Supporting Online Material for

Total Synthesis of Schilancidilactones A, B and Schilancitrilactone A, 20-*epi*-Schilancitrilactone A via Late-stage Nickel-catalyzed cross coupling

Hengtao Wang, Xiunan Zhang and Pingping Tang*

*To whom correspondence should be addressed. E-mail: ptang@nankai.edu.cn

Table of contents

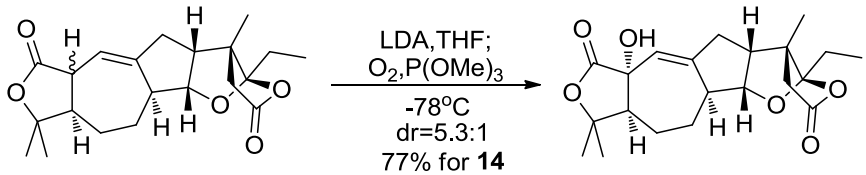
Materials and Methods

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Tetrahydrofuran (THF), toluene and 1,4–dioxane were distilled immediately before use from sodium–benzophenone ketyl. Methylene chloride (CH_2Cl_2), triethylamine (Et_3N), *N*, *N*–dimethylformide (DMF) were distilled from calcium hydride and stored under an argon atmosphere. Methanol (MeOH) was distilled from magnesium and stored under an argon atmosphere. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvents for chromatography were used as supplied by Tianjin Reagents chemical. Reactions were monitored by thin layer chromatography (TLC) carried out on silica gel Huanghai HSGF254 plates using UV light as visualizing agent and aqueous phosphomolybdic acid or basic aqueous potassium permanganate as developing agent. 200–300 mesh silica gel purchased from Qingdao Haiyang Chemical Co., China was used for flash column chromatography. Semipreparative HPLC was performed on an UltiMate 3000 liquid chromatography with a Thermo HG–C18, 21.2 mm × 15 cm column. NMR spectra were recorded on Bruker AVANCE AV 400 (400MHz, 101MHz and 376MHz) instrument and calibrated by using residual undeuterated chloroform (δ_H=7.26 ppm) and $CDCl_3$ (δ_C=77.16 ppm) as internal references. The following abbreviations are used to designate multiplicities: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, quint=quintet, br=broad. IR spectra were recorded on a Bruker Tensor 27 instrument. High–resolution mass spectra (HRMS) were obtained on Varian 7.0T FTMS. Circular dichroism spectra (CD) were obtained from JASCO J–715 Spectropolarmeter. Optical rotations were measured with an Insmark IP 120 digital polarimeter. X–ray diffraction was realized on a Rigaku 007 Saturn 70 instrument.

Experimental Data

Experimental Procedures and Compound Characterization

Synthesis of compound 14

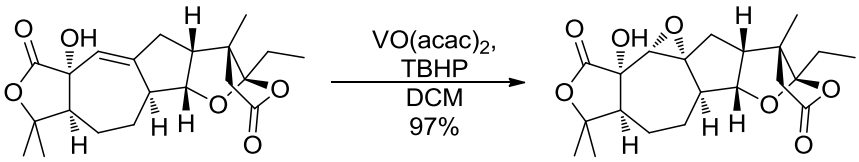


9 **14**

To a stirred solution of compounds **9**[1] (138 mg, 0.382 mmol, 1.00 equiv) in THF (13.8 mL) was slowly added LDA (lithium *N*, *N*-diisopropylamide) (2.0 M in THF, 0.57 mL, 1.16 mmol, 3.00 equiv) at –78 ℃ under the atmosphere of N_2. 30 min later, the reaction mixture was degassed with O_2 for 3 times followed by addition of $P(OMe)_3$ (89.4 μL, 0.764 mmol, 2.00 equiv). After stirring for 3 h, the reaction was quenched with saturated aqueous NH_4Cl. The resulting mixture was extracted with EtOAc (3 × 10.0 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc: petroleum

ether = 1/5 to 1/2) to give the product **14** (110 mg, 0.294 mmol, dr=5.3:1, 77% yield for **14**); **14**: R_f = 0.4 (silica, EtOAc: petroleum ether = 1:1); $[\alpha]_D^{25}$ = 59.0 (*c* = 0.42 in $CHCl_3$); IR (film): ν_{max} = 3435, 2961, 2926, 2855, 1766, 1680, 1462, 1452, 1388, 1374, 1260, 1122, 1089, 1024, 937, 906, 894, 798, 758, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.74 (s, 1H), 4.32 (d, *J* = 2.6 Hz, 1H), 3.10 (t, *JJ* = 7.9 Hz, 1H), 2.74 (d, *J* = 18.5 Hz, 1H), 2.58 (d, *J* = 18.1 Hz, 2H), 2.54–2.42 (m, 3H), 2.36 (dd, *J* = 11.3, 4.1 Hz, 1H), 2.12–1.99 (m, 1H), 1.83–1.73 (m, 3H), 1.52 (s, 3H), 1.51–1.41 (m, 1H), 1.36–1.29 (m, 1H), 1.28 (s, 3H), 1.24 (s, 3H), 1.11 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.9, 174.0, 152.2, 120.7, 119.2, 89.7, 85.2, 77.3, 53.6, 53.3, 50.0, 45.3, 45.1, 35.3, 29.2, 29.2, 25.0, 24.6, 22.2, 19.5, 7.8. HRMS (m/z): $[M+H]^+$ calcd for $C_{21}H_{28}O_6H^+$ 377.1964, found 377.1959.

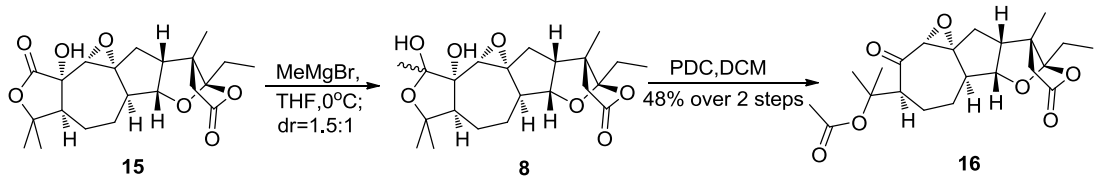
Synthesis of compound 15



14 **15**

To a round–bottom flask covered with tinfoil was added compound **14** (173 mg, 0.458 mmol, 1.00 equiv) and $VO(acac)_2$ (35.2 mg, 0.138 mmol, 0.30 equiv), DCM (8.0 mL). A solution of TBHP (25% v/v in DCM, 2.0 mL, 5.50 mmol, 12.0 equiv) was slowly added to the reaction mixture. After stirring for 3.5 hours, TLC showed the disappearance of the starting material and the reaction mixture was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 2/3 to 1/1) to give the product **15** (174 mg, 0.444 mmol, 97% yield); **15**: R_f = 0.4 (silica, EtOAc: petroleum ether = 2:1); $[\alpha]_D^{25}$ = 32.1 (*c* = 0.23 in $CHCl_3$); IR (film): ν_{max} = 3474, 3455, 2959, 2925, 2854, 1769, 1652, 1636, 1464, 1376, 1261, 1238, 1089, 1070, 1051, 1024, 938, 799, 778, 761, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.40 (d, *J* = 5.5 Hz, 1H), 3.34 (s, 1H), 3.24 (s, 1H), 2.79–2.69 (m, 2H), 2.63–2.52 (m, 2H), 2.35–2.19 (m, 2H), 1.97–1.65 (m, 5H), 1.56–1.43 (m, 3H), 1.52(s, 3H), 1.38 (ddd, *J* = 13.1, 8.4, 4.0 Hz, 1H), 1.32 (s, 3H), 1.25 (s, 3H), 1.14 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 173.8, 120.6, 89.4, 84.2, 74.2, 68.4, 56.6, 53.6, 52.4, 50.9, 45.6, 43.8, 33.4, 29.1, 28.4, 25.9, 24.8, 22.5, 19.6, 7.7. HRMS (m/z): $[M+H]^+$ calcd for $C_{21}H_{28}O_7H^+$ 393.1902, found 393.1908.

Synthesis of compound 16

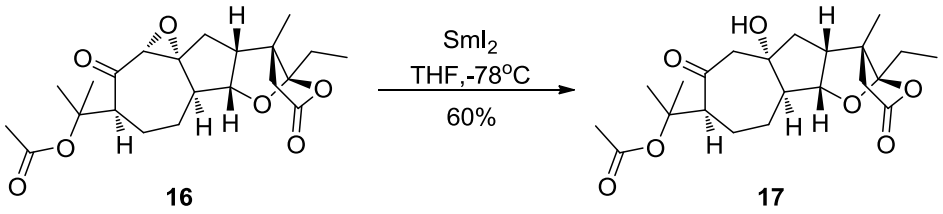


15 **8** **16**

To a stirred solution of compound **15** (174 mg, 0.444 mmol, 1.00 equiv) in THF (17 mL) was slowly added MeMgBr (1.0 M in THF, 1.0 mL, 1.02 mmol, 2.30 equiv) at 0 ℃ under the atmosphere of N_2. 3 hours later, the reaction mixture was quenched with MeOH (1 mL). The resulting mixture was carefully evaporated under reduced pressure. The remainder was filtered with silica gel (EtOAc), and the solvent was evaporated to give the crude product **8**

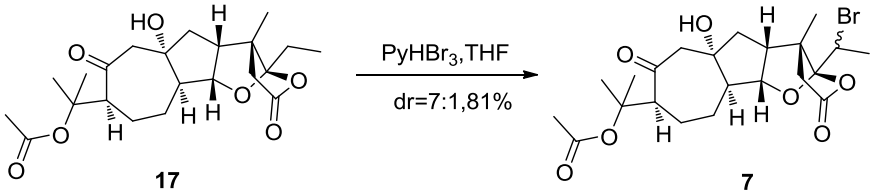
(dr=1.5:1). To a stirred solution of compounds **8** in DCM (17 mL) was slowly added PDC (500 mg, 1.33 mmol, 3.00 equiv). After stirring for 3 hours, the reaction mixture was filtered through silica gel and the residue was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 1/4 to 2/1) to give the product **16** (86.7 mg, 0.213 mmol, 48% yield over 2 steps) and recovering of the material **15** (26.1 mg, 0.067 mmol, 15% yield); **16**: R_f = 0.4 (silica, EtOAc: petroleum ether = 1:1); $[\alpha]_D^{25}$ = 12.0 (*c* = 0.38 in $CHCl_3$); IR (film): ν_{max} = 2924, 2850, 1768, 1729, 1711, 1463, 1454, 1368, 1250, 1124, 1021, 939, 914, 758, 711, 666, 607, 506, 466 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.27 (d, *J* = 4.5 Hz, 1H), 3.70 (s, 1H), 3.55 (t, *J* = 9.4 Hz, 1H), 3.32 (s, 1H), 2.74 (brd, *J* = 18.8 Hz, 1H), 2.61 (brd, *J* = 18.8 Hz, 1H), 2.56–2.47 (m, 2H), 2.14 (dd, *J* = 14.2, 11.0 Hz, 1H), 2.07–1.89 (m, 2H), 1.95 (s, 3H), 1.86–1.76 (m, 2H), 1.72–1.56 (m, 5H), 1.55 (s, 3H), 1.26 (s, 3H), 1.16 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 173.9, 170.3, 119.7, 88.9, 83.0, 72.5, 67.8, 52.4, 50.3, 48.1, 45.8, 44.9, 35.6, 29.6, 28.8, 24.2, 24.0, 24.0, 22.6, 19.7, 7.8. HRMS (m/z): $[M+H]^+$ calcd for $C_{22}H_{30}O_7H^+$ 407.2059, found 407.2064.

Synthesis of compound 17



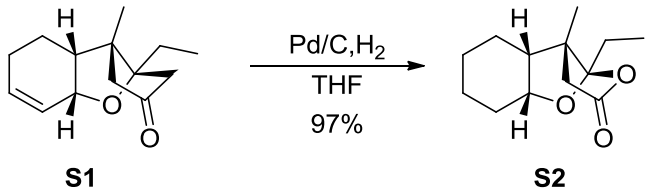
To a stirred solution of compound **16** (32.0 mg, 0.079 mmol, 1.00 equiv) in THF (1.5 mL) was slowly added freshly prepared SmI_2[2] (0.1 M in THF, 1.7 mL, 0.170 mmol, 2.10 equiv) at –78 ℃ under the atmosphere of N_2. 5 hours later, TLC showed the disappearance of the starting material and the reaction was quenched with saturated aqueous NH_4Cl. The resulting mixture was extracted with EtOAc (3 × 5.0 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 2/3 to 1/1) to give the product **17** (19.4 mg, 0.047 mmol, 60% yield); **17**: R_f = 0.4 (silica, EtOAc: petroleum ether = 2:1); $[\alpha]_D^{25}$ = –53.2 (*c* = 0.32 in $CHCl_3$); IR (film): ν_{max} = 3468, 2961, 2925, 2857, 1766, 1730, 1695, 1463, 1453, 1387, 1369, 1258, 1213, 1160, 1131, 1109, 1090, 1021, 938, 918, 876, 799, 758, 666, 616 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.58 (dd, *J* = 7.7, 5.9 Hz, 1H), 3.14 (d, *J* = 11.5 Hz, 1H), 2.81 (s, 1H), 2.78 (dd, *J* = 11.1, 5.9 Hz, 1H), 2.70 (brd, *J* = 17.8 Hz, 1H), 2.56 (brd, *J* = 17.8 Hz, 1H), 2.48–2.38 (m, 1H), 2.28 (dd, *J* = 11.5, 1.1 Hz, 1H), 2.23–2.17 (m, 1H), 2.10–1.90 (m, 5H), 1.91–1.68 (m, 5H), 1.52 (s, 3H), 1.48 (s, 3H), 1.20 (s, 3H), 1.10 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.4, 173.6, 170.0, 122.0, 84.3, 82.4, 81.0, 62.6, 53.8, 50.3, 50.1, 49.9, 46.0, 41.9, 28.0, 25.0, 24.7, 23.5, 22.5, 19.7, 19.1, 7.6. HRMS (m/z): $[M+H]^+$ calcd for $C_{22}H_{32}O_7H^+$ 409.2218, found 409.2221.

Synthesis of compound 7



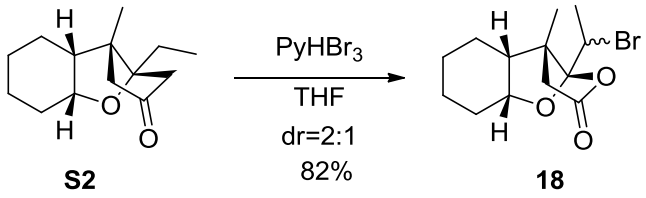
To a stirred solution of compound **17** (19.3 mg, 0.0473 mmol, 1.00 equiv) in THF (1.9 mL) at room temperature was added $PyHBr_3$ (18 mg, 0.0567 mmol, 1.20 equiv). Stirring continued for 30 min, TLC showed the disappearance of the starting material and the organic solvent was removed under reduced pressure to give the crude product **7**. Crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 2/3 to 1/1) to give a mixture of compounds **7** (18.6 mg, 0.0383 mmol, 81% yield; dr=7:1); **7-Major**: R_f = 0.3 (silica, EtOAc: petroleum ether = 2:1); $[\alpha]_D^{25}$ = –61.1 (*c* = 0.13 in $CHCl_3$); IR (film): ν_{max} = 3413, 2958, 2924, 2853, 1769, 1731, 1696, 1462, 1376, 1260, 1215, 1097, 1019, 950, 922, 859, 800, 761, 696, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.66–4.55 (m, 1H), 4.34–4.22 (m, 1H), 3.15 (d, *J* = 11.5 Hz, 1H), 2.88–2.69 (m, 4H), 2.51–2.39 (m, 1H), 2.36–2.20 (m, 3H), 2.08–1.73 (m, 10H), 1.52 (d, *J* = 9.8 Hz, 4H), 1.48 (d, *J* = 9.6 Hz, 3H), 1.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.3, 172.7, 170.0, 119.1, 84.5, 82.4, 81.0, 77.4, 62.7, 53.4, 52.0, 51.2, 50.3, 47.5, 41.8, 25.0, 24.7, 23.6, 22.5, 21.4, 19.9, 19.5.HRMS (m/z): $[M+H]^+$ calcd for $C_{22}H_{31}BrO_7H^+$ 487.1326, found 487.1323.

Synthesis of compound S2



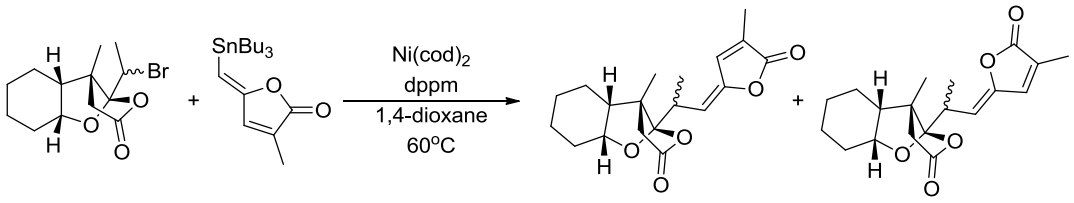
To a round bottom flask was added compound **S1**[1] (830.1 mg, 3.74 mmol, 1.00 equiv) and Pd/C (79.5 mg, 0.747 mmol, 0.20 equiv). The flask was degassed with H_2 for 3 times and THF (25 mL) was added. 3 hours later, the mixture was filtered with Celite pad and the solvent was removed under reduced pressure to give the crude product **S2**. Crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 1/10 to 1/5) to give compound **S2** (816 mg, 3.63 mmol, 97% yield); **S2**: R_f = 0.3 (silica, EtOAc: petroleum ether = 1:5); $[\alpha]_D^{25}$ = 23.1 (*c* = 0.63 in $CHCl_3$); IR (film): ν_{max} = 2940, 2882, 2857, 1778, 1466, 1446, 1422, 1365, 1299, 1272, 1262, 1234, 1196, 1166, 1124, 1093, 1051, 1019, 983, 952, 940, 872, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.19 (d, *J* = 2.9 Hz, 1H), 2.74 (brd, *J* = 19.0 Hz, 1H), 2.53 (brd, *J* = 19.0 Hz, 1H), 2.11 (dd, *J* = 15.7, 2.7 Hz, 1H), 1.86–1.72 (m, 3H), 1.72–1.66 (m, *J* = 8.5 Hz, 3H), 1.64–1.45 (m, 1H), 1.44–1.31 (m, 1H), 1.19 (s, 3H), 1.17–1.05 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 119.1, 74.1, 51.0, 49.0, 45.2, 29.6, 27.4, 24.4, 24.3, 20.1, 18.9, 8.0. HRMS (m/z): $[M+H]^+$ calcd for $C_{13}H_{20}O_3H^+$ 225.1485, found 225.1485.

Synthesis of compound 18



To a stirred solution of compound **S2** (816 mg, 3.65 mmol, 1.00 equiv) in THF (40 mL) was added $PyHBr_3$ (1.39 g, 4.37 mmol, 1.20 equiv). Stirring continued for 20 min before the organic solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (silica, EtOAc: petroleum ether = 1:10 to 1:5) to give the diastereisomers of compounds **18** (920 mg, 3.03 mmol, 82%, 2:1). **18-Major**: R_f = 0.3 (silica, EtOAc: petroleum ether = 1:5); $[\alpha]_D^{25}$ = –15.3 (*c* = 0.80 in $CHCl_3$); IR (film): ν_{max} = 2930, 2869, 1771, 1452, 1419, 1377, 1260, 1238, 1200, 1164, 1089, 1071, 1040, 1025, 980, 953, 865, 800, 741, 658 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.28–4.14 (m, 2H), 2.79 (brd, *J* = 19.1 Hz, 1H), 2.66 (brd, *J* = 19.1 Hz, 1H), 2.18–2.08 (m, 1H), 1.90 (d, *J* = 6.9 Hz, 3H), 1.87–1.81 (m, 1H), 1.77–1.45 (m, 6H), 1.44 (s, 3H), 1.21–1.07 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 117.2, 74.8, 52.6, 49.8, 47.2, 46.5, 27.5, 24.1, 23.6, 22.1, 20.2, 19.3. HRMS (m/z): $[M+H]^+$ calcd for $C_{13}H_{19}BrO_3H^+$ 303.0592, found 303.0590.

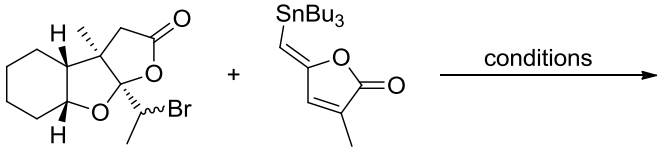
Synthesis of compound 19 and 19'



Compound **18** (10 mg, 0.0330 mmol, 1.00 equiv), **6** (132 mg, 0.330 mmol, 10.0 equiv), bis(diphenylphosphino)methane (7.6 mg, 0.0185 mmol, 0.60 equiv) , $Ni(cod)_2$ (3.6 mg, 0.0123 mmol, 0.40 equiv) and 1,4-dioxane (0.2 mL) were added to a 2.0 mL sealed vial in the glove box. The reaction mixture was heated to 60 ℃, and stirring continued for 12 hours. The mixture was directly purified by the silica gel column chromatography (EtOAc: petroleum ether = 1:10 to 1:3) to give the compound **19'-Major** (2.6 mg, 0.00792 mmol, 24% yield), **19 – Major** (2.4 mg, 0.0726 mmol, 22% yield) and a mixture of **19'-Minor** and **19-Minor**. Further purification was carried through preparative TLC (DCM as developing solvent) to yield **19'-Minor** (R_f = 0.1, 2.0 mg, 0.0594 mmol, 18% yield) and **19-Minor** (R_f = 0.2, 1.5 mg, 0.0462 mmol, 14% yield). **19'-Major**: R_f = 0.1 (silica, EtOAc: petroleum ether = 1:1); $[\alpha]_D^{25}$ = –28.31 (*c* = 0.47 in $CHCl_3$); IR (film): ν_{max} = 2929, 2867, 1766, 1667, 1452, 1378, 1260, 1058, 1019, 937, 867, 800, 759, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 5.74 (d, *J* = 11.0 Hz, 1H), 4.18 (s, 1H), 3.01–2.91 (m, 1H), 2.77 (brd, *J* = 19.1 Hz, 1H), 2.59 (brd, *J* = 19.1 Hz, 1H), 2.96 (dq, *J* = 13.6, 6.8 Hz, 1H), 2.04 (s, 3H), 1.82–1.69 (m, 2H), 1.64–1.48 (m , 4H), 1.33 (d, *J* = 6.8 Hz, 3H), 1.21 (s, 3H), 1.16–1.05 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 170.7, 148.5, 133.3, 131.9, 118.4, 114.3, 76.8, 52.4, 49.5, 46.1, 37.8, 27.3, 24.3, 24.1, 20.3, 19.5, 18.1, 11.1. HRMS (m/z): $[M+H]^+$ calcd for $C_{19}H_{25}O_5H^+$ 333.1697, found 333.1697. **19'-Minor**: R_f = 0.3 (silica, EtOAc: petroleum ether = 1:1); $[\alpha]_D^{25}$ = 81.77 (*c* = 0.26

in $CHCl_3$); IR (film): ν_{max} = 3093, 2960, 2925, 2852, 1765, 1668, 1457, 1376, 1260, 1229, 1163, 1089, 1056, 1045, 1018, 955, 933, 859, 800, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 5.62 (d, *J* = 10.7 Hz, 1H), 4.18 (d, *J* = 2.8 Hz, 1H), 2.98 (dq, *J* = 13.8, 6.9 Hz, 1H), 2.73 (brd, *J* = 19.1 Hz, 1H), 2.54 (brd, *J* = 19.1 Hz, 1H), 2.14–2.05 (m, 1H), 2.04 (s, 3H), 1.80–1.74 (m, 1H), 1.75–1.68 (m, 1H), 1.68–1.46 (m, 4H), 1.34 (d, *J* = 6.9 Hz, 3H), 1.18 (s, 3H), 1.17–1.08 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 170.5, 149.2, 133.3, 132.1, 117.9, 113.0, 74.0, 52.1, 49.6, 45.3, 38.6, 27.4, 24.6, 24.2, 20.19, 18.0, 11.1. HRMS (m/z): $[M+H]^+$ calcd for $C_{19}H_{25}O_5H^+$ 333.1697, found 333.1696. **19-Minor**: R_f = 0.1 (silica, EtOAc: petroleum ether = 1:1); $[\alpha]_D^{25}$ = –44.03 (*c* = 0.40 in $CHCl_3$); IR (film): ν_{max} = 3061, 2927, 2853, 1768, 1675, 1457, 1420, 1377, 1258, 1236, 1215, 1087, 1055, 1015,990, 951, 932, 801, 756, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 0.9 Hz, 1H), 5.19 (d, *J* = 10.3 Hz, 1H), 4.19 (d, *J* = 2.8 Hz, 1H), 3.35 (dq, *J* = 10.3, 6.8 Hz, 1H), 2.73 (brd, *J* = 19.1 Hz, 1H), 2.48 (brd, *J* = 19.0 Hz, 1H), 2.16–2.07 (m, 1H), 2.00 (s, 3H), 1.80–1.67 (m, 2H), 1.68–1.60 (m, 1H), 1.57–1.47 (m, 2H), 1.42–1.34 (m, 1H), 1.30 (d, *J* = 6.8 Hz, 3H), 1.26–1.20 (m, 1H), 1.16 (s, 3H), 1.13–1.06 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 170.9, 147.9, 137.8, 130.1, 118.3, 113.7, 74.1, 52.0, 49.4, 45.1, 38.1, 27.5, 24.5, 24.2, 20.2, 19.3, 16.6, 10.7. HRMS (m/z): $[M+H]^+$ calcd for $C_{19}H_{25}O_5H^+$ 333.1697, found 333.1700. **19-Major**: R_f = 0.5 (silica, EtOAc: petroleum ether = 1:1); $[\alpha]_D^{25}$ = 108.12 (*c* = 0.78 in $CHCl_3$); IR (film): ν_{max} = 3061, 2928, 2868, 1766, 1676, 1620, 1458, 1421, 1378, 1313, 1293, 1260, 1241, 1213, 1163, 1093, 1055, 1016, 989, 962, 935, 800, 757, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 1.4 Hz, 1H), 5.31 (d, *J* = 10.3 Hz, 1H), 4.15 (dd, *J* = 6.4, 3.2 Hz, 1H), 3.38 (dq, *J* = 10.3, 6.8 Hz, 1H), 2.74 (brd, *J* = 19.1 Hz, 1H), 2.59 (brd, *J* = 19.0 Hz, 1H), 2.10–2.02 (m, 1H), 2.00 (d, *J* = 1.0 Hz, 3H), 1.81–1.74 (m, 1H), 1.73–1.66 (m, 1H), 1.61–1.43 (m, 3H), 1.32–1.27 (m, 1H), 1.25 (d, *J* = 5.3 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H), 1.20–1.05 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 170.9, 147.8, 138.0, 130.0, 118.7, 114.9, 74.4, 52.1, 49.6, 45. 7, 37.2, 27.4, 24.2, 24.2, 20.3, 19.3, 16.5, 10.7. HRMS (m/z): $[M+H]^+$ calcd for $C_{19}H_{25}O_5H^+$ 333.1697, found 333.1697.

Reactions performed according to former references

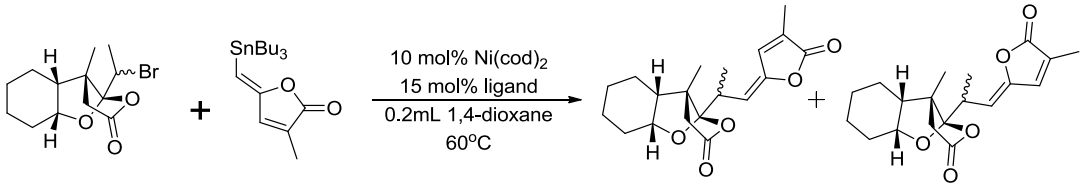


18 **6**

Table S1: Reactions performed according to former references

Entry	Condition	Yield/%
1	AIBN, Toluene, 80 ℃[5]	ND
2	Et_3B, Et_2O, O_2, N_2[6]	ND
3	$Ir(ppy)_3$, MeCN, hν, N_2[7]	ND
4	Zn, CuI, Pyrdine, H_2O, ultrasound[8]	ND
5	$SnCl_4$,$NiCl_2$,*t*-BuOK,Pybox,*t*-BuOH,*i*-BuOH[9]	ND
6	AIBN,*n*-Bu_3SnH,NaI,4Å MS, Toluene, 100 ℃[1]	ND
7	$Ni(acac)_2$,terpyridine,1,4-dioxane[10]	trace

Effects of ligands on the reaction

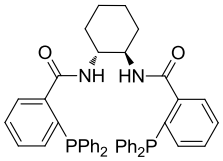


18 **6** (2.5 equiv) **19'** **19**

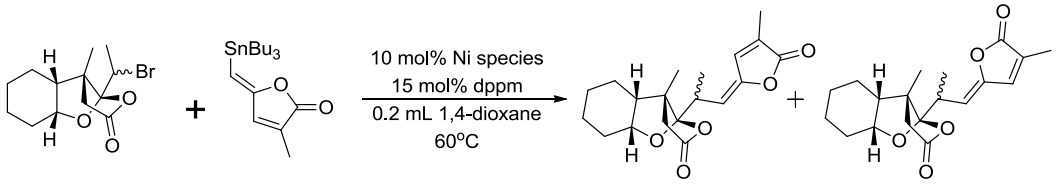
In a glove box, compound **18** (10 mg, 0.0330 mmol, 1.00 equiv), **6** (33.0 mg, 0.0825 mmol, 2.50 equiv), ligand (0.0185 mmol, 0.15 equiv), $Ni(cod)_2$ (0.9 mg, 0.0123 mmol, 0.10 equiv) and 1,4-dioxane (0.2 mL) were added to a 2.0 mL sealed vial. The reaction mixture was heated to 60 ℃, and stirring continued for 12 hours. The mixture was filtered with silica gel, and benzyl chloride (10 μL, 0.0870 mmol, 2.64 equiv) was added as internal standard.

The yields were determined by the ^{1}H NMR and reported in Table S2.

Table S2: Effects of ligands on the reaction

Ligand	**Yield/%** **(19'-major:19'-minor:19-major:19-minor)**
–	0
1,10–Phenanthroline	0
4,4',4''–tri–*tert*–butyl–2,2':6',2''–terpyridine	0
4,4'–di–*tert*–butyl–2,2'–bipyridine	0
PyBox	0
PPh_3	Trace
PCy_3	Trace
dppf	Trace
dppm	**18:10:18:10**
dppp	0
dppBz	trace
xantphos	0
Butyldi–1–adamantylphosphine	0
IPrHCl (0.15 equiv t–BuOK was added)	0
	2:2:2:2

Effects of Ni species on the reaction



18 **6** (2.5 equiv) **19'** **19**

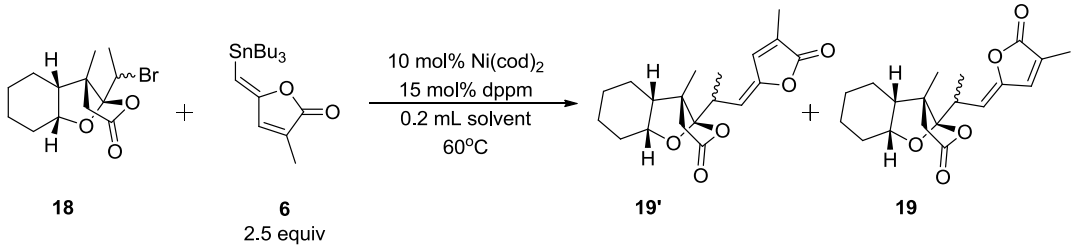
In a glove box, compound **18** (10 mg, 0.0330 mmol, 1.00 equiv), **6** (33.0 mg, 0.0825 mmol,

2.50 equiv), dppm (1.9 mg, 0.0185 mmol, 0.15 equiv), Ni species (0.0123 mmol, 0.10 equiv) and 1,4-dioxane (0.2 mL) were added to a 2.0 mL sealed vial. The reaction mixture was heated to 60 ℃, and stirring continued for 12 hours. The mixture was filtered with silica gel, and benzyl chloride (10 μL, 0.0870 mmol, 2.64 equiv) was added as internal standard. The yields were determined by the ^{1}H NMR and reported in Table S3.

Table S3: Effects of Ni species on the reaction

Ni species	Yield/% (19'-major:19'-minor:19-major:19-minor)
$Ni(cod)_2$	**18:10:18:10**
$NiCl_2$	0
$Ni(acac)_2$	0
$NiCl_2$ glycol	0
$NiBr_2$	0
NiO	0

Effects of solvents on the reaction

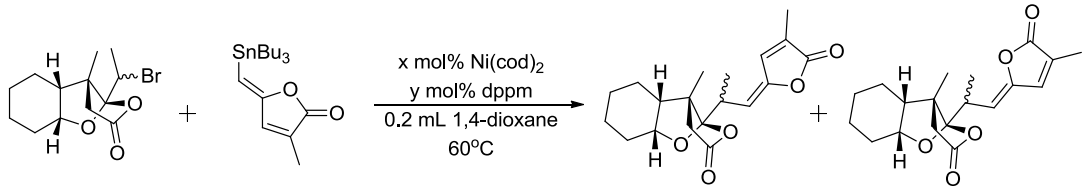


In a glove box, compound **18** (10 mg, 0.0330 mmol, 1.00 equiv), **6** (33.0 mg, 0.0825 mmol, 2.50 equiv), dppm (1.9 mg, 0.0185 mmol, 0.15 equiv), $Ni(cod)_2$ (0.9 mg, 0.0123 mmol, 0.10 equiv) and solvent (0.2 mL) were added to a 2.0 mL sealed vial. The reaction mixture was heated to 60 ℃, and stirring continued for 12 hours. The mixture was filtered with silica gel, and benzyl chloride (10 μL, 0.0870 mmol, 2.64 equiv) was added as internal standard. The yields were determined by the ^{1}H NMR and reported in Table S4.

Table S4: Effects of solvents on the reaction

Solvent	Yield/% (19'-major:19'-minor:19-major:19-minor)
DME	18:10:18:10
THF	14:6:14:6
Toluene	18:10:18:10
DMF	22:10:16:10
EtOAc	18:10:18:10
Et_2O	16:10:16:10
1,4 – dioxane	**18:10:18:10**

Effects of amounts of $Ni(cod)_2$ and dppm on the reaction

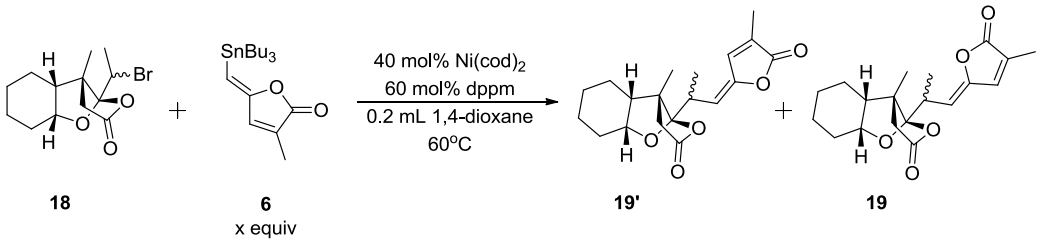


In a glove box, compound **18** (10 mg, 0.0330 mmol, 1.00 equiv), **6** (33.0 mg, 0.0825 mmol, 2.50 equiv), ligand (y mol%), $Ni(cod)_2$ (x mol%) and 1,4-dioxane (0.2 mL) were added to a 2.0 mL sealed vial. The reaction mixture was heated to 60 ℃, and stirring continued for 12 hours. The mixture was filtered with silica gel, and benzyl chloride (10 μL, 0.0870 mmol, 2.64 equiv) was added as internal standard. The yields were determined by the ^{1}H NMR and reported in Table S5.

Table S5: Effects of amounts of $Ni(cod)_2$ and dppm on the reaction

$Ni(cod)_2$/x	**dppm/y**	**Yield/% (19'-major:19'-minor:19-major:19-minor)**
10	20	18:10:18:10
25	40	20:10:20:10
40	**60**	**26:14:26:14**
55	80	22:12:22:12

Effects of amounts of compound 6 on the reaction

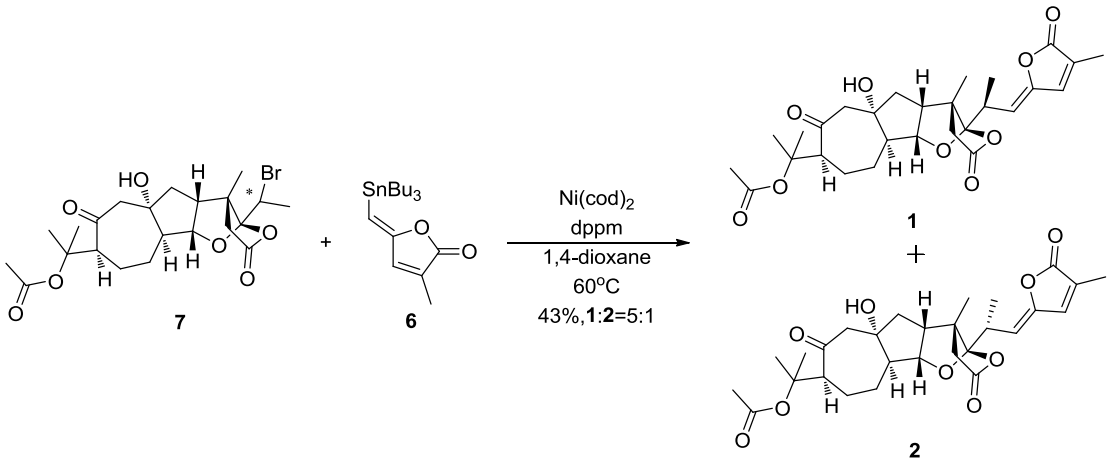


In a glove box, compound **18** (10 mg, 0.0330 mmol, 1.00 equiv), **6** (x equiv), bis(diphenylphosphino)methane (7.6 mg, 0.0185 mmol, 0.60 equiv), $Ni(cod)_2$ (3.6 mg, 0.0123 mmol, 0.40 equiv) and 1,4-dioxane (0.2 mL) were added to a 2.0 mL sealed vial. The reaction mixture was heated to 60 ℃, and stirring continued for 12 hours. The mixture was filtered with silica gel, and benzyl chloride (10 μL, 0.0870 mmol, 2.64 equiv) was added as internal standard. The yields were determined by the ^{1}H NMR and reported in Table S6.

Table S6: Effects of amounts of compound 6 on the reaction

Substrate 6/x	**Yield/% (19'-major:19'-minor:19-major:19-minor)**
2.5	26:14:26:14
5.0	26:14:26:14
7.5	26:14:26:14
10.0	26:14:26:14

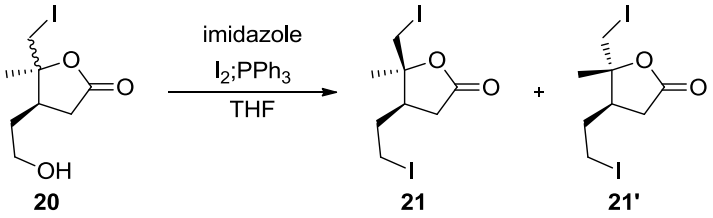
Synthesis of compound 1, 2



In a glove box, compound **7** (15 mg, 0.0308 mmol, 1.00 equiv), **6** (123 mg, 0.308 mmol, 10.0 equiv), bis(diphenylphosphino)methane (7.1 mg, 0.0185 mmol, 0.60 equiv), $Ni(cod)_2$ (3.4 mg, 0.0123 mmol, 0.40 equiv) and 1,4-dioxane (0.2 mL) were added to a 2.0 mL sealed vial. The reaction mixture was heated to 60 ℃, and stirring continued for 12 hours. The mixture was purified by the silica gel column chromatography (petroleum ether/ ethyl acetate=1:4 to 1:1) to gain the mixture of compounds **1** and **2**. Further purification was carried through preparative HPLC[3] (3 mL/min, detector UV λ_{max} 275 nm, MeOH/H_2O 55:45) to yield **1** (55 min, 5.7 mg, 0.011 mmol, 36% yield) and **2** (72 min, 1.1mg, 0.0022mmol, 7% yield). The ^{1}H NMR of compound **1** shows a minor impurity (d.r.=11:1) that we assumes to be a double bond geometrical isomer. Due to the limited mass, the exact structure can't be confirmed. **1**: R_f = 0.3 (silica, EtOAc: petroleum ether = 3:1); $[\alpha]_D^{25}$ = 73.8 (*c* = 0.07 in $CHCl_3$); IR (film): ν_{max} = 3429, 2960, 2919, 2851, 1767, 1698, 1621, 1458, 1374, 1260, 1094, 1019, 874, 800, 759, 664 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 1.5 Hz, 1H), 5.28 (d, *J* = 9.9 Hz, 1H), 4.55 (dd, *J* = 7.8, 5.8 Hz, 1H), 3.40–3.29 (m, 1H), 3.15 (d, *J* = 11.5 Hz, 1H), 2.80–2.73 (m, 2H), 2.72 (ABd, *J* = 18.1 Hz, 1H), 2.65 (ABd, *J* = 18.0 Hz, 1H), 2.44–2.34 (m, 1H), 2.26 (d, *J* = 11.6 Hz, 1H), 2.24–2.18 (m, 1H), 2.08 – 2.00 (m, 4H), 1.99 (s, 3H), 1.98–1.73 (m, 4H), 1.51 (s, 3H), 1.51–1.46 (m, 1H), 1.48 (s, 3H), 1.23 (s, 3H), 1.22 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.4, 173.1, 170.8, 170.0, 147.9, 137.9, 130.2, 121.5, 113.5, 84.2, 82.4, 81.0, 62.7, 53.4, 51.0, 50.7, 50.3, 46.5, 41.9, 36. 1, 25.0, 24.7, 23.5, 22.6, 19.8, 19.3, 16.1, 10.8. HRMS (m/z): $[M+NH_4]^+$ calcd for $C_{28}H_{36}O_9NH_4^+$ 534.2703, found 534.2692. **2:** R_f = 0.2 (silica, EtOAc: petroleum ether = 1:5); $[\alpha]_D^{25}$ = –80.0 (*c* = 0.04 in $CHCl_3$); IR (film): ν_{max} = 3453, 2962, 2925, 2854, 1767, 1737, 1730, 1461, 1415, 1377, 1262, 1096, 1017, 864, 803, 742, 705 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 1.4 Hz, 1H), 4.99 (d, *J* = 10.5 Hz, 1H), 4.57 (dd, *J* = 7.8, 6.1 Hz, 1H), 3.41–3.32 (m, 1H), 3.13 (d, *J* = 11.5 Hz, 1H), 2.81–2.74 (m, 1H), 2.73 (s, 1H), 2.66 (ABd, *J* = 17.9 Hz, 1H), 2.46 (ABd, *J* = 17.9 Hz, 1H), 2.43–2.34 (M, 1H), 2.27 (d, *J* = 11.5 Hz, 1H), 2.45–2.18 (m, 1H), 2.12–2.05 (m, 1H), 2.02 (s, 3H), 1.99 (s, 3H), 1.92–1.75 (m, 4H), 1.52 (s, 3H), 1.53–1.48 (m, 1H), 1.49 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 3H), 1.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.3, 173.8, 170.4, 170.0, 148.6, 137.6, 131.0, 121.6, 111.5, 83.8, 82.5, 80.9, 62.6, 53.6, 50.9, 50.4, 50.3, 46.5, 41.9, 36.5, 25.0, 24.7, 23.4, 22.8, 22.5, 19.7, 19.0, 16.2, 10.8. HRMS (m/z): $[M+H]^+$ calcd for

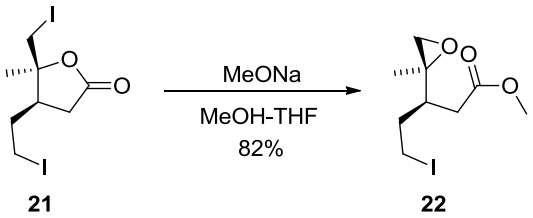
$C_{28}H_{36}O_9H^+$ 517.2438, found 517.2435.

Synthesis of compound 21



To a round–bottom flask containing compounds **20**[1] (3.12 g, 11.0 mmol, 1.00 equiv), PPh_3 (3.75g, 14.3 mmol, 1.30 equiv), imidazole (0.786g, 11.5 mmol, 1.05 equiv) and THF (26 mL) was added a solution of I_2 (3.63 g, 14.3 mmol, 1.30 equiv) in THF (5 mL) at 0 ℃. 30 min later, the reaction mixture was warmed to room temperature, and stirring continued for 1hour. The reaction was quenched with saturated aqueous $Na_2S_2O_3$. The resulting mixture was extracted with EtOAc (3 × 5.0 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 1/10 to 1/5) to give the products **21'** (1.35 g, 3.41 mmol, 31% yield) and **21** (2.69 g, 6.82 mmol, 62% yield) whose structure was confirmed by X–ray crystallograph; **21**: R_f = 0.2 (silica, EtOAc: petroleum ether = 1:5); $[\alpha]_D^{25}$ = − 28.6 (*c* = 1.77 in $CHCl_3$); IR (film): ν_{max} = 2958, 2923, 2852, 1767, 1415, 1379, 1258, 1213, 1182, 1110, 1095, 1049, 1030, 982, 952, 911, 799, 763, 668, 609, 522, 441 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.36–3.24 (m, 3H), 3.09–2.99 (m, 1H), 2.76–2.60 (m, 2H), 2.50 (dd, *J* = 16.0, 9.3 Hz, 1H), 2.18–2.05 (m, 1H), 2.04–1.91 (m, 1H), 1.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 84.5, 45.3, 34.2, 32.5, 27.2, 9.2, 2.9.HRMS (m/z): $[M+H]^+$ calcd for $C_8H_{12}I_2O_2H^+$ 394.8993, found 394.8999. **21':** R_f = 0.2 (silica, EtOAc: petroleum ether = 1:5); $[\alpha]_D^{25}$ = − 47.6 (*c* = 0.90 in $CHCl_3$); IR (film): ν_{max} = 2960, 2924, 2851, 1770, 1454, 1416, 1380, 1308, 1260, 1225, 1161, 1096, 1047, 1028, 924, 800, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.48 (ABd, *J* = 11.1 Hz, 1H), 3.39 (ABd, *J* = 11.1 Hz, 1H), 3.30–3.18 (m, 1H), 3.03 (dd, *J* = 16.6, 9.2 Hz, 1H), 2.89–2.61 (m, 2H), 2.31 (dd, *J* = 16.8, 10.2 Hz, 1H), 2.19–2.01 (m, 1H), 1.97–1.81 (m, 1H), 1.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 84.6, 44.1, 34.4, 34.2, 21.2, 13.6, 2.3. HRMS (m/z): $[M+NH_4]^+$ calcd for $C_8H_{12}I_2O_2NH_4^+$ 412.927, found 412.926.

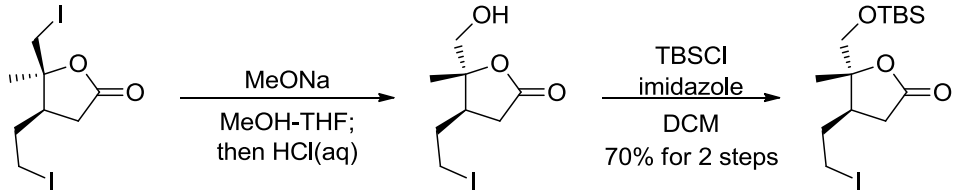
Synthesis of compound 22



To a suspension of compound **21** (200 mg, 0.51 mmol, 1.00 equiv) in MeOH (2.1 mL) and THF (0.4 mL) was added MeONa (82.7 mg, 1.52 mmol, 3.00 equiv). 1 min later, the reaction mixture turned clear and TLC showed the disappearance of the starting material. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with EtOAc (3 × 5.0 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and

evaporated under reduced pressure. The crude product was purified by neutral aluminum oxide gel column chromatography (EtOAc: petroleum ether = 1/10) to give the product **22** (124.1 mg, 0.42 mmol, 82% yield). **22**: R_f = 0.3 (silica, EtOAc: petroleum ether = 1:5); $[\alpha]_D^{25}$ = 11.3 (*c* = 0.18 in $CHCl_3$); IR (film): ν_{max} = 2960, 2922, 2851, 1734, 1436, 1378, 1362, 1260, 1174, 1091, 1021, 871 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 3.31–3.18 (m, 1H), 2.55 (dd, *J* = 20.4, 4.7 Hz, 2H), 2.30 (dd, *J* = 7.4, 1.9 Hz, 2H), 2.22–2.11 (m, 1H), 2.01–1.79 (m, 2H), 1.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 57.9, 53.1, 52.0, 43.3, 36.5, 36.3, 17.3, 2.7.

Synthesis of compound 23

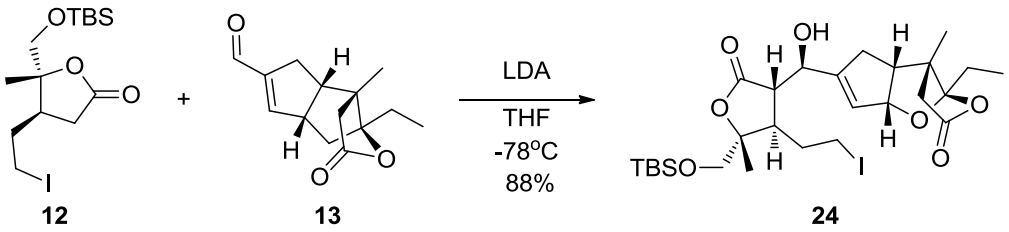


21 **23** **12**

To a suspension of compound **21** (800 mg, 2.03 mmol, 1.00 equiv) in MeOH (8.3 mL) and THF (1.7 mL) was added MeONa (329.1 mg, 6.09 mmol, 3.00 equiv). 1 min later, the reaction mixture turned clear and 1M HCl (6 mL) was added. After stirring continued for 40 min, organic solvents were evaporated under reduced pressure. The residual aqueous phase was extracted with EtOAc (3 × 5.0 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 1/4 to 1/1) to give the product **23** (438 mg, 1.54 mmol, 76% yield). **23**: R_f = 0.3 (silica, EtOAc: petroleum ether = 1:1); $[\alpha]_D^{25}$ = –79.1 (*c* = 0.41 in $CHCl_3$); IR (film): ν_{max} = 3418, 2959, 2924, 1777, 1754, 1729, 1462, 1453, 1390, 1260, 1215, 1102, 1067, 1019, 952, 800, 762 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.73 (ABd, *J* = 12.5 Hz, 1H), 3.54 (ABd, *J* = 12.5 Hz, 1H), 3.22 (ddd, *J* = 9.9, 8.2, 5.2 Hz, 1H), 3.05 (dt, *J* = 9.9, 7.9 Hz, 1H), 2.87–2.66 (m, 2H), 2.39–2.26 (m, 1H), 2.08–1.97 (m, 1H), 1.96–1.81 (m, 1H), 1.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 88.2, 66.8, 39.6, 34.1, 33.9, 17.9, 2.4. HRMS (m/z): $[M+H]^+$ calcd for $C_8H_{13}IO_3H^+$ 284.9777, found 284.9982.

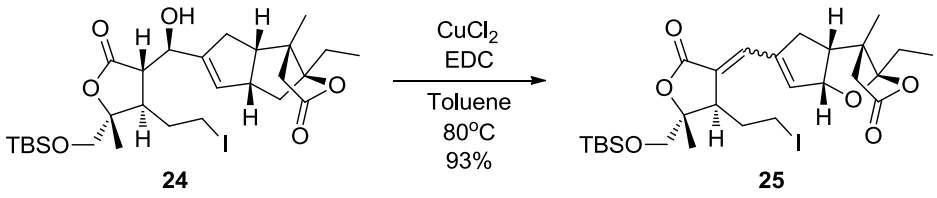
To a stirred solution of compound **23** (438 mg, 1.54 mmol, 1.00 equiv) in DCM (7.5 mL) was sequentially added TBSCl (465 mg, 3.08 mmol, 2.00 equiv) and imidazole (210 mg, 3.08 mmol, 2.00 equiv). After stirring for 2 hours, the reaction mixture was filtered through Celite pad, and the solvent was evaporated under reduced pressure to give the crude product. The crude product was purified by the silica gel column chromatography (EtOAc: petroleum ether = 1/10) to give the product **12** (566 mg, 1.42 mmol, 92% yield). **12**: R_f = 0.3 (silica, EtOAc: petroleum ether = 1:10); $[\alpha]_D^{25}$ = –56.7 (*c* = 0.56 in $CHCl_3$); IR (film): ν_{max} = 2955, 2927, 2856, 1787, 1462, 1378, 1300, 1258, 1236, 1160, 1103, 1017, 955, 837, 779, 671, 513 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.66 (ABd, *J* = 10.8 Hz, 1H), 3.57 (ABd, *J* = 10.8 Hz, 1H), 3.34–3.18 (m, 1H), 3.03 (dd, *J* = 16.7, 9.1 Hz, 1H), 2.82–2.65 (m, 2H), 2.33–2.16 (m, 1H), 2.13–2.00 (m, 1H), 1.86–1.74 (m, 1H), 1.23 (s, 3H), 0.90 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 87.6, 68.6, 40.6, 34.3, 34.2, 26.0, 18.4, 18.3, 3.1, –5.3, –5.4. HRMS (m/z): $[M+H]^+$ calcd for $C_{14}H_{27}IO_3SiH^+$ 399.0837, found 399.0847.

Synthesis of compound 24



To a solution of lithium diisopropylamide (0.82 mL, *c* = 2.00 M in THF, 1.63 mmol, 1.30 equiv) in tetrahydrofuran (7.9 mL) was slowly added a solution of compound **12** (650 mg, 1.63 mmol, 1.30 equiv) in tetrahydrofuran (3.5 mL) at –78 ℃. After 30 min, compound **13**[1] (297 mg, 1.26 mmol, 1.00 equiv) in tetrahydrofuran (3.5 mL) was added at –78 ℃ and stirring continued for 1 h before the reaction was quenched with saturated aqueous NH_4Cl. The resultant mixture was extracted with EtOAc (3 × 15.0 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 3/7) to give compound **24** (702 mg, 1.11 mmol, 88% yield). **24**: R_f = 0.3 (silica, EtOAc: petroleum ether = 1/2); $[\alpha]_D^{25}$ =–5.0 (*c* = 0.12 in $CHCl_3$); IR (film): ν_{max} = 3482, 2959, 2925, 1768, 1463, 1377, 1260, 1099, 1020, 838, 801 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.86 (d, *J* = 1.1 Hz, 1H), 5.30 (d, *J* = 7.8 Hz, 1H), 4.52 (dd, *J* = 7.0, 3.3 Hz, 1H), 3.81 (d, *J* = 3.4 Hz, 1H), 3.72 (d, *J* = 11.2 Hz, 1H), 3.51 (d, *J* = 11.2 Hz, 1H), 3.19 (ddd, *J* = 10.1, 7.6, 5.2 Hz, 1H), 3.04–2.95 (m, 1H), 2.91 (td, *J* = 8.7, 3.2 Hz, 1H), 2.74–2.62 (m, 3H), 2.54–2.44 (m, 2H), 2.33 (dd, *J* = 17.6, 9.0 Hz, 1H), 2.05–1.93 (m, 1H), 1.85–1.64 (m, 3H), 1.26 (s, 3H), 1.18 (s, 3H), 1.10 (t, *J* = 7.3 Hz, 3H), 0.91 (s, 9H), 0.09 (d, *J* = 5.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 173.7, 147.2, 128.0, 121. 9, 88.2, 87.2, 70.9, 68.6, 50.7, 49.8, 49.2, 45.4, 41.2, 33.8, 31.4, 27.7, 26.0, 18.6, 18.4, 17.1, 7.5, 2.5, –5.2, –5.3. HRMS (m/z): $[M+Na]^+$ calcd for $C_{27}H_{43}IO_7SiNa^+$ 657.1720, found 657.1715.

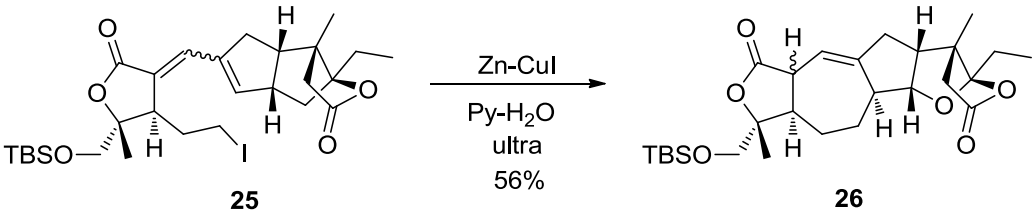
Synthesis of compound 25



To a solution of compound **24** (500 mg, 0.788 mmol, 1.00 equiv) in toluene (30.0 mL) was added EDC (1–(3–*N*,*N*-dimethylaminopropyl)–3–ethylcarbodiimide) (0.28 mL, 1.58 mmol, 2.00 equiv) and $CuCl_2$ (53 mg, 0.39 mmol, 0.50 equiv) at 80 ℃, and stirring continued for 1 h. The reaction mixture was filtered with Celite pad and evaporated to gain the crude product, which was purified by silica gel column chromatography (EtOAc: petroleum ether = 1/4) to give compounds **25** (452 mg, 0.733 mmol, 93% yield, 1:0.34). **25 Major**: R_f = 0.6 (silica, EtOAc: petroleum ether = 1/2); $[\alpha]_D^{25}$ =–35.9 (*c* = 0.54 in $CHCl_3$); IR (film): ν_{max} = 2954, 2927, 2856, 1757, 1649, 1464, 1379, 1361, 1300, 1258, 1234, 1160, 1102, 1050, 1033, 941, 910, 873, 839, 801, 780, 757, 667, 591, 542 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 1H), 6.21 (s, 1H), 5.35 (d, *J* = 7.6 Hz, 1H), 3.49 (s, 2H), 3.36–3.29 (m, 1H), 3.15 (t, *J* = 7.6 Hz, 2H), 2.96 (td, *J* = 8.1, 3.1 Hz, 1H), 2.76–2.59 (m, 3H), 2.50 (d, *J* = 17.4 Hz, 1H), 2.26–2.14

(m, 1H), 2.22–1.91 (m, 1H), 1.72 (q, *J* = 7.3 Hz, 2H), 1.39 (s, 3H), 1.17 (s, 3H), 1.10 (t, *J* = 7.3 Hz, 3H), 0.83 (s, 9H), 0.01 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 170.6, 141.8, 136.3, 133.2, 130.2, 121.5, 87.9, 85.2, 70.1, 50.9, 50.5, 45.3, 44.3, 35.9, 34.6, 27.8, 25.8, 18.4, 18.2, 17.1, 7.5, 1.8, –5.5, –5.6. HRMS (m/z): $[M+Na]^+$ calcd for $C_{27}H_{41}IO_6SiNa^+$ 639.1615, found 639.1609. **25 Minor**: R_f = 0.6 (silica, EtOAc: petroleum ether = 1/2); $[\alpha]_D^{25}$ =–51.1 (*c* = 0.15 in $CHCl_3$); IR (film): ν_{max} = 2961, 2926, 2854, 1751, 1652, 1647, 1457, 1417, 1398, 1377, 1260, 1100, 1020, 908, 799, 702, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 1H), 6.22 (s, 1H), 5.32 (d, *J* = 7.6 Hz, 1H), 3.63–3.47 (m, 5H), 2.95 (td, *J* = 8.6, 3.2 Hz, 1H), 2.85–2.59 (m, 3H), 2.50 (d, *J* = 17.4 Hz, 1H), 2.24–2.12 (m, 1H), 1.89–1.79 (m, 1H), 1.72 (q, *J* = 7.4 Hz, 2H), 1.40 (d, *J* = 3.6 Hz, 3H), 1.16 (d, *J* = 9.0 Hz, 3H), 1.10 (t, *J* = 7.4 Hz, 3H), 0.83 (d, *J* = 4.5 Hz, 9H), 0.04–0.00 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 170.7, 141.9, 136.4, 134.1, 130.2, 121.5, 87.8, 85.23, 70.0, 50.9, 50.7, 45.3, 42.4, 40.4, 34.5, 27.8, 25.8, 18.5, 18.2, 17.1, 7.5, 0.1, –5.5, –5.6. HRMS (m/z): $[M+H]^+$ calcd for $C_{27}H_{41}IO_6SiH^+$ 617.1786, found 617.1790.

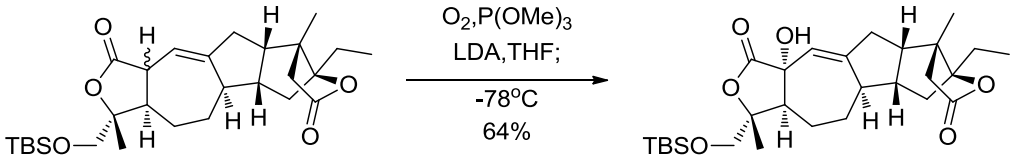
Synthesis of compound 26



25 **26**

To the emulsion of compounds **25** (246 mg, 0.399 mmol, 1.00 equiv) in pyridine (11.5 mL) and water (44.6 mL) was added zinc (332 mg, 5.07 mmol, 12.7 equiv) and cuprous iodide (338 mg, 1.75 mmol, 4.38 equiv) in 3 portions at room temperature. The reaction was carried out under sonication for 8 h. The resultant mixture was filtered with Celite pad, the filtrate was extracted with DCM (5 × 25.0 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 3/1 to 1/1) to give compounds **26** (109 mg, 0.223 mmol, 56% yield, 1:0.14). **26 Major**: R_f = 0.5 (silica, EtOAc: petroleum ether = 1/2); $[\alpha]_D^{25}$ = –29.3 (*c* = 0.35 in $CHCl_3$); IR (film): ν_{max} = 2957, 2929, 2857, 1768, 1463, 1386, 1361, 1298, 1259, 1214, 1105, 1057, 1022, 957, 938, 907, 838, 799, 780, 758, 714, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (s, 1H), 4.28 (dd, *J* = 5.0, 1.8 Hz, 1H), 3.62 (dd, *J* = 30.3, 10.8 Hz, 2H), 3.21–3.11 (m, 1H), 2.82–2.67 (m, 3H), 2.58 (d, *J* = 18.5 Hz, 1H), 2.45–2.26 (m, 3H), 2.15–2.06 (m, 1H), 1.89–1.73 (m, 3H), 1.69–1.55 (m, 2H), 1.23 (d, *J* = 2.5 Hz, 6H), 1.12 (t, *J* = 7.3 Hz, 3H), 0.92–0.84 (m, 9H), 0.06 (d, *J* = 3.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 174.2, 148.1, 120.4, 118.5, 90.5, 86.3, 68.1, 53.3, 49.6, 45.7, 45.4, 44.0, 43.8, 36.6, 29.6, 29.2, 25.9, 24.8, 19.4, 18.4, 18.3, 7.8, –5.2, –5.3. HRMS (m/z): $[M+H]^+$ calcd for $C_{27}H_{42}O_6SiH^+$ 491.2824, found 491.2823.

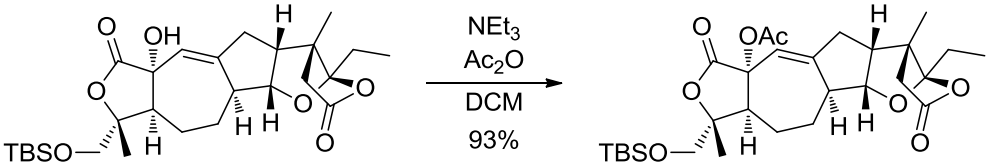
Synthesis of compound 27



26 **27**

To a stirred solution of compounds **26** (149 mg, 0.304 mmol, 1.00 equiv) in THF (20.0 mL) was slowly added LDA (2.0 M in THF, 0.50 mL, 0.913 mmol, 3.00 equiv) at –78 ℃ under the atmosphere of N_2. 30 min later, the reaction mixture was degassed with O_2 for 3 times followed by addition of $P(OMe)_3$ (72 μL, 0.609 mmol, 2.00 equiv). After stirring for 3 h, the reaction was quenched with saturated aqueous NH_4Cl. The resulting mixture was extracted with EtOAc (3 × 10.0 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 1/5 to 1/2) to give the product **27** (98.4 mg, 0.195 mmol, 64% yield); **27**: R_f = 0.4 (silica, EtOAc: petroleum ether = 1:1); $[\alpha]_D^{25}$ = 61.5 (*c* = 0.27 in $CHCl_3$); IR (film): ν_{max} = 3433, 2957, 2926, 2855, 1768, 1462, 1377, 1259, 1215, 1099, 1024, 937, 908, 892, 837, 758, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.80 (s, 1H), 4.29 (s, 1H), 4.12 (s, 1H), 3.74 (d, *J* = 10.8 Hz, 1H), 3.60 (d, *J* = 10.7 Hz, 1H), 3.12 (t, *J* = 9.2 Hz, 1H), 2.75 (d, *J* = 18.6 Hz, 1H), 2.60 (d, *J* = 18.6 Hz, 1H), 2.55 – 2.46 (m, 3H), 2.43 (dd, *J* = 12.2, 2.6 Hz, 1H), 2.02–1.87 (m, 1H), 1.83–1.68 (m, 3H), 1.39–1.23 (m, 8H), 1.11 (t, *J* = 7.3 Hz, 3H), 0.94–0.89 (m, 9H), 0.12 (d, *J* = 1.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 174.5, 150.7, 120.5, 118.9, 89.2, 85.9, 77.4, 69.9, 53.9, 50.0, 48.7, 45.4, 43.6, 34.7, 29.3, 26.0, 25.6, 22.6, 20.3, 19.7, 18.6, 7.8, –5.4, –5.4. HRMS (m/z): $[M+Na]^+$ calcd for $C_{27}H_{42}O_7SiNa^+$ 529.2597, found 529.2592.

Synthesis of compound 11

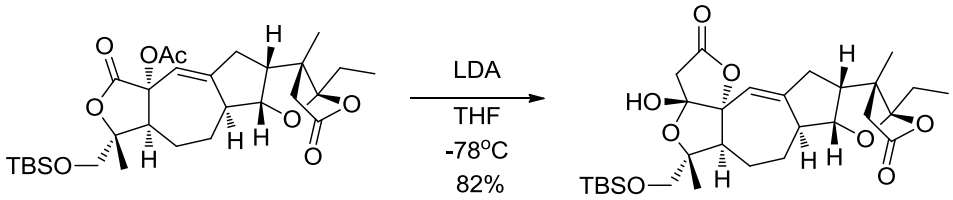


27 **11**

To a stirred solution of compound **27** (88.0 mg, 0.174 mmol, 1.00 equiv) in DCM (1.7 mL) was sequentially added NEt_3 (0.24 mL, 1.74 mmol, 10.0 equiv) and Ac_2O (49 μL, 0.521 mmol, 3.00 equiv) at room temperature. After stirring for 3 hours, the reaction was quenched with saturated aqueous $NaHCO_3$. The resulted mixture was extracted with DCM (3 × 3.0 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 1/5 to 1/2) to give the product **11** (88.8 mg, 0.162 mmol, 93% yield); **27**: R_f = 0.5 (silica, EtOAc: petroleum ether = 1:1); $[\alpha]_D^{25}$ = 26.1 (*c* = 0.33 in $CHCl_3$); IR (film): ν_{max} = 2956, 2929, 2857, 1778, 1741, 1464, 1387, 1370, 1299, 1258, 1226, 1158, 1104, 1029, 973, 931, 906, 838, 801, 781, 757, 714, 666, 611, 538, 502 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.54 (s, 1H), 4.40–4.28 (m, 1H), 3.70 (s, 2H), 3.18–3.11 (m, 1H),

2.85 (dd, *J* = 11.3, 4.7 Hz, 1H), 2.74 (d, *J* = 18.4 Hz, 1H), 2.58 (d, *J* = 18.4 Hz, 1H), 2.55–2.46 (m, *J* = 36.8, 17.6 Hz, 3H), 2.09 (s, 3H), 2.00–1.87 (m, 1H), 1.79 (q, *J* = 7.3 Hz, 2H), 1.75–1.64 (m, 2H), 1.46–1.34 (m, 1H), 1.25 (s, 6H), 1.12 (t, *J* = 7.3 Hz, 3H), 0.88 (s, 9H), 0.07 (d, *J* = 4.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 173.8, 170.0, 154.4, 120.9, 115.3, 90.5, 85.5, 81.2, 69.6, 53.6, 49.9, 48. 0, 46.0, 45.3, 35.8, 29.0, 26.0, 23.8, 23.5, 21.3, 20.6, 19.4, 18.4, 7.8, –5.4, ‒5.4. HRMS (m/z): $[M+H]^+$ calcd for $C_{29}H_{44}O_8SiH^+$ 549.2880, found 549.2878.

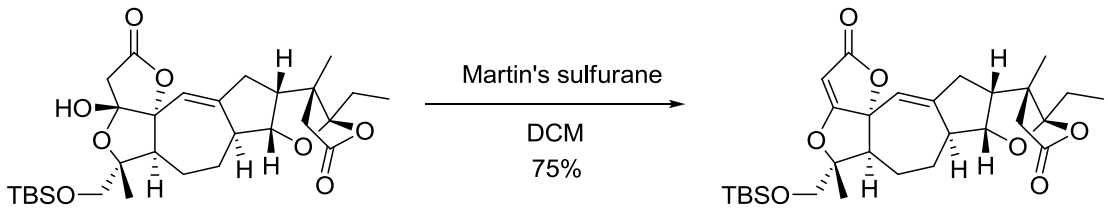
Synthesis of compound 28



11 **28**

To a stirred solution of compounds **11** (157 mg, 0.286 mmol, 1.00 equiv) in THF (9.5 mL) was slowly added LDA (2.0 M in THF, 0.43 mL, 0.857 mmol, 3.00 equiv) at –78 ℃ under the atmosphere of N_2. After stirring for 3 h, the reaction was quenched with saturated aqueous NH_4Cl. The resulting mixture was extracted with EtOAc (3 × 10.0 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 1/5 to 1/2) to give the product **28** (129 mg, 0.235 mmol, 82% yield); **28**: R_f = 0.2 (silica, EtOAc: petroleum ether = 1:1); $[\alpha]_D^{25}$ = –11.0 (*c* = 0.36 in $CHCl_3$); IR (film): ν_{max} = 3396, 2956, 2926, 2855, 1768, 1462, 1413, 1377, 1287, 1259, 1235, 1191, 1162, 1097, 1024, 984, 938, 905, 890, 870, 838, 800, 778, 761, 722, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (s, 1H), 4.28 (d, *J* = 3.7 Hz, 1H), 3.51–3.38 (m, 2H), 3.17 ‒ 3.06 (m, 1H), 2.93–2.83 (m, 2H), 2.80–2.71 (m, 2H), 2.66–2.61 (m, 1H), 2.61–2.42 (m, 4H), 1.96–1.83 (m, 1H), 1.82–1.71 (m, 2H), 1.69–1.55 (m, 1H), 1.52–1.36 (m, 1H), 1.26 (d, *J* = 3.0 Hz, 6H), 1.23–1.15 (m, 1H), 1.12 (t, *J* = 7.3 Hz, 3H), 0.88 (s, 9H), 0.04 (d, *J* = 3.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 172.4, 152.4, 120.5, 115. 6, 108.4, 98.0, 89.3, 88.9, 70.7, 54.0, 50.1, 49.4, 45.4, 43.5, 42.2, 34.5, 29.4, 26.6, 26.0, 23.6, 21.7, 19.8, 18.3, 7.9, –5.2, –5.4. HRMS (m/z): $[M+H]^+$ calcd for $C_{29}H_{44}O_8SiH^+$ 549.2878, found 549.2883.

Synthesis of compound 29

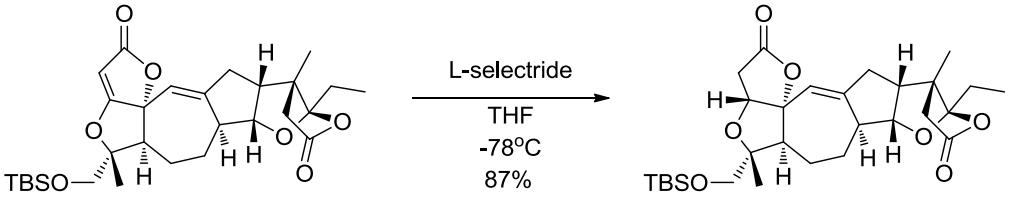


28 **29**

To a stirred solution of compound **28** (131 mg, 0.283 mmol, 1.00 equiv) in DCM (12 mL) was sequentially added Martin's sulfurane (289 mg, 0.429 mmol, 1.80 equiv). After stirring for 3 hours, the reaction was quenched with saturated aqueous NH_4Cl. The resulted mixture was extracted with DCM (3 × 10.0 mL) and the combined organic extracts were dried over

anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 1/5 to 1/2) to give the product **29** (113 mg, 0.212 mmol, 75% yield); **29**: R_f = 0.5 (silica, EtOAc: petroleum ether = 1:1); $[\alpha]_D^{25}$ = –60.7 (*c* = 0.38 in $CHCl_3$); IR (film): ν_{max} = 2955, 2925, 2854, 1770, 1657, 1462, 1377, 1357, 1260, 1100, 1021, 939, 887, 838, 801, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.53 (s, 1H), 4.88 (s, 1H), 4.41–4.32 (m, 1H), 3.64 (d, *J* = 11.3 Hz, 1H), 3.51 (d, *J* = 11.3 Hz, 1H), 3.06 (s, 1H), 2.81–2.75 (m, 1H), 2.71 (d, *J* = 18.1 Hz, 1H), 2.55 (d, *J* = 18.1 Hz, 1H), 2.52–2.45 (m, 2H), 2.45–2.34 (m, 1H), 2.20–2.08 (m, 1H), 1.88–1.72 (m, 4H), 1.44–1.36 (m, 1H), 1.36 (s, 3H), 1.21 (s, 3H), 1.12 (t, *J* = 7.3 Hz, 3H), 0.86 (s, 9H), 0.05 (d, *J* = 2.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.9, 174.5, 173.8, 153.3, 121.5, 117.6, 101.7, 90.0, 86.4, 86.2, 68.3, 53.0, 49.7, 47.8, 47.3, 45.4, 35.5, 28.8, 25.9, 23.7, 21.9, 20.3, 19.0, 18.3, 7.7, –5.3, –5.4. HRMS (m/z): $[M+H]^+$ calcd for $C_{29}H_{42}O_7SiH^+$ 531.2773, found 531.2777.

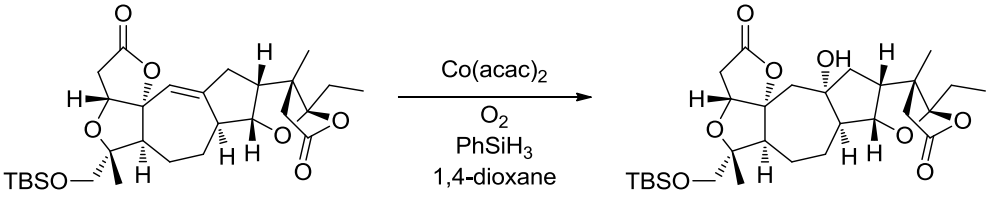
Synthesis of compound 30



29 **30**

To a stirred solution of compound **29** (46.2 mg, 0.0871 mmol, 1.00 equiv) in THF (1.6 mL) was slowly added L–selectride (1.0 M in THF, 0.26 mL, 0.261 mmol, 3.00 equiv) at –78 ℃ under the atmosphere of N_2. After stirring for 5 h, the reaction was quenched with saturated aqueous NH_4Cl. The resulting mixture was extracted with EtOAc (3 × 10.0 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc: petroleum ether = 1/3 to 1/1) to give the product **30** (40.3 mg, 0.768 mmol, 87% yield); **30**: R_f = 0.3 (silica, EtOAc: petroleum ether = 1:1); $[\alpha]_D^{25}$ = –15.3 (*c* = 0.10 in $CHCl_3$); IR (film): ν_{max} = 2957, 2925, 2853, 1770, 1462, 1376, 1259, 1204, 1170, 1100, 1064, 1022, 934, 837, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.46 (s, 1H), 4.31 (d, *J* = 4.2 Hz, 1H), 4.28 (d, *J* = 3.9 Hz, 1H), 3.56–3.46 (m, 2H), 3.26–3.16 (m, 1H), 2.79–2.50 (m, 6H), 2.49–2.33 (m, 2H), 1.98–1.85 (m, 1H), 1.75 (q, *J* = 7.1 Hz, 2H), 1.32–1.17 (m, 6H), 1.11 (t, *J* = 7.3 Hz, 3H), 1.07 (s, 3H), 0.88 (s, 9H), 0.05 (d, *J* = 1.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 153.51, 120.5, 116.2, 97.4, 89.1, 87.5, 80.9, 70.0, 54.0, 51.8, 50.1, 45.4, 43.9, 36.2, 34.1, 29.3, 26.0, 25.7, 23.7, 19.6, 18.4, 17.9, 7.8, –5.2, –5.4. HRMS (m/z): $[M+H]^+$ calcd for $C_{29}H_{44}O_7SiH^+$ 533.2929, found 533.2939.

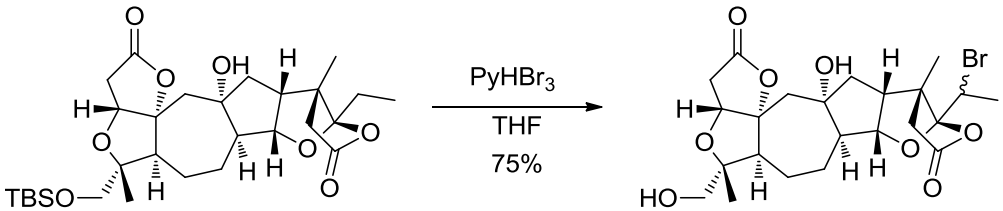
Synthesis of compound 31



30 **31**

To a stirred solution of compound **30** (18.3 mg, 0.0344 mmol, 1.00 equiv) and $Co(acac)_2$ (1.9 mg, 0.00689 mmol, 0.20 equiv) in 1,4–dioxane (0.35 mL) was slowly added $PhSiH_3$ (12.7 μL, 0.103 mmol, 3.00 equiv) at room temperature under the atmosphere of O_2. 12 hours later, the reaction was quenched with saturated aqueous $Na_2S_2O_3$. The resulted mixture was extracted with EtOAc (3 × 2.0 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (MeOH/DCM = 1/100 to 1/50) to give the product **31** (8.5 mg, 0.0.155 mmol, 45% yield); **31**: R_f = 0.4 (silica, MeOH: DCM = 1:25); $[\alpha]_D^{25}$ = 33.1 (*c* = 0.10 in $CHCl_3$); IR (film): ν_{max} = 3560, 2956, 2925, 2853, 1769, 1462, 1377, 1260, 1097, 1020, 916, 871, 836, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.49 (dd, *J* = 8.1, 5.5 Hz, 1H), 4.16 (d, *J* = 3.6 Hz, 1H), 3.65 (s, 1H), 3.53 (d, *J* = 10.4 Hz, 1H), 3.48 (d, *J* = 10.4 Hz, 1H), 2.76–2.65 (m, 3H), 2.65–2.57 (m, 1H), 2.54 (d, *J* = 17.7 Hz, 1H), 2.47 (q, *J* = 8.8 Hz, 1H), 2.35 (d, *J* = 5.2 Hz, 1H), 2.07–1.98 (m, 1H), 1.94 (d, *J* = 15.0 Hz, 1H), 1.90–1.58 (m, 7H), 1.43–1.31 (m, 1H), 1.20 (s, 3H), 1.10 (t, *J* = 7.4 Hz, 3H), 1.07 (s, 3H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 173.7, 122.5, 98.7, 87.0, 85.4, 82.9, 81.01, 69.3, 55.2, 53.6, 50.1, 49.9, 46.3, 42.3, 41.4, 35.3, 27.6, 26.0, 24.1, 22.31, 19.1, 18.4, 17.8, 7.6, –5.2, –5.4. HRMS (m/z): $[M+H]^+$ calcd for $C_{29}H_{46}O_8SiH^+$ 551.3029, found 551.3035.

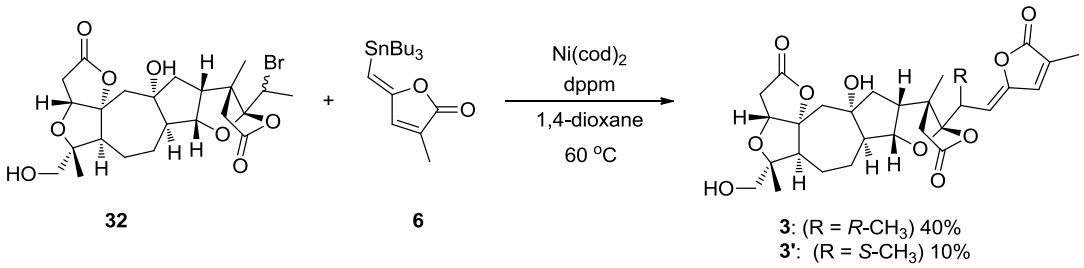
Synthesis of compound 32



31 **32**

To a stirred solution of compound **31** (19 mg, 0.0345 mmol, 1.00 equiv) in THF (1.6 mL) was added $PyHBr_3$ (13.2 mg, 0.0414 mmol, 1.20 equiv). Stirring continued for 2 hours before the organic solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (MeOH/DCM = 1:100 to 1:50) to give the diastereisomers of compounds **32** (13.3 mg, 0.0259 mmol, 75% yield, 2:1). **32**: R_f = 0.2 (silica, MeOH/DCM =1:25); $[\alpha]_D^{25}$ = 44.8 (*c* = 0.44 in $CHCl_3$); IR (film): ν_{max} = 3423, 2954, 2923, 2852, 1769, 1453, 1378, 1327, 1260, 1241, 1201, 1176, 1158, 1096, 1068, 1026, 920, 800, 735, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.55–4.44 (m, 1.54H), 4.31 (m, 1H), 4.19 (d, *J* = 4.4 Hz, 1.54H), 4.17–4.07 (m, 0.61H), 3.78–3.67 (m, 1.54H), 3.64–3.52 (m, 2.1H), 3.46–3.36 (m, 1.68H), 2.97–2.58 (m, 8.38H), 2.57–2.44 (m, 2.68H), 2.21–2.11 (m, 1.87H), 2.12–2.01 (m, 1.27H), 2.00–1.77 (m, 11.34H), 1.77–1.67 (m, 2.06H), 1.68–1.48 (m, 4H), 1.48–1.42 (m, 3.73H), 1.39 (d, *J* = 10.8 Hz, 2.24H), 1.30–1.20 (m, 3.18H), 1.06 (s, 4.99H), 0.88 (t, *J* = 9.0 Hz, 0.91H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 173.0, 119.3, 119.0, 100.1, 98.6, 87.4, 85.6, 82.9, 82.8, 80.9, 66.9, 53.3, 53.2, 52.6, 52.6, 52.0, 51.7, 51.3, 50.8, 47.8, 47.6, 47.6, 42.0, 41.5, 35.1, 29.8, 24.1, 24.0, 21.8, 21.7, 21.2, 21.1, 19.2, 18.1, 17.5. HRMS (m/z): $[M+H]^+$ calcd for $C_{23}H_{31}BrO_8H^+$ 515.1272, found 515.1275.

Synthesis of compound 3 and 3'



Compound **32** (27 mg, 0.0527 mmol, 1.00 equiv), **6** (211 mg, 0.527 mmol, 10.0 equiv), bis(diphenylphosphino)methane (12.2 mg, 0.0316 mmol, 0.60 equiv) , $Ni(cod)_2$ (5.8 mg, 0.0211 mmol, 0.40 equiv) and dioxane (0.3 mL) was added to a 2.0 mL sealed vial in the glove box. The reaction mixture was heated to 60 ℃, and stirring continued 12 hours. The mixture was purified by the silica gel column chromatography (MeOH/ DCM=1:50) to gain the mixture of **3**, **3'** and other byproducts. Further purification was carried through preparative HPLC[4] (3 mL/min, detector UV λ_{max} 275 nm, MeCN/H_2O 35:55) to yield **3** (34 min, 2.9 mg, 0.00527 mmol, 10% yield) and preparative HPLC[4] (3 mL/min, detector UV λ_{max} 275 nm, MeCN/H_2O 50:50) to yield **3'** (30 min, 11.6 mg, 0.0211 mmol, 40% yield). **3**: R_f = 0.4 (silica, MeOH: DCM = 4:100); $[\alpha]_D^{25}$ = 13.0 (*c* = 0.11 in $CHCl_3$); IR (film): ν_{max} = 3451, 2920, 2850, 1776, 1766, 1452, 1462, 1390, 1258, 1245, 1101, 1061, 990, 915, 804, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H), 4.97 (d, *J* = 10.5 Hz, 1H), 4.52–4.42 (m, 1H), 4.19 (d, *J* = 4.7 Hz, 1H), 3.64 (s, 1H), 3.57 (d, *J* = 11.7 Hz, 1H), 3.49–3.29 (m, 2H), 2.81–2.60 (m, 5H), 2.49–2.34 (m, 3H), 2.11–2.02 (m, 1H), 2.01 (s, 3H), 1.94–1.81 (m, 4H), 1.73–1.66 (m, 1H), 1.56–1.48 (m, 1H), 1.43–1.27 (m, 1H), 1.25 (d, *J* = 4.6 Hz, 3H), 1.19 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 173.6, 170.4, 148.6, 137.6, 130.9, 122.0, 111.5, 98.6, 87.31, 84.93, 82.84, 81.03, 66.95, 53.53, 53.03, 50.73, 50.59, 46.84, 42.14, 41.45, 36.31, 35.1, 23.9, 21.7, 19.0, 17.5, 16.2, 10.8. HRMS (m/z): $[M+H]^+$ calcd for $C_{26}H_{36}O_{10}H^+$ 545.2387, found 545.2385. **3'**: R_f = 0.4 (silica, MeOH: DCM = 4:100); $[\alpha]_D^{25}$ = –108.4 (*c* = 0.26 in $CHCl_3$); IR (film): ν_{max} = 3491, 2961, 2924, 2854, 1765, 1461, 1453, 1402, 1378, 1260, 1061, 1019, 918, 873, 803, 756, 694, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 1.3 Hz, 1H), 5.38 (d, *J* = 9.7 Hz, 1H), 4.45 (dd, *J* = 8.0, 4.4 Hz, 1H), 4.19 (d, *J* = 3.9 Hz, 1H), 3.77 (s, 1H), 3.57 (d, *J* = 10.5 Hz, 1H), 3.45–3.26 (m, 2H), 2.86 (dd, *J* = 13.2, 4.0 Hz, 1H), 2.77–2.70 (m, 2H), 2.69–2.57 (m, 2H), 2.55–2.46 (m, 2H), 2.45–2.39 (m, 1H), 2.08–2.02 (m, 1H), 1.99 (s, 3H), 1.97–1.87 (m, 2H), 1.86–1.74 (m, 2H), 1.69 (dd, *J* = 13.5, 9.1 Hz, 1H), 1.59–1.48 (m, 1H), 1.46–1.34 (m, 1H), 1.22 (d, *J* = 6.9 Hz, 3H), 1.21 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 173.2, 170.9, 147.6, 138.0, 129.9, 121.9, 113.9, 98.7, 87.38, 86.2, 82.8, 80.8, 66.6, 52.9, 51.8, 51.0, 50.8, 46.8, 41.7, 41.6, 36.0, 35.1, 24.4, 21.8, 19.4, 17.5, 16.3, 10.7. HRMS (m/z): $[M+H]^+$ calcd for $C_{26}H_{36}O_{10}H^+$ 545.2387, found 545.2376.

Reference

[1] L.Wang, H.-T. Wang,Y.-H. Li. *Angew. Chem. Int. Ed.* **2015**, *54*, 5732.

[2] P. Girard, J. L. Namy, H. B. Kagan. *J. Am. Chem. Soc.* **1980**, *102*, 2693.

[3] X. Luo, C. Ying, X.-J. Zhang, J.-X. Pu, X.-M. Li Gao, Y.-L. Wu, R.-R. Wang, W.-L. Xiao, Y.-T. Zheng, Y. Lu, G.-Q. Chen, Q.-T. Zheng, H.-D. Sun, *Tetrahedron Lett.* **2009**, *50*, 5962.

[4] X. Luo, Y.-M. Shi, R.-H. Luo, S.-H. Luo, X.-N. Li, R.-R. Wang, S.-H. Li, Y.-T. Zheng, X. Du, W.-L. Xiao, J.-X. Pu, H.-D. Sun, *Org. Lett.* **2012**, *14*, 1286.

[5] J. E. Baldwin, D. R. Kelly, *J. Chem. Soc. Chem. Commun.* **1985,**682.

[6] D. L. J. Clive, H. W. Manning, T. L. B. Boivin, M. H. D. Postema. *J. Org. Chem.* **1993**,*58*, 6857–6873

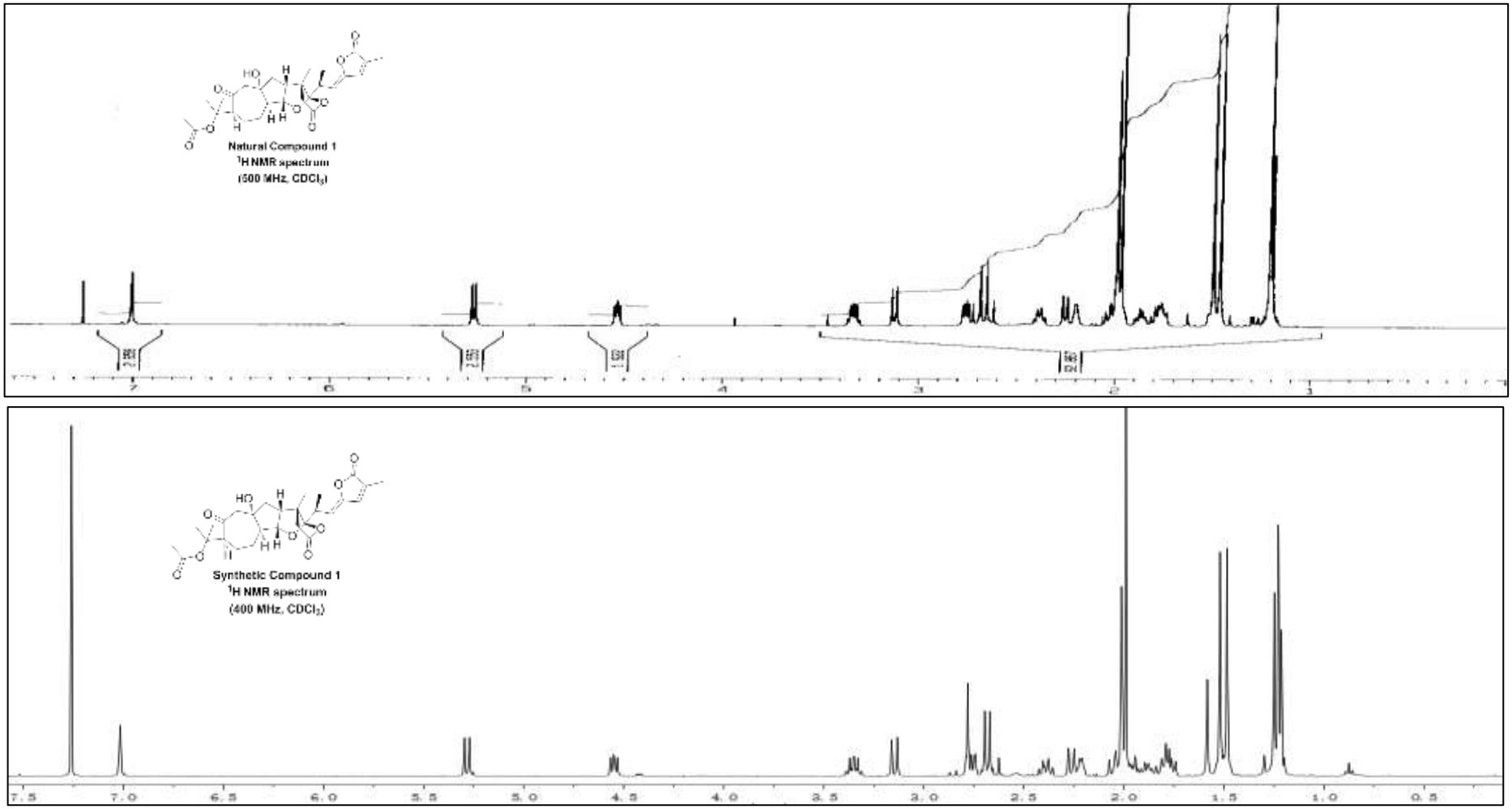
[7] J. D. Nguyen, E.. M. D'Amato, J. M. R. Narayanam , C. R. J. Stephenson. *Nat. Chem.* **2012**, *4*, 854–859.

[8] J. L. Luche, C. Allavena. *Tetrahedron Lett.* **1988**, *29*, 5369.

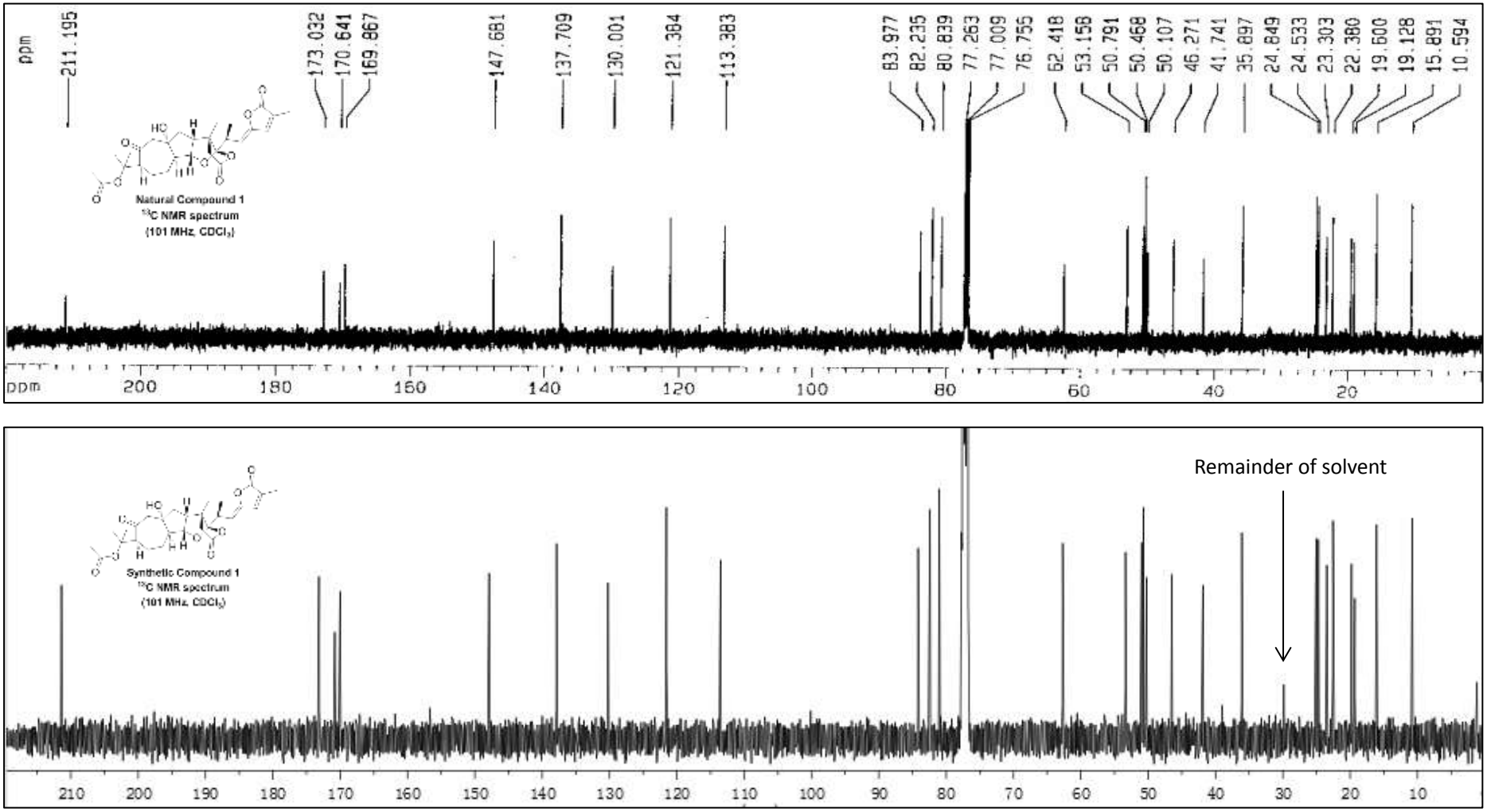
[9] D. A. Powell, T. Maki, and G. C. Fu. *J. Am. Chem. Soc.* **2005**, *127*, 510.

[10] J. Yi, X. Lu, Y.-Y. Sun, B. Xiao, L. Liu. *Angew. Chem. Int. Ed.* **2013**, *52*, 12409.

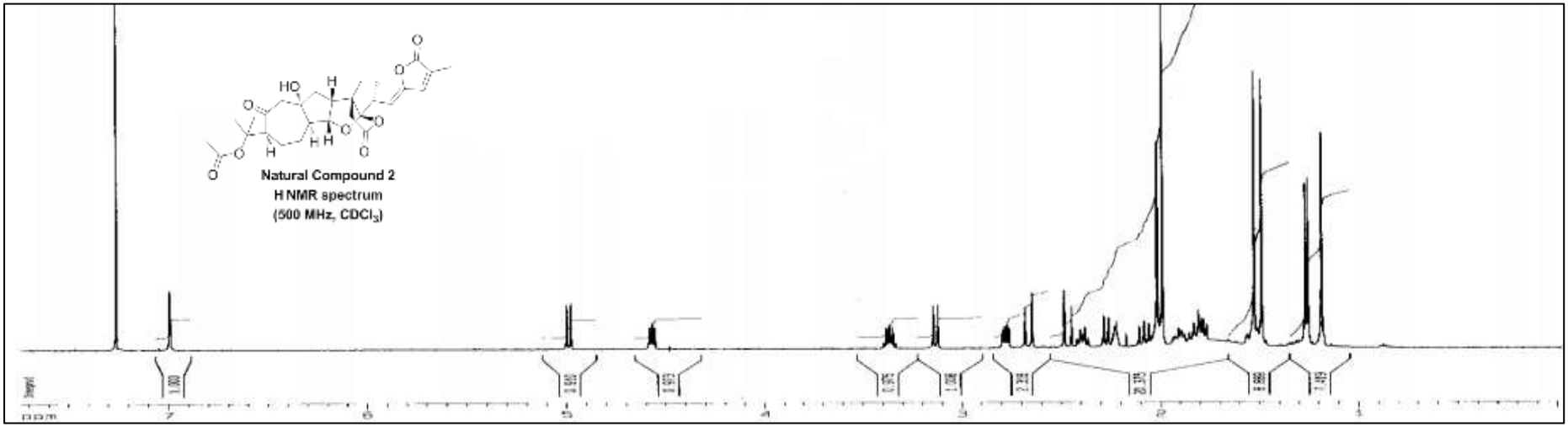
Comparison of the 1H NMR spectra of compound 1

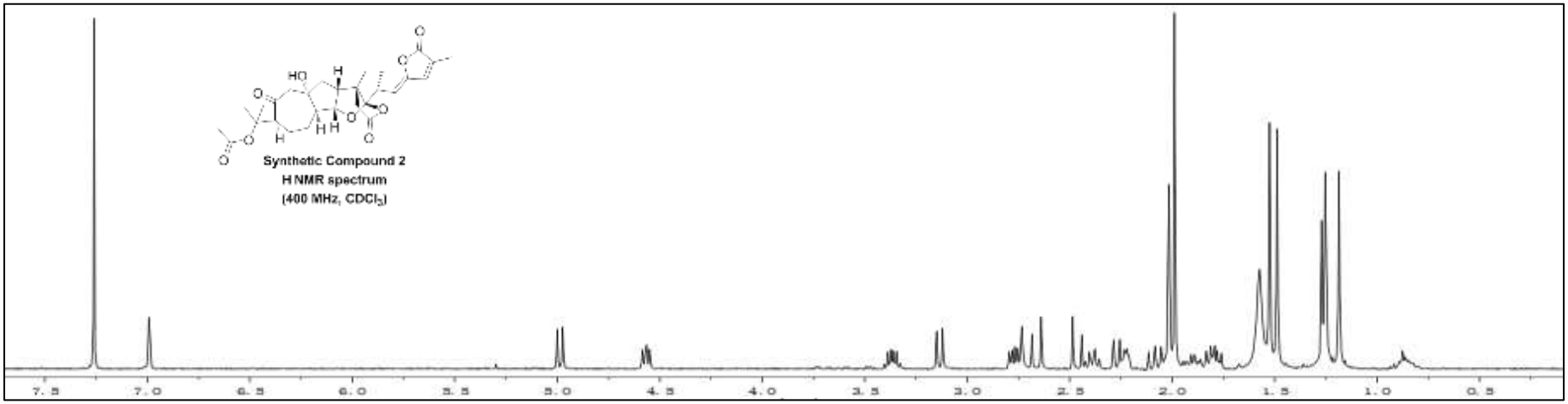


Comparison of the ^{13}C NMR spectra of compound 1

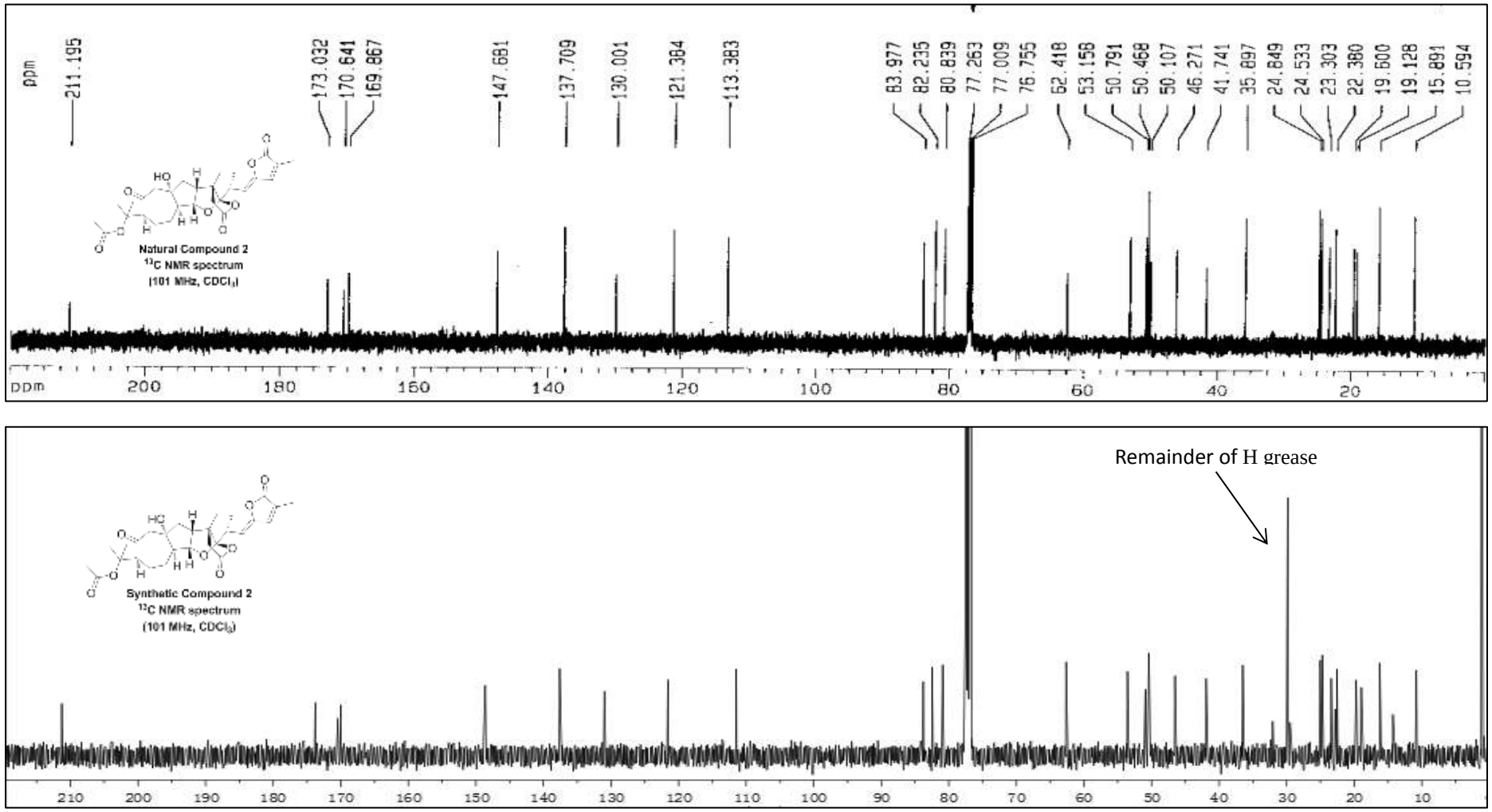


Comparison of the 1H NMR spectra of compound 2

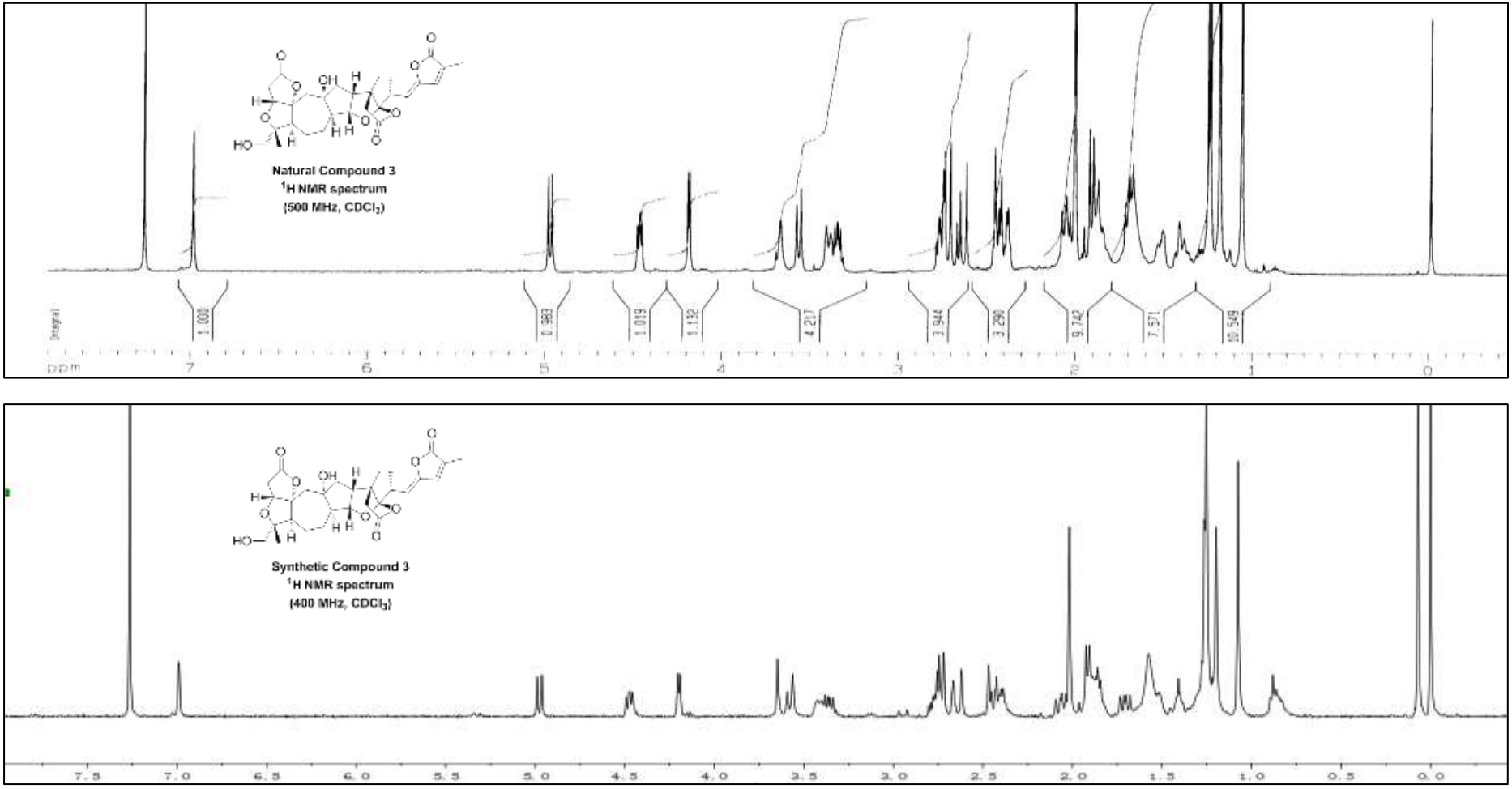




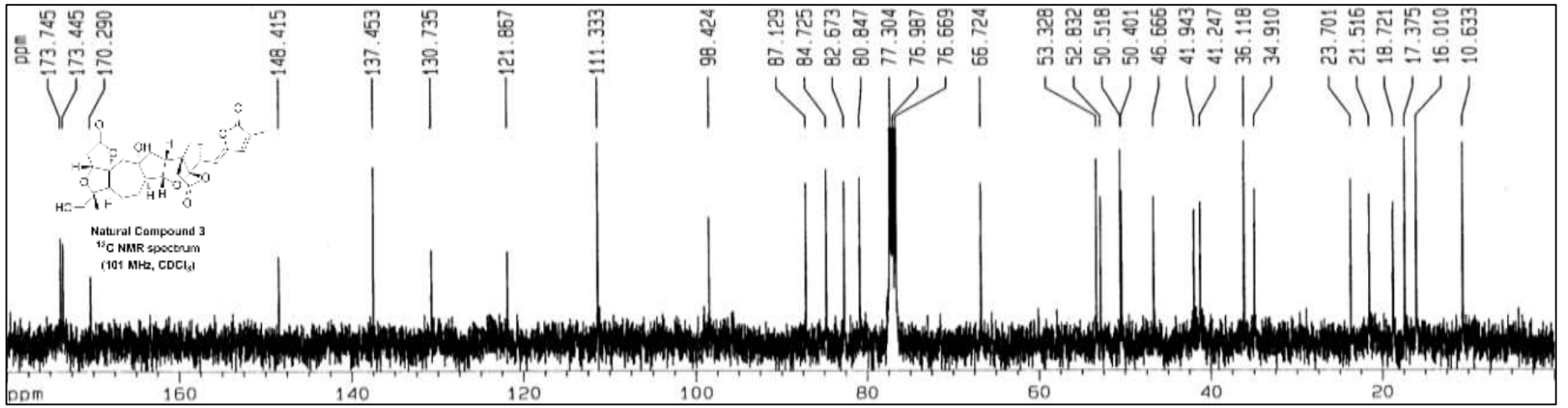
Comparison of the ^{13}C NMR spectra of compound 2

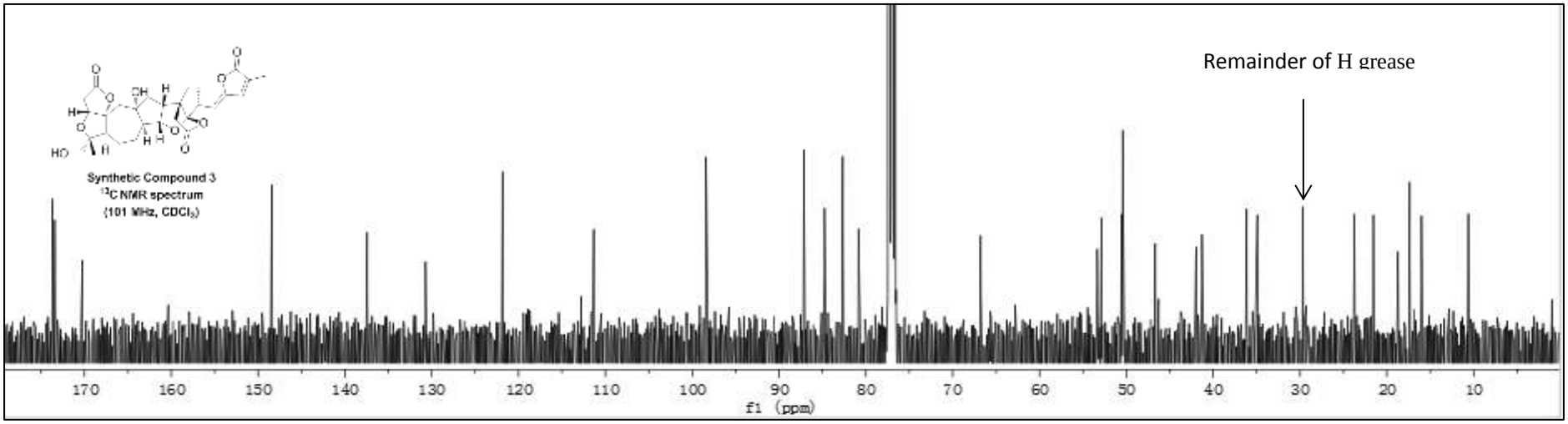


Comparison of the ^{1}H NMR spectra of compound 3



Comparison of the ^{13}C NMR spectra of compound 3





Comparison of the CD spectrum of compound 3

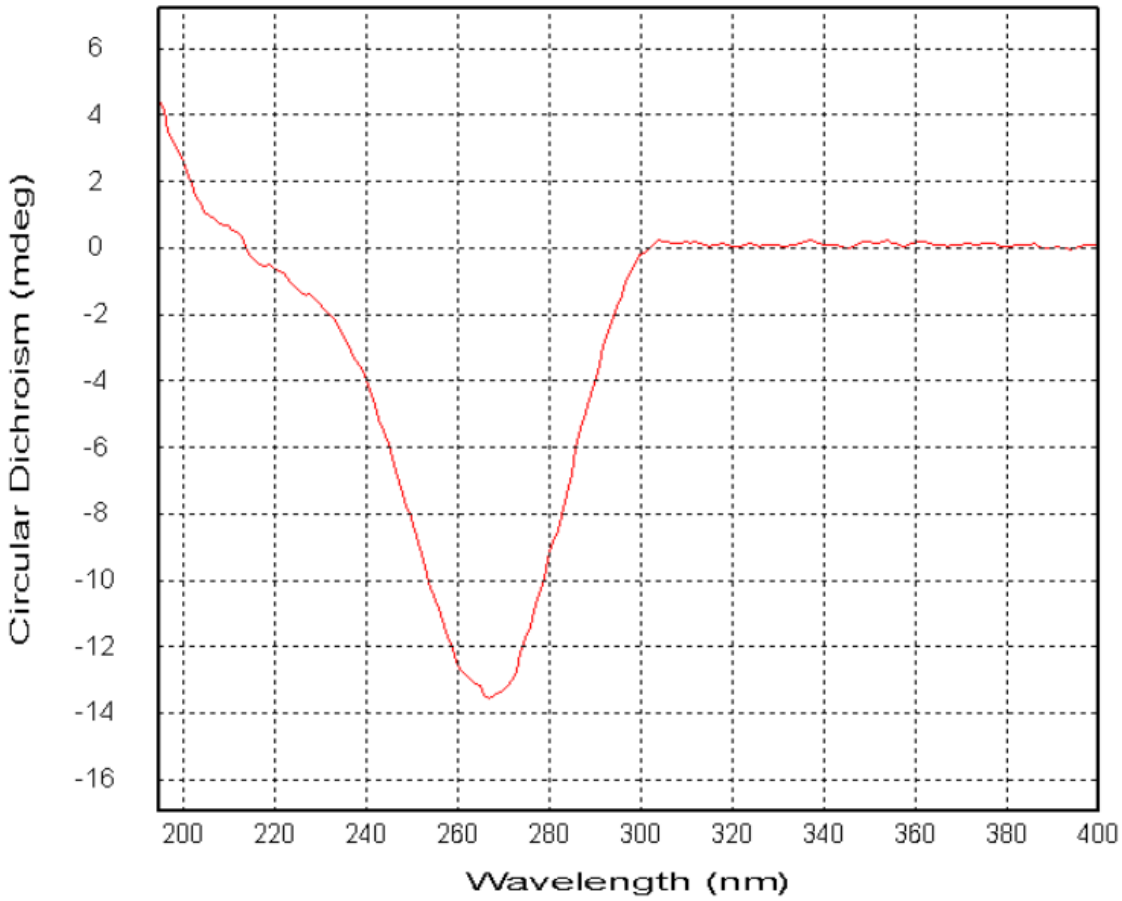


Figure S1. CD spectrum of natural compound 3

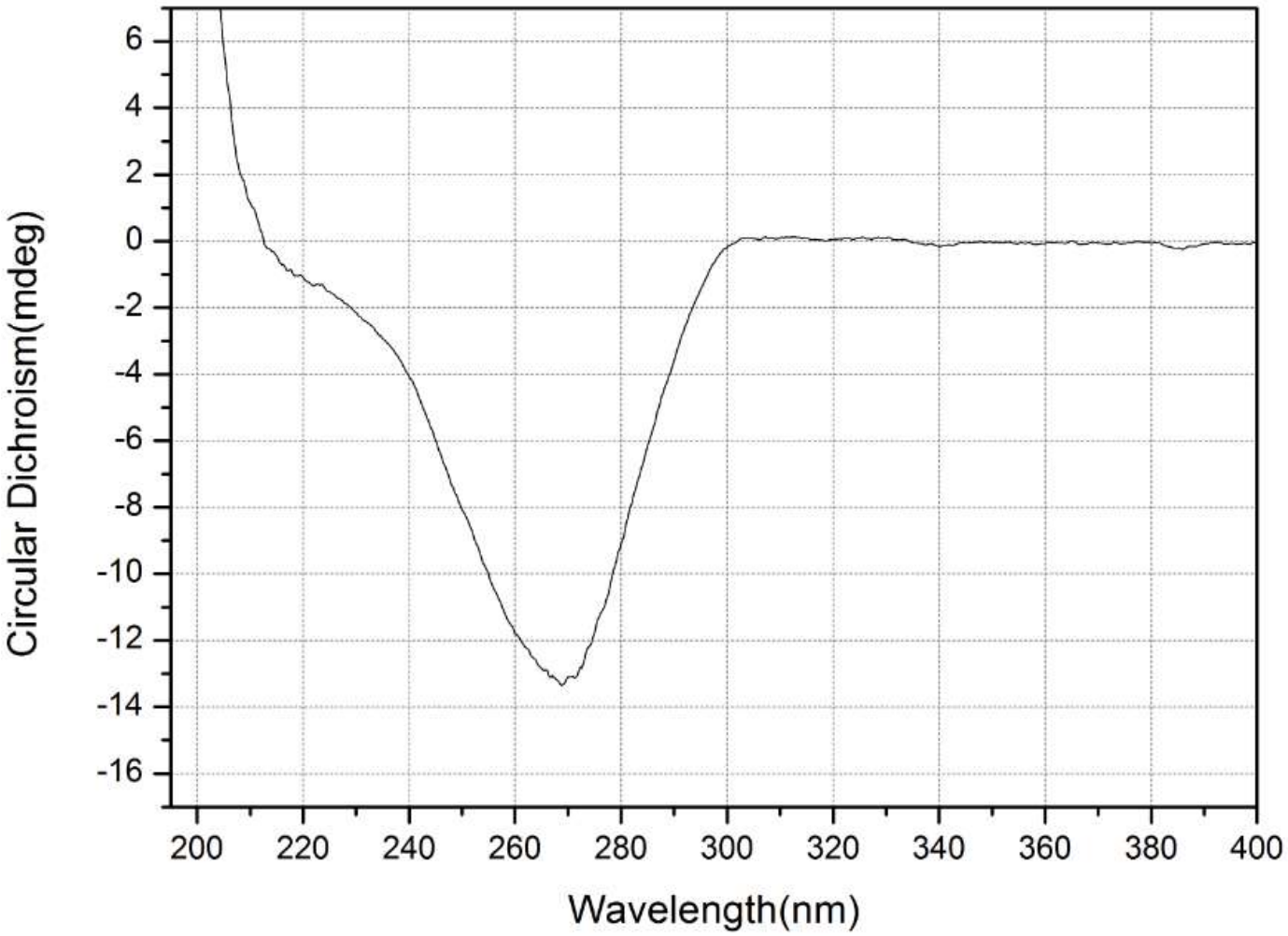


Figure S2. CD spectrum of synthetic compound 3

CD spectrum of synthetic compound 3'

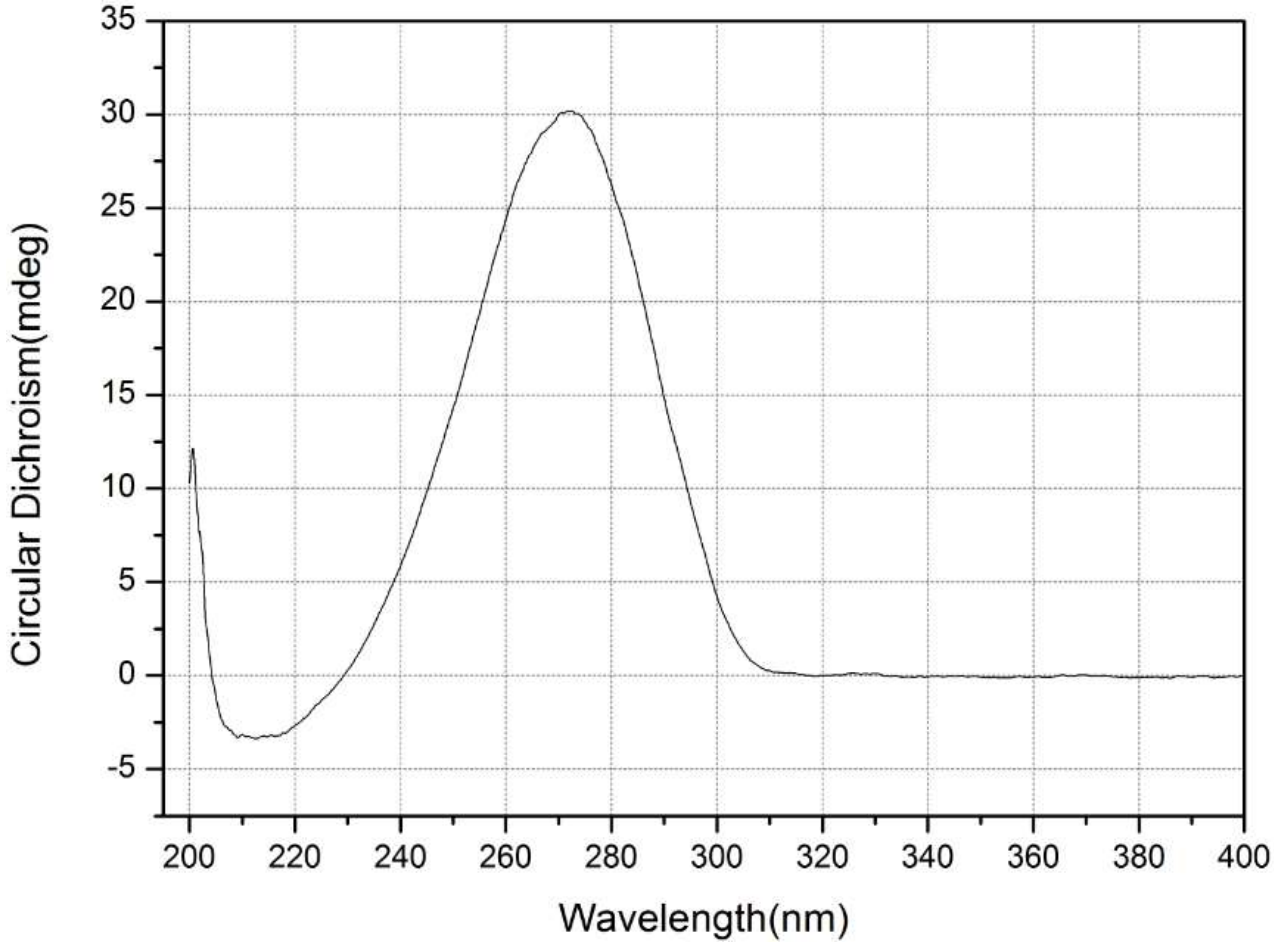
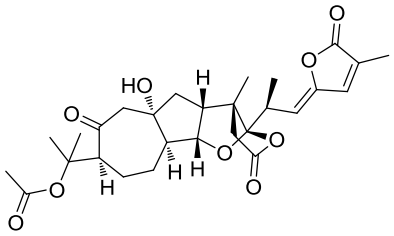


Figure S2. CD spectrum of synthetic compound 3'

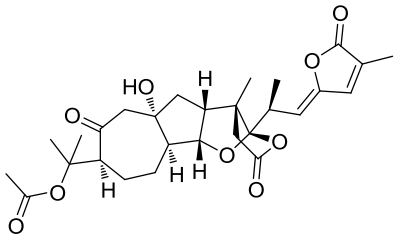
Table S7. Comparison of the ^{1}H NMR ($CDCl_3$) data of natural and synthetic compound **1**



Compound 1-6

Natural δ ^{1}H [ppm, mult, *J*(Hz)] 500 MHz	**Synthetic** δ^{1}H [ppm, mult, *J*(Hz)] 400 MHz	**Err** (narural–synthetic) **Δ**δ (ppm)
7.01 (d, 1.2)	7.02 (d, 1.5)	− 0.01
5.28 (d, 9.9)	5.28 (d, 9.9)	0
4.54 (dd,6.0, 7.5	4.55 (dd, 7.8, 5.8)	− 0.01
3.34 (m)	3.35 (m)	−
3.13 (ABd, 11.5)	3.15 (ABd, 11.6)	− 0.02
2.76 (m)	2.76 (m)	0
2.71 (d, 18.0)	2.72 (d, 18)	− 0.01
2.64 (d, 18.0)	2.65 (d, 18)	− 0.01
2.39 (m)	2.39 (m)	−
2.26 (ABd, 11.5)	2.26 (d, 11.6)	0
2.20 (m)	2.21 (m)	−
2.03 (overlapped)	2.03 (overlapped	−
2.00 (s)	2.01 (d, 1.5)	− 0.01
1.98 (s)	1.99 (s)	–0.01
1.96–2.02 (m)	1.96–2.02 (m)	−
1.76 (overlapped)	1.76 (overlapped	−
1.75–2.00 (m)	1.75–2.00 (m)	−
1.75–2.00 (m)	1.75–2.00 (m)	−
1.50 (s)	1.51 (s)	− 0.01
1.47 (s)	1.48 (s)	− 0.01
1.46–1.51 (m)	1.46–1.51 (m)	−
1.22 (s)	1.23 (s)	− 0.01
1.20 (d, 7.4)	1.22 (d)	− 0.02

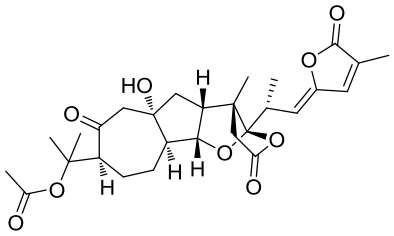
Table S8. Comparison of the ^{13}C NMR ($CDCl_3$) data of natural and synthetic compound **1**



Compound 1-6

Natural δ ^{13}C (ppm) 126 MHz	**Synthetic** δ^{13}C (ppm) 101 MHz	**Err** (narural–synthetic) **Δ**δ (ppm)
211.2	211.2	0.0
173.0	172.9	0.1
170.6	170.6	0.1
169.9	169.8	0.1
147.7	147.7	0.0
137.7	137.6	0.1
130.0	130.0	0.0
121.4	121.3	0.0
113.4	113.3	0.1
84.0	84.0	0.0
82.2	82.2	0.1
80.8	80.8	0.0
62.4	62.5	–0.1
53.2	53.2	0.0
50.8	50.8	0.0
50.5	50.5	0.0
50.1	50.0	0.1
46.3	46.3	0.0
41.7	41.7	0.1
35.9	35.9	0.0
24.8	24.8	0.0
24.5	24.5	0.0
23.3	23.3	0.0
22.4	22.3	0.0
19.6	19.6	0.0
19.1	19.1	0.0
15.9	15.9	0.0
10.6	10.6	0.0

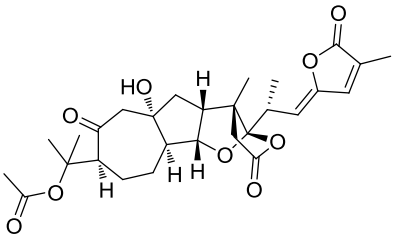
Table S9. Comparison of the ^{1}H NMR ($CDCl_3$) data of natural and synthetic compound **2**



Compound 1-7

Natural δ ^{1}H [ppm, mult, *J*(Hz)] 500 MHz	**Synthetic** δ^{1}H [ppm, mult, *J*(Hz)] 400 MHz	**Err** (narural–synthetic) **Δ**δ (ppm)
7.00 (d, 1.6)	6.99 (d, 1.4)	0.01
4.99 (d, 10.4)	4.99 (d, 10.5)	0
4.57 (dd, 6.4, 8.0)	4.57 (dd, 6.1,7.8)	0
3.37 (m)	3.37 (m)	–
3.13 (ABd, 11.6)	3.13 (d, 11.5)	0
2.78 (m)	2.77 (m)	–
2.67 (d, 18.0)	2.66 (d, 17.9)	0.01
2.47 (d, 18.0)	2.46 (d, 17.9)	0.01
2.38 (m)	2.39 (m)	–
2.27 (ABd, 11.6)	2.27 (d, 11.5)	0
2.23 (m)	2.22 (m)	–
2.08 (overlapped)	2.08 (overlapped)	–
2.02 (s)	2.02 (s)	0
1.99–2.02 (m)	1.99–2.02 (m)	–
1.99 (s)	1.99 (s)	0
1.80–1.92 (m)	1.80–1.92 (m)	–
1.80–1.91 (m)	1.80–1.91 (m)	–
1.78 (overlapped)	1.78 (overlapped)	–
1.53 (s)	1.52 (s)	0.01
1.49 (s)	1.49 (s)	0
1.48–1.53 (m)	1.48–1.54 (m)	–
1.26 (d, 6.8)	1.26 (d, 6.9)	0
1.19 (s)	1.19 (s)	0

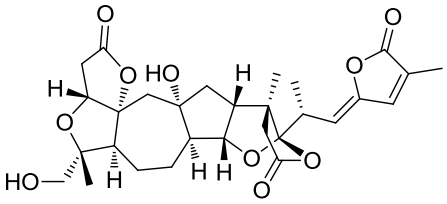
Table S10. Comparison of the ^{13}C NMR ($CDCl_3$) data of natural and synthetic compound **2**



Compound 1-7

Natural δ ^{13}C (ppm) 126 MHz	**Synthetic** δ^{13}C (ppm) 101 MHz	**Err** (narural–synthetic) **Δ**δ (ppm)
211.1	211.1	0.0
173.6	173.6	0.0
170.2	170.3	0.0
169.8	169.8	0.0
148.4	148.4	0.0
137.4	137.4	0.0
130.8	130.8	0.0
121.4	121.4	0.0
111.3	111.3	0.0
83.6	83.6	0.0
82.3	82.3	0.0
80.7	80.7	0.0
62.5	62.5	0.0
53.4	53.4	0.0
50.8	50.7	0.0
50.3	50.2	0.0
50.2	50.2	0.0
46.4	46.4	0.0
41.8	41.7	0.0
36.3	36.3	0.0
24.9	24.9	0.0
24.6	24.6	0.0
23.3	23.2	0.0
22.4	22.4	0.0
19.6	19.5	0.0
18.8	18.8	0.0
16.0	16.0	0.0
10.6	10.6	0.0

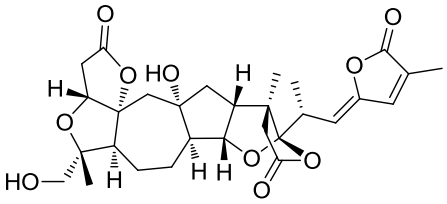
Table S11. Comparison of the ^{1}H NMR ($CDCl_3$) data of natural and synthetic compound **2**



compound 3

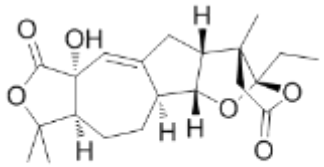
Natural δ ^{1}H [ppm, mult, *J*(Hz)] 500 MHz	**Synthetic** δ^{1}H [ppm, mult, *J*(Hz)] 400 MHz	**Err** (narural–synthetic) **Δ**δ (ppm)
6.98 (brd, 0.8)	6.99 (d, 1.2)	0.01
4.97 (d, 10.5)	4.97 (d, 10.5)	0
4.47 (dd, 7.9, 5.7)	4.47 (dd, 8.3,5.5)	0
4.19 (brd, 5.0)	4.19(brd, 4.7)	0
3.57 (d, 12.0)	3.57(d, 12.3)	0
3.40 (d, 12.0)	3.40(overlap)	–
3.34 (m)	3.34(overlap)	–
2.77 (m)	2.77(m)	–
2.76 (brdd,18.1)	2.76 (overlap)	0
2.69 (d, 18.1)	2.69 (d, 18.5)	0
2.63 (Abd, 17.7)	2.63 (Abd, 17.8)	0
2.44 (Abd, 17.7)	2.44 (Abd, 17.8)	0
2.43 (m)	2.43 (m)	–
2.38 (m)	2.38 (m)	–
2.05 (m)	2.05 (m)	–
2.01 (s)	2.01 (s)	0
1.91 (overlap)	1.91 (overlap)	–
1.91 (overlap)	1.91 (overlap)	–
1.86 (overlap)	1.86 (overlap)	–
1.86 (overlap)	1.86 (overlap)	–
1.70 (m)	1.70 (m)	–
1.52 (m)	1.52 (m)	0
1.40 (m)	1.40 (m)	0
1.25 (d, 6.7)	1.25 (d, 6.5)	0
1.19 (s)	1.19 (s)	0
1.06 (s)	1.07 (s)	– 0.01

Table S12. Comparison of the ^{13}C NMR ($CDCl_3$) data of natural and synthetic compound **3**

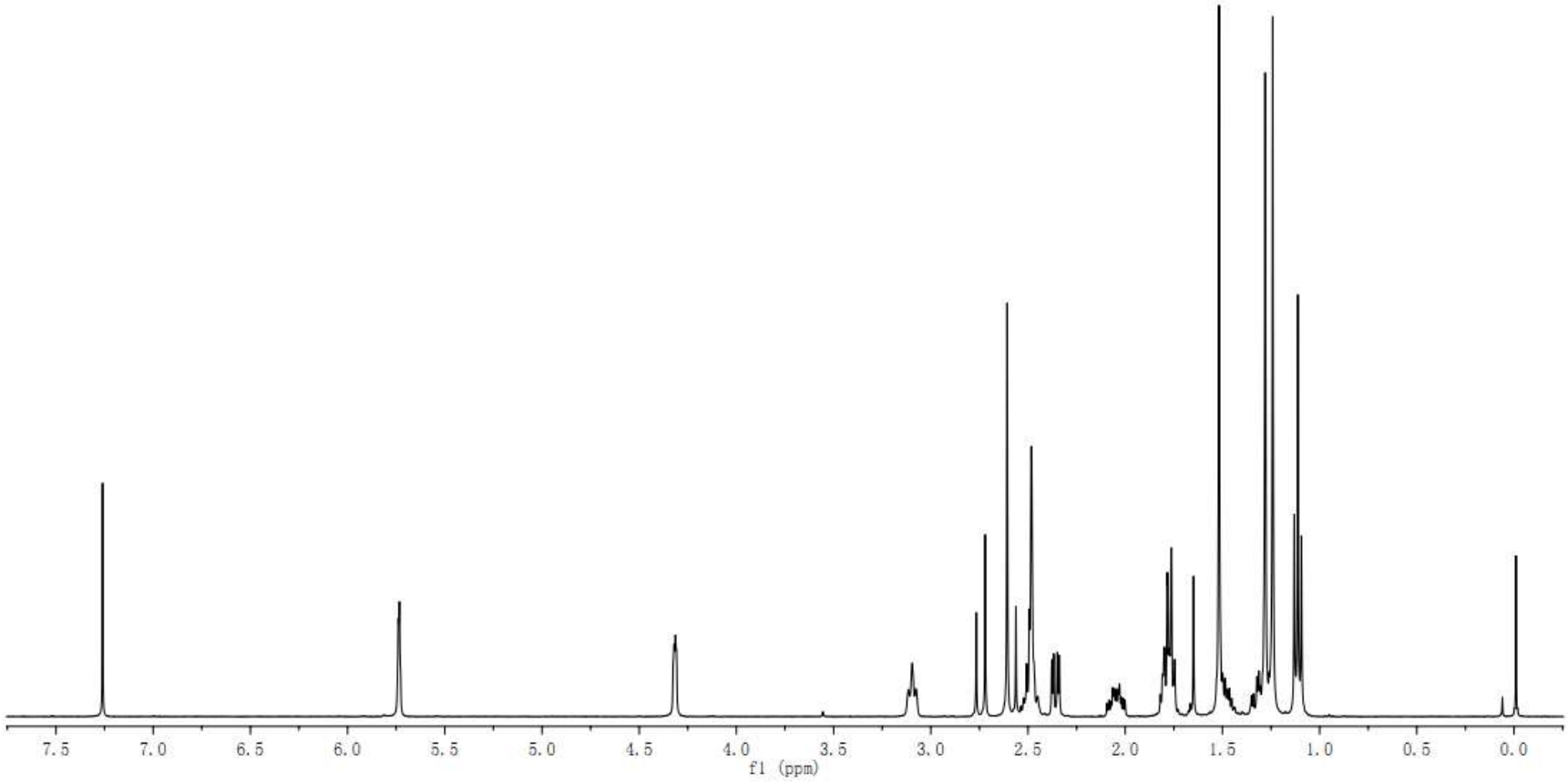


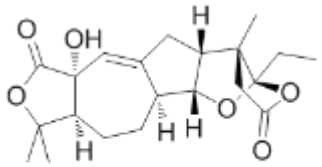
compound 3

Natural δ ^{13}C (ppm) 126 MHz	**Synthetic** δ^{13}C (ppm) 101 MHz	**Err** (narural–synthetic) **Δ**δ (ppm)
173.7	173.7	0.0
173.4	173.4	0.0
170.3	170.3	0.0
148.4	148.4	0.0
137.5	137.4	0.1
130.7	130.7	0.0
121.9	121.8	0.1
111.3	111.3	0.0
98.4	98.4	0.0
87.1	87.1	0.0
84.7	84.8	‑ 0.1
82.7	82.7	0.0
80.8	80.9	‑ 0.1
66.7	66.8	–0.1
53.3	53.4	–0.1
52.8	52.9	–0.1
50.5	50.6	–0.1
50.4	50.4	0.0
46.7	46.7	0.0
41.9	42.0	–0.1
41.2	41.3	–0.1
36.1	36.1	0.0
34.9	34.9	0.0
23.7	23.7	0.0
21.5	21.5	0.0
18.7	18.7	0.0
17.4	17.4	0.0
16.0	16.0	0.0
10.6	10.6	0.0

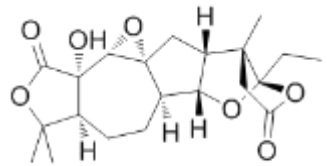


^{1}H NMR spectrum of 14

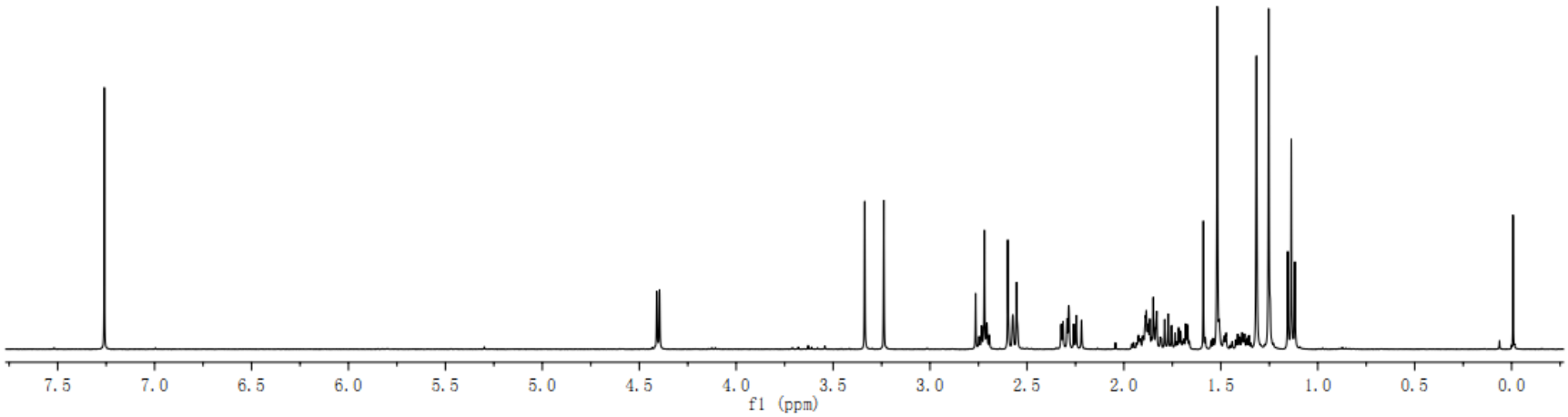


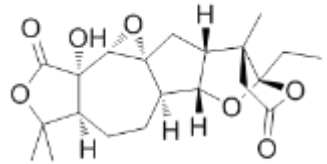


^{13}C NMR spectrum of 14

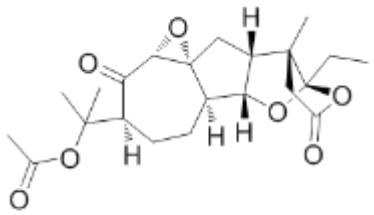


^{1}H NMR spectrum of 15

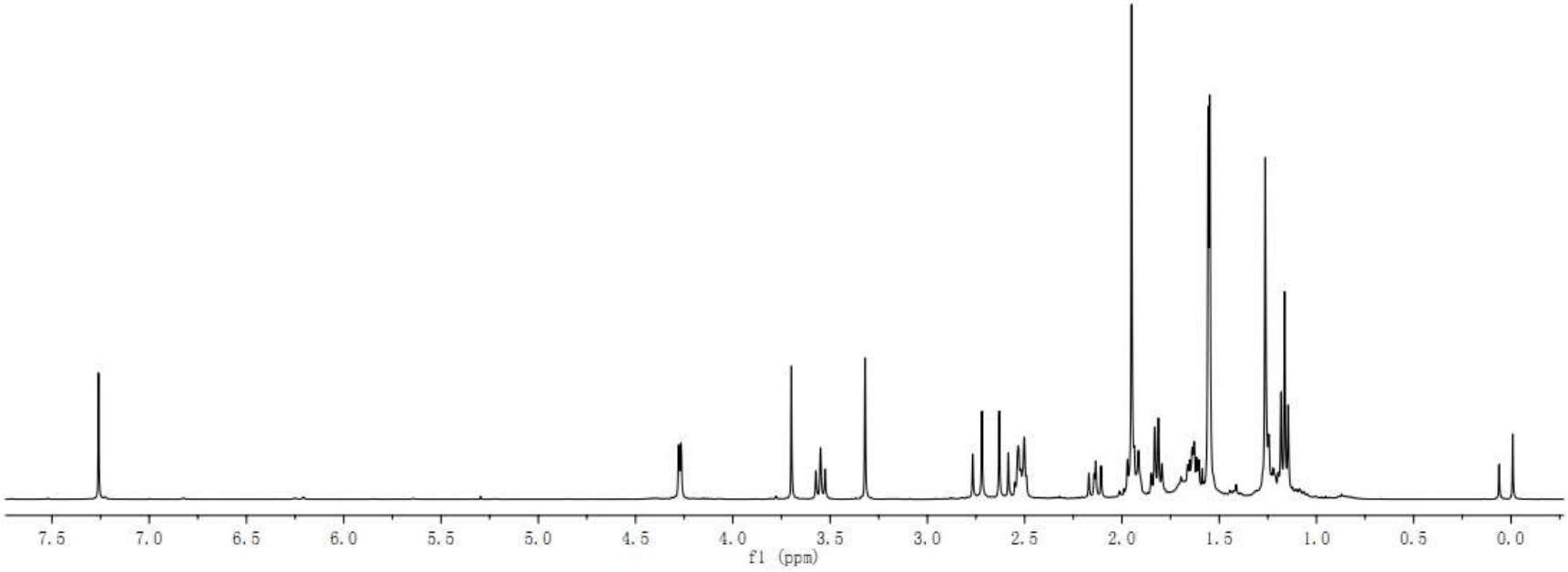


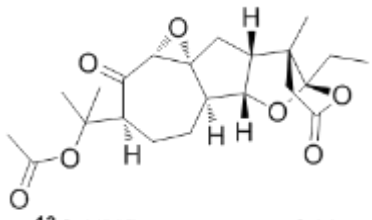


^{13}C NMR spectrum of 15

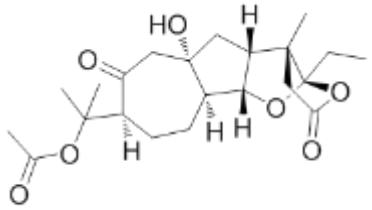


^{1}H NMR spectrum of 16

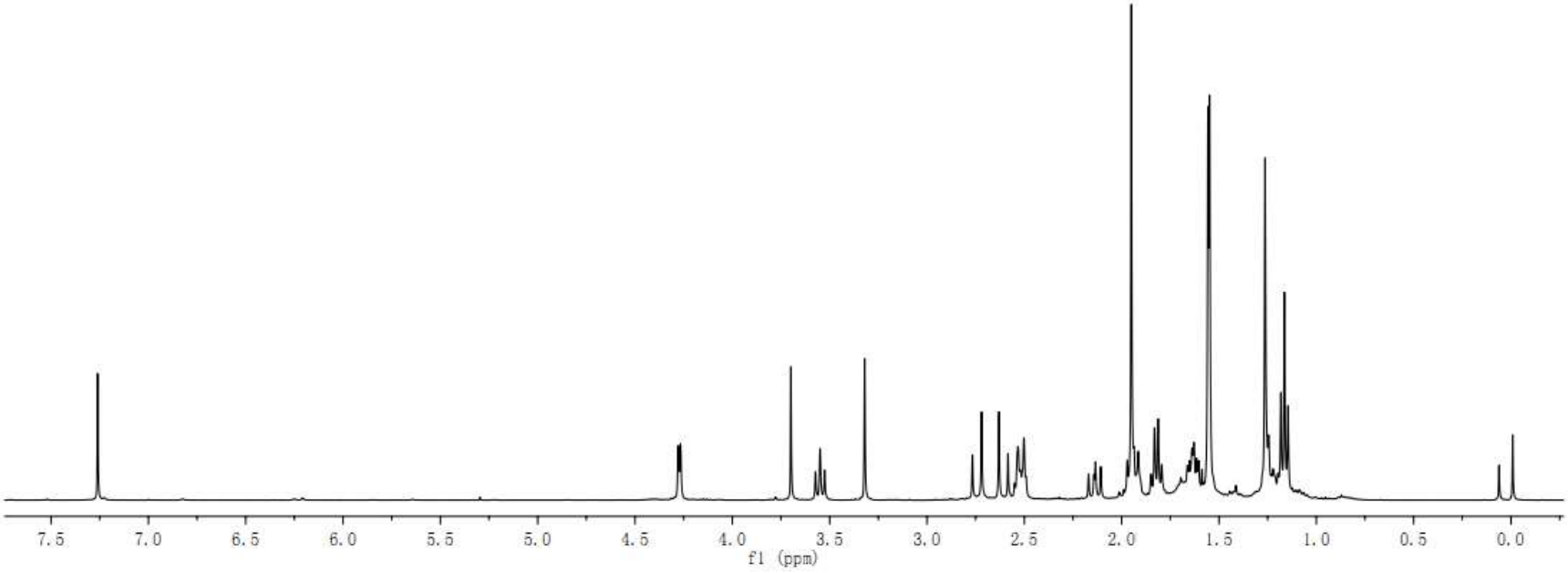


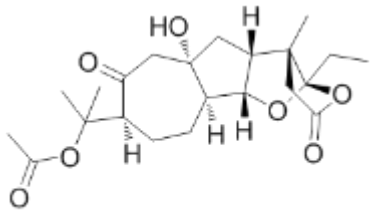


^{13}C NMR spectrum of 16

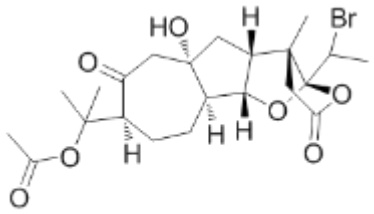


^{1}H NMR spectrum of 17

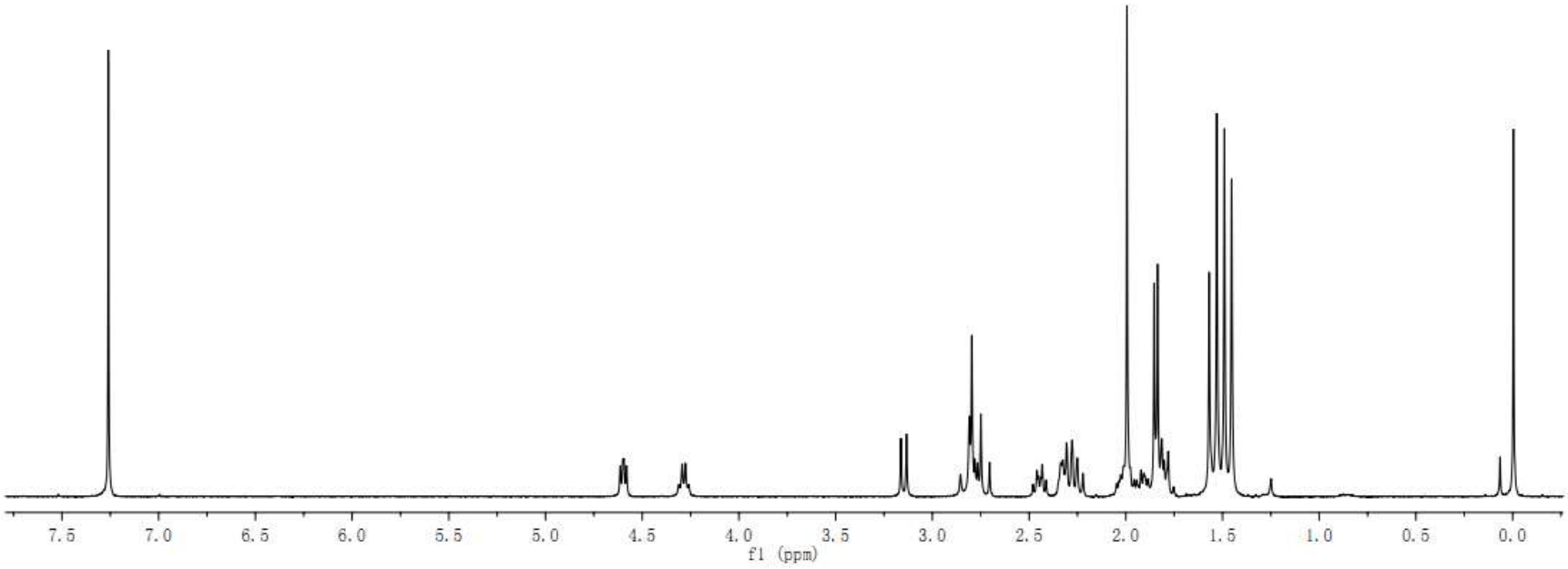


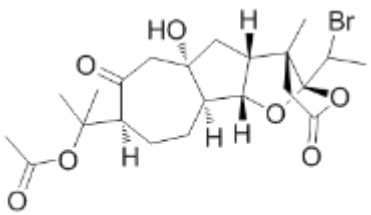


^{13}C NMR spectrum of 17

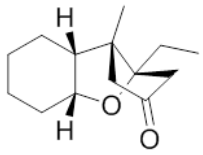


^{1}H NMR spectrum of 7

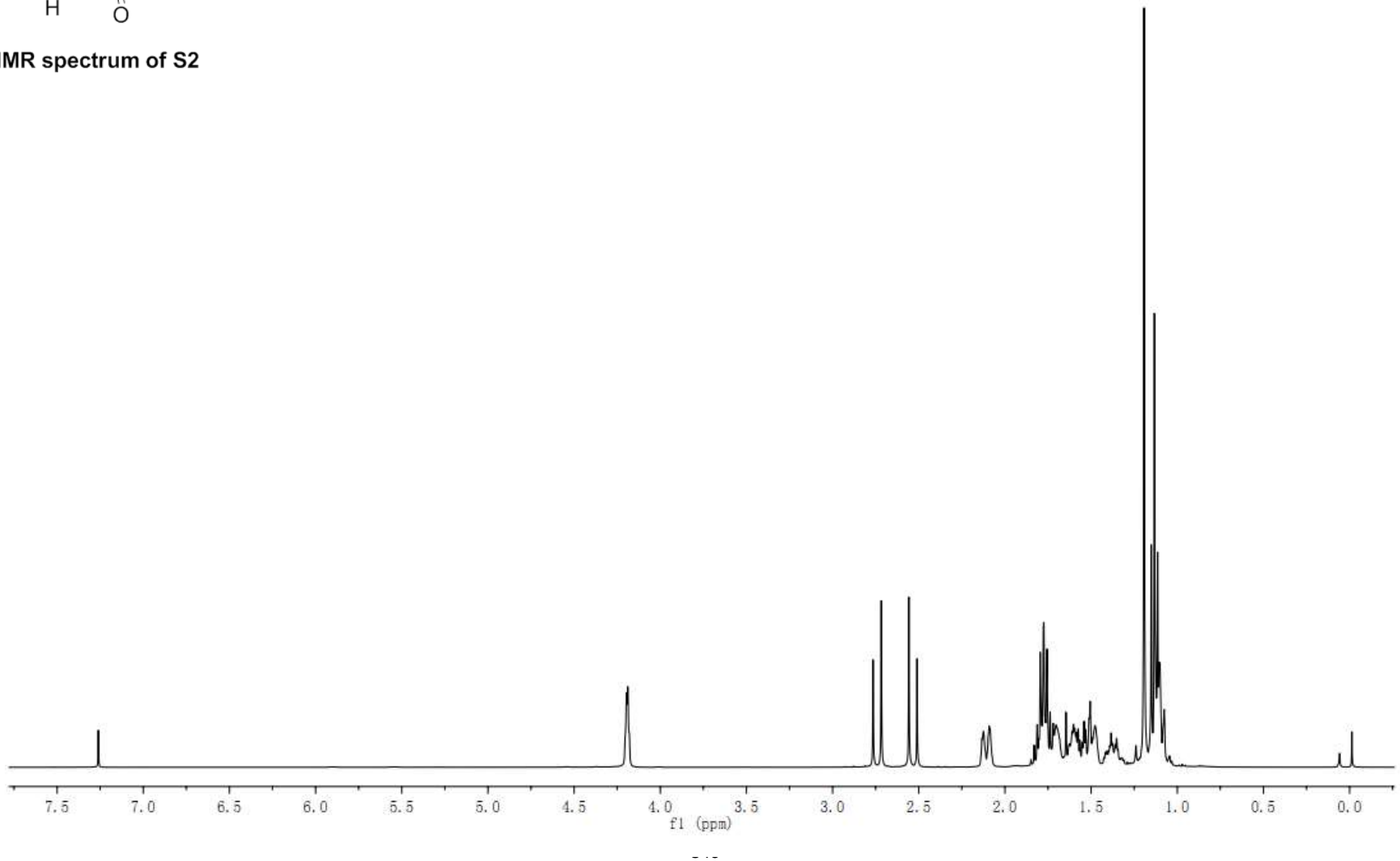


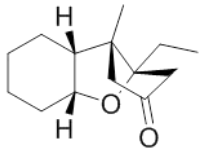


^{13}C NMR spectrum of 7

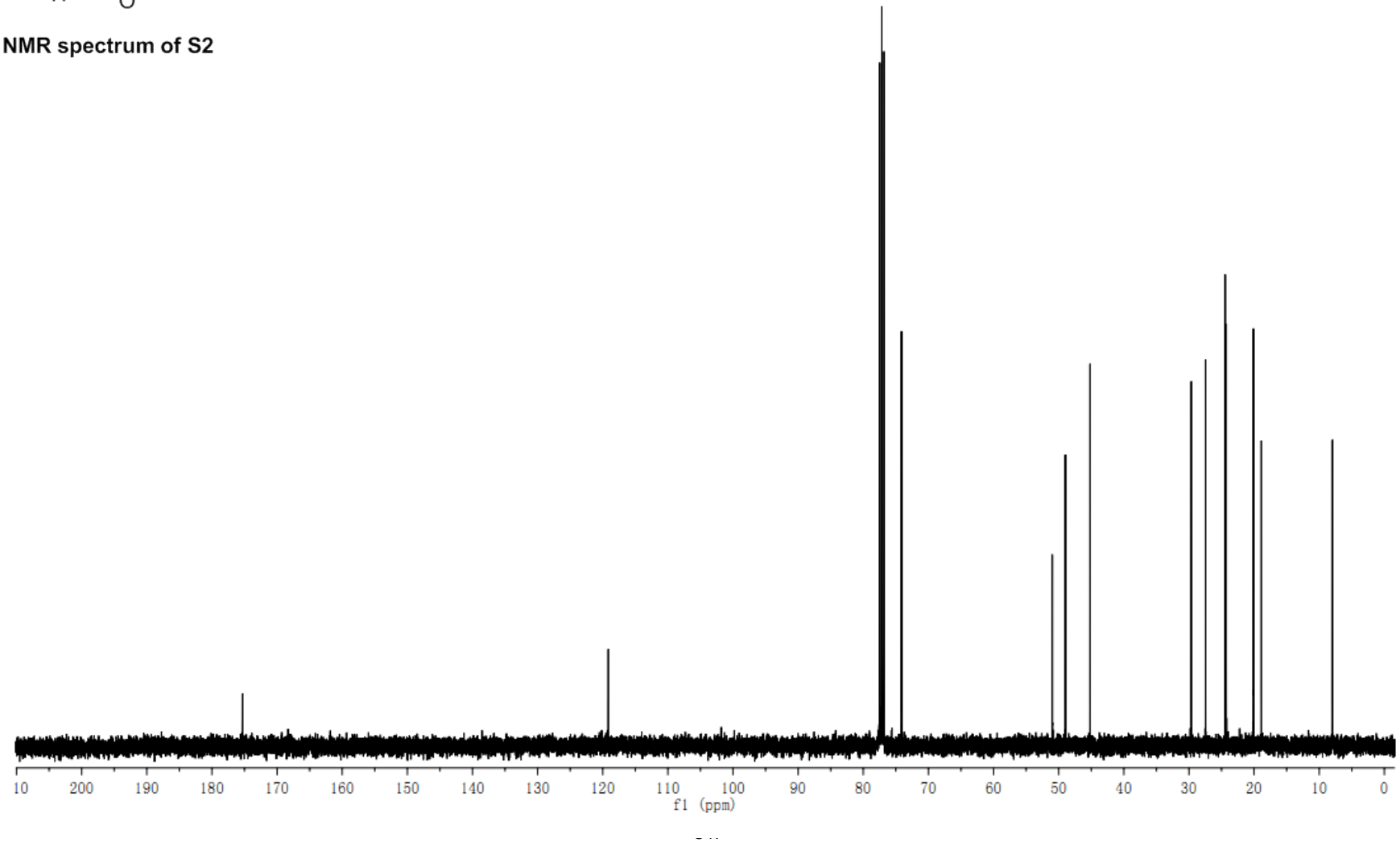


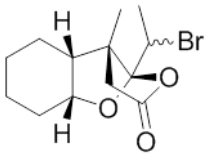
^{1}H NMR spectrum of S2



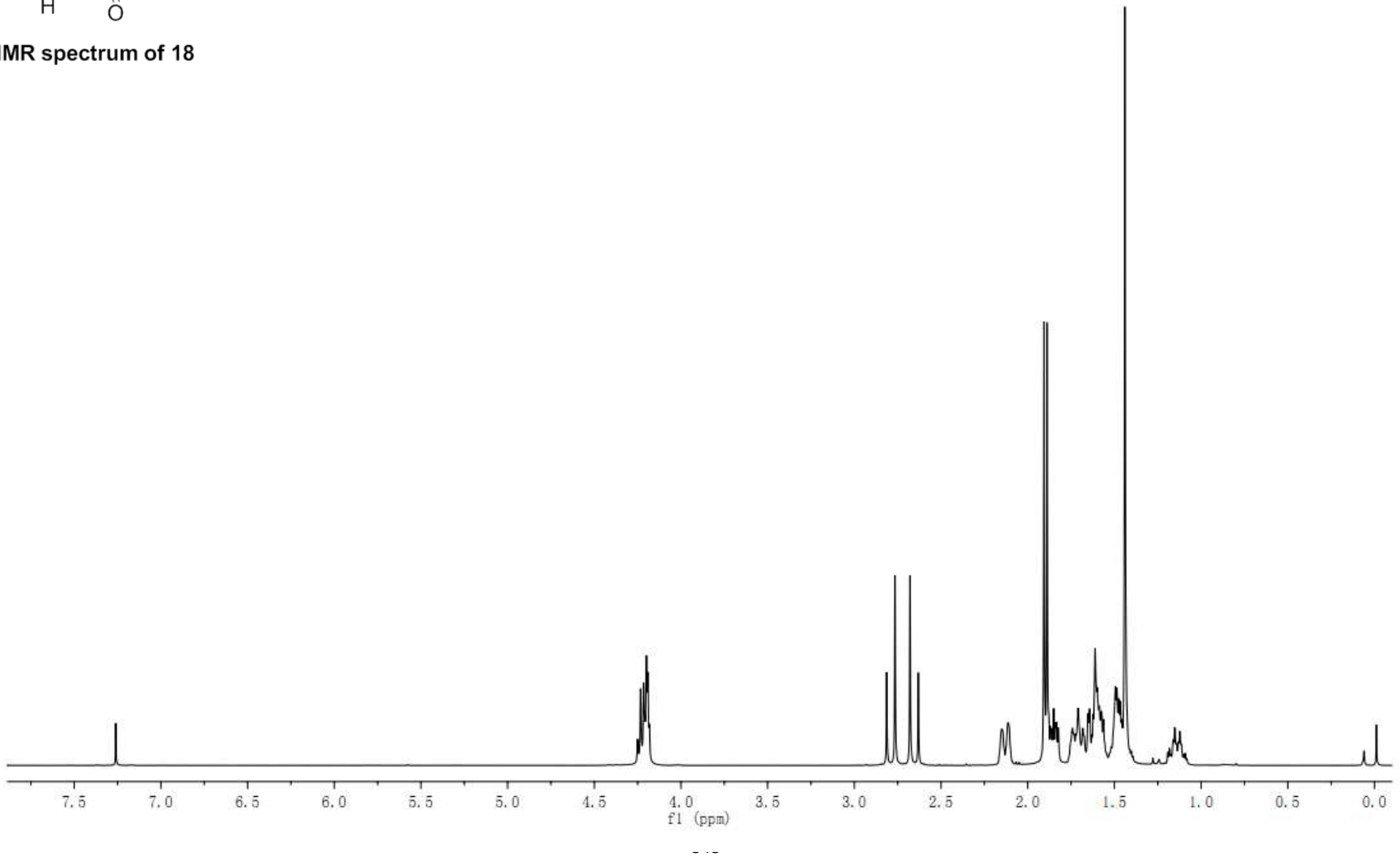


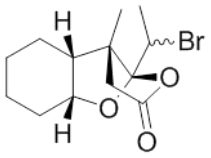
^{13}C NMR spectrum of S2



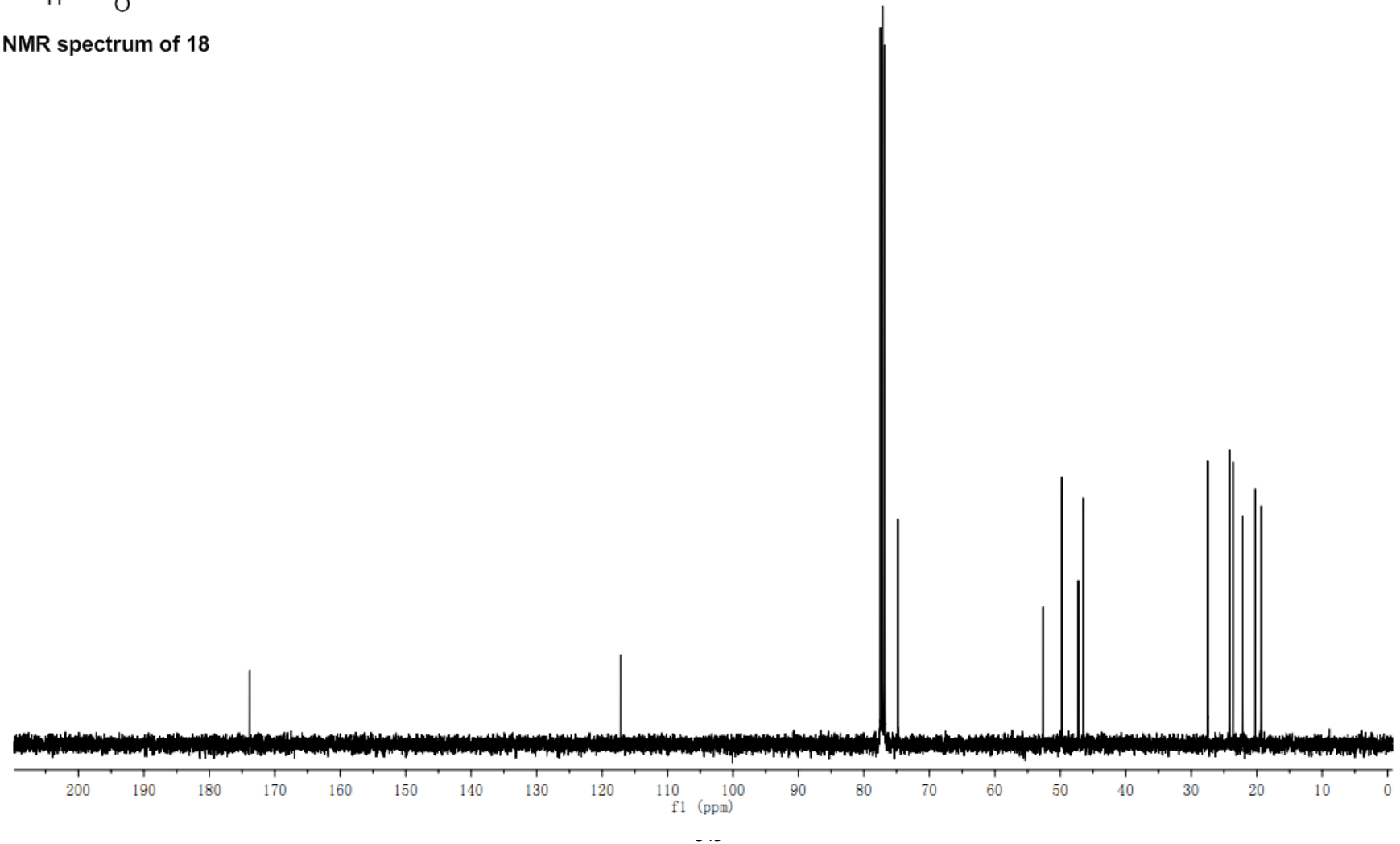


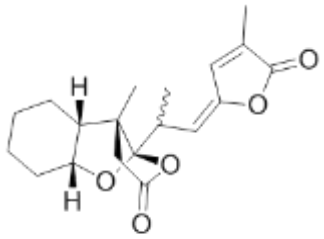
^{1}H NMR spectrum of 18



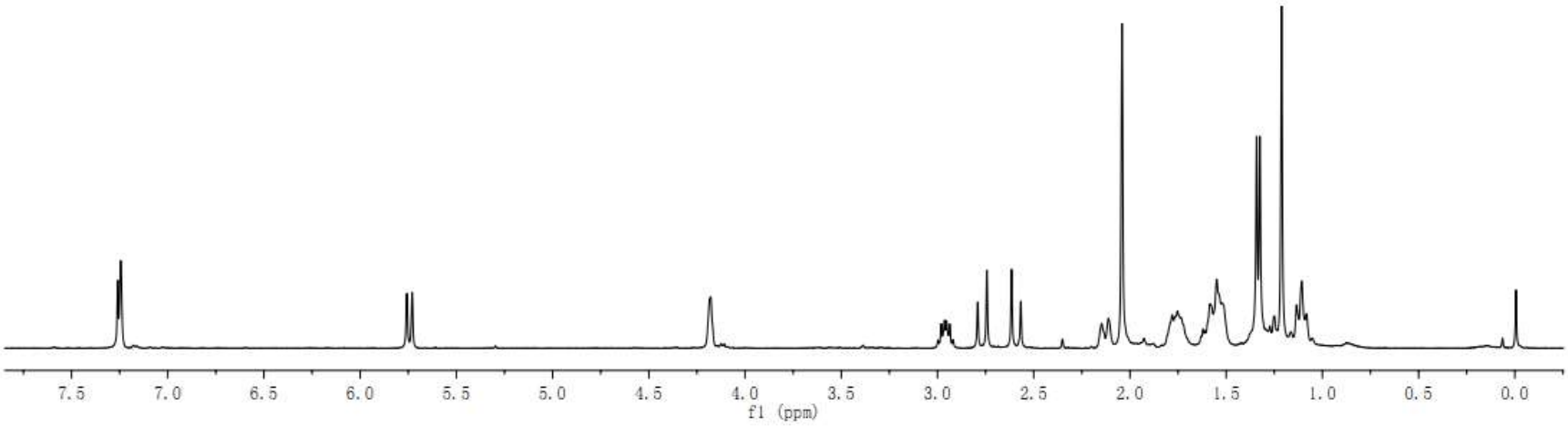


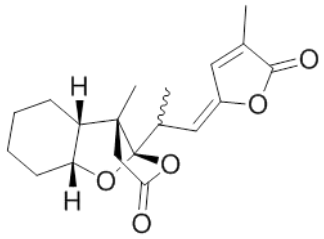
^{13}C NMR spectrum of 18



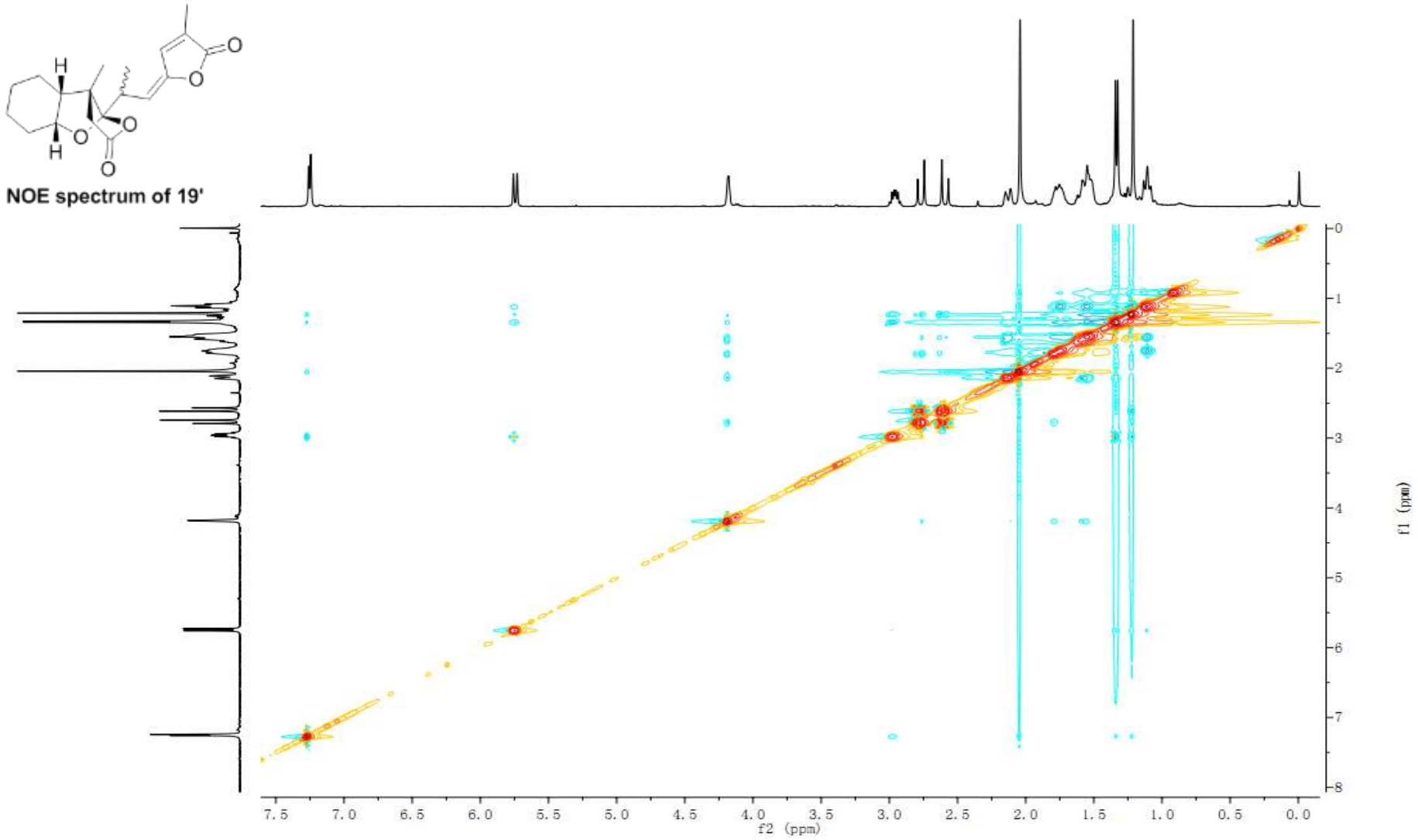


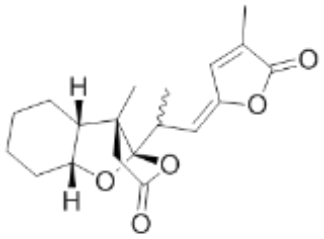
^{1}H NMR spectrum of 19'



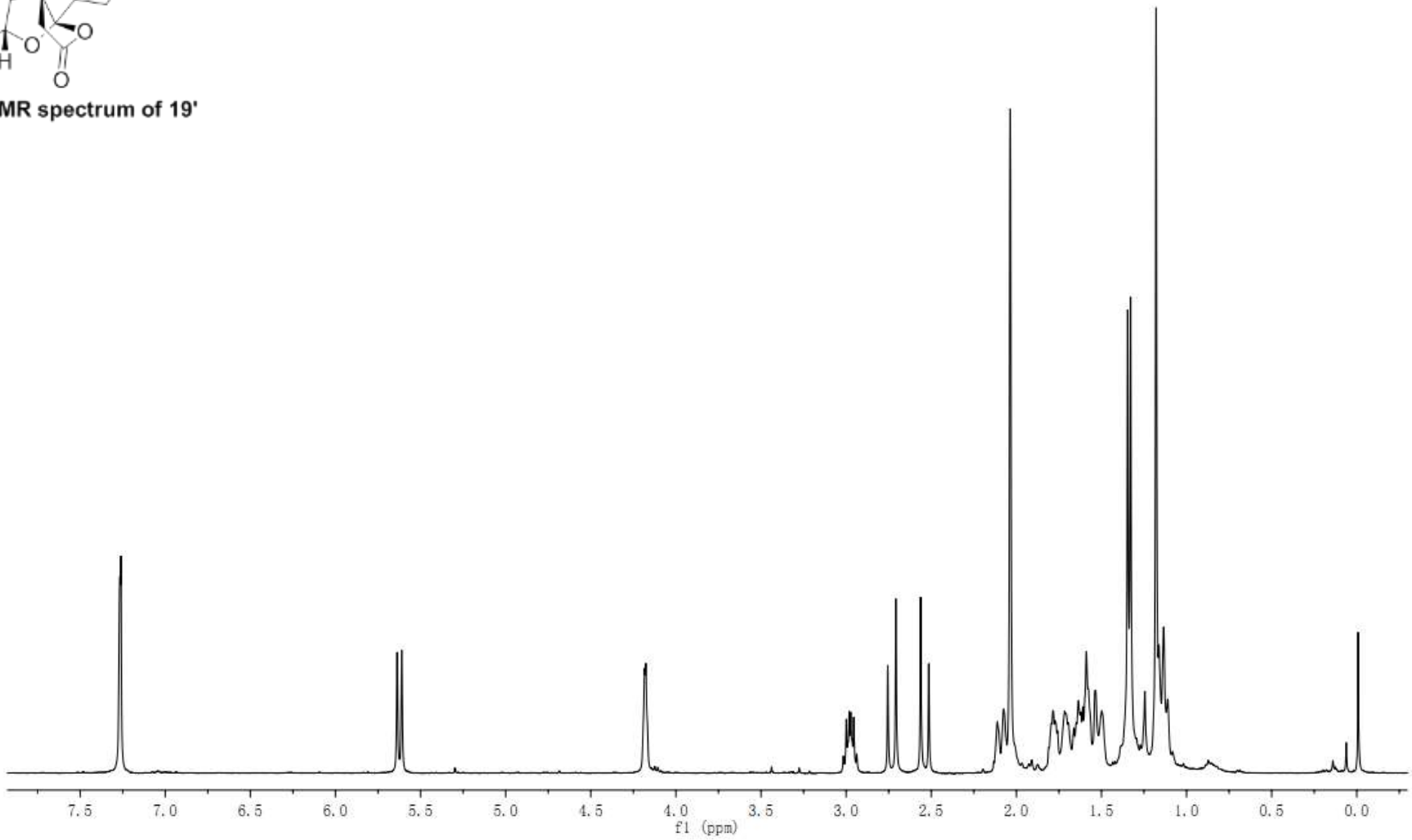


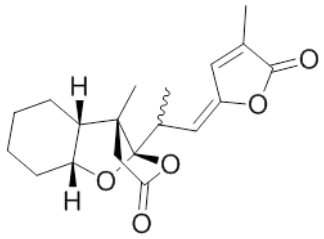
^{13}C NMR spectrum of 19'


NOE spectrum of 19'
f2 (ppm)
f1 (ppm)

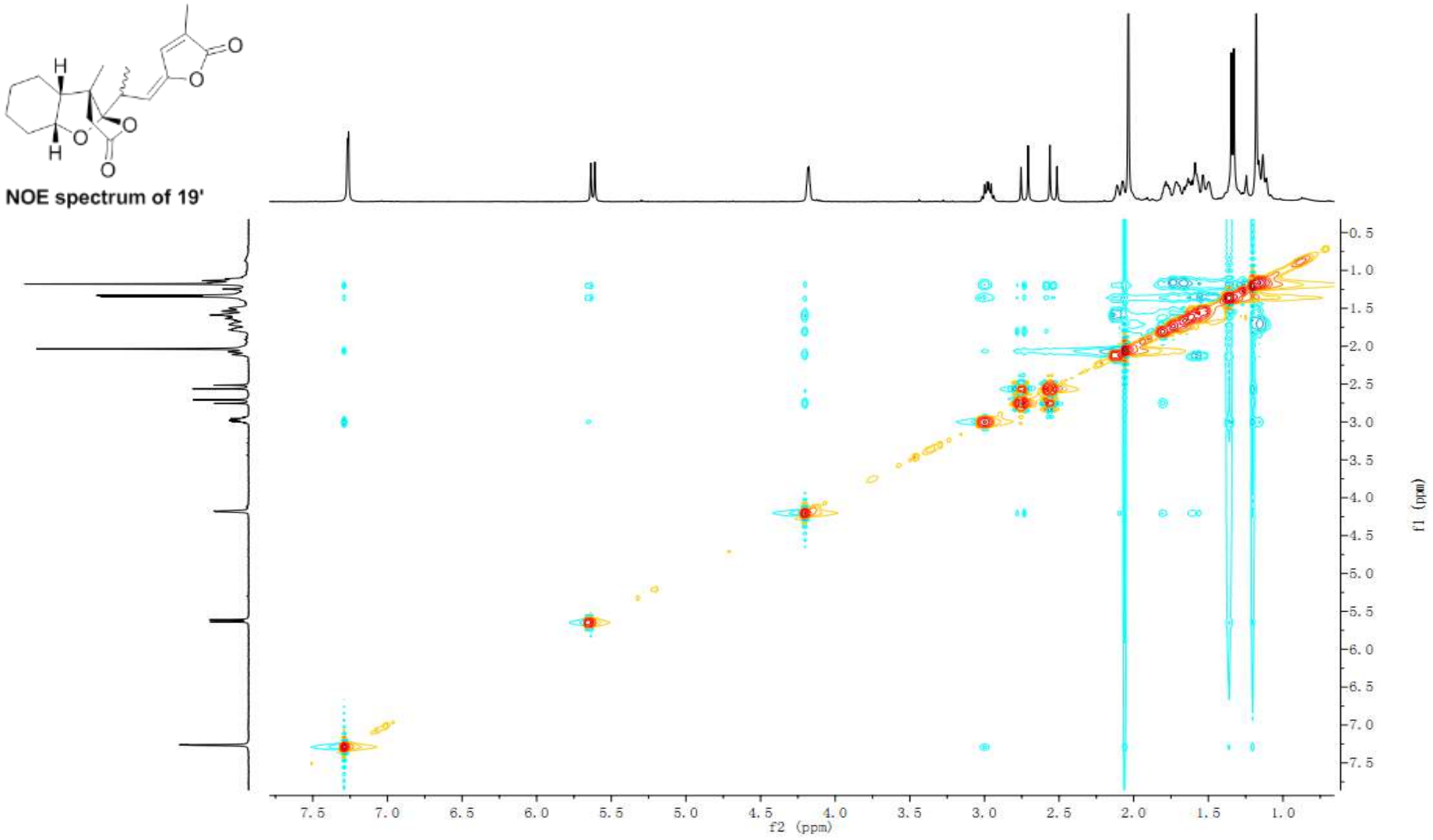


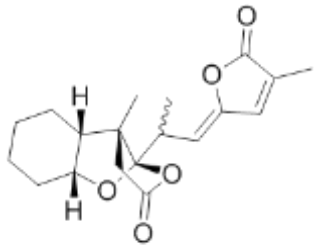
^{1}H NMR spectrum of 19'



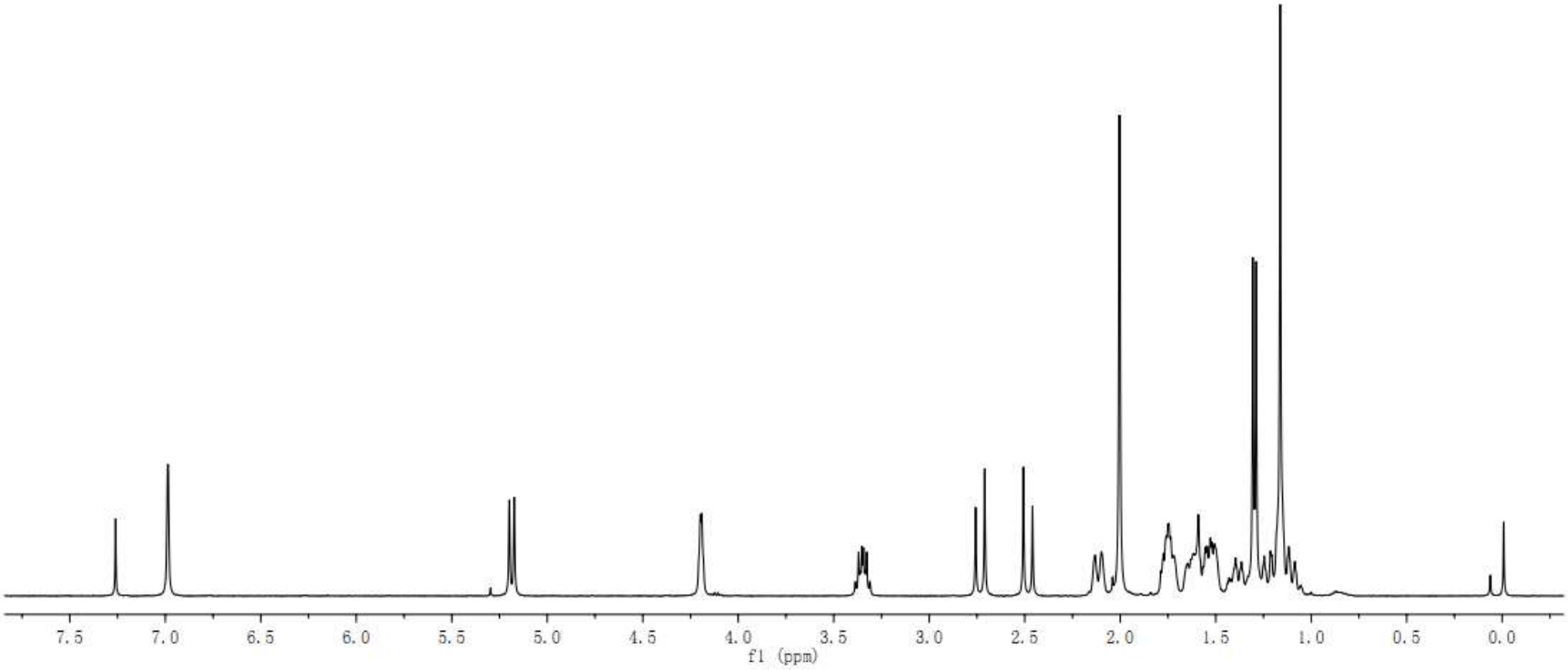


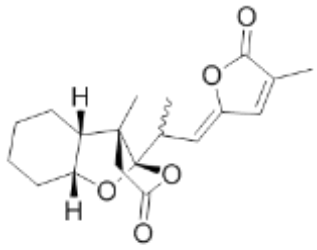
^{13}C NMR spectrum of 19'


NOE spectrum of 19'
f2 (ppm)
f1 (ppm)

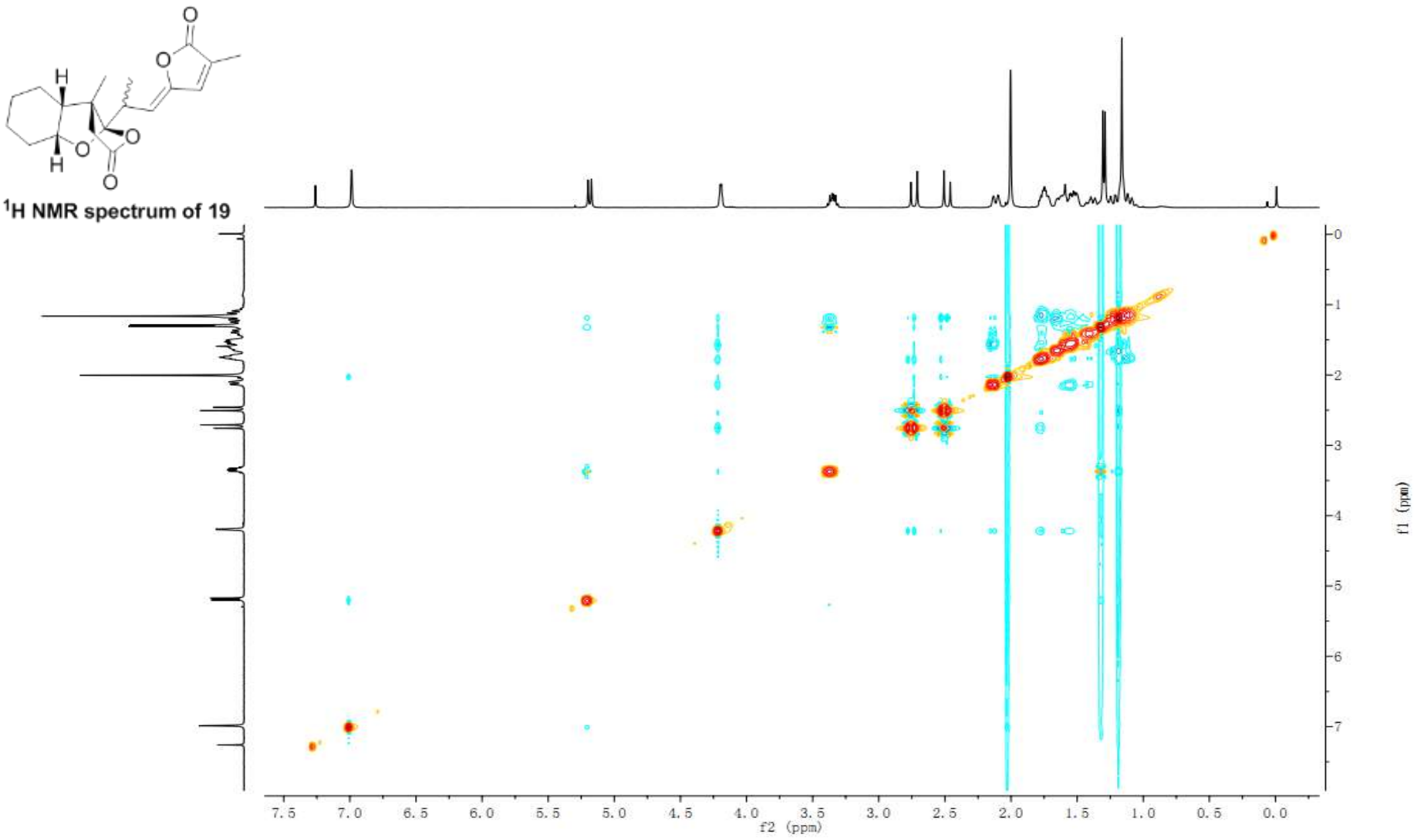


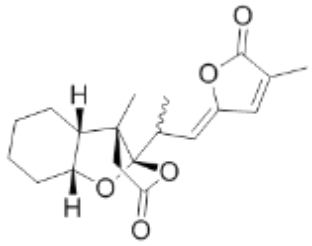
^{1}H NMR spectrum of 19



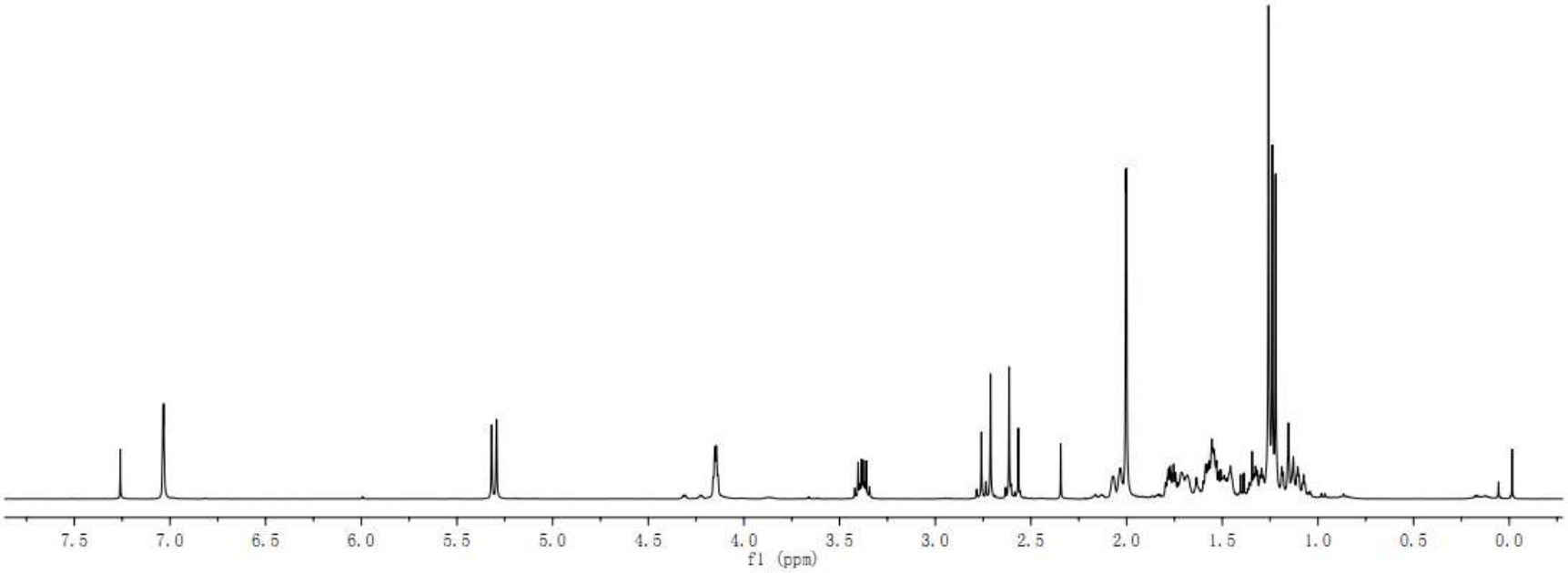


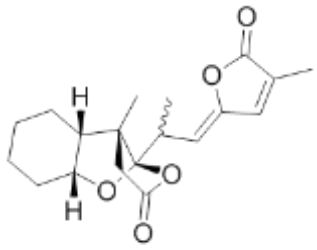
^{13}C NMR spectrum of 19


H
O
O
O
O
H
O
1H NMR spectrum of 19
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
f1 (ppm)

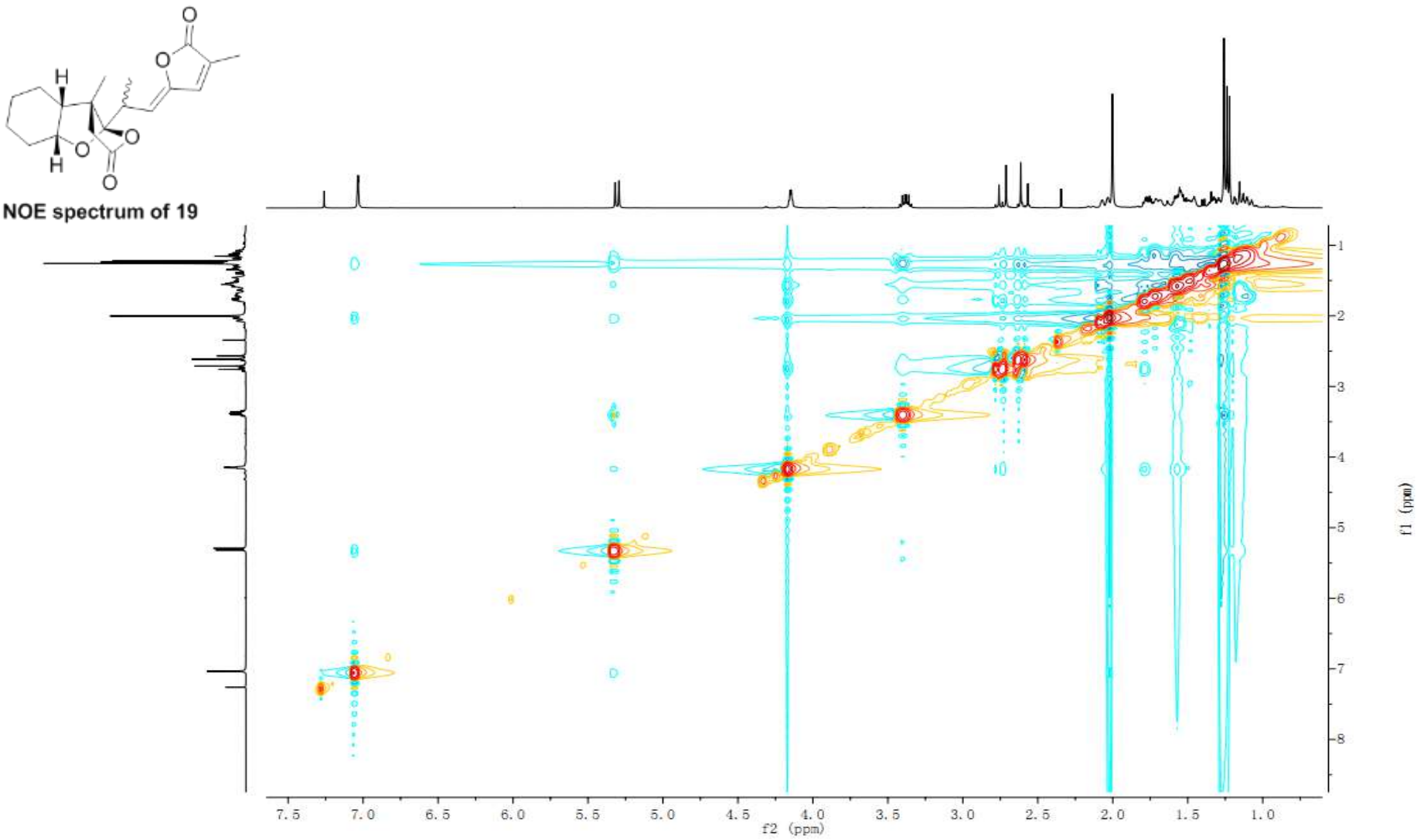


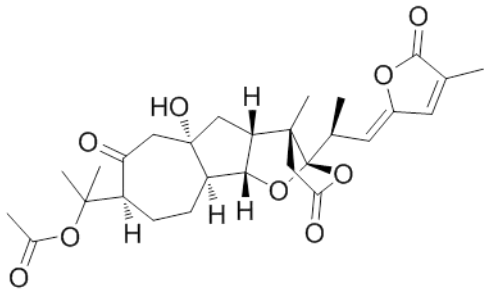
^{1}H NMR spectrum of 19



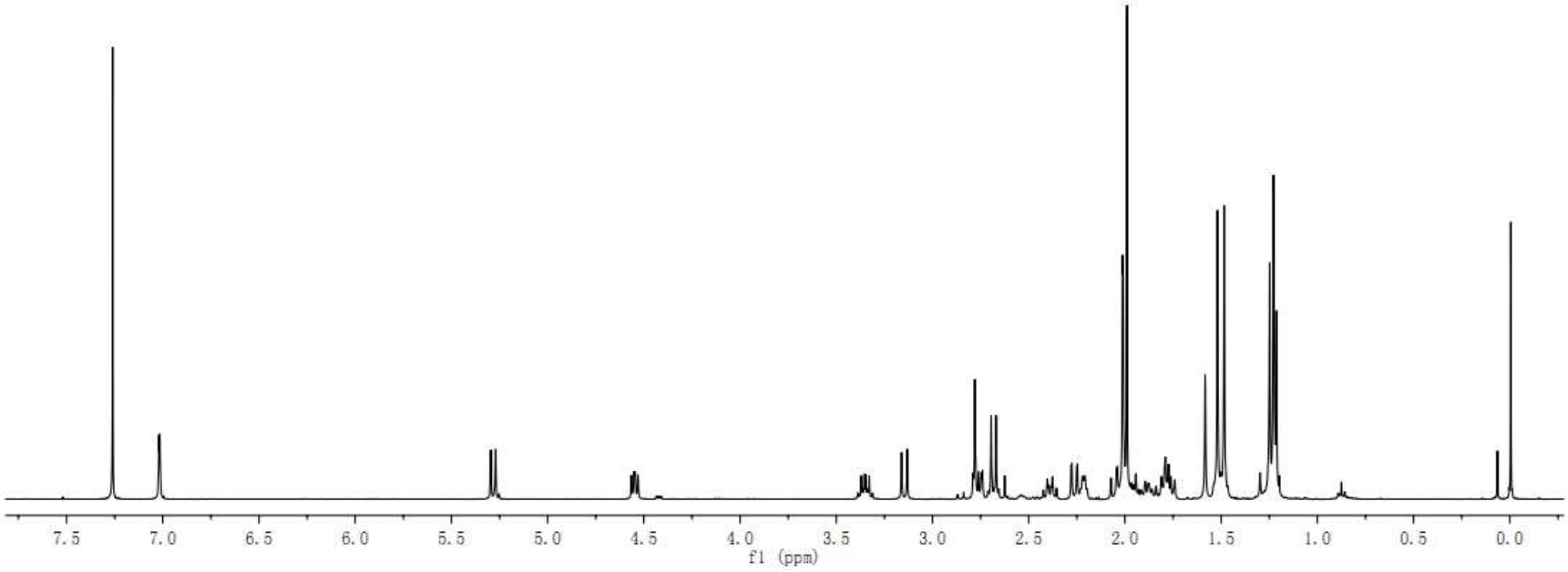


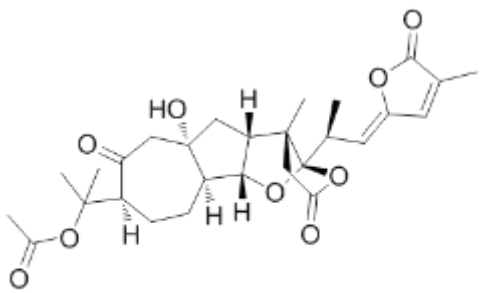
^{13}C NMR spectrum of 19


O
O
H
O
O
H
O
NOE spectrum of 19
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1
2
3
4
5
6
7
8
f1 (ppm)

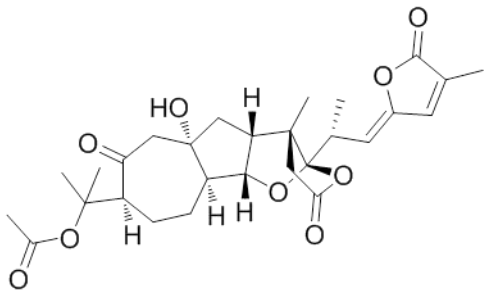


^{1}H NMR spectrum of 1

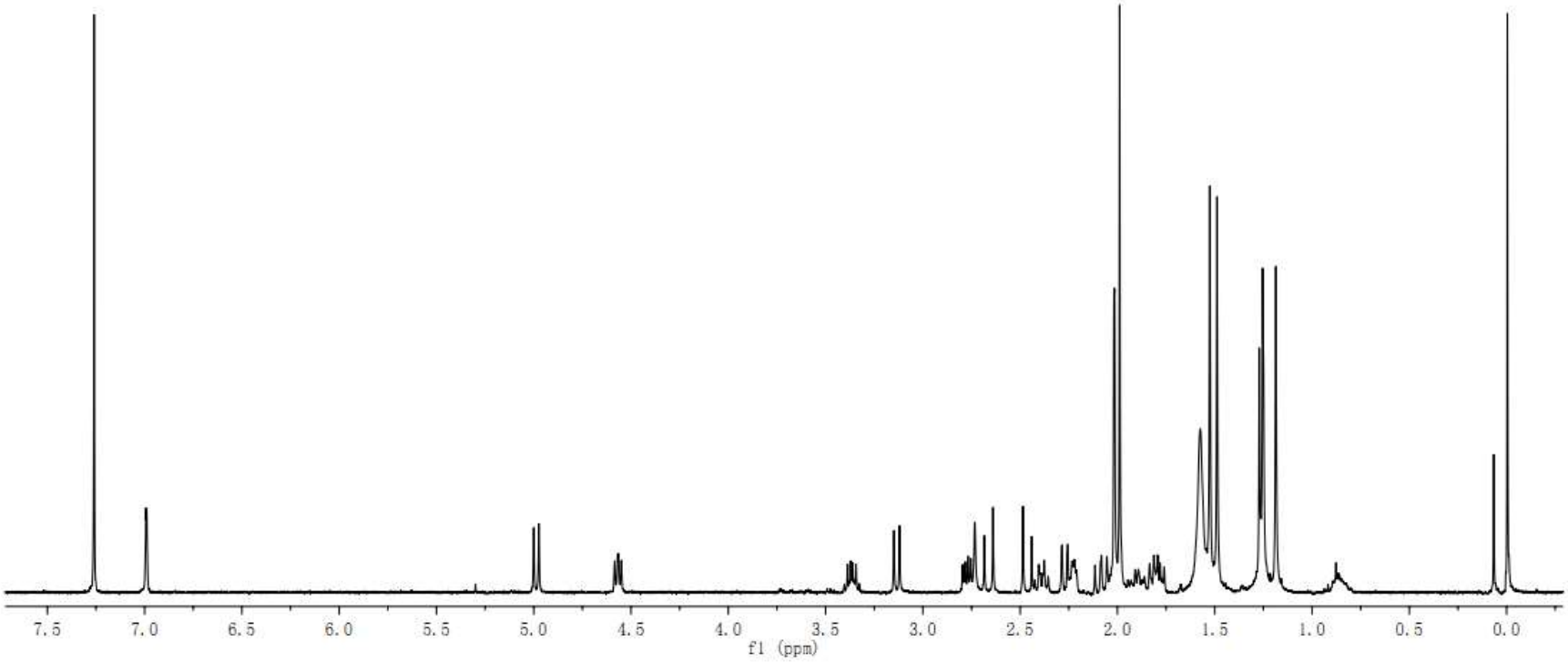


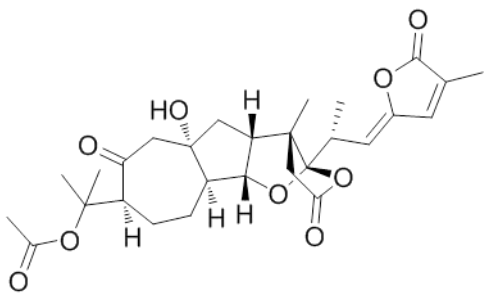


^{13}C NMR spectrum of 1

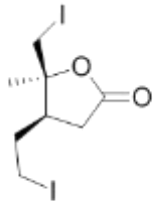


^{1}H NMR spectrum of 2

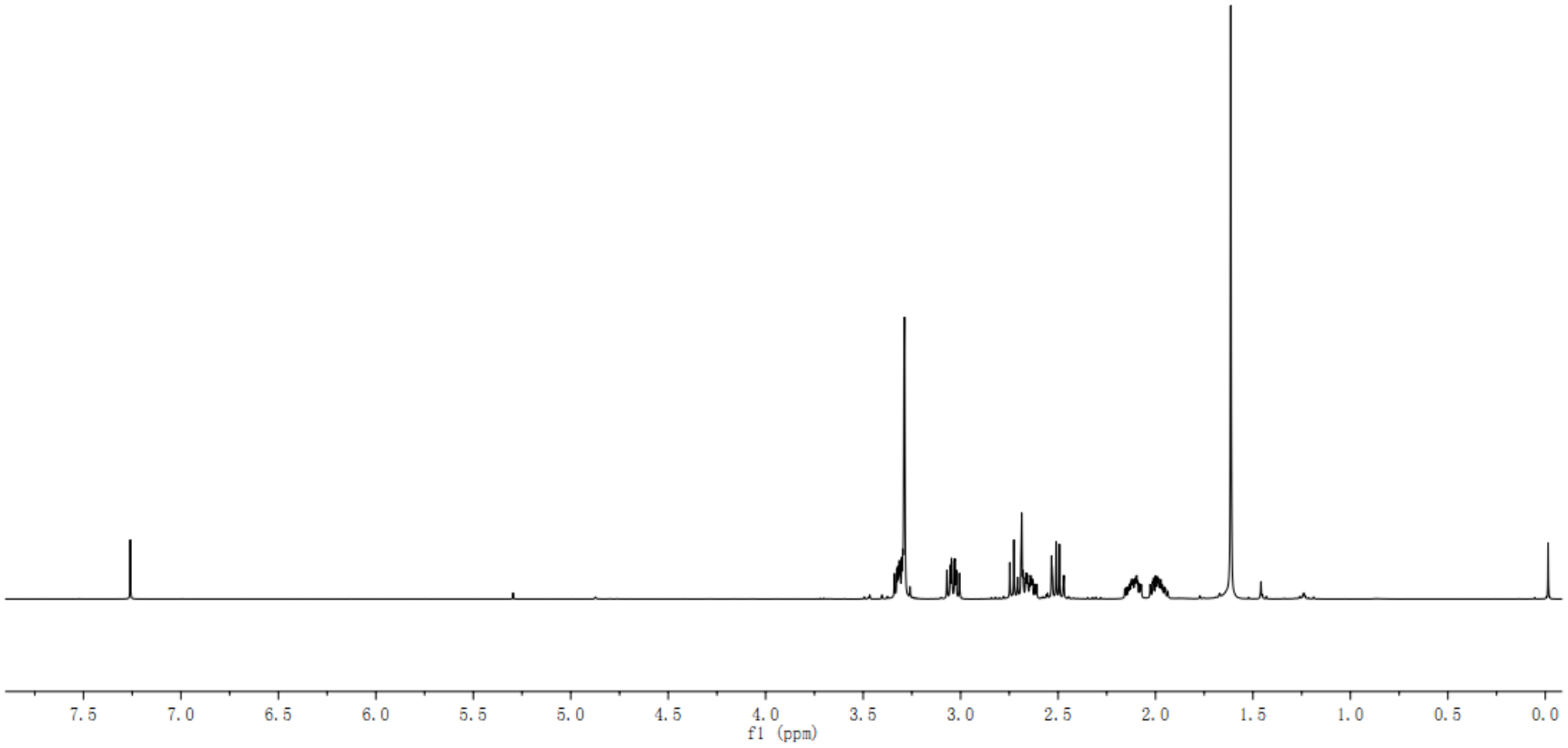


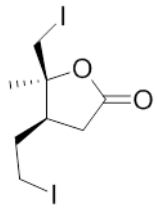


^{13}C NMR spectrum of 2

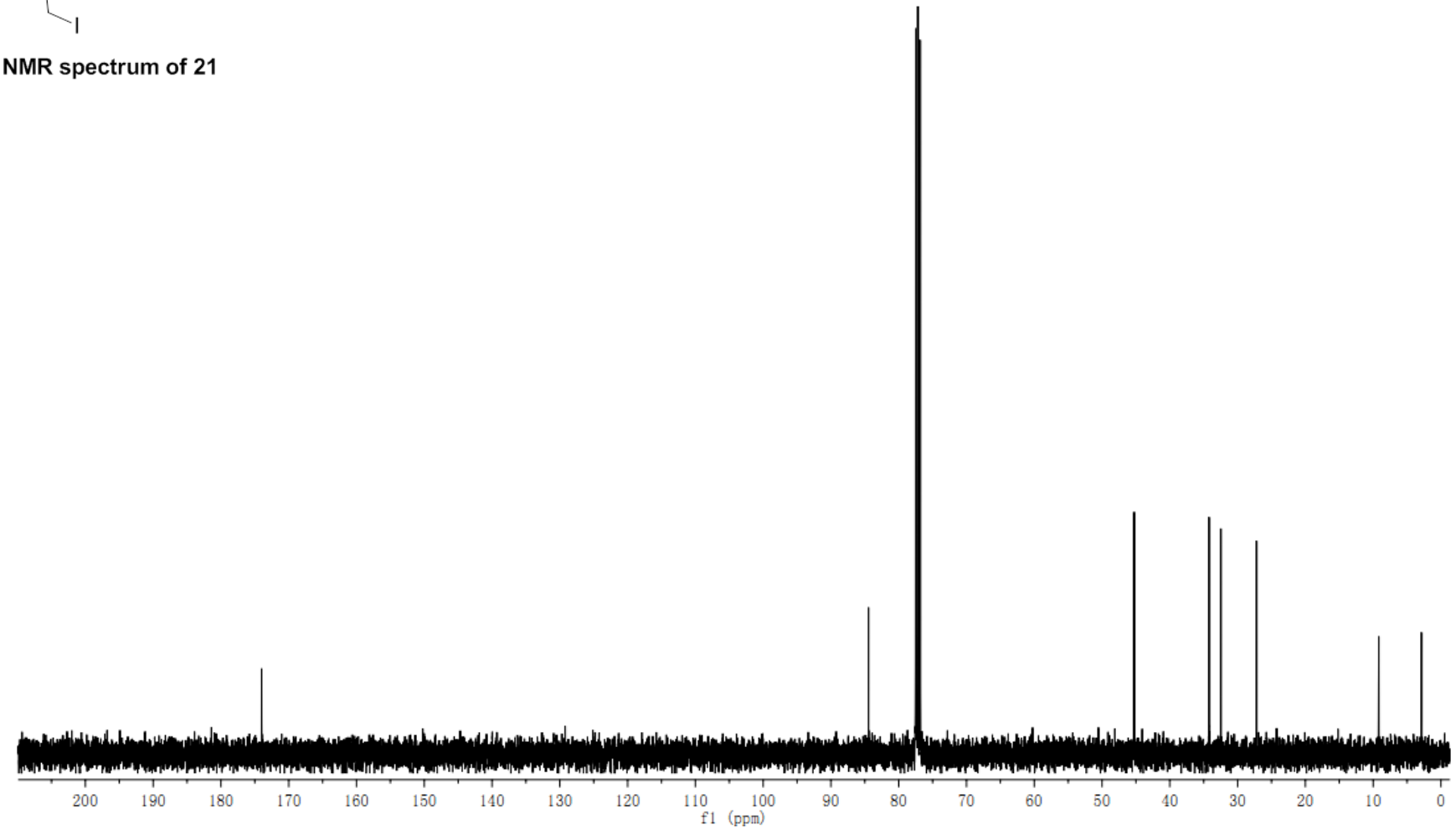


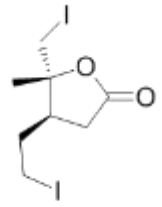
^{1}H NMR spectrum of 21



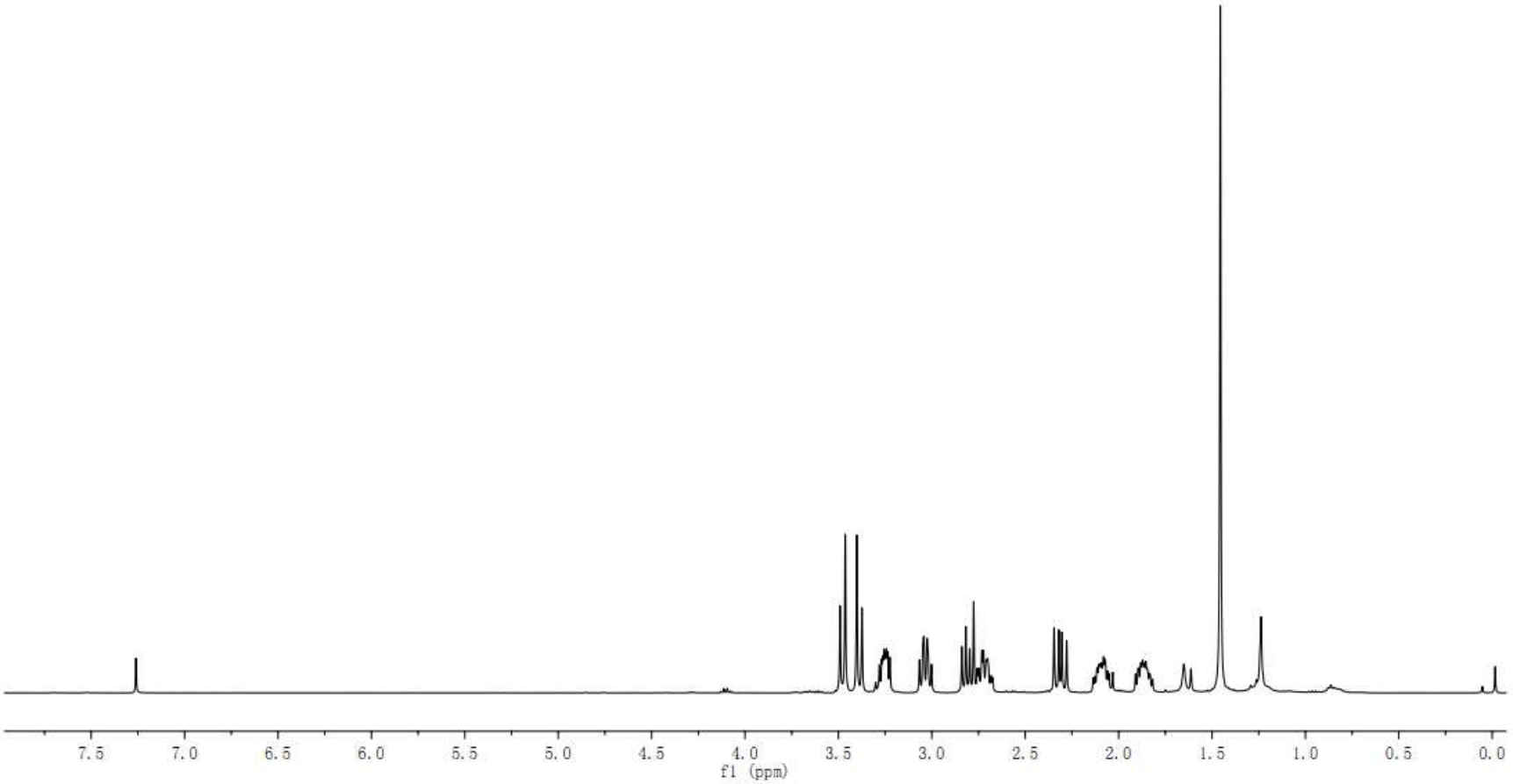


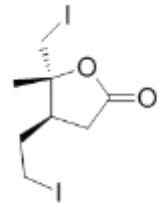
^{13}C NMR spectrum of 21



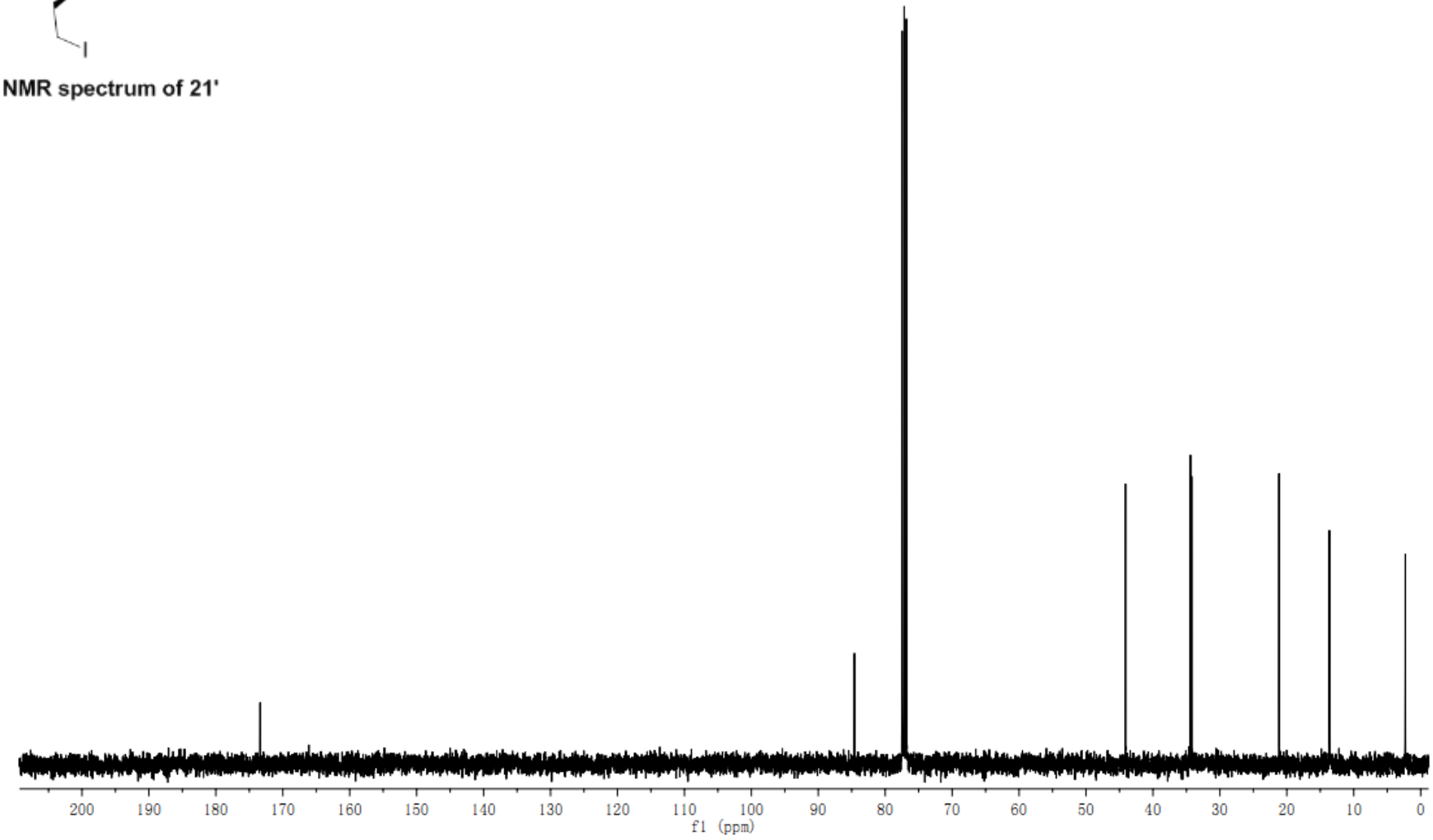


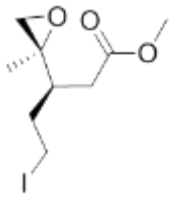
^{1}H NMR spectrum of 21'



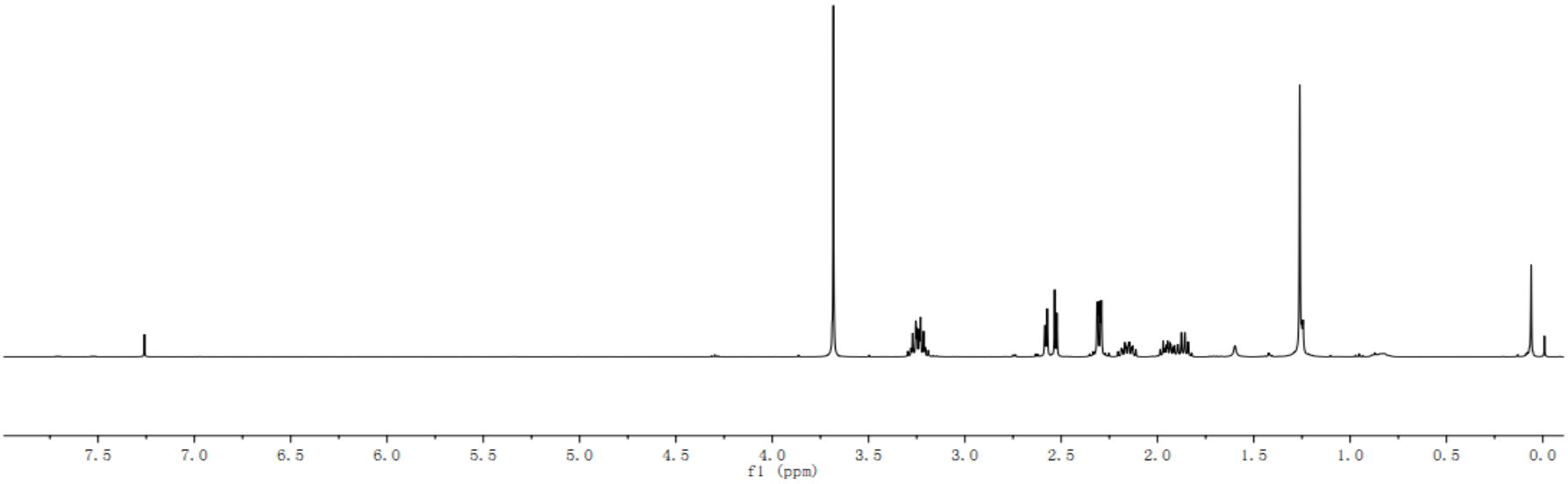


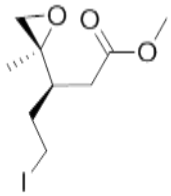
^{13}C NMR spectrum of 21'



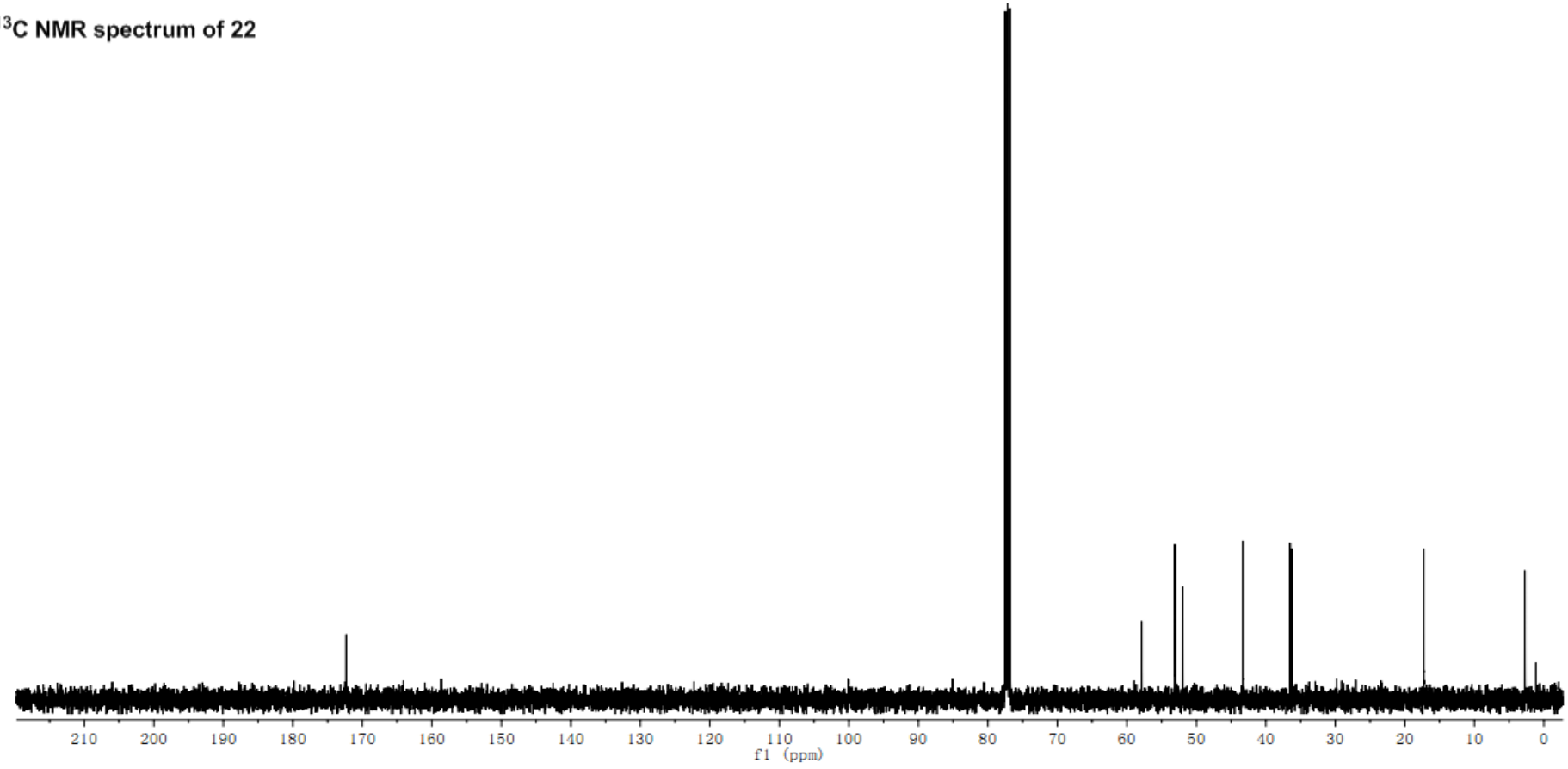


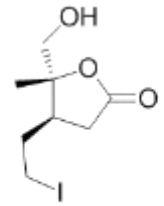
^{1}H NMR spectrum of 22



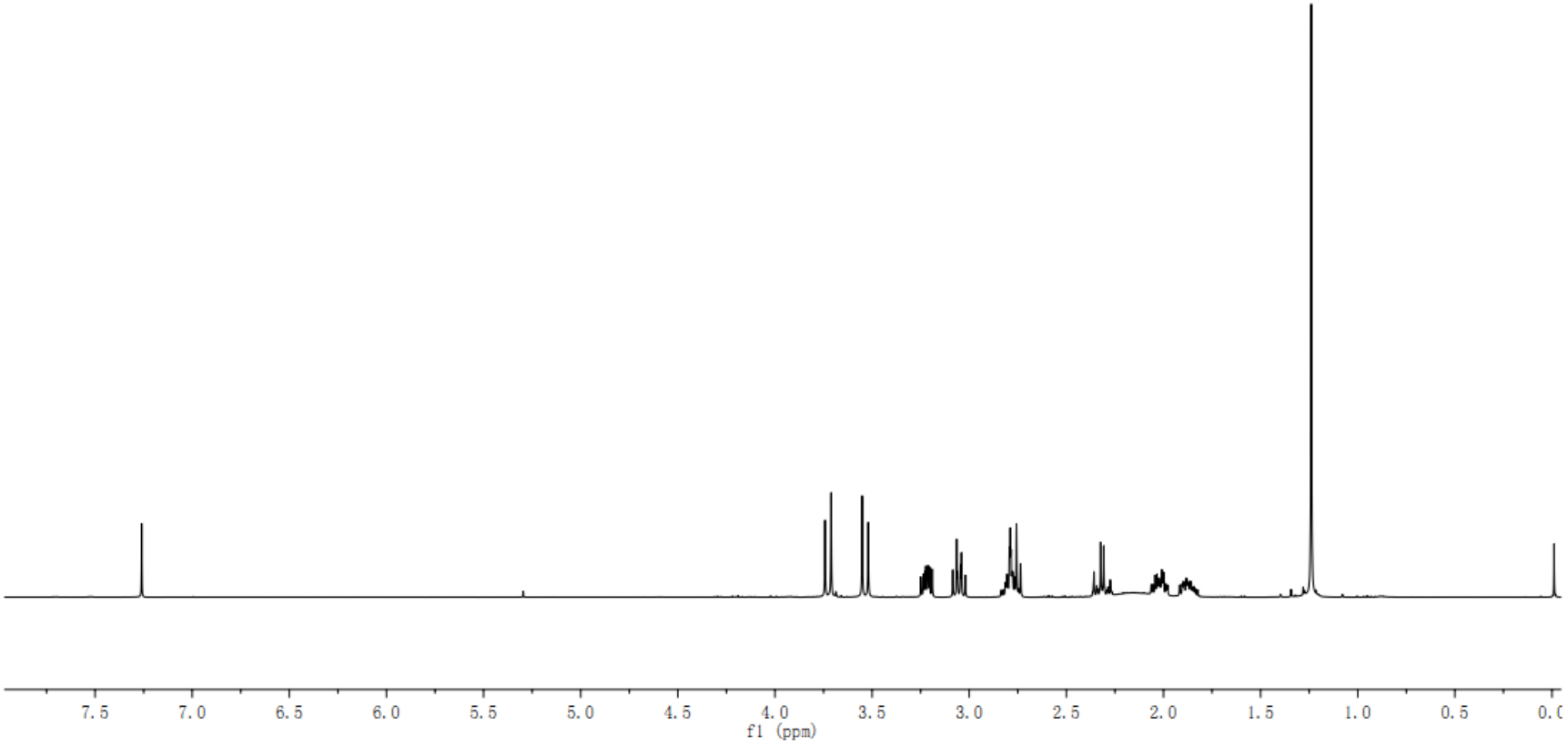


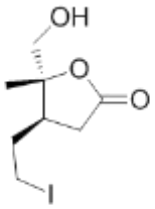
^{13}C NMR spectrum of 22



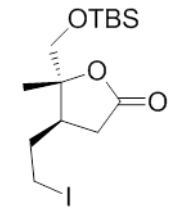


^{1}H NMR spectrum of 23

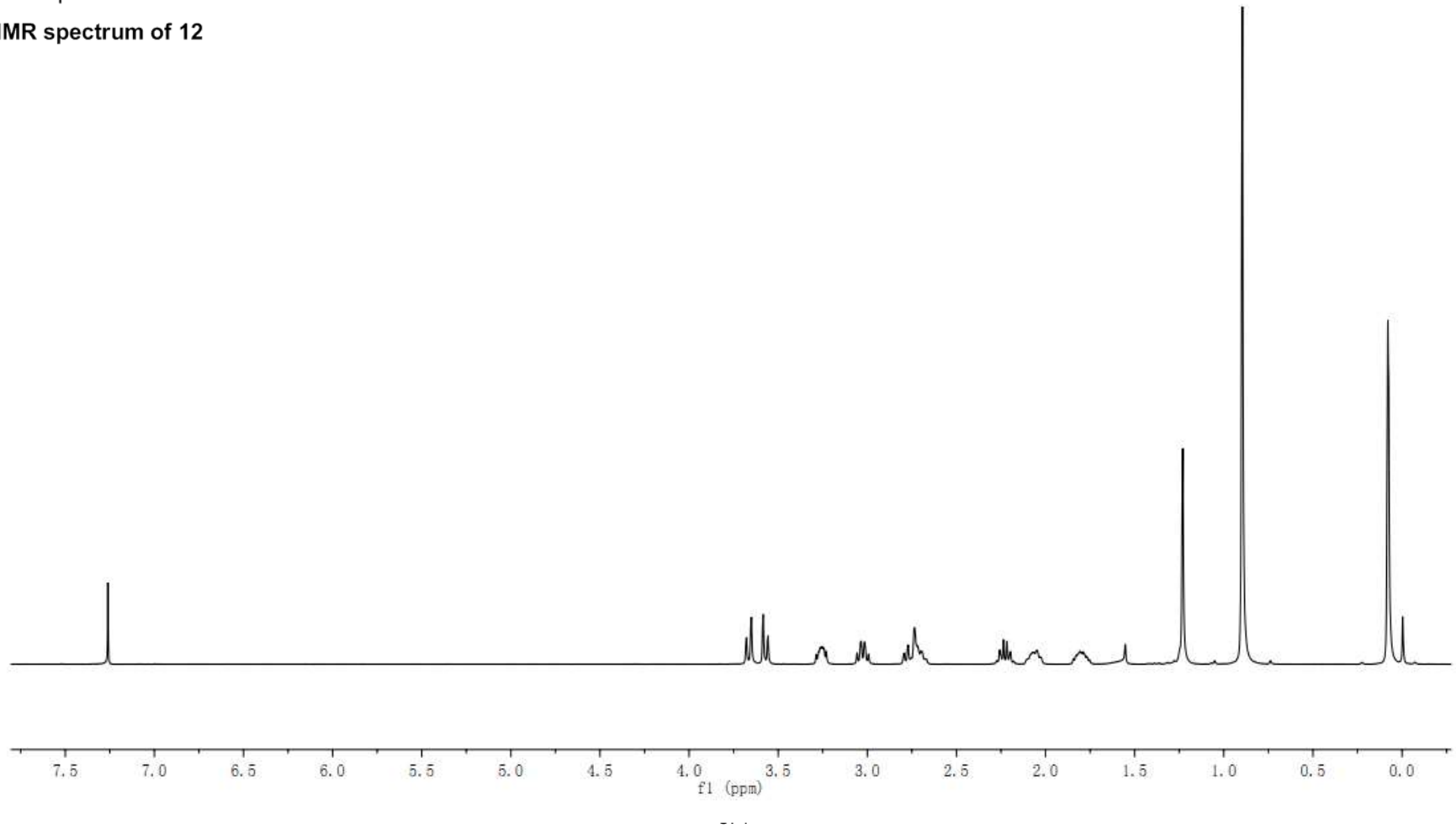


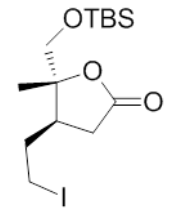


^{13}C NMR spectrum of 23

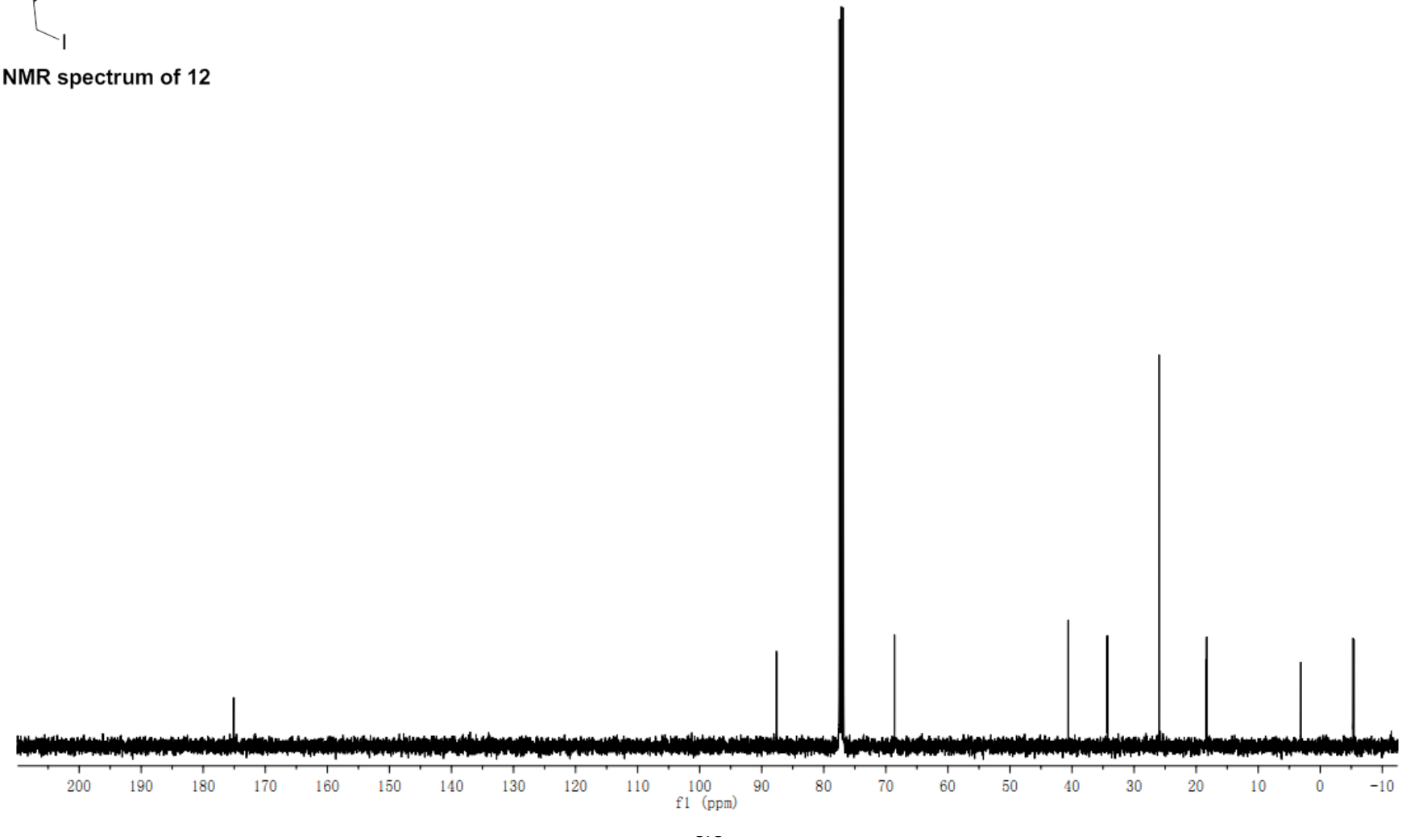


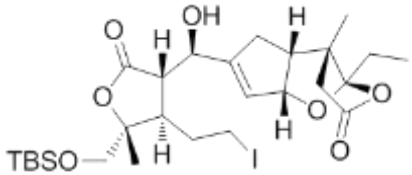
^{1}H NMR spectrum of 12



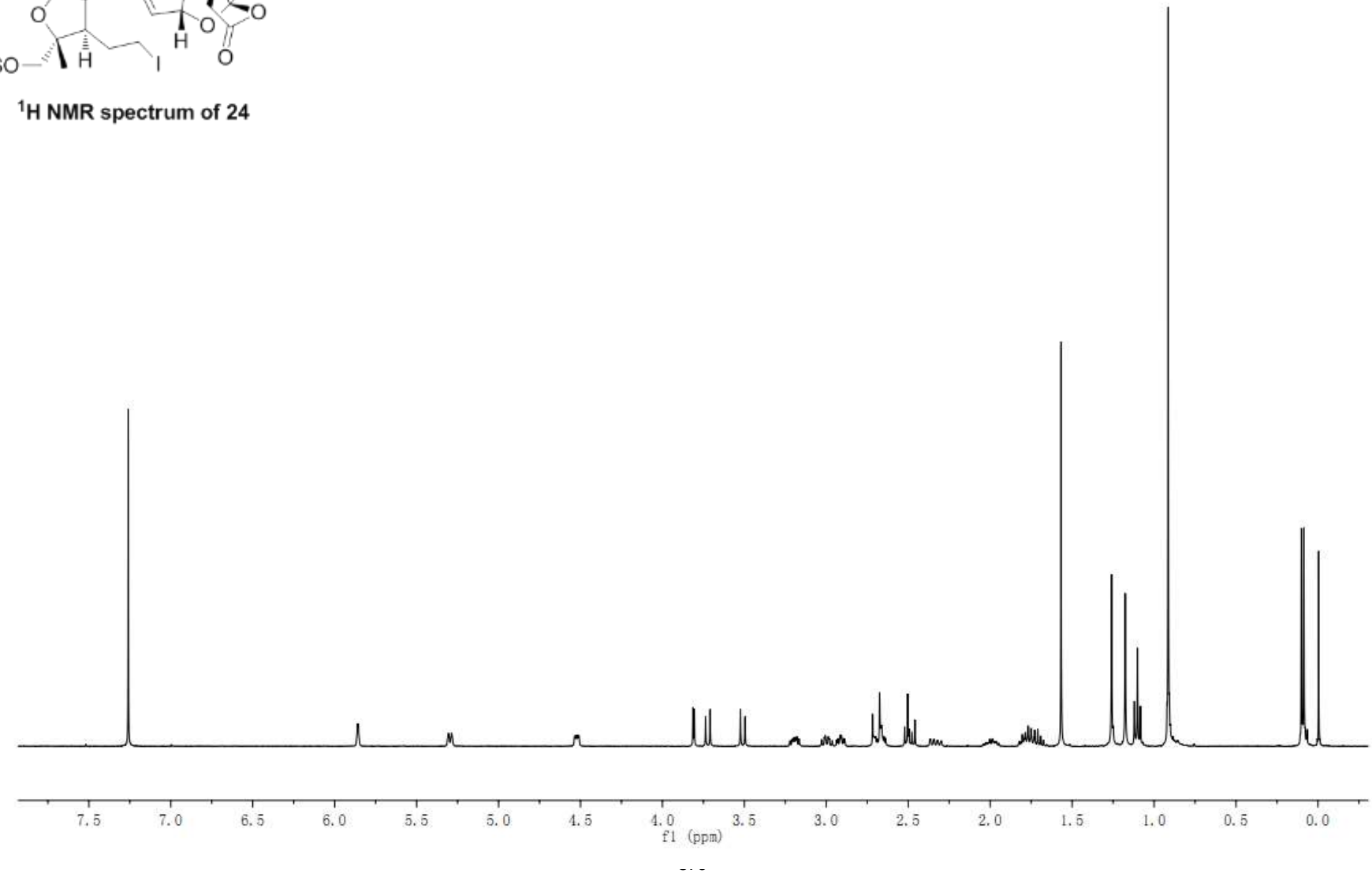


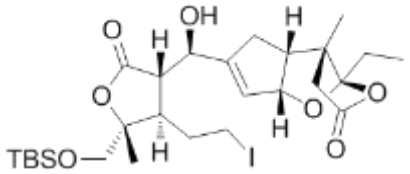
^{13}C NMR spectrum of 12



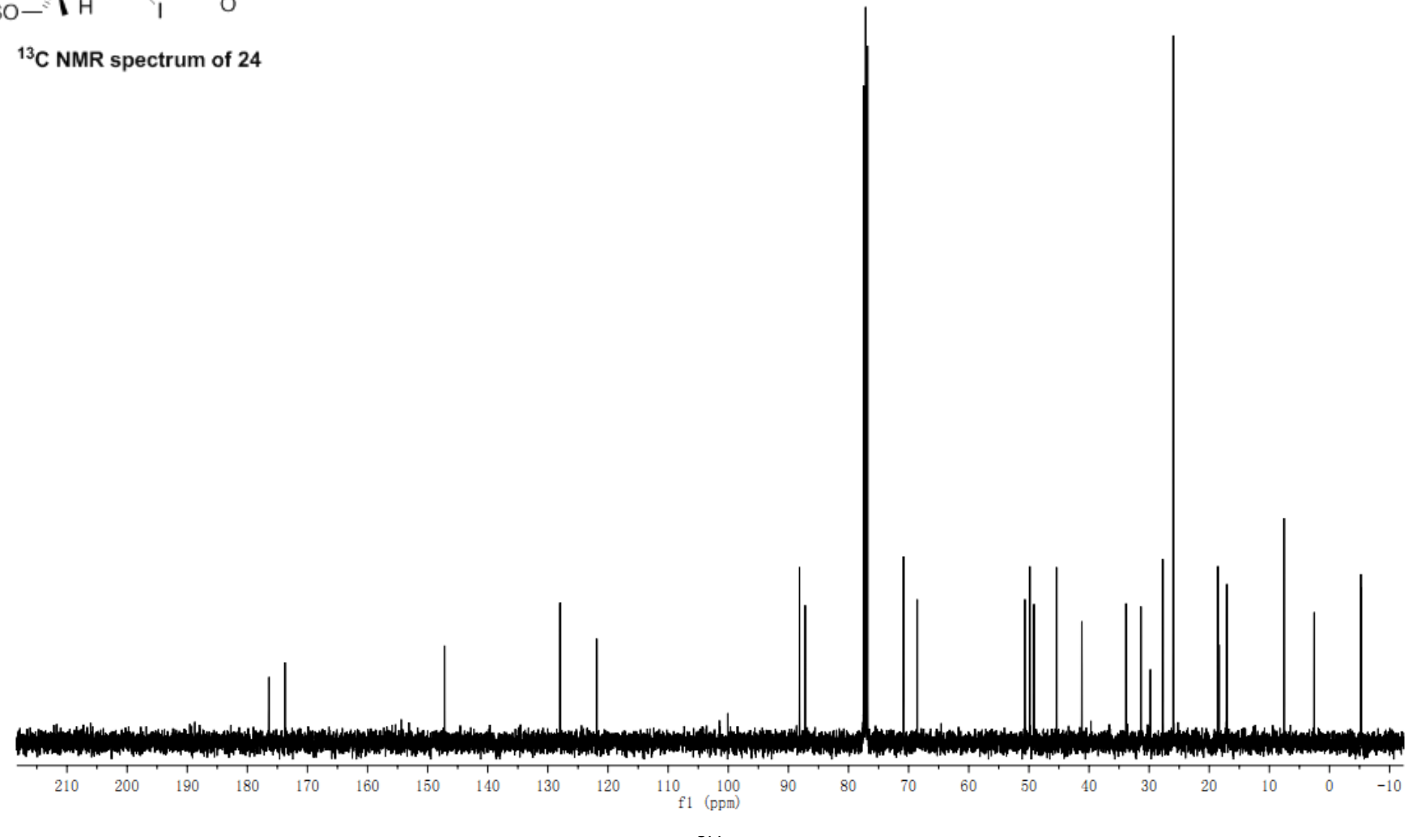


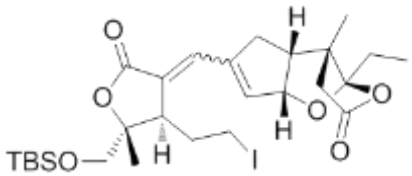
^{1}H NMR spectrum of 24



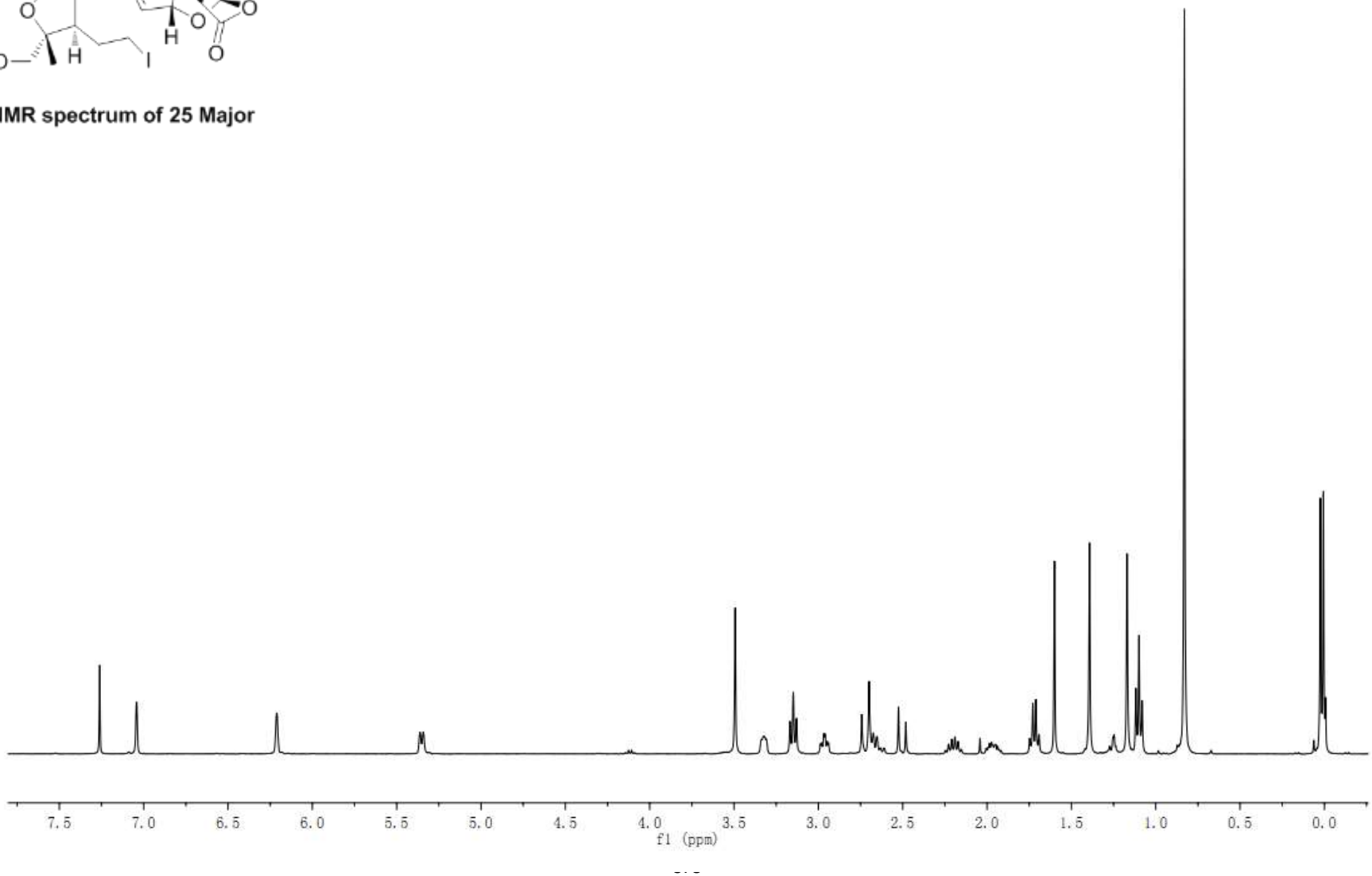


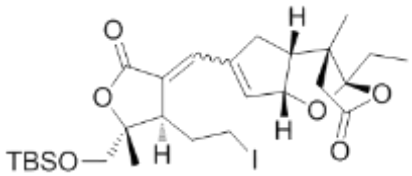
^{13}C NMR spectrum of 24



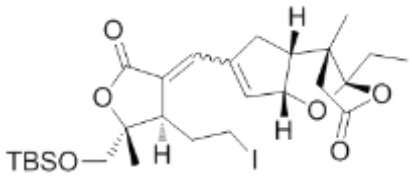


^{1}H NMR spectrum of 25 Major

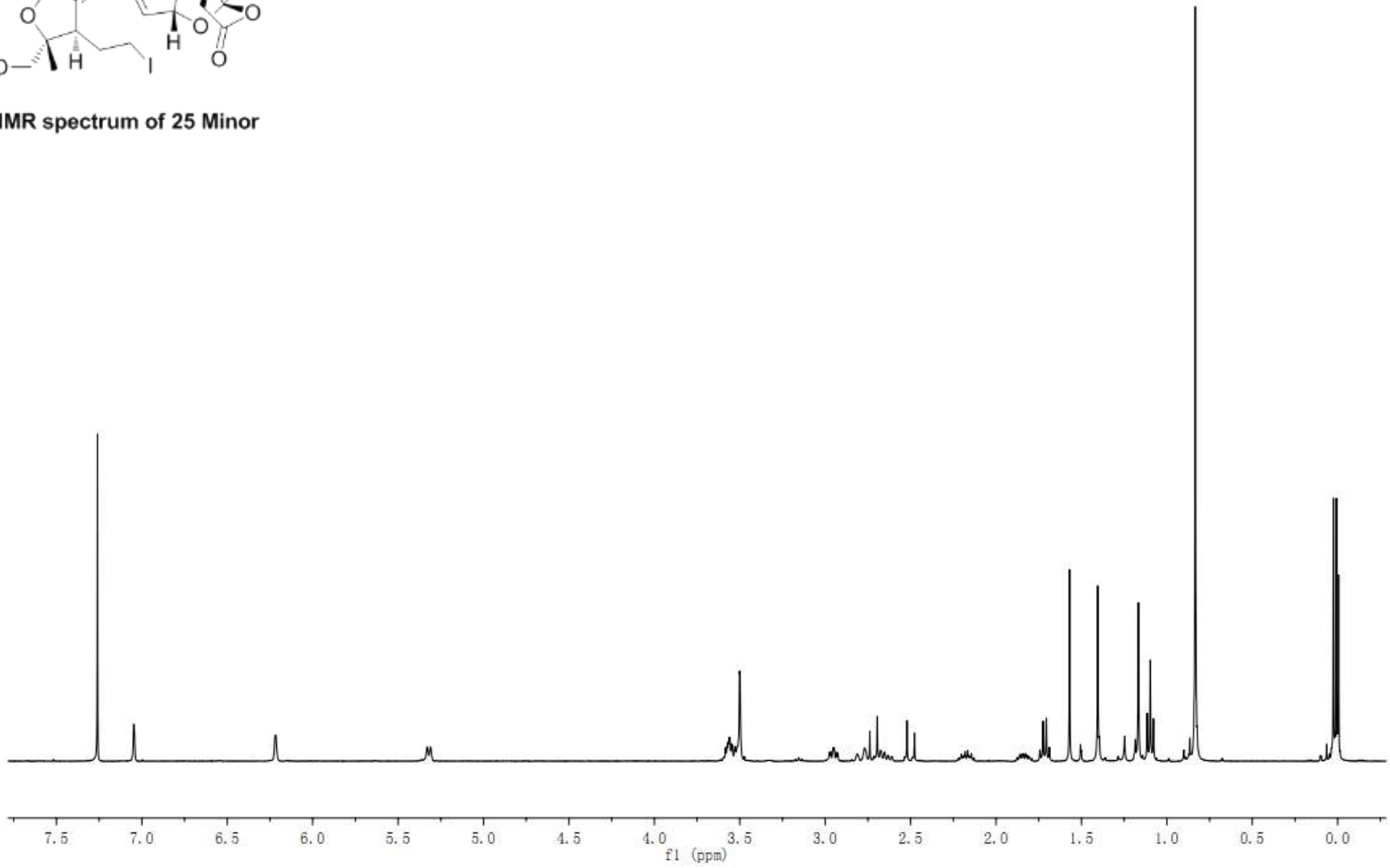


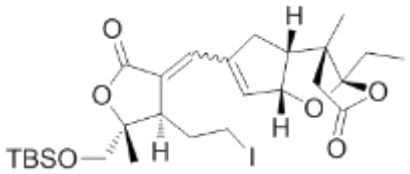


^{13}C NMR spectrum of 25 Major

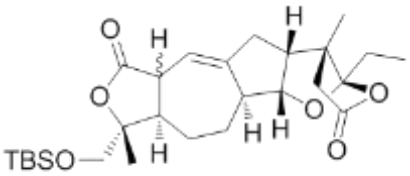


^{1}H NMR spectrum of 25 Minor

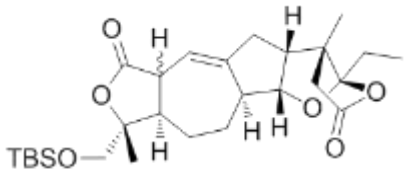




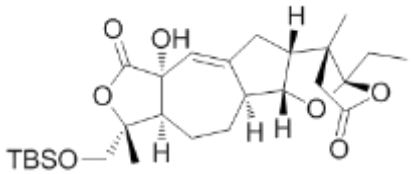
^{13}C NMR spectrum of 25 Minor



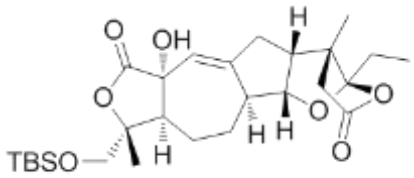
^{1}H NMR spectrum of 26 Major



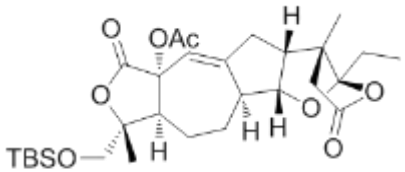
^{13}C NMR spectrum of 26 Major



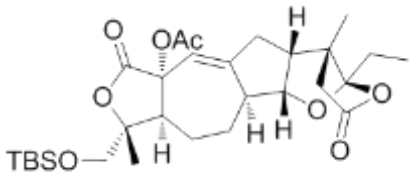
^{1}H NMR spectrum of 27



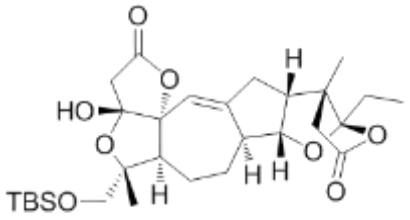
^{13}C NMR spectrum of 27



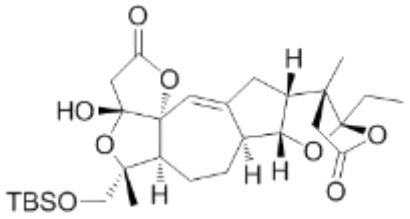
^{1}H NMR spectrum of 11



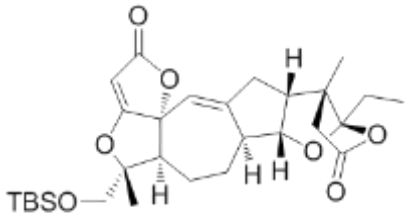
^{13}C NMR spectrum of 11



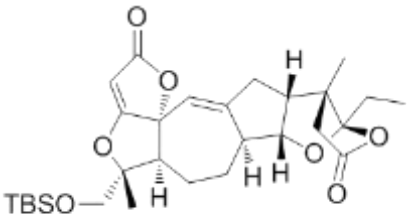
^{1}H NMR spectrum of 28



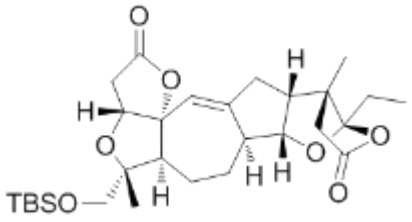
^{13}C NMR spectrum of 28



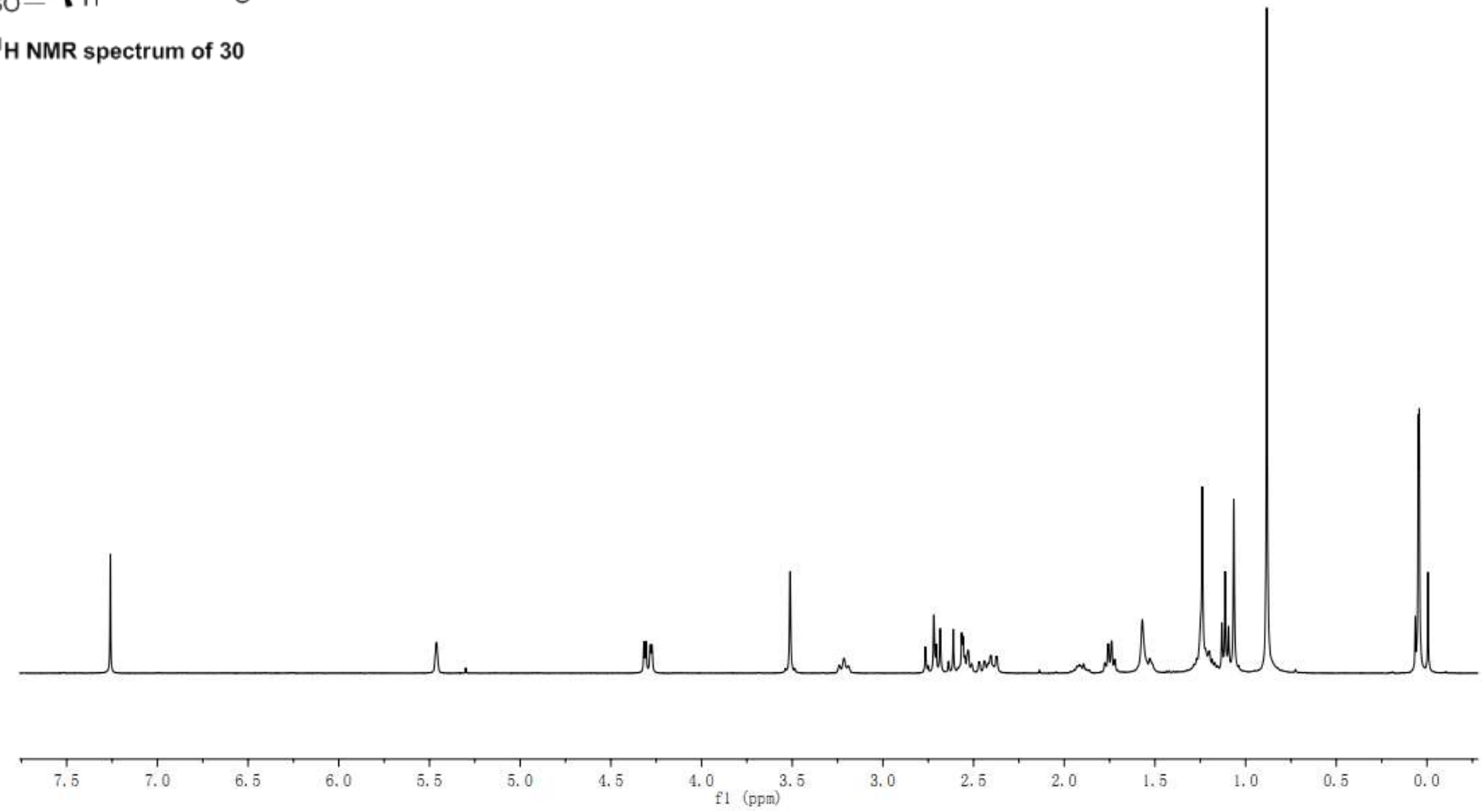
^{1}H NMR spectrum of 29

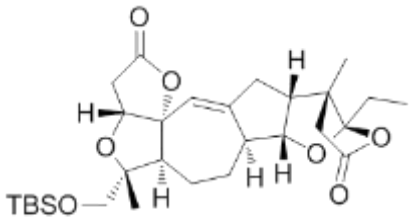


^{13}C NMR spectrum of 29

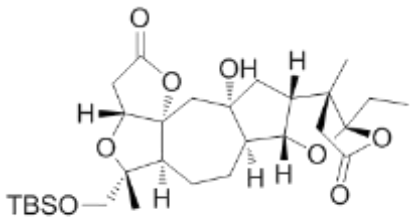


^{1}H NMR spectrum of 30

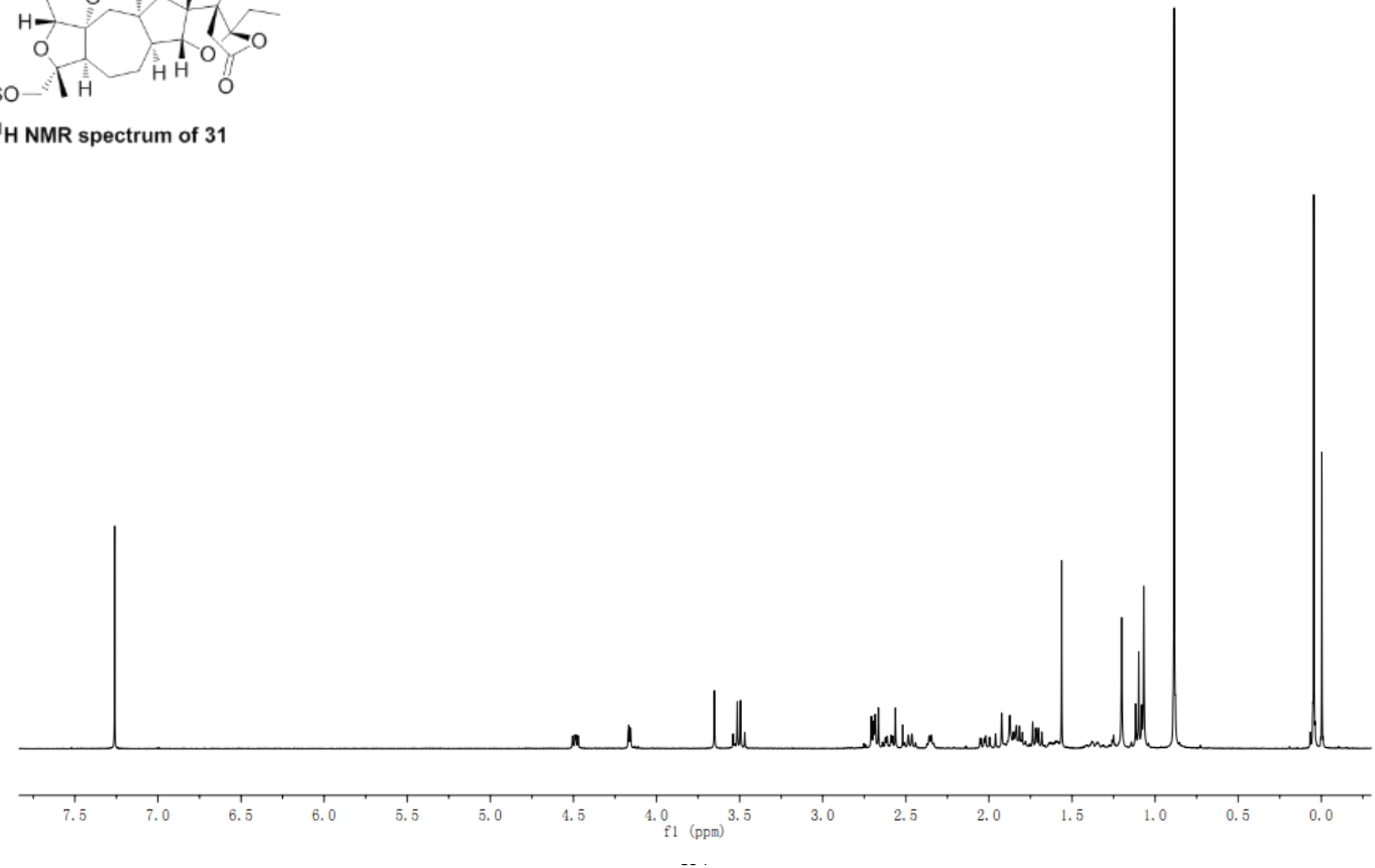


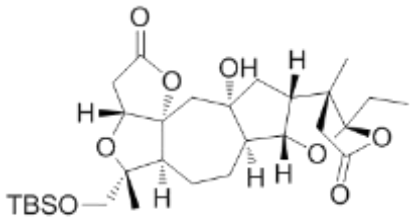


^{13}C NMR spectrum of 30

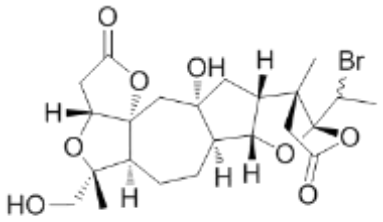


^{1}H NMR spectrum of 31

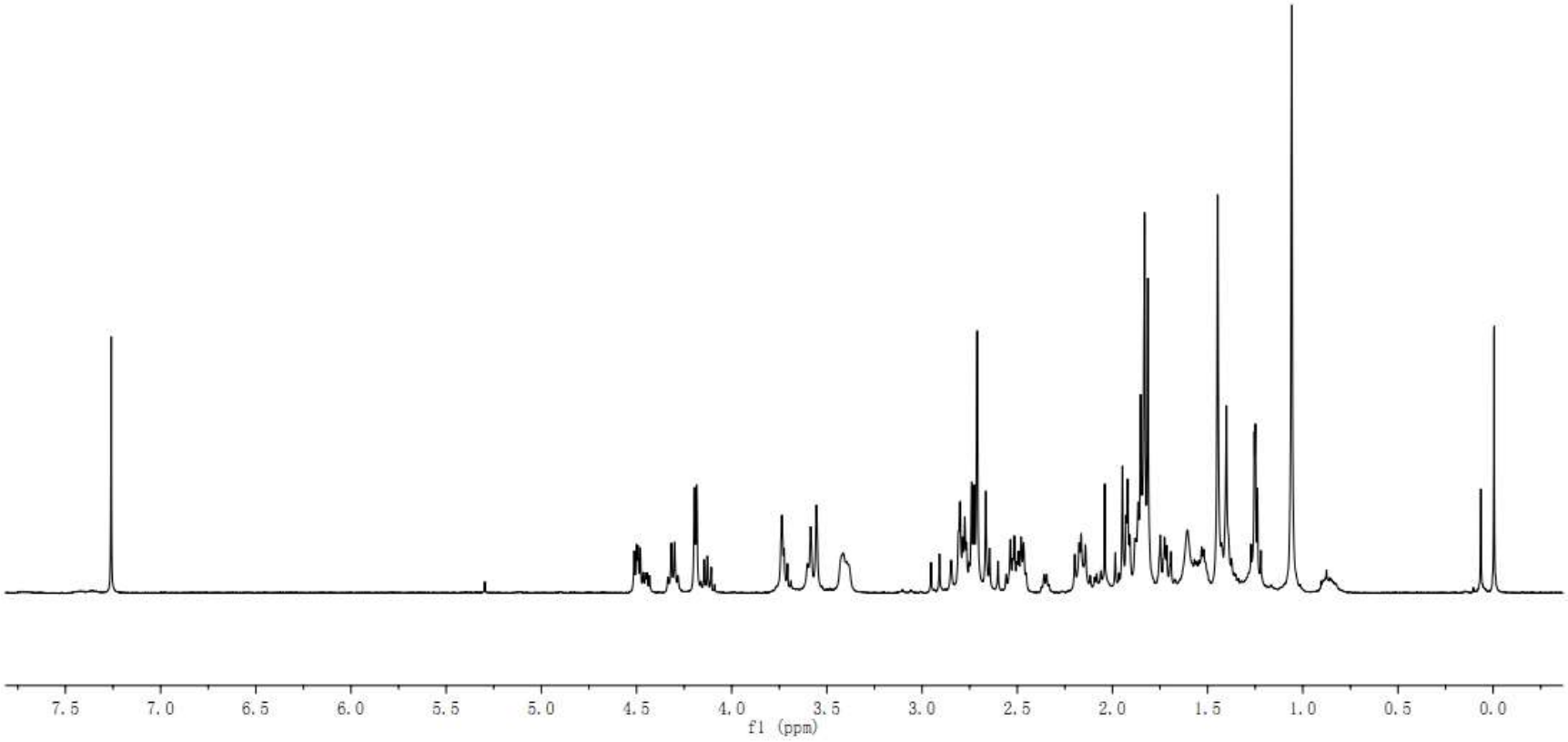


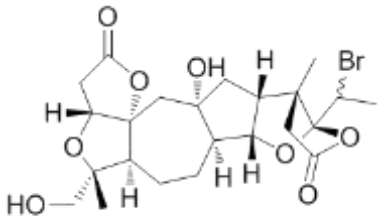


^{13}C NMR spectrum of 31

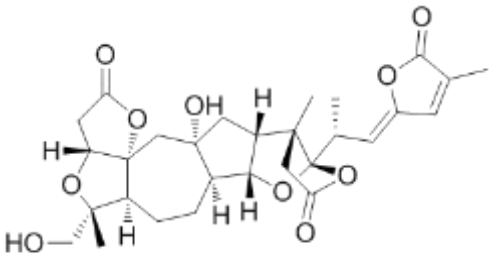


^{1}H NMR spectrum of 32

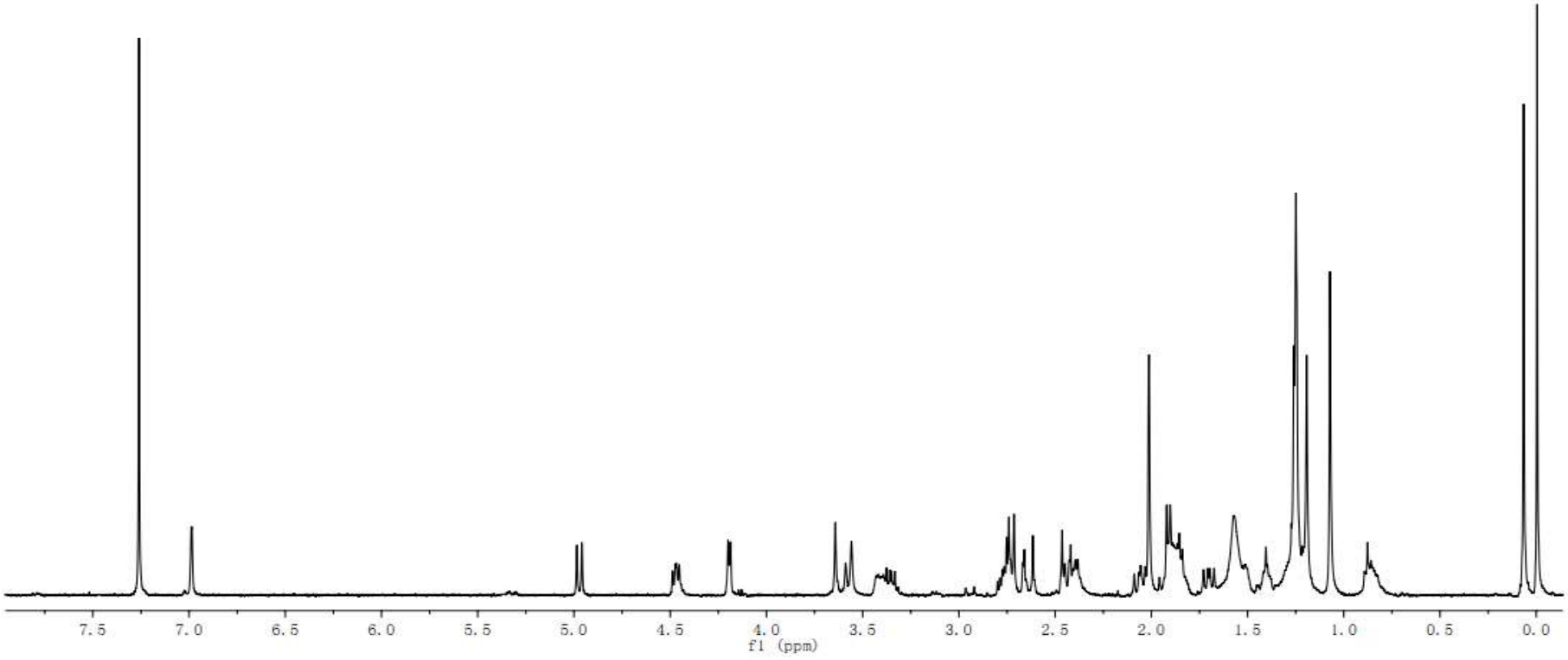


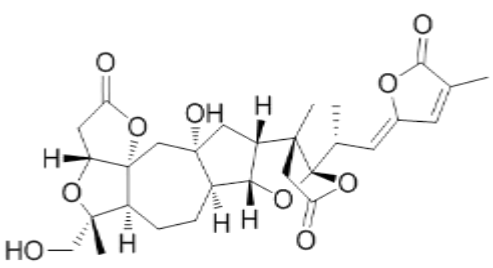


^{13}C NMR spectrum of 32

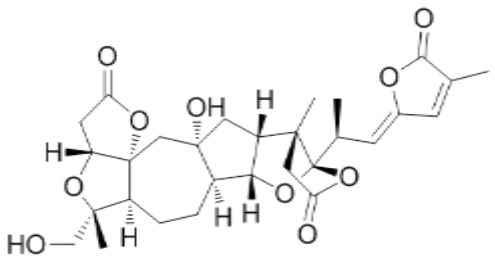


^{1}H NMR spectrum of 3

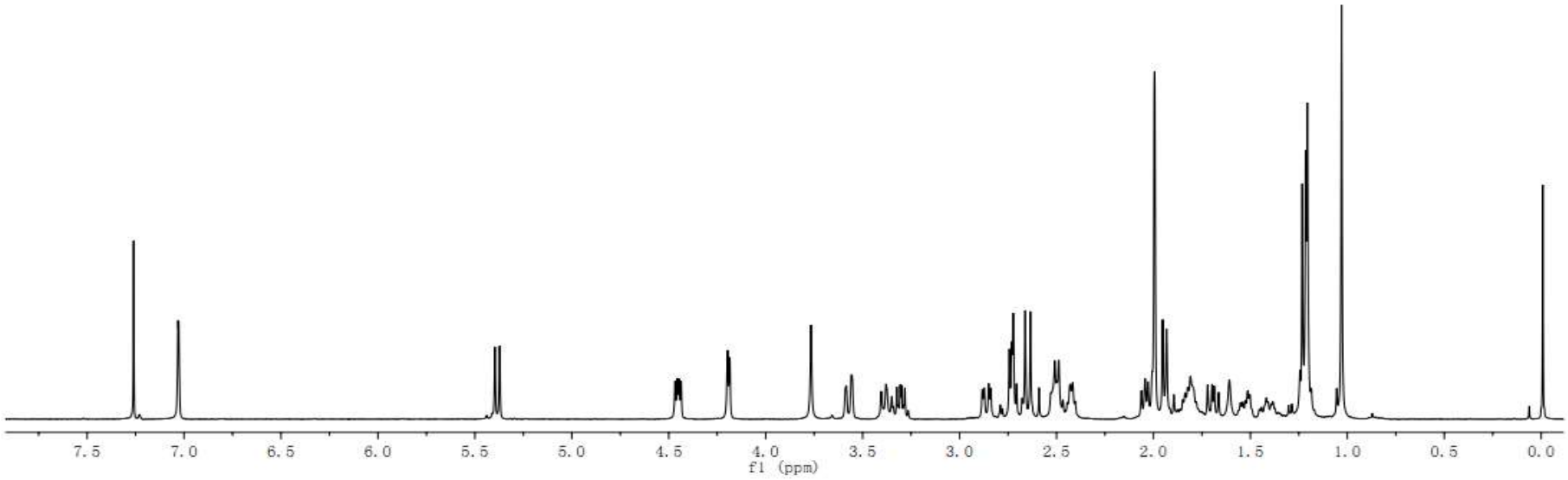


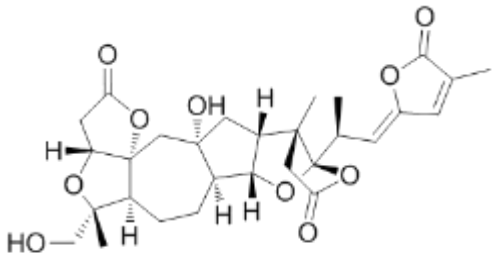


^{13}C NMR spectrum of 3

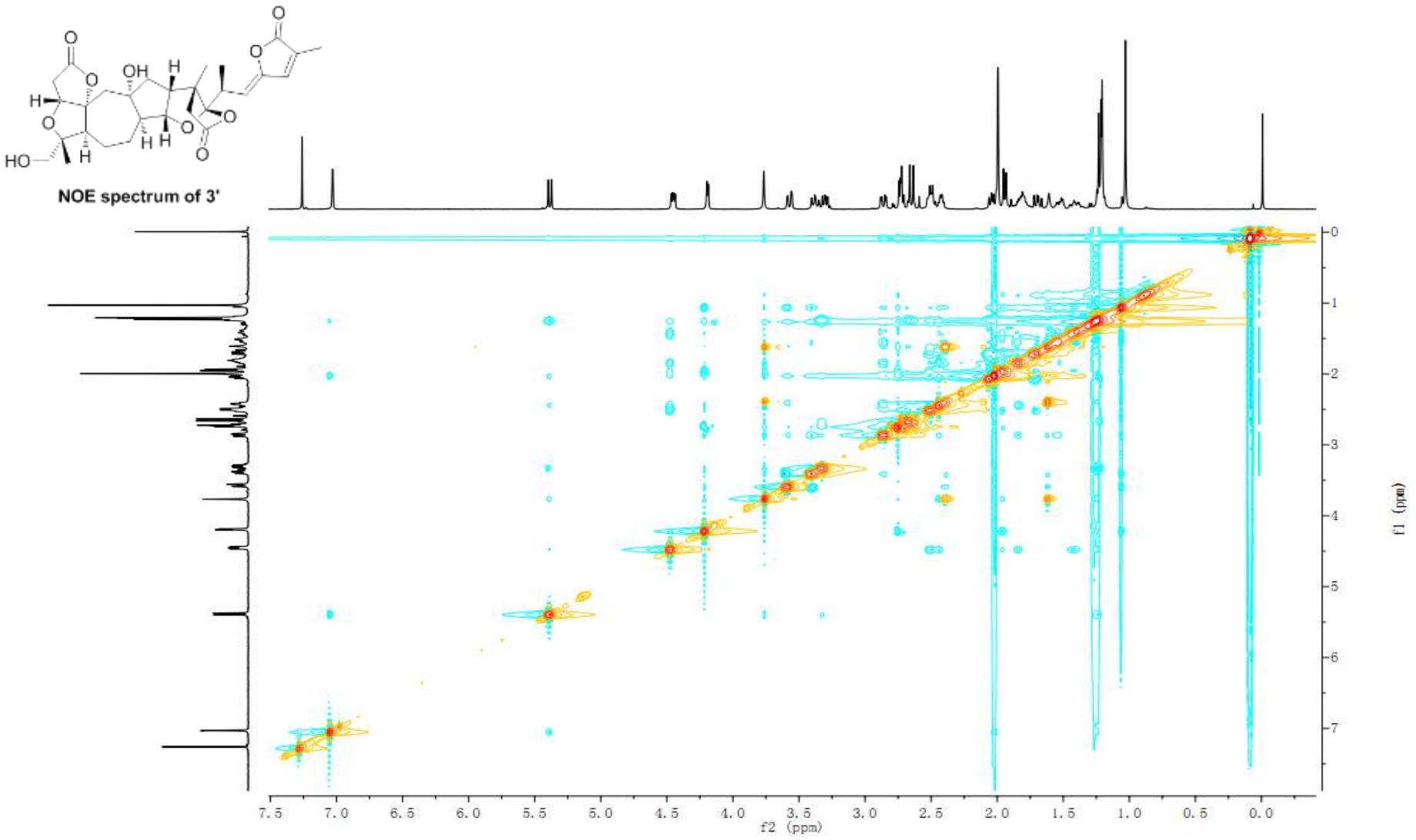


^{1}H NMR spectrum of 3'





^{13}C NMR spectrum of 3'


NOE spectrum of 3'
f2 (ppm)
f1 (ppm)

X–ray Crystal Structure Data

X–ray Crystal Structure Data for compound 15 (CCDC 1535911)

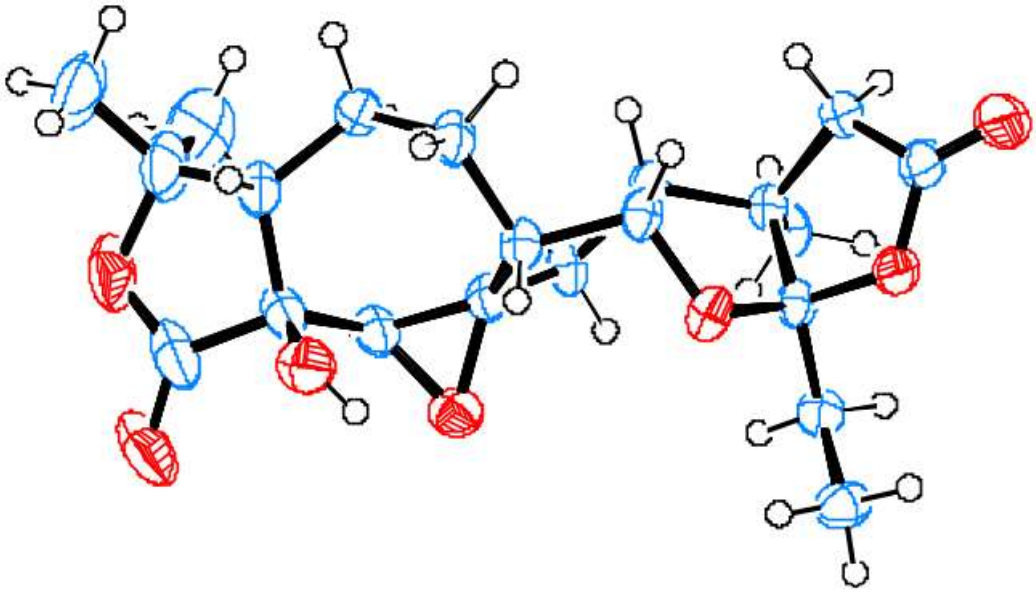


Table S13. Crystal data and structure refinement for shelxl.

Identification code	**shelxl**
Empirical formula	**C21 H28 O7**
Formula weight	**392.43**
Temperature	**173(2) K**
Wavelength	**1.54187 A**
Crystal system, space group	**Orthorhombic, P2(1)2(1)2(1)**
Unit cell dimensions	**a = 8.087(2) A alpha = 90 deg.** **b = 10.797(3) A beta = 90 deg.** **c = 22.609(6) A gamma = 90 deg.**
Volume	**1974.1(9) A^3**
Z, Calculated density	**4, 1.320 Mg/m^3**
Absorption coefficient	**0.817 mm^–1**

F(000)	**840**
Crystal size	**0.180 x 0.160 x 0.140 mm**
Theta range for data collection	**6.731 to 75.109 deg.**
Limiting indices	**–10<=h<=10, –13<=k<=10, –19<=l<=27**
Reflections collected / unique	**16798 / 4036 [R(int) = 0.0238]**
Completeness to theta = 67.687	**99.6 %**
Absorption correction	**Semi–empirical from equivalents**
Max. and min. transmission	**0.892 and 0.794**
Refinement method	**Full–matrix least–squares on F^2**
Data / restraints / parameters	**4036 / 0 / 262**
Goodness–of–fit on F^2	**1.071**
Final R indices [I>2sigma(I)]	**R1 = 0.0314, wR2 = 0.0828**
R indices (all data)	**R1 = 0.0331, wR2 = 0.0841**
Absolute structure parameter	**0.01(4)**
Extinction coefficient	**0.0018(4)**
Largest diff. peak and hole	**0.202 and –0.170 e.A^–3**

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for shelxl.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	5765(2)	2910(1)	2494(1)	47(1)
O(2)	5891(3)	1494(2)	3585(1)	83(1)
O(3)	3253(3)	2047(2)	3637(1)	73(1)
O(4)	5770(2)	720(1)	1943(1)	42(1)
O(5)	5223(2)	1352(1)	441(1)	35(1)
O(6)	4840(2)	940(1)	–556(1)	37(1)
O(7)	3113(2)	1568(2)	–1259(1)	62(1)
C(1)	4444(3)	2151(2)	2682(1)	39(1)
C(2)	4653(4)	1846(2)	3343(1)	59(1)
C(3)	1914(4)	2454(3)	3240(1)	59(1)
C(4)	2812(3)	2864(2)	2673(1)	37(1)
C(5)	1790(2)	2768(2)	2107(1)	37(1)
C(6)	2737(3)	3170(2)	1557(1)	38(1)
C(7)	4107(2)	2271(2)	1337(1)	31(1)
C(8)	4185(2)	1043(2)	1672(1)	31(1)
C(9)	4359(3)	958(2)	2316(1)	36(1)
C(10)	3352(3)	23(2)	1311(1)	35(1)
C(11)	2645(2)	684(2)	756(1)	30(1)
C(12)	3730(2)	1837(2)	708(1)	31(1)
C(13)	4812(2)	408(2)	38(1)	29(1)
C(14)	2966(2)	36(2)	159(1)	29(1)
C(15)	2022(2)	675(2)	–350(1)	34(1)
C(16)	3309(3)	1117(2)	–779(1)	40(1)
C(17)	1082(5)	3541(4)	3544(1)	81(1)
C(18)	754(5)	1356(3)	3170(1)	84(1)
C(19)	6113(2)	–598(2)	51(1)	34(1)
C(20)	7863(3)	–125(2)	–44(1)	42(1)
C(21)	2626(3)	–1361(2)	160(1)	36(1)

Table S15. Bond lengths [A] and angles [deg] for shelxl.

O(1)–C(1)	**1.413(3)**
O(1)–H(1)	**0.82(4)**
O(2)–C(2)	**1.203(3)**
O(3)–C(2)	**1.331(4)**
O(3)–C(3)	**1.474(3)**
O(4)–C(9)	**1.441(3)**
O(4)–C(8)	**1.463(2)**
O(5)–C(13)	**1.407(2)**
O(5)–C(12)	**1.448(2)**
O(6)–C(16)	**1.351(3)**
O(6)–C(13)	**1.461(2)**
O(7)–C(16)	**1.199(2)**
C(1)–C(4)	**1.528(3)**
C(1)–C(9)	**1.533(3)**
C(1)–C(2)	**1.538(3)**
C(3)–C(17)	**1.518(4)**
C(3)–C(18)	**1.520(5)**
C(3)–C(4)	**1.538(3)**
C(4)–C(5)	**1.527(3)**
C(4)–H(4)	**1.0000**
C(5)–C(6)	**1.525(3)**
C(5)–H(5A)	**0.9900**
C(5)–H(5B)	**0.9900**
C(6)–C(7)	**1.555(3)**
C(6)–H(6A)	**0.9900**
C(6)–H(6B)	**0.9900**
C(7)–C(12)	**1.528(2)**
C(7)–C(8)	**1.528(2)**
C(7)–H(7)	**1.0000**
C(8)–C(9)	**1.465(2)**
C(8)–C(10)	**1.527(2)**
C(9)–H(9)	**1.0000**
C(10)–C(11)	**1.553(2)**
C(10)–H(10A)	**0.9900**
C(10)–H(10B)	**0.9900**
C(11)–C(12)	**1.526(2)**
C(11)–C(14)	**1.542(2)**
C(11)–H(11)	**1.0000**
C(12)–H(12)	**1.0000**
C(13)–C(19)	**1.512(2)**

C(13)–C(14)	**1.570(3)**
C(14)–C(21)	**1.533(3)**
C(14)–C(15)	**1.544(2)**
C(15)–C(16)	**1.502(3)**
C(15)–H(15A)	**0.9900**
C(15)–H(15B)	**0.9900**
C(17)–H(17A)	**0.9800**
C(17)–H(17B)	**0.9800**
C(17)–H(17C)	**0.9800**
C(18)–H(18A)	**0.9800**
C(18)–H(18B)	**0.9800**
C(18)–H(18C)	**0.9800**
C(19)–C(20)	**1.520(3)**
C(19)–H(19A)	**0.9900**
C(19)–H(19B)	**0.9900**
C(20)–H(20A)	**0.9800**
C(20)–H(20B)	**0.9800**
C(20)–H(20C)	**0.9800**
C(21)–H(21A)	**0.9800**
C(21)–H(21B)	**0.9800**
C(21)–H(21C)	**0.9800**

C(1)–O(1)–H(1)	**107(2)**
C(2)–O(3)–C(3)	**111.67(17)**
C(9)–O(4)–C(8)	**60.61(12)**
C(13)–O(5)–C(12)	**109.52(13)**
C(16)–O(6)–C(13)	**112.69(14)**
O(1)–C(1)–C(4)	**110.86(16)**
O(1)–C(1)–C(9)	**110.96(17)**
C(4)–C(1)–C(9)	**112.18(17)**
O(1)–C(1)–C(2)	**109.52(19)**
C(4)–C(1)–C(2)	**102.47(18)**
C(9)–C(1)–C(2)	**110.53(16)**
O(2)–C(2)–O(3)	**122.1(2)**
O(2)–C(2)–C(1)	**127.0(3)**
O(3)–C(2)–C(1)	**110.9(2)**
O(3)–C(3)–C(17)	**106.3(2)**
O(3)–C(3)–C(18)	**106.6(2)**
C(17)–C(3)–C(18)	**112.1(3)**
O(3)–C(3)–C(4)	**104.3(2)**
C(17)–C(3)–C(4)	**111.3(2)**
C(18)–C(3)–C(4)	**115.4(2)**
C(5)–C(4)–C(1)	**116.36(15)**
C(5)–C(4)–C(3)	**115.0(2)**

C(1)–C(4)–C(3)	**104.55(18)**
C(5)–C(4)–H(4)	**106.8**
C(1)–C(4)–H(4)	**106.8**
C(3)–C(4)–H(4)	**106.8**
C(6)–C(5)–C(4)	**113.13(17)**
C(6)–C(5)–H(5A)	**109.0**
C(4)–C(5)–H(5A)	**109.0**
C(6)–C(5)–H(5B)	**109.0**
C(4)–C(5)–H(5B)	**109.0**
H(5A)–C(5)–H(5B)	**107.8**
C(5)–C(6)–C(7)	**116.15(15)**
C(5)–C(6)–H(6A)	**108.2**
C(7)–C(6)–H(6A)	**108.2**
C(5)–C(6)–H(6B)	**108.2**
C(7)–C(6)–H(6B)	**108.2**
H(6A)–C(6)–H(6B)	**107.4**
C(12)–C(7)–C(8)	**101.68(14)**
C(12)–C(7)–C(6)	**110.27(15)**
C(8)–C(7)–C(6)	**114.40(15)**
C(12)–C(7)–H(7)	**110.1**
C(8)–C(7)–H(7)	**110.1**
C(6)–C(7)–H(7)	**110.1**
O(4)–C(8)–C(9)	**58.97(12)**
O(4)–C(8)–C(10)	**116.02(15)**
C(9)–C(8)–C(10)	**121.86(16)**
O(4)–C(8)–C(7)	**116.79(15)**
C(9)–C(8)–C(7)	**123.37(15)**
C(10)–C(8)–C(7)	**110.06(15)**
O(4)–C(9)–C(8)	**60.42(12)**
O(4)–C(9)–C(1)	**115.52(17)**
C(8)–C(9)–C(1)	**119.30(16)**
O(4)–C(9)–H(9)	**116.6**
C(8)–C(9)–H(9)	**116.6**
C(1)–C(9)–H(9)	**116.6**
C(8)–C(10)–C(11)	**105.23(14)**
C(8)–C(10)–H(10A)	**110.7**
C(11)–C(10)–H(10A)	**110.7**
C(8)–C(10)–H(10B)	**110.7**
C(11)–C(10)–H(10B)	**110.7**
H(10A)–C(10)–H(10B)	**108.8**
C(12)–C(11)–C(14)	**102.19(13)**
C(12)–C(11)–C(10)	**102.73(14)**
C(14)–C(11)–C(10)	**115.87(15)**
C(12)–C(11)–H(11)	**111.8**

C(14)–C(11)–H(11)	**111.8**
C(10)–C(11)–H(11)	**111.8**
O(5)–C(12)–C(11)	**102.41(14)**
O(5)–C(12)–C(7)	**109.41(15)**
C(11)–C(12)–C(7)	**107.40(14)**
O(5)–C(12)–H(12)	**112.4**
C(11)–C(12)–H(12)	**112.4**
C(7)–C(12)–H(12)	**112.4**
O(5)–C(13)–O(6)	**107.80(13)**
O(5)–C(13)–C(19)	**110.07(15)**
O(6)–C(13)–C(19)	**106.83(14)**
O(5)–C(13)–C(14)	**107.30(13)**
O(6)–C(13)–C(14)	**106.00(14)**
C(19)–C(13)–C(14)	**118.36(14)**
C(21)–C(14)–C(11)	**114.57(14)**
C(21)–C(14)–C(15)	**110.59(15)**
C(11)–C(14)–C(15)	**111.46(15)**
C(21)–C(14)–C(13)	**114.96(15)**
C(11)–C(14)–C(13)	**101.34(13)**
C(15)–C(14)–C(13)	**103.07(13)**
C(16)–C(15)–C(14)	**106.35(15)**
C(16)–C(15)–H(15A)	**110.5**
C(14)–C(15)–H(15A)	**110.5**
C(16)–C(15)–H(15B)	**110.5**
C(14)–C(15)–H(15B)	**110.5**
H(15A)–C(15)–H(15B)	**108.7**
O(7)–C(16)–O(6)	**121.18(19)**
O(7)–C(16)–C(15)	**128.5(2)**
O(6)–C(16)–C(15)	**110.35(15)**
C(3)–C(17)–H(17A)	**109.5**
C(3)–C(17)–H(17B)	**109.5**
H(17A)–C(17)–H(17B)	**109.5**
C(3)–C(17)–H(17C)	**109.5**
H(17A)–C(17)–H(17C)	**109.5**
H(17B)–C(17)–H(17C)	**109.5**
C(3)–C(18)–H(18A)	**109.5**
C(3)–C(18)–H(18B)	**109.5**
H(18A)–C(18)–H(18B)	**109.5**
C(3)–C(18)–H(18C)	**109.5**
H(18A)–C(18)–H(18C)	**109.5**
H(18B)–C(18)–H(18C)	**109.5**
C(13)–C(19)–C(20)	**113.82(16)**
C(13)–C(19)–H(19A)	**108.8**
C(20)–C(19)–H(19A)	**108.8**

C(13)–C(19)–H(19B)	**108.8**
C(20)–C(19)–H(19B)	**108.8**
H(19A)–C(19)–H(19B)	**107.7**
C(19)–C(20)–H(20A)	**109.5**
C(19)–C(20)–H(20B)	**109.5**
H(20A)–C(20)–H(20B)	**109.5**
C(19)–C(20)–H(20C)	**109.5**
H(20A)–C(20)–H(20C)	**109.5**
H(20B)–C(20)–H(20C)	**109.5**
C(14)–C(21)–H(21A)	**109.5**
C(14)–C(21)–H(21B)	**109.5**
H(21A)–C(21)–H(21B)	**109.5**
C(14)–C(21)–H(21C)	**109.5**
H(21A)–C(21)–H(21C)	**109.5**
H(21B)–C(21)–H(21C)	**109.5**

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters (A^2 x 10^3) for shelxl.
The anisotropic displacement factor exponent takes the form:
–2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	48(1)	35(1)	58(1)	–14(1)	–10(1)	1(1)
O(2)	129(2)	65(1)	55(1)	–10(1)	–50(1)	31(1)
O(3)	120(2)	72(1)	27(1)	5(1)	–3(1)	27(1)
O(4)	45(1)	32(1)	49(1)	–5(1)	–8(1)	9(1)
O(5)	39(1)	29(1)	37(1)	–6(1)	9(1)	–8(1)
O(6)	38(1)	44(1)	30(1)	12(1)	7(1)	7(1)
O(7)	56(1)	91(1)	38(1)	30(1)	7(1)	21(1)
C(1)	55(1)	32(1)	31(1)	–3(1)	–12(1)	5(1)
C(2)	102(2)	37(1)	38(1)	–7(1)	–26(1)	16(1)
C(3)	83(2)	63(2)	31(1)	7(1)	11(1)	9(1)
C(4)	53(1)	32(1)	27(1)	–1(1)	1(1)	6(1)
C(5)	39(1)	39(1)	33(1)	–1(1)	1(1)	6(1)
C(6)	59(1)	30(1)	27(1)	2(1)	0(1)	11(1)
C(7)	42(1)	23(1)	28(1)	–1(1)	2(1)	–2(1)
C(8)	38(1)	25(1)	30(1)	–1(1)	0(1)	2(1)
C(9)	48(1)	27(1)	32(1)	1(1)	–7(1)	5(1)
C(10)	53(1)	27(1)	26(1)	2(1)	1(1)	–8(1)
C(11)	36(1)	28(1)	26(1)	1(1)	4(1)	–4(1)
C(12)	41(1)	25(1)	26(1)	1(1)	5(1)	–2(1)
C(13)	37(1)	25(1)	24(1)	2(1)	3(1)	–1(1)
C(14)	34(1)	28(1)	25(1)	0(1)	2(1)	–2(1)
C(15)	36(1)	38(1)	28(1)	2(1)	0(1)	2(1)
C(16)	44(1)	44(1)	32(1)	7(1)	6(1)	11(1)
C(17)	101(2)	100(2)	42(1)	–1(1)	27(1)	27(2)
C(18)	100(2)	88(2)	63(2)	25(2)	29(2)	–12(2)
C(19)	40(1)	28(1)	36(1)	2(1)	0(1)	3(1)
C(20)	38(1)	40(1)	48(1)	9(1)	4(1)	6(1)
C(21)	46(1)	30(1)	31(1)	–2(1)	–1(1)	–8(1)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for shelxl.

	x	y	z	U(eq)
H(4)	3094	3760	2725	45
H(5A)	1424	1899	2056	44
H(5B)	790	3289	2148	44
H(6A)	3253	3984	1638	46
H(6B)	1932	3290	1232	46
H(7)	5209	2691	1349	37
H(9)	3841	223	2510	43
H(10A)	2455	–372	1541	42
H(10B)	4163	–619	1196	42
H(11)	1452	903	807	36
H(12)	3207	2500	463	37
H(15A)	1260	84	–544	41
H(15B)	1369	1382	–197	41
H(17A)	1908	4179	3632	97
H(17B)	570	3260	3913	97
H(17C)	231	3887	3283	97
H(18A)	351	1098	3559	101
H(18B)	1348	668	2983	101
H(18C)	–185	1595	2921	101
H(19A)	5855	–1215	–259	41
H(19B)	6060	–1026	438	41
H(20A)	7947	256	–436	51
H(20B)	8642	–818	–16	51
H(20C)	8128	492	260	51
H(21A)	3311	–1761	462	43
H(21B)	2894	–1705	–229	43
H(21C)	1456	–1508	248	43
H(1)	6390(40)	2470(30)	2298(15)	75(10)

Table S18. Torsion angles [deg] for shelxl.

C(3)–O(3)–C(2)–O(2)	**–179.1(2)**
C(3)–O(3)–C(2)–C(1)	**2.1(3)**
O(1)–C(1)–C(2)–O(2)	**–47.5(3)**
C(4)–C(1)–C(2)–O(2)	**–165.2(2)**
C(9)–C(1)–C(2)–O(2)	**75.1(3)**
O(1)–C(1)–C(2)–O(3)	**131.2(2)**
C(4)–C(1)–C(2)–O(3)	**13.5(3)**
C(9)–C(1)–C(2)–O(3)	**–106.2(2)**
C(2)–O(3)–C(3)–C(17)	**–134.6(2)**
C(2)–O(3)–C(3)–C(18)	**105.7(3)**
C(2)–O(3)–C(3)–C(4)	**–16.9(3)**
O(1)–C(1)–C(4)–C(5)	**92.6(2)**
C(9)–C(1)–C(4)–C(5)	**–32.1(2)**
C(2)–C(1)–C(4)–C(5)	**–150.65(19)**
O(1)–C(1)–C(4)–C(3)	**–139.40(18)**
C(9)–C(1)–C(4)–C(3)	**95.9(2)**
C(2)–C(1)–C(4)–C(3)	**–22.6(2)**
O(3)–C(3)–C(4)–C(5)	**153.16(19)**
C(17)–C(3)–C(4)–C(5)	**–92.6(3)**
C(18)–C(3)–C(4)–C(5)	**36.6(3)**
O(3)–C(3)–C(4)–C(1)	**24.3(2)**
C(17)–C(3)–C(4)–C(1)	**138.5(2)**
C(18)–C(3)–C(4)–C(1)	**–92.2(3)**
C(1)–C(4)–C(5)–C(6)	**–56.6(2)**
C(3)–C(4)–C(5)–C(6)	**–179.34(18)**
C(4)–C(5)–C(6)–C(7)	**72.5(2)**
C(5)–C(6)–C(7)–C(12)	**119.85(18)**
C(5)–C(6)–C(7)–C(8)	**6.0(2)**
C(9)–O(4)–C(8)–C(10)	**–113.07(18)**
C(9)–O(4)–C(8)–C(7)	**114.54(17)**
C(12)–C(7)–C(8)–O(4)	**117.28(16)**
C(6)–C(7)–C(8)–O(4)	**–123.88(17)**
C(12)–C(7)–C(8)–C(9)	**–173.75(18)**
C(6)–C(7)–C(8)–C(9)	**–54.9(3)**
C(12)–C(7)–C(8)–C(10)	**–17.77(19)**
C(6)–C(7)–C(8)–C(10)	**101.07(18)**
C(8)–O(4)–C(9)–C(1)	**–110.65(17)**
C(10)–C(8)–C(9)–O(4)	**103.24(19)**
C(7)–C(8)–C(9)–O(4)	**–103.51(19)**
O(4)–C(8)–C(9)–C(1)	**104.4(2)**

C(10)–C(8)–C(9)–C(1)	**–152.32(19)**
C(7)–C(8)–C(9)–C(1)	**0.9(3)**
O(1)–C(1)–C(9)–O(4)	**11.6(2)**
C(4)–C(1)–C(9)–O(4)	**136.18(17)**
C(2)–C(1)–C(9)–O(4)	**–110.1(2)**
O(1)–C(1)–C(9)–C(8)	**–57.4(2)**
C(4)–C(1)–C(9)–C(8)	**67.2(2)**
C(2)–C(1)–C(9)–C(8)	**–179.1(2)**
O(4)–C(8)–C(10)–C(11)	**–139.15(16)**
C(9)–C(8)–C(10)–C(11)	**152.69(17)**
C(7)–C(8)–C(10)–C(11)	**–3.7(2)**
C(8)–C(10)–C(11)–C(12)	**23.75(18)**
C(8)–C(10)–C(11)–C(14)	**134.24(16)**
C(13)–O(5)–C(12)–C(11)	**35.14(17)**
C(13)–O(5)–C(12)–C(7)	**148.85(14)**
C(14)–C(11)–C(12)–O(5)	**–41.54(16)**
C(10)–C(11)–C(12)–O(5)	**78.89(15)**
C(14)–C(11)–C(12)–C(7)	**–156.72(14)**
C(10)–C(11)–C(12)–C(7)	**–36.30(18)**
C(8)–C(7)–C(12)–O(5)	**–76.94(17)**
C(6)–C(7)–C(12)–O(5)	**161.31(14)**
C(8)–C(7)–C(12)–C(11)	**33.49(18)**
C(6)–C(7)–C(12)–C(11)	**–88.25(18)**
C(12)–O(5)–C(13)–O(6)	**99.75(15)**
C(12)–O(5)–C(13)–C(19)	**–144.07(15)**
C(12)–O(5)–C(13)–C(14)	**–14.03(17)**
C(16)–O(6)–C(13)–O(5)	**–105.74(18)**
C(16)–O(6)–C(13)–C(19)	**135.99(17)**
C(16)–O(6)–C(13)–C(14)	**8.90(19)**
C(12)–C(11)–C(14)–C(21)	**156.83(16)**
C(10)–C(11)–C(14)–C(21)	**46.0(2)**
C(12)–C(11)–C(14)–C(15)	**–76.64(18)**
C(10)–C(11)–C(14)–C(15)	**172.56(15)**
C(12)–C(11)–C(14)–C(13)	**32.43(16)**
C(10)–C(11)–C(14)–C(13)	**–78.38(17)**
O(5)–C(13)–C(14)–C(21)	**–136.67(15)**
O(6)–C(13)–C(14)–C(21)	**108.35(16)**
C(19)–C(13)–C(14)–C(21)	**–11.5(2)**
O(5)–C(13)–C(14)–C(11)	**–12.53(17)**
O(6)–C(13)–C(14)–C(11)	**–127.51(14)**
C(19)–C(13)–C(14)–C(11)	**112.68(16)**
O(5)–C(13)–C(14)–C(15)	**102.91(16)**
O(6)–C(13)–C(14)–C(15)	**–12.07(17)**
C(19)–C(13)–C(14)–C(15)	**–131.88(16)**

C(21)–C(14)–C(15)–C(16)	**–112.13(17)**
C(11)–C(14)–C(15)–C(16)	**119.18(17)**
C(13)–C(14)–C(15)–C(16)	**11.24(19)**
C(13)–O(6)–C(16)–O(7)	**178.7(2)**
C(13)–O(6)–C(16)–C(15)	**–1.5(2)**
C(14)–C(15)–C(16)–O(7)	**173.1(2)**
C(14)–C(15)–C(16)–O(6)	**–6.7(2)**
O(5)–C(13)–C(19)–C(20)	**–53.5(2)**
O(6)–C(13)–C(19)–C(20)	**63.3(2)**
C(14)–C(13)–C(19)–C(20)	**–177.34(16)**

Symmetry transformations used to generate equivalent atoms:

X–ray Crystal Structure Data for compound 21(CCDC 1535913)

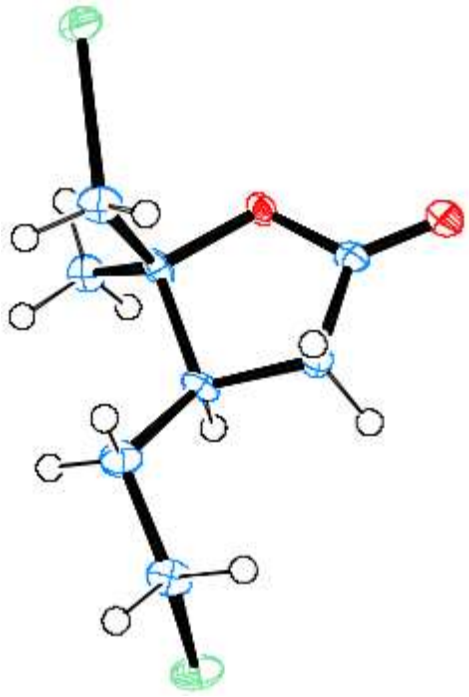


Table S19. Crystal data and structure refinement for A160909B.

Identification code	**a160909b**
Empirical formula	**C8 H12 I2 O2**
Formula weight	**393.98**
Temperature	**135.00(10) K**
Wavelength	**0.71073 A**
Crystal system, space group	**Orthorhombic, P2(1)2(1)2(1)**
Unit cell dimensions	**a = 7.2879(3) A alpha = 90 deg.** **b = 11.3154(5) A beta = 90 deg.** **c = 13.6084(5) A gamma = 90 deg.**
Volume	**1122.23(9) A^3**
Z, Calculated density	**4, 2.332 Mg/m^3**
Absorption coefficient	**5.569 mm^-1**
F(000)	**728**

Crystal size	**? x ? x ? mm**
Theta range for data collection	**3.325 to 25.009 deg.**
Limiting indices	**-7<=h<=8, -13<=k<=11, -16<=l<=11**
Reflections collected / unique	**4456 / 1981 [R(int) = 0.0398]**
Completeness to theta = 25.009	**99.7 %**
Absorption correction	**Semi-empirical from equivalents**
Max. and min. transmission	**1.00000 and 0.54419**
Refinement method	**Full-matrix least-squares on F^2**
Data / restraints / parameters	**1981 / 0 / 111**
Goodness-of-fit on F^2	**1.036**
Final R indices [I>2sigma(I)]	**R1 = 0.0305, wR2 = 0.0618**
R indices (all data)	**R1 = 0.0321, wR2 = 0.0634**
Absolute structure parameter	**0.00(4)**
Extinction coefficient	**0.0115(5)**
Largest diff. peak and hole	**1.020 and -0.988 e.A^-3**

Table S20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for A160909B. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
I(1)	2654(1)	8682(1)	9837(1)	25(1)
I(2)	2223(1)	5920(1)	4554(1)	25(1)
O(1)	4943(7)	8369(5)	7811(4)	15(1)
O(2)	7782(8)	7662(5)	7649(4)	21(1)
C(1)	3041(11)	7974(7)	7655(6)	16(2)
C(2)	6153(10)	7516(7)	7546(6)	14(2)
C(3)	5158(9)	6483(8)	7124(6)	17(2)
C(4)	3281(10)	6978(7)	6871(6)	16(2)
C(5)	2317(12)	7490(6)	8611(5)	21(2)
C(6)	1937(11)	9003(7)	7266(6)	19(2)
C(7)	1742(11)	6083(7)	6795(6)	20(2)
C(8)	2070(11)	5162(6)	6008(5)	18(2)

Table S21. Bond lengths [A] and angles [deg] for A160909B.

I(1)-C(5)	2.159(7)
I(2)-C(8)	2.161(7)
O(1)-C(1)	1.472(9)
O(1)-C(2)	1.356(9)
O(2)-C(2)	1.207(9)
C(1)-C(4)	1.562(11)
C(1)-C(5)	1.507(10)
C(1)-C(6)	1.511(11)
C(2)-C(3)	1.491(11)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(3)-C(4)	1.518(10)
C(4)-H(4)	0.9800
C(4)-C(7)	1.515(11)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(7)-C(8)	1.512(10)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(2)-O(1)-C(1)	111.0(6)
O(1)-C(1)-C(4)	102.2(6)
O(1)-C(1)-C(5)	108.4(6)
O(1)-C(1)-C(6)	108.6(6)
C(5)-C(1)-C(4)	111.5(6)
C(5)-C(1)-C(6)	113.3(7)
C(6)-C(1)-C(4)	112.1(6)
O(1)-C(2)-C(3)	110.2(6)
O(2)-C(2)-O(1)	120.8(7)
O(2)-C(2)-C(3)	129.1(8)
C(2)-C(3)-H(3A)	111.0
C(2)-C(3)-H(3B)	111.0
C(2)-C(3)-C(4)	103.7(6)
H(3A)-C(3)-H(3B)	109.0
C(4)-C(3)-H(3A)	111.0

C(4)-C(3)-H(3B)	**111.0**
C(1)-C(4)-H(4)	**107.2**
C(3)-C(4)-C(1)	**102.2(6)**
C(3)-C(4)-H(4)	**107.2**
C(7)-C(4)-C(1)	**116.5(6)**
C(7)-C(4)-C(3)	**115.8(7)**
C(7)-C(4)-H(4)	**107.2**
I(1)-C(5)-H(5A)	**108.8**
I(1)-C(5)-H(5B)	**108.8**
C(1)-C(5)-I(1)	**113.6(5)**
C(1)-C(5)-H(5A)	**108.8**
C(1)-C(5)-H(5B)	**108.8**
H(5A)-C(5)-H(5B)	**107.7**
C(1)-C(6)-H(6A)	**109.5**
C(1)-C(6)-H(6B)	**109.5**
C(1)-C(6)-H(6C)	**109.5**
H(6A)-C(6)-H(6B)	**109.5**
H(6A)-C(6)-H(6C)	**109.5**
H(6B)-C(6)-H(6C)	**109.5**
C(4)-C(7)-H(7A)	**109.0**
C(4)-C(7)-H(7B)	**109.0**
H(7A)-C(7)-H(7B)	**107.8**
C(8)-C(7)-C(4)	**113.1(7)**
C(8)-C(7)-H(7A)	**109.0**
C(8)-C(7)-H(7B)	**109.0**
I(2)-C(8)-H(8A)	**109.1**
I(2)-C(8)-H(8B)	**109.1**
C(7)-C(8)-I(2)	**112.5(5)**
C(7)-C(8)-H(8A)	**109.1**
C(7)-C(8)-H(8B)	**109.1**
H(8A)-C(8)-H(8B)	**107.8**

Symmetry transformations used to generate equivalent atoms:

Table S22. Anisotropic displacement parameters (A^2 x 10^3) for A160909B. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
I(1)	28(1)	29(1)	17(1)	-6(1)	0(1)	3(1)
I(2)	42(1)	18(1)	16(1)	0(1)	-2(1)	2(1)
O(1)	12(3)	16(3)	17(3)	0(3)	-1(2)	-4(2)
O(2)	20(3)	24(3)	20(3)	-1(3)	-3(3)	1(3)
C(1)	13(4)	11(4)	25(4)	3(4)	-5(4)	-3(4)
C(2)	17(4)	19(5)	8(3)	4(4)	0(3)	-5(4)
C(3)	14(4)	22(5)	16(4)	0(4)	1(3)	1(4)
C(4)	17(4)	13(4)	18(4)	0(4)	-5(4)	-5(4)
C(5)	27(5)	13(4)	22(4)	0(4)	-1(4)	-4(4)
C(6)	22(4)	15(4)	21(4)	2(4)	1(4)	-4(4)
C(7)	25(4)	17(5)	19(4)	-1(4)	-1(4)	0(4)
C(8)	27(4)	10(4)	15(3)	8(3)	-6(4)	0(4)

Table S23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for A160909B.

	x	y	z	U(eq)
H(3A)	5060	5849	7601	21
H(3B)	5775	6188	6542	21
H(4)	3387	7364	6229	19
H(5A)	2946	6755	8757	25
H(5B)	1023	7313	8534	25
H(6A)	1872	9611	7757	29
H(6B)	720	8742	7106	29
H(6C)	2518	9312	6687	29
H(7A)	1601	5689	7424	24
H(7B)	605	6494	6653	24
H(8A)	1082	4587	6026	21
H(8B)	3206	4749	6149	21

Table 8. Torsion angles [deg] for A160909B.

O(1)-C(1)-C(4)-C(3)	**31.5(7)**
O(1)-C(1)-C(4)-C(7)	**158.8(6)**
O(1)-C(1)-C(5)-I(1)	**52.1(8)**
O(1)-C(2)-C(3)-C(4)	**17.6(8)**
O(2)-C(2)-C(3)-C(4)	**-161.1(9)**
C(1)-O(1)-C(2)-O(2)	**-177.7(7)**
C(1)-O(1)-C(2)-C(3)	**3.4(8)**
C(1)-C(4)-C(7)-C(8)	**179.1(7)**
C(2)-O(1)-C(1)-C(4)	**-22.3(8)**
C(2)-O(1)-C(1)-C(5)	**95.6(7)**
C(2)-O(1)-C(1)-C(6)	**-140.9(6)**
C(2)-C(3)-C(4)-C(1)	**-29.7(8)**
C(2)-C(3)-C(4)-C(7)	**-157.5(6)**
C(3)-C(4)-C(7)-C(8)	**-60.6(9)**
C(4)-C(1)-C(5)-I(1)	**163.9(5)**
C(4)-C(7)-C(8)-I(2)	**-62.6(8)**
C(5)-C(1)-C(4)-C(3)	**-84.2(8)**
C(5)-C(1)-C(4)-C(7)	**43.2(9)**
C(6)-C(1)-C(4)-C(3)	**147.5(7)**
C(6)-C(1)-C(4)-C(7)	**-85.1(8)**
C(6)-C(1)-C(5)-I(1)	**-68.5(8)**

Symmetry transformations used to generate equivalent atoms: