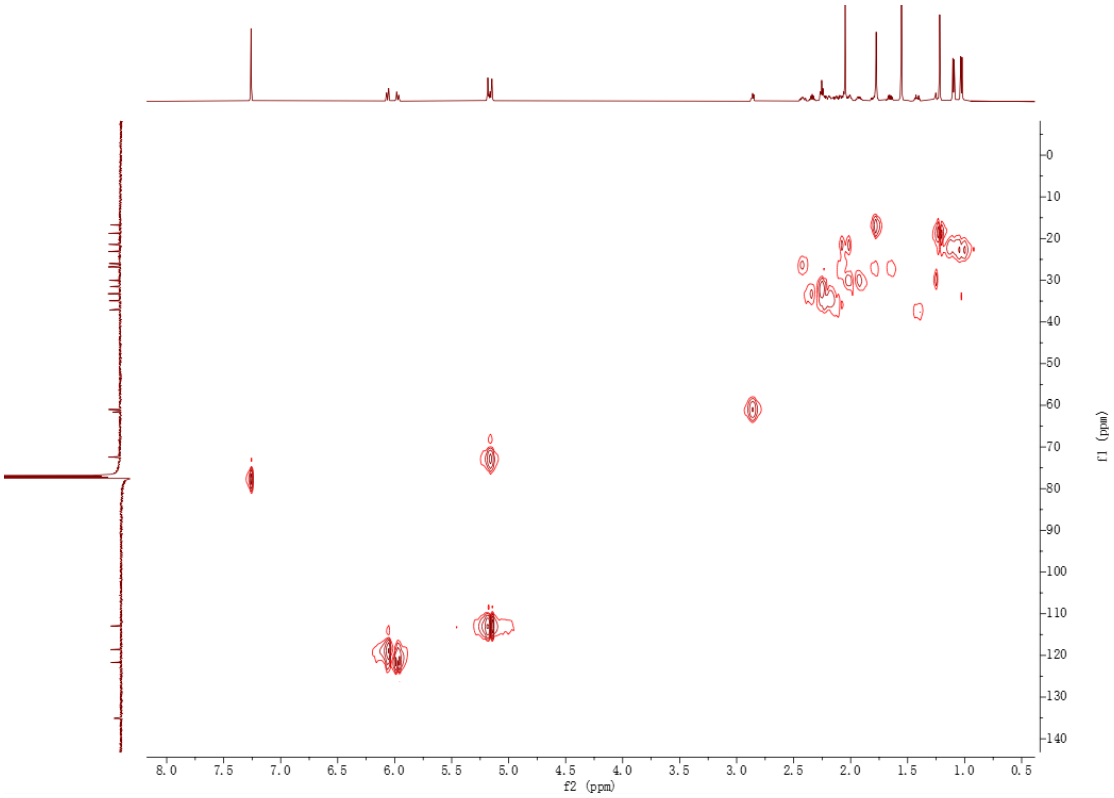


Figure S1.3. HSQC spectrum (600 MHz) of compound **1** in $CDCl_3$.

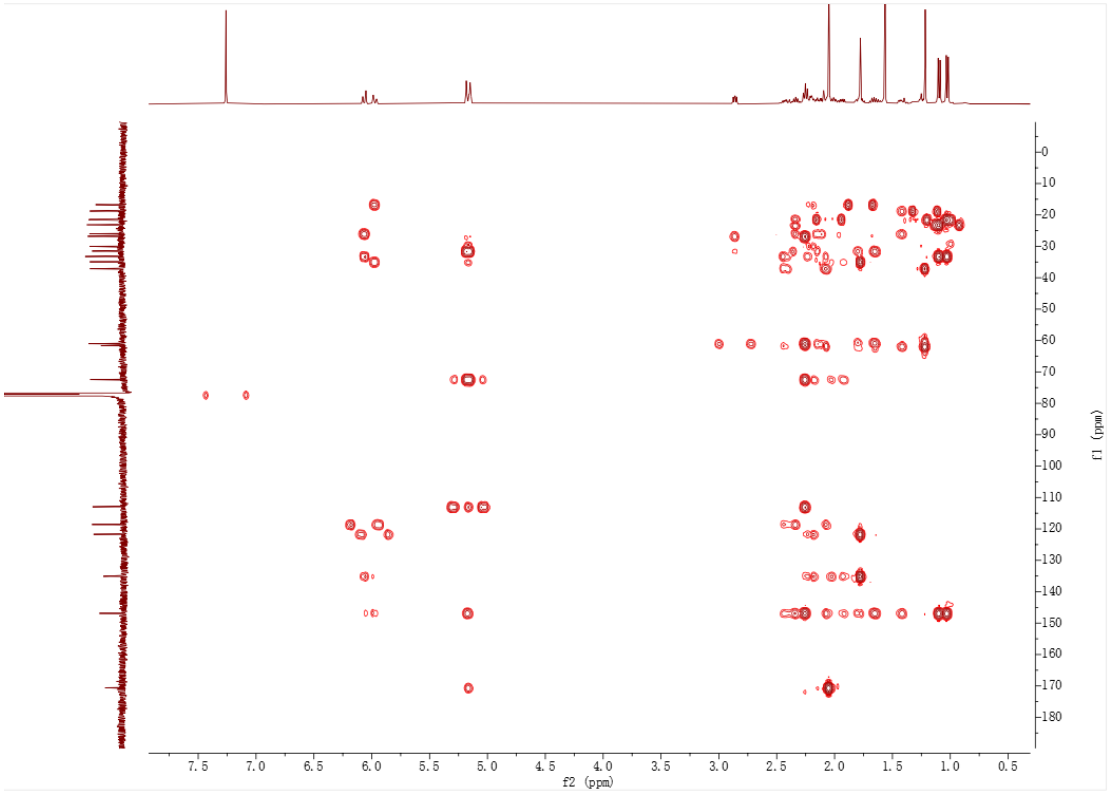


Figure S1.4. HMBC spectrum (600 MHz) of compound **1** in $CDCl_3$.

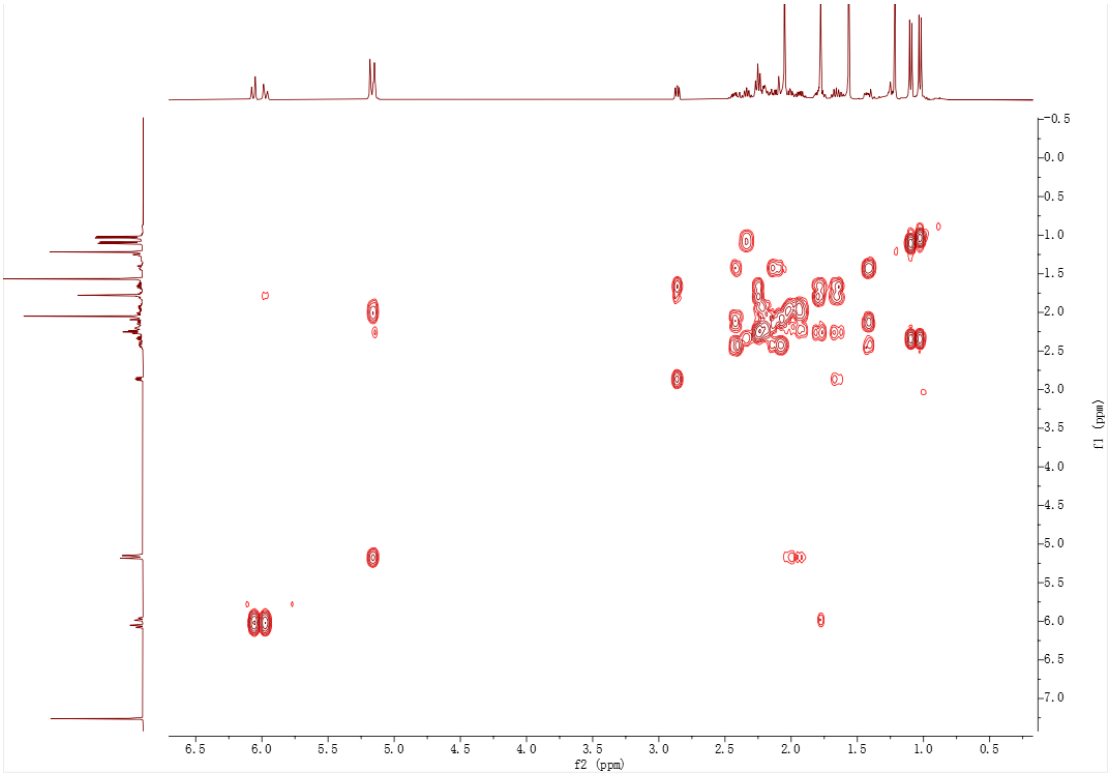


Figure S1.5. ^{1}H-^{1}H COSY spectrum (600 MHz) of compound **1** in $CDCl_3$.

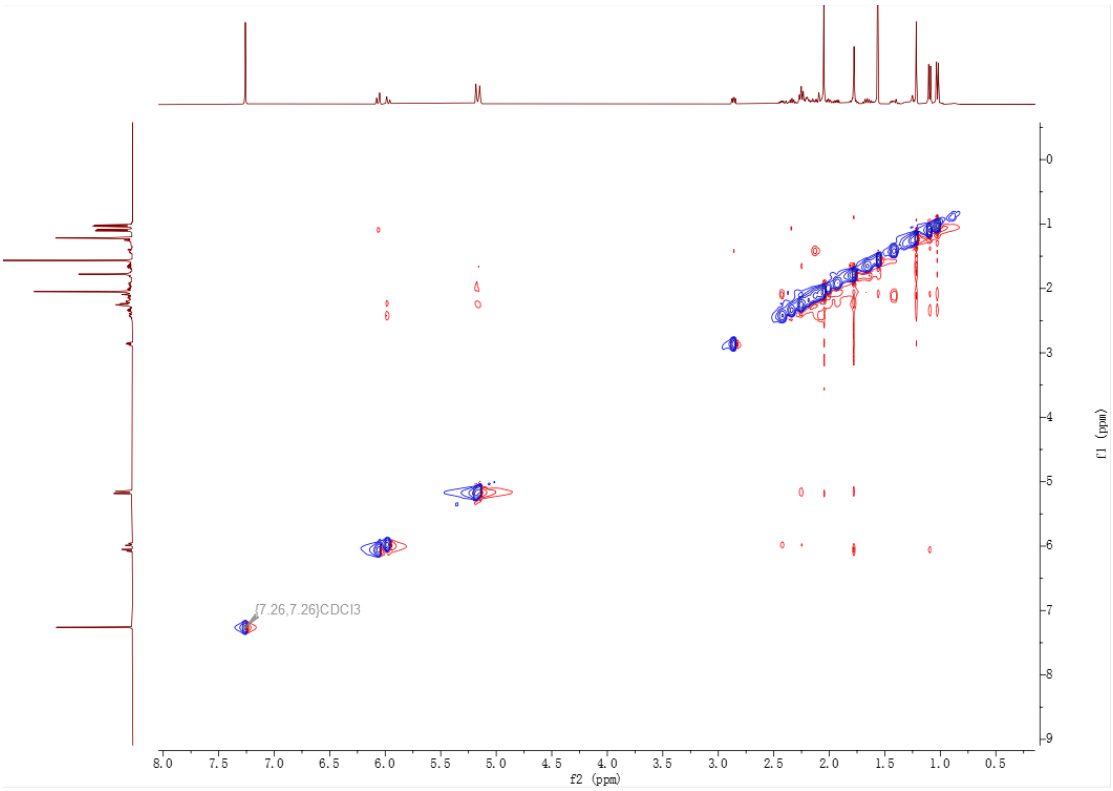
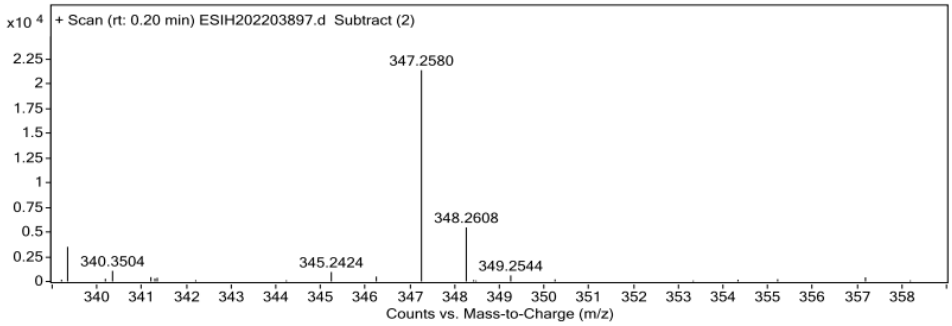


Figure S1.6. NOESY spectrum (600 MHz) of compound **1** in $CDCl_3$.

Data Filename	ESIH202203897.d	**Sample Name**	A8-Y2C13-3B
Sample ID		**Position**	P1-A8
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	10/17/2022 13:26:41	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by fangsu

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
170	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
347.258	347.2581	0.04	0.12	C22 H35 O3	(M+H)+

Figure S1.7. HR-EIMS spectrum of compound **1**.

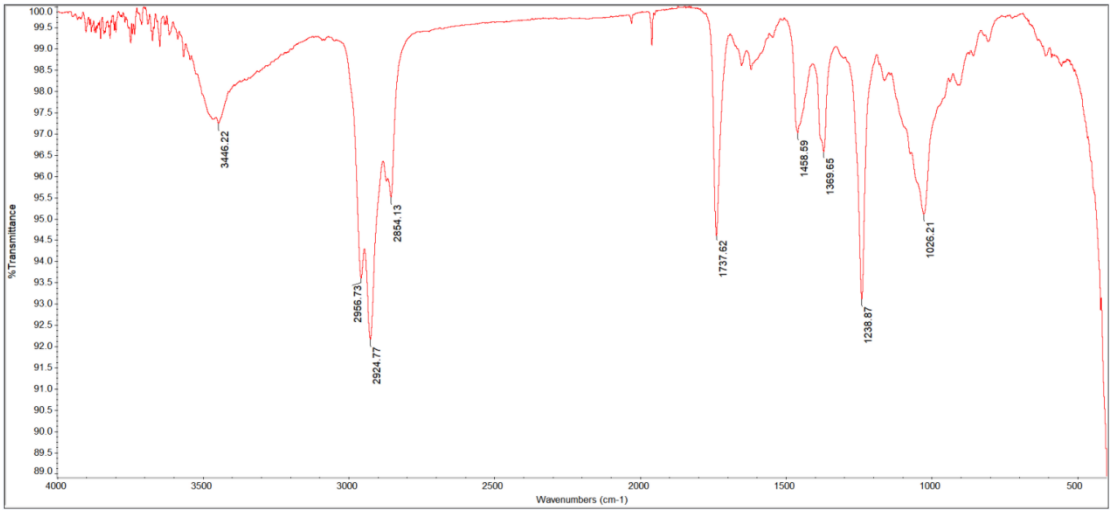


Figure S1.8. IR spectrum of compound **1**.

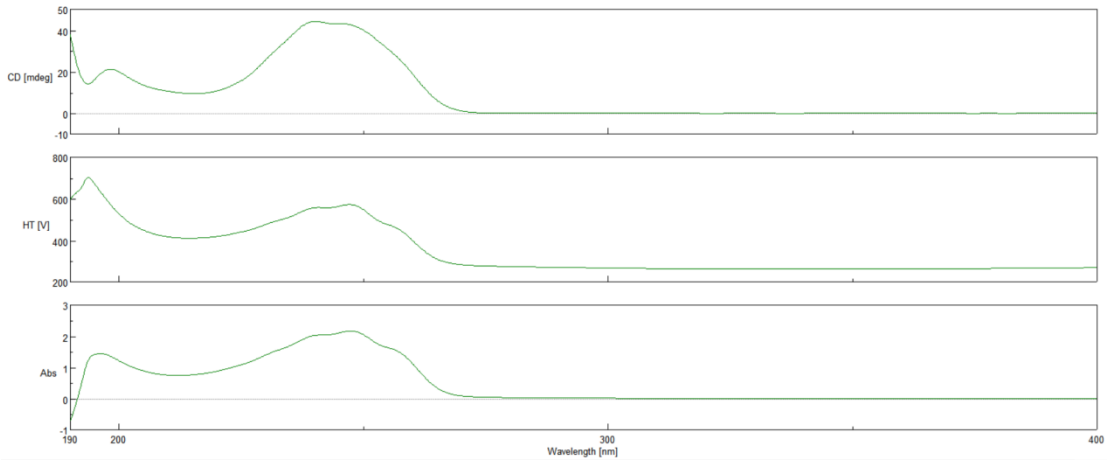


Figure S1.9. CD and UV spectra of compound **1**.

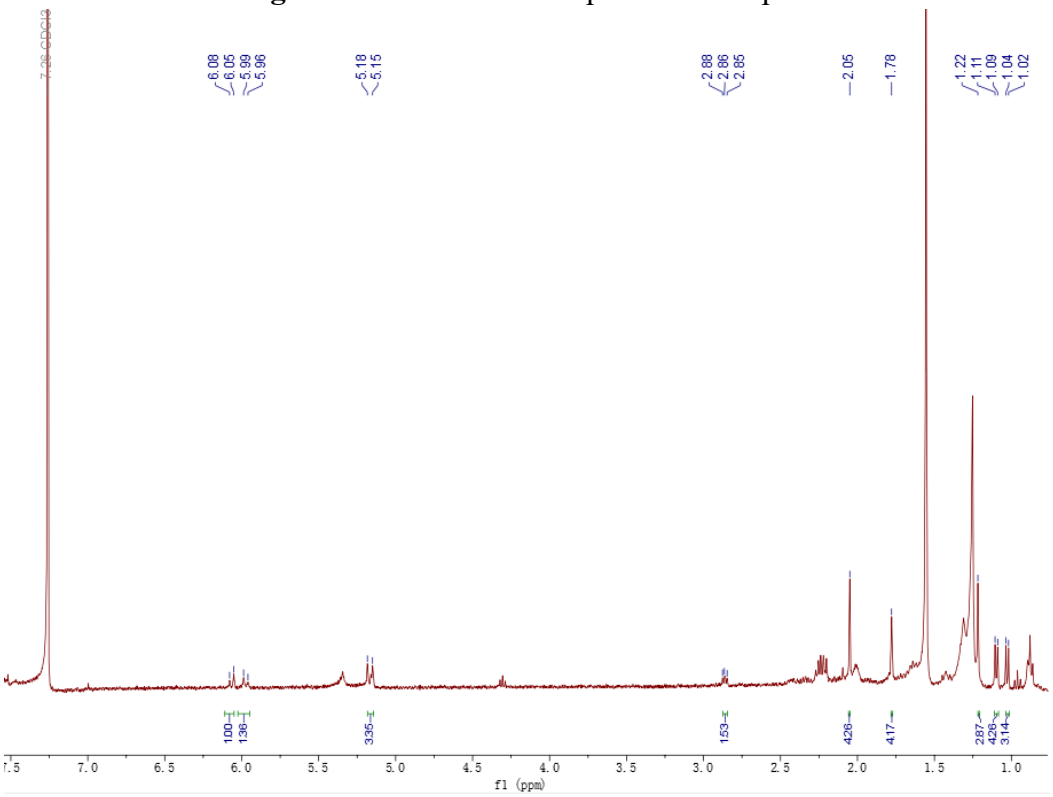


Figure S1.10. ^{1}H NMR spectrum (400 MHz) of compound **1a** in $CDCl_3$.

3. Spectra of compound 2

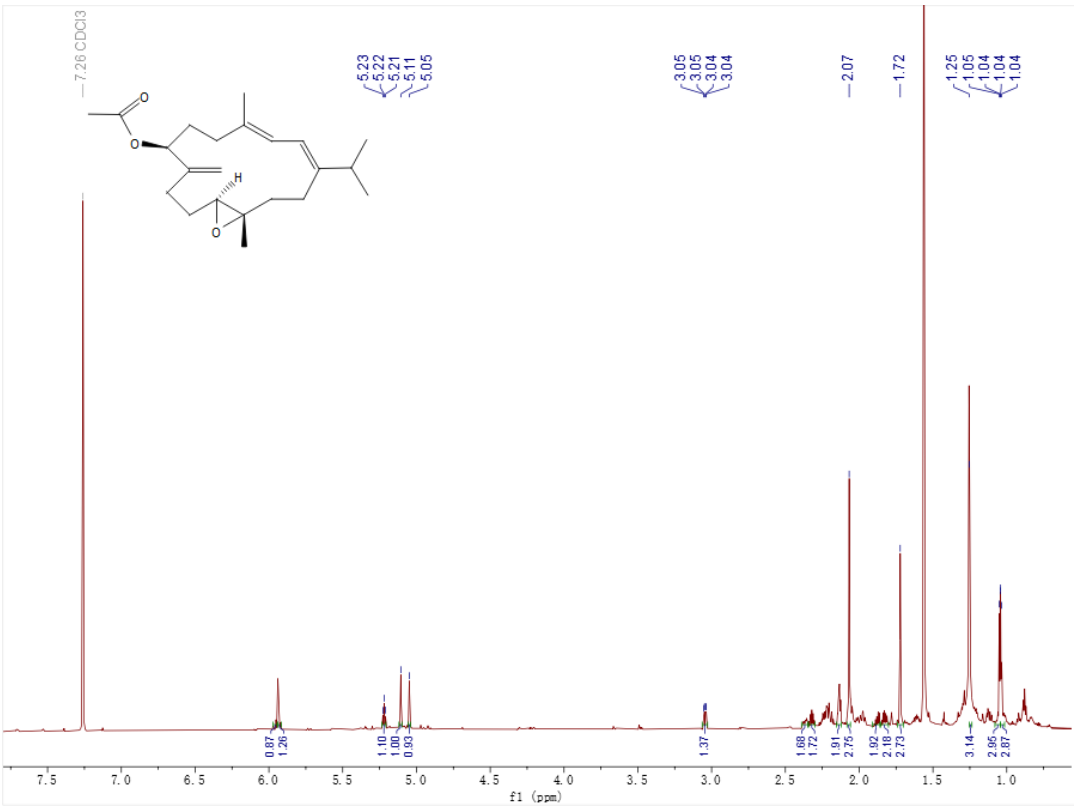


Figure S2.1. ^{1}H NMR spectrum (800 MHz) of compound **2** in $CDCl_3$.

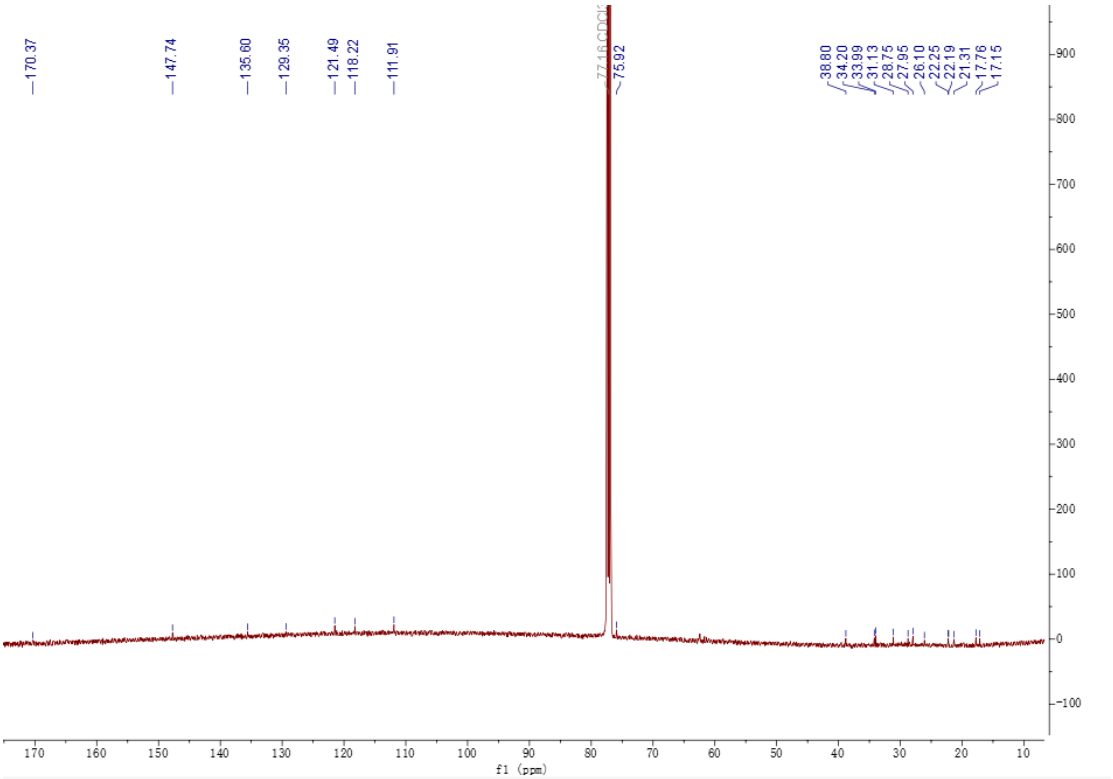


Figure S2.2. ^{13}C NMR spectrum (150 MHz) of compound **2** in $CDCl_3$.

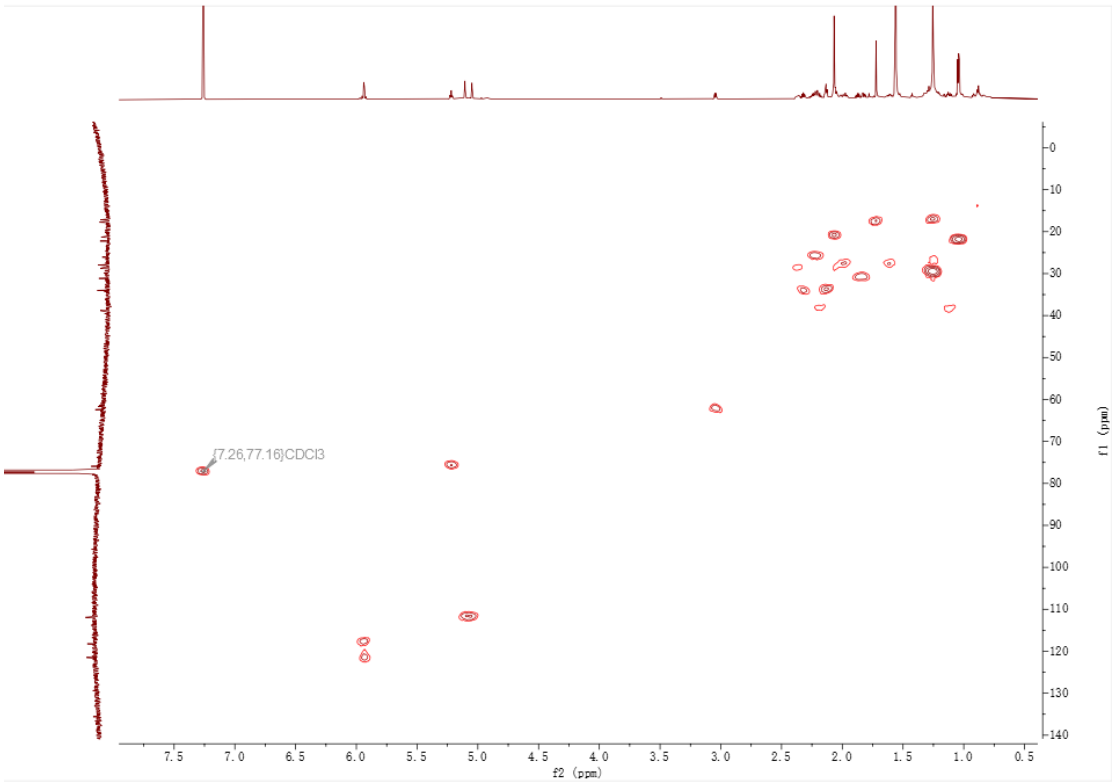


Figure S2.3. HSQC spectrum (800 MHz) of compound **2** in $CDCl_3$.

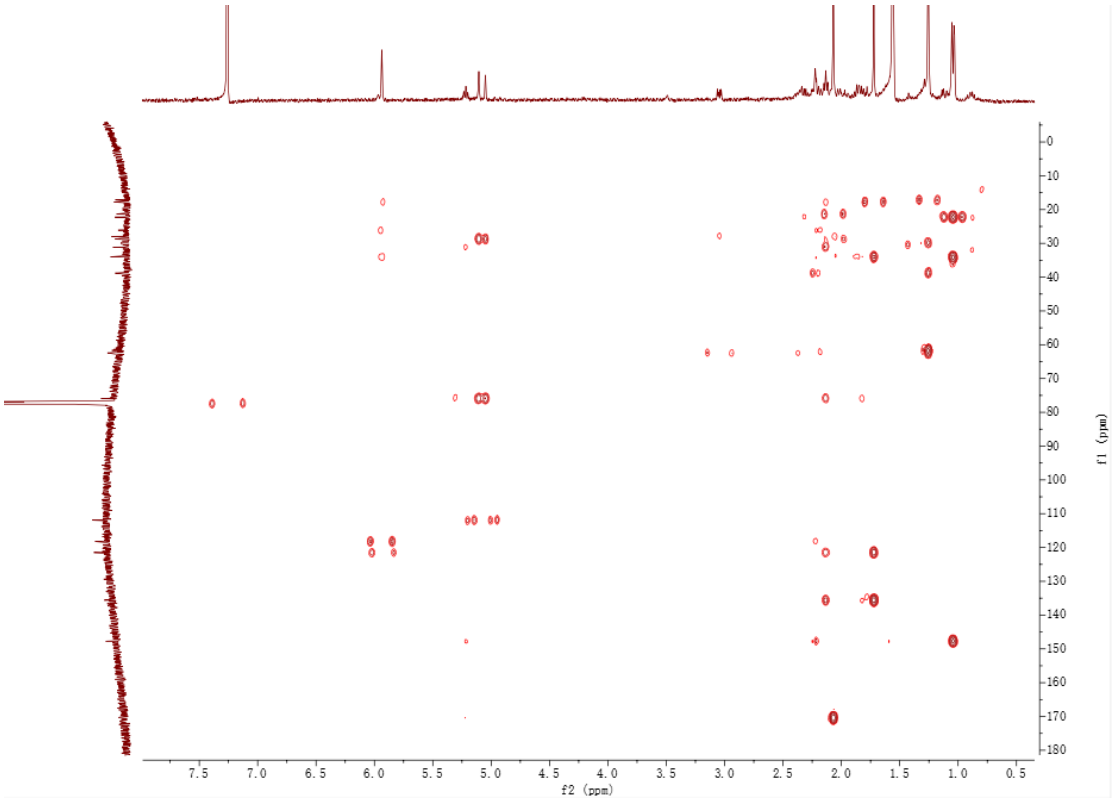


Figure S2.4. HMBC spectrum (800 MHz) of compound **2** in $CDCl_3$.

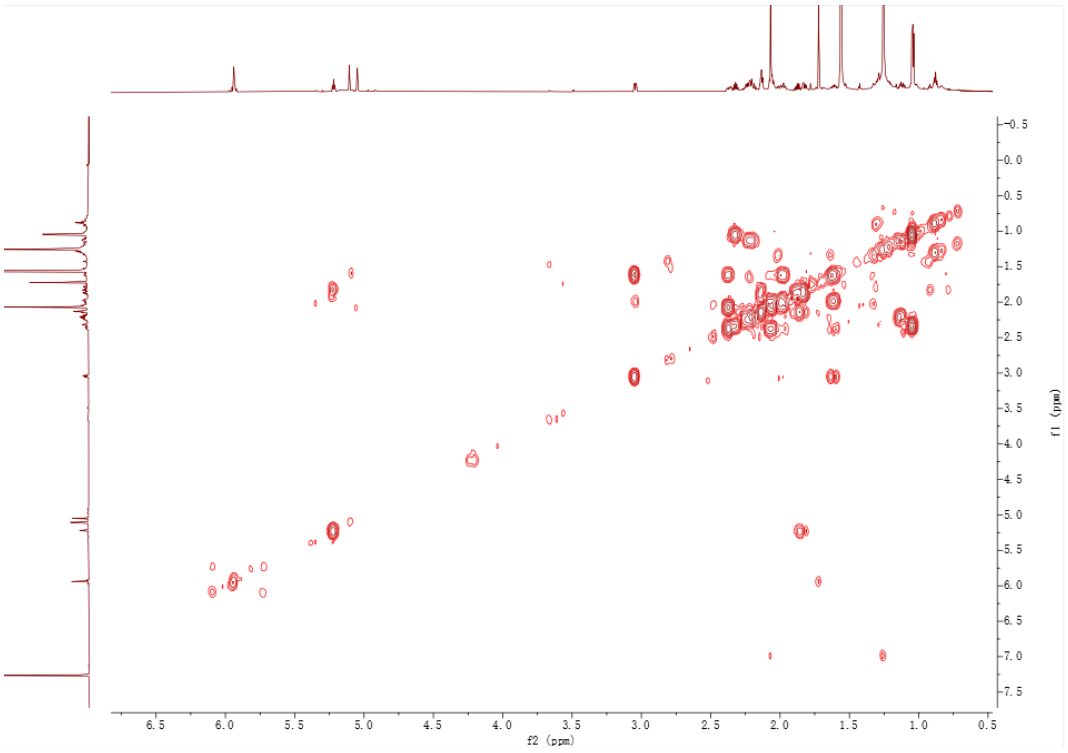


Figure S2.5. ^{1}H-^{1}H COSY spectrum (800 MHz) of compound **2** in $CDCl_3$.

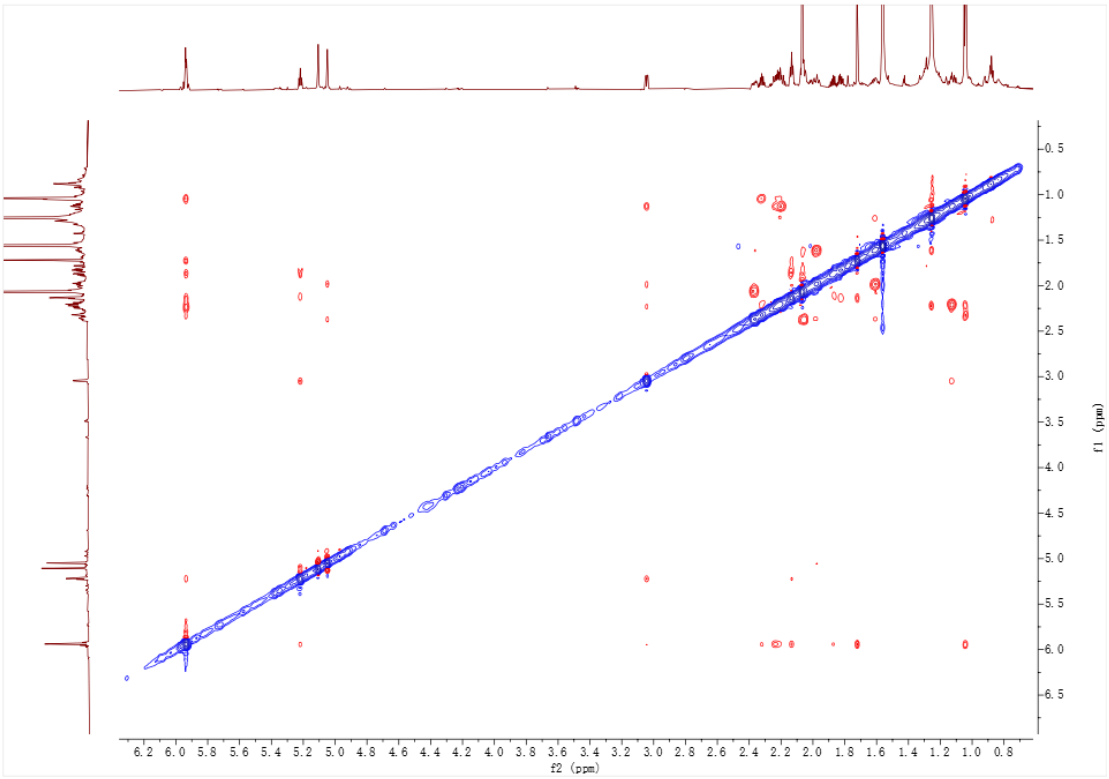


Figure S2.6. NOESY spectrum (800 MHz) of compound **2** in $CDCl_3$.

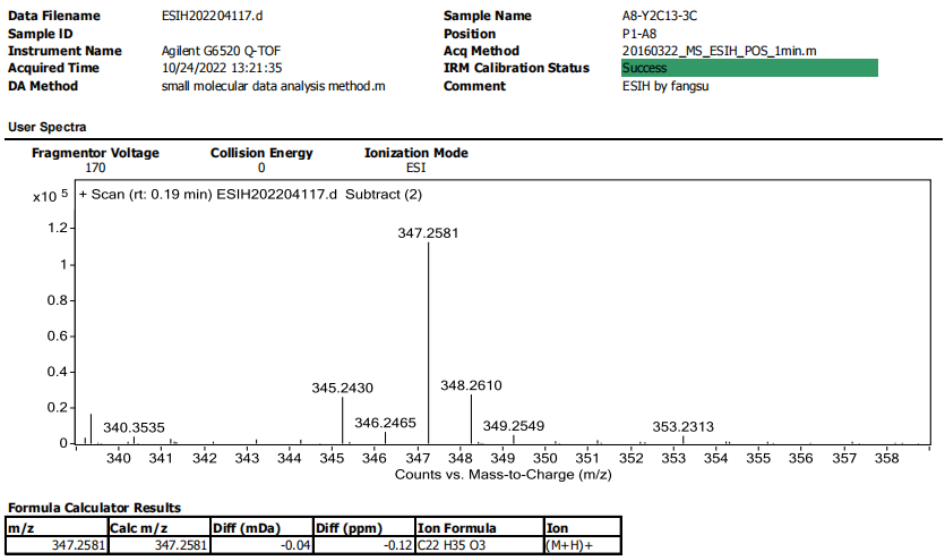


Figure S2.7. HR-EIMS spectrum of compound **2**.

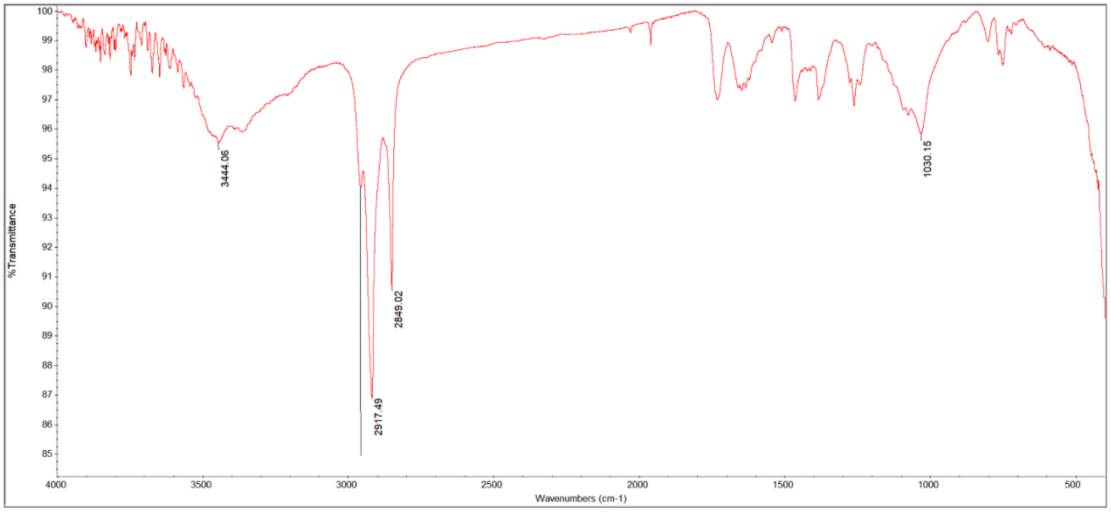


Figure S2.8. IR spectrum of compound **2**.

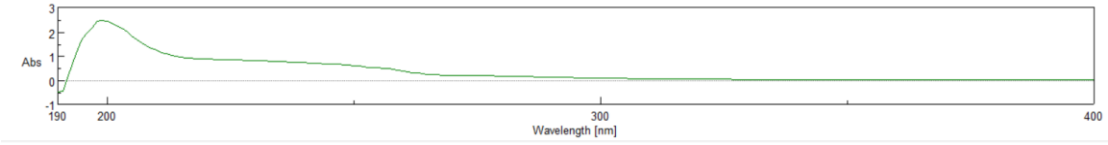


Figure S2.9. UV spectrum of compound **2**.

4. Spectra of compound 3

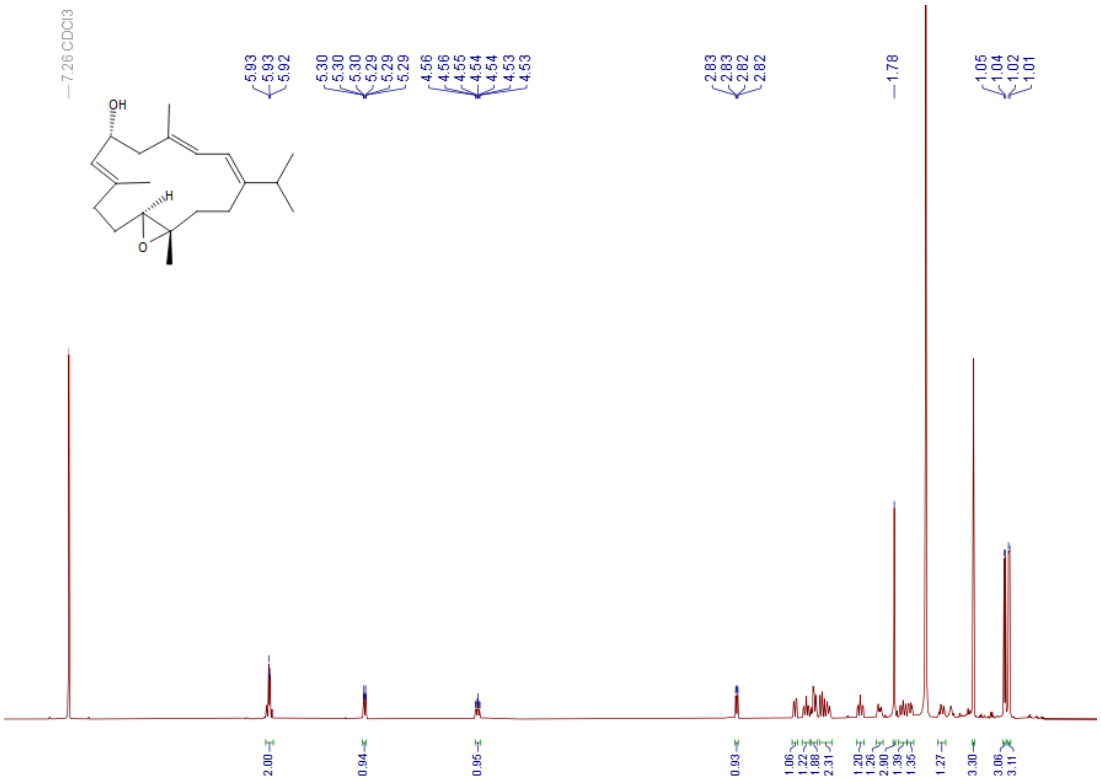


Figure S3.1. ^{1}H NMR spectrum (800 MHz) of compound **3** in $CDCl_3$.

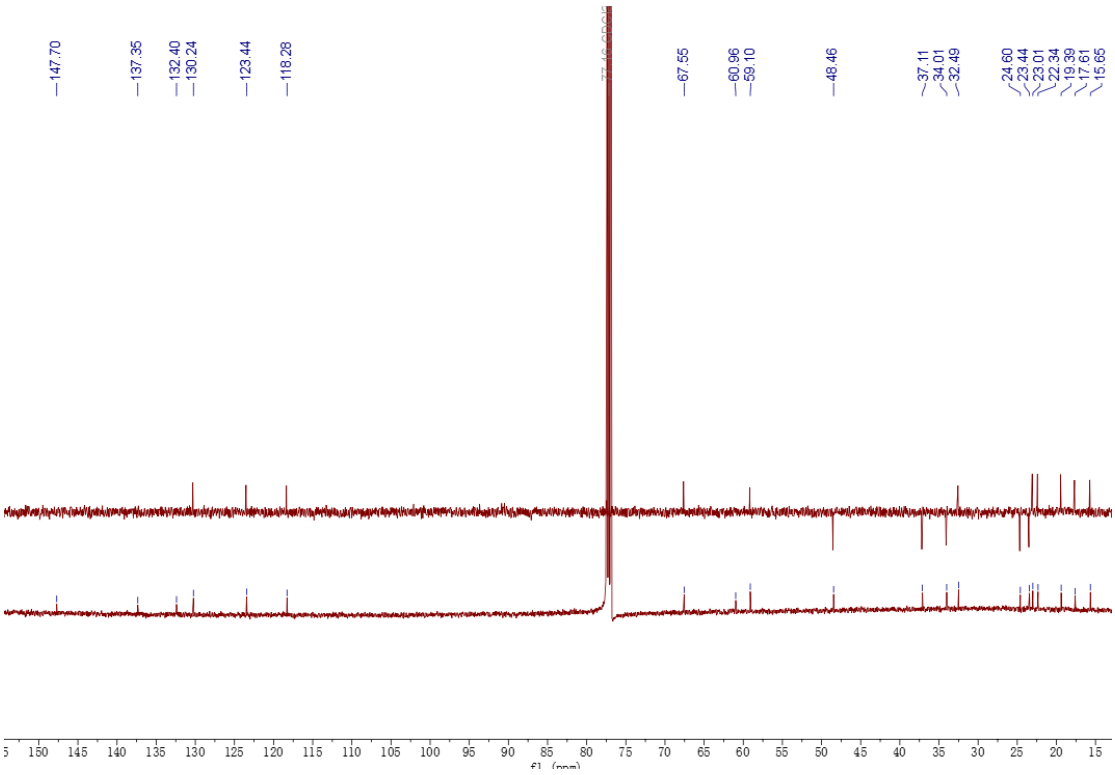


Figure S3.2. ^{13}C NMR spectrum (150 MHz) of compound **3** in $CDCl_3$.

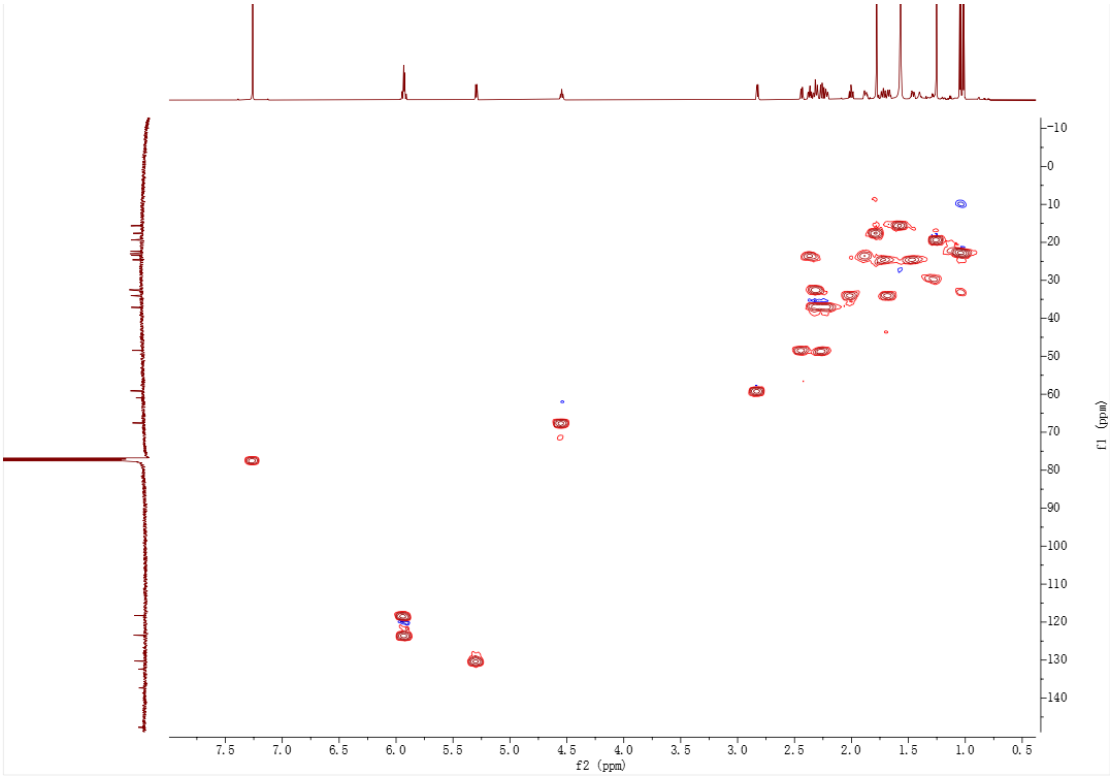


Figure S3.3. HSQC spectrum (800 MHz) of compound **3** in $CDCl_3$.

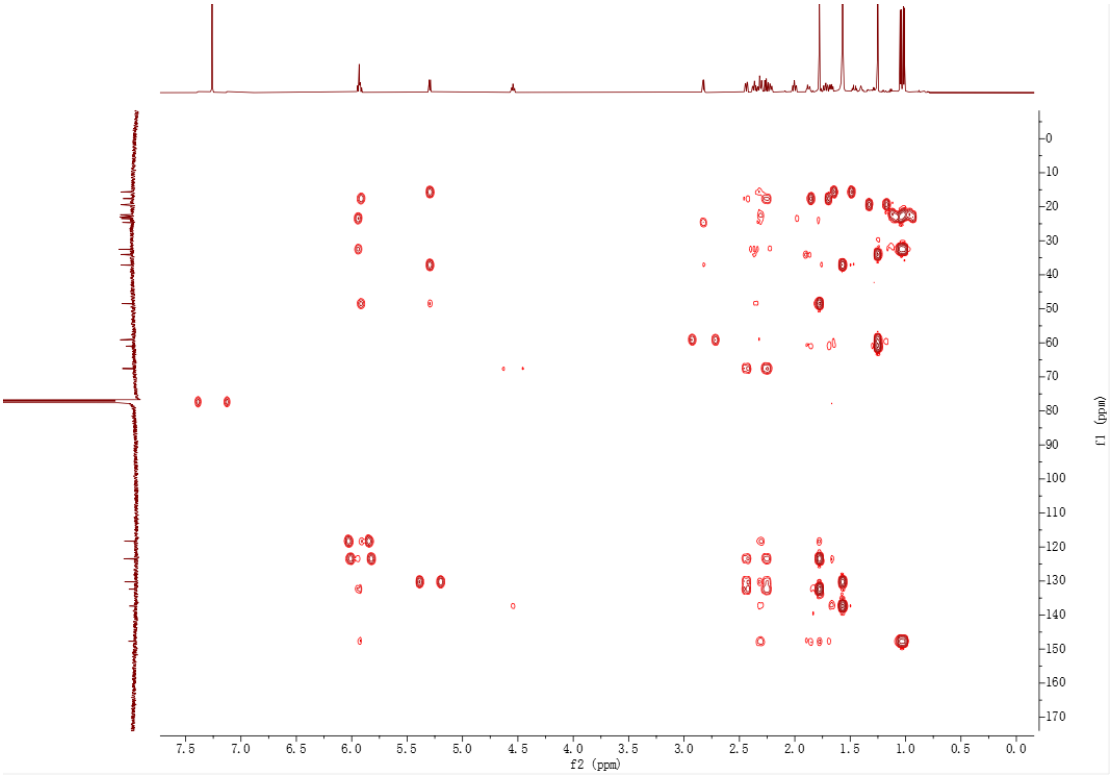


Figure S3.4. HMBC spectrum (800 MHz) of compound **3** in $CDCl_3$.

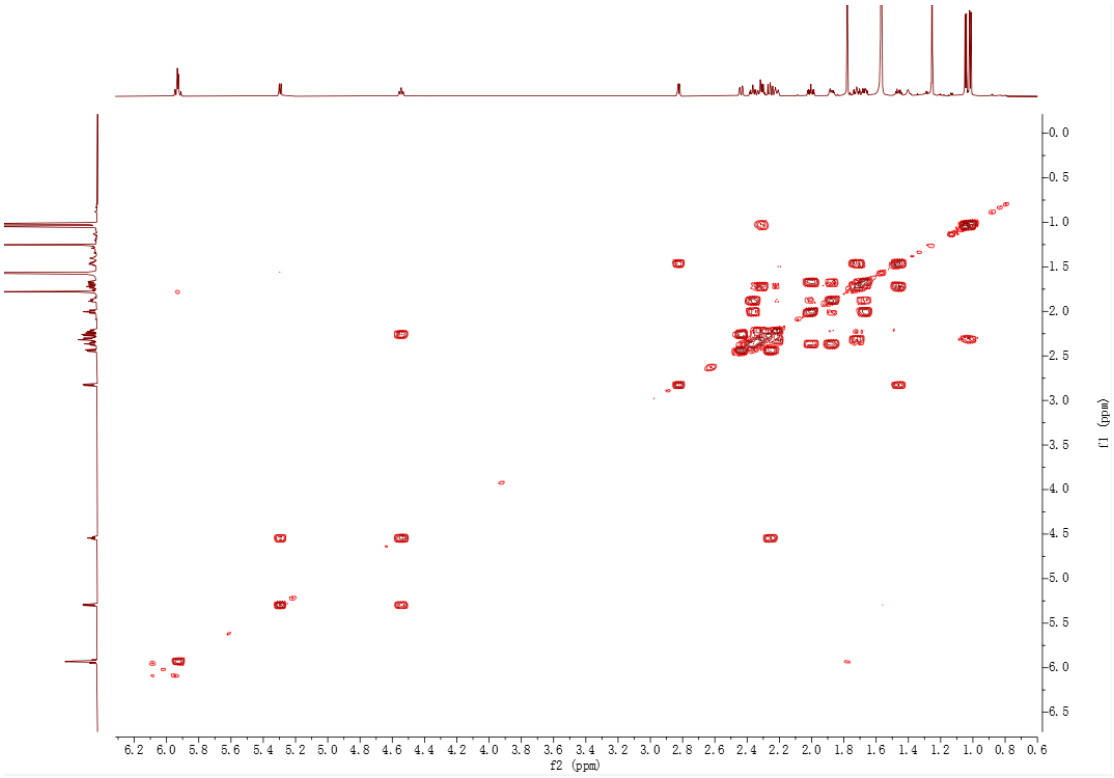


Figure S3.5. ^{1}H-^{1}H COSY spectrum (800 MHz) of compound **3** in $CDCl_3$.

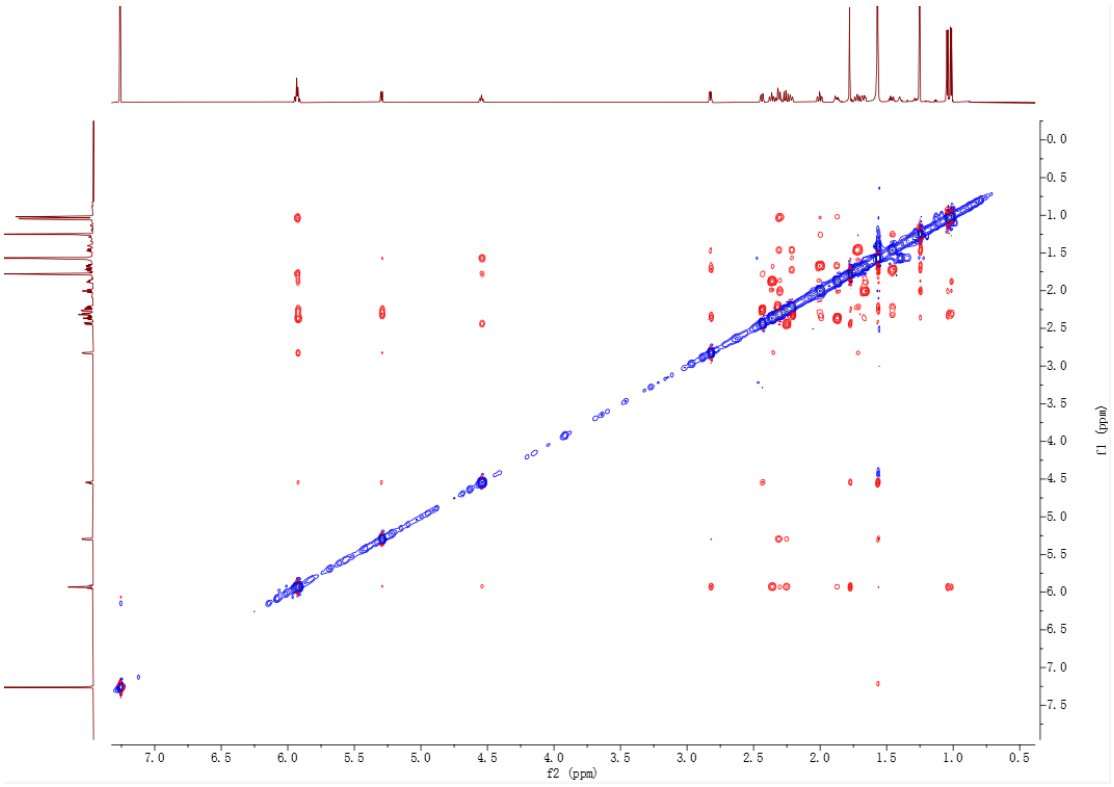


Figure S3.6. NOESY spectrum (800 MHz) of compound **3** in $CDCl_3$.

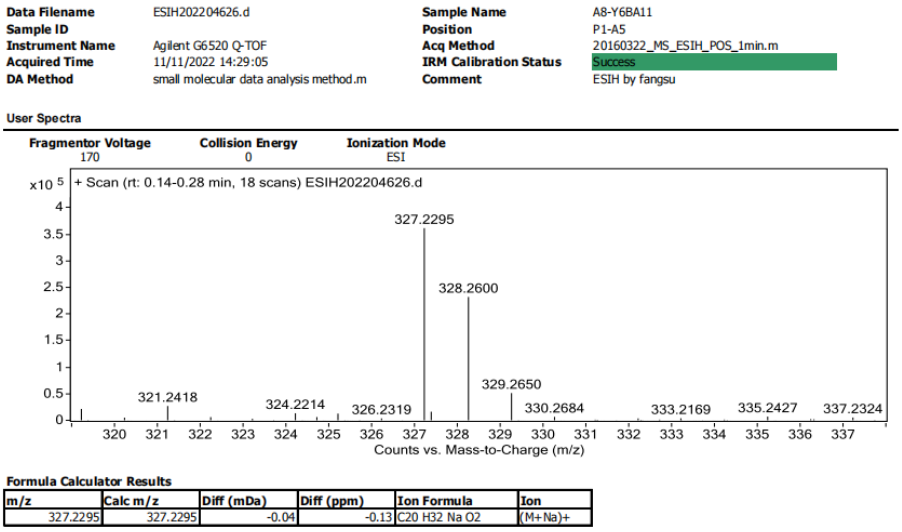


Figure S3.7. HR-EIMS spectrum of compound **3**.

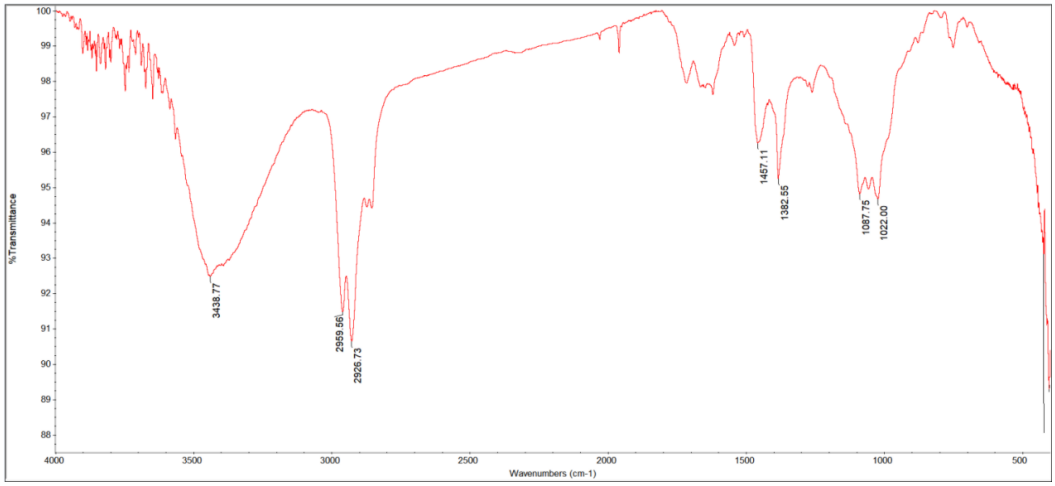


Figure S3.8. IR spectrum of compound **3**.

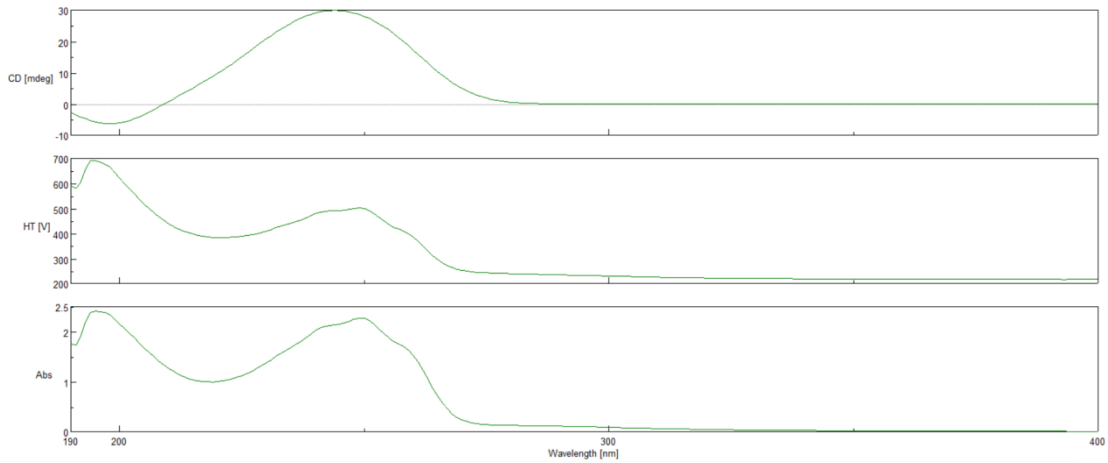


Figure S3.9. CD and UV spectrum of compound **3**.

5. Spectra of compound 4

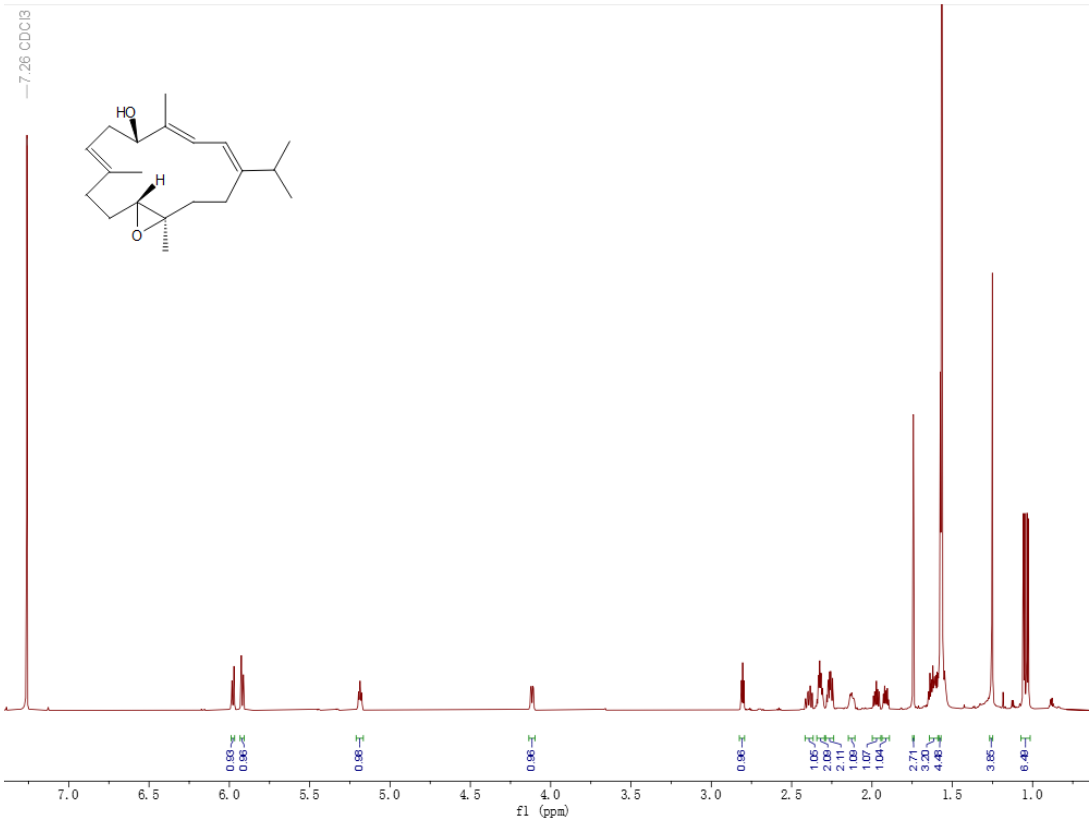


Figure S4.1. ^{1}H NMR spectrum (800 MHz) of compound **4** in $CDCl_3$.

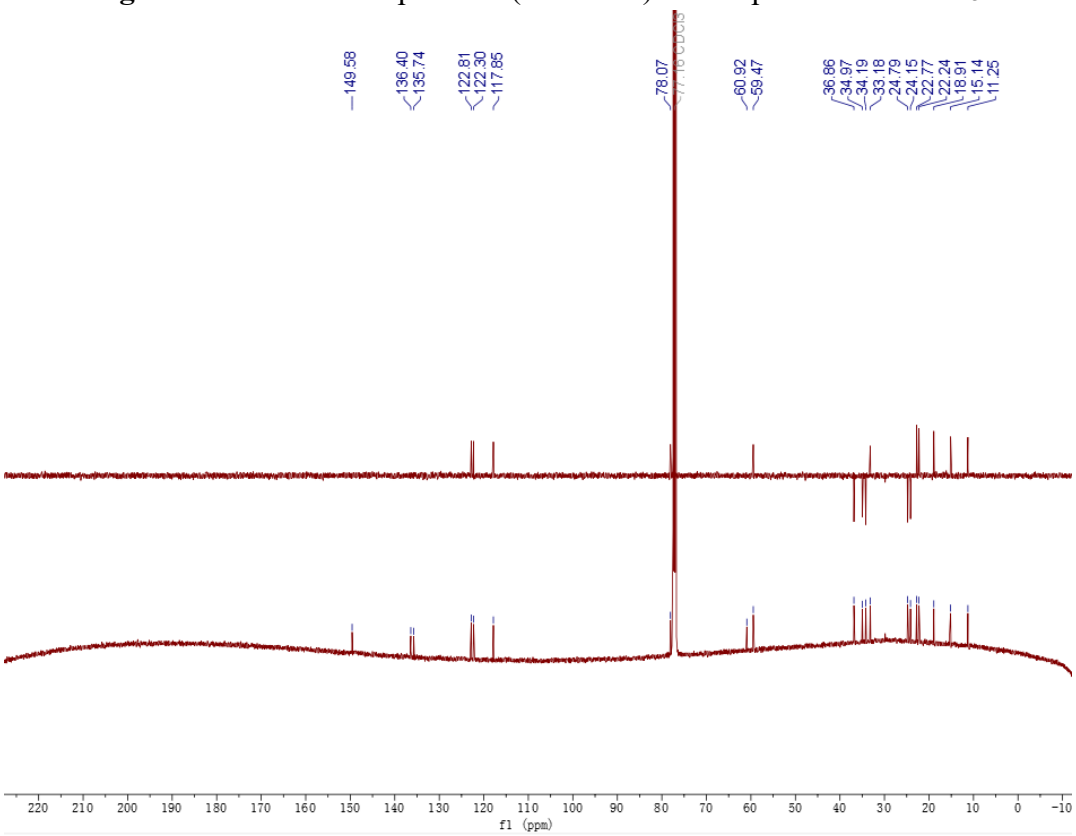


Figure S4.2. ^{13}C NMR spectrum (150 MHz) of compound **4** in $CDCl_3$.

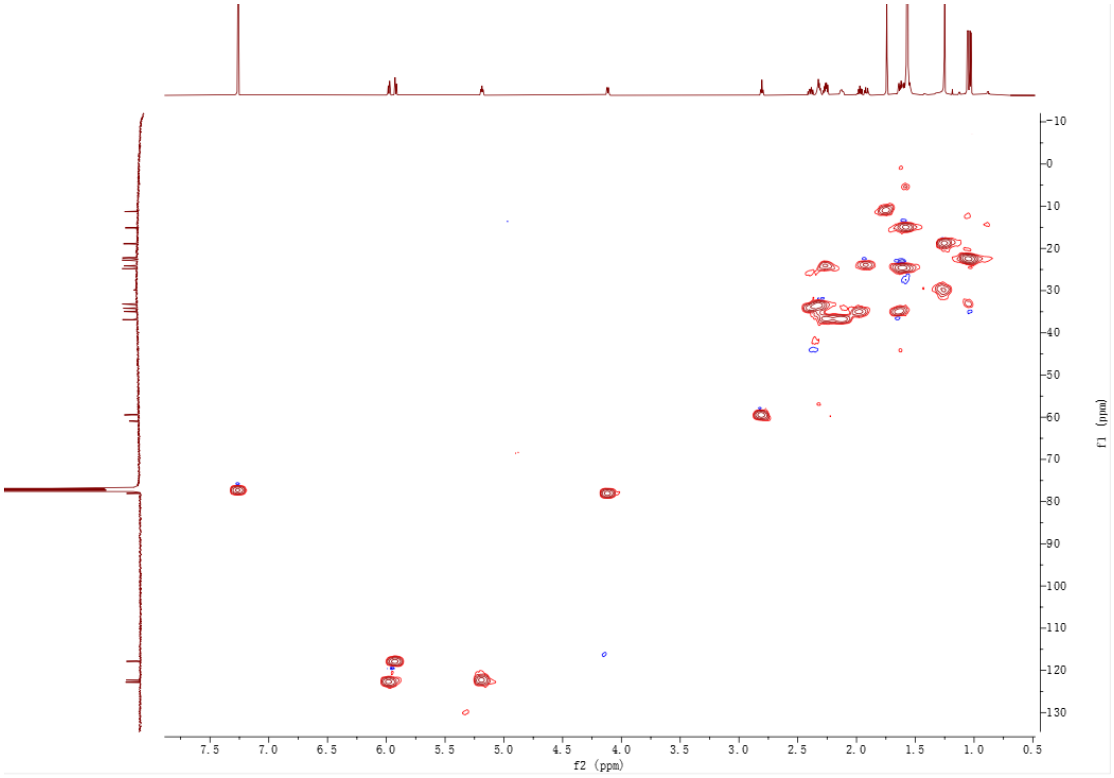


Figure S4.3. HSQC spectrum (800 MHz) of compound **4** in $CDCl_3$.

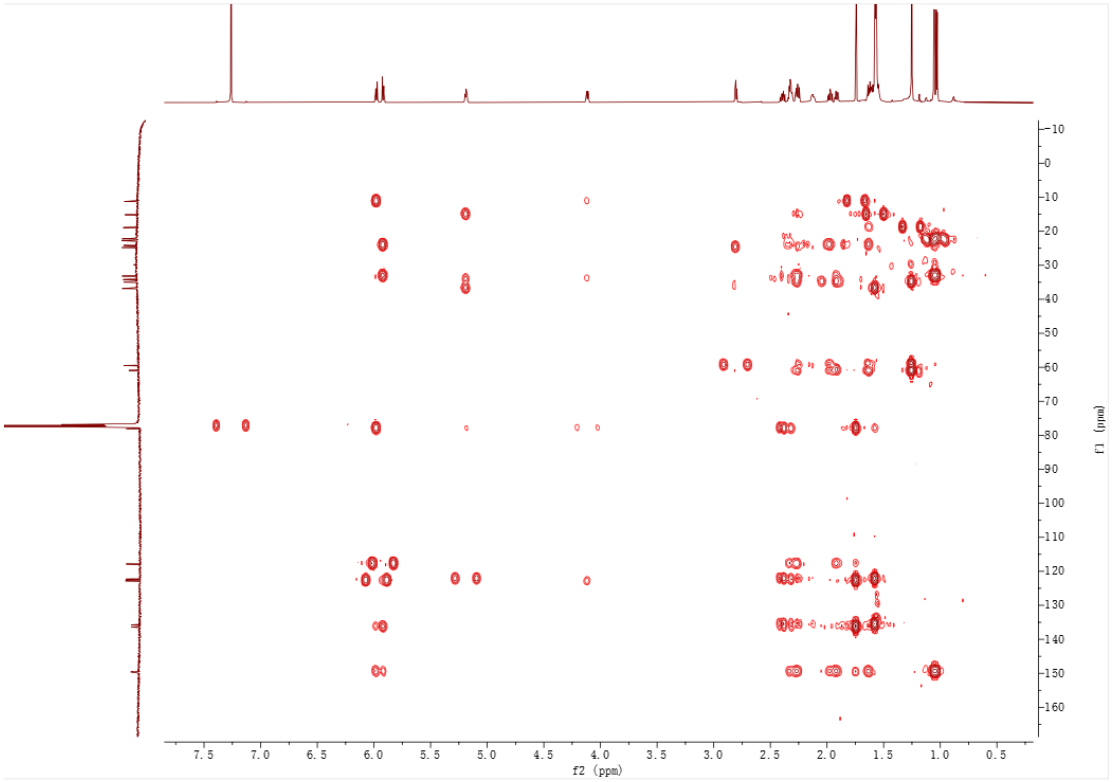


Figure S4.4. HMBC spectrum (800 MHz) of compound **4** in $CDCl_3$.

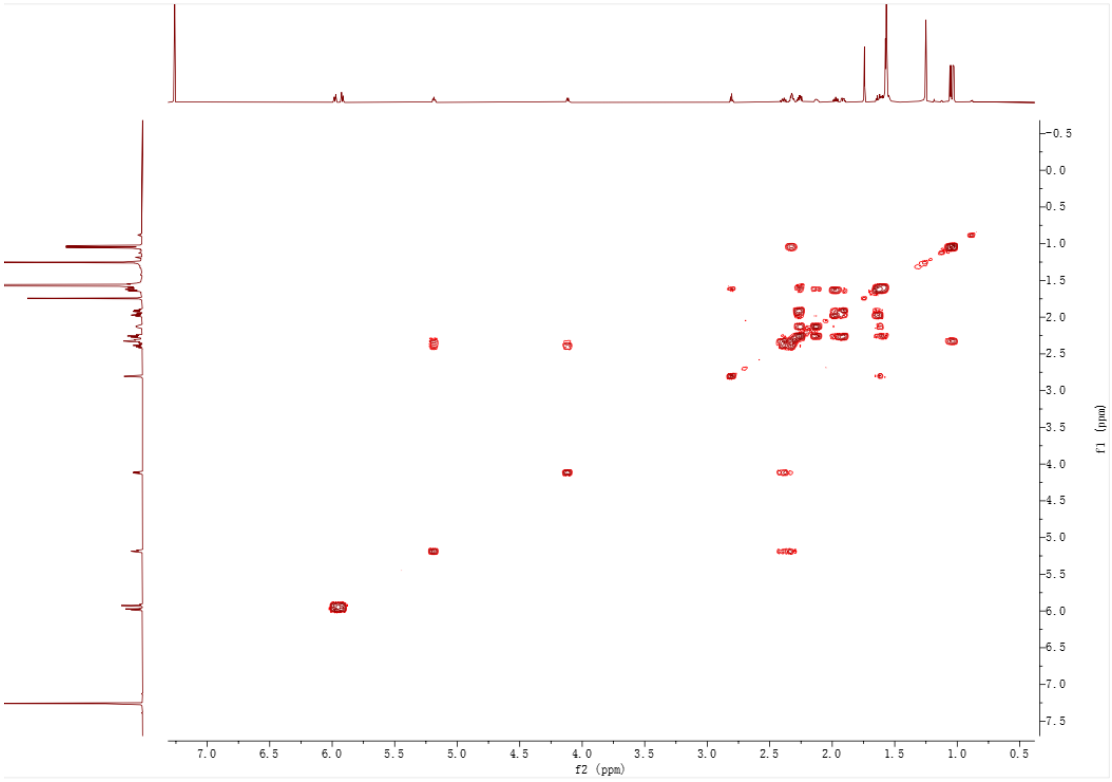


Figure S4.5. ^{1}H-^{1}H COSY spectrum (800 MHz) of compound **4** in $CDCl_3$.

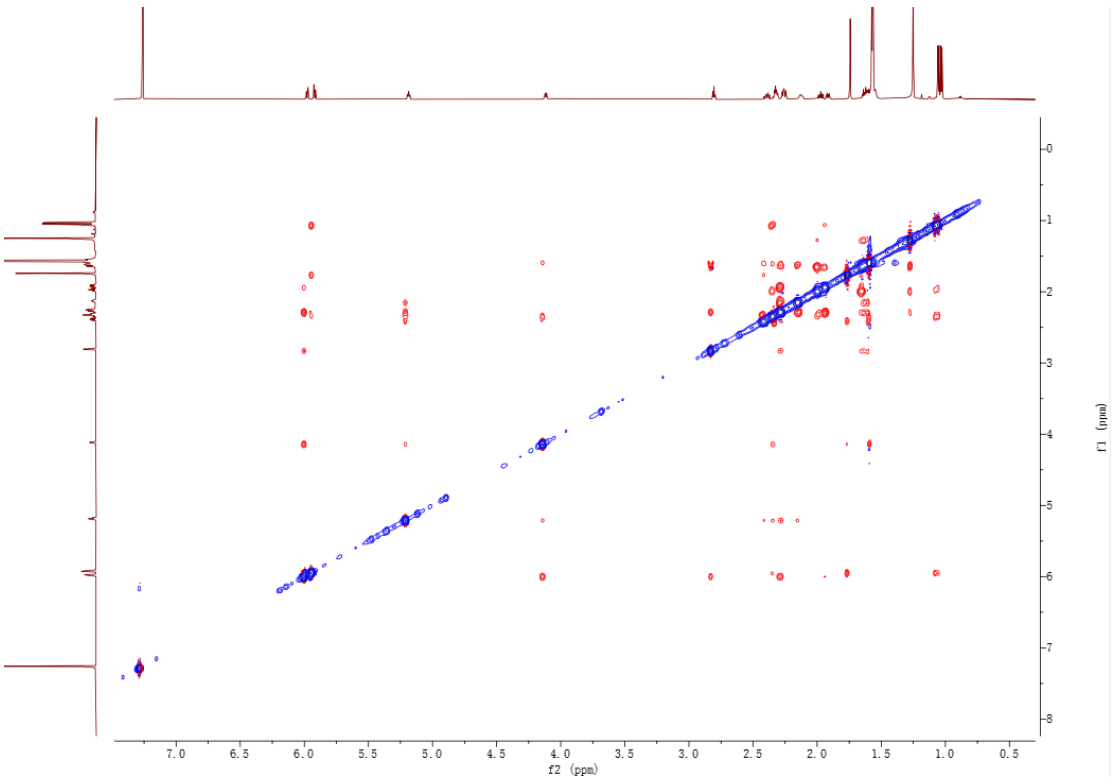
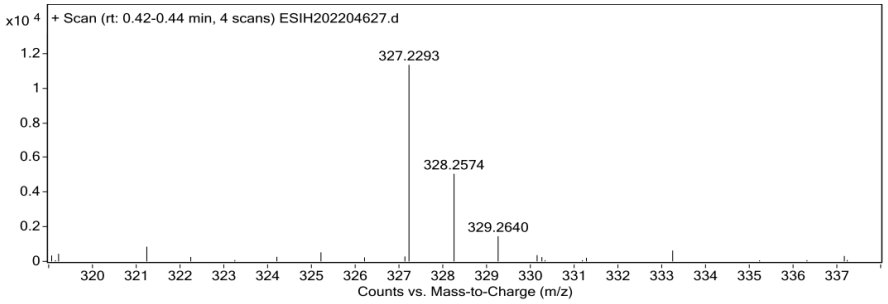


Figure S4.6. NOESY spectrum (800 MHz) of compound **4** in $CDCl_3$.

Data Filename	ESIH202204627.d	**Sample Name**	A8-Y6BA12
Sample ID		**Position**	P1-A6
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	11/11/2022 14:30:22	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by fangsu

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
170	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
327.2293	327.2295	0.15	0.45	C20 H32 Na O2	(M+Na)+

Figure S4.7. HR-EIMS spectrum of compound **4**.

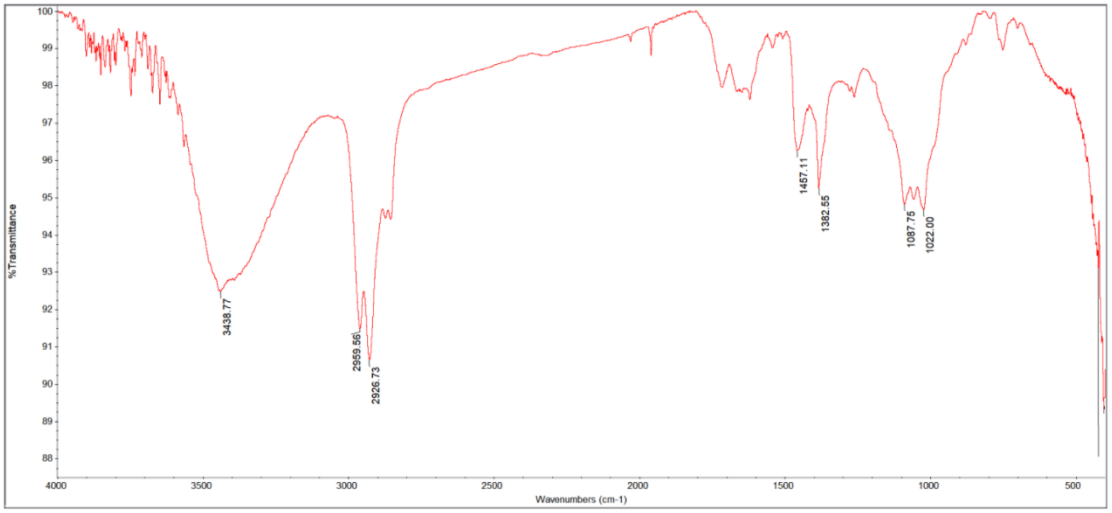


Figure S4.8. IR spectrum of compound **4**.

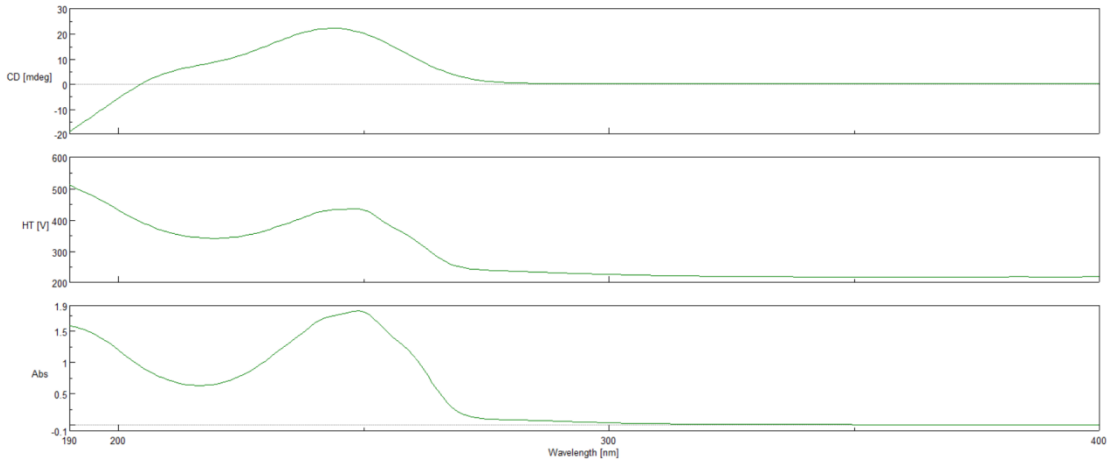


Figure S4.9. CD and UV spectrum of compound **4**.

6. Spectra of compound 5

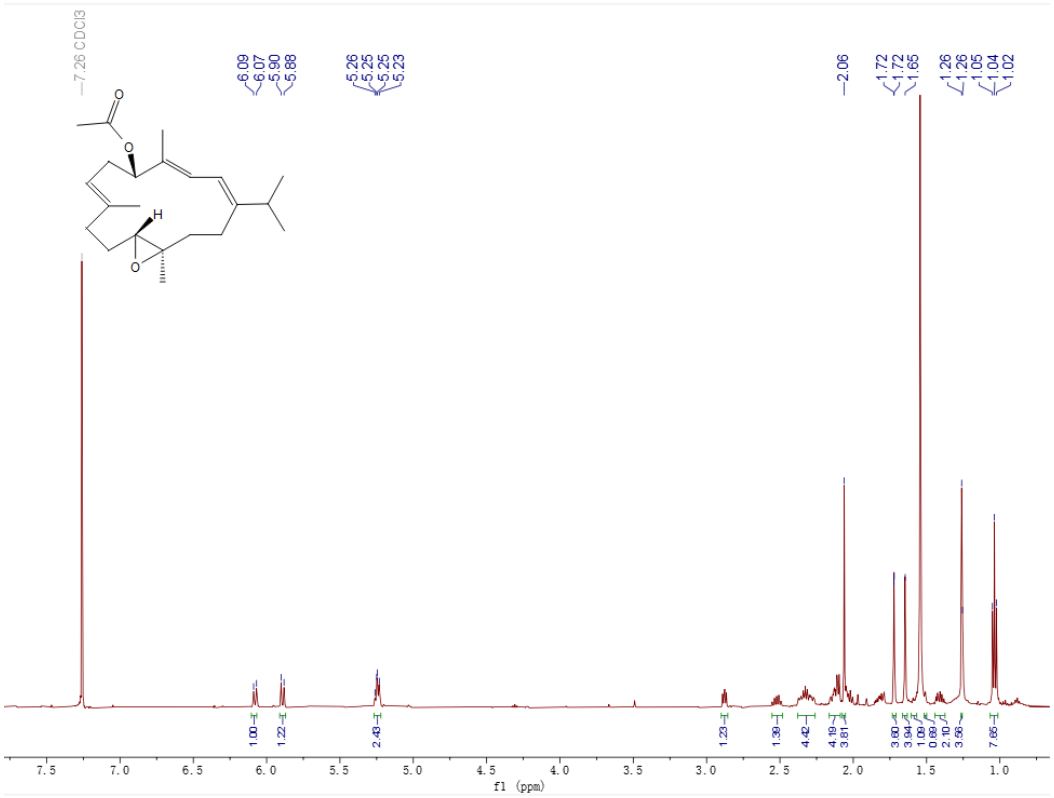


Figure S5.1. ^{1}H NMR spectrum (600 MHz) of compound **5** in $CDCl_3$.

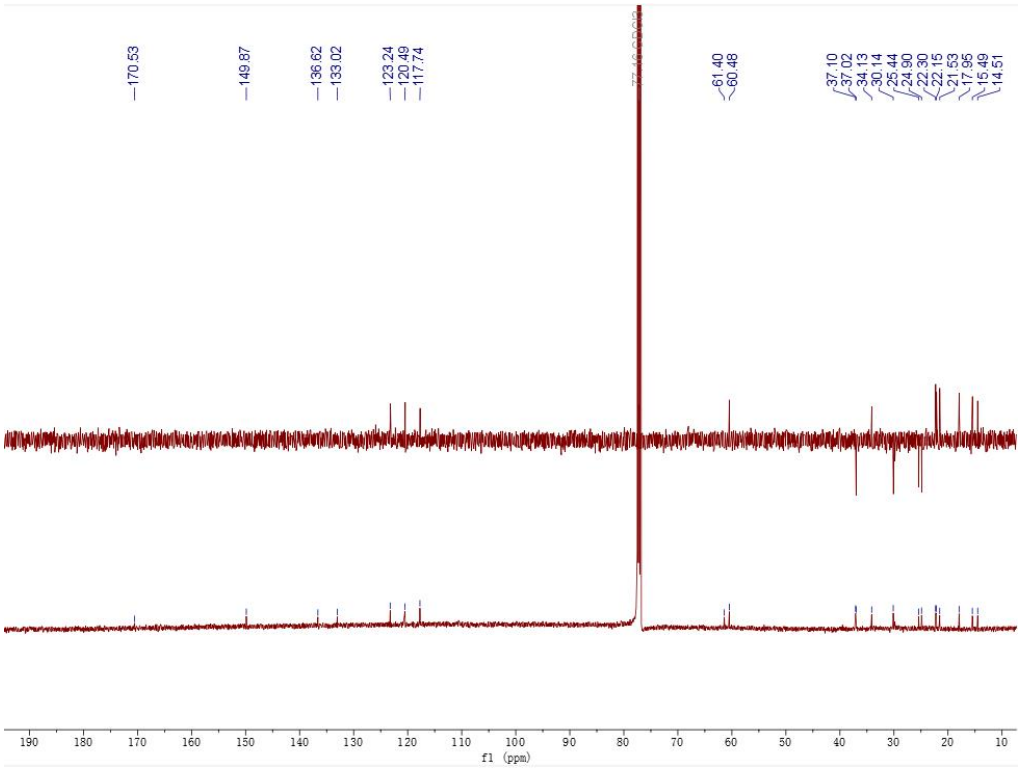


Figure S5.2. ^{13}C NMR spectrum (150 MHz) of compound **5** in $CDCl_3$.

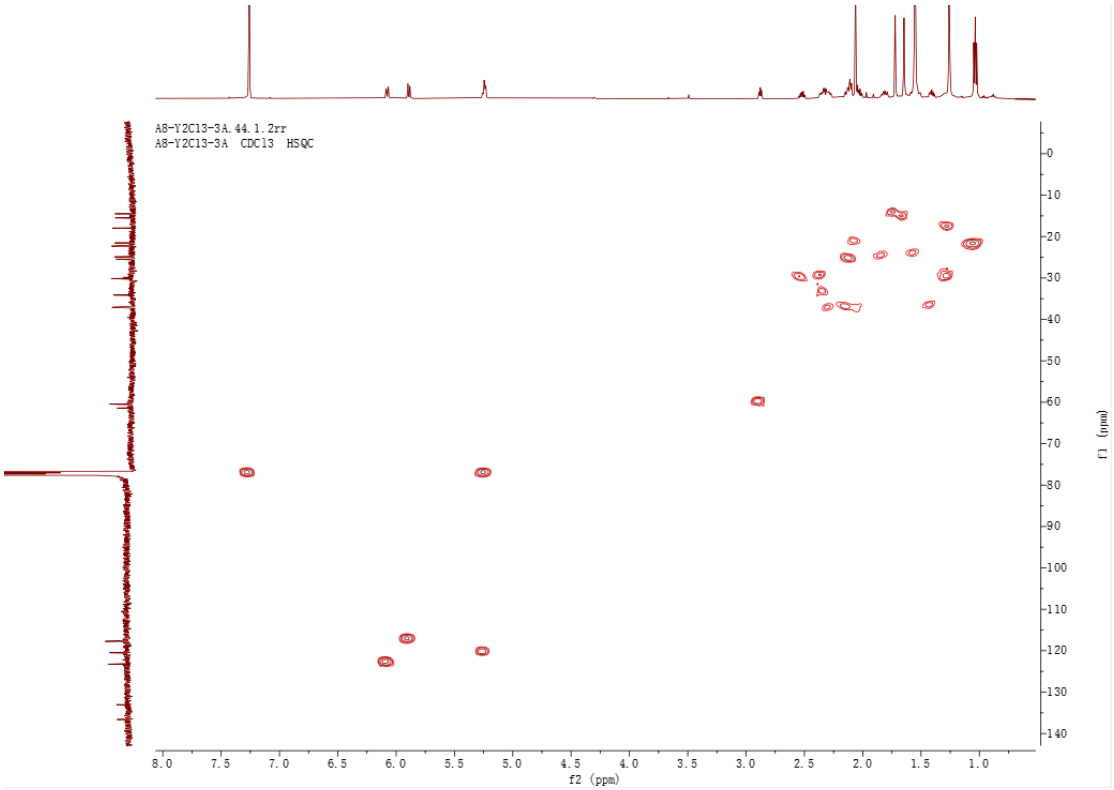


Figure S5.3. HSQC spectrum (600 MHz) of compound **5** in $CDCl_3$.

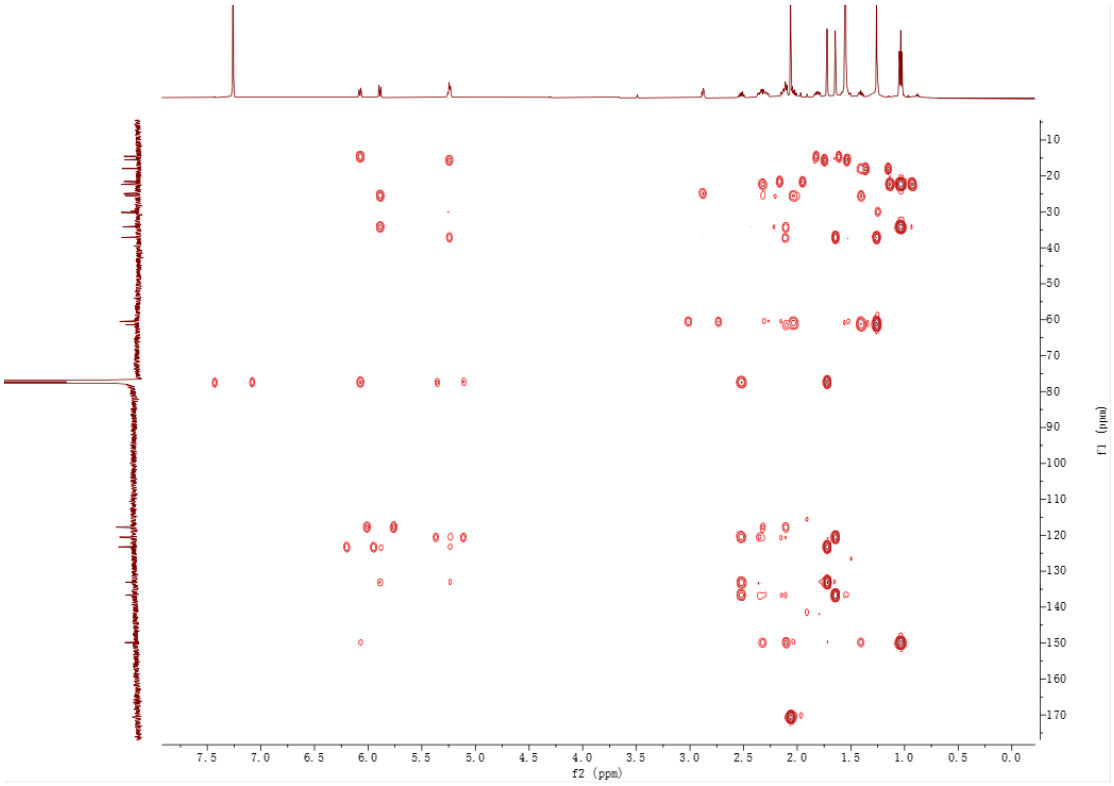


Figure S5.4. HMBC spectrum (600 MHz) of compound **5** in $CDCl_3$.

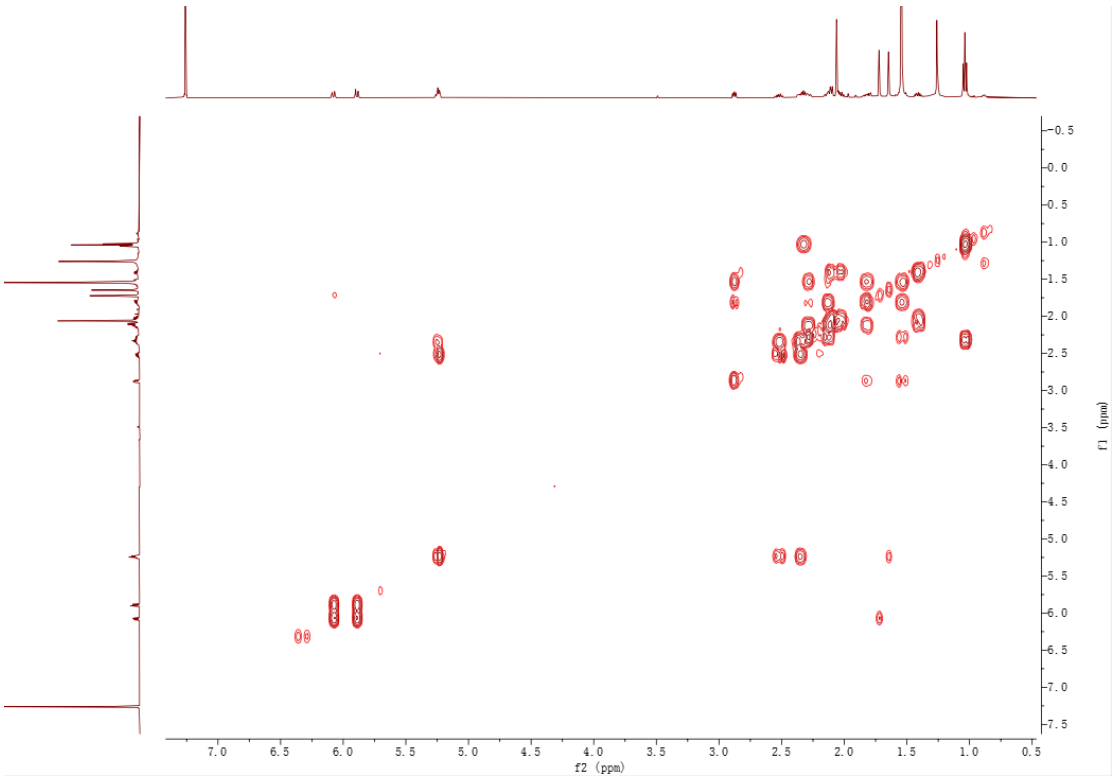


Figure S5.5. ^{1}H-^{1}H COSY spectrum (600 MHz) of compound **5** in $CDCl_3$.

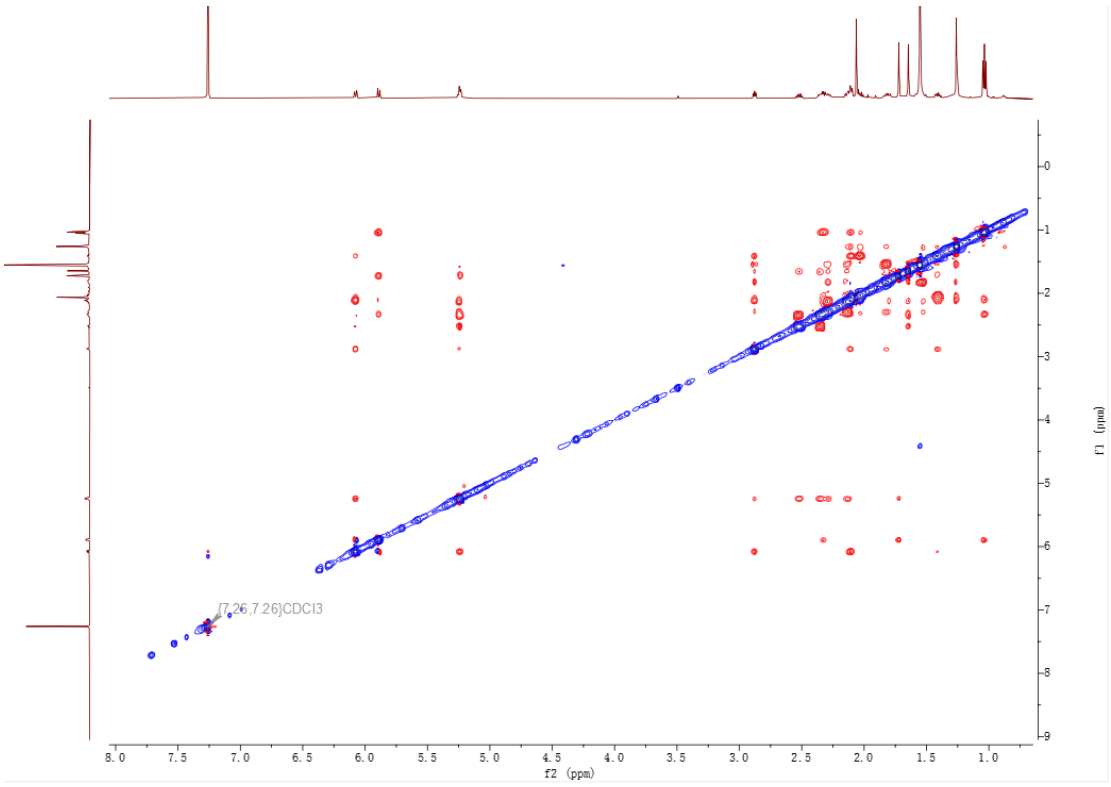
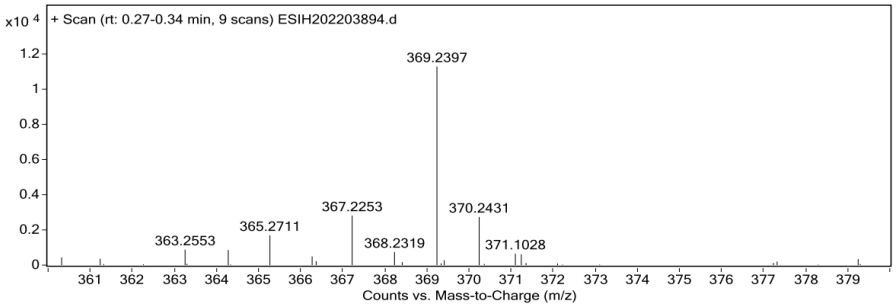


Figure S5.6. NOESY spectrum (600 MHz) of compound **5** in $CDCl_3$.

Data Filename	ESIH202203894.d	**Sample Name**	A8-Y2C13-3A
Sample ID		**Position**	P1-A5
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	10/17/2022 13:22:49	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by fangsu

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
170	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
369.2397	369.24	0.36	0.98	C22 H34 Na O3	(M+Na)+

Figure S5.7. HR-EIMS spectrum of compound **5**.

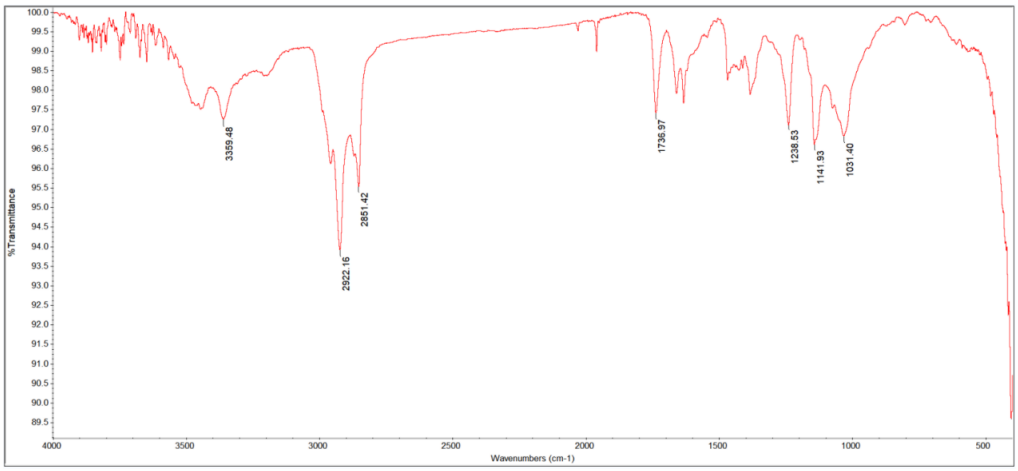


Figure S5.8. IR spectrum of compound **5**.

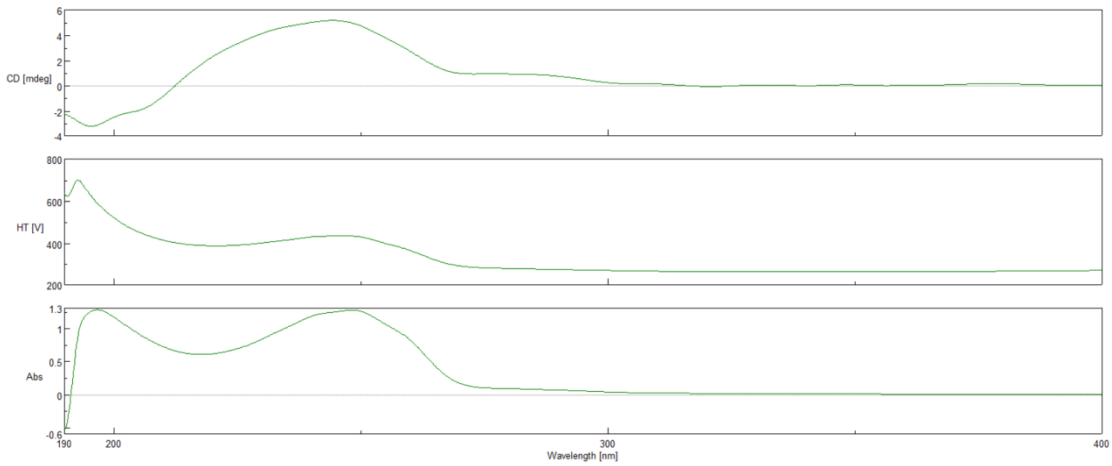


Figure S5.9. CD and UV spectrum of compound **5**.

7. Spectra of compound 9

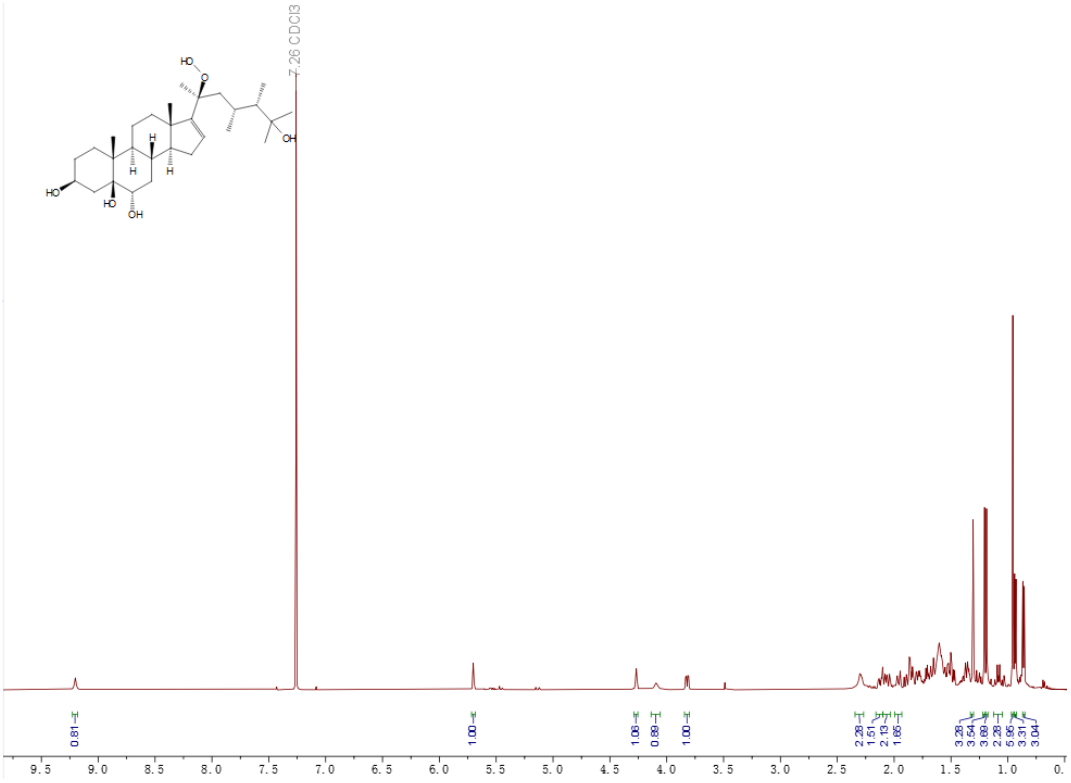


Figure S6.1. ^{1}H NMR spectrum (600 MHz) of compound **9** in $CDCl_3$.

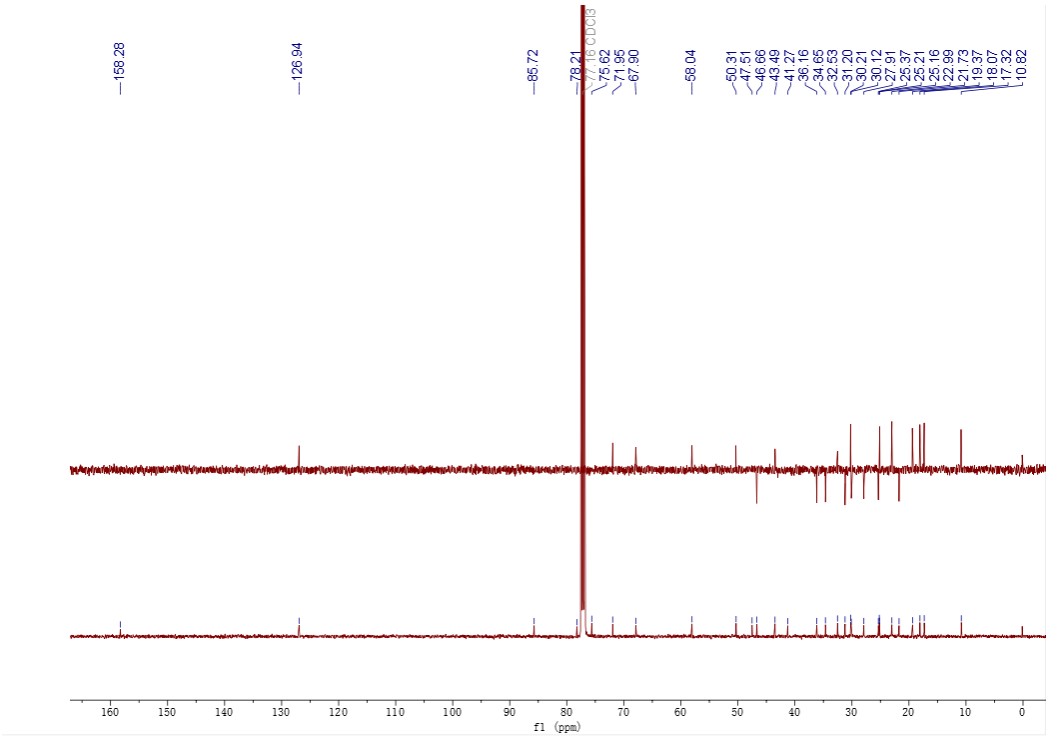


Figure S6.2. ^{13}C NMR spectrum (150 MHz) of compound **9** in $CDCl_3$.

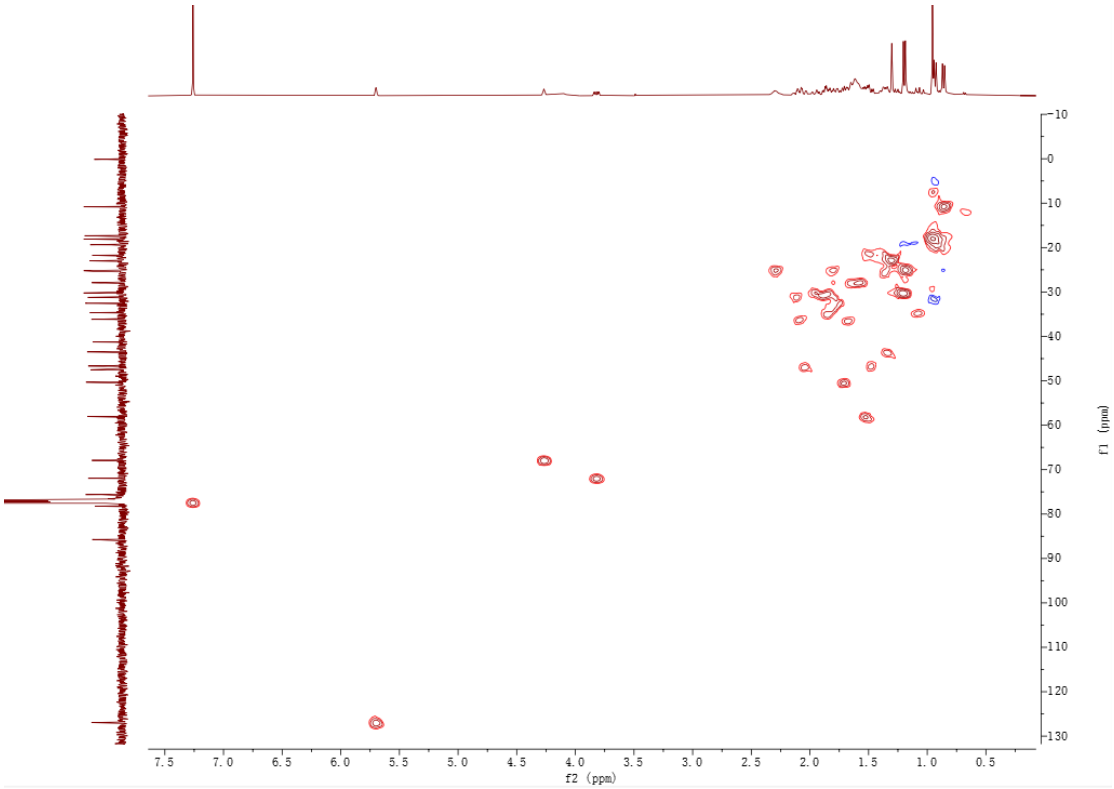


Figure S6.3. HSQC spectrum (600 MHz) of compound **9** in $CDCl_3$.

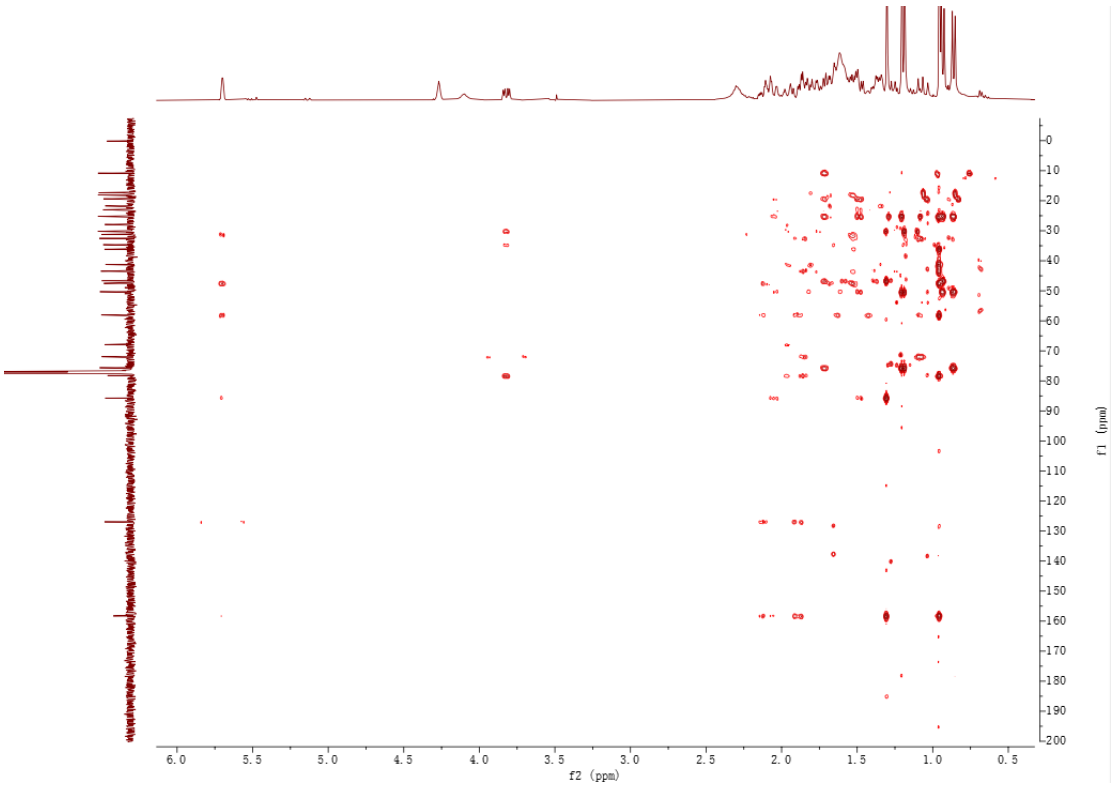


Figure S6.4. HMBC spectrum (600 MHz) of compound **9** in $CDCl_3$.

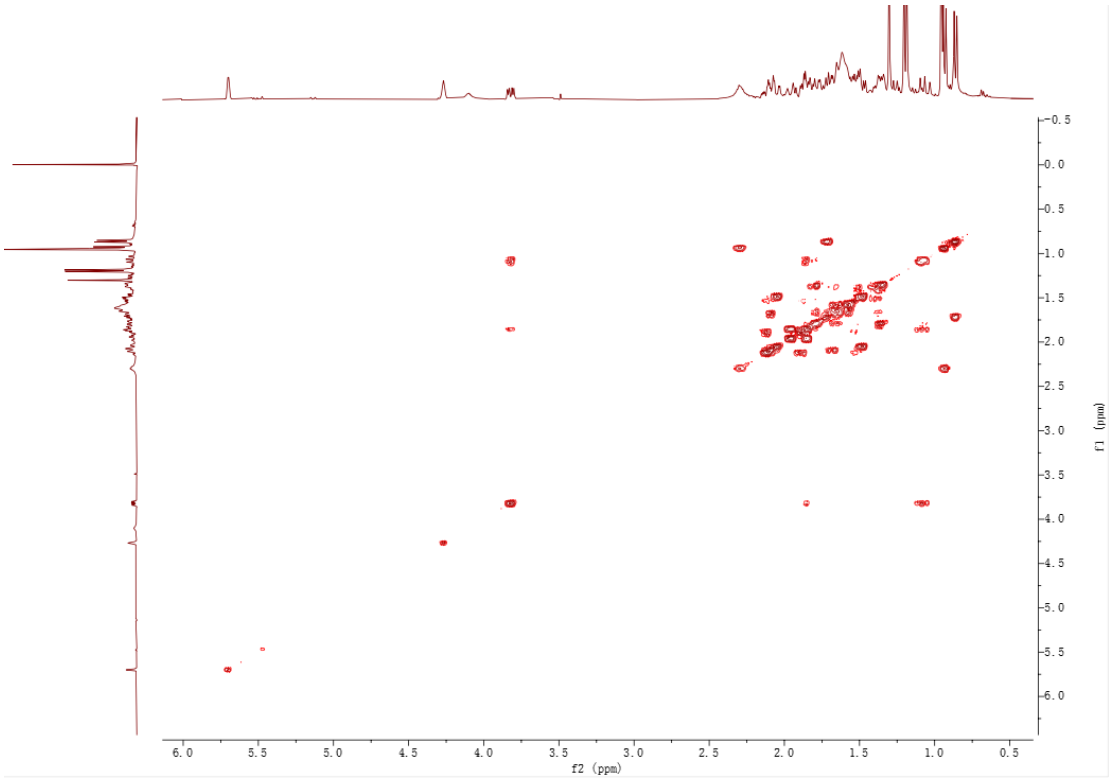


Figure S6.5. ^{1}H-^{1}H COSY spectrum (600 MHz) of compound **9** in $CDCl_3$.

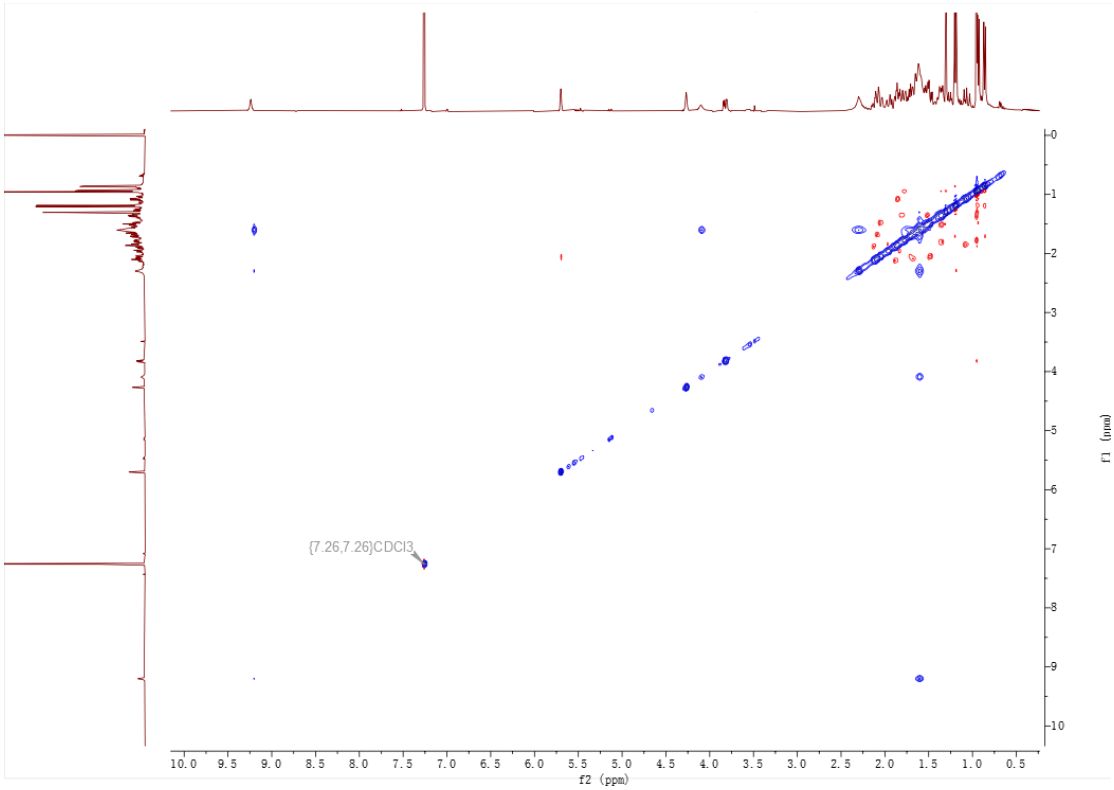
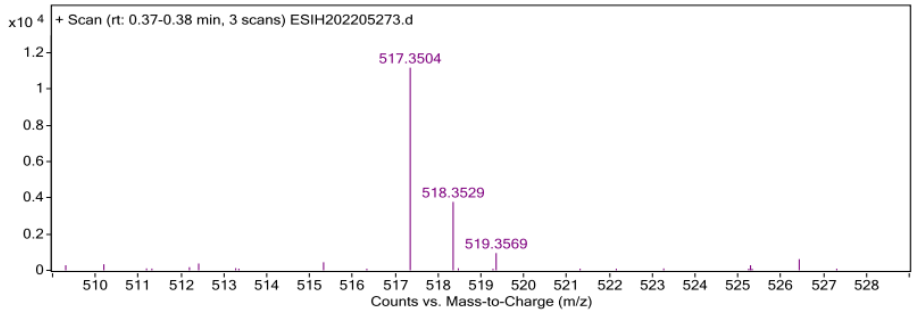


Figure S6.6. NOESY spectrum (600 MHz) of compound **9** in $CDCl_3$.

Data Filename	ESIH202205273.d	**Sample Name**	A8-Y9BEC
Sample ID		**Position**	P1-A3
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/6/2022 14:22:34	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by fangsu

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
170	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
517.3504	517.35	-0.41	-0.79	C29 H50 Na O6	(M+Na)+

Figure S6.7. HR-EIMS spectrum of compound **9**.

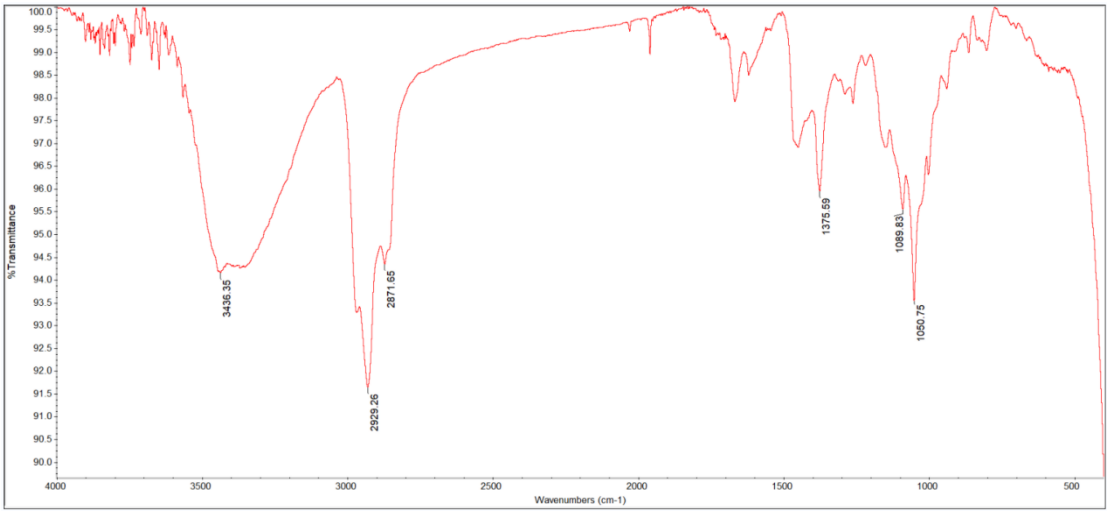


Figure S6.8. IR spectrum of compound **9**.

8. Spectra of compound 10

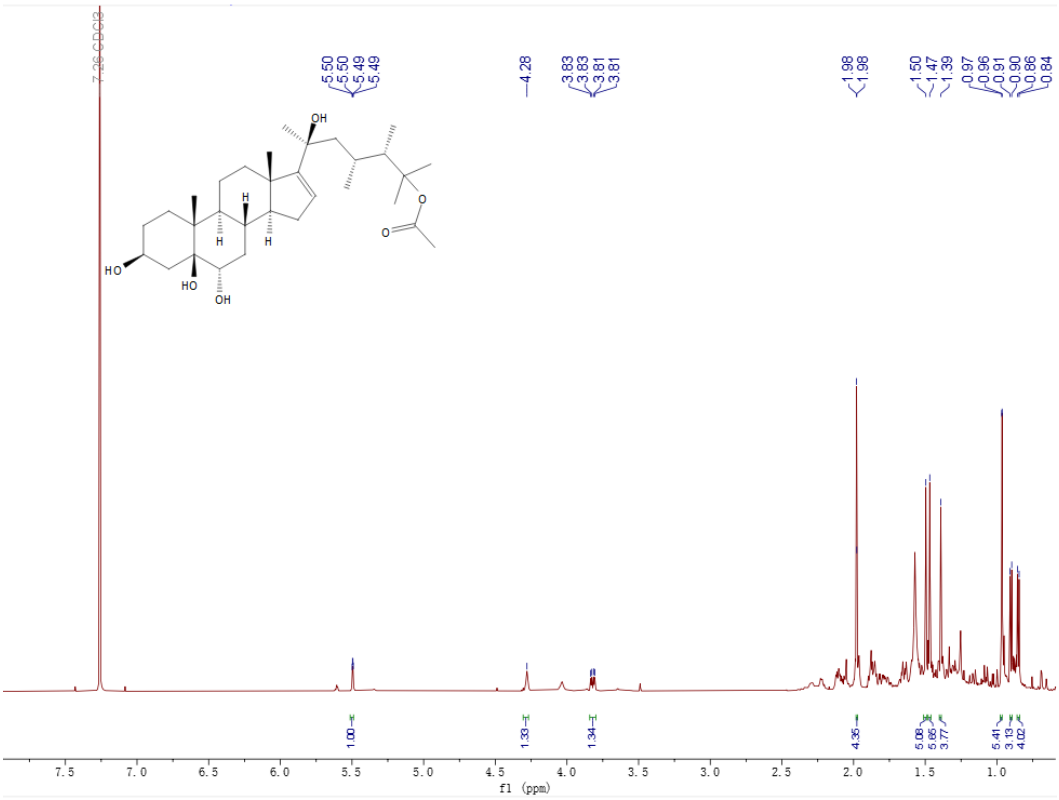


Figure S7.1. ^{1}H NMR spectrum (600 MHz) of compound **10** in $CDCl_3$.

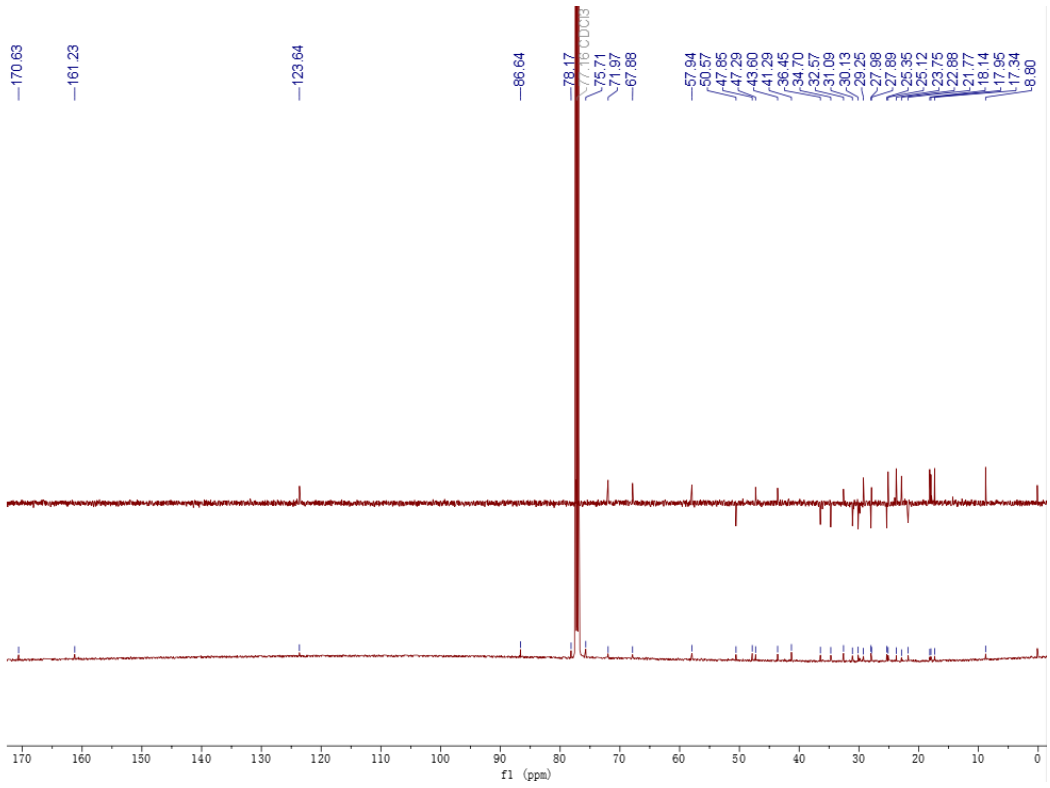


Figure S7.2. ^{13}C NMR spectrum (150 MHz) of compound **10** in $CDCl_3$.

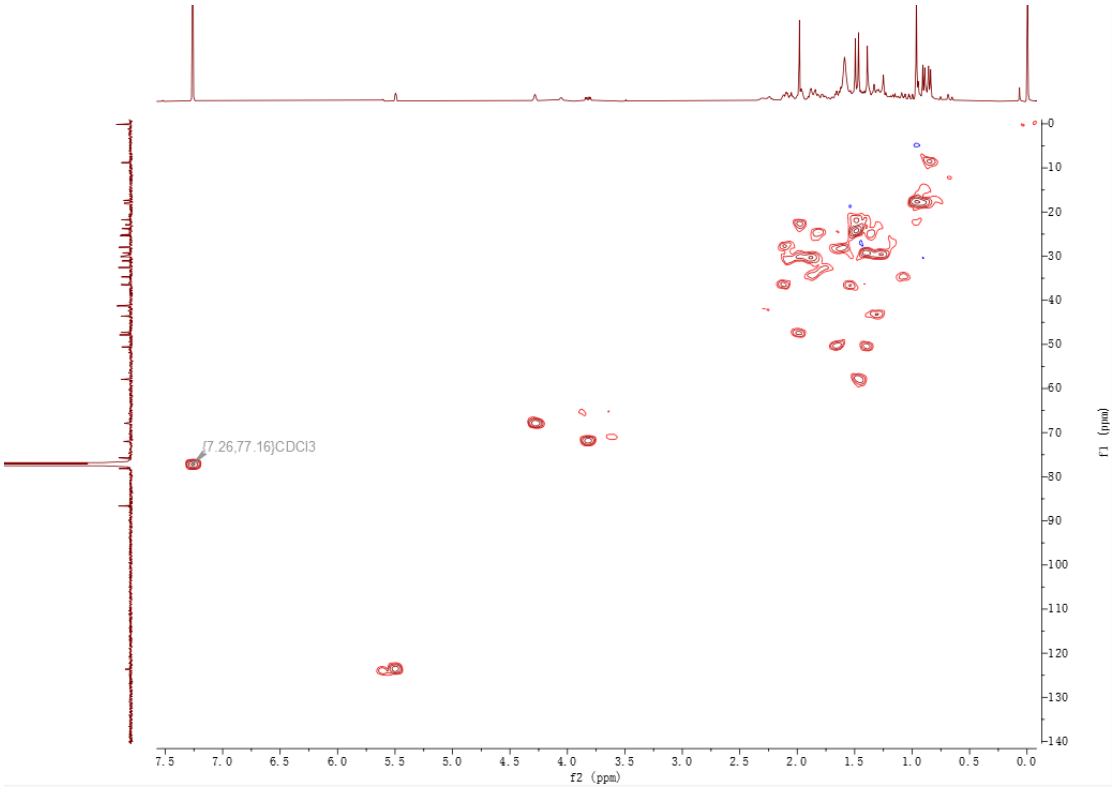


Figure S7.3. HSQC spectrum (600 MHz) of compound **10** in $CDCl_3$.

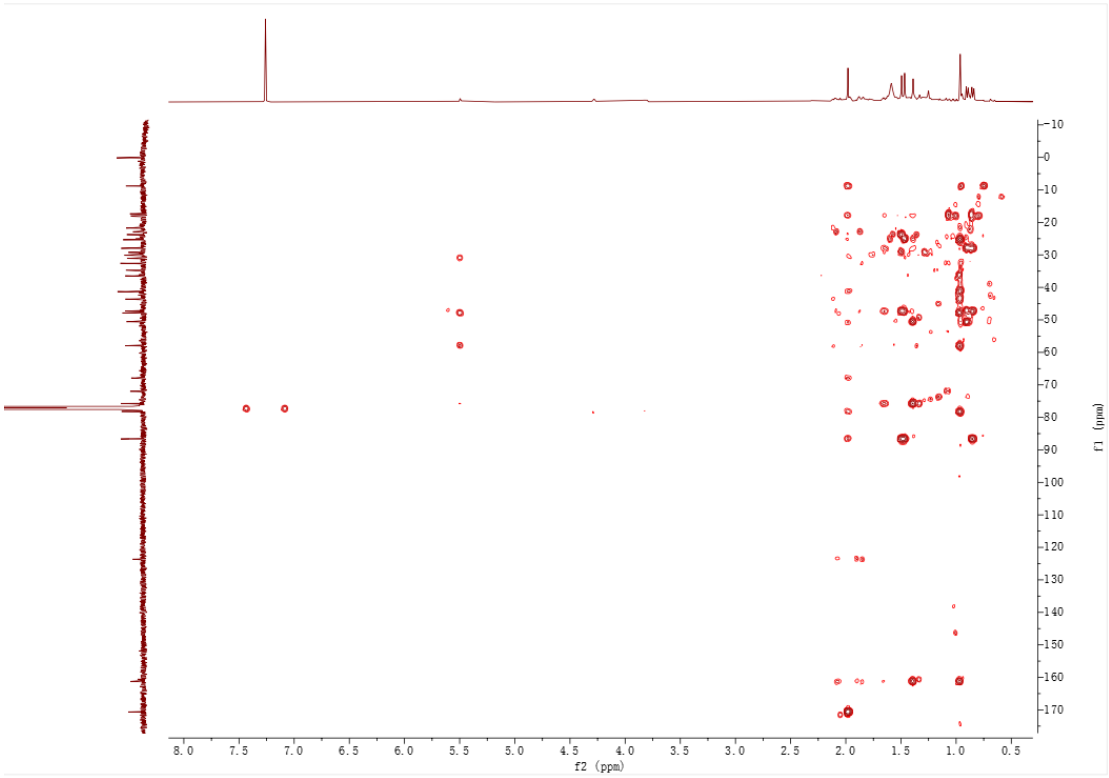


Figure S7.4. HMBC spectrum (600 MHz) of compound **10** in $CDCl_3$.

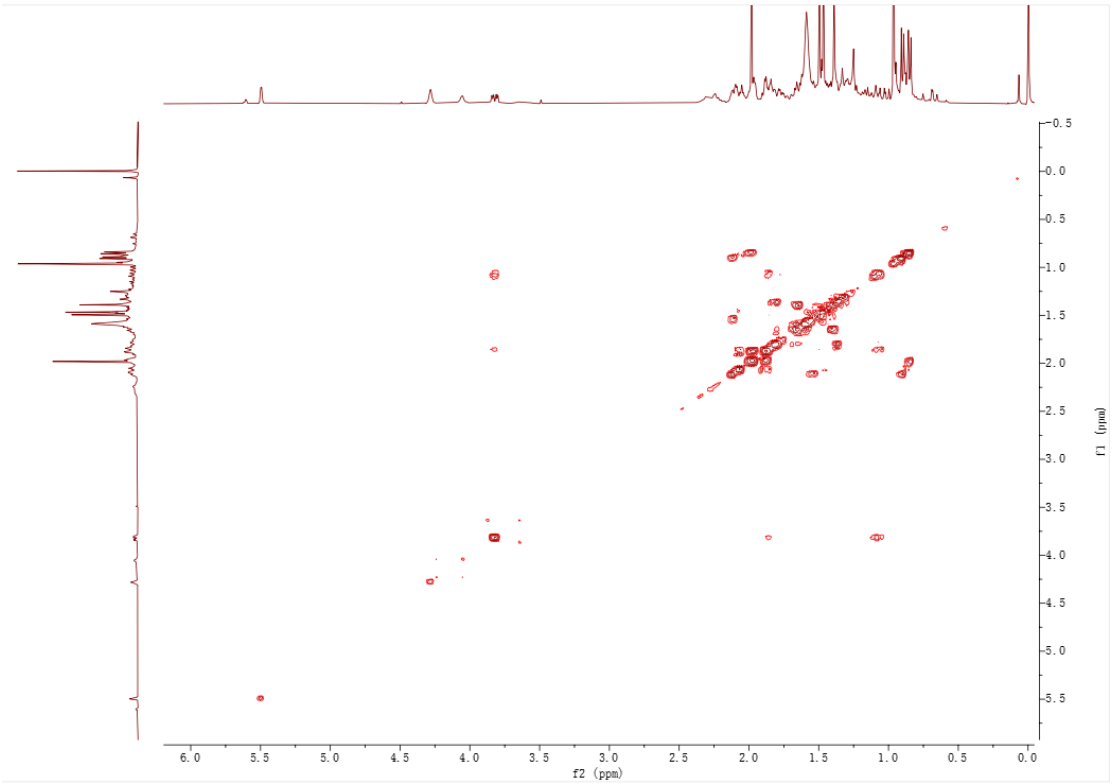


Figure S7.5. ^{1}H-^{1}H COSY spectrum (600 MHz) of compound **10** in $CDCl_3$.

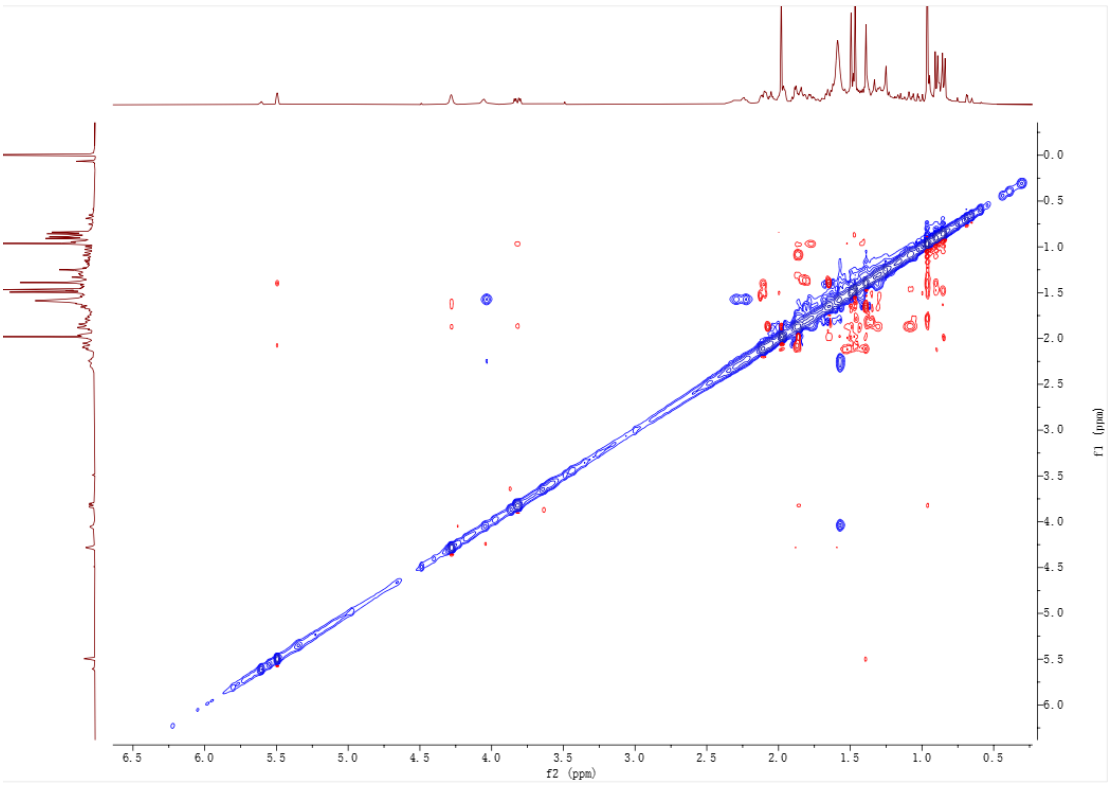
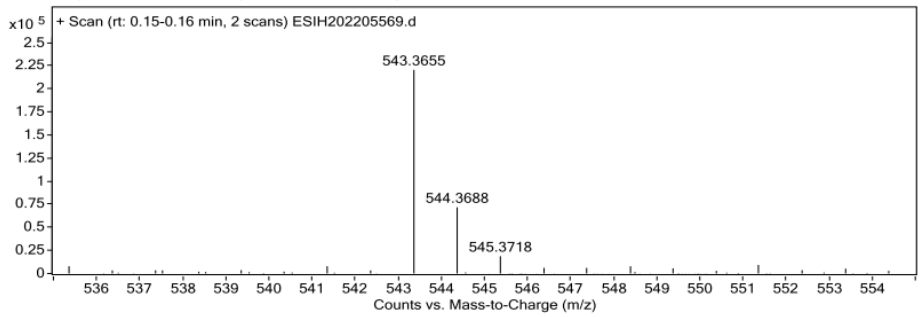


Figure S7.6. NOESY spectrum (600 MHz) of compound **10** in $CDCl_3$.

Data Filename	ESIH202205569.d	**Sample Name**	A8-Y9ADFGC
Sample ID		**Position**	P1-A4
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/15/2022 10:27:19	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by fangsu

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
170	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
543.3655	543.3656	0.08	0.14	C31 H52 Na O6	(M+Na)+

Figure S7.7. HR-EIMS spectrum of compound **10**.

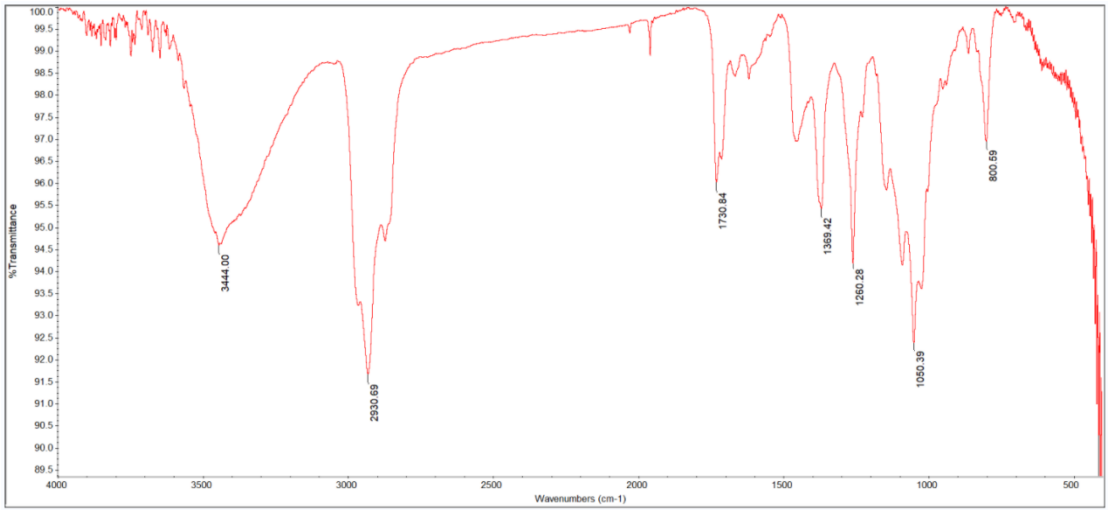


Figure S7.8. IR spectrum of compound **10**.

9. Spectra of compound 11

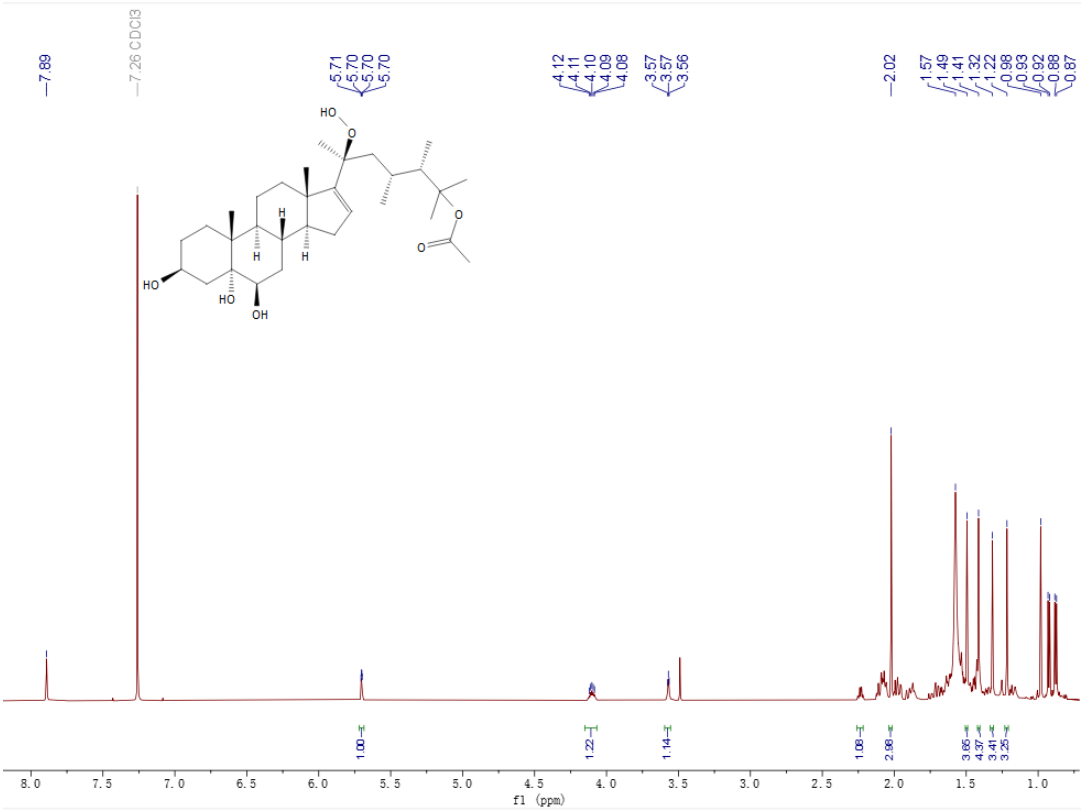


Figure S8.1. ^{1}H NMR spectrum (600 MHz) of compound **11** in $CDCl_3$.

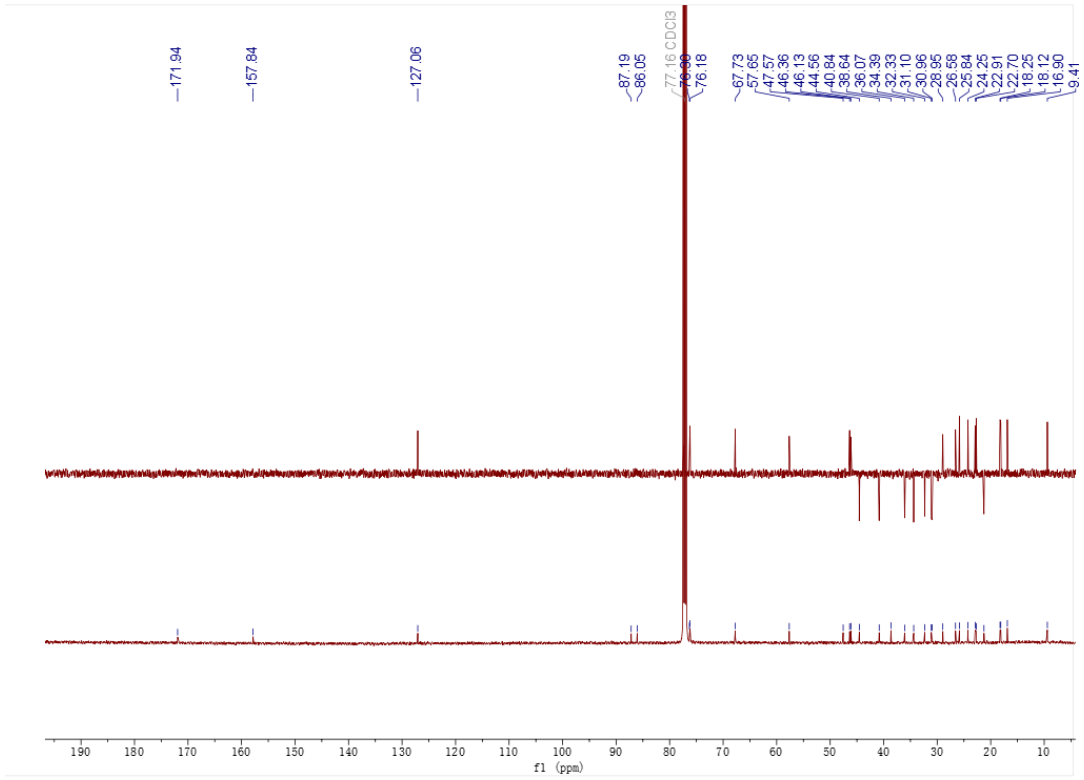


Figure S8.2. ^{13}C NMR spectrum (150 MHz) of compound **11** in $CDCl_3$.

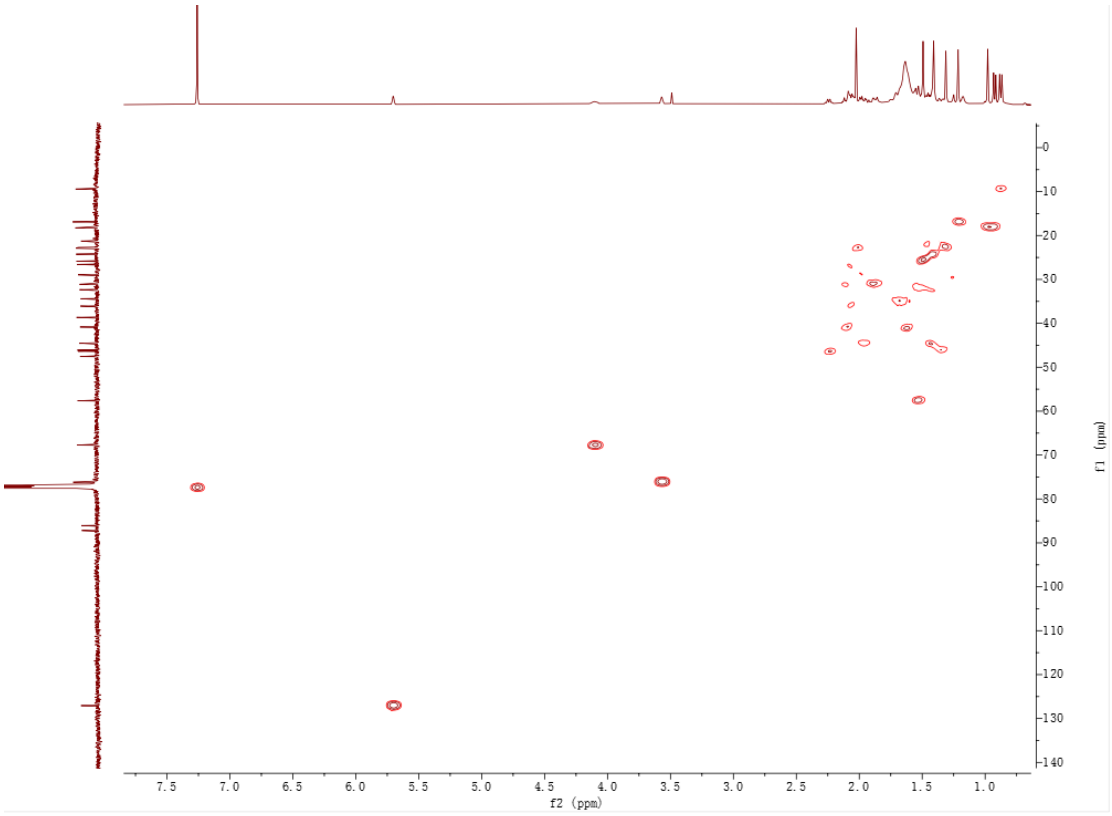


Figure S8.3. HSQC spectrum (600 MHz) of compound **11** in $CDCl_3$.

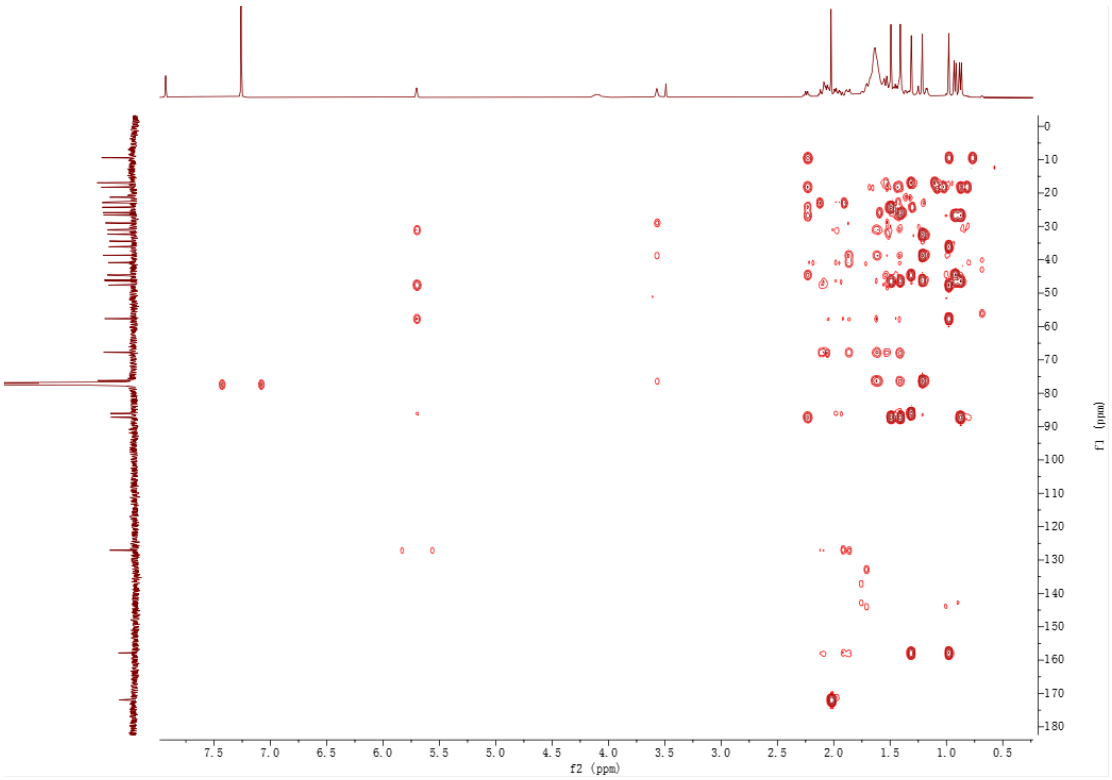


Figure S8.4. HMBC spectrum (600 MHz) of compound **11** in $CDCl_3$.

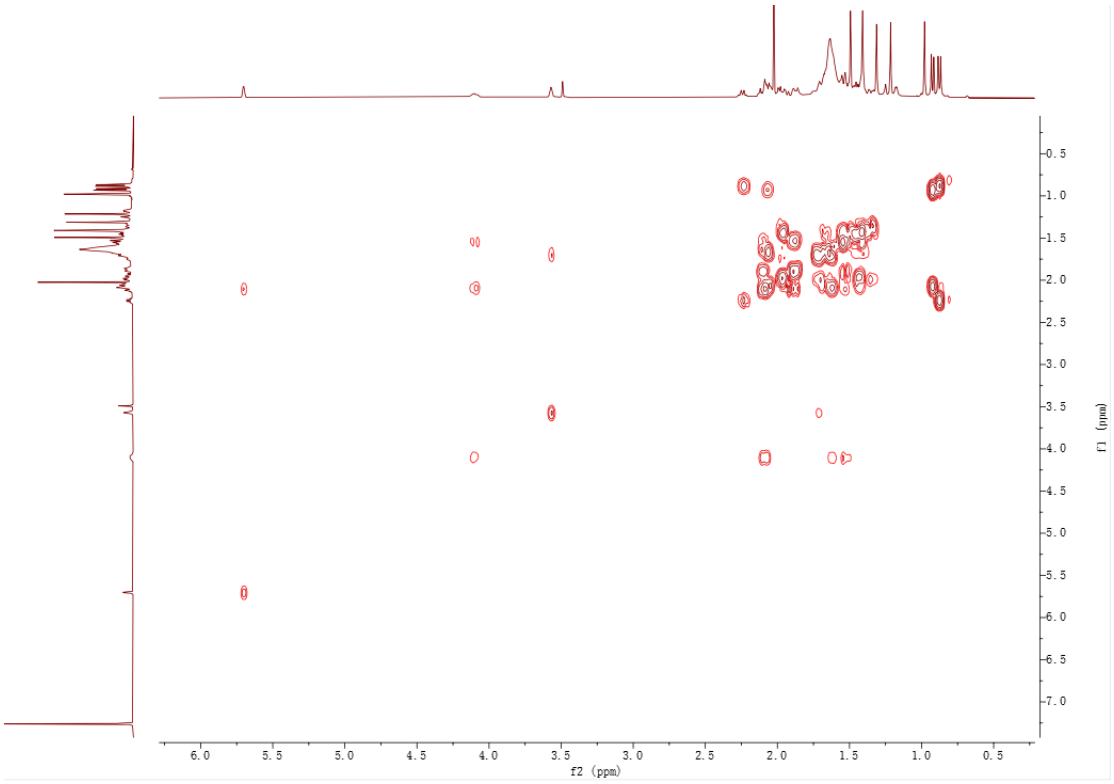


Figure S8.5. ^{1}H-^{1}H COSY spectrum (600 MHz) of compound **11** in $CDCl_3$.

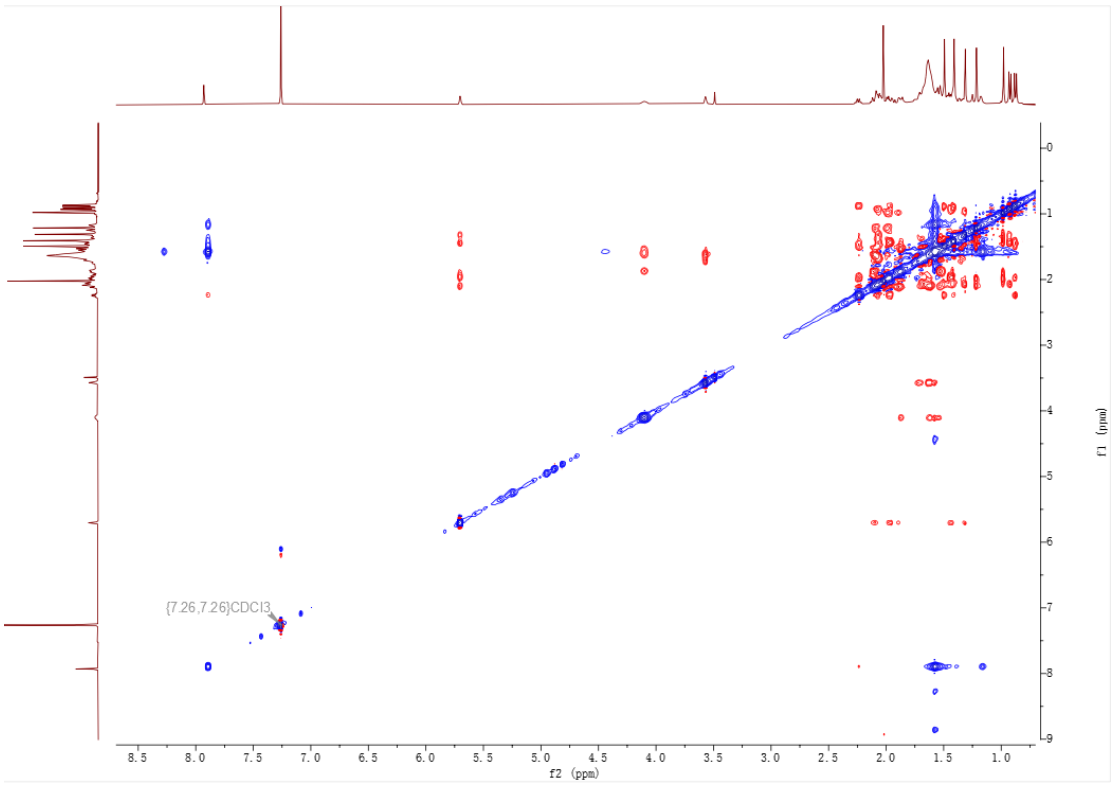
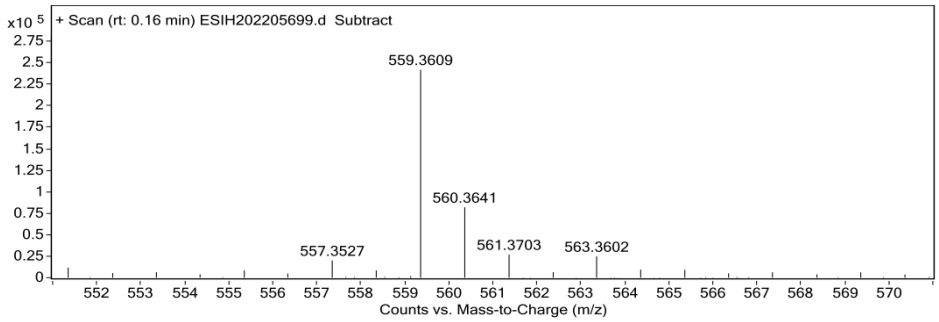


Figure S8.6. NOESY spectrum (600 MHz) of compound **11** in $CDCl_3$.

Data Filename	ESIH202205699.d	**Sample Name**	A8-A8-Y9ADFE
Sample ID		**Position**	P1-D9
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/16/2022 12:37:30	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by fangsu

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
170	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
559.3609	559.3605	-0.35	-0.62	C31 H52 Na O7	(M+Na)+

Figure S8.7. HR-EIMS spectrum of compound **11**.

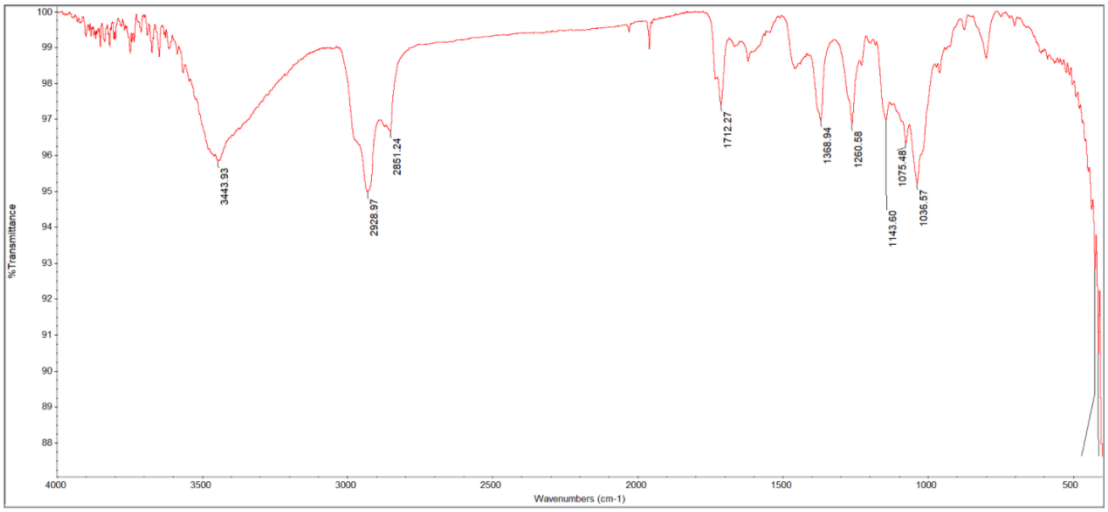


Figure S8.8. IR spectrum of compound **11**.

10.Spectra of compound 12

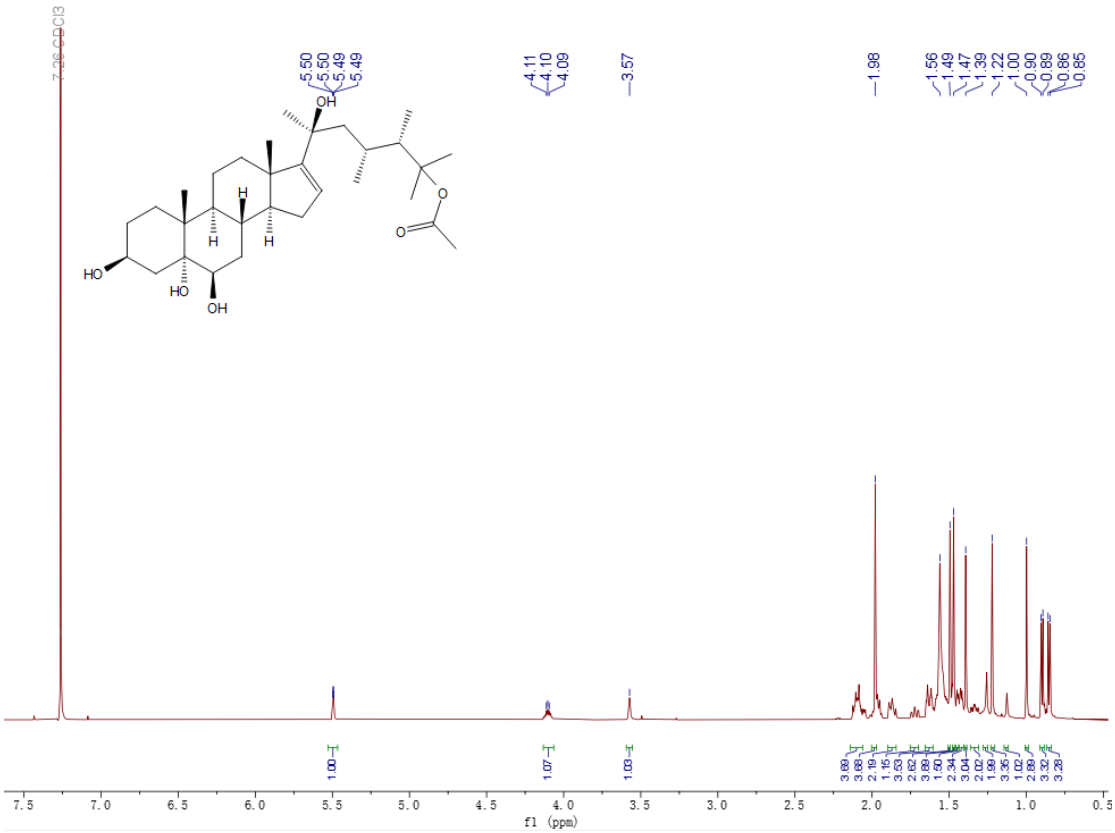


Figure S9.1. ^{1}H NMR spectrum (600 MHz) of compound **12** in $CDCl_3$.

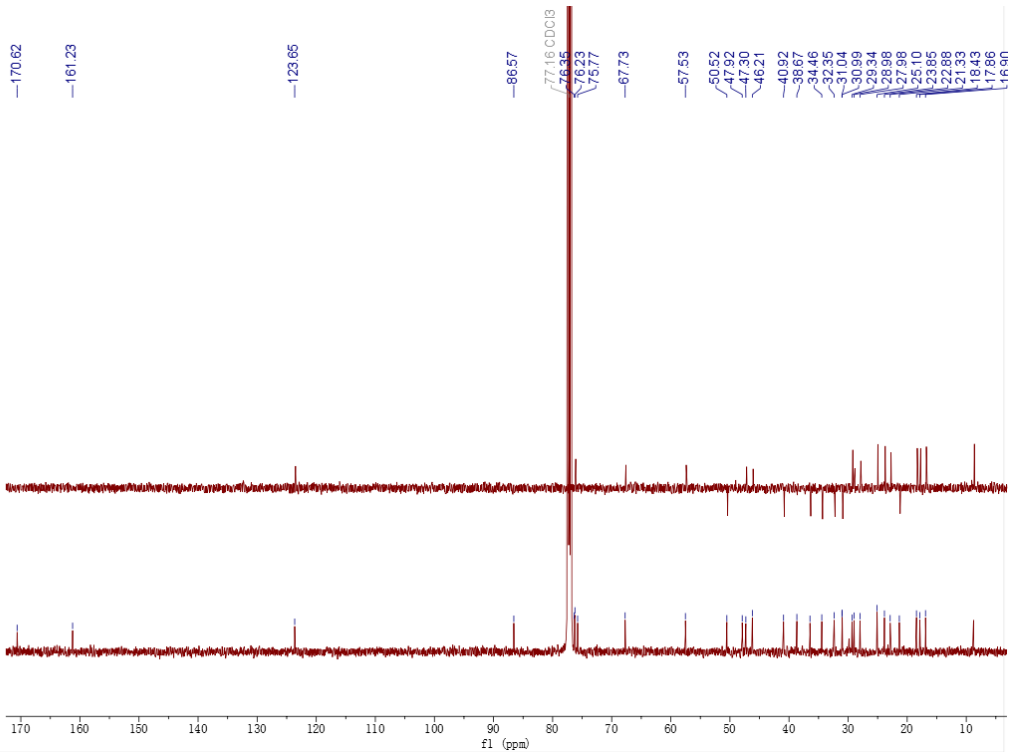


Figure S9.2. ^{13}C NMR spectrum (150 MHz) of compound **12** in $CDCl_3$.

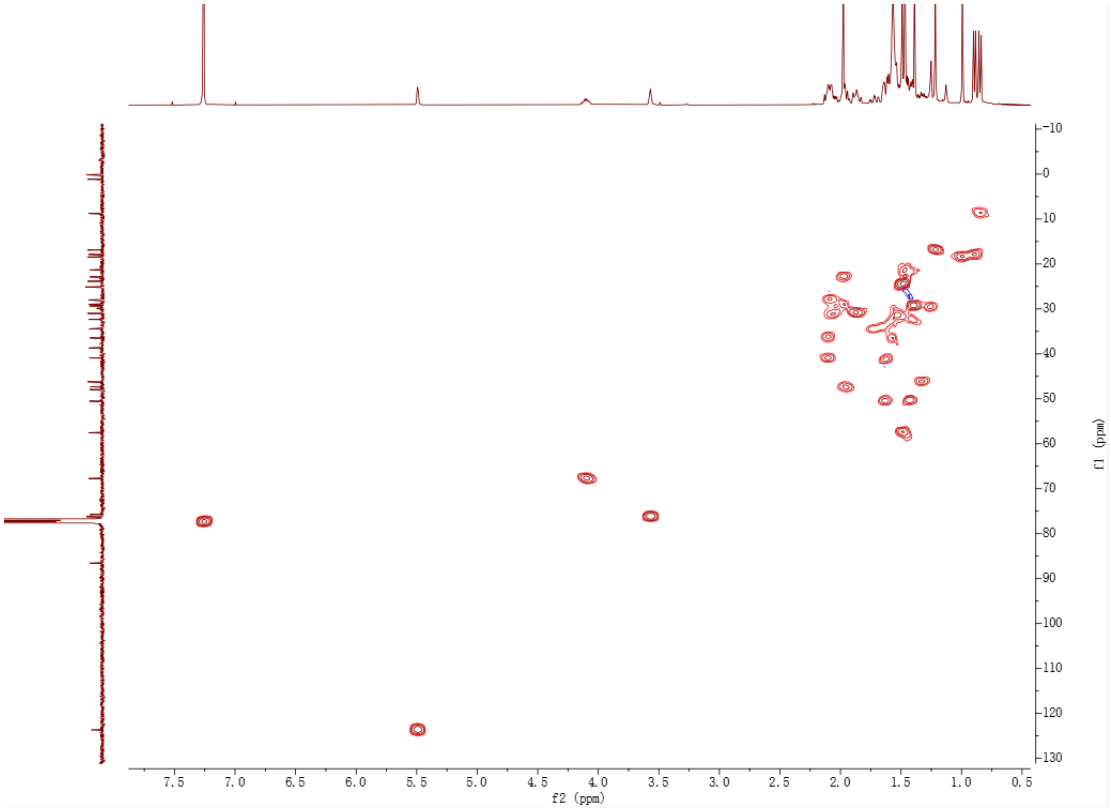


Figure S9.3. HSQC spectrum (600 MHz) of compound **12** in $CDCl_3$.

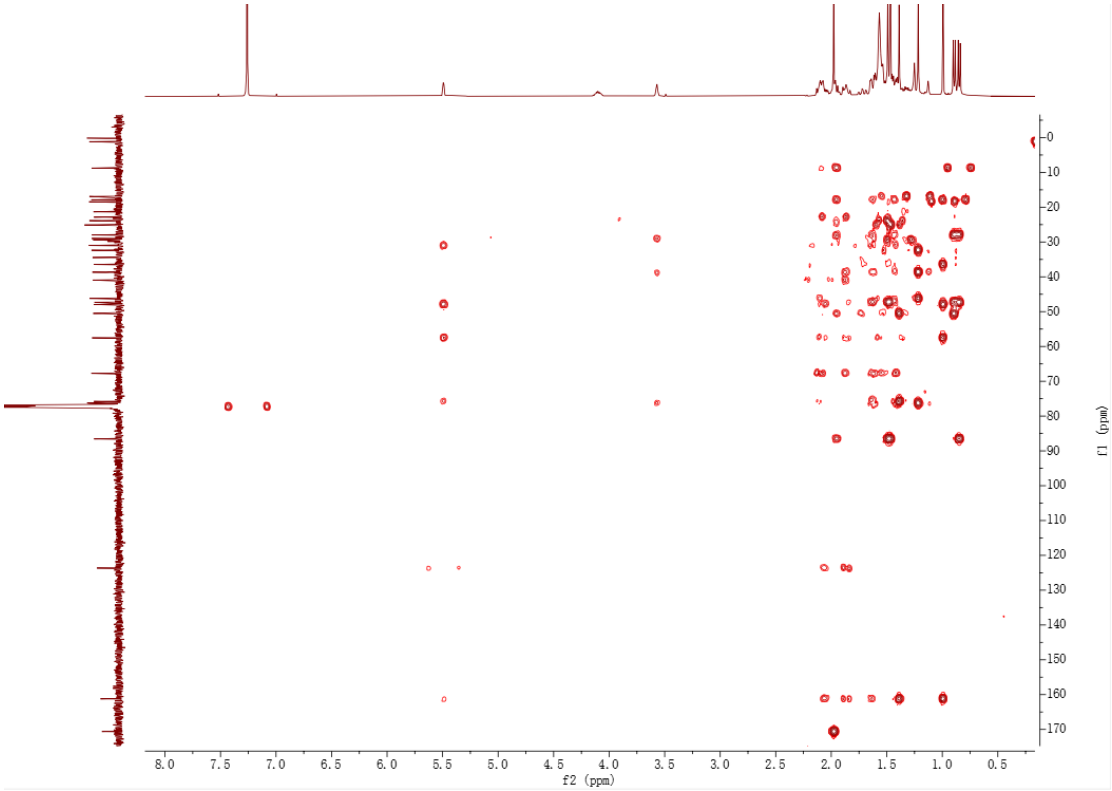


Figure S9.4. HMBC spectrum (600 MHz) of compound **12** in $CDCl_3$.

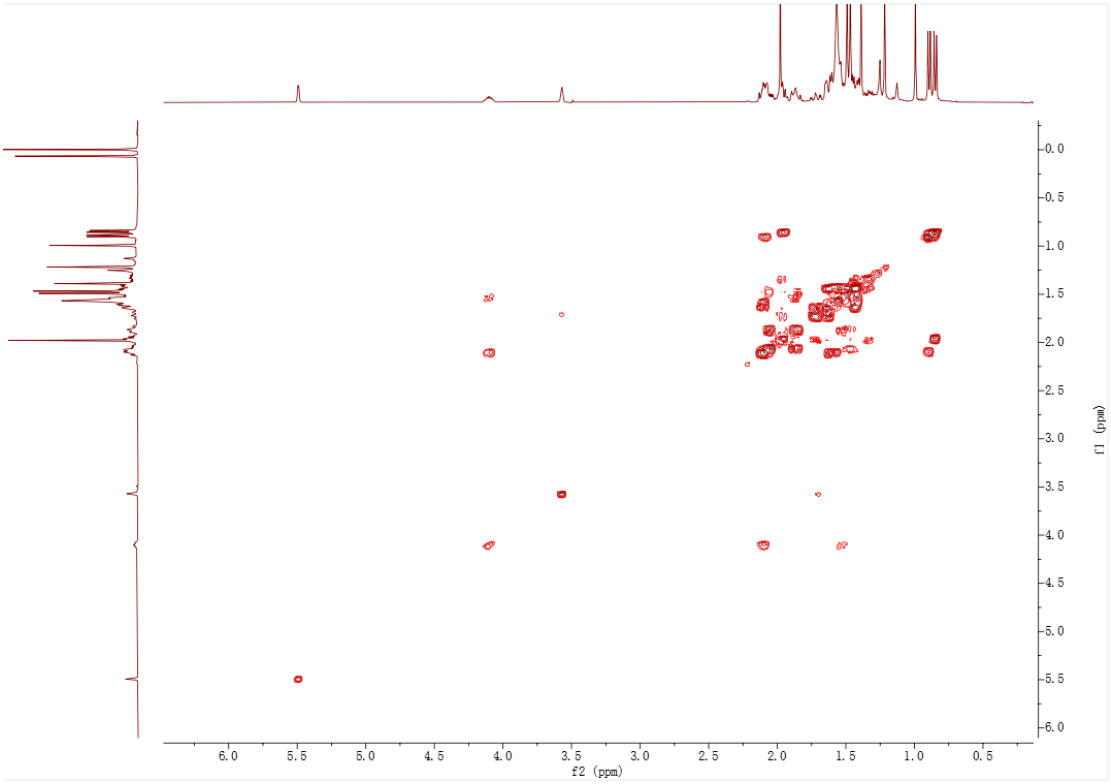


Figure S9.5. ^{1}H-^{1}H COSY spectrum (600 MHz) of compound **12** in $CDCl_3$.

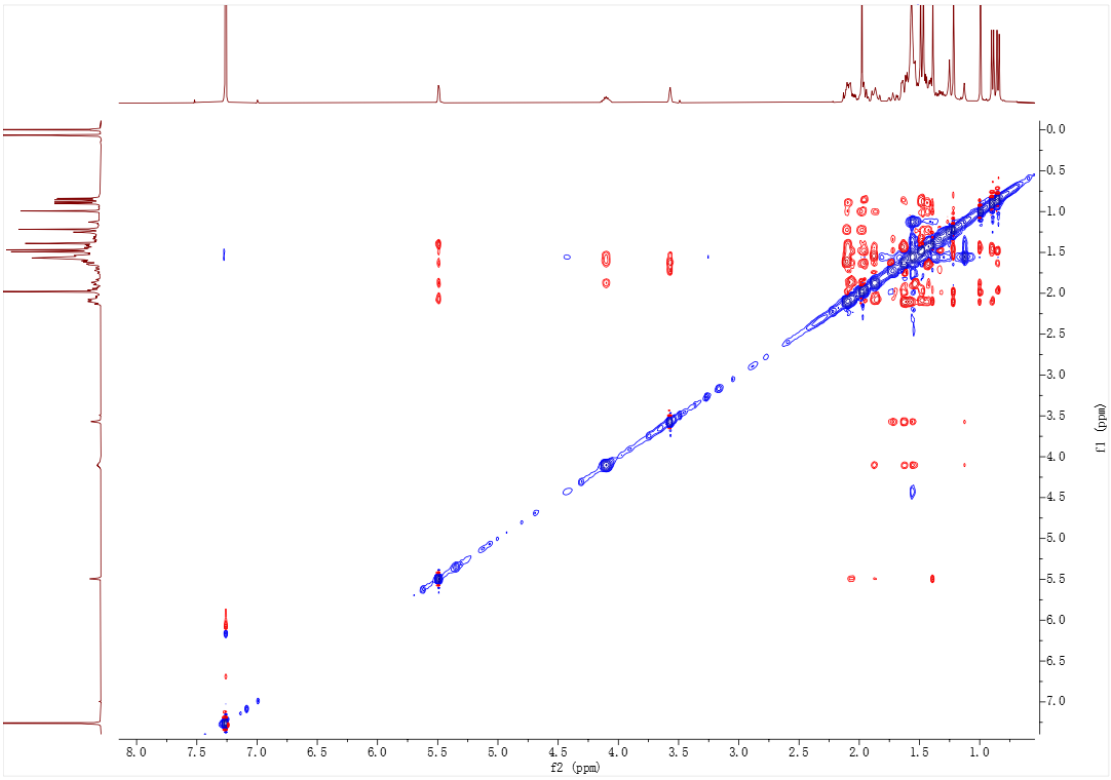


Figure S9.6. NOESY spectrum (600 MHz) of compound **12** in $CDCl_3$.

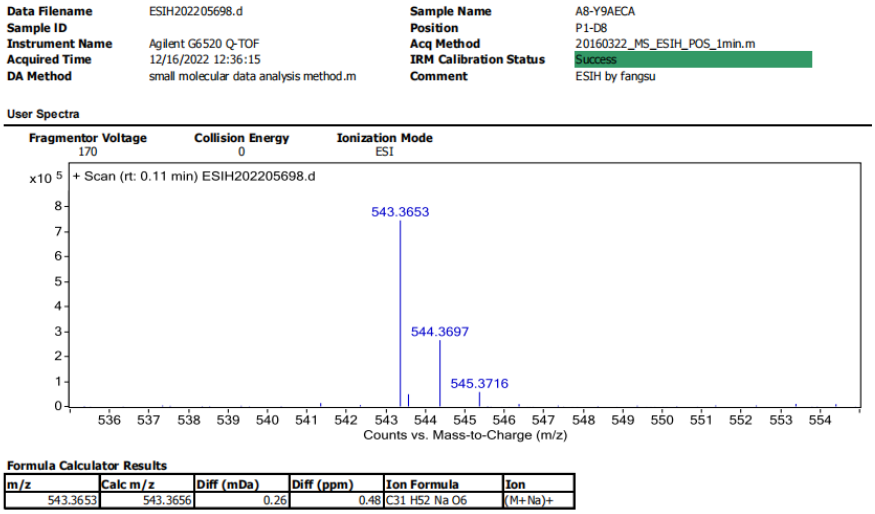


Figure S9.7. HR-EIMS spectrum of compound **12**.

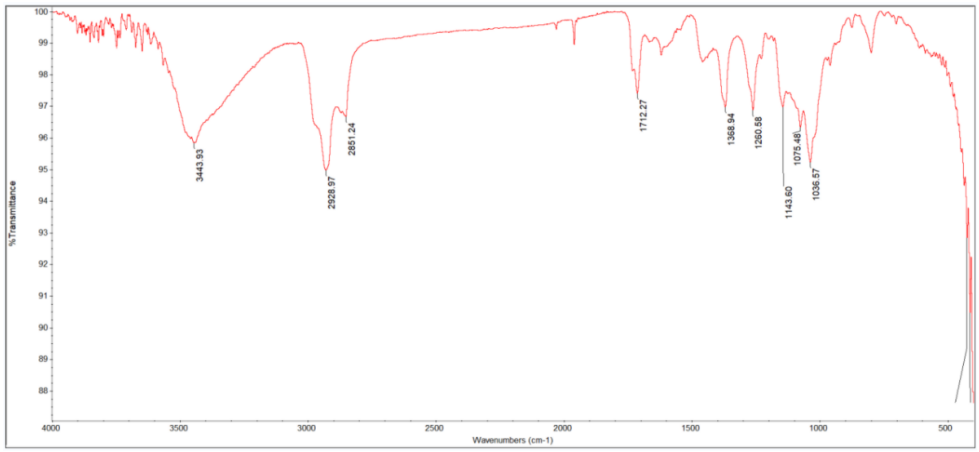


Figure S9.8. IR spectrum of compound **12**.

11.Spectra of compound 15a

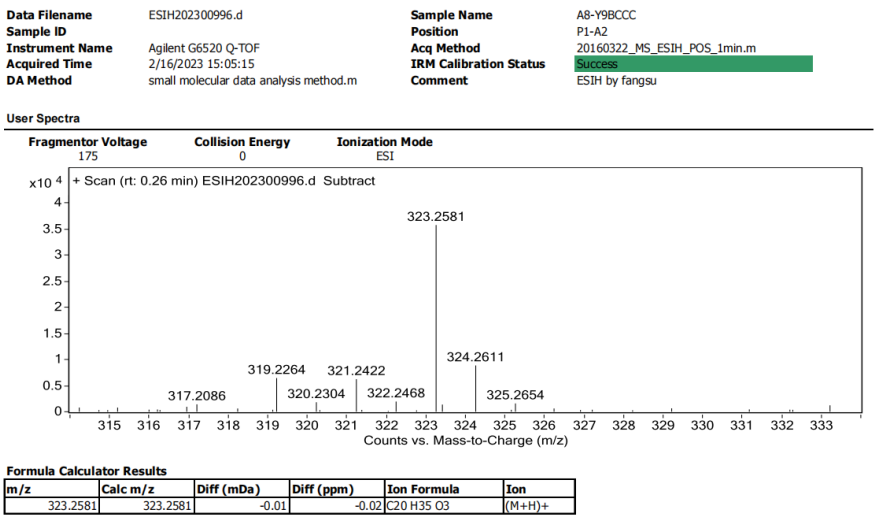


Figure S10.1. HR-EIMS spectrum of compound **15a**.

12.QM-NMR calculation

Torsional sampling (MCMM) conformational searches using OPLS_2005 force field were carried out by the means of conformational search module in Macro model 9.9.223 software (Schrodinger, http://www.schrodinger.com/MacroModel), applying an energy window of 21 kJ/mol (5.02 kcal/mol) for saving structures. Conformers above 1% population were re-optimized with Gaussian 09 at the B3LYP/6-311G(d,p) level with IEFPCM solvent model for acetonitrile.

The following DFT calculations were performed using Gaussian 09, and the dominant conformers were re-optimized at B3LYP/6-311G(d,p) level of theory. Magnetic shielding constants (σ) were calculated by means of the gauge including atomic orbitals (GIAO) method at mPW1PW91/6–31 G(d) level of theory as recommended for DP4+ analysis.

12.1. Structure of studied isomers of compound **3**.

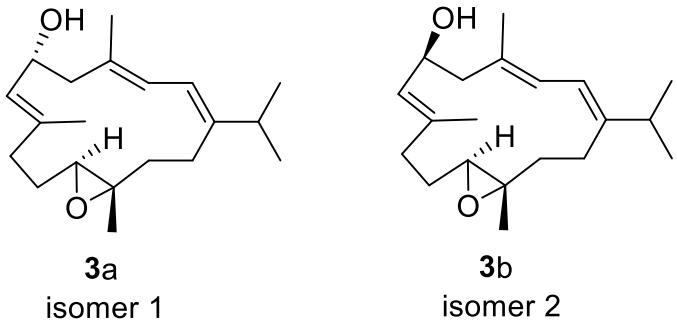


Figure S11.1. Two possible configurations of compound **3**.

12.2. SCF energies computed at the PCM/mPW1PW91/6-31G* level of theory for all conformers of studied isomers.

3a_6R11S12S_1: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56192291 a. u.

3a_6R11S12S_2: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56473866 a. u.

3a_6R11S12S_3: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56474077 a. u.

3a_6R11S12S_4: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56150640 a. u.

3a_6R11S12S_5: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56244883 a. u.

3a_6R11S12S_6: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56399453 a. u.

3a_6R11S12S_7: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56239668 a. u.

3a_6R11S12S_8: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56355852 a. u.

3a_6R11S12S_9: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55897310 a. u.

3b_6S11S12S_1: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55843435 a. u.

3b_6S11S12S_2: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55519468 a. u.

3b_6S11S12S_3: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55217040 a. u.

3b_6S11S12S_4: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55473068 a. u.

3b_6S11S12S_5: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55773570 a. u.

3b_6S11S12S_6: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55806553 a. u.

3b_6S11S12S_7: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55198124 a. u.

3b_6S11S12S_8: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55451696 a. u.

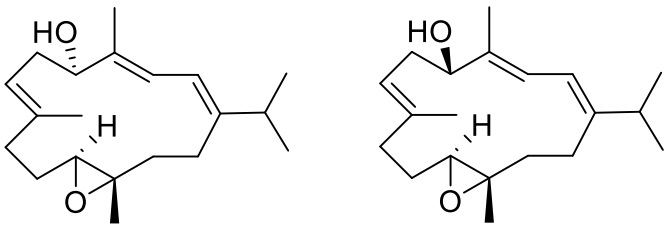
3b_6S11S12S_9: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55131077 a. u.

3b_6S11S12S_10: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55806506 a. u.

12.3. DP4+ results obtained using experimental ^{1}H and ^{13}C data of compound **3** versus isomers **3a-3b**.

Functional	Solvent?	Basis Set	Type of Data			
mPW1PW91	PCM	6-31G(d)	Shielding Tensors			
	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	100.00%	0.00%	–	–	–	–
sDP4+ (C data)	67.24%	32.76%	–	–	–	–
sDP4+ (all data)	100.00%	0.00%	–	–	–	–
uDP4+ (H data)	100.00%	0.00%	–	–	–	–
uDP4+ (C data)	55.50%	44.50%	–	–	–	–
uDP4+ (all data)	100.00%	0.00%	–	–	–	–
DP4+ (H data)	100.00%	0.00%	–	–	–	–
DP4+ (C data)	71.91%	28.09%	–	–	–	–
DP4+ (all data)	100.00%	0.00%	–	–	–	–

12.4. Structure of studied isomers of compound **4**.



4a
isomer 1

4b
isomer 2

Figure S11.2. Two possible configurations of compound **4**.

12.5. SCF energies computed at the PCM/mPW1PW91/6-31G* level of theory for all conformers of studied isomers.

4a_5R11S12S_1: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56095132 a. u.

4a_5R11S12S_2: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56479510 a. u.

4a_5R11S12S_3: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56033711 a. u.

4a_5R11S12S_4: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56528750 a. u.

4a_5R11S12S_5: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55940219 a. u.

4a_5R11S12S_6: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56486809 a. u.

4a_5R11S12S_7: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56362976 a. u.

4a_5R11S12S_8: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56321472 a. u.

4a_5R11S12S_9: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55994482 a. u.

4a_5R11S12S_10: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56227741 a. u.

4b_5S11S12S_1: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56559011 a. u.

4b_5S11S12S_2: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56612488 a. u.

4b_5S11S12S_3: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56559008 a. u.

4b_5S11S12S_4: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56513833 a. u.

4b_5S11S12S_5: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56568095 a. u.

4b_5S11S12S_6: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55884239 a. u.

4b_5S11S12S_7: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56066577 a. u.

4b_5S11S12S_8: SCF energy (PCM/mPW1PW91/6-31G*) = -931.55451696 a. u.

4b_5S11S12S_9: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56230067 a. u.

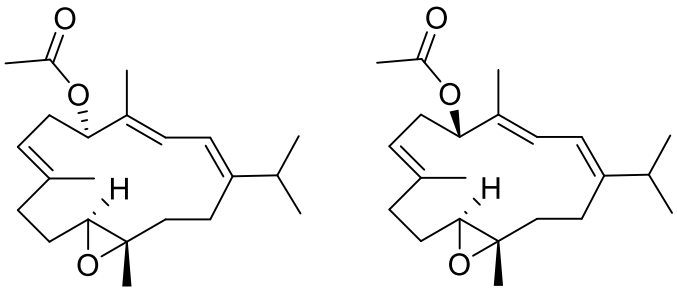
4b_5S11S12S_10: SCF energy (PCM/mPW1PW91/6-31G*) = -931.56376243 a. u.

12.6. DP4+ results obtained using experimental ^{1}H and ^{13}C data of compound **4** versus isomers**4a-4b**.

Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-31G(d)	Shielding Tensors

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	96.82%	3.18%	–	–	–	–
sDP4+ (C data)	99.17%	0.83%	–	–	–	–
sDP4+ (all data)	99.97%	0.03%	–	–	–	–
uDP4+ (H data)	97.65%	2.35%	–	–	–	–
uDP4+ (C data)	98.70%	1.30%	–	–	–	–
uDP4+ (all data)	99.97%	0.03%	–	–	–	–
DP4+ (H data)	99.92%	0.08%	–	–	–	–
DP4+ (C data)	99.99%	0.01%	–	–	–	–
DP4+ (all data)	100.00%	0.00%	–	–	–	–

12.7. Structure of studied isomers of compound **5**.



5a
isomer 1

5b
isomer 2

Figure S11.3. Two possible configurations of compound **5**.

12.8. SCF energies computed at the PCM/mPW1PW91/6-31G* level of theory for all conformers of studied isomers.

5a_5R11S12S_1: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18727565 a. u.

5a_5R11S12S_2: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.19113432 a. u.

5a_5R11S12S_4: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.19102676 a. u.

5a_5R11S12S_5: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.19029245 a. u.

5a_5R11S12S_6: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18339270 a. u.

5a_5R11S12S_7: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18710949 a. u.

5a_5R11S12S_8: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18545285 a. u.

5a_5R11S12S_9: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18849334 a. u.

5a_5R11S12S_10: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18228246 a. u.

5b_5S11S12S_1: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18629387 a. u.

5b_5S11S12S_2: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18791705 a. u.

5b_5S11S12S_3: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18759467 a. u.

5b_5S11S12S_4: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18796802a. u.

5b_5S11S12S_5: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18761750 a. u.

5b_5S11S12S_6: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18735303 a. u.

5b_5S11S12S_7: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18695579 a. u.

5b_5S11S12S_8: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18614398 a. u.

5b_5S11S12S_9: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.19250519 a. u.

5b_5S11S12S_10: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18269693 a. u.

5b_5S11S12S_11: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.19269867 a. u.

5b_5S11S12S_12: SCF energy (PCM/mPW1PW91/6-31G*) = -1084.18521306 a. u

12.9. DP4+ results obtained using experimental ^{13}C data of compound **5** versus isomers **5a-5b**.

Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-31G(d)	Shielding Tensors

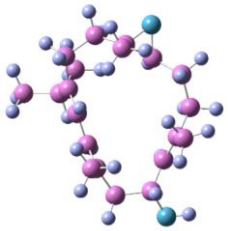
	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	–	–	–	–	–	–
sDP4+ (C data)	81.76%	18.24%	–	–	–	–
sDP4+ (all data)	81.76%	18.24%	–	–	–	–
uDP4+ (H data)	–	–	–	–	–	–
uDP4+ (C data)	97.89%	2.11%	–	–	–	–
uDP4+ (all data)	97.89%	2.11%	–	–	–	–
DP4+ (H data)	–	–	–	–	–	–
DP4+ (C data)	99.52%	0.48%	–	–	–	–
DP4+ (all data)	99.52%	0.48%	–	–	–	–

13.TDDFT-ECD calculation

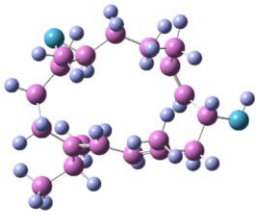
Conformational searches were done following the general protocols previously described for DP4+ calculation. For the resulting geometries, ECD spectra were obtained by TDDFT calculations performed with the same functional, basis set and solvent model as the energy optimization. Finally, the Boltzmann-averaged ECD spectra of **3**, **4**, **5** was obtained with SpecDis1.62 software.

Re-optimized conformers of (6*R*, 11*S,* 12*S*)-**3**, (5S, 11*R,* 12*R*)-**4** and (5S, 11*R,* 12*R*)-**5** calculated at the B3LYP/6-311G(d,p) level with IEFPCM solvent model for acetonitrile.

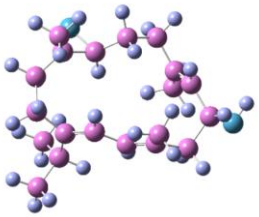
(6*R*,11*S,12S*)-**3:**



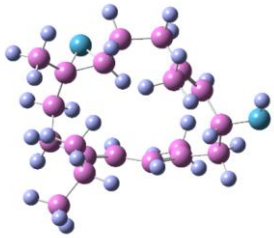
Conf.1
46.351%
-932.02316965



Conf.2
6.996%
-932.02637025



Conf.3
6.069%
-932.02637081



Conf.4
4.414%
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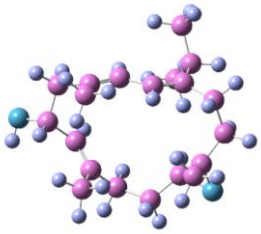

Conf.5
3.548%
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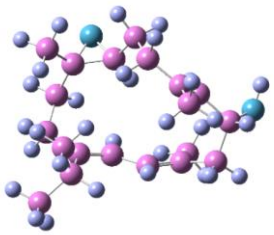
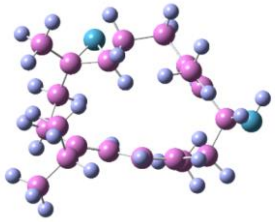


Conf.6
2.465%
-932.02549192



Conf.7
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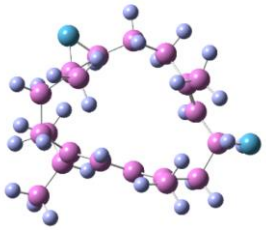

Conf.8
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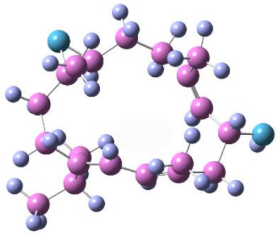

Conf.9
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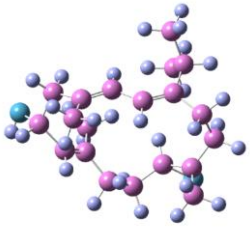

Conf.10
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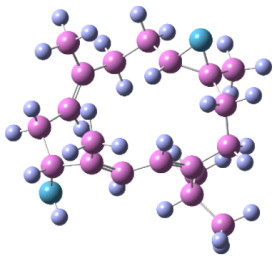
-932.02014682

(5S,11*R,12R*)-**4:**



Conf.1
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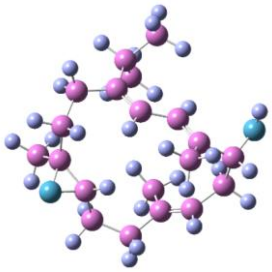

Conf.2
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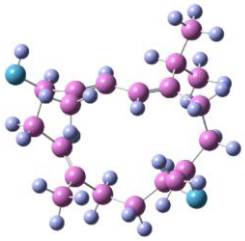

Conf.3
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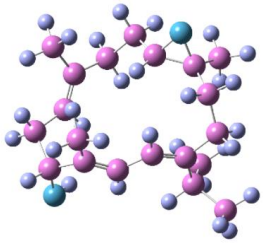

Conf.4
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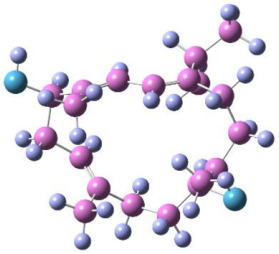

Conf.5
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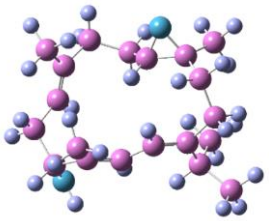
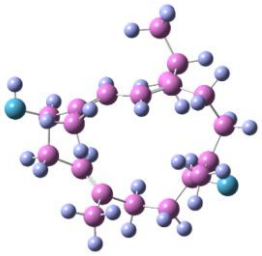


Conf.6
6.102%
-932.01914903



Conf.7
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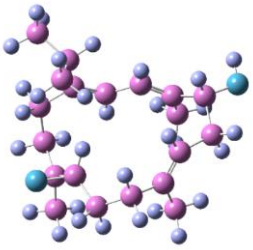

Conf.8
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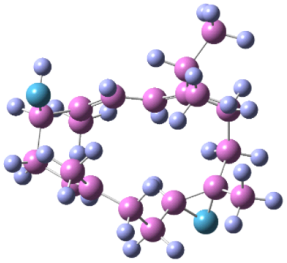

Conf.9
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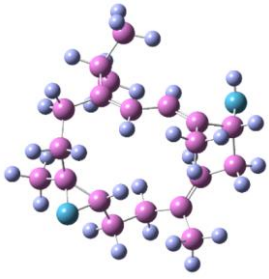
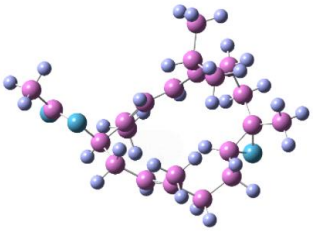


Conf.10
1.887%
-932.01638942

(5S,11*R,12R*)-**5:**



Conf.1
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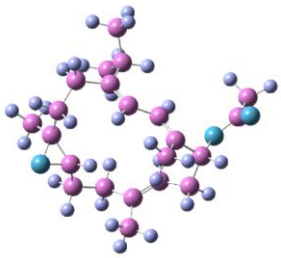

Conf.2
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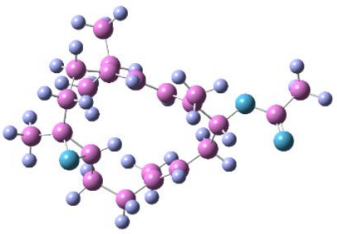

Conf.3
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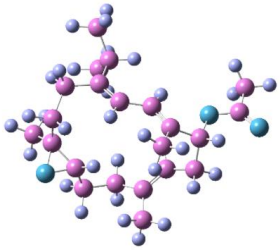

Conf.4
7.200%
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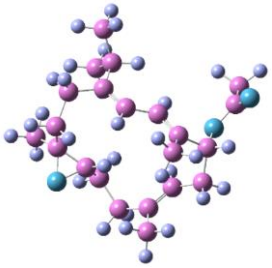

Conf.5
2.739%
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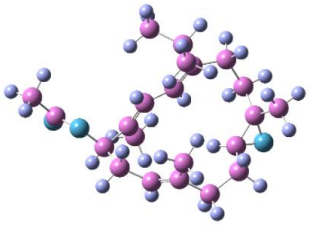

Conf.6
1.926%
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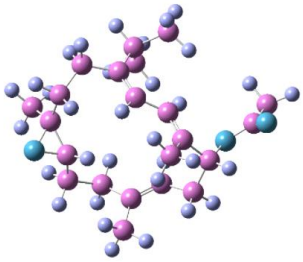

Conf.7
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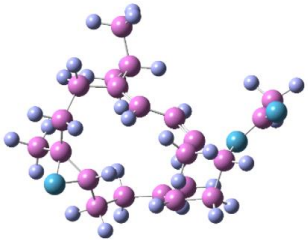

Conf.8
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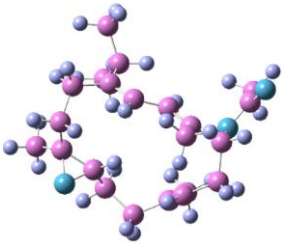

Conf.9
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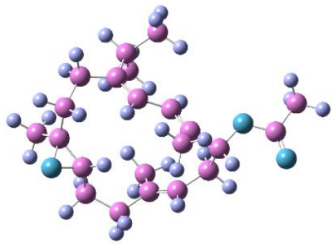

Conf.10
1.065%
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