Supporting Information

Efficient and Convenient Synthesis of Methyl (S)-5-Chloro-2-Hydroxy-1-Oxo-2,3-Dihydro-1H-Indene-2-Carboxylate: A Key Intermediate for (S)-Indoxacarb Using Aqueous TBHP as Oxidant

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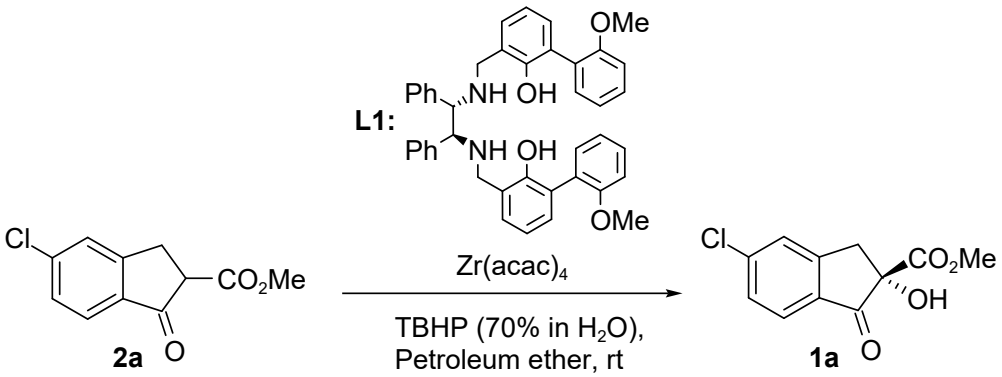
1. General Information

TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light. Column chromatography was performed on silica gel (200-300 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Agilent-400 MHz. Chemical shifts are reported in ppm versus tetramethylsilane with either tetramethylsilane or the residual solvent resonance used as an internal standard. Abbreviations were used in the description of NMR data as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constant (*J*, Hz). Mass spectra were determined on an Agilent 6520 QTOF., using electron spray ionization (ESI). Melting points are performed on an SGWX-4 digital visual melting point apparatus without correction. All other commercial chemicals were used without further purification.

2. Reaction optimization tables

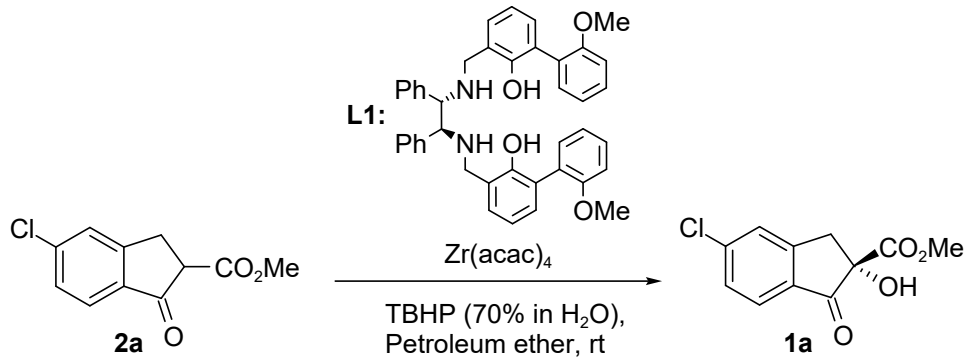
2.1 Optimization of the amount of $Zr(acac)_4$ and **L1** (Table S1)



Entry[a]	Zr(acac)$_4$ (equiv.)	L1 (equiv.)	Yield[b]	ee[c]
1	0.100	0.110	88%	99%
2	0.050	0.055	88%	99%
3	0.040	0.044	89%	99%
4	0.030	0.033	82%	99%
5	0.020	0.022	32%	99%

[a] Reaction conditions: $Zr(acac)_4$ (x equiv.), **L1** (y equiv.), Petroleum ether (4.3 mL), 30 min. Then, **2a** (0.25 mmol, 1.0 equiv.), TBHP (70% in H_2O) (0.375 mmol, 1.5 equiv.), 24 h. [b] Isolated yield and purification by filtration. [c] Determined by chiral HPLC.

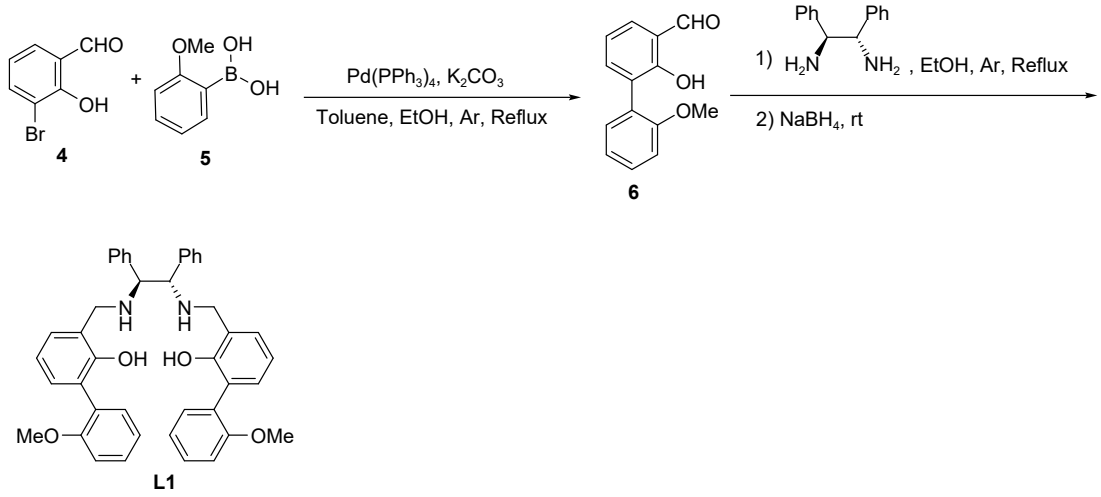
2.2 Optimization of the amount of TBHP and the volume of petroleum ether (Table S2)



Entry[a]	TBHP (70% in H_2O) (equiv.)	Volume of petroleum ether	Yield[b]	ee[c]
1	1.5	4.3 mL	89%	99%
2	2.0	4.3 mL	82%	99%
3	1.2	4.3 mL	84%	99%
4	1.0	4.3 mL	78%	99%
5	1.5	3.5 mL	92%	99%
6	1.5	3.0 mL	86%	99%

[a] Reaction conditions: $Zr(acac)_4$ (0.01 mmol, 0.04 equiv.), **L1** (0.011 mmol, 0.044 equiv.), Petroleum ether (x mL), 30 min. Then, **2a** (0.25 mmol, 1.0 equiv.), TBHP (70% in H_2O) y equiv.), 24 h. [b] Isolated yield and purification by filtration. [c] Determined by chiral HPLC.

3. Preparation of chiral ligan L1

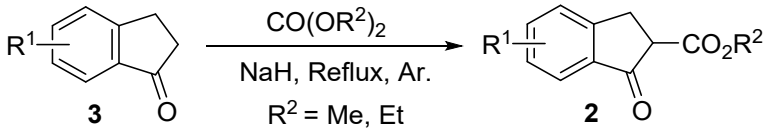


Under argon, 60 mL of toluene and 15 mL of ethanol were added to a mixture of 3-bromo-2-hydroxybenzaldehyde (2.010 g, 10 mmol), (2-methoxyphenyl) boronic acid (1.823 g, 12 mmol) and $Pd(PPh_3)_4$ (0.254 g, 0.22 mmol), giving a yellow solution, to which solid anhydrous K_2CO_3 (3.040 g, 22 mmol) was added. The reaction mixture was stirred for 4 hours under reflux and then allowed to cool to room temperature. Afterwards, the mixture was transferred to a separating funnel to which water and ethyl acetate were added. The water phase was extracted with ethyl acetate, and the organic phase was combined and dried with Na_2SO_4. Purification using column chromatography on silica gel (petroleum ether/dichloromethane = 3/1) to give the desired product **6** as a white solid (2.043 g, 89%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.31 (s, 1H), 9.94 (s, 1H), 7.56 (t, J = 8.3 Hz, 2H), 7.38 (t, J = 7.9 Hz, 1H), 7.29 (d, J = 7.4 Hz, 1H), 7.12 – 6.98 (m, 3H), 3.80 (s, 3H). Analytical data are in agreement with those reported in the literature [1].

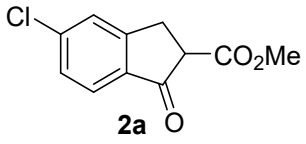
To a solution of (1*S*,2*S*)-1,2-diphenylethane-1,2-diamine (0.849 g, 4.0 mmol) in ethanol (120 mL) was added 2-hydroxy-2'-methoxy-[1,1'-biphenyl]-3-carbaldehyde **6** (1.826 g, 8.0 mmol). The reaction mixture refluxed for 14 h under argon. After cooling to 0 ℃, to the above reaction mixture was added sodium borohydride (0.454 g, 12 mmol). The resulting mixture was stirred at room temperature for 5 h, and a second portion of sodium borohydride (0.227 g, 6 mmol) was added. After stirring at room temperature for 1 h, the reaction mixture was poured into water 50 mL and the ethanol

was removed in vacuo. The suspension was extracted with dichloromethane and the combined organic layers were washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to **L1** as a white solid (2.394 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.31 (dd, *J* = 7.4, 1.5 Hz, 2H), 7.24 – 7.18 (m, 6H), 7.16 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.98 – 6.93 (m, 4H), 6.86 – 6.82 (m, 2H), 6.79 (t, *J* = 7.4 Hz, 2H), 4.01 (s, 2H), 3.86 (d, *J* = 13.5 Hz, 2H), 3.77 (s, 6H), 3.65 (d, *J* = 13.5 Hz, 2H). Analytical data are in agreement with those reported in the literature [2].

4. General procedure for the synthesis of β-keto esters [2,3]



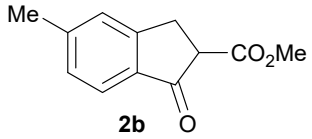
To a suspension of NaH (7.5 mmol, 60% dispersion in mineral oil) in dimethyl carbonate or diethyl carbonate (4.8 mL) was added a solution of indanone **3** (3.0 mmol) in dimethyl carbonate or diethyl carbonate (4.8 mL) dropwise at room temperature. The resulting mixture was heated to reflux until full conversion of **3** as indicated by TLC. The resulting solid was dissolved in H_2O (12 mL) and HCl (2 M, 3 mL), extracted with DCM and dried over Na_2SO_4. Purification using column chromatography on silica gel to give the desired product **2**.



2a

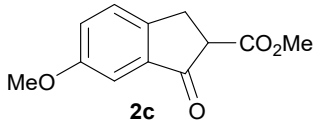
Following general procedure and **2a** was obtained as a yellow solid (579 mg, 86%) after purification by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (duplicate signals are observed for some hydrogens; asterisks indicate those corresponding to the enol rotamer) 10.34* (s, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.56* (d, *J* = 8.2 Hz, 1H), 7.51

(s, 1H), 7.46* (s, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 3.86* (s, 3H), 3.80 (s, 3H), 3.76 (dd, *J* = 8.3, 3.9 Hz, 1H), 3.56 (dd, *J* = 17.6, 4.0 Hz, 1H), 3.51* (s, 2H), 3.36 (dd, *J* = 17.5, 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (duplicate signals are observed for some carbons; asterisks indicate those corresponding to the enol rotamer) 198.1, 169.2, 155.1, 144.8*, 142.2, 135.5*, 133.7, 128.8, 127.5*, 126.9, 125.9, 125.3*, 121.8*, 53.3, 53.11*, 53.09, 51.5*, 32.5*, 30.0. Analytical data are in agreement with those reported in the literature [2].



2b

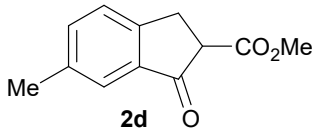
Following general procedure and **2b** was obtained as a brown liquid (490 mg, 80%) after purification by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (duplicate signals are observed for some hydrogens; asterisks indicate those corresponding to the enol rotamer) 10.46* (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.54* (d, *J* = 7.8 Hz, 1H), 7.31 (s, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 3.85* (s, 3H), 3.80 (s, 3H), 3.74 (dd, *J* = 8.2, 4.0 Hz, 1H), 3.52 (dd, *J* = 17.3, 3.7 Hz, 1H), 3.48* (s, 2H), 3.33 (dd, *J* = 17.2, 8.2 Hz, 1H), 2.46 (s, 3H), 2.44* (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (duplicate signals are observed for some carbons; asterisks indicate those corresponding to the enol rotamer) 199.0, 169.8, 154.3, 147.0, 133.0, 129.3*, 129.2, 127.0*, 126.9, 124.64, 124.60*, 53.5, 53.4*, 52.9, 52.8*, 32.4*, 30.2, 22.3, 22.2*. Analytical data are in agreement with those reported in the literature [2].



2c

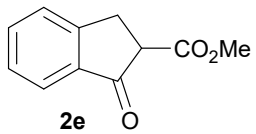
Following general procedure and **2c** was obtained as a yellow solid (362 mg, 55%) after purification by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (duplicate signals are observed for some hydrogens; asterisks indicate those corresponding to the enol rotamer) 10.39* (s, 1H), 7.77* (s, 1H), 7.58 – 7.47* (m, 1H), 7.39 (d, *J* = 7.9 Hz,

1H), 7.25 – 7.18 (m, 2H), 7.00* (d, *J* = 7.8 Hz, 1H), 3.98* (d, *J* = 26.9 Hz, 2H), 3.85* (s, 3H), 3.84 (s, 3H), 3.80 (s, 3H), 3.75* (s, 3H), 3.65 (d, *J* = 16.8 Hz, 1H), 3.47 (d, *J* = 17.4 Hz, 1H), 3.31 (dd, *J* = 16.8, 7.6 Hz, 1H), 3.18* (d, *J* = 16.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (duplicate signals are observed for some carbons; asterisks indicate those corresponding to the enol rotamer) 200.9*, 199.6, 172.1*, 169.7, 159.9*, 159.8, 146.7, 145.3*, 136.5, 134.8*, 127.3, 125.8*, 125.5*, 125.2, 106.3*, 105.7, 56.1*, 55.8, 54.0, 53.6*, 52.9, 51.4*, 38.8*, 29.7. Analytical data are in agreement with those reported in the literature [2].



2d

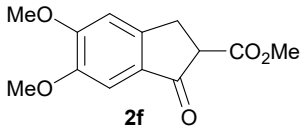
Following general procedure and **2d** was obtained as a gray solid (412 mg, 67%) after purification by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (duplicate signals are observed for some hydrogens; asterisks indicate those corresponding to the enol rotamer) 10.38* (s, 1H), 7.57 (s, 1H), 7.51 – 7.42 (m, 2H), 7.39* (d, *J* = 8.0 Hz, 1H), 7.35* (d, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 3.85 (s, 3H), 3.79* (s, 3H), 3.74 (dd, *J* = 8.1, 3.8 Hz, 1H), 3.51 (dd, *J* = 17.2, 3.4 Hz, 1H), 3.46* (s, 2H), 3.33 (dd, *J* = 17.1, 8.1 Hz, 1H), 2.43 (s, 3H), 2.40* (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (duplicate signals are observed for some carbons; asterisks indicate those corresponding to the enol rotamer) 199.7, 169.8, 151.1, 140.5*, 138.0, 136.9, 136.8*, 135.5, 130.6*, 126.3, 124.7, 124.5*, 121.2*, 53.6, 52.9, 51.3*, 32.2*, 30.0, 21.5*, 21.2. Analytical data are in agreement with those reported in the literature [2].



2e

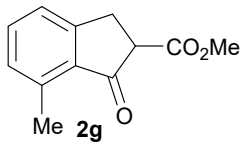
Following general procedure and **2e** was obtained as an orange liquid (437 mg, 77%) after purification by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (duplicate signals are observed for some hydrogens; asterisks indicate those corresponding to the

enol rotamer) 10.39* (s, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.44* (m, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 3.86* (s, 3H), 3.80 (s, 3H), 3.75 (dd, *J* = 8.0, 3.9 Hz, 1H), 3.58 (dd, *J* = 17.2, 3.6 Hz, 1H), 3.52* (s, 2H), 3.39 (dd, *J* = 17.3, 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (duplicate signals are observed for some carbons; asterisks indicate those corresponding to the enol rotamer) 199.6, 169.6, 153.7, 135.7, 135.53*, 135.45, 135.2*, 128.3*, 127.5, 126.8, 126.5*, 124.9, 124.7*, 53.4, 53.1*, 53.0, 52.8*, 30.3, 30.0*. Analytical data are in agreement with those reported in the literature [2].



2f

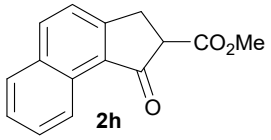
Following general procedure and **2f** was obtained as a white solid (709 mg, 94%) after purification by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 6.92 (s, 1H), 3.99 (s, 3H), 3.91 (s, 3H), 3.80 (s, 3H), 3.74 (dd, *J* = 7.8, 3.5 Hz, 1H), 3.47 (dd, *J* = 17.0, 3.3 Hz, 1H), 3.29 (dd, *J* = 17.1, 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 170.0, 156.2, 149.9, 149.4, 128.0, 107.4, 104.9, 56.5, 56.3, 53.5, 52.9, 30.1. Analytical data are in agreement with those reported in the literature [2].



2g

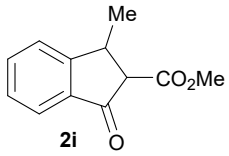
Following general procedure and **2g** was obtained as a white solid (527 mg, 86%) after purification by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (duplicate signals are observed for some hydrogens; asterisks indicate those corresponding to the enol rotamer) 10.76* (s, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 3.83* (s, 2H), 3.78 (s, 3H), 3.69 (dd, *J* = 8.4, 4.3 Hz, 1H), 3.49 (dd, *J* = 17.2, 4.2 Hz, 1H), 3.44* (s, 1H), 3.30 (dd, *J* = 17.2, 8.4 Hz, 1H), 2.63* (s, 3H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (duplicate signals are observed for some carbons; asterisks indicate those corresponding to the enol rotamer) 200.3, 169.9, 154.3,

143.9*, 139.9, 134.8, 132.7, 129.7, 129.3*, 128.9*, 123.9, 122.3*, 53.6, 52.77*, 52.76, 51.2*, 32.2*, 29.9, 18.5*, 18.4.



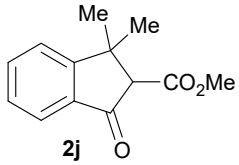
2h

Following general procedure and **2h** was obtained as a yellow solid (539 mg, 75%) after purification by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 3.87 – 3.82 (m, 1H), 3.81 (s, 3H), 3.63 (dd, *J* = 17.5, 2.4 Hz, 1H), 3.42 (dd, *J* = 17.6, 7.8 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 169.9, 157.4, 136.8, 132.9, 129.6, 129.4, 129.3, 128.4, 127.0, 124.0, 123.7, 53.7, 52.9, 30.7.



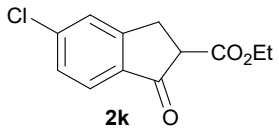
2i

Following general procedure and **2i** was obtained as a brown liquid (346 mg, 56%) after purification by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (duplicate signals are observed for some hydrogens; asterisks indicate those corresponding to the enol rotamer) 10.55* (s, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.64 – 7.60* (m, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.45* (m, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 3.88* (s, 3H), 3.87 – 3.82 (m, 1H), 3.81 (s, 3H), 3.73* (s, 1H), 3.67* (dd, *J* = 14.5, 7.3 Hz, 1H), 3.32 (d, *J* = 4.5 Hz, 1H), 1.50 (d, *J* = 7.1 Hz, 3H), 1.42* (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (duplicate signals are observed for some carbons; asterisks indicate those corresponding to the enol rotamer) 199.0, 169.6, 158.1, 135.7, 135.6*, 134.8, 129.8*, 128.1, 127.1*, 125.2, 124.5, 123.6*, 120.9*, 62.1, 58.1*, 52.8, 51.3*, 39.3*, 37.7, 20.1, 17.1*.



2j

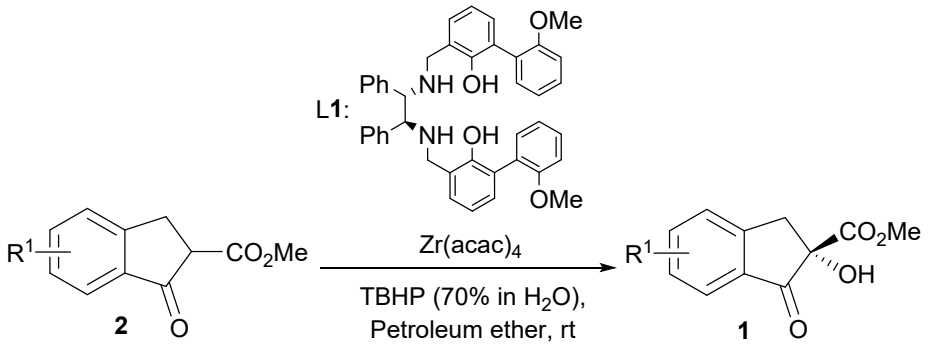
Following general procedure and **2j** was obtained as a brown liquid (519 mg, 79%) after purification by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (duplicate signals are observed for some hydrogens; asterisks indicate those corresponding to the enol rotamer) 10.70* (s, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.61* (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.42* (m, 2H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.35* (td, *J* = 7.4, 1.0 Hz, 1H), 3.89* (s, 3H), 3.75 (s, 3H), 3.50 (s, 1H), 1.57 (s, 3H), 1.43* (s, 6H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (duplicate signals are observed for some carbons; asterisks indicate those corresponding to the enol rotamer) 199.9, 169.7, 162.3, 155.2*, 135.8, 134.3, 134.2*, 130.2*, 128.1, 127.0*, 124.3, 123.5, 121.9*, 121.1*, 111.7*, 65.4, 52.2, 51.3*, 45.2*, 42.8, 30.6, 26.3*, 24.7.



2k

Following general procedure and **2k** was obtained as a brown liquid (473 mg, 66%) after purification by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (duplicate signals are observed for some hydrogens; asterisks indicate those corresponding to the enol rotamer) 10.43* (s, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.56* (d, *J* = 8.0 Hz, 1H), 7.51 (s, 1H), 7.46* (s, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.36* (s, 1H), 4.33* (q, *J* = 6.7 Hz, 2H), 4.25 (q, *J* = 6.9 Hz, 2H), 3.74 (dd, *J* = 8.0, 3.2 Hz, 1H), 3.55 (dd, *J* = 17.3, 3.9 Hz, 1H), 3.51* (s, 1H), 3.36 (dd, *J* = 17.4, 8.2 Hz, 1H), 1.37* (t, *J* = 7.2 Hz, 1H), 1.32 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (duplicate signals are observed for some carbons; asterisks indicate those corresponding to the enol rotamer) 198.2, 168.8, 155.2, 144.8*, 142.2, 135.6*, 133.8, 128.8, 127.5*, 126.9, 125.9, 125.3*, 121.7*, 62.1, 60.4*, 53.5, 32.6*, 30.1, 29.8*, 14.6*, 14.3.

5. General procedure for the enantioselective hydroxylation of β-keto ester



General procedure A:

To a solution of **L1** (0.014 g, 0.022 mmol) in petroleum ether (7.00 mL) was added $Zr(acac)_4$ (0.010 g, 0.020 mmol). The mixture was stirred at room temperature for 30 min. Then, β-keto ester **2** (0.50 mmol) and TBHP (70% in H_2O, 0.096 mL, 0.75 mmol) were added sequentially. The resulting solution was stirred at room temperature for 24 hours. The precipitates were formed during the course of the reaction, which was filtered and washed thoroughly with cold petroleum ether to give the desired product **1**.

General procedure B:

To a solution of **L1** (0.014 g, 0.022 mmol) in petroleum ether (7.00 mL) was added $Zr(acac)_4$ (0.010 g, 0.020 mmol). The mixture was stirred at room temperature for 30 min. Then, β-keto ester **2** (0.50 mmol) and TBHP (70% in H_2O, 0.096 mL, 0.75 mmol) were added sequentially, and the resulting solution was stirred at room temperature. After 24 hours, additional TBHP (70% in H_2O, 0.048 mL, 0.375 mmol) was added once every 8 hours for a total of 3 times. The precipitates were formed during the course of the reaction, which was filtered and washed thoroughly with cold petroleum ether to give the desired product **1**.

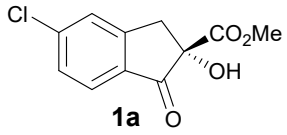
General procedure C:

To a solution of **L1** (0.014 g, 0.022 mmol) in petroleum ether (7.00 mL) was added $Zr(acac)_4$ (0.010 g, 0.020 mmol). The mixture was stirred at room temperature for 30

min. Then, β-keto ester **2** (0.50 mmol) and TBHP (70% in H_2O, 0.096 mL, 0.75 mmol) were added sequentially, and the resulting solution was stirred at room temperature. After 24 hours, additional TBHP (70% in H_2O, 0.048 mL, 0.375 mmol) was added once every 8 hours for a total of 3 times. The mixture was concentrated under vacuum. The residue was purified by column chromatography to give the desired product **1**.

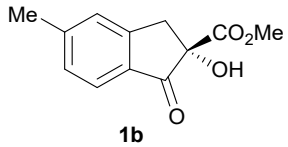
General procedure D:

To a solution of **L1** (0.014 g, 0.022 mmol) in petroleum ether (7.00 mL) was added $Zr(acac)_4$ (0.010 g, 0.020 mmol). The mixture was stirred at room temperature for 30 min. Then, β-keto ester **2** (0.50 mmol) and TBHP (70% in H_2O, 0.096 mL, 0.75 mmol) were added sequentially. The resulting solution was stirred at room temperature for 24 hours. The mixture was concentrated under vacuum. The residue was purified by column chromatography to give the desired product **1**.



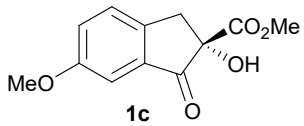
1a

Following general procedure A and **1a** was obtained as a solid (111 mg, yield 92%, ee 99%) after purification by filtration. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.74 (d, J = 8.2 Hz, 1H), 7.50 (s, 1H), 7.42 (d, J = 8.2 Hz, 1H), 4.00 (s, 1H), 3.75 (s, 3H), 3.70 (d, J = 17.5 Hz, 1H), 3.24 (d, J = 17.5 Hz, 1H). ^{13}C NMR($CDCl_3$, 100 MHz): δ = 199.6, 171.7, 153.7, 143.0, 132.0, 129.2, 126.9, 126.5, 80.5, 53.8, 39.0. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{11}H_9ClNaO_4$: 263.0082; found: 263.0078. HPLC analysis CHIRALPAK OD-H, Hexane: *i*-PrOH=9:1, 25 ℃, 1.0 mL/min flow rate, detection at 254 nm, t1=13.99 min (major), t2=17.75 min (minor). Analytical data are in agreement with those reported in the literature [2,3].



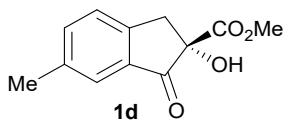
1b

Following general procedure A and **1b** was obtained as a solid (109 mg, yield 99%, ee 97%) after purification by filtration. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.30 (s, 1H), 7.24 (brs, 1H), 3.94 (s, 1H), 3.74 (s, 3H), 3.68 (d, *J* = 17.2 Hz, 1H), 3.21 (d, *J* = 17.2 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 200.7, 172.0, 152.6, 147.3, 131.2, 129.4, 127.2, 124.4, 80.0, 52.4, 40.7, 21.8. HRMS (ESI): calcd for $C_{12}H_{13}O_4$ $[M+H]^+$: 221.0808, found: 221.0805. HPLC analysis CHIRALPAK OD-H, Hexane: *i*-PrOH=47:3, 25 ℃, 0.8 mL/min flow rate, detection at 254 nm, t1=20.20 min (major), t2=24.92 min (minor). Analytical data are in agreement with those reported in the literature [2].



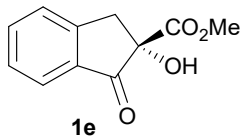
1c

Following general procedure A and **1c** was obtained as a solid (106 mg, yield 90%, ee 94%) after purification by filtration. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 1H), 7.28 (s, 1H), 7.22 (s, 1H), 4.11 (s, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 3.66 (d, *J* = 17.1 Hz, 1H), 3.18 (d, *J* = 16.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 172.1, 159.9, 145.3, 134.8, 127.3, 125.8, 106.3, 81.2, 55.8, 53.6, 38.8. HRMS (ESI): calcd for $C_{12}H_{13}O_5$ $[M+H]^+$: 237.0757, found: 237.0767. HPLC analysis CHIRALPAK OD-H, Hexane: *i*-PrOH=9:1, 25 ℃, 1.0 mL/min flow rate, detection at 254 nm, t1=13.95 min (major), t2=15.94 min (minor). Analytical data are in agreement with those reported in the literature [2].



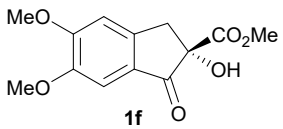
1d

Following general procedure B and **1d** was obtained as a solid (90 mg, yield 81%, ee 95%) after purification by filtration. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 4.03 (s, 1H), 3.74 (s, 3H), 3.69 (d, *J* = 17.2 Hz, 1H), 3.21 (d, *J* = 17.2 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 172.2, 149.8, 138.4, 137.6, 133.8, 126.3, 125.3, 80.8, 53.6, 39.1, 21.2. HRMS (ESI): calcd for $C_{12}H_{12}NaO_4$ $[M+Na]^+$: 243.0628, found: 243.0636. HPLC analysis CHIRALPAK OD-H, Hexane: *i*-PrOH=47:3, 25 ℃, 0.8 mL/min flow rate, detection at 254 nm, t1=18.07 min (major), t2=21.32 min (minor). Analytical data are in agreement with those reported in the literature [2].



1e

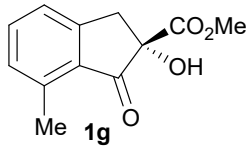
Following general procedure B and **1e** was obtained as a solid (87 mg, yield 85%, ee 90%) after purification by filtration. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 4.07 (s, 1H), 3.82 – 3.66 (m, 4H), 3.27 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 171.9, 152.2, 136.3, 133.5, 128.3, 127.1, 124.5, 79.7, 52.5, 40.9. HRMS (ESI): calcd for $C_{11}H_{11}O_4$ $[M+H]^+$: 207.0652, found: 207.0655. HPLC analysis CHIRALPAK AD-H, Hexane: *i*-PrOH=22:3, 25 ℃, 1.0 mL/min flow rate, detection at 254 nm, t1=18.07 min (major), t2=19.53 min (minor). Analytical data are in agreement with those reported in the literature [2].



1f

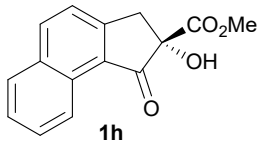
Following general procedure C and **1f** was obtained as a solid (60 mg, yield 45%, ee 97%) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 6.91 (s, 1H), 4.00 (s, 3H), 3.96 (d, *J* = 11.0 Hz, 1H), 3.92 (s, 3H), 3.75 (s, 3H), 3.65 (d, *J* = 17.0 Hz, 1H), 3.17 (d, *J* = 17.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

199.3, 172.3, 156.8, 150.0, 148.3, 126.2, 107.4, 105.3, 80.8, 56.5, 56.2, 53.5, 39.1. HRMS (ESI): calcd for $C_{13}H_{15}O_6$ $[M+H]^+$: 267.0863, found: 267.0860. HPLC analysis CHIRALPAK AD-H, Hexane: *i*-PrOH=3:1, 25 ℃, 1.0 mL/min flow rate, detection at 254 nm, t1=19.22 min (major), t2=23.06 min (minor). Analytical data are in agreement with those reported in the literature [2].



1g

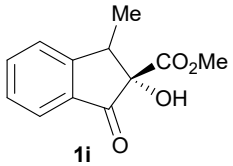
Following general procedure C and **1g** was obtained as a solid (69 mg, yield 62%, ee 53%) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 13.4, 5.9 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 4.03 (s, 1H), 3.74 (s, 3H), 3.70 (d, *J* = 17.3 Hz, 1H), 3.20 (d, *J* = 17.3 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 172.2, 152.9, 140.6, 135.6, 131.2, 130.0, 123.8, 80.5, 53.6, 38.8, 18.5. HRMS (ESI): calcd for $C_{12}H_{13}O_4$ $[M+H]^+$: 221.0808, found: 221.0804. HPLC analysis CHIRALPAK OD-H, Hexane: *i*-PrOH=9:1, 25 ℃, 1.0 mL/min flow rate, detection at 254 nm, t1=9.22 min (major), t2=11.40 min (minor).



1h

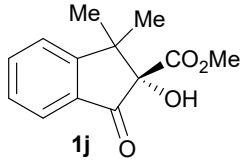
Following general procedure C and **1h** was obtained as a solid (39 mg, yield 30%, ee 30%) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 4.12 (s, 1H), 3.84 (d, *J* = 14.7 Hz, 1H), 3.74 (s, 3H), 3.37 (d, *J* = 17.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 172.2, 156.1, 137.6, 133.1, 129.8, 129.7, 128.6, 127.9, 127.3, 124.2, 123.7, 80.7, 53.6, 39.6. HRMS (ESI): calcd for $C_{15}H_{13}O_4$ $[M+H]^+$: 257.0808, found: 257.0808.

HPLC analysis CHIRALPAK OD-H, Hexane: *i*-PrOH=9:1, 25 ℃, 1.0 mL/min flow rate, detection at 254 nm, t1=16.85 min (major), t2=19.27 min (minor).



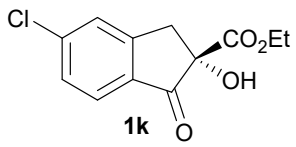
1i

Following general procedure C and **1i** was obtained as a solid (47 mg, yield 42%, ee 63%) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.70 (td, *J* = 7.7, 1.1 Hz, 1H), 7.53 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 3.92 (s, 1H), 3.80 (q, *J* = 7.3 Hz, 1H), 3.73 (s, 3H), 1.34 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 172.5, 158.6, 136.4, 132.8, 128.3, 125.6, 125.2, 82.1, 53.7, 42.6, 16.2. HRMS (ESI): calcd for $C_{12}H_{13}O_4$ $[M+H]^+$: 221.0808, found: 221.0807. HPLC analysis CHIRALPAK OD-H, Hexane: *i*-PrOH=22:3, 25 ℃, 1.0 mL/min flow rate, detection at 254 nm, t1=7.64 min (major), t2=8.74 min (minor).



1j

Following general procedure B and **1j** was obtained as a solid (63 mg, yield 53%, ee 2%) after purification by filtration. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 3.95 (s, 1H), 3.61 (s, 3H), 1.39 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 172.0, 160.9, 136.1, 133.1, 128.0, 124.6, 123.3, 87.7, 53.3, 46.8, 29.9, 21.4. HRMS (ESI): calcd for $C_{13}H_{15}O_4$ $[M+H]^+$: 235.0965, found: 235.0961. HPLC analysis CHIRALPAK OD-H, Hexane: *i*-PrOH=23:2, 25 ℃, 0.8 mL/min flow rate, detection at 254 nm, t1=11.52 min (major), t2=12.60 min (minor).



1k

Following general procedure D and **1k** was obtained as a solid (44 mg, yield 35%, ee 83%) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 4.22 (q, *J* = 6.2, 2H), 4.03 (s, 1H), 3.70 (d, *J* = 17.8 Hz, 1H), 3.23 (d, *J* = 17.7 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 171.2, 153.8, 142.9, 132.1, 129.1, 126.8, 126.5, 80.4, 63.1, 39.1, 14.1. HRMS (ESI): calcd for $C_{12}H_{11}ClNaO_4$ $[M+Na]^+$: 277.0238, found: 277.0254. HPLC analysis CHIRALPAK OD-H, Hexane: *i*-PrOH=9:1, 25 ℃, 1.0 mL/min flow rate, detection at 254 nm, t1=10.29 min (major), t2=12.49 min (minor). Analytical data are in agreement with those reported in the literature [3].

6. Gram-scale experiment

To a solution of **L1** (0.841 g, 1.32 mmol) in petroleum ether (420.00 mL) was added $Zr(acac)_4$ (0.585 g, 1.20 mmol). The mixture was stirred at room temperature for 30 min. Then, methyl 5-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate **2a** (6.739 g, 30.0 mmol) and TBHP (70% in H_2O, 5.79 mL, 45 mmol) were added sequentially. The resulting solution was stirred at room temperature for 36 hours. Fine white precipitates were formed during the course of the reaction. The white solid product **1a** was isolated by filtration and washed thoroughly with cold petroleum ether: the amount of the obtained product **1a** was 7.053 g (yield 98%, ee 91%).

7. The recyclability of the catalytic system

To a solution of **L1** (0.140 g, 0.22 mmol) in petroleum ether (70.0 mL) was added $Zr(acac)_4$ (0.098 g, 0.20 mmol). The mixture was stirred at room temperature for 30 min. Then, methyl 5-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate **2a** (1.123 g, 5.0 mmol) and TBHP (70% in H_2O, 7.5 mmol) were added sequentially. The resulting solution was stirred at room temperature for 24 hours. Fine white precipitates were

formed during the course of the reaction. The white solid was isolated by filtration. Firstly, the filtrate solution containing the catalyst was decanted into another flask and fresh portions of ester **2a** and TBHP (70% in H_2O) were added to initiate the reaction, and the reaction was reperformed over 3 cycles. Then, the solid was washed thoroughly with cold petroleum ether to give the product **1a**.

First cycle: the amount of the obtained product **1a** was 1.095 g (yield 91%, ee 99%)

Second cycle: the amount of the obtained product **1a** was 0.902 g (yield 75%, ee 63%)

Third cycle: the amount of the obtained product **1a** was 0.517 g (yield 43%, ee 16%)

8. Mechanistic studies

8.1 HRMS Study

To a solution of **L1** (7.0 mg, 0.011 mmol) in petroleum ether (3.5 mL) was added $Zr(acac)_4$ (5.0 mg, 0.010 mmol). The mixture was stirred at room temperature for 30 min. Then, a small amount of the mixture was taken in dichloromethane for high resolution mass spectrometry. The HRMS of the in situ generated Zr(IV)-**L1** complex exhibits a ion peak at m/z 824.2404, whose mass correspond to $[Zr^{IV}(\mathbf{L1})(acac)]^+$ (calculated m/z = 824.2397) (Figure S1)

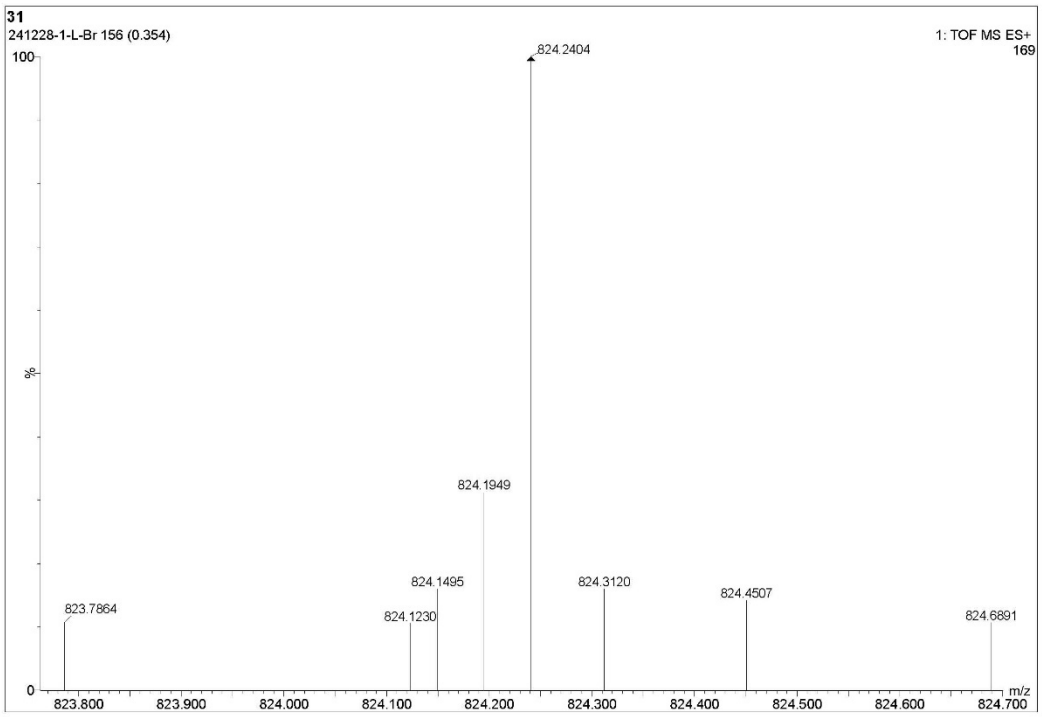


Figure S1 HRMS spectrum of Zr(IV)-**L1** generated in situ in the reaction of $Zr(acac)_4$ and **L1** in petroleum ethe at room temperature.

8.2 NMR Study

A NMR tube was charged with L1 (2.0 mg, 0.0031 mmol), $Zr(acac)_4$ (1.4 mg, 0.028 mmo) and cyclohexane-d_{12} (1.0 mL) and the resulting solution was stirred at room temperature. After 30 min, the mixture was determined by ^1H NMR analysis. The full ^1H NMR spectra were given in Figure S2, compared with the ^1H NMR spectra of $Zr(acac)_4$, acetylacetone and **L1**, significant chemical shift changes were observated at δ 5.48-5.06 ppm and 2.00-1.35 ppm. The spectra from δ 5.48 ppm to 5.06 ppm were enlarged in Figure S3. From Figure S3, the α-H (-CH-) of $acac^-$ in $Zr(acac)_4$ (δ 5.33 ppm) disappeared and the α-H (-CH-) of $acac^-$ in Zr(IV)-**L1** complex (δ 5.32 ppm) appeared. Furthermore, Figure S4 showed that the CH_3 of $acac^-$ in $Zr(acac)_4$ (δ 1.80 ppm) disappeared and the CH_3 of $acac^-$ in Zr(IV)-**L1** complex (δ 1.45 ppm) appeared.

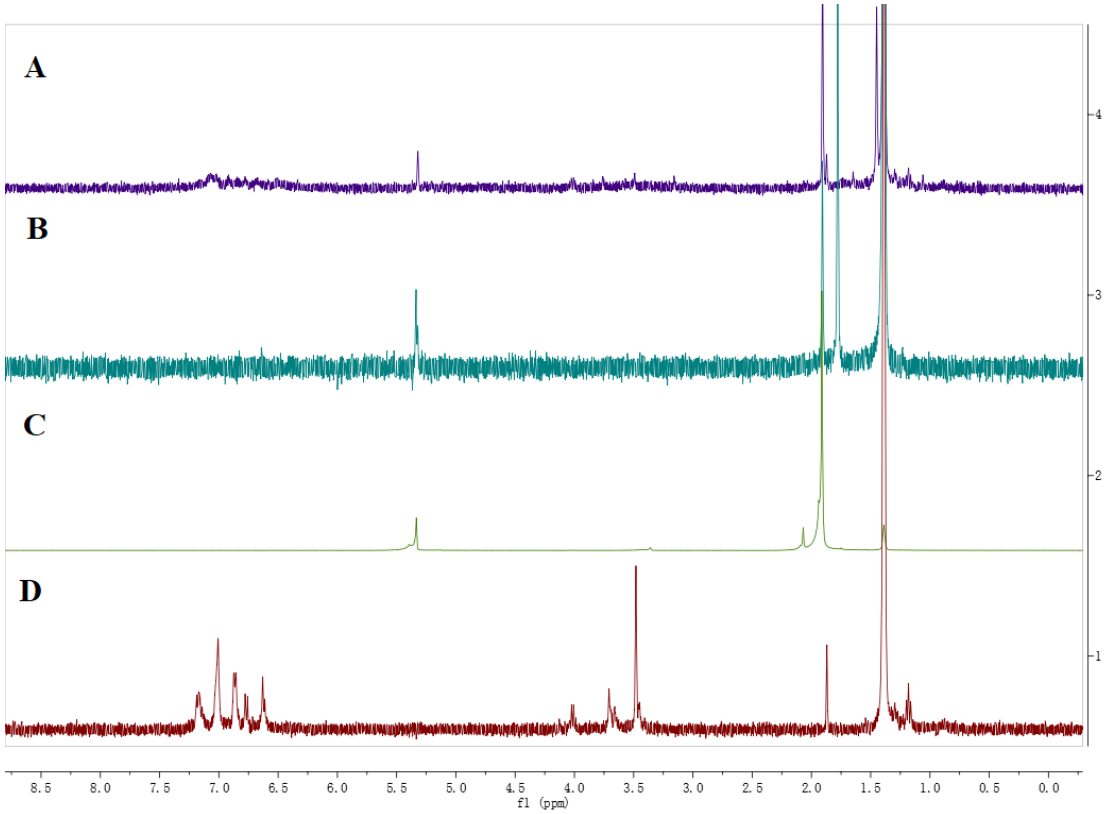


Figure S2 The formation of Zr(IV)-**L1** complex evidenced by 1 H NMR analysis. (**A**) the resulting solution of the reaction between **L1** and $Zr(acac)_4$; (**B**) $Zr(acac)_4$; (**C**) acetylacetone (Hacac); (**D**) **L1**.

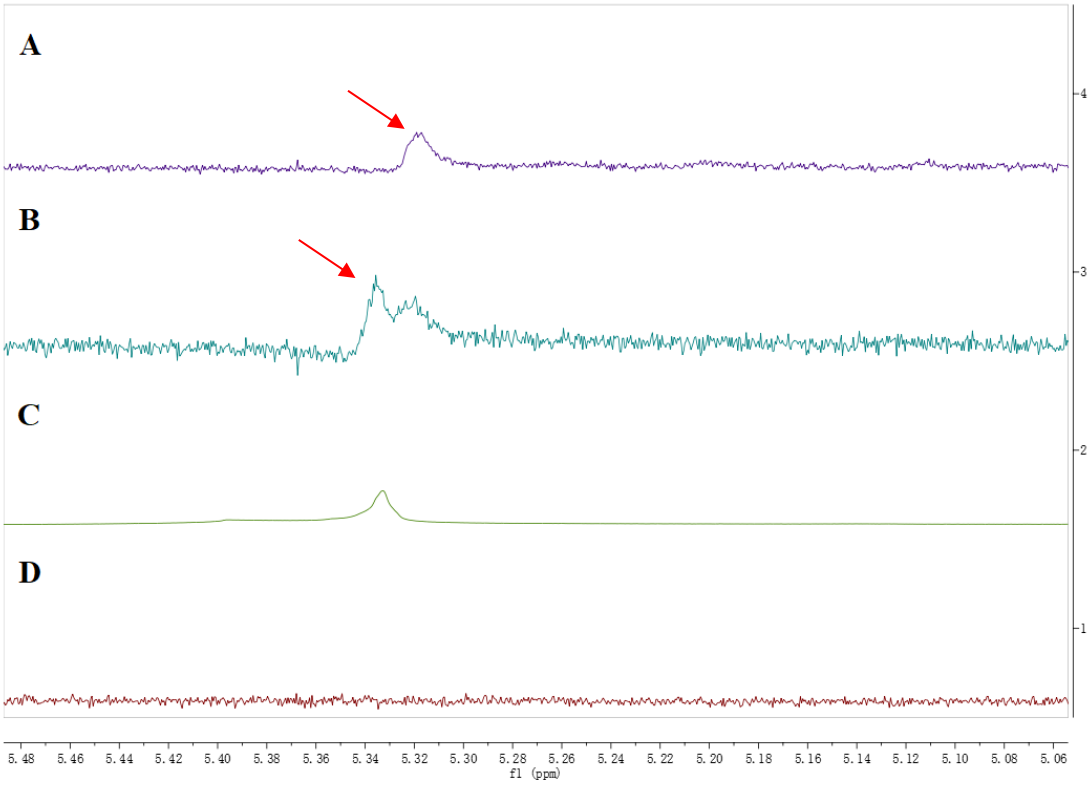


Figure S3 The enlarged spectra of Figure S2 scaled from δ 5.48 to 5.06 ppm. (**A**) the resulting solution of the reaction between **L1** and $Zr(acac)_4$; (**B**) $Zr(acac)_4$; (**C**) acetylacetone (Hacac); (**D**) **L1**.

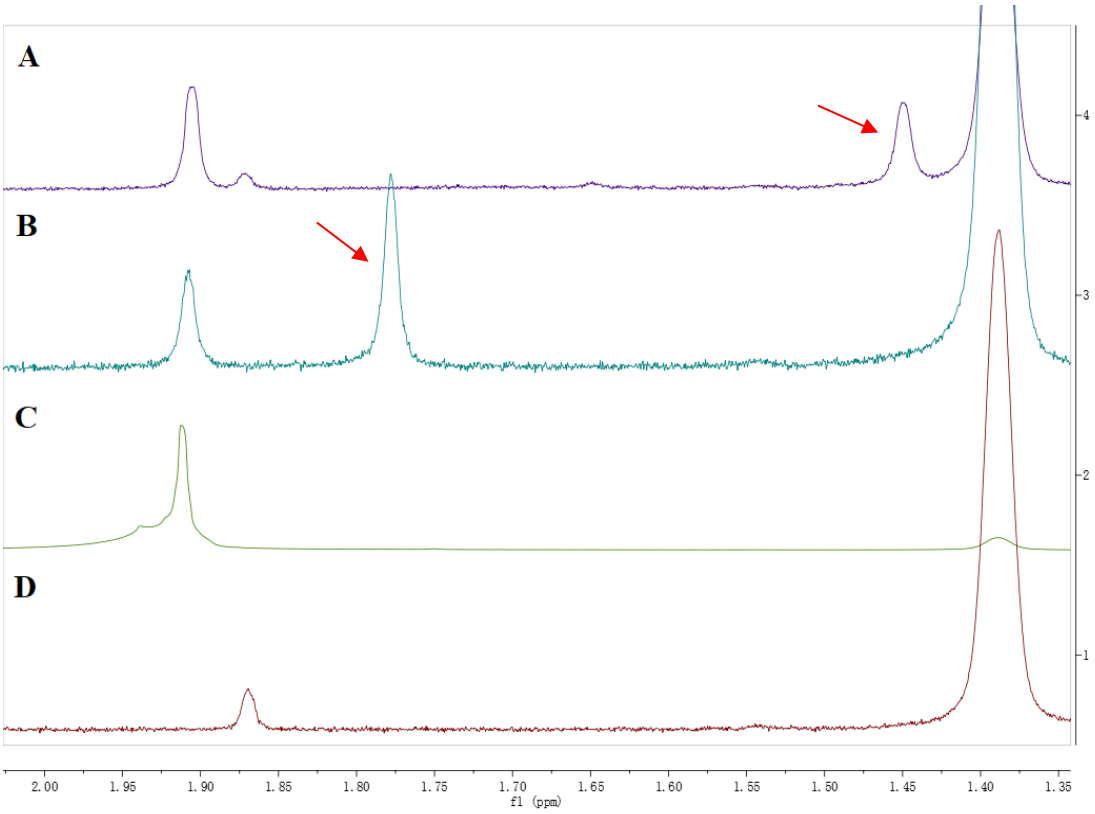


Figure S4 The enlarged spectra of Figure S2 scaled from δ 2.00 to 1.35 ppm. (**A**) the resulting solution of the reaction between **L1** and $Zr(acac)_4$; (**B**) $Zr(acac)_4$; (**C**) acetylacetone (Hacac); (**D**) **L1**.

9. References

[1] H.-L. Mu, W.-P. Ye, D.-P. Song, Y.-S. Li, *Organometallics*, 2010, **29**, 6282.

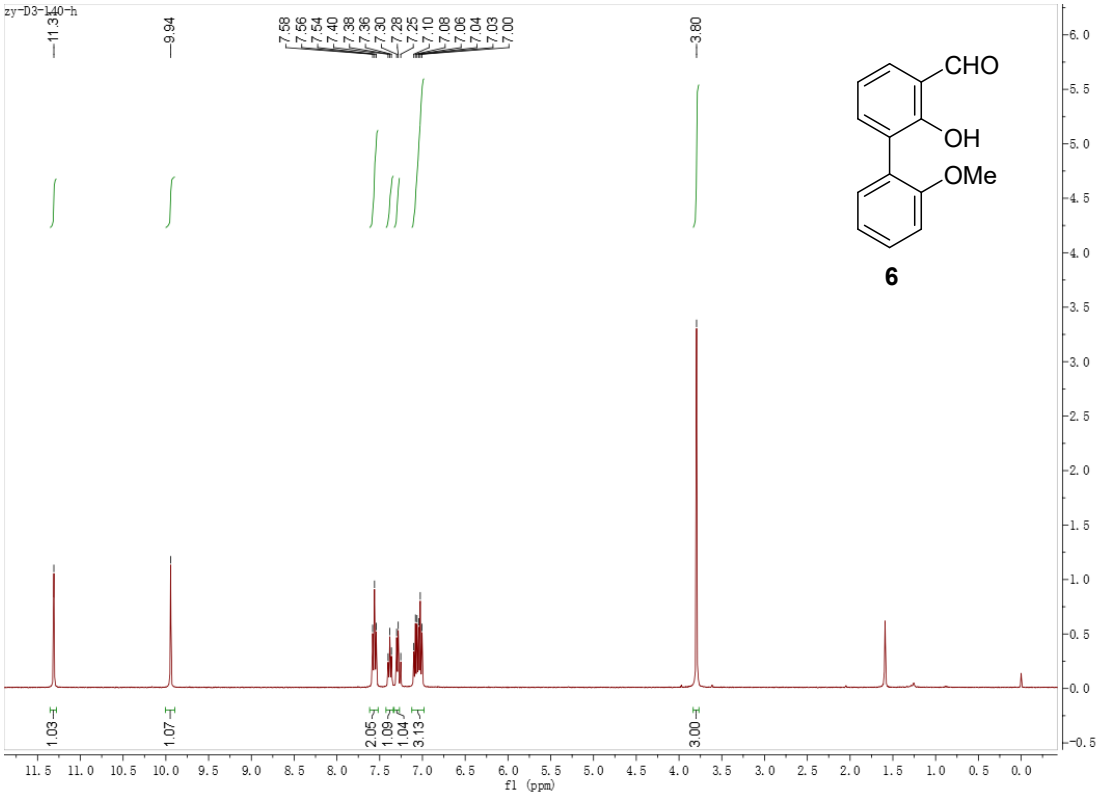
[2] J. Chen, H.-Y. Gu, X.-Y. Zhu, W.-W. Nam and B. Wang, *Adv. Synth. Catal.,* 2020, **362**, 2976.

[3] F. Yang, J. Zhao, X. Tang, G. Zhou, W. Song, Q. Meng, *Org. Lett.,* 2017, **19**, 448.

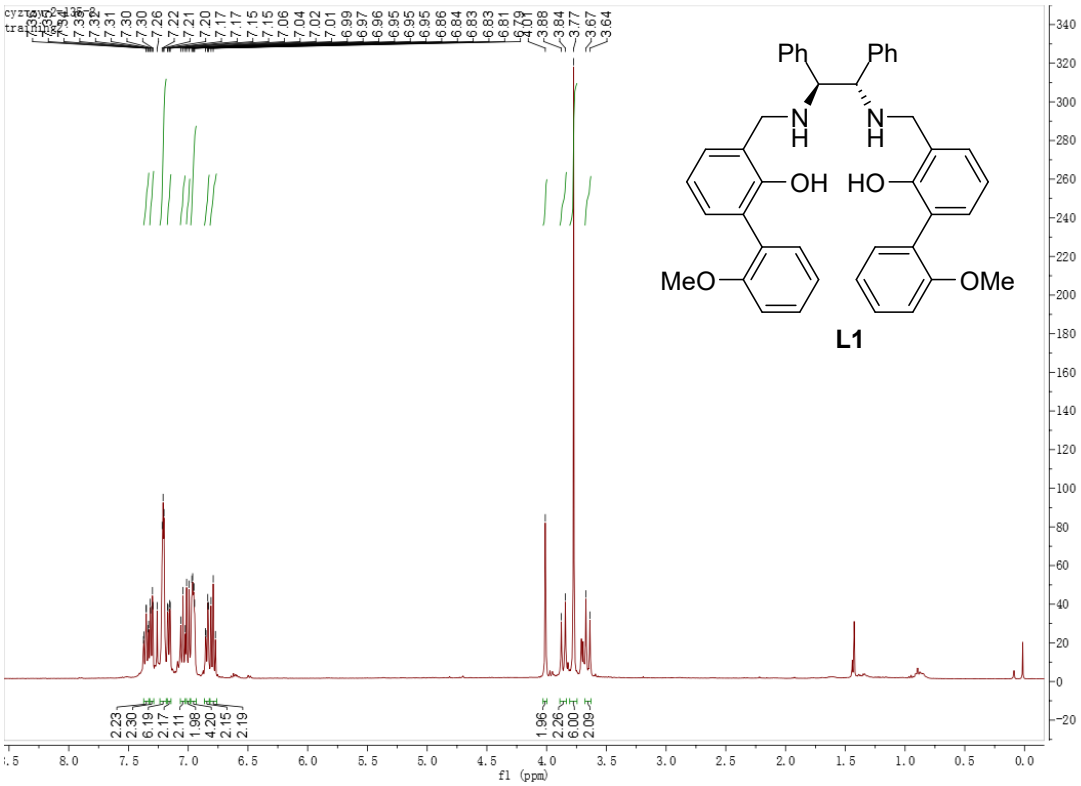
10. Copies of ^{1}H and ^{13}C NMR spectra

10.1 chiral ligan L1

^{1}H NMR of compound 6

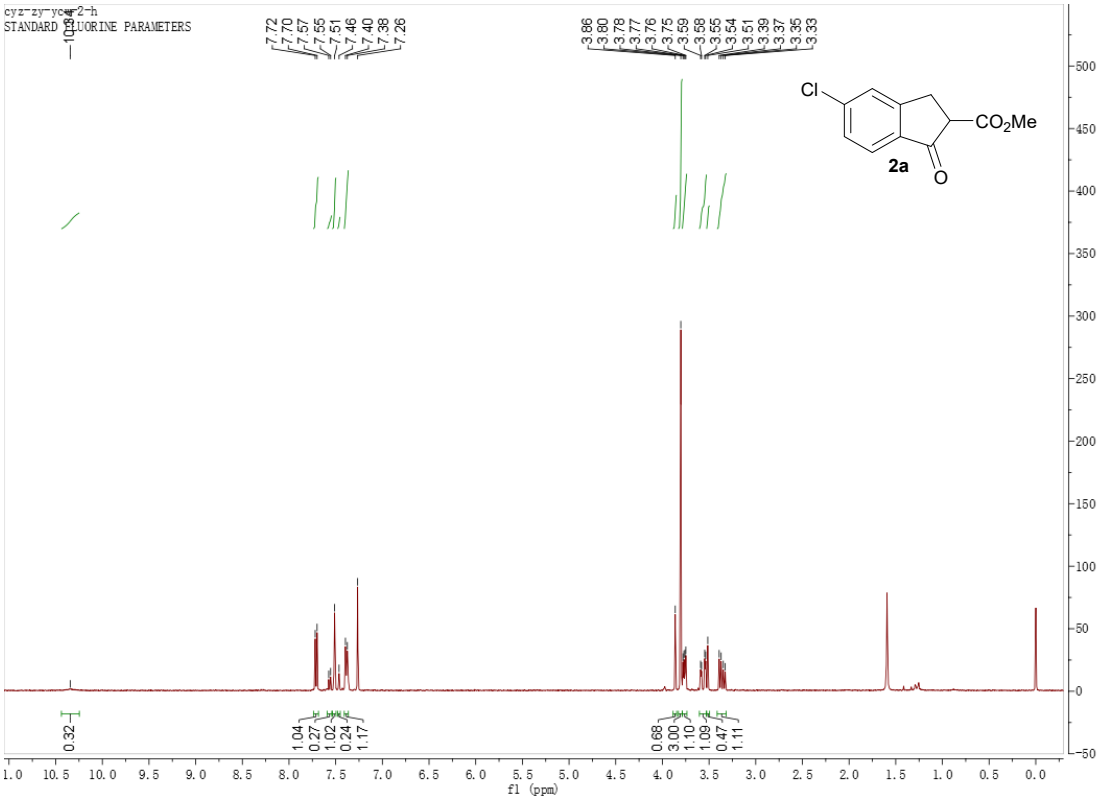


^{1}H NMR of compound L1

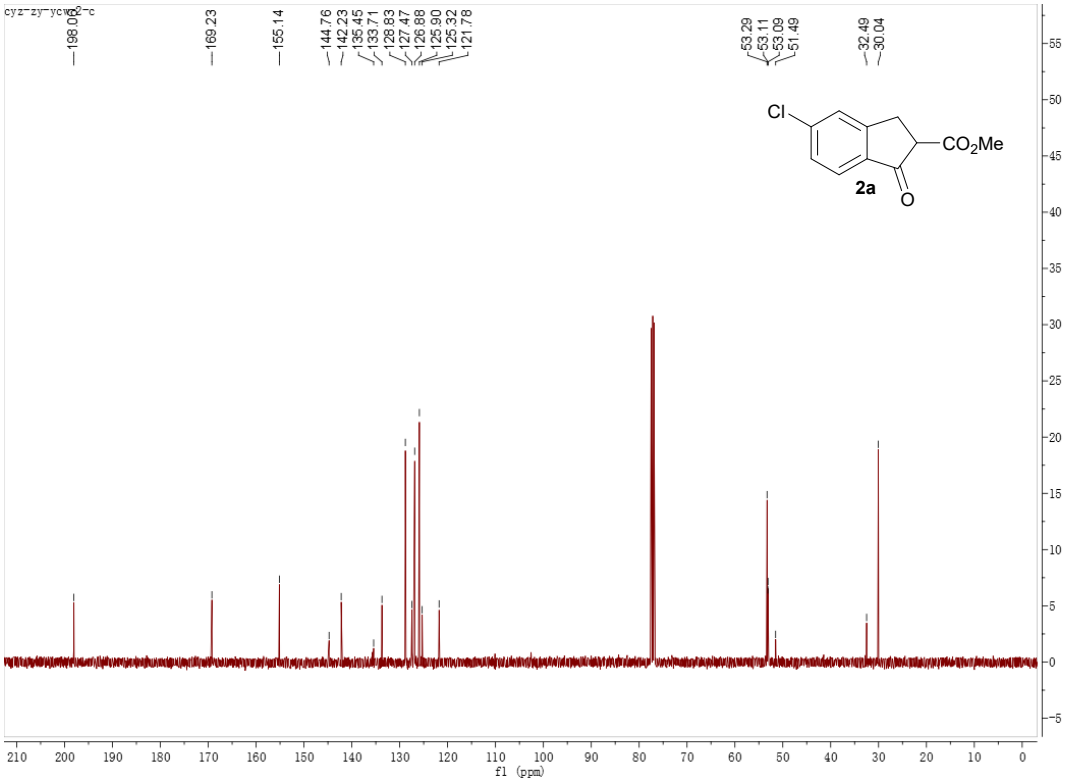


10.2 β-keto esters

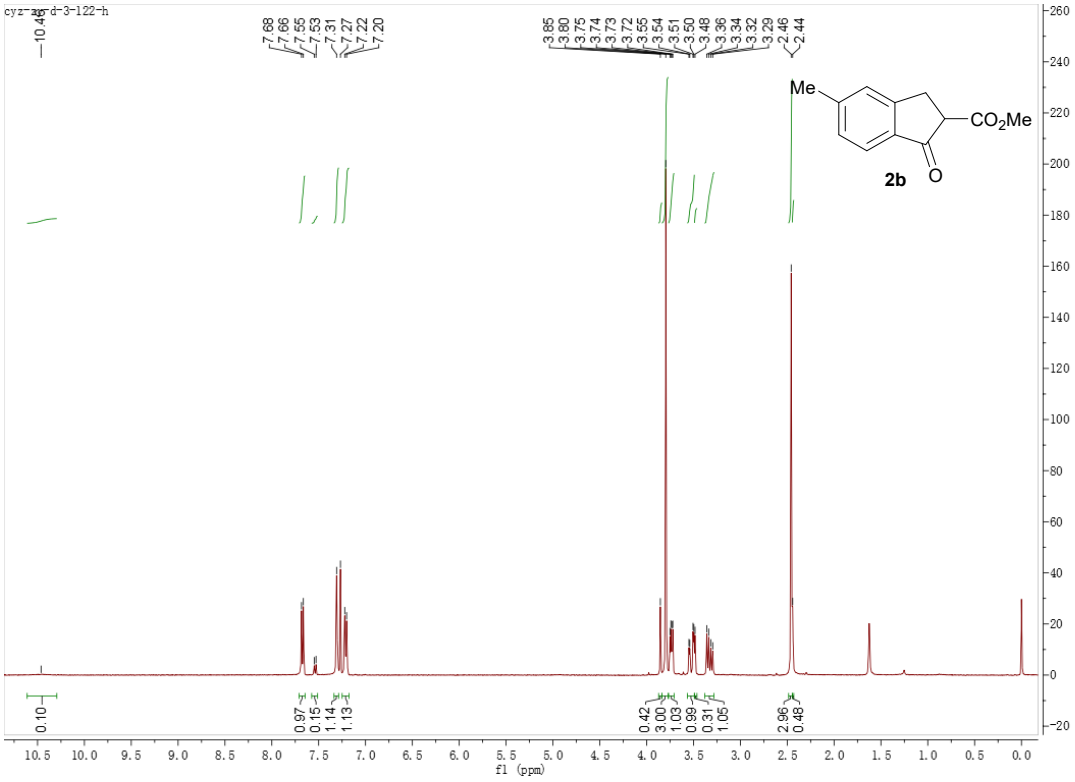
^{1}H NMR of compound 2a



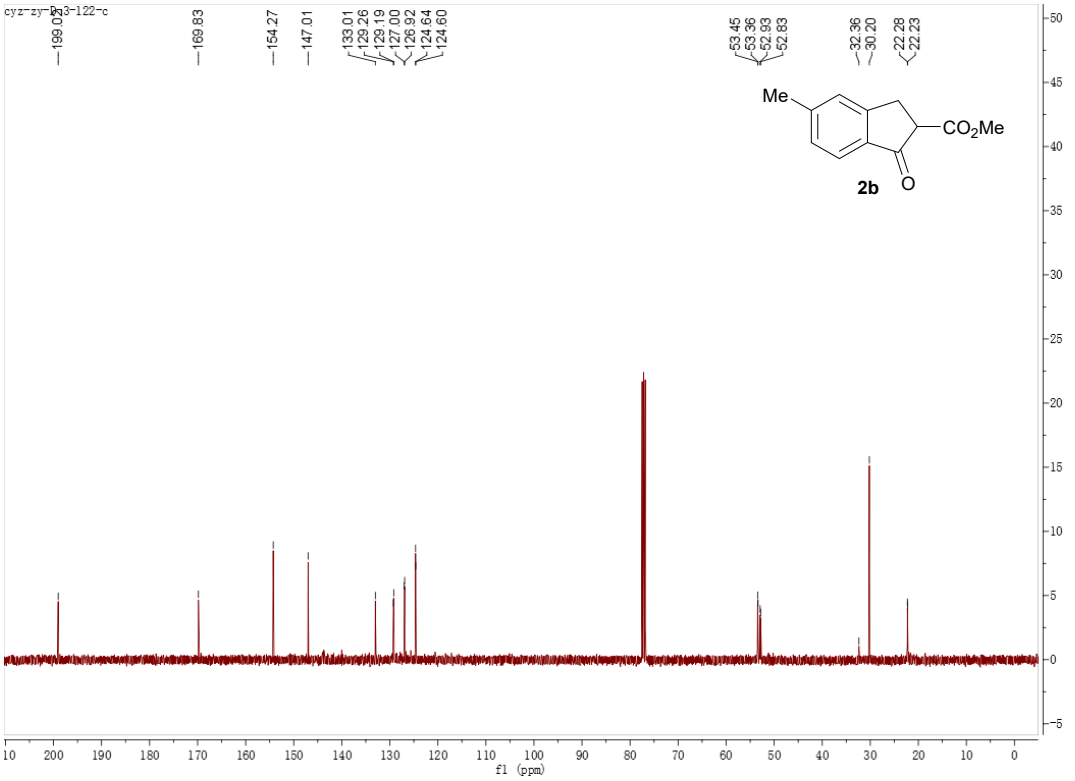
^{13}C NMR of compound 2a



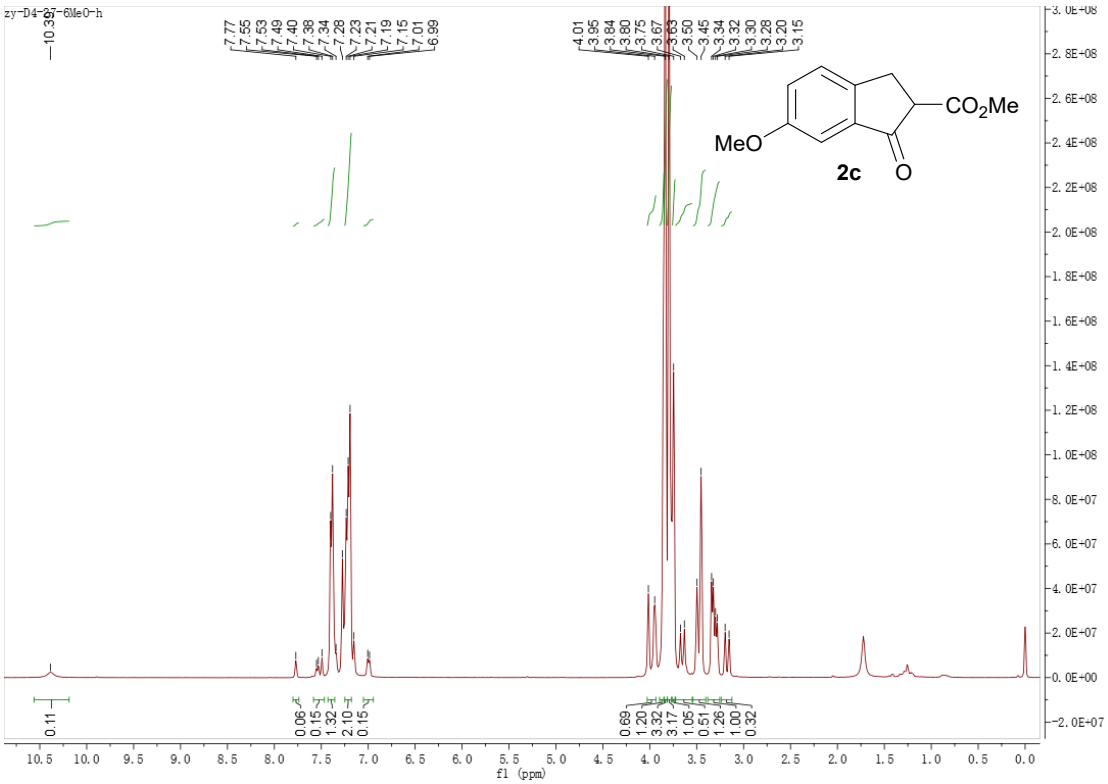
^{1}H NMR of compound 2b



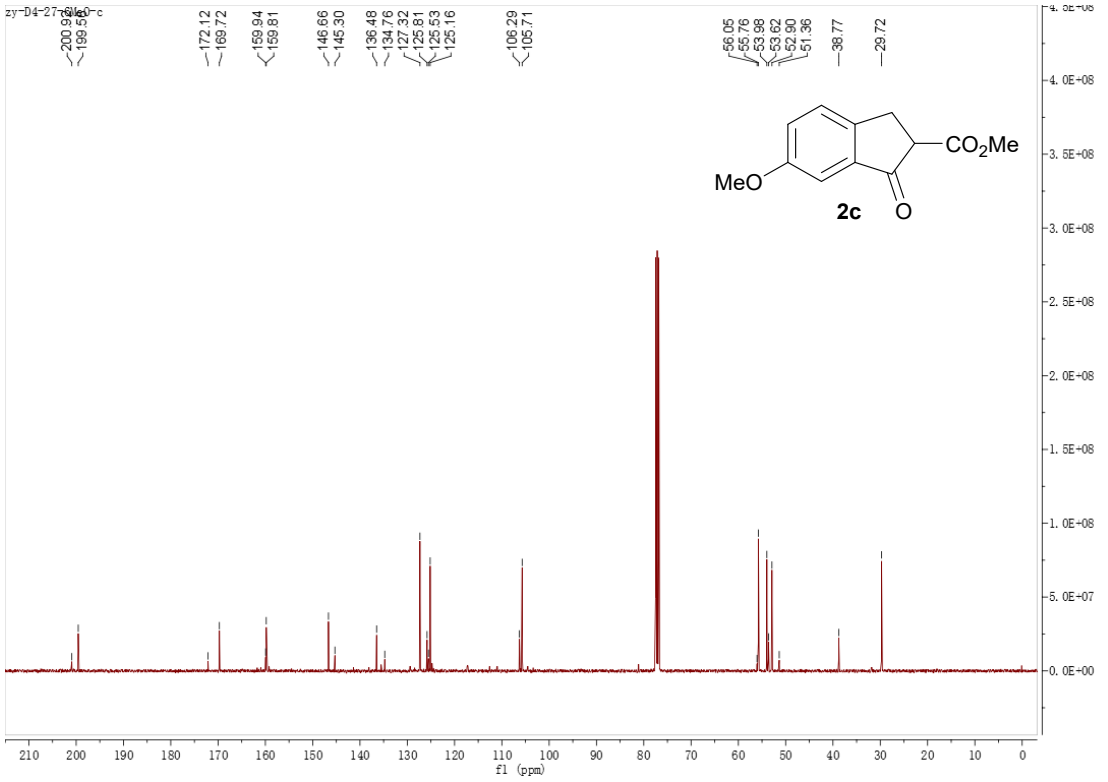
^{13}C NMR of compound 2b



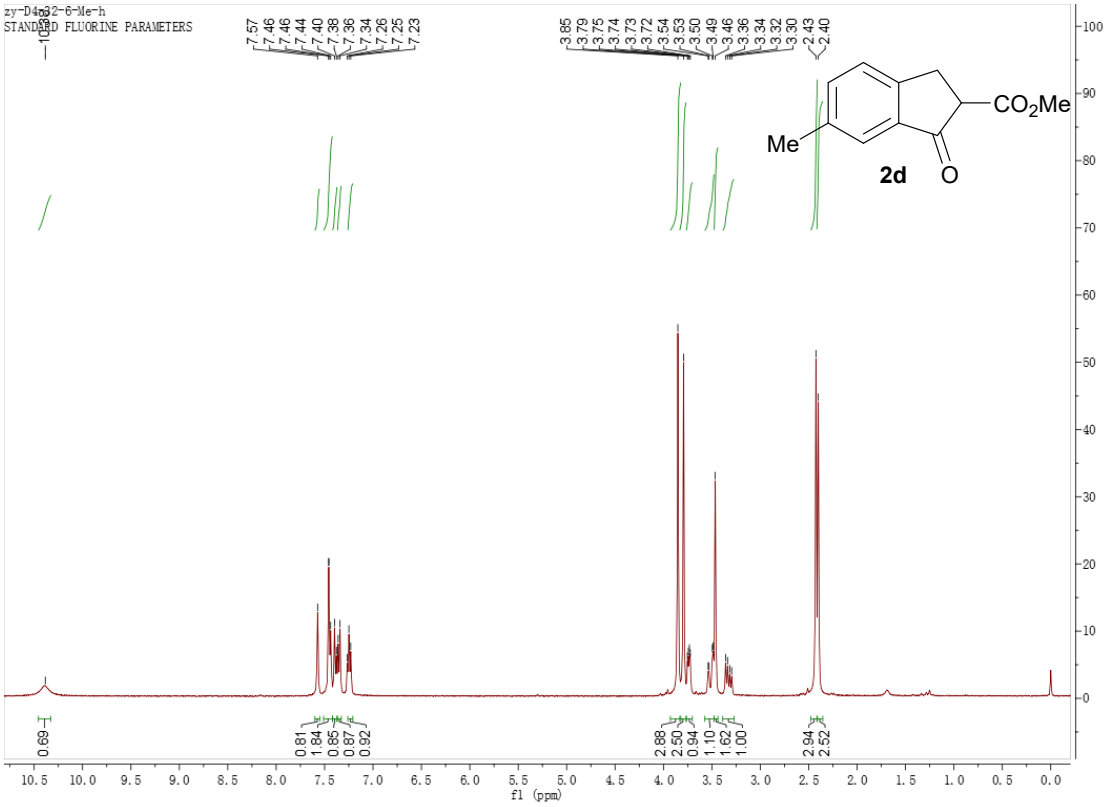
^{1}H NMR of compound 2c



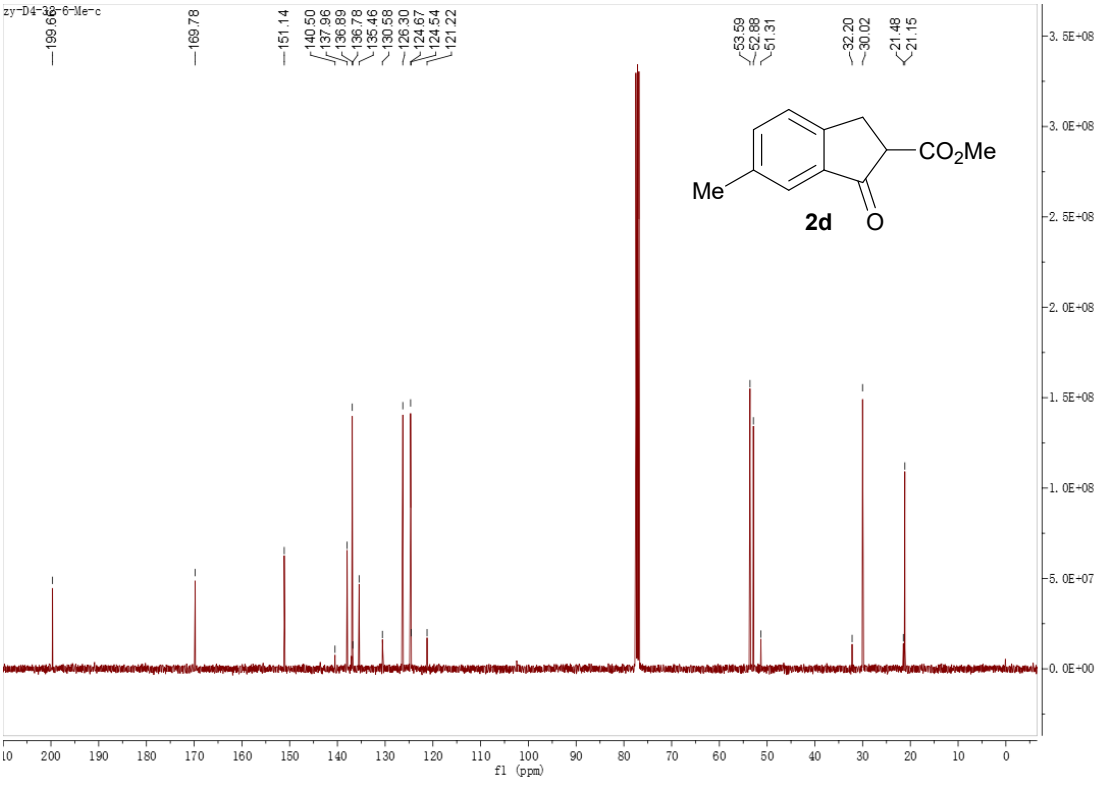
^{13}C NMR of compound 2c



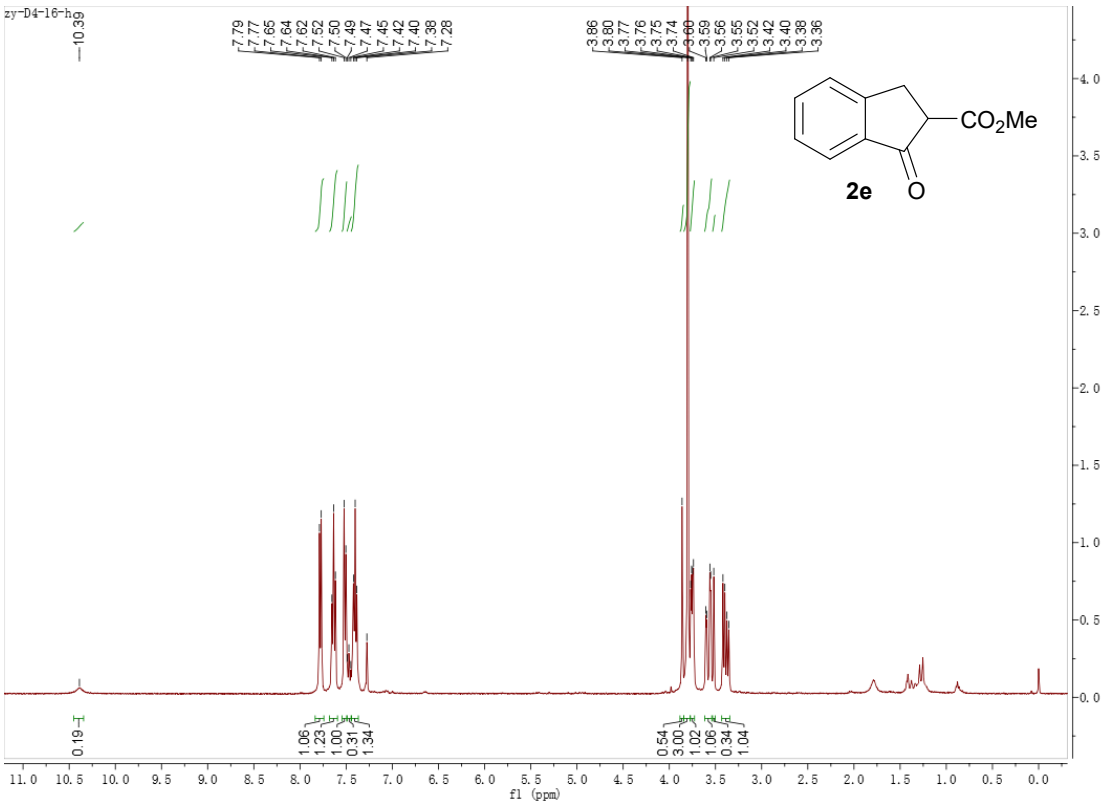
^{1}H NMR of compound 2d



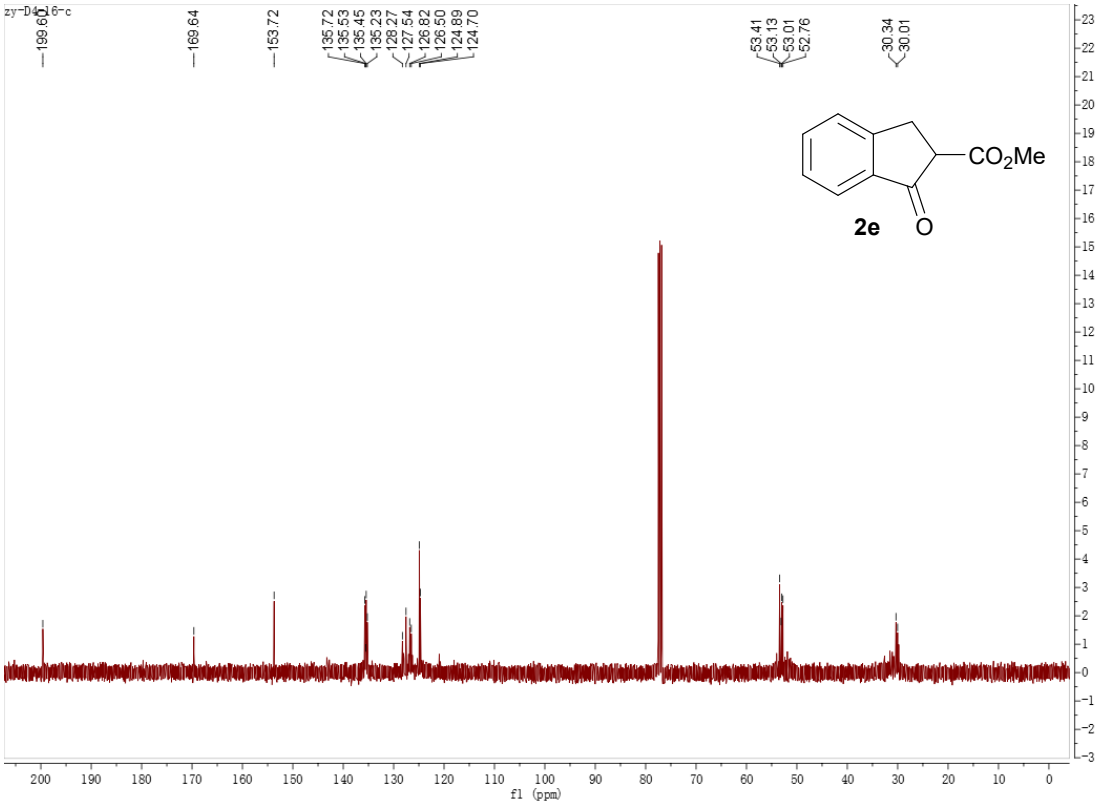
^{13}C NMR of compound 2d



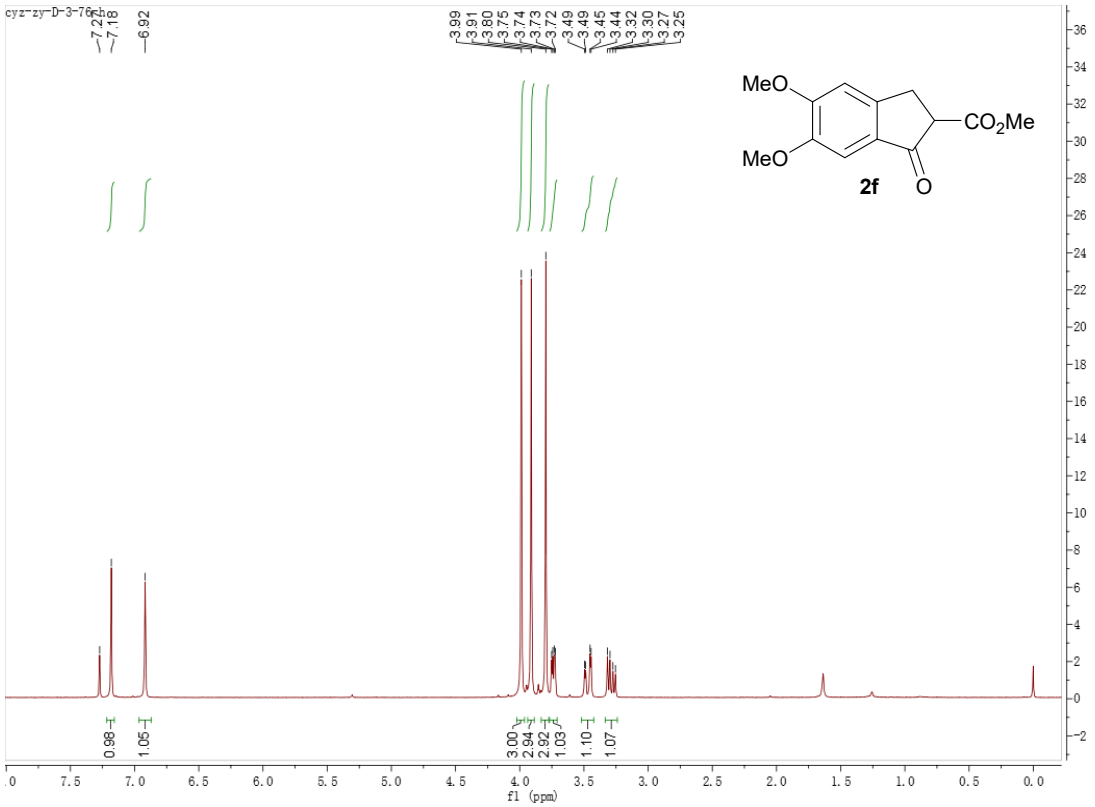
^{1}H NMR of compound 2e



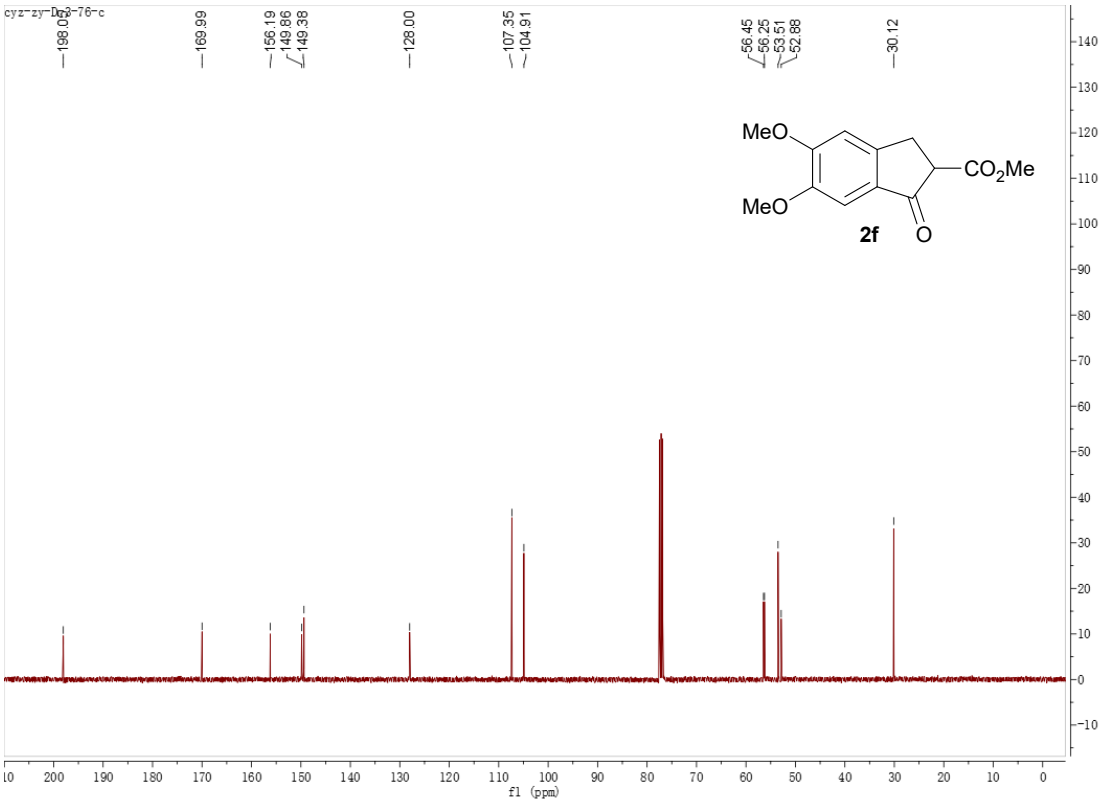
^{13}C NMR of compound 2e



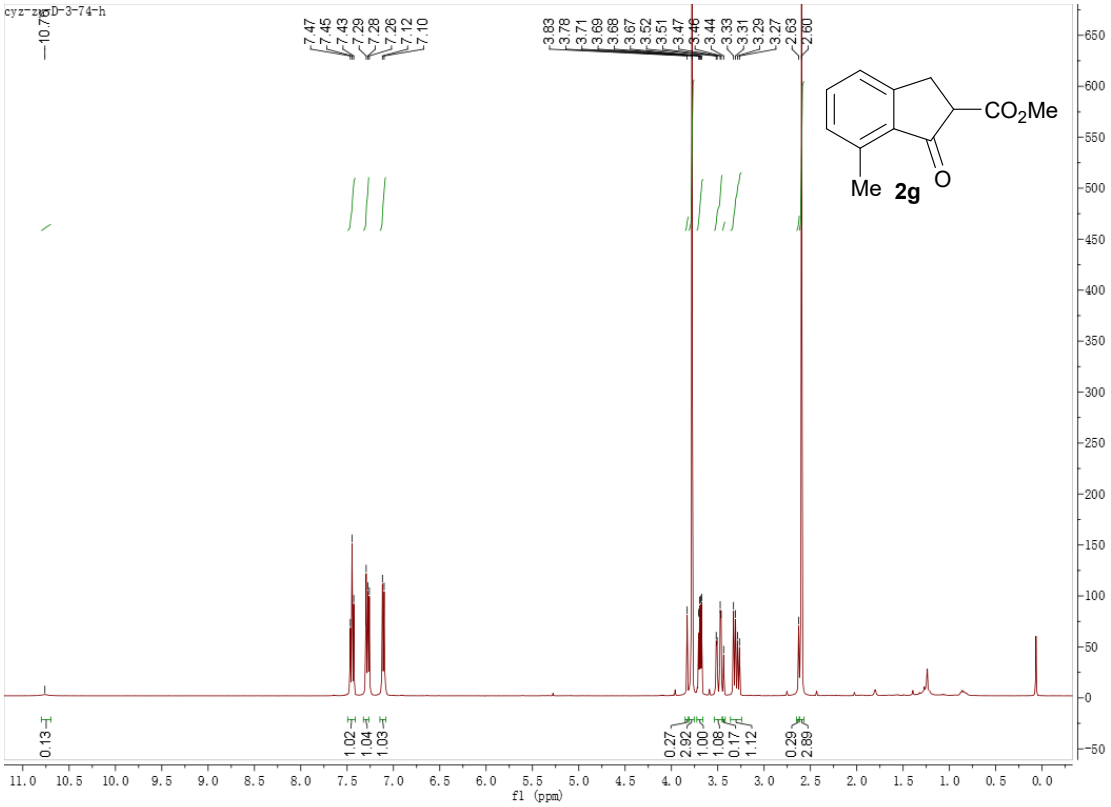
^{1}H NMR of compound 2f



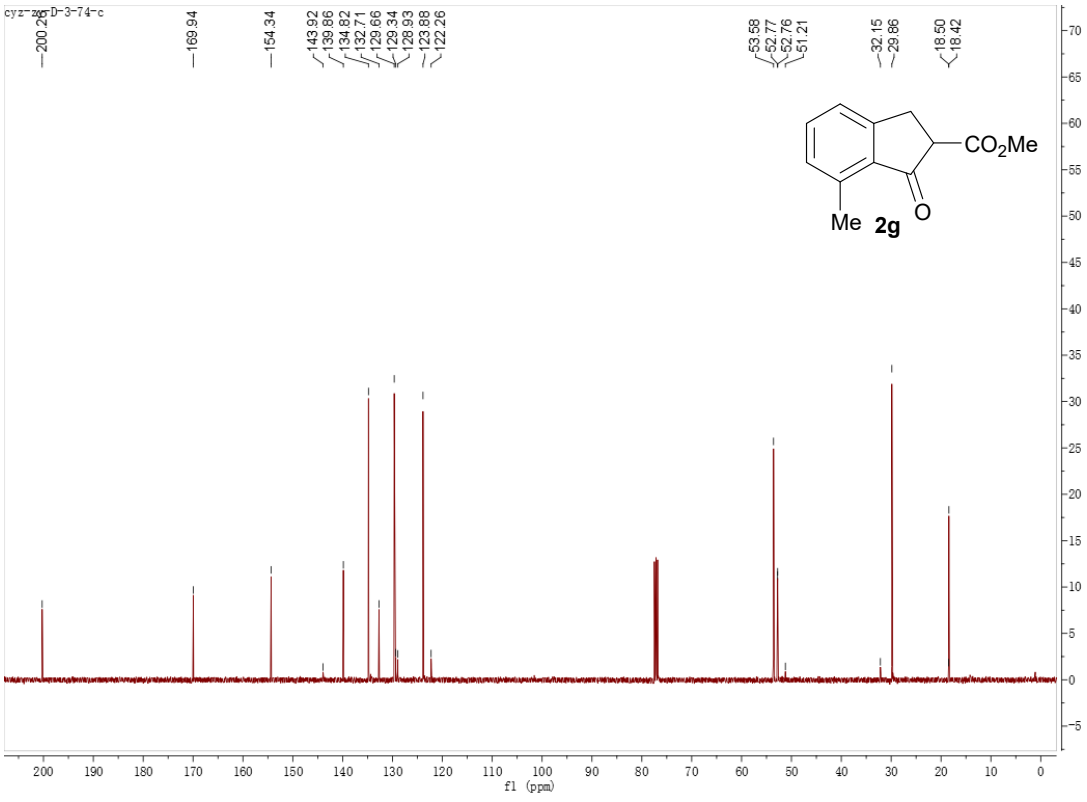
^{13}C NMR of compound 2f



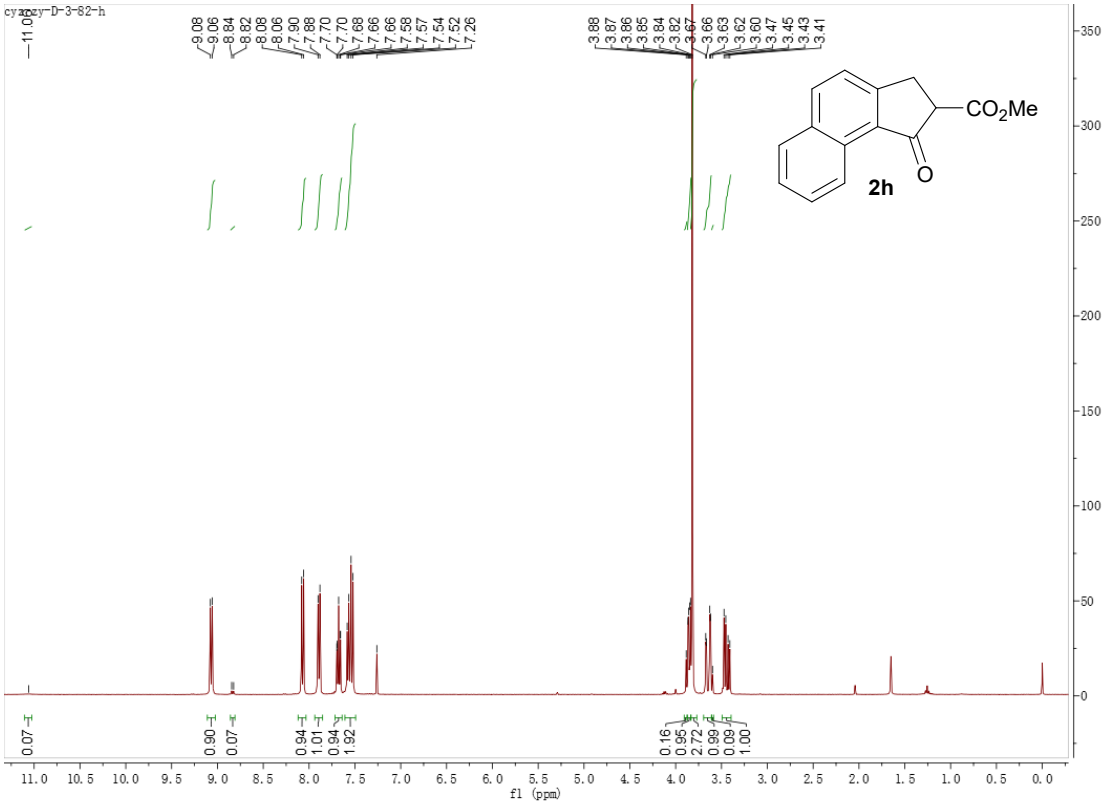
^{1}H NMR of compound 2g



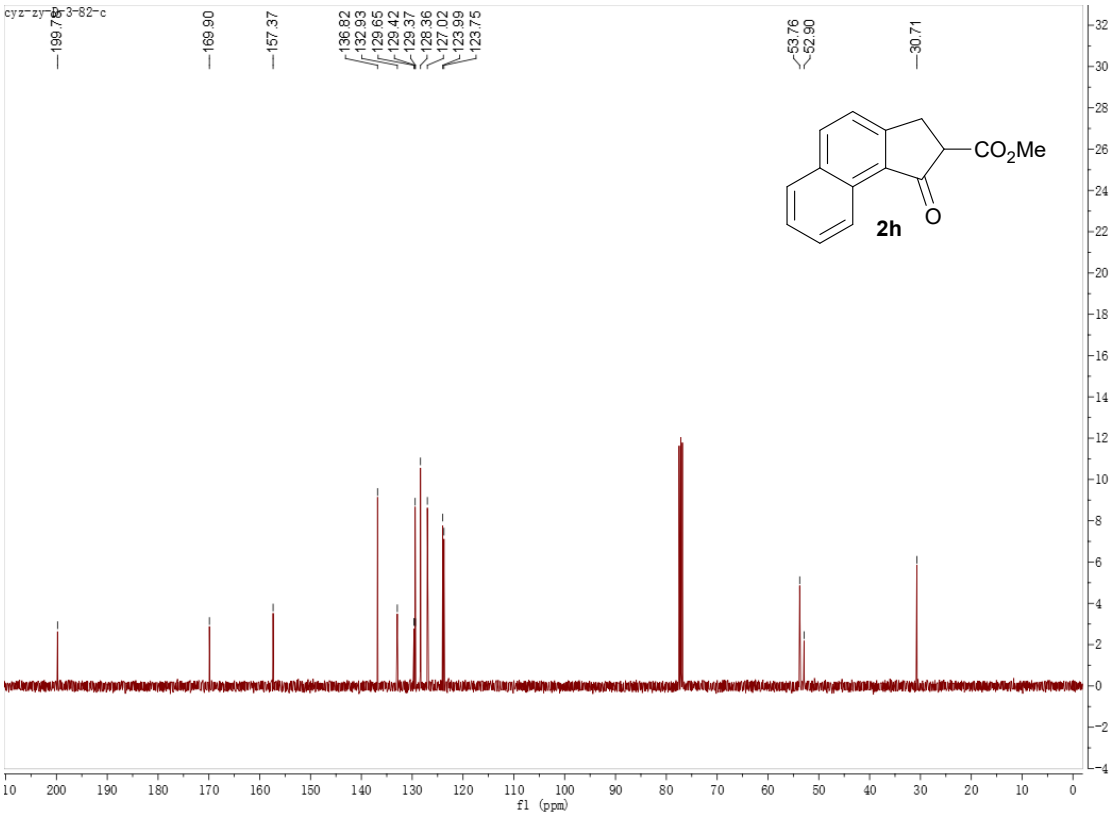
^{13}C NMR of compound 2g



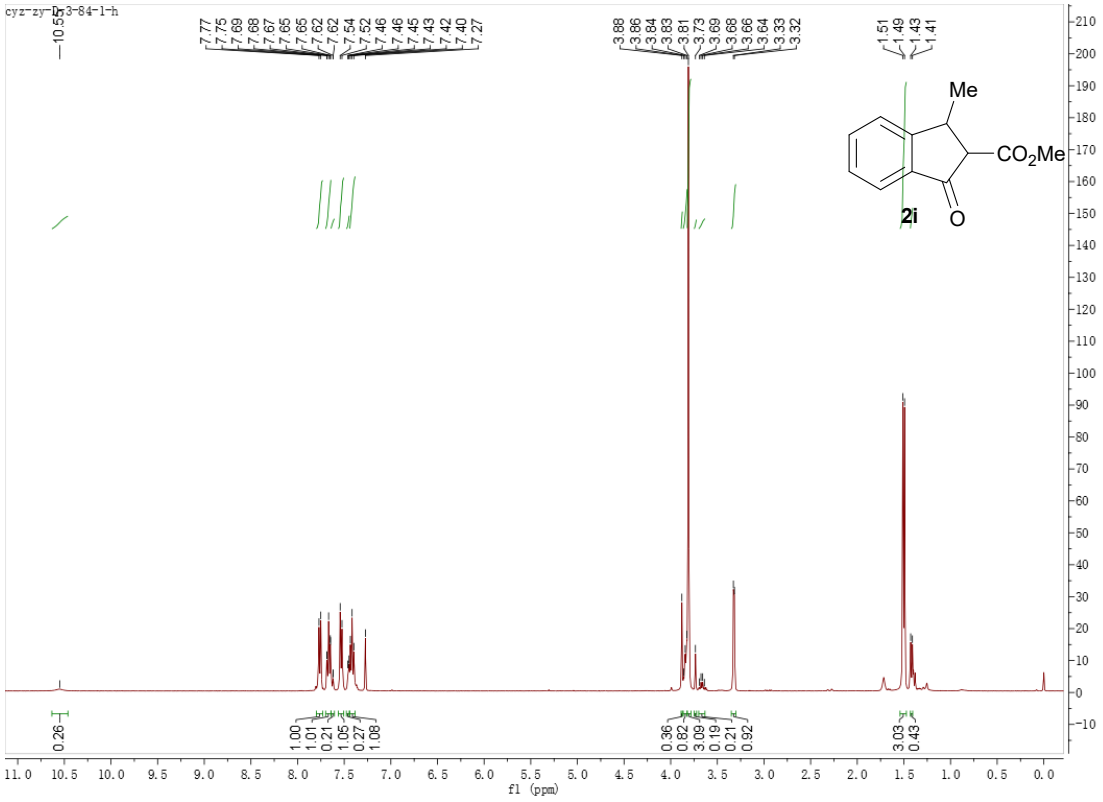
^{1}H NMR of compound 2h



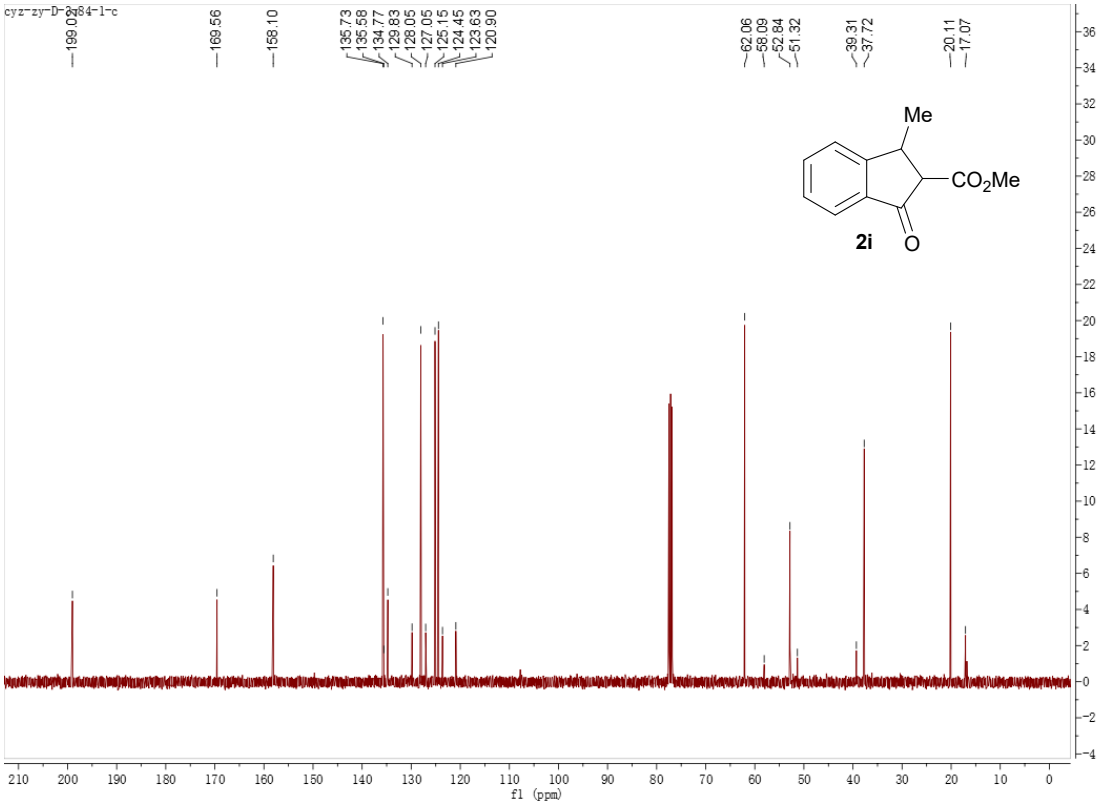
^{13}C NMR of compound 2h



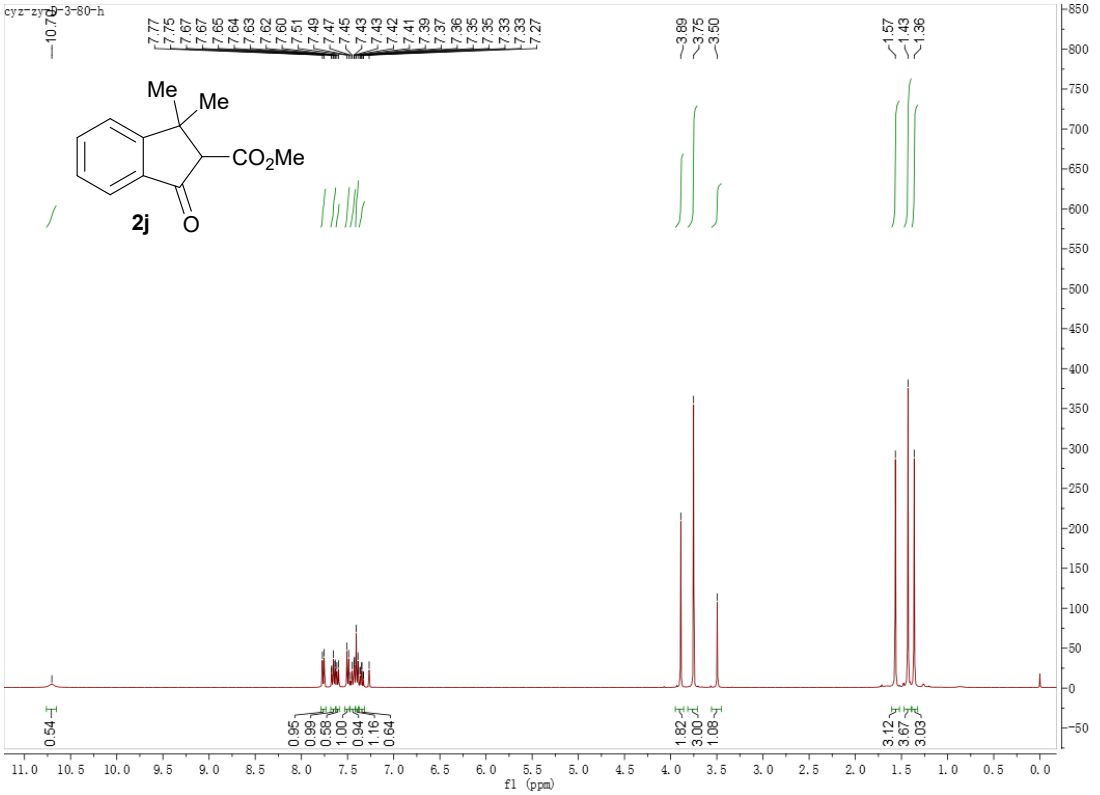
^{1}H NMR of compound 2i



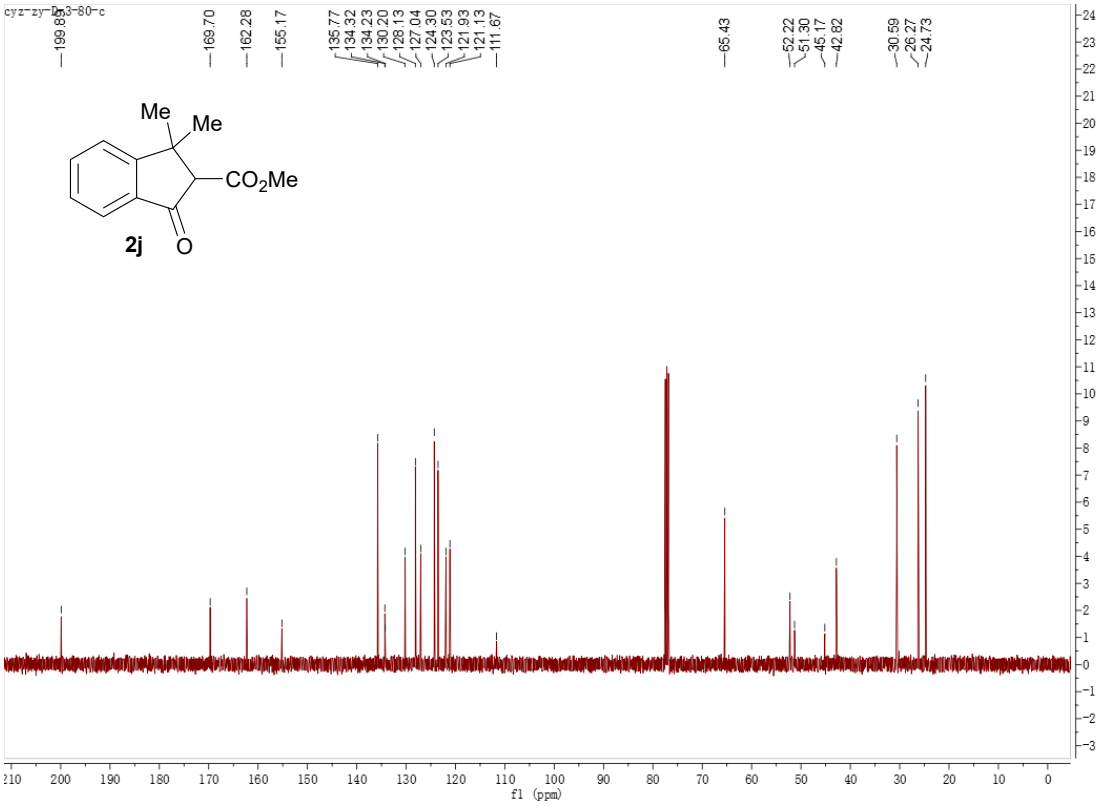
^{13}C NMR of compound 2i



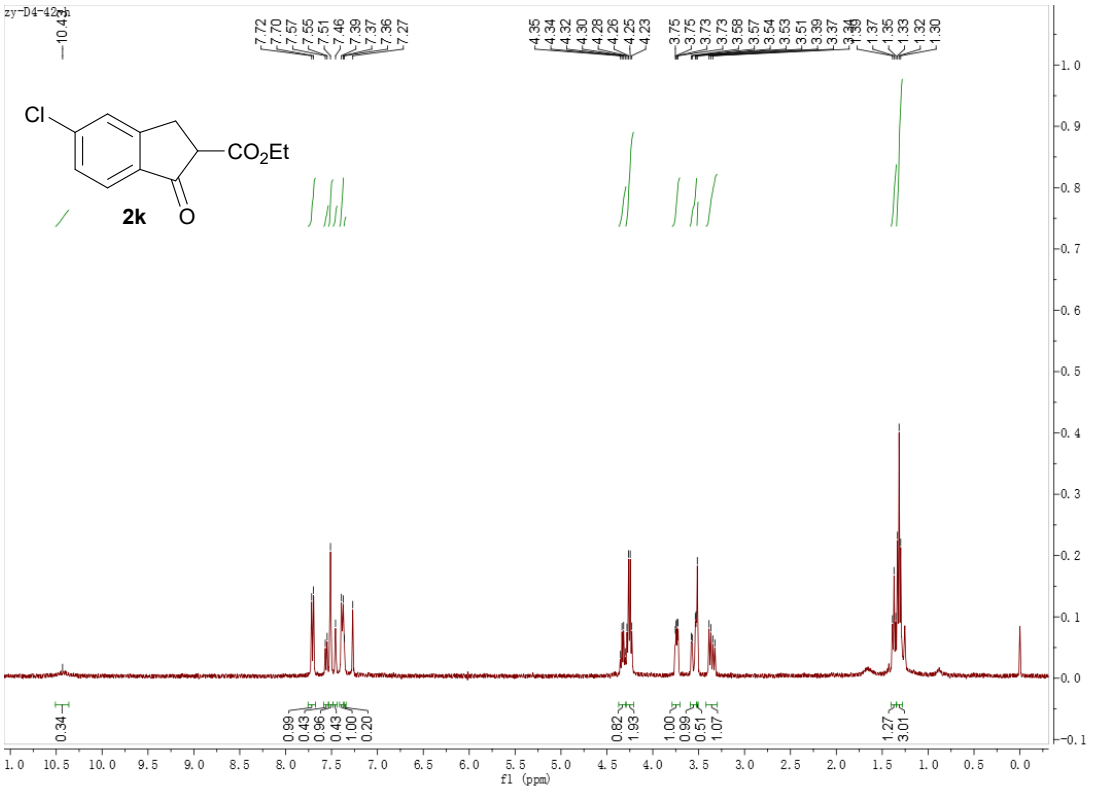
^{1}H NMR of compound 2j



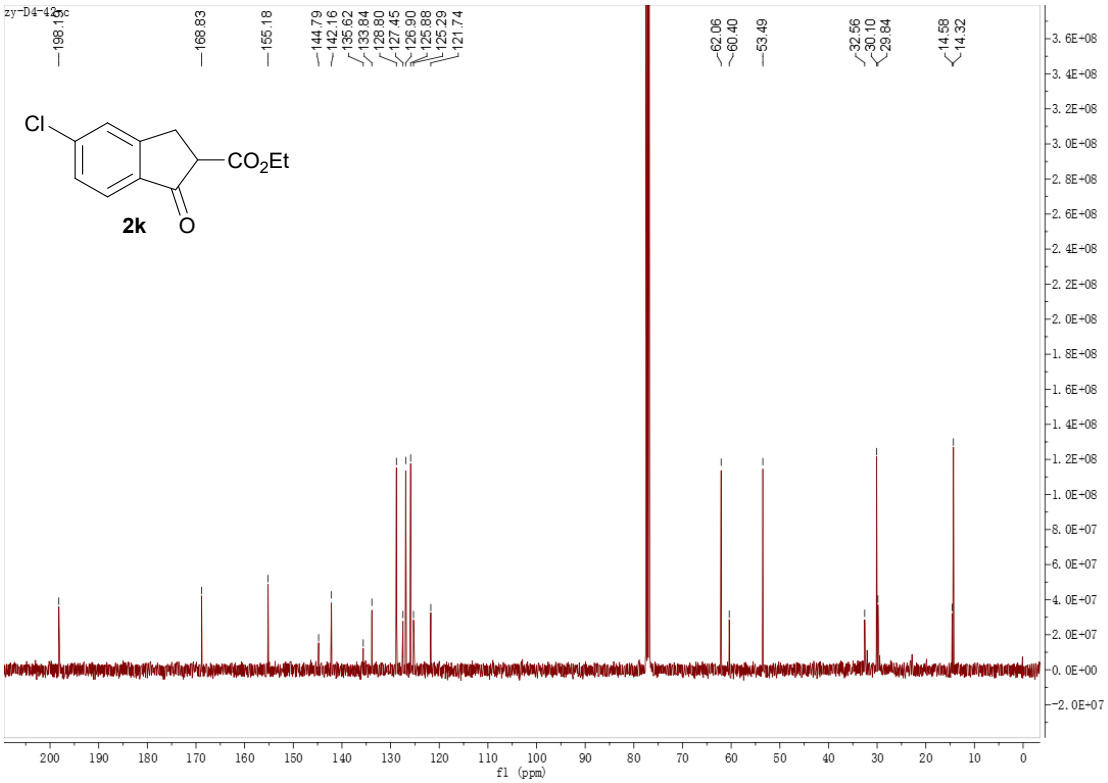
^{13}C NMR of compound 2j



^{1}H NMR of compound 2k

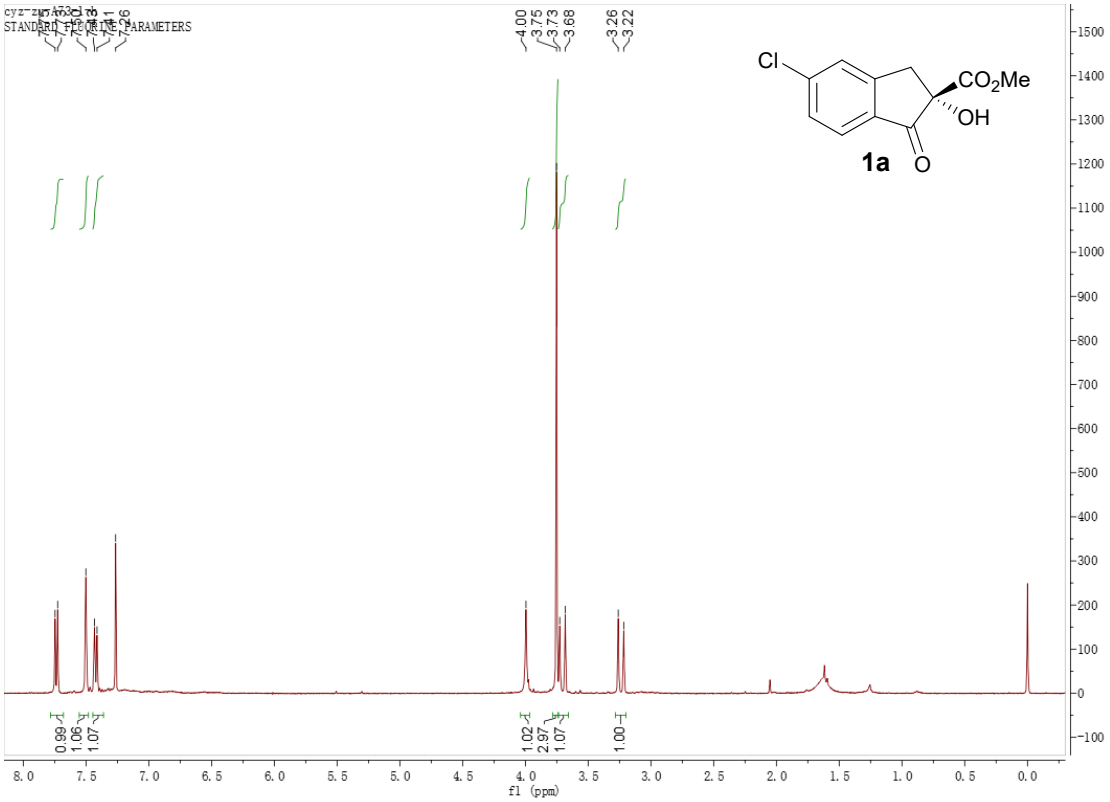


^{13}C NMR of compound 2k

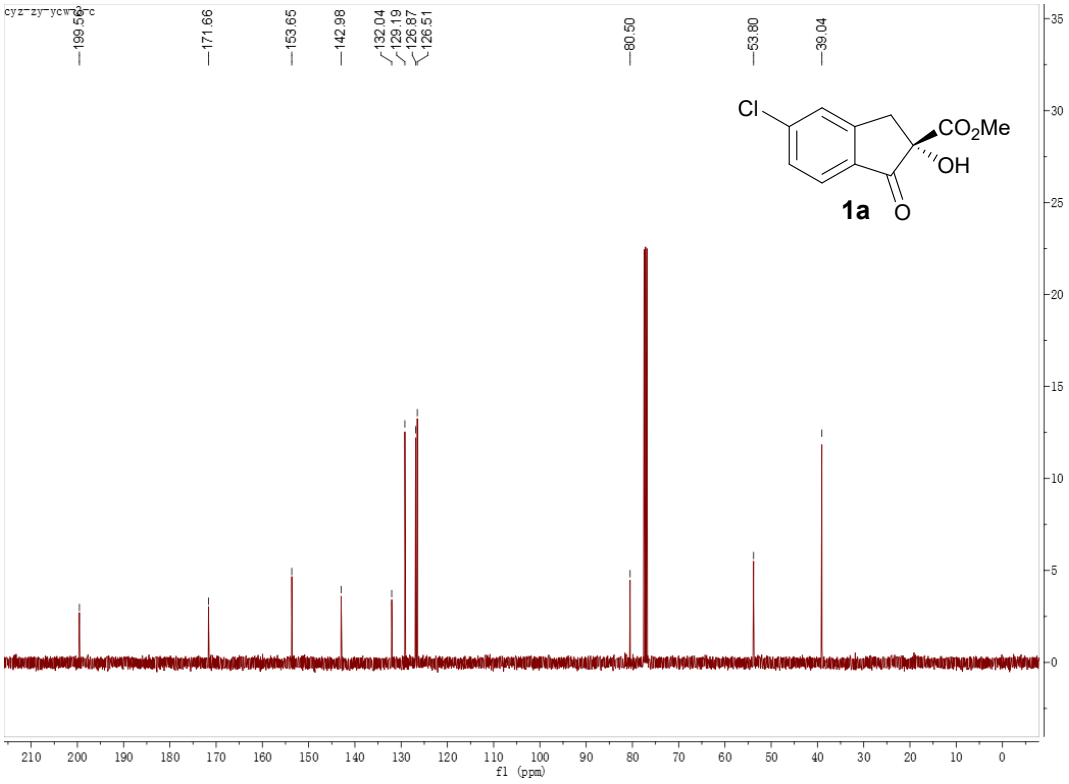


10.3 The products of enantioselective hydroxylation

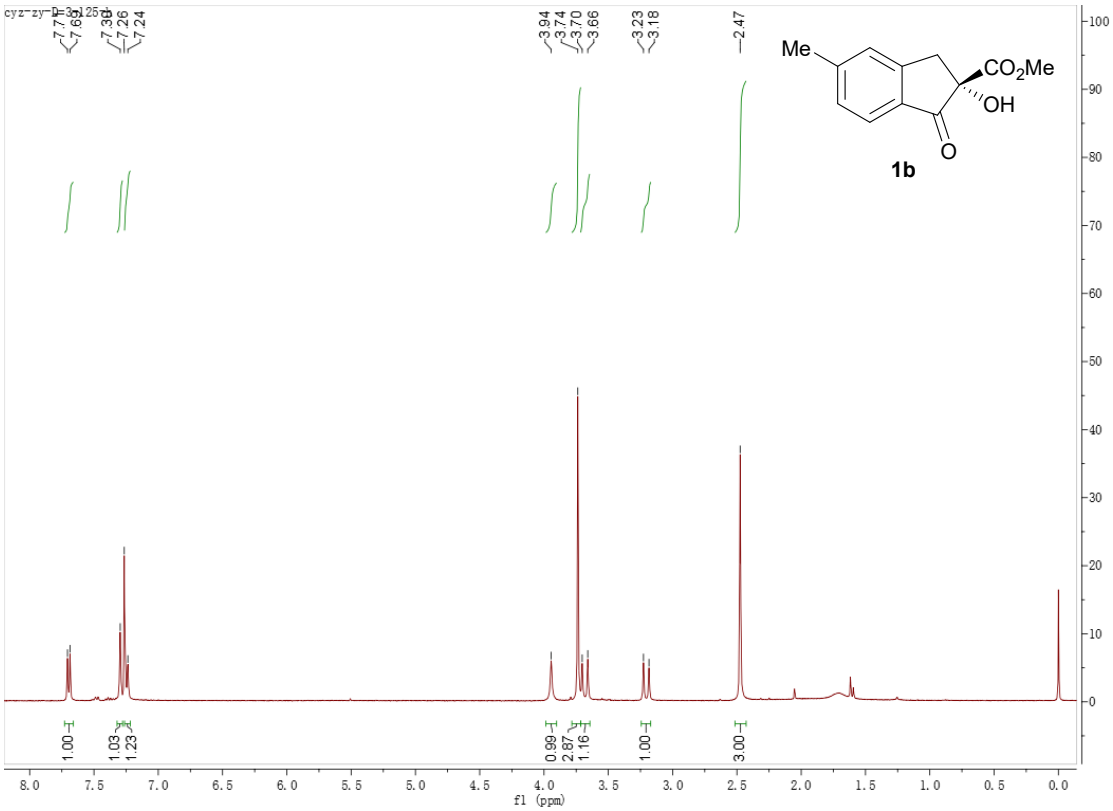
^{1}H NMR of compound 1a



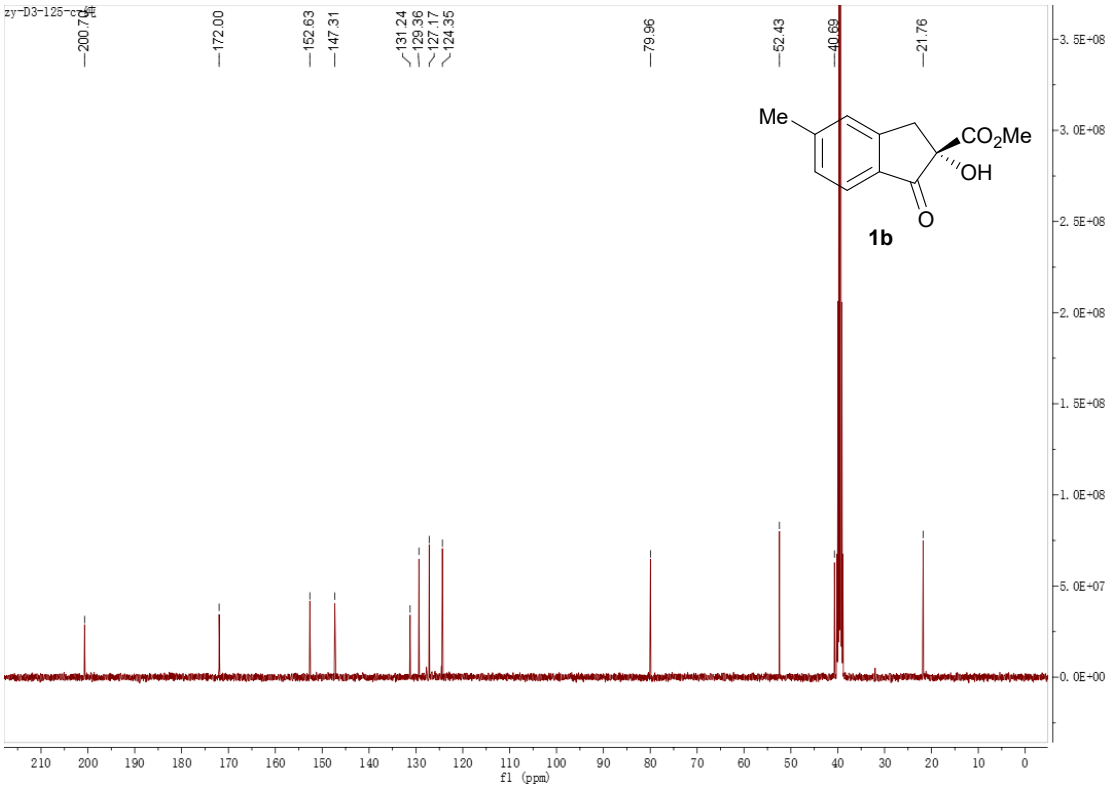
^{13}C NMR of compound 1a



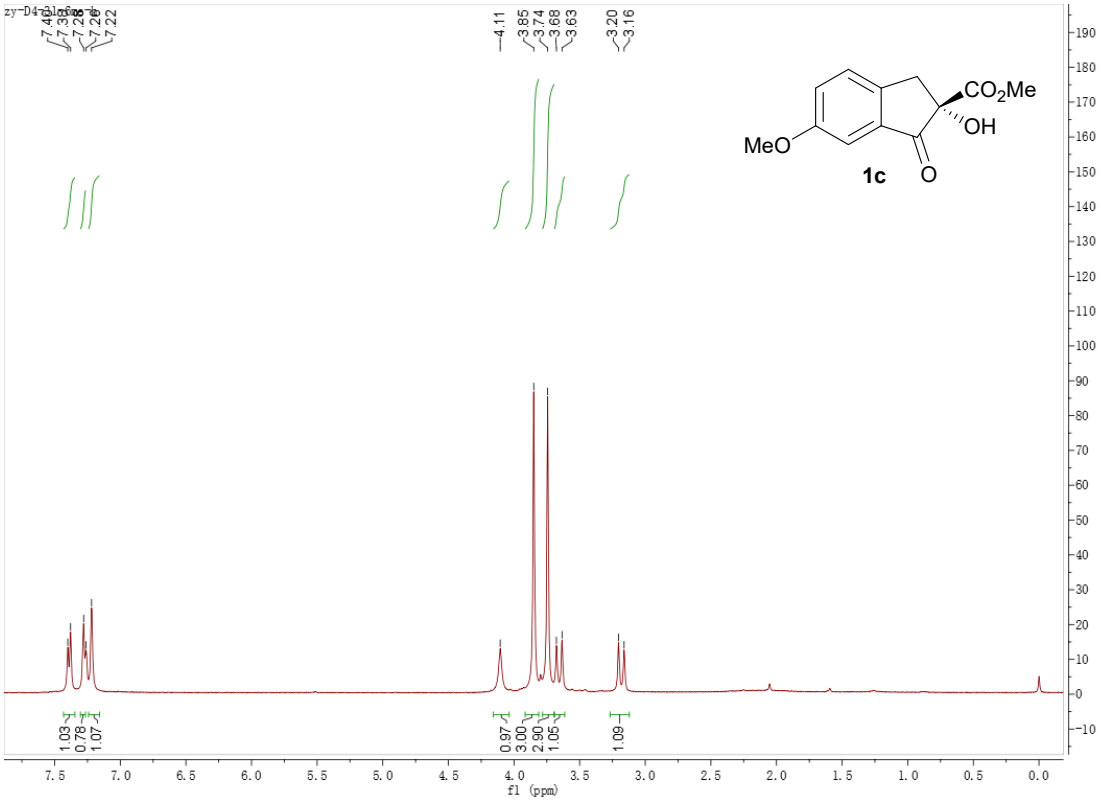
^{1}H NMR of compound 1b



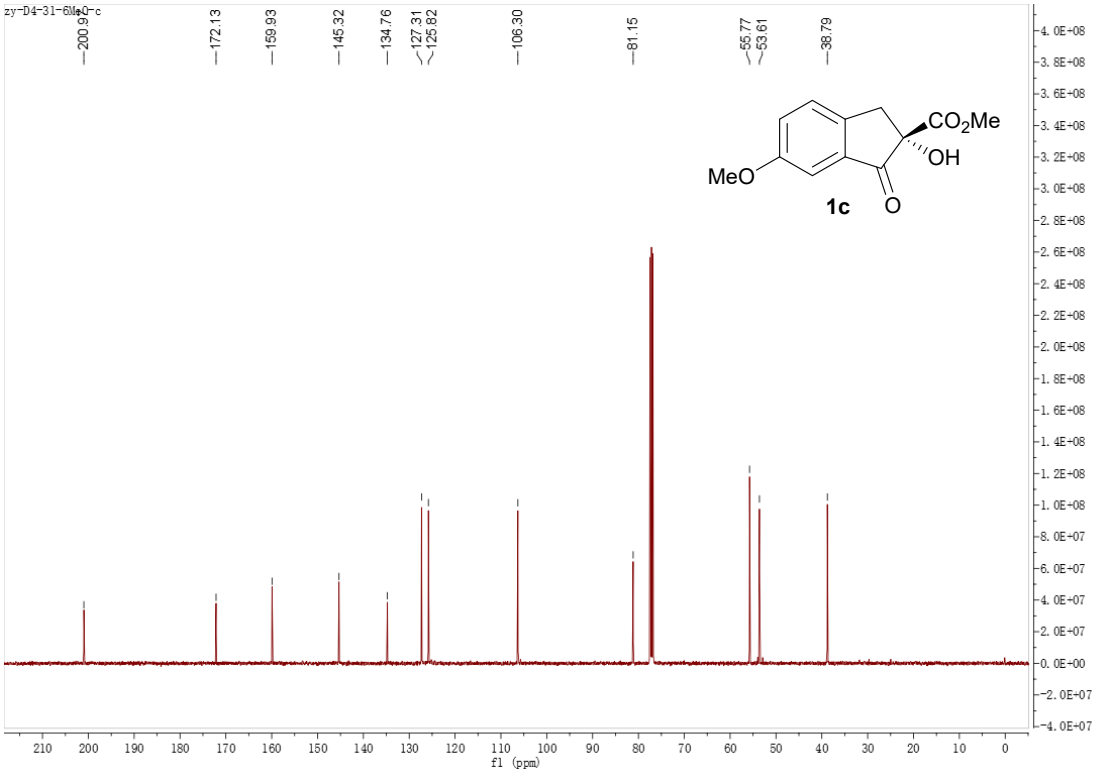
^{13}C NMR of compound 1b



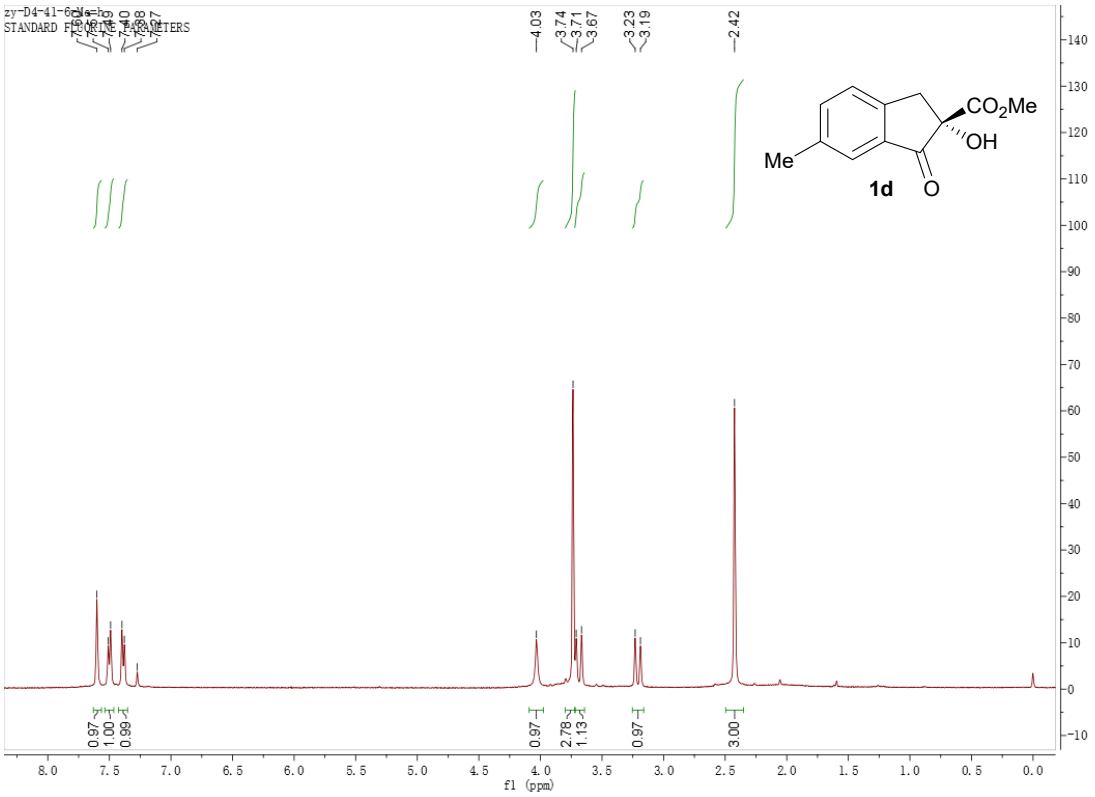
^{1}H NMR of compound 1c



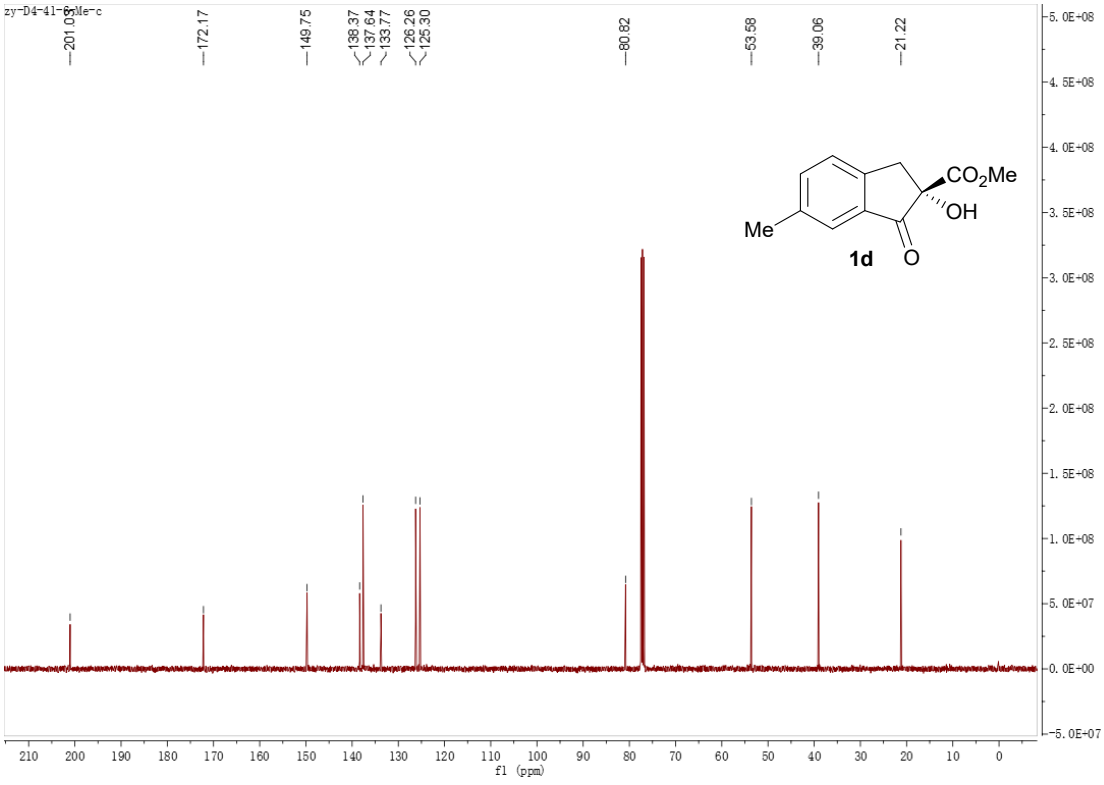
^{13}C NMR of compound 1c



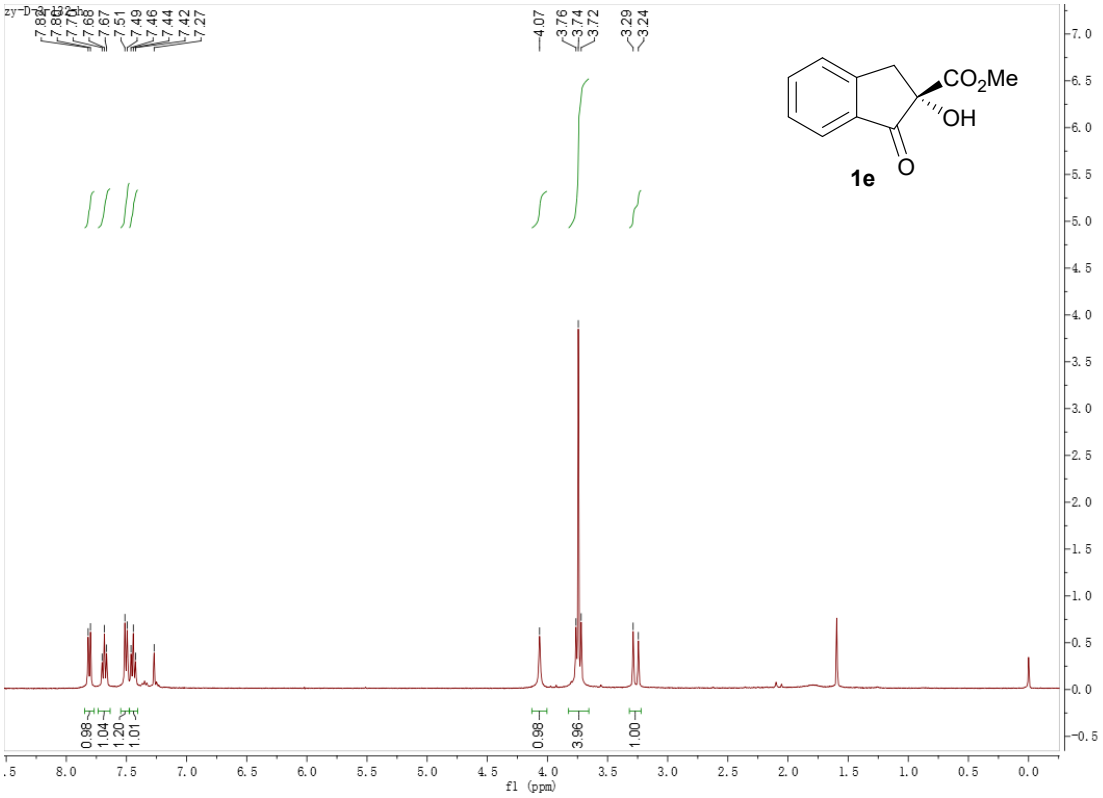
^{1}H NMR of compound 1d



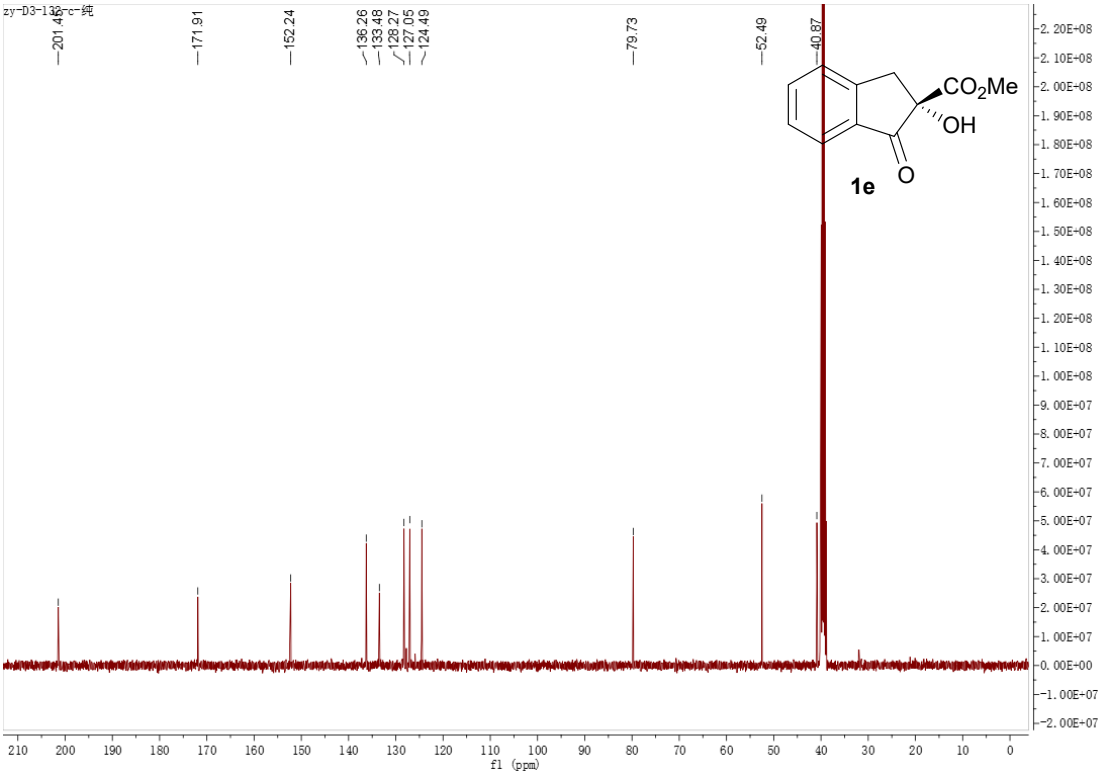
^{13}C NMR of compound 1d



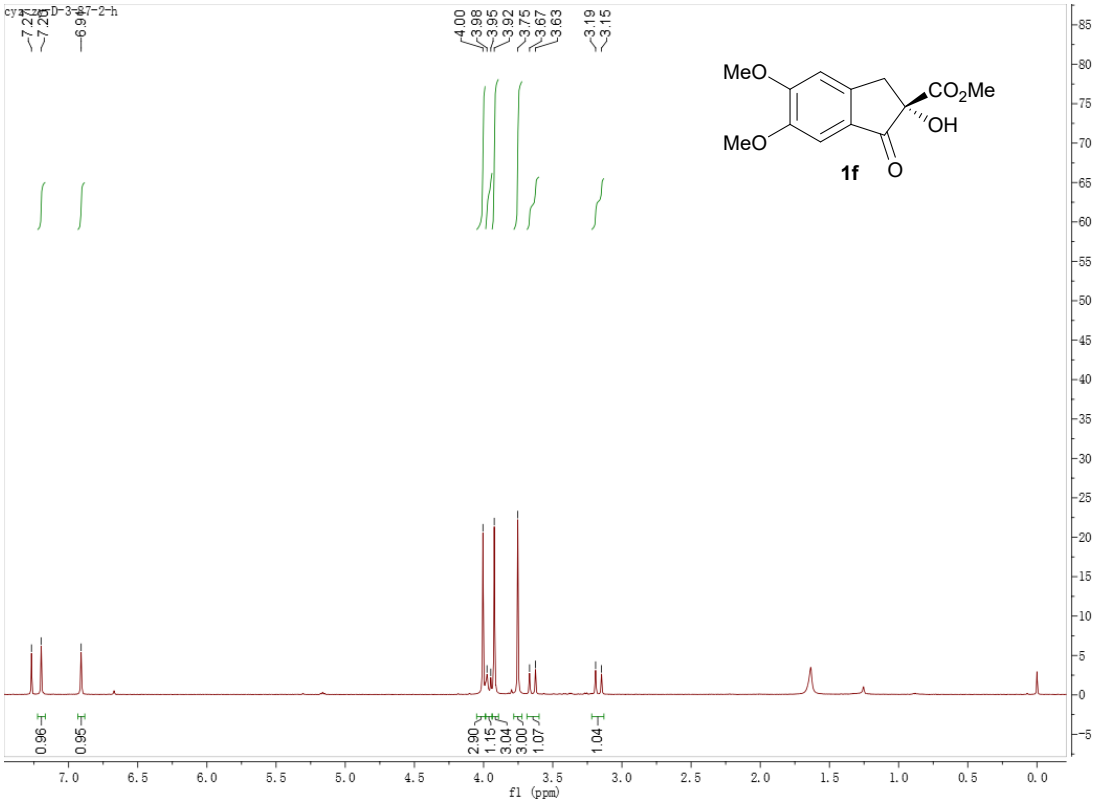
^{1}H NMR of compound 1e



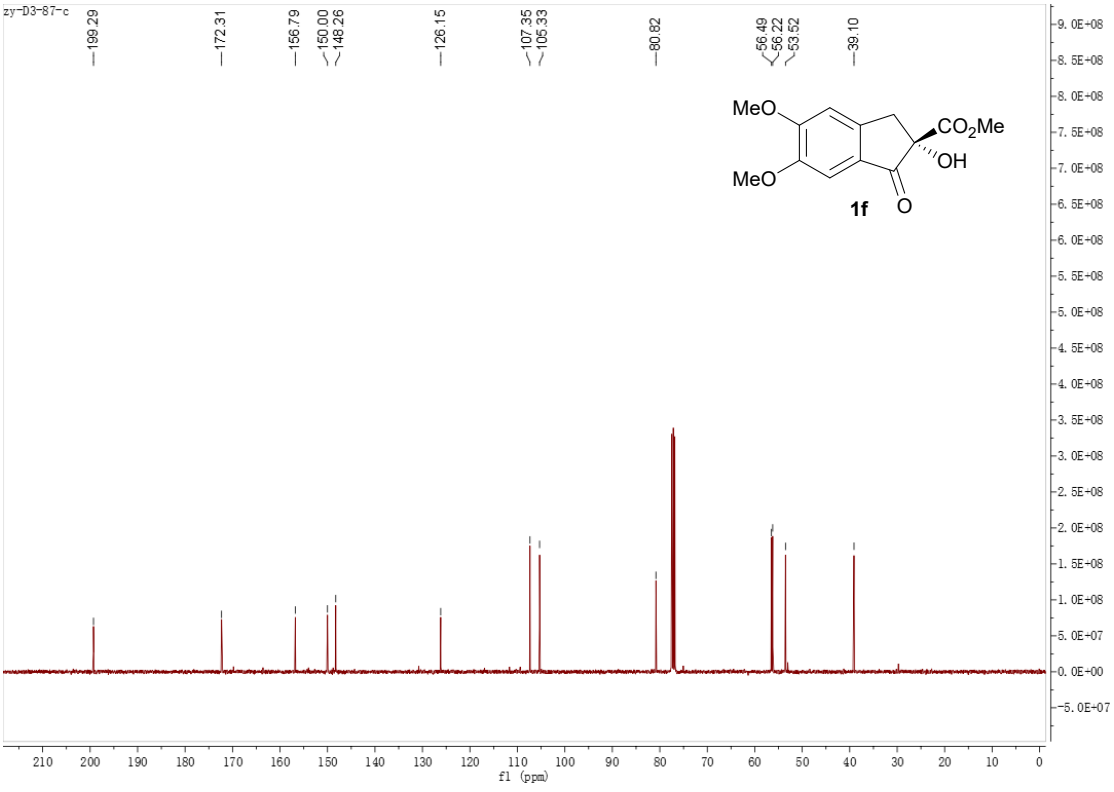
^{13}C NMR of compound 1e



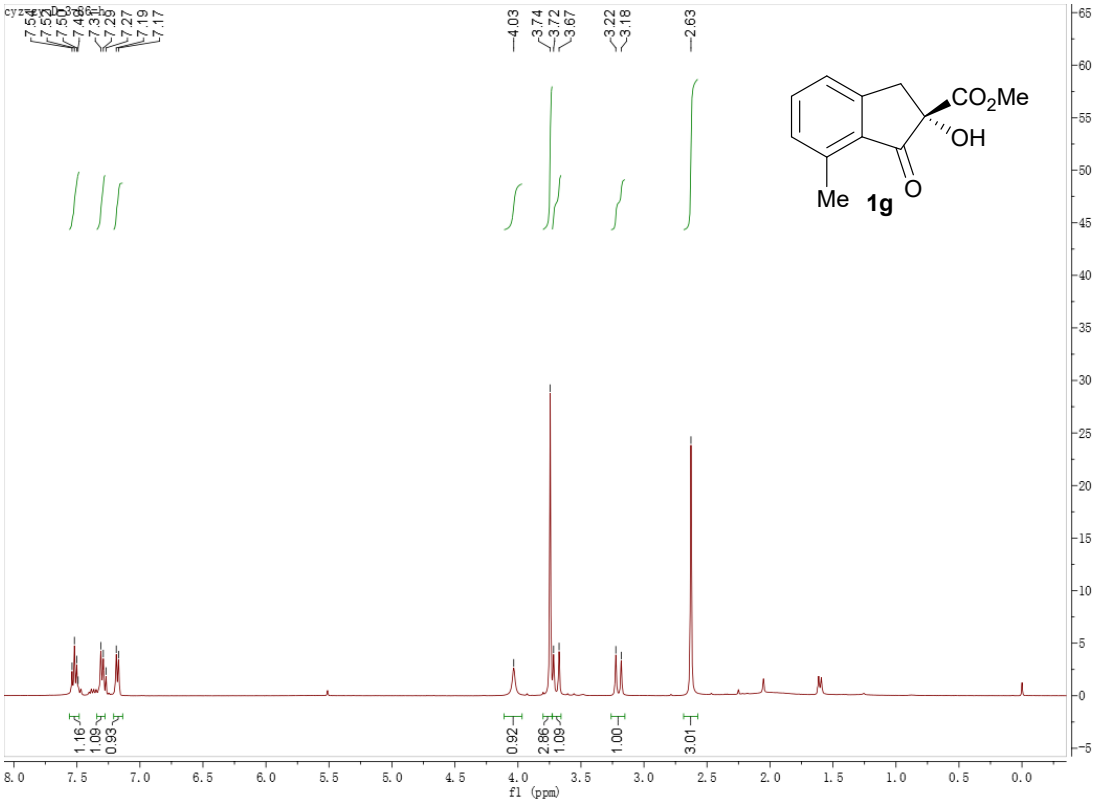
^{1}H NMR of compound 1f



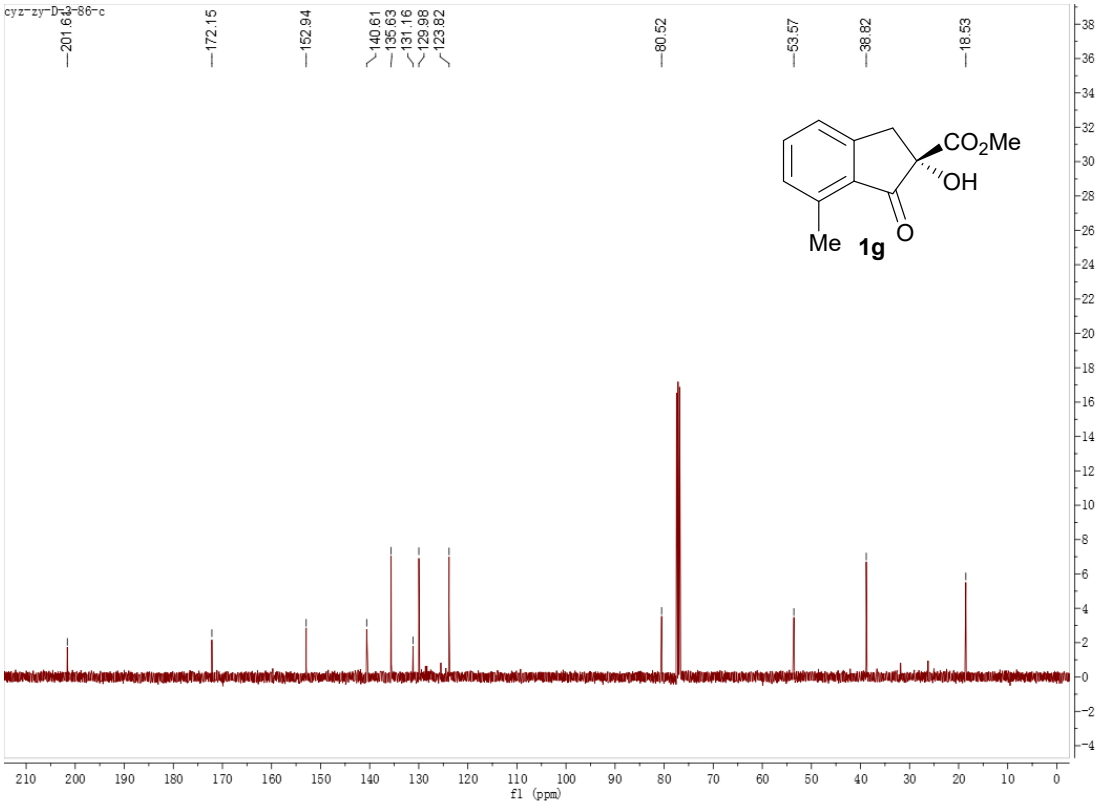
^{13}C NMR of compound 1f



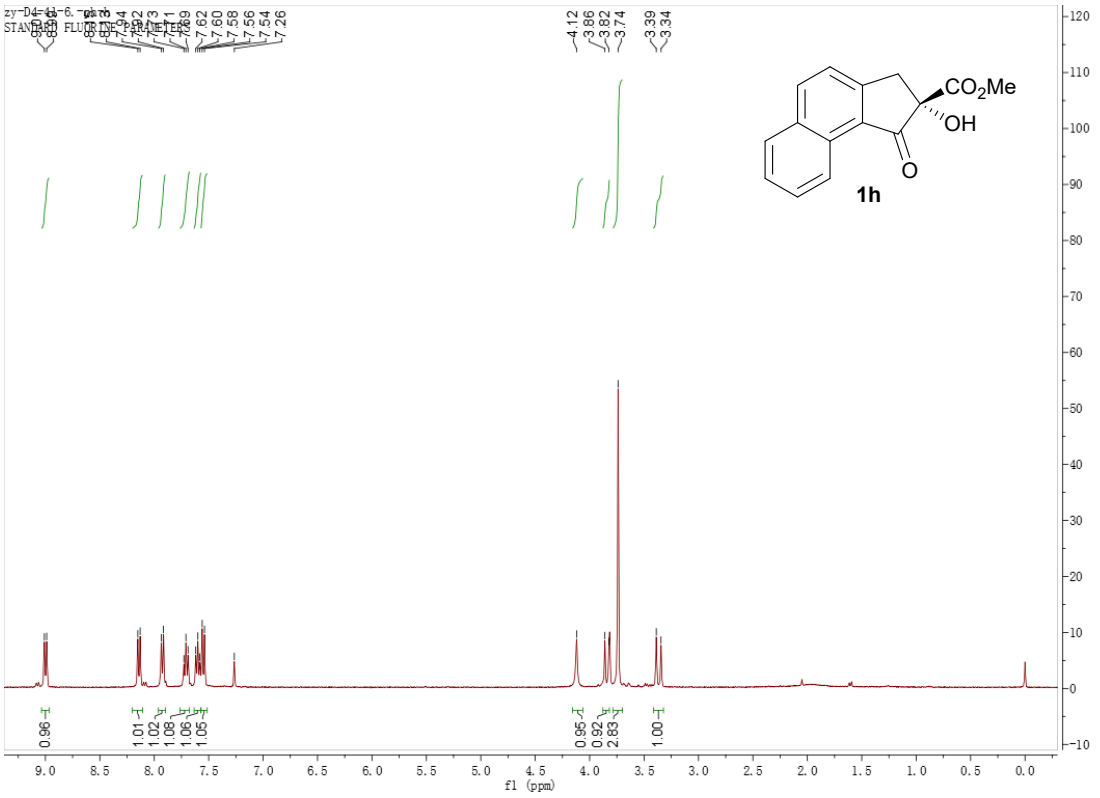
^{1}H NMR of compound 1g



^{13}C NMR of compound 1g



^{1}H NMR of compound 1h



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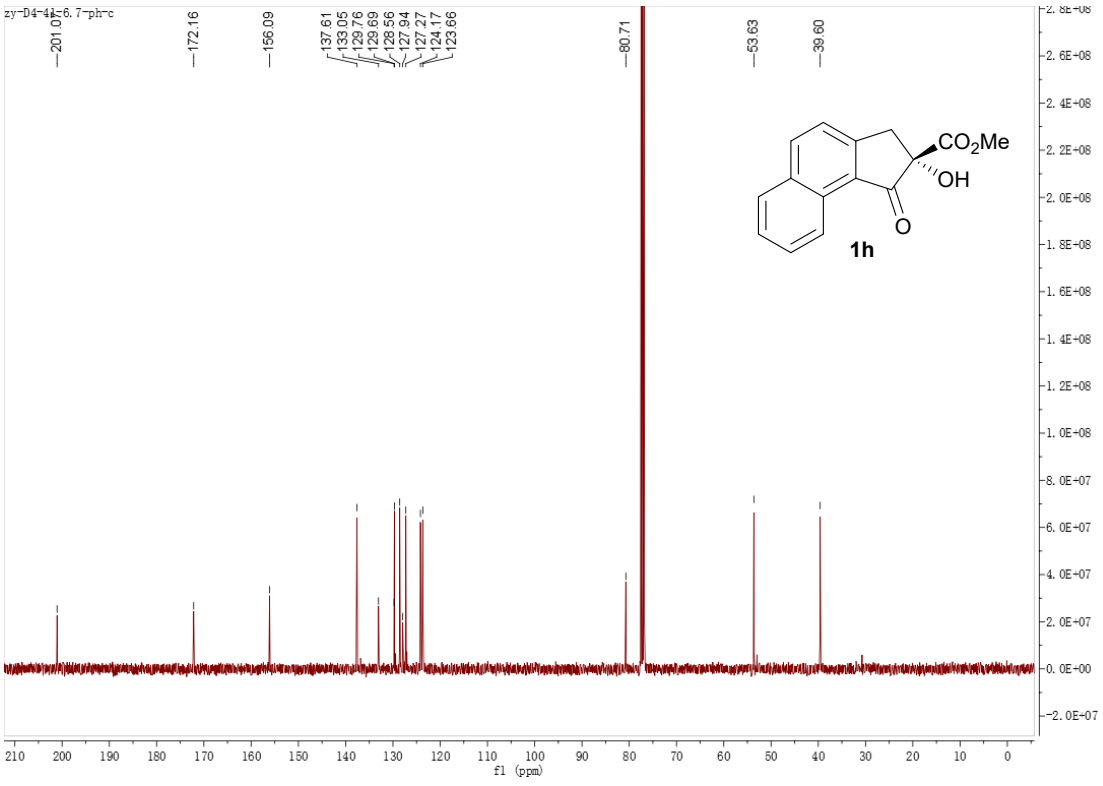
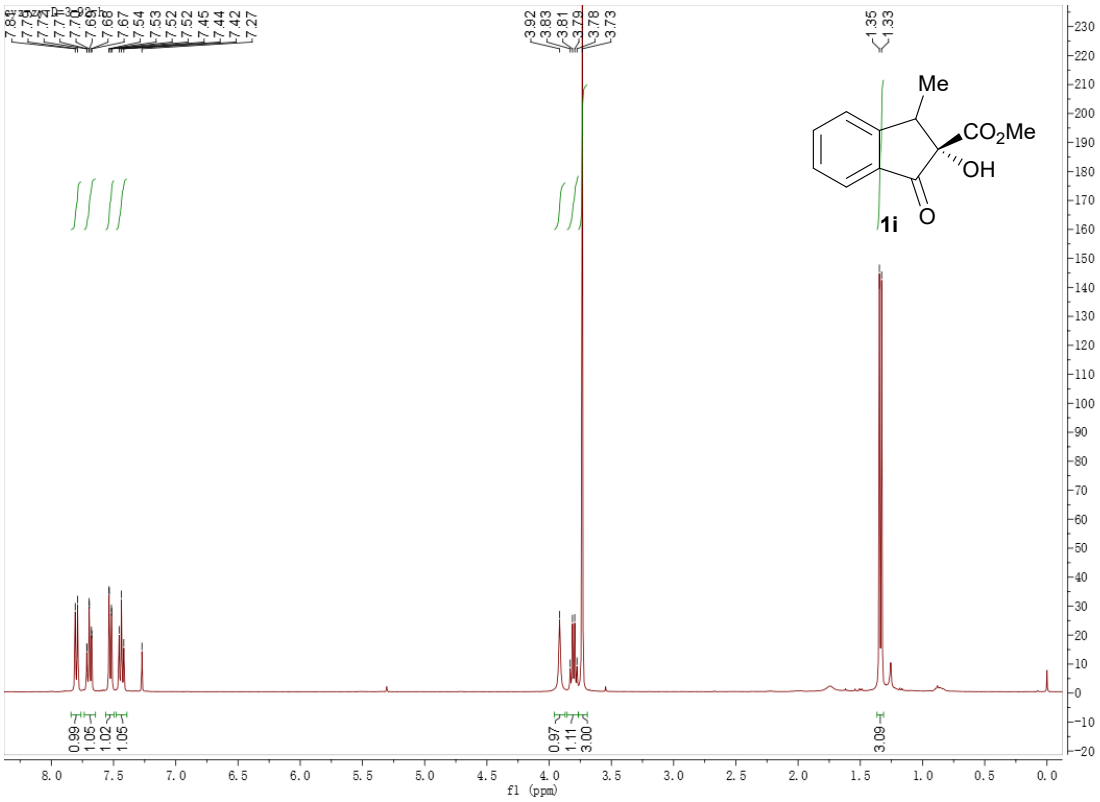
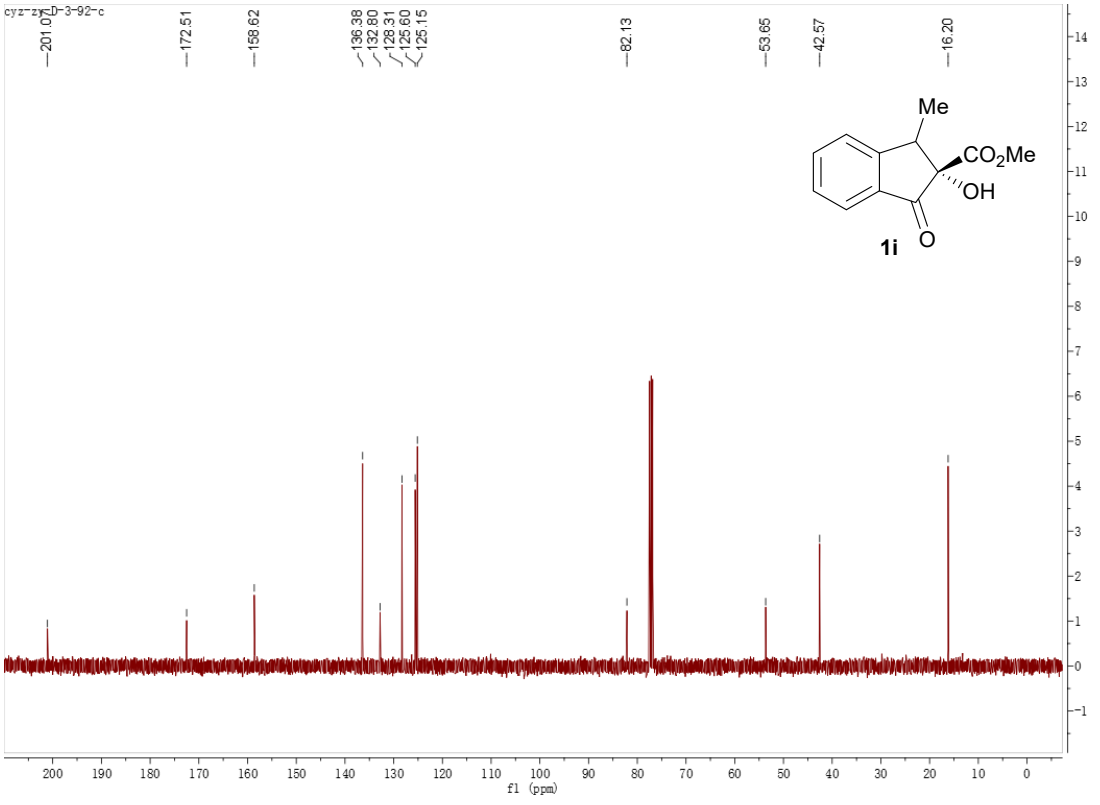


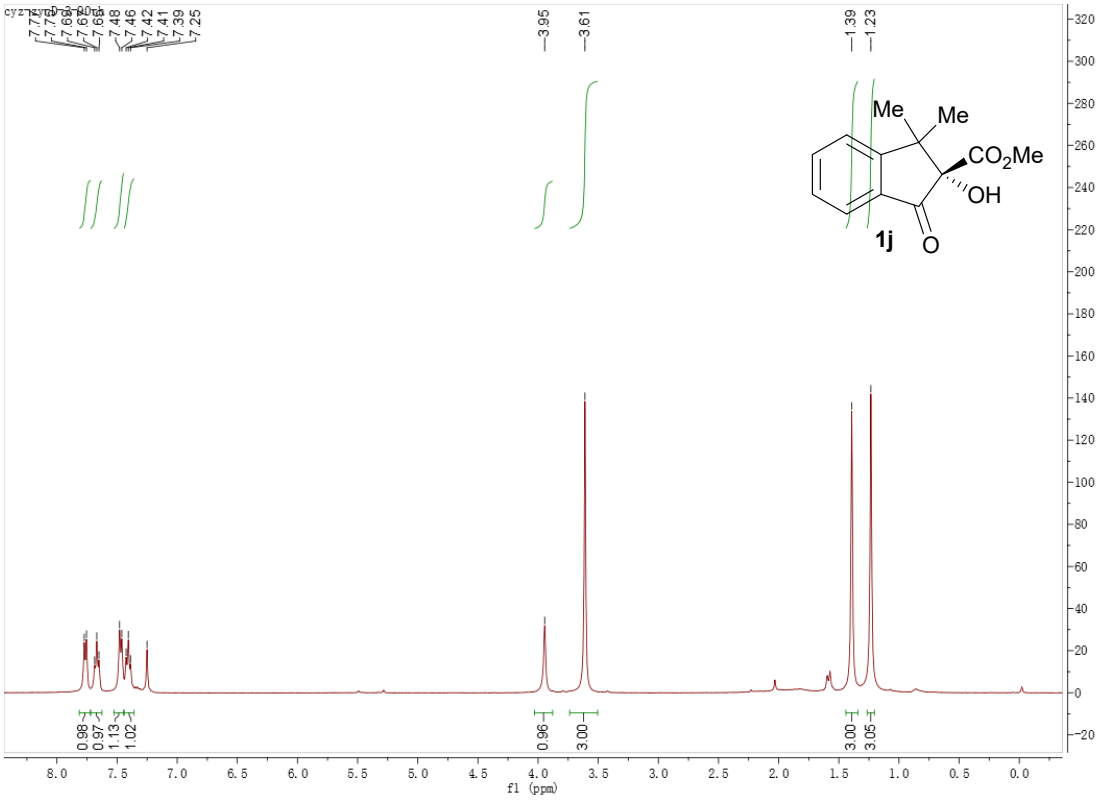
^{1}H NMR of compound 1i



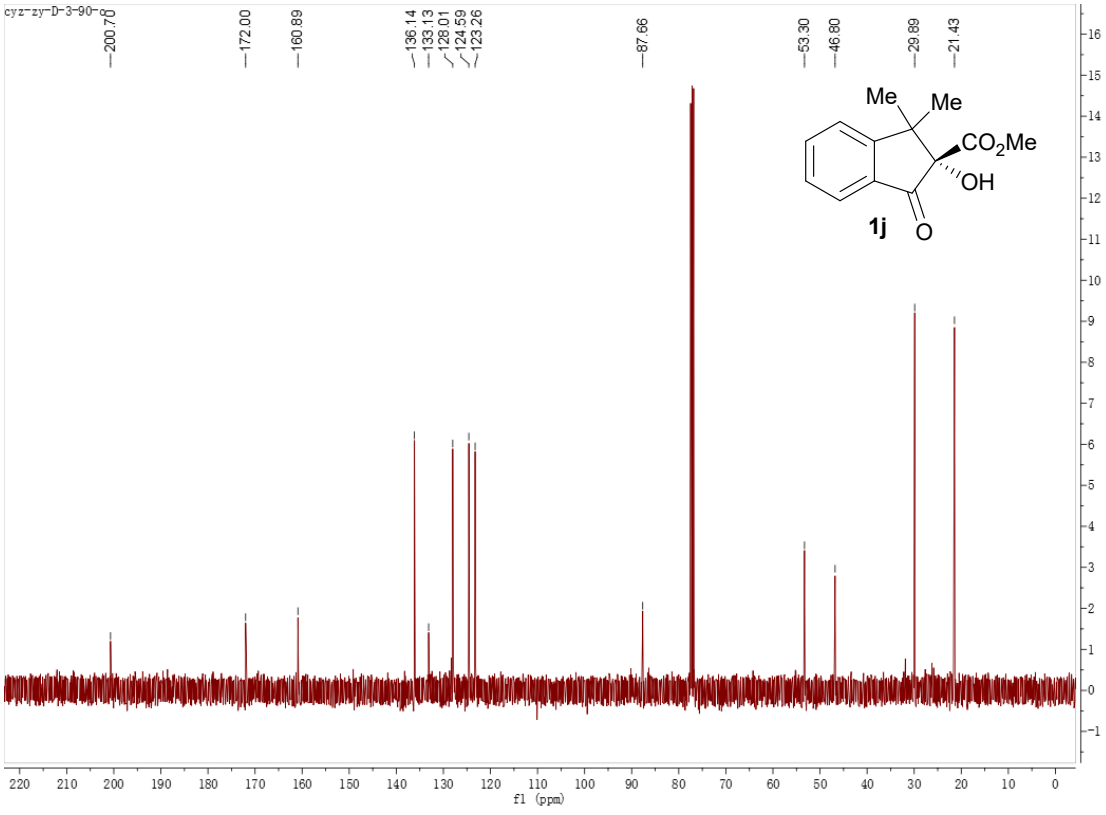
^{13}C NMR of compound 1i



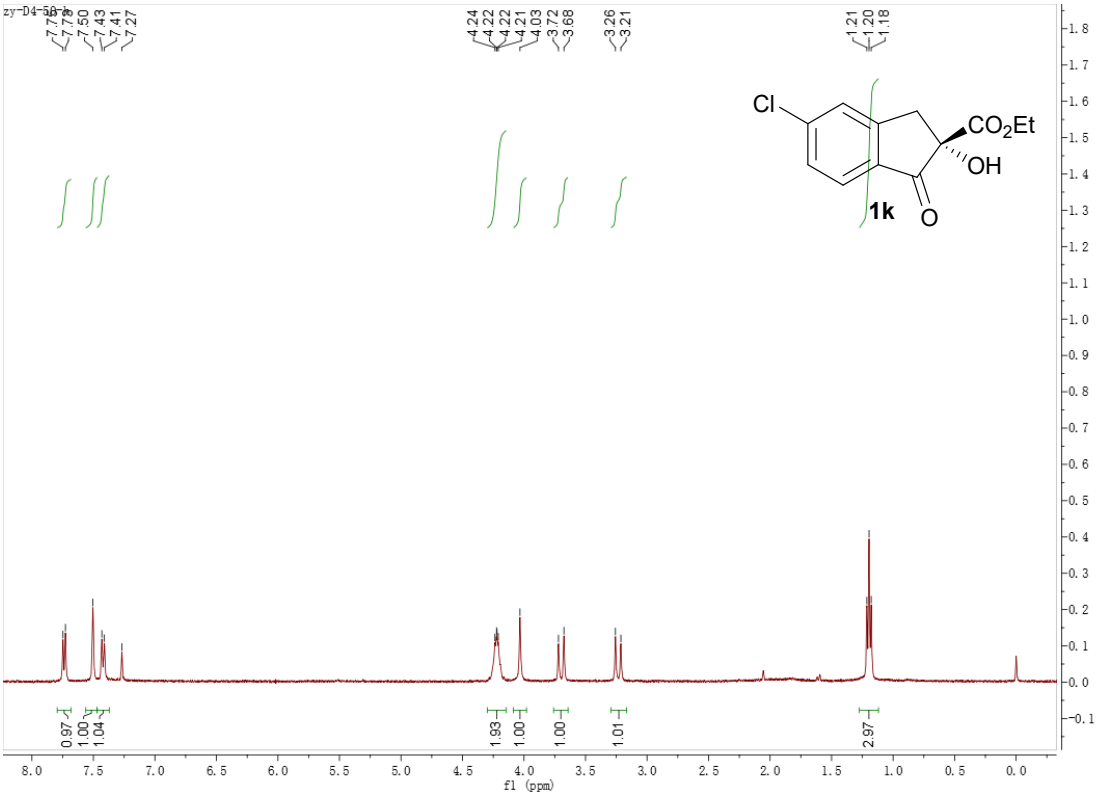
^{1}H NMR of compound 1j



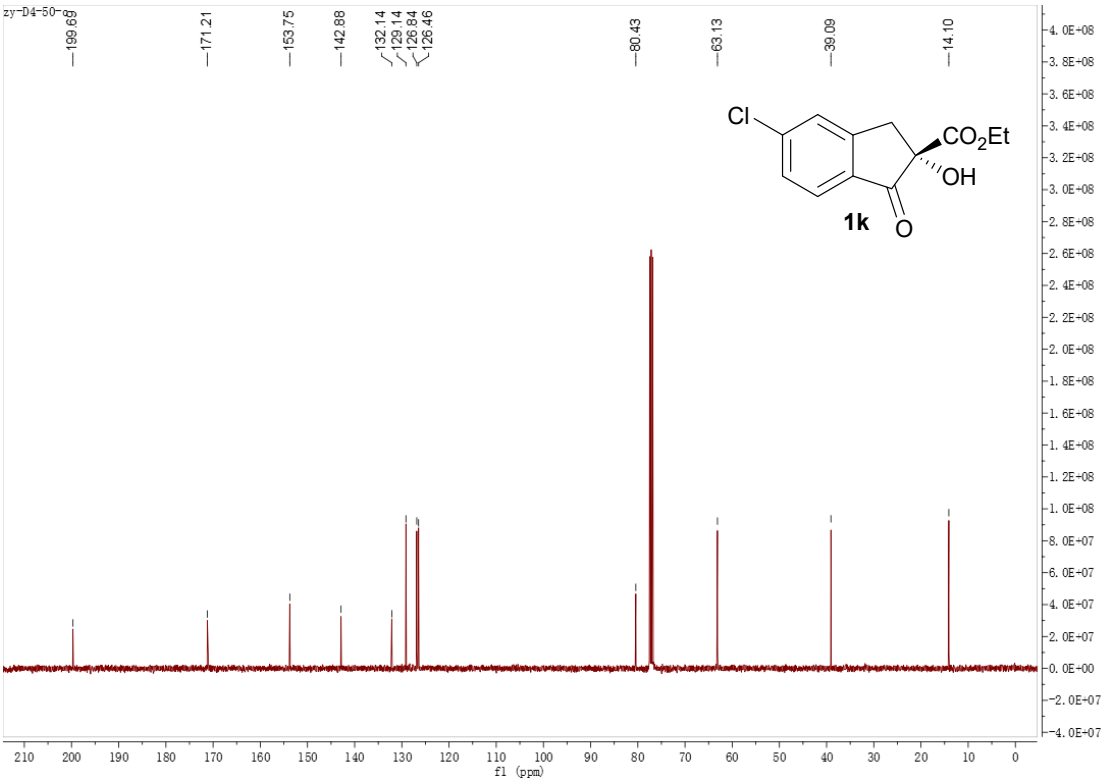
^{13}C NMR of compound 1j



^{1}H NMR of compound 1k



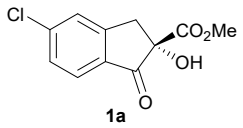
^{13}C NMR of compound 1k



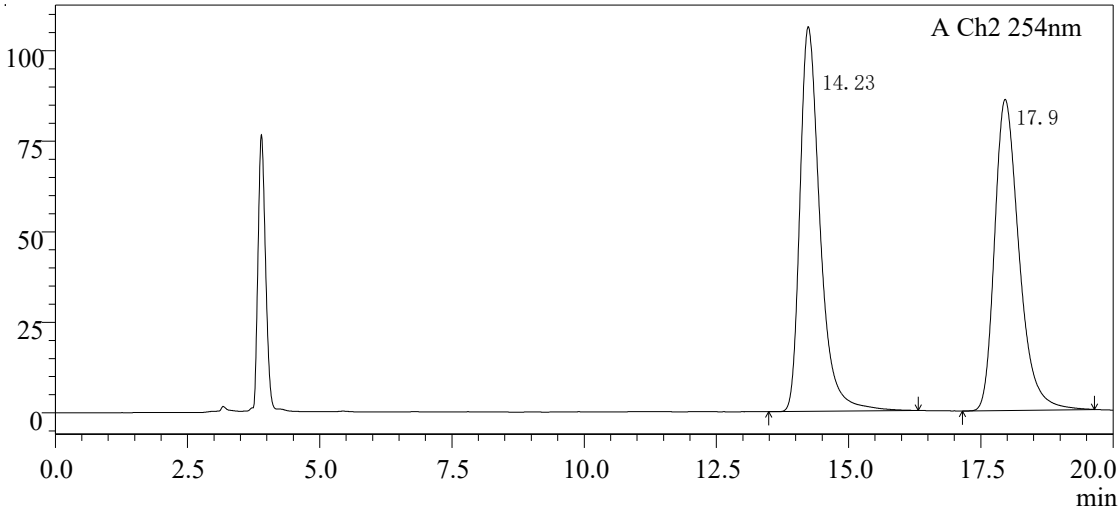
11. Copies of HPLC chromatogram

11.1 HPLC chromatogram of the Products

HPLC chromatogram of 1a



1a



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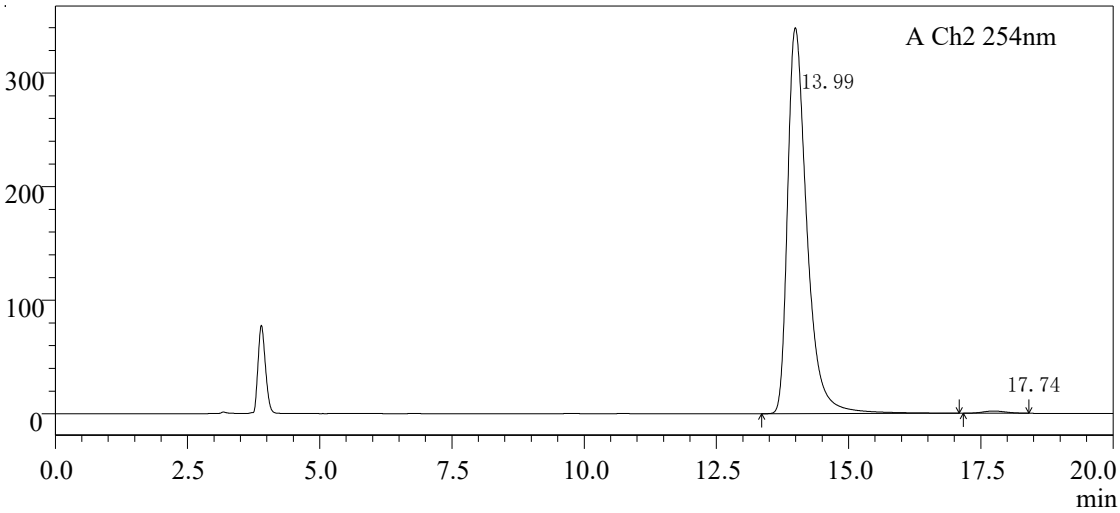

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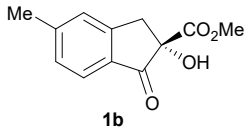
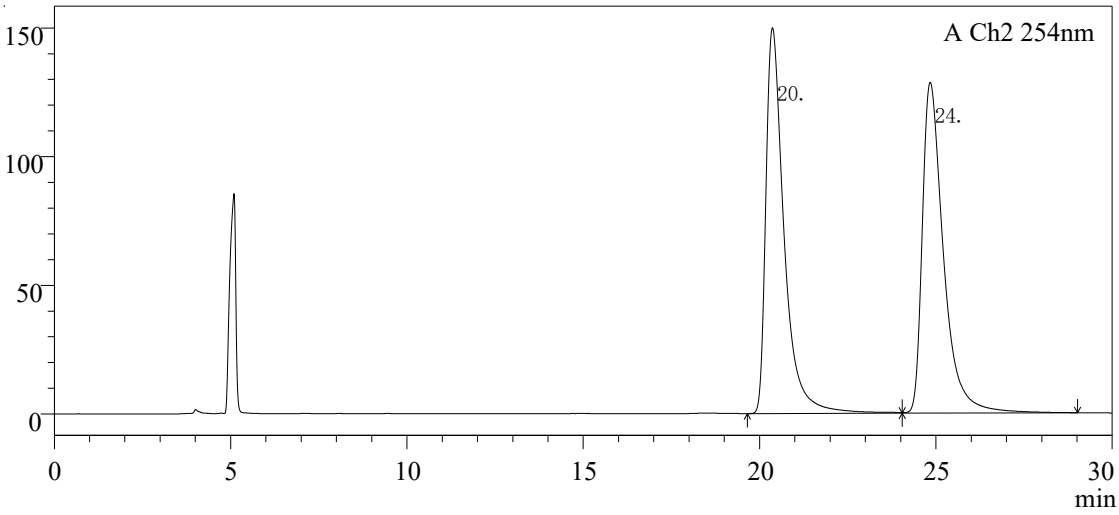
HPLC chromatogram of 1b



1b



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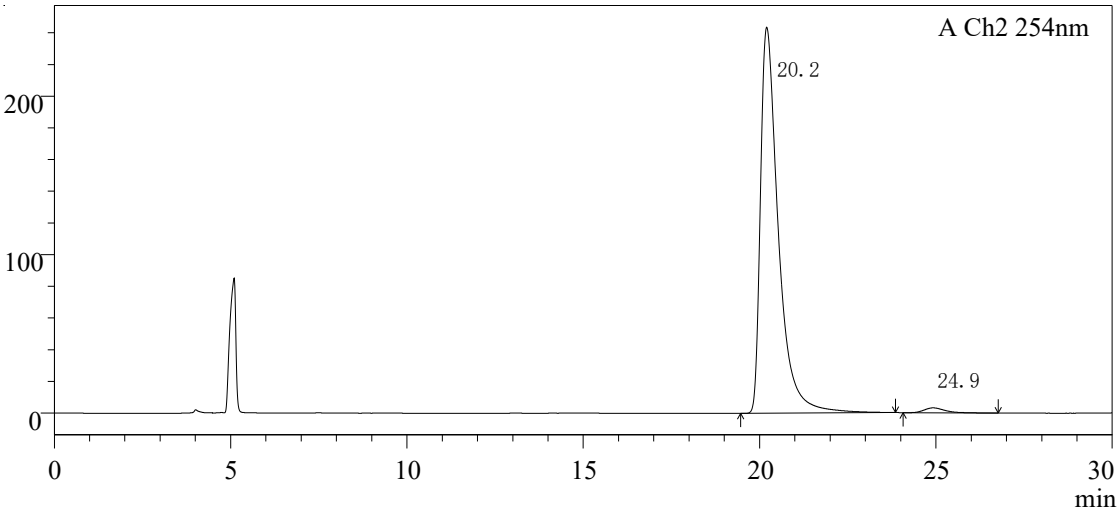
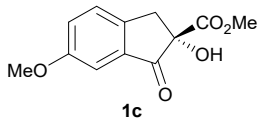
1	20.364	5405857	149908	50.064	--
2	24.838	5392134	128585	49.936	4.669

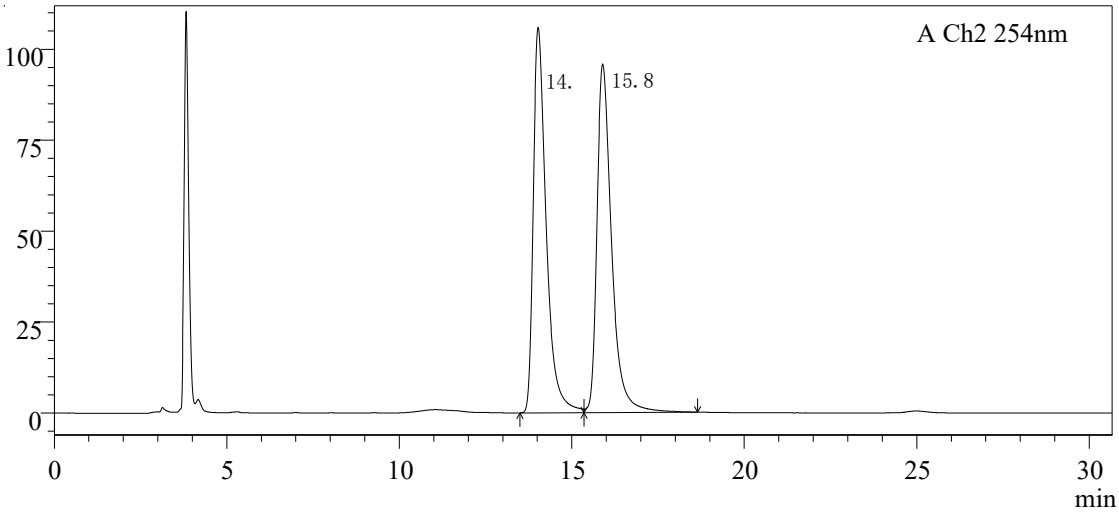


ID#	Ret. Time	Area	Height	Area %	Resolution
1	20.201	8633736	243759	98.554	--
2	24.920	126653	3108	1.446	4.852

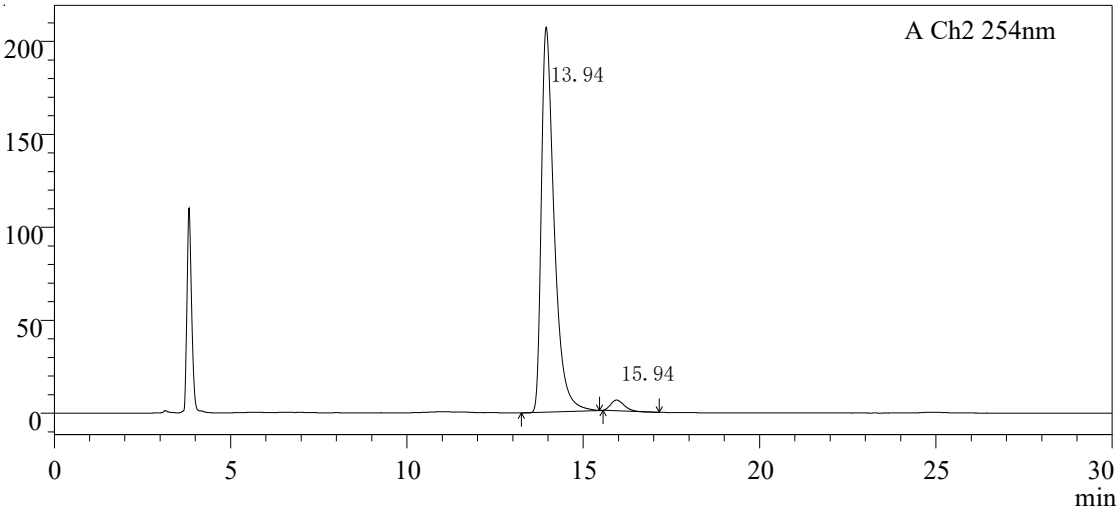
HPLC chromatogram of 1c



1c

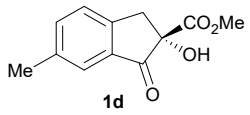


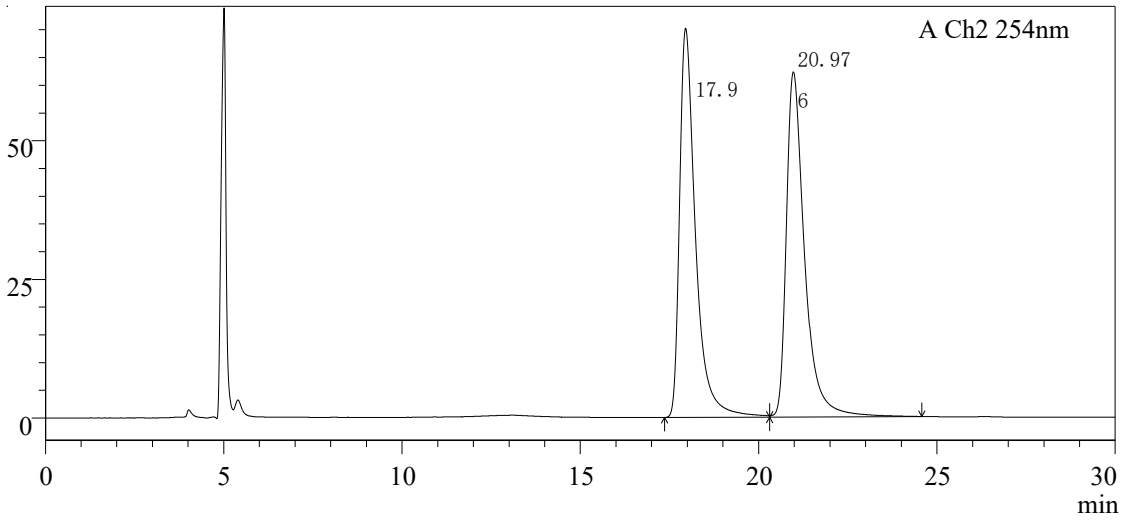
ID#	Ret. Time	Area	Height	Area %	Resolution
1	14.026	2771384	105971	49.488	--
2	15.898	2828716	95792	50.512	2.691



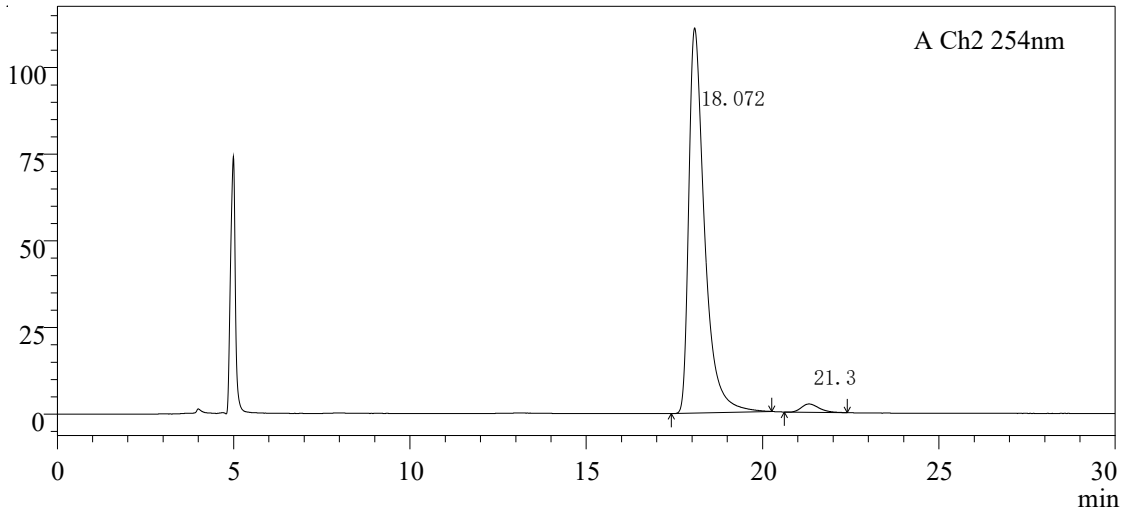
ID#	Ret. Time	Area	Height	Area %	Resolution
1	13.948	5264852	207216	97.216	--
2	15.944	150797	5746	2.784	2.945

HPLC chromatogram of 1d



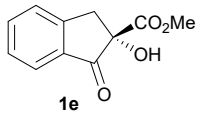


ID#	Ret. Time	Area	Height	Area %	Resolution
1	17.950	2194267	70188	49.776	--
2	20.976	2214056	62258	50.224	3.694

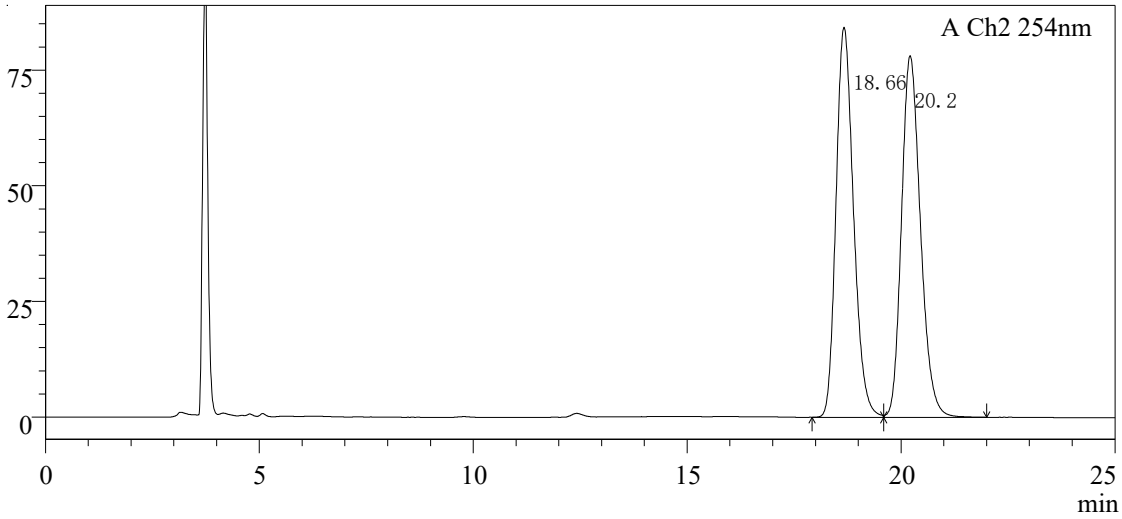


ID#	Ret. Time	Area	Height	Area %	Resolution
1	18.072	3470787	111158	97.652	--
2	21.321	83465	2399	2.348	3.872

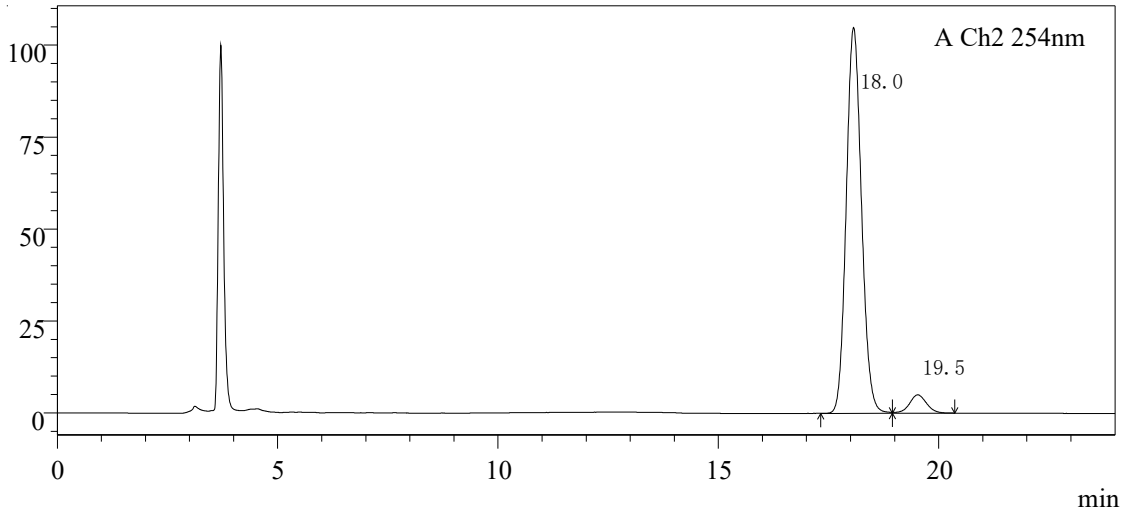
HPLC chromatogram of 1e



1e

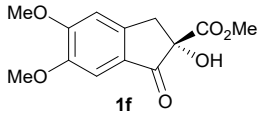


ID#	Ret. Time	Area	Height	Area %	Resolution
1	18.666	2395628	84315	49.865	--
2	20.212	2408642	78160	50.135	1.999

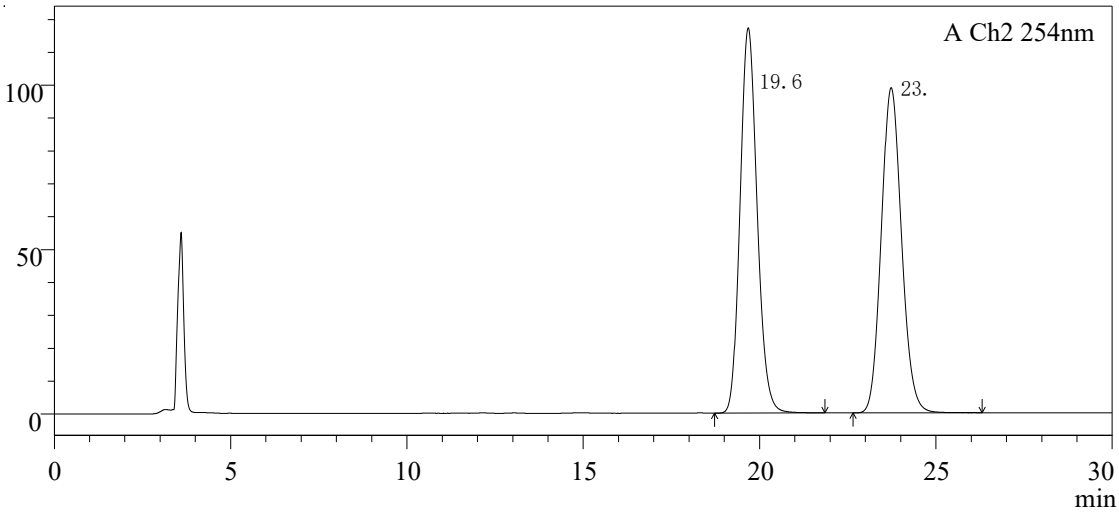


ID#	Ret. Time	Area	Height	Area %	Resolution
1	18.068	2522781	104962	94.879	--
2	19.526	136152	4992	5.121	2.179

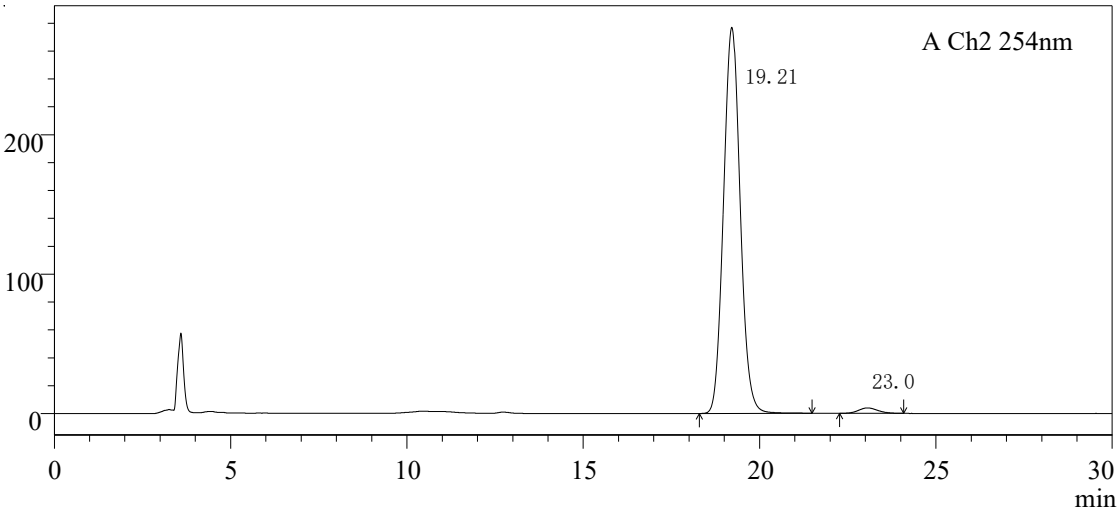
HPLC chromatogram of 1f



1f

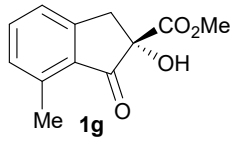


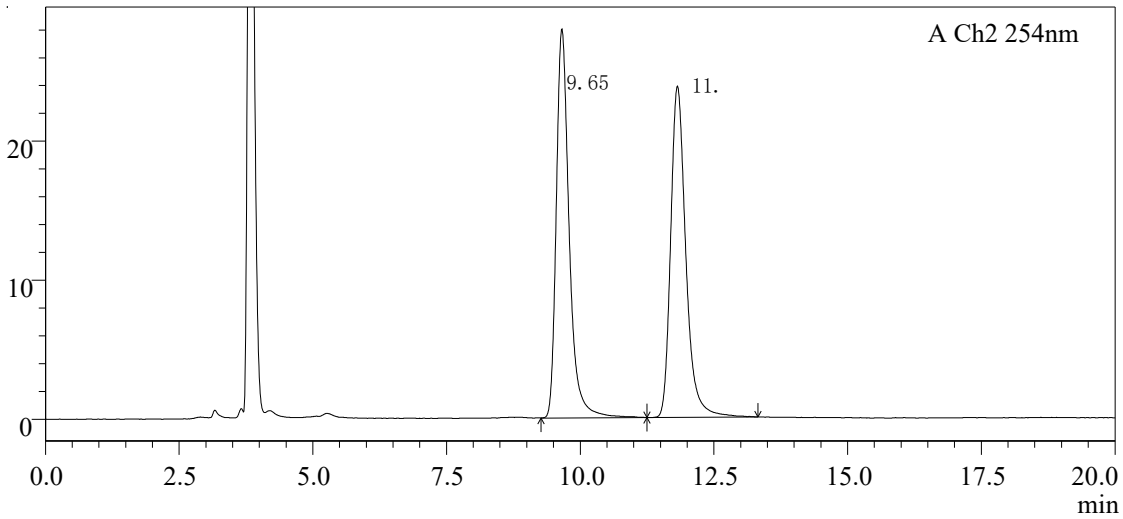
ID#	Ret. Time	Area	Height	Area %	Resolution
1	19.674	3943280	117186	50.033	--
2	23.727	3938122	98908	49.967	4.202



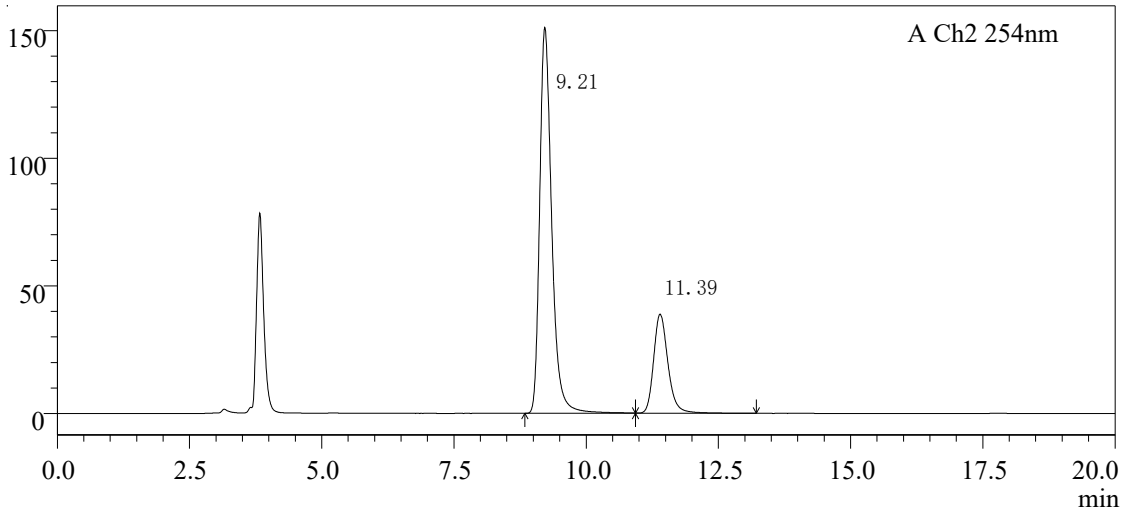
ID#	Ret. Time	Area	Height	Area %	Resolution
1	19.215	9030907	276886	98.389	--
2	23.061	147825	3880	1.611	4.128

HPLC chromatogram of 1g



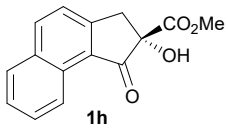


ID#	Ret. Time	Area	Height	Area %	Resolution
1	9.656	471840	27986	49.967	--
2	11.817	472456	23838	50.033	4.660

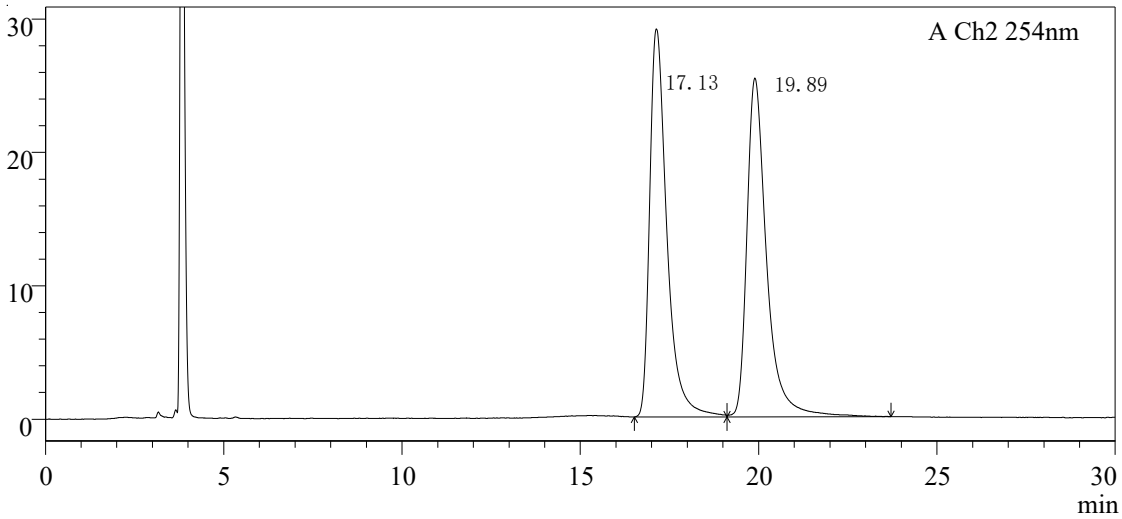


ID#	Ret. Time	Area	Height	Area %	Resolution
1	9.219	2383650	151142	76.506	--
2	11.398	731981	38859	23.494	4.933

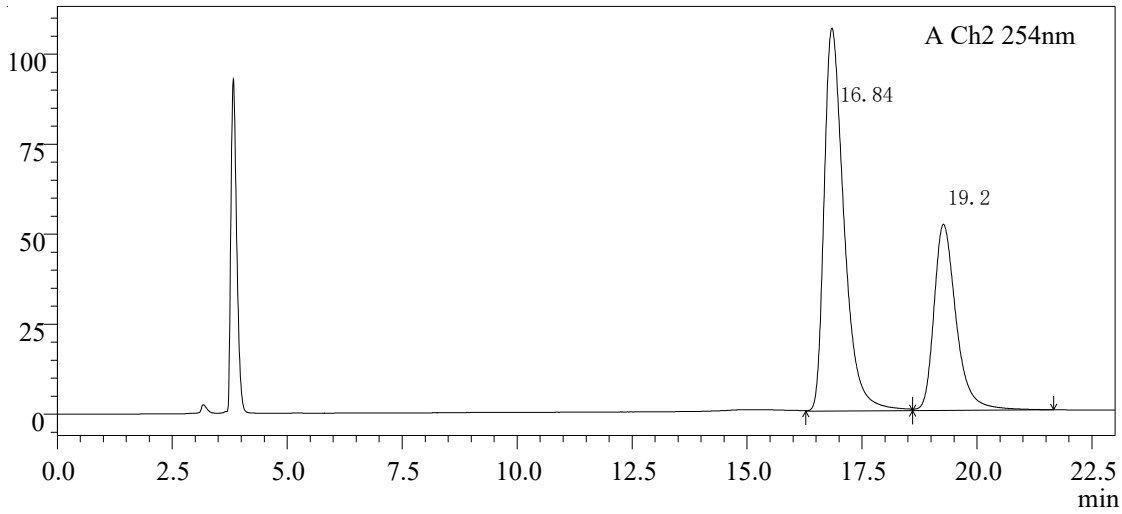
HPLC chromatogram of 1h



1h

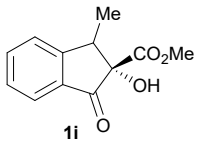


ID#	Ret. Time	Area	Height	Area %	Resolution
1	17.134	965728	29101	49.651	--
2	19.893	979312	25395	50.349	3.131

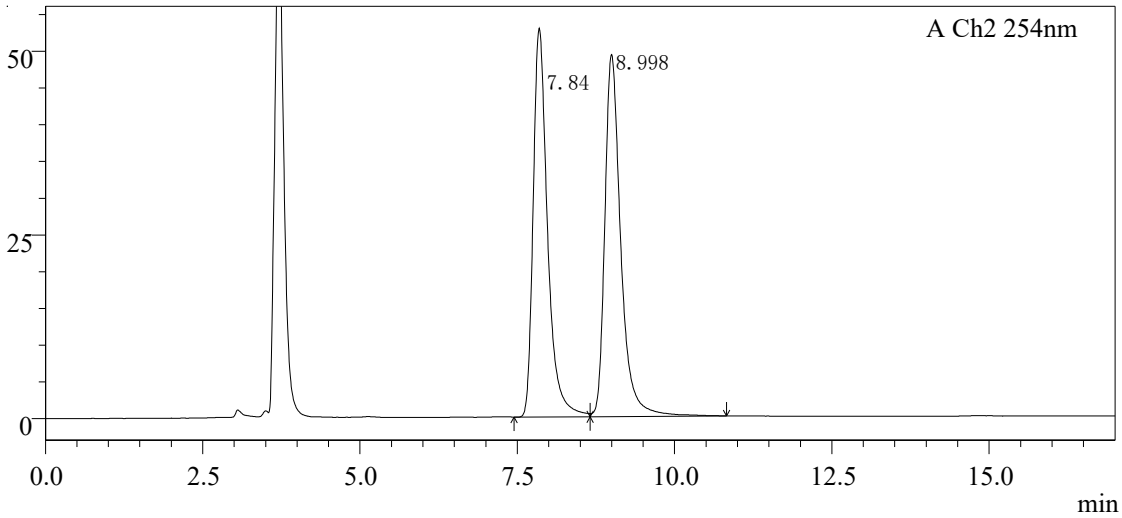


ID#	Ret. Time	Area	Height	Area %	Resolution
1	16.845	3197817	106386	64.839	--
2	19.270	1734149	51706	35.161	3.016

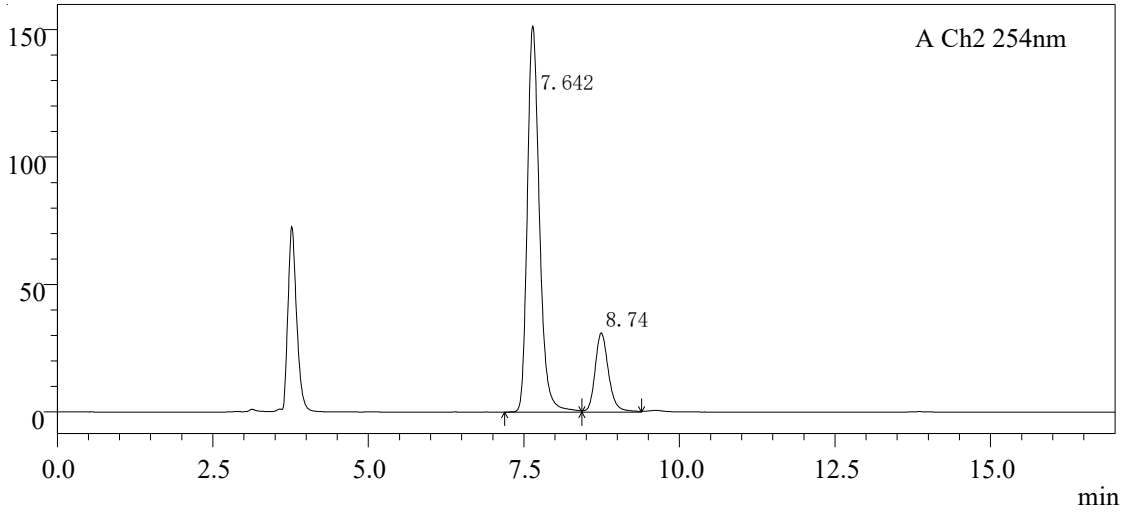
HPLC chromatogram of 1i



1i

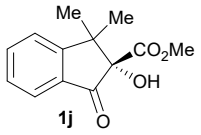


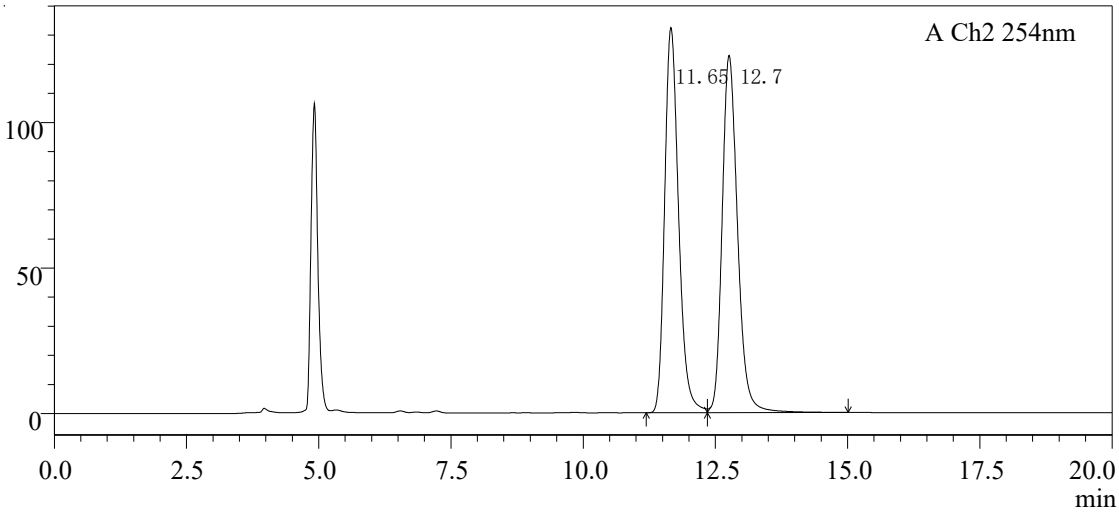
ID#	Ret. Time	Area	Height	Area %	Resolution
1	7.848	840912	52921	49.182	--
2	8.998	868874	49266	50.818	2.733



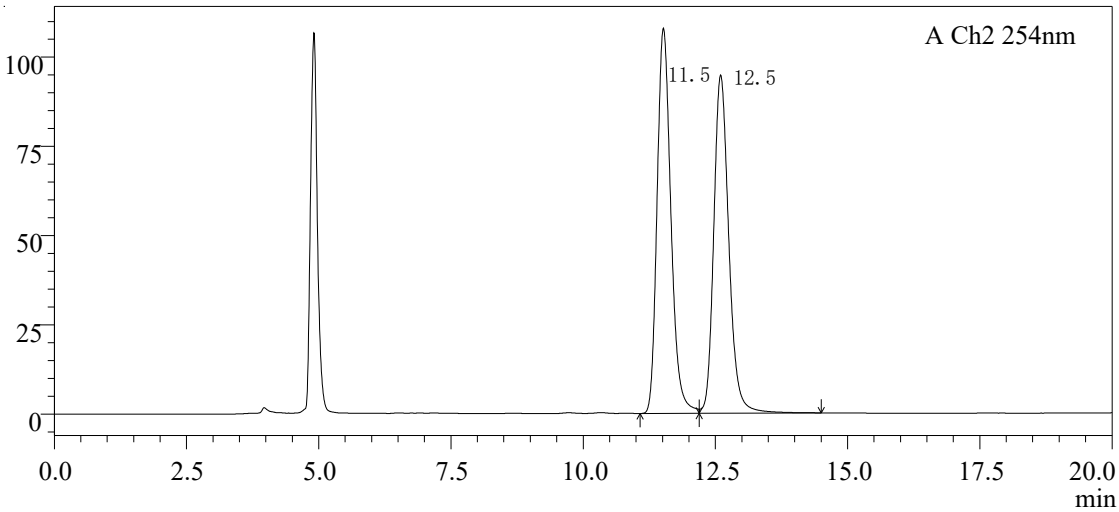
ID#	Ret. Time	Area	Height	Area %	Resolution
1	7.642	2052377	151496	81.487	--
2	8.743	466283	31046	18.513	2.988

HPLC chromatogram of 1j



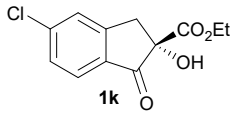


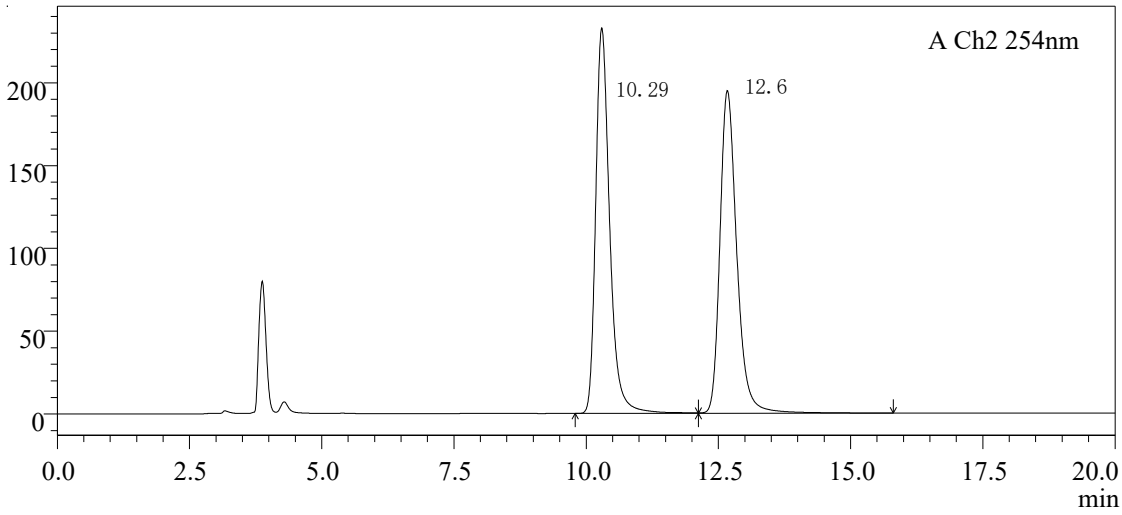
ID#	Ret. Time	Area	Height	Area %	Resolution
1	11.658	2435065	132387	49.519	--
2	12.759	2482350	122777	50.481	2.206



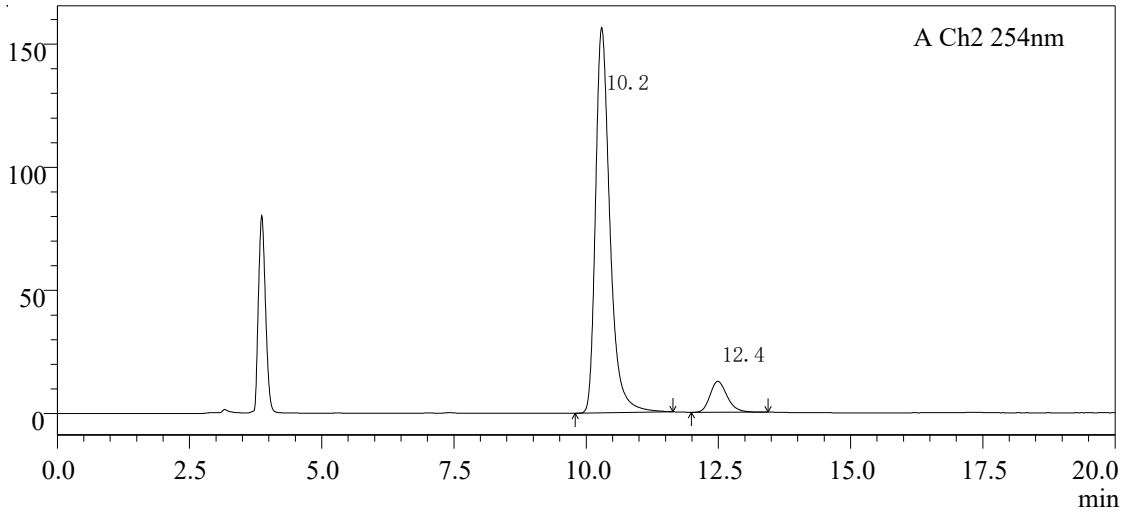
ID#	Ret. Time	Area	Height	Area %	Resolution
1	11.516	1954801	107965	50.970	--
2	12.599	1880401	94763	49.030	2.207

HPLC chromatogram of 1k





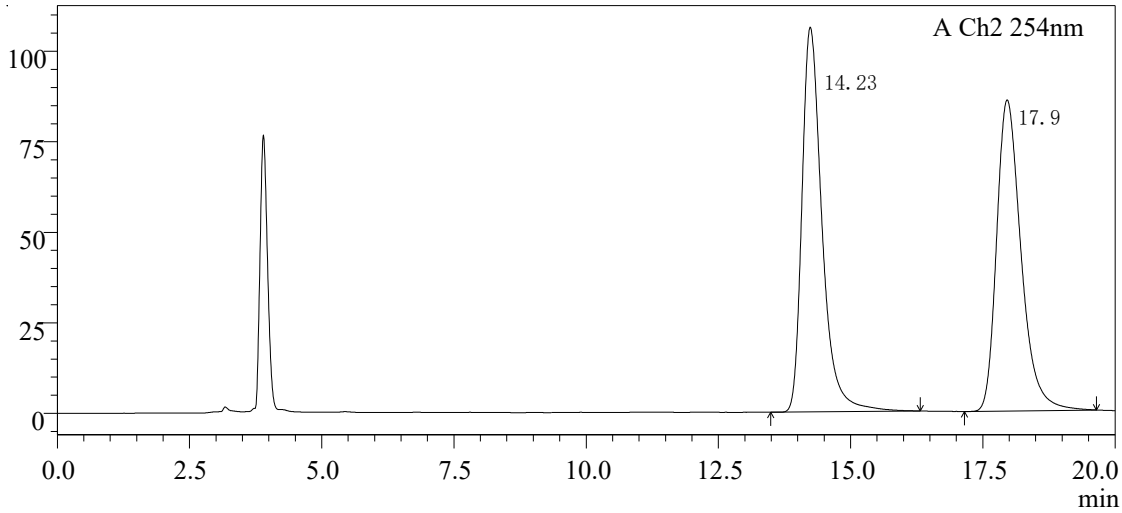
ID#	Ret. Time	Area	Height	Area %	Resolution
1	10.294	4292526	232864	49.857	--
2	12.670	4317075	194856	50.143	4.608



ID#	Ret. Time	Area	Height	Area %	Resolution
1	10.293	2965045	156536	91.258	--
2	12.490	284018	12559	8.742	4.106

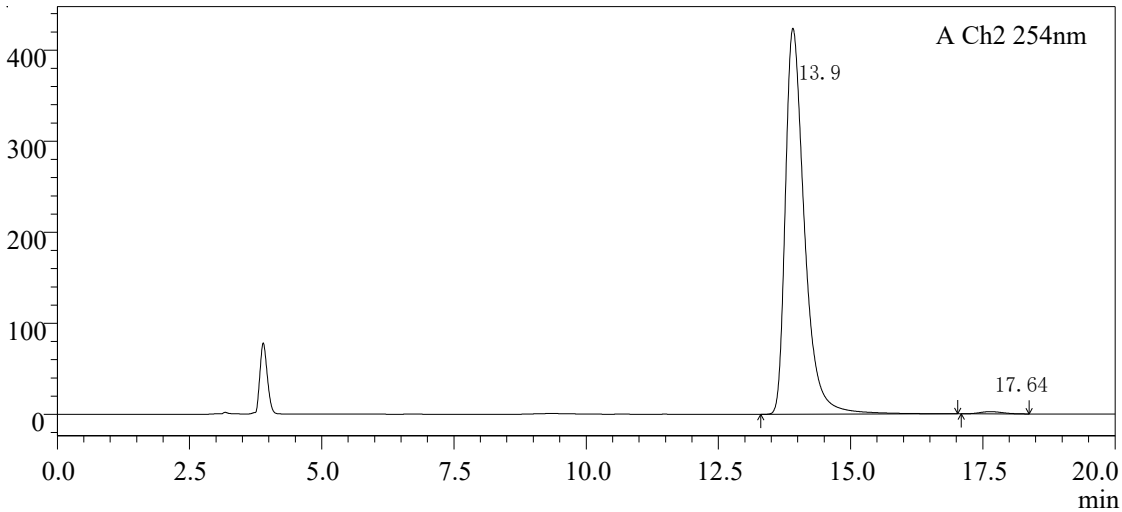
11.2 HPLC chromatogram of the recyclability of the catalytic system

racemate



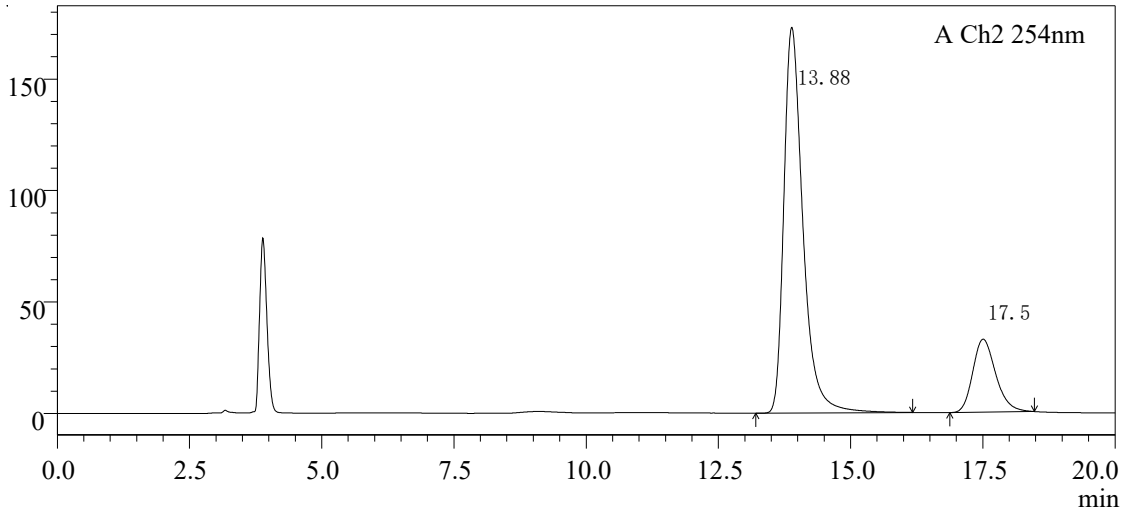
ID#	Ret. Time	Area	Height	Area %	Resolution
1	14.238	2800481	106246	50.367	--
2	17.959	2759621	85968	49.633	5.010

First cycle



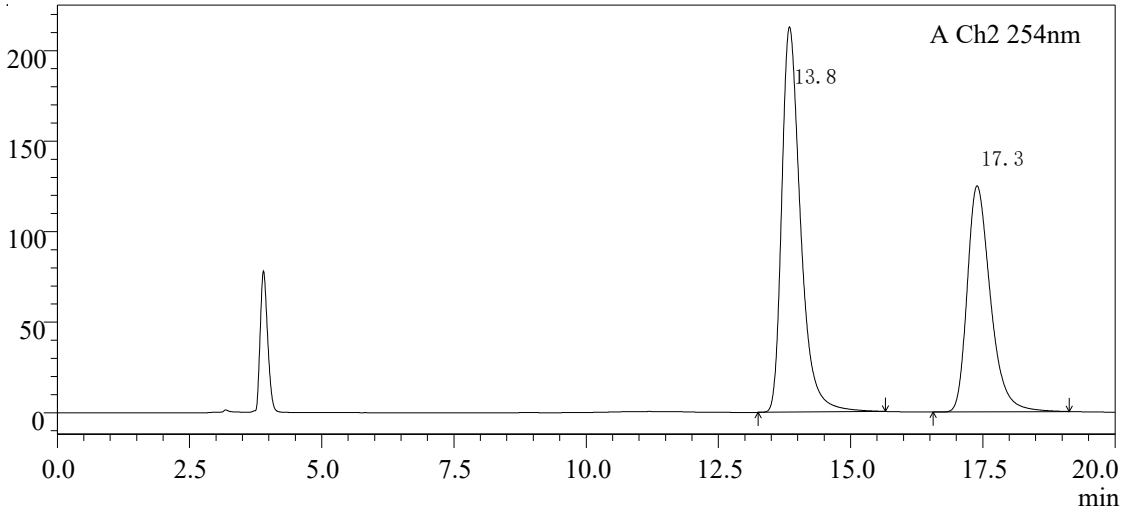
ID#	Ret. Time	Area	Height	Area %	Resolution
1	13.909	10672976	423955	99.300	--
2	17.646	75200	2527	0.700	5.240

Second cycle



ID#	Ret. Time	Area	Height	Area %	Resolution
1	13.887	4352306	173029	81.433	--
2	17.505	992315	32783	18.567	5.085

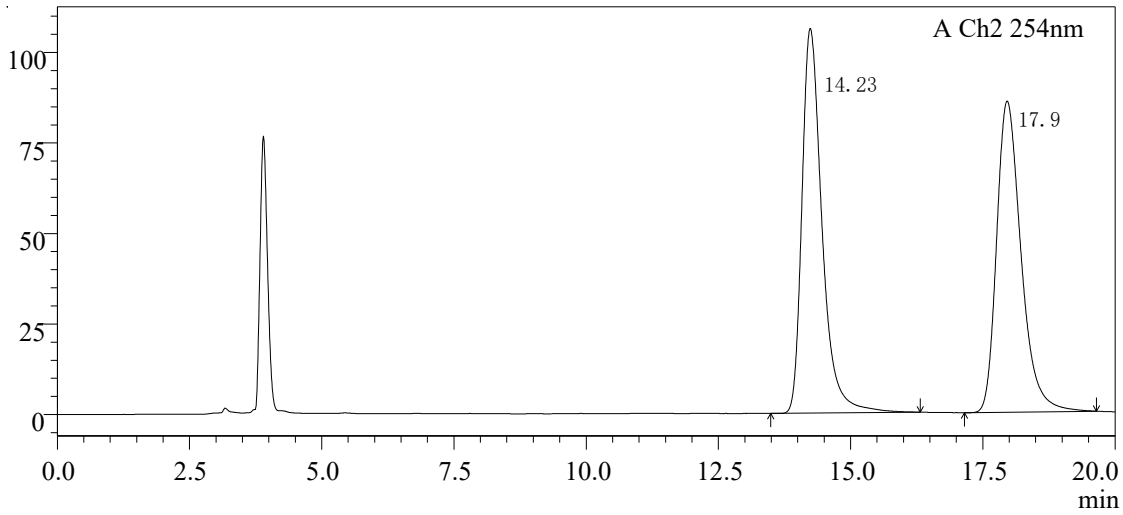
Third cycle



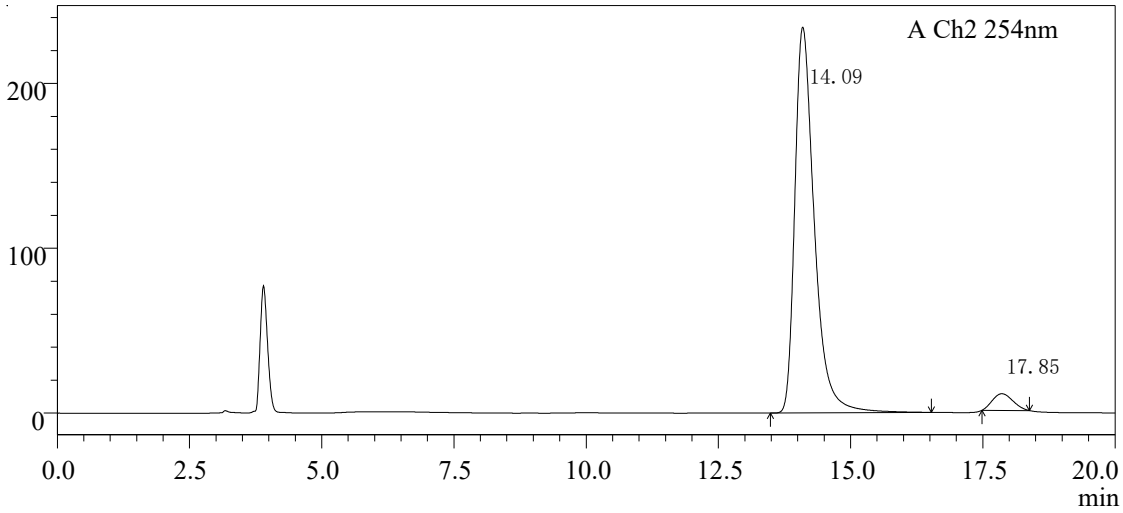
ID#	Ret. Time	Area	Height	Area %	Resolution
1	13.844	5279032	212910	58.058	--
2	17.392	3813669	124911	41.942	5.028

11.3 HPLC chromatogram of gram-scale experiment

racemate



ID#	Ret. Time	Area	Height	Area %	Resolution
1	14.238	2800481	106246	50.367	--
2	17.959	2759621	85968	49.633	5.010



ID#	Ret. Time	Area	Height	Area %	Resolution
1	14.096	6012567	234063	95.657	--
2	17.859	272968	10143	4.343	5.413