Supporting Information

Flueggines A and B, Two New Dimeric Indolizidine Alkaloids from *Flueggea virosa*

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List of Supporting Information

General Experimental Procedures

All melting points were obtained on an X-5 micro melting point apparatus without correction. Optical rotations were measured on a Jasco P-1020 polarimeter with a 1 cm cell at room temperature. UV spectra were determined on a Jasco V-550 UV/VIS spectrophotometer. CD spectra were obtained on a Jasco J-810 spectropolarimeter at room temperature. IR spectra were recorded on a Jasco FT/IR-480 plus Fourier Transform infrared spectrometer using KBr pellets. HR-ESI-MS spectra were acquired on Agilent 6210 LC/MSD TOF mass spectrometer. NMR spectra were measured on Bruker AV-600 (^{1}H: 600 MHz, ^{13}C: 150 MHz) spectrometer. TLC analyses were carried out using precoated silica gel GF_{254} plates (Qingdao Marine Chemical Plant, Qingdao, P. R. China). Column chromatography was performed on Silica gel (200-300 mesh, Qingdao Marine Chemical Plant, Qingdao, P. R. China) and reversed-phase C_{18} silica gel (Merck, Darmstadt, Germany). All solvents used in column chromatography and HPLC were of analytical grade (Shanghai Chemical Plant, Shanghai, P. R. China) and chromatographic grade (Fisher Scientific, New Jersey, U. S. A), respectively.

Plant material

The air-dried twigs and leaves of *Flueggea virosa* were collected from Conghua county, Guangdong Province, P. R. China, in May of 2008, and authenticated by Prof. Guang-Xiong Zhou (Jinan University). A voucher specimen (No. 20080527) was deposited in the Institute of Traditional Chinese Medicine & Natural Products, Jinan University, Guangzhou, P. R. China.

Extraction and Isolation

The air-dried powdered material (50 kg) was percolated with 95 % EtOH at room temperature to give 7.5 kg crude extract, which was suspended in H_2O and acidified with 10 % HCl to pH 3. The acidic suspension was partitioned with $CHCl_3$ to remove the neutral components. The aqueous layer was then basified with $NH_3 \cdot H_2O$ to pH 9 and re-extracted with $CHCl_3$ to obtain a 450 g total alkaloids. The alkaloid extract was subjected to silica gel column chromatography eluting with $CHCl_3$:CH_3OH (100:0→0:100) to afford ten major fractions (Fr. 1-10). Fr. 5 (22.7 g) was resubjected to silica gel column chromatography ($CHCl_3$:CH_3OH, 100:0→0:100) to afford two subfractions (Fr. 5a and 5b). Fr. 5a (2.2 g) was then subsequently purified on RP-18 silica gel column (CH_3OH:H_2O, 50:50) to give compounds **1** (7.5 mg) and **2** (6.3 mg).

Physico-chemical constants of 1-2

Flueggine A (**1**): colorless needles; mp 221-222℃; $[\alpha]_{20}^{D}$ -31.9° (*c* = 0.25, CH_3OH); UV (CH_3OH) λ_{max} (lg ε) 216 (4.19), 253 (4.05) nm; CD (CH_3OH) 237 ($\Delta\varepsilon$ +3.44), 268 ($\Delta\varepsilon$ -8.00) nm; IR (KBr) λ_{max} 3450, 1756, 1643, 1215, 923 cm^{-1}; HR-ESI-MS *m/z* 439.1866 ($[M + H]^+$, calcd for $C_{24}H_{27}N_2O_6$: 439.1864).

Flueggine B (**2**): colorless needles; mp 235-236℃; $[\alpha]_{20}^{D}$ +159.9° (*c* = 0.25, CH_3OH); UV (CH_3OH) λ_{max} (lgε) 214 (4.12), 256 (3.27) nm; CD (CH_3OH) 228 ($\Delta\varepsilon$ +1.24), 268 ($\Delta\varepsilon$ +2.22) nm; IR (KBr) λ_{max} 3419, 2938, 1755, 1645, 1059, 918 cm^{-1}; HR-ESI-MS *m/z* 425.2072 ($[M + H]^+$, calcd for $C_{24}H_{29}N_2O_5$: 425.2071).

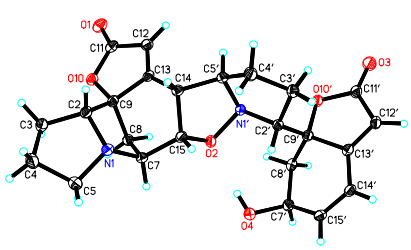
Cell lines and cell culture

Human breast cancer cell line MCF-7 and MDA-MB-231 cells were obtained from the American Type Culture Collection. The doxorubicin -resistant human breast cancer cell line MCF-7/ADR was kindly provided by Prof. Li-Wu Fu (State Key Laboratory of Oncology in South China, Cancer Center, Sun Yat-Sen University). All of the cell lines were cultured in the RPMI 1640 medium, supplemented with 10% FBS (v/v) at 37 ℃ in a humidified atmosphere of 5% CO_2 (v/v).

Cell viability assay

Cells were seeded into 96-well plates at the density of 5000 cell/well and allowed to grow for 24 h. After that, cells were treated with compounds **1** & **2** at various concentrations for 72 h. 30 μL of MTT solution (5 mg/mL) was added into each well and incubated for another 4 h. Subsequently, medium was discarded and 100 μL of DMSO was added to dissolve the produced formazan. The absorbance was measured at 570 nm using a microplate Reader (Thermo scientific multiskan MK3, USA). IC50 values were calculated from cell survival curves using Prism software.

Single crystal X-ray data and structures of 1 and 2



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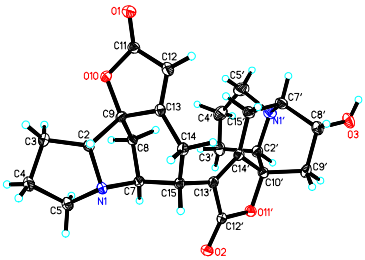

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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.    R-factors based
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H4BA H -0.1141 0.8100 0.5635 0.043 Uiso 1 1 calc R . .
H4BB H 0.0049 0.7000 0.5127 0.043 Uiso 1 1 calc R . .
C5B C -0.1119(4) 0.7635(3) 0.4009(3) 0.0353(8) Uani 1 1 d . . .
H5BA H -0.0492 0.8416 0.4069 0.042 Uiso 1 1 calc R . .
H5BB H -0.0575 0.7008 0.3463 0.042 Uiso 1 1 calc R . .
C7B C -0.3535(4) 0.7201(3) 0.2646(3) 0.0251(7) Uani 1 1 d . . .
H7BA H -0.2820 0.7673 0.2274 0.030 Uiso 1 1 calc R . .
C8B C -0.5533(4) 0.7381(3) 0.2523(3) 0.0315(8) Uani 1 1 d . . .
H8BA H -0.5887 0.7060 0.1778 0.038 Uiso 1 1 calc R . .
C9B C -0.6643(4) 0.6662(3) 0.3141(3) 0.0299(7) Uani 1 1 d . . .
H9BA H -0.7291 0.7214 0.3692 0.036 Uiso 1 1 calc R . .
H9BB H -0.7507 0.6080 0.2674 0.036 Uiso 1 1 calc R . .
C10B C -0.5353(4) 0.5996(3) 0.3619(2) 0.0227(7) Uani 1 1 d . . .
O11B O -0.6284(3) 0.52167(18) 0.41376(17) 0.0255(5) Uani 1 1 d . . .

C12B C -0.5829(4) 0.4054(3) 0.3675(2) 0.0230(7) Uani 1 1 d . . .
C13B C -0.4576(4) 0.4023(3) 0.2805(2) 0.0213(6) Uani 1 1 d . . .
C14B C -0.4314(4) 0.5168(3) 0.2773(2) 0.0211(6) Uani 1 1 d . . .
C15B C -0.3263(4) 0.5832(3) 0.2142(3) 0.0255(7) Uani 1 1 d . . .
H15E H -0.3691 0.5558 0.1417 0.031 Uiso 1 1 calc R . .
H15F H -0.2003 0.5688 0.2159 0.031 Uiso 1 1 calc R . .
O1 O -0.2658(3) 0.3825(2) 0.54444(18) 0.0328(5) Uani 1 1 d . . .
O2 O 0.6510(3) 0.5103(2) 0.94970(17) 0.0280(5) Uani 1 1 d . . .
O3 O 0.6748(3) -0.0149(2) 0.5525(2) 0.0389(6) Uani 1 1 d . . .
H3A H 0.6443 -0.0507 0.4913 0.058 Uiso 1 1 calc R . .
N1 N 0.1866(3) 0.6973(2) 0.8858(2) 0.0245(6) Uani 1 1 d . . .
C2 C 0.0415(4) 0.6837(3) 0.8035(3) 0.0238(7) Uani 1 1 d . . .
H2A H 0.0800 0.7277 0.7544 0.029 Uiso 1 1 calc R . .
C3 C -0.1230(4) 0.7383(3) 0.8627(3) 0.0313(8) Uani 1 1 d . . .
H3B H -0.1854 0.7832 0.8246 0.038 Uiso 1 1 calc R . .
H3C H -0.2056 0.6755 0.8742 0.038 Uiso 1 1 calc R . .
C4 C -0.0430(5) 0.8230(3) 0.9663(3) 0.0345(8) Uani 1 1 d . . .
H4A H -0.1315 0.8390 1.0209 0.041 Uiso 1 1 calc R . .
H4B H 0.0059 0.8996 0.9587 0.041 Uiso 1 1 calc R . .
C5 C 0.1046(4) 0.7498(3) 0.9899(3) 0.0314(7) Uani 1 1 d . . .
H5A H 0.1921 0.8020 1.0403 0.038 Uiso 1 1 calc R . .
H5B H 0.0552 0.6861 1.0172 0.038 Uiso 1 1 calc R . .
C7 C 0.2458(4) 0.5726(3) 0.8719(2) 0.0229(7) Uani 1 1 d . . .
H7A H 0.2845 0.5650 0.9394 0.027 Uiso 1 1 calc R . .
C8 C 0.0755(4) 0.4907(3) 0.8304(2) 0.0207(6) Uani 1 1 d . . .
H8A H 0.1003 0.4058 0.8010 0.025 Uiso 1 1 calc R . .
H8B H -0.0140 0.4987 0.8840 0.025 Uiso 1 1 calc R . .
C9 C 0.0207(4) 0.5451(3) 0.7462(2) 0.0217(6) Uani 1 1 d . . .
O10 O -0.1549(3) 0.50192(19) 0.70082(16) 0.0243(5) Uani 1 1 d . . .
C11 C -0.1369(4) 0.4350(3) 0.5974(3) 0.0252(7) Uani 1 1 d . . .
C12 C 0.0531(4) 0.4416(3) 0.5713(3) 0.0282(7) Uani 1 1 d . . .
H12A H 0.1006 0.4060 0.5057 0.034 Uiso 1 1 calc R . .
C13 C 0.1460(4) 0.5072(3) 0.6571(2) 0.0212(6) Uani 1 1 d . . .
C14 C 0.3399(4) 0.5460(3) 0.6807(3) 0.0248(7) Uani 1 1 d . . .
H14A H 0.3630 0.6281 0.6771 0.030 Uiso 1 1 calc R . .
H14B H 0.4112 0.4928 0.6280 0.030 Uiso 1 1 calc R . .
C15 C 0.3982(4) 0.5425(3) 0.7912(2) 0.0221(7) Uani 1 1 d . . .
H15A H 0.4957 0.6060 0.8169 0.026 Uiso 1 1 calc R . .
N1' N 0.3646(4) 0.0528(2) 0.6838(2) 0.0314(6) Uani 1 1 d . . .
C2' C 0.4452(4) 0.1282(3) 0.7875(3) 0.0290(7) Uani 1 1 d . . .
H2'A H 0.5210 0.0774 0.8137 0.035 Uiso 1 1 calc R . .
C3' C 0.2887(5) 0.1610(3) 0.8609(3) 0.0364(8) Uani 1 1 d . . .
H3'A H 0.2451 0.2381 0.8609 0.044 Uiso 1 1 calc R . .
H3'B H 0.3224 0.1657 0.9321 0.044 Uiso 1 1 calc R . .
C4' C 0.1489(5) 0.0561(4) 0.8141(3) 0.0482(10) Uani 1 1 d . . .
H4'A H 0.1737 -0.0149 0.8344 0.058 Uiso 1 1 calc R . .
H4'B H 0.0293 0.0790 0.8357 0.058 Uiso 1 1 calc R . .
C5' C 0.1690(5) 0.0326(4) 0.6985(3) 0.0504(10) Uani 1 1 d . . .
H5'A H 0.1261 -0.0502 0.6600 0.060 Uiso 1 1 calc R . .
H5'B H 0.1023 0.0883 0.6743 0.060 Uiso 1 1 calc R . .
C7' C 0.4087(5) 0.1056(3) 0.5979(3) 0.0305(7) Uani 1 1 d . . .
H7'A H 0.3461 0.0560 0.5329 0.037 Uiso 1 1 calc R . .
C8' C 0.6128(4) 0.1041(3) 0.5826(3) 0.0307(7) Uani 1 1 d . . .

H8'A H 0.6468 0.1439 0.5297 0.037 Uiso 1 1 calc R . .
C9' C 0.7064(4) 0.1755(3) 0.6887(3) 0.0287(7) Uani 1 1 d . . .
H9'A H 0.7735 0.1213 0.7145 0.034 Uiso 1 1 calc R . .
H9'B H 0.7895 0.2395 0.6796 0.034 Uiso 1 1 calc R . .
C10' C 0.5649(4) 0.2307(3) 0.7673(3) 0.0250(7) Uani 1 1 d . . .
O11' O 0.6456(3) 0.31030(19) 0.86367(17) 0.0277(5) Uani 1 1 d . . .
C12' C 0.5937(4) 0.4256(3) 0.8767(3) 0.0231(7) Uani 1 1 d . . .
C13' C 0.4704(4) 0.4240(3) 0.7904(3) 0.0231(7) Uani 1 1 d . . .
C14' C 0.4544(4) 0.3095(3) 0.7252(2) 0.0232(7) Uani 1 1 d . . .
C15' C 0.3591(4) 0.2395(3) 0.6238(3) 0.0298(7) Uani 1 1 d . . .
H15B H 0.3970 0.2726 0.5682 0.036 Uiso 1 1 calc R . .
H15C H 0.2305 0.2440 0.6310 0.036 Uiso 1 1 calc R . .
O1W O -0.4536(4) 0.9409(3) 0.1307(2) 0.0461(7) Uani 1 1 d . . .
H1WA H -0.368(7) 1.008(5) 0.156(4) 0.069 Uiso 1 1 d . . .
H1WB H -0.457(7) 0.928(5) 0.066(5) 0.069 Uiso 1 1 d . . .
O2W O 0.4606(4) 0.8851(3) 0.9161(2) 0.0435(6) Uani 1 1 d . . .
H2WA H 0.372(7) 0.828(5) 0.904(4) 0.065 Uiso 1 1 d . . .
H2WB H 0.505(7) 0.875(5) 0.852(4) 0.065 Uiso 1 1 d . . .
O3W O 0.5303(6) 0.8485(3) 0.7012(2) 0.0590(9) Uani 1 1 d . . .
H3WA H 0.463(8) 0.902(6) 0.681(5) 0.089 Uiso 1 1 d . . .
H3WB H 0.660(8) 0.861(5) 0.667(5) 0.089 Uiso 1 1 d . . .

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C14A 0.0210(15) 0.0229(16) 0.0247(17) 0.0028(14) -0.0004(13) 0.0031(12)
C15A 0.0179(14) 0.0221(16) 0.0207(16) 0.0028(13) 0.0007(12) 0.0016(12)
O2B 0.0241(11) 0.0265(12) 0.0279(12) 0.0093(10) 0.0030(9) 0.0009(9)
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C14B 0.0181(14) 0.0228(16) 0.0218(16) 0.0058(14) 0.0000(12) 0.0023(12)
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O1 0.0325(13) 0.0322(13) 0.0299(13) 0.0046(11) -0.0033(10) -0.0010(10)
O2 0.0297(12) 0.0273(13) 0.0242(12) 0.0040(11) -0.0022(10) -0.0002(10)
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N1 0.0238(13) 0.0201(14) 0.0266(14) 0.0021(12) 0.0005(11) 0.0044(10)
C2 0.0233(15) 0.0213(16) 0.0260(17) 0.0058(14) -0.0011(13) 0.0026(12)
C3 0.0255(17) 0.0302(18) 0.036(2) 0.0059(16) 0.0005(15) 0.0092(14)
C4 0.0325(18) 0.0291(18) 0.037(2) 0.0013(17) 0.0062(15) 0.0078(14)
C5 0.0320(17) 0.0331(19) 0.0245(18) 0.0013(15) 0.0056(14) 0.0061(14)
C7 0.0217(15) 0.0244(16) 0.0215(16) 0.0049(14) -0.0014(12) 0.0045(12)
C8 0.0243(15) 0.0193(15) 0.0181(15) 0.0051(13) 0.0000(12) 0.0029(12)
C9 0.0168(14) 0.0215(16) 0.0266(17) 0.0073(14) -0.0018(12) 0.0007(12)
O10 0.0181(10) 0.0262(11) 0.0265(12) 0.0051(10) 0.0008(9) 0.0009(8)
C11 0.0279(16) 0.0206(16) 0.0259(18) 0.0055(15) -0.0036(14) 0.0020(13)
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C14 0.0231(16) 0.0227(16) 0.0288(18) 0.0080(14) 0.0041(13) 0.0030(12)
C15 0.0222(15) 0.0196(16) 0.0249(17) 0.0072(14) 0.0002(13) 0.0036(12)
N1' 0.0327(15) 0.0249(15) 0.0353(16) 0.0088(13) -0.0003(13) -0.0048(12)
C2' 0.0292(17) 0.0242(17) 0.0332(19) 0.0079(15) 0.0011(14) 0.0034(13)
C3' 0.0398(19) 0.035(2) 0.036(2) 0.0134(17) 0.0092(16) 0.0055(15)
C4' 0.035(2) 0.056(3) 0.057(3) 0.024(2) 0.0068(18) 0.0006(18)
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C15' 0.0330(18) 0.0252(17) 0.0289(19) 0.0046(15) -0.0029(14) 0.0044(14)
O1W 0.0483(16) 0.0440(16) 0.0422(16) 0.0121(15) -0.0053(13) -0.0161(13)
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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C13B C14B 1.339(4) . ?
C14B C15B 1.496(4) . ?
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O3 C8' 1.422(4) . ?
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N1 C7 1.495(4) . ?
N1 C2 1.510(4) . ?
C2 C3 1.531(4) . ?
C2 C9 1.547(4) . ?
C3 C4 1.524(5) . ?
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C7 C8 1.529(4) . ?
C7 C15 1.553(4) . ?
C8 C9 1.517(4) . ?
C9 O10 1.437(4) . ?
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C14 C15 1.555(4) . ?
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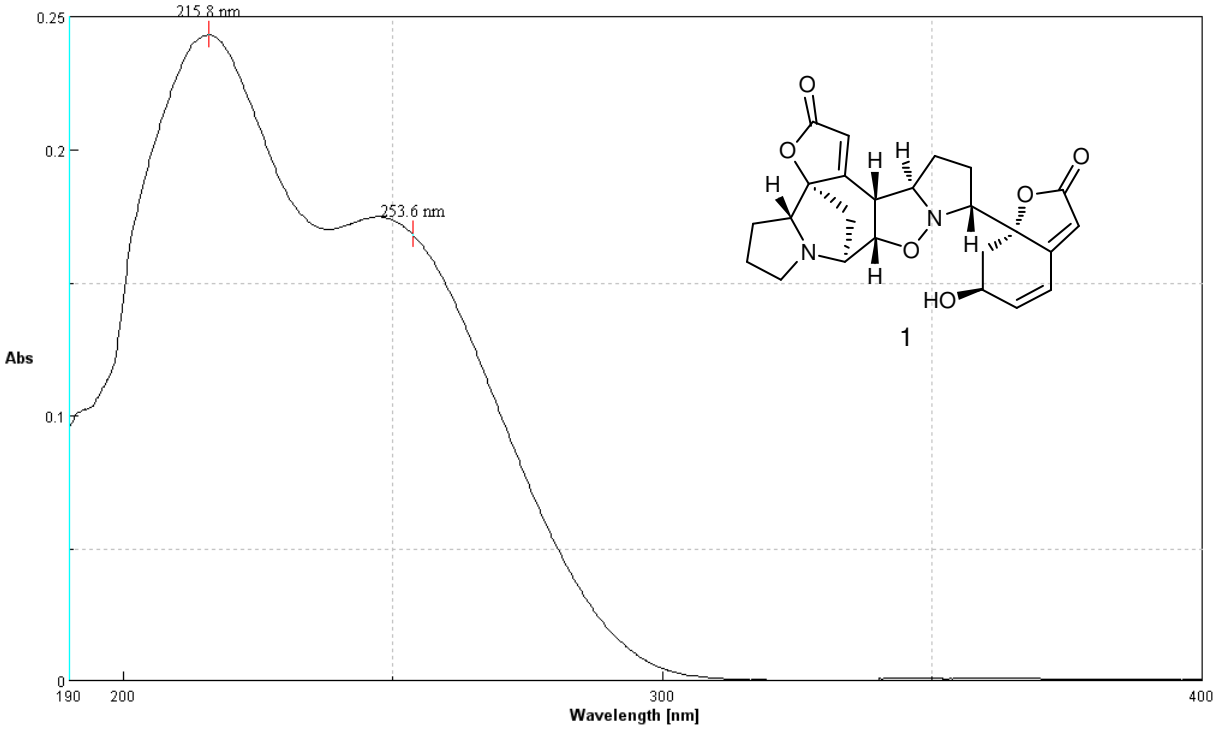

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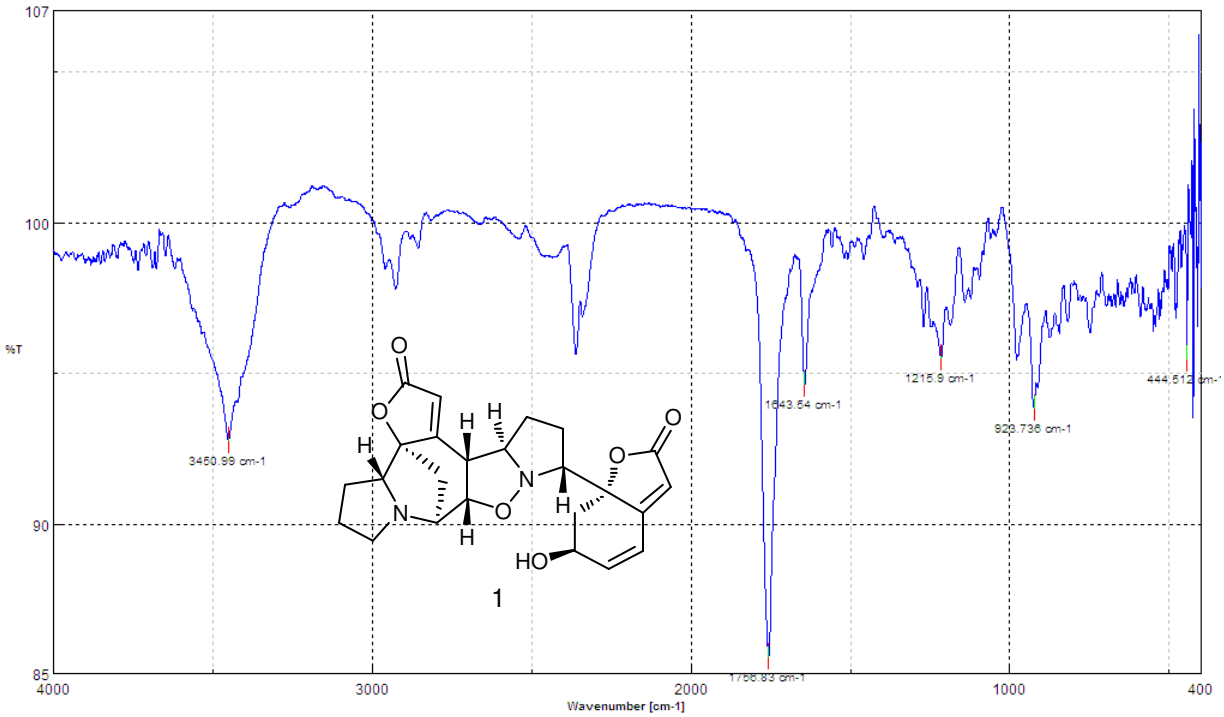

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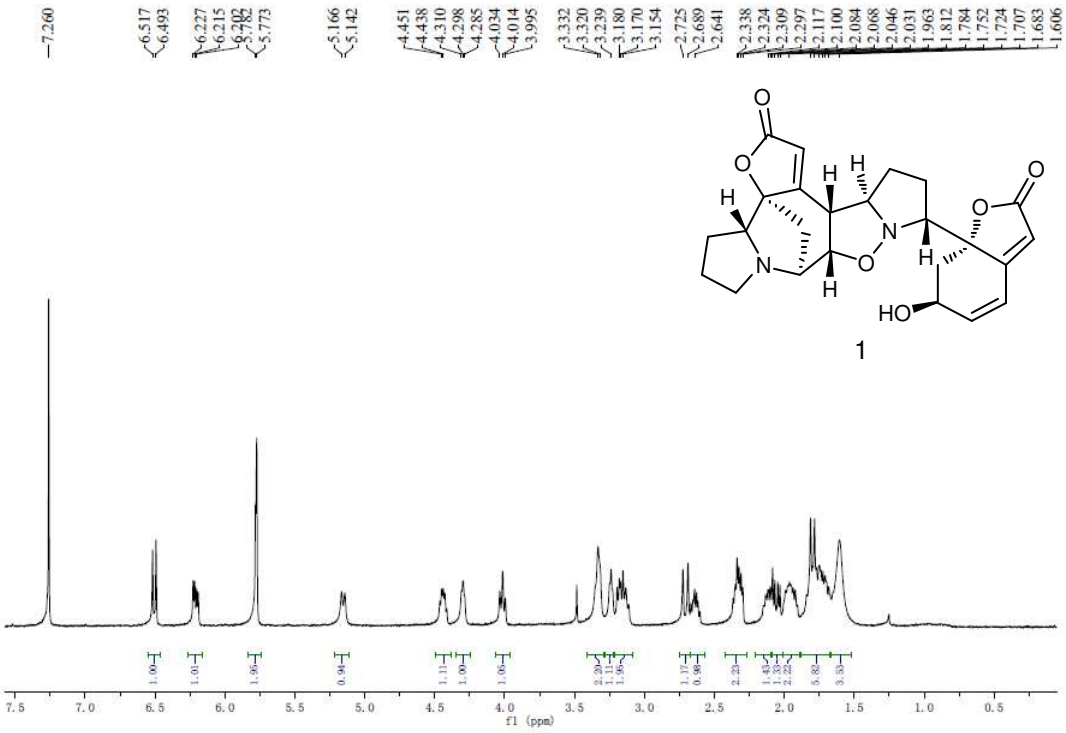

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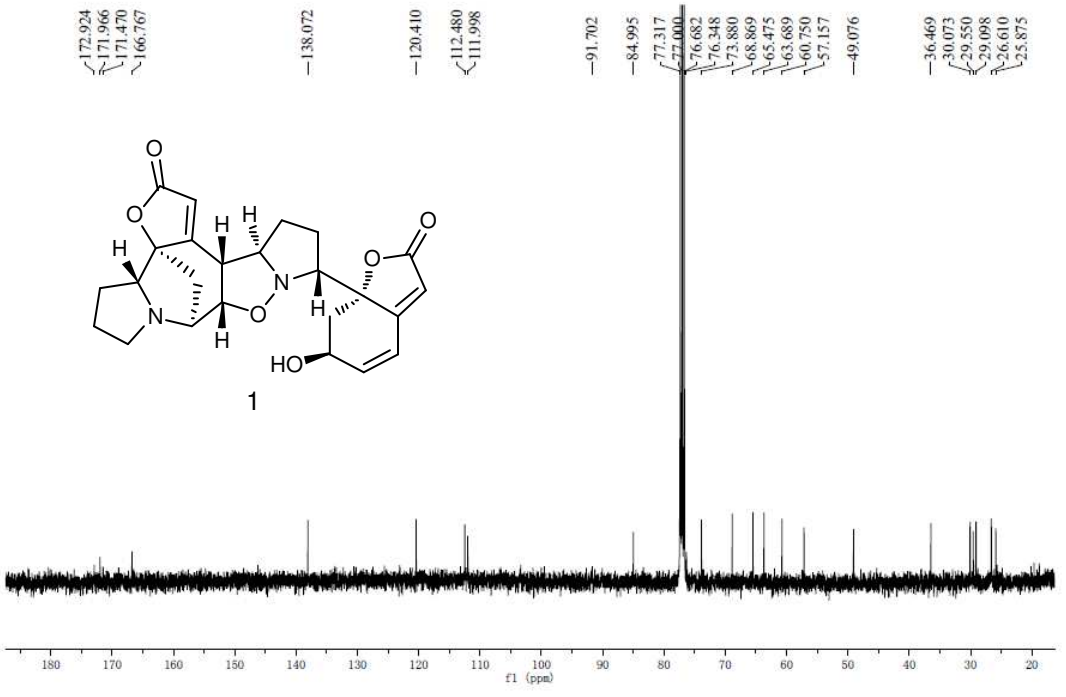

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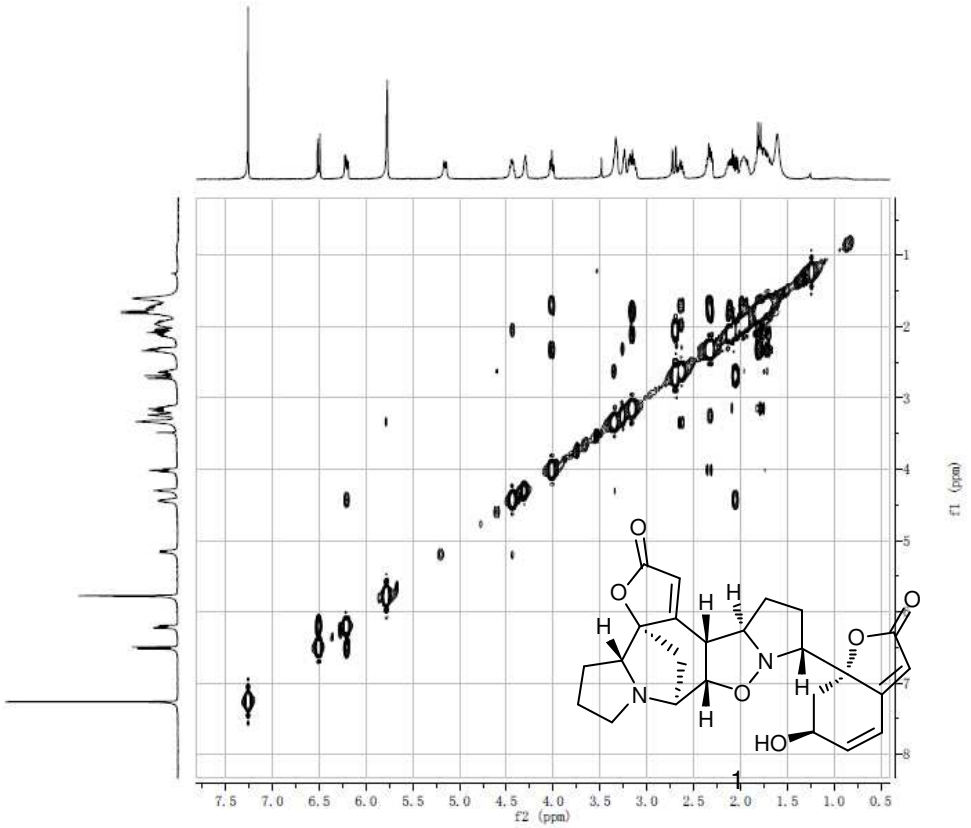
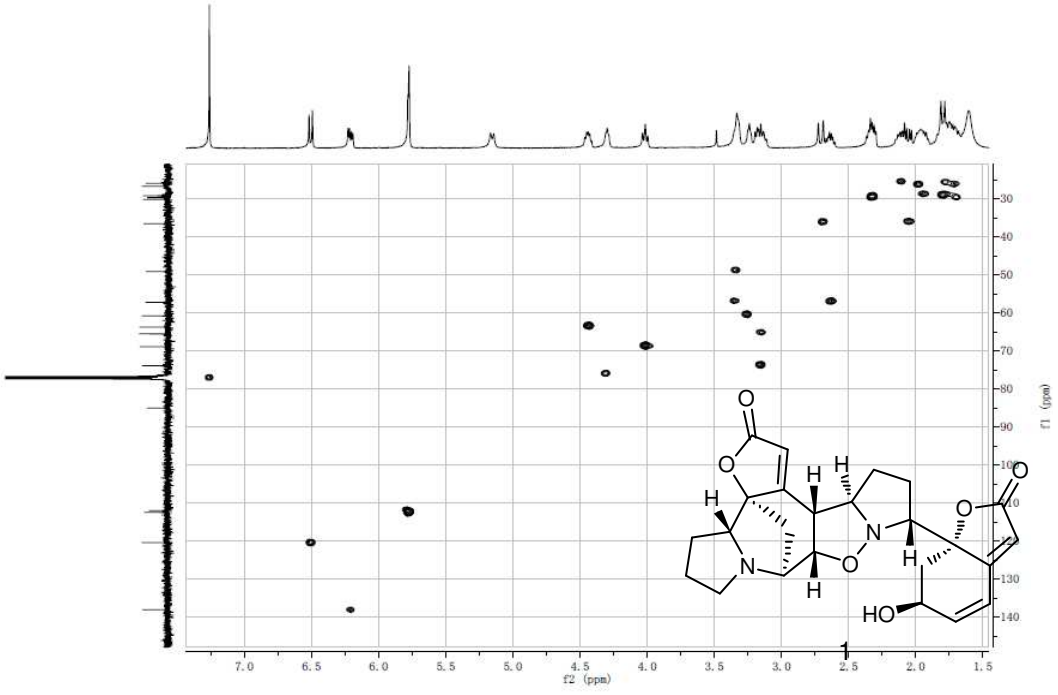
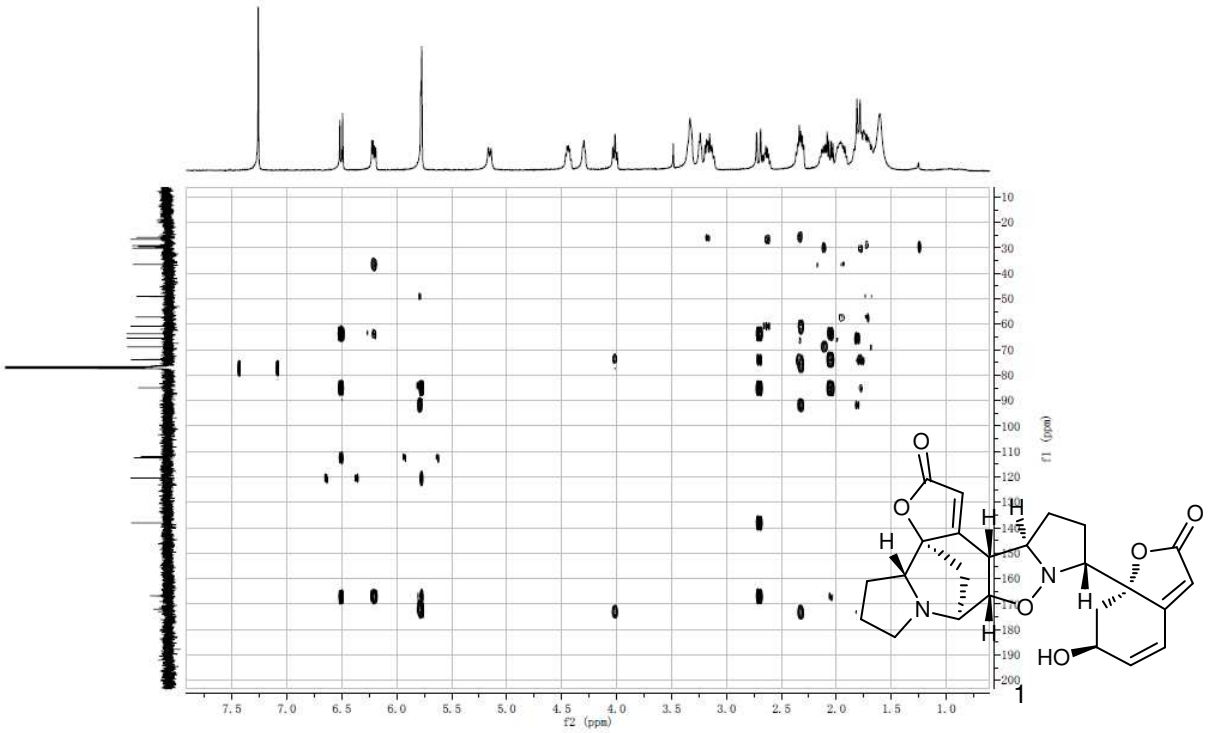


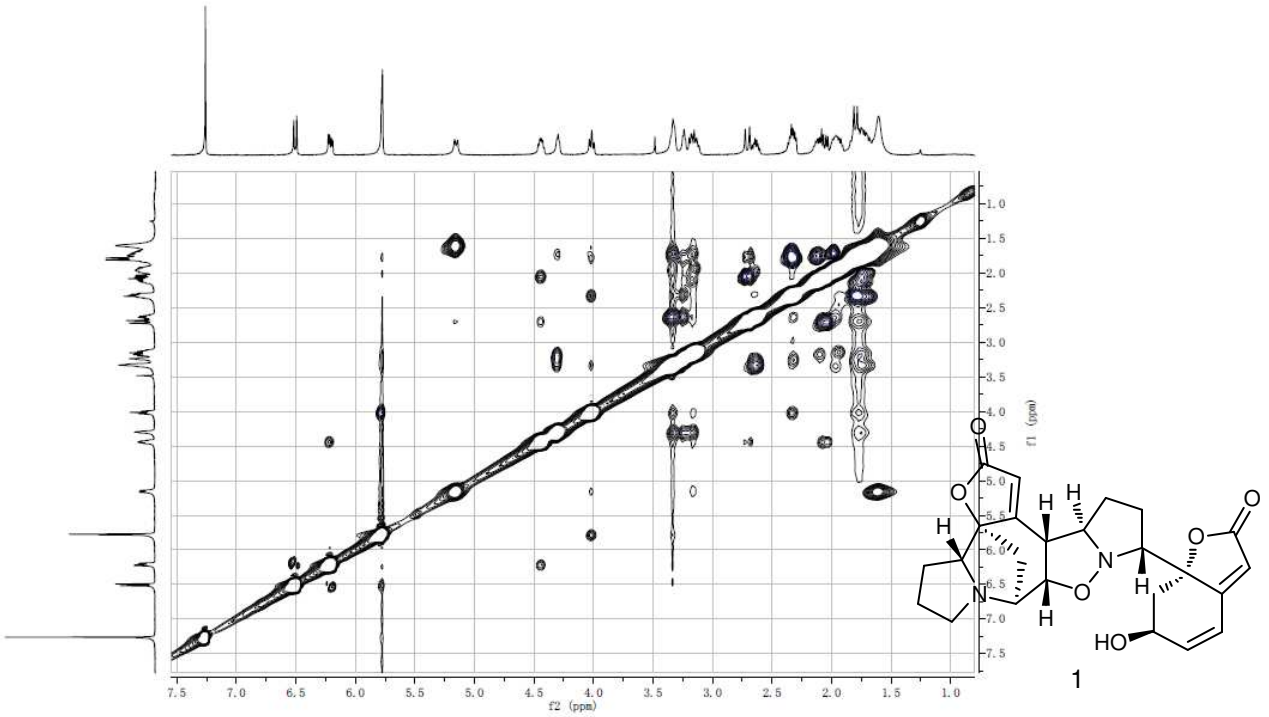
^{1}H-^{1}H COSY spectrum of **1** in $CDCl_3$



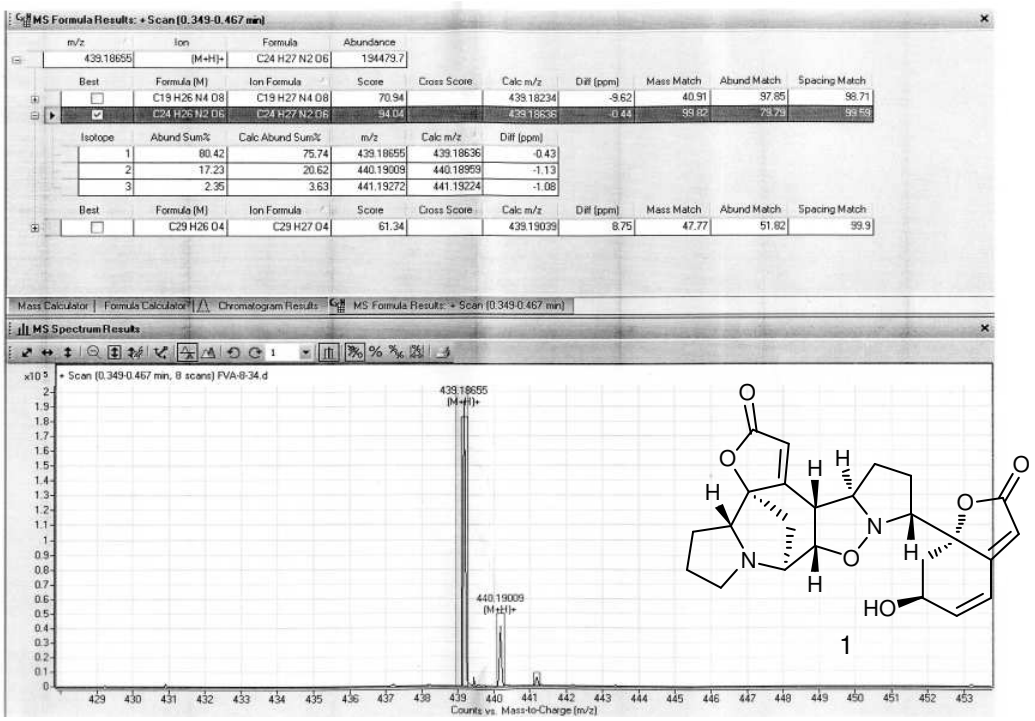
HSQC spectrum of **1** in $CDCl_3$



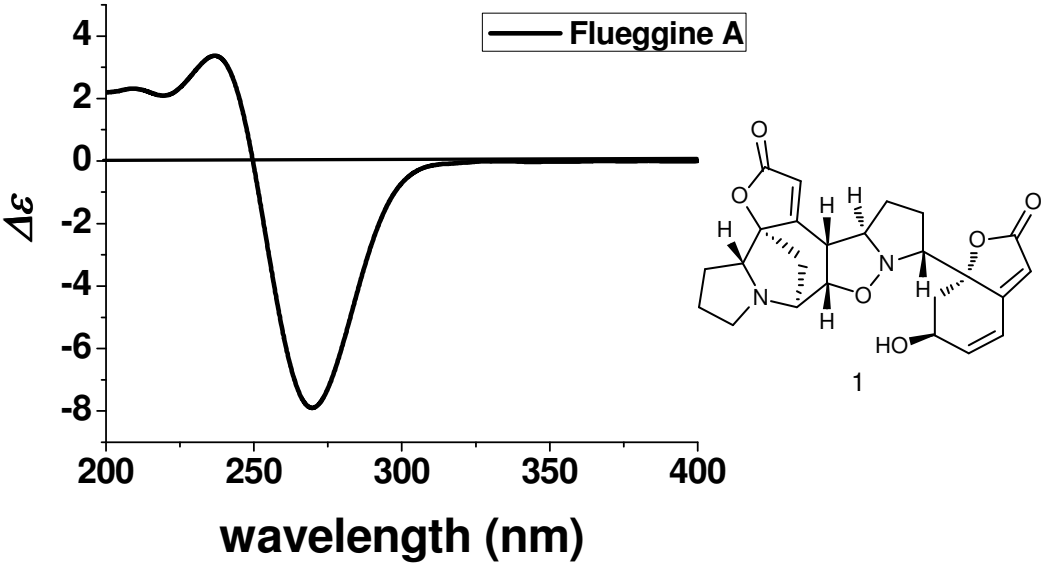
HMBC spectrum of **1** in $CDCl_3$



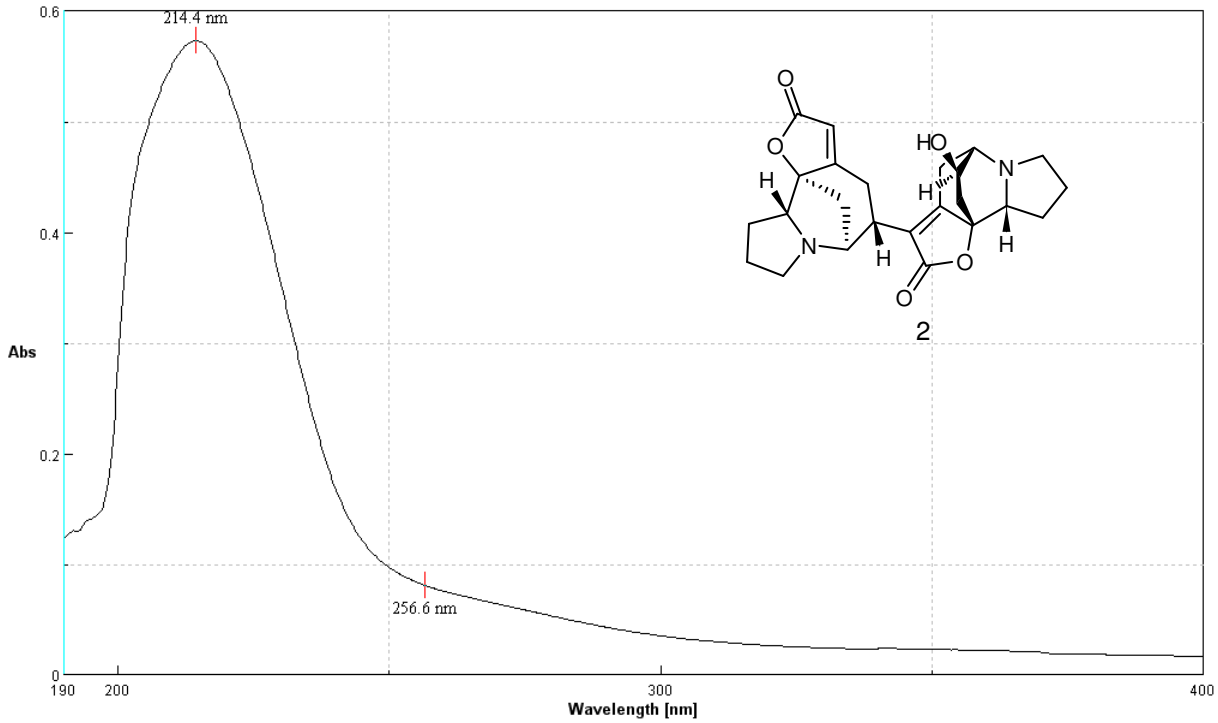
ROESY spectrum of **1** in $CDCl_3$



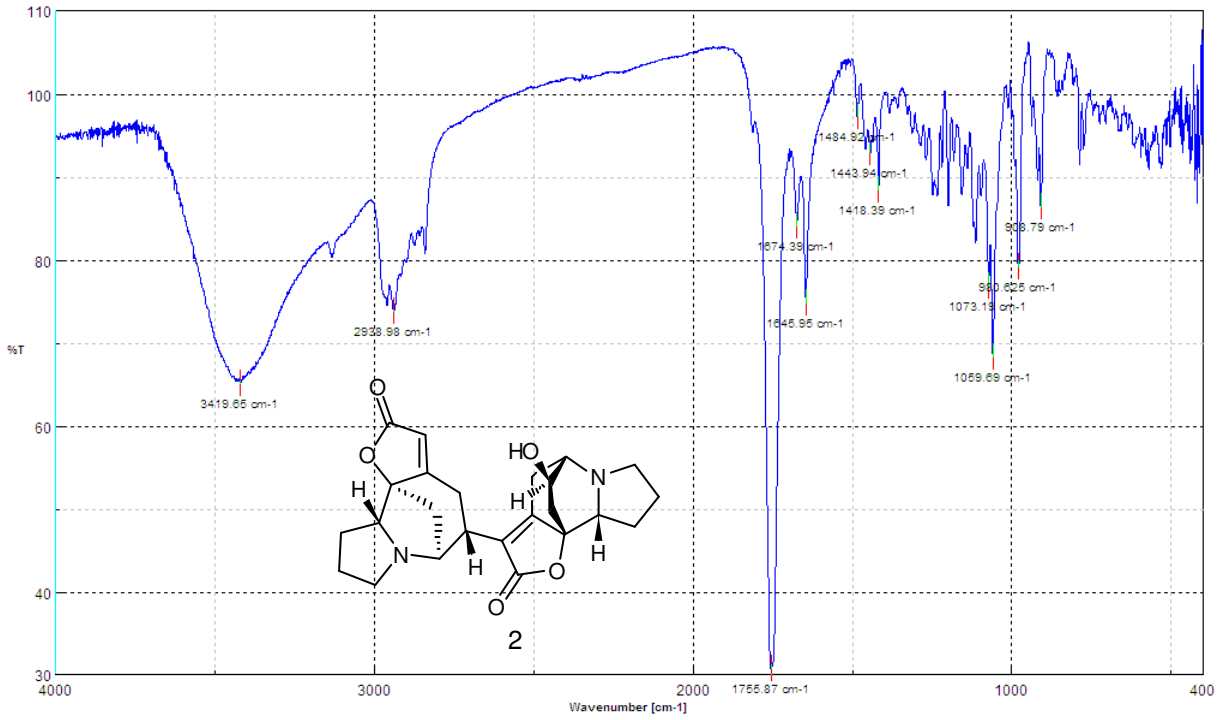
HR-ESI-MS spectrum of **1**



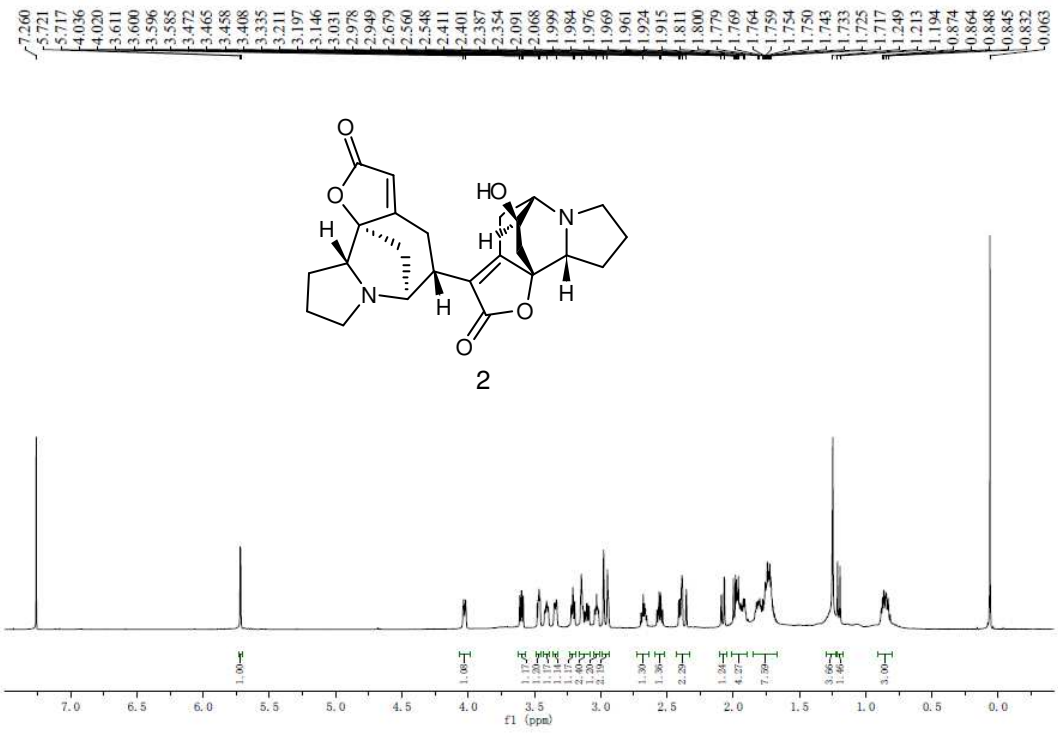
CD spectrum of **1** (CH_3OH)



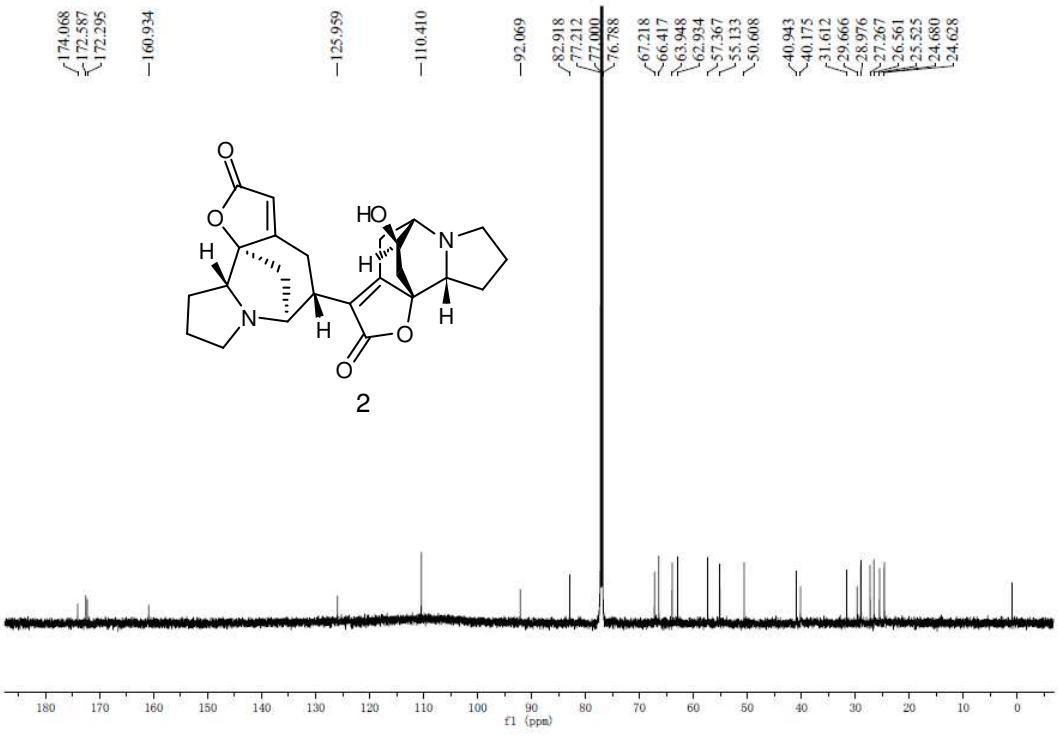
UV spectrum of **2** (CH_3OH)



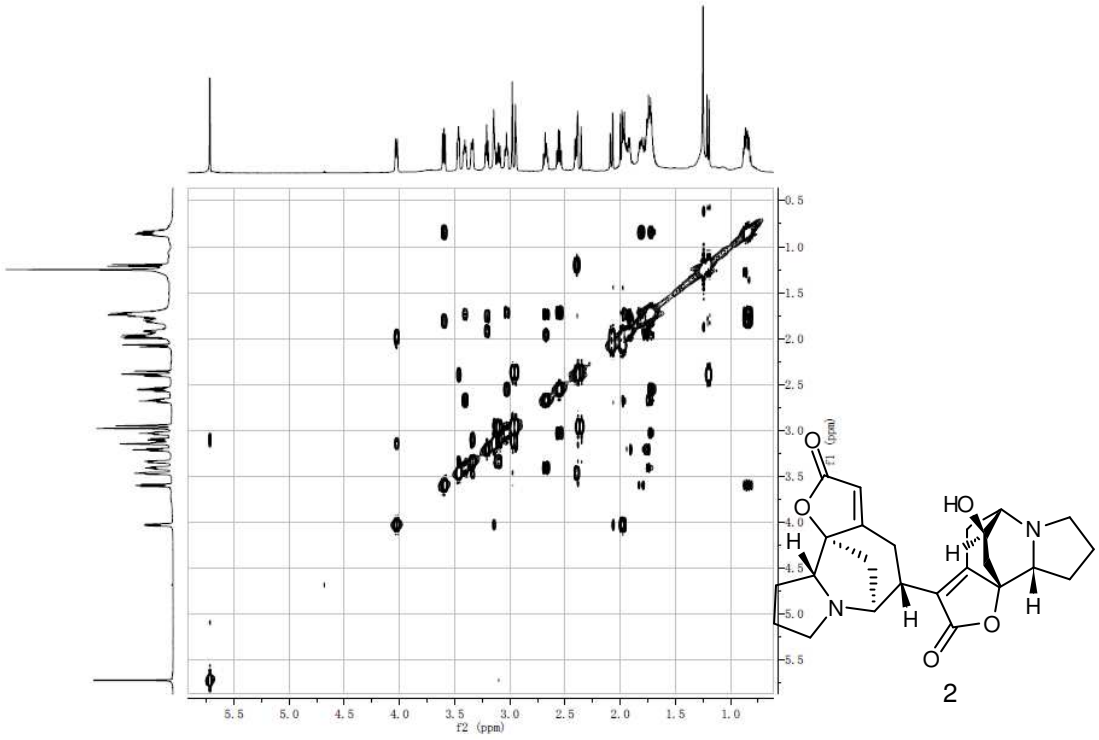
IR spectrum of **2** (KBr disc)



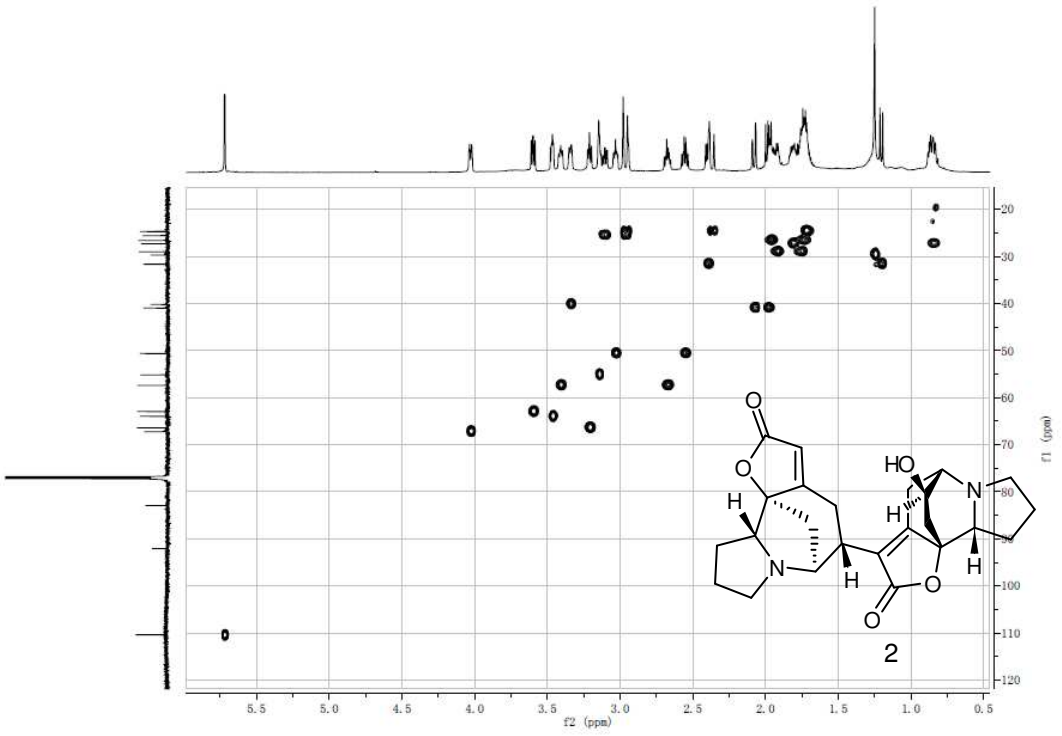
^{1}H NMR spectrum of **2** in $CDCl_3$



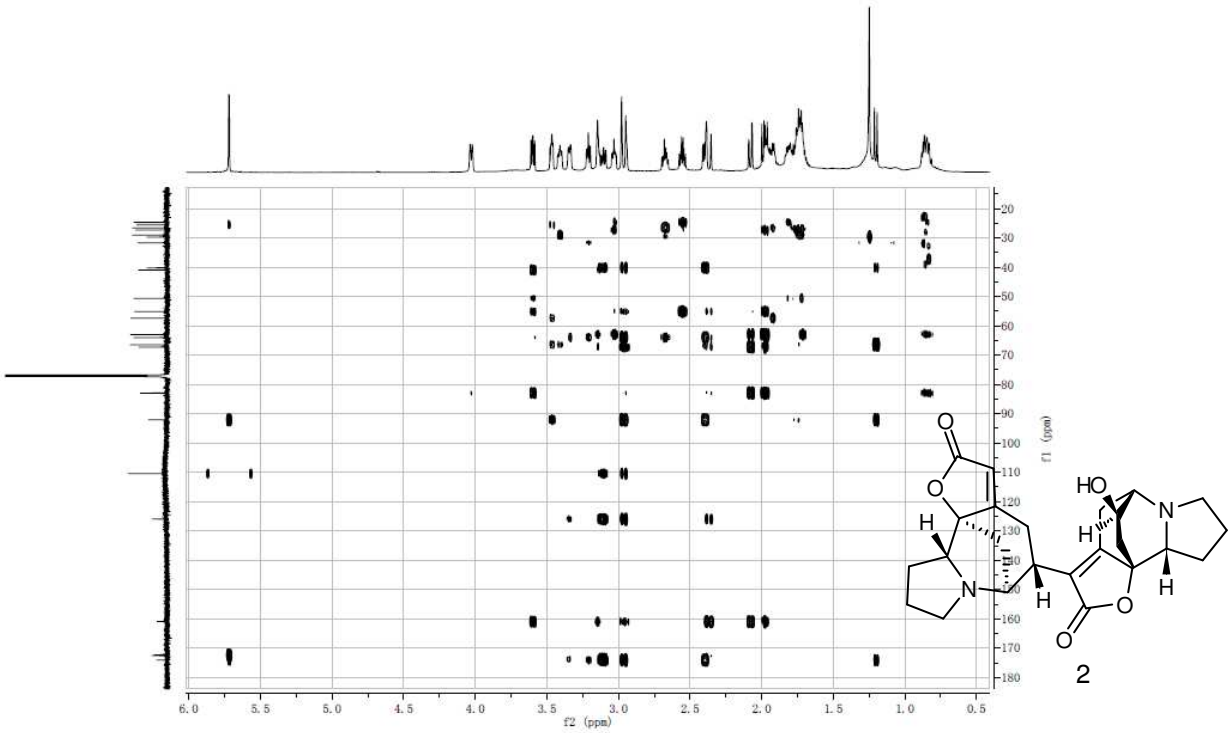
^{13}C NMR spectrum of **2** in $CDCl_3$



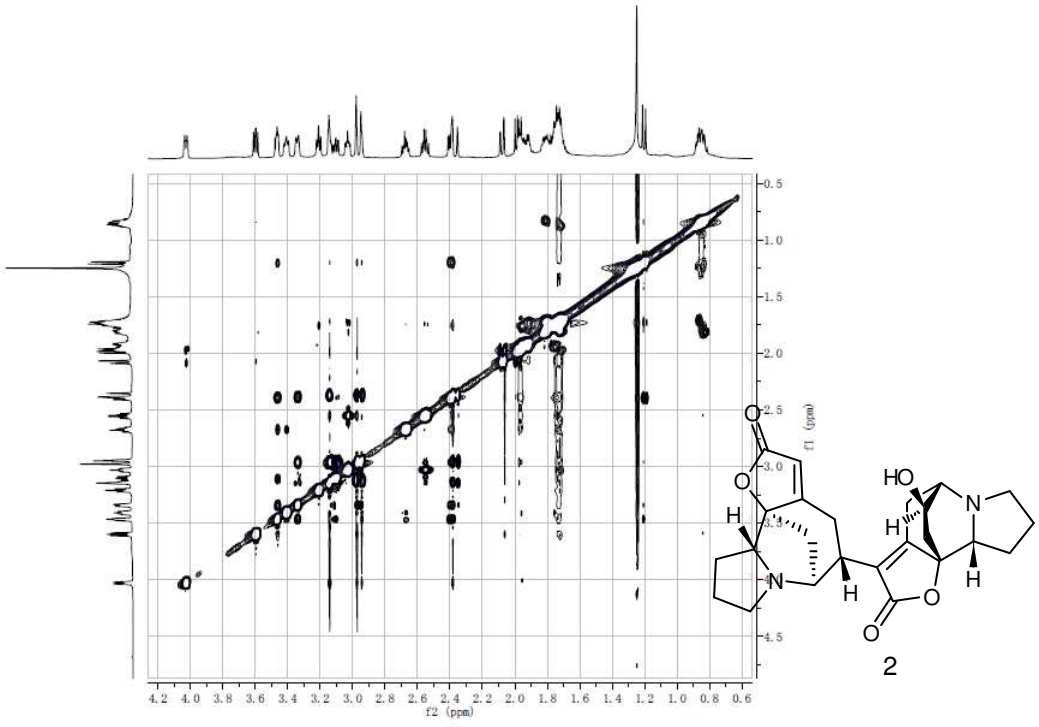
^{1}H-^{1}H COSY spectrum of **2** in $CDCl_3$



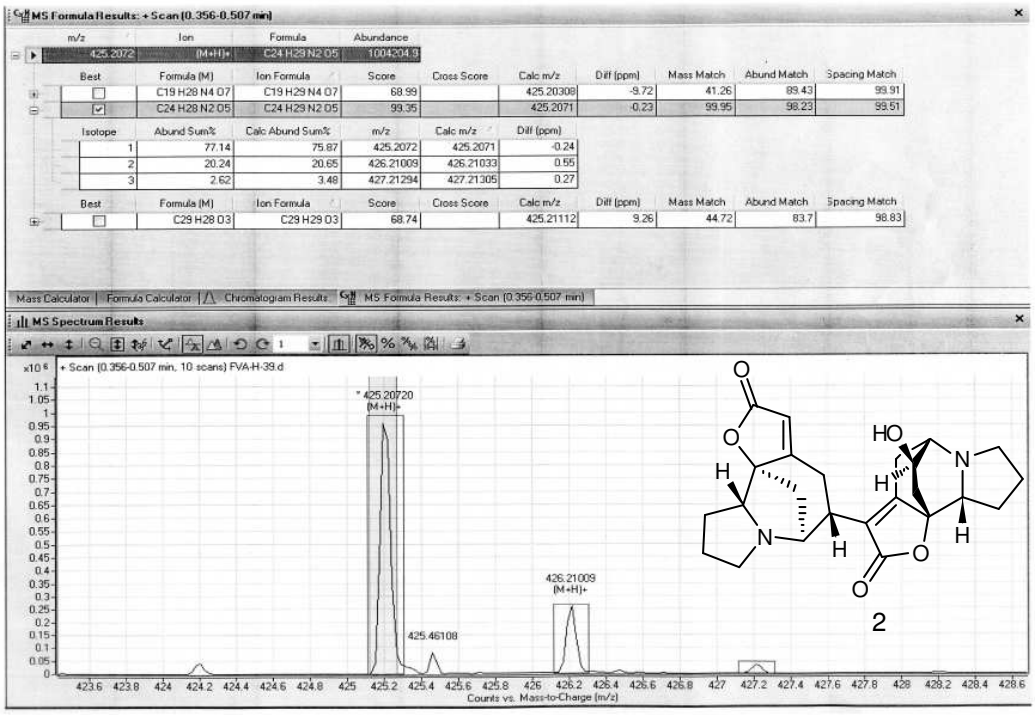
HSQC spectrum of **2** in $CDCl_3$



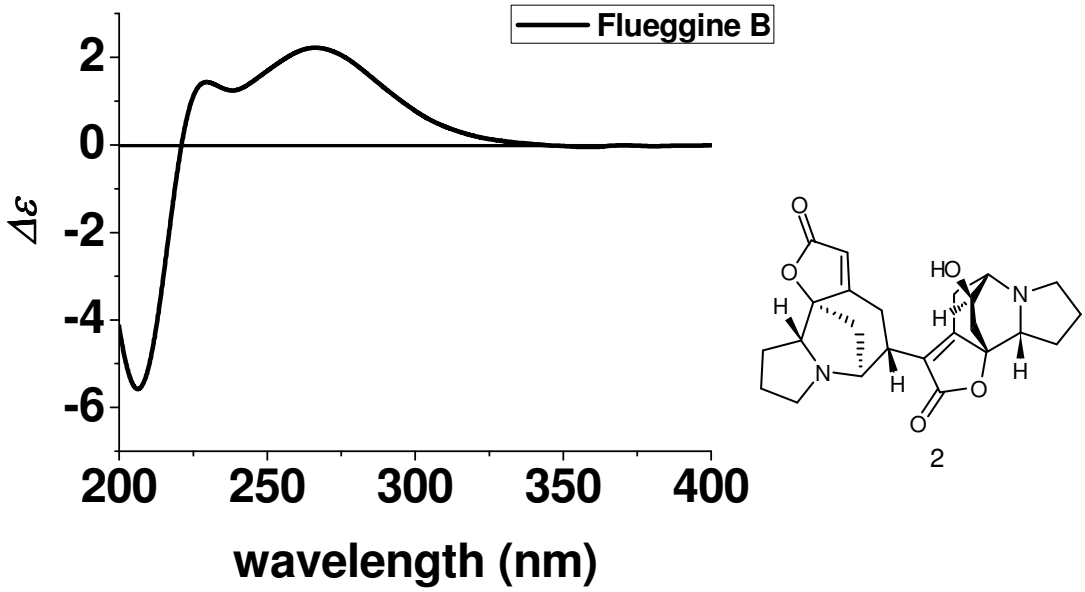
HMBC spectrum of **2** in $CDCl_3$



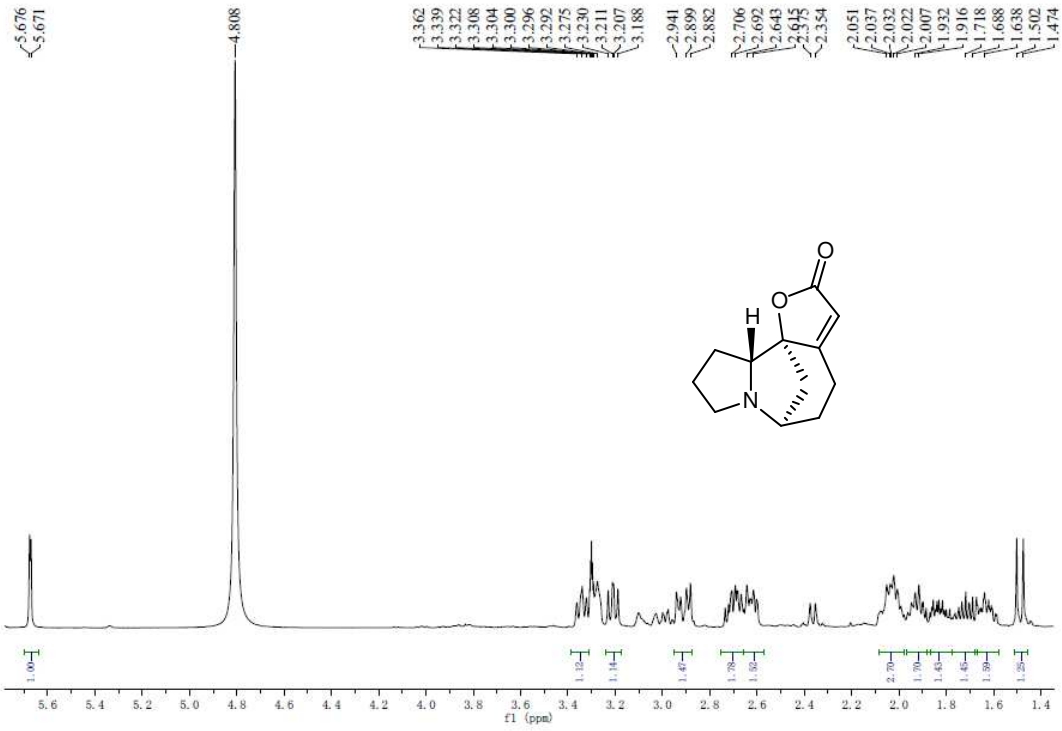
ROESY spectrum of **2** in $CDCl_3$



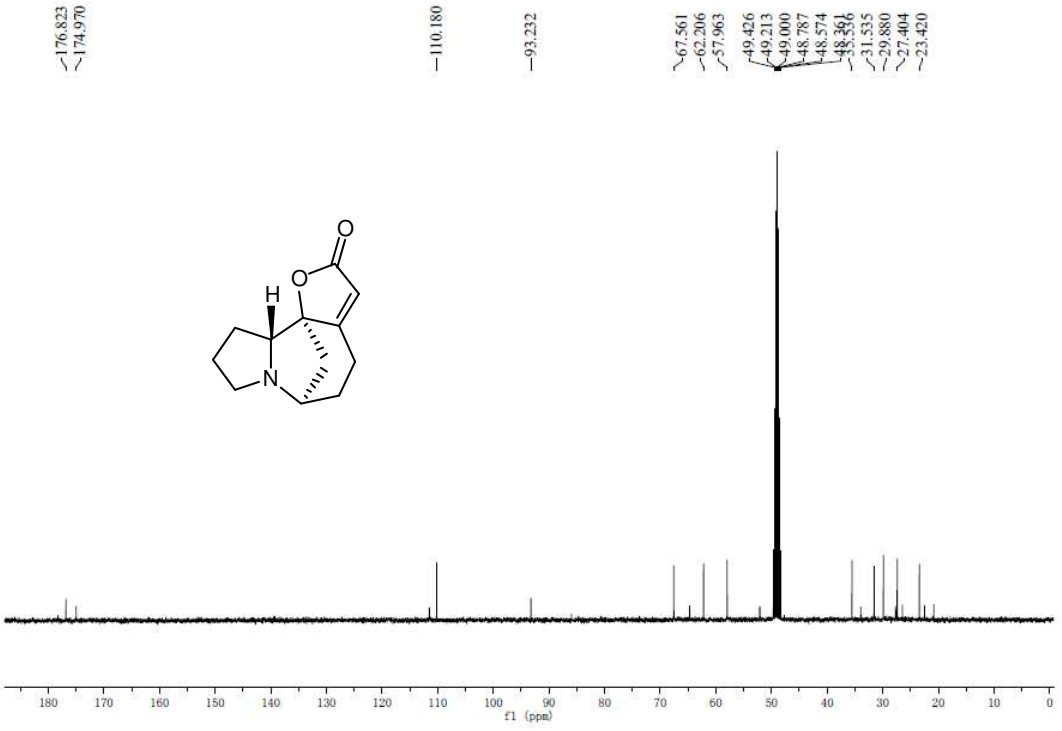
HR-ESI-MS spectrum of **2**



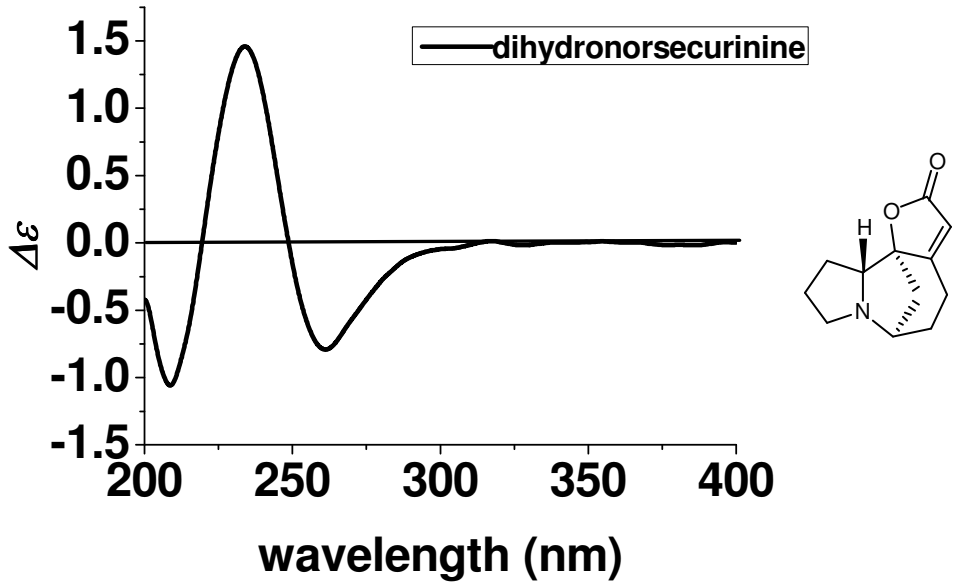
CD spectrum of **2** (CH_3OH)



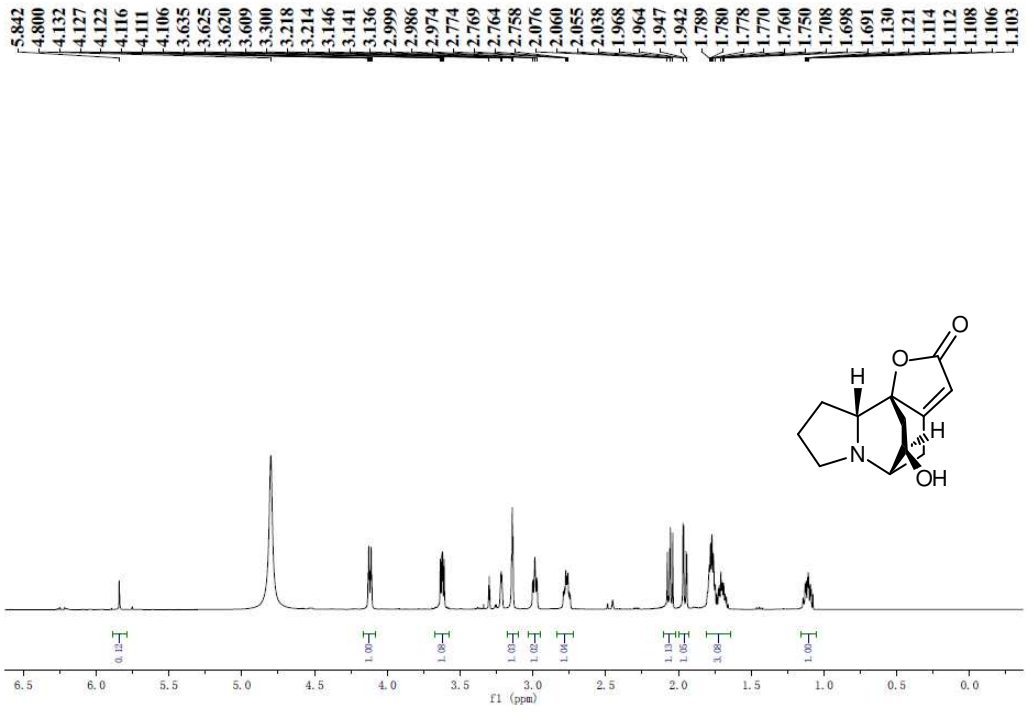
^{1}H NMR spectrum of dihydronorsecurinine in CD_3OD



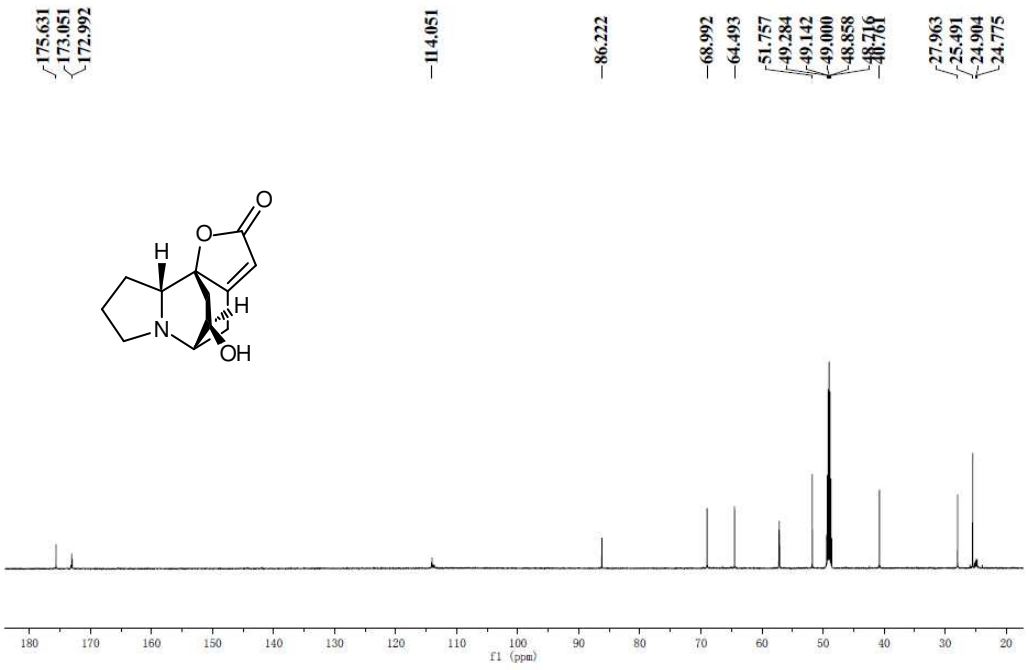
^{13}C NMR spectrum of dihydronorsecurinine in CD_3OD



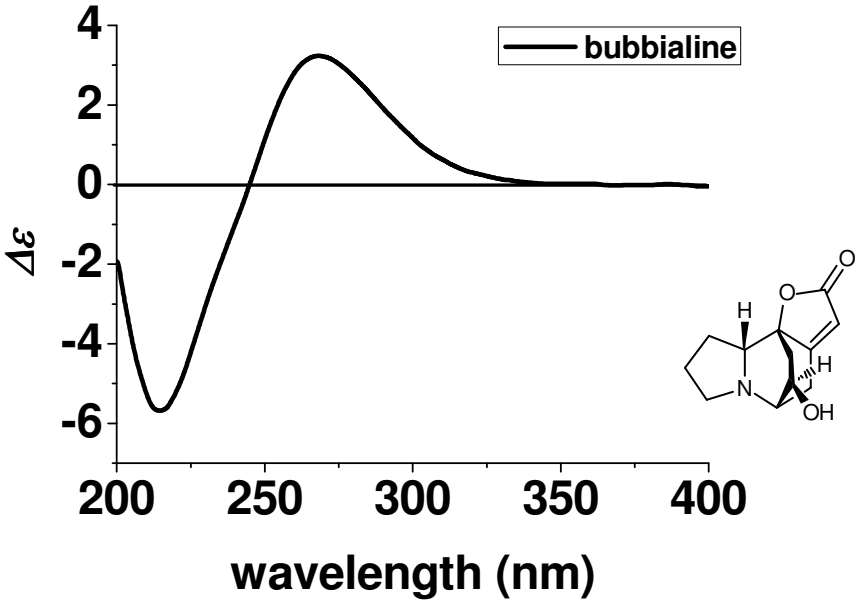
CD spectrum of dihydronorsecurinine (CH_3OH)



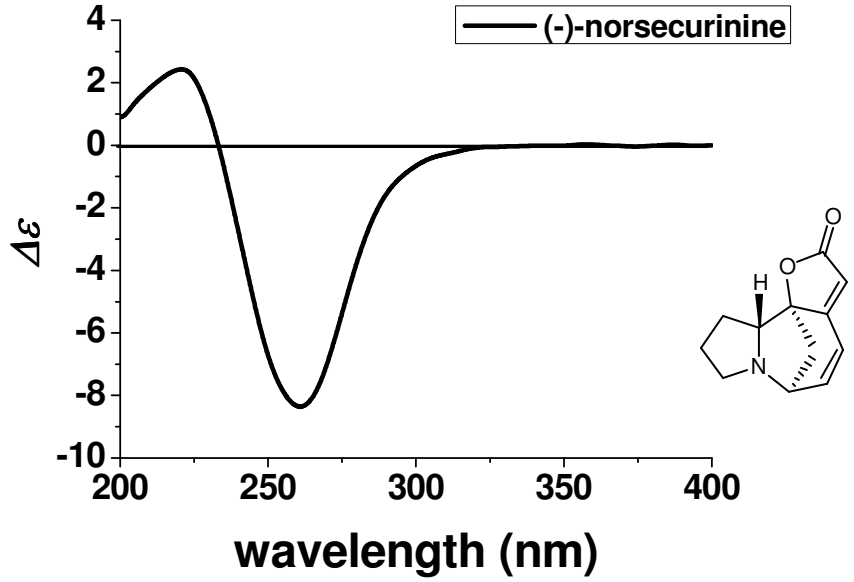
^1H NMR spectrum of bubbialine in CD_3OD



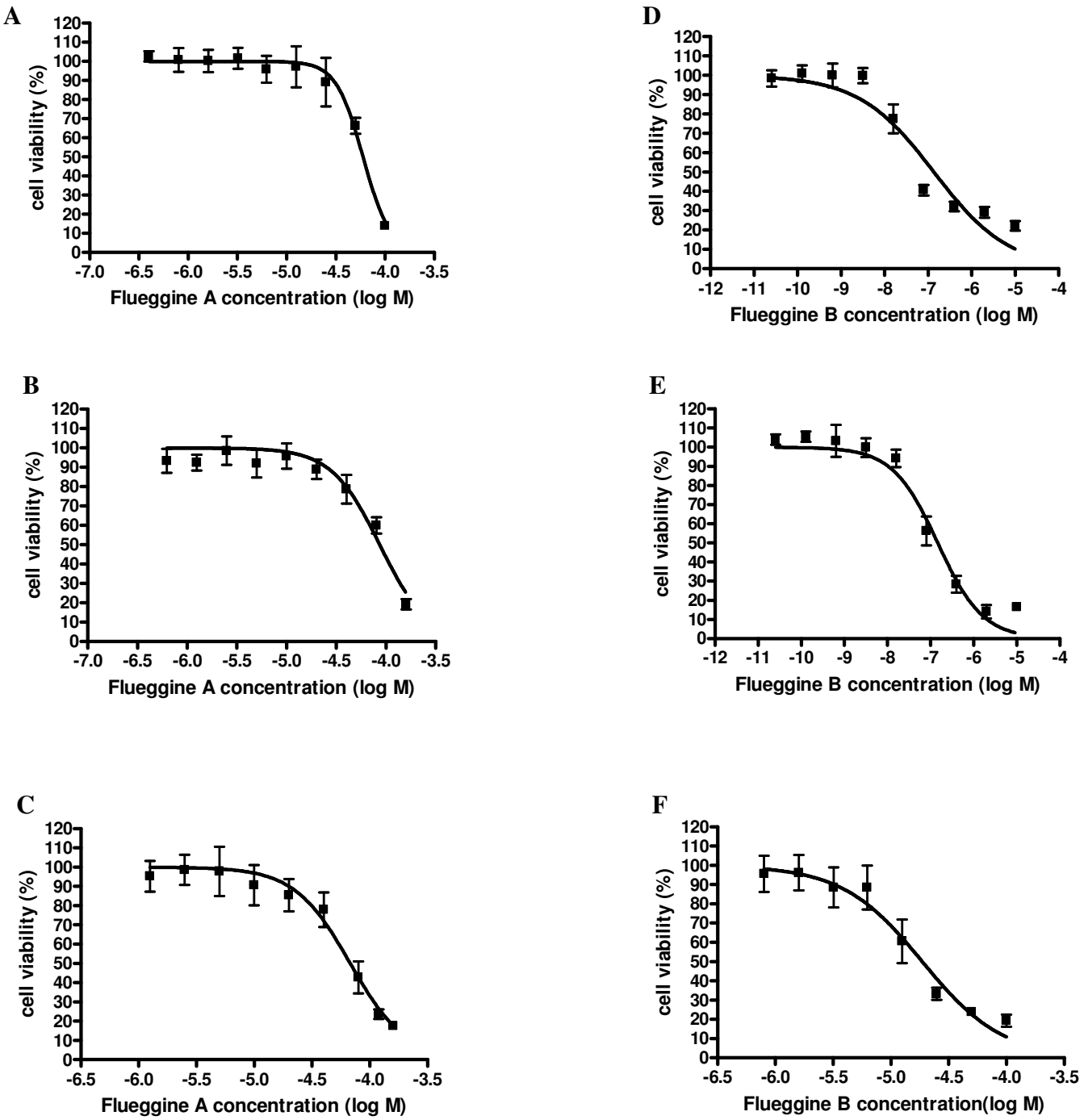
^{13}C NMR spectrum of bubbialine in CD_3OD



CD spectrum of bubbialine (CH_3OH)



CD spectrum of (-)-norsecurinine (CH_3OH)



Drug sensitivity to breast cancer cells was analyzed by MTT assay. The survival curves of MCF-7 (A and D), MDA-MB-231 (B and E) and MCF-7/ADR (C and F) cells at the different concentrations of **1** (flueggine A) and **2** (flueggine B). Data points are the means ± SD of six replicates. Representative curves of three independent experiments are shown.