Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

For

Pd-catalyzed diastereoselective allylation of aldehydes with 3-bromomethyl-5*H*-furan-2-one: Stereoselective synthesis of *syn* configuration of *β*-(Hydroxymethylaryl/ alkyl)-*α*-methylene-*γ*-butyrolactones

List of the Contents

1-General details

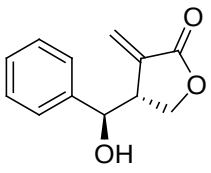
Unless otherwise specified, the reactions were carried out in oven-dried glassware under an argon atmosphere. All commercially available reagents were used without further purification. THF, Et_2O, toluene and xylene were refluxed over and distilled from sodium-benzophenone ketyl. CH_2Cl_2 and CH_3CN was refluxed over and distilled from P_2O_5. Preparative separation was performed by column chromatography on silica gel 100-200m. Thin layer chromatography (TLC) was performed on glass backed plates pre-coated with silica (GF254), which were developed using standard visualizing agents. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, and chemical shifts were represented as d-values relative to the internal standard TMS. ^{1}H: Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, sept = sepetet), integration, coupling constants (*J*) in Hz. ^{13}C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ 77.0 ppm). IR spectra were recorded on a Varian 2000 Infrared spectrophotometer and are reported as cm^{-1}. High-resolution mass spectra (HRMS) recorded for accurate mass analysis, were performed on a Q-TOF micro (Waters) spectrometer.

Melting points were uncorrected.

2-Procedure A: Allylation of aromatic aldehydes

In a Schlenk tube, $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and toluene(1.3 ml) were added under argon. The reaction mixture was stirred at 30℃ for 30m in, then the bromolactone 2 (44 mg, 0.25 mmol) in toluene (0.3 ml), aldehydes (0.3 mmol) in toluene (0.2 ml) and Me_2Zn (0.6 ml, 1.0M in toluene, 0.6 mmol) were added sequentially. The reaction mixture was stirred at 30℃ for 4-6h before quenching with saturated NH_4Cl (aq.). After stirring for 30min, ethyl acetate (10 ml) was added and the organic phase was separated, washed with brine, dried ($NaSO_4$) and evaporated to give the crude homoallylic alcohol products. Purification was achieved via flash column chromatography (petroleum ether/ethyl acetate).

3- **Characterization data for lactones 3a-3m**



3a

4-(Hydroxy(phenyl)methyl)-3-methylenedihydrofuran-2(3*H*)-one (3a):

Following procedure A, a solution of 1a (32 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05

mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in toluene (1.8 ml) was stirred at 30℃ for 2h to give the desired 3a (39.8 mg, 78%) as a colourless oil.

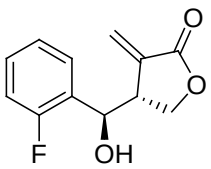
^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.29 (5 H, dt, *J* 14.4, 7.5), 6.35 (1 H, d, *J* 2.5), 5.70 (1 H, d, *J* 2.0), 5.37 (1 H, d, *J* 4.7，H-4), 3.90 – 3.75 (2 H, m), 3.09 (1 H, d, *J* 2.4,H-5).

Discernable data for minor diastereoisomer: 4.68 (1 H, d, *J* = 7 Hz, H-4), 3.43 (1H, m, H-5).

^{13}C NMR (100 MHz, $CDCl_3$) : 168.93, 138.52, 134.53, 127.86, 127.58, 124.52, 122.84, 79.85, 62.38, 49.03.

IR (neat): 3460br, 1767s, 1663s, 1269s, 1134br.

HRMS (ESI) *m/z* calcd for $C_{12}H_{12}O_3$ 204.0786; found 203.0711



3b

4-(2-Flurophenyl)(hydroxy)methyl)-3-methylenedihydrofuran-2(3*H*)-one (3b):

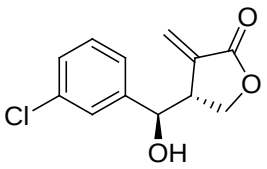
Following procedure A, a solution of 1b (37.2 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in toluene (1.8 ml) was stirred at 30℃ for 6h to give the desired 3b (43.8 mg, 79%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) : δ7.27 (2 H, td, *J* 7.5, 1.8), 7.10 (1 H, t, *J* 7.5), 7.04 (1 H, d, *J* 10.2), 6.38 (1 H, d, *J* 2.5), 5.73 (1 H, d, *J* 2.2), 5.56 (1 H, d, *J* 4.5), 3.87 (2 H, ddd, *J* 16.8, 10.9, 5.4), 3.13 (1 H, m).

^{13}C NMR (100 MHz, $CDCl_3$) : 170.08, 161.14, 158.69, 135.41, 130.34, 127.26, 126.87, 124.55, 124.20, 115.94, 115.74, 76.23, 63.55, 49.07.

IR (neat): 3450s, 1776s, 1543s, 1125s.

HRMS (ESI) *m/z* calcd for $C_{12}H_{11}FO_3$ (M + Na^+) 245.0692, found 245.0584



3c

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

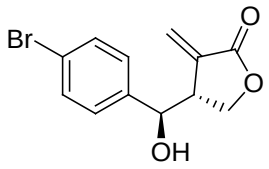
Following procedure A, a solution of 1c (42.2 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in toluene (1.8 ml) was stirred at 30℃ for 6h to give the desired 3c (50.6mg, 85.4%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.32 (3 H, m), 7.22 (1 H, s), 6.43 (1 H, d, *J* 2.6), 5.77 (1 H, d, *J* 2.2), 5.43 (1 H, d, *J* 4.6), 3.90 (2 H, m), 3.14 (1 H, m), 2.19 (1 H, m).

^{13}C NMRδ (100 MHz, $CDCl_3$) : 169.72, 141.71, 134.90, 130.22, 128.70, 125.68, 124.41, 123.60, 80.05, 63.47, 49.92.

IR (neat): 3453s, 1766s, 1477s, 1271s.

HRMS (ESI) *m/z* calcd for $C_{12}H_{11}ClO_3$ ($M+H^+$) 239.0397; found 239.0472



3d

4-(4-Bromophenyl)(hydroxy)methyl)-3-methylenedihydrofuran-2(3*H*)-one (3d):

Following procedure A, a solution of 1d (55.5 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in toluene (1.8 ml) was stirred at 30℃ for 6h to give the desired 3d (57.8 mg, 82.5%) as a white solid.

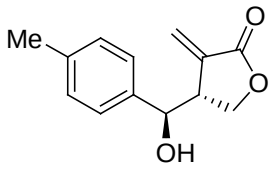
m.p : 51-54℃

^{1}H NMR (400 MHz, $CDCl_3$): δ7.42 (2 H, d, *J* 8.3), 7.12 (2 H, d, *J* 8.3), 6.32 (1 H, d, *J* 2.4), 5.68 (1 H, d, *J* 2.0), 5.34 (1 H, d, *J* 4.6), 3.79 (2 H, m), 3.03 (1 H, d, *J* 2.1), 2.42 (1 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): 169.00, 137.59, 134.01, 130.97, 126.22, 123.36, 121.52, 79.38, 62.31, 48.89.

IR (neat): 3469s, 1747s, 1490s, 1263s.

HRMS (ESI) *m/z* calcd for $C_{12}H_{11}BrO_3$ 281.9892; found 279.0941



3e

4-(4-Methylphenyl)(hydroxy)methyl)-3-methylenedihydrofuran-2(3*H*)-one (3e):

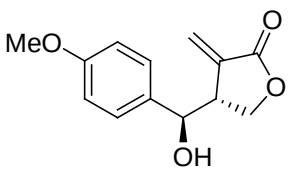
Following procedure A, a solution of 1e (36 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in toluene (1.8 ml) was stirred at 30℃ for 4h to give the desired 3e (45.2 mg, 83.7%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.11 (4 H, d, *J* 4.1), 6.30 (1 H, d, *J* 2.6), 5.67 (1 H, d, *J* 2.2), 5.31 (1 H, d, *J* 4.8), 3.76 (2 H, m), 3.05 (1 H, dd, *J* 7.0, 4.0), 2.27 (3 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): 169.28, 137.48, 135.42, 134.72, 128.49, 124.59, 122.79, 80.07, 62.22, 48.99, 20.12.

IR (neat): 3450br, 1766s, 1751s, 1270s.

HRMS (ESI) *m/z* calcd for $C_{13}H_{14}O_3$ 218.0943; found 218.2115



3f

4-(4-Methoxylphenyl)(hydroxy)methyl)-3-methylenedihydrofuran-2(3*H*)-one (3f):

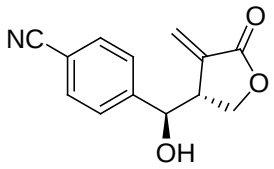
Following procedure A, a solution of 1f (41 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in toluene (1.8 ml) was stirred at 30℃ for 4h to give the desired 3f (48.6 mg, 83.2%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) :δ 7.25 (2 H, d, *J* 8.5), 6.90 (2 H, d, *J* 8.5), 6.39 (1 H, d, *J* 2.1), 5.77 (1 H, d, *J* 1.6), 5.38 (1 H, d, *J* 4.8), 3.84 (5 H, m), 3.16 (1 H, d, *J* 2.2), 2.53 (1 H, s).

^{13}C NMR (100 MHz, $CDCl_3$) : 169.25, 158.80, 134.85, 130.30, 126.22, 122.70, 113.19, 80.08, 62.12, 54.31, 48.84.

IR (neat): 3457br, 1762s, 1516s, 1251s.

HRMS (ESI) *m/z* calcd for $C_{13}H_{14}O_4$ ($M+H^+$) 235.0892; found 235.0967.



3g

4-(Hydroxy(4-methylene-5-oxotetrahydrofuran-3-yl)methyl)benzonitrile (3g):

Following procedure A, a solution of 1g (39 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in toluene (1.8 ml)

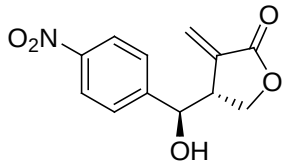
was stirred at 50℃ for 4h to give the desired 3g (39.5 mg, 69%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.62 (2 H, d, *J* 8.2), 7.42 (2 H, d, *J* 8.2), 6.38 (1 H, d, *J* 2.5), 6.31 (0 H, m), 5.71 (1 H, d, *J* 2.0), 5.47 (1 H, d, *J* 4.5), 3.86 (2 H, m), 3.05 (1 H, m).

^{13}C NMR (100 MHz, $CDCl_3$) : 168.23, 144.00, 133.23, 131.68, 125.06, 123.80, 117.31, 111.38, 78.73, 62.67, 48.80.

IR (neat): 3536s, 1745s, 1460s, 1164s.

HRMS (ESI) *m/z* calcd for $C_{13}H_{11}NO_3$ ($M+H^+$) 230.0739; found 230.2476



3h

4-(4-Nitrophenyl)(hydroxy)methyl)-3-methylenedihydrofuran-2(3*H*)-one (3h):

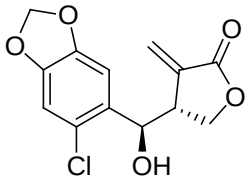
Following procedure A, a solution of 1h (45.3 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in toluene (1.8 ml) was stirred at 50℃ for 4h to give the desired 3h (44.8 mg, 71.2%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.17 (2 H, d, *J* 8.6), 7.48 (2 H, d, *J* 8.5), 6.38 (1 H, d, *J* 2.1), 5.72 (1 H, s), 5.54 (1 H, d, *J* 4.4), 3.86 (2 H, t, *J* 7.4), 3.08 (1 H, m), 2.15 (1 H, s).

^{13}C NMR (100 MHz, $CDCl_3$) :168.44, 146.80, 145.93, 133.14, 125.27, 124.00, 123.09, 78.72, 62.65, 48.83.

IR (neat): 3440s, 1747s, 1560s, 1350, 1171s.

HRMS (ESI) *m/z* calcd for $C_{12}H_{11}NO_5$ 249.0637; found 249.2940



3i

4-(6-Chlorobenzo[d][1,3]dioxol-5-yl)(hydroxy)methyl)-3-methylenedihydrofuran-2(3*H*)-one (3i):

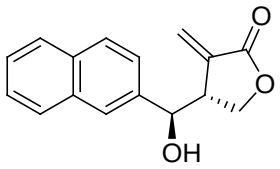
Following procedure A, a solution of 1i (55.2 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in toluene (1.8 ml) was stirred at 30℃ for 6h to give the desired 3i (50.0 mg, 71%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) : δ 6.91 (0 H, s), 6.78 (1 H, s), 6.69 (1 H, s), 6.37 (1 H, d, *J* 2.4), 5.94 (2 H, m), 5.73 (1 H, d, *J* 2.1), 5.59 (1 H, d, *J* 4.0), 3.94 (1 H, dd, *J* 10.8, 5.4), 3.84 (1 H, m), 3.02 (1 H, dd, *J* 5.0, 2.2).

^{13}C NMR (100 MHz, $CDCl_3$) : 170.59, 149.01, 148.11, 136.09, 131.08, 125.19, 124.36, 110.88, 107.09, 102.87, 78.36, 64.40, 50.34.

IR (neat): 3468s, 1748s, 1487s, 1243s, 1117s.

HRMS (ESI) *m/z* calcd for $C_{13}H_{11}ClO_5$ ($M+H^+$) 283.0295; found 283.0369



3j

4-Hydroxy(naphthalen-2-yl)methyl)-3-methylenedihydrofuran-2(3*H*) -one(3j):

Following procedure A, a solution of 1j (46.8 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in toluene (1.8 ml) was stirred at 30℃ for 4h to give the desired 3j (51.4 mg, 81.4%) as a white solid.

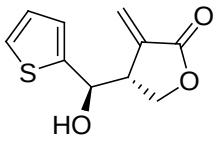
m.p : 63-66℃

^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.11 (1 H, d, *J* 7.5), 7.89 (1 H, m), 7.83 (1 H, dd, *J* 7.1, 2.0), 7.54 (2 H, m), 7.43 (2 H, d, *J* 7.3), 6.41 (1 H, d, *J* 2.0), 6.26 (1 H, d, *J* 3.2), 5.70 (1 H, d, *J* 1.8), 3.98 (1 H, dd, *J* 10.9, 7.1), 3.90 (1 H, dd, *J* 11.0, 5.4), 3.29 (1 H, dd, *J* 3.4, 1.8), 2.91 (1 H, s).

^{13}C NMR (100 MHz, $CDCl_3$) : 169.85, 134.18, 133.85, 132.76, 128.68, 128.03, 125.68, 125.02, 124.22, 123.79, 121.58, 77.19, 62.82, 48.58.

IR (neat): 3510br, 1758s, 1264s, 1121s.

HRMS (ESI) *m/z* calcd for $C_{16}H_{14}O_3$ ($M+H^+$) 255.0943; found 255.1019



3k

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

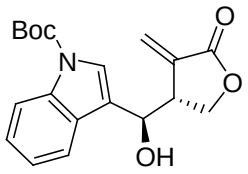
Following procedure A, a solution of 1k (33.6 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in toluene (1.8 ml) was stirred at 30℃ for 4h to give the desired 3k (39.4 mg, 75%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.27 (1 H, dd, *J* 5.1, 1.2), 7.05 (1 H, d, *J* 3.5), 6.94 (1 H, dd, *J* 5.0, 3.6), 6.35 (1 H, d, *J* 2.7), 5.73 (1 H, d, *J* 2.4), 5.59 (1 H, d, *J* 5.2), 3.83 (2 H, dt, *J* 15.6, 5.3), 3.27 (1 H, m), 1.90 (1 H, t, *J* 5.2).

^{13}C NMR (100 MHz, $CDCl_3$) : 168.18, 140.81, 134.29, 126.08, 125.43, 125.14, 122.94, 75.94, 61.84, 48.98.

IR (neat): 3445, 1758, 1645, 1263, 1123.

HRMS (ESI) *m/z* calcd for $C_{10}H_{10}SO_3$ ($M+Na^+$) 233.0351; found 233.0240



3l

***tert*-Butyl 3-(-Hydroxy-4-methylene-5-oxotetrahydrofuran-3-yl)methyl)-1*H*-indole-1-carboxylate (3l):**

Following procedure A, a solution of 1l (73.4 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in toluene (1.8 ml) was stirred at 30℃ for 4h to give the desired 3l (63.5 mg, 74%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (1 H, d, *J* 8.2), 7.52 (2 H, m), 7.29 (1 H, t, *J* 7.7), 7.19 (1 H, t, *J* 3.5), 6.40 (1 H, d, *J* 2.3), 5.74 (1 H, d, *J* 1.9), 5.65 (1 H, d, *J* 4.4), 3.86 (2 H, m), 3.37 (1 H, m), 1.60 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): 170.36, 154.61, 136.20, 128.27, 125.80, 124.92, 124.13, 123.72, 120.12, 119.57, 116.31, 85.01, 76.26, 64.28, 48.26, 28.88.

IR (neat): 3468s, 1741s, 1735s, 1374s, 1139s.

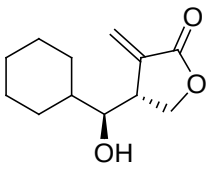
HRMS (ESI) *m/z* calcd for $C_{19}H_{21}NO_5$ ($M+H^+$) 344.1420; found 344.1499.

4-Procedure B: Allylation of aliphatic aldehydes

In a Schlenk tube, $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and THF(1.3 ml) were added under argon. The reaction mixture was stirred at 30℃ for 30min, then the bromolactone 2 (44 mg, 0.25

mmol) inTHF(0.3 ml), aldehydes(0.3 mmol) in THF(0.2 ml) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) were added sequentially. The reaction mixture was stirred at 30℃ for 2-4h before quenching with saturated NH_4Cl (aq.). After stirring for 30min, ethyl acetate (10 ml) was added and the organic phase was separated, washed with brine, dried ($NaSO_4$) and evaporated to give the crude homoallylic alcohol products. Purification was achieved via flash column chromatography (petroleum ether/ethyl acetate).

5-Characterization data for lactones 3m-3t



3m

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

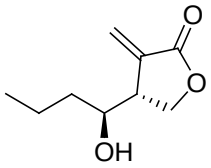
Following procedure B, a solution of 1m (33.6 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in THF (1.8 ml) was stirred at 30℃ for 4h to give the desired 3m (39.9 mg, 76%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.24 (1 H, d, *J* 2.2), 5.67 (1 H, d, *J* 1.8), 4.13 (1 H, dd, *J* 5.6, 3.7), 3.64 (2 H, dt, *J* 16.5, 10.5), 2.95 (1 H, m), 2.22 (1 H, s), 1.68 (6 H, m), 1.47 (1 H, m), 1.15 (4 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): 169.37, 135.45, 122.44, 83.33, 63.66, 43.03, 41.69, 27.22, 26.38, 25.18, 24.78, 24.60.

IR (neat): 3486, 1745, 1650, 1263, 1132.

HRMS (ESI) *m/z* calcd for $C_{12}H_{18}O_3$ ($M+Na^+$) 233.1154; found 233.1146.



3n

4-(1-Hydroxybutyl)-3-methylenedihydrofuran-2(3H)-one (3n):

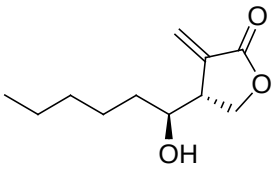
Following procedure B, a solution of 1n (21.6 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in THF (1.8 ml) was stirred at 30℃ for 4h to give the desired 3n (33.6 mg, 79%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.27 (1 H, s), 5.64 (1 H, d, *J* 8.6), 4.35 (1 H, dd, *J* 11.4, 5.4), 3.69 (2 H, d, *J* 5.8), 2.81 (1 H, d, *J* 3.1), 1.82 (1 H, s), 1.59 (2 H, m), 1.42 (2 H, m), 0.90 (3 H, t, *J* 7.3).

^{13}C NMR (100 MHz, $CDCl_3$): 170.20, 136.23, 123.50, 80.58, 63.89, 46.88, 38.16, 18.33, 13.77.

IR (neat): 3445s, 1758s, 1465, 1129.

HRMS (ESI) *m/z* calcd for $C_9H_{14}O_3$ ($M+Na^+$) 193.0841; found 193.0830.



3o

4-(1-Hydroxyhexyl)-3-methylenedihydrofuran-2(3H)-one (3o):

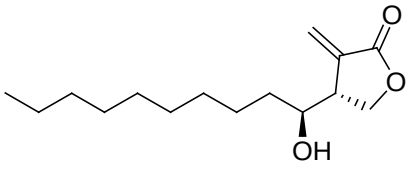
Following procedure B, a solution of 1o (30.0 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in THF (1.8 ml) was stirred at 30℃ for 4h to give the desired 3o (39.4 mg, 79.6%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.34 (1 H, d, *J* 1.7), 5.74 (1 H, s), 4.42 (1 H, dd, *J* 10.5, 5.9), 3.77 (2 H, d, *J* 5.9), 2.89 (1 H, d, *J* 2.7), 2.06 (1 H, s), 1.69 (2 H, dd, *J* 14.2, 6.9), 1.48 (2 H, m), 1.33 (4 H, m), 0.91 (3 H, s).

^{13}C NMR (100 MHz, $CDCl_3$):170.19, 136.25, 123.50, 80.81, 63.91, 46.86, 36.07, 31.47, 24.65, 22.48, 13.97.

IR (neat): 3453s, 1766s, 1460, 1125.

HRMS (ESI) *m/z* calcd for $C_{11}H_{18}O_3$ ($M+Na^+$) 221.1148; found 221.1155.



3p

4-(1-Hydroxydecyl)-3-methylenedihydrofuran-2(3*H*)-one (3p):

Following procedure B, a solution of 1p (46.9 mg, 0.3 mmol), 2 (44

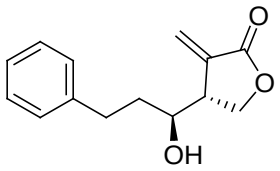
mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in THF (1.8 ml) was stirred at 30℃ for 4h to give the desired 3p (52.1 mg, 82.5%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.26 (1 H, d, *J* 2.6), 5.65 (1 H, d, *J* 2.2), 4.33 (1 H, dd, *J* 10.8, 6.4), 3.68 (2 H, d, *J* 4.4), 2.81 (1 H, m), 1.88 (1 H, s), 1.61 (2 H, m), 1.19 (14 H, s), 0.81 (3 H, t, *J* 6.8).

^{13}C NMR (100 MHz, $CDCl_3$): 169.11, 135.23, 122.45, 79.75, 62.90, 45.84, 35.09, 30.84, 28.44, 28.30, 28.26, 23.96, 21.64, 13.08.

IR (neat): 2955s, 1778s, 1465, 1119.

HRMS (ESI) *m/z* calcd for $C_{15}H_{26}O_3$ ($M+Na^+$) 277.1882; found 277.1899.



3q

4-(1-Hydroxy-3-phenylpropyl)-3-methylenedihydrofuran-2(3*H*)-one (3q):

Following procedure B, a solution of 1q (40.2 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in THF (1.8 ml) was stirred at 30℃ for 4h to give the desired 3q (47 mg, 81%) as a pale

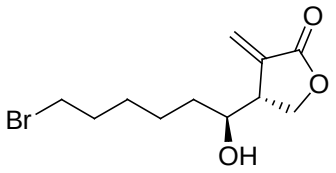
yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (2 H, m), 7.14 (3 H, d, *J* 6.9), 6.28 (1 H, s), 5.66 (1 H, s), 4.34 (1 H, m), 3.67 (2 H, d, *J* 5.9), 2.81 (2 H, m), 2.69 (1 H, dd, *J* 14.8, 6.9), 1.93 (2 H, dd, *J* 14.3, 6.9), 1.82 (1 H, s).

^{13}C NMR (100 MHz, $CDCl_3$):169.09, 139.66, 134.96, 127.53, 127.41, 125.17, 122.74, 78.99, 62.78, 45.87, 36.87 , 30.36.

IR (neat): 3455s, 1758s, 1650, 1254, 1119.

HRMS (ESI) *m/z* calcd for $C_{14}H_{16}O_3$ ($M+Na^+$)255.0992; found 255.0990.



3r

4-(1-Hydroxy-6-bromohexyl)-3-methylenedihydrofuran-2(3*H*)-one (3r):

Following procedure B, a solution of 1r (53.4 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in THF (1.8 ml) was stirred at 30℃ for 4h to give the desired 3r (52.4 mg, 76.2%) as a pale yellow oil.

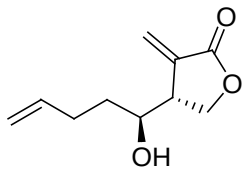
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.27 (1 H, d, *J* 2.6), 5.64 (1 H, dd, *J* 9.8, 2.2), 4.35 (1 H, dd, *J* 12.1, 5.1), 3.70 (2 H, d, *J* 6.3), 3.35 (2 H, t, *J* 6.7),

2.81 (1 H, qd, *J* 6.4, 3.2), 1.81 (2 H, m), 1.64 (2 H, dt, *J* 11.1, 5.5), 1.43 (4 H, m), 1.18 (1 H, s).

^{13}C NMR (100 MHz, $CDCl_3$):168.91, 134.99, 122.57, 79.49, 62.87, 45.83, 34.93, 32.63, 31.48, 26.75, 23.26.

IR (neat): 3425s, 1765s, 1458s, 1126s.

HRMS (ESI) *m/z* calcd for $C_{11}H_{17}BrO_3$ ($M+Na^+$) 299.0361; found 299.0365.



3s

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

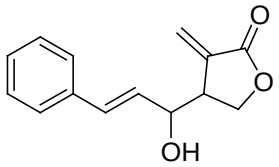
Following procedure B, a solution of 1s (25.2 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in THF (1.8 ml) was stirred at 30℃ for 4h to give the desired 3s (34.1 mg, 75.2%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.27 (1 H, t, *J* 3.4), 6.23, 5.75 (1 H, ddt, *J* 16.9, 10.2, 6.6), 5.65 (1 H, m), 4.99 (2 H, m), 4.37 (1 H, dd, *J* 10.9, 6.4), 3.70 (2 H, d, *J* 6.1), 2.83 (1 H, m), 2.18 (2 H, ddt, *J* 22.4, 14.8, 7.3), 1.94 (1 H, s), 1.72 (2 H, dd, *J* 14.4, 7.3).

^{13}C NMR (100 MHz, $CDCl_3$): 168.99, 135.95, 135.02, 122.62, 114.73, 79.04, 62.84, 45.81, 34.26, 28.21.

IR (neat): 3445s, 1760s, 1640s, 1270, 1116s.

HRMS (ESI) *m/z* calcd for $C_{10}H_{14}O_3$ ($M+Na^+$) 205.0943; found 205.1499.



3t

4-(1-Hydroxy-3-phenylprop-2-en-1-yl)-3-methylenedihydrofuran-2(3*H*)-one (3t):

Following procedure B, a solution of 1t (25.2 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in THF (1.8 ml) was stirred at 30℃ for 4h to give the desired 3t (47.7 mg, 83%) as a pale yellow oil.

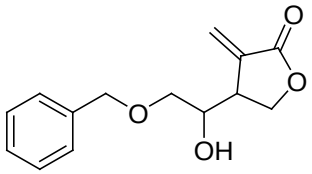
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (10 H, m), 6.61 (1 H, d, *J* 2.0), 6.57 (1.13 H, d, *J* 2.0), 6.32 (2.14 H, dd, *J* 4.6, 2.4), 6.08 (2.2 H, dt, *J* 15.9, 7.0), 5.83 (1.14 H, d, *J* 2.0), 5.68 (1 H, d, *J* 2.2), 4.34 (5 H, m), 4.22 (1 H, dd, *J* 9.6, 4.1), 3.23 (2 H, dddd, *J* 12.8, 8.3, 4.1, 2.1), 2.04 (2 H, dd, *J* 7.0, 5.1).

^{13}C NMR (100 MHz, $CDCl_3$): 169.70, 169.54, 134.68, 133.84, 133.71, 132.67, 132.53, 127.72, 127.36, 126.63, 126.16, 125.65, 124.04, 123.62,

73.41, 73.06, 66.31, 66.21, 43.30, 43.22.

IR (neat): 3448s, 1762s, 1665, 1273s, 1120s.

HRMS (ESI) *m/z* calcd for $C_{14}H_{14}O_3$ ($M+Na^+$) 253.0943; found 253.1299.



3u

4-(1-Hydroxy-2-benzyloxyethyl)-3-methylenedihydrofuran-2(3*H*)-one (3u):

Following procedure B, a solution of 1u (25.2 mg, 0.3 mmol), 2 (44 mg, 0.25 mmol), $Pd(PhCN)_2Cl_2$(10 mg, 0.025 mmol), PPh_3(14 mg,0.05 mmol) and Me_2Zn(0.6 ml, 1.0M in toluene, 0.6 mmol) in THF (1.8 ml) was stirred at 30℃ for 4h to give the desired 3u (50.5 mg, 81.5%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (8 H, m), 6.38 (1 H, d, *J* 2.4), 6.36 (0.6 H, d, *J* 2.4), 5.88 (1 H, d, *J* 2.0), 5.62 (0.6 H, d, *J* 2.1), 4.56 (5 H, m), 4.35 (1.86 H, t, *J* 9.0), 4.23 (1.08 H, dd, *J* 9.5, 4.4), 3.92 (1.74 H, m), 3.59 (0.74 H, d, *J* 3.6), 3.55 (1.76H, dd, *J* 9.6, 3.9), 3.47 (1.08H, dd, *J* 9.5, 6.7), 3.33 (1 H, tdd, *J* 6.9, 4.5, 2.2), 3.27 (0.6 H, ddd, *J* 8.0, 4.0, 2.1), 2.62 (1 H, d, *J* 4.5), 2.52 (0.6 H, d, *J* 5.2).

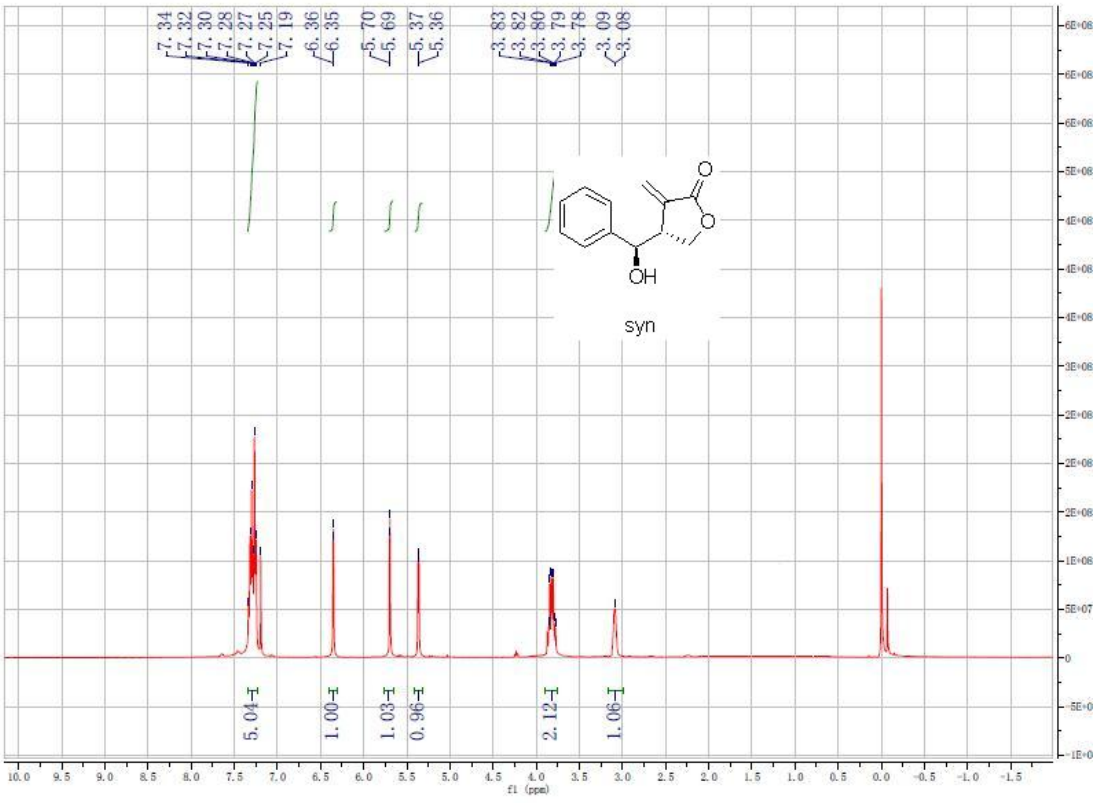
^{13}C NMR (100 MHz, $CDCl_3$): 169.44, 136.24, 134.26, 133.57, 127.59, 127.12, 126.85, 123.98, 122.91, 72.60, 70.73, 69.85, 69.77, 69.71,

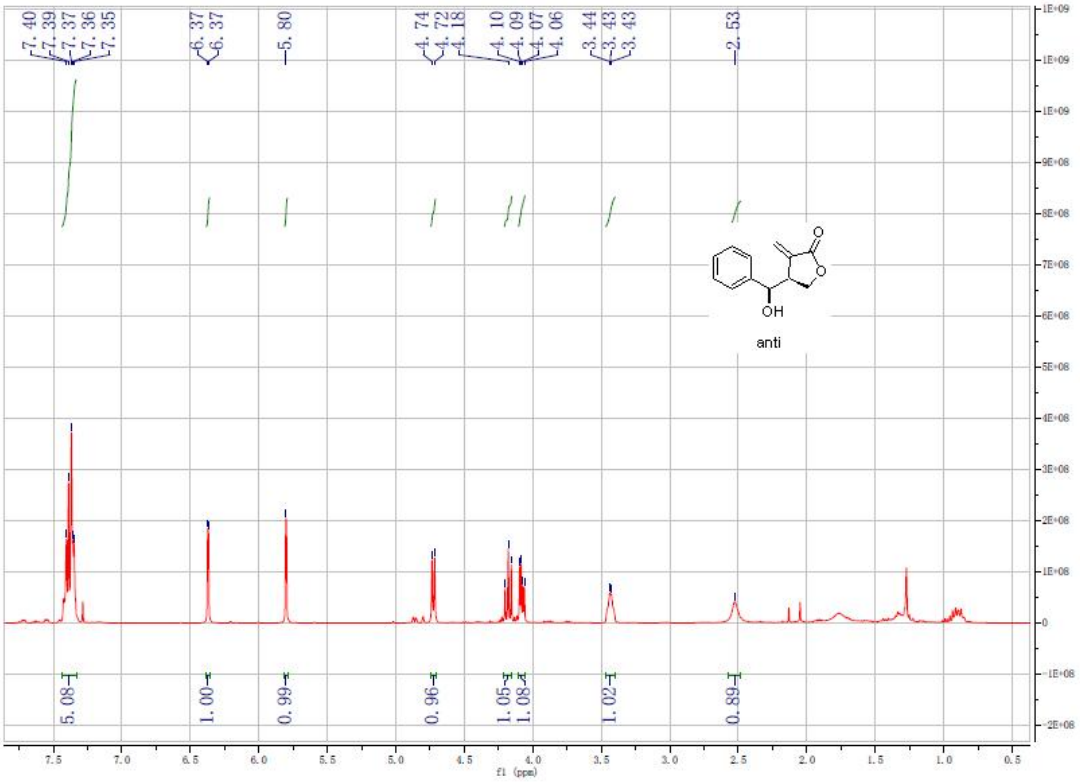
66.24, 66.01, 40.96, 40.45.

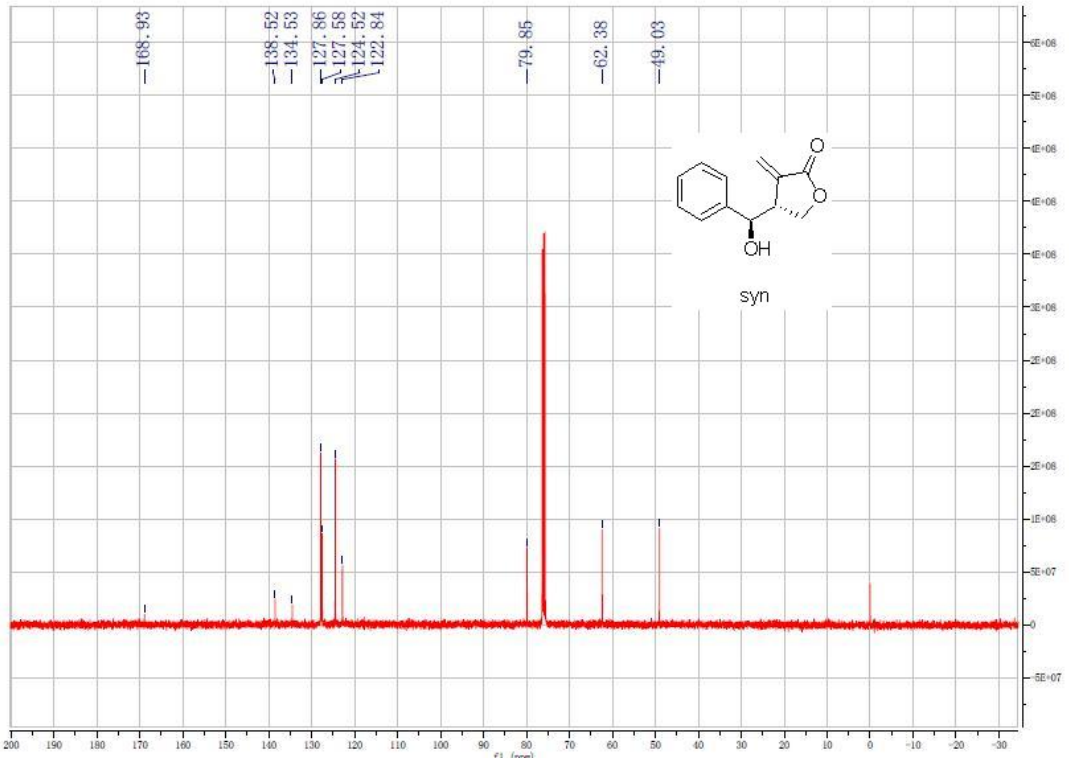
IR (neat): 3559s, 1756s, 1586, 1258s.

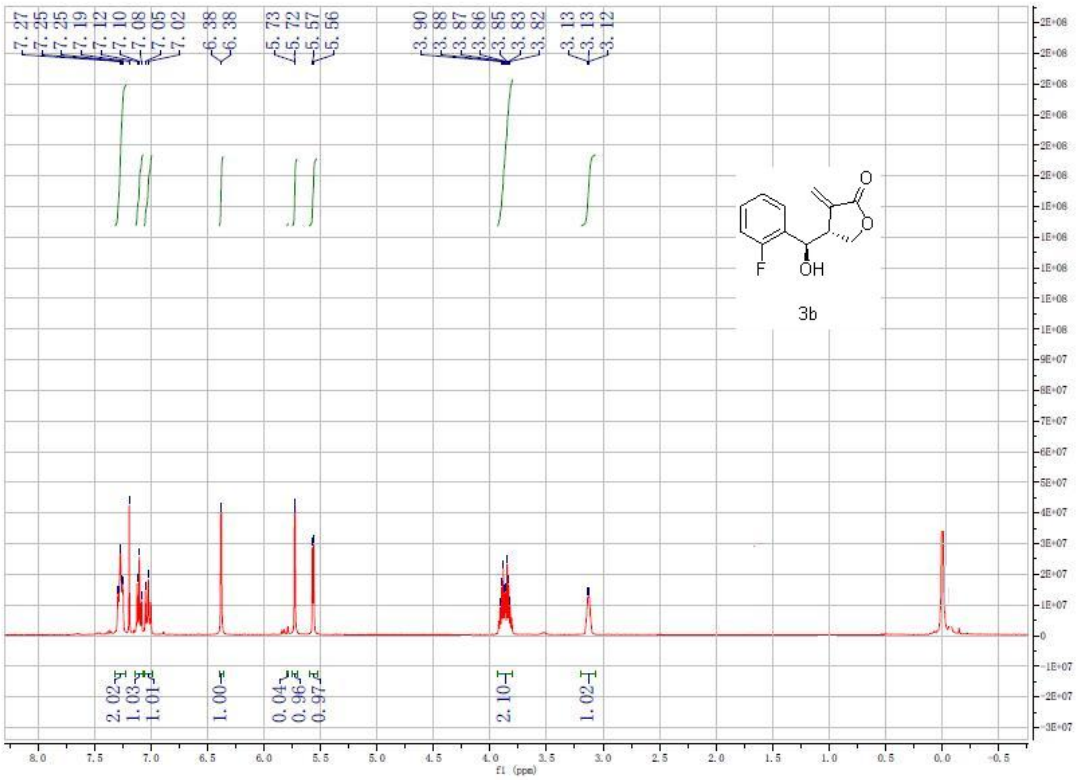
HRMS (ESI) *m/z* calcd for $C_{14}H_{16}O_4$ ($M+Na^+$) 271.1049; found 271.1289.

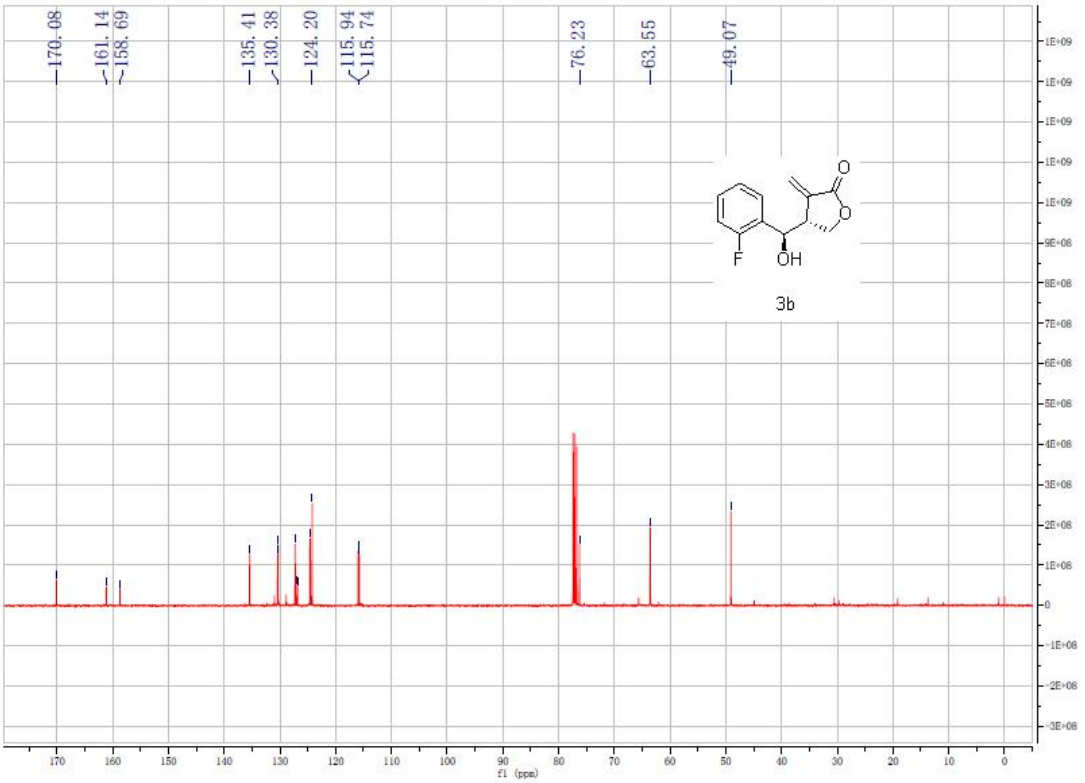
6. ^{1}H and ^{13}C Spectra

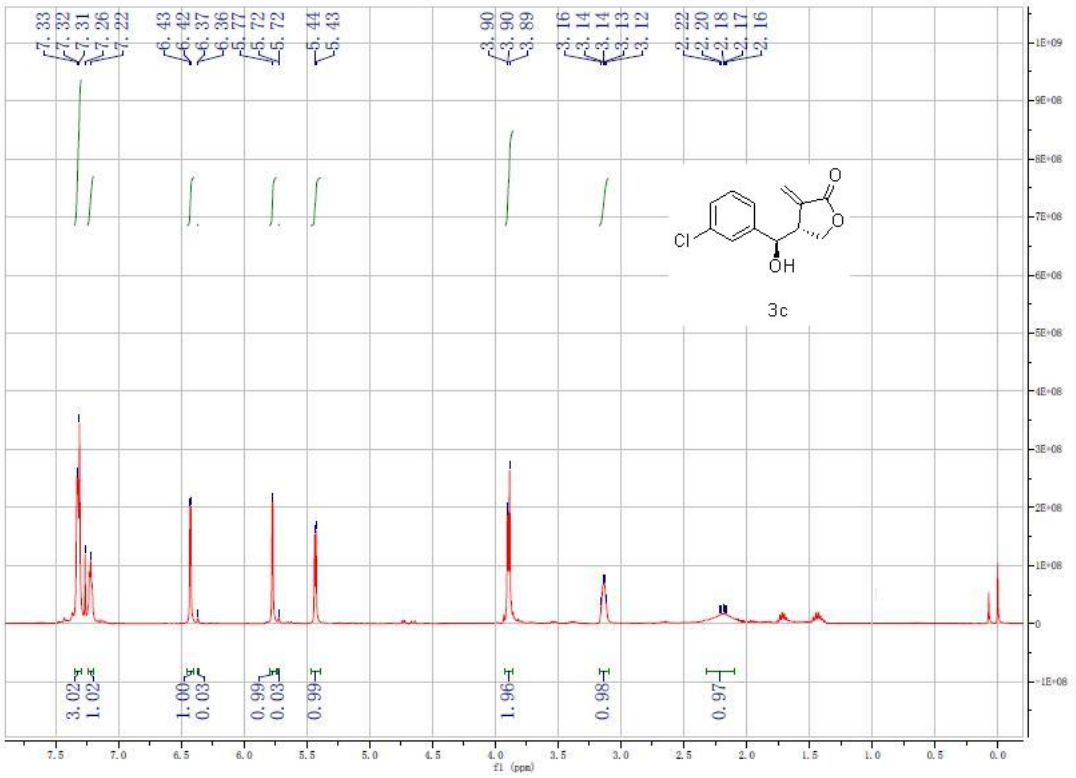


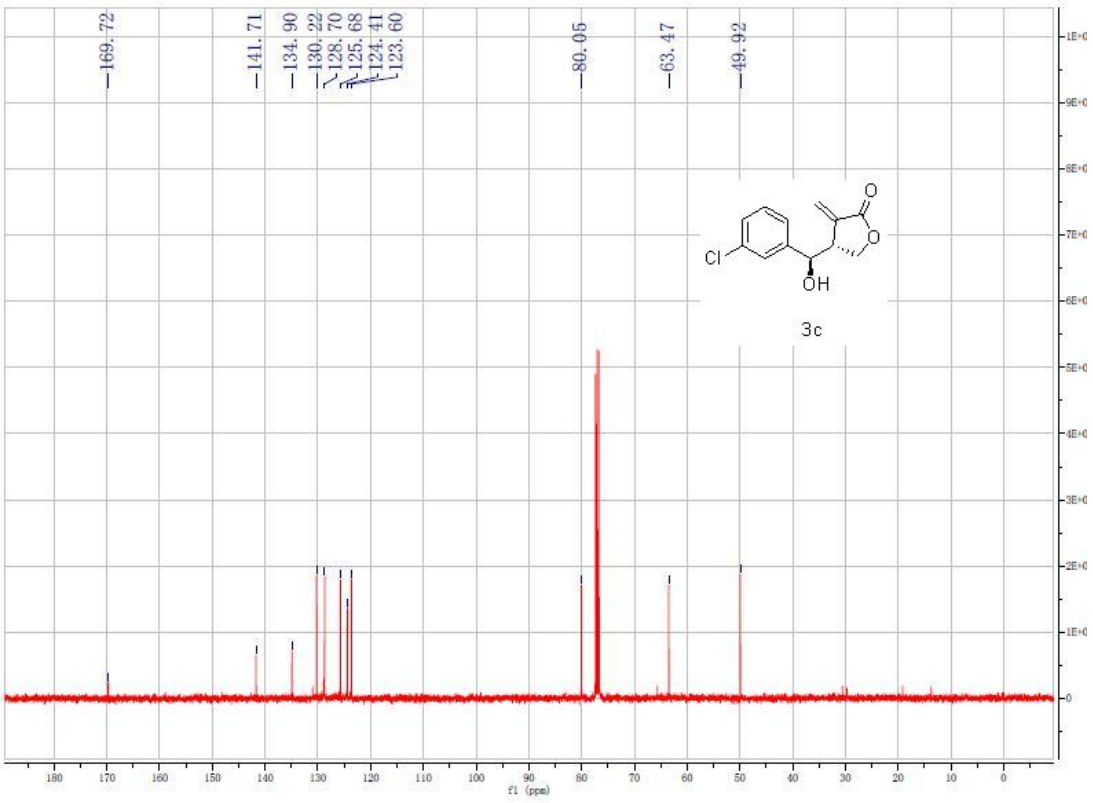


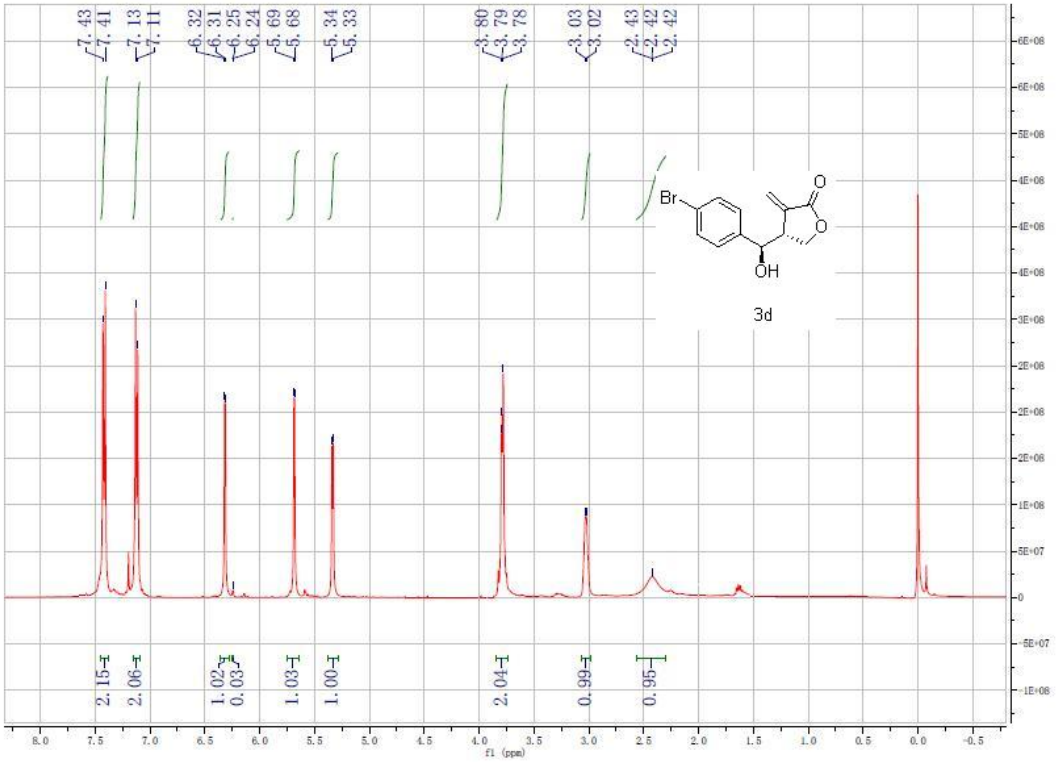


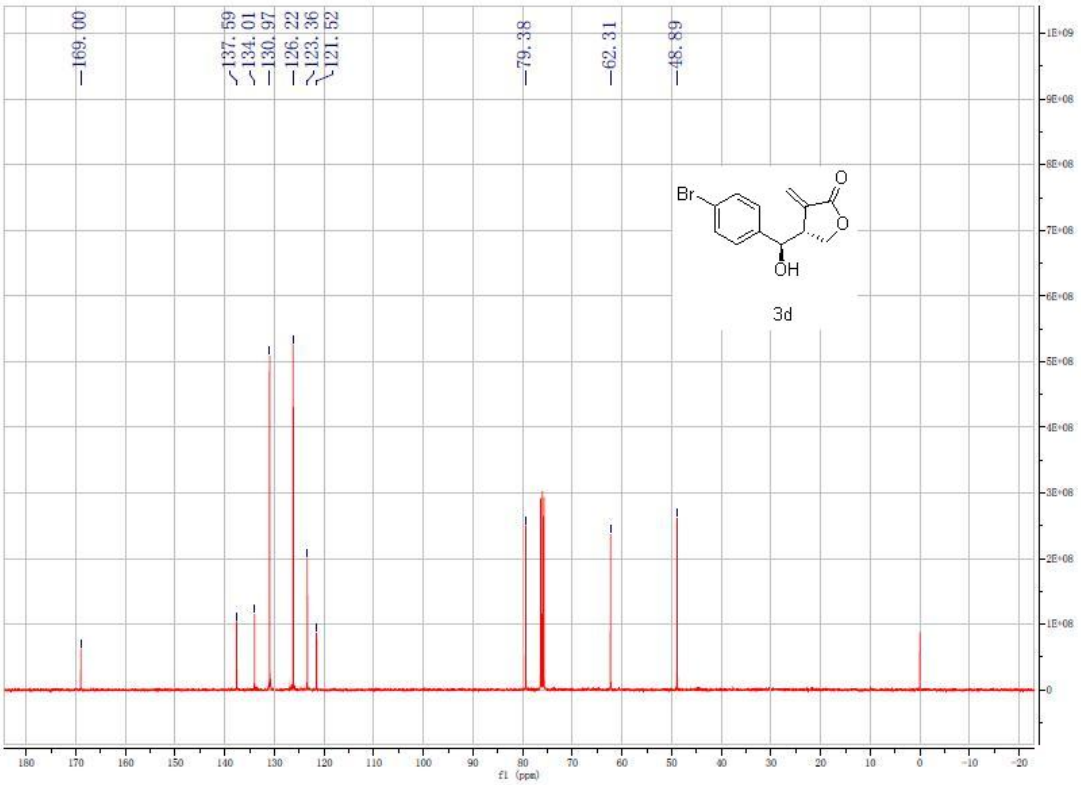


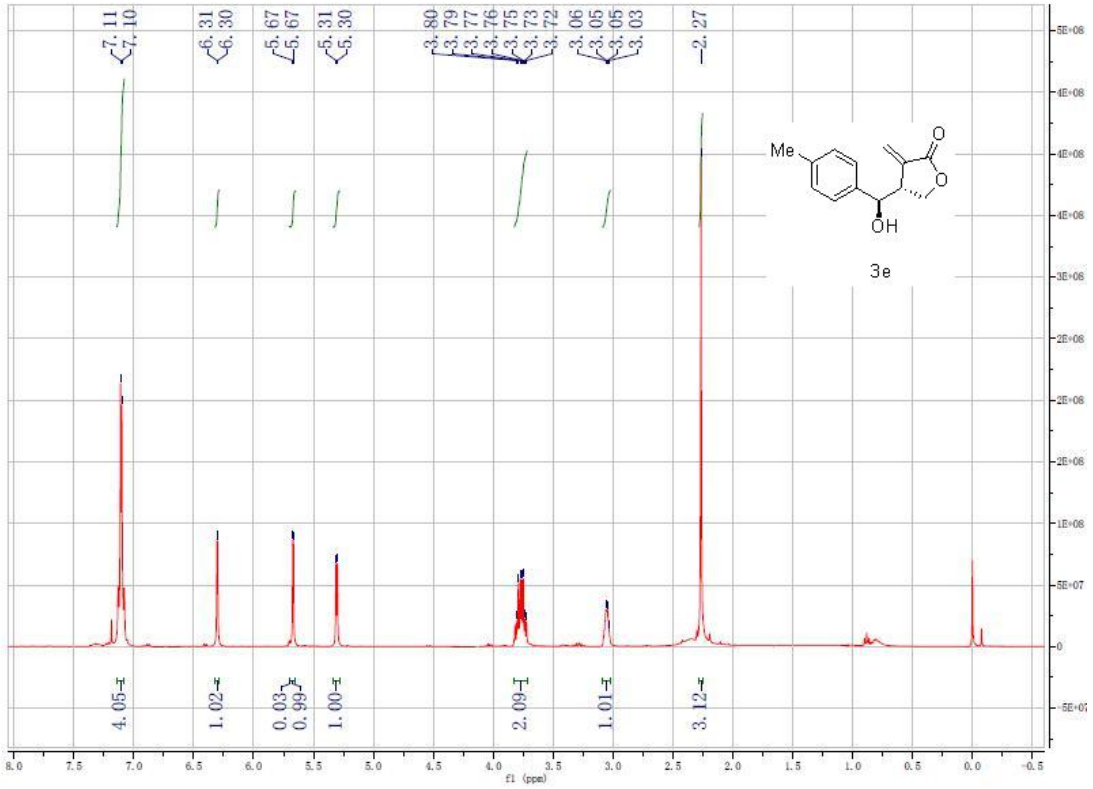


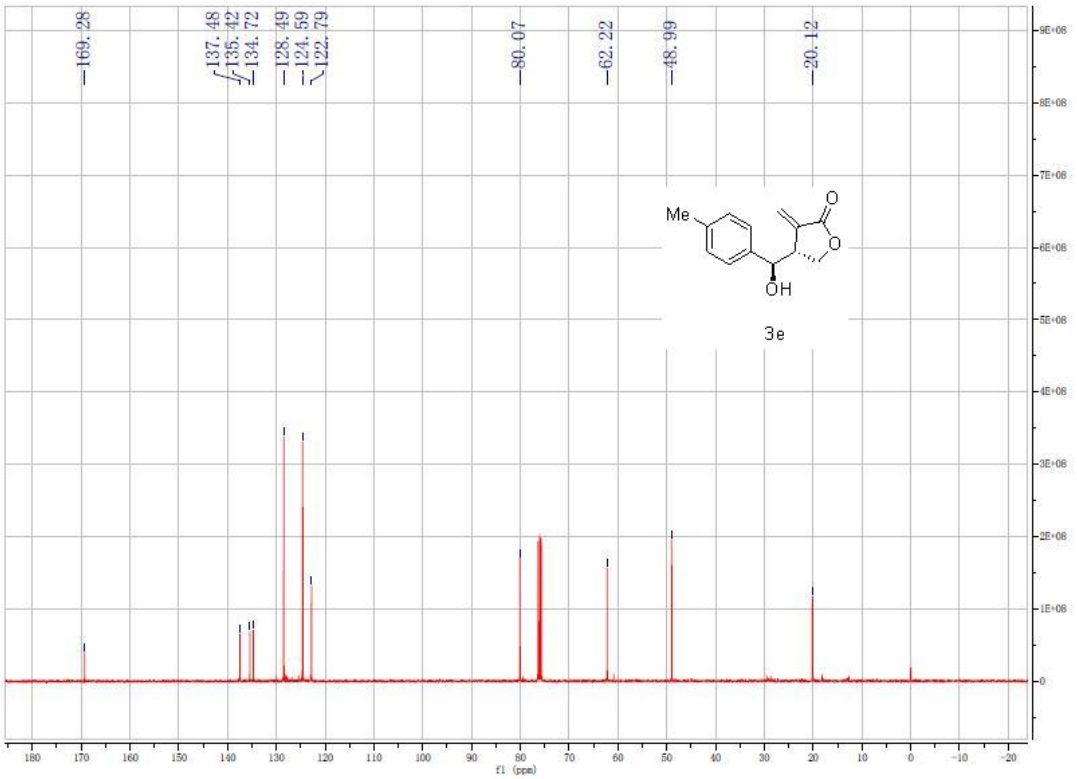


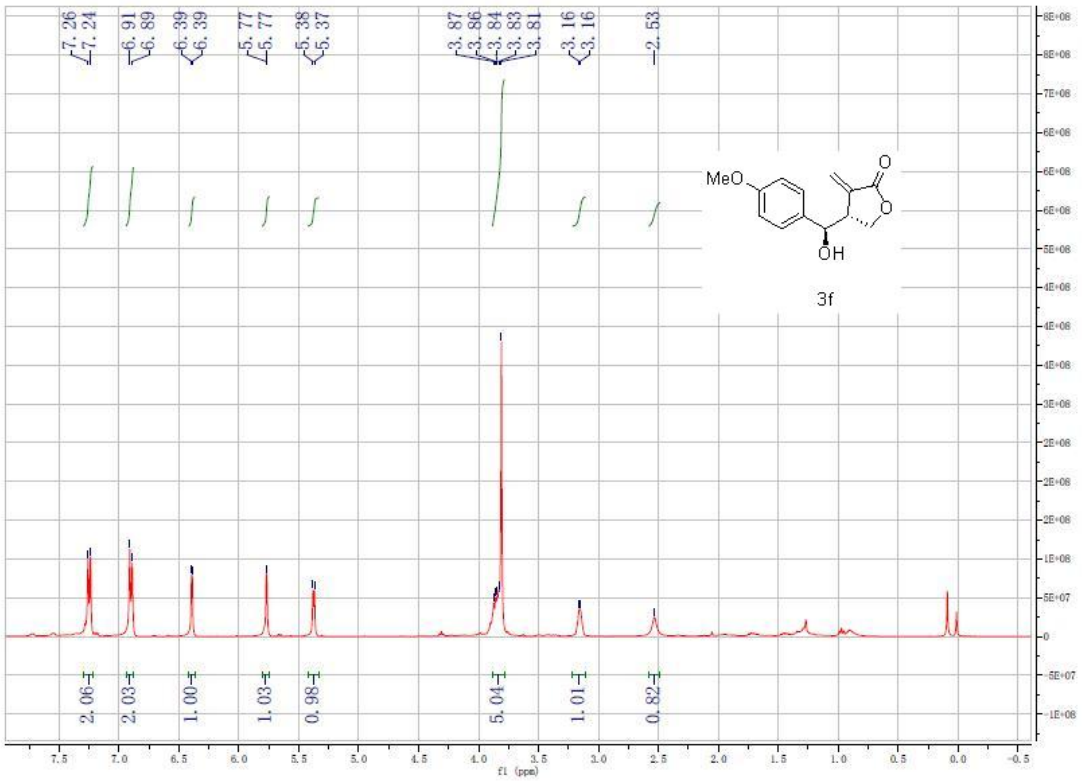


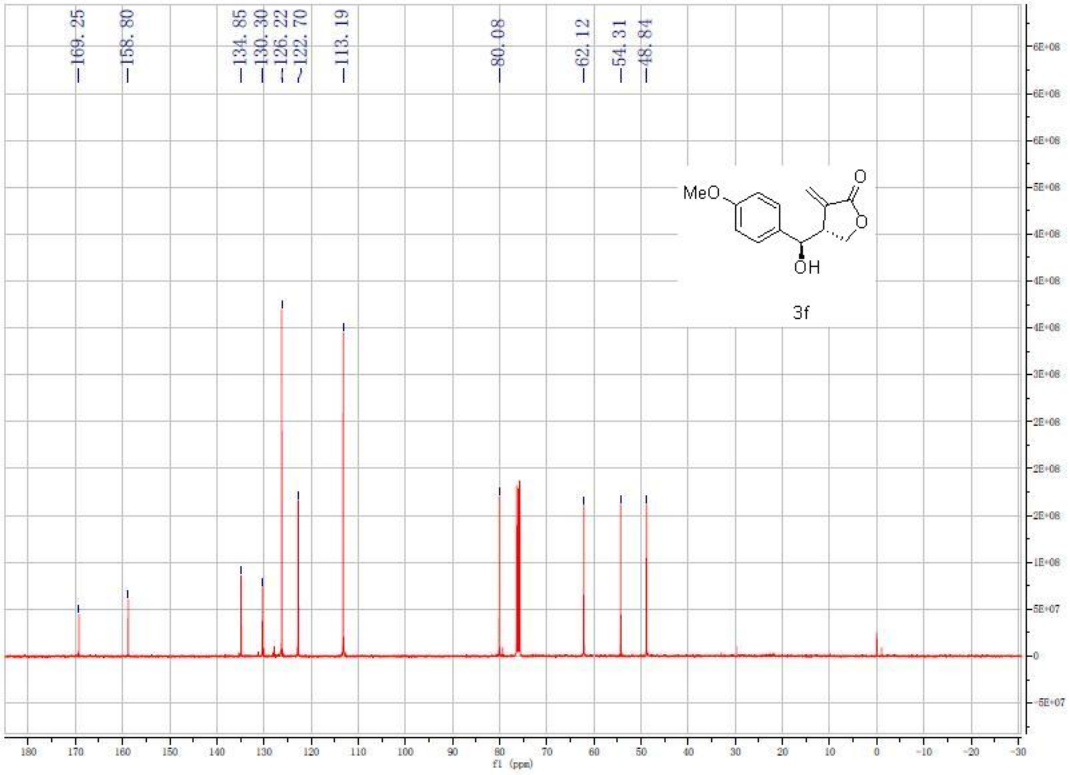


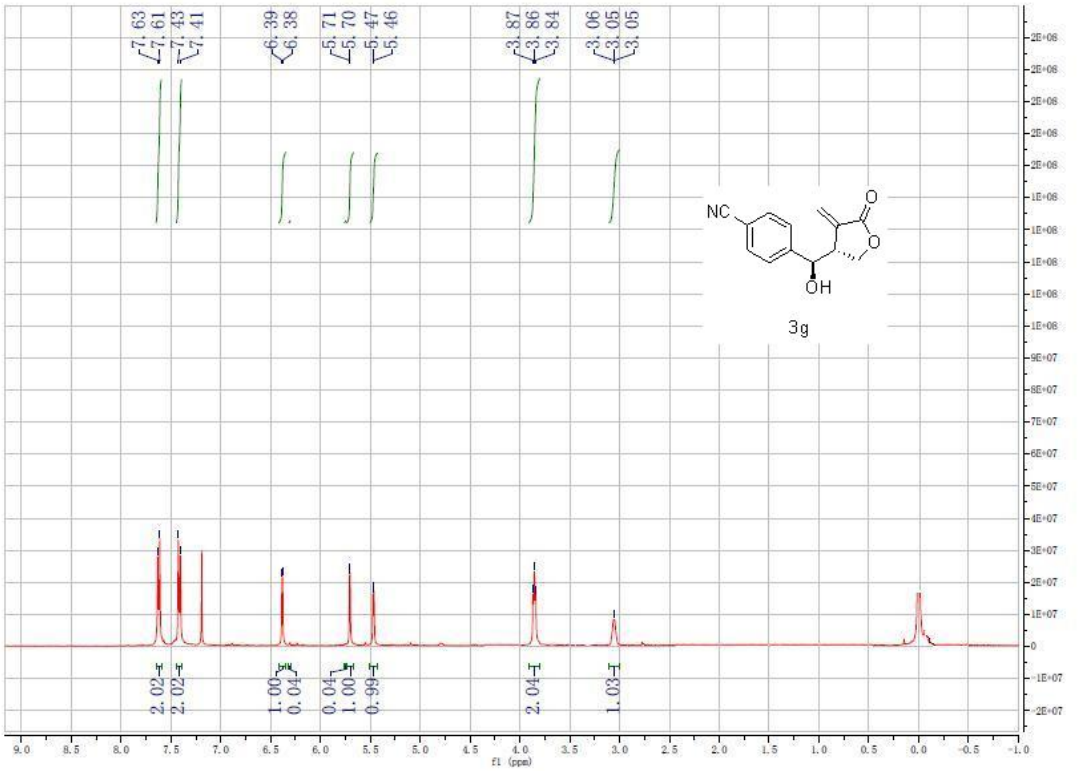


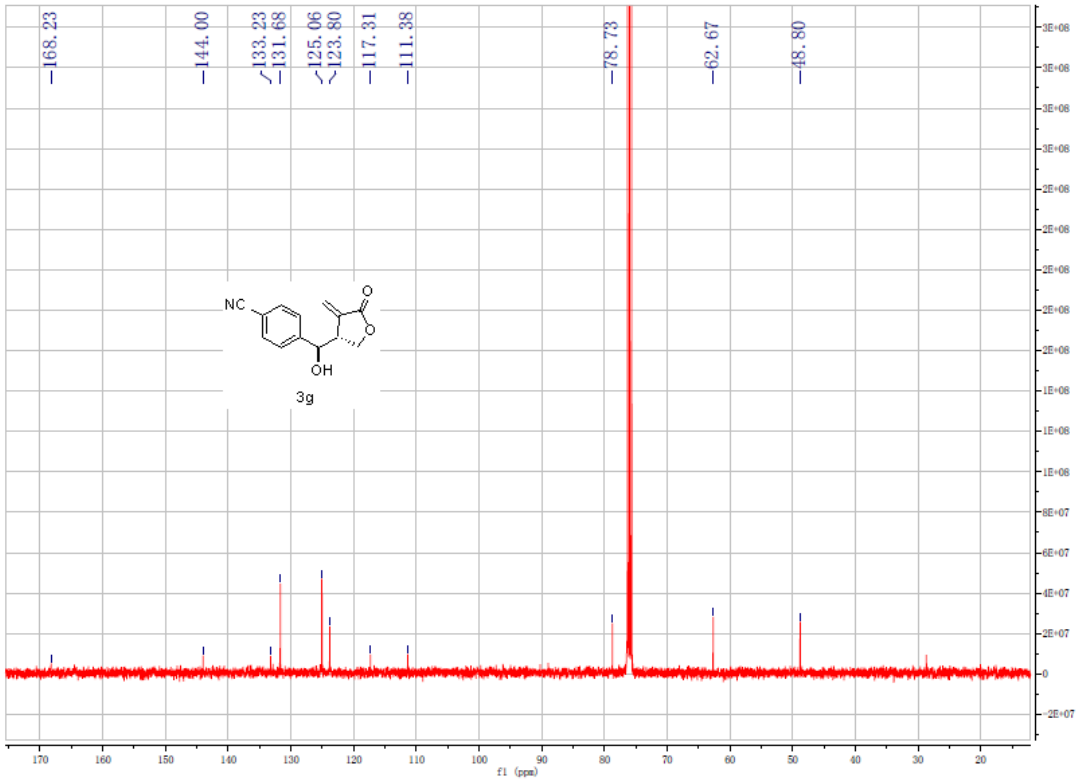


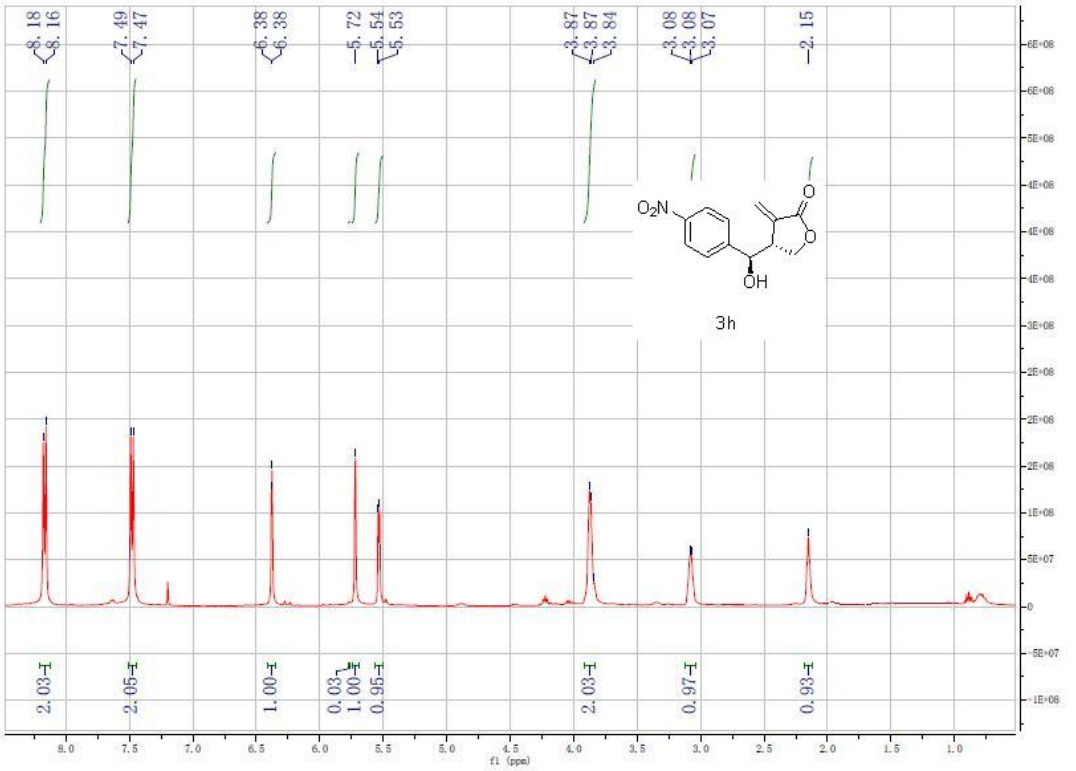


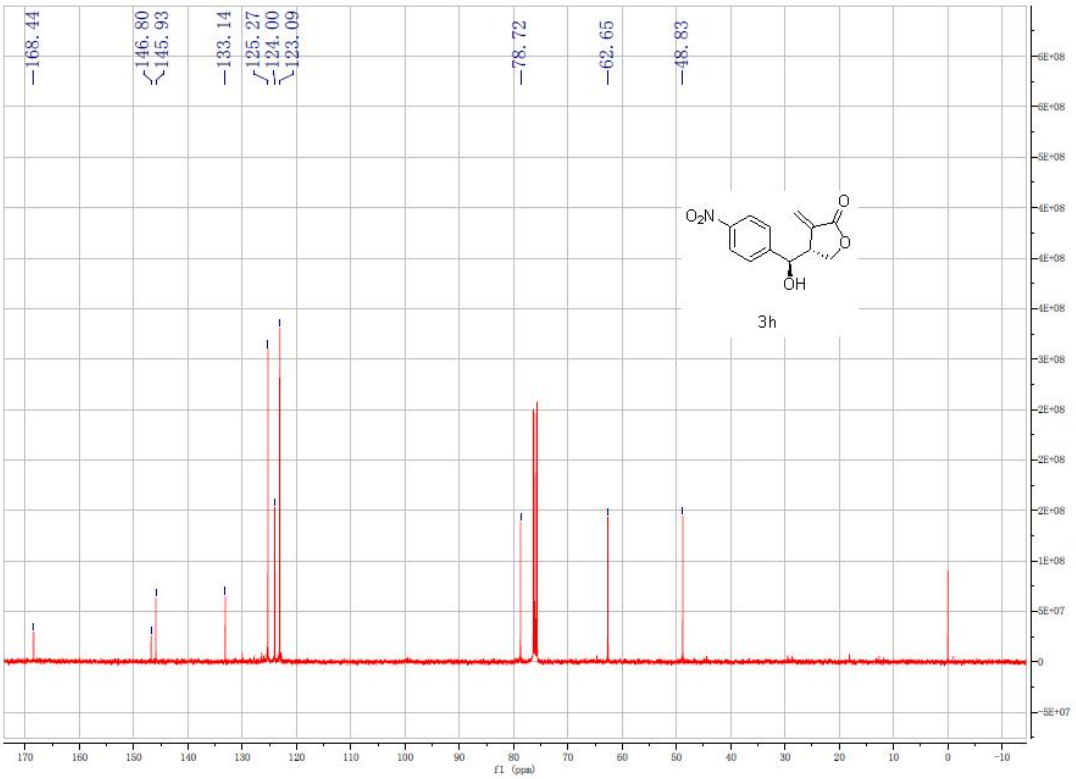


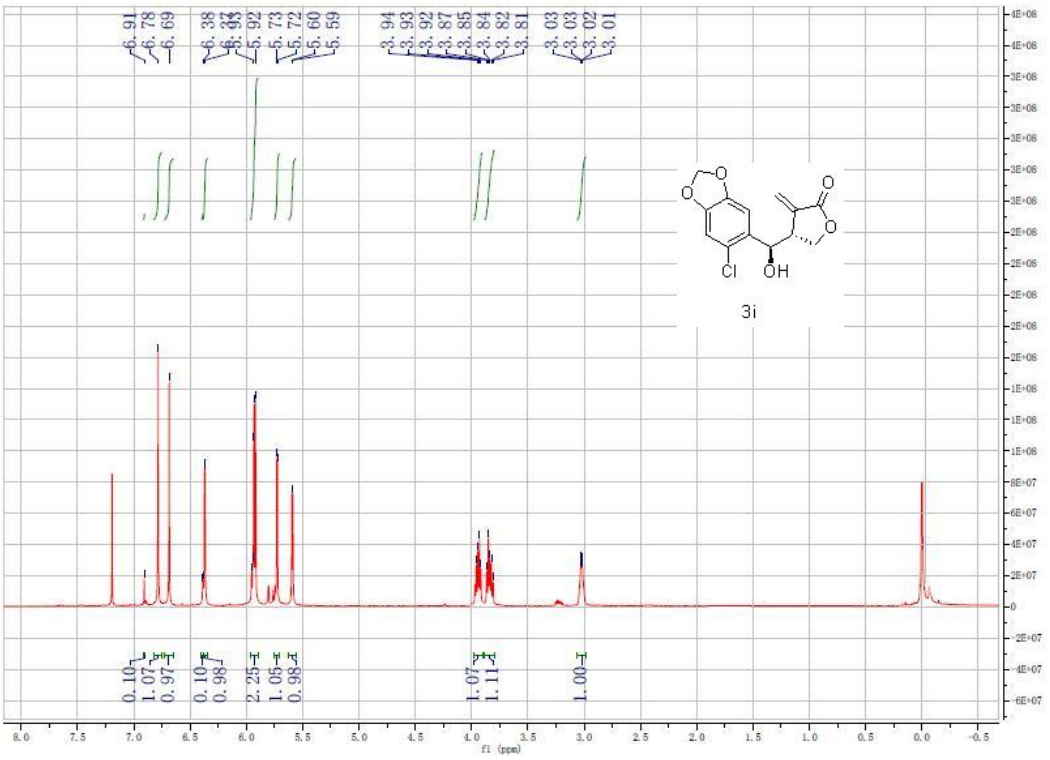


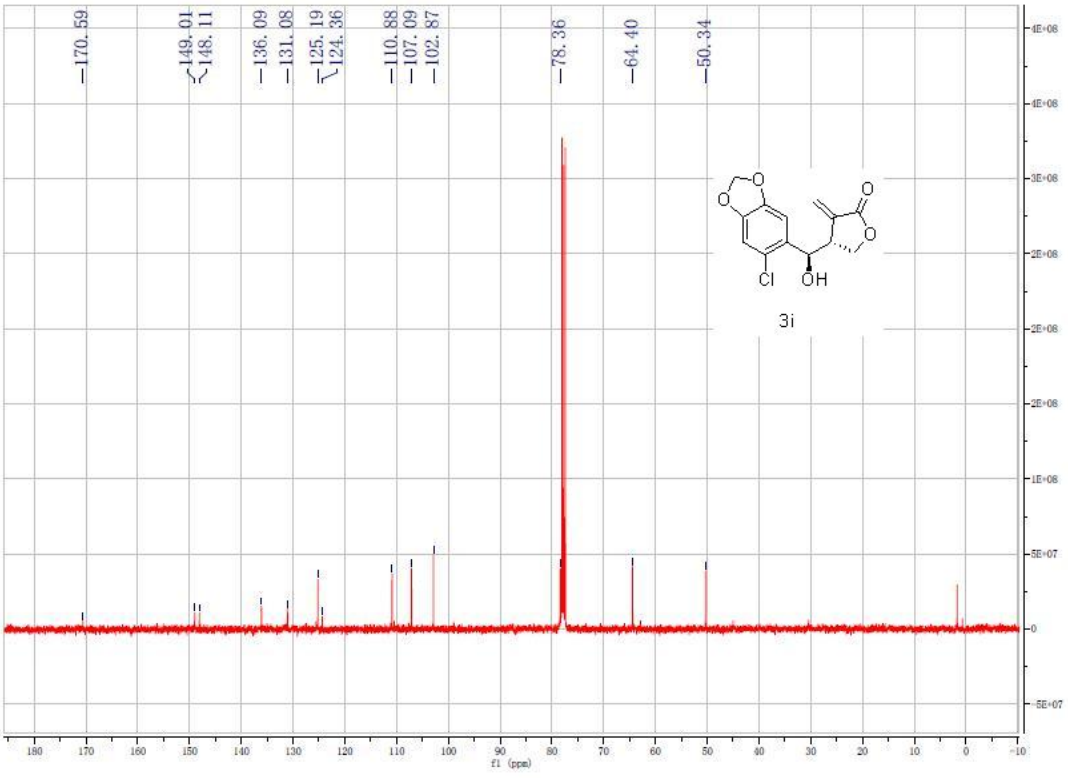


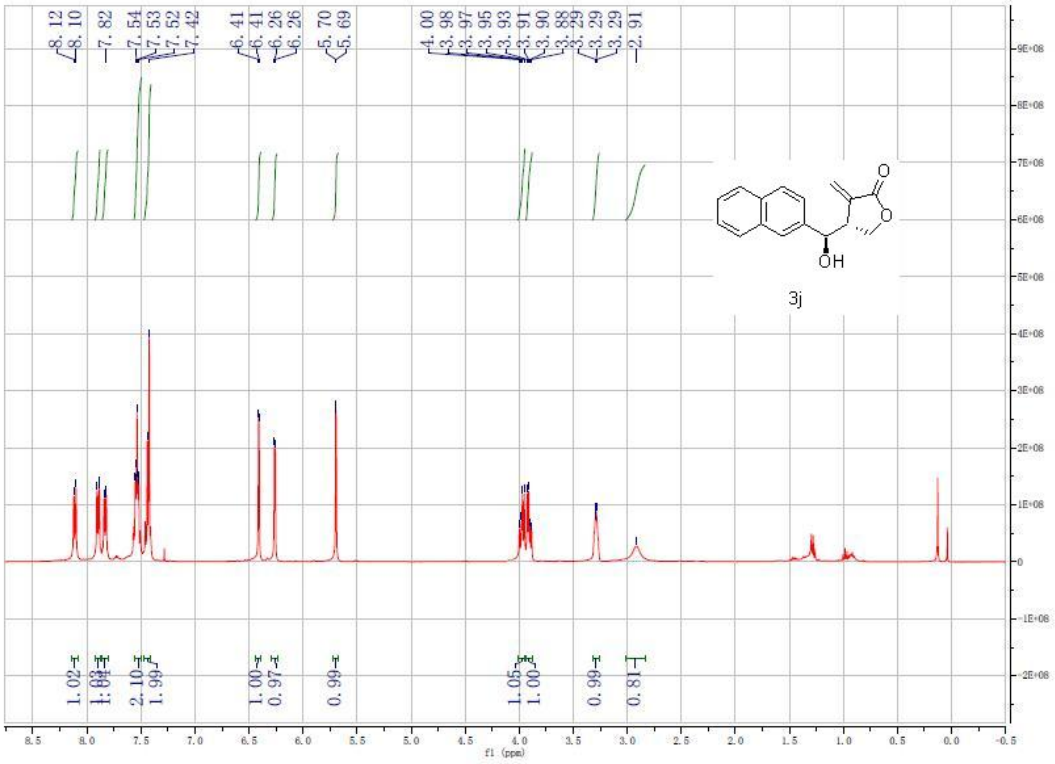


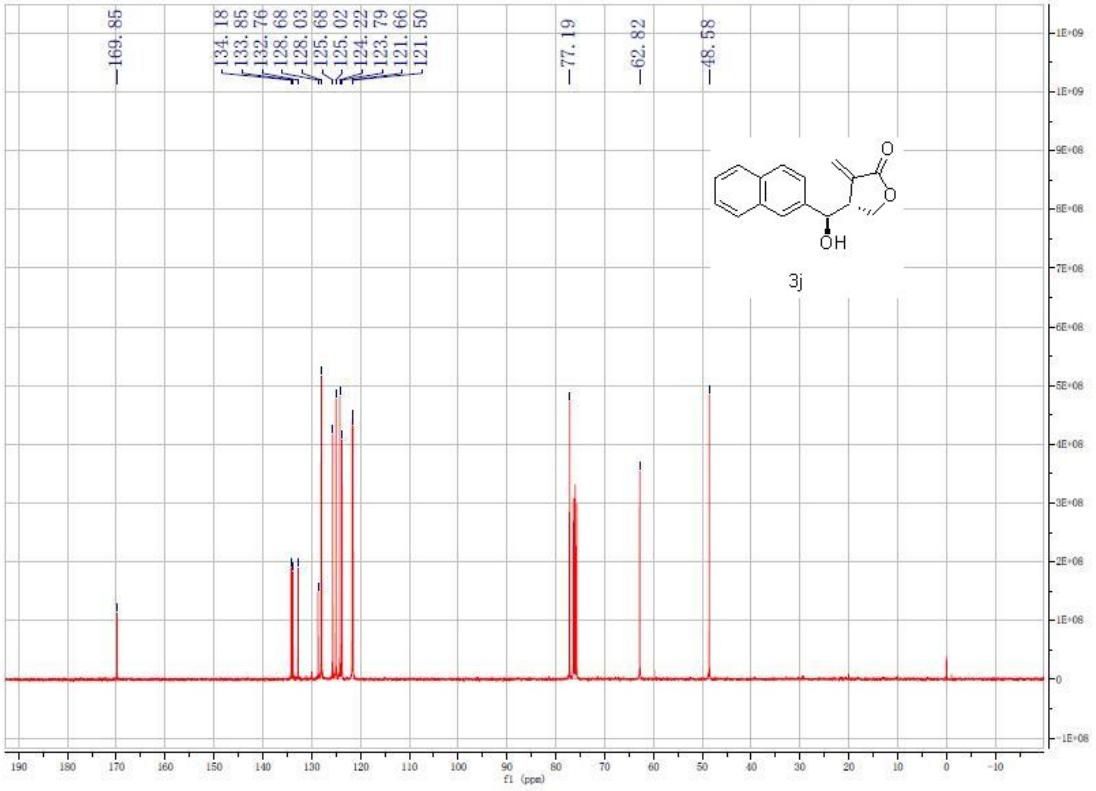


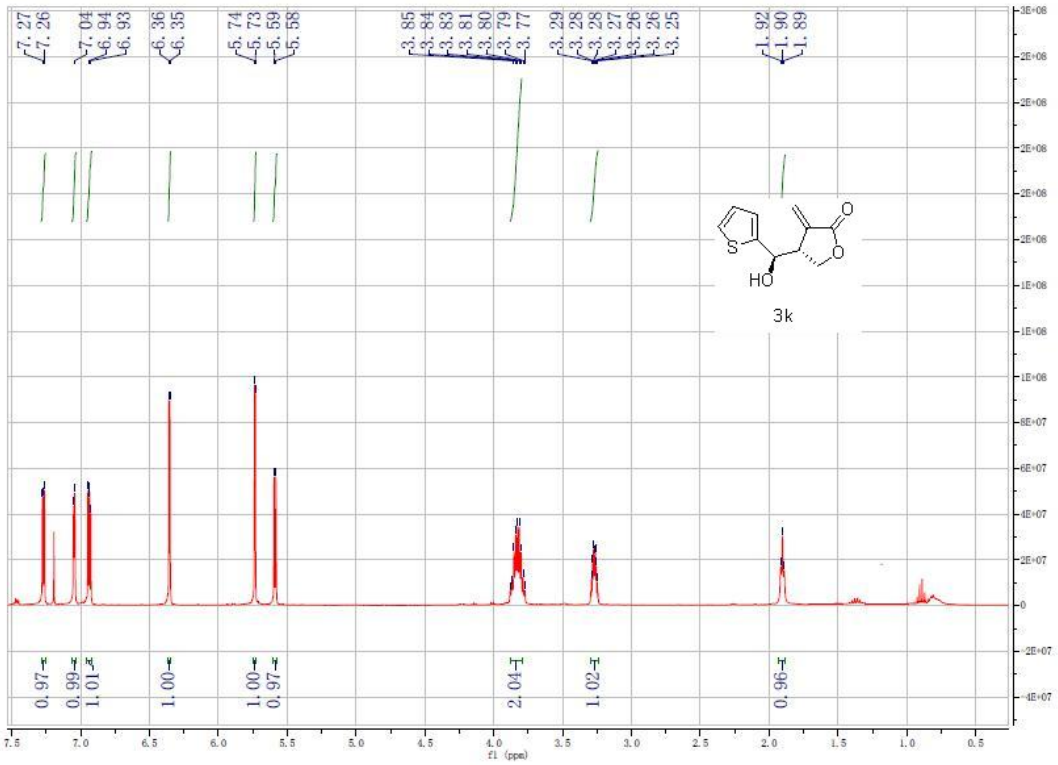


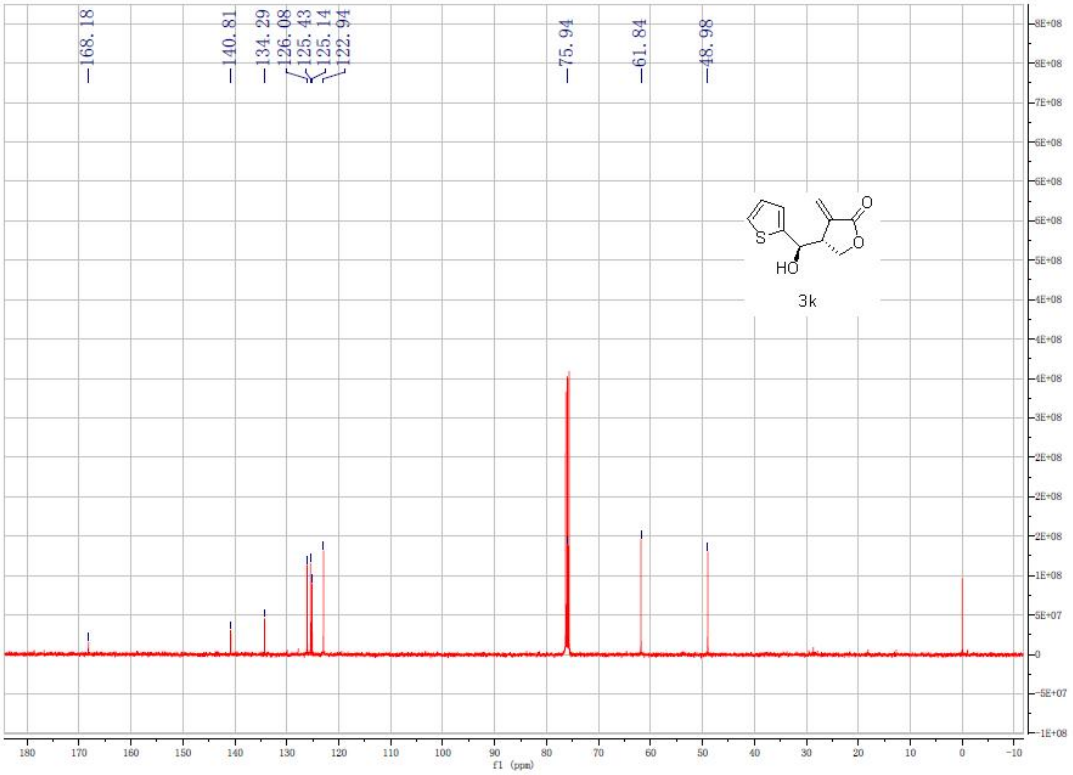


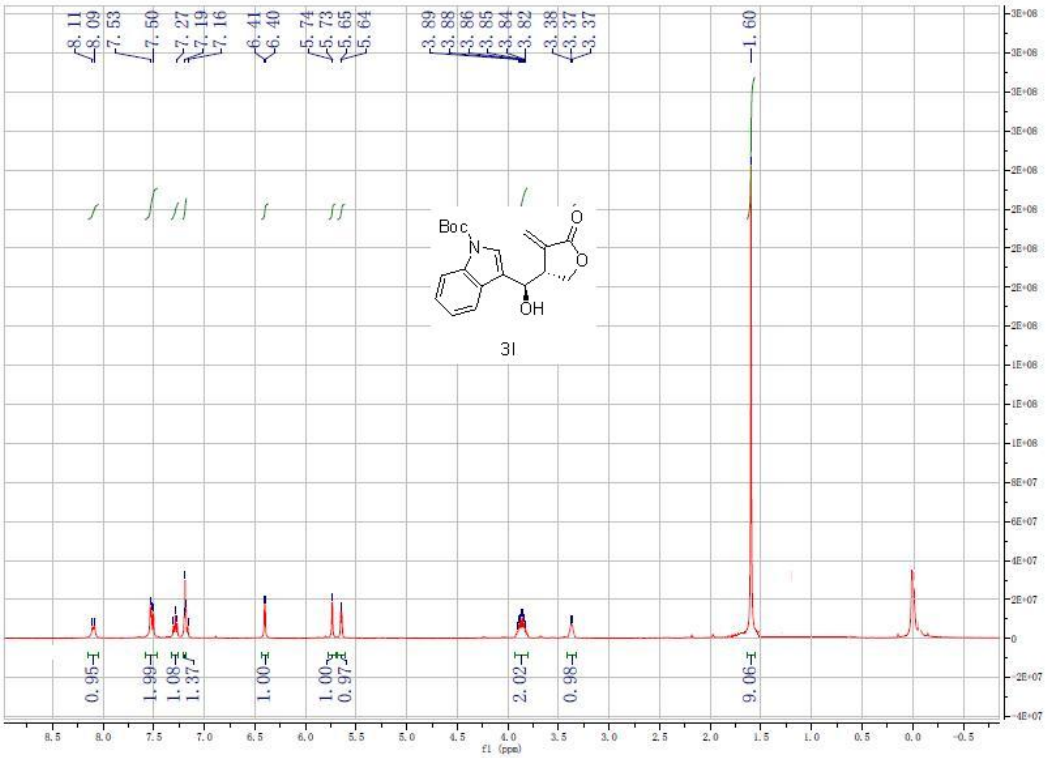












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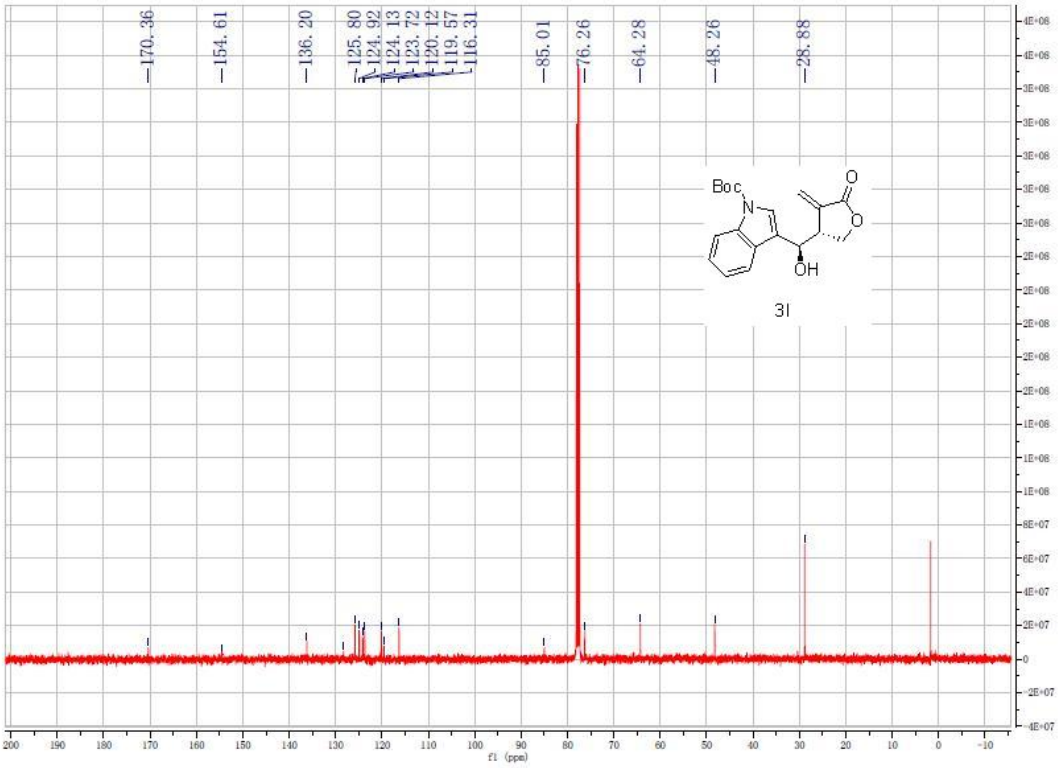

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