Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Zinc and indium-mediated Barbier-type allylation of aldehydes with 3-bromomethyl-5*H*-furan-2-one: an efficient synthesis of α-methylene-γ-butyrolactone

YuZhe Gao, Xue Wang, LongGuan Xie and XiaoHua Xu*

State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China.

xiaohuaxu@nankai.edu.cn; Fax:+88 22 23504284

CONTENTS

1-General details

Unless otherwise noted, all commercial materials were used as received. Et $_2$O, THF were distilled over sodium under nitrogen, CH_2Cl_2 was distilled over sodium hydride under nitrogen. IR spectra were recorded as thin films or KBr discs, using a MAGNA-560 FTIR spectrophotometer. NMR spectra were recorded on Bruker spectrometer at 400 or 300 (^{1}H NMR), 100 or 75 (^{13}C NMR) MHz with $CDCl_3$ as solvent. Data are expressed as chemical shifts in parts per million (ppm) relative to residual chloroform (^{1} H δ 7.27), $CDCl_3$ (^{13}C δ 77.0) as the internal standard on the δ scale. The multiplicity of each signal is designated by the following abbreviations; s, singlet; d, doublet; t, triplet; br, broad. Allylation diastereoselectivity was determined by 1 H-NMR integrations of the methylene signals. Melting points were measured on X4 apparatus and uncorrected. High-resolution mass Spectra were conducted using an Ionspec 7.0T spectrometer by ESI-FTICR technique.

2-Procedure A: Allylation using indium

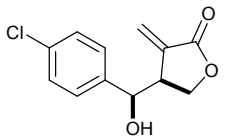
to a reaction vessel were added sequentially aldehyde (1 mmol), 3-bromomethyl-5*H*-furan-2-one (1.5 mmol), water (1.0 ml) and indium powder (2 mmol). the mixture was stirred vigorously at rt. After 12h the reaction mixture was filterated by diatomite, extracted with diethyl ether (20 ml × 3), washed with brine (20 mL), and dried over anhydrous Na_2SO_4. Evaporation under reduced pressure gave a residue which was chromatographed.

3-Procedure B: Allylation using zinc

to a reaction vessel were added sequentially aldehyde (1 mmol), 3-bromomethyl-5*H*-furan-2-one (1.5 mmol), THF (1 ml), saturated aqueous NH_4Cl (0.5 ml) and activated zinc powder (1.7 mmol). The mixture was stirred for 15 minetes at rt and filterated by diatomite. Extracted with diethyl ether (20 ml × 3), washed with brine (20 ml) and dried over anhydrous Na_2SO_4. Evaporation under reduced pressure gave a residue which was chromatographed.

4-Characterization data for lactones 2a-2i

4-(4-Chlorophenyl)(hydroxy)methyl-3-methylenedihydrofuran-2(3H)-one (2a)



Following procedure A, using 4-chlorobenzaldehyde (135mg, 0.96 mmol), afforded the above alcohol 2a (214mg, 93%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36 (d, *J*=1.9 Hz, 1H), 7.35 (t, *J*=2.3Hz, 1H), 7.29 (d, *J*=2.0Hz, 1H), 7.27 (d, *J*=4.2Hz, 1H), 6.32(d, *J*=2.3Hz, 1H), 5.69 (d, *J*=1.8Hz, 1H), 4.73 (d, *J*=7.1Hz, 1H), 4.21(dd, *J*=8.2, 9.6Hz, 1H), 4.10(dd, *J*=4.1, 9.6Hz, 1H), 3.33-3.39(m, 1H), 2.81(br s, 1H).

Discernable data for minor diastereoisomer: 6.20(d, *J*=2.4Hz, 1H), 5.08(d, *J*=2.1Hz, 1H), 4.54(dd, *J*=9.6, 3.9Hz, 1H), 4.35(dd, *J*=9.6, 7.9Hz, 1H).

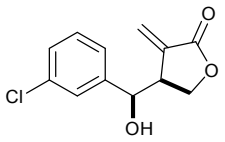
^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.8, 139.1, 134.5, 134.3, 128.9, 127.9, 125.6, 74.8, 67.6, 45.4.

IR (neat), ν (cm^{-1}) 3457, 1759, 1660, 1272, 1132, 822.

HRMS (ESI): M+Na^+ found 260.0291, $C_{12}H_{11}ClO_3Na$ requires 261.0297.

Following procedure B, using 4-chlorobenzaldehyde (141mg, 1.00 mmol), afforded the above alcohol 2a (216mg, 90%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

(2) Synthesis of 4-(3-Chlorophenyl) (hydroxy) methyl)-3-methylenedihydrofuran-2(3H)-one (2b)



Following procedure A, using 3-chlorobenzaldehyde (139mg, 0.99mmol), afforded the above alcohol 2b (212mg, 90%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35(s, 1H), 7.29-7.31(m, 2H), 7.18-7.23(m, 1H), 6.31(d, *J*=2.2Hz, 1H), 5.67(d, *J*=1.8, 1H), 4.72(d, *J*=7.1Hz, 1H), 4.23(t, *J*=9.5Hz, 1H), 4.12(dd, *J*=9.6, 4.1Hz, 1H), 3.33-3.40(m, 1H), 2.91(s, 1H).

Discernable data for minor diastereoisomer: 6.22(d, *J*=2.2Hz, 1H), 5.12(d, *J*=2.1Hz, 1H), 4.54(dd, *J*=9.6, 3.9Hz, 1H), 4.34(t, *J*=8.1Hz, 1H).

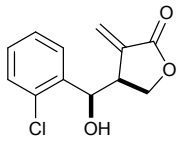
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 142.8, 134.8, 134.4, 130.0, 128.6, 125.8, 124.8, 67.7, 45.4.

IR (neat), ν (cm^{-1}) 3455, 1758, 1659, 1274, 1138, 807.

HRMS (ESI): $M+Na^+$ found 261.0289, $C_{12}H_{11}ClO_3Na$ requires 261.0297.

The reaction of 1b(140mg, 1.00mmol), 3-bromomethyl-5*H*-furan-2-one (262mg, 1.49mmol), activated zinc powder (106mg, 166mmol), THF (1 ml), and saturated aqueous NH_4Cl (0.5 ml) at rt for 15 min afforded 2b (219mg, 92%).

4-(2-Chlorophenyl)(hydroxy)methyl)-3-methylenedihydrofuran-2(3H)-one (2c)



Following procedure A, using 2-chlorobenzaldehyde (138mg, 0.99mmol), afforded the above alcohol 2c (226mg, 96%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

mp: 94-108 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50(dd, J=7.5, 1.9Hz, 1H), 7.40(dd, J=7.5, 1.7Hz, 1H), 7.27-7.34(m, 2H), 6.27(d, J=2.2Hz, 1H), 5.28(d, J=3.6Hz, 1H), 5.27(s, 1H), 4.37(t, J=9.3Hz, 1H), 4.32(dd, J=9.4, 3.9Hz, 1H), 3.46-3.52(m, 1H), 2.67(br s, 1H).

Discernable data for minor diastereoisomer: 7.62(dd, J=7.7, 1.7Hz, 1H), 7.14-7.19(m, 3H), 6.31(d, J=2.5Hz, 1H), 5.59(s, 1H), 5.46(d, J=4.0Hz, 1H), 4.55(dd, J=9.5, 4.1Hz, 1H), 4.21(t, J=8.3Hz, 1H).

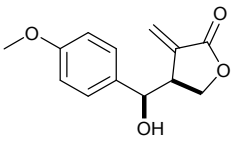
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 138.0, 133.8, 131.9, 129.6, 129.4, 128.5, 127.1, 125.6, 71.9, 68.6, 43.6.

IR (neat), ν (cm-1) 3453, 1742, 1659, 1274, 1141, 768.

HRMS (ESI): $M+Na^+$ found 260.0289, $C_{12}H_{11}ClO_3Na$ requires 261.0297.

Following procedure B, using 2-chlorobenzaldehyde (135mg, 0.96mmol), afforded the above alcohol 2c (212mg, 92%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

4-(4-Methoxyphenyl)(hydroxy)methyl)-3-methylenedihydrofuran-2(3H)-one (2d)



Following procedure A, using 4-methoxybenzaldehyde (140mg, 1.03mmol), afforded the above alcohol 2d (215mg, 89%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26(d, J=8.2Hz, 2H), 6.91(d, J=8.7Hz, 2H), 6.36(d, J=2.2Hz, 1H), 5.85(d, J=1.6Hz, 1H), 4.65(d, J=7.9Hz, 1H), 4.16(dd, J=8.4, 9.5Hz, 1H), 4.02(dd, J=4.5, 9.6Hz, 1H), 3.81(s, 3H), 3.36-3.42(m, 1H), 2.40(br s, 1H).

Discernable data for minor diastereoisomer: 7.84(d, J=8.8Hz, 2H), 7.02(d, J=8.7Hz, 2H), 6.17(d, J=2.4Hz, 1H),

4.97(d, J=2.0Hz, 1H), 4.40(dd, J=9.4, 7.9Hz, 1H), 4.31(t, J=6.7Hz, 1H), 3.89(s, 3H).

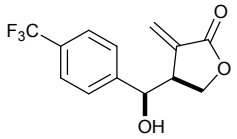
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 159.8, 135.2, 132.8, 127.8, 125.4, 114.2, 75.3, 67.5, 55.3, 45.5.

IR (neat), ν (cm-1) 3454, 1759, 1658, 1465, 1250, 1120, 819.

HRMS (ESI): M+ Na^+ found 257.0787, $C_{13}H_{14}O_4Na$ required 257.0792.

Following procedure B, using 4-methoxybenzaldehyde (134mg, 0.98mmol), afforded the above alcohol 2d (215mg, 93%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

4-(4-Trifluoromethylphenyl)(hydroxy)methyl)-3-methylenedihydrofuran-2(3H)-one (2e)



Following procedure A, using 4-trifluoromethylbenzaldehyde (170mg, 0.98mmol), afforded the above alcohol 2e (242mg, 91%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

mp: 76 - 90 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69(d, J=8.1Hz, 2H), 7.52(d, J=8.1Hz, 2H), 6.39(d, J=2.1Hz, 1H), 5.69(d, J=1.7Hz, 1H), 4.87(d, J=7.0Hz, 1H), 4.28(t, J=9.6Hz, 1H), 4.18(dd, J=9.6, 3.9Hz, 1H), 3.41-3.46(m, 1H), 2.62(br s, 1H).

Discernable data for minor diastereoisomer: 8.14(d, J=7.9Hz, 2H), 7.80(d, J=8.1Hz, 2H), 6.29(d, J=2.4Hz, 1H), 5.98(s, 1H), 5.17(d, J=2.0Hz, 1H).

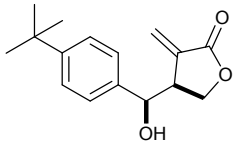
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 144.5, 134.4, 127.0, 125.8, 125.77, 125.73, 75.0, 67.5, 45.5.

IR (neat), ν (cm-1) 3466, 1735, 1662, 1276, 1124, 828.

HRMS (ESI): M+Na^+ found 295.0546, $C_{13}H_{11}O_3F_3Na$ required 295.1560.

Following procedure B, using 4-trifluoromethylbenzaldehyde (176mg, 1.01mmol), afforded the above alcohol 2e (251mg, 91%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

4-(4-Tert-butylphenyl)(hydroxy)methyl)-3-methylenedihydrofuran-2(3H)-one (2f)



Following procedure A, using 4-tert-butylbenzaldehyde (161mg, 0.99mmol), afforded the above alcohol 2f (233mg, 90%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.43(d, J=8.3Hz, 2H), 7.29(d, J=8.8Hz, 2H), 6.39(d, J=2.0Hz, 1H), 5.89(d, J=1.4Hz, 1H), 4.68(d, J=8.1Hz, 1H), 4.18(t, J=9.5Hz, 1H), 4.04(dd, J=9.6, 4.5Hz, 1H), 3.41-3.46(m, 1H), 2.17(br s, 1H), 1.33(s, 3H).

Discernable data for minor diastereoisomer: 7.73-7.71(m, 2H), 7.55(dd, J=6.1, 2.9Hz, 2H), 6.22(d, J=2.4Hz, 1H), 5.84(d, J=1.8Hz, 1H), 5.04(d, J=2.0Hz, 1H), 4.42(dd, J=9.4, 8.1Hz, 1H), 4.33(t, J=6.8Hz, 1H).

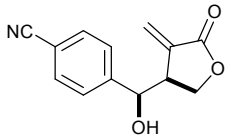
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 150.9, 136.6, 134.2, 125.3, 124.8, 124.4, 74.5, 66.5, 44.4, 33.6, 30.3.

IR (neat), ν (cm-1) 3305, 1764, 1656, 1286, 1124, 837.

HRMS (ESI): M+Na^+ found 283.1309, $C_{16}H_{20}O_3Na$ requied 283.1310.

Following procedure B, using 4-tert-butylbenzaldehyde (176mg, 1.09mmol), afforded the above alcohol 2f (234mg, 88%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

4-(4-cyanophenyl) (hydroxy) methyl)-3-methylenedihydrofuran-2(3H)-one (2g)



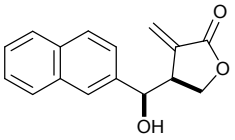
Following procedure A, using 4-cyanobenzaldehyde (134mg, 1.02mmol), afforded the above alcohol 2g (204mg, 87%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71(d, *J*=8.0Hz, 2H), 7.51(d, *J*=8.1Hz, 2H), 6.37(s, 1H), 5.61(s, 1H), 4.88(d, *J*=6.6Hz, 1H), 4.29(t, *J*=9.4Hz, 1H), 4.19(dd, *J*=3.6, 9.6Hz, 1H), 3.4(s, 1H), 2.48(br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 145.5, 134.0, 132.5, 127.6, 127.2, 125.7, 118.2, 112.4, 74.8, 67.2, 45.3.

Following procedure B, using 4-cyanobenzaldehyde (129mg, 0.98mmol), afforded the above alcohol 2f (221mg, 98%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

4-(Hydroxy(naphthalen-3-yl)methyl)-3-methylenedihydrofuran-2(3H)-one (2h)



Following procedure A, using β-nahpthaldehyde (160mg, 1.03mmol), afforded the above alcohol 2h (232mg, 89%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.86(m, 3H), 7.75(s, 1H), 7.50-7.52(m, 2H), 7.44(d, J=8.4Hz, 1H), 6.34(s, 1H), 5.75(s, 1H), 4.82(d, J=7.5Hz, 1H), 4.15(t, J=9.1Hz, 1H), 4.08(dd, J=9.3, 4.1Hz, 1H), 3.47(s, 1H), 2.66(br s, 1H).

Discernable data for minor diastereoisomer: 7.20(d, J=8.9Hz, 1H), 6.17(d, J=2.4Hz, 1H), 4.97(d, J=2.1Hz, 1H), 4.64(dd, J=9.7, 4.1Hz, 1H), 4.39(dd, J=9.4, 7.8Hz, 1H).

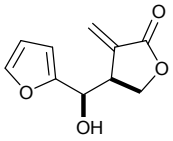
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 137.0, 133.9, 132.3, 132.0, 127.9, 127.0, 126.7, 125.6, 125.5, 124.9, 124.5, 122.9, 74.7, 66.7, 44.3.

IR (neat), ν (cm-1) 3443, 1759, 1658, 1273, 1123.

HRMS (ESI): $M+Na^+$ found 277.0828, $C_{16}H_{14}O_3Na$ required 277.0841.

Following procedure B, using β-nahpthaldehyde (153mg, 0.98mmol), afforded the above alcohol 2h (212mg, 85%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

4-(Hydroxy(furan-3-yl)methyl)-3-methylenedihydrofuran-2(3H)-one (2i)



Following procedure A, using 2-furaldehyde (101mg, 1.05mmol), afforded the above alcohol 2i (149mg, 73%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43(d, J=1.0Hz, 1H), 6.40(d, J=3.7Hz, 2H), 6.36(d, J=3.3Hz, 1H), 5.78(d, J=2.0Hz, 1H), 4.80(d, J=7.4Hz, 1H), 4.39(t, J=9.5Hz, 1H), 4.21(dd, J=9.6, 4.3Hz, 1H), 3.59-3.65(m, 1H), 2.67(br s, 1H).

Discernable data for minor diastereoisomer: 7.45(s, 1H), 6.28(d, J=2.5Hz, 1H), 5.24(d, J=2.2Hz, 1H), 4.77(d, J=7.6Hz, 1H), 4.58(dd, J=9.6, 4.3Hz, 1H), 4.49(t, J=8.1Hz, 1H).

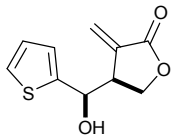
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 152.2, 141.8, 133.2, 124.7, 109.5, 107.2, 68.2, 66.4, 42.3.

IR (neat), ν (cm-1) 3418, 1755, 1660, 1274, 1123.

HRMS (ESI): M+Na^+ found 217.0470, $C_{10}H_{10}O_4Na$ required 2170.477.

Following procedure B, using 2-furaldehyde (98mg, 1.02mmol), afforded the above alcohol 2i (187mg, 94%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

4-(Hydroxy(thiophene-3-yl)methyl)-3-methylenedihydrofuran-2(3H)-one (2j)



Following procedure A, using 2-thiophenaldehyde (115mg, 1.03mmol), afforded the above alcohol 2j (184mg, 85%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32(dd, J=4.9, 1.1Hz, 1H), 6.98-7.02(m, 2H), 6.39(d, J=2.3Hz, 1H), 5.90(d, J=1.8Hz, 1H), 4.98(d, J=7.7Hz, 1H), 4.28(t, J=9.7Hz, 1H), 4.13(dd, J=9.7, 4.4Hz, 1H), 3.44-3.50(m, 1H), 2.75(br s, 1H).

Discernable data for minor diastereoisomer: 7.25(d,J=5.1Hz, 1H), 6.91(dd, J=4.9, 3.6Hz, 1H), 6.81(d, J=2.7Hz, 1H), 6.26(d, J=2.5Hz, 1H), 5.20(d, J=2.1Hz, 1H), 4.56(dd, J=9.8, 4.2Hz, 1H), 4.45(t, J=8.1Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 143.3, 133.6, 126.0, 124.9, 124.3, 70.6, 66.4, 44.9.

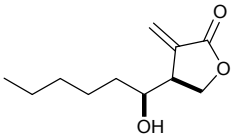
IR (neat), ν (cm-1) 3443, 1759, 1659, 1276, 1125.

HRMS (ESI): M+Na^+ found 233.0240, $C_{10}H_{10}O_3SNa$ required 233.0248.

Following procedure B, using 2-thiophenaldehyde (113mg, 1.01mmol), afforded the above alcohol 2j (197mg, 93%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

5- Characterization data for lactones 4a-4h

4-(1-Hydroxyhexyl)-3-methylenedihydrofuran-2(3H)-one (4a)



Following procedure A, using n-hexaldehyde (103mg, 1.03mmol), afforded the above alcohol 4a (192mg, 94%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31(d, J=2.0Hz, 1H), 5.75(d, J=1.6Hz, 1H), 4.36(dd, J=9.3, 8.2Hz, 1H), 4.20(dd, J=9.4, 3.7Hz, 1H), 3.64(dd, J=11.6, 5.9Hz, 1H), 3.04-3.09(m, 1H), 1.83(br s, 1H), 1.18-1.46(m, 8H), 0.85(t, J=6.5Hz, 3H).

Discernable data for minor diastereoisomer: 6.01(d, J=1.0Hz, 1H), 5.47(d, J=0.8Hz, 1H), 3.14-3.33(m, 1H).

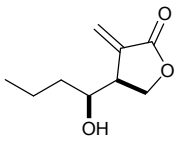
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 135.2, 124.6, 73.2, 68.1, 44.5, 33.5, 31.6, 25.4, 22.6, 14.0.

IR (neat), ν (cm-1) 3445, 1765, 1661, 1270, 1129.

HRMS (ESI): M+Na^+ found 221.1146, $C_{10}H_{18}O_3Na$ required 221.1154.

Following procedure B, using n-hexaldehyde (100mg, 1mmol), afforded the above alcohol 4a (193mg, 97%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

4-(1-Hydroxybutyl)-3-methylenedihydrofuran-2(3H)-one (4b)



Following procedure A, using butyraldehyde (80mg, 1.11mmol), afforded the above alcohol 4b (176mg, 93%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37(d, J=2.1Hz, 1H), 5.82(d, J=1.8Hz, 1H), 4.42(t,J=9.2Hz, 1H), 4.30(dd, J=9.4, 3.7Hz, 1H), 3.68-3.72(m, 1H), 3.13-3.15(m, 1H), 2.08(br s, 1H), 1.34-1.60(m, 4H), 0.97(t, J=7.2Hz, 3H).

Discernable data for minor diastereoisomer: 6.17(d, J=2.2Hz, 1H), 5.61(d, J=2.0Hz, 1H), 4.61(t, J=9.1Hz, 1H).

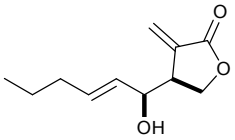
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 135.1, 124.6, 72.9, 68.1, 44.6, 35.6, 18.9, 13.9.

IR (neat), ν (cm-1) 3453, 1761, 1660, 1274, 1123.

HRMS (ESI): $M+Na^+$ found 193.0830, $C_9H_{14}O_3Na$ required 193.0841.

Following procedure B, using butyraldehyde (75mg, 1.04mmol), afforded the above alcohol 4b (170mg, 96%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

(E)-4-(1-Hydroxyhex-2-en-1-yl)-3-methylenedihydrofuran-2(3H)-one (4c)



Following procedure A, using (E)-2-hexenal (97mg, 0.99mmol), afforded the above alcohol 4c (162mg, 83%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38(d, J=2.2Hz, 1H), 5.88(d, J=1.8Hz, 1H), 5.74-5.82(m, 1H), 5.48(dd, J=15.4,7.3Hz, 1H), 4.37(t, J=9.4Hz, 1H), 4.26(dd, J=8.5, 4.1Hz, 1H), 4.20(t, J=7.0Hz, 1H), 3.21-3.25(m, 1H), 2.00-2.10(m, 2H), 1.99(br s, 1H), 1.37-1.47(m, 2H), 0.94(t, J=7.3Hz, 3H);

Discernable data for minor diastereoisomer: 6.17(d, J=2.3Hz, 1H), 5.93(d, J=1.8Hz, 1H).

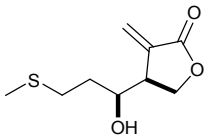
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 135.9, 135.2, 128.2, 124.6, 74.6, 67.3, 44.1, 34.3, 22.2, 13.6.

IR (neat), ν (cm-1) 3454, 1760, 1662, 1274, 1124.

HRMS (ESI): $M+Na^+$ found 219.0990, $C_{11}H_{16}O_3Na$ 219.0997.

Following procedure B, using (E)-2-hexenal (101mg, 1.03mmol), afforded the above alcohol 4c (192mg, 95%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

4-(3-Methylthio-1-hydroxypropyl)-3-methylenedihydrofuran-2(3H)-one (4d)



Following procedure A, using 3-(Methylthio)propionaldehyde (104mg, 1mmol), afforded the above alcohol 4d (162mg, 80%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38(d, J=2.1Hz, 1H), 5.83(d, J=1.7Hz, 1H), 4.44(t, J=9.4Hz, 1H), 4.31(dd, J=9.4, 3.6Hz, 1H), 3.87-3.93(m, 1H), 3.17-3.22(m, 1H), 2.71(t, J=6.7Hz, 2H), 2.52(br s, 1H), 2.12(s, 3H), 1.68-1.83(m, 2H);

Discernable data for minor diastereoisomer: 5.76(d, J=2.1Hz, 1H), 3.81-3.43(m, 1H), 2.35(br s, 1H).

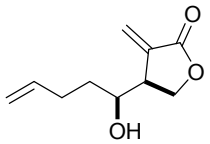
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 134.0, 123.8, 71.4, 66.8, 43.6, 30.6, 29.9, 14.4.

IR (neat), ν (cm-1) 3453, 1762, 1660, 1414, 1279, 1122.

HRMS (ESI): M+Na^+ found 225.0562, $C_9H_{14}O_3SNa$ required 225.0561.

Following procedure B, using 3-(Methylthio)propionaldehyde (107mg, 1.03mmol), afforded the above alcohol 4d (198mg, 95%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

4-(1-Hydroxypent-4-en-1-yl)-3-methylenedihydrofuran-2(3H)-one (4e)



Following procedure A, using 4-pentenal (90mg, 1.07mmol), afforded the above alcohol 4e (177mg, 91%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37(d, *J*=1.5Hz, 1H), 5.76-5.86(m, 2H), 5.09(d, *J*=17.1Hz, 1H), 5.02(d, *J*=10.1Hz, 1H), 4.41(t, *J*=9.2Hz, 1H), 4.27(dd, *J*=9.4, 3.6Hz, 1H), 3.69-3.74(m, 1H), 3.14(s, 1H), 2.25-2.31(m, 2H), 2.12-2.21(m, 1H), 1.54-1.60(m, 2H).

Discernable data for minor diastereoisomer: 5.72(d, *J*=1.9Hz, 1H), 3.83-3.88(m, 1H).

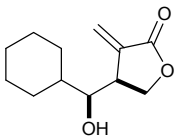
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 138.2, 135.6, 125.3, 116.3, 73.2, 68.6, 45.1, 33.1, 30.6.

IR (neat), ν (cm^{-1}) 3444, 1760, 1660, 1271, 1123.

HRMS (ESI): M+Na^+ found 182.0940, $C_{10}H_{14}O_3Na$ required 182.0943.

Following procedure B, using 4-pentenal (86mg, 1.02mmol), afforded the above alcohol 4e (166mg, 89%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

4-(Hydroxy(cyclohex-2-yl)methyl)-3-methylenedihydrofuran-2(3H)-one (4f)



Following procedure A, using cyclohexanal (114mg, 1.02mmol), afforded the above alcohol 4f (205mg, 96%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32(d, J=2.1Hz, 1H), 5.77(d, J=1.6Hz, 1H), 4.37(t, J=8.8Hz, 1H), 4.14(dd, J=9.1, 4.2Hz, 1H), 3.35(t, J=6.1Hz, 1H), 3.17-3.23(m, 1H), 1.63-1.76(m, 6H), 1.35-1.37(m, 1H), 1.02-1.18(m, 5H);

Discernable data for minor diastereoisomer: 6.10(d, J=1.8Hz, 1H), 5.56(d, J=1.2Hz, 1H), 4.54(t, J=8.9Hz, 1H).

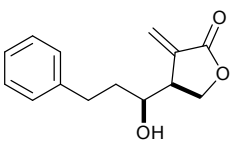
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 134.2, 123.7, 75.7, 67.6, 40.0, 39.4, 29.0, 26.2, 25.2, 25.1, 24.9.

IR (neat), ν (cm-1) 3490, 1741, 1659, 1265, 1134.

HRMS (ESI): M+Na^+ found 233.1146, $C_{12}H_{18}O_3Na$ required 233.1154.

Following procedure B, using cyclohexanal (116mg, 1.04mmol), afforded the above alcohol 4f (201mg, 92%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

4-(3-phenyl-1-hydroxypropyl)-3-methylenedihydrofuran-2(3H)-one (4g)



Following procedure A, using 3-phenylpropanal (142mg, 1.06mmol), afforded the above alcohol 4g (162mg, 80%)

via column chromatography (petroleum ether/ethyl acetate, 1:1).

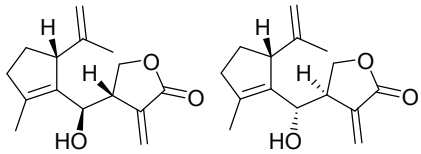
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33(t, *J*=7.3Hz, 2H), 7.24(dd, *J*=7.2, 11.8Hz, 3H), 6.37(d, *J*=1.6Hz, 1H), 5.79(d, *J*=1.0Hz, 1H), 4.40(t, *J*=8.9Hz, 1H), 4.24(dd, *J*=3.4, 9.4Hz, 1H), 3.71(t, *J*=9.2Hz, 1H), 3.13(s, 1H), 2.93(m, 1H), 2.75(m, 1H), 2.05(br s, 1H), 1.84(m, 2H);

Discernable data for minor diastereoisomer: 5.70(d, *J*=1.7Hz, 1H), 4.40(t, *J*=8.9Hz, 1H), 4.24(dd, *J*=3.4, 9.4Hz, 1H), 3.71(t, *J*=9.2Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 141.1, 135.0, 128.6, 128.4, 126.3, 124.8, 72.4, 68.0, 44.7, 35.2, 32.0.

Following procedure B, using 3-phenylpropanal (130mg, 0.97mmol), afforded the above alcohol 4g (189mg, 84%) via column chromatography (petroleum ether/ethyl acetate, 1:1)

4-(Hydroxy-(5-isopropenyl-2-methyl-1-en-cyclopentyl) methyl) -3-methylenedihydrofuran-2(3H)-one (4h)



4hI 4hII

Following procedure A, using 5-isopropenyl-2-methyl-1-en-cyclopentane-carboxaldehyde (153mg, 1.02mmol), afforded the above alcohol 4h (220mg, 87%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

4hI (81mg, 32%) : $[\alpha]_D^{20}$ = -150.7 (*c* = 0.01, EtOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34(s, 1H), 5.93(s,1H), 4.78(s, 1H), 4.72(s, 1H), 4.30(d, *J*=9.4Hz, 1H), 4.22(t, *J*=8.8Hz, 1H), 3.97(dd, *J*=9.4, 3.4Hz, 1H), 3.53(d, *J*=8.6Hz, 1H), 3.32(s, 1H), 2.44-2.52(m, 1H), 2.22-2.28(t, *J*=9.6Hz, 1H), 2.00-2.10(m, 1H), 1.93(s, 1H), 1.81(s, 3H), 1.66-1.72(m, 1H), 1.64(s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 148.5, 141.0, 135.8, 134.7, 125.2, 111.5, 70.3, 67.8, 53.7, 43.4, 38.3, 29.0, 19.1, 14.7.

IR (neat) ν (cm^{-1}) 3481, 1766, 1659, 1275, 1119.

HRMS (ESI) $M+Na^+$ found 271.1313, $C_{15}H_{20}O_3Na$ required 271.1305.

4hII (139, 55%) : $[\alpha]_D^{20}$ = +2.8 (*c* = 0.01, EtOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33(dd, *J*=2.4, 0.8Hz, 1H), 6.04(dd, *J*=2.2, 0.9Hz, 1H), 4.85(s, 1H), 4.78(t, *J*=1.5Hz, 1H), 4.48(dd, *J*=9.2, 5.9Hz, 1H), 4.26(dd, *J*=9.4, 8.5Hz, 1H), 3.86(dd, *J*=9.5, 5.0Hz, 1H), 3.27-3.33(m, 1H), 2.41-2.50(m, 1H), 2.23-2.29(m, 2H), 1.95-2.06(m, 1H), 1.76(s, 3H), 1.64-1.71(m, 1H).

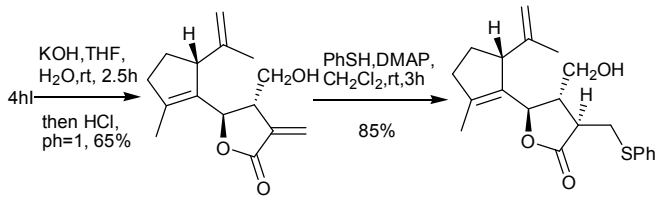
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 151.3, 141.4, 135.9, 133.7, 125.0, 110.7, 71.0, 67.3, 53.1, 43.6, 37.5, 28.9, 19.7, 14.3.

IR (neat) ν (cm^{-1}) 3481, 1766, 1658, 1276, 1121.

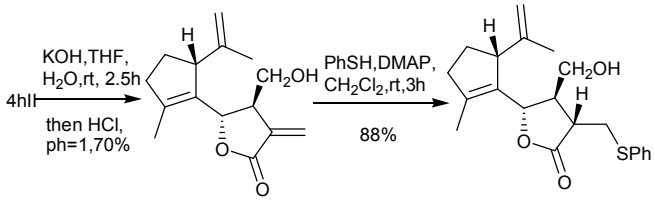
HRMS (ESI) $M+Na^+$ found 271.1311, $C_{15}H_{20}O_3Na$ required 271.1305.

Following procedure B, using 5-isopropenyl-2-methyl-1-en-cyclopentane-carboxaldehyde (150mg, 1.0mmol), afforded the above alcohol 4h (221mg, 89%) via column chromatography (petroleum ether/ethyl acetate, 1:1).

6-Procedure for 4h into 8

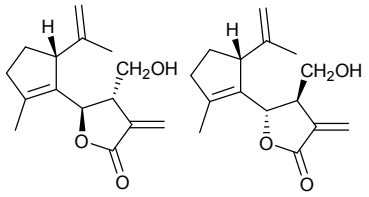


5 6



7 8

Synthesis of 4-Hydroxymethyl-5-(5-isopropenyl-2-methyl-1-en-cyclopentyl)-3-methylenedihydrofuran-2(3H)-one (5,7)



5 7

A mixture of lactone 4hI (296mg, 1.19mmol), NaOH (220mg, 5.5mmol) were combined in 6 ml of a 1:1 mixture of THF and water for 2 h. The mixture was carefully acidified to pH 1 and extracted with CH_2Cl_2. The combined extracts were dried, concentrated and chromatographed to give 5(178mg, 60%): oil.

$[\alpha]_D^{20}$ = -150.0 (*c* = 0.01, EtOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.29(d, *J*=2.6Hz, 1H), 5.65(d, *J*=1.8Hz, 1H), 5.16(d, *J*=5.6Hz, 1H), 4.72(d, *J*=1.8Hz, 1H), 4.63(t, *J*=1.4Hz, 1H), 3.81(dd, *J*=10.9, 5.8Hz, 1H), 3.73(dd, *J*=10.9, 5.4Hz, 1H), 3.47(d, *J*=9.4Hz, 1H), 3.08-3.12(m, 1H), 2.43-2.52(m, 1H), 2.22-2.26(m, 1H), 2.01-2.11(m, 2H), 1.79(s, 3H), 1.64-1.69(m, 1H), 1.63(s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 148.0, 141.7, 136.7, 132.5, 122.5, 111.7, 77.7, 63.2, 53.2, 45.7, 38.3, 28.8, 18.9, 14.3.

IR (neat) ν (cm^{-1}) 3457, 1732, 1659, 1269, 1141.

HRMS (ESI) M+Na^+ found 271.1301, $C_{15}H_{20}O_3Na$ required 271.1305.

Compound 7 was prepared according to the same procedure. The reaction of 4hII (251mg, 0.93mmol), NaOH (193mg, 4.8mmol) and 1:1 mixture of THF and water (6 ml) afforded 7 (190mg, 70%): oil.

$[\alpha]_D^{20}$ = -70.7 (*c* = 0.01, EtOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27(d, *J*=2.5Hz, 1H), 5.69(d, *J*=2.5Hz, 1H), 5.22(d, *J*=5.0Hz, 1H), 4.61(s, 1H), 4.60(d, *J*=1.2Hz, 1H), 3.80(dd, *J*=10.8, 6.2Hz, 1H), 3.74(dd, *J*=10.8, 5.6Hz, 1H), 3.46(d, *J*=8.2Hz, 1H), 3.13-3.17(m, 1H), 2.43-2.51(m, 1H), 2.26-2.34(m, 1H), 1.99-2.06(m, 2H), 1.81(s, 3H), 1.65-1.72(m, 1H), 1.62(s, 3H).

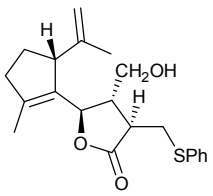
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 148.1, 143.8, 137.0, 132.5, 122.3, 111.4, 76.9, 63.7, 53.9, 44.9, 38.2, 28.1, 17.8, 14.2.

IR (neat) ν (cm^{-1}) 3439, 1747, 1661, 1271, 1153.

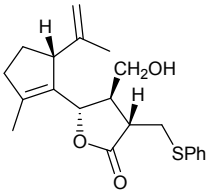
HRMS (ESI) M+Na^+ found 271.1304, $C_{15}H_{20}O_3Na$ required 271.1305.

Synthesis of

4-Hydroxymethyl-5-(5-isopropenyl-2-methyl-1-en-cyclopentyl)-3-phenthiomethyl-dihydrofuran-2(3H)-one (6, 8)



6



8

To a solution of the 5 (160 mg, 0.59 mmol) and DMAP (11mg) in CH_2Cl_2 (4 mL) was added benzenethiol (190 µl, 1.9 mmol) at ice cold temperature. After stirring at room temperature for 3 h, the solution was concentrated directly, and the crude oil was chromatographed to give thioether 6 (180mg, 85%): white solid.

mp = 52-56 ℃; $[\alpha]_D^{20}$ = -96.0 (c = 0.01, EtOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40(d, *J*=7.3Hz, 2H), 7.34(t, *J*=7.4Hz, 2H), 7.24(t, *J*=7.1Hz, 1H), 5.05(d, *J*=9.9Hz, 1H), 4.79(d, *J*=1.6Hz, 1H), 4.67(s, 1H), 3.85(dd, *J*=11.3, 3.5Hz, 1H), 3.56-3.65(m, 3H), 2.88-2.97(m, 2H), 2.45-2.58(m, 2H), 2.23-2.29(m, 1H), 2.02-2.12(m, 1H), 1.89(s, 1H), 1.78(s, 3H), 1.65-1.72(m, 1H), 1.63(s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 148.6, 142.6, 134.8, 130.9, 129.5, 139.3, 126.8, 111.8, 76.9, 60.1, 53.2, 48.0, 41.9, 38.4, 33.9, 28.6, 18.6, 14.4.

IR (neat) ν (cm^{-1}) 3388, 1748, 1670, 1277, 1191.

HRMS (ESI) M+Na^+ found 381.1499, $C_{21}H_{26}O_3SNa$ required 381.1495.

Compound 8 was prepared according to the same procedure. The reaction of 6 (219mg, 0.81mmol), DMAP (15mg), benzenethiol (248ul, 2.4mmol) in CH_2Cl_2 (6 ml) afforded 8 (271mg, 88%): white solid.

mp = 115-118 ℃; $[\alpha]_D^{20}$ = -20.8 (*c* = 0.01, EtOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41(d, *J*=7.8Hz, 2H), 7.35(t, *J*=7.6Hz, 2H), 7.26(t, *J*=7.0Hz, 1H), 5.05(d, *J*=9.5Hz, 1H), 4.73(s, 1H), 4.68(s, 1H), 3.81(d, *J*=11.2Hz, 1H), 3.69(dd, *J*=11.3, 4.0Hz, 2H), 3.52(s, 1H), 2.84-2.96(m, 2H), 2.66(s, 1H), 2.45-2.49(m, 1H), 2.30-2.34(m, 1H), 2.04(s, 1H), 1.89(s, 1H), 1.79(s, 1H), 1.69-1.73(m, 1H), 1.65(s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 148.8, 145.8, 134.5, 130.4, 129.6, 129.3, 126.9, 111.1, 76.0, 60.9, 54.1, 46.9, 42.0, 38.2, 34.1, 28.0, 18.0, 14.3.

IR (neat) ν (cm^{-1}) 3422, 1768, 1664, 1315, 1197.

HRMS (ESI) M+Na^+ found 381.1497, $C_{21}H_{26}O_3SNa$ required 381.1495.

7-References

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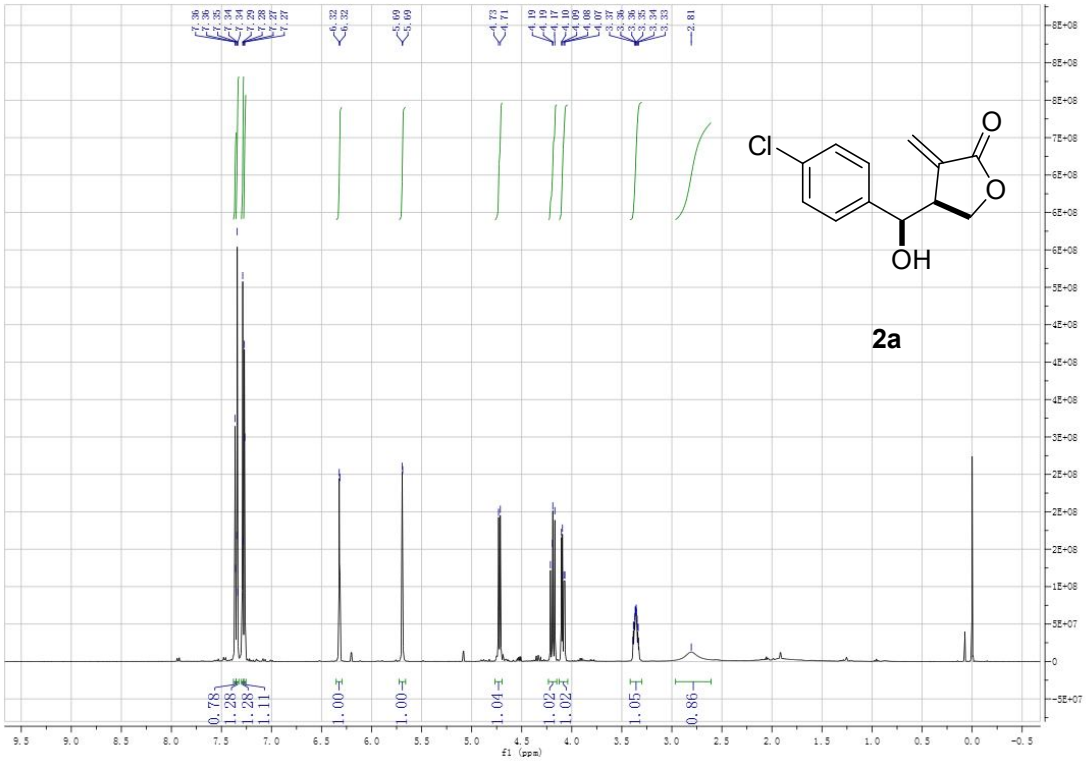
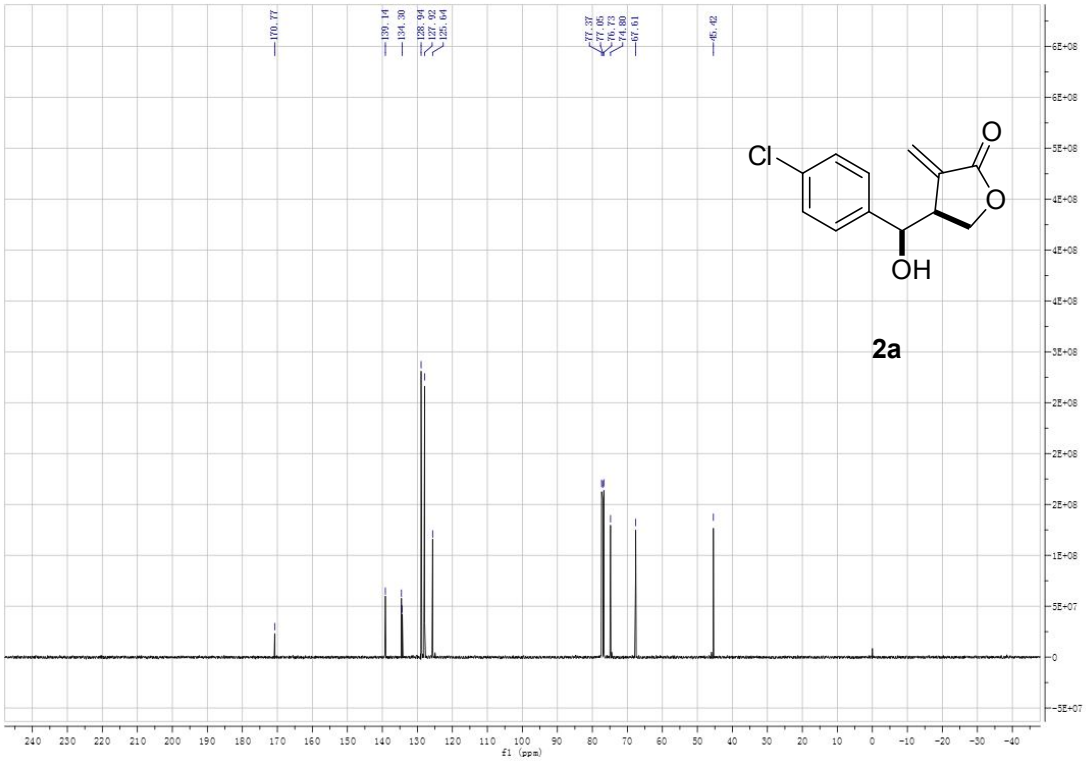
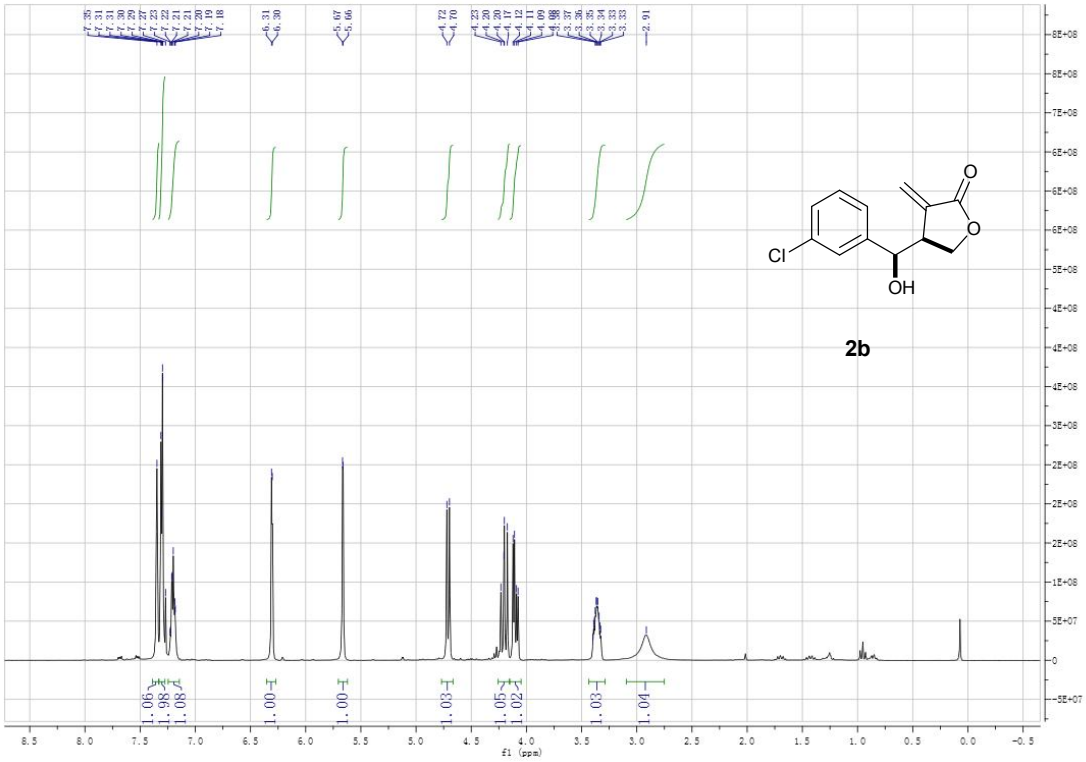
8-^{1}H and ^{13}C Spectra



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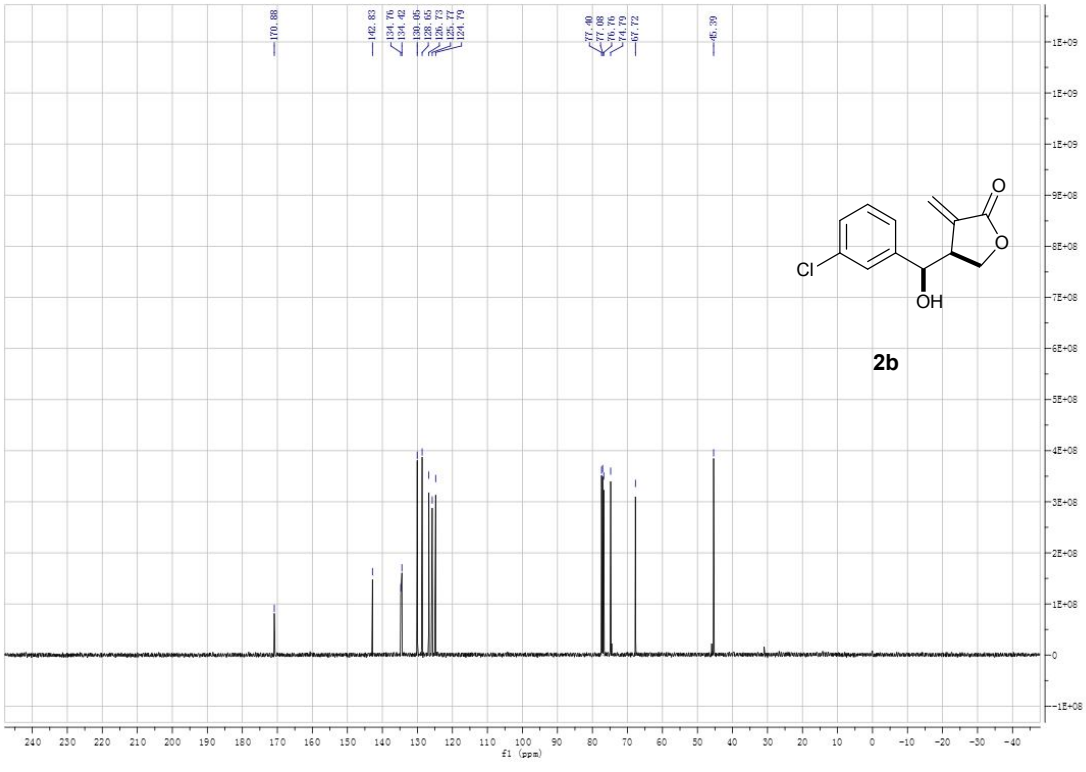
O
OH
2b
f1 (ppm)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O
OH
2b
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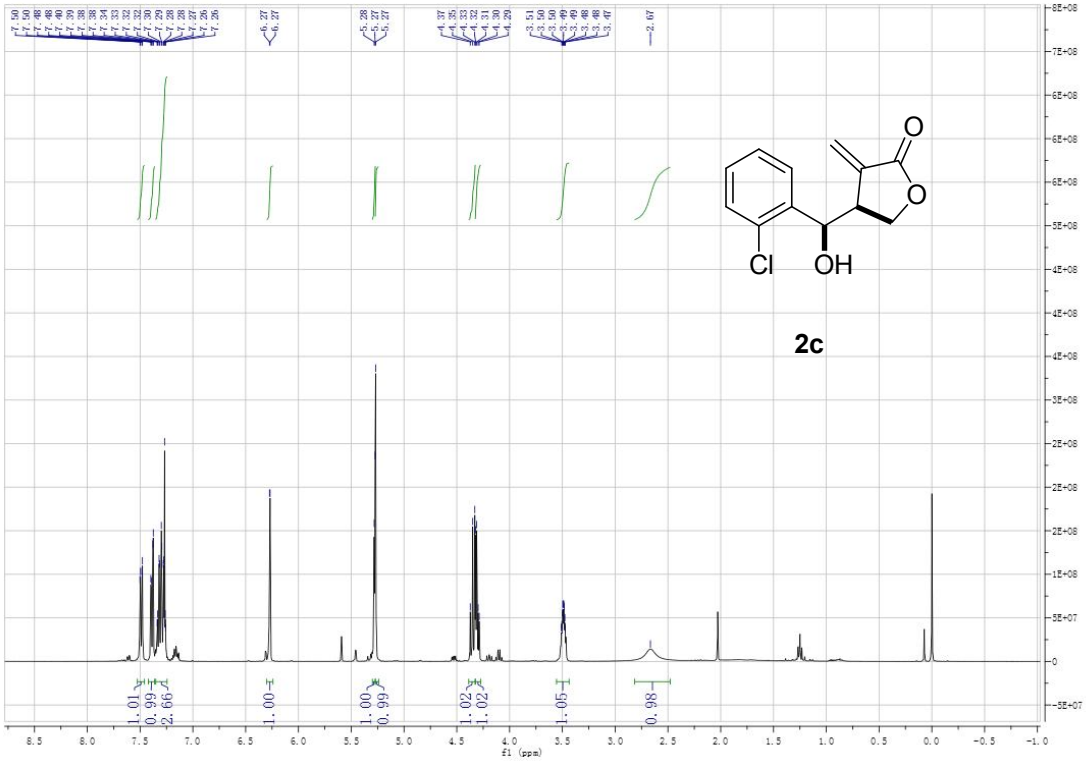

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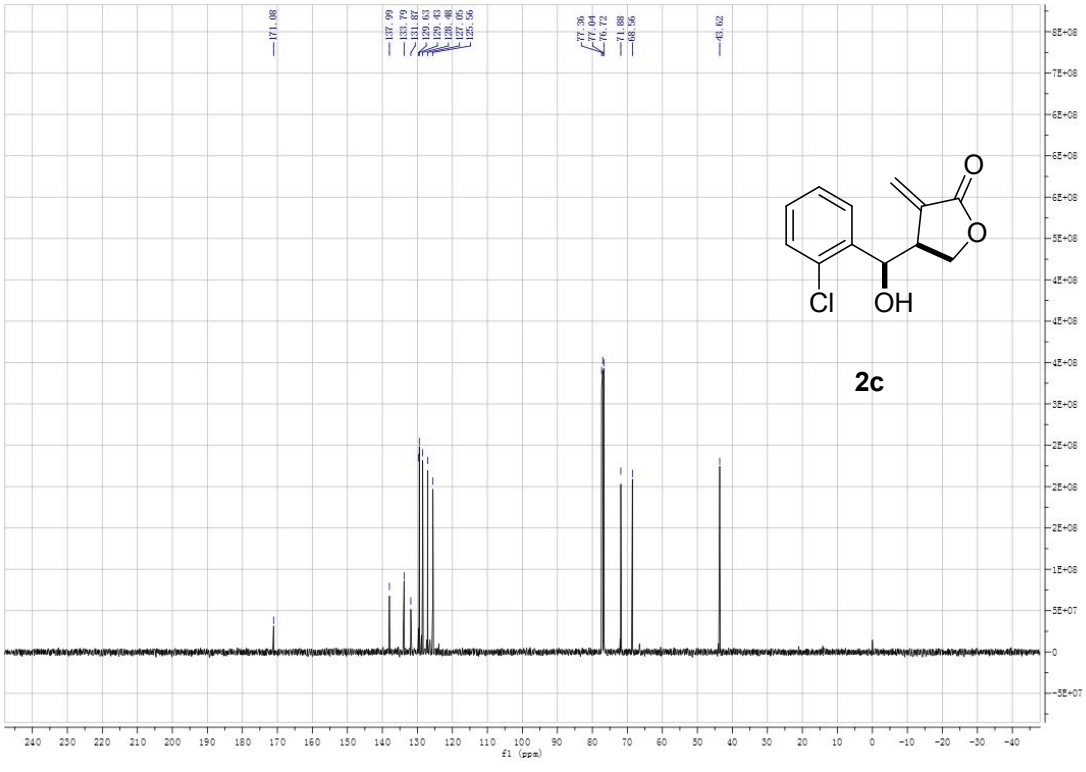

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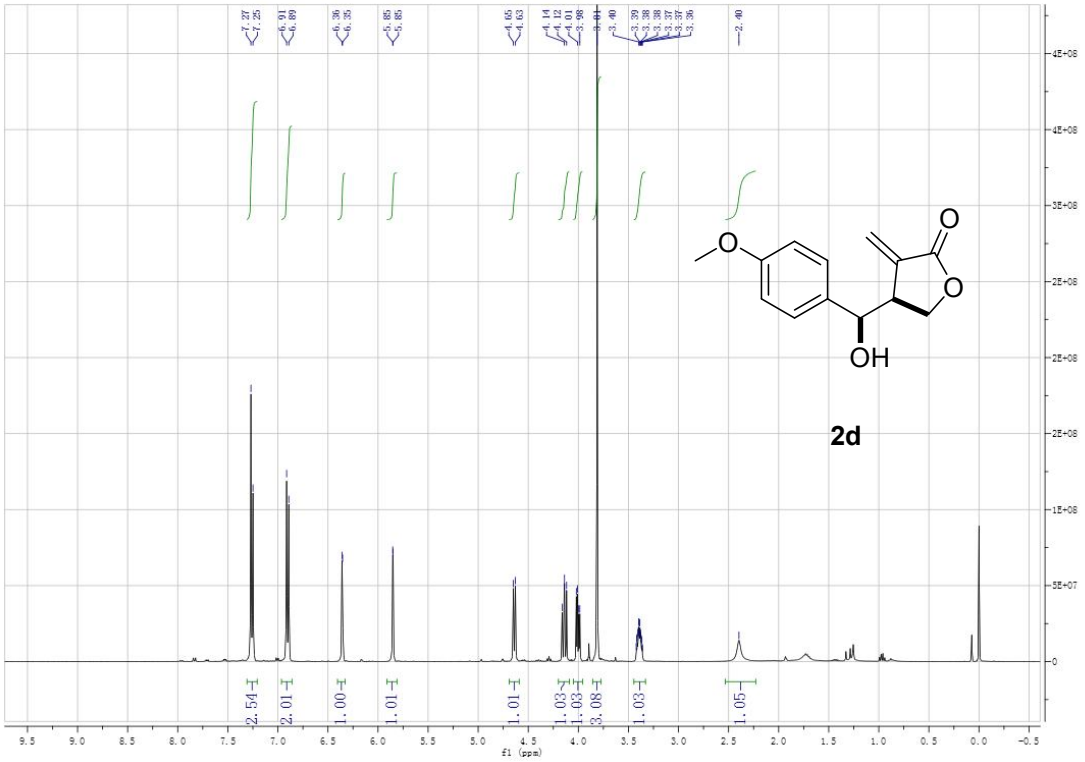
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4.01
3.98
3.40
3.39
3.38
3.37
3.36
2.40
O
O
O
OH
2d
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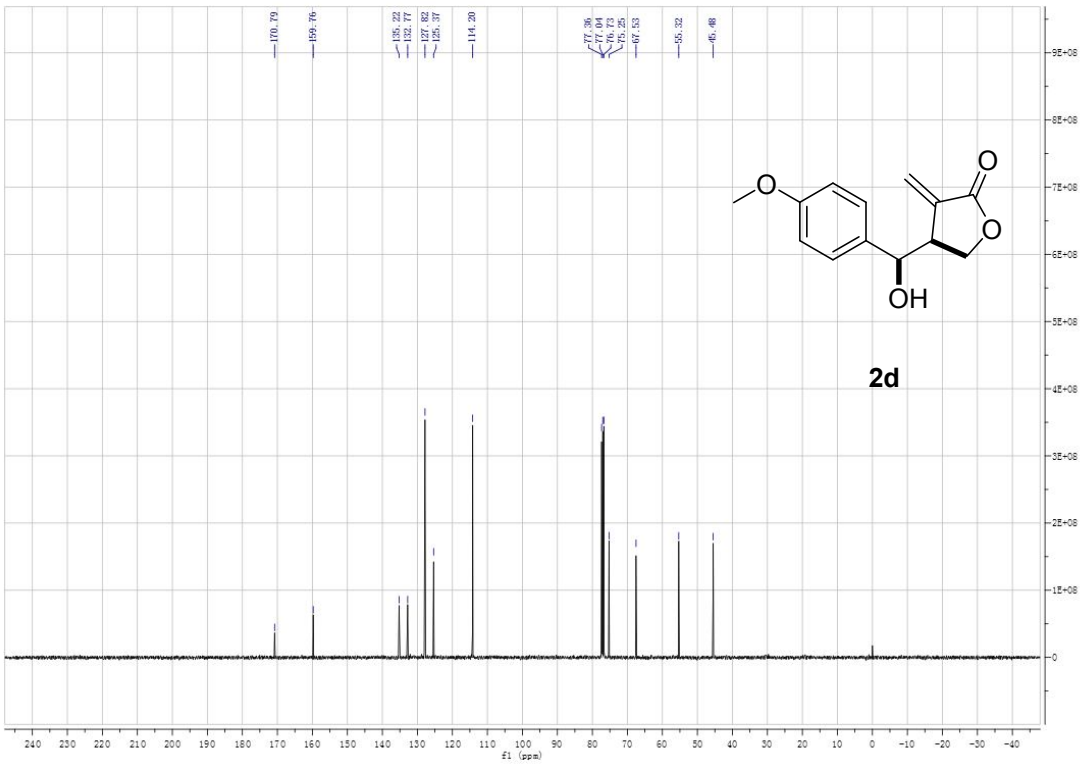
1.00
1.01
1.01
1.03
1.03
3.08
1.03
1.05
f1 (ppm)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75.25
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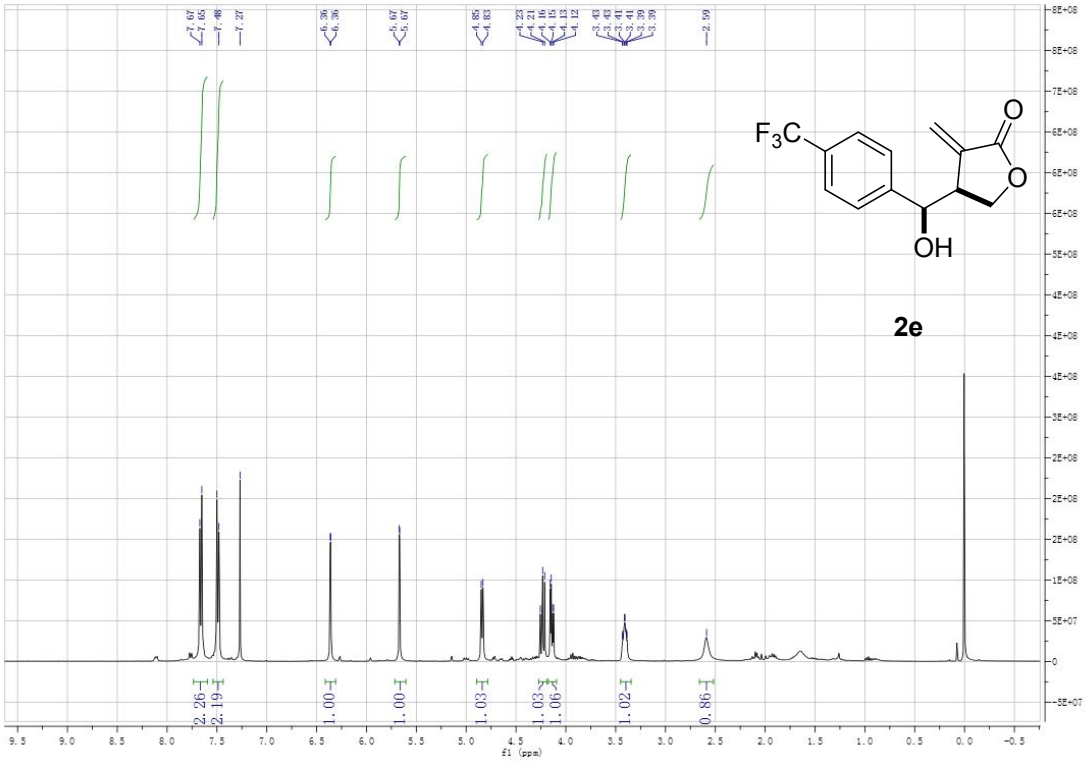
55.32
45.48
O
O
O
OH
2d
f1 (ppm)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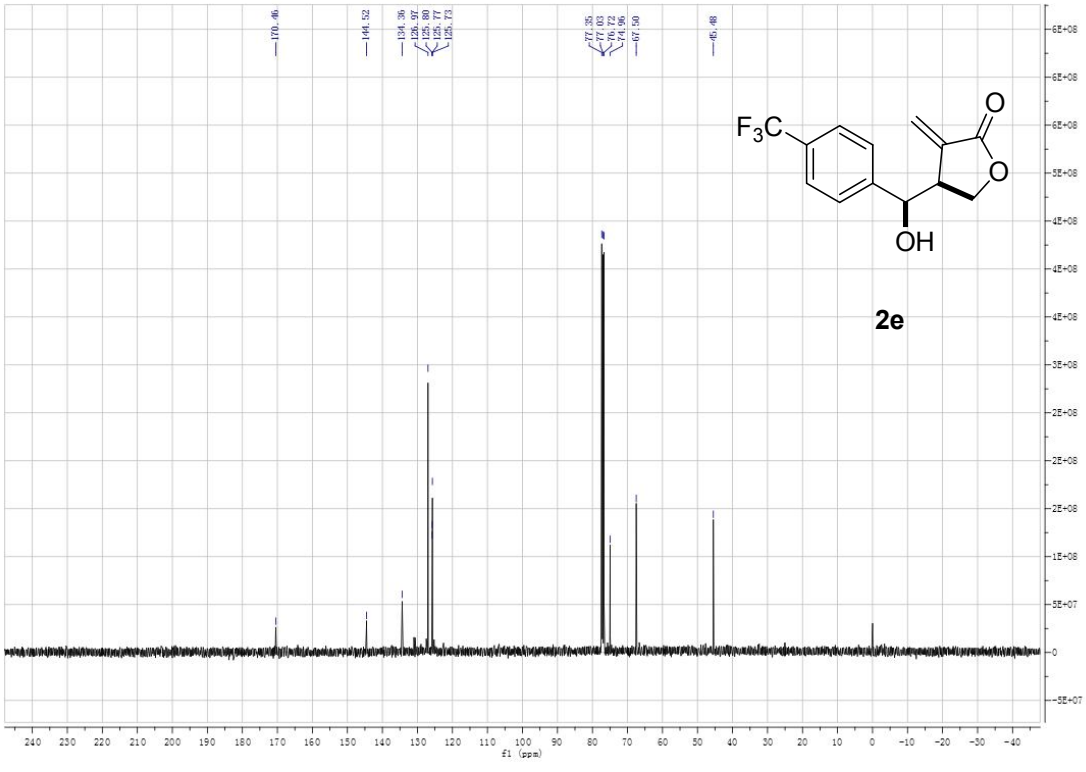
O
OH
2e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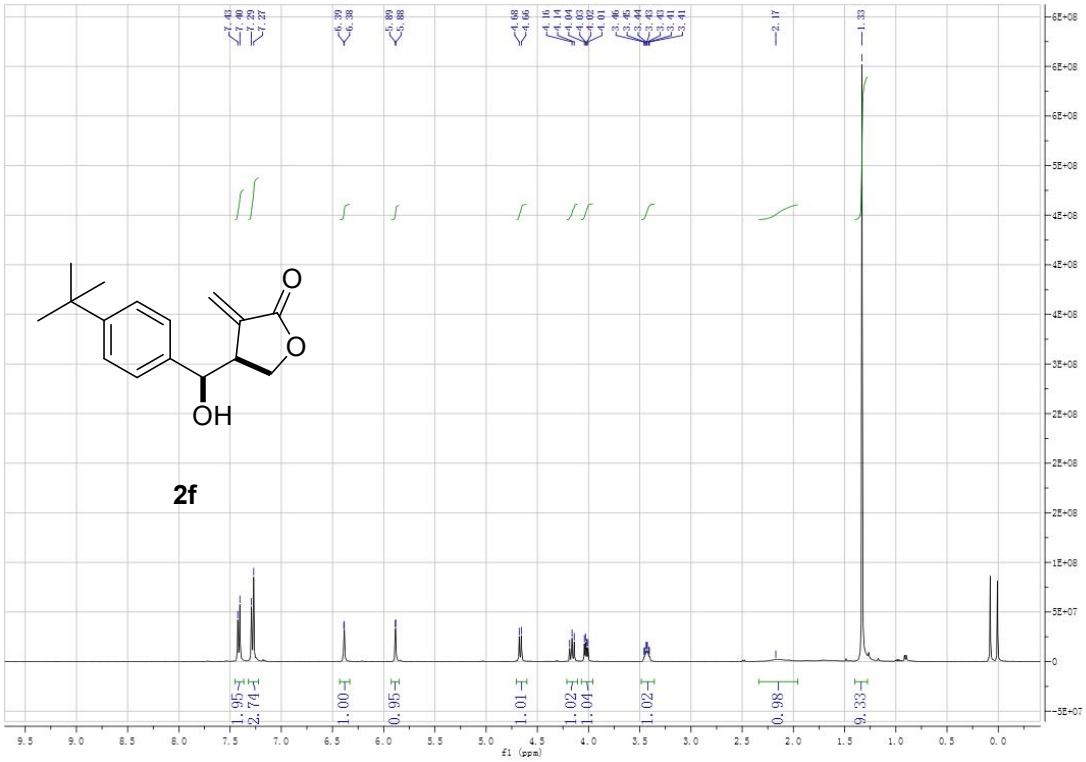
O
O
OH
2e



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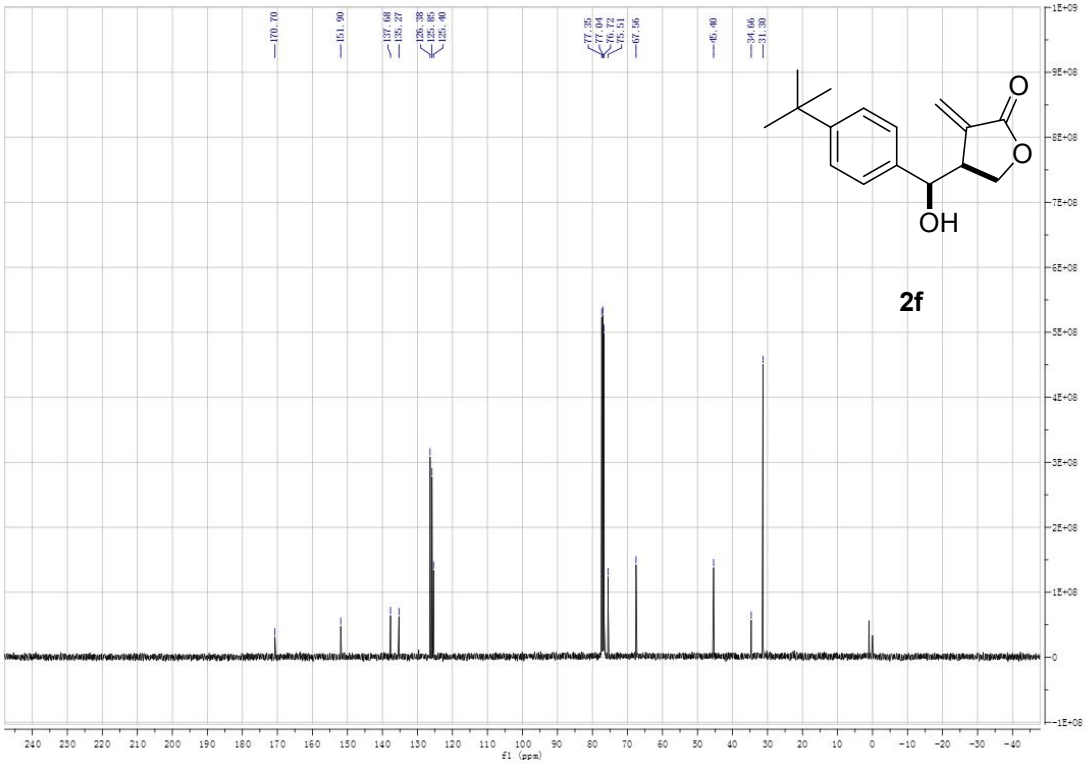

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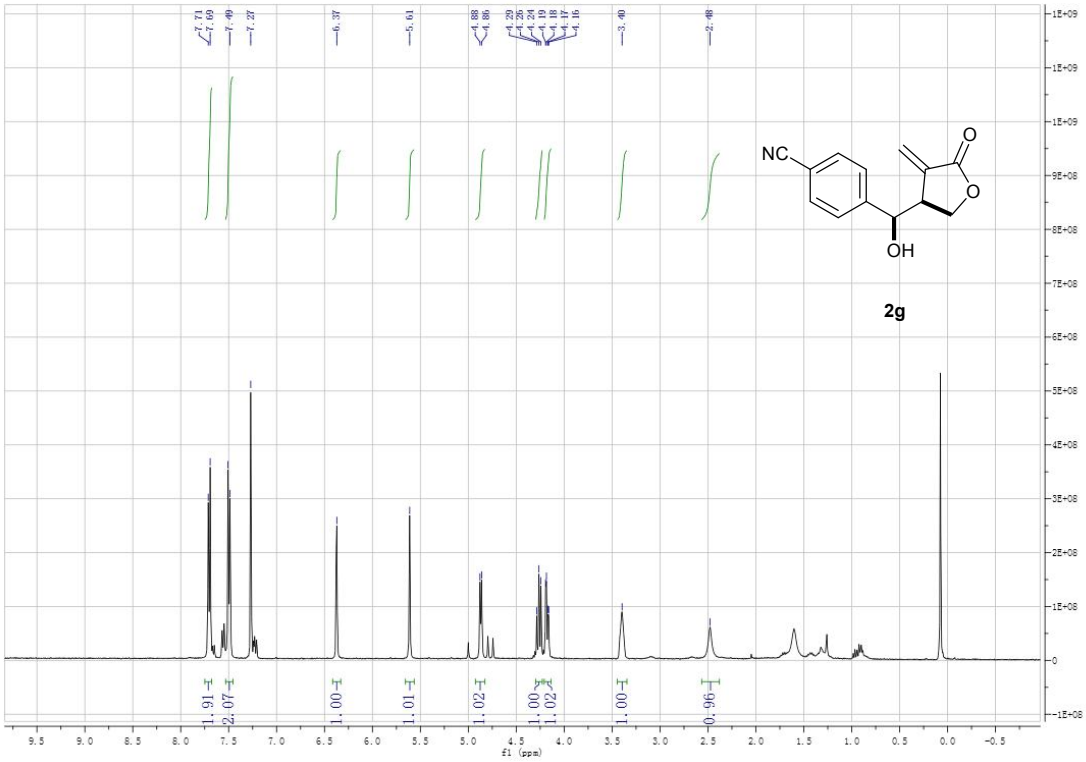
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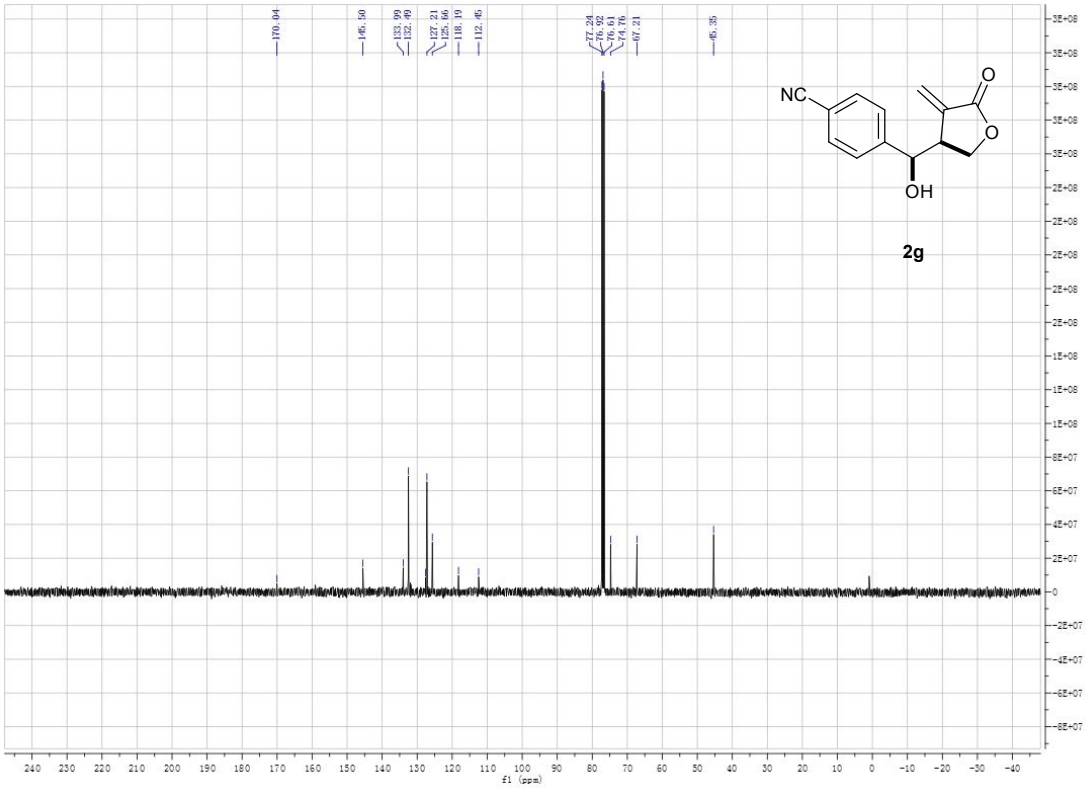
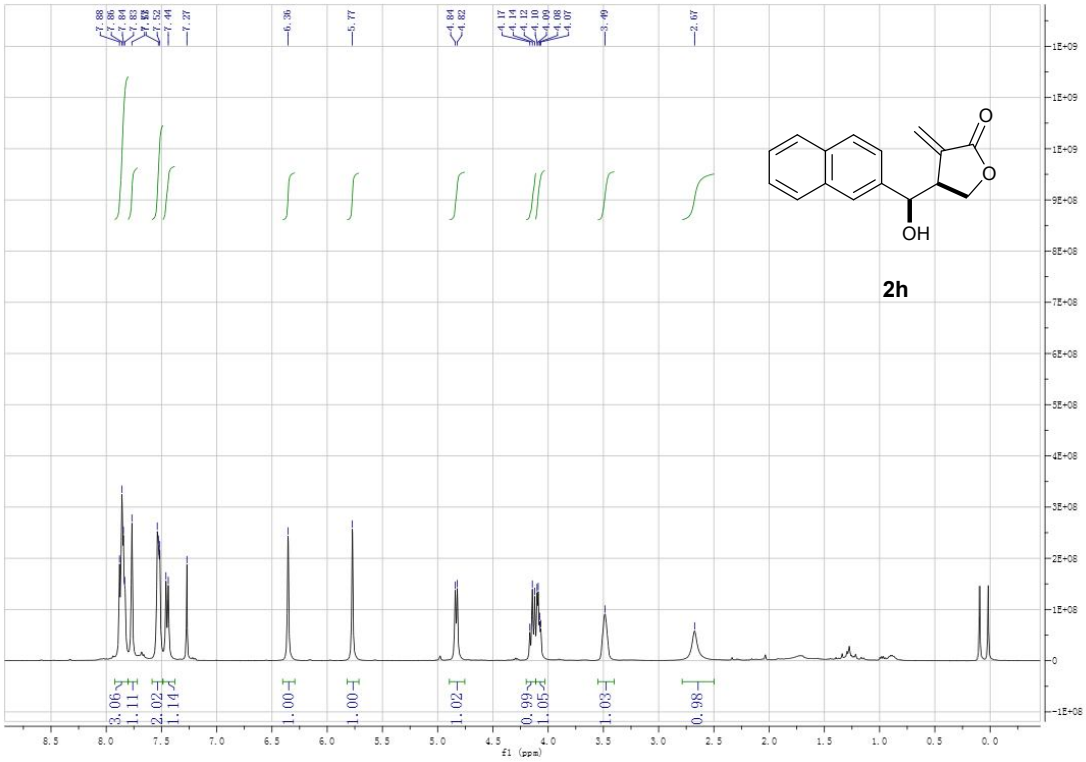
O
OH
2g


NC
O
O
OH
2g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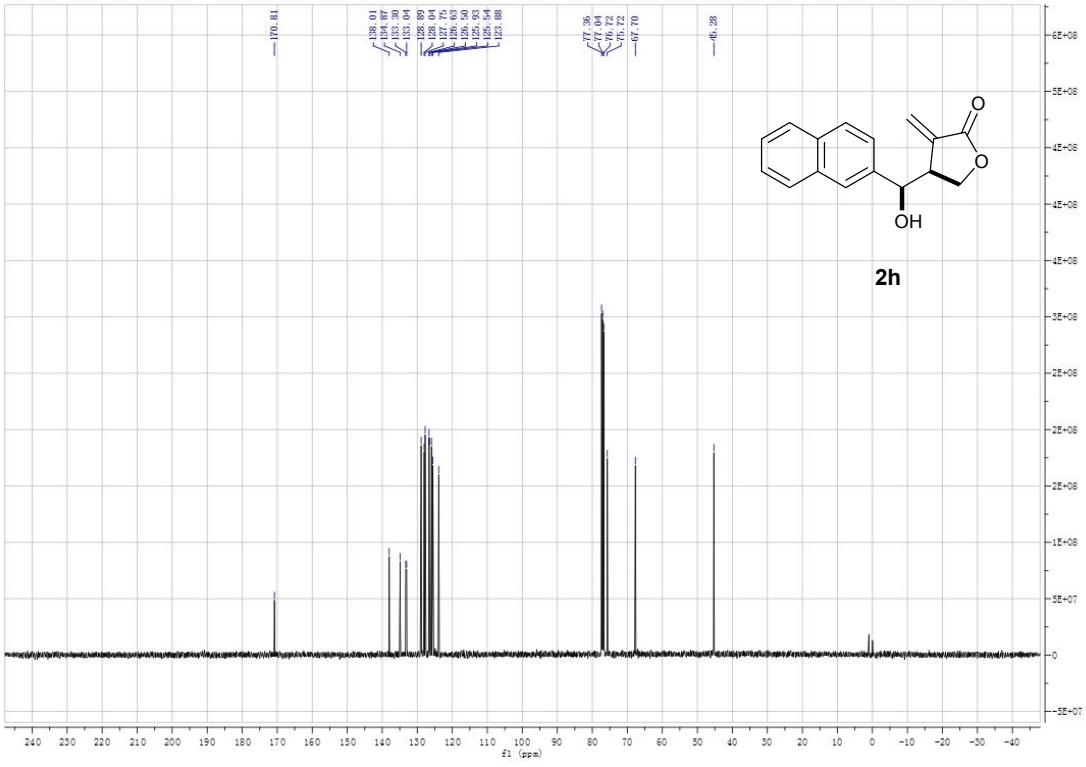
4.14
4.12
4.10
4.09
4.08
4.07
3.49
2.67
O
O
OH
2h
3.06
1.11
2.02
1.14
1.00
1.00
1.02
0.99
1.05
1.03
0.98
f1 (ppm)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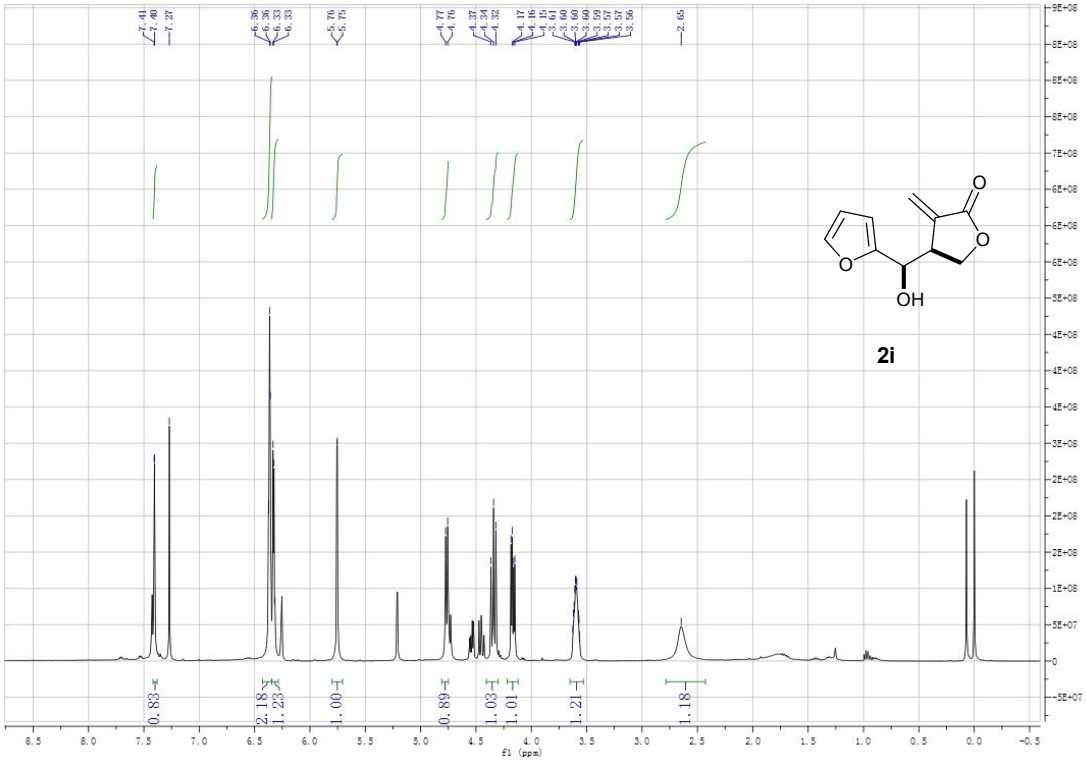
77.36
77.04
76.72
75.72
67.70
45.28
O
O
OH
2h
f1 (ppm)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4.34
4.32
4.17
4.16
4.15
4.14
3.60
3.60
3.59
3.57
3.57
3.56
2.65
O
O
O
OH
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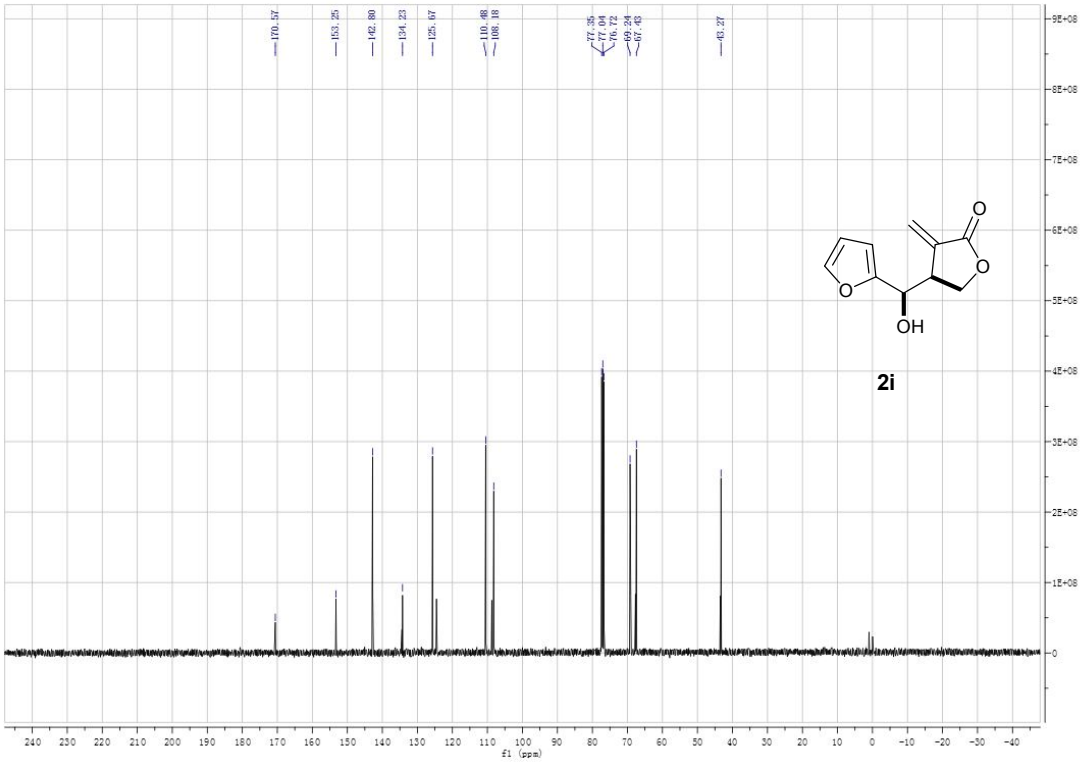
0.89
1.03
1.01
1.21
1.18
f1 (ppm)

2i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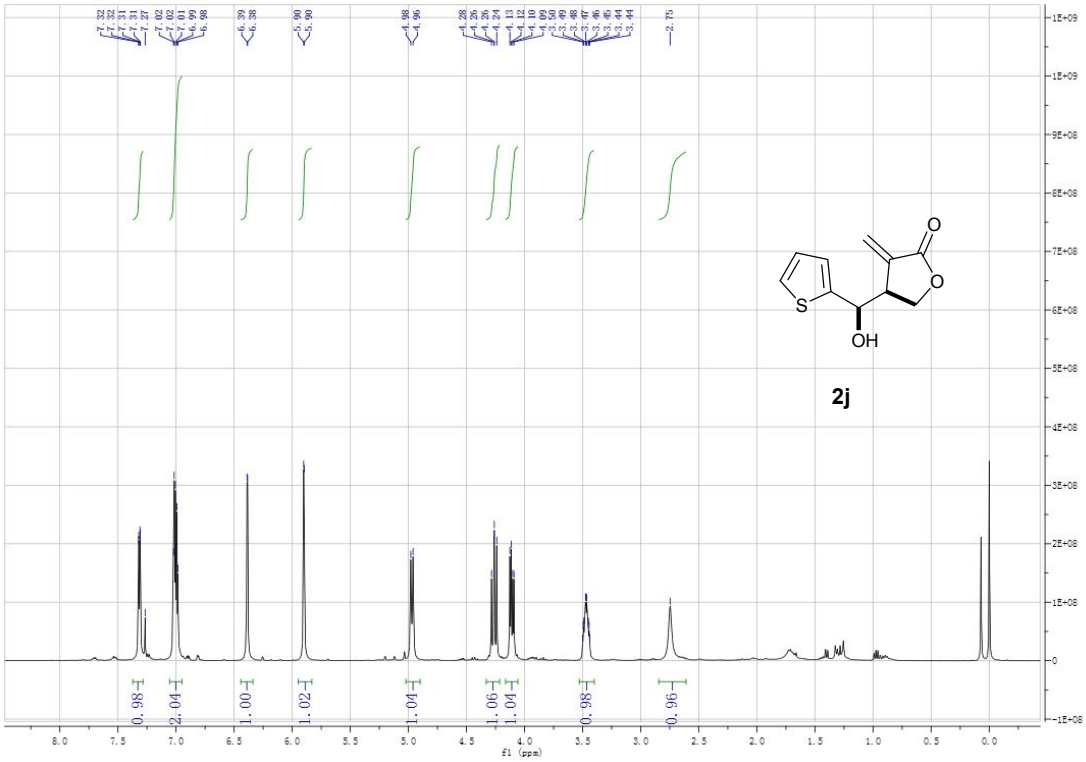
O
O
O
OH
f1 (ppm)

2i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6.39
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4.26
4.26
4.24
4.15
4.12
4.10
4.09
4.09
3.99
3.48
3.47
3.46
3.45
3.44
3.44
2.75
0.98
2.04
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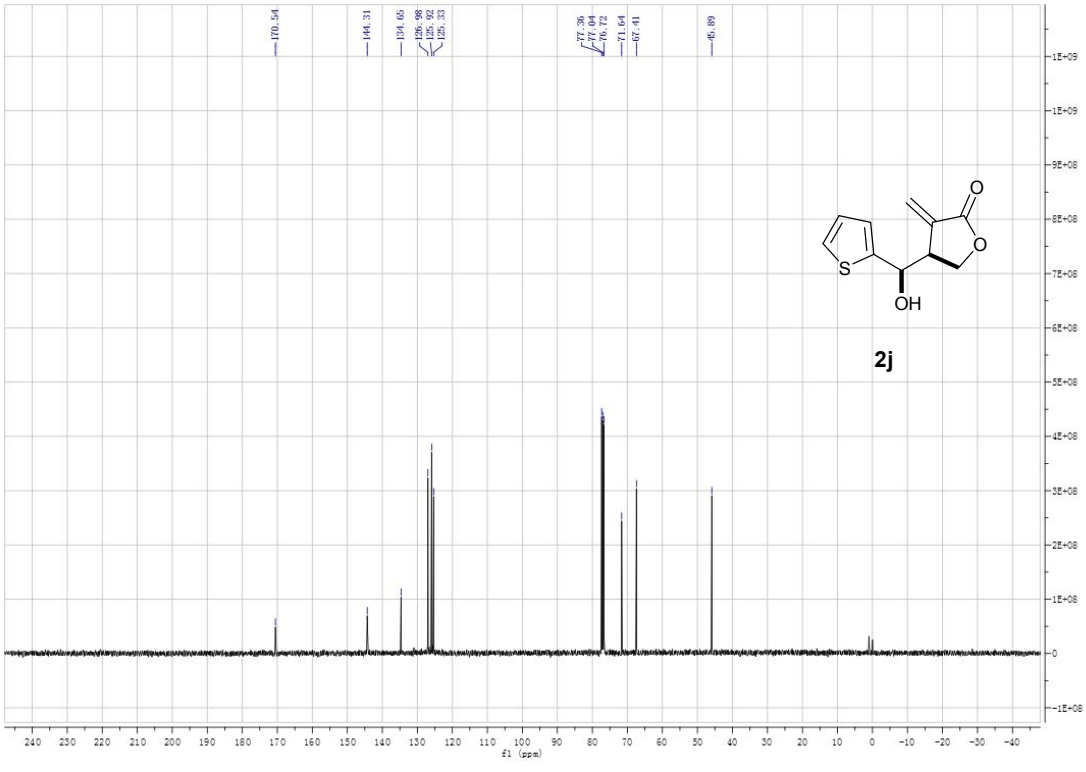
1.04
1.06
1.04
0.98
0.96
f1 (ppm)
O
O
S
OH

2j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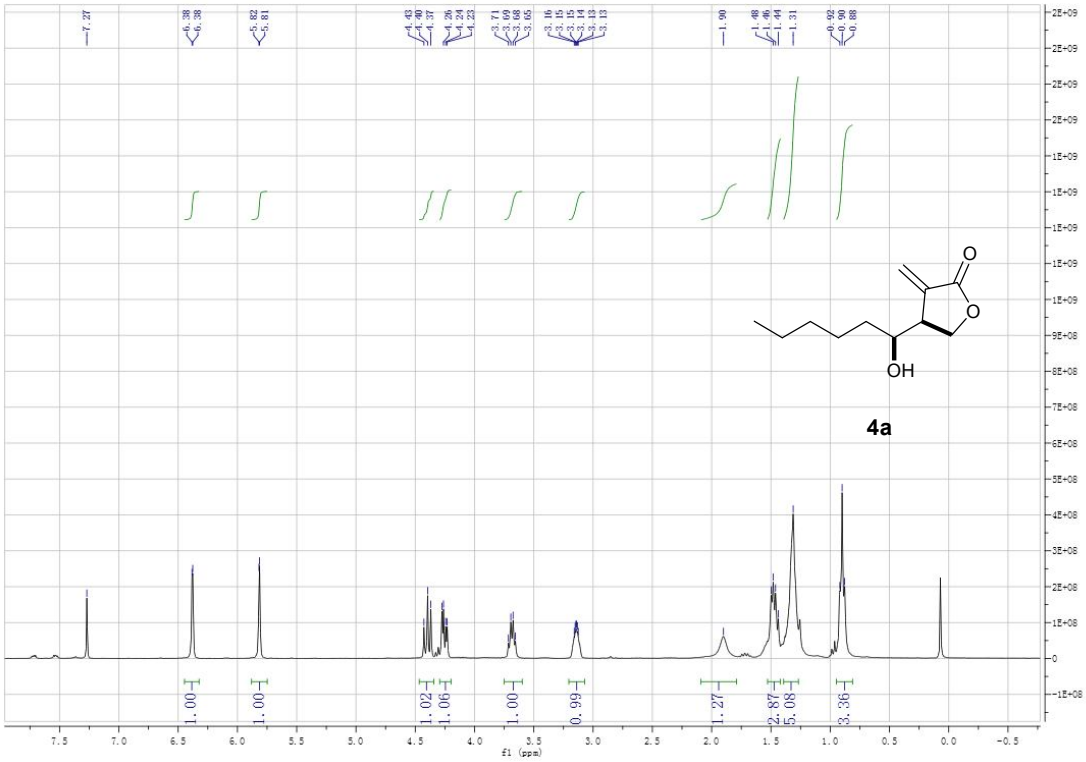
O
S
OH

2j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3.69
3.68
3.65
3.16
3.15
3.14
3.13
3.13
1.90
1.48
1.46
1.44
1.31
0.92
0.90
0.88
1.00
1.00
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0.99
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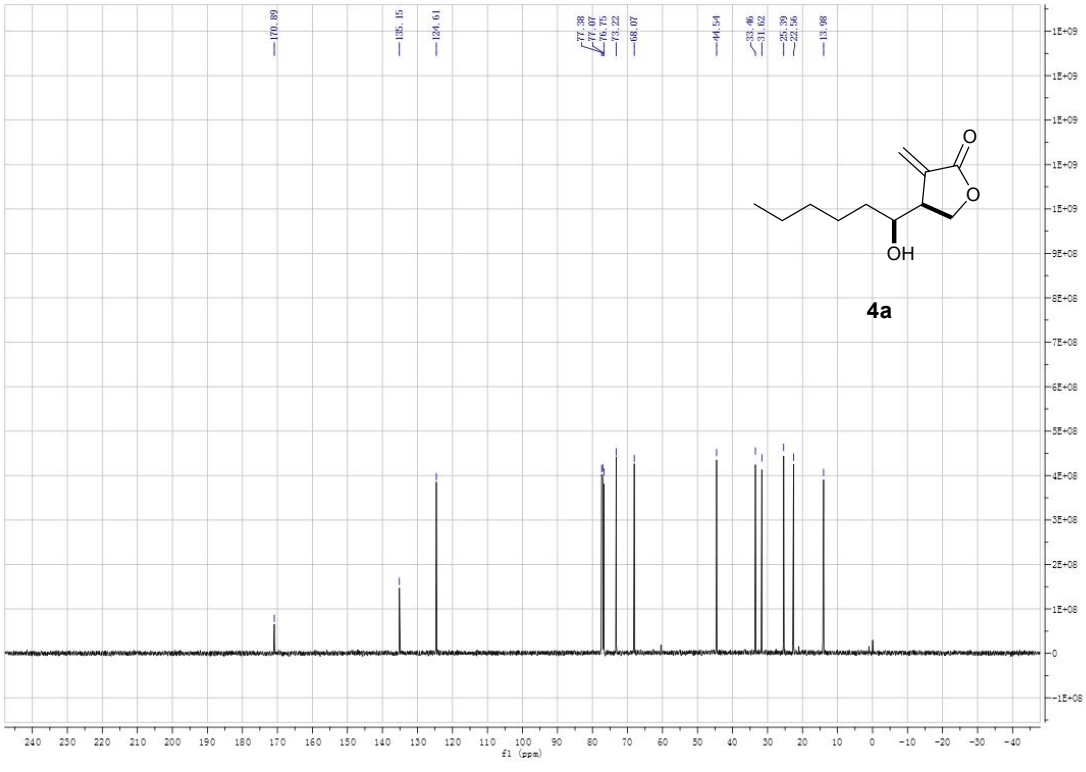
5.08
3.36
f1 (ppm)
O
O
OH
4a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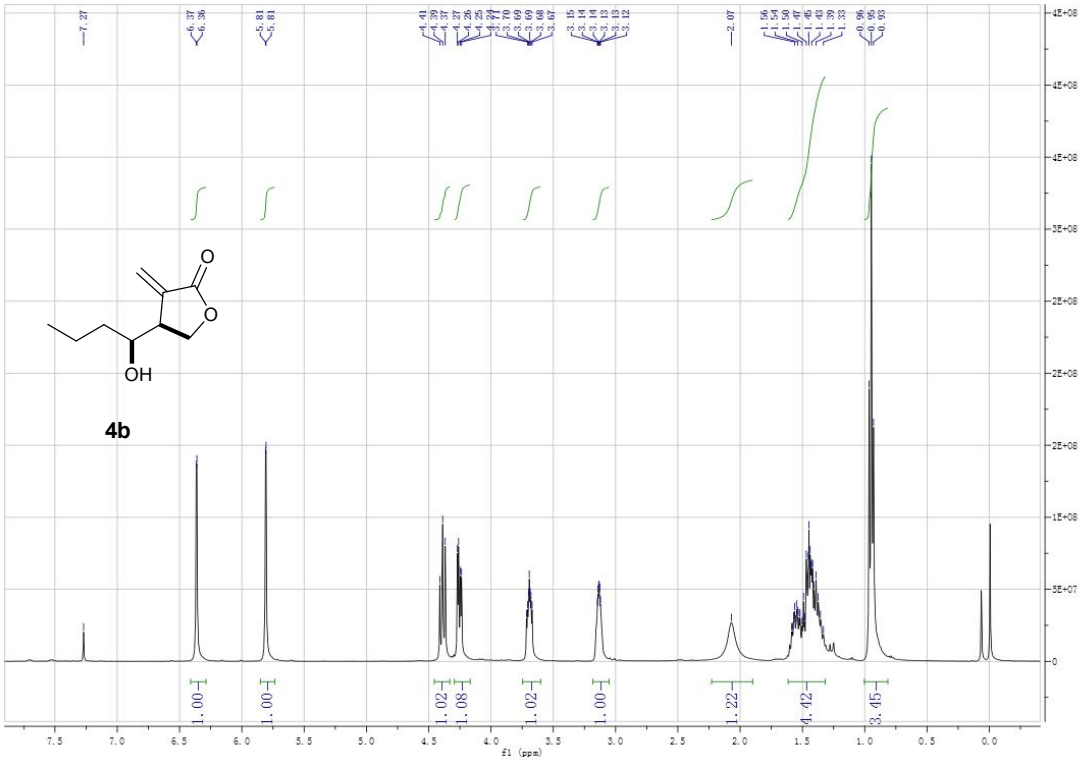
22.56
13.98
f1 (ppm)
O
O
OH
4a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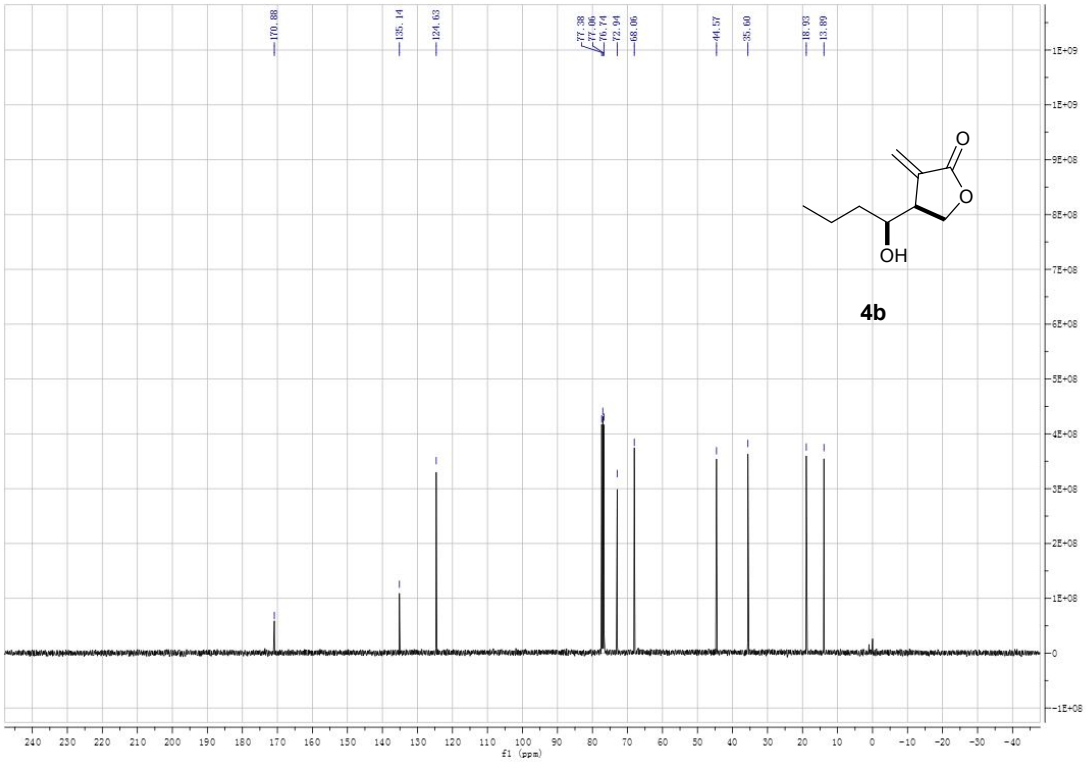
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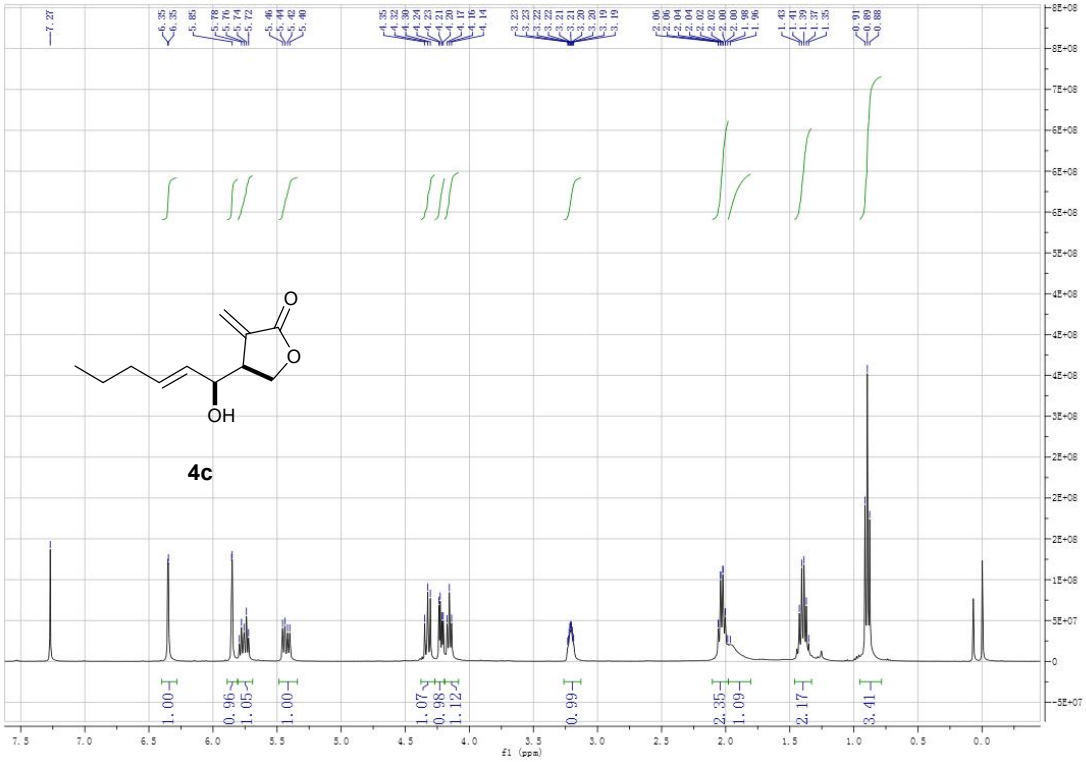

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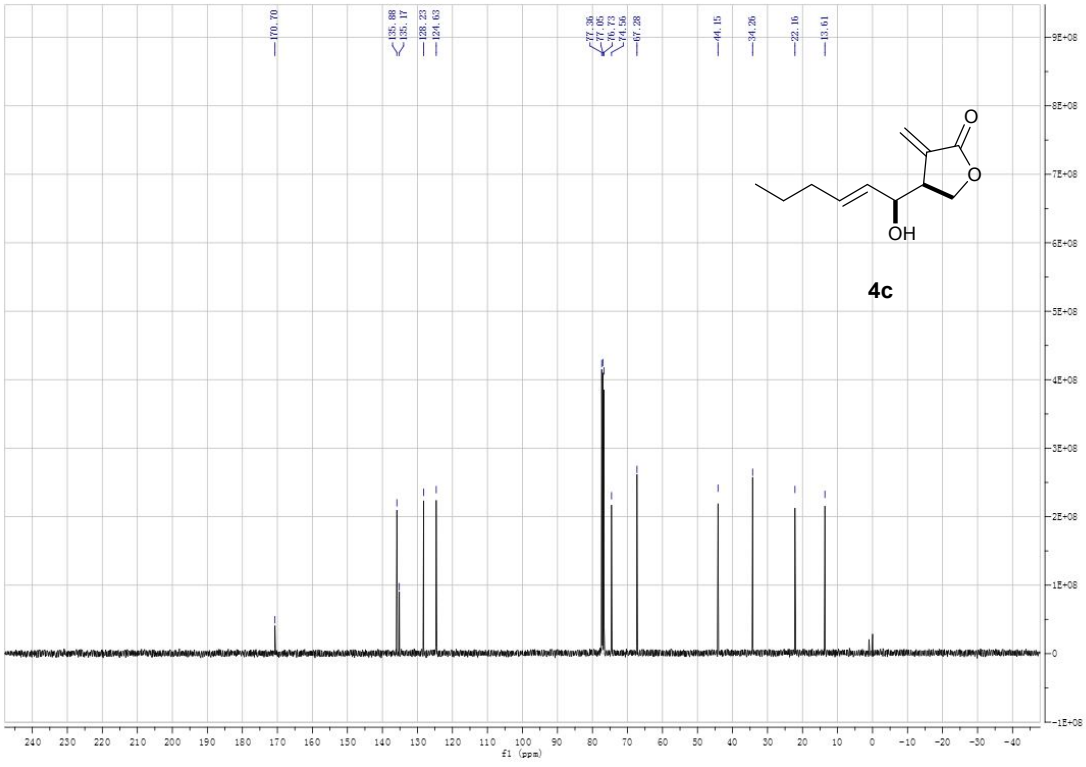

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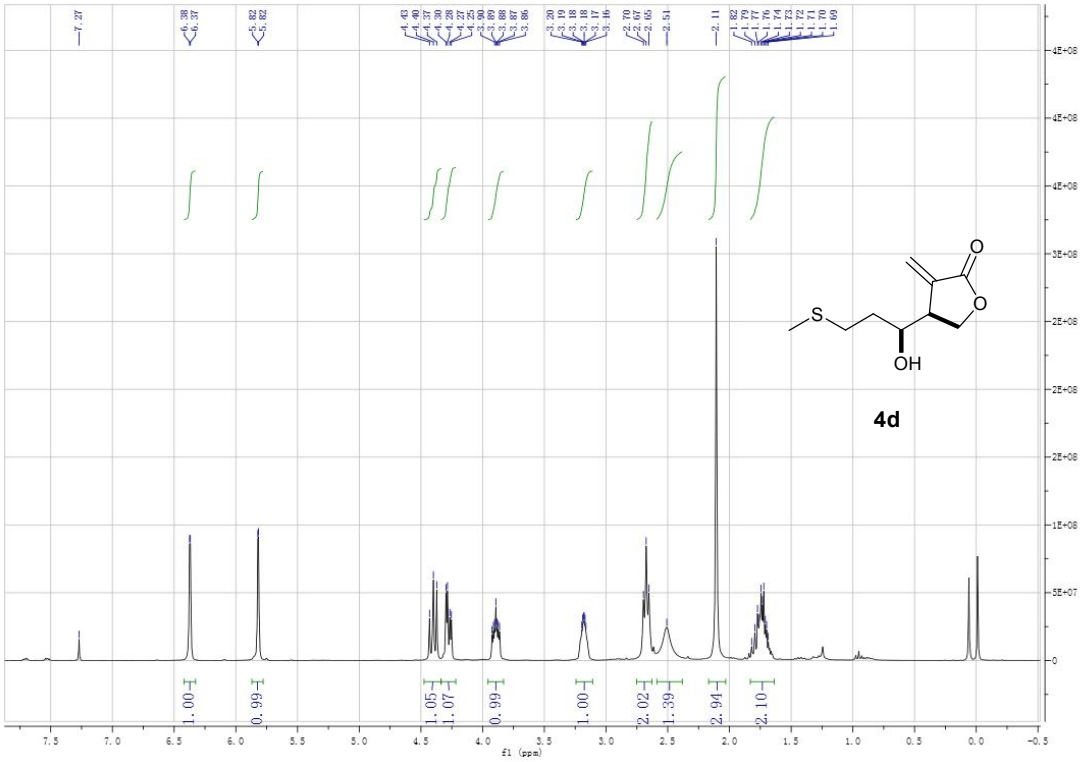
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4.08
3.89
3.88
3.87
3.86
3.20
3.19
3.18
3.17
3.16
2.70
2.67
2.65
2.51
2.11
1.82
1.79
1.77
1.76
1.74
1.73
1.72
1.71
1.70
1.69
1.00
0.99
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1.07
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1.00
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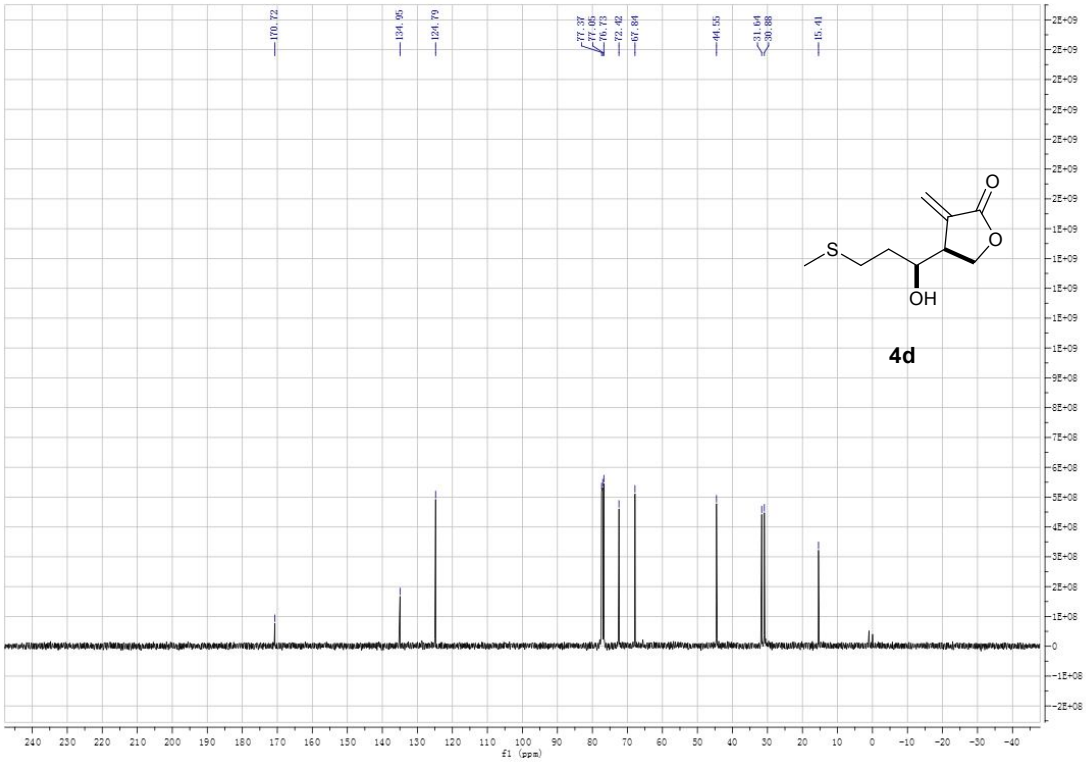
2.94
2.10
f1 (ppm)
O
O
S
OH
4d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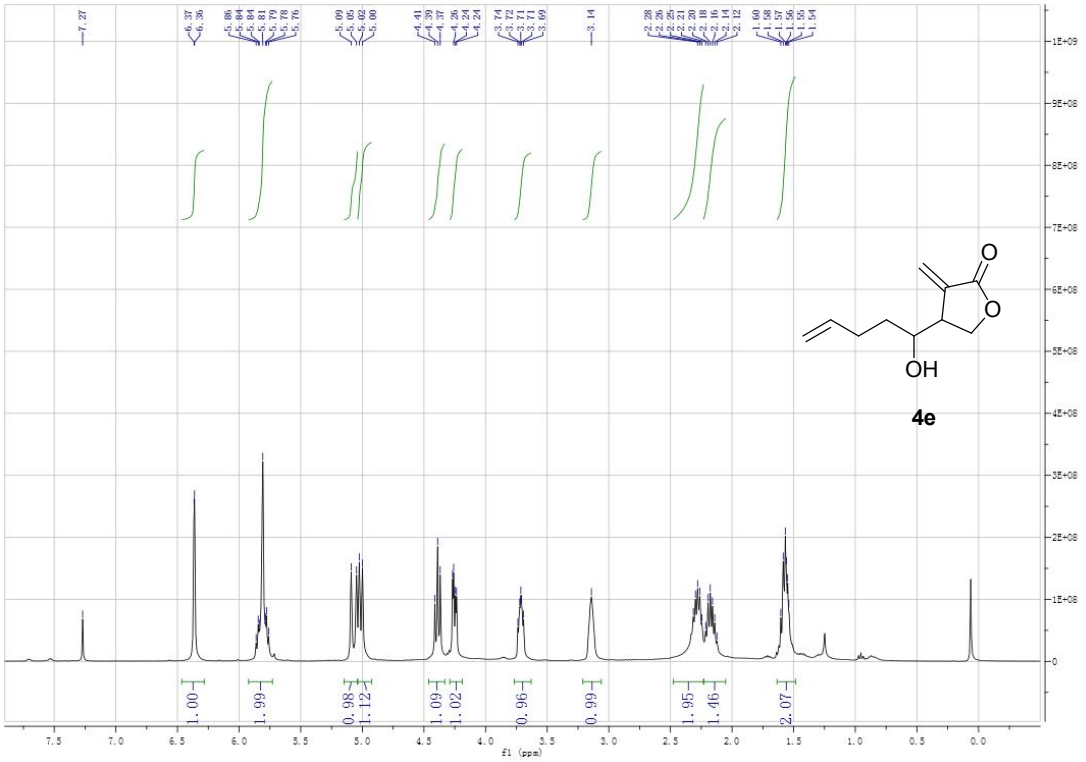
O
S
OH
4d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5.00
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4.24
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3.71
3.71
3.69
3.14
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2.26
2.25
2.21
2.20
2.18
2.16
2.14
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1.58
1.57
1.56
1.55
1.54
1.00
1.99
0.98
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2.07
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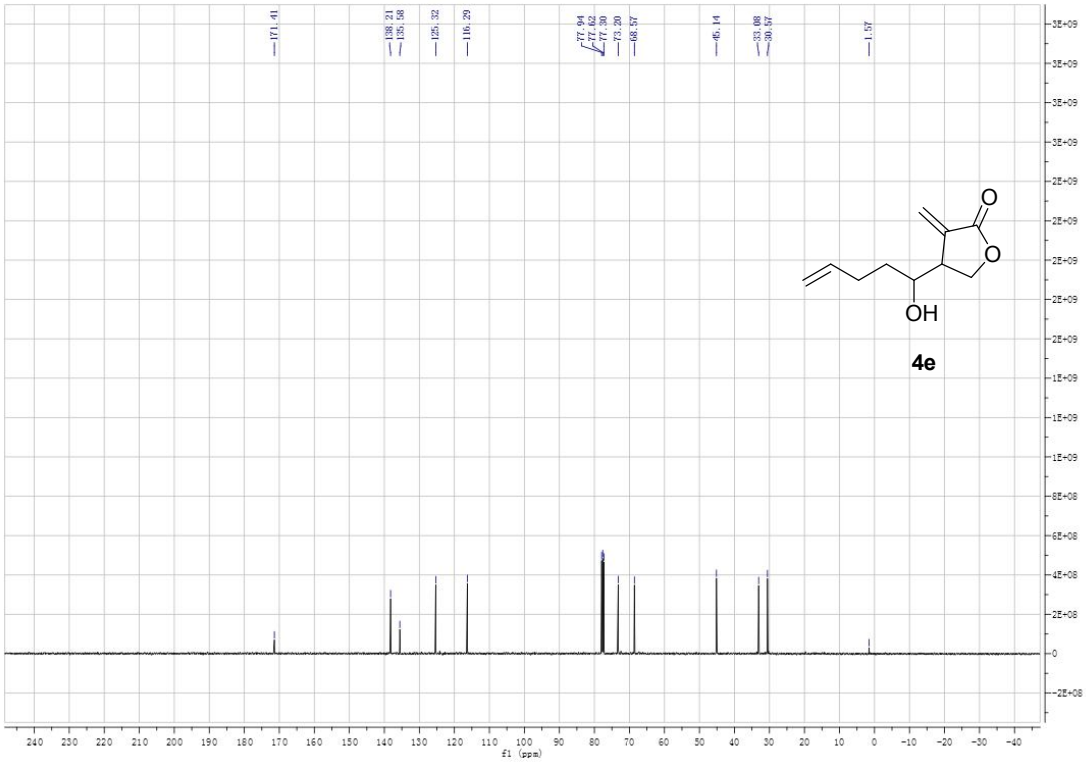
O
OH
4e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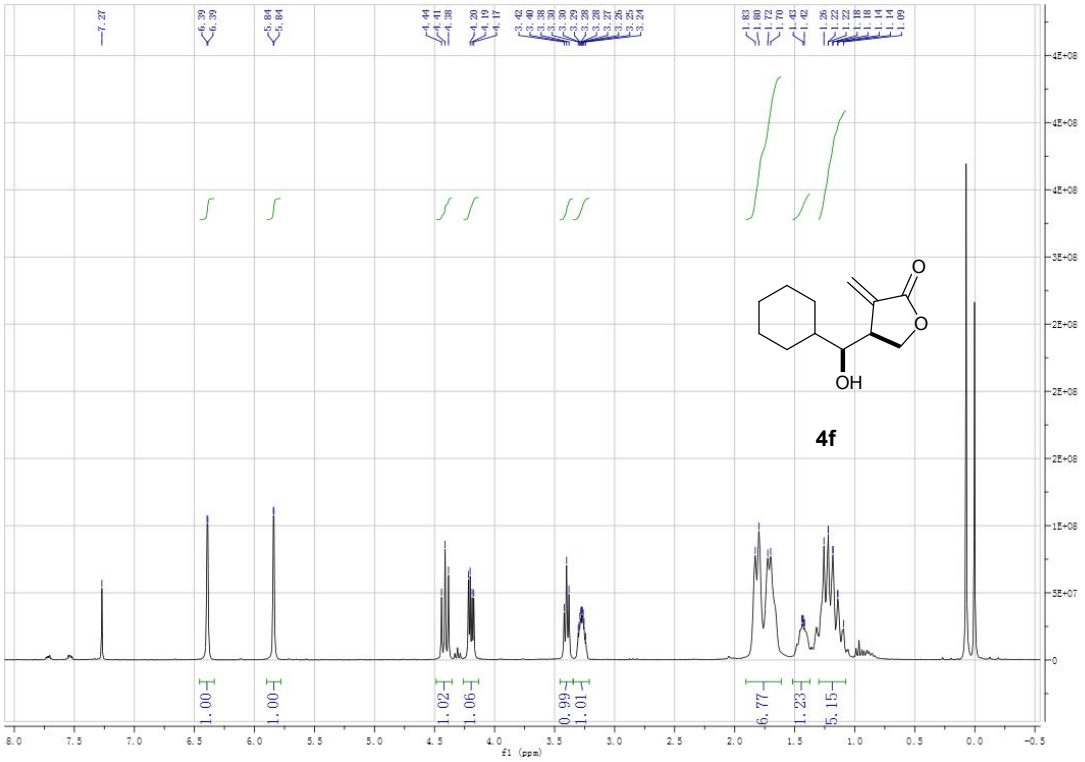
O
O
OH
4e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3.29
3.28
3.28
3.27
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3.24
1.83
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1.70
1.43
1.42
1.26
1.22
1.22
1.18
1.18
1.14
1.14
1.09
1.00
1.00
1.02
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0.99
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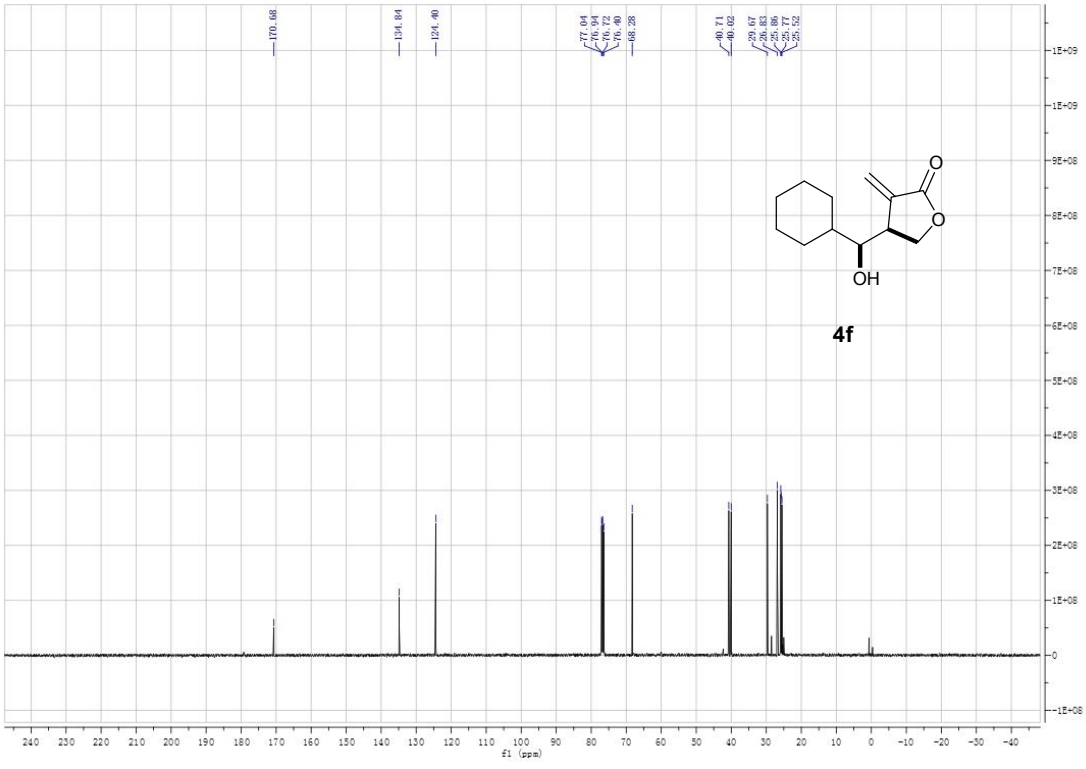
1.23
5.15
f1 (ppm)
O
O
OH
4f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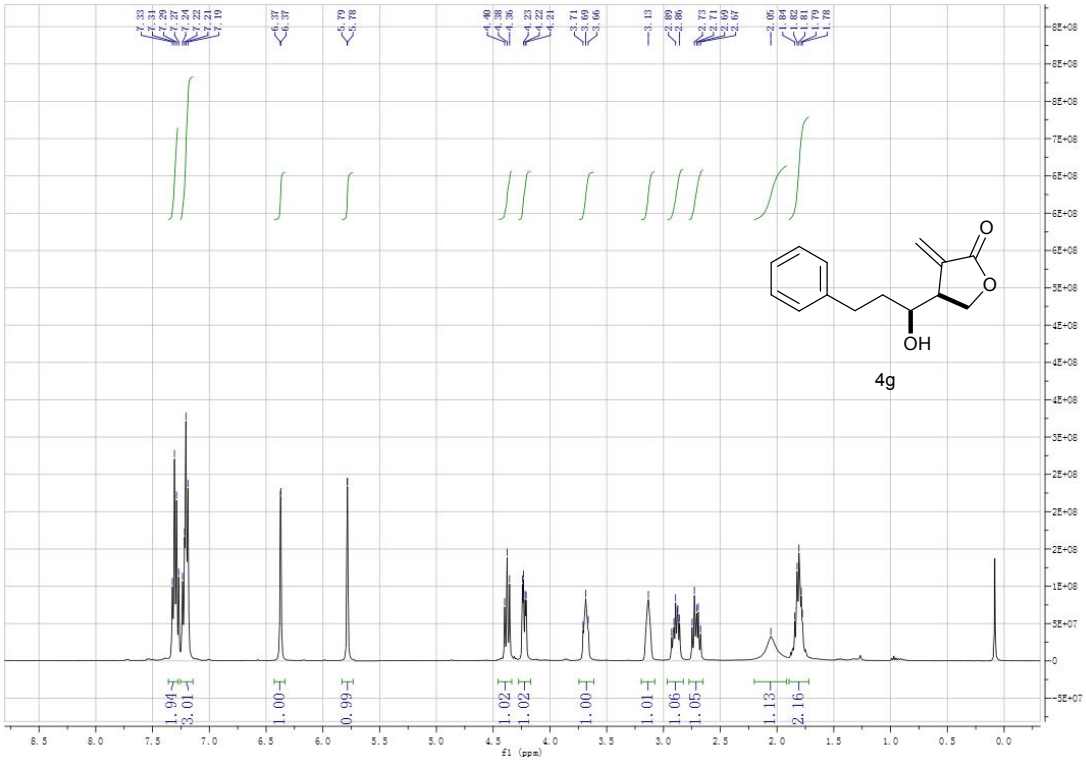
25.77
25.52
f1 (ppm)
O
O
OH
4f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6.37
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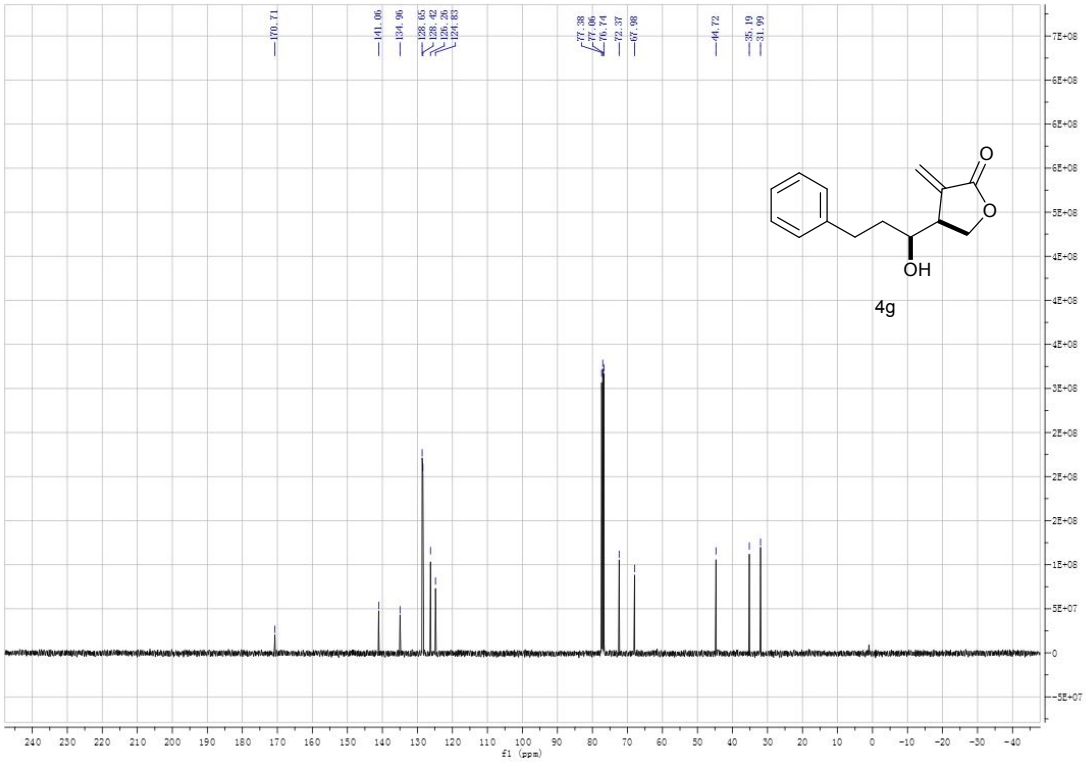
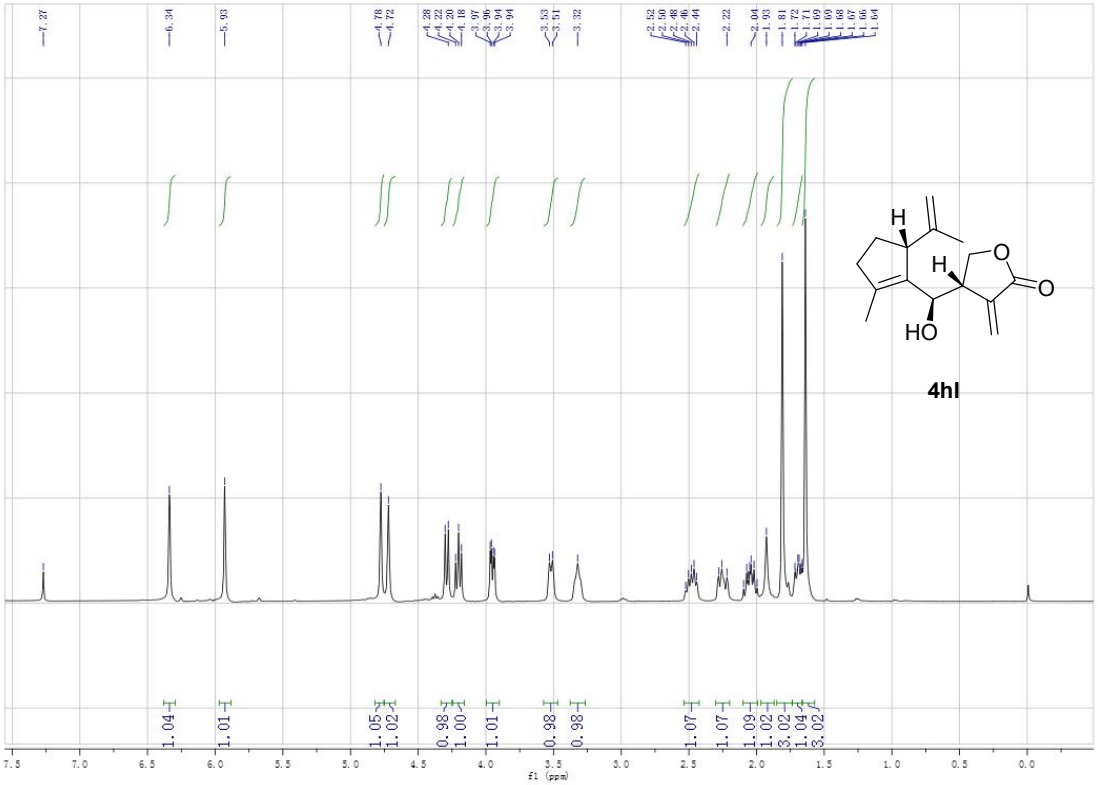
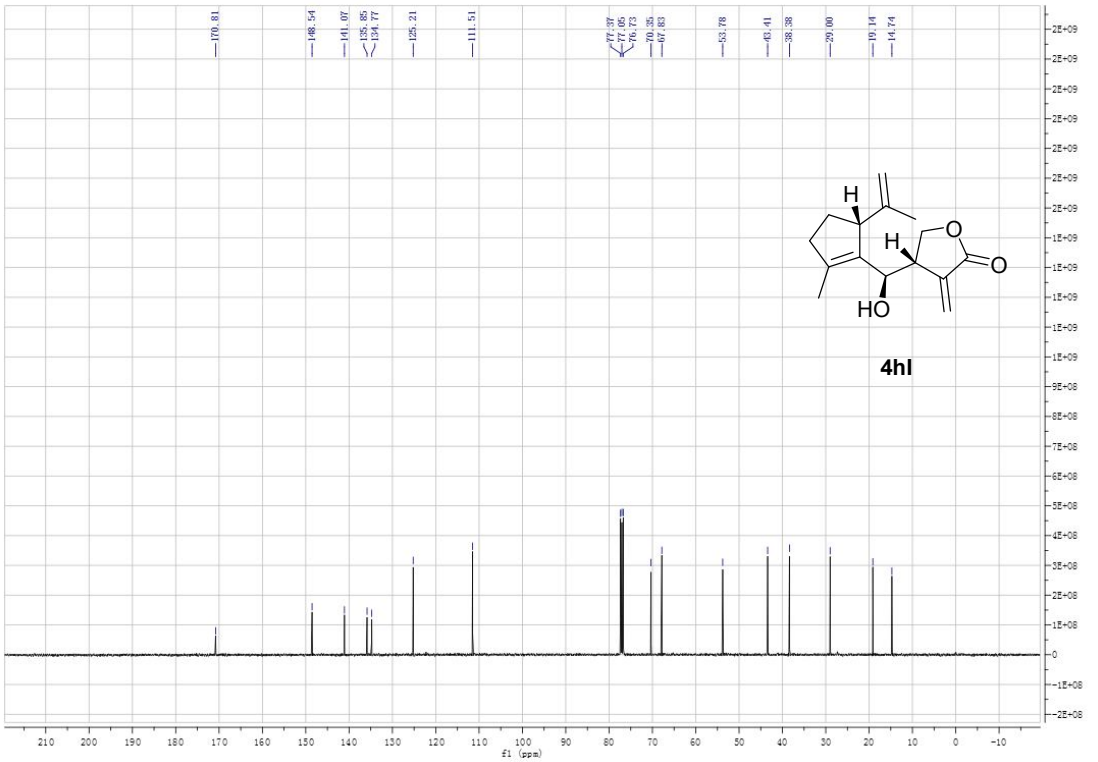
5.79
5.78
4.40
4.38
4.36
4.23
4.22
4.21
3.71
3.69
3.66
3.13
2.89
2.86
2.73
2.71
2.69
2.67
2.05
1.84
1.82
1.81
1.79
1.78
1.94
3.01
1.00
0.99
1.02
1.02
1.00
1.01
1.06
1.05
1.13
2.16
O
O
OH
4g
f1 (ppm)

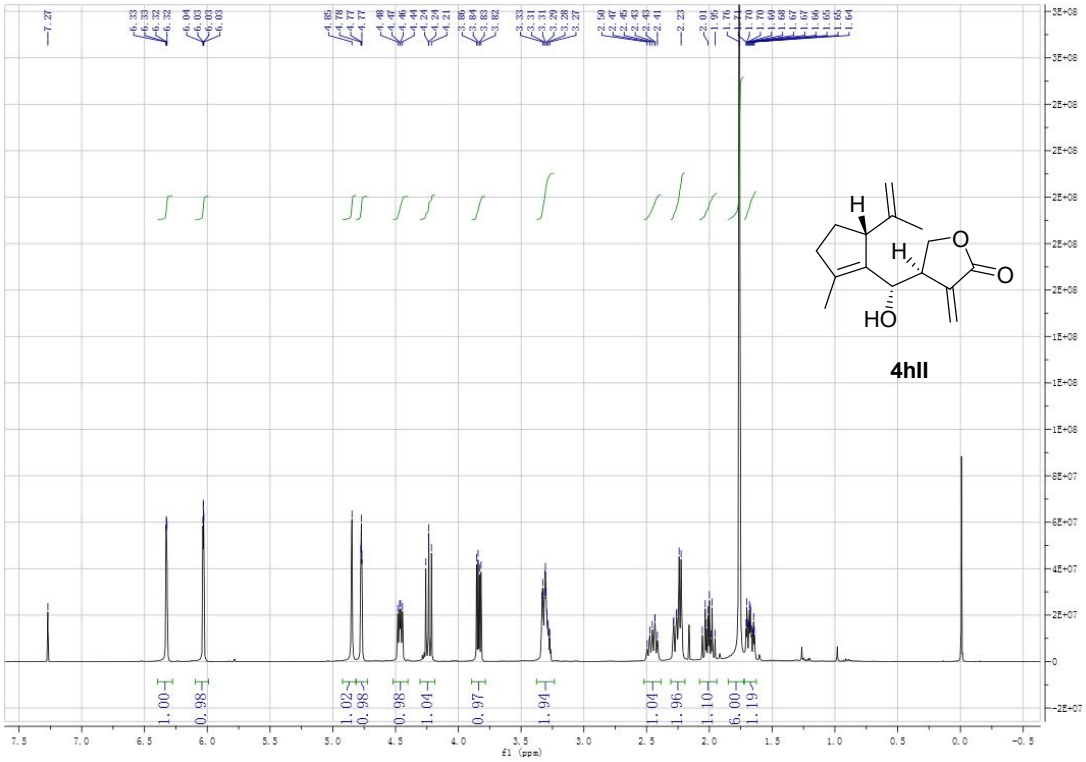

170.71
141.06
134.96
128.55
128.42
126.26
124.85
77.38
77.06
76.74
72.37
67.98
44.72
35.19
31.99
O
O
OH
4g
f1 (ppm)

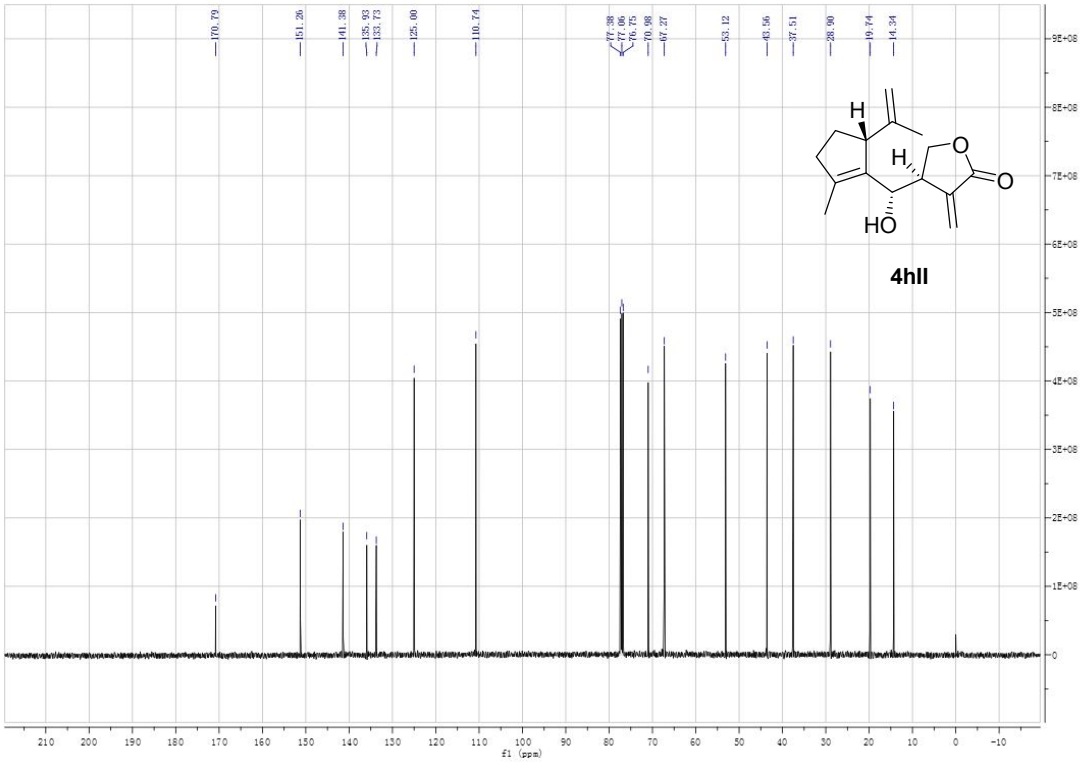


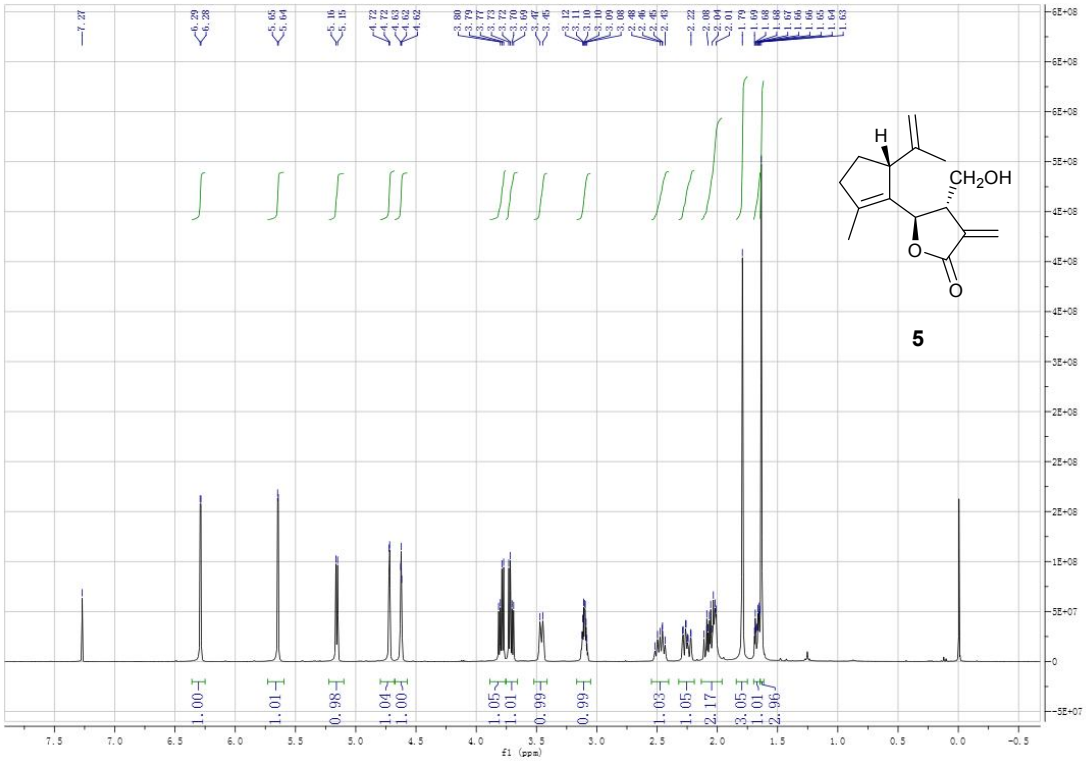
4hl

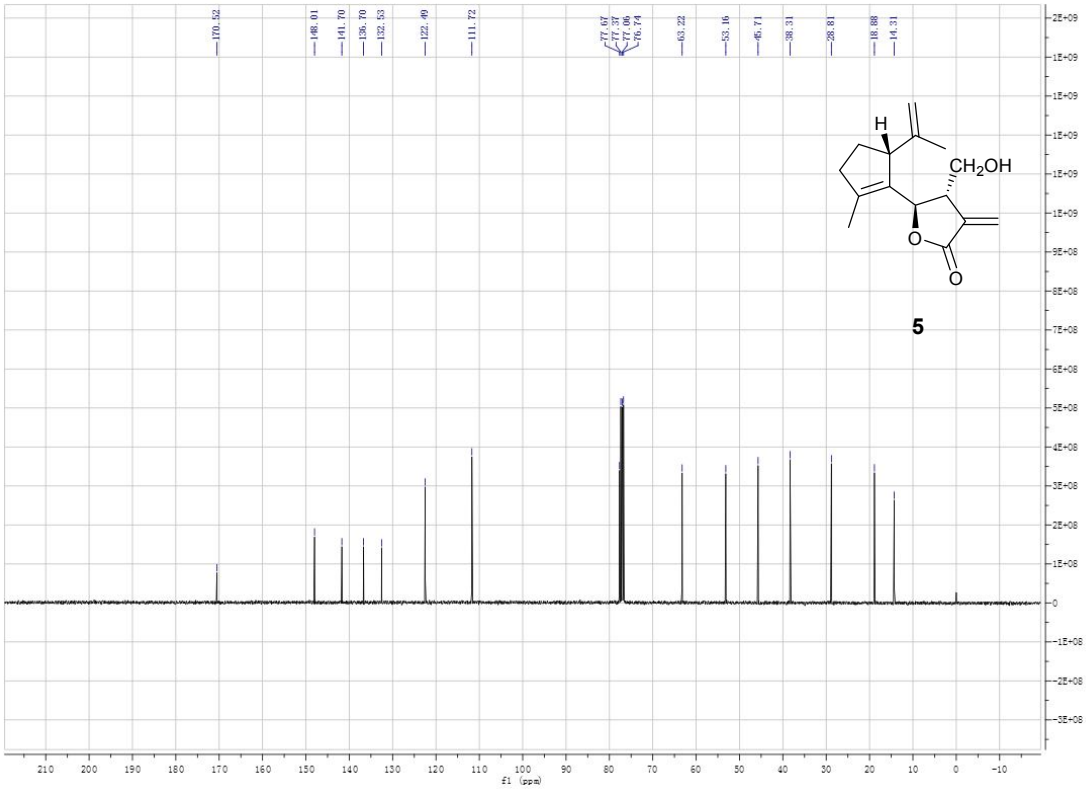


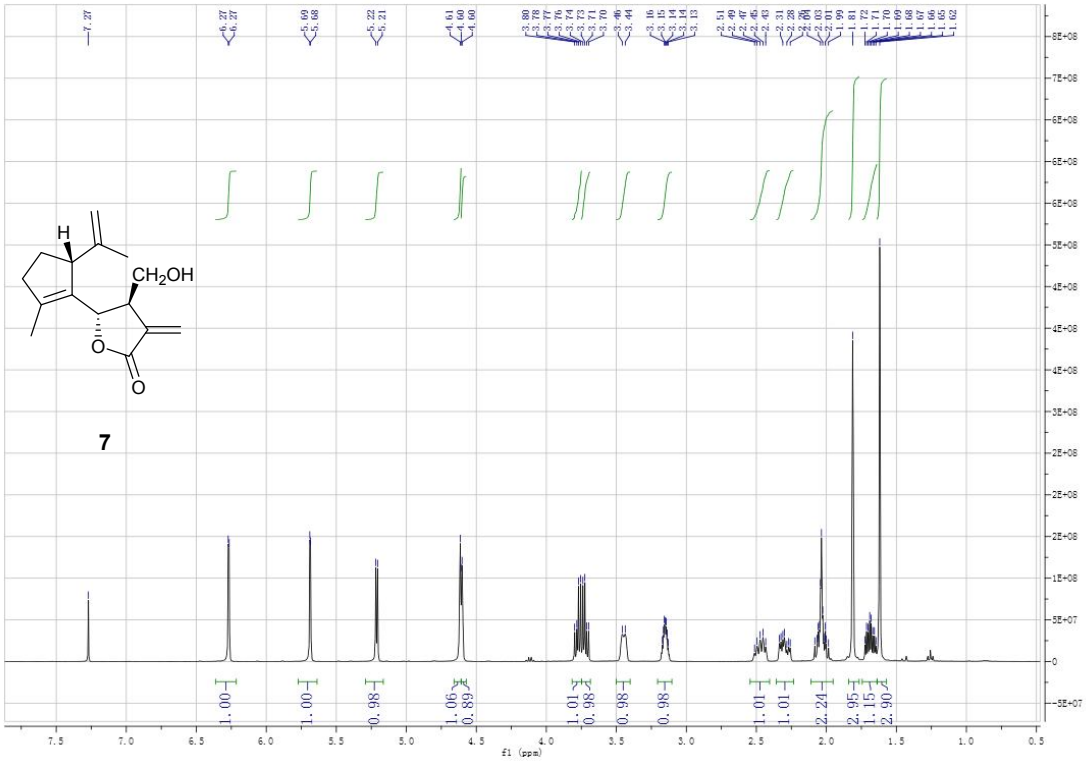
4hl

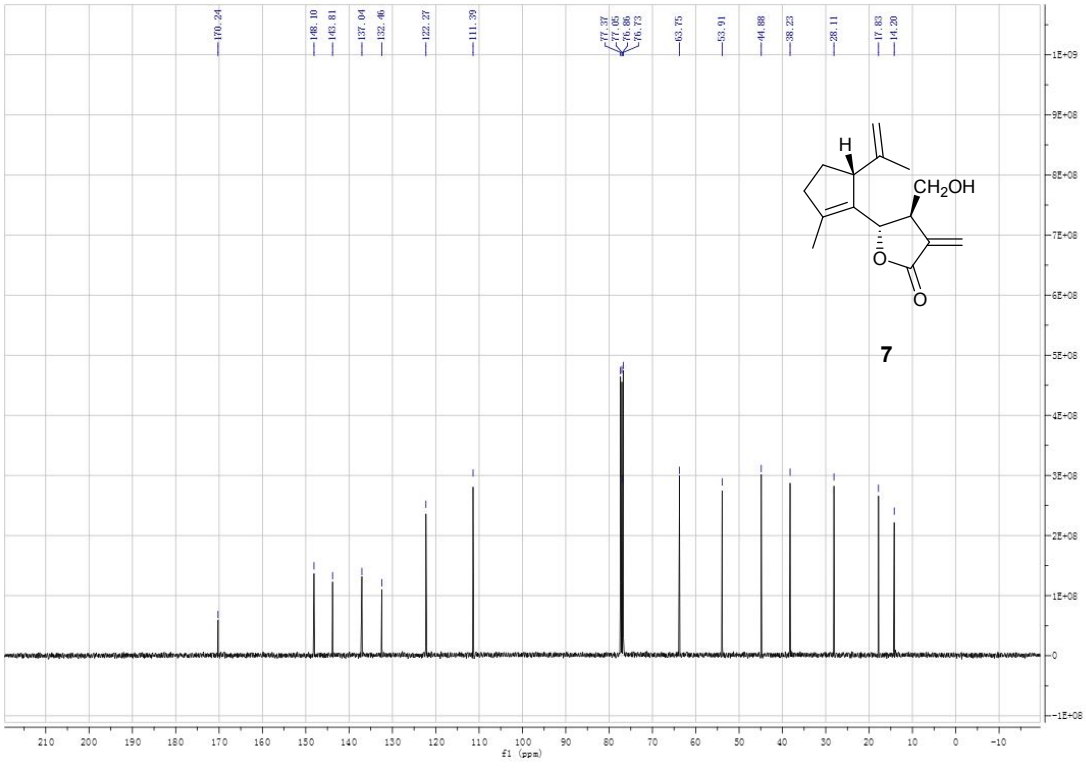

H
H
O
O
HO
4hll

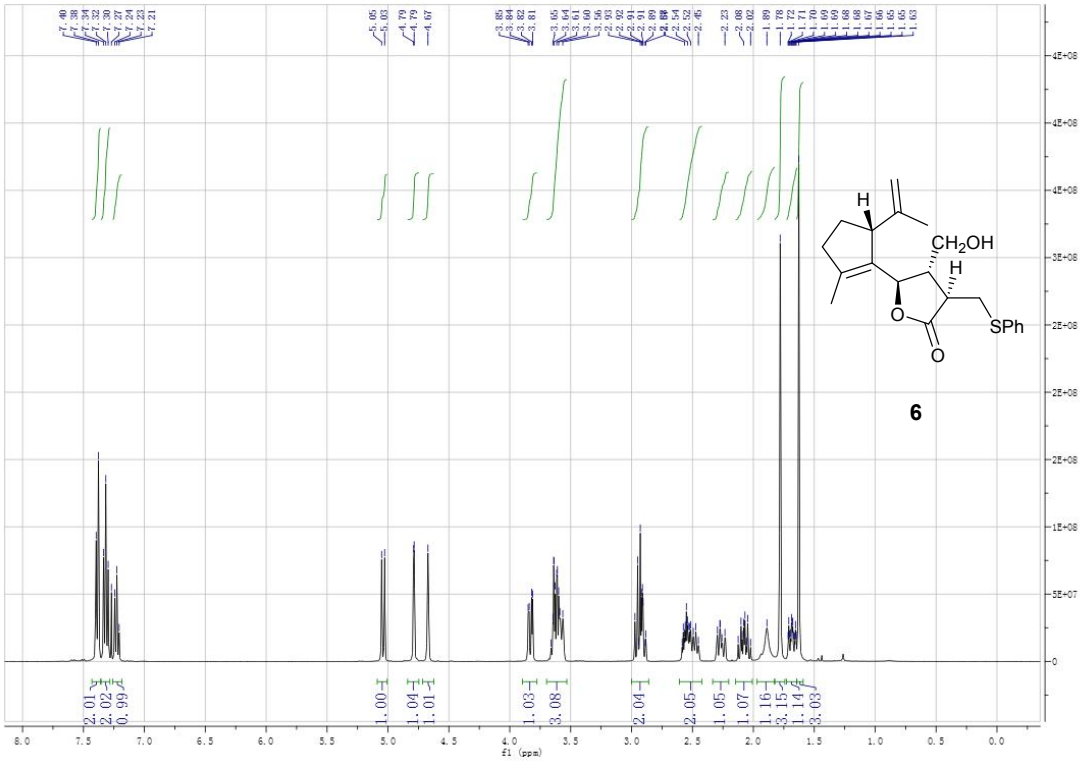

H
H
O
O
HO
4hll

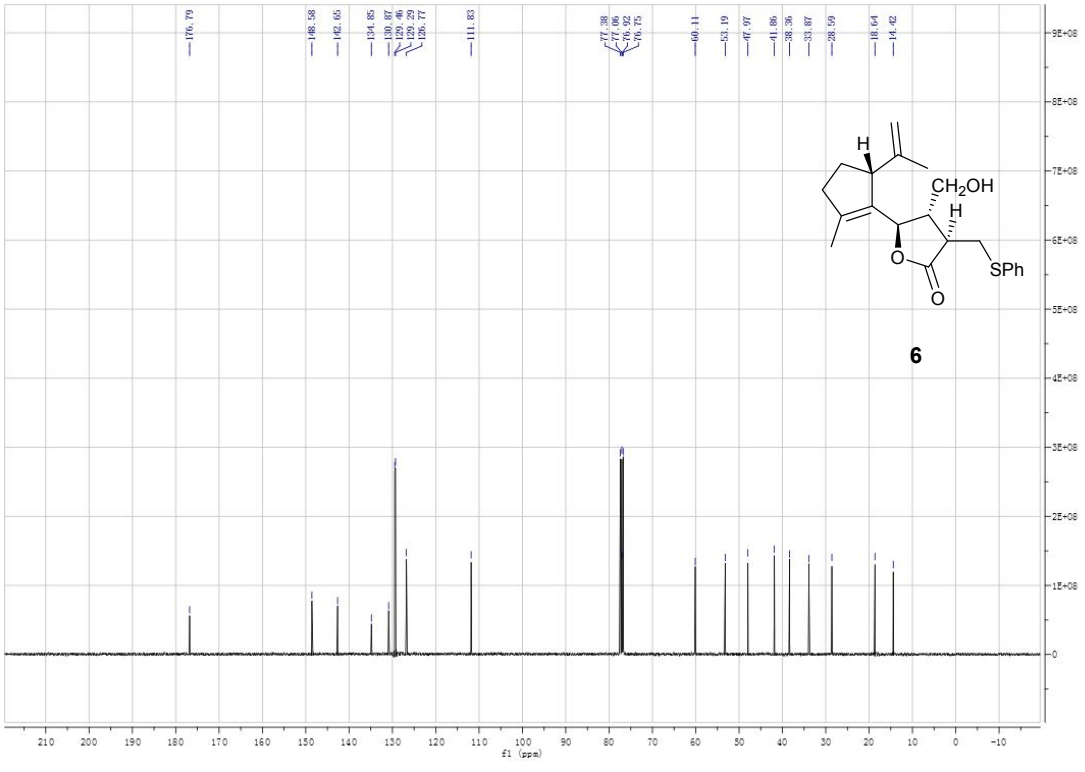

H
CH2OH
O
O
5

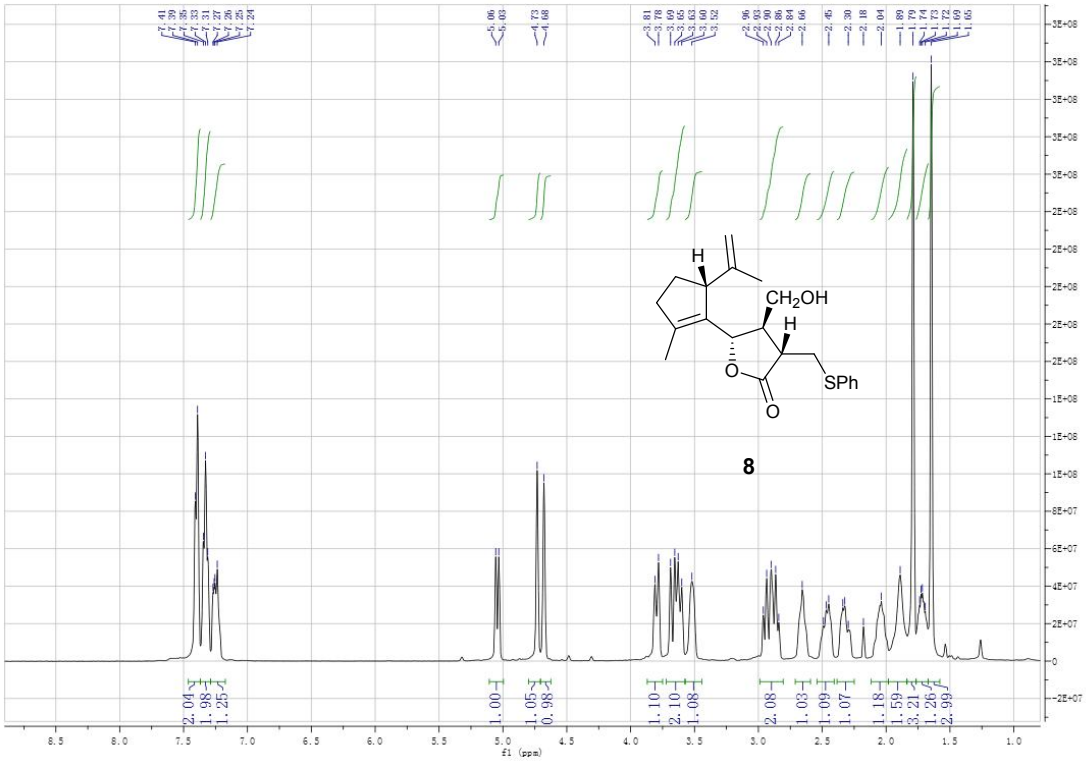

H
CH2OH
O
O
5

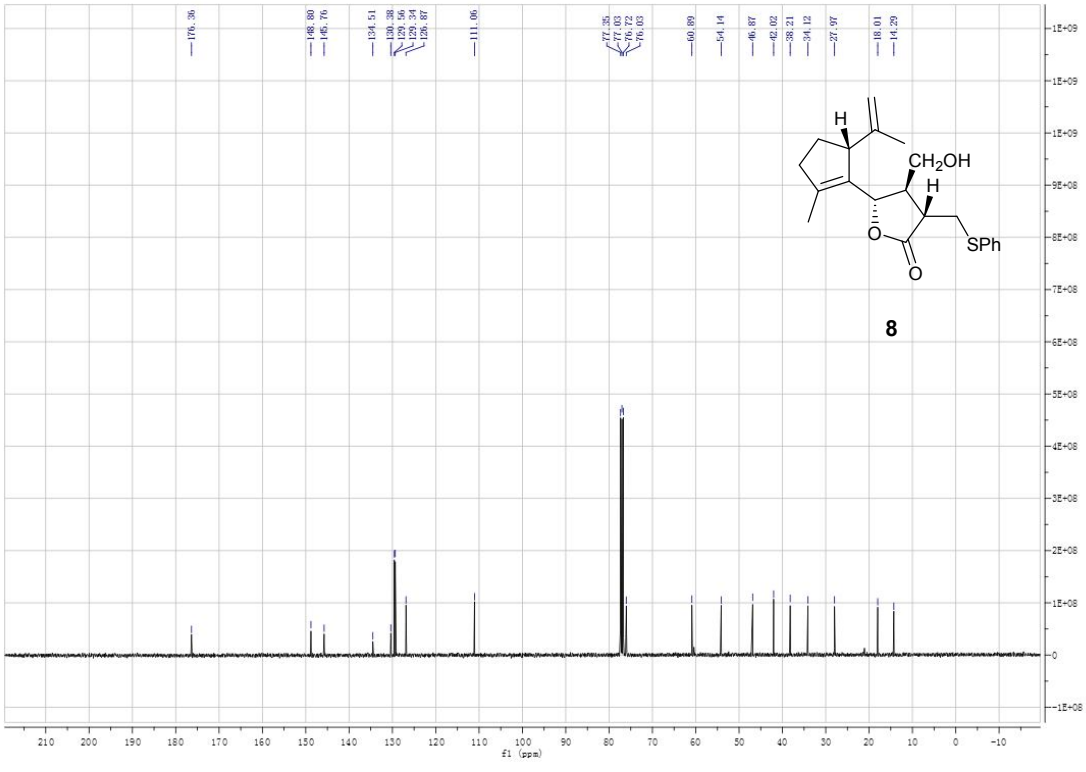

H
CH2OH
O
O
7


H
CH2OH
O
O
7


H
CH2OH
H
O
O
SPh
6

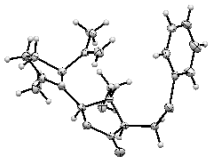

H
CH2OH
H
O
O
SPh
6


H
CH2OH
H
O
O
SPh
8


H
CH2OH
H
O
O
SPh
8

9-Structure of 6, 8 by X-ray

Structure of 6



Structure of 8