Asymmetric bis(oxazolines)-Ni(II) catalyzed α-hydroxylation of cyclic β-keto esters under visible light

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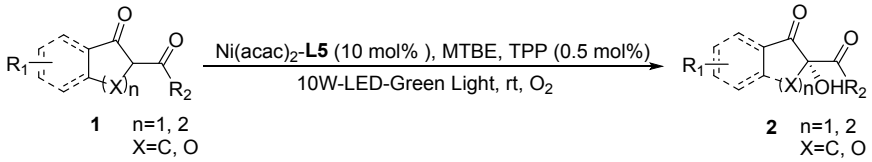
List of Contents

1. General information

Unless otherwise stated, all regents were purchased from commercial suppliers and used without purifications. 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 254 nm. Column chromatography was performed on silica-gel. ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ on Bruker AVANCE III (600 MHz), Bruker AVANCE III (500 MHz) or Bruker Ascend 400 (400 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. Chemical shifts (d) are expressed in ppm and coupling constants J are given in Hz. Melting points (m.p.) were obtained using a Büchi B-545 apparatus and uncorrected. 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 MassHunter software. Chiral HPLC analyses were performed using a JASCO LC-2000 Plus and an Agilent 1260 chromatograph (for compound **2**). Specific rotations were performed on a Rudolph Autopol IV automatic polarimeter. The photocatalytic oxidation reactions were carried out in a temperature controlled WATTCAS Parallel Light Reactor (WP-TEC-1020HSL).

All admantyl esters substrates **1** were prepared by transesterification[1] of methyl ester which was prepared according to the previous method[2]. The ethyl ester substrate **1o** and the isopropyl ester substrate **1q** and the tert-butyl ester substrates **1r,1s** were prepared according to the reported procedures.[3,4,5]

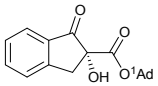
2. Typical experimental procedure for the enantioselective hydroxylation under visible light conditions



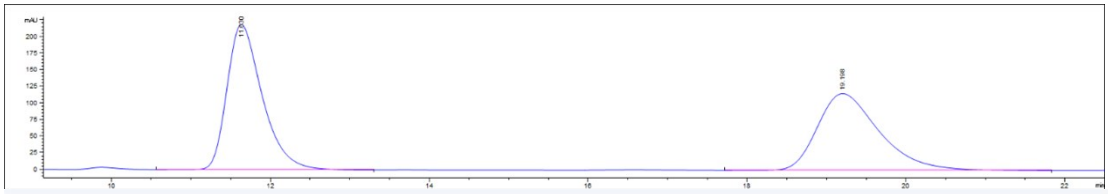
$Ni(acac)_2$(2.57 mg, 0.01 mmol), **L5** (4.86 mg, 0.01 mmol) and MTBE (2 mL) were added to a test tube. The solution was stirred at room temperature for 0.5 h. Then the 1-adamantyl (1-Ad) indanone carboxylate **1** (0.1 mmol) and TPP (0.3 mg, 0.0005 mmol) were added. After the air in the tube is vacuumed and replaced with oxygen. The mixture was stirred for 3h under an irradiation of 525 nm green light and the completion of the reaction was checked by TLC. The reaction mixture was condensed and purified by column chromatography on silica gel to give the product **2**. The enantiomeric excess was determined by HPLC using a Chiralpak AD-H or OD-H or ID column.

3. Characterization data and HPLC spectra

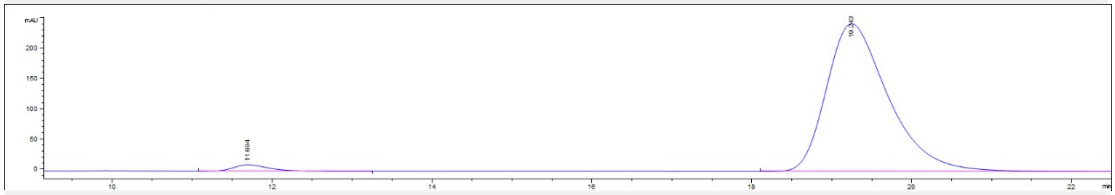
(R)-1-Adamantanyl 2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2a)



Compound was isolated as a white solid (99% yield, 32.3 mg) after column chromatography on silica-gel. mp: 80-82 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ7.80 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 4.06 (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. $[\alpha]_D^{18}$ =-28 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/i-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R =19.243 min, minor enantiomer: t_R =11.694 min. 95% *ee*. HRMS exact mass calcd for $C_{20}H_{22}O_4Na^+$ (M+Na) requires *m/z* 349.1410. Found *m/z* 349.1417.

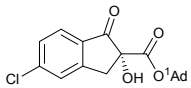


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.63	6756.4	219.1	0.4697	0.65	51.782	BB
2	19.198	6291.5	116	0.8248	0.647	48.218	BB

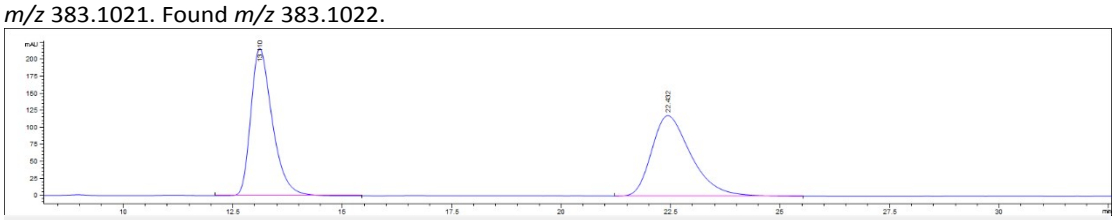


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.694	316.3	10.5	0.4573	0.669	2.368	BB
2	19.243	13040.1	242.9	0.8143	0.639	97.632	BB

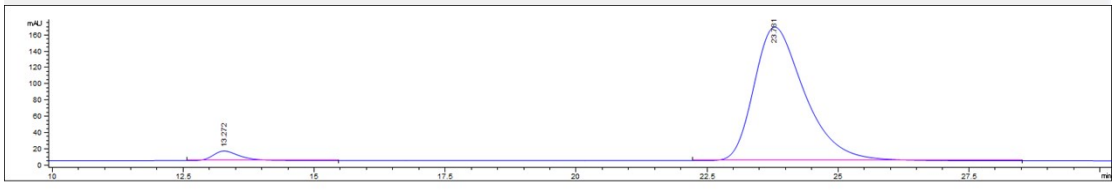
(R)-1-Adamantanyl 2-hydroxy-5-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2b)



Compound was isolated as a white solid (97% yield, 34.9 mg) after column chromatography on silica-gel. mp: 162-165 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.48 (s, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 4.09 (s, 1H), 3.63 (d, *J* = 17.3 Hz, 1H), 3.20 (d, *J* = 17.3 Hz, 1H), 2.13 (s, 3H), 1.97 (s, 6H), 1.61 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.0, 169.8, 153.7, 142.4, 132.5, 128.8, 126.5, 126.1, 84.2, 80.5, 40.9, 39.3, 35.8, 30.8. $[\alpha]_D^{18}$ = -56 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/i-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R =23.781 min, minor enantiomer: t_R =13.272 min. 93% ee. HRMS exact mass calcd for $C_{20}H_{21}ClO_4Na^+$ (M+Na) requires *m/z* 383.1021. Found *m/z* 383.1022.

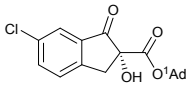


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.11	7388.7	216.5	0.5182	0.661	49.917	BB
2	22.432	7413.2	118.1	0.952	0.655	50.083	BB

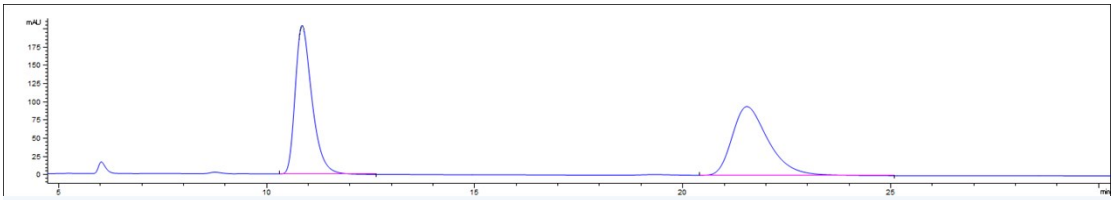


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.272	417.9	11.8	0.5333	0.647	3.627	BB
2	23.781	11103.3	165.1	1.0184	0.649	96.373	BB

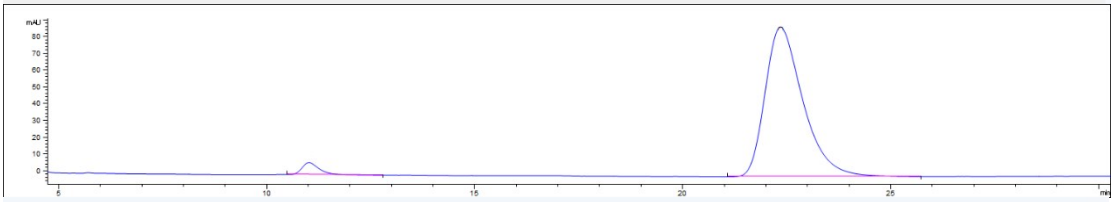
(R)-1-Adamantanyl 2-hydroxy-6-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2c)



Compound was isolated as a yellow solid (98% yield, 35.1 mg) after column chromatography on silica-gel. mp: 89-91 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 1.5 Hz, 1H), 7.62 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 4.06 (s, 1H), 3.63 (d, *J* = 17.2 Hz, 1H), 3.19 (d, *J* = 17.2 Hz, 1H), 2.15 (s, 3H), 1.98 (d, *J* = 2.5 Hz, 6H), 1.62 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.3, 169.8, 150.4, 135.8, 135.5, 134.2, 127.5, 124.7, 84.3, 80.9, 40.9, 39.2, 35.8, 30.8. $[\alpha]_D^{18}$ = -20 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/i-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R =22.353 min, minor enantiomer: t_R =11.012 min. 93% ee. HRMS exact mass calcd for $C_{20}H_{21}ClO_4Na^+$ (M+Na) requires *m/z* 383.1021. Found *m/z* 383.1023.

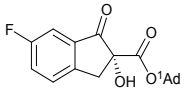


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.844	5653.3	202.9	0.4211	0.643	49.905	BB
2	21.544	5674.8	93.8	0.9179	0.644	50.095	BB

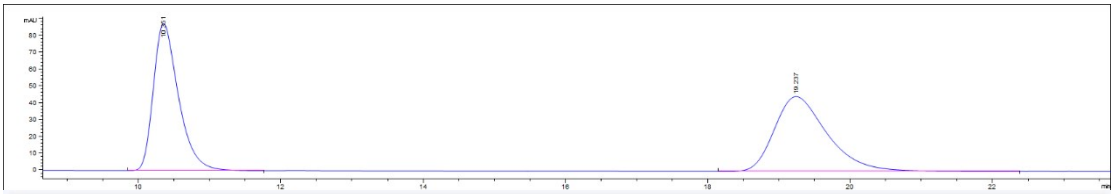


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.012	208.1	7.2	0.4321	0.635	3.522	BB
2	22.353	5700.9	89.9	0.9576	0.642	96.478	BB

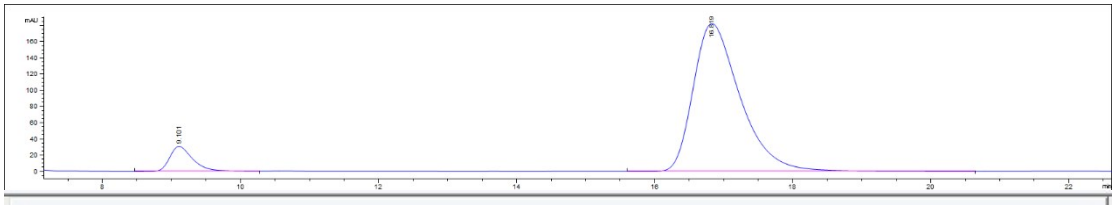
(R)-1-Adamantyl 2-hydroxy-6-fluorine-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2d)



Compound was isolated as a white solid (92% yield, 31.7 mg) after column chromatography on silica-gel. mp: 57-59 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.5, 4.6 Hz, 1H), 7.44 (dd, *J* = 7.5, 2.5 Hz, 1H), 7.37 (td, *J* = 8.5, 2.5 Hz, 1H), 4.10 (s, 1H), 3.62 (d, *J* = 16.9 Hz, 1H), 3.19 (d, *J* = 16.8 Hz, 1H), 2.14 (s, 3H), 1.97 (d, *J* = 2.9 Hz, 6H), 1.61 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.6, 169.8, 162.4(d, $^1J_{C\text{-}F}$=247.4), 147.8(d, $^4J_{C\text{-}F}$=2.1), 135.7(d, $^3J_{C\text{-}F}$=7.5), 127.7(d, $^3J_{C\text{-}F}$=7.8), 123.5(d, $^2J_{C\text{-}F}$=23.5), 110.7(d, $^2J_{C\text{-}F}$=22.0), 84.2, 81.2, 40.9, 39.1, 35.8, 30.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ -113.36 (s, 1F). $[\alpha]_D^{18}$ = -16 (c =1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R = 16.819 min, minor enantiomer: t_R = 9.101 min. 85% ee. HRMS exact mass calcd for $C_{20}H_{21}FO_4Na^+$ (M+Na) requires m/z 367.1316. Found m/z 367.1320.

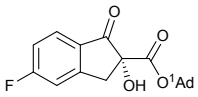


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.351	2130.1	87	0.3717	0.643	48.303	BB
2	19.237	2279.7	44.2	0.7794	0.654	51.697	BB

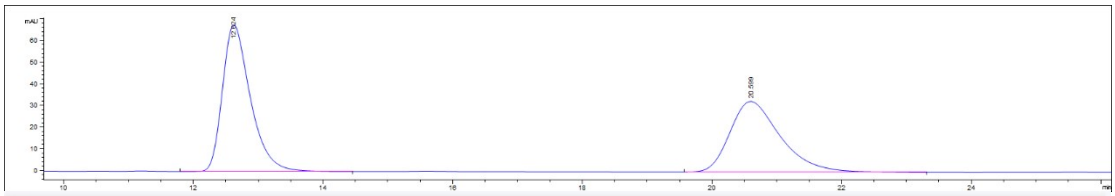


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.101	714	30.7	0.349	0.631	7.697	BB
2	16.819	8562.8	181.6	0.716	0.619	92.303	BB

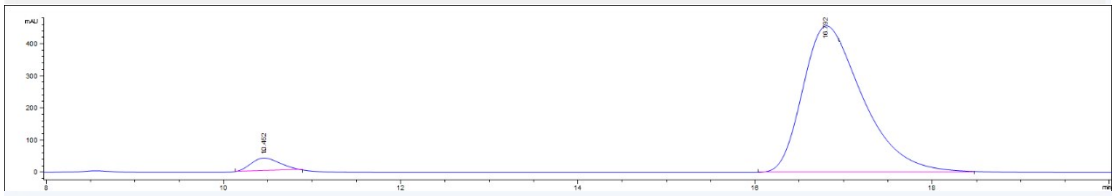
(*R*)-1-Adamantanyl 2-hydroxy-5-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2e)



Compound was isolated as a white solid (94% yield, 32.3 mg) after column chromatography on silica-gel. mp: 120-122 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.4, 5.3 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.13 (t, *J* = 8.7 Hz, 1H), 4.08 (s, 1H), 3.65 (d, *J* = 17.3 Hz, 1H), 3.22 (d, *J* = 17.3 Hz, 1H), 2.14 (s, 3H), 1.98 (d, *J* = 2.9 Hz, 6H), 1.61 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.5, 169.9, 167.7(d, $^{1}J_{C\text{-}F}$=256.7), 155.3(d, $^{3}J_{C\text{-}F}$=10,4), 130.4(d, $^{4}J_{C\text{-}F}$=1.7), 127.4(d, $^{3}J_{C\text{-}F}$=10.6), 116.3(d, $^{2}J_{C\text{-}F}$=23.7), 113.1(d,$^{2}J_{C\text{-}F}$=22.5), 84.2, 80.7, 40.9, 39.4, 35.9, 30.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ -100.35 (s, 1F). $[\alpha]_D^{18}$ = -48 (c =1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R =16.792 min, minor enantiomer: t_R =10.452 min. 92% *ee.* HRMS exact mass calcd for $C_{20}H_{21}FO_4Na^+$ (M+Na) requires *m/z* 367.1316. Found *m/z* 367.1319.



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	12.624	2013.3	67.4	0.4525	0.646	53.473	BB
2	20.599	1751.8	32.4	0.8185	0.656	46.527	BB



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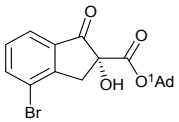
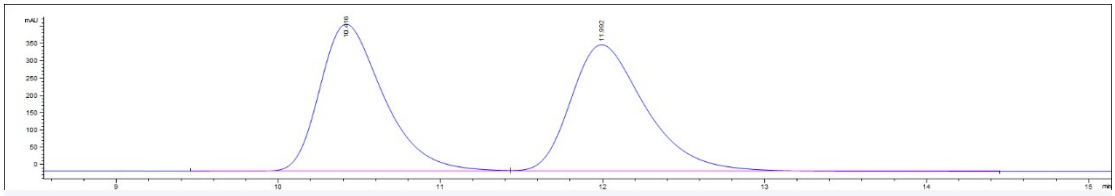
1	10.452	888.1	39.6	0.3737	0.79	3.982	MM
2	16.792	21413.8	457.2	0.7806	0.633	96.018	MM

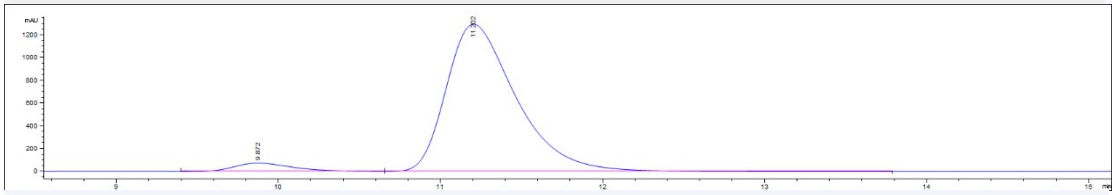
(R)-1-Adamantyl 2-hydroxy-4-bromine-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2f)



Compound was isolated as a white solid (94 % yield, 38.0 mg) after column chromatography on silica-gel. mp: 152-154 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 4.09 (s, 1H), 3.61 (d, *J* = 17.5 Hz, 1H), 3.16 (d, *J* = 17.5 Hz, 1H), 2.15 (s, 3H), 1.99 (d, *J* = 2.9 Hz, 6H), 1.62 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.8, 169.7, 152.1, 138.5, 136.0, 130.0, 123.8, 121.7, 84.3, 80.3, 40.9, 40.7, 35.8, 30.8. $[\alpha]_D^{18}$ =-78 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R =11.202 min, minor enantiomer: t_R =9.872 min. 91% *ee.* HRMS exact mass calcd for $C_{20}H_{21}BrO_4Na^+$ (M+Na) requires *m/z* 427.0515. Found *m/z* 427.0514.

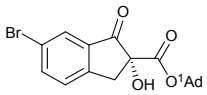


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.416	11636.1	424.4	0.4178	0.661	49.767	BV
2	11.992	11744.9	365.5	0.4869	0.658	50.233	VB

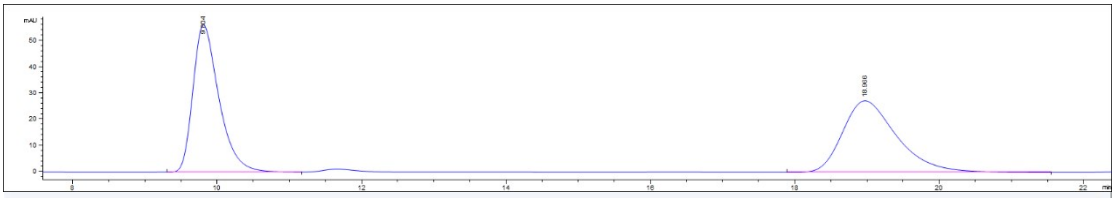


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.872	1846	73.9	0.3775	0.645	4.553	BV
2	11.202	38700.9	1295	0.4527	0.602	95.447	VB

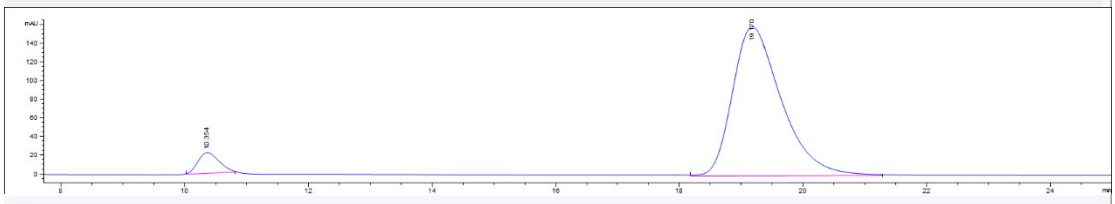
(R)-1-Adamantyl 2-hydroxy-6-bromine-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2g)



Compound was isolated as a colorless oil (89 % yield, 36.0 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 4.09 (s, 1H), 3.61 (d, *J* = 17.2 Hz, 1H), 3.16 (d, *J* = 17.2 Hz, 1H), 2.14 (s, 3H), 1.97 (d, *J* = 2.5 Hz, 6H), 1.61 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.1, 169.7, 150.9, 138.5, 135.8, 127.8, 122.0, 84.3, 80.7, 77.3, 40.9, 39.2, 35.8, 30.8. $[\alpha]_D^{18}$ = -23 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R =19.170 min, minor enantiomer: t_R =10.354 min. 88% *ee.* HRMS exact mass calcd for $C_{20}H_{21}BrO_4Na^+$ (M+Na) requires *m/z* 427.0515. Found *m/z* 427.0515.

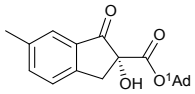


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.804	1407.3	56.3	0.3775	0.641	49.649	BB
2	18.966	1427.2	27.4	0.7948	0.66	50.351	BB

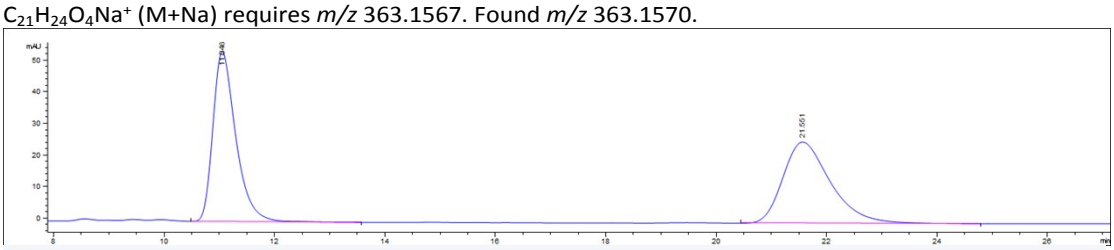


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.354	549.8	22.7	0.4033	0.782	5.882	MM
2	19.17	8797.7	159.6	0.919	0.657	94.118	MM

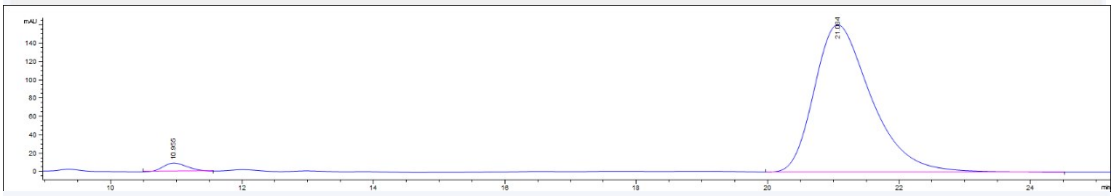
(R)-1-Adamantyl 2-hydroxy-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2h)



Compound was isolated as a white solid (95% yield, 32.3mg) after column chromatography on silica-gel. mp: 104-106 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 4.02 (s, 1H), 3.62 (d, *J* = 16.9 Hz, 1H), 3.17 (d, *J* = 16.9 Hz, 1H), 2.43 (s, 3H), 2.13 (s, 3H), 1.99 (d, *J* = 2.9 Hz, 6H), 1.62 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.5, 170.3, 149.8, 137.9, 137.1, 134.1, 125.9, 124.9, 83.8, 80.8, 40.9, 39.2, 35.9, 30.8, 21.1. $[\alpha]_D^{18}$ = -15 (c =1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R =21.064 min, minor enantiomer: t_R =10.955 min. 95% *ee.* HRMS exact mass calcd for $C_{21}H_{24}O_4Na^+$ (M+Na) requires *m/z* 363.1567. Found *m/z* 363.1570.

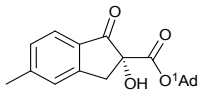


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.046	1552.1	53.9	0.4362	0.641	50.094	BB
2	21.551	1546.3	25.8	0.9103	0.664	49.906	BB

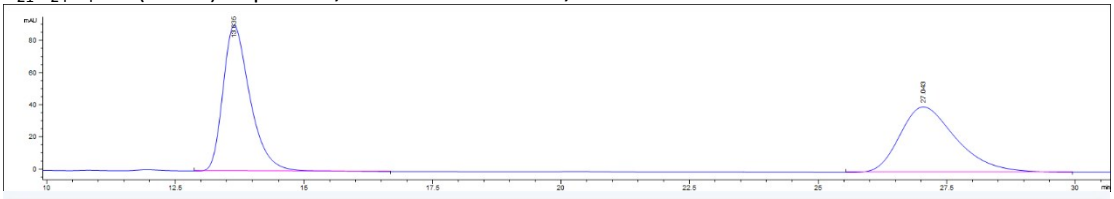


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.955	235.4	9.1	0.4004	0.762	2.384	BB
2	21.064	9640.8	160.2	0.9021	0.649	97.616	BB

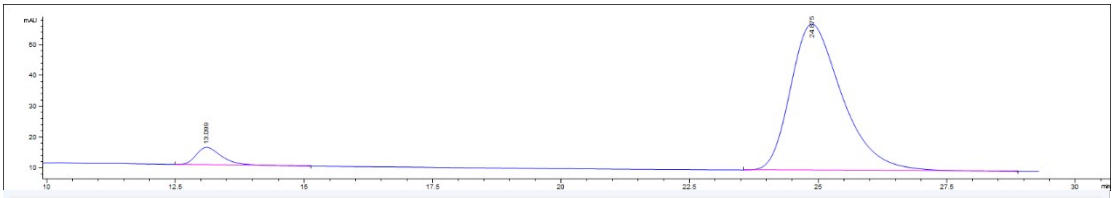
(R)-1-Adamantyl 2-hydroxy-5-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2i)



Compound was isolated as a white solid (91% yield, 30.9 mg) after column chromatography on silica-gel. mp: 125-128 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.28 (s, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 4.02 (s, 1H), 3.62 (d, *J* = 17.0 Hz, 1H), 3.17 (d, *J* = 17.0 Hz, 1H), 2.47 (s, 3H), 2.13 (s, 3H), 1.99 (d, *J* = 3.1 Hz, 6H), 1.62 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.8, 170.4, 152.9, 147.3, 131.7, 129.2, 126.6, 124.9, 83.8, 80.7, 40.9, 39.4, 35.9, 30.8, 22.3. $[\alpha]_D^{18}$ = -41 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R =24.875 min, minor enantiomer: t_R =13.099 min. 89% *ee.* HRMS exact mass calcd for $C_{21}H_{24}O_4Na^+$ (M+Na) requires *m/z* 363.1567. Found *m/z* 363.1567.

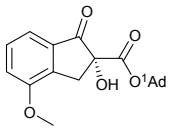


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.635	3348.8	91.4	0.5536	0.652	51.567	BB
2	27.043	3145.3	41.1	1.1613	0.676	48.433	BB

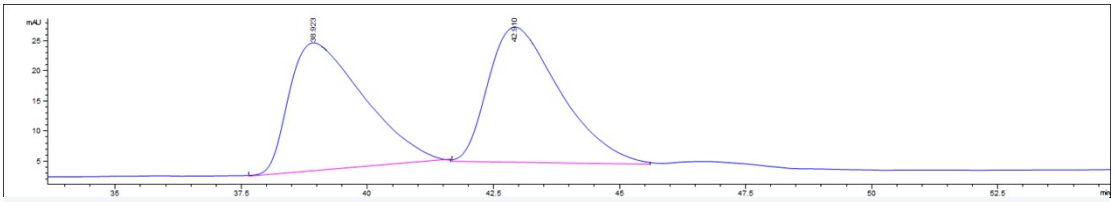


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.099	198.9	5.7	0.5264	0.627	5.666	BB
2	24.875	3311.8	47.4	1.0694	0.654	94.334	BB

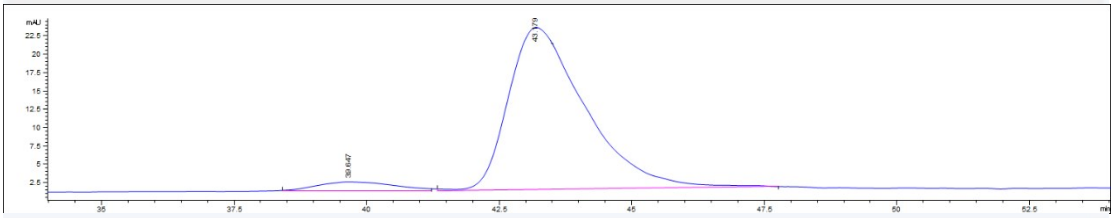
(R)-1-Adamantyl 2-hydroxy-4-methoxyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2j)



Compound was isolated as a white solid (92% yield, 32.8 mg) after column chromatography on silica-gel. mp: 115-118 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 1.8 Hz, 1H), 7.39 (s, 1H), 7.11 – 7.09 (m, 1H), 4.01 (s, 1H), 3.93 (s, 3H), 3.60 (d, *J* = 17.4 Hz, 1H), 3.09 (d, *J* = 17.5 Hz, 1H), 2.14 (s, 3H), 2.00 (d, *J* = 3.1 Hz, 6H), 1.62 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.6, 170.4, 156.6, 141.4, 135.3, 129.4, 116.5, 116.0, 83.9, 80.3, 55.6, 40.9, 36.4, 35.9, 30.8. $[\alpha]_D^{18}$ = -33 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak OD-H column at 254 nm (n-hexane/*i*-PrOH =99/1), 1.0 mL/min; Major enantiomer: t_R =43.179 min, minor enantiomer: t_R =39.647 min. 90 % *ee*. HRMS exact mass calcd for $C_{21}H_{24}O_5Na^+$ (M+Na) requires *m/z* 379.1516. Found *m/z* 379.1518.

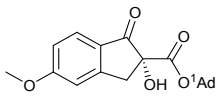


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	38.923	2198.6	21.4	1.7098	0.485	49.404	MM
2	42.91	2251.7	22.7	1.6561	0.569	50.596	MM

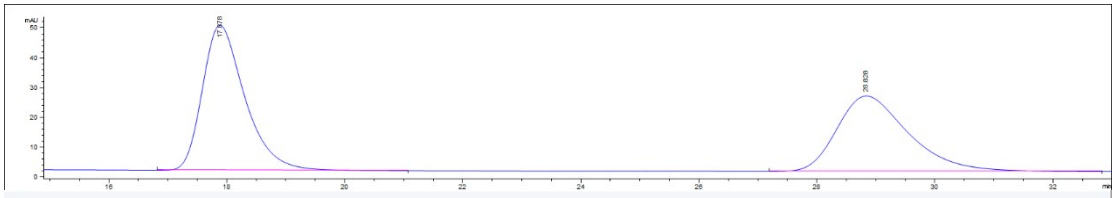


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	39.647	124.2	1.2	1.6803	0.667	5.245	MM
2	43.179	2244.3	22.2	1.6849	0.548	94.755	MM

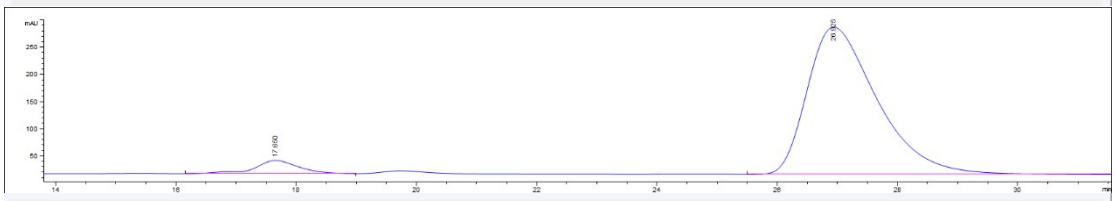
(R)-1-Adamantyl 2-hydroxy-5-methoxyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2k)



Compound was isolated as a white solid (93% yield, 33.1 mg) after column chromatography on silica-gel. mp: 102-104 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5 Hz, 1H), 6.94 (d, *J* = 10.7 Hz, 1H), 6.91 (s, 1H), 4.04 (s, 1H), 3.92 (s, 3H), 3.62 (d, *J* = 17.1 Hz, 1H), 3.17 (d, *J* = 17.1 Hz, 1H), 2.13 (s, 3H), 2.00 (d, *J* = 2.9 Hz, 6H), 1.62 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.4, 170.4, 166.2, 155.5, 127.1, 126.9, 1159, 109.5, 83.7, 80.8, 55.8, 41.0, 39.5, 35.9, 30.8. $[\alpha]_D^{18}$ = -36 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R =26.925 min, minor enantiomer: t_R =17.650 min. 89 % *ee*. HRMS exact mass calcd for $C_{21}H_{24}O_5Na^+$ (M+Na) requires *m/z* 379.1516. Found *m/z* 379.1517.

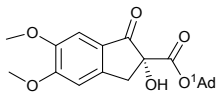


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	17.878	2452.6	49	0.7598	0.662	53.334	BB
2	28.828	2145.9	25.5	1.2708	0.659	46.666	BB

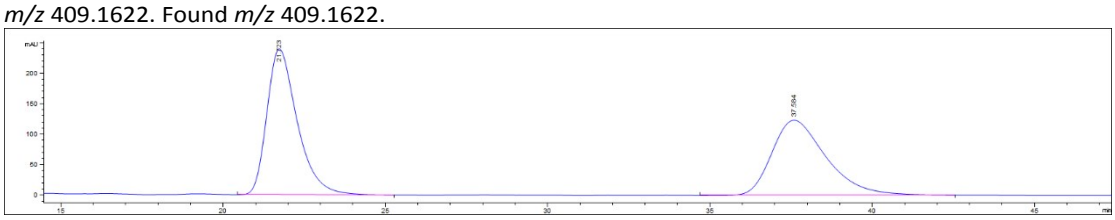


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	17.65	1229.8	24.2	0.7502	0.929	5.337	BB
2	26.925	21813.5	270.4	1.2311	0.571	94.663	BBA

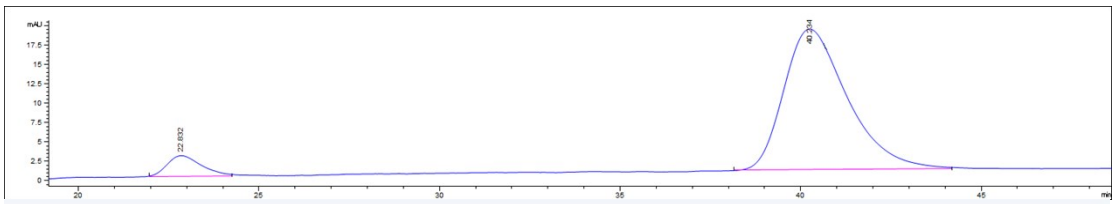
(R)-1-Adamantyl 2-hydroxy-5,6-di-methoxyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2l)



Compound was isolated as a yellow solid (98% yield, 37.8 mg) after column chromatography on silica-gel. mp: 151-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 6.89 (s, 1H), 4.06 (s, 1H), 4.00 (s, 3H), 3.92 (s, 3H), 3.58 (d, *J* = 16.9 Hz, 1H), 3.12 (d, *J* = 16.9 Hz, 1H), 2.13 (s, 3H), 2.00 (d, *J* = 2.3 Hz, 6H), 1.61 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.9, 170.6, 156.3, 149.7, 148.3, 126.5, 107.1, 105.2, 83.8, 80.8, 56.4, 56.1, 40.9, 39.3, 35.9, 30.8. $[\alpha]_D^{18}$ = -65 (c =1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R =40.234 min, minor enantiomer: t_R =22.832 min. 85% *ee.* HRMS exact mass calcd for $C_{22}H_{26}O_6Na^+$ (M+Na) requires *m/z* 409.1622. Found *m/z* 409.1622.

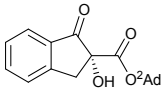


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	21.723	15598.8	239.9	0.9827	0.649	52.004	BB
2	37.584	14396.8	123.6	1.7549	0.651	47.996	BB

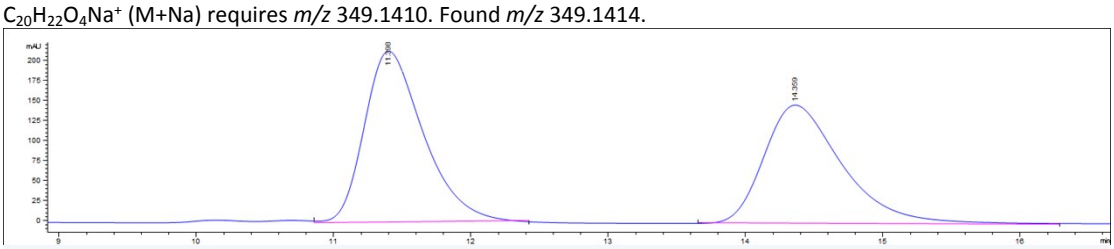


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	22.832	183.2	2.7	1.1181	0.687	7.556	MM
2	40.234	2241	18.3	2.0447	0.655	92.444	MM

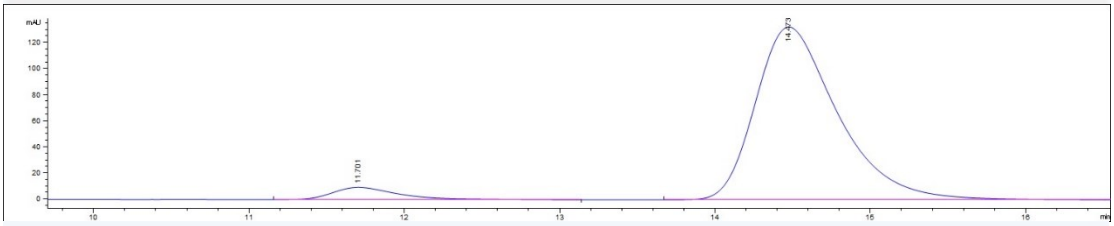
(R)-2-Adamantyl 2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2m)



Compound was isolated as a white solid (95% yield, 30.9 mg) after column chromatography on silica-gel. mp: 84-85 °C. ^{1}H NMR (600 MHz, $CDCl_3$) 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 – 1.57 (m, 10H), 1.45 – 1.22 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.1, 170.7, 152.0, 136.0, 134.1, 128.1, 126.3, 125.1, 81.0, 79.8, 39.6, 37.1, 36.1, 36.0, 31.7, 31.5, 31.3, 26.8, 26.7. $[\alpha]_D^{18}$ = -47 (c = 1 in CH_3Cl). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R =14.473 min, minor enantiomer: t_R =11.701 min. 89 % *ee.* HRMS exact mass calcd for $C_{20}H_{22}O_4Na^+$ (M+Na) requires *m/z* 349.1410. Found *m/z* 349.1414.

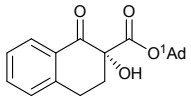


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.398	6402.5	213.9	0.4989	0.682	51.975	MM
2	14.359	5915.9	147.9	0.6667	0.634	48.025	MM

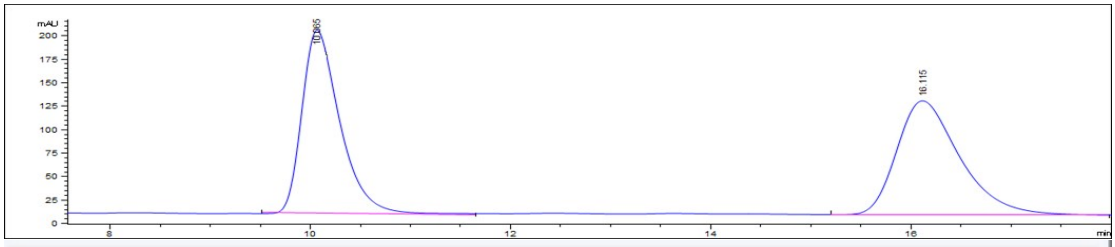


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.701	272.7	9.3	0.4391	0.604	5.311	BB
2	14.473	4861	132.4	0.5544	0.642	94.689	BB

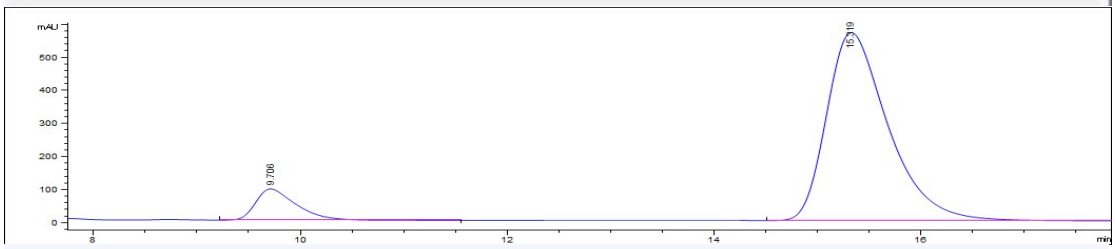
(R)-1-Adamantyl 2-hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2n)



Compound was isolated as a white solid (91% yield, 30.9 mg) after column chromatography on silica-gel. mp: 105-107 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 1H), 7.54 (td, *J* = 7.5, 1.3 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 4.26 (s, 1H), 3.15-3.13 (m, 3H), 2.66 (dt, *J* = 13.5, 5.2 Hz, 1H), 2.27-2,22 (m, 1H), 2.14 (s, 3H), 2.03 (s, 6H), 1.63 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.9, 169.7, 143.8, 134.1, 130.7, 128.8, 128.0, 126.9, 83.5, 77.8, 41.0, 36.0, 32.9, 30.8, 25.8.$[\alpha]_D^{18}$ =-21 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R =15.319 min, minor enantiomer: t_R =9.706 min. 80% *ee.* HRMS exact mass calcd for $C_{21}H_{24}O_4Na^+$ (M+Na) requires *m/z* 363.1567. Found *m/z* 363.1568.

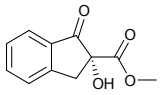


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.065	5207.7	196.4	0.442	0.632	49.232	MM
2	16.115	5370.3	122.4	0.7315	0.675	50.768	MM

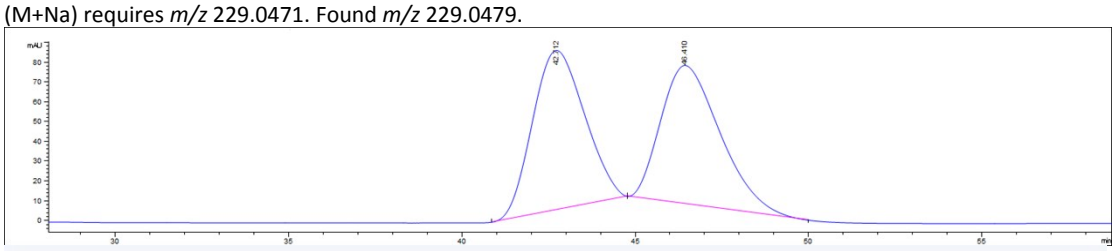


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.706	2543.9	94.3	0.3986	0.553	9.793	BB
2	15.319	23432.9	569.4	0.6221	0.628	90.207	BB

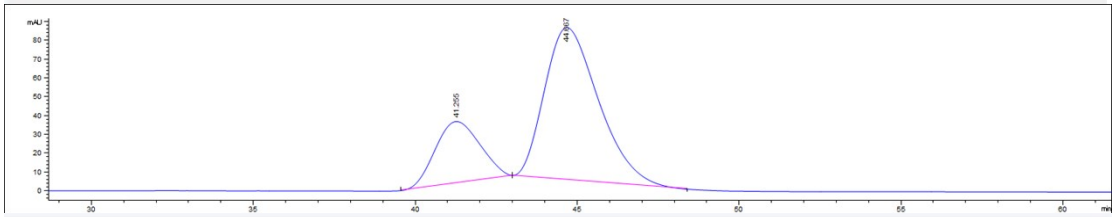
(R)-Methyl 2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2o)



Compound was isolated as a white solid (95% yield, 19.6 mg) after column chromatography on silica-gel. mp: 126-128 °C. ^{1}H NMR (600 MHz, $CDCl_3$) 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. $[\alpha]_D^{18}$ = -15 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH =95/5), 1.0 mL/min; Major enantiomer: t_R =44.667 min, minor enantiomer: t_R =41.255 min. 50%; *ee.* HRMS exact mass calcd for $C_{11}H_{10}O_4Na^+$ (M+Na) requires *m/z* 229.0471. Found *m/z* 229.0479.

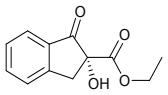


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	42.712	8385.7	80.6	1.6152	0.837	50.141	BB
2	46.41	8338.4	70	1.8363	0.65	49.859	BB

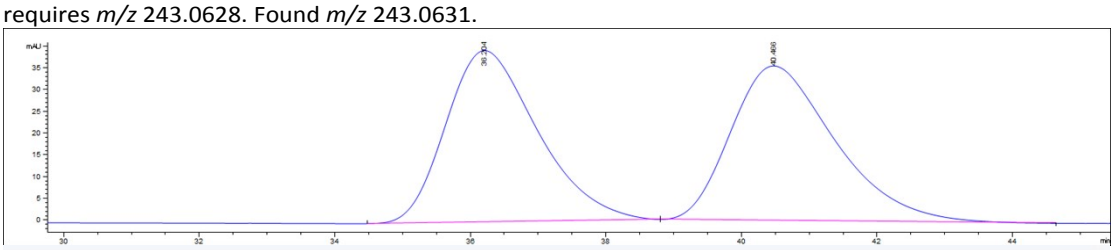


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	41.255	3140.7	32.8	1.4785	0.892	24.999	BB
2	44.667	9422.7	81.2	1.7964	0.667	75.001	BB

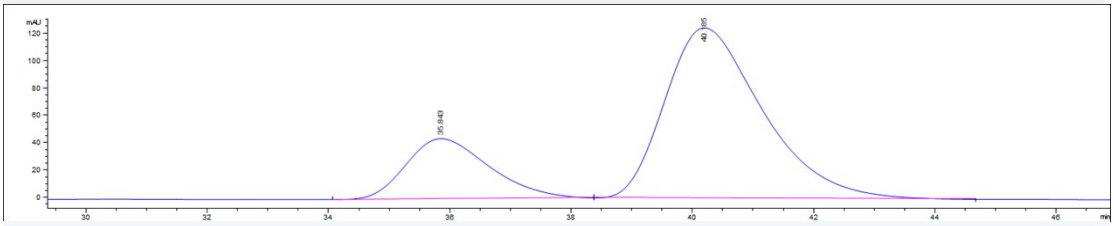
Ethyl (R)-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2p)



Compound was isolated as a colourless oil (96 % yield,21.1 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 201.1, 171.5, 152.3, 136.1, 133.6, 128.1, 126.5, 125.2, 80.3, 62.7, 39.4, 14.0. $[\alpha]_D^{18}$ = -19 (c =1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH =95/5), 1.0 mL/min; Major enantiomer: t_R =40.185 min, minor enantiomer: t_R =35.843 min. 54% *ee.* HRMS exact mass calcd for $C_{12}H_{12}O_4Na^+$ (M+Na) requires *m/z* 243.0628. Found *m/z* 243.0631.

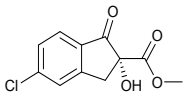


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	36.204	3686	39.3	1.4292	0.704	49.378	BB
2	40.466	3778.9	35.4	1.6035	0.657	50.622	BB

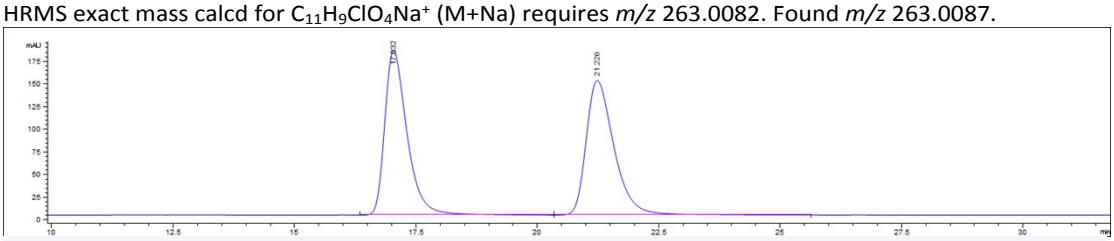


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	35.843	4209.3	44.2	1.4363	0.698	23.112	BB
2	40.185	14003.3	125	1.6728	0.64	76.888	BB

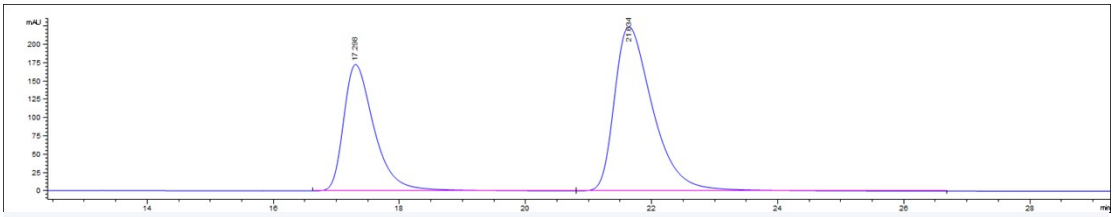
Methyl (R)-5-chloro-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2q)



Compound was isolated as a white solid (95% yield, 22.8 mg) after column chromatography on silica-gel. mp: 133-135 °C. ^{1}H NMR (600 MHz, $CDCl_3$) 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. $[\alpha]_D^{18}$ = -31 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak OD-H column at 254 nm (n-hexane/*i*-PrOH =90/10), 1.0 mL/min; Major enantiomer: t_R =21.634 min, minor enantiomer: t_R =17.298 min. 24% *ee.* HRMS exact mass calcd for $C_{11}H_9ClO_4Na^+$ (M+Na) requires *m/z* 263.0082. Found *m/z* 263.0087.

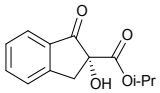


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	17.032	5846.1	182.4	0.488	0.605	49.537	BB
2	21.226	5955.3	149	0.6082	0.611	50.463	BB

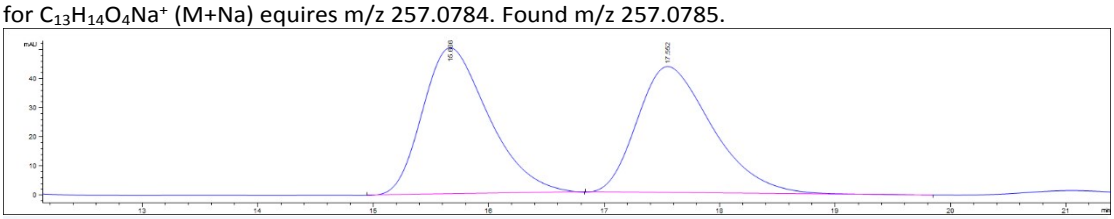


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	17.298	5826.3	172.5	0.5121	0.591	38.073	BB
2	21.634	9476.8	224.3	0.6409	0.561	61.927	BB

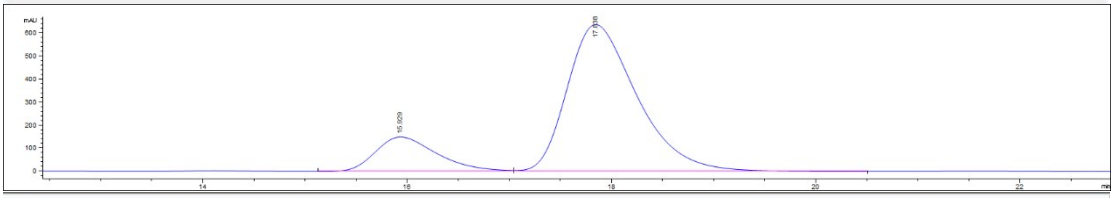
Isopropyl (R)-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2r)



Compound was isolated as a yellow oil (94% yield, 22.0 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, $CDCl_3$) 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), 4.09 (s, 1H), 3.71 (d, *J* = 17.1 Hz, 1H), 3.25 (d, *J* = 17.1 Hz, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.14 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.0, 171.0, 152.4, 136.0, 133.7, 128.1, 126.4, 125.2, 80.3, 70.9, 39.3, 21.6, 21.4. $[\alpha]_D^{18}$ = -53 (c =1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/i-PrOH =95/5), 1.0 mL/min; Major enantiomer: t_R =17.838 min, minor enantiomer: t_R =15.929 min. 66% ee. HRMS exact mass calcd for $C_{13}H_{14}O_4Na^+$ (M+Na) equires m/z 257.0784. Found m/z 257.0785.

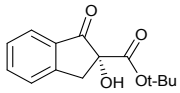


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	15.666	2003.1	50.1	0.612	0.682	50.525	BB
2	17.552	1961.5	43.3	0.7046	0.647	49.475	BB

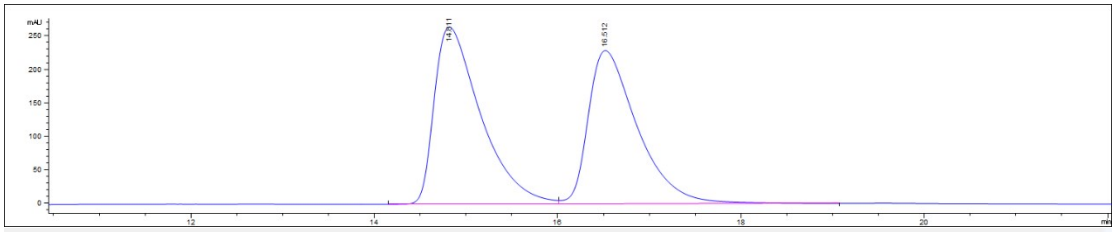


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	15.929	6242.7	149.3	0.6319	0.656	17.094	BV
2	17.838	30278.1	638.6	0.7292	0.649	82.906	VB

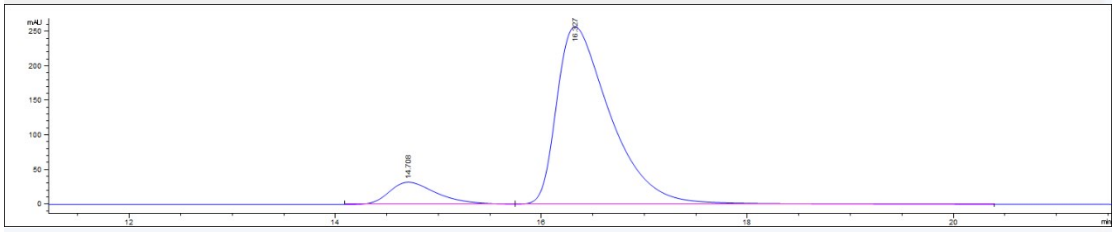
tert-butyl (R)-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2s)



Compound was isolated as a yellow oil (98 % yield, 24.3 mg) after column chromatography on silica-gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 4.07 (s, 1H), 3.67 (d, *J* = 17.2 Hz, 1H), 3.24 (d, *J* = 17.2 Hz, 1H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 170.6, 152.4, 135.9, 133.9, 128.0, 126.3, 125.1, 84.0, 80.5, 39.5, 27.7. $[\alpha]_D^{18}$ =-62 (c =1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak OD-H column at 254 nm (n-hexane/*i*-PrOH =97/3), 1.0 mL/min; Major enantiomer: t_R =16.327 min, minor enantiomer: t_R =14.708 min. 80% *ee.* HRMS exact mass calcd for $C_{14}H_{16}O_4Na^+$ (M+Na) equires *m/z* 271.0941. Found *m/z* 271.0942.

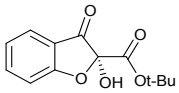


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	14.811	9316.5	264.4	0.5311	0.446	52.231	BV
2	16.512	8520.5	228.7	0.5627	0.497	47.769	VB

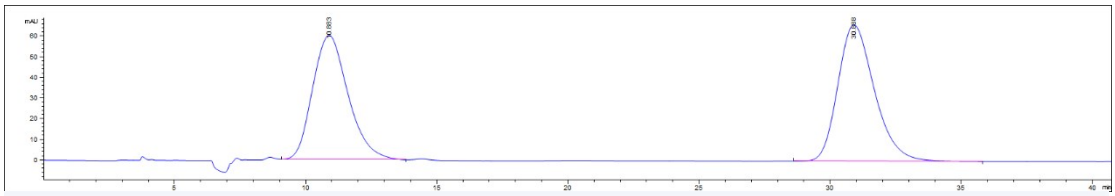


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	14.708	1011.6	31.8	0.4854	0.639	9.838	BB
2	16.327	9271	255.9	0.5447	0.474	90.162	BB

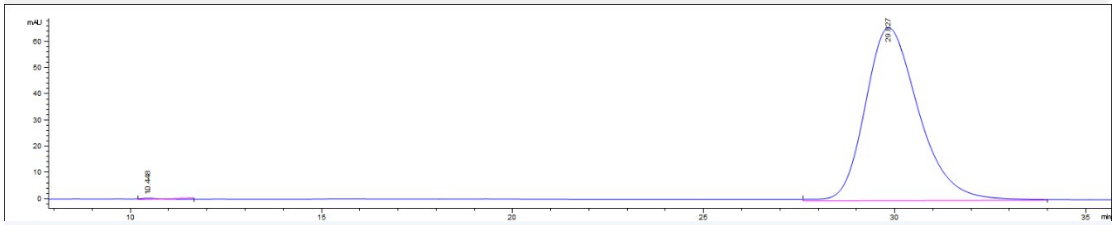
tert-butyl (S)-2-hydroxy-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (2t)



Compound was isolated as a brown solid (97 % yield, 24.3 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. $[\alpha]_D^{18}$ = -34 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH =80/20), 1.0 mL/min; Major enantiomer: t_R =29.827 min, minor enantiomer: t_R =10.448 min. 99% *ee.* HRMS exact mass calcd for $C_{13}H_{14}O_5Na^+$ (M+Na) requires *m/z* 273.0733. Found *m/z* 273.0736.

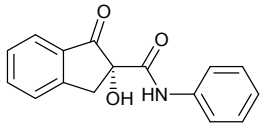


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.883	5638.8	60	1.4502	0.818	46.908	BB
2	30.888	6382.1	65.9	1.4941	0.737	53.092	BB

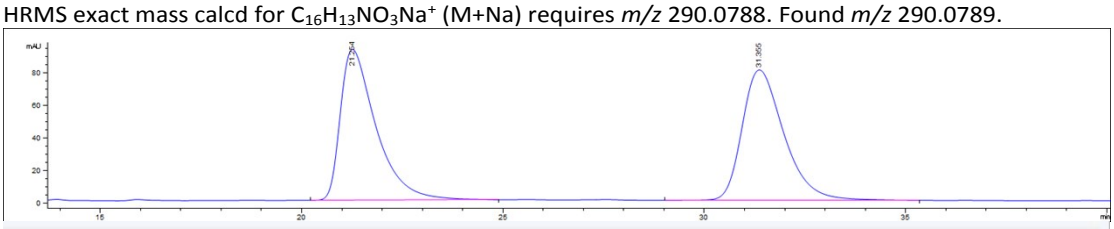


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.448	13.7	4.8E-1	0.4812	0.819	0.209	MM
2	29.827	6540.8	66.5	1.6393	0.751	99.791	MM

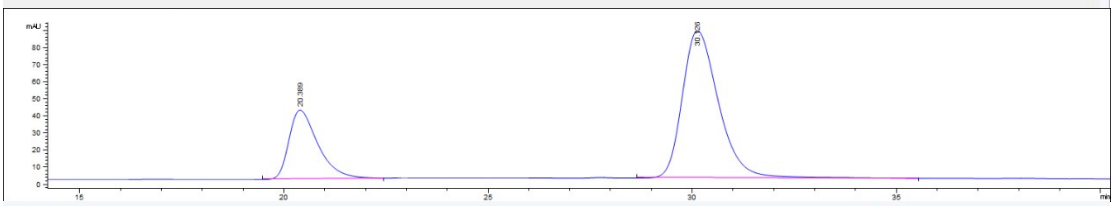
(R)-2-hydroxy-1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (2u)



Compound was isolated as a brown solid (96 % yield, 25.6 mg) after column chromatography on silica-gel. mp: 128-130 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 3H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 3.98 (s, 1H), 3.89 (d, *J* = 16.7 Hz, 1H), 3.22 (d, *J* = 16.7 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 203.1, 168.3, 153.0, 136.9, 136.5, 133.7, 129.0, 128.2, 126.4, 125.2, 124.8, 119.7, 82.7, 40.9. $[\alpha]_D^{25}$ = -9 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak OD-H column at 254 nm (n-hexane/*i*-PrOH =90/10), 1.0 mL/min; Major enantiomer: t_R =30.126 min, minor enantiomer: t_R =20.389 min. 46% *ee.* HRMS exact mass calcd for $C_{16}H_{13}NO_3Na^+$ (M+Na) requires *m/z* 290.0788. Found *m/z* 290.0789.

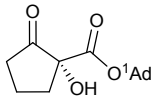


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	21.254	5687.1	92.4	0.9162	0.476	49.632	BB
2	31.355	5771.4	79.8	1.1141	0.657	50.368	BB

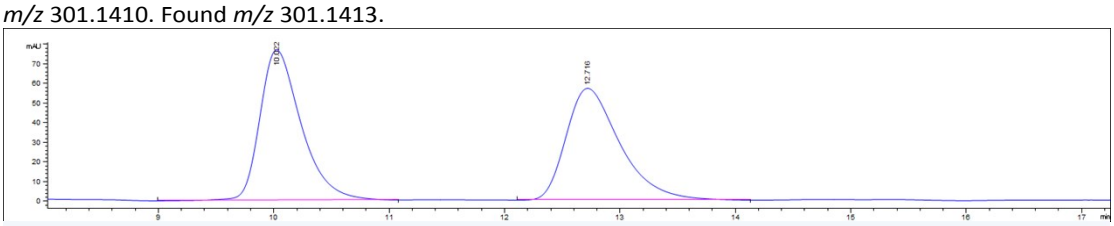


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	20.389	1994.1	40.3	0.7546	0.58	27.110	BB
2	30.126	5361.5	86.4	0.9496	0.671	72.890	BB

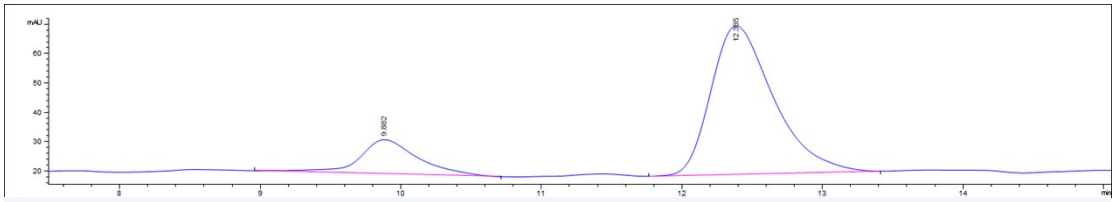
(R)-1-Adamantyl 1-hydroxy-2-oxo-cyclopentane-carboxylate (2v)



Compound was isolated as a white solid (93 % yield, 25.8 mg) after column chromatography on silica-gel. mp: 70-72 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ 3.73 (s, 1H), 2.44 (dd, *J* = 14.4, 7.3 Hz, 3H), 2.20 (s, 3H), 2.10 (d, *J* = 11.3 Hz, 8H), 1.67 (s, 6H), 1.27 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 213.9, 170.5, 84.0, 79.8, 41.1, 35.9, 34.9, 30.9, 18.4. $[\alpha]_D^{25}$ = -9 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 210 nm (n-hexane/*i*-PrOH =90/10), 1.0 mL/min; Major enantiomer: t_R =12.385 min, minor enantiomer: t_R =9.882 min. 65% *ee.* HRMS exact mass calcd for $C_{16}H_{22}O_4Na^+$ (M+Na) requires *m/z* 301.1410. Found *m/z* 301.1413.

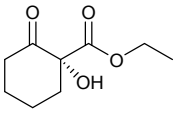


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.022	1902.8	76.6	0.3758	0.647	50.731	BB
2	12.716	1848	56.8	0.4953	0.624	49.269	BB

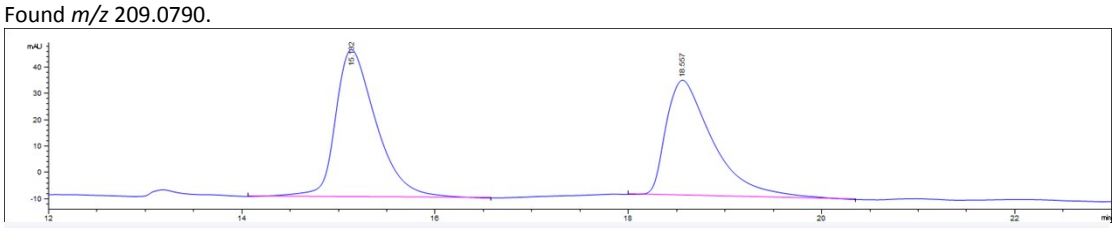


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.882	337.7	11.6	0.4227	0.743	17.759	BB
2	12.385	1563.8	50.6	0.4708	0.644	82.241	BB

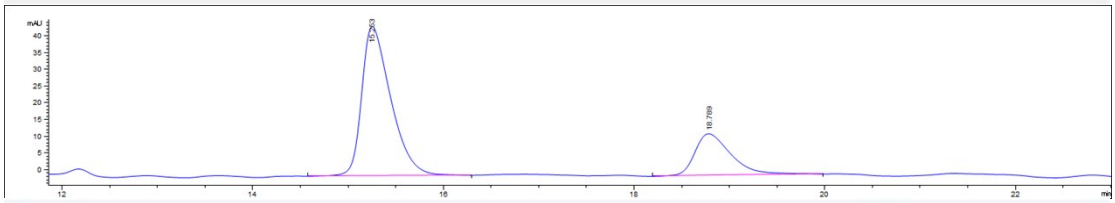
(R)-Ethyl 1-Hydroxy-2-oxocyclohexane-1-carboxylate (2w)



Compound was isolated as a colourless oil (86 % yield, 16.0 mg) after column chromatography on silica-gel. ^{1}H NMR (600 MHz, $CDCl_3$) 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.$[\alpha]_D^{25}$ = 38 (c = 1 in $CHCl_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 210 nm (n-hexane/*i*-PrOH =95/5), 1.0 mL/min; Major enantiomer: t_R =15.253 min, minor enantiomer: t_R =18.789 min. 48% *ee.* HRMS exact mass calcd for $C_9H_{14}O_4Na^+$ (M+Na) requires *m/z* 209.0784. Found *m/z* 209.0790.

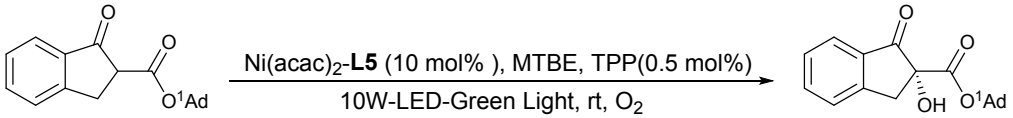


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	15.132	1637.1	55.8	0.4442	0.624	52.548	BB
2	18.557	1478.4	43.6	0.5072	0.49	47.452	BB



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	15.253	942.6	44.4	0.3196	0.545	73.957	BB
2	18.789	331.9	12.4	0.4017	0.58	26.043	BB

4. Scale-up experiment

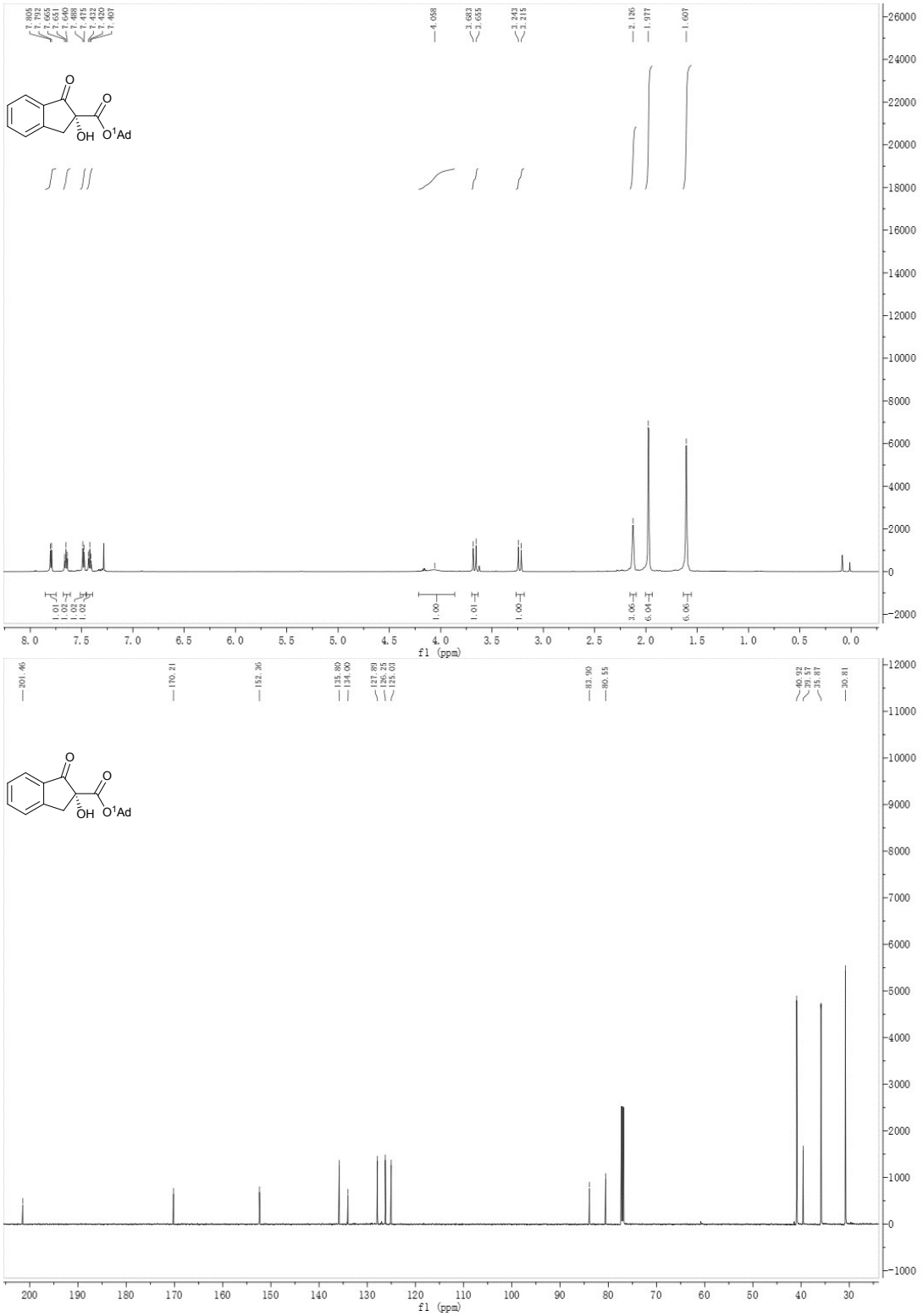


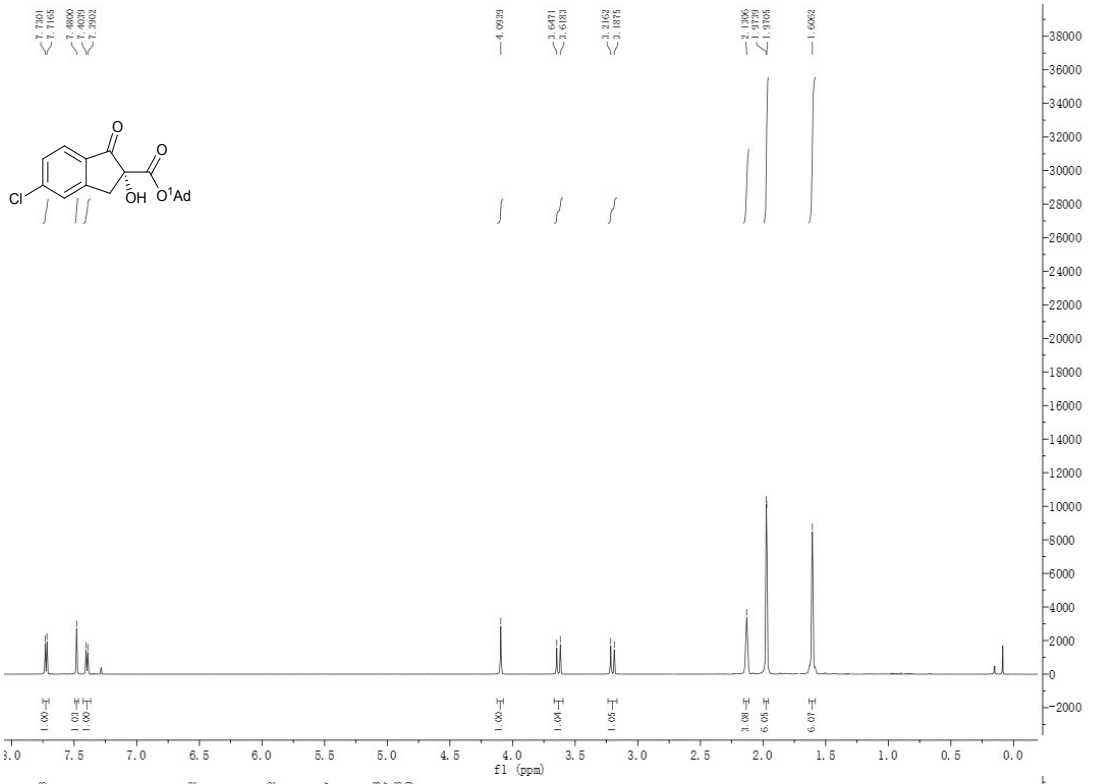
1a 1.085 g (3.5 mmol)

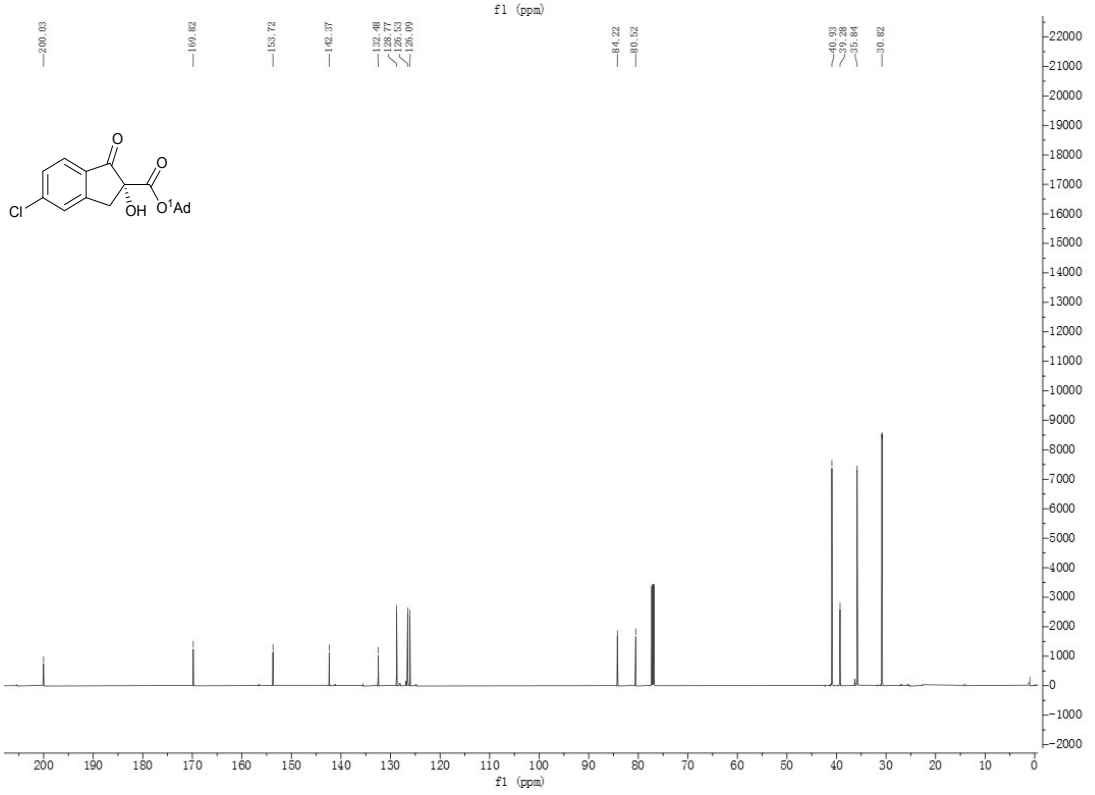
2a 1.08g, 95% yield, 94% ee

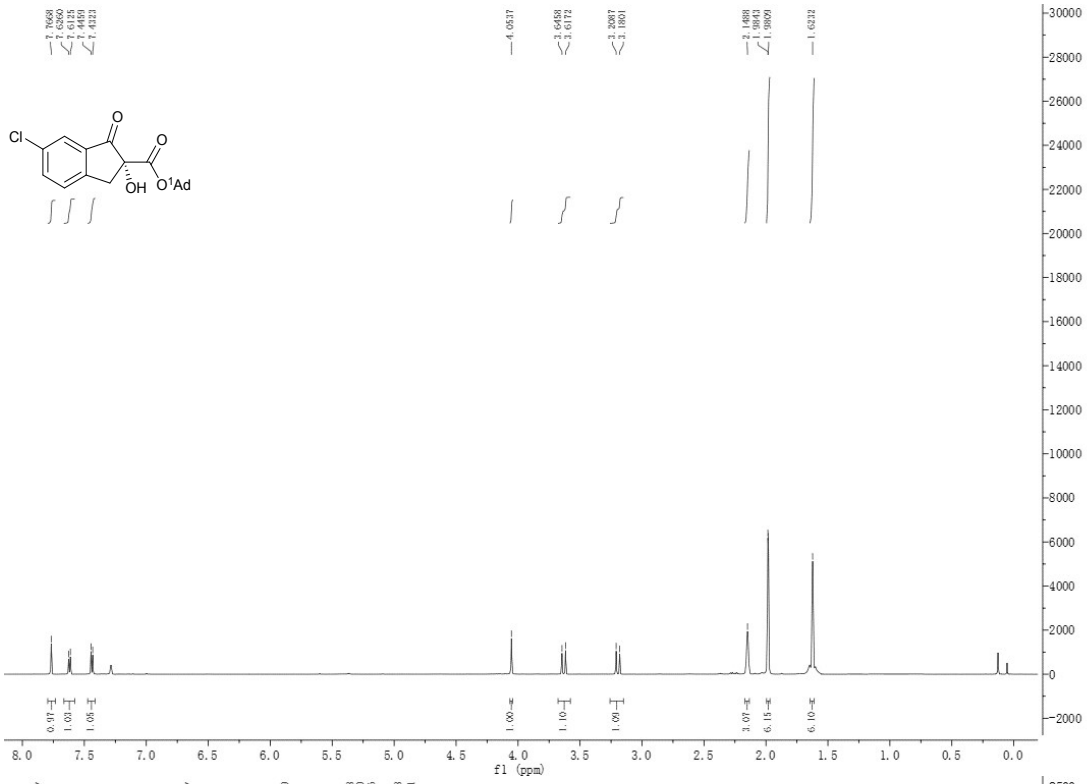
$Ni(acac)_2$ (90.0 mg, 0.35 mmol), **L5** (170.1 mg, 0.35 mmol) and MTBE (70 mL) were added to a test tube. The solution was stirred at room temperature for 0.5 h. Then the 1-adamantyl (1-Ad) indanone carboxylate **1a** (3.5 mmol) and TPP (10.5 mg, 0.0175 mmol) were added. After the air in the tube is vacuumed and replaced with oxygen. The mixture was stirred for 3h under an irradiation of 525 nm green light and the completion of the reaction was checked by TLC. The reaction mixture was condensed and purified by column chromatography on silica gel to to give the product **2a** in 95% yield (1.08 g, 94% ee).

5. NMR spectra of product




7.7301
7.7165
7.4890
7.4039
7.3902
4.0939
3.6471
3.6183
3.2162
3.1976
2.1896
2.1739
1.9705
1.6062
Cl
OH
O
O
O
1Ad
1.00
1.03
1.00
1.00
1.04
1.05
3.08
6.05
6.07
f1 (ppm)


200.03
169.82
153.72
142.37
132.48
128.77
126.53
126.09
84.22
80.52
40.93
39.28
35.84
30.82
Cl
OH
O
O
O
1Ad
f1 (ppm)


7.7668
7.6360
7.6175
7.4459
7.4323
4.0537
3.6458
3.6172
3.2087
3.1801
2.1488
1.9844
1.9809
1.6232
Cl
O
O
OH
O1Ad
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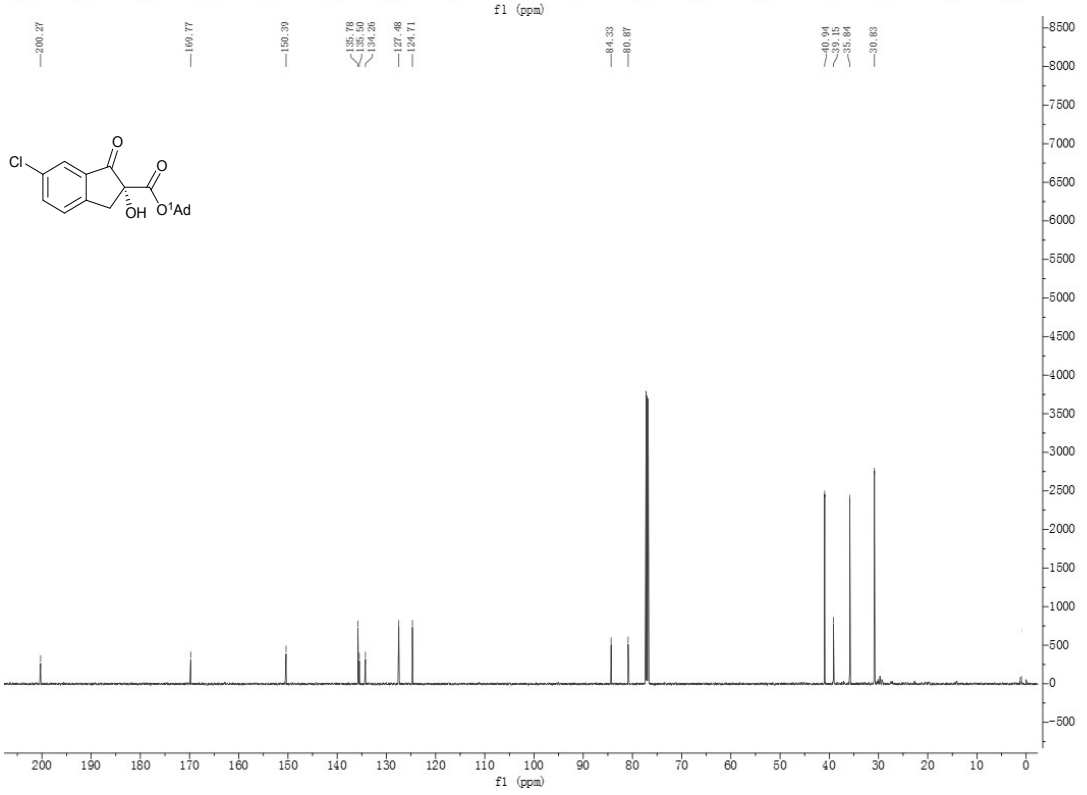
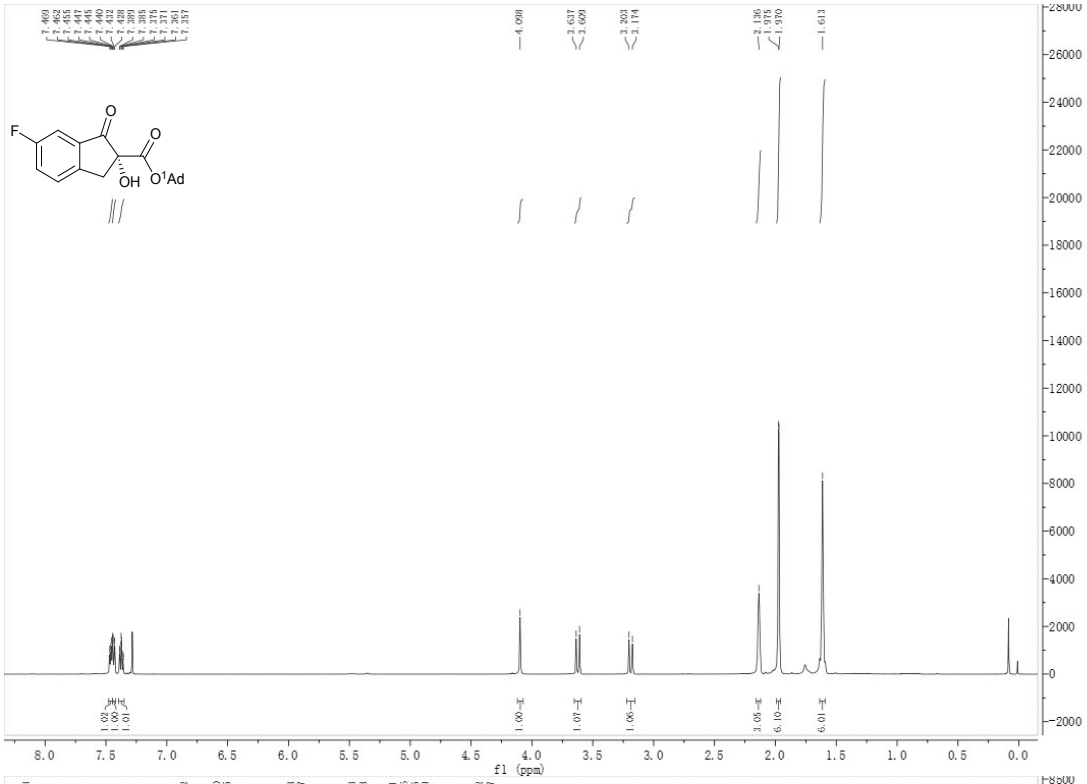
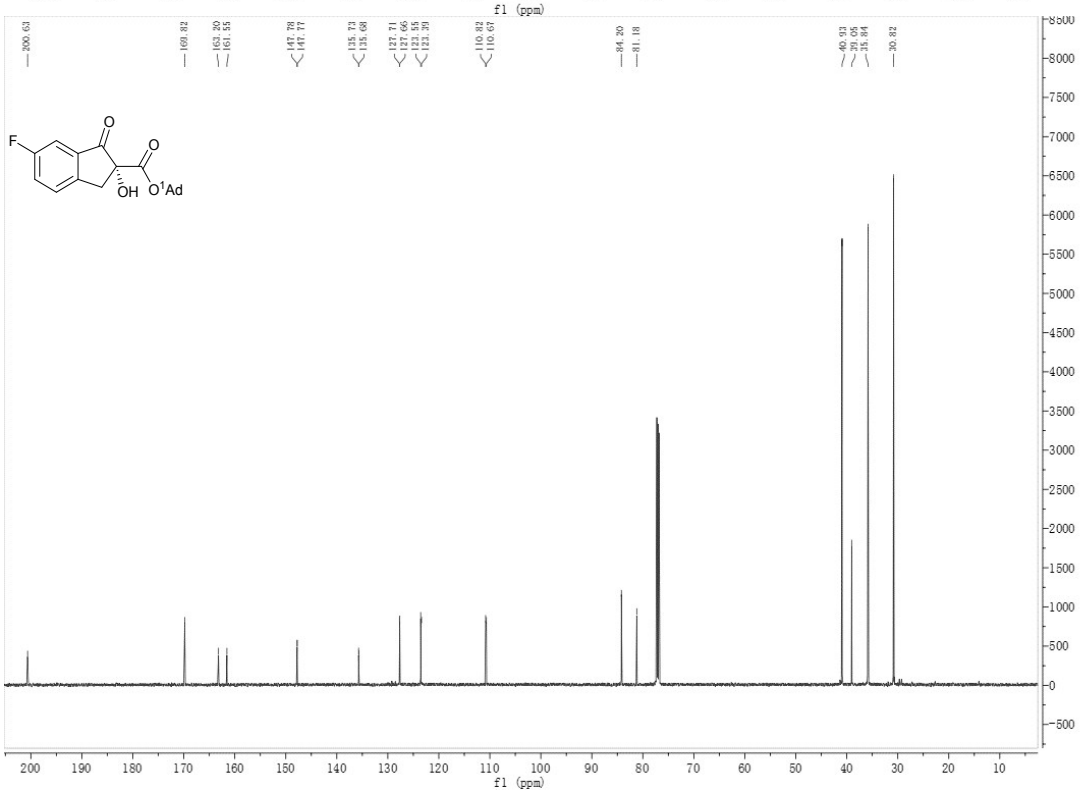
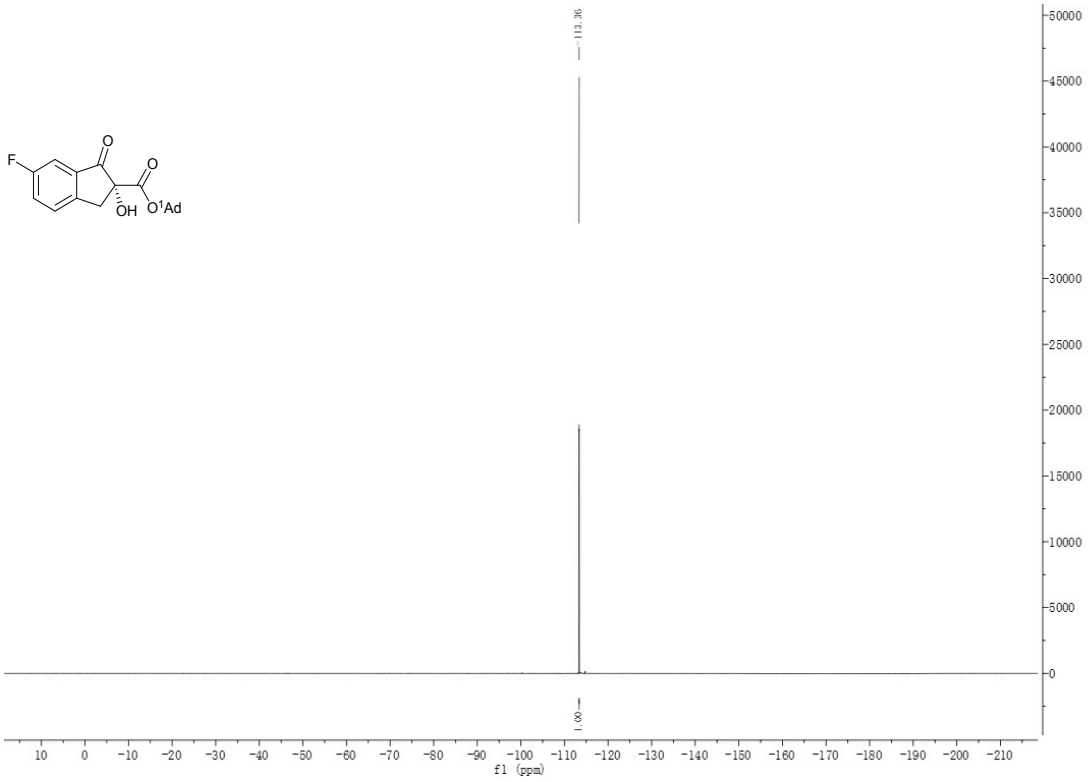
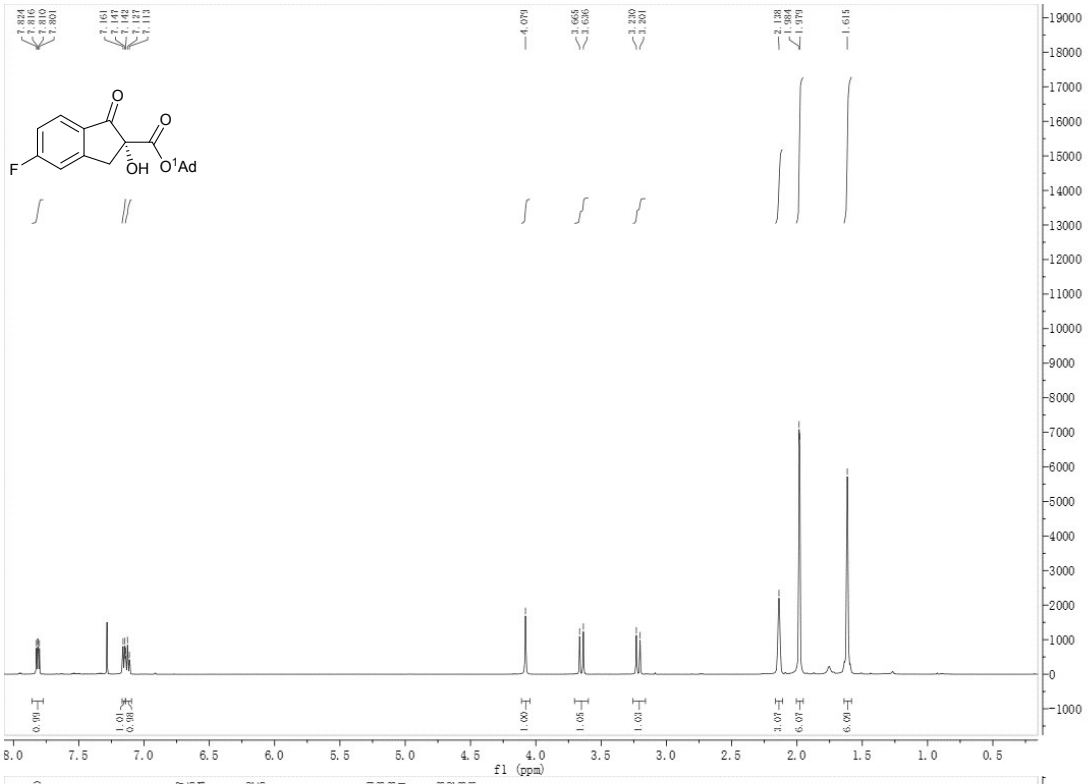
1.03
1.05
1.00
1.10
1.09
3.07
6.15
6.10
f1 (ppm)

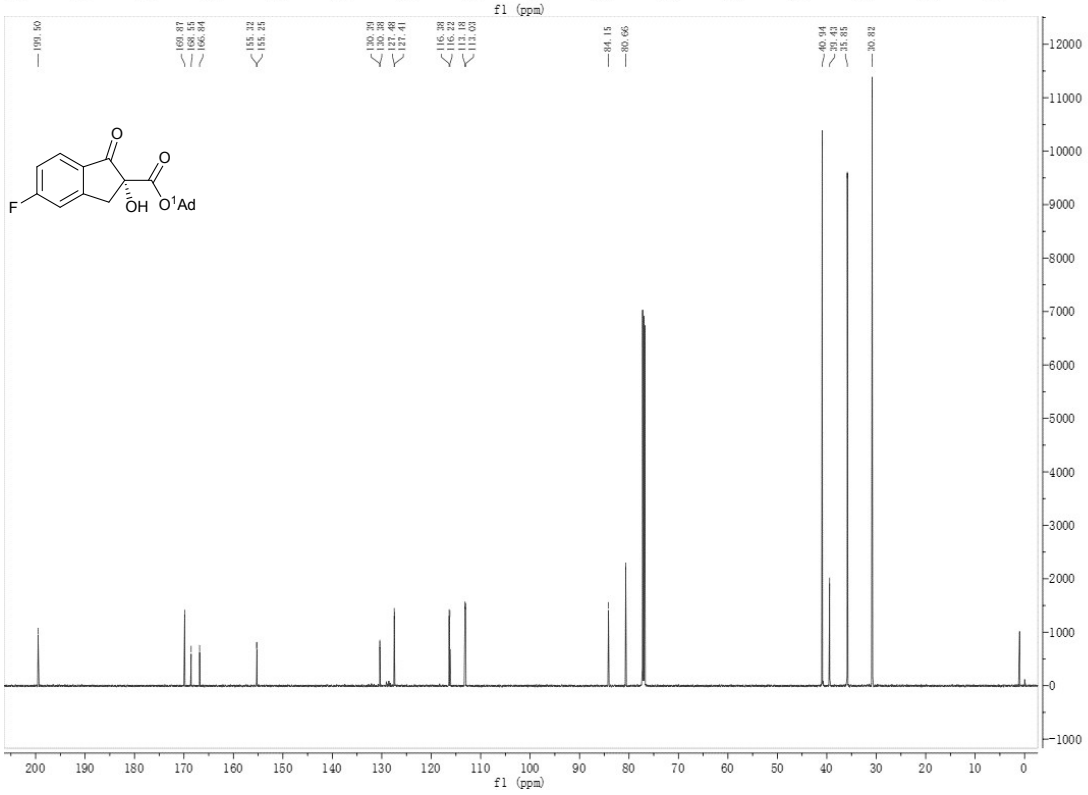

200.27
169.77
150.39
135.78
135.50
134.26
127.48
124.71
84.33
80.87
40.94
39.15
35.84
30.83
Cl
O
O
OH
O1Ad
f1 (ppm)

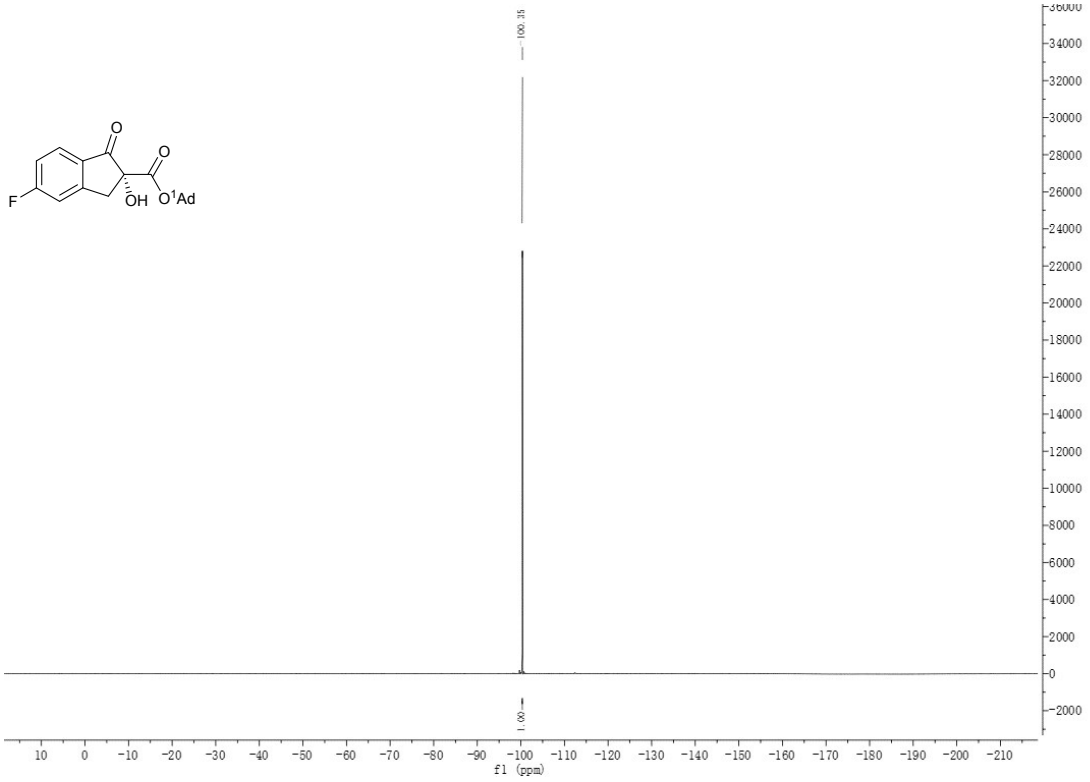

F
O
O
OH
O1Ad
fl (ppm)

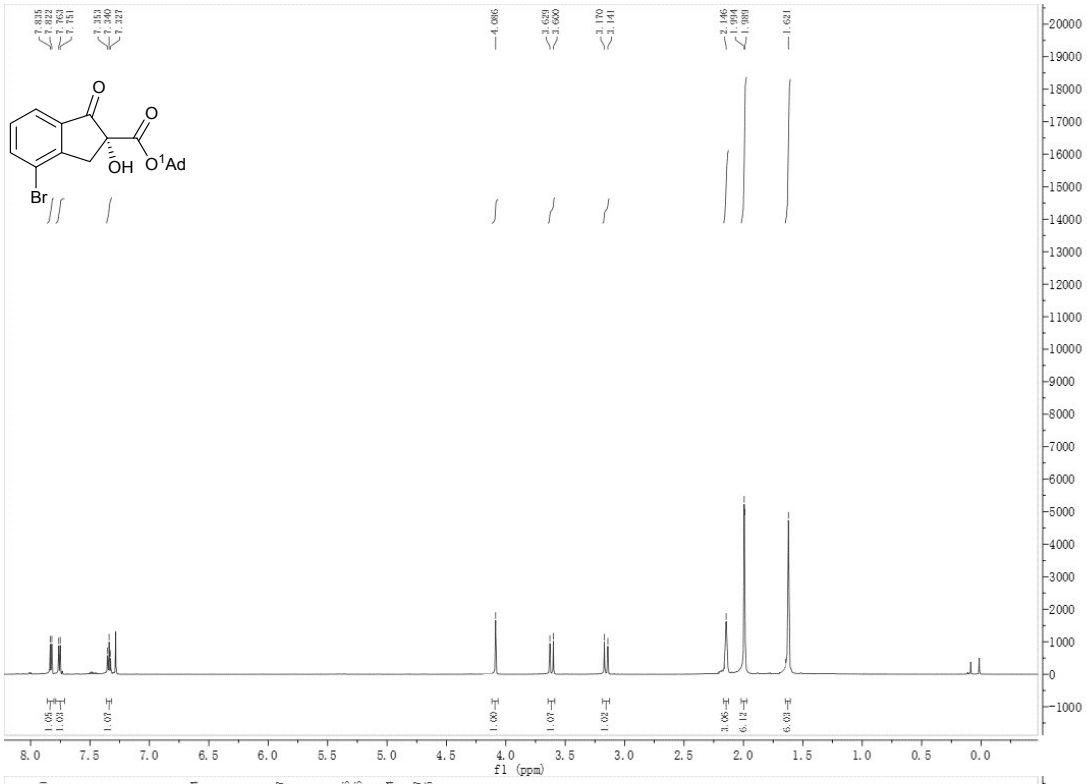

F
O
O
OH
O1Ad
fl (ppm)


F
O
O
OH
O1Ad
-113.36
1.00
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
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)


F
OH
O
O
O
O1Ad
fl (ppm)


F
OH
O
O
O
O1Ad
fl (ppm)


O
O
F
OH
O1Ad
-100.35
1.00
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)
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000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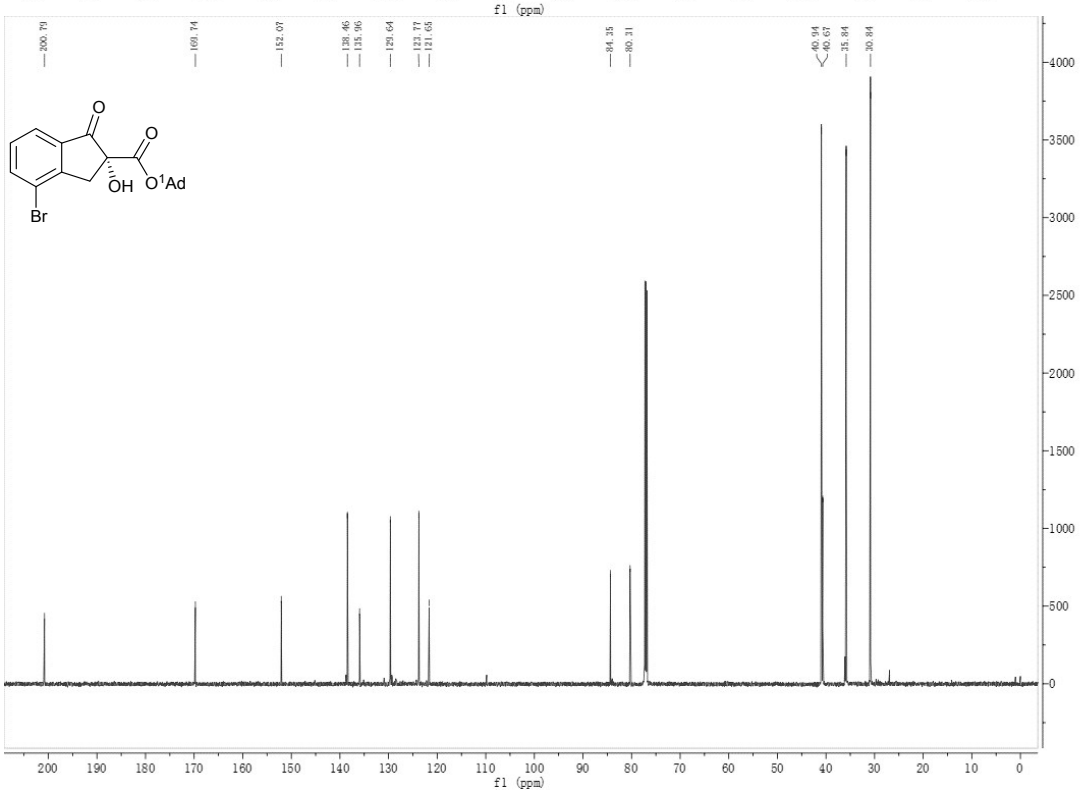
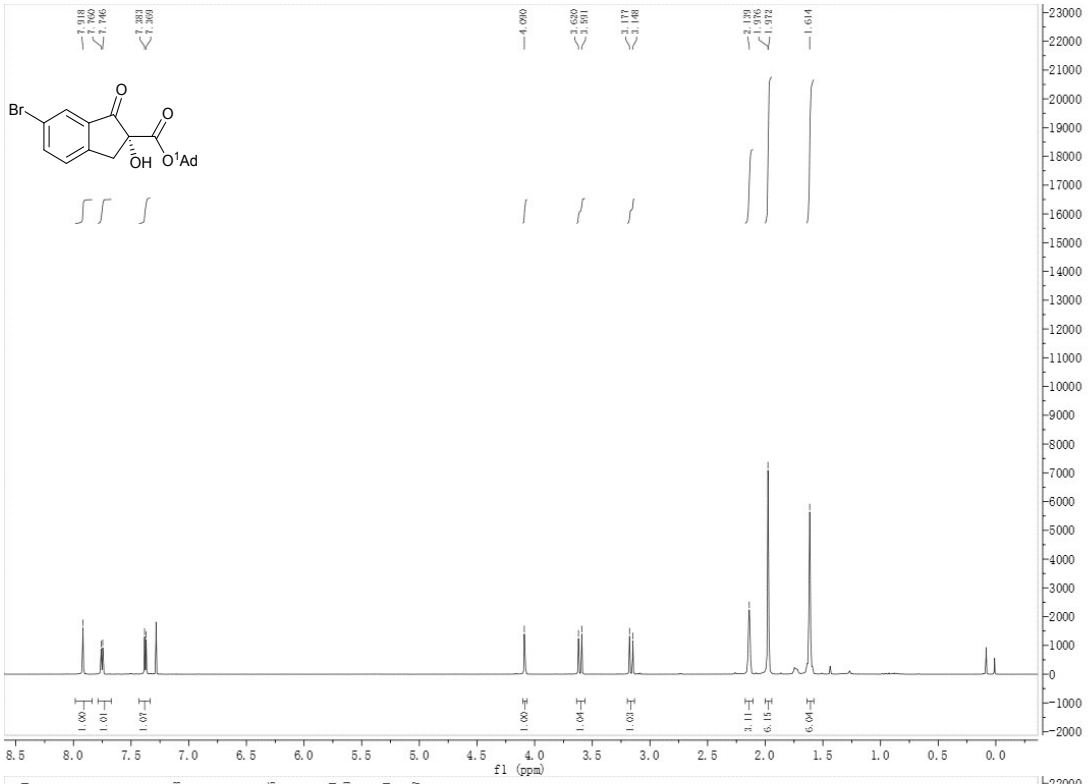
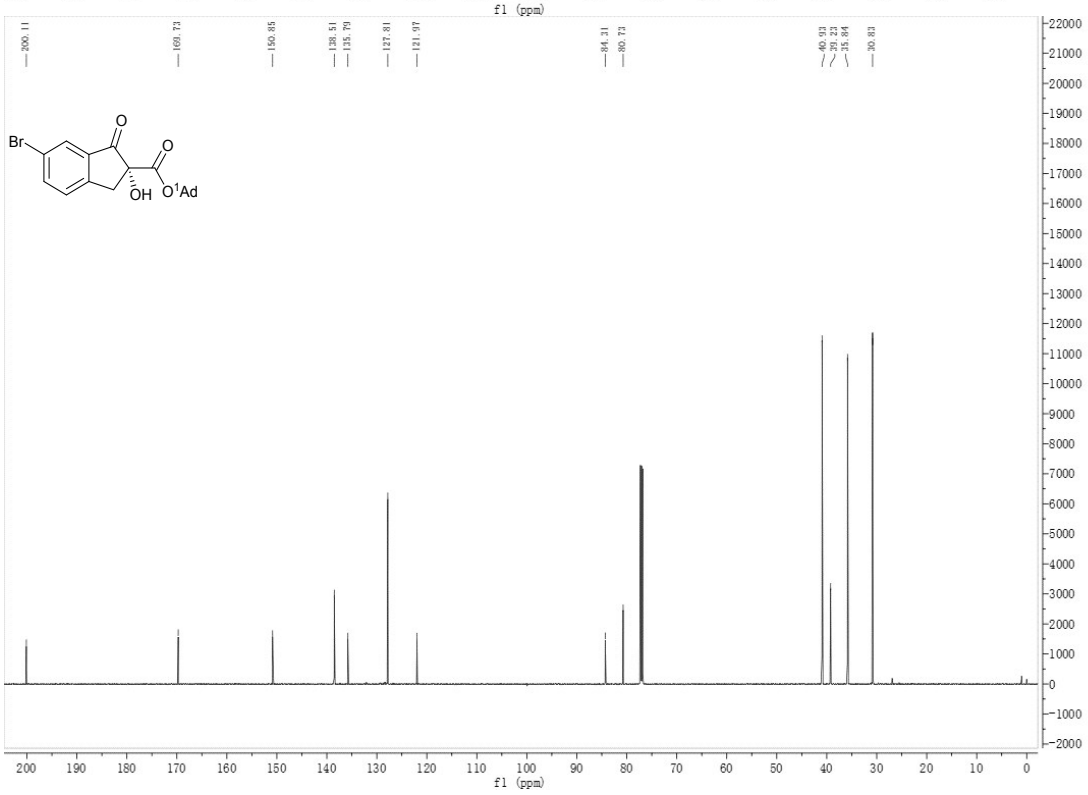
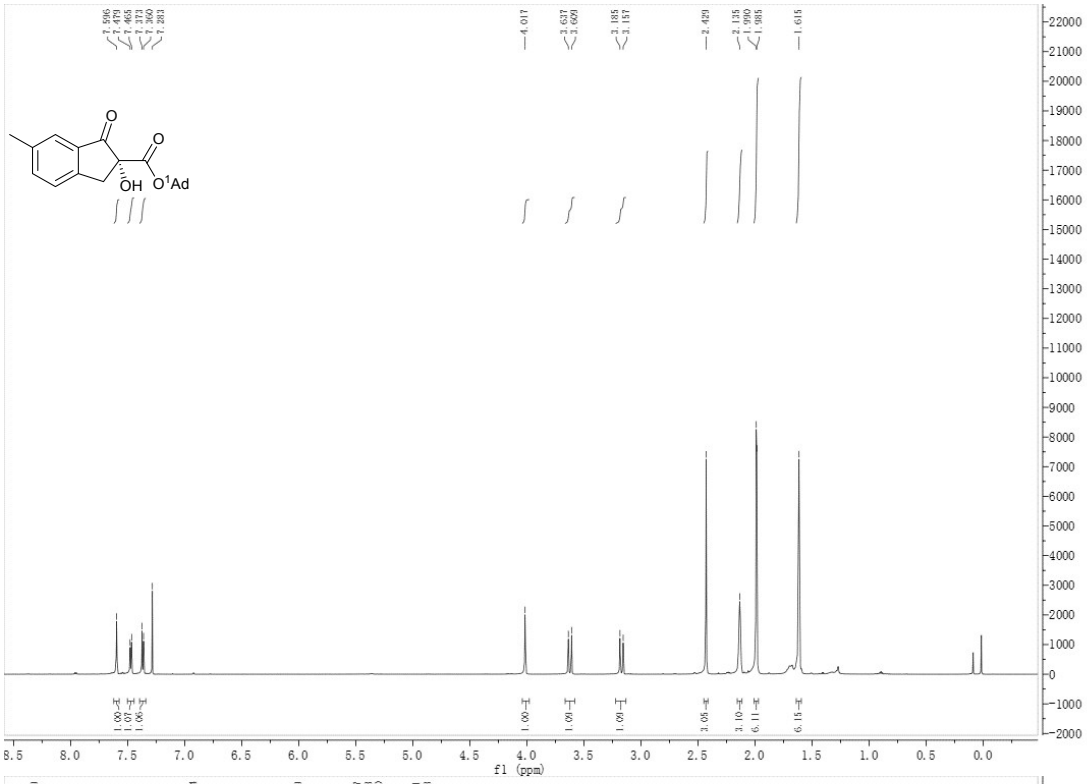
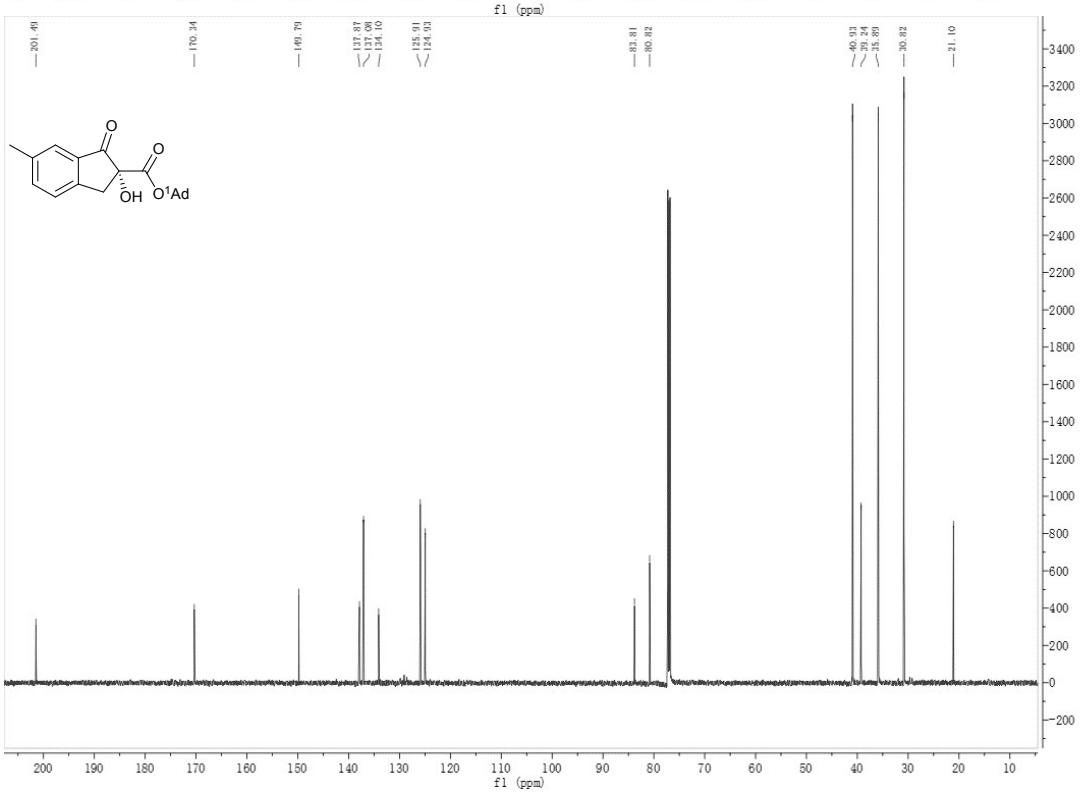
7.822
7.753
7.751
7.353
7.340
7.327
4.086
3.629
3.600
3.170
3.141
2.146
1.994
1.989
1.621
O
O
OH
O1Ad
Br
1.05
1.03
1.07
1.07
1.00
1.07
1.02
3.06
6.12
6.03
f1 (ppm)

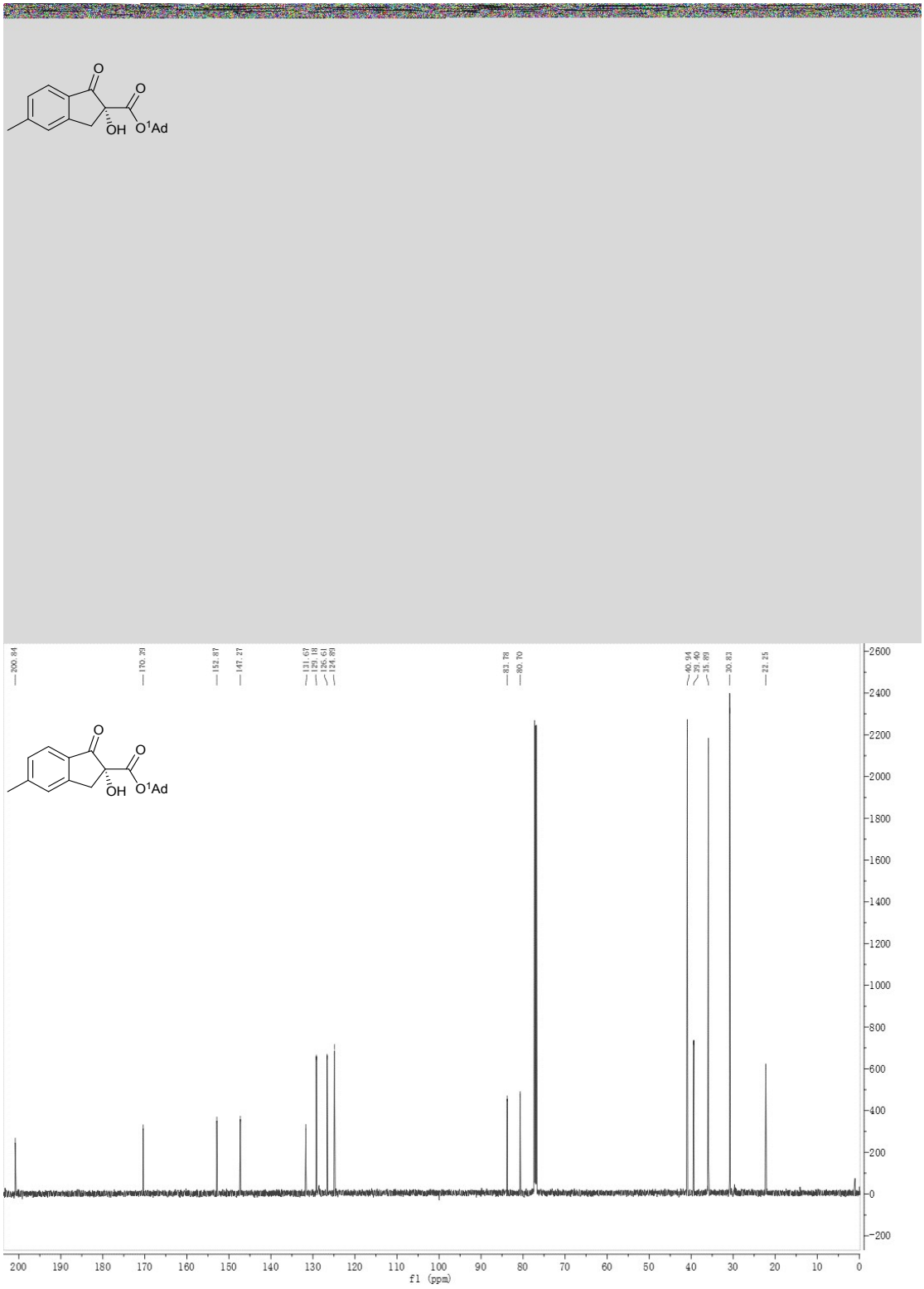

200.79
169.74
152.07
138.46
135.96
129.64
123.77
121.65
84.35
80.31
40.94
40.67
35.84
30.84
O
O
OH
O1Ad
Br
f1 (ppm)


Br
O
O
OH
O1Ad
fl (ppm)


Br
O
O
OH
O1Ad
fl (ppm)


O
O
OH
O1Ad
f1 (ppm)


O
O
OH
O1Ad
f1 (ppm)


O
O
OH
O1Ad
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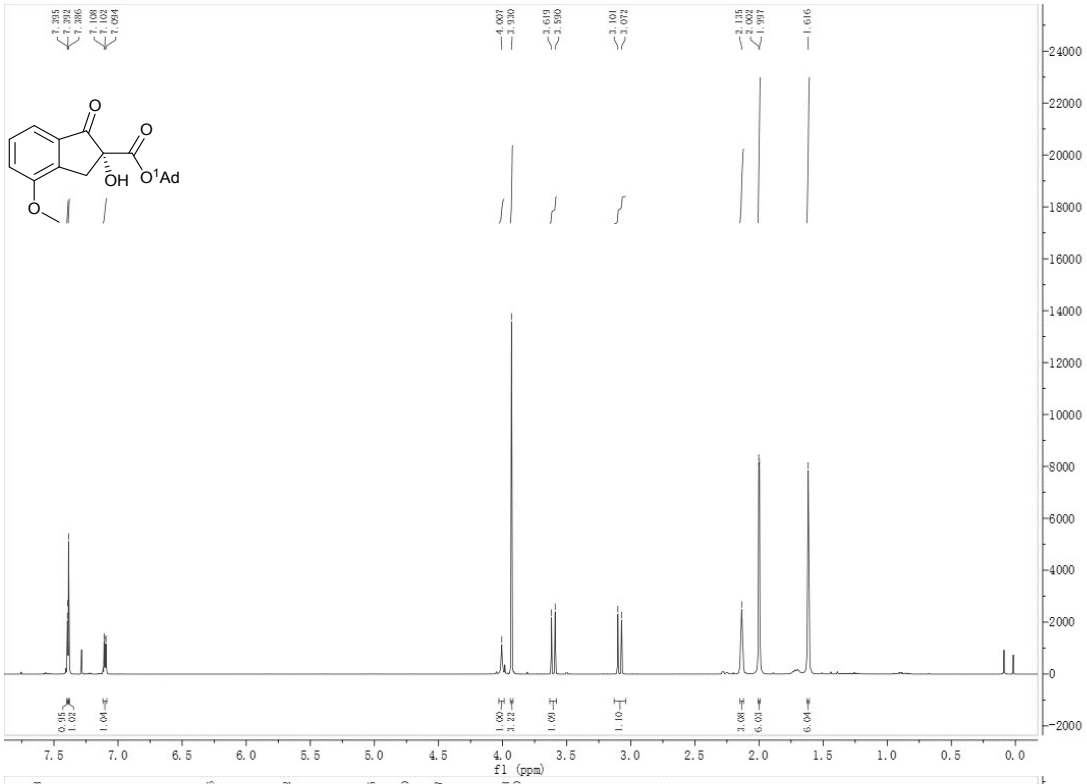
152.87
147.27
131.67
129.38
126.61
124.89
83.78
80.70
40.94
39.46
35.89
30.83
22.25
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.102
7.094
4.607
3.930
3.619
3.590
3.101
3.072
2.135
2.002
1.997
1.616
O
O
OH
O1Ad
O
0.95
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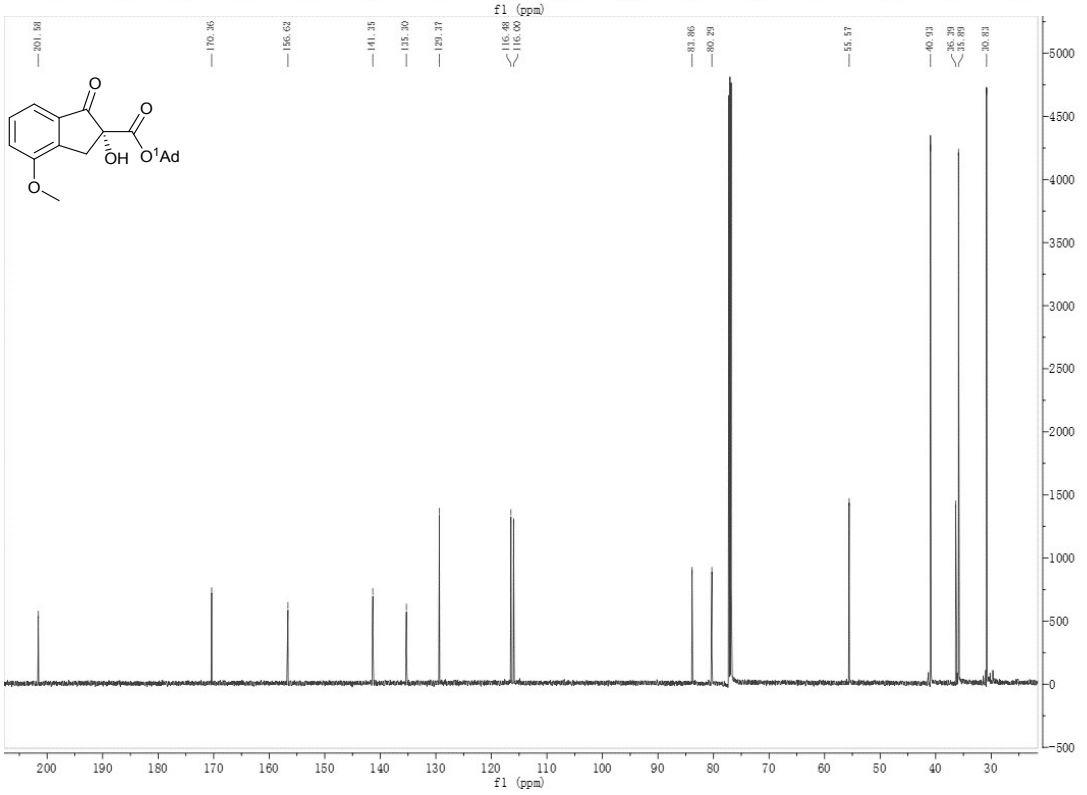
1.04
1.00
3.22
1.09
1.10
3.08
6.03
6.04
f1 (ppm)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116.00
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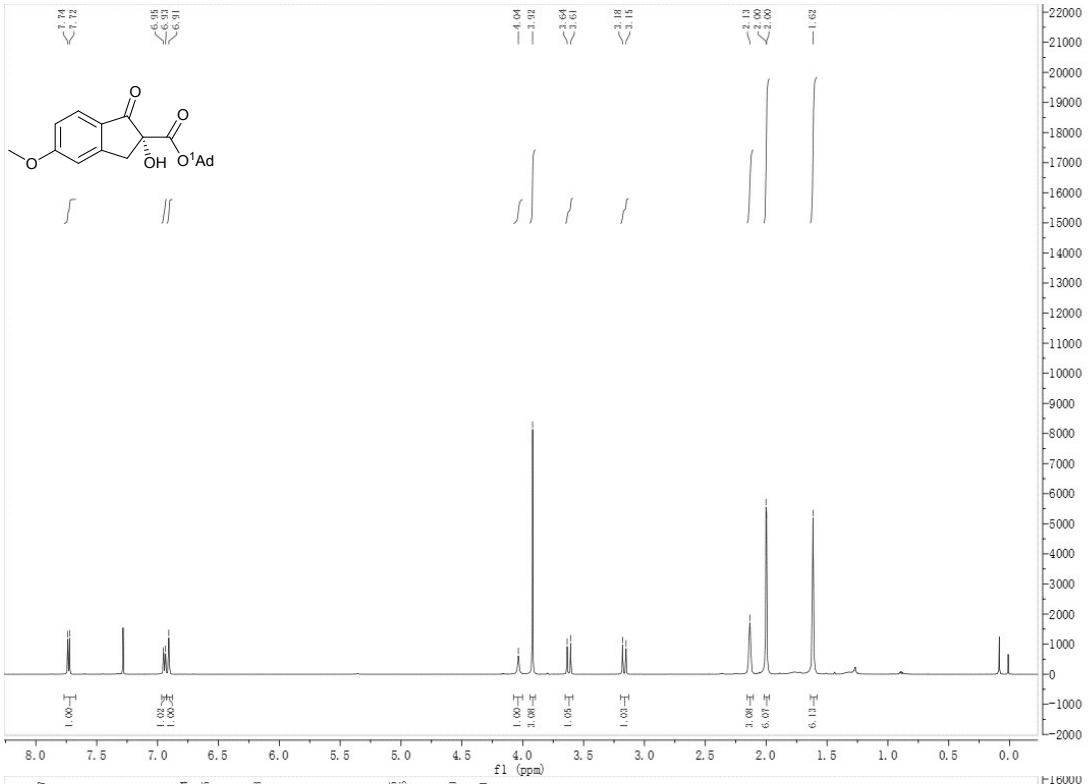
36.39
35.89
30.83
O
O
OH
O1Ad
O
f1 (ppm)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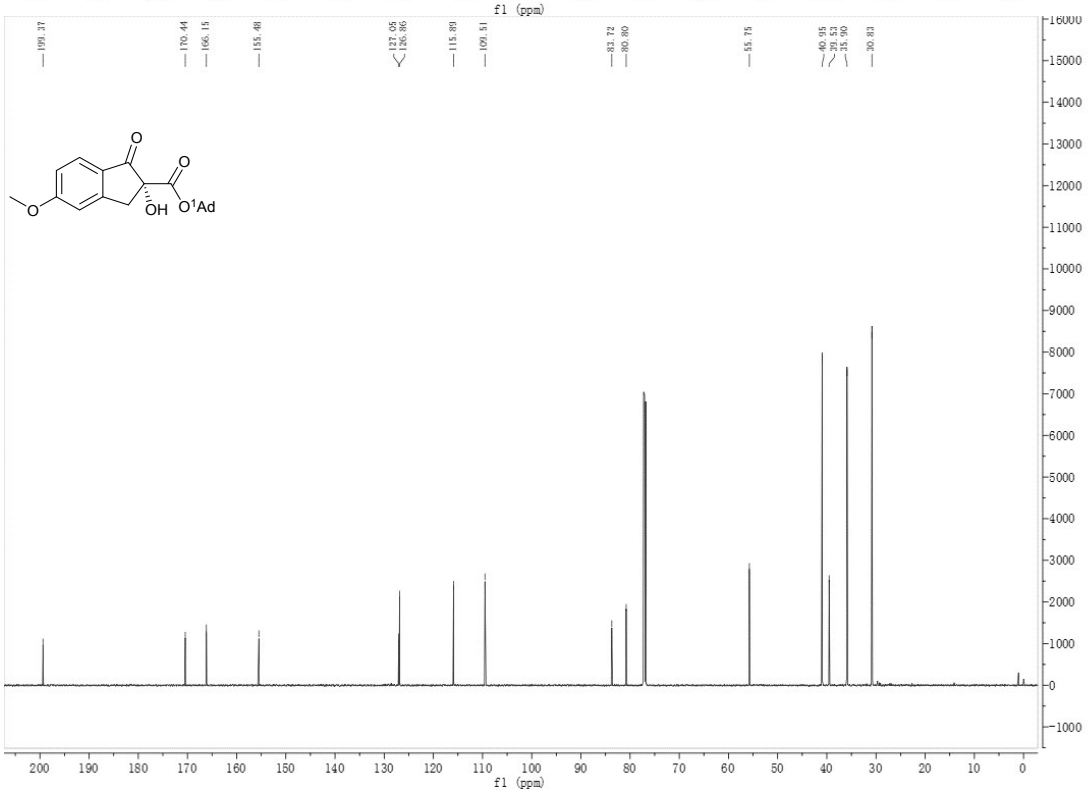
3.64
3.61
3.18
3.15
2.13
2.00
2.00
1.62
O
O
O
OH
O1Ad
1.00
1.02
1.00
1.00
3.08
1.05
1.03
3.08
6.07
6.13
f1 (ppm)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115.89
109.51
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55.75
40.95
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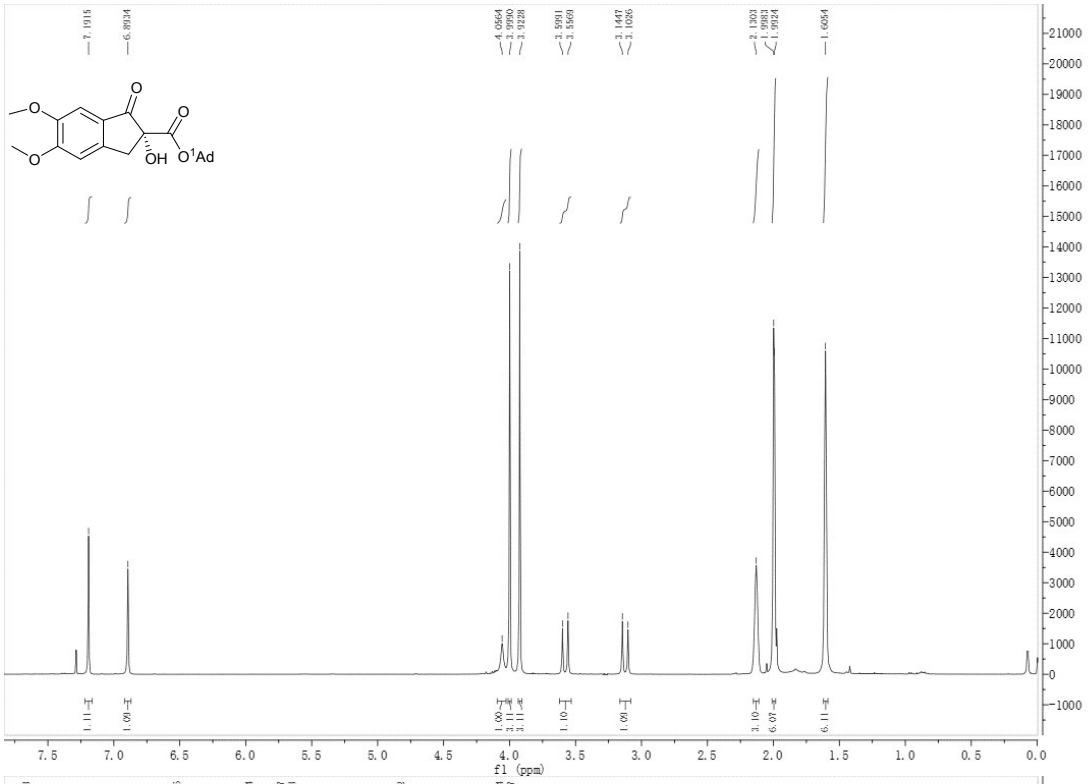
20.83
O
O
O
OH
O1Ad
f1 (ppm)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4.0864
3.9990
3.9228
3.5991
3.5569
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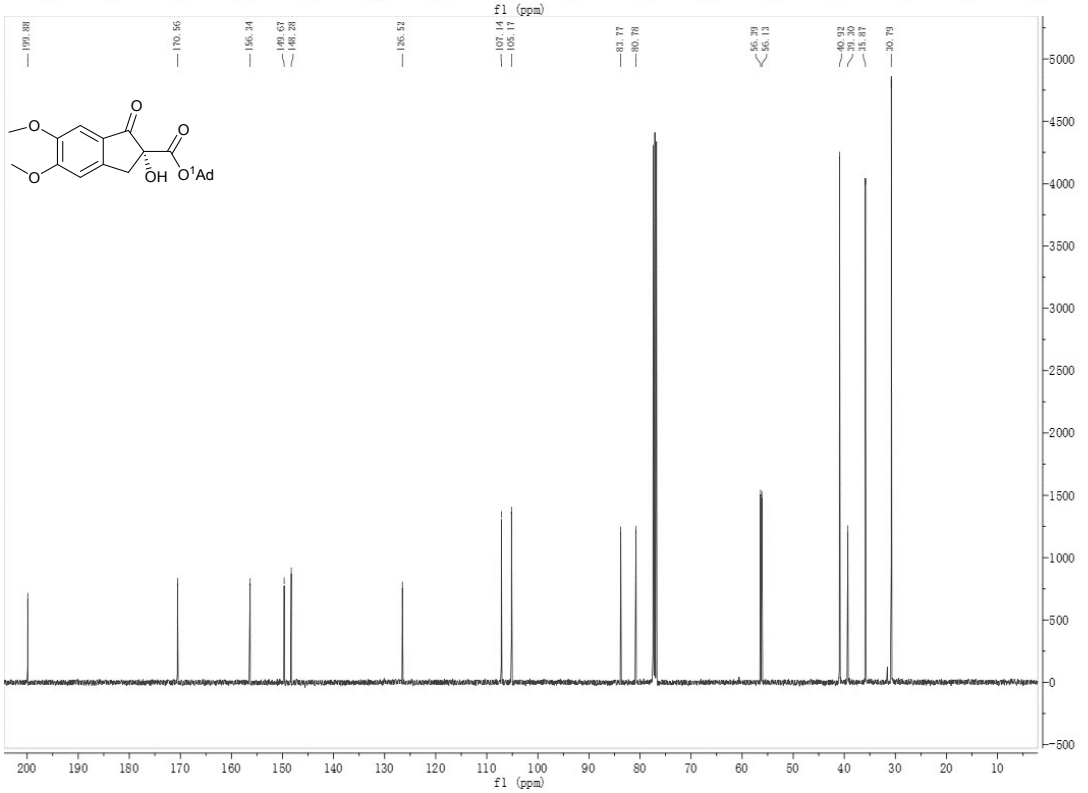
2.1303
1.9983
1.9924
1.6064
O
O
O
OH
O1Ad
f1 (ppm)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148.28
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107.14
105.17
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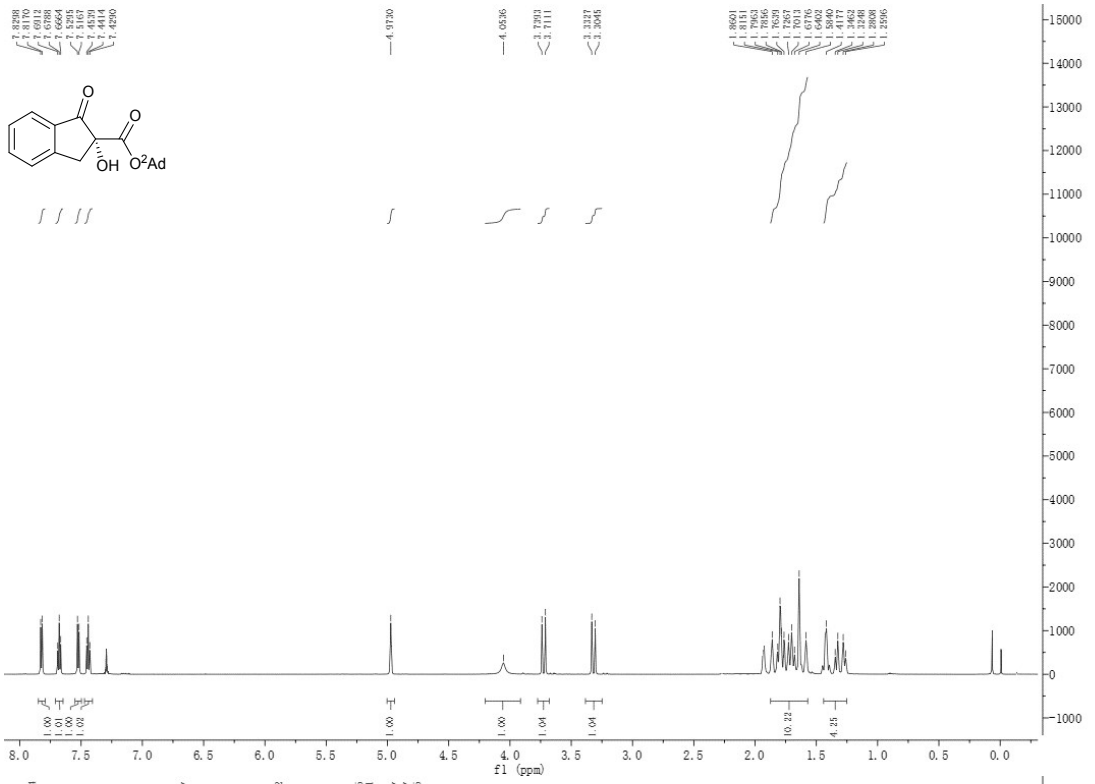
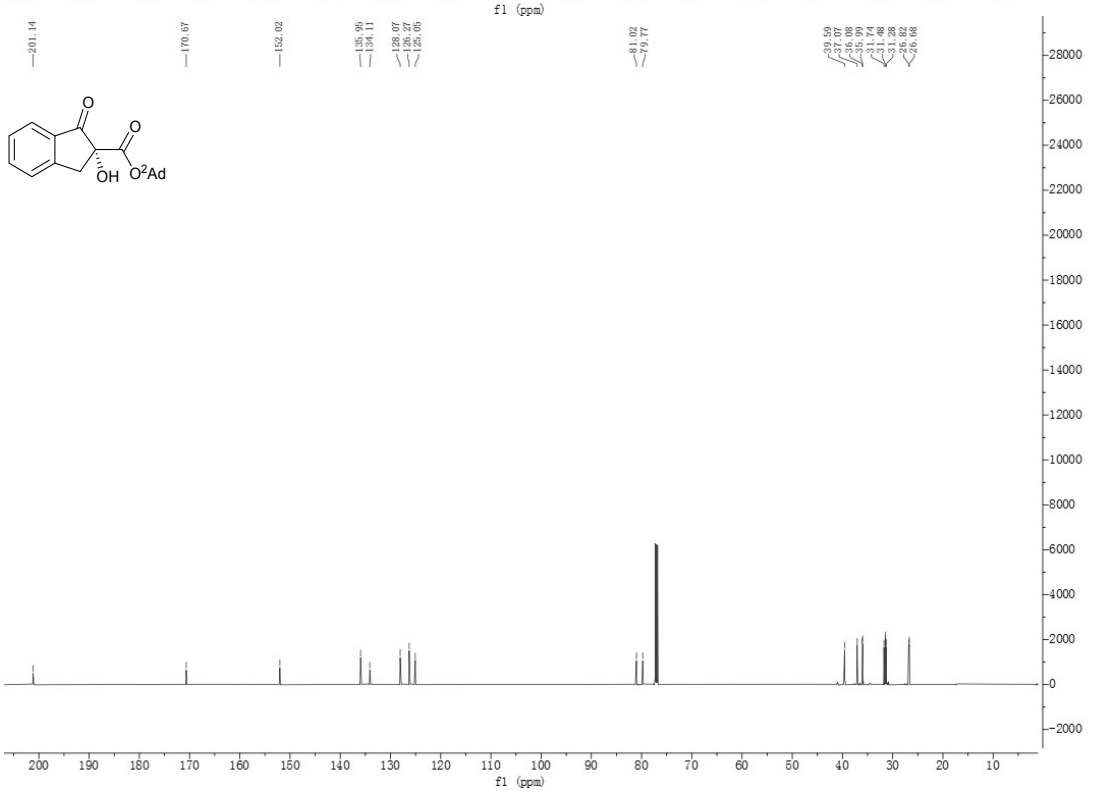
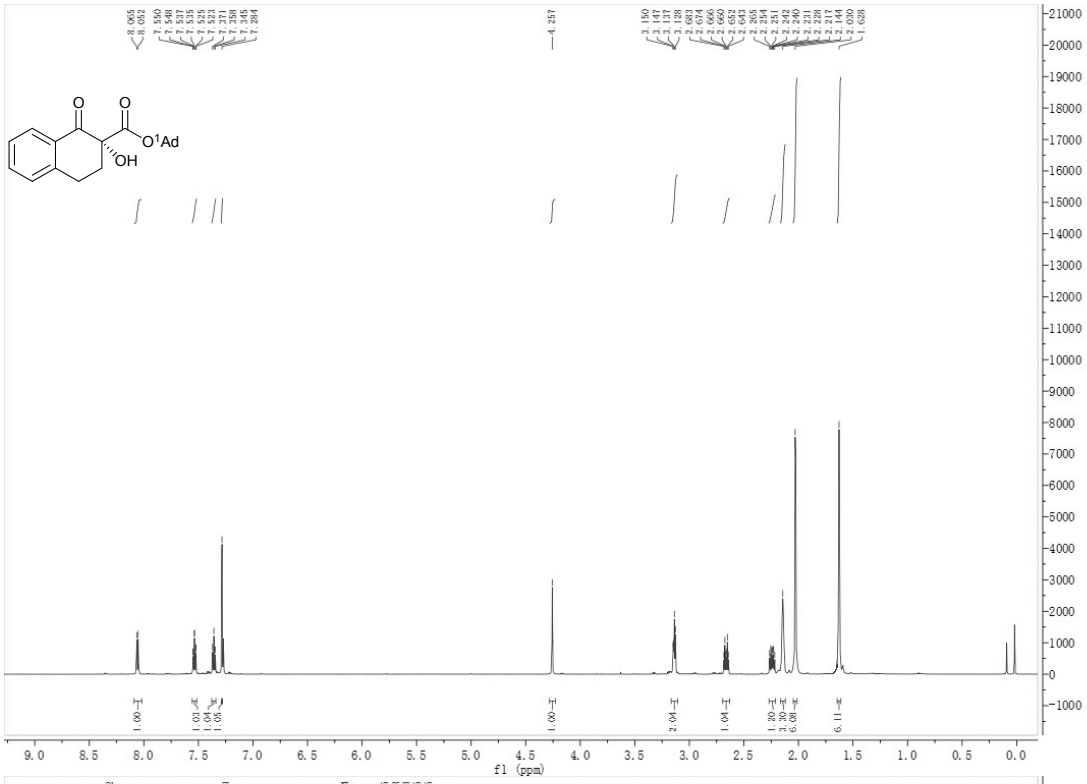
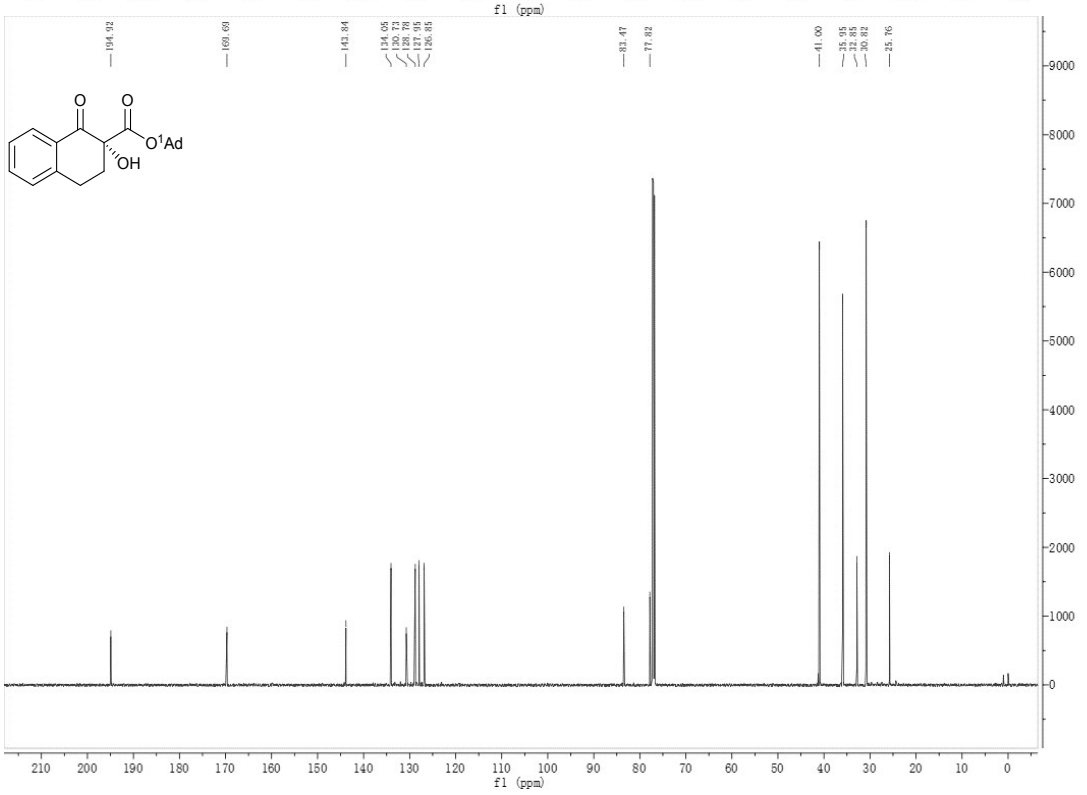
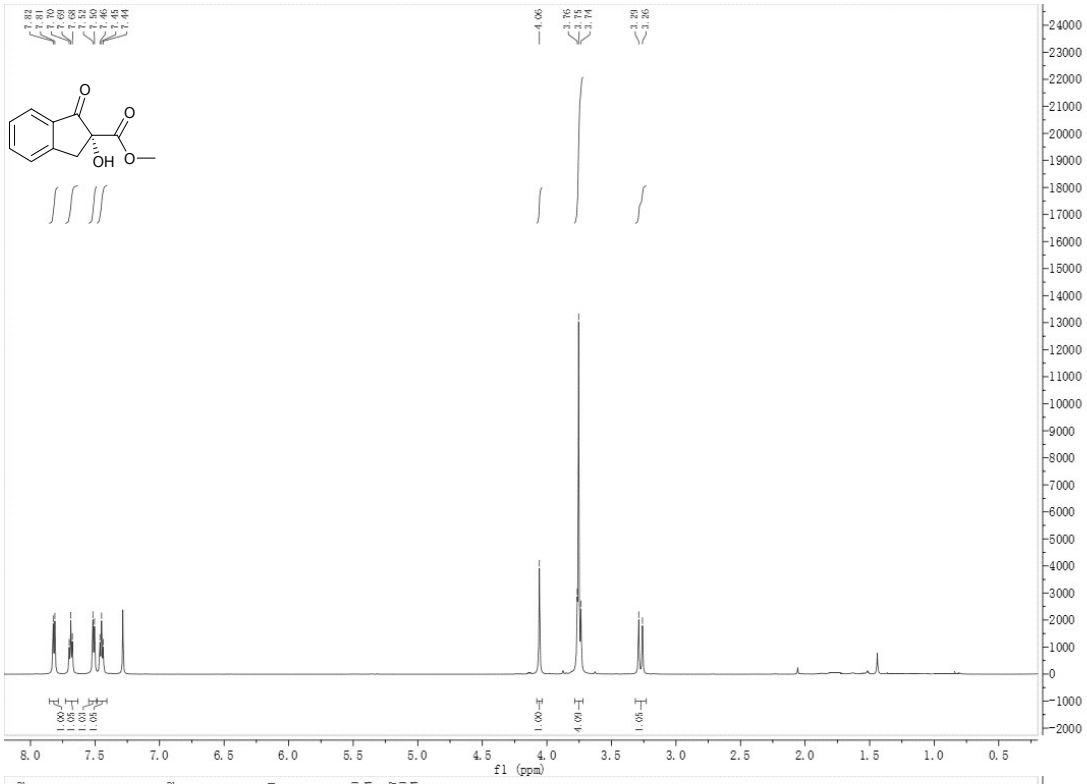
56.13
40.92
29.30
25.87
20.79
O
O
O
OH
O1Ad
f1 (ppm)


O
O
OH
O2Ad
f1 (ppm)


O
O
OH
O2Ad
f1 (ppm)


O
O
O1Ad
OH
f1 (ppm)


O
O
O1Ad
OH
f1 (ppm)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7.45
7.44
4.06
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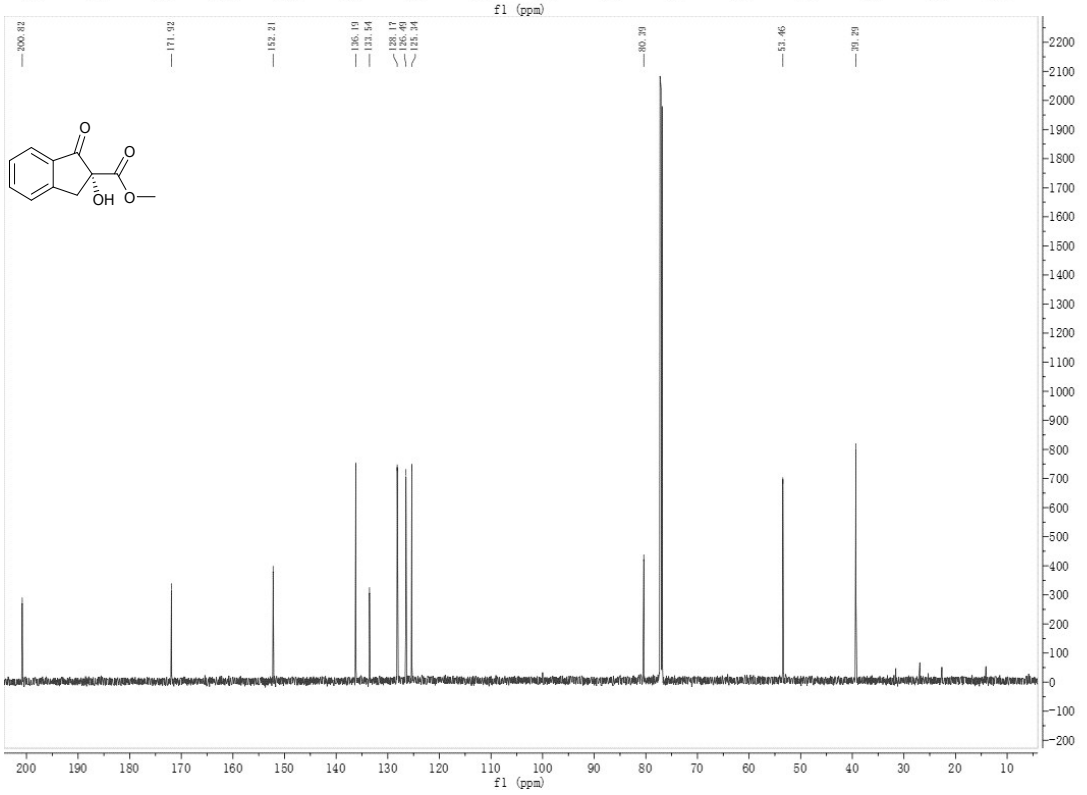
3.75
3.74
3.29
3.26
O
O
OH
O
1.00
1.05
1.03
1.05
1.00
4.09
1.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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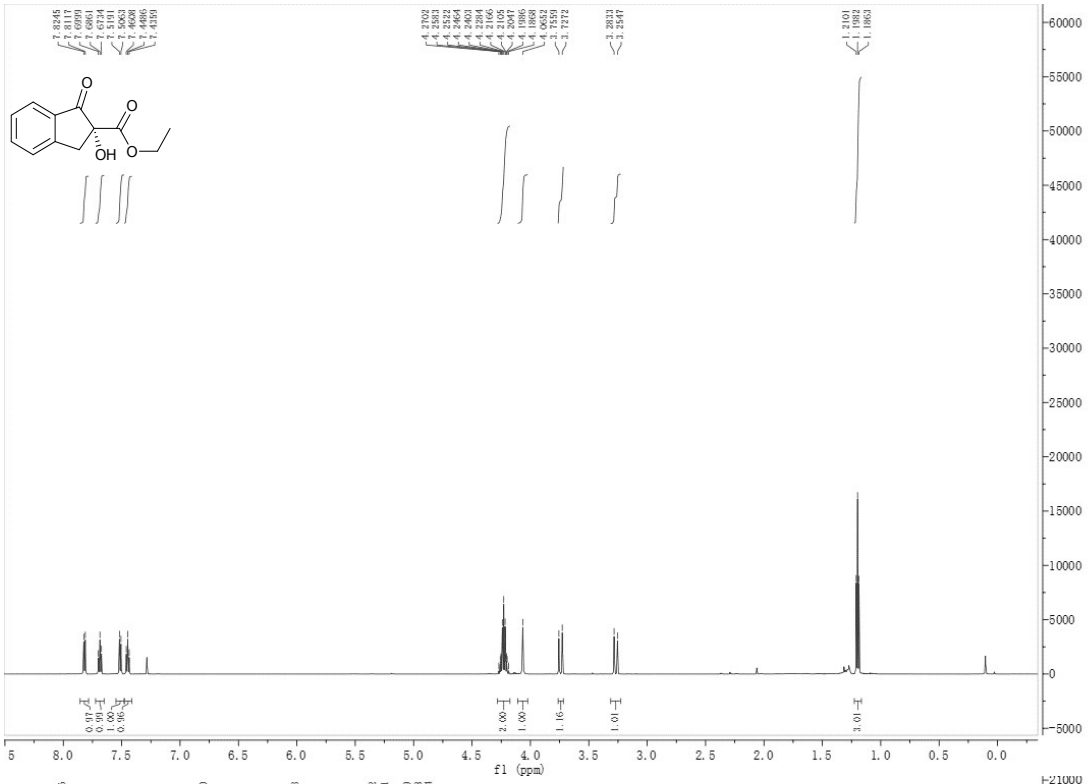
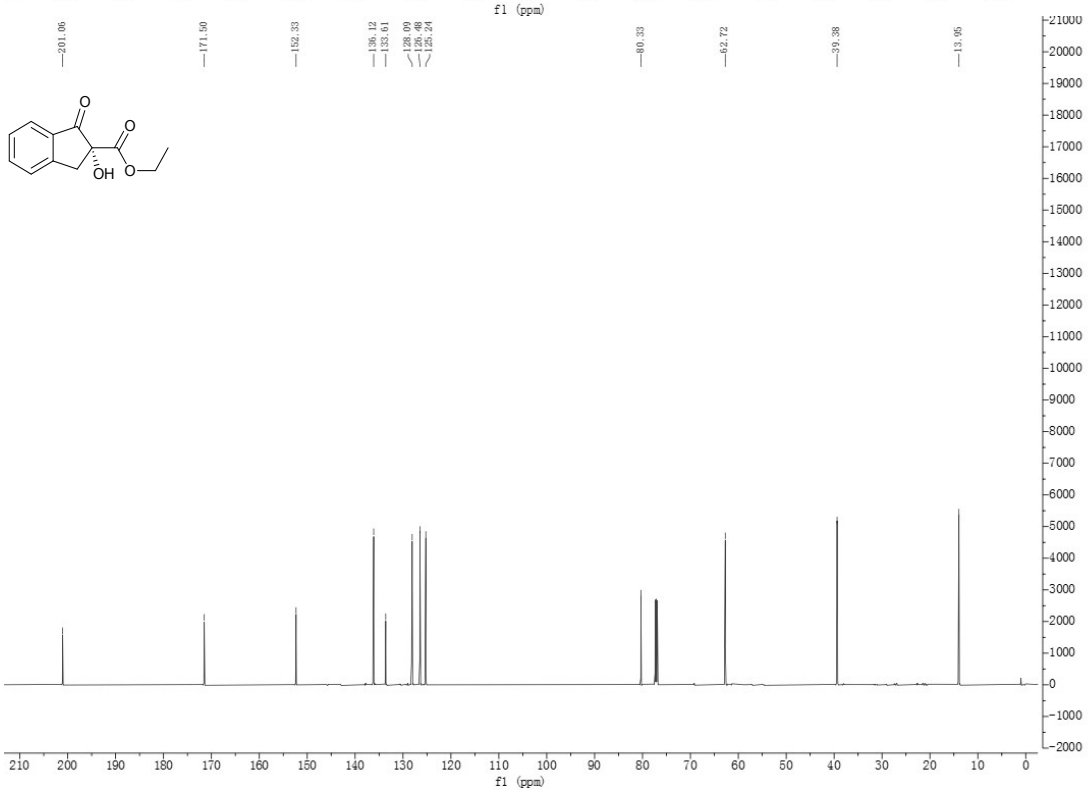
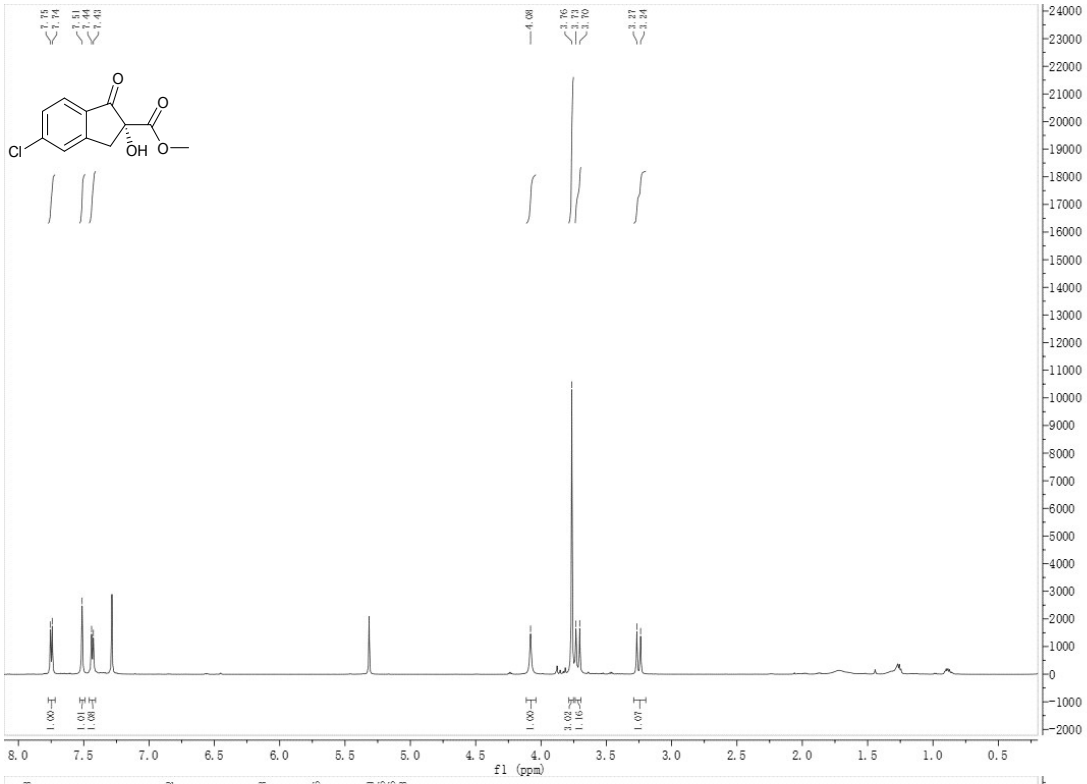
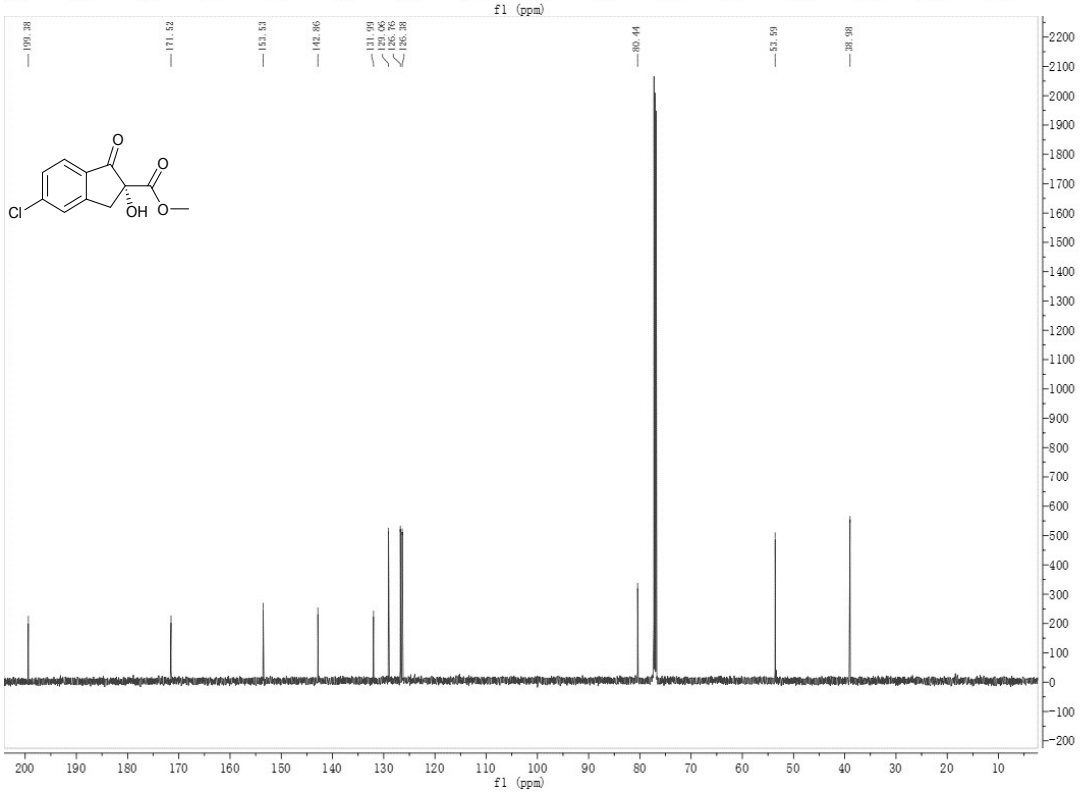
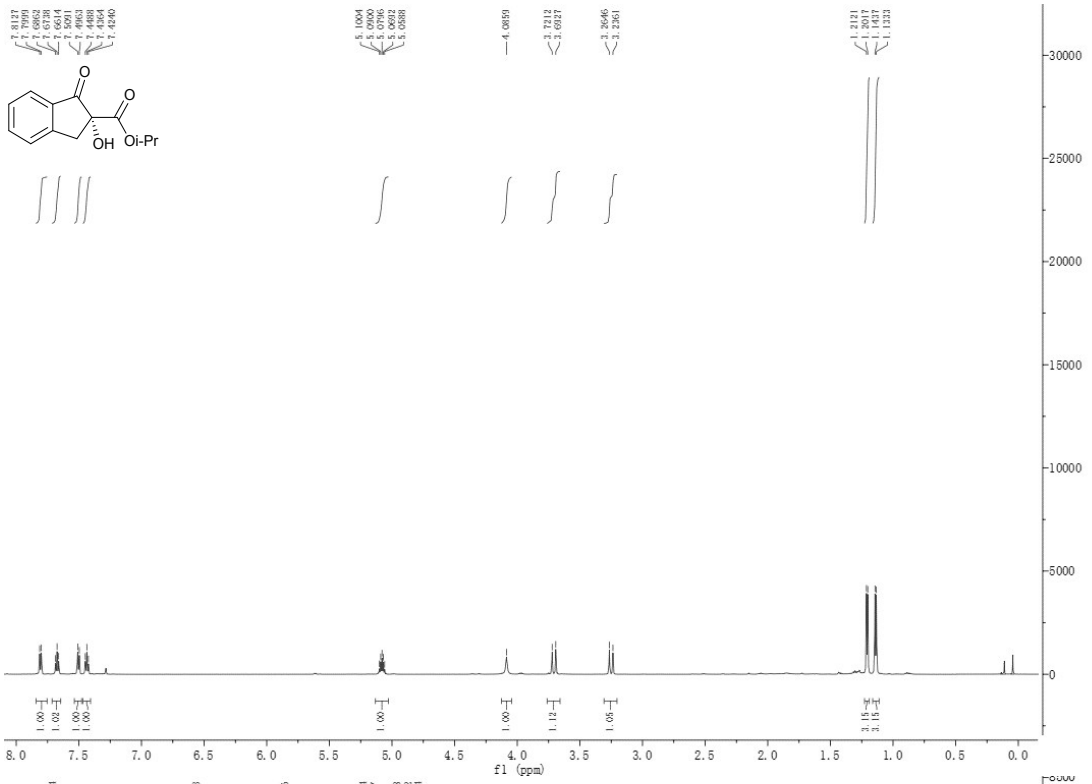
133.54
128.17
126.49
125.34
80.39
53.46
39.29
O
O
OH
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.8345
7.8117
7.6999
7.6861
7.6674
7.5191
7.5063
7.4606
7.4496
7.4359
4.2702
4.2532
4.2464
4.2403
4.2294
4.2256
4.2105
4.2047
4.1986
4.1898
4.0652
3.7559
3.7272
3.2833
3.2547
1.2101
1.1952
1.1863
0.97
0.97
1.00
0.96
2.00
1.00
1.16
1.01
3.01
f1 (ppm)


201.06
171.50
152.33
136.12
133.61
128.09
126.48
125.24
80.33
62.72
39.38
13.95
f1 (ppm)


7.75
7.74
7.51
7.44
7.43
4.08
3.76
3.73
3.70
3.27
3.24
O
O
Cl
OH
O
1.00
1.01
1.08
1.00
3.02
1.16
1.07
f1 (ppm)


199.38
171.52
153.53
142.86
131.99
129.95
126.95
126.38
80.44
53.59
28.98
O
O
Cl
OH
O
f1 (ppm)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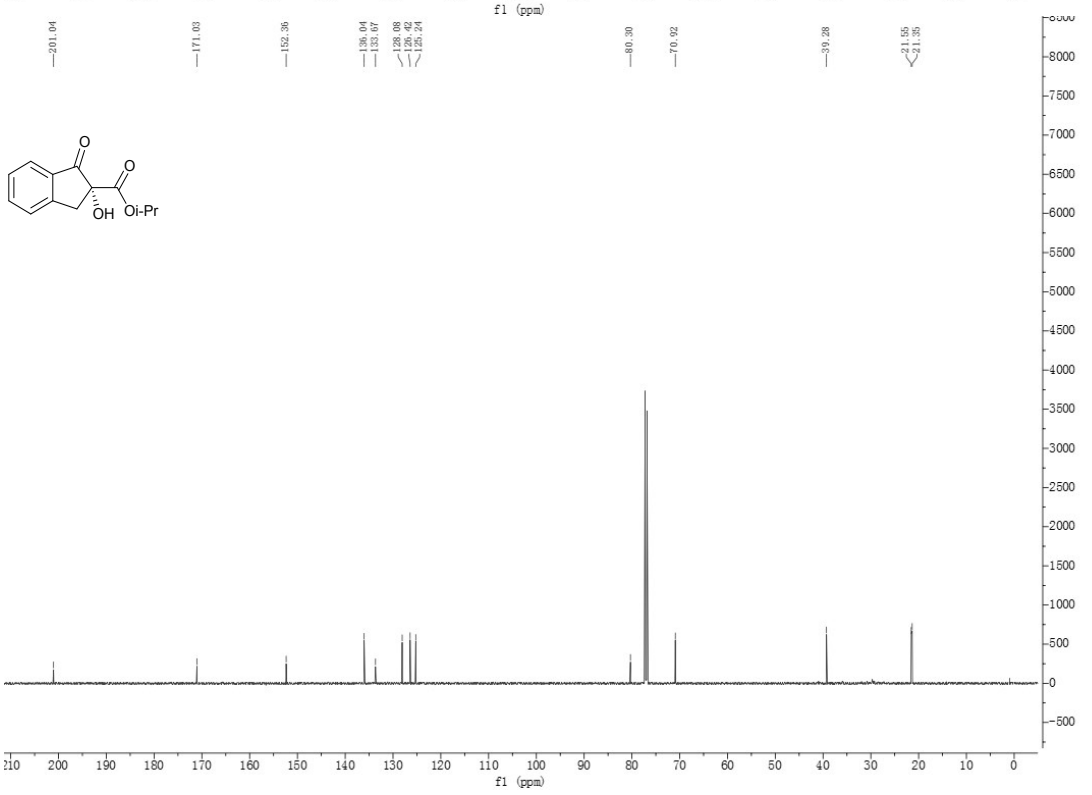
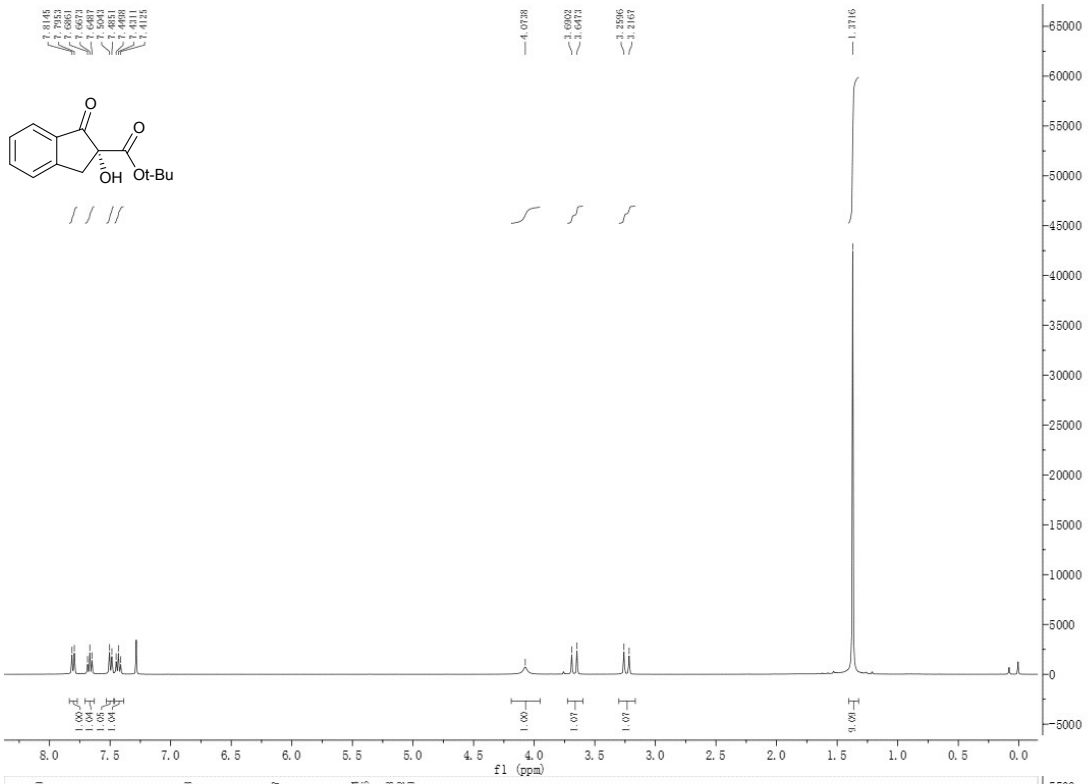
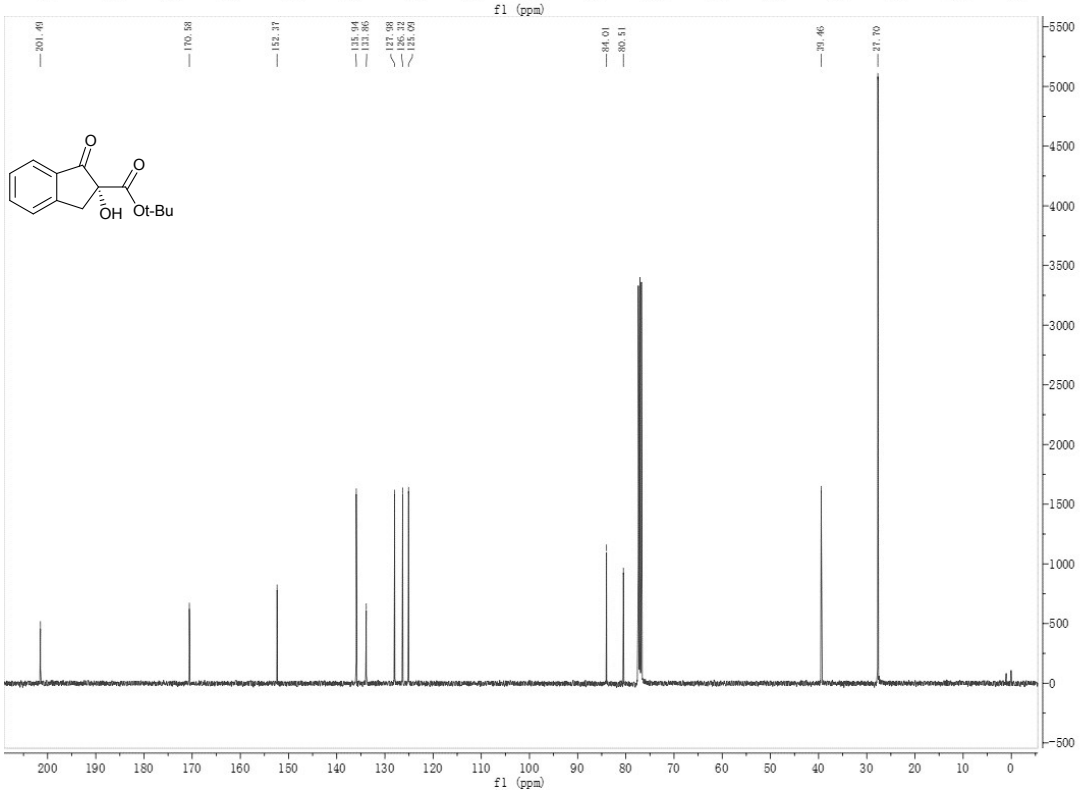
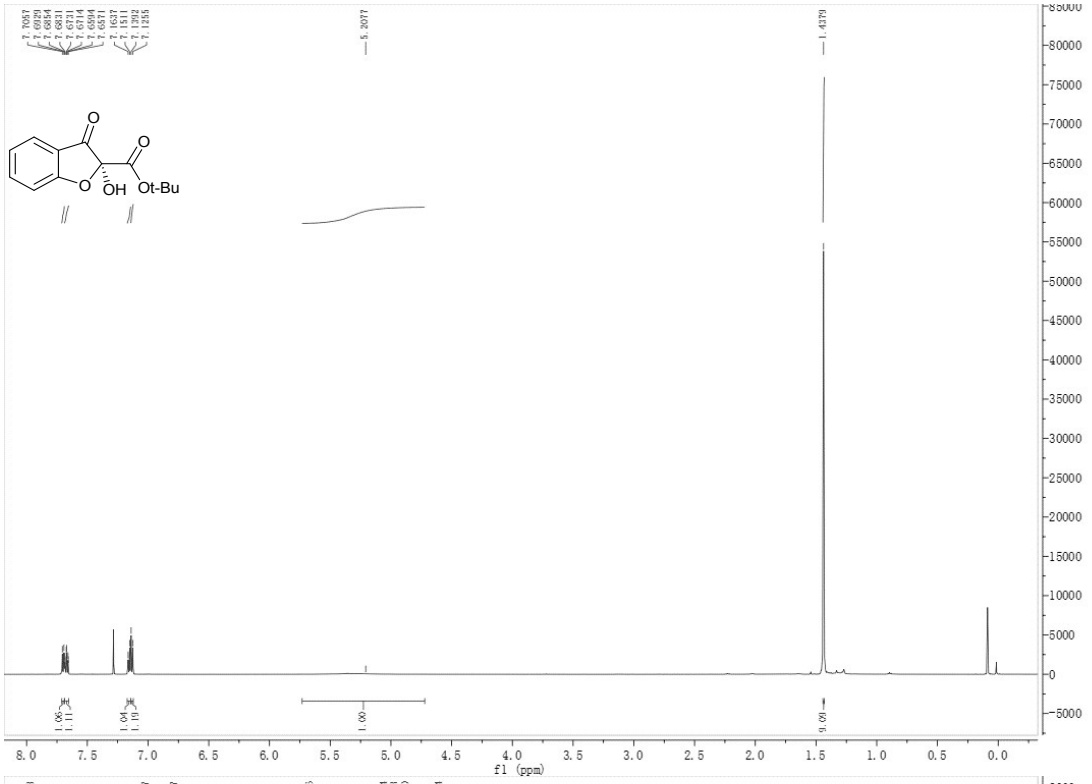
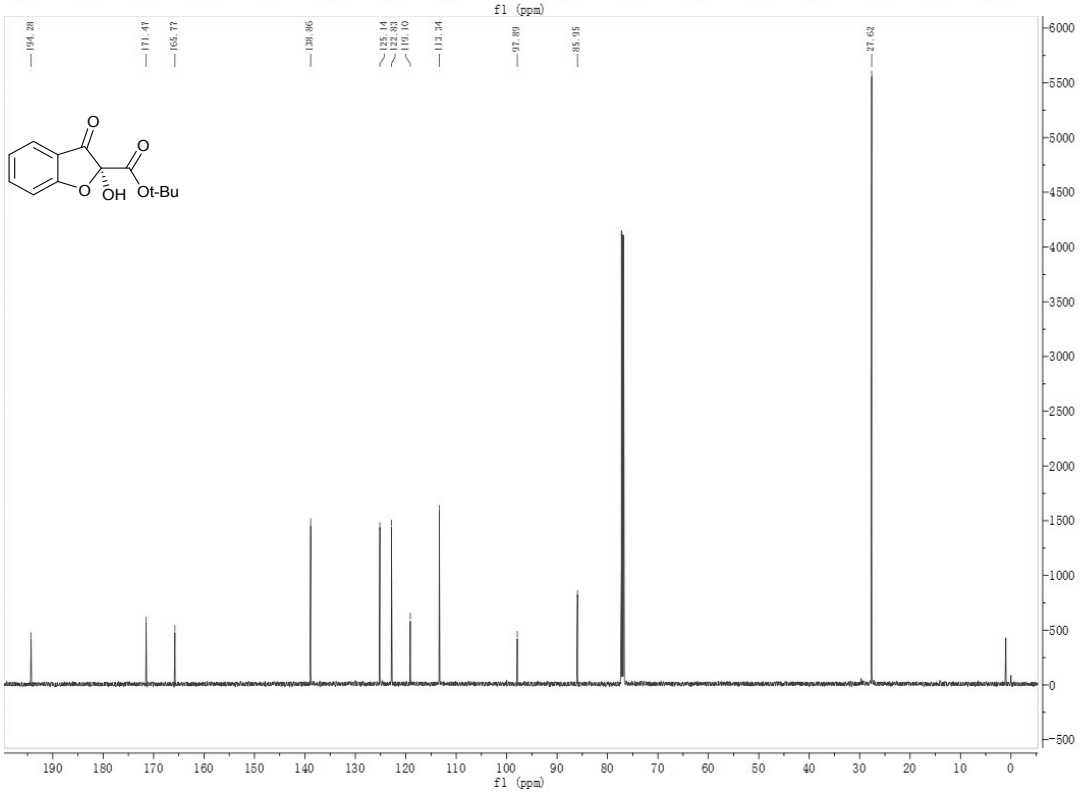
7.7999
7.6862
7.6738
7.6644
7.5091
7.4963
7.4488
7.4364
7.4240
5.1004
5.0900
5.0796
5.0692
5.0588
4.0659
3.7212
3.6927
3.3646
3.2361
1.2121
1.2017
1.1437
1.1333
O
O
OH
Oi-Pr
1.00
1.02
1.00
1.00
1.00
1.12
1.05
3.15
3.15
f1 (ppm)

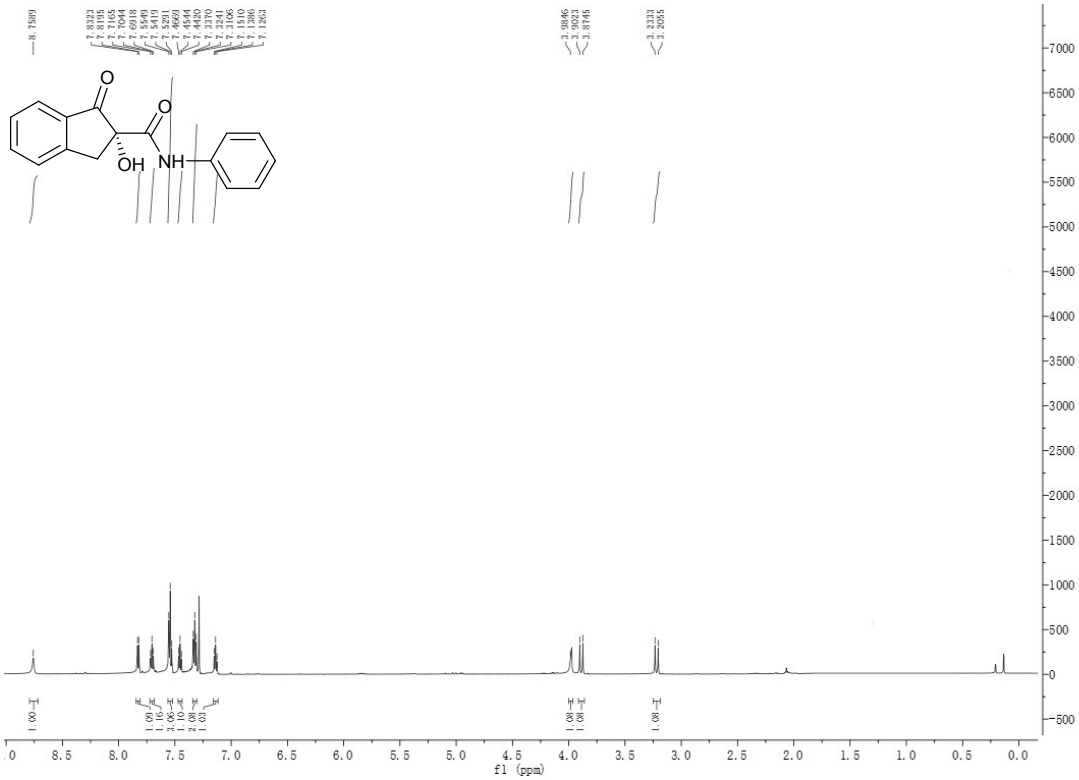

201.04
171.03
152.36
136.04
133.67
128.08
126.62
125.24
80.30
70.92
39.28
21.55
21.35
O
O
OH
Oi-Pr
f1 (ppm)

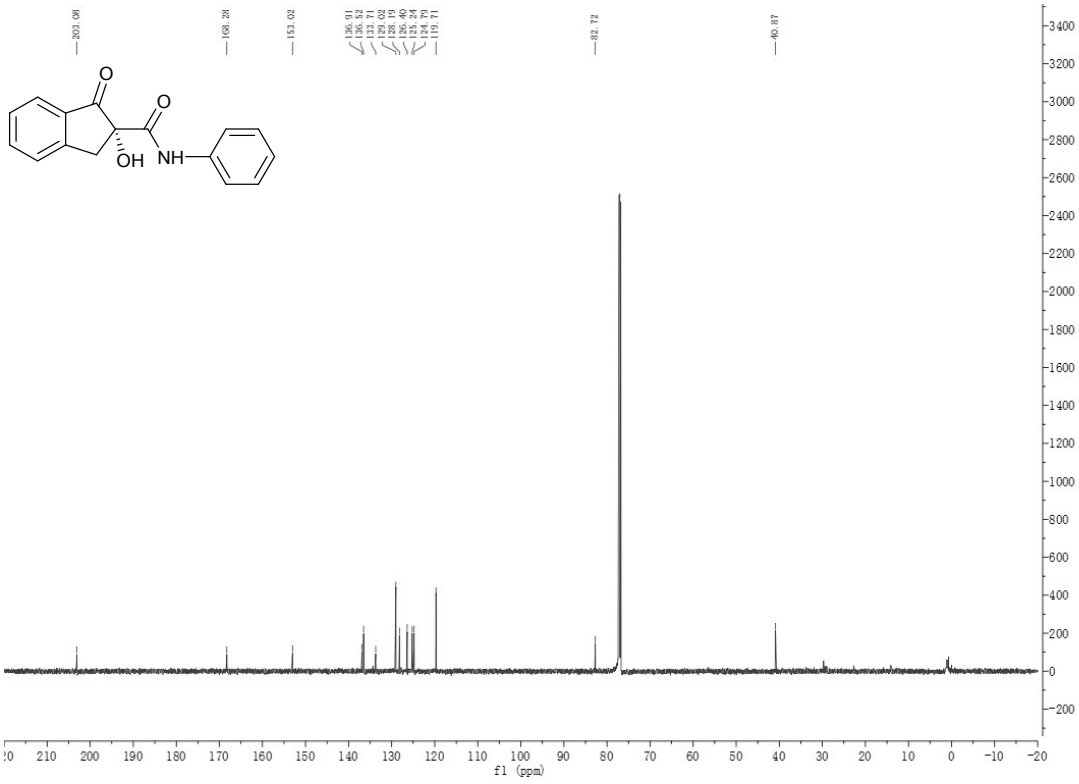

7.8145
7.7953
7.6861
7.6673
7.6487
7.6454
7.4651
7.4498
7.4311
7.4125
4.0738
3.6902
3.6473
3.2596
3.2167
1.3716
O
O
OH
Ot-Bu
1.00
1.04
1.04
1.04
1.00
1.07
1.07
9.09
f1 (ppm)

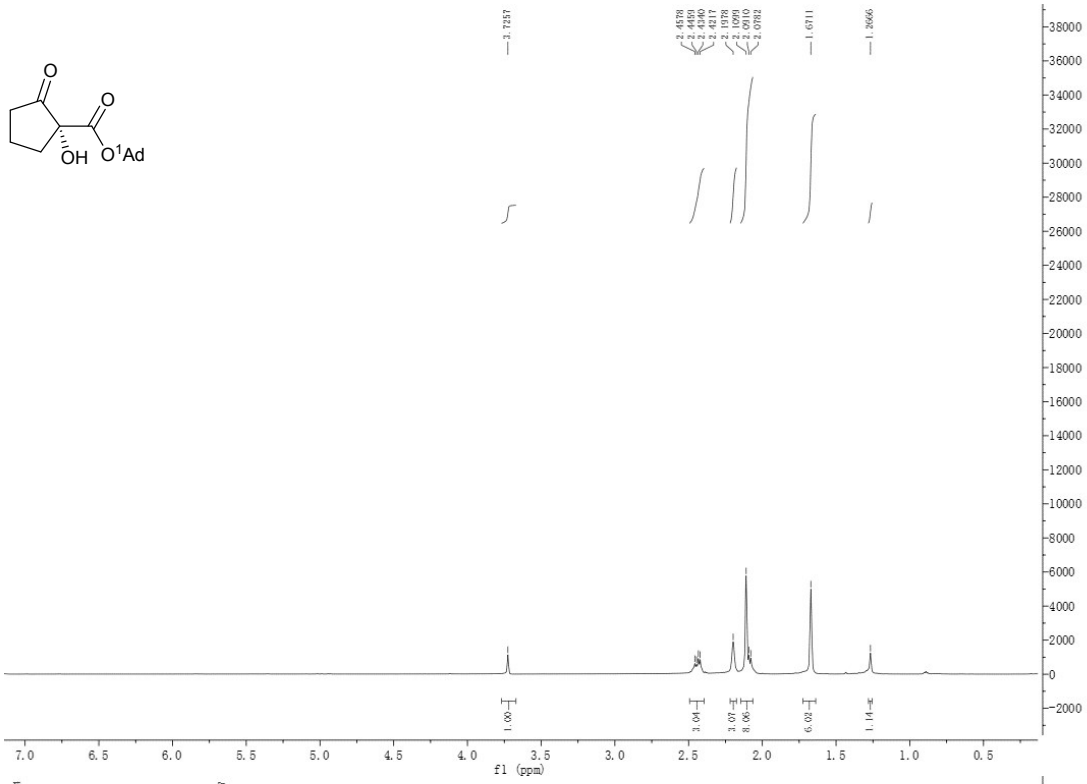

201.49
170.58
152.37
135.94
133.86
127.98
126.32
125.09
84.01
80.51
29.46
27.70
O
O
OH
Ot-Bu
f1 (ppm)

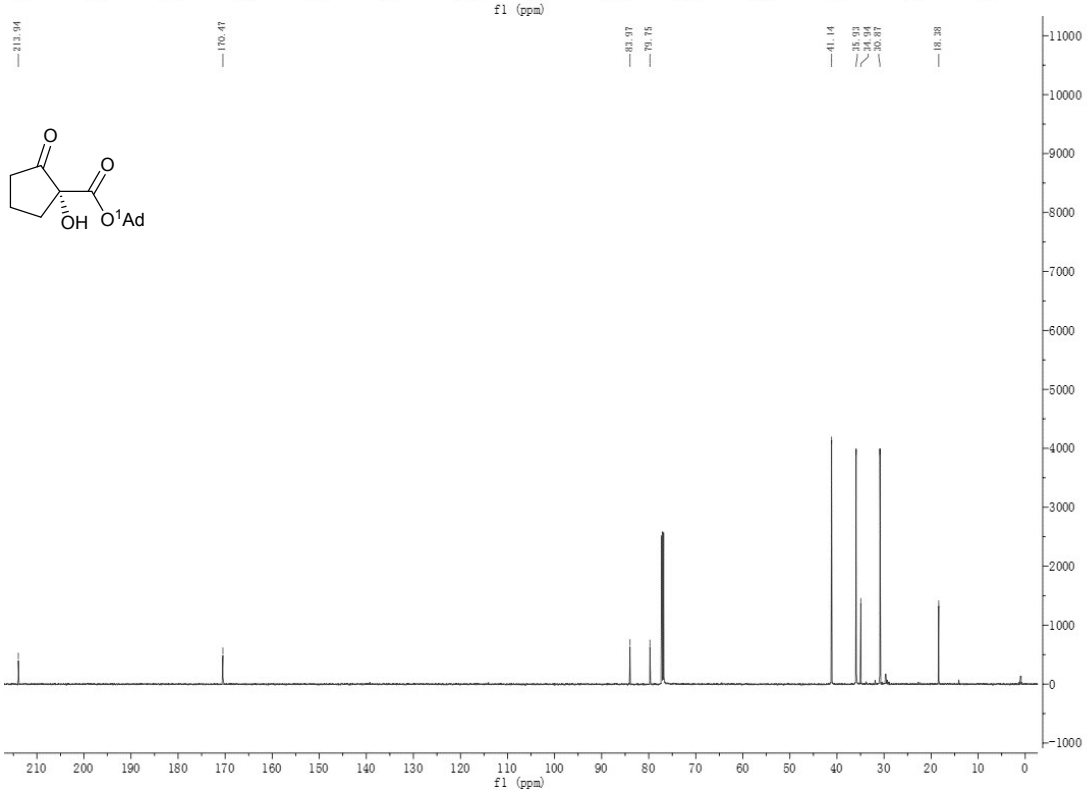

7.7057
7.6929
7.6854
7.6831
7.6731
7.6714
7.6594
7.6571
7.6437
7.1511
7.1392
7.1255
5.2077
1.4379
O
O
O
OH
Ot-Bu
1.06
1.11
1.04
1.10
1.00
9.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

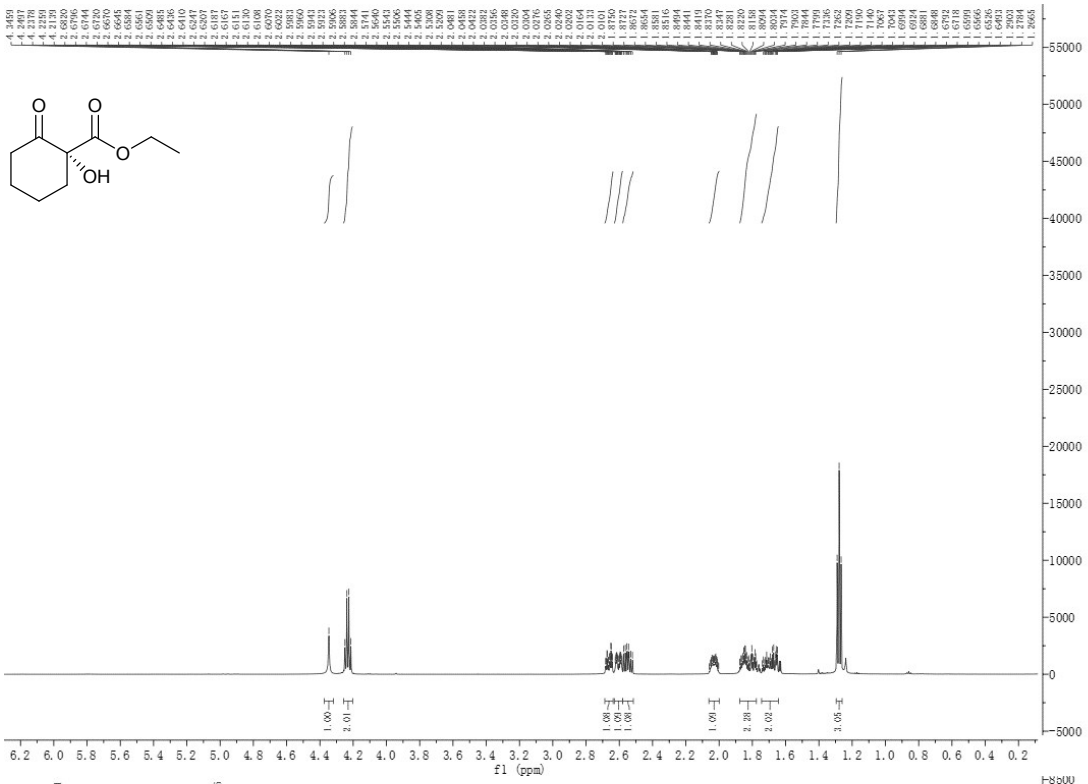

194.28
171.47
165.77
138.86
125.14
123.83
119.10
113.34
97.89
85.95
27.62
O
O
O
OH
Ot-Bu
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

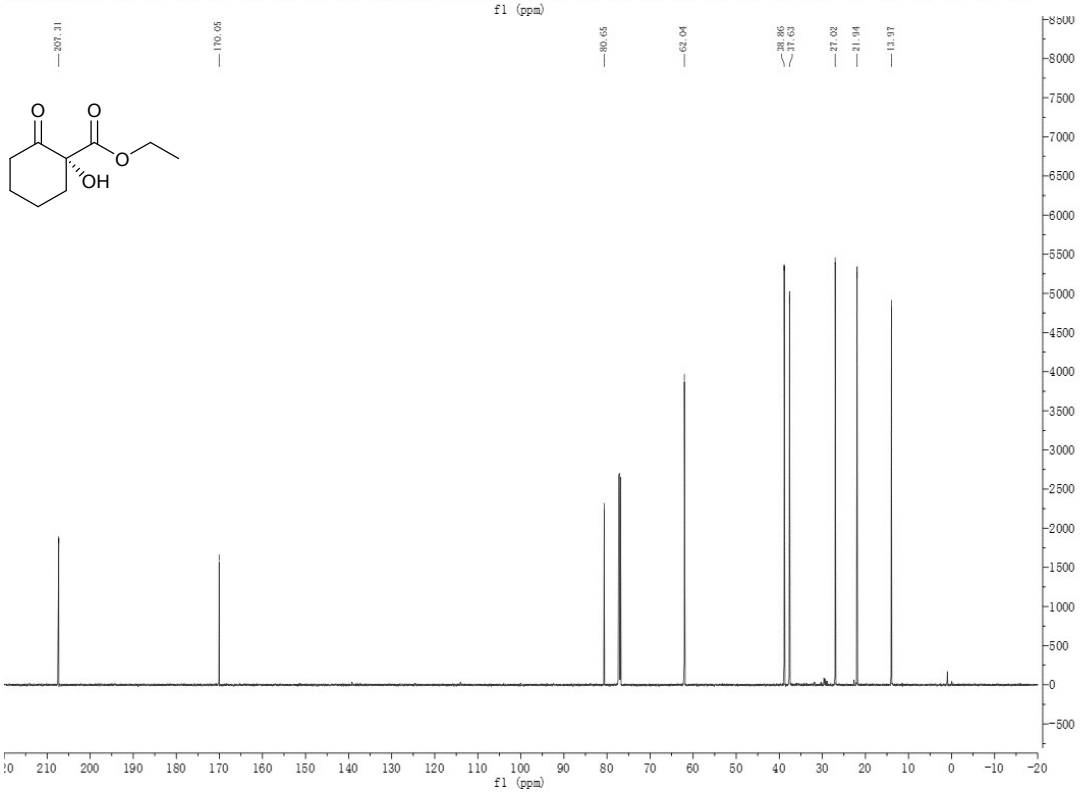

O
O
OH
NH
f1 (ppm)


O
O
OH
NH
f1 (ppm)


O
O
OH
O1Ad
3.7257
2.4578
2.4450
2.4306
2.4217
2.1978
2.1099
2.0910
2.0782
1.6711
1.2666
1.00
3.04
3.07
8.06
6.02
1.14
f1 (ppm)


O
O
OH
O1Ad
213.94
170.47
83.97
79.75
41.14
35.93
34.94
30.87
18.38
f1 (ppm)





6. References:

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[2] House, H. O.; Hudson, C. B. *J. Org. Chem.* **1970**, *35*, 647.

[3] Nakajima, M.; Yamamoto, S.; Yamaguchi, Y.; Nakamura, S.; Hashimoto, S. *Tetrahedron.* **2003**, *59*, 7307.

[4] Fusco, C. D; Meninno, S.; Tedesco, C.; Lattanzi, A. *Org. Biomol. Chem.* **2013**, *11*, 896.

[5] Zhao, L.; Huang, G.-X.; Guo, B.-B.; Xu, L.-J.; Chen, J.; Cao, W.-G.; Zhao, G.; Wu, X.-Y. *Org. Lett*. **2014**, *16*, 5584-5587.