Supporting Information

Hydroxyl effect on antioxidant properties of 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one to Scavenge Free Radicals

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Experimental procedures and analytical data

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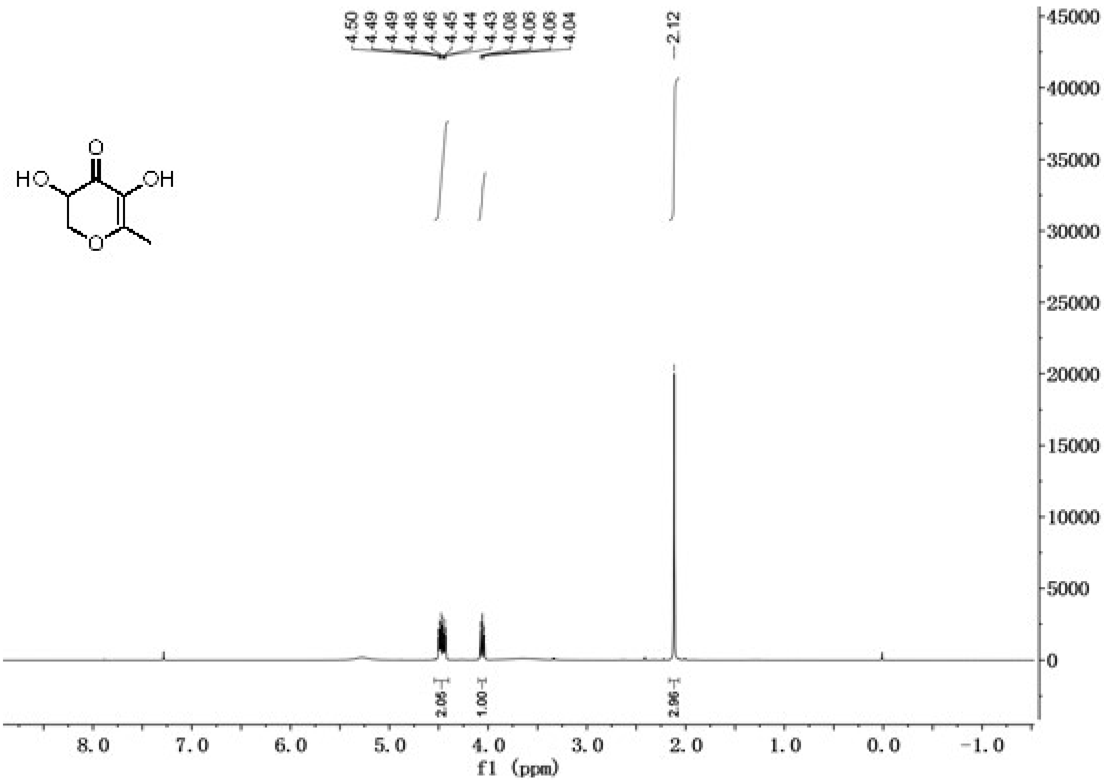
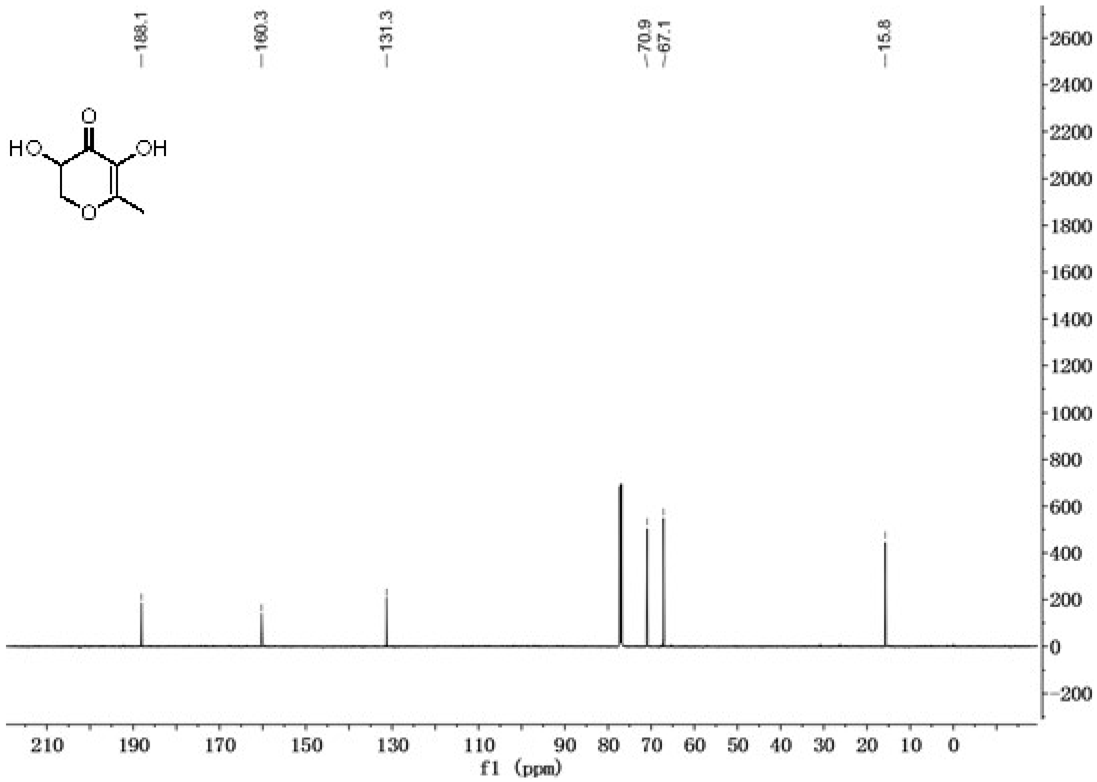
1. General considerations

All the manipulations of air- and/or moisture-sensitive compounds were carried out under nitrogen atmosphere using the standard Schlenk techniques. The solvents were dried and distilled prior to use by the literature methods. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker DRX-600 spectrometer and all chemical shift values refer to δ_{TMS} = 0.00 ppm, $CDCl_3$ (δ (^{1}H), 7.26 ppm; δ (^{13}C), 77.16 ppm). TLC analysis was performed by using glass-backed plates coated with 0.2 mm silica gel. Flash column chromatography was performed on silica gel (200-300 meshes). All chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

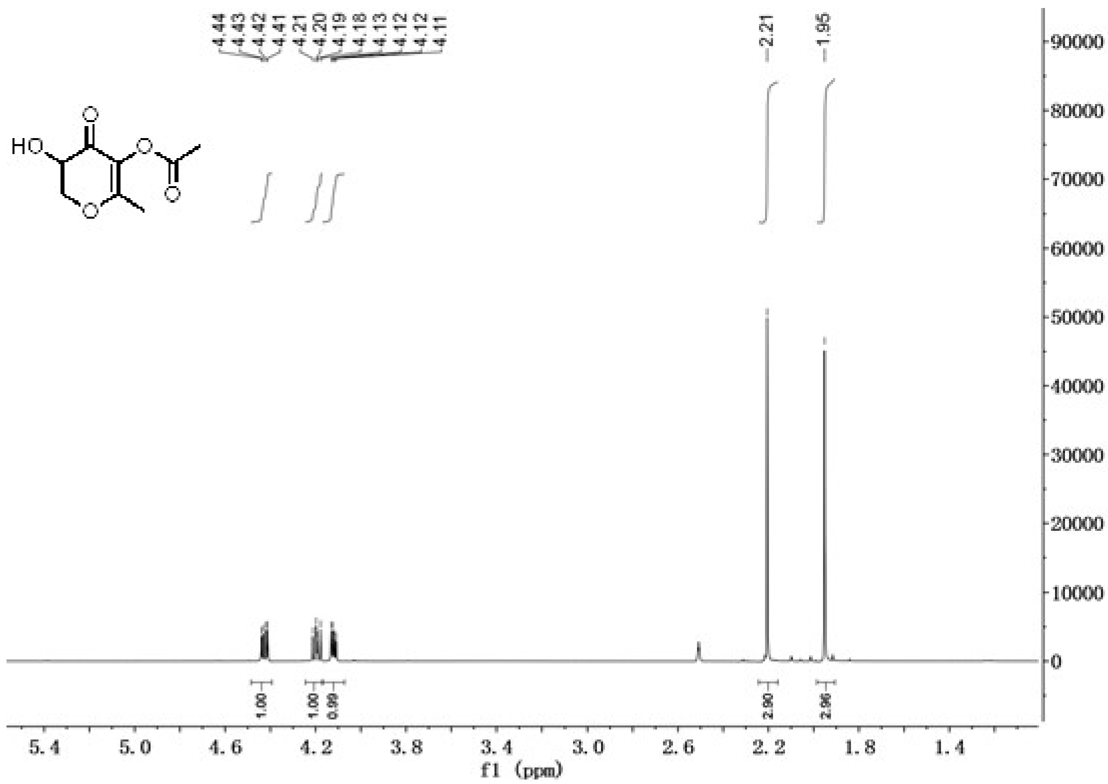
2. Copies of NMR spectra

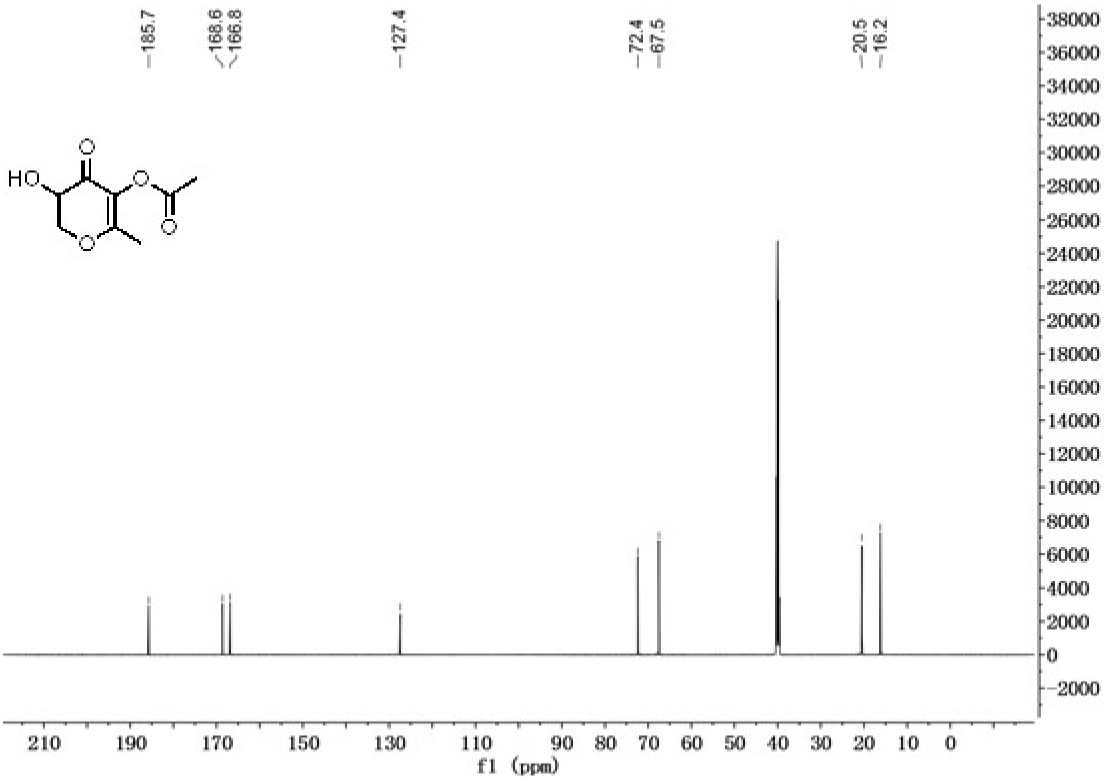
3,5-dihydroxy-6-methyl-2H-pyran-4(3H)-one (1)



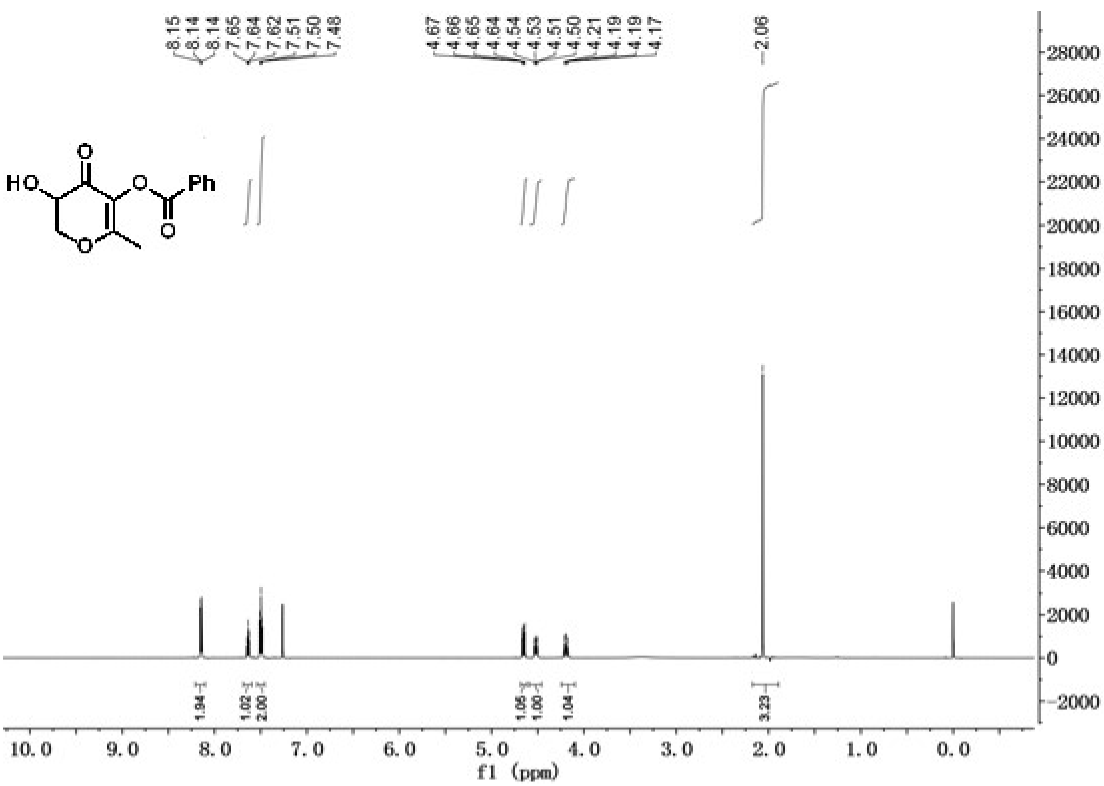


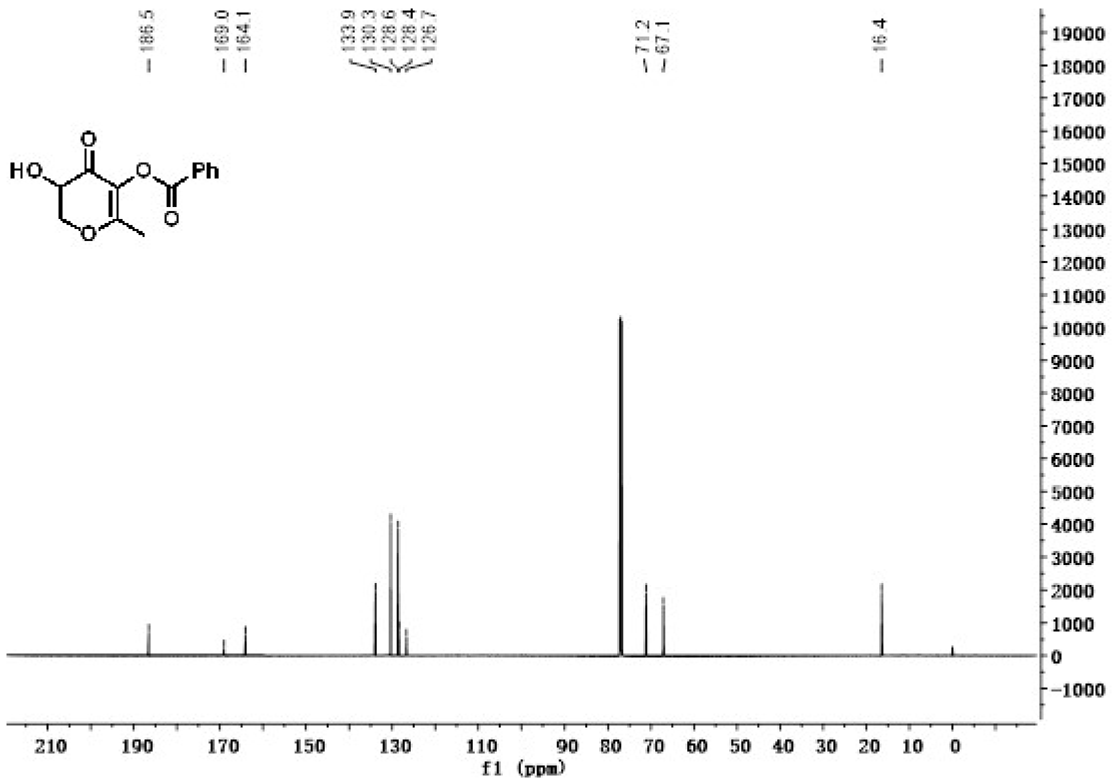
3-hydroxy-6-methyl-4-oxo-3,4-dihydro-2H-pyran-5-yl acetate (2a)



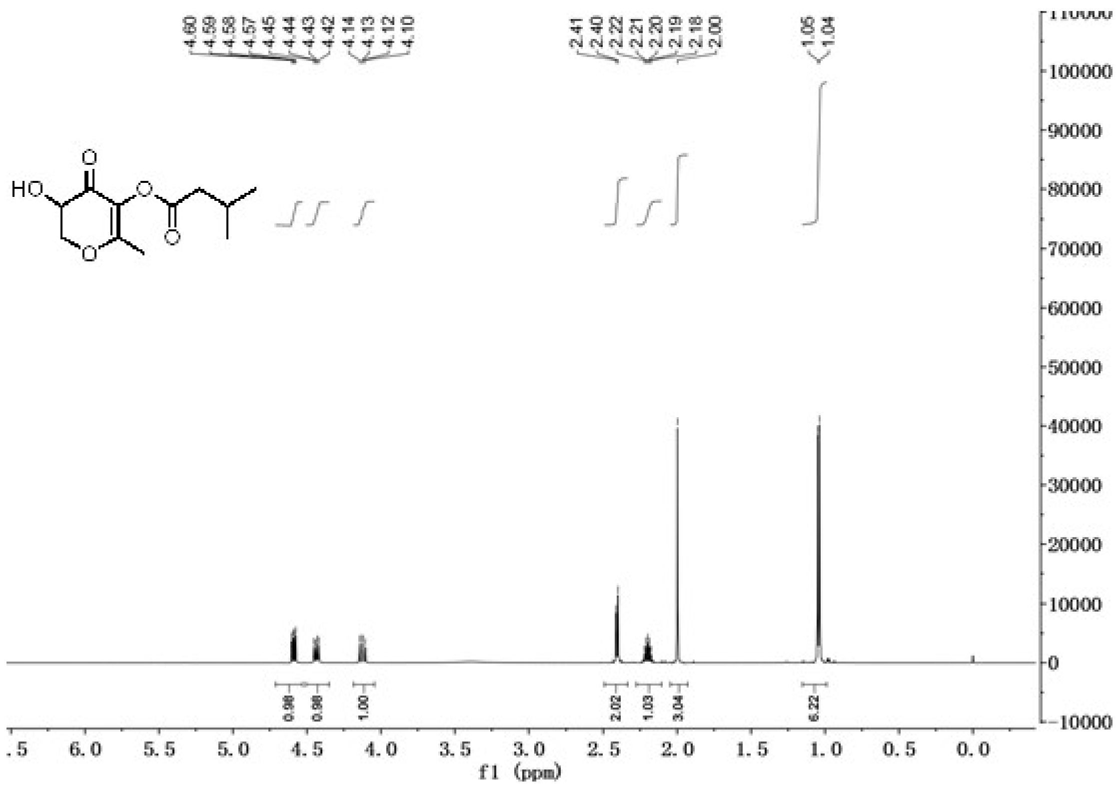


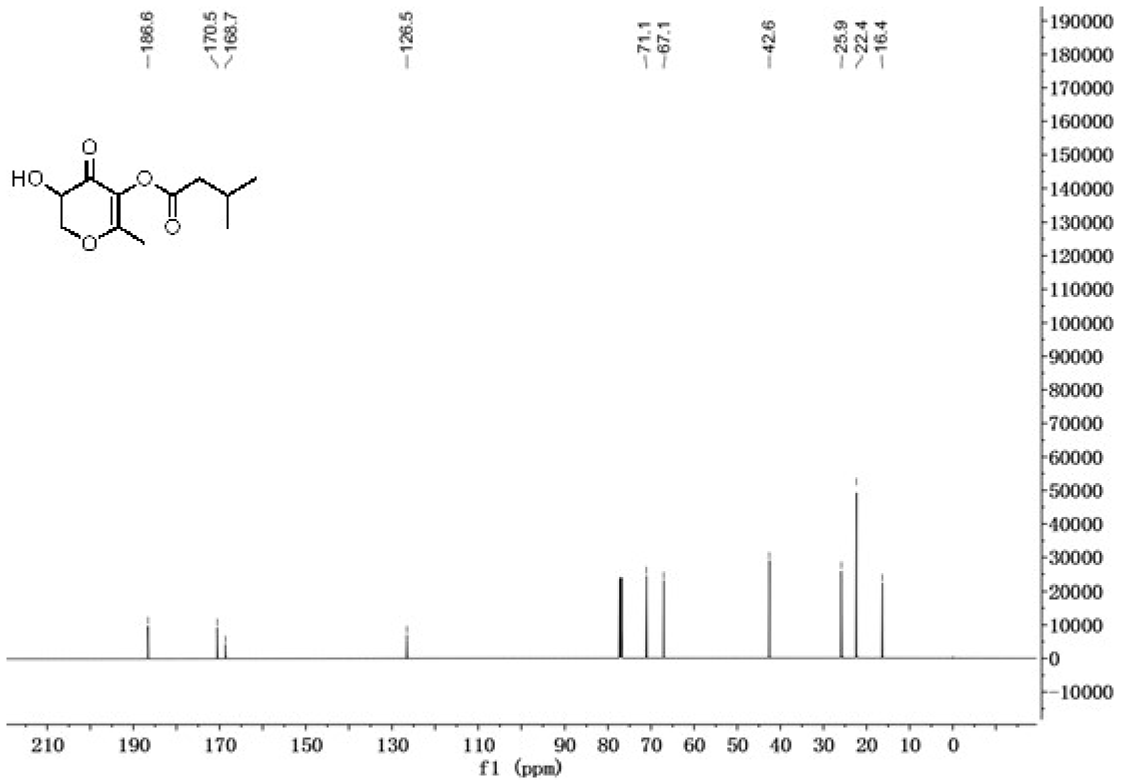
3-hydroxy-6-methyl-4-oxo-3,4-dihydro-2H-pyran-5-yl benzoate (2b)



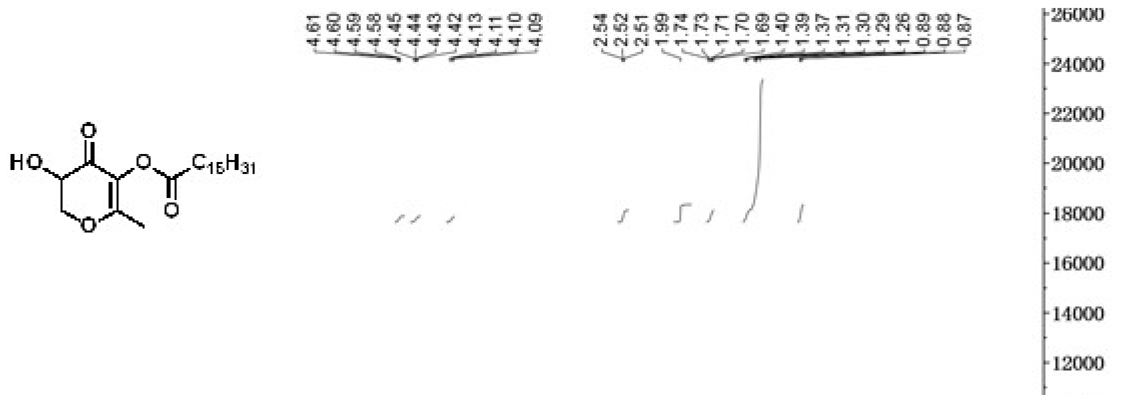


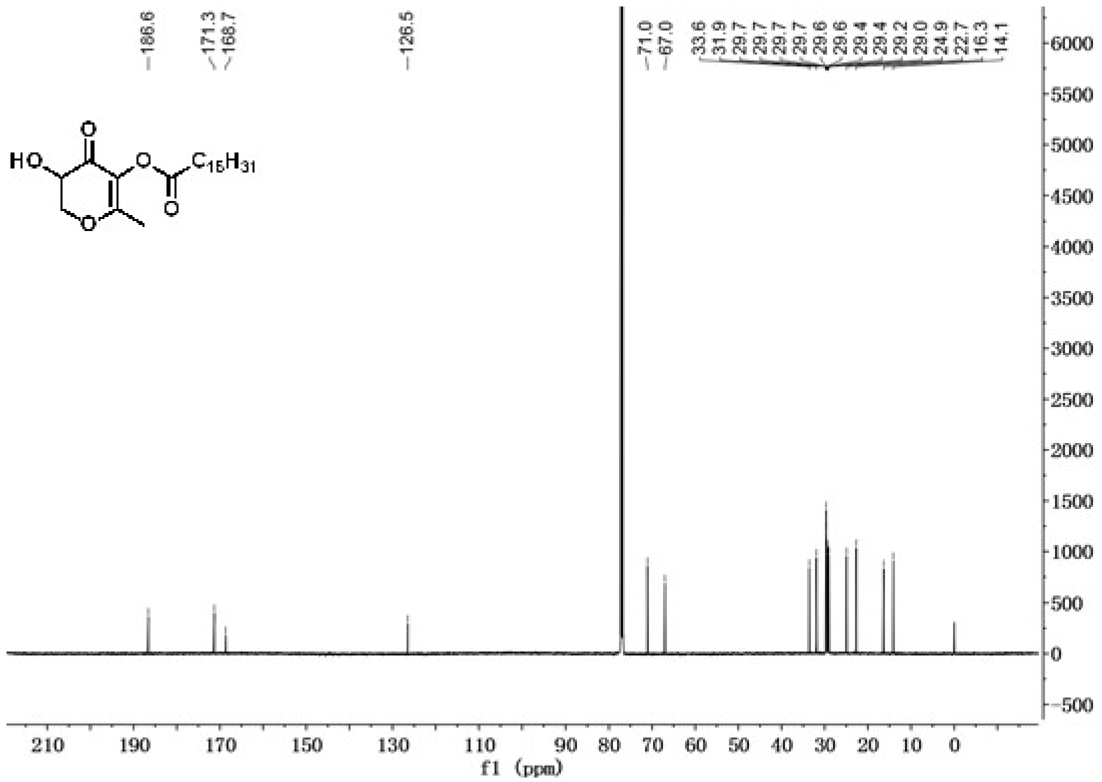
3-hydroxy-6-methyl-4-oxo-3,4-dihydro-2H-pyran-5-yl 3-methylbutanoate (2c)



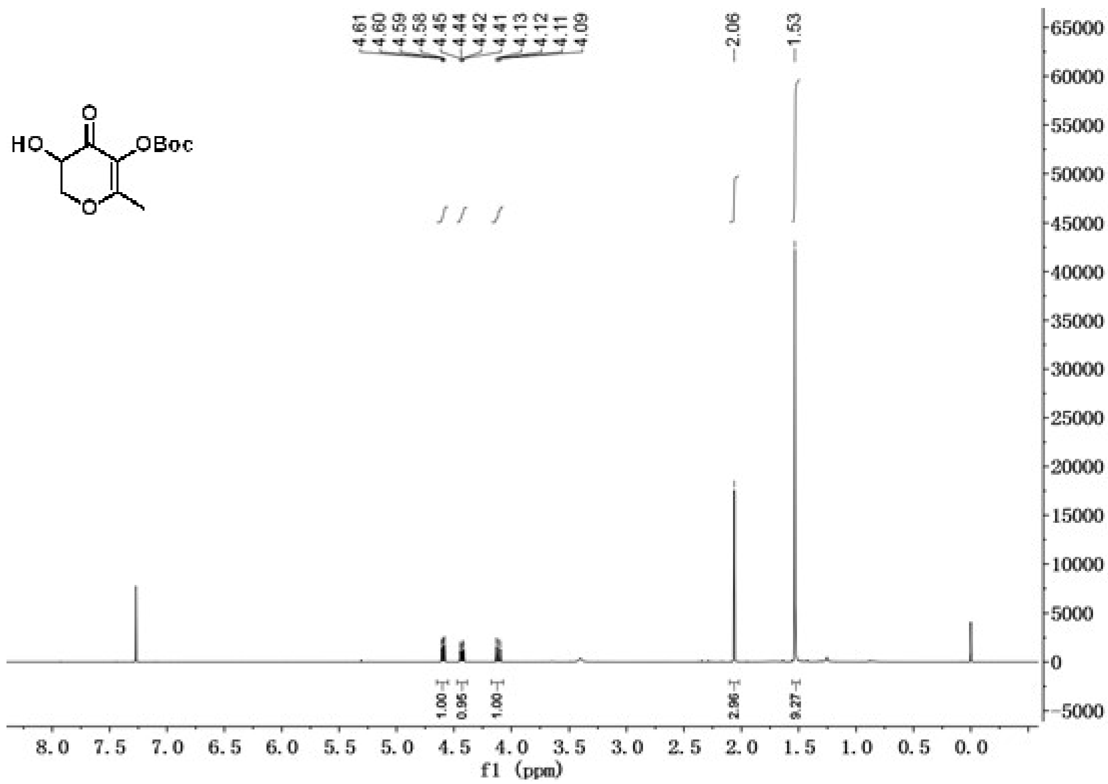


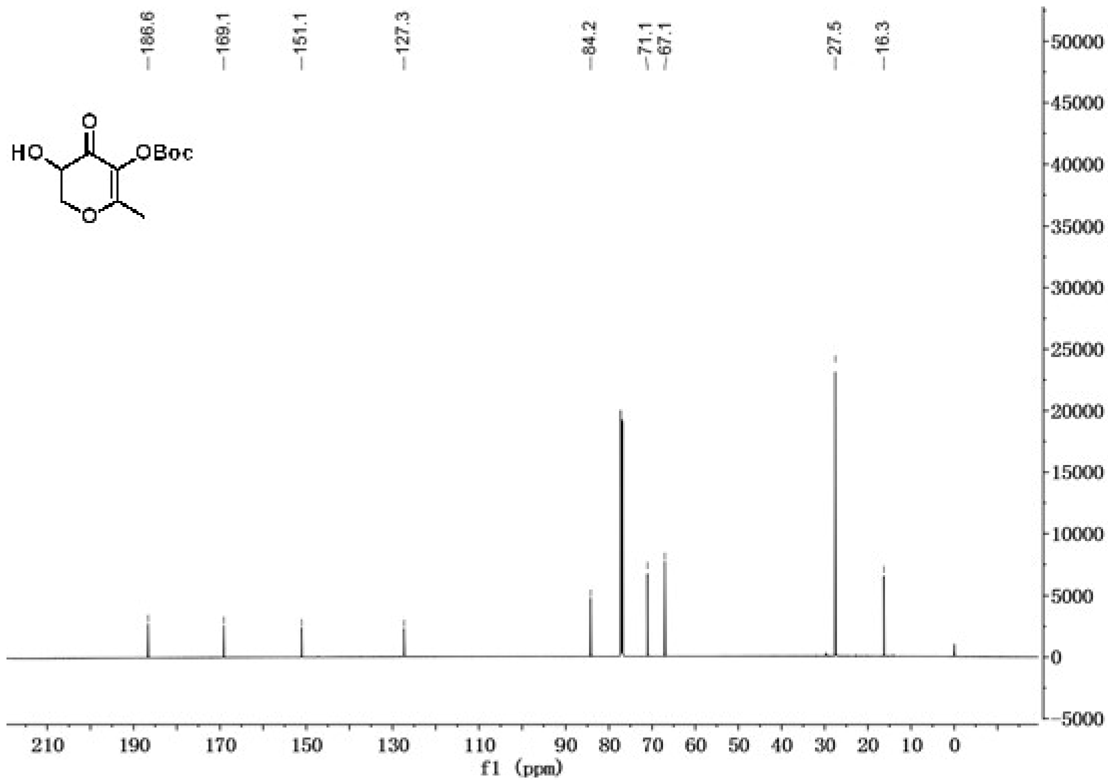
3-hydroxy-6-methyl-4-oxo-3,4-dihydro-2H-pyran-5-yl palmitate (2d)



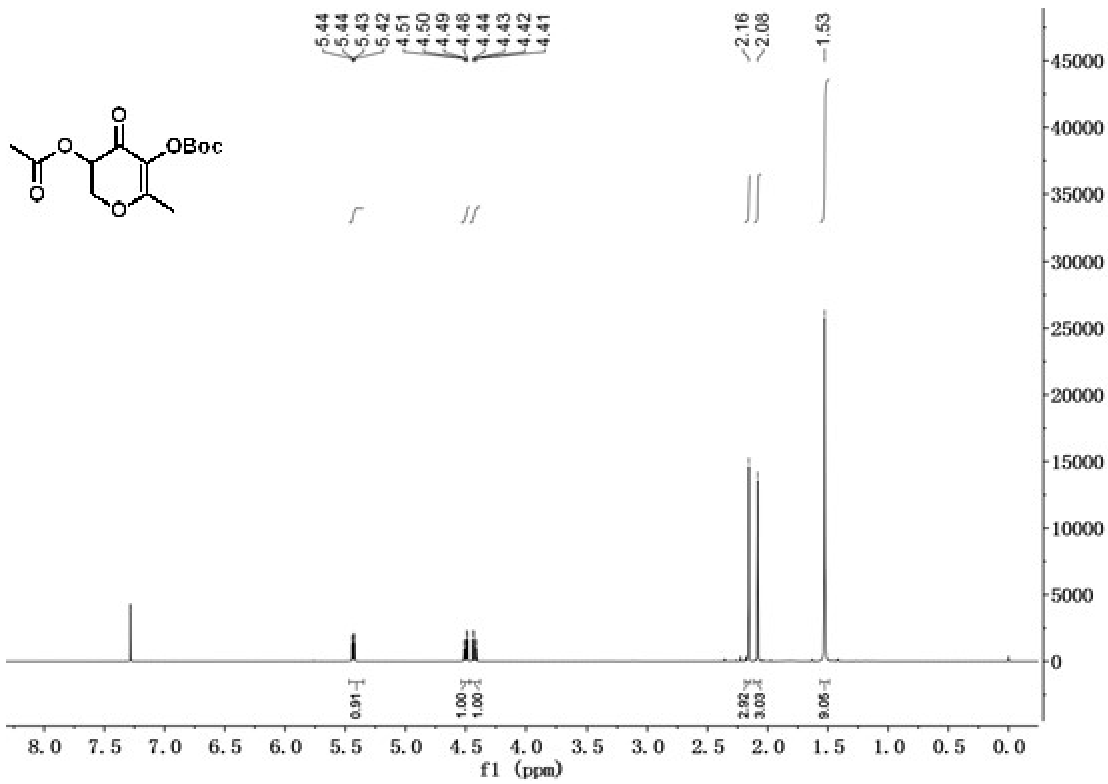


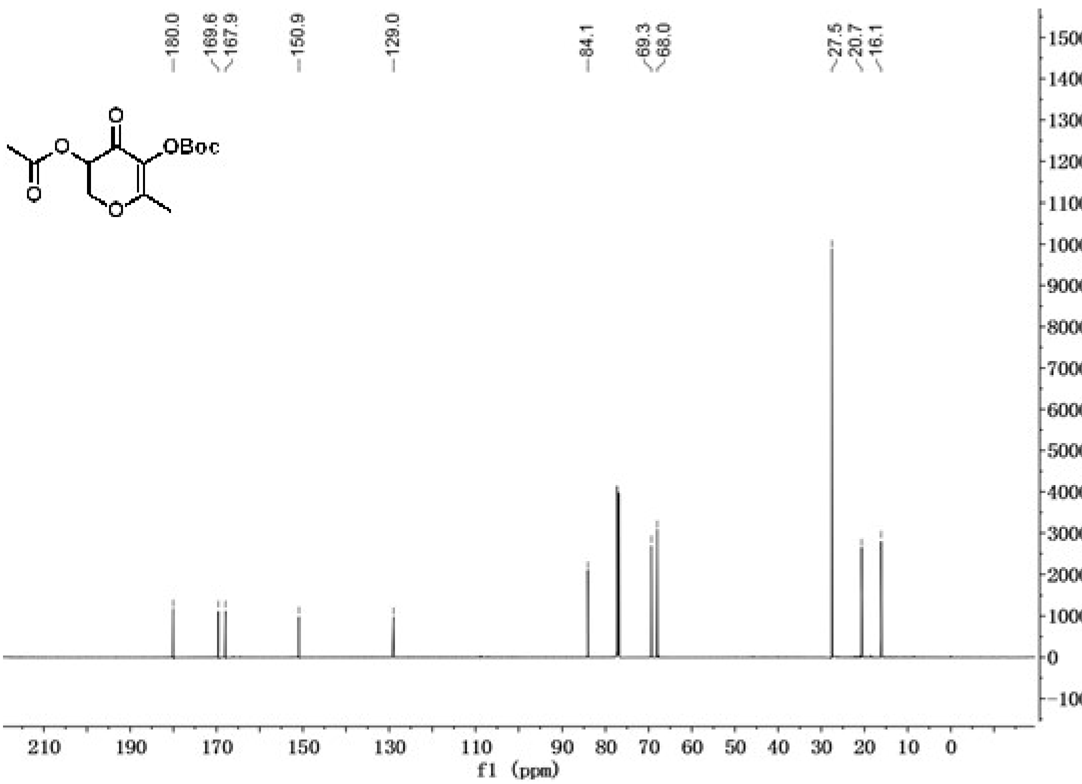
tert-butyl (3-hydroxy-6-methyl-4-oxo-3,4-dihydro-2H-pyran-5-yl) carbonate (3)



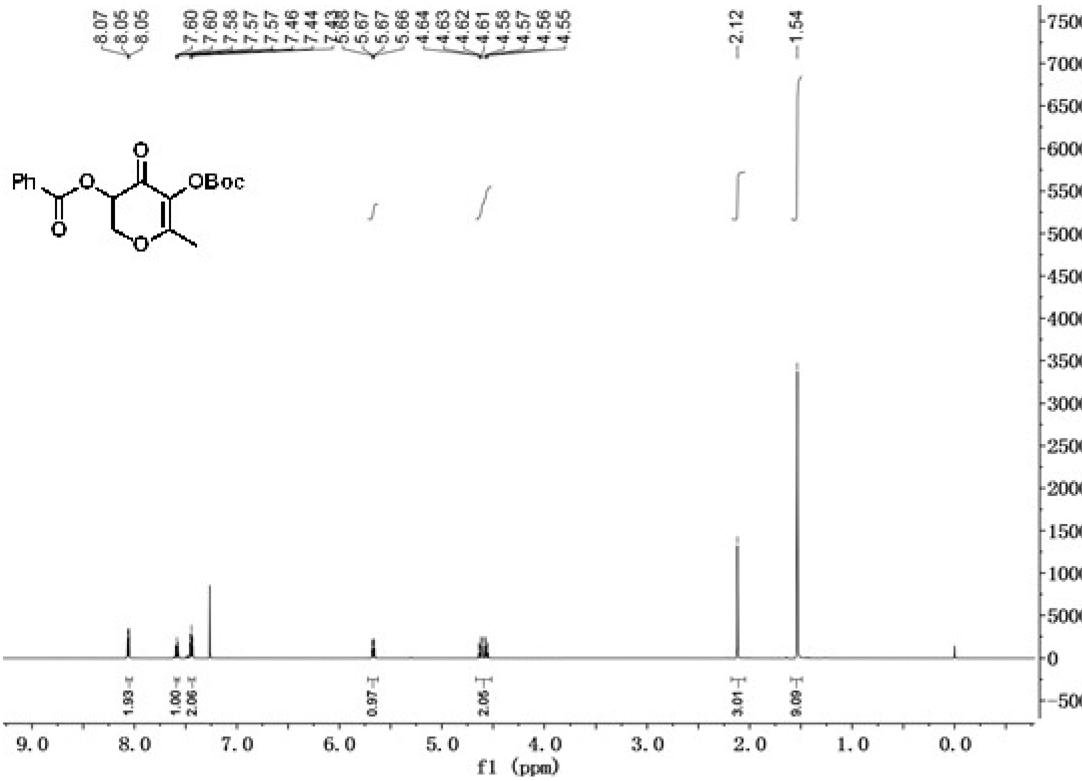


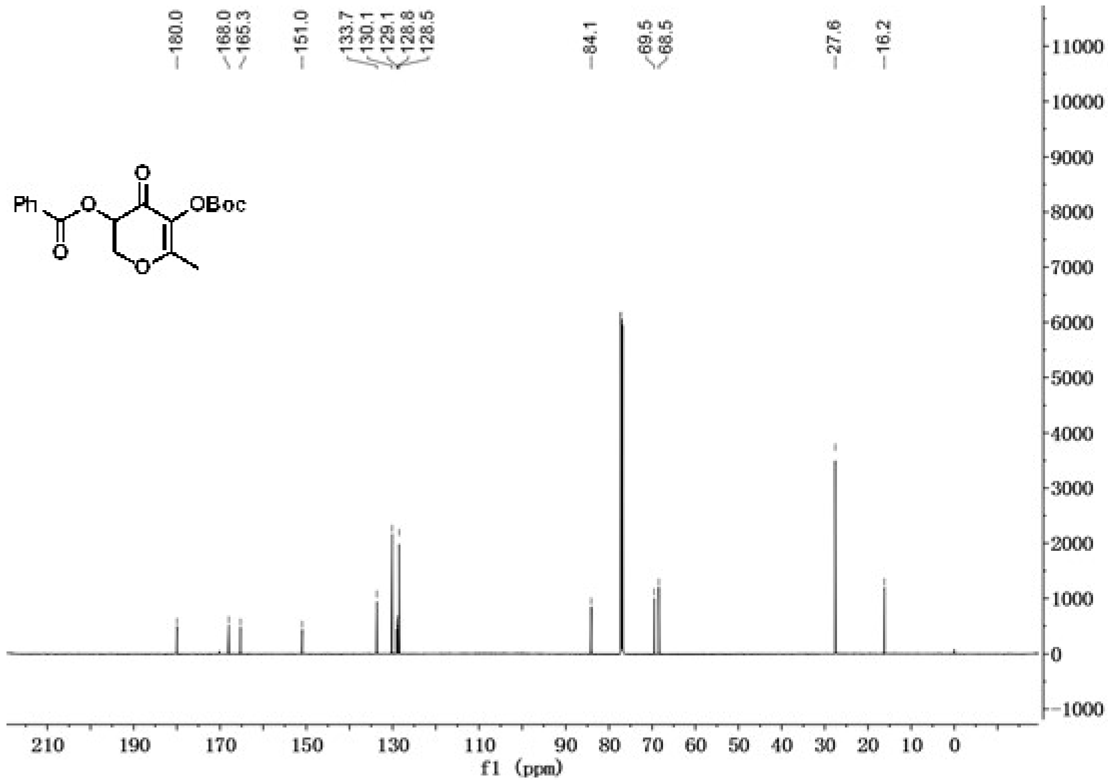
5-((tert-butoxycarbonyl)oxy)-6-methyl-4-oxo-3,4-dihydro-2H-pyran-3-yl acetate (4a)



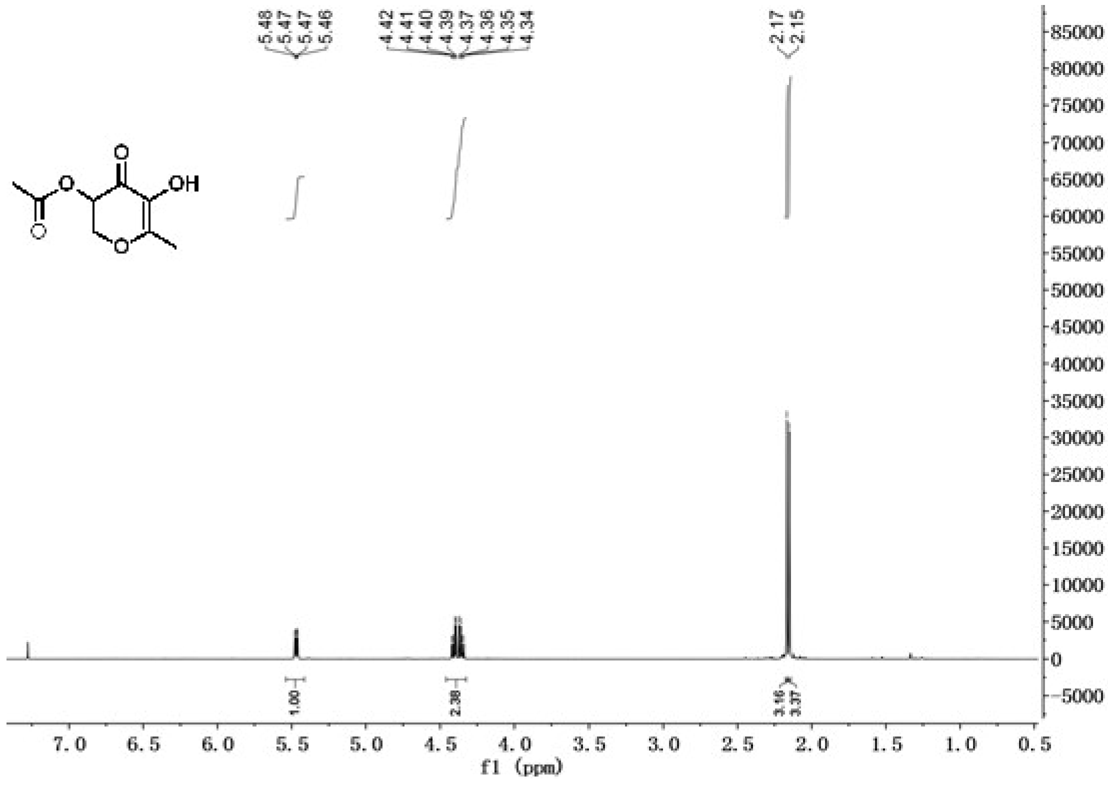


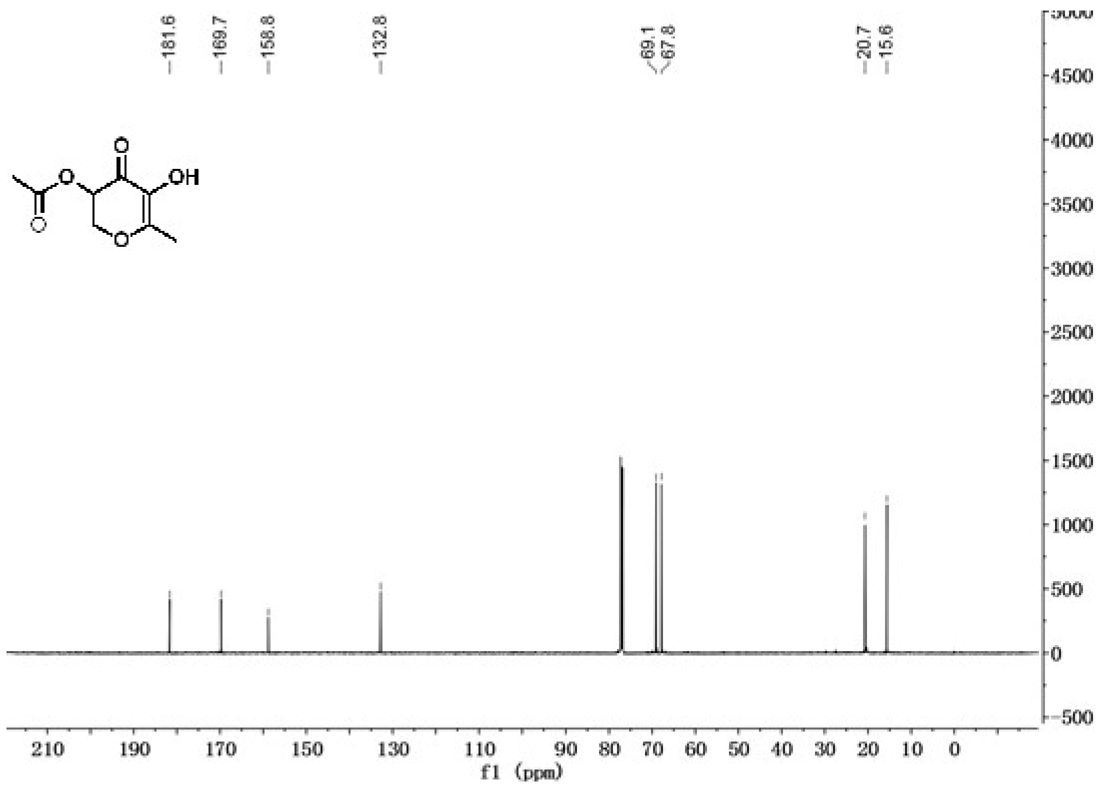
5-((tert-butoxycarbonyl)oxy)-6-methyl-4-oxo-3,4-dihydro-2H-pyran-3-yl benzoate (4b)



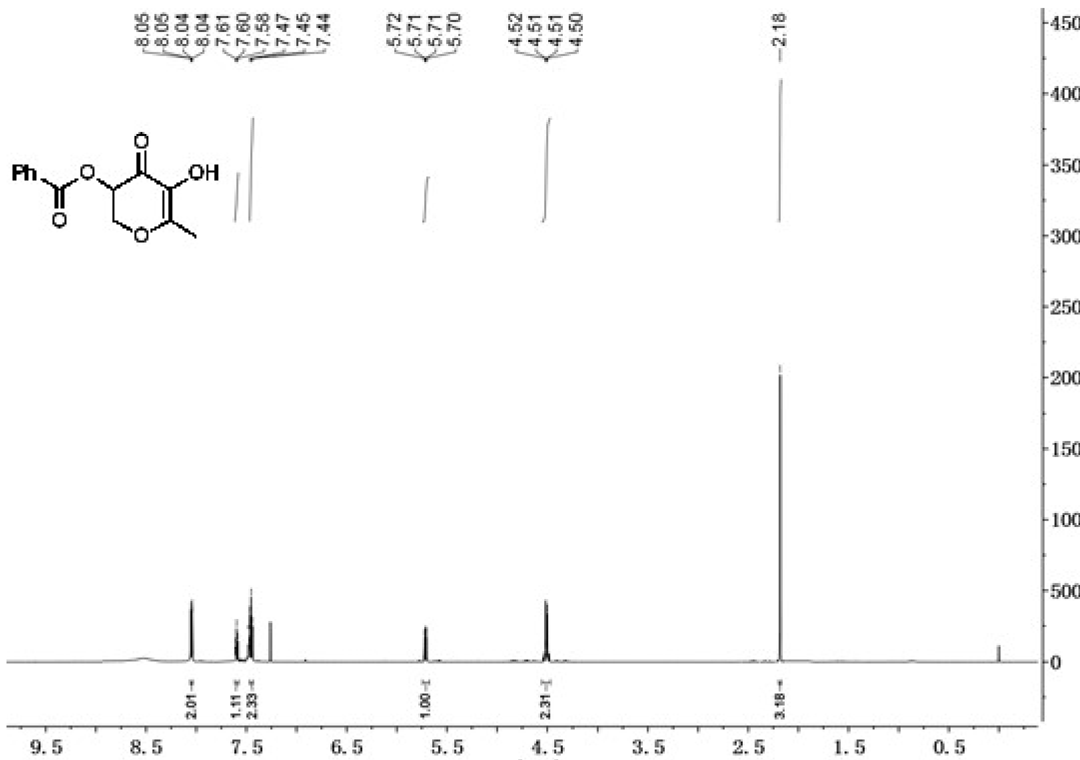


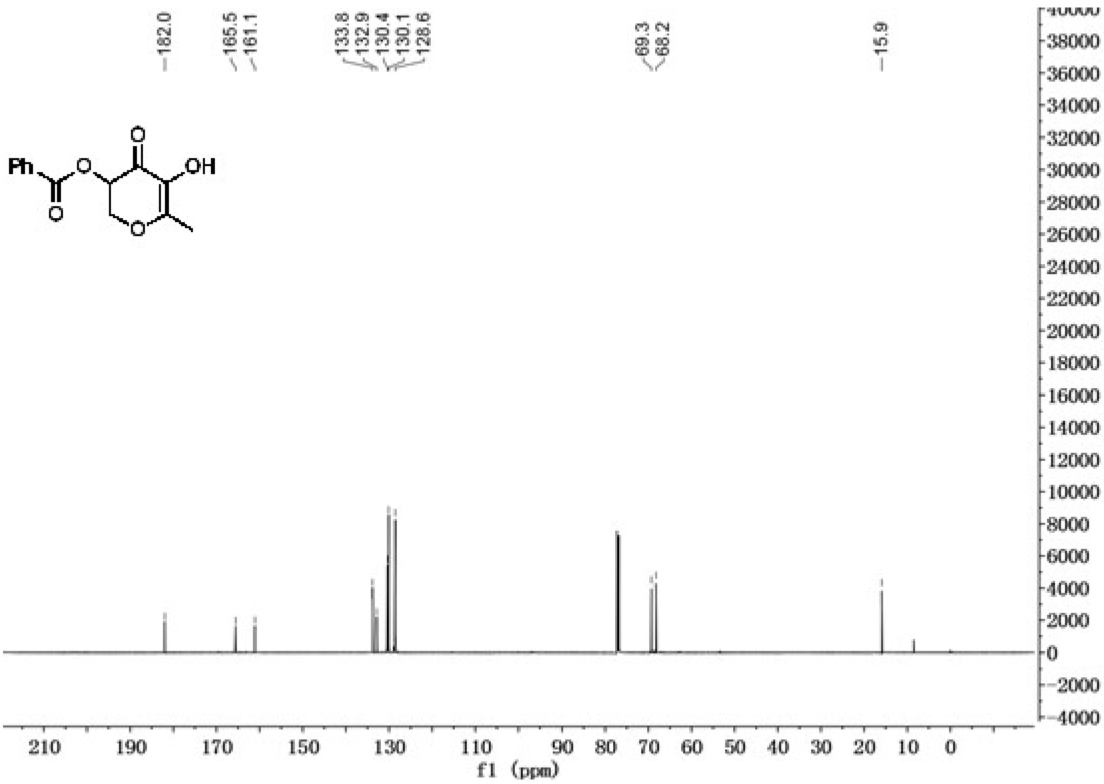
5-hydroxy-6-methyl-4-oxo-3,4-dihydro-2H-pyran-3-yl acetate (5a)





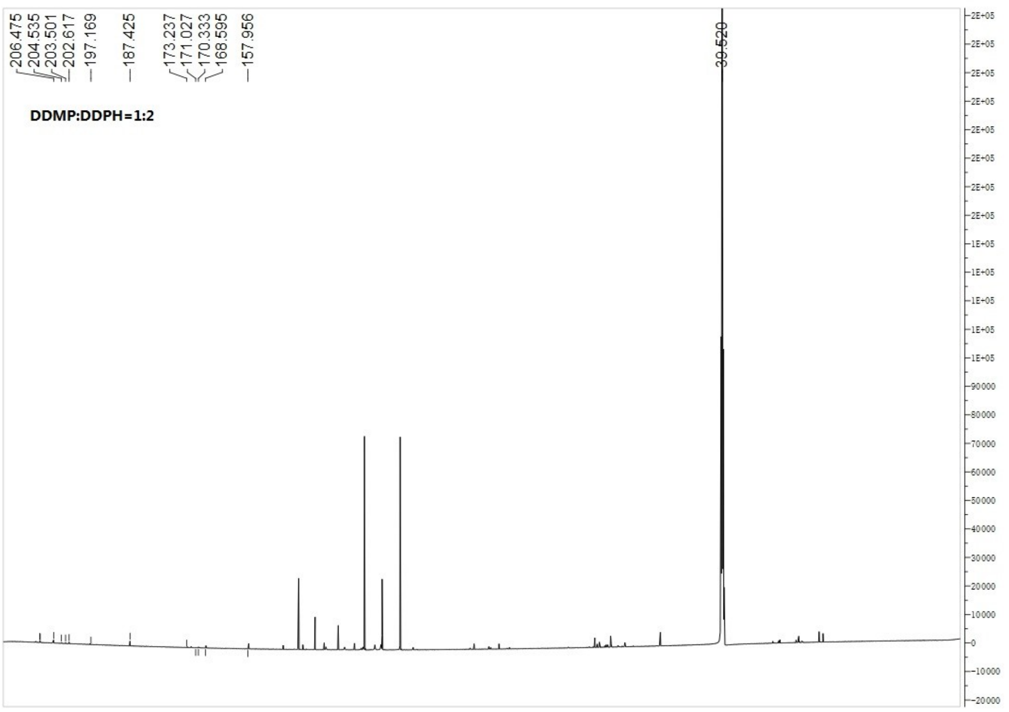
5-hydroxy-6-methyl-4-oxo-3,4-dihydro-2H-pyran-3-yl benzoate (5b)





Reaction of DDMP with DPPH.

When the ratio of DDMP to DPPH was 1:2, DDMP was almost completely consumed. Several carbon signals at chemical shift δ206~197 and δ174~168 on the ^{13}C NMR spectrum were found.



4. Results of scavenging radicals.

Table 1S Equation of [ABTS$^{+\cdot}$] ~ t and its differential style (-d[ABTS$^{+\cdot}$]/dt ~ t), reaction rate at t = 0 (r_0), and rate constant (k) [a].

Compound	Equation of [ABTS$^{+\cdot}$ (μM)] ~ t (s)	Equation of -d[ABTS$^{+\cdot}$]/dt ~ t	r_0 (μM·s^{-1})	k (mM^{-1}·s^{-1})
1	$[ABTS^{+\bullet}]=13.86e^{-\frac{t}{7.20}}+19.53e^{-\frac{t}{256.00}}+14.59$	$-\frac{d[ABTS^{+\bullet}]}{dt}=1.93e^{-\frac{t}{7.20}}+0.08e^{-\frac{t}{256.00}}$	2.01	2.40
2a	$[ABTS^{+\bullet}]=7.81e^{-\frac{t}{3.95}}+9.29e^{-\frac{t}{105.27}}+30.53$	$-\frac{d[ABTS^{+\bullet}]}{dt}=1.98e^{-\frac{t}{3.95}}+0.09e^{-\frac{t}{105.27}}$	2.07	6.19×10^{-2}
2b	$[ABTS^{+\bullet}]=8.16e^{-\frac{t}{5.11}}+7.69e^{-\frac{t}{114.76}}+31.70$	$-\frac{d[ABTS^{+\bullet}]}{dt}=1.60e^{-\frac{t}{5.11}}+0.07e^{-\frac{t}{114.76}}$	1.67	4.99×10^{-2}
2c	$[ABTS^{+\bullet}]=5.91e^{-\frac{t}{4.11}}+2.68e^{-\frac{t}{274.48}}+39.05$	$-\frac{d[ABTS^{+\bullet}]}{dt}=1.44e^{-\frac{t}{4.11}}+0.01e^{-\frac{t}{274.48}}$	1.45	4.34×10^{-2}
2d	$[ABTS^{+\bullet}]=6.77e^{-\frac{t}{4.58}}+3.78e^{-\frac{t}{114.33}}+37.06$	$-\frac{d[ABTS^{+\bullet}]}{dt}=1.48e^{-\frac{t}{4.58}}+0.03e^{-\frac{t}{114.33}}$	1.51	4.53×10^{-2}
5a	$[ABTS^{+\bullet}]=8.33e^{-\frac{t}{8.36}}+10.78e^{-\frac{t}{202.23}}+28.17$	$-\frac{d[ABTS^{+\bullet}]}{dt}=1.00e^{-\frac{t}{8.36}}+0.05e^{-\frac{t}{202.23}}$	1.05	1.26
5b	$[ABTS^{+\bullet}]=6.19e^{-\frac{t}{7.28}}+8.82e^{-\frac{t}{254.51}}+32.20$	$-\frac{d[ABTS^{+\bullet}]}{dt}=0.85e^{-\frac{t}{7.28}}+0.03e^{-\frac{t}{254.51}}$	0.88	1.06
6	$[ABTS^{+\bullet}]=7.41e^{-\frac{t}{4.72}}+9.61e^{-\frac{t}{107.96}}+30.62$	$-\frac{d[ABTS^{+\bullet}]}{dt}=1.57e^{-\frac{t}{4.72}}+0.09e^{-\frac{t}{107.96}}$	1.66	1.99

[a] The concentrations of **1**, **5a**, **5b** and **6** were 17.5 μM, the concentrations of **2a**, **2b**, **2c**, and **2d** were 700 μM. The concentration of ABTS$^{+\cdot}$ is 47.68 μM.

Table 2S Equation of [DPPH] ~ *t* and its differential style (-*d*[DPPH]/*dt* ~ *t*), reaction rate at *t* = 0 (***r*₀**), and rate constant (***k***) [a].

Compound	Equation of [DPPH (μM)] ~ *t* (s)	Equation of -*d*[DPPH]/*dt* ~ *t*	r_0 (μM·s⁻¹)	*k* (mM⁻¹·s⁻¹)
1	$[\mathrm{DPPH}] = 65.86e^{-\frac{t}{2.76}} + 91.61e^{-\frac{t}{614.15}} + 141.88$	$-\frac{d[\mathrm{DPPH}]}{dt} = 23.86e^{-\frac{t}{2.76}} + 0.15e^{-\frac{t}{614.45}}$	24.01	1.15
2a	$[\mathrm{DPPH}] = 64.34e^{-\frac{t}{1.34}} + 37.82e^{-\frac{t}{1500.28}} + 197.34$	$-\frac{d[\mathrm{DPPH}]}{dt} = 48.01e^{-\frac{t}{1.34}} + 0.03e^{-\frac{t}{1500.28}}$	48.04	0.11
2b	$[\mathrm{DPPH}] = 66.51e^{-\frac{t}{1.60}} + 24.58e^{-\frac{t}{1216.64}} + 208.41$	$-\frac{d[\mathrm{DPPH}]}{dt} = 41.57e^{-\frac{t}{1.60}} + 0.02e^{-\frac{t}{1216.64}}$	41.59	0.10
2c	$[\mathrm{DPPH}] = 61.95e^{-\frac{t}{1.22}} + 13.00e^{-\frac{t}{1200.09}} + 224.56$	$-\frac{d[\mathrm{DPPH}]}{dt} = 50.78e^{-\frac{t}{1.22}} + 0.01e^{-\frac{t}{1200.09}}$	50.79	0.12
2d	$[\mathrm{DPPH}] = 61.68e^{-\frac{t}{1.24}} + 28.13e^{-\frac{t}{1228.93}} + 209.70$	$-\frac{d[\mathrm{DPPH}]}{dt} = 49.74e^{-\frac{t}{1.24}} + 0.02e^{-\frac{t}{1228.93}}$	49.76	0.12
5a	$[\mathrm{DPPH}] = 27.56e^{-\frac{t}{1.43}} + 81.99e^{-\frac{t}{1914.14}} + 189.96$	$-\frac{d[\mathrm{DPPH}]}{dt} = 19.27e^{-\frac{t}{1.43}} + 0.04e^{-\frac{t}{1914.14}}$	19.31	0.92
5b	$[\mathrm{DPPH}] = 22.27e^{-\frac{t}{1.11}} + 32.07e^{-\frac{t}{1610.58}} + 245.16$	$-\frac{d[\mathrm{DPPH}]}{dt} = 20.06e^{-\frac{t}{1.11}} + 0.02e^{-\frac{t}{1610.58}}$	20.08	0.96
6	$[\mathrm{DPPH}] = 31.65e^{-\frac{t}{1.51}} + 70.02e^{-\frac{t}{1244.20}} + 197.83$	$-\frac{d[\mathrm{DPPH}]}{dt} = 20.96e^{-\frac{t}{1.51}} + 0.06e^{-\frac{t}{1244.20}}$	21.02	1.00

[a] The concentrations of **1**, **5a**, **5b**, and **6** were 70 μM, the concentration of **2a**, **2b**, **2c**, and **2d** were 1400 μM. The concentration of DPPH is 299.51 μM.

Table 3S Equation of [galvinoxyl] ~ *t* and its differential style (-*d*[galvinoxyl]/*dt* ~ *t*), reaction rate at *t* = 0 (r_0), and rate constant (***k***) [a].

Compound	Equation of [galvinoxyl (μM)] ~ *t* (s)	Equation of -*d*[galvinoxyl]/*dt* ~ *t*	r_0 (μM·s^{-1})	*k* (mM^{-1}·s^{-1})
1	$[galvinoxyl]=0.94e^{-\frac{t}{2.28}}+8.64e^{-\frac{t}{469.40}}+1.37$	$-\frac{d[galvinoxyl]}{dt}=0.41e^{-\frac{t}{2.28}}+0.02e^{-\frac{t}{469.40}}$	0.43	2.25
2a	$[galvinoxyl]=0.95e^{-\frac{t}{2.15}}+1.89e^{-\frac{t}{1344.76}}+6.80$	$-\frac{d[galvinoxyl]}{dt}=0.44e^{-\frac{t}{2.15}}+0.001e^{-\frac{t}{1344.76}}$	0.44	0.06
2b	$[galvinoxyl]=1.10e^{-\frac{t}{2.12}}+2.21e^{-\frac{t}{1714.24}}+6.42$	$-\frac{d[galvinoxyl]}{dt}=0.52e^{-\frac{t}{2.12}}+0.001e^{-\frac{t}{1714.24}}$	0.52	0.08
2c	$[galvinoxyl]=0.85e^{-\frac{t}{2.05}}+1.47e^{-\frac{t}{2449.80}}+7.32$	$-\frac{d[galvinoxyl]}{dt}=0.41e^{-\frac{t}{2.05}}+0.001e^{-\frac{t}{2449.80}}$	0.41	0.06
2d	$[galvinoxyl]=0.86e^{-\frac{t}{1.78}}+3.11e^{-\frac{t}{3214.08}}+5.67$	$-\frac{d[galvinoxyl]}{dt}=0.48e^{-\frac{t}{1.78}}+0.001e^{-\frac{t}{3214.08}}$	0.48	0.07
5a	$[galvinoxyl]=0.57e^{-\frac{t}{4.25}}+4.23e^{-\frac{t}{1843.37}}+6.15$	$-\frac{d[galvinoxyl]}{dt}=0.13e^{-\frac{t}{4.25}}+0.002e^{-\frac{t}{1843.37}}$	0.14	0.71
5b	$[galvinoxyl]=0.71e^{-\frac{t}{8.69}}+1.50e^{-\frac{t}{1471.10}}+8.73$	$-\frac{d[galvinoxyl]}{dt}=0.08e^{-\frac{t}{8.69}}+0.001e^{-\frac{t}{1471.10}}$	0.08	0.43
6	$[galvinoxyl]=0.57e^{-\frac{t}{3.71}}+5.07e^{-\frac{t}{1601.79}}+5.31$	$-\frac{d[galvinoxyl]}{dt}=0.15e^{-\frac{t}{3.71}}+0.0031e^{-\frac{t}{1601.79}}$	0.16	0.82

[a] The concentrations of **1**, **5a**, **5b**, and **6** were17.5 μM, the concentrations of **2a**, **2b**, **2c**, and **2d** was 700 μM. The concentration of galvinoxyl is 10.95 μM.