Supporting Information

Exploring the natural piericidins as anti-renal cell carcinoma agents targeting peroxiredoxin 1

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Table S2. Volcano.

Table S3. Intersection of DEGs from three groups (PA50_Control, PA25_Control, PA50_PA25).

Table S4. KEGG enrichment analysis.

Table S5. CytoscapeInput-edges-PA-turquoise.txt default edge.

Table S6. CytoscapeInput-edges-PA-turquoise.txt default node.

Table S7. Deduced ORFs of Piericidin A Biosynthetic Gene Cluster of SCSIO NS126

Query_name	Query_ length	Description	Protein Homolog and Origin	Identity/ Similarity (%)	GenBank Accession Number
Query_1522	199	PieR	*Streptomyces piomogenus*	81.9	AEZ54373.1
Query_1523	2482	PieA1	*Streptomyces piomogenus*	73.5	AEZ54374.1
Query_1524	3379	PieA2	*Streptomyces piomogenus*	79.6	AEZ54375.1
Query_1525	1725	PieA3	*Streptomyces piomogenus*	79.2	AEZ54376.1
Query_1526	2161	PieA4	*Streptomyces piomogenus*	80.2	AEZ54377.1
Query_1527	1860	PieA5	*Streptomyces piomogenus*	79.9	AEZ54378.1
Query_1528	2354	PieA6	*Streptomyces piomogenus*	79.7	AEZ54379.1
Query_1529	228	PieB1	*Streptomyces piomogenus*	84.6	AEZ54380.1
Query_1530	170	PieC	*Streptomyces piomogenus*	89.4	AEZ54381.1
Query_1531	613	PieD	*Streptomyces piomogenus*	87.2	AEZ54382.1
Query_1532	257	PieB2	*Streptomyces piomogenus*	89.4	AEZ54383.1
Query_1533	589	PieE	*Streptomyces piomogenus*	89.4	AEZ54384.1

Table S8. 16S rRNA sequence of the strains *Streptomyces psammoticus* SCSIO NS126

TCGGGGTAACCTTCGACGGCTCATCCCTTACGGGTTAGGCCACCGGCTTCGGGTGTTACCGACTTTCGTGACGTGACGG

GCGGTGTGTACAAGGCCCGGGAACGTATTCACCGCAGCATGCTGATCTGCGATTACTAGCAACTCCAACTTCATGGGGT

CGAGTTGCAGACCCCAATCCGAACTGAGGCCGGCTTTTTGGGATTCGCTCCGCCTCACGGCATCGCAGCCCTTTGTACC

GACCATTGTAGCACGTGTGCAGCCCAAGACATAAGGGGCATGATGATTTGACGTCGTCCCCACCTTCCTCCGAGTTGAC

CCCGGCAGTCTCCTGTGAGTCCCCGACATTACTCGCTGGCAACACAGAACAAGGGTTGCGCTCGTTGCGGGACTTAAC

CCAACATCTCACGACACGAGCTGACGACAACCATGCACCACCTGTATACCGACCACAAGGGGGCACCCATCTCTGGAT

GTTTCCGGCATATGTCAAGCCTTGGTAAGGTTCTTCGCGTTGCGTCGAATTAAGCCACATGCTCCGCTGCTTGTGCGGG

CCCCCGTCAATTCCTTTGAGTTTTAGCCTTGCGGCCGTACTCCCCAGGCGGGGAACTTAATGCGTTAGCTGCGGCACCG

ACGACGTGGAATGTCGCCAACACCTAGTTCCCAACGTTTACGGCGTGGACTACCAGGGTATCTAATCCTGTTCGCTCCC

CACGCTTTCGCTCCTCAGCGTCAGTAATGGCCCAGAGATCCGCCTTCGCCACCGGTGTTCCTCCTGATATCTGCGCATTT

CACCGCTACACCAGGAATTCCGATCTCCCCTACCACACTCTAGCCTGCCCGTATCGAATGCAGACCCGGGGTTAAGCCC

CGGGCTTTCACATCCGACGCGACAGGCCGCCTACGAGCTCTTTACGCCCAATAATTCCGGACAACGCTCGCACCCTACG

TATTACCGCGGCTGCTGGCACGTAGTTAGCCGGTGCTTCTTCTGCAGGTACCGTCACTTGCGCTTCTTCCCTGCTGAAA

GAGGTTTACAACCCGAAGGCCGTCATCCCTCACGCGGCGTCGCTGCATCAGGCTTTCGCCCATTGTGCAATATTCCCCA

CTGCTGCCTCCCGTAGGAGTCTGGGCCGTGTCTCAGTCCCAGTGTGGCCGGTCGCCCTCTCAGGCCGGCTACCCGTCG

TCGCCTTGGTAGGCCATTACCCCACCAACAAGCTGATAGGCCGCGGGCTCATCCTGCACCGCCGGAGCTTTCCACCAA

CCCCCATGCGGAGGAAGGTCATATCCGGTATTAGACCCCGTTTCCAGGGCTTGTCCCAGAGTGCAGGGCAGATTGCCC

ACGTGTTACTCACCCGTTCGCCACTGATCCACCCCGAAGGGCTTCACCGTTCGACTGCAGGGTAAGCAGCT

Table S9. RT-qPCR primer sequence

Gene	Forward primer	Reverse primer
PRDX1	TCCTTTGGTATCAGACCCGA	TAAAAAGGCCCCTGAACGAG
EGFR	GACGCAGATAGTCGCCCAAA	ACGGTAGAAGTTGGAGTCTGTAGGA
ETS1	AGGAGATGGGGAAAGAGGAA	GTGTACCCCAGCAGGCTCT
SOD2	CTGATTTGGACAAGCAGCAA	CTGGACAAACCTCAGCCCTA
HK2	GATTTCACCAAGCGTGGACT	CCACACCCACTGTCACTTTG
SLC2A1	AAGGTGATCGAGGAGTTCTACA	ATGCCCCCAACAGAAAAGATG
LDHA	CAGCTTGGAGTTTGCAGTTAC	TGATGGATCTCCAACATGG
MET	GAGAAGCCCAAGCCCATCC	GCCCAGGGCTCAGAGCTT
VHL	CGTAGCGGTTGGTGACTTG	CCCTGGTTTGTTCCTCTGAC
β-ACTIN	ACGTGGACATCCGCAAAGAC	CAAGAAAGGGTGTAACGCAACTA

Table S10. Baseline clinical characteristics of human kidney samples

Characteristics	Group	number	Percentage (%)
Gender	Male	3	50
	Female	3	50
Age（years）	18-37	1	16.7
	37-65	5	83.3
Cancer	Clear cell carcinoma	6	100
	Non-cancer	0	0

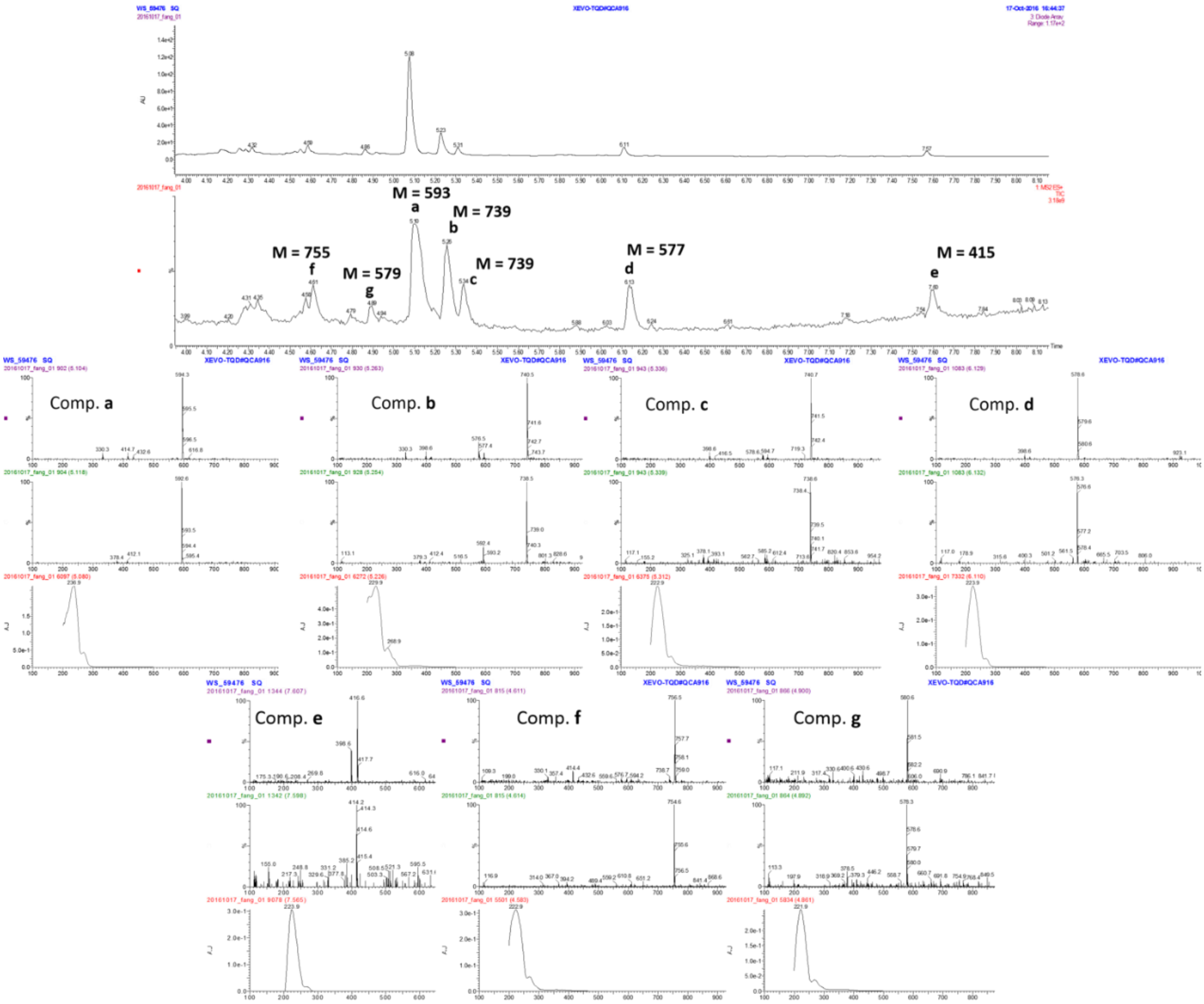

Figure S1. HPLC/MS spectra of the extract of strain NS126.

Piericidins present characteristic UV/vis spectra, one strong absorbance peak at 220–235 nm, and one weak absorbance peak at 260–270 nm. Aglycones or glycosides of piericidins could be determined by MS data. Peak **e** (7.6 min) of the TIC (total ion chromatogram) with molecular ion peak (*m/z* 416.6 $[M + H]^+$) suggested that it is possibly piericidin A or its isomer. Moreover, peaks **a** (5.1 min), **d** (6.1 min), and **g** (4.9 min) of the TIC were suggested to be monoglycosides, while peaks **b** (5.2 min), **c** (5.3 min), and **f** (4.6 min) were diglycosides of piericidin.

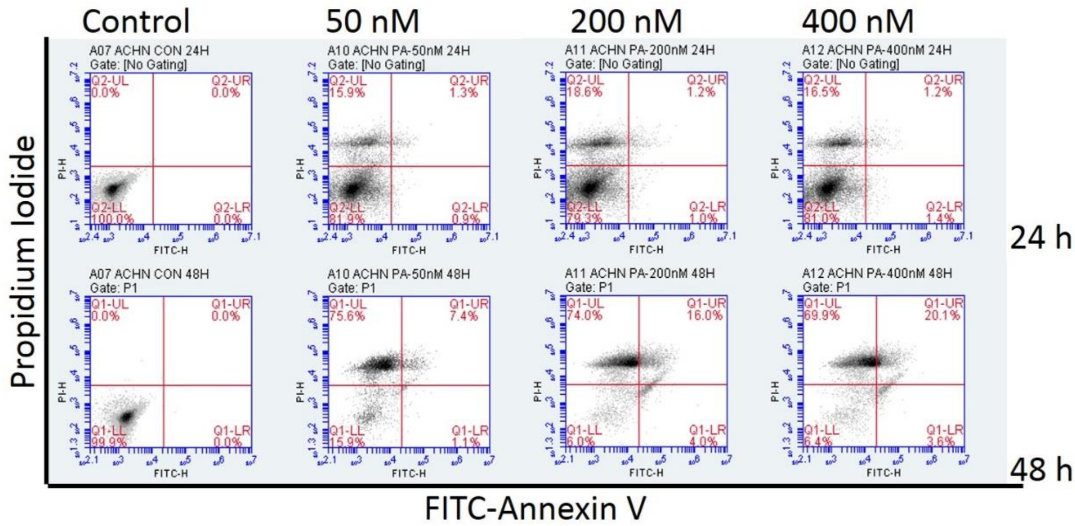

Figure S2. Cell apoptosis of ACHN cells induced by **1**.

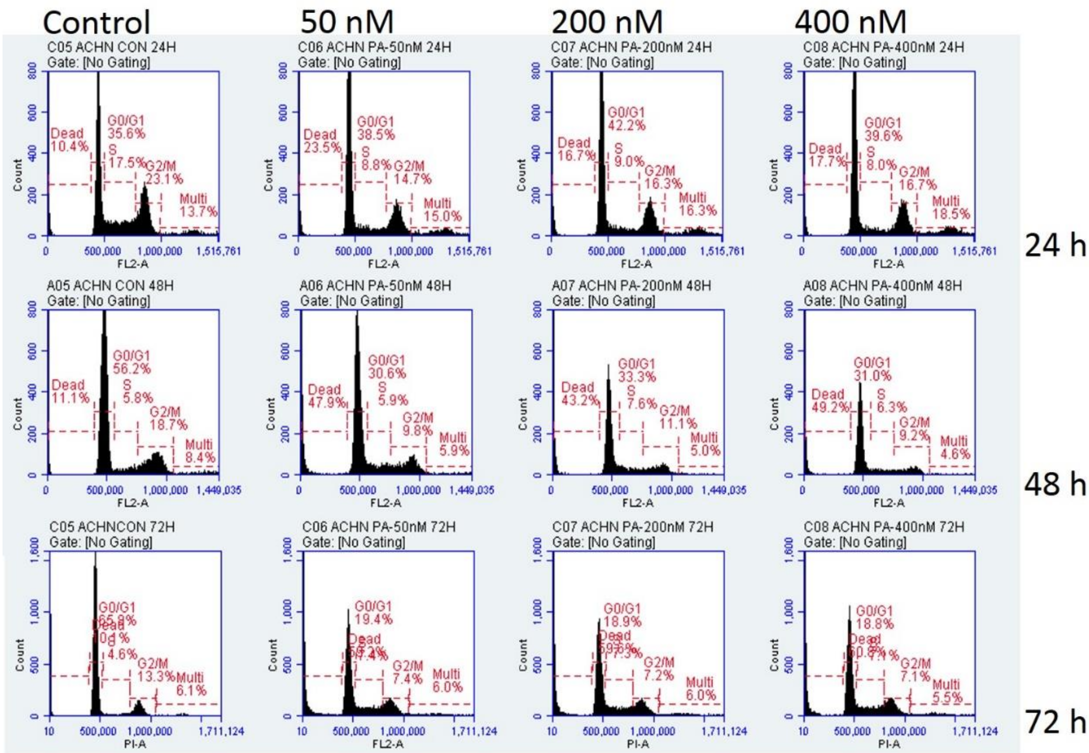

Figure S3. Cell cycle of ACHN cells treated with **1**.

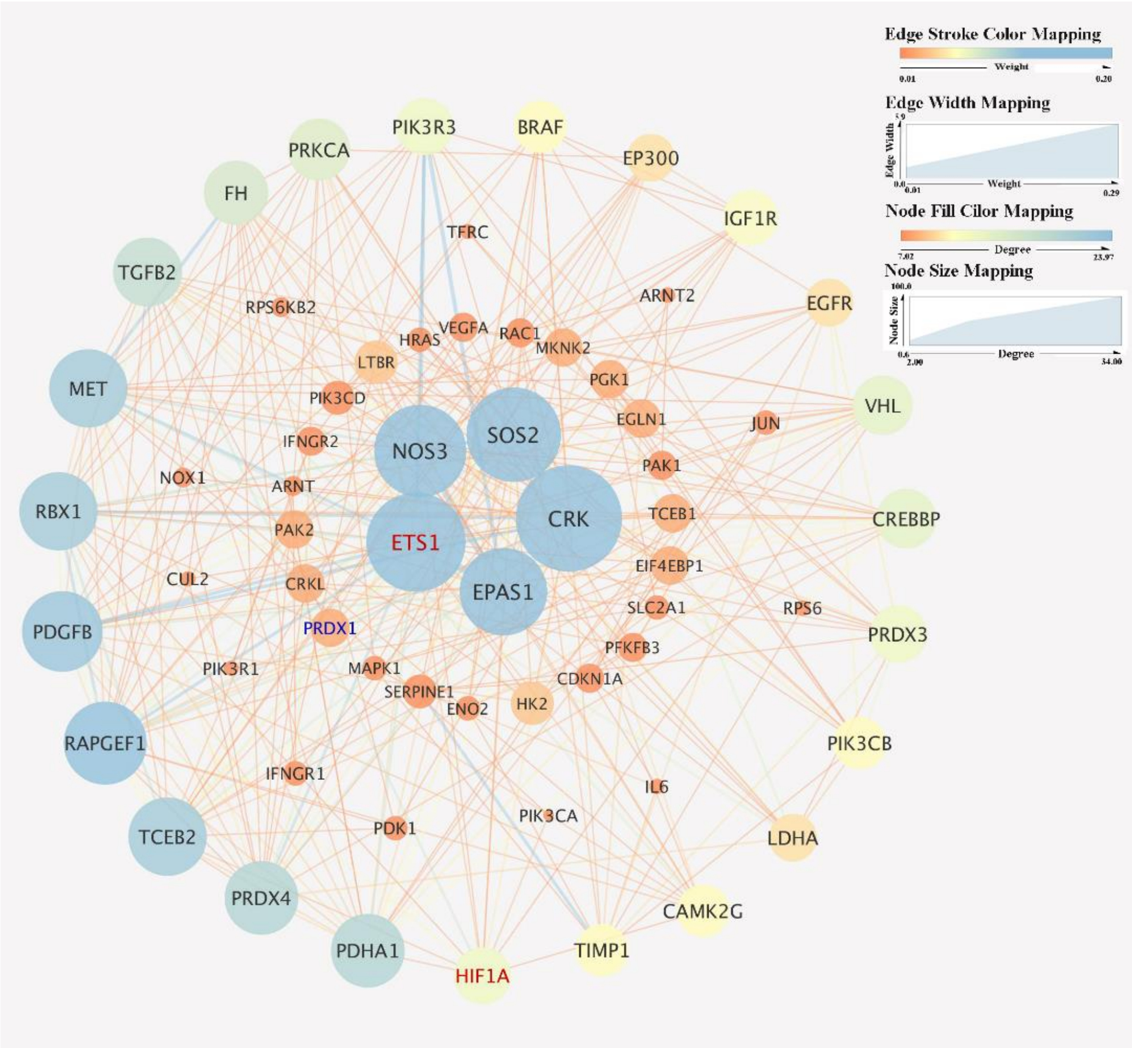

Figure S4. Weighted gene co-expression network of 63 DEGs genes analyzed in GSE40435. Bigger circle size and blue mapping bar means higher connectivity. There are 63 genes of a total of 71 genes which were included in the analysis using Microarray data from 101 tumors (GSE40435) were belonged to the unique Turquoise Module when the minimum module size was set to 20 genes per module, which were visualized in Cytoscape.

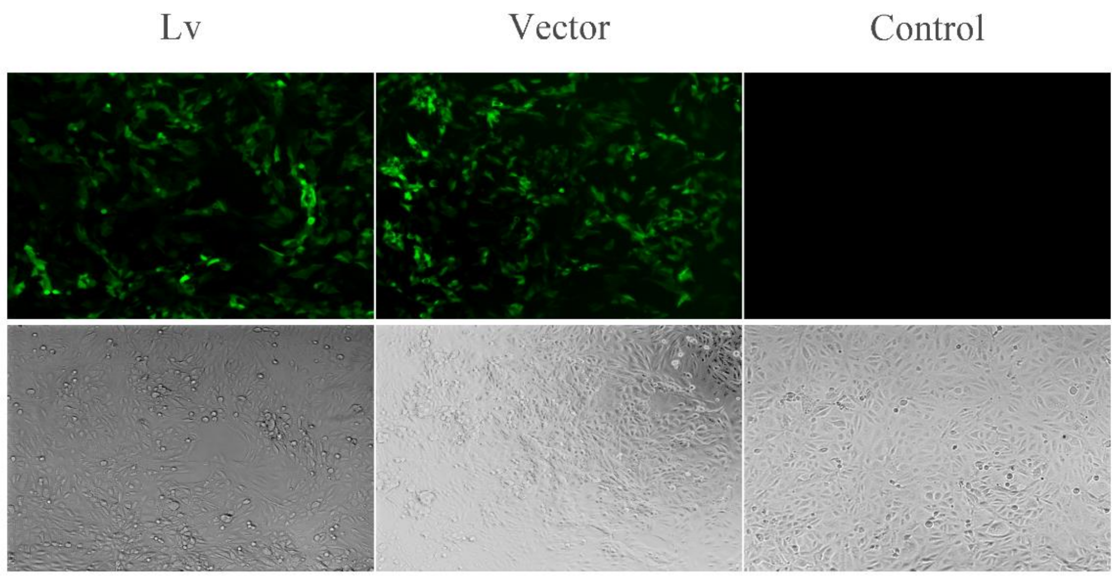

Figure S5. Representative images of immunofluorescence staining of shPRDX1 ACHN cells with 100X magnification in 72h. Lentivirus PRDX1 shRNA was diluted in enhance infection solution (Genechem, China). After 6-hour infection, complete medium containing puromycin (1μg/mL) was add to select the PRDX1 knockdown ACHN cells. The GFP microscope (green) indicates the shPRDX1 ACHN cells, compared with light microscope.

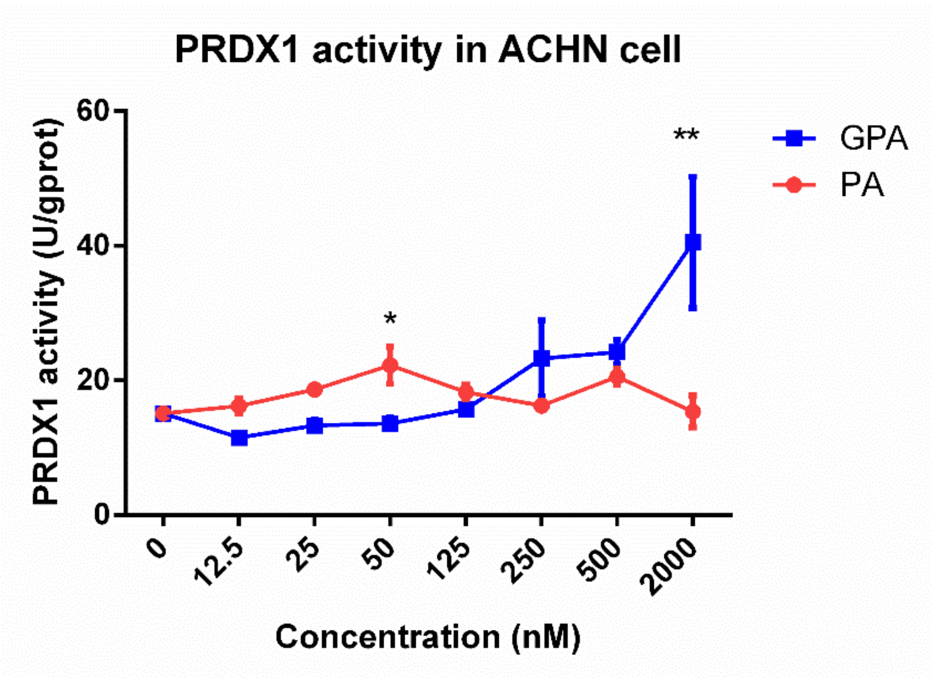

Figure S6. Antioxidant activities of PRDX1 after treated with PA/GPA in 24h using ELISA assay.

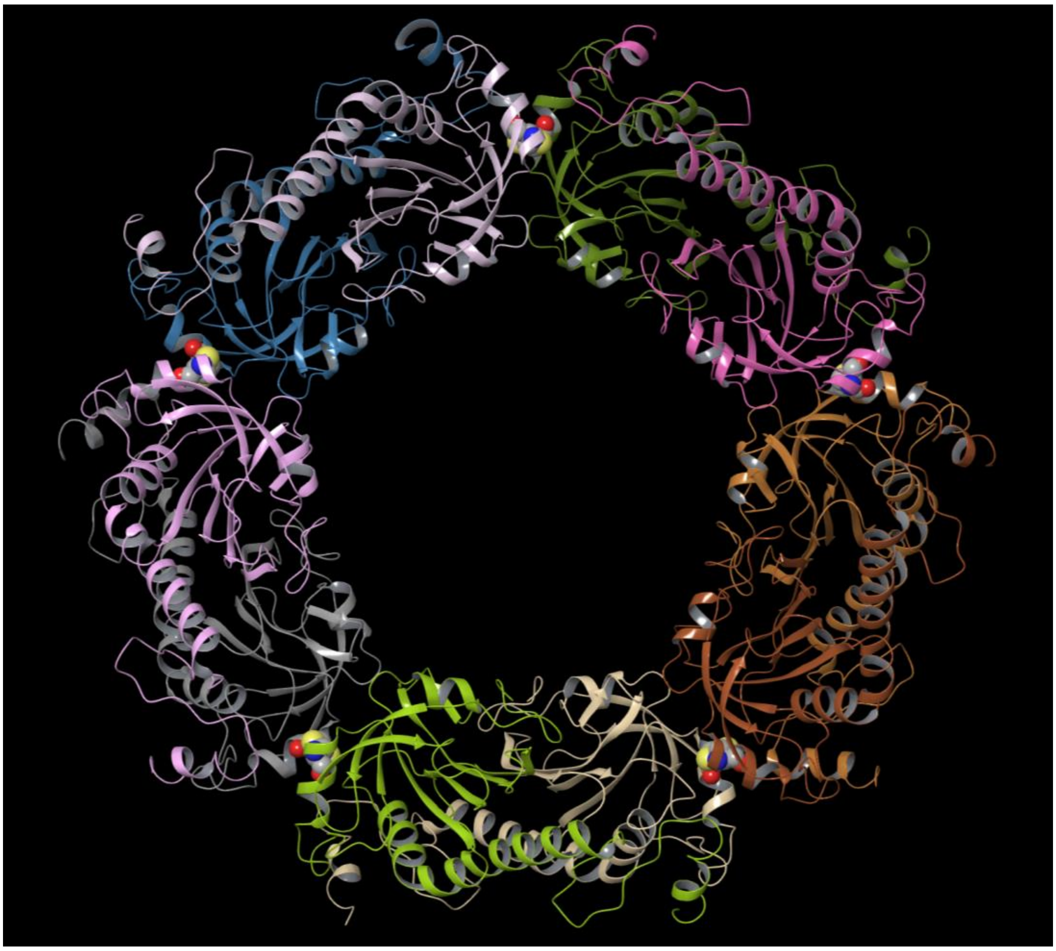

Figure S7. The structure of decameric form of PRDX1 (PDB entry 2Z9S).

Supplementary Structure Elucidation

Structure elucidation of compounds 1-27.

Compound **1**, the main metabolism of the strain SCSIO NS104, was established with its molecular formula $C_{25}H_{37}NO_4$, by HPLC/HRESIMS analysis in the extract of the fermentation. The structure of the purified **1** was characterized by comparison of its ^{1}H and ^{13}C NMR date with literature data[1] and was determined to be piericidin A (**1**, also piericidin A1).

Compound **2** was isolated as pale yellow oil. Its molecular formula was established by HR-ESIMS (*m/z* 402.2649 $[M + H]^+$) to be $C_{24}H_{35}NO_4$. Comparison of its ^{1}H and ^{13}C NMR date with those of piericidin A (**1**) indicated that they shared the piericidin skeleton. The only difference was the absence of the 14-Me in **2**, which was confirmed by the HMBC correlations from H-10 (δ_H 3.75, dd, J = 7.6, 7.6 Hz) to C-11 (δ_C 132.2), H-11 (δ_H 5.46, dd, J = 7.6, 15.2 Hz) to C-13 (δ_C 18.1), H-12 (δ_H 5.70, dq, J = 15.2, 6.4 Hz) to C-10 (δ_C 77.5), and H_3-13 (δ_H 1.72, d, J = 6.4 Hz) to C-12 (δ_C 129.1), together with COSY correlations H_3-13/H-12/H-11/H-10/H-9/H-8 (H_3-15) (**Figure S8**). The 2*E*, 5*E*, 7*E* and 11*E* configurations of the double bonds were also deduced by the NOESY correlations (**Figure S8**). Thus, compound **2** was identified as 11-demethyl-piericidin A (**2**).

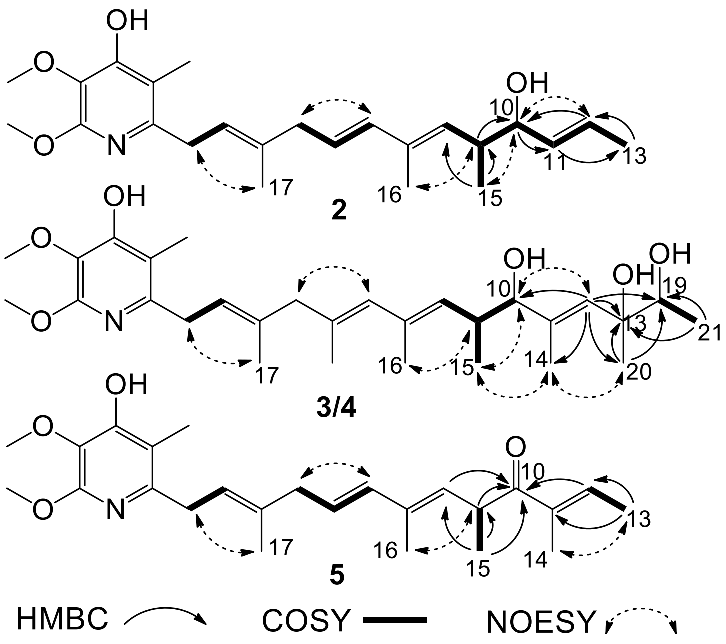

Figure S8. Key HMBC, ^{1}H-^{1}H COSY and NOESY correlations of **2–5.**

Compound **3** was isolated as pale yellow oil. Comparison of its ^{1}H and ^{13}C NMR date with those of IT-143-A [2] and piericidin C$_8$[3] indicated that they shared the piericidins skeleton. The only difference was an additional oxygenated methine (δ_C 75.1, δ_H 3.66, CH-19) and oxygenated quaternary carbon (δ_C 76.5, C-13) in **3**, instead of the olefinic bond in IT-143-A. Two hydroxyl groups on C-13 and C-19, confirmed by the HMBC correlations from H-12 (δ_H 5.46, s), H-20 (δ_H 1.28, s, 3H), H-21 (δ_H 1.14, d, J = 6.4 Hz, 3H) to C-13 and C-19 (**Figure S8**), were also supported by molecular formula $C_{29}H_{45}NO_6$ established by HRESIMS, rather than the epoxide moiety. All of the double bonds and C-9/C-10 in **3** were deduced to be the same configurations (2*E*, 5*E*, 7*E*, 11*E*, 9*R*, 10*R*) with those reported piericidins, by the NOESY correlations, coupling constants, and also a biosynthetic point of view.

Compound **4** has a same molecular formula $C_{29}H_{46}NO_6$ with **3**, as deduced from its HRESIMS. Its 1D and 2D NMR spectra showed resonances exactly similar with those of **3**, meanwhile the configurations (2*E*, 5*E*, 7*E*, 11*E*, 9*R*, 10*R*) of the four double bonds and C-9/C-10 were also the same. The small difference of C-12 (δ_C 132.8 in **3**, and δ_C 132.0 in **4**) and H-19 (δ_H 3.83 in **3**, and δ_H 3.77 in **4**) chemical shifts, by comparison of ^{1}H and ^{13}C NMR (in $CDCl_3$) date of **3** and **4** (**Tables S11, S12**), as well as their different ECD curves (**Figure S9**), suggested **4** as a C-13/C-19 epimer of **3**. The absence of NOESY correlation between H_3-20 and H-19 of **3**/**4** suggested an *anti*-relationship between 13-OH and 19-OH. The Boltzmann-weighted ECD curve of (13*S*, 19*R*)-**3** was calculated and compared with the experimental ECD curves of **3**/**4** (**Figure S9**), which led to the determination of 13*S*, 19*R* absolute configuration of **3**, and 13*R*, 19*S* absolute configuration of **4**. Consequently, compounds **3** (13*S*,19*R*) and **4** (13*R*,19*S*) were identified as a pair of epimers of (2*E*,5*E*,7*E*,11*E*,9*R*,10*R*,13*S**,19*R**)-13,19-dihydroxyl-IT-143-A.

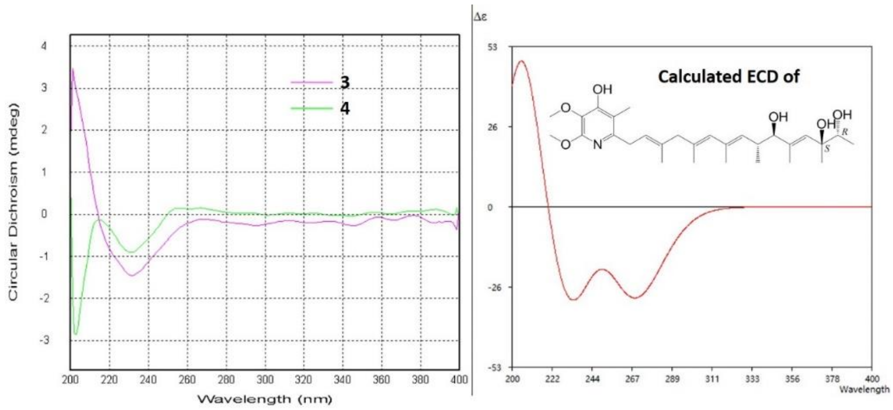

Figure S9. ECD spectrum of **3**, **4** and the calculated ECD curve of (13*S*, 19*R*)-**3**.

Compound **5** was isolated as clear oil. Its molecular formula was established by HR-ESIMS to be $C_{25}H_{35}NO_4$. Comparison of its ^{1}H and ^{13}C NMR date with those of piericidin A (**1**) (**Tables S11, S12**) showed that, the only difference was the replacement of the CHOH-10 in **1** by a ketone carbonyl group in **5**, which was confirmed by the HMBC correlations showed in **Figure S8**. C-10 ketone piericidin A was previously reported as a synthetic analogue of **1**.[4] The specific rotations (**5**: $[\alpha]_D^{20}$ – 5.5, *c* 0.2, $CHCl_3$; C-10 ketone piericidin A[4]: $[\alpha]_D^{25}$ – 14, *c* 0.1, CH_2Cl_2) indicated that **5** shared the same absolute configuration (9*R*) as those synthetic C-10 ketone piericidin A. Thus, (9*R*) 10-ketone piericidin A (**5**) was obtained in this study as a new natural product.

The structures of the other five known piericidin aglycones (**6–9**) were characterized by comparison of their NMR and MS data with literature data and were determined to be piericidins C2 (**6**), C1(**7**), and A2 (**8**) [1a], and 7-demethylpiericidin A1 (**9**).[5]

Compound **10** was suggested to be a piericidin glycoside, with molecular weight 577 and similar UV curve with piericidin A (molecular weight 415), by HPLC/HRESIMS analysis in the extract of the strain SCSIO NS126 fermentation. The structure of the purified **10** was characterized by comparison of its ^{1}H and ^{13}C NMR date with literature data[6] and was determined to be glucopiericidin A (**10**).

Compound **11** was suggested to be an oxidative product of **10** because of its molecular weight 593 given by HPLC/HRESIMS. It was determined to be 13-hydroxyglucopiericidin A (**11**) by comparison of its ^{1}H and ^{13}C NMR date with literature data.[7]

Compound **12** was obtained with its molecular formula $C_{30}H_{45}NO_9$, established by HR-ESIMS (*m/z* 564.3185 $[M + H]^+$). Comparison of its ^{1}H and ^{13}C NMR date with those of **10** indicated that they shared the piericidin glycoside skeleton. The only difference was the absence of the 16-Me linked to C-7 in **12**, which was confirmed by the HMBC correlations like from H-5 (δ_H 5.54, dt, J = 13.9, 7.1 Hz) to C-7 (δ_C 131.0), and from H-9 (δ_H 2.45, m) to C-7, together with H_2-4/H-5/H-6/H-7/H-8/H-9/H-10 COSY correlations (**Figure S10**). Compound **12** was suggested to be the glycoside of 7-demethylpiericidin A1 (**9**). The ^{1}H and ^{13}C NMR spectrum (CD_3OD) showed signals due to a D-glucose group [δ_H 4.20 (d, J = 7.8 Hz, H-1″); 3.19 (d, J = 8.9, 7.8 Hz, H-2″); 3.30 (dd, J = 8.9, 8.7 Hz, H-3″); 3.29 (dd, J = 9.1, 8.7 Hz, H-4″); 3.11(ddd, J = 9.1, 5.3, 2.5 Hz, H-5″); 3.62 (dd, J = 11.8, 5.4 Hz, H-6″a); 3.74 (dd, J = 11.8, 2.5 Hz, H-6″b); δ_C 104.2 (C-1″), 75.7 (C-2″), 78.3 (C-3″), 71.6, (C-4″), 77.7 (C-5″), and 62.8 (C-6″)], which was also confirmed by the acid hydrolysis of **12**. The coupling constant of the anomeric proton (δ_H 4.20, d, J = 7.8 Hz) indicated that the glycosyl linkage is of *β*-configuration, and the 10-*O*-D-glucoside linkage was determined by the down-field shift of C-10 (δ_C

93.7) and the HMBC correlations from H-1″ to C-10.[6] The double bonds in side chain and C-9/C-10 were deduced to be the same configurations (2*E*,5*E*,7*E*,11*E*,9*R*,10*R*) with those of obtaned piericidin aglycones, by the NOESY correlations, coupling constants, and also a biosynthetic point of view. Thus, **12** was characterized as 7-demethylglucopiericidin A (**12**).

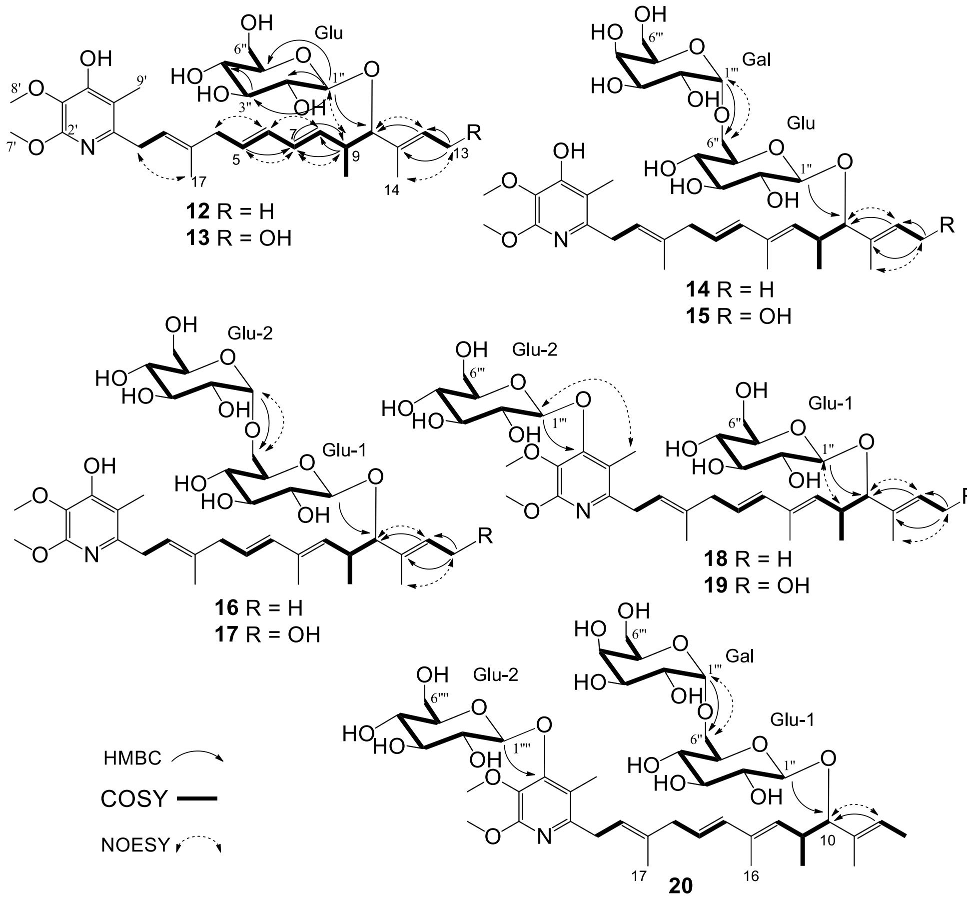

Figure S10. Key HMBC, COSY and NOESY correlations of **12–20.**

Compound **13** was obtained with its molecular formula $C_{30}H_{45}NO_{10}$, established by HR-ESIMS (*m/z* 580.3126 [M + H]$^+$). Comparison of its ^{1}H and ^{13}C NMR date with those of **12** indicated that they shared the piericidin glycoside skeleton (**Tables S13, S15**). The only difference was the replacement of the 13-Me in **12** by an oxygenated methylene in **13**, which was confirmed by the HMBC correlations from H$_2$-13 (δ_H 3.90, dd, J = 13.0, 6.3 Hz; 3.98, dd, J = 13.0, 6.3 Hz) to C-11 (δ_C 135.4) and C-12 (δ_C 128.7), and COSY correlations of H$_2$-13/H-12 (δ_H 5.43, t, J = 6.3 Hz). The glycosyl linkage and the configurations were also confirmed by HMBC, COSY and NOESY correlations showed in **Figure S10**. Compound **13** was characterized as 7-demethyl-13-hydroxyglucopiericidin A (**13**).

Compound **14** was obtained with its molecular formula $C_{37}H_{57}NO_{14}$, established by HR-ESIMS (*m/z* 738.3712 [M – H]$^-$). Comparison of its ^{1}H and ^{13}C NMR date with those of **10** indicated that **14** is also a piericidin glycoside with an additional glycosyl group (**Table S13, S15**). NMR tube degradation method for sugar analysis of **14** revealed that another sugar was D-galactose (**Figure S11**),[8] also supported by ^{1}H and ^{13}C NMR date (**Figure S12**).[9] The coupling constant of the two anomeric protons (δ_H 4.09, d, J = 7.8 Hz, H-1″ of Glu; δ_H 4.64, d, J = 2.2 Hz, H-1‴ of Gal) indicated that the glycosyl linkage were of β- and α- configurations for glucose and galactose, respectively. The galactose linkage was established at C-6″ of the glucosyl residue by an HMBC correlations from δ_H

4.64 (H-1‴ of Gal) to δ_C 67.2 (C-6″ of Glu). Thus, compound **14** was characterized as piericidin A 10-*O*-α-D-galactose (1→6)-β-D-glucoside (**14**). This structure was reported recently without clear determination.[9]

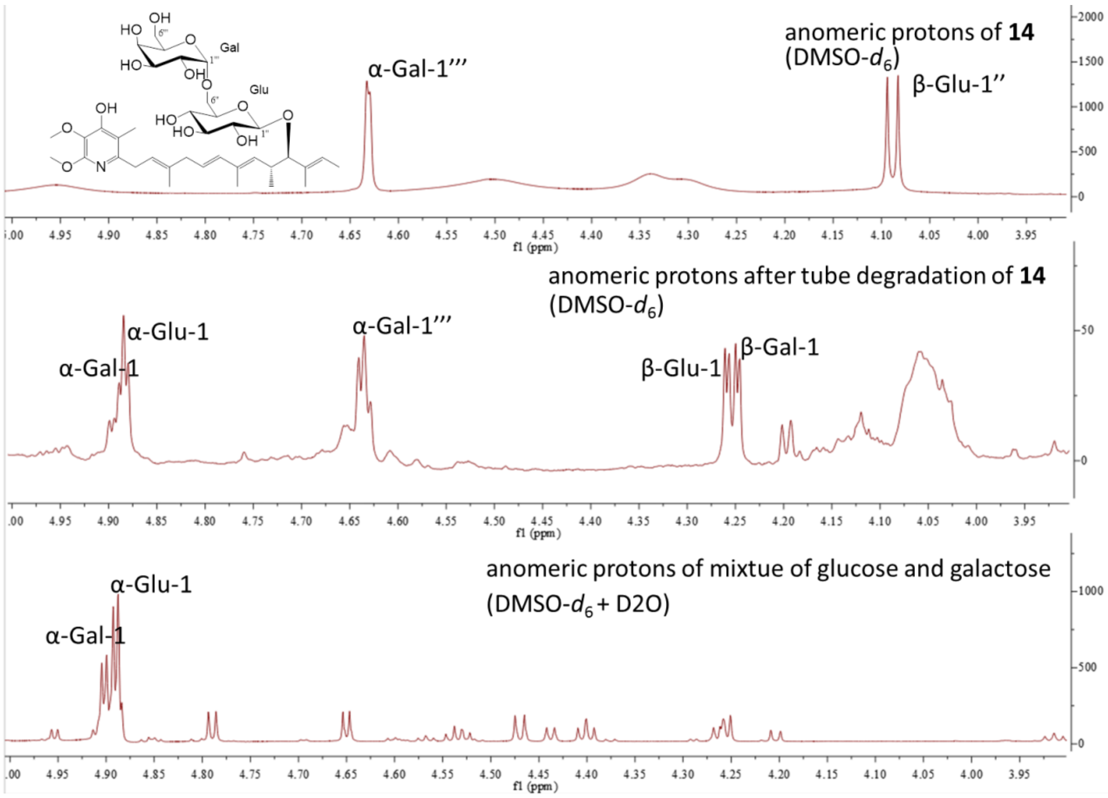

Figure S11. Anomeric protons analysis of **14** before and after NMR tube degradation.

Compound **15** was obtained with its molecular formula $C_{37}H_{57}NO_{15}$, established by HR-ESIMS (*m/z* 754.3646 $[M-H]^-$). Comparison of its ^1H and ^{13}C NMR date with those of **14** indicated that they shared the piericidin diglycosides skeleton. The only difference was the replacement of the 13-Me in **14** by an oxygenated methylene in **15**, which was confirmed by the HMBC correlations from (3.96, dd, J = 13.0, 6.3 Hz; 4.00, dd, J = 13.0, 6.3 Hz) to C-11 (δ_C 134.3) and C-12 (δ_C 128.8), and COSY correlations of H_2-13/H-12 (δ_H 5.42, t, J = 6.3 Hz) (**Figure S10**). The coupling constant of the two anomeric protons (δ_H 4.11, d, J = 8.0 Hz, H-1″ of Glu; δ_H 4.64, d, J = 2.9 Hz, H-1‴ of Gal) indicated that the same glycosyl linkage (*β*-D-glucose and *α*-D-galactose configurations) in **15** as those in **14**. Compound **15** was characterized as 13-hydroxypiericidin A 10-*O*-*α*-D-galactose (1→6)-*β*-D-glucoside (**15**).

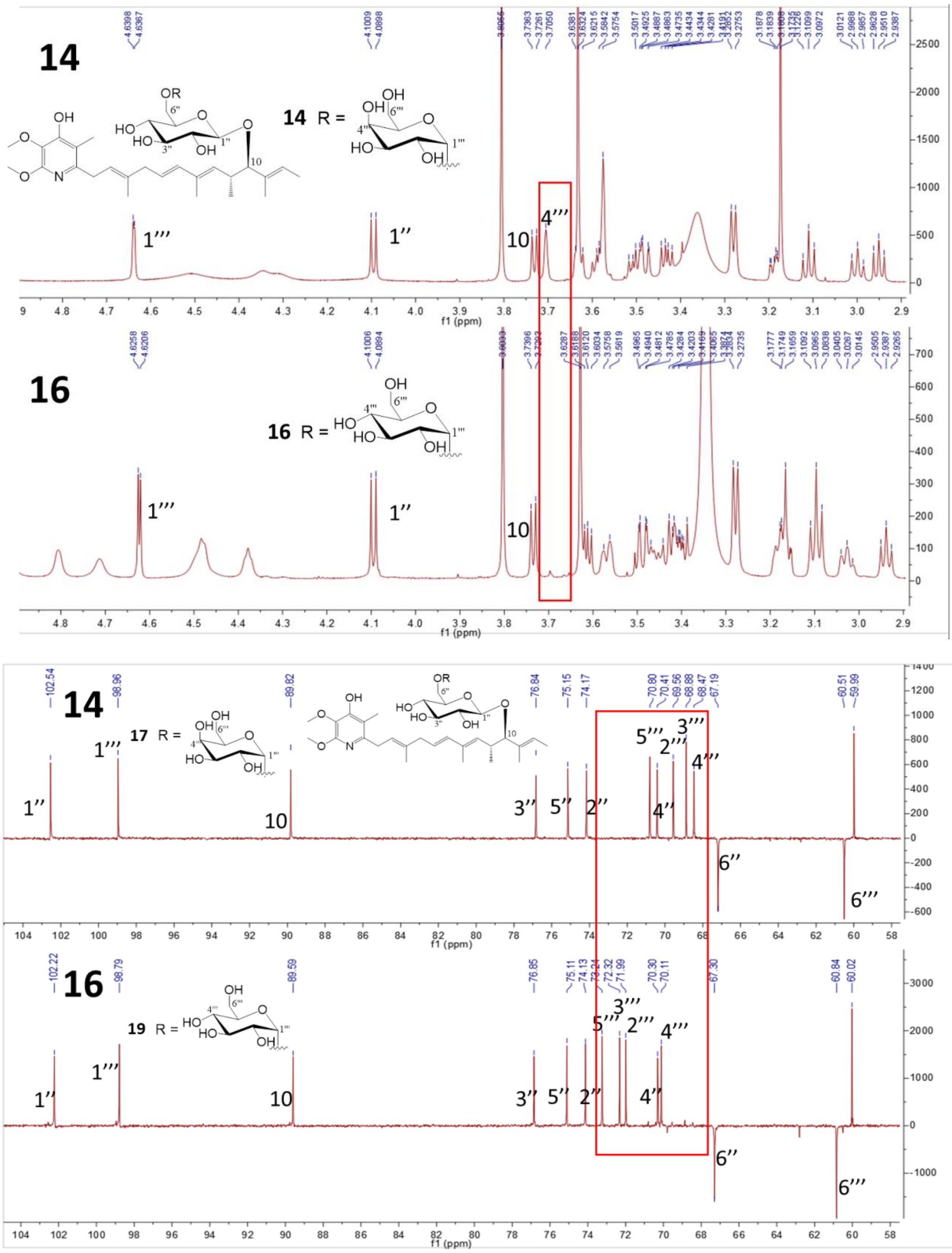

Figure S12. Comparison of the sugar moieties of **14** and **16** in ^{1}H and ^{13}C NMR spectrum.

Compound **16** was also suggested to be a piericidin diglycoside, based on the molecular formula $C_{37}H_{57}NO_{14}$ established by HR-ESIMS (*m/z* 738.3702 $[M - H]^-$). The NMR data of **16** were similar to those of **14**, except for some small differences of the ^{1}H and ^{13}C chemical shifts of position CH-2‴, CH-3‴, CH-4‴ (**Figure S12**, **Tables S13, S15**). Only glucose was yield after acid hydrolysis of **16**, suggesting diglucoside of **16**. The coupling constant of the two anomeric protons (δ_H 4.10, d, J = 7.8 Hz, H-1″ of Glu-1; δ_H 4.62, d, J = 3.6 Hz, H-1‴ of Glu-2) indicated that the glycosyl linkage were of *β*- and *α*- configurations for two glucoses. The Glu-2 linkage was established at C-6″ of the Glu-1 by an HMBC correlations from δ_H 4.62 (H-1‴ of Glu-2) to δ_C 67.3 (C-6″ of Glu-1) (**Figure S10**). Thus, compound **16** was characterized as piericidin A 10-*O*-*α*-D-glucose (1→6)-*β*-D-glucoside (**16**). This structure was reported as the name BE-14324 in the Japanese patent. [10]

Compound **17** was obtained with its molecular formula $C_{37}H_{57}NO_{15}$, established by HR-ESIMS (*m/z* 754.3660 $[M-H]^-$). Comparison of its ^{1}H and ^{13}C NMR date with those of **16** indicated that they shared the piericidin diglucosides skeleton (**Table S13, S15**). The only difference was the replacement of the 13-Me in **16** by an oxygenated methylene in **17**, which was confirmed by the HMBC correlations from H_2-13 (3.97, dd, J = 13.0, 6.3 Hz; 4.01, dd, J = 13.0, 6.3 Hz) to C-11 (δ_C 134.0) and C-12 (δ_C 129.0), and COSY correlations of H_2-13/H-12 (δ_H 5.42, m) (**Figure S10**). The coupling constant of the two anomeric protons (δ_H 4.12, d, J = 7.8 Hz, H-1′′ of Glu-1; δ_H 4.64, d, J = 3.6 Hz, H-1′′′ of Glu-2) indicated that the same glycosyl linkage in **17** as those in **16**. Compound **17** was characterized as 13-hydroxypiericidin A 10-*O*-*α*-D-glucose (1→6)-*β*-D-glucoside (**17**).

Compound **18** was also suggested to be a piericidin diglucoside, based on the molecular formula $C_{37}H_{57}NO_{14}$ established by HR-ESIMS (*m/z* 738.3684 $[M-H]^-$). Comparison of its NMR date with those of glucopiericidin A (**10**) indicated that the only difference was an additional glycosyl group linked on OH-4′ of the pyridine ring, which was confirmed by the HMBC correlations from H-1′′′ (δ_H 5.09, d, J = 7.4 Hz) to C-4′ (δ_C 154.3), and NOESY correlations of H-1′′′/H-9′ (δ_H 2.07, s, 3H) (**Figure S10**). The coupling constant of the two anomeric protons, indicated that both of the glucoses were *β* glucosyl linkage. So, the structure of **18** was characterized as 4′-*O*-*β*-D-glucose glucopiericidin A (**18**).

Compound **19** was obtained with its molecular formula $C_{37}H_{57}NO_{15}$, established by HR-ESIMS (*m/z* 756.3829 $[M+H]^+$). Comparison of its ^{1}H and ^{13}C NMR date with those of **18** indicated that they shared the piericidin diglucosides skeleton (**Tables S13, S15**). The only difference was the replacement of the 13-Me in **18** by an oxygenated methylene in **19**, which was confirmed by the HMBC correlations from H_2-13 (4.05, dd, J = 12.8, 7.2 Hz; 4.17, dd, J = 12.8, 7.2 Hz) to C-11 (δ_C 139.1) and C-12 (δ_C 128.8), and COSY correlations of H_2-13/H-12 (δ_H 5.58, t, J = 6.2 Hz) (**Figure S10**). The coupling constant of the two anomeric protons indicated that both of the glucoses were *β* glucosyl linkage. So, the structure of **19** was characterized as 4′-*O*-*β*-D-glucose 13-hydroxyglucopiericidin A (**19**).

Compound **20** was obtained with its molecular formula $C_{43}H_{67}NO_{19}$, established by HR-ESIMS (*m/z* 902.4390 $[M+H]^+$). Its NMR date indicated three glycosyl groups in the structure, with three anomeric protons (δ_H 4.25, d, J = 7.8 Hz, H-1′′ of Glu-1; δ_H 4.84, d, J = 3.2 Hz, H-1′′′ of Gal; δ_H 5.23, d, J = 7.5 Hz, H-1′′′′ of Glu-2). Comparison of its NMR date with those of **14** indicated that **20** had the same α-D-galactose (1→6)-β-D-glucoside moiety linked on C-10, and comparison with those of **18** and **19** revealed a *β*-D-glucose group linked on OH-4′ of the pyridine ring in **20**. The structure of this piericidin triglycoside was confirmed by the HMBC, COSY, and NOESY correlations (**Figure S10**), and characterized as 4′-*O*-*β*-D-glucose piericidin A 10-*O*-*α*-D-glucose (1→6)-*β*-D-glucoside (**20**).

Compound **21** was obtained with its molecular formula $C_{32}H_{51}NO_{11}$, established by HR-ESIMS (*m/z* 626.3543 $[M+H]^+$). Comparison of its ^{1}H and ^{13}C NMR date with those of glucopiericidin A (**10**) indicated that they shared the piericidin glycoside skeleton. The only difference was the replacement of the C-5/C-6 olefinic methines in **10** by two oxygenated methines and another oxygenated methyl in **21**. The moiety of -OH on C-5 and -OMe on C-6 was confirmed by the HMBC correlations from H_2-4 (2.51, br.d, J = 13.9 Hz; 2.03, dd, J = 13.9, 8.9 Hz) to C-5 (δ_C 70.1), from H-6 (δ_H 3.20, d, J = 8.4 Hz) to C-4 (δ_C 43.2), C-5, C-8 (δ_C 137.5), C-16 (δ_C 11.3), from H_3-(6-OMe) (δ_H 3.11, s) to C-6 (δ_C 92.3), and COSY correlations of H_2-4/H-5 (δ_H 3.69, ddd, J = 8.9, 8.4, 2.7 Hz)/H-6 (**Figure S13**). The NMR data (**Tables S14, S15**) indicated the presence of a *β*-D-glucose group in **21**, same as in **10–13**. All the double bonds in side chain were deduced to be *E* configurations by the NOESY correlations.

The C-9/C-10 configurations were considered as 9*R*, 10*R*, as same as those of all the obtaines piericidins, on a biosynthetic point of view. The relative configurations of C-5/C-6 were determined by the coupling constant ($J_{H\text{-}5/H\text{-}6}$ = 8.4 Hz), and the NOESY correlation of H-(6-OMe) and H-10 indicated they were on the same side of the C-7/C-8 double bond (**Figure S13**). Accordingly, compound **21** was characterized as 5-hydroxy-6-hydroxymethyl glucopiericidin A (**21**).

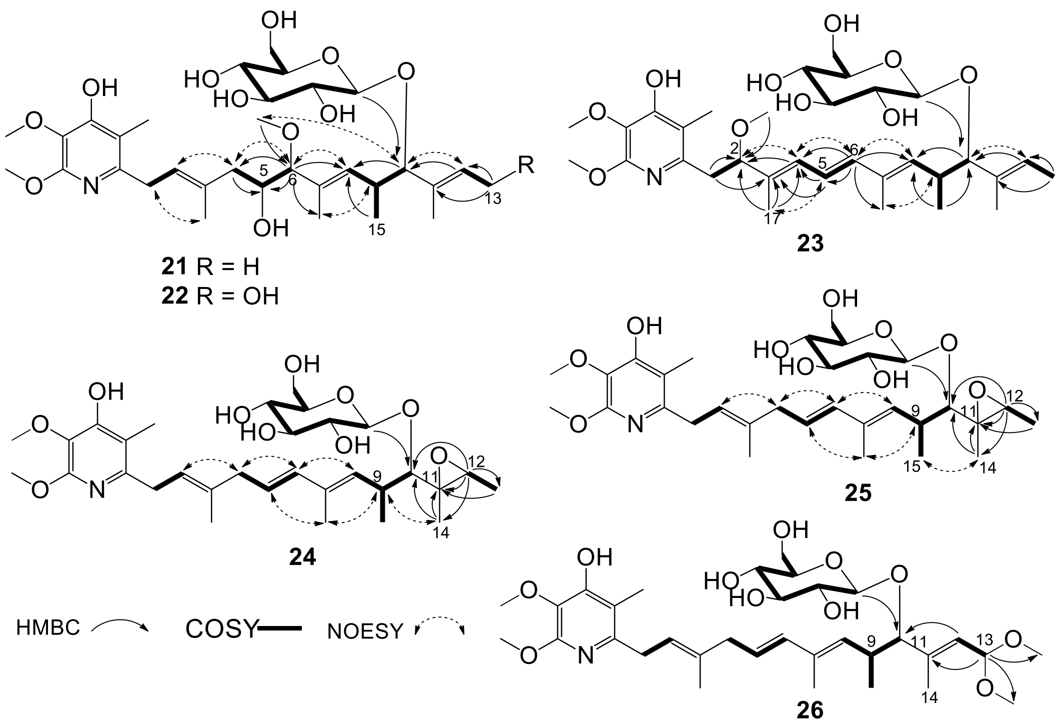

Figure S13. Key HMBC, COSY and NOESY correlations of **21**–**26.**

Compound **22** was obtained with its molecular formula $C_{32}H_{51}NO_{12}$, established by HR-ESIMS (*m/z* 642.3481 $[M + H]^+$). The NMR data (**Tables S14, S15**) of **22** were similar to those of **21**, except for the replacement of the 13-Me in **21** by an oxygenated methylene in **22**, which was confirmed by the HMBC correlations from H_2-13 (4.05, dd, *J* = 12.8, 6.0 Hz; 4.18, dd, *J* = 12.8, 6.0 Hz) to C-11 (δ_C 139.0) and C-12 (δ_C 129.2), and COSY correlations of H_2-13/H-12 (δ_H 5.58, t, *J* = 6.3 Hz) (**Figure S13**). All the configurations were determined by the NOESY correlations, coupling constants, as well as a biosynthetic point of view. Thus, compound **22** was characterized as 5-hydroxy-6-hydroxymethyl-13-hydroxyglucopiericidin A (**22**).

Compound **23** was obtained with its molecular formula $C_{32}H_{49}NO_{10}$, established by HR-ESIMS (*m/z* 608.3444 $[M + H]^+$). Comparison of its ^{1}H and ^{13}C NMR date with those of glucopiericidin A (**10**) indicated that they shared the piericidin glycoside skeleton, but there were some differences with the chemical shifts on position 1–6 of the side chain (**Tables S14, S15**), together with an additional hydroxymethyl group. The hydroxymethyl was linked on C-2, and the conventional C-2/C-3 double bond was moved to C-3/C-4 here. This usual moiety in piericidins were clearly determined by the HMBC correlations from H_2-1 (δ_H 2.97, dd, J = 13.7, 8.6 Hz; 2.73, dd, *J* = 13.7, 8.6 Hz), H-4 (δ_H 5.93, d, *J* = 10.9 Hz), H_3-17 (δ_H 1.79, s), H_3-(2-OMe) (δ_H 3.16, s) to C-2 (δ_C 88.0), from H_2-1, H-5 (δ_H 6.35, dd, *J* = 5.2, 10.9 Hz), H_3-17 to C-3 (δ_C 136.9), from H-5, H-6 (δ_H 6.21, d, *J* = 15.2 Hz), H_3-17 to C-4 (δ_C 129.8), and COSY correlations of H_2-1/H-2 (δ_H 4.08, t, *J* = 8.6 Hz), and H-4/H-5/H-6 (**Figure S13**). The NMR data (**Tables S14, S15**), especially the coupling constants of the protons in the sugar group, indicated the presence of a *β*-D-glucose group in **23**. The configurations of the double bonds in side chain and C-9/C-10 were deduced by the NOESY correlations and coupling constants, as illuminated in other piericidins above. The absolute configuration of C-2 was remained to be defined. Accordingly, compound **23** was characterized as 2-hydroxymethyl-*Δ*3, 4-glucopiericidin A (**23**).

Compound **24** was obtained with its molecular formula $C_{31}H_{47}NO_{10}$, established by HRESIMS (*m/z* 594.3269 $[M + H]^+$). Comparison of its ^1H and ^{13}C NMR date with those of **10** indicated that they shared the piericidin glycoside skeleton. The only difference was the replacement of the C-11/C-12 olefinic methines in **10** by C-11/C-12 epoxy ring in **24**, which was confirmed by the HRESIMS and HMBC correlations like from H-12 (δ_H 2.97 q, J = 5.5 Hz) to C-10 (δ_C 86.1), C-11 (δ_C 61.2), C-13 (δ_C 13.1), and C-14 (δ_C 13.4) (**Figure S13**). Comparison of its NMR date with those of piericidin C1 (**7**) indicated that **24** was the 10-*O*-glucoside of piericidin C1. The configurations of the glucose, double bonds in side chain and C-9/C-10 were deduced by the NOESY correlations and coupling constants, as illuminated in other piericidins above. The NOESY correlations from H-9 to H-14 suggested the same side of the H-9 and CH_3-14 (**Figure S13**). So the configurations of the C-11/C-12 epoxy ring were determined to be 11*S*, 12*R*. So, compound **24** was characterized as (11*S*, 12*R*) piericidin C1 10-*O*-*β*-D-glucoside (**24**).

Compound **25** was obtained with its molecular formula $C_{31}H_{47}NO_{10}$, established by HRESIMS (*m/z* 594.3288 $[M + H]^+$). The NMR data (**Table S14, S15**) of **25** were similar to those of **24**, except for some small difference of the chemical shifts of CH-10, C-11, CH-12, CH_3-13, and CH_3-14. The HMBC and COSY correlations revealed **25** had the same planer structure with **24,** including the C-11/C-12 epoxy ring. The differences of the specific rotations (**24**: $[\alpha]_D^{20}$ + 2.0, *c* 0.6, $CHCl_3$; **25**: $[\alpha]_D^{20}$ + 0.9, *c* 0.6, $CHCl_3$) and ECD curves (**Figure S14**) suggested **25** to be a C-11/C-12 epimer of **24**. The NOESY correlations from H_3-15 (δ_H 0.91, d, J = 6.9 Hz) to H-14 suggested the same side of the H_3-15 and CH_3-14 (**Figure S13**). So the configurations of the C-11/C-12 epoxy ring were determined to be 11*R*, 12*S*. Accordingly, compound **25** was characterized as (11*R*, 12*S*) piericidin C1 10-*O*-*β*-D-glucoside (**25**).

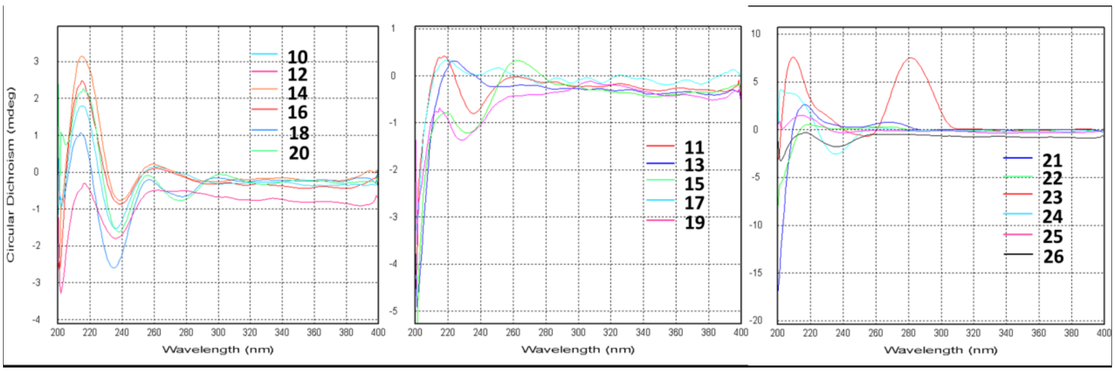

Figure S14. ECD spectrum of **10–26**.

Compound **26** was obtained with its molecular formula $C_{33}H_{51}NO_{11}$, established by HRESIMS (*m/z* 638.3535 $[M + H]^+$). Comparison of its ^1H and ^{13}C NMR date with those of **11** indicated that they shared the piericidin glycoside skeleton (**Tables S14, S15**). The only difference was the replacement of the C-13 oxygenated CH_2 in **11** by oxygenated CH (δ_H 5.06, d, J = 6.5 Hz, δ_C 101.5) in **26**, which was confirmed by the coupling constant of CH-12 (δ_H 5.46, d, J = 6.5 Hz). The chemical shifts of CH-13 and the molecular formula suggested two methoxy groups linked on C-13, which were supported by HMBC correlations from H-13 to C-11 (δ_C 142.9) and –OMe (δ_C 52.0) and COSY correlation from H-13 and H-12 (**Figure S13**). Thus, compound **26** was characterized as 13-dimethoxy glucopiericidin A (**26**).

Compound **27** was obtained with its molecular formula $C_{30}H_{45}NO_8$, established by HRESIMS (*m/z* 548.3215 $[M + H]^+$). It was determined to be glucopiericidin C (**27**) by comparison of its ^1H and ^{13}C NMR date with literature data.[1b]

Methods of the Glycosides Hydrolyzation.

Compound **11** (5.0 mg) was refluxed with 2 M HCl/MeOH (1:1, 5 mL) for 6 h at 60 °C. The reaction mixture was evaporated to dryness and diluted with H_2O (5 mL). After extraction with EtOAc (3 × 5 mL), the aqueous layer was concentrated and heated with L-cycteine methyl ester hydrochloride (5 mg) in pyridine (1 ml) at 60 °C for 1 h.[1] Then *O*-tolyl isothiocyanate (0.4 ml) was added to the reaction mixture, which was then stirred at 60 °C for 1 h. Sugar (D-glucose/D-galactose) standards (Sigma) were also derivatized using L-cycteine methyl ester hydrochloride in the same manner. Then *O*-tolyl isothiocyanate was added to the reaction mixture, stirred at 60 °C for 1h. The reaction mixtures were analyzed by using HPLC under the followed conditions: an YMC-Pack ODS-A column (250 × 4.6 mm); a UV detector; CH_3CN/H_2O mobile phase (25/75, v/v); a detection wavelength of 250 nm; 0.8 ml/min flow rate. The retention times of the derivatized standards were as follow: D-glucose 21.5 min, D-galactose 19.0 min. By comparing the retention times with those of the standards, the sugar in compound **11** was determined to be D-glucose.[11] Hydrolyzation of **12** (0.8 mg) and **16** (1.0 mg) were taken in the same way, and only D-glucose was determined in the reaction mixtures.

NMR tube degradation method for sugar analysis of **14** (1.0 mg) was taken as reported. [8] Briefly, after measuring the ^1H NMR spectrum (700 MHz, in DMSO-d_6) of **14**, 2 M DCl/D_2O (Deuterium Chloride) was added into the NMR tube and heated to 90 °C for 3 h. The ^1H NMR spectrum (700 MHz) of the mixture in the tube was acquired after the hydrolyzation. The mixture of D-glucose and D-galactose was also measured in DMSO-d_6 with a little D_2O. D-Glucose and D-galactose were determined in the degradation mixture of **14**, comparing with the anomeric protons of the hydrolysis products and those of sugar (D-glucose/D-galactose) standards acquired and in reference. [8]

Table S11. ^1H NMR (700 MHz) Spectroscopic Data for **2-5**.

	2 ($CDCl_3$)	**3** (CD_3OD)	**3** ($CDCl_3$)	**4** ($CDCl_3$)	**5** ($CDCl_3$)
1	3.37 (d, 6.9) 2H	3.38 (d, 6.9) 2H	3.38 (d, 6.8) 2H	3.38 (d, 6.9) 2H	3.36 (d, 6.9) 2H
2	5.41 (t, 6.9)	5.33 (t, 6.9)	5.41 (t, 6.9)	5.41 (t, 6.9)	5.40 (t, 6.9)
4	2.79 (d,7.0) 2H	2.70 (s) 2H	2.70 (s) 2H	2.70 (s) 2H	2.77 (d, 6.9) 2H
5	5.60 (dt, 15.5, 7.0)	/	/	/	5.59 (m)
6	6.08 (d, 15.5)	5.68 (s)	5.69 (s)	5.69 (s)	6.03 (d, 15.5)
8	5.21 (d, 9.8)	5.16 (d, 9.4)	5.06 (d, 9.9)	5.06 (d, 9.9)	5.35 (d, 9.6)
9	2.56 (m)	2.66 (m)	2.65 (m)	2.65 (m)	4.14 (m)
10	3.75 (dd, 7.6, 7.6)	3.66 *	3.59 (d, 8.7)	3.61 (d, 8.5)	/
11	5.46 (dd, 7.6, 15.2)	/	/	/	/
12	5.70 (dq, 15.2, 6.4)	5.46 (s)	5.46 (s)	5.43 (s)	6.73 (q, 7.0)
13	1.72 (d, 6.4)	/	/	/	1.84 (d, 6.9) 3H
14	/	1.87 (s) 3H	1.91 (s) 3H	1.92 (s) 3H	1.77 (s) 3H
15	0.92 (d, 6.8) 3H	0.90 (d, 6.9) 3H	0.87 (d, 6.7) 3H	0.89 (d, 6.7) 3H	1.15 (d, 6.8) 3H

16	1.77 (s) 3H	1.73 (s) 3H	1.78 (s) 3H	1.78 (s) 3H	1.79 (s) 3H
17	1.75 (s) 3H	1.68 (s) 3H	1.68 (s) 3H	1.68 (s) 3H	1.73 (s) 3H
18	/	1.68 (s) 3H	1.67 (s) 3H	1.67 (s) 3H	/
19	/	3.66 *	3.83 (q, 6.4)	3.77 (q, 6.3)	/
20	/	1.28 (s) 3H	1.29 (s) 3H	1.27 (s) 3H	/
21	/	1.14 (d, 6.4) 3H	1.14 (d, 6.4) 3H	1.15 (d, 6.4) 3H	/
7’	3.95 (s) 3H	3.91 (s) 3H	3.95 (s) 3H	3.95 (s) 3H	3.94 (s) 3H
8’	3.86 (s) 3H	3.68 (s) 3H	3.86 (s) 3H	3.86 (s) 3H	3.86 (s) 3H
9’	2.09 (s) 3H	2.06 (s) 3H	2.09 (s) 3H	2.09 (s) 3H	2.09 (s) 3H

* overlapped

Table S12. ^{13}C NMR (175 MHz) Spectroscopic Data for **2-5**.

	2 ($CDCl_3$)	**3** (CD_3OD)	**3** ($CDCl_3$)	**4** ($CDCl_3$)	**5** ($CDCl_3$)
1	34.7, CH_2	35.3, CH_2	34.7, CH_2	34.7, CH_2	34.5, CH_2
2	122.5, CH	124.8, CH	123.8, CH	123.8, CH	122.3, CH
3	135.1, C	135.0, C	133.9, C	134.0, C	134.9, C
4	43.4, CH_2	49.8, CH_2	51.1, CH_2	51.3, CH_2	43.2, CH_2
5	127.0, CH	134.6, C	134.9, C	134.9, C	126.9, CH
6	136.1, CH	131.9, CH	130.9, CH	130.9, CH	135.7, CH
7	136.0, C	134.2, C	136.2, C	136.1, C	133.7, C
8	132.8, CH	133.7, CH	130.1, CH	130.1, CH	131.3, CH
9	39.7, CH	37.5, CH	37.1, CH	37.0, CH	39.7, CH
10	77.5, CH	84.5, CH	83.3, CH	83.1, CH	203.4, C
11	132.2, CH	140.2, CH	139.3, CH	139.5, CH	137.8, C
12	129.1, CH	131.6, CH	132.8, CH	132.0, CH	137.1, CH
13	18.1, CH_3	76.5, C	75.9, C	75.8, C	15.0, CH_3
14	/	12.8, CH_3	12.2, CH_3	12.4, CH_3	11.6, CH_3
15	17.3,CH_3	18.5, CH_3	17.8, CH_3	17.8, CH_3	18.3, CH_3
16	13.4, CH_3	17.6, CH_3	17.5, CH_3	17.5, CH_3	12.9, CH_3
17	17.0,CH_3	16.0, CH_3	16.0, CH_3	16.0, CH_3	16.8, CH_3
18	/	17.6, CH_3	17.7, CH_3	17.8, CH_3	/
19	/	75.1, CH	73.3, CH	73.7, CH	/
20	/	24.3, CH_3	22.9, CH_3	22.7, CH_3	/
21	/	17.8, CH_3	17.0, CH_3	16.8, CH_3	/
2’	153.5,C	156.0, C	153.7,C	153.7,C	153.7, C
3’	127.8, C	130.0, C	127.9, C	127.9, C	127.9, C
4’	154.3, C	156.7, C	154.1, C	154.1, C	154.1, C
5’	111.8, C	114.5, C	112.1, C	112.1, C	112.1, C
6’	150.8, C	150.3, C	151.1, C	151.1, C	151.0, C
7’	53.3, CH_3	52.0, CH_3	53.2, CH_3	53.2, CH_3	53.2, CH_3
8’	61.0, CH_3	60.8, CH_3	60.8, CH_3	60.8, CH_3	60.8, CH_3
9’	10.8, CH_3	10.9, CH_3	10.6, CH_3	10.6, CH_3	10.6, CH_3

Table S13. [1]H NMR (700 MHz) Spectroscopic Data for **12-19**.

	12 (CD_3OD)	**13** (DMSO-d_6)	**14** (DMSO-d_6)	**15** (DMSO-d_6)	**16** (DMSO-d_6)	**17** (DMSO-d_6)	**18** (DMSO-d_6)	**19** (CD_3OD)
1	3.34 (d, 6.9) 2H	3.26 (d, 6.9) 2H	3.28 (d, 6.9) 2H	3.28 (d, 6.9) 2H	3.28 (d, 6.9) 2H	3.28 (d, 6.9) 2H	3.34 *	3.40 (d, 6.9) 2H
2	5.29 (t, 6.9)	5.28 (t, 6.9)	5.33 (t, 6.9)	5.33 (t, 6.9)	5.32 (t, 6.9)	5.32 (t, 6.9)	5.37 (t, 6.9)	5.37 (t, 6.9)
4	2.70 (d, 6.9) 2H	2.70 (d, 7.0) 2H	2.74 (m) 2H	2.74 (m) 2H	2.73 (m) 2H	2.73 (m) 2H	2.75 (m) 2H	2.77 (d, 7.0) 2H
5	5.54 (dt, 13.9, 7.1)	5.54 (dt, 13.9, 7.0)	5.54 (dt, 15.5, 7.3)	5.44 (dt, 15.5, 7.3)	5.45 (dt, 15.5, 7.1)	5.47 (dt, 15.5, 7.1)	5.47 (dt, 15.5, 7.1)	5.54 (dt, 15.5, 7.1)
6	6.04 *	5.99 *	6.04 (d, 15.5)	6.04 (d, 15.5)	6.04 (d, 15.5)	6.04 (d, 15.5)	6.04 (d, 15.5)	6.09 (d, 15.5)
7	6.07 *	6.02 *	/	/	/	/		
8	5.79 (dd, 14.3, 7.1)	5.88 (dd, 14.4, 6.3)	5.42 (d, 9.0)	5.43 (d, 9.0)	5.41 (d, 9.0)	5.43 (d, 9.0)	5.40 (d, 9.0)	5.40 (d, 9.0)
9	2.45 (m)	2.37 (m)	2.66 (m)	2.67 (m)	2.66 (m)	2.67 (m)	2.67 (m)	2.81 (m)
10	3.66 (d, 8.9)	3.60 *	3.73 (d, 7.1)	3.74 (d, 7.0)	3.73 (d, 7.2)	3.75 (d, 7.0)	3.76 (d, 8.9)	3.75 (d, 8.9)
12	6.46 (q, 6.7)	5.43 (t, 6.3)	5.36 (q, 6.8)	5.42 (t, 6.3)	5.37 (q, 6.8)	5.42 (m)*	5.37 (q, 6.8)	5.58 (t, 6.2)
13	1.62 (d, 6.7) 3H	3.90 (dd, 13.0, 6.3)	1.56 (d, 6.8) 3H	3.96 (dd, 13.0, 6.3)	1.56 (d, 6.8) 3H	3.97 (dd, 13.0, 6.3)	1.55 (d, 6.8) 3H	4.05 (dd, 12.8, 7.2)
		3.98 (dd, 13.0, 6.3)		4.00 (dd, 13.0, 6.3)		4.01 (dd, 13.0, 6.3)		4.17 (dd, 12.8, 7.2)
14	1.60 (s) 3H	1.52 (s) 3H	1.51 (s) 3H	1.52 (s) 3H	1.51 (s) 3H	1.53 (s) 3H	1.52 (s) 3H	1.67 (s) 3H
15	0.85 (d, 6.9) 3H	0.82 (d, 6.9) 3H	0.81 (d, 6.9) 3H	0.83 (d, 6.9) 3H	0.79 (d, 6.9) 3H	0.82 (d, 6.9) 3H	0.79 (d, 6.9) 3H	0.88 (d, 6.9) 3H
16	/	/	1.65 (s) 3H	1.66 (s) 3H	1.65 (s) 3H	1.65 (s) 3H	/	1.74 (s) 3H
17	1.74 (s) 3H	1.69 (s) 3H	1.70 (s) 3H	1.69 (s) 3H	1.69 (s) 3H	1.70 (s) 3H	1.70 (s) 3H	1.74 (s) 3H
7′	3.90 (s) 3H	3.78 (s) 3H	3.81 (s) 3H	3.81 (s) 3H	3.80 (s) 3H	3.80 (s) 3H	3.83 (s) 3H	3.92 (s) 3H
8′	3.73 (s) 3H	3.62 (s) 3H	3.63 (s) 3H	3.63 (s) 3H	3.63 (s) 3H	3.62 (s) 3H	3.71 (s) 3H	3.81 (s) 3H
9′	2.04 (s) 3H	1.96 (s) 3H	1.98 (s) 3H	1.98 (s) 3H	1.98 (s) 3H	1.97 (s) 3H	2.07 (s) 3H	2.15 (s) 3H
1″	4.20 (d, 7.8)	4.07 (d, 7.8)	4.09 (d, 7.8)	4.11 (d, 8.0)	4.10 (d, 7.8)	4.12 (d, 7.8)	4.08 (d, 7.8)	4.24 (d, 7.8)
2″	3.19 (d, 8.9, 7.8)	2.96 (dd, 8.7, 7.8)	2.95 (dd, 8.8, 7.8)	2.96 (dd, 8.8, 7.8)	2.94 (dd, 8.8, 7.8)	2.96 (dd, 8.8, 7.8)	2.93 (m)*	3.16 (m)*
3″	3.30 (dd, 8.9, 8.7)	3.10 (dd, 8.7, 8.6)	3.11 (dd, 8.8, 8.8)	3.10 (dd, 8.8, 8.8)	3.10 (dd, 8.8, 8.8)	3.12 (dd, 8.8, 8.8)	3.22 (m)*	3.32 (m)*
4″	3.29 (dd, 9.1, 8.7)	2.99 (m)*	3.00 (dd, 9.3, 8.8)	3.02 (dd, 9.3, 8.8)	3.02 (dd, 9.6, 8.8)	3.04 (dd, 9.6, 8.8)	3.03 (dd, 9.3, 9.0)	3.22 (dd, 9.6, 8.8)

5′′	3.11 (ddd, 9.1, 5.3, 2.5)	2.98 (m)*	3.18 (ddd, 9.3, 5.3, 1.8)	3.20 (ddd, 9.3, 5.3, 1.8)	3.17 (m)	3.17 (m)	3.09 (m)*	3.26 (ddd, 9.6, 5.3, 1.8)
6′′	3.62 (dd, 11.8, 5.4)	3.36 *	3.48 (dd, 10.5, 1.8)	3.48 (dd, 10.5, 1.8)	3.50 (dd, 10.8, 1.8)	3.50 (br.d 10.8)	3.62 (br.d 11.5)	3.67 (dd, 12.1, 5.3)
	3.74 (dd, 11.8, 2.5)	3.60 *	3.58 (dd, 10.5, 5.3)	3.58 (dd, 10.5, 5.3)	3.60 (dd, 10.8, 6.0)	3.62 (m) *	3.42 (m) *	3.79 (m) *
1′′′	/	/	4.64, d (2.2)	4.64, d (2.9)	4.62, d (3.6)	4.64, d (3.6)	5.09 (d, 7.4)	5.23 (d, 7.4)
2′′′	/	/	3.58 (m)*	3.57 (m)*	3.18 (dd, 8.9, 2.0)	3.18 (m)	3.21 (m)*	3.46 (m)*
3′′′	/	/	3.70 (br.s)	3.70 (br.s)	3.40 (m)	3.40 (m)	3.07 (m)*	3.46 (m)*
4′′′	/	/	3.58 (m)*	3.56 (m)*	3.10 (dd, 8.8, 8.8)	3.10 (dd, 8.8, 8.8)	3.12 (dd, 9.3, 9.0)	3.40 (m)*
5′′′	/	/	3.62 (m)*	3.61 (m)	3.43 (m)	3.42 (m)	2.93 (m)*	3.16 (m)*
6′′′	/	/	3.43 (dd, 10.7, 6.3)	3.42 (dd, 10.7, 6.3)	3.46 (dd, 9.7, 6.6)	3.46 (dd, 11.6, 5.2)	3.56 (br.d 11.5)	3.59 (dd, 11.9, 6.1)
			3.51 (dd, 10.7, 6.3)	3.51 (dd, 10.7, 6.3)	3.57 (br.d, 9.7)	3.58 (br.d, 11.6)	3.42 (m) *	3.79 (m) *

* overlapped

Table S14. [1]H NMR (700 MHz) Spectroscopic Data for **20-26**.

	20 (CD_3OD)	**21** (CD_3OD)	**22** (CD_3OD)	**23** (CD_3OD)	**24** ($CDCl_3$)	**25** ($CDCl_3$)	**26** (CD_3OD)
1	3.39 (d, 6.9) 2H	3.38 (d, 6.8) 2H	3.28 (d, 6.8) 2H	2.97 (dd, 13.7, 8.6)	3.37 (d, 6.8) 2H	3.36 (d, 6.8) 2H	3.45 (d, 6.7) 2H
				2.73 (dd, 13.7, 8.6)			
2	5.35 (t, 6.9)	5.37 (t, 6.8)	5.32 (t, 6.8)	4.08 (t, 8.6)	5.38 (t, 6.8)	5.38 (t, 6.8)	5.26 (t, 6.7)
4	2.77 (d, 7.0) 2H	2.51(br.d, 13.9)	2.51(br.d, 14.0)	5.93 (d, 10.9)	2.77 (d/, 6.9) 2H	2.77 (d, 6.9) 2H	2.78 (d, 6.9) 2H
		2.03 (dd, 13.9, 8.9)	2.04 (dd, 14.0, 9.0)				
5	5.54 (dt, 15.5, 6.9)	3.69 (ddd, 8.9, 8.4, 2.7)	3.68 (ddd, 9.0, 8.3, 2.7)	6.35 (dd, 15.2, 10.9)	5.61 (dt, 15.6, 6.9)	5.63 (dt, 15.6, 6.9)	5.54 (dt, 15.6, 6.9)
6	6.09 (d, 15.5)	3.20 (d, 8.4)	3.21 (d, 8.3)	6.21 (d, 15.2)	6.03 (d, 15.6)	6.04 (d, 15.6)	6.08 (d, 15.6)
OMe	/	3.11 (s) 3H	3.13 (s) 3H	3.16 (s) 3H	/	/	3.31 (s) 6H*
8	5.41 (d, 9.0)	5.30 (d, 9.3)	5.31 (d, 9.3)	5.52 (d, 9.2)	5.26 (d, 9.8)	5.21 (d, 9.8)	5.41 (d, 9.5)
9	2.80 (m)	2.77 (m)	2.79 (m)	2.82 (m)	2.92 (m)	2.73 (m)	2.84 (m)
10	3.75 (d, 7.0)	3.60 (d, 9.3)	3.62 (d, 9.3)	3.74 *	3.11 (d, 6.6)	2.70 (d, 9.5)	3.83 (d, 6.9)
12	5.48 (q, 6.7)	5.47 (q, 6.6)	5.58 (t, 6.3)	5.48 (q, 6.5)	2.97 (q, 5.5)	2.87 (q, 5.5)	5.46 (d, 6.5)

13	1.64 (d, 6.8) 3H	1.63 (d, 6.8) 3H	4.05 (dd, 12.8, 6.0) 4.18 (dd, 12.8, 6.0)	1.62 (d, 6.8) 3H	1.22 (d, 5.5)	1.30 (d, 5.5)	5.06 (d, 6.5)
14	1.62 (s) 3H	1.60 (s) 3H	1.61 (s) 3H	1.63 (s) 3H	1.27 (s) 3H	1.29 (s) 3H	1.73 (s) 3H
15	0.83 (d, 6.9) 3H	0.79 (d, 6.9) 3H	0.84 (d, 6.9) 3H	0.83 (d, 6.9) 3H	1.05 (d, 6.9) 3H	0.91 (d, 6.9) 3H	0.96 (d, 6.9) 3H
16	1.74 (s) 3H	1.64 (s) 3H	1.69 (s) 3H	1.81 (s) 3H	1.77 (s) 3H	1.78 (s) 3H	1.76 (s) 3H
17	1.75 (s) 3H	1.82 (s) 3H	1.82 (s) 3H	1.79 (s) 3H	1.74 (s) 3H	1.74 (s) 3H	1.73 (s) 3H
7′	3.92 (s) 3H	3.91 (s) 3H	3.99 (s) 3H	3.91 (s) 3H	3.94 (s) 3H	3.95 (s) 3H	4.06 (s) 3H
8′	3.81 (s) 3H	3.73 (s) 3H	3.76 (s) 3H	3.73 (s) 3H	3.85 (s) 3H	3.86 (s) 3H	3.80 (s) 3H
9′	1.90 (s) 3H	2.07 (s) 3H	2.10 (s) 3H	2.07 (s) 3H	2.09(s) 3H	2.09(s) 3H	2.10(s) 3H
1′′	4.25 (d, 7.8)	4.16 (d, 7.9)	4.19 (d, 7.8)	4.21 (d, 7.9)	4.30 (d, 7.8)	4.18 (d, 7.9)	4.27 (d, 7.8)
2′′	3.16 (dd, 8.8, 7.8)	3.10 (m)*	3.11 (dd, 9.0, 7.8)	3.13 (dd, 9.0, 7.8)	3.27 (dd, 8.8, 7.8)	3.32 (dd, 8.8,7.9)	3.19 (dd, 9.0, 7.8)
3′′	3.32 (m)*	3.29 (m)*	3.29 (dd, 9.0, 9.0)	3.31 (dd, 9.0, 6.8)	3.51 (dd, 8.8, 8.8)	3.50 (dd, 8.8, 8.8)	3.34 (dd, 9.0, 8.7)
4′′	3.29 (m)*	3.27 (dd, 9.6, 8.8)	3.20 (dd, 9.8, 9.0)	3.29 (dd, 9.2, 6.8)	3.58 (dd, 9.6, 8.8)	3.39 (dd, 8.8, 8.7)	3.27 (dd, 8.7, 8.7)
5′′	3.37 (m)	3.10 (m)*	3.15 (m)	3.11 (ddd, 9.2, 5.2, 2.5)	3.37 (m)*	3.44 (ddd, 8.7, 8.7, 2.8)	3.16 (ddd, 8.7, 5.6, 2.3)
6′′	3.56 (dd, 10.7, 2.2) 3.94 (dd, 10.7, 4.2)	3.62 (dd, 12.1, 5.3) 3.73 (m) *	3.57 (dd, 11.7, 6.1) 3.79 (dd, 11.7, 2.0)	3.63 (dd, 11.8, 5.2) 3.75 (dd, 11.8, 2.5)	3.83 (m) * 3.87 (m) *	3.63 (dd, 11.8, 8.7) 3.92 (dd, 11.8, 2.8)	3.62 (dd, 11.8, 5.6) 3.77 (dd, 11.8, 2.3)
1′′′	4.84, d (3.2)	/	/	/	/	/	/
2′′′	3.75 (m)*	/	/	/	/	/	/
3′′′	3.90 (br.d, 1.8)	/	/	/	/	/	/
4′′′	3.75 (m)*	/	/	/	/	/	/
5′′′	3.86 (m)*	/	/	/	/	/	/
6′′′	3.68 (dd, 10.7, 6.5) 3.80 (dd, 10.7, 2.3)	/	/	/	/	/	/
1′′′′	5.23 (d, 7.5)	/	/	/	/	/	/
2′′′′	3.46 (m)*	/	/	/	/	/	/
3′′′′	3.37 (m)*	/	/	/	/	/	/

4′′′′	3.42 (m)*	/	/	/	/	/	/
5′′′′	3.25 (ddd, 9.6, 5.3, 2.3)	/	/	/	/	/	/
6′′′′	3.68 (dd, 10.7, 5.3)	/	/	/	/	/	/
	3.80 (m)*						

* overlapped

Table S15. ^{13}C NMR (175 MHz) Spectroscopic Data for **12-26**.

	12 [a]	**13** [b]	**14** [b]	**15** [b]	**16** [b]	**17** [b]	**18** [b]	**19** [a]	**20** [a]	**21** [a]	**22** [a]	**23** [a]	**24** [c]	**25** [c]	**26**
1	35.3, CH_2	34.2, CH_2	34.1, CH_2	34.0, CH_2	34.0, CH_2	34.2, CH_2	34.0, CH_2	35.5, CH_2	35.5, CH_2	35.3, CH_2	36.0, CH_2	39.9, CH_2	34.6, CH_2	34.6, CH_2	33.8, CH_2
2	123.6, CH	122.4, CH	121.6, CH	121.9, CH	121.8, CH	122.3, CH	121.6, CH	123.1, CH	123.1, CH	125.4, CH	124.4, CH	88.0, CH	122.5, CH	122.5, CH	121.8, CH
3	135.6, C	133.8, C	132.2, C	132.2, C	132.1, C	132.2, C	132.5, C	134.8, C	134.6, C	134.3, C	134.6, C	136.9, C	134.0, C	134.8, C	137.4, C
4	43.8, CH_2	42.1, CH_2	42.5, CH_2	42.5, CH_2	42.5, CH_2	42.4, CH_2	42.5, CH_2	44.1, CH_2	44.1, CH_2	43.2, CH_2	45.1, CH_2	129.8, CH	43.1, CH	43.2, CH	43.9, CH
5	133.3, CH	128.8, CH	122.0, CH	124.7, CH	121.9, CH	124.7, CH	121.8, CH	126.6, CH	126.5, CH	70.1, CH	70.1, CH	123.0, CH	127.2, CH	127.7, CH	126.3, CH
6	132.0, CH	129.5, CH	136.1, CH	136.2, CH	136.2, CH	136.1, CH	136.2, CH	137.4, CH	137.4, CH	92.3, CH	92.4, CH	139.1, CH	135.4, CH	135.0, CH	137.6, CH
OMe	/	/	/	/	/	/	/	/	/	56.0, CH_3	56.0, CH_3	56.3, CH_3	/	/	52.0, CH_3
7	131.0, CH	131.9, CH	135.4, C	134.9, C	135.3, C	134.8, C	135.4, C	136.1, C	136.2, C	133.1, C	133.4, C	135.2, C	134.8, C	134.9, C	134.3, C
8	137.0, CH	135.8, CH	134.7, CH	134.5, CH	134.8, CH	134.6, CH	134.9, CH	135.5, CH	135.9, CH	137.5, CH	137.0, CH	138.4, CH	132.7, CH	133.5, CH	134.8, CH
9	40.3, CH	38.0, CH	35.6, CH	35.5, CH	35.4, CH	35.4, CH	35.2, CH	36.8, CH	36.8, CH	36.1, CH	36.0, CH	37.0, CH	35.8, CH	36.1, CH	36.9, CH
10	93.7, CH	90.0, CH	89.8, CH	89.2, CH	89.6, CH	89.2, CH	89.5, CH	93.1, CH	93.9, CH	94.2, CH	93.6, CH	93.8, CH	86.1, CH	93.4, CH	91.7, CH
11	137.1, C	135.4, C	134.2, C	134.3, C	134.3, C	134.0, C	134.6, C	139.1, C	136.5, C	136.5, C	139.0, C	136.7, C	61.2, C	61.4, C	142.9, CH
12	124.2, CH	128.7, CH	124.7, CH	128.8, CH	124.6, CH	129.0, CH	124.6, CH	128.8, CH	124.8, CH	124.6, CH	129.2, CH	124.5, CH	57.3, CH	57.9, CH	125.9, CH
13	13.2, CH_3	57.2, CH_2	13.0, CH_3	57.4, CH_2	13.1, CH_3	57.5, CH_2	13.0, CH_3	59.0, CH_2	13.1, CH_3	13.2, CH_3	59.0, CH_2	13.0, CH_3	13.1, CH_3	13.3, CH_3	101.5, CH
14	11.7, CH_3	12.0, CH_3	11.8, CH_3	12.2, CH_3	11.9, CH_3	12.3, CH_3	11.9, CH_3	12.0, CH_3	11.8, CH_3	11.4 CH_3	11.9 CH_3	11.9 CH_3	13.4, CH_3	11.7 CH_3	13.5, CH_3
15	17.0, CH_3	15.9, CH_3	17.6, CH_3	17.5, CH_3	17.6, CH_3	17.5, CH_3	17.4, CH_3	17.8, CH_3	17.8, CH_3	17.7, CH_3	17.6, CH_3	17.6, CH_3	14.4, CH_3	17.1, CH_3	18.0, CH_3
16	/	/	16.4, CH_3	16.4, CH_3	16.4, CH_3	16.4, CH_3	16.4, CH_3	12.3 CH_3	12.0 CH_3	11.3 CH_3	11.3 CH_3	13.2 CH_3	13.6, CH_3	13.4, CH_3	13.1, CH_3
17	16.7, CH_3	16.4, CH_3	12.7, CH_3	12.7, CH_3	12.7, CH_3	12.7, CH_3	12.6, CH_3	16.7, CH_3	16.7, CH_3	17.2, CH_3	17.2, CH_3	11.9, CH_3	16.7, CH_3	16.8, CH_3	16.7, CH_3
2′	156.1, C	154.3, C	154.3, C	154.3, C	154.3, C	154.3, C	155.3, C	157.1, C	157.1, C	156.2, C	155.9, C	160.0, C	154.2, C	154.1, C	155.7, C

3′	130.4, C	128.5, C	128.4, C	128.3, C	128.3, C	128.6, C	132.1, C	134.4, C	134.4, C	129.6, C	129.9, C	130.4, C	128.0, C	127.7, C	131.3, C
4′	158.6, C	157.6, C	155.5, C	155.1, C	155.2, C	156.3, C	154.3, C	155.9, C	155.9, C	156.6, C	159.8, C	158.2, C	153.7, C	153.7, C	162.6, C
5′	115.0, C	113.1, C	112.9, C	112.7, C	112.7, C	113.1, C	118.1, C	120.0, C	120.0, C	118.3, C	117.9, C	116.3, C	112.2, C	112.2, C	116.3, C
6′	151.3, C	149.5, C	149.6, C	149.7, C	149.7, C	149.4, C	149.8, C	152.1, C	152.1, C	151.2, C	150.9, C	148.4, C	134.0, C	151.0, C	149.7, C
7′	53.9, CH_3	52.4, CH_3	52.5, CH_3	52.5, CH_3	52.5, CH_3	52.5, CH_3	52.8, CH_3	53.4, CH_3	53.7, CH_3	53.7, CH_3	53.9, CH_3	53.8, CH_3	53.2, CH_3	53.3, CH_3	56.6, CH_3
8′	60.8, CH_3	59.9, CH_3	60.0, CH_3	60.0, CH_3	60.0, CH_3	59.9, CH_3	60.2, CH_3	61.2, CH_3	61.2, CH_3	60.8, CH_3	61.1, CH_3	60.8, CH_3	60.8, CH_3	60.8, CH_3	61.3, CH_3
9′	10.9, CH_3	10.6, CH_3	10.6, CH_3	10.6, CH_3	10.5, CH_3	10.7, CH_3	11.4, CH_3	13.2, CH_3	13.3, CH_3	11.0, CH_3	10.8, CH_3	11.2, CH_3	10.6, CH_3	10.6, CH_3	10.7, CH_3
1′′	104.2, CH	102.7, CH	102.5, CH	102.4, CH	102.2, CH	102.2, CH	102.0, CH	104.2, CH	104.0, CH	104.2, CH	104.6, CH	104.1, CH	103.8, CH	104.4, CH	105.1, CH
2′′	75.7, CH	74.1, CH	74.2, CH	74.1, CH	74.1, CH	74.2, CH	74.3, CH	75.7, CH	75.8, CH	75.4, CH	75.3, CH	75.7, CH	73.2, CH	74.7, CH	75.7, CH
3′′	78.3, CH	77.1, CH	76.8, CH	76.9, CH	76.9, CH	77.0, CH	76.5, CH	77.9, CH	78.0, CH	78.0, CH	78.1, CH	78.3, CH	76.1, CH	77.7, CH	78.1, CH
4′′	71.6, CH	70.2, CH	70.4, CH	70.4, CH	70.3, CH	70.3, CH	70.0, CH	71.7, CH	71.7, CH	71.6, CH	71.8, CH	71.5, CH	70.4, CH	71.4, CH	71.5, CH
5′′	77.7, CH	76.8, CH	75.2, CH	75.1, CH	75.1, CH	75.1, CH	77.4, CH	78.3, CH	78.2, CH	77.6, CH	77.8, CH	77.7, CH	75.5, CH	76.2, CH	77.9, CH
6′′	62.8, CH_2	61.8, CH_2	67.2, CH_2	67.1, CH_2	67.3, CH_2	67.2, CH_2	60.8, CH_2	62.5, CH_2	67.2, CH_2	62.8, CH_2	63.0, CH_2	62.7, CH_2	62.4, CH_2	63.2, CH_2	62.8, CH_2
1′′′	/	/	99.0, CH	99.0, CH	98.8, CH	98.8, CH	102.7, CH	104.6, CH	100.3, CH	/	/	/	/	/	/
2′′′	/	/	69.6, CH	69.6, CH	72.0, CH	72.0, CH	74.1, CH	75.6, CH	71.3, CH	/	/	/	/	/	/
3′′′	/	/	68.9, CH	68.9, CH	72.3, CH	72.4, CH	76.9, CH	78.0, CH	70.5, CH	/	/	/	/	/	/
4′′′	/	/	68.4, CH	68.4, CH	70.1, CH	70.1, CH	69.8, CH	71.4, CH	71.0, CH	/	/	/	/	/	/
5′′′	/	/	70.8, CH	70.9, CH	73.2, CH	73.3, CH	70.0, CH	78.2, CH	72.2, CH	/	/	/	/	/	/
6′′′	/	/	60.5, CH_2	60.5, CH_2	60.8, CH_2	60.9, CH_2	61.1, CH_2	62.9, CH_2	62.5, CH_2	/	/	/	/	/	/
1′′′′	/	/	/	/	/	/	/	/	104.2, CH	/	/	/	/	/	/
2′′′′	/	/	/	/	/	/	/	/	75.7, CH	/	/	/	/	/	/
3′′′′	/	/	/	/	/	/	/	/	76.5, CH	/	/	/	/	/	/
4′′′′	/	/	/	/	/	/	/	/	71.4, CH	/	/	/	/	/	/
5′′′′	/	/	/	/	/	/	/	/	78.4, CH	/	/	/	/	/	/
6′′′′	/	/	/	/	/	/	/	/	62.7, CH_2	/	/	/	/	/	/

[a] in CD_3OD; [b] in DMSO-d_6; [c] in $CDCl_3$.

References

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Spectra of the compounds

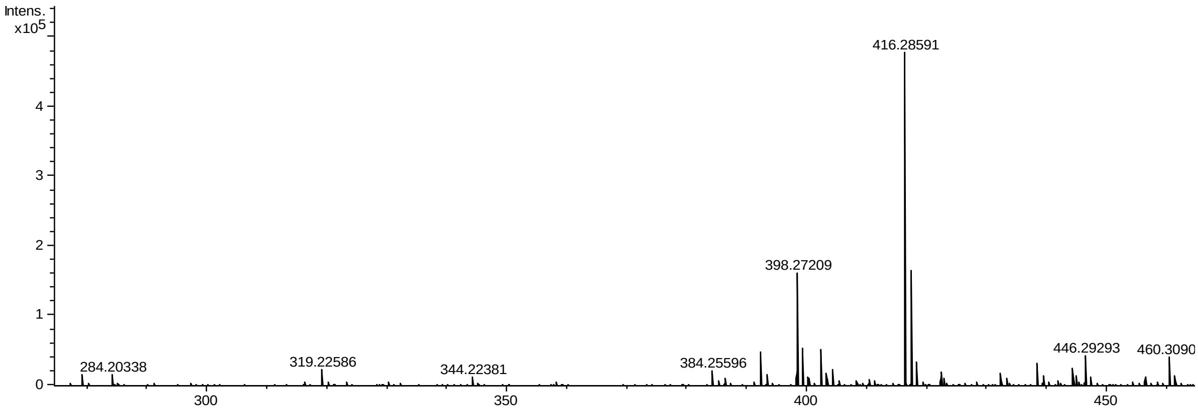


Figure SS-1-1. HRESIMS (+) spectrum of **1**.

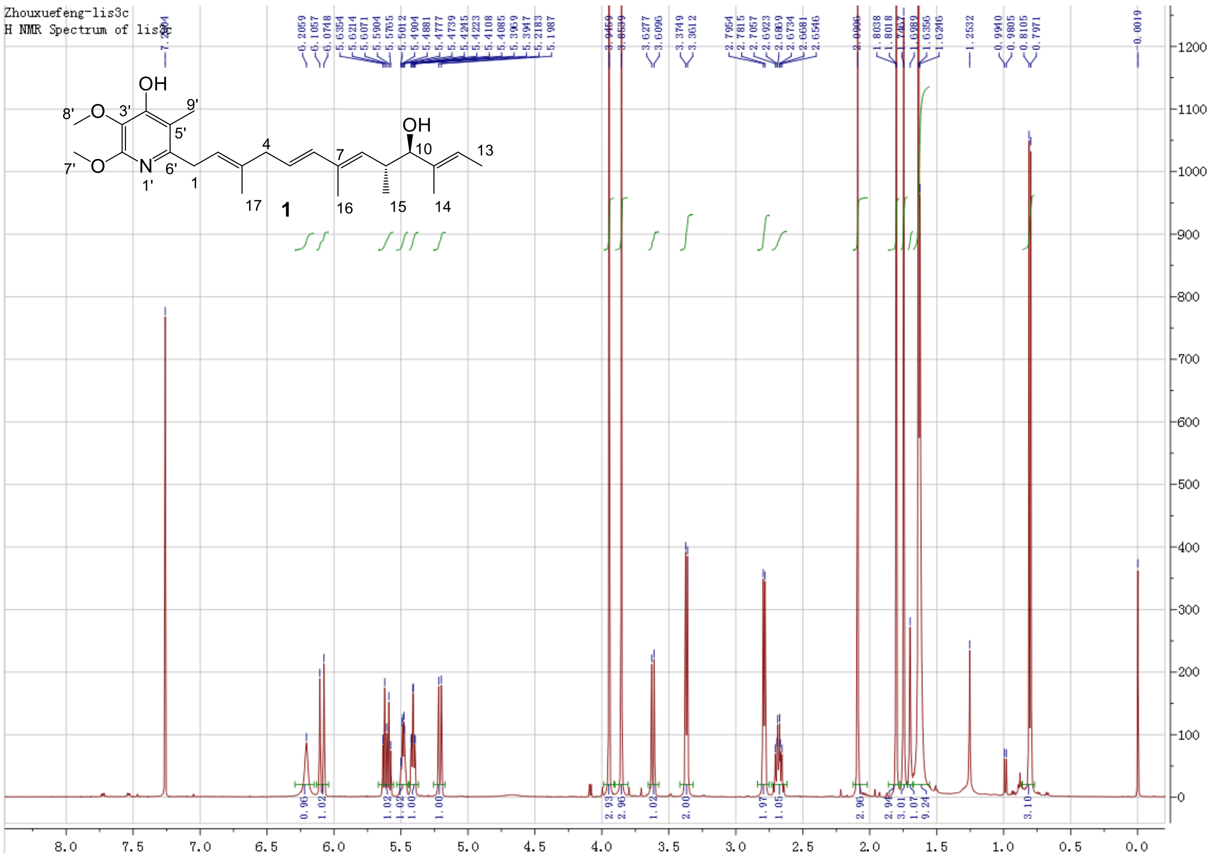


Figure SS-1-2. [1]H NMR spectrum of **1** (in $CDCl_3$, 500 MHz).

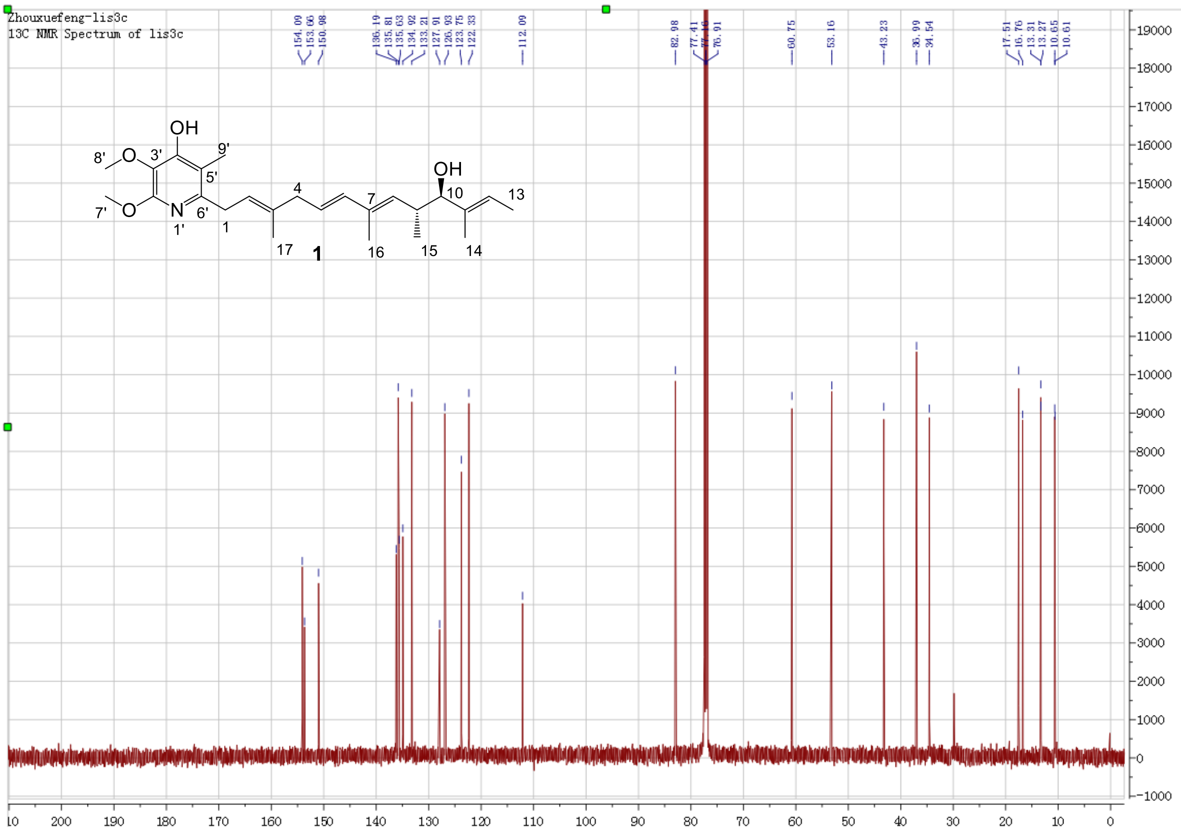


Figure SS-1-3. ^{13}C NMR spectrum of **1** (in $CDCl_3$, 125 MHz).

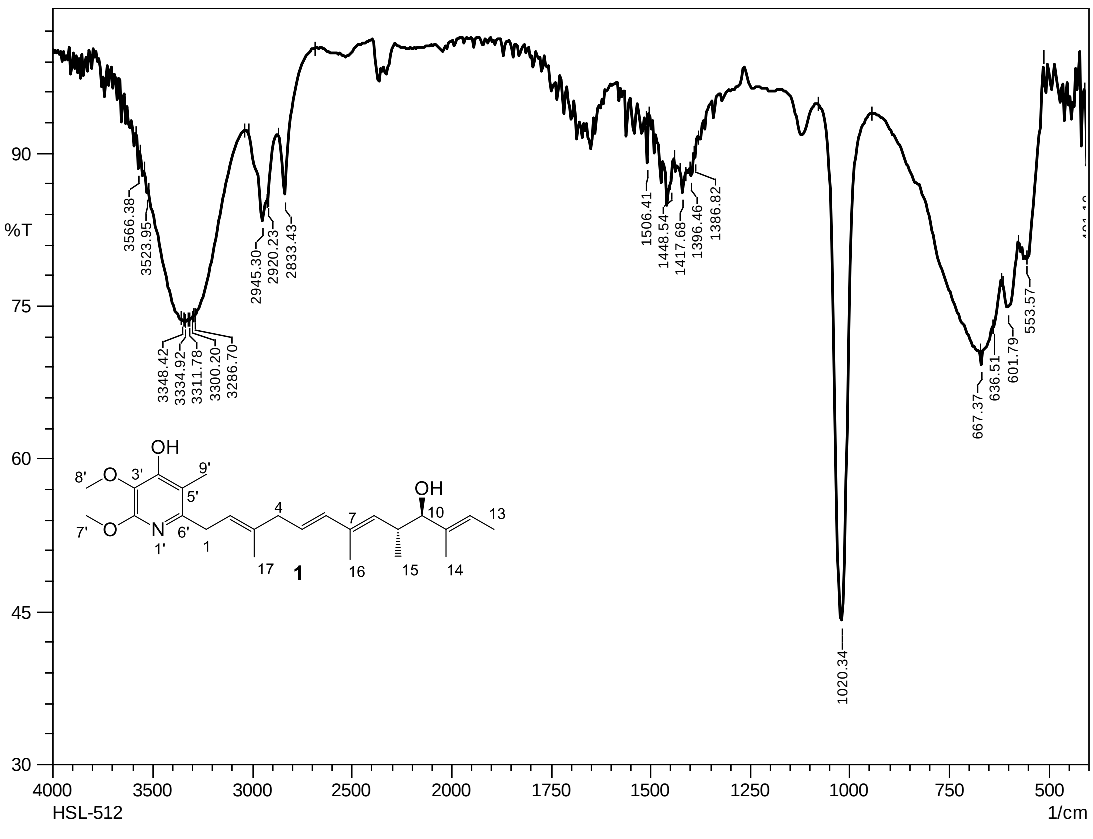
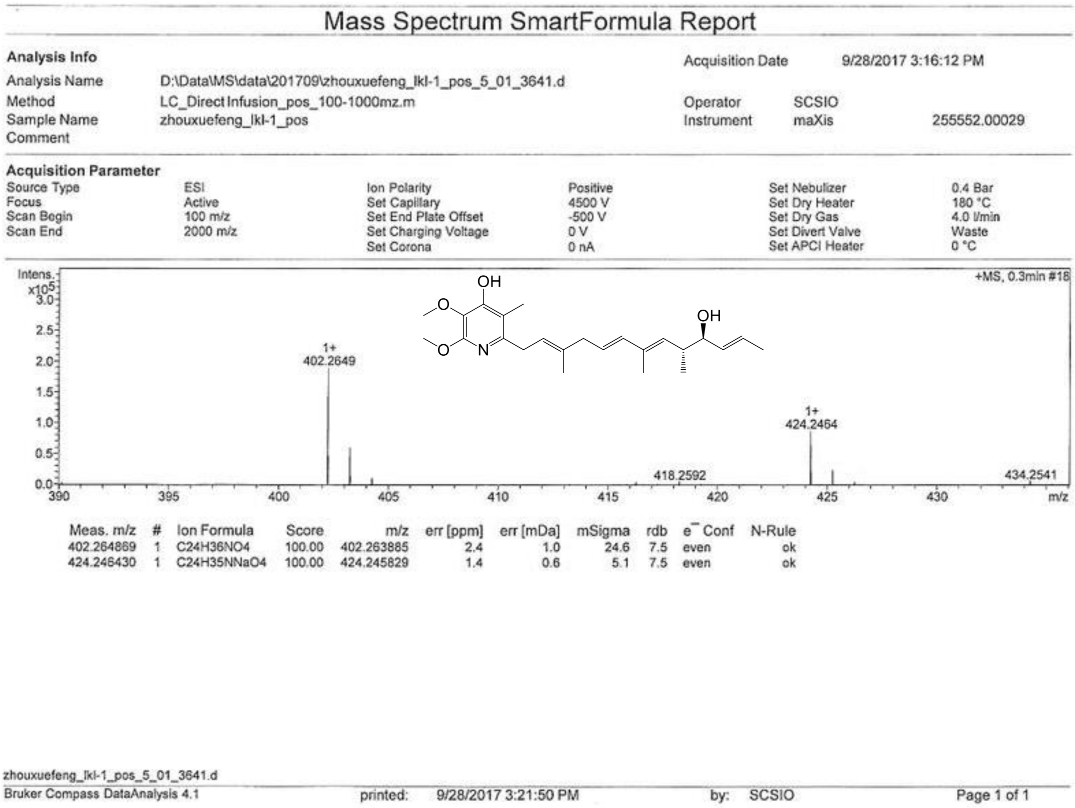


Figure SS-2-1. IR spectrum of **2**.



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Comment			

Acquisition Parameter

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zhouxuefeng_lkl-1_pos_5_01_3641.d

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Figure SS-2-2. HRESIMS (+) spectrum of **2**.

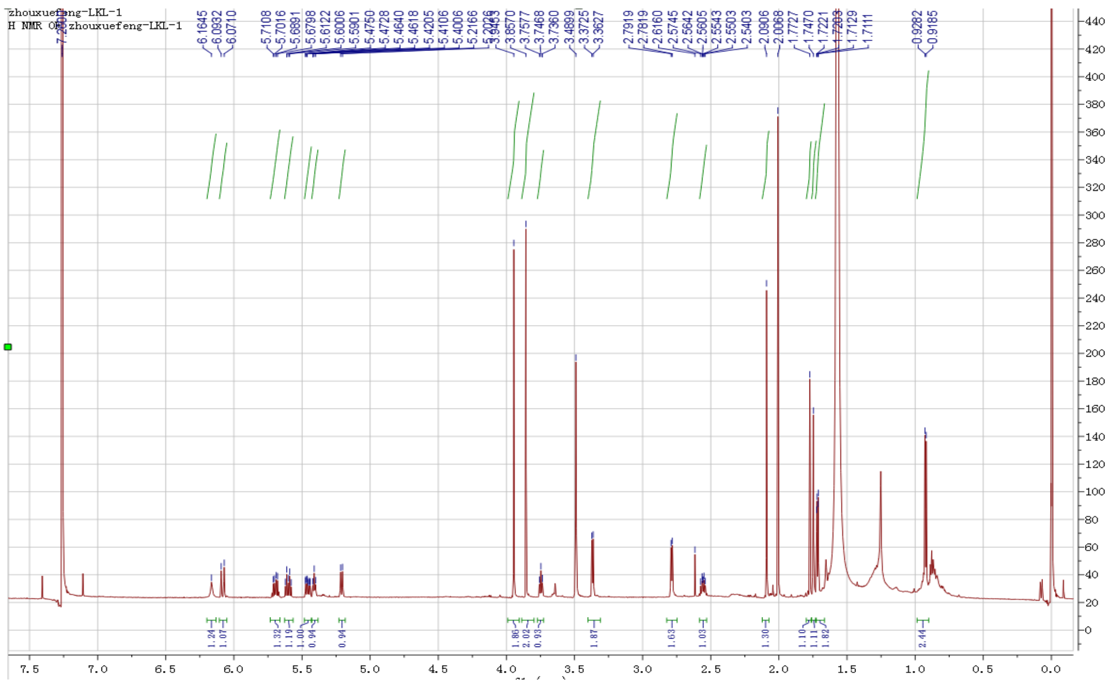


Figure SS-2-3. ^{1}H NMR spectrum of **2** (in $CDCl_3$, 700 MHz).

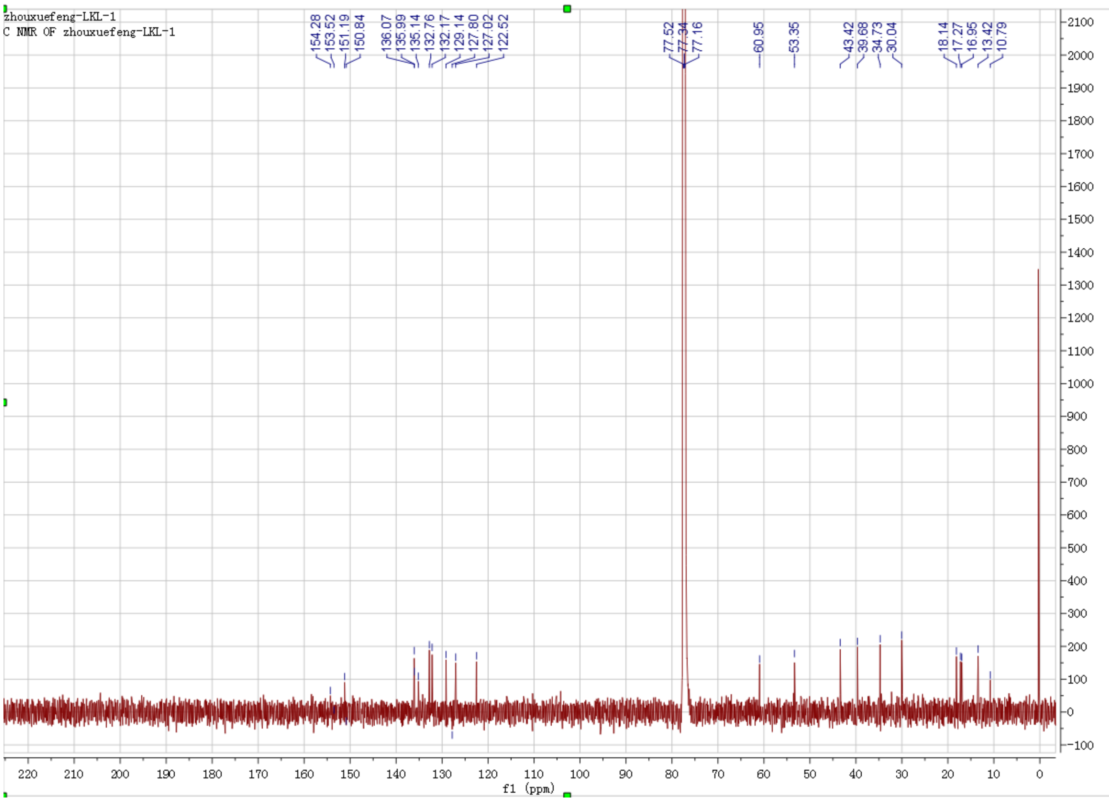


Figure SS-2-4. ^{13}C NMR spectrum of **2** (in $CDCl_3$, 175 MHz).

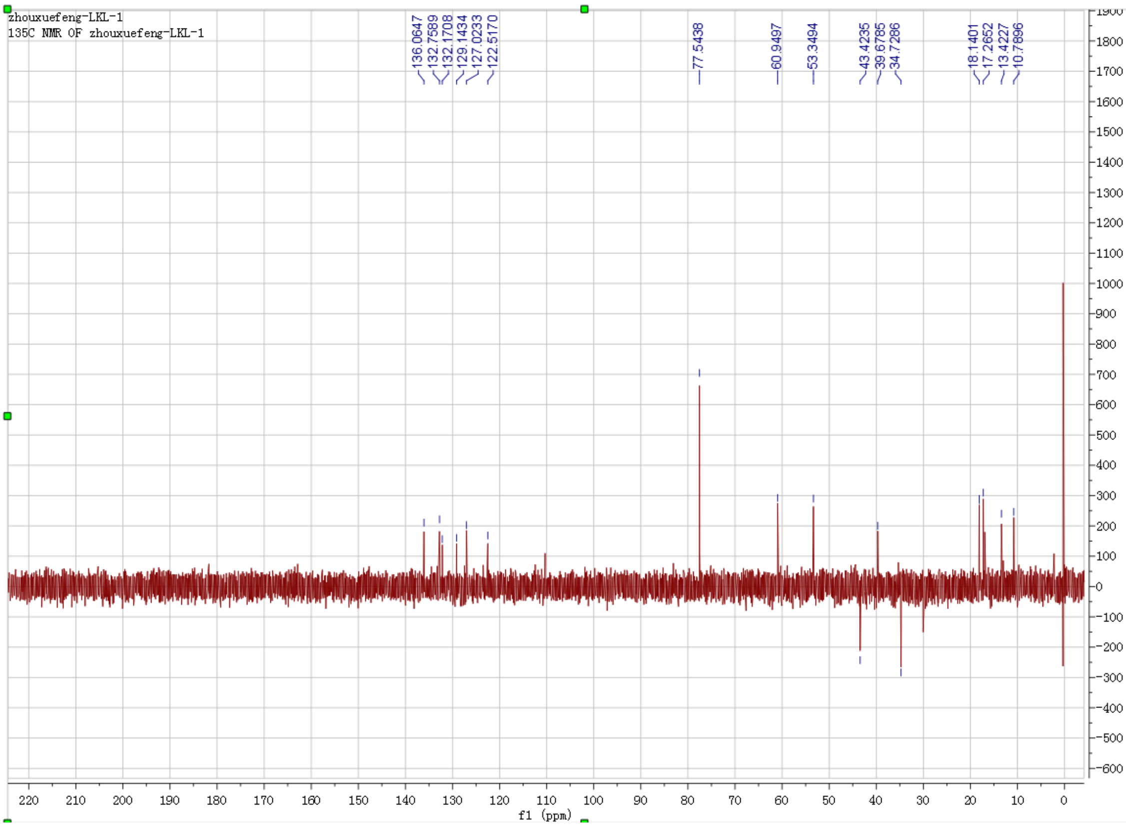


Figure SS-2-5. DEPT spectrum of **2** (in $CDCl_3$, 175 MHz).

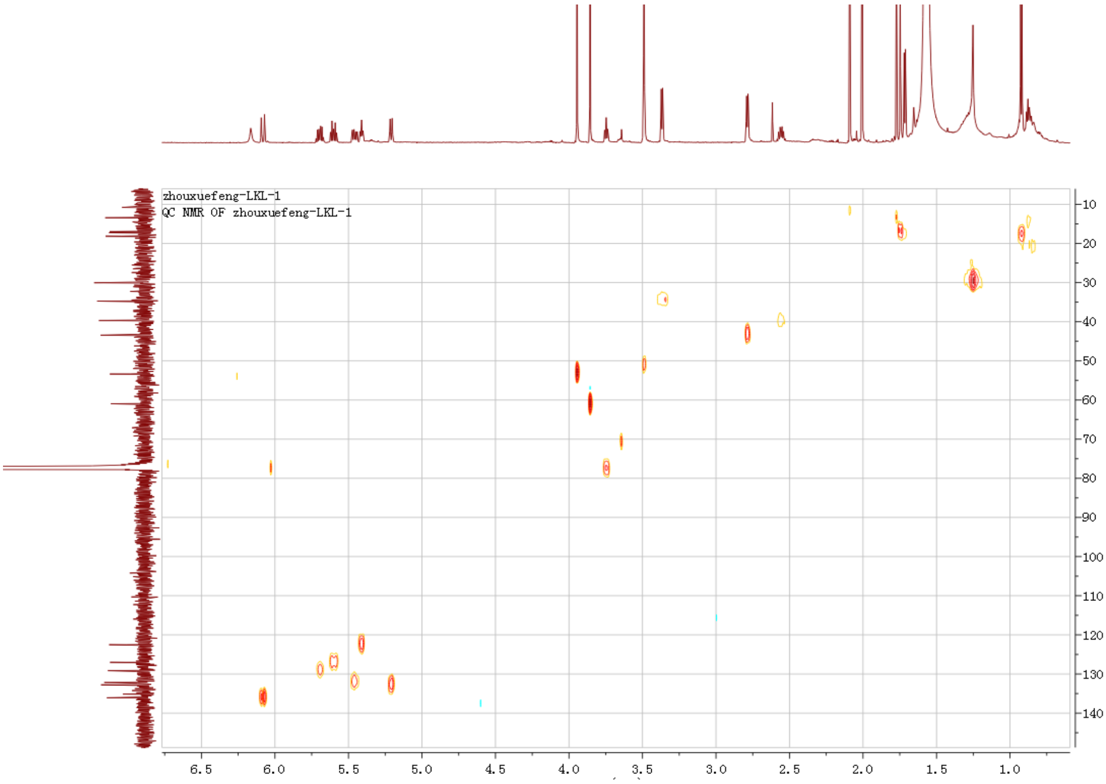


Figure SS-2-6. HSQC spectrum of **2** (in $CDCl_3$).

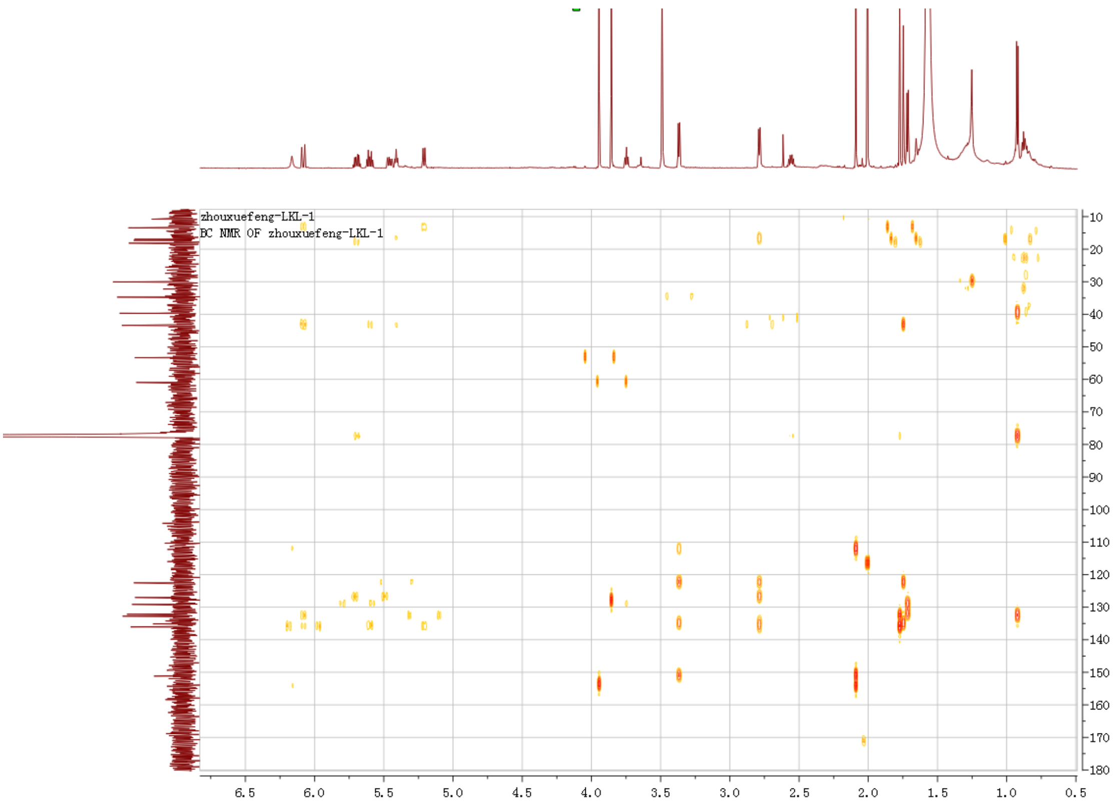


Figure SS-2-7. HMBC spectrum of **2** (in $CDCl_3$).

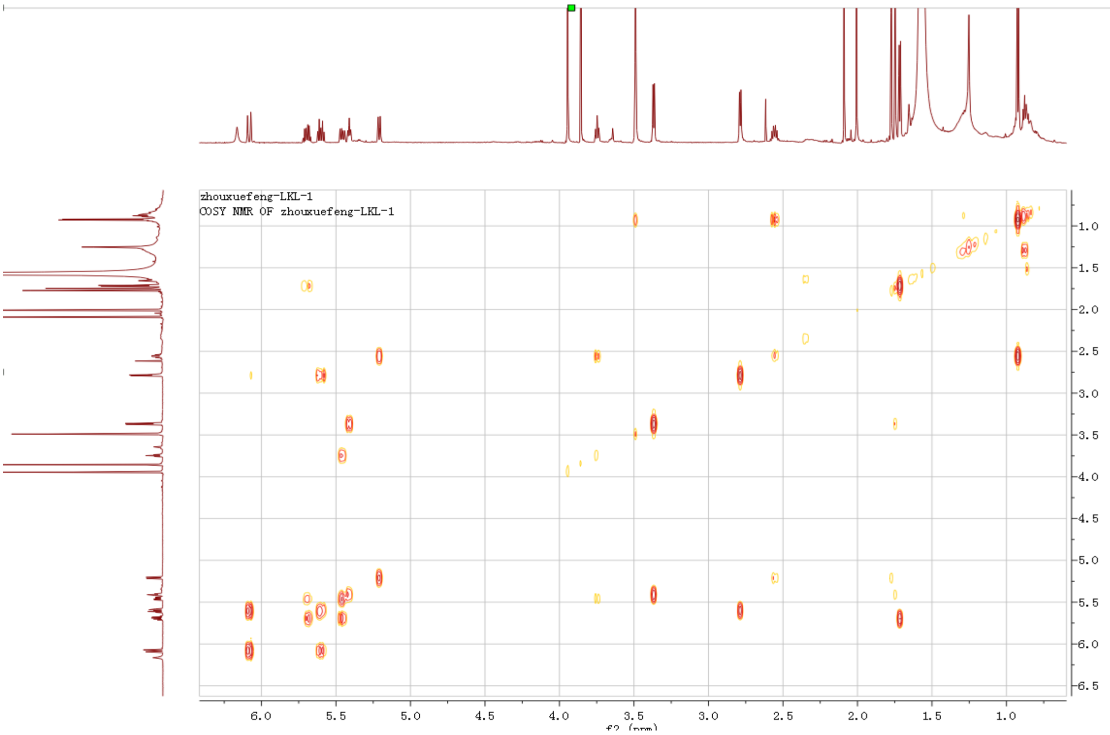


Figure SS-2-8. ^1H-^1H COSY spectrum of **2** (in $CDCl_3$).

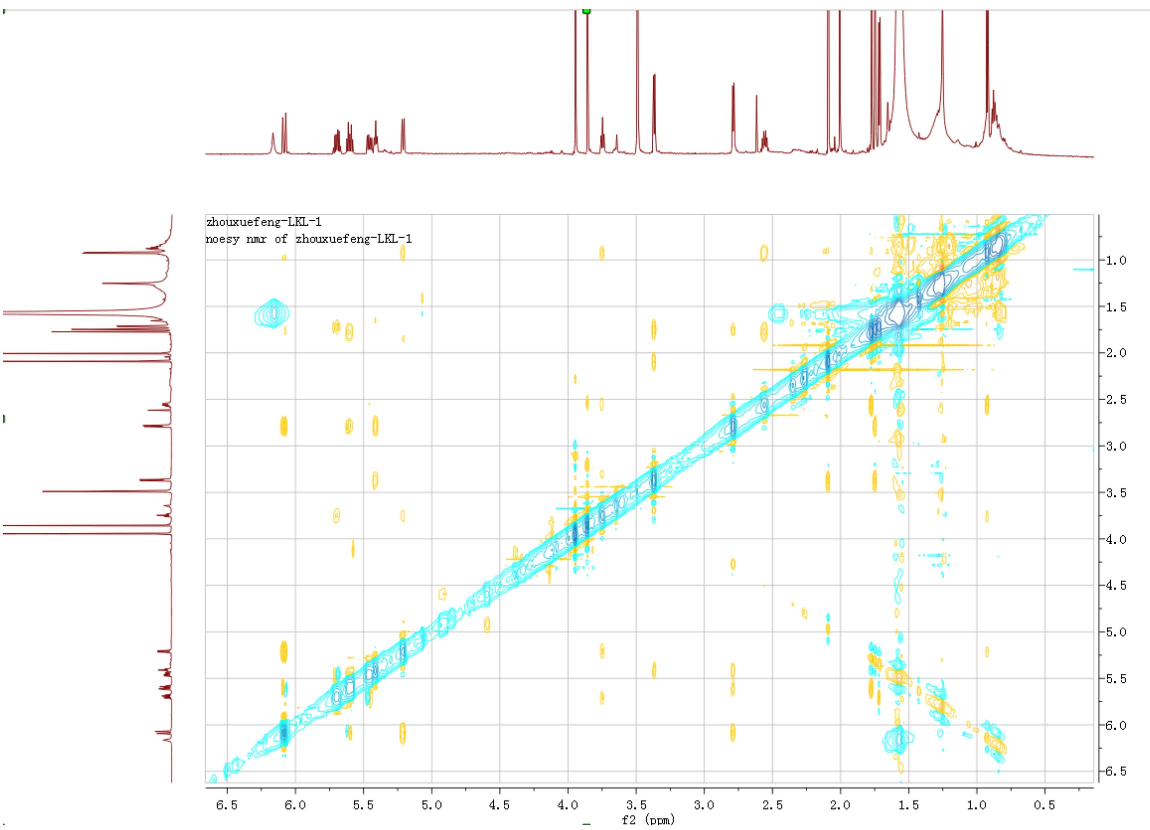


Figure SS-2-9. NOESY spectrum of **2** (in $CDCl_3$).

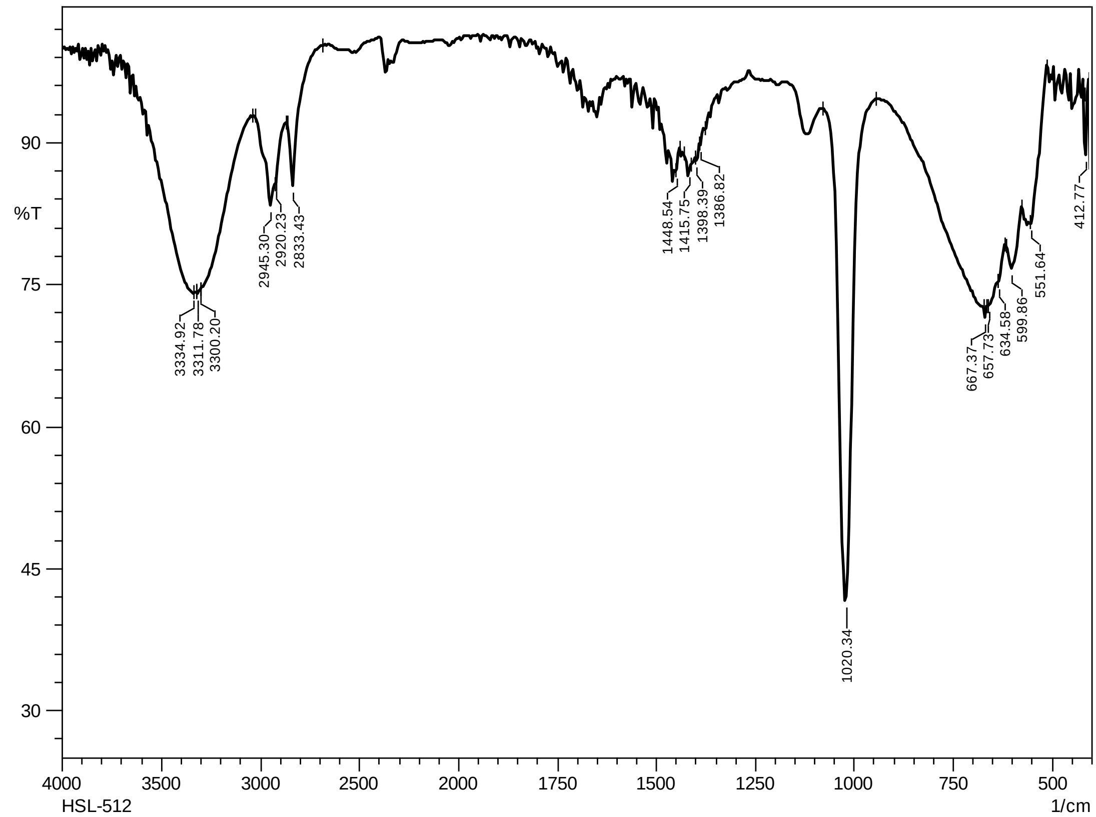
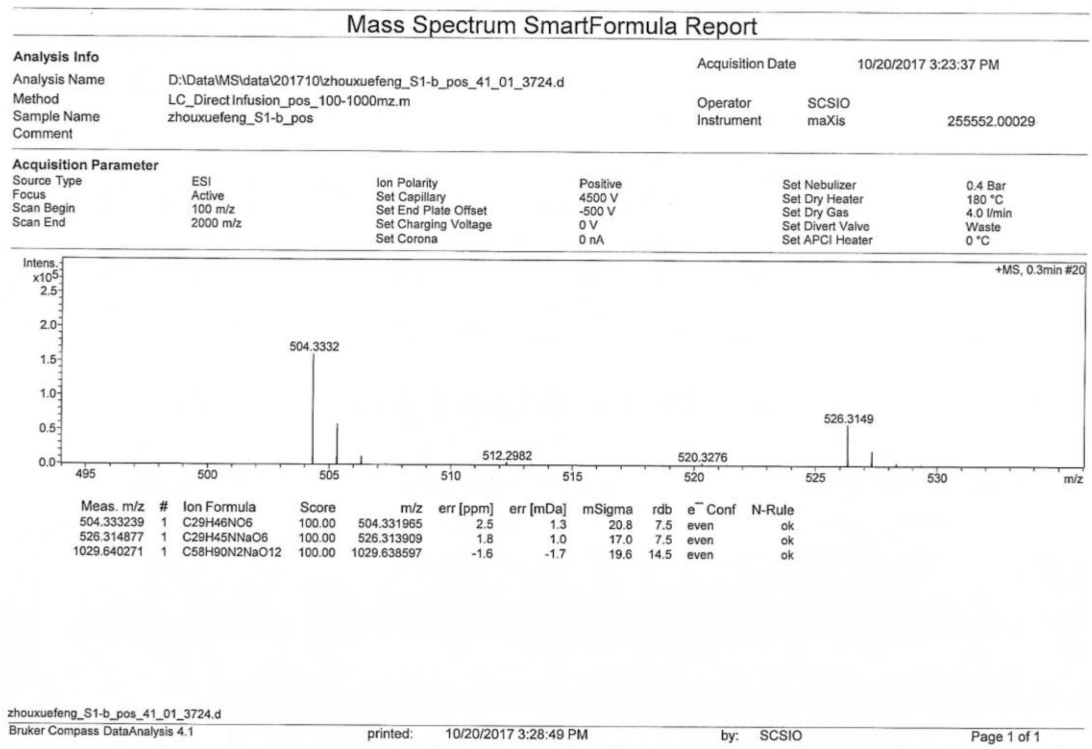


Figure SS-3-1. IR spectrum of **3**.



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Comment			

Acquisition Parameter

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Scan End	2000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C

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zhouxuefeng_S1-b_pos_41_01_3724.d

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Figure SS-3-2. HRESIMS (+) spectrum of **3**.

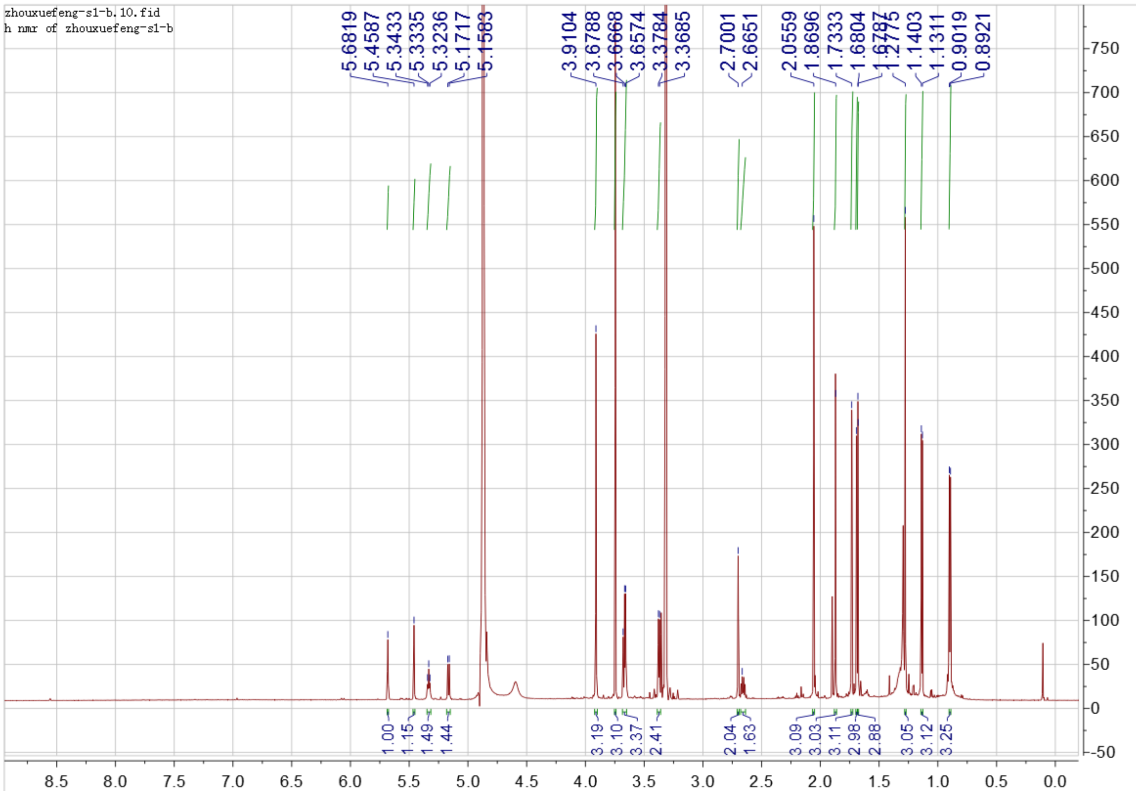

Figure SS-3-3. ¹H NMR spectrum of **3** (in CD_3OD, 700 MHz).

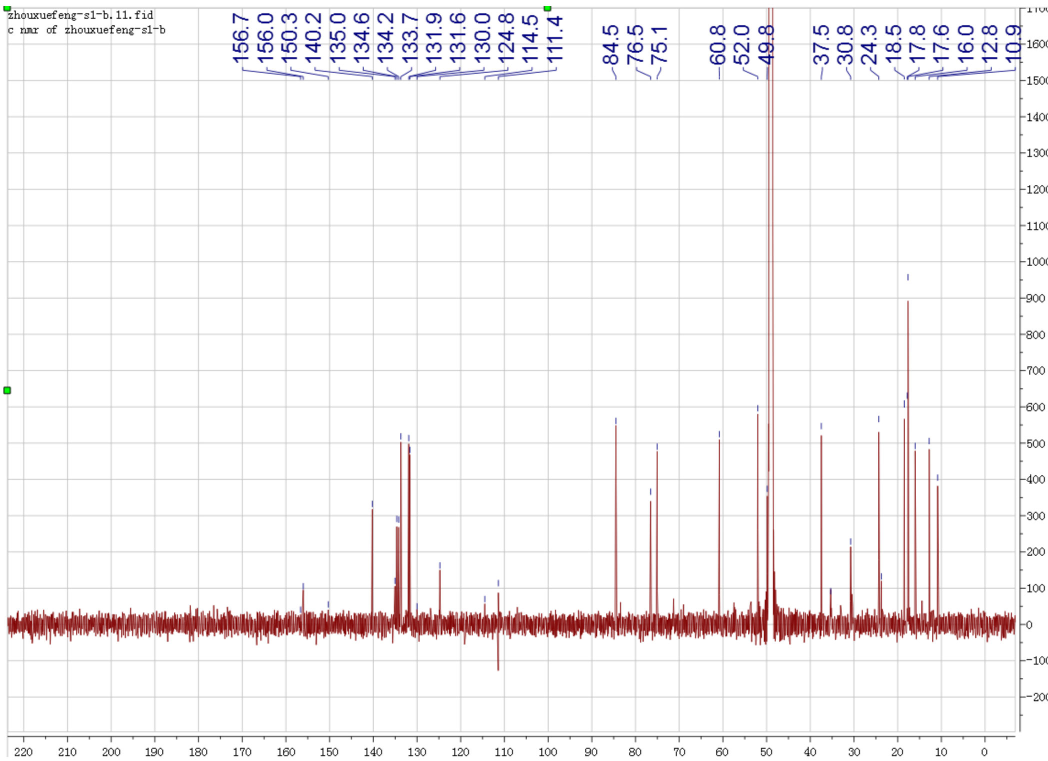

Figure SS-3-4. ¹³C NMR spectrum of **3** (in CD_3OD, 175 MHz).

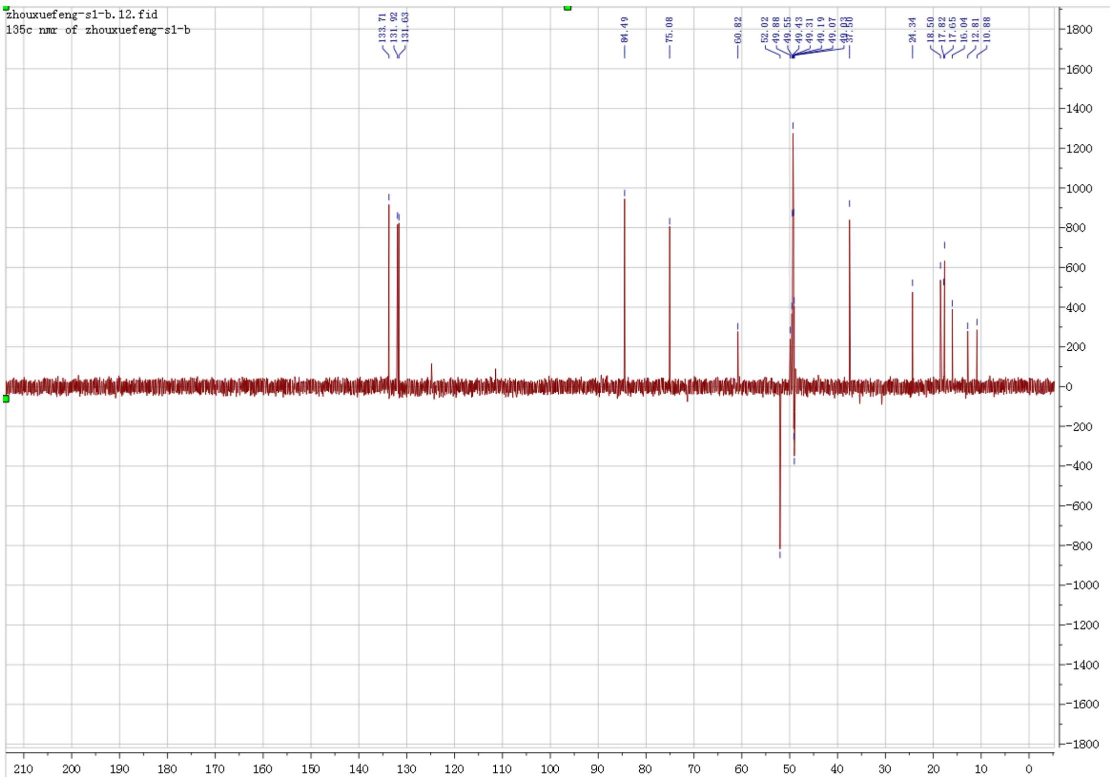

Figure SS-3-5. DEPT spectrum of **3** (in CD_3OD, 175 MHz).

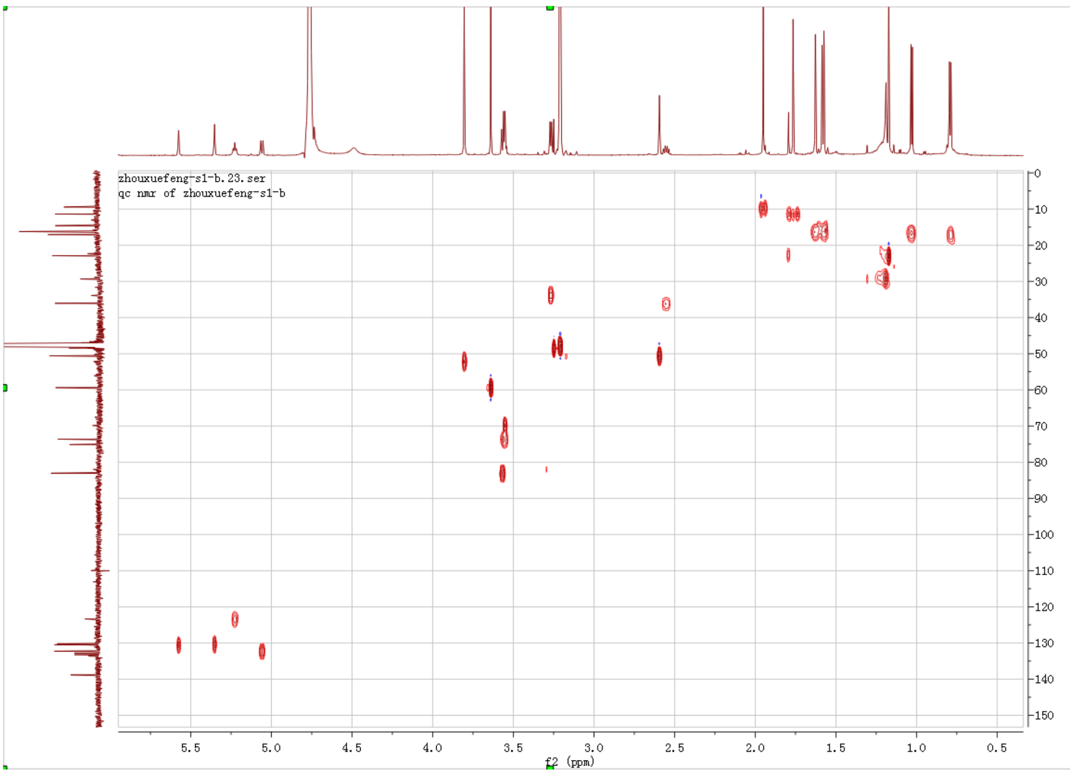

Figure SS-3-6. HSQC spectrum of **3** (in CD_3OD).

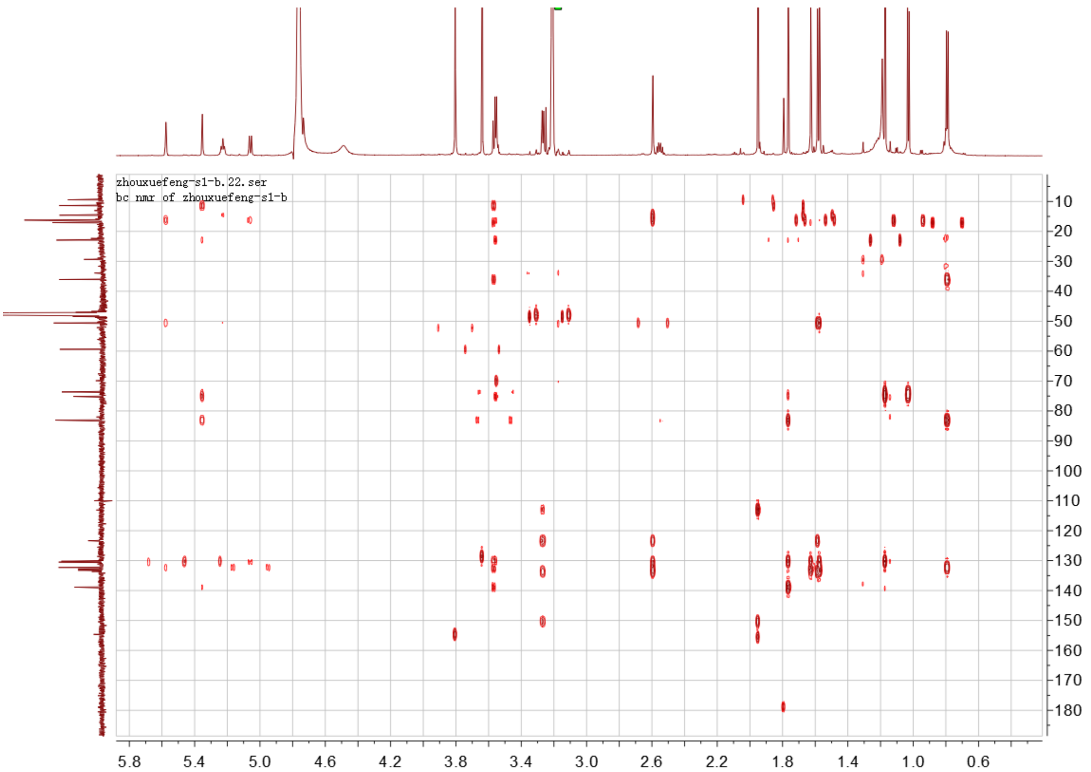

Figure SS-3-7. HMBC spectrum of **3** (in CD_3OD).

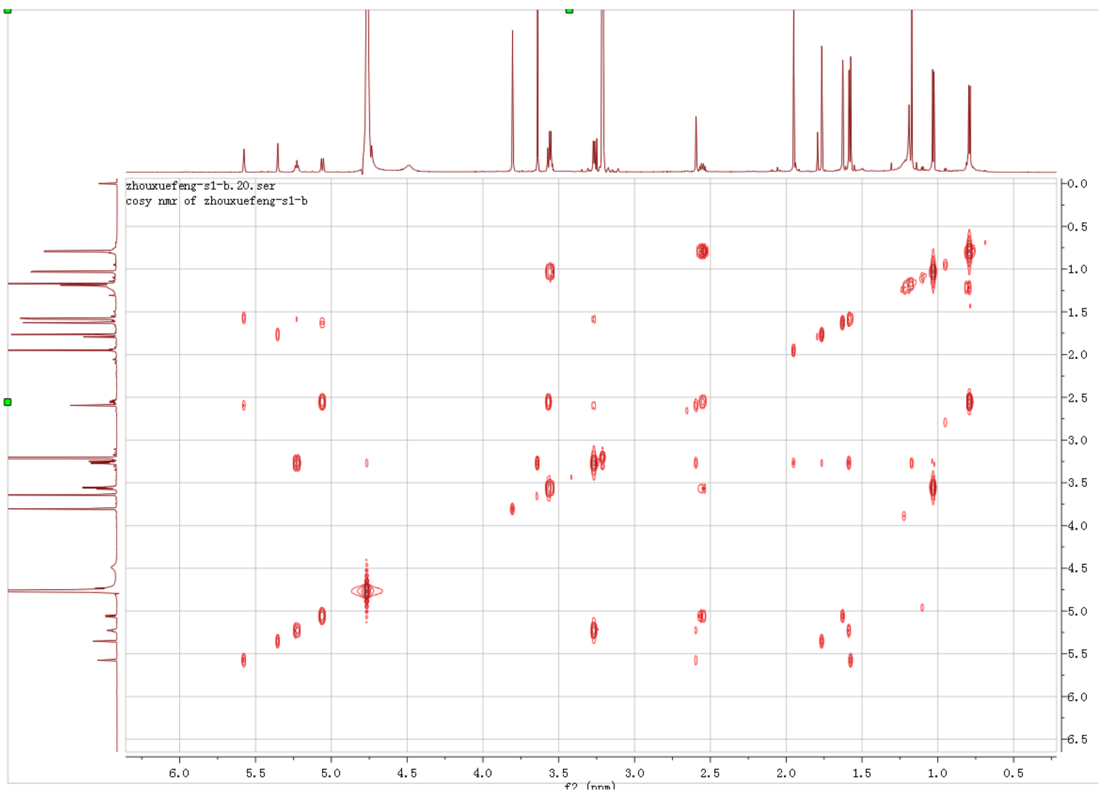

Figure SS-3-8. ^1H-^1H COSY spectrum of **3** (in CD_3OD).

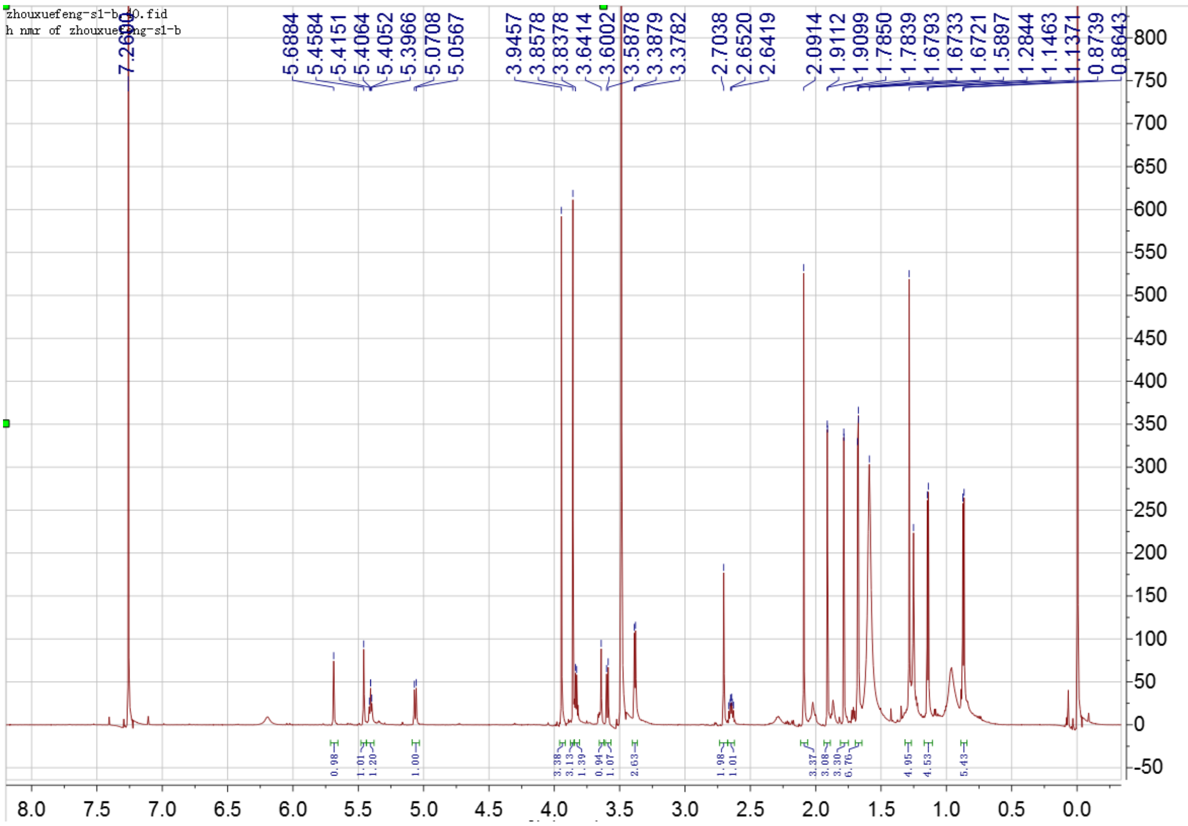

Figure SS-3-9. ^{1}H NMR spectrum of **3** (in $CDCl_3$, 700 MHz).

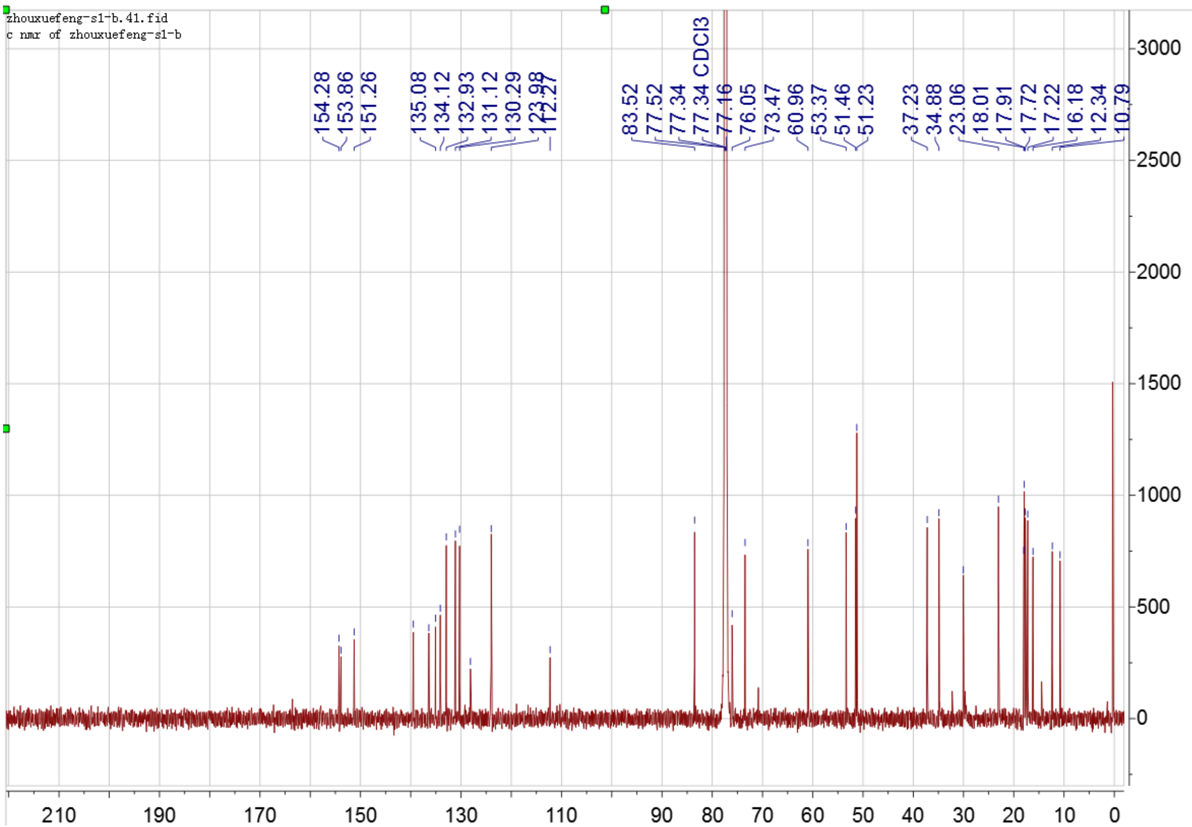

Figure SS-3-10. ^{13}C NMR spectrum of **3** (in $CDCl_3$, 175 MHz).

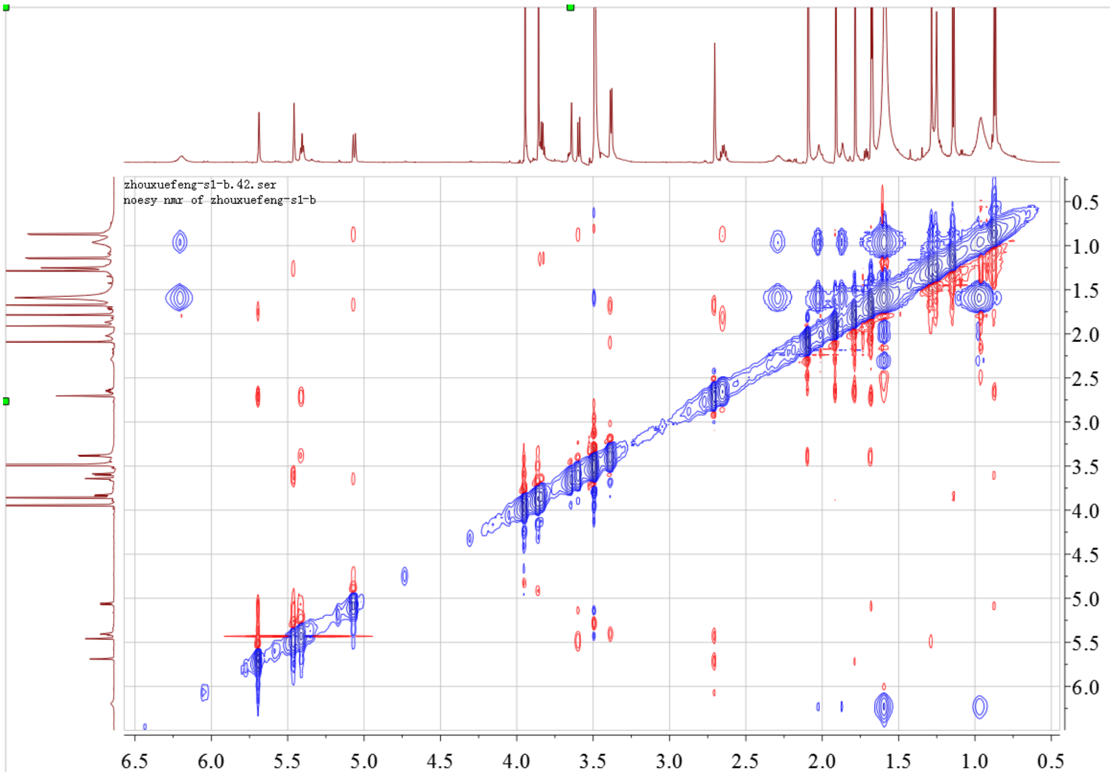

Figure SS-3-11. NOESY spectrum of **3** (in $CDCl_3$).

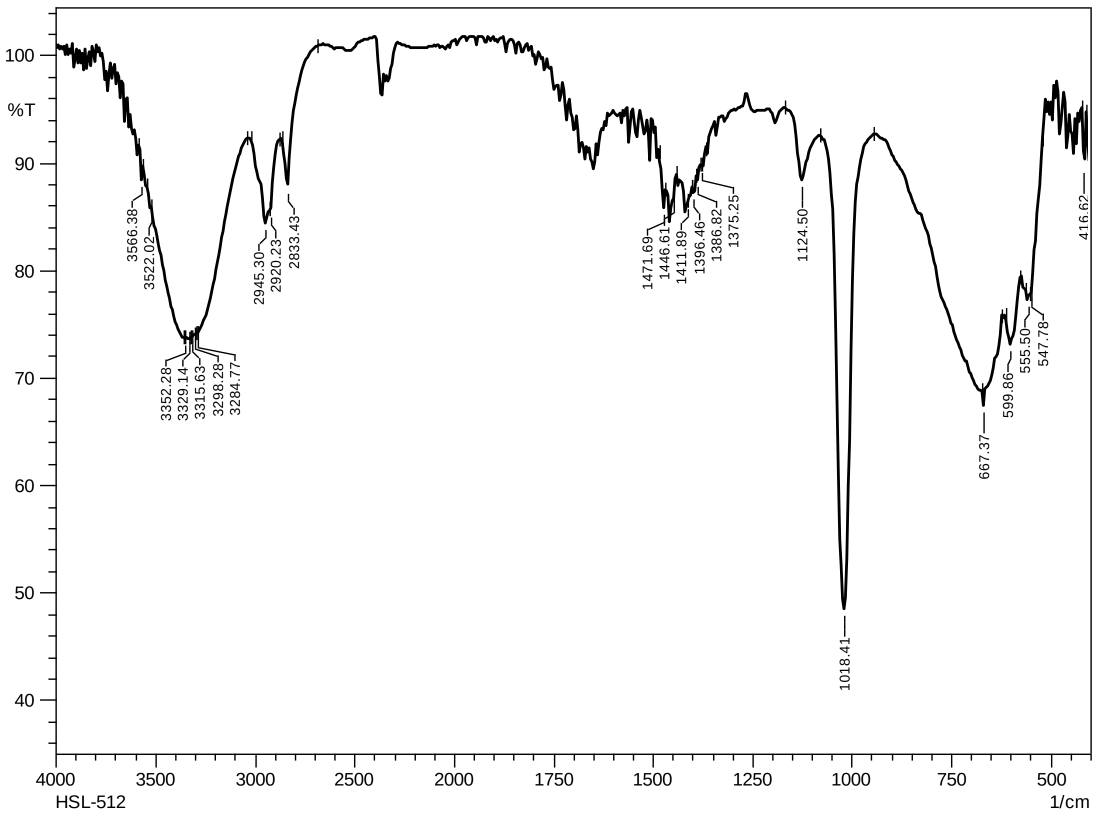

Figure SS-4-1. IR spectrum of **4**.

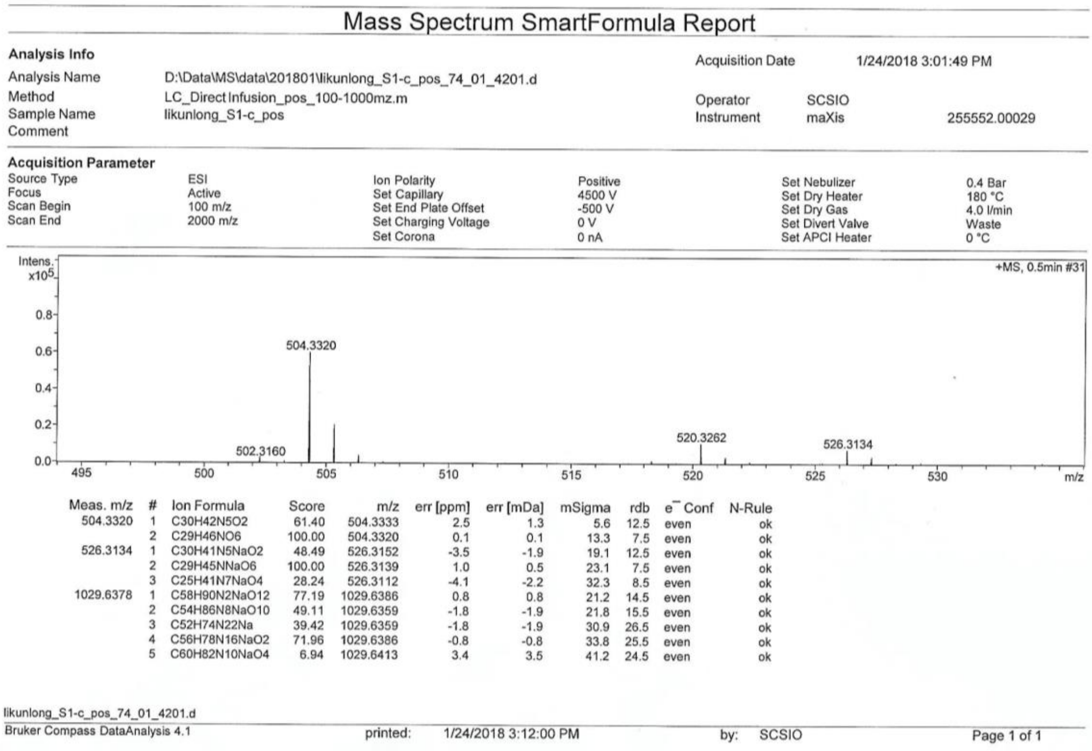

Figure SS-4-2. HRESIMS (+) spectrum of **4**.

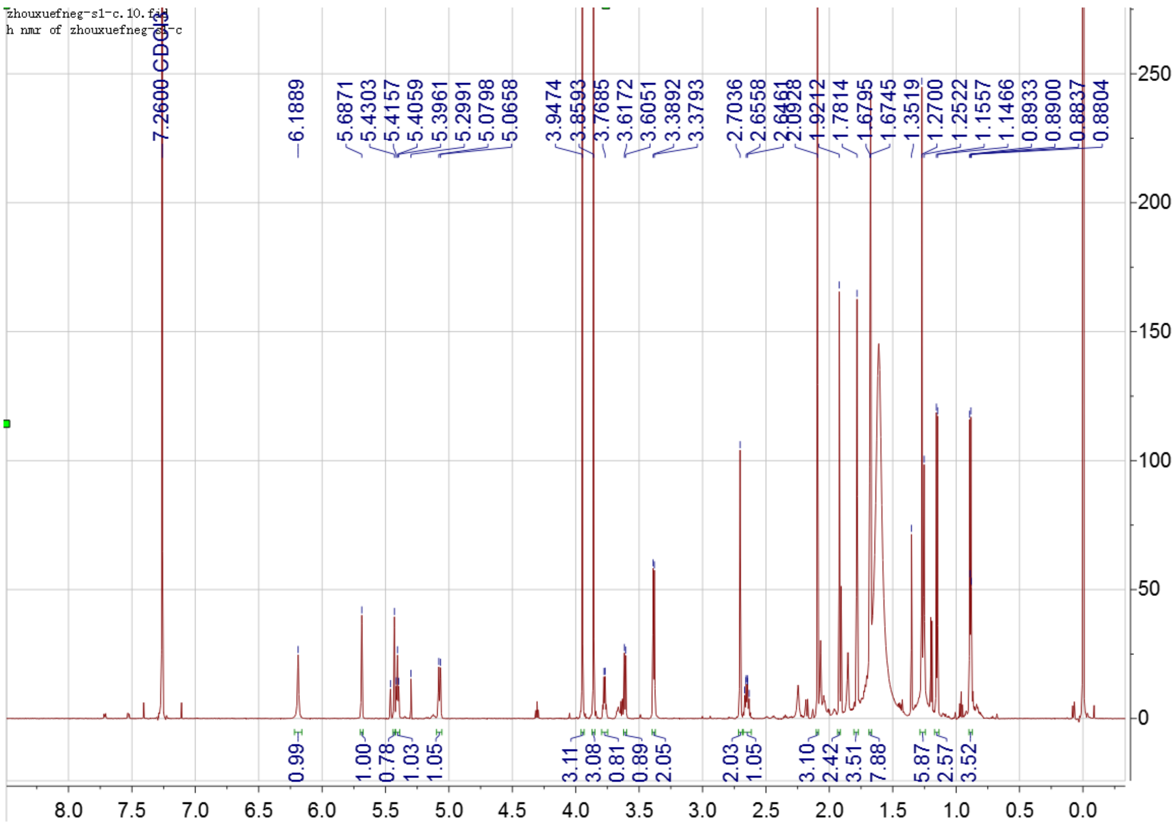

Figure SS-4-3. ^{1}H NMR spectrum of **4** (in $CDCl_3$, 700 MHz).

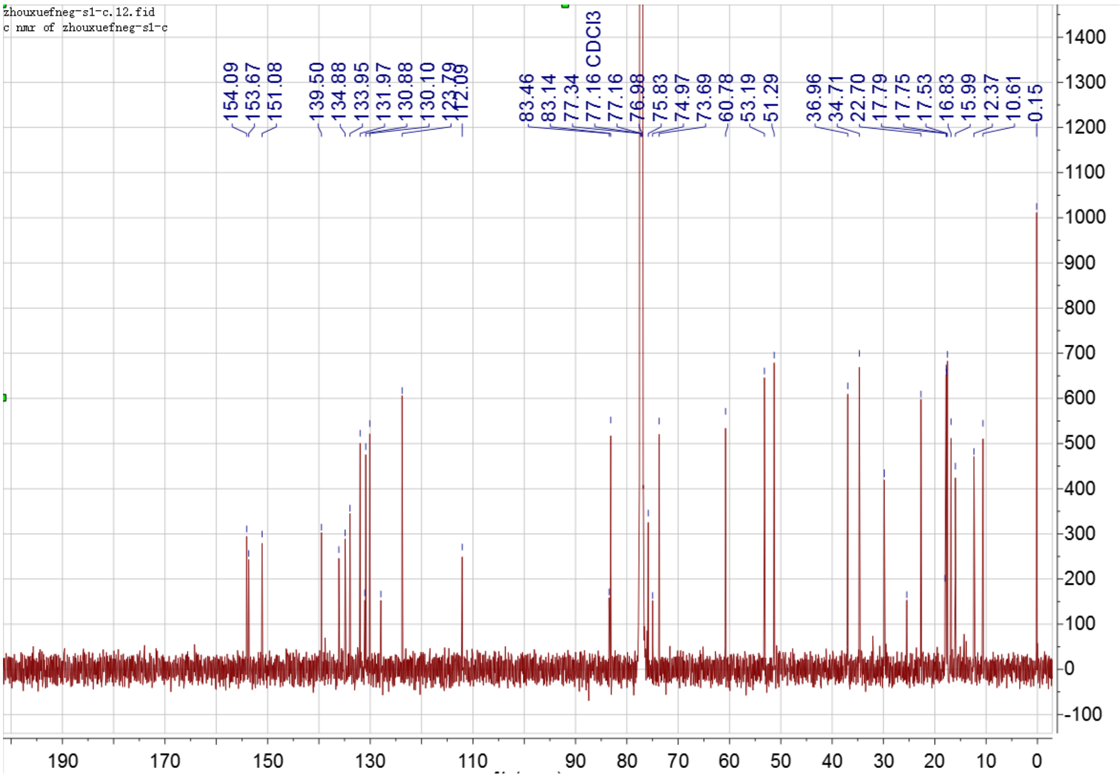

Figure SS-4-4. ^{13}C NMR spectrum of **4** (in $CDCl_3$, 175 MHz).

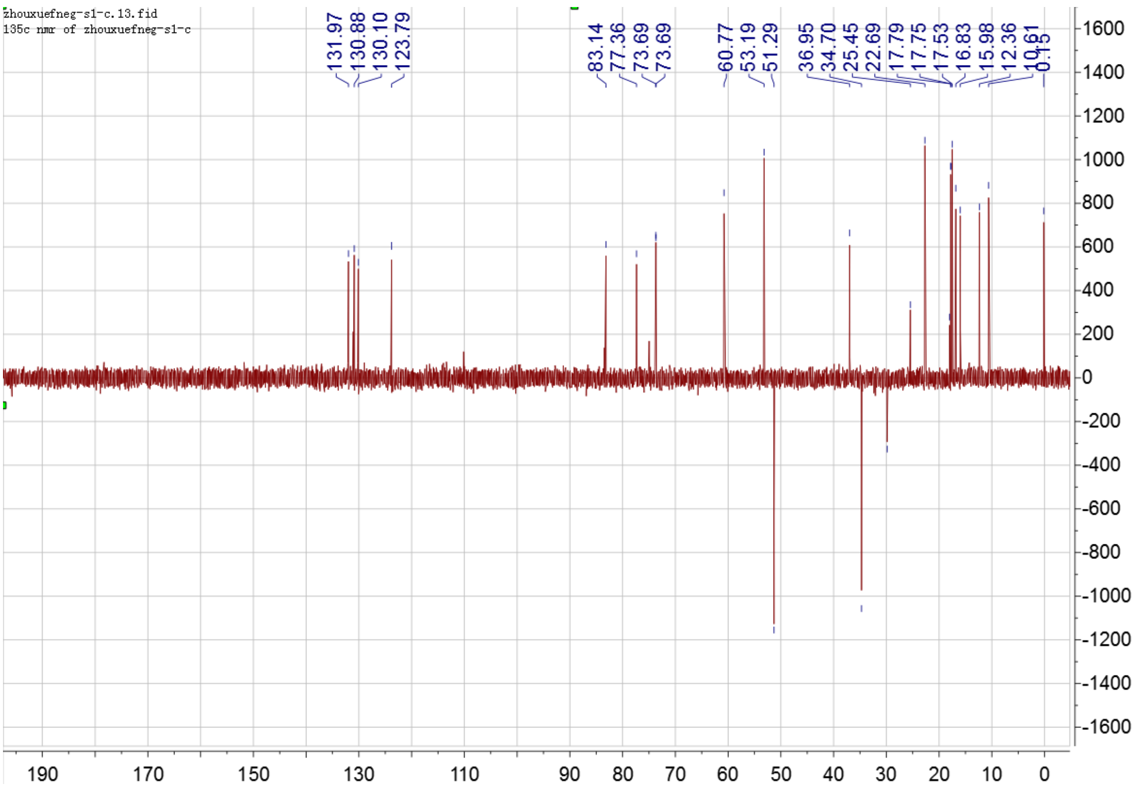

Figure SS-4-5. DEPT spectrum of **4** (in $CDCl_3$, 175 MHz).

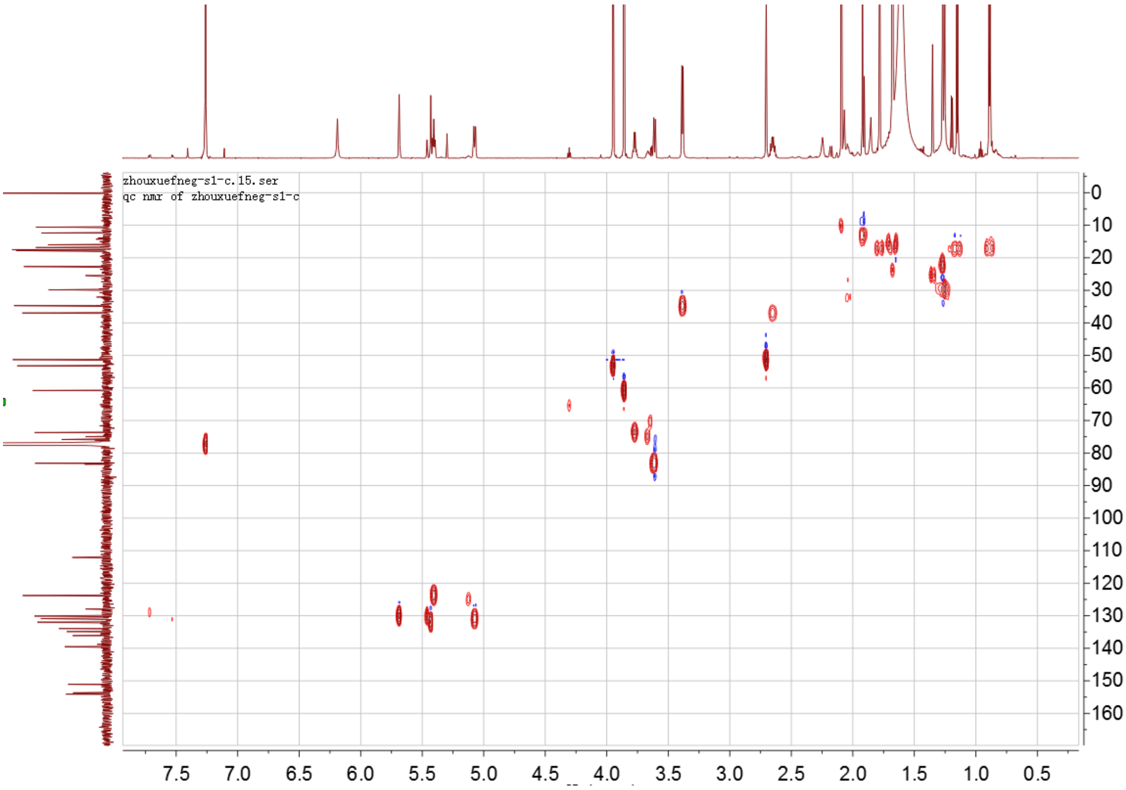

Figure SS-4-6. HSQC spectrum of **4** (in $CDCl_3$).

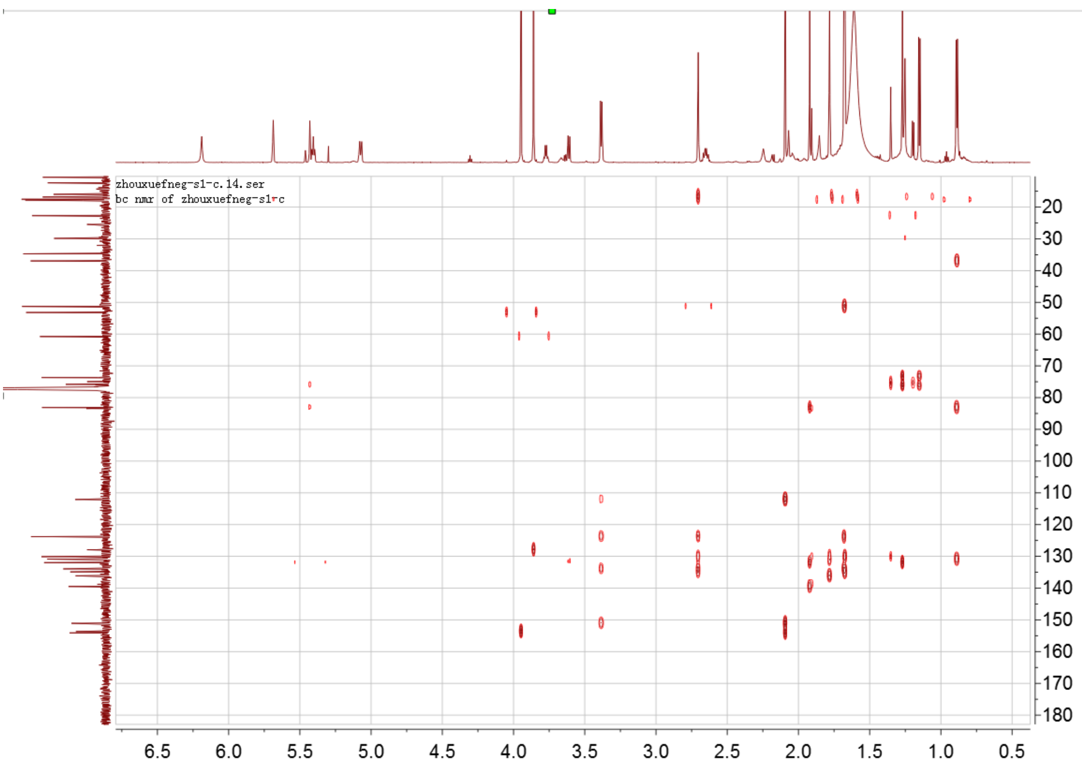

Figure SS-4-7. HMBC spectrum of **4** (in $CDCl_3$).

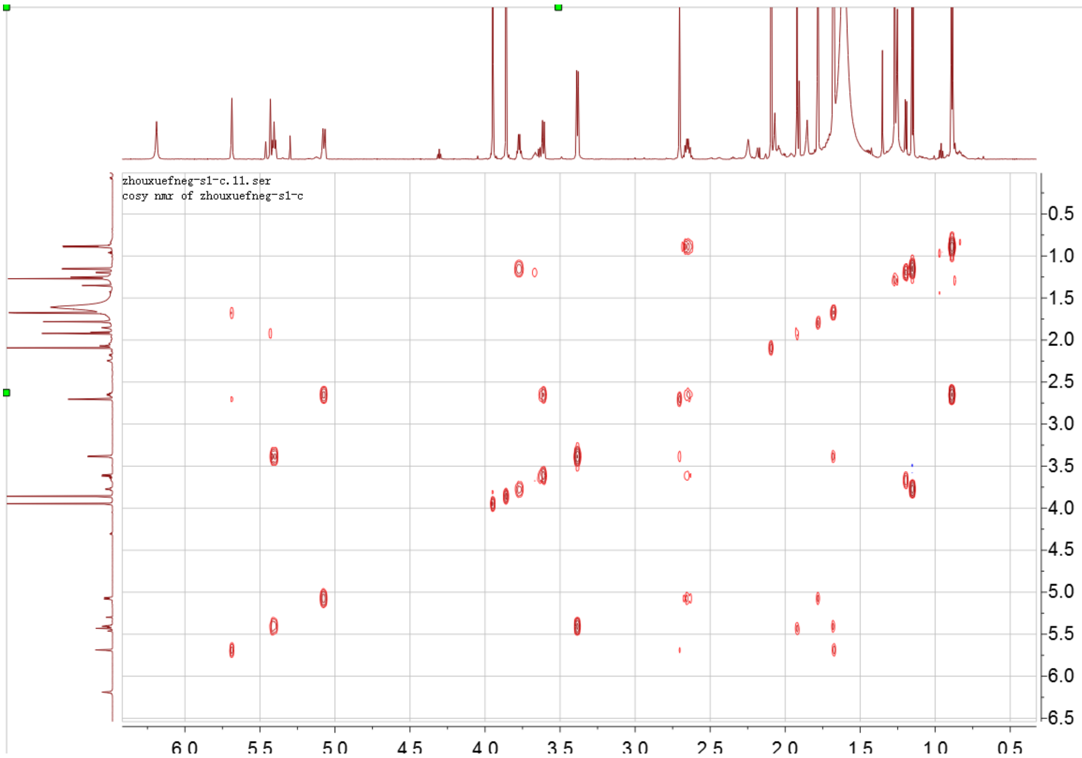

Figure SS-4-8. ^{1}H-^{1}H COSY spectrum of **4** (in $CDCl_3$).

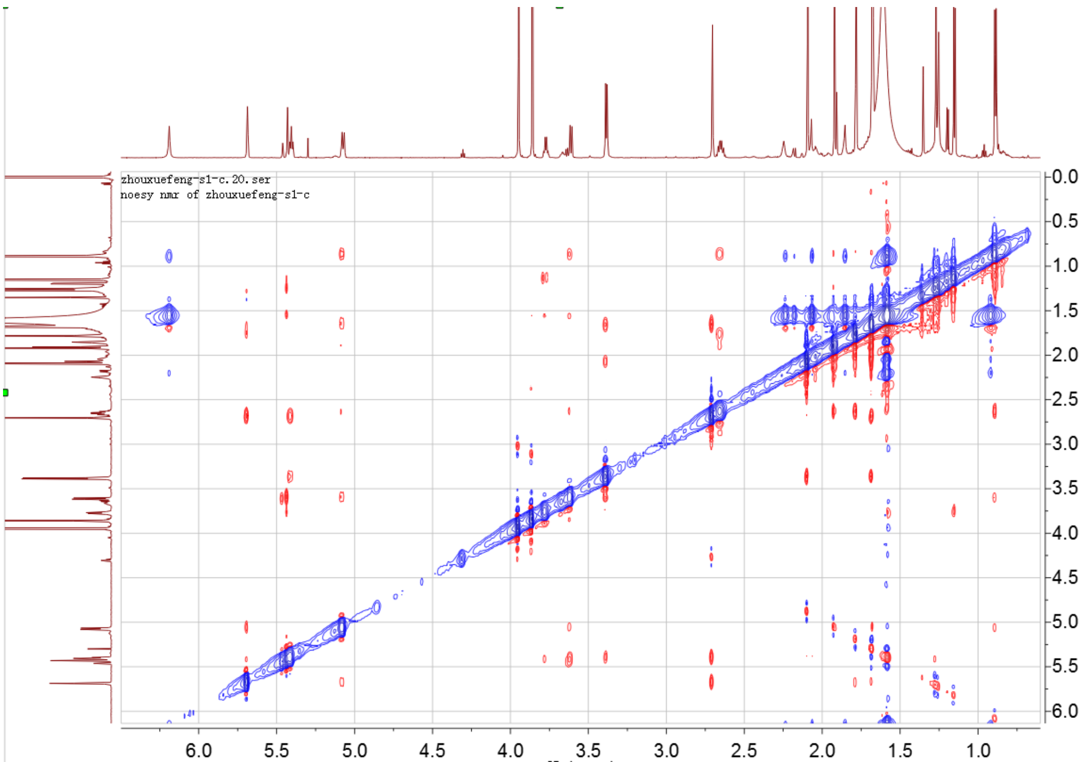

Figure SS-4-9. NOESY spectrum of **4** (in $CDCl_3$).

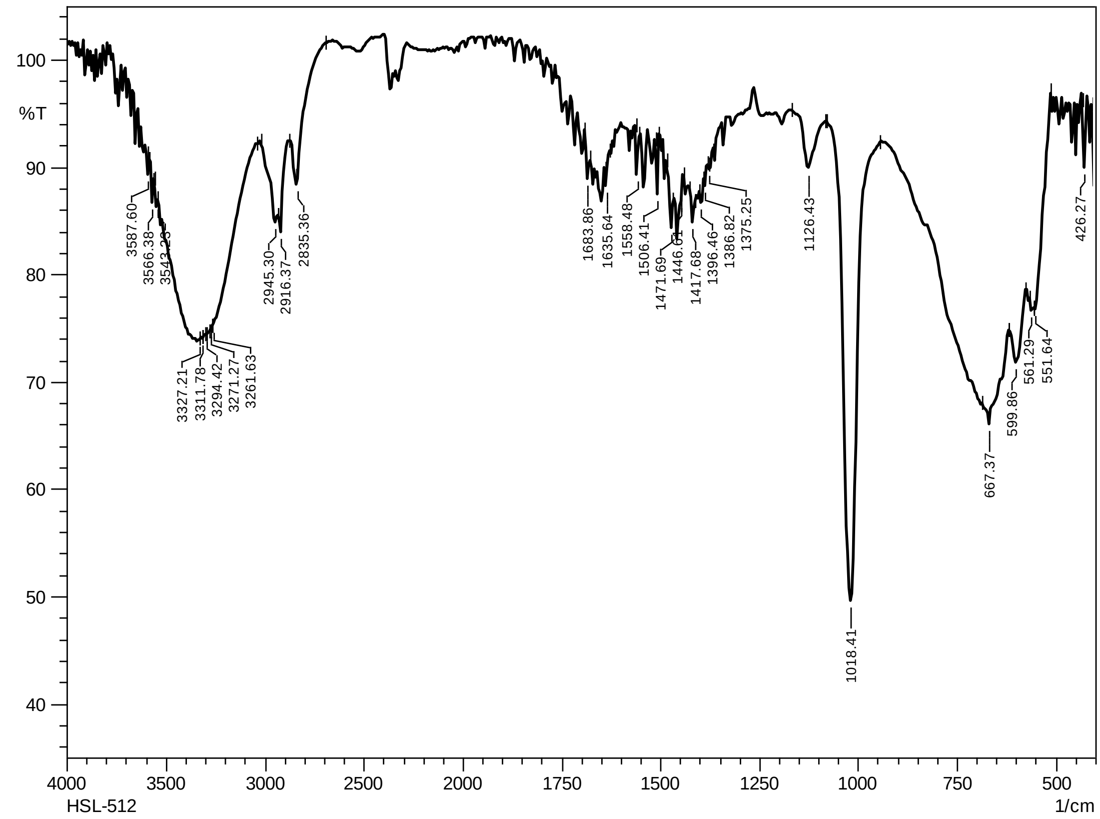

Figure SS-5-1. IR spectrum of **5**.

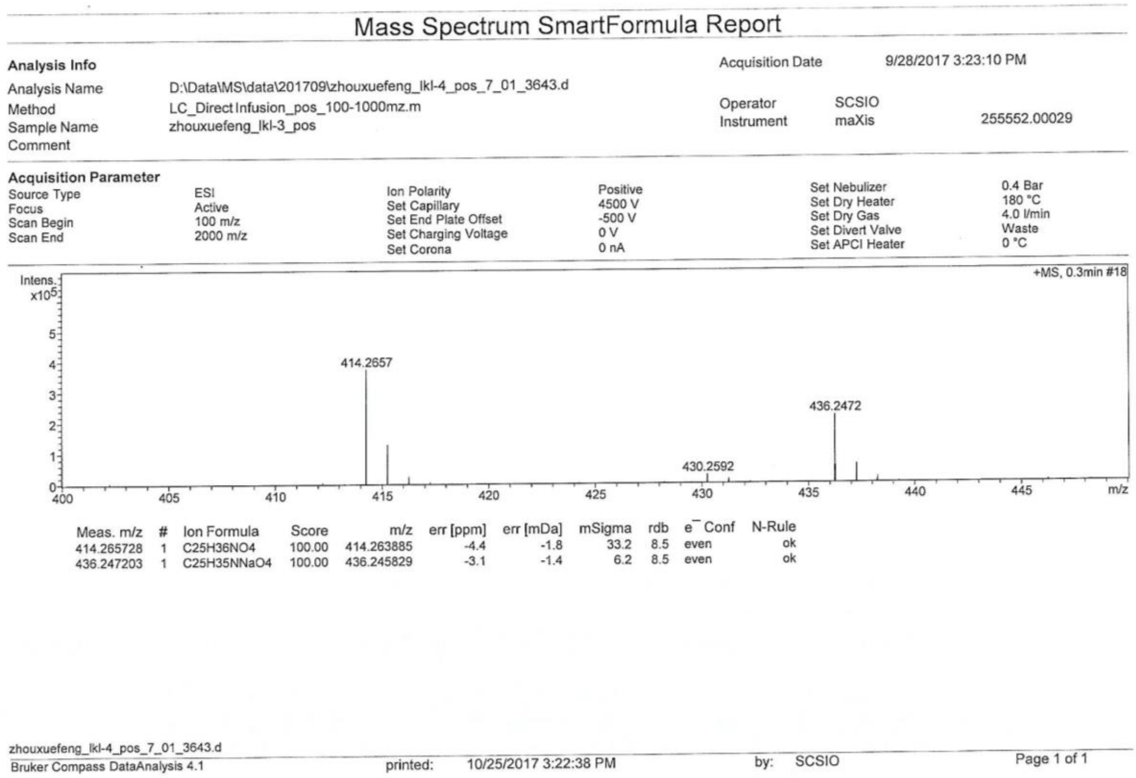

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Figure SS-5-2. HRESIMS (+) spectrum of **5**.

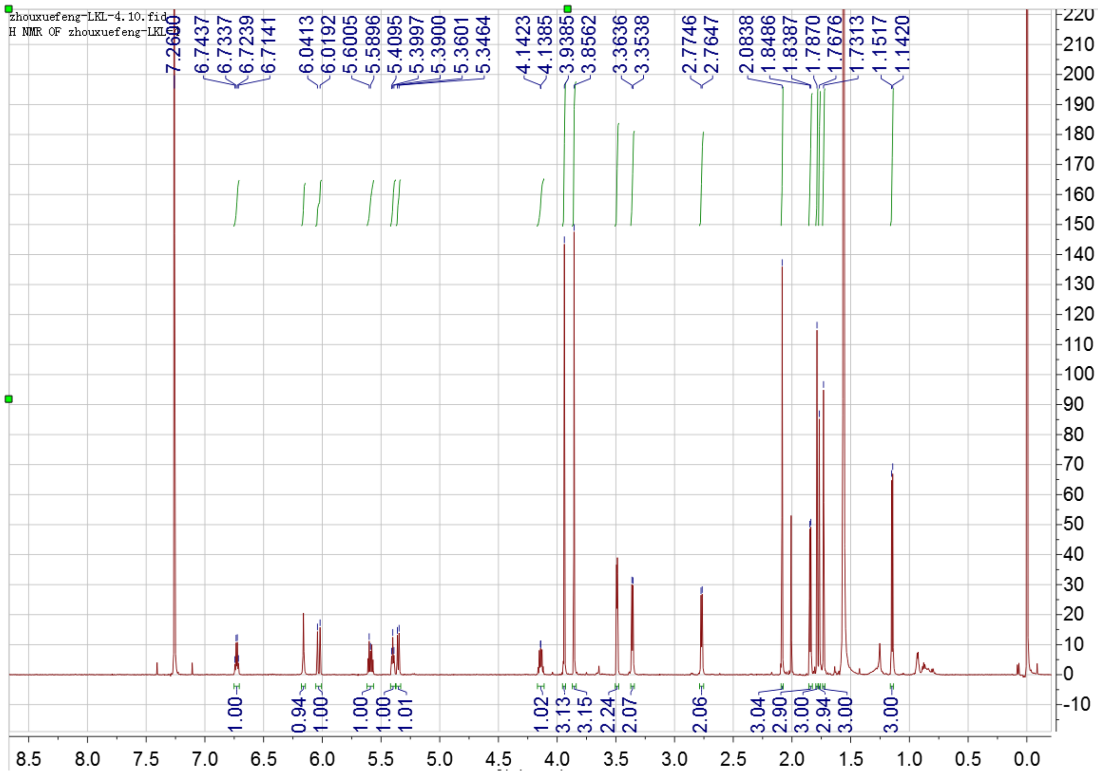


Figure SS-5-3. ^{1}H NMR spectrum of **5** (in $CDCl_3$, 700 MHz).

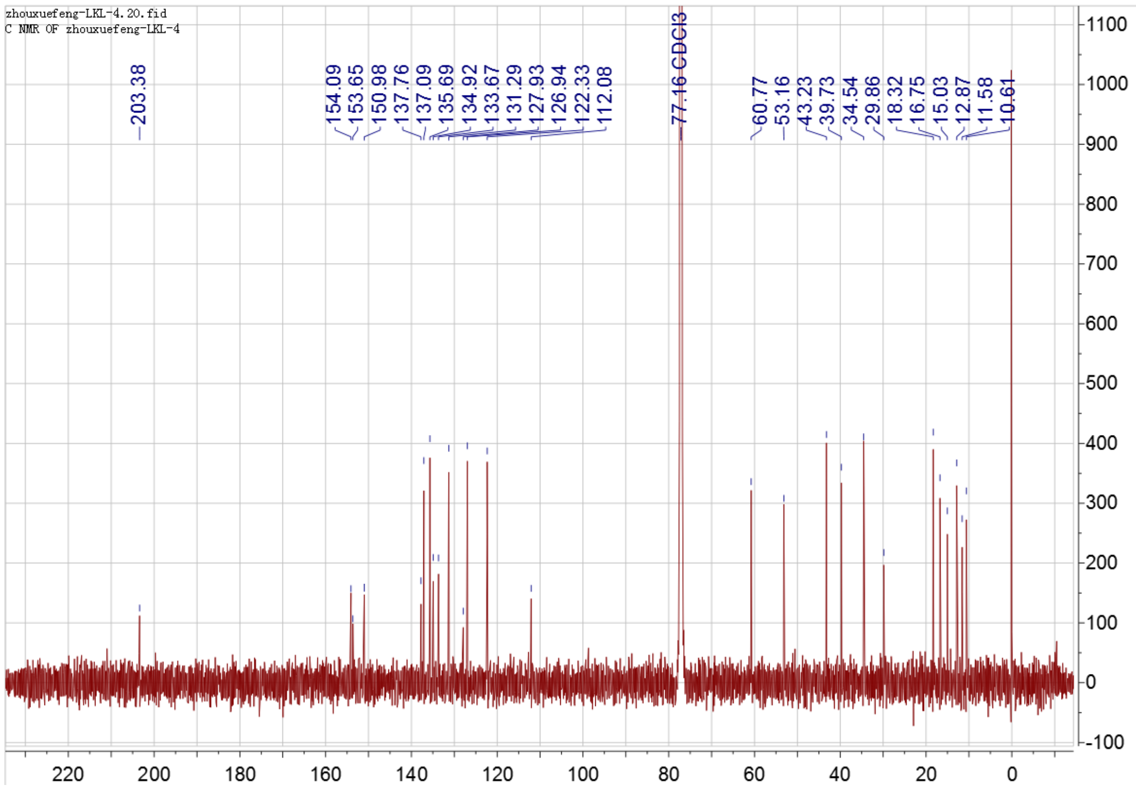


Figure SS-5-4. ^{13}C NMR spectrum of **5** (in $CDCl_3$, 175 MHz).

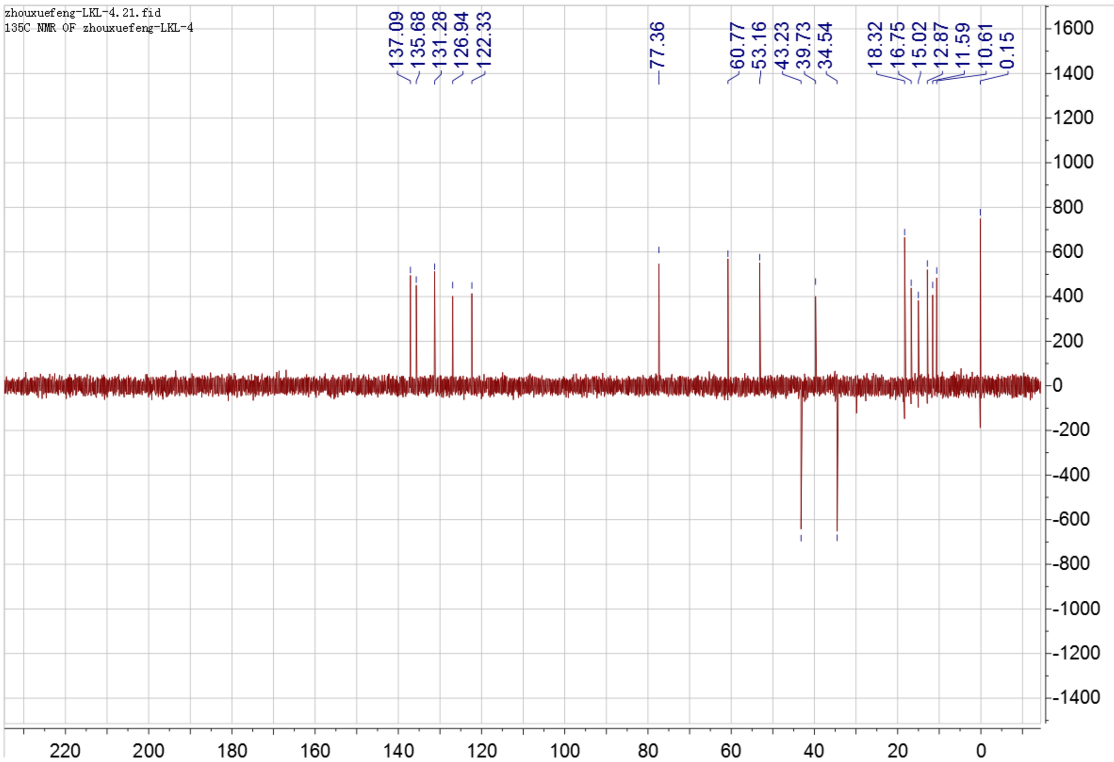


Figure SS-5-5. DEPT spectrum of **5** (in $CDCl_3$, 175 MHz).

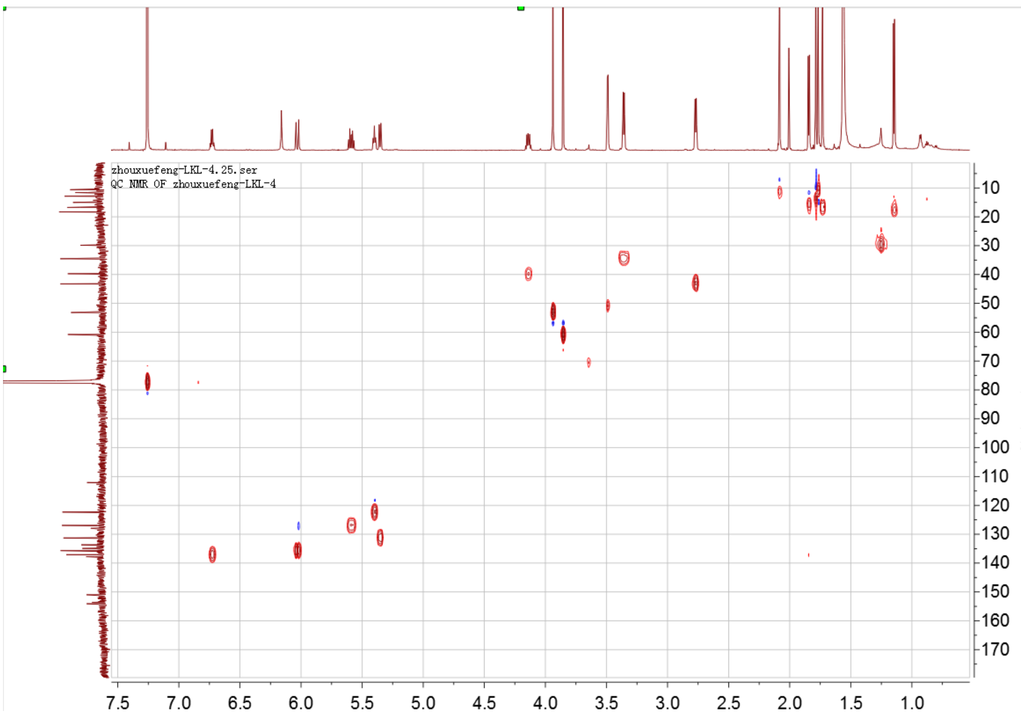


Figure SS-5-6. HSQC spectrum of **5** (in $CDCl_3$).

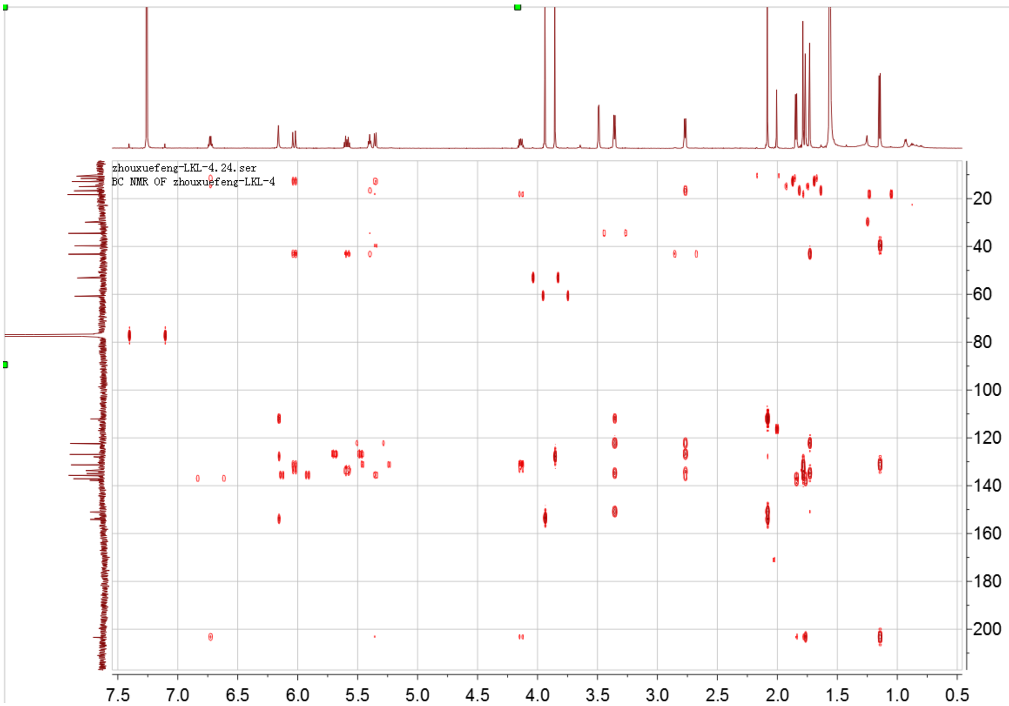


Figure SS-5-7. HMBC spectrum of **5** (in $CDCl_3$).

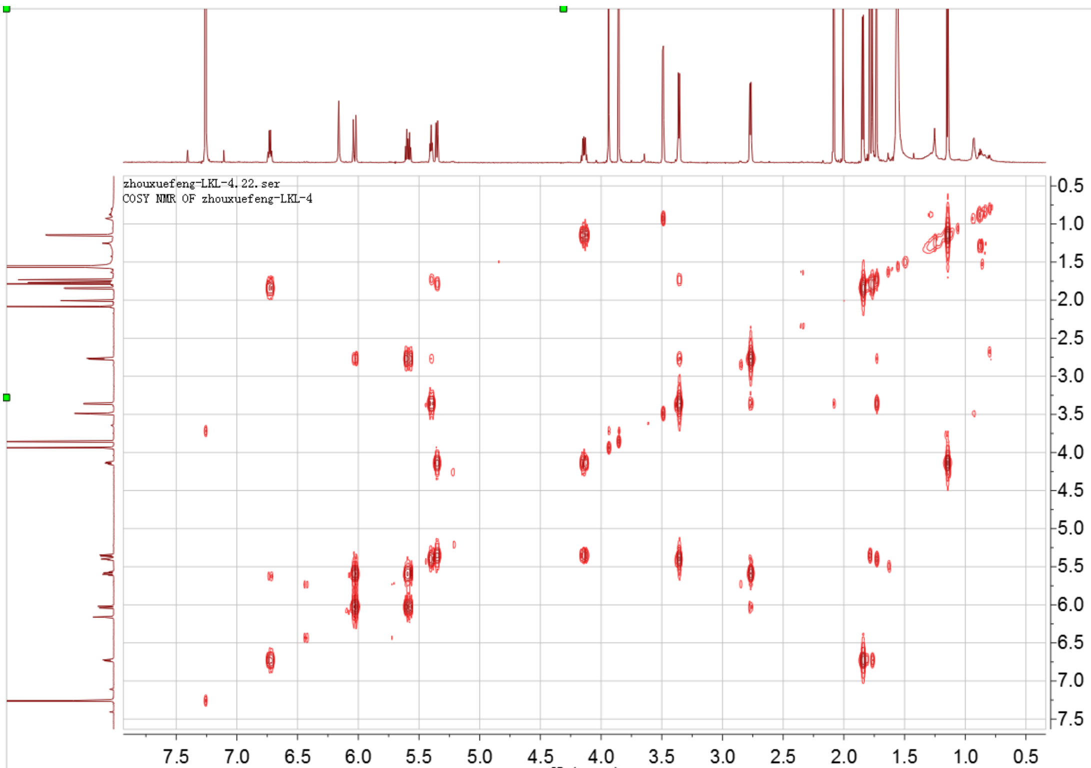


Figure SS-5-8. ^1H-^1H COSY spectrum of **5** (in $CDCl_3$).

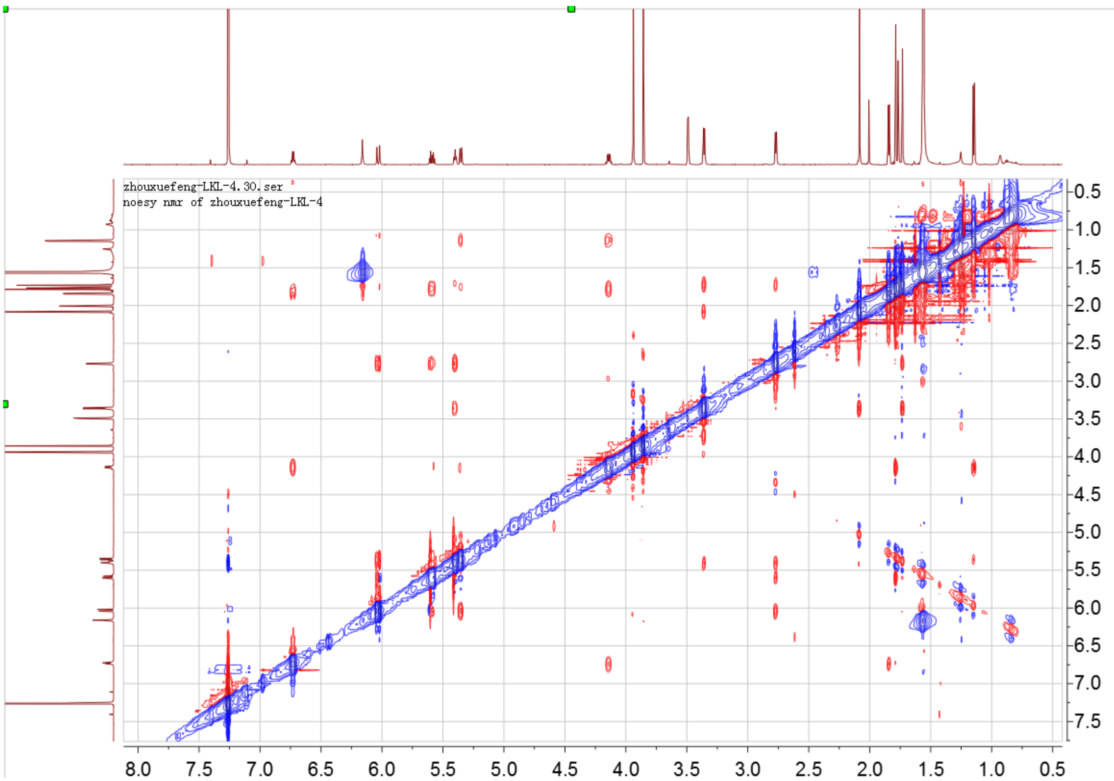


Figure SS-5-9. NOESY spectrum of **5** (in $CDCl_3$).

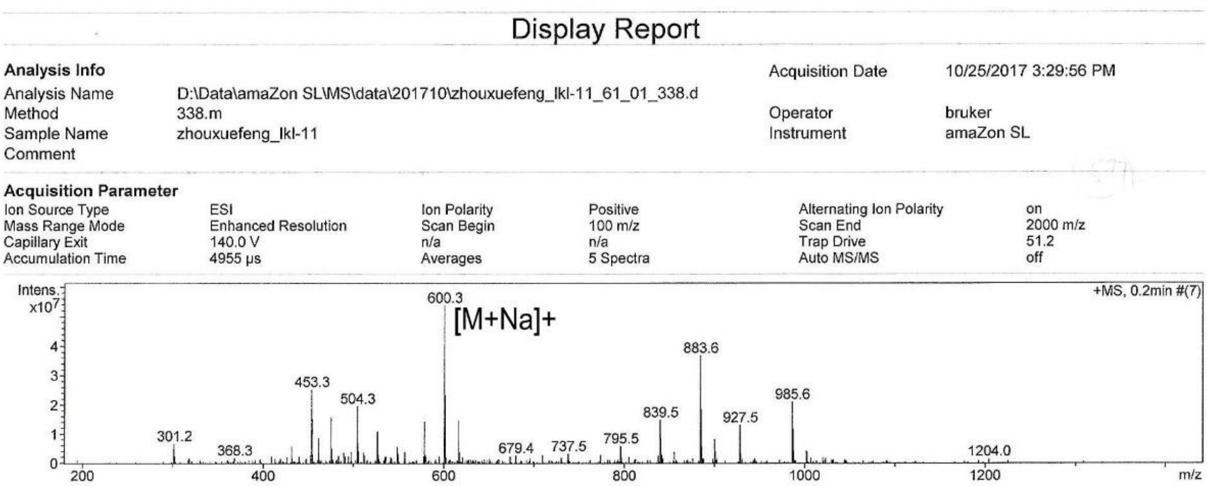


Figure SS-6-1. ESIMS (+) spectrum of **10**.

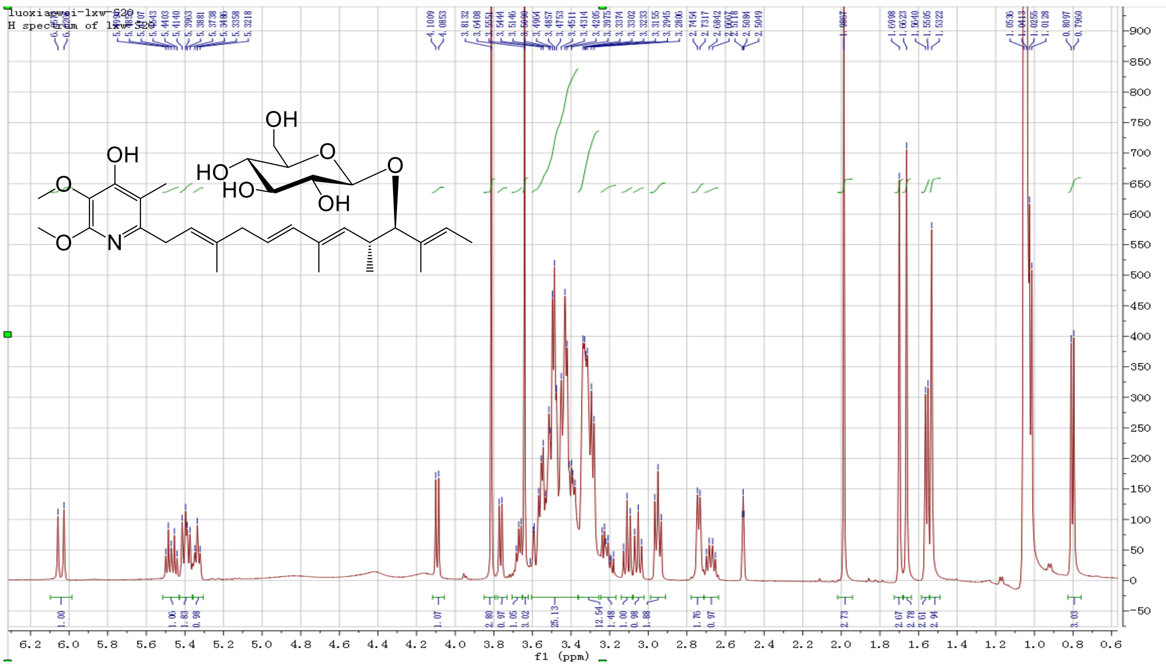


Figure SS-6-2. ^{1}H NMR spectrum of **10** (in DMSO-d_6, 700 MHz).

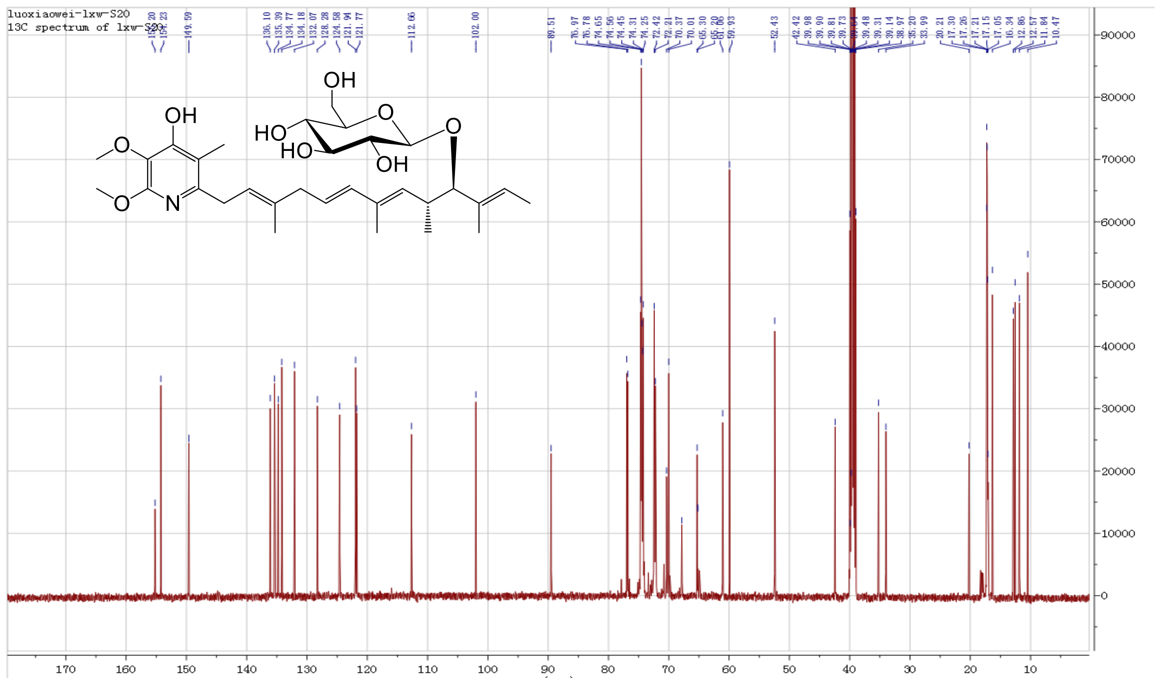


Figure SS-6-3. ^{13}C NMR spectrum of **10** (in DMSO-d_6, 175 MHz).

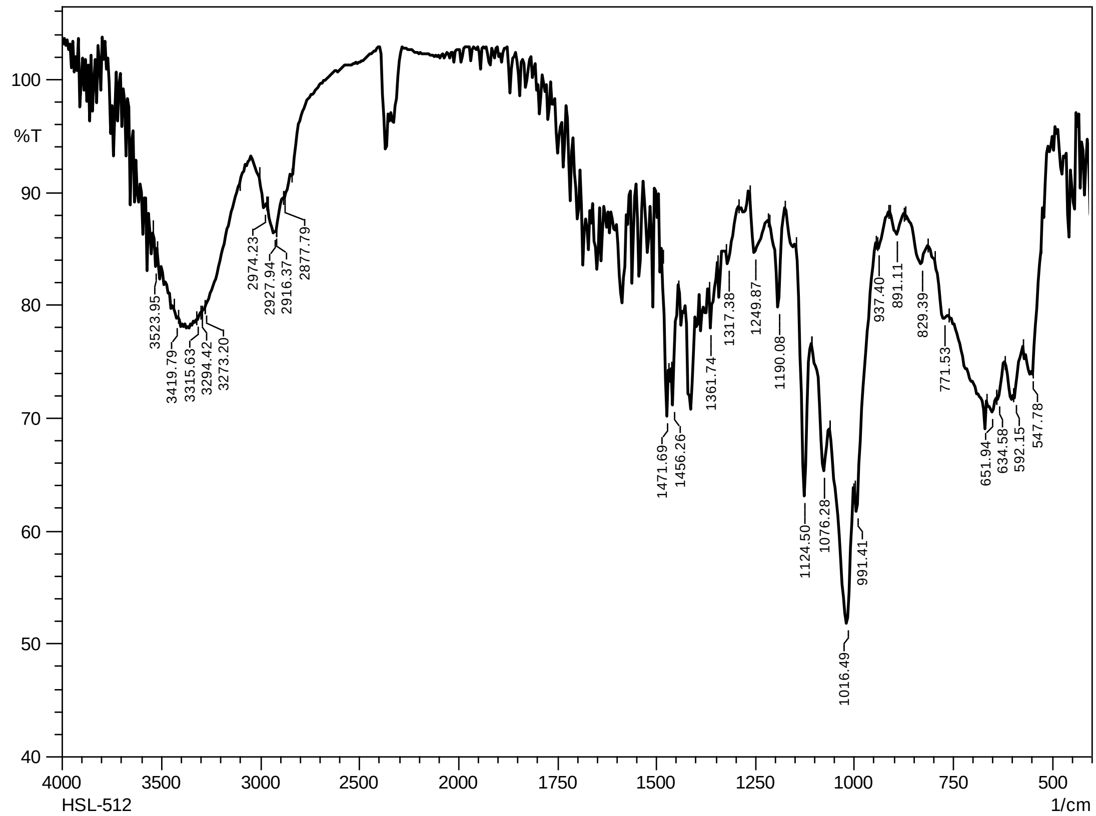
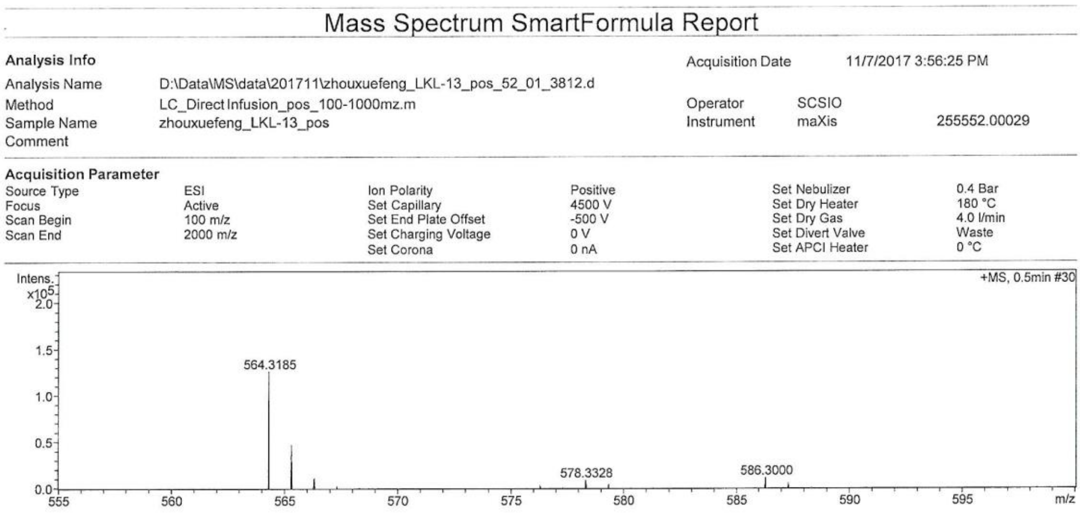


Figure SS-7-1. IR spectrum of **12**.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf	N-Rule
564.318512	1	C30H46NO9	100.00	564.316708	3.2	1.8	19.9	8.5	even	ok
586.300000	1	C30H45NNaO9	100.00	586.298653	-2.3	-1.3	10.5	8.5	even	ok
1149.608528	1	C60H90N2NaO18	100.00	1149.608085	0.4	0.4	27.4	16.5	even	ok

Figure SS-7-2. HRESIMS (+) spectrum of **12**.

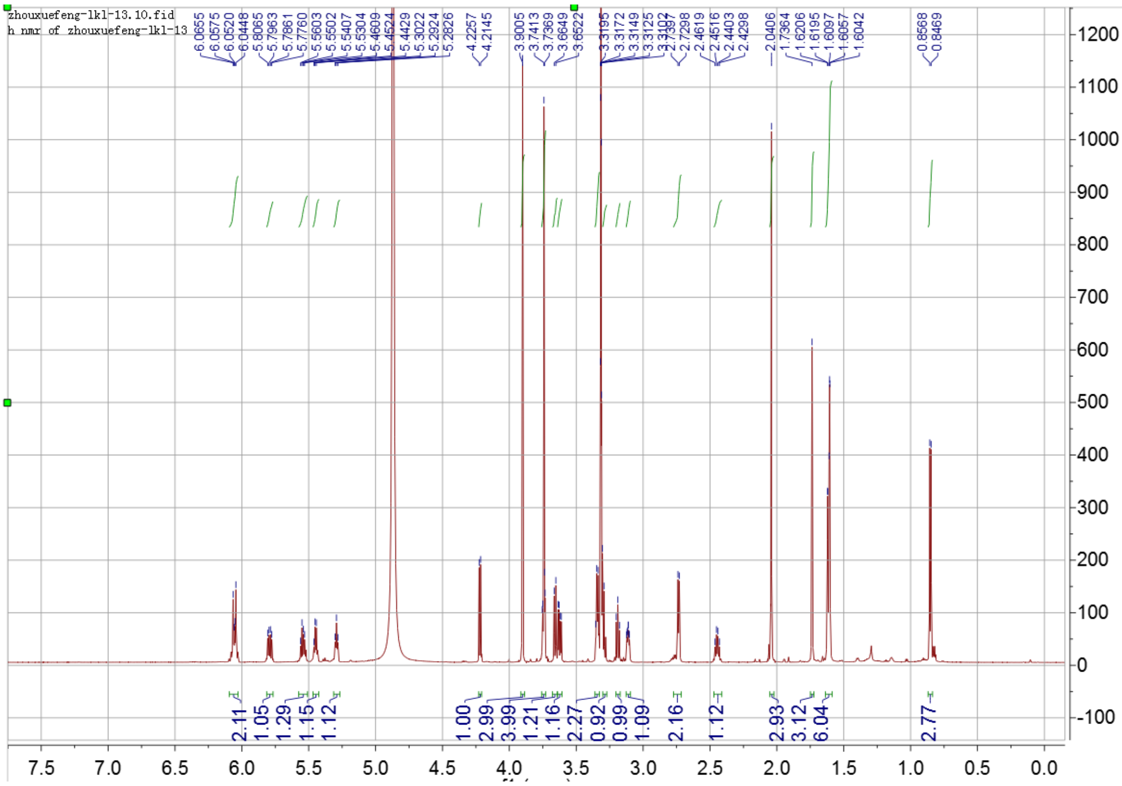


Figure SS-7-3. ^{1}H NMR spectrum of **12** (in CD_3OD, 700 MHz).

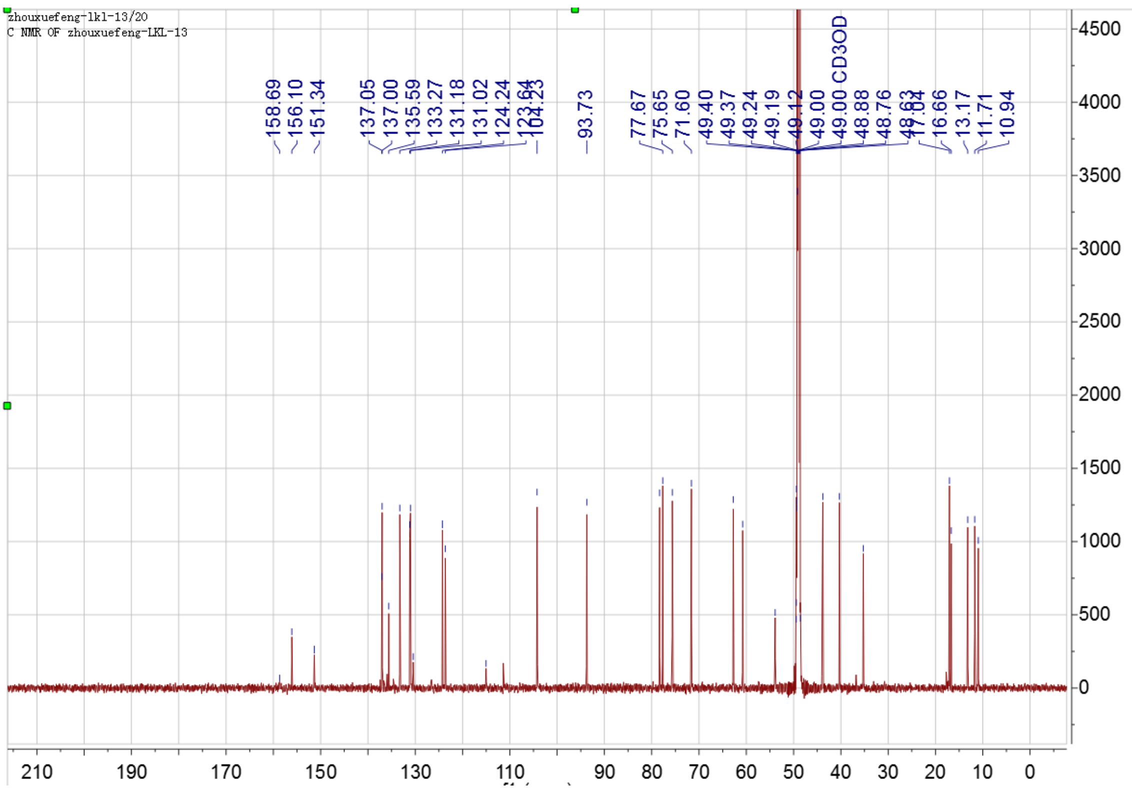


Figure SS-7-4. ^{13}C NMR spectrum of **12** (in CD_3OD, 175 MHz).

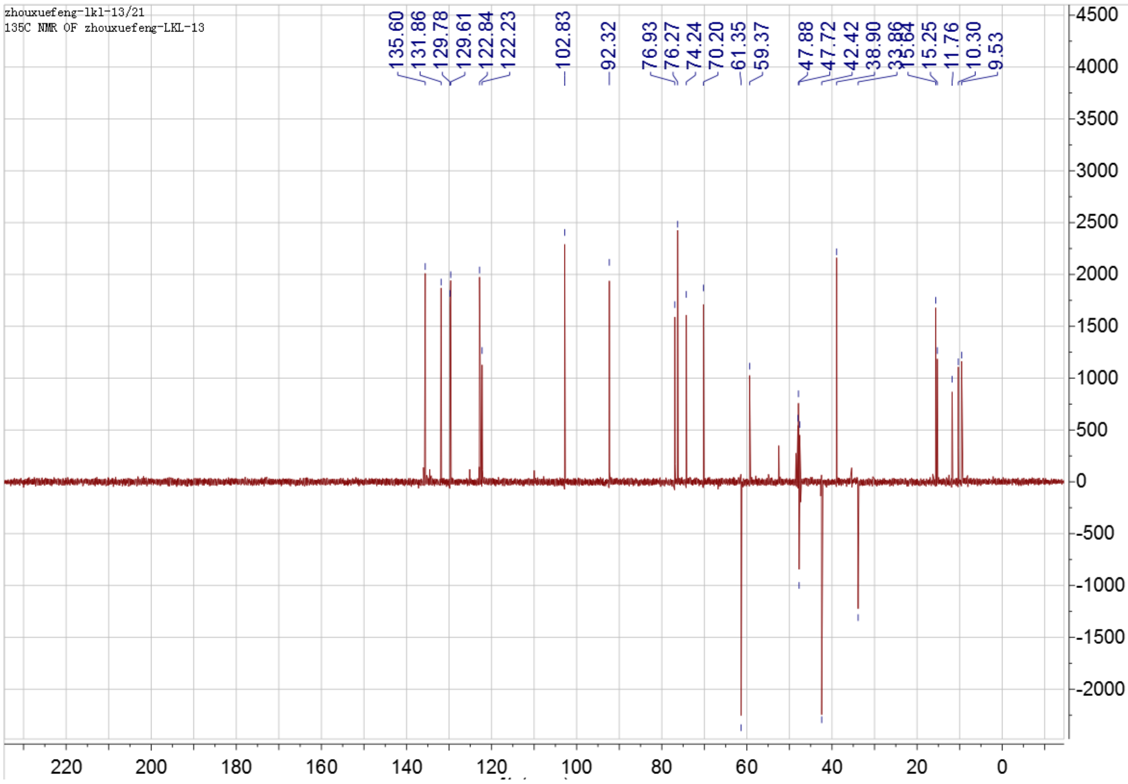


Figure SS-7-5. DEPT spectrum of **12** (in CD_3OD, 175 MHz).

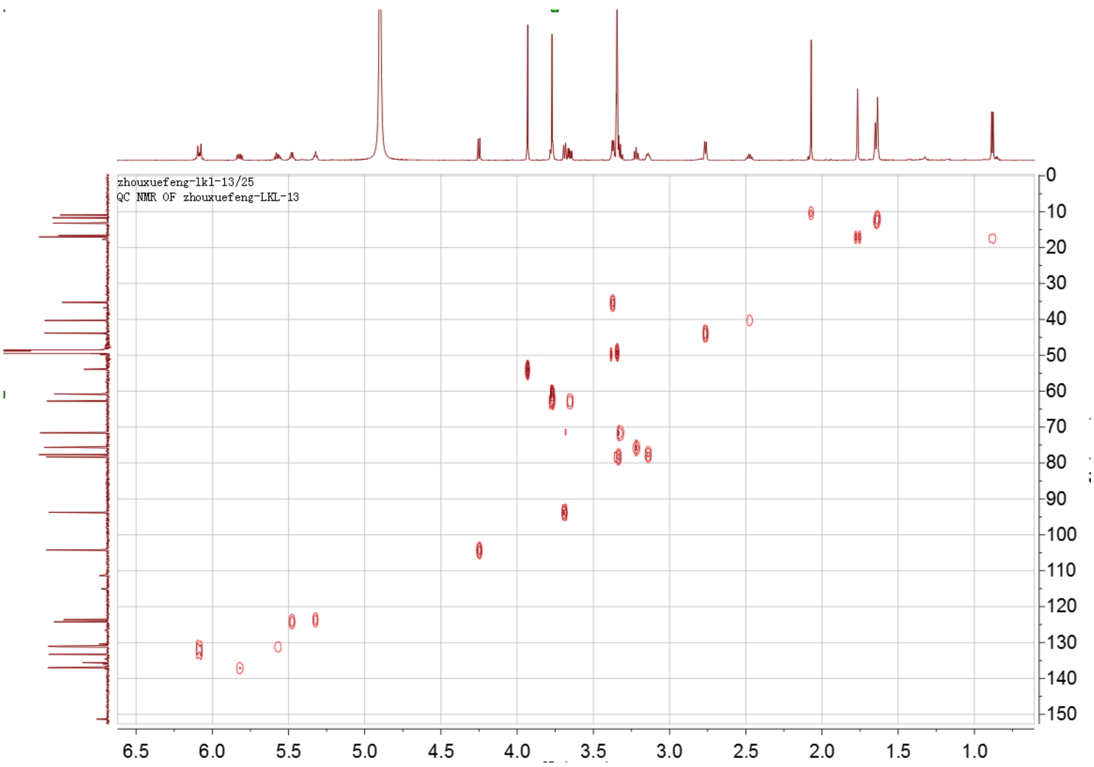


Figure SS-7-6. HSQC spectrum of **12** (in CD_3OD).

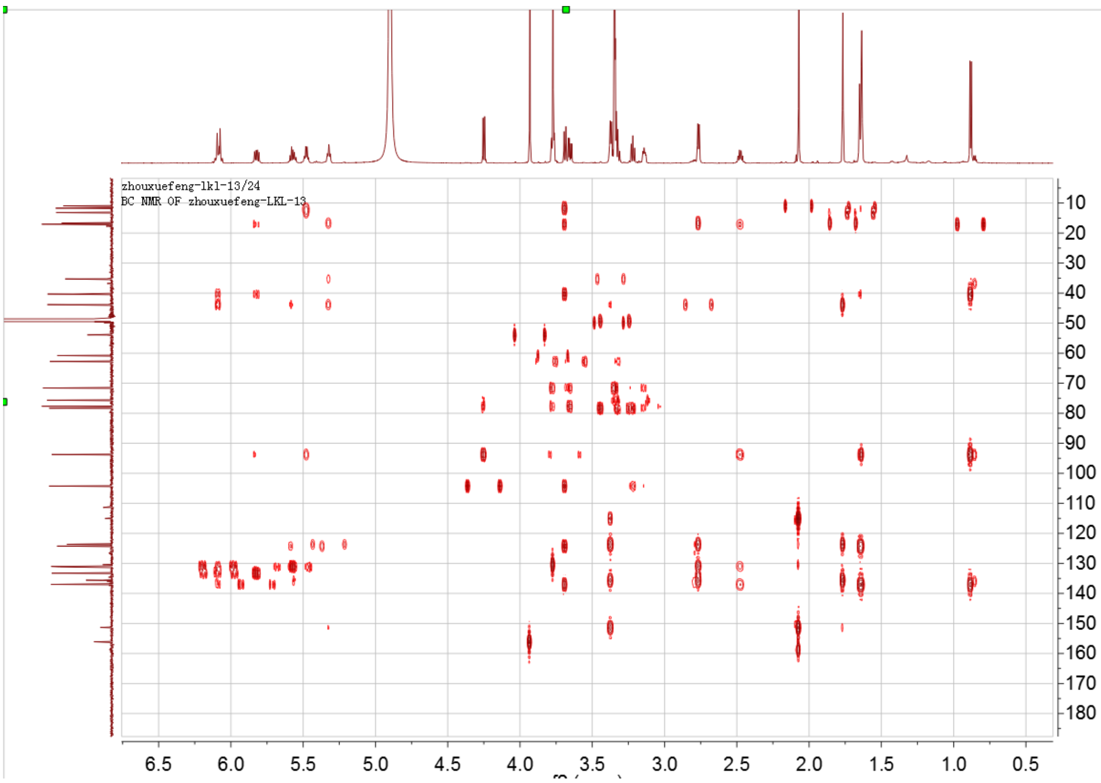


Figure SS-7-7. HMBC spectrum of **12** (in CD_3OD).

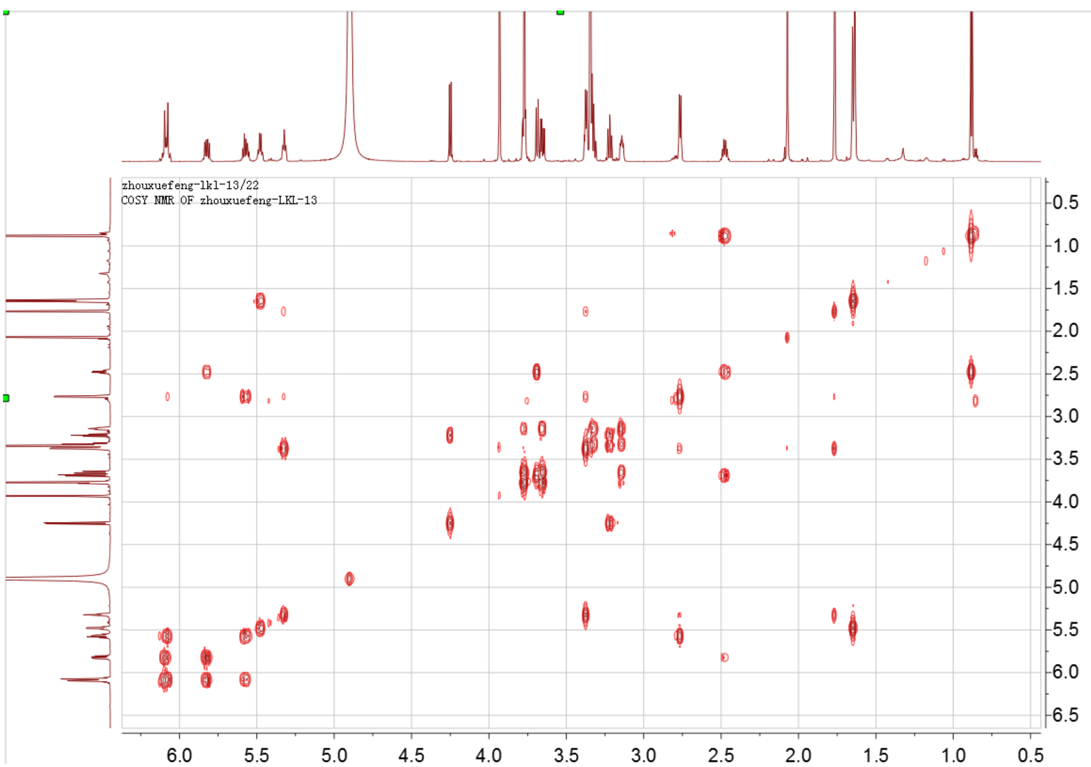


Figure SS-7-8. ^{1}H-^{1}H COSY spectrum of **12** (in CD_3OD).

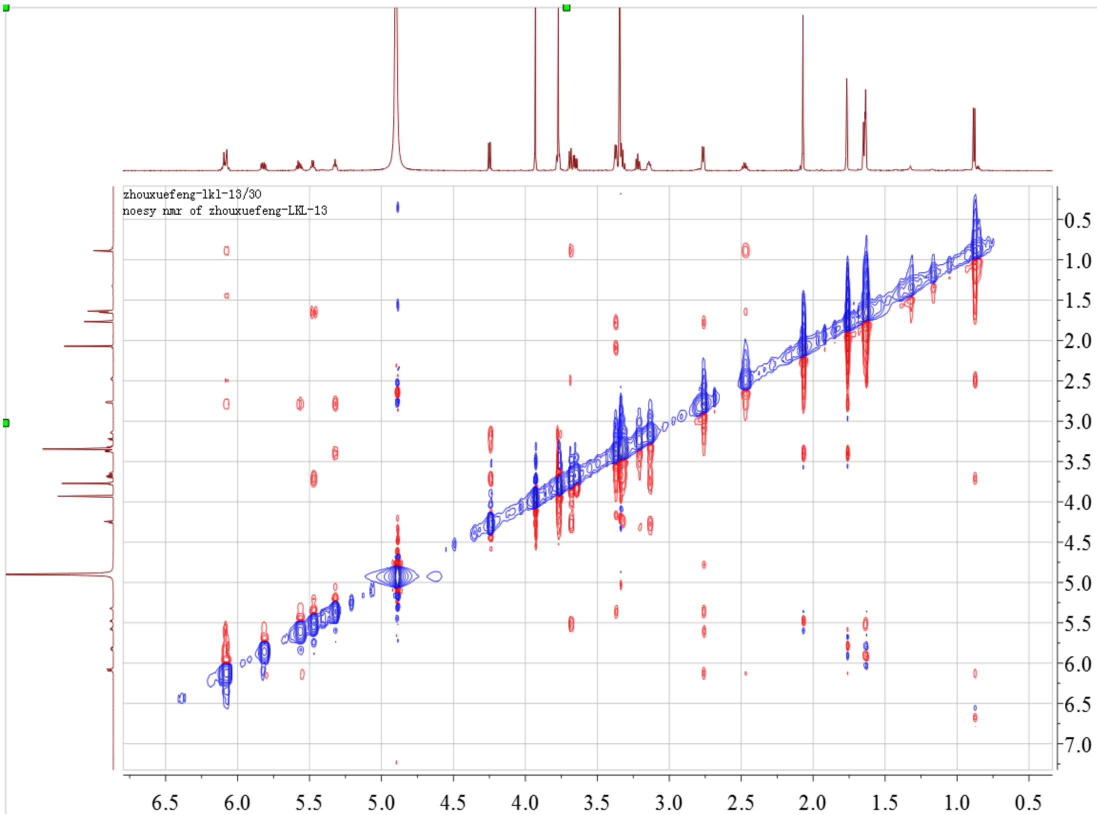


Figure SS-7-9. NOESY spectrum of **12** (in CD_3OD).

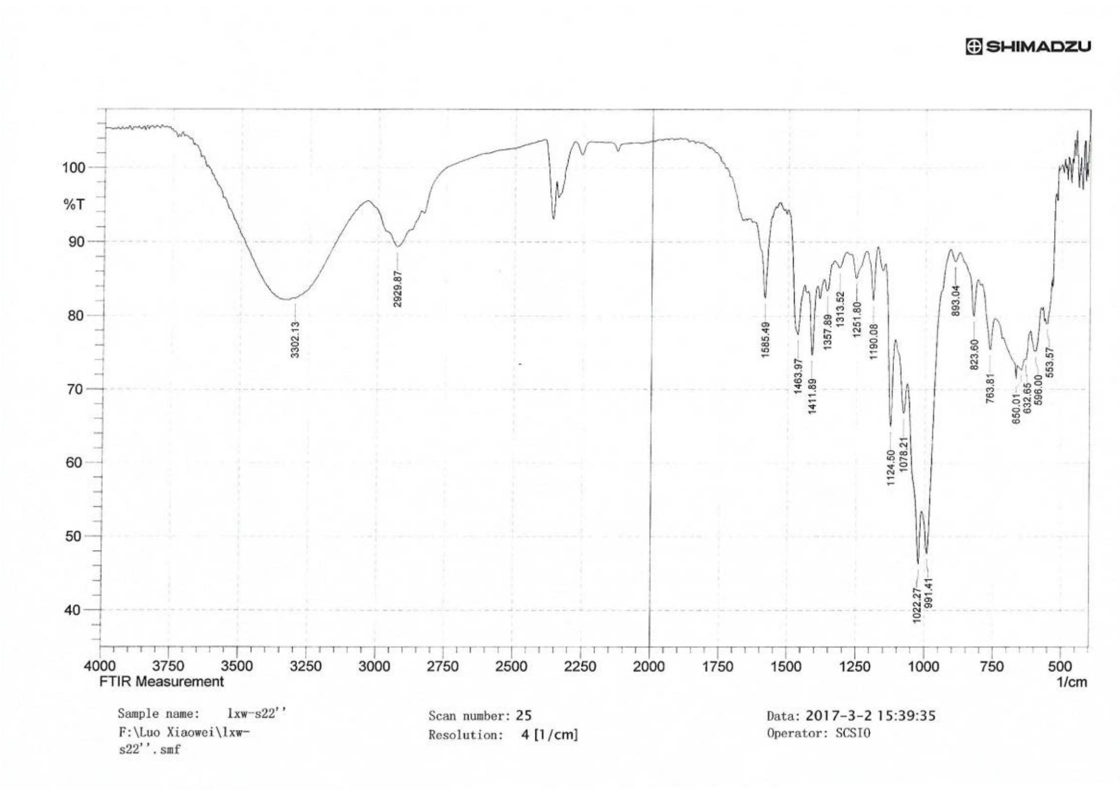
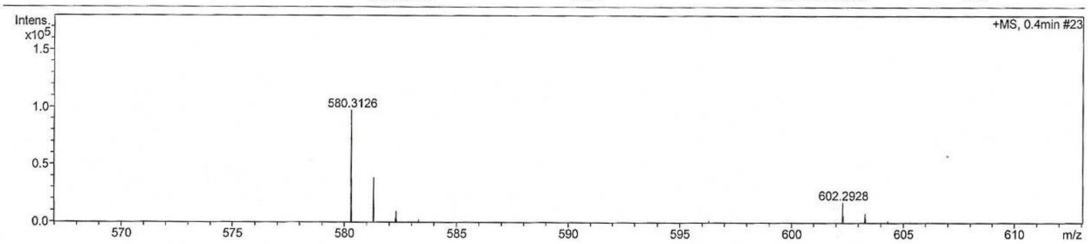


Figure SS-8-1. IR spectrum of **13**.

Mass Spectrum SmartFormula Report

Analysis Info			
Analysis Name	D:\Data\MS\data\201801\likunlong_LKL-19_pos_73_01_4200.d	Acquisition Date	1/24/2018 2:58:20 PM
Method	LC_Direct Infusion_pos_100-1000mz.m	Operator	SCSIO
Sample Name	likunlong_LKL-19_pos	Instrument	maXis 255552.00029
Comment			

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf	N-Rule
580.3126	1	C32H38N9O2	55.30	580.3143	-2.9	-1.7	14.1	18.5	even	ok
	2	C31H42N5O6	100.00	580.3130	-0.6	-0.4	22.8	13.5	even	ok
	3	C30H46NO10	57.42	580.3116	-1.7	-1.0	33.3	8.5	even	ok
602.2928	1	C30H45NNaO10	100.00	602.2936	-1.2	-0.7	2.6	8.5	even	ok
	2	C31H41N5NaO6	37.00	602.2949	3.4	2.1	10.0	13.5	even	ok
1159.6174	1	C60H91N2O20	51.73	1159.6160	-1.2	-1.4	31.0	16.5	even	ok
	2	C62H83N10O12	52.60	1159.6186	-1.1	-1.2	35.6	26.5	even	ok
	3	C60H71N24O2	41.06	1159.6186	1.1	1.2	44.9	37.5	even	ok
	4	C64H75N18O4	3.48	1159.6213	3.4	3.9	48.3	36.5	even	ok
1181.5989	1	C60H90N2NaO20	96.63	1181.5979	-0.8	-1.0	8.6	16.5	even	ok
	2	C62H82N10NaO12	37.85	1181.6006	-1.4	-1.7	24.5	26.5	even	ok

likunlong_LKL-19_pos_73_01_4200.d

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Figure SS-8-2. HRESIMS (+) spectrum of **13**.

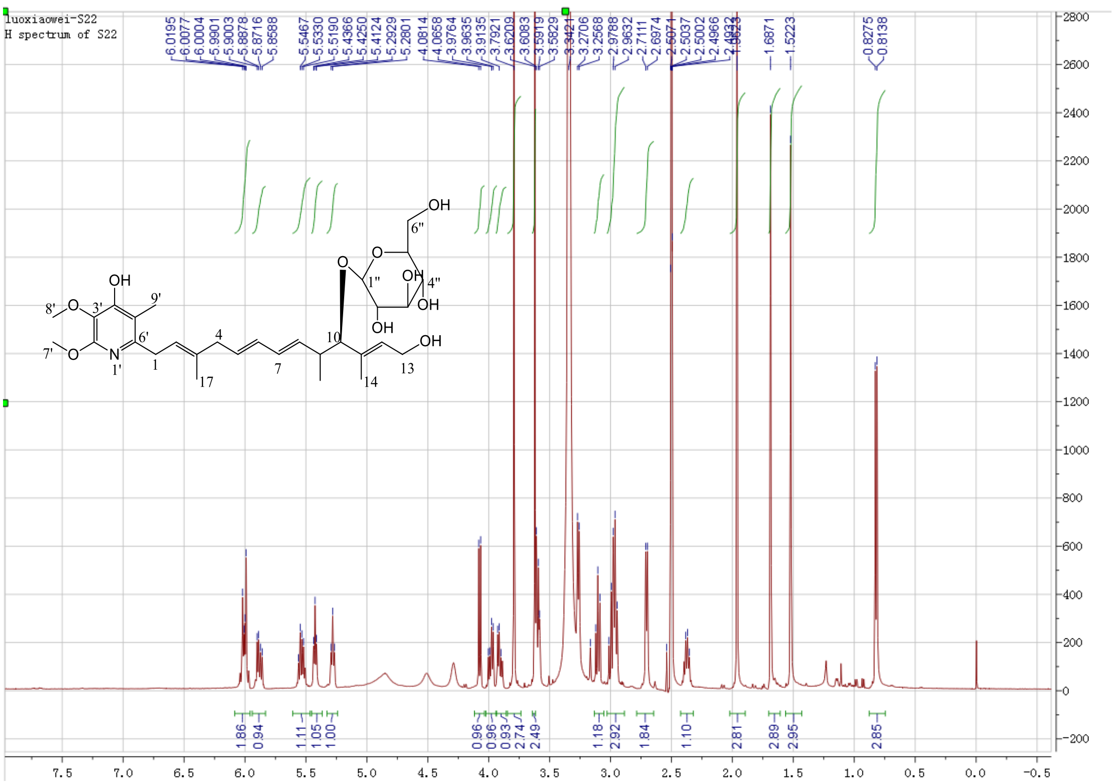


Figure SS-8-3. ^{1}H NMR spectrum of **13** (in DMSO-d_6, 700 MHz).

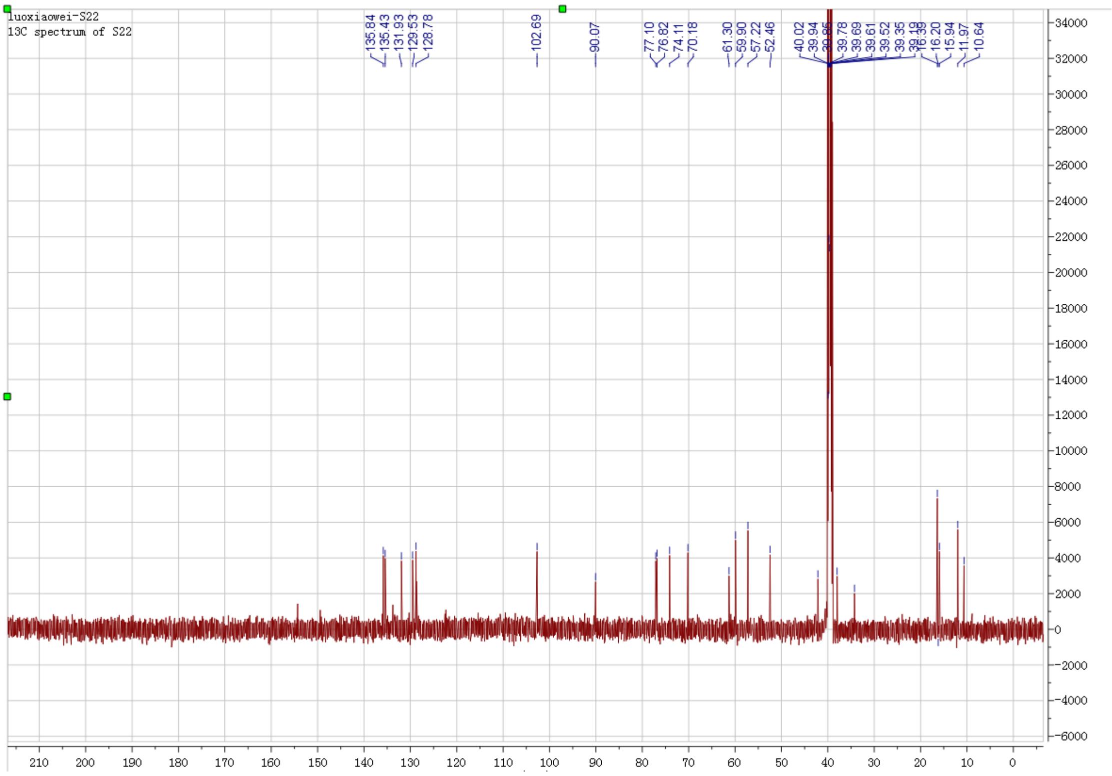


Figure SS-8-4. ^{13}C NMR spectrum of **13** (in DMSO-d_6, 175 MHz).

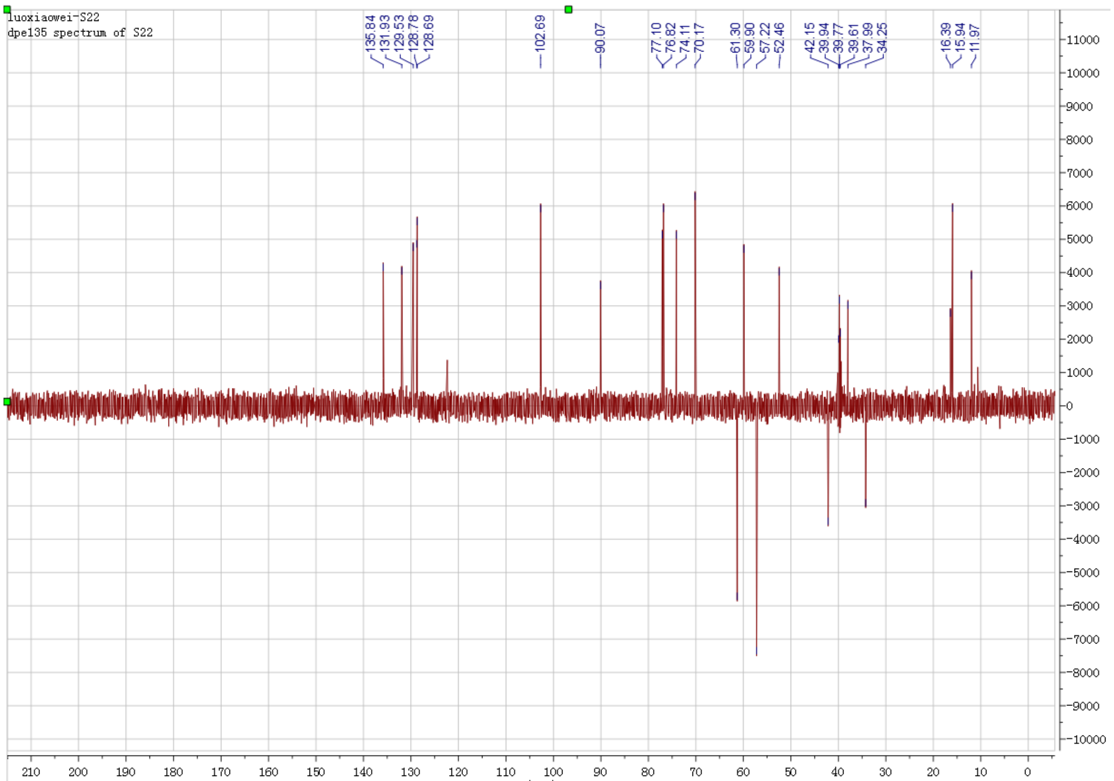


Figure SS-8-5. DEPT spectrum of **13** (in DMSO-d_6, 175 MHz).

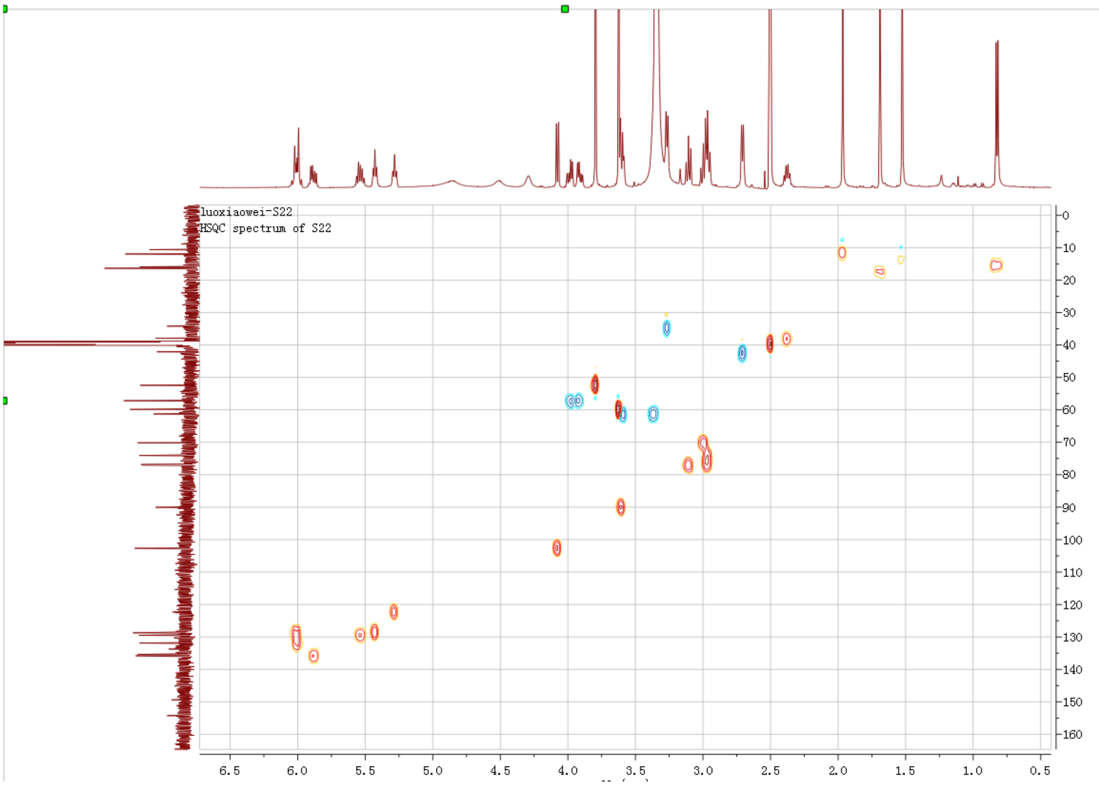


Figure SS-8-6. HSQC spectrum of **13** (in DMSO-d_6).

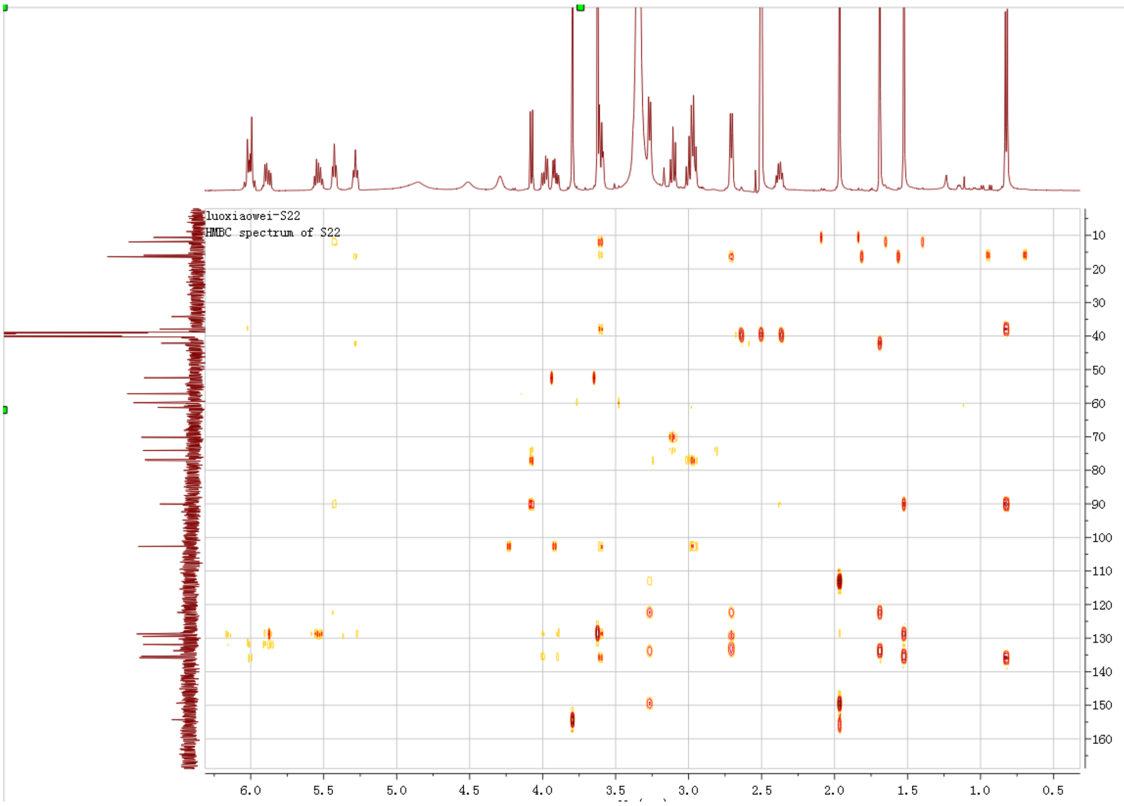


Figure SS-8-7. HMBC spectrum of **13** (in DMSO-d_6).

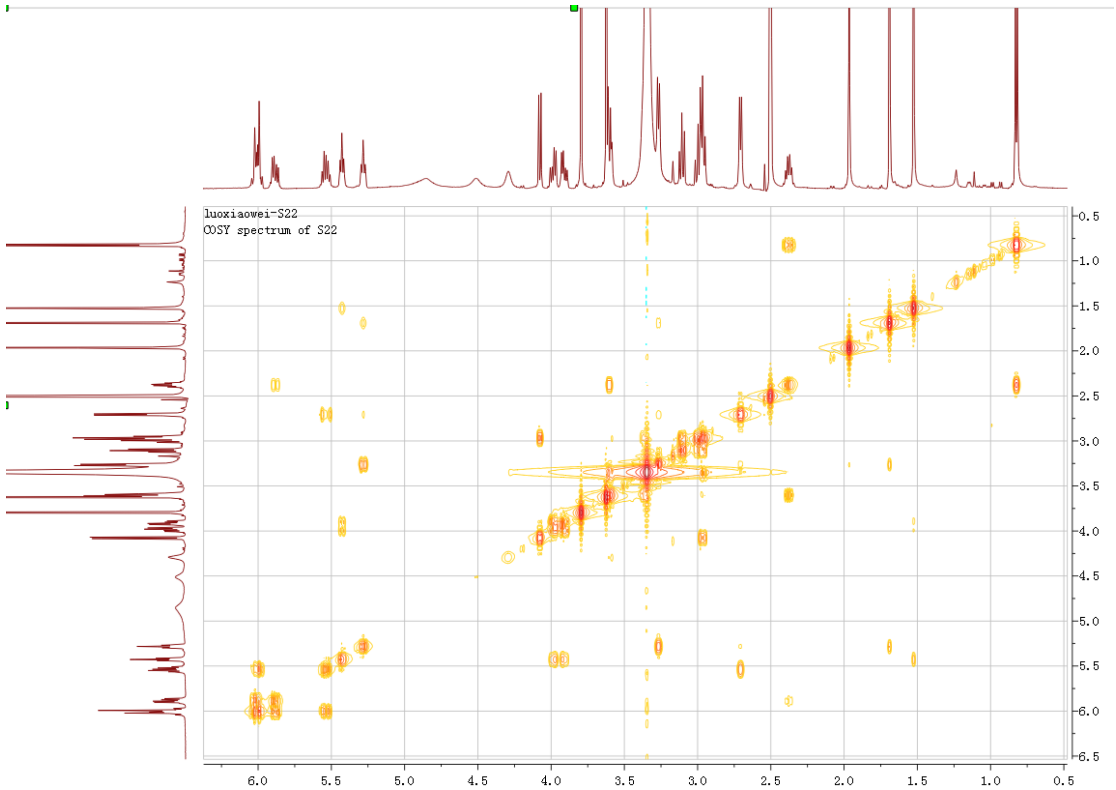


Figure SS-8-8. ^{1}H-^{1}H COSY spectrum of **13** (in DMSO-d_6).

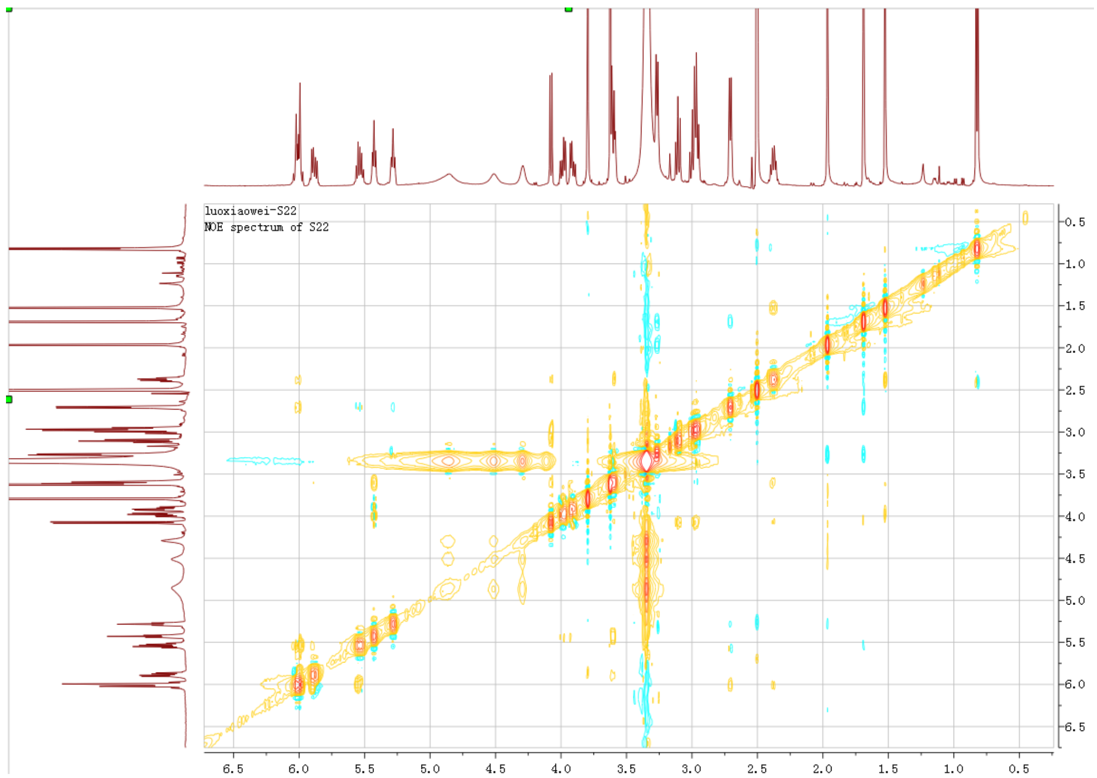


Figure SS-8-9. NOESY spectrum of **13** (in DMSO-d_6).

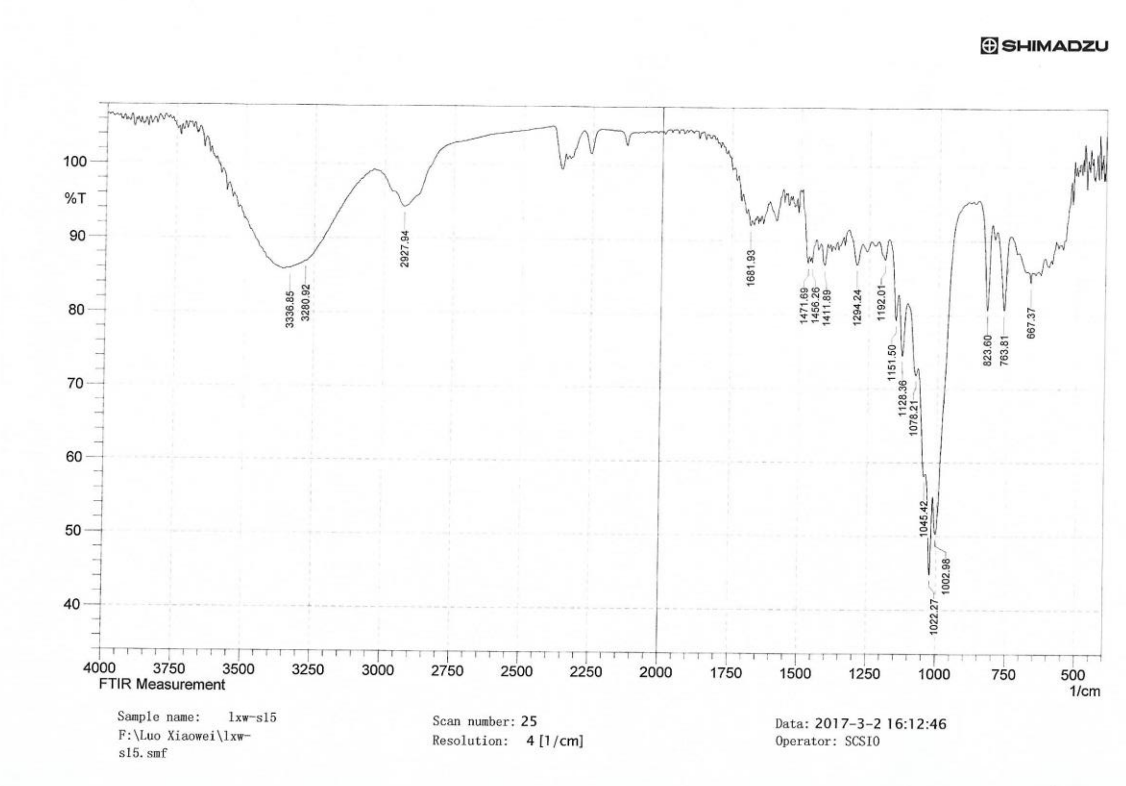


Figure SS-9-1. IR spectrum of **14**.

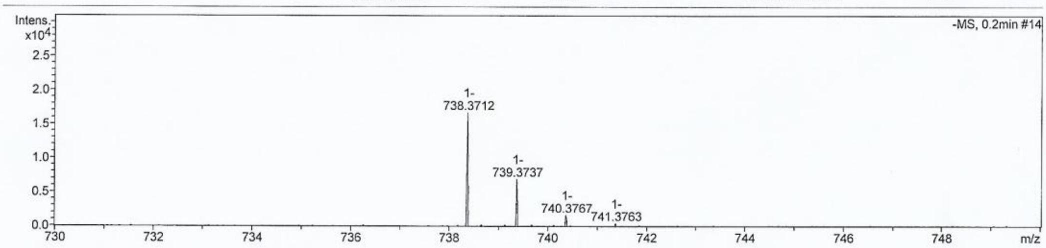
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\MS\data\201612\zhouxuefeng_lxw-s15_neg.d	Acquisition Date	12/28/2016 3:04:12 PM
Method	tune_wide_neg_20160911.m	Operator	SCSIO
Sample Name	zhouxuefeng_lxw-s15_neg	Instrument	maXis 255552.00029
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3000 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf	N-Rule
738.371223	1	C34H48N11O8	35.56	738.369281	2.6	1.9	5.1	16.5	even	ok
	2	C37H56NO14	100.00	738.370629	0.8	0.6	6.7	10.5	even	ok
	3	C31H40N21O2	10.02	738.367933	-4.5	-3.3	9.0	22.5	even	ok
	4	C33H52N7O12	9.85	738.367944	-4.4	-3.3	10.4	11.5	even	ok
	5	C35H44N15O4	68.21	738.370619	0.8	0.6	14.9	21.5	even	ok
	6	C38H52N5O10	62.50	738.371966	1.0	0.7	15.7	15.5	even	ok
	7	C39H48N9O6	20.60	738.373304	-2.8	-2.1	26.8	20.5	even	ok
	8	C40H44N13O2	4.52	738.374641	4.6	3.4	38.4	25.5	even	ok
	9	C50H48N3O3	13.33	738.370116	-1.5	-1.1	70.7	28.5	even	ok
	10	C55H48NO	1.29	738.374139	3.9	2.9	93.6	32.5	even	ok

zhouxuefeng_lxw-s15_neg.d

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Figure SS-9-2. HRESIMS (-) spectrum of **14**.

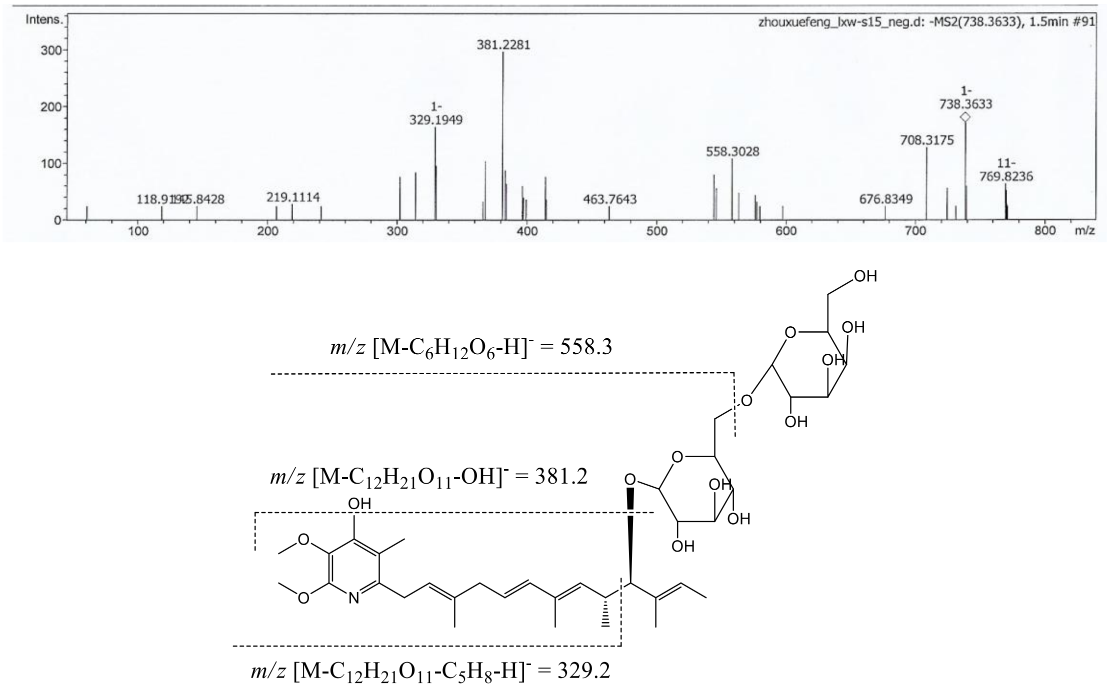


Figure SS-9-3. HRESI-MS/MS (-) spectrum of **14**.

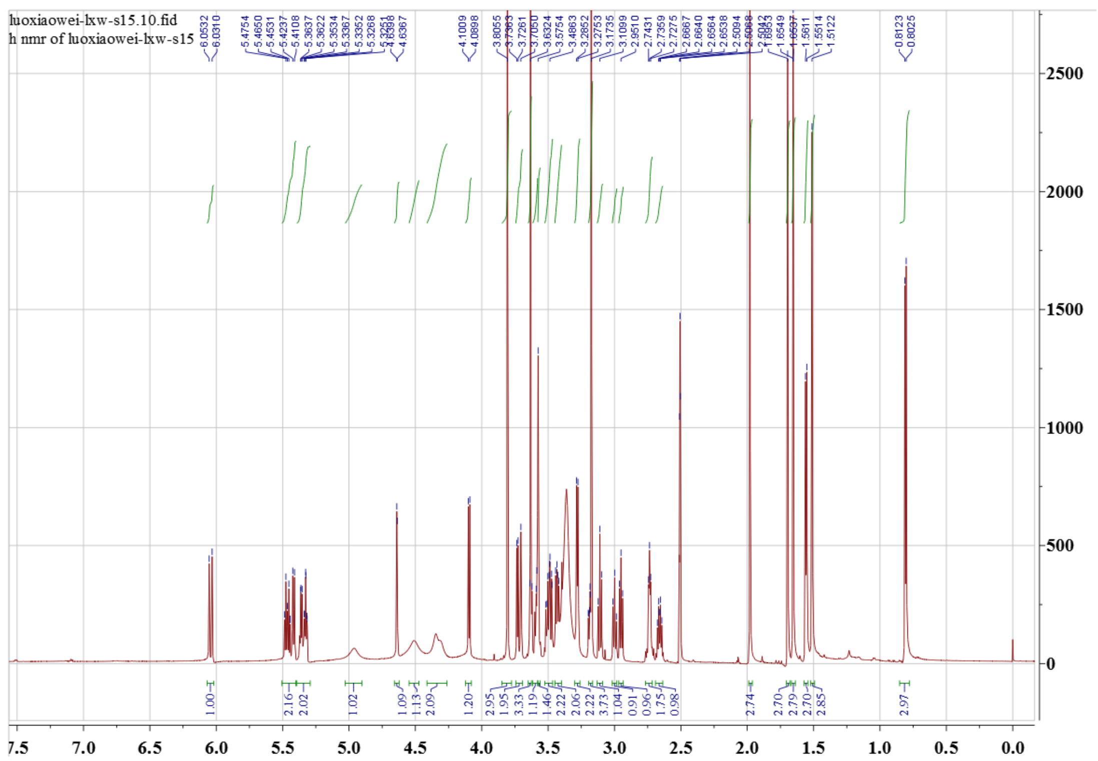


Figure SS-9-4. [1]H NMR spectrum of **14** (in DMSO-d_6, 700 MHz).

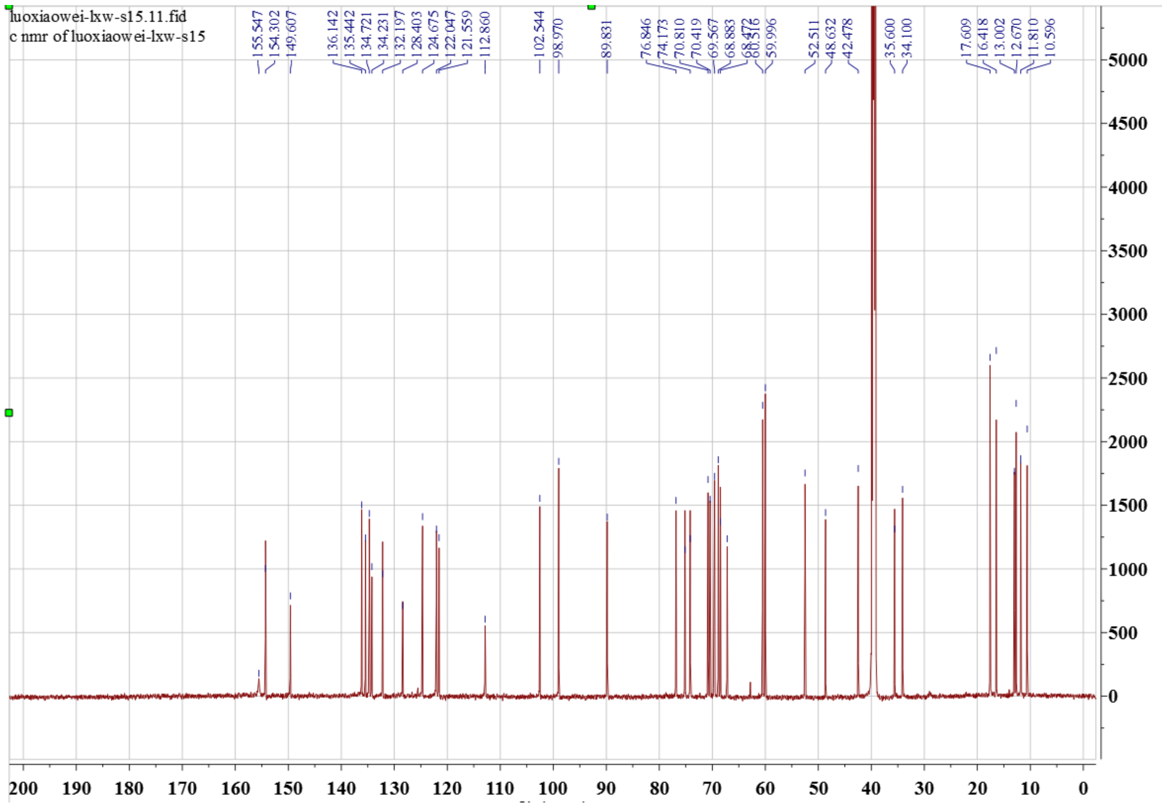


Figure SS-9-5. ^{13}C NMR spectrum of **14** (in DMSO-d_6, 175 MHz).

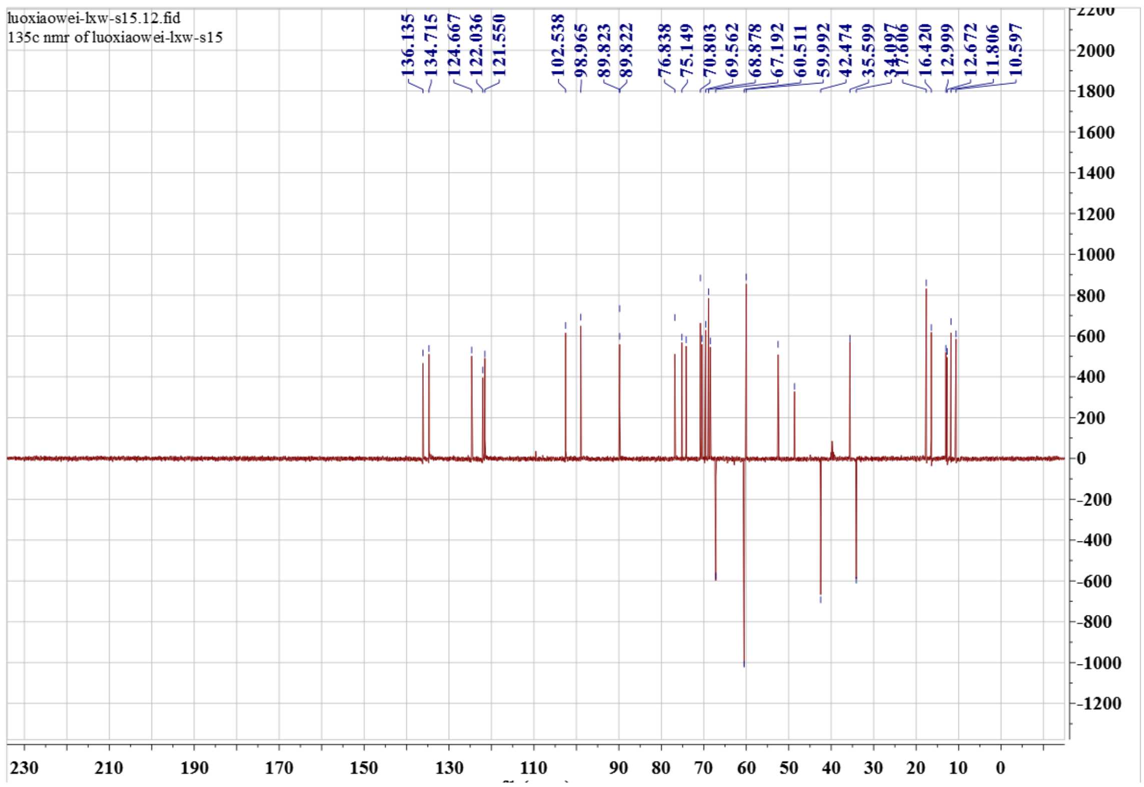


Figure SS-9-6. DEPT spectrum of **14** (in DMSO-d_6, 175 MHz).

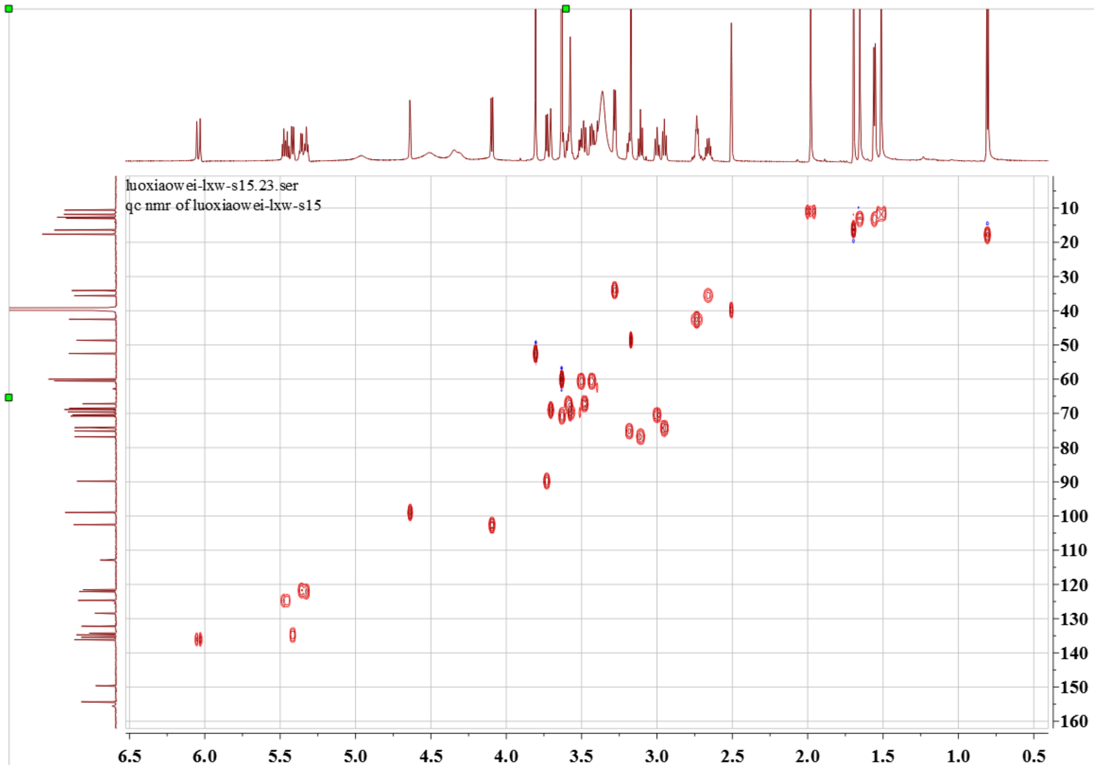


Figure SS-9-7. HSQC spectrum of **14** (in DMSO-d_6).

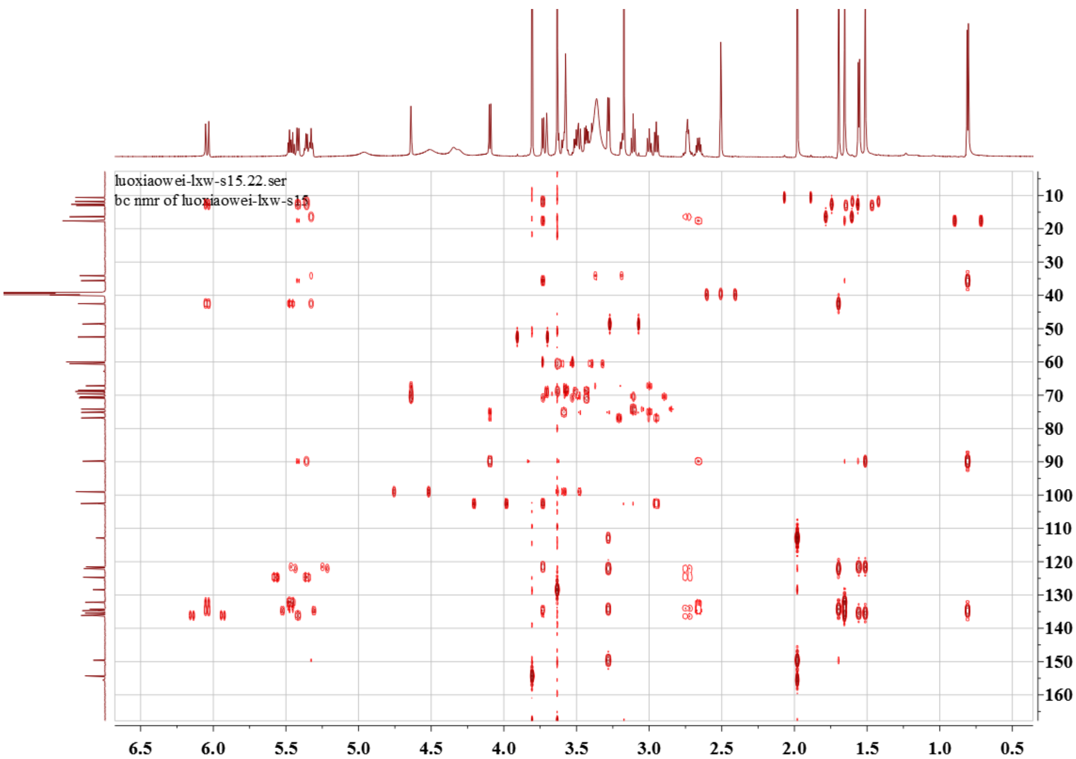


Figure SS-9-8. HMBC spectrum of **14** (in DMSO-d_6).

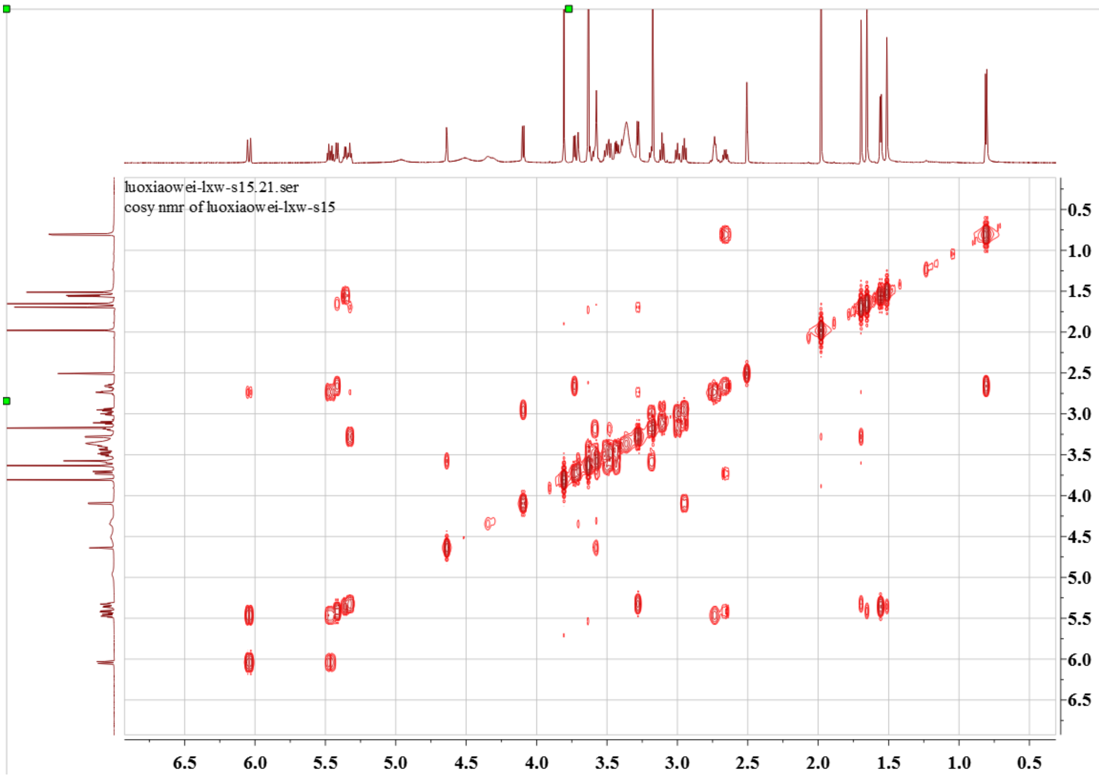


Figure SS-9-9. ^{1}H-^{1}H COSY spectrum of **14** (in DMSO-d_6).

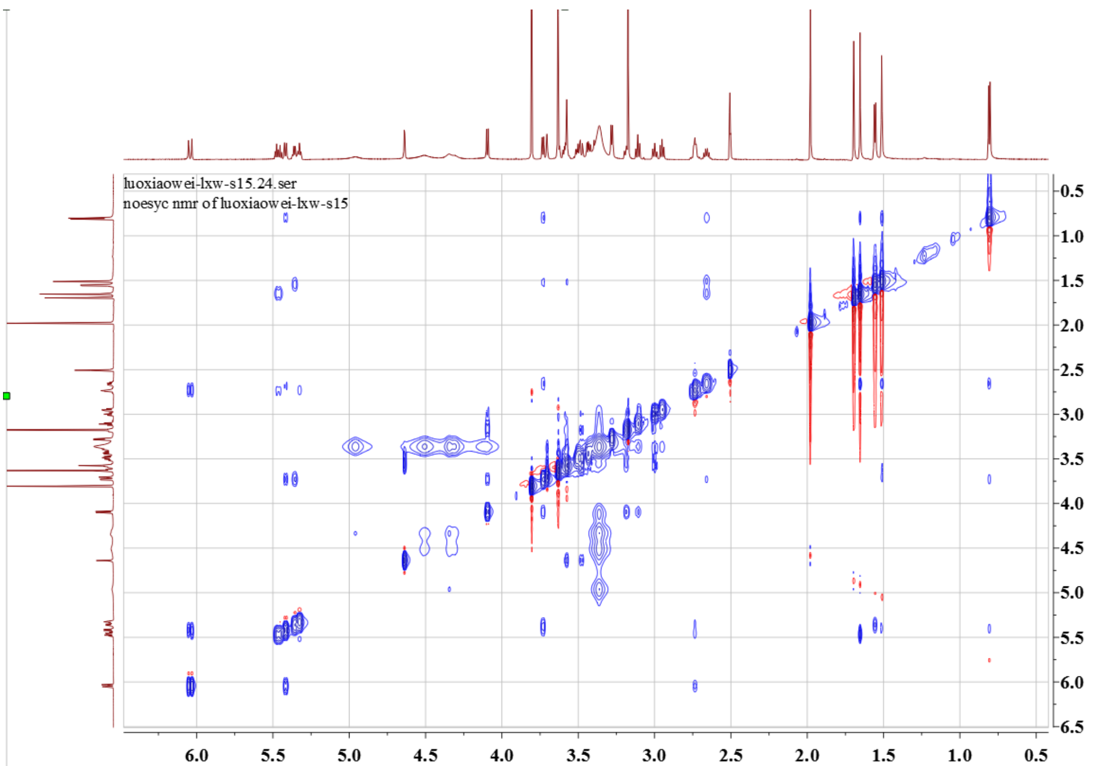


Figure SS-9-10. NOESY spectrum of **14** (in DMSO-d_6).

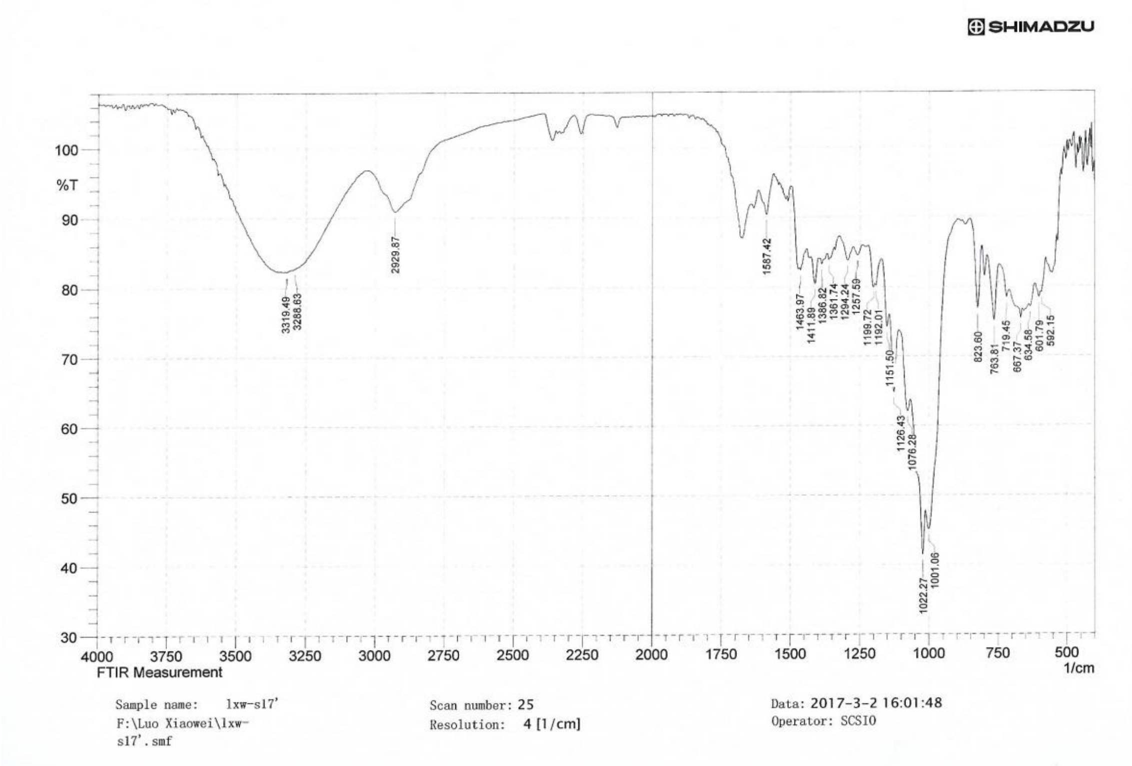


Figure SS-10-1. IR spectrum of **15**.

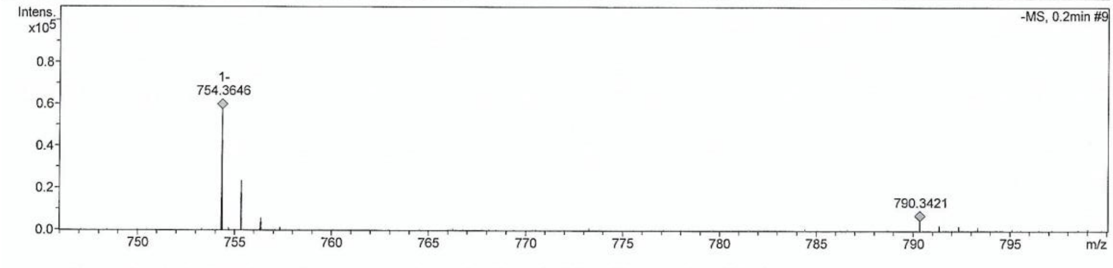
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\MS\data\201612\zhouxuefeng_lxw-s17_neg_61_01_2955.d	Acquisition Date	1/13/2017 10:18:44 AM
Method	LC ms2_Direct Infusion_neg_100-1000mz.m	Operator	SCSIO
Sample Name	zhouxuefeng_lxw-s17_neg	Instrument	maXis 255552.00029
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	3800 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	0 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf	N-Rule
754.364639	1	C37H56NO15	100.00	754.365544	1.2	0.9	6.6	10.5	even	ok
790.342093	1	C37H57ClNO15	100.00	790.342221	-0.2	-0.1	42.9	9.5	even	ok

zhouxuefeng_lxw-s17_neg_61_01_2955.d

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Figure SS-10-2. HRESIMS (-) spectrum of **15**.

Figure SS-10-3. ^{1}H NMR spectrum of **15** (in DMSO-d_6, 700 MHz).

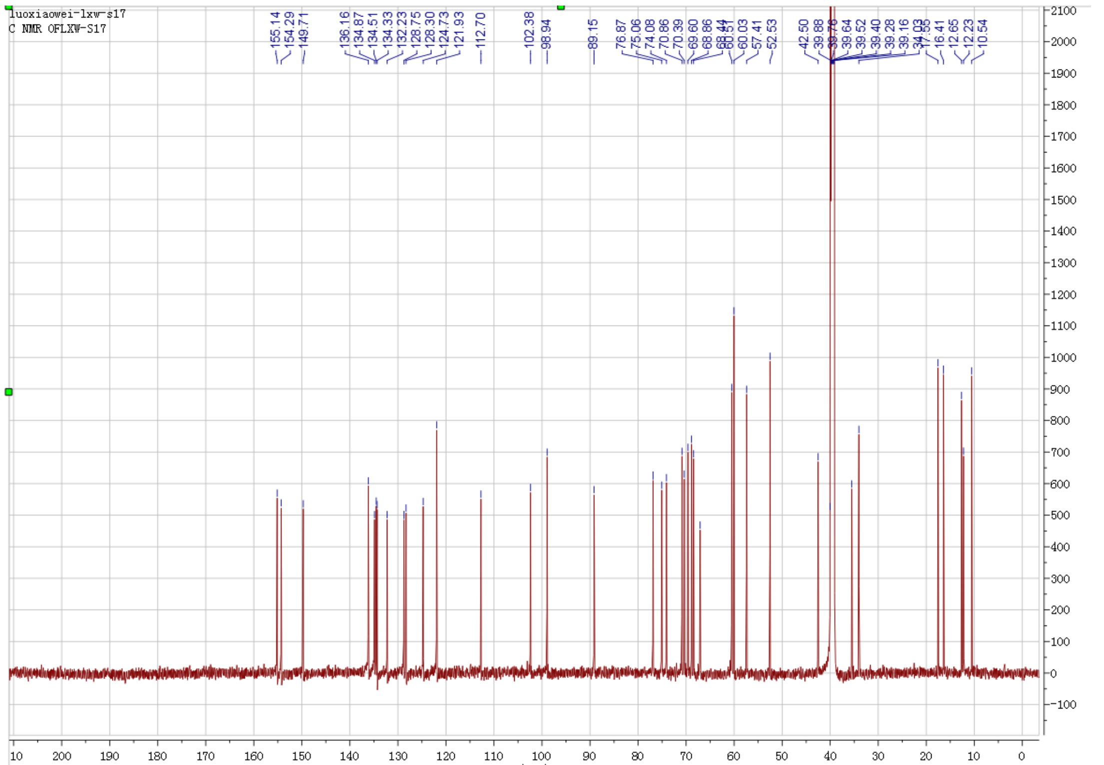


Figure SS-10-4. ^{13}C NMR spectrum of **15** (in DMSO-d_6, 175 MHz).

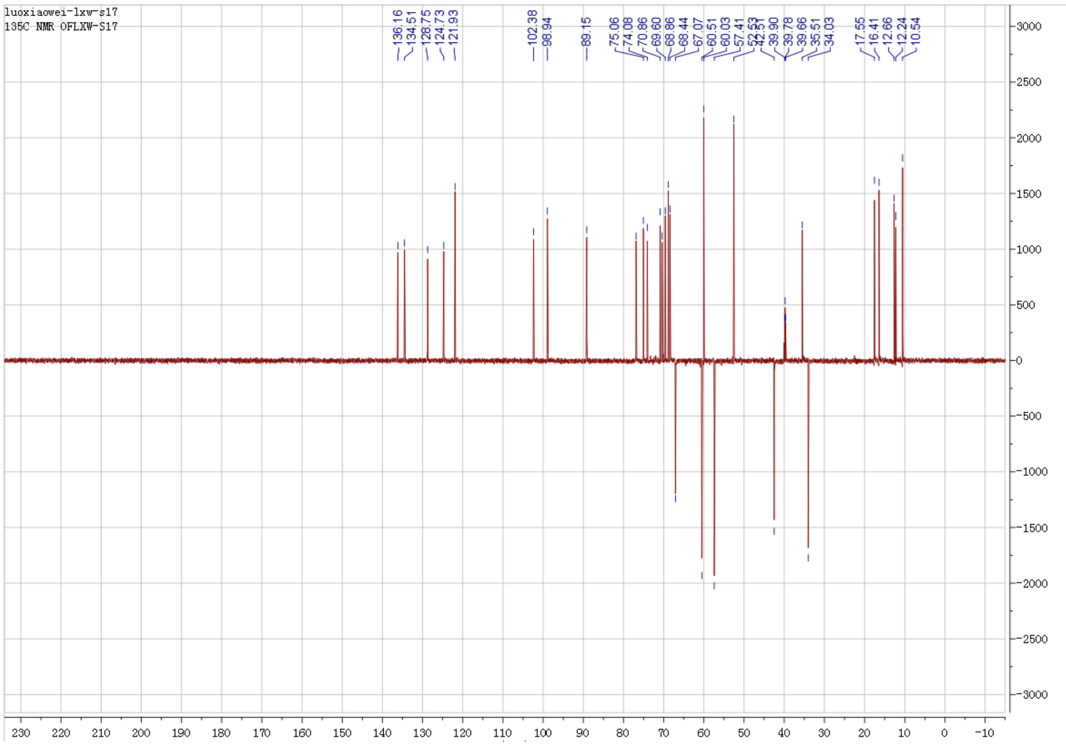


Figure SS-10-5. DEPT spectrum of **15** (in DMSO-d_6, 175 MHz).

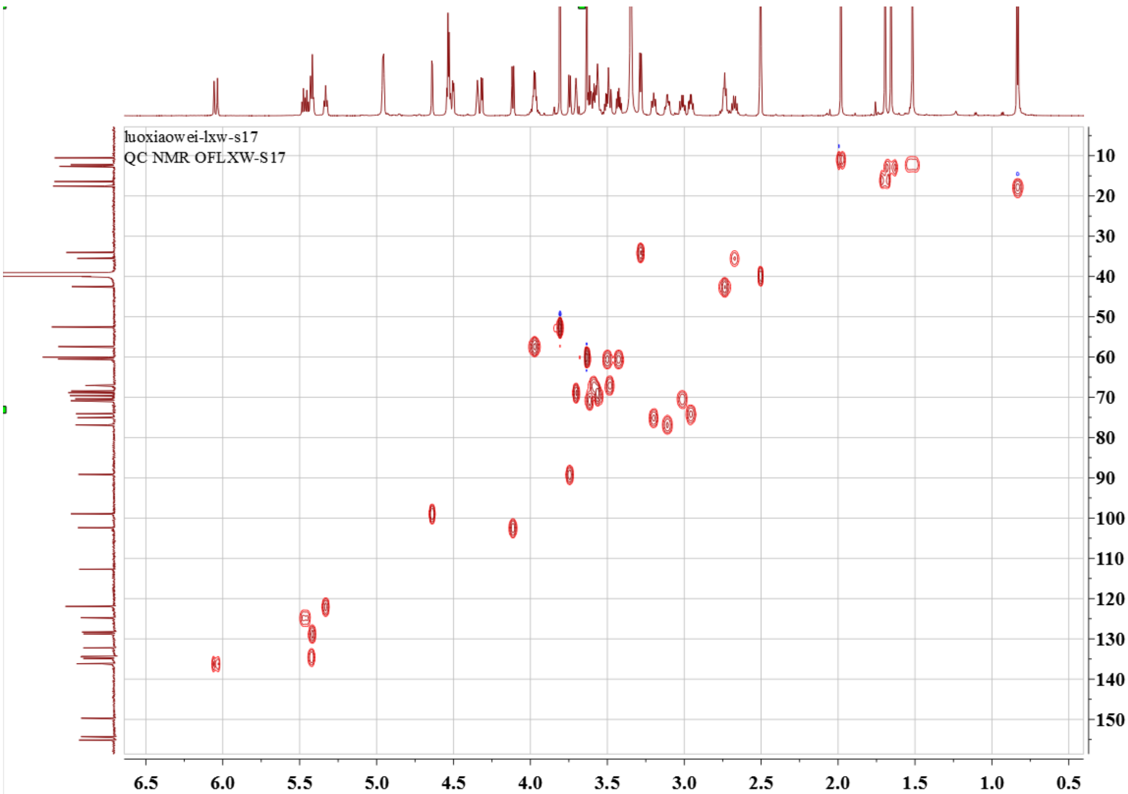


Figure SS-10-6. HSQC spectrum of **15** (in DMSO-d_6).

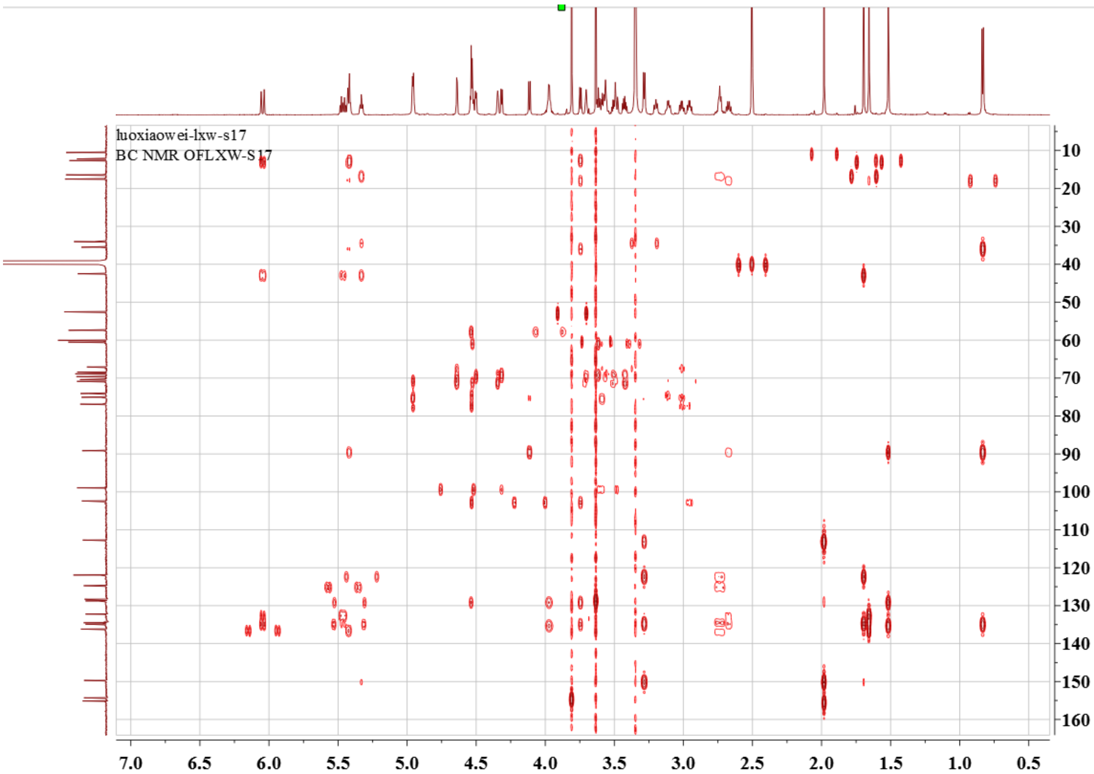


Figure SS-10-7. HMBC spectrum of **15** (in DMSO-d_6).

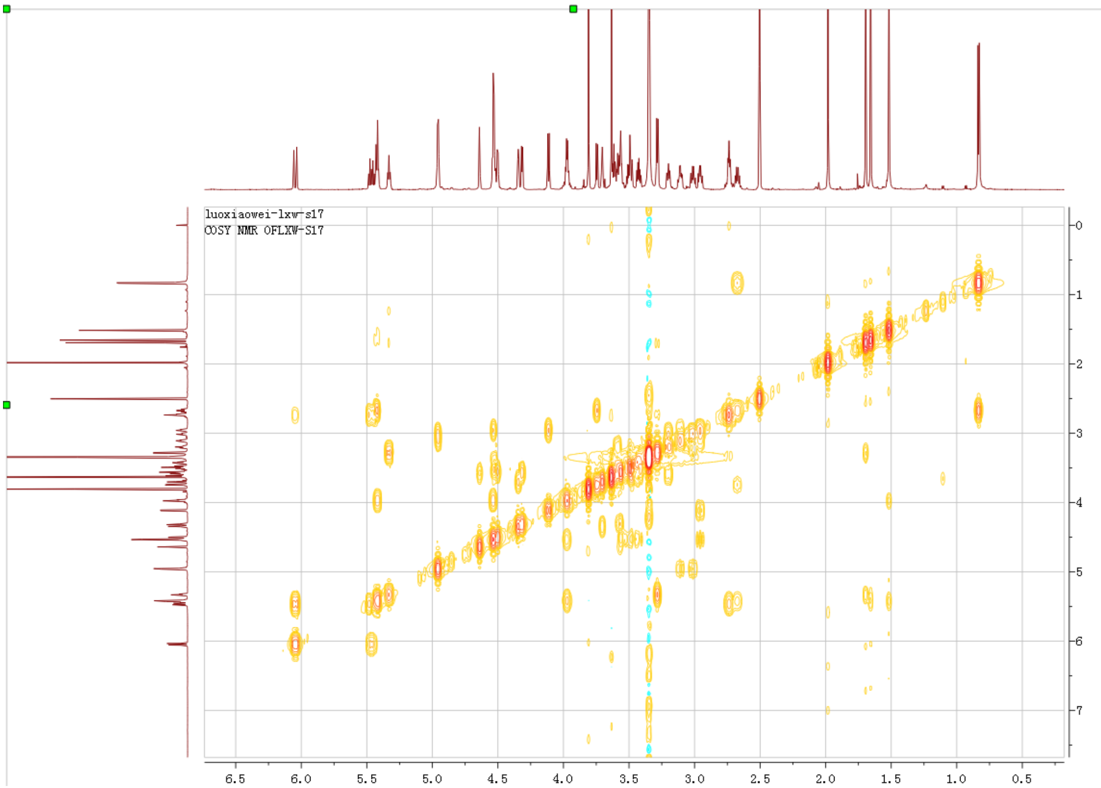


Figure SS-10-8. ^{1}H-^{1}H COSY spectrum of **15** (in DMSO-d_6).

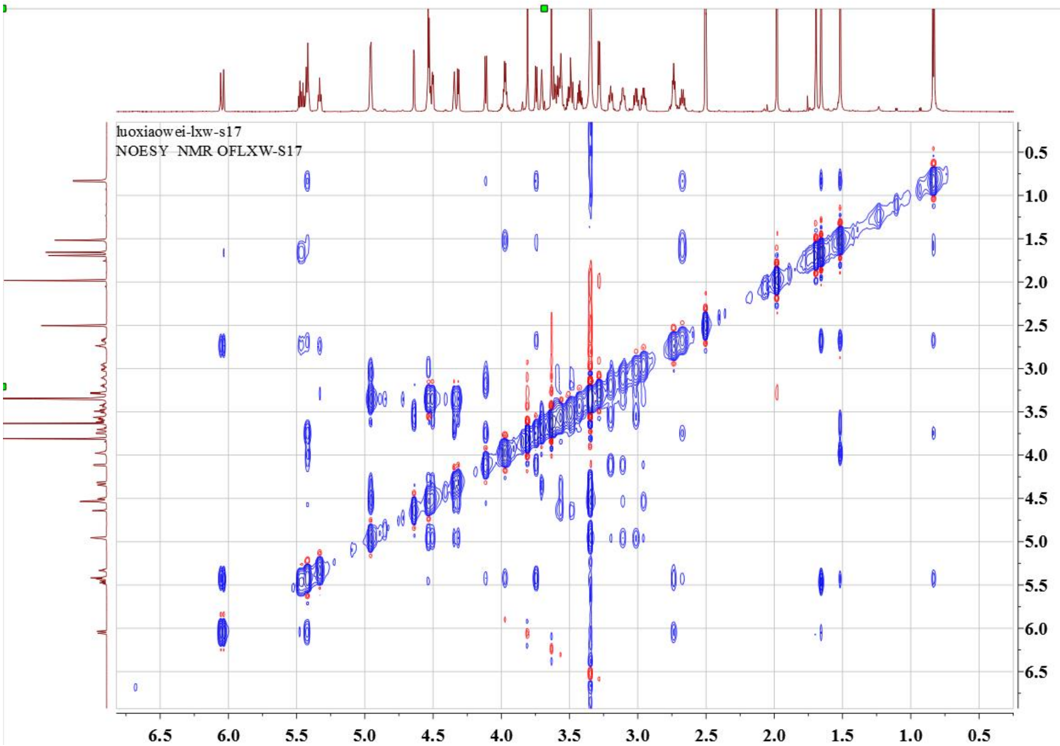


Figure SS-10-9. NOESY spectrum of **15** (in DMSO-d_6).

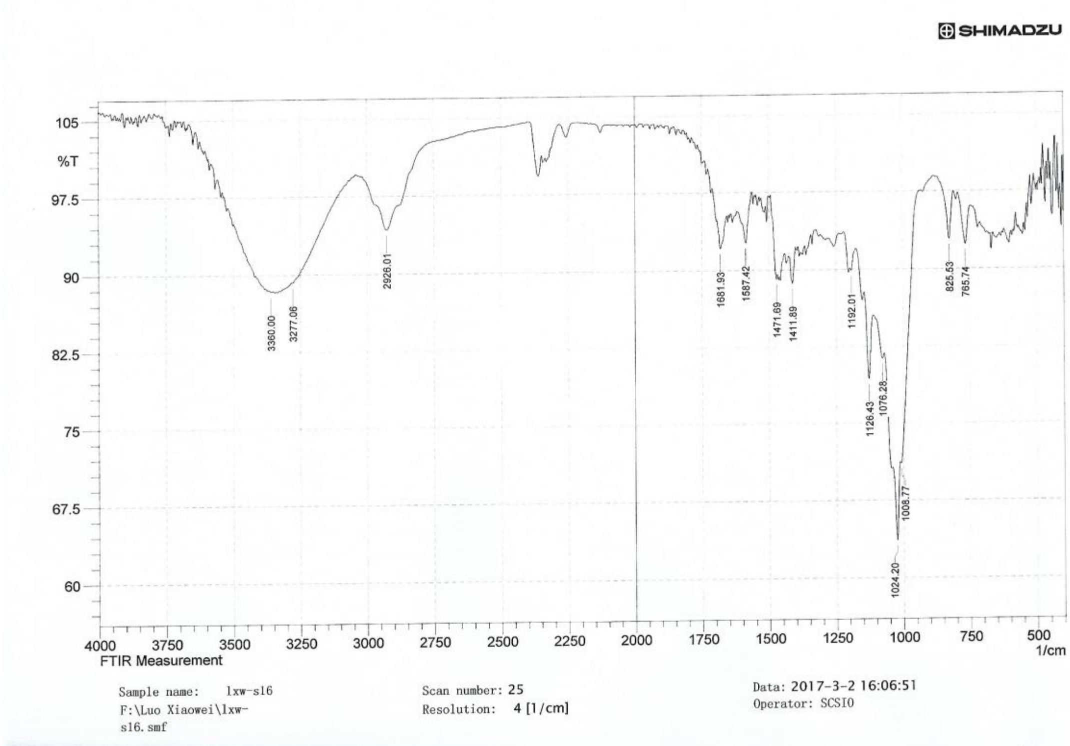
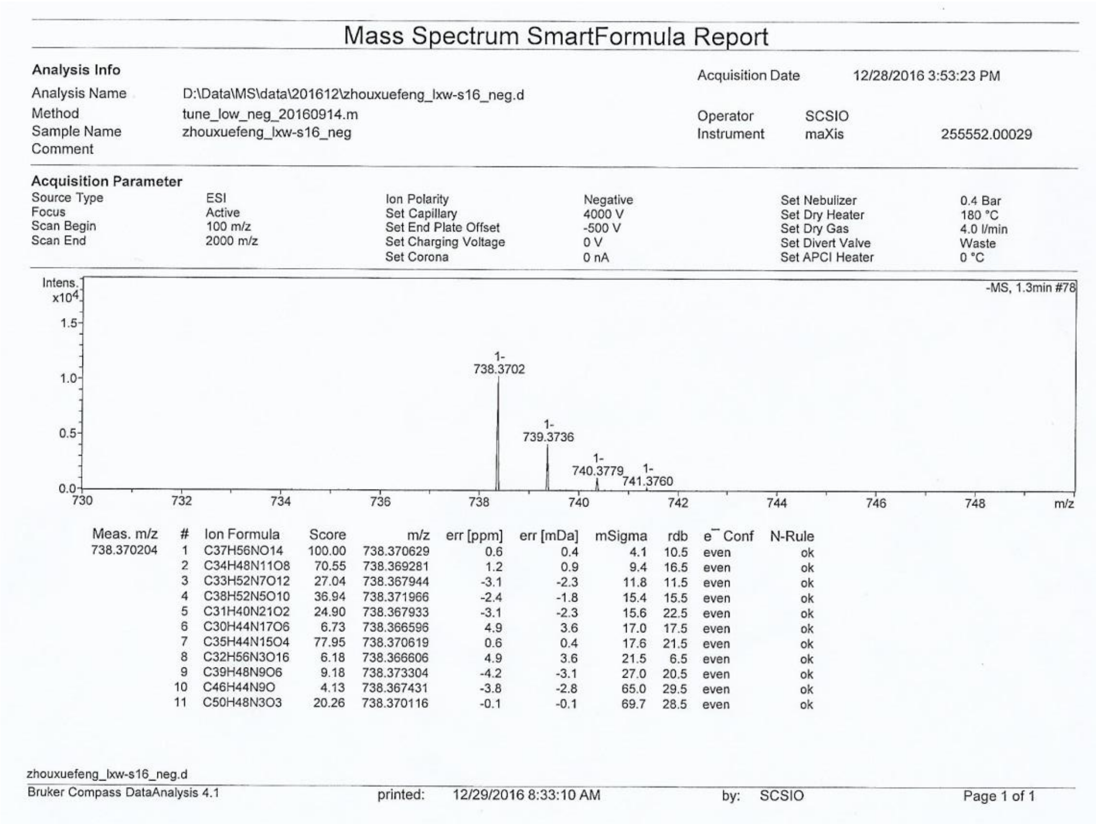


Figure SS-11-1. IR spectrum of **16**.



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\MS\data\201612\zhouxuefeng_lxw-s16_neg.d	Acquisition Date	12/28/2016 3:53:23 PM
Method	tune_low_neg_20160914.m	Operator	SCSIO
Sample Name	zhouxuefeng_lxw-s16_neg	Instrument	maXis 255552.00029
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.4 Bar		
Focus	Active	Set Capillary	4000 V	Set Dry Heater	180 °C		
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min		
Scan End	2000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste		
		Set Corona	0 nA	Set APCI Heater	0 °C		

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf	N-Rule
738.370204	1	C37H56NO14	100.00	738.370629	0.6	0.4	4.1	10.5	even	ok
	2	C34H48N11O8	70.55	738.369281	1.2	0.9	9.4	16.5	even	ok
	3	C33H52N7O12	27.04	738.367944	-3.1	-2.3	11.8	11.5	even	ok
	4	C38H52N5O10	36.94	738.371966	-2.4	-1.8	15.4	15.5	even	ok
	5	C31H40N21O2	24.90	738.367933	-3.1	-2.3	15.6	22.5	even	ok
	6	C30H44N17O6	6.73	738.366596	4.9	3.6	17.0	17.5	even	ok
	7	C35H44N15O4	77.95	738.370619	0.6	0.4	17.6	21.5	even	ok
	8	C32H56N3O16	6.18	738.366606	4.9	3.6	21.5	6.5	even	ok
	9	C39H48N9O6	9.18	738.373304	-4.2	-3.1	27.0	20.5	even	ok
	10	C46H44N9O	4.13	738.367431	-3.8	-2.8	65.0	29.5	even	ok
	11	C50H48N3O3	20.26	738.370116	-0.1	-0.1	69.7	28.5	even	ok

zhouxuefeng_lxw-s16_neg.d
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Figure SS-11-2. HRESIMS (-) spectrum of **16**.

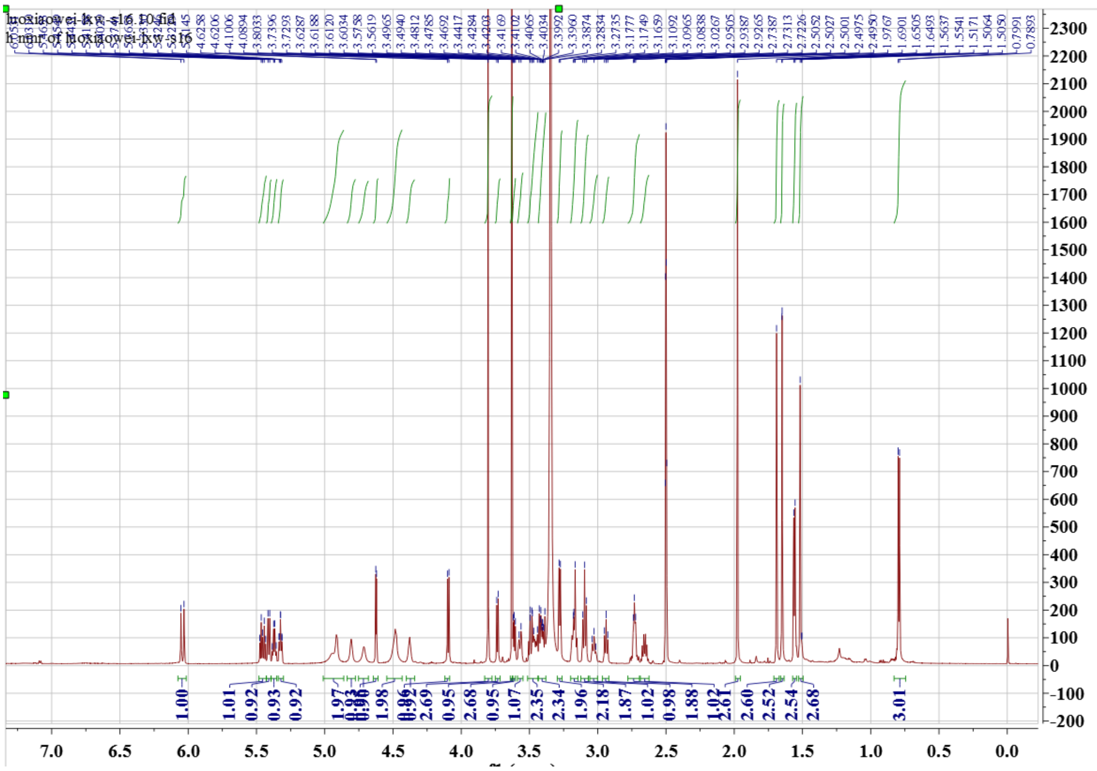


Figure SS-11-3. [1]H NMR spectrum of **16** (in DMSO-d_6, 700 MHz).

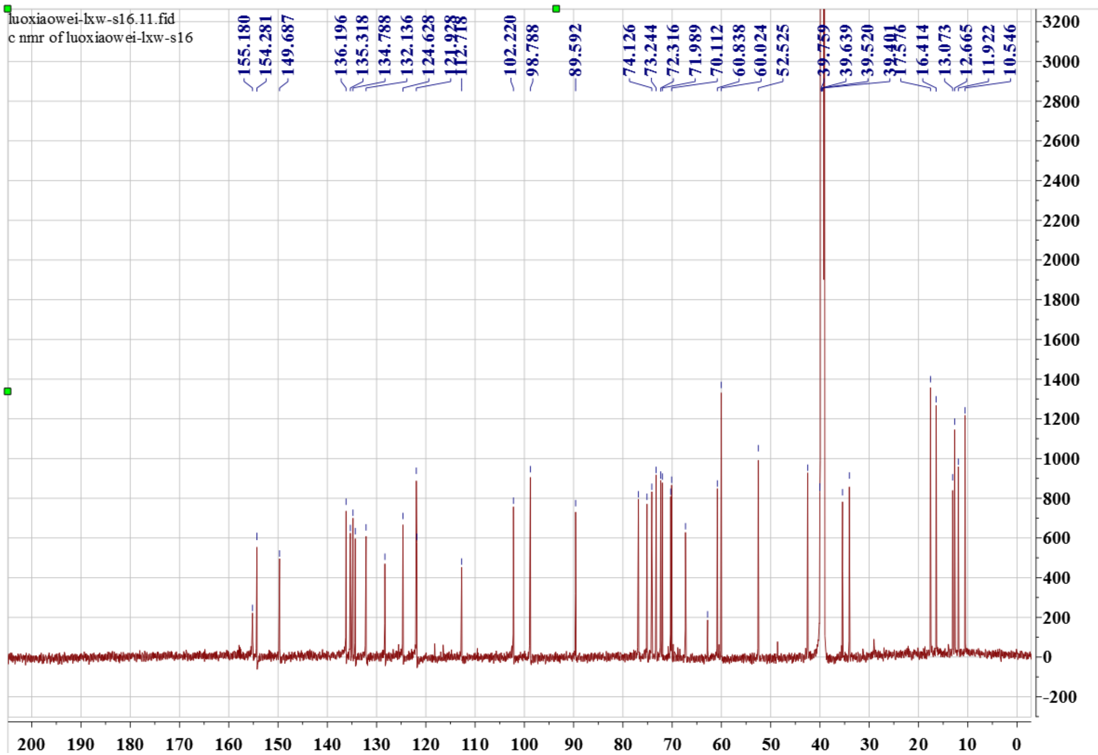


Figure SS-11-4. ^{13}C NMR spectrum of **16** (in DMSO-d_6, 175 MHz).

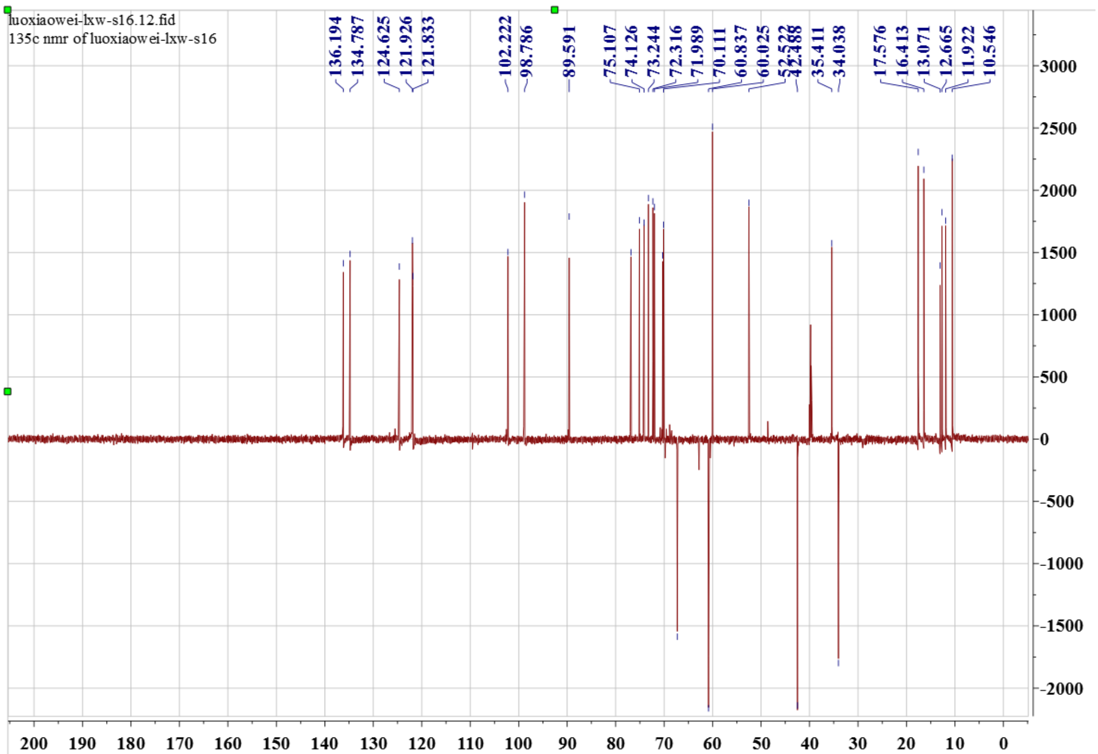


Figure SS-11-5. DEPT spectrum of **16** (in DMSO-d_6, 175 MHz).

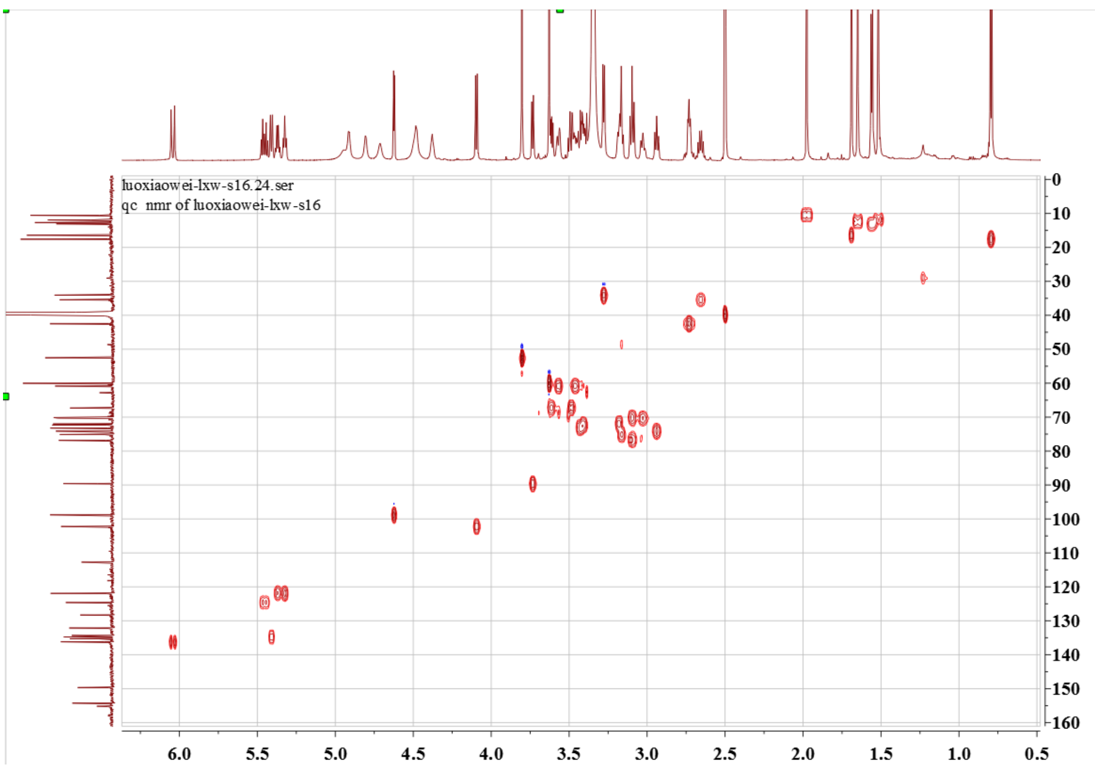


Figure SS-11-6. HSQC spectrum of **16** (in DMSO-d_6).

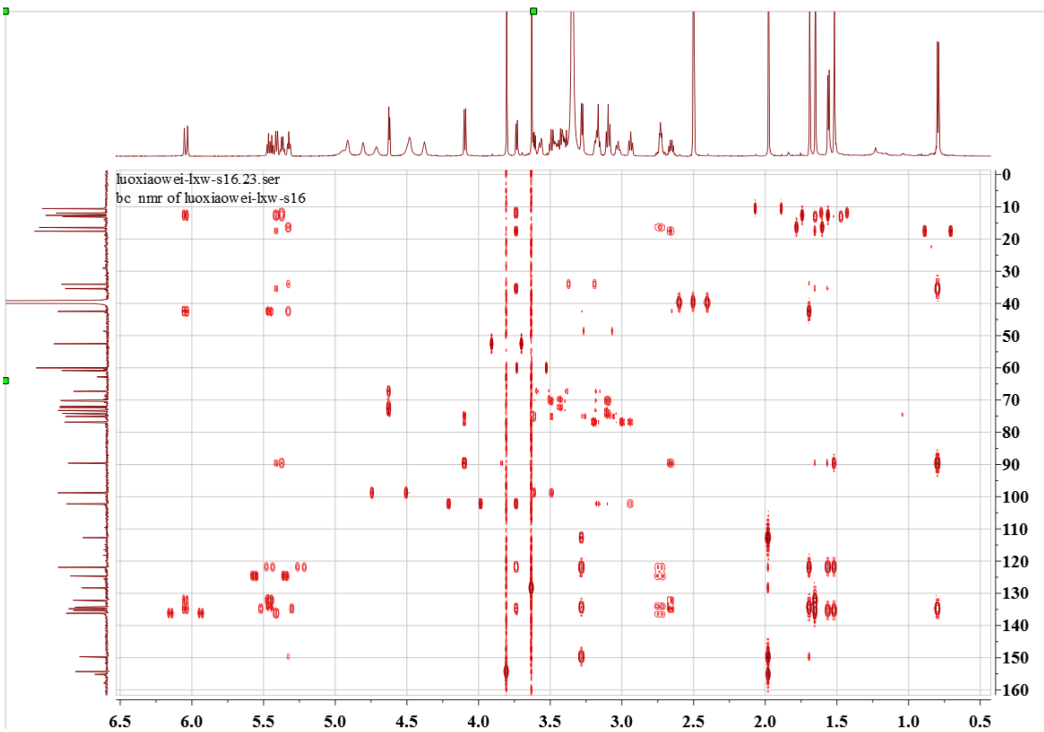


Figure SS-11-7. HMBC spectrum of **16** (in DMSO-d_6).

Figure SS-11-8. ^1H-^1H COSY spectrum of **16** (in DMSO-d_6).

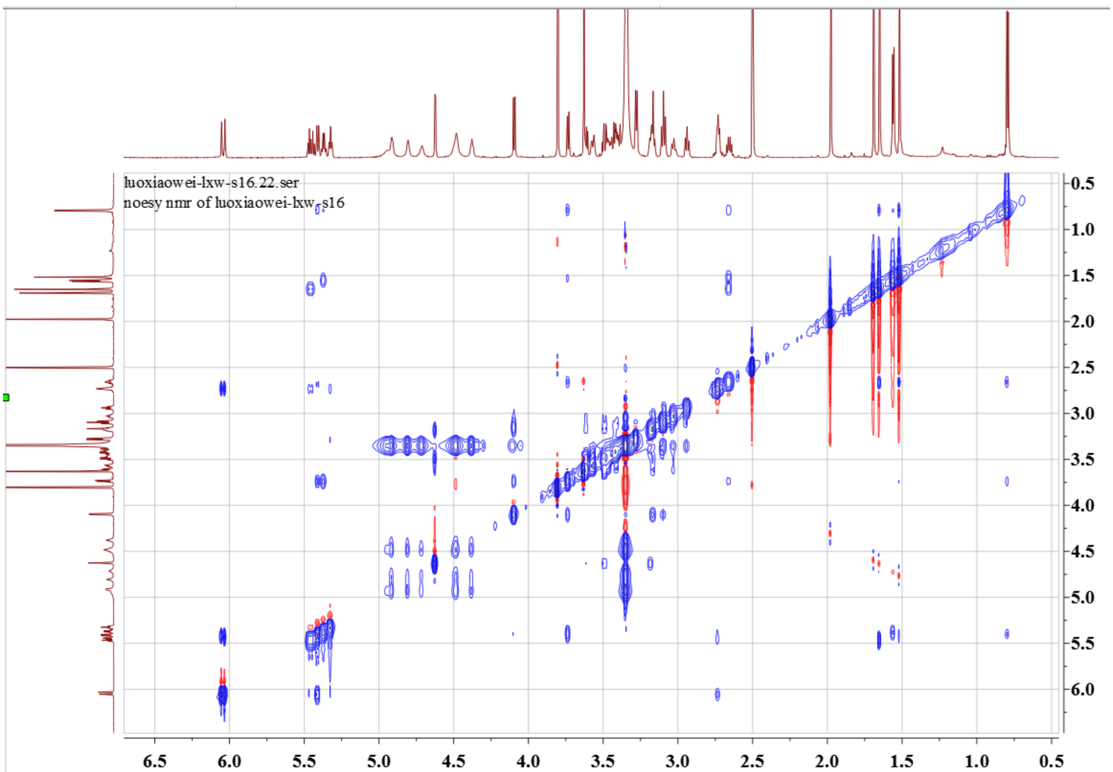


Figure SS-11-9. NOESY spectrum of **16** (in DMSO-d_6).

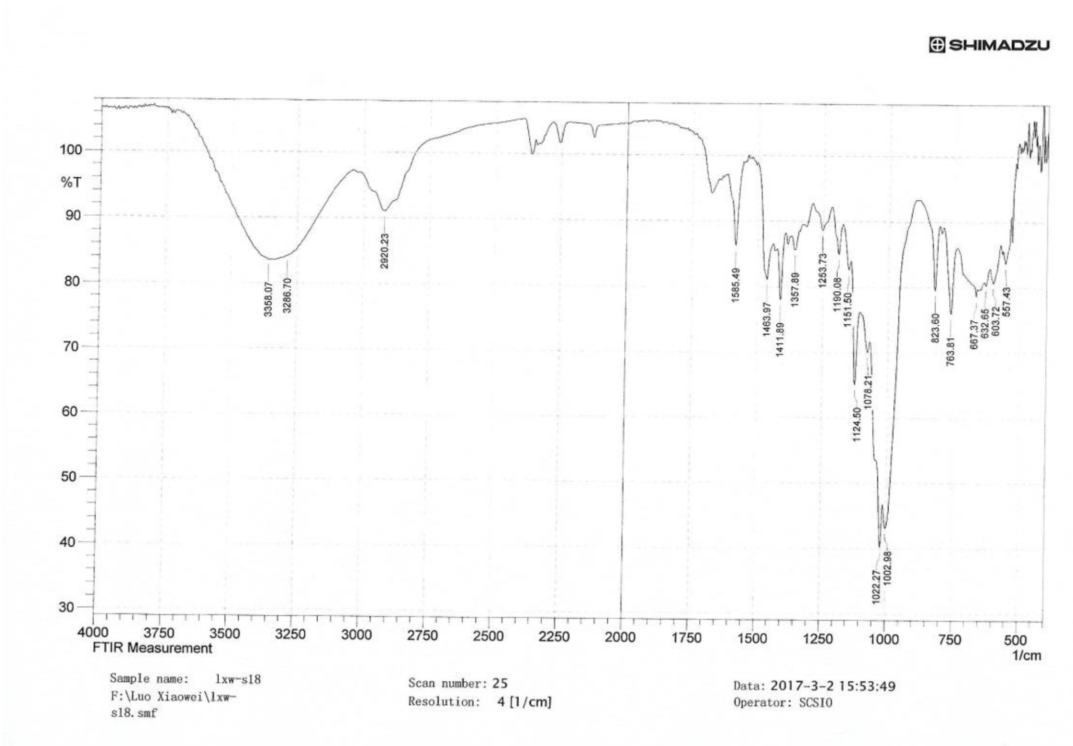
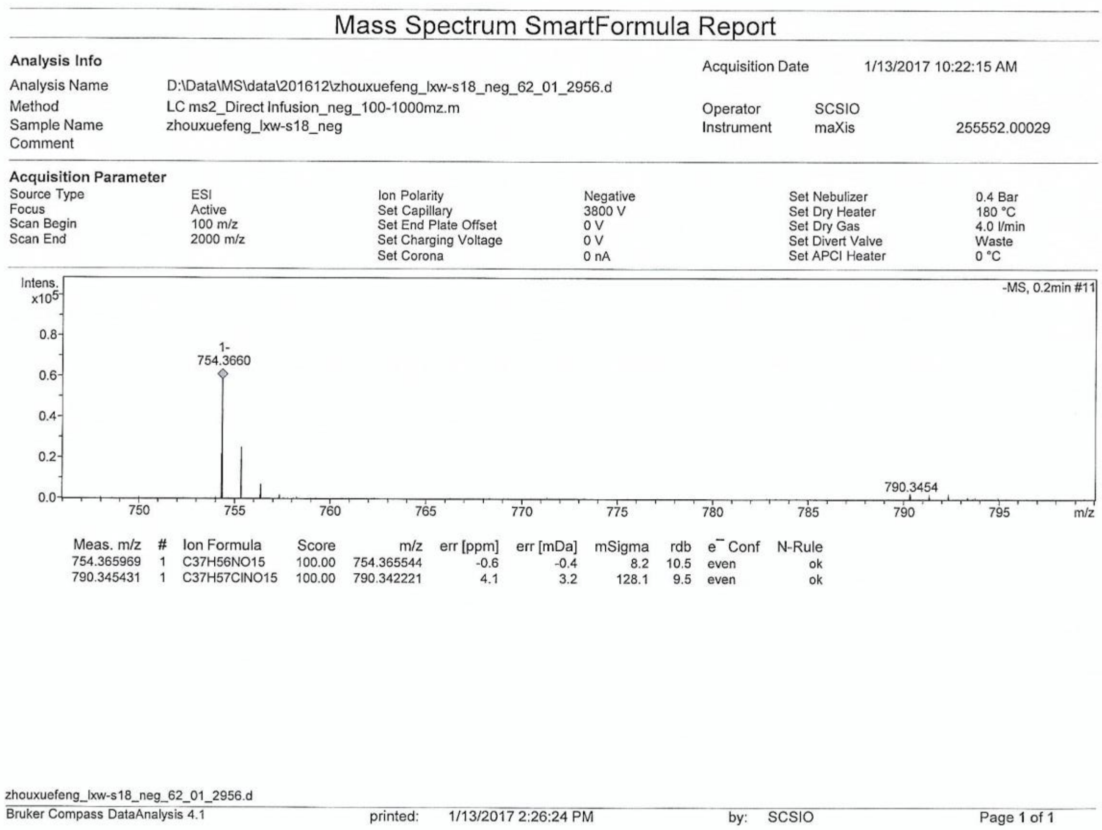


Figure SS-12-1. IR spectrum of **17**.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf	N-Rule
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790.345431	1	C37H57ClNO15	100.00	790.342221	4.1	3.2	128.1	9.5	even	ok

Figure SS-12-2. HRESIMS (-) spectrum of **17**.

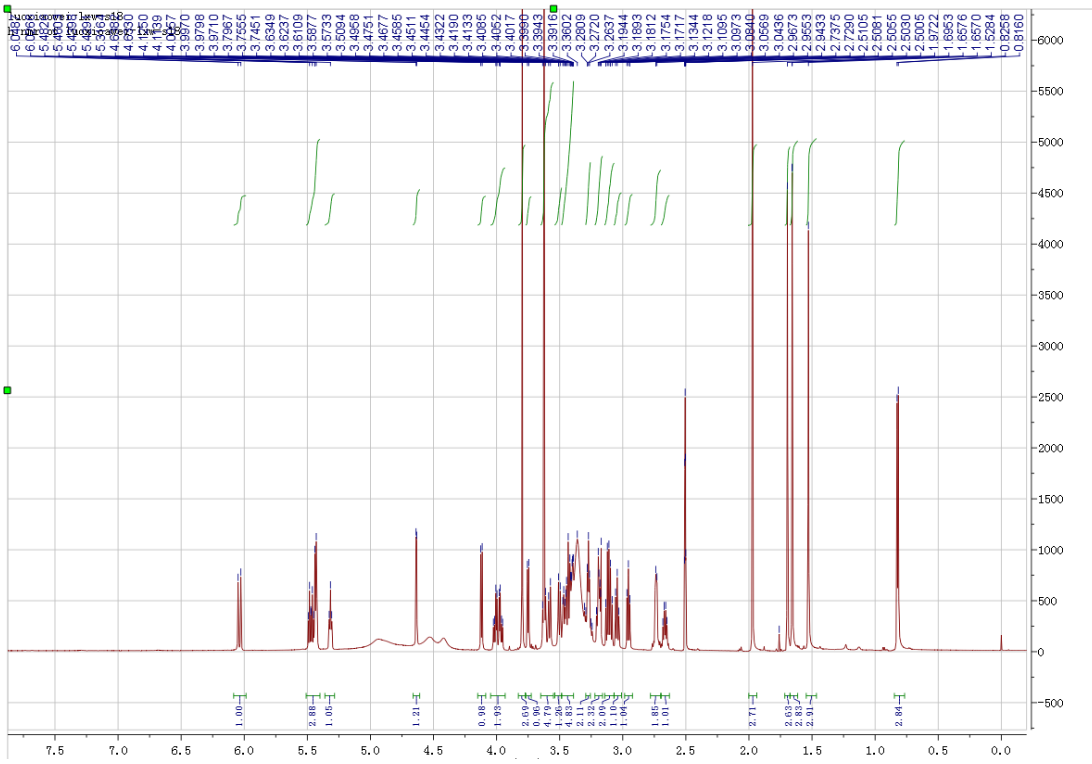


Figure SS-12-3. ^{1}H NMR spectrum of **17** (in DMSO-d_6, 700 MHz).

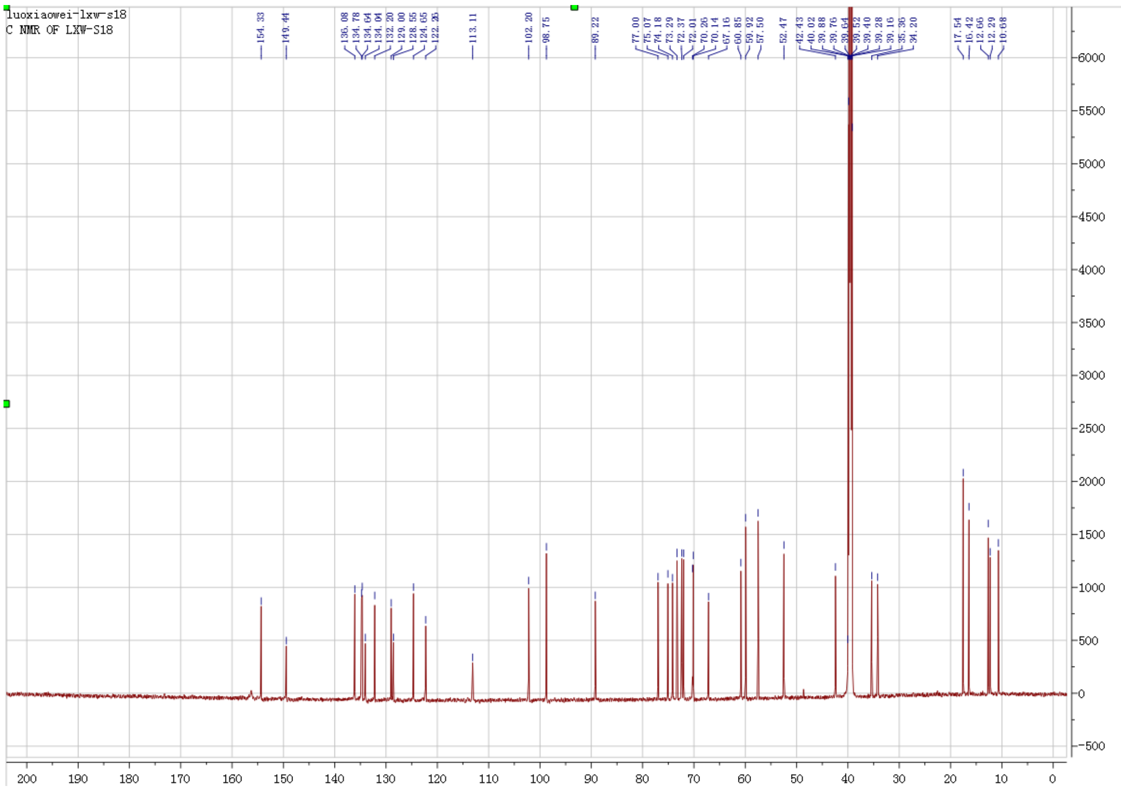


Figure SS-12-4. ^{13}C NMR spectrum of **17** (in DMSO-d_6, 175 MHz).

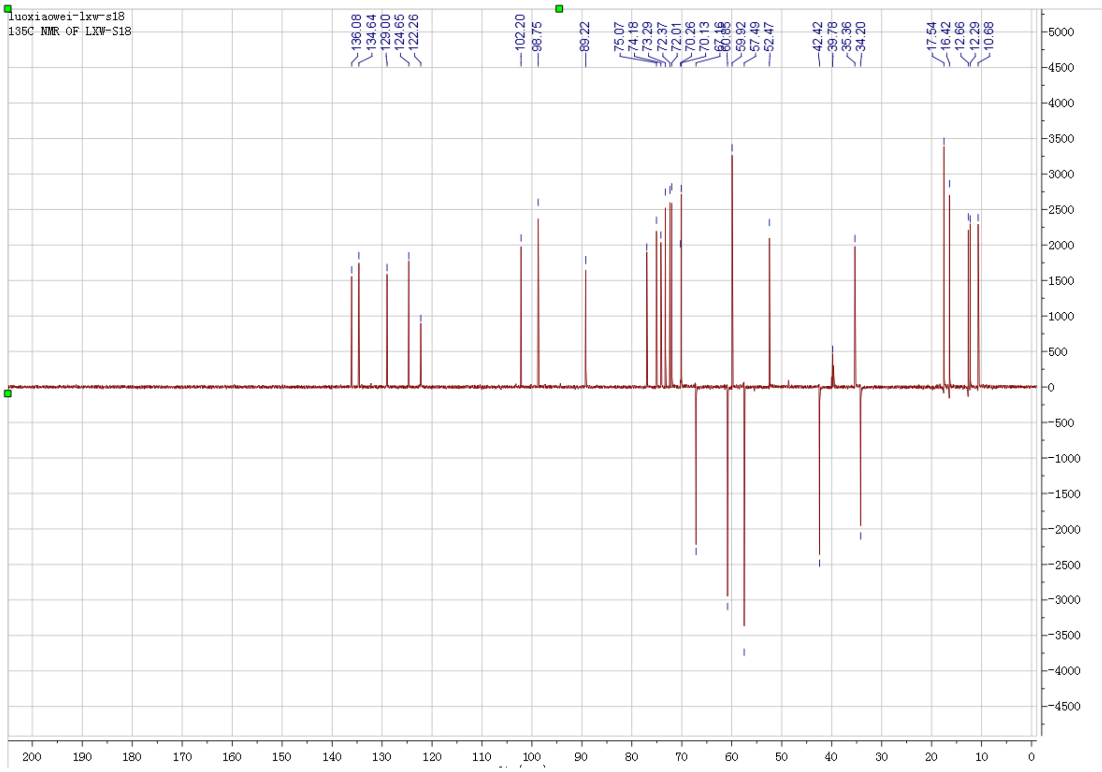


Figure SS-12-5. DEPT spectrum of **17** (in DMSO-d_6, 175 MHz).

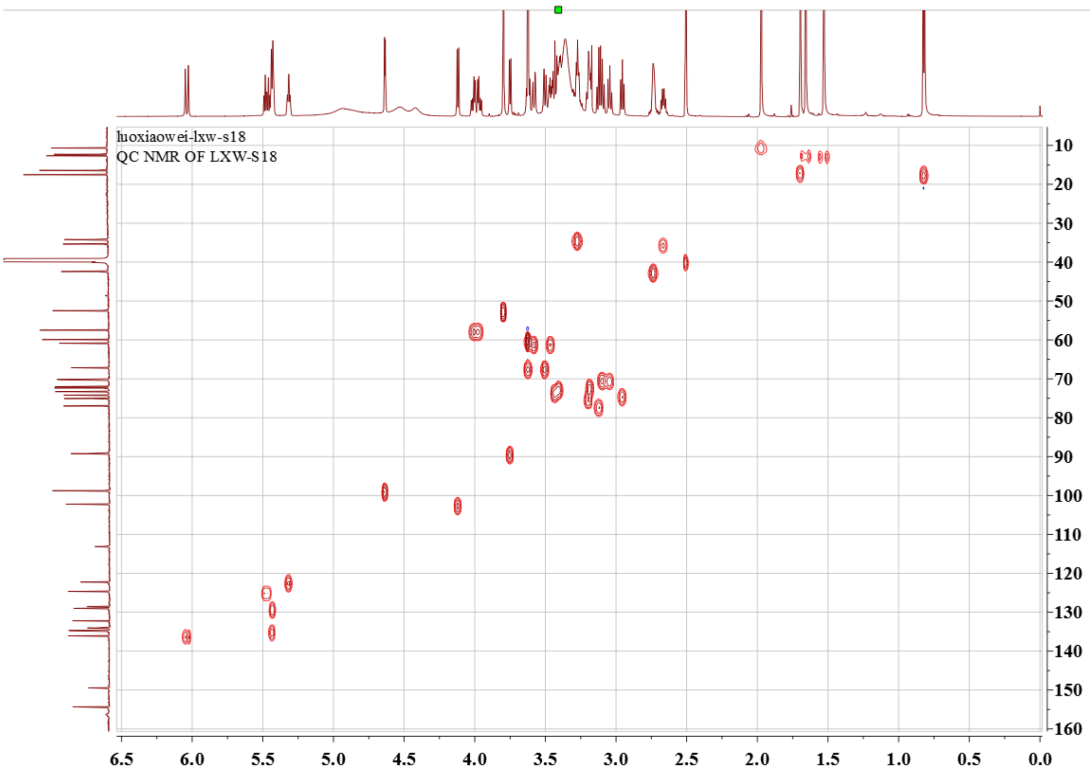


Figure SS-12-6. HSQC spectrum of **17** (in DMSO-d_6).

Figure SS-12-7. HMBC spectrum of **17** (in DMSO-d_6).

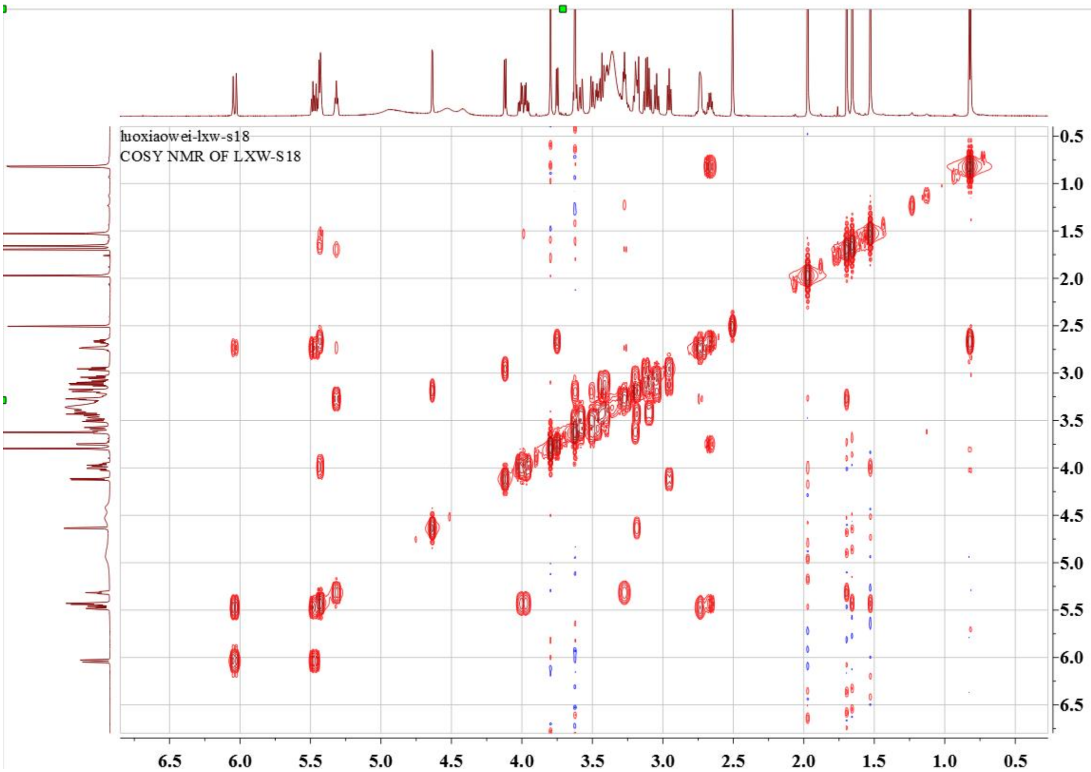


Figure SS-12-8. ^{1}H-^{1}H COSY spectrum of **17** (in DMSO-d_6).

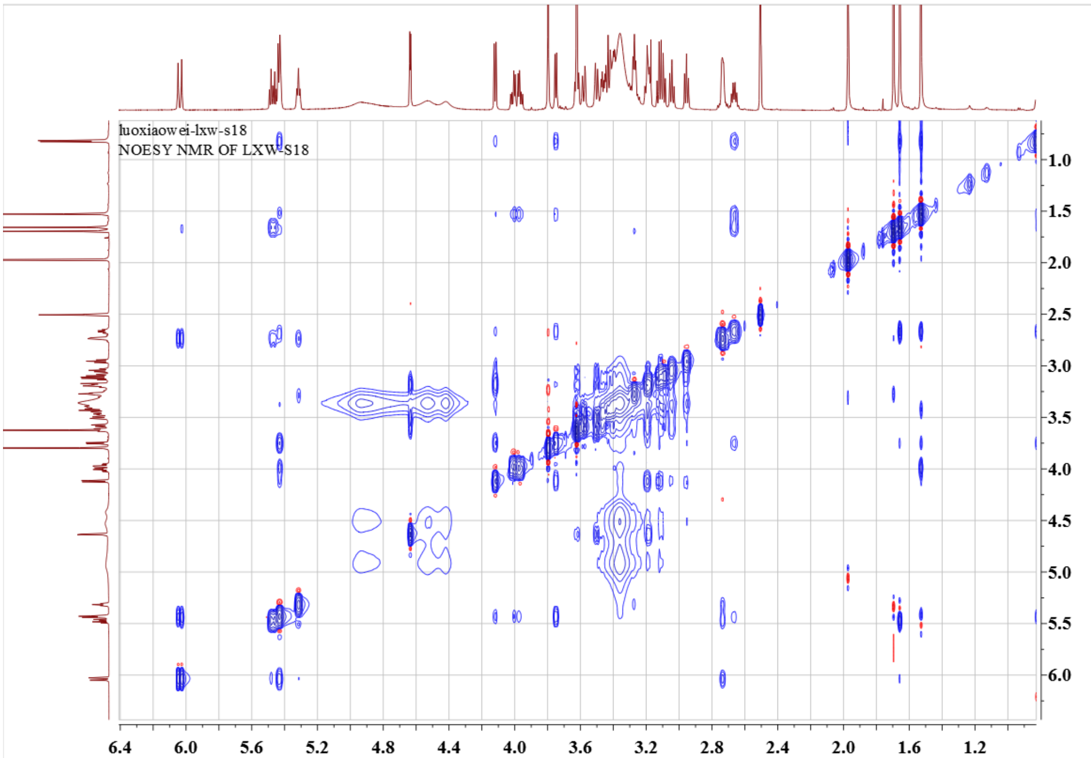


Figure SS-12-9. NOESY spectrum of **17** (in DMSO-d_6).

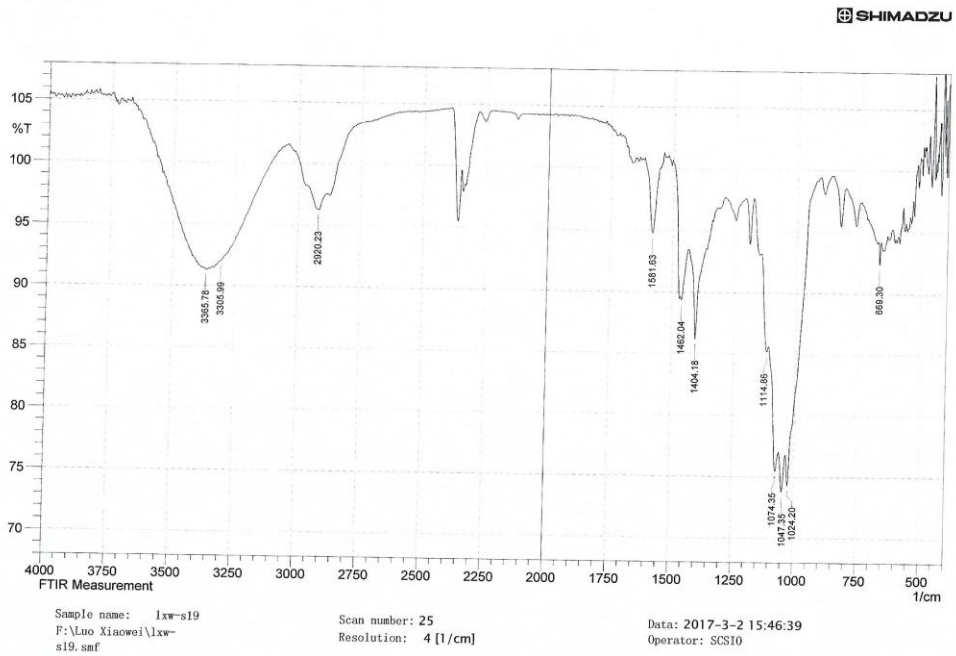


Figure SS-13-1. IR spectrum of **18**.

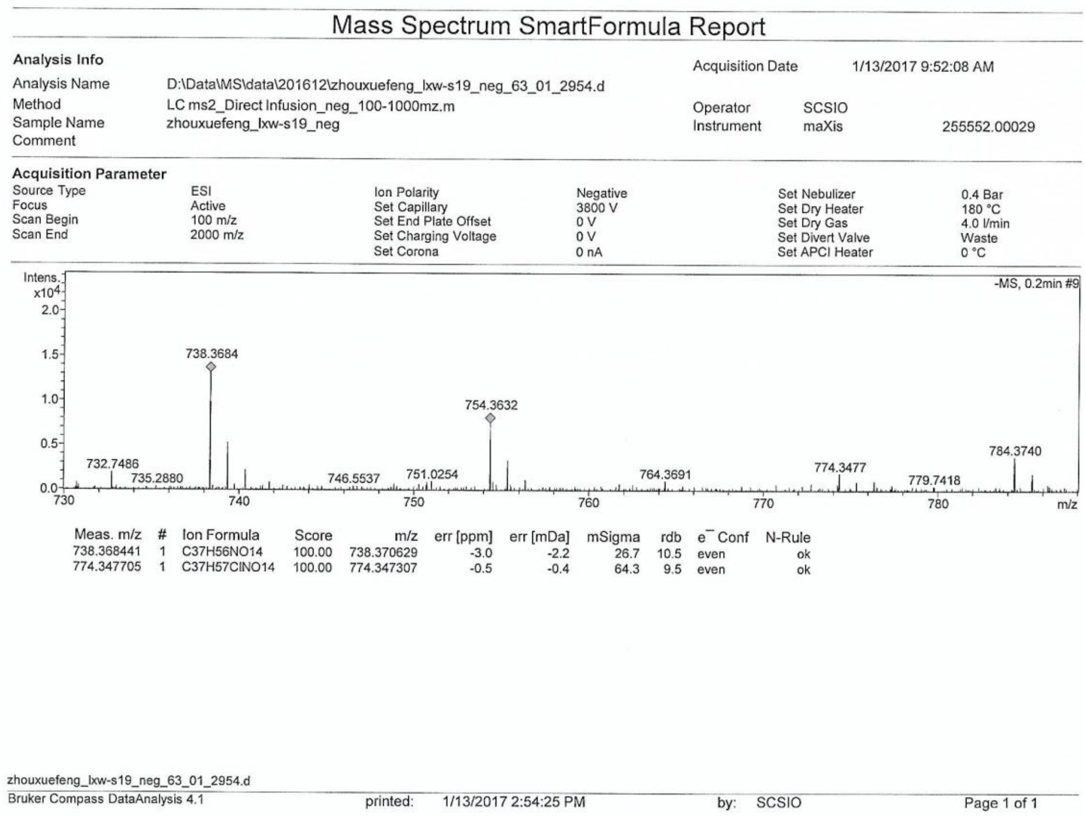


Figure SS-13-2. HRESIMS (+) spectrum of **18**.

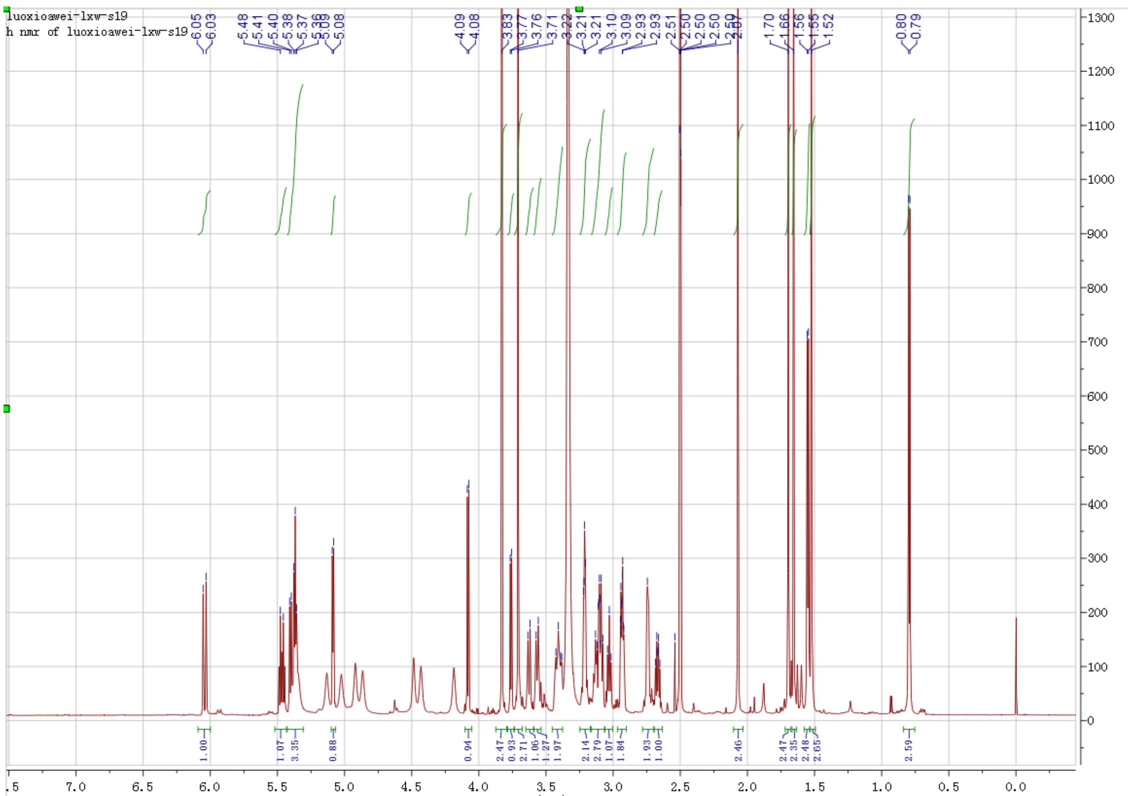


Figure SS-13-3. [1]H NMR spectrum of **18** (in DMSO-d_6, 700 MHz).

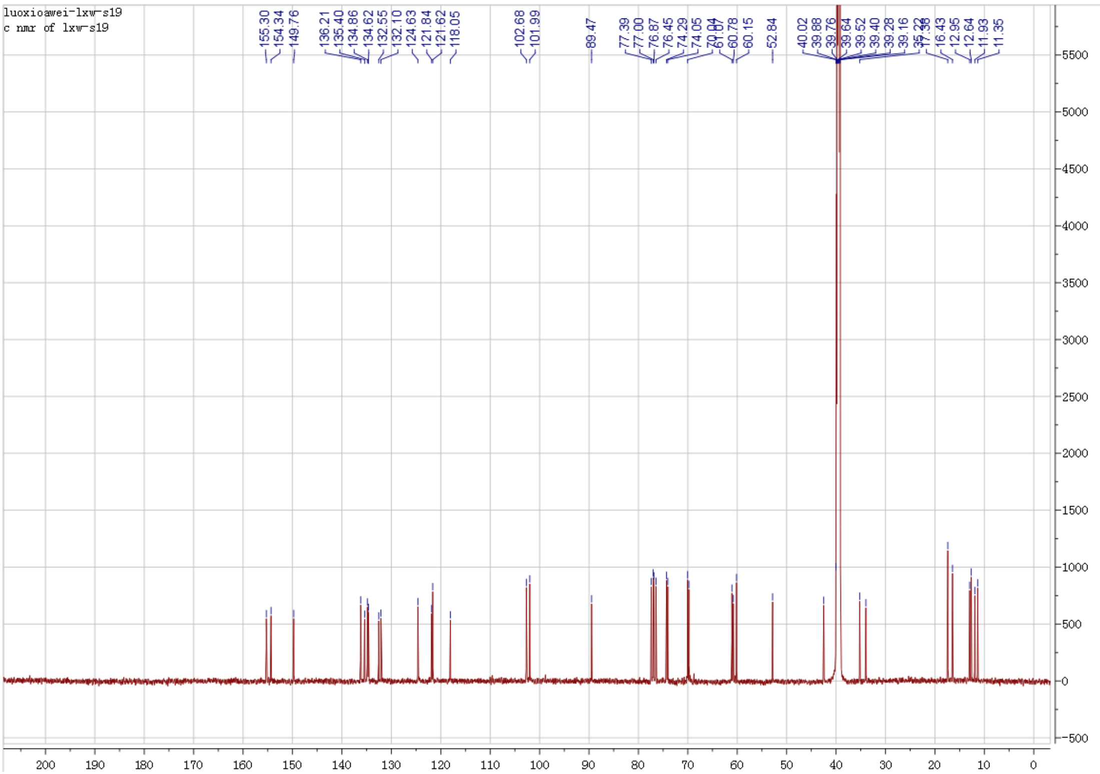


Figure SS-13-4. ^{13}C NMR spectrum of **18** (in DMSO-d_6, 175 MHz).

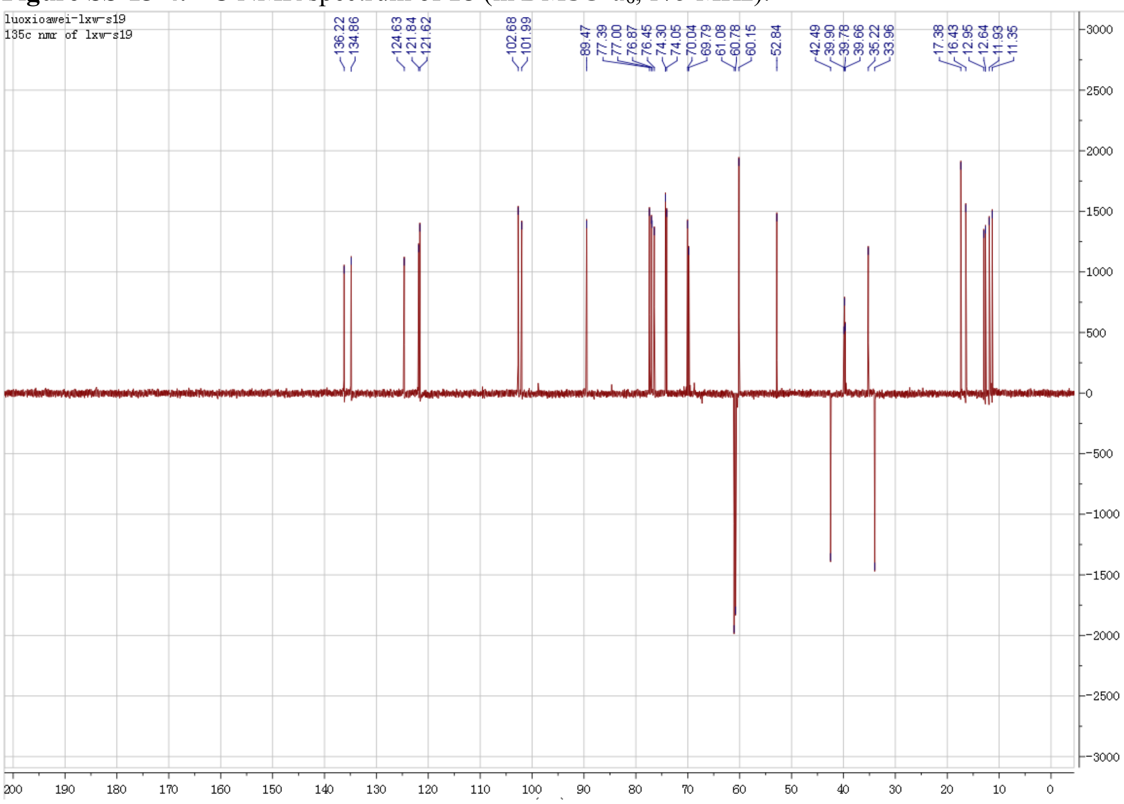


Figure SS-13-5. DEPT spectrum of **18** (in DMSO-d_6, 175 MHz).

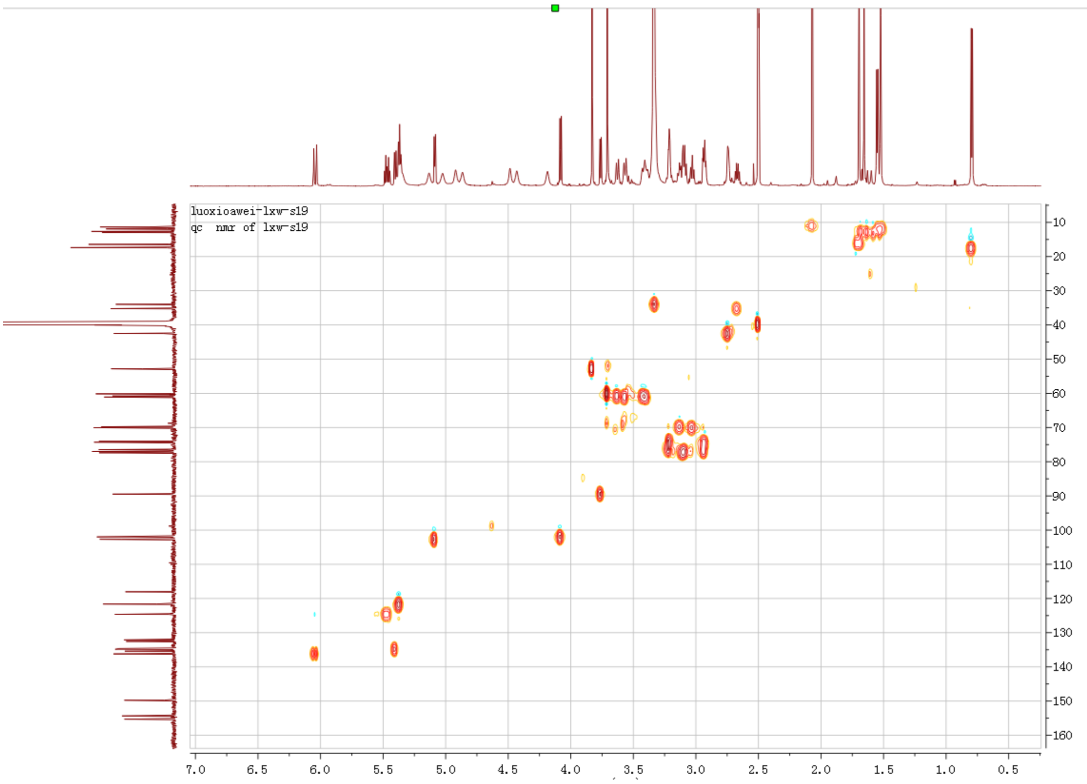


Figure SS-13-6. HSQC spectrum of **18** (in DMSO-d_6).

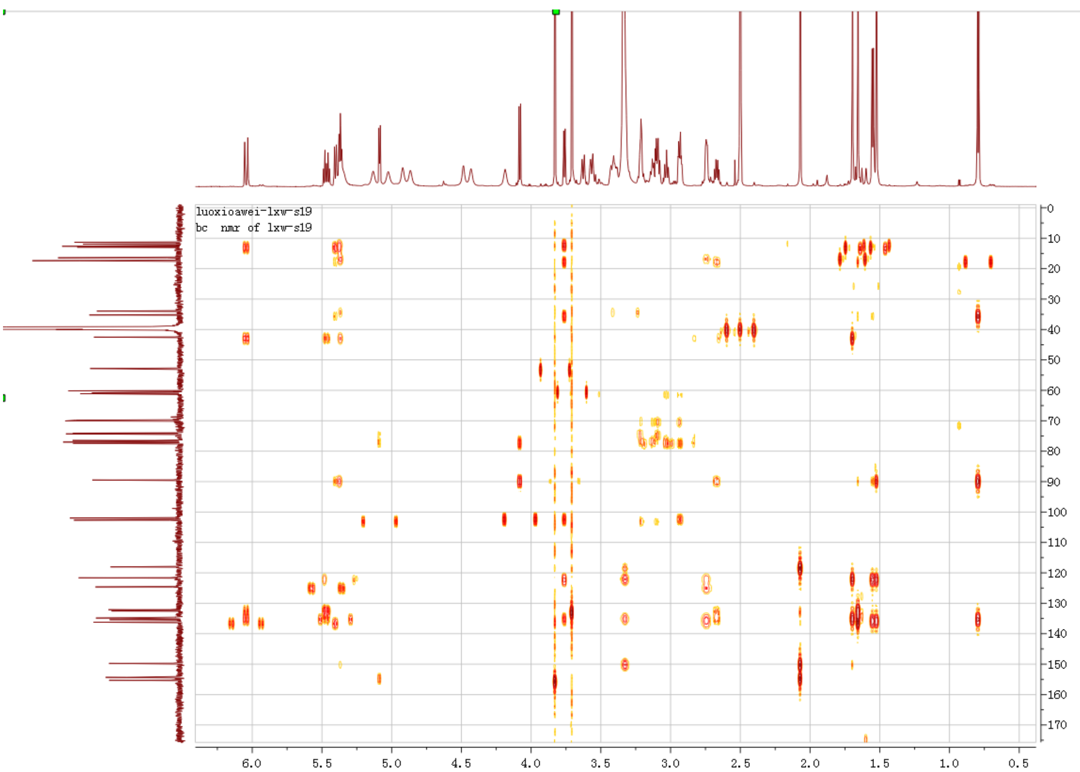


Figure SS-13-7. HMBC spectrum of **18** (in DMSO-d_6).

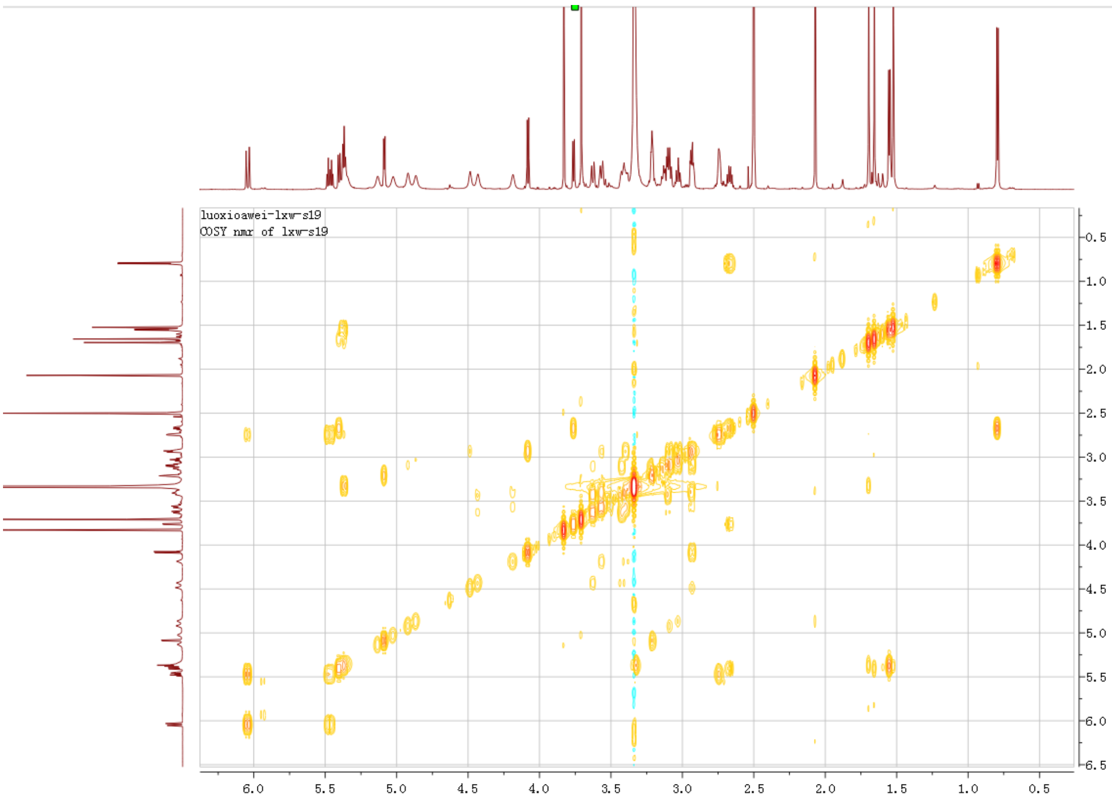


Figure SS-13-8. ^{1}H-^{1}H COSY spectrum of **18** (in DMSO-d_6).

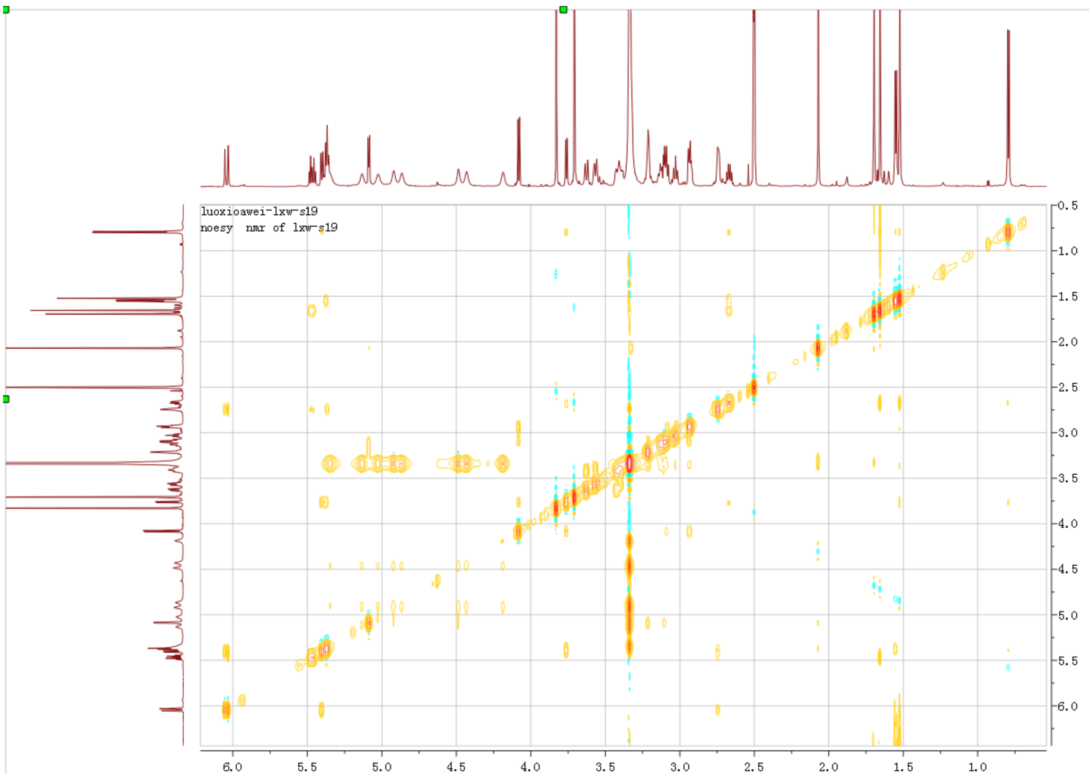


Figure SS-13-9. NOESY spectrum of **18** (in DMSO-d_6).

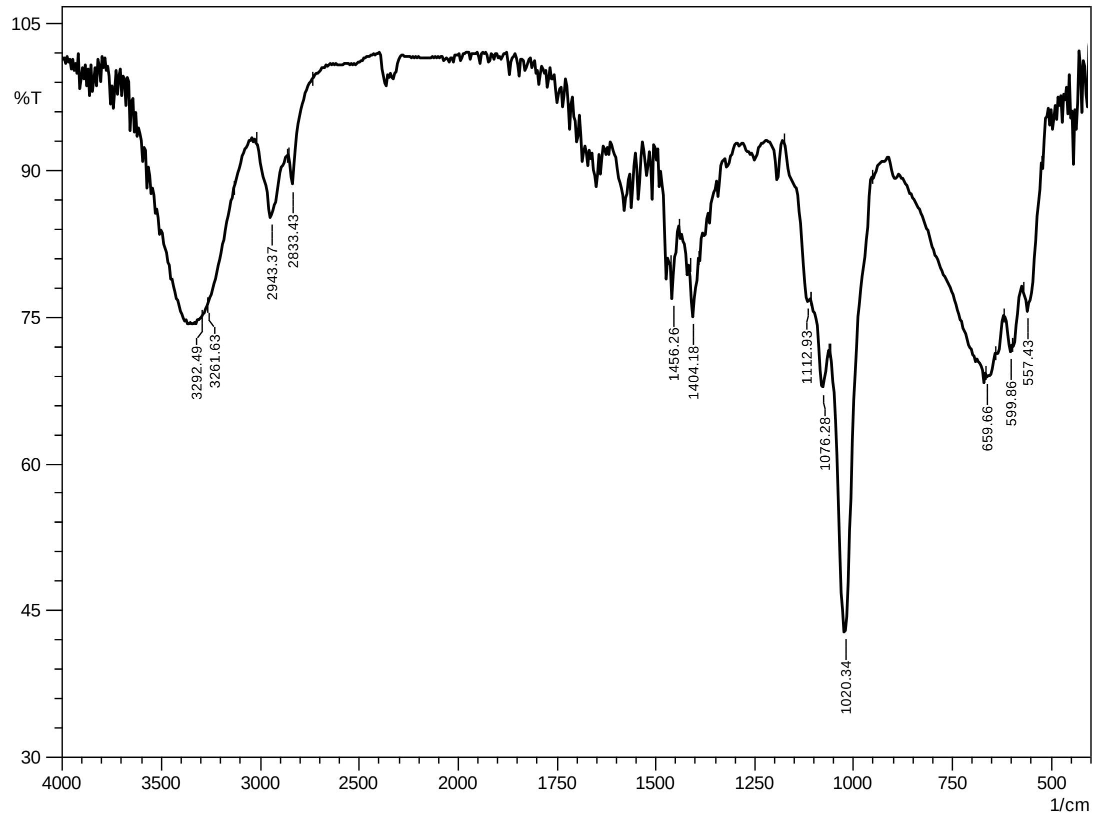
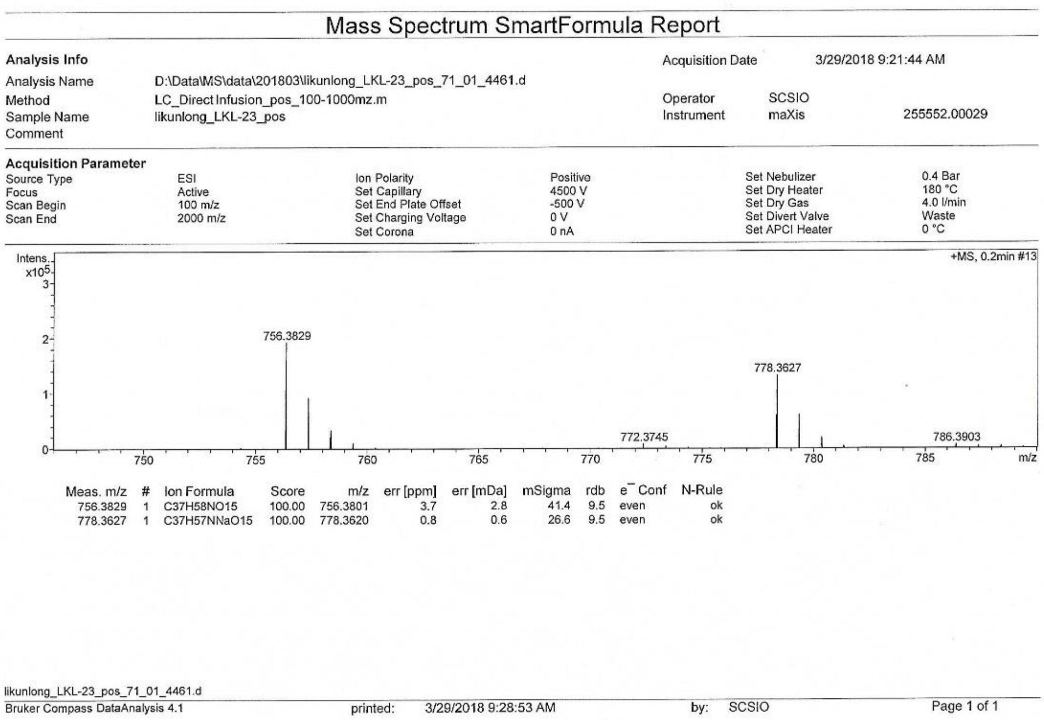


Figure SS-14-1. IR spectrum of **19**.



Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	likunlong_LKL-23_pos	Instrument	maXis	255552.00029
Comment				

Acquisition Parameter

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Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf	N-Rule
756.3829	1	C37H58NO15	100.00	756.3801	3.7	2.8	41.4	9.5	even	ok
778.3627	1	C37H57NNaO15	100.00	778.3620	0.8	0.6	26.6	9.5	even	ok

likunlong_LKL-23_pos_71_01_4461.d

Bruker Compass DataAnalysis 4.1 printed: 3/29/2018 9:28:53 AM by: SCSIO Page 1 of 1

Figure SS-14-2. HRESIMS (+) spectrum of **19**.

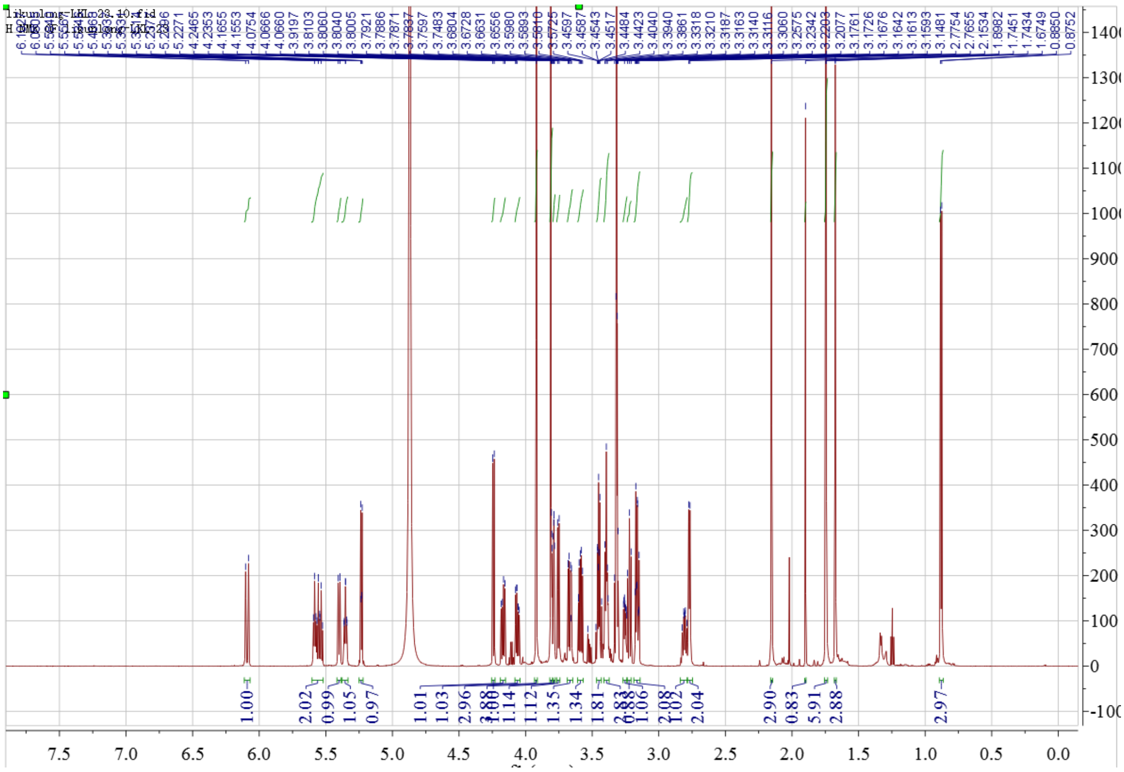

Figure SS-14-3. ^{1}H NMR spectrum of **19** (in CD_3OD, 700 MHz).

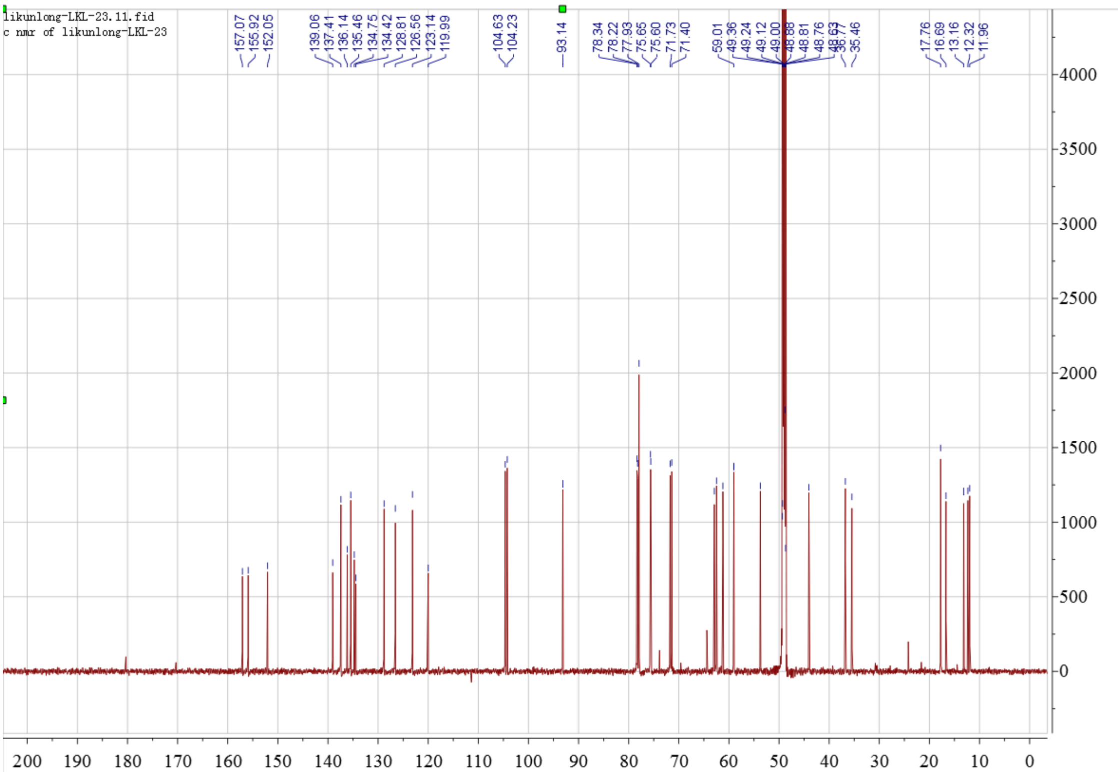

Figure SS-14-4. ^{13}C NMR spectrum of **19** (in CD_3OD, 175 MHz).

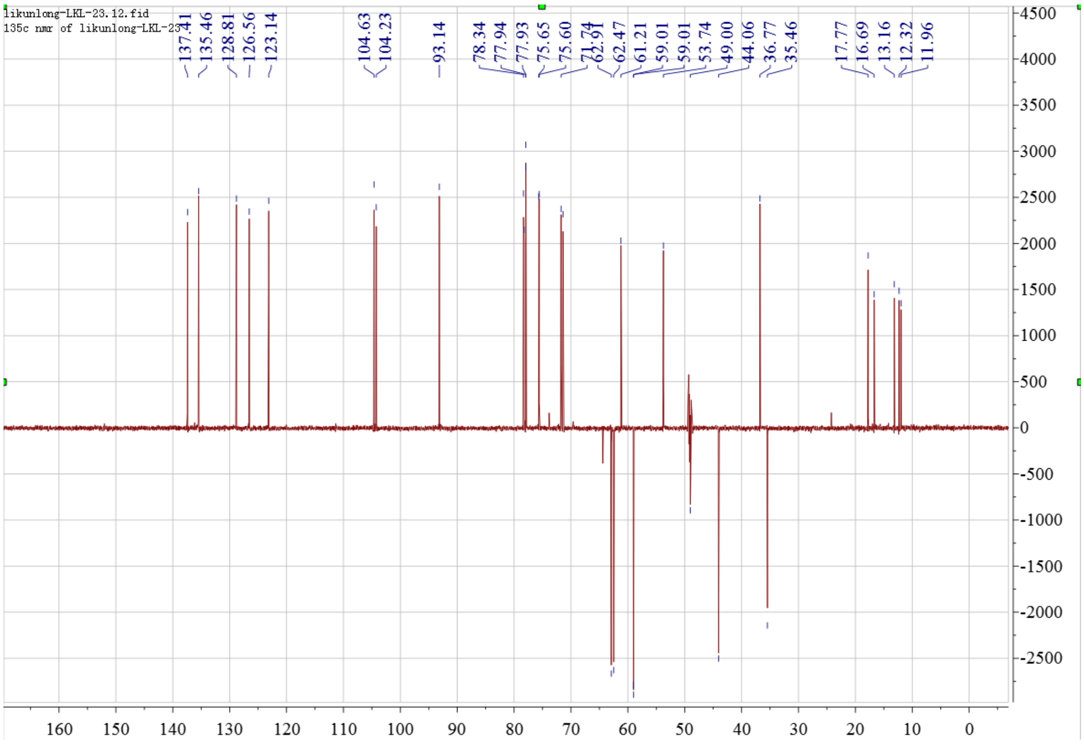

Figure SS-14-5. DEPT spectrum of **19** (in CD_3OD, 175 MHz).

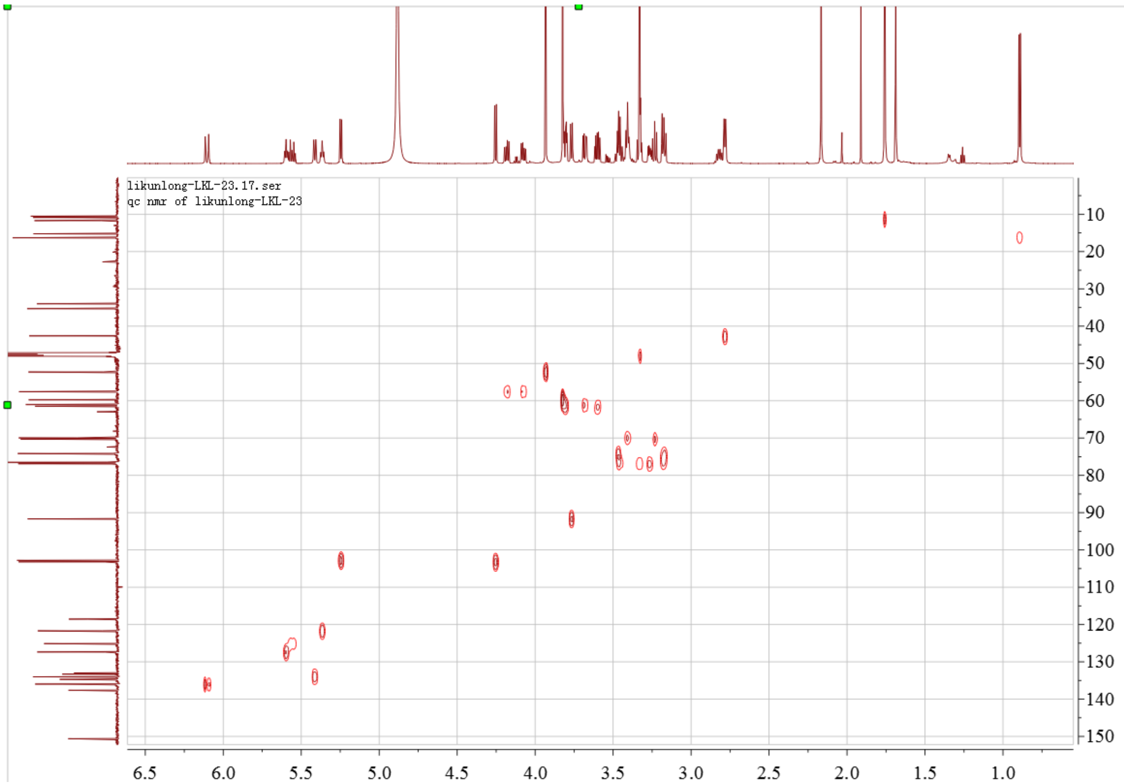

Figure SS-14-6. HSQC spectrum of **19** (in CD_3OD).

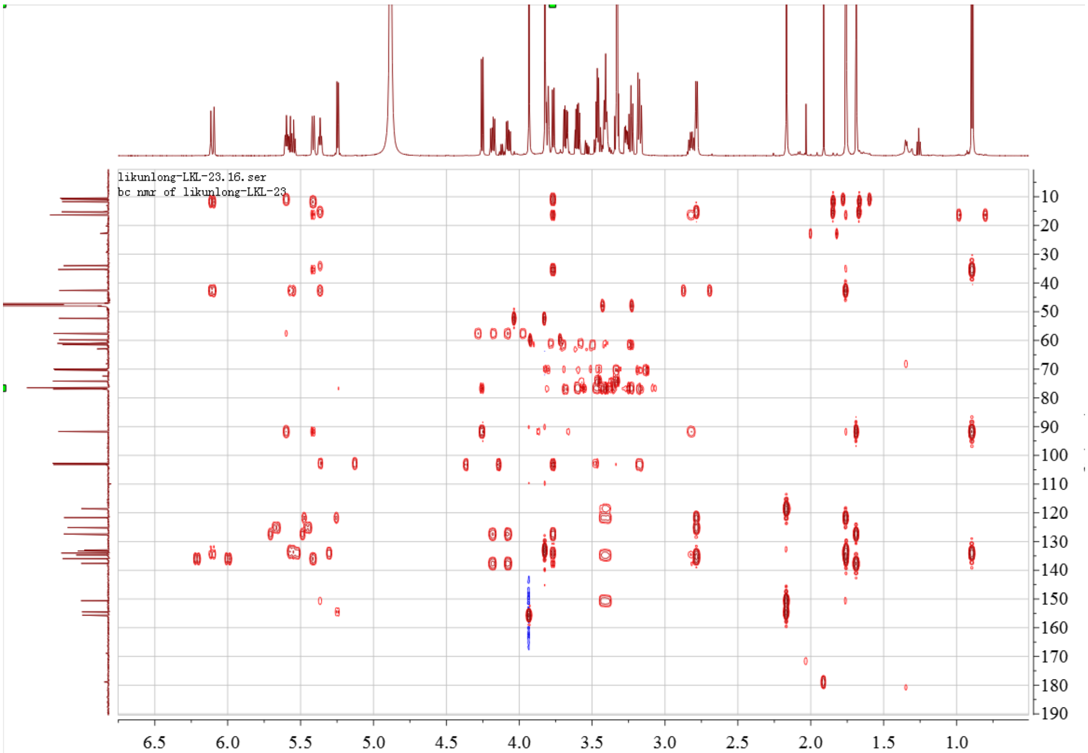

Figure SS-14-7. HMBC spectrum of **19** (in CD_3OD).

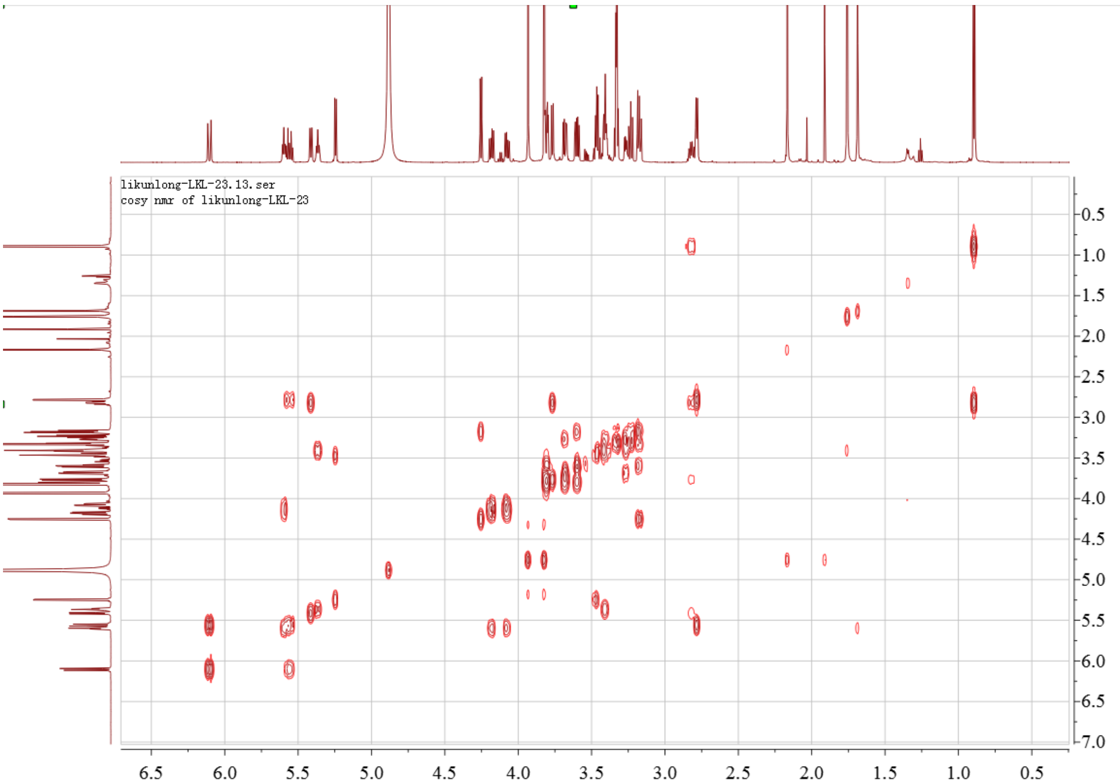

Figure SS-14-8. ^{1}H-^{1}H COSY spectrum of **19** (in CD_3OD).

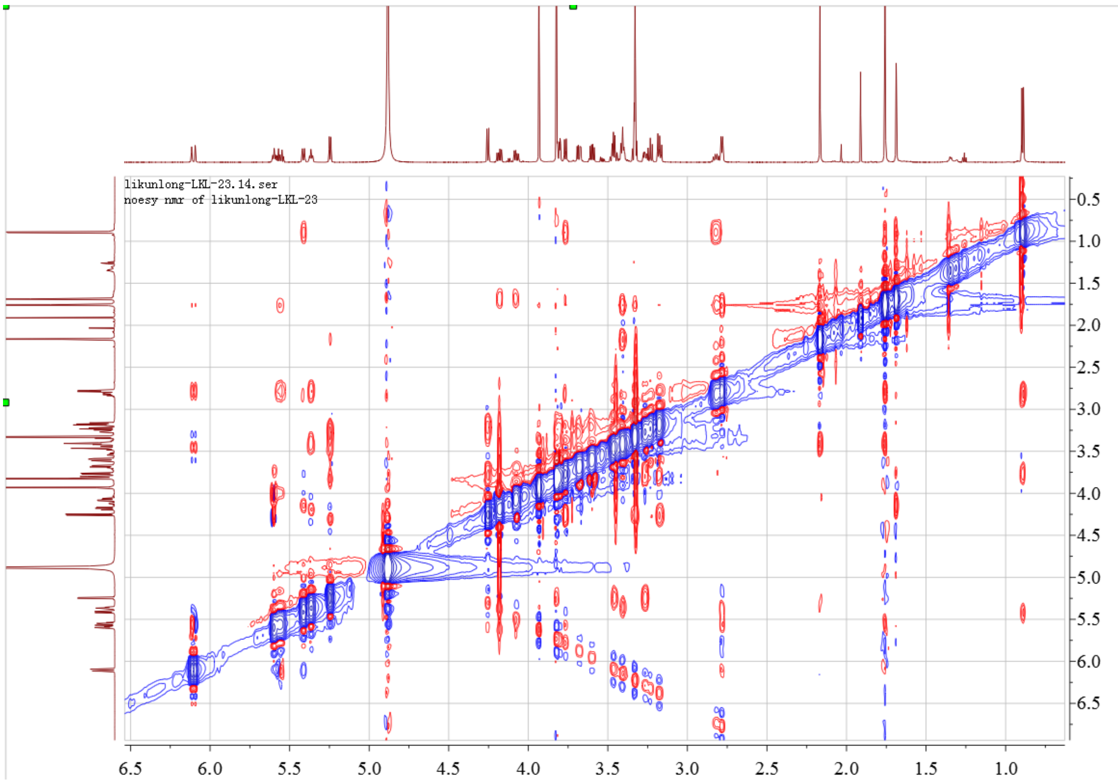

Figure SS-14-9. NOESY spectrum of **19** (in CD_3OD).

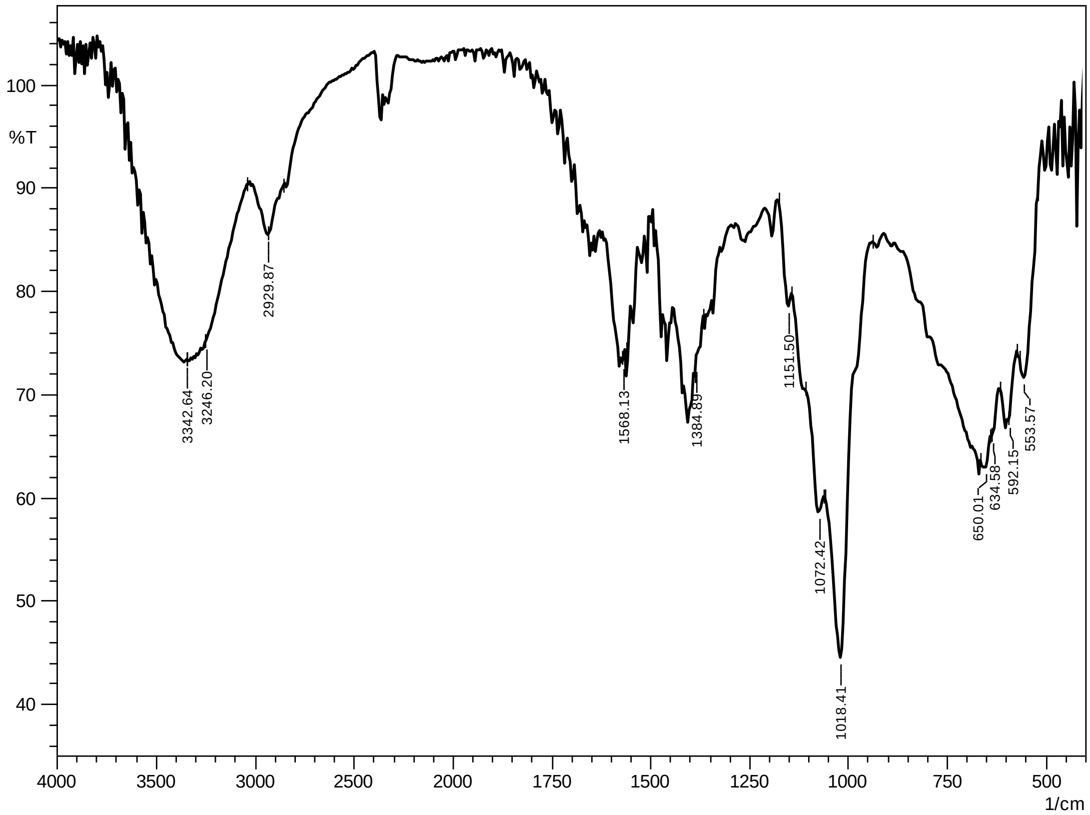

Figure SS-15-1. IR spectrum of **20**.

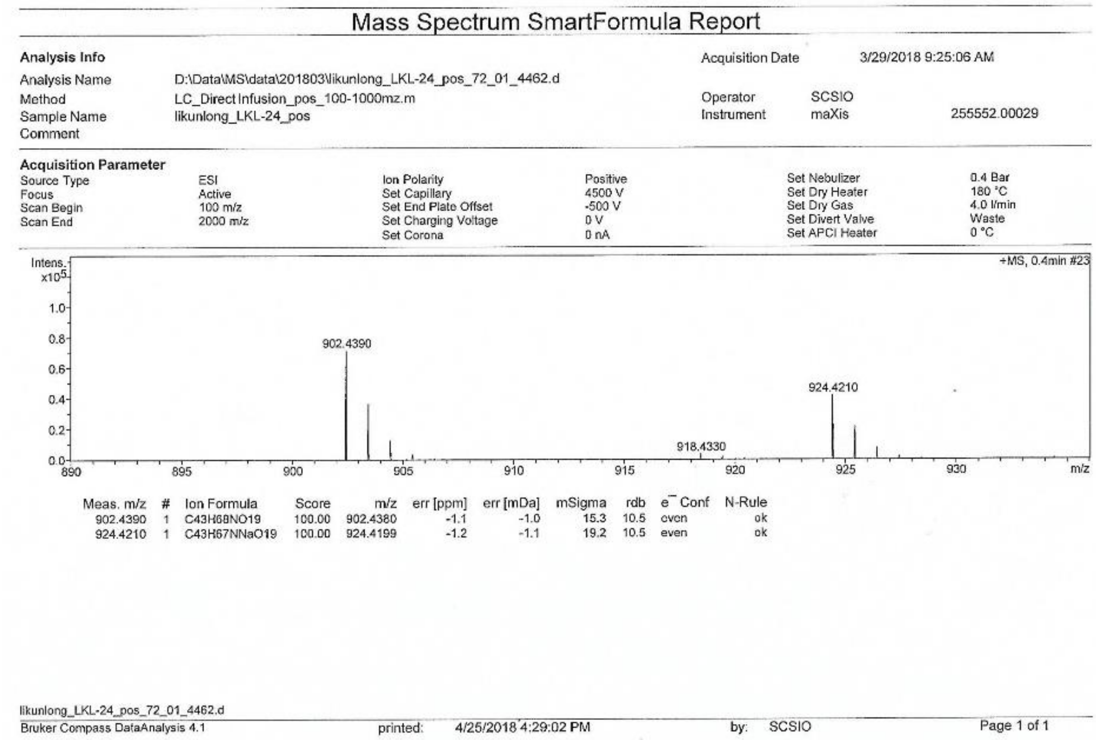

Figure SS-15-2. HRESIMS (+) spectrum of **20**.

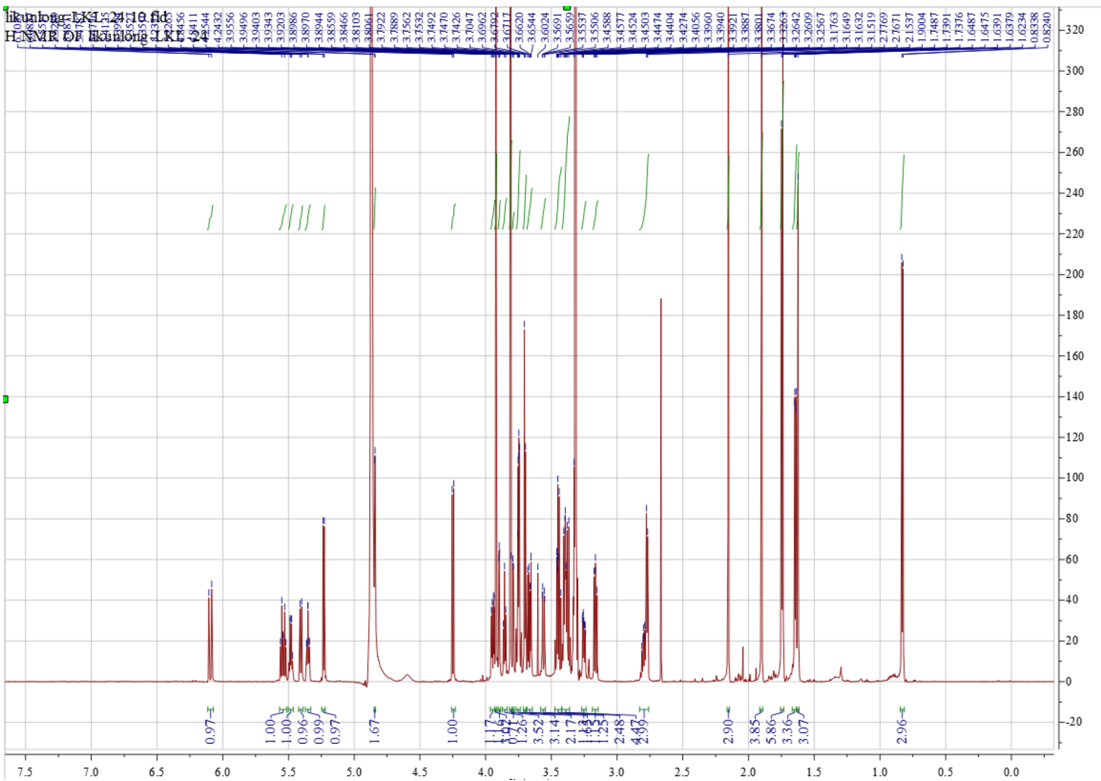

Figure SS-15-3. [1]H NMR spectrum of **20** (in CD_3OD, 700 MHz).

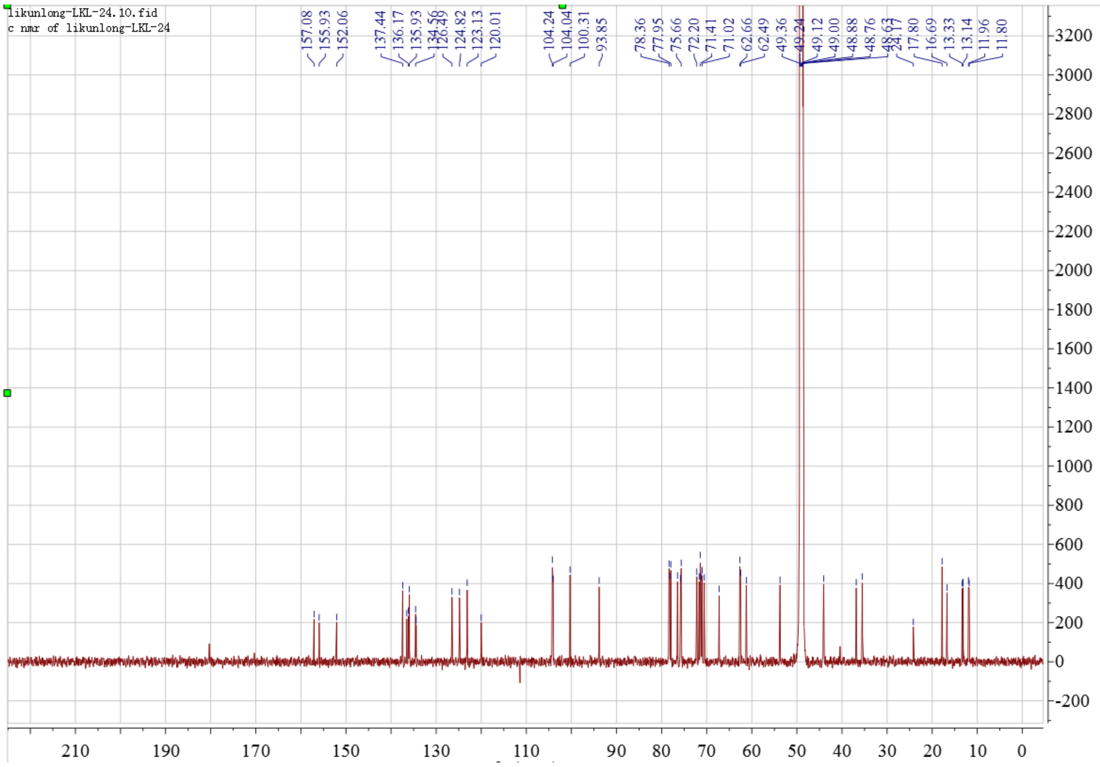

Figure SS-15-4. ^{13}C NMR spectrum of **20** (in CD_3OD, 175 MHz).

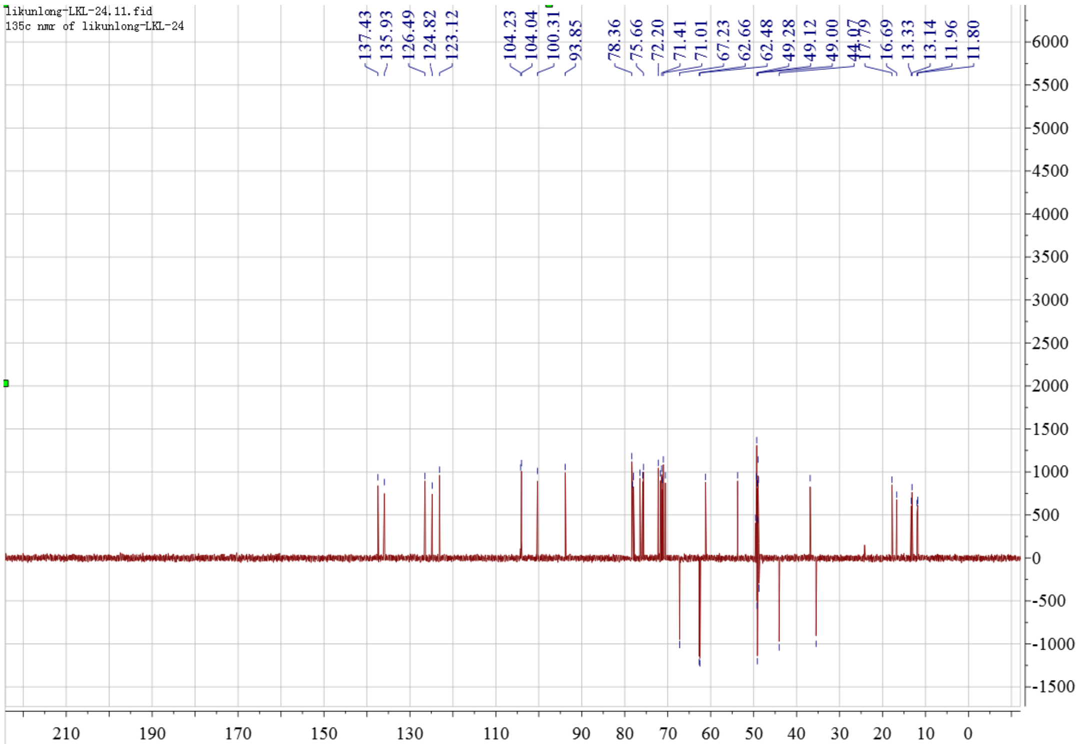

Figure SS-15-5. DEPT NMR spectrum of **20** (in CD_3OD, 175 MHz).

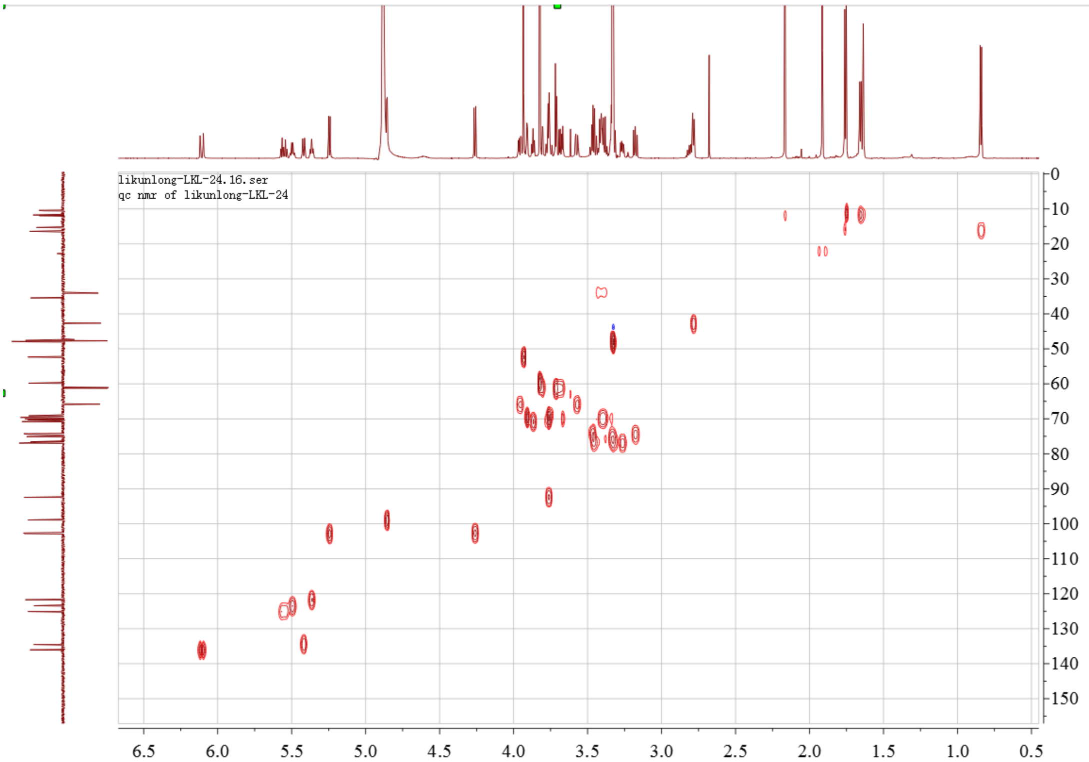

Figure SS-15-6. HSQC spectrum of **20**.

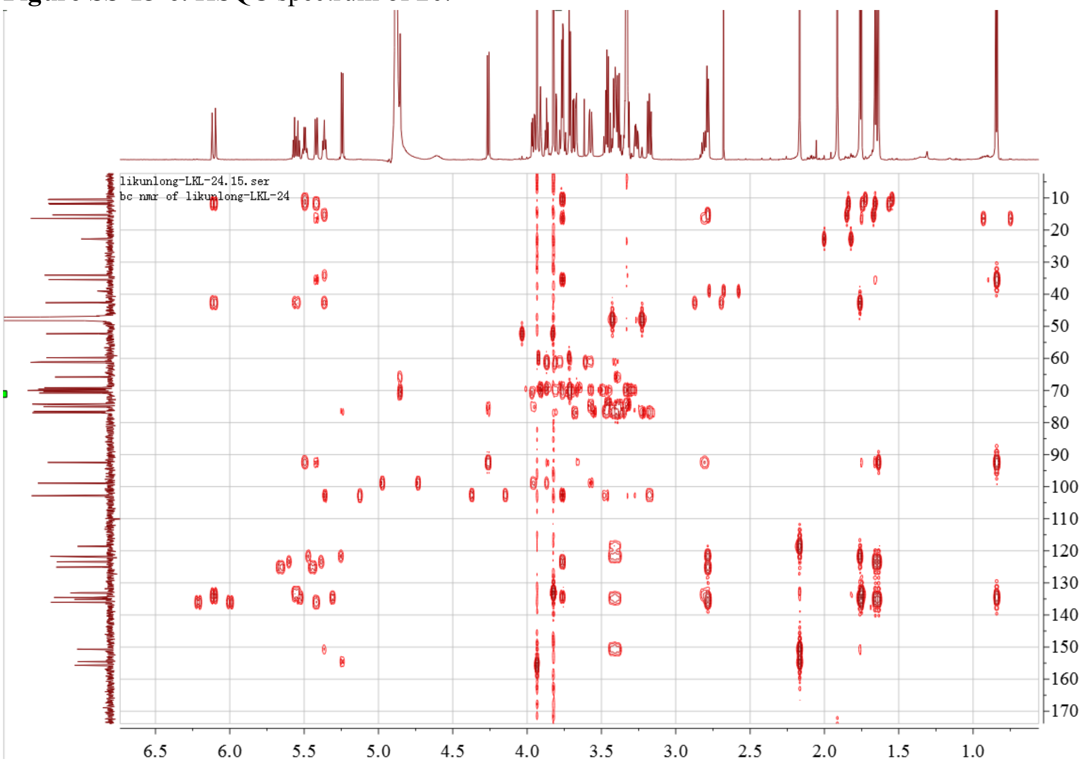

Figure SS-15-7. HMBC spectrum of **20**.

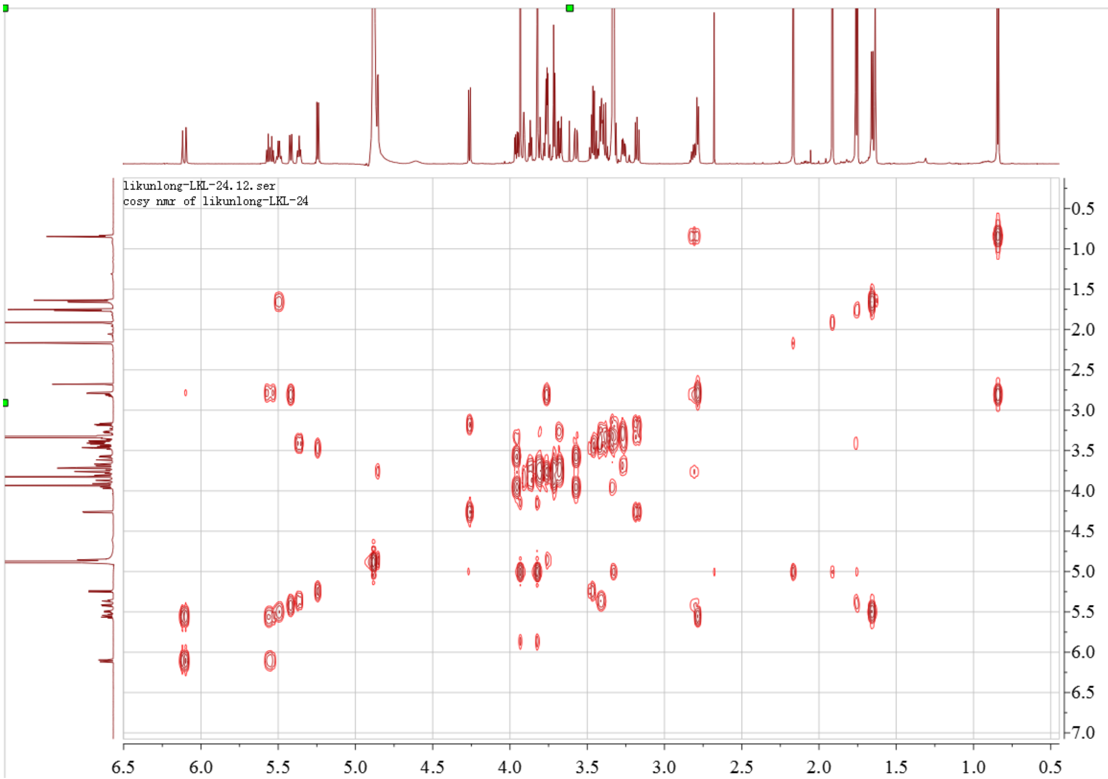

Figure SS-15-8. HMBC spectrum of **20**.

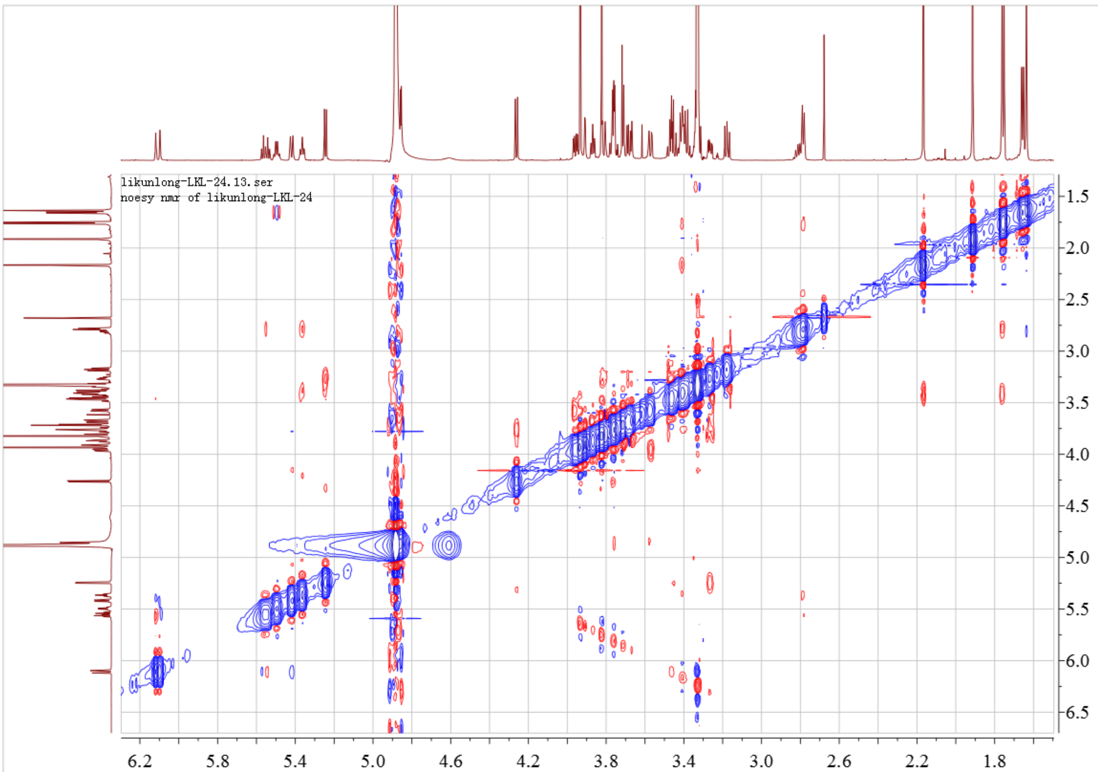

Figure SS-15-9. NOESY spectrum of **20**.

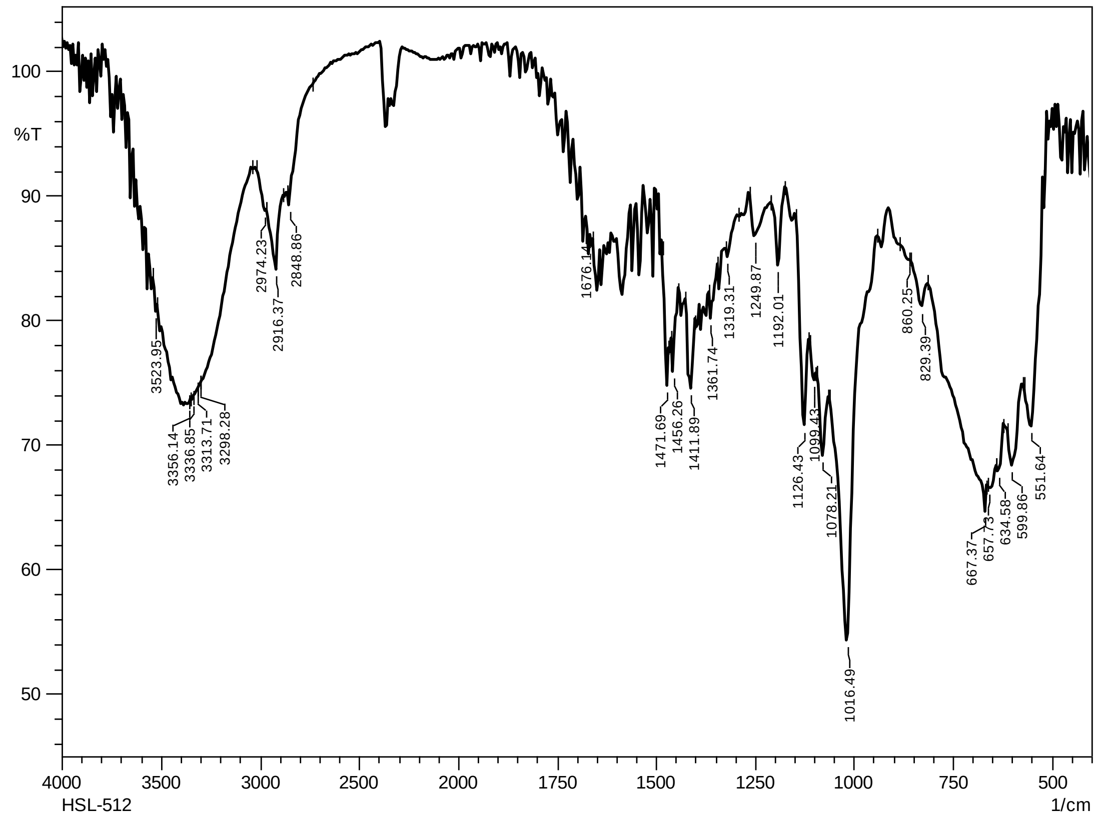

Figure SS-16-1. IR spectrum of **21**.

Mass Spectrum SmartFormula Report

Analysis Info		Acquisition Date	11/8/2017 3:10:38 PM
Analysis Name	D:\Data\MS\data\201711\zhouxuefeng_LKL-8_pos_51_01_3819.d		
Method	LC_Direct Infusion_pos_100-1000mz.m	Operator	SCSIO
Sample Name	zhouxuefeng_LKL-8_pos	Instrument	maXis 255552.00029
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
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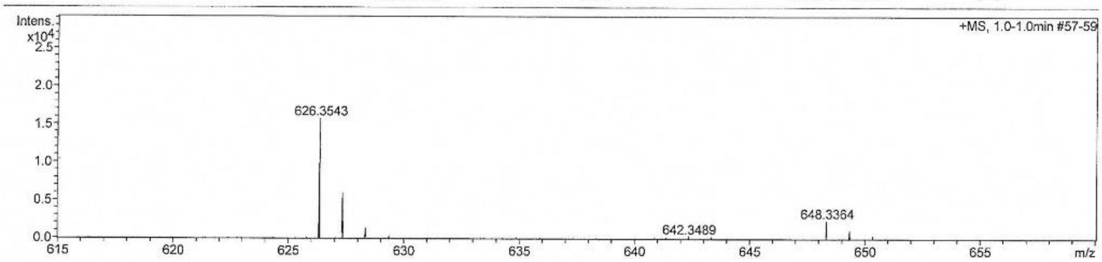

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf	N-Rule
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648.336355	1	C32H51NNaO11	76.08	648.335432	1.4	0.9	10.6	7.5	even	ok

Figure SS-16-2. HRESIMS (+) spectrum of **21**.

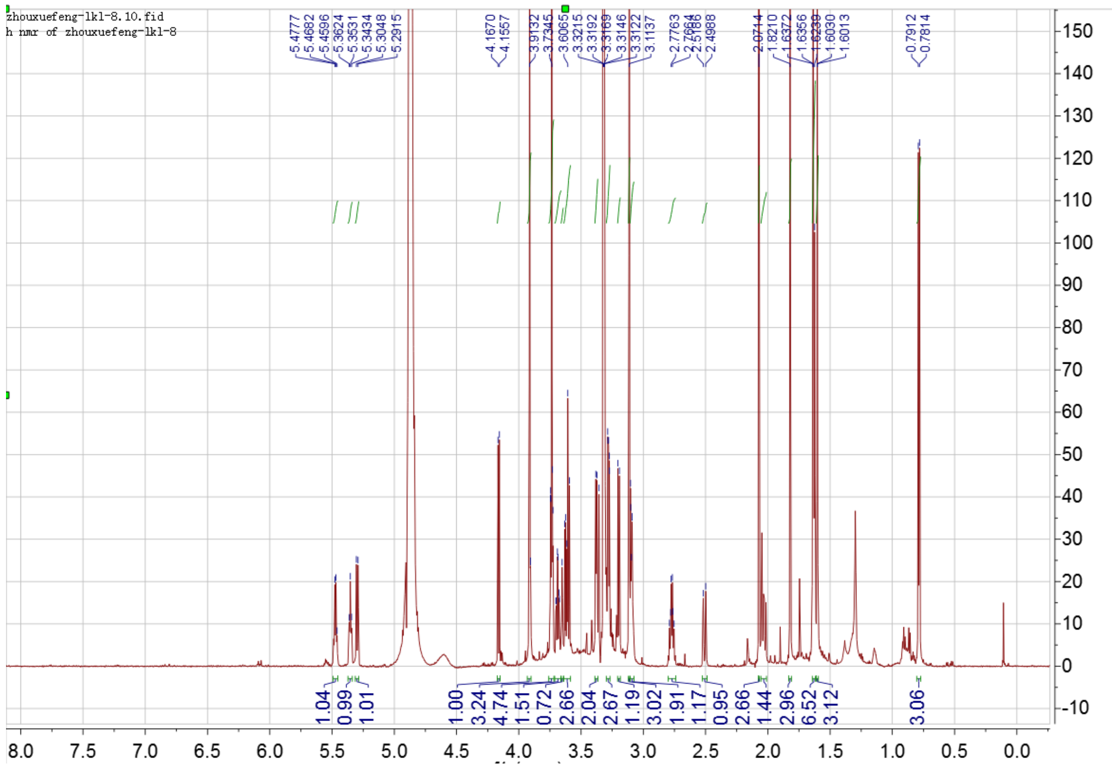


Figure SS-16-3. ^{1}H NMR spectrum of **21** (in CD_3OD, 700 MHz).

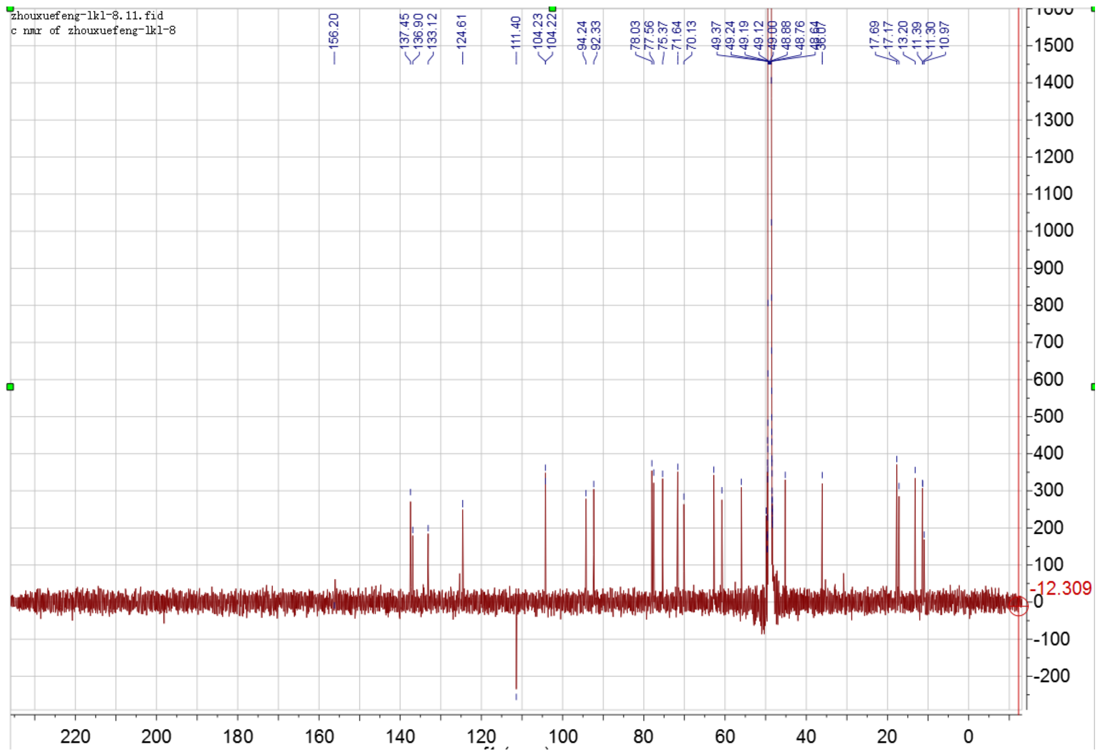


Figure SS-16-4. ^{13}C NMR spectrum of **21** (in CD_3OD, 175 MHz).

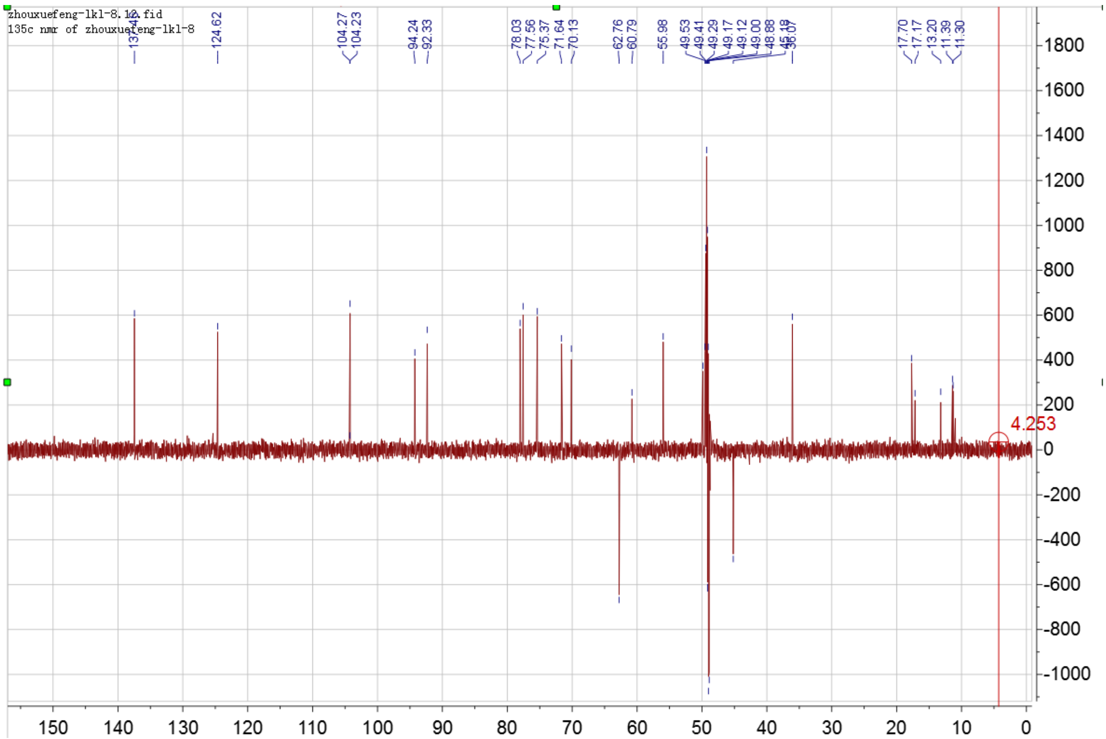


Figure SS-16-5. DEPT spectrum of **21** (in CD_3OD, 175 MHz).

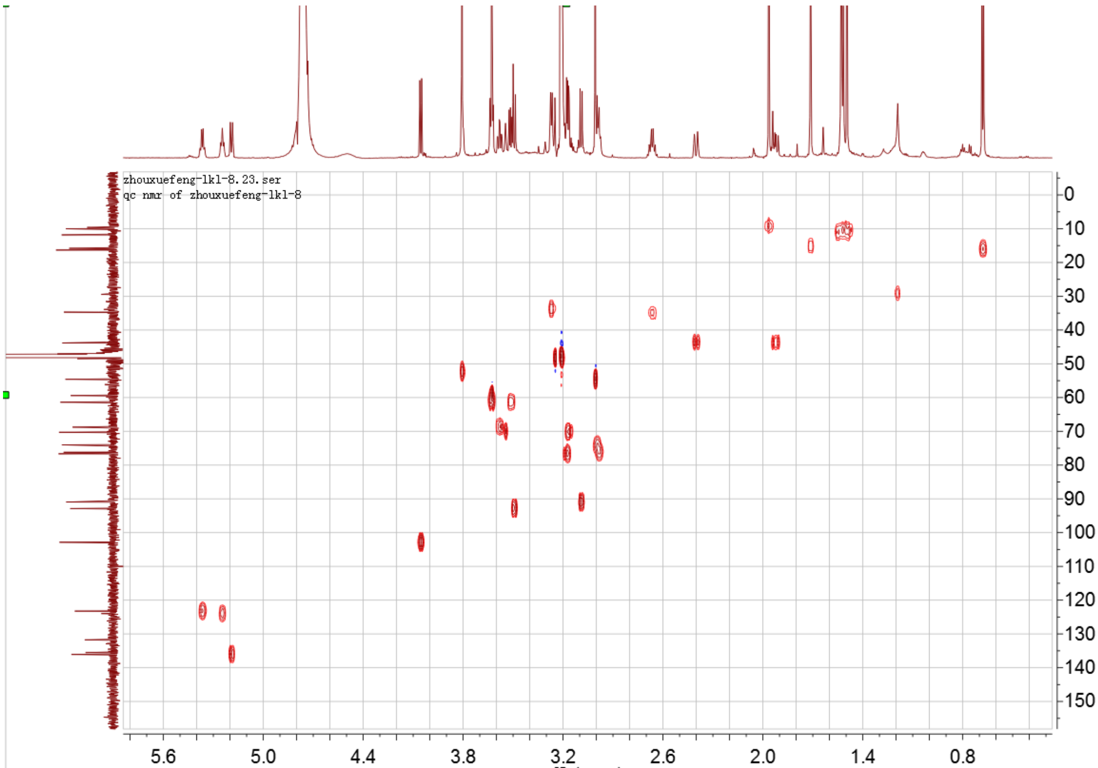


Figure SS-16-6. HSQC spectrum of **21** (in CD_3OD).

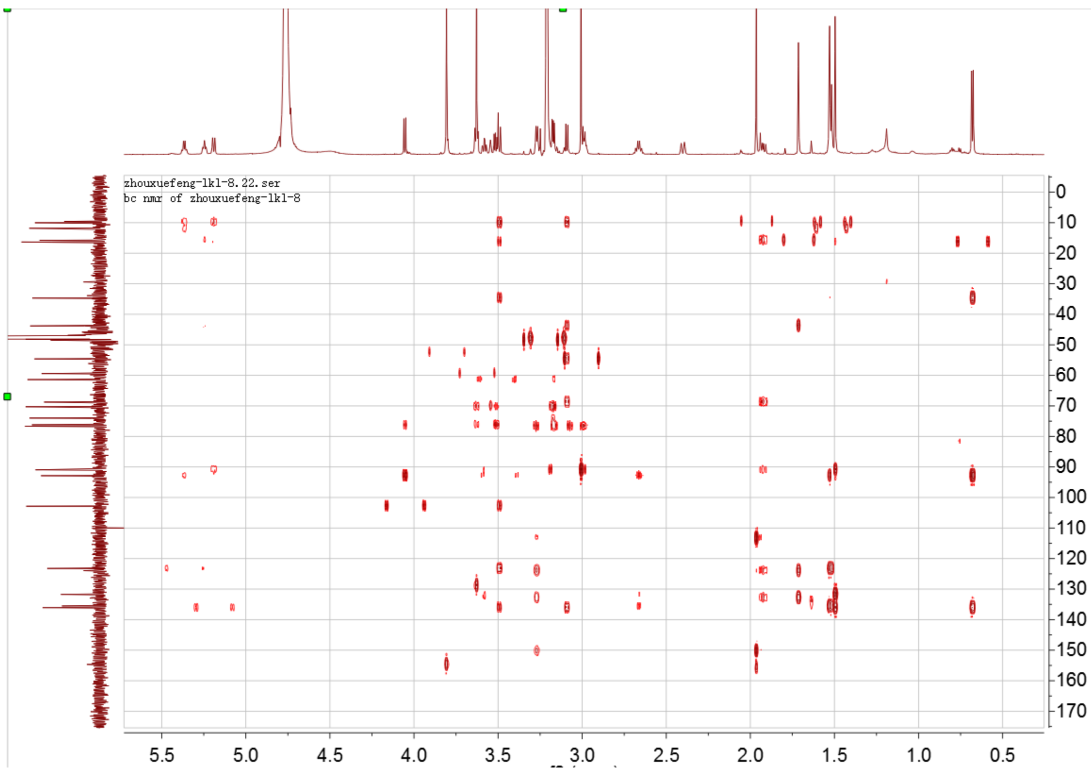


Figure SS-16-7. HMBC spectrum of **21** (in CD_3OD).

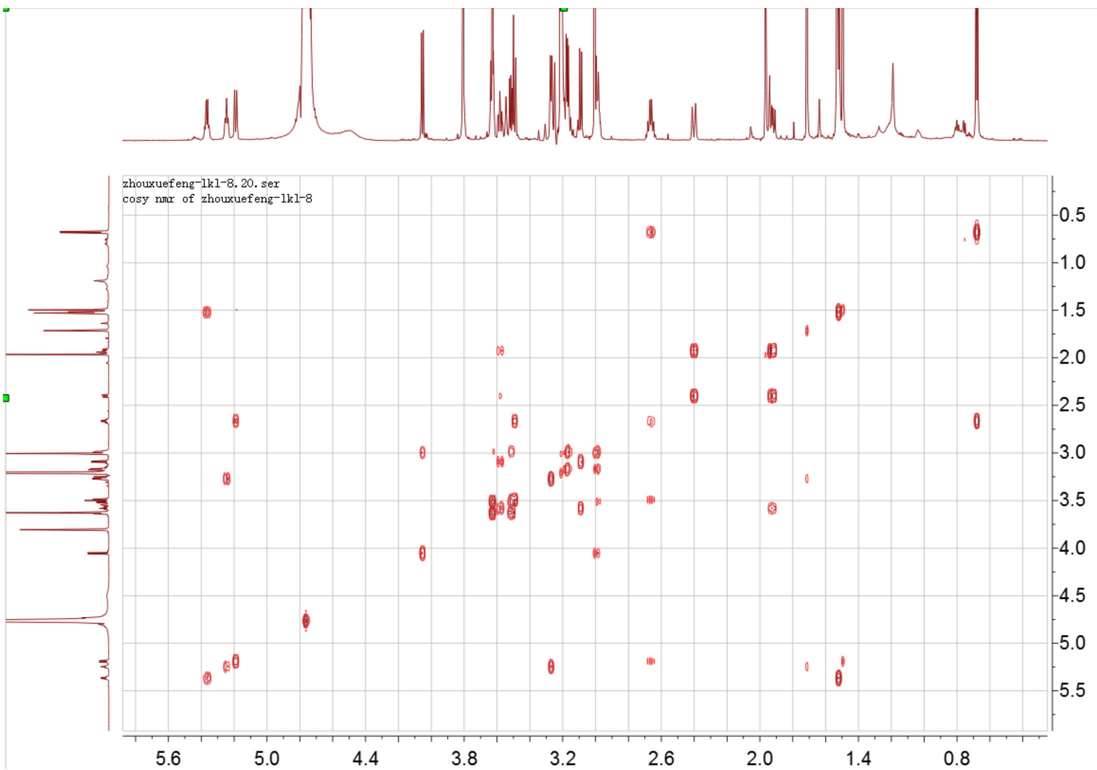


Figure SS-16-8. ^{1}H-^{1}H COSY spectrum of **21** (in CD_3OD).

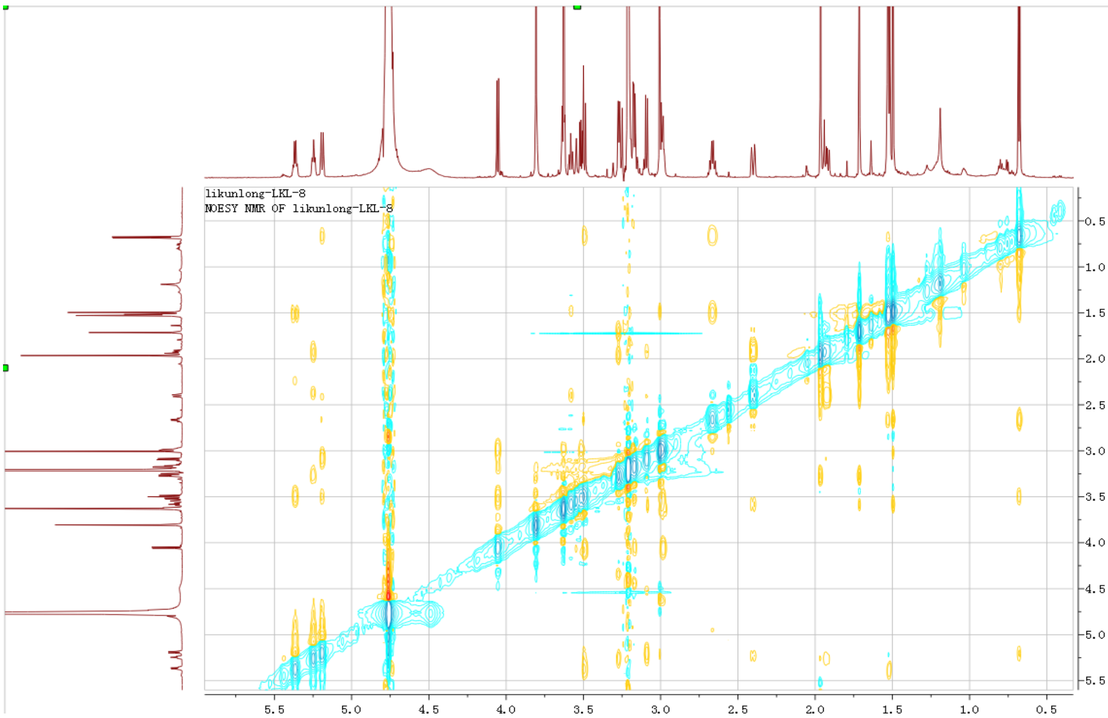


Figure SS-16-9. NOESY spectrum of **21** (in CD_3OD).

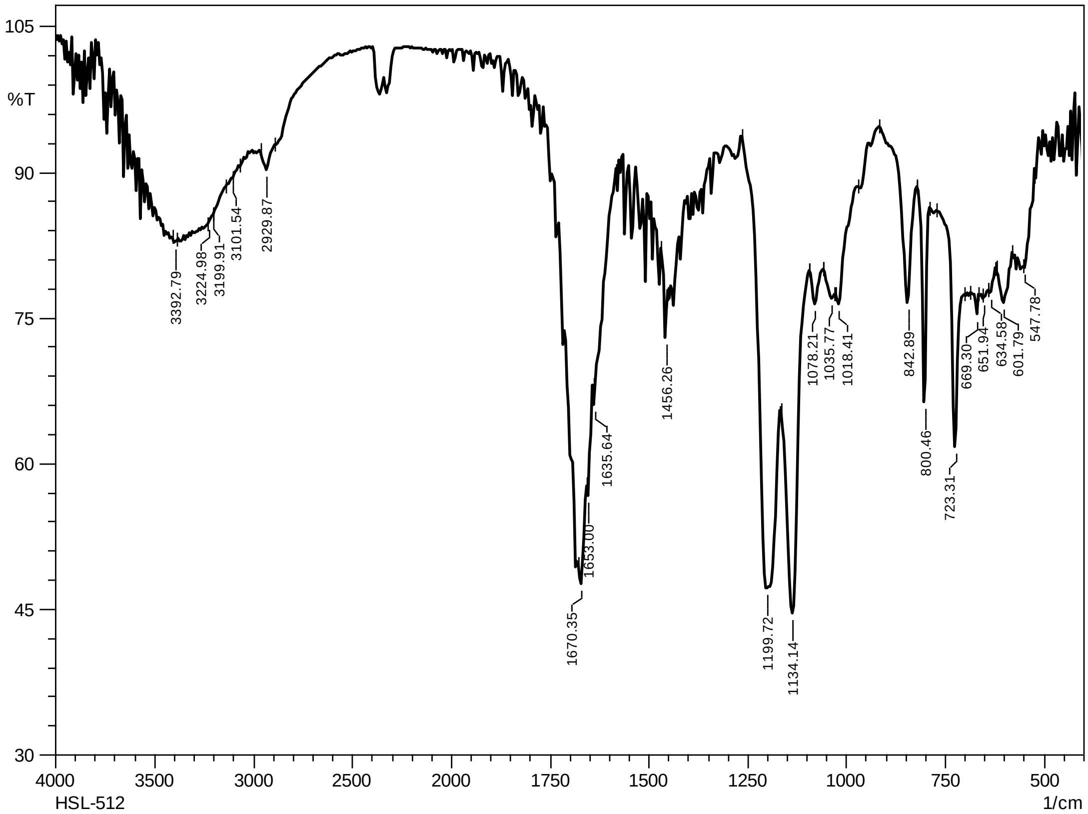
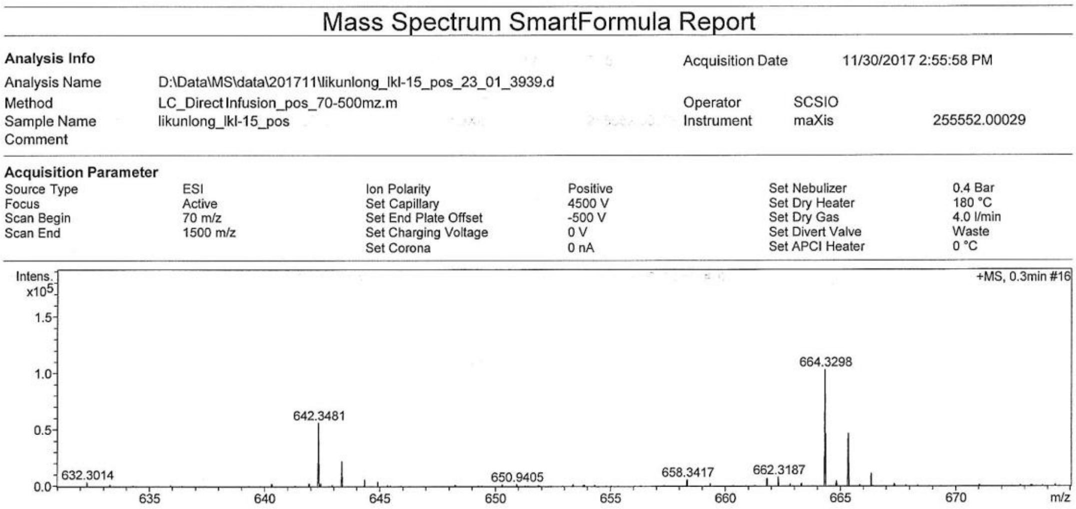


Figure SS-17-1. IR spectrum of **22**.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf	N-Rule
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664.329752	1	C32H51NNaO12	100.00	664.330347	-0.9	-0.6	46.6	7.5	even	ok

Figure SS-17-2. HRESIMS (+) spectrum of **22**.

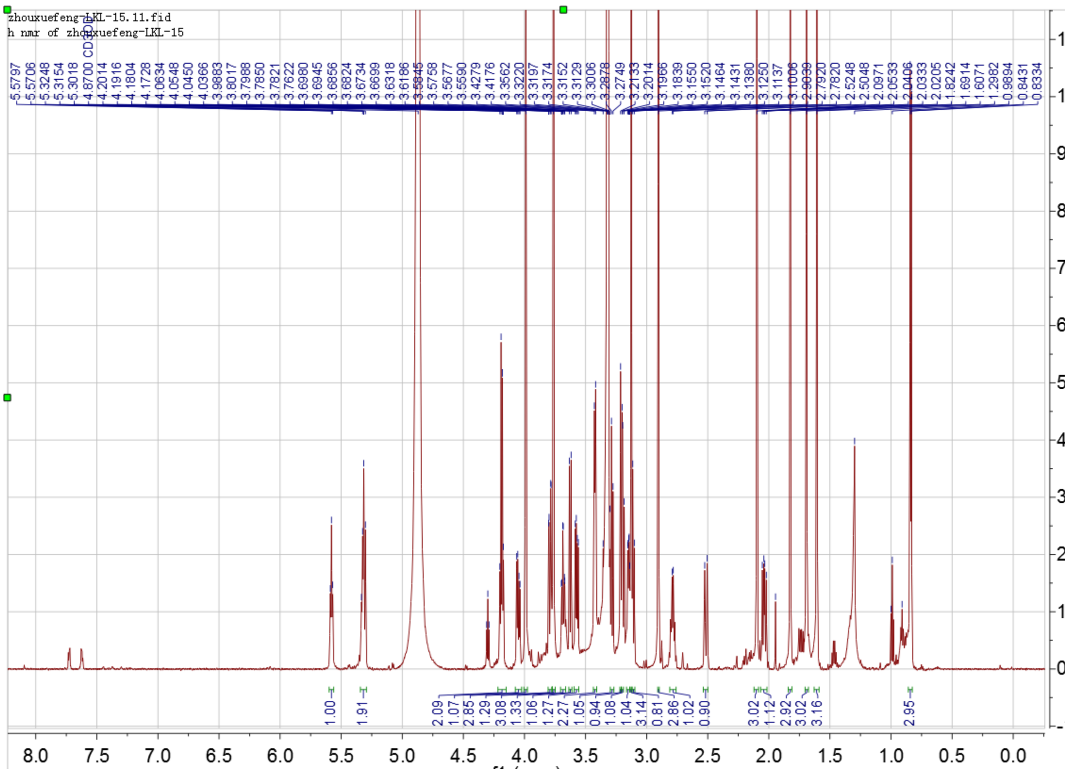

Figure SS-17-3. ^{1}H NMR spectrum of **22** (in CD_3OD, 700 MHz).

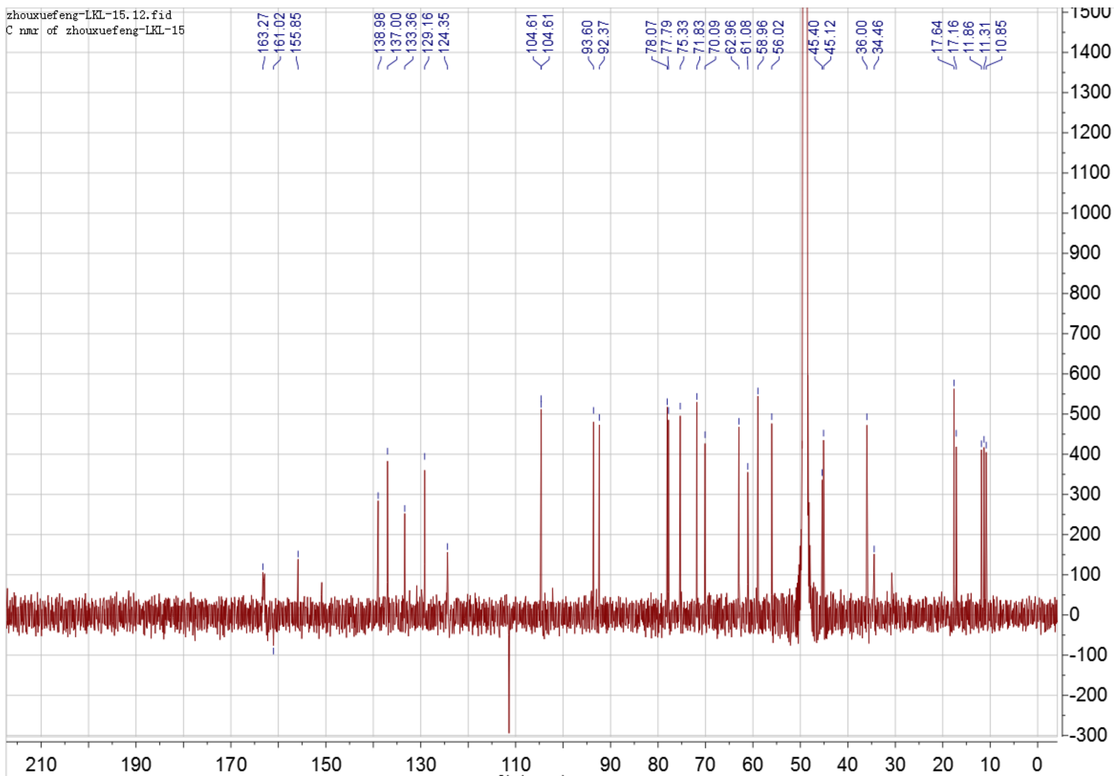

Figure SS-17-4. ^{13}C NMR spectrum of **22** (in CD_3OD, 175 MHz).

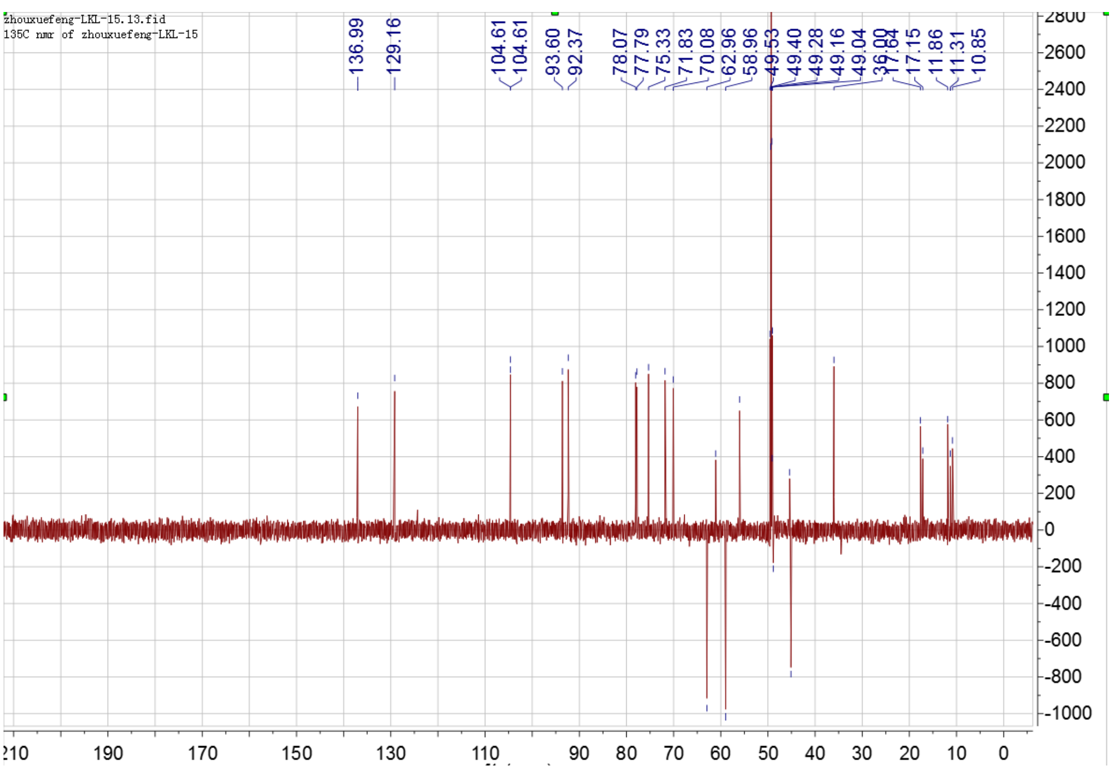

Figure SS-17-5. DEPT spectrum of **22** (in CD_3OD, 175 MHz).

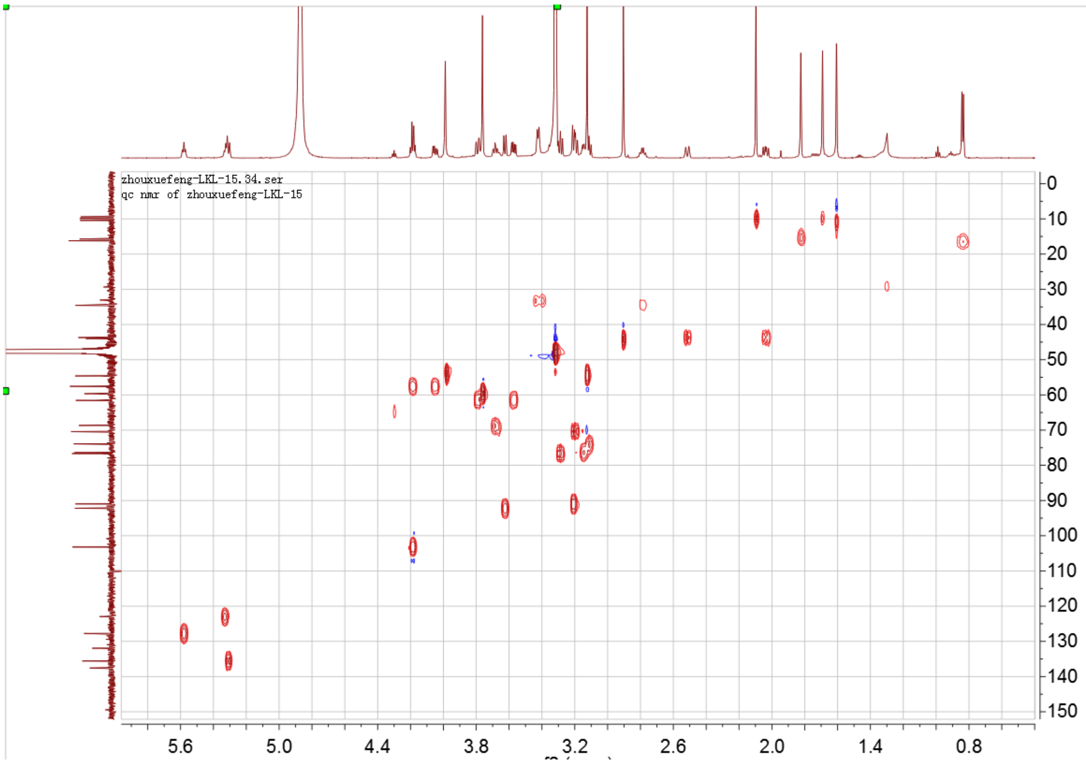

Figure SS-17-6. HSQC spectrum of **22** (in CD_3OD).

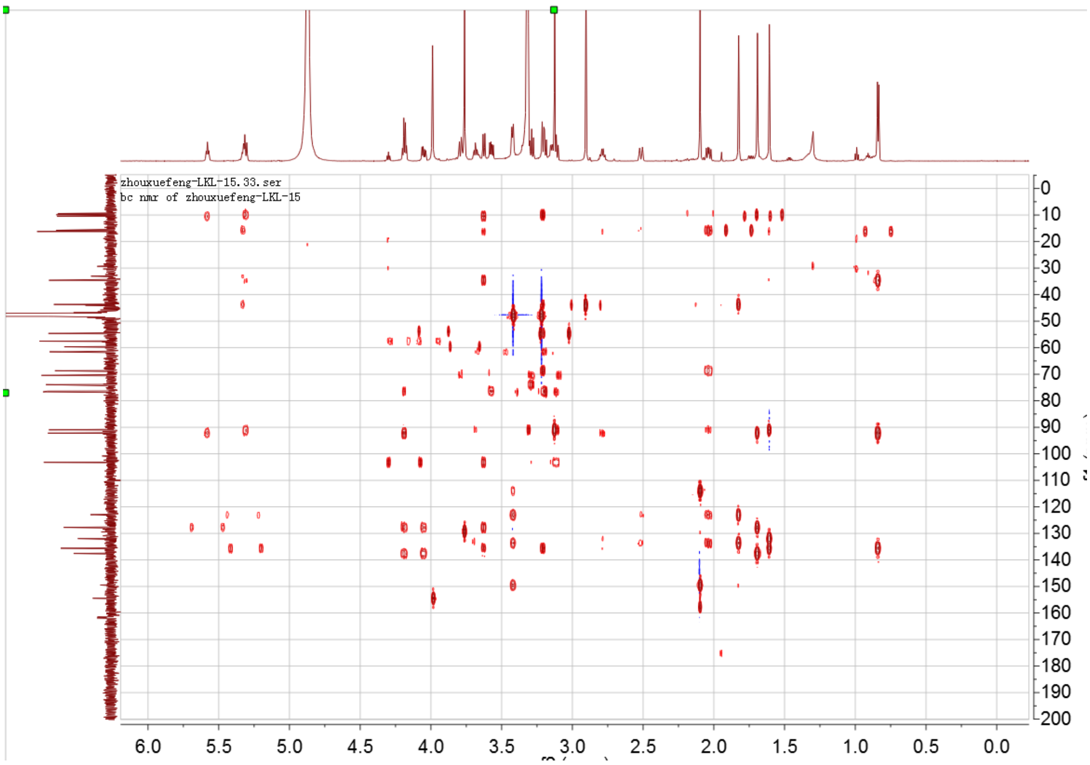

Figure SS-17-7. HMBC spectrum of **22** (in CD_3OD).

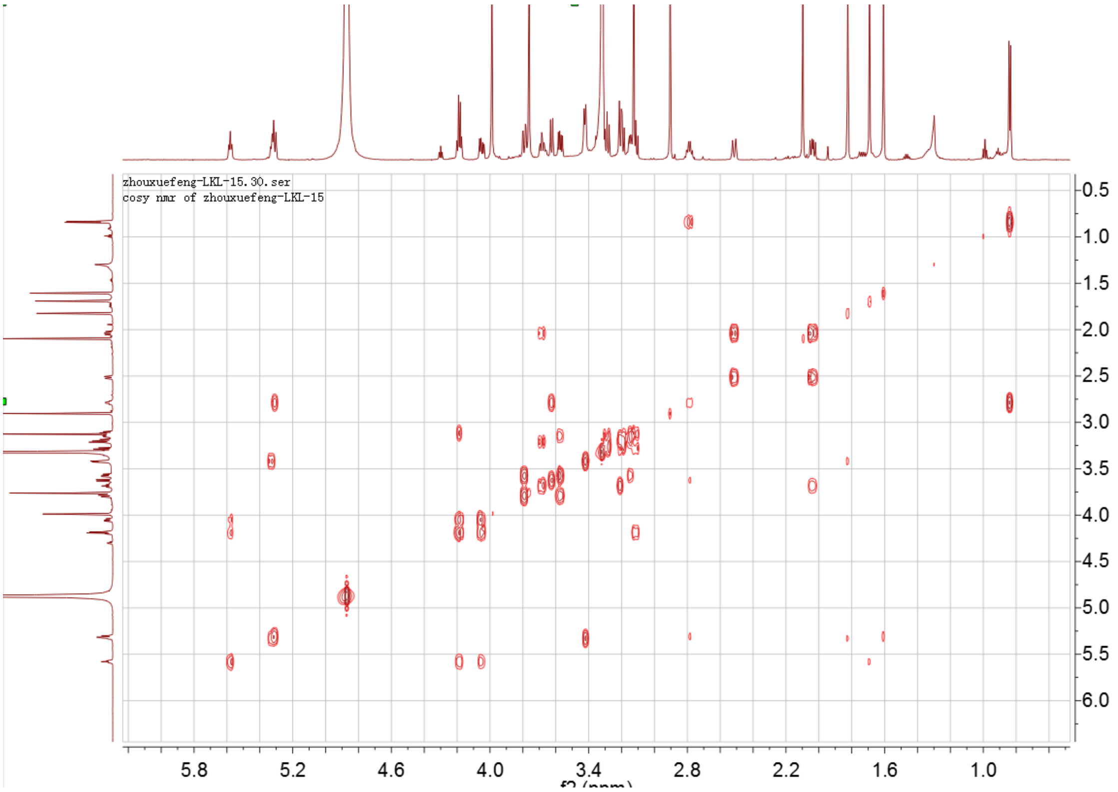

Figure SS-17-8. ^{1}H-^{1}H COSY spectrum of **22** (in CD_3OD).

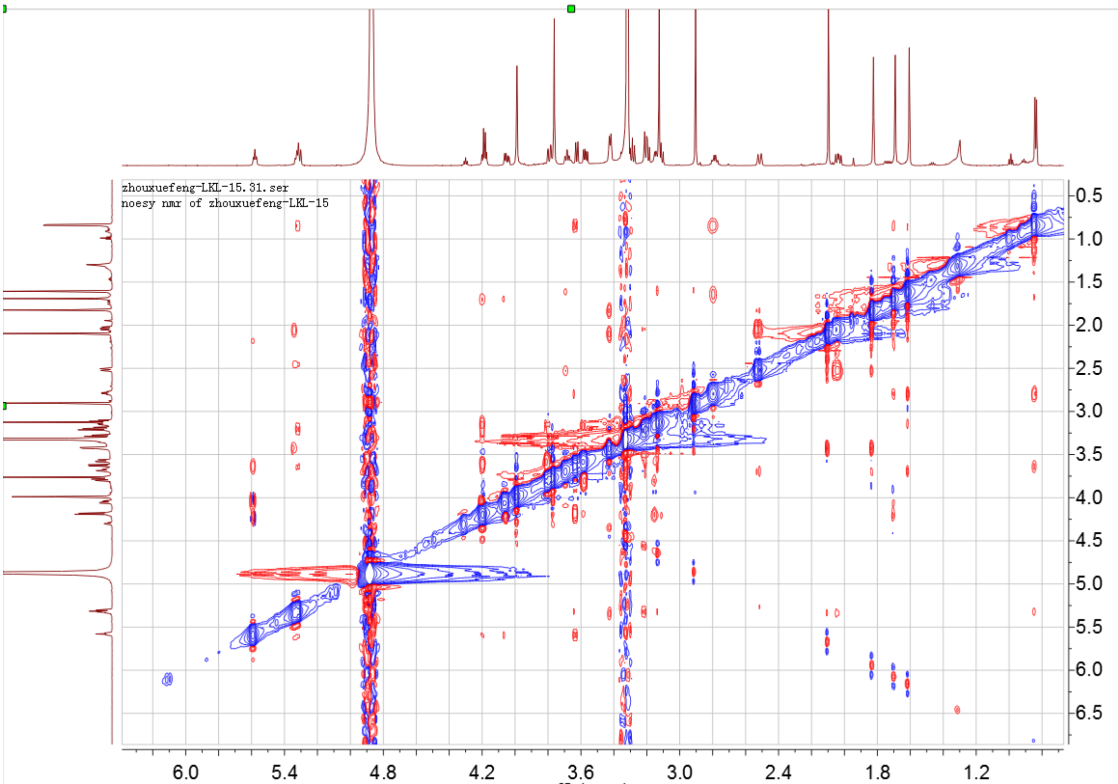

Figure SS-17-9. NOESY spectrum of **22** (in CD_3OD).

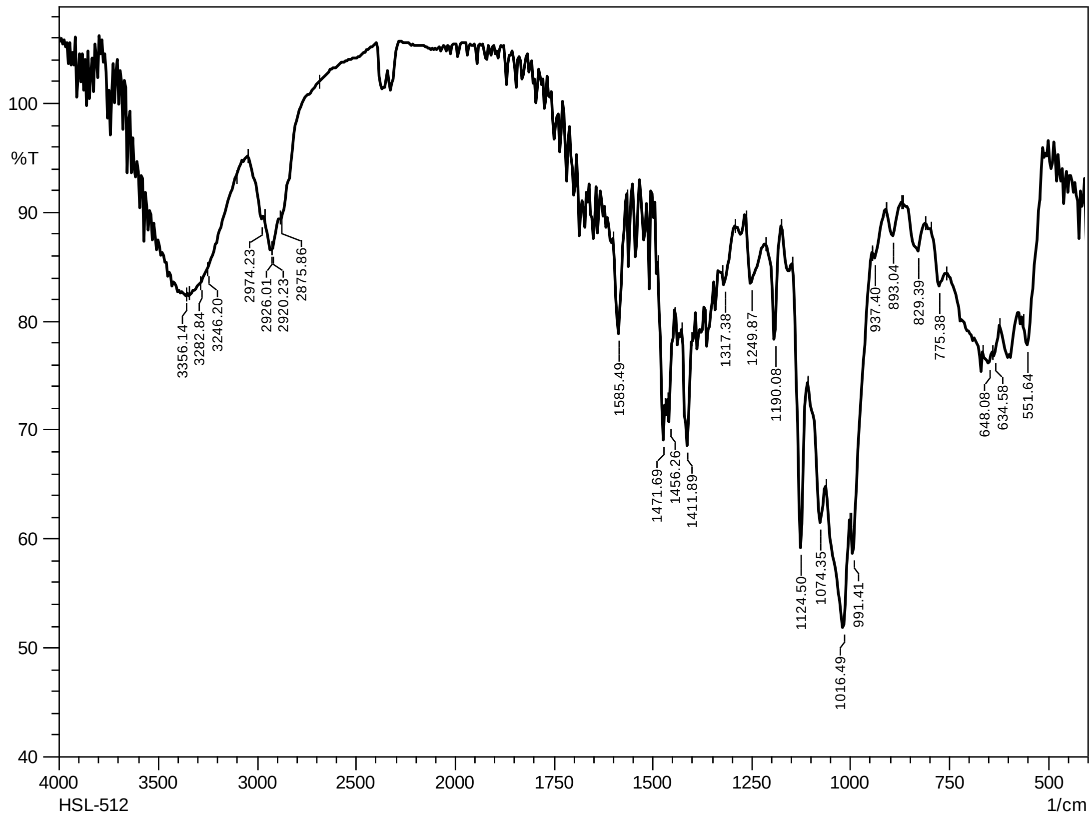

Figure SS-18-1. IR spectrum of **23**.

Mass Spectrum SmartFormula Report

Analysis Info			
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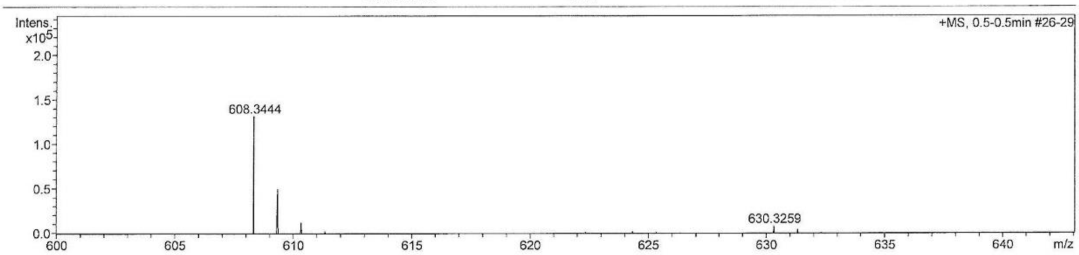
Method	LC_DirectInfusion_pos_100-1000mz.m	Operator	SCSIO
Sample Name	zhouxuefeng_LKL-12_pos	Instrument	maXis 255552.00029
Comment			

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf	N-Rule
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630.325859	1	C32H49NNaO10	100.00	630.324867	1.6	1.0	6.7	8.5	even	ok
1237.663688	1	C64H98N2NaO20	100.00	1237.660514	-2.6	-3.2	18.0	16.5	even	ok

zhouxuefeng_LKL-12_pos_51_01_3811.d
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Figure SS-18-2. HRESIMS (+) spectrum of **23**.

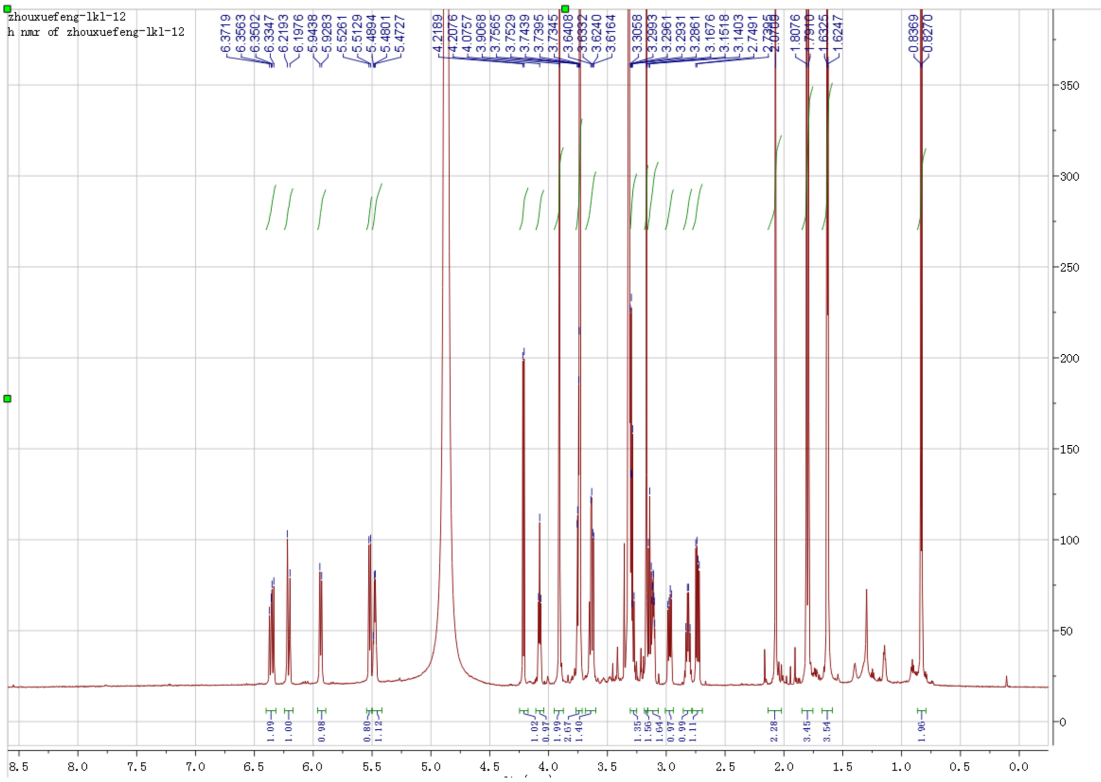


Figure SS-18-3. ^{1}H NMR spectrum of **23** (in CD_3OD, 700 MHz).

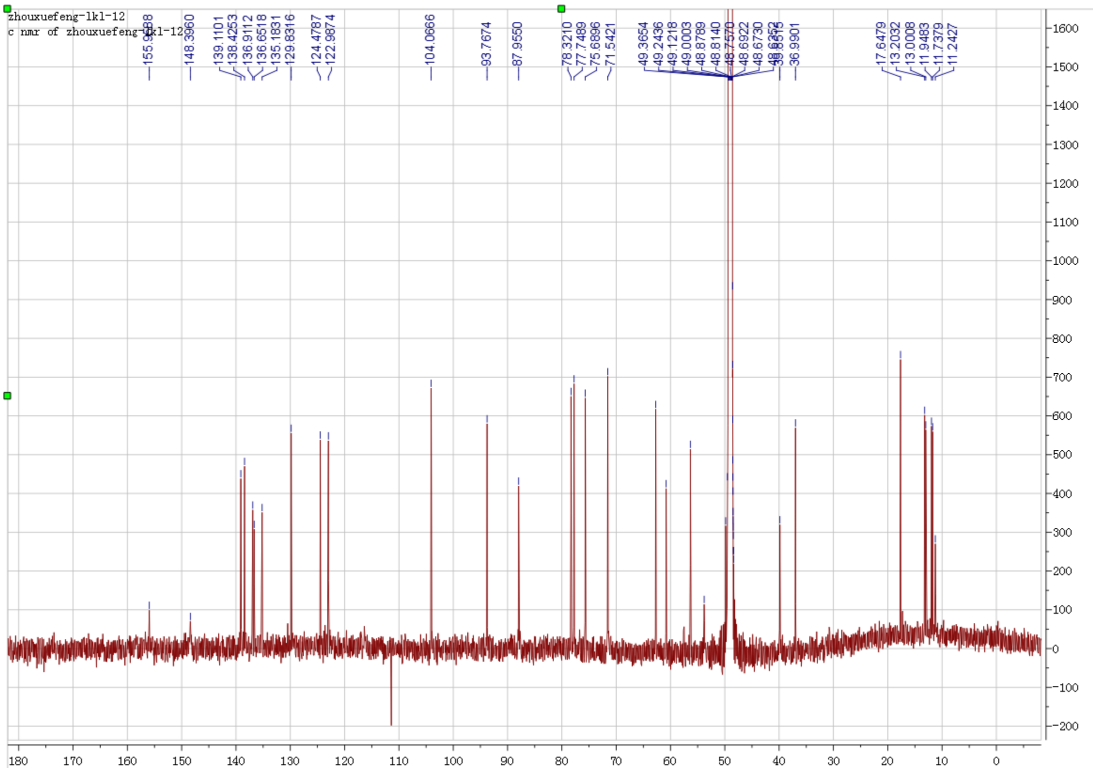


Figure SS-18-4. ^{13}C NMR spectrum of **23** (in CD_3OD, 175 MHz).

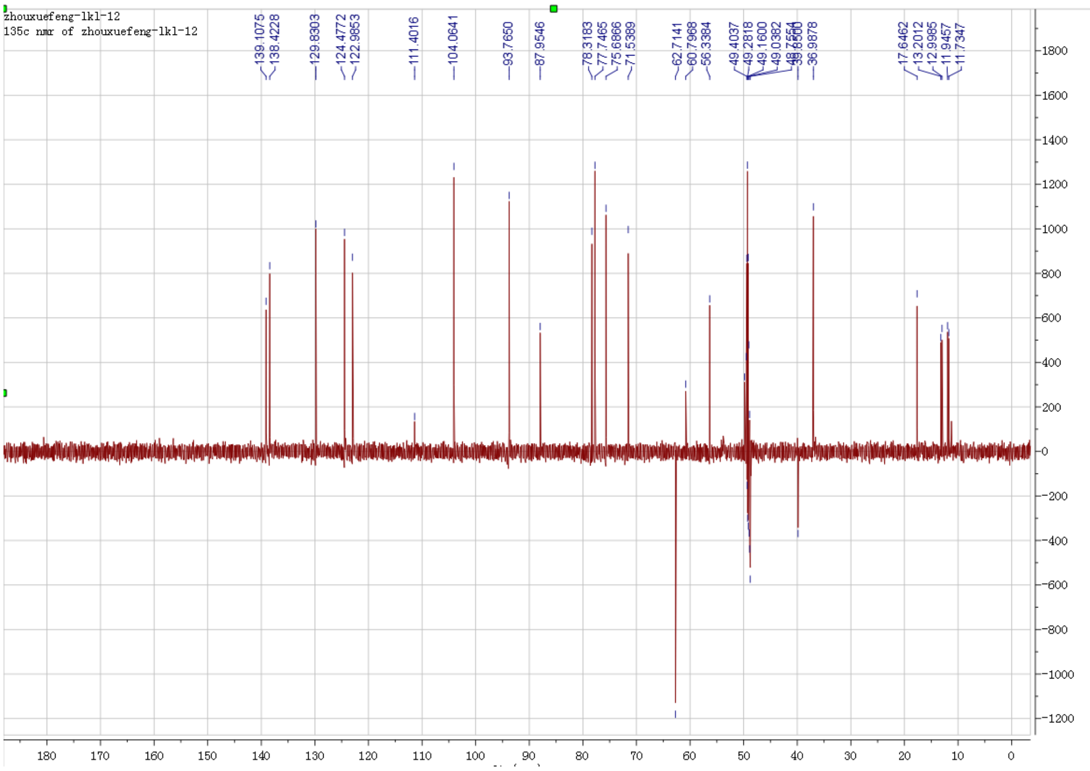


Figure SS-18-5. DEPT spectrum of **23** (in CD_3OD, 175 MHz).

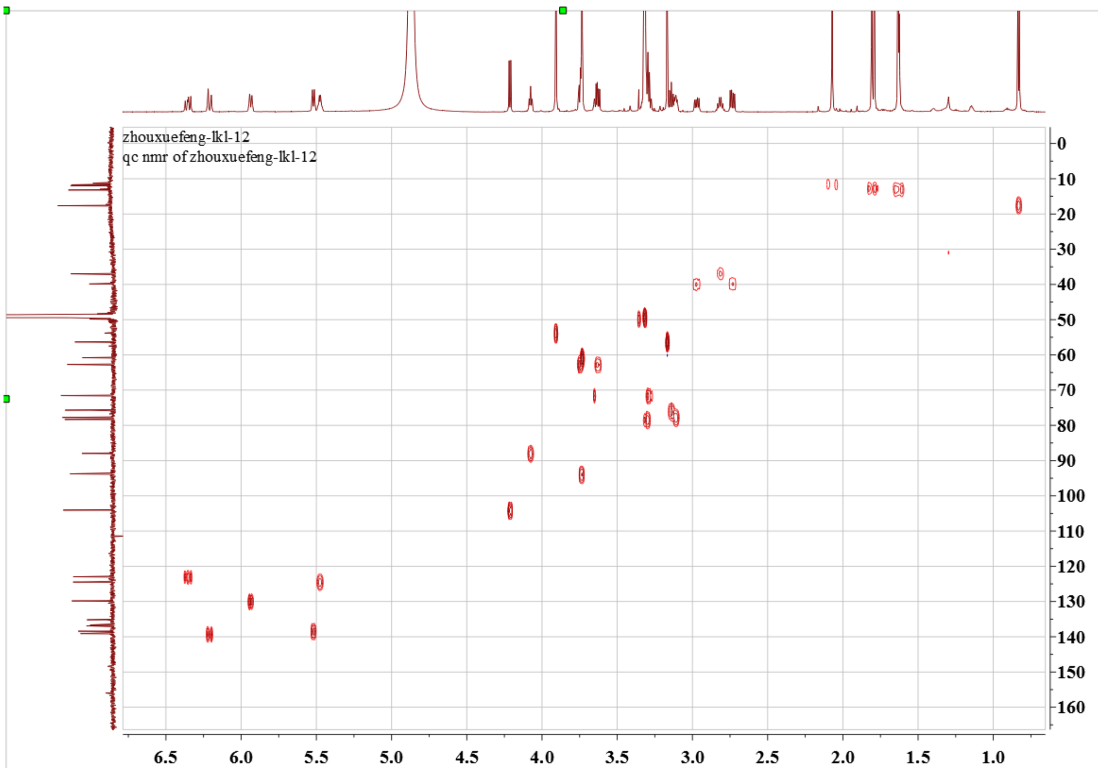


Figure SS-18-6. HSQC spectrum of **23** (in CD_3OD).

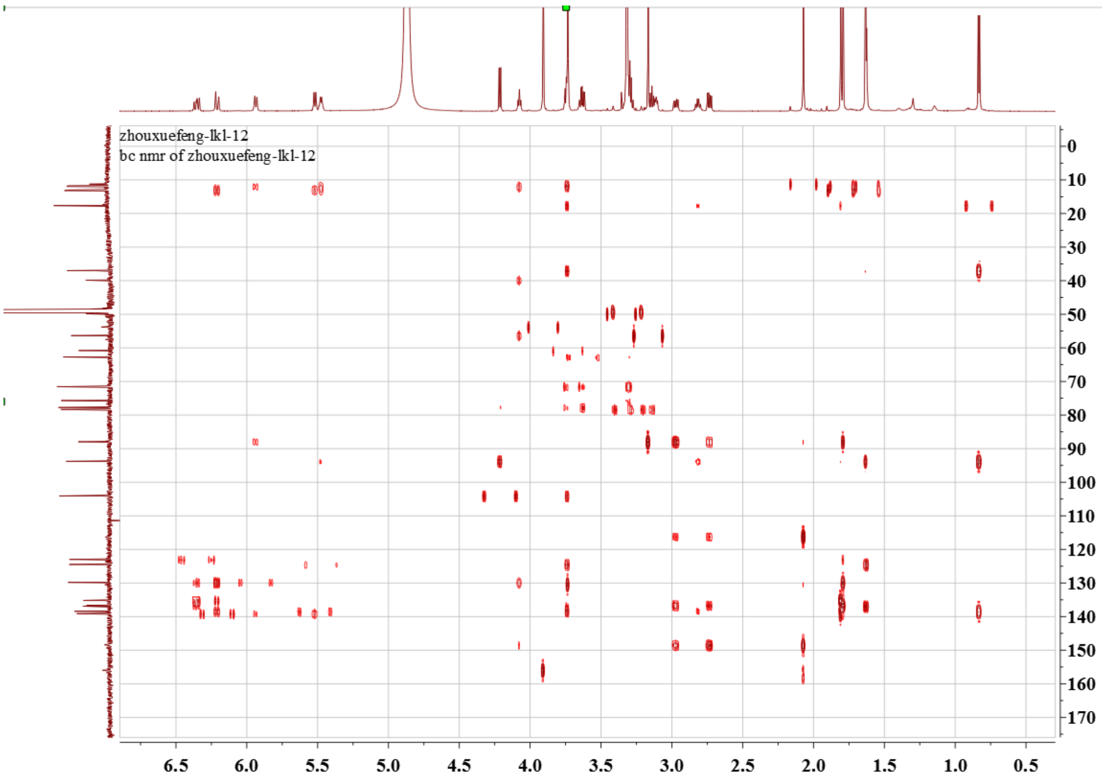


Figure SS-18-7. HMBC spectrum of **23** (in CD_3OD).

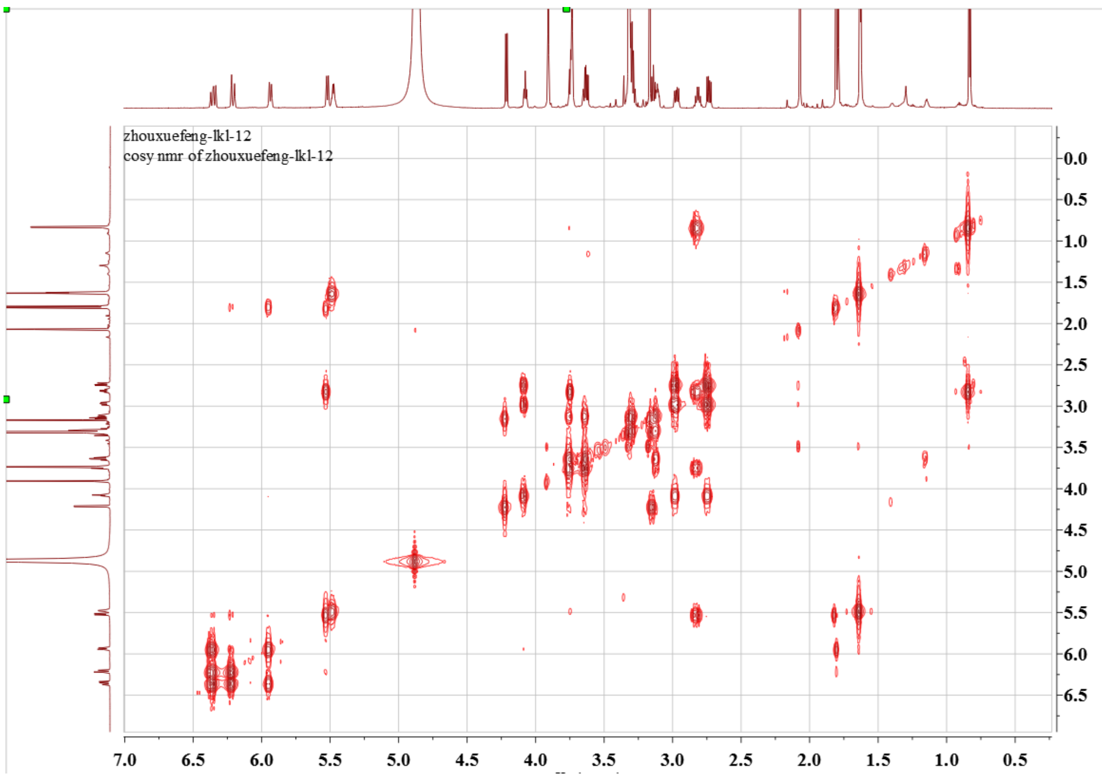


Figure SS-18-8. ^1H-^1H COSY spectrum of **23** (in CD_3OD).

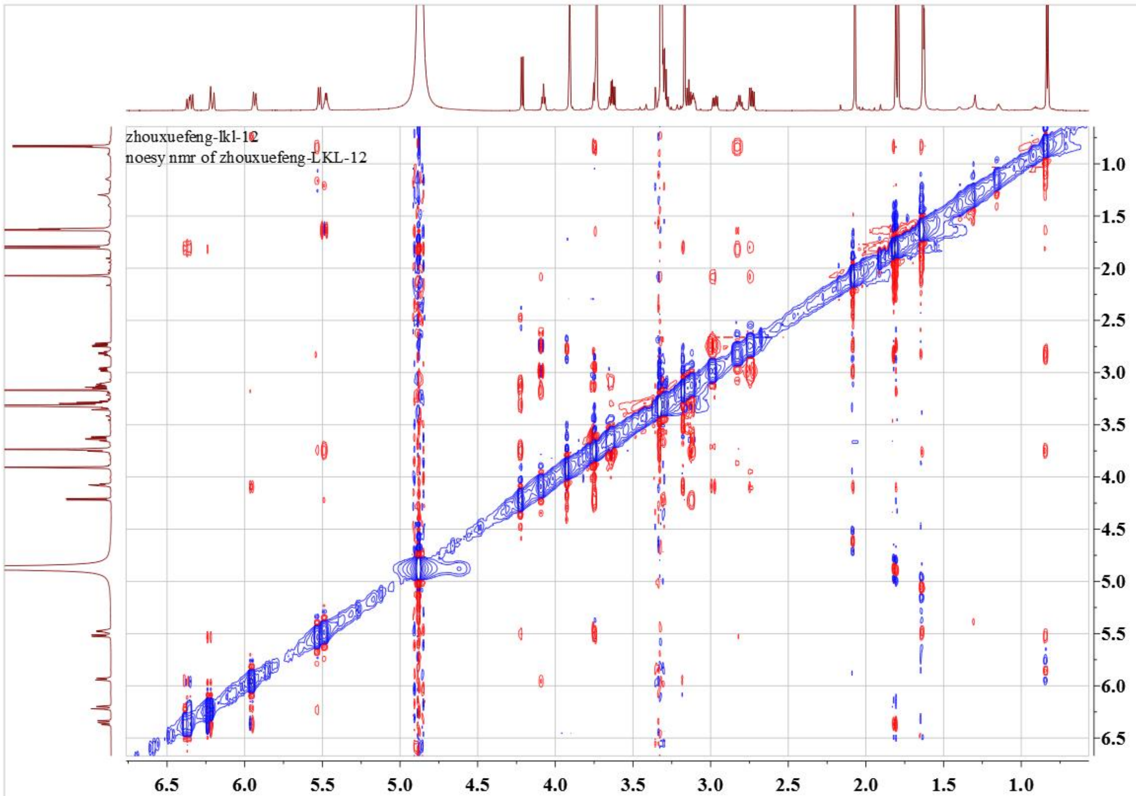


Figure SS-18-9. NOESY spectrum of **23** (in CD_3OD).

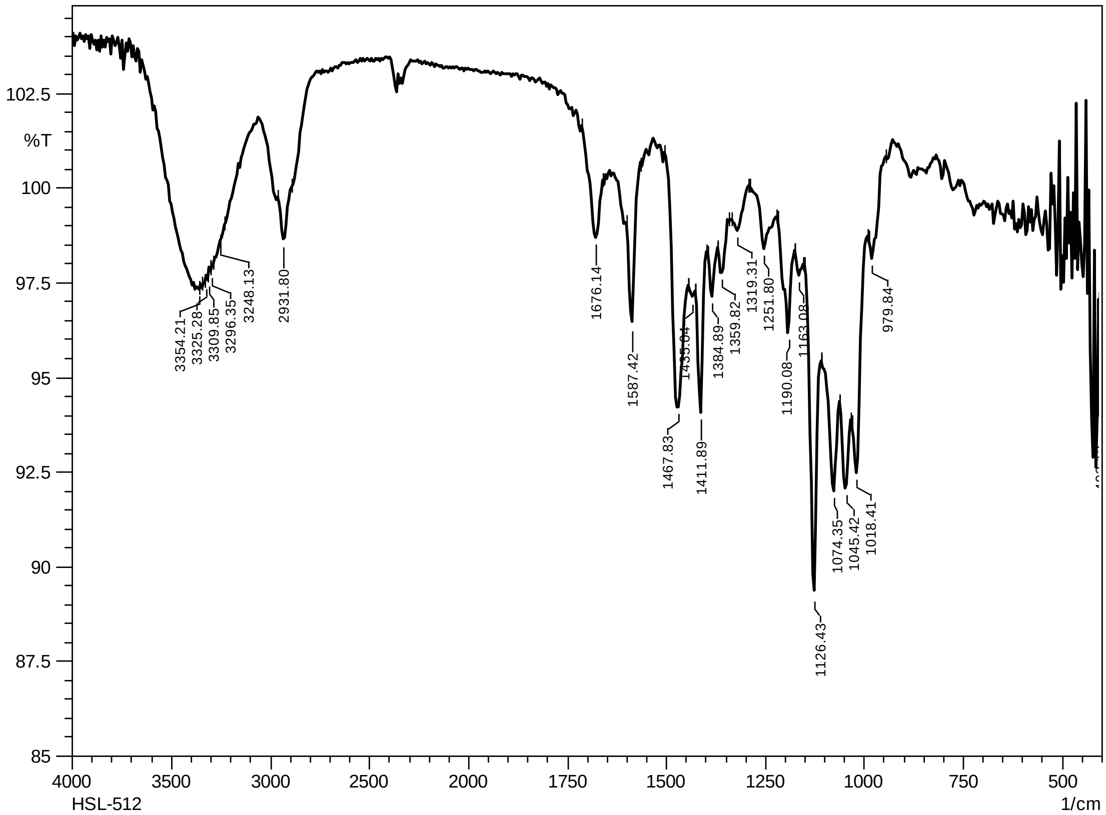
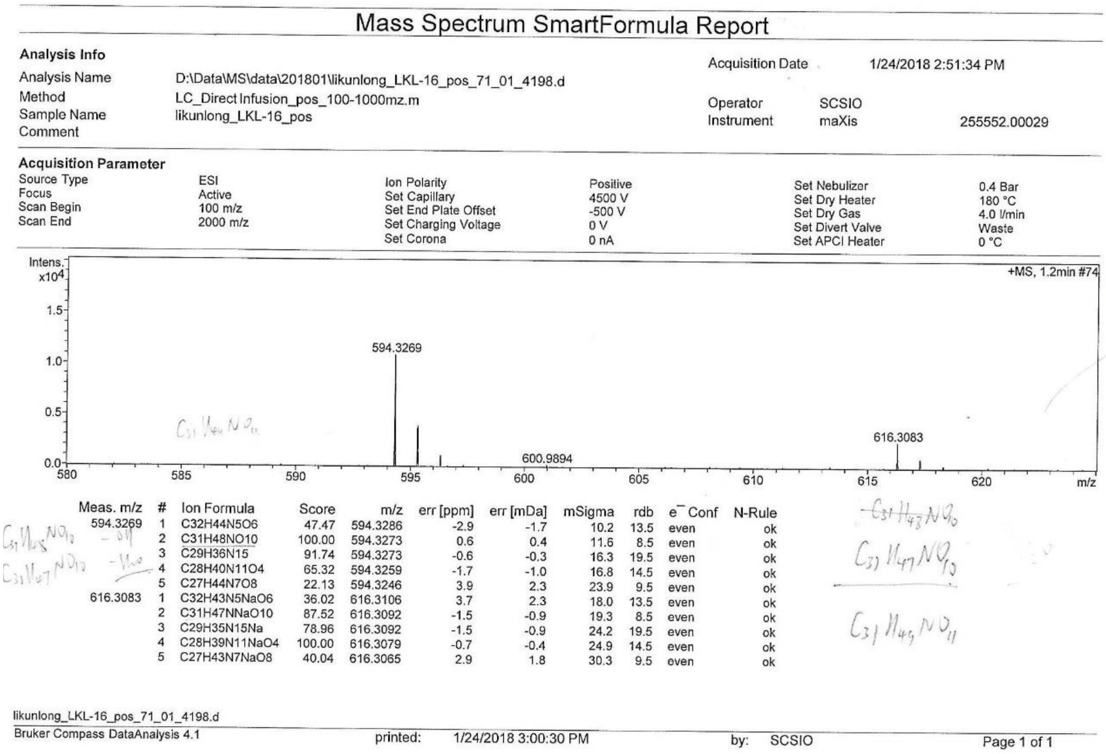


Figure SS-19-1. IR spectrum of **24**.



Mass Spectrum SmartFormula Report

Analysis Info			
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Method	LC_Direct Infusion_pos_100-1000mz.m	Operator	SCSIO
Sample Name	likunlong_LKL-16_pos	Instrument	maXis 255552.00029
Comment			

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf	N-Rule
594.3269	1	C32H44N5O6	47.47	594.3286	-2.9	-1.7	10.2	13.5	even	ok
	2	C31H48NO10	100.00	594.3273	0.6	0.4	11.6	8.5	even	ok
	3	C29H36N15	91.74	594.3273	-0.6	-0.3	16.3	19.5	even	ok
	4	C28H40N11O4	65.32	594.3259	-1.7	-1.0	16.8	14.5	even	ok
	5	C27H44N7O8	22.13	594.3246	3.9	2.3	23.9	9.5	even	ok
616.3083	1	C32H43N5NaO6	36.02	616.3106	3.7	2.3	18.0	13.5	even	ok
	2	C31H47NNaO10	87.52	616.3092	-1.5	-0.9	19.3	8.5	even	ok
	3	C29H35N15Na	78.96	616.3092	-1.5	-0.9	24.2	19.5	even	ok
	4	C28H39N11NaO4	100.00	616.3079	-0.7	-0.4	24.9	14.5	even	ok
	5	C27H43N7NaO8	40.04	616.3065	2.9	1.8	30.3	9.5	even	ok

likunlong_LKL-16_pos_71_01_4198.d
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Figure SS-19-2. HRESIMS (+) spectrum of **24**.

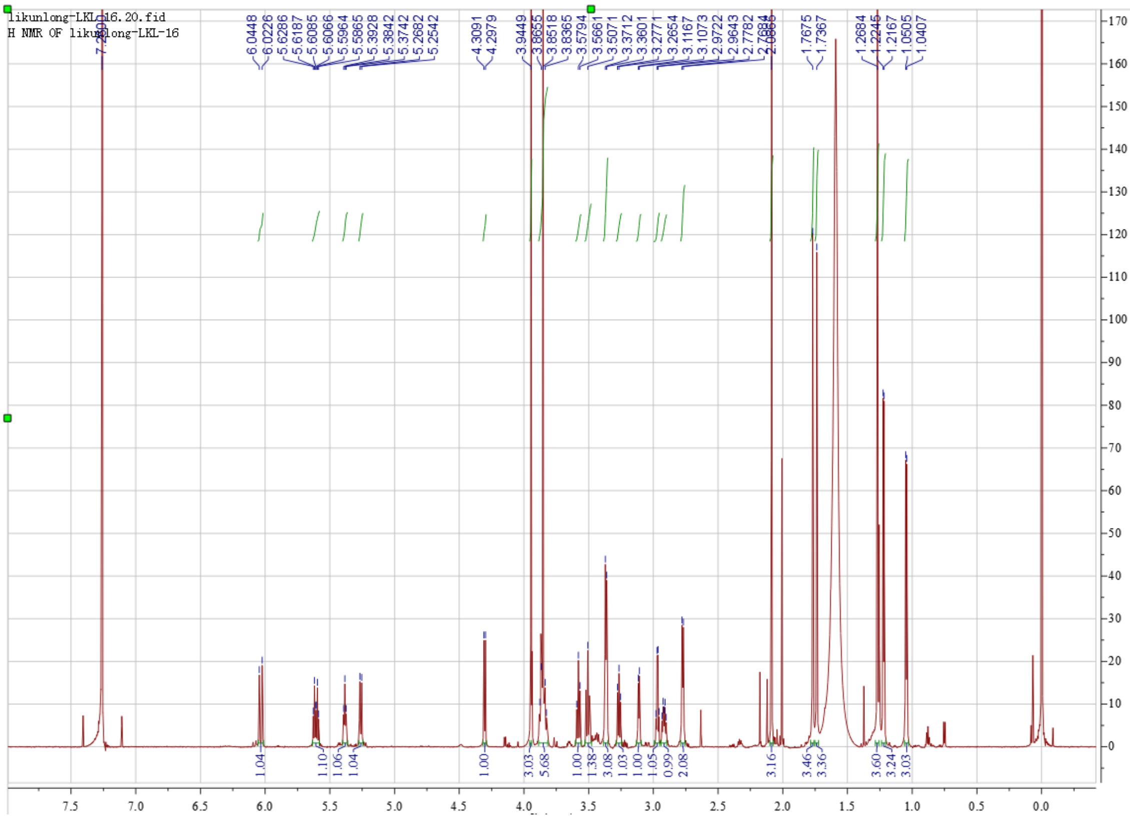

Figure SS-19-3. ^{1}H NMR spectrum of **24** (in $CDCl_3$, 700 MHz).

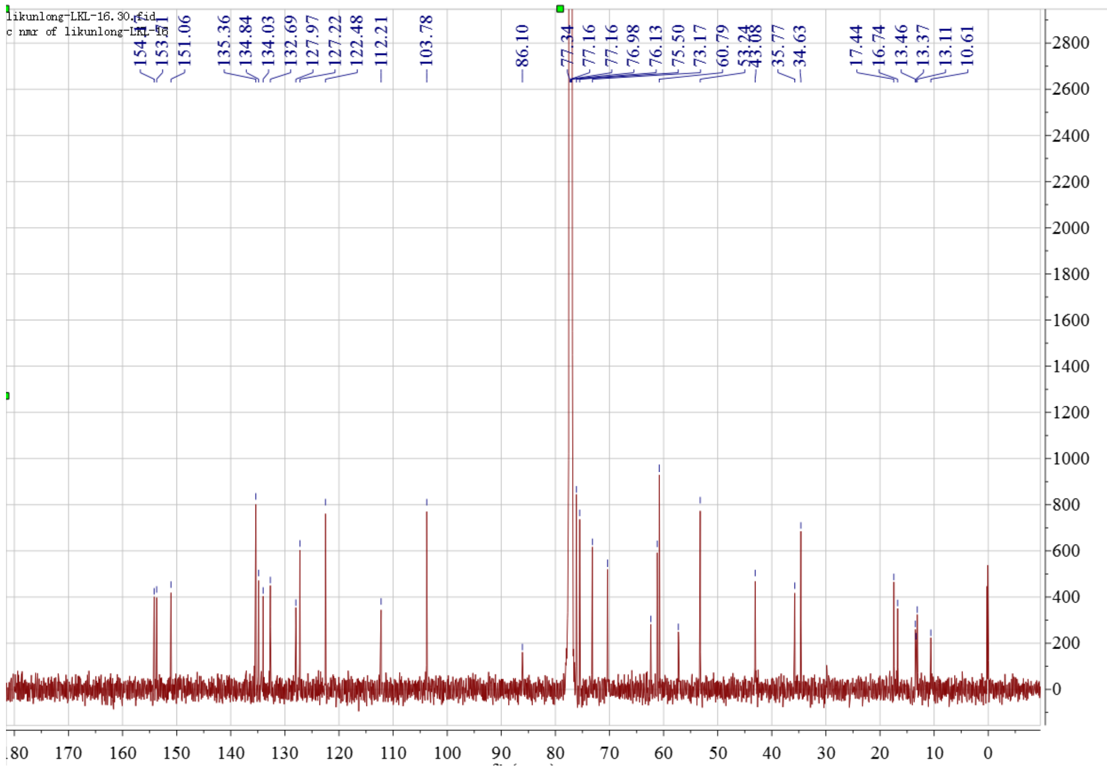

Figure SS-19-4. ^{13}C NMR spectrum of **24** (in $CDCl_3$, 175 MHz).

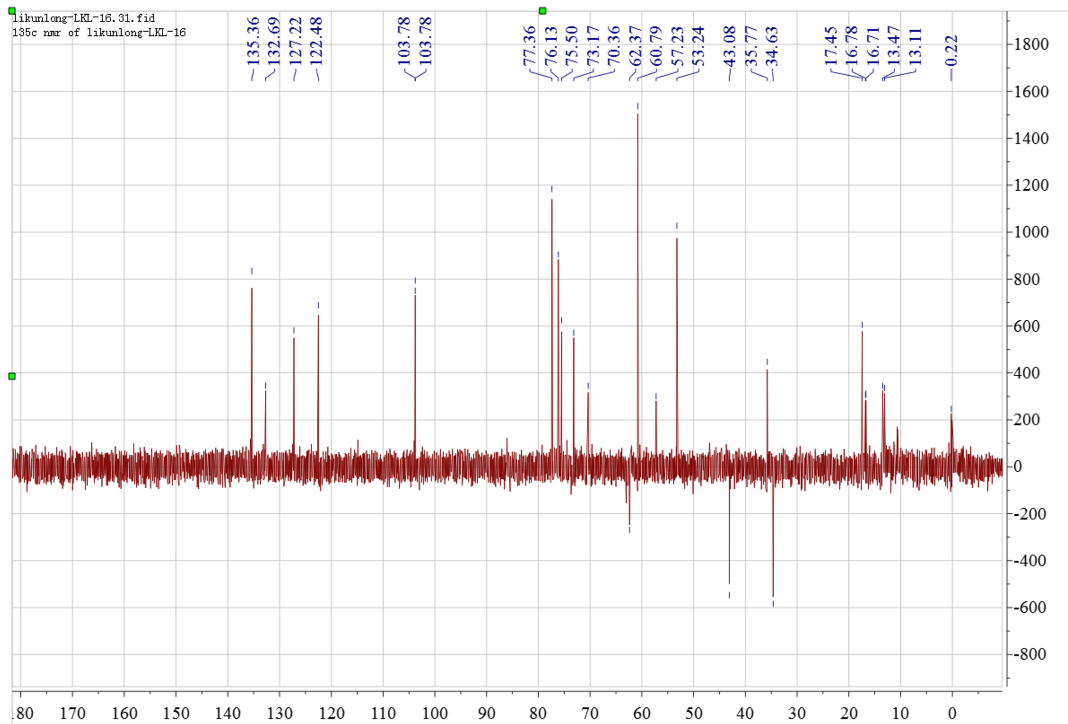

Figure SS-19-5. DEPT spectrum of **24** (in $CDCl_3$, 175 MHz).

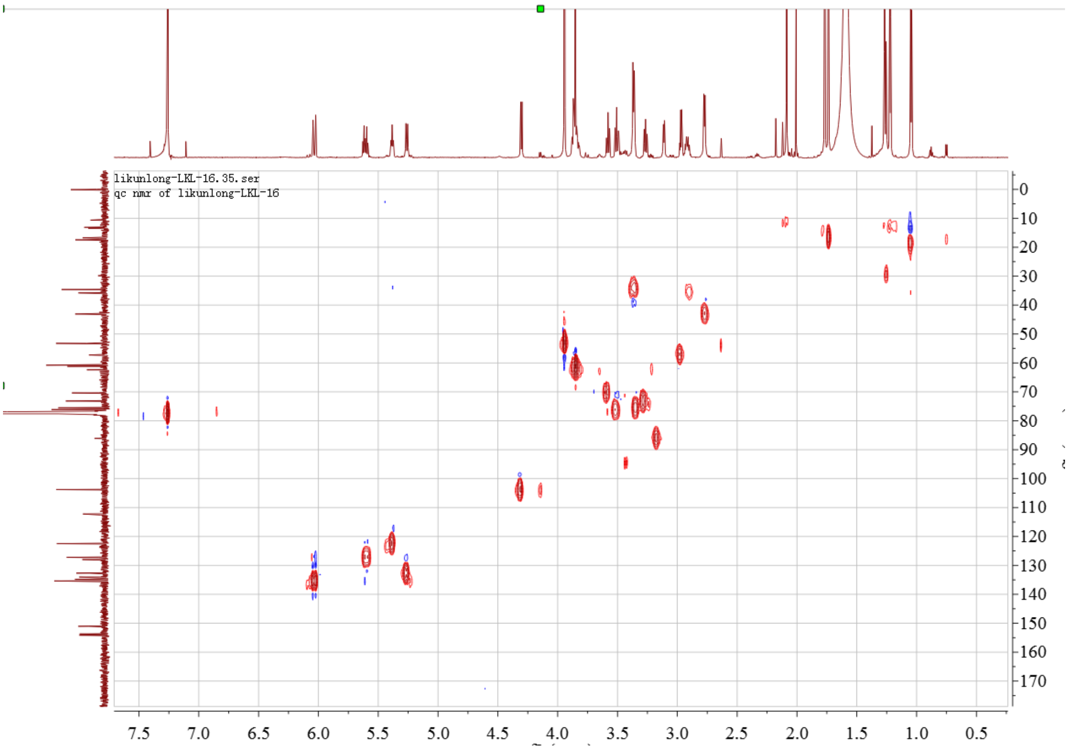

Figure SS-19-6. HSQC spectrum of **24** (in $CDCl_3$).

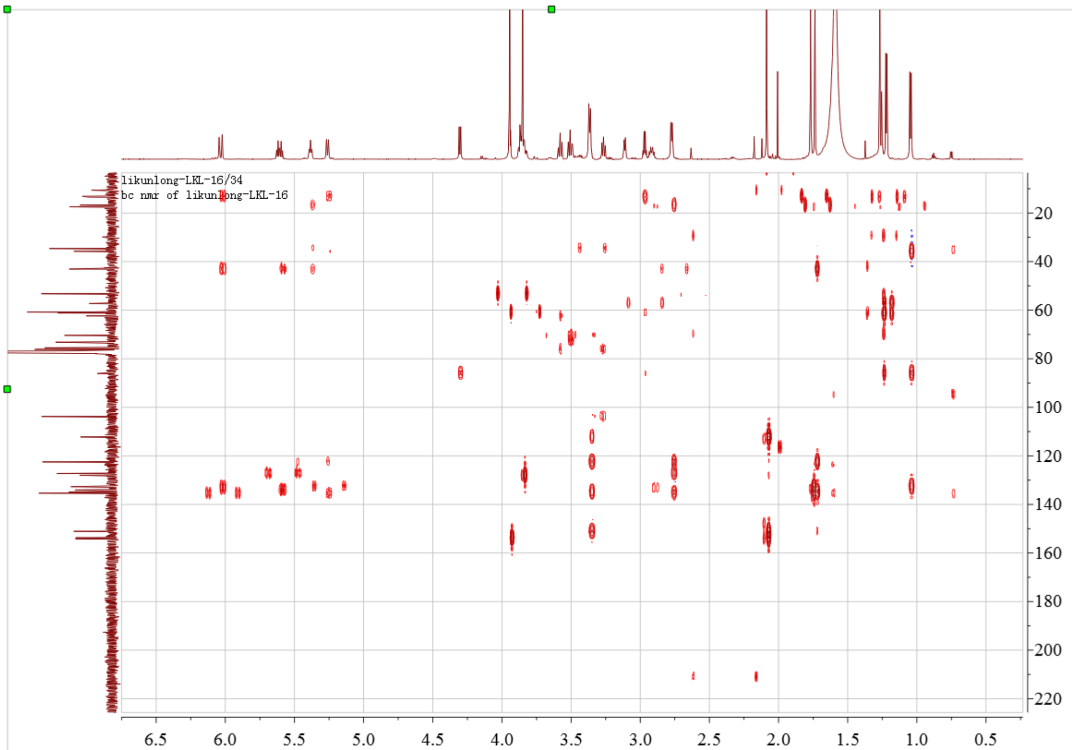

Figure SS-19-7. HMBC spectrum of **24** (in $CDCl_3$).

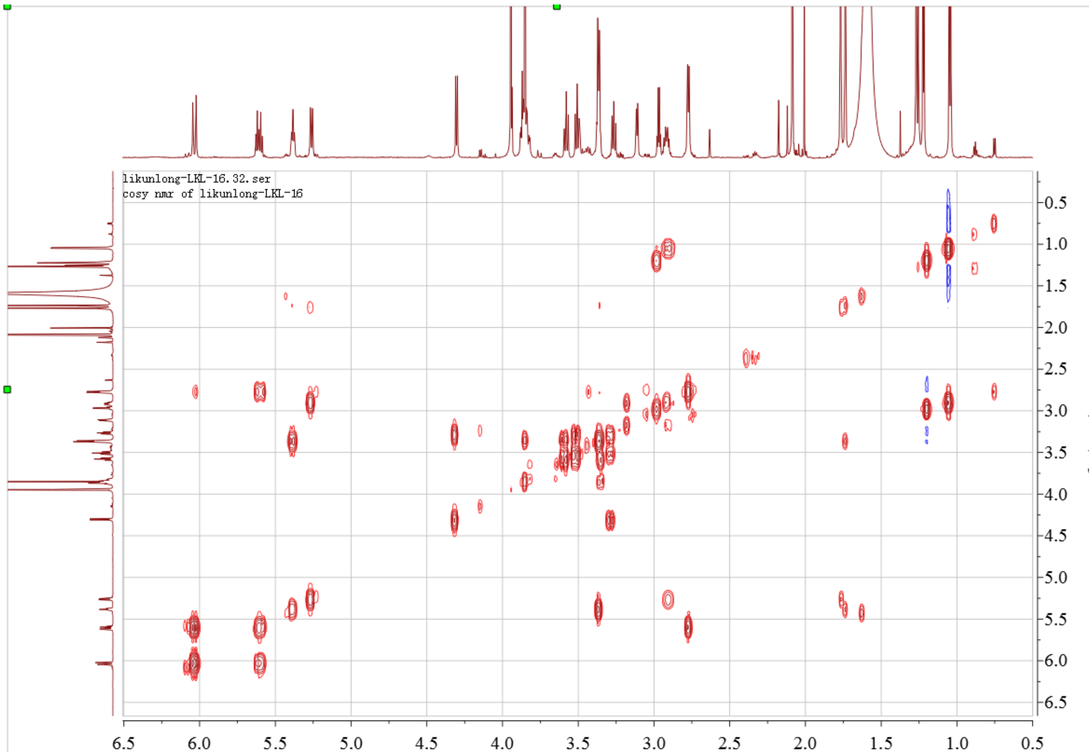

Figure SS-19-8. ^{1}H-^{1}H COSY spectrum of **24** (in $CDCl_3$).

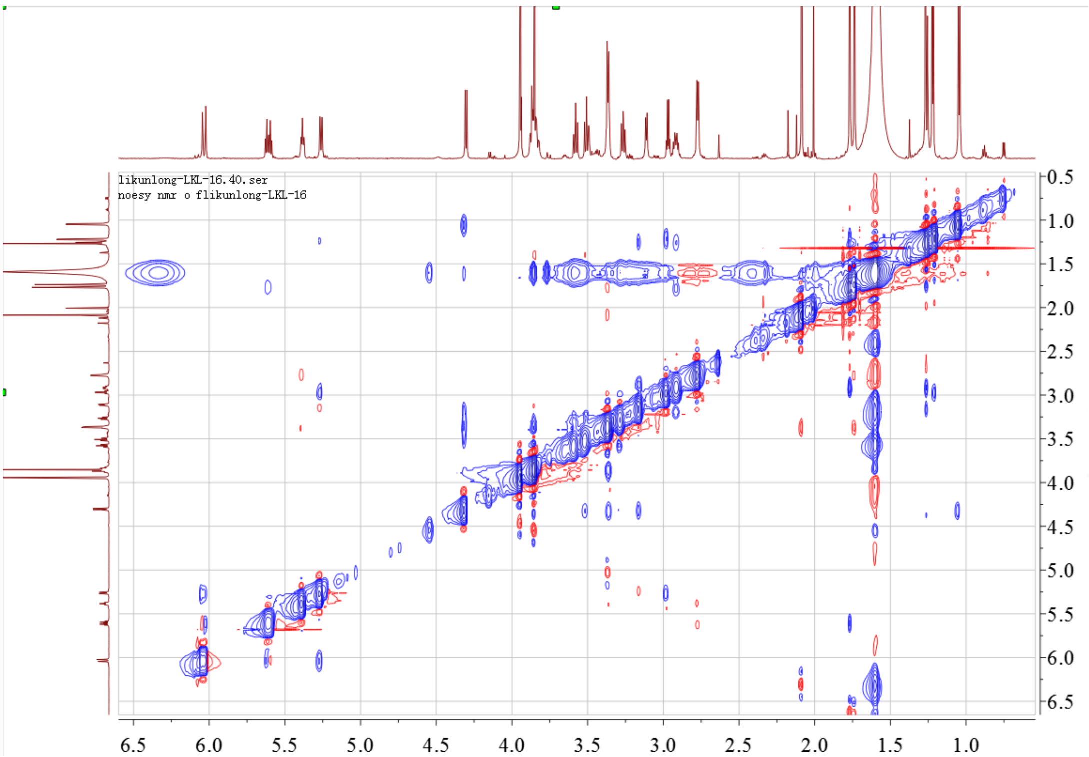

Figure SS-19-9. NOESY spectrum of **24** (in $CDCl_3$).

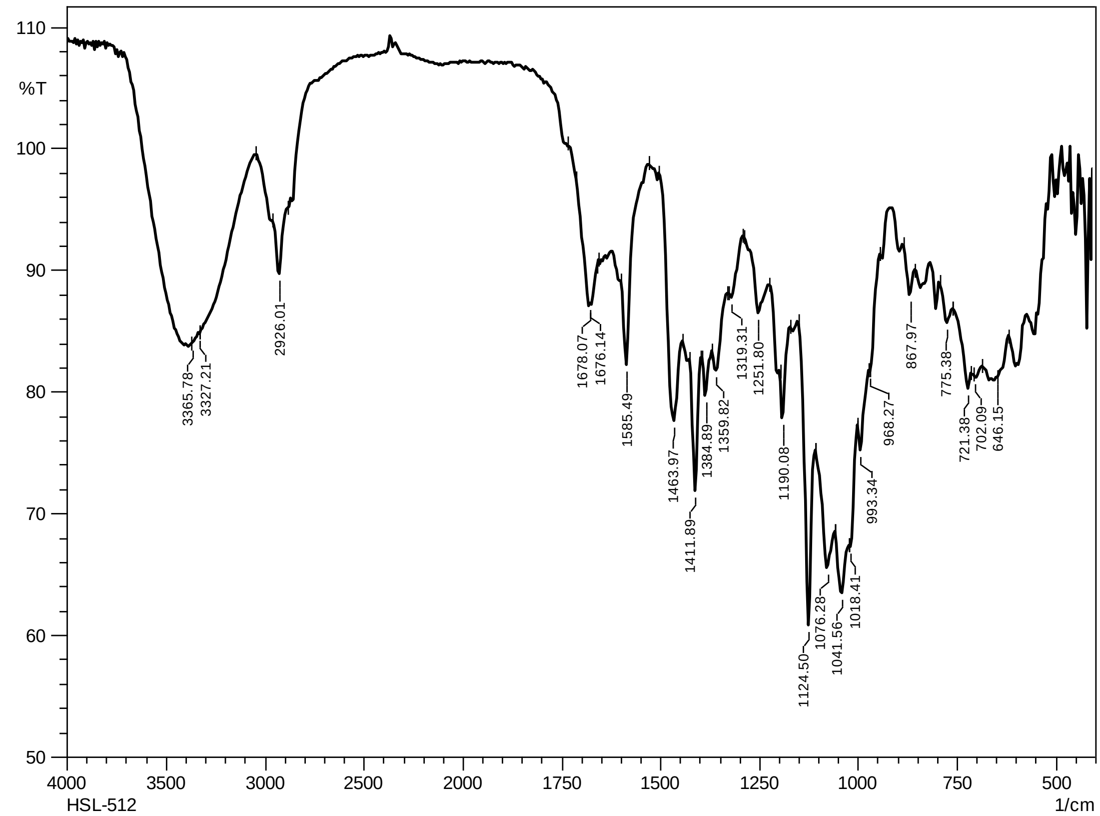

Figure SS-20-1. IR spectrum of **25**.

Mass Spectrum SmartFormula Report

Analysis Info

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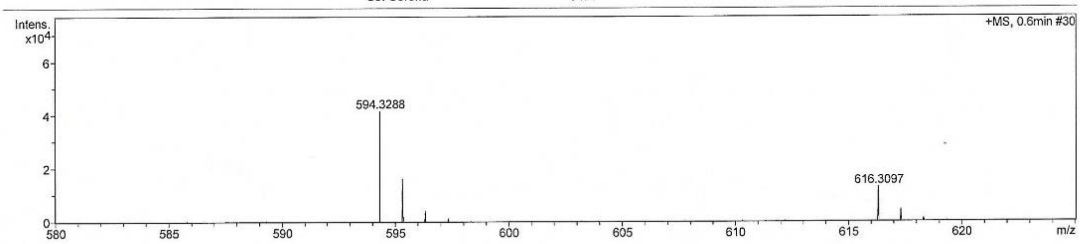
Method	LC_Direct Infusion_pos_100-1000mz.m	Operator	SCSIO
Sample Name	likunlong_LKL-17_pos	Instrument	maXis 255552.00029
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf	N-Rule
594.3288	1	C33H40N9O2	66.95	594.3299	-1.9	-1.1	10.0	18.5	even	ok
	2	C32H44N5O6	100.00	594.3286	-0.3	-0.2	14.3	13.5	even	ok
	3	C29H36N15	43.31	594.3273	-2.6	-1.5	19.0	19.5	even	ok
	4	C31H48NO10	39.09	594.3273	-2.6	-1.5	24.1	8.5	even	ok
	5	C28H40N11O4	12.36	594.3259	-4.8	-2.9	26.9	14.5	even	ok
616.3097	1	C31H47NNaO10	100.00	616.3092	-0.8	-0.5	4.3	8.5	even	ok
	2	C28H39N11NaO4	40.78	616.3079	3.0	1.9	8.7	14.5	even	ok
	3	C32H43N5NaO6	71.50	616.3106	-1.3	-0.8	14.4	13.5	even	ok
	4	C29H35N15Na	78.94	616.3092	-0.9	-0.5	16.7	19.5	even	ok
	5	C33H39N9NaO2	23.02	616.3119	3.5	2.2	25.9	18.5	even	ok

likunlong_LKL-17_pos_72_01_4199.d

Bruker Compass DataAnalysis 4.1 printed: 1/24/2018 3:03:31 PM by: SCSIO Page 1 of 1

Figure SS-20-2. HRESIMS (+) spectrum of **25**.

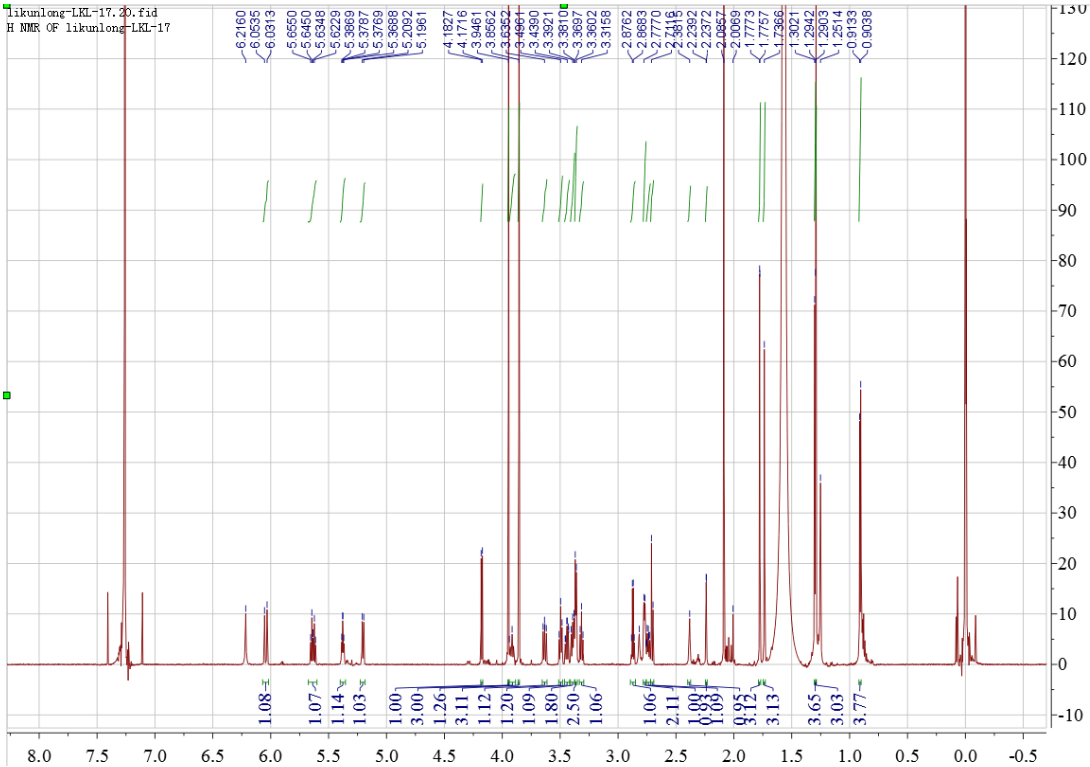


Figure SS-20-3. ^{1}H NMR spectrum of **25** (in $CDCl_3$, 700 MHz).

Figure SS-20-4. ^{13}C NMR spectrum of **25** (in $CDCl_3$, 175 MHz).

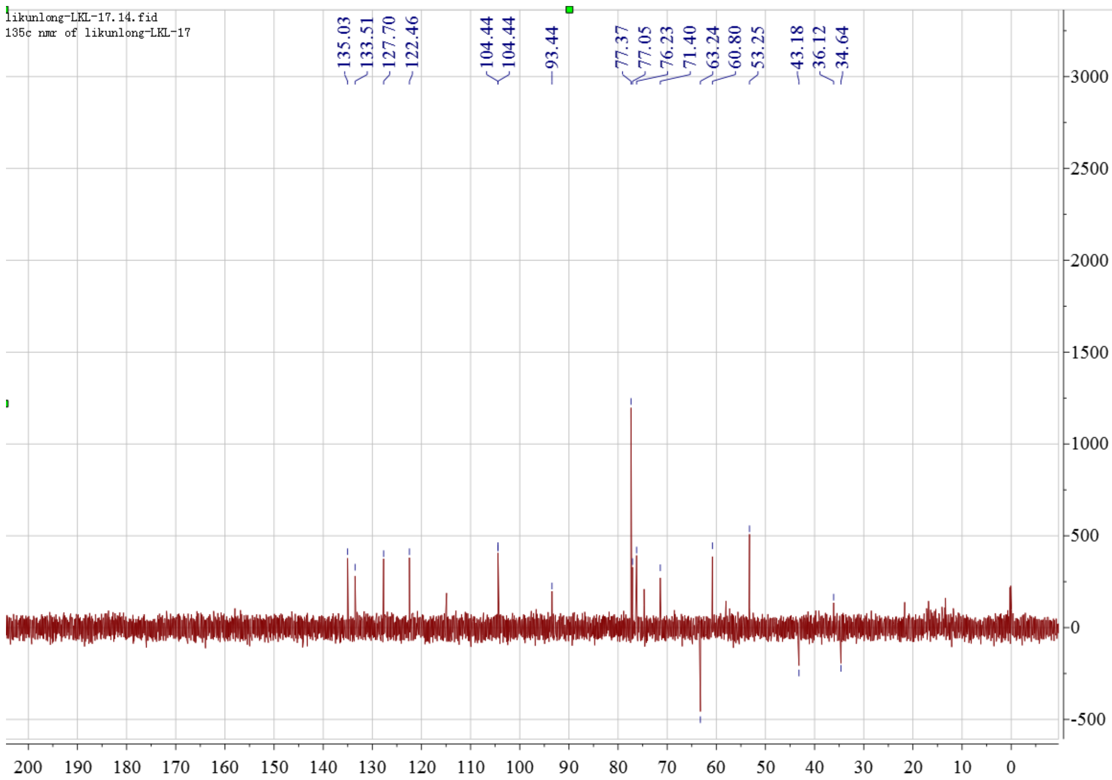


Figure SS-20-5. DEPT spectrum of **25** (in $CDCl_3$, 175 MHz).

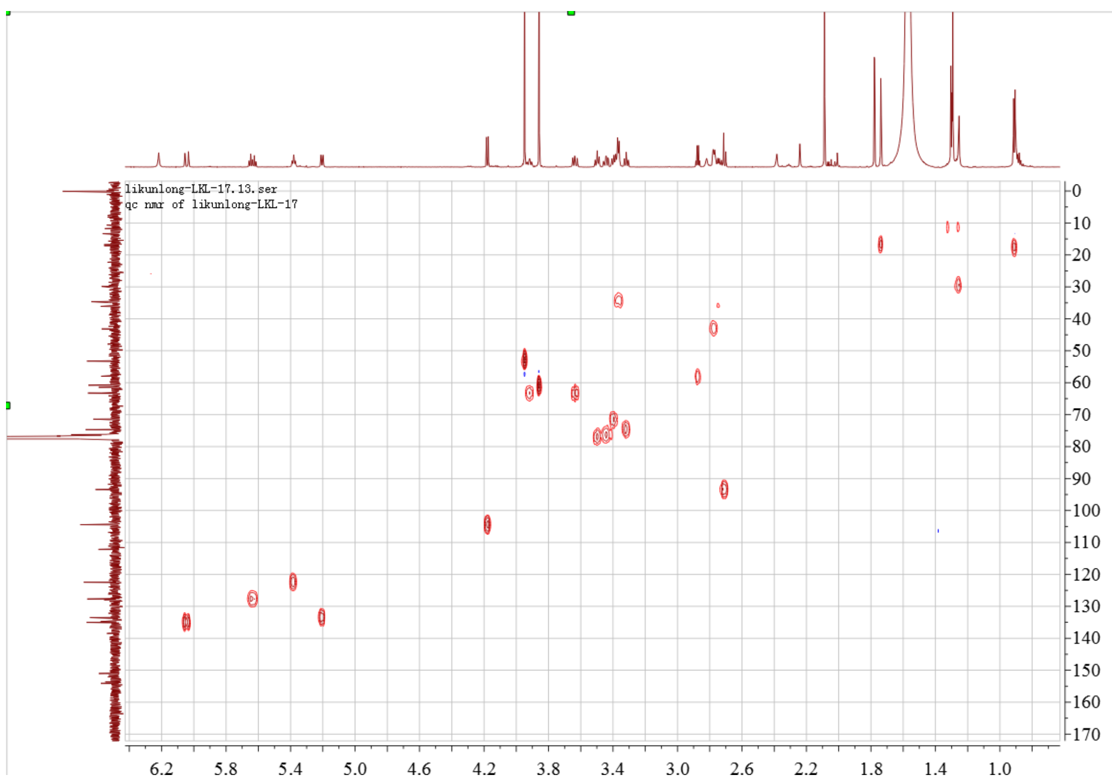


Figure SS-20-6. HSQC spectrum of **25** (in $CDCl_3$).

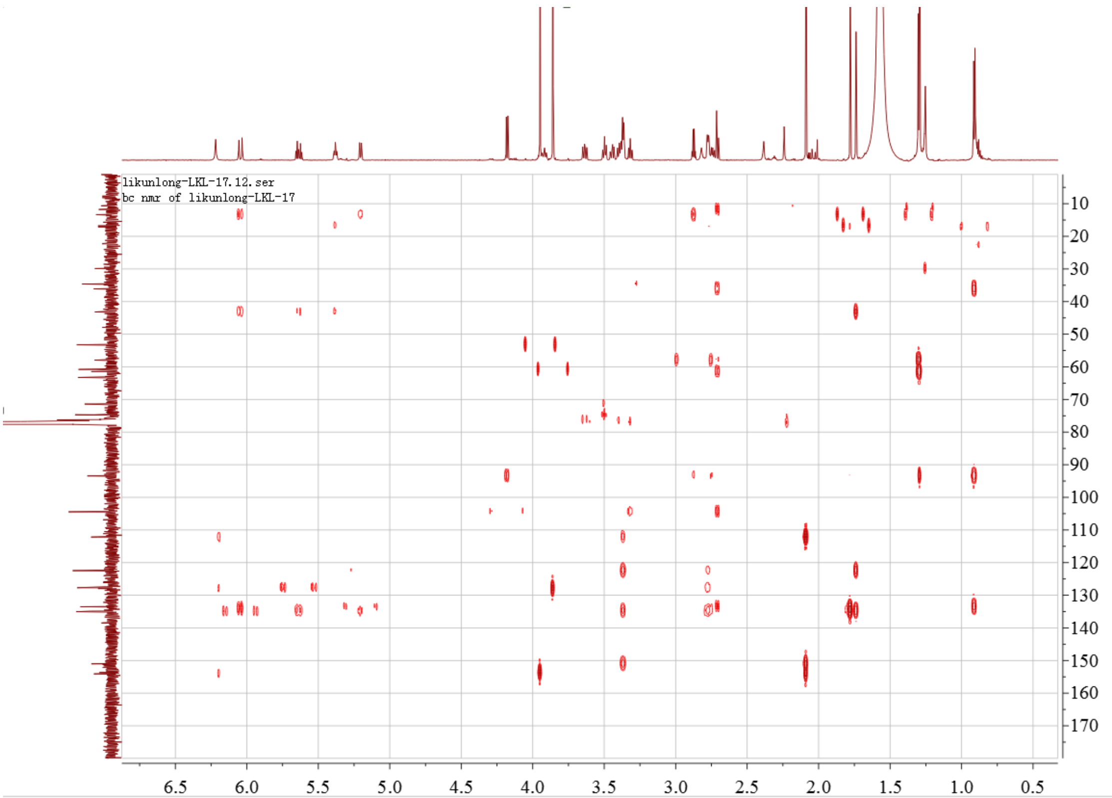


Figure SS-20-7. HMBC spectrum of **25** (in $CDCl_3$).

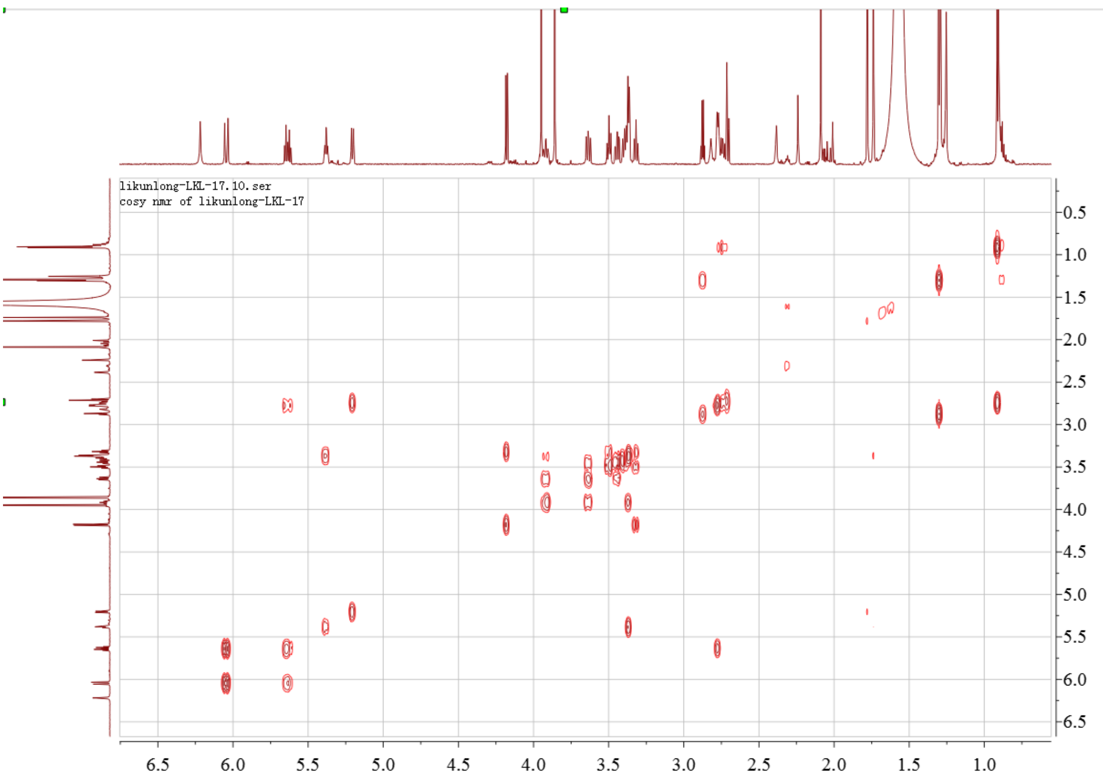


Figure SS-20-8. ^1H-^1H COSY spectrum of **25** (in $CDCl_3$).

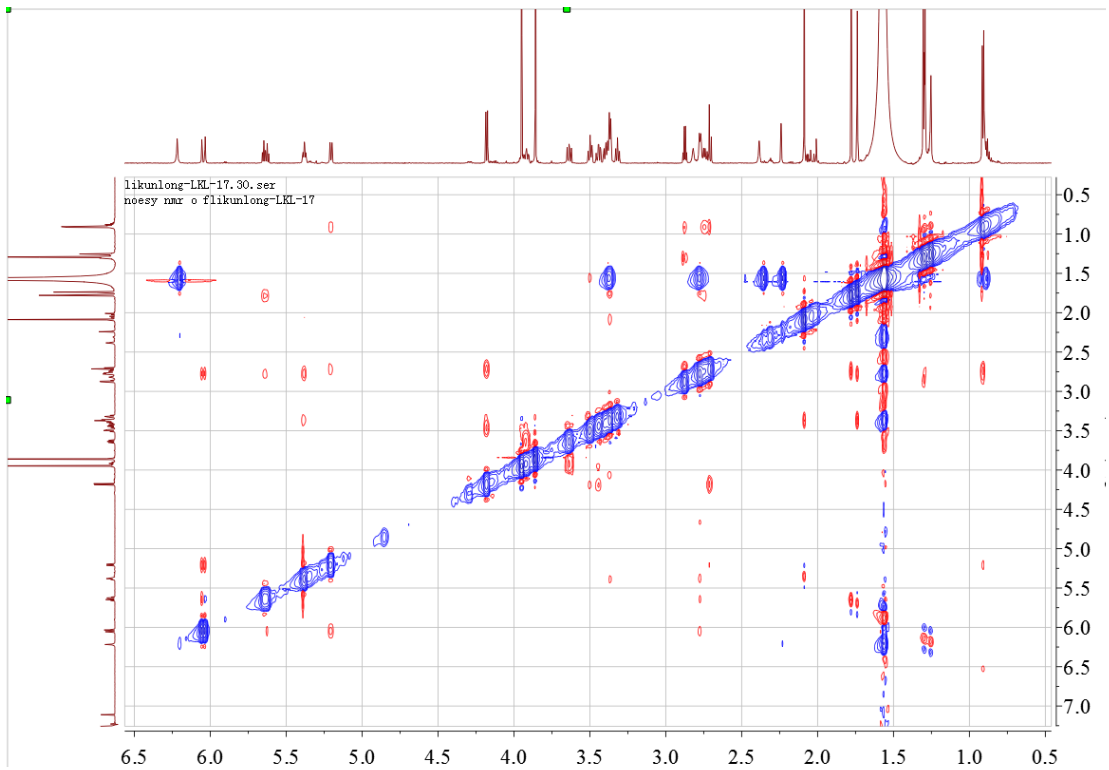


Figure SS-20-9. NOESY spectrum of **25** (in $CDCl_3$).

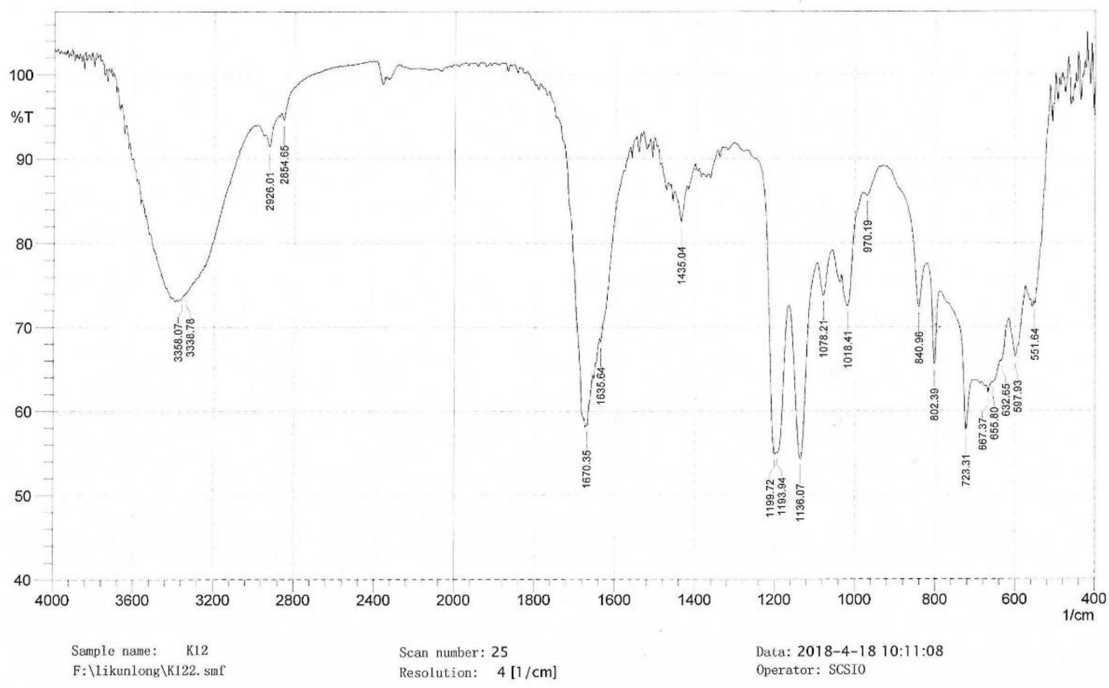


Figure SS-21-1. IR spectrum of **26**.

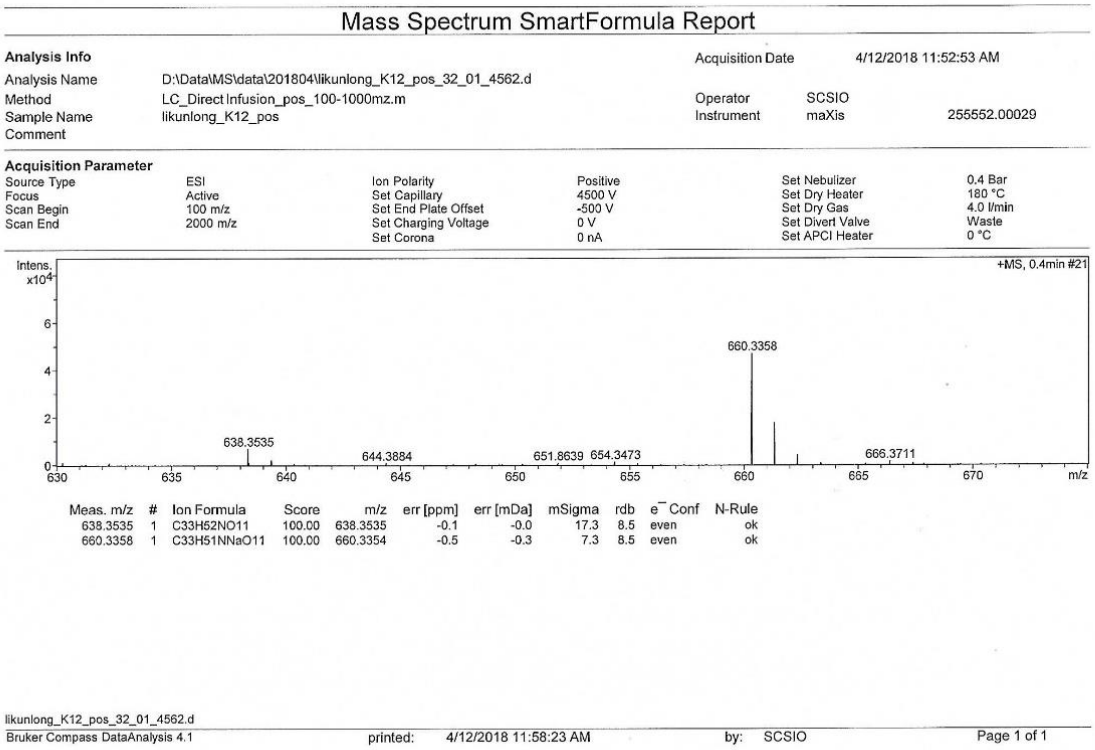


Figure SS-21-2. HRESIMS spectrum of **26**.

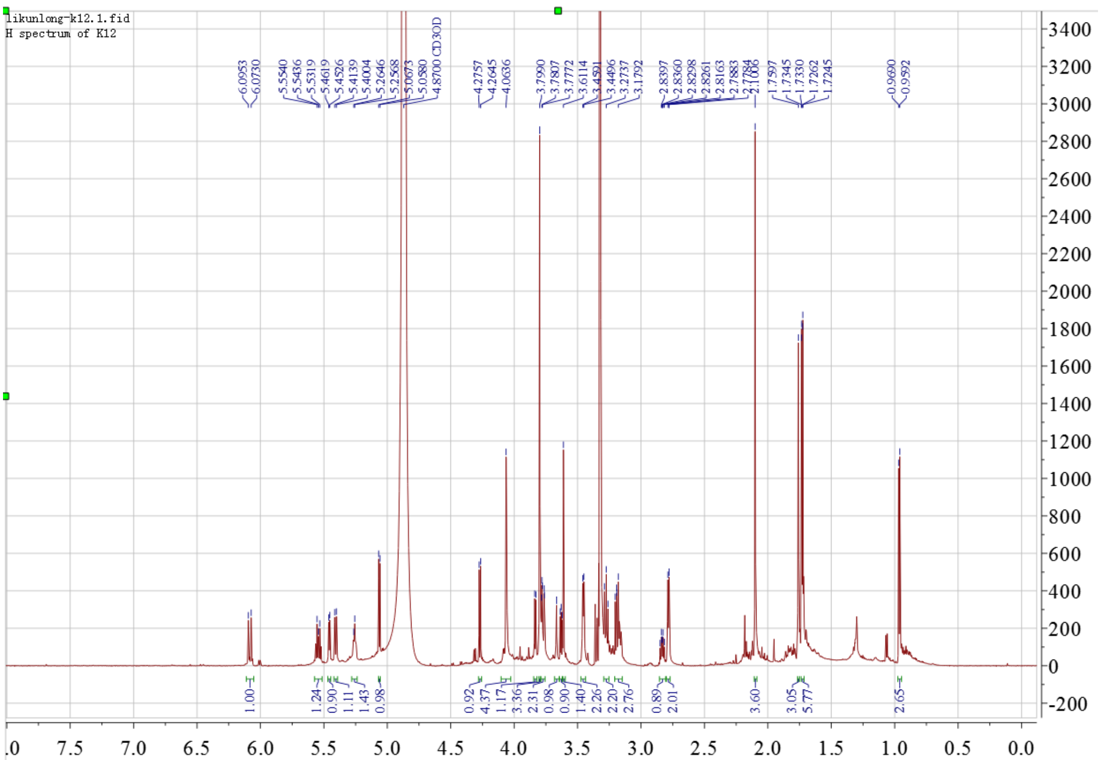


Figure SS-21-3. ^{1}H-NMR spectrum of **26** (in MeOD, 700 MHz).

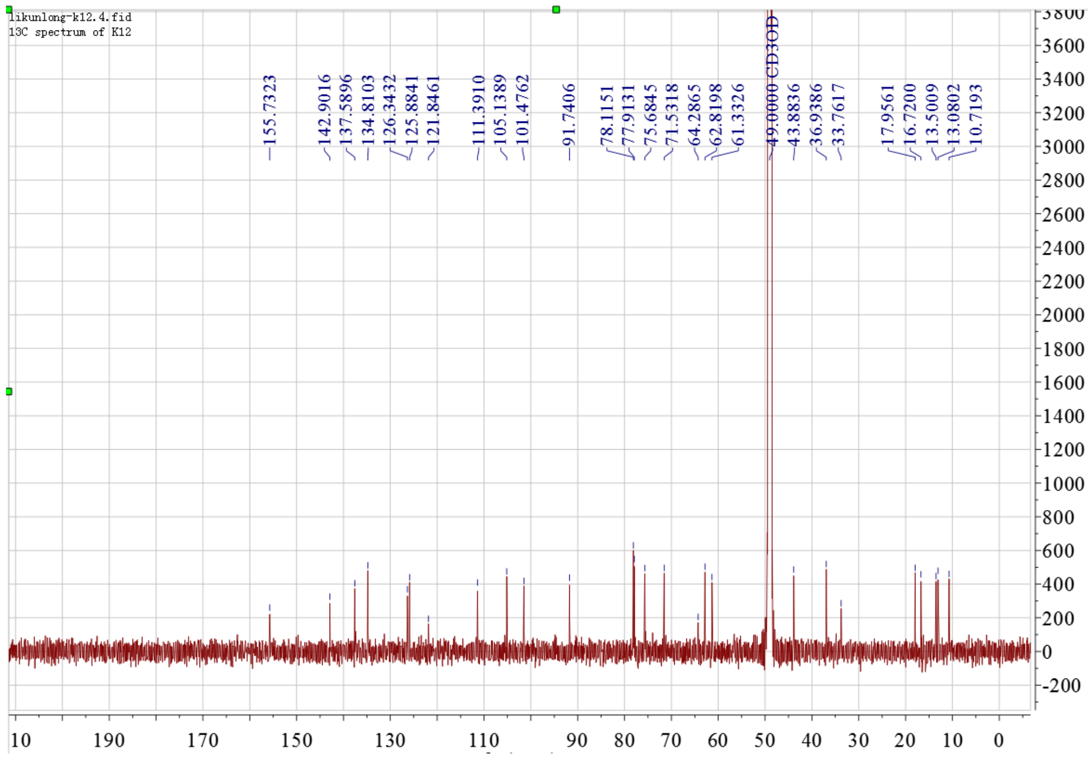


Figure SS-21-4. ^{13}C-NMR spectrum of **26** (in MeOD, 175 MHz).

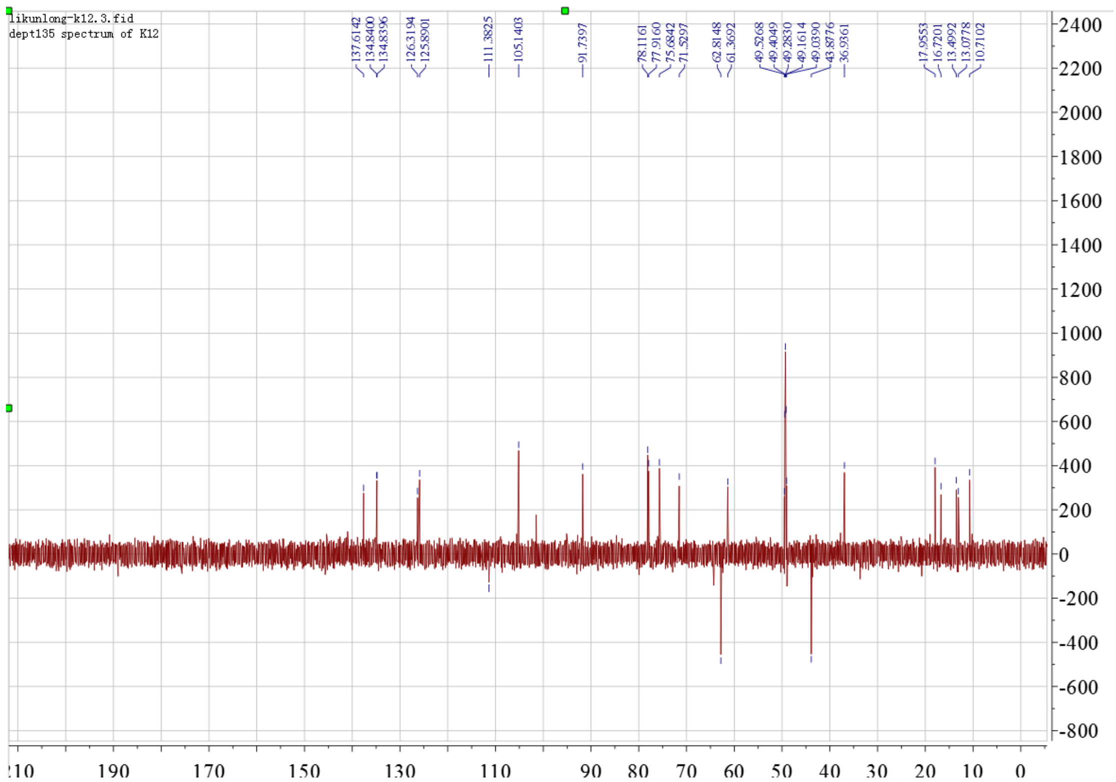


Figure SS-21-5. DEPT spectrum of **26** (in MeOD, 175 MHz).

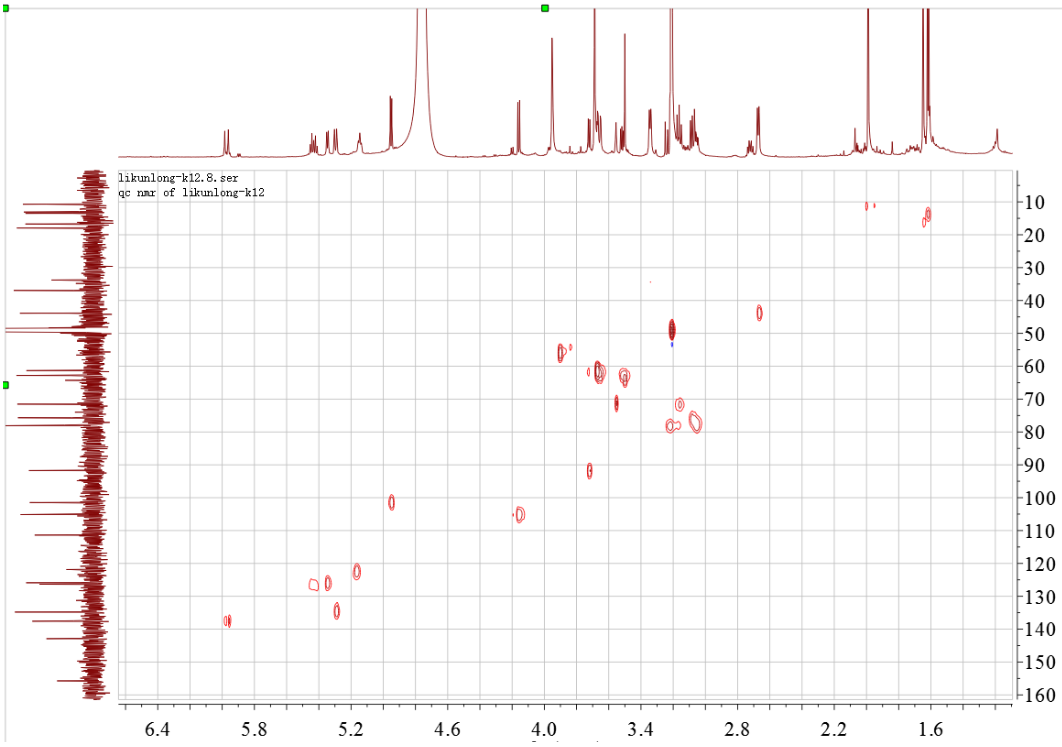


Figure SS-21-6. HSQC spectrum of **26** (in MeOD).

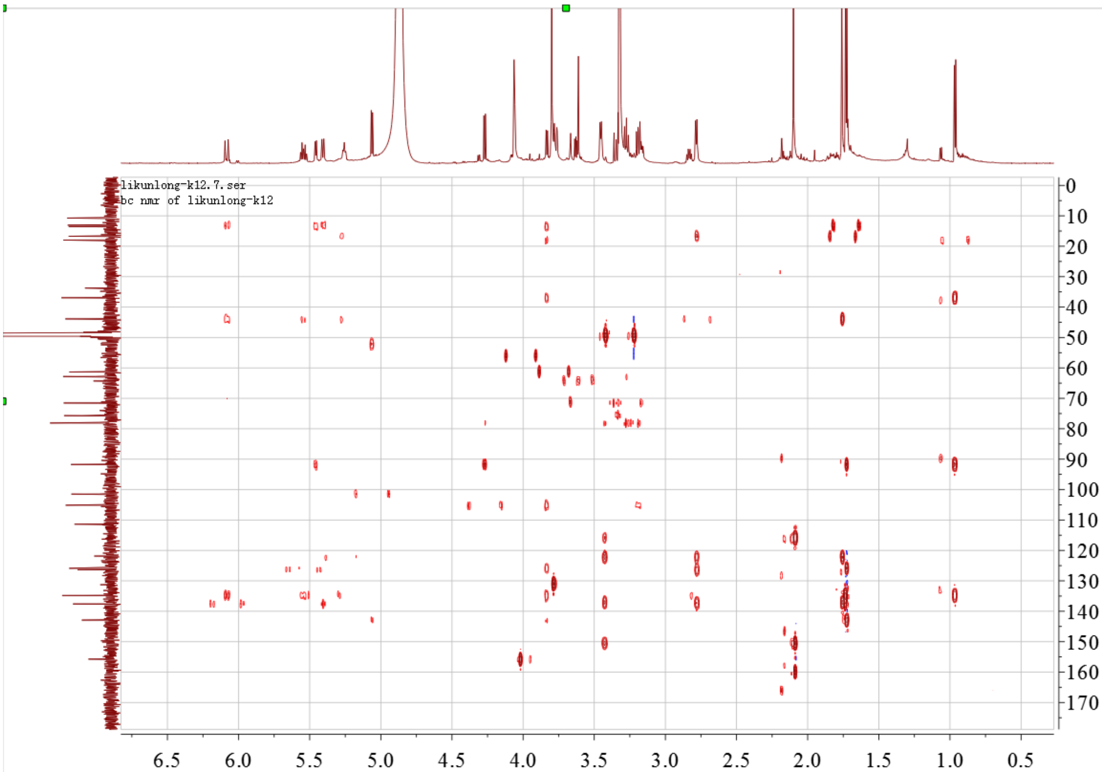


Figure SS-21-7. HMBC spectrum of **26** (in MeOD).

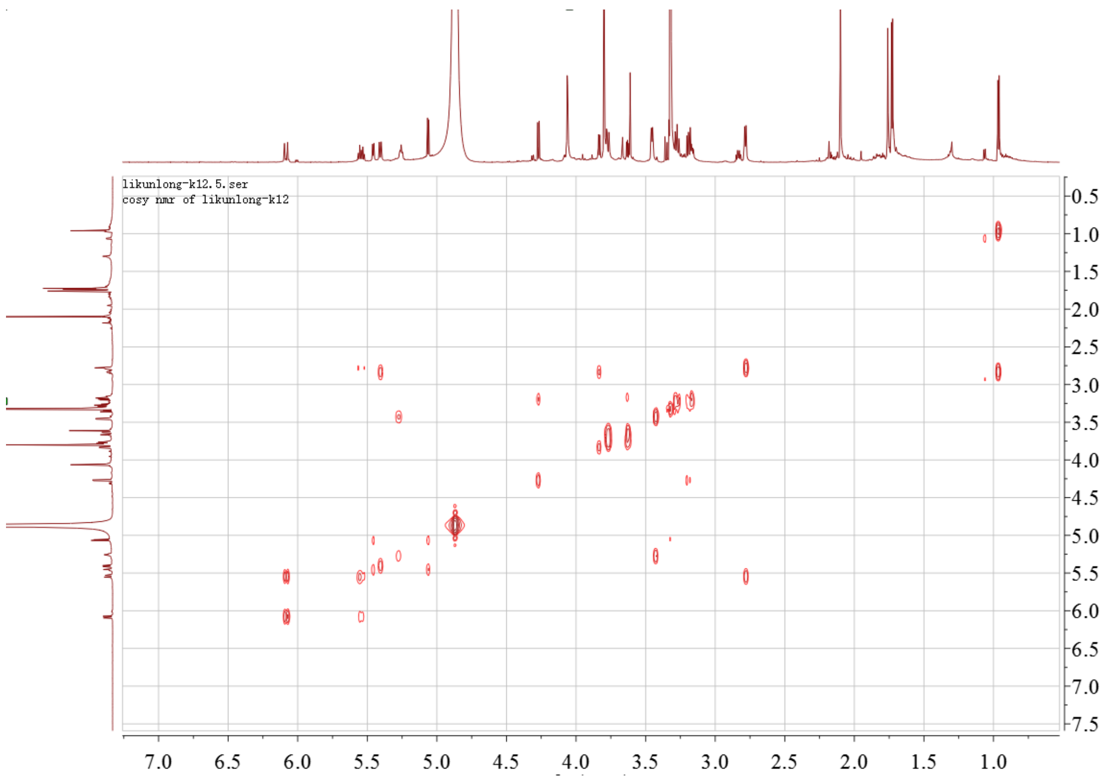


Figure SS-21-8. COSY spectrum of **26** (in MeOD).