Visible Light-induced Oxidative α-Hydroxylation of β-Dicarbonyl Compounds Catalyzed by Ethylenediamine-Copper(II)

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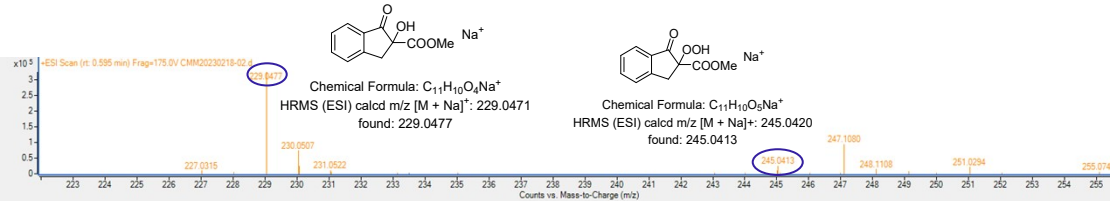
1. General information

Unless otherwise stated, all regents were purchased from commercial suppliers and used without purifications. The β-keto esters [1] were synthesized according to the known method. All reactions were carried out in glassware. Reactions were monitored by TLC on silica gel precoated on glass plates, and spots were visualized with UV light at 254nm. Flash column chromatography was performed on silica-gel.^{1}H and ^{13}C NMR were recorded in $CDCl_3$ on Bruker ASCEND (600 MHz). TMS served as internal standard (d= 0 ppm) for ^{1}H NMR and $CDCl_3$ was used as internal standard (d= 77.0 ppm) for ^{13}C NMR; High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6545 Q-TOF LCMS spectrometer equipped with an ESI source and controlled by using Mass Hunter software.

[1] Pericas, À.; Shafir, A.; Vallribera, A. *Tetrahedron.* **2008**, *64*, 9258.

2. Mass spectrum of the control experiment

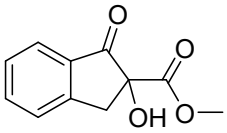


3. General procedure for the synthesis of 2

Copper acetate (1.81 mg, 0.01 mmol) and ethylenediamine **L_1** (0.6 mg, 0.01 mmol) were added to the test tube containing tetrahydrofuran (2 mL). The mixture was stirred at room temperature for 0.5 h. The β-keto esters **1** (0.1 mmol) and TPP (0.006 mg, 0.01 mol%) were added to above prepared catalyst solution, The resulting mixture was vented with air and stirred under the irradiation of 10 W-525 nm green light for 7 h, the reaction was monitored by thin-layer chromatography (TLC). After completion, the reaction mixture was concentrated in vacuo and purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to afford the desired product.

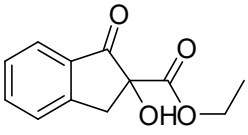
4. Characterization data of products 2

Methyl 2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2a)



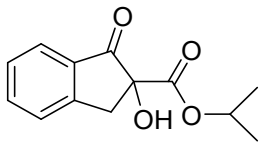
Compound was isolated as a white solid (99% yield, 20.4 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 4.06 (s, 1H), 3.79 – 3.72 (m, 4H), 3.27 (d, *J* = 17.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.8, 171.9, 152.2, 136.2, 133.5, 128.2, 126.5, 125.3, 80.4, 53.5, 39.3. HRMS exact mass calcd for $C_{11}H_{10}O_4Na^+$ (M+Na) requires *m/z* 229.0471. Found *m/z* 229.0479.

Ethyl-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2b)



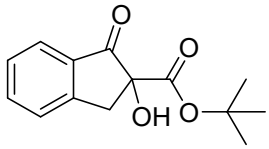
Compound was isolated as a white solid (97 % yield, 21.3 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 4.23 (p, *J* = 7.1 Hz, 2H), 4.07 (s, 1H), 3.74 (d, *J* = 17.2 Hz, 1H), 3.27 (d, *J* = 17.2 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.0, 171.5, 152.3, 136.1, 133.6, 128.1, 126.5, 125.3, 80.3, 62.8, 39.3, 14.0. HRMS exact mass calcd for $C_{12}H_{12}O_4Na^+$ (M+Na) requires *m/z* 243.0628. Found *m/z* 243.0631.

Isopropyl 2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2c)



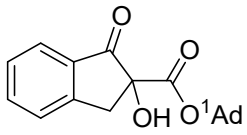
Compound was isolated as a white solid (94% yield, 22.0 mg) after column chromatography on silica-gel. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 5.08 (p, *J* = 6.3 Hz, 1H), 4.05 (s, 1H), 3.70 (d, *J* = 17.2 Hz, 1H), 3.25 (d, *J* = 17.2 Hz, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.14 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.0, 171.0, 152.3, 136.0, 133.7, 128.0, 126.4, 125.2, 80.3, 70.9, 39.3, 21.5, 21.3. HRMS exact mass calcd for $C_{13}H_{14}O_4Na^+$ (M+Na) requires *m/z* 257.0784. Found *m/z* 257.0785.

tert-butyl 2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2d)



Compound was isolated as a white solid (96% yield, 23.8 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 4.04 (s, 1H), 3.67 (d, *J* = 17.1 Hz, 1H), 3.24 (d, *J* = 17.1 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.4, 170.5, 152.3, 135.9, 133.9, 127.9, 126.3, 125.1, 83.9, 80.5, 39.5, 27.7. HRMS exact mass calcd for $C_{14}H_{16}O_4Na^+$ (M+Na) requires *m/z* 271.0941. Found *m/z* 271.0946.

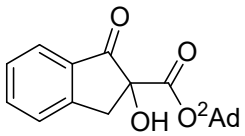
1-Adamantanyl 2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2e)



Compound was isolated as a white solid (96% yield, 31.2 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 4.07 (s, 1H), 3.67 (d, *J* = 17.0 Hz, 1H), 3.23 (d, *J*

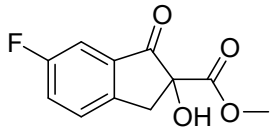
= 17.0 Hz, 1H), 2.13 (s, 3H), 1.98 (s, 6H), 1.61 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.5, 170.2, 152.4, 135.8, 134.0, 127.9, 126.3, 125.0, 83.9, 80.6, 40.9, 39.6, 35.9, 30.8. HRMS exact mass calcd for $C_{20}H_{22}O_4Na^+$ (M+Na) requires *m/z* 349.1410. Found *m/z* 349.1411.

2-Adamantanyl 2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2f)



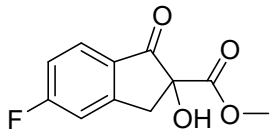
Compound was isolated as a pink solid (94% yield, 30.6 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 4.97 (s, 1H), 4.05 (s, 1H), 3.73 (d, *J* = 16.9 Hz, 1H), 3.32 (d, *J* = 16.9 Hz, 1H), 1.88 – 1.55 (m, 10H), 1.44 – 1.25 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.1, 170.7, 152.0, 135.9, 134.1, 128.1, 126.3, 125.1, 81.0, 79.8, 39.6, 37.1, 36.1, 36.0, 31.7, 31.5, 31.5, 31.3, 26.8, 26.7. HRMS exact mass calcd for $C_{20}H_{22}O_4Na^+$ (M+Na) requires *m/z* 349.1410. Found *m/z* 349.1417.

Methyl 6-fluoro-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2g)



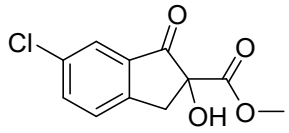
Compound was isolated as a white solid (97% yield, 21.7 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 (dd, *J* = 8.4, 4.5 Hz, 1H), 7.45 (dd, *J* = 7.3, 2.5 Hz, 1H), 7.41 (td, *J* = 8.5, 2.5 Hz, 1H), 4.08 (s, 1H), 3.76 (s, 3H), 3.71 (d, *J* = 17.0 Hz, 1H), 3.23 (d, *J* = 17.0 Hz, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 200.0, 171.6, 162.5(d, $^1J_{C\text{-}F}$=247.9), 147.6(d, $^4J_{C\text{-}F}$=2.1), 135.2(d, $^3J_{C\text{-}F}$=7.5), 127.9(d, $^3J_{C\text{-}F}$=7.83), 123.9(d, $^2J_{C\text{-}F}$=23.6), 111.0(d, $^2J_{C\text{-}F}$=22.0), 81.03, 53.58, 38.77. HRMS exact mass calcd for $C_{11}H_9FO_4Na^+$ (M+Na) requires *m/z* 247.0377. Found *m/z* 247.0382.

Methyl 5-fluoro-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2h)



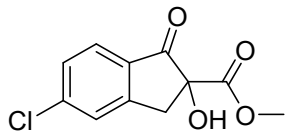
Compound was isolated as a brown solid (96% yield, 21.5 mg) after column chromatography on silica-gel.^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 8.4, 5.3 Hz, 1H), 7.22 – 7.09 (m, 2H), 4.05 (s, 1H), 3.77 (s, 3H), 3.73 (d, *J* = 17.4 Hz, 1H), 3.26 (d, *J* = 17.4 Hz, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 198.9, 171.6, 167.9(d, $^1J_{C\text{-}F}$=257.5), 155.2(d, $^3J_{C\text{-}F}$=10.2), 129.9(d, $^4J_{C\text{-}F}$=1.74), 127.8(d, $^3J_{C\text{-}F}$=10.7), 116.6(d, $^2J_{C\text{-}F}$=23.5), 113.4(d, $^2J_{C\text{-}F}$=22.6), 80.54, 53.56, 39.14. HRMS exact mass calcd for $C_{11}H_9FO_4Na^+$ (M+Na) requires *m/z* 247.0377. Found *m/z* 247.0379.

Methyl 6-chloro-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2i)



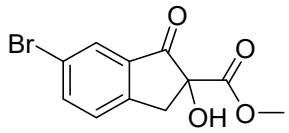
Compound was isolated as a white solid (97% yield, 23.2 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 1.8 Hz, 1H), 7.65 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 4.05 (s, 1H), 3.77 (s, 3H), 3.71 (d, *J* = 17.3 Hz, 1H), 3.24 (d, *J* = 17.3 Hz, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 199.6, 171.5, 150.2, 136.2, 135.0, 134.6, 127.7, 125.0, 80.8, 53.6, 38.9. HRMS exact mass calcd for $C_{11}H_9ClO_4Na^+$ (M+Na) requires *m/z* 263.0082. Found *m/z* 263.0083.

Methyl 5-chloro-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2j)



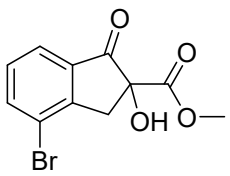
Compound was isolated as a white solid (99% yield, 23.7 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.51 (s, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 4.08 (s, 1H), 3.76 (s, 3H), 3.72 (d, *J* = 17.4 Hz, 1H), 3.25 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.4, 171.5, 153.5, 142.9, 132.0, 129.1, 126.8, 126.4, 80.4, 53.6, 39.0. HRMS exact mass calcd for $C_{11}H_9ClO_4Na^+$ (M+Na) requires *m/z* 263.0082. Found *m/z* 263.0082.

Methyl 6-bromine-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2k)



Compound was isolated as a white solid (98% yield, 27.8 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.79 (d, *J* = 10.1 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 4.03 (s, 1H), 3.77 (s, 3H), 3.69 (d, *J* = 17.3 Hz, 1H), 3.21 (d, *J* = 17.4 Hz, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 199.5, 171.5, 150.7, 138.9, 135.4, 128.1, 128.0, 122.3, 80.6, 53.6, 38.9. HRMS exact mass calcd for $C_{11}H_9BrO_4Na^+$ (M+Na) requires *m/z* 306.9576. Found *m/z* 306.9579

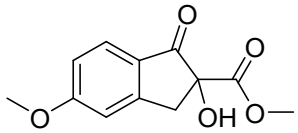
Methyl 4-bromine-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2l)



Compound was isolated as a white solid (84% yield, 23.8 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 7.4 Hz, 1H),

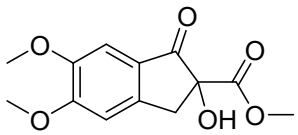
7.37 (t, *J* = 7.5 Hz, 1H), 4.04 (s, 1H), 3.79 (s, 3H), 3.69 (d, *J* = 17.8 Hz, 1H), 3.20 (d, *J* = 17.7 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 200.2, 171.5, 151.9, 138.9, 135.5, 129.9, 124.1, 121.9, 80.0, 53.7, 40.4. HRMS exact mass calcd for $C_{11}H_9BrO_4Na^+$ (M+Na) requires *m/z* 306.9576. Found *m/z* 306.9581.

Methyl 5-methoxy-2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2m)



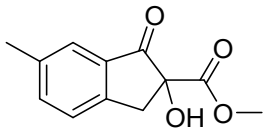
Compound was isolated as a white solid (97% yield, 22.9 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.6 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.93 (s, 1H), 4.60 (s, 1H), 3.93 (s, 4H), 3.81 (s, 3H), 3.66 (d, *J* = 17.6 Hz, 1H), 3.54 (d, *J* = 17.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.31, 169.46, 166.70, 155.02, 127.37, 126.92, 116.53, 109.76, 91.02, 55.88, 53.16, 36.76. HRMS exact mass calcd for $C_{12}H_{12}O_5Na^+$ (M+Na) requires *m/z* 259.0577. Found *m/z* 259.0578.

Methyl 5,6-dimethoxy-2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2n)



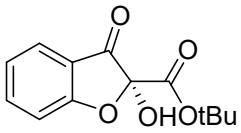
Compound was isolated as a white solid (87% yield, 23.1 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.19 (s, 1H), 6.90 (s, 1H), 4.08 (s, 1H), 3.99 (s, 3H), 3.91 (s, 3H), 3.74 (s, 3H), 3.64 (d, *J* = 16.9 Hz, 1H), 3.16 (d, *J* = 16.9 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 199.1, 172.2, 156.8, 150.0, 148.1, 126.1, 107.3, 105.4, 80.8, 56.4, 56.1, 53.4, 39.0. HRMS exact mass calcd for $C_{13}H_{14}O_6Na^+$ (M+Na) requires *m/z* 289.0683. Found *m/z* 289.0685.

Methyl 6-methyl-2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2o)



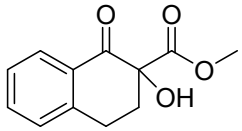
Compound was isolated as a white solid (93% yield, 20.4 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 4.02 (s, 1H), 3.75 (s, 3H), 3.70 (d, *J* = 17.1 Hz, 1H), 3.22 (d, *J* = 17.1 Hz, 1H), 2.43 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 200.9, 172.0, 149.6, 138.3, 137.5, 133.7, 126.1, 125.2, 80.7, 53.4, 39.0, 21.1. HRMS exact mass calcd for $C_{12}H_{12}O_4Na^+$ (M+Na) requires *m/z* 243.0628. Found *m/z* 243.0630.

tert-butyl-2-hydroxy-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (2p)



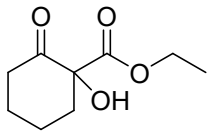
Compound was isolated as a yellow solid (93% yield, 23.2 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.7 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 5.21 (s, 1H), 1.44 (s, 9H).^{13}C NMR (151 MHz, $CDCl_3$) δ 194.3, 171.5, 165.8, 138.9, 125.1, 122.8, 119.1, 113.3, 97.9, 86.0, 27.6. HRMS exact mass calcd for $C_{13}H_{14}O_5Na^+$ (M+Na) requires *m/z* 273.0733. Found *m/z* 273.0735.

Methyl 2-hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2q)



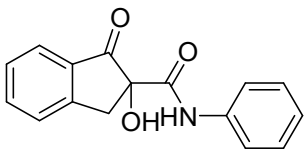
Compound was isolated as a colorless oil (89% yield, 19.6 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.25 (m, 1H), 4.41 (s, 1H), 3.74 (s, 3H), 3.13 (q, *J* = 4.4, 4.0 Hz, 2H), 2.71 (dt, *J* = 13.5, 5.1 Hz, 1H), 2.25 (ddd, *J* = 14.8, 8.9, 6.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.5, 171.1, 144.0, 134.4, 130.1, 128.9, 128.2, 127.0, 77.7, 53.0, 32.7, 21.0. HRMS exact mass calcd for $C_{12}H_{12}O_4Na^+$ (M+Na) requires *m/z* 243.0628. Found *m/z* 243.0636.

(R)-Ethyl 1-Hydroxy-2-oxocyclohexane-1-carboxylate (2r)



Compound was isolated as a colourless oil (76 % yield, 14.1 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.35 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.66 (dtd, *J* = 14.1, 4.5, 1.5 Hz, 1H), 2.60 (dddd, *J* = 13.5, 4.7, 3.6, 2.3 Hz, 1H), 2.55 (ddd, *J* = 14.1, 11.8, 6.0 Hz, 1H), 2.03 (ddtt, *J* = 14.3, 8.3, 4.5, 2.3 Hz, 1H), 1.88 – 1.77 (m, 2H), 1.74 – 1.64 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.3, 170.1, 80.7, 62.0, 38.9, 37.6, 27.0, 21.9, 14.0. HRMS exact mass calcd for $C_9H_{14}O_4Na^+$ (M+Na) requires *m/z* 209.0784. Found *m/z* 209.0789.

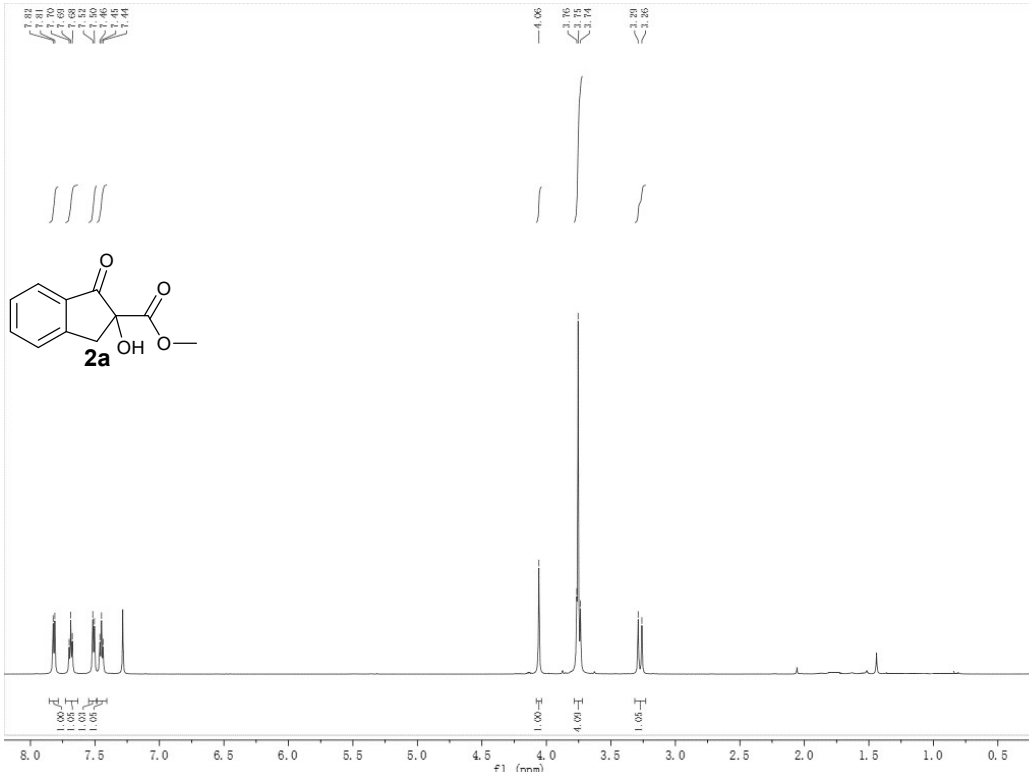
2-hydroxy-1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (2s)

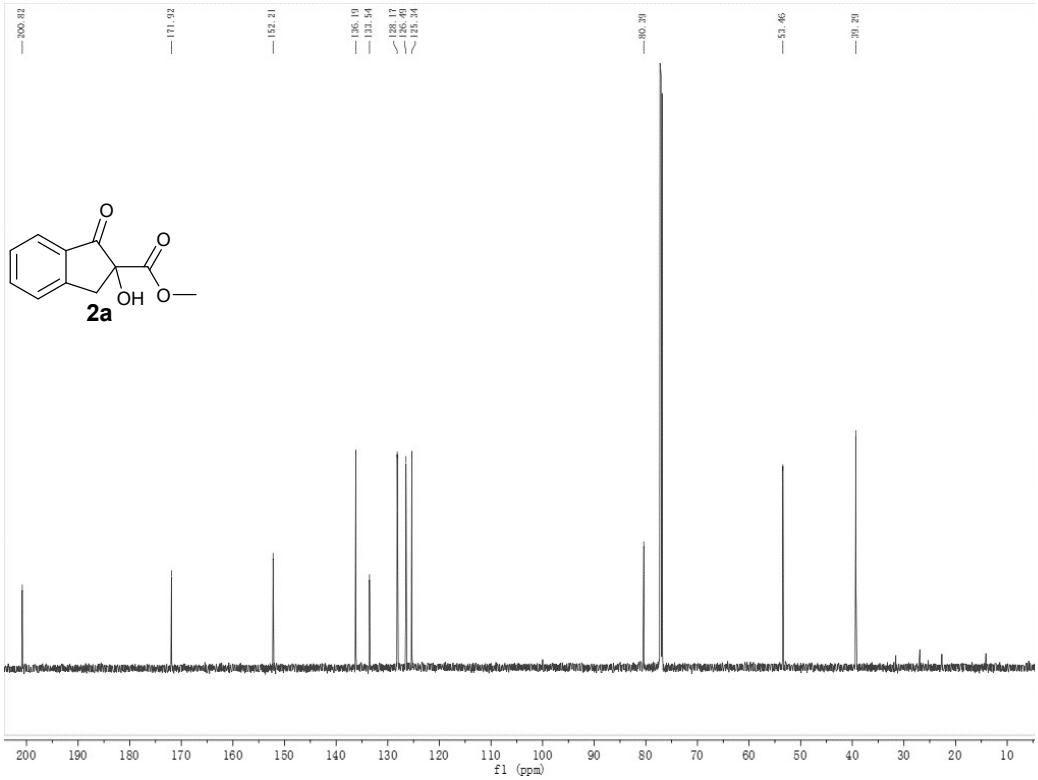


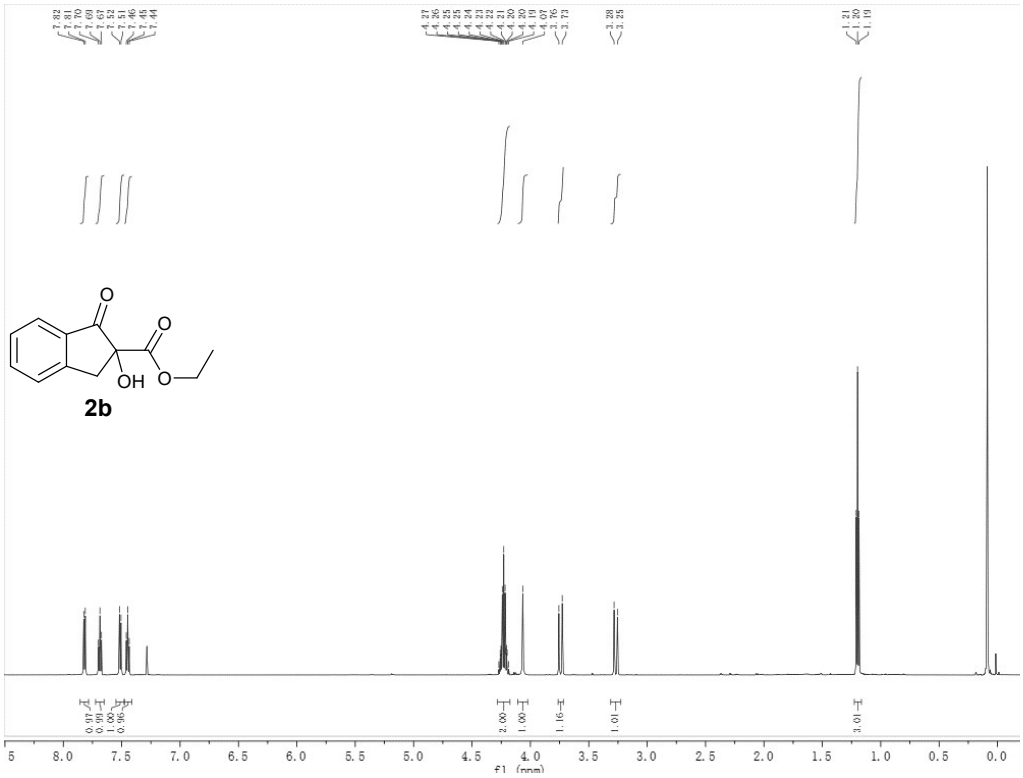
Compound was isolated as a brown solid (96% yield, 25.6 mg) after column chromatography on silica-gel. mp: 128-130 ^{o}C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.79 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.70 (td, *J* = 7.6, 1.1 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.29 (m,

2H), 7.16 – 7.11 (m, 1H), 4.21 (s, 1H), 3.88 (d, J = 16.7 Hz, 1H), 3.21 (d, J = 16.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.2, 168.4, 153.1, 136.9, 136.5, 129.0, 128.2, 126.4, 125.2, 124.8, 119.7, 82.7, 40.9. HRMS exact mass calcd for $C_{16}H_{13}NO_3Na^+$ (M+Na) requires *m/z* 290.0788. Found *m/z* 290.0789.

5. NMR spectra of products 2



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7.51
7.46
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4.26
4.25
4.25
4.24
4.23
4.22
4.21
4.20
4.20
4.19
4.07
2.76
2.73
2.28
2.25
1.21
1.20
1.19
1.10
O
O
O
OH
2b
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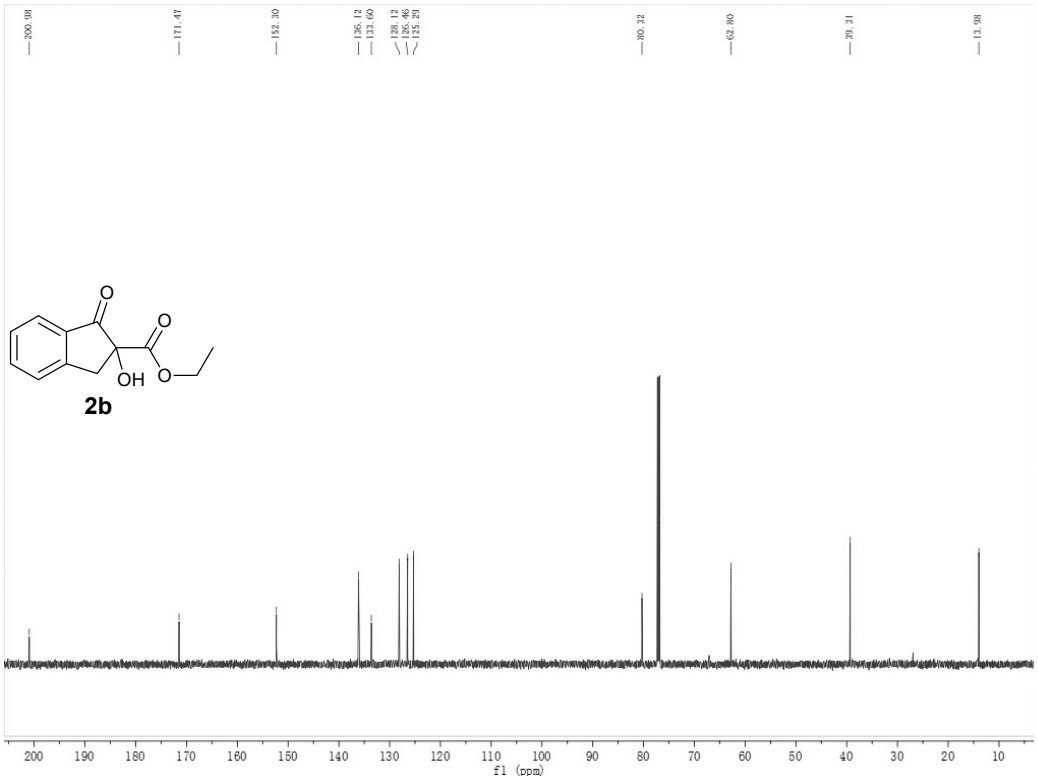
0.98
1.00
0.96
2.00
1.00
1.16
1.01
3.01
f1 (ppm)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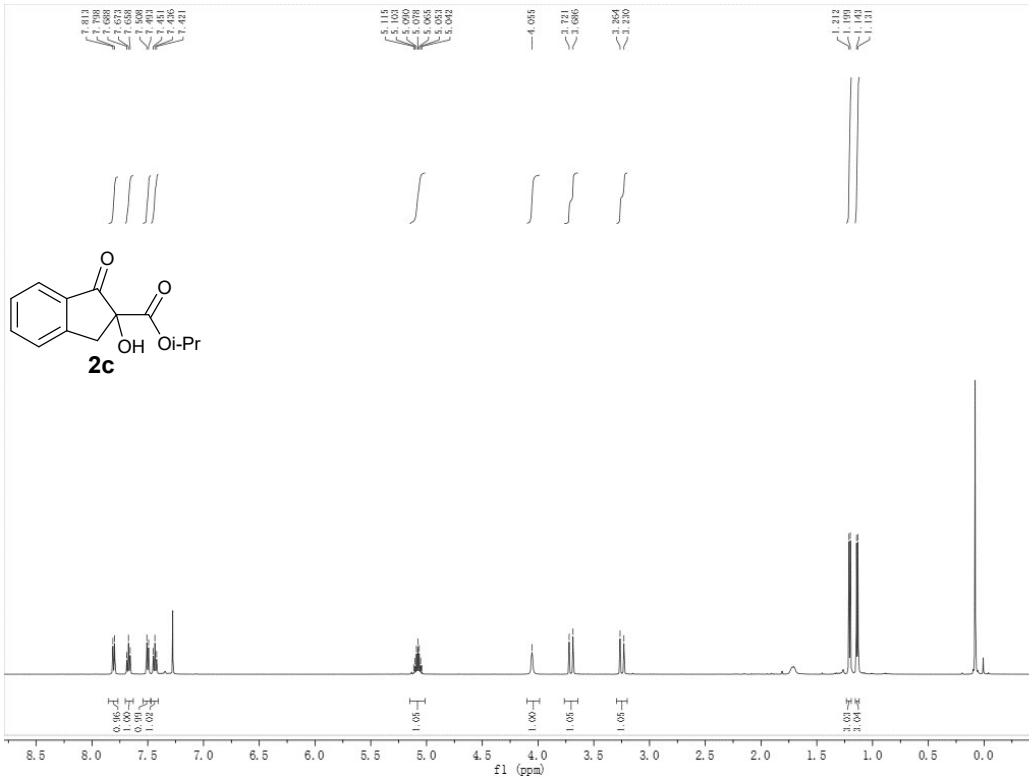
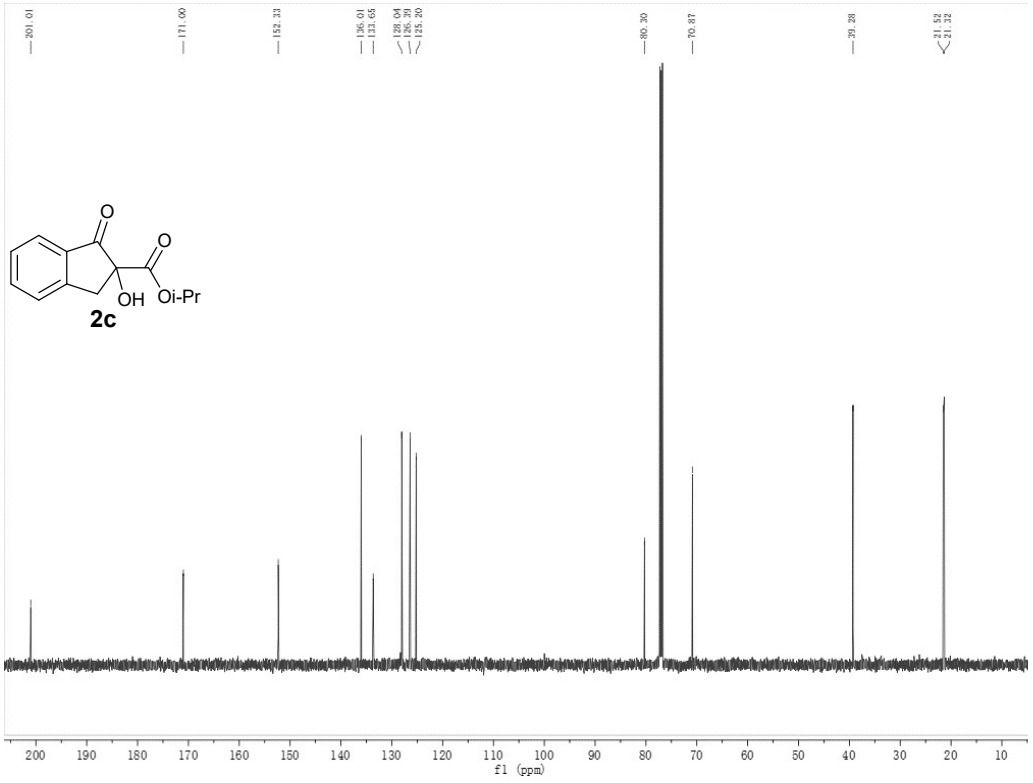
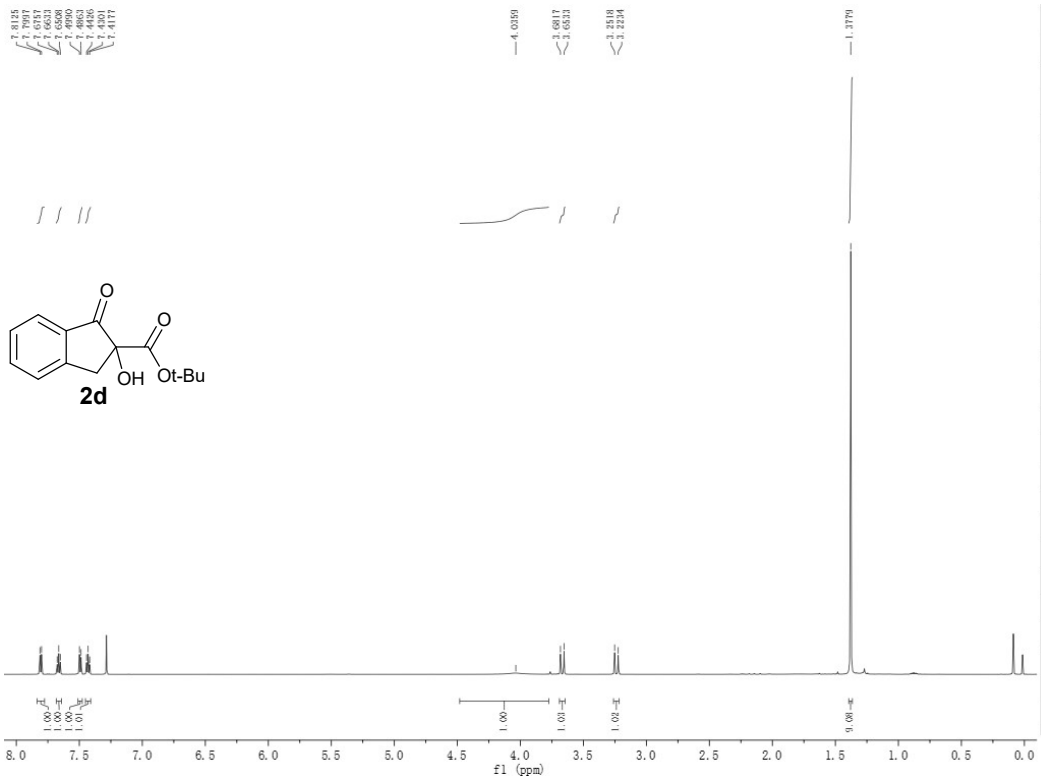
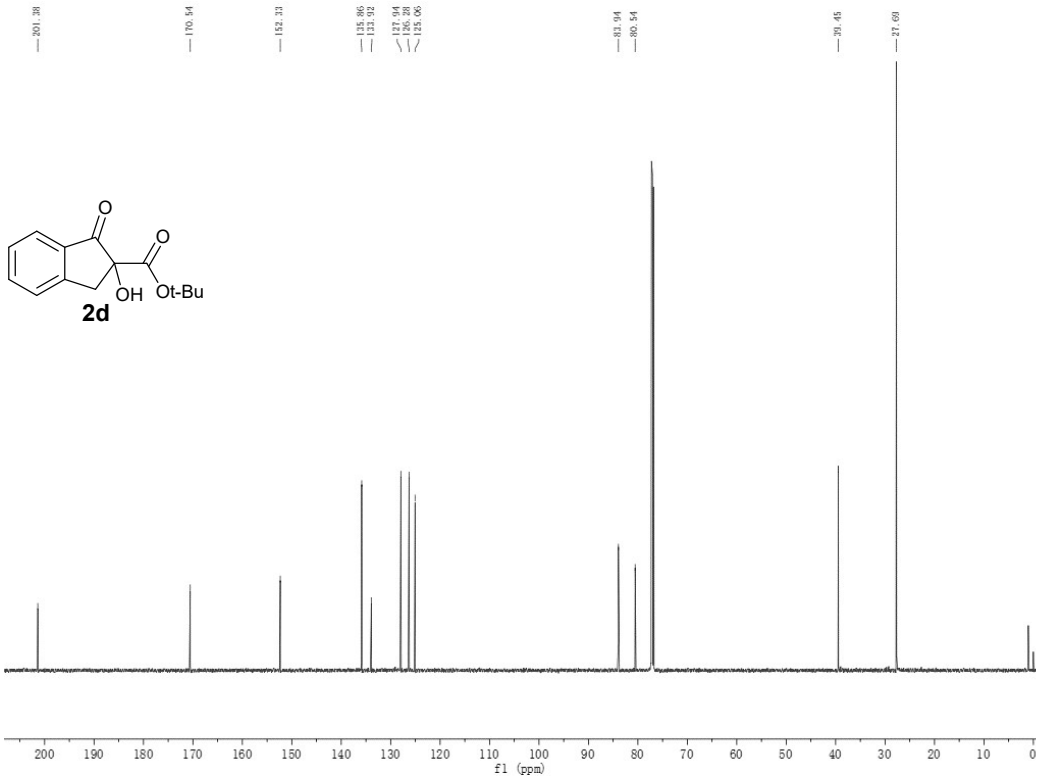
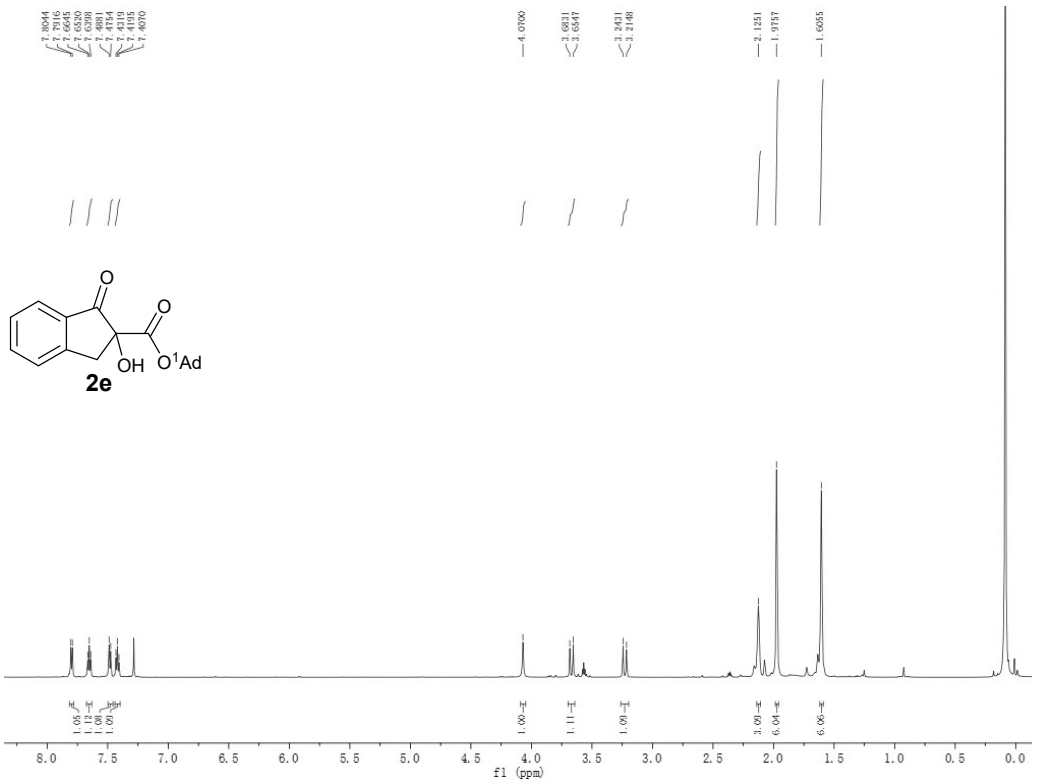
20.31
13.98
O
O
O
OH
2b
f1 (ppm)


O
O
OH
Oi-Pr
2c
f1 (ppm)


O
O
OH
Oi-Pr
2c
f1 (ppm)


OH
Ot-Bu
2d
f1 (ppm)


OH
Ot-Bu
2d
f1 (ppm)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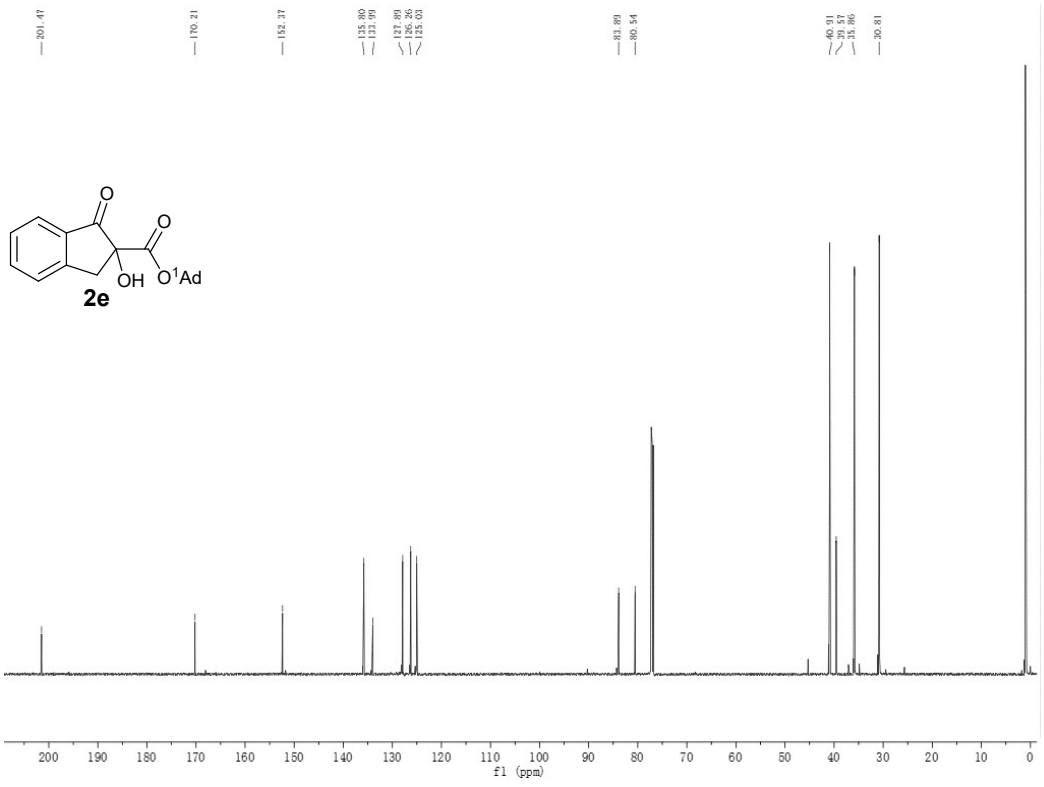
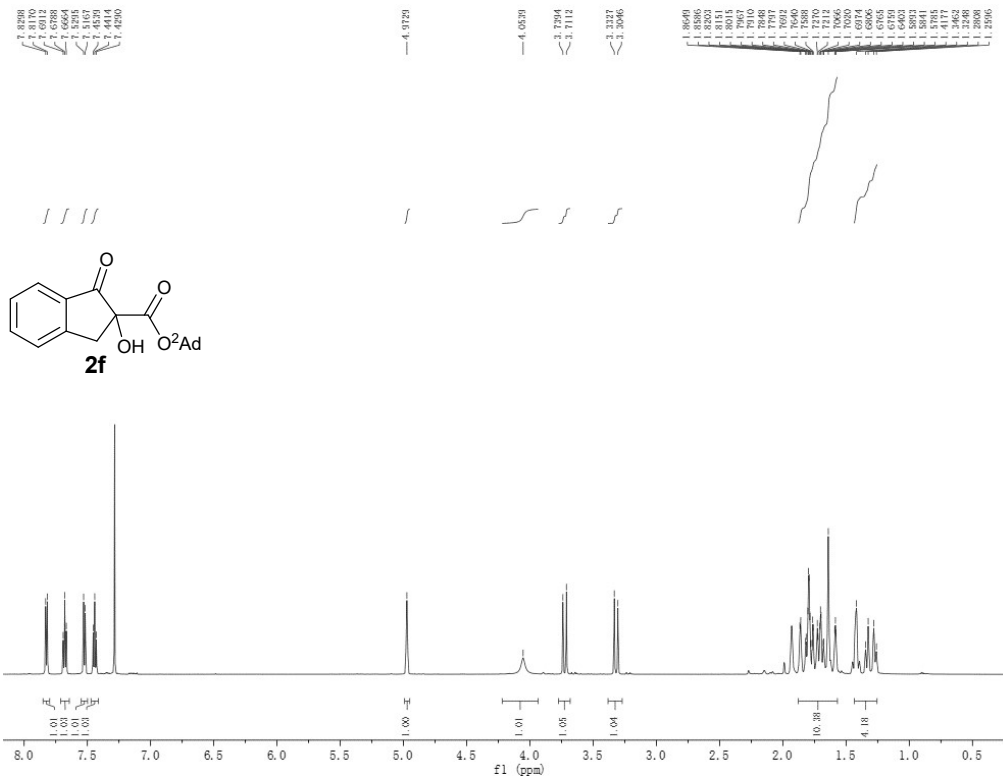
O
OH
O1Ad
2e
f1 (ppm)


O
O
OH
O1Ad
2e
f1 (ppm)



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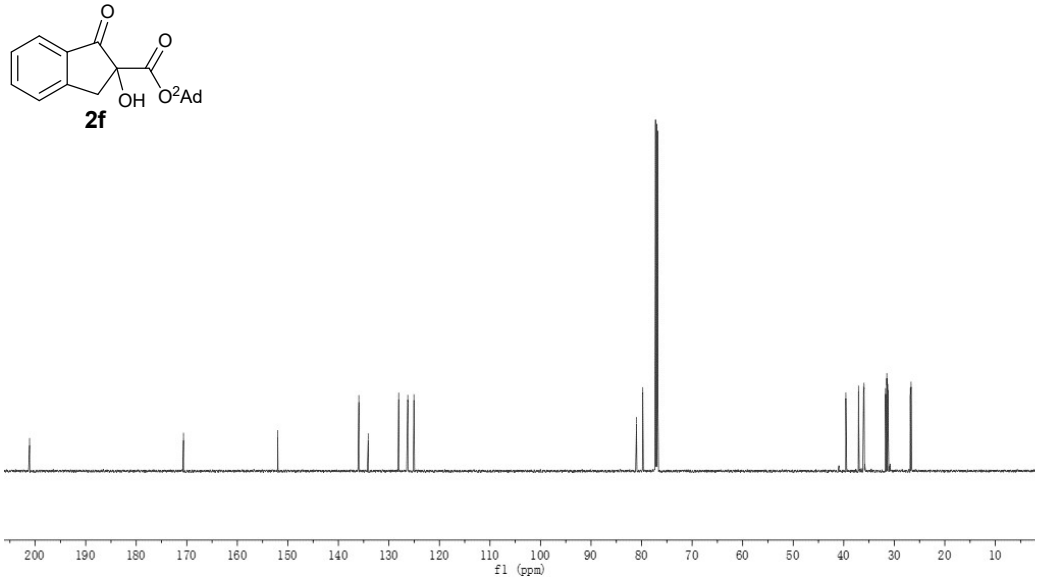
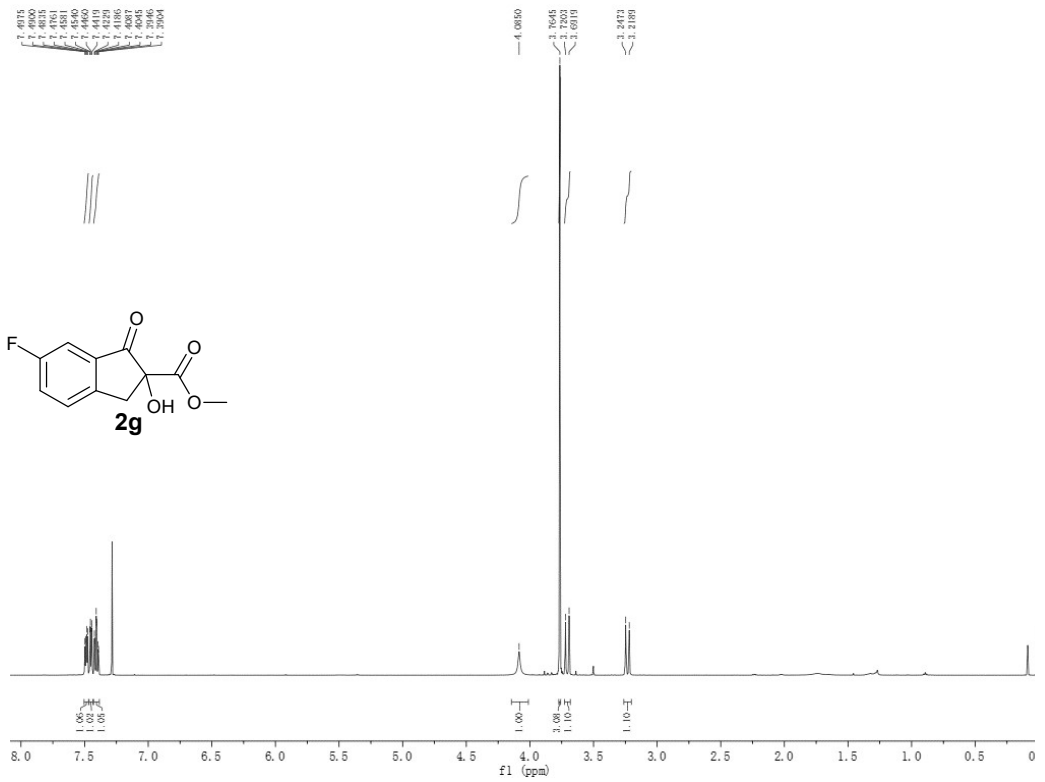


2f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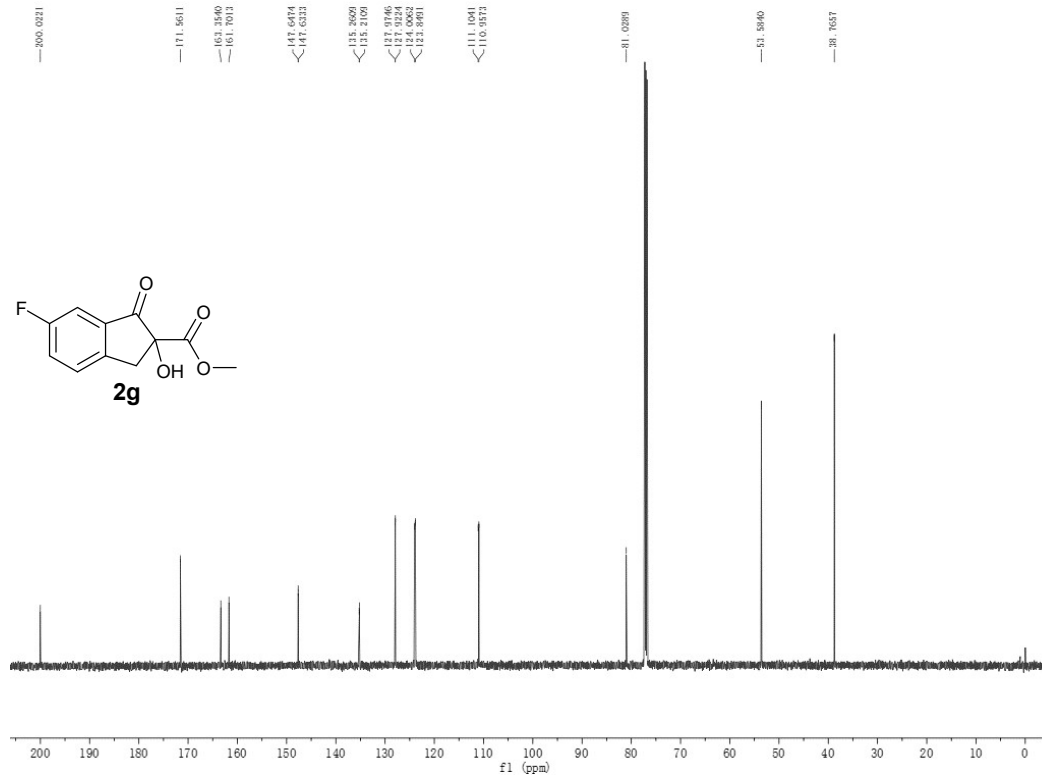
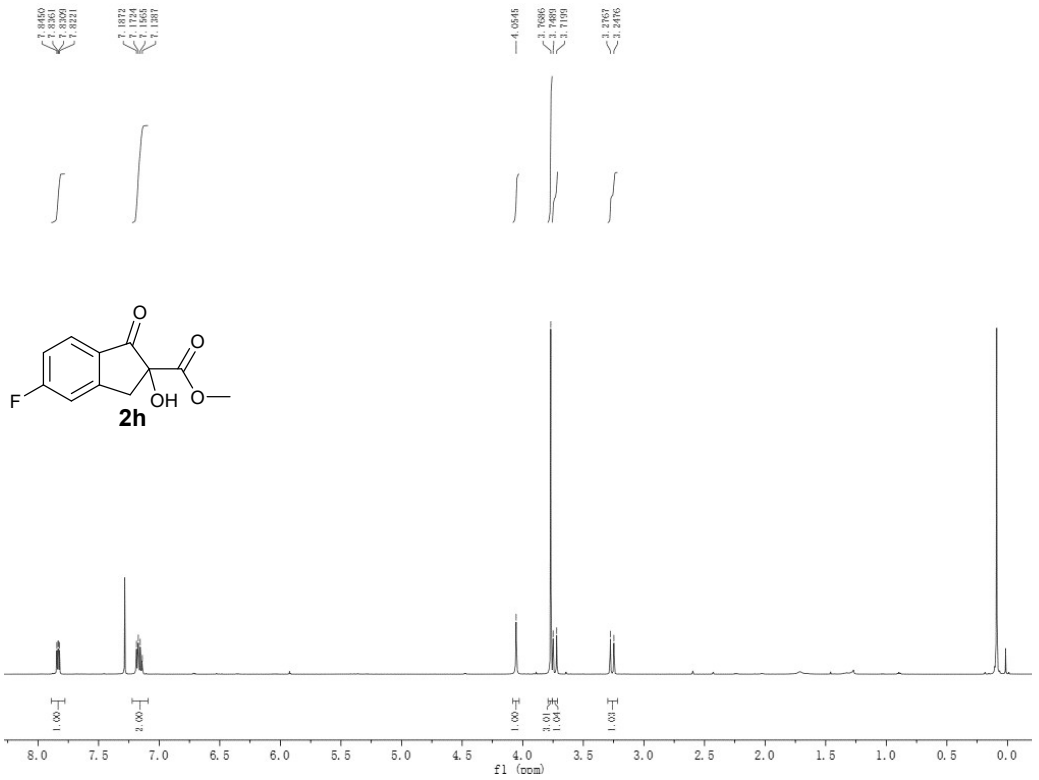
O
O
O
OH
2g
f1 (ppm)


F
O
O
O
OH
2g
f1 (ppm)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4.0545
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3.7489
3.7199
3.2767
2.2476
O
O
F
OH
O
2h
1.00
2.00
1.00
3.01
1.04
1.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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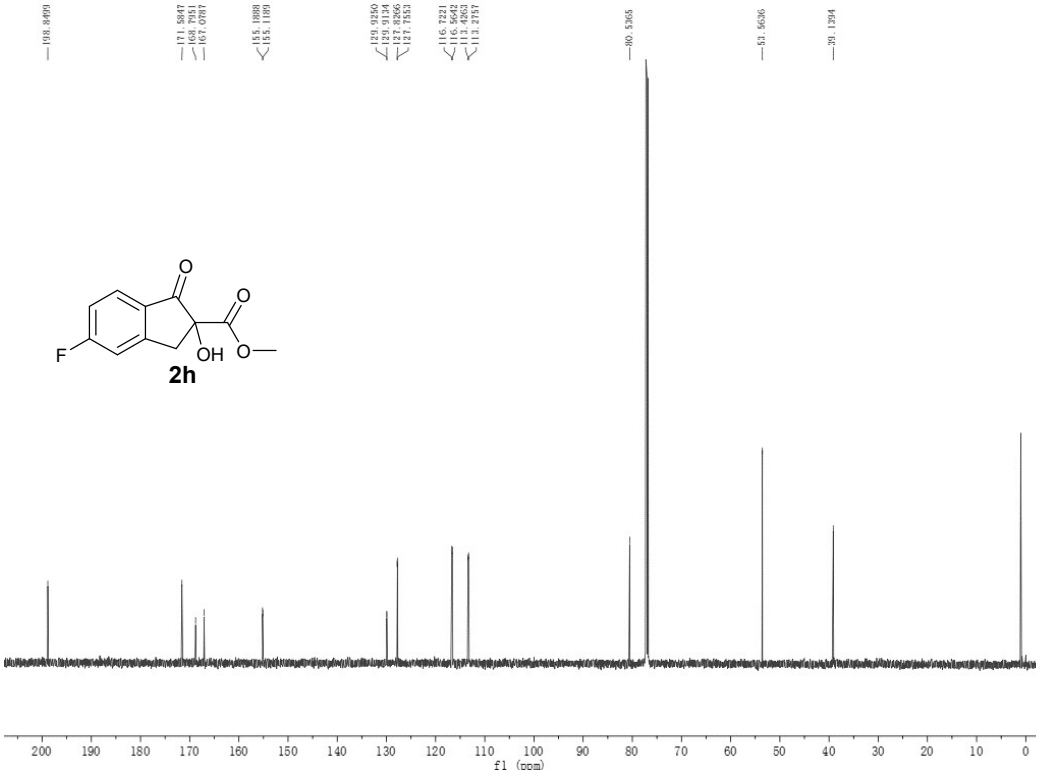
0.0
f1 (ppm)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167.0787
155.1888
155.1089
129.9250
129.9134
127.8265
127.7953
116.7221
116.5642
113.4583
113.2757
80.5365
53.8536
39.1394
O
O
F
OH
O
2h
200
190
180
170
160
150
140
130
120
110
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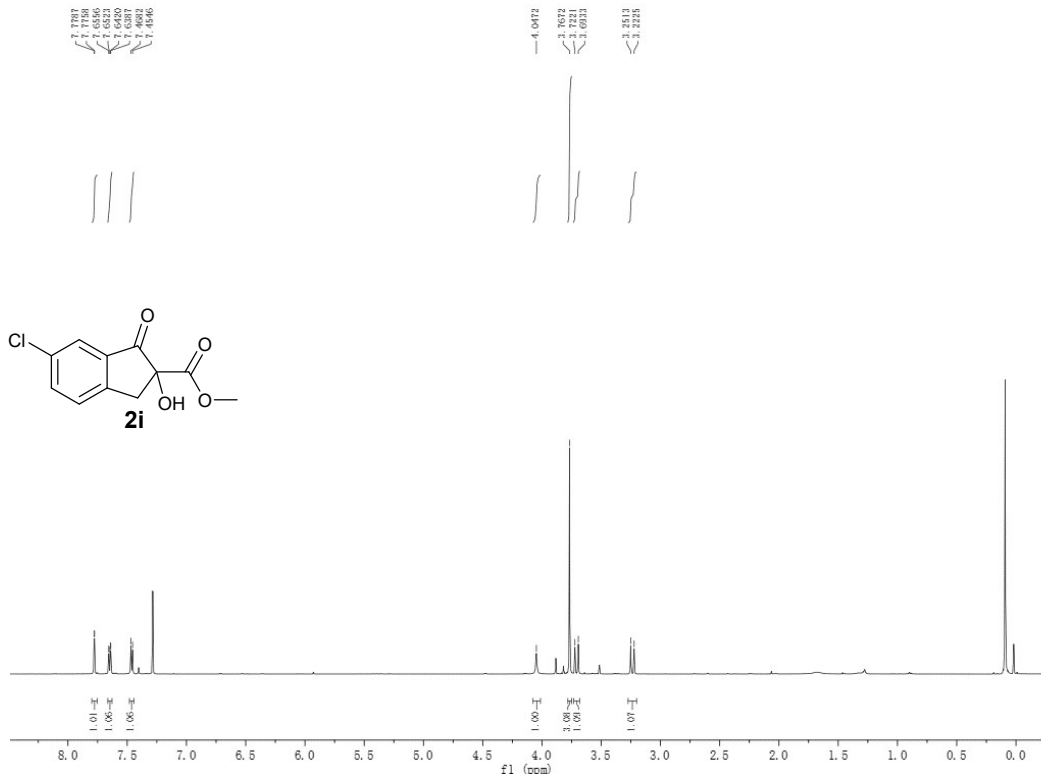
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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O
OH
O
2i
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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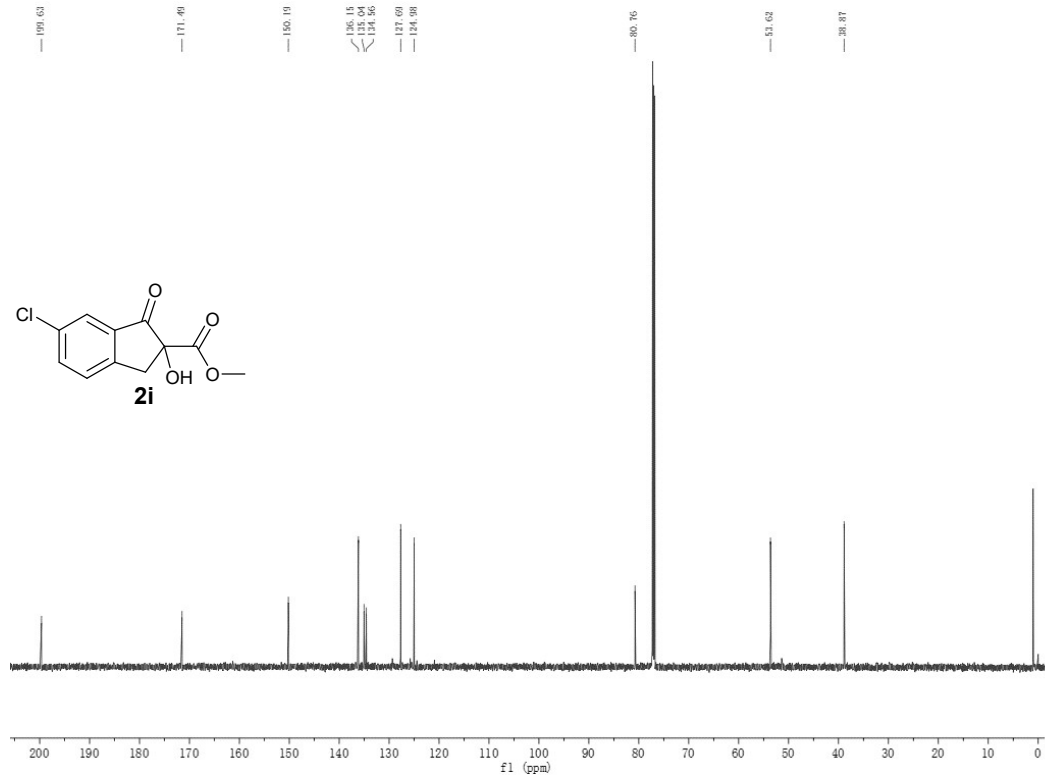
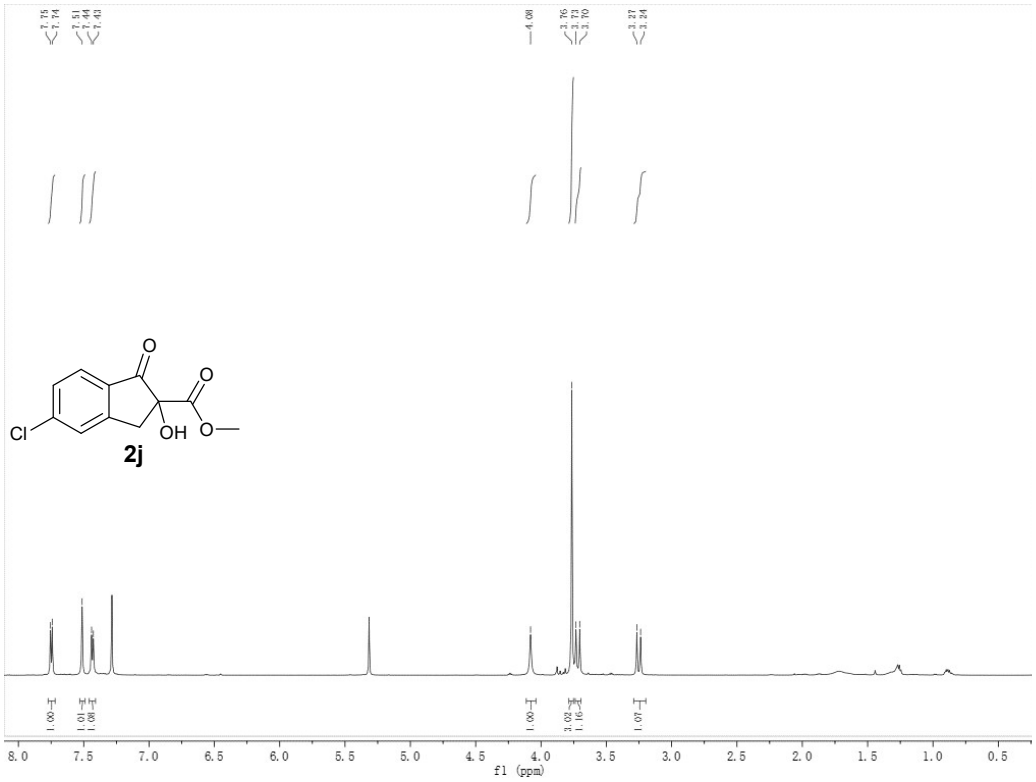
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Cl
O
O
OH
O
2i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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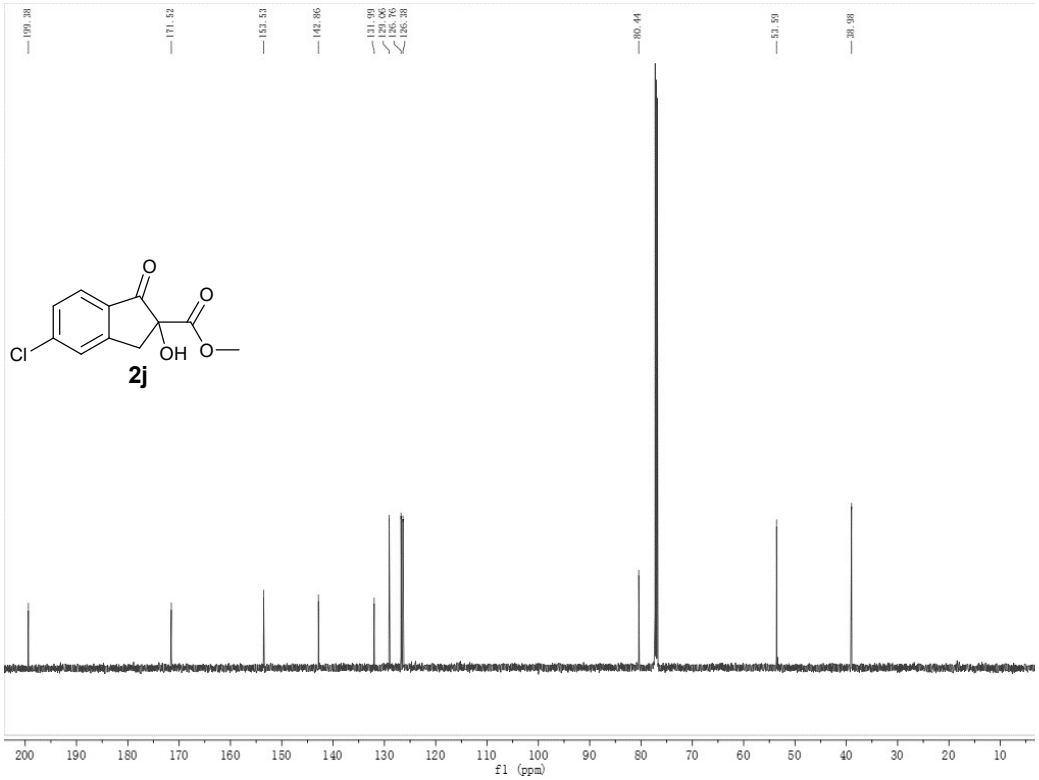
3.27
3.24
Cl
OH
O
O
O
2j
1.00
1.01
1.00
1.00
3.02
1.16
1.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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153.53
142.86
131.99
129.06
126.95
126.38
80.44
53.89
39.98
Cl
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O
O
2j
200
190
180
170
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140
130
120
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100
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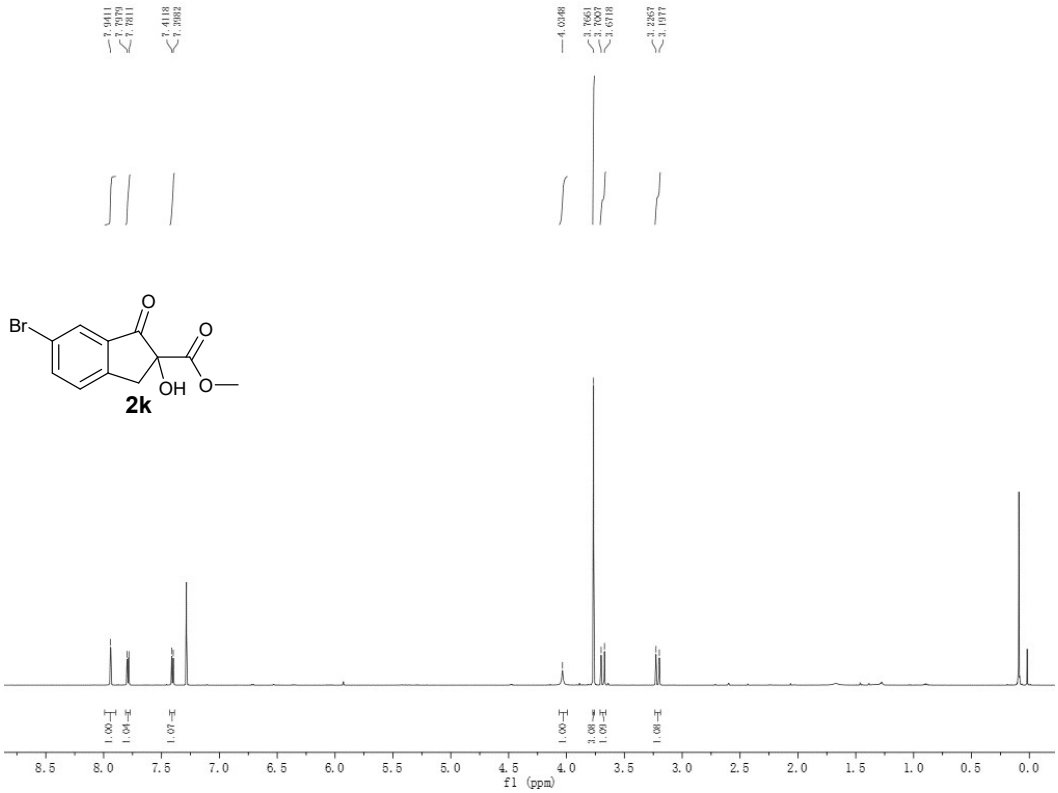
60
50
40
30
20
10
f1 (ppm)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7.7811
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7.3982
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3.7661
3.7007
3.6718
3.2267
3.1977
Br
O
O
OH
O
2k
1.00
1.04
1.07
1.00
3.08
1.07
1.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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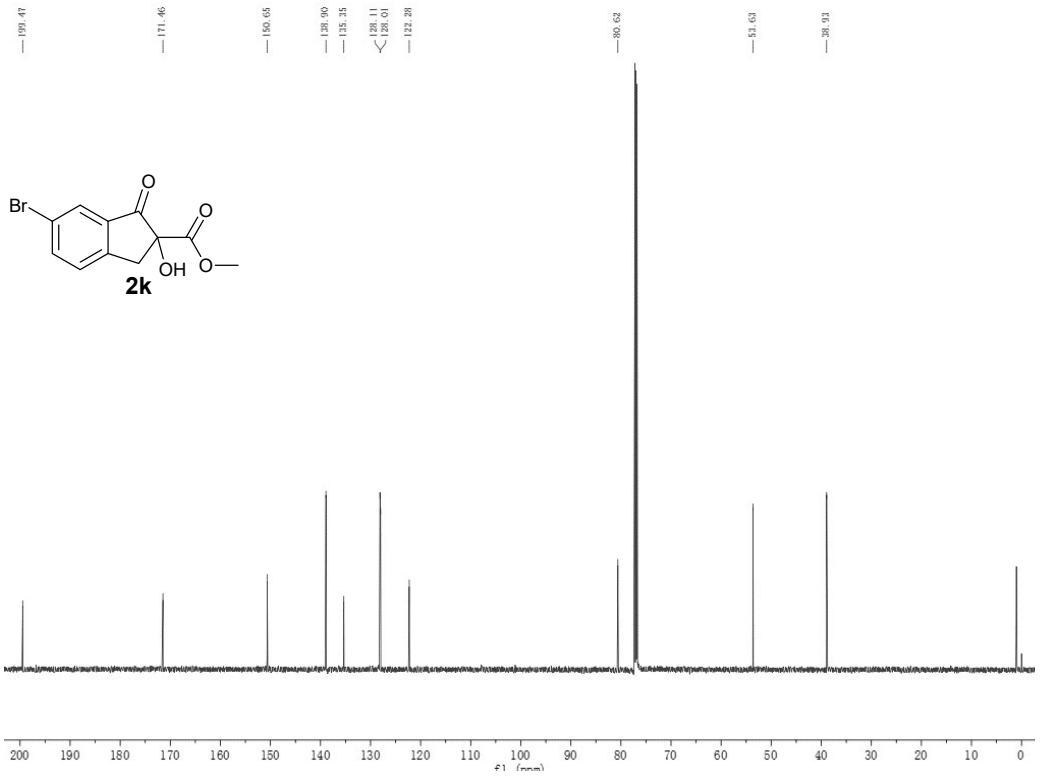
0.0
f1 (ppm)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135.35
128.11
128.01
122.28
80.62
53.63
28.93
Br
O
O
OH
O
2k
200
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150
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110
100
90
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70
60
50
40
30
20
10
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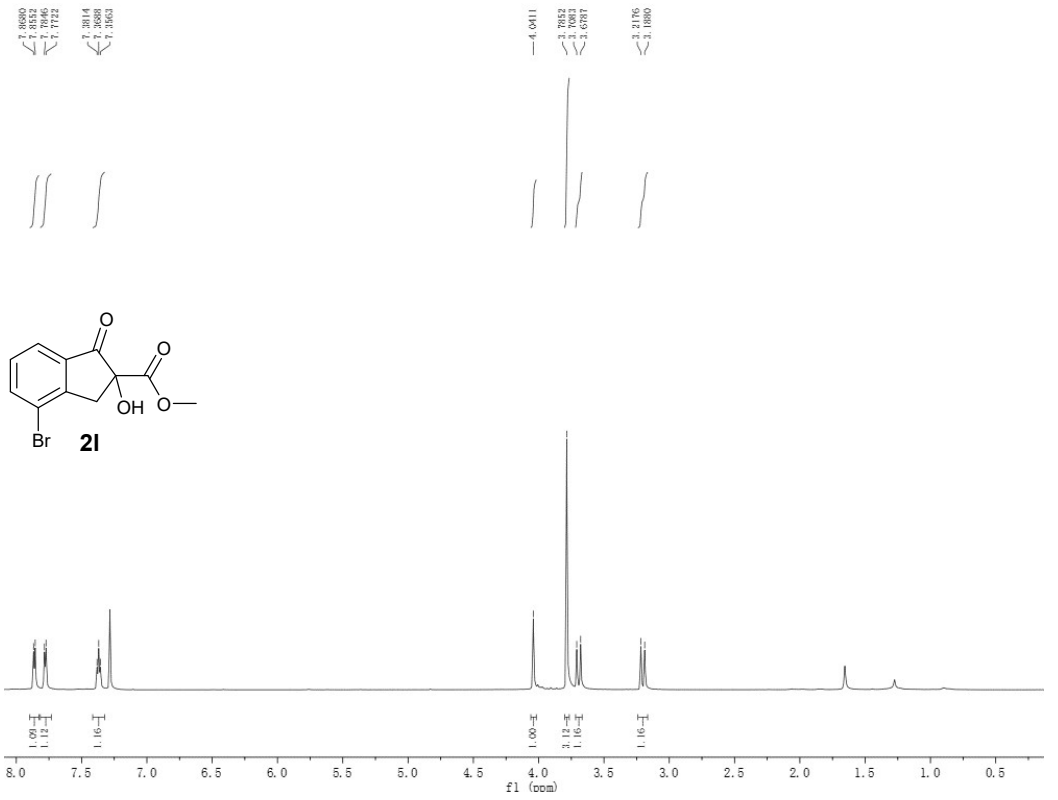
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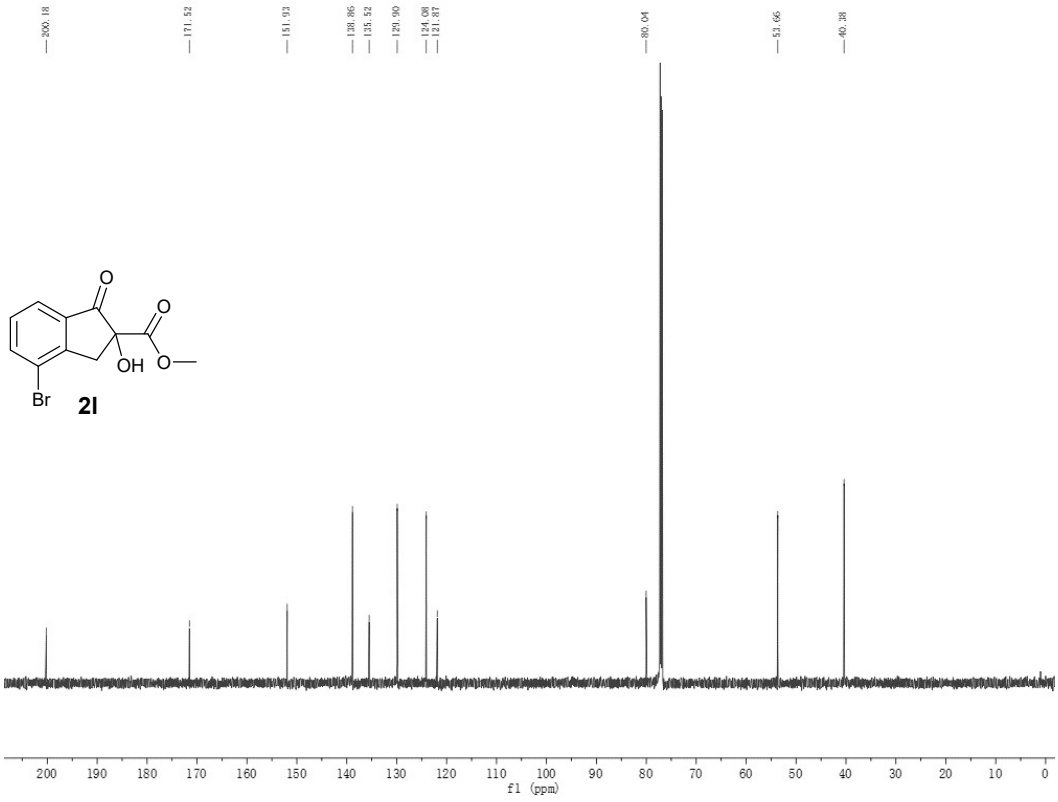
3.7852
3.7063
3.6787
3.2176
1.1680
O
O
OH
O—
Br
2l
1.09
1.12
1.16
1.00
2.12
1.16
1.16
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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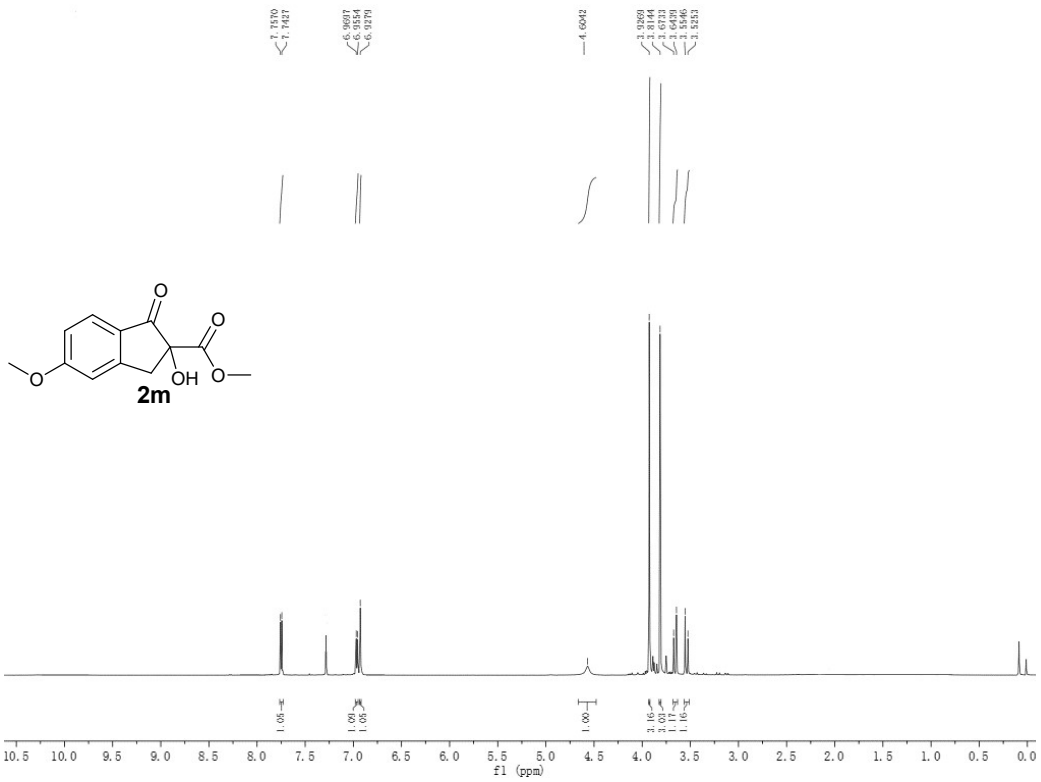
138.86
135.52
129.90
124.08
121.87
80.04
53.66
40.38
O
O
OH
O—
Br
2l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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3.9269
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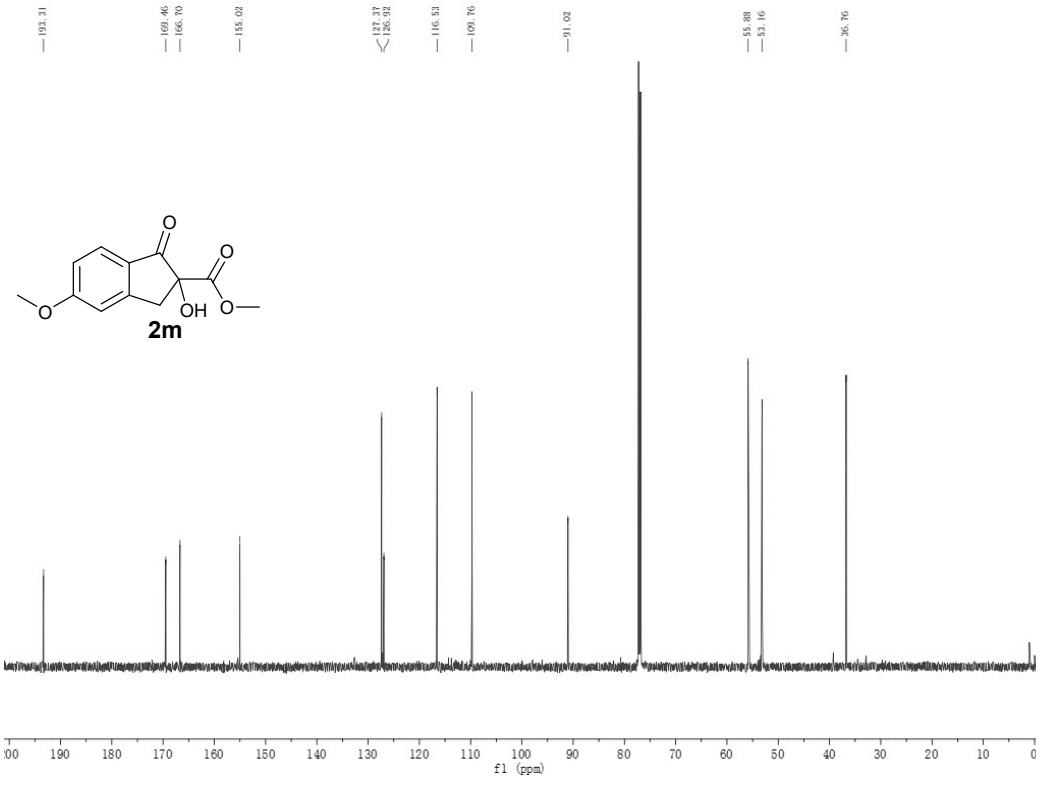
3.6733
3.6589
3.5546
3.5253
O
O
O
OH
O
2m
1.05
1.09
1.05
1.00
3.16
3.03
3.17
1.16
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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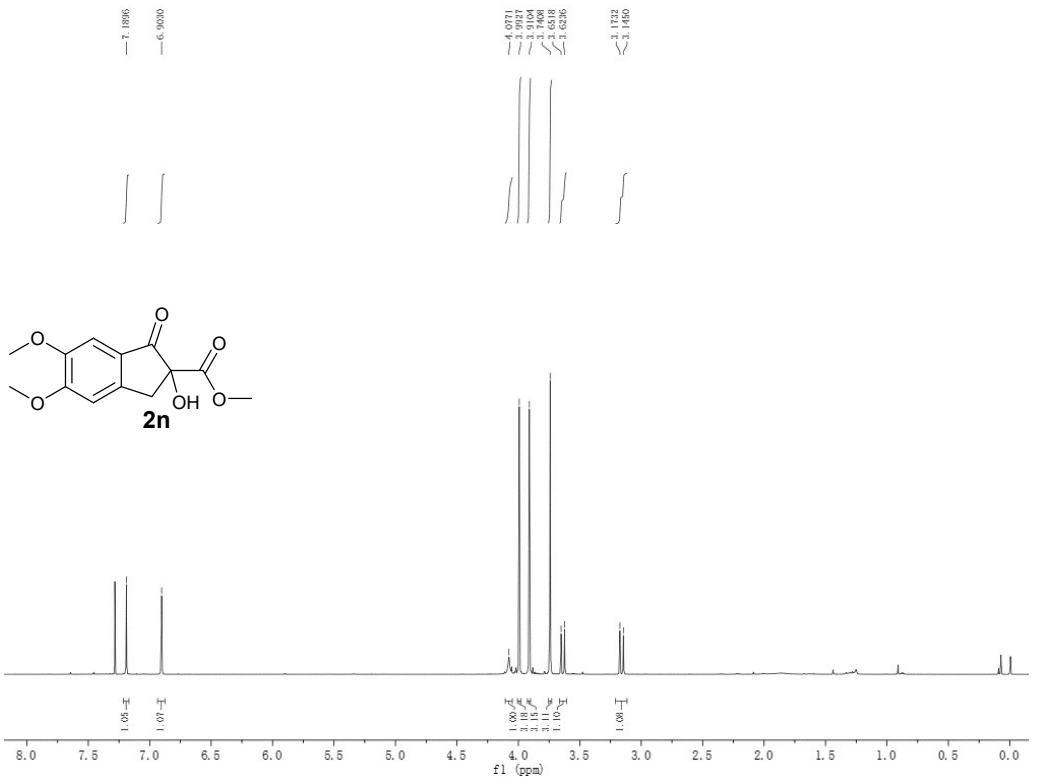
127.37
126.92
116.53
109.76
91.02
55.88
53.16
35.76
O
O
O
OH
O
2m
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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3.1732
3.1450
O
O
O
O
OH
O
2n
1.05
1.07
1.00
3.18
3.15
3.11
1.10
1.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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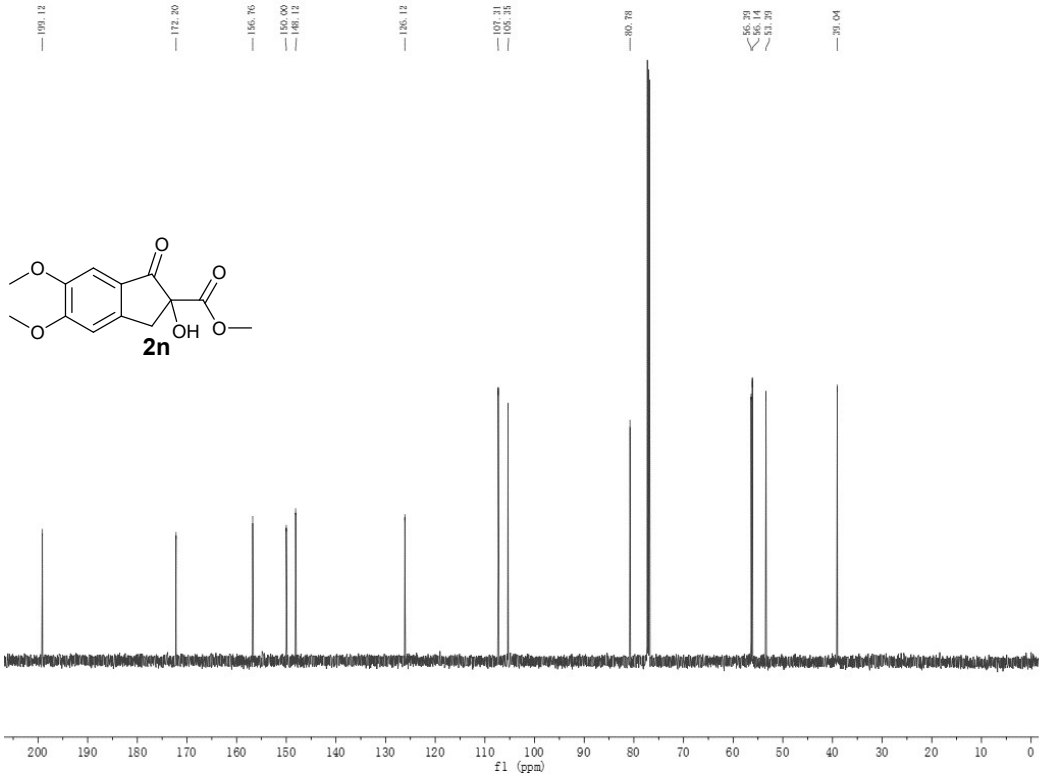
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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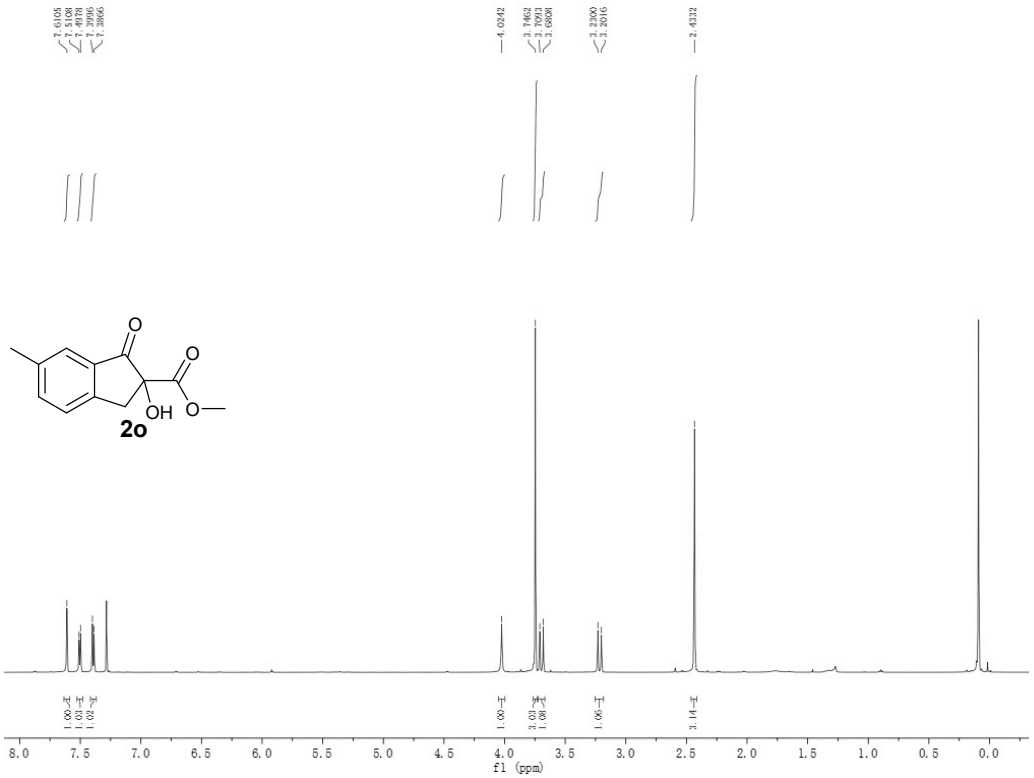
80.78
56.39
56.14
53.39
39.04
O
O
O
O
OH
O
2n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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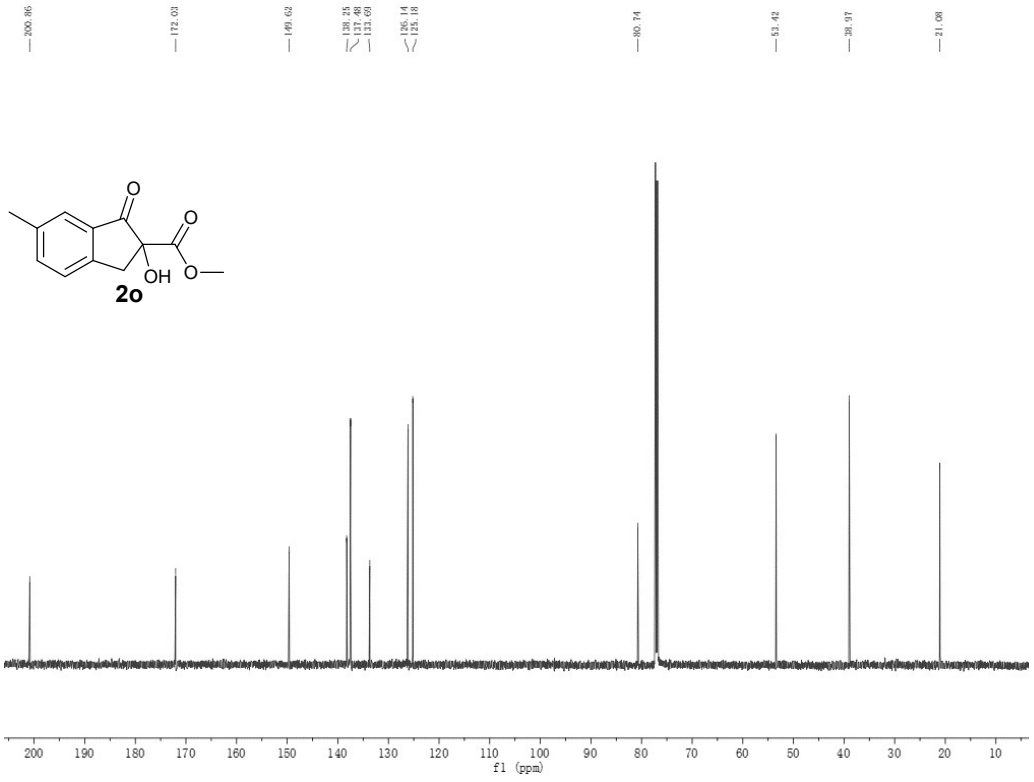
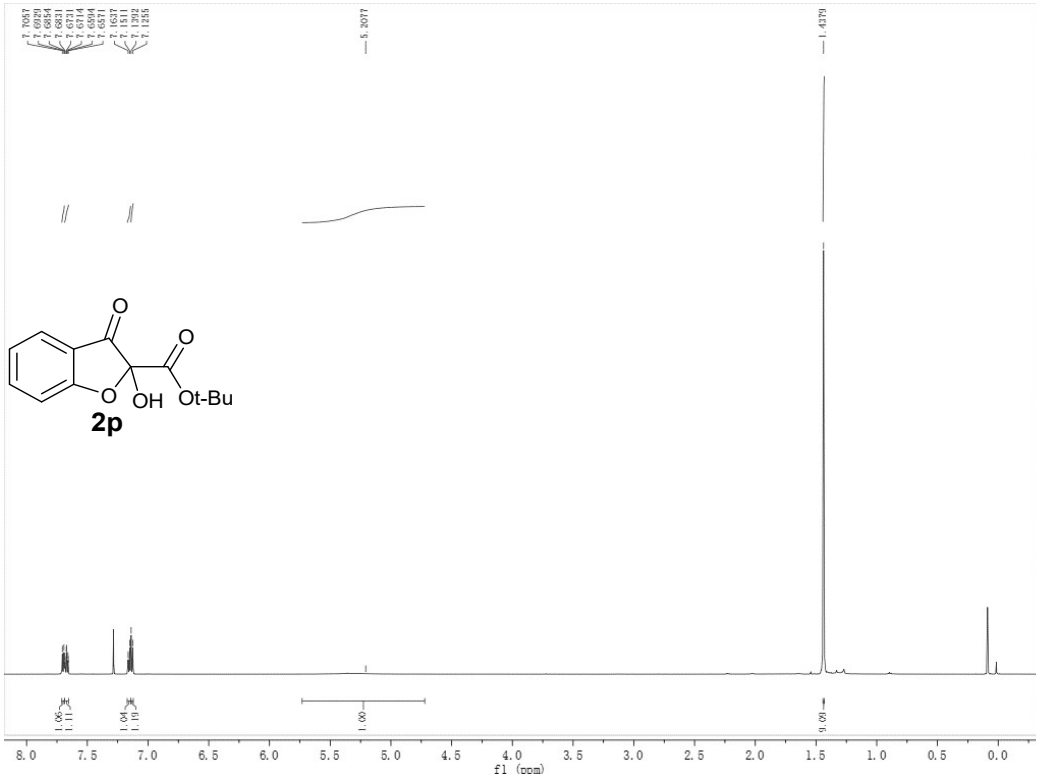
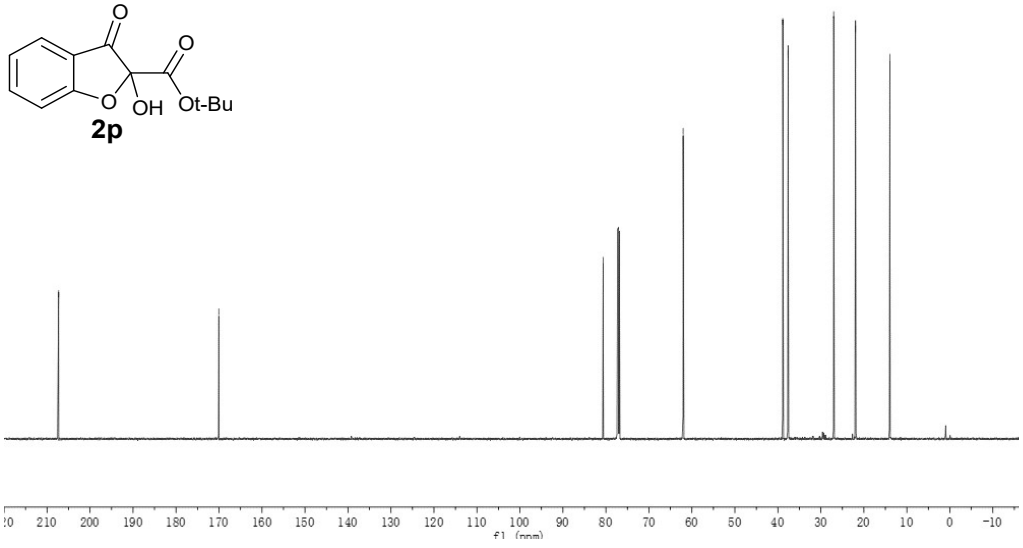
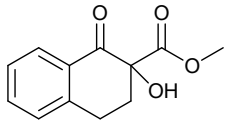
7.5108
7.4978
7.3996
7.3865
4.0242
3.7462
3.7091
3.6868
3.2300
3.2016
2.4332
O
O
OH
O
2o
1.00
1.01
1.02
1.00
3.03
1.08
1.06
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


200.86
172.03
149.62
138.25
137.48
133.69
126.14
125.18
80.74
53.42
28.97
21.08
O
O
OH
O
2o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
O
O
OH
Ot-Bu
2p
fl (ppm)


O
O
O
OH
Ot-Bu
2p
fl (ppm)



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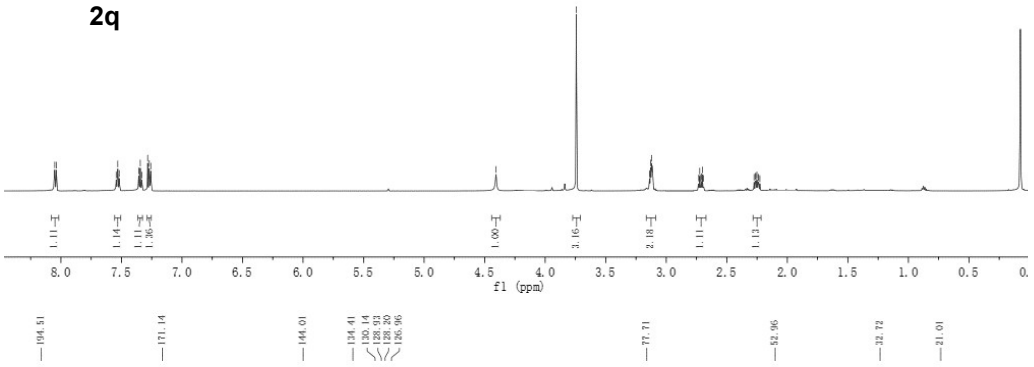

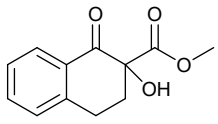

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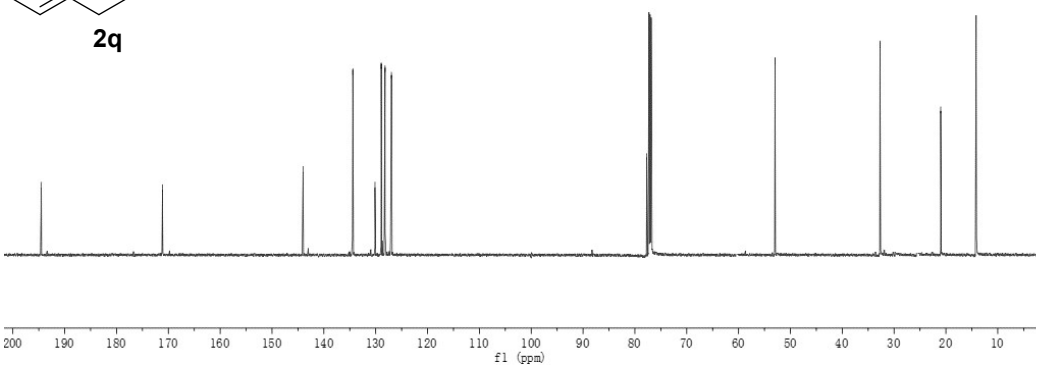

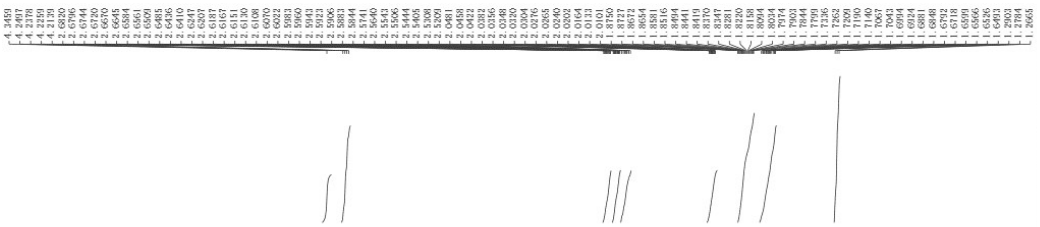

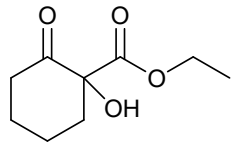

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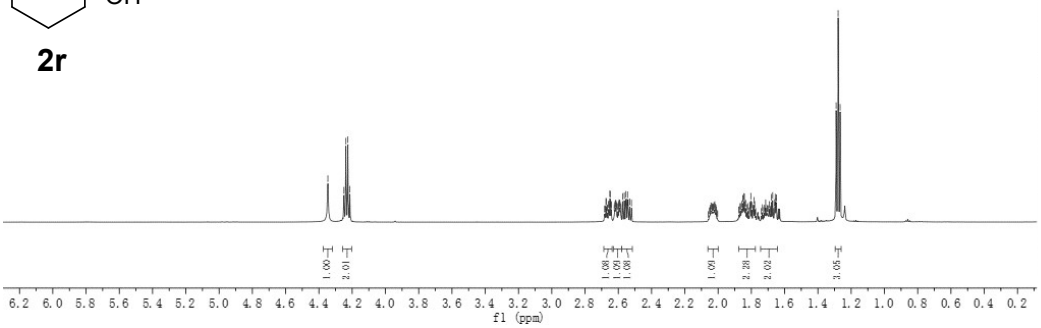

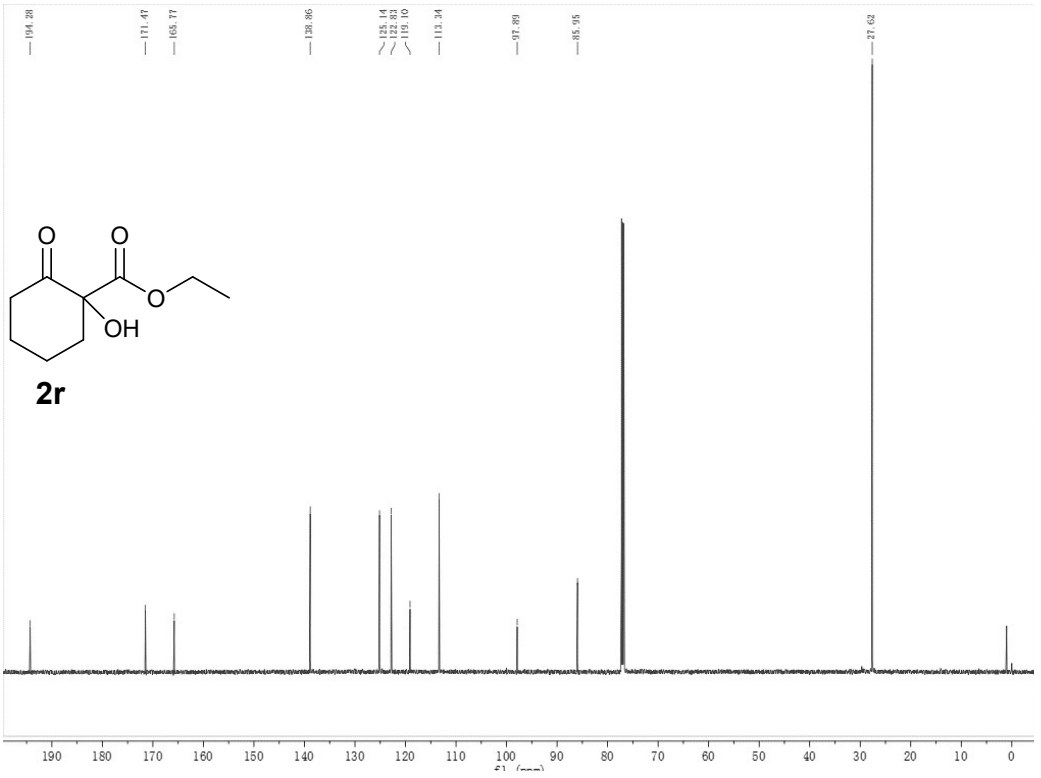

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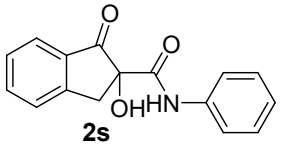

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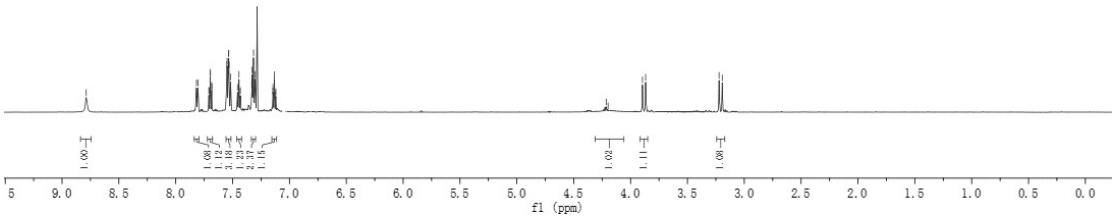

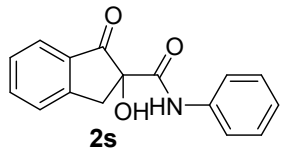

2s