Supporting Information

Enantioselective photooxygenation of β-dicarbonyl compounds in batch and flow photomicroreactor

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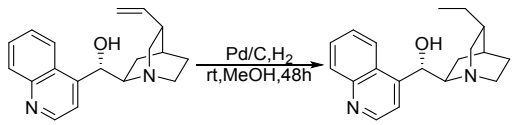
1. General Information

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 (200-300 mesh). Melting points were determined with a hot plate apparatus. Optical rotations were measured on a digital polarimeter with a sodium lamp at 20ºC (10 cm cell, c given in g/100 mL). ^{1}H NMR (400 MHz or 500 MHz) spectra was obtained at 25 ºC; ^{13}C NMR (101 MHz) were recorded on a VARIAN INOVA-400M and AVANCE II 400 spectrometer at 25 ºC. Chemical shifts are reported as δ (ppm) values relative to TMS as internal standard and coupling constants (J) in Hz. High resolution mass spectrometry data were obtained with UPLC/Q-Tof Mass Spectrometer and were determined by electrospray ionization (ESI). The enantiomeric ratio (ee) were determined by HPLC. HPLC analyses were performed on equipped with Diacel Chiralpak AD-H, OD-H and AS-H chiral column (0.46cm × 25 cm), using mixtures of n-hexane/isopropyl alcohol as mobile phase, at 25 °C with an injection volume of 20 μL at a flow rate of 1 mL/min.

2. Synthesis of Catalysts

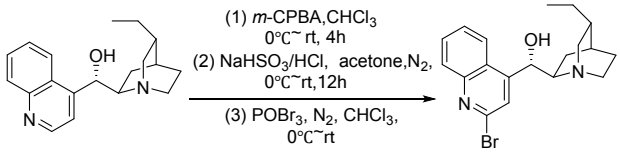
2.1 Preparation of Cn-3



Cn Cn-1
97% yield

Cn-1 was prepared partly according to Jeong's method[1]. Cn (8.83 g, 30 mmol) and 10% Pd/C (1.77 g) were added to MeOH (150 mL) under H_2. The reaction was left to stir for 48 h at room temperature. The reaction mixture was filtered and washed with chloroform/MeOH(8/2, 3× 200 mL). The solution was concentrated in vacuo to give a white solid of Cn-1 (8.63 g, 97% yield). $[a]_D^{20}$ = +96 (c 0.1, $CHCl_3$); m.p. 284-286 ºC;

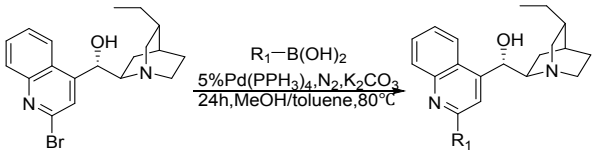
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.82 (d, J = 4.4 Hz, 1H), 8.24 (d, J = 8.5 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.71 (t, J = 7.7 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 7.51 (d, J = 4.5 Hz, 1H), 5.61 (s, 1H), 5.34 – 5.21 (m, 1H), 2.98 (q, J = 8.6 Hz, 1H), 2.77 – 2.52 (m, 3H), 1.81 (s, 1H), 1.64 (s, 1H), 1.54 – 1.27 (m, 6H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d and Methanol-d_4 (4:1)) δ 150.34, 149.54, 147.33, 129.26, 129.17, 126.84, 125.49, 122.85, 118.32, 70.90, 59.72, 50.73, 50.03, 37.11, 26.74, 26.01, 24.89, 19.51, 11.77. HRMS (ESI/[M+H]$^+$): Calculated for $C_{19}H_{25}N_2O$ requires m/z 297.1961, found m/z 297.1956.



Cn-1 Cn-2
49% yield

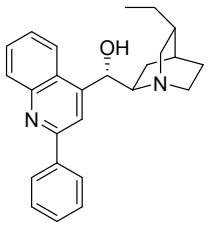
Cn-2 was prepared partly according to Deng's method[2]. Cn-1 (5.93 g, 20 mmol) and *m*-CPBA (75%, 11.53 g, 50 mmol) was added to $CHCl_3$ (100 mL) at 0ºC. The resulting suspension was allowed to warm to room temperature and stirred for 3 hours, during which time the reaction mixture

became a clear yellow solution. The reaction was quenched with NaOH (*aq*) (10% in H_2O) until pH = 10. The resulting two-phase mixture was extracted with a mixed solvent of $CHCl_3$/MeOH (10/1, 6×100 mL). The organic phase was collected and evaporated in vacuo to give the crude product A. This crude product A was used in the next step without further purification. To the solution of product A in acetone (10 mL) at 0ºC was added dropwise an aqueous solution of 65% $NaHSO_3$ /37% HCl /H_2O(9.6 g/ 6.08 g/ 40 g) under N_2. The resulting mixture was warmed to room temperature for 1 h. The resulting mixture was stirred overnight. Then, the acetone was removed under vacuum, and it was adjusted to pH=8 with NH_4OH *aq*. Chloroform (5×250 mL) was used to extract the aqueous layer and concentrated in vacuo. This crude product B was used in the next step without further purification. At 0ºC, to the solution of product B in $CHCl_3$ (100 mL) was added dropwise the solution of $POBr_3$ (22.9 g, 80 mmol) in $CHCl_3$ (20 mL) under N_2. Then orange solution was warmed to room temperature and stirred overnight. $CHCl_3$ (50 mL) was added and the mixture was poured into ice-water (50 mL). Then it was adjusted to pH=8 with NH_4OH (*aq*). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (5×100 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (MeOH/EA/PE/Et_3N=10/40/48/2) to afford Cn-2 as a white solid (3.68 g, 49% yield). $[a]_D^{20}$ = +141.2 (c 0.1, $CHCl_3$); m.p. 231-232 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.28 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.71 – 7.56 (m, 2H), 5.79 (d, *J* = 4.9 Hz, 1H), 5.22 (dd, *J* = 7.8, 5.1 Hz, 1H), 2.97 (q, *J* = 8.4 Hz, 1H), 2.73 – 2.57 (m, 2H), 2.49 – 2.38 (m, 2H), 1.76 (dd, *J* = 13.2, 8.7 Hz, 1H), 1.64 (s, 1H), 1.54 – 1.27 (m, 6H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d* and Methanol-d_4 (2:1)) δ 152.93, 148.19, 141.98, 130.08, 128.47, 127.05, 124.24, 122.98, 122.75, 70.60, 59.61, 50.54, 49.83, 36.93, 26.54, 25.82, 24.72, 19.29, 11.53. HRMS (ESI/[M+H]$^+$): Calculated for $C_{19}H_{24}BrN_2O$ requires m/z 375.1067, found m/z 375.1065.



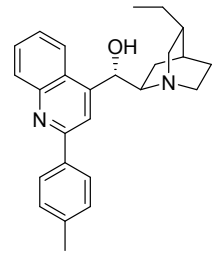
Cn-2 Cn-3
83-96% yield

To a flame-dried flask equipped with a magnetic stirring bar and a reflux condenser, Cn-2 (0.38 g, 1.0 mmol), substituted phenylboronic acid (1.2 mmol), K_2CO_3 (0.28 g, 2.0 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol) and MeOH/toluene (4 mL/ 4 mL) were added; the solution was stirred at 80ºC under nitrogen atmosphere for 24 hours. The reaction was quenched by water (5 mL). $CHCl_3$ (2×10 mL) was used to extract the aqueous layer. The organic layer were combined, washed by brine (10 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (MeOH/EA/PE/Et_3N=5/40/53/2) to afford Cn-3.



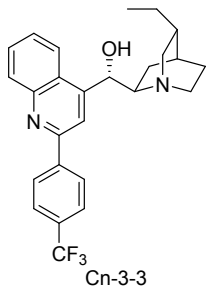
Cn-3-1

The general procedure was followed using Cn-2 (0.38 g, 1.0 mmol), phenylboronic acid (0.15 g, 1.2 mmol), K_2CO_3 (0.28 g, 2.0 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol). The product Cn-3-1 was obtained as a white solid (0.35 g, 0.94 mmol, 94% yield). $[a]_D^{20}$ = +108.0 (c 0.1, MeOH); m.p. 248-250 ºC; ^{1}H NMR (400 MHz, Methanol-d_4) δ 8.17 (d, J = 8.5 Hz, 1H), 8.10 (dd, J = 17.3, 7.5 Hz, 4H), 7.75 (t, J = 7.7 Hz, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.52 (dt, J = 15.6, 7.2 Hz, 3H), 5.80 (d, J = 2.9 Hz, 1H), 3.40 (dd, J = 13.4, 7.3 Hz, 2H), 3.10 (dt, J = 10.9, 5.3 Hz, 1H), 3.02 – 2.90 (m, 2H), 2.82 (dt, J = 13.3, 8.9 Hz, 1H), 2.20 (dd, J = 13.1, 9.3 Hz, 1H), 1.75 (d, J = 4.3 Hz, 1H), 1.56 (qt, J = 14.1, 7.0 Hz, 5H), 1.08 (ddd, J = 13.8, 9.2, 4.6 Hz, 1H), 0.93 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Methanol-d_4 and Chloroform-d (1:1)) δ 158.38, 151.15, 148.70, 140.31, 130.22, 130.16, 130.06, 129.39, 128.40, 127.32, 125.18, 123.42, 117.46, 71.42, 60.70, 51.32, 50.53, 37.65, 27.06, 26.69, 25.54, 20.20, 12.19. HRMS (ESI/[M+H]$^+$): Calculated for $C_{25}H_{29}N_2O$ requires m/z 373.2274, found m/z 373.2268.



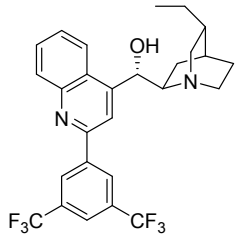
Cn-3-2

The general procedure was followed using Cn-2 (0.38 g, 1.0 mmol), *p*-tolylboronic acid (0.16 g, 1.2 mmol), K_2CO_3 (0.28 g, 2.0 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol). The product Cn-3-2 was obtained as a white solid (0.32 g, 0.83 mmol, 83% yield). $[a]_D^{20}$ = +101.5 (c 0.1, $CHCl_3$); m.p. 283-284 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (dd, J = 22.9, 6.6 Hz, 3H), 8.06 (d, J = 6.5 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.7 Hz, 1H), 7.35 (d, J = 7.8 Hz, 2H), 5.68 (s, 1H), 5.39 (s, 1H), 3.08 (d, J = 8.0 Hz, 1H), 2.86 (s, 1H), 2.80 – 2.55 (m, 3H), 2.42 (s, 3H), 1.93 (s, 1H), 1.70 (s, 1H), 1.47 (ddt, J = 37.8, 19.8, 8.7 Hz, 6H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Methanol-d_4 and Chloroform-d (3:2)) δ 158.19, 150.74, 148.47, 140.08, 137.30, 129.94, 128.16, 126.95, 124.86, 123.17, 117.15, 71.21, 60.43, 51.18, 50.42, 37.47, 26.93, 26.50, 25.37, 21.44, 19.88, 12.13. HRMS (ESI/[M+H]$^+$): Calculated for $C_{26}H_{31}N_2O$ requires m/z 387.2431, found m/z 387.2428.



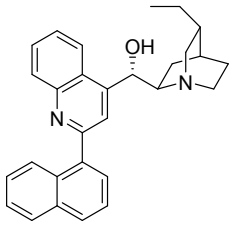
Cn-3-3

The general procedure was followed using Cn-2 (0.38 g, 1.0 mmol), (4-(trifluoromethyl)phenyl)boronic acid (0.23 g, 1.2 mmol), K_2CO_3 (0.28 g, 2.0 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol). The product Cn-3-3 was obtained as a white solid (0.41 g, 0.93 mmol, 93% yield). $[a]_D^{20}$ = +109.3 (c 0.1, $CHCl_3$); m.p. 276-278 ºC; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.28 (d, J = 8.0 Hz, 2H), 8.19 (d, J = 8.5 Hz, 1H), 8.09 (d, J = 1.7 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.82 – 7.66 (m, 3H), 7.48 (dd, J = 8.6, 6.6 Hz, 1H), 5.72 (d, J = 4.7 Hz, 1H), 3.41 (s, 1H), 3.11 (td, J = 9.2, 4.6 Hz, 1H), 3.04 – 2.82 (m, 3H), 2.74 (dt, J = 13.3, 8.8 Hz, 1H), 2.00 – 1.87 (m, 1H), 1.54 – 1.45 (m, 2H), 1.44 – 1.34 (m, 3H), 1.30 – 1.14 (m, 2H), 0.86 (td, J = 7.1, 2.1 Hz, 3H). ^{13}C NMR (101 MHz, Methanol-d_4 and Chloroform-d (1:1)) δ 156.45, 151.61, 148.69, 143.70, 130.45, 130.30, 128.68, 127.66, 126.18, 126.14, 125.38, 124.75 (d, J = 274.7 Hz, CF_3), 117.03, 71.51, 60.59, 51.27, 50.50, 37.66, 27.15, 26.62, 25.48, 20.21, 12.16. HRMS (ESI/[M+H]$^+$): Calculated for $C_{26}H_{28}F_3N_2O$ requires m/z 441.2148, found m/z 441.2147.



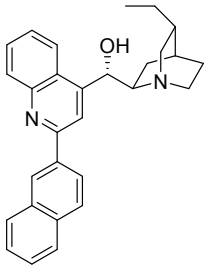
Cn-3-4

The general procedure was followed using Cn-2 (0.38 g, 1.0 mmol), (3,5-bis(trifluoromethyl)phenyl)boronic acid (0.31 g, 1.2 mmol), K_2CO_3 (0.28 g, 2.0 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol). The product Cn-3-4 was obtained as a white solid (0.49 g, 0.96 mmol, 96% yield). $[a]_D^{20}$ = +65.0 (c 0.1, $CHCl_3$); m.p. 162-164 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.89 (s, 2H), 8.44 – 8.30 (m, 2H), 8.25 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 5.75 (d, *J* = 5.3 Hz, 1H), 5.35 (dd, *J* = 8.3, 4.8 Hz, 1H), 3.16 (q, *J* = 8.5 Hz, 1H), 2.80 – 2.58 (m, 2H), 2.44 (q, J = 6.8, 5.6 Hz, 2H), 1.90 – 1.73 (m, 1H), 1.67 (s, 1H), 1.51 (dddd, *J* = 31.3, 20.9, 11.4, 5.8 Hz, 4H), 1.34 (q, *J* = 8.4, 7.4 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.51, 151.48, 148.34, 141.83, 132.24 (q, *J* = 33.3 Hz) 130.88, 129.76, 127.67, 127.60, 127.16, 125.03, 123.57 (q, *J* = 273.7 Hz, CF_3), 122.88 – 122.76 (m), 122.64, 115.32, 71.69, 60.31, 51.20, 50.34, 37.43, 29.83, 27.07, 26.39, 25.21, 20.51, 12.05. HRMS (ESI/[M+H]$^+$): Calculated for $C_{27}H_{27}F_6N_2O$ requires m/z 509.2022, found m/z 509.2023.



Cn-3-5

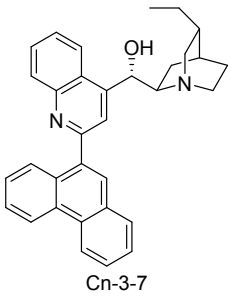
The general procedure was followed using Cn-2 (0.38 g, 1.0 mmol), naphthalen-1-ylboronic acid (0.21 g, 1.2 mmol), K_2CO_3 (0.28 g, 2.0 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol). The product Cn-3-5 was obtained as a white solid (0.40 g, 0.95 mmol, 95% yield). $[a]_D^{20}$ = +87.7 (c 0.1, $CHCl_3$); m.p. 168-170 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.08 (q, *J* = 7.9, 6.7 Hz, 3H), 7.86 – 7.73 (m, 3H), 7.67 (q, *J* = 8.3 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 5.72 (s, 1H), 5.36 (t, *J* = 6.1 Hz, 1H), 3.09 (q, *J* = 8.3 Hz, 1H), 2.72 (t, *J* = 8.9 Hz, 2H), 2.57 (t, J = 8.3 Hz, 2H), 1.83 (t, *J* = 10.7 Hz, 1H), 1.66 (s, 1H), 1.59 – 1.26 (m, 6H), 0.86 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Methanol-d_4 and Chloroform-*d* (5:2)) δ 159.32, 150.59, 134.18, 129.93, 129.75, 129.54, 128.71, 127.90, 127.22, 126.85, 126.31, 125.74, 125.56, 124.74, 123.18, 120.98, 71.34, 60.23, 51.10, 50.42, 37.47, 27.09, 26.44, 25.25, 20.00, 12.09. HRMS (ESI/[M+H]$^+$): Calculated for $C_{29}H_{31}N_2O$ requires m/z 423.2431, found m/z 423.2428.



Cn-3-6

The general procedure was followed using Cn-2 (0.38 g, 1.0 mmol), naphthalen-2-ylboronic acid (0.21 g, 1.2 mmol), K_2CO_3 (0.28 g, 2.0 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol). The product Cn-3-6 was obtained as a white solid (0.36 g, 0.86 mmol, 86% yield). $[a]_D^{20}$ = +77.0 (c 0.1, MeOH); m.p. 248-249 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 1.8 Hz, 1H), 8.37 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.28 – 8.20 (m, 2H), 8.06 – 7.95 (m, 3H), 7.90 (dt, *J* = 6.2, 3.4 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.54 (dt, *J* = 6.2, 3.2 Hz, 2H), 7.48 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 5.76 (d, *J* = 4.5 Hz, 1H), 3.42 (s, 1H), 3.14 (td, *J* = 9.2, 4.6 Hz, 1H), 3.04 (dd, *J* = 14.3, 6.4 Hz, 1H), 2.97 – 2.85 (m, 2H), 2.76 (dt, *J* = 13.1, 9.0 Hz, 1H), 2.05 – 1.93 (m, 1H), 1.55 – 1.37 (m, 5H), 1.31 – 1.17 (m, 2H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Methanol-d_4 and Chloroform-*d* (5:1)) δ 157.25, 150.31, 148.15, 136.99, 133.80, 133.41, 129.92, 129.40, 128.75, 128.48, 127.66, 127.38, 126.75, 126.52, 126.35, 125.14, 124.42, 122.60, 116.61, 71.09, 59.79, 50.89 , 50.17 , 37.19, 26.79, 26.13, 24.97, 19.28, 11.89. HRMS

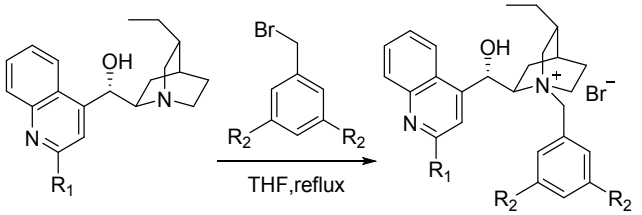
(ESI/[M+H]$^+$): Calculated for $C_{29}H_{31}N_2O$ requires m/z 423.2431, found m/z 423.2430.



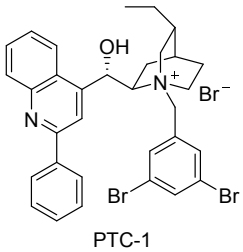
Cn-3-7

The general procedure was followed using Cn-2 (0.38 g, 1.0 mmol), phenanthren-9-ylboronic acid (0.27 g, 1.2 mmol), K_2CO_3 (0.28 g, 2.0 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol). The product Cn-3-6 was obtained as a white solid (0.41 g, 0.87 mmol, 87% yield). $[a]_D^{20}$ = +62.6 (c 0.1, $CHCl_3$); m.p. 140-142 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.98 (d, J = 8.4 Hz, 1H), 8.93 (d, J = 8.2 Hz, 1H), 8.38 (d, J = 8.5 Hz, 1H), 8.21 – 8.09 (m, 3H), 8.07 (s, 1H), 7.84 (s, 1H), 7.71 (dddd, J = 46.5, 21.2, 15.8, 7.8 Hz, 6H), 5.76 (d, J = 4.8 Hz, 1H), 5.37 (t, J = 6.1 Hz, 1H), 3.10 (q, J = 8.4 Hz, 1H), 2.70 (q, J = 13.0, 10.3 Hz, 2H), 2.58 (q, J = 10.3, 8.0 Hz, 2H), 1.82 (dd, J = 13.3, 8.6 Hz, 1H), 1.65 (s, 1H), 1.44 (ddp, J = 43.3, 23.6, 8.1, 7.1 Hz, 6H), 0.85 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Methanol-d_4 and Chloroform-d (3:1)) δ 159.27, 150.42, 148.03, 137.44, 131.46, 131.02, 130.78, 130.50, 129.93, 129.75, 129.34, 128.93, 127.58, 127.25, 127.02, 127.00, 126.65, 124.74, 123.28, 123.12, 122.83, 120.93, 71.14, 60.20, 51.04, 50.37, 37.33, 26.93, 26.34, 25.15, 19.87, 12.01. HRMS (ESI/[M+H]$^+$): Calculated for $C_{33}H_{33}N_2O$ requires m/z 473.2587, found m/z 473.2587.

2.2 Preparation of cinchonine-derived phase-transfer catalysts (PTC)



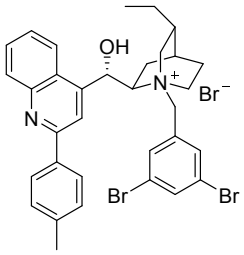
The phase-transfer catalysts (PTCs) were synthesized according to known procedures. To a flame-dried flask equipped with a magnetic stirring bar and a reflux condenser, the Cn-3 (0.2 mmol), the desired bromide (0.24 mmol) and THF (4 mL) were added. The mixture was heated to reflux under N_2 for 12 hours. The mixture was cooled to room temperature and poured into Et_2O and isolated by filtration. Then, the crude product was recrystallized from MeOH/Et_2O to afford corresponding product.



PTC-1

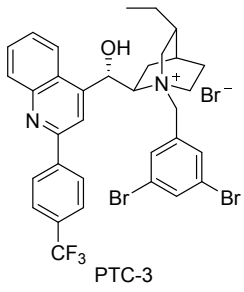
The general procedure was followed using Cn-3-1 (0.075 g, 0.2 mmol), 1,3-dibromo-5-(bromomethyl)benzene (0.079 g, 0.24 mmol). The product PTC-1 was obtained as a white solid (0.105 g, 0.15 mmol, 75% yield). $[a]_D^{20}$ = +79.3 (c 0.1, MeOH); m.p. 257-258 ºC; ^{1}H NMR (400 MHz, Methanol-d_4) δ 8.31 (d, J = 7.5 Hz, 1H), 8.25 (s, 1H), 8.11 (d, J = 7.5 Hz, 2H), 7.95 (d, J = 7.5 Hz, 3H), 7.78 (s, 1H), 7.58 (t, J = 7.4 Hz, 2H), 7.54 (d, J = 7.0 Hz, 1H), 7.47 (dd, J = 10.0, 5.5 Hz, 2H), 6.43 (s, 1H), 5.62 (d, J = 12.1 Hz, 1H), 5.09 (d, J = 12.1 Hz, 1H), 4.16 (dt, J = 29.1, 10.3 Hz, 3H), 3.35 (t, J = 5.7 Hz, 1H), 2.86 (q, J = 10.2 Hz, 1H), 2.23 (t, J = 12.2 Hz, 1H), 1.89 (s, 1H), 1.73 (dq, J = 43.6, 10.1, 9.5 Hz, 3H), 1.57 (hept, J = 6.8 Hz, 2H), 0.92 (q, J = 8.4, 7.2 Hz, 4H). ^{13}C NMR (101 MHz, Methanol-d_4 and Chloroform-d (5:2)) δ 157.47, 147.80, 145.77, 139.59, 136.58, 135.53, 131.36, 130.00, 129.92, 129.72, 129.23, 128.09,

127.92, 123.86, 123.53, 123.35, 118.20 , 68.09, 66.00, 60.88, 57.08, 56.79, 36.17, 24.72, 24.46, 24.34, 21.57, 11.52. HRMS (ESI/[M-Br^-]$^+$): Calculated for $C_{32}H_{33}Br_2N_2O$ requires m/z 619.0954, found m/z 619.0958.



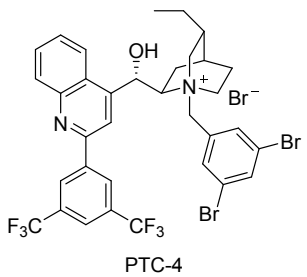
PTC-2

The general procedure was followed using Cn-3-2 (0.077 g, 0.2 mmol), 1,3-dibromo-5-(bromomethyl)benzene (0.079 g, 0.24 mmol). The product PTC-2 was obtained as a white solid (0.125 g, 0.174 mmol, 87% yield). $[a]_D^{20}$ = +129.3 (c 0.1, $CHCl_3$); m.p. 243-245 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (d, J = 11.5 Hz, 2H), 8.21 (d, J = 7.9 Hz, 2H), 8.15 (d, J = 8.4 Hz, 1H), 8.10 (s, 3H), 7.86 (t, J = 7.7 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 7.8 Hz, 2H), 6.76 (s, 1H), 6.47 (s, 1H), 5.06 (d, J = 12.4 Hz, 1H), 4.86 (d, J = 12.4 Hz, 1H), 3.90 (ddd, J = 45.7, 21.3, 9.9 Hz, 3H), 3.51 (t, J = 11.2 Hz, 1H), 3.00 (q, J = 10.1 Hz, 1H), 2.42 (s, 3H), 2.39 – 2.31 (m, 1H), 1.91 – 1.64 (m, 4H), 1.54 (dt, J = 14.0, 7.0 Hz, 2H), 1.10 (q, J = 10.2, 6.6 Hz, 1H), 0.87 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 156.27, 147.32, 144.34, 139.38, 137.16, 136.30, 135.15, 131.10, 129.77, 129.63, 128.38, 127.64, 126.90, 123.49, 123.11, 122.27, 117.29, 67.55, 65.91, 59.57, 56.62, 56.17, 36.09, 24.50, 24.30, 23.98, 21.67, 21.48, 15.36, 11.45. HRMS (ESI/[M-Br^-]$^+$): Calculated for $C_{33}H_{35}Br_2N_2O$ requires m/z 633.1111, found m/z 633.1107.



PTC-3

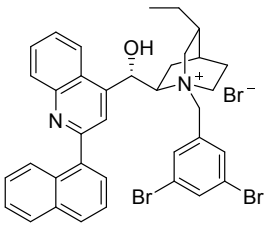
The general procedure was followed using Cn-3-3 (0.088 g, 0.2 mmol), 1,3-dibromo-5-(bromomethyl)benzene (0.079 g, 0.24 mmol). The product PTC-3 was obtained as a white solid (0.112 g, 0.146 mmol, 73% yield). $[a]_D^{20}$ = +107.3 (c 0.1, MeOH); m.p. 246-248 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.54 (d, J = 8.1 Hz, 2H), 8.42 (s, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 4.2 Hz, 3H), 7.97 (d, J = 8.2 Hz, 2H), 7.91 (t, J = 7.7 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 6.81 (d, J = 3.6 Hz, 1H), 6.51 (s, 1H), 5.09 (d, J = 12.4 Hz, 1H), 4.87 (d, J = 12.4 Hz, 1H), 3.93 (ddd, J = 35.1, 19.0, 8.0 Hz, 3H), 3.51 (t, J = 11.1 Hz, 1H), 3.00 (q, J = 10.0 Hz, 1H), 2.37 (t, J = 11.8 Hz, 1H), 1.90 – 1.65 (m, 4H), 1.56 (h, J = 6.7 Hz, 2H), 1.12 (dq, J = 13.7, 7.4, 5.6 Hz, 1H), 0.87 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.08, 147.62, 146.66, 142.37, 135.49, 135.04, 132.54, 130.11, 129.71 (q, J = 31.3 Hz), 128.09, 127.74, 125.87 – 125.75 (m), 124.25 (q, J = 273.7 Hz, CF_3), 123.94, 123.78, 122.77, 117.26, 67.87, 65.05, 60.26, 56.19, 56.06, 34.82, 24.06, 23.61, 20.29, 11.36. HRMS (ESI/[M-Br^-]$^+$): Calculated for $C_{33}H_{32}Br_2F_3N_2O$ requires m/z 687.0828, found m/z 687.0825.



PTC-4

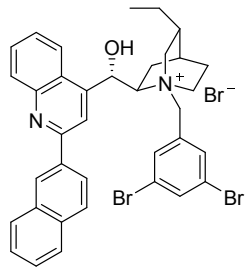
The general procedure was followed using Cn-3-4 (0.102 g, 0.2 mmol), 1,3-dibromo-5-(bromomethyl)benzene (0.079 g, 0.24 mmol). The product PTC-4 was obtained as a white solid (0.07 g, 0.084 mmol, 42% yield). $[a]_D^{20}$ = +91.1 (c 0.1, $CHCl_3$); m.p. 288-289 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.91 (s, 2H), 8.54 (s, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.33 (s, 1H), 8.28 (d, J = 8.4 Hz, 1H), 8.11 (s, 3H), 7.94 (t, J = 7.7 Hz, 1H), 7.82 (t, J = 7.6 Hz, 1H), 6.81 (s, 1H), 6.53 (s, 1H), 5.07 (d, J = 12.5 Hz, 1H), 4.85 (d, J = 12.5 Hz, 1H), 4.04 – 3.76 (m, 3H), 3.52 (t, J = 11.2 Hz, 1H),

3.00 (q, J = 10.1 Hz, 1H), 2.40 (t, J = 11.8 Hz, 1H), 1.94 – 1.64 (m, 4H), 1.56 (dt, J = 14.2, 7.1 Hz, 2H), 1.09 (s, 1H), 0.87 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.12, 147.39, 147.15, 140.97, 135.47, 135.04, 132.67, 130.9 (q, J = 32.3 Hz), 130.09, 127.89, 127.59, 124.15, 124.10, 123.33 (q, J =273.71 Hz, CF_3), 122.91, 122.74, 117.04, 68.21, 65.45, 60.03, 56.14, 55.89, 34.90, 24.09, 23.67, 23.59, 20.41, 11.35. HRMS (ESI/[M-Br$^-$]$^+$): Calculated for $C_{34}H_{31}Br_2F_6N_2O$ requires m/z 755.0702, found m/z 755.0706.



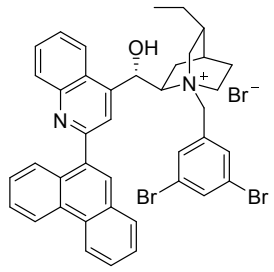
PTC-5

The general procedure was followed using Cn-3-5 (0.085 g, 0.2 mmol), 1,3-dibromo-5-(bromomethyl)benzene (0.079 g, 0.24 mmol). The product PTC-5 was obtained as a white solid (0.084 g, 0.112 mmol, 56% yield). $[a]_D^{20}$ = +97.8 (c 0.1, MeOH); m.p. 252-254 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.40 (d, J = 8.4 Hz, 1H), 8.19 (t, J = 7.5 Hz, 2H), 8.15 – 8.01 (m, 6H), 7.93 (t, J = 7.7 Hz, 1H), 7.82 (t, J = 7.1 Hz, 2H), 7.72 (t, J = 7.8 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 6.76 (s, 1H), 6.54 (s, 1H), 5.11 (d, J = 12.4 Hz, 1H), 4.88 (d, J = 12.5 Hz, 1H), 4.09 – 3.79 (m, 3H), 3.50 (t, J = 11.5 Hz, 1H), 3.01 (q, J = 10.0 Hz, 1H), 2.33 (t, J = 11.8 Hz, 1H), 1.75 (dt, J = 35.0, 11.1 Hz, 3H), 1.47 (h, J = 7.2 Hz, 2H), 1.26 (dd, J = 16.5, 9.3 Hz, 1H), 0.83 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 158.18, 146.91, 144.64, 138.54, 136.29, 135.13, 134.12, 131.18, 131.04, 129.73, 129.38, 128.74, 128.59, 127.99, 127.32, 126.69, 126.08, 125.77, 125.55, 123.52, 123.46, 122.16, 121.60, 67.33, 65.60, 59.56, 56.59, 56.17, 35.94, 24.44, 24.20, 23.89, 21.71, 11.36. HRMS (ESI/[M-Br$^-$]$^+$): Calculated for $C_{36}H_{35}Br_2N_2O$ requires m/z 669.1111, found m/z 669.1109.



PTC-6

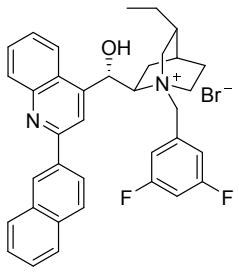
The general procedure was followed using Cn-3-6 (0.085 g, 0.2 mmol), 1,3-dibromo-5-(bromomethyl)benzene (0.079 g, 0.24 mmol). The product PTC-6 was obtained as a white solid (0.136 g, 0.181 mmol, 91% yield). $[a]_D^{20}$ = +142.8 (c 0.1, $CHCl_3$); m.p. 249-251 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.87 (s, 1H), 8.51 (d, J = 9.0 Hz, 2H), 8.33 (d, J = 8.4 Hz, 1H), 8.22 (t, J = 8.8 Hz, 2H), 8.13 (d, J = 17.3 Hz, 4H), 8.06 – 7.99 (m, 1H), 7.90 (t, J = 7.7 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.68 – 7.56 (m, 2H), 6.82 (s, 1H), 6.51 (s, 1H), 5.08 (d, J = 12.4 Hz, 1H), 4.86 (d, J = 12.4 Hz, 1H), 3.99 (t, J = 10.6 Hz, 1H), 3.88 (d, J = 13.7 Hz, 2H), 3.65 – 3.45 (m, 2H), 3.01 (q, J = 10.2 Hz, 1H), 2.43 (t, J = 11.6 Hz, 1H), 1.86 (s, 1H), 1.82 – 1.68 (m, 3H), 1.58 (h, J = 6.6 Hz, 2H), 1.21 – 1.10 (m, 1H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 155.93, 147.59, 144.35, 136.32, 135.15, 133.88, 133.54, 131.13, 129.98, 129.02, 128.53, 127.77, 127.18, 126.69, 126.33, 125.19, 123.55, 123.37, 117.46, 68.04, 67.82, 59.66, 56.67, 56.19, 36.13, 25.69, 24.52, 24.33, 24.01, 21.73, 11.47. HRMS (ESI/[M-Br$^-$]$^+$): Calculated for $C_{36}H_{35}Br_2N_2O$ requires m/z 669.1111, found m/z 669.1109.



PTC-7

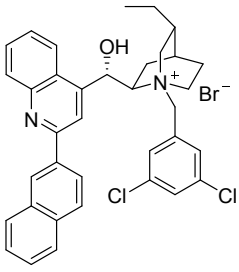
The general procedure was followed using Cn-3-7 (0.095 g, 0.2 mmol), 1,3-dibromo-5-(bromomethyl)benzene (0.079 g, 0.24 mmol). The product PTC-7 was obtained as a white solid (0.120 g, 0.15 mmol, 75% yield). $[a]_D^{20}$ = +25 (c 0.1, $CHCl_3$); m.p. 251-253 ºC; ^{1}H NMR (400

MHz, DMSO-d_6) δ 9.02 (d, J = 8.4 Hz, 1H), 8.96 (d, J = 8.3 Hz, 1H), 8.41 (d, J = 8.5 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H), 8.14 – 8.02 (m, 6H), 7.94 (t, J = 7.7 Hz, 1H), 7.80 (ddd, J = 17.6, 14.2, 7.9 Hz, 4H), 7.64 (t, J = 7.6 Hz, 1H), 6.78 (d, J = 3.7 Hz, 1H), 6.55 (s, 1H), 5.09 (d, J = 12.4 Hz, 1H), 4.85 (d, J = 12.4 Hz, 1H), 3.91 (t, J = 9.9 Hz, 3H), 3.50 (t, J = 11.4 Hz, 1H), 3.00 (q, J = 10.2 Hz, 1H), 2.33 (t, J = 11.6 Hz, 1H), 1.89 (s, 1H), 1.77 (dt, J = 27.4, 10.9 Hz, 3H), 1.45 (dq, J = 13.9, 6.8 Hz, 2H), 1.25 (d, J = 19.3 Hz, 1H), 0.81 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 158.21, 147.00, 144.83, 137.18, 136.31, 135.18, 131.31, 131.10, 131.06, 130.58, 130.21, 129.71, 129.24, 129.04, 128.93, 127.50, 127.42, 127.07, 126.85, 126.64, 123.60, 123.50, 123.23, 122.70, 122.40, 121.73, 67.41, 65.68, 59.68, 56.65, 56.23, 35.98, 24.43, 24.20, 23.89, 21.75, 11.35. HRMS (ESI/[M-Br$^-$]$^+$): Calculated for $C_{40}H_{37}Br_2N_2O$ requires m/z 719.1267, found m/z 719.1267.



PTC-8

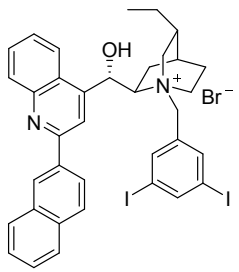
The general procedure was followed using Cn-3-6 (0.095 g, 0.2 mmol), 1-(bromomethyl)-3,5-difluorobenzene (0.050 g, 0.24 mmol). The product PTC-8 was obtained as a white solid (0.082 g, 0.13 mmol, 65% yield). $[\alpha]_D^{20}$ = +166.7 (c 0.1, $CHCl_3$); m.p. 262-263 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.88 (s, 1H), 8.60 – 8.45 (m, 2H), 8.36 (d, J = 8.4 Hz, 1H), 8.23 (t, J = 8.4 Hz, 2H), 8.14 (d, J = 8.6 Hz, 1H), 8.07 – 7.97 (m, 1H), 7.90 (t, J = 7.7 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.70 – 7.58 (m, 4H), 7.54 (t, J = 9.5 Hz, 1H), 6.87 (d, J = 3.5 Hz, 1H), 6.54 (s, 1H), 5.12 (d, J = 12.4 Hz, 1H), 4.90 (d, J = 12.3 Hz, 1H), 3.95 (dq, J = 29.0, 10.2 Hz, 3H), 3.58 (q, J = 11.2, 9.6 Hz, 1H), 3.00 (q, J = 10.1 Hz, 1H), 2.43 (t, J = 11.8 Hz, 1H), 1.85 (s, 1H), 1.74 (dd, J = 23.2, 13.9 Hz, 3H), 1.64 – 1.49 (m, 2H), 1.18 (d, J = 12.1 Hz, 1H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Methanol-d_4 and Chloroform-d (3:1))δ 164.37, 164.27, 161.88, 161.75, 157.02, 147.93, 145.36, 136.81, 134.13, 133.64, 130.98, 129.80, 129.70 , 129.01, 128.86, 127.94, 127.76, 127.64, 127.19, 126.76, 125.20, 123.53, 123.33, 118.13, 117.33, 117.07, 106.33, 77.86, 77.54, 77.22, 68.05 , 66.27, 60.93, 57.09, 56.67, 36.15, 24.72, 24.38, 24.34, 21.57 , 11.46. HRMS (ESI/[M-Br$^-$]$^+$): Calculated for $C_{36}H_{35}F_2N_2O$ requires m/z 549.2712, found m/z 549.2710.



PTC-9

The general procedure was followed using Cn-3-6 (0.095 g, 0.2 mmol), 1-(bromomethyl)-3,5-dichlorobenzene (0.058 g, 0.24 mmol). The product PTC-9 was obtained as a white solid (0.09 g, 0.136 mmol, 68% yield). $[\alpha]_D^{20}$ = +147.5 (c 0.1, $CHCl_3$); m.p. 268-270 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.88 (s, 1H), 8.52 (d, J = 9.7 Hz, 2H), 8.34 (d, J = 8.5 Hz, 1H), 8.23 (t, J = 8.5 Hz, 2H), 8.14 (d, J = 8.7 Hz, 1H), 8.07 – 8.00 (m, 1H), 7.99 – 7.82 (m, 4H), 7.76 (t, J = 7.6 Hz, 1H), 7.68 – 7.55 (m, 2H), 6.85 (s, 1H), 6.52 (s, 1H), 5.10 (d, J = 12.4 Hz, 1H), 4.89 (d, J = 12.4 Hz, 1H), 4.00 (t, J = 10.1 Hz, 1H), 3.90 (d, J = 14.7 Hz, 2H), 3.54 (t, J = 11.4 Hz, 1H), 3.09 – 2.93 (m, 1H), 2.42 (d, J = 11.7 Hz, 1H), 1.86 (s, 1H), 1.77 (dt, J = 20.5, 11.0 Hz, 3H), 1.59 (p, J = 7.7, 7.2 Hz, 2H), 1.16 (s, 1H), 0.89 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 155.86, 147.53, 144.29, 136.89, 135.65, 133.83, 133.49, 131.90, 130.67, 130.61, 129.93, 128.95, 128.46, 127.72, 127.11, 126.65, 126.28, 125.13, 123.31, 117.39, 67.73, 59.72, 56.63, 56.14, 36.06, 24.50, 24.26, 23.98, 21.68, 11.41. HRMS (ESI/[M-Br$^-$

]$^+$): Calculated for $C_{36}H_{35}Cl_2N_2O$ requires m/z 581.2121, found m/z 581.2120.



PTC-10

The general procedure was followed using Cn-3-6 (0.095 g, 0.2 mmol), 1,3-diiodo-5-(iodomethyl)benzene (0.113 g, 0.24 mmol). The product PTC-10 was obtained as a white solid (0.105 g, 0.124 mmol, 62% yield). $[\alpha]_D^{20}$ = +142.3 (c 0.1, $CHCl_3$); m.p. 240-241 ºC;^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 8.53 – 8.28 (m, 3H), 8.10 (d, *J* = 11.3 Hz, 4H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.54 (p, *J* = 7.0 Hz, 2H), 7.06 (dt, *J* = 20.4, 7.0 Hz, 2H), 6.67 (d, *J* = 5.6 Hz, 1H), 6.54 – 6.38 (m, 1H), 6.24 (d, *J* = 11.9 Hz, 1H), 5.25 (d, *J* = 11.9 Hz, 1H), 4.20 (q, *J* = 9.3 Hz, 2H), 4.09 (t, *J* = 11.3 Hz, 1H), 3.20 (t, *J* = 10.6 Hz, 1H), 2.66 (q, *J* = 10.1 Hz, 1H), 2.09 (t, *J* = 12.3 Hz, 1H), 1.86 (s, 1H), 1.79 – 1.59 (m, 3H), 1.49 (dq, *J* = 21.3, 13.5, 10.9 Hz, 3H), 0.83 (q, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.02, 147.68, 147.57, 144.46, 141.45, 137.00, 133.94, 133.60, 131.17, 130.02, 129.07, 128.67, 128.56, 127.80, 127.25, 126.72, 126.35, 125.25, 123.50, 122.83, 117.55, 95.42, 67.95, 59.55, 56.70, 56.26, 36.21, 24.57, 24.42, 24.04, 21.75, 11.51. HRMS (ESI/[M-Br$^-$]$^+$): Calculated for $C_{36}H_{35}I_2N_2O$ requires m/z 765.0833, found m/z 765.0834.

3. General procedure in the flow photomicroreactors

3.1The general procedure in the flow photomicroreactor

Due to the limitations of the microreactor material, the reaction conditions were not exactly the same as the batch. Substrate 1 (0.1 mmol), 20 mol% PTC-6 and 0.1 mol% TPP were dissolved in 10 mL of $PhCH_3$. In the pump 1, the $PhCH_3$ (organic phase) flow rate was 1.5 mL/min, and in the pump 2, 10% K_2HPO_4 solution (aqueous phase) flow rate was 1.5 mL/min. O_2 flow rate was 10 mL/min and the reaction pressure was 3 atm. The reaction was carried out at 0ºC under white light. After completion of the reaction, 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 column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, 5/1) to afford the product 2. The ee of the product was determined by chiral HPLC.

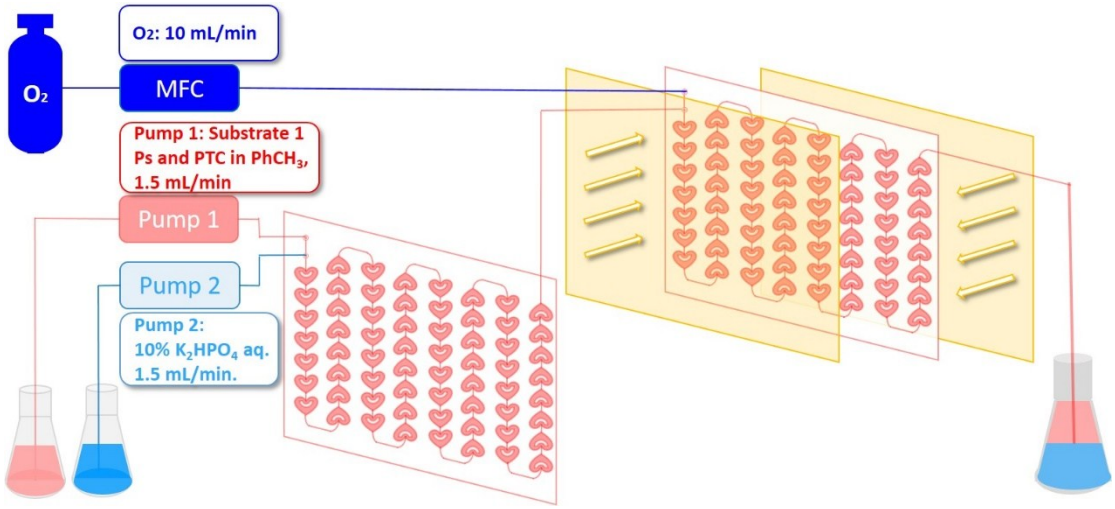


Figure S1. Schematic representation of flow photomicroreactor for asymmetric photocatalytic oxidation of β-dicarbonyl compounds

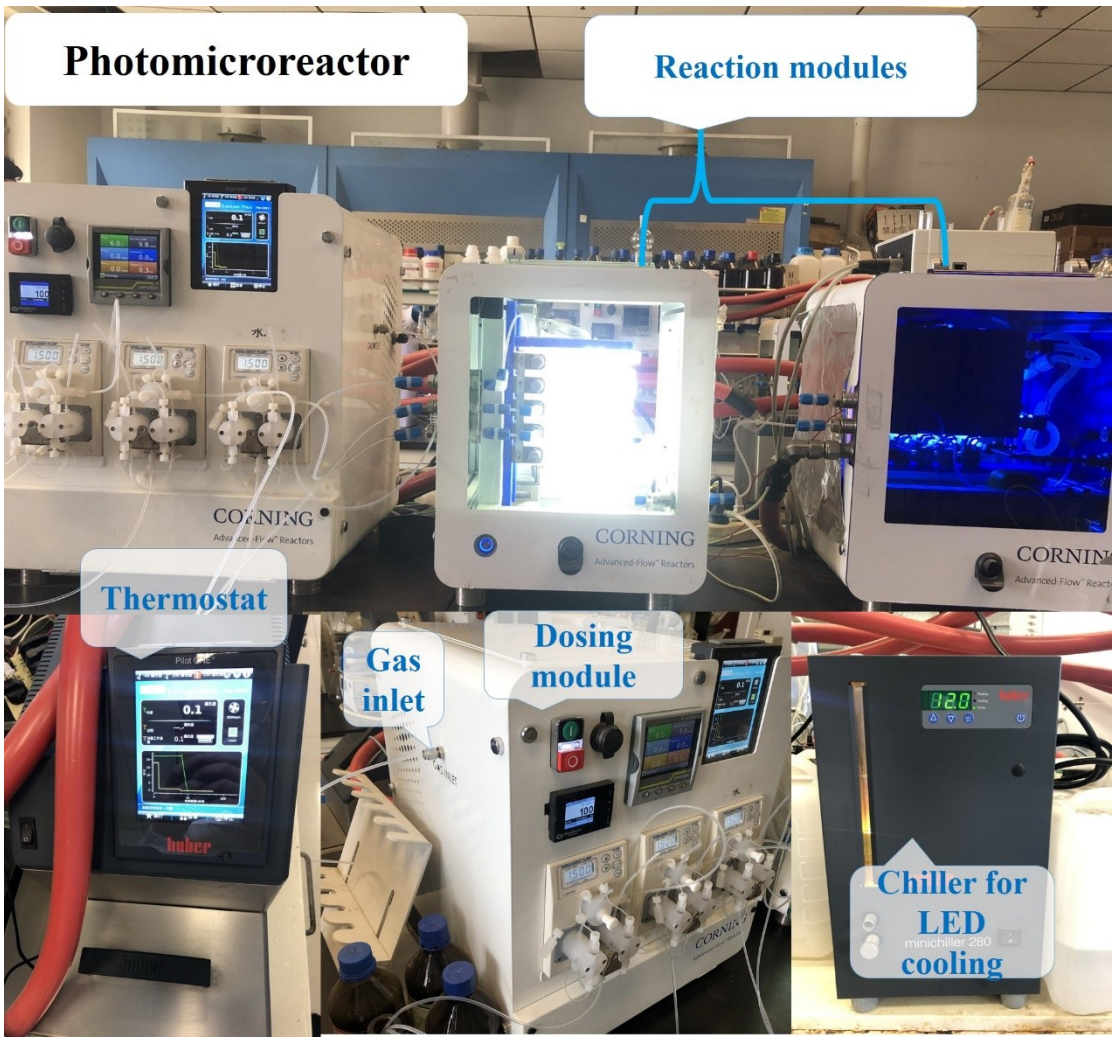


Figure S2. Corning Advanced Flow Reactor. The reaction system contains a dosing module, two reaction modules, two thermostat (for controlling the reaction temperature) and a chiller (for LED cooling). The dosing module equipped with 3 liguid dosing lines (based on HPLC type metal free pumps), a gas dosing line (using mass flow gas controller, with control panel), a thermostat control panel and a gas control panel. The two reaction modules were both equipped with a back pressure regulator at the outlet. O_2 in an oxygen cylinder was transfer to the reaction system with the gas inlet in the dosing module. The reaction mixture was inlet to the reaction modules with the liquid dosing line in the dosing module.

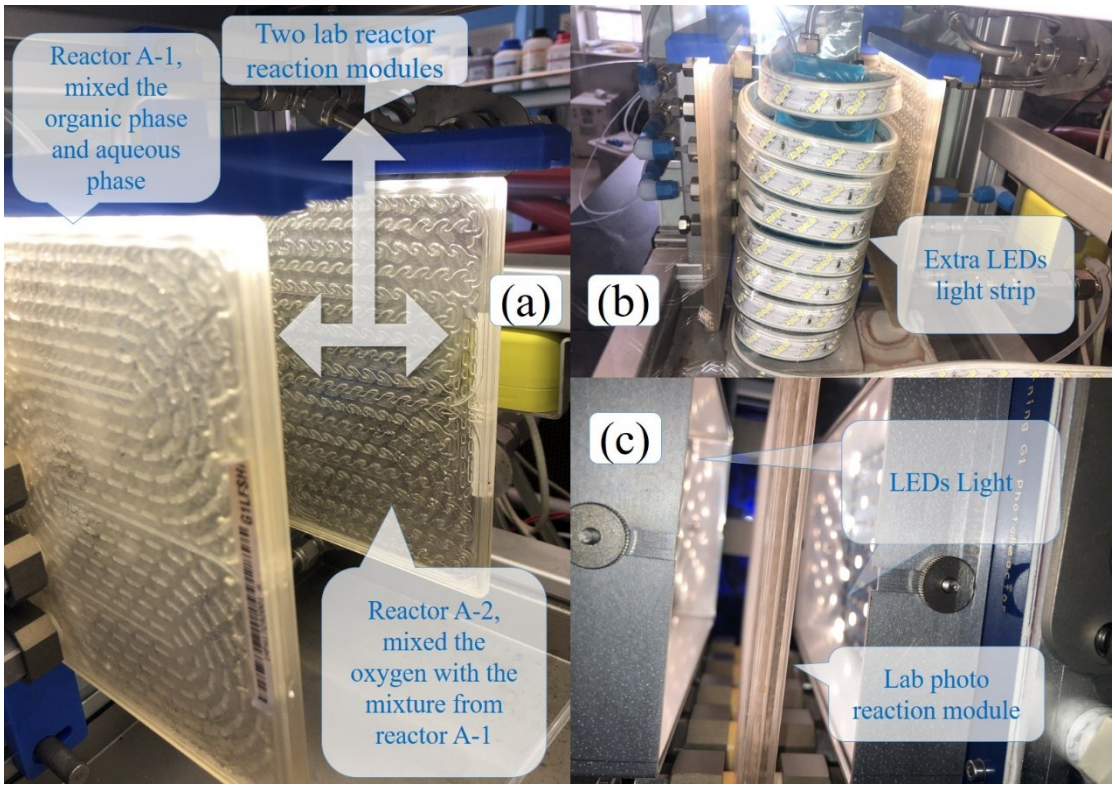


Figure S3. The description of the light for the reaction in the flow photomicroreactor. (a) Two lab reactor reaction modules (Reactor A-1 and A-2, L× W× H: 155 mm×125 mm×8 mm) have no photo module to provide light. Organic phase and aqueous phase was mixed in the Reactor A-1, and after that, it was mixed with oxygen in the Reactor A-2. (b) The white LEDs light strip (2 m, 20W, (10 W/m, 4000K)) was wrapped around a shelf and then put the shelf between the two lab reactor reaction modules to provide light. (c) The lab photo reaction module (Reactor A-3, L× W× H: 155 mm×125 mm×8 mm) has a LEDs Light module (original) to provide light (20 W, 4000 K, 100 mW/cm^2, white light). And the mixture reacted in the Reactor A-2 and A-3 under white light.

3.2 The resident time in the flow photomicroreactor

$$Resident\ time = \frac{V}{v_{liq} + v_{gas}}$$

$$v_{liq} = v_1 + v_2$$

$$v_{gas} = \frac{T^* \times p}{T \times p^*} \times v_{o_2}$$

Therefore:

$$Resident\ time = \frac{V}{v_1 + v_2 + \frac{T^* \times p}{T \times p^*} \times v_{o_2}}$$

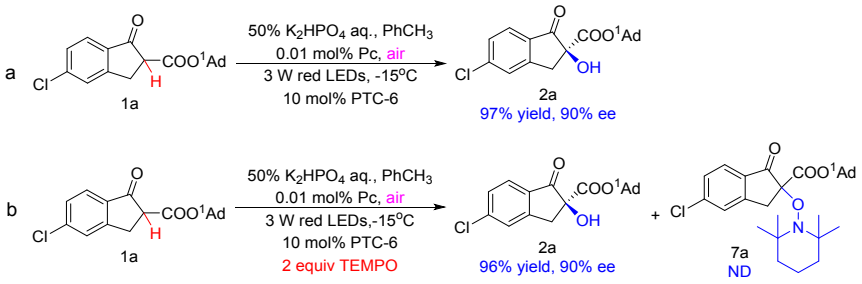
V refers to the total volume of the reaction module (Reactor A-2 and Reactor A-3), V =5.4 mL. v_{liq} and v_{o_2} refer to the flow rate of the reaction mixture and O_2, respectively. v_1 refers to the flow rate of the organic phase (pump 1) and v_2 refers to the flow rate of the aqueous phase (pump 2). v_1= 1.5 mL/min, and v_2= 1.5 mL/min. v_{gas} refers to the flow rate of the oxygen in the reactor under pressure, and p is 1 atm (standard state), and p^* is the reaction pressure, T is 298.15 K and T^* is

the reaction temperature. v_{o_2}= 10 mL/min.

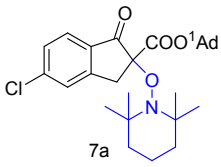
4. Control experiments and mechanistic studies

4.1 Radical Trapping Experiments[3]

According to Tan's report[4], α-oxyamination **7a** was synthesised from β-dicarbonyl compounds **1a** by visible-light-induced photocatalytic oxidation with 43% yield. However, addition of 2 *equiv.* TEMPO into our reaction systems still produced the α-hydroxylation product **2a** with 96% yield and 90% ee. And, no α-oxyamination were detected from the reaction mixture. According to these results, we believe that the radical pathway is not crucial in the current reaction.



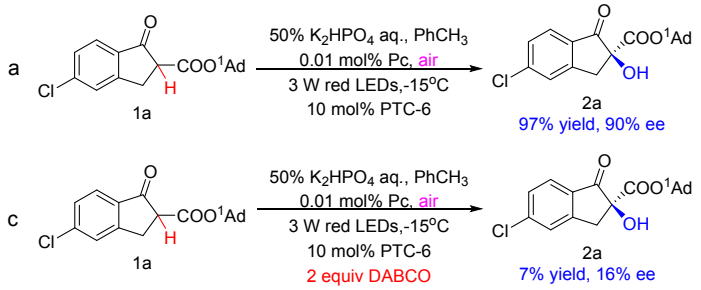
1-adamantanyl-5-chloro-1-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2,3-dihydro-1H-indene-2-carboxylate (7a):



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 1.7 Hz, 1H), 7.32 (dd, *J* = 8.2, 1.7 Hz, 1H), 4.57 (d, *J* = 17.7 Hz, 1H), 3.29 (d, *J* = 17.7 Hz, 1H), 2.14 – 2.08 (m, 3H), 2.02 (d, *J* = 3.0 Hz, 6H), 1.60 (t, *J* = 3.0 Hz, 6H), 1.58 – 1.51 (m, 2H), 1.48 – 1.40 (m, 2H), 1.33 (s, 3H), 1.33 – 1.25 (m, 2H), 1.18 (s, 3H), 1.10 (s, 3H), 0.56 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.30 , 168.35 , 154.68 , 141.74 , 132.99 , 128.13 , 126.20 , 125.51 , 89.92 , 82.74 , 60.48 , 59.36 , 40.91 , 40.44 , 40.18 , 35.92 , 33.82 , 32.29 , 31.97 , 30.75 , 20.77 , 20.46 , 16.89 . HRMS calculated for $C_{29}H_{39}ClNO_4$ [(M+H)$^+$]: 500.2562, found: 500.2560.

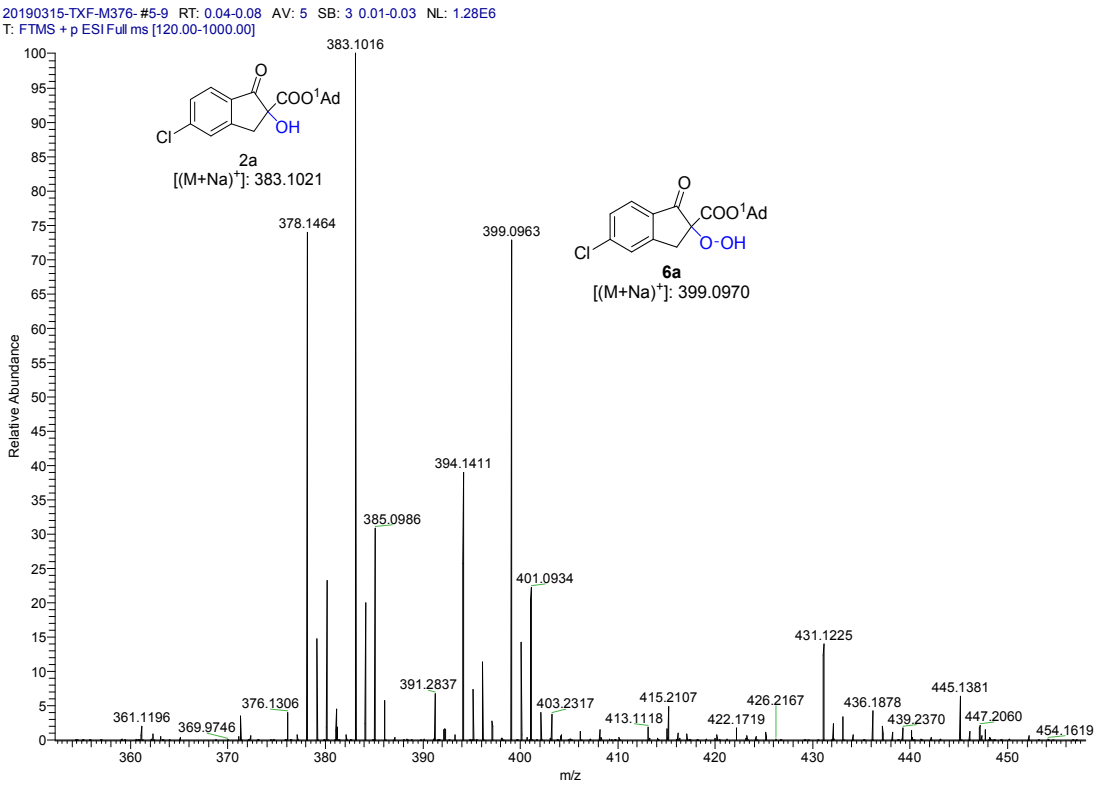
4.2 Study for Singlet Oxygen

We carried out control experiments trying to verify the presence of photoexcited singlet oxygen. When the singlet oxygen quencher, 1,4-diazabicyclo[2.2.2]octane (DABCO), was added to the 1a reaction system, a greatly reduced product yield and enantioselectivity was observed (7% yield and 16% ee).

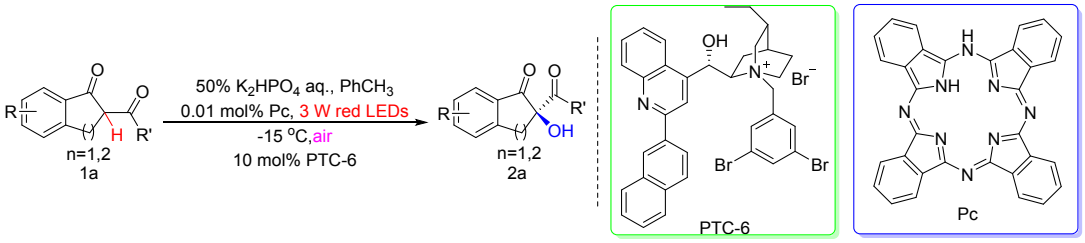


4.3 Study for the α-Hydroperoxide Intermediate

With further research, the α-hydroperoxide β-ketoester intermediate **6a** has been observed by HRMS of the reaction solution. In the photomicroreactor (CORNING Advanced-Flow Reactors), substrate **1a** (0.1 mmol), PTC-6 (10 mol%) and TPP (5 mol%) were dissolved in toluene (10 mL). Under 5 atm of O_2 and visible light generated from a white LED lamp (100mW/cm^2) at 0 ºC, the residence time was 1.12 minutes. Under this condition, the α-hydroperoxide **6a** was detected by HRMS. However, because of the strong oxidability and instability of **6a**, we could not get the separated pure **6a**.

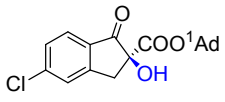


5. General procedure for the asymmetric α-hydroxylation of β-dicarbonyl compounds



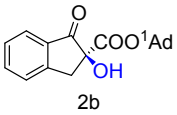
Substrate 1 (0.1 mmol), PTC-6 (10 mol %), 50% K_2HPO_4 aq (4 mL) and Pc (0.01mol %) were added to a test tube equipped with a stirring bar and dissolved in $PhCH_3$ (10 mL). It was stirred at -15 ºC covered by a 3w LED red lamp. After completion of the reaction (confirmed by TLC), the mixture was diluted 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 column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, 5/1) to afford the product 2a-2t. The ee of the product was determined by chiral HPLC.

(*S*)-1-adamantanyl 2-hydroxy-5-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2a)


2a

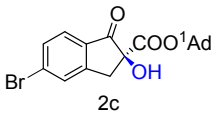
Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) to give **2a** as white solid (35.0 mg, 97% yield, 90% ee). $[a]_D^{20}$ = +81.6 (c 0.1, $CHCl_3$); m.p. 152-156 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.48 (s, 1H), 7.44 – 7.35 (m, 1H), 4.04 (s, 1H), 3.63 (d, *J* = 17.3 Hz, 1H), 3.20 (d, *J* = 17.3 Hz, 1H), 2.13 (s, 3H), 1.97 (d, *J* = 3.0 Hz, 6H), 1.61 (d, *J* = 2.9 Hz, 6H). HPLC conditions: Chiralpak AD-H column (250×4.6mm), hexane/*i*-PrOH = 80:20, 1.0 mL/min; 254 nm, τ_R (major) = 11.3 min, τ_R (minor) = 18.3 min.

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


2b

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) to give **2b** as colorless oil (31.3 mg, 96% yield, 86% ee). $[a]_D^{20}$ = +30.0 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.41 (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), 2.18 – 2.07 (m, 3H), 1.96 (d, *J* = 2.9 Hz, 6H), 1.60 (t, *J* = 2.9 Hz, 6H). HPLC conditions: Chiralpak AD-H column (250×4.6mm), hexane/*i*-PrOH = 80:20, 1.0 mL/min; 254 nm, τ_R (major) = 10.7 min, τ_R (minor) = 16.9 min.

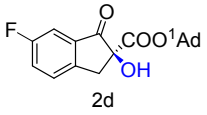
(*S*)-1-Adamantanyl 2-hydroxy-5-bromo-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2c)


2c

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) to give **2c** as white solid (38.9 mg, 96% yield, 89% ee). $[a]_D^{20}$ = +79.0 (c 0.1, $CHCl_3$); m.p. 192-194 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 9.4 Hz, 2H),

7.56 (d, *J* = 8.1 Hz, 1H), 4.01 (s, 1H), 3.63 (d, *J* = 17.3 Hz, 1H), 3.20 (d, *J* = 17.3 Hz, 1H), 2.13 (t, *J* = 3.3 Hz, 3H), 1.97 (d, *J* = 2.9 Hz, 6H), 1.61 (d, *J* = 3.0 Hz, 6H). HPLC conditions: Chiralpak AD-H column (250×4.6mm), hexane/*i*-PrOH = 80:20, 1.0 mL/min; 254 nm, τ_R (major) = 12.5 min, τ_R (minor) = 20.3 min.

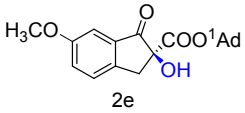
(*S*)-1-Adamantanyl 2-hydroxy-6-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2d)



2d

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) to give **2d** as white solid (31.7 mg, 92% yield, 84% ee). $[a]_D^{20}$ = +22.4 (c 0.1, $CHCl_3$); m.p. 58-60 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (td, *J* = 7.6, 6.5, 3.4 Hz, 2H), 7.36 (td, *J* = 8.4, 2.5 Hz, 1H), 4.04 (s, 1H), 3.61 (d, *J* = 16.9 Hz, 1H), 3.18 (d, *J* = 16.9 Hz, 1H), 2.13 (d, *J* = 4.1 Hz, 3H), 1.96 (d, *J* = 2.9 Hz, 6H), 1.60 (d, *J* = 3.0 Hz, 6H). HPLC conditions: Chiralpak AD-H column (250×4.6mm), hexane/*i*-PrOH = 80:20, 1.0 mL/min; 254 nm, τ_R (major) = 9.1 min, τ_R (minor) = 16.5 min.

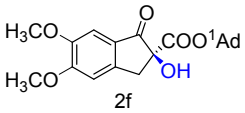
(*S*)-1-Adamantyl 2-hydroxy-6-methoxyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2e)



2e

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) to give **2e** as white solid (32.8 mg, 92% yield, 79% ee). $[a]_D^{20}$ = +20.5 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.3 Hz, 1H), 7.26 – 7.16 (m, 2H), 4.02 (s, 1H), 3.85 (s, 3H), 3.58 (d, *J* = 16.8 Hz, 1H), 3.13 (d, *J* = 16.7 Hz, 1H), 2.18 – 2.07 (m, 3H), 1.98 (d, *J* = 3.0 Hz, 6H), 1.60 (d, *J* = 3.1 Hz, 6H). HPLC conditions: Chiralpak AD-H column (250×4.6mm), hexane/*i*-PrOH = 80:20, 1.0 mL/min; 254 nm, τ_R (major) = 12.5 min, τ_R (minor) = 20.6 min.

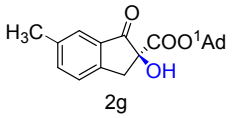
(*S*)-1-Adamantyl 2-hydroxy-5,6-dimethoxyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2f)



2f

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 5/1) to give **2f** as white solid (35.2 mg, 91% yield, 80% ee). $[a]_D^{20}$ = +73.2 (c 0.1, $CHCl_3$); m.p. 145-148 ºC;^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (s, 1H), 6.88 (s, 1H), 3.99 (d, *J* = 2.9 Hz, 4H), 3.92 (s, 3H), 3.57 (d, *J* = 16.8 Hz, 1H), 3.12 (d, *J* = 16.8 Hz, 1H), 2.22 – 2.11 (m, 3H), 2.00 (d, *J* = 3.0 Hz, 6H), 1.61 (d, *J* = 3.0 Hz, 6H). HPLC conditions: Chiralpak AD-H column (250×4.6mm), hexane/*i*-PrOH = 80:20, 1.0 mL/min; 254 nm, τ_R (major) = 19.0 min, τ_R (minor) = 30.9 min.

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

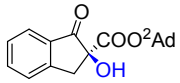


2g

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) to give **2g** as white solid (30.3 mg, 89% yield, 78% ee). $[a]_D^{20}$ = +35.8 (c 0.1, $CHCl_3$); m.p. 113-115 ºC;^{1}H NMR (400 MHz,

Chloroform-*d*) δ 7.58 (s, 1H), 7.46 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 3.99 (s, 1H), 3.61 (d, *J* = 16.9 Hz, 1H), 3.15 (d, *J* = 17.0 Hz, 1H), 2.41 (s, 3H), 2.12 (t, *J* = 3.4 Hz, 3H), 1.97 (d, *J* = 3.0 Hz, 6H), 1.60 (d, *J* = 3.0 Hz, 6H). HPLC conditions: Chiralpak AD-H column (250×4.6mm), hexane/*i*-PrOH = 80:20, 1.0 mL/min; 254 nm, τ_R (major) = 9.4 min, τ_R (minor) = 16.1 min.

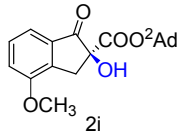
(*S*)-2-Adamantyl 2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2h)



2h

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) to give **2h** as white solid (30.0 mg, 92% yield, 77% ee). $[a]_D^{20}$ = +19.2 (c 0.1, $CHCl_3$); m.p. 58-59 ºC;^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 4.96 (s, 1H), 4.03 (s, 1H), 3.71 (d, *J* = 17.0 Hz, 1H), 3.30 (d, *J* = 17.0 Hz, 1H), 1.94 – 1.83 (m, 2H), 1.81 – 1.60 (m, 8H), 1.41 (d, *J* = 3.5 Hz, 2H), 1.33 – 1.24 (m, 2H). HPLC conditions: Chiralpak AD-H column (250×4.6mm), hexane/*i*-PrOH = 95:5, 1.0 mL/min; 254 nm, τ_R (major) = 21.7 min, τ_R (minor) = 28.5 min.

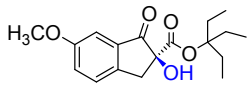
(*S*)-2-Adamantyl 2-hydroxy-4-methoxyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2i)



2i

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) to give **2i** as colorless oil (31.4 mg, 88% yield, 77% ee). $[a]_D^{20}$ = +38.4 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 4.3 Hz, 2H), 7.10 (p, *J* = 4.1 Hz, 1H), 5.01 – 4.90 (m, 1H), 4.02 (s, 1H), 3.91 (s, 3H), 3.66 (d, *J* = 17.4 Hz, 1H), 3.13 (d, *J* = 17.4 Hz, 1H), 1.89 (dd, *J* = 29.2, 3.6 Hz, 2H), 1.81 – 1.57 (m, 8H), 1.50 – 1.37 (m, 2H), 1.36 – 1.25 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.36, 170.87, 156.80, 141.08, 135.55, 129.63, 116.59, 116.29, 81.05, 79.78, 55.77, 37.23, 36.47, 36.21, 36.12, 31.84, 31.59, 31.57, 31.41, 27.02, 26.82. HRMS calculated for $C_{21}H_{25}O_5$ [(M+H)$^+$]: 357.1697, found: 357.1695. HPLC conditions: Chiralpak AD-H column (250×4.6mm), hexane/*i*-PrOH = 90:10, 1.0 mL/min; 254 nm, τ_R (major) = 24.7 min, τ_R (minor) = 34.4 min.

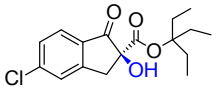
(*S*)-3-ethylpentan-3-yl 2-hydroxy-6-methoxyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2j)



2j

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) to give **2j** as colorless oil (26.6 mg, 83% yield, 66% ee). $[a]_D^{20}$ = +22.4 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.18 (m, 2H), 4.04 (s, 1H), 3.85 (s, 3H), 3.56 (d, *J* = 16.7 Hz, 1H), 3.16 (d, *J* = 16.7 Hz, 1H), 1.71 (qd, *J* = 7.5, 1.5 Hz, 6H), 0.67 (t, *J* = 7.5 Hz, 9H). HPLC conditions: Chiralpak AD-H column (250×4.6mm), hexane/i-PrOH = 95:5, 1.5 mL/min; 254 nm, τ_R (minor) = 13.6 min, τ_R (major) = 15.5 min.

(*S*)-3-ethylpentan-3-yl 5-chloro-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2k)

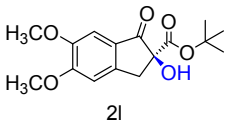


2k

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) to give **2k** as white solid (29.9 mg, 92% yield, 64% ee). $[a]_D^{20}$ = +24.6 (c 0.1, $CHCl_3$); m.p. 133-135 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.48 (s, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 4.05 (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: Chiralpak AS-H column (250×4.6mm), hexane/i-PrOH = 90:10, 1.0 mL/min; 254 nm, τ_R (minor) = 8.2 min, τ_R (major) = 9.9 min.

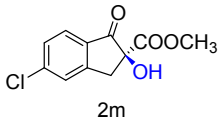
(*S*)-*t*-butyl 2-hydroxy-5,6-dimethoxyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2l)



2l

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 5/1) to give **2l** as white solid (23.7 mg, 77% yield, 61% ee). $[a]_D^{20}$ = +42.4 (c 0.1, $CHCl_3$); m.p. 113-116 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (s, 1H), 6.89 (s, 1H), 3.99 (s, 3H), 3.98 (s, 1H), 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: Chiralpak AS-H column (250×4.6mm), hexane/i-PrOH = 90:10, 1.0 mL/min; 254 nm, τ_R (minor) = 31.5 min, τ_R (major) = 43.9 min.

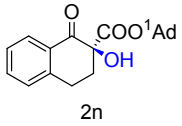
(*S*)-Methyl 2-hydroxy-5-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2m)



2m

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 5/1) to give **2m** as white solid (20.0 mg, 83% yield, 54% ee). $[a]_D^{20}$ = +53.6 (c 0.1, $CHCl_3$); m.p. 133-135 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.50 (s, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 4.06 (d, *J* = 2.0 Hz, 1H), 3.78 – 3.74 (m, 3H), 3.71 (d, *J* = 17.5 Hz, 1H), 3.24 (d, *J* = 17.5 Hz, 1H). HPLC conditions: Chiralpak OD-H column (250×4.6mm), hexane/i-PrOH = 90:10, 1.0 mL/min; 254 nm, τ_R (major) = 13.2 min, τ_R (minor) = 16.2 min.

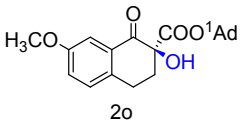
(*S*)-1-Adamantyl 2-hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2n)



2n

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) to give **2n** as yellow solid (27.9 mg, 82% yield, 70% ee). $[a]_D^{20}$ = -8.0 (c 0.1, $CHCl_3$); m.p. 95-96 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.25 (s, 1H), 4.23 (s, 1H), 3.12 (t, *J* = 6.3 Hz, 2H), 2.64 (dt, *J* = 13.6, 5.2 Hz, 1H), 2.22 (dt, *J* = 14.1, 7.6 Hz, 1H), 2.17 – 2.07 (m, 3H), 2.01 (d, *J* = 2.9 Hz, 6H), 1.60 (d, *J* = 3.0 Hz, 6H). HPLC conditions: Chiralpak OD-H column (250×4.6mm), hexane/i-PrOH = 90:10, 1.0 mL/min; 254 nm, τ_R (minor) = 7.4 min, τ_R (major) = 9.8 min.

(*S*)-1-Adamantyl 2-hydroxy-7-methoxyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2o)

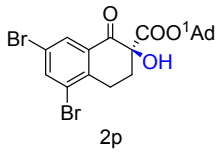


2o

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) to give **2o** as colorless oil (30.7 mg, 83% yield, 65% ee). $[a]_D^{20}$ = -12.0 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 2.7 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 7.10 (dd, *J* = 8.5, 2.8 Hz, 1H), 4.21 (s, 1H), 3.85 (s, 3H), 3.05 (dd, *J* = 7.4, 5.2 Hz, 2H), 2.62 (dt, *J* = 13.5, 5.1 Hz, 1H), 2.25 – 2.17 (m, 1H), 2.16 – 2.08 (m, 3H), 2.02 (d, *J* = 2.9 Hz, 6H), 1.61 (d, *J* = 3.1 Hz, 6H). HPLC conditions: Chiralpak AD-H column

(250×4.6mm), hexane/i-PrOH = 80:20, 1.0 mL/min; 254 nm, τ_R (major) = 10.8 min, τ_R (minor) = 17.1 min.

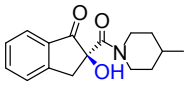
(*S*)-1-Adamantyl 2-hydroxy-5,7-dibromine-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2p)



2p

Prepared according to the general procedure with a reaction time of 8 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) to give **2p** as colorless oil (38.4 mg, 77% yield, 59% ee). $[a]_D^{20}$ = -1.9 (c 0.1, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 2.1 Hz, 1H), 7.93 (d, *J* = 2.1 Hz, 1H), 4.10 (s, 1H), 3.11 (dt, *J* = 18.2, 5.6 Hz, 1H), 2.99 (ddd, *J* = 18.2, 9.1, 5.3 Hz, 1H), 2.64 (dt, *J* = 13.9, 5.4 Hz, 1H), 2.23 (td, *J* = 8.9, 4.5 Hz, 1H), 2.18 – 2.10 (m, 3H), 2.01 (d, *J* = 2.9 Hz, 6H), 1.62 (t, *J* = 3.0 Hz, 6H). HPLC conditions: Chiralpak AD-H column (250×4.6mm), hexane/i-PrOH = 90:10, 1.0 mL/min; 254 nm, τ_R (major) = 9.0 min, τ_R (minor) = 14.7 min.

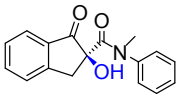
(*S*)- 2-hydroxy-2-(4-methylpiperidine-1-carbonyl)-2,3-dihydro-1*H*-inden-1-one (2q)



2q

Prepared according to the general procedure with a reaction time of 24 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 5/1) to give **2q** as colorless oil (15.6 mg, 57% yield, 72% ee). $[a]_D^{20}$ = -16.3 (c 0.1, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 7.7 Hz, 1H), 7.67 (td, *J* = 7.5, 1.3 Hz, 1H), 7.54 – 7.40 (m, 2H), 5.54 (d, *J* = 25.8 Hz, 1H), 4.59 (d, *J* = 36.4 Hz, 1H), 3.45 (d, *J* = 17.8 Hz, 1H), 3.31 (d, *J* = 18.1 Hz, 1H), 3.07 (s, 1H), 2.78 (d, *J* = 40.9 Hz, 2H), 1.60 (d, *J* = 29.0 Hz, 3H), 1.01 (d, *J* = 13.9 Hz, 2H), 0.92 (d, *J* = 6.4 Hz, 3H). HPLC conditions: Chiralpak AD-H column (250×4.6mm), hexane/i-PrOH = 90:10, 1.0 mL/min; 254 nm, τ_R (minor) = 25.5 min, τ_R (major) = 28.6 min.

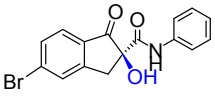
(*S*)-2-hydroxy-N-methyl-1-oxo-N-phenyl-2,3-dihydro-1*H*-indene-2-carboxamide (2r)



2r

Prepared according to the general procedure with a reaction time of 24 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 5/1) to give **2r** as yellow solid (12.9 mg, 46% yield, 54% ee). $[a]_D^{20}$ = -15.0 (c 0.1, $CHCl_3$); m.p. 92-94 ºC; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.31 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.12 – 6.65 (m, 6H), 5.41 (s, 1H), 3.55 (d, *J* = 18.0 Hz, 1H), 3.34 (s, 3H), 3.12 (d, *J* = 18.0 Hz, 1H). HPLC conditions: Chiralpak OD-H column (250×4.6mm), hexane/i-PrOH = 95:5, 1.0 mL/min; 254 nm, τ_R (minor) = 33.1 min, τ_R (major) = 38.0 min.

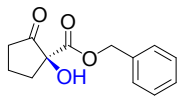
(*S*)-5-bromo-2-hydroxy-1-oxo-N-phenyl-2,3-dihydro-1*H*-indene-2-carboxamide (2s)



2s

Prepared according to the general procedure with a reaction time of 24 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 5/1) to give **2s** as white solid (23.2 mg, 67% yield, 18% ee). $[a]_D^{20}$ = +9.2 (c 0.1, $CHCl_3$); m.p. 187-189 ºC; ^1H NMR (400 MHz, Methanol-d_4) δ 7.81 – 7.74 (m, 1H), 7.69 – 7.53 (m, 4H), 7.35 – 7.29 (m, 2H), 7.17 – 7.08 (m, 1H), 3.85 (d, *J* = 17.3 Hz, 1H), 3.17 (d, *J* = 17.3 Hz, 1H). HPLC conditions: Chiralpak OD-H column (250×4.6mm), hexane/i-PrOH = 90:10, 1.0 mL/min; 254 nm, τ_R (major) = 23.0 min, τ_R (minor) = 33.4 min.

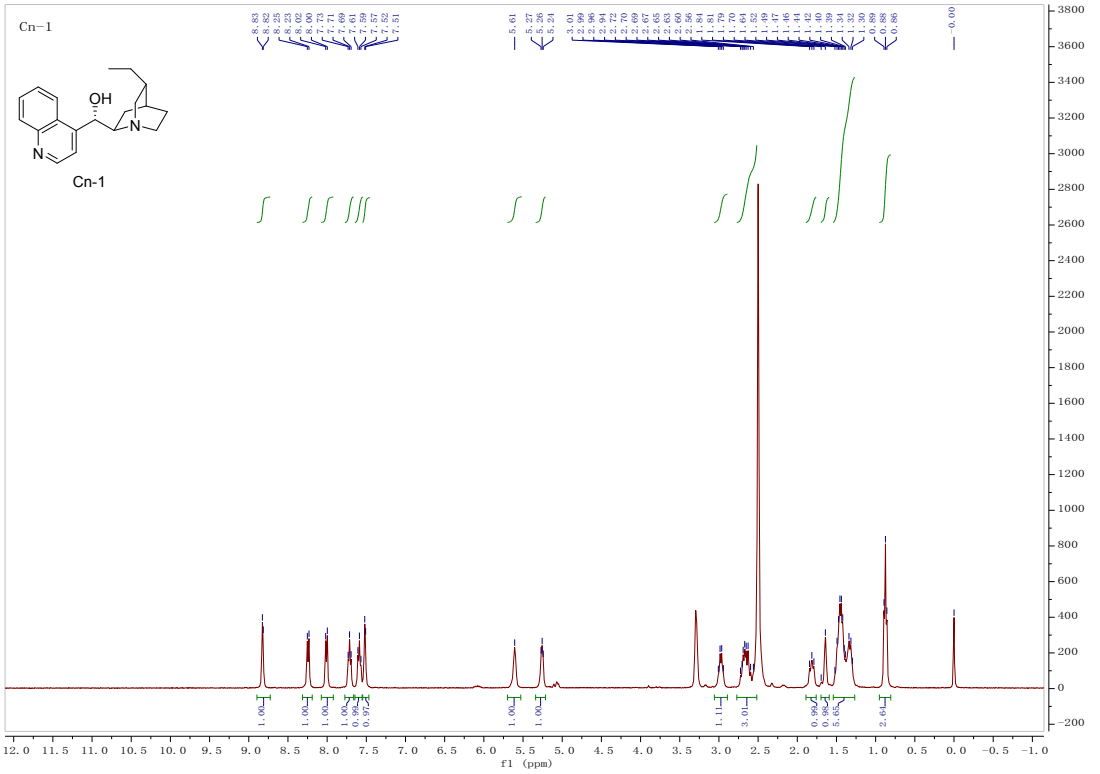
(*S*)-benzyl -1-hydroxy-2-oxocyclopentane-1-carboxylate (2t)

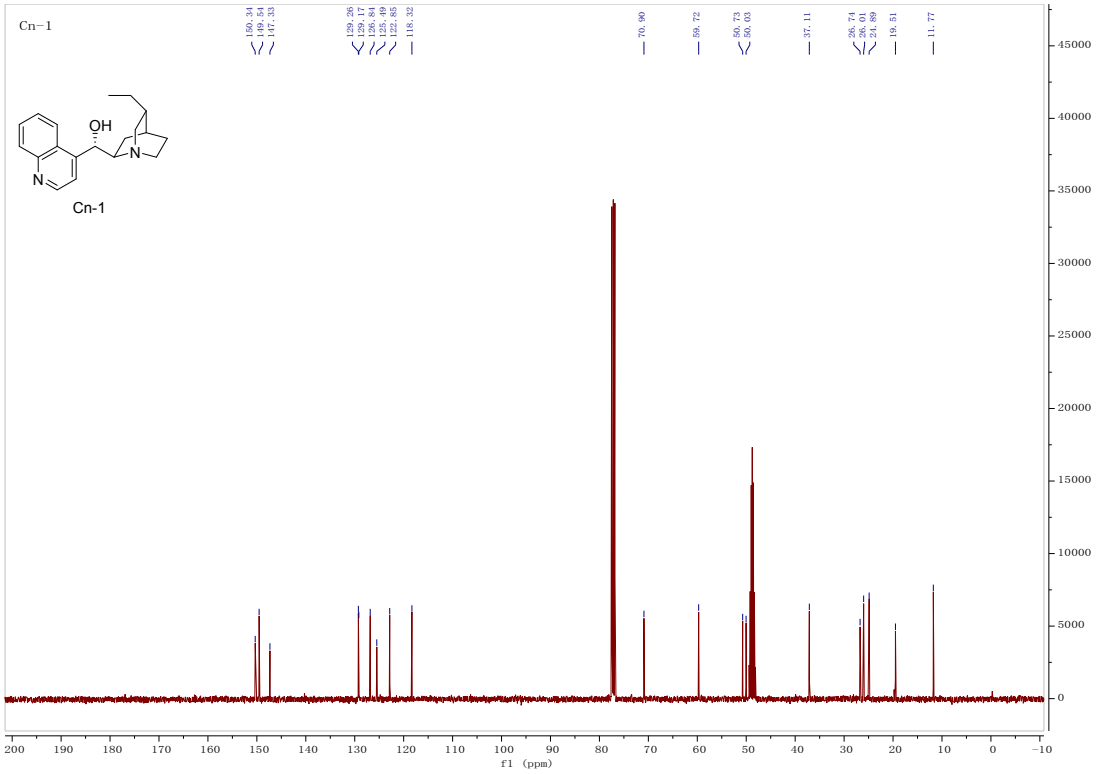


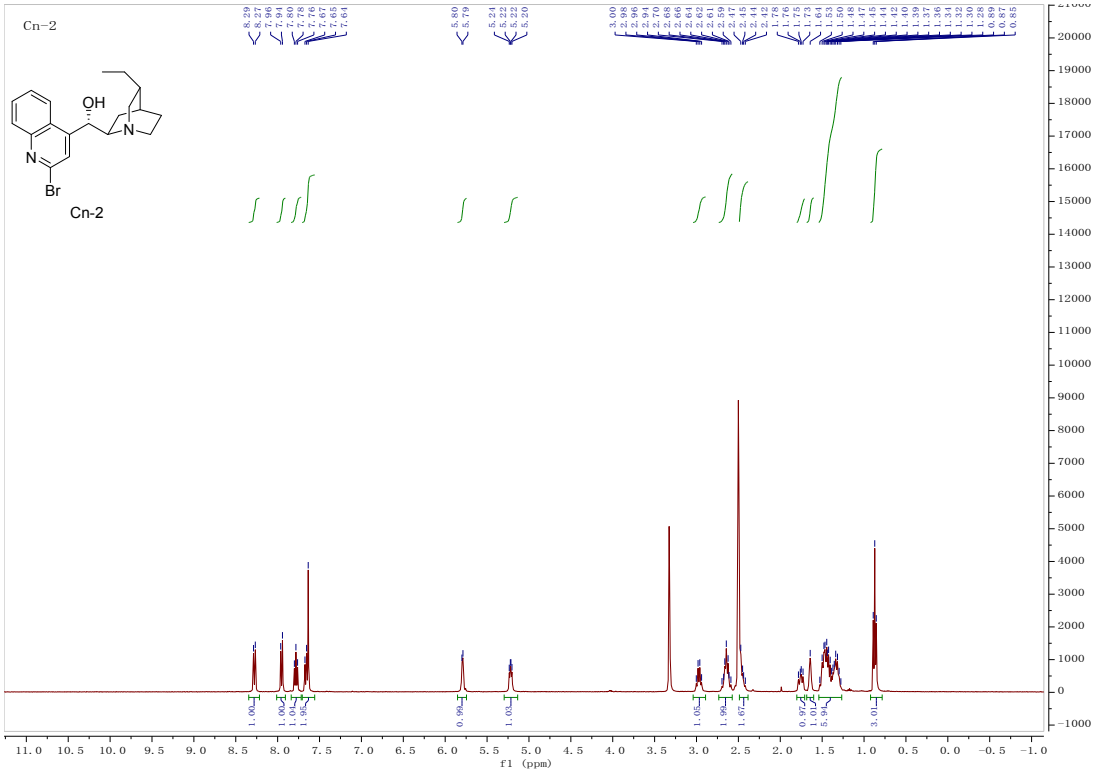
2t

Prepared according to the general procedure with a reaction time of 24 hours. After column chromatography (silica gel, petroleum ether/ethyl acetate = 5/1) to give **2t** as colorless oil (12.9 mg, 55% yield, 4% ee). $[a]_D^{20}$ = -0.2 (c 0.1, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.36 (td, *J* = 5.4, 2.5 Hz, 3H), 7.30 (dd, *J* = 7.5, 2.1 Hz, 2H), 5.22 (q, *J* = 12.2 Hz, 2H), 3.69 (s, 1H), 2.61 – 2.36 (m, 3H), 2.21 – 1.99 (m, 3H). HPLC conditions: Chiralpak OD-H column (250×4.6mm), hexane/i-PrOH = 95:5, 1.0 mL/min; 220 nm, τ_R (major) = 14.4 min, τ_R (minor) = 16.0 min.

6. Copies of NMR Spectra



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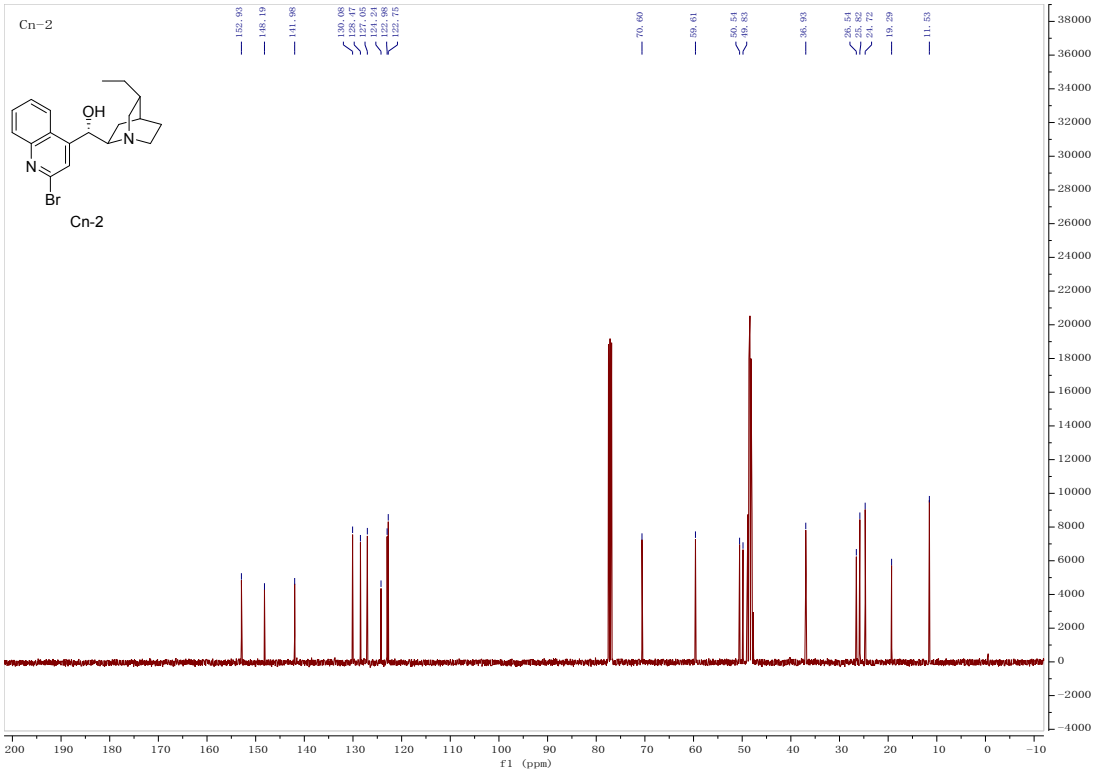
N
Br
Cn-2
f1 (ppm)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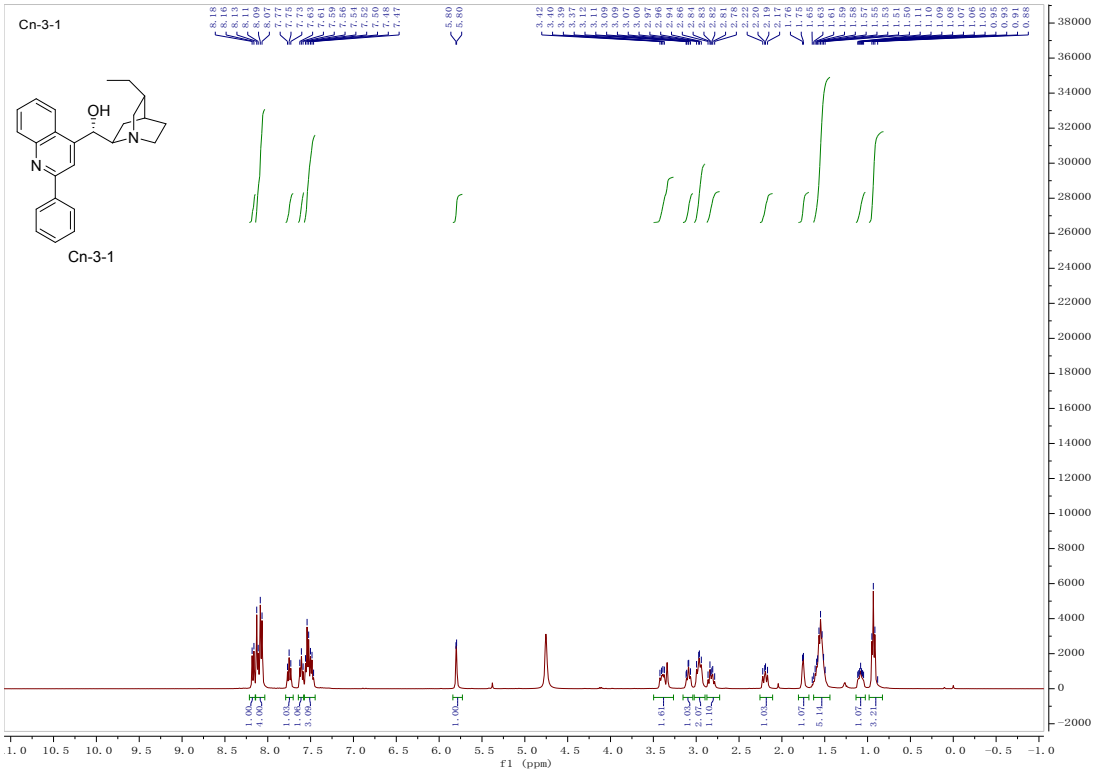
N
N
Br
Cn-2
f1 (ppm)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N
N
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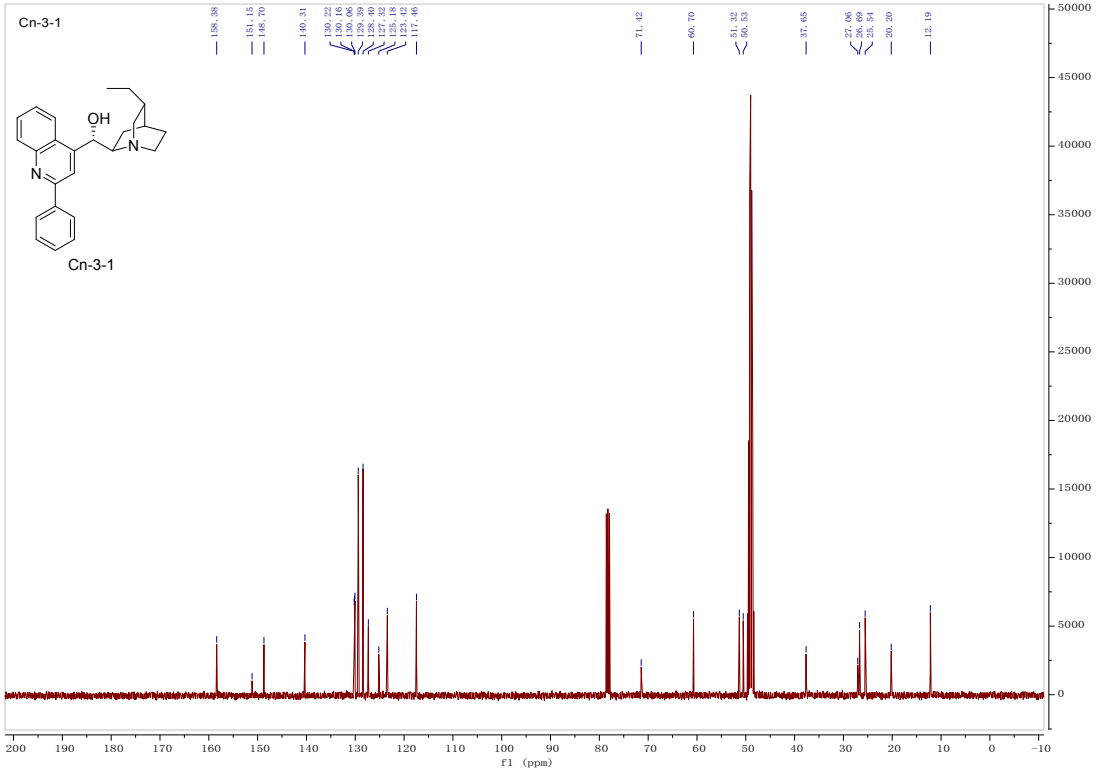
f1 (ppm)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N
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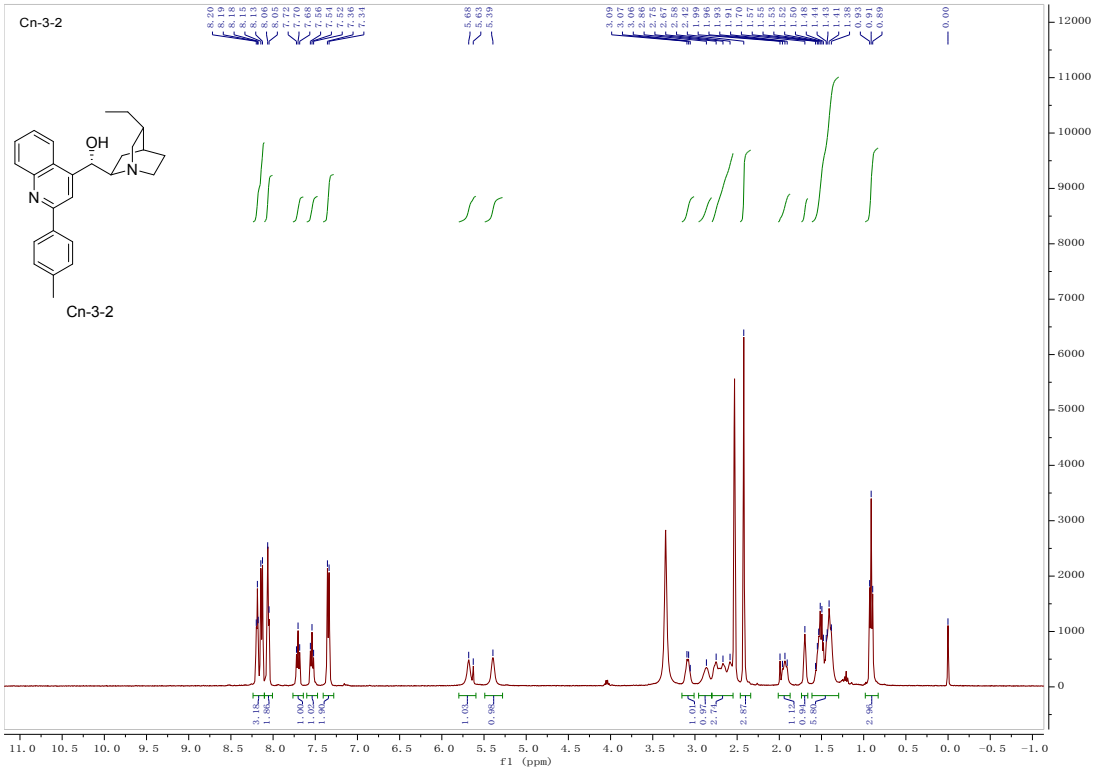
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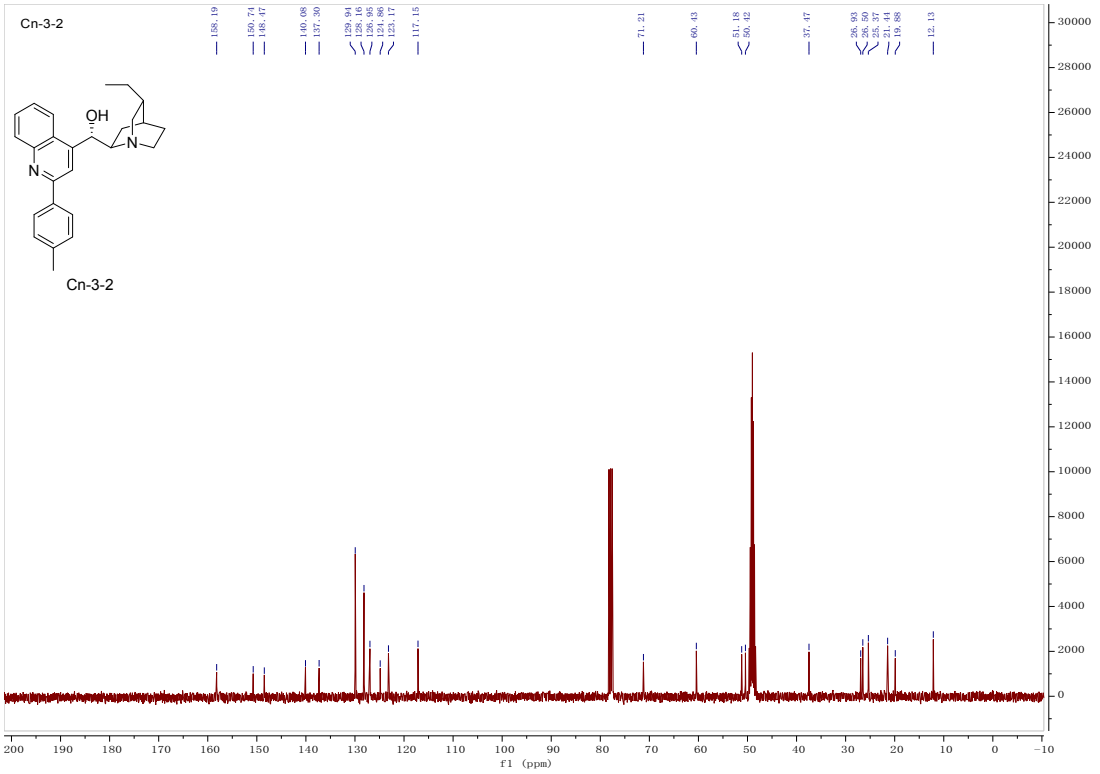
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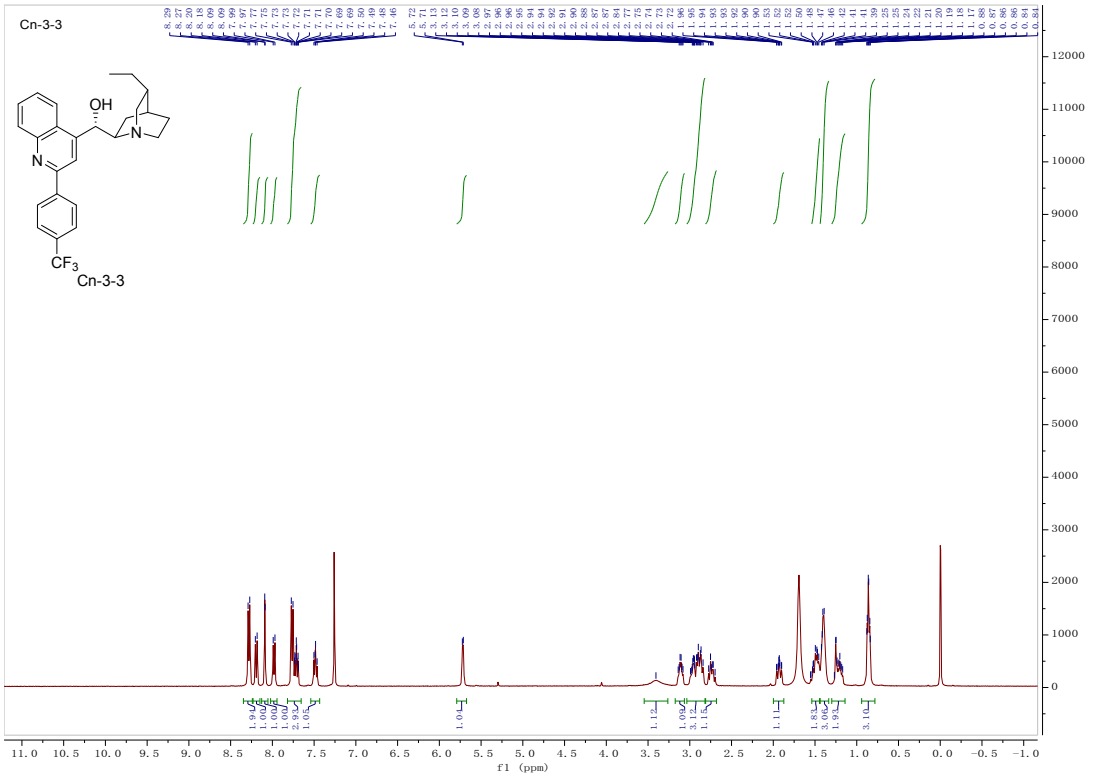
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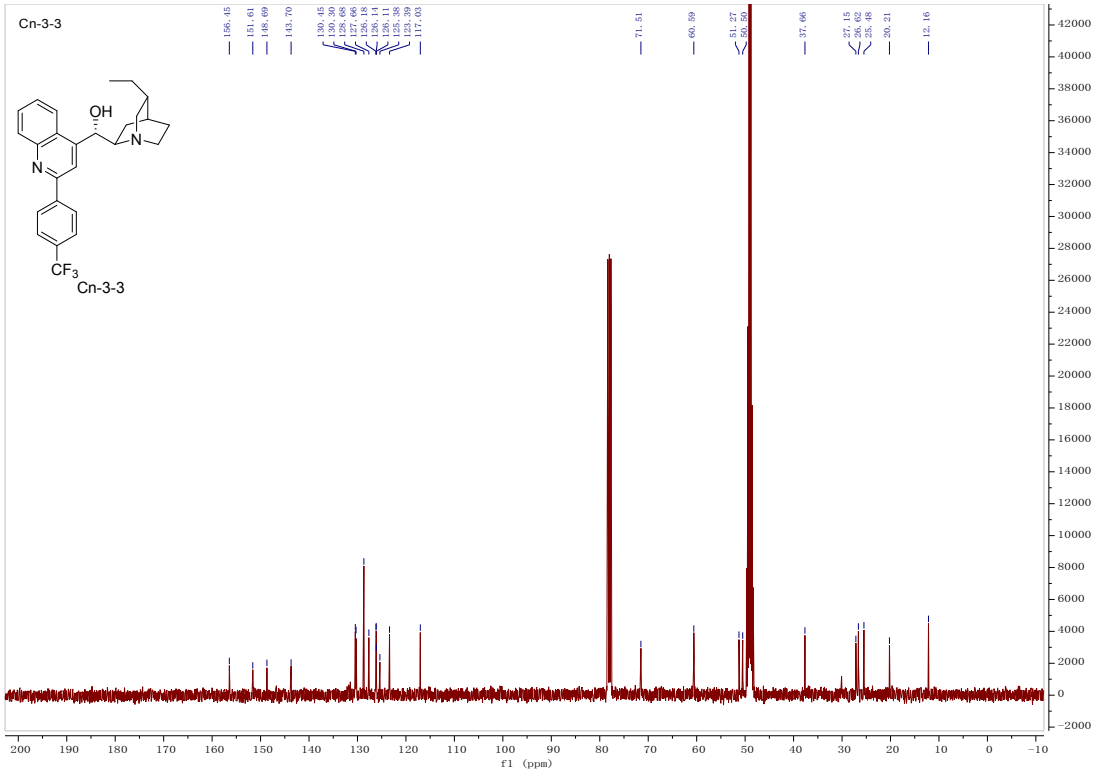
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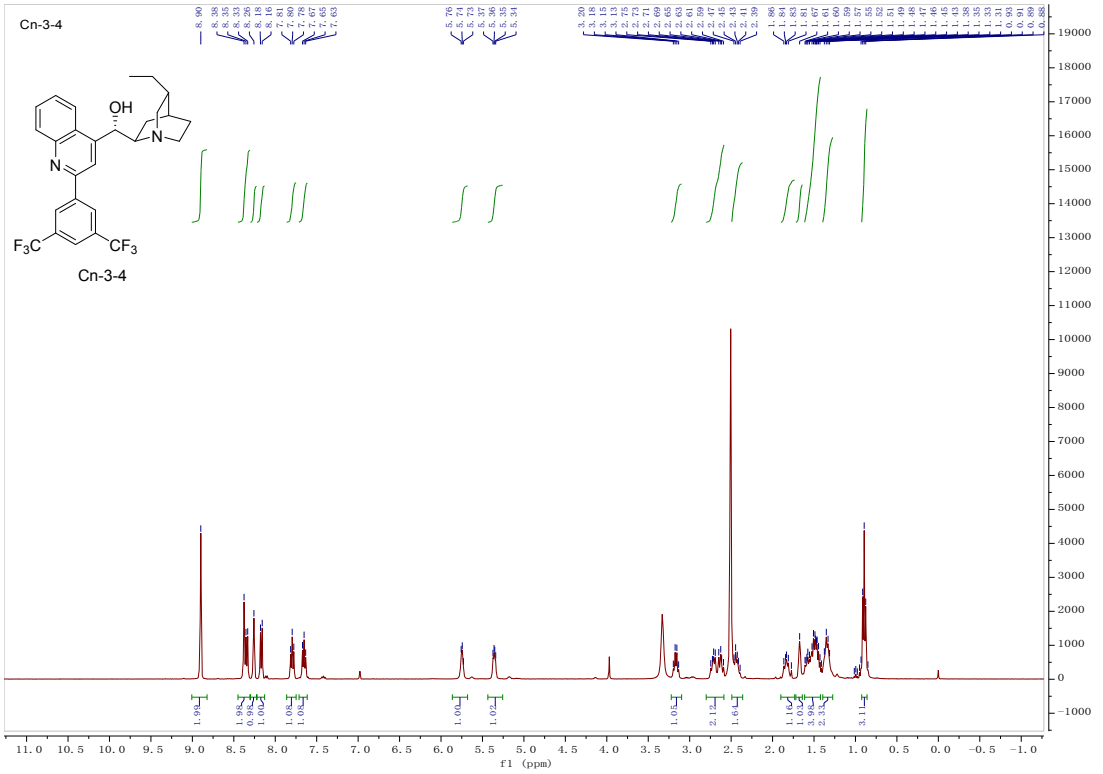
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N
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CF3
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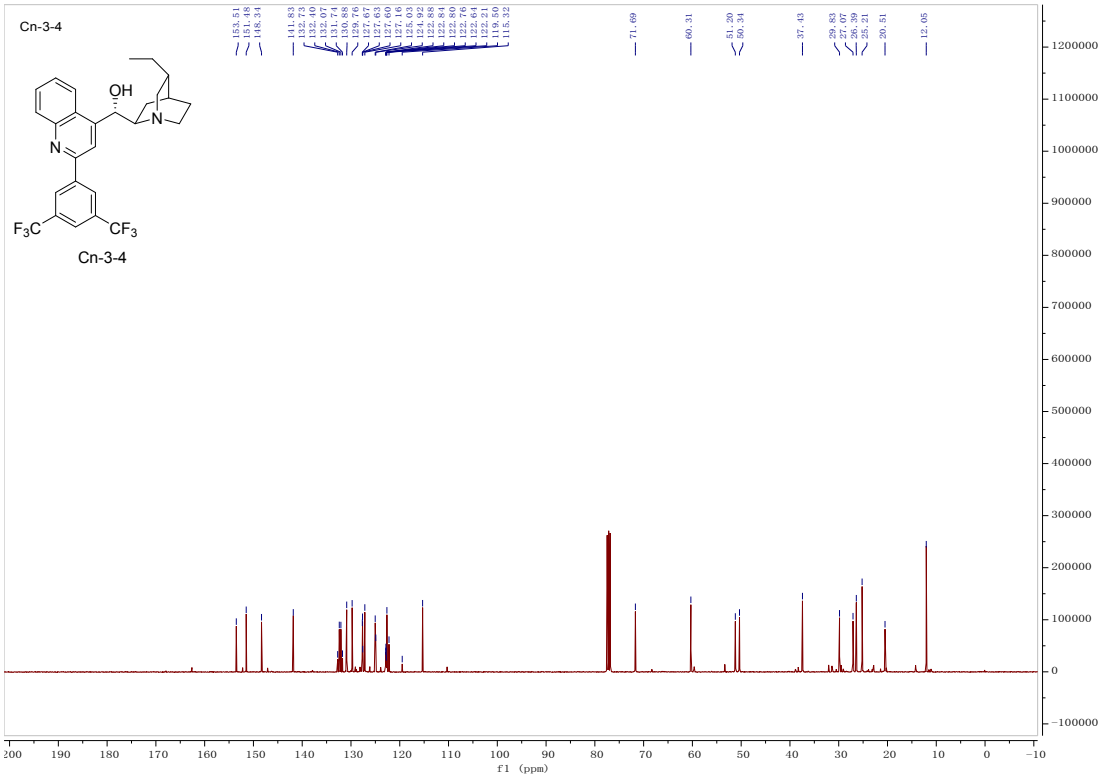
f1 (ppm)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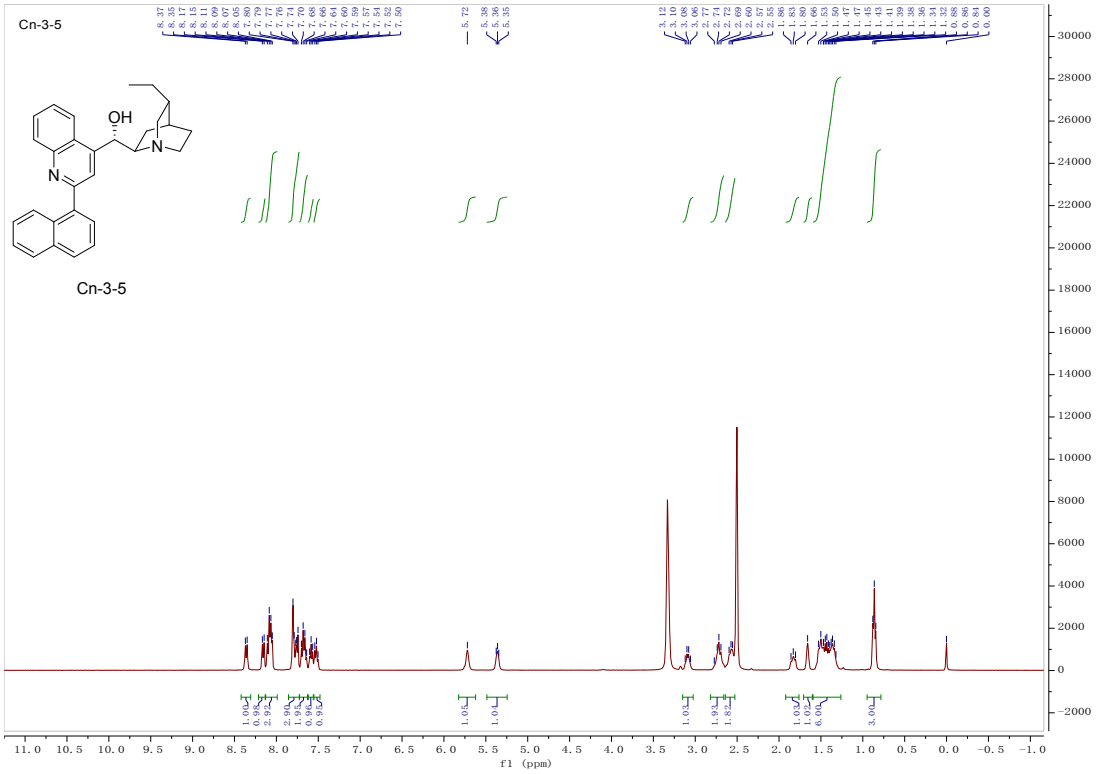
Cn-3-4
f1 (ppm)


Cn-3-5
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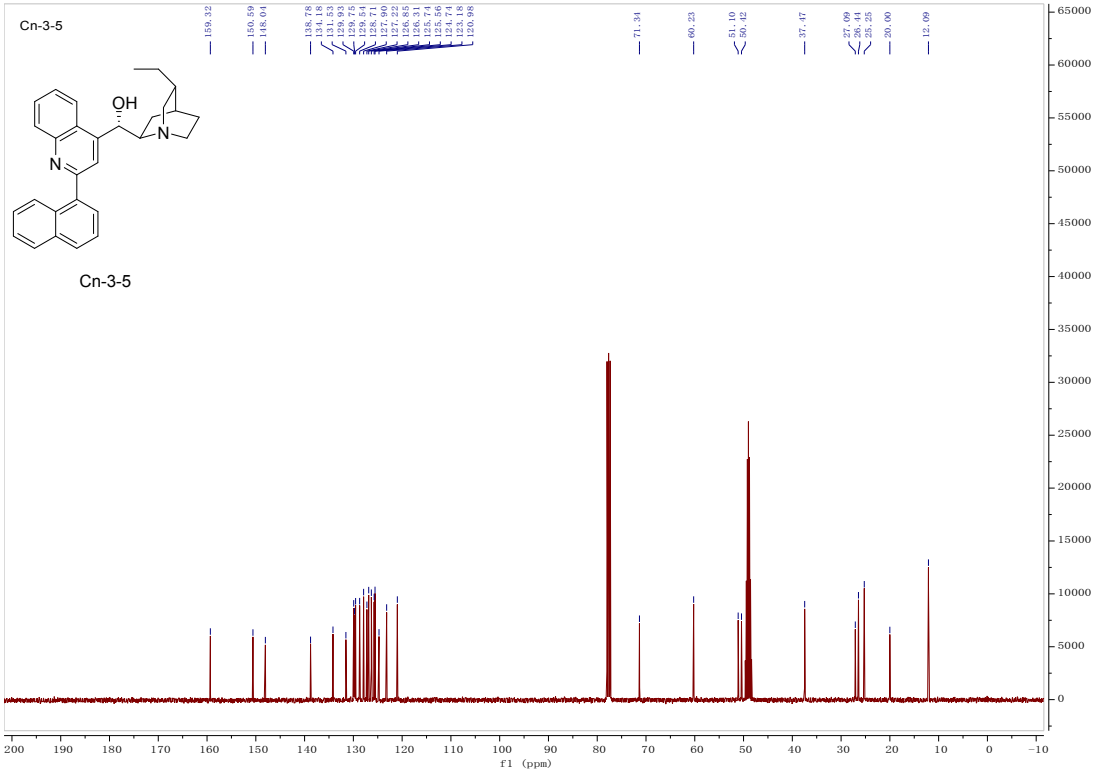
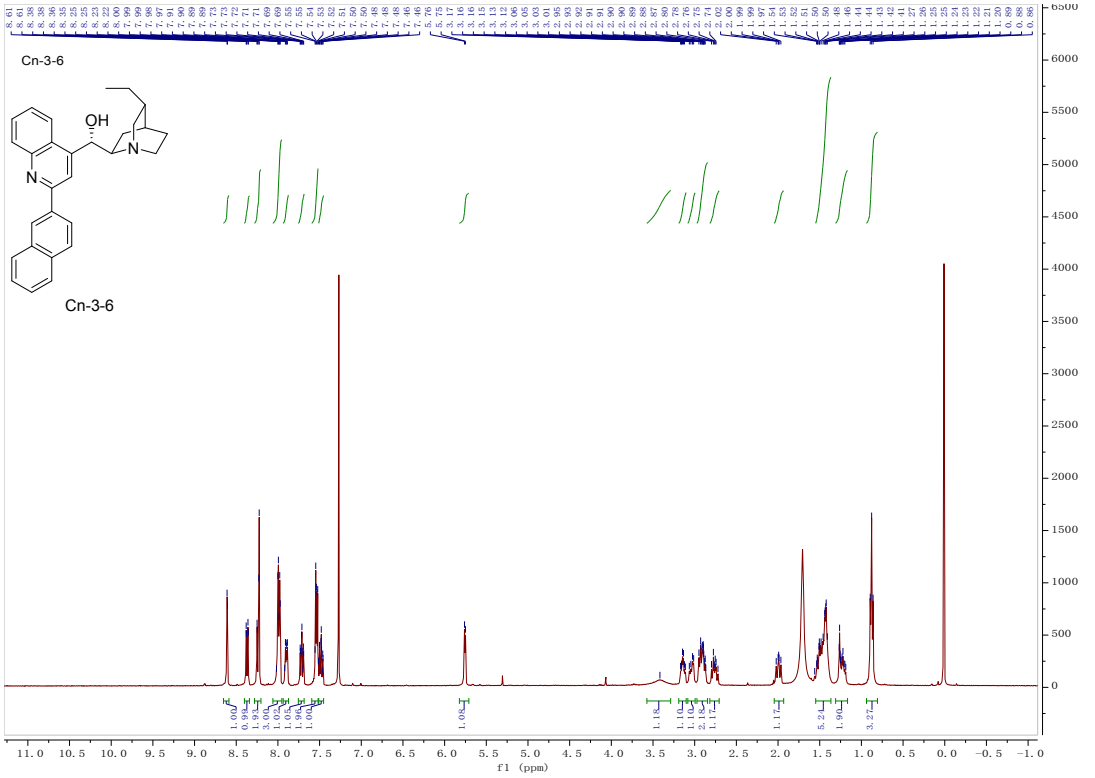
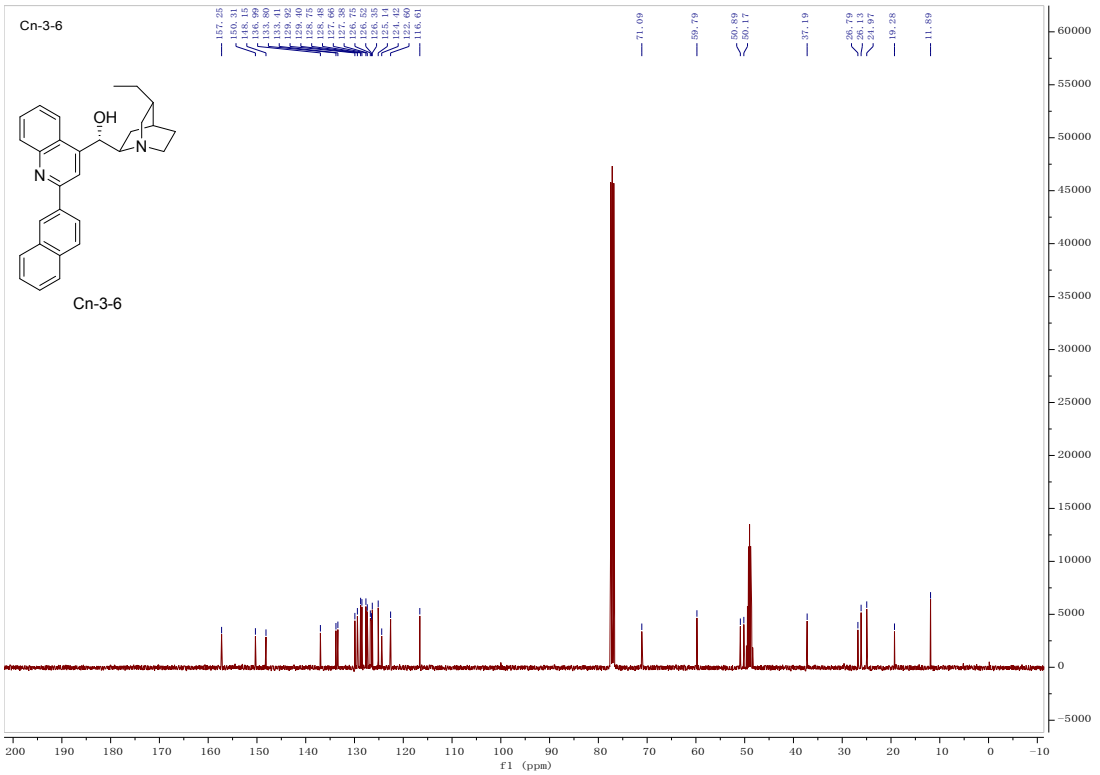
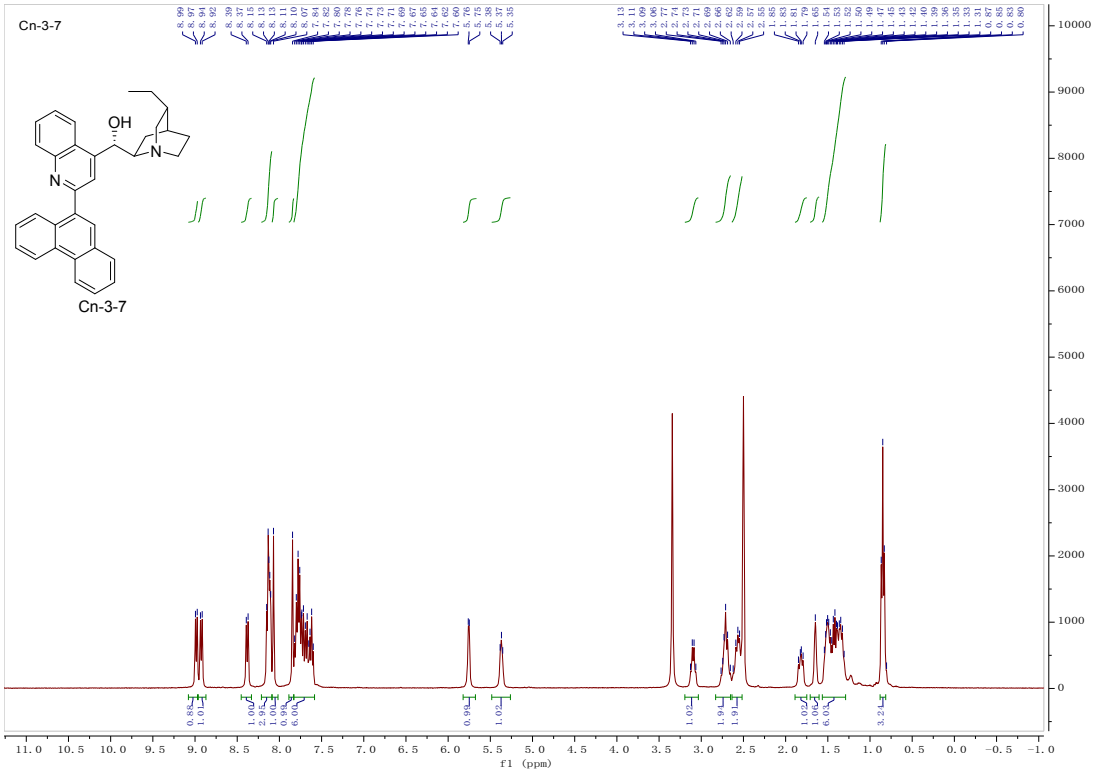
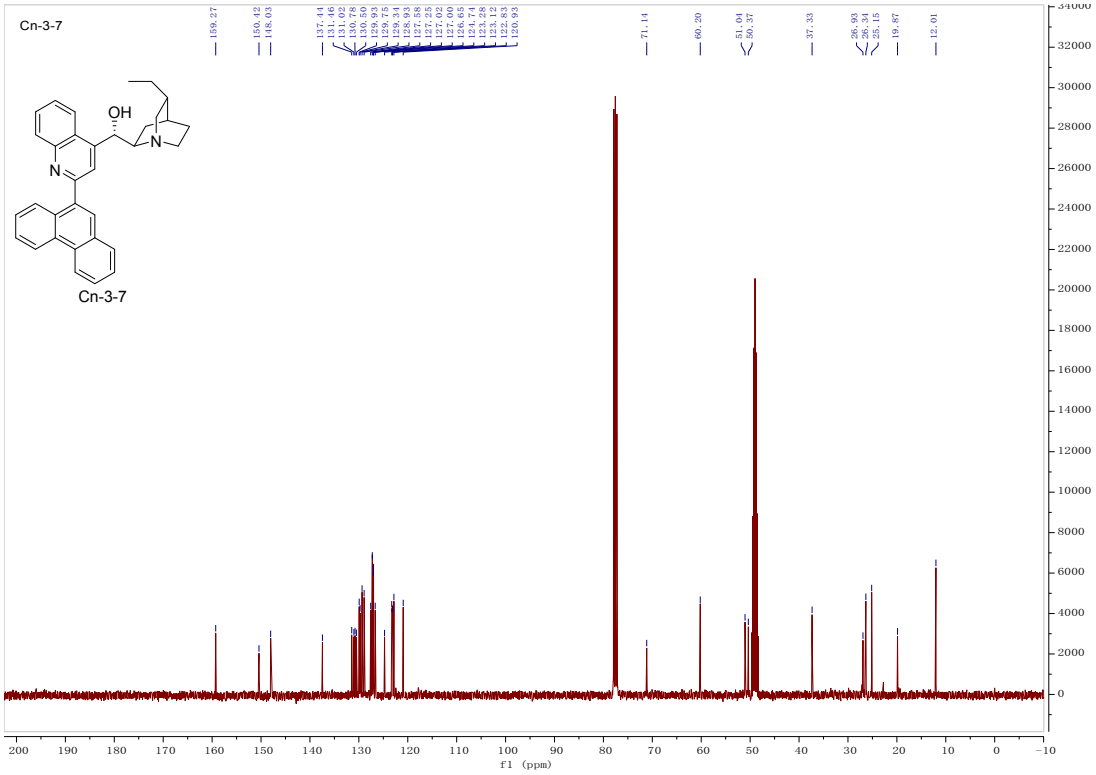
N
Cn-3-5
f1 (ppm)

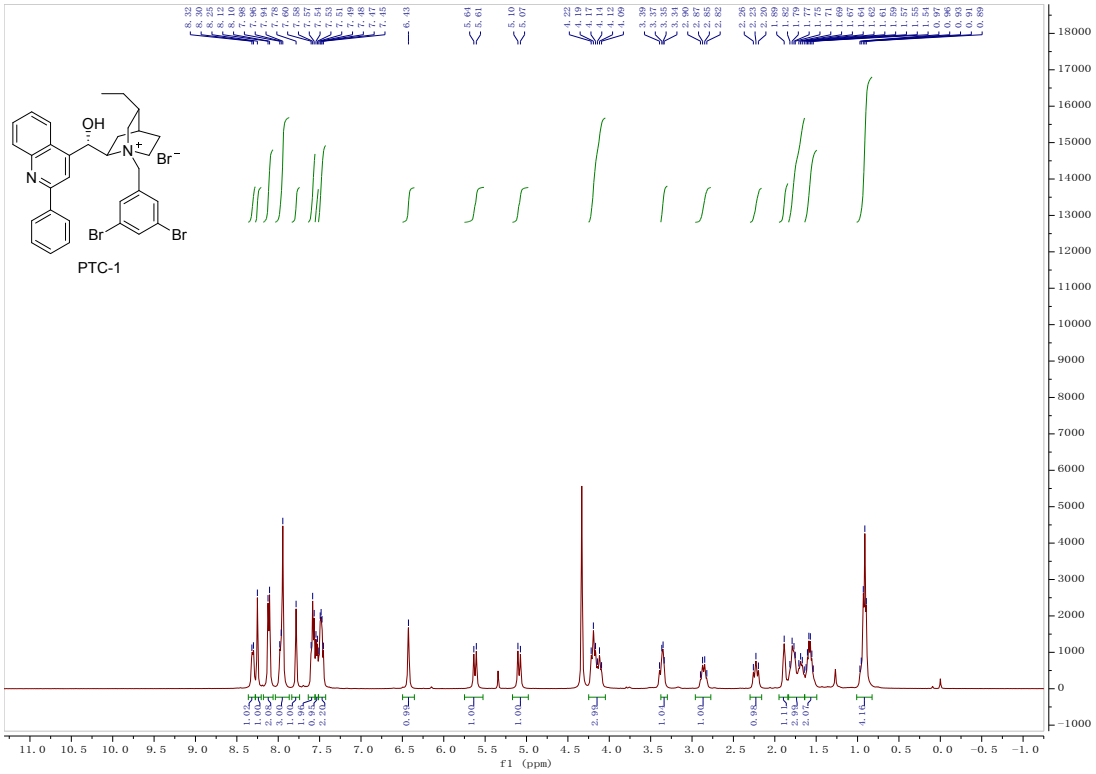

Cn-3-5
OH
N
N
Cn-3-5
f1 (ppm)

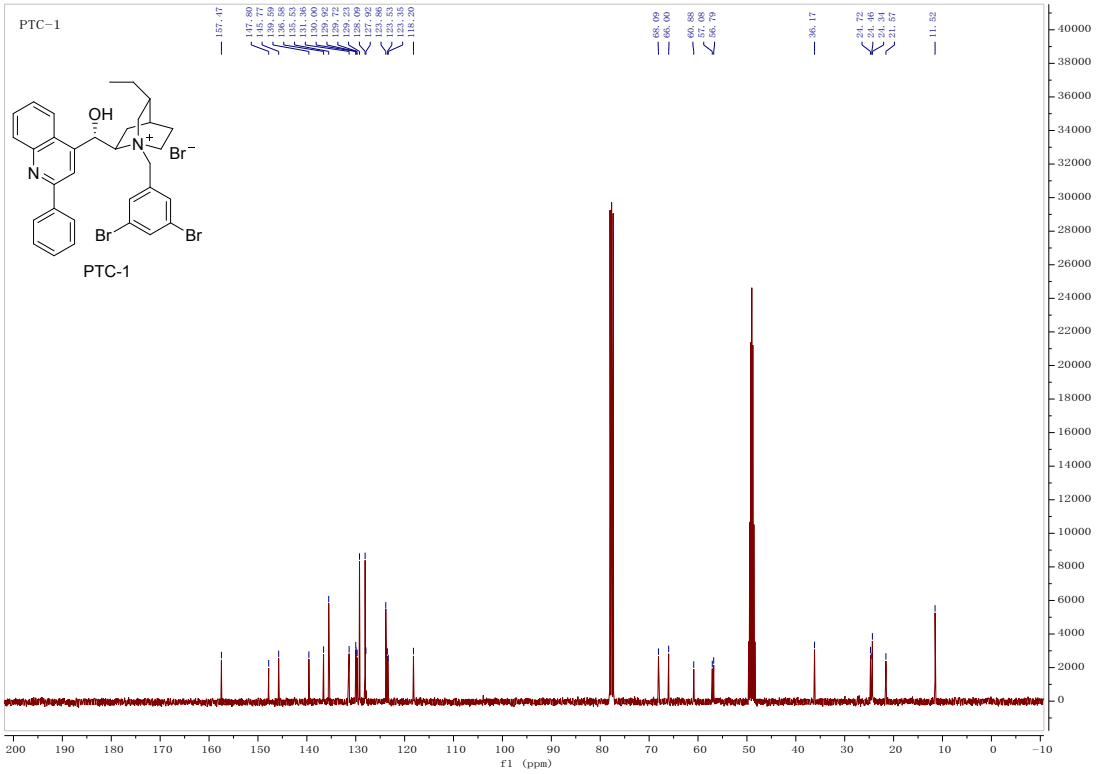

Cn-3-6
OH
N
N
Cn-3-6
f1 (ppm)

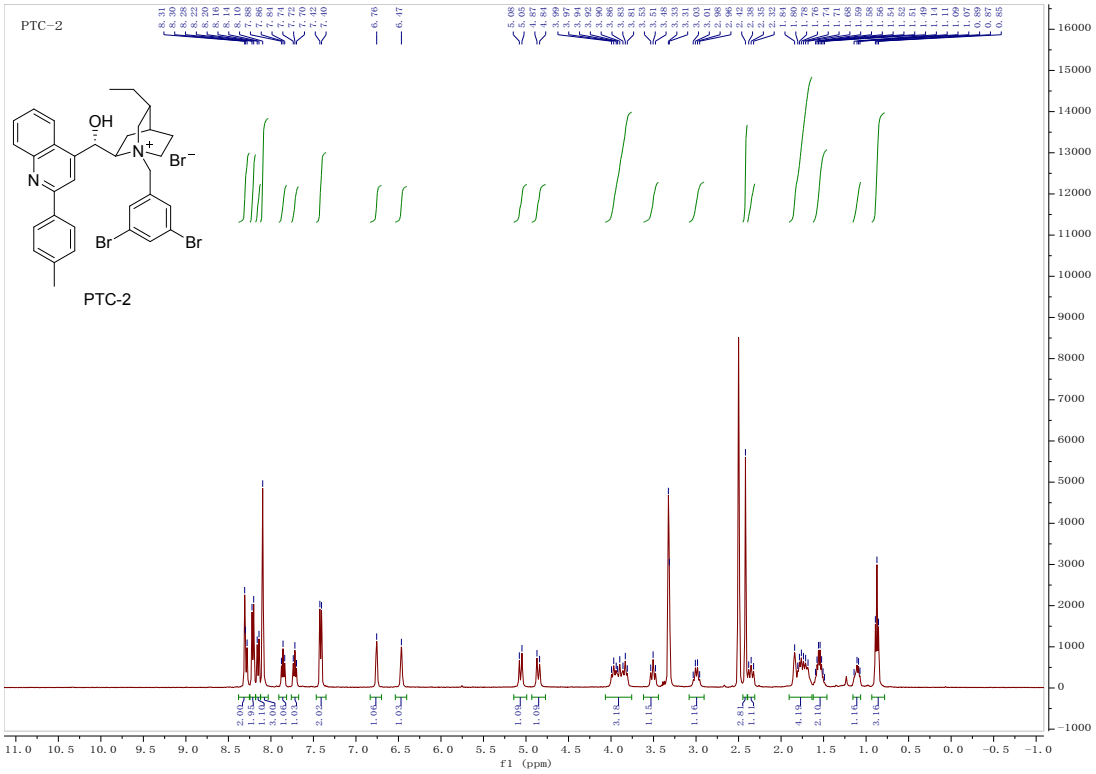

Cn-3-6
OH
N
N
Cn-3-6
f1 (ppm)

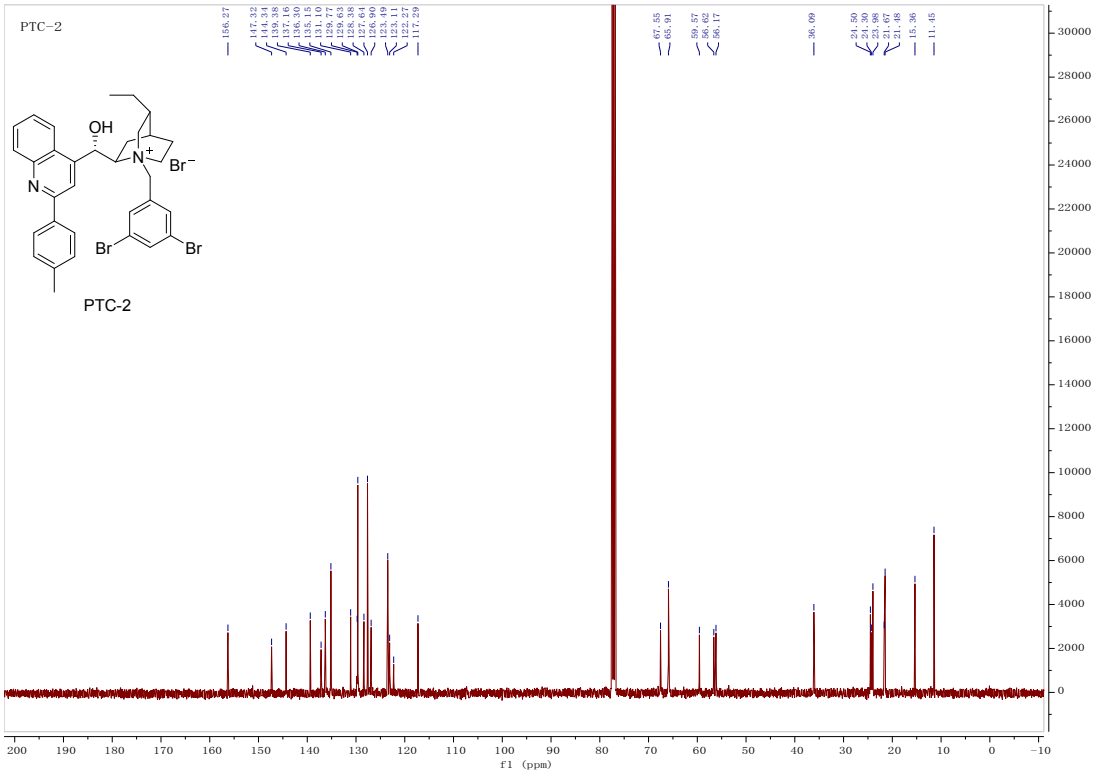

Cn-3-7
OH
N
N
Cn-3-7
f1 (ppm)

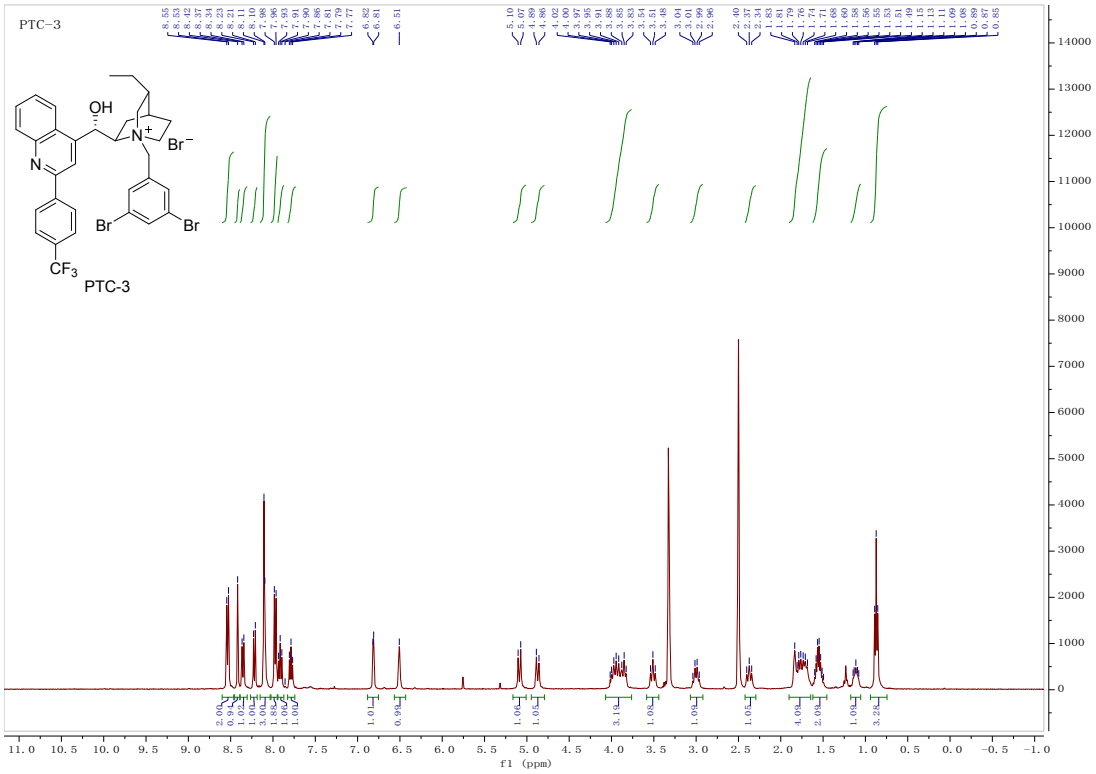

Cn-3-7
OH
N
N
Cn-3-7
f1 (ppm)

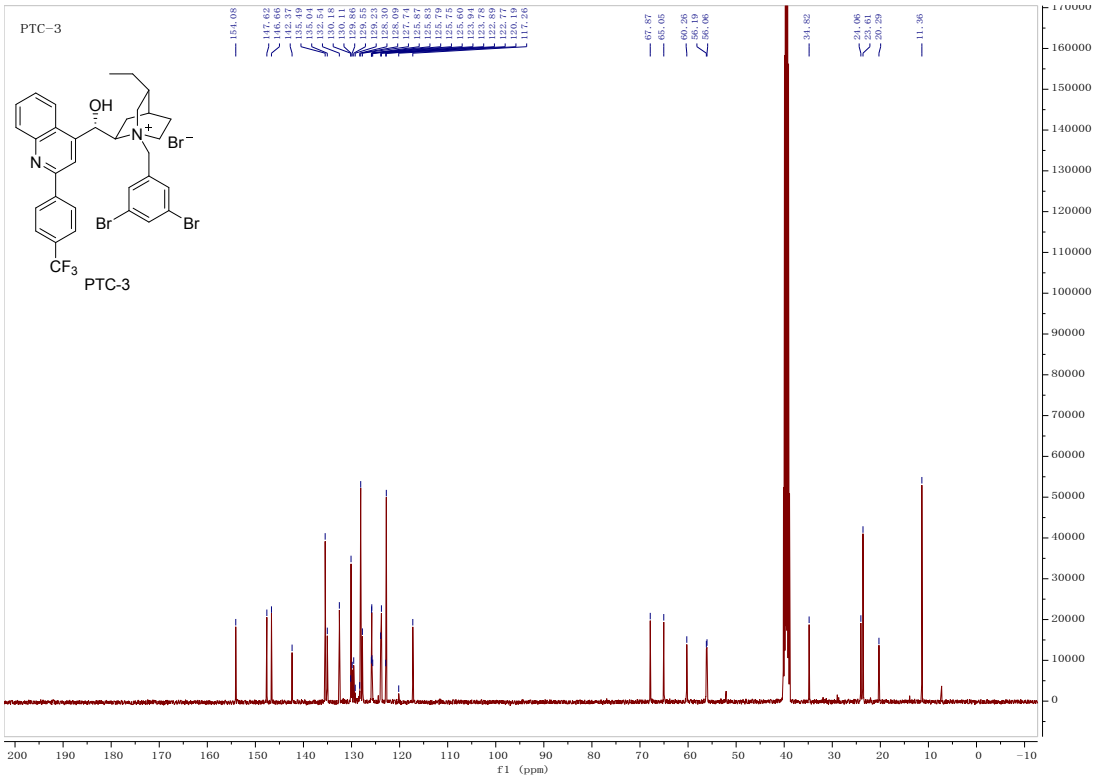

PTC-1
f1 (ppm)

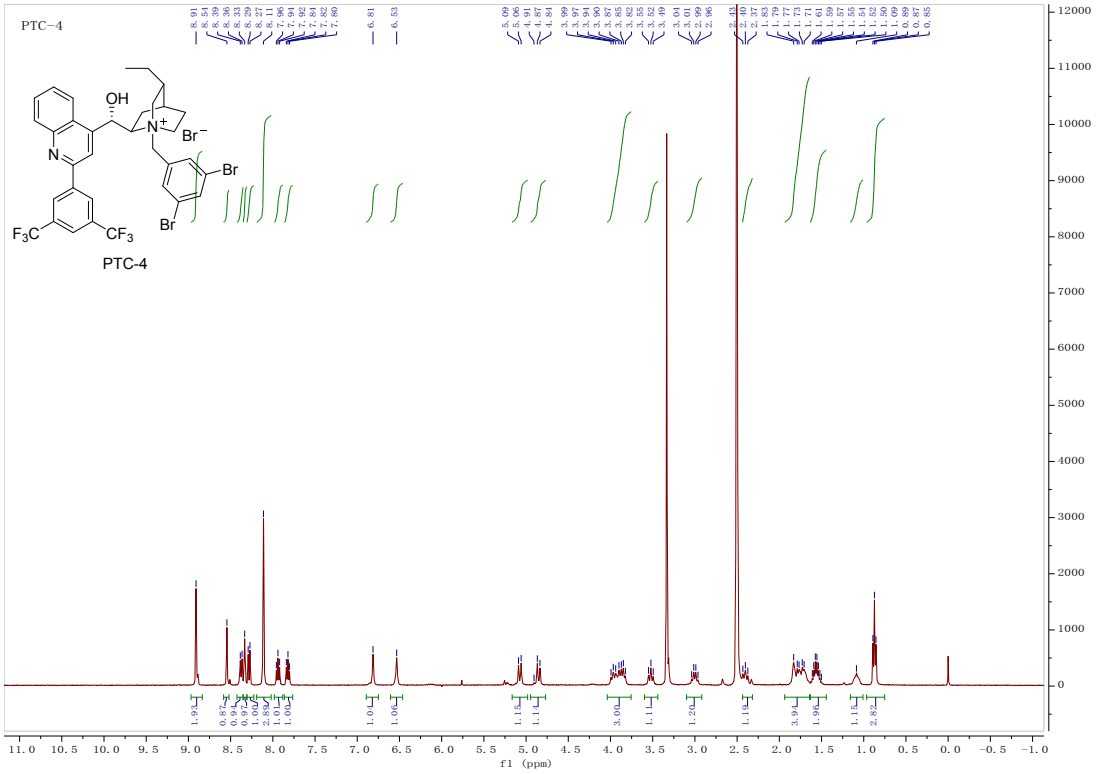

PTC−1
PTC-1
f1 (ppm)

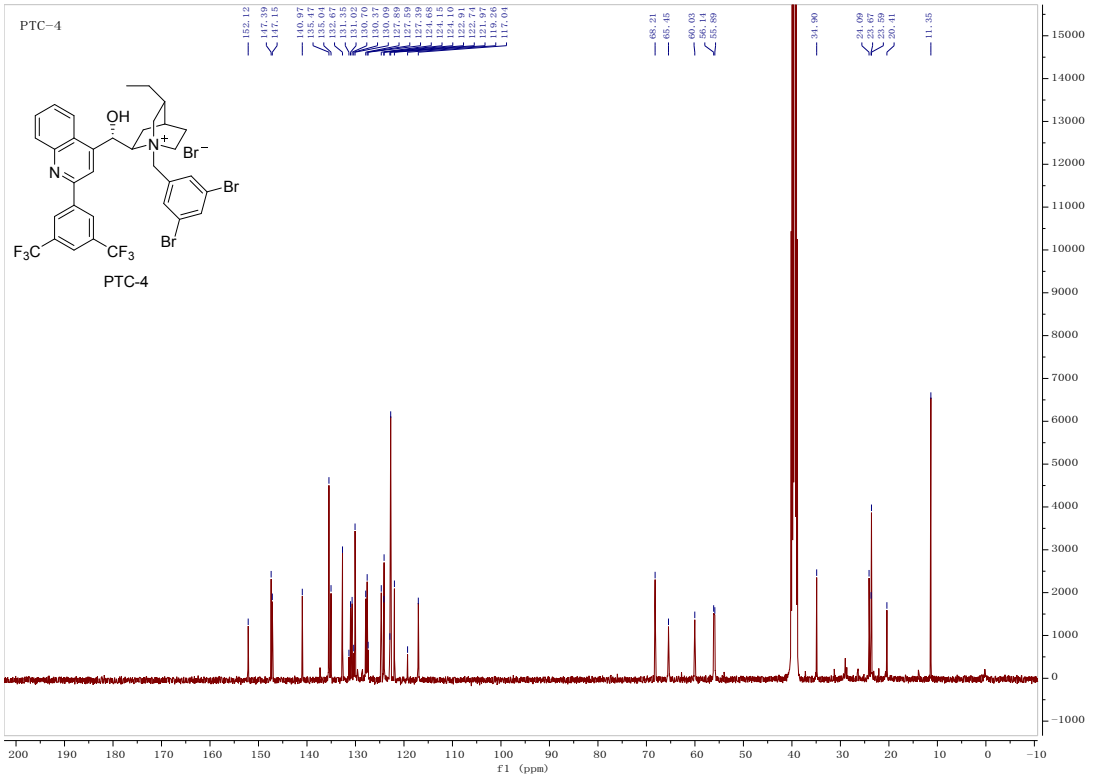

PTC-2
OH
N
Br⁻
Br
Br
PTC-2
f1 (ppm)

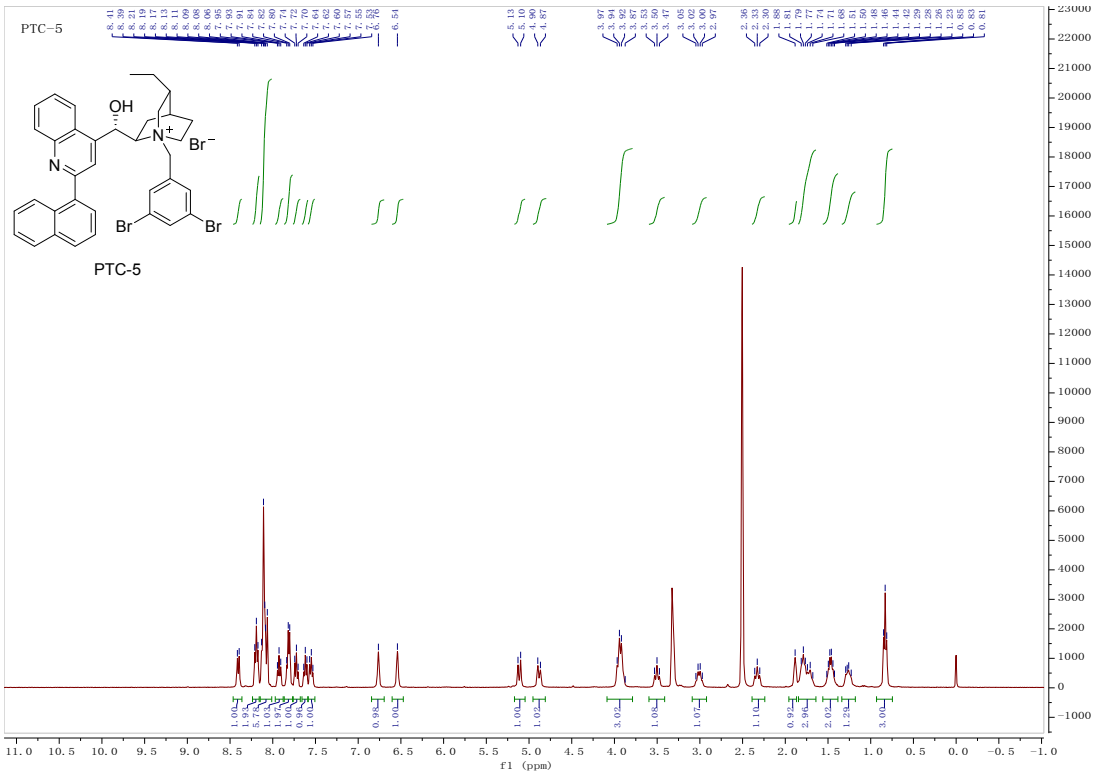

PTC-2
OH
N
Br⁻
Br
Br
PTC-2
f1 (ppm)

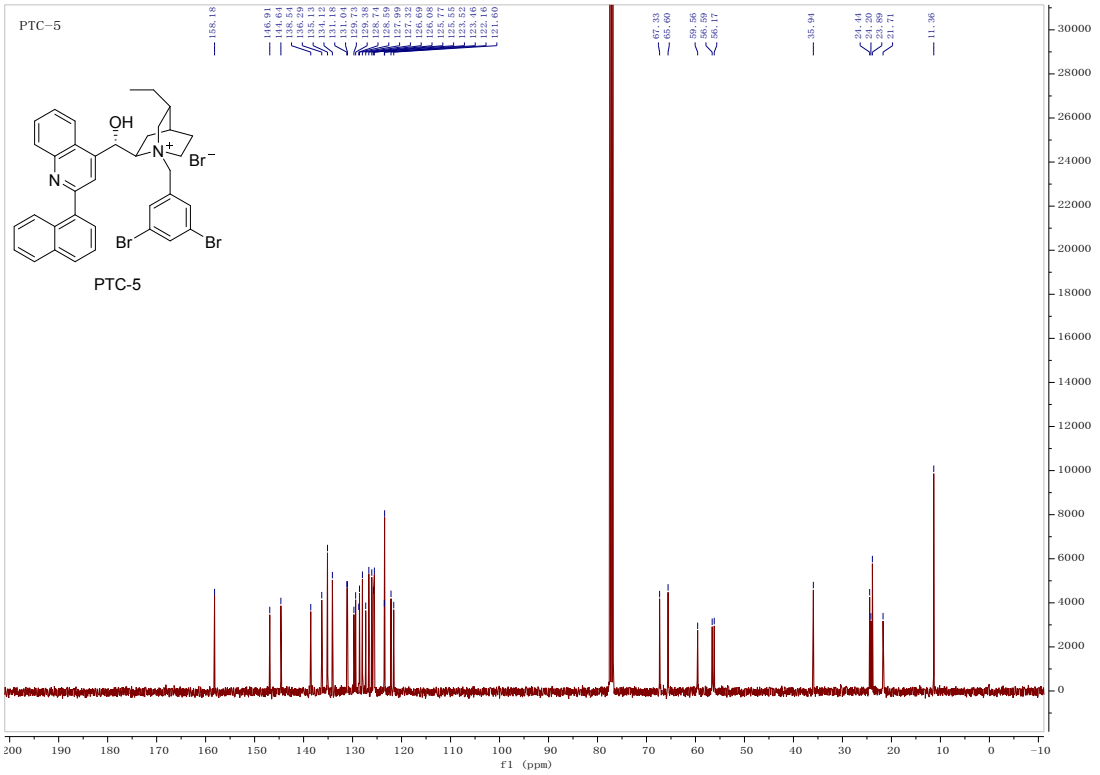

PTC−3
OH
N
Br⁻
Br
Br
CF3
PTC-3
f1 (ppm)

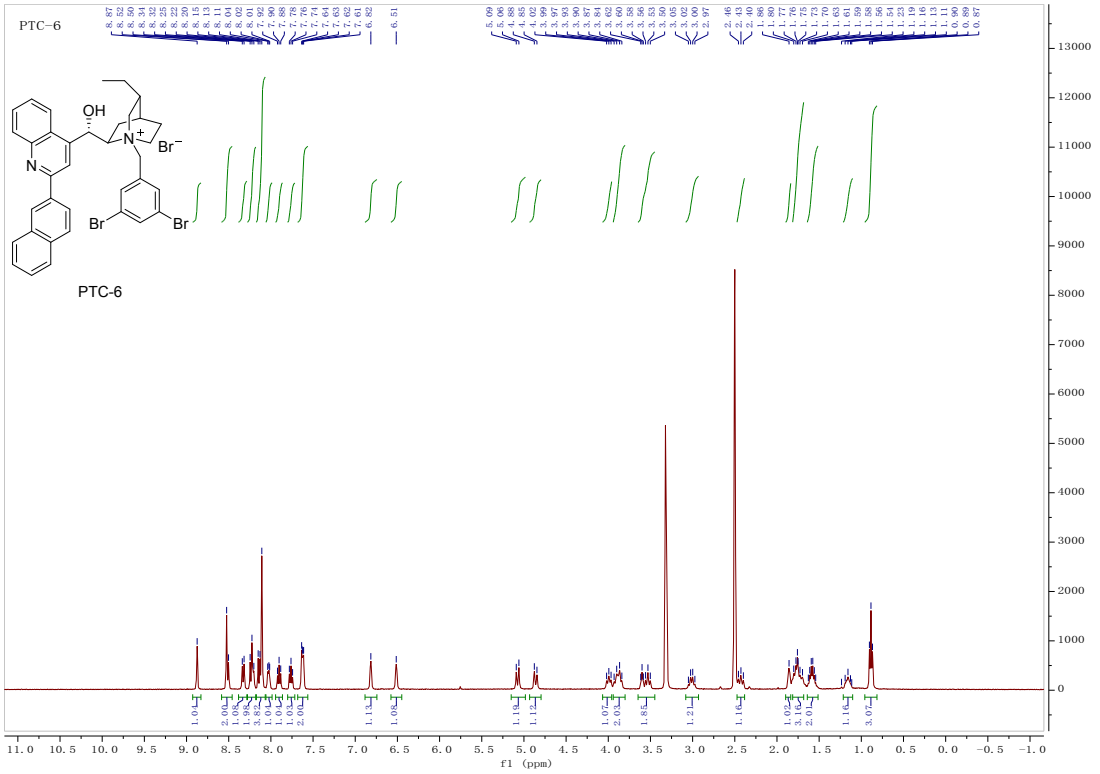

PTC−3
OH
N
Br⁻
Br
Br
CF3
PTC-3
f1 (ppm)

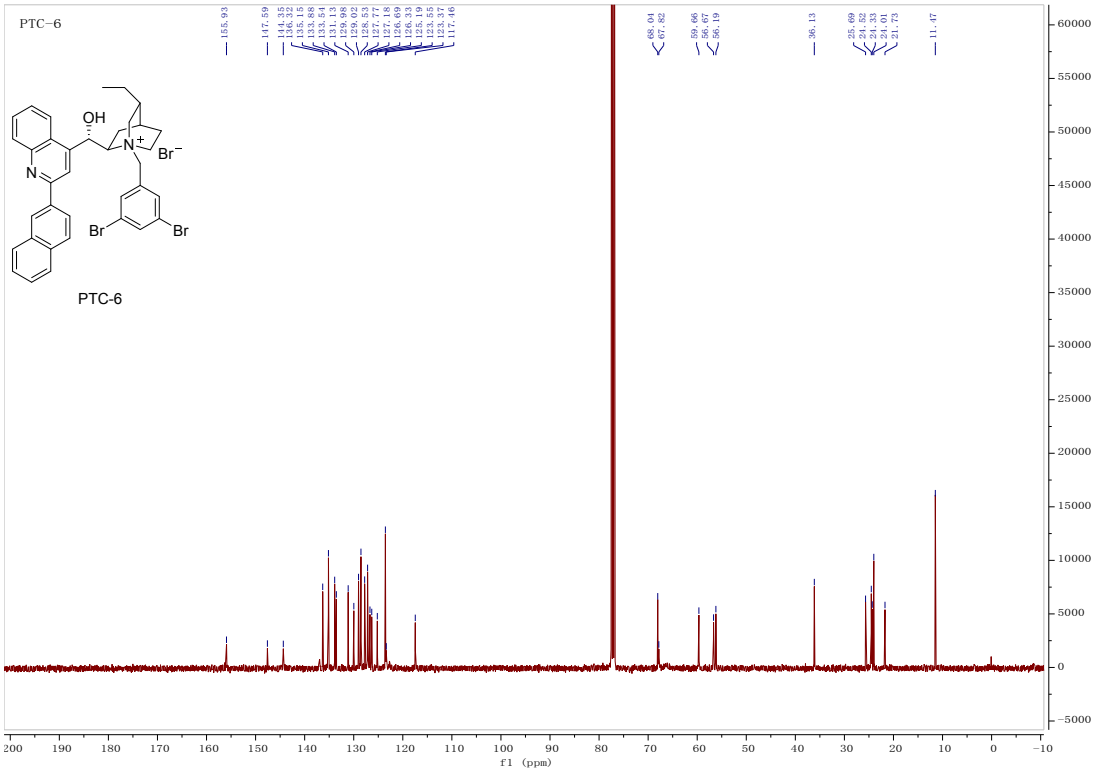

PTC−4
PTC-4
f1 (ppm)

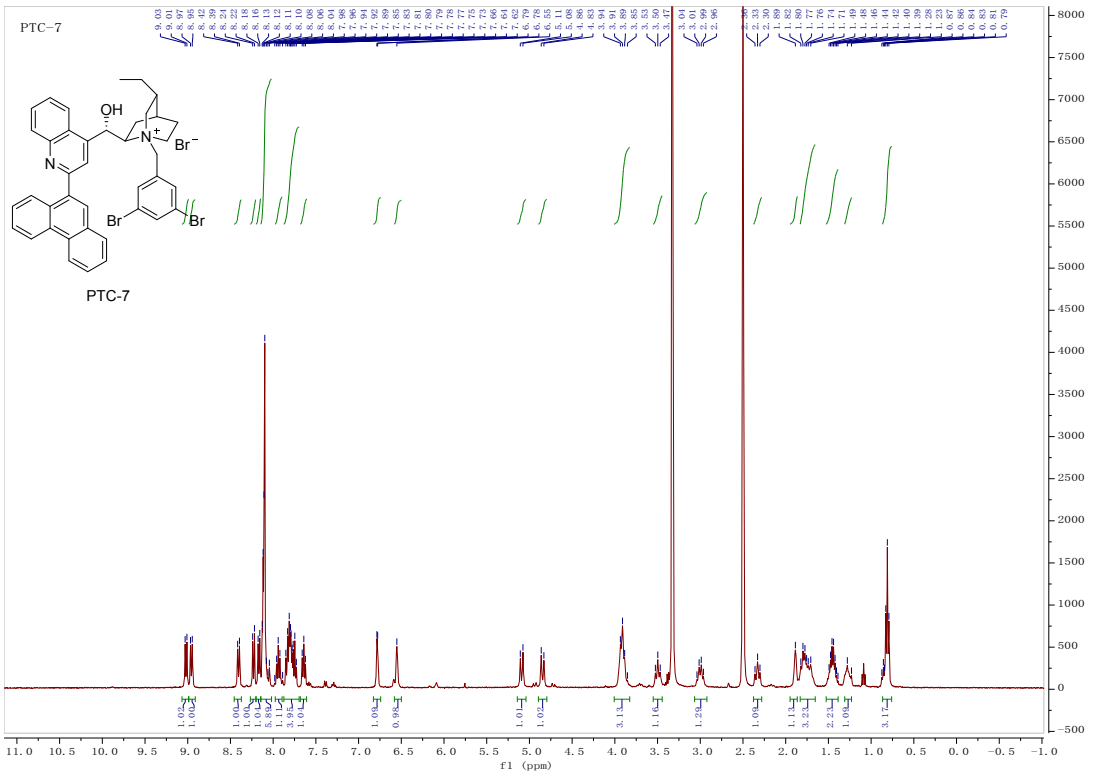

PTC−4
PTC-4
f1 (ppm)

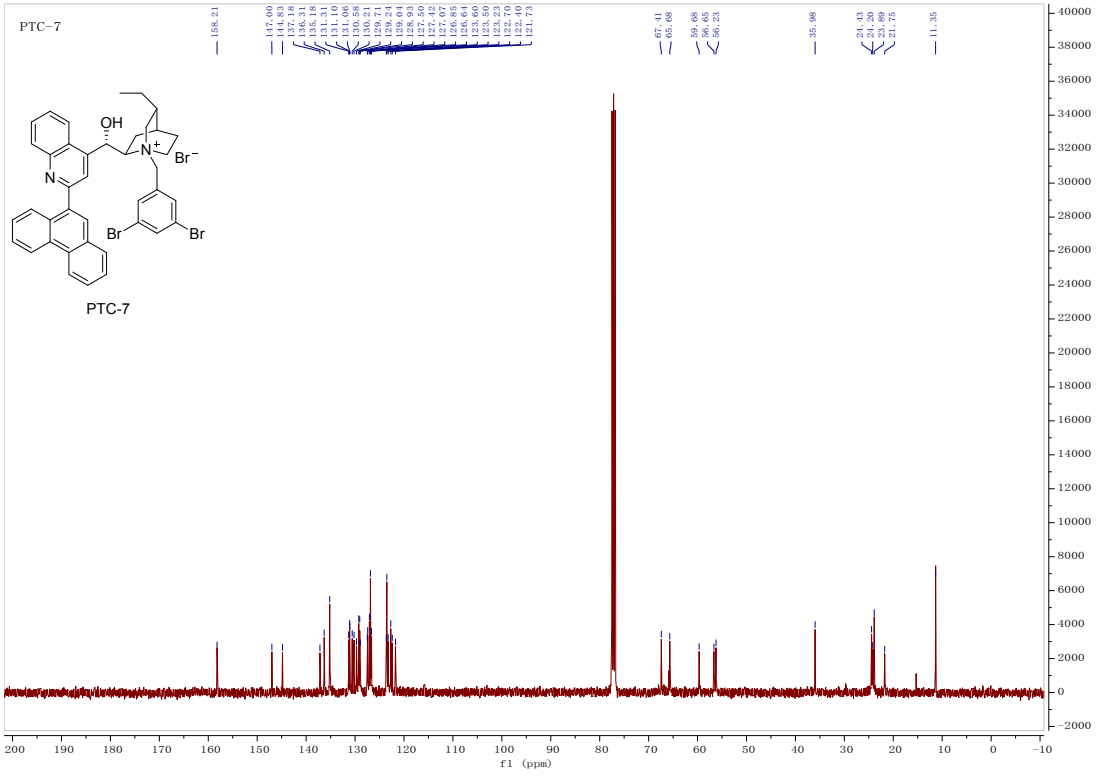

PTC−5
PTC-5
f1 (ppm)

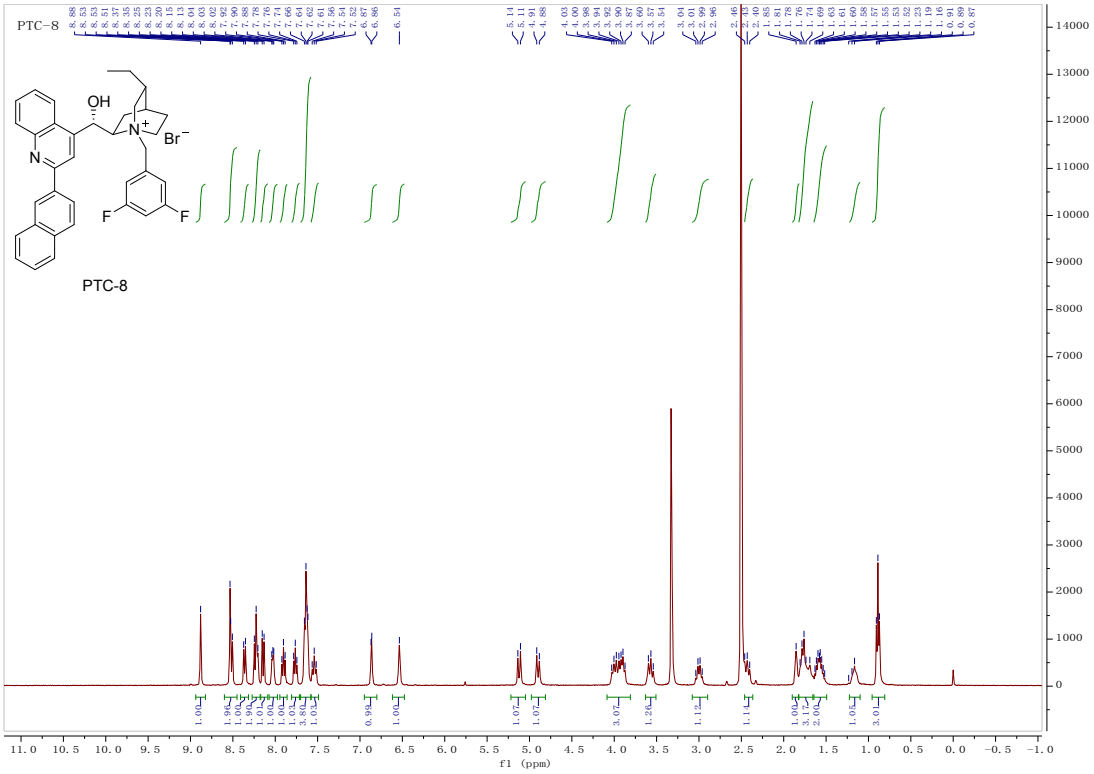

PTC−5
PTC-5
f1 (ppm)

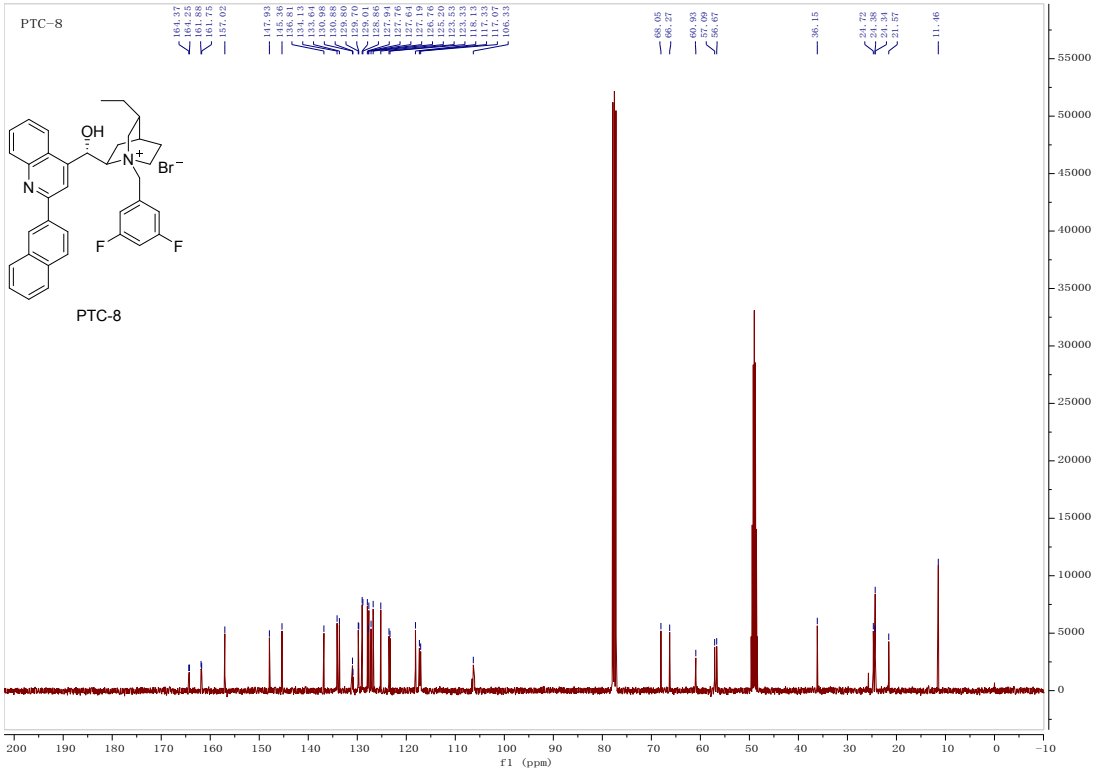

PTC−6
PTC-6
f1 (ppm)

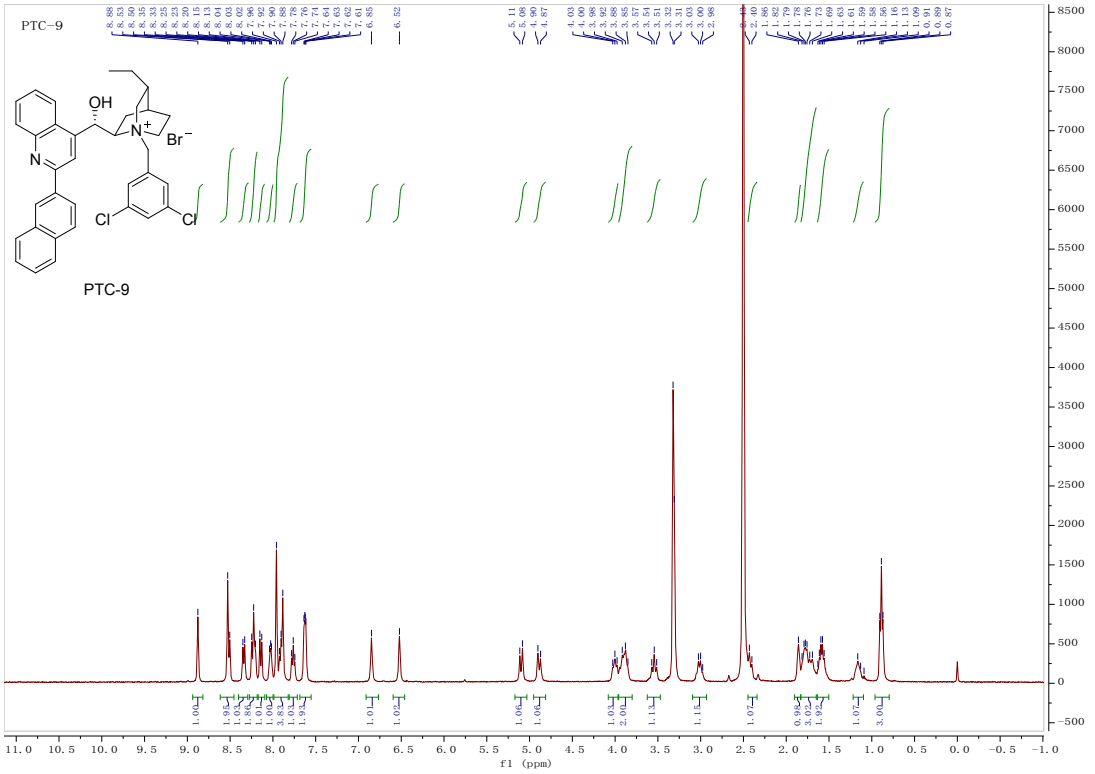

PTC−6
PTC-6
f1 (ppm)

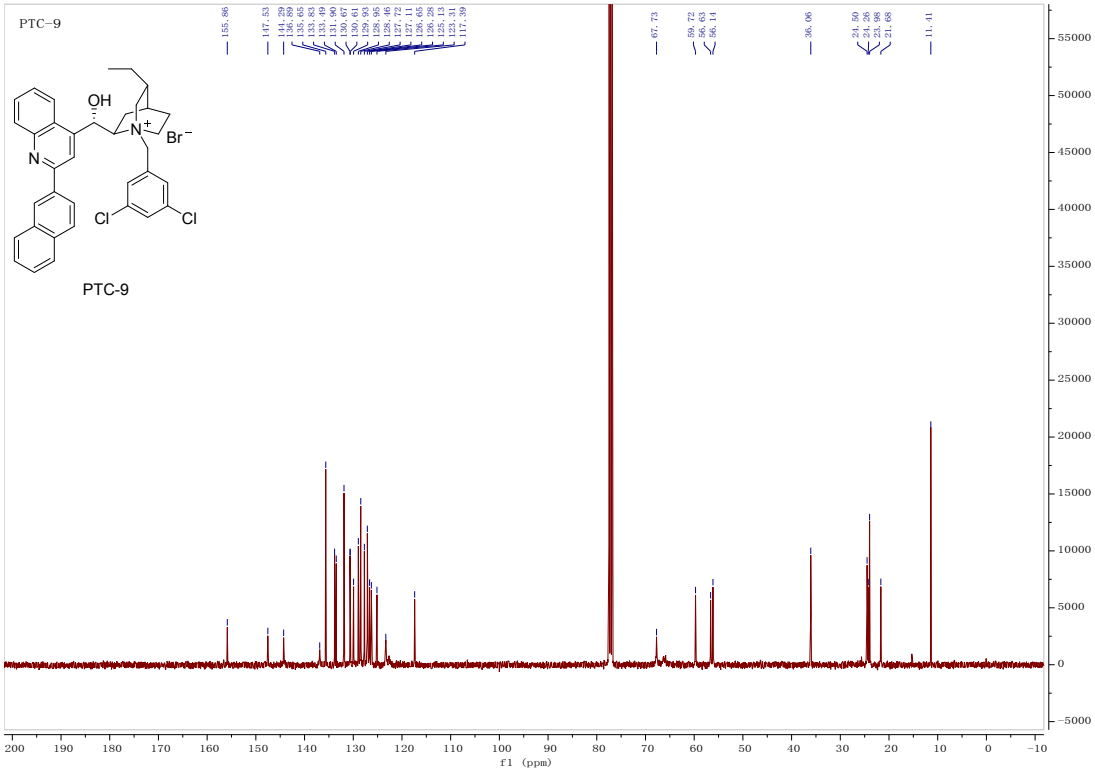

PTC−7
PTC-7
f1 (ppm)

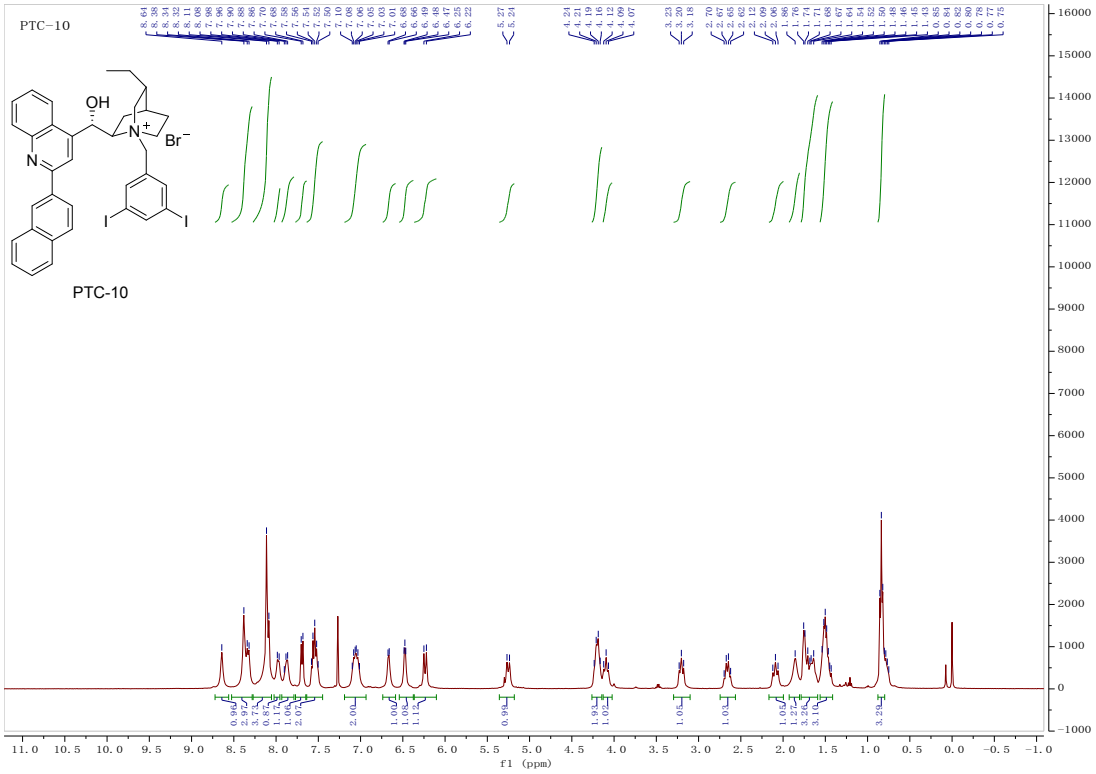

PTC−7
PTC-7
f1 (ppm)

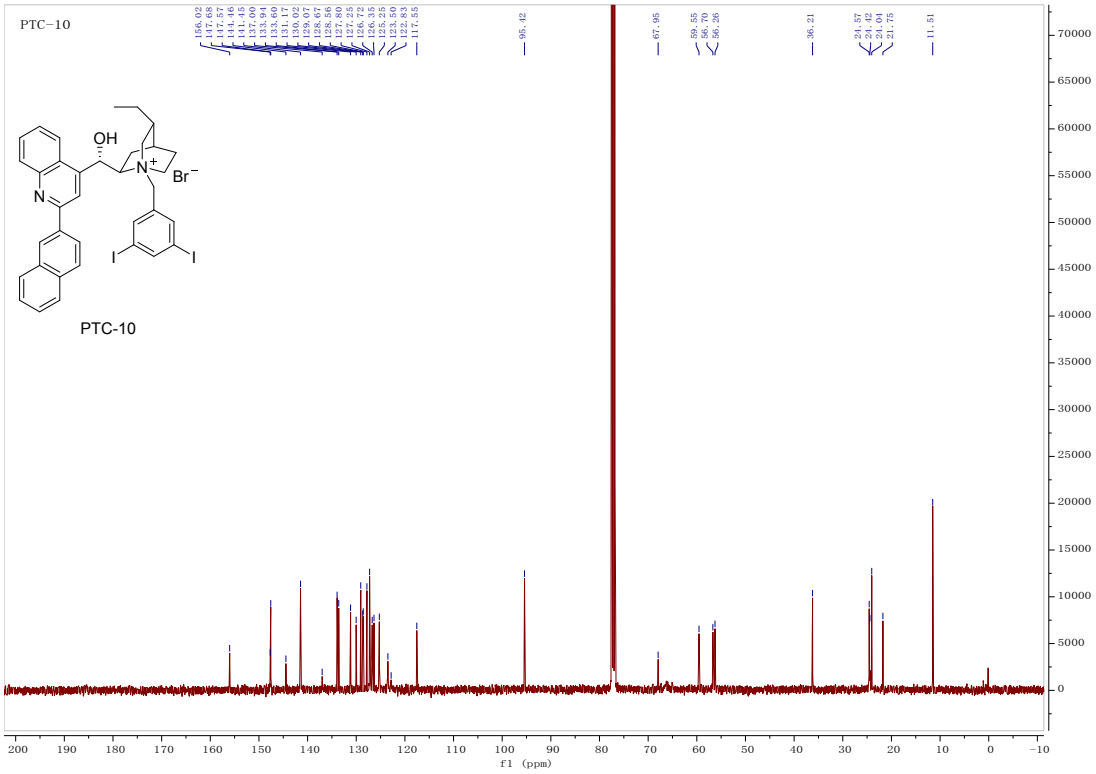

PTC−8
PTC-8
f1 (ppm)

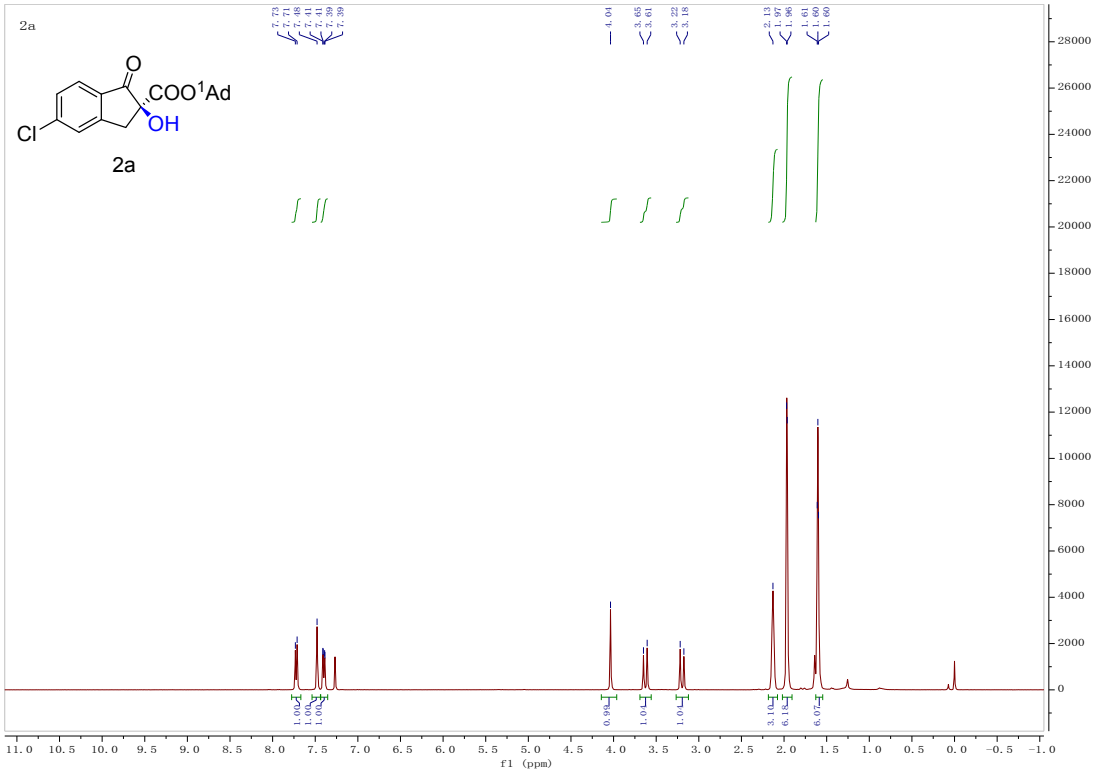

PTC−8
PTC-8
f1 (ppm)

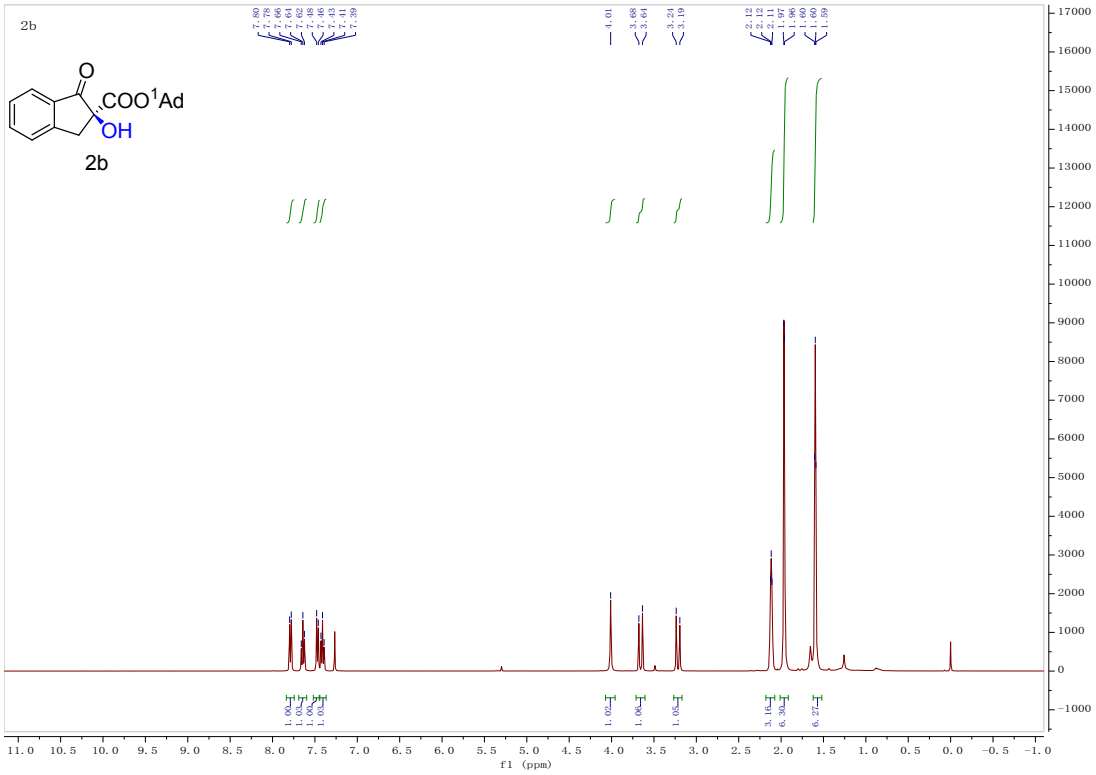

PTC-9
PTC-9
f1 (ppm)

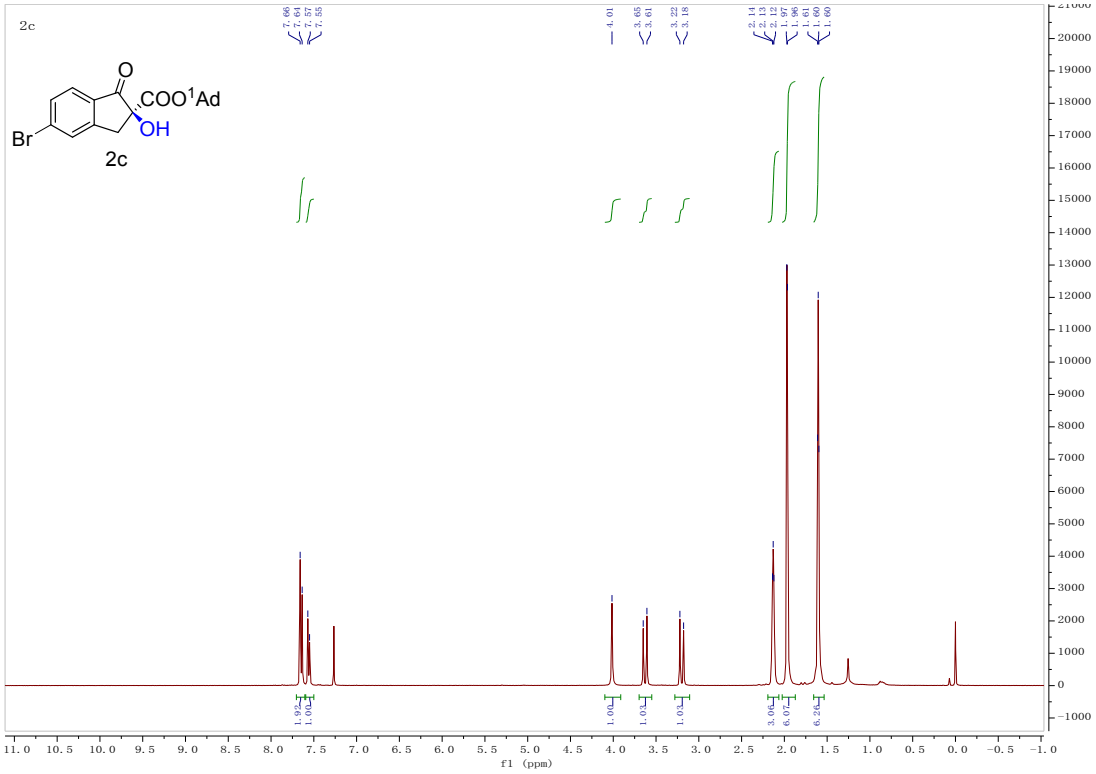

PTC-9
PTC-9
f1 (ppm)

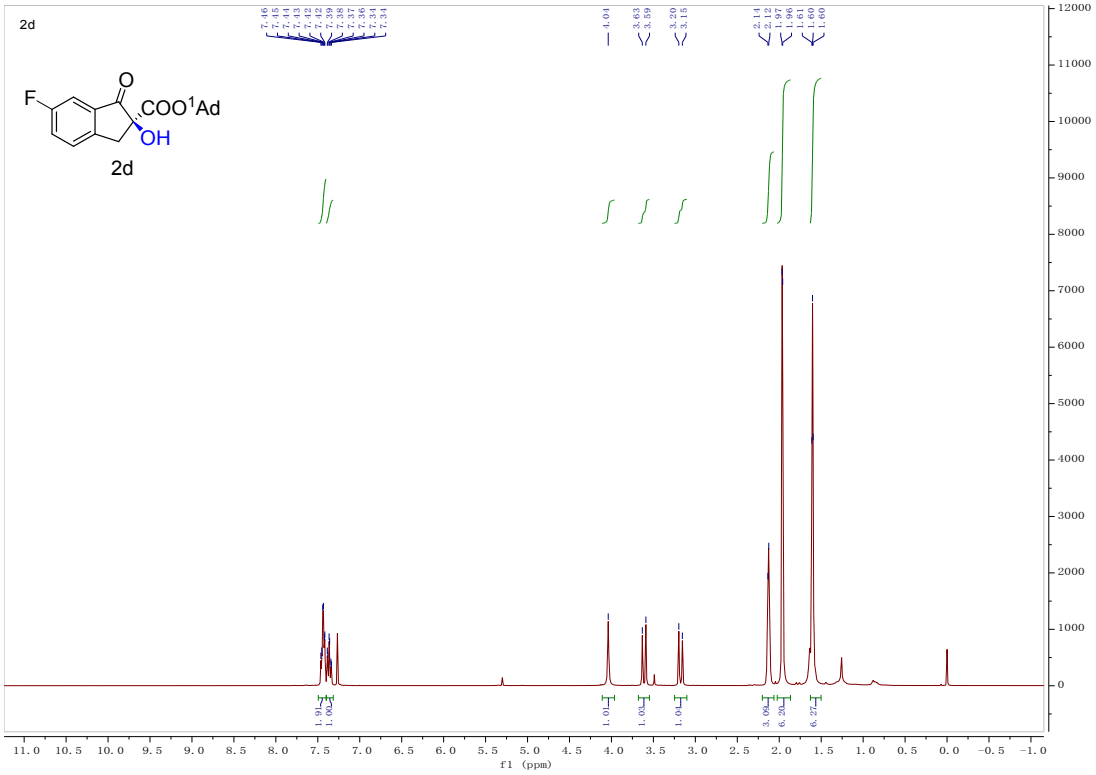

PTC−10
OH
N
N+
Br−
I
I
PTC-10
f1 (ppm)

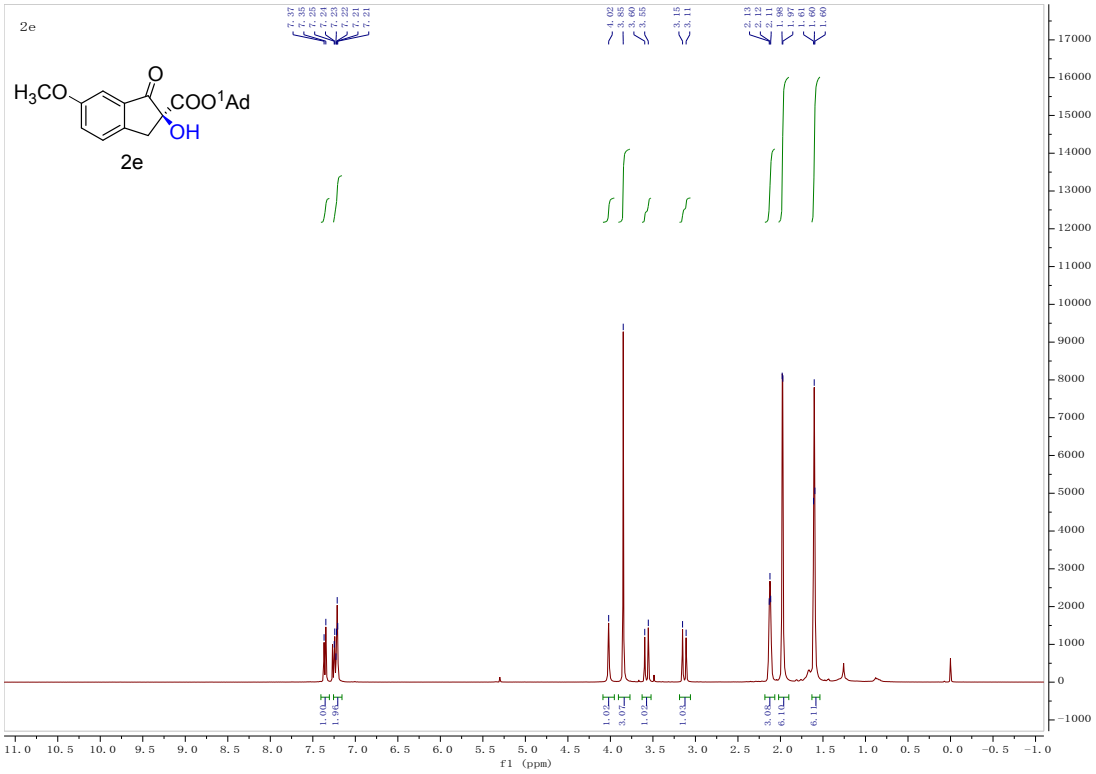

PTC−10
OH
N
N+
Br−
I
I
PTC-10
f1 (ppm)

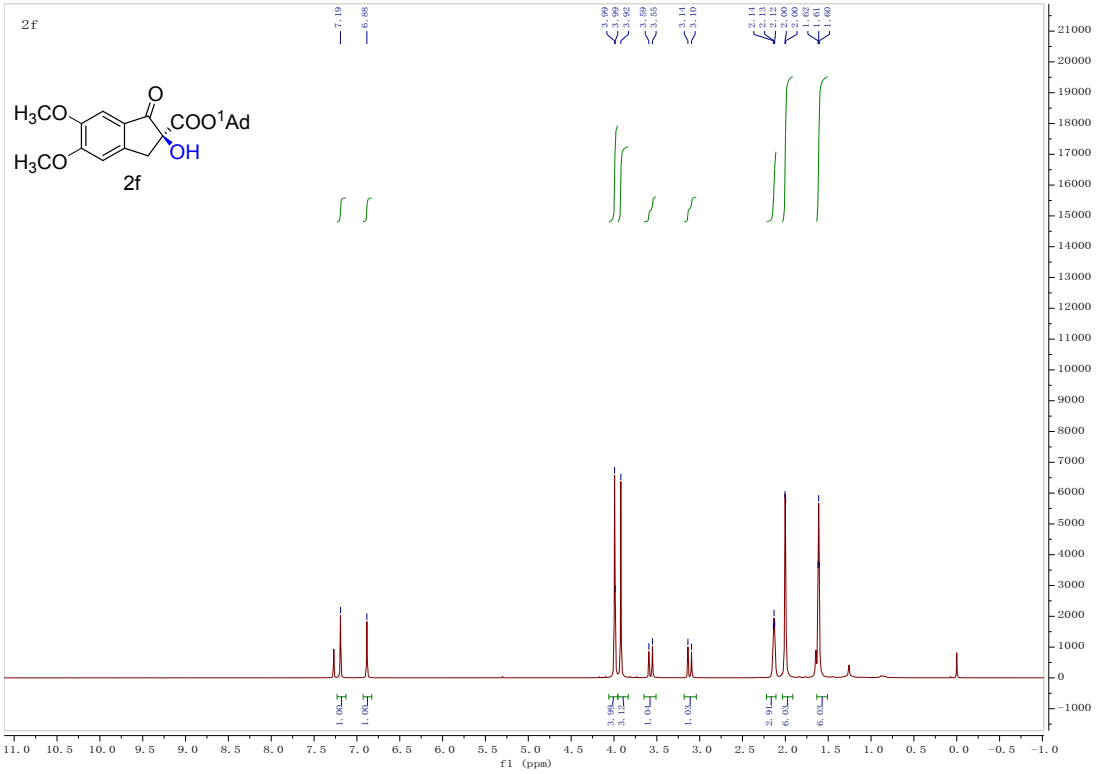

2a
O
COO1Ad
OH
Cl
2a
f1 (ppm)

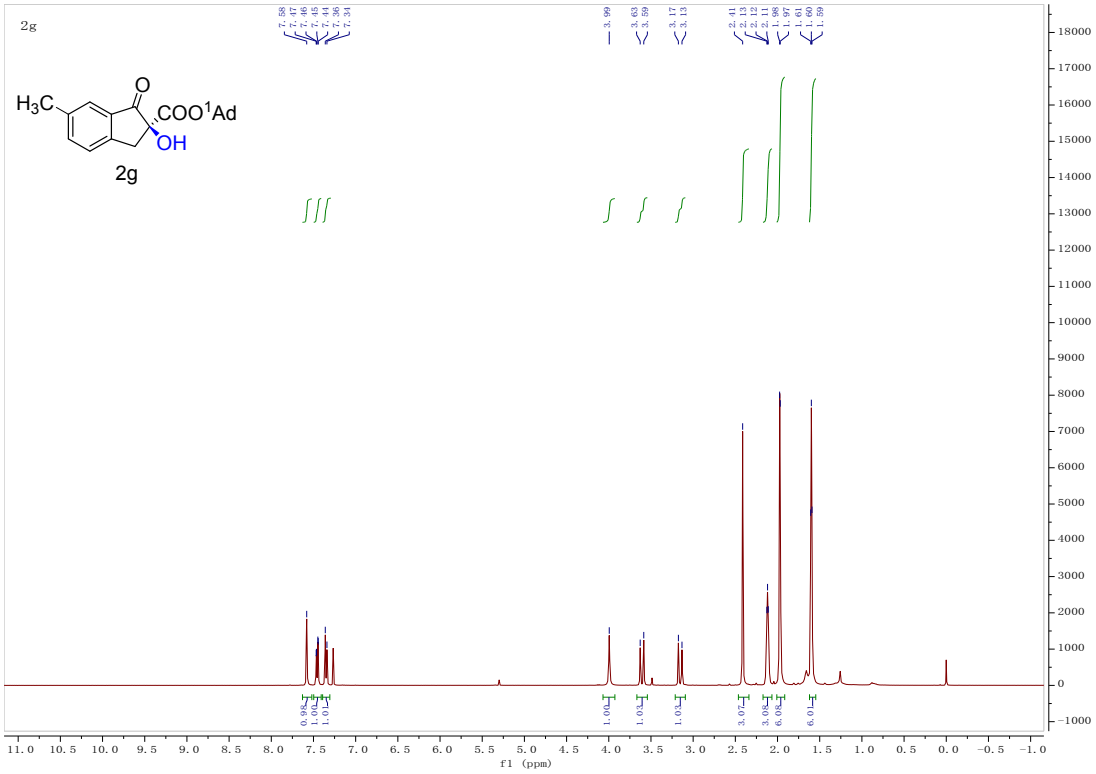

2b
O
COO1Ad
OH
2b
f1 (ppm)

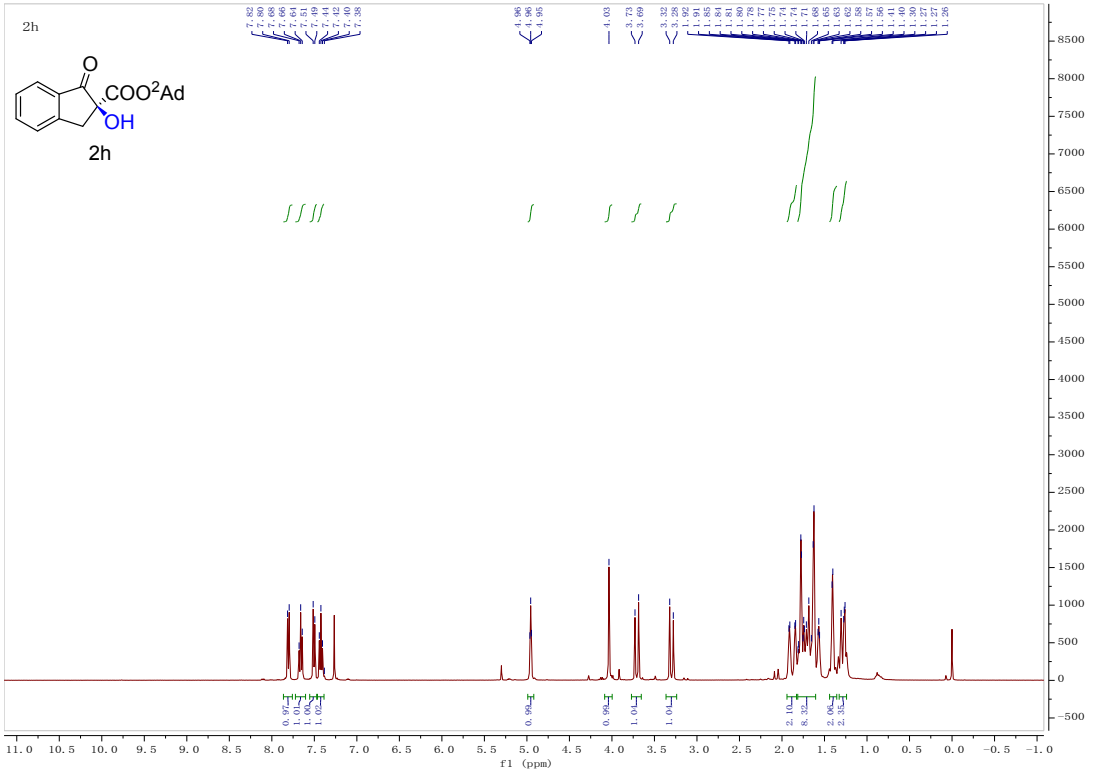

2c
O
COO1Ad
OH
Br
2c
f1 (ppm)

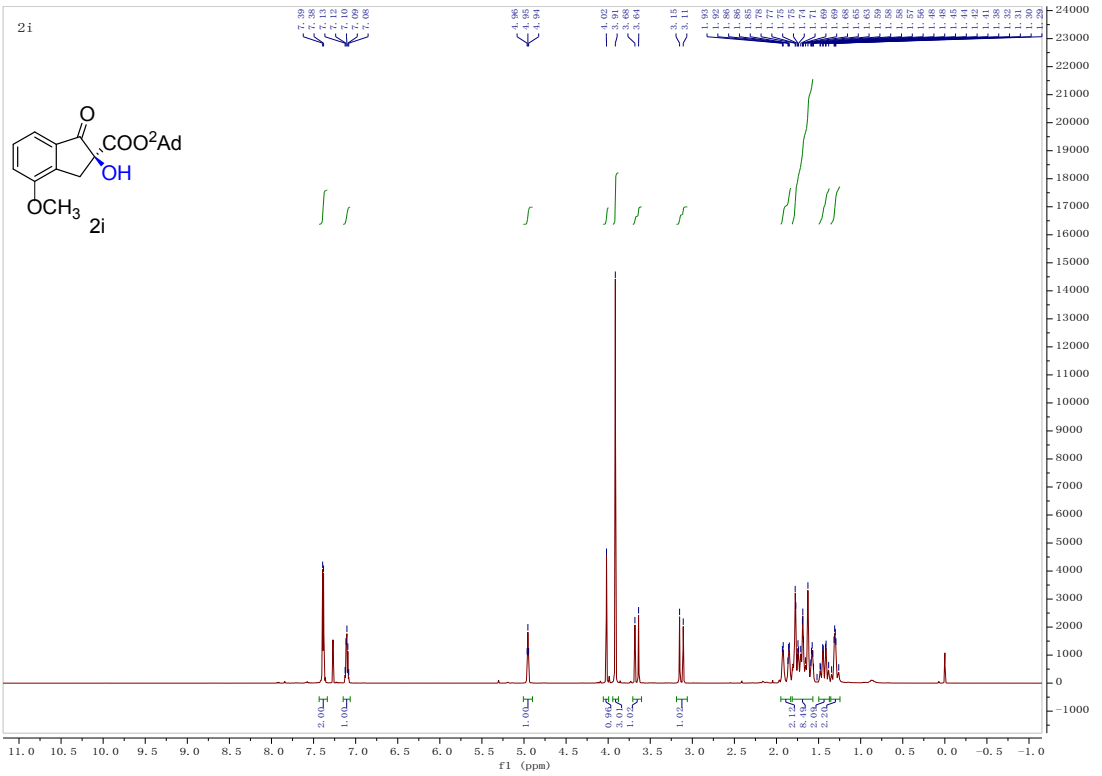

2d
O
COO1Ad
OH
F
2d
f1 (ppm)

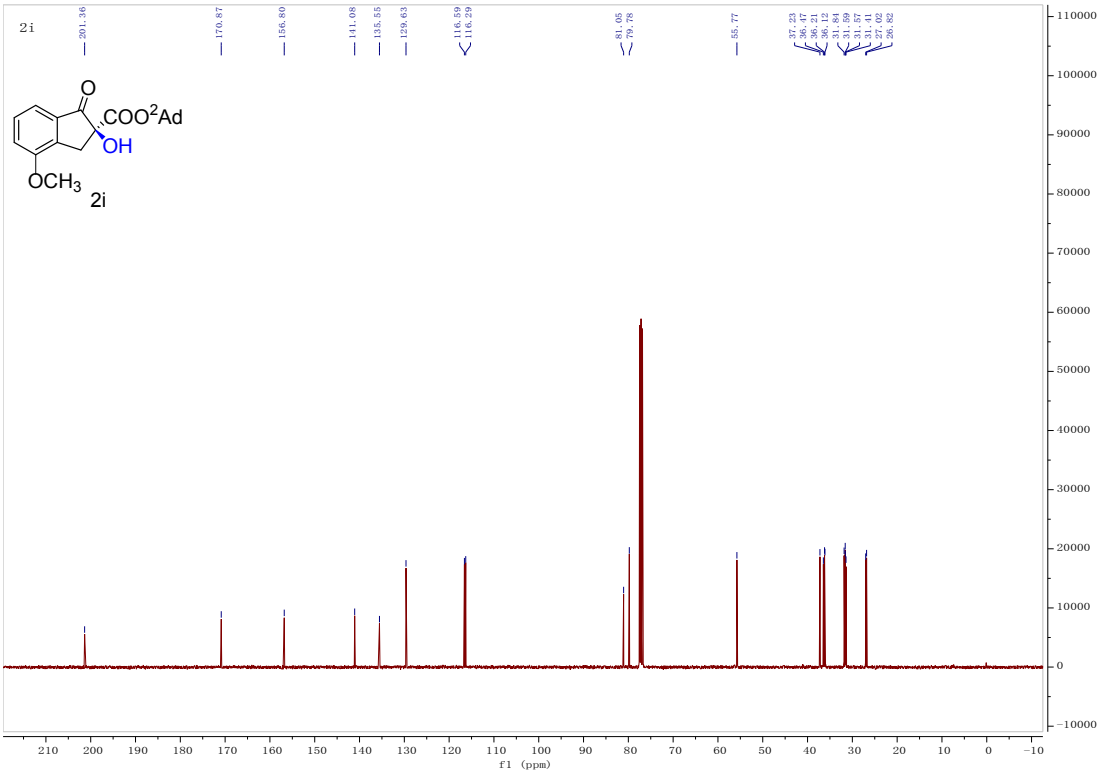

2e
H3CO
O
COO1Ad
OH
2e
f1 (ppm)

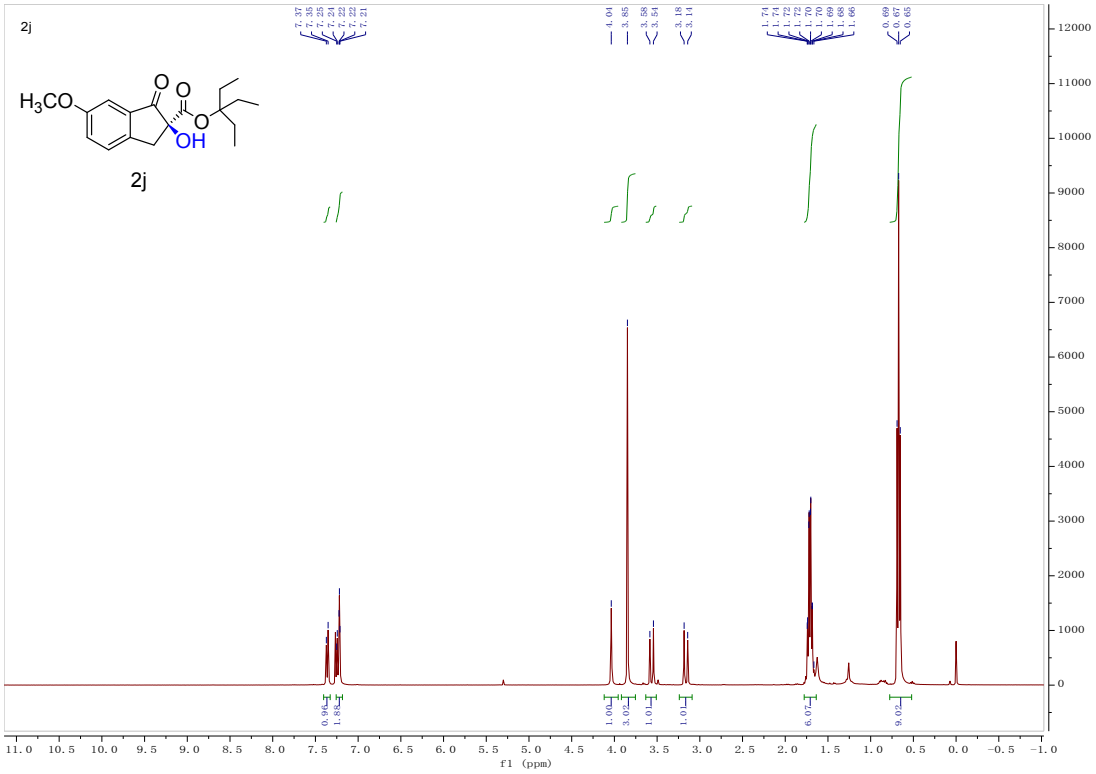

2f
H3CO
H3CO
O
COO1Ad
OH
2f
f1 (ppm)

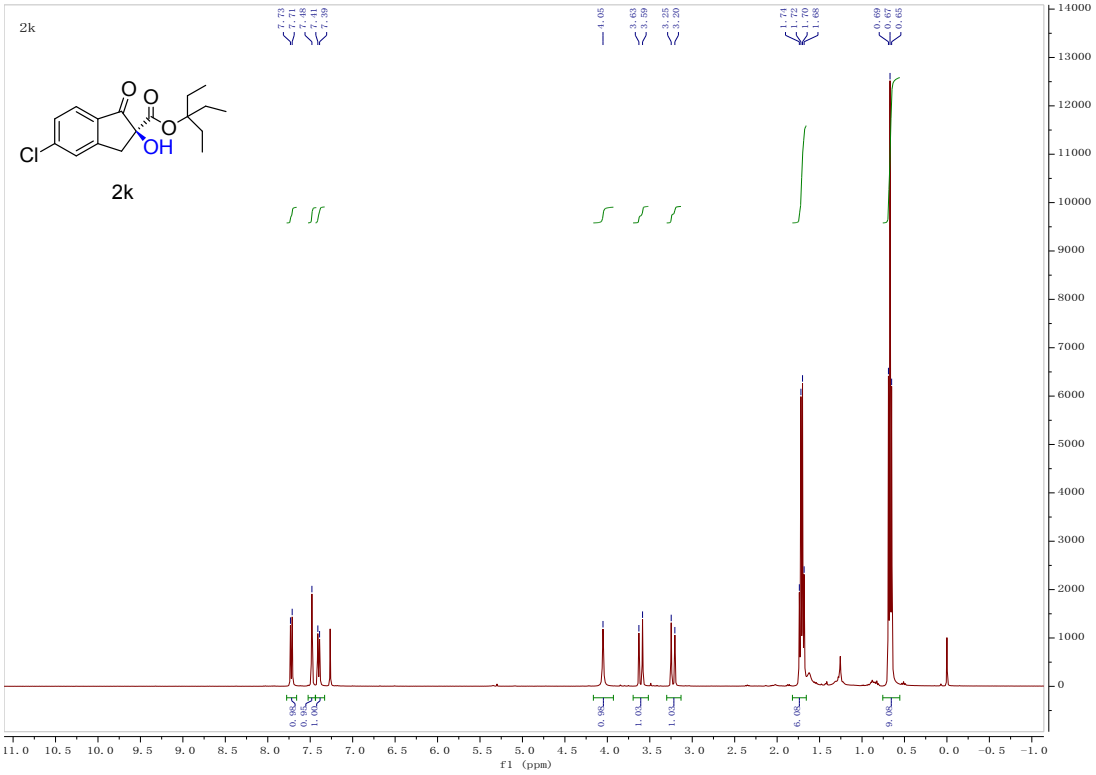

2g
H3C
O
COO1Ad
OH
2g
f1 (ppm)

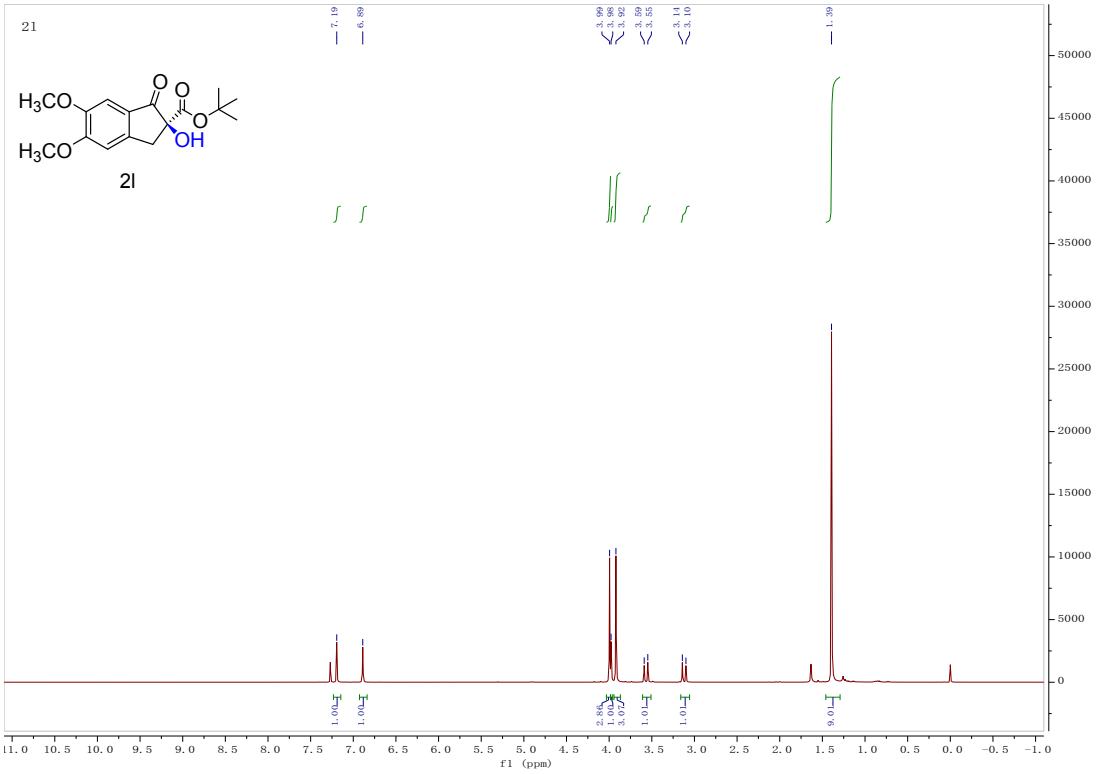

2h
O
COO2Ad
OH
2h
f1 (ppm)

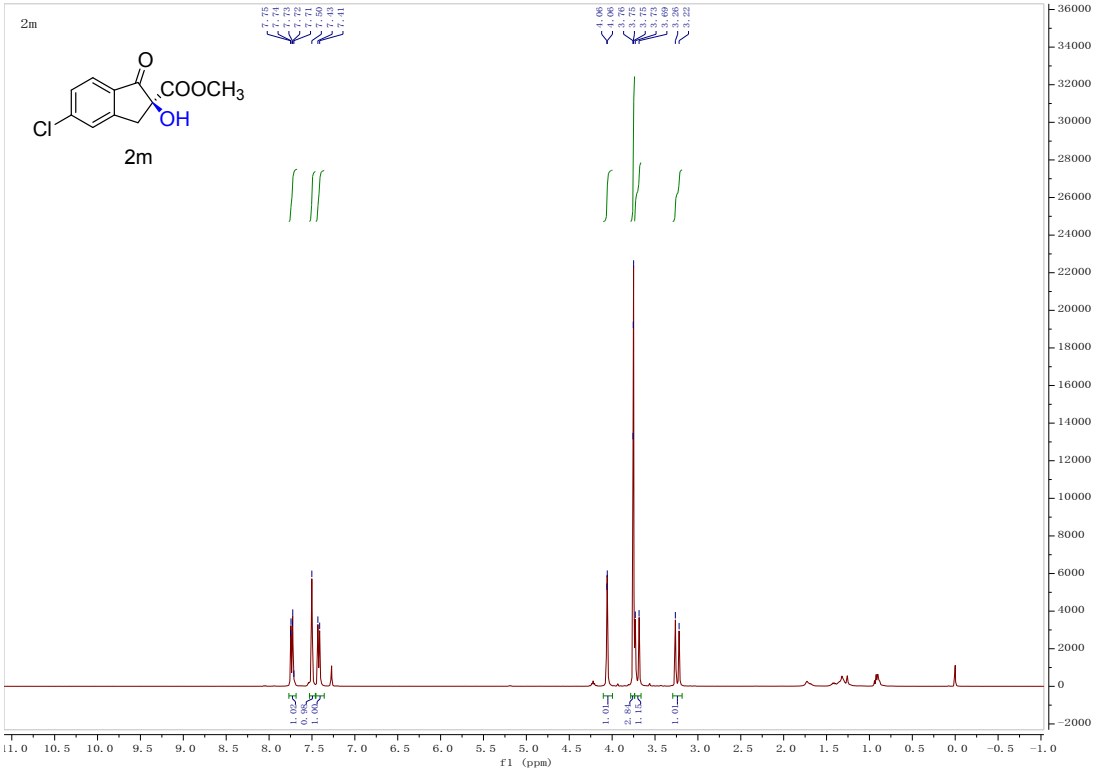

2i
O
COO2Ad
OH
OCH3
2i
f1 (ppm)

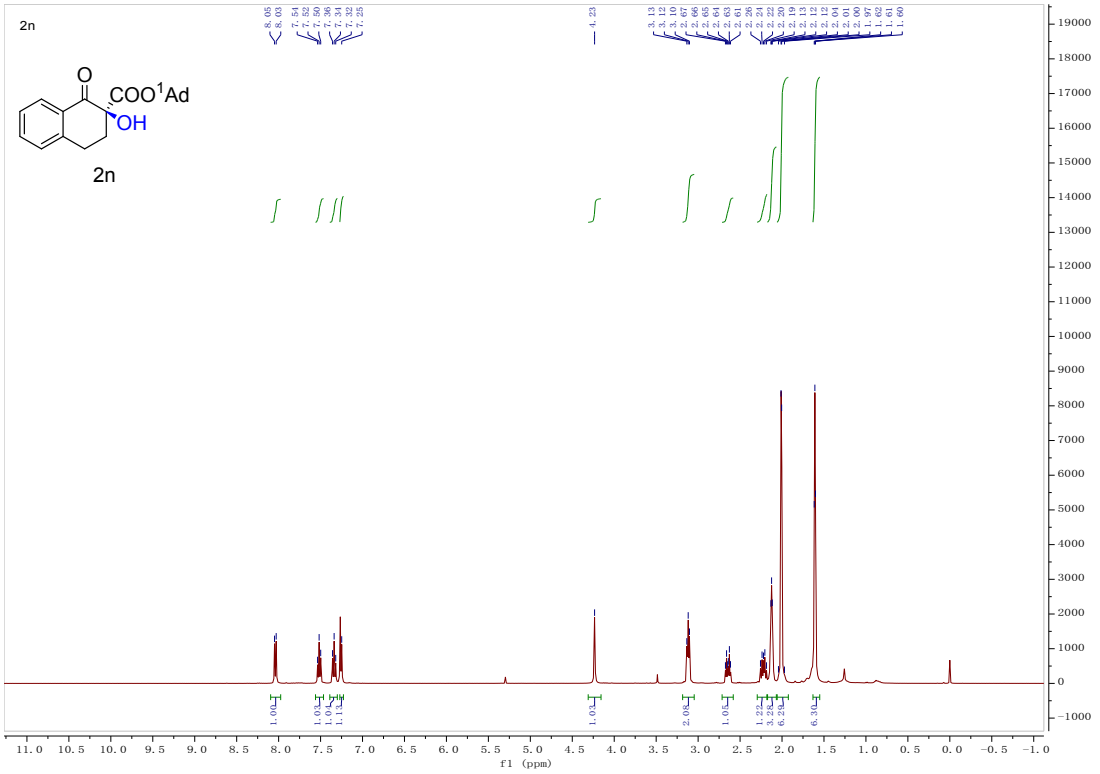

2i
O
COO2Ad
OH
OCH3
2i
f1 (ppm)

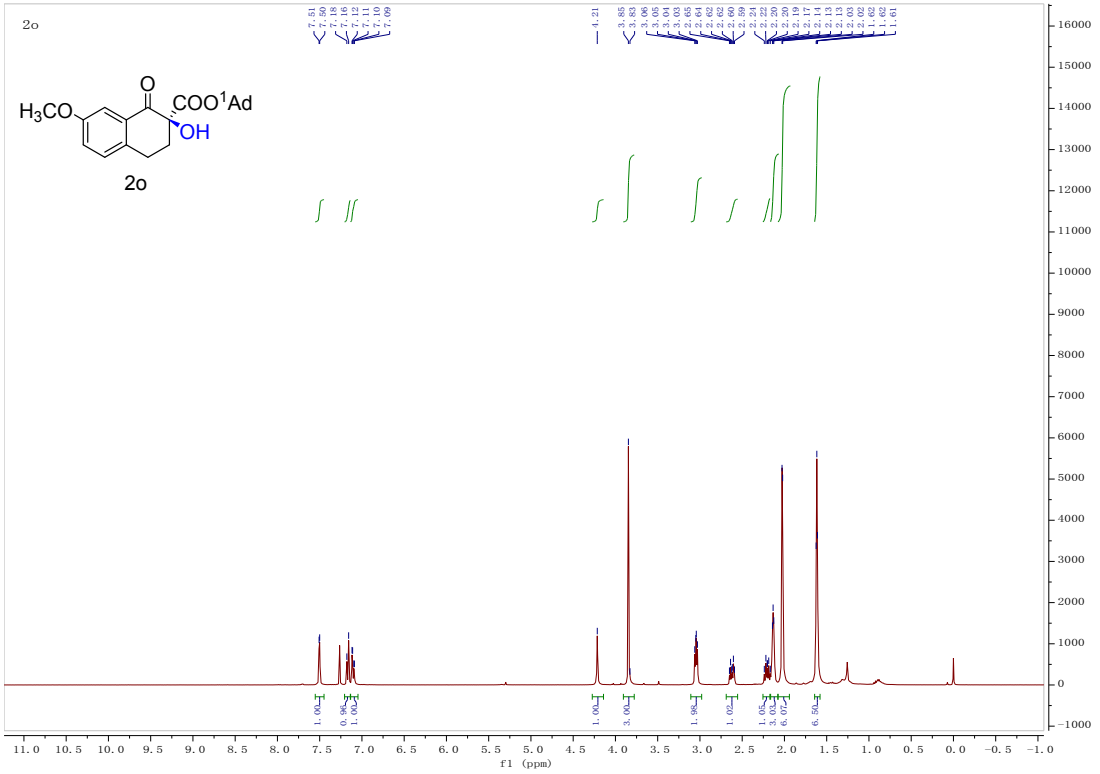

2j
H3CO
O
O
O
OH
2j
f1 (ppm)

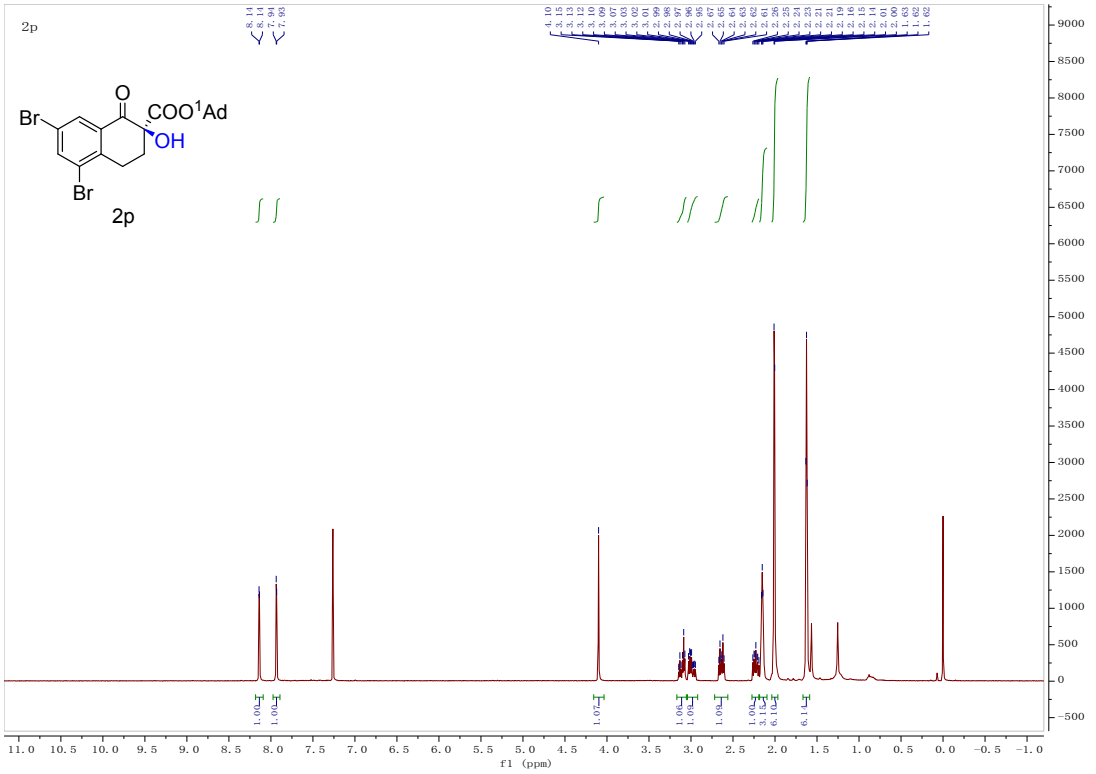

2k
Cl
O
O
O
OH
2k
f1 (ppm)

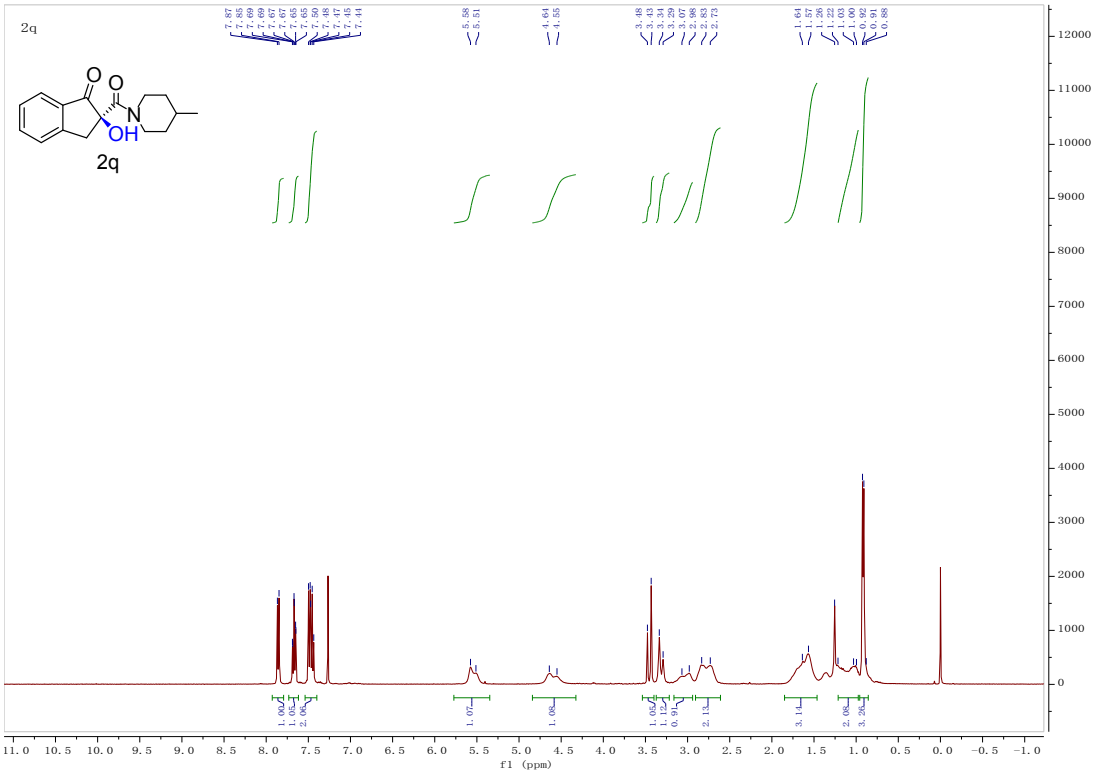

21
H3CO
H3CO
O
O
O
OH
2l
7.19
6.89
3.99
3.98
3.92
3.59
3.55
3.14
3.10
1.39
f1 (ppm)

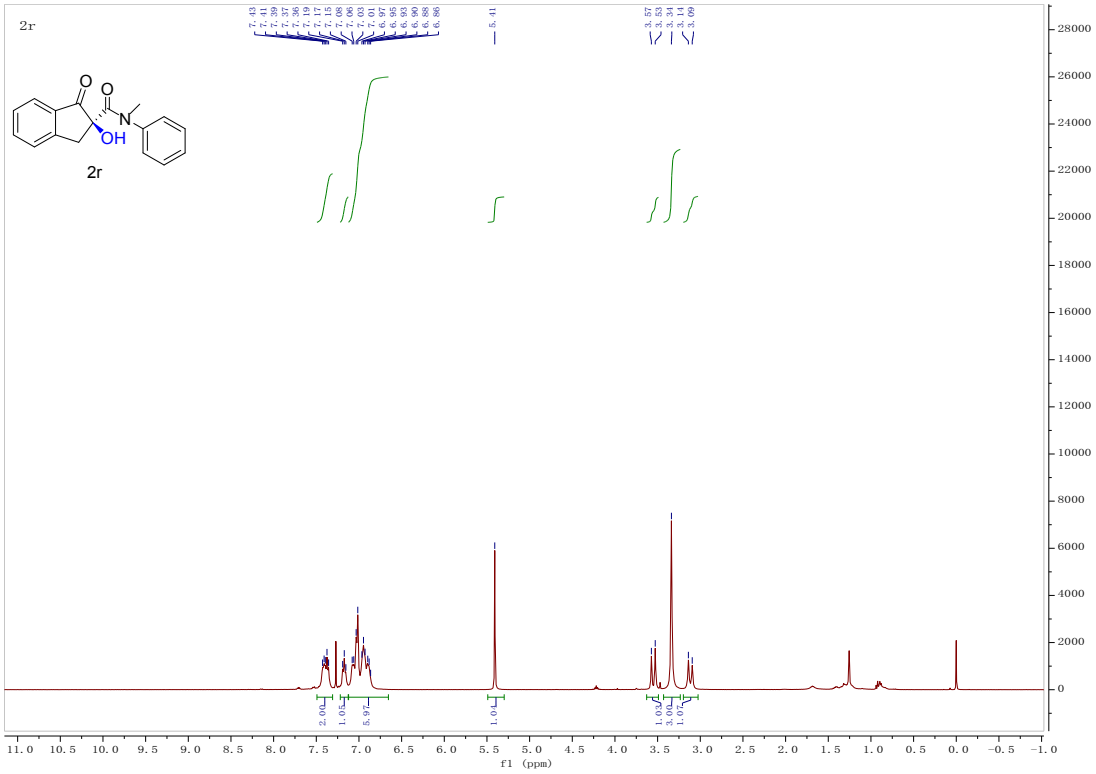

2m
O
COOCH3
Cl
OH
2m
7.75
7.74
7.73
7.72
7.71
7.71
7.50
7.43
7.41
4.06
4.06
3.76
3.75
3.75
3.73
3.69
3.26
3.22
f1 (ppm)

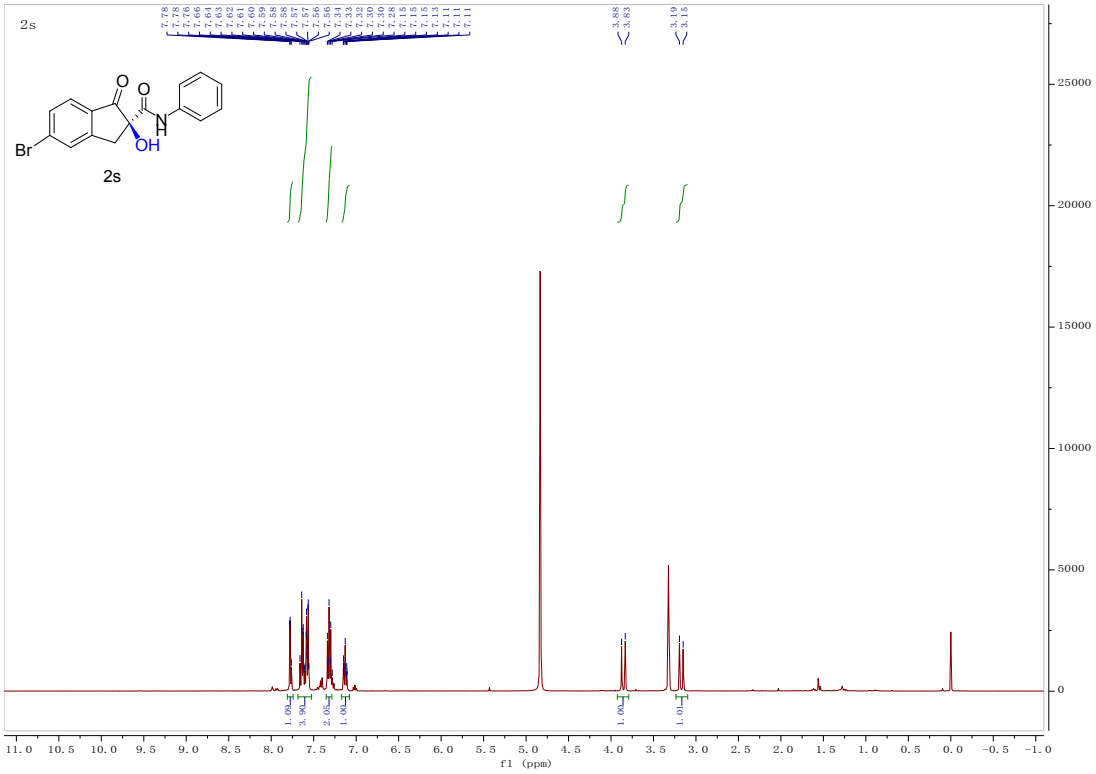

2n
O
COO1Ad
OH
2n
f1 (ppm)

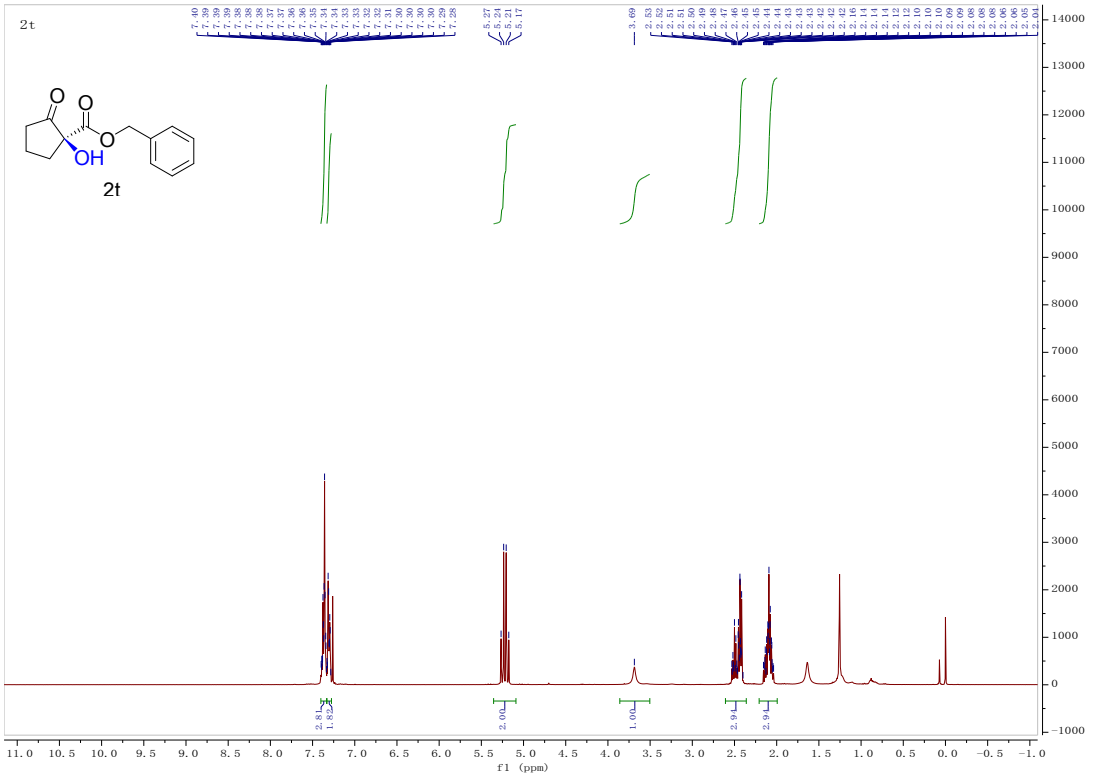

2o
H3CO
O
COO1Ad
OH
2o
f1 (ppm)

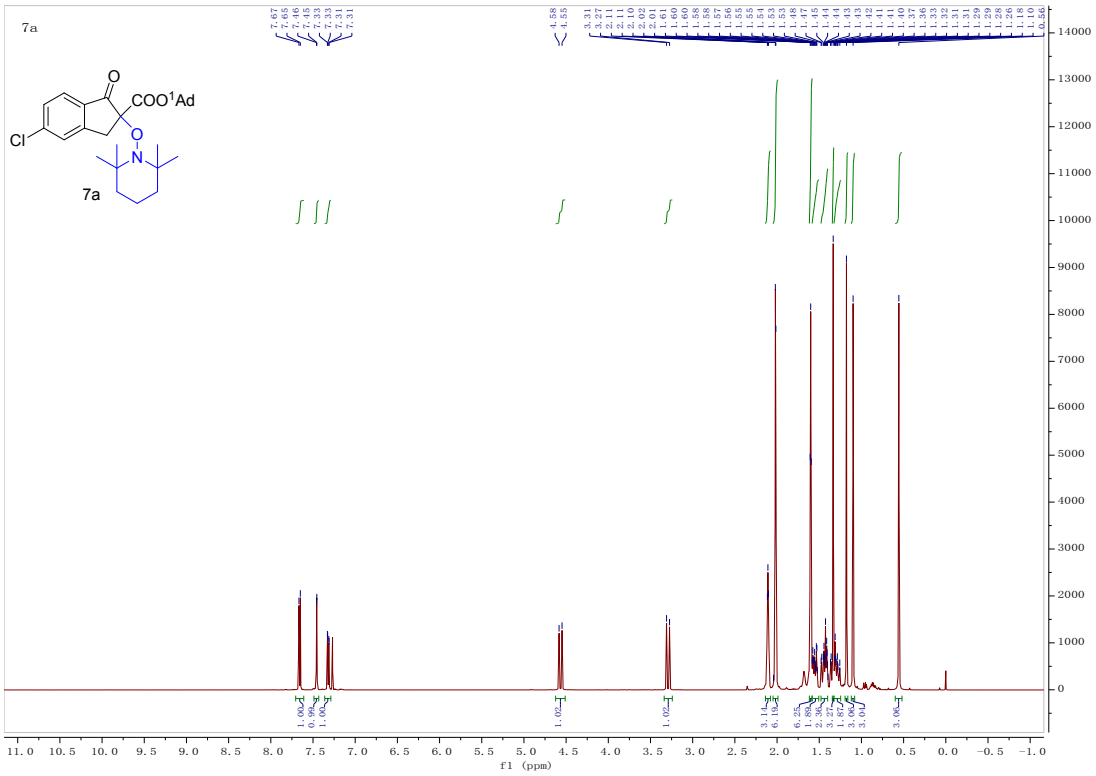

2p
Br
O
COO1Ad
OH
Br
2p
f1 (ppm)

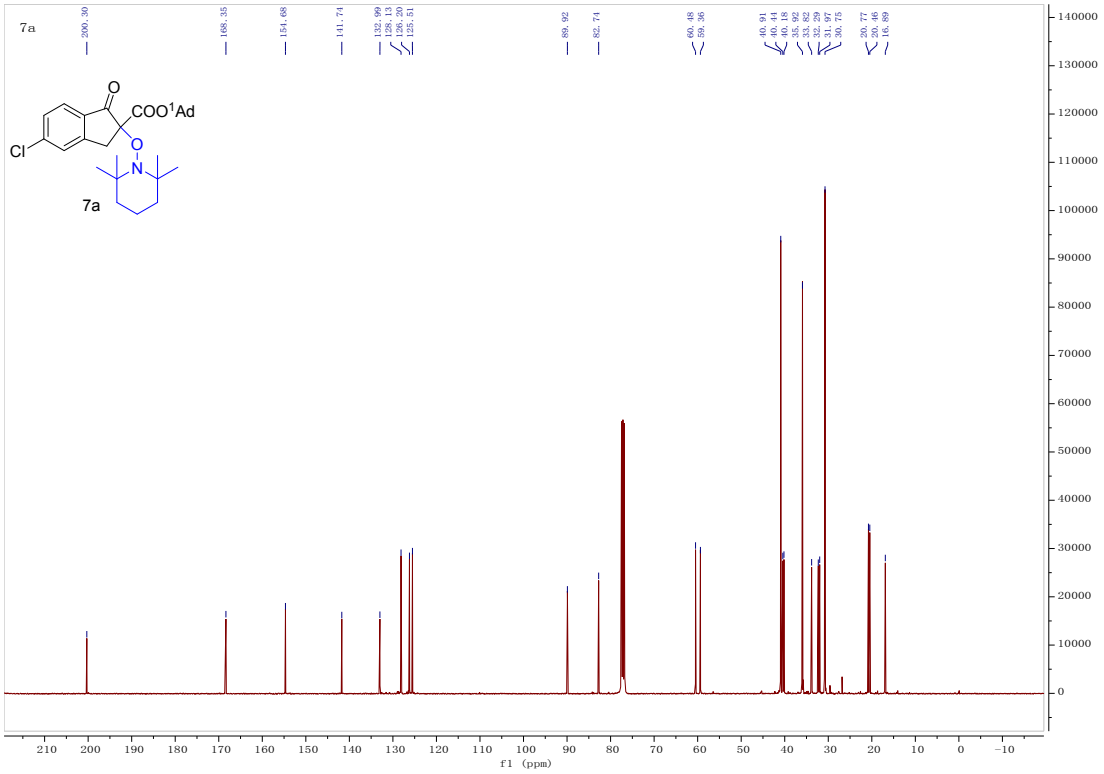

2q
O
O
N
OH
2q
f1 (ppm)


2r
2r

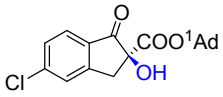

2s
Br
2s


2t
O
O
O
OH
2t
f1 (ppm)

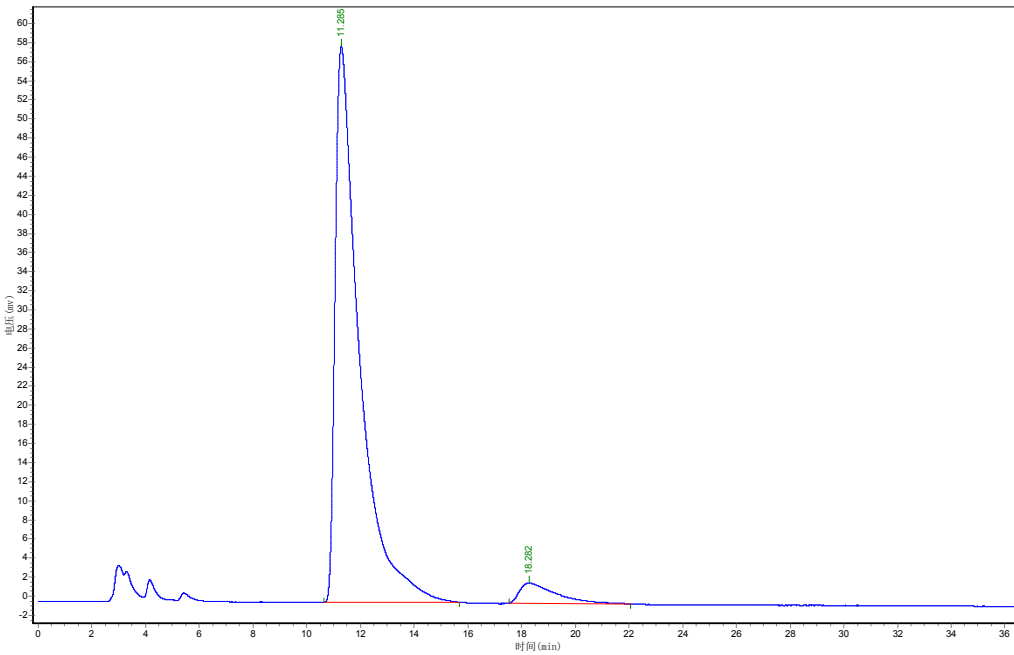

7a
O
COO¹Ad
Cl
O
N
7a
f1 (ppm)


7a
200.30
168.35
154.68
141.74
132.99
128.13
126.20
125.51
89.92
82.74
60.48
59.36
40.91
40.44
40.18
35.92
33.82
32.29
31.97
30.75
20.77
20.46
16.89
O
COO1Ad
Cl
O
N
7a
f1 (ppm)

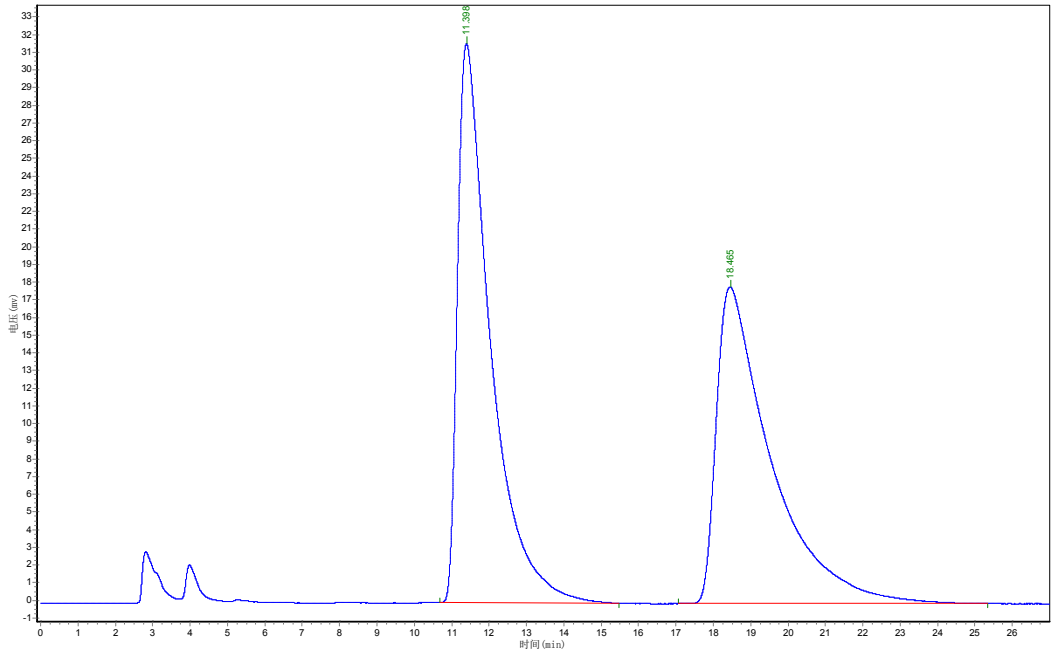
7. Copies of HPLC Spectra



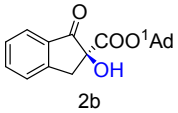
2a



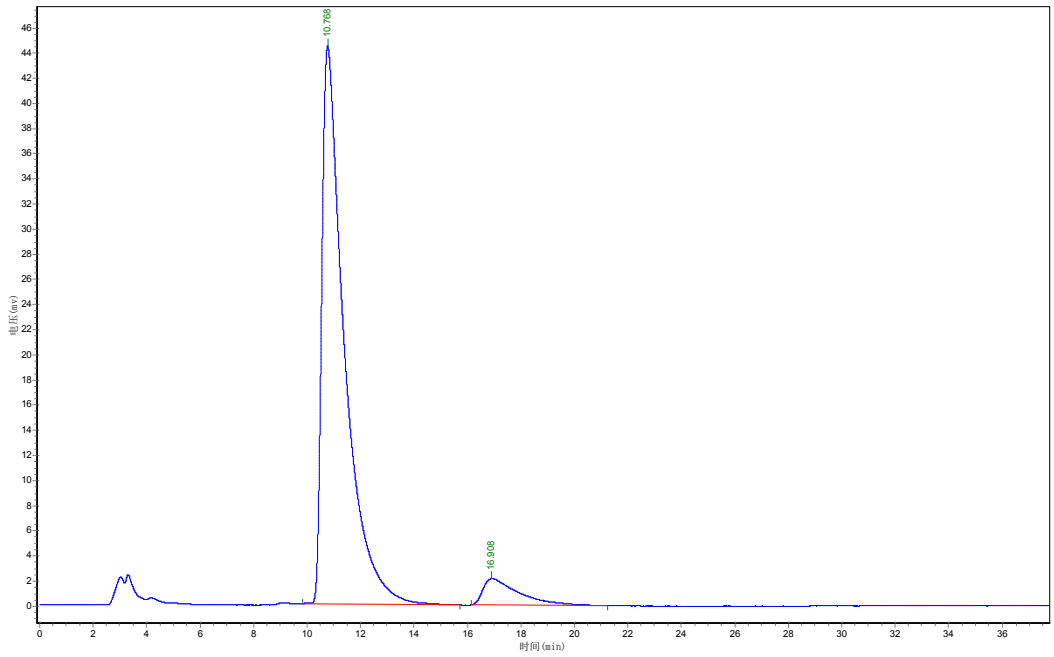
Peak	RetTime	Height	Area	Area%
1	11.285	58275.480	3642204.000	94.8479
2	18.282	2110.641	197843.141	5.1521



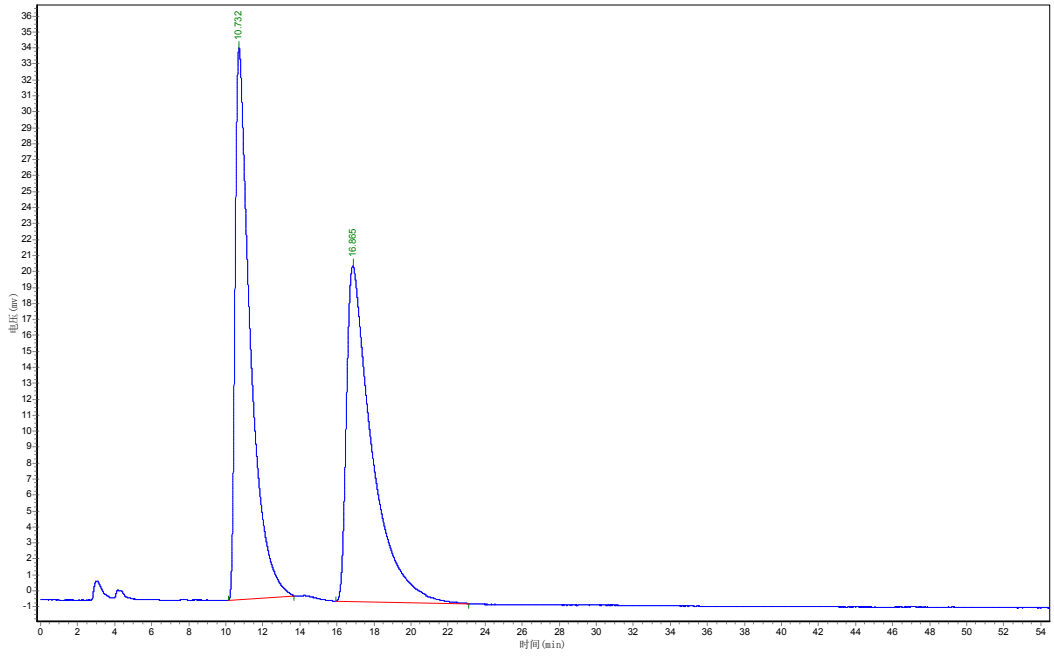
Peak	RetTime	Height	Area	Area%
1	11.398	31641.277	1943232.000	51.7408
2	18.465	17906.307	1812471.625	48.2592



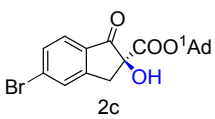
2b



Peak	RetTime	Height	Area	Area%
1	10.768	44397.836	2595911.750	92.9923
2	16.908	2113.575	195621.594	7.0077



Peak	RetTime	Height	Area	Area%
1	10.732	34526.410	1980273.250	49.8493
2	16.865	21005.838	1992247.750	50.1507



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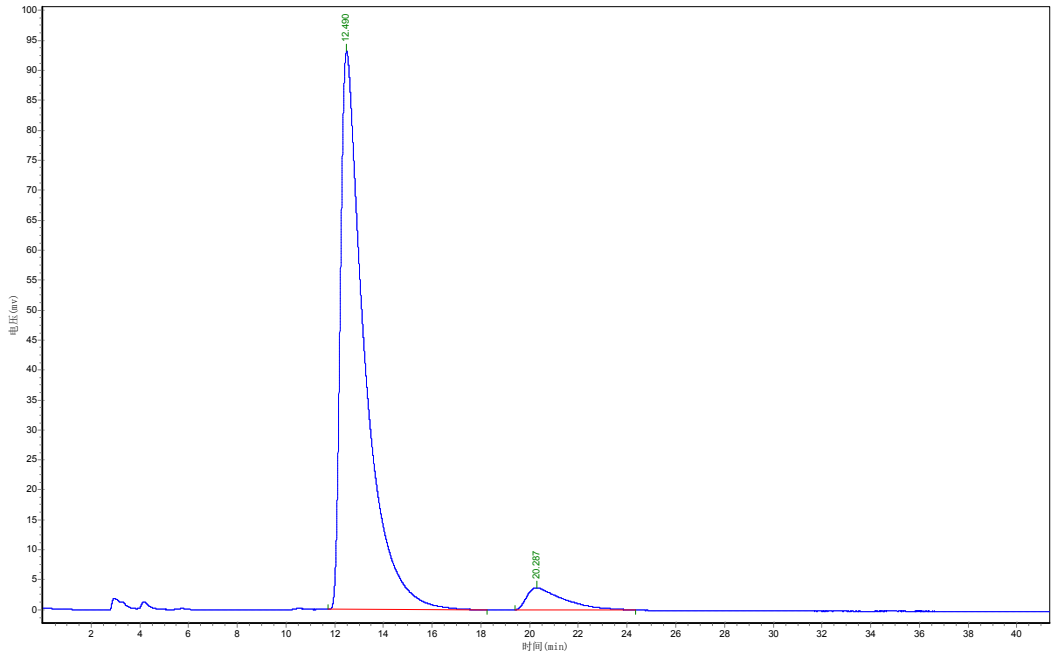
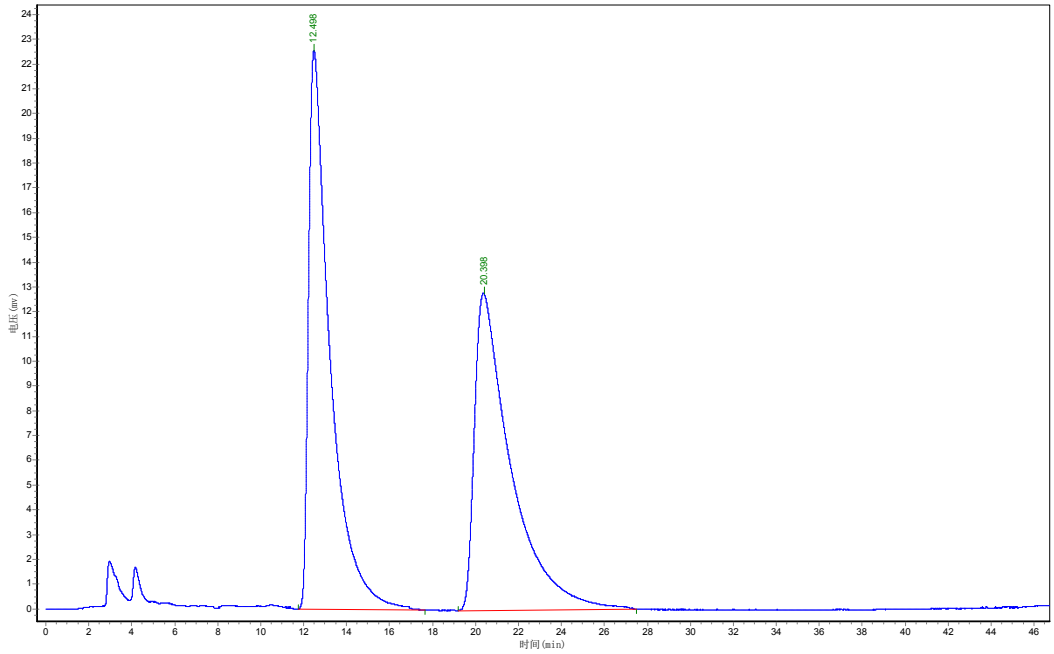
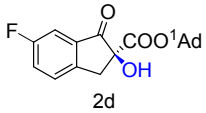


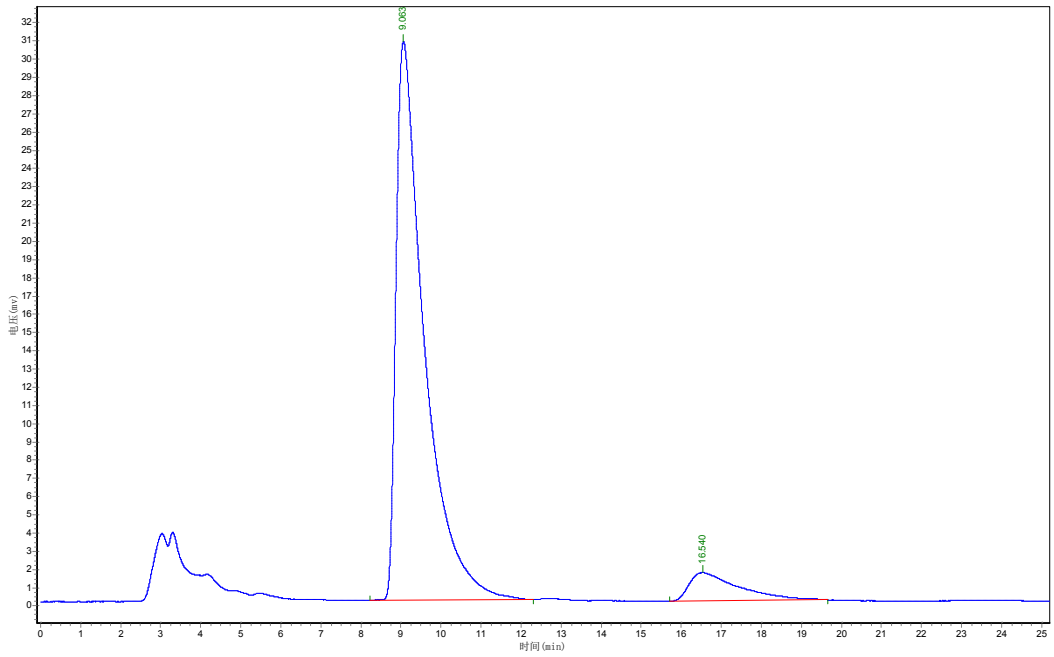
Peak	RetTime	Height	Area	Area%
1	12.490	93177.172	6397412.500	94.2895
2	20.287	3700.715	387450.188	5.7105



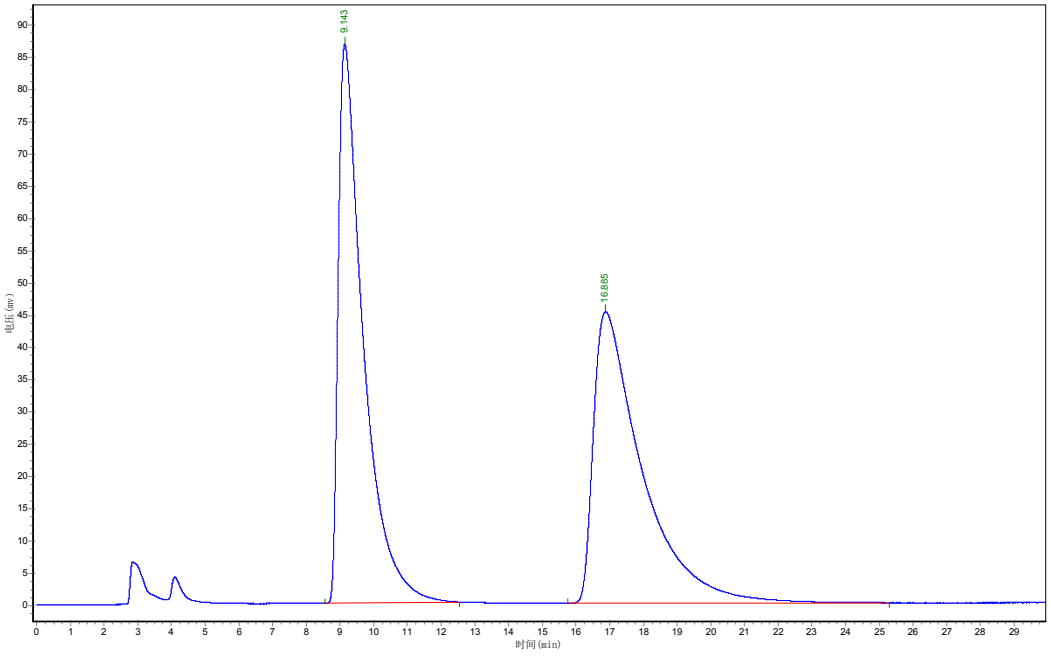
Peak	RetTime	Height	Area	Area%
1	12.498	22548.375	1565998.250	51.0996
2	20.398	12801.829	1498601.375	48.9004



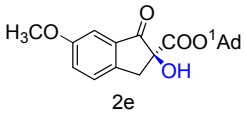
2d



Peak	RetTime	Height	Area	Area%
1	9.063	30639.209	1501242.875	91.8714
2	16.540	1548.476	132827.188	8.1286



Peak	RetTime	Height	Area	Area%
1	9.143	86719.742	4476201.000	49.8436
2	16.885	45202.719	4504300.500	50.1564



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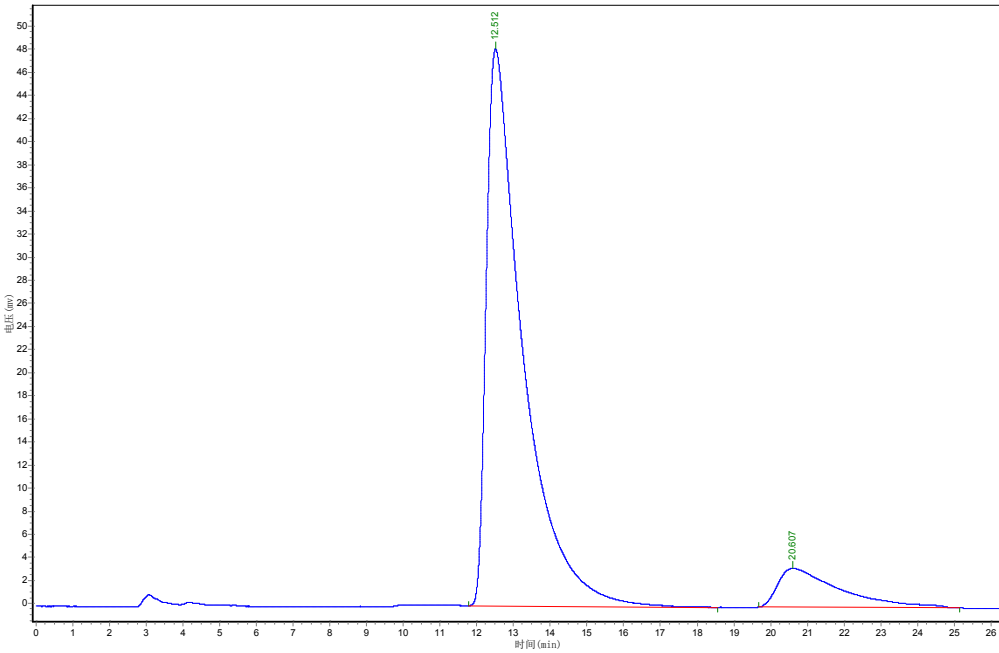
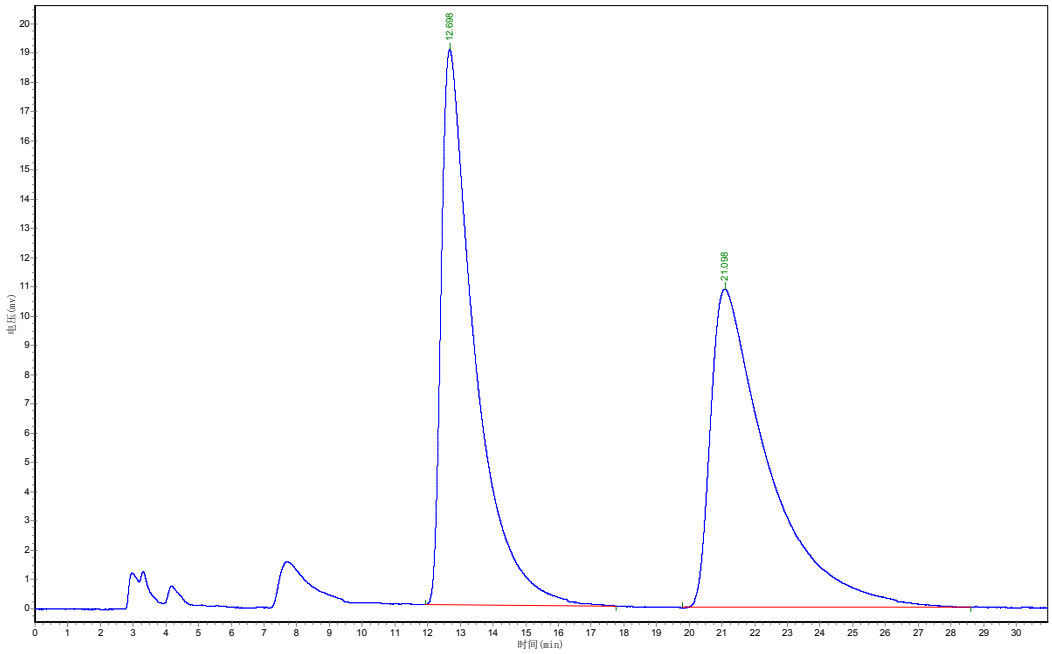
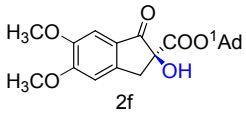


Peak	RetTime	Height	Area	Area%
1	12.512	48260.758	3343454.250	89.4594
2	20.607	3378.211	393942.313	10.5406



Peak	RetTime	Height	Area	Area%
1	12.698	18983.652	1351248.875	50.3943
2	21.098	10890.447	1330101.000	49.6056



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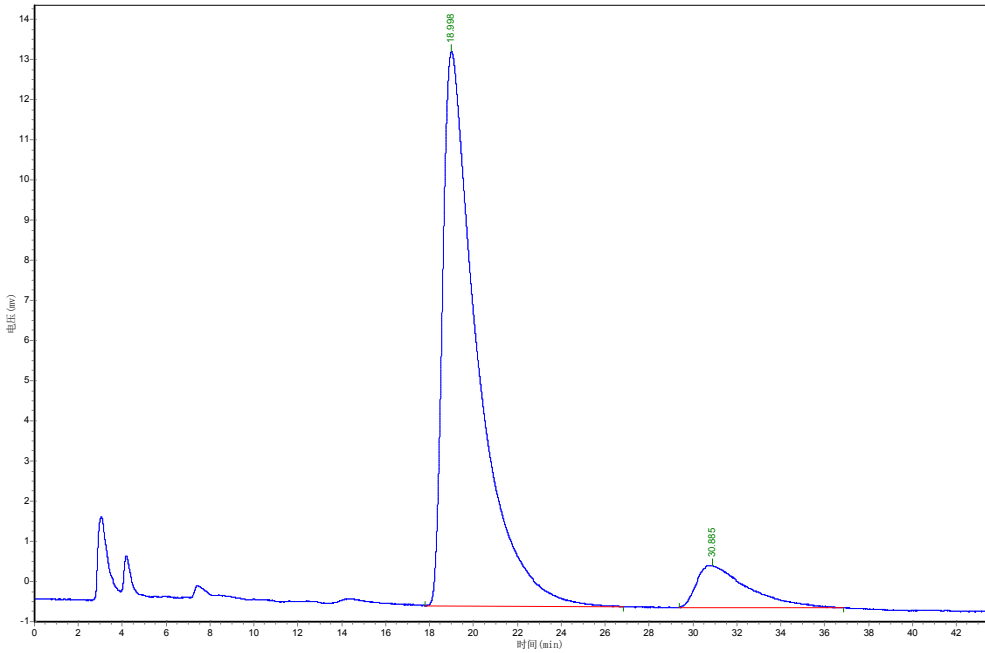
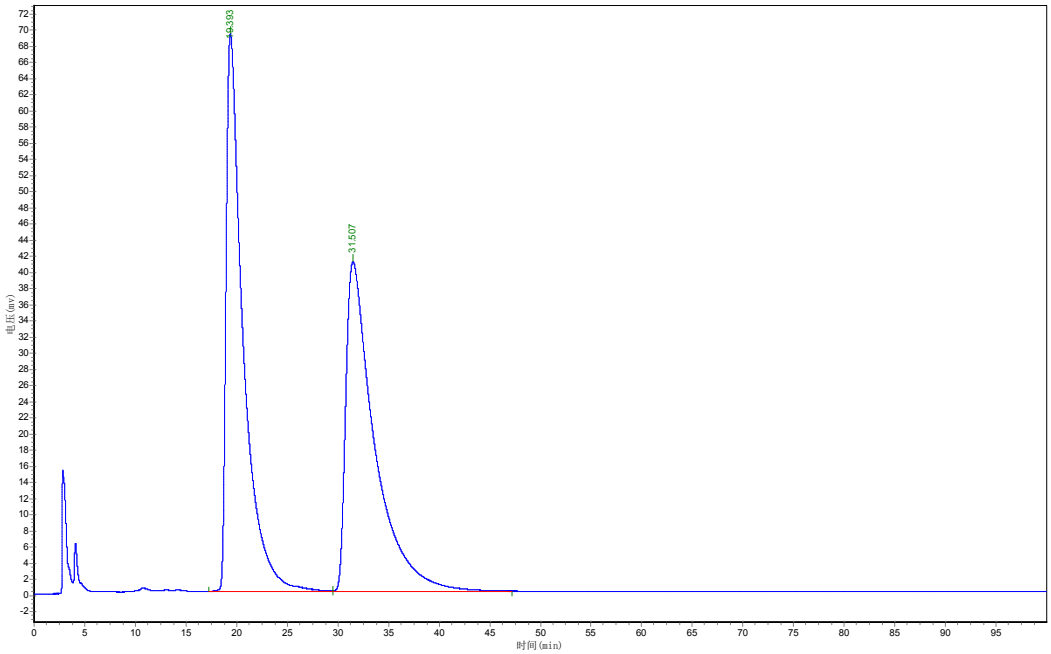
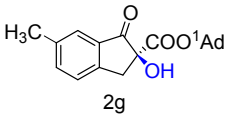


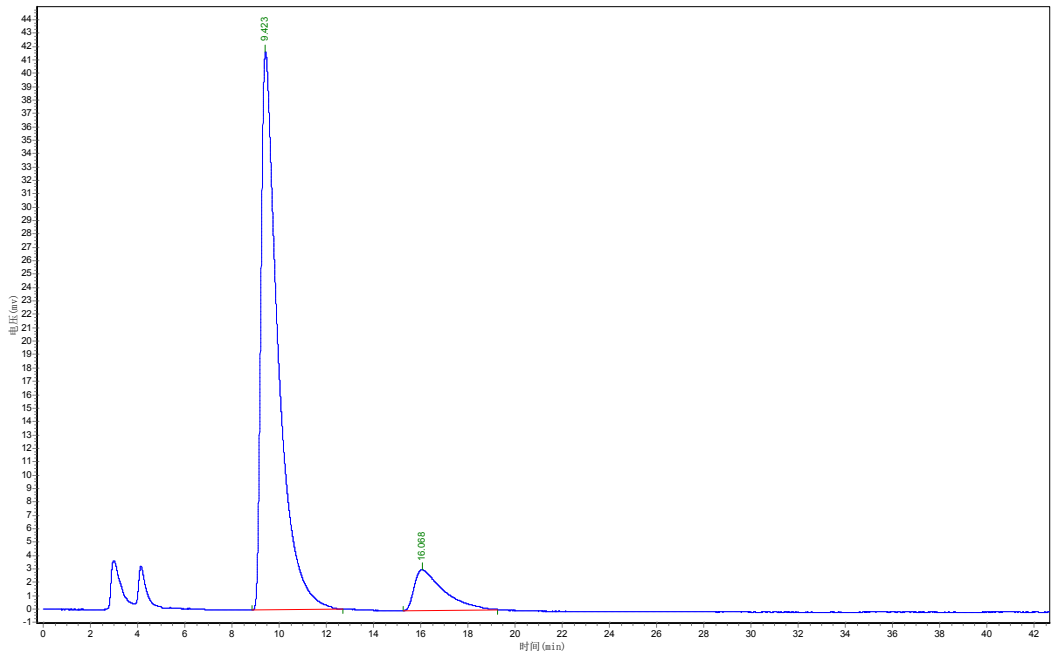
Peak	RetTime	Height	Area	Area%
1	18.998	13812.267	1513618.250	90.0184
2	30.885	1046.821	167835.109	9.9816



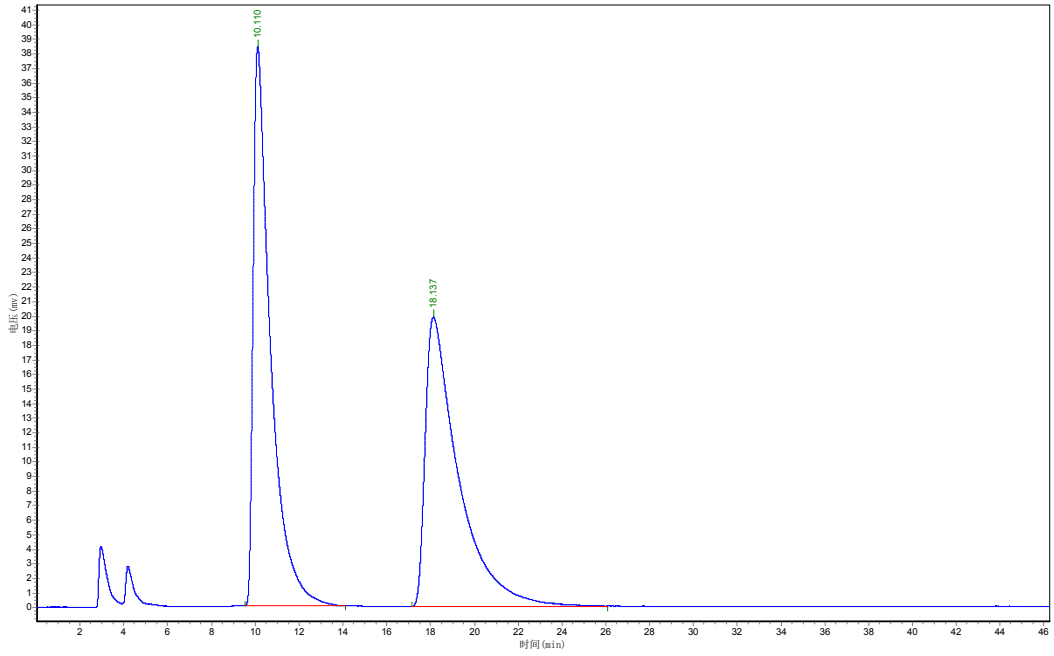
Peak	RetTime	Height	Area	Area%
1	19.393	69034.383	8054553.000	50.1677
2	31.507	40805.063	8000711.000	49.8323



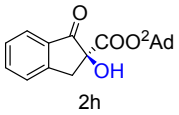
2g



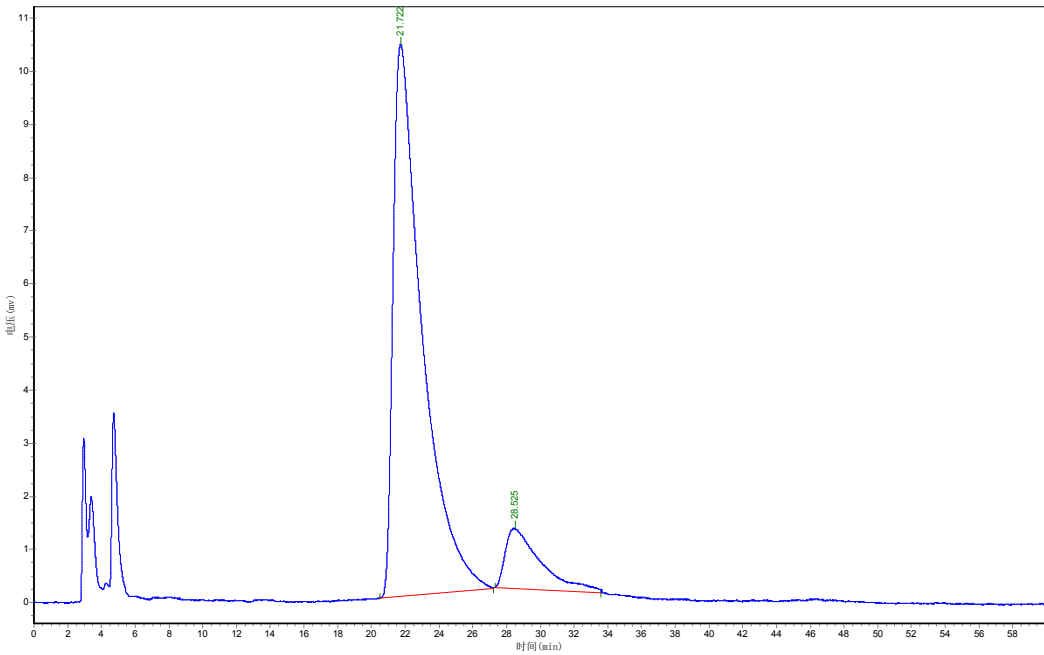
Peak	RetTime	Height	Area	Area%
1	9.423	41635.164	2099102.250	88.9404
2	16.068	3040.480	261019.656	11.0596



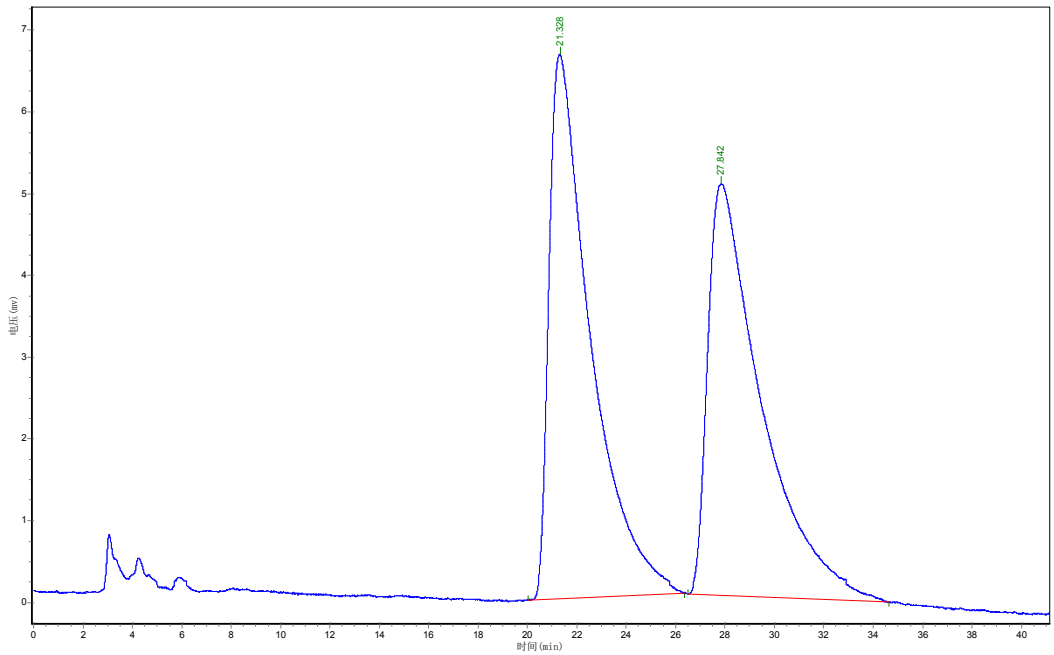
Peak	RetTime	Height	Area	Area%
1	10.110	38343.734	2107903.250	50.3546
2	18.137	19875.275	2078213.375	49.6454



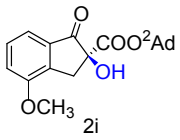
2h



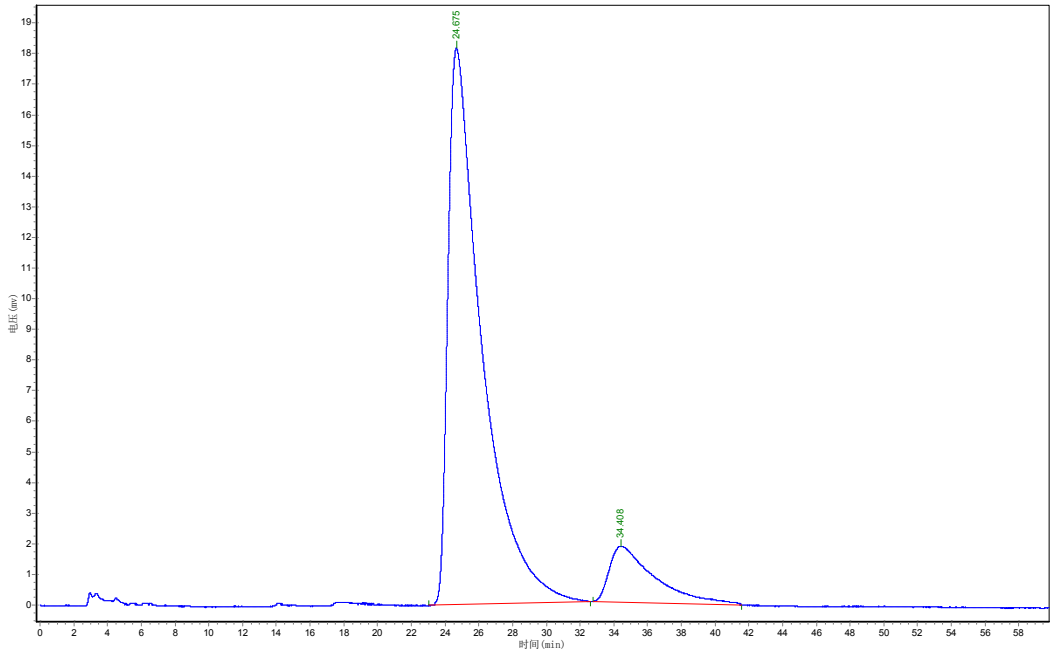
Peak	RetTime	Height	Area	Area%
1	21.722	10379.418	1236899.500	88.3194
2	28.525	1129.648	163585.813	11.6807



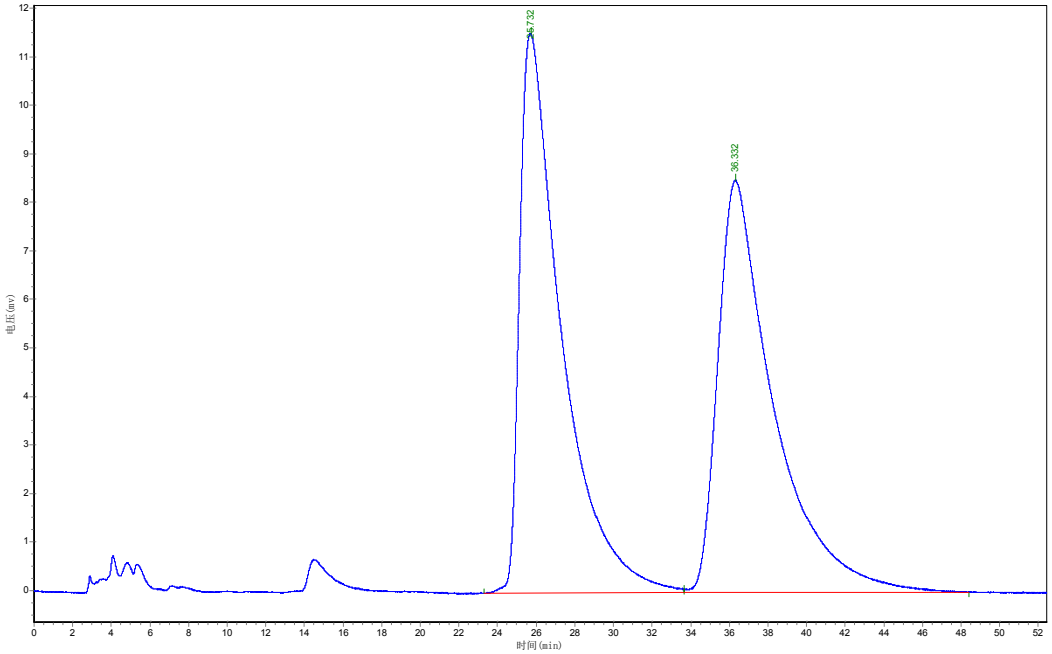
Peak	RetTime	Height	Area	Area%
1	21.328	6658.484	777516.250	50.5989
2	27.842	5034.317	759111.375	49.4011



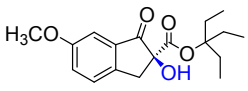
2i



Peak	RetTime	Height	Area	Area%
1	24.675	18168.904	2529881.250	88.2851
2	34.408	1819.010	335699.281	11.7149



Peak	RetTime	Height	Area	Area%
1	25.732	11524.771	1736184.875	50.5857
2	36.332	8491.057	1695983.875	49.4143



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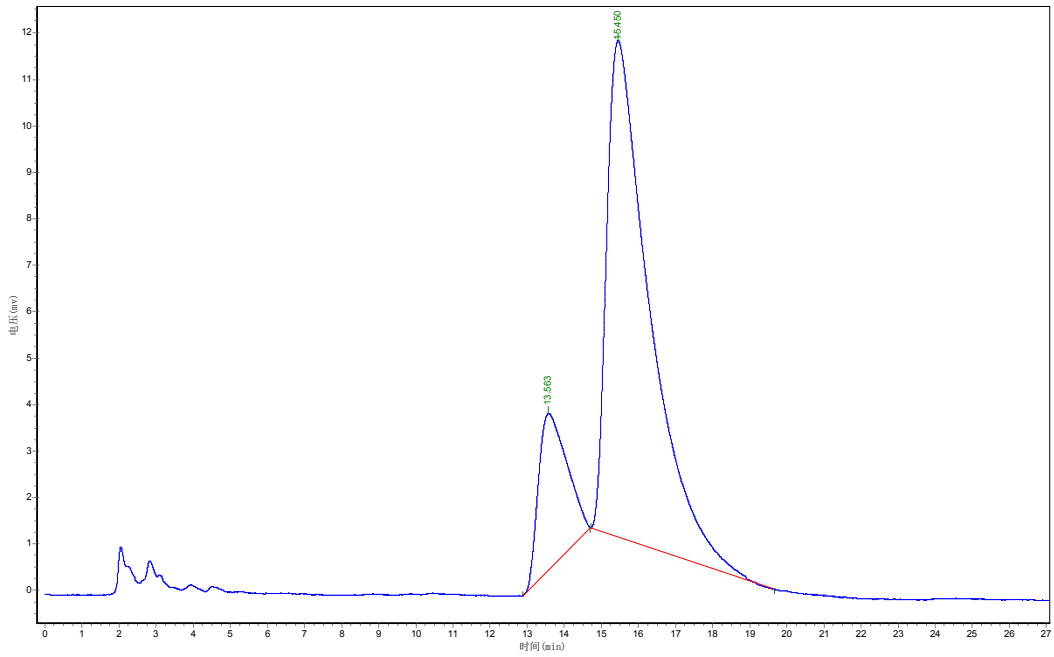
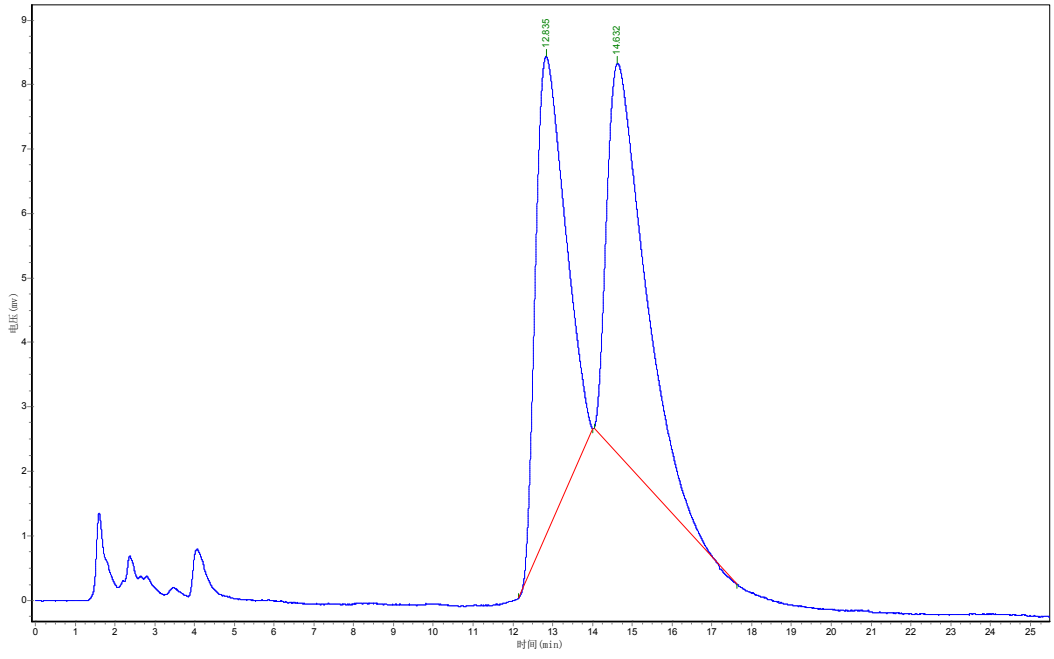
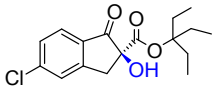


Peak	RetTime	Height	Area	Area%
1	13.563	3376.964	178124.297	17.1674
2	15.450	10696.258	859451.250	82.8326



Peak	RetTime	Height	Area	Area%
1	12.835	7438.766	382969.031	48.4829
2	14.632	6060.933	406937.031	51.5171



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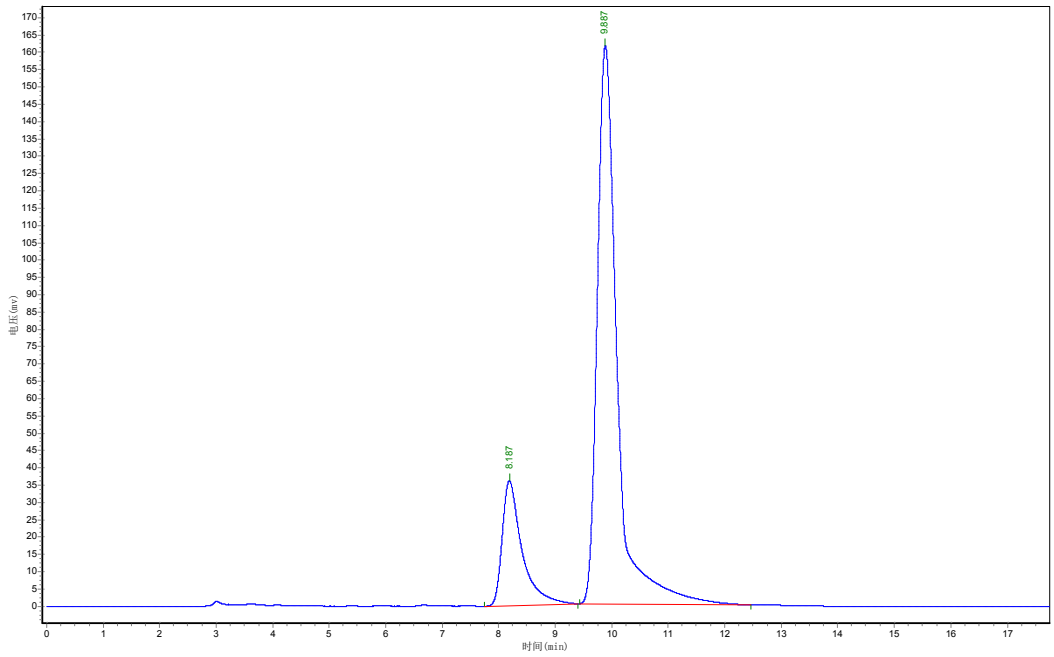
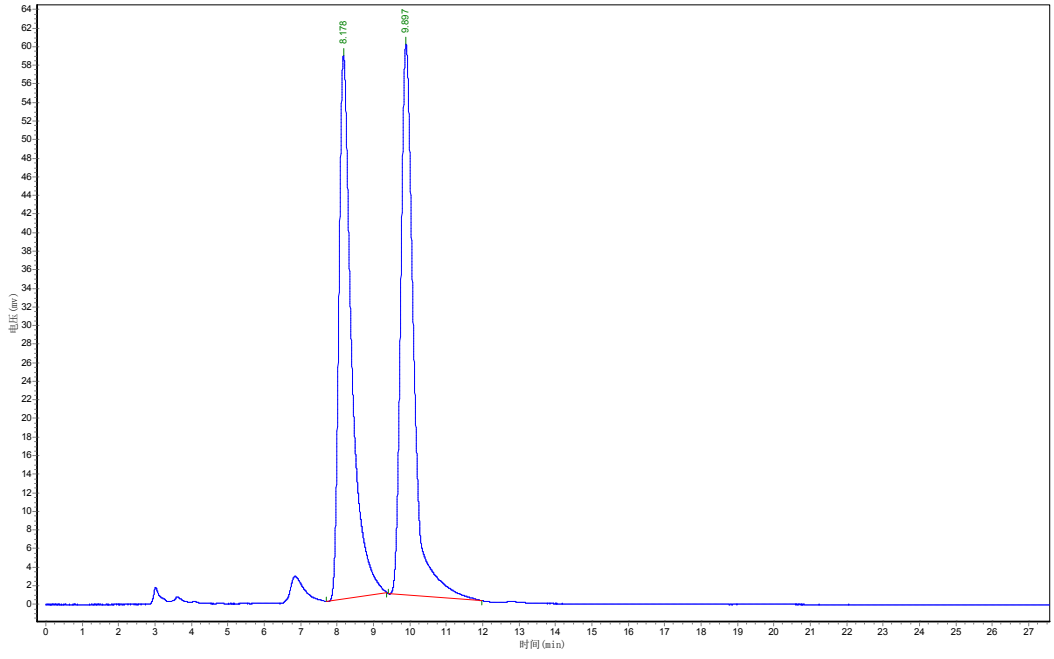
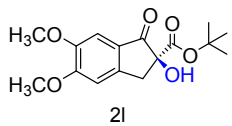


Peak	RetTime	Height	Area	Area%
1	8.187	36041.023	874505.813	18.1714
2	9.887	161151.328	3938022.250	81.8286



Peak	RetTime	Height	Area	Area%
1	8.178	58511.852	1430676.375	49.3589
2	9.897	59265.402	1467840.125	50.6411



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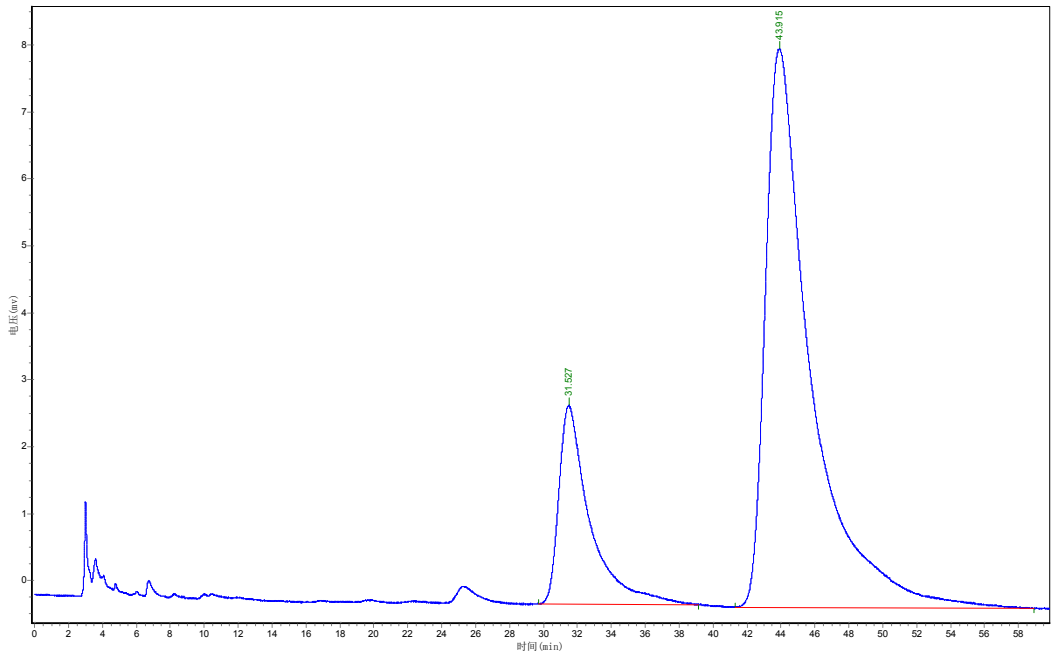
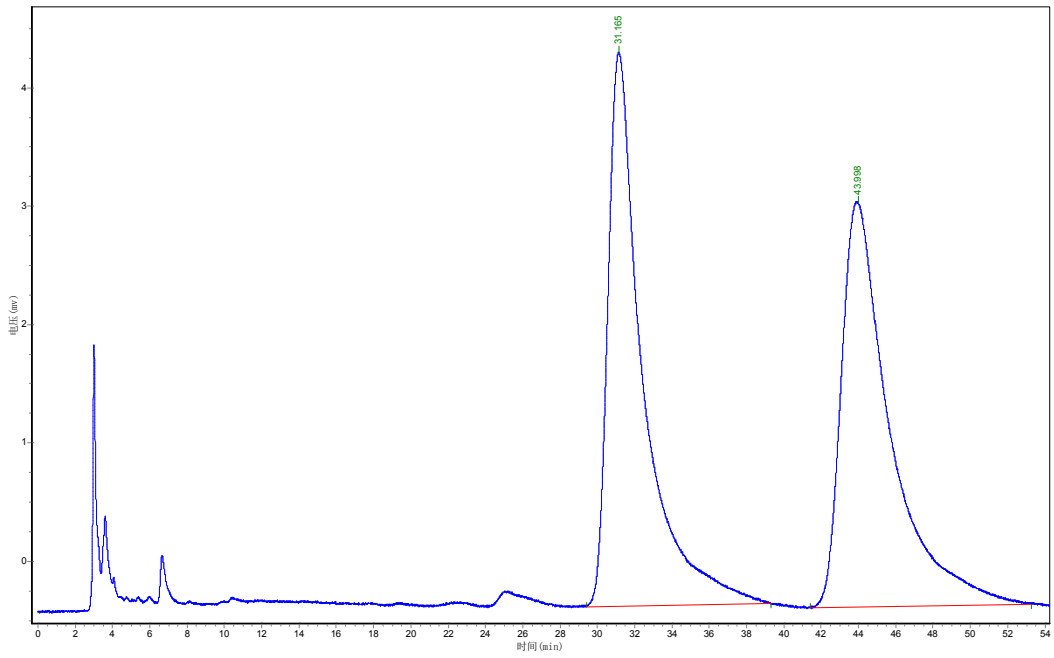
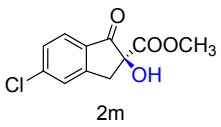


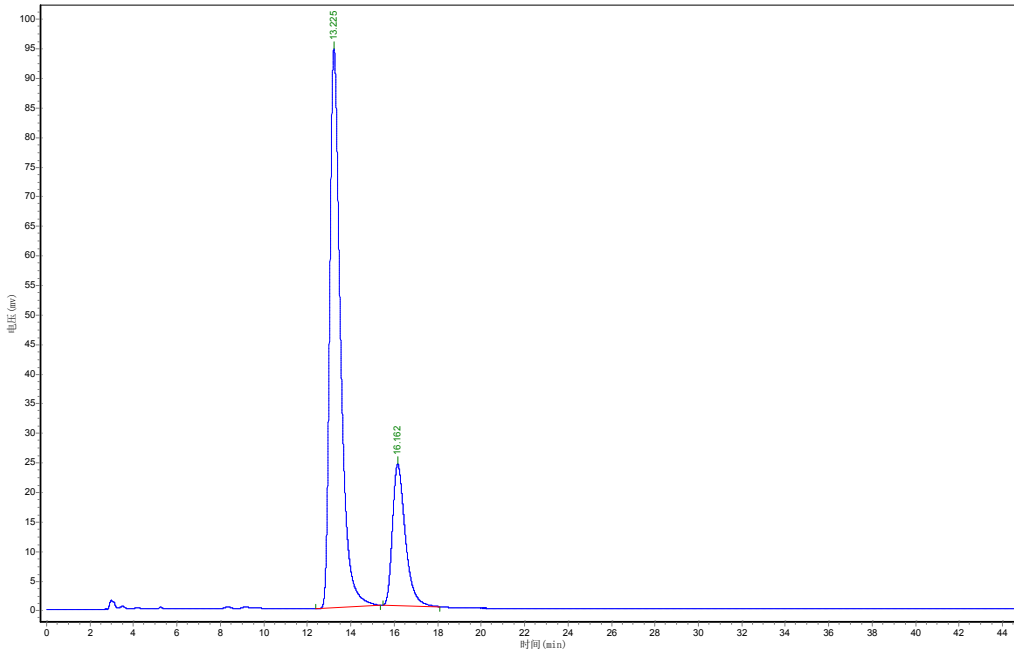
Peak	RetTime	Height	Area	Area%
1	31.527	2969.728	377926.563	19.5678
2	43.915	8345.824	1553439.750	80.4322



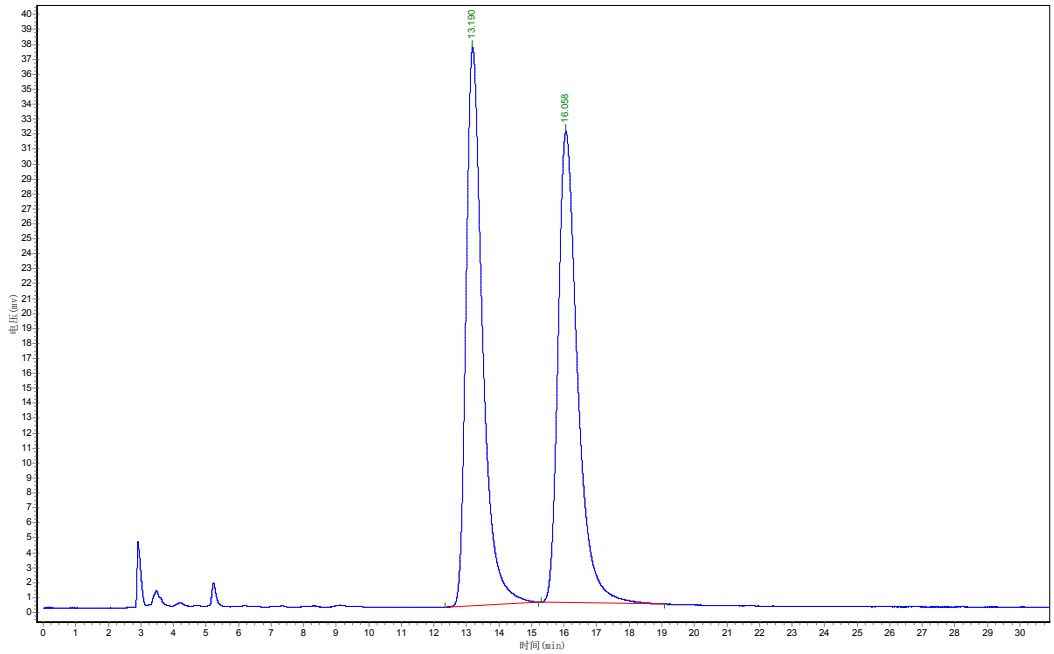
Peak	RetTime	Height	Area	Area%
1	31.165	4670.549	608210.875	49.6910
2	43.998	3418.674	615774.500	50.3090



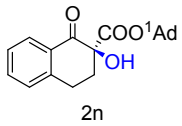
2m



Peak	RetTime	Height	Area	Area%
1	13.225	94542.797	3266573.000	76.9001
2	16.162	23935.619	981238.125	23.0999



Peak	RetTime	Height	Area	Area%
1	13.190	37338.070	1311683.625	50.1650
2	16.058	31516.746	1303054.000	49.8350



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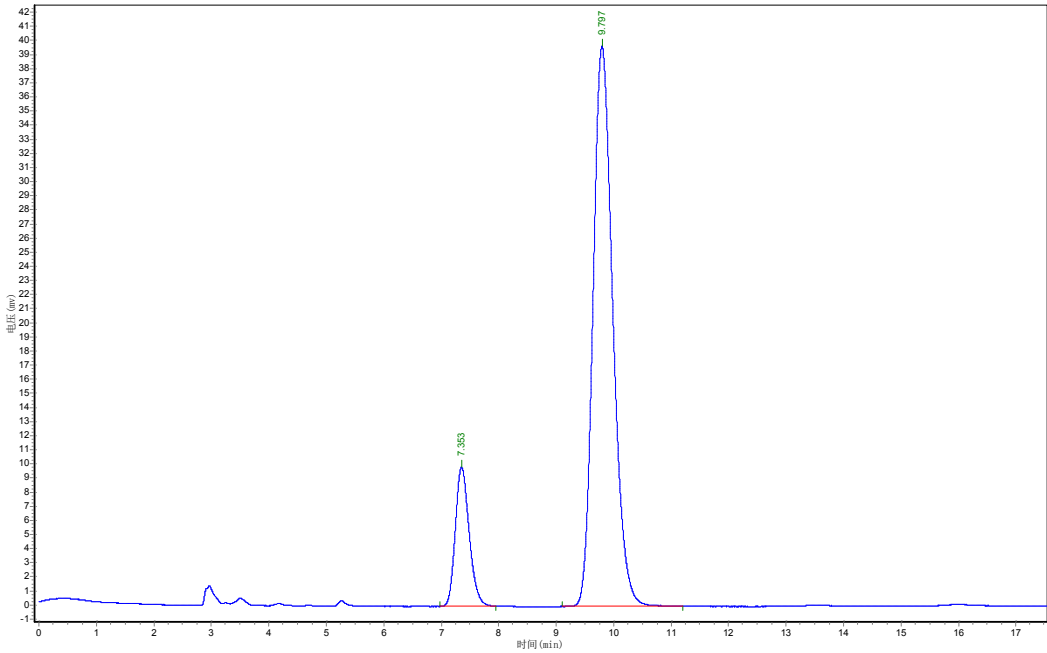
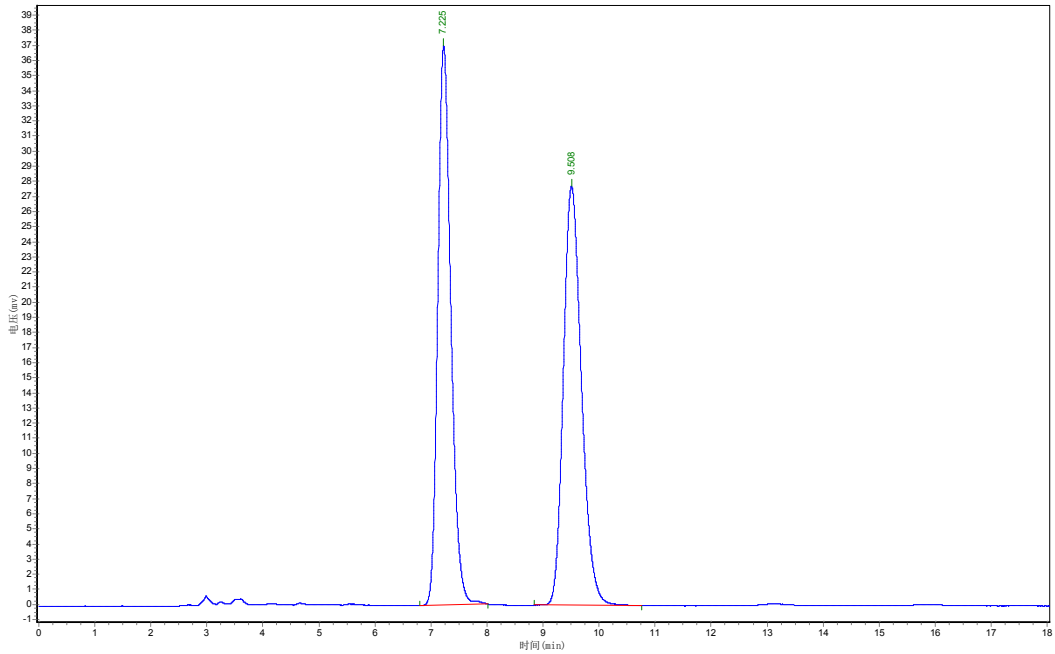
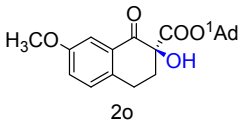


Peak	RetTime	Height	Area	Area%
1	7.353	9859.950	165367.906	14.9158
2	9.797	39685.785	943307.688	85.0842



Peak	RetTime	Height	Area	Area%
1	7.225	37017.117	600876.188	49.1471
2	9.508	27721.977	621731.813	50.8529



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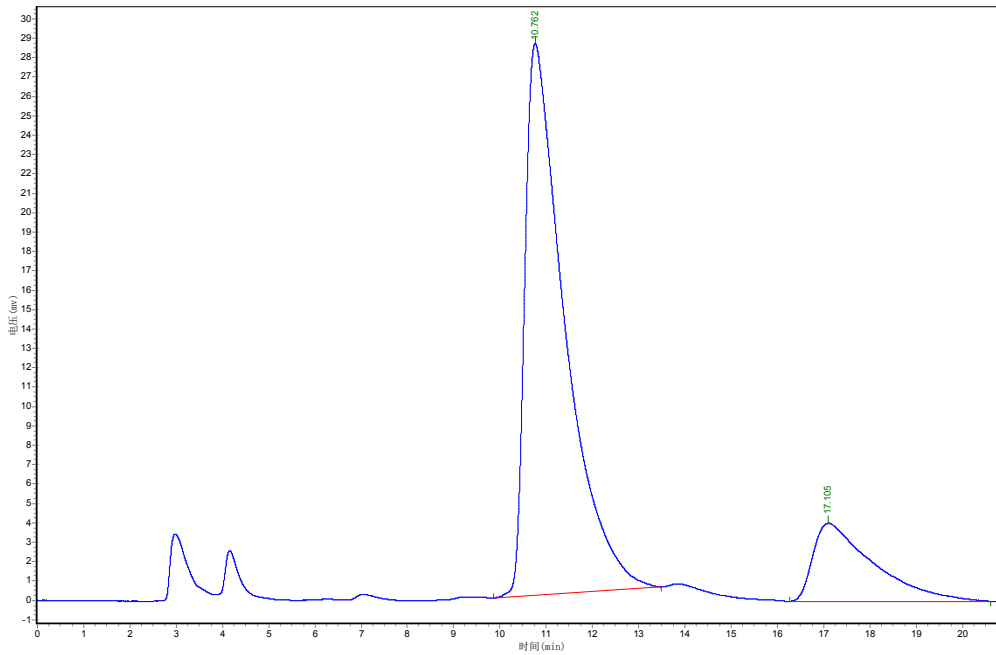
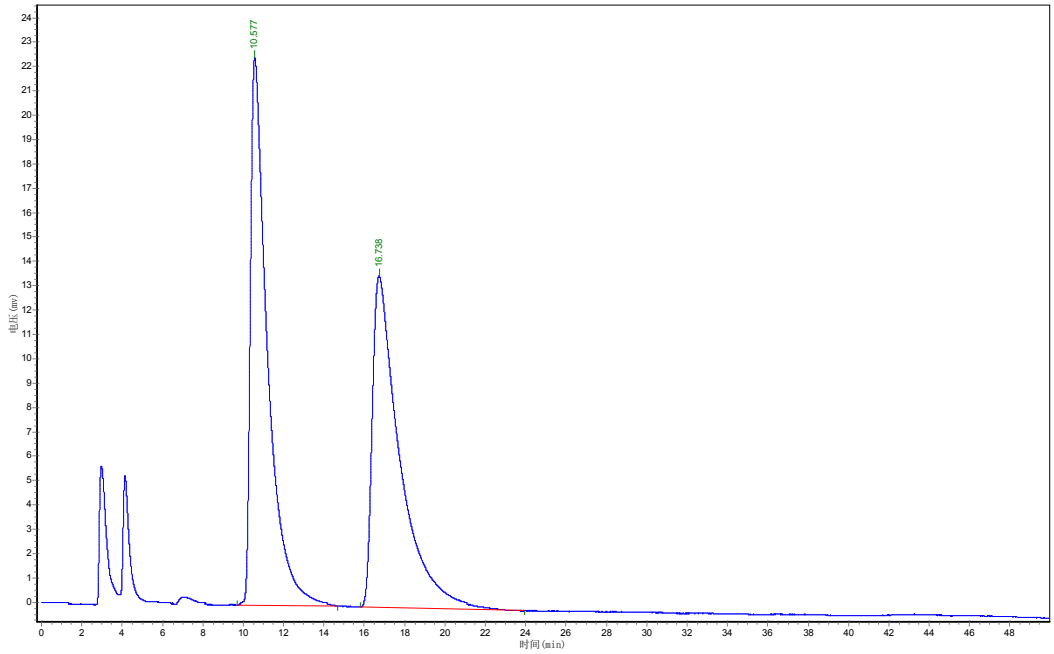
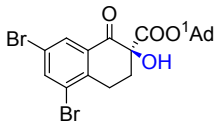


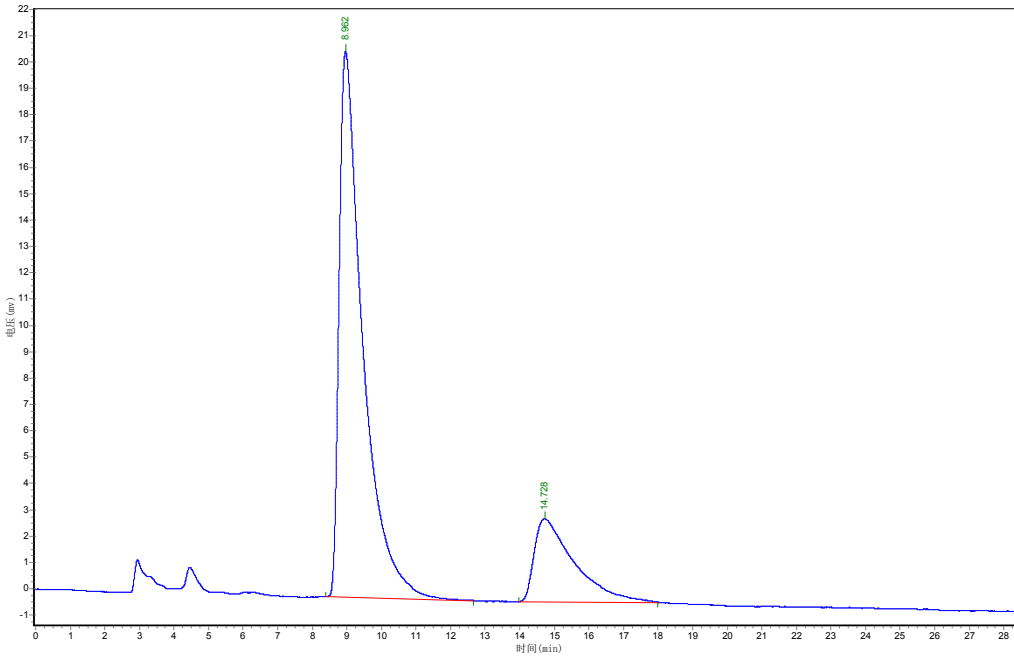
Peak	RetTime	Height	Area	Area%
1	10.762	28468.848	1705628.000	82.4618
2	17.105	4021.543	362757.781	17.5382



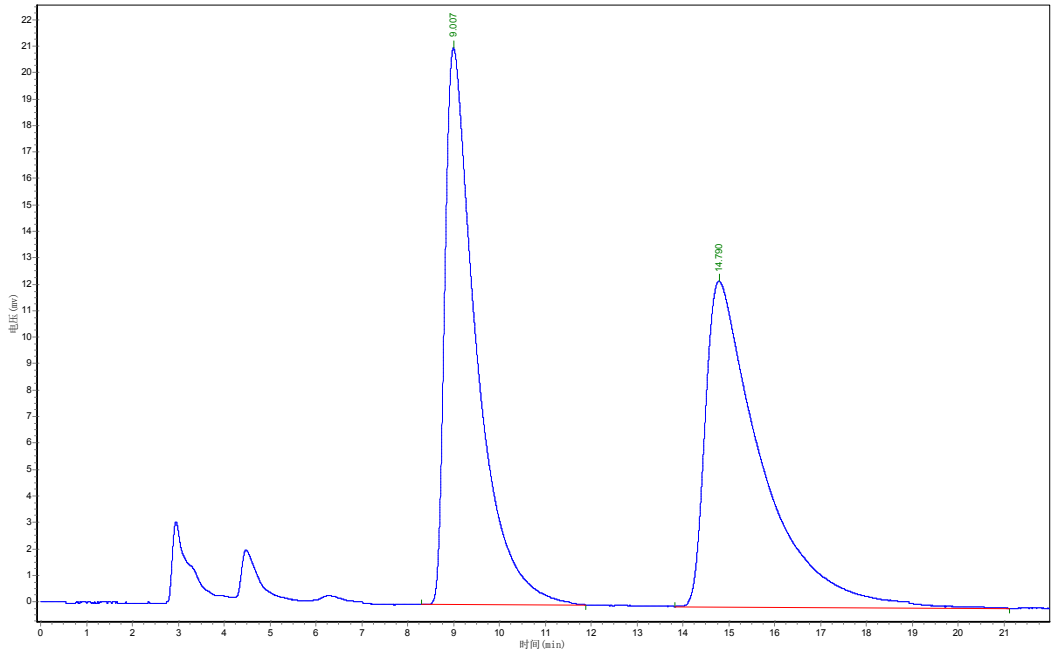
Peak	RetTime	Height	Area	Area%
1	10.577	22484.283	1322801.750	50.6488
2	16.738	13609.563	1288914.750	49.3512



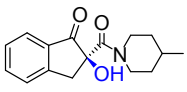
2p



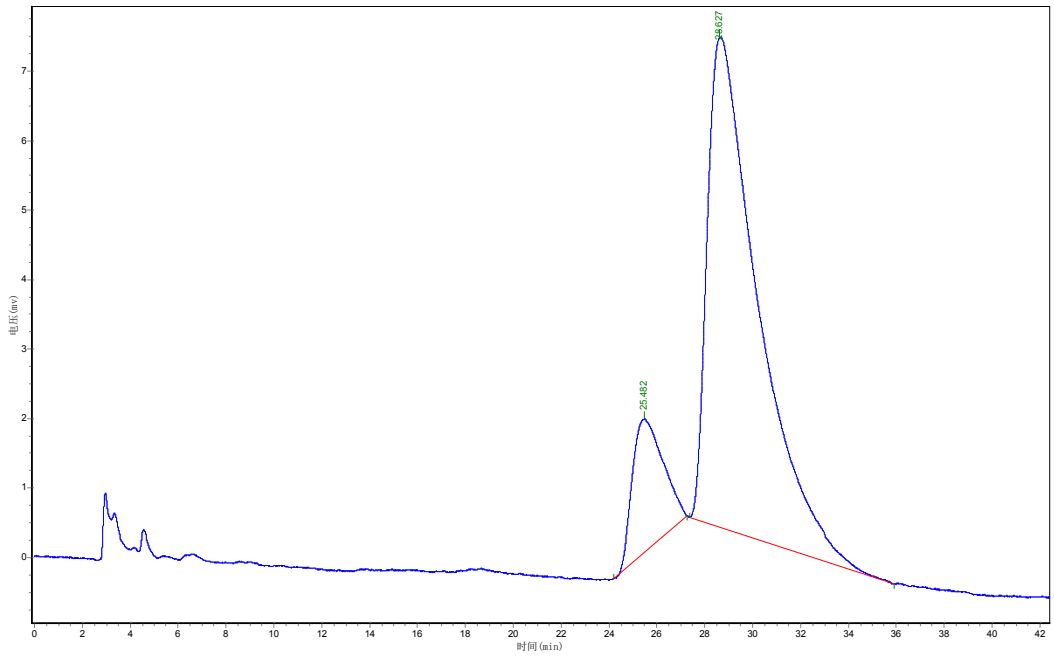
Peak	RetTime	Height	Area	Area%
1	8.962	20705.207	982955.125	79.6210
2	14.728	3152.496	251587.406	20.3790



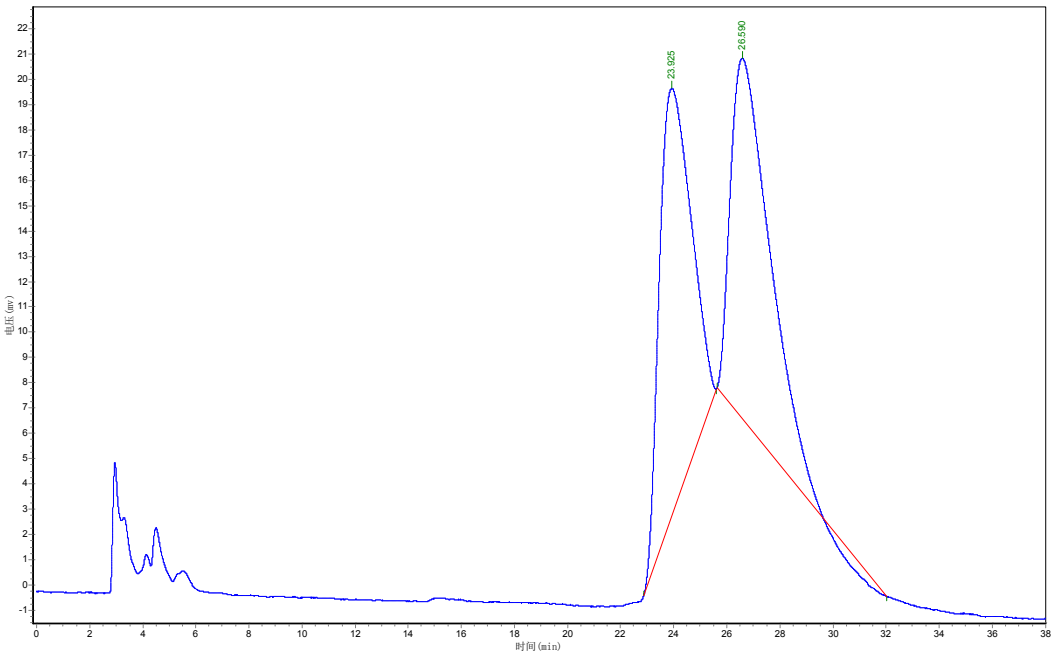
Peak	RetTime	Height	Area	Area%
1	9.007	21033.711	999876.000	49.1205
2	14.790	12290.932	1035682.188	50.8795



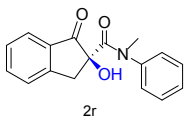
2q



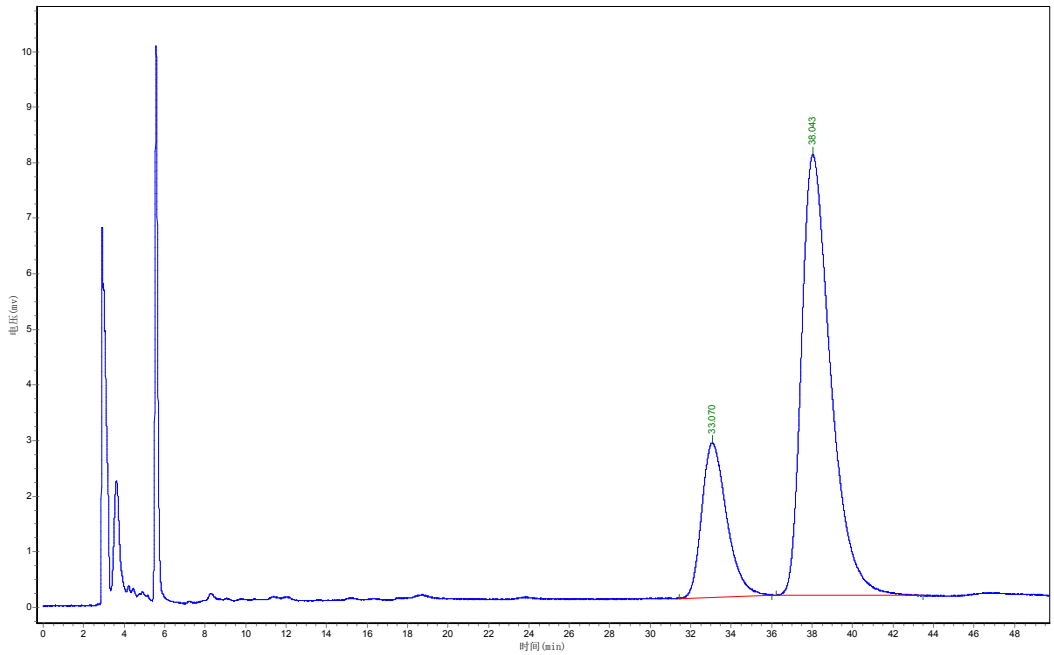
Peak	RetTime	Height	Area	Area%
1	25.482	1921.454	170151.906	14.1393
2	28.627	7054.237	1033243.938	85.8607



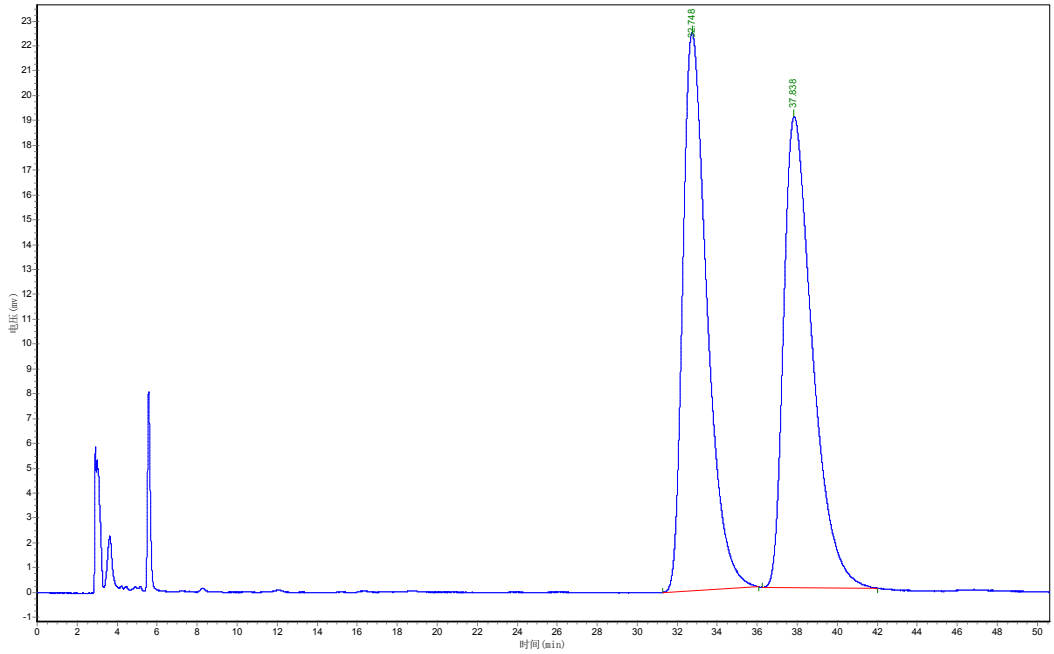
Peak	RetTime	Height	Area	Area%
1	23.925	16911.932	1397439.125	48.8369
2	26.590	14261.473	1464004.375	51.1631



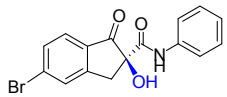
2r



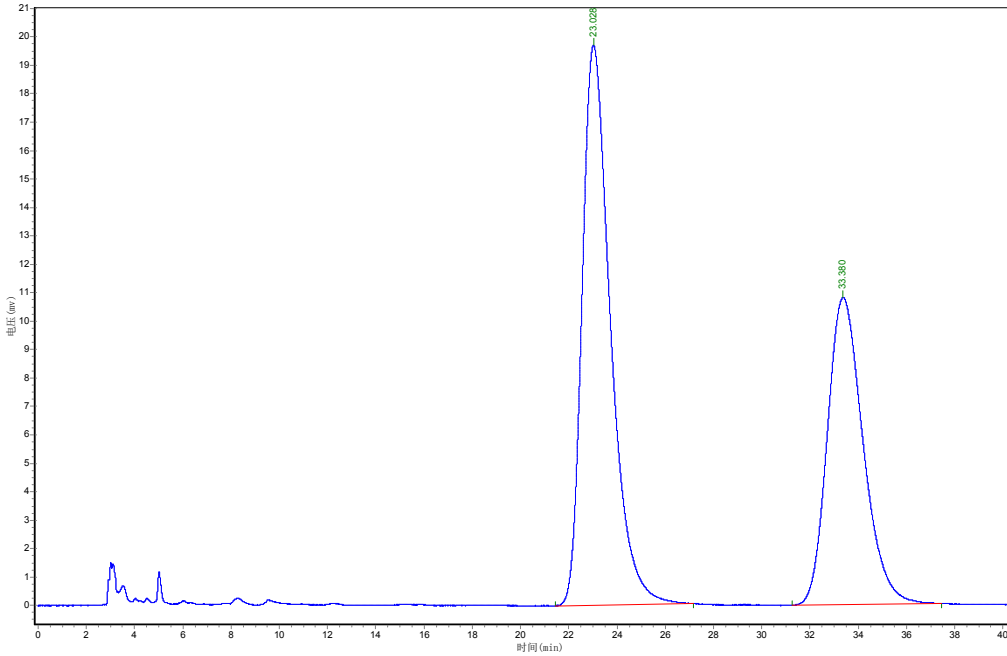
Peak	RetTime	Height	Area	Area%
1	33.070	2781.233	238009.188	23.1548
2	38.043	7931.999	789893.625	76.8452



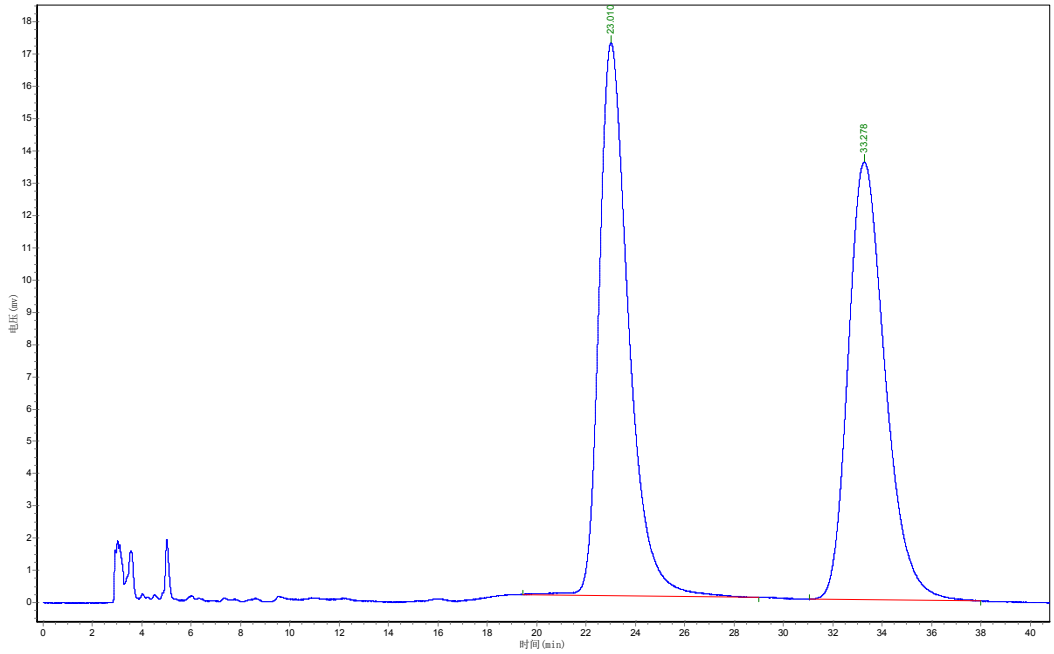
Peak	RetTime	Height	Area	Area%
1	32.748	22453.492	1888366.375	50.0054
2	37.838	18960.984	1887959.000	49.9946



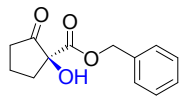
2s



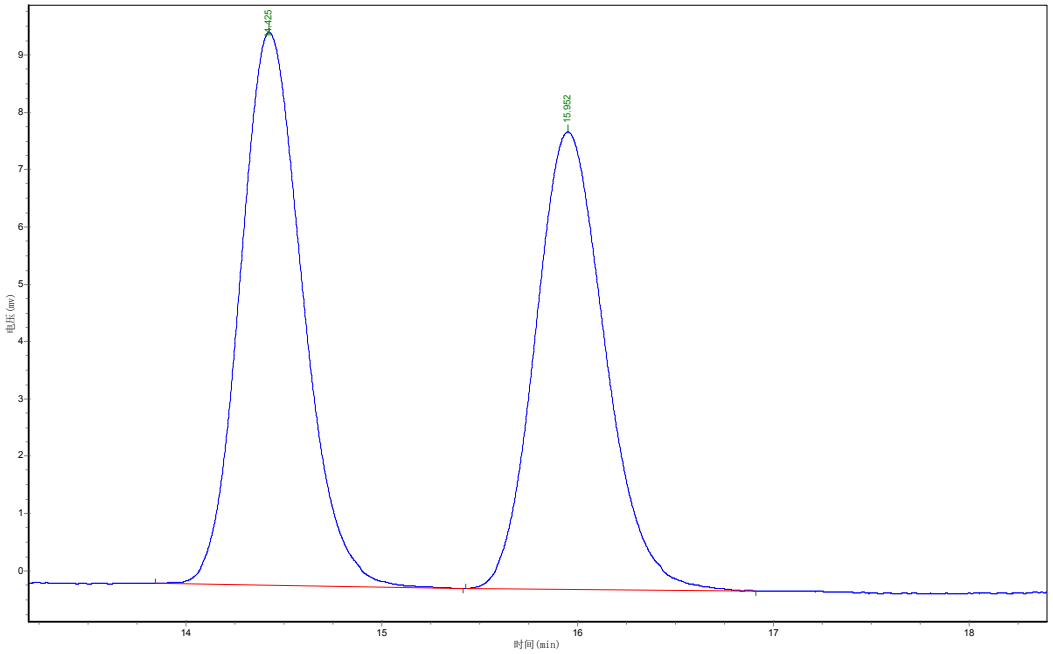
Peak	RetTime	Height	Area	Area%
1	23.028	19692.123	1603593.500	59.0838
2	33.380	10797.882	1110506.250	40.9162



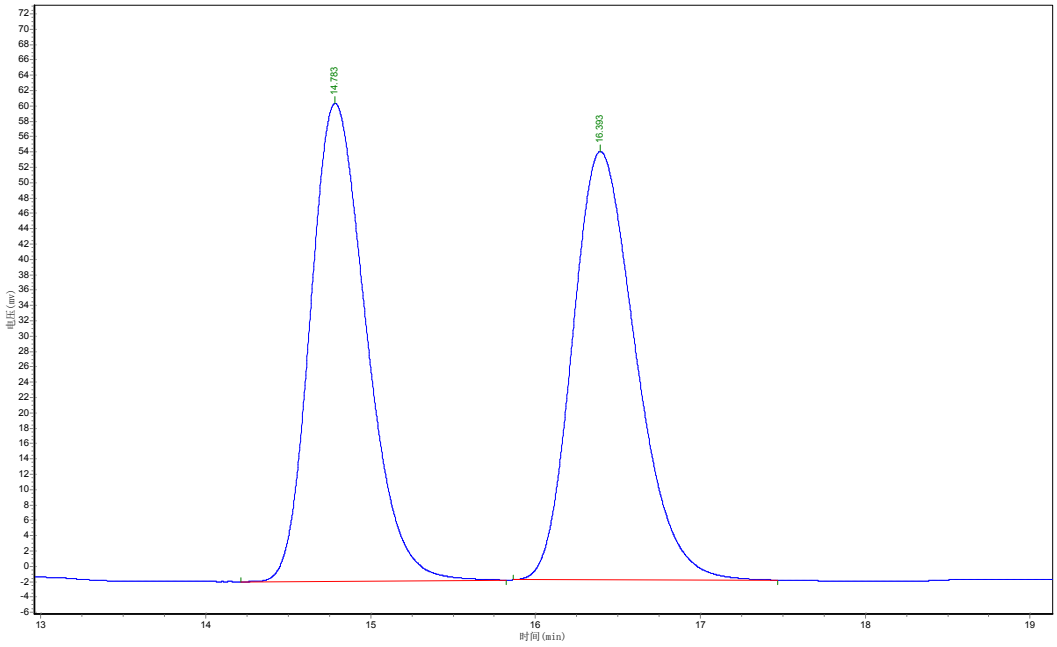
Peak	RetTime	Height	Area	Area%
1	23.010	17124.611	1416533.875	50.1111
2	33.278	13572.252	1410253.625	49.8889



2t



Peak	RetTime	Height	Area	Area%
1	14.425	9653.582	214550.156	52.0070
2	15.952	7987.054	197990.500	47.9930



Peak	RetTime	Height	Area	Area%
1	14.783	62261.758	1459611.875	49.5063
2	16.393	55818.898	1488721.125	50.4937

8. References

1. J. H. Lee, M. S. Yoo, J. H. Jung, S. S. Jew, H. G. Park, B. S. Jeong, *Tetrahedron,* **2007**, *63,* 7906-7915.
2. (a) Y. Wu, R. P. Singh, L. Deng, *J. Am. Chem. Soc.* **2011**, *133*, 12458-12461; (b) Y. Wu, L. Deng, *J. Am. Chem. Soc.* **2012**, *134*, 14334-14337.
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