Supporting Information

Organocatalytic 1,4-Conjugate Addition of Ascorbic Acid to Unsaturated Aldehydes: Bio-inspired Total Syntheses of Leucodrin, Leudrin and Proposed Structure of Dilaspirolactone

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Part 1: General methods and materials:

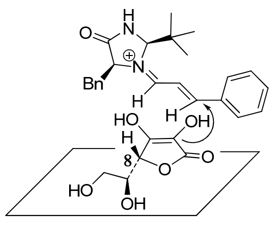
Unless otherwise mentioned, all reactions were carried out under a nitrogen atmosphere under anhydrous conditions and all reagents were purchased from commercial suppliers without further purification. Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials.
Reactions were monitored by Thin Layer Chromatography on plates (GF254) supplied by Yantai Chemicals (China) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. If not specially mentioned, flash column chromatography uses silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China).
NMR spectra were recorded on Bruker AV400 instrument. TMS was used as internal standard for 1H NMR (0 ppm), and solvent signal was used as reference for ^{13}C NMR (CHLOROFORM-D, 77.160 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, td = triple doublet, qd = quarter doublet, m = multiplet.
Infrared (IR) spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker ESI-Q/TOF MS.

Part 2: Experimental details and characteristic data for organocatalytic addition of ascorbic acid with α, β-unsaturated aldehydes

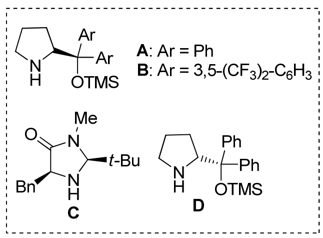
General Procedure:

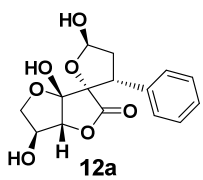
A mixture of **11** (1.5 mmol), **9** (1.0 mmol), and the catalyst **C**/BA (0.2 mmol) in 2.0 ml solvents (H_2O/MeOH = 1:4) was stirred at 50°C for 12 h. The solvent was removed directly by concentration and the residual was purified by column chromatography (hexane/EtOAc = 1:2 to 1:5) to give the desired product **12** as a mixture of **C-2** diastereoisomers which cannot be separated by chromatography. The ratios of α-isomer/β-isomer vary from 1:5 to 1:7. Only the NMR data of β-isomer were documented in the following characteristic data of **12a-m**.

Rationalization of the stereochemical result of the above transformation:
Notably, although four stereogenic centers were generated in this reaction, **12** was only obtained as a mixture of C-2 diastereoisomers, and no other diastereoisomers were observed. We think that the high diastereoselectivity of the reaction was mainly controlled by the substrate ascorbic acid itself (mainly the C-8 stereogenetic center of ascorbic acid), but not the chiral catalyst. As shown below, when the electrophile approached to ascorbic acid, it should attack from the less hindered top side of the c ring. Meanwhile, the aromatic moiety was oriented far away from the c ring. It is the most favorable transition state compared with others, which may explain why we always got only one diastereoisomer with different catalysts. Moreover, we also tried the enantiomer of catalyst A (Cat. **D**) in the reaction, and it also gave comparable yield (86%) of **12a** with the same stereochemical outcome. This result further proved that the diastereoselectivity of the transformation is mainly controlled by the substrate, but not the catalyst.



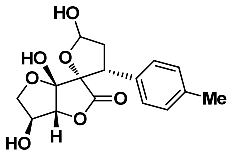
favorable transition state





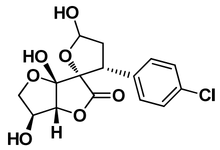
12a

Characteristic data of 12a: IR ν_{max} (film): 3448, 2954, 1785, 1113, 1017 cm^{-1}; $[\alpha]^{20}_{D}$ = -29.0 (*c* = 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, CD_3OD) (major isomer) δ = 6.60-6.55 (m, 2H), 6.53-6.49 (m, 3H), 5.31 (d, *J* = 4.3 Hz, 1H), 4.06-3.97 (m, 3H), 3.85 (d, *J* = 4.7 Hz, 1H), 3.68 (s, 1H), 2.88 (ddd, *J* = 10.9, 10.3, 4.3 Hz, 1H), 2.37 (dd, *J* = 10.1, 5.3 Hz, 1H); ^{13}C NMR (756 MHz, CD_3OD) δ = 174.3, 134.2, 128.8, 128.5, 128.0, 106.0, 98.3, 91.3, 87.4, 74.9, 74.0, 46.7, 38.6 ppm; HRMS (ESI) m/z calcd for $C_{15}H_{16}NaO_7$ $[M+Na]^+$: 331.0788; found: 331.0789.



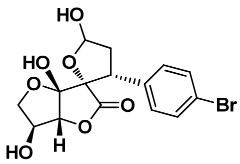
12b

Characteristic data of 12b: IR ν_{max} (film): 3435, 2954, 1785, 1109, 1022, 818 cm^{-1}; $[\alpha]^{20}_{D}$ = -19.0 (c = 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, CD_3OD) (major isomer) δ = 7.27 (d, J = 8.1 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H), 5.80 (d, J = 5.3 Hz, 1H), 4.29 – 4.08 (m, 3H), 3.99 (dd, J = 8.4, 2.5 Hz, 1H), 3.79 (s, 1H), 2.73 (ddd, J = 13.7, 12.7, 5.4 Hz, 1H), 2.31 (s, 3H), 2.11 (dd, J = 12.6, 6.7 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 174.3, 137.9, 131.0, 129.1, 128.6, 106.0, 98.2, 91.3, 87.3, 74.9, 74.0, 46.3, 38.6, 19.9 ppm; HRMS (ESI) m/z calcd for $C_{16}H_{18}NaO_7$ $[M+Na]^+$: 345.0945; found: 345.0946.



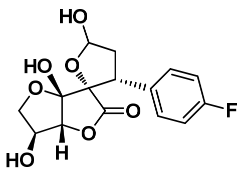
12c

Characteristic data of 12c: IR vmax (film): 3464, 2967, 1797, 1092, 1009 cm^{-1}; $[\alpha]^{20}_{D}$ = -35.0 (c = 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, CD_3OD) (major isomer) δ 7.42 – 7.31 (m, 4H), 5.81 (d, J = 5.3 Hz, 1H), 4.25 – 4.15 (m, 3H), 4.05 – 3.91 (m, 1H), 3.77 (s, 1H), 2.73 (ddd, J = 13.6, 12.7, 5.4 Hz, 1H), 2.15 (dd, J = 12.6, 6.7 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 175.4, 135.3, 134.7, 131.8, 129.9, 107.3, 99.7, 92.6, 89.0, 76.2, 75.6, 47.6, 40.0 ppm; HRMS (ESI) m/z calcd for $C_{15}H_{15}ClNaO_7$ $[M+Na]^+$: 365.0398; found: 365.0440.



12d

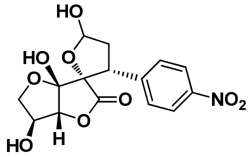
Characteristic data of 12d: IR vmax (film): 3460, 2967, 1789, 1071, 1022 cm^{-1}; $[\alpha]^{20}_{D}$ = -12.0 (c = 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, CD_3OD) (major isomer) δ 7.50 (d, J = 7.7 Hz, 2H), 7.31 (d, J = 7.7 Hz, 2H), 5.81 (d, J = 5.2 Hz, 1H), 4.25 – 4.15(m, 3H), 3.99 (dd, J = 8.7, 2.2 Hz, 1H), 3.78 (s, 1H), 2.73 (td, J = 12.6, 4.7 Hz, 1H), 2.14 (dd, J = 12.6, 6.6 Hz, 1H).; ^{13}C NMR (125 MHz, CD_3OD) δ 175.5, 135.2, 133.0, 132.2, 123.3, 107.4, 99.7, 92.6, 89.0, 76.3, 75.6, 47.7, 40.0 ppm; HRMS (ESI) m/z calcd for $C_{15}H_{15}BrNaO_7$ $[M+Na]^+$: 408.9893; found: 408.9892.



12e

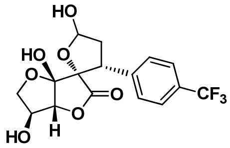
Characteristic data of 12e: IR vmax (film): 3456, 2958, 1785, 1515, 1009, 835 cm^{-1}; $[\alpha]^{20}_{D}$ = -26.0 (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, CD_3OD) (major isomer)δ 7.46 – 7.36 (m, 2H), 7.12 – 7.01 (m, 2H), 5.81 (d, J = 5.3 Hz, 1H), 4.27 – 4.09 (m, 3H), 4.03 – 3.95 (m, 1H), 3.78 (s, 1H), 2.73 (ddd, J = 13.6, 12.7, 5.4 Hz, 1H), 2.14 (dd, J = 12.6, 6.7 Hz, 1H).; ^{13}C NMR (125 MHz,

CD_3OD) δ 175.5, 163.1, 132.1, 132.0, 116.6, 116.5, 107.4, 99.6, 88.9, 76.2, 75.5, 47.4, 40.1 ppm; HRMS (ESI) m/z calcd for $C_{15}H_{15}FNaO_7$ $[M+Na]^+$: 349.0694; found:349.0693.



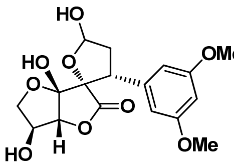
12f

Characteristic data of 12f: IR vmax (film): 3377, 2917, 2357, 1789, 1519, 1349, 1076 cm^{-1}; $[\alpha]^{20}_D$ = -14.5 (*c* = 0.2, $CHCl_3$); ^1H NMR (500 MHz, CD_3OD) δ 8.20 (dd, *J* = 8.8, 1.9 Hz, 2H), 7.76-7.58 (m, 2H), 5.84 (d, *J* = 5.3 Hz, 1H), 4.34 (dd, *J* = 13.1, 6.7 Hz, 1H), 4.23– 4.09 (m, 3H), 4.05– 3.90 (m, 1H), 3.76 (s, 1H), 2.97 – 2.69 (m, 1H), 2.20 (dd, *J* = 13.1, 7.3 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 175.1, 149.4, 144.0, 131.5, 124.8, 107.3, 99.9, 92.7, 89.2, 76.3, 75.6, 48.1, 40.1 ppm; HRMS (ESI) m/z calcd for $C_{15}H_{15}NNaO_9$ $[M+Na]^+$: 376.0639; found:376.0642.



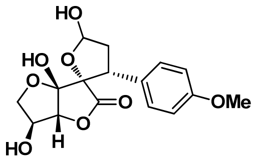
12g

Characteristic data of 12g: IR vmax (film): 3427, 1789, 1324, 1113, 1071, 1009 cm^{-1}; $[\alpha]^{20}_D$ = -24.5 (*c* = 0.2, $CHCl_3$); ^1H NMR (300 MHz, CD_3OD) δ 7.70 – 7.55 (m, 4H), 5.84 (d, *J* = 5.3 Hz, 1H), 4.31 (dd, *J* = 13.5, 6.6 Hz, 1H), 4.24 – 4.13 (m, 2H), 4.00 (dd, *J* = 7.8, 2.1 Hz, 1H), 3.76 (s, 1H), 2.87 – 2.72 (m, 1H), 2.20 (dd, *J* = 12.6, 6.8 Hz, 1H).; ^{13}C NMR (75 MHz, CD_3OD) δ 175.3, 140.8, 131.1, 131.0, 126.7, 126.7, 107.4, 99.8, 92.7, 89.1, 76.3, 75.6, 48.1, 40.0 ppm; HRMS (ESI) m/z calcd for $C_{16}H_{19}F_3NaO_7$ $[M+Na]^+$: 394.1108; found:394.1106.



12h

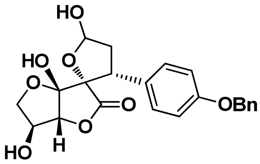
Characteristic data of 12h: IR vmax (film): 3448, 2921, 1781, 1586, 1204, 1059, 1022 cm^{-1}; $[\alpha]^{20}_D$ = -68.0 (*c* = 0.2, $CHCl_3$); ^1H NMR (300 MHz, CD_3OD) δ 6.55 (d, *J* = 2.2 Hz, 2H), 6.43 (s, 1H), 5.79 (d, *J* = 5.3 Hz, 1H), 4.23 – 4.07 (m, 3H), 4.00 (dd, *J* = 8.9, 3.1 Hz, 1H), 3.91 (s, 1H), 3.76 (s, 6H), 2.70 (td, *J* = 13.2, 5.4 Hz, 1H), 2.13 (dd, *J* = 12.6, 6.7 Hz, 1H).; ^{13}C NMR (75 MHz, CD_3OD) δ 175.9, 162.5, 137.9, 108.2, 107.5, 101.2, 99.7, 92.6, 89.1, 76.3, 75.5, 55.9, 55.9, 48.3, 40.1 ppm; HRMS (ESI) m/z calcd for $C_{17}H_{20}NaO_9$ $[M+Na]^+$: 391.0999; found:391.0999;



12i

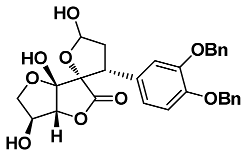
Characteristic data of 12i: IR vmax (film): 3435, 2958, 2357, 1785, 1511, 1022, 831 cm^{-1}; $[\alpha]^{20}_D$ = -26.5 (*c* = 0.2, $CHCl_3$); ^1H NMR (300 MHz, METHANOL-D_3) δ 7.31 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.78 (d, *J* = 5.3 Hz, 1H), 4.24 – 4.08 (m, 3H), 4.02 – 3.93 (m, 1H), 3.80 – 3.75 (m, 4H), 2.78 – 2.66 (m, 1H), 2.10 (dd, J = 12.6, 6.7 Hz, 1H).; ^{13}C NMR (150 MHz, CD_3OD)

δ 175.9, 161.2, 131.2, 127.2, 115.2, 107.5, 99.6, 92.6, 88.8, 76.3, 75.6, 55.9, 47.4, 40.1 ppm; HRMS (ESI) m/z calcd for $C_{16}H_{18}NaO_8$ $[M+Na]^+$: 361.0894; found:361.0893.



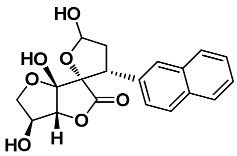
12j

Characteristic data of 12j: IR vmax (film): 3440, 2958, 2353, 1789, 1511, 1246, 1022 cm^{-1}; $[\alpha]^{20}_D$ = -15.5 (*c* = 0.2, $CHCl_3$); ^1H NMR (500 MHz, CD_3OD) δ 7.45 – 7.25 (m, 7H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.79 (d, *J* = 5.3 Hz, 1H), 5.02 (s, 2H), 4.26 – 4.11 (m, 3H), 3.99 (dd, *J* = 9.4, 3.6 Hz, 1H), 3.82 (s, 1H), 2.81 – 2.64 (m, 1H), 2.10 (dd, *J* = 12.6, 6.7 Hz, 1H).; ^{13}C NMR (125 MHz, CD_3OD) δ 175.8, 160.3, 138.7, 131.3, 129.6, 129.0, 128.7, 127.5, 116.2, 107.5, 99.6, 92.6, 88.8, 76.2, 75.6, 71.2, 47.4, 40.0 ppm; HRMS (ESI) m/z calcd for $C_{22}H_{22}NaO_8$ $[M+Na]^+$: 437.1207; found:437.1209.



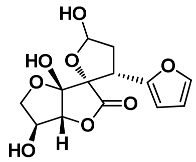
12k

Characteristic data of 12k: R_f = 0.65 (silica gel, CH_2Cl_2/MeOH = 10/1); $[\alpha]^{20}_D$ = -6 (*c* = 0.2, $CHCl_3$); IR ν_{max} (film): 3647, 2984, 2897, 1408, 1259, 1064, 815, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.49 – 7.20 (m, 10H), 6.96 (s, 1H), 6.89 (s, 2H), 5.17 – 5.07 (m, 4H), 4.27 (d, *J* = 4.0 Hz, 1H), 4.19 – 4.12 (m, 2H), 4.03 (dd, *J* = 10.5, 4.3 Hz, 1H), 3.77 (s, 1H), 3.09 (dd, *J* = 17.4, 13.2 Hz, 1H), 2.83 (dd, *J* = 17.4, 8.4 Hz, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.0, 170.7, 149.4, 148.8, 136.8, 136.7, 128.5, 128.5, 128.0, 127.9, 127.4, 127.3, 124.3, 121.9, 115.4, 114.9, 105.4, 88.9, 86.0, 85.9, 76.1, 73.3, 71.4, 71.1, 45.0, 33.8 ppm; HRMS m/z calcd for $C_{29}H_{26}O_9$ $[M+Na]^+$: 541.1469.; found: 541.1470.



12l

Characteristic data of 12l: IR vmax (film): 3435, 2958, 1789, 1337, 1117, 1013, 823, 748, 731 cm^{-1}; $[\alpha]^{20}_D$ = -31.5 (*c* = 0.2, $CHCl_3$); ^1H NMR (300 MHz, CD_3OD) δ 8.18 – 7.72 (m, 4H), 7.56 – 7.37 (m, 3H), 5.87 (d, *J* = 5.3 Hz, 1H), 4.39 (dd, *J* = 13.7, 6.6 Hz, 1H), 4.25 – 4.11 (m, 2H), 4.02 – 3.97 (m, 1H), 3.75 (s, 1H), 2.91 (ddd, *J* = 13.6, 12.7, 5.4 Hz, 1H), 2.23 (dd, *J* = 12.6, 6.7 Hz, 1H).; ^{13}C NMR (75 MHz, CD_3OD) δ 175.8, 134.9, 134.8, 133.2, 129.5, 129.4, 129.1, 128.8, 127.7, 127.5, 127.4, 107.4, 99.8, 92.8, 88.9, 76.3, 75.5, 48.3, 40.1 ppm; HRMS (ESI) m/z calcd for $C_{19}H_{22}NO_7$ $[M+NH_4]^+$: 376.1391; found:376.1391.

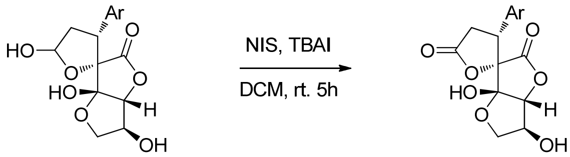


12m

Characteristic data of 12m: IR vmax (film): 3427, 2357, 1785, 1113, 1013, 740 cm^{-1}; $[\alpha]^{20}_D$ = +2.5 (c = 0.2, $CHCl_3$); ^1H NMR (500 MHz, CD_3OD) δ 7.45 (dd, J = 1.8, 0.8 Hz, 1H), 6.68 – 6.25 (m, 2H), 5.77 (d, J = 5.2 Hz, 1H), 4.41 – 4.25 (m, 2H), 4.23 – 4.17 (m, 2H), 4.07 – 3.98 (m, 1H), 2.69 (td, J = 12.9, 5.3 Hz, 1H), 2.17 (dd, J = 12.6, 6.9 Hz, 1H).; ^{13}C NMR (75 MHz, CD_3OD) δ 175.3, 150.9, 144.1, 111.8, 109.9, 109.7, 107.5, 99.7, 89.1, 76.6, 75.5, 42.4, 38.8 ppm; HRMS (ESI) m/z calcd for $C_{13}H_{14}NaO_8$ $[M+NH_4]^+$: 321.0581; found:321.0581.

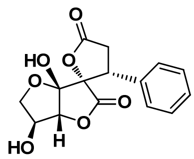
Part 3: Experimental details and characteristic data for selective oxidation of the hemiketal moiety

General Procedure:



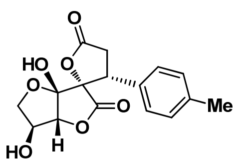
12 **13**

Synthesis of 13: A mixture of **12** (1.0 mmol), N-iodosuccinimide (5.0 mmol), and tetrabutylammonium iodide (1.0 mmol) in 5.0 ml DCM was stirred at 50°C for 5 h. Then 10 mL water was added followed by 10 ml DCM. The organic layer was separated and aqueous phase was extracted with DCM twice. The combined extract was washed with 10 ml H_2O and brine, and then dried with Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (hexane/EtOAc = 5:1) to give the desired product **13a-l**.



13a

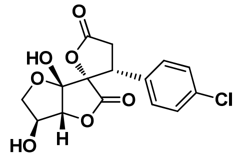
Characteristic data of 13a: IR ν_{max} (film): 3456, 2888, 2900, 1801, 1710, 1217, 1117, 1071, 1030, 777 cm^{-1}; $[\alpha]^{20}_D$ = -7.0 (c = 0.2, $CHCl_3$); ^1H NMR (300 MHz, CD_3OD) δ 7.45 – 7.40 (m, 2H), 7.39 – 7.33 (m, 3H), 4.30 (dd, J = 12.9, 8.6 Hz, 1H), 4.25 – 4.15 (m, 2H), 4.04 – 3.98 (m, 1H), 3.81 (s, 1H), 3.26 – 3.18 (m, 1H), 2.92 (dd, J = 17.4, 8.6 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 159.4, 157.1, 126.1, 123.0, 122.9, 122.1, 104.2, 91.7, 90.5, 80.2, 79.0, 56.4, 46.4 ppm; HRMS (ESI) m/z calcd for $C_{15}H_{15}O_7$ $[M+H]^+$: 307.0812; found: 307.0814.



13b

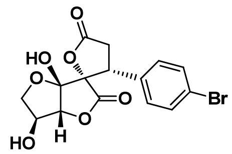
Characteristic data of 13b: IR ν_{max} (film): 3469, 2971, 2921, 1805, 1208, 1121, 1034, 901 cm^{-1}; $[\alpha]^{20}_D$ = -5.0 (c = 0.2, $CHCl_3$); ^1H NMR (300 MHz, CD_3OD) δ 7.27 (d, J = 8.2 Hz, 2H), 7.17

(d, J = 8.1 Hz, 2H), 4.38 (d, J = 4.0 Hz, 1H), 4.33 – 4.19 (m, 2H), 4.12 (dd, J = 10.6, 4.3 Hz, 1H), 3.90 (s, 1H), 3.25 (dd, J = 17.4, 13.3 Hz, 1H), 2.90 (dd, J = 17.4, 8.4 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 174.0, 170.6, 139.5, 130.2, 128.7, 128.7, 124.6, 105.9, 89.2, 86.0, 73.8, 45.4, 34.0, 21.4 ppm; HRMS (ESI) m/z calcd for $C_{16}H_{17}O_7$ $[M+H]^+$: 321.0969; found: 321.0972.



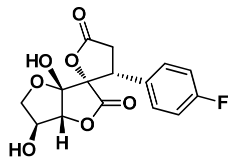
13c

Characteristic data of 13c: IR ν_{max} (film): 3477, 2975, 2896, 1801, 1212, 1121, 1026, 897 cm^{-1}; $[\alpha]^{20}_D$ = -36 (c = 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, CD_3OD) δ 7.44 – 7.36 (m, 4H), 4.34 – 4.17 (m, 3H), 4.01 (dd, J = 12.4, 3.3 Hz, 1H), 3.84 (s, 1H), 3.22 (dd, J = 17.4, 12.8 Hz, 1H), 2.93 (dd, J = 17.4, 8.6 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 175.5, 172.6, 136.0, 133.1, 131.8, 130.3, 106.7, 90.8, 89.8, 76.7, 75.2, 46.3, 34.4 ppm; HRMS (ESI) m/z calcd for $C_{15}H_{14}ClO_7$ $[M+H]^+$: 341.0423; found: 341.0426.



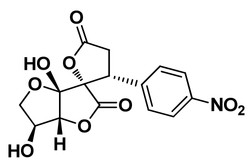
13d

Characteristic data of 13d: IR ν_{max} (film): 3402, 2892, 2336, 1801, 1706, 1208, 1117, 1030, 827 cm^{-1}; $[\alpha]^{20}_D$ = -5.5 (c = 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, CD_3OD) δ 7.47 (dd, J = 8.1, 1.7 Hz, 2H), 7.38 (dd, J = 8.4, 1.5 Hz, 2H), 4.33 – 4.17 (m, 3H), 4.02 (dd, J = 9.4, 3.3 Hz, 1H), 3.84 (s, 1H), 3.20 (dd, J = 17.3, 12.8 Hz, 1H), 2.92 (dd, J = 17.3, 8.5 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 175.5, 172.6, 133.5, 133.3, 132.0, 124.0, 106.7, 90.7, 89.8, 76.7, 75.2, 46.4, 34.3 ppm; HRMS (ESI) m/z calcd for $C_{15}H_{14}BrO_7$ $[M+H]^+$: 384.9917; found: 384.9914.



13e

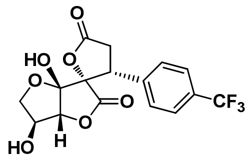
Characteristic data of 13e: IR ν_{max} (film): 3448, 2988, 1801, 1511, 1225, 1121, 1076, 1030, 843 cm^{-1}; $[\alpha]^{20}_D$ = -11.0 (c = 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, CD_3OD) δ 7.47 (dd, J = 9.2, 5.3 Hz, 2H), 7.13 (t, J = 8.9 Hz, 2H), 4.48 – 4.15 (m, 2H), 4.04 (dd, J = 9.3, 3.3 Hz, 1H), 3.84 (s, 1H), 3.24 (dd, J = 17.4, 12.8 Hz, 1H), 2.95 (dd, J = 17.5, 8.6 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 173.5, 170.8, 130.2, 130.1, 128.2, 115.1, 114.8, 104.7, 87.8, 74.7, 73.2, 44.2, 32.6 ppm; HRMS (ESI) m/z calcd for $C_{15}H_{14}FO_7$ $[M+H]^+$: 325.0718; found: 325.0721.



13f

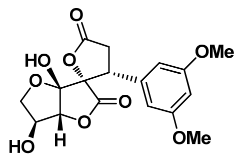
Characteristic data of 13f: IR ν_{max} (film): 3464, 2992, 1793, 1723, 1345, 1084, 860 cm^{-1};

$[\alpha]^{20}_{D}$ = -5.5 (*c* = 0.2, $CHCl_3$); ^1H NMR (300 MHz, CD_3OD) δ 8.16 (dd, *J* = 9.1, 1.3 Hz, 2H), 7.60 (d, *J* = 9.2 Hz, 2H), 4.24 – 4.19(m, 1H), 4.17 – 4.06 (m, 1H), 4.02 – 3.85 (m, 2H), 3.55 – 3.44 (m, 1H), 3.35 (s, 1H), 2.93 – 2.77 (m, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 176.4, 174.4, 147.1, 131.5, 125.1, 124.1, 108.6, 88.1, 81.5, 75.9, 75.6, 47.0, 35.9 ppm.; HRMS (ESI) m/z calcd for $C_{15}H_{14}NO_9$ $[M+H]^+$: 352.0663; found: 352.0667.



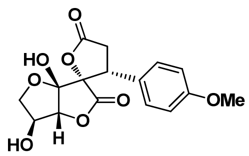
13g

Characteristic data of 13g: IR ν_{max} (film): 3440, 1785, 1714, 1324, 1118, 1063, 1017, 835 cm^{-1}; $[\alpha]^{20}_{D}$ = -7.5 (*c* = 0.2, $CHCl_3$); ^1H NMR (300 MHz, CD_3OD) δ 7.64 (q, *J* = 8.5 Hz, 4H), 4.40 (dd, *J* = 12.5, 8.6 Hz, 1H), 4.28 – 4.10 (m, 2H), 4.01 (dd, *J* = 9.3, 3.2 Hz, 1H), 3.81 (s, 1H), 3.29 – 3.15 (m, 1H), 2.97 (dd, *J* = 17.5, 8.6 Hz, 0H).; ^{13}C NMR (75 MHz, CD_3OD) δ 175.3, 172.5, 139.0, 139.0, 131.9, 131.0, 127.0, 127.0, 106.7, 89.8, 76.7, 75.2, 46.6, 34.4 ppm; HRMS (ESI) m/z calcd for $C_{16}H_{14}F_3O_7$ $[M+H]^+$: 375.0686; found: 375.0687.



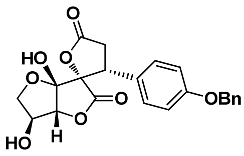
13h

Characteristic data of 13h: IR ν_{max} (film): 3452, 2361, 1793, 1727, 1594, 1208, 1154, 1067 cm^{-1}; $[\alpha]^{20}_{D}$ = -20.5 (*c* = 0.2, $CHCl_3$); ^1H NMR (300 MHz, CD_3OD) δ 6.58 (d, *J* = 2.2 Hz, 2H), 6.47 (t, *J* = 2.2 Hz, 1H), 4.31 – 4.17 (m, 3H), 4.04 (dd, *J* = 9.4, 3.3 Hz, 1H), 3.97 (s, 1H), 3.22 (dd, *J* = 17.4, 12.9 Hz, 1H), 2.92 (dd, *J* = 17.4, 8.6 Hz, 1H).; ^{13}C NMR (75 MHz, CD_3OD) δ 150.4, 148.2, 140.1, 118.9, 96.3, 95.3, 91.2, 82.6, 81.7, 71.2, 70.0, 54.6, 47.5, 37.5 ppm; HRMS (ESI) m/z calcd for $C_{17}H_{19}O_9$ $[M+H]^+$: 367.1024; found:367.1024.



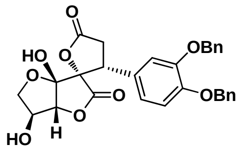
13i

Characteristic data of 13i: IR ν_{max} (film): 3464, 2967, 2361, 1801, 1611, 1511, 1254, 1067, 1030 cm^{-1}; $[\alpha]^{20}_{D}$ = -22.0 (*c* = 0.2, $CHCl_3$); ^1H NMR (300 MHz, CD_3OD) δ 7.32 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.39 (d, *J* = 3.6 Hz, 1H), 4.29 (dd, *J* = 13.3, 8.4 Hz, 1H), 4.22 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.13 (dd, *J* = 10.4, 4.4 Hz, 1H), 3.93 (s, 1H), 3.80 (s, 3H), 3.22 (dd, *J* = 17.4, 13.3 Hz, 1H), 2.92 (dd, *J* = 17.4, 8.4 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 174.43, 171.0, 160.3, 130.0, 123.4, 114.9, 105.8, 100.1, 89.3, 86.3, 73.7, 55.5, 34.0, 29.9 ppm; HRMS (ESI) m/z calcd for $C_{16}H_{17}O_8$ $[M+H]^+$: 337.0918; found:337.0921.



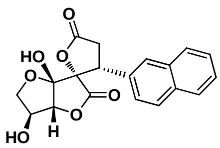
13j

Characteristic data of 13j: IR ν_{max} (film): 3286, 2925, 2357, 1801, 1698, 1183, 1121, 1030, 823 cm^{-1}; $[\alpha]^{20}_{D}$ = -9.5 (c = 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, CD_3OD) δ 7.42 – 7.28 (m, 7H), 7.98 (dd, J = 8.7, 1.8 Hz, 1H), 5.50 (s, 2H), 4.23 – 4.17 (m, 2H), 4.33 – 4.09 (m, 3H), 3.84 (s, 1H), 3.19 (dd, J = 17.6, 12.5 Hz, 1H), 2.87 (dd, J = 17.6, 8.5 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 175.8, 172.9, 160.7, 138.6, 131.2, 129.7, 129.1, 128.8, 125.9, 116.5, 106.7, 91.0, 89.6, 76. 7, 75.2, 71.2, 46.3, 34.6 ppm; HRMS (ESI) m/z calcd for $C_{22}H_{21}O_8$ $[M+H]^+$: 413.1231; found:413.1231.



13k

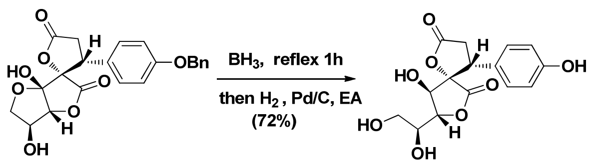
Characteristic data of 13k: R_f = 0.65 (silica gel, CH_2Cl_2/MeOH = 10/1); IR ν_{max} (film): 2969, 1793, 1518, 1273, 1024, 823, 736 cm^{-1}; $[\alpha]^{20}_{D}$ = -29.0 (c = 0.2, $CHCl_3$); 1H NMR (400 MHz, CD_3OD) δ = 7.49 – 7.20 (m, 10H), 6.96 (s, 1H), 6.89 (s, 2H), 5.17 – 5.07 (m, 4H), 4.27 (d, J = 4.0 Hz, 1H), 4.19 – 4.12 (m, 2H), 4.03 (dd, J = 10.5, 4.3 Hz, 1H), 3.77 (s, 1H), 3.09 (dd, J = 17.4, 13.2 Hz, 1H), 2.83 (dd, J = 17.4, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ = 174.0, 170.7, 149.4, 148.8, 136.8, 136.7, 128.5, 128.5, 128.0, 127.9, 127.4, 127.3, 124.3, 121.9, 115.4, 114.9, 105.4, 88.9, 86.0, 85.9, 76.1, 73.3, 71.4, 71.1, 45.0, 33.8 ppm; HRMS m/z calcd for C29H26O9 [M+Na]+: 541.1469.; found: 541.1470.



13l

Characteristic data of 13k: IR ν_{max} (film): 3452, 2349, 1797, 1718, 1208, 1117, 1080, 1026, 823, 752 cm^{-1}; $[\alpha]^{20}_{D}$ = -21.0 (c = 0.2, $CHCl_3$); ^{1}H NMR (301 MHz, CD_3OD) δ 7.97 – 7.74 (m, 4H), 7.61 – 7.43 (m, 3H), 4.50 (dd, J = 12.8, 8.6 Hz, 1H), 4.23 – 4.17 (m, 2H), 4.10 – 3.98 (m, 1H), 3.82 (s, 1H), 3.41 (dd, J = 17.4, 12.8 Hz, 1H), 3.01 (dd, J = 17.4, 8.6 Hz, 1H).; ^{13}C NMR (75 MHz, CD_3OD) δ 175. 8, 172.9, 135.0, 134.8, 131.5, 130.0, 129.6, 129.2, 128.8, 127.9, 127.8, 127.2, 106.8, 91.1, 89.7, 76.7, 75.1, 47.1, 34.6 ppm; HRMS (ESI) m/z calcd for $C_{19}H_{17}O_7$ $[M+H]^+$: 357.0969; found:357.0969.

Part 4: Experimental details and characteristic data for syntheses of leucodrin, leudrin and proposed structure of diaspirolactone A.



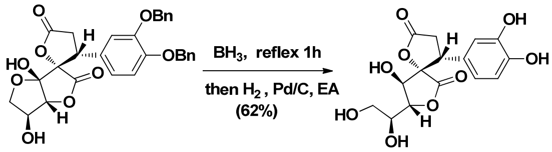
13 j

Leucodrin (5)

Synthesis of leucodrin (5): To a solution of **13j** (165 g, 0.4 mmol) in anhydrous THF (5 mL) was added BH_3 (1.0 M in THF, 0.8 mmol, 0.8 mL). The solution was heated to reflux and was stirred for 1 h. The reaction was quenched with water and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo* to give a white solid that was used immediately in the next step without further purification.

To a solution of the above crude product in EtOAc/THF (5 mL, v/v 1:1) at room temperature was added 10% Pd/C (30mg). The solution was stirred under hydrogen atmosphere for 4 h and then filtered. The filtrate was concentrated *in vacuo*, and the residue was purified with flash column chromatography (silica gel, DCM/MeOH = 10:1) to afford Leucodrin (**5**) as a white solid (93 mg, 72% for 2 steps).

Characteristic data of leucodrin (5): R_f = 0.46 (silica gel, CH_2Cl_2/MeOH = 10/1); $[\alpha]^{20}_D$ = -11.9 (*c* = 1.0, 95% EtOH), (lit.$[\alpha]^{20}_D$ = -11.2, (c=1.0, 95%EtOH); IR ν_{max} (film): 3382, 1781, 16007, 1511, 1167, 1109, 1022, 835, 765, 678 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 9.49 (s, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.71 (d, *J* = 8.1 Hz, 2H), 6.59 (d, *J* = 5.1 Hz, 1H), 5.16 (d, *J* = 6.3 Hz, 1H), 4.73 – 4.60 (m, 2H), 4.29 (dd, *J* = 12.5, 8.8 Hz, 1H), 3.70 (dd, *J* = 8.5, 1.7 Hz, 1H), 3.54-3.49 (m, 1H), 3.22 – 3.06 (m, 2H), 2.92 (dd, *J* = 17.4, 8.8 Hz, 1H);^{13}C NMR (100 MHz, DMSO-d_6) δ = 174.6, 171.9, 157.1, 129.9, 123.4, 115.4, 89.9, 79.8, 69.1, 67.9, 61.2, 41.0, 33.1 ppm; HRMS m/z calcd for $C_{15}H_{16}O_8$ $[M+Na]^+$: 347.0737; found: 347.0741.

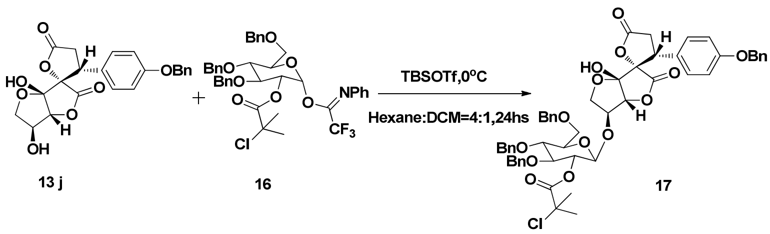


13 k

Leudrin (6)

Synthesis of leudrin (6): The same procedure was employed as that for the synthesis of **5**, with **l**eudrin (**6**) obtained in yield of 61.2%.

Characteristic data of leucodrin (5): R_f = 0.35 (silica gel, CH_2Cl_2/MeOH = 10/1); $[\alpha]^{20}_D$ = -13.0, (*c* =0.25, 95%EtOH), (lit.$[\alpha]^{20}_D$ = -16.7, (c=0.88, 95%EtOH); IR ν_{max} (film): 3386, 2917, 1794, 1259, 1200, 1113, 1038, 802 cm^{-1}; ^1H NMR (400 MHz, CD_3CN–d_3) δ 6.94 (s, 2H), 6.87 (s, 1H), 6.80 – 6.75 (m, 2H), 4.71 (d, *J* = 8.5 Hz, 1H), 4.59 (s, 1H), 4.29 (dd, *J* = 12.6, 8.7 Hz, 1H), 3.67 (dd, *J* = 8.5, 2.6 Hz, 1H), 3.64 (s, 1H), 3.47 (dd, *J* = 10.8, 6.0 Hz, 1H), 3.36 (dd, *J* = 10.8, 6.8 Hz, 1H), 3.11 (dd, *J* = 17.4, 12.7 Hz, 1H), 2.84 (dd, *J* = 17.4, 8.8 Hz, 1H); 13C NMR (101 MHz, CD_3CN–d_3) δ = 174.5, 171.9, 144.7, 144.6, 125.2, 121.0, 115.7, 115.4, 89.8, 80.3, 69.9, 69.2, 62.0, 41.6, 33.5 ppm; HRMS m/z calcd for C15H16O8 [M+Na]+: 347.0737; found: 347.0741.



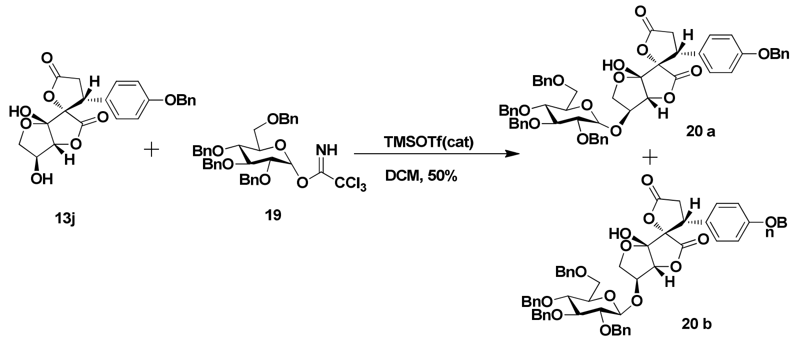
13 j 16 17

Synthesis of 17: To a mixture of **13j** (116 mg, 0.28 mmol), **16** (472 mg, 0.65 mmol), and 4 Å MS (1.0 g) was added dry CH_2Cl_2 (1.6 mL) and hexane (0.4 mL). The mixture was stirred for 45 min at 25 °C before it was cooled to 0 °C. TBSOTf (30 mg, 113μmol) in CH_2Cl_2 (100 μL) was added dropwise and the reaction was allowed to stir for another 24 h before quenched by addition of

NEt_3. The mixture was filtrated and concentrated in *vacuo* to afford crude material, which was purified by preparative TLC (EtOAc/petroleum ether = 1/1) to give β-glycoside **17** (62 mg，46%) as a white foam.

Characteristic data of 17: R_f = 0.30 (silica gel, EtOAc/petroleum ether = 1/1); $[\alpha]^{20}_D$ = +6.5 (*c* = 0.2, $CHCl_3$); IR ν_{max} (film): 2980, 2897, 2360, 2329, 1552, 1264, 1061, 836, 736, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.43 – 7.23 (m, 20H), 7.17-7.15 (m, 2H), 6.94 (d, *J* = 8.7 Hz, 1H), 5.02 (s, 2H), 4.99 (t, *J* = 8.4 Hz, 1H, H_2'), 4.80 – 4.70 (m, 3H), 4.57 – 4.39 (m, 5H), 4.29 – 4.25 (m, 2H), 4.04 (dd, *J* = 10.5, 4.1 Hz, 2H), 3.89 (s, 2H), 3.73 (dd, *J* = 5.2, 3.6 Hz, 1H), 3.67 – 3.60 (m, 1H), 3.47 (s, 1H), 3.21 (dd, *J* = 17.3, 13.3 Hz, 1H), 2.88 (dd, *J* = 17.3, 8.4 Hz, 1H), 1.76-1.62 (m, 6H, $CClMe_2$);^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.8, 171.0, 170.4, 159.2, 137.8, 137.6, 136.5, 129.9, 128.7, 128.5, 128.5, 128.4, 128.2, 128.0, 127.9, 127.9, 127.8, 127.7, 127.5, 127.3, 123.8, 115.5, 105.2, 100.6, 88.4, 84.5, 82.2, 79.5, 77.2, 75.3, 75.2, 75.1, 74.7, 74.5, 73.5, 70.1, 68.2, 64.3, 44.6, 33.9, 29.7, 29.4.ppm; HRMS m/z calcd for $C_{53}H_{53}ClO_{14}$ $[M+Na]^+$: 971.3016; found: 971.3003.

Note: **17** was assigned as β-glycoside based on the observed coupling constant between H1' and H2' ($J_{H1'-H2'}$ = 8.4 Hz), and the 12-OH glycoside was confirmed by the observed HMBC signal between $H_{1'}$ and C_{12}.



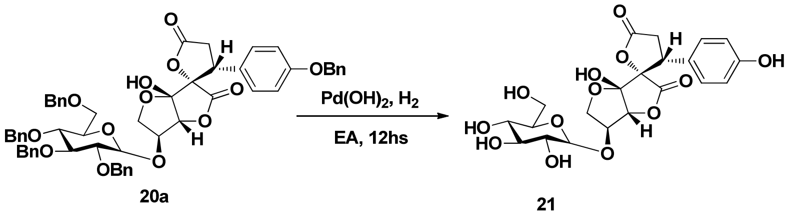
Synthesis of 20a and 20b: Compound **13j** (225 mg, 0.55 mmol) and **19** (748 mg, 1.10 mmol) was dried in *vacuo* for 2 h. Powdered 4Å molecular sieves (2 g) was added and the mixture was dissolved in CH_2Cl_2 (6 mL). The mixture was stirred for 1 h at r.t. before it was cooled to 0 °C. A solution of TMSOTf (16 mg, 70 μmol) in CH_2Cl_2 (100 μL) was added dropwise. After being stirred for 12 h, the reaction was quenched by addition of several drops of NEt_3. The mixture was filtrated, and concentrated in *vacuo* to afford crude material, which was purified by preparative TLC (CH_2Cl_2/MeOH = 50/1) to afford β-glycoside **20b** (85 mg，17%) and α-glycoside **20a** (170 mg，33%).

Characteristic data of β-Anomer（20b）: $[\alpha]^{20}_D$ = -33.5 (*c* = 0.2, $CHCl_3$); R_f = 0.28 (silica gel, CH_2Cl_2/MeOH = 50/1); IR ν_{max} (film): 2962, 2912, 1817, 1510, 1445, 1257, 1070, 1020, 836, 740, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.47 – 7.24 (m, 25H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 4.98 – 4.88 (m, 6H), 4.83 – 4.76 (m, 2H),, 4.63 (d, *J* = 11.2 Hz, 1H), 4.51 – 4.43 (m, 2H), 4.39 (d, *J* = 7.6 Hz, 1H, H1'), 4.37 (dd, *J* = 5.2, 10.4 Hz, 1H), 4.33 (dd, *J* = 2.0, 5.2 Hz, 1H), 4.11 (dd, *J* = 10.4, 5.2 Hz, 1H), 3.88 (s, 1H), 3.84 (t, *J* = 9.3 Hz, 1H), 3.68 – 3.51 (m, 5H), 3.43 – 3.39 (m, 1H), 3.12 (dd, *J* = 17.1, 13.6 Hz, 1H), 2.64 (dd, *J* = 17.1, 8.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.1, 170.6, 159.2, 138.3, 138.2, 137.9, 137.8, 136.5, 129.7, 128.6, 128.6, 128.5, 128.5, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 123.5, 115.3, 105.6, 102.8, 88.9, 85.4, 85.1, 81.6, 80.0, 77.3, 76.2, 75.3, 75.1, 74.8, 74.8, 73.4, 70.0, 68.4, 44.9, 33.7ppm.

Note: **20b** was assigned as β-glycoside based on the observed coupling constant between H1' and H2' ($J_{H1'-H2'}$ = 7.6 Hz), and the 12-OH glycoside was confirmed by the observed HMBC signal between $H_{1'}$ and C_{12}.

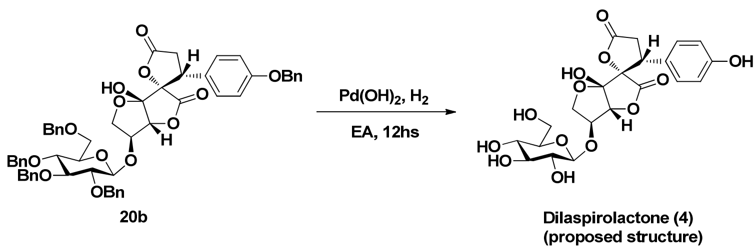
Characteristic data of α-Anomer（20a）:$[\alpha]^{20}_D$ = +77.5 (*c* = 0.2, $CHCl_3$); R_f = 0.30 (silica gel, CH_2Cl_2/MeOH = 50/1); IR ν_{max} (film): 2963, 2925, 1806, 1263, 1500, ,1440, 1000, 799, 600 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 – 7.26 (m, 25H), 7.17 – 7.07 (m, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 5.09 – 5.02 (m, 2H), 4.94 – 4.87 (m, 2H), 4.82 – 4.77 (m, 2H), 4.70 (d, *J* = 3.8 Hz, 1H, $H_{1'}$), 4.58 (dd, *J* = 12.0, 10.9 Hz, 2H), 4.49 – 4.42 (m, 2H), 4.29 (d, *J* = 2.3 Hz, 1H), 4.27 – 4.21 (m, 2H), 3.90 (S, 1H), 3.88 – 3.81 (m, 2H), 3.71 – 3.65 (m, 3H), 3.59 – 3.53 (m, 2H), 3.20 (dd, *J* = 17.3, 13.1 Hz, 1H), 2.89 (dd, *J* = 17.3, 8.5 Hz, 1H), ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.2, 170.6, 159.3, 138.5, 137.8, 137.7, 137.2, 136.7, 130.0, 129.0, 128.9, 128.8, 128.8, 128.7, 128.6, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.7, 124.2, 115.8, 105.7, 94.5, 88.5, 84. 6, 81.6, 78.9, 77.4, 75.8, 75.6, 74.5, 73.8, 71.5, 70.2, 70.2, 68.2, 44.7, 34.2 ppm; HRMS m/z calcd for $C_{56}H_{54}O_{13}$ $[M+Na]^+$: 957.3457; found: 957.3458.

Note: **20a** was assigned as α-glycoside based on the observed coupling constant between H1' and H2' ($J_{H1'-H2'}$ = 3.8 Hz), and the 12-OH glycoside was confirmed by the observed HMBC signal between $H_{1'}$ and C_{12}.



Synthesis of 21: To a solution of **20a** (20 mg, 0.02 mmol) in EtOAc (0.4 mL) was added $Pd(OH)_2$ (5mg). The suspension was stirred at r.t. under hydrogen atmosphere (balloon pressure) for 12 h. The reaction mixture was filtered through celite, washed with acetone three times. The combined solution was evaporated to afford **21** (9.6 mg, quant.).

Characteristic data of 21: IR ν_{max} (film): 3356, 2900, 1810, 1780, 1558, 1170, 881 cm^{-1}; $[\alpha]^{20}_D$ = +43.5 (*c* = 0.2, MeOH); ^{1}H NMR (400 MHz, Pyridiene-D_5, containing 1% D_2O) δ = 7.63 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.43 (d, *J* = 3.7 Hz, 1H), 5.23 (s, 1H), 4.82 – 4.70 (m, 2H), 4.61 – 4.40 (m, 6H), 4.33 (t, *J* = 9.3 Hz, 1H), 4.14 (dd, *J* = 9.8, 3.9 Hz, 1H), 3.41 (dd, *J* = 17.4, 10.9 Hz, 1H), 3.15 (dd, *J* = 17.5, 8.9 Hz, 1H); ^{13}C NMR (101 MHz, Pyridiene-D_5, containing 1% D_2O) δ = 174.6, 171.6, 159.1, 130.3, 124.2, 116.5, 107.0, 102.7, 90.4, 86.5, 83.4, 74.7, 74.7, 73.9, 73.3, 71.4, 62.2, 45.2, 34.3 ppm; HRMS m/z calcd for $C_{21}H_{24}O_{13}$ $[M+Na]^+$: 507.1109; found:507.1106.

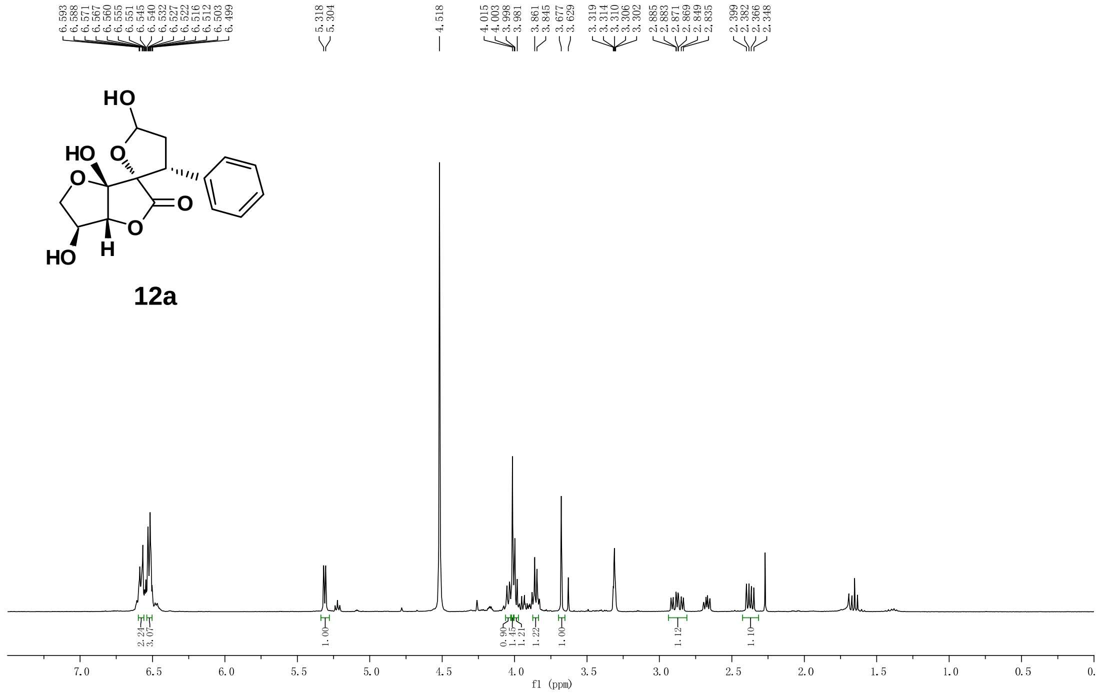


Synthesis of 4: The same procedure was employed as that for the synthesis of **21**, with **4** obtained in almost quantitatively yield.

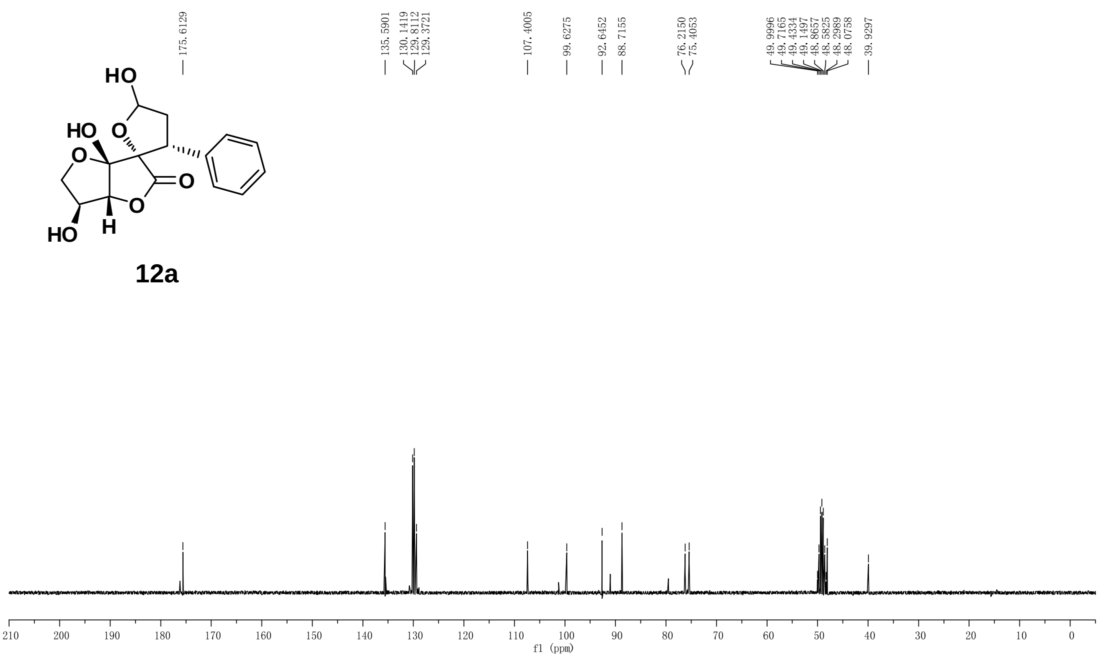
Characteristic data of 4: IR ν_{max} (film): 3389, 2925, 1800, 1615, 1518, 1230, 881, 842 cm^{-1};

$[\alpha]^{20}_{D}$ = +7.0 (*c* = 0.4, MeOH); ^{1}H NMR (400 MHz, Pyridine-D_5, containing 1% D_2O) δ = 7.64 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 4.93 (s, 1H), 4.85 (d, *J* = 8.0 Hz, 1H), 4.82 – 4.75 (m, 2H), 4.67 (dd, *J* = 10.0, 4.4 Hz, 1H), 4.56 – 4.50 (m, 2H), 4.29 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.21 (t, *J* = 9.2 Hz, 1H), 4.14 (t, *J* = 9.2 Hz, 1H), 3.99 (t, *J* = 8.4 Hz, 1H), 3.90 – 3.87 (m, 1H), 3.55 (dd, *J* = 17.4, 12.6 Hz, 1H), 3.12 (dd, *J* = 17.4, 8.7 Hz, 1H); ^{13}C NMR (101 MHz, Pyridine-D_5, containing 1% D_2O) δ = 175.7, 173.1, 159.9, 131.4, 124.1, 117.4, 107.0, 105.1, 91.2, 88.1, 82.6, 79.2, 78.5, 75.5, 75.3, 72.0, 63.1, 46.2, 34.9 ppm; HRMS m/z calcd for $[M+Na]^{+}$: 507.1109; found: 507.1104.

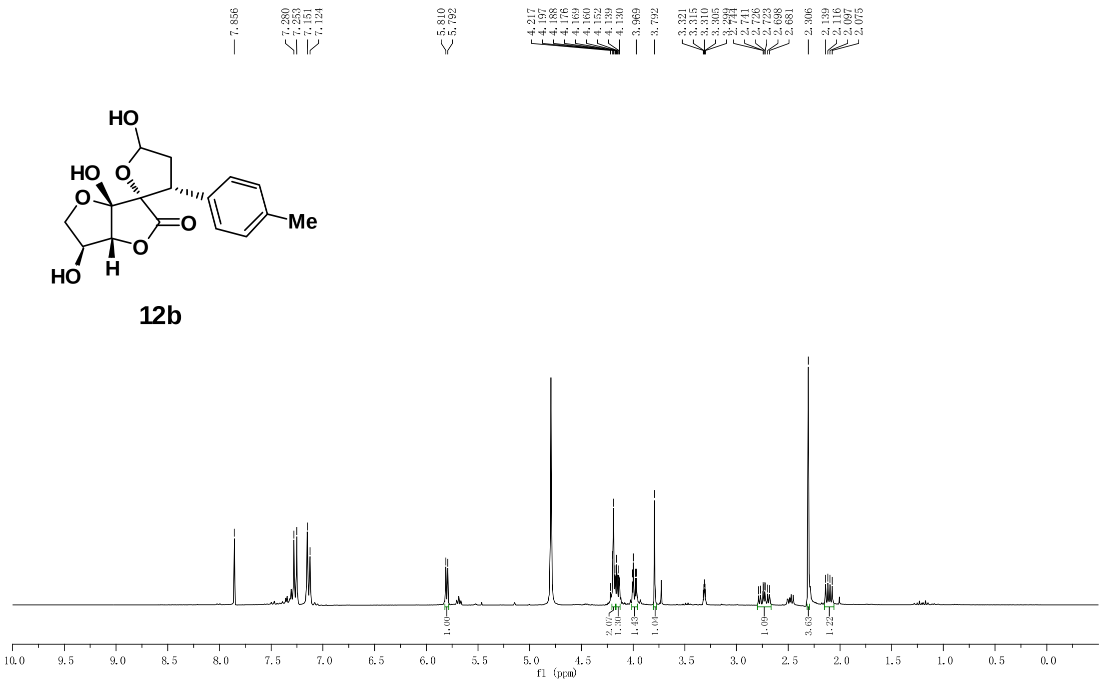
Part 5: NMR spectra



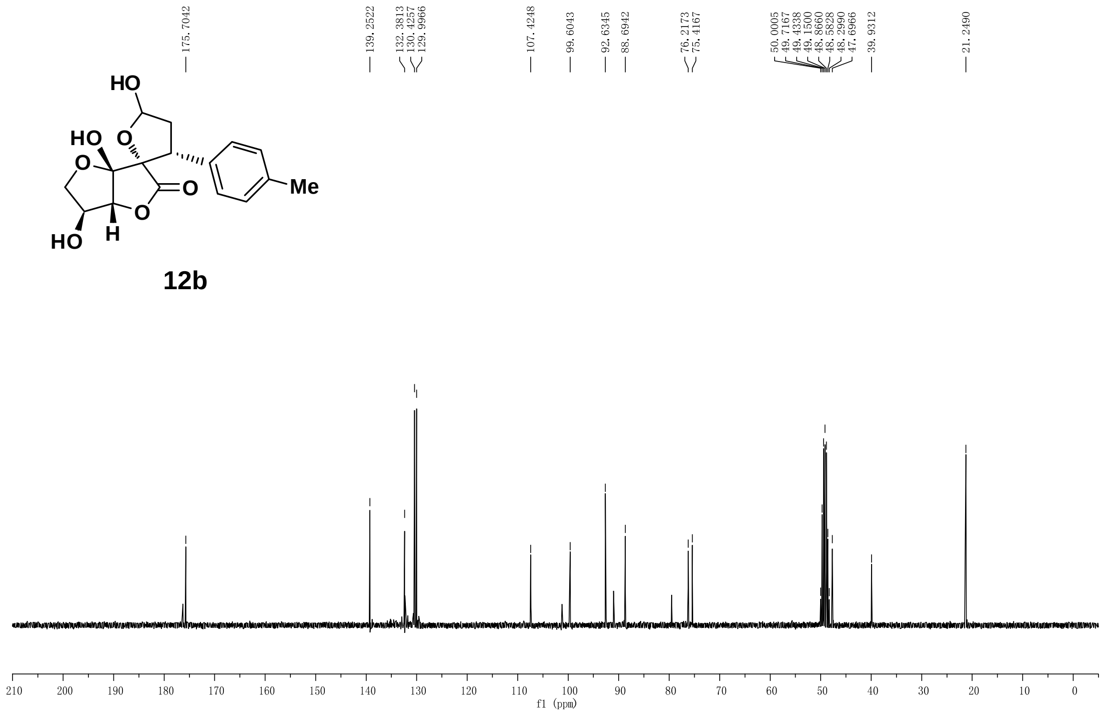
^{1}H NMR Spectrum for **12a** (300 MHz, CD_3OD)



^{13}C NMR Spectrum for **12a** (75 MHz, CD_3OD)



^{1}H NMR Spectrum for **12b** (300 MHz, CD_3OD)



^{13}C NMR Spectrum for **12b** (75 MHz, CD_3OD)

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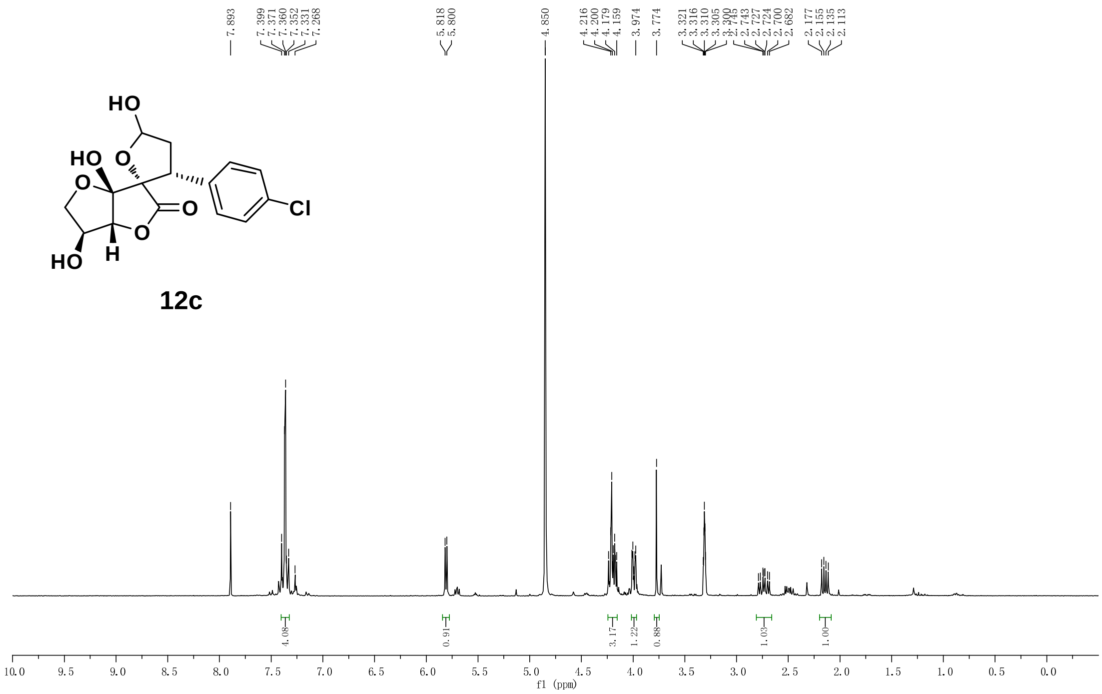
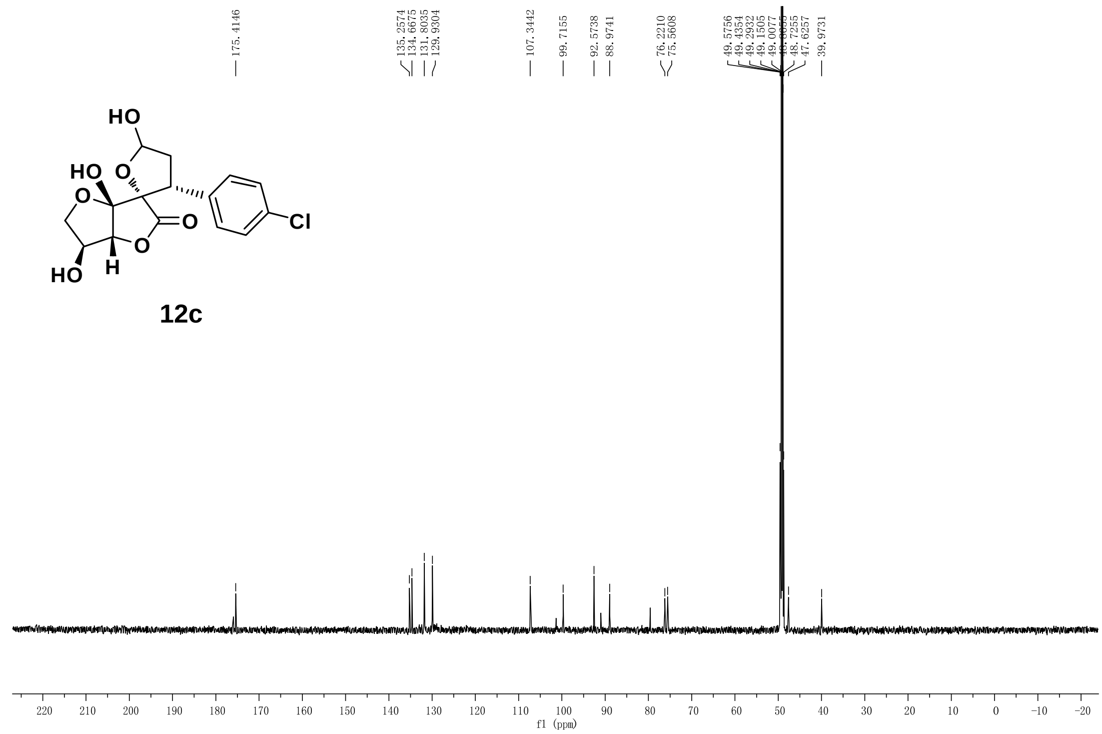
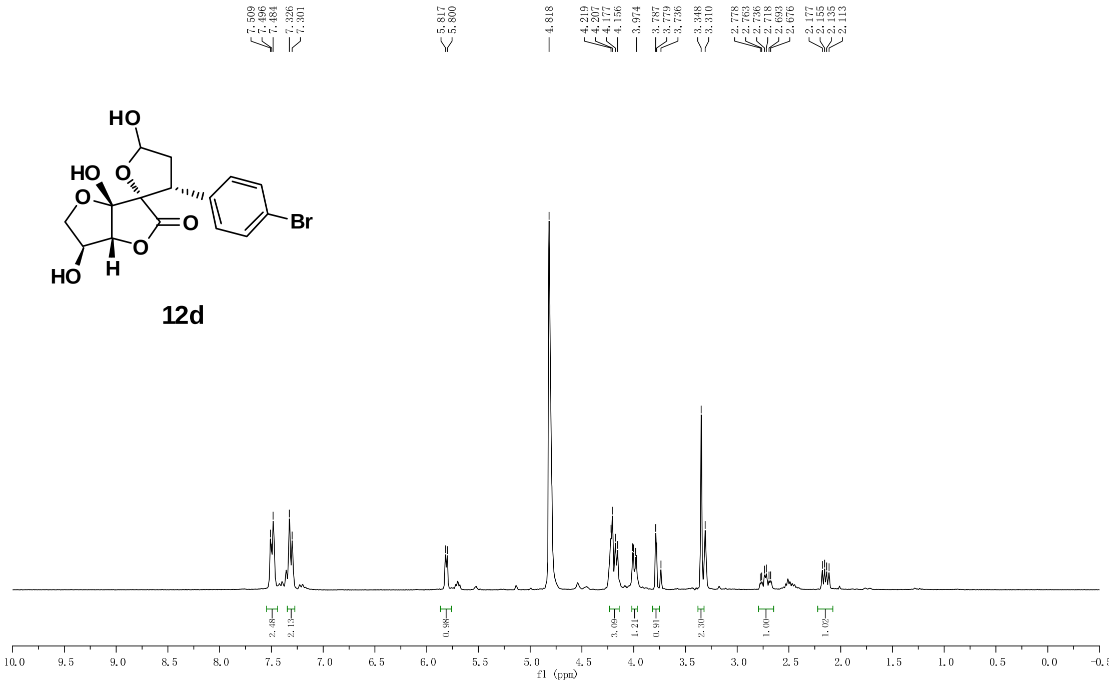


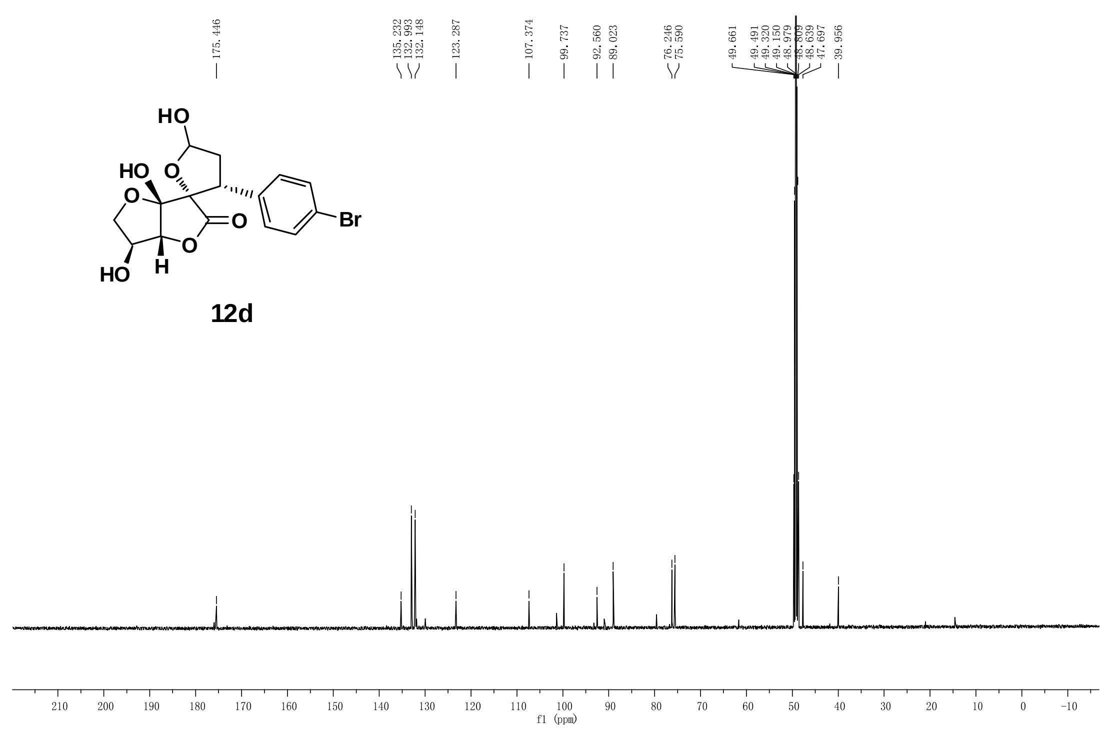
^{1}H NMR Spectrum for **12c** (300 MHz, CD_3OD)



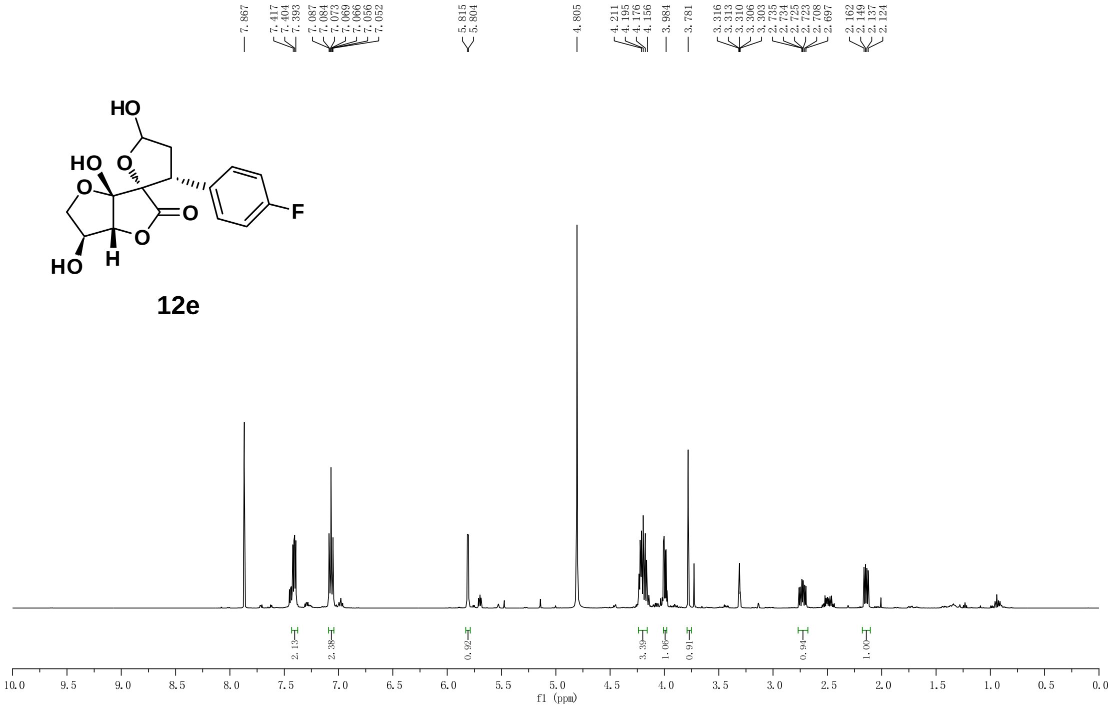
^{13}C NMR Spectrum for **12c** (150 MHz, CD_3OD)



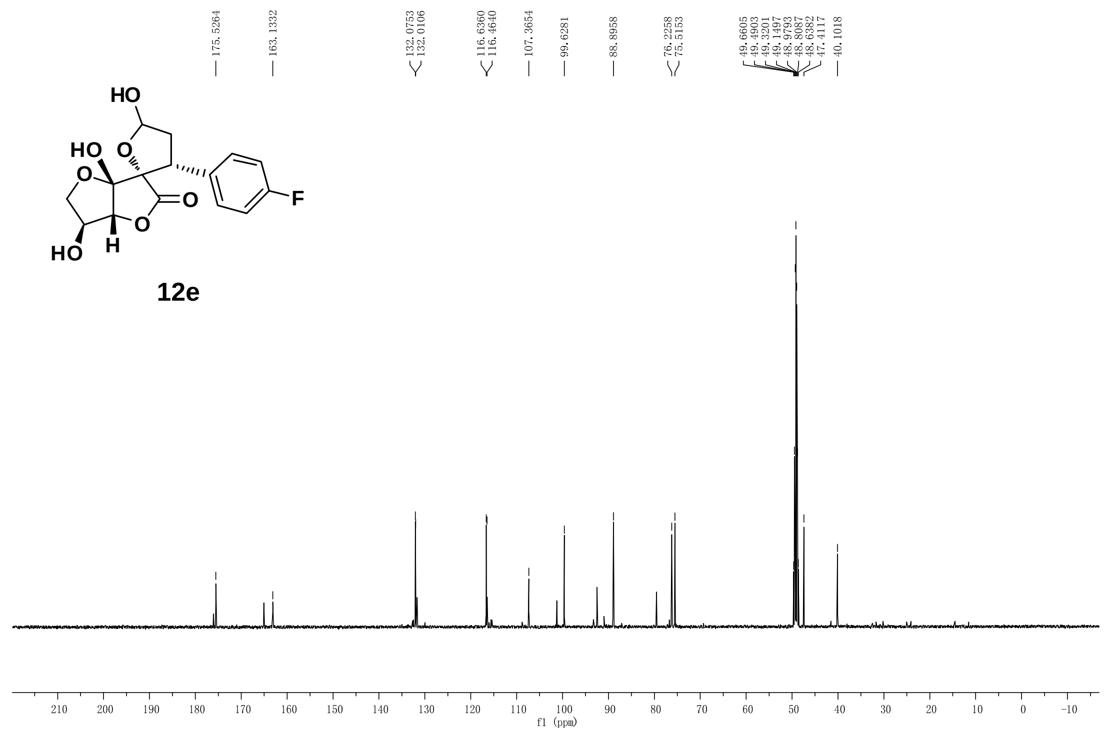
^{1}H NMR Spectrum for **12d** (300 MHz, CD_3OD)



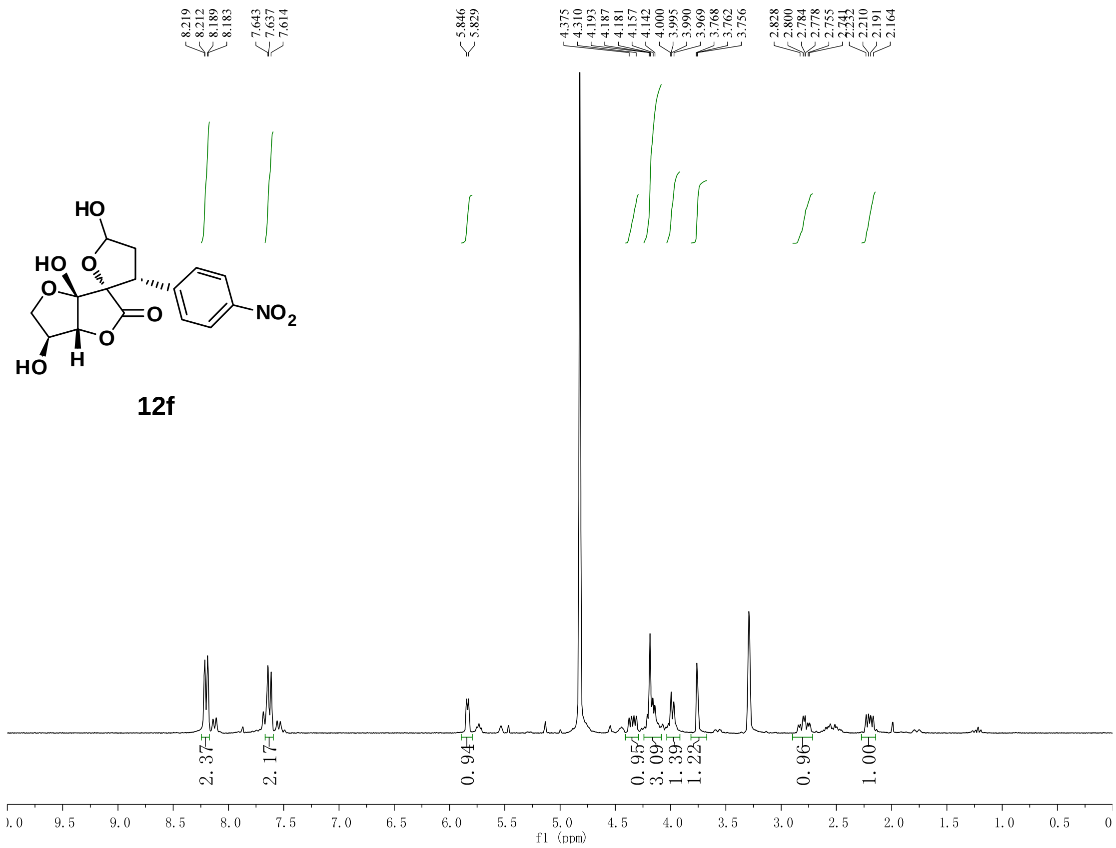
^{13}C NMR Spectrum for **12d** (125 MHz, CD_3OD)



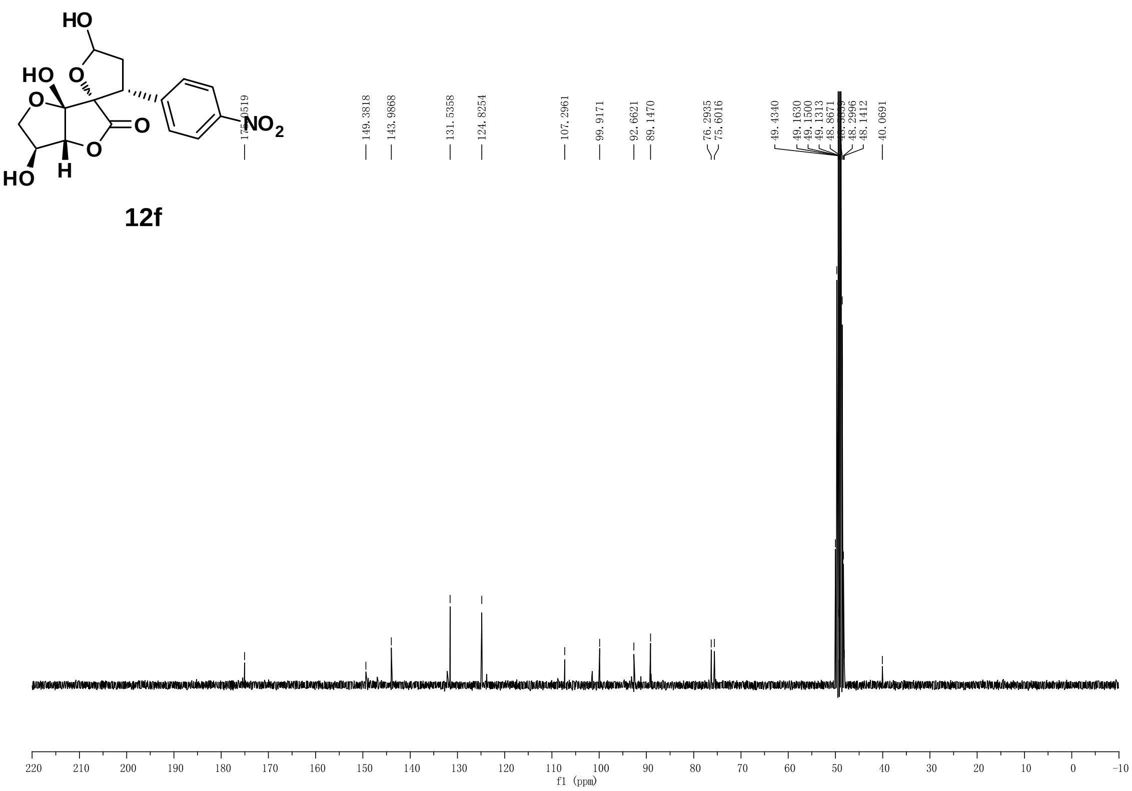
^{1}H NMR Spectrum for **12e** (500 MHz, CD_3OD)



^{13}C NMR Spectrum for **12e** (125 MHz, CD_3OD)

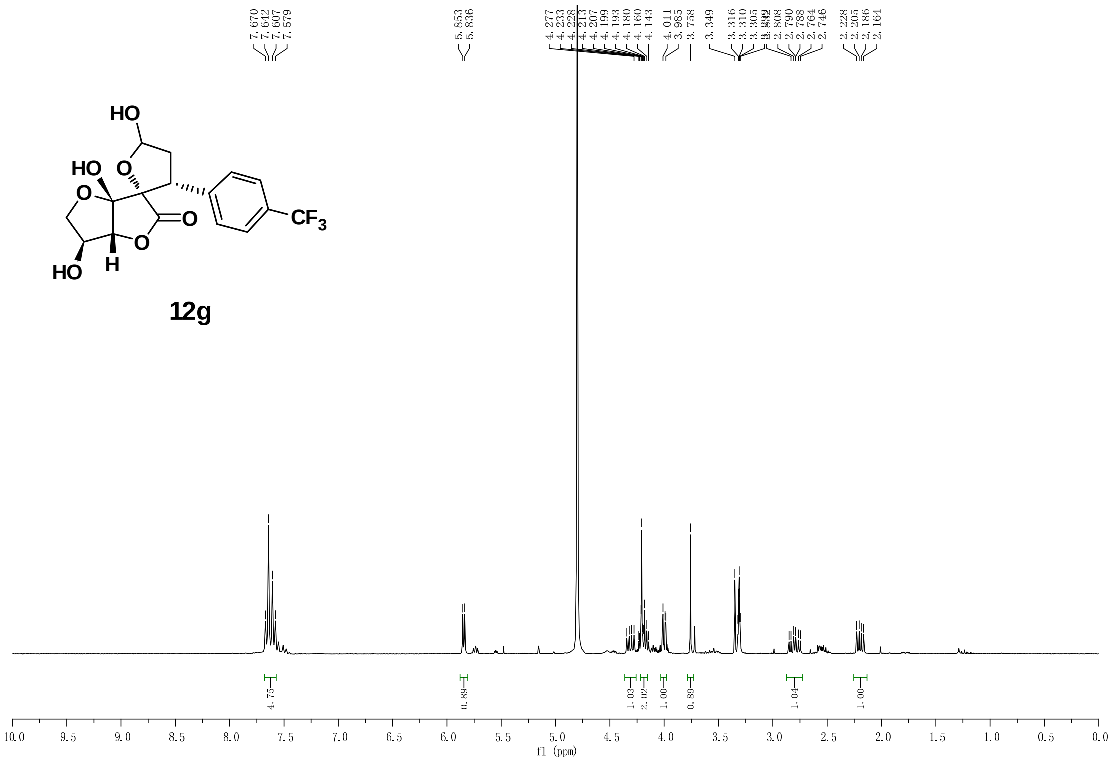


^{1}H NMR Spectrum for **12f** (300 MHz, CD_3OD)

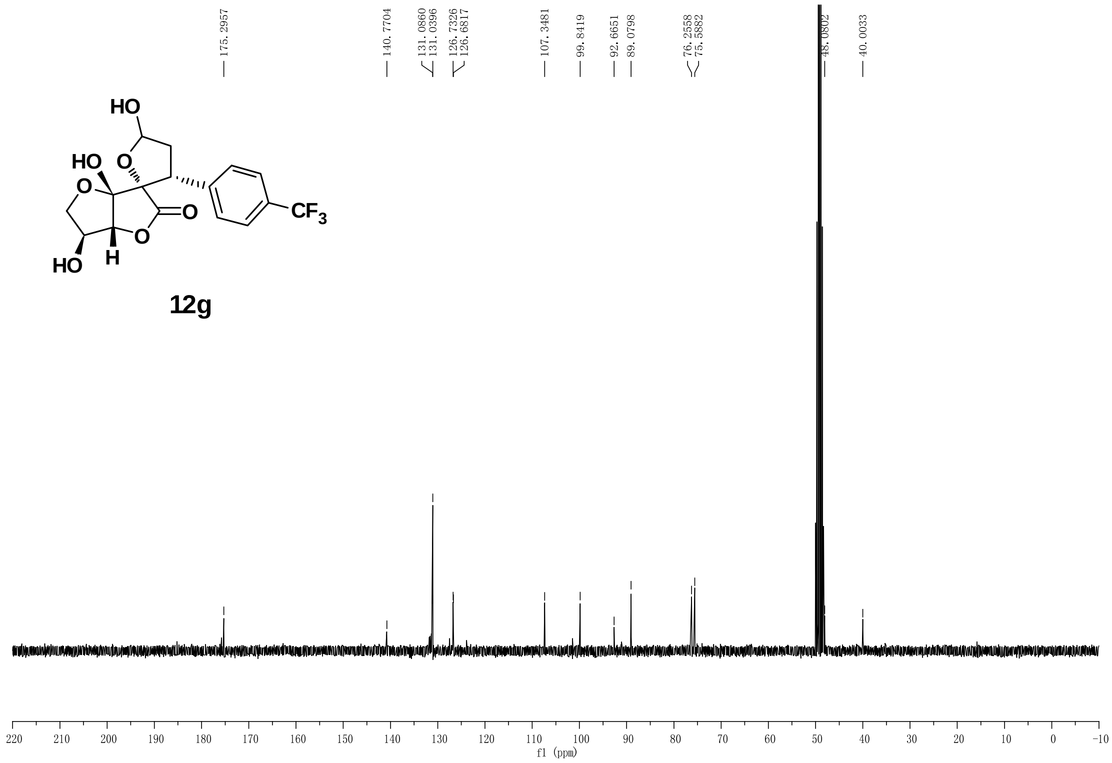


^{13}C NMR Spectrum for **12f** (75 MHz, CD_3OD)

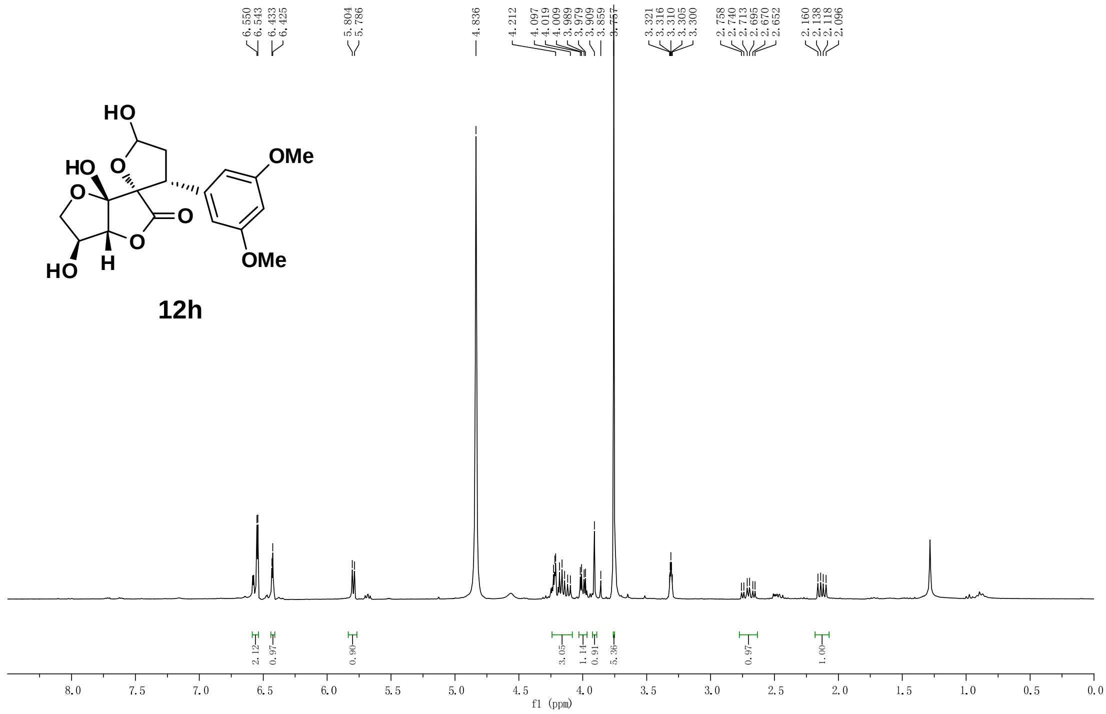
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



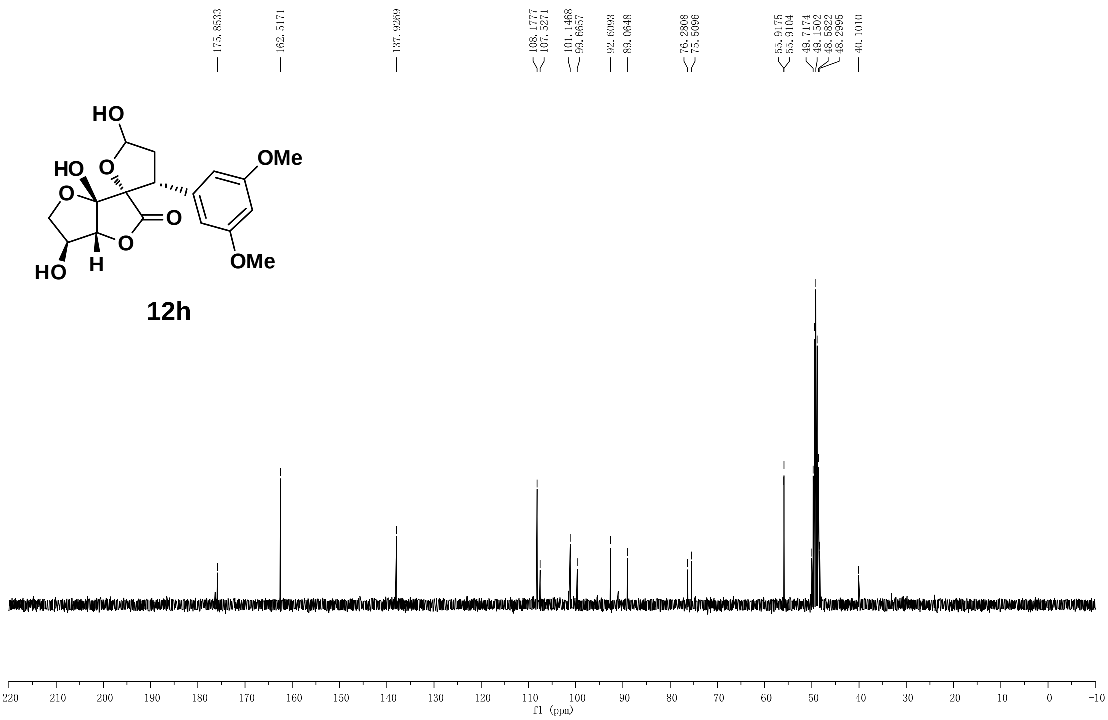
[1]H NMR Spectrum for **12g** (300 MHz, CD_3OD)



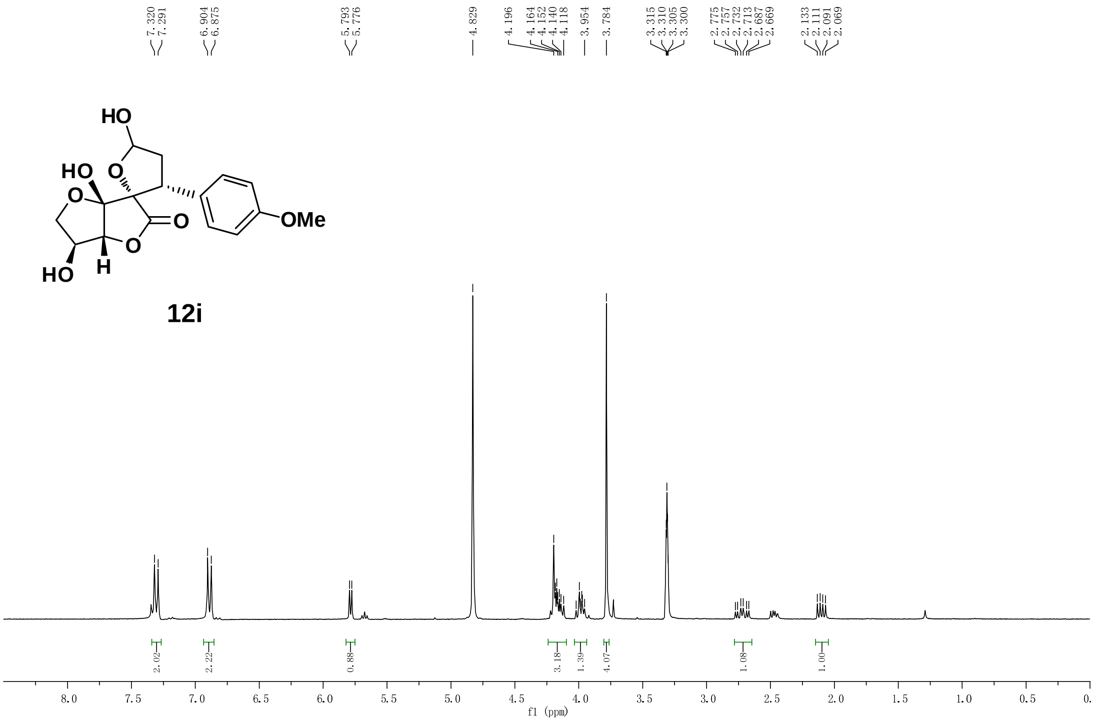
[13]C NMR Spectrum for **12g** (75 MHz, CD_3OD)



^{1}H NMR Spectrum for **12h** (300 MHz, CD_3OD)

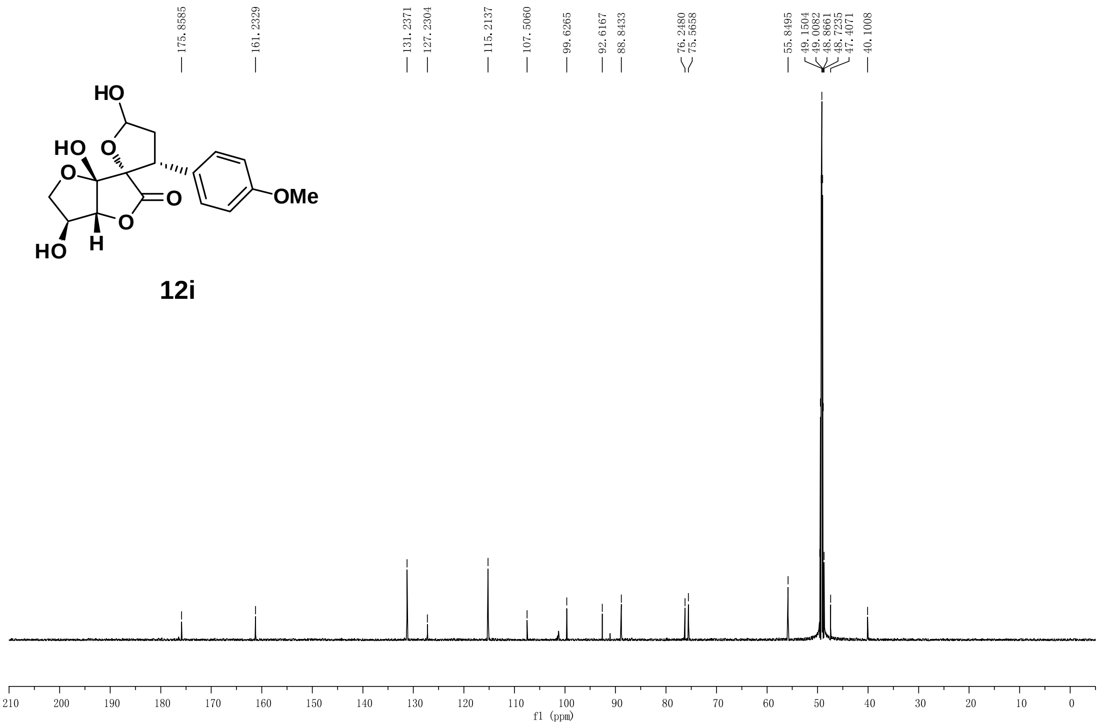


^{13}C NMR Spectrum for **12h** (75 MHz, CD_3OD)



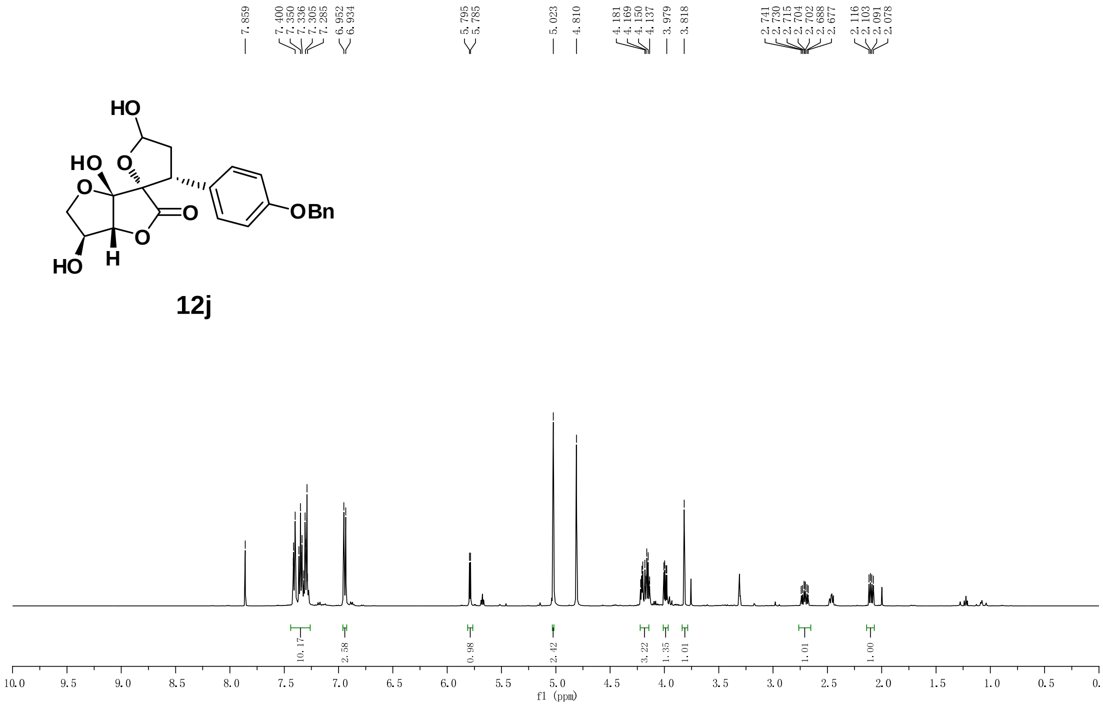
12i

^{1}H NMR Spectrum for **12i** (300 MHz, CD_3OD)

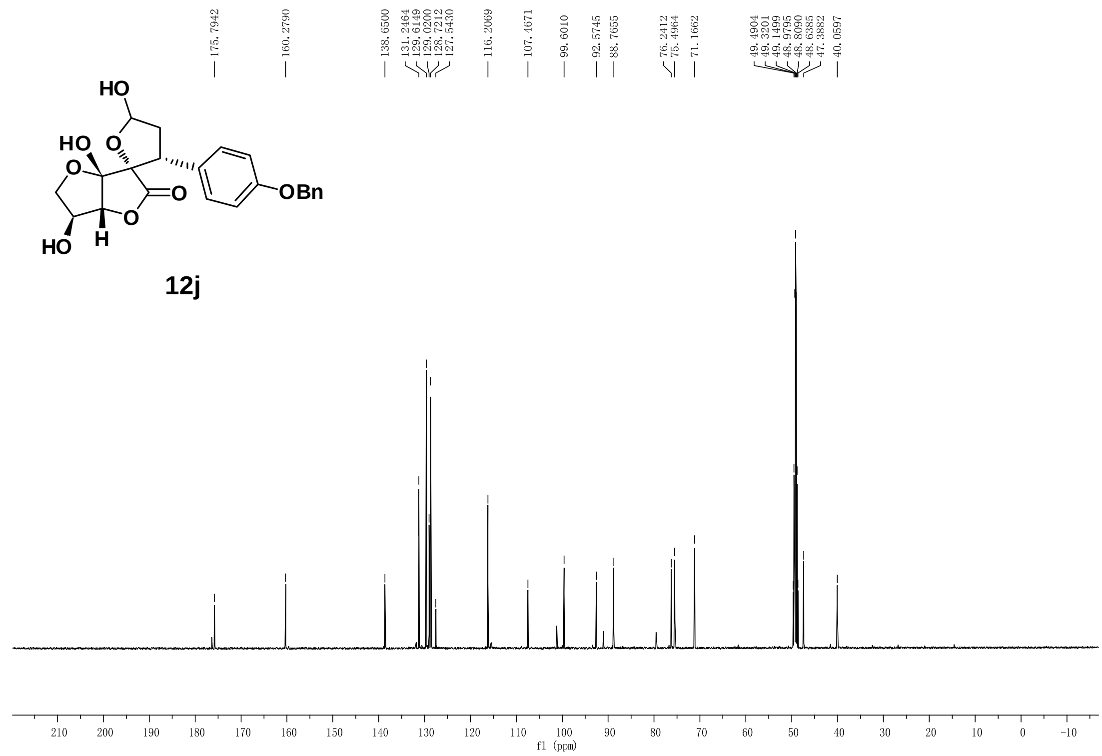


12i

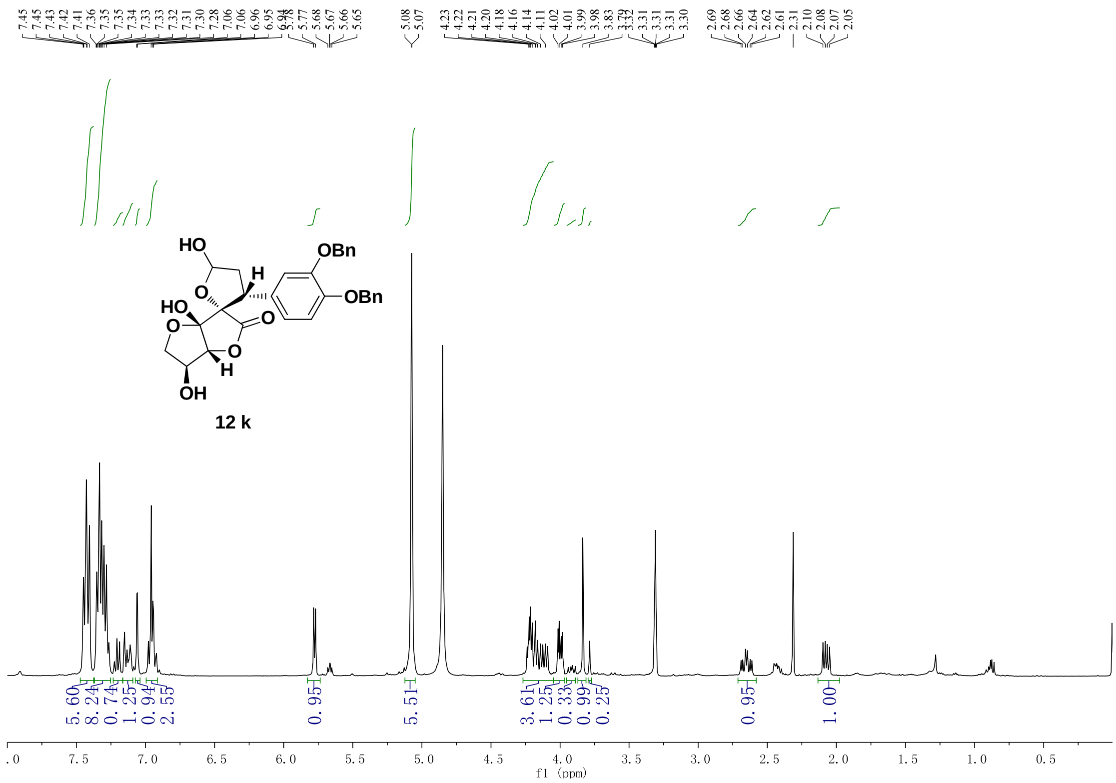
^{13}C NMR Spectrum for **12i** (75 MHz, CD_3OD)



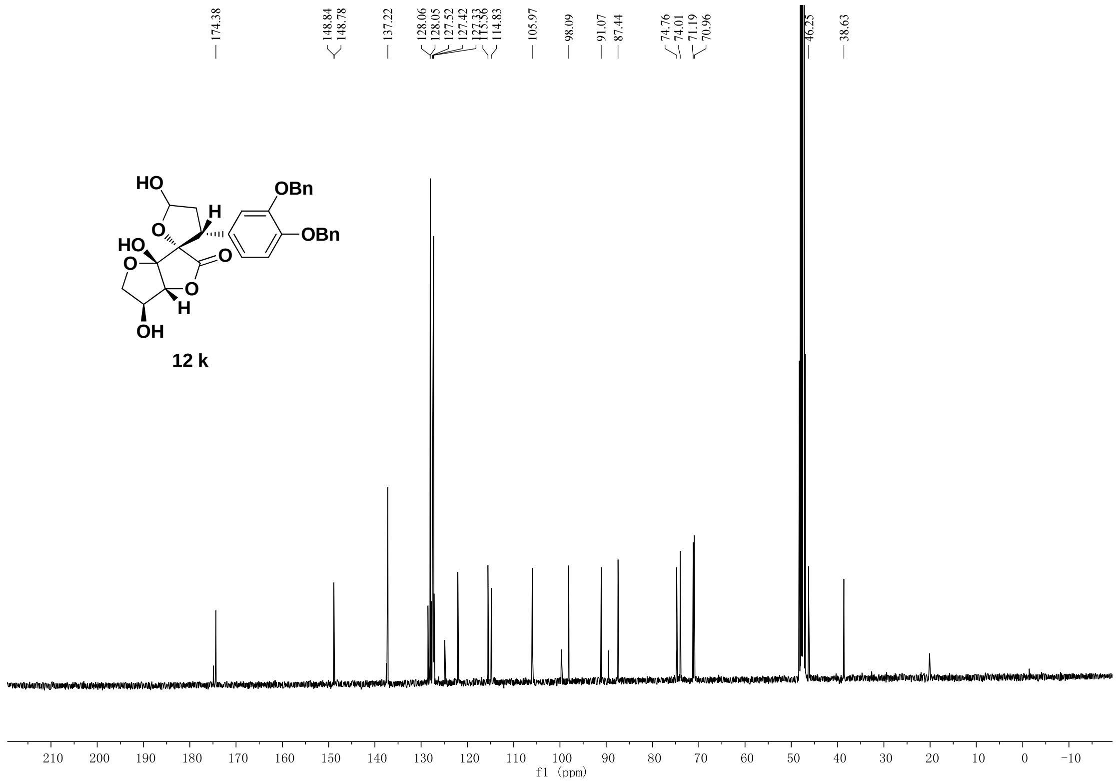
^{1}H NMR Spectrum for **12j** (500 MHz, CD_3OD)



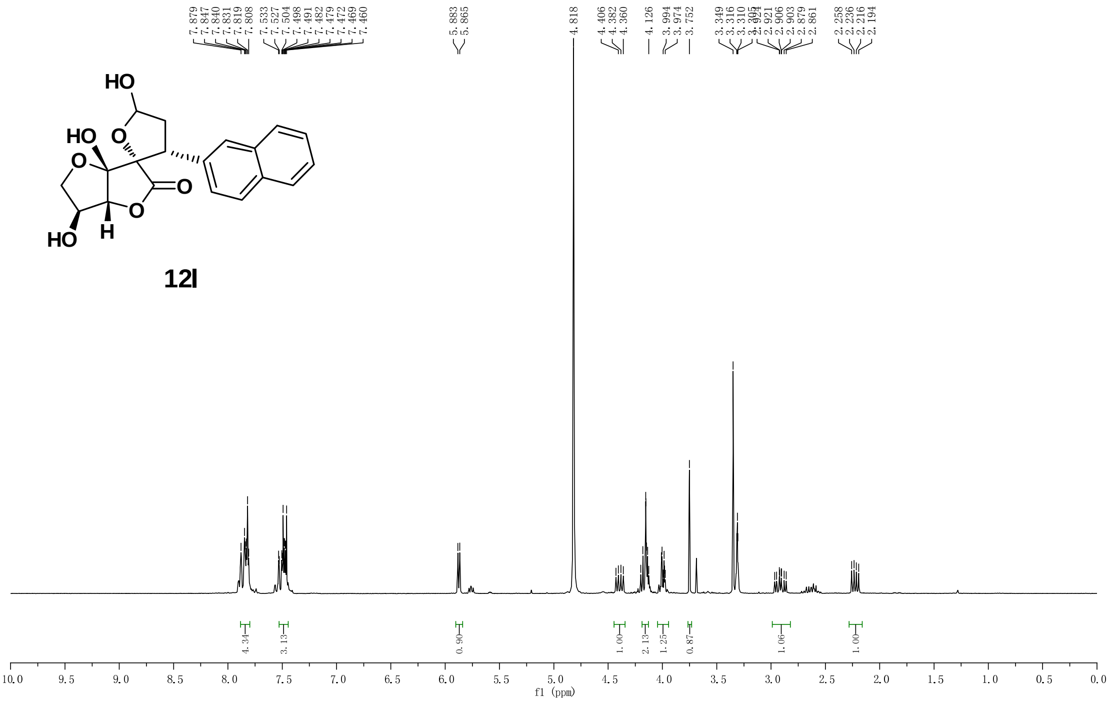
^{13}C NMR Spectrum for **12j** (125 MHz, CD_3OD)



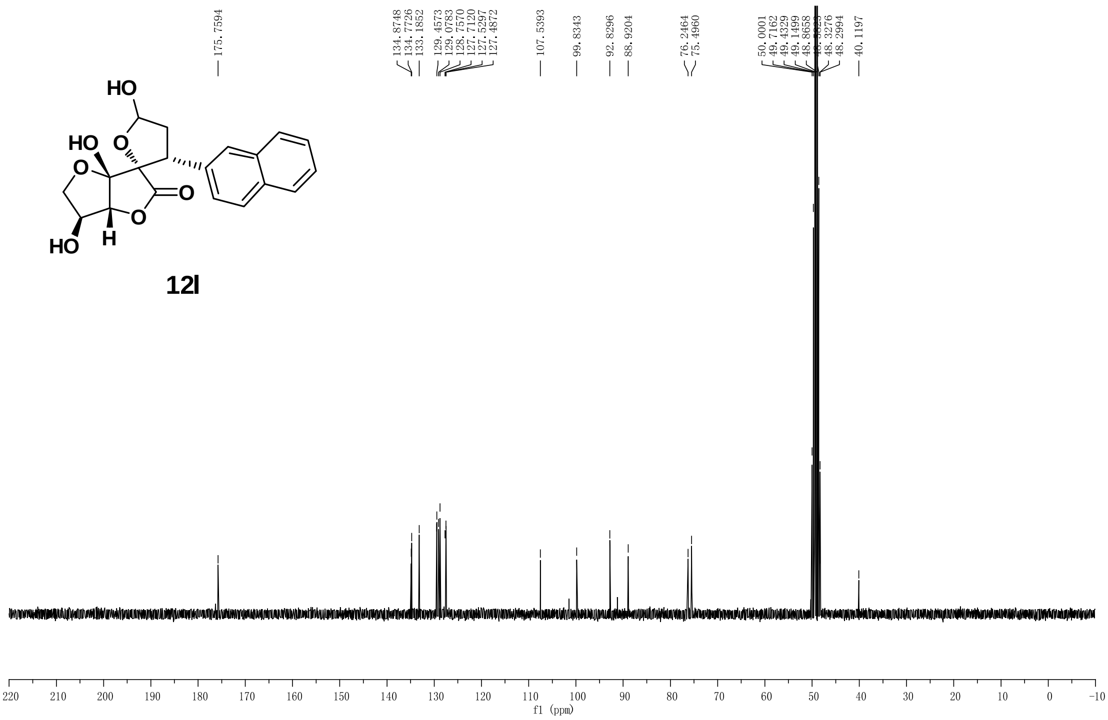
^{1}H NMR Spectrum for **12k** (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum for **12k** (400 MHz, $CDCl_3$)



[1]H NMR Spectrum for **12l** (300 MHz, CD_3OD)



[13]C NMR Spectrum for **12l** (75 MHz, CD_3OD)

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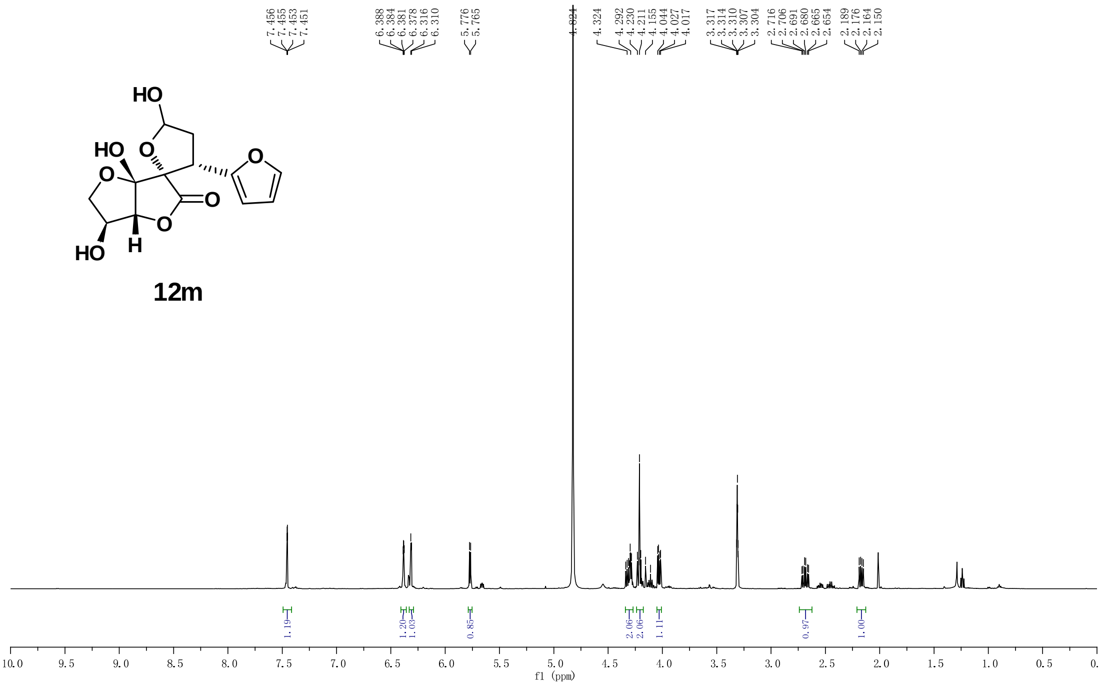
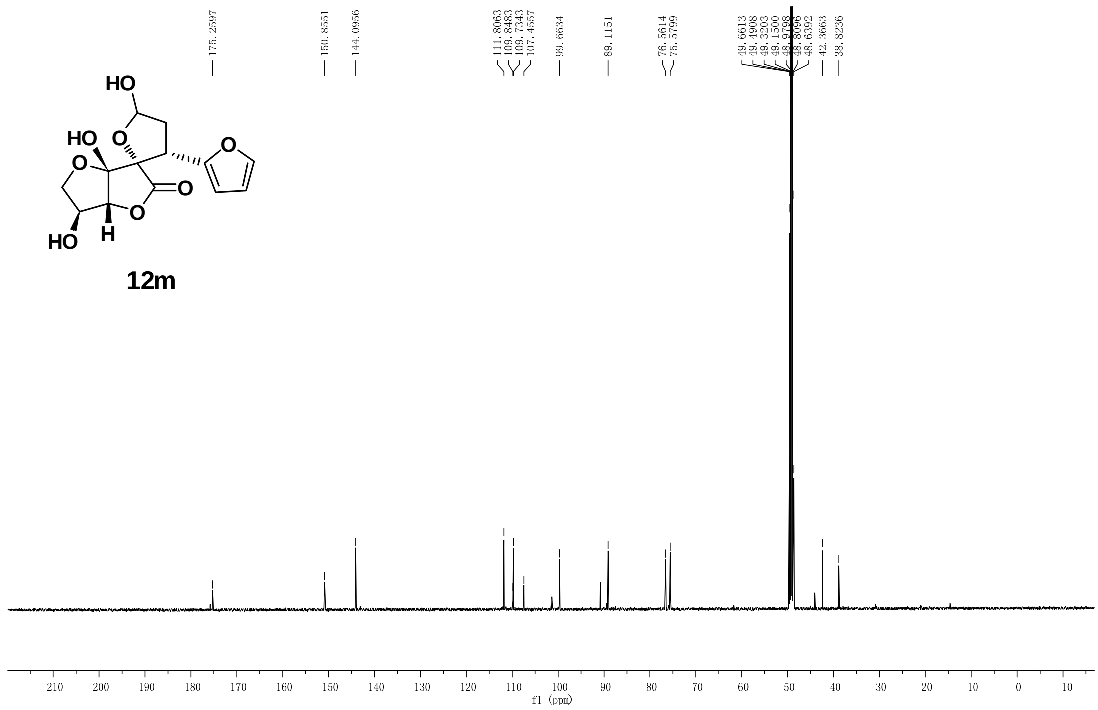
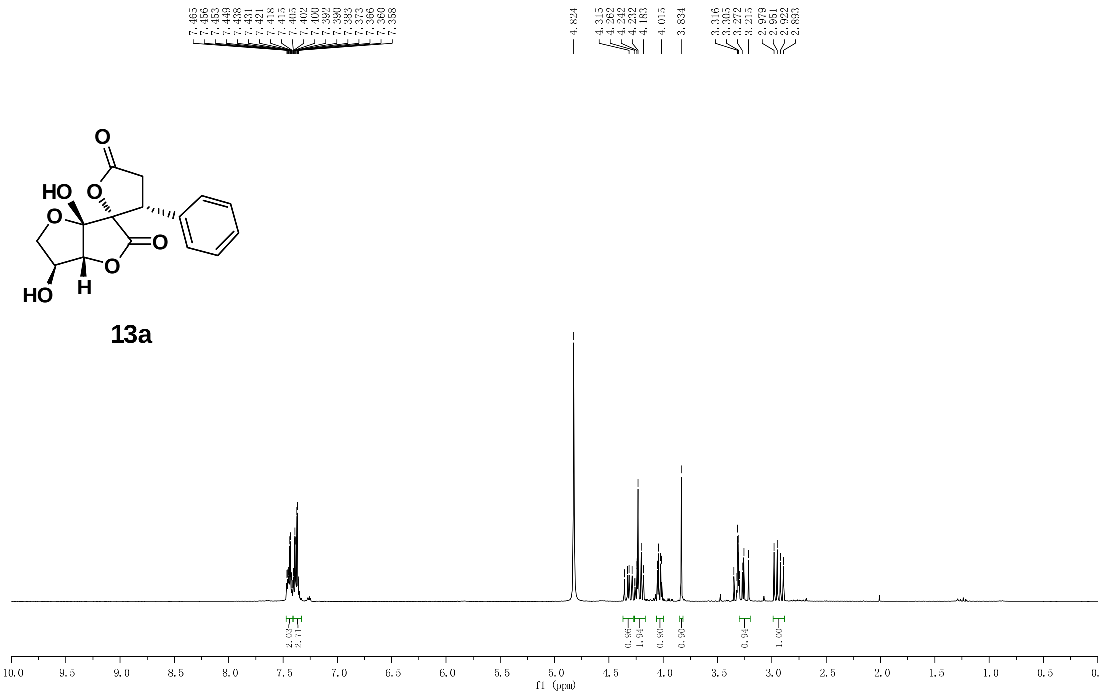


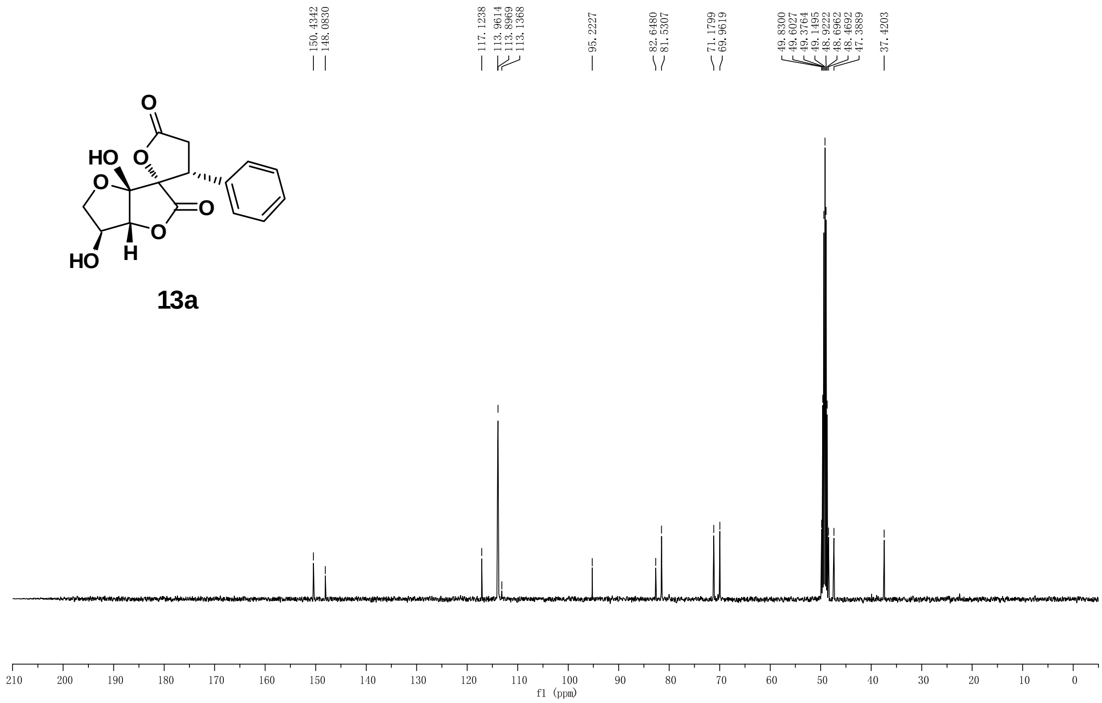
^{1}H NMR Spectrum for **12m** (500 MHz, CD_3OD)



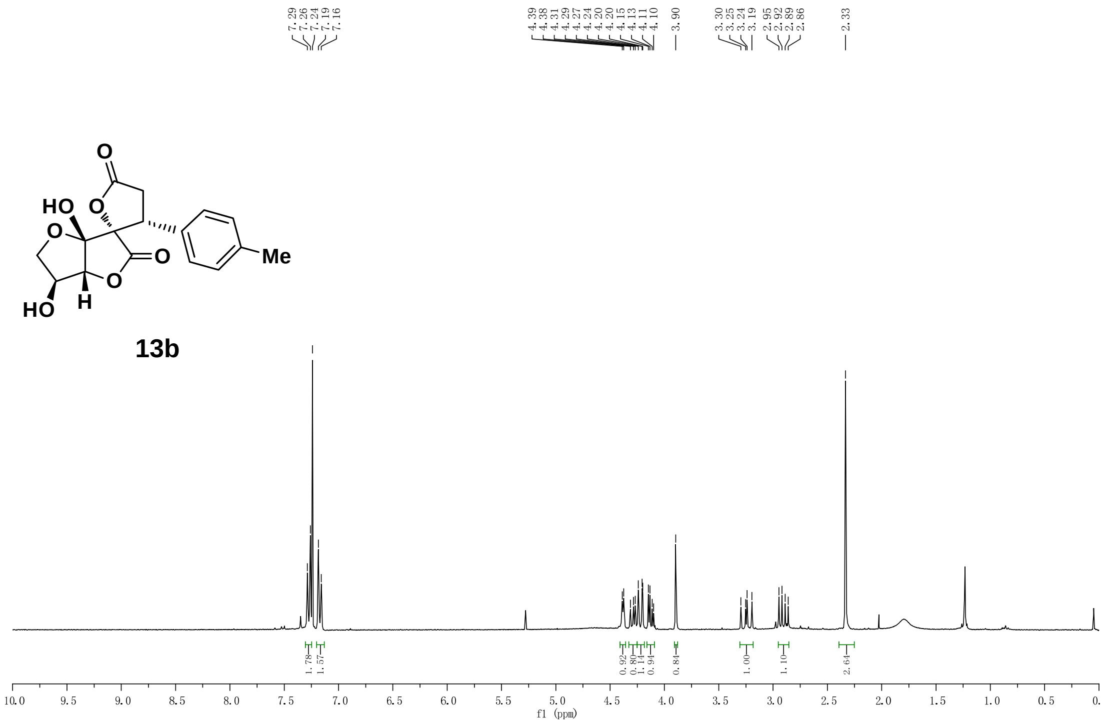
^{13}C NMR Spectrum for **12m** (75 MHz, CD_3OD)



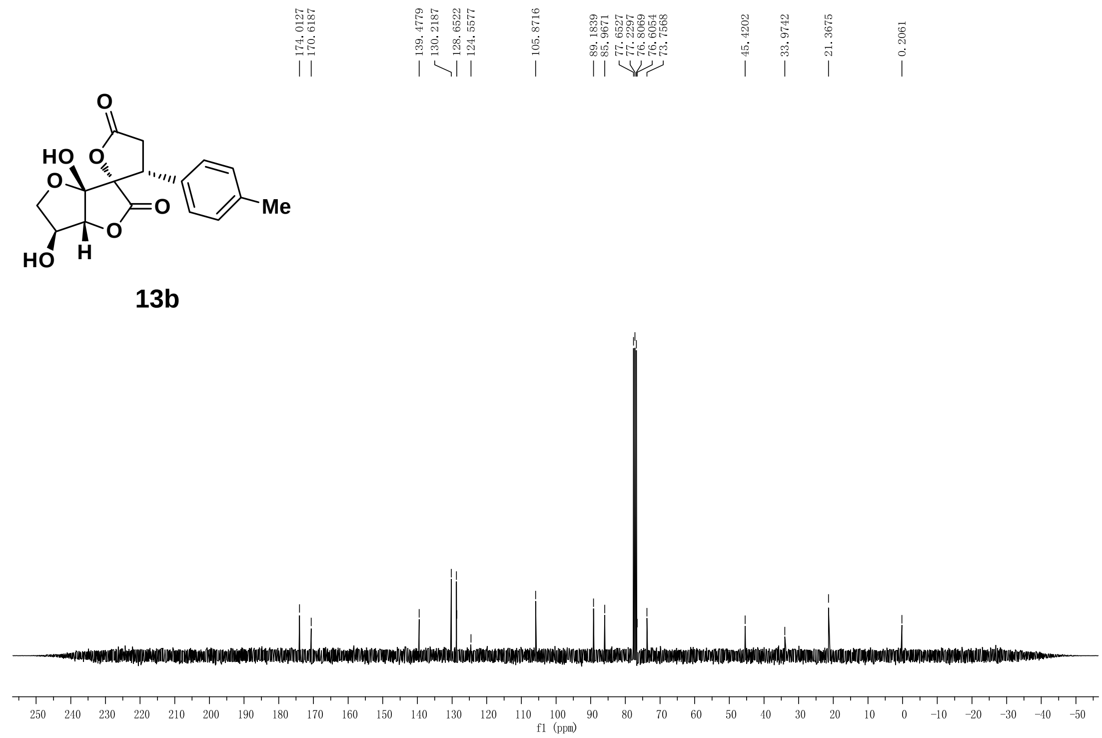
[1]H NMR Spectrum for **13a** (300 MHz, CD_3OD)



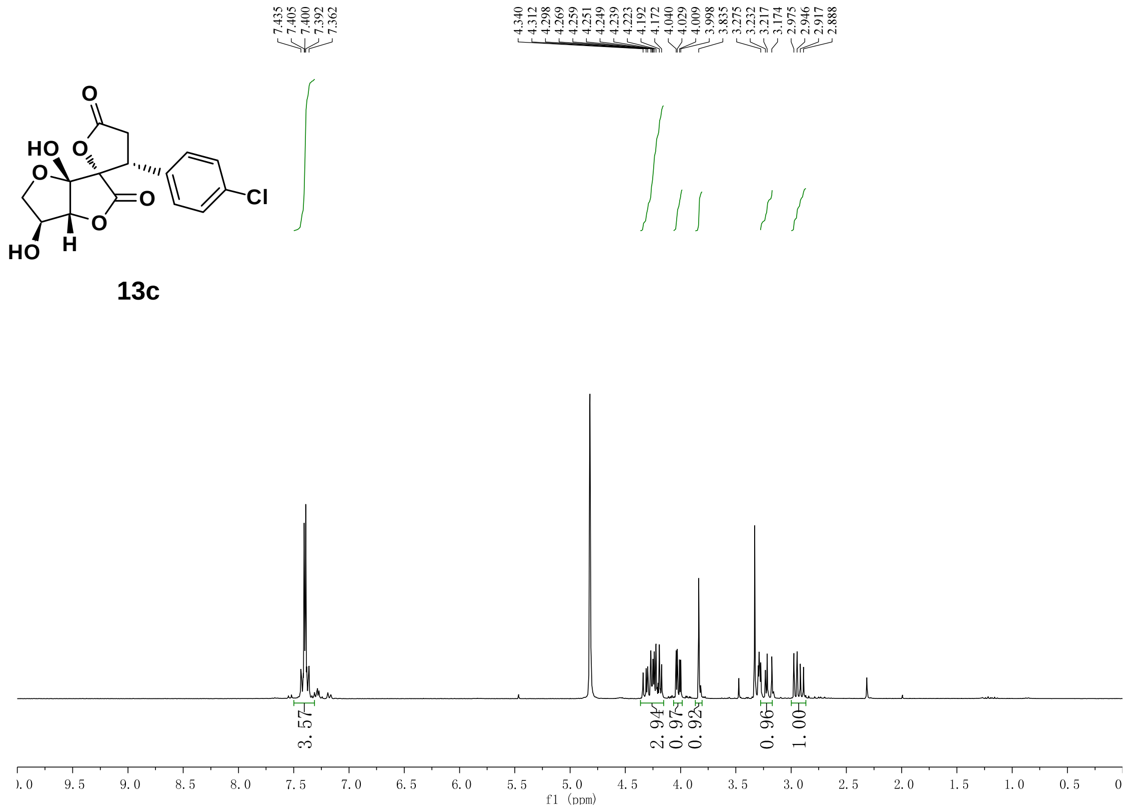
[13]C NMR Spectrum for **13a** (75 MHz, CD_3OD)



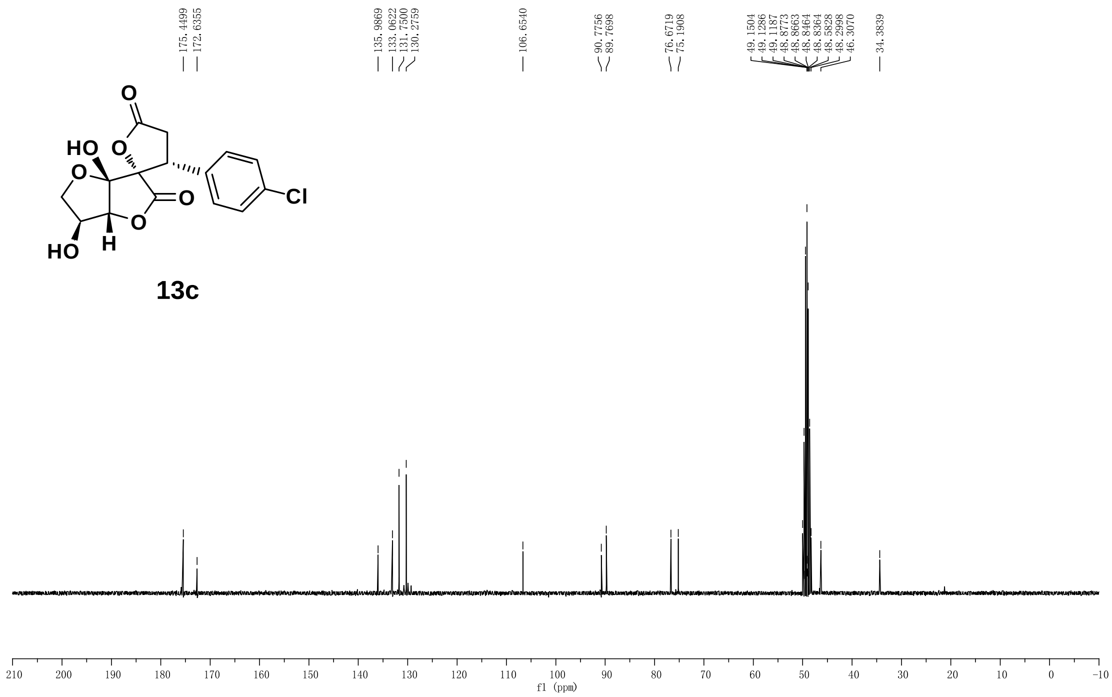
^{1}H NMR Spectrum for **13b** (300 MHz, $CDCl_3$)



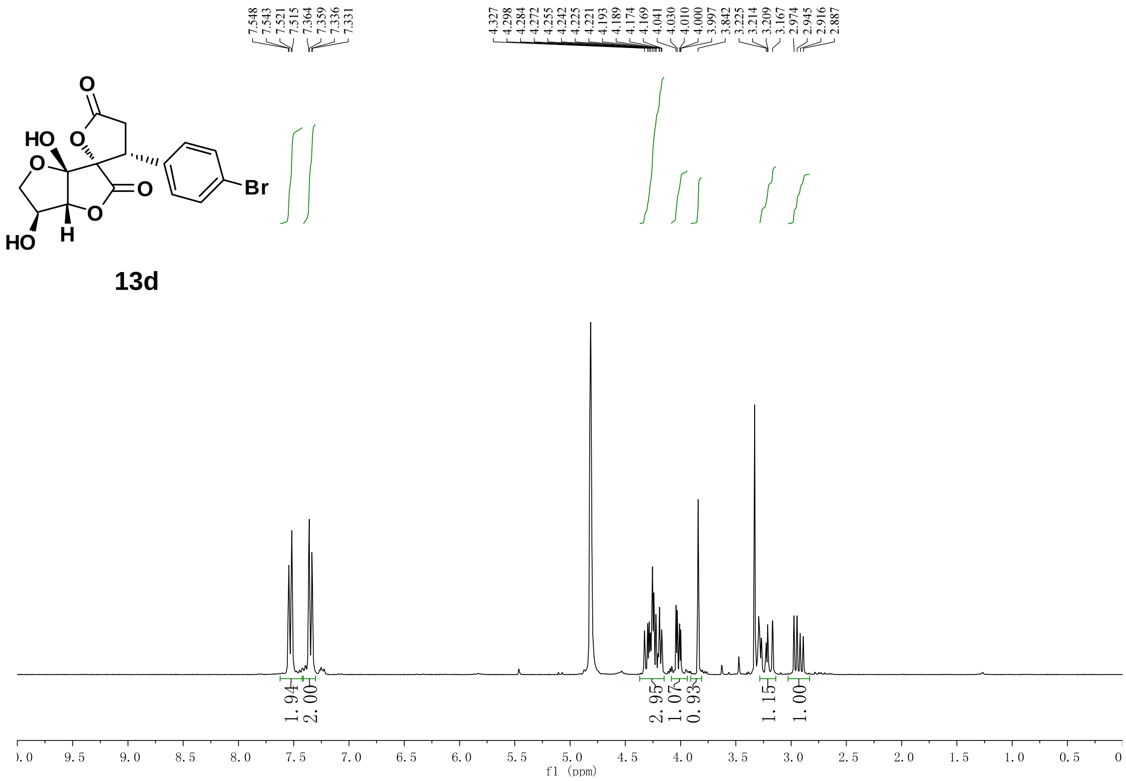
^{13}C NMR Spectrum for **13b** (301 MHz, $CDCl_3$)



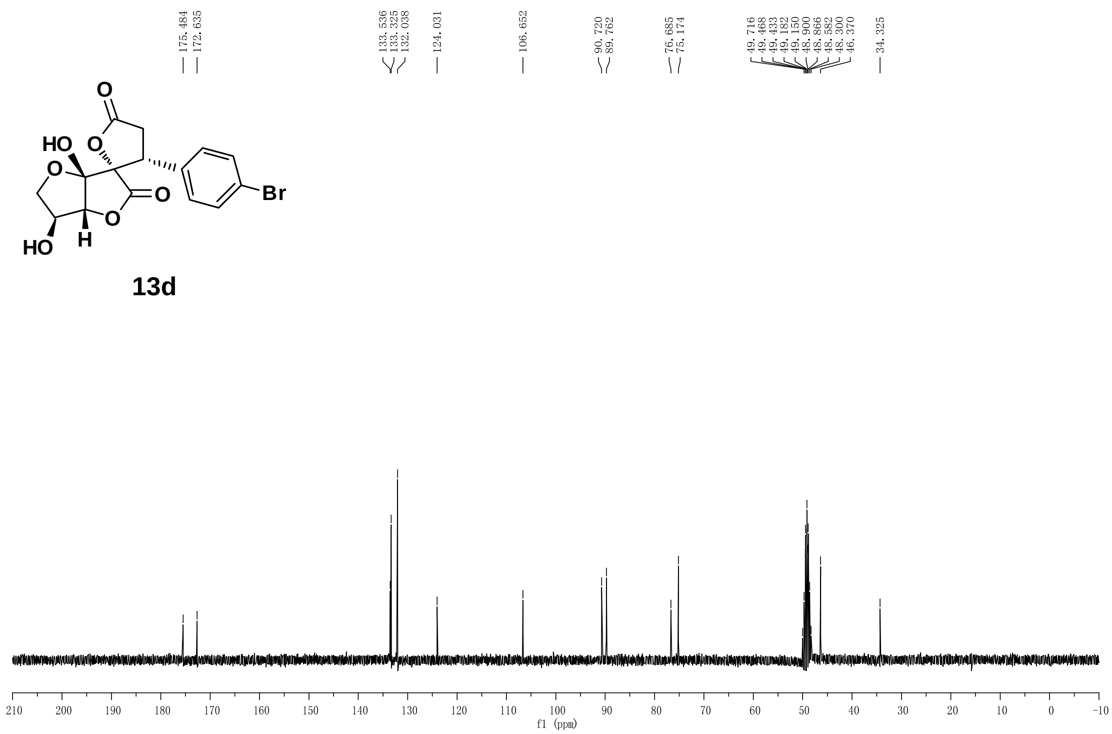
^{1}H NMR Spectrum for **13c** (300 MHz, CD_3OD)



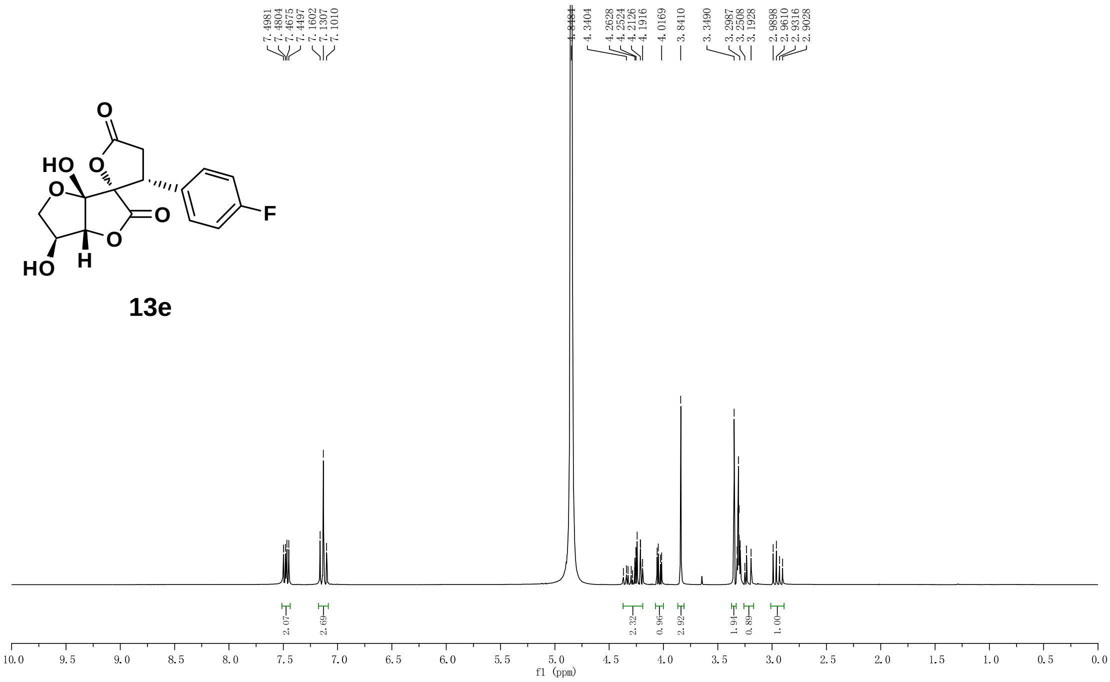
^{13}C NMR Spectrum for **13c** (75 MHz, CD_3OD)



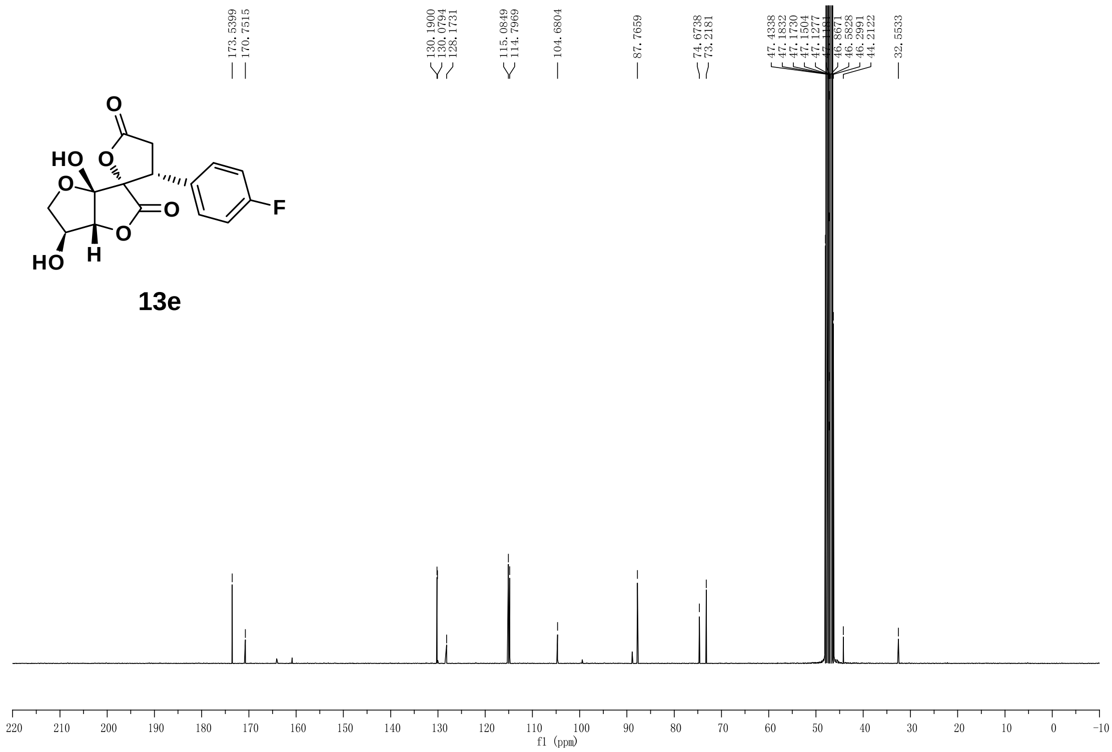
^{1}H NMR Spectrum for **13d** (300 MHz, CD_3OD)



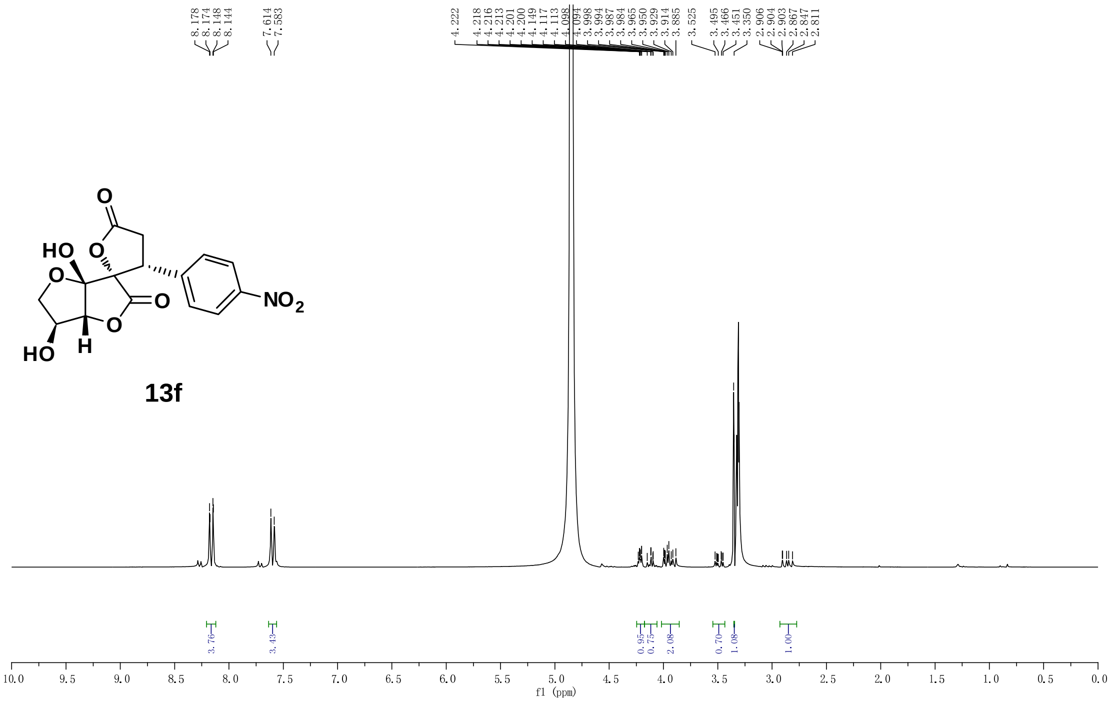
^{13}C NMR Spectrum for **13d** (75 MHz, CD_3OD)



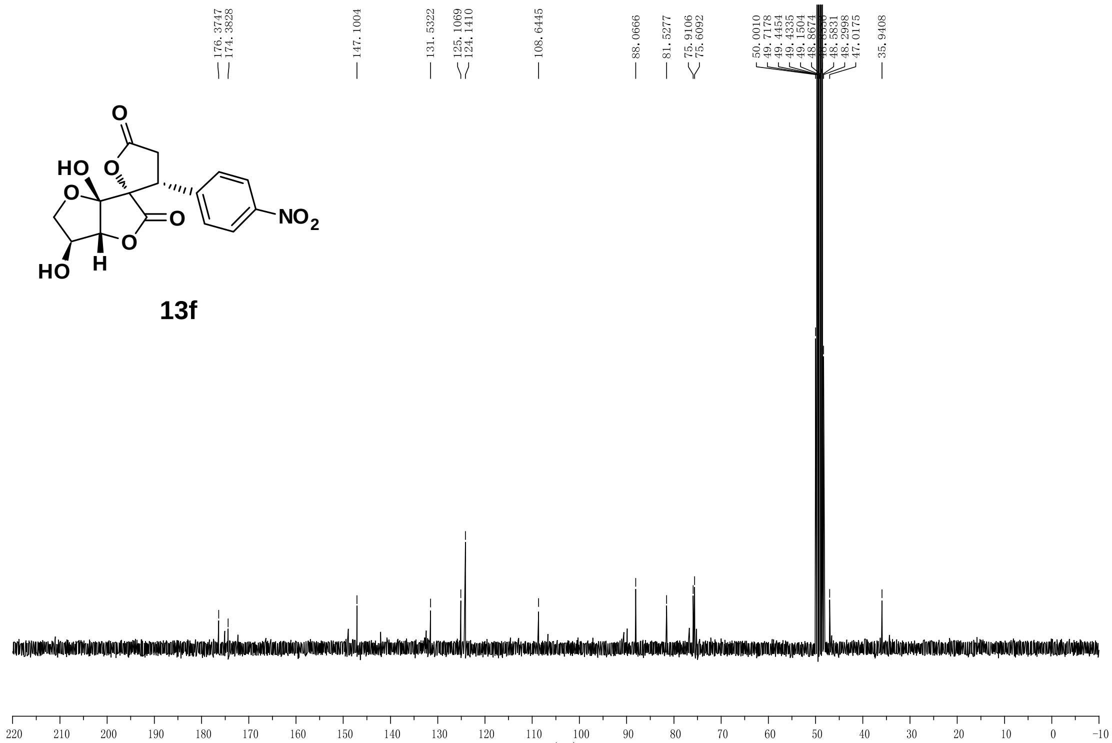
^{1}H NMR Spectrum for **13e** (300 MHz, CD_3OD)



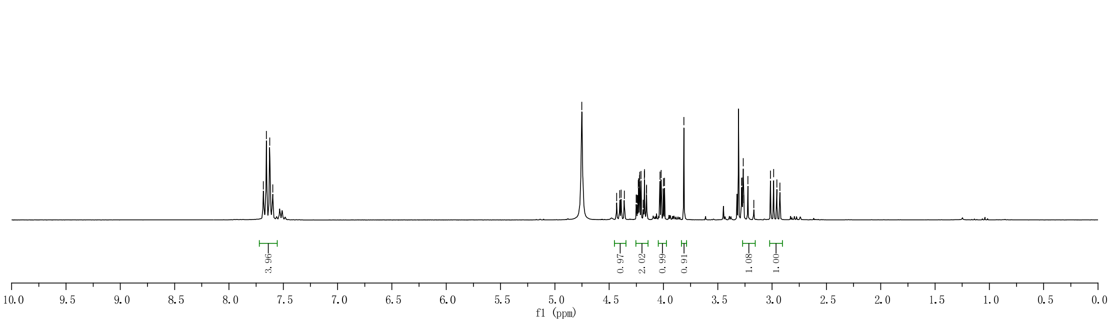
^{13}C NMR Spectrum for **13e** (75 MHz, CD_3OD)

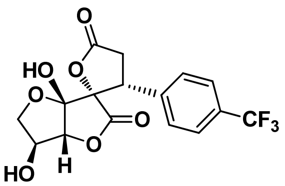


^{1}H NMR Spectrum for **13f** (300 MHz, CD_3OD)



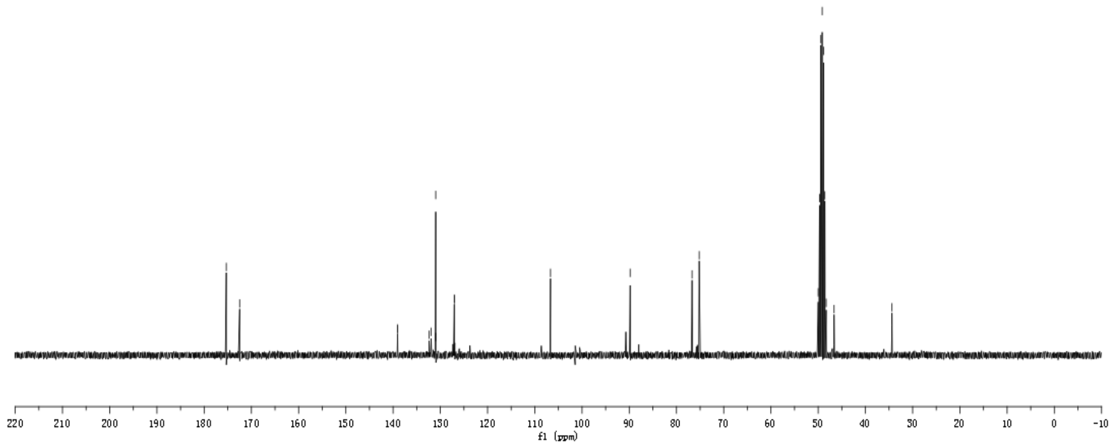
^{13}C NMR Spectrum for **13f** (75 MHz, CD_3OD)

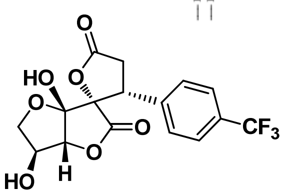




13g

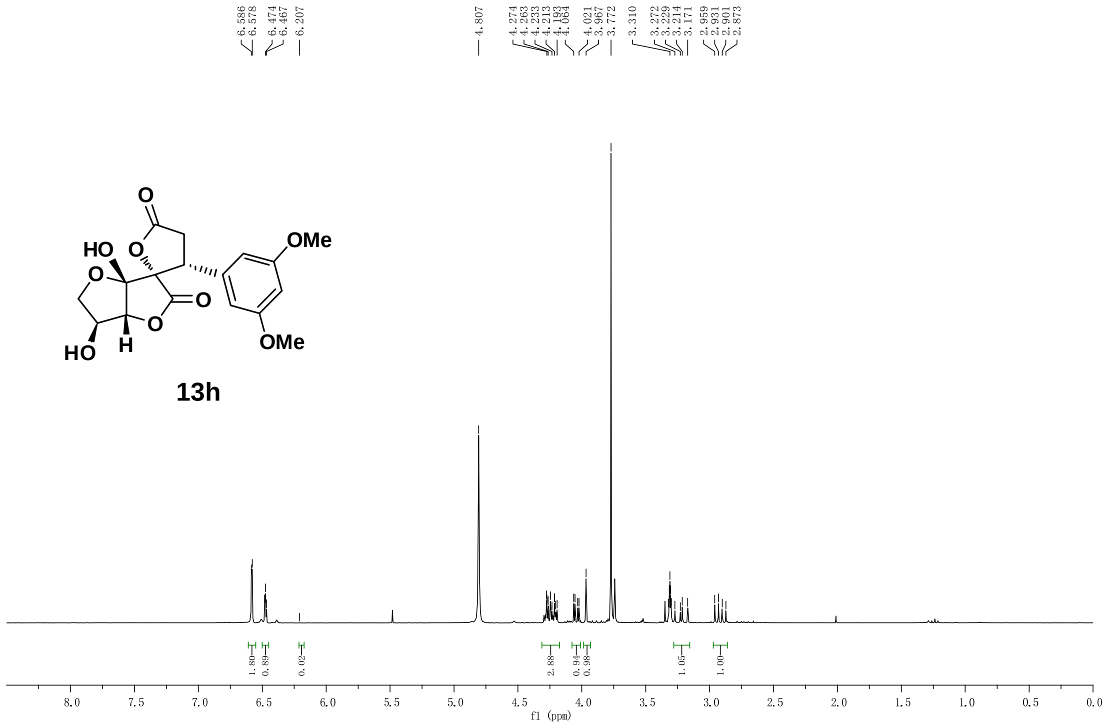
^{1}H NMR Spectrum for **13g** (300 MHz, CD_3OD)



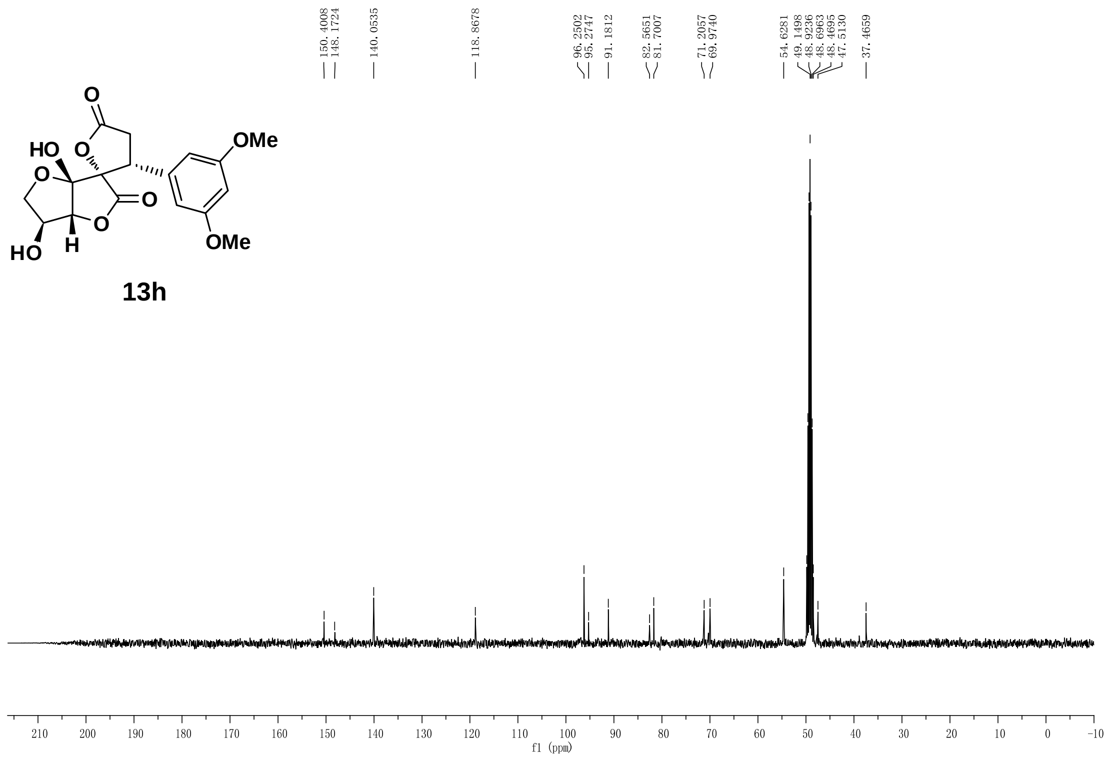


13g

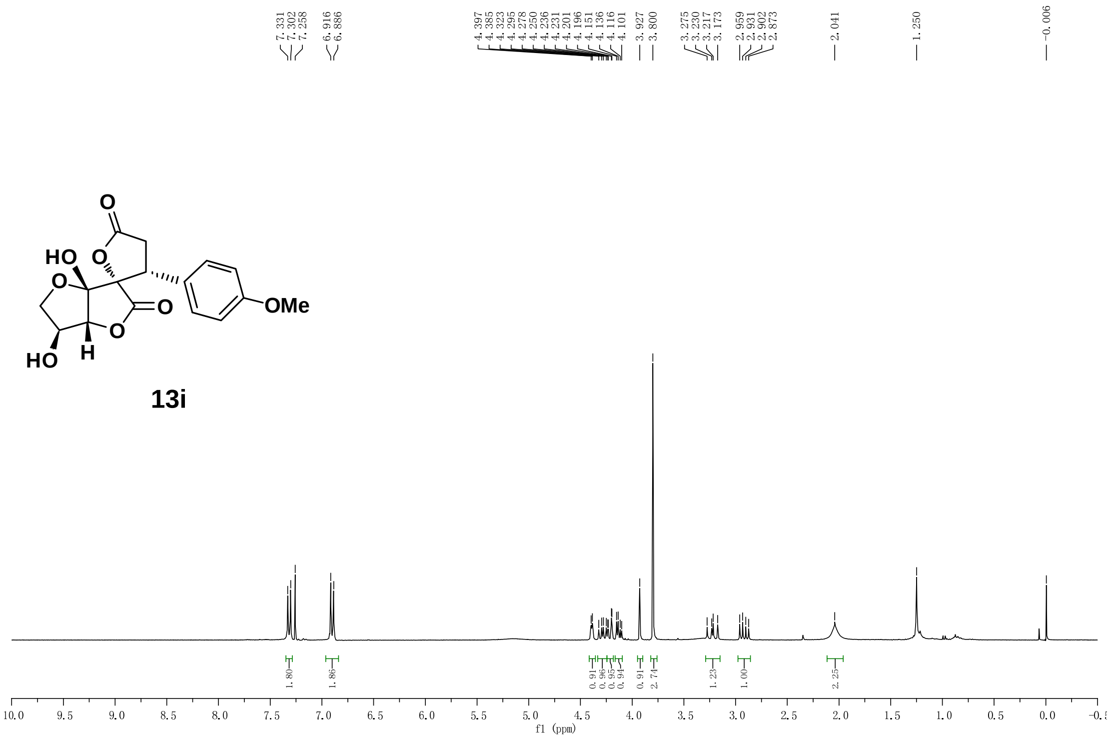
^{13}C NMR Spectrum for **13g** (75 MHz, CD_3OD)



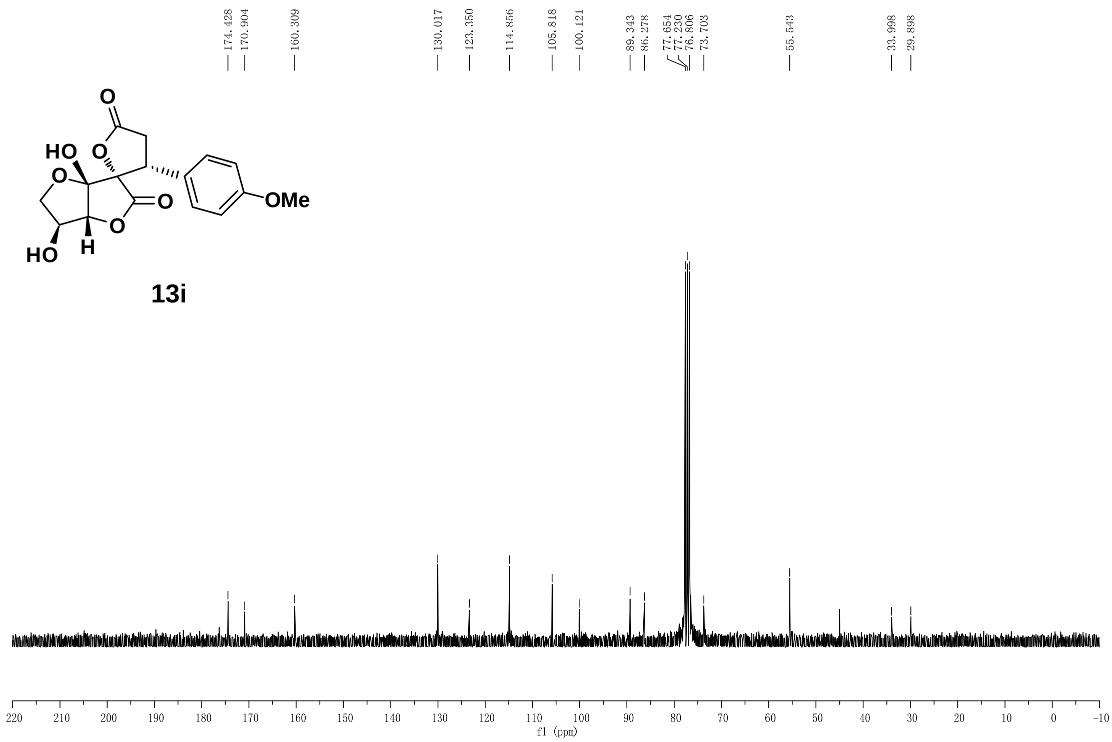
^{1}H NMR Spectrum for **13h** (300 MHz, CD_3OD)



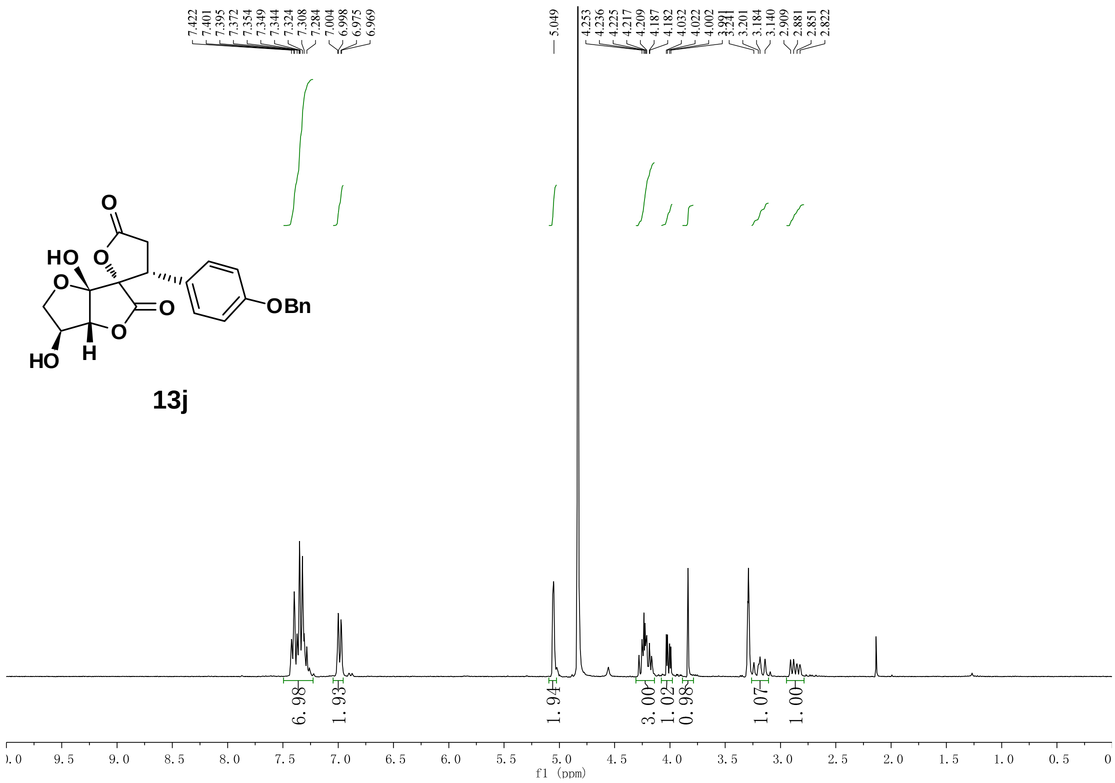
^{13}C NMR Spectrum for **13h** (75 MHz, CD_3OD)



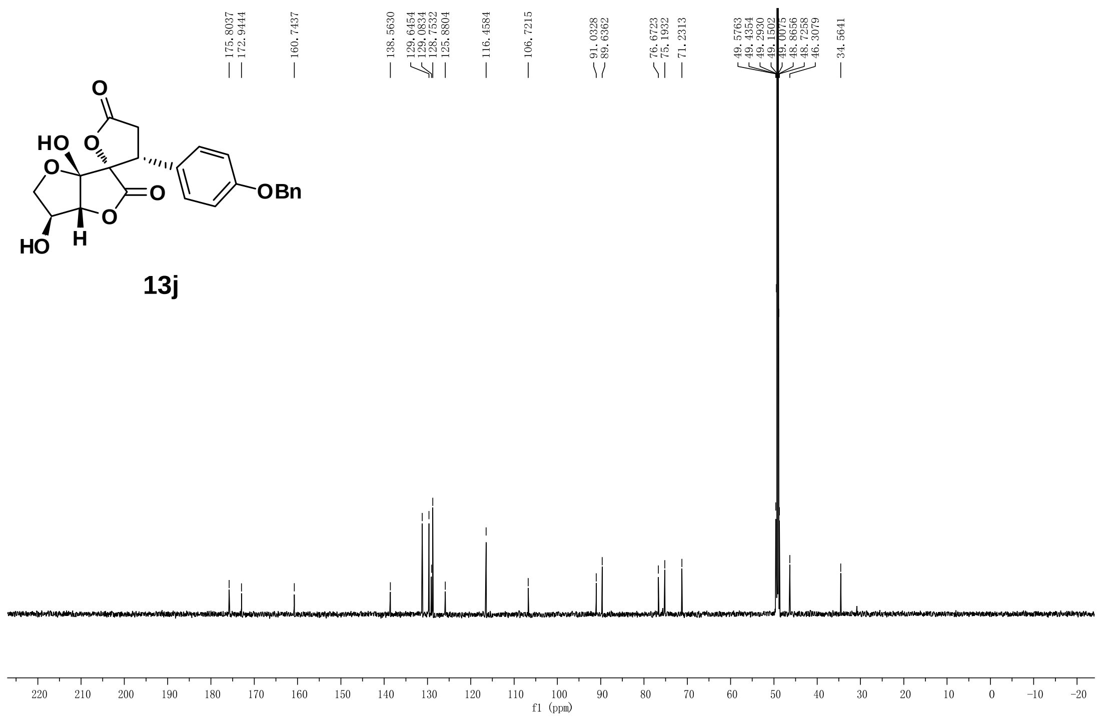
[1]H NMR Spectrum for **13i** (300 MHz, CD_3OD)



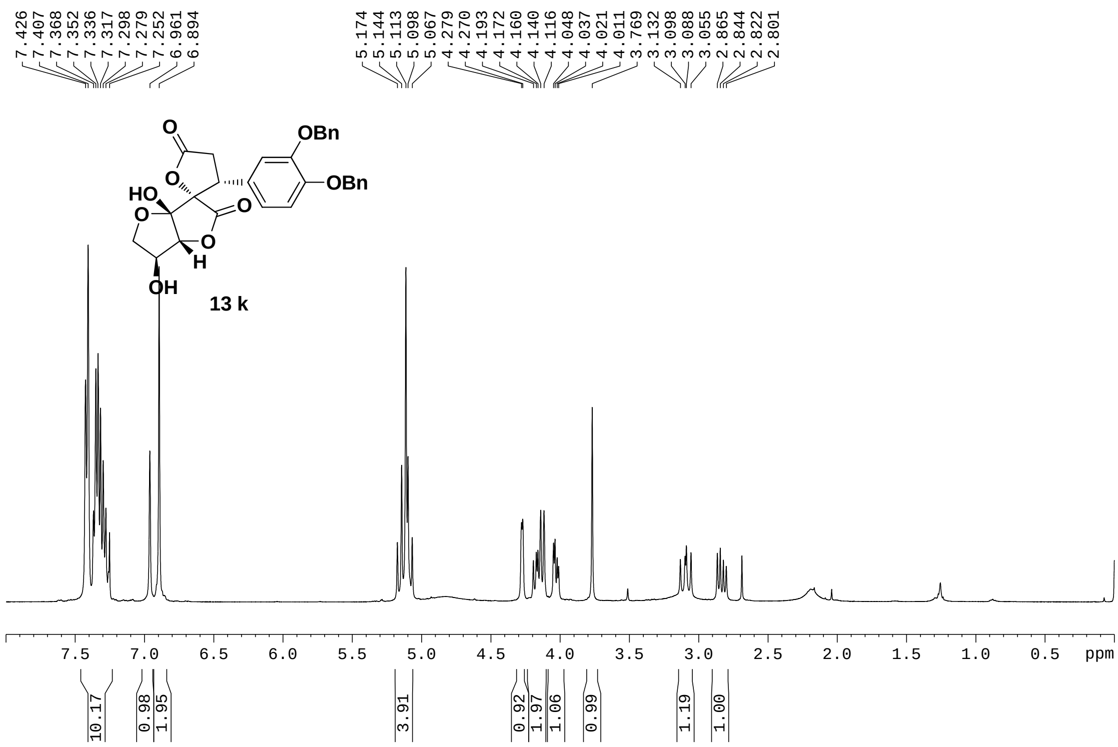
[13]C NMR Spectrum for **13i** (75 MHz, CD_3OD)



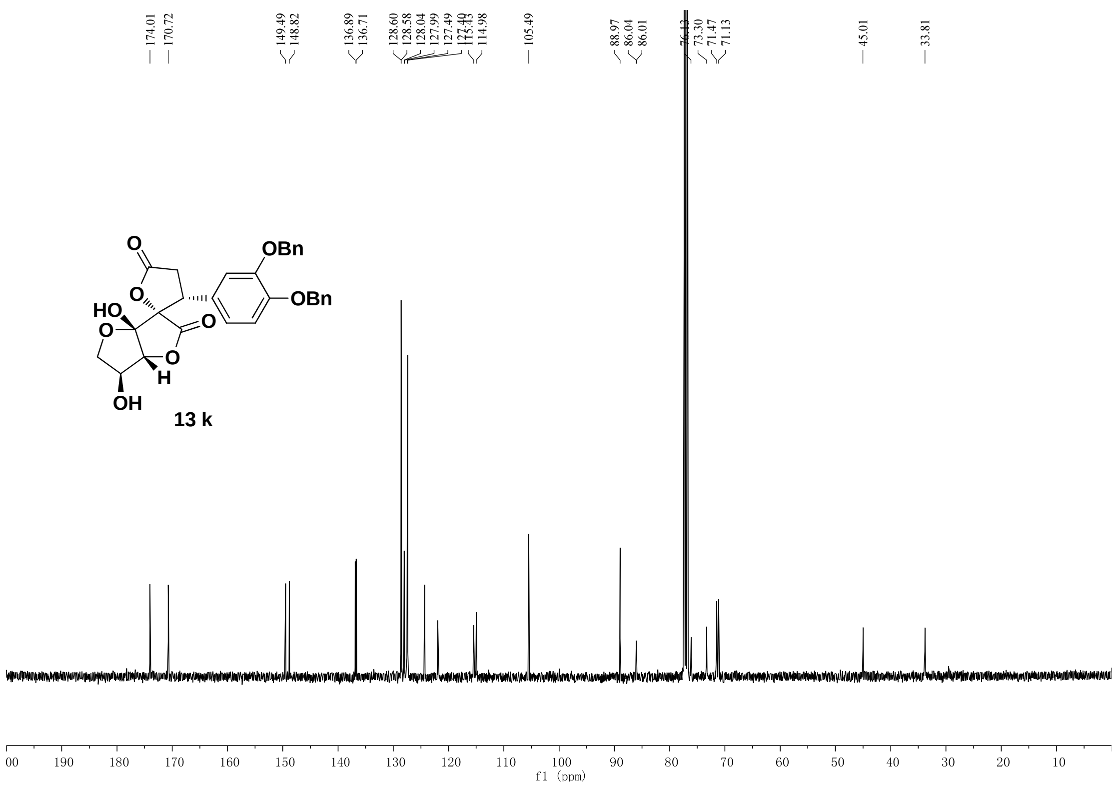
^{1}H NMR Spectrum for **13j** (300 MHz, CD_3OD)



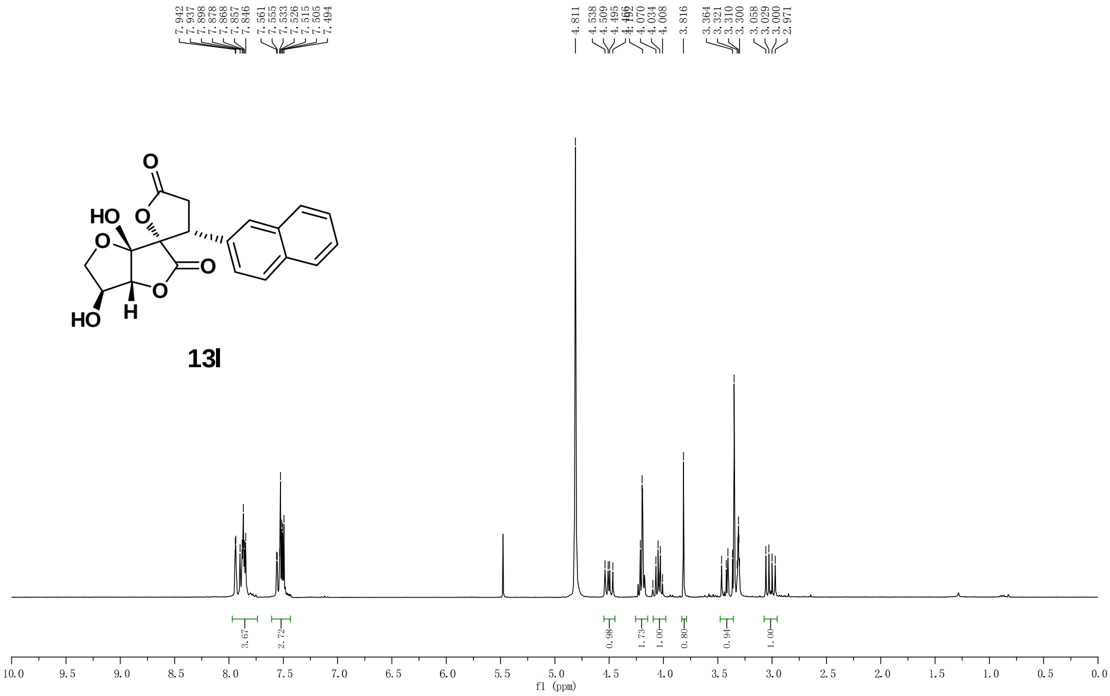
^{13}C NMR Spectrum for **13j** (75 MHz, CD_3OD)



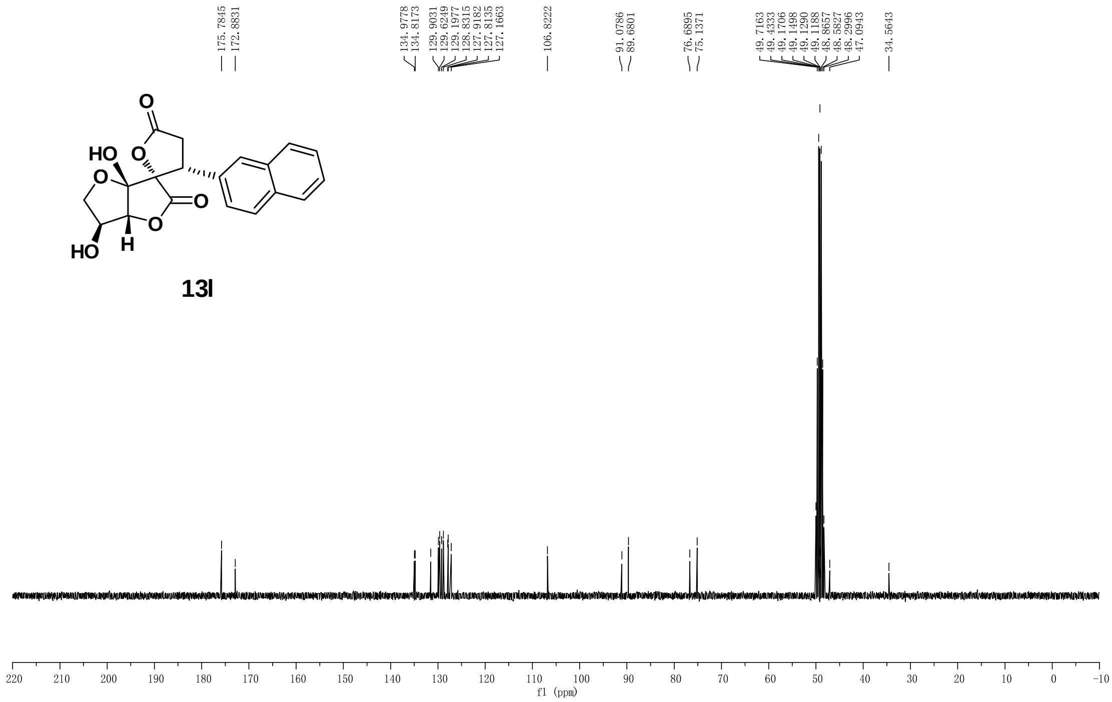
[1]H NMR Spectrum for **13k** (400 MHz，CDCl$_3$)



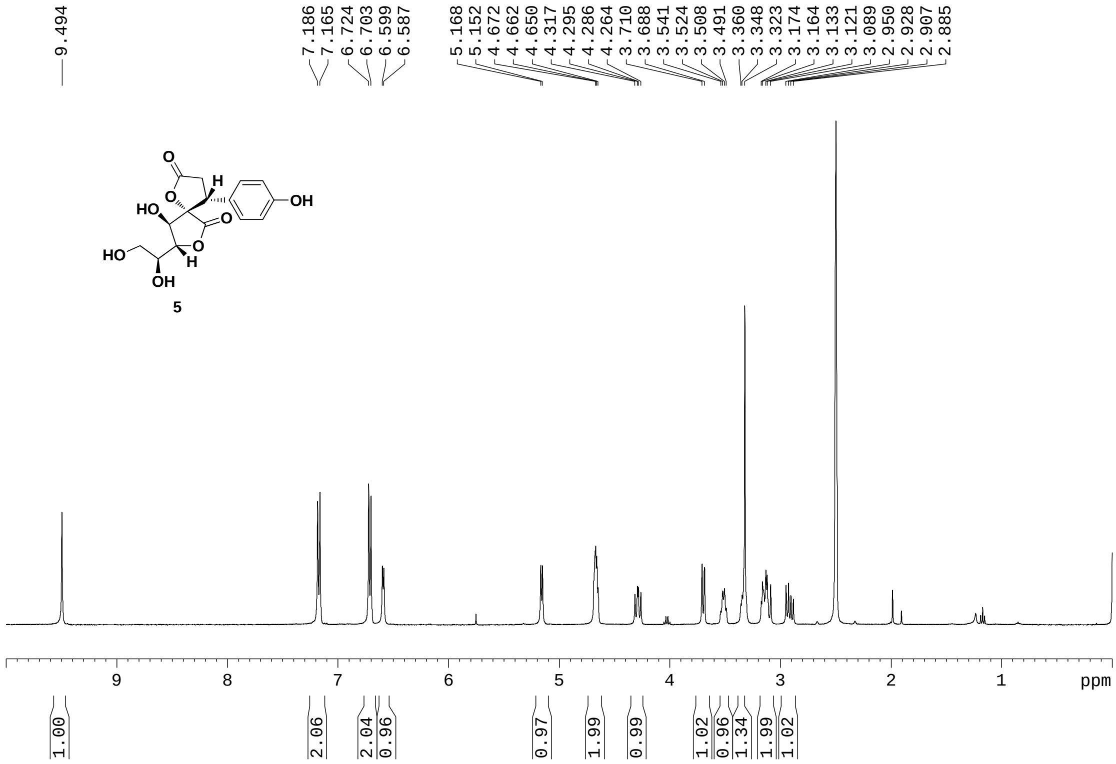
[13]C NMR Spectrum for **13k** (100 MHz，CDCl$_3$)



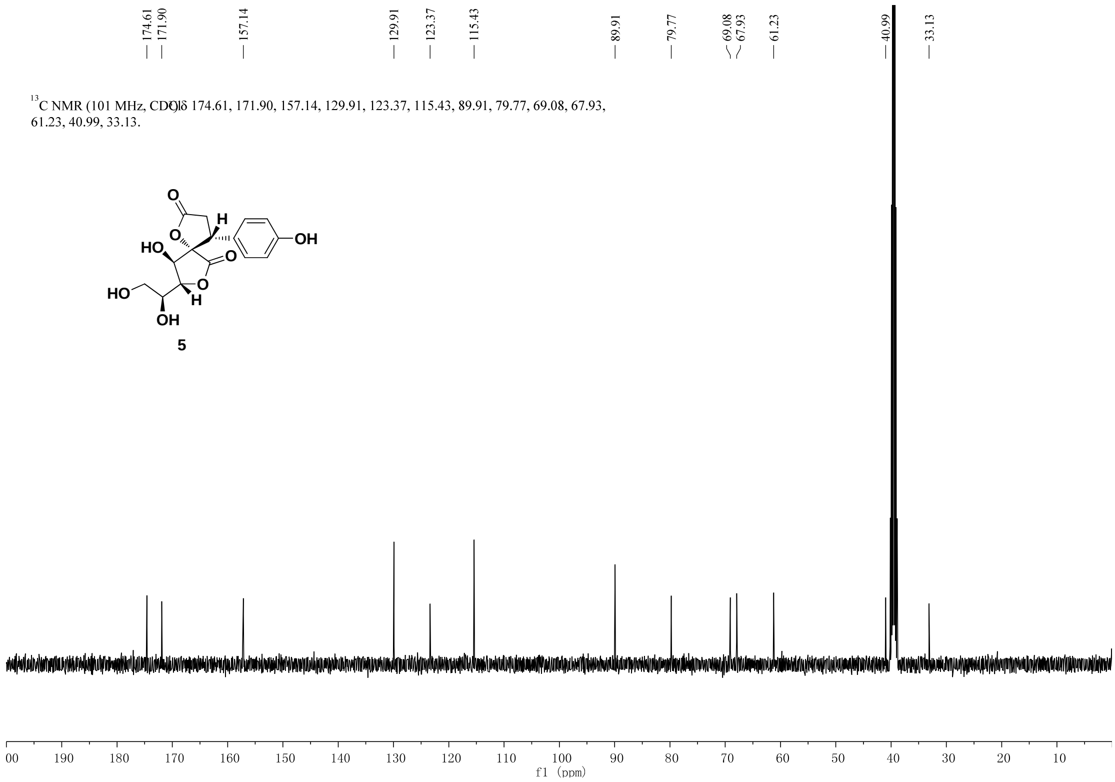
[1]H NMR Spectrum for **13l** (300 MHz, CD_3OD)



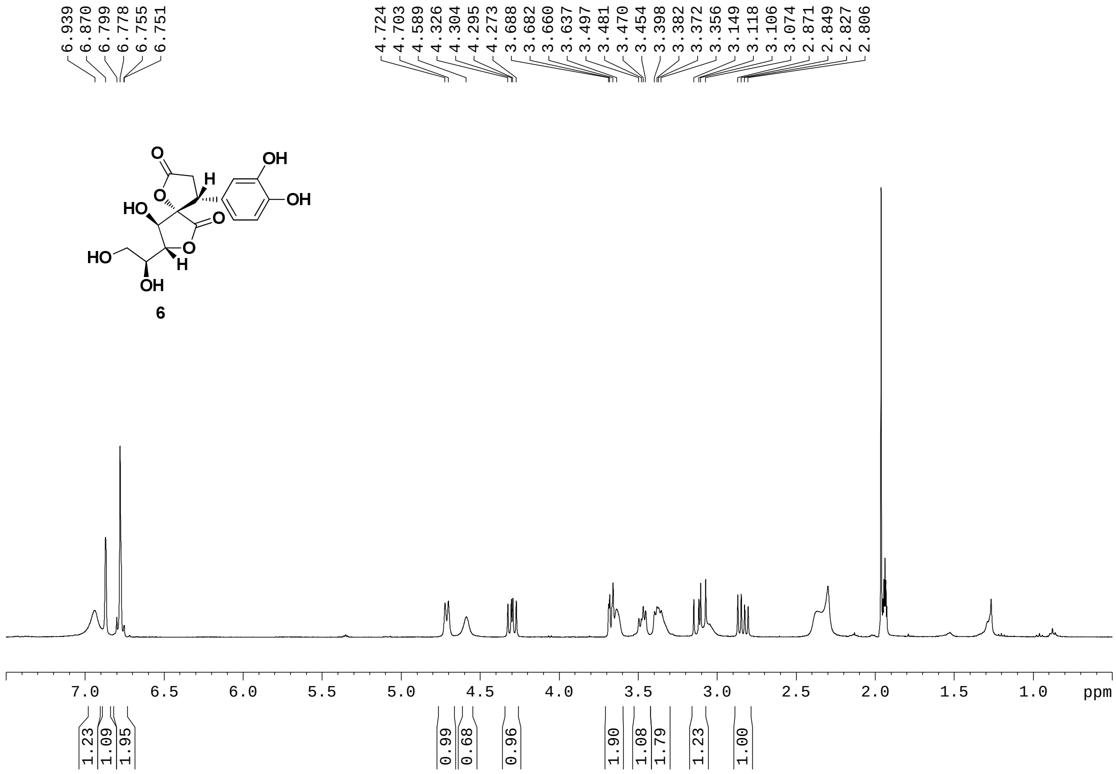
[13]C NMR Spectrum for **13l** (75 MHz, CD_3OD)



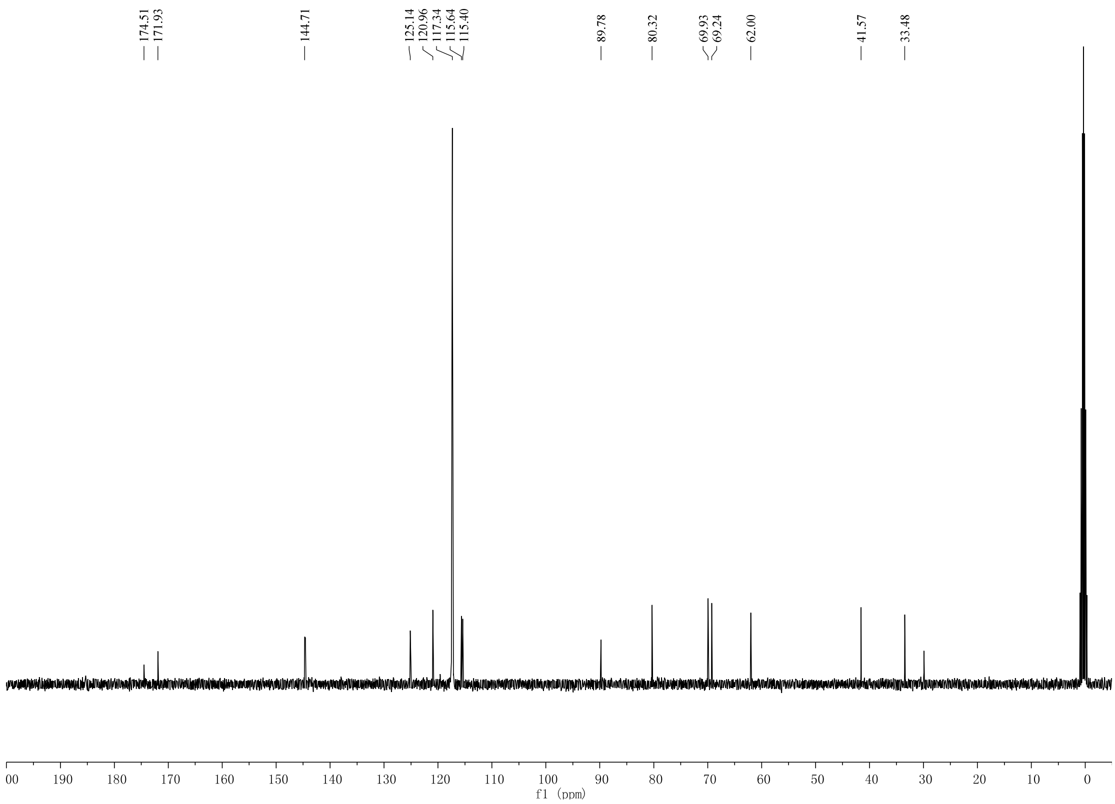
^{1}H NMR Spectrum for **5** (400 MHz，DMSO-d_6)



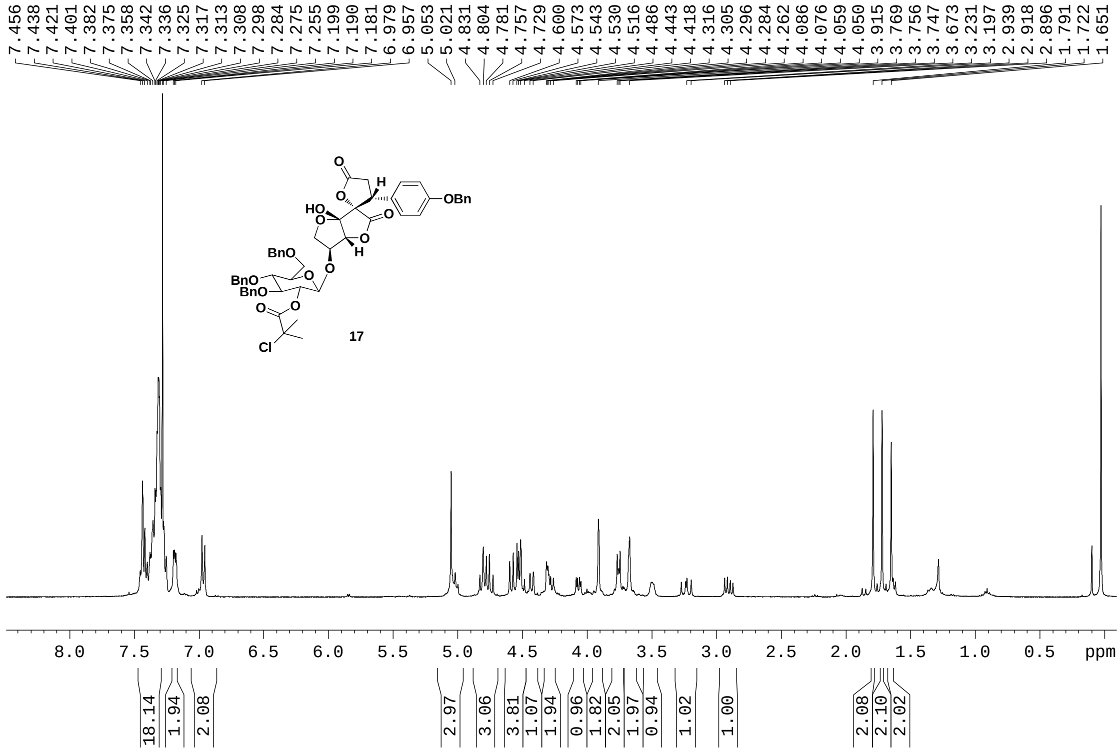
^{13}C NMR Spectrum for **5** (100 MHz，DMSO-d_6,)



^{1}H NMR Spectrum for **6** (400 MHz， CD_3CN)

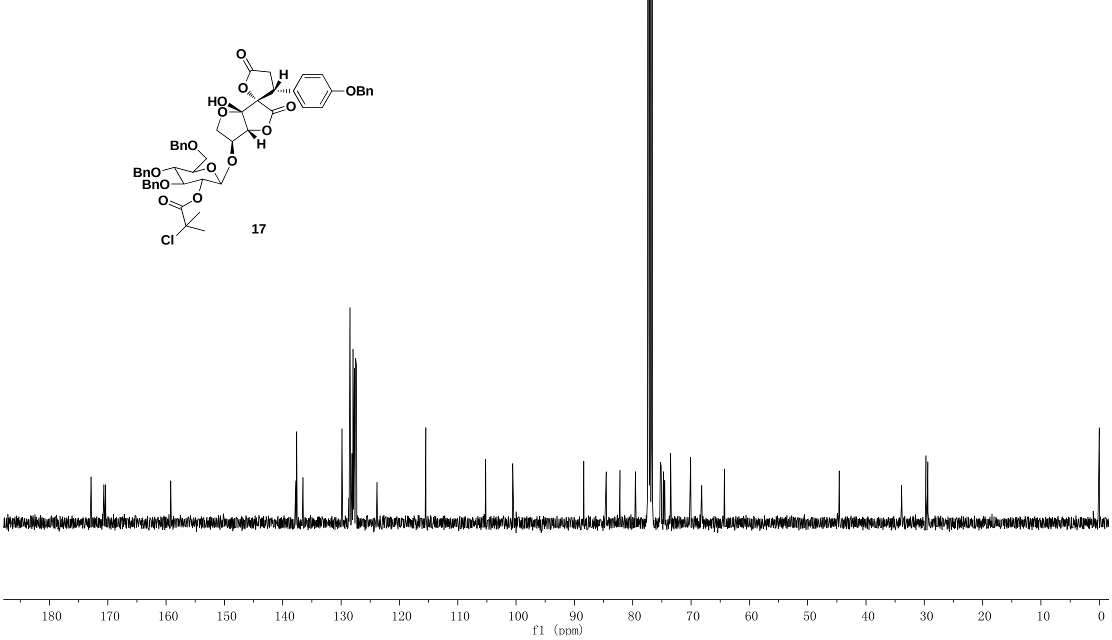


^{13}C NMR Spectrum for **6** (101 MHz， CD_3CN)

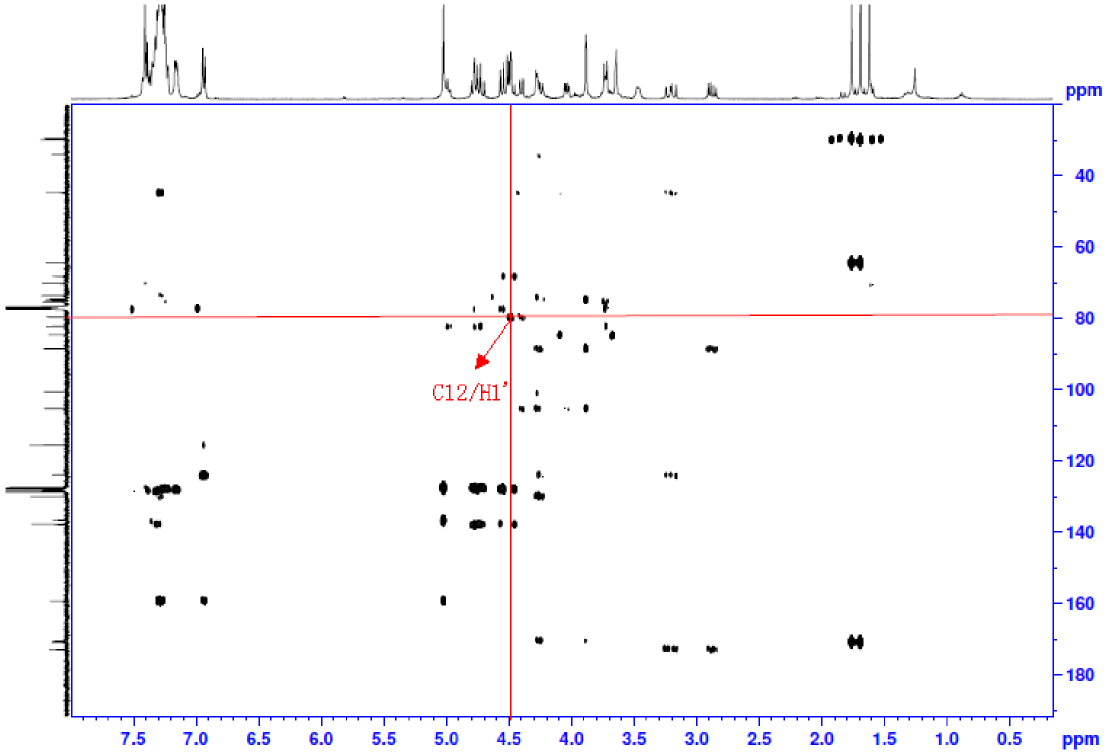


^{1}H NMR Spectrum for **17** (400 MHz, $CDCl_3$)

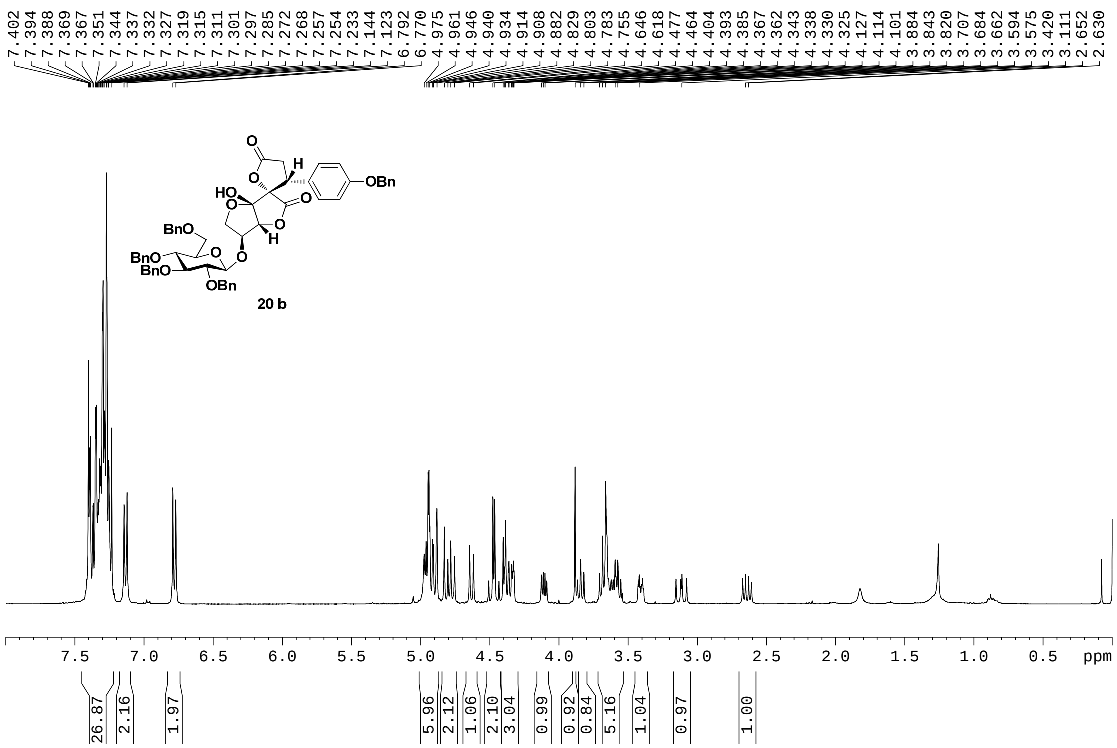
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.84, 170.69, 170.37, 159.19, 137.76, 137.62, 136.54, 129.86, 128.66, 128.50, 128.47, 128.45, 128.16, 127.97, 127.93, 127.90, 127.82, 127.72, 127.52, 127.34, 123.83, 115.47, 105.22, 100.57, 88.40, 84.53, 82.19, 79.53, 77.22, 75.29, 75.25, 75.11, 74.73, 74.50, 73.51, 70.08, 68.18, 64.29, 44.57, 33.90, 29.74, 29.41.



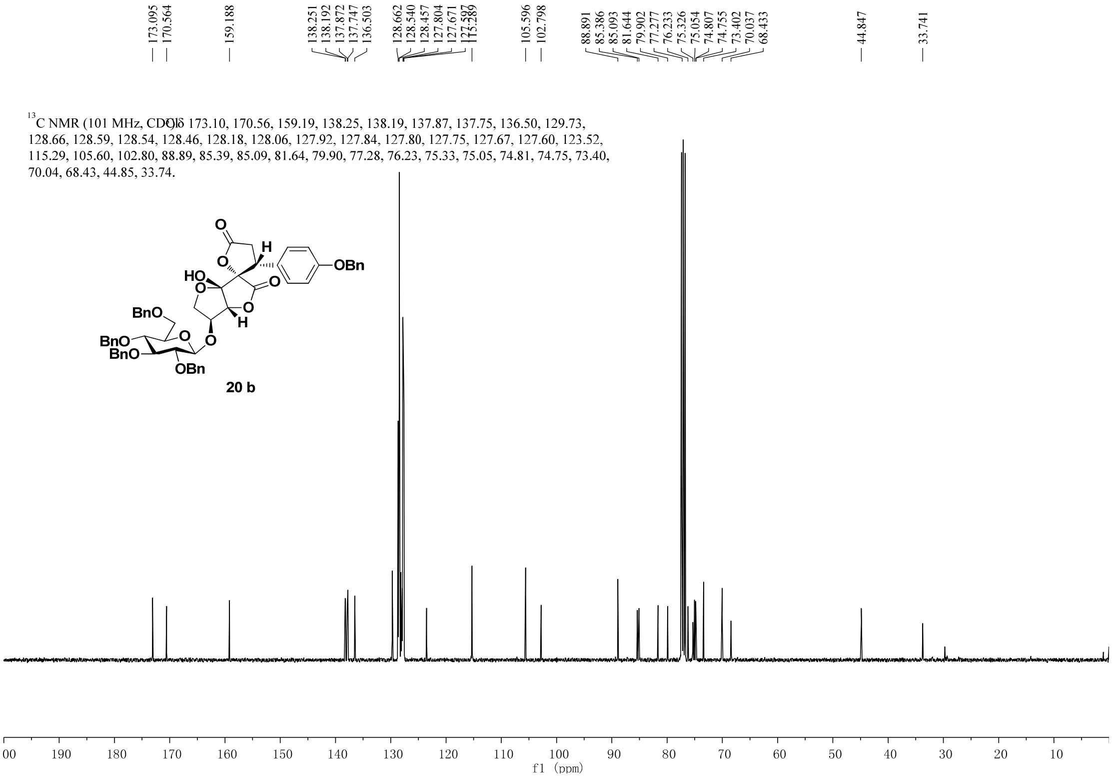
^{13}C NMR Spectrum for **17** (100 MHz, $CDCl_3$)



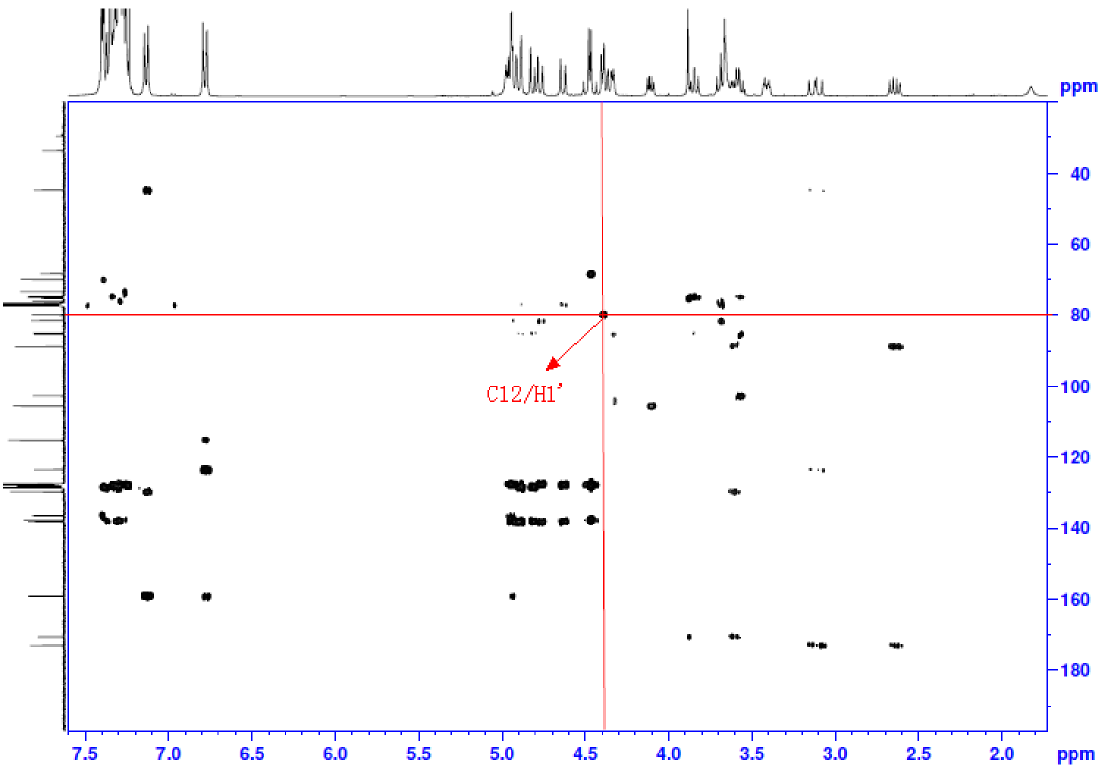
HMBC Spectrum for **17** (400 MHz， $CDCl_3$)



^{1}H NMR Spectrum for **20b** (400 MHz， $CDCl_3$)

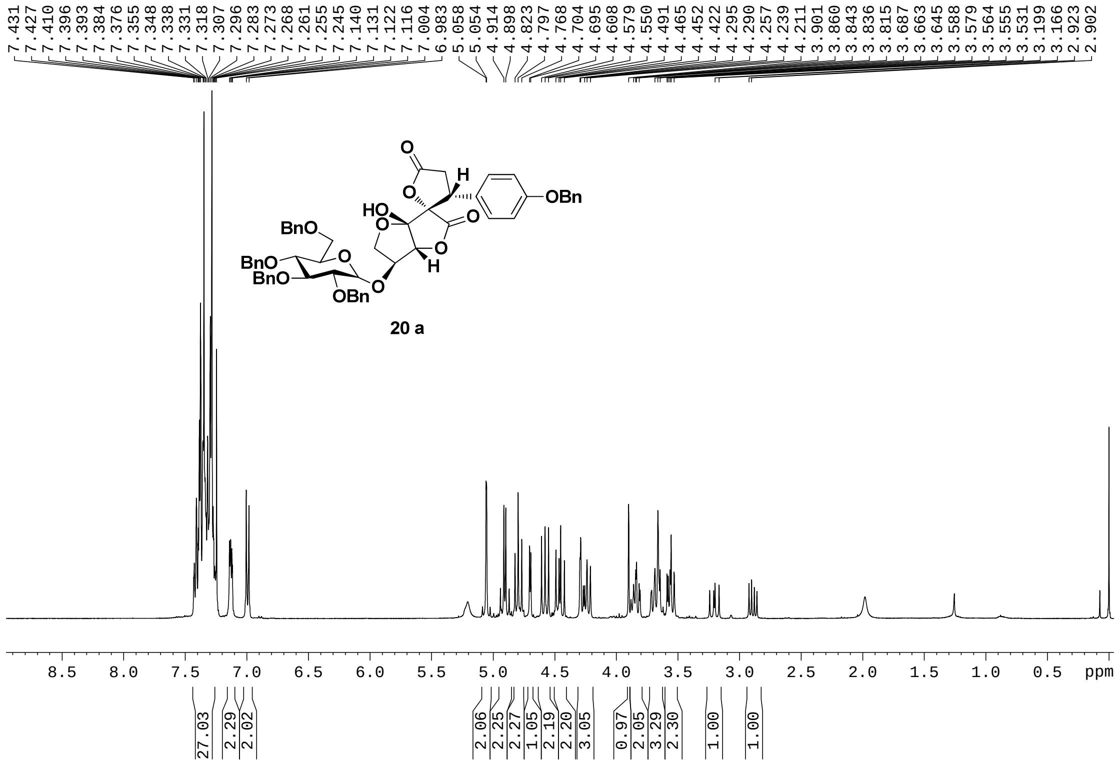


^{13}C NMR Spectrum for **20b** (101 MHz，$CDCl_3$)



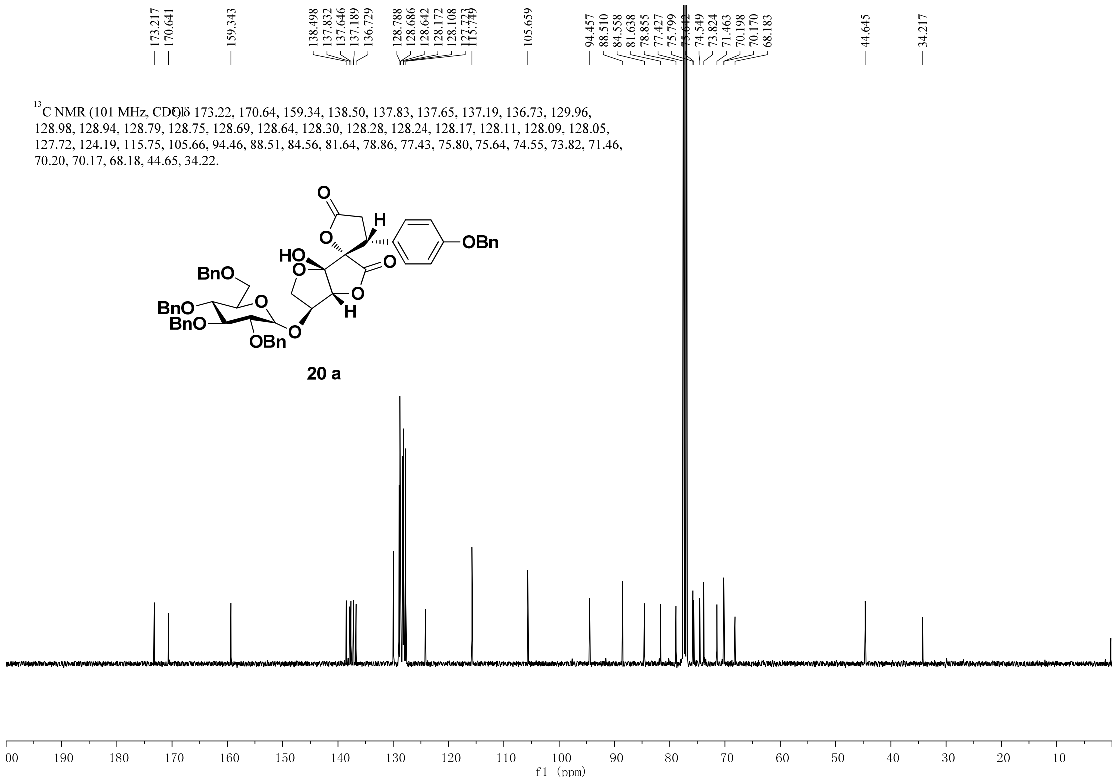
HMBC Spectrum for **20b** (400 MHz，$CDCl_3$)

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

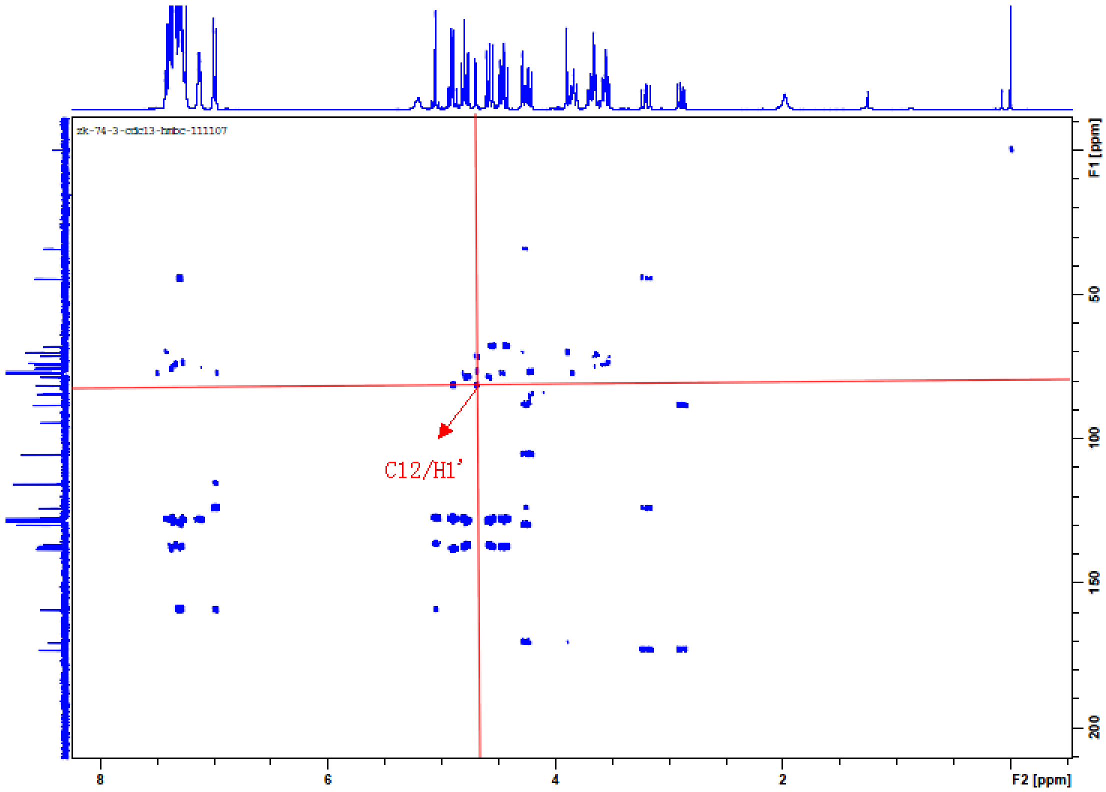


^{1}H NMR Spectrum for **20a** (400 MHz, $CDCl_3$)

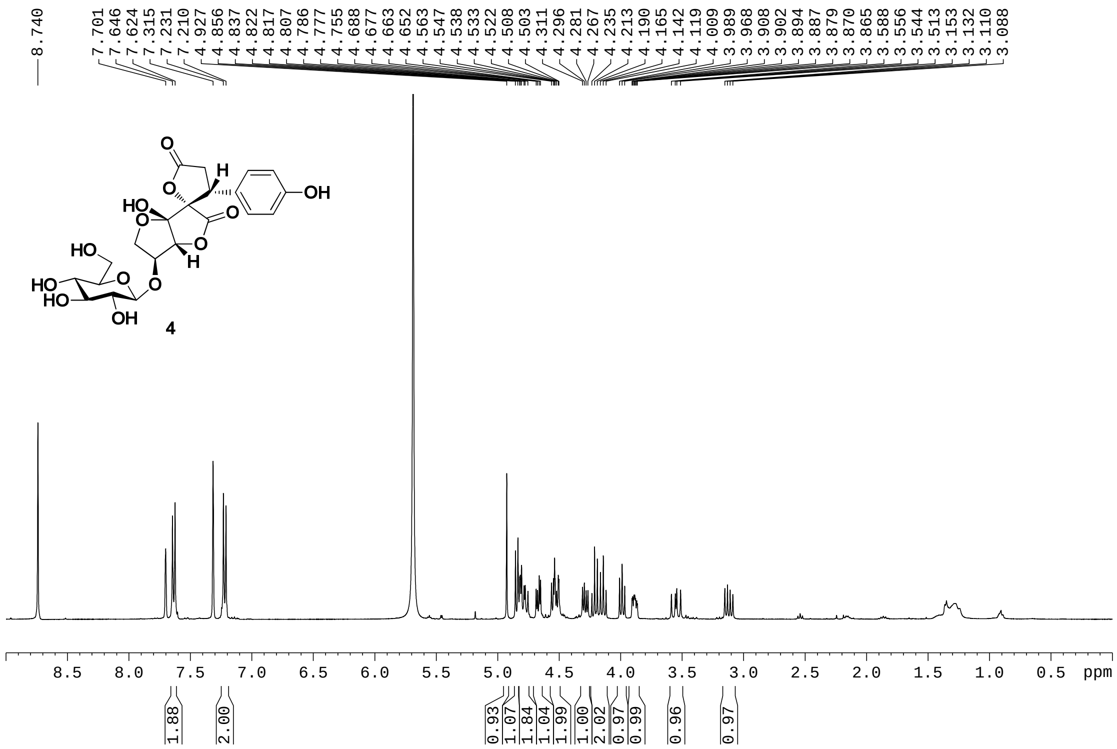
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.22, 170.64, 159.34, 138.50, 137.83, 137.65, 137.19, 136.73, 129.96, 128.98, 128.94, 128.79, 128.75, 128.69, 128.64, 128.30, 128.28, 128.24, 128.17, 128.11, 128.09, 128.05, 127.72, 124.19, 115.75, 105.66, 94.46, 88.51, 84.56, 81.64, 78.86, 77.43, 75.80, 75.64, 74.55, 73.82, 71.46, 70.20, 70.17, 68.18, 44.65, 34.22.



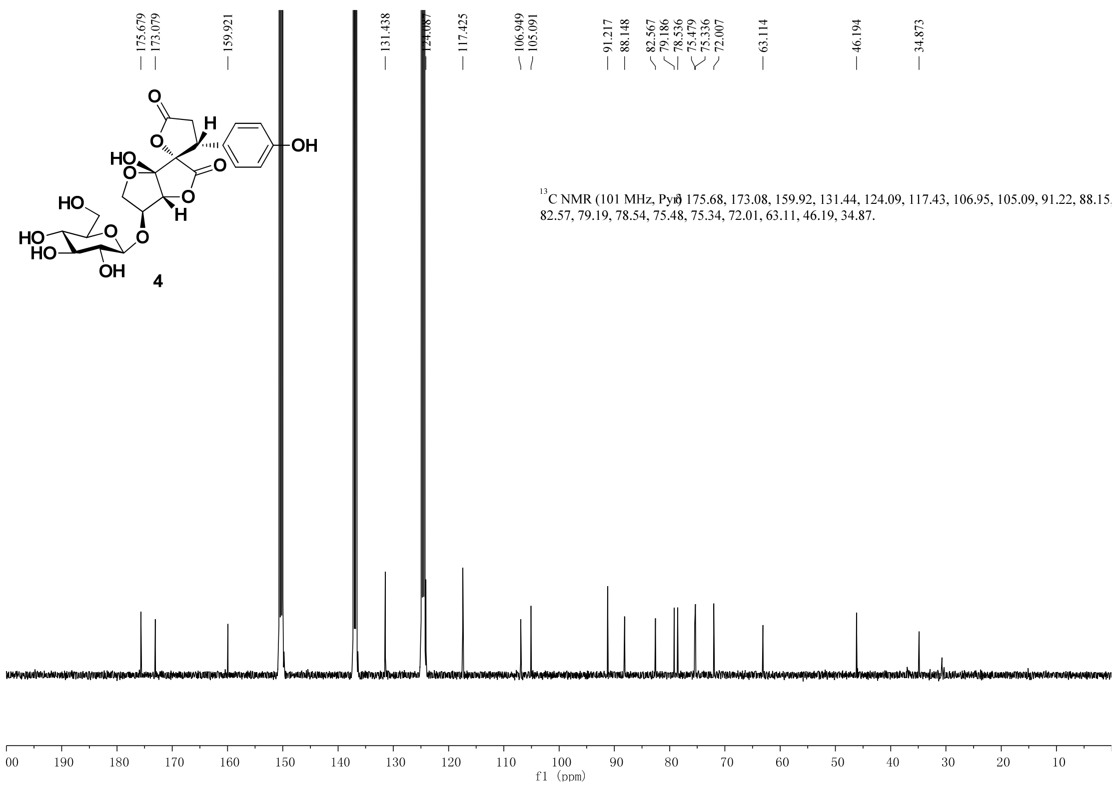
^{13}C NMR Spectrum for **20a** (400 MHz, $CDCl_3$)



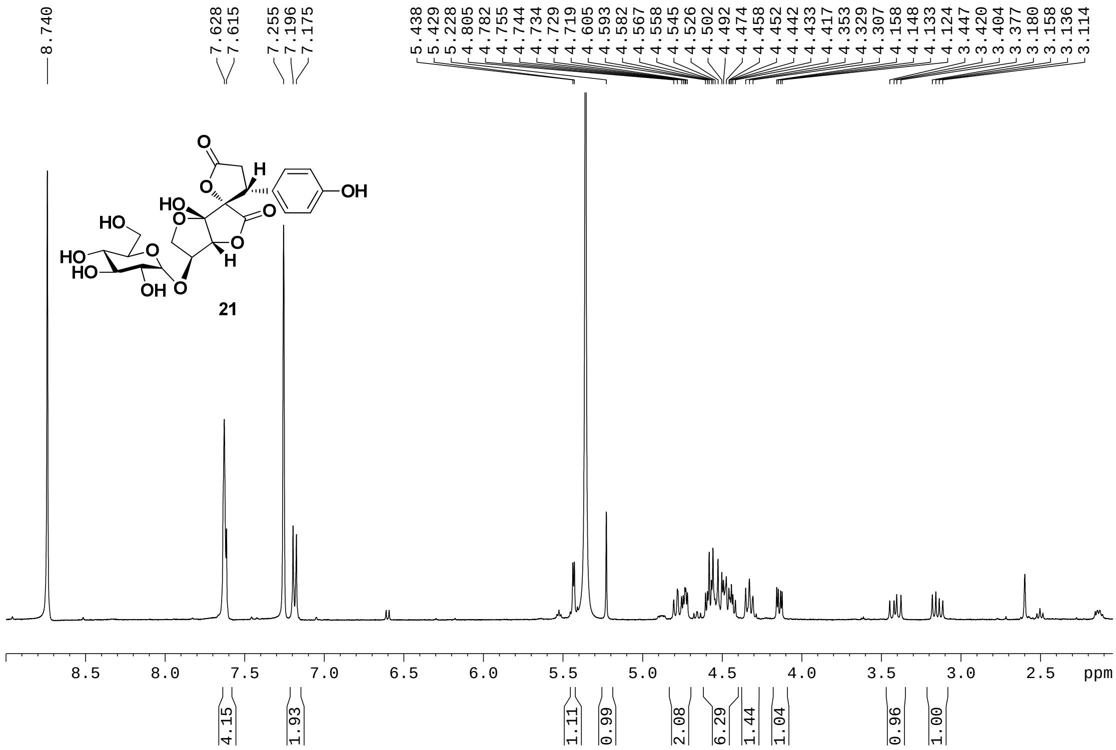
HMBC Spectrum for **20a** (400 MHz， $CDCl_3$)



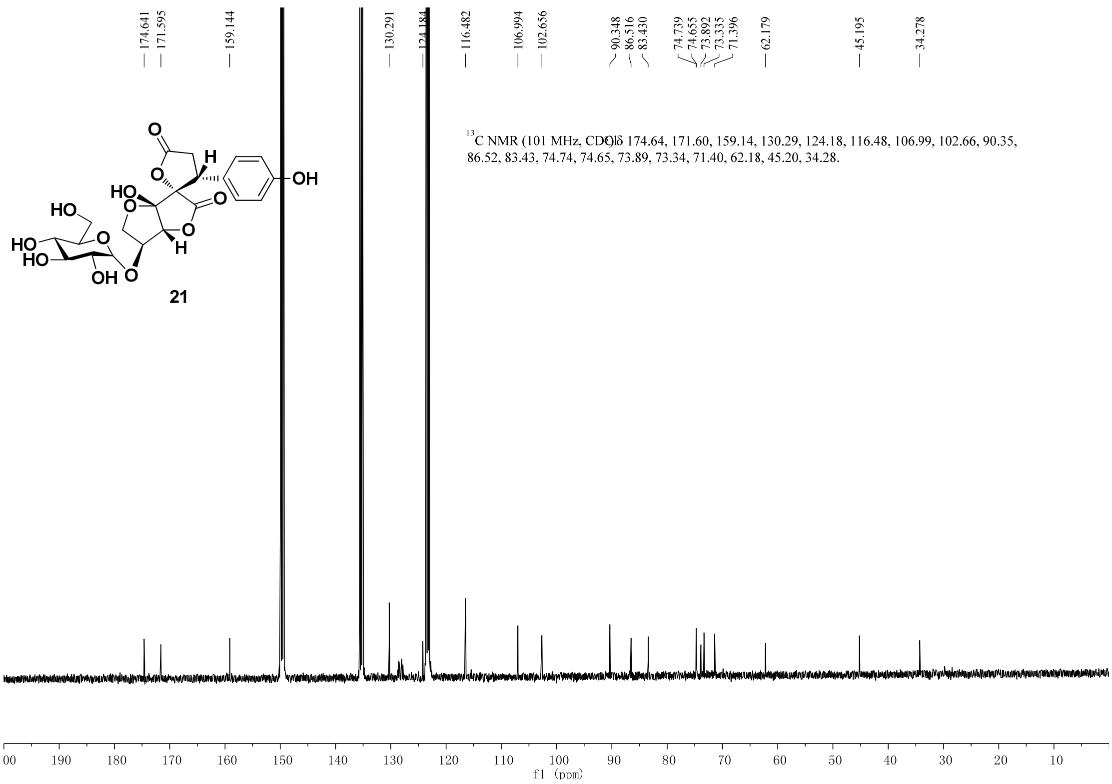
^{1}H NMR Spectrum for **4** (400 MHz，Pyridiene-D_5, Containing 1% D_2O)



^{13}C NMR Spectrum for **4** (400 MHz，Pyridiene-D_5, Containing 1% D_2O)



^{1}H NMR Spectrum for **21** (400 MHz，Pyridiene-D_5, Containing 1% D_2O)



^{13}C NMR Spectrum for **21** (400 MHz，Pyridiene-D_5, Containing 1% D_2O)

Part 6: X-ray Cryatallographic Studies for 12j

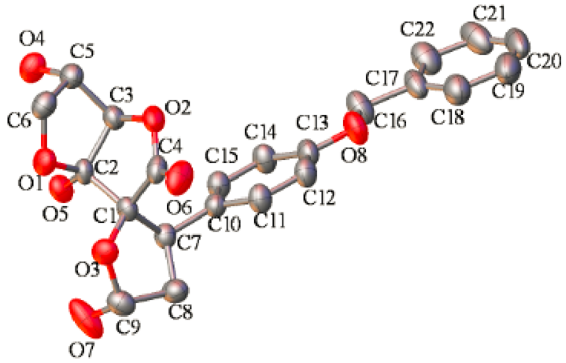


Table 1. Crystal data and structure refinement for 12j

Identification code	12j
Empirical formula	C22 H22 O8
Formula weight	414.40
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 6.690(2) A alpha = 90 deg.
	b = 7.080(2) A beta = 95.955(5) deg.
	c = 20.692(6) A gamma = 90 deg.
Volume	974.7(5) A^3
Z, Calculated density	2, 1.412 Mg/m^3
Absorption coefficient	0.108 mm^-1
F(000)	436
Crystal size	0.50 x 0.38 x 0.09 mm
Theta range for data collection	2.97 to 27.46 deg.
Limiting indices	-7<=h<=8, -9<=k<=9, -22<=l<=26
Reflections collected / unique	7441 / 2407 [R(int) = 0.0419]
Completeness to theta = 27.46	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6044
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2407 / 2 / 272
Goodness-of-fit on F^2	1.119
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.0973
R indices (all data)	R1 = 0.0498, wR2 = 0.0992
Absolute structure parameter	10(10)
Largest diff. peak and hole	0.171 and -0.160 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 12j.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	7592(3)	4635(3)	9526(1)	47(1)
O(2)	6632(3)	5467(3)	8148(1)	48(1)
O(3)	10373(3)	2581(3)	8968(1)	44(1)
O(4)	3238(3)	5358(4)	9439(1)	50(1)
O(5)	5896(3)	1811(3)	9287(1)	45(1)
O(6)	9907(4)	5445(4)	8003(1)	60(1)
O(7)	10294(4)	-602(4)	9247(1)	75(1)
O(8)	3847(3)	1929(4)	5638(1)	59(1)
C(1)	8480(4)	2893(4)	8601(1)	35(1)
C(2)	6809(4)	3359(4)	9031(1)	36(1)
C(3)	5344(4)	4550(4)	8584(1)	38(1)
C(4)	8518(5)	4707(5)	8219(1)	43(1)
C(5)	4657(4)	6068(5)	9031(1)	44(1)
C(6)	6589(4)	6460(5)	9452(1)	44(1)
C(7)	8073(4)	1123(4)	8154(1)	36(1)
C(8)	10194(4)	322(5)	8153(1)	47(1)
C(9)	11074(4)	696(5)	8841(2)	46(1)
C(10)	6934(4)	1402(4)	7489(1)	37(1)
C(11)	7753(4)	2302(5)	6976(1)	46(1)
C(12)	6683(5)	2455(5)	6372(1)	47(1)
C(13)	4758(5)	1704(5)	6262(1)	45(1)
C(14)	3913(4)	821(5)	6758(1)	48(1)
C(15)	5014(4)	679(5)	7366(1)	43(1)
C(16)	1898(5)	1172(6)	5500(2)	61(1)
C(17)	1169(6)	1457(5)	4788(1)	55(1)
C(18)	2398(6)	2139(6)	4345(2)	65(1)
C(19)	1650(7)	2337(7)	3691(2)	76(1)
C(20)	-281(7)	1797(6)	3492(2)	73(1)
C(21)	-1490(7)	1126(6)	3929(2)	75(1)
C(22)	-776(6)	965(6)	4578(2)	66(1)

Table 3. Bond lengths [A] and angles [deg] for 12j.

O(1)-C(2)	1.425(3)
O(1)-C(6)	1.457(4)
O(2)-C(4)	1.366(4)
O(2)-C(3)	1.462(3)
O(3)-C(1)	1.424(3)
O(3)-C(9)	1.448(4)
O(4)-C(5)	1.426(4)
O(4)-H(4)	0.8400
O(5)-C(2)	1.386(3)
O(5)-H(5)	0.8400
O(6)-C(4)	1.193(4)
O(7)-C(9)	1.382(4)
O(7)-H(7)	0.8401
O(8)-C(13)	1.379(3)
O(8)-C(16)	1.412(4)
C(1)-C(4)	1.510(4)
C(1)-C(2)	1.535(4)
C(1)-C(7)	1.565(4)
C(2)-C(3)	1.530(4)
C(3)-C(5)	1.520(4)
C(3)-H(3)	1.0000
C(5)-C(6)	1.507(4)
C(5)-H(5A)	1.0000
C(6)-H(6B)	0.9900
C(6)-H(6A)	0.9900
C(7)-C(10)	1.515(4)
C(7)-C(8)	1.528(4)
C(7)-H(7A)	1.0000
C(8)-C(9)	1.508(4)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9)	1.0000
C(10)-C(15)	1.382(4)
C(10)-C(11)	1.398(4)
C(11)-C(12)	1.380(4)
C(11)-H(11)	0.9500
C(12)-C(13)	1.390(4)
C(12)-H(12)	0.9500
C(13)-C(14)	1.373(4)

C(14)-C(15)	1.393(4)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(16)-C(17)	1.517(4)
C(16)-H(16B)	0.9900
C(16)-H(16A)	0.9900
C(17)-C(22)	1.373(5)
C(17)-C(18)	1.381(5)
C(18)-C(19)	1.399(5)
C(18)-H(18)	0.9500
C(19)-C(20)	1.369(6)
C(19)-H(19)	0.9500
C(20)-C(21)	1.360(6)
C(20)-H(20)	0.9500
C(21)-C(22)	1.382(5)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(2)-O(1)-C(6)	110.8(2)
C(4)-O(2)-C(3)	110.8(2)
C(1)-O(3)-C(9)	109.5(2)
C(5)-O(4)-H(4)	109.5
C(2)-O(5)-H(5)	106.3
C(9)-O(7)-H(7)	116.2
C(13)-O(8)-C(16)	117.0(2)
O(3)-C(1)-C(4)	110.4(2)
O(3)-C(1)-C(2)	112.7(2)
C(4)-C(1)-C(2)	100.0(2)
O(3)-C(1)-C(7)	106.4(2)
C(4)-C(1)-C(7)	112.5(2)
C(2)-C(1)-C(7)	115.0(2)
O(5)-C(2)-O(1)	111.7(2)
O(5)-C(2)-C(3)	112.7(2)
O(1)-C(2)-C(3)	104.5(2)
O(5)-C(2)-C(1)	115.3(2)
O(1)-C(2)-C(1)	108.5(2)
C(3)-C(2)-C(1)	103.2(2)
O(2)-C(3)-C(5)	107.2(2)
O(2)-C(3)-C(2)	103.6(2)
C(5)-C(3)-C(2)	103.7(2)
O(2)-C(3)-H(3)	113.8
C(5)-C(3)-H(3)	113.8
C(2)-C(3)-H(3)	113.8
O(6)-C(4)-O(2)	122.3(3)

O(6)-C(4)-C(1)	128.7(3)
O(2)-C(4)-C(1)	109.1(2)
O(4)-C(5)-C(6)	107.8(2)
O(4)-C(5)-C(3)	111.9(3)
C(6)-C(5)-C(3)	100.8(2)
O(4)-C(5)-H(5A)	111.9
C(6)-C(5)-H(5A)	111.9
C(3)-C(5)-H(5A)	111.9
O(1)-C(6)-C(5)	104.8(2)
O(1)-C(6)-H(6B)	110.8
C(5)-C(6)-H(6B)	110.8
O(1)-C(6)-H(6A)	110.8
C(5)-C(6)-H(6A)	110.8
H(6B)-C(6)-H(6A)	108.9
C(10)-C(7)-C(8)	115.3(2)
C(10)-C(7)-C(1)	118.2(2)
C(8)-C(7)-C(1)	101.1(2)
C(10)-C(7)-H(7A)	107.2
C(8)-C(7)-H(7A)	107.2
C(1)-C(7)-H(7A)	107.2
C(9)-C(8)-C(7)	101.8(2)
C(9)-C(8)-H(8A)	111.4
C(7)-C(8)-H(8A)	111.4
C(9)-C(8)-H(8B)	111.4
C(7)-C(8)-H(8B)	111.4
H(8A)-C(8)-H(8B)	109.3
O(7)-C(9)-O(3)	110.7(3)
O(7)-C(9)-C(8)	108.8(3)
O(3)-C(9)-C(8)	103.3(2)
O(7)-C(9)-H(9)	111.2
O(3)-C(9)-H(9)	111.2
C(8)-C(9)-H(9)	111.2
C(15)-C(10)-C(11)	117.3(2)
C(15)-C(10)-C(7)	119.3(2)
C(11)-C(10)-C(7)	123.3(2)
C(12)-C(11)-C(10)	121.1(3)
C(12)-C(11)-H(11)	119.4
C(10)-C(11)-H(11)	119.4
C(11)-C(12)-C(13)	120.2(3)
C(11)-C(12)-H(12)	119.9
C(13)-C(12)-H(12)	119.9
C(14)-C(13)-O(8)	125.2(3)
C(14)-C(13)-C(12)	119.9(2)
O(8)-C(13)-C(12)	114.9(3)

C(13)-C(14)-C(15)	119.2(3)
C(13)-C(14)-H(14)	120.4
C(15)-C(14)-H(14)	120.4
C(10)-C(15)-C(14)	122.3(3)
C(10)-C(15)-H(15)	118.9
C(14)-C(15)-H(15)	118.9
O(8)-C(16)-C(17)	110.0(3)
O(8)-C(16)-H(16B)	109.7
C(17)-C(16)-H(16B)	109.7
O(8)-C(16)-H(16A)	109.7
C(17)-C(16)-H(16A)	109.7
H(16B)-C(16)-H(16A)	108.2
C(22)-C(17)-C(18)	119.2(3)
C(22)-C(17)-C(16)	118.2(3)
C(18)-C(17)-C(16)	122.5(3)
C(17)-C(18)-C(19)	119.9(4)
C(17)-C(18)-H(18)	120.0
C(19)-C(18)-H(18)	120.0
C(20)-C(19)-C(18)	119.7(4)
C(20)-C(19)-H(19)	120.2
C(18)-C(19)-H(19)	120.2
C(21)-C(20)-C(19)	120.3(3)
C(21)-C(20)-H(20)	119.8
C(19)-C(20)-H(20)	119.8
C(20)-C(21)-C(22)	120.3(4)
C(20)-C(21)-H(21)	119.8
C(22)-C(21)-H(21)	119.8
C(17)-C(22)-C(21)	120.5(4)
C(17)-C(22)-H(22)	119.8
C(21)-C(22)-H(22)	119.8

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 12j.
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)	56(1)	35(1)	-13(1)	-4(1)	-1(1)
O(2)	67(1)	42(1)	34(1)	5(1)	8(1)	5(1)
O(3)	37(1)	49(1)	45(1)	-7(1)	-5(1)	-4(1)
O(4)	42(1)	60(2)	50(1)	-11(1)	5(1)	-8(1)
O(5)	44(1)	50(1)	40(1)	10(1)	5(1)	-5(1)
O(6)	79(2)	50(1)	57(1)	-3(1)	31(1)	-19(1)
O(7)	79(2)	75(2)	62(2)	31(2)	-29(1)	-35(2)
O(8)	67(1)	70(2)	36(1)	6(1)	-9(1)	-8(1)
C(1)	37(1)	38(2)	29(1)	-1(1)	-2(1)	-4(1)
C(2)	41(1)	42(2)	26(1)	-1(1)	2(1)	-5(1)
C(3)	44(1)	40(2)	30(1)	1(1)	-1(1)	0(1)
C(4)	60(2)	40(2)	31(1)	-5(1)	11(1)	-6(2)
C(5)	50(2)	42(2)	38(1)	-4(1)	2(1)	3(1)
C(6)	45(2)	44(2)	45(2)	-10(1)	9(1)	-6(1)
C(7)	41(1)	36(1)	32(1)	-2(1)	3(1)	-6(1)
C(8)	48(2)	43(2)	48(2)	-5(2)	1(1)	6(2)
C(9)	41(2)	44(2)	52(2)	4(2)	-5(1)	-4(1)
C(10)	42(1)	38(2)	32(1)	-2(1)	4(1)	0(1)
C(11)	49(2)	51(2)	37(1)	1(1)	5(1)	-10(2)
C(12)	59(2)	49(2)	34(1)	3(1)	7(1)	-7(2)
C(13)	59(2)	46(2)	30(1)	-1(1)	-2(1)	0(2)
C(14)	45(2)	59(2)	40(1)	0(2)	-1(1)	-8(2)
C(15)	46(2)	48(2)	36(1)	1(1)	4(1)	-7(1)
C(16)	77(2)	57(2)	44(2)	9(2)	-12(2)	-13(2)
C(17)	85(2)	42(2)	35(1)	2(2)	-9(2)	2(2)
C(18)	81(2)	62(2)	49(2)	-3(2)	1(2)	5(2)
C(19)	113(3)	67(3)	49(2)	5(2)	17(2)	18(3)
C(20)	123(4)	55(2)	36(2)	-5(2)	-11(2)	21(2)
C(21)	105(3)	53(2)	60(2)	-3(2)	-31(2)	-1(2)
C(22)	87(3)	51(2)	57(2)	7(2)	-9(2)	-10(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 12j.

	x	y	z	U(eq)
H(4)	2314	4790	9212	76
H(5)	6696	1422	9598	67
H(7)	10880	-682	9625	112
H(3)	4216	3806	8353	46
H(5A)	4143	7214	8784	52
H(6B)	7424	7379	9239	53
H(6A)	6312	6970	9879	53
H(7A)	7288	204	8394	44
H(8A)	10165	-1046	8054	56
H(8B)	10954	989	7836	56
H(9)	12575	640	8882	56
H(11)	9070	2818	7045	55
H(12)	7263	3076	6029	57
H(14)	2594	313	6688	58
H(15)	4424	64	7707	52
H(16B)	966	1803	5773	73
H(16A)	1917	-194	5604	73
H(18)	3749	2474	4483	78
H(19)	2478	2844	3388	91
H(20)	-778	1891	3046	87
H(21)	-2833	765	3787	90
H(22)	-1637	511	4880	79

Table 6. Torsion angles [deg] for 12j.

C(9)-O(3)-C(1)-C(4)	-128.5(2)
C(9)-O(3)-C(1)-C(2)	120.6(3)
C(9)-O(3)-C(1)-C(7)	-6.2(3)
C(6)-O(1)-C(2)-O(5)	-117.0(2)
C(6)-O(1)-C(2)-C(3)	5.2(3)
C(6)-O(1)-C(2)-C(1)	114.8(2)
O(3)-C(1)-C(2)-O(5)	-84.0(3)
C(4)-C(1)-C(2)-O(5)	158.9(2)
C(7)-C(1)-C(2)-O(5)	38.2(3)
O(3)-C(1)-C(2)-O(1)	42.2(3)
C(4)-C(1)-C(2)-O(1)	-74.9(2)
C(7)-C(1)-C(2)-O(1)	164.4(2)
O(3)-C(1)-C(2)-C(3)	152.7(2)
C(4)-C(1)-C(2)-C(3)	35.5(3)
C(7)-C(1)-C(2)-C(3)	-85.2(3)
C(4)-O(2)-C(3)-C(5)	119.7(2)
C(4)-O(2)-C(3)-C(2)	10.4(3)
O(5)-C(2)-C(3)-O(2)	-154.2(2)
O(1)-C(2)-C(3)-O(2)	84.3(2)
C(1)-C(2)-C(3)-O(2)	-29.1(3)
O(5)-C(2)-C(3)-C(5)	93.9(3)
O(1)-C(2)-C(3)-C(5)	-27.6(3)
C(1)-C(2)-C(3)-C(5)	-141.0(2)
C(3)-O(2)-C(4)-O(6)	-166.3(3)
C(3)-O(2)-C(4)-C(1)	13.4(3)
O(3)-C(1)-C(4)-O(6)	29.9(4)
C(2)-C(1)-C(4)-O(6)	148.7(3)
C(7)-C(1)-C(4)-O(6)	-88.8(4)
O(3)-C(1)-C(4)-O(2)	-149.7(2)
C(2)-C(1)-C(4)-O(2)	-30.8(3)
C(7)-C(1)-C(4)-O(2)	91.6(3)
O(2)-C(3)-C(5)-O(4)	174.7(2)
C(2)-C(3)-C(5)-O(4)	-76.1(3)
O(2)-C(3)-C(5)-C(6)	-71.0(3)
C(2)-C(3)-C(5)-C(6)	38.3(3)
C(2)-O(1)-C(6)-C(5)	19.4(3)
O(4)-C(5)-C(6)-O(1)	82.1(3)
C(3)-C(5)-C(6)-O(1)	-35.3(3)
O(3)-C(1)-C(7)-C(10)	-146.7(2)
C(4)-C(1)-C(7)-C(10)	-25.7(3)
C(2)-C(1)-C(7)-C(10)	87.9(3)

O(3)-C(1)-C(7)-C(8)	-19.8(3)
C(4)-C(1)-C(7)-C(8)	101.1(3)
C(2)-C(1)-C(7)-C(8)	-145.3(2)
C(10)-C(7)-C(8)-C(9)	165.8(3)
C(1)-C(7)-C(8)-C(9)	37.1(3)
C(1)-O(3)-C(9)-O(7)	-85.9(3)
C(1)-O(3)-C(9)-C(8)	30.4(3)
C(7)-C(8)-C(9)-O(7)	75.7(3)
C(7)-C(8)-C(9)-O(3)	-42.0(3)
C(8)-C(7)-C(10)-C(15)	129.2(3)
C(1)-C(7)-C(10)-C(15)	-111.0(3)
C(8)-C(7)-C(10)-C(11)	-48.2(4)
C(1)-C(7)-C(10)-C(11)	71.5(4)
C(15)-C(10)-C(11)-C(12)	-0.1(5)
C(7)-C(10)-C(11)-C(12)	177.4(3)
C(10)-C(11)-C(12)-C(13)	-0.2(5)
C(16)-O(8)-C(13)-C(14)	-0.7(5)
C(16)-O(8)-C(13)-C(12)	179.3(3)
C(11)-C(12)-C(13)-C(14)	0.6(5)
C(11)-C(12)-C(13)-O(8)	-179.4(3)
O(8)-C(13)-C(14)-C(15)	179.5(3)
C(12)-C(13)-C(14)-C(15)	-0.5(5)
C(11)-C(10)-C(15)-C(14)	0.2(5)
C(7)-C(10)-C(15)-C(14)	-177.4(3)
C(13)-C(14)-C(15)-C(10)	0.2(5)
C(13)-O(8)-C(16)-C(17)	-177.1(3)
O(8)-C(16)-C(17)-C(22)	-174.0(3)
O(8)-C(16)-C(17)-C(18)	7.7(5)
C(22)-C(17)-C(18)-C(19)	0.6(6)
C(16)-C(17)-C(18)-C(19)	178.8(4)
C(17)-C(18)-C(19)-C(20)	-2.0(6)
C(18)-C(19)-C(20)-C(21)	2.1(7)
C(19)-C(20)-C(21)-C(22)	-0.7(7)
C(18)-C(17)-C(22)-C(21)	0.9(6)
C(16)-C(17)-C(22)-C(21)	-177.4(4)
C(20)-C(21)-C(22)-C(17)	-0.8(6)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 12j [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)