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Supporting Information

Synthesis of tetronic acids from propargylic alcohols and CO_2

Guo Shen,[a] Wen-Jun Zhou,[a,b,*] Xiao-Bo Zhang,[a] Guang-Mei Cao,[a] Zhen Zhang,[a,c] Jian-Heng Ye,[a] Li-Li Liao,[a] Jing Li,[a] and Da-Gang Yu[a,*]

[a] *Key Laboratory of Green Chemistry & Technology of Ministry of Education, College of Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu 610064 (P. R. China) E-mail: dgyu@scu.edu.cn*

[b] *College of Chemistry and Chemical Engineering, Neijiang Normal University, Neijiang 641112 (P. R. China)*

[c] *College of Pharmacy and Biological Engineering, Chengdu University, Chengdu 610106 (P. R. China)*

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General considerations

All reactions were set up using 25 mL Schlenk techniques and carried out under a carbon dioxide atmosphere. All commercially available compounds were purchased from Accela, TCI, Adamas, Across, J&K or Micxy, and used as received unless otherwise noted. CO_2 (99.99% purity) was commercially available. Cesium carbonate (99%) was purchased from Accela. 1,3-Dimethyl-2-Imidazolidinone (DMI, >99.0% purity) was purchased from TCI and used directly without dehydration. The substrates of propargyl alcohol were synthesized according to the literature procedure. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.2±0.03 mm using UV light as a visualizing agent and iodine vapor to visualize the course of reaction.

A SHIMADZU-GL Wonda Cract ODS-2 column (5.0 µm, 4.6 x 150 mm) was used for the separation. The mobile phases were H_2O containing 1‰ HCOOH and MeOH. LC method A: A isocratic elution of 65:35 (v/v) MeOH/water over 11 min at a flow rate of 1.0 mL/min was used as a mobile phase. LC method B: A isocratic elution of 55:45 (v/v) MeOH/water for 4 min, then a linear gradient from 55:45 (v/v) MeOH/water (4 min) to 90% MeOH/water (6 min), next a isocratic elution 55:45 (v/v) MeOH/water from 6 min to 10 min, finally a linear gradient from 55:45 (v/v) MeOH/water (10 min) to 90% MeOH/water (11 min) and a isocratic elution 55:45 (v/v) MeOH/water from 11 min to 12 min at a flow rate of 1.0 mL/min was used as a mobile phase. UV detections were conducted at 254 nm. Metal element contents were obtained on a thermo ICP-AES (IRIS Adv.).

Flash column chromatography was performed over silica gel (200-300 mesh). Exact ESI mass spectra were performed on a SHIMADZU LCMS-IT-TOF. UPLC and UPLC-MS were obtained on a Waters UPLC and Thermo-ITQ.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Brüker Advance 400 spectrometer (^{1}H: 400 MHz, ^{19}F: 376 MHz, ^{13}C: 101 MHz,). Chemical shifts (δ) for ^{1}H, ^{19}F and ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), b (broad), dd (doublet of doublet). The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale (DMSO-d_6: δH = 2.50 ppm, δC = 39.52 ppm).

GC-MS was obtained using electron ionization (Agilent Technologies 7890B/GC-System and 5977A/MSD). Exact ESI mass spectra were recorded on a SHIMADZU LCMS-IT-TOF. ESI-MS were obtained on a Thermo-ITQ. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm.

Synthesis of substrates

The substrates **1b-1j** and **1x** were prepared according to procedures described in the literatures reported before.[1]

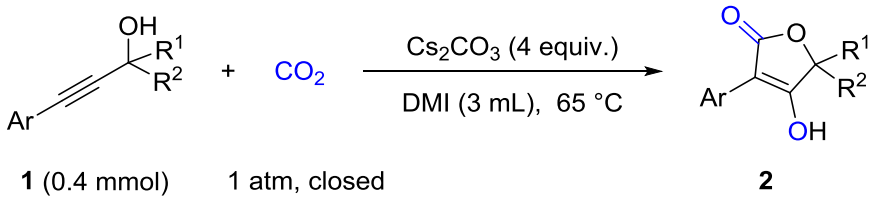
The substrates **1a**, **1k-1w** and **1y** were prepared according to procedures described in the literatures reported before.[2]

The intermediate **3h** was prepared according to procedures described in the literatures reported before.[3]

The compound **4h** was prepared according to procedures described in the literatures reported before.[4]

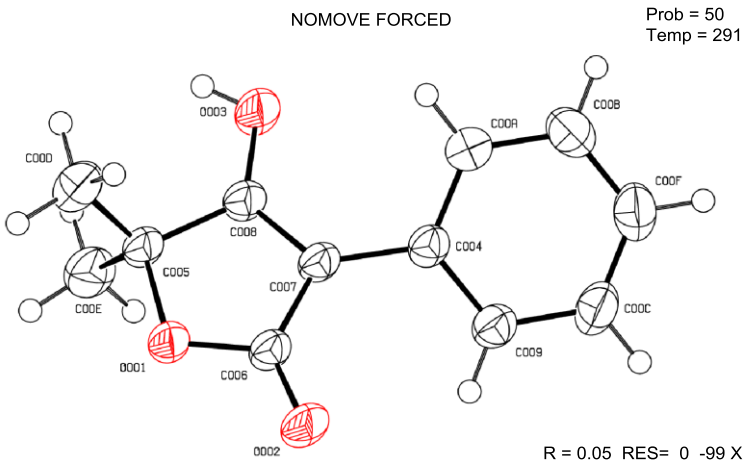
All the protocols were employed without any optimization of the reaction conditions.

Synthesis of tetronic acid derivation



Propargyl alcohols **1** (0.4 mmol, 1.0 equiv.) were added into an oven-dried 25 mL Schlenk tube (synthware, F580825) equipped with a stirring bar, then added Cs_2CO_3 (1.6 mmol, 4.0 equiv.) in the glovebox. The tube was moved out and then evacuated and back-filled with CO_2 for 3 times. Once DMI (3 mL) was charged under CO_2 atmosphere, the Schlenk tube was sealed at atmospheric pressure of CO_2. The resulting solution was stirred at 65 °C. Then, the mixture was cooled to room temperature, quenched with 3 mL HCl solution (2 M) and the reaction mixture was extracted by EtOAc for 6-8 times. The combined organic layer was concentrated in vacuo. The residue was purified by flash silica gel chromatography (MeOH/DCM = 1:10) to give the tetronic acid products **2**.

Crystal data for 2h （CCDC 1815711）



Datablock:

Bond precision: C-C = 0.0021 A Wavelength=0.71073

Cell: a=6.7868(6) b=8.5848(10) c=9.4383(8)
alpha=87.679(8) beta=83.576(7) gamma=73.938(9)

Temperature: 291 K

	Calculated	Reported
Volume	525.10(9)	525.10(9)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C12 H12 O3	C12 H12 O3
Sum formula	C12 H12 O3	C12 H12 O3
Mr	204.22	204.22
Dx,g cm-3	1.292	1.292
Z	2	2
Mu (mm-1)	0.093	0.093
F000	216.0	216.0
F000’	216.12	
h,k,lmax	8,10,11	8,10,11
Nref	2156	2152
Tmin,Tmax	0.967,0.991	0.739,1.000
Tmin’	0.946	

Correction method= # Reported T Limits: Tmin=0.739 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 26.363

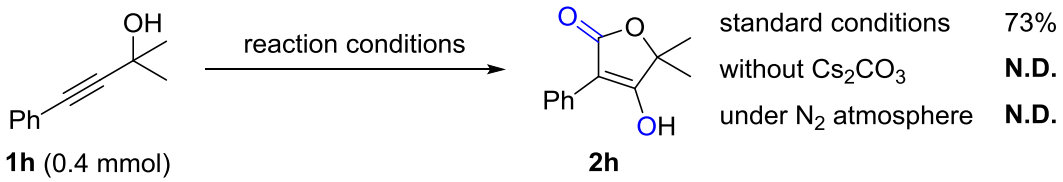
R(reflections)= 0.0479(1794) wR2(reflections)= 0.1337(2152)

S = 1.053 Npar= 139

Mechanistic studies

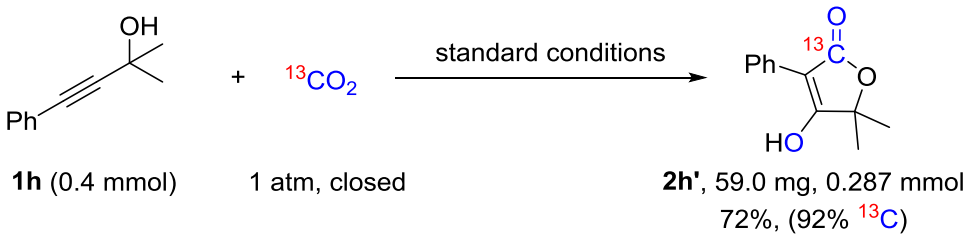
Carbonyl source confirmation

The role of each reaction component



2-methyl-4-phenylbut-3-yn-2-ol **1h** (0.4 mmol, 64.1 mg, 1.0 equiv.) were added into a 25 mL Schlenk tube equipped with a stirring bar, then added Cs_2CO_3 (1.6 mmol, 521.3 mg, 4.0 equiv., no Cs_2CO_3 in entry 3) in the glovebox. The tube was moved out and then evacuated and back-filled with CO_2 or N_2 for 3 times. Then the Schlenk tube was sealed at atmospheric pressure of CO_2 or N_2. The resulting solution was stirred for 48 h at 65 °C. Then, the mixture was cooled to room temperature, quenched with 3 mL HCl solution (2 M) and extracted with EA (6-8 times). The combined organic solution was concentrated at the reduced pressure. Column chromatography on silica gel (MeOH/DCM = 1:10) afforded the tetronic acid product **2h**.

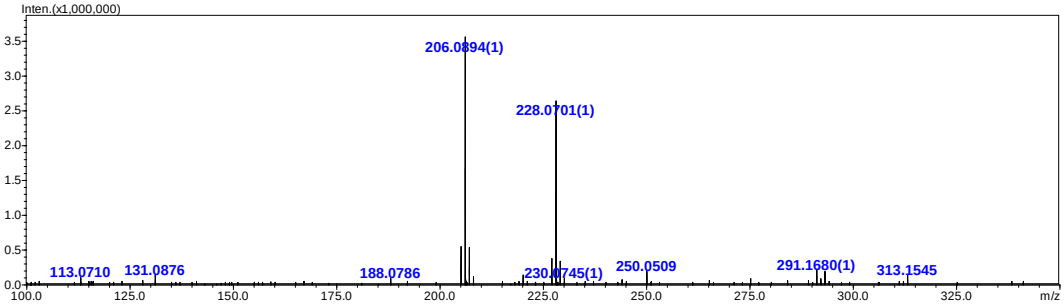
Carbon ($^{13}CO_2$) labeling experiment



An oven-dried 25 mL Schlenk tube (synthware, F580825) equipped with a magnetic stir bar was charged with 2-methyl-4-phenylbut-3-yn-2-ol **1h** (0.4 mmol, 64.1 mg, 1.0 equiv.) and Cs_2CO_3 (1.6 mmol, 521.3 mg, 4.0 equiv.) in the glovebox. The tube was moved out and then evacuated and back-filled with $^{13}CO_2$ for 3 times, DMI (3 mL) was injected in the Schlenk tube at room temperature under $^{13}CO_2$. The Schlenk tube was sealed at atmospheric pressure of $^{13}CO_2$ (1 atm). The resulting mixture was stirred at 65 °C for 48 h. Then, the mixture was cooled to room temperature, quenched with 3 mL HCl solution (2 M) and extracted with EA (6-8 times). The combined organic solution was concentrated at the reduced pressure. Column chromatography on silica gel affordedtetronic acid **2h'** in 72% yield. The ^{13}C-content was determined to be 92% by **HRMS (ESI+)**.

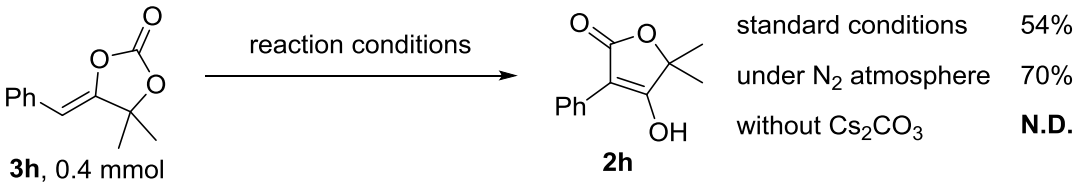
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 – 7.87 (m, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.25 – 7.18 (m, 1H), 1.51 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 181.08 (d, J = 11.4 Hz),

171.42, 131.37 (d, *J* = 3.9 Hz), 128.40, 127.03 (d, *J* = 2.2 Hz), 126.59, 96.31 (d, *J* = 71.5 Hz), 80.03, 24.54. **HRMS (ESI+)**: calculated for $C_{11}{}^{13}CH_{12}O_3^+$ $[M+H]^+$ 206.0893, found 206.0894.



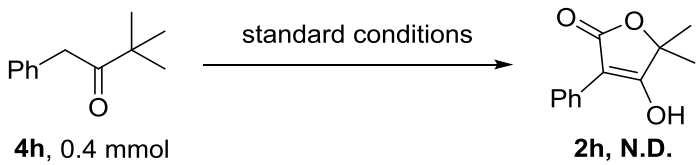
The determination of the intermediate

The role of the cyclic carbonate



An oven-dried 25 mL Schlenk tube (synthware, F580825) equipped with a magnetic stir bar was charged with cyclic carbonate **3h** (0.4 mmol, 81.7 mg, 1.0 equiv.) and Cs_2CO_3 (1.6 mmol, 521.3 mg, 4.0 equiv.) in the glovebox. The tube was moved out and then evacuated and back-filled with CO_2 or N_2 for 3 times, DMI (3 mL) was injected in the Schlenk tube at room temperature under CO_2 or N_2. The Schlenk tube was sealed at atmospheric pressure of CO_2 or N_2 (1 atm). The resulting mixture was stirred at 65 °C for 48 h. Then, the mixture was cooled to room temperature, quenched with 3 mL HCl solution (2 M) and extracted with EA (6-8 times). The combined organic solution was concentrated at the reduced pressure. Column chromatography on silica gel afforded product **2h**. These yields evidences proved alkylidene cyclic carbonates was the key intermediate, and control experiments revealed that Cs_2CO_3 was necessary in the conversion to products. The higher yield under N_2 than CO_2 atmosphere might indicate that basic property could affect the ring-opening process and CO_2 could decrease the alkaline of the system.

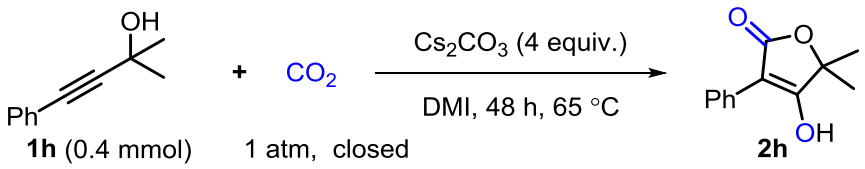
The role of the α-hydroxyl ketone



An oven-dried 25 mL Schlenk tube (synthware, F580825) equipped with a magnetic

stir bar was charged with α-hydroxyl ketone **4h** (0.4 mmol 71.3 mg, 1.0 equiv.) and Cs_2CO_3 (1.6 mmol, 521.3 mg, 4.0 equiv.) in the glovebox. The tube was moved out and then evacuated and back-filled with CO_2 for 3 times, DMI (3 mL) was injected in the Schlenk tube at room temperature under CO_2. Then the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The resulting mixture was stirred at 65 °C for 11 h. Then, the mixture was cooled to room temperature, quenched with 3 mL HCl solution (2 M), and **2h** wasn't detected by ESI-MS.

Demonstration of metal-free

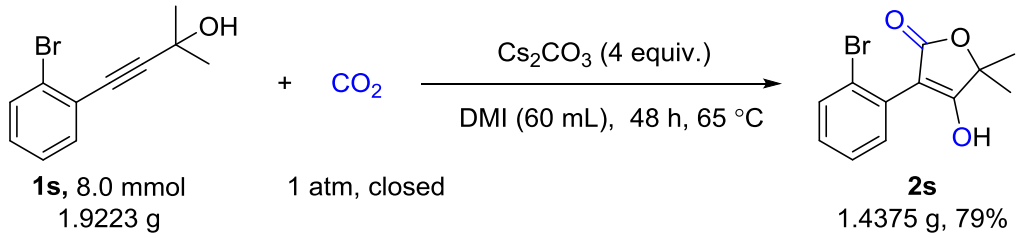


Co/ppm	Cu/ppm	Fe/ppm	Ni/ppm	Ag/ppm	Rh/ppm	Pd/ppm	Mn/ppm	Ru/ppm
0.0118	**0.0165**	**0.5186**	**0.0155**	**0.0096**	**0.0438**	**0.0151**	**0.0199**	**0.0051**

An oven-dried 25 mL Schlenk tube (synthware, F580825) equipped with a magnetic stir bar was charged with substance **1h** (0.4 mmol, 64.1 mg, 1.0 equiv.) and Cs_2CO_3 (1.6 mmol, 521.3 mg, 4.0 equiv.) in the glovebox. The tube was moved out and then evacuated and back-filled with carbon dioxide for 3 times, DMI (3 mL) was injected in the Schlenk tube at room temperature under CO_2. The Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The resulting mixture was stirred at 65 °C for 48 h. Then, the mixture was cooled to room temperature. The reaction mixture was concentrated at the reduced pressure. The residue was diluted to 30.7 mg/mL, and mixed again for ICP experiment.

Gram-scale reaction

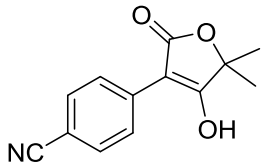
3-(2-bromophenyl)-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one (2s)



An oven-dried 250 mL Schlenk flask equipped with a magnetic stir bar was charged with substance **1s** (8.0 mmol, 1.9129 g, 1.0 equiv.) and Cs_2CO_3 (32 mmol, 10.4769 g, 4.0 equiv.) in the glovebox. The tube was moved out and then evacuated and back-filled with carbon dioxide for 3 times, DMI (60 mL) was injected in the Schlenk flask at room temperature under CO_2. The resulting mixture in sealed tube was stirred at 65 °C for 48 h (Re-fill with CO_2 was performed at 36 h.). Then, the mixture was cooled to room temperature, quenched with HCl solution (2 M) and extracted with EA (6-8 times). The combined organic solution was concentrated at the reduced pressure. Twice column chromatography on silica gel afforded product **2s** in 79% yield since we didn't get the pure product for the first purification.

Characterization data

4-(4-hydroxy-5,5-dimethyl-2-oxo-2,5-dihydrofuran-3-yl)benzonitrile (2a)

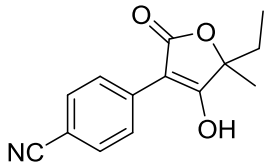


82.3 mg, 0.359 mmol, 90%; White powder; **R**$_f$ (MeOH/DCM 1/10): 0.12;

^{1}**H NMR** (400 MHz, DMSO-d_6) δ 8.36 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 1.35 (s, 6H); ^{13}**C NMR** (101 MHz, DMSO-d_6) δ 193.12, 173.91, 141.68, 131.73, 123.62, 120.73, 103.50, 87.27, 80.51, 25.01.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{13}H_{11}NO_3$] [M-H]$^-$: 228.0666, found: 228.0669.

4-(4-hydroxy-5-methyl-2-oxo-5-phenyl-2,5-dihydrofuran-3-yl)benzonitrile (2b)

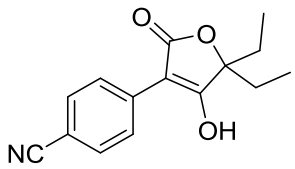


78.4 mg, 0.322 mmol, 81%; White powder; **R**$_f$ (MeOH/DCM 1/10): 0.12;

^{1}**H NMR** (400 MHz, DMSO-d_6) δ 8.47 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 1.67 – 1.46 (m, 2H), 1.19 (s, 3H), 0.71 (t, J = 7.4 Hz, 3H); ^{13}**C NMR** (101 MHz, DMSO-d_6) δ 187.53, 172.87, 139.02, 132.07, 125.28, 120.17, 105.93, 92.61, 83.07, 29.64, 23.52, 7.89.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{14}H_{13}NO_3$] [M-H]$^-$: 304.0979, found: 304.0973.

4-(5,5-diethyl-4-hydroxy-2-oxo-2,5-dihydrofuran-3-yl)benzonitrile (2c)



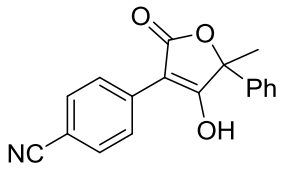
64.1 mg, 0.249 mmol, 62%; White powder; **R**$_f$ (MeOH/DCM 1/10): 0.11;

^{1}**H NMR** (400 MHz, DMSO-d_6) δ 8.18 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 1.94 – 1.78 (m, 4H), 0.73 (t, J = 7.3 Hz, 6H); ^{13}**C NMR** (101 MHz, DMSO-d_6) δ 181.36, 171.86, 136.65, 132.42, 126.69, 119.72, 108.09, 97.63, 85.87, 28.49, 7.50.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{15}H_{15}NO_3$] [M-H]$^-$: 282.1136, found:

282.1129.

4-(4-hydroxy-5-methyl-2-oxo-5-phenyl-2,5-dihydrofuran-3-yl)benzonitrile （2d）

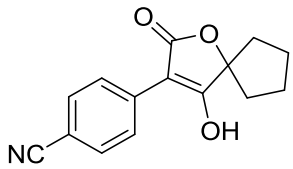


102.8 mg, 0.353 mmol, 88%, (2 equiv. Cs_2CO_3, 48 h); 101.9 mg, 0.350 mmol, 87%, (4 equiv. Cs_2CO_3, 2 h); White powder; $\mathbf{R}_f$ (MeOH/DCM 1/10): 0.07;

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.43 (d, J = 8.3 Hz, 2H), 7.49 (dd, J = 16.4, 8.0 Hz, 4H), 7.36 – 7.26 (m, 2H), 7.26 – 7.19 (m, 1H), 1.60 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 192.09, 174.60, 142.59, 142.15, 131.70, 128.31, 127.38, 125.49, 123.18, 120.84, 103.00, 85.82, 82.82, 25.05.

HRMS (ESI-MS, m/z): calculated m/z for $[C_{18}H_{13}NO_3]$ $[M-H]^-$: 290.0823, found: 290.0812.

4-(4-hydroxy-2-oxo-1-oxaspiro[4.6]undec-3-en-3-yl)benzonitrile (2e)

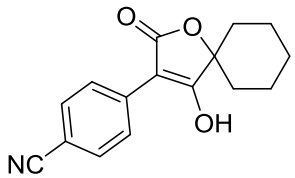


86.6 mg, 0.339 mmol, 85%; White powder; $\mathbf{R}_f$ (MeOH/DCM 1/10): 0.10;

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (d, J = 8.6 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H), 2.22 – 2.08 (m, 2H), 1.89 – 1.78 (m, 4H), 1.78 – 1.68 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 182.37, 171.32, 137.22, 132.33, 126.39, 119.79, 107.68, 95.38, 90.49, 36.55, 25.15.

HRMS (ESI-MS, m/z): calculated m/z for $[C_{15}H_{13}NO_3]$ $[M-H]^-$: 254.0823, found: 254.0823.

4-(4-hydroxy-2-oxo-1-oxaspiro[4.5]dec-3-en-3-yl)benzonitrile (2f)



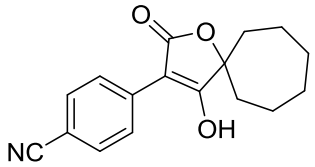
96.6 mg, 0.359 mmol, 90%, (2 equiv. Cs_2CO_3, 48 h); 100.5 mg, 0.373 mmol, 93%, (4 equiv. Cs_2CO_3, 2 h); White powder; $\mathbf{R}_f$ (MeOH/DCM 1/10): 0.10;

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (d, J = 8.6 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H), 1.99 – 1.91 (m, 2H), 1.73 – 1.70 (m, 3H), 1.61 – 1.48 (m, 4H), 1.28 – 1.18 (m, 1H); **^{13}C NMR**

(101 MHz, DMSO-d_6) δ 185.51, 171.63, 137.68, 132.25, 126.35, 119.86, 107.38, 93.77, 81.82, 32.50, 24.48, 22.07.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{16}H_{15}NO_3$] [M-H]$^-$: 268.0979, found: 268.0972.

4-(4-hydroxy-2-oxo-1-oxaspiro[4.6]undec-3-en-3-yl)benzonitrile (2g)

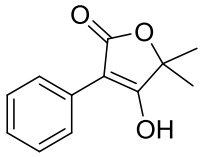


93.6 mg, 0.330 mmol, 83%; White powder; **R**$_f$ (MeOH/DCM 1/10): 0.09;

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14 (d, *J* = 8.6 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 2H), 2.15 – 2.01 (m, 2H), 1.80 – 1.61 (m, 8H), 1.61 – 1.48 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 190.76, 173.10, 139.91, 131.93, 124.92, 120.36, 105.16, 89.69, 84.65, 36.63, 28.33, 22.61.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{17}H_{17}NO_3$] [M-H]$^-$: 282.1136, found: 282.1129.

4-hydroxy-5,5-dimethyl-3-phenylfuran-2(5*H*)-one (2h)

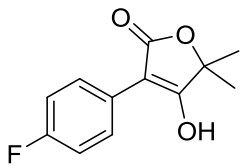


59.6 mg, 0.292 mmol, 73%; White powder; **R**$_f$ (MeOH/DCM 1/10): 0.38;

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 – 7.86 (m, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.26 – 7.20 (m, 1H), 1.52 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 181.06, 171.41, 131.36, 128.40, 127.03, 126.60, 96.33, 80.03, 24.54.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{12}H_{12}O_3$] [M+H]$^+$: 205.0859, found: 205.0857.

3-(4-fluorophenyl)-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one (2i)



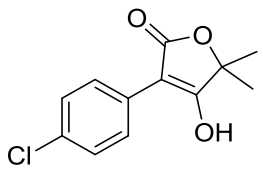
63.0 mg, 0.284 mmol, 71%; White powder; **R**$_f$ (MeOH/DCM 1/10): 0.25;

^{1}H NMR (400 MHz, DMSO-d_6) (400 MHz, DMSO-d_6) 8.03 – 7.97 (m, 2H), 7.18 (t, *J* = 9.0 Hz, 2H), 1.49 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 182.24, 171.79, 160.56 (d, *J*

= 242.9 Hz), 128.46 (d, *J* = 7.5 Hz), 128.39, 115.11 (d, *J* = 20.9 Hz), 94.47, 80.18, 24.57; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -115.08.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{12}H_{11}FO_3$] [M-H]$^-$: 221.0619, found: 221.0618.

3-(4-chlorophenyl)-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one （2j）

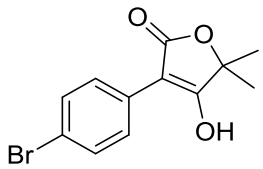


75.3 mg, 0.316 mmol, 79%; White powder; **R**$_f$ (MeOH/DCM 1/10): 0.20;

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 1.49 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 183.10, 171.63, 131.01, 130.26, 128.32, 128.08, 94.15, 80.25, 24.55.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{12}H_{11}ClO_3$] [M+H]$^+$: 239.0469, found: 239.0469.

3-(4-bromophenyl)-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one (2k)

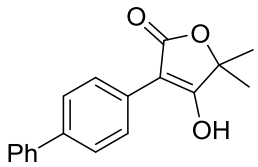


97.3 mg, 0.344 mmol, 86%; White powder; **R**$_f$ (MeOH/DCM 1/10): 0.15;

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 1.50 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 181.51, 171.09, 131.39, 130.63, 128.82, 119.44, 95.42, 80.25, 24.44.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{12}H_{11}BrO_3$] [M-H]$^-$: 280.9819, found: 280.9835.

3-([1,1'-biphenyl]-4-yl)-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one (2l)



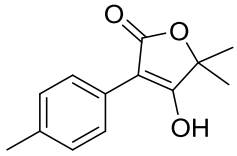
90.5 mg, 0.323 mmol, 81%; White powder; **R**$_f$ (MeOH/DCM 1/10): 0.3;

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 – 7.97 (m, 2H), 7.72 – 7.67 (m, 4H), 7.47 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.39 – 7.33 (m, 1H), 1.54 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ

180.69, 171.25, 140.29, 138.28, 130.38, 129.39, 127.79, 127.58, 126.90, 126.64, 96.47, 80.13, 24.53.

HRMS (ESI-MS, m/z): calculated m/z for $[C_{18}H_{16}O_3]$ $[M-H]^-$: 279.1027, found: 279.1030.

4-hydroxy-5,5-dimethyl-3-(*p*-tolyl)furan-2(5*H*)-one (2m)

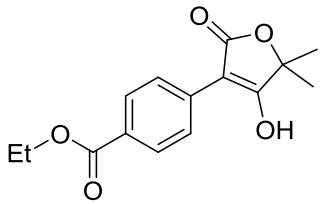


50.5 mg, 0.231mmol, 58%; White powder; $\mathbf{R_f}$ (MeOH/DCM 1/10): 0.4;

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 1.50 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 180.16, 171.42, 135.77, 128.98, 128.31, 127.01, 96.58, 79.96, 24.55, 21.31.

HRMS (ESI-MS, m/z): calculated m/z for $[C_{13}H_{14}O_3]$ $[M+H]^+$: 219.1016, found: 219.1016.

ethyl 4-(4-hydroxy-5,5-dimethyl-2-oxo-2,5-dihydrofuran-3-yl)benzoate (2n)

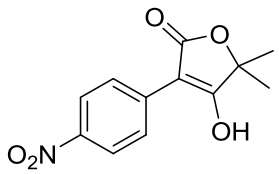


85.4 mg, 0.309 mmol, 77% (2 equiv. Cs_2CO_3, 48 h); 83.8 mg, 0.303 mmol, 76% (4 equiv. Cs_2CO_3, 2 h); White powder; $\mathbf{R_f}$ ((MeOH/DCM): 0.20;

^{1}H NMR (400 MHz, DMSO-d_6)δ 8.23 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.41 (s, 6H), 1.32 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 187.78, 172.52, 166.26, 138.98, 129.16, 125.49, 125.00, 91.81, 80.34, 60.72, 24.73, 14.70.

HRMS (ESI-MS, m/z): calculated m/z for $[C_{15}H_{16}O_5]$ $[M-H]^-$: 275.0925, found: 275.0922.

4-hydroxy-5,5-dimethyl-3-(4-nitrophenyl)furan-2(5*H*)-one (2o)

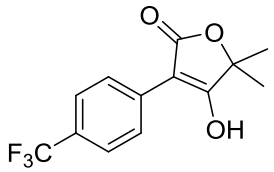


72.2 mg, 0.290 mmol, 72%; Yellow powder; $\mathbf{R_f}$ (MeOH/DCM 1/10): 0.13;

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.37 – 8.30 (m, 2H), 8.22 – 8.14 (m, 2H), 1.47 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 187.45, 171.69, 143.95, 140.73, 125.65, 123.83, 92.54, 80.61, 24.56.

HRMS (ESI-MS, m/z): calculated m/z for $[C_{12}H_{11}NO_5]$ $[M+H]^+$:248.0564, found: 248.0564.

4-hydroxy-5,5-dimethyl-3-(4-(trifluoromethyl)phenyl)furan-2(5*H*)-one (2p)

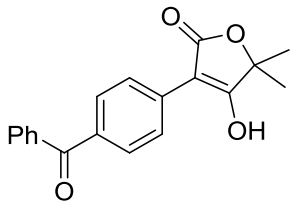


83.8 mg, 0.308 mmol, 77% (2 equiv. Cs_2CO_3, 48 h); 86.2 mg, 0.317 mmol, 79% (4 equiv. Cs_2CO_3, 2 h); Yellow powder; $\mathbf{R_f}$ (MeOH/DCM 1/10): 0.18;

^{1}H NMR (400 MHz, DMSO-d_6)δ 8.17 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 1.53 (s, 6H); **^{13}C NMR** (101 MHz, DMSO) δ 182.92, 170.97, 135.72, 127.08, 126.60 (q, *J* = 31.7 Hz), 125.26 (q, *J* = 3.8, 3.3 Hz), 124.84 (q, *J* = 271.8 Hz), 95.19, 80.36, 24.41; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -61.46.

HRMS (ESI-MS, m/z): calculated m/z for $[C_{13}H_{11}F_3O_3]$ $[M-H]^-$: 271.0588, found: 271.0596.

3-(4-benzoylphenyl)-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one (2q)

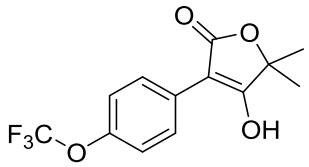


103.5 mg, 0.328 mmol, 84%; White powder; $\mathbf{R_f}$ (MeOH/DCM 1/10): 0.25;

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 – 8.00 (m, 2H), 7.69 (dd, *J* = 8.3, 1.9 Hz, 4H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.34 (m, 1H), 1.54 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 195.71, 182.65, 170.91, 137.78, 135.93, 134.70, 132.95, 130.12, 129.99, 129.00, 126.59, 95.83, 80.32, 24.44.

HRMS (ESI-MS, m/z): calculated m/z for $[C_{19}H_{16}O_4]$ $[M-H]^-$: 307.0976, found: 307.0965.

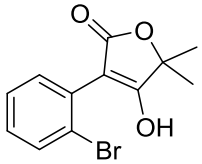
4-hydroxy-5,5-dimethyl-3-(4-(trifluoromethoxy)phenyl)furan-2(5*H*)-one (2r)



89.8 mg, 0.312 mmol, 78%; White powder; $\mathbf{R}_f$ (MeOH/DCM 1/10): 0.28;

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, J = 9.0 Hz, 2H), 7.37 (d, J = 7.9 Hz, 2H), 1.52 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 186.03, 175.80, 151.56 (d, J = 2.1 Hz), 135.37, 133.44, 125.86, 125.33 (q, J = 255.9 Hz), 100.32, 85.02, 29.15; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -56.86.
HRMS (ESI-MS, m/z): calculated m/z for [$C_{13}H_{11}F_3O_4$] [M-H]$^-$: 287.0537, found: 287.0539.

3-(2-bromophenyl)-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one (2s)

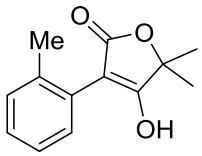


95.5 mg, 0.337 mmol, 84%; White powder; $\mathbf{R}_f$ (MeOH/DCM 1/10): 0.30;

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 – 7.64 (m, 1H), 7.42 – 7.37 (m, 1H), 7.31 – 7.25 (m, 2H), 1.49 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 180.32, 170.87, 133.32, 132.68, 131.69, 130.13, 127.82, 125.40, 99.50, 81.08, 24.57.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{12}H_{11}BrO_3$] [M-H]$^-$: 280.9819, found: 280.9811.

4-hydroxy-5,5-dimethyl-3-(*o*-tolyl)furan-2(5*H*)-one (2t)

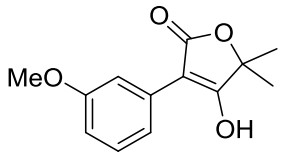


54.4 mg, 0.249 mmol, 62%, White powder; $\mathbf{R}_f$ (MeOH/DCM 1/10): 0.50;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.22 (s, 1H), 7.25 – 7.11 (m, 4H), 2.16 (s, 3H), 1.50 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 179.71, 171.51, 137.87, 131.25, 130.16, 129.73, 128.09, 125.79, 99.22, 80.75, 24.73, 19.94.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{13}H_{14}O_3$] [M+H]$^+$: 219.1016, found: 219.1014.

4-hydroxy-3-(3-methoxyphenyl)-5,5-dimethylfuran-2(5*H*)-one (2u)

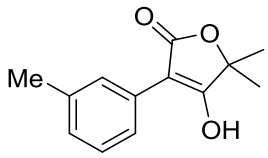


76.9 mg, 0.328 mmol, 82%; White powder; **R**$_f$ (MeOH/DCM 1/10): 0.28;

^{1}H NMR (400 MHz, DMSO-d_6) 7.50 (dd, J = 7.5, 1.5 Hz, 2H), 7.28 (t, J = 8.1 Hz, 1H), 6.83 – 6.79 (m, 1H), 3.75 (s, 3H), 1.51 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 180.78, 171.19, 159.34, 132.41, 129.43, 119.56, 112.64, 112.29, 96.53, 79.96, 55.32, 24.49.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{13}H_{14}O_4$] $[M+H]^+$: 235.0965, found: 235.0967.

4-hydroxy-5,5-dimethyl-3-(*m*-tolyl)furan-2(5*H*)-one (2v)

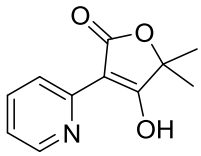


55.7 mg, 0.255 mmol, 64%; White powder; **R**$_f$ (MeOH/DCM 1/10): 0.38;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.55 (s, 1H), 7.74 – 7.66 (m, 2H), 7.23 (t, J = 7.7 Hz, 1H), 7.04 – 6.99 (m, 1H), 2.30 (s, 3H), 1.50 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 181.25, 171.54, 137.19, 131.36, 128.26, 127.62, 127.18, 124.27, 96.24, 79.99, 24.57, 21.73.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{13}H_{14}O_3$] $[M+H]^+$: 219.1016, found: 219.1014.

4-hydroxy-5,5-dimethyl-3-(pyridin-2-yl)furan-2(*5H*)-one (2w)

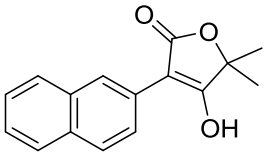


61.2 mg, 0.298 mmol, 75%; White powder; **R**$_f$ (MeOH/DCM 1/10): 0.78;

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.37 – 8.34 (m, 1H), 8.31 (d, J = 8.7 Hz, 1H), 8.18 – 8.12 (m, 1H), 7.29 – 7.24 (m, 1H), 1.34 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 197.64, 172.30, 149.90, 143.66, 138.33, 119.19, 117.88, 83.24, 82.63, 24.36.

HRMS (ESI-MS, m/z): calculated m/z for [$C_{11}H_{11}NO_3$] $[M+H]^+$: 206.0812, found: 206.0812.

4-hydroxy-5,5-dimethyl-3-(naphthalen-2-yl)furan-2(*5H*)-one (2x)



74.1 mg, 0.291 mmol, 73%; White powder; **R**$_f$ (MeOH/DCM 1/10): 0.25;

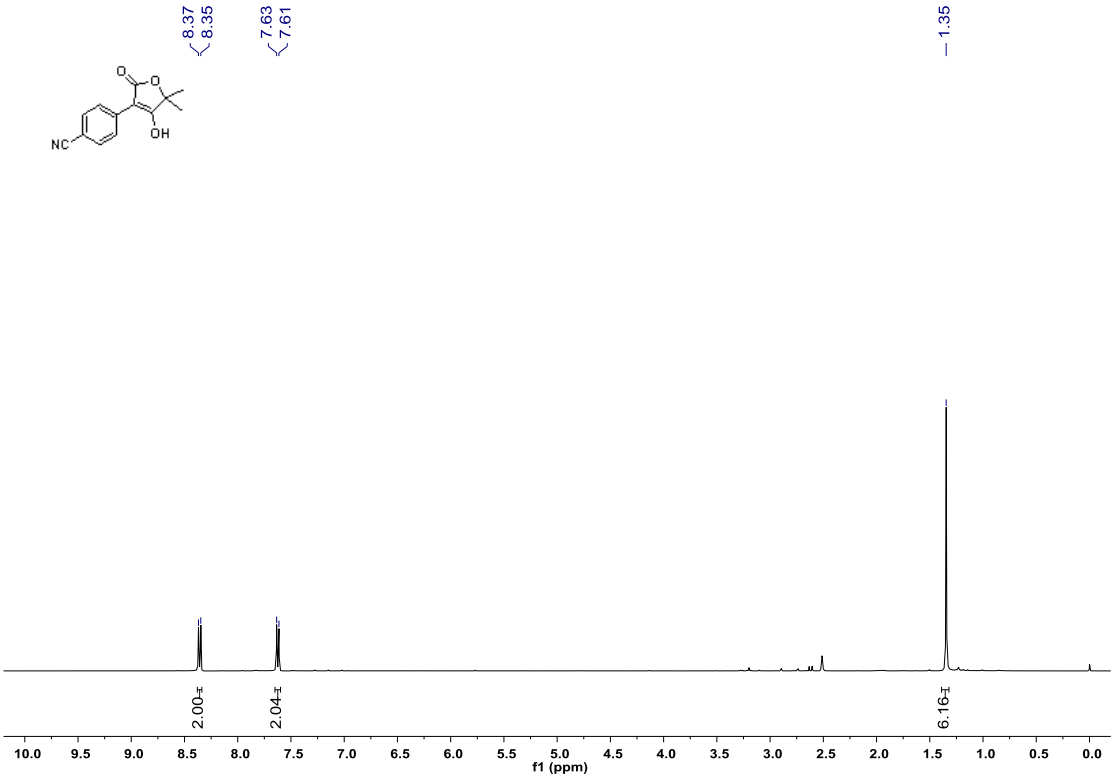
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.44 (d, J = 3.5 Hz, 1H), 8.16 – 8.06 (m, 1H), 7.93 – 7.82 (m, 3H), 7.55 – 7.42 (m, 2H), 1.56 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 181.81, 171.62, 133.31, 131.91, 129.19, 128.32, 127.86, 127.65, 126.48, 126.02, 125.54, 125.41, 96.22, 80.21, 24.61.
HRMS (ESI-MS, m/z): calculated m/z for [$C_{16}H_{14}O_3$] $[M-H]^-$: 253.0870, found: 253.0868.

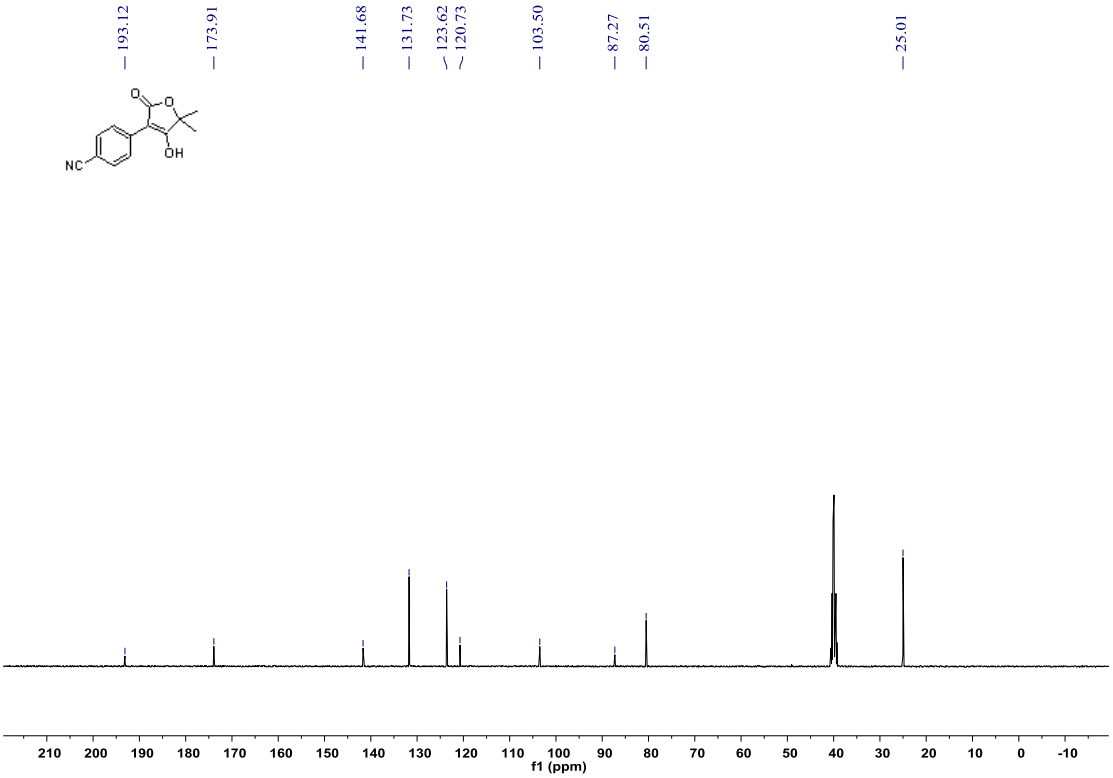
References

1. L. Ye, W. He and L. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 8550.
2. N. Okamoto, T. Sueda, H. Minami, Y. Miwa and R. Yanada, *Org. Lett.*, 2015, **17**, 1336.
3. Q.-W. Song, W.-Q. Chen, R. Ma, A. Yu, Q.-Y. Li, Y. Chang and L.-N. He, *ChemSusChem*, 2015, **8**, 821.
4. H. He, C. Qi, X. Hu, Y. Guan and H. Jiang, *Green Chem.*, 2014, **16**, 3729.

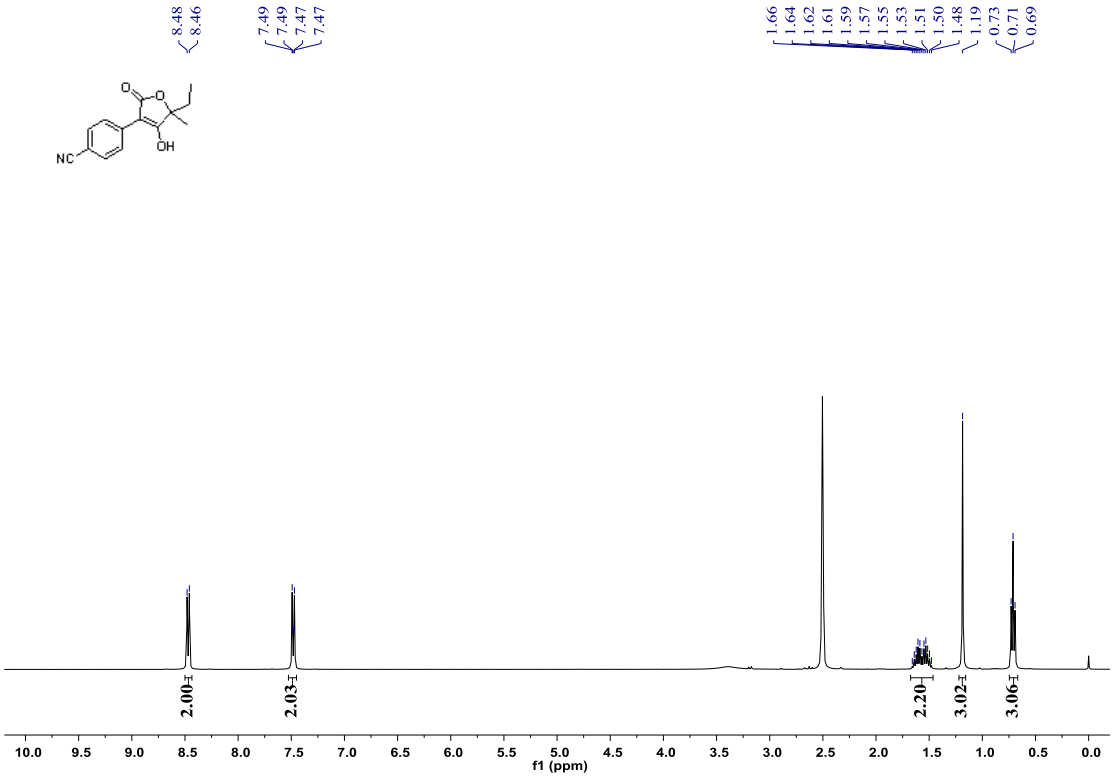
^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra

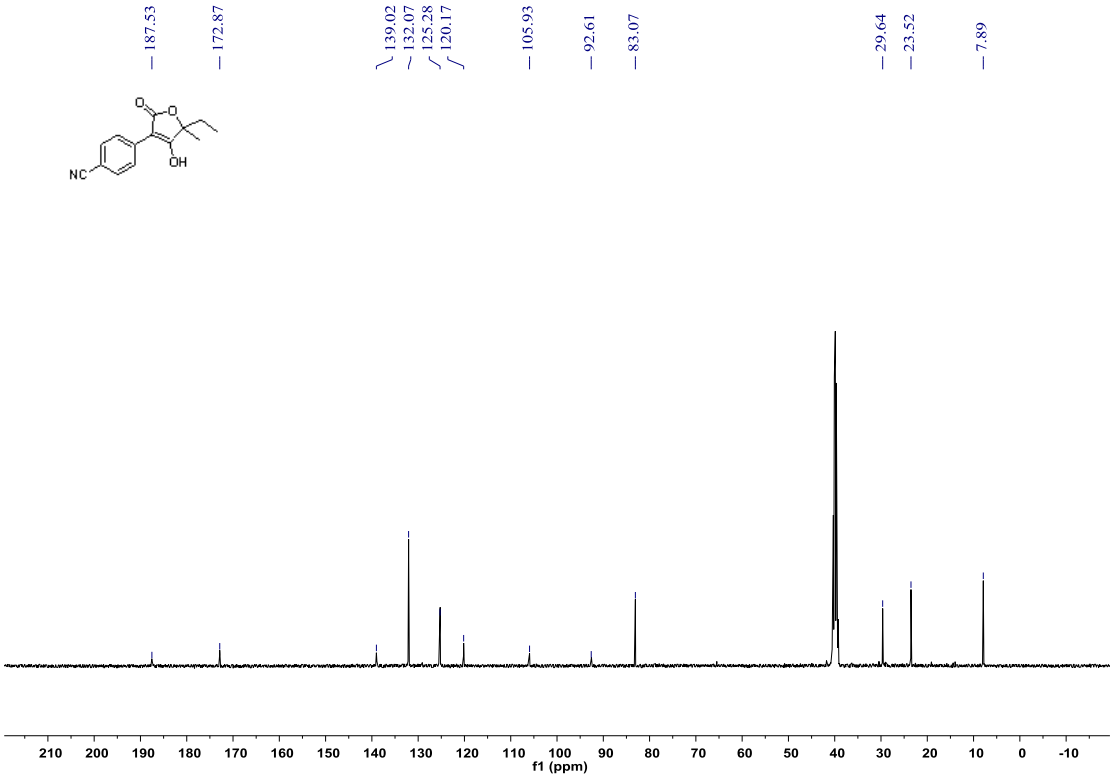
4-(4-hydroxy-5,5-dimethyl-2-oxo-2,5-dihydrofuran-3-yl)benzonitrile (2a)



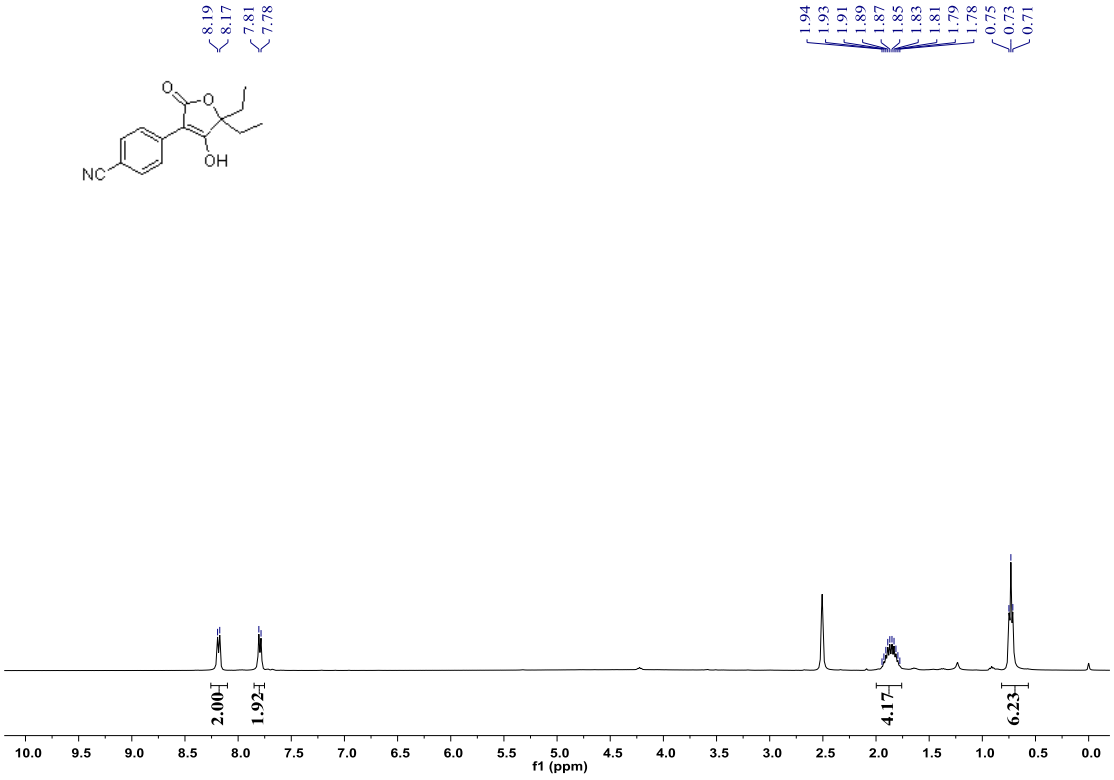


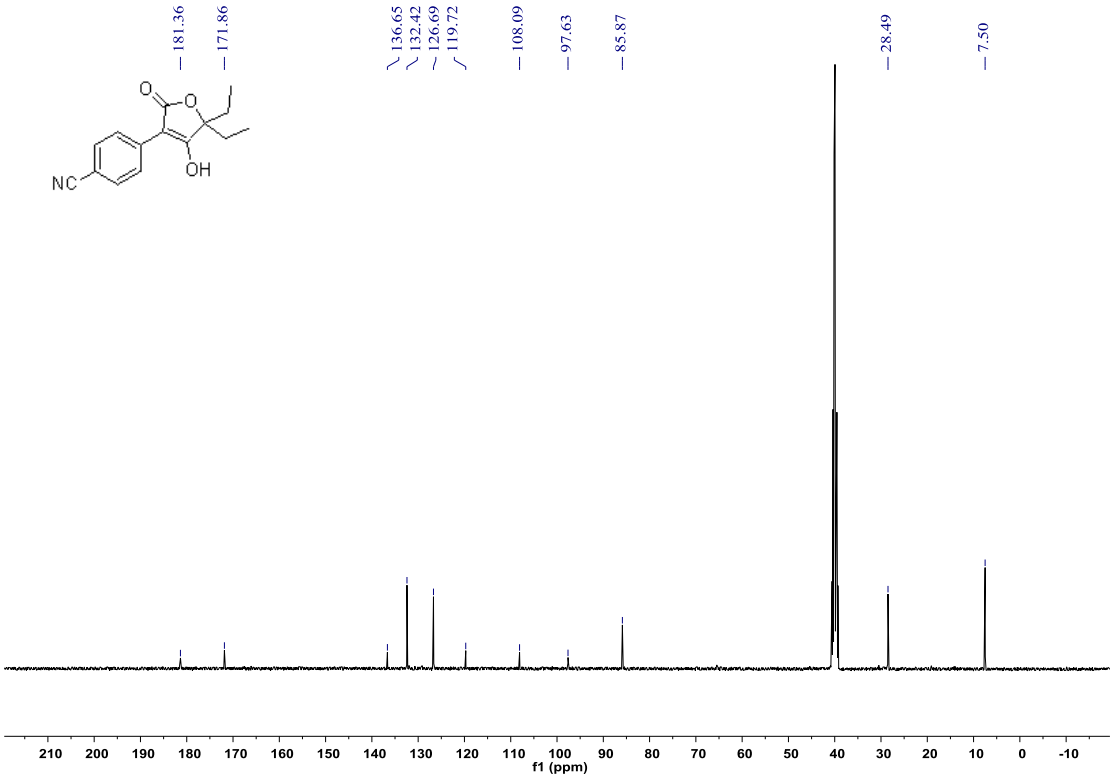
4-(4-hydroxy-5-methyl-2-oxo-5-phenyl-2,5-dihydrofuran-3-yl)benzonitrile (2b)



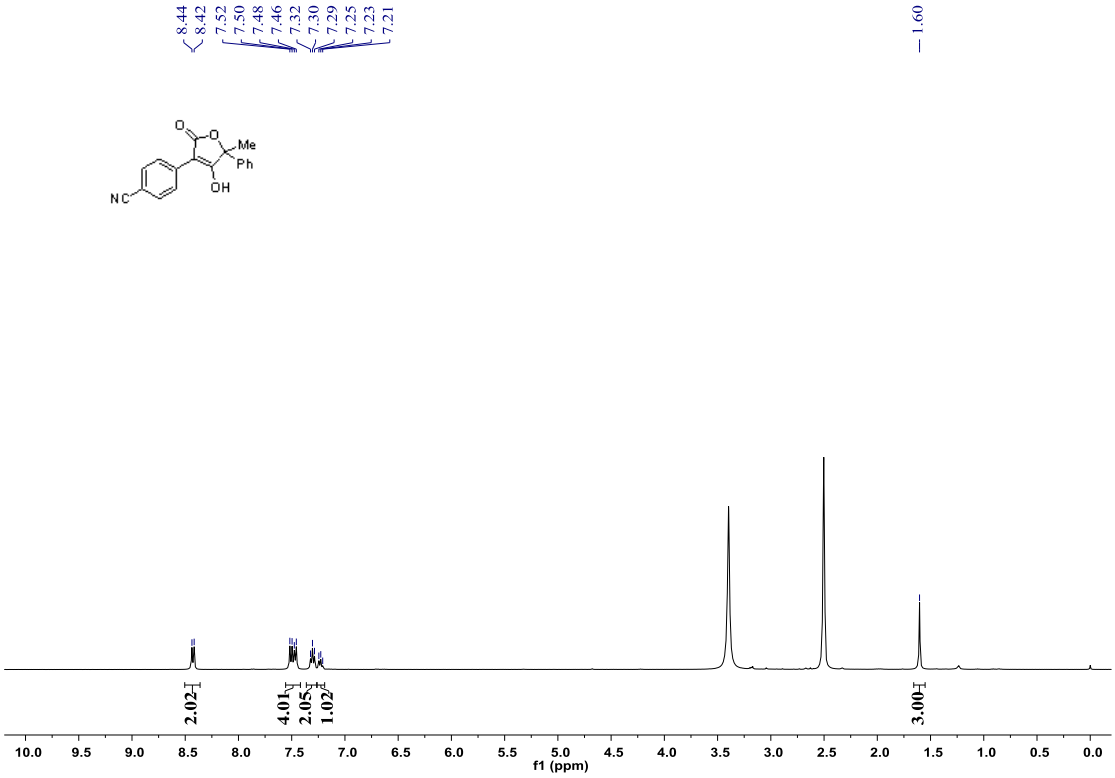


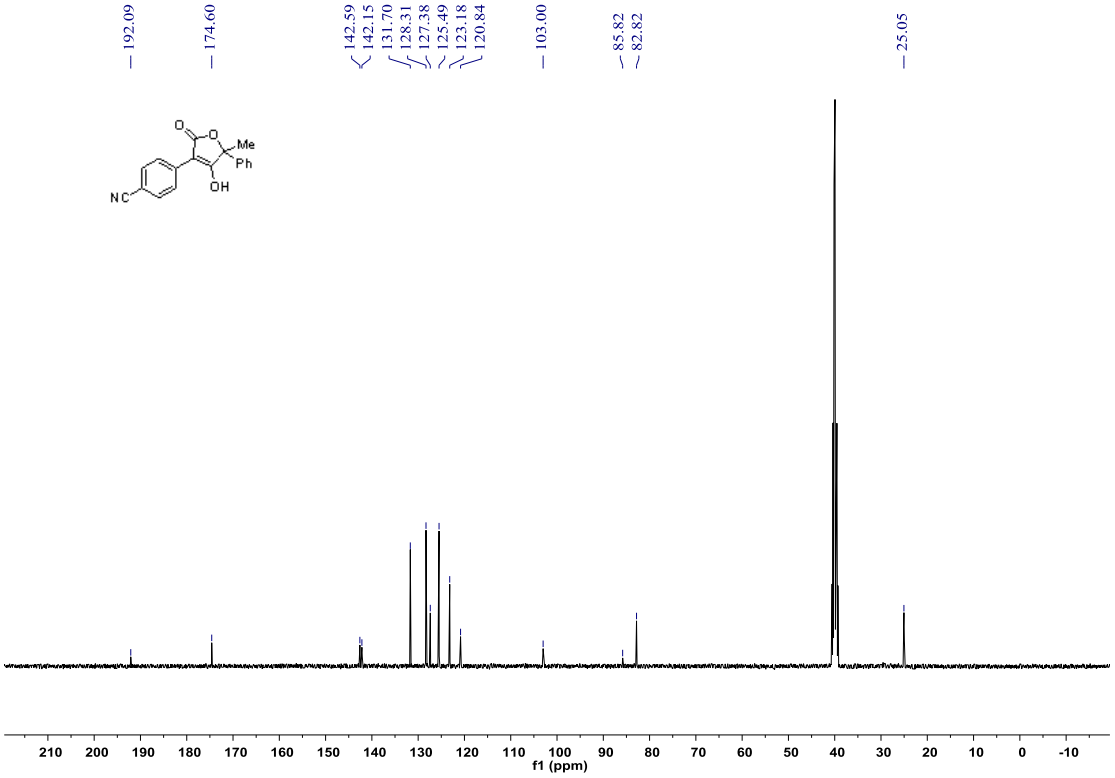
4-(5,5-diethyl-4-hydroxy-2-oxo-2,5-dihydrofuran-3-yl)benzonitrile (2c)



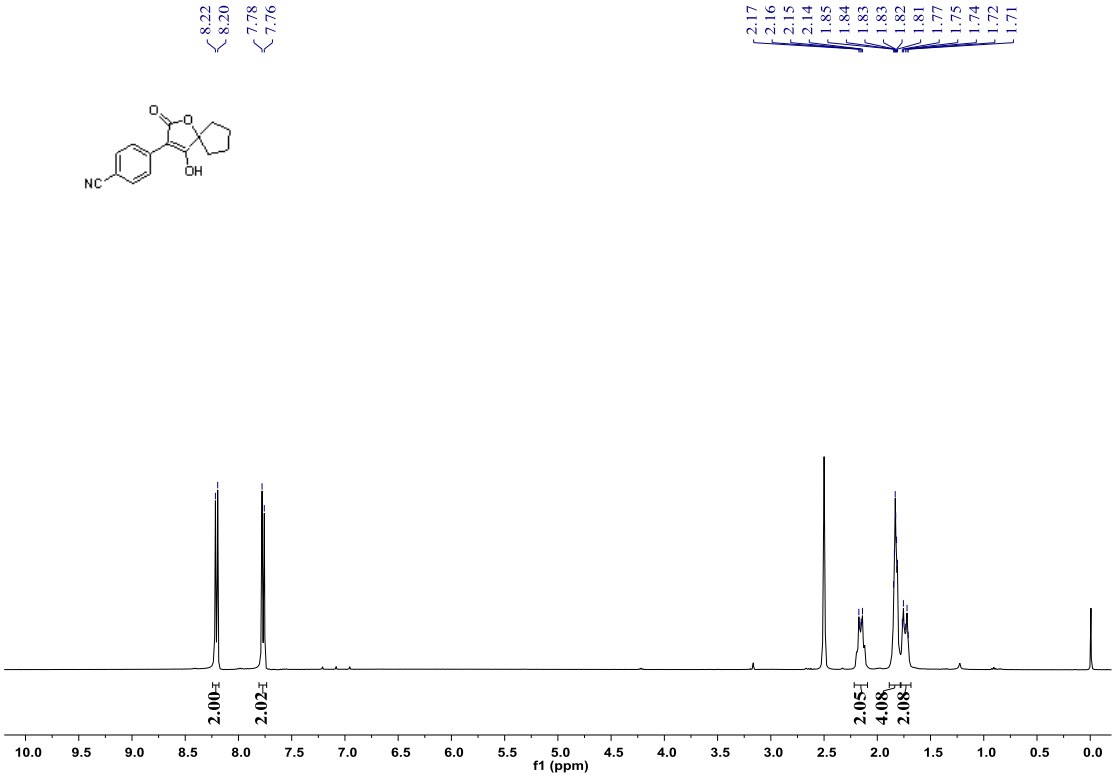


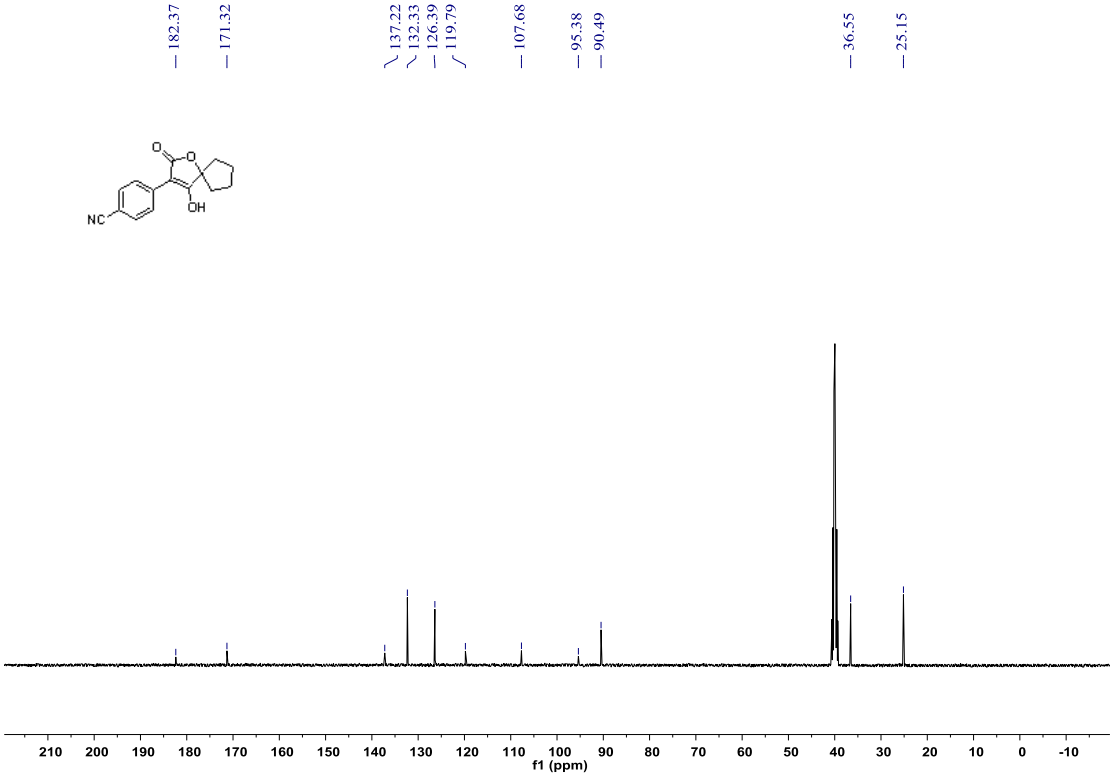
4-(4-hydroxy-5-methyl-2-oxo-5-phenyl-2,5-dihydrofuran-3-yl)benzonitrile （2d）



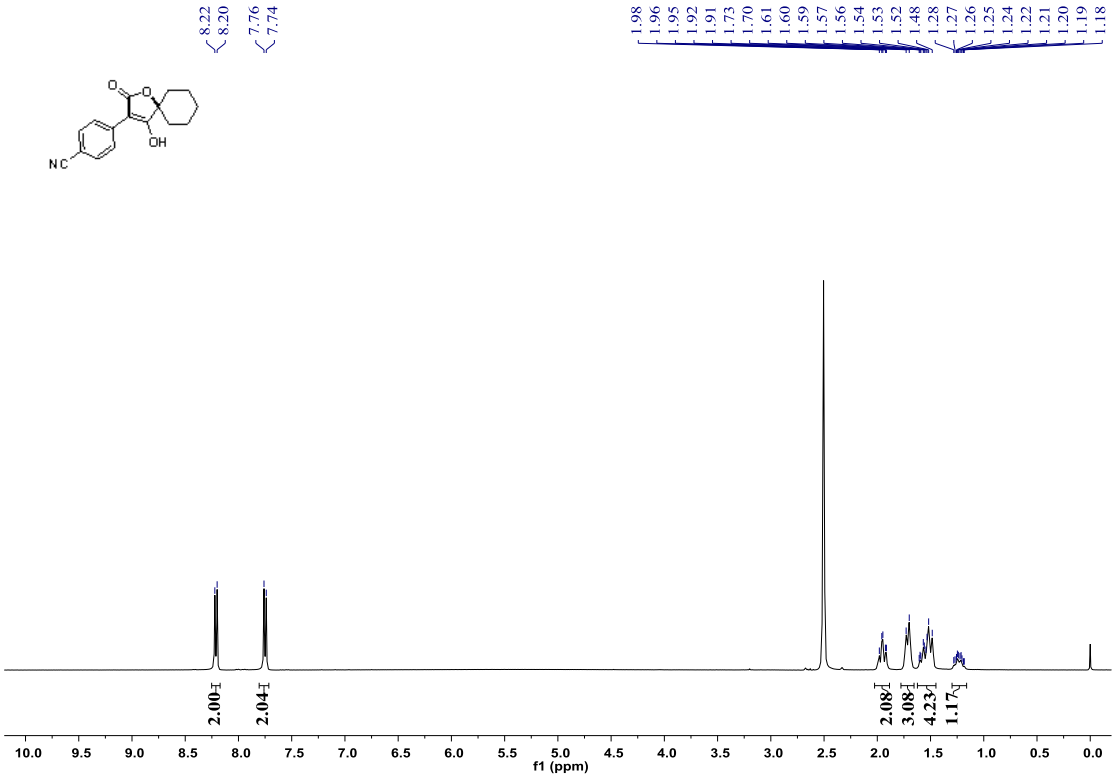


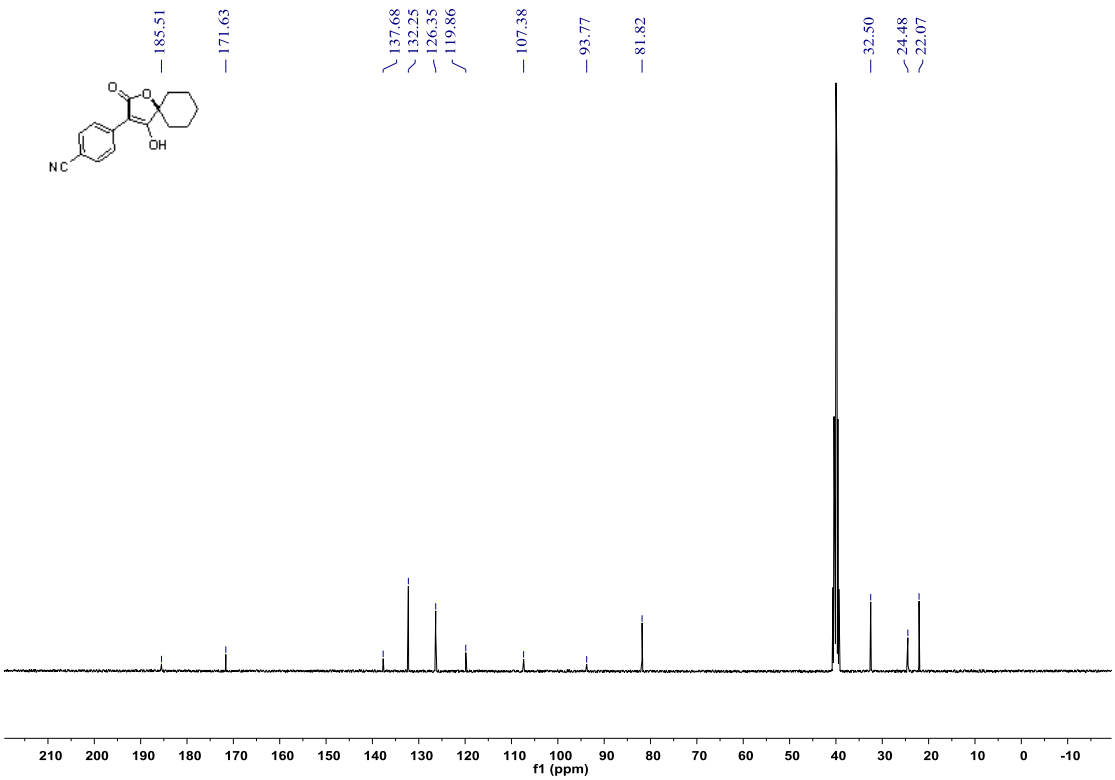
4-(4-hydroxy-2-oxo-1-oxaspiro[4.6]undec-3-en-3-yl)benzonitrile (2e)



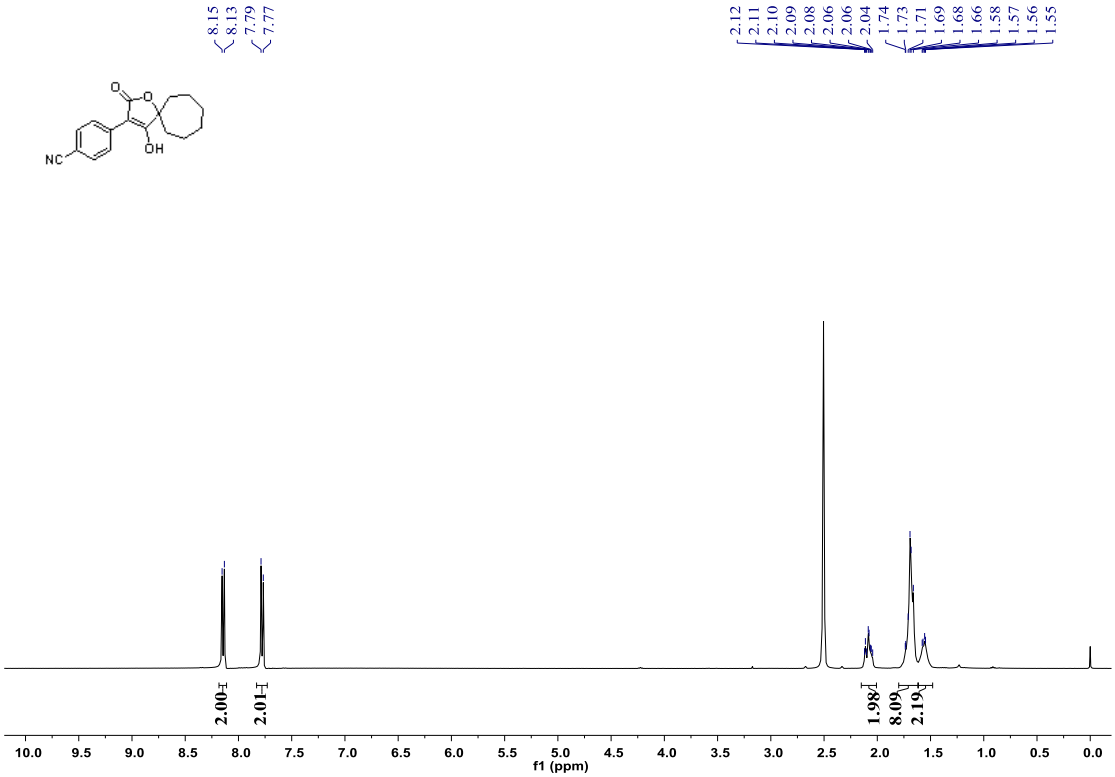


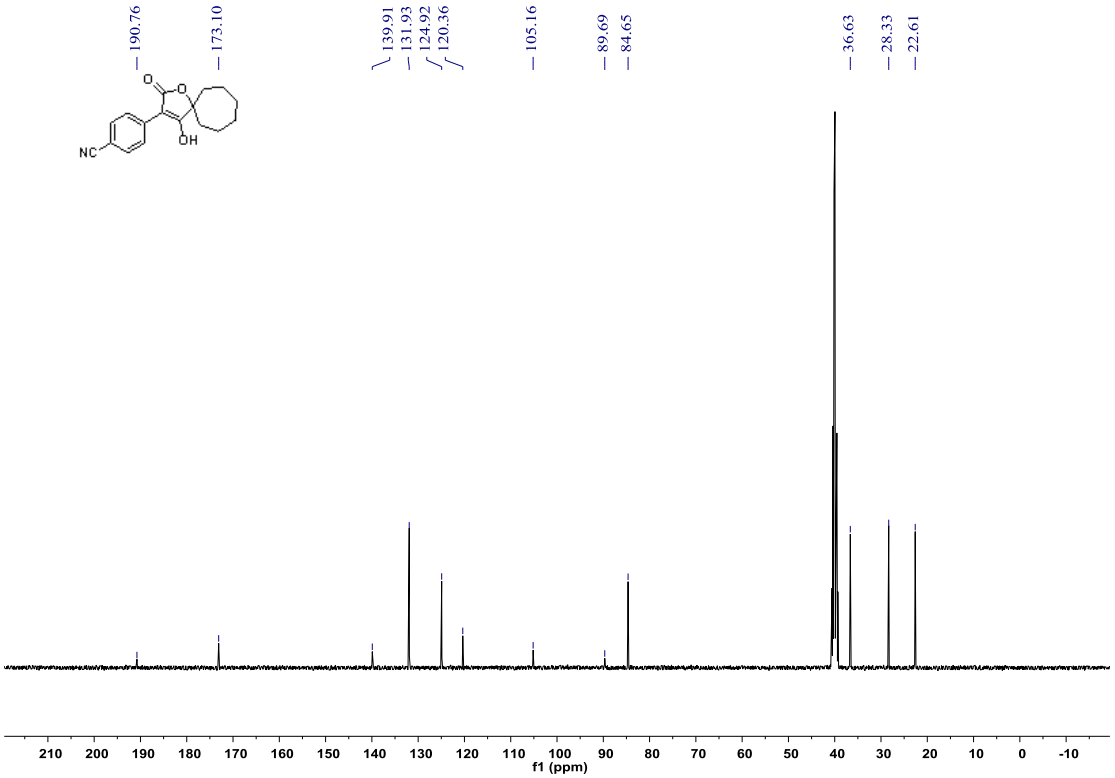
4-(4-hydroxy-2-oxo-1-oxaspiro[4.5]dec-3-en-3-yl)benzonitrile (2f)



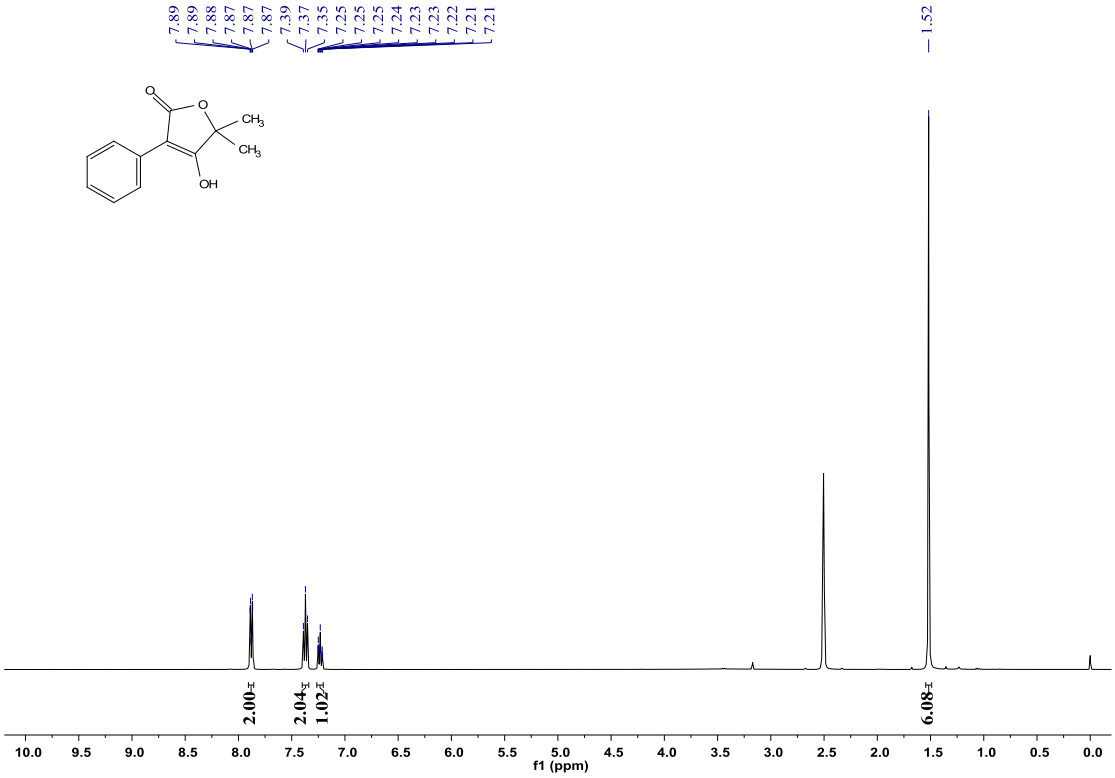


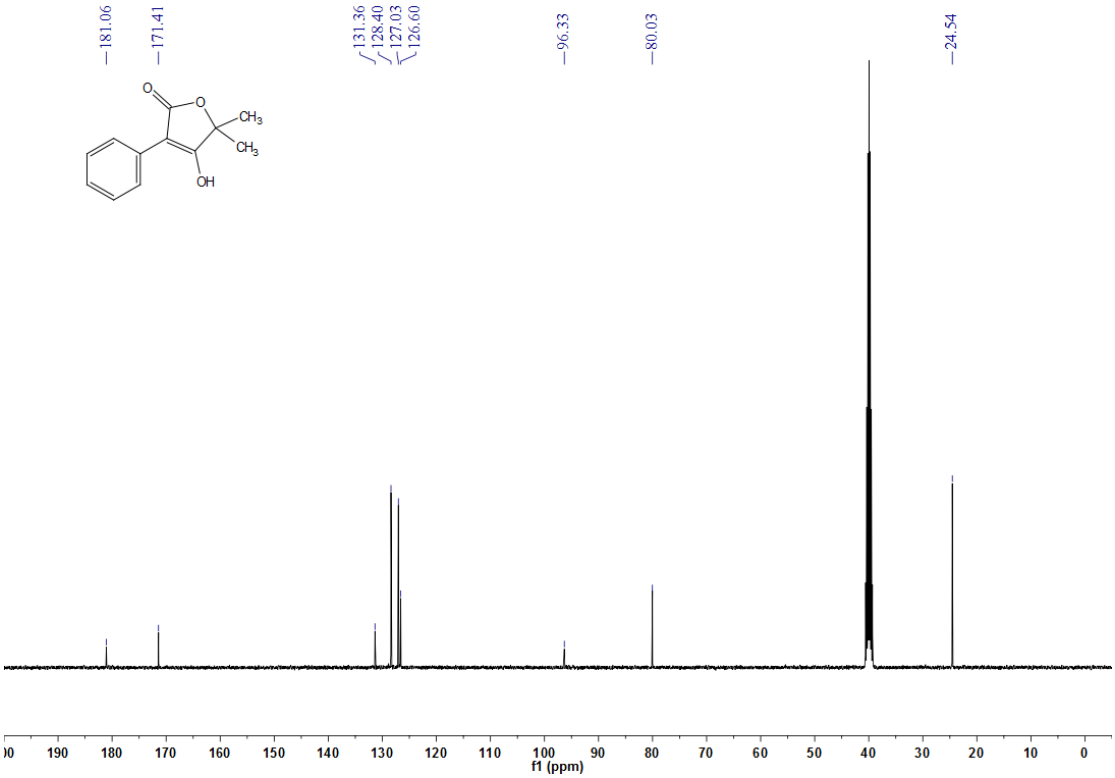
4-(4-hydroxy-2-oxo-1-oxaspiro[4.6]undec-3-en-3-yl)benzonitrile (2g)



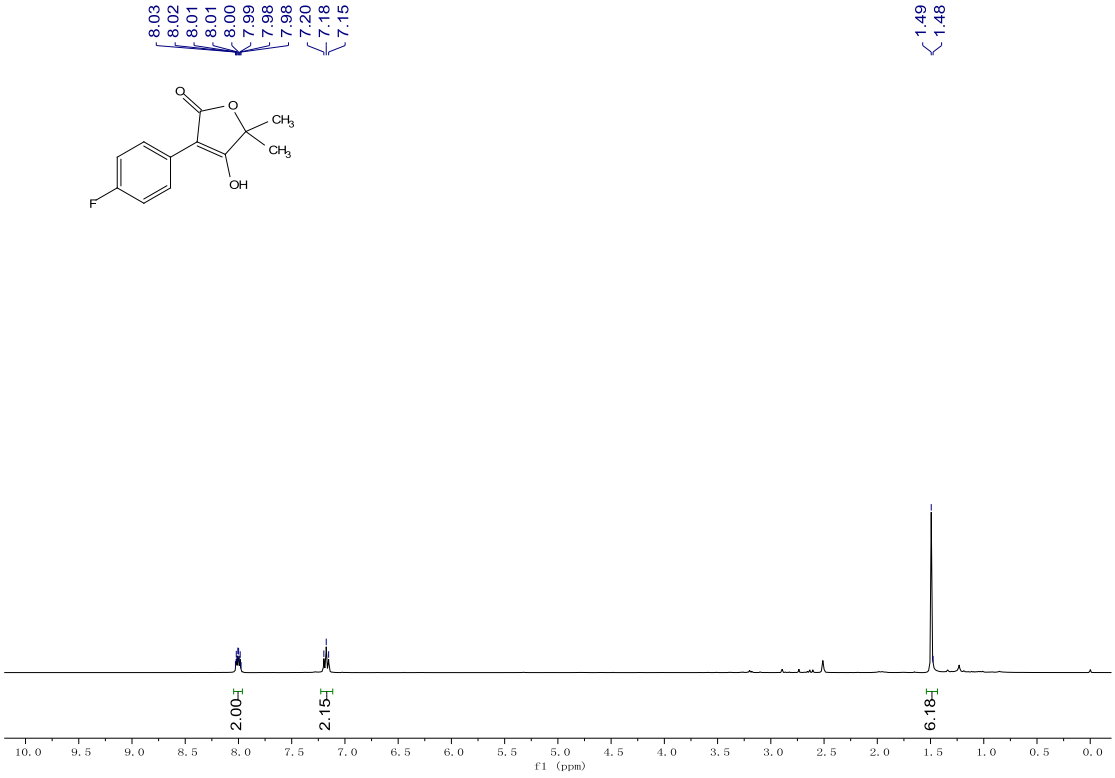


4-hydroxy-5,5-dimethyl-3-phenylfuran-2(5*H*)-one (2h)





3-(4-fluorophenyl)-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one (2i)



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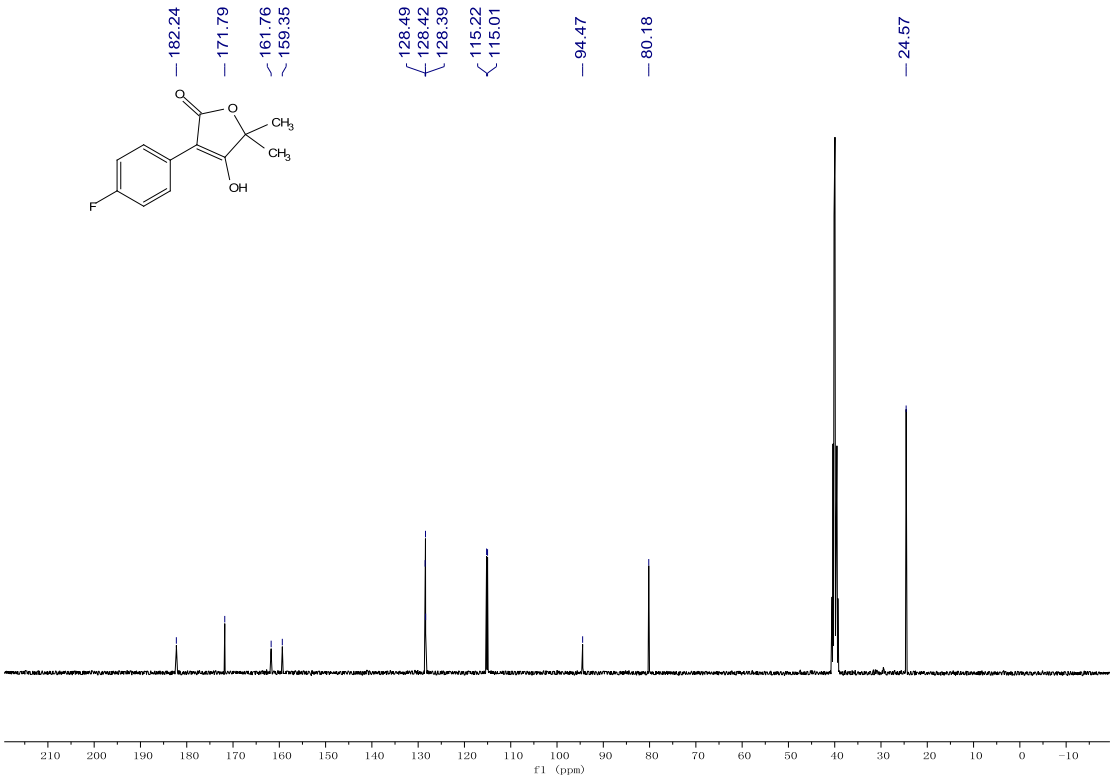

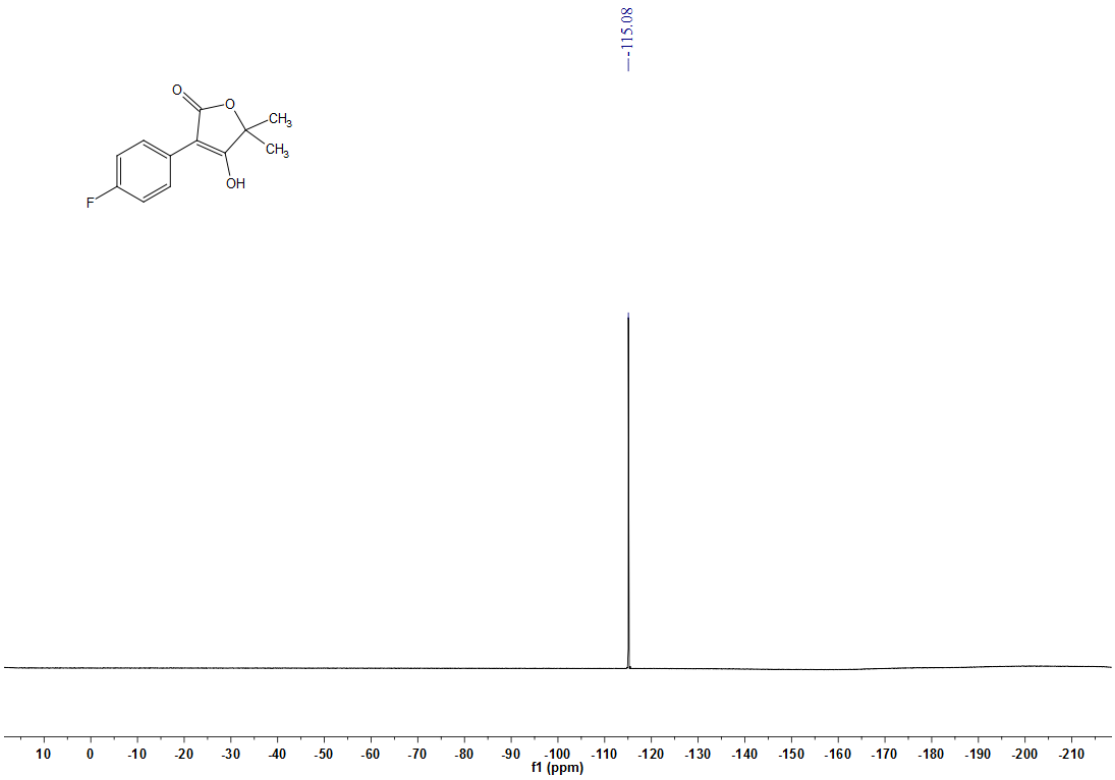
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O
CH3
CH3
OH
F
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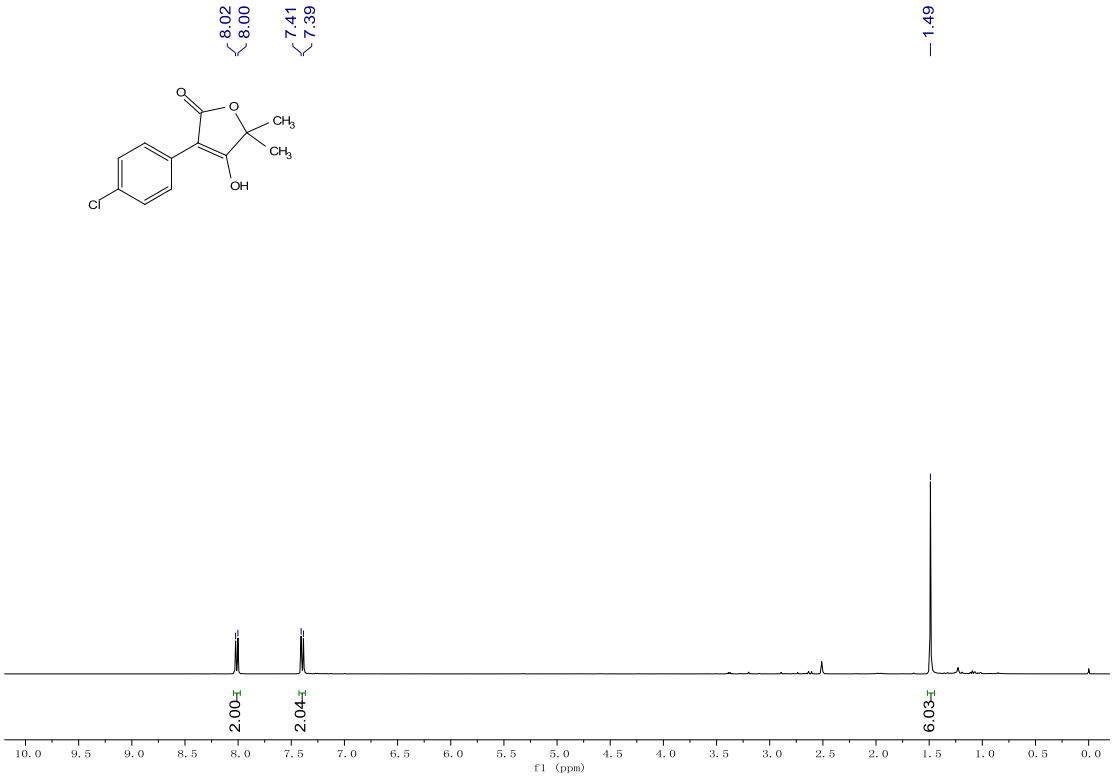
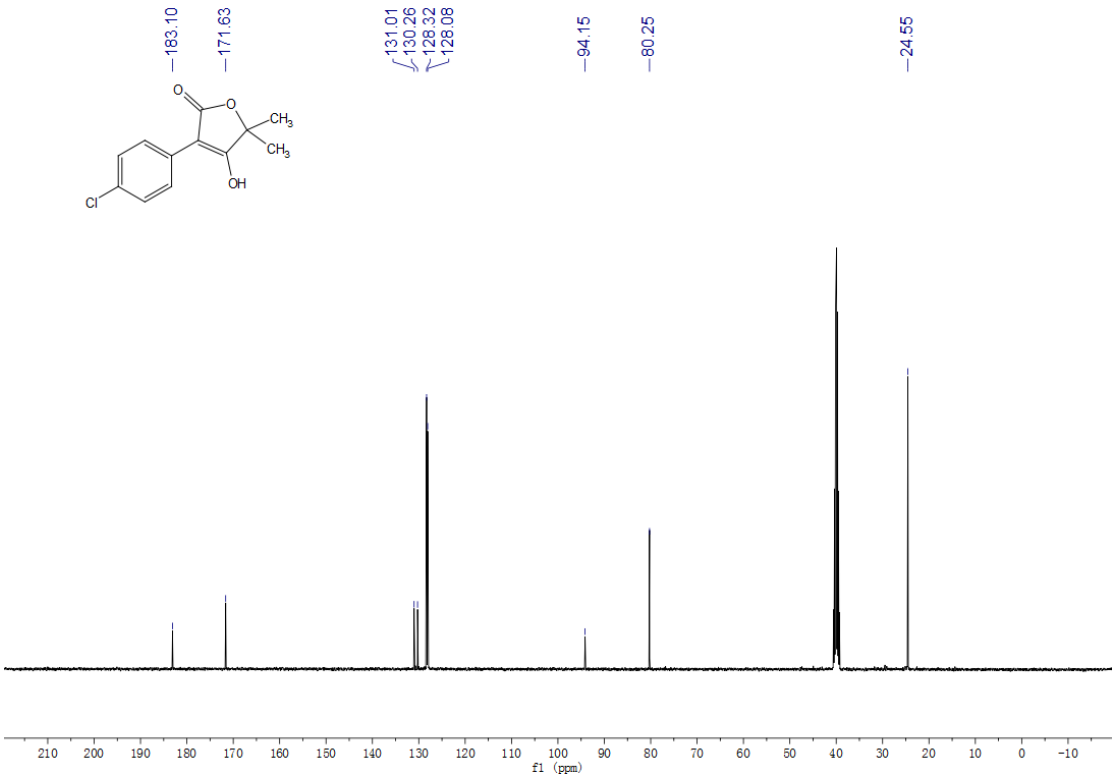
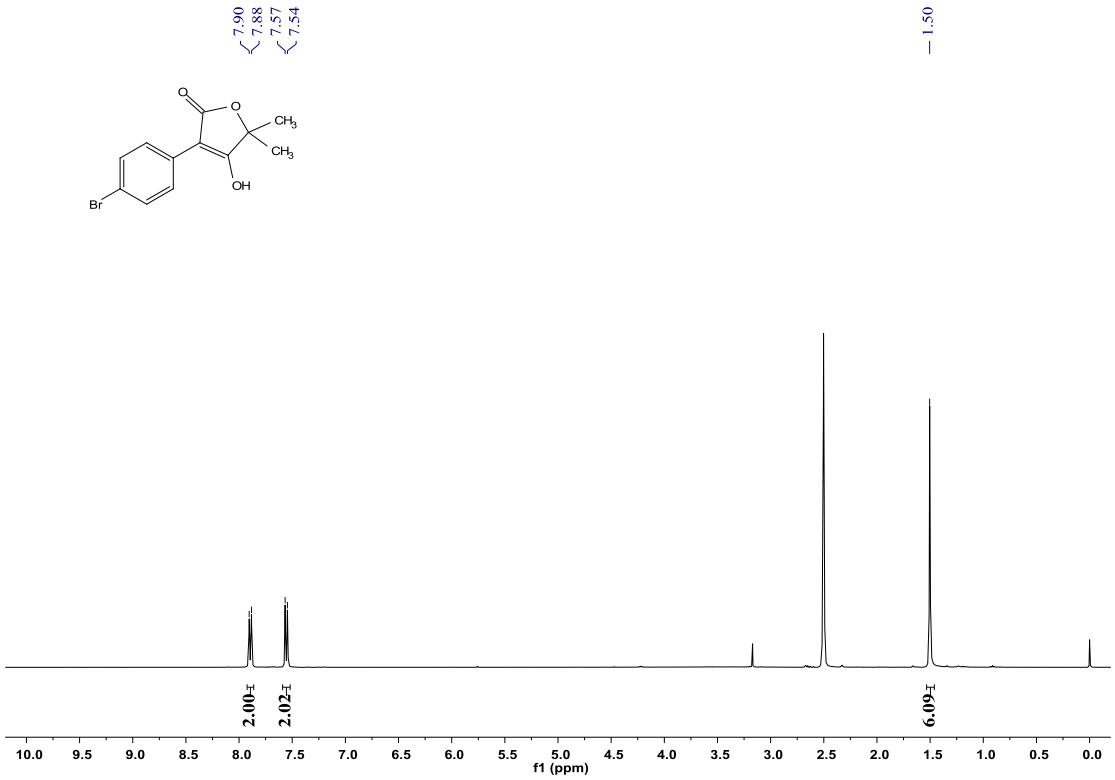
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

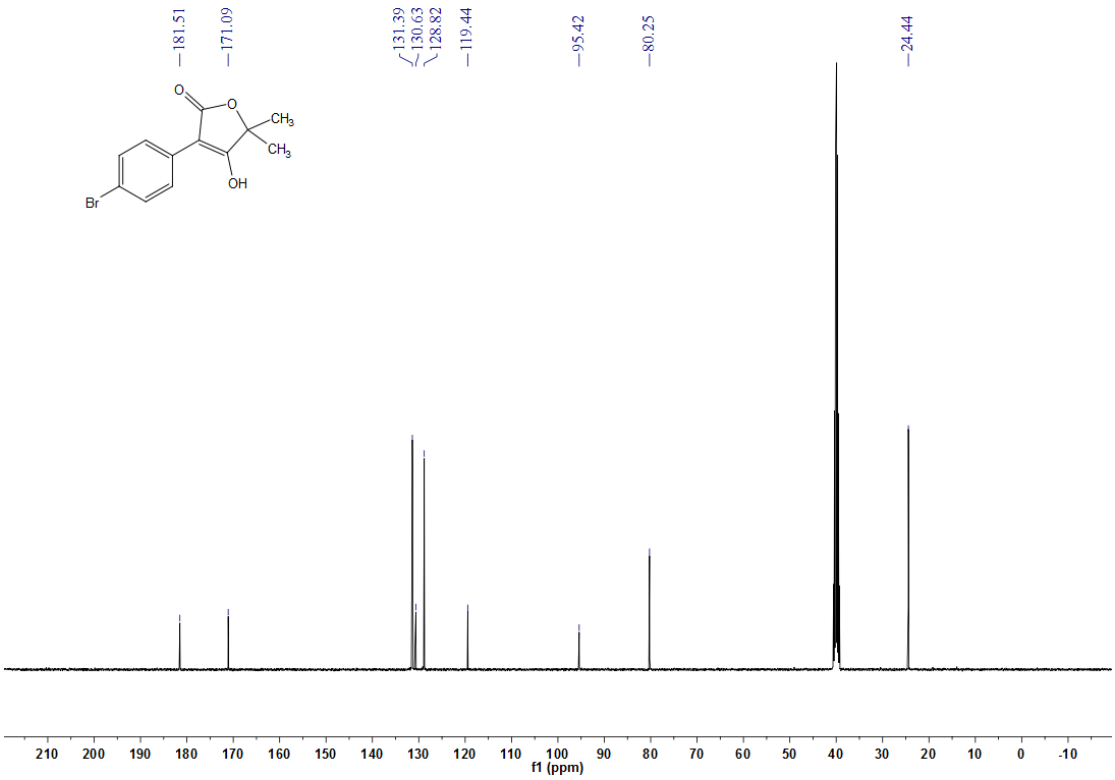
3-(4-chlorophenyl)-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one （2j）



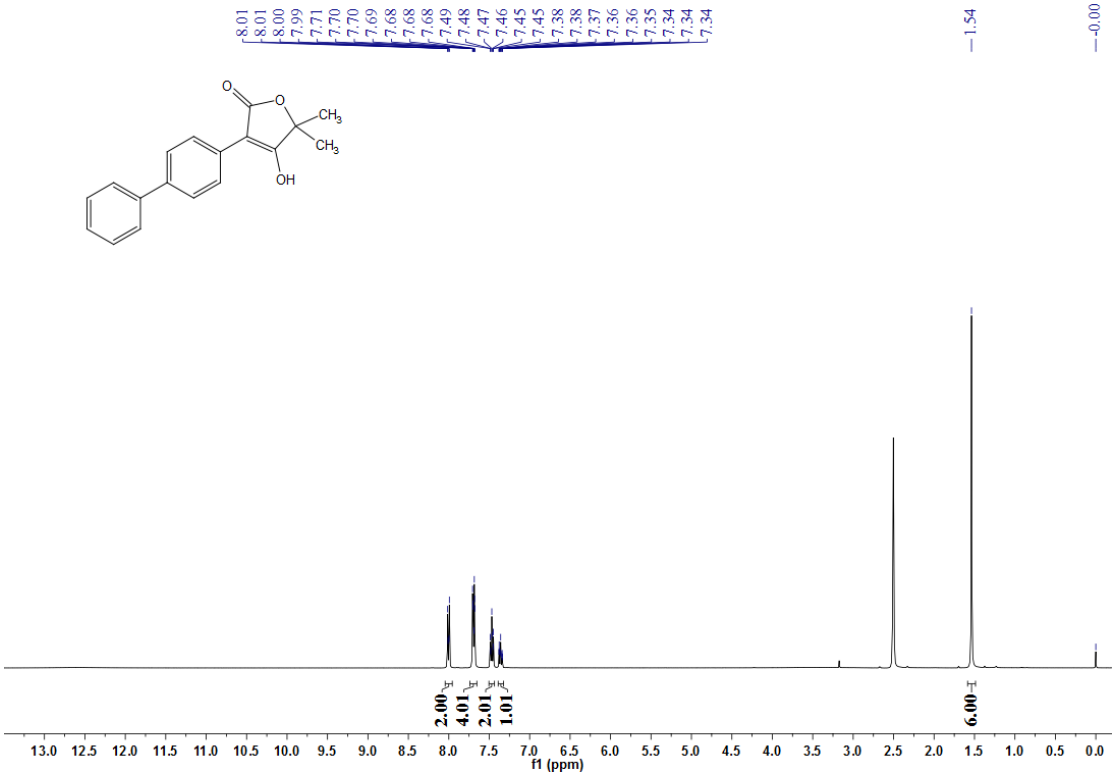


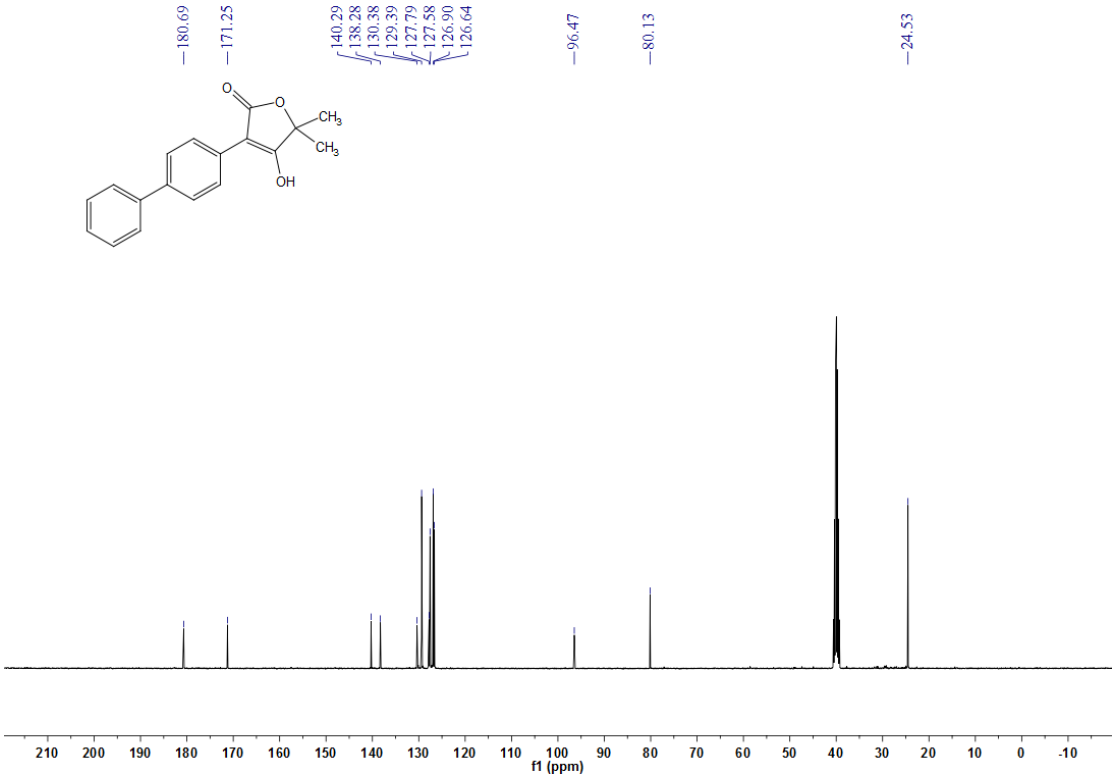
3-(4-bromophenyl)-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one (2k)



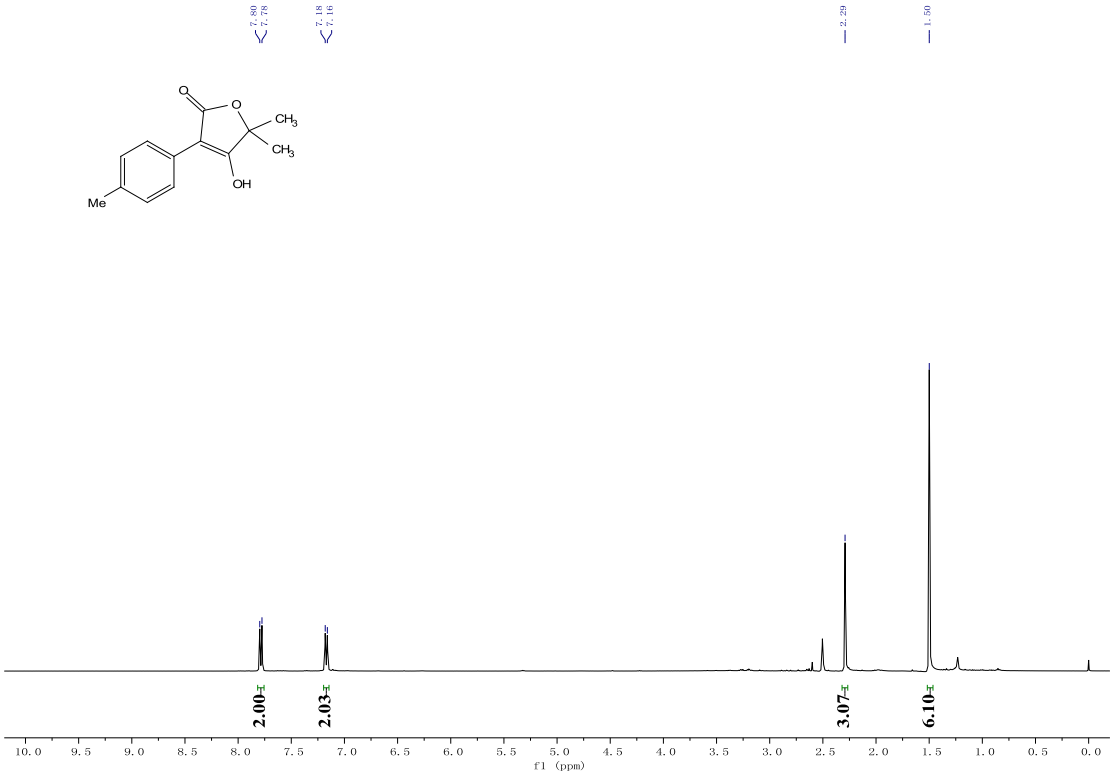


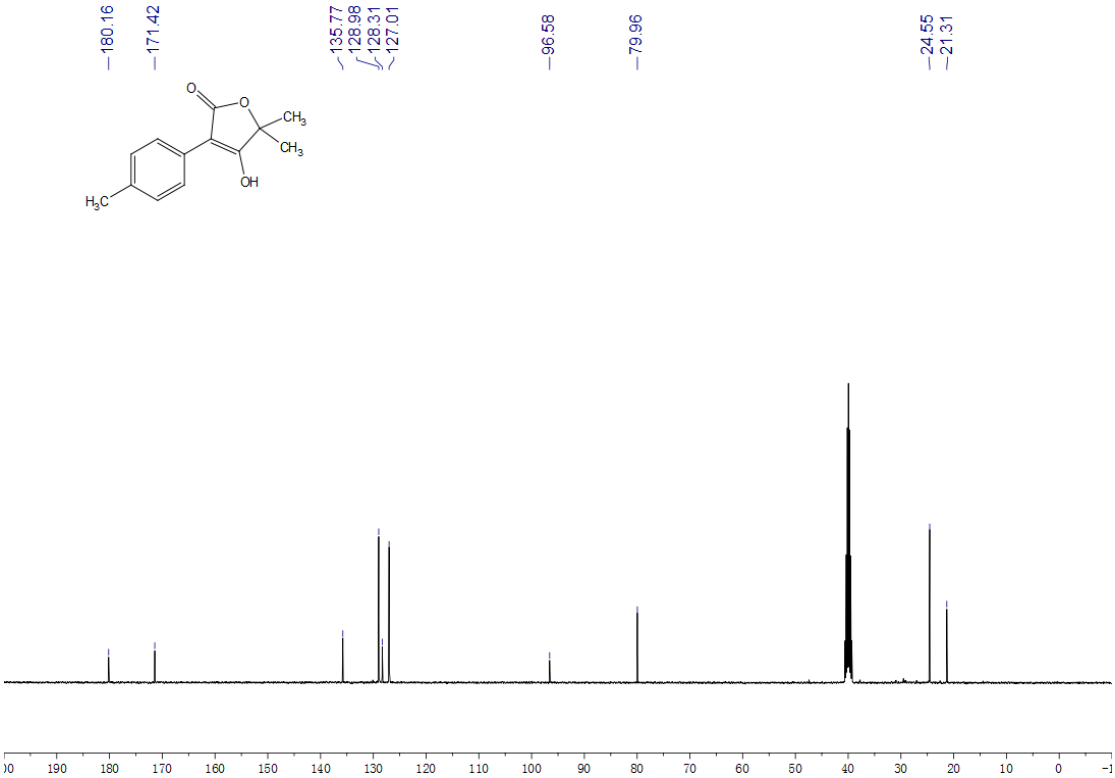
3-([1,1'-biphenyl]-4-yl)-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one (2l)



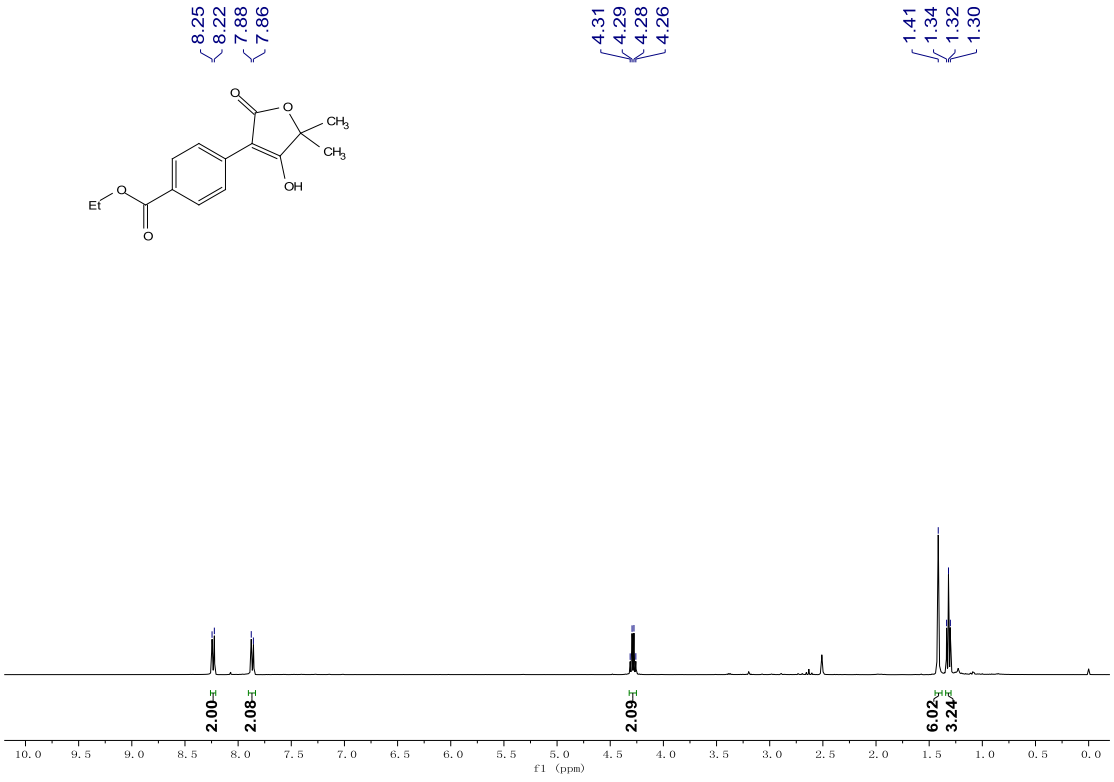


4-hydroxy-5,5-dimethyl-3-(p-tolyl)furan-2(5*H*)-one (2m)





ethyl 4-(4-hydroxy-5,5-dimethyl-2-oxo-2,5-dihydrofuran-3-yl)benzoate (2n)



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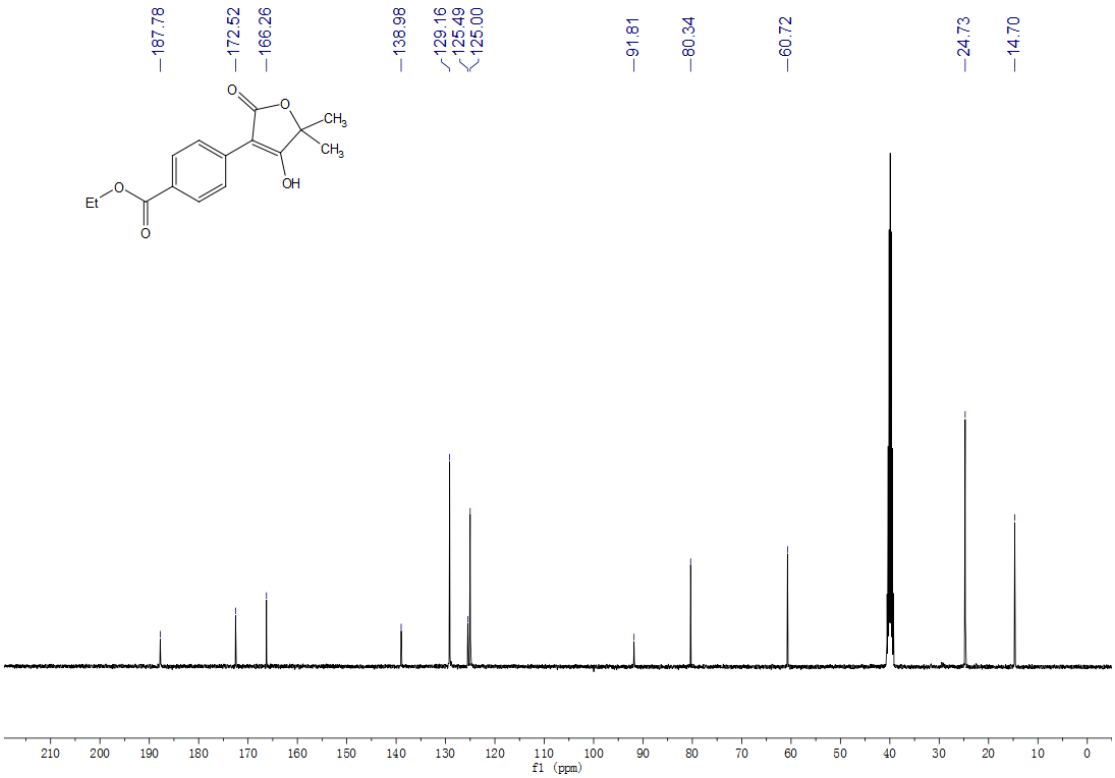
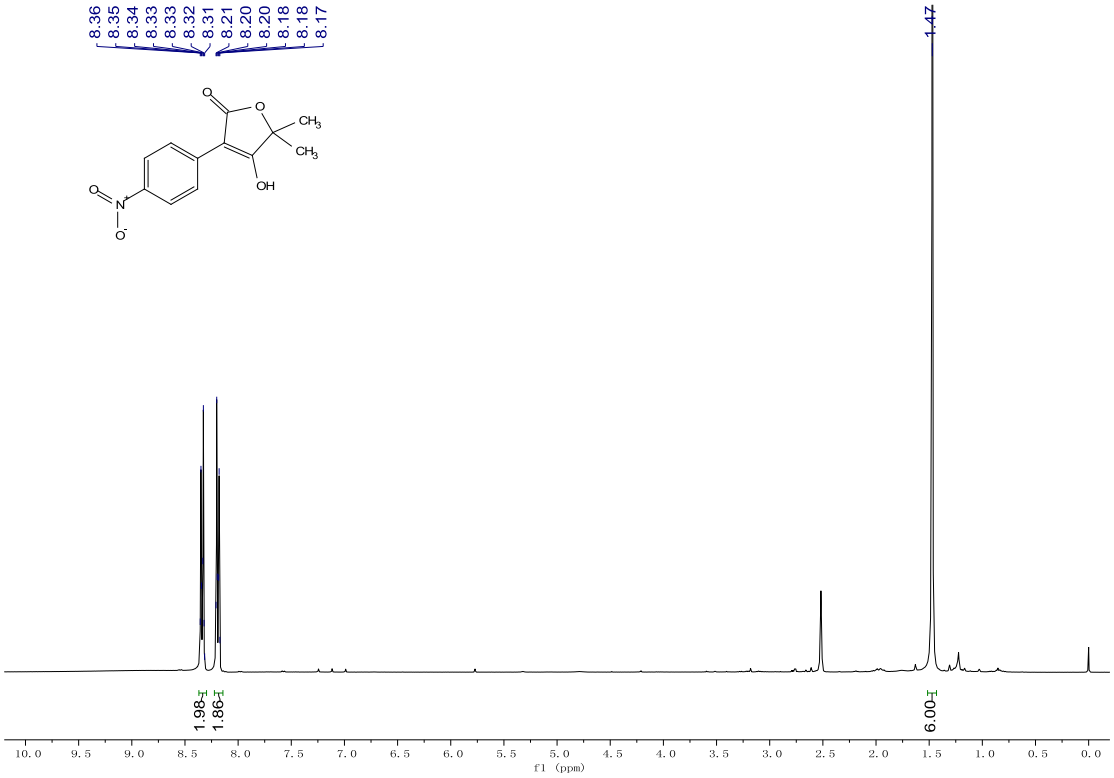
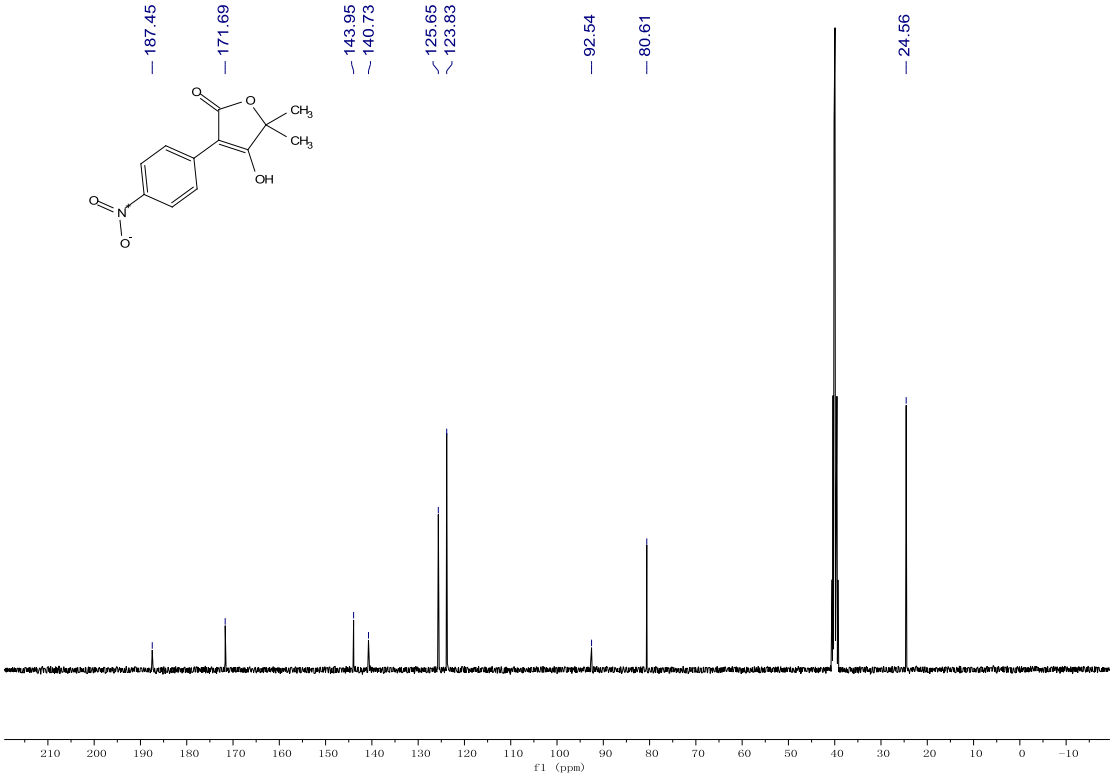
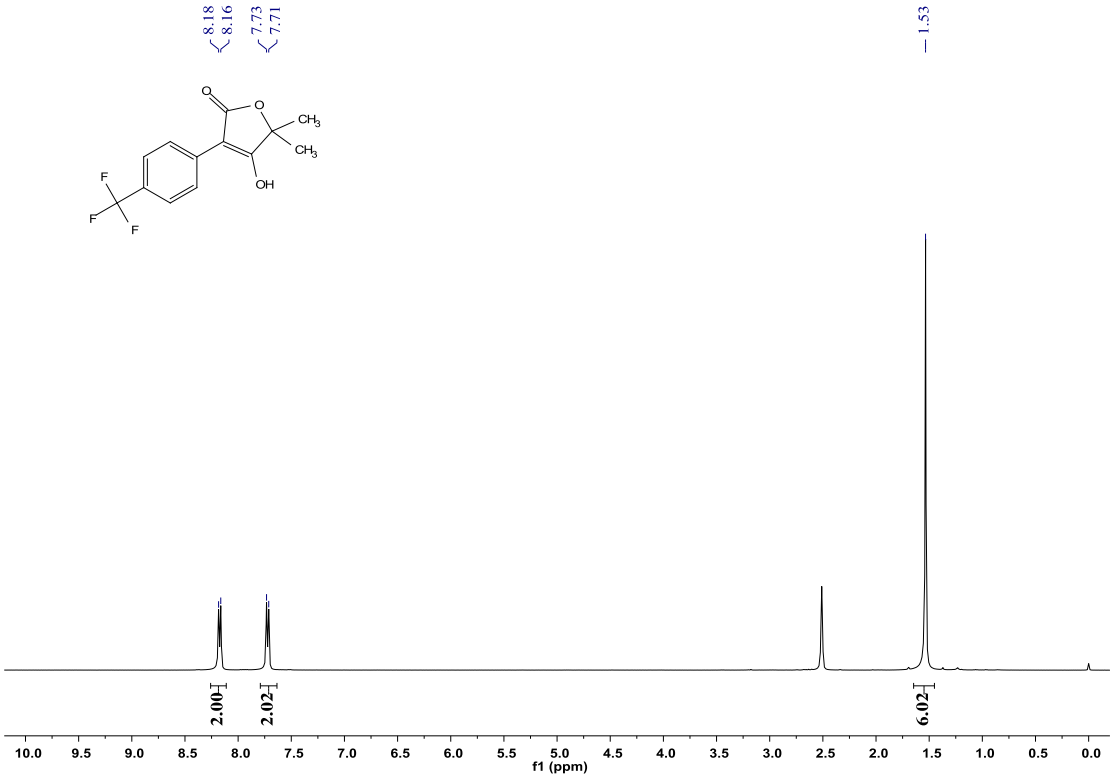


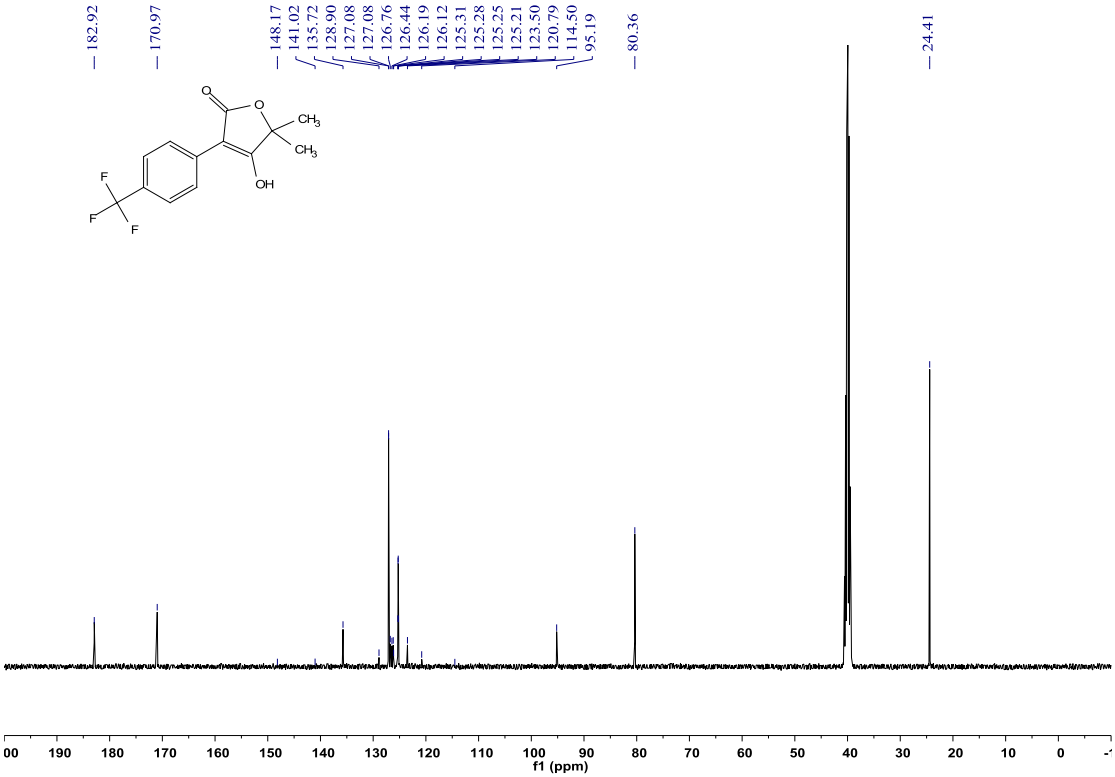
4-hydroxy-5,5-dimethyl-3-(4-nitrophenyl)furan-2(5*H*)-one (2o)

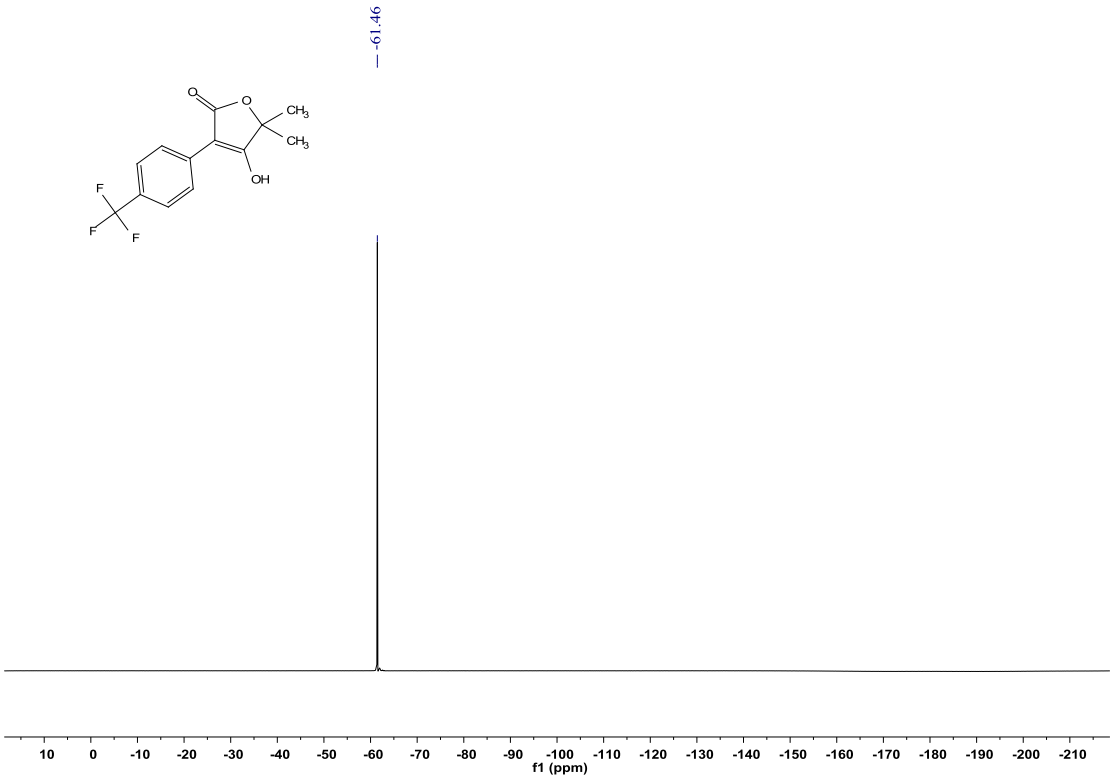




4-hydroxy-5,5-dimethyl-3-(4-(trifluoromethyl)phenyl)furan-2(5*H*)-one (2p)



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O
CH3
CH3
OH
F
F
F
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0
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-60
-70
-80
-90
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-110
-120
-130
-140
-150
-160
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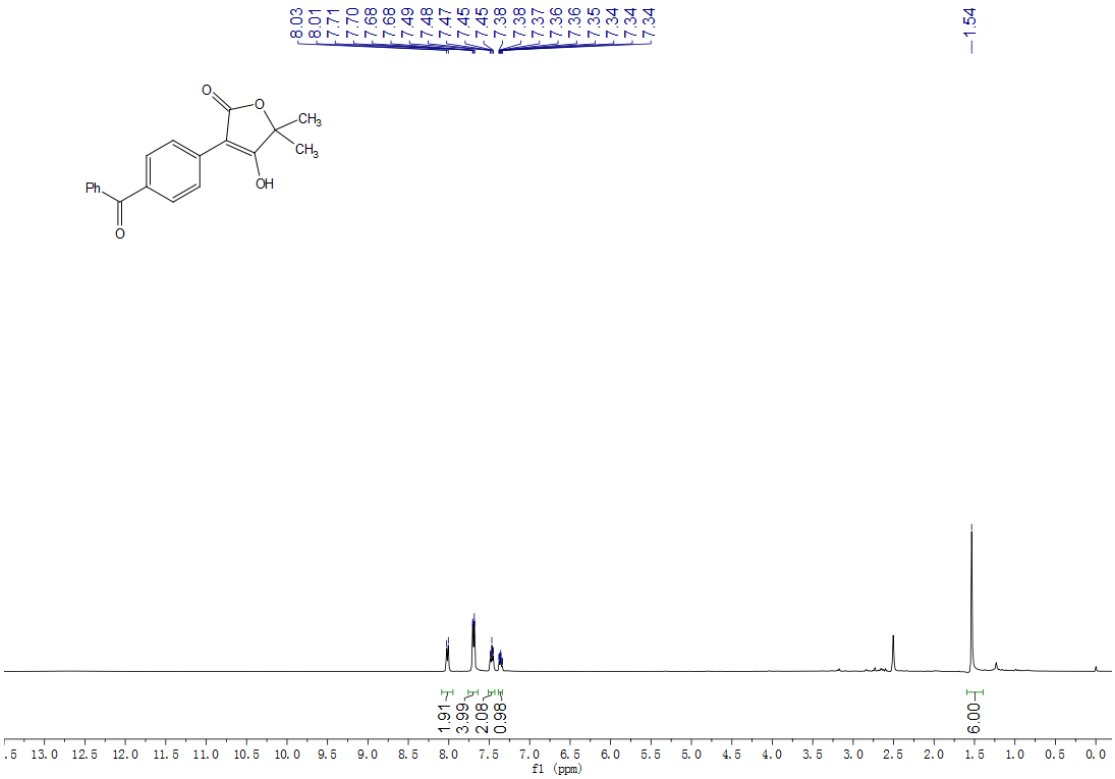
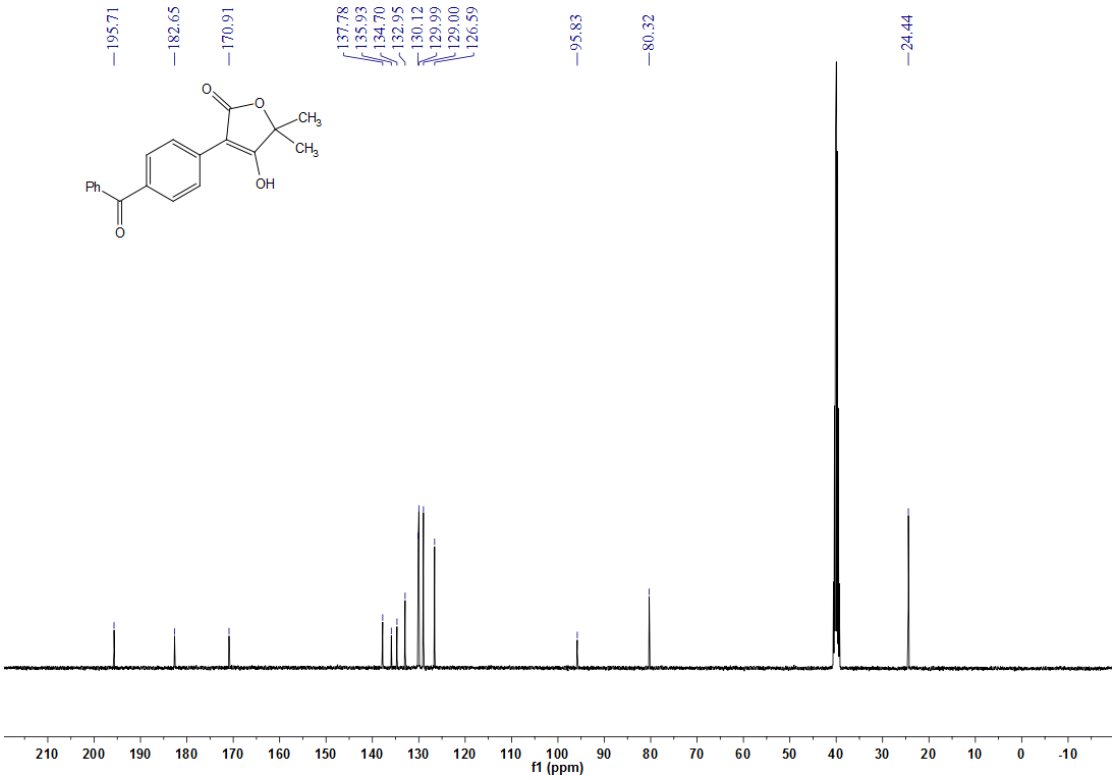
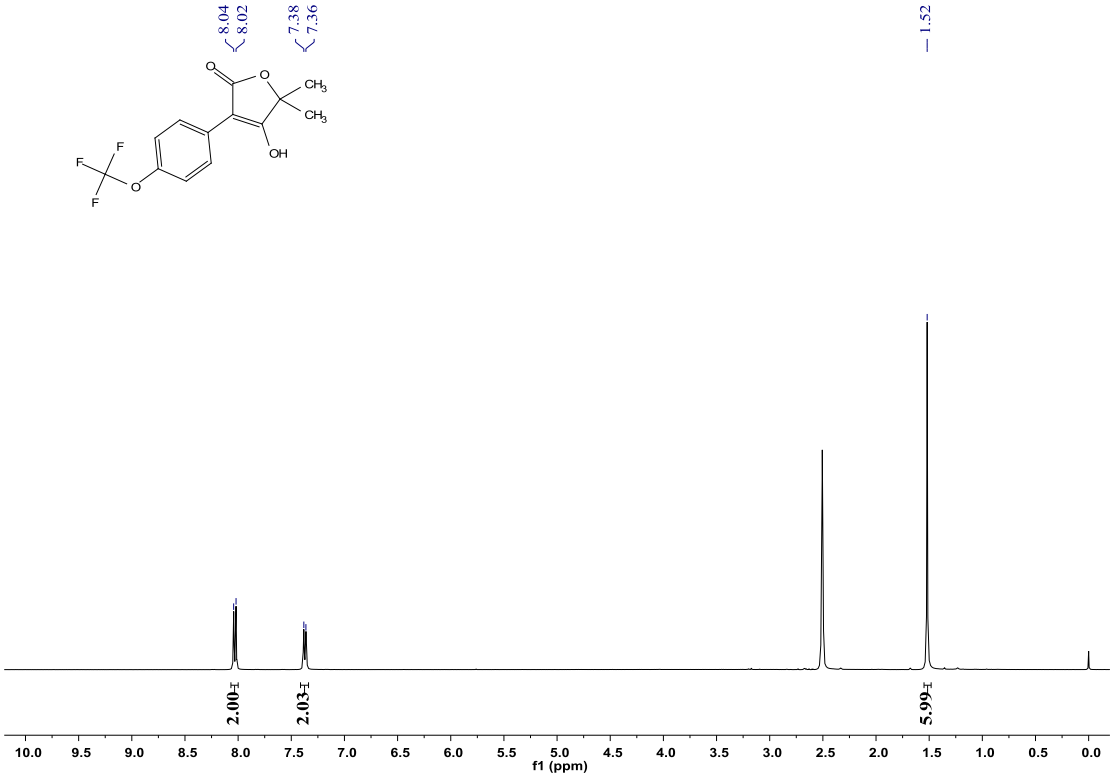
-200
-210
f1 (ppm)

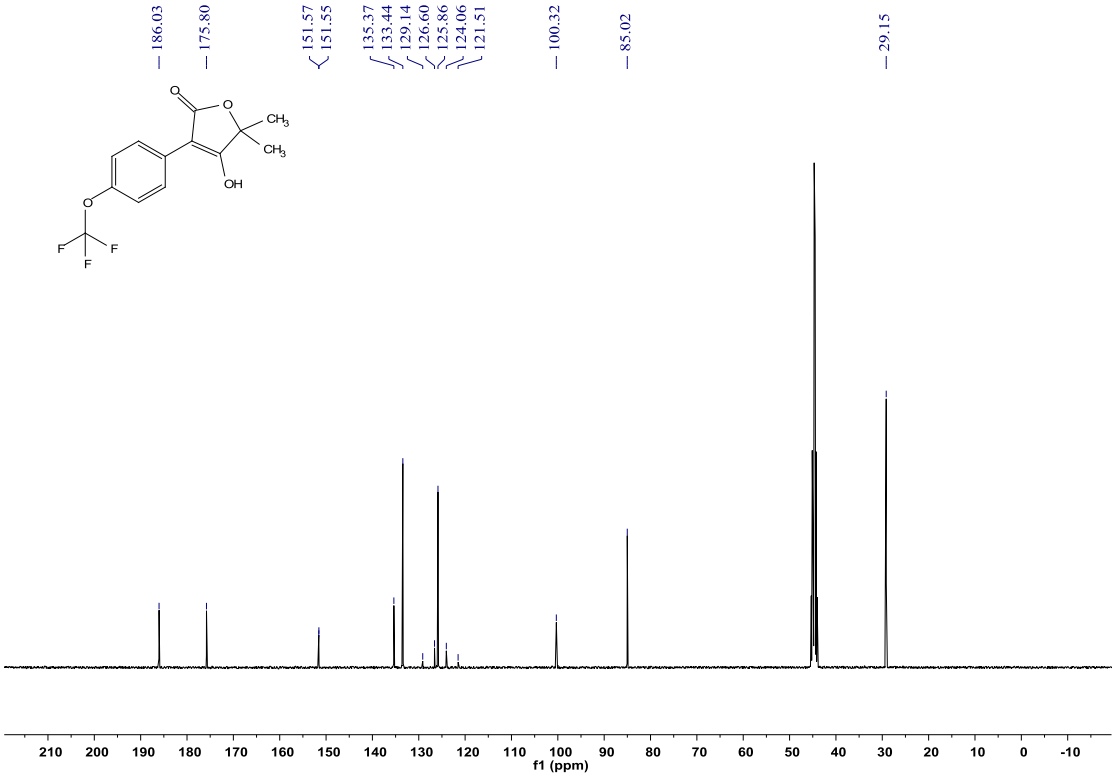
3-(4-benzoylphenyl)-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one (2q)

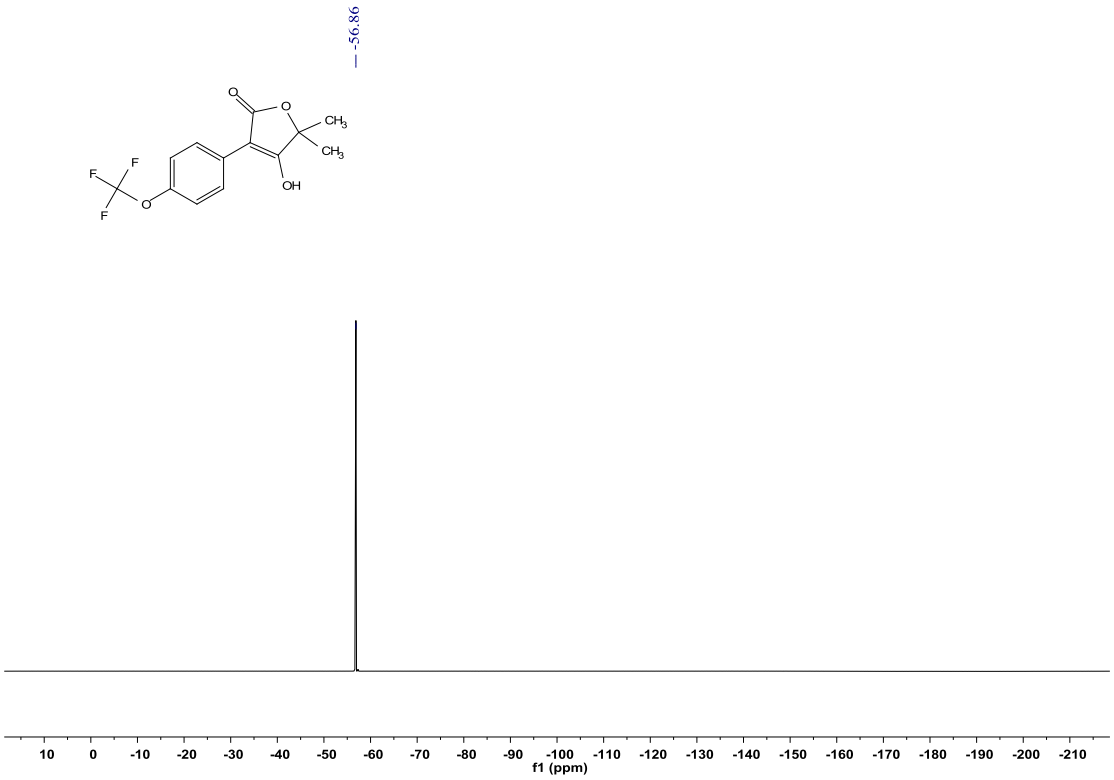




4-hydroxy-5,5-dimethyl-3-(4-(trifluoromethoxy)phenyl)furan-2(5*H*)-one (2r)



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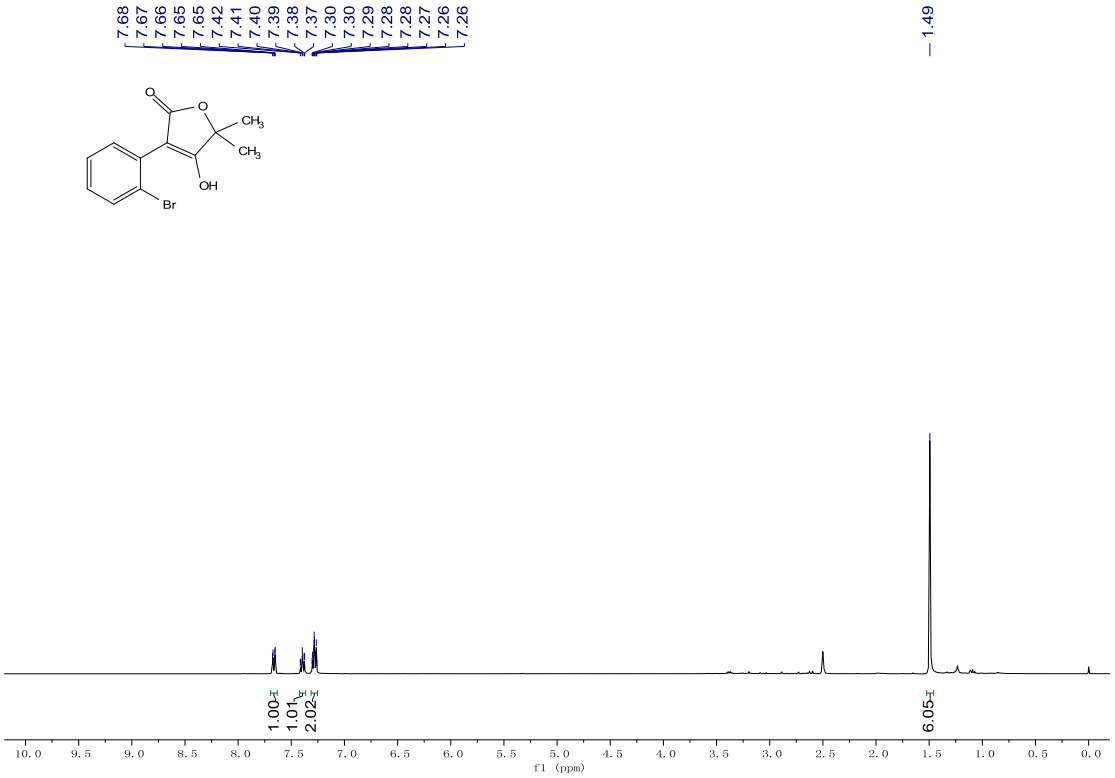
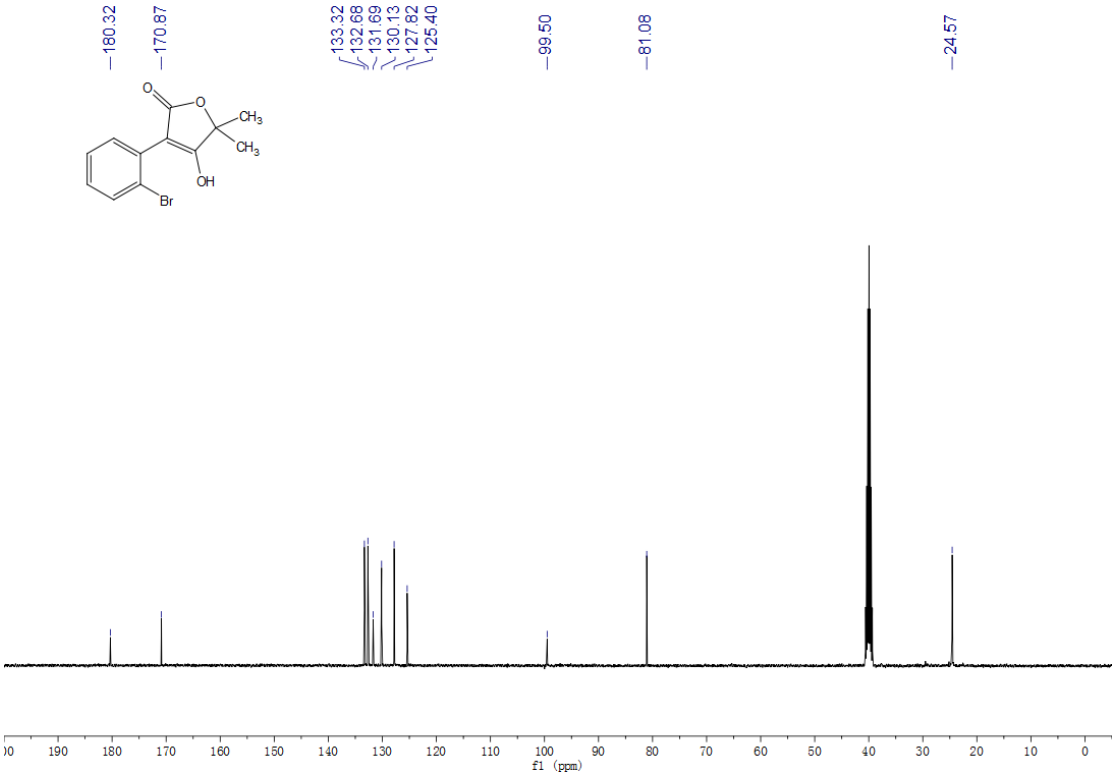
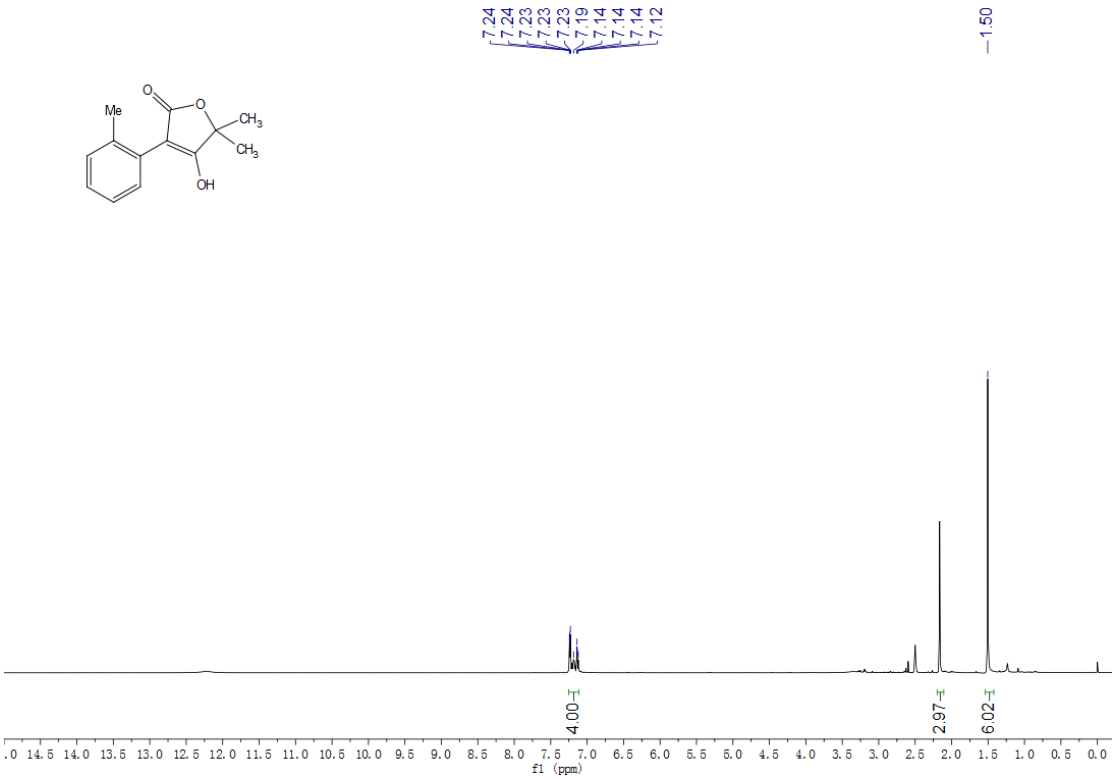
CH3
OH
F
F
F
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

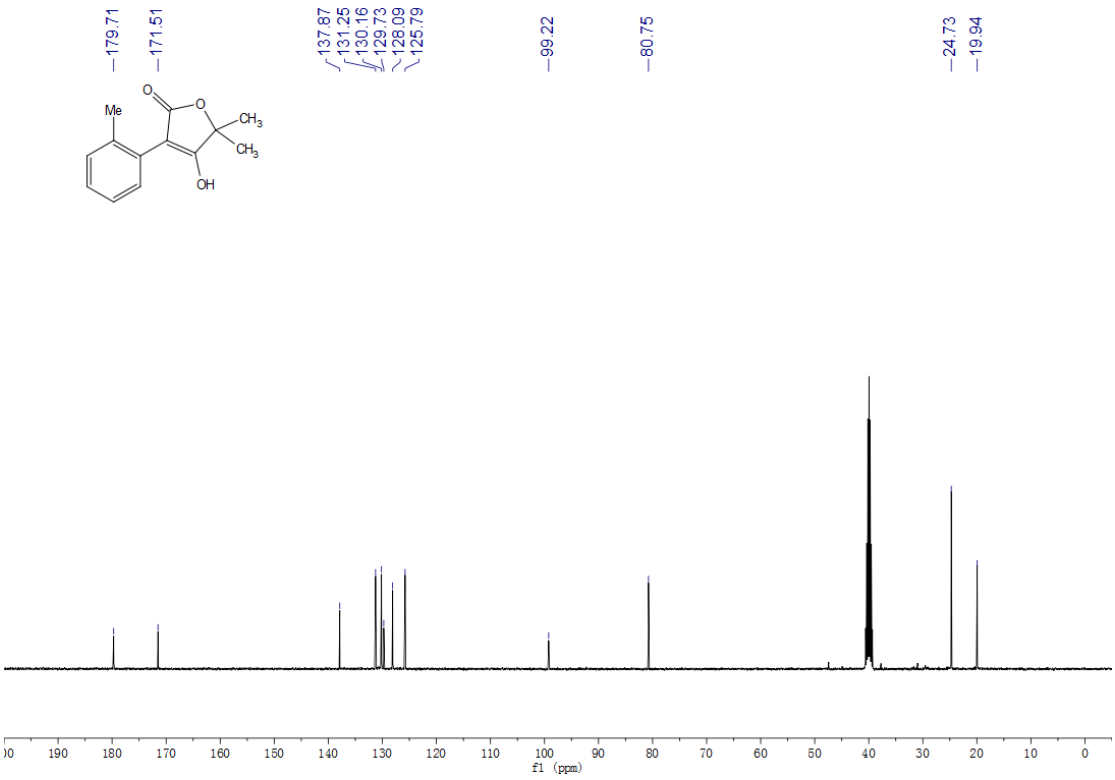
3-(2-bromophenyl)-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one (2s)



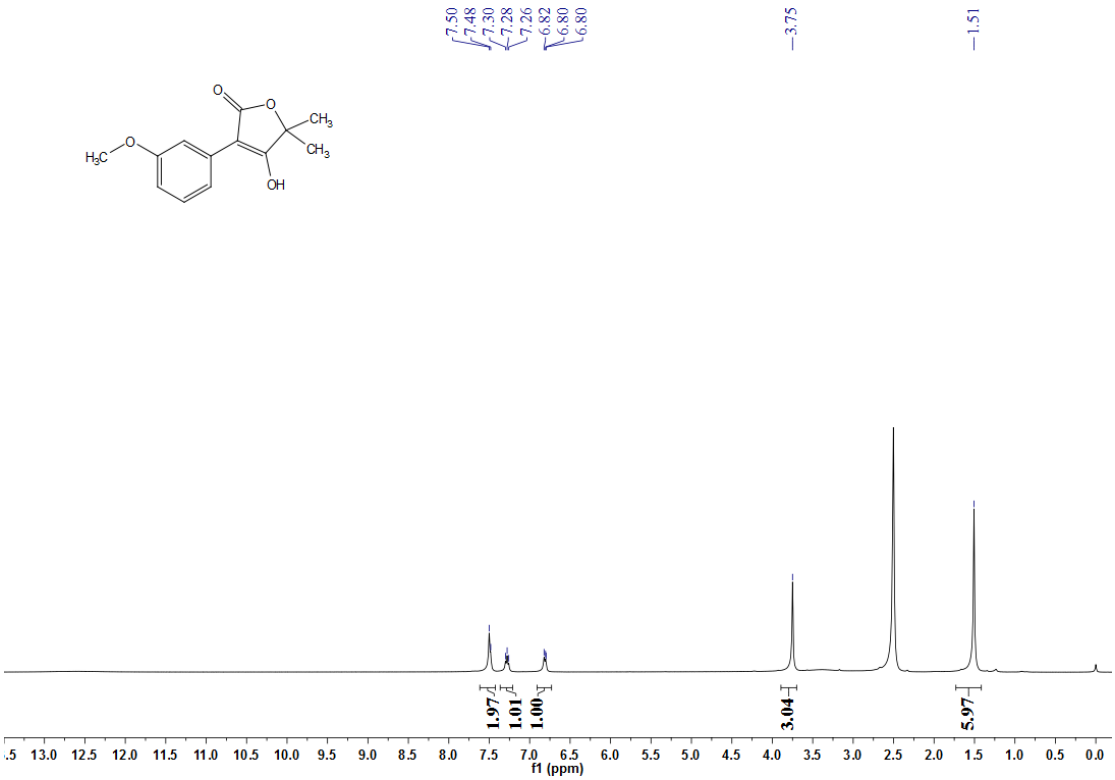


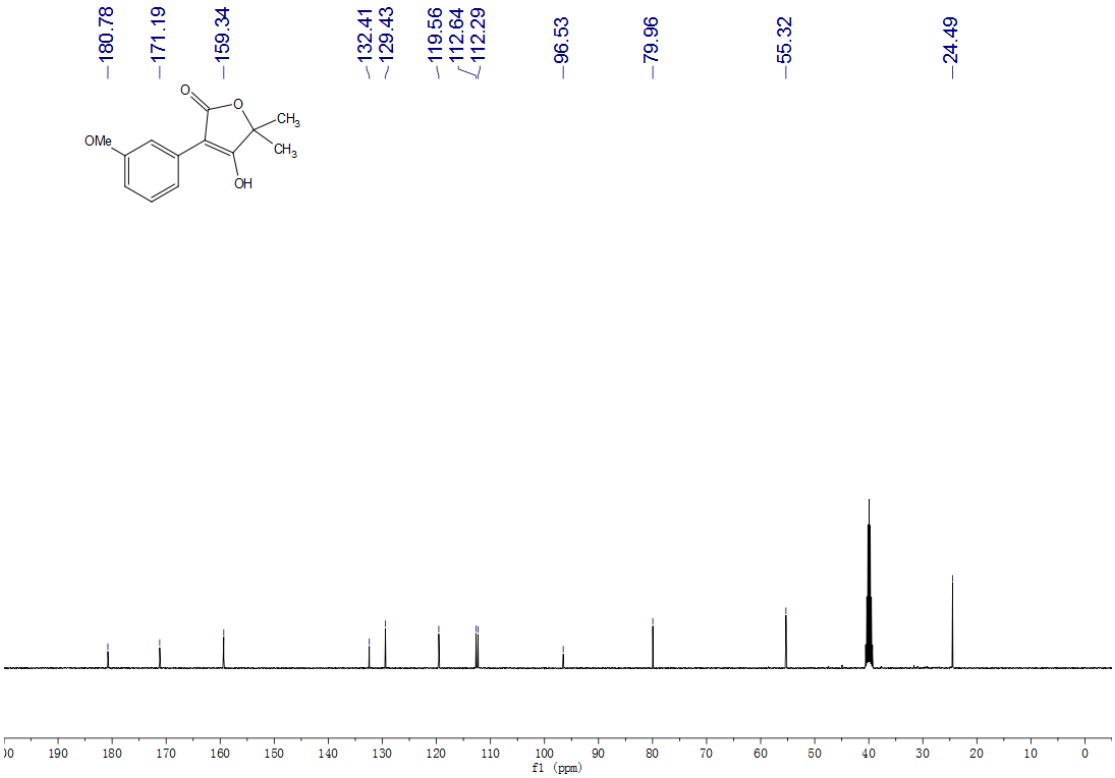
4-hydroxy-5,5-dimethyl-3-(o-tolyl)furan-2(5*H*)-one (2t)



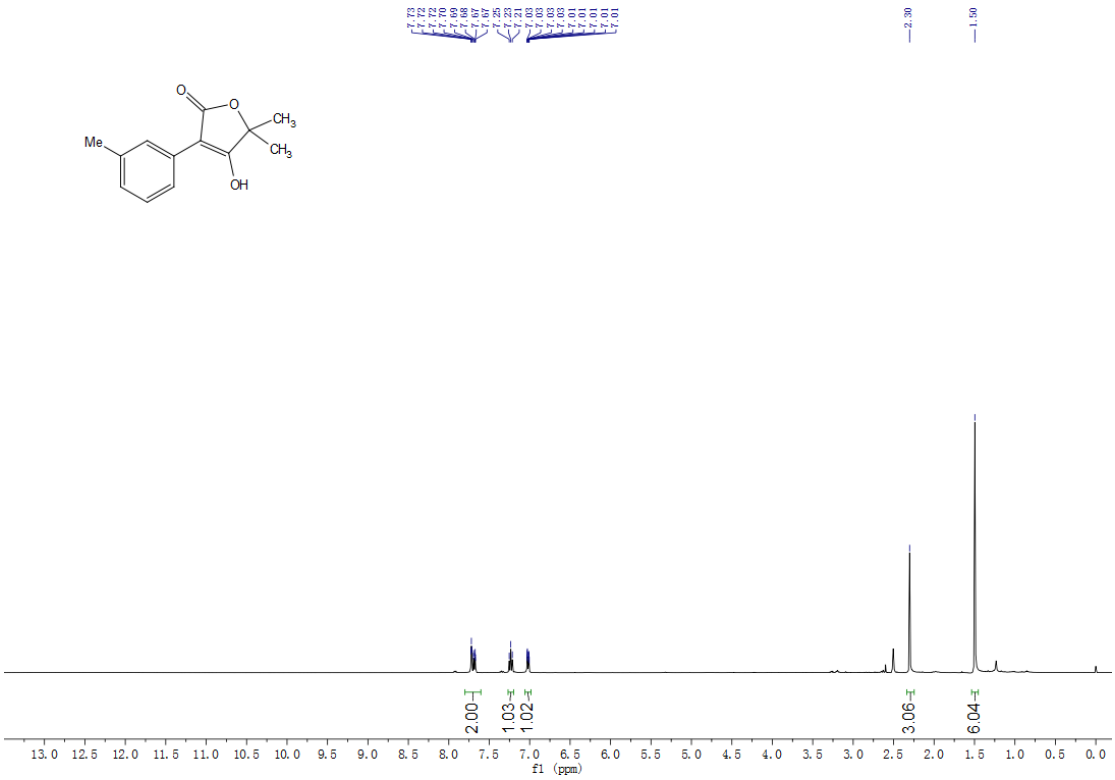


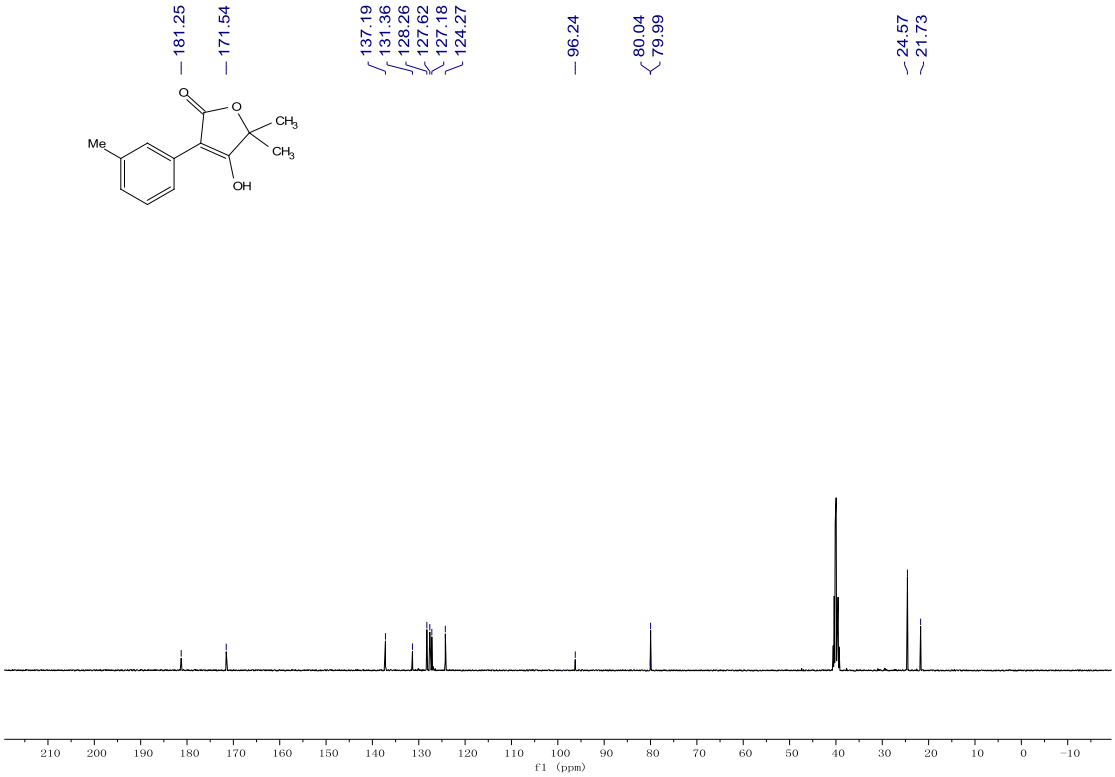
4-hydroxy-3-(3-methoxyphenyl)-5,5-dimethylfuran-2(5*H*)-one (2u)



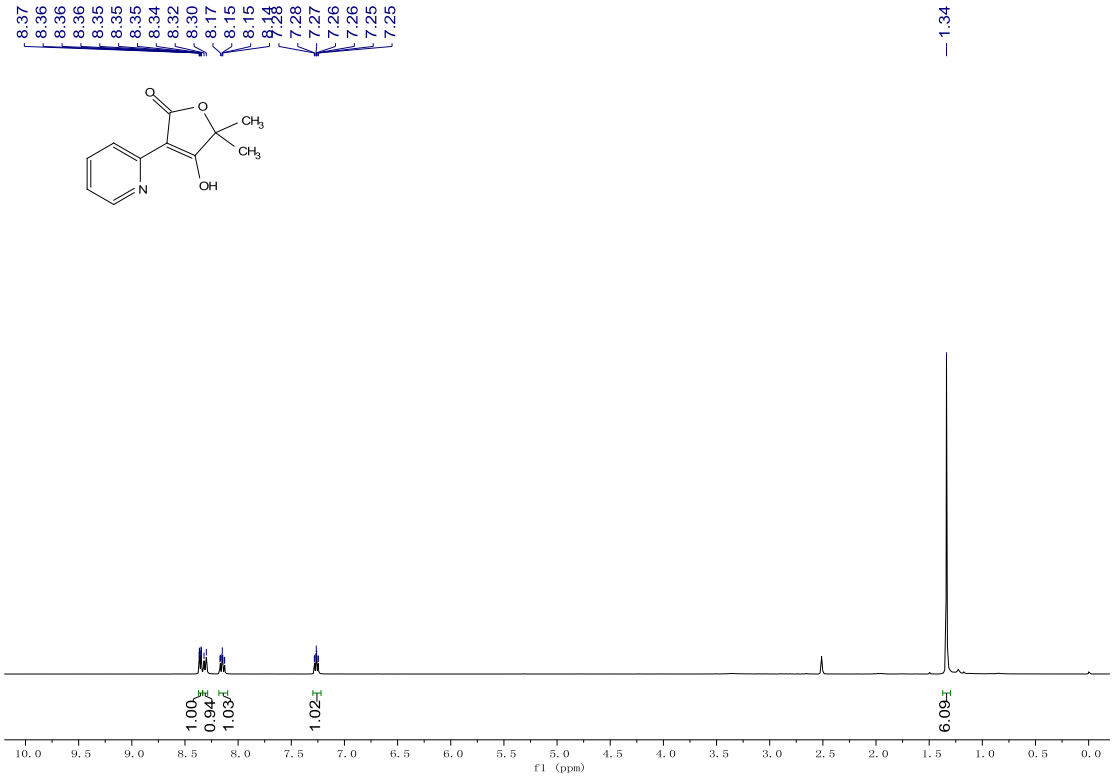


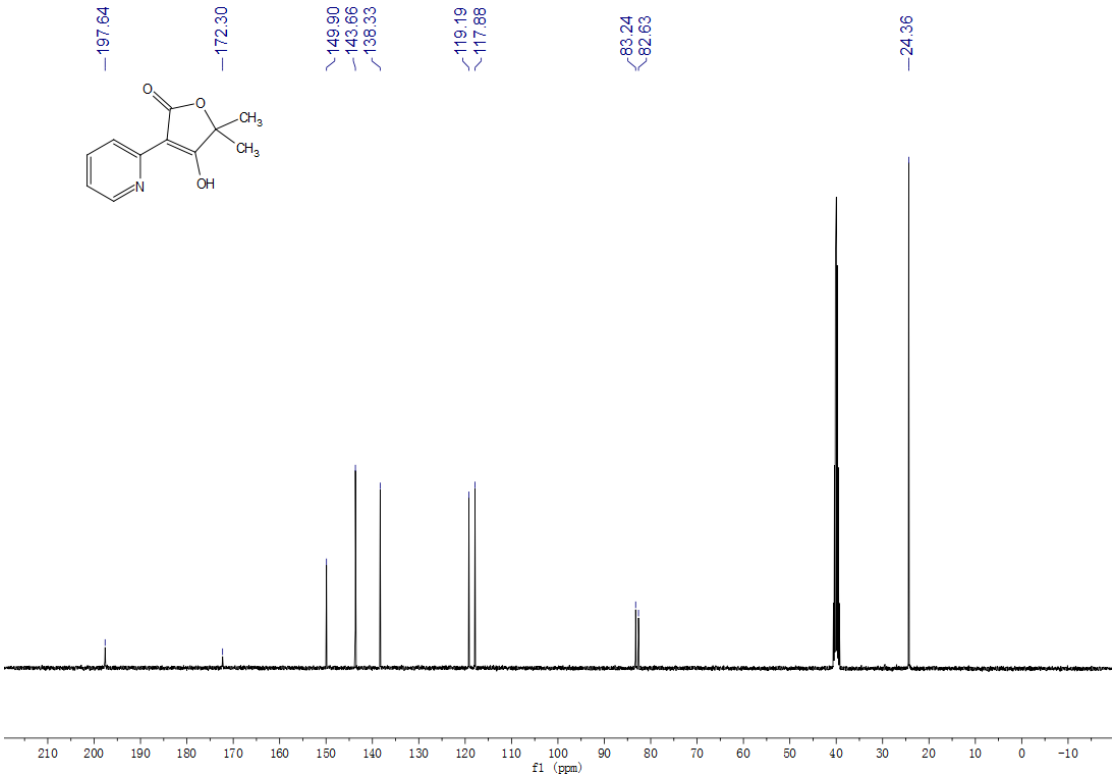
4-hydroxy-5,5-dimethyl-3-(m-tolyl)furan-2(5*H*)-one (2v)



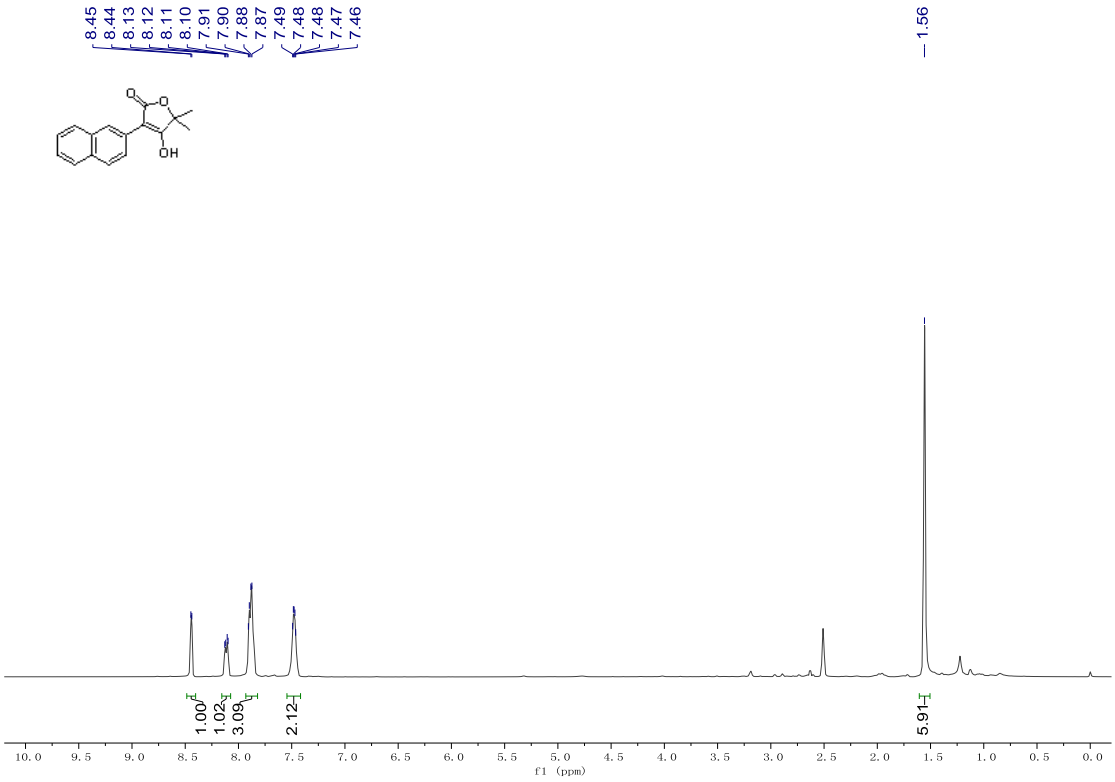


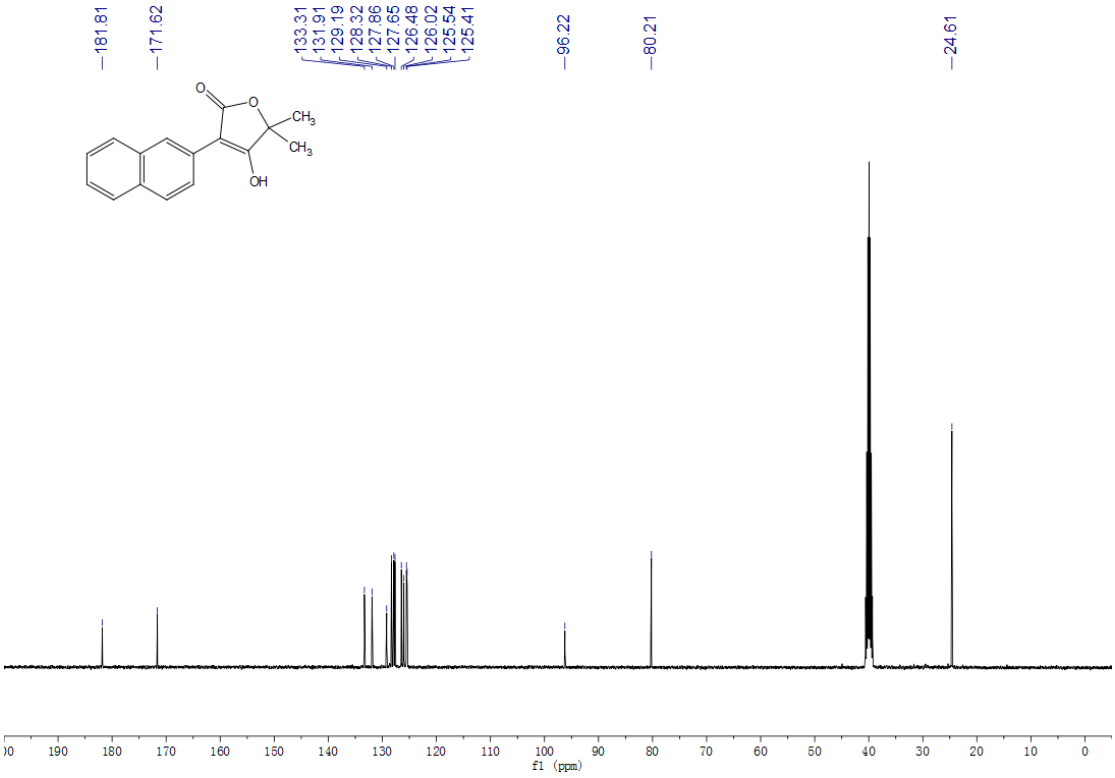
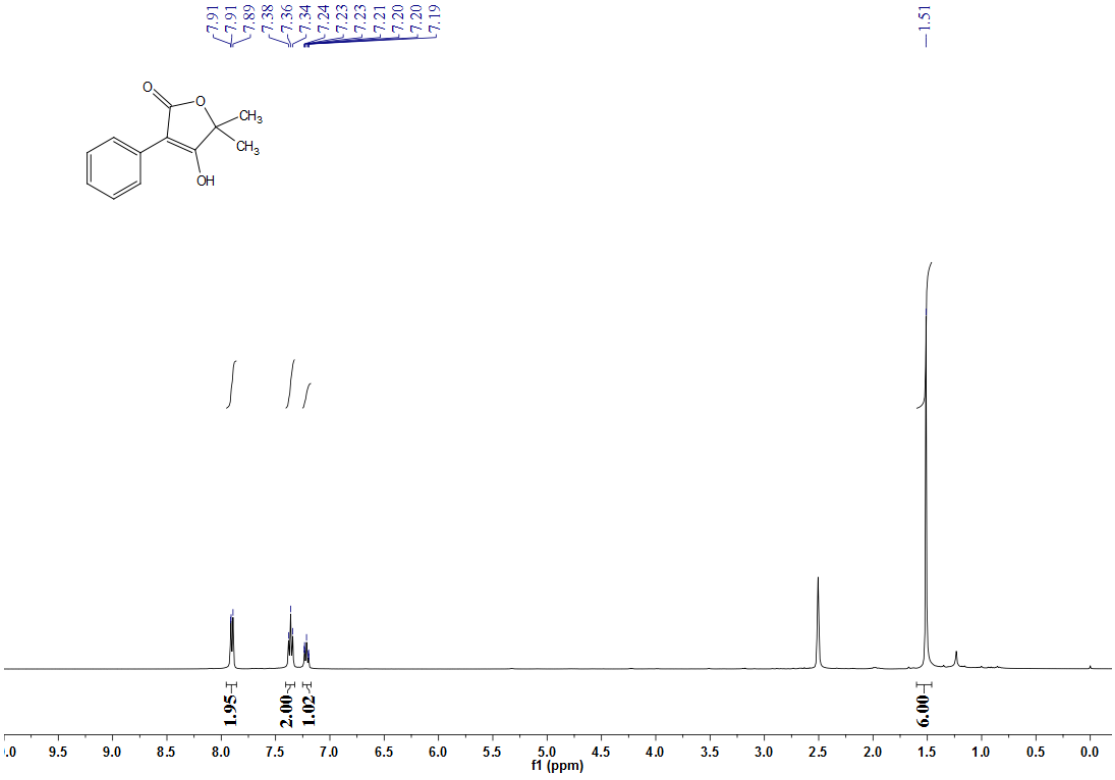
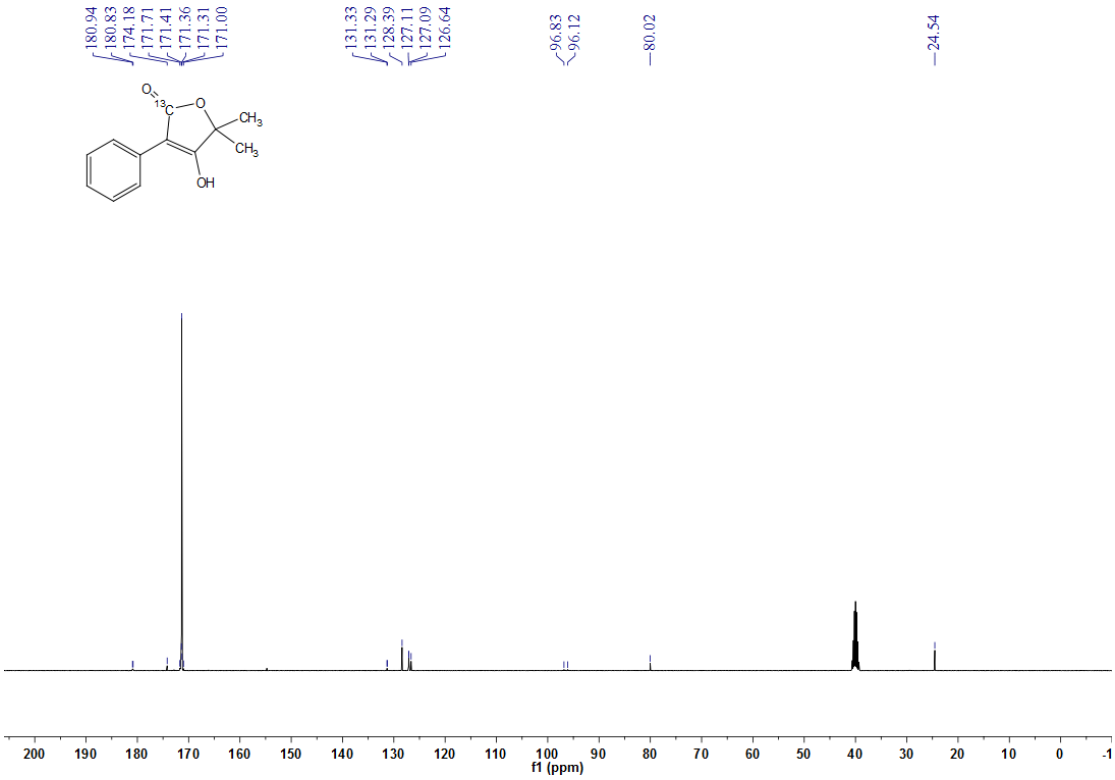
4-hydroxy-5,5-dimethyl-3-(pyridin-2-yl)furan-2(5*H*)-one (2w)





4-hydroxy-5,5-dimethyl-3-(naphthalen-2-yl)furan-2(5*H*)-one (2x)





4-hydroxy-5,5-dimethyl-3-phenylfuran-2(5*H*)-one-2-^{13}C (2h')