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Supporting Information

Photo-organocatalytic enantioselective α-hydroxylation of β-keto esters and β-keto amides with oxygen under phase transfer catalysis

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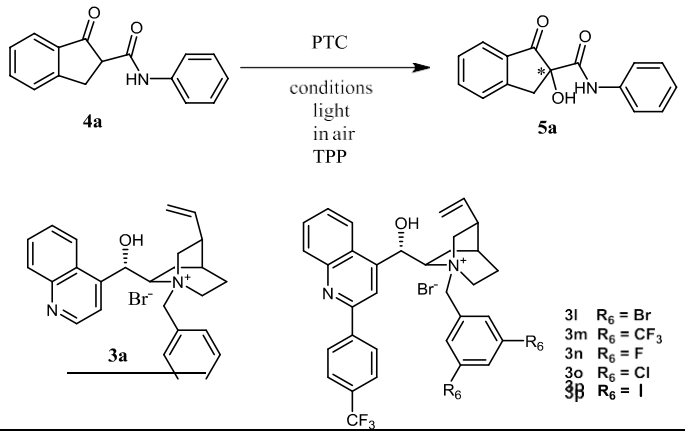
General

Unless otherwise stated, all commercial reagents and solvents were used without further additional purification. Analytical TLC was visualized with UV light at 254 nm. Thin layer chromatography was carried out on TLC aluminum sheets with silica gel 60 F_{254}. Purification of reaction products was carried out with chromatography on silica gel 60 (200-400 mesh). Melting points were determined with a hot plate apparatus. Optical rotations were measured on a digital polarimeter with a sodium lamp at room temperature. ^{1}H NMR (400 MHz) or (500 MHz) spectra was obtained at 25 °C; ^{13}C NMR (126 MHz) were recorded on a VARIAN INOVA-400M and AVANCE II 400 spectrometer at 25 °C. Chemical shifts are reported as δ (ppm) values relative to TMS as internal standard and coupling constants (J) in Hz. The enantiomeric excesses (*ee*) were determined by HPLC. HPLC analyses were performed on equipped with Diacel Chiralpak AD-H, OD-H and AS-H chiral column (0.46 cm × 25 cm), using mixtures of n-hexane/isopropyl alcohol as mobile phase, at 25 °C. Mass spectra are reported by using electron ionization and electrospray ionization techniques. Melting points were determined with a hot plate apparatus. Optical rotations were measured on a digital polarimeter with a sodium lamp at 20 ^{o}C or 25 ^{o}C .

Optimization of reaction conditions of the α-hydroxylation of β-keto amides

Table 1. Optimization of the reaction conditions for α-hydroxylation of β-keto amide **4a**



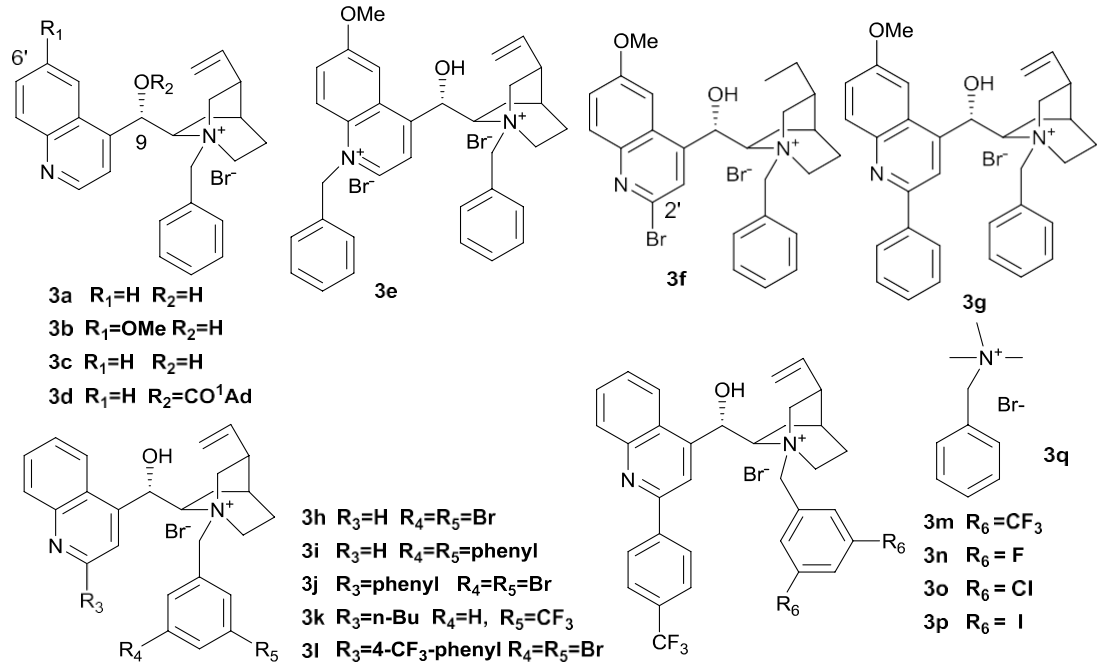
Entry	Solvent	**PTC** (2.5 mol%)	base	T [°C]	Reaction time	Con [%][b]	ee [%][c]
1	PhMe/$CHCl_3$ =8:2	**3a**	50%K_2HPO_4	15	120 min	75	20
2	**PhMe/$CHCl_3$ =8:2**	**3l**	**50%K_2HPO_4**	**15**	**30 min**	**>99**	**39**
3	PhMe/$CHCl_3$ =8:2	**3m**	50%K_2HPO_4	15	30 min	>99	35
4	PhMe/$CHCl_3$ =8:2	**3n**	50%K_2HPO_4	15	40 min	>99	27
5	PhMe/$CHCl_3$ =8:2	**3o**	50%K_2HPO_4	15	30 min	>99	39
6	PhMe/$CHCl_3$ =8:2	**3p**	50%K_2HPO_4	15	30 min	>99	35
7	PhMe	**3l**	50%K_2HPO_4	15	45 min	>99	39
8	$CHCl_3$	**3l**	50%K_2HPO_4	15	60 min	>99	17
9	PhMe/$CHCl_3$ =8:2	**3l**	20%K_2HPO_4	15	120 min	95	38
10	PhMe/$CHCl_3$ =8:2	**3l**	30%K_2CO_3	15	30 min	95	31
11	PhMe/$CHCl_3$ =8:2	**3l**	50%K_2HPO_4	-5	180 min	>99	19

[a] The reaction was conducted with substrate (0.1 mmol) in the presence of **PTC** (2.5 mol%) and TPP (0.5 mol%) in a mixture containing solvent (10 mL) and K_2HPO_4 (4 mL, 50% aq.) at room temprature, with exposure to a 3-W LED yellow lamp for the given reaction period. [b] Yield of isolated product. [c] The enantiomeric excess was determined by HPLC analysis of the product using a chiral column (DAICEL Chiralcel OD-H) with n-hexane/2-propanol = 8:2 as the eluent.

We tried to further optimize reaction conditions of the α-hydroxylation of β-keto amides. Table 1 summarizes the effect of several parameters on this reaction. We screened the

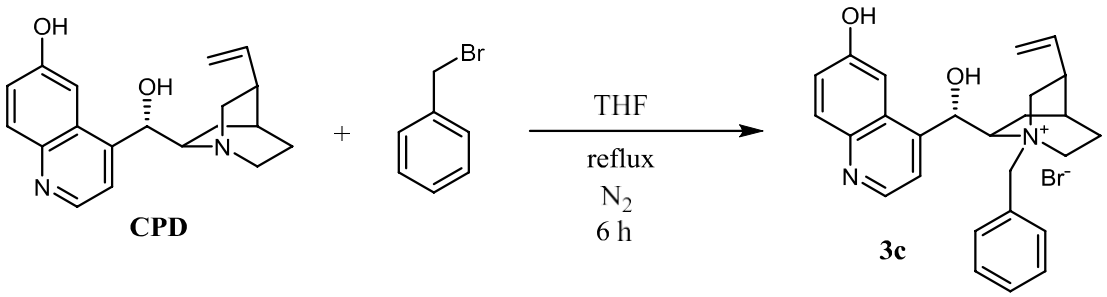
PTC 3a, **3l-3p**. **PTC 3l** was found to be the best catalyst compared with others. In the solvent screening, toluene was found to give a moderate ee value, but the stereoselectivity in chloroform was poor. We also tested other bases such as 20%K_2HPO_4 or 30% K_2CO_3. But the ee value was not further improved. Finally, reduction of temperature to -5 ^oC also led to poor results. We hold the opinion that with the H atom in N-position was sensitive to this method. In the main text, when we use **4d** instead of **4a**, the enantioselectivity of **5d** was further improved to 66%, although the reaction time was extended to 4h. After all, we need to develop new **PTC** to further improve the enantioselectivity of β-keto amides

General Procedure for the Synthesis of Catalysts



PTC **3a, 3b, 3d** was prepared according to our previous paper (*Eur. J. Org. Chem.* **2010**, *34*, 6525–6530; *J. Org.Chem.* **2012**, 77, 9601–9608.) PTC **3q** was purchased from Aladdin.

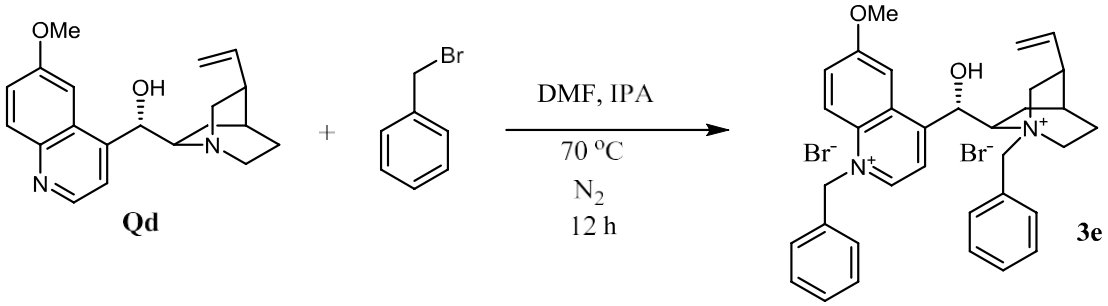
Preparation of PTC 3c



CPD was prepared according to our previous paper (*Synlett*. **2014**, *25*, 2155–2160). To a flame-dried flask equipped with a magnetic stirring bar and a reflux condenser was added **CPD** (0.93 g, 3 mmol), THF (50 mL), and benzyl bromide (0.67g, 3.9 mmol). The mixture was heated to reflux under N_2 for 6 hours until judged to be complete by TLC-analysis (CH_2Cl_2/MeOH 9:1) and then cooled to room temperature and poured onto Et_2O (150 mL) with stirring. The resulting suspension was stirred for 1 h and the precipitated solids were isolated by filtration, which was recrystallized from MeOH/Et_2O to afford the product as offwhite crystal (1.08 g, 75% yield). m. p. 264-267 °C, $[\alpha]_D^{25}$ +214.0 (*c* 0.1, MeOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.11 (s, 1H), 8.74 (d, *J* = 4.4 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.83 – 7.73 (m, 2H), 7.68 (d, *J* = 4.4 Hz, 1H), 7.64 – 7.54 (m, 4H), 7.37 (dd, *J*

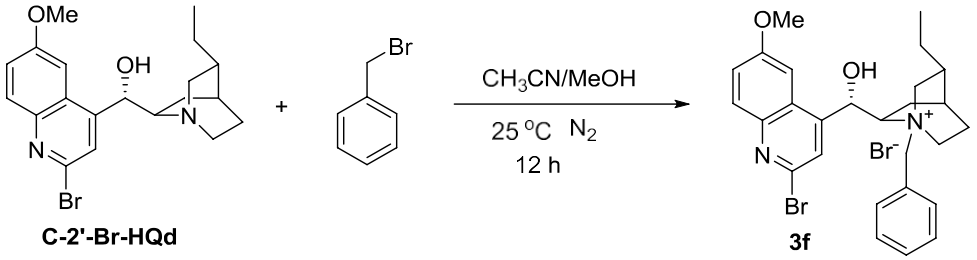
= 9.1, 2.4 Hz, 1H), 6.72 (d, *J* = 3.8 Hz, 1H), 6.34 (t, *J* = 3.0 Hz, 1H), 6.01 (m, 1H), 5.32 – 5.15 (m, 2H), 5.12 – 4.94 (m, 2H), 4.19 (ddd, *J* = 11.9, 8.3, 2.7 Hz, 1H), 4.04 – 3.86 (m, 2H), 3.56 – 3.43 (m, 1H), 3.04 – 2.89 (m, 1H), 2.65 (d, *J* = 9.0 Hz, 1H), 2.33 (t, *J* = 11.6 Hz, 1H), 1.98 – 1.68 (m, 3H), 1.24 – 1.01 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 155.91, 146.65, 142.89, 142.68, 137.12, 133.80, 131.37, 130.13, 128.92, 127.74, 125.56, 121.71, 119.80, 116.98, 104.55, 67.07, 64.65, 62.28, 56.05, 53.65, 36.60, 26.30, 23.01, 20.53. HRMS calcd. for $[C_{26}H_{29}N_2O_2Br\text{-}Br]^+$ requires m/z 401.2229, found m/z 401.2206.

Preparation of PTC 3e



Catalyst **Q-2** was prepared partly according to Yasuda's method (*Angew. Chem. Int. Ed.* **2014**, *53*, 8375 –8378). A slurry of quinidine (0.81 g, 2.5 mmol) and benzyl bromide (1.07 g, 6.25 mmol) in IPA (0.5 mL) and DMF (3 mL) was degassed, heated to 70 °C under nitrogen atmosphere and held for 12 h. The reaction mixture was cooled to 15 °C and EtOAc (50 mL) was added over 10 min with vigorous stirring. The resulting slurry was aged at 15 °C for 1 to 2 h, filtered, rinsed with EtOAc (twice, 20 mL each) and hexanes (twice, 20 mL each). The solid was dried under vacuum to give 1.35 g of **3e** as a yellow solid in 81% yield. m. p. 127-129 °C, $[\alpha]_D^{25}$ +143.0 (*c* 0.1, MeOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.67 (d, *J* = 5.7 Hz, 1H), 8.63 – 8.46 (m, 2H), 7.92 (dd, *J* = 9.8, 2.5 Hz, 1H), 7.86 – 7.71 (m, 3H), 7.58 (q, *J* = 2.6 Hz, 3H), 7.43 – 7.35 (m, 5H), 6.87 (s, 1H), 6.52 – 6.33 (m, 2H), 6.16 – 5.93 (m, 1H), 5.32 – 5.21 (m, 2H), 5.13 (d, *J* = 10.4 Hz, 1H), 4.83 (dt, *J* = 12.7, 4.0 Hz, 1H), 4.19 (t, *J* = 1.7 Hz, 4H), 4.02 (q, *J* = 5.0, 2.9 Hz, 3H), 3.52 (m, 2H), 3.01 – 2.86 (m, 1H), 2.70 (q, *J* = 8.6 Hz, 1H), 2.43 – 2.30 (m, 1H), 1.96 – 1.88 (m, 1H), 1.86 – 1.74 (m, 2H), 1.25 (s, 1H). ^{13}C NMR (126 MHz, DMSO) δ 159.32, 155.76, 146.31, 137.10, 133.95, 133.69, 132.81, 130.17, 129.09, 128.99, 128.70, 128.27, 127.64, 127.13, 126.99, 121.92, 121.78, 117.08, 105.19, 79.34, 66.85, 65.15, 63.34, 60.00, 56.62, 56.15, 53.77, 36.68, 26.28, 22.97, 20.58. HRMS calcd. for $[(C_{34}H_{38}N_2O_2Br_2\text{-}2Br)/2]^+$ requires m/z 253.1466, found m/z 253.1449.

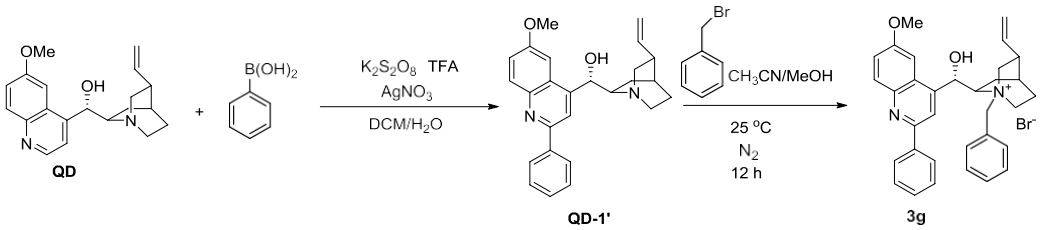
Preparation of PTC 3f



To a flame-dried flask equipped with a magnetic stirring bar and a reflux condenser was added **C-2'-Br-HQd** (0.2 g) (**C-2'-Br-HQd** was prepared according to our previous paper (*Adv. Synth. Catal.* **2016**, *358*, 737 – 745)), CH_3CN (3 mL),MeOH (0.75 mL) and benzyl bromide (0.21 g). The mixture was heated to reflux under N_2 for 12 hours and then cooled to

room temperature. The residue was subjected to silica gel column chromatography (40% EtOAc, 15% MeOH, 2% Et_3N in PE) to afford **3f** as a white solid (0.23 g, 80% yield). m. p. 132-135 °C, $[\alpha]_D^{25}$ +132.0 (*c* 0.1, MeOH). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.80 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.40 (s, 1H), 7.34 – 7.26 (m, 3H), 7.23 – 7.14 (m, 1H), 6.78 (d, *J* = 5.9 Hz, 1H), 6.44 (t, *J* = 3.6 Hz, 1H), 5.69 (d, *J* = 12.0 Hz, 1H), 5.34 (d, *J* = 12.0 Hz, 1H), 4.30 – 4.15 (m, 2H), 4.03 (d, *J* = 9.3 Hz, 1H), 3.90 (s, 3H), 3.38 (s, 1H), 2.87 (d, *J* = 10.5 Hz, 1H), 2.28 (s, 1H), 1.93 – 1.76 (m, 2H), 1.71 – 1.44 (m, 5H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 157.86, 147.48, 143.92, 138.21, 133.58, 130.31, 130.11, 129.00, 127.77, 124.65, 124.20, 122.59, 103.15, 67.33, 64.58, 63.23, 56.09, 55.74, 55.66, 45.59, 34.68, 20.16, 11.31, 8.51. HRMS calcd. for $[C_{27}H_{32}N_2O_2Br_2\text{-}Br]^+$ requires m/z 495.1642, found m/z 495.1623.

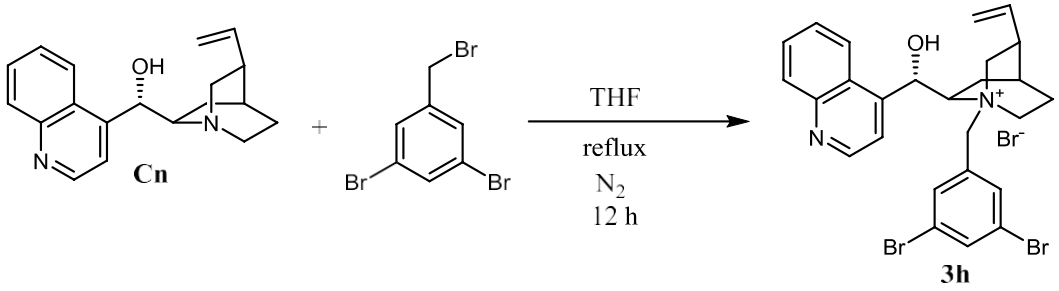
Preparation of PTC 3g



Qd-1'was prepared according to Baran's method(*J. Am. Chem. Soc.* **2010**, *132*, 13194–13196).To a solution of quinidine (3.24 g, 10 mmol), phenylboronic acid (2.44 g, 20 mmol, 2.0 equiv), potassium persulfate (5.44 g, 20 mmol, 2.0 equiv) in dichloromethane (50 mL) and water (30 mL) was added trifluoroacetic acid (2.24 mL, 3.0 equiv) followed by silver (I) nitrate (340 mg, 2 mmol, 0.2 equiv) in water (5 mL) and the solution was stirred vigorously at room temperature and monitored by thin-layer chromatography (40% EtOAc, 5% MeOH, 2% Et_3N inPE). After 4 h, phenylboronic acid (1.22 g, 10 mmol, 1.0 equiv) was added, and the reaction was stirred for 9 h, diluted with dichloromethane (30 mL) and washed with 2 M NaOH (30 mL). The layers were separated, and the aqueous layer was extracted with 90%CH_2Cl_2, 10% isopropyl alcohol (6 x 40 mL), the combined organic layers were concentrated under reduced pressure. The residue was applied to silica gel (40% EtOAc, 5% MeOH, 2% Et_3N in PE); to afford **QD-1'** as a light yellow solid (1.68 g, 42% yield).

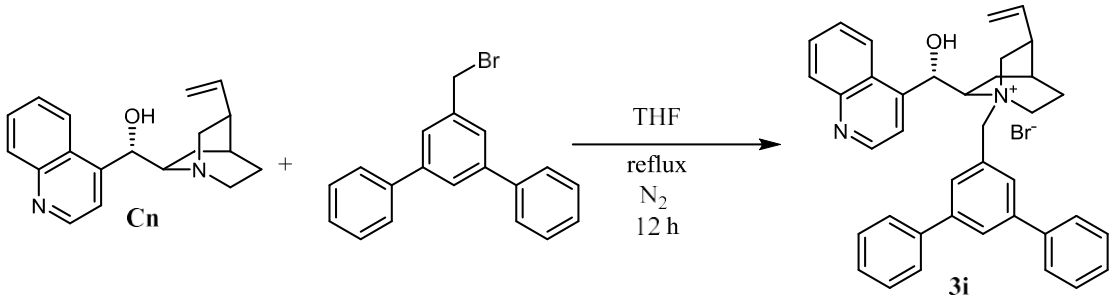
PTC 3g was synthesized by the same procedure as mentioned above for catalyst **3f** from **QD-1'** as a white solid (0.35 g, 95% yield). m. p. 143-145 °C, $[\alpha]_D^{25}$ +153.0 (*c* 0.1, MeOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.31 – 8.22 (m, 3H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.73 (dd, *J* = 6.3, 3.1 Hz, 2H), 7.66 – 7.46 (m, 8H), 6.97 (d, *J* = 3.8 Hz, 1H), 6.67 – 6.52 (m, 1H), 6.23 – 6.03 (m, 1H), 5.31 – 5.19 (m, 2H), 5.08 (d, *J* = 12.9 Hz, 1H), 4.80 (d, *J* = 12.5 Hz, 1H), 4.24 (d, *J* = 3.4 Hz, 1H), 4.09 (s, 3H), 3.96 (d, *J* = 37.0 Hz, 2H), 3.52 (s, 1H), 3.07 (d, *J* = 7.4 Hz, 3H), 2.92 (d, *J* = 10.5 Hz, 1H), 2.67 (d, *J* = 8.8 Hz, 1H), 1.91 (d, *J* = 5.1 Hz, 1H), 1.83 – 1.71 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 157.93, 153.61, 145.11, 144.25, 139.24, 137.80, 134.15, 132.04, 130.62, 129.78, 129.49, 129.37, 128.31, 127.41, 125.16, 122.33, 117.83, 117.48, 102.97, 79.75, 68.14, 65.72, 63.68, 56.44, 56.13, 54.24, 49.05, 46.09, 37.37, 26.84, 23.62, 21.07, 9.09. HRMS calcd. for $[C_{33}H_{35}N_2O_2Br\text{-}Br]^+$ requires m/z 491.2699, found m/z 491.2675.

Preparation of PTC 3h



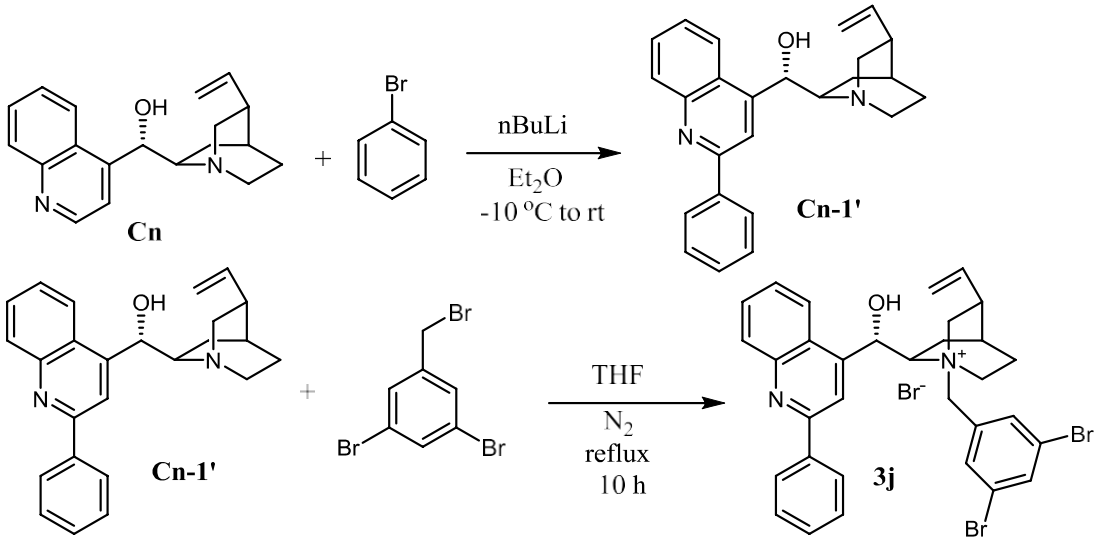
PTC 3h was synthesized by the same procedure as mentioned above for catalyst **3c** from cinchonine as a white solid (0.35 g, 95% yield). m. p. 286-289 °C, $[\alpha]_D^{25}$ +139.0 (*c* 0.1, MeOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.99 (d, *J* = 4.5 Hz, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 8.14 – 8.08 (m, 3H), 7.92 – 7.70 (m, 3H), 6.72 (d, *J* = 3.6 Hz, 1H), 6.45 (t, *J* = 3.0 Hz, 1H), 6.00 (ddd, *J* = 17.3, 10.1, 6.8 Hz, 1H), 5.39 – 5.18 (m, 2H), 5.08 (d, *J* = 12.5 Hz, 1H), 4.85 (d, *J* = 12.7 Hz, 1H), 4.24 (ddd, *J* = 11.9, 8.4, 2.7 Hz, 1H), 3.84 (dd, *J* = 24.9, 15.5 Hz, 2H), 3.59 – 3.22 (m, 3H), 3.09 – 2.95 (m, 1H), 2.76 – 2.60 (m, 1H), 2.29 (m, 1H), 1.96 – 1.67 (m, 3H), 1.07 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 150.04, 137.11, 135.43, 135.08, 132.36, 129.69, 129.49, 127.21, 124.31, 123.62, 122.81, 120.03, 117.00, 67.67, 64.72, 60.60, 56.00, 54.31, 36.67, 26.26, 22.98, 20.50. HRMS calcd. for $[C_{26}H_{27}N_2OBr_3\text{-}Br]^+$ requires m/z 541.0485, found m/z 541.0478.

Preparation of PTC 3i



PTC 3i was synthesized by the same procedure as mentioned above for catalyst **3h** from cinchonine as a white solid (0.41 g, 81% yield). m. p. 257-259 °C, $[\alpha]_D^{25}$ +157.0 (*c* 0.1, MeOH). ^{1}H NMR (500 MHz, Methanol-d_4) δ 8.97 (d, *J* = 4.6 Hz, 1H), 8.38 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.06 (d, *J* = 1.7 Hz, 1H), 8.03 – 7.97 (m, 3H), 7.88 – 7.78 (m, 6H), 7.53 (t, *J* = 7.7 Hz, 4H), 7.48 – 7.41 (m, 2H), 6.70 (s, 1H), 6.10 (m, 1H), 5.36 – 5.26 (m, 3H), 5.18 (m, 1H), 4.53 (m, 1H), 4.09 (m, 2H), 3.78 (m, 1H), 3.31 – 3.22 (m, 1H), 2.70 (m, 1H), 2.59 – 2.49 (m, 1H), 2.04 – 1.80 (m, 4H), 1.11 (m, 1H). ^{13}C NMR (126 MHz, MeOD) δ 151.05, 148.76, 147.33, 144.27, 141.17, 137.69, 132.25, 131.17, 130.29, 130.17, 130.07, 129.23, 129.20, 128.77, 128.38, 126.16, 124.46, 121.24, 117.97, 69.25, 66.99, 64.65, 58.30, 56.36, 38.97, 28.52, 24.82, 22.35. HRMS calcd. for $[C_{38}H_{37}N_2OBr\text{-}Br]^+$ requires m/z 537.2906, found m/z 537.2878.

Preparation of PTC 3j

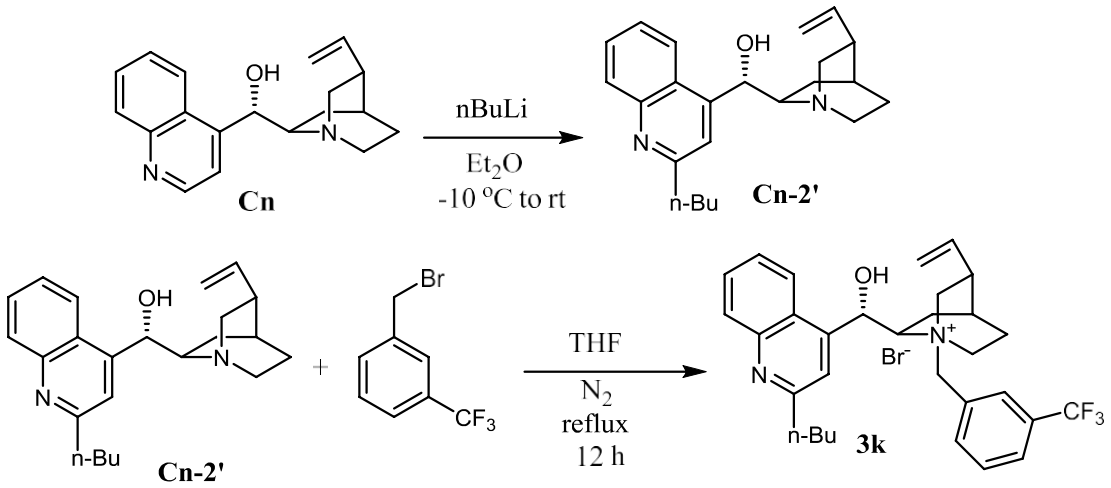


Cn-1' was synthesized partly according to Englert's method *(Angew. Chem* . **2007**, *119*, 5256 –5259).To a dried flask equipped with a magnetic stirring bar, *n*BuLi (10.4 mL , 25.5 mmol, 2.4 M) was added to a 10 mL diethyl ether solution of bromobenzene (4g, 25.5 mmol). The reaction cooled to -10 ℃ (ice/EtOH bath) under an nitrogen atmosphere for 2 hours. After the organo-lithium compound was prepared, it was added at once to the vigorously stirred dried diethyl ether solution of cinchonine (3g, 10.2 mmol) and stirred at -10 ℃ for 1h. Then the mixture was warmed to ambient temperature and stirred over 2 h. The reaction is quenched by dropwise addition of AcOH (5 mL) with strong stirring and cooling, followed by addition of water (50 mL) and EtOAc (50 mL). Solid iodine (2.5 g) was added in several portions and the mixture shaken vigorously after each addition until all the solids had dissolved. Then a solution of sodium metabisulfite ($Na_2S_2O_5$: 1 g) in water (20 mL) is added to quench excess iodine. The mixture was made basic with the addition of aqueous ammonia (concentrated, 20%) and shaken thoroughly. The organic phase is washed with NaCl aq. and the aqueous phase was extracted with CH_2Cl_2 (40 mL). The collected organic phases are dried (Na_2SO_4), followed by filtration and evaporation. The crude product was purified by column chromatography on silica gel (15% MeOH, 2% Et_3N, 40% EtOAc in PE) to give the crude product, and then recrystallized from EtOAc to give the pure **Cn-1'**(0.80 g, 22% yield) as white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.24 – 8.13 (m, 3H), 8.08 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.68 (dd, *J* = 8.3, 6.8 Hz, 1H), 7.52 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.44 (dt, *J* = 15.7, 7.4 Hz, 2H), 6.03 (m, 1H), 5.78 (s, 1H), 5.13 – 4.98 (m, 2H), 3.34 (s, 1H), 3.13 (d, *J* = 4.3 Hz, 1H), 2.94 (dd, *J* = 13.3, 9.9 Hz, 2H), 2.83 – 2.73 (m, 1H), 2.33 – 2.18 (m, 1H), 2.06 (m, 1H), 1.77 (s, 1H), 1.63 – 1.47 (m, 2H), 1.22 (m, 1H).

To a flame-dried flask equipped with a magnetic stirring bar and a reflux condenser was added **Cn-1'** (0.37 g, 1 mmol), THF (20 mL), and 1,3-dibromo-benzyl bromide (0.43g, 1.3 mmol). The mixture was heated to reflux under N_2 for 10 hours until judged to be complete by TLC-analysis (CH_2Cl_2/MeOH=15:1) and then cooled to room temperature and poured onto Et_2O (50 mL) with stirring. The resulting suspension was stirred for 1 h and the precipitated solids were isolated by filtration, which was recrystallized from MeOH/Et_2O to afford the product **3j** as white solid (0.56 g, 81% yield). m. p. 258-261 ℃, $[\alpha]_D^{25}$ +127.0 (*c* 0.1, MeOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.40 – 8.24 (m, 4H), 8.18 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.14 – 8.07 (m, 3H), 7.88 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.74 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.65 – 7.53 (m, 3H), 6.83 (d, *J* = 13.3 Hz, 1H), 6.51 (s, 1H), 6.17 – 6.04 (m, 1H), 5.34 – 5.21 (m, 2H), 5.12 (d, *J* = 12.5 Hz, 1H), 4.93 (d, *J* = 12.4 Hz, 1H), 4.35 – 4.14 (m, 1H), 4.00 – 3.78 (m, 2H), 3.54 (t, *J* = 11.4 Hz, 1H), 3.15 – 2.99 (m, 1H), 2.67 (d, *J* = 8.9 Hz, 1H), 2.40 (t, *J* = 11.7 Hz, 1H), 1.87 (s, 1H), 1.82 – 1.72 (m, 2H), 1.20 – 1.12 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 155.66, 147.71, 146.04, 138.61, 137.24, 135.46, 135.08, 132.39, 130.04, 129.89, 129.77, 128.97, 127.23, 127.05, 123.48, 122.81, 117.09, 117.04, 67.86, 65.09, 60.62, 56.00, 54.36,

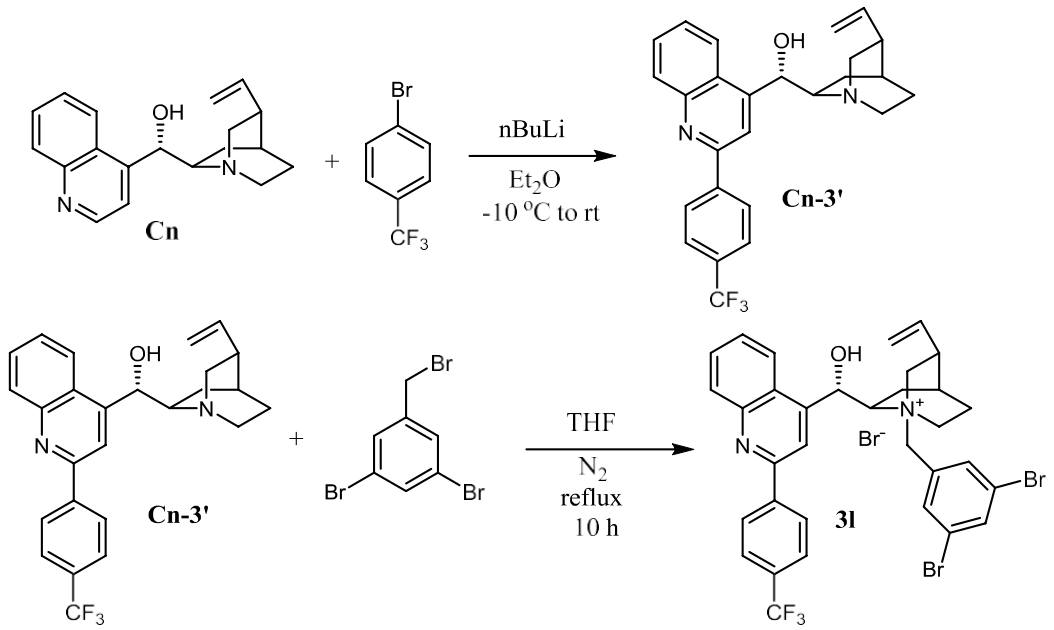
36.97, 26.32, 23.06, 20.44. HRMS Calcd. for $[C_{32}H_{31}N_2OBr_3\text{-}Br]^+$ requires m/z 617.0803, found m/z 617.0780.

Preparation of PTC 3k



Cn-2' was synthesized by the same procedure as mentioned above for **Cn-1'** from cinchonine and *n*BuLi (2.5 equiv) as a white solid (53% yield). **PTC 3k** was synthesized by the same procedure as mentioned above for **PTC 3j** from **Cn-2'** and 3-trifluoromethyl- benzyl bromide (1.5 equiv) as a white solid (87% yield). m. p. 192-194 °C, $[\alpha]_D^{25}$ +103.0 (*c* 0.1, MeOH).^{1}H NMR (500 MHz, DMSO-d_6) δ 8.31 – 8.25 (m, 1H), 8.21 (s, 1H), 8.03 (ddd, *J* = 32.8, 29.7, 7.8 Hz, 3H), 7.88 – 7.77 (m, 2H), 7.74 – 7.64 (m, 2H), 6.74 (d, *J* = 3.7 Hz, 1H), 6.48 (t, *J* = 3.0 Hz, 1H), 6.03 (ddd, *J* = 17.3, 10.5, 7.0 Hz, 1H), 5.34 – 5.14 (m, 3H), 5.08 – 4.98 (m, 1H), 4.25 (s, 1H), 4.04 – 3.79 (m, 2H), 3.49 (t, *J* = 11.4 Hz, 1H), 2.98 (tt, *J* = 7.6, 4.0 Hz, 3H), 2.65 (d, *J* = 9.1 Hz, 1H), 2.42 – 2.29 (m, 1H), 1.88 (s, 1H), 1.77 (q, *J* = 7.4 Hz, 4H), 1.39 (q, *J* = 7.4 Hz, 2H), 1.17 – 1.04 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 162.01, 147.44, 144.84, 137.96, 137.14, 130.27, 130.08, 129.32, 129.21, 126.87, 126.25, 123.41, 122.92, 120.05, 117.02, 67.60, 64.66, 61.36, 55.84, 54.01, 37.99, 36.72, 31.26, 26.36, 22.96, 21.89, 20.44, 13.81. HRMS Calcd. for $[C_{31}H_{36}F_3N_2OBr\text{-}Br]^+$ requires m/z 509.2780, found m/z 509.2754.

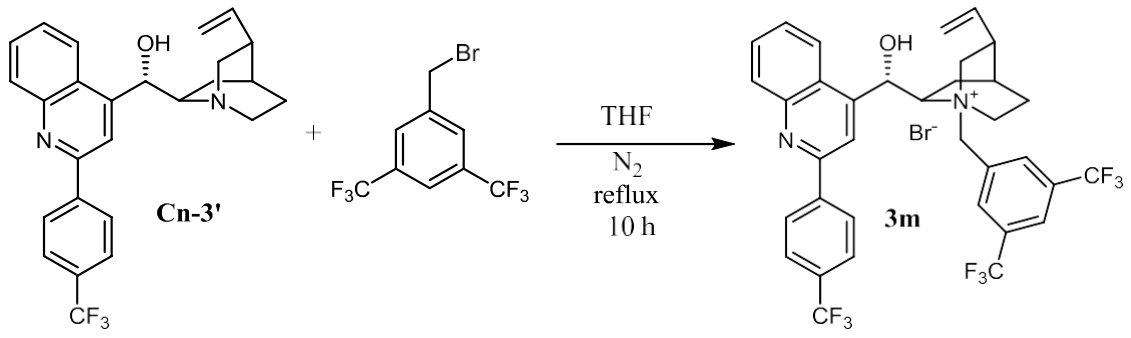
Preparation of PTC 3l



Cn-3' was synthesized by the same procedure as mentioned above for **Cn-1'** from cinchonine , 4-bromobenzotrifluoride and *n*BuLi (2.5 equiv) as a light orange solid (42% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 8.1 Hz, 2H), 8.19 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.10 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.74 – 7.68 (m, 1H), 7.53 – 7.44 (m, 1H), 6.00 (m, 1H), 5.82 (d, *J* = 4.4 Hz, 1H), 5.13 – 4.96 (m, 2H), 3.34 (d, *J* = 13.0 Hz, 1H), 3.17 (td, *J* = 9.2, 4.4 Hz, 1H), 2.96 (dd, *J* = 13.7, 9.7 Hz, 2H), 2.86 – 2.72 (m, 1H), 2.27 (m, 1H), 2.12 – 2.02 (m, 1H), 1.80 (s, 1H), 1.64 – 1.45 (m, 2H), 1.27 (m, 1H).

PTC 3l was synthesized by the same procedure as mentioned above for **PTC 3j** from **Cn-3'** and 3,5-dibromo-benzyl bromide (1.3 equiv) as a white solid (89% yield). m. p. 230-233 °C, $[\alpha]_D^{25}$ +113.0 (*c* 0.1, MeOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.52 (d, *J* = 8.1 Hz, 2H), 8.39 (d, *J* = 9.0 Hz, 2H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.12 (dd, *J* = 15.1, 1.8 Hz, 3H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.92 (t, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 3.8 Hz, 1H), 6.54 (t, *J* = 3.0 Hz, 1H), 6.21 – 6.05 (m, 1H), 5.34 – 5.22 (m, 2H), 5.14 (d, *J* = 12.3 Hz, 1H), 4.94 (d, *J* = 12.4 Hz, 1H), 4.24 (ddd, *J* = 11.9, 8.3, 2.7 Hz, 1H), 4.04 – 3.84 (m, 2H), 3.55 (t, *J* = 11.4 Hz, 1H), 3.16 – 3.01 (m, 1H), 2.76 – 2.65 (m, 1H), 2.42 (t, *J* = 11.7 Hz, 1H), 1.99 – 1.70 (m, 3H), 1.16 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 154.11, 147.64, 146.61, 142.38, 137.22, 135.48, 135.07, 132.41, 130.15, 129.85, 129.60, 128.05, 127.69, 125.87, 125.84, 125.81, 125.31, 123.84, 123.79, 123.15, 122.78, 67.79, 65.08, 60.46, 55.97, 54.31, 37.03, 26.34, 23.06, 20.47. HRMS calcd. for $[C_{33}H_{30}F_3N_2OBr_3\text{-}Br]^+$ requires m/z 685.0677, found m/z 685.0655.

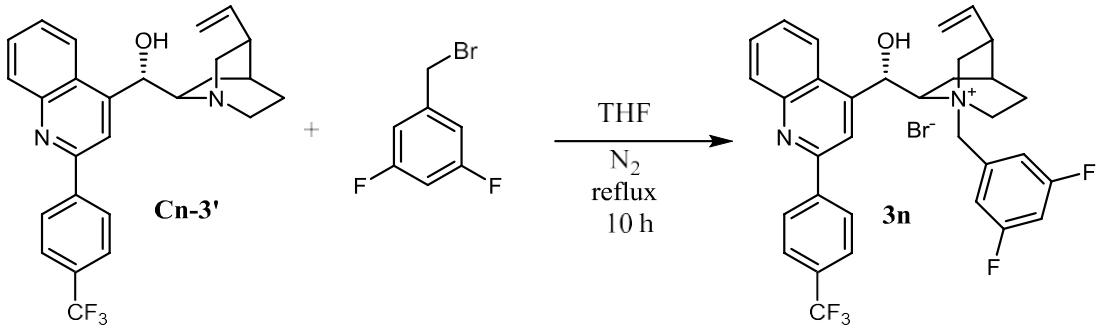
Preparation of PTC 3m



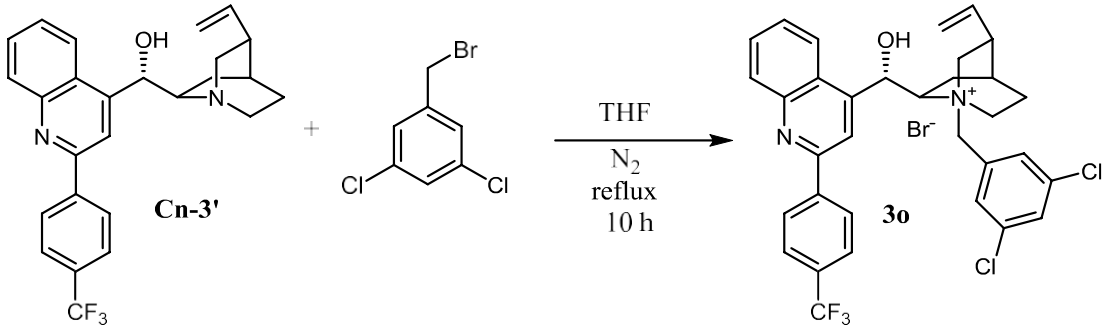
To a flame-dried flask equipped with a magnetic stirring bar and a reflux condenser was added **Cn-3'** (0.24 g, 0.55 mmol), THF (15 mL) and 3,5-di-CF_3-benzyl bromide (0.305g, 1.1 mmol). The mixture was heated to reflux under N_2 for 10 hours until judged to be complete

by TLC-analysis (10%MeOH, 2%Et_3N, 40%EtOAC in PE) and then cooled to room temperature. The crude product was purified by column chromatography on silica gel (15% MeOH, 2% Et_3N, 40% EtOAc in PE) to give the crude product, and then recrystallized from Et_2O to give the pure **PTC 3m** (0.31 g, 76% yield) as light yellow solid. m. p. 205-209 °C, $[\alpha]_D^{25}$ +93.0 (*c* 0.1, MeOH). ^{1}H NMR (500 MHz, Methanol-d_4) δ 8.59 – 8.38 (m, 6H), 8.32 – 8.20 (m, 2H), 7.97 – 7.79 (m, 4H), 6.69 (d, *J* = 2.6 Hz, 1H), 6.13 (m, 1H), 5.48 – 5.39 (m, 1H), 5.38 – 5.24 (m, 3H), 4.58 (ddd, *J* = 11.7, 8.4, 2.8 Hz, 1H), 4.12 (dt, *J* = 34.5, 10.1 Hz, 2H), 3.61 (t, *J* = 11.3 Hz, 1H), 3.23 – 3.11 (m, 1H), 2.78 – 2.53 (m, 2H), 2.07 – 1.84 (m, 3H), 1.21 (m, 1H). ^{13}C NMR (126 MHz, MeOD) δ 156.68, 149.52, 147.61, 144.10, 137.57, 135.57, 133.81, 133.54, 132.17, 131.39, 131.35, 129.32, 129.25, 126.89, 126.86, 126.83, 125.63, 125.57, 125.31, 124.41, 123.47, 118.65, 118.13, 69.90, 67.31, 62.79, 58.02, 56.43, 38.95, 28.47, 24.73, 22.33. HRMS calcd. for $[C_{35}H_{30}F_9N_2OBr\text{-}Br]^+$ requires m/z 665.2209, found m/z 665.2217.

Preparation of PTC 3n

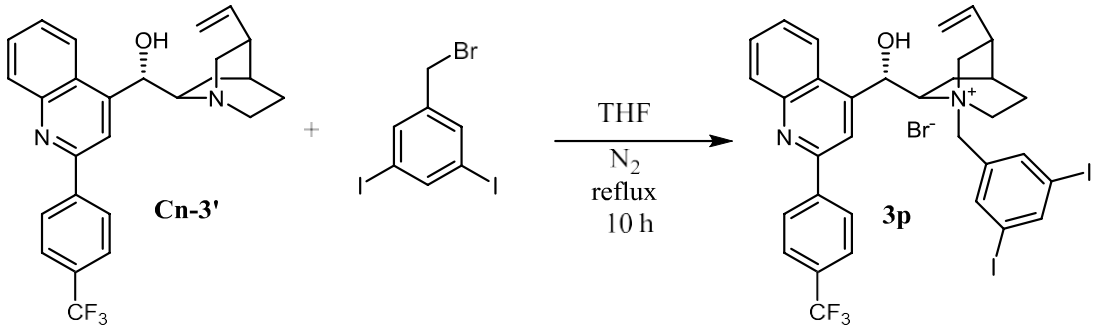


PTC 3n was synthesized by the same procedure as mentioned above for catalyst **3m** from **Cn-3'** and 3,5-di-F-benzyl bromide as a light yellow solid (0.55 g, 85% yield). m. p. 193-196 °C, $[\alpha]_D^{25}$ +101.0 (*c* 0.1, MeOH). ^{1}H NMR (500 MHz, Methanol-d_4) δ 8.49 – 8.42 (m, 3H), 8.38 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.23 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.97 – 7.76 (m, 4H), 7.59 – 7.45 (m, 2H), 7.35 – 7.18 (m, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 6.12 (ddd, *J* = 17.4, 10.5, 7.1 Hz, 1H), 5.39 – 5.28 (m, 2H), 5.20 (d, *J* = 12.4 Hz, 1H), 5.08 (d, *J* = 12.5 Hz, 1H), 4.49 (ddd, *J* = 11.8, 8.5, 2.8 Hz, 1H), 4.22 – 4.06 (m, 1H), 3.97 (td, *J* = 9.7, 4.8 Hz, 1H), 3.69 (ddd, *J* = 12.2, 10.4, 1.6 Hz, 1H), 3.22 – 3.05 (m, 2H), 2.69 (q, *J* = 8.8 Hz, 1H), 2.63 – 2.51 (m, 1H), 1.93 (m, 3H), 1.16 (m, 1H). ^{13}C NMR (126 MHz, MeOD) δ 165.66, 165.56, 163.68, 163.58, 156.73, 149.56, 147.68, 144.13, 137.59, 132.54, 131.41, 129.31, 129.20, 126.94, 126.91, , 125.34, 124.18, 118.65, 118.21, 118.06, 117.99, 107.15, 69.69, 67.29, 63.27, 58.34, 56.35, 38.98, 28.36, 24.74, 22.32. HRMS calcd. for $[C_{33}H_{30}F_5N_2OBr\text{-}Br]^+$ requires m/z 565.2273, found m/z 565.2243.



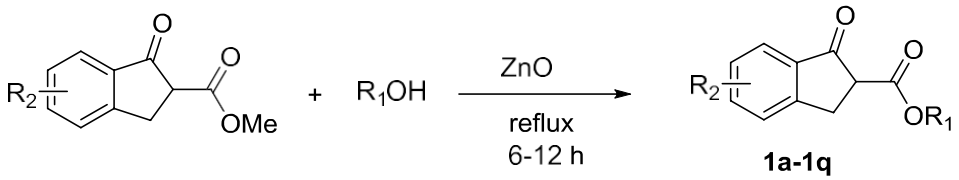
PTC 3o was synthesized by the same procedure as mentioned above for catalyst **3m** from **Cn-3'** and 3,5-di-Cl-benzyl bromide as a white solid (0.46 g, 68% yield). m. p. 251-253 °C, $[\alpha]_D^{25}$ +106.0 (*c* 0.1, MeOH). ^{1}H NMR (500 MHz, Methanol-d_4) δ 8.49 – 8.41 (m, 3H), 8.37

(dd, *J* = 8.4, 1.3 Hz, 1H), 8.25 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.95 – 7.80 (m, 6H), 7.74 (d, *J* = 1.9 Hz, 1H), 6.65 (d, *J* = 2.5 Hz, 1H), 6.13 (ddd, *J* = 17.4, 10.4, 7.1 Hz, 1H), 5.41 – 5.26 (m, 2H), 5.18 (d, *J* = 12.5 Hz, 1H), 5.05 (d, *J* = 12.5 Hz, 1H), 4.49 (ddd, *J* = 11.8, 8.5, 2.8 Hz, 1H), 4.09 (t, *J* = 9.7 Hz, 1H), 4.03 – 3.91 (m, 1H), 3.76 – 3.58 (m, 2H), 3.19 (dt, *J* = 11.9, 9.2 Hz, 1H), 2.70 (q, *J* = 8.8 Hz, 1H), 2.65 – 2.51 (m, 1H), 2.05 – 1.85 (m, 3H), 1.39 – 1.12 (m, 2H). ^{13}C NMR (126 MHz, MeOD) δ 156.75, 149.57, 147.66, 144.12, 137.59, 137.02, 133.40, 132.60, 132.51, 132.34, 131.77, 131.43, 129.31, 129.22, 126.91, 126.88, 125.34, 124.62, 124.18, 118.64, 118.09, 69.71, 67.30, 63.10, 58.25, 56.41, 38.99, 28.41, 24.74, 22.31. HRMS calcd. for $[C_{33}H_{30}Cl_2F_3N_2OBr\text{-}Br]^+$ requires m/z 597.1682, found m/z 597.1663.



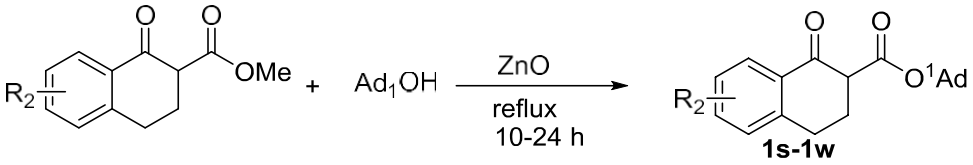
PTC 3p was synthesized by the same procedure as mentioned above for catalyst **3m** from **Cn-3'** and 3,5-di-Cl-benzyl bromide as a light yellow solid (0.43 g, 82% yield). m. p. 247-249 °C, $[\alpha]_D^{25}$ +108.0 (*c* 0.1, MeOH). ^{1}H NMR (500 MHz, Methanol-d_4) δ 8.49 – 8.41 (m, 3H), 8.37 (t, *J* = 1.5 Hz, 1H), 8.35 – 8.24 (m, 2H), 8.19 (d, *J* = 1.5 Hz, 2H), 7.96 – 7.78 (m, 4H), 6.64 (d, *J* = 2.5 Hz, 1H), 6.13 (m, 1H), 5.51 (s, 1H), 5.41 – 5.28 (m, 2H), 5.12 – 4.93 (m, 2H), 4.52 – 4.43 (m, 1H), 4.04 (t, *J* = 9.6 Hz, 1H), 3.88 (d, *J* = 11.4 Hz, 1H), 3.74 – 3.55 (m, 1H), 3.23 – 3.11 (m, 1H), 2.71 (d, *J* = 8.9 Hz, 1H), 2.58 (t, *J* = 11.9 Hz, 1H), 2.05 – 1.85 (m, 3H), 1.19 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 154.10, 147.63, 146.64, 145.75, 142.37, 141.24, 137.26, 132.20, 130.15, 129.84, 129.59, 128.04, 127.68, 125.87, 125.84, 125.31, 123.80, 123.15, 117.22, 117.13, 96.64, 67.71, 65.04, 60.35, 55.93, 54.25, 36.99, 30.91, 26.38, 20.44. HRMS calcd. for $[C_{33}H_{30}I_2F_3N_2OBr\text{-}Br]^+$ requires m/z 781.0394, found m/z 781.0368.

General proceduce for Preparation of β-keto esters and β-keto amides



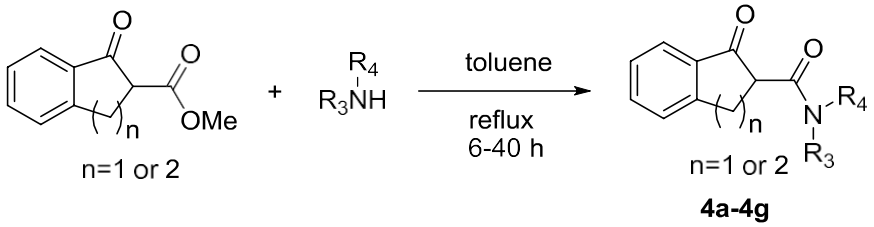
1a-1q

β-keto esters **1a**-**1q** were prepared according to the literature procedure （*Eur. J. Org. Chem.* **2010**, *34*, 6525–6530）To a flask equipped with a Dean-Stark trap and reflux condenser was added β-keto methyl ester (1 mmol), corresponding alcohol, the transesterification catalyst or ZnO and toluene or cyclohexane. The mixture was heated to reflux, distilling the methanol formed during the reaction. The mixture was refluxed until complete conversion was observed by TLC, then concentrated under reduced pressure and the crude residue was purified by column chromatography.



1s-1w

β-keto esters **1s**-**1w** were prepared as above. To a flask equipped with a Dean-Stark trap and reflux condenser was added β-keto methyl ester (1 mmol), corresponding alcohol, the transesterification catalyst ZnO and toluene or cyclohexane. The mixture was heated to reflux, distilling the methanol formed during the reaction. The mixture was refluxed for 10-24 h until complete conversion was observed by TLC, then concentrated under reduced pressure and the crude residue was purified by column chromatography.

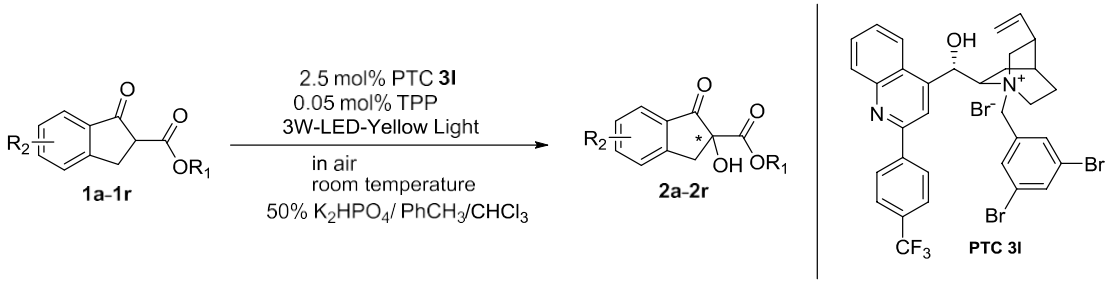


4a-4g

β-keto amides **4a**-**4g** were prepared partly according to the literature procedure (*Synlett*. **2011**, 425–429). To a flask equipped with a Dean-Stark trap and reflux condenser was added *β*-keto methyl ester (1 mmol), corresponding amine and toluene. The mixture was refluxed for 10-24 h until complete conversion was observed by TLC. then concentrated under reduced pressure and the crude residue was purified by column chromatography or recrystallization to give the desired product.

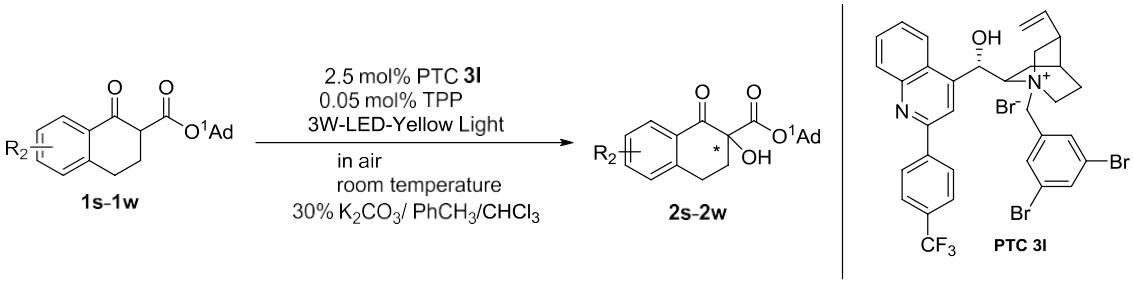
General proceduce for the asymmetric *α*-hydroxylation of *β*-keto esters and *β*-keto amides.

α-hydroxylation of β-indanone esters



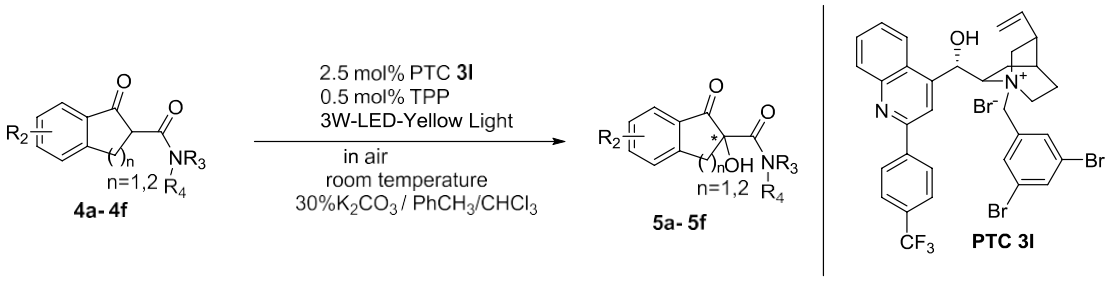
The reaction was conducted with substrate **1a-1r** (0.1 mmol) in the presence of PTC **3l** (2.5 mol%) and tetraphenylporphine (TPP) (0.05 mol%) in a mixture containing $PhCH_3/CHCl_3$=8:2 (10 mL) and K_2HPO_4 (4 mL, 50% aq.) at room temprature, with exposure to a 3-W LED yellow lamp for the given reaction period. After completion of the reaction (confirmed by TLC analysis,), the mixture was diluted with EtOAc (50 mL), washed with water (3× 20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography to give **2a-2r**. The ee of the product was determined by chiral HPLC.

α-hydroxylation of 1-tetralone-derived adamantly β-keto esters

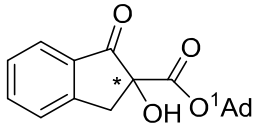


The reaction was conducted with substrate **1s-1w** (0.1 mmol) in the presence of PTC **3l** (2.5 mol%) and tetraphenylporphine (TPP) (0.05 mol%) in a mixture containing $PhCH_3/CHCl_3$=8:2 (10 mL) and K_2CO_3 (4 mL, 30% aq.) at room temprature, with exposure to a 3-W LED yellow lamp for the given reaction period. After completion of the reaction (confirmed by TLC analysis,), the mixture was diluted with EtOAc (50 mL), washed with water (3× 20 mL), dried over anhydrous Na2SO4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography to give **2s-2w**. The ee of the product was determined by chiral HPLC.

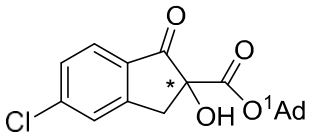
α-hydroxylation of β-keto amides



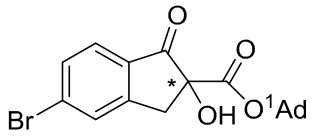
The reaction was conducted with substrate **4a-4f** (0.1 mmol) in the presence of PTC **3l** (2.5 mol%) and tetraphenylporphine (TPP) (0.5 mol%) in a mixture containing $PhCH_3/CHCl_3$=8:2 (10 mL) and K_2HPO_4 (4 mL, 50% aq.) or K_2CO_3 (4 mL, 30% aq.) at room temprature, with exposure to a 3-W LED yellow lamp for the given reaction period. After completion of the reaction (confirmed by TLC analysis), the mixture was diluted with EtOAc (50 mL), washed with water (3× 20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography to give **5a-5f**. The ee of the product was determined by chiral HPLC.



1-Adamantyl 2-hydroxy-1-oxo-2,3-dihydro-1H-inde-ne-2-carboxylate (**2a**); colorless oil; (32.0 mg, 98% yield, 90% ee); $[\alpha]_D^{25}$ 28.7 (*c* 0.47, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.65 (td, *J* = 7.5, 1.1 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 4.01 (s, 1H), 3.66 (d, *J* = 17.1 Hz, 1H), 3.22 (d, *J* = 17.1 Hz, 1H), 2.12 (s, 3H), 1.96 (s, 6H), 1.60 (s, 6H).HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 80 / 20, 1 mL / min, 254 nm, τ_R (major) = 12.5 min, τ_R (minor) = 21.1 min.

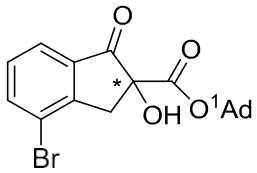


1-Adamantyl 2-hydroxy-5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate(**2b**); white solid; mp:152-156 ℃; (35.1 mg, 97% yield, 87% ee); $[\alpha]_D^{25}$ 67.5 (*c* 0.54, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.40 (dd, *J* = 8.2, 1.7 Hz, 1H), 4.00 (s, 1H), 3.62 (d, *J* = 17.3 Hz, 1H), 3.19 (d, *J* = 17.3 Hz, 1H), 2.13 (m, 3H), 1.97 (s, 6H), 1.60 (sz, 6H). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 80 / 20, 1 mL / min, 254 nm, τ_R (major) = 12.6 min, τ_R (minor) = 21.9 min.

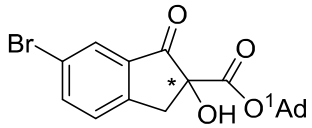


1-Adamantyl 2-hydroxy-5-bromine-1-oxo-2,3-dihydro-1H-indene-2-carboxylate(**2c**); white was; (38.5 mg, 96% yield, 83% ee) ; $[\alpha]_D^{25}$ 63.6 (*c* 0.69, $CHCl_3$);^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 – 7.61 (m, 2H), 7.56 (d, *J* = 8.2 Hz, 1H), 4.05 (s, 1H), 3.63 (d, *J* = 17.3 Hz, 1H), 3.20 (d, *J* = 17.3 Hz, 1H), 2.13 (s, 3H), 1.97 (s, 6H), 1.60 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.24, 169.77, 153.77, 132.85, 131.62, 131.28, 129.60, 126.13, 84.27, 80.40,

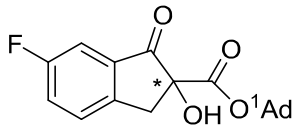
40.93, 39.19, 35.84, 30.82. HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 80 / 20, 1 mL / min, 254 nm, τ_R (major) = 14.1 min, τ_R (minor) = 22.5 min. HRMS calcd. for $[C_{20}H_{21}BrO_4+Na]^+$ requires m/z 427.0521, found m/z 427.0530.



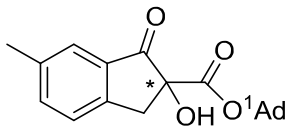
1-Adamantyl 2-hydroxy-4-bromine-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2d**); colorless oil; (35.8 mg, 88% yield, 89% ee); $[\alpha]_D^{25}$ 48.5 (*c* 0.64, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 – 7.69 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 4.05 (s, 1H), 3.60 (d, *J* = 17.6 Hz, 1H), 3.14 (d, *J* = 17.6 Hz, 1H), 2.20 – 2.05 (s, 3H), 1.98 (s, 6H), 1.61 (s, 6H). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 80 / 20, 0.8 mL / min, 254 nm, τ_R (major) = 13.2 min, τ_R (minor) = 15.2 min.



1-Adamantyl 2-hydroxy-6-bromine-1-oxo-2,3-dihydro-1H-indene-2-carboxylate(**2e**); colorless oil; (37.1 mg, 92% yield, 85% ee); $[\alpha]_D^{25}$ -19.3 (*c* 0.68, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 1.9 Hz, 1H), 7.74 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 4.01 (s, 1H), 3.59 (d, *J* = 17.2 Hz, 1H), 3.15 (d, *J* = 17.2 Hz, 1H), 2.20 – 2.08 (m, 3H), 1.96 (m, 6H), 1.60 (m, 6H). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 80 / 20, 1.0 mL / min, 254 nm, τ_R (major) = 11.8 min, τ_R (minor) = 23.5 min.

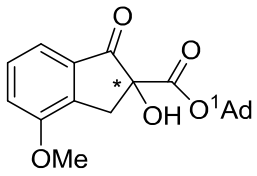


1-Adamantyl 2-hydroxy-6-fluorine-1-oxo-2,3-dihydro-1H-indene-2-carboxylate(**2f**); colorless oil; (30.9 mg, 89% yield, 85% ee); $[\alpha]_D^{25}$ 18.4 (*c* 0.57, $CHCl_3$)^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.40 (m, 2H), 7.39 – 7.33 (m, 1H), 4.04 (s, 1H), 3.61 (d, *J* = 16.9 Hz, 1H), 3.18 (d, *J* = 16.9 Hz, 1H), 2.20 – 2.08 (m, 3H), 1.96 (m, 6H), 1.60 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.62, 169.81, 163.36, 161.38, 147.77, 135.73, 127.71, 123.57 110.84, 84.21, 81.16, 40.92, 39.03, 35.83, 30.81. HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 80 / 20, 1.0 mL / min, 254 nm, τ_R (major) = 9.9 min, τ_R (minor) = 19.4 min. HRMS calcd. for $[C_{20}H_{21}FO_4+Na]^+$ requires m/z 367.1322, found m/z 367.1307.

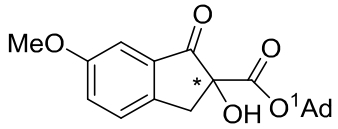


1-Adamantyl 2-hydroxy-6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate(**2g**); white wax; (32.9 mg, 97% yield, 82% ee); $[\alpha]_D^{25}$ 39.7 (*c* 0.56, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 4.00 (s, 1H), 3.61 (d, *J* = 16.9 Hz, 1H), 3.15 (d, *J* = 16.9 Hz, 1H), 2.41 (s, 3H), 2.14 – 2.06 (m, 3H), 1.97 (m, 6H), 1.60 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.45, 169.32, 148.77, 136.84, 136.05, 133.07, 124.89, 123.90, 82.76, 79.78, 39.90, 38.22, 34.85, 29.79, 20.08. HPLC conditions: Chiralcel

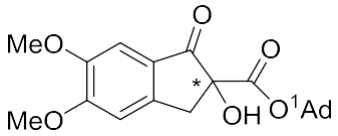
AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 80 / 20, 1.0 mL / min, 254 nm, τ_R (major) = 10.9 min, τ_R (minor) = 20.7 min. HRMS Calcd. for $[C_{21}H_{24}O_4+Na]^+$ requires m/z 363.1572, found m/z 363.1560.



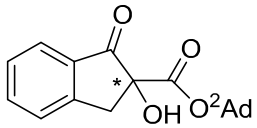
1-Adamantyl 2-hydroxy-4-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate(**2h**);white wax ; (33.1 mg, 93% yield, 84% ee); $[\alpha]_D^{25}$ 44.8 (*c* 0.61, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.33 (m, 2H), 7.09 (dd, *J* = 5.3, 3.6 Hz, 1H), 4.00 (s, 1H), 3.91 (s, 3H), 3.59 (d, *J* = 17.5 Hz, 1H), 3.07 (d, *J* = 17.5 Hz, 1H), 2.22 – 2.04 (m, 3H), 1.98 (m, 6H), 1.60 (m, 6H). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 80 / 20, 1.0 mL / min, 254 nm, τ_R (major) = 15.9 min, τ_R (minor) = 22.7 min.



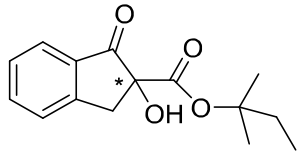
1-Adamantyl 2-hydroxy-6-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate(**2i**);white wax ; (35.0 mg, 98% yield, 85% ee); $[\alpha]_D^{25}$ 22.6 (*c* 0.67, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.19 (m, 2H), 4.03 (s, 1H), 3.58 (d, *J* = 16.8 Hz, 1H), 3.13 (d, *J* = 16.7 Hz, 1H), 2.24 – 2.07 (m, 3H), 1.98 (d, *J* = 3.0 Hz, 6H), 1.60 (t, *J* = 3.0 Hz, 6H). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 80 / 20, 1.0 mL / min, 254 nm, τ_R (major) = 13.5 min, τ_R (minor) = 23.7 min.



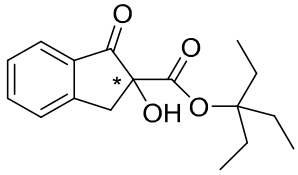
*1-Adamanty*l 2-hydroxy-5,6-di-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate(**2j**); yellow solid: mp:145-148 ℃;(37.5 mg, 97% yield, 88% ee); $[\alpha]_D^{25}$ 71.8 (*c* 0.71, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.19 (s, 1H), 6.89 (s, 1H), 4.05 (s, 1H), 3.99 (s, 3H), 3.92 (s, 3H), 3.58 (d, *J* = 16.9 Hz, 1H), 3.12 (d, *J* = 16.9 Hz, 1H), 2.21 – 2.09 (m, 3H), 2.00 (m, 6H), 1.61 (m, 6H). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 80 / 20, 1.0 mL / min, 254 nm, τ_R (major) = 22.1 min, τ_R (minor) = 38.7 min.



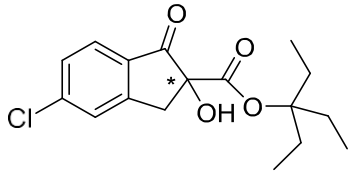
2-Adamantyl 2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2k**); white wax ; (31.6 mg, 97% yield, 81% ee); $[\alpha]_D^{25}$ 20.6 (*c* 0.54, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 4.95 (t, *J* = 3.5 Hz, 1H), 4.06 (s, 1H), 3.71 (d, *J* = 17.0 Hz, 1H), 3.30 (d, *J* = 17.0 Hz, 1H), 1.94 – 1.56 (m, 10H), 1.44 – 1.27 (m, 4H). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 80 / 20, 1.0 mL / min, 254 nm, τ_R (major) = 11.7 min, τ_R (minor) = 14.7 min.



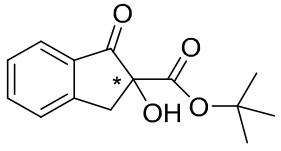
tert-pentyl 2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2l**);colorless oil; (25.1 mg, 96% yield, 78% ee); $[\alpha]_D^{25}$ 36.5 (*c* 0.42, $CHCl_3$)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.64 (td, *J* = 7.5, 1.2 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 4.02 (s, 1H), 3.64 (d, *J* = 17.1 Hz, 1H), 3.23 (d, *J* = 17.1 Hz, 1H), 1.58 (t, *J* = 7.5 Hz, 2H), 1.34 (d, *J* = 4.4 Hz, 6H), 0.62 (t, *J* = 7.5 Hz, 3H). HPLC conditions: Chiralcel OD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 95 / 5, 0.8 mL / min, 254 nm, τ_R (major) = 11.5 min, τ_R (minor) = 12.4 min.



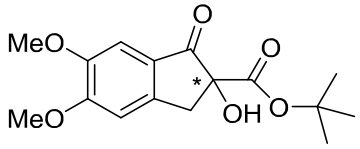
3-ethyl amyl 2-hydroxy-1-oxo-2,3-dihydro-1H-ind-ene-2-carboxylate (**2m**);colorless oil; (29.5 mg, 99% yield, 70% ee); $[\alpha]_D^{25}$ 26.7 (*c* 0.25, $CHCl_3$) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.64 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.48 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.42 (td, *J* = 7.5, 0.9 Hz, 1H), 4.04 (s, 1H), 3.64 (d, *J* = 16.9 Hz, 1H), 3.34 – 3.17 (d, *J* = 16.9 Hz, 1H), 1.70 (q, *J* = 7.5 Hz, 6H), 0.65 (t, *J* = 7.5 Hz, 9H). HPLC conditions: Chiralcel AS-H column (250 × 4.6 mm), hexane / *i*-PrOH = 9 / 1, 1.0 mL / min, 254 nm, τ_R (major) = 11.6 min, τ_R (minor) = 14.0 min.



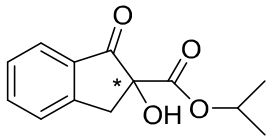
3-ethyl amyl 2-hydroxy-5- chloro -1-oxo-2,3-dihydro-1H-ind-ene-2-carboxylate (**2n**); white wax; (29.5 mg, 97% yield, 69% ee); $[\alpha]_D^{25}$ 24.3 (*c* 0.23, $CHCl_3$) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.40 (dd, *J* = 8.3, 1.7 Hz, 1H), 4.07 (s, 1H), 3.61 (d, *J* = 17.2 Hz, 1H), 3.23 (d, *J* = 17.2 Hz, 1H), 1.71 (q, *J* = 7.5 Hz, 6H), 0.67 (t, *J* = 7.5 Hz, 9H). HPLC conditions: Chiralcel AS-H column (250 × 4.6 mm), hexane / *i*-PrOH = 9 / 1, 1.0 mL / min, 254 nm, τ_R (major) = 7.9 min, τ_R (minor) = 10.5 min.



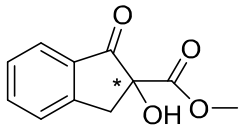
tert-butyl 2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate(**2o**); white solid; mp 128-129 °C. (24.1 mg, 97% yield, 76% ee); $[\alpha]_D^{25}$ 25.3 (*c* 0.15, $CHCl_3$) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.64 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.48 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.42 (td, *J* = 7.5, 1.0 Hz, 1H), 3.99 (s, 1H), 3.65 (dd, *J* = 17.0, 0.8 Hz, 1H), 3.30 – 3.16 (m, 1H), 1.36 (s, 9H). HPLC conditions: Chiralcel OD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 9 / 1, 1.0 mL / min, 254 nm, τ_R (major) = 6.6 min, τ_R (minor) = 7.3 min.



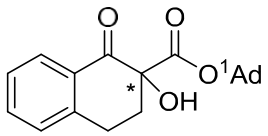
tert-butyl 2-hydroxy-5,6-di-methoxyl -1-oxo-2,3-dihydro-1H-indene-2-carboxylate(**2p**); light yellow oil; (28.2 mg, 92% yield, 72% ee); $[\alpha]_D^{25}$48.2 (*c* 0.55, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.19 (s, 1H), 6.89 (s, 1H), 4.00 (s, 3H), 3.92 (s, 3H), 3.57 (d, *J* = 16.8 Hz, 1H), 3.12 (d, *J* = 16.8 Hz, 1H), 1.39 (s, 9H). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 9 / 1, 1.0 mL / min, 254 nm, τ_R (major) = 36.9 min, τ_R (minor) = 41.3 min.



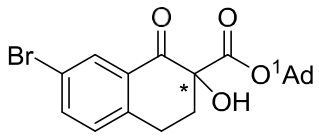
Isopropyl 2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2q**); white solid ; mp 67-71 °C; (22.5 mg, 96% yield, 65% ee); $[\alpha]_D^{25}$ 27.3 (*c* 0.23, $CHCl_3$) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.67 (td, *J* = 7.5, 1.2 Hz, 1H), 7.49 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.46 – 7.39 (m, 1H), 5.15 – 4.99 (m, 1H), 3.70 (d, *J* = 17.4 Hz, 1H), 3.24 (d, *J* = 17.2 Hz, 1H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.13 (d, *J* = 6.2 Hz, 3H). HPLC conditions: Chiralcel OD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 95 / 5, 1.0 mL / min, 254 nm, τ_R (major) = 9.8 min, τ_R (minor) = 10.8 min.



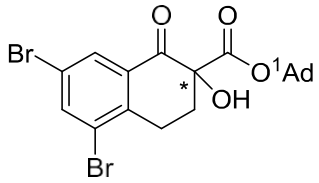
Methyl 2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2r**); white solid ; mp 134-136 °C; (20.2 mg, 98% yield, 62% ee); $[\alpha]_D^{25}$ 47.4 (*c* 0.25, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.67 (td, *J* = 7.5, 1.2 Hz, 1H), 7.54 – 7.40 (m, 2H), 3.74 (m, 4H), 3.26 (d, *J* = 17.2 Hz, 1H). HPLC conditions: Chiralcel OD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 9 / 1, 1.0 mL / min, 254 nm, τ_R (major) = 12.1 min, τ_R (minor) = 14.4 min.



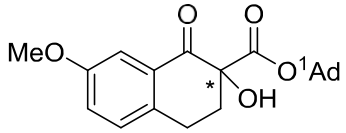
1-Adamantyl 2-hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate(**2s**);colorless oil; (29.8 mg, 92% yield, 74% ee); $[\alpha]_D^{25}$ -5.4 (*c* 0.51, $CHCl_3$);^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.52 (td, *J* = 7.5, 1.4 Hz, 1H), 7.34 (s, 1H), 7.27 – 7.24 (m, 1H), 4.22 (s, 1H), 3.12 (m, 2H), 2.65 (d, *J* = 13.5 Hz, 1H), 2.22 (m, 1H), 2.17 – 2.08 (m, 3H), 2.01 (d, *J* = 3.0 Hz, 6H), 1.68 – 1.54 (m, 6H). HPLC conditions: Chiralcel OD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 9 / 1, 1.0 mL / min, 254 nm, τ_R (major) = 7.8 min, τ_R (minor) = 10.8 min.



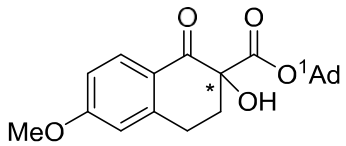
1-Adamantyl 2-hydroxy-7-bromine-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate(**2t**); colorless oil; (37.1 mg, 89% yield, 68% ee); $[\alpha]_D^{25}$ -19.3 (*c* 0.68, $CHCl_3$);^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 2.2 Hz, 1H), 7.62 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 4.17 (s, 1H), 3.19 – 2.97 (m, 2H), 2.61 (m, 1H), 2.30 – 2.19 (m, 1H), 2.18 – 2.10 (m, 3H), 2.02 (m, 6H), 1.62 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.58, 169.48, 142.55, 136.76, 132.24, 130.62, 130.58, 120.81, 83.85, 41.02, 35.91, 32.60, 30.83, 25.31. HPLC conditions: Chiralcel OD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 9 / 1, 1.0 mL / min, 254 nm, τ_R (major) = 7.7 min, τ_R (minor) = 11.6 min. HRMS Calcd. for $[C_{21}H_{23}BrO_4+Na]^+$ requires m/z 441.0677, found m/z 441.0682.



1-Adamantyl 2-hydroxy-5,7-di-bromine-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**2u**); colorless oil; (34.8 mg, 70% yield,71% ee); $[\alpha]_D^{25}$ -2.1 (*c* 0.27, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 2.0 Hz, 1H), 7.93 (d, *J* = 2.0 Hz, 1H), 4.12 (s, 1H), 3.19 – 2.91 (m, 2H), 2.63 (m, 1H), 2.23 (m, 1H), 2.18 – 2.12 (m, 3H), 2.01 (m, 6H), 1.63 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.78, 169.04, 141.72, 139.75, 133.53, 130.05, 125.30, 120.98, 84.13, 41.02, 35.89, 31.64, 30.84, 26.38. HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 9 / 1, 1.0 mL / min, 254 nm, τ_R (major) = 10.1 min, τ_R (minor) = 18.2 min. HRMS Calcd. for $[C_{21}H_{23}Br_2O_4+Na]^+$ requires m/z 518.9783, found m/z 518.9775.

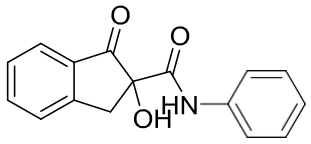


1-Adamantyl 2-hydroxy-7-methoxyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**2v**); light yellow wax; (34.1 mg, 93% yield, 80% ee); $[\alpha]_D^{25}$-22.0 (*c* 0.66, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 2.8 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.10 (dd, *J* = 8.4, 2.8 Hz, 1H), 4.23 (s, 1H), 3.84 (s, 3H), 3.04 (dd, *J* = 7.4, 5.2 Hz, 2H), 2.67 – 2.56 (m, 1H), 2.25 – 2.19 (m, 1H), 2.17 – 2.09 (m, 3H), 2.02 (m, 6H), 1.61 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.88, 169.76, 158.42, 136.51, 131.41, 130.01, 122.64, 109.61, 83.44, 55.52, 41.00, 35.95, 33.09, 30.82, 24.98. HPLC conditions:Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 8/ 2, 1.0 mL / min, 254 nm, τ_R (major) = 13.6 min, τ_R (minor) = 22.9 min.HRMS Calcd. for $[C_{22}H_{26}O_5+Na]^+$ requires m/z 393.1678, found m/z 393.1667.

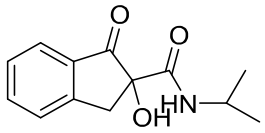


1-Adamantyl 2-hydroxy-6-methoxyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**2w**); light yellow wax; (32.2 mg, 87% yield, 74% ee); $[\alpha]_D^{25}$ -8.3 (*c* 0.55, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.7 Hz, 1H), 6.86 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.70 (d, *J* = 2.5 Hz, 1H), 4.26 (s, 1H), 3.87 (s, 3H), 3.17 – 3.01 (m, 2H), 2.62 (m, 1H), 2.24 – 2.10 (m, 4H), 2.03 (m, 6H), 1.61 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.46, 169.89, 164.17, 146.49, 130.48, 124.10, 113.62, 112.55, 83.25, 55.50, 41.01, 35.96, 32.83, 30.82, 26.12. HPLC conditions:Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 8/ 2, 1.0 mL /

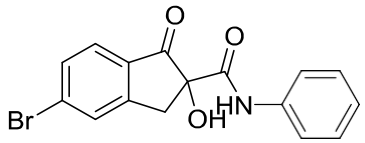
min, 254 nm, τ_R (major) = 21.3 min, τ_R (minor) = 29.8 min. HRMS Calcd. for $[C_{22}H_{26}O_5+Na]^+$ requires m/z 393.1678, found m/z 393.1666.



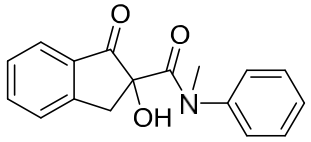
2-hydroxy-1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (**5a**). white solid; mp 149-151 ℃ (24.6 mg, 92% yield, 39% ee). $[\alpha]_D^{25}$ 17.5 (*c* 0.31, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.76 (s, 1H), 7.77 (m, 1H), 7.65 (m, 1H), 7.50 (m, 2H), 7.41 (m, 1H), 7.31 – 7.24 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 3.85 (d, *J* = 16.8 Hz, 1H), 3.17 (d, *J* = 16.8 Hz, 1H). HPLC conditions:Chiralcel OD-H column (250 × 4.6 mm), hexane / *i*-PrOH =9/ 1, 1.0 mL / min, 254 nm, τ_R (major) = 9.8 min, τ_R (minor) = 14.1 min.



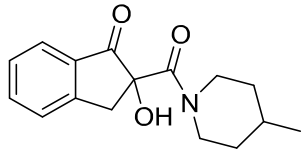
2-hydroxy-1-oxo-N-isopropyl-2,3-dihydro-1H-indene-2-carboxamide (**5b**). Colorless wax; (23.2 mg, 99% yield, 5% ee). $[\alpha]_D^{25}$ -0.2 (*c* 0.21, $CHCl_3$) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.65 (td, *J* = 7.5, 1.3 Hz, 1H), 7.54 – 7.35 (m, 2H), 6.63 (s, 1H), 4.07 – 3.90 (m, 1H), 3.73 (d, *J* = 16.7 Hz, 1H), 3.11 (d, *J* = 16.7 Hz, 1H), 1.17 (m, 6H). HPLC conditions:Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH =8/2, 1.0 mL / min, 254 nm, τ_R (major) = 4.6 min, τ_R (minor) = 5.5 min.



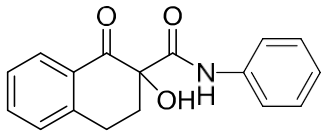
2-hydroxy-1-oxo-5-bromine-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (**5c**). Colorless wax; (32.4 mg, 94% yield, 52% ee). $[\alpha]_D^{25}$ 35.3 (*c* 0.25, $CHCl_3$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 8.13 – 7.94 (m, 1H), 7.74 – 7.28 (m, 7H), 7.13 (t, *J* = 7.4 Hz, 1H), 3.84 (d, *J* = 16.9 Hz, 1H), 3.18 (d, *J* = 16.9 Hz, 1H). HPLC conditions: Chiralcel OD-H column (250 × 4.6 mm), hexane / *i*-PrOH = 80 / 20, 1 mL / min, 254 nm, τ_R (major) = 11.8 min, τ_R (minor) =15.4 min.



2-hydroxy-1-oxo-N-phenyl- N-methyl-2,3-dihydro-1H-indene-2-carboxamide (**5d**). white wax; (20.5 mg, 73% yield, 66% ee). $[\alpha]_D^{25}$ -19.7 (*c* 0.26, $CHCl_3$)^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49 – 7.30 (m, 2H), 7.23 – 6.74 (m, 7H), 5.40 (s, 1H), 3.55 (d, *J* = 18.0 Hz, 1H), 3.40 – 3.24 (m, 3H), 3.12 (d, *J* = 18.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.26, 171.33, 151.17, 135.02, 134.49, 129.05, 128.82, 127.31, 125.85, 124.76, 79.18, 41.53. HPLC conditions:Chiralcel OD-H column (250 × 4.6 mm), hexane / *i*-PrOH =9/1, 1.0 mL / min, 254 nm, τ_R (major) = 29.3 min, τ_R (minor) = 25.5 min. HRMS Calcd. for $[C_{17}H_{15}NO_3+Na]^+$ requires m/z 304.0950, found m/z 304.0939.

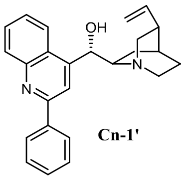


2-hydroxy-1-oxo-N-phenyl-N-4-methylpiperidine-2,3-dihydro-1H-indene-2-carboxamide (**5e**). colorless oil; (19.4 mg, 71% yield, 63% ee); $[\alpha]_D^{25}$ 18.6 (*c* 0.24, $CHCl_3$) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.53 – 7.42 (m, 2H), 5.54 (s, 1H), 4.74 – 4.47 (m, 1H), 3.45 (d, *J* = 18.70 Hz, 1H), 3.31 (d, *J* = 18.0 Hz, 1H), 2.99 (s, 1H), 2.78 (m, 2H), 1.89 – 1.36 (m, 4H), 0.92 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.94, 134.13, 128.35, 127.00, 125.42, 41.00, 30.95, 29.69, 21.47. HPLC conditions:Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH =9/1, 1.0 mL / min, 254 nm, τ_R (major) = 34.9 min, τ_R (minor) = 29.9 min. HRMS Calcd. for $[C_{16}H_{19}NO_3+Na]^+$ requires m/z 296.1263, found m/z 296.1252.

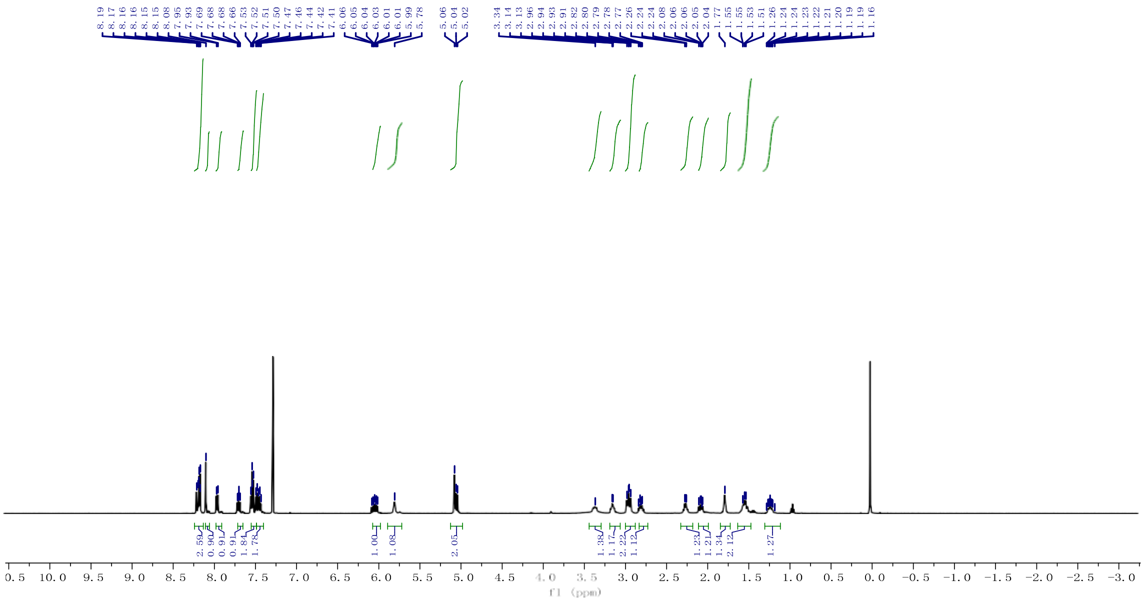


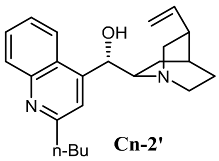
2-hydroxy-N-phenyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate(**5f**).brown oil; (23.6 mg, 84% yield, 25% ee); $[\alpha]_D^{25}$ -6.9 (*c* 0.49, $CHCl_3$) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.81 (s, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.54 (dd, *J* = 13.5, 7.8 Hz, 3H), 7.38 – 7.23 (m, 4H), 7.10 m, 1H), 4.84 (s, 1H), 3.62 (m, 1H), 3.06 – 2.92 (m, 1H), 2.61 (m, 1H), 2.33 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.05, 167.81, 145.69, 136.94, 134.65, 130.66, 129.01, 128.00, 126.72, 124.66, 119.64, 78.26, 77.28, 77.22, 34.63, 26.33. HPLC conditions:Chiralcel AD-H column (250 × 4.6 mm), hexane / *i*-PrOH =8/2, 1.0 mL / min, 254 nm, τ_R (major) = 14.4 min, τ_R (minor) = 18.6 min. HRMS Calcd. for $[C_{17}H_{15}NO_3+Na]^+$ requires m/z 304.0950, found m/z 304.0938.

NMR spectra and HPLC

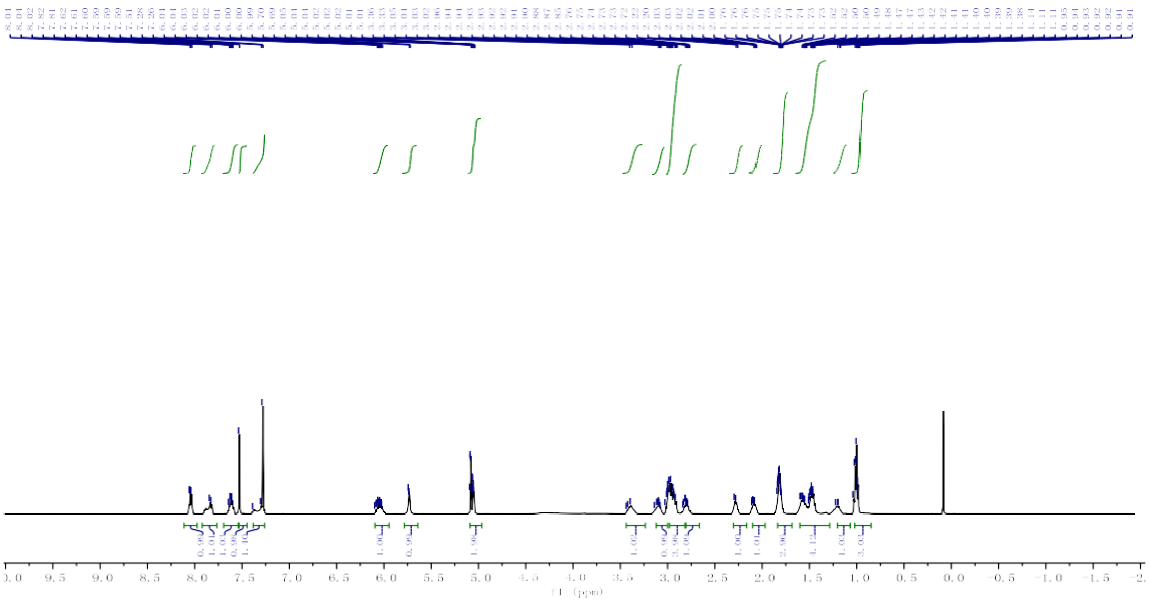


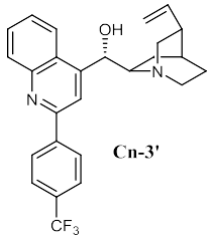
Cn-1'



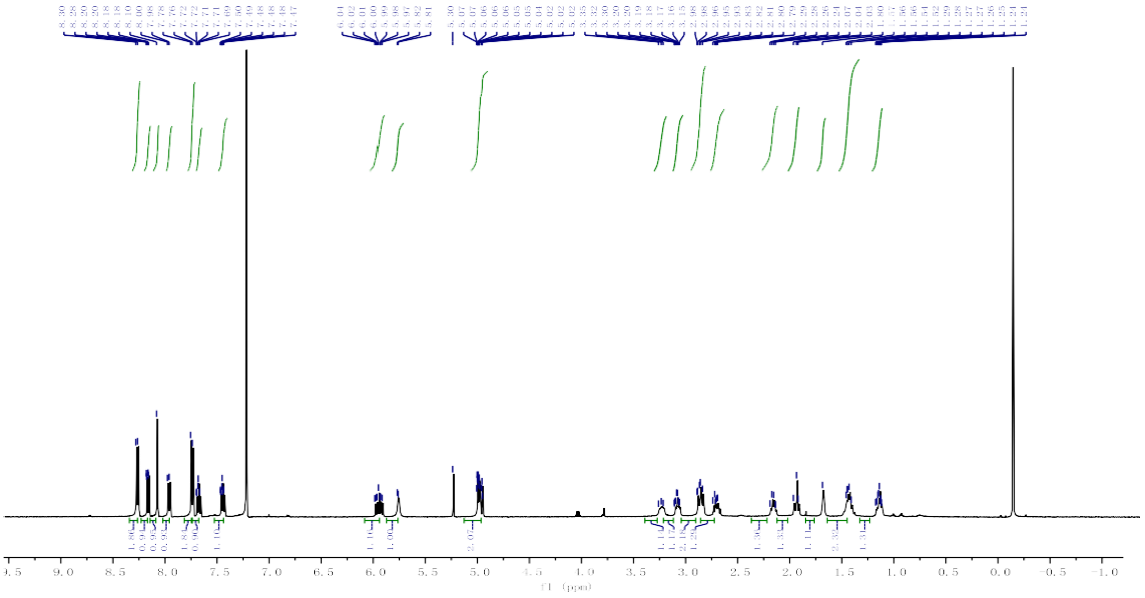


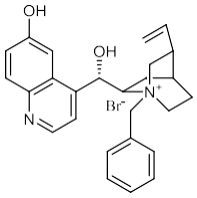
Cn-2'





Cn-3'

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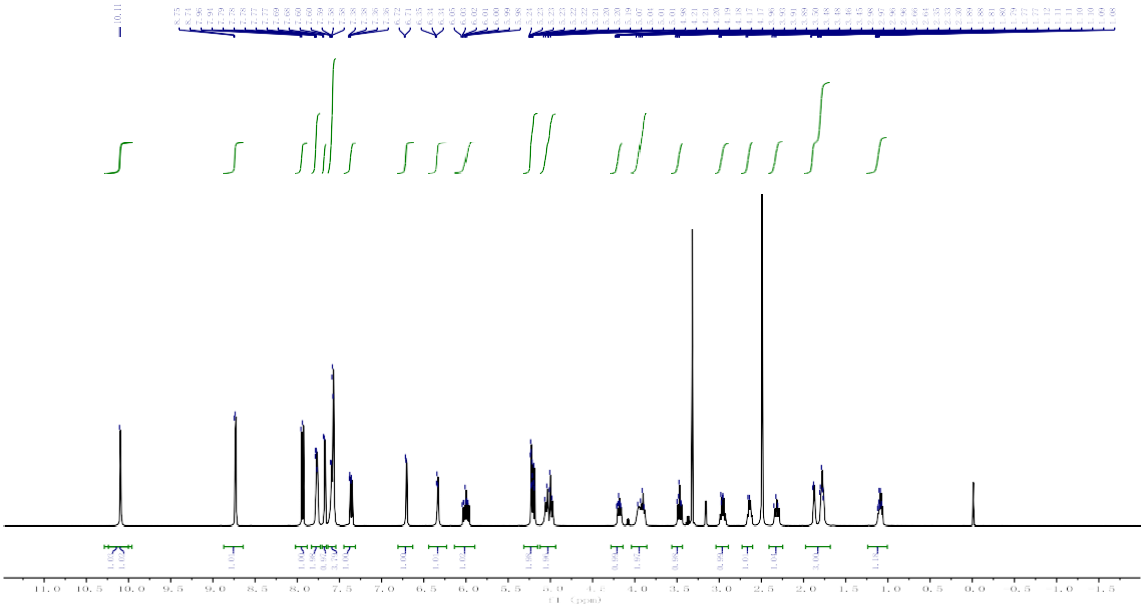
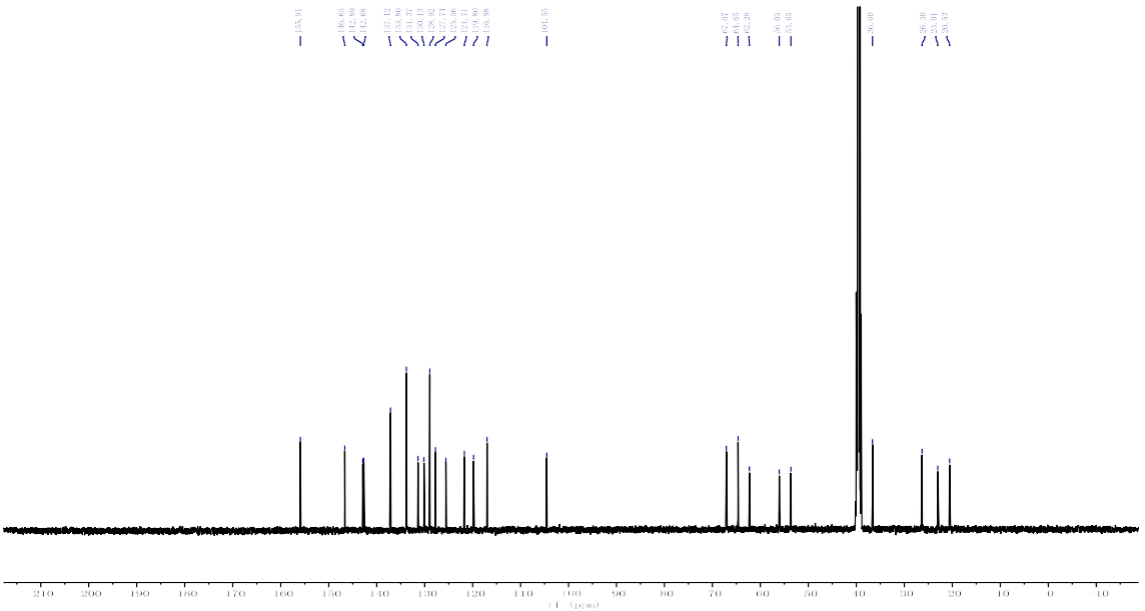
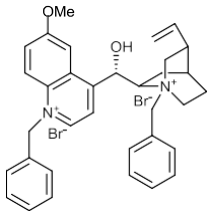
OH
Br⁻
N⁺
N






OMe
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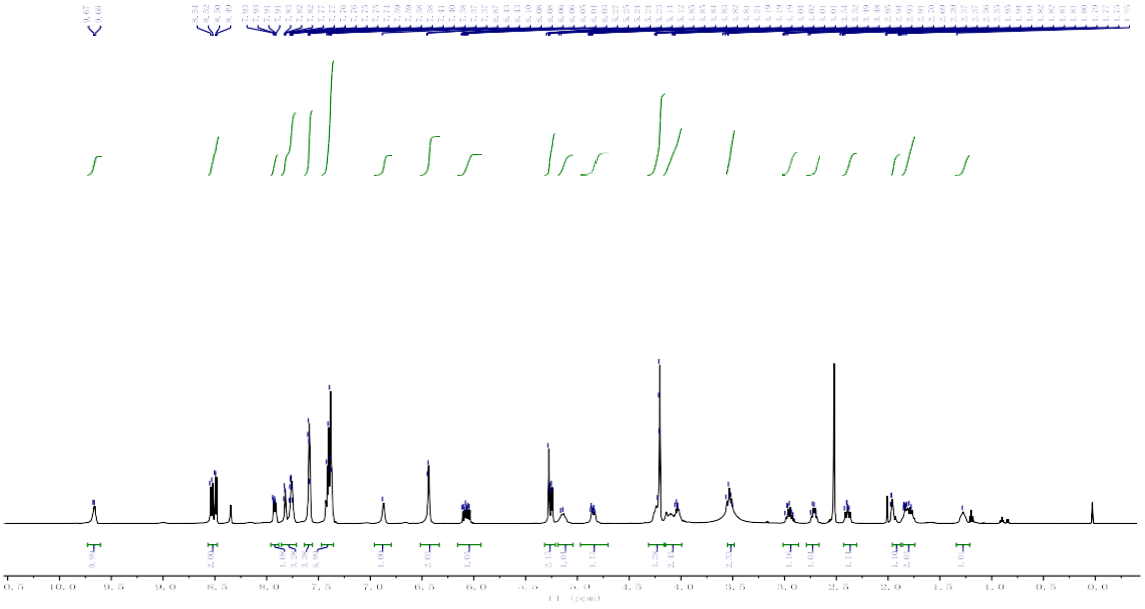
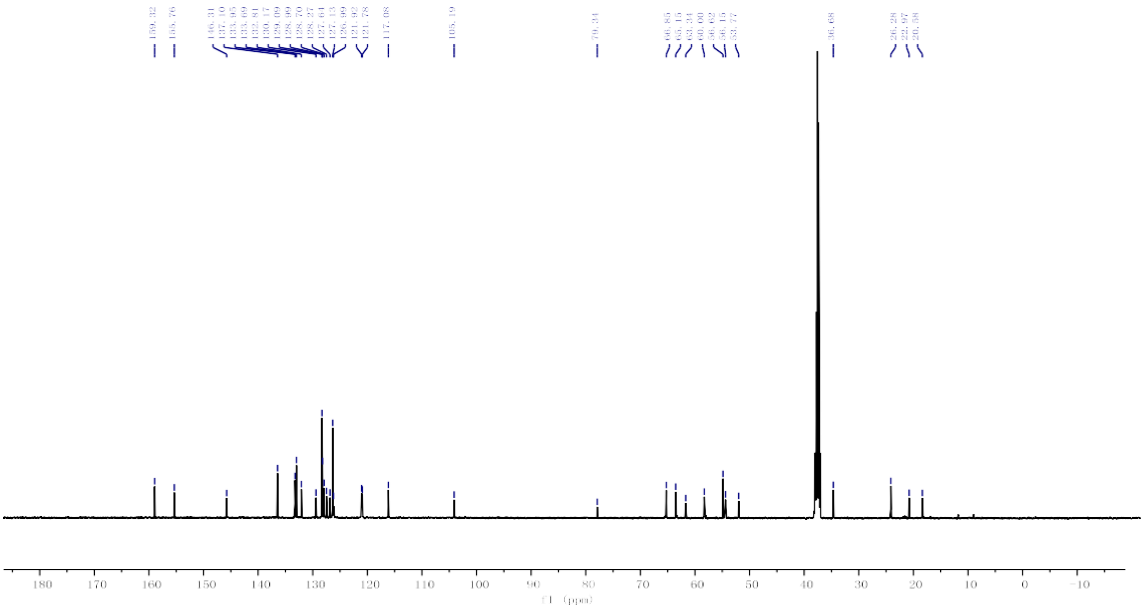
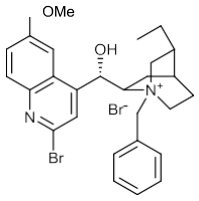
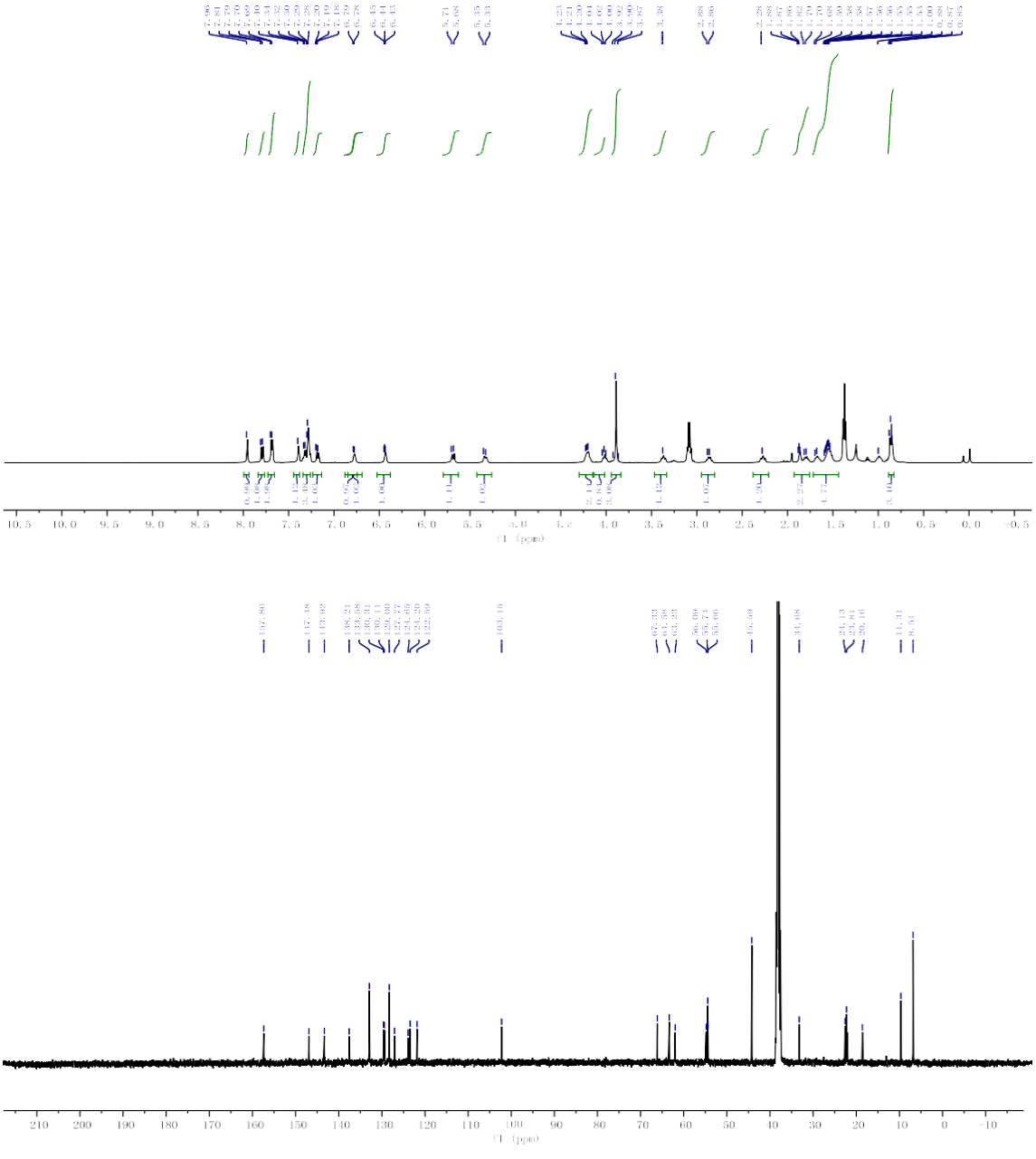
N+
Br-
N+
Br-

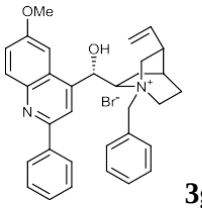




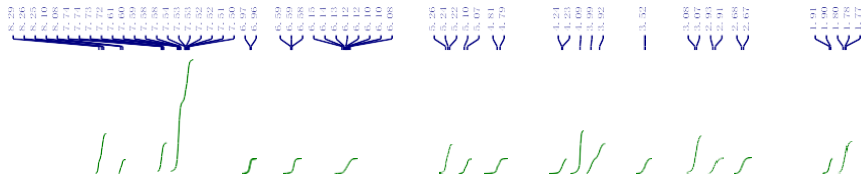


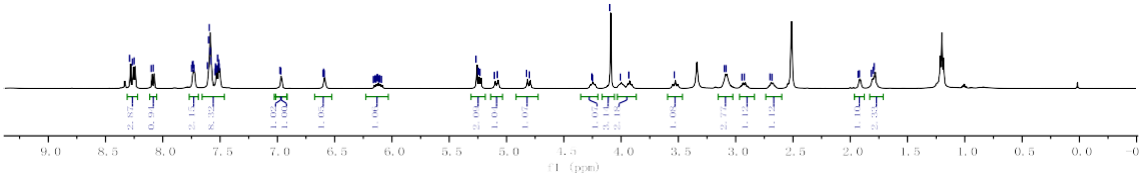
3f

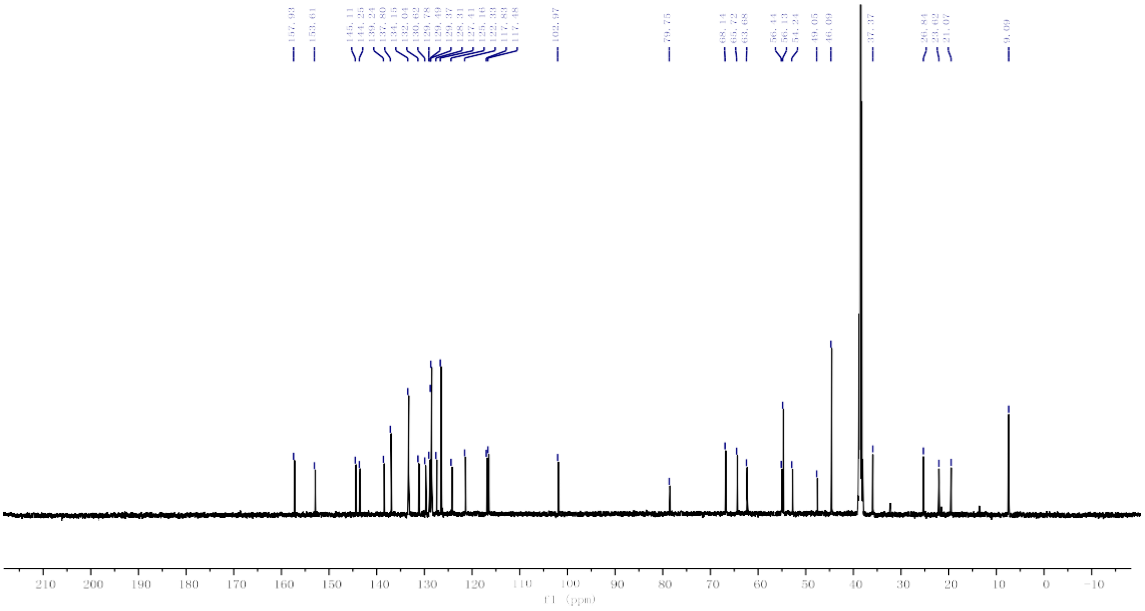


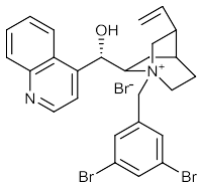


3g









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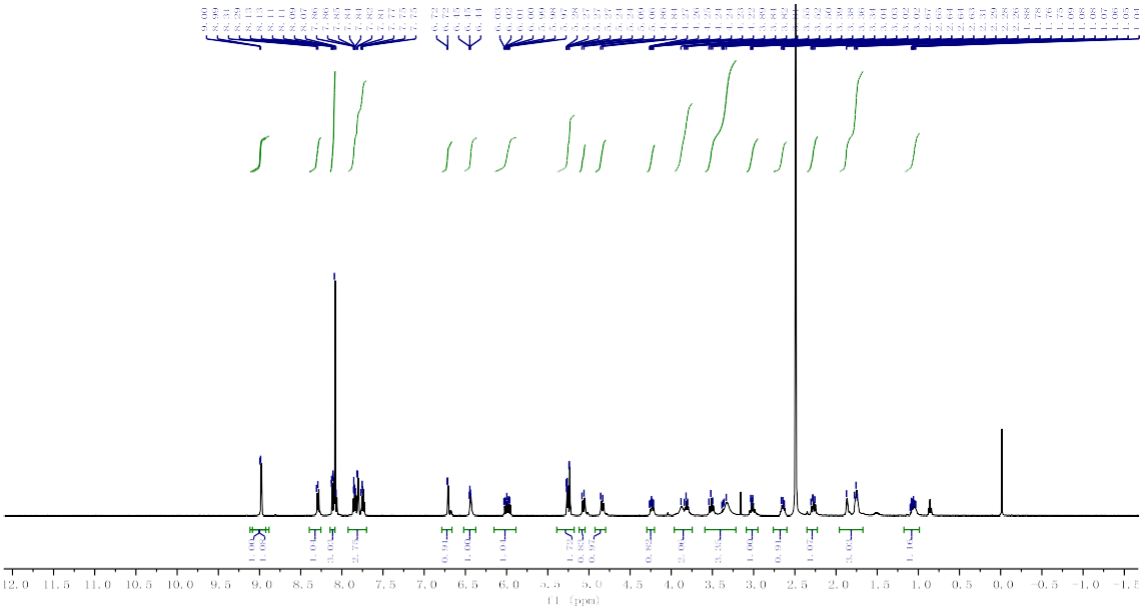

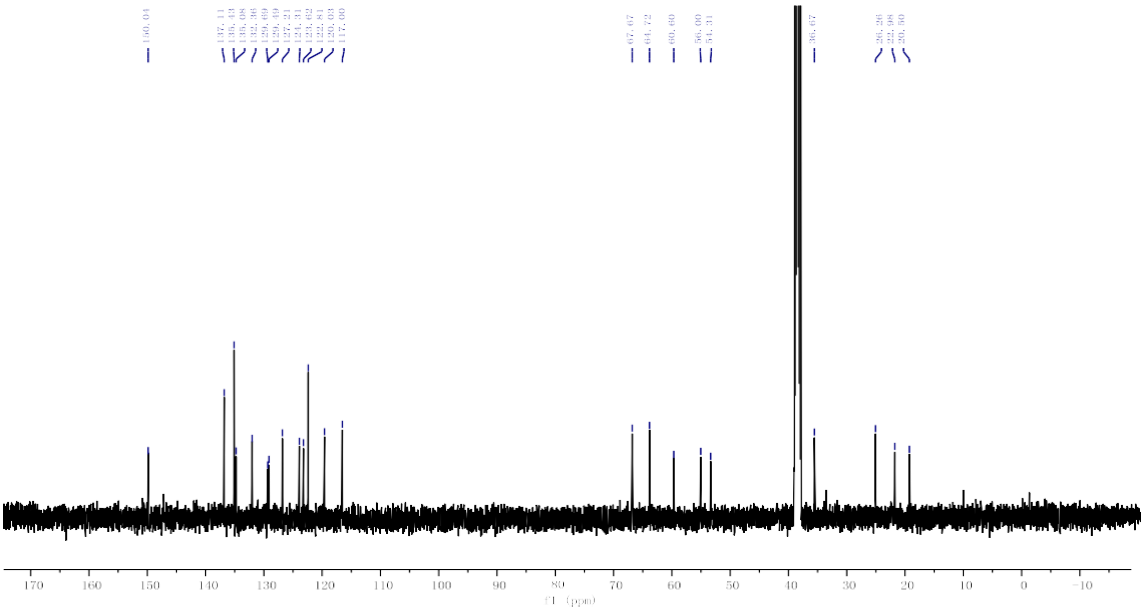

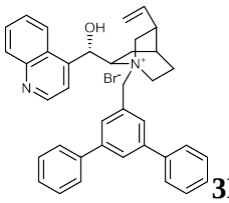

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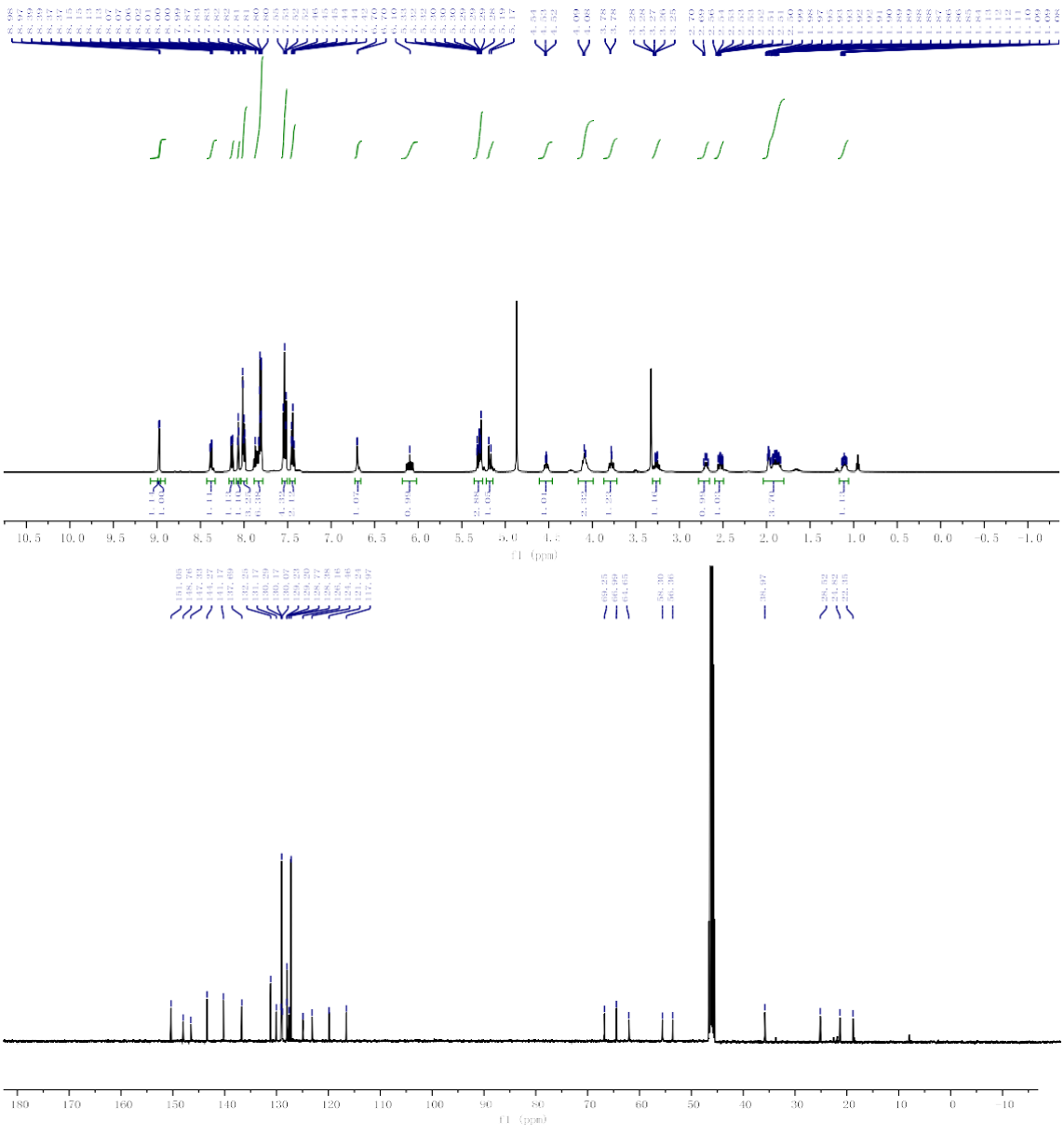

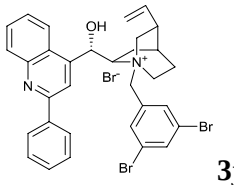

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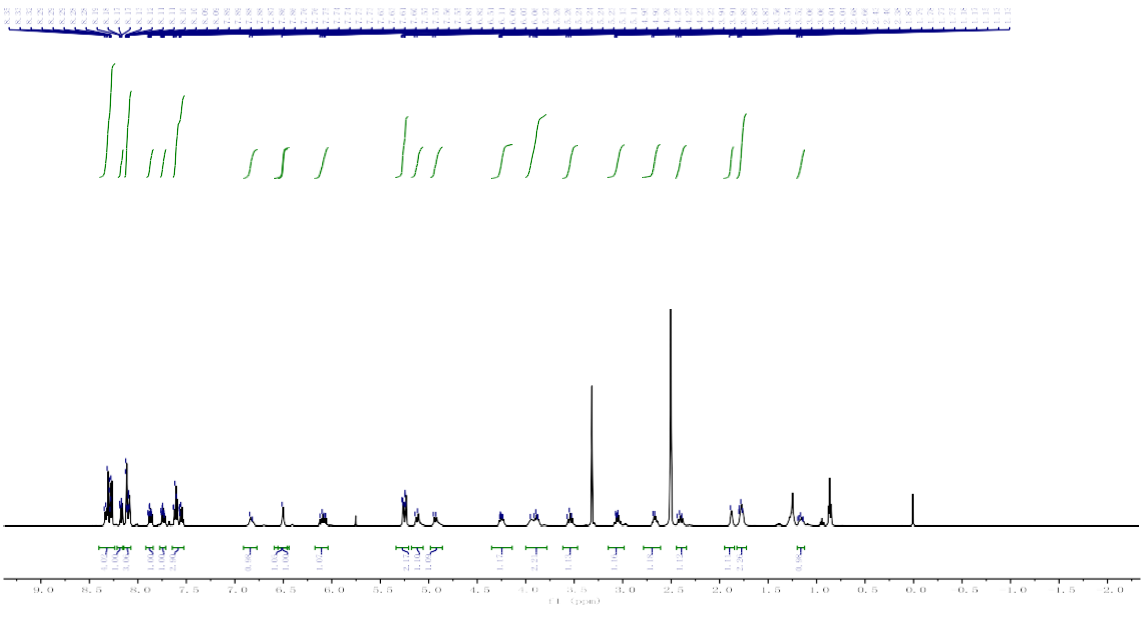

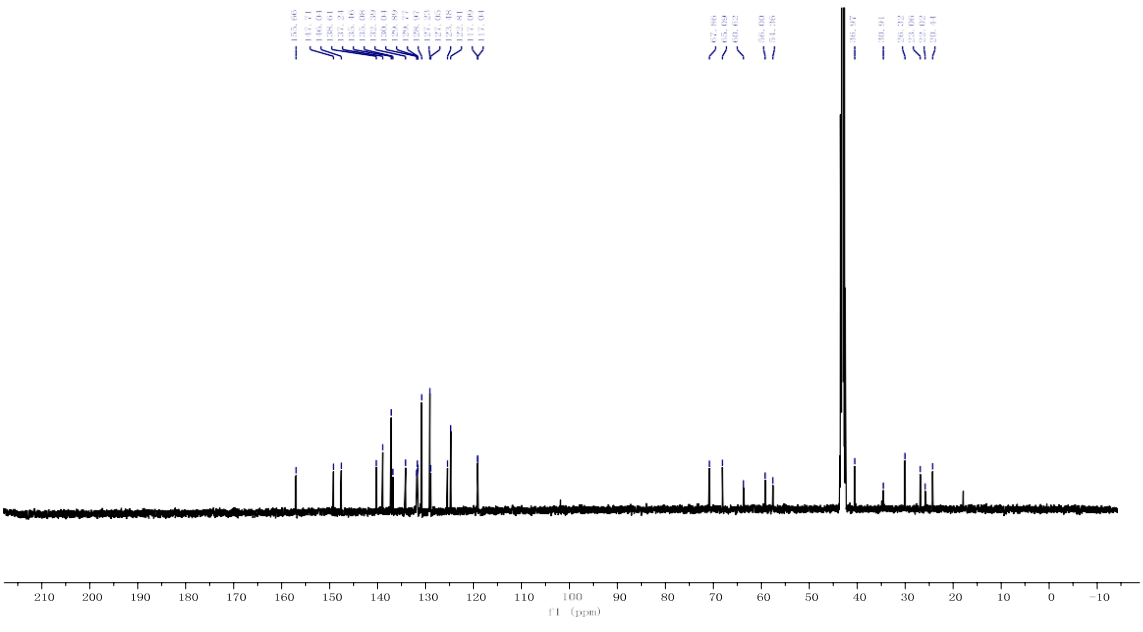

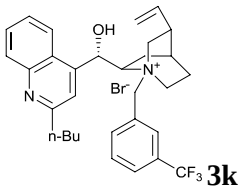

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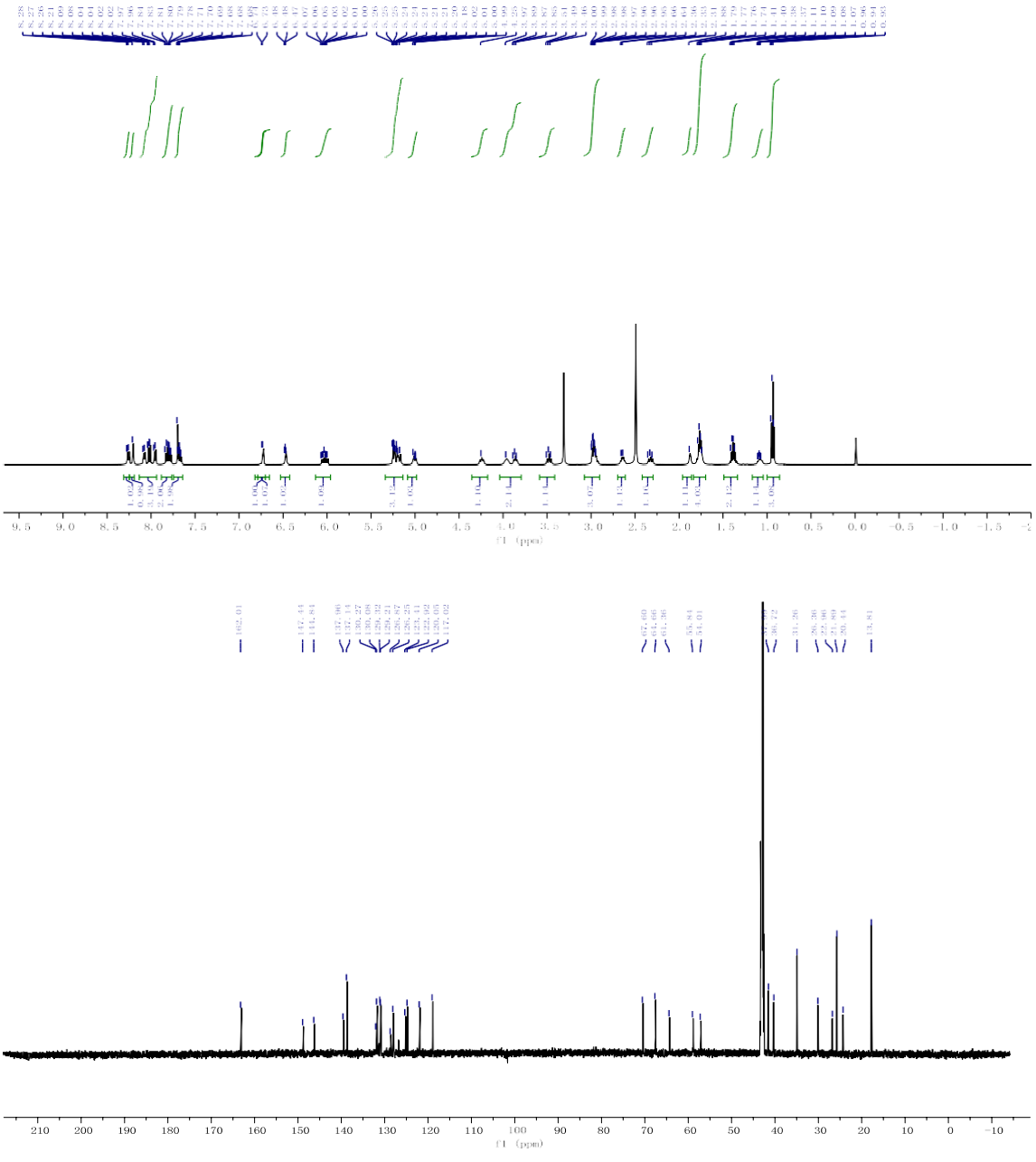

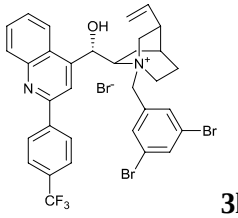

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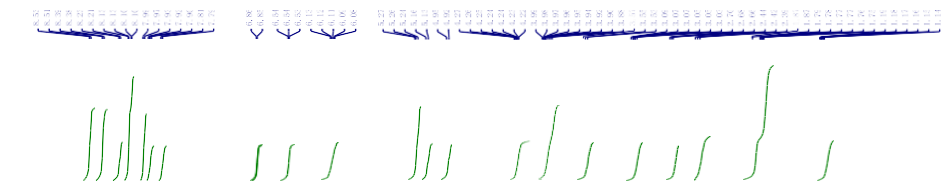
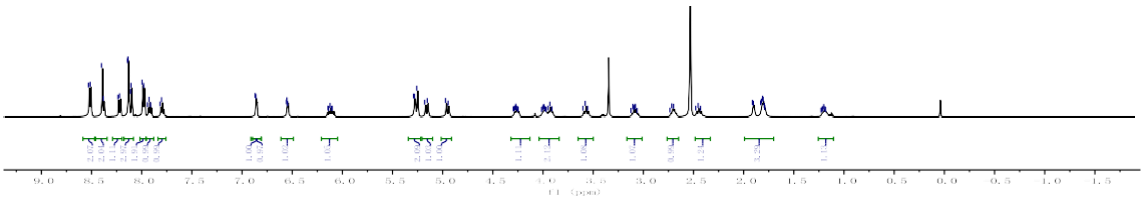
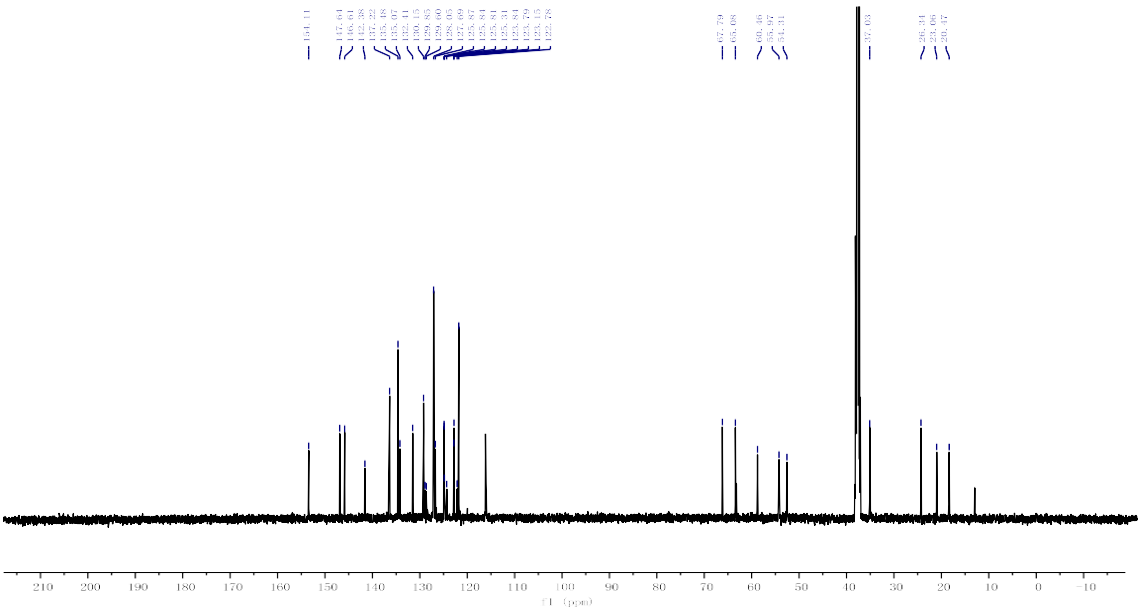
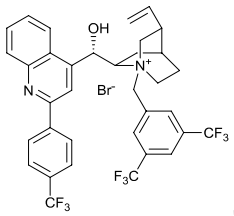
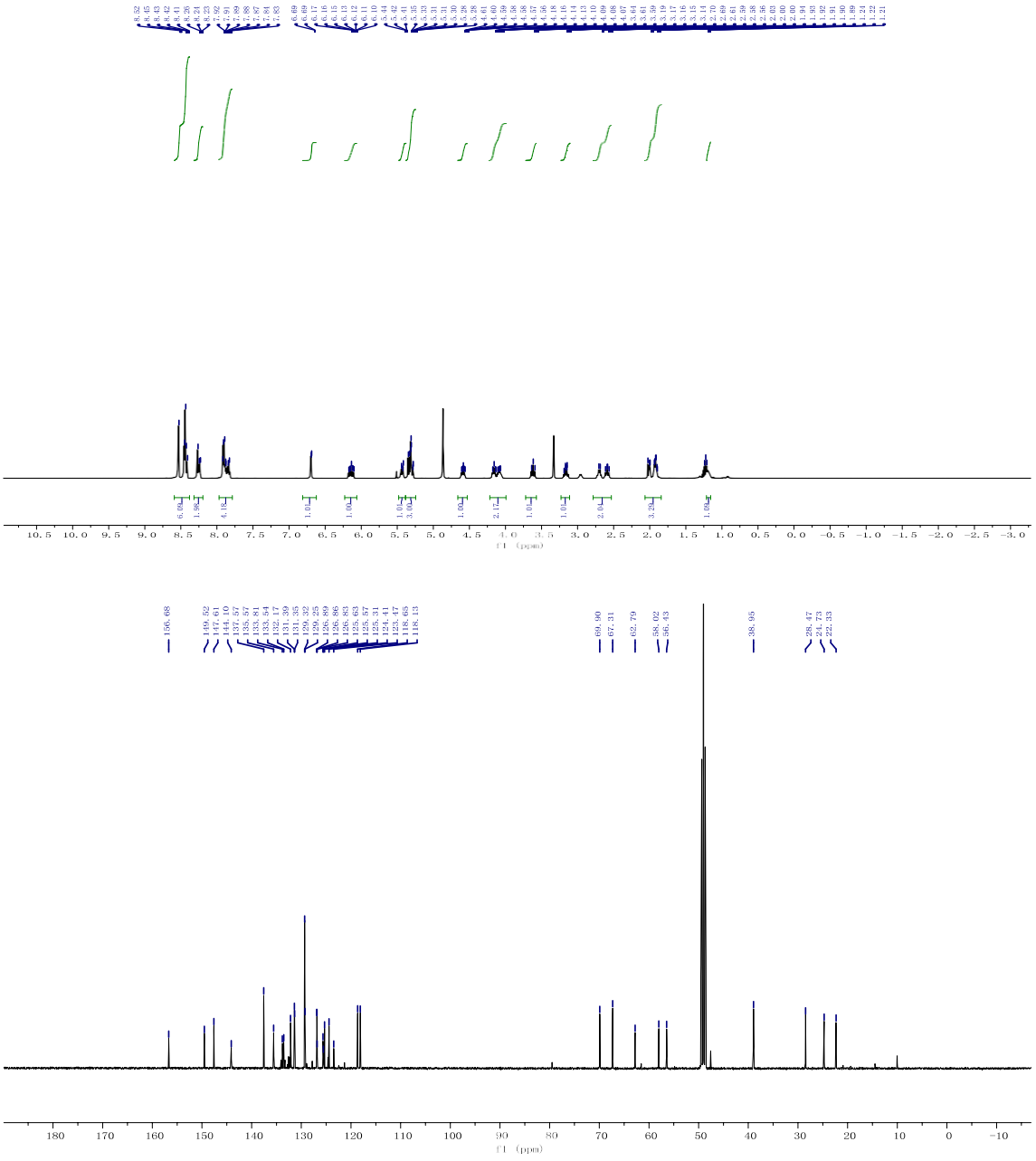


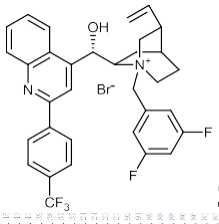




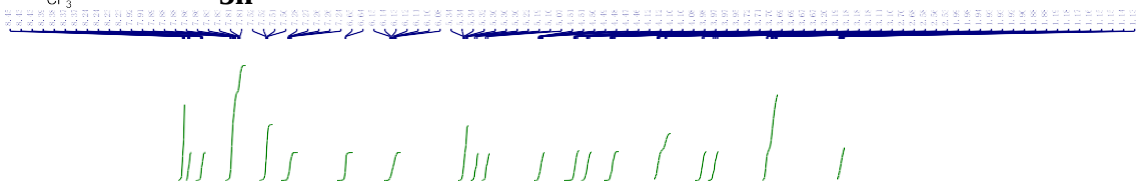

OH
N
N+
Br-
CF3
F3C
CF3

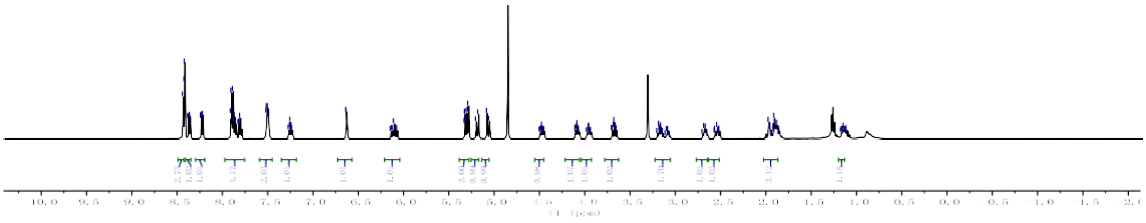
3m

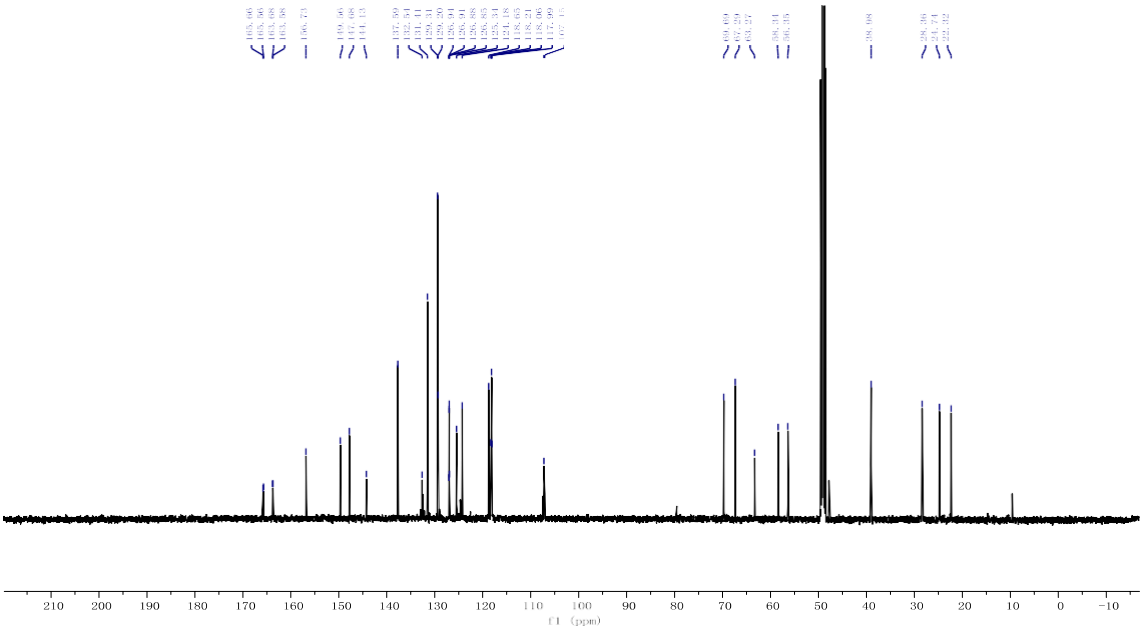

8.52
8.45
8.43
8.42
8.41
8.26
8.24
8.23
8.22
7.91
7.89
7.88
7.87
7.84
7.83
6.09
6.08
6.17
6.16
6.15
6.13
6.12
6.11
6.10
5.44
5.43
5.41
5.35
5.33
5.31
5.30
5.28
5.28
4.61
4.60
4.59
4.58
4.58
4.57
4.56
4.18
4.16
4.14
4.11
4.10
4.09
4.08
4.07
4.04
3.61
3.59
3.19
3.17
3.16
3.15
3.14
2.70
2.69
2.61
2.59
2.58
2.35
2.35
2.00
2.00
1.94
1.93
1.92
1.91
1.90
1.89
1.34
1.22
1.21
6.08
1.98
4.18
1.04
1.00
1.03
3.00
1.00
2.17
1.04
1.01
2.04
3.28
1.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0
f1 (ppm)
156.68
149.52
147.61
144.10
137.57
135.57
133.84
133.54
132.17
131.39
131.35
130.32
129.25
126.89
126.86
126.83
125.62
125.57
125.31
124.41
123.47
118.46
118.13
69.90
67.31
62.79
58.02
56.43
38.95
28.47
24.73
22.33
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

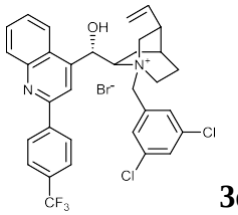


3n

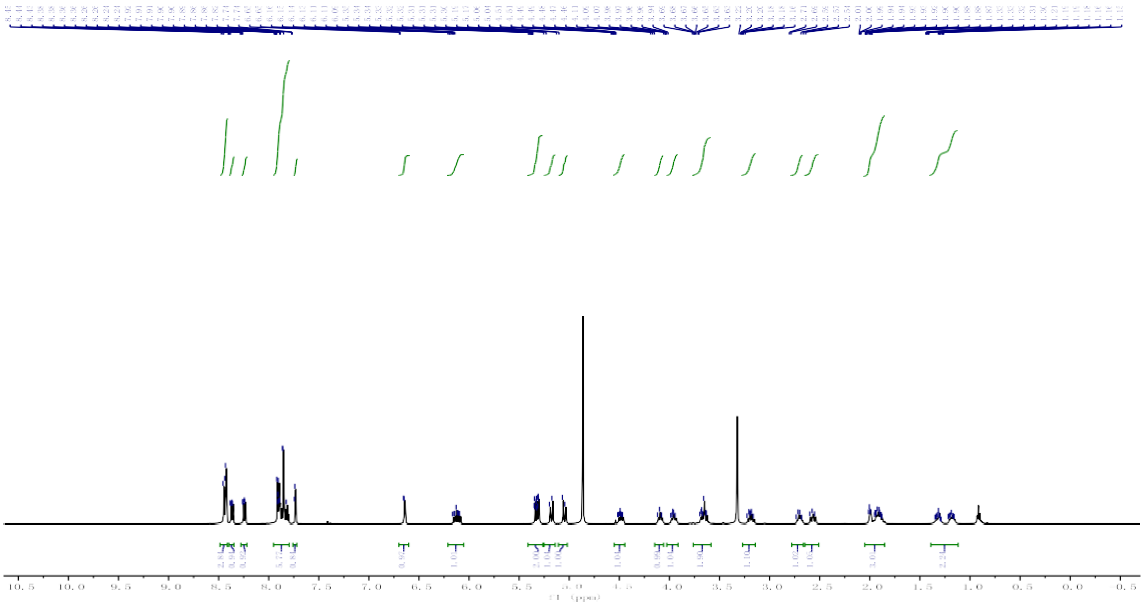


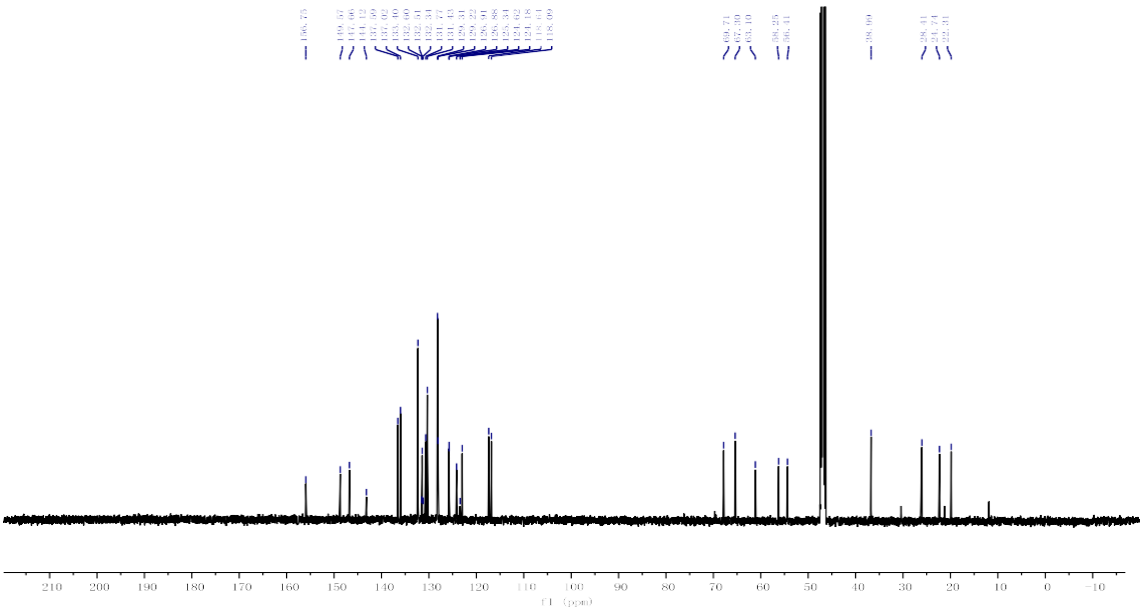


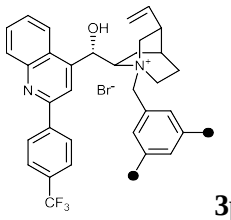




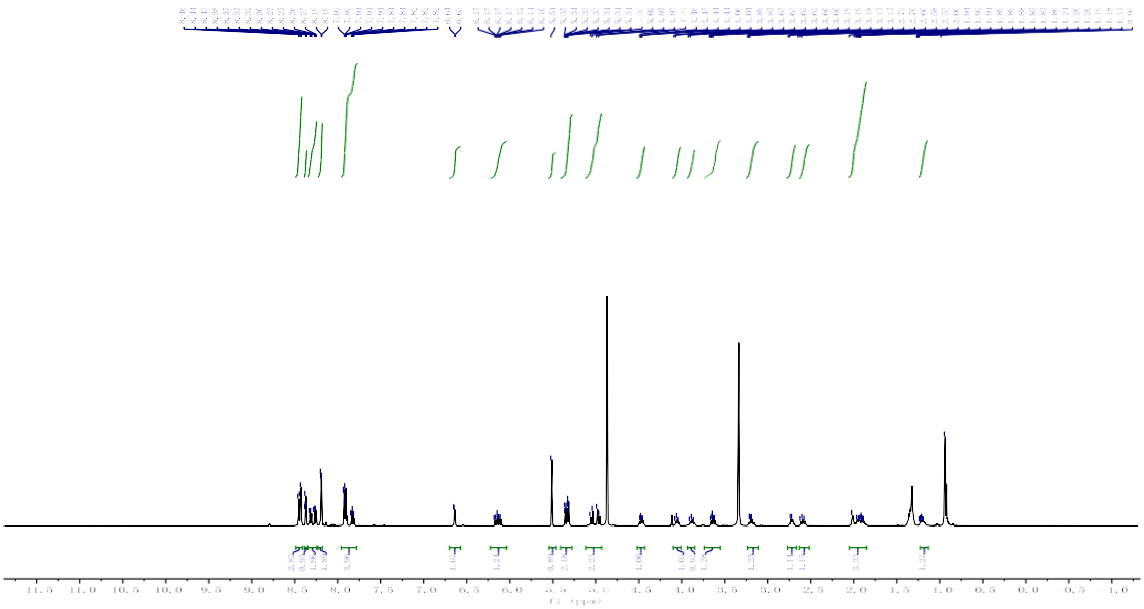
3o

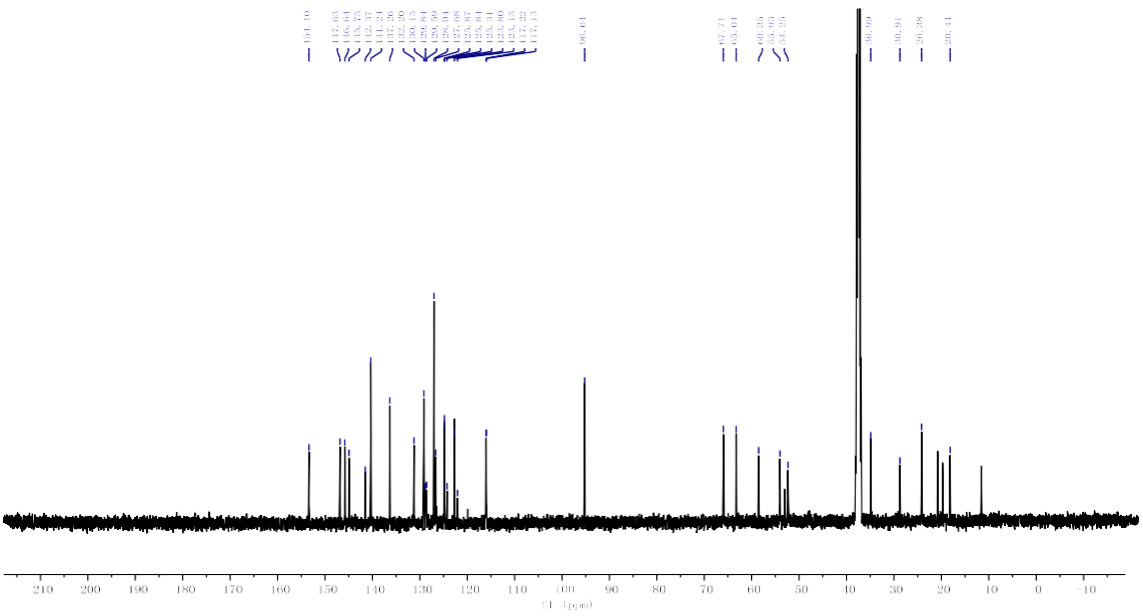


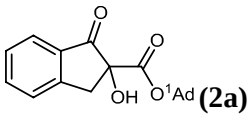




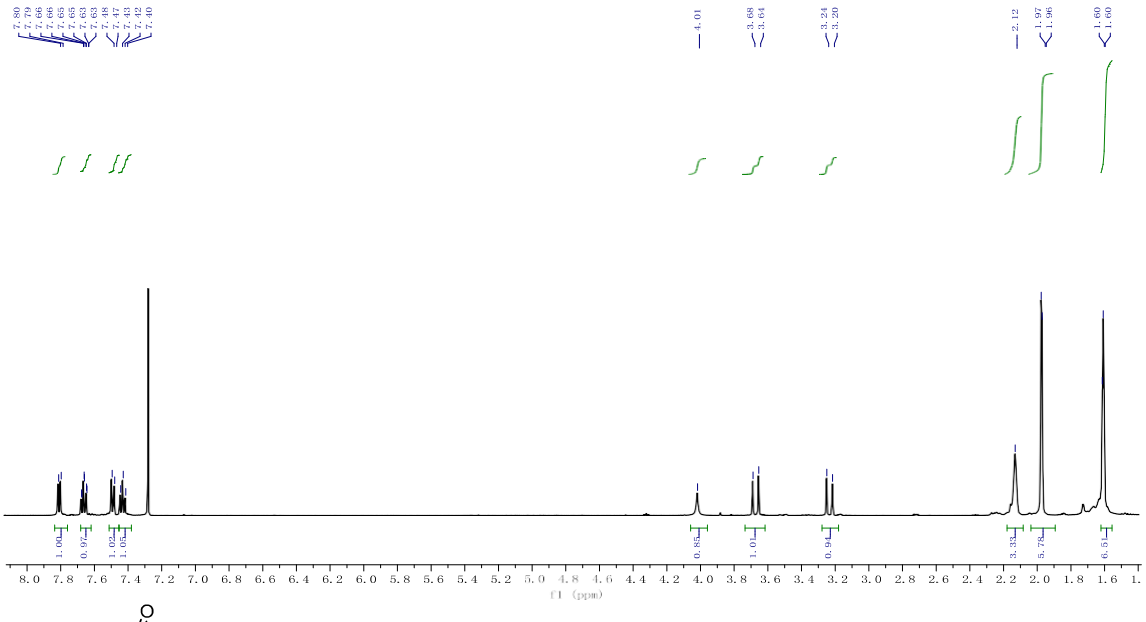
3p

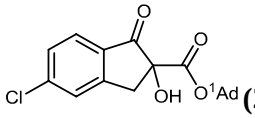




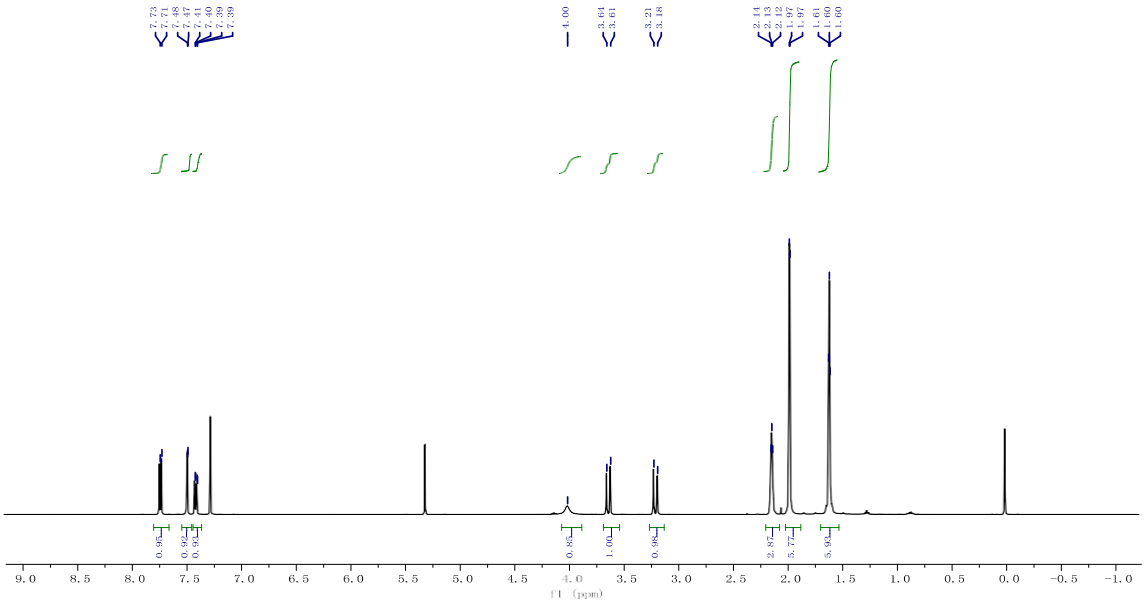


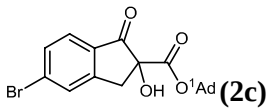
(2a)



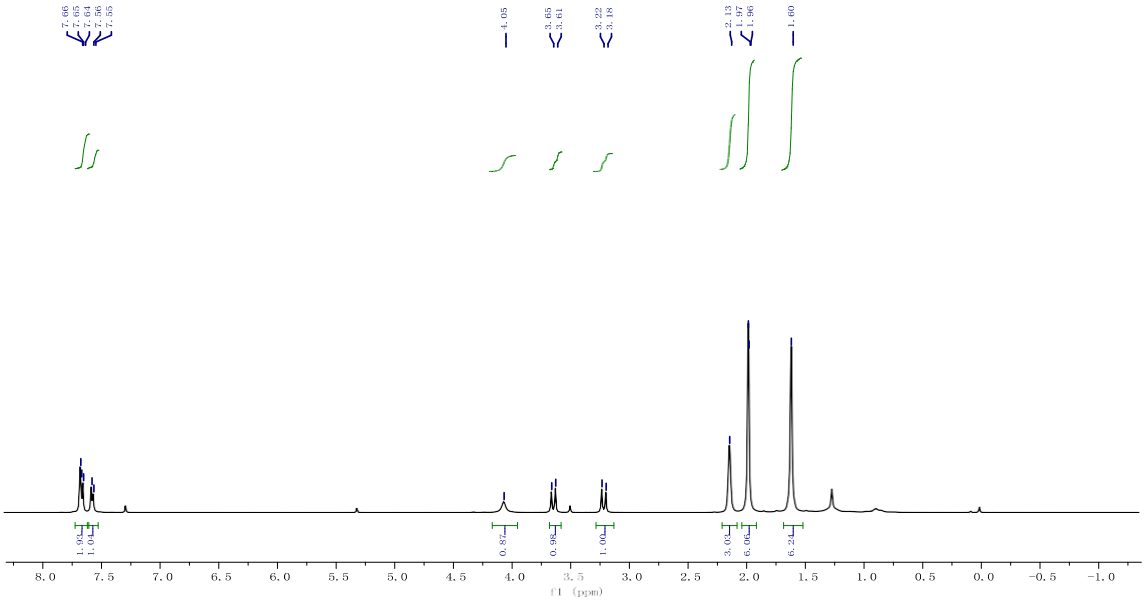


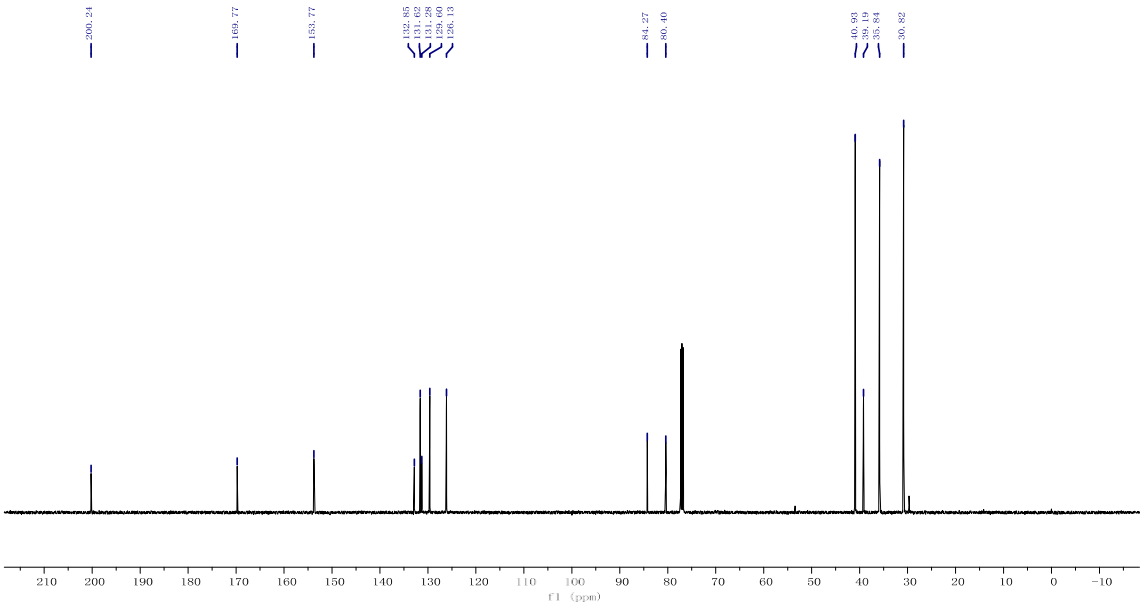
(2b)



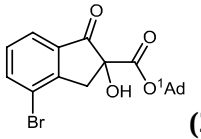

O
O
Br
OH
O1Ad

(2c)

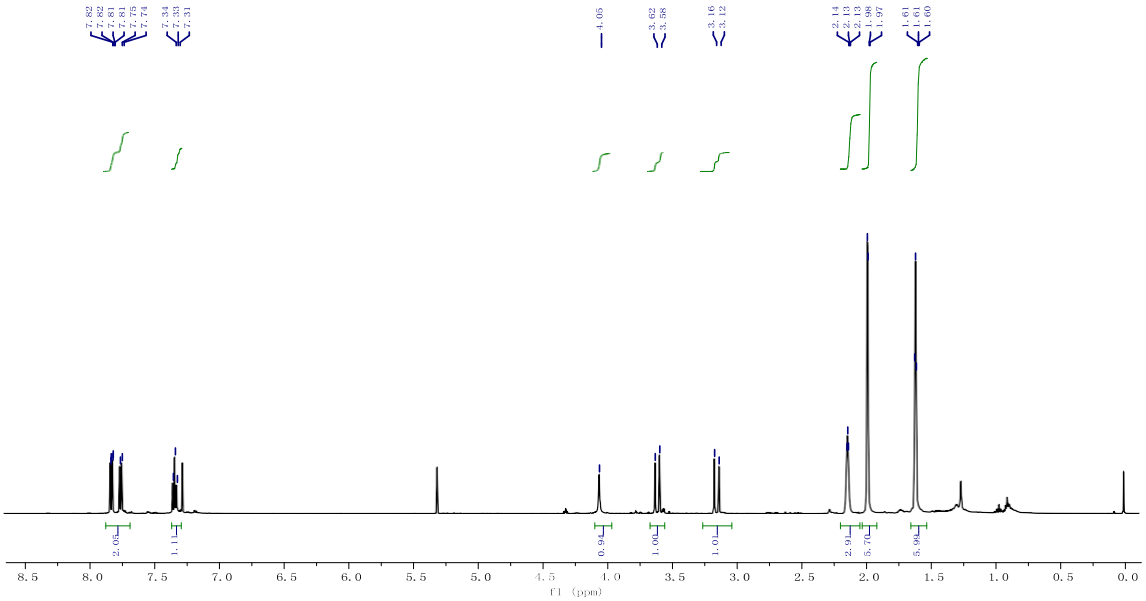

7.66
7.65
7.64
7.56
7.55
4.05
3.65
3.61
3.22
3.18
2.13
1.97
1.96
1.60
1.93
1.04
0.87
0.98
1.00
3.03
6.06
6.24
f1 (ppm)

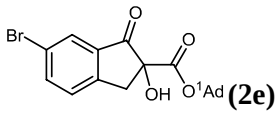

200.24
169.77
153.77
132.85
131.62
131.28
129.60
126.13
84.27
80.40
40.93
39.19
35.84
30.82
f1 (ppm)

(2c)

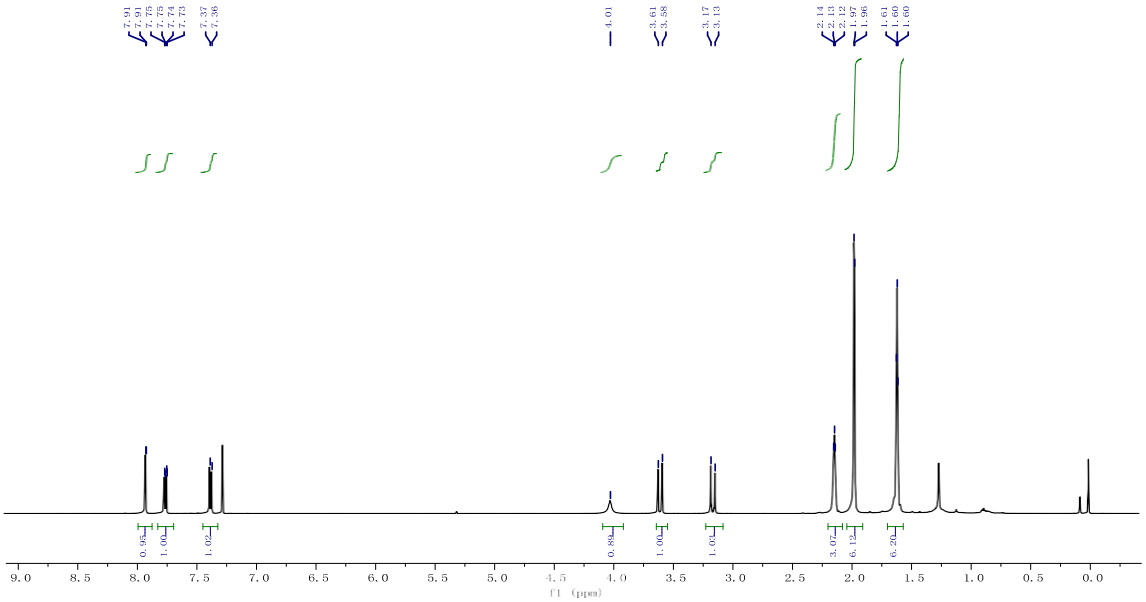

O
O
OH
O1Ad
Br

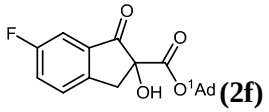
(2d)


7.82
7.82
7.81
7.81
7.75
7.74
7.34
7.33
7.31
4.05
3.62
3.58
3.16
3.12
2.14
2.13
2.13
1.98
1.97
1.61
1.61
1.60
2.06
1.11
0.94
1.00
1.01
2.91
5.70
5.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

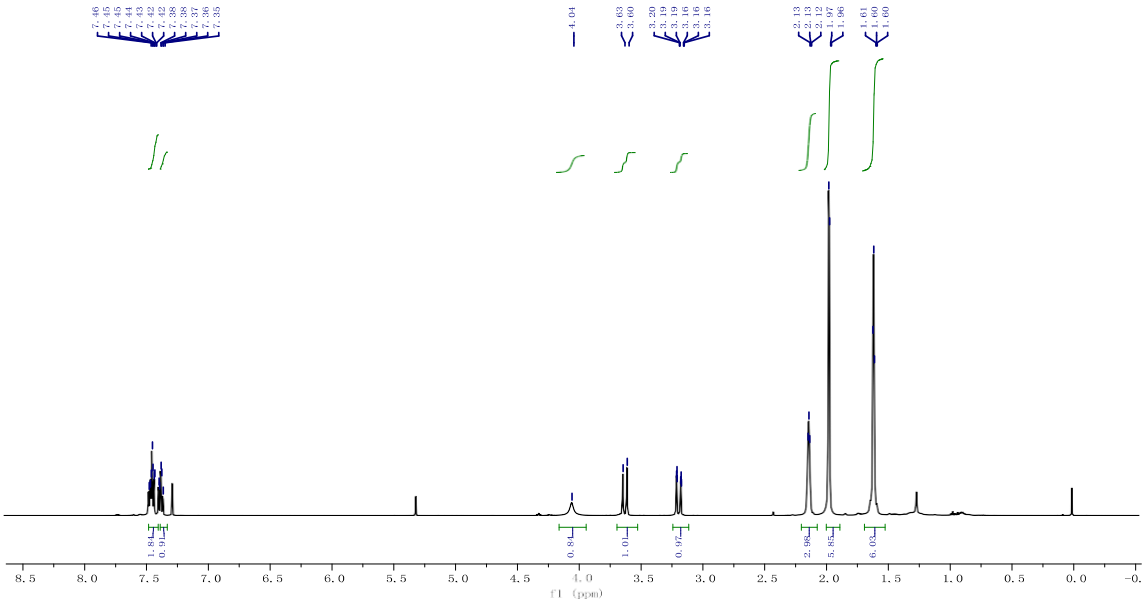

O
O
Br
OH
O1Ad

(2e)


7.91
7.91
7.75
7.75
7.74
7.73
7.37
7.36
4.01
3.61
3.58
3.17
3.13
2.14
2.13
2.12
1.97
1.96
1.61
1.60
1.60
0.96
1.00
1.02
0.88
1.00
1.01
3.07
6.12
6.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


F
O
O
OH
O
1Ad

(2f)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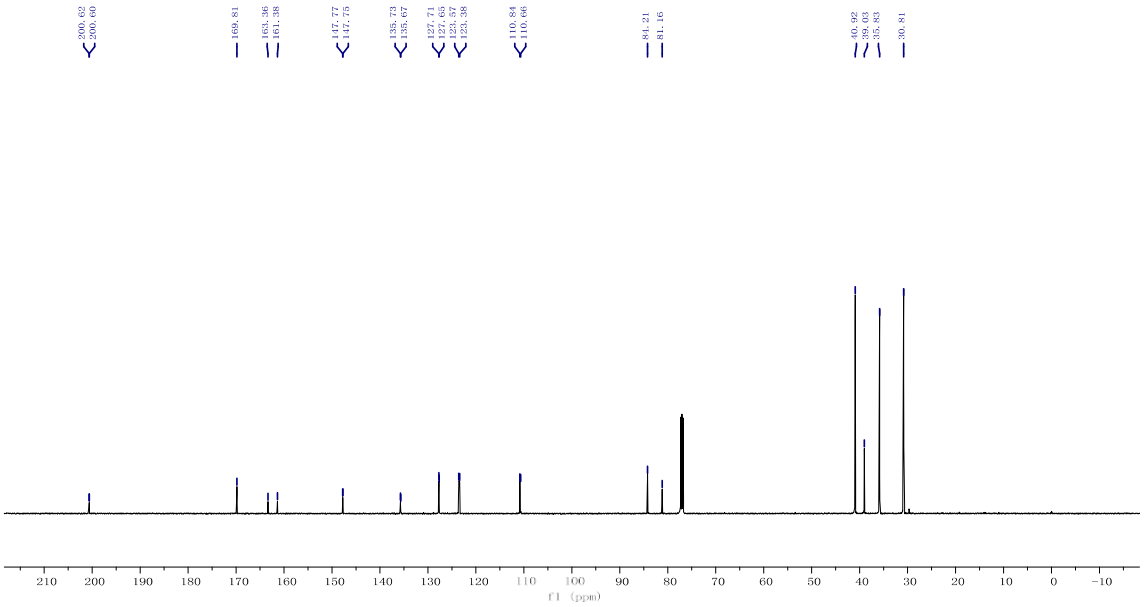
7.45
7.44
7.43
7.42
7.38
7.38
7.37
7.36
7.35
4.04
3.63
3.60
3.20
3.19
3.18
3.16
3.16
3.16
2.13
2.13
2.12
1.97
1.96
1.61
1.60
1.60
1.84
0.91
0.84
1.01
0.97
2.98
5.85
6.03
f1 (ppm)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200.60
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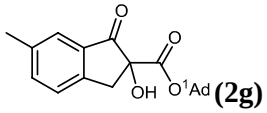
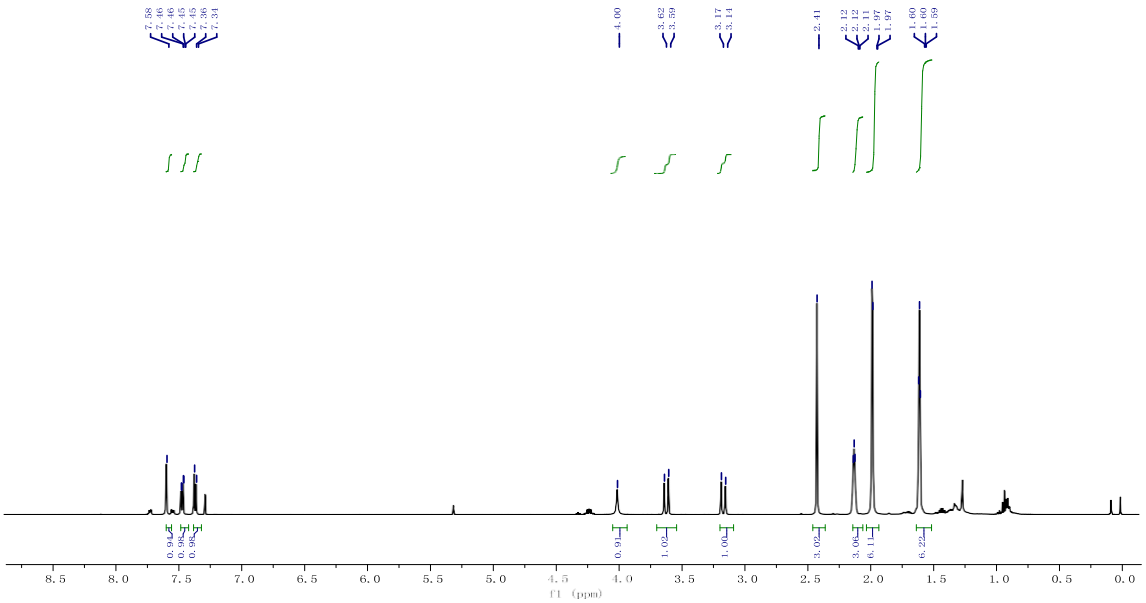
163.36
161.38
147.77
147.75
135.73
135.67
127.71
127.65
123.97
123.38
110.84
110.66
84.21
81.16
40.92
39.03
35.83
30.81
f1 (ppm)


O
O
OH
O
1Ad

(2g)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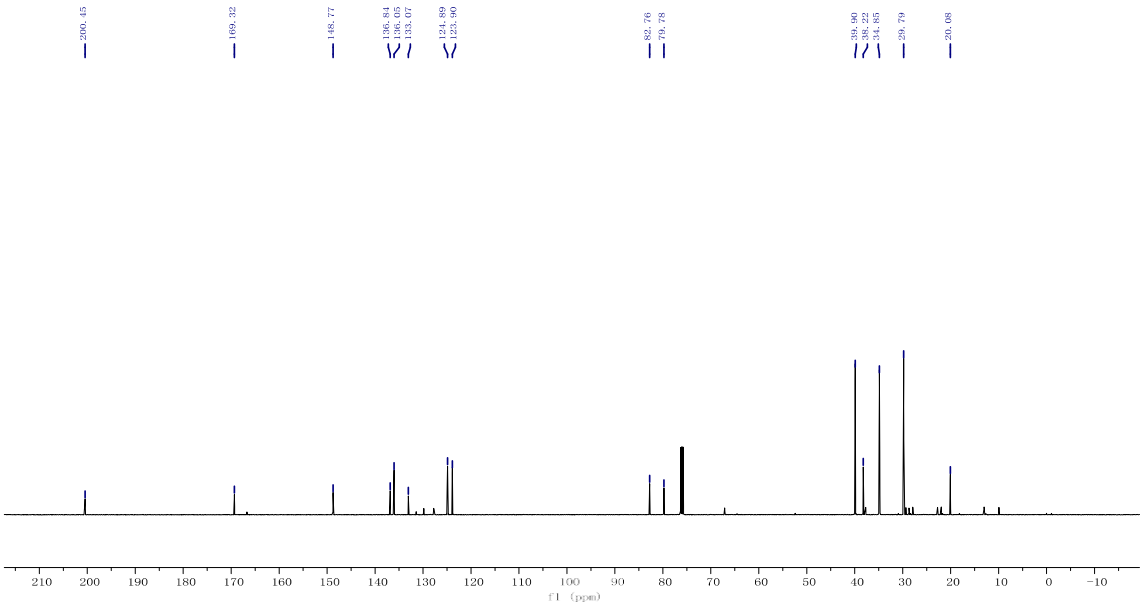
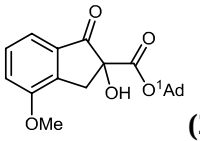
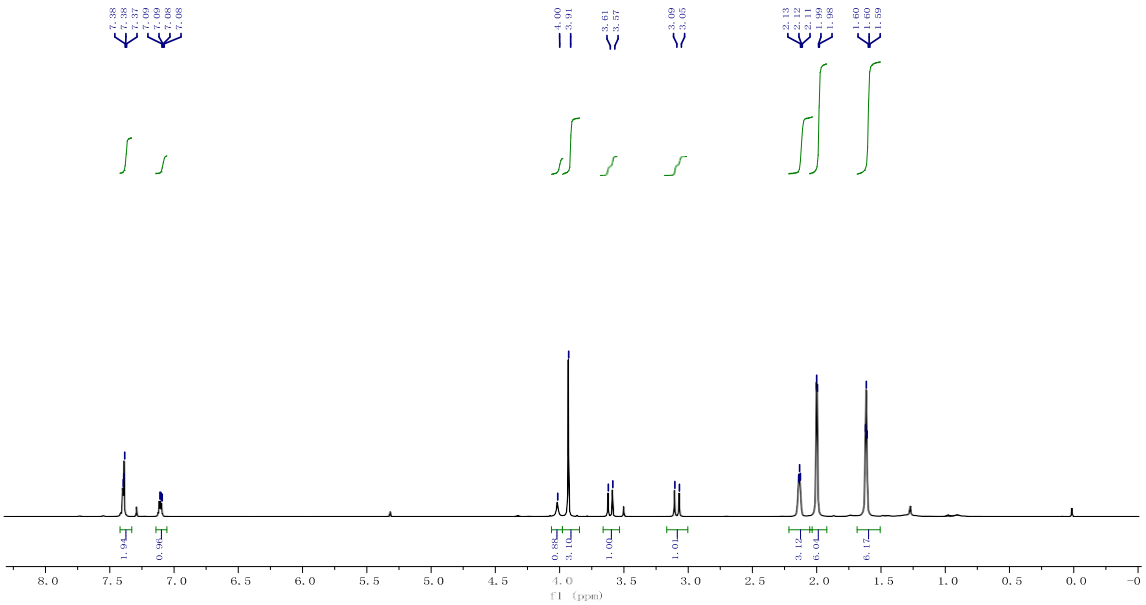
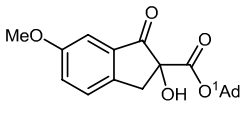
7.46
7.46
7.45
7.45
7.36
7.34
4.00
3.62
3.59
3.17
3.14
2.41
2.12
2.12
2.11
1.97
1.97
1.60
1.60
1.59
0.94
0.98
0.98
0.91
1.02
1.00
3.02
3.06
6.11
6.22
f1 (ppm)


200.45
169.32
148.77
136.84
136.05
133.07
124.89
123.90
82.76
79.78
39.90
38.22
34.85
29.79
20.08
f1 (ppm)

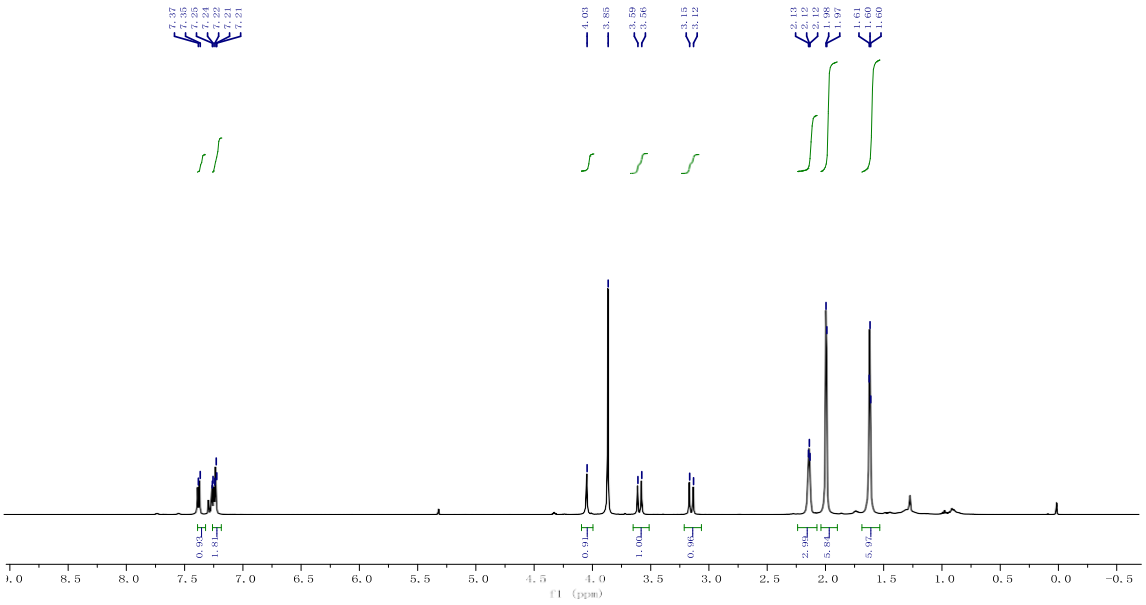


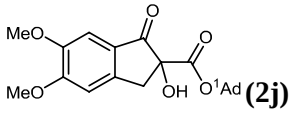
(2h)



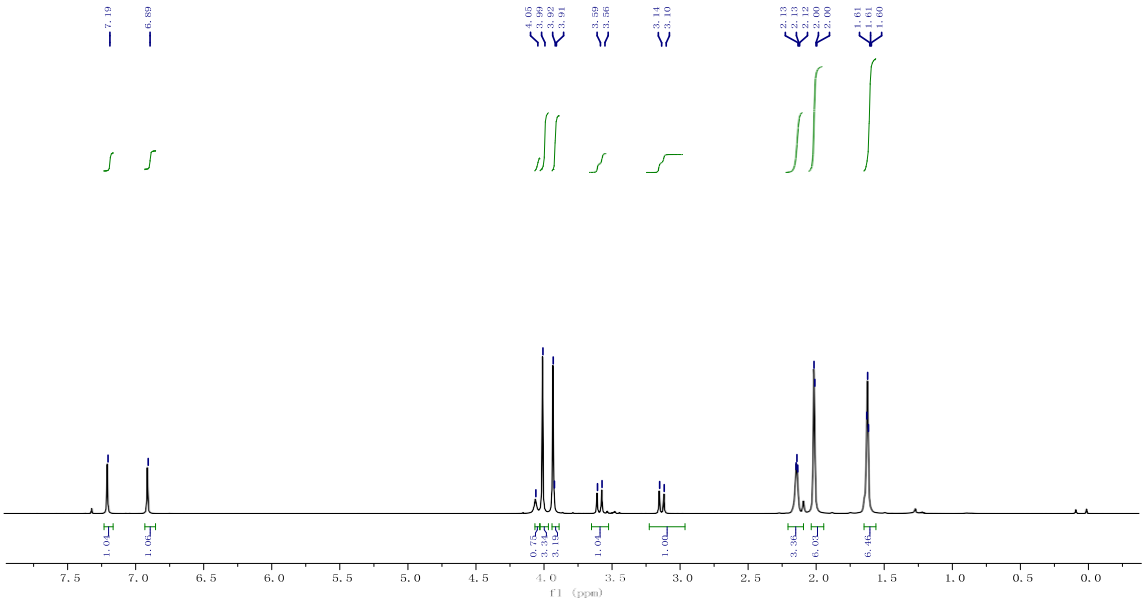


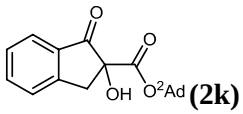
(2i)



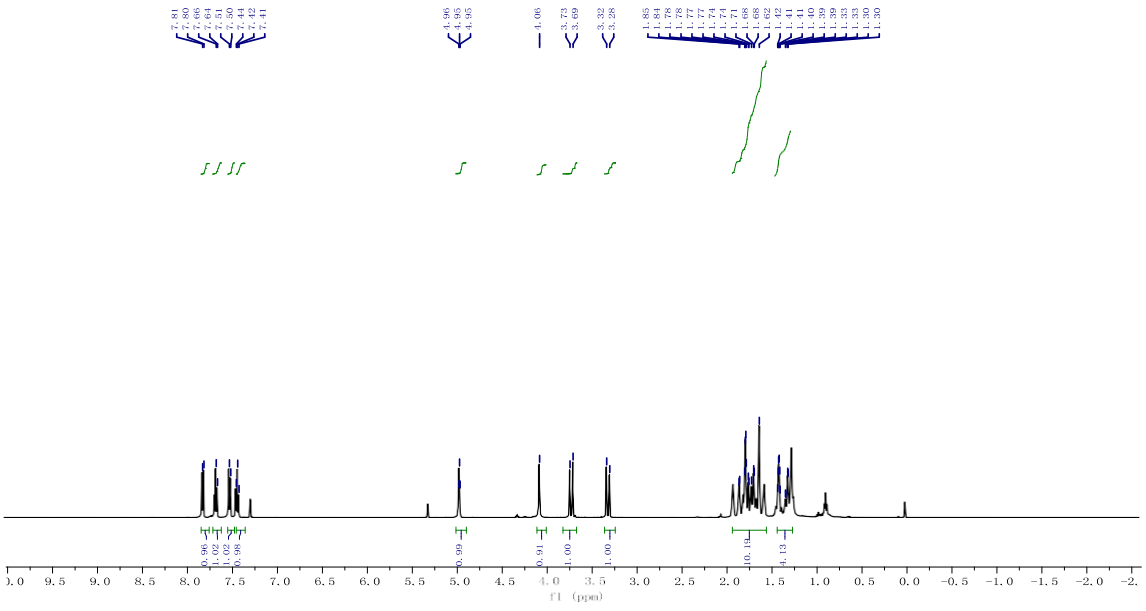


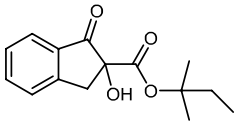
(2j)



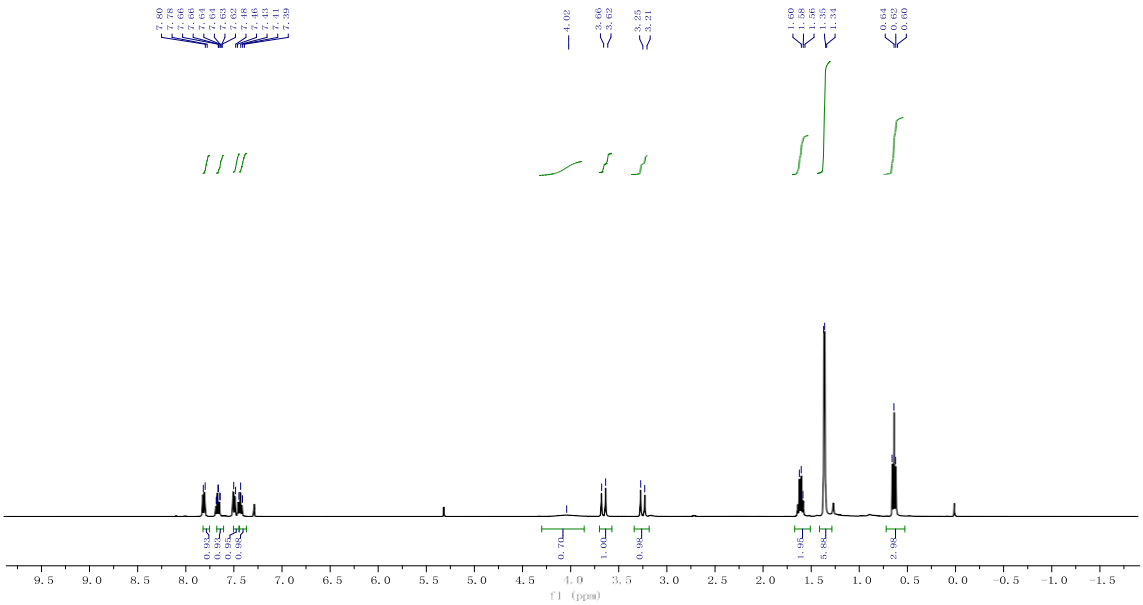


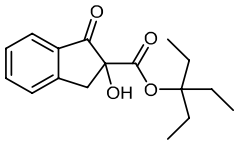
(2k)



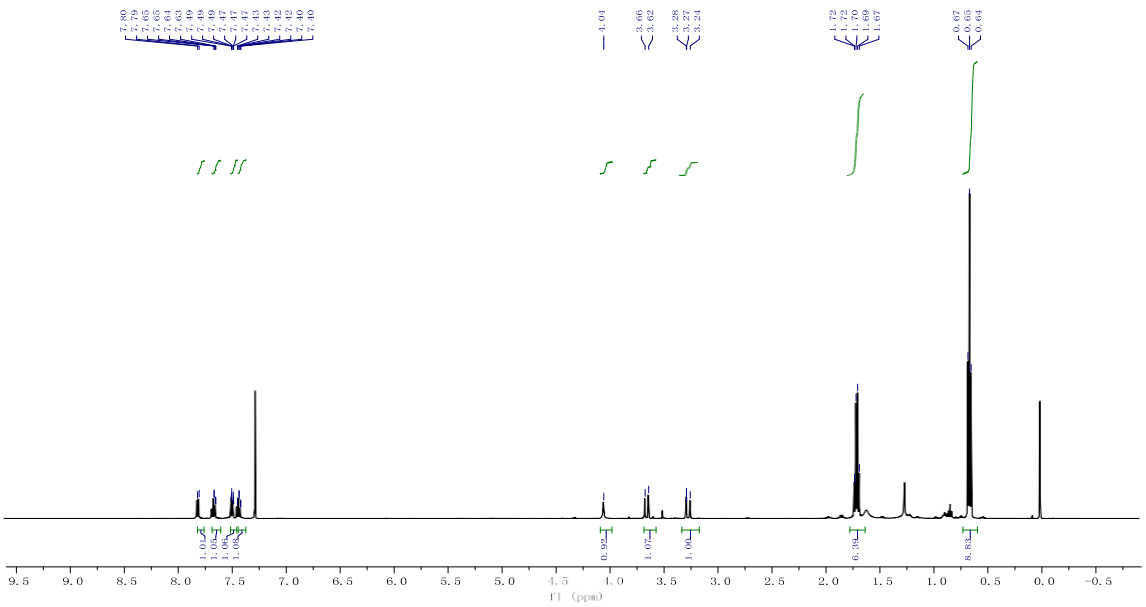

O
O
OH
O

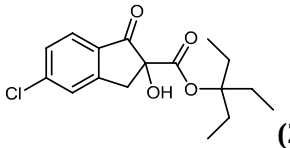
(2l)


7.89
7.78
7.66
7.64
7.63
7.62
7.48
7.46
7.45
7.41
7.39
4.02
3.66
3.62
3.25
3.21
1.60
1.58
1.56
1.35
1.34
0.64
0.62
0.60
0.95
0.95
0.95
0.98
0.70
1.00
0.98
1.98
5.84
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

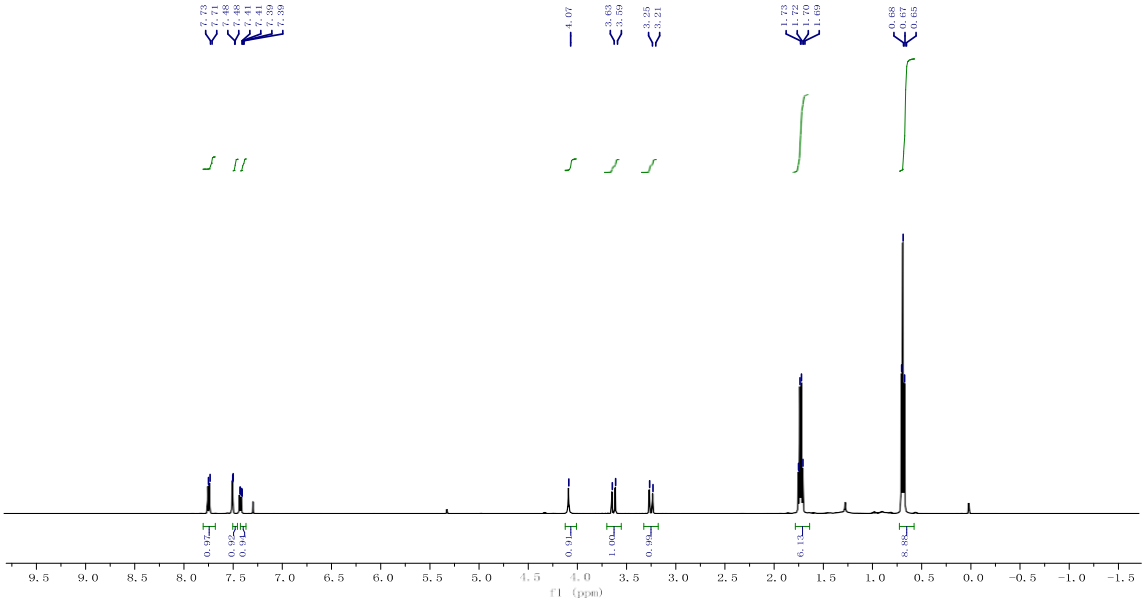

O
O
OH
O

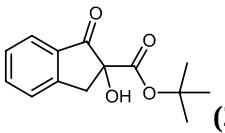
(2m)


7.80
7.79
7.65
7.64
7.63
7.49
7.49
7.47
7.47
7.43
7.43
7.42
7.40
7.40
4.04
3.66
3.62
3.28
3.27
3.24
1.72
1.72
1.70
1.69
1.67
0.67
0.65
0.64
1.01
1.03
1.06
1.08
0.92
1.07
1.00
6.39
8.83
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

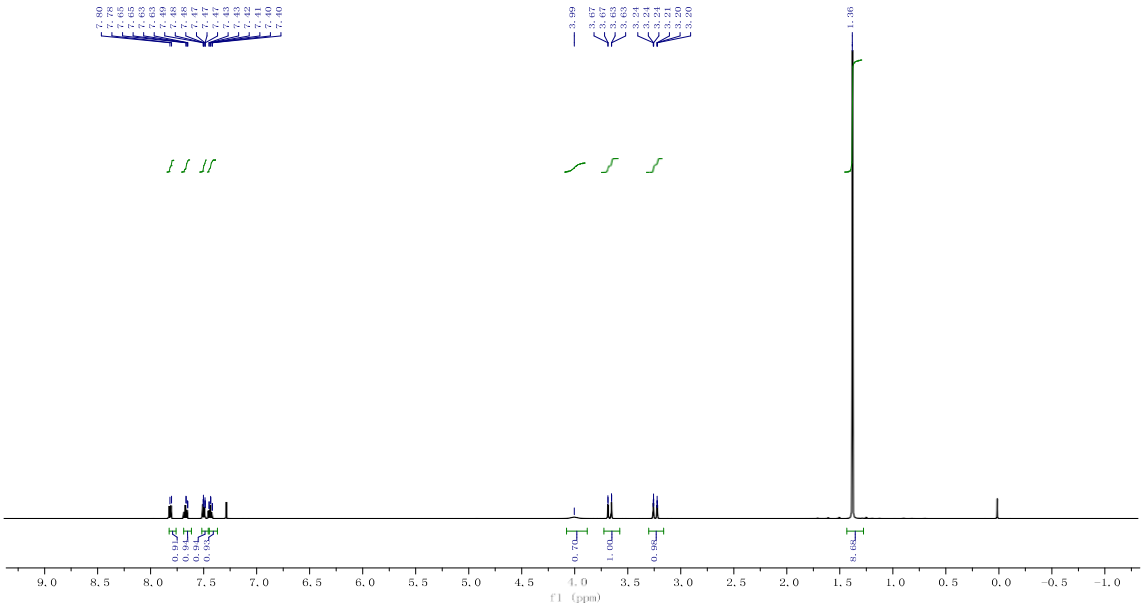

O
O
Cl
OH
O

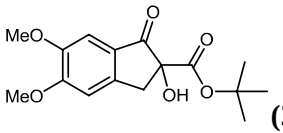
(2n)


7.73
7.71
7.48
7.48
7.41
7.39
7.39
4.07
3.63
3.59
3.25
3.21
1.73
1.72
1.70
1.69
0.68
0.67
0.65
0.97
0.92
0.94
0.91
1.00
0.99
6.13
8.88
f1 (ppm)

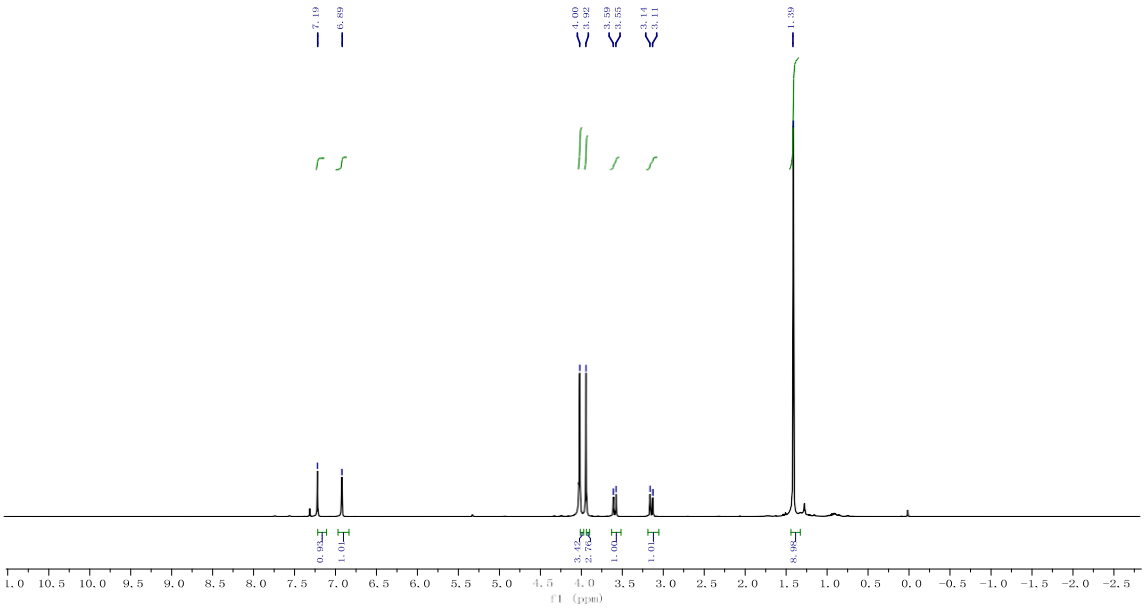

O
O
OH
O

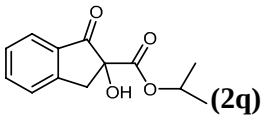
(2o)


7.80
7.78
7.65
7.65
7.63
7.63
7.49
7.48
7.47
7.47
7.43
7.43
7.42
7.41
7.40
7.40
3.99
3.67
3.65
3.63
3.24
3.24
3.21
3.20
3.20
1.36
0.97
0.94
0.94
0.92
0.70
1.00
0.98
8.68
f1 (ppm)

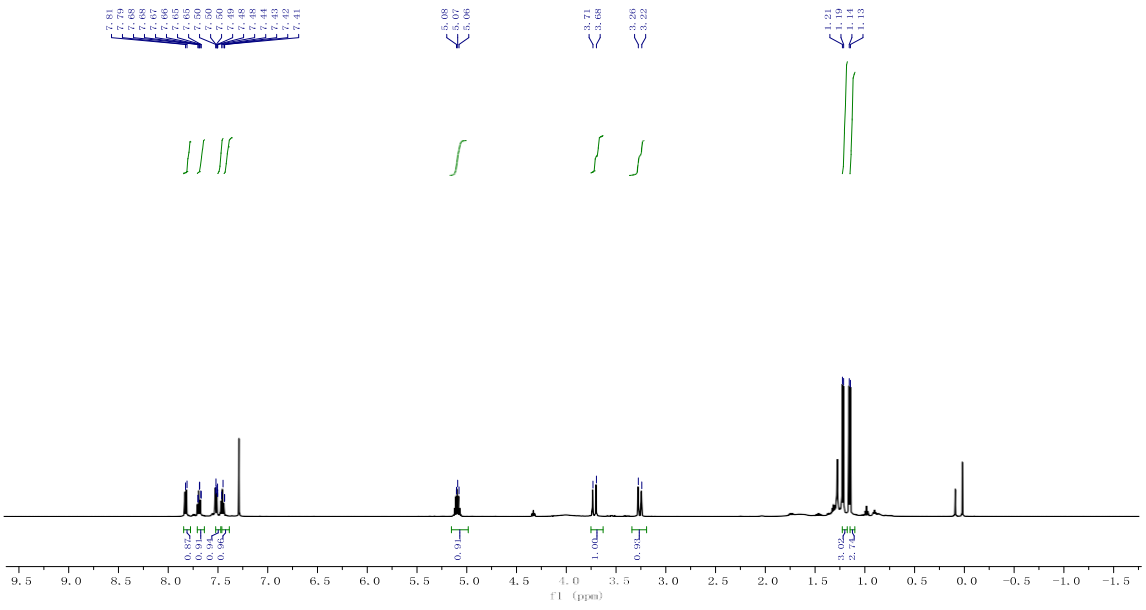

MeO
MeO
O
O
OH
O

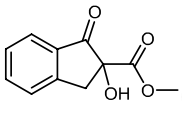
(2p)


7.19
6.89
4.00
3.92
3.59
3.55
3.14
3.11
1.39
f1 (ppm)

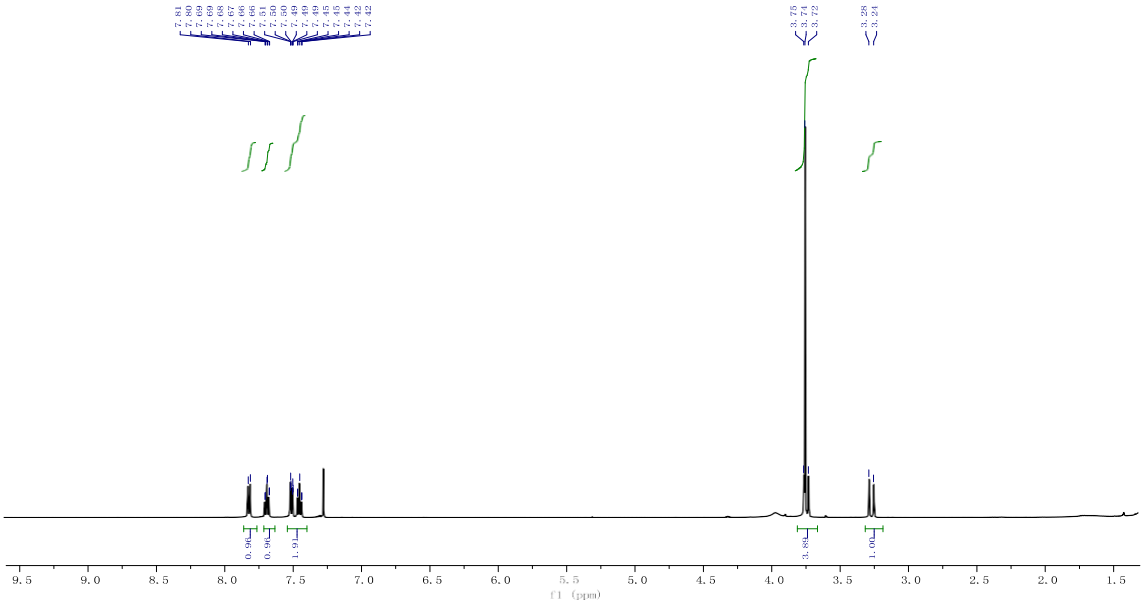

O
O
OH
O

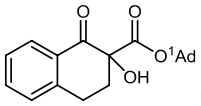
(2q)


7.81
7.79
7.68
7.66
7.65
7.65
7.50
7.50
7.49
7.48
7.46
7.44
7.43
7.42
7.41
5.08
5.07
5.06
3.71
3.68
3.98
3.22
1.21
1.19
1.14
1.13
f1 (ppm)

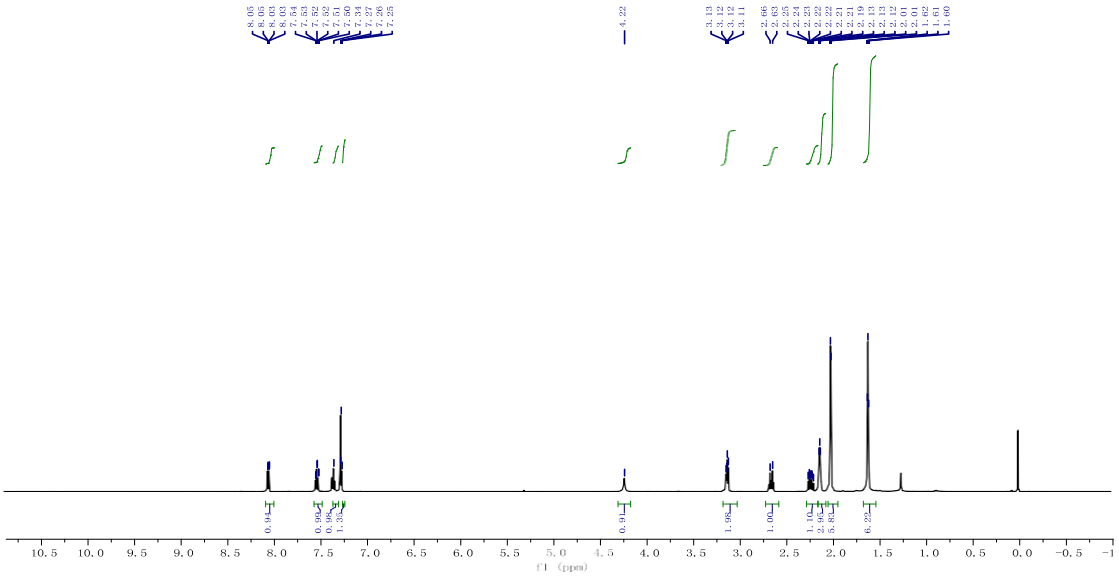


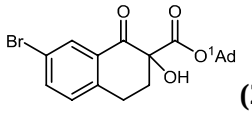
(2r)



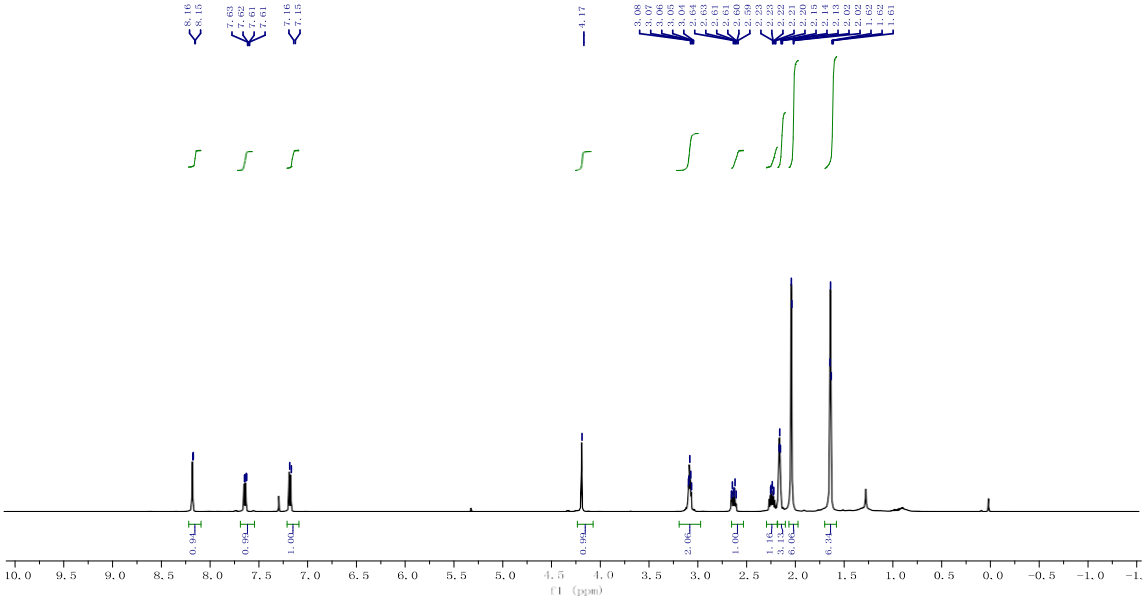


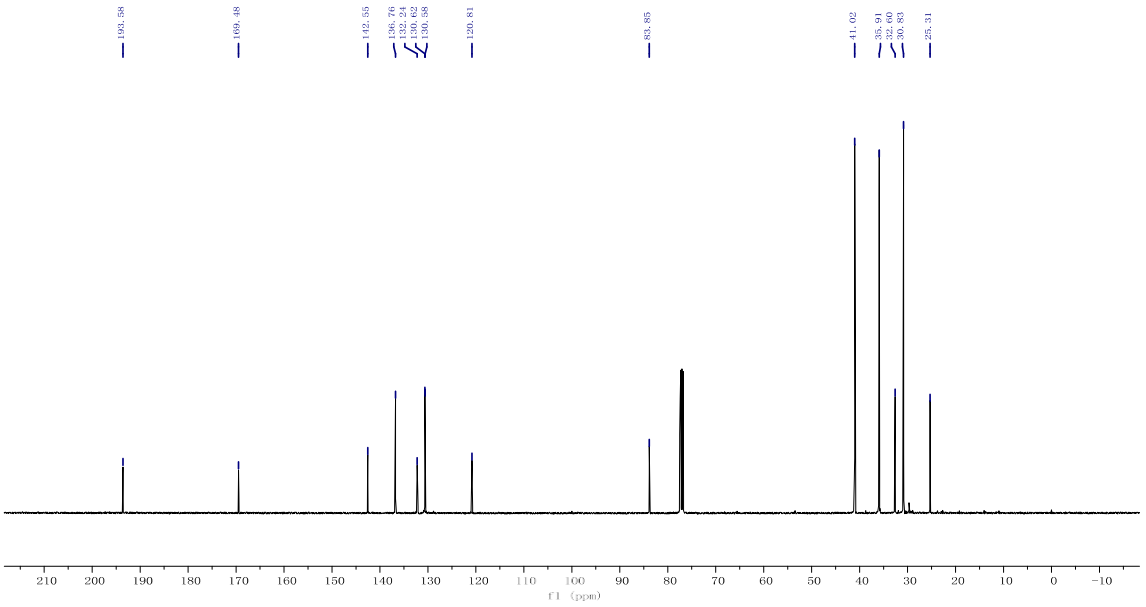
(2s)

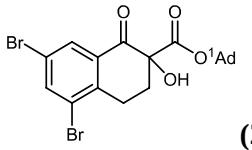



Br
O
O
O
1Ad
OH

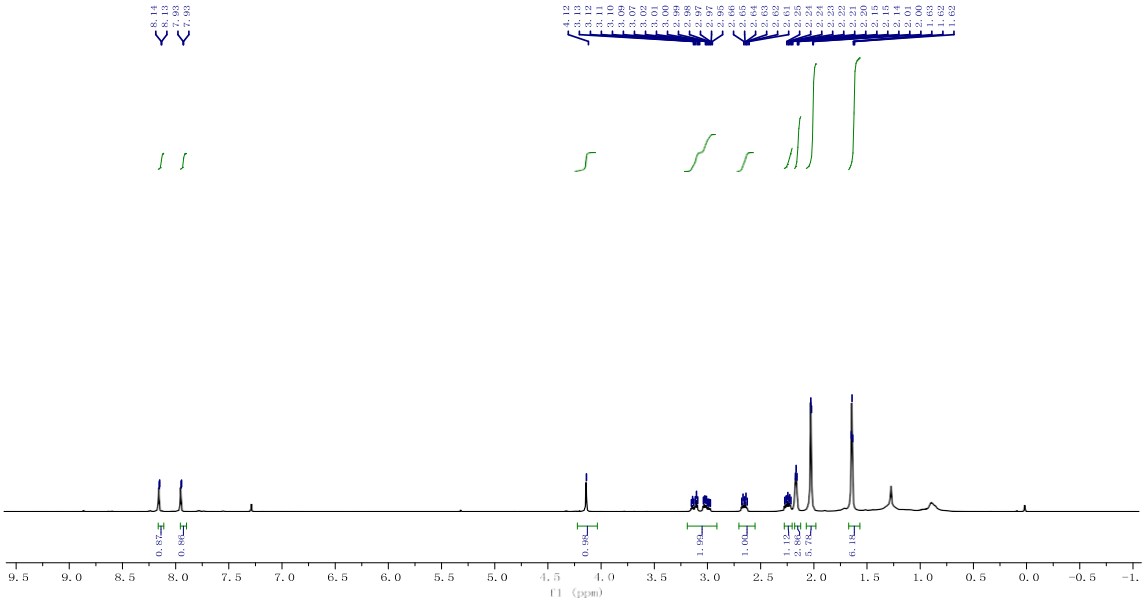
(2t)

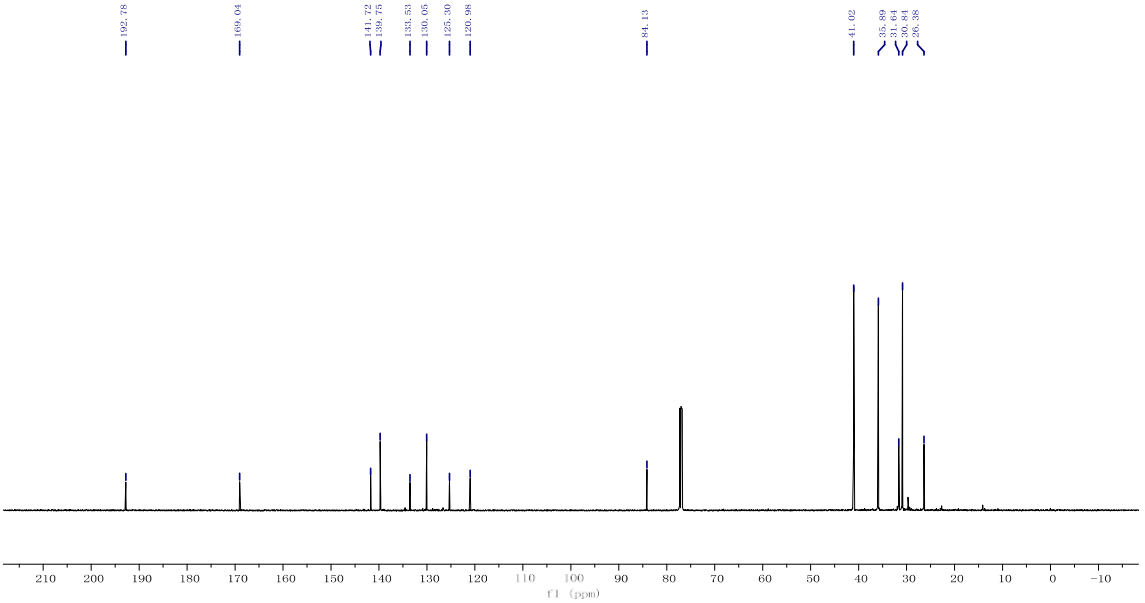

8.16
8.15
7.63
7.62
7.61
7.61
7.16
7.15
4.17
3.08
3.07
3.06
3.05
3.04
2.64
2.63
2.61
2.61
2.60
2.59
2.23
2.23
2.22
2.21
2.20
2.15
2.14
2.13
2.02
2.02
1.62
1.61
0.94
0.96
1.00
0.99
2.06
1.06
1.10
3.13
6.06
6.34
f1 (ppm)

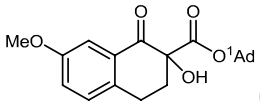

193.58
169.48
142.55
136.76
132.24
130.62
130.58
120.81
83.85
41.02
35.91
32.60
30.83
25.31
f1 (ppm)



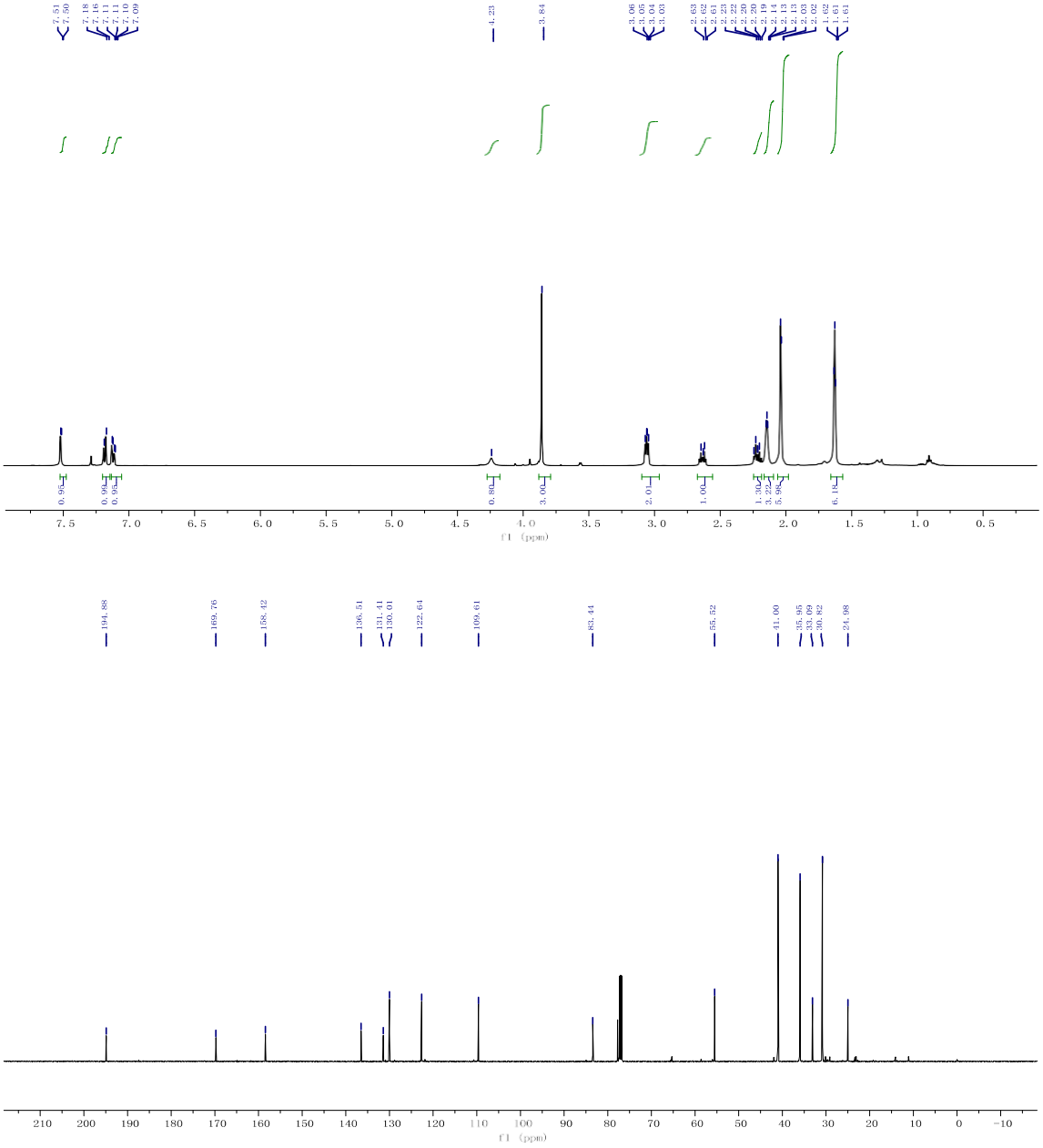
(2u)

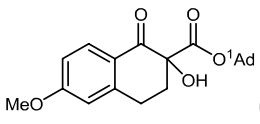




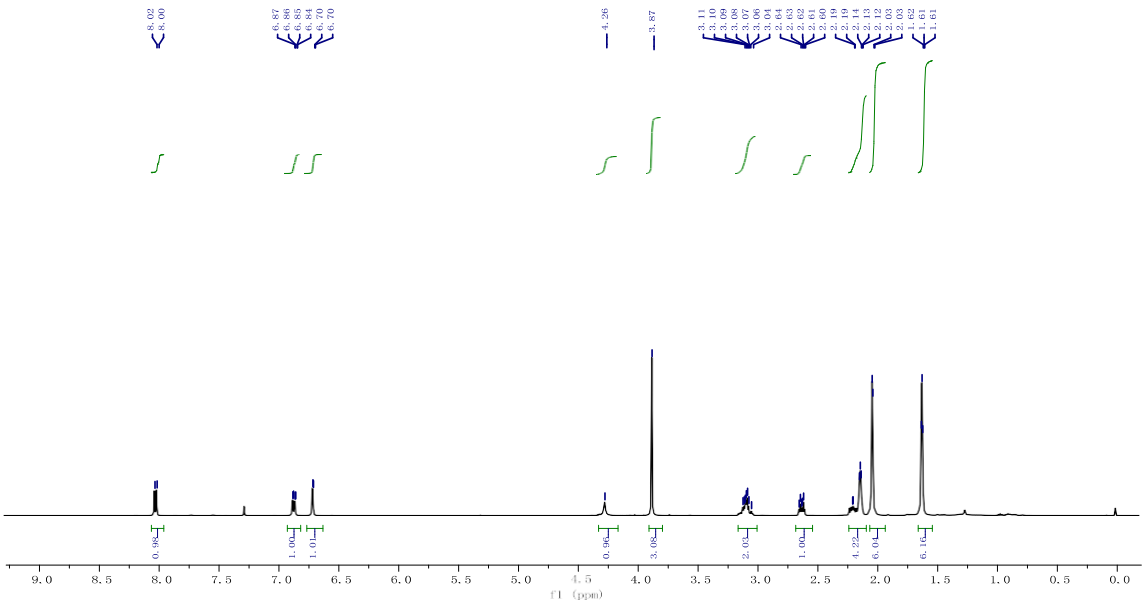

MeO
O
O
O
O1Ad
OH

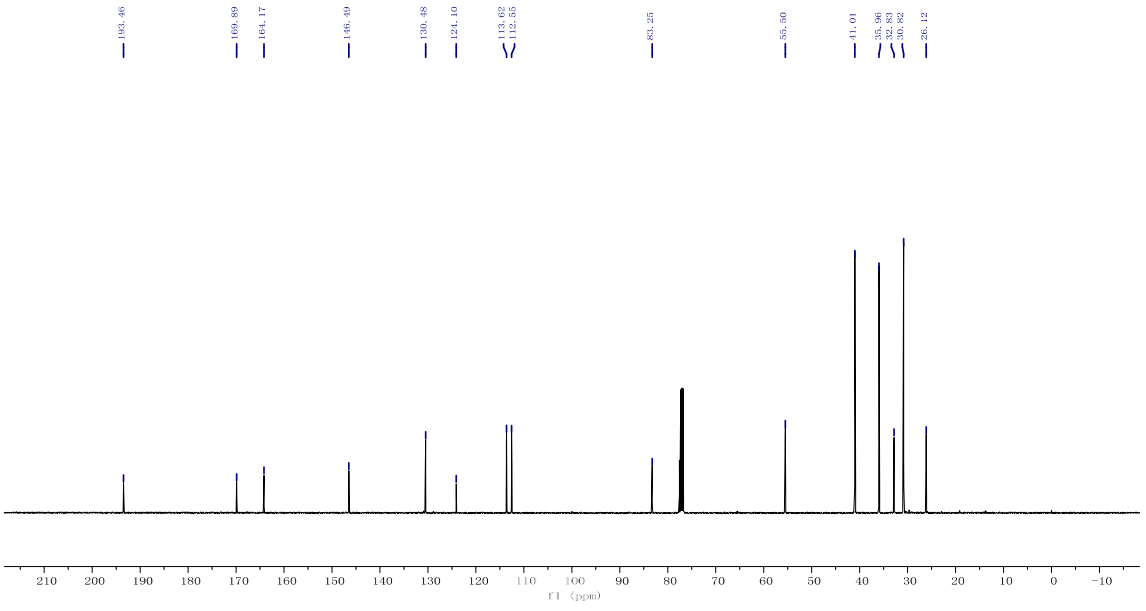
(2v)

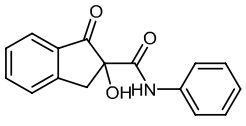

7.51
7.50
7.18
7.16
7.11
7.11
7.10
7.09
4.23
3.84
3.06
3.05
3.04
3.03
2.63
2.62
2.61
2.23
2.22
2.20
2.20
2.19
2.14
2.13
2.03
2.02
1.62
1.61
1.61
0.95
0.99
0.98
0.86
3.00
2.01
1.00
1.30
5.22
5.98
6.18
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
194.88
169.76
158.42
136.51
131.41
130.01
122.64
109.61
83.44
55.52
41.00
35.95
33.69
30.82
24.98
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
O1Ad
OH
MeO

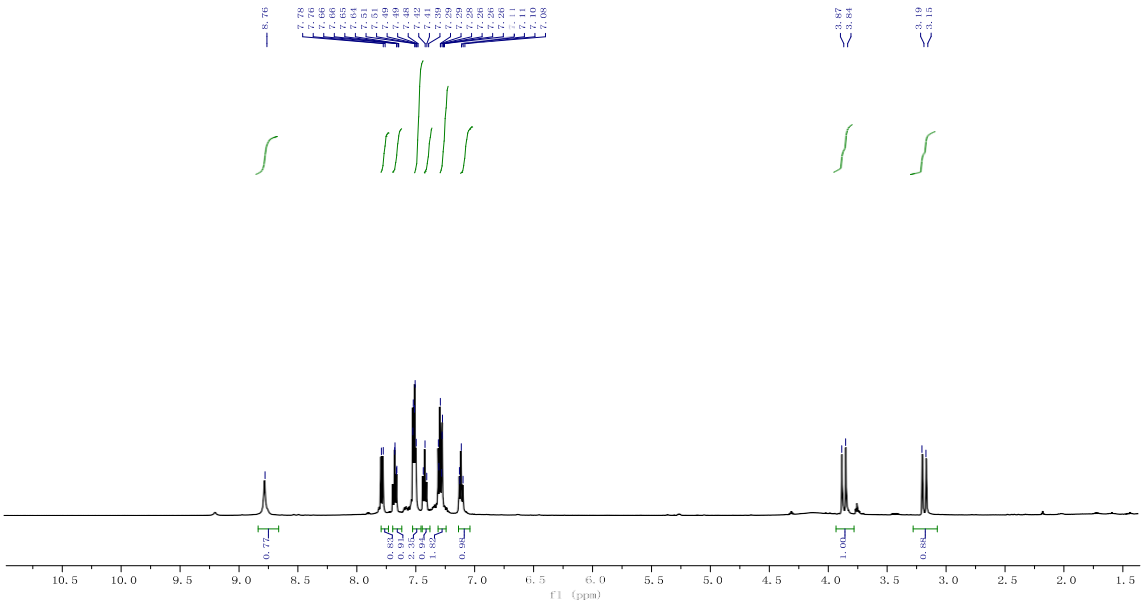
(2w)

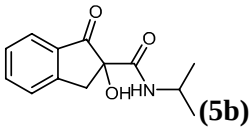

8.02
8.00
6.87
6.86
6.85
6.84
6.70
6.70
4.26
3.87
3.11
3.10
3.09
3.08
3.07
3.06
3.04
2.64
2.63
2.62
2.61
2.60
2.19
2.14
2.13
2.12
2.03
2.02
1.62
1.61
0.98
1.00
1.01
0.96
3.08
2.01
1.00
4.22
6.04
6.16
f1 (ppm)


193.46
169.89
164.17
146.49
130.48
124.10
113.62
112.55
83.25
55.50
41.01
35.96
32.83
30.82
26.12
f1 (ppm)

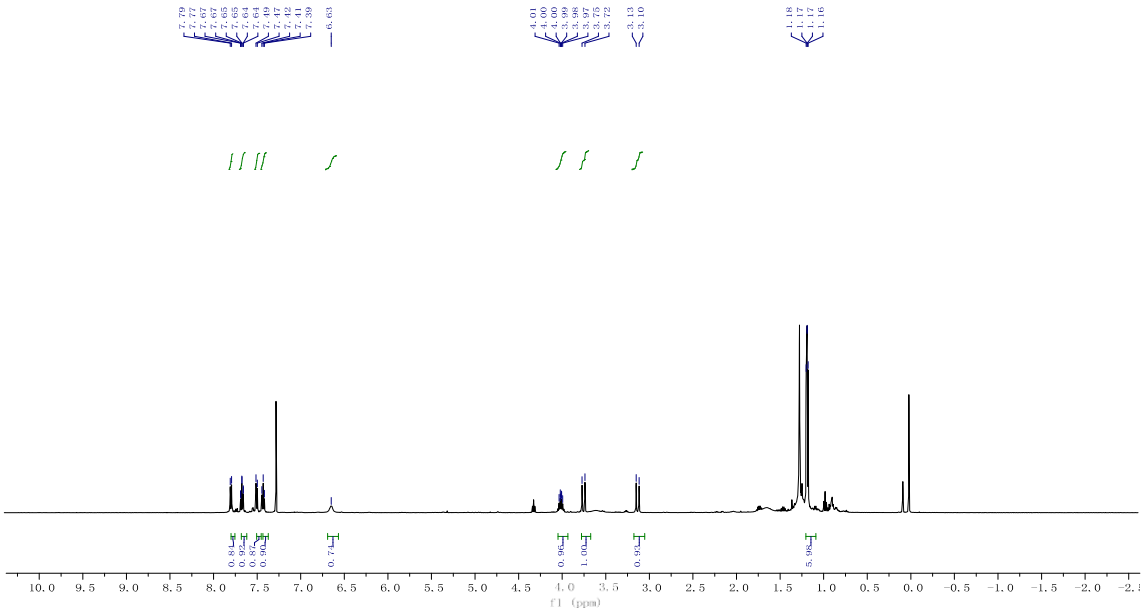


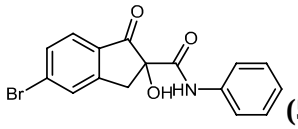
(5a)



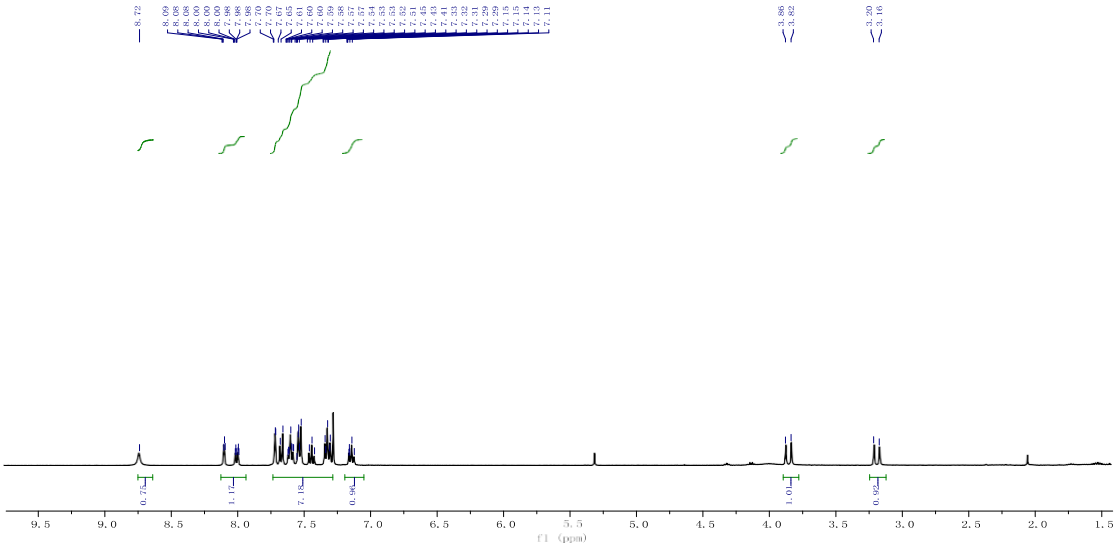


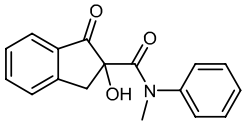
(5b)



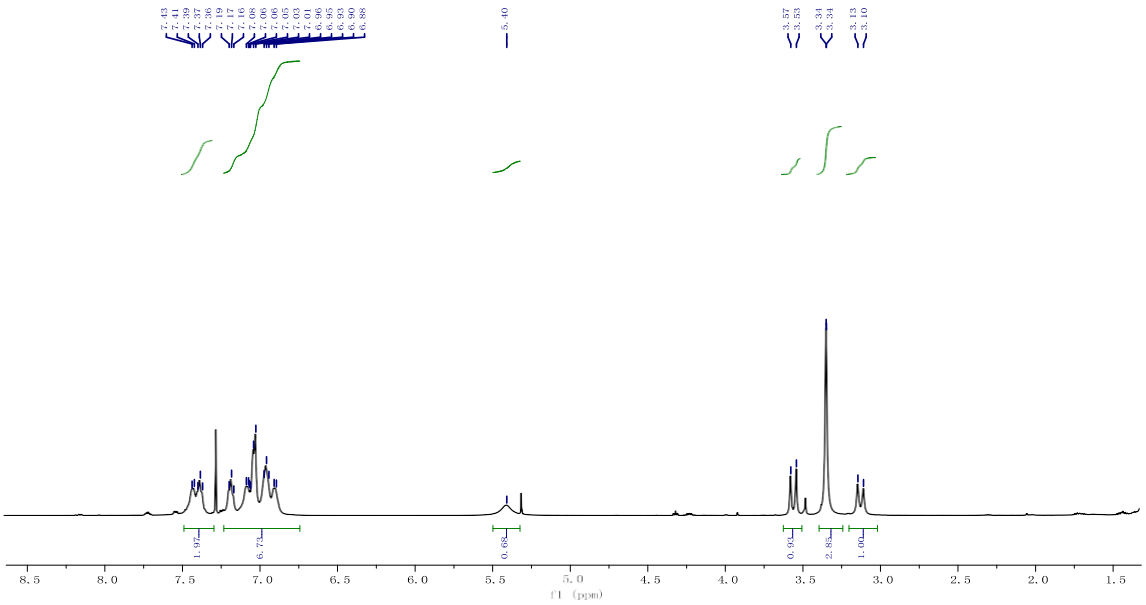

O
O
Br
OH
HN

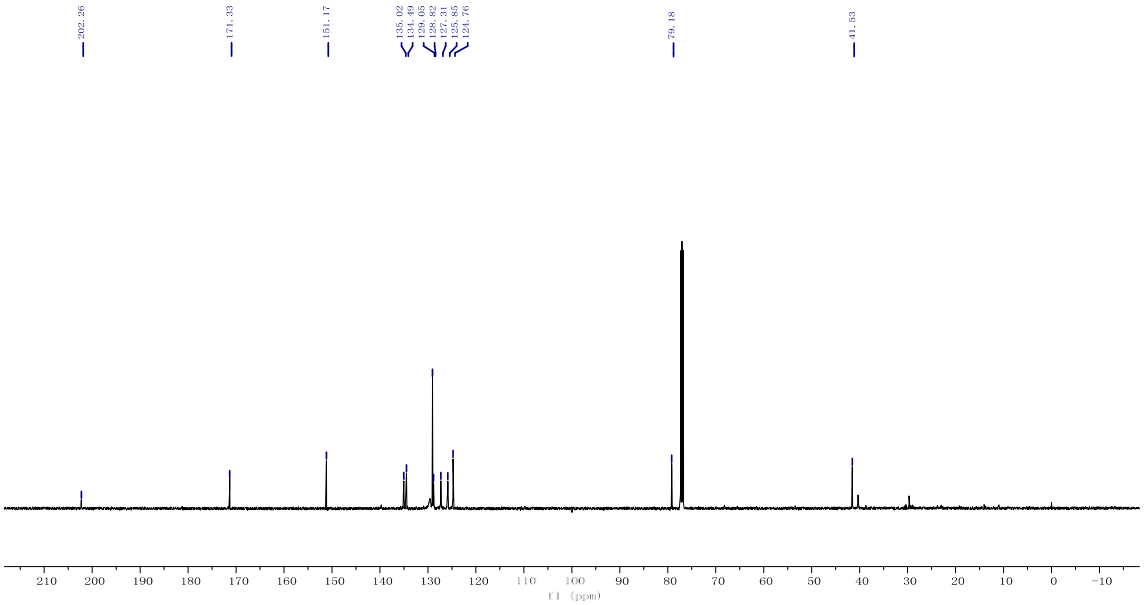
(5c)

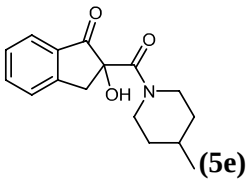

8.72
8.09
8.08
8.08
8.06
8.06
8.00
7.98
7.98
7.70
7.70
7.67
7.65
7.61
7.60
7.60
7.59
7.58
7.57
7.54
7.53
7.53
7.52
7.51
7.45
7.45
7.41
7.33
7.32
7.31
7.29
7.29
7.15
7.15
7.14
7.13
7.11
3.86
3.82
3.20
3.16
0.75
1.17
7.18
0.98
1.01
0.92
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


O
O
OH
N

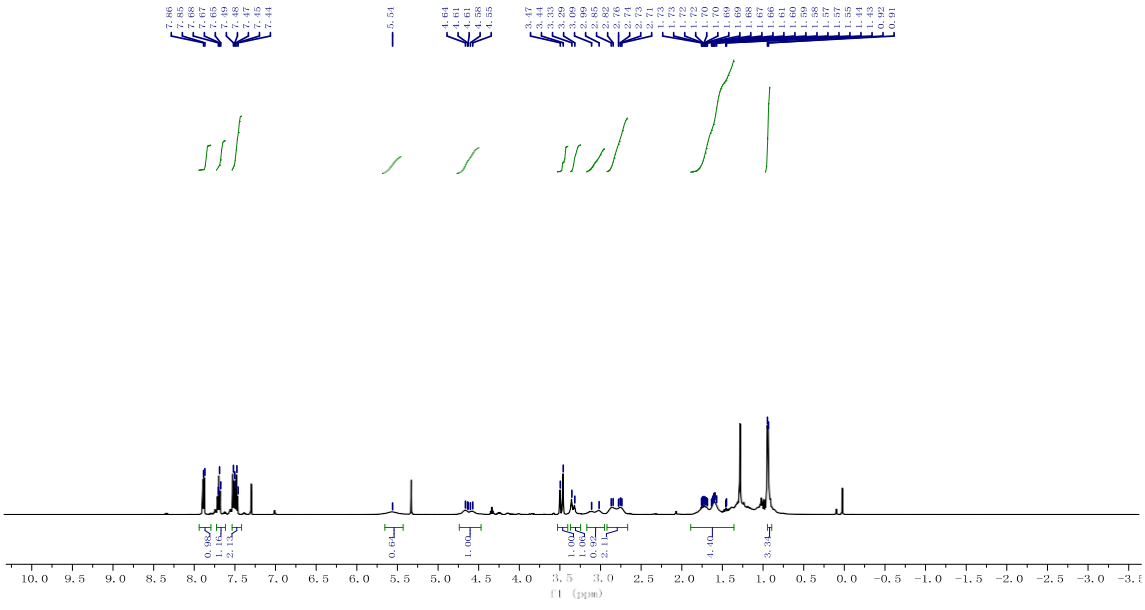
(5d)

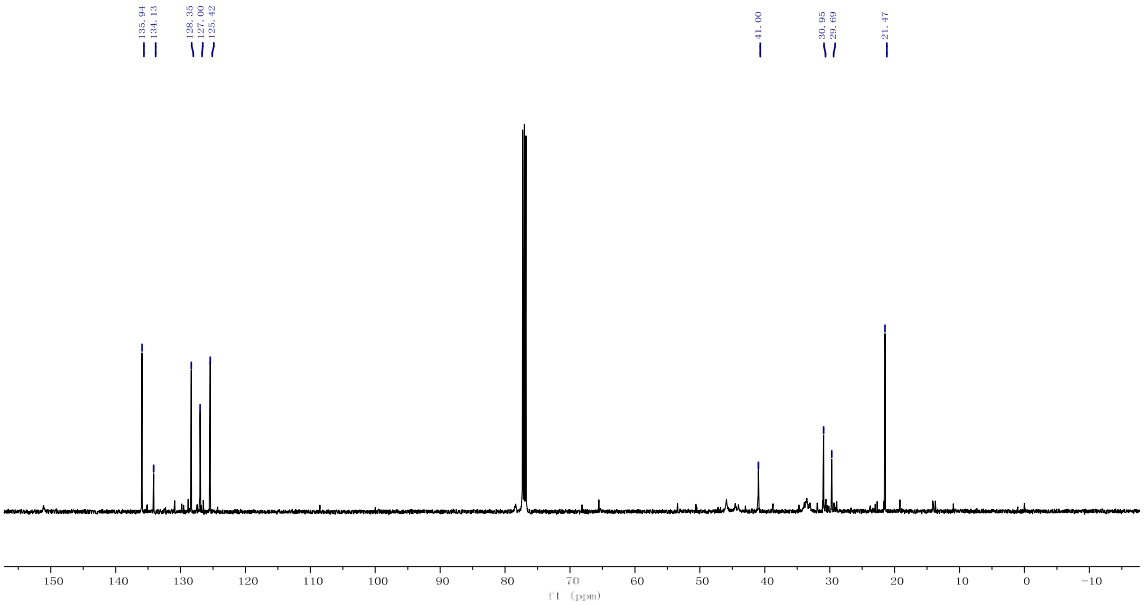

7.43
7.41
7.39
7.37
7.36
7.19
7.17
7.16
7.08
7.06
7.06
7.05
7.03
7.01
6.96
6.95
6.93
6.90
6.88
5.40
3.57
3.53
3.34
3.34
3.13
3.10
1.97
6.73
0.68
0.93
2.85
1.90
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

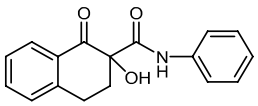

202.26
171.33
151.17
135.02
134.49
129.65
128.82
127.31
125.85
124.76
79.48
41.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
OH
N

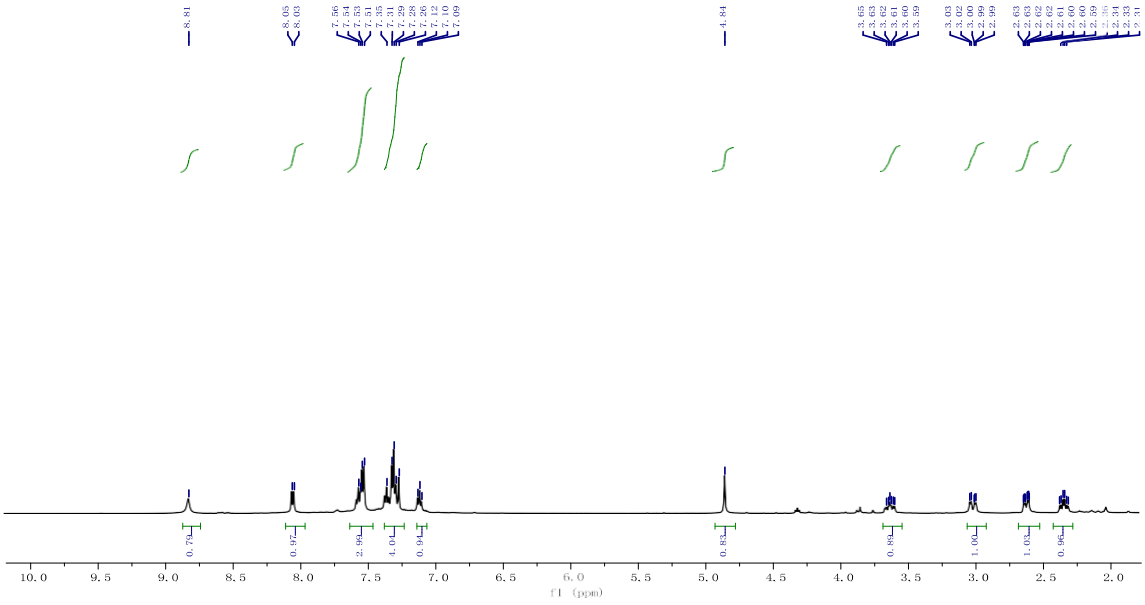
(5e)

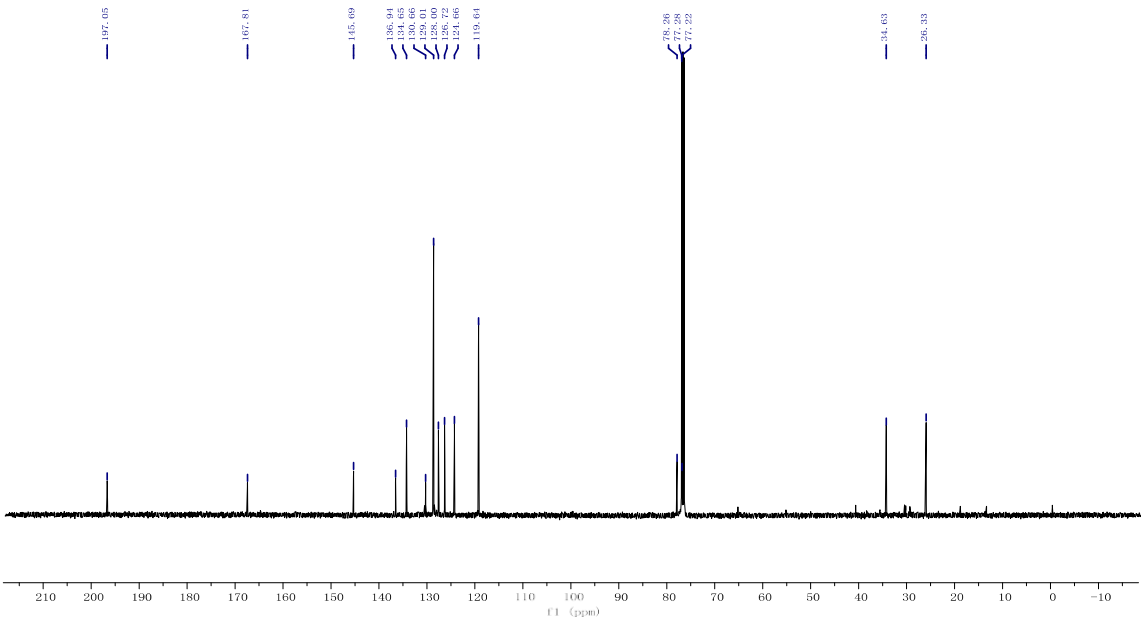

7.86
7.85
7.68
7.67
7.65
7.64
7.48
7.47
7.45
7.44
5.54
4.64
4.61
4.61
4.58
4.55
3.47
3.44
3.33
3.30
3.09
2.99
2.85
2.82
2.76
2.71
2.73
2.71
1.73
1.72
1.72
1.70
1.70
1.69
1.69
1.68
1.67
1.66
1.61
1.60
1.59
1.58
1.57
1.57
1.55
1.44
1.43
0.92
0.91
0.98
1.16
2.13
0.64
1.00
1.00
1.06
0.92
2.14
4.40
3.34
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0
f1 (ppm)

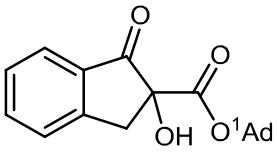

135.94
134.13
128.35
127.00
125.42
41.00
30.95
29.69
21.47
f1 (ppm)


O
O
N
H
OH

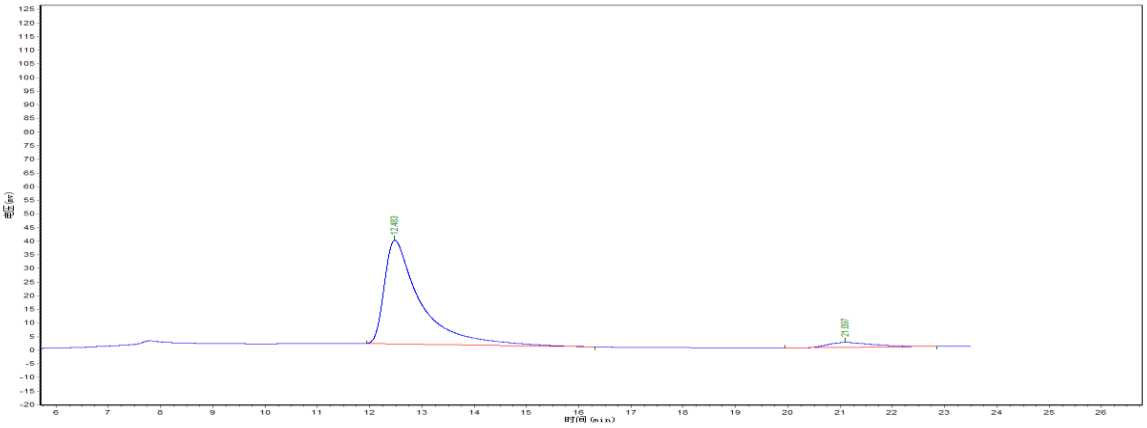
(5f)


8.81
8.05
8.03
7.56
7.54
7.53
7.51
7.35
7.31
7.29
7.28
7.12
7.10
7.09
4.84
3.65
3.63
3.62
3.61
3.60
3.59
3.03
3.02
3.00
2.99
2.99
2.63
2.63
2.62
2.62
2.61
2.60
2.60
2.59
2.35
2.34
2.31
0.70
0.97
2.99
4.01
0.94
0.83
0.88
1.00
1.03
0.98
f1 (ppm)


197.05
167.81
145.69
136.94
134.65
130.66
129.01
128.60
126.72
124.66
119.64
78.26
77.28
77.22
34.63
26.33
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

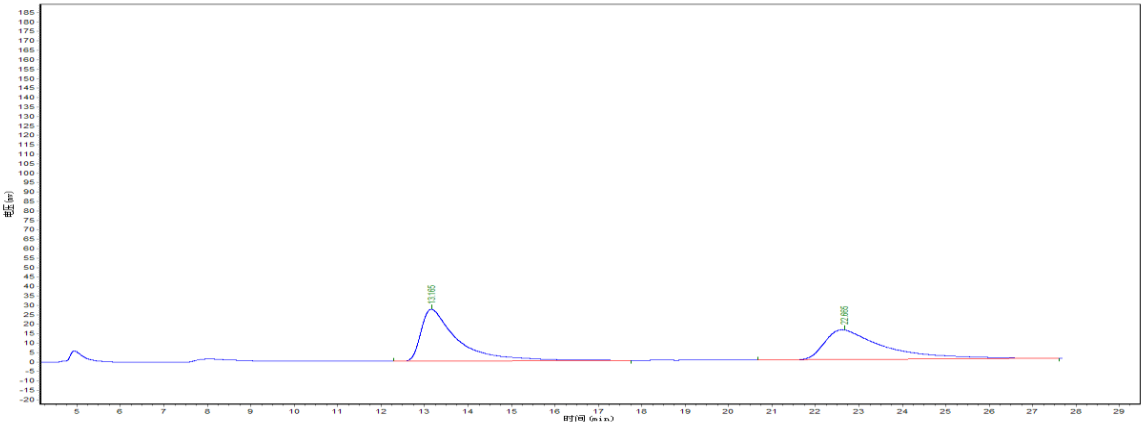


(2a)

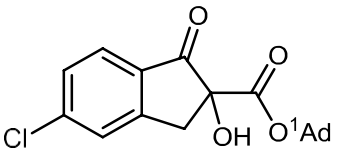


R.Time	Area	Area%
12.483	**2090179.750**	**94.8473**
21.097	**113552.734**	**5.1527**

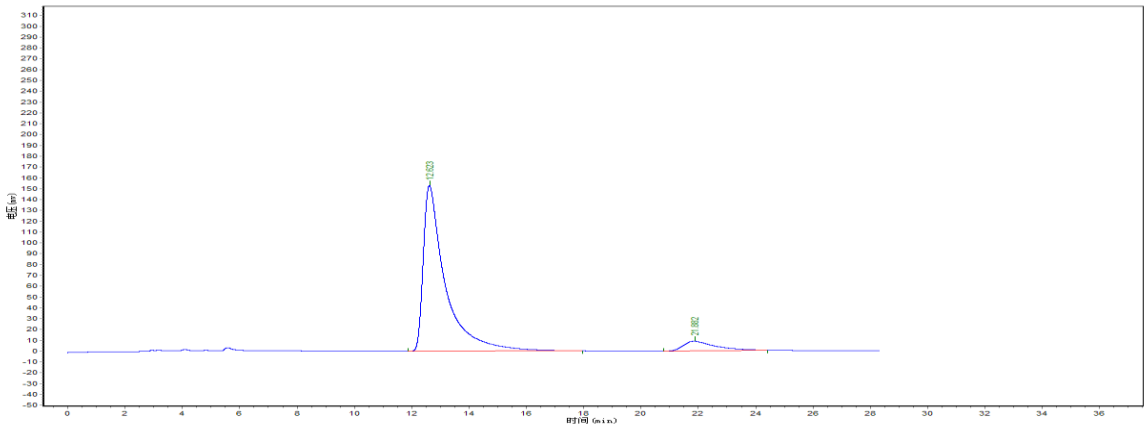
ee=90%



R.Time	Area	Area%
13.165	**1614498.125**	**51.7971**
22.665	**1502466.000**	**48.2029**

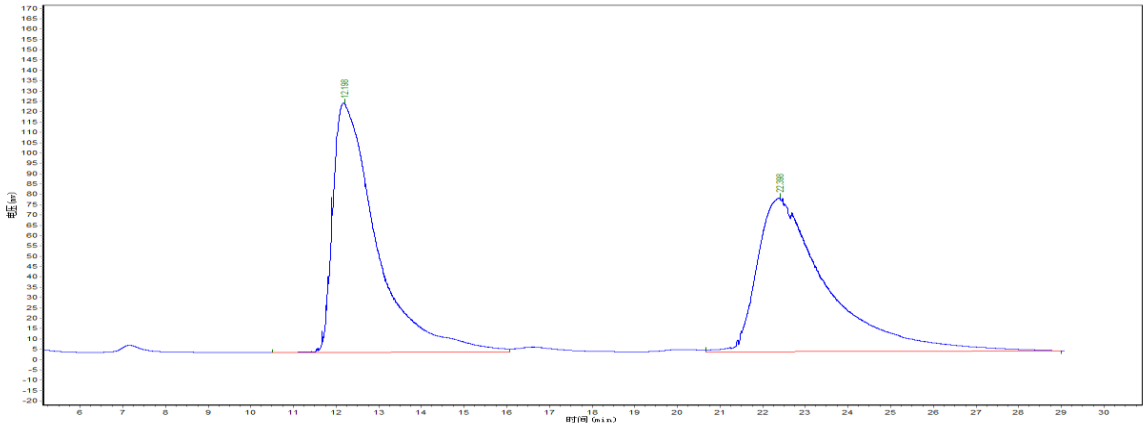


(2b)

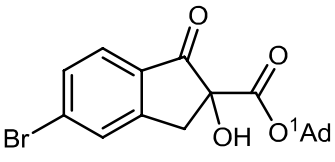


R.Time	Area	Area%
12.617	**8176033.500**	**93.6272**
21.880	**556510.688**	**6.3728**

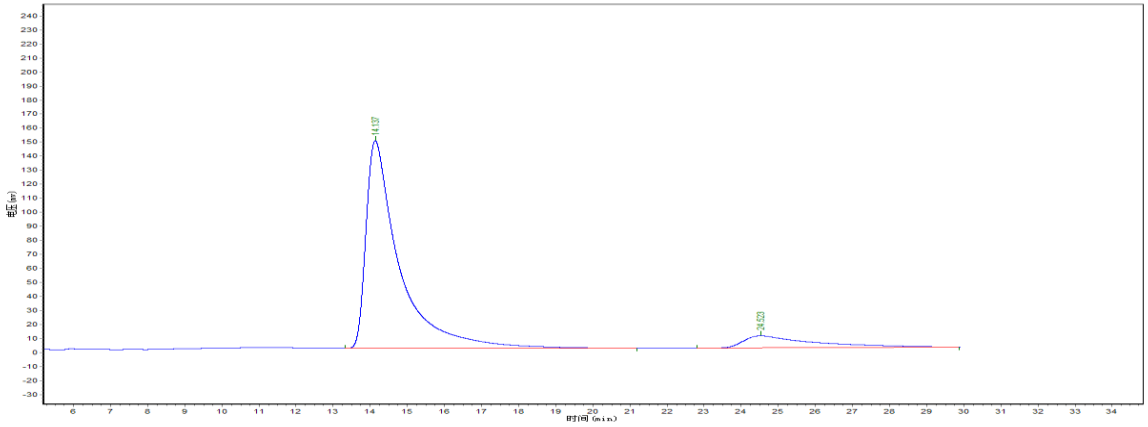
ee=87%



R.Time	Area	Area%
12.198	**8563164.000**	**50.6368**
22.398	**8347784.000**	**49.3632**

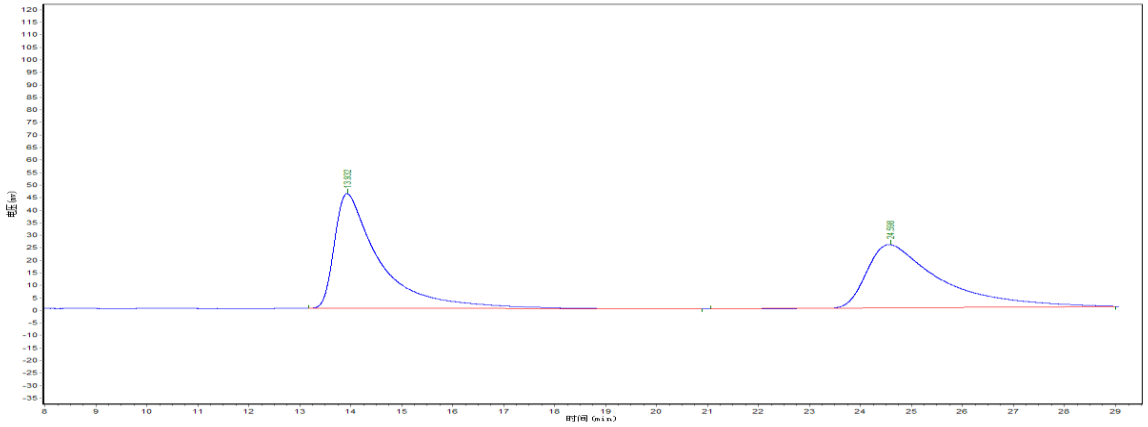


(2c)

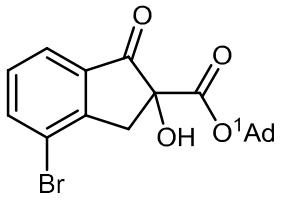


R.Time	Area	Area%
14.137	**9241228.000**	**91.5248**
24.523	**855740.313**	**8.4752**

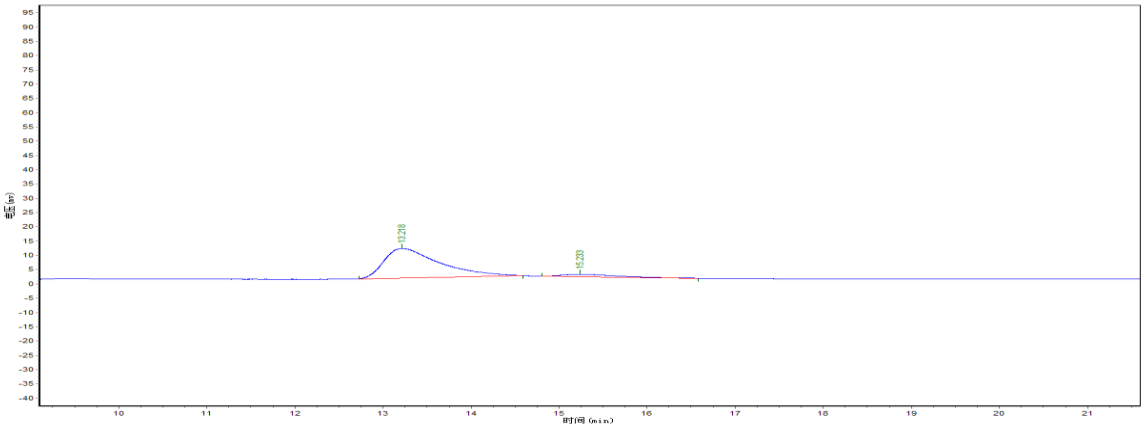
ee=83%



R.Time	Area	Area%
13.932	**2884313.500**	**50.3097**
24.598	**2875892.250**	**49.6903**

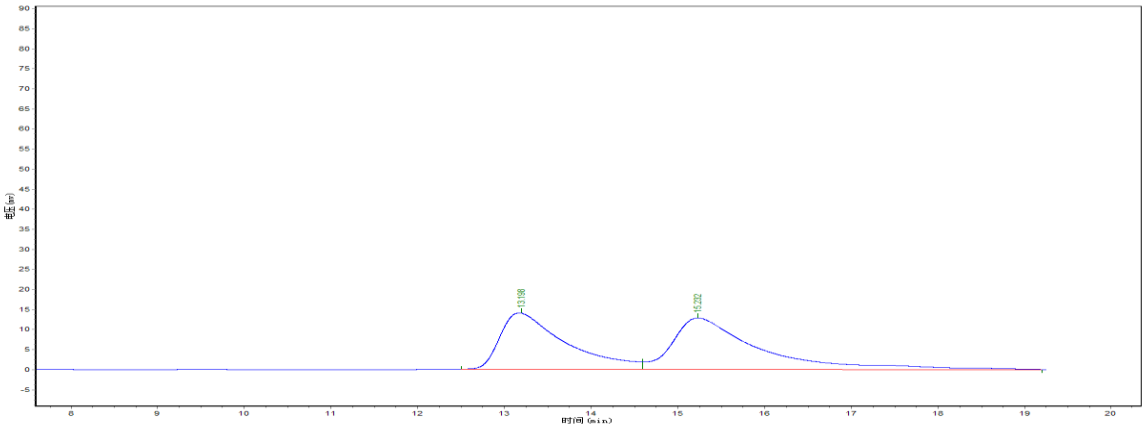


(2d)

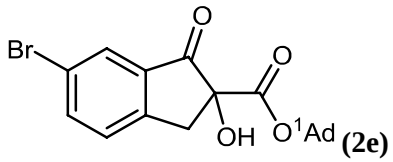


R.Time	Area	Area%
13.218	**450118.938**	**94.4090**
15.233	**26656.711**	**5.5910**

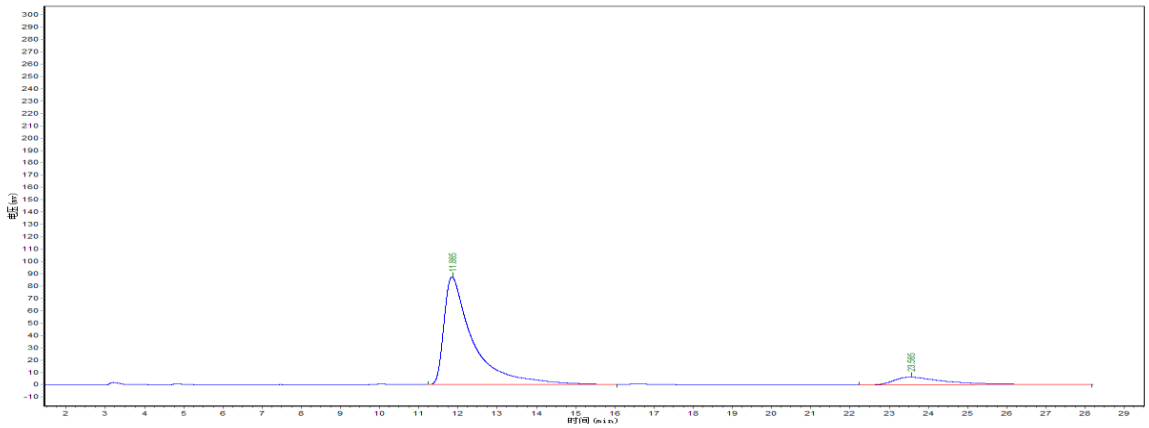
ee=89%



R.Time	Area	Area%
13.168	**590485.500**	**50.2262**
15.228	**585167.375**	**49.7738**

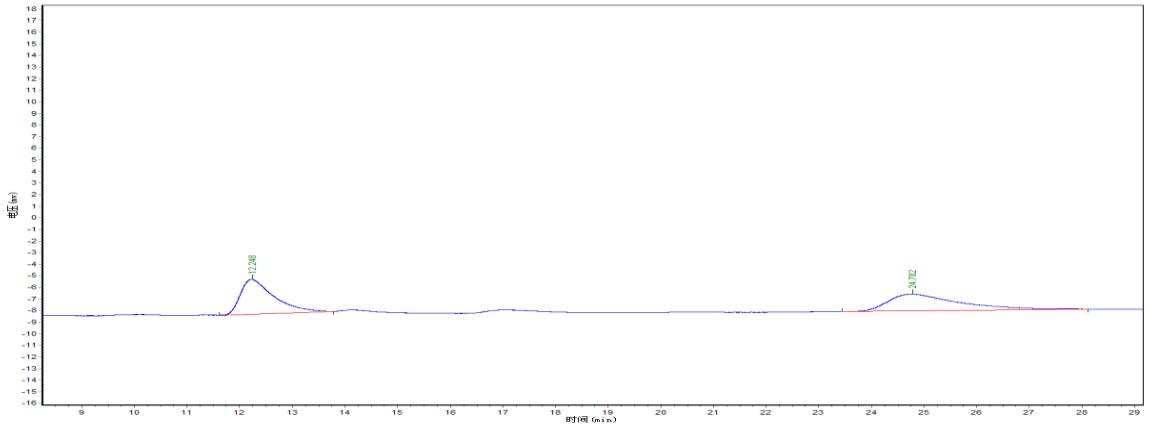


(2e)

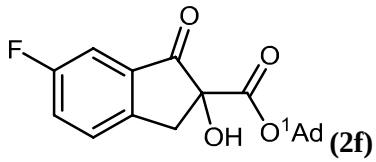


R.Time	Area	Area%
11.843	**4478572.500**	**92.0610**
23.540	**386213.125**	**7.9390**

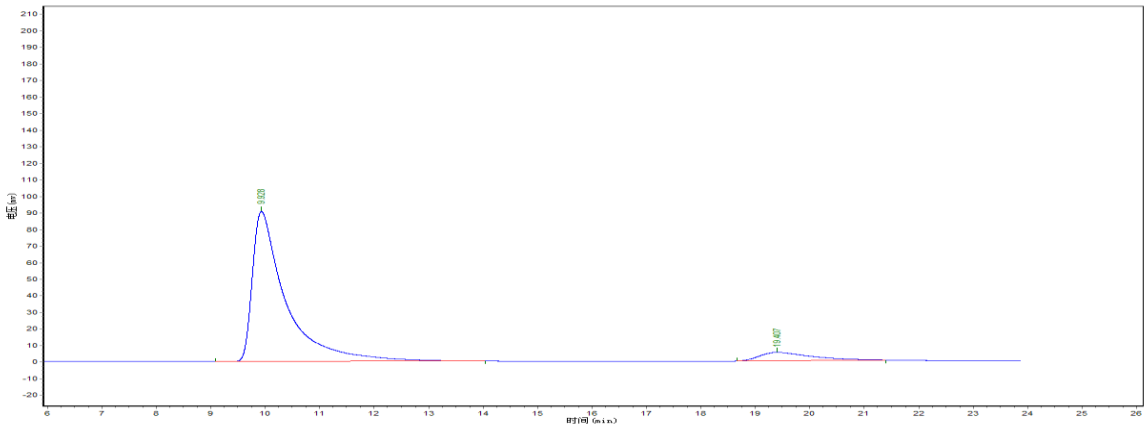
ee=85%



R.Time	Area	Area%
12.248	**146012.484**	**50.4497**
24.782	**143409.469**	**49.5503**

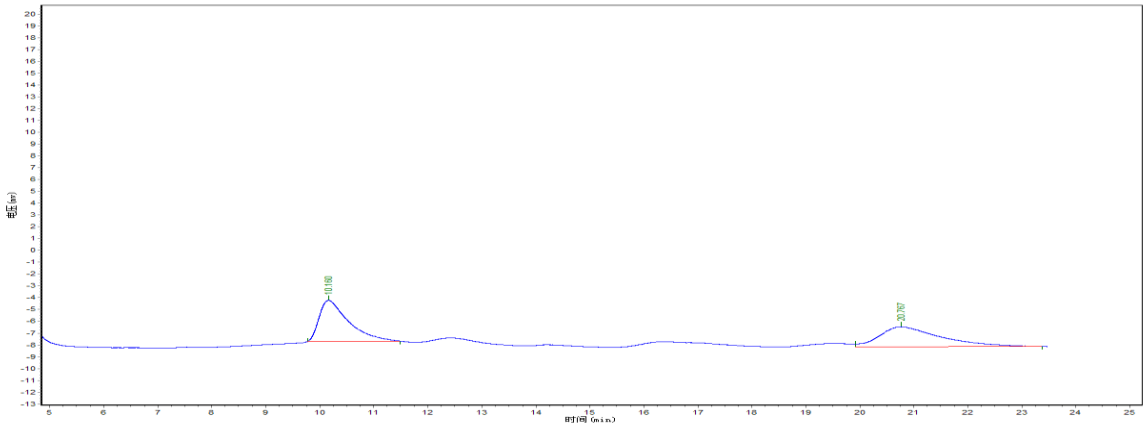


(2f)

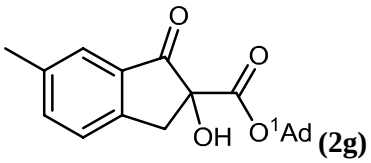


R.Time	Area	Area%
9.928	**3854453.250**	**92.6175**
19.407	**307236.188**	**7.3825**

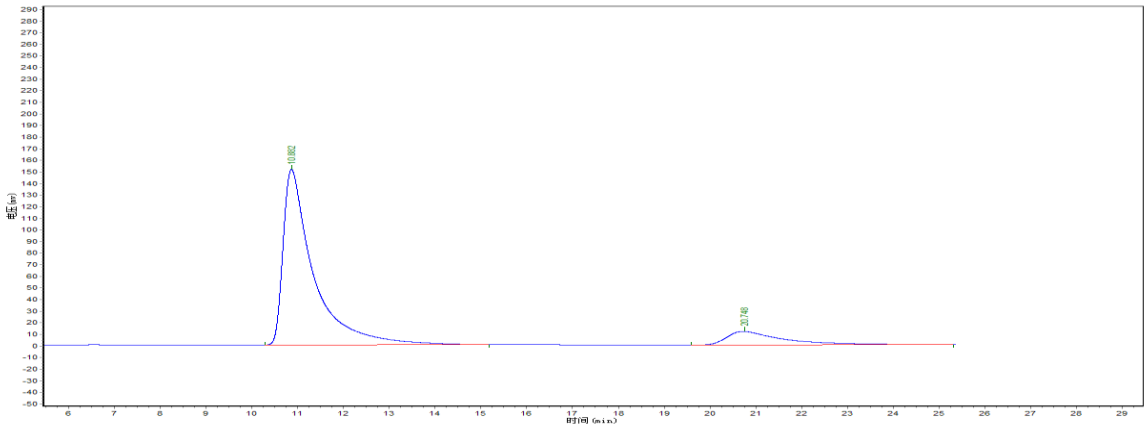
ee=85%



R.Time	Area	Area%
10.160	**129962.289**	**49.1846**
20.767	**134271.172**	**50.8154**

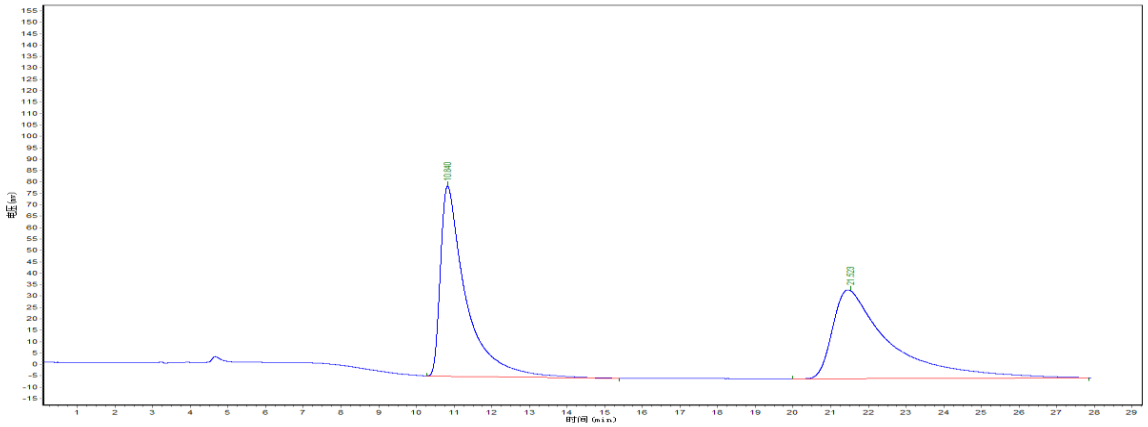


(2g)

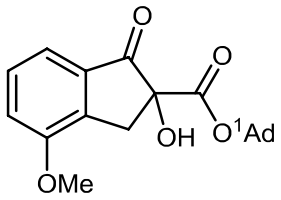


R.Time	Area	Area%
10.867	**6956524.500**	**90.9239**
20.723	**694407.188**	**9.0761**

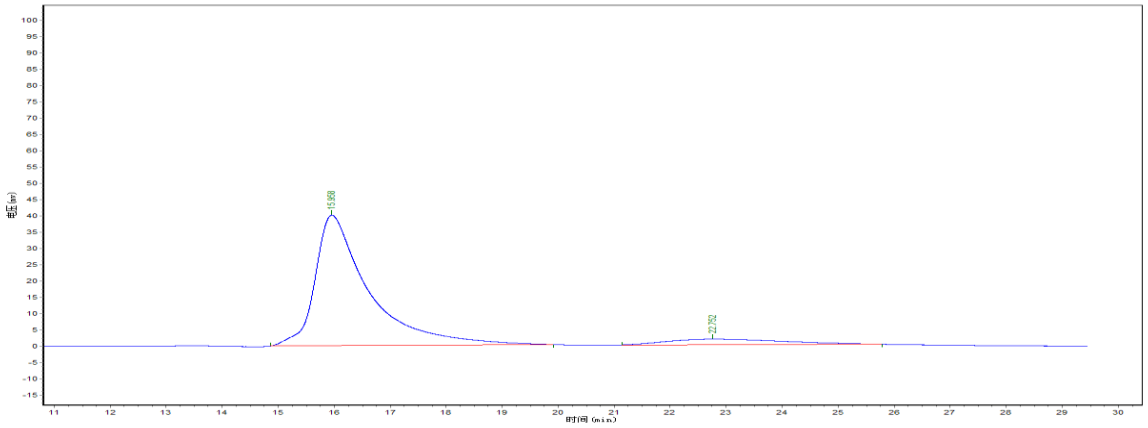
ee=82%



R.Time	Area	Area%
10.840	**3884723.000**	**48.9036**
21.523	**4058912.250**	**51.0964**

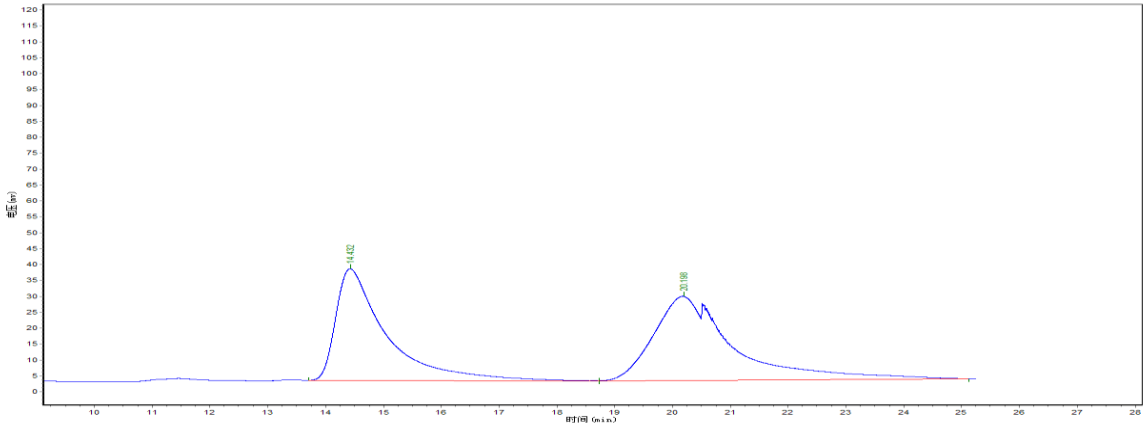


(2h)

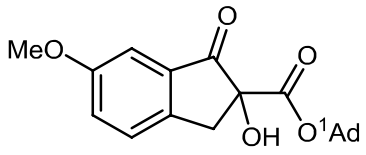


R.Time	Area	Area%
15.958	**2669792.250**	**91.8966**
22.752	**235419.750**	**8.1034**

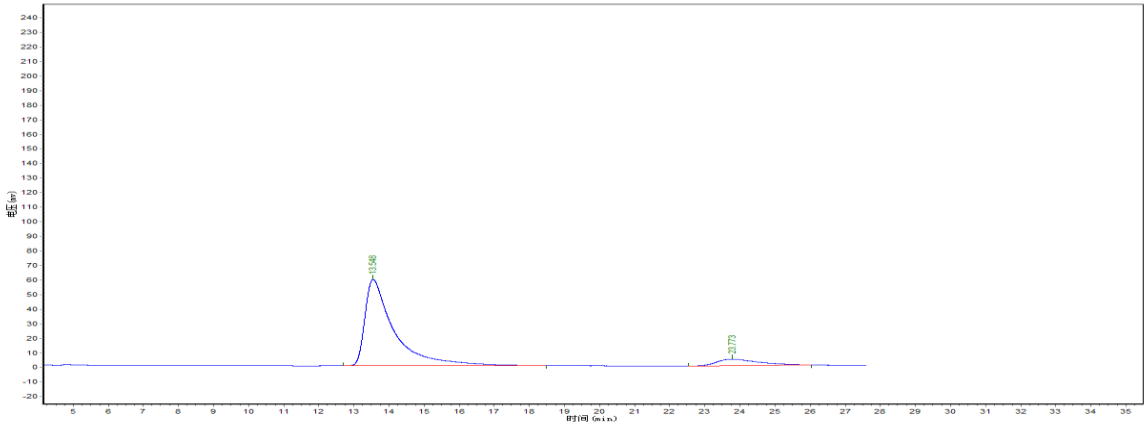
ee= 84%



R.Time	Area	Area%
14.423	**2111805.250**	**48.0913**
20.175	**2279438.250**	**51.9087**

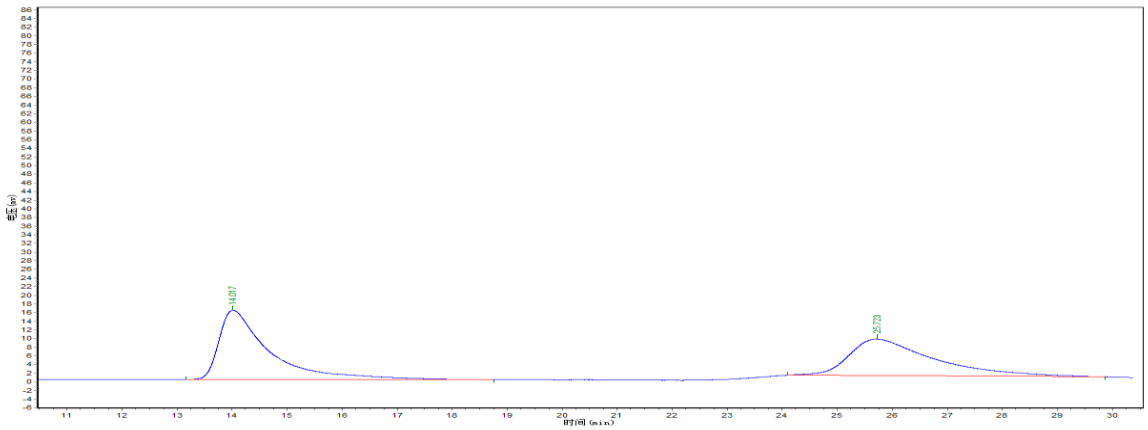


(2i)

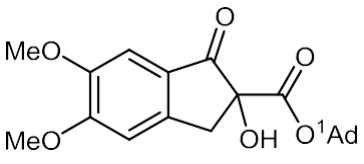


R.Time	Area	Area%
13.545	**3414776.250**	**92.5740**
23.768	**273922.313**	**7.4260**

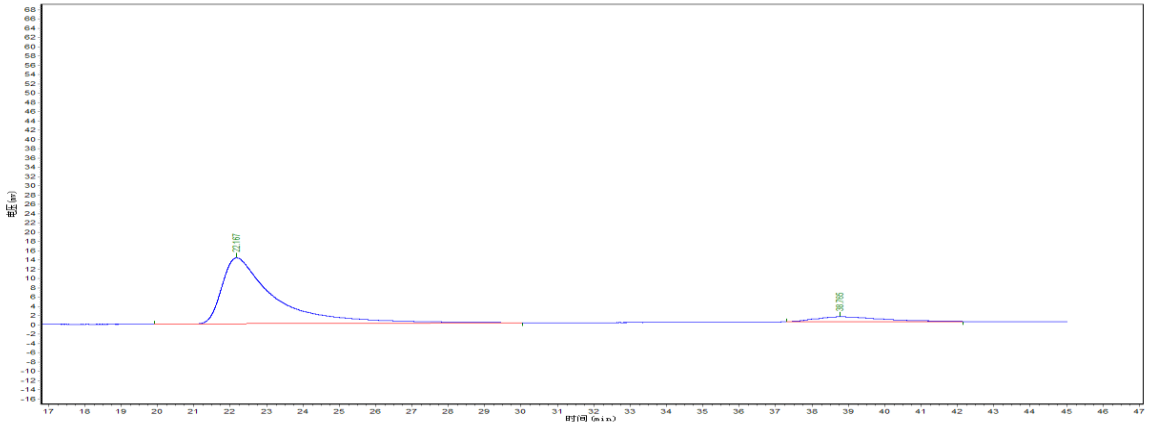
ee= 85%



R.Time	Area	Area%
14.017	**1019550.188**	**52.9519**
25.723	**905875.188**	**47.0481**

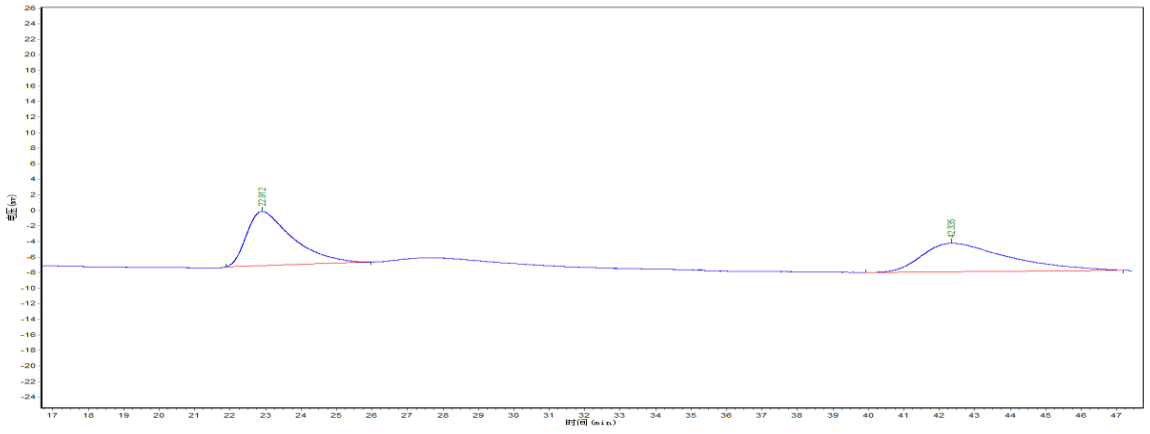


(2j)

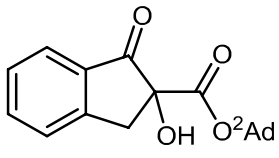


R.Time	Area	Area%
22.167	**1423643.000**	**94.0405**
38.765	**90219.219**	**5.9595**

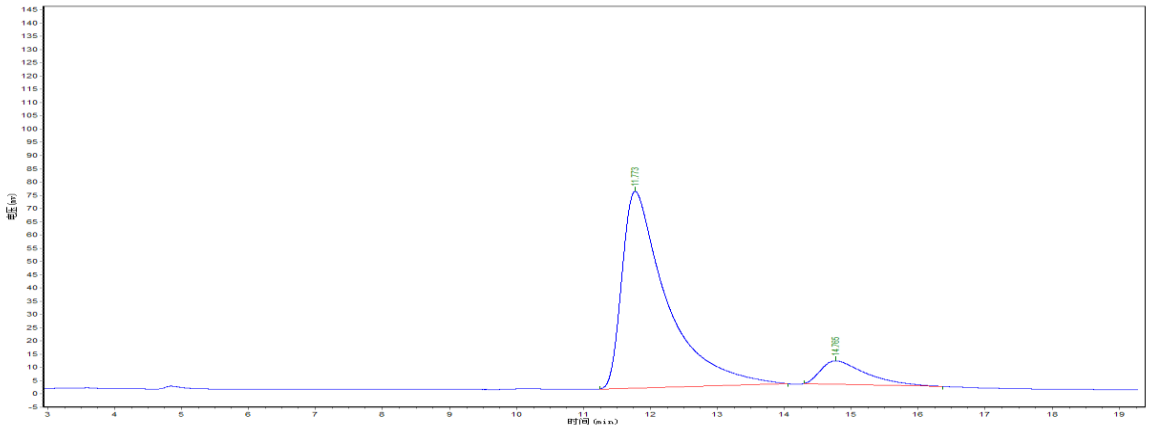
ee=88%



R.Time	Area	Area%
22.912	**626721.875**	**50.4635**
42.335	**615209.500**	**49.5365**

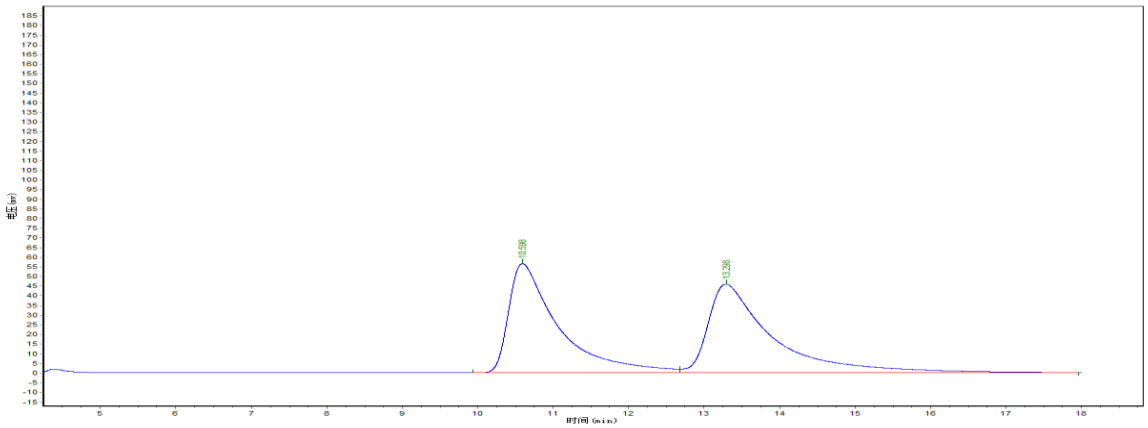


(2k)

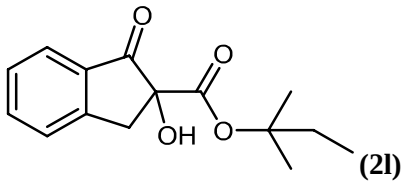


R.Time	Area	Area%
11.773	**3445304.500**	**90.3046**
14.765	**369899.031**	**9.6954**

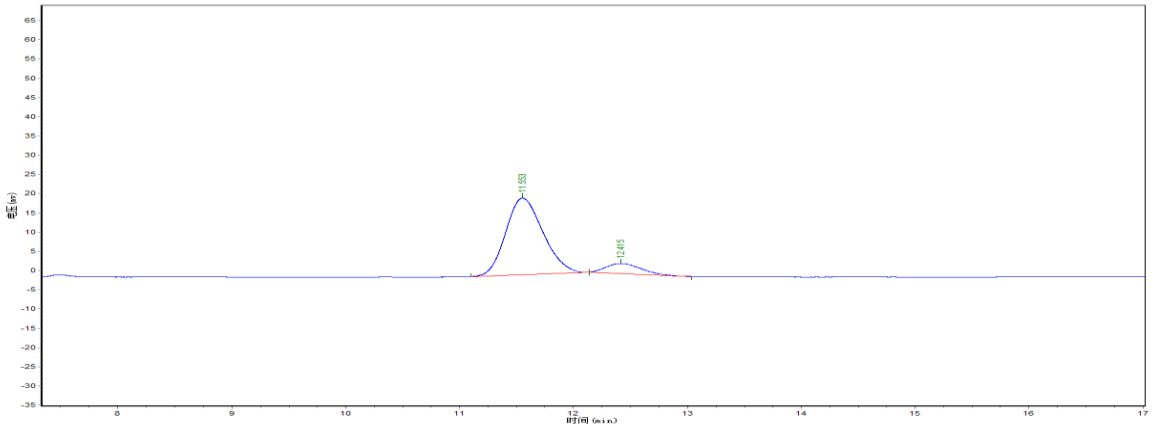
ee=81%



R.Time	Area	Area%
10.598	**2566851.250**	**48.9743**
13.298	**2674364.500**	**51.0257**

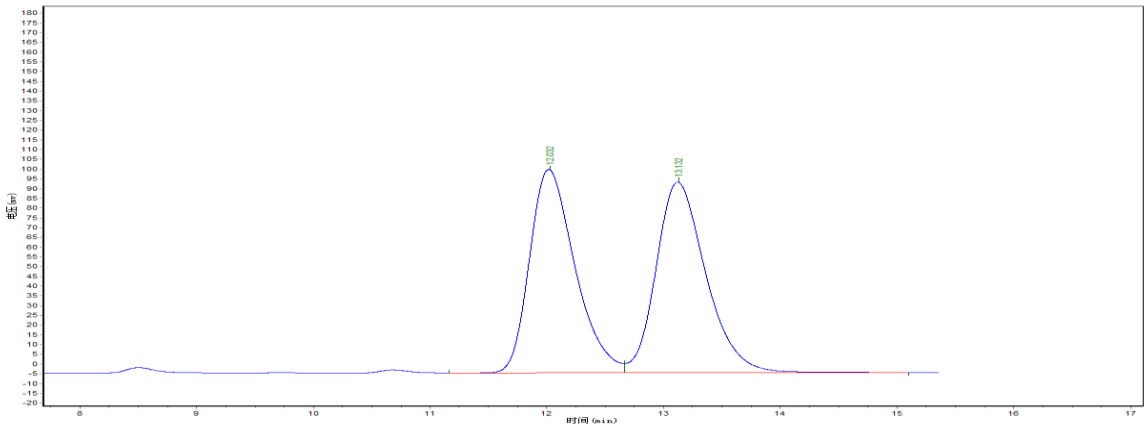


(2l)

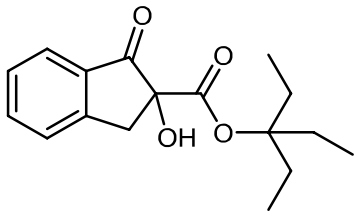


R.Time	Area	Area%
11.553	**451732.000**	**89.0018**
12.415	**55821.703**	**10.9982**

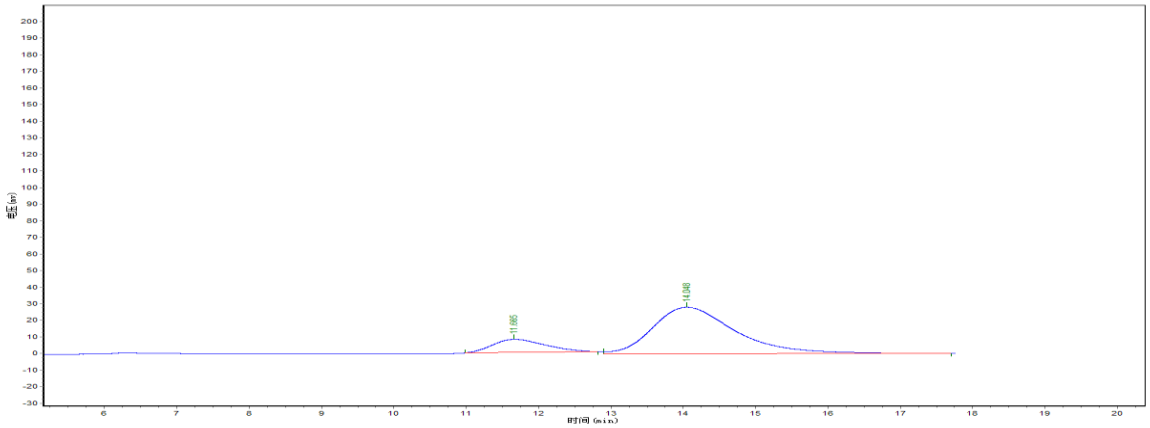
ee=78%



R.Time	Area	Area%
12.032	**2818960.000**	**49.2797**
13.132	**2901372.000**	**50.7203**

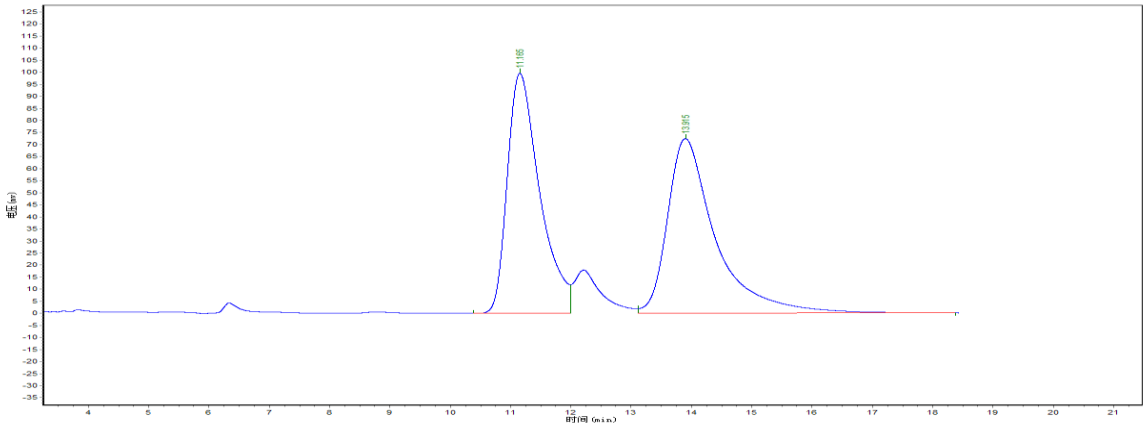


(2m)

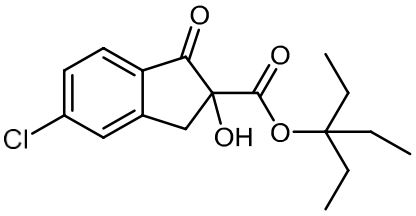


R.Time	Area	Area%
11.665	**389527.781**	**14.9715**
14.048	**2212274.500**	**85.0285**

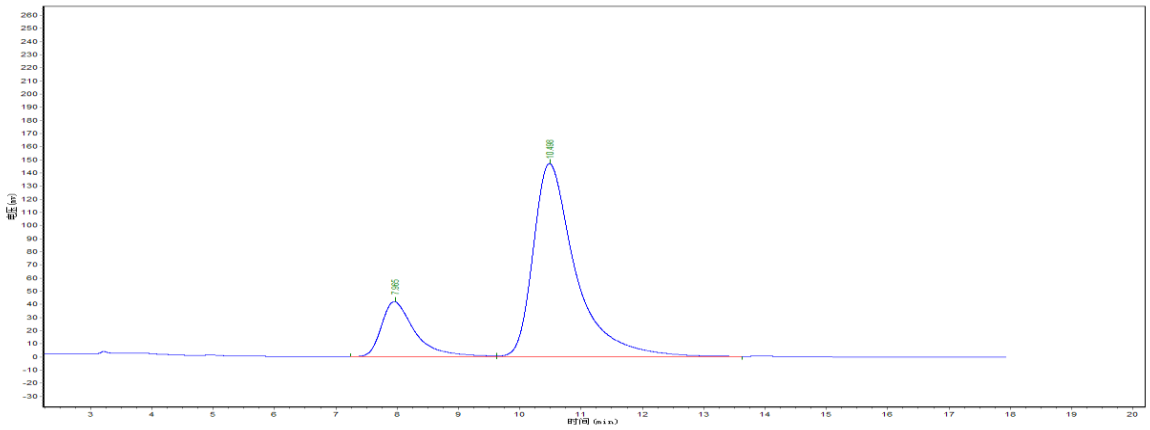
ee=70%



R.Time	Area	Area%
11.165	**3714998.000**	**48.1631**
13.915	**3998375.000**	**51.8369**

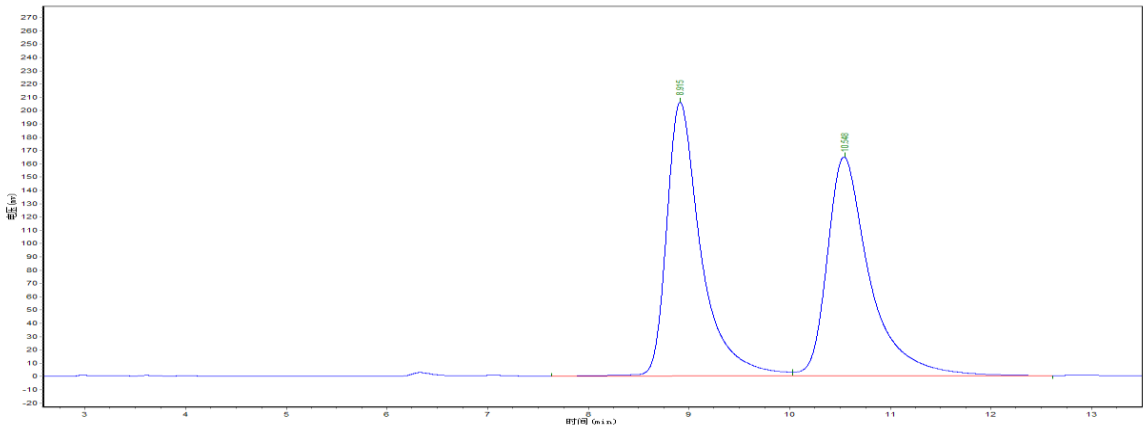


(2n)

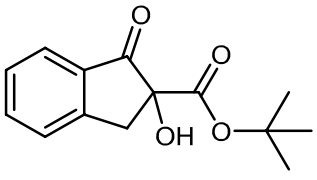


R.Time	Area	Area%
7.950	**1284281.125**	**15.5014**
10.482	**7000680.500**	**84.4986**

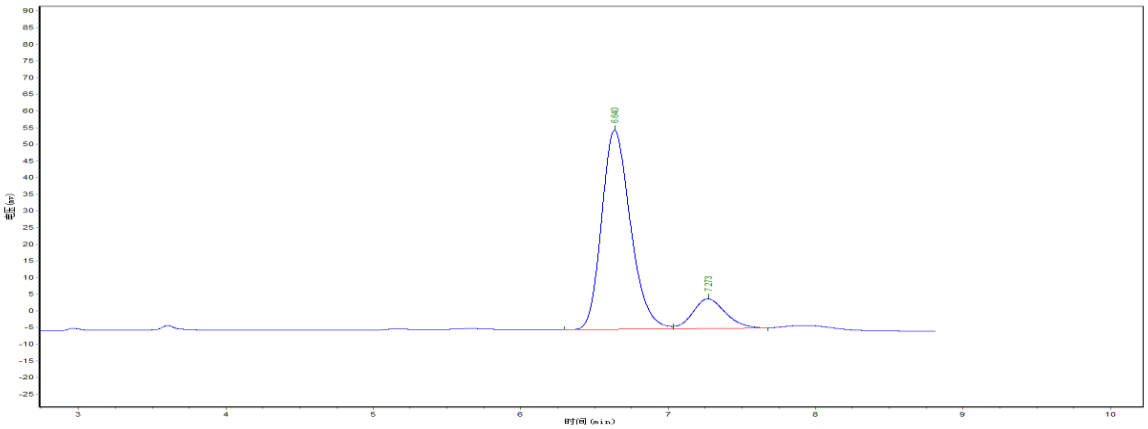
ee=69%



R.Time	Area	Area%
8.915	**4896782.500**	**50.2509**
10.548	**4847879.500**	**49.7491**

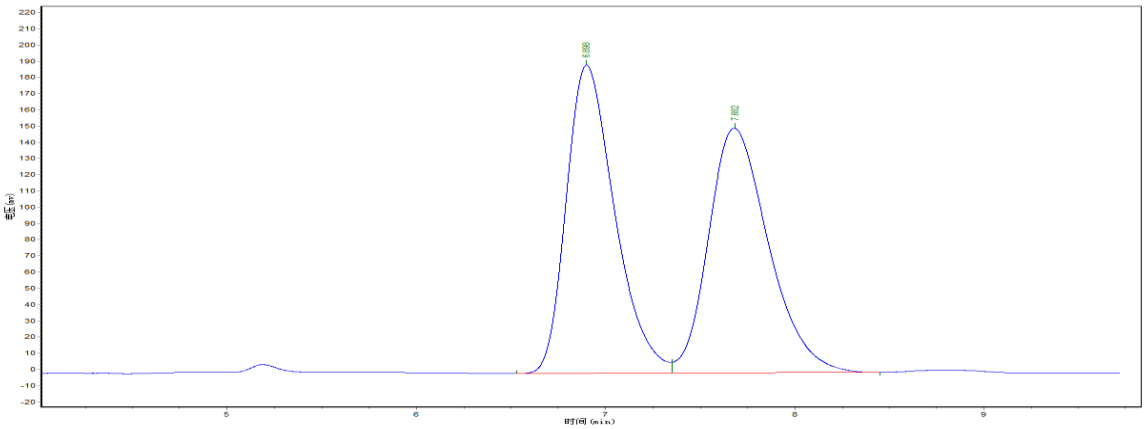


(2o)

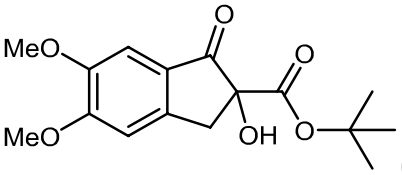


R.Time	Area	Area%
6.637	**810483.563**	**88.0220**
7.268	**110289.906**	**11.9780**

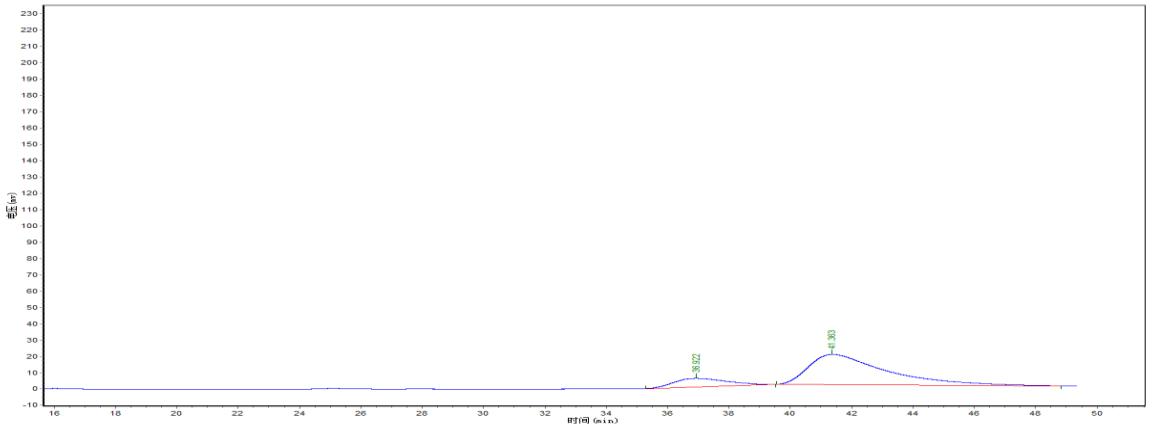
ee=76%



R.Time	Area	Area%
6.898	**3377434.750**	**50.2499**
7.682	**3343838.000**	**49.7501**

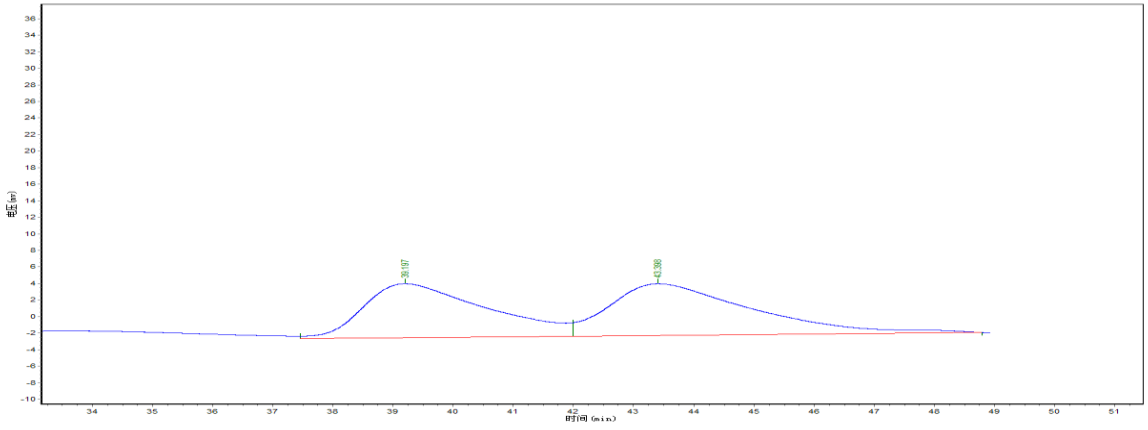


(2p)

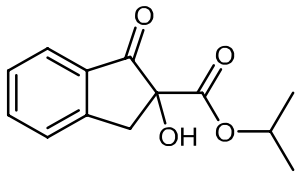


R.Time	Area	Area%
36.922	**528894.875**	**13.9745**
41.363	**3255832.250**	**86.0256**

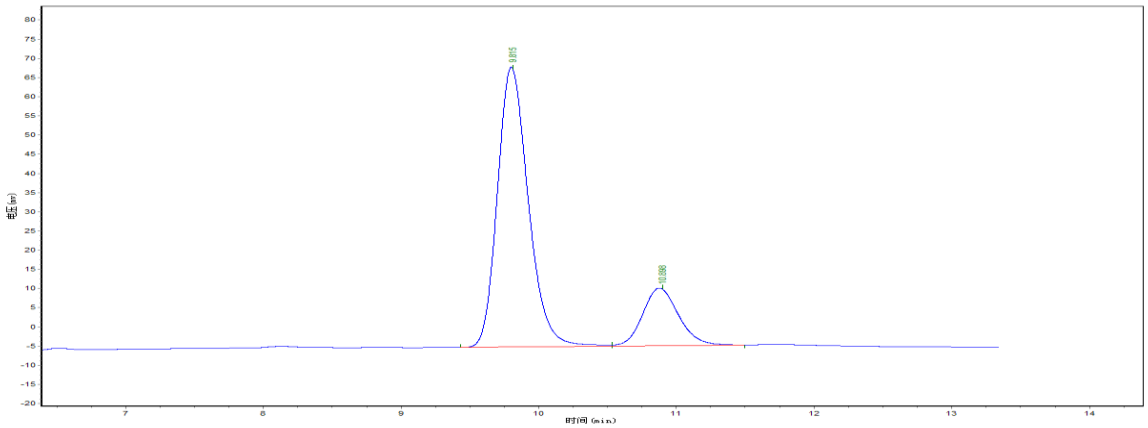
ee=72%



R.Time	Area	Area%
39.197	**922402.438**	**47.4933**
43.398	**1019771.750**	**52.5067**

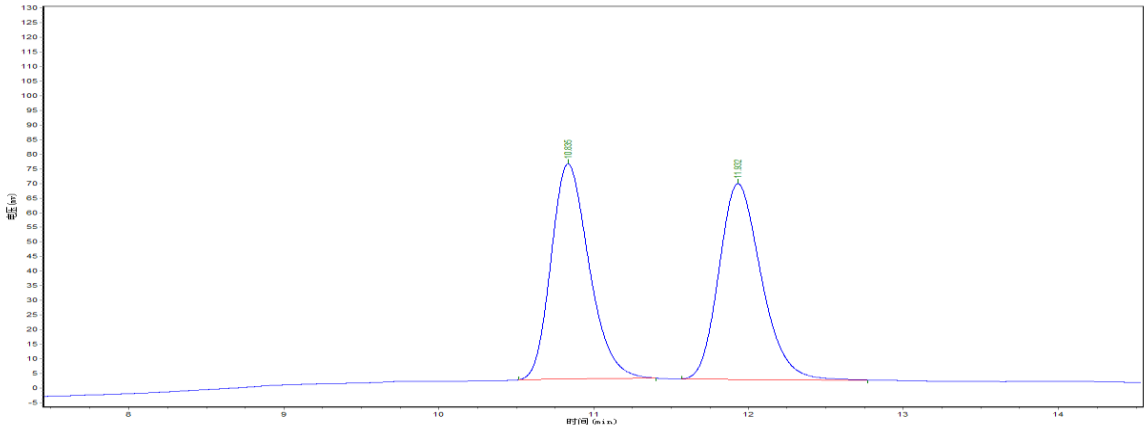


(2q)

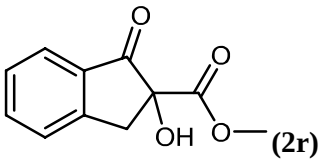


R.Time	Area	Area%
9.802	**1137032.625**	**82.6814**
10.875	**238164.250**	**17.3186**

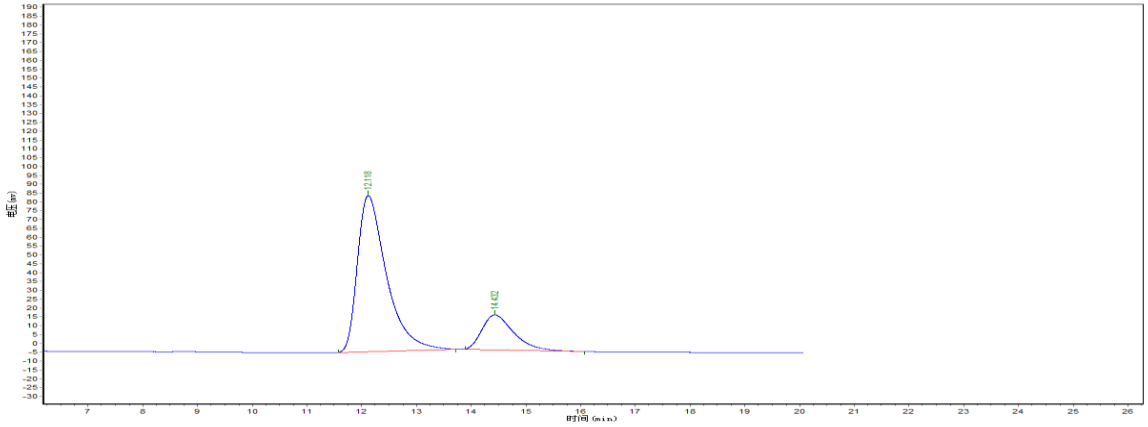
ee=65%



R.Time	Area	Area%
10.835	**1255820.000**	**49.7940**
11.932	**1266209.875**	**50.2060**

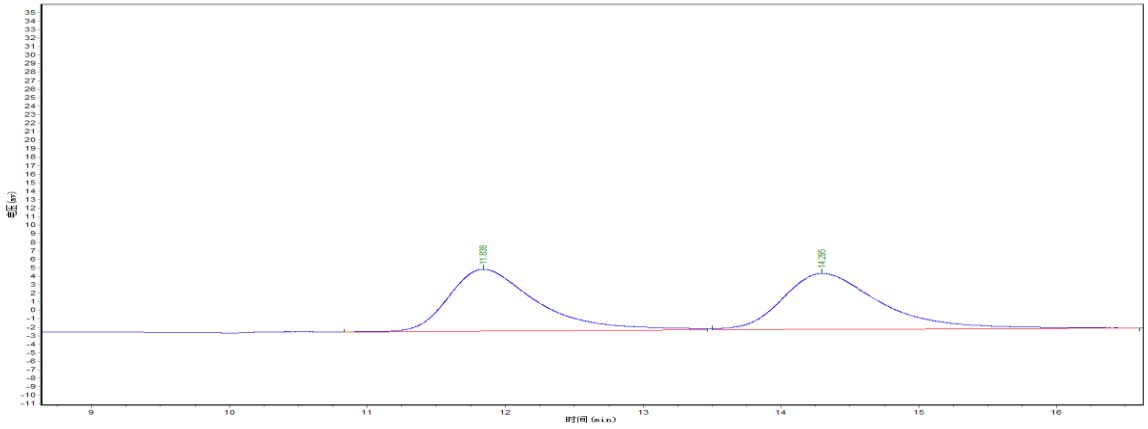


(2r)

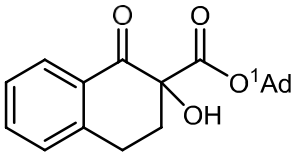


R.Time	Area	Area%
12.118	**3385920.500**	**81.3388**
14.432	**776814.625**	**18.6612**

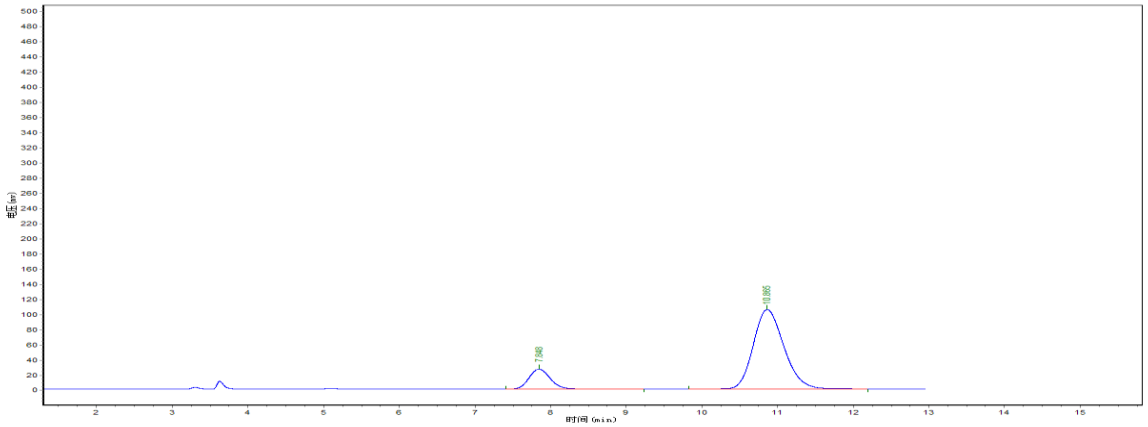
ee=63%



R.Time	Area	Area%
11.838	**323318.844**	**49.9446**
14.295	**324036.250**	**50.0554**

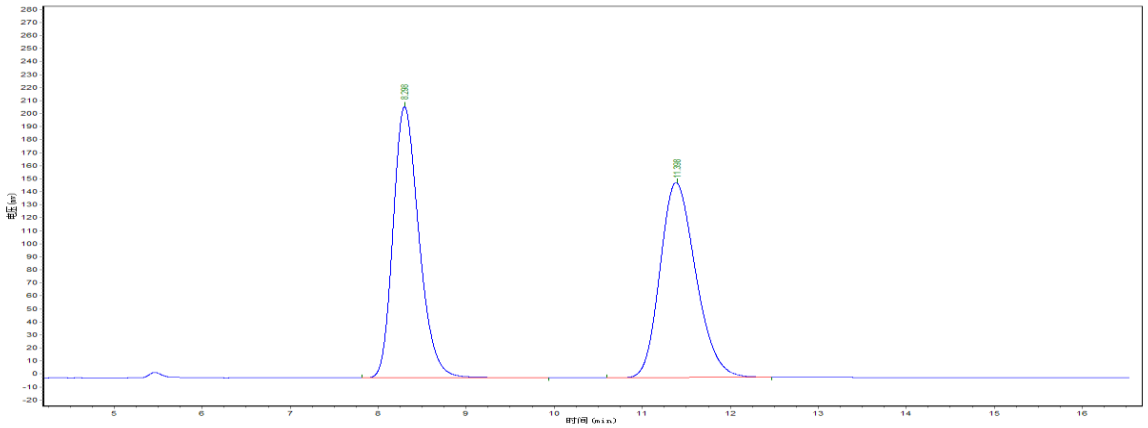


(2s)

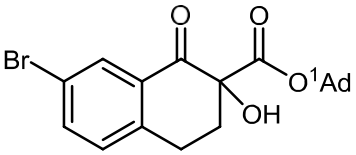


R.Time	Area	Area%
7.847	**445040.781**	**13.1717**
10.863	**2933723.750**	**86.8283**

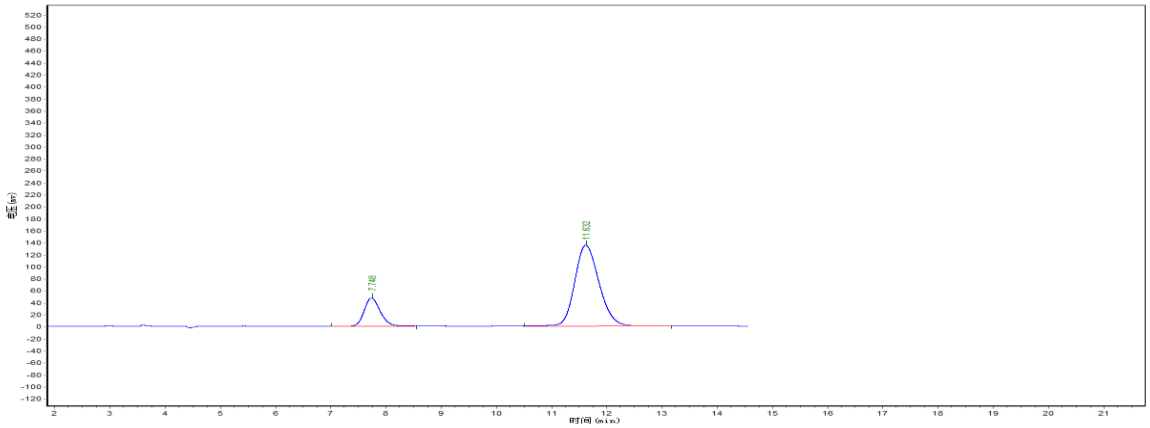
ee=74%



R.Time	Area	Area%
8.298	**4240629.000**	**49.9887**
11.398	**4242541.000**	**50.0113**

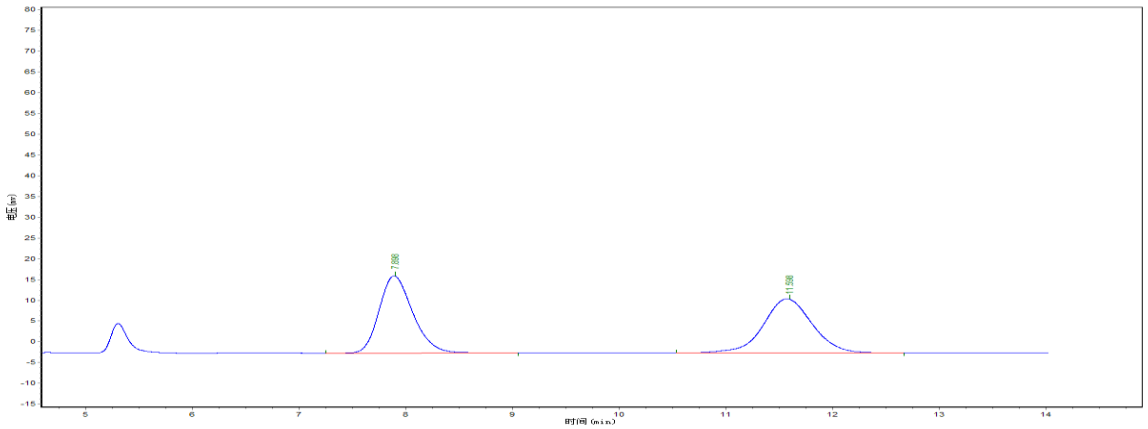


(2t)

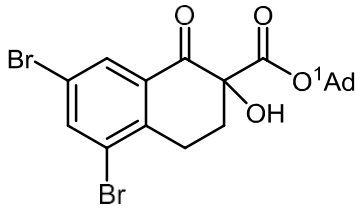


R.Time	Area	Area%
7.737	**794120.063**	**16.1775**
11.618	**4114671.000**	**83.8225**

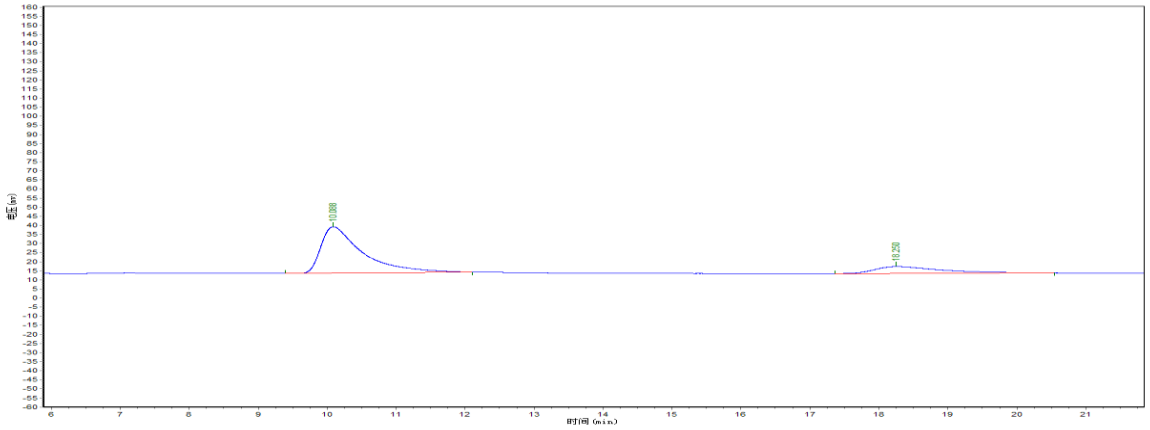
ee=68%



R.Time	Area	Area%
7.898	**409742.906**	**49.6735**
11.598	**415129.188**	**50.3265**

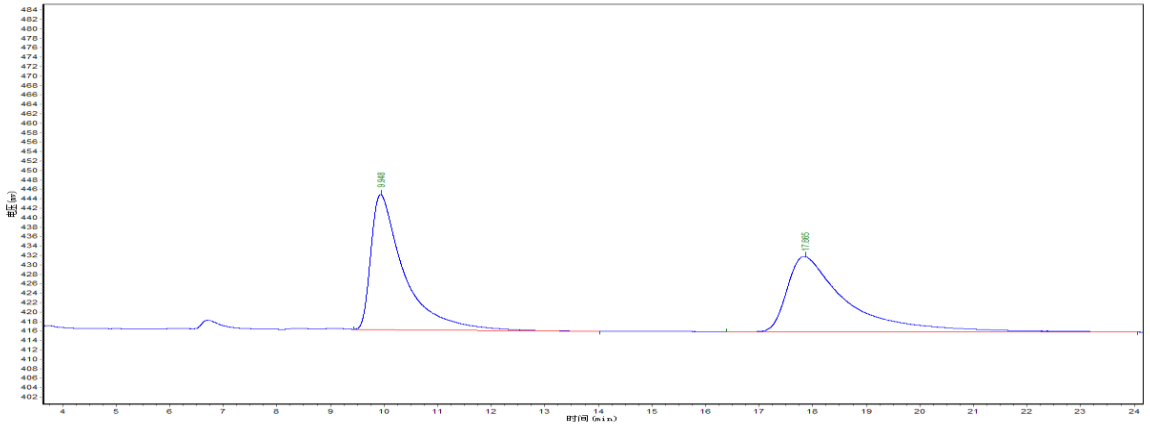


(2u)

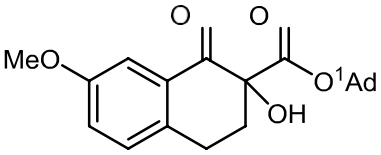


R.Time	Area	Area%
10.088	**1056456.250**	**85.5056**
18.250	**179083.781**	**14.4944**

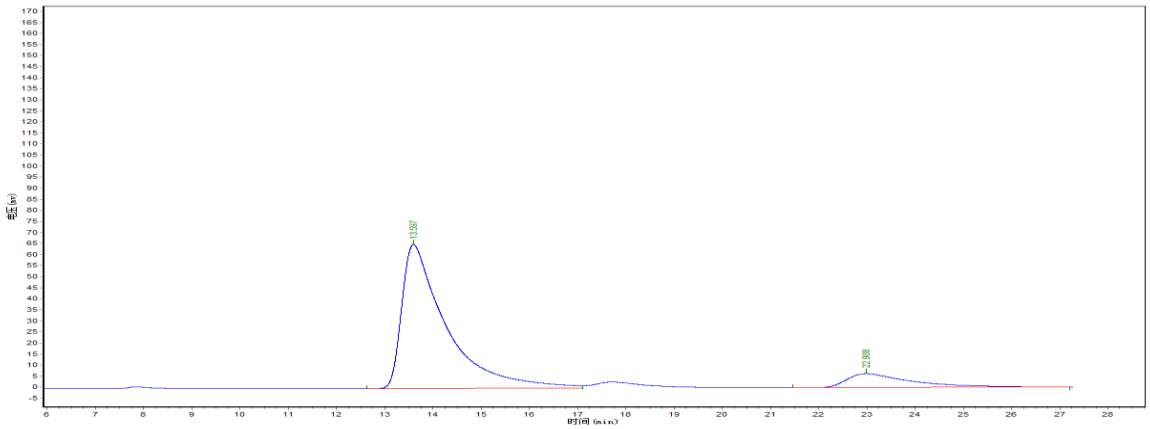
ee=71%



R.Time	Area	Area%
9.948	**1246465.625**	**50.2949**
17.865	**1231848.000**	**49.7051**

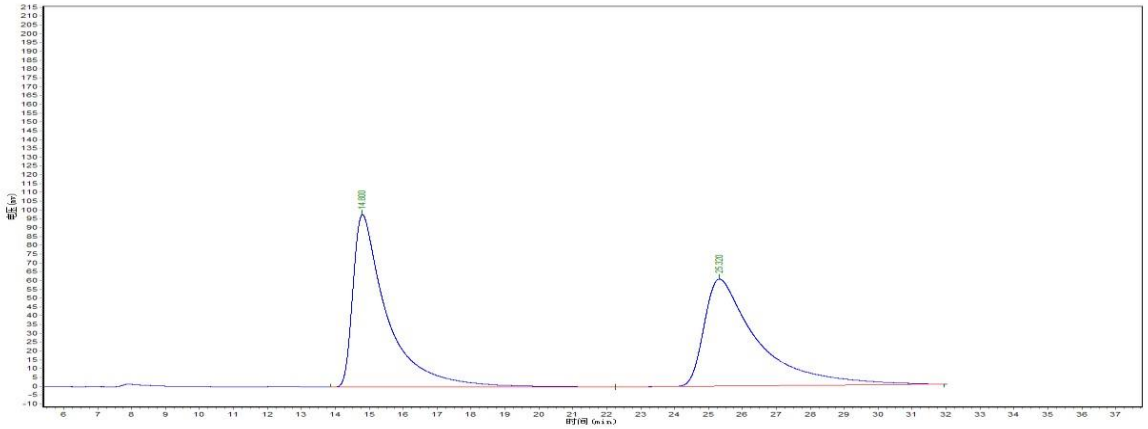


(2v)

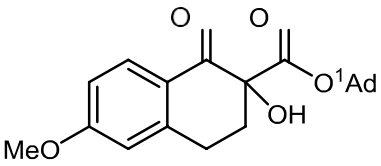


R.Time	Area	Area%
13.597	**4145673.500**	**90.2687**
22.988	**446919.969**	**9.7313**

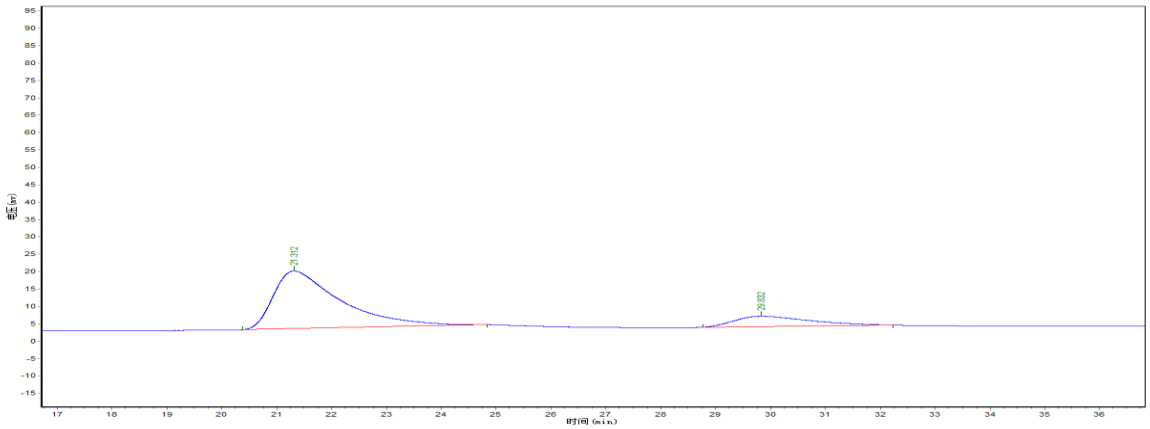
ee =80%



R.Time	Area	Area%
14.800	**6802411.000**	**50.7966**
25.320	**6589046.000**	**49.2034**

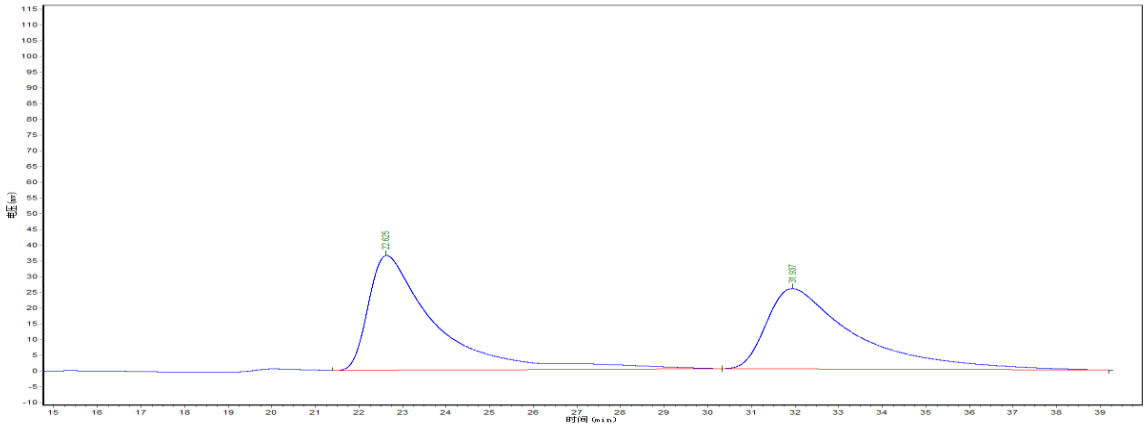


(2w)

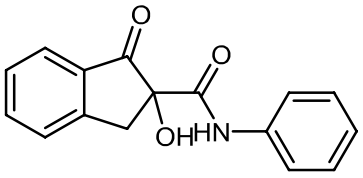


R.Time	Area	Area%
21.312	**1402812.000**	**86.9442**
29.832	**210649.766**	**13.0558**

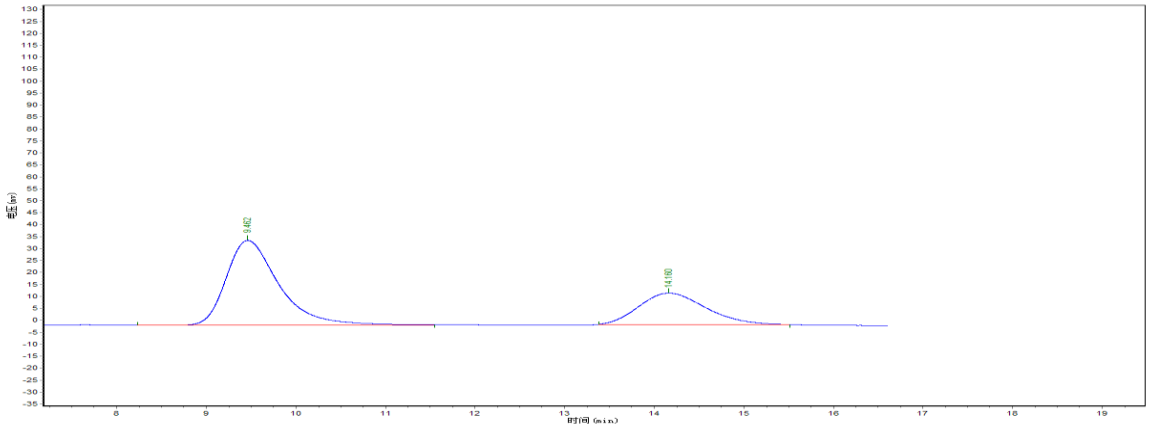
ee =74%



R.Time	Area	Area%
22.625	**3870567.750**	**52.0343**
31.937	**3567925.500**	**47.9657**

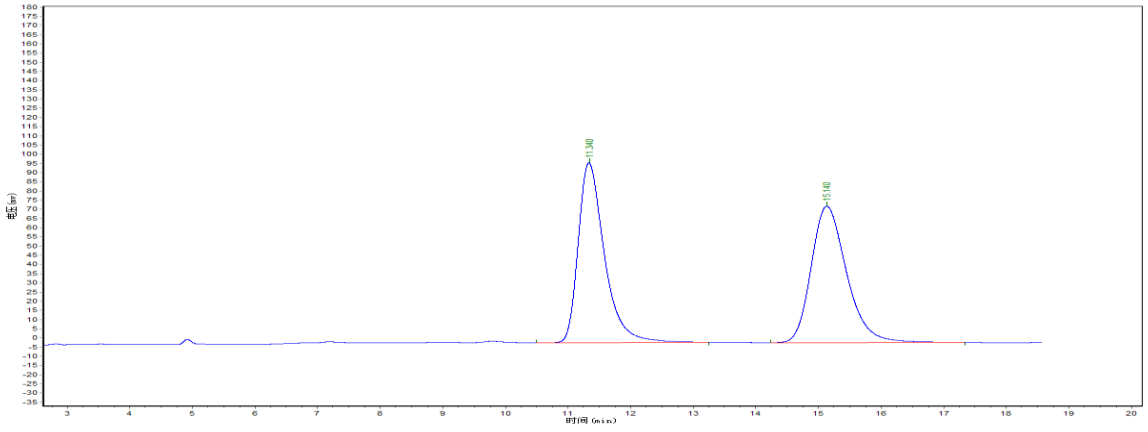


(5a)

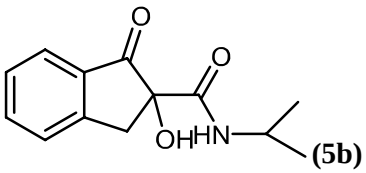


R.Time	Area	Area%
9.862	**1457887.000**	**69.3169**
14.160	**645332.500**	**30.6831**

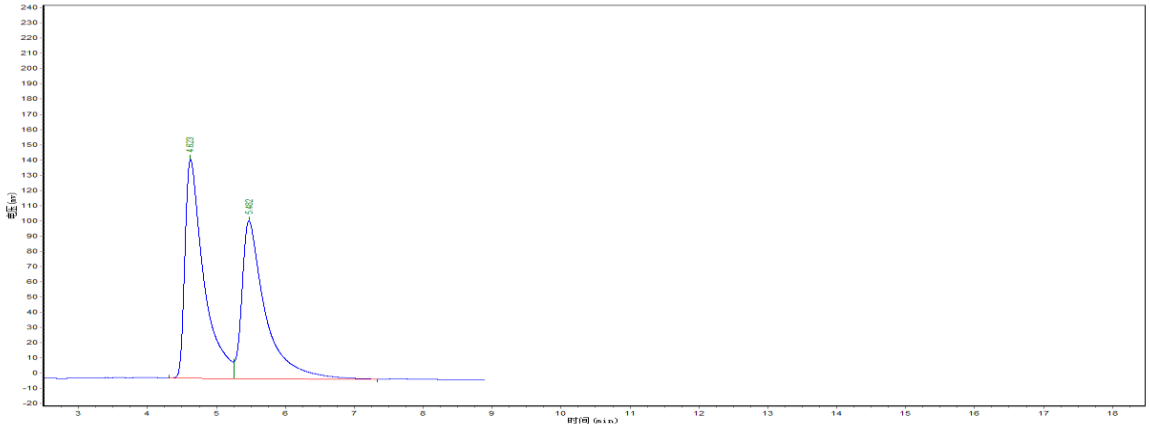
ee=39%



R.Time	Area	Area%
11.140	**2839808.750**	**49.3376**
15.140	**2916067.250**	**50.6624**

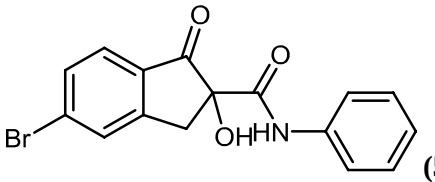


(5b)

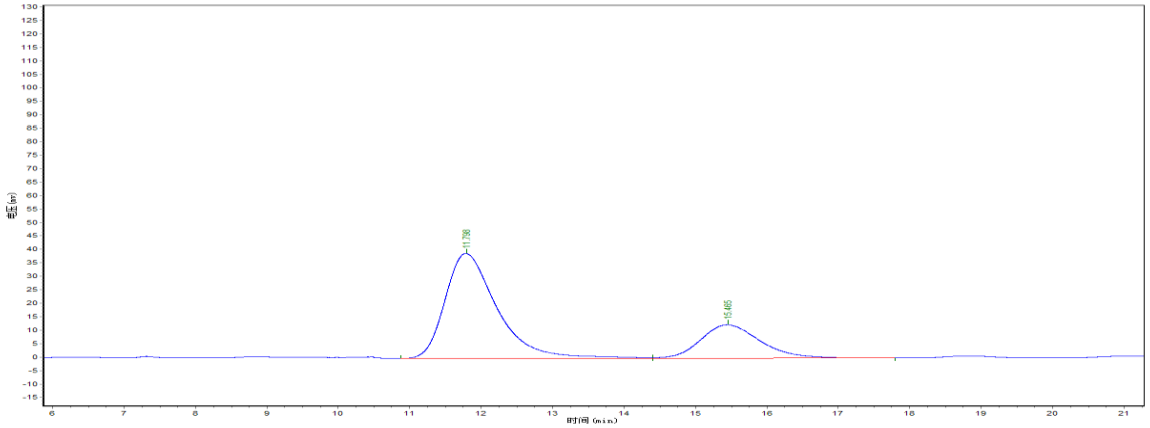


R.Time	Area	Area%
4.623	**2750132.500**	**52.6800**
5.482	**2470317.250**	**47.3200**

ee=5%

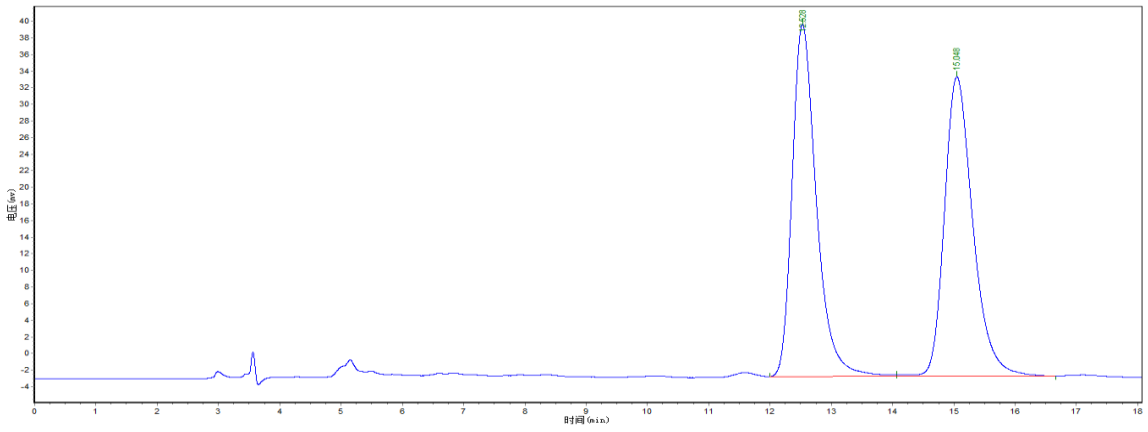


(5c)

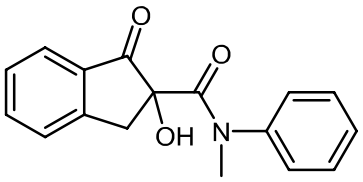


R.Time	Area	Area%
11.782	**1966707.625**	**75.8787**
15.447	**632053.063**	**24.1213**

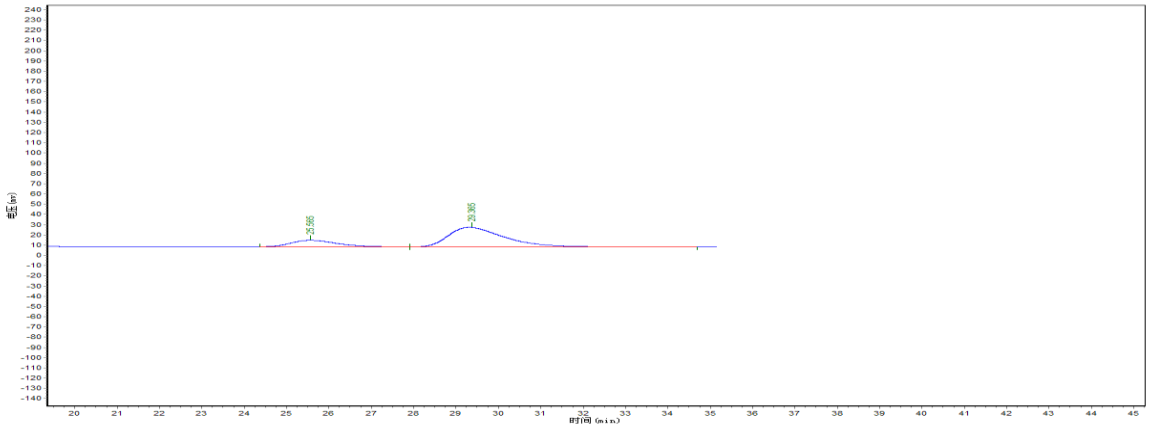
ee=52%



R.Time	Area	Area%
12.328	**1166018.625**	**50.0**
15.048	**1163762.500**	**50.0**

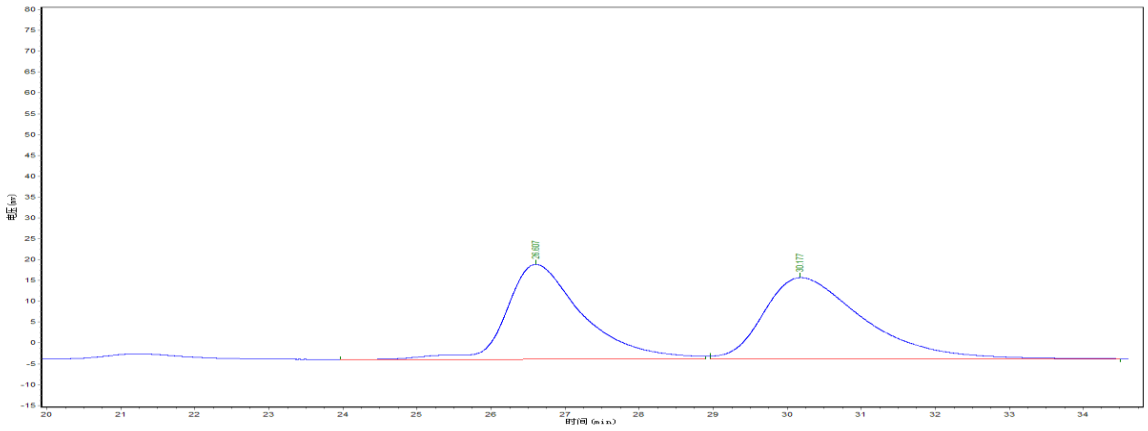


(5d)

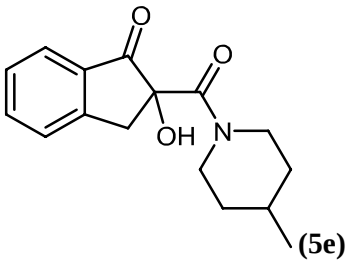


R.Time	Area	Area%
25.547	**364933.125**	**17.1495**
29.305	**1763023.500**	**82.8505**

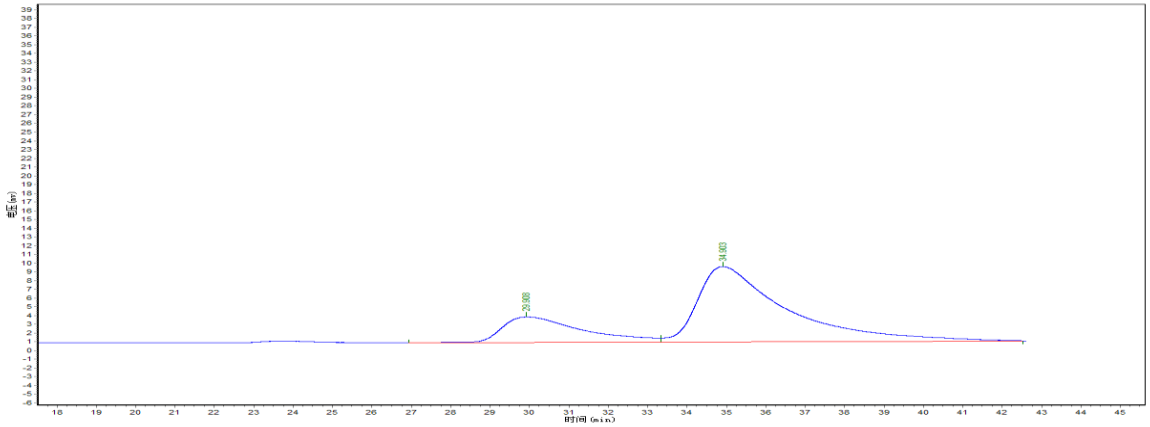
ee=66%



R.Time	Area	Area%
26.607	**1617886.750**	**49.0286**
30.177	**1652331.750**	**50.9714**

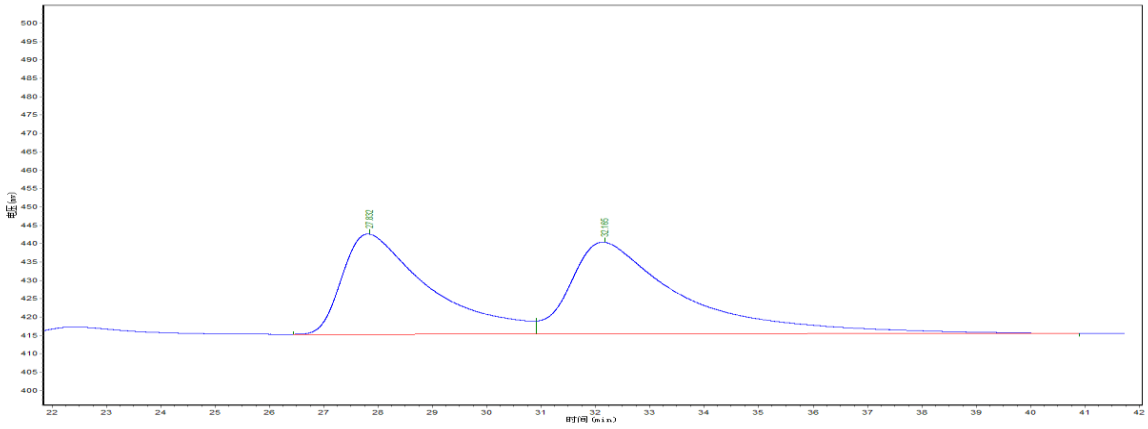


(5e)

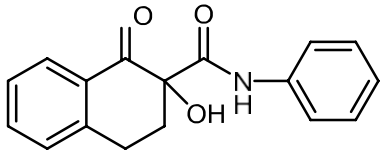


R.Time	Area	Area%
29.908	**306869.781**	**18.7286**
34.903	**1331639.250**	**81.2714**

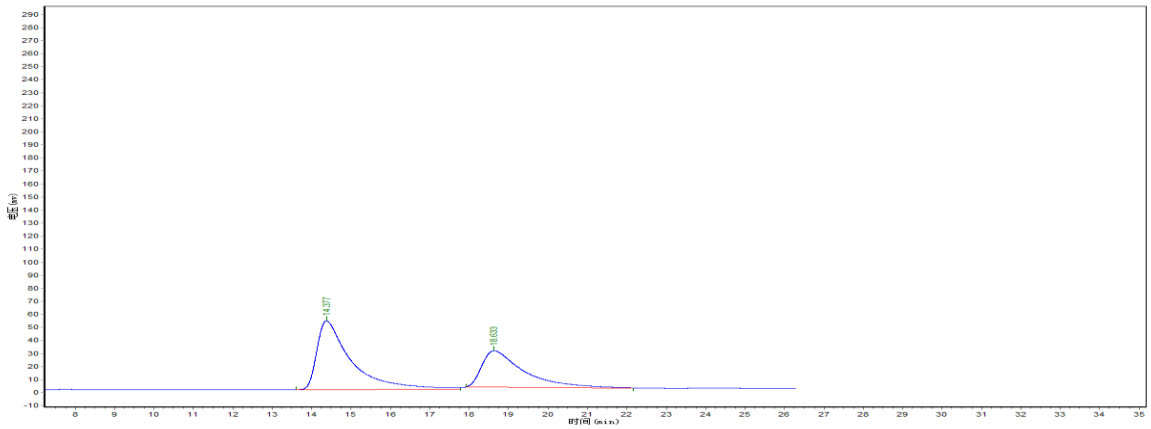
ee=63%



R.Time	Area	Area%
27.802	**2538531.750**	**50.1118**
32.128	**2527204.250**	**49.8882**



(5f)



R.Time	Area	Area%
14.377	**3188516.750**	**62.7687**
18.633	**1891268.125**	**37.2313**

ee=25%