Supplementary Information (SI) for Organic & Biomolecular Chemistry.
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Asymmetric [3+3] Annulation of 3-Hydroxyquinolin-2-ones via NHC Organocatalysis

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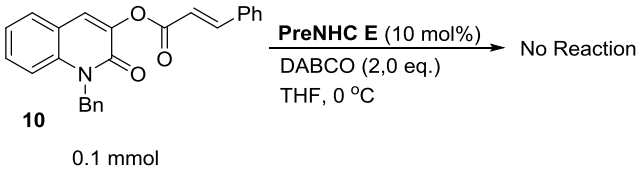
Content

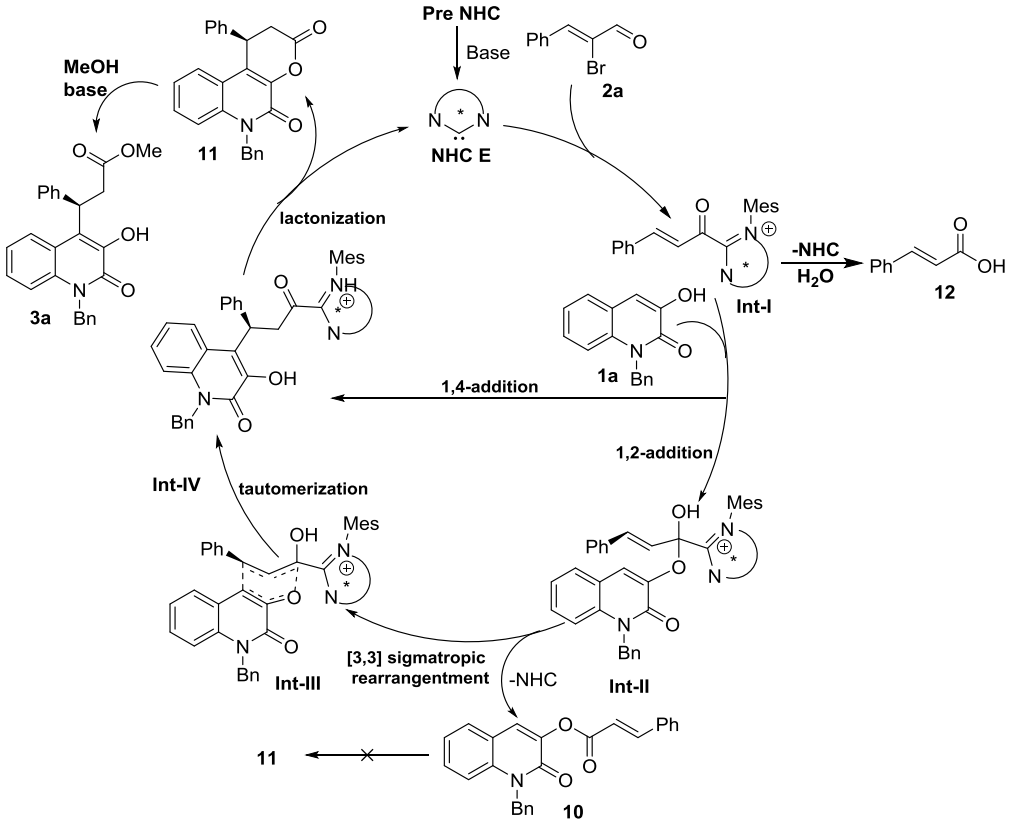
1 General Information

^{1}H NMR spectra were recorded at 400/600 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublet, br = broad), coupling constants (Hz), integration. ^{13}C{^{1}H} NMR data were collected at 100/150 MHz with complete proton decoupling. Enantiomeric excesses (*ee*) were determined by chiral HPLC analysis on Daicel Chiralcel IA, IB, IC, ID, IE and IF columns in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent CH_2Cl_2). The high-resolution mass spectra (HRMS) were recorded on Thermo Q-Exactive Focus (FTMS $^{+}$c ESI); or recorded on a Waters XEVO G2-S TOF Premier using ESI ionization and data were reported as (m/z). Melting points were measured using a SGWX-4A microscopy melting point meter and are uncorrected. X-ray crystallographic data were collected by a Bruker D8 Venture Photon II. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All NHC precatalyst and 2-bromoenals mentioned in the manuscript and supporting information were synthesized according to the literatures [1-6].

2 Control experiment and proposed reaction mechanism



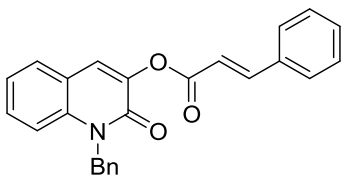
Under standard reaction conditions, the isolated esterification product **10** could not be converted into intermediate **11** and other compounds, as confirmed by TLC and NMR analysis. Therefore, this esterification product possibly does not participate in the [3+3] cyclization reaction.



Scheme S1. Proposed reaction mechanism.

3 characterization of the byproduct

1-benzyl-2-oxo-1,2-dihydroquinolin-3-yl cinnamate (10)

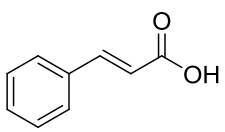


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 16.0 Hz, 1H), 7.67 (s, 1H), 7.63 – 7.52 (m, 3H), 7.47 – 7.38 (m, 4H), 7.26 (m, 7H) , 6.71 (d, J = 16.0 Hz, 1H), 5.60 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 158.0, 147.7, 140.6, 137.7, 136.1, 134.3, 130.9, 130.2, 129.1, 129.0, 128.5, 128.2, 128.2, 127.5, 126.9, 123.0, 119.8, 116.5, 116.5, 115.2, 46.8.

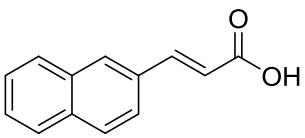
HRMS (ESI-TOF), m/z calcd for $C_{25}H_{20}NO_3^+$ ($[M + H]^+$) 382.1438, found 382.1443.

cinnamic acid (12)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 16.0 Hz, 1H), 7.57 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.46 – 7.38 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H).

3-(naphthalen-2-yl) acrylic acid (13)

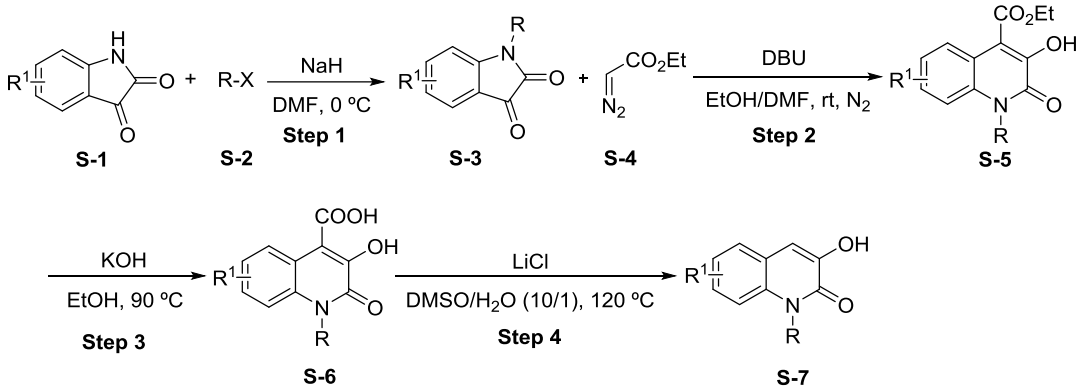


^{1}H NMR (400 MHz, DMSO-d_6) δ 12.44 (s, 1H), 8.18 (s, 1H), 7.94 (dd, *J* = 8.6, 3.6 Hz, 3H), 7.87 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.75 (d, *J* = 16.0 Hz, 1H), 7.56 (dt, *J* = 4.9, 3.3 Hz, 2H), 6.67 (d, *J* = 16.0 Hz, 1H).

4 Substrates synthesis and characterization

4.1 General procedure for synthesis 3-hydroxyquinolin

Substrates **1k**, **1n**, and **1o** were synthesized according to literature procedures [7-9], while other 3-hydroxyquinolin substrates were synthesized through the following general procedure.



Step 1:

A solution of **S-1** (1.0 equiv.) in DMF was treated with NaH (2.0 equiv.) at 0 ℃. After stirring for several minutes, **S-2** (1.2 equiv.) was added dropwise. The reaction was maintained at 0 ℃ for 4 h. The mixture was quenched with water, and the aqueous phase was extracted with EA three times. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was recrystallized from petroleum ether and ethyl acetate to afford the corresponding substrate **S-3**.

Step 2:

S-3 (1.0 equiv.) was placed in a round-bottom flask and backfilled with N_2 for three times. A mixture of EtOH and DMF (5:1) was added, followed by **S-4** (2.0 equiv.) and DBU (0.15 equiv.). The reaction was allowed to proceed at room temperature and stirred overnight. A 6 N hydrochloric acid aqueous solution was added to the reaction mixture, resulting in copious precipitation. The solid was collected by suction filtration to afford substrate **S-5**.

Step 3:

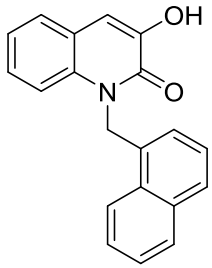
S-5 (1.0 equiv.) was dissolved in EtOH, followed by the addition of KOH (5.0 equiv.). The mixture was heated at 90 ℃ with stirring overnight. Upon completion of the reaction, 6 N hydrochloric acid aqueous solution was added to the reaction mixture, leading to the precipitation of a significant amount of solid. The solid was collected by suction filtration to afford substrate **S-6**.

Step 4:

S-6 (1.0 equiv.) was dissolved in a mixture of DMSO and water (5:1), followed by the addition of LiCl (3.0 equiv.). The reaction mixture was heated at 120 ℃ with stirring overnight. Upon completion of the reaction, water was added to the reaction mixture. The solid was collected by suction filtration to afford the product **S-7**.

4.2 Characterization of substrates

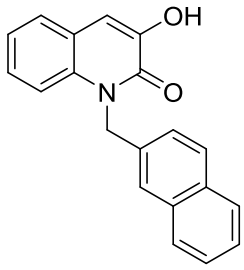
3-hydroxy-1-(naphthalen-1-ylmethyl) quinolin-2(1*H*)-one (1a)



Synthesized according procedure with 12 mmol 1-(bromomethyl) naphthalene as started material. 602 mg, yellow solid, 20% yield, m.p. = 296.2 – 297.3 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.74 (s, 1H), 8.35 – 8.00 (m, 1H), 7.99 – 7.58 (m, 4H), 7.42 – 7.00 (m, 5H), 6.57 (s, 1H), 6.04 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 158.6, 145.3, 134.1, 133.4, 131.2, 130.3, 128.8, 127.4, 126.9, 126.8, 126.6, 126.2, 125.5, 123.1, 122.7, 121.6, 121.5, 114.9, 112.8, 43.9.

HRMS (ESI-TOF), m/z calcd for $C_{20}H_{16}NO_2^+$ ([M + H]$^+$) 302.1176, found 302.1173.

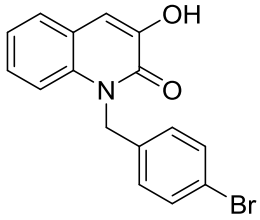
3-hydroxy-1-(naphthalen-2-ylmethyl) quinolin-2(1*H*)-one (1b)



Synthesized according procedure with 12 mmol 2-(bromomethyl) naphthalene as started material. 693 mg, pink solid, 23% yield, m.p. = 163.8– 164.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.75 – 7.70 (m, 1H), 7.60 (s, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.35 – 7.16 (m, 5H), 5.79 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 144.3, 134.1, 133.4, 133.2, 132.80, 128.9, 127.8, 127.7, 127., 127.3, 126.4, 126.0, 125.3, 124.6, 123.3, 121.9, 115.1, 112.1, 47.2.

HRMS (ESI-TOF), m/z calcd for $C_{20}H_{16}NO_2^+$ ([M + H]$^+$) 302.1176, found 302.1183.

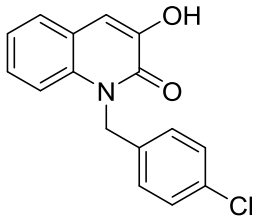
1-(4-bromobenzyl)-3-hydroxyquinolin-2(1*H*)-one (1c)



Synthesized according procedure with 12 mmol 1-bromo-4-(bromomethyl)benzene as started material. 594 mg, yellow solid, 18% yield, m.p. = 194.2 – 195.8 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.29 (m, 1H), 7.29 – 7.16 (m, 3H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.03 (s, 1H), 5.57 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 158.6, 145.2, 136.1, 133.7, 131.5, 128.8, 126.9, 126.8, 122.6, 121.4, 120.2, 114.7, 112.6 , 44.9.

HRMS (ESI-TOF), m/z calcd for $C_{16}H_{13}ClNO_2^+$ ([M + H]$^+$) 330.0125 (332.0104 for ^{81}Br), found 330.0124 (332.0105 for ^{81}Br).

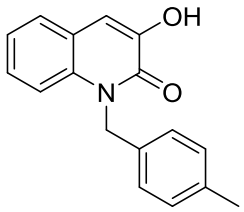
1-(4-chlorobenzyl)-3-hydroxyquinolin-2(1*H*)-one (1d)



Synthesized according procedure with 12 mmol 1-(bromomethyl)-4-chlorobenzene as started material. 600 mg, white solid, 21% yield, m.p. = 176.4 - 177.7 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.38 – 7.24 (m, 3H), 7.24 – 7.11 (m, 5H), 7.03 (s, 1H), 5.58 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 144.2, 134.3, 134.0, 133.5, 129.2, 128.2, 127.7, 127.5, 123.5, 121.9, 114.8, 112.2, 46.4.

HRMS (ESI-TOF), m/z calcd for $C_{16}H_{13}ClNO_2^+$ ($[M + H]^+$) 286.0630 (288.0600 for ^{37}Cl), found 286.0631 (288.0602 for ^{37}Cl).

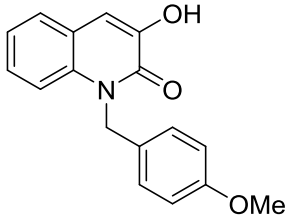
3-hydroxy-1-(4-methylbenzyl) quinolin-2(1*H*)-one (1e)



Synthesized according procedure with 12 mmol 1-(bromomethyl)-4-methylbenzene as started material. 610 mg, white solid, 23% yield, m.p. = 178.2 – 179.4 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.25 (m,2H), 7.24 – 7.15 (m, 2H), 7.15 - 7.00 (m, 5H), 5.59 (s, 2H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 144.3, 137.3, 134.2, 132.8, 129.6, 127.5, 127.3, 126.7, 123.3, 121.9, 115.1, 111.9, 46.8, 21.2.

HRMS (ESI-TOF), m/z calcd for $C_{17}H_{16}NO_2^+$ ($[M + H]^+$) 266.1176, found 266.1177.

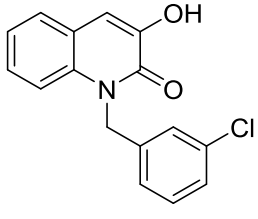
3-hydroxy-1-(4-methoxybenzyl) quinolin-2(1*H*)-one (1f)



Synthesized according procedure with 12 mmol 1-(bromomethyl)-4-methoxybenzene as started material. 703 mg, white solid, 25% yield, m.p. = 156.9– 160.8 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 3.9 Hz, 2H), 7.19 (dt, *J* = 18.7, 4.3 Hz, 4H), 7.08 (s, 1H), 6.83 (d, *J* = 8.2 Hz, 2H), 5.56 (s, 2H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 159.0, 144.3, 134.1, 128.1, 127.8, 127.5, 127.3, 123.3, 121.9, 115.1, 114.3, 111.9, 55.3, 46.5.

HRMS (ESI-TOF), m/z calcd for $C_{17}H_{16}NO_2^+$ ($[M + H]^+$) 282.1125, found 282.1125.

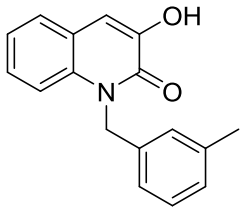
1-(3-chlorobenzyl)-3-hydroxyquinolin-2(1*H*)-one (1g)



Synthesized according procedure with 12 mmol 1-(bromomethyl)-3-chlorobenzene as started material. 743 mg, yellow solid, 26% yield, m.p. = 154.8 – 155.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.2 Hz, 1H), 7.39 – 7.29 (m, 1H), 7.25 –7.19 (m, 6H), 7.10 –7.06 (m, 1H), 7.02 (s, 1H), 5.59 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 144.2, 137.9, 135.0, 134.0, 130.3, 128.0, 127.7, 127.5, 126.8, 124.8, 123.5, 121.9, 114.8, 112.3, 46.5.

HRMS (ESI-TOF), m/z calcd for $C_{16}H_{13}ClNO_2^+$ ($[M + H]^+$) 286.0630 (288.0600 for ^{37}Cl), found 286.0628 (288.0605 for ^{37}Cl).

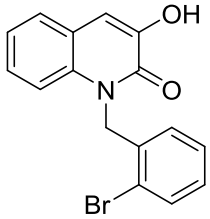
3-hydroxy-1-(3-methylbenzyl) quinolin-2(1*H*)-one (1h)



Synthesized according procedure with 12 mmol 1-(bromomethyl)-3-methylbenzene as started material. 637 mg, pink solid, 24% yield, m.p. = 114.8 – 115.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.25 – 7.16 (m, 3H), 7.06 (d, *J* = 8.0 Hz,2H), 7.00 (d, *J* = 8.0 Hz, 2fH), 5.59 (s, 2H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 144.3, 138.7, 135.7, 134.2, 128.8, 128.4, 127.5, 127.3, 127.2, 123.7, 123.3, 121.9, 115.1, 112.0, 47.1, 21.5.

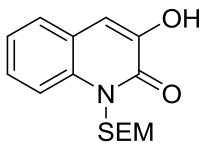
HRMS (ESI-TOF), m/z calcd for $C_{17}H_{16}NO_2^+$ ($[M + H]^+$) 266.1176, found 266.1176.

1-(2-bromobenzyl)-3-hydroxyquinolin-2(1*H*)-one (1i)



Synthesized according **procedure A** with 12 mmol 1-bromo-2-(bromomethyl)benzene as started material. 925 mg, white solid, 28% yield, m.p. = 227.8 – 228.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 1H), 7.54 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.36 – 7.20 (m, 3H), 7.13 (dd, *J* = 5.9, 3.5 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.64 (dd, *J* = 5.7, 3.7 Hz, 1H), 5.66 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 144.1, 134.2, 133.9, 133.1, 129.1, 128.0, 127.7, 127.7, 126.9, 123.6, 122.6, 121.8, 115.1, 112.2, 47.5. **HRMS** (ESI-TOF), m/z calcd for $C_{16}H_{13}BrNO_2^+$ ($[M + H]^+$) 330.0125 (332.0104 for ^{81}Br), found 330.0125 (332.0106 for ^{81}Br).

3-hydroxy-1-((2-(trimethylsilyl) ethoxy) methyl) quinolin-2(1*H*)-one (1j)

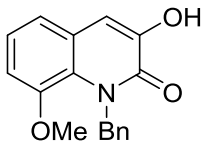


Synthesized according procedure with 12 mmol 2-(Trimethylsilyl) ethoxymethyl chloride as started material. 554 mg, red solid, 19% yield, m.p. = 88.7 – 89.9 ℃. **^{1}H NMR (**400 MHz, $CDCl_3$**)** δ 7.59 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.12 (s, 1H), 6.98 (s, 1H), 5.84 (s, 2H), 3.68 (t, *J* = 8.1 Hz, 2H), 0.94 (t, *J* = 8.1 Hz, 2H), -0.04 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$**)** δ 160.1, 143.9, 133.9, 127.4, 127.3, 123.7, 121.6, 115.6, 112.5, 72.5, 66.8, 18.1, -1.3.

HRMS (ESI-TOF), m/z calcd for $C_{15}H_{23}NO_3Si^+$ ($[M + H]^+$) 292.1364, found 292.1364.

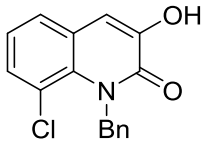
1-benzyl-3-hydroxy-8-methoxyquinolin-2(1*H*)-one (1l)



Synthesized according procedure with 12 mmol (bromomethyl)benzene as started material. 760 mg, white solid, 27% yield, m.p. = 213.9 – 214.7 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.6 Hz, 1H), 7.36 – 7.19 (m, 6H), 7.14 (s, 1H), 6.91 – 6.78 (m, 2H), 6.75 (d, *J* = 2.3 Hz, 1H), 5.59 (s, 2H), 3.73 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 159.0, 158.4, 143.1, 136.8, 135.2, 128.7, 128.1, 127.2, 126.7, 115.0, 112.9, 110.0, 99.9, 55.3, 45.4.

HRMS (ESI-TOF), m/z calcd for $C_{17}H_{16}NO_3^+$ ($[M + H]^+$) 282.1125, found 282.1121.

1-benzyl-8-chloro-3-hydroxyquinolin-2(1*H*)-one (1m)

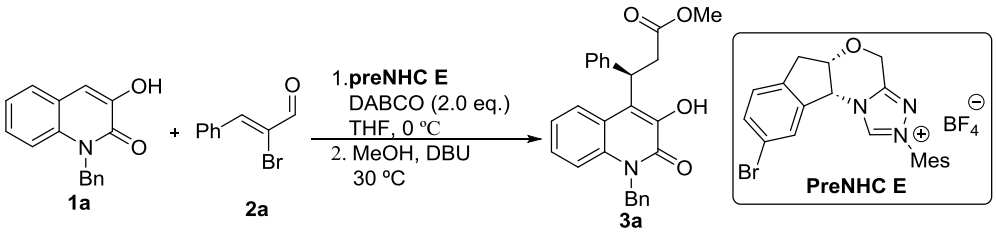


Synthesized according procedure with 12 mmol (bromomethyl) benzene as started material. 686 mg, yellow solid, 24% yield, m.p. = 142.7 – 143.6 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (m, 2H), 7.26 (m, 3H), 7.18 – 6.95 (m, 6H), 6.08 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.3, 144.2, 137.7, 132.0, 131.5, 128.5, 127.2, 126.9, 125.9, 125.2, 124.1, 120.4, 112.2, 50.5.

HRMS (ESI-TOF), m/z calcd for $C_{16}H_{13}ClNO_2^+$ ($[M + H]^+$) 286.0630 (288.0600 for ^{37}Cl), found 286.0633 (288.0608 for ^{37}Cl).

5 General procedure for synthesis of products 3a and 4a-4v

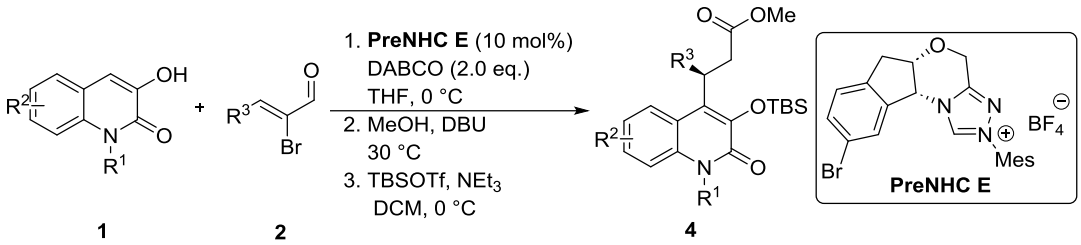
5.1 General procedure for synthesis of 3a



To a dried reaction tube equipped with a magnetic stir bar were added 10 mol% of **PreNHC E** (5.0 mg), **1a** (0.1 mmol, 1.0 equiv.), and DABCO (0.2 mmol, 2.0 equiv.), followed by the addition of 1 mL of solvent. The mixture was cooled to 0 ℃ and stirred for several minutes, after which **2a** (0.2 mmol, 2.0 equiv.) was added slowly. The reaction was stirred at 0 ℃ for 24 hours, then solvent was evaporated and residue purified by column chromatography on silica gel (PE/EA = 2:1) to afford the ring-closed product.

Subsequently, the cyclization product was transferred to a reaction tube equipped with a stir bar. DBU (0.1 mmol, 1.0 equiv.) and methanol (1.0 mL) were added to the reaction mixture. The reaction was stirred at 30 ℃ until complete conversion of the cyclization substrate (monitored by TLC). After concentration under reduced pressure, the crude product was purified by flash column chromatography on silica gel (PE/EA = 10:1) to afford **3a** as a red solid.

5.2 General procedure for synthesis of 4a-4v



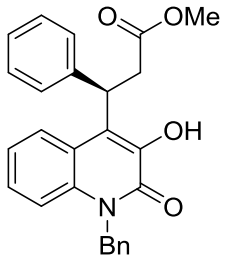
To a dried reaction tube equipped with a magnetic stir bar were added 10 mol% of **preNHC E** (5.0 mg), substrate **1** (0.1 mmol, 1.0 equiv.), and DABCO (0.2 mmol, 2.0 equiv.), followed by the addition of 1 mL of solvent. The mixture was cooled to 0 ℃ and stirred for several minutes, after which substrate **2** (0.2 mmol, 2.0 equiv.) was added slowly. The reaction was stirred at 0 ℃ for 24 hours, then purified by column chromatography on silica gel (PE/EA = 2:1) to afford the ring-closed product.

Subsequently, the cyclization product was transferred to a reaction tube equipped with a stir bar. DBU (0.1 mmol, 1.0 equiv.) and methanol (1.0 mL) were added to the reaction mixture. The reaction was stirred at 30 ℃ until complete conversion of the cyclization substrate (monitored by TLC).

After concentration under reduced pressure, TBSOTf (0.2 mmol, 2.0 equiv.) was added to the residue followed by DCM (1.0 mL). The mixture was cooled to 0 ℃ and allowed to stir for several minutes before dropwise addition of Et_3N (0.3 mmol, 3.0 equiv.) at this temperature. The reaction was maintained at 0 ℃ for 2 hours, then purified by column chromatography on silica gel (PE/EA = 30:1) to afford product **4**.

5.3 Characterization Products

Methyl (R)-3-(1-benzyl-3-hydroxy-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (3a)

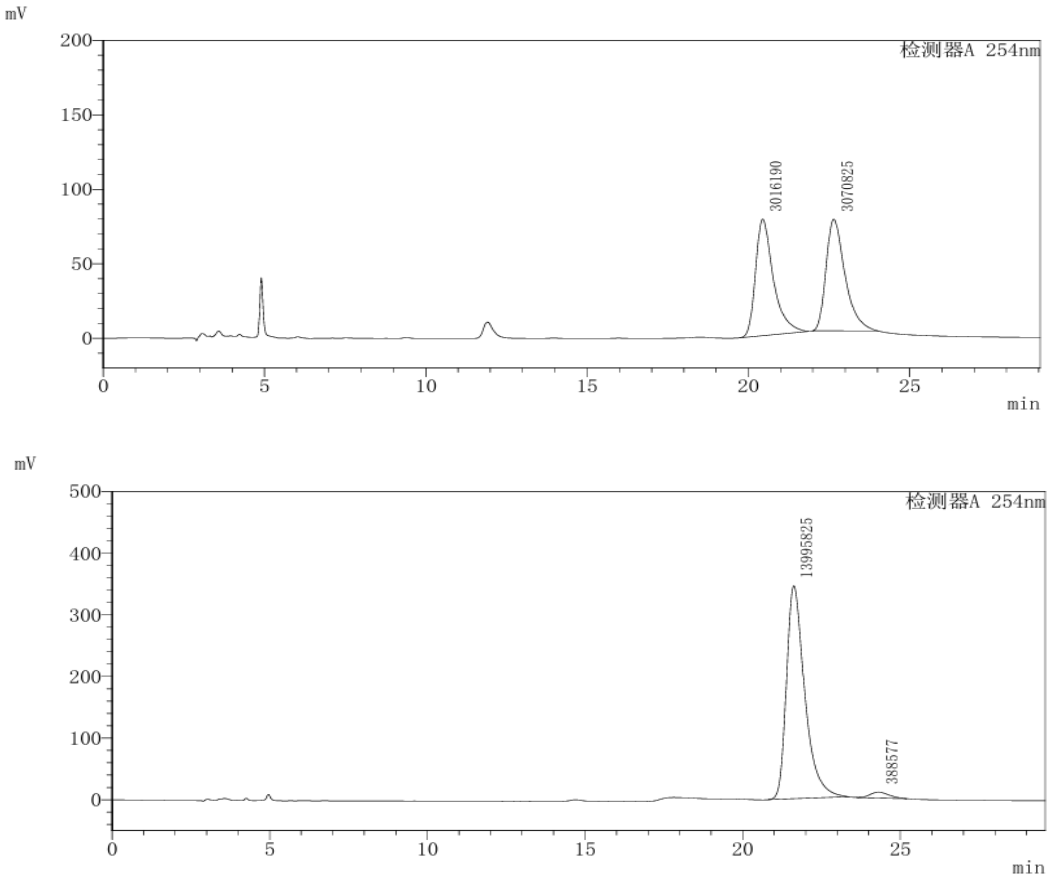


Compound **3a**: Prepared in 0.1 mmol scale at 0 ℃ for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 7:1. red solid, 63% yield (26.0 mg), 94% *ee*, m.p. = 112.5 – 113.4 ℃. HPLC (chiral IF column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 21.62 min, *tr* (minor) = 24.30 min. $[\alpha]^{25}_D$ = -154.0 (c = 0.09, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.43 (m, 3H), 7.36 – 7.17 (m, 11H), 5.62 (d, *J* = 4.3 Hz, 2H), 5.21 (t, *J* = 7.6 Hz, 1H), 3.66 – 3.54 (m, 4H), 3.42 (dd, *J* = 16.6, 7.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 159.4, 141.9, 141.7, 135.7, 133.9, 129.0, 128.7, 127.8, 127.6, 127.3, 126.9, 126.6, 124.5, 123.6, 123.5, 121.6, 115.6, 51.9, 47.4, 39.3, 38.1.

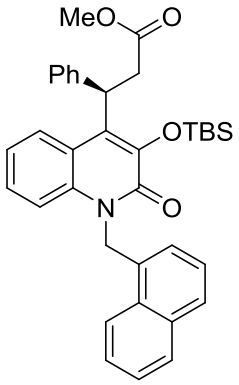
HRMS (ESI-TOF), m/z calcd for $C_{26}H_{24}NO_4^+$ ([M + H]$^+$) 414.1700, found 414.1704.



Racemic			
	Retention Time	Area	%Area
1	20.445	3016190	49.551
2	22.647	3070825	50.449

Enantioenriched			
	Retention Time	Area	%Area
1	21.622	13995825	97.299
2	24.304	388577	2.701

Methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(naphthalen-1-ylmethyl)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4a)



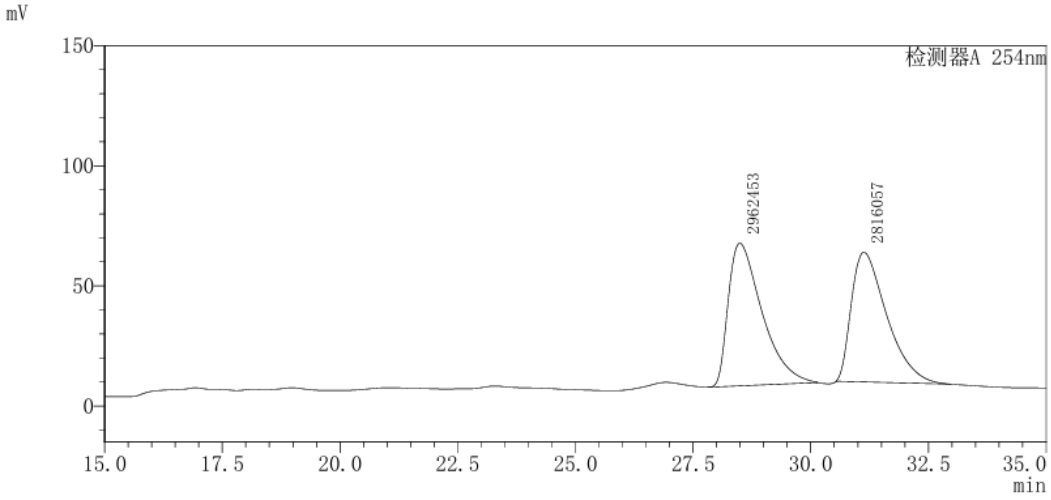
Compound **4a**: Prepared in 0.1 mmol scale at 0 °C for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. yellow solid, 55% yield (31.7 mg), 91，% *ee*, m.p. = 126.3 – 127.9 ℃. HPLC (chiral IB column), hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min, λ = 254 nm, *tr* (minor) = 28.34 min, tr (major) = 30.38 min. $[\alpha]^{25}_D$ = -167.0 (c = 0.09, CH_2Cl_2)

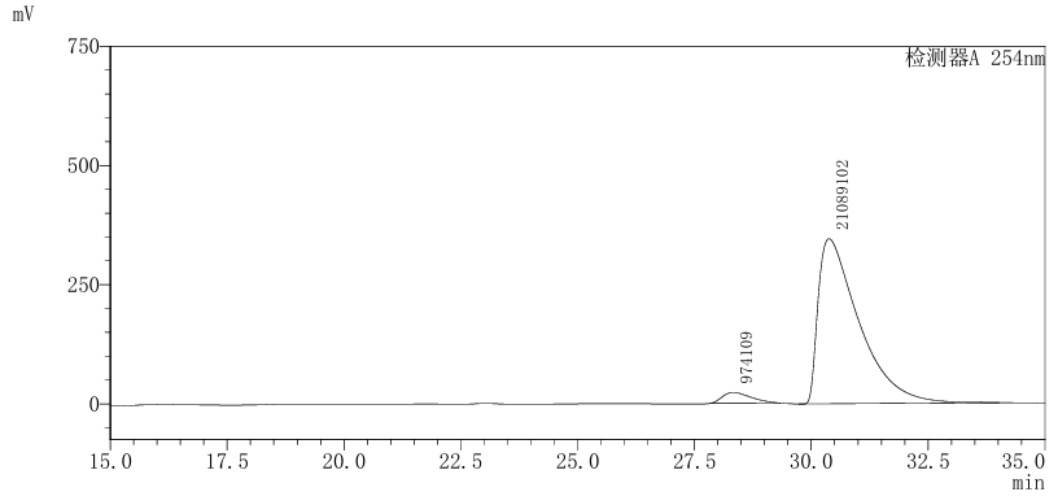
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.75 - 7.42 (m, 2H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.18 (m, 6H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.95 (dd, *J* = 17.1, 8.4 Hz, 2H), 6.75 (d, *J* = 7.2 Hz, 1H), 6.20 – 5.95 (m, 2H), 5.86 (t, *J*

= 7.4 Hz, 1H), 3.71 (s, 3H), 3.59 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.11 (dd, *J* = 15.8, 5.9 Hz, 1H), 0.97 (s, 9H), 0.43 (s, 3H), 0.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 159.3, 142.9, 141.5, 135.5, 133.9, 131.1, 130.7, 130.5, 129.2, 128.9, 127.8, 127.2, 126.8, 126.5, 126.5, 126.1, 125.9, 125.7, 122.5, 122.3, 122.3, 120.4, 115.6, 52.1, 45.0, 37.7, 37.0, 19.3, -2.7, -3.2.

HRMS (ESI-TOF), m/z calcd for $C_{36}H_{40}NO_4Si^+$ ($[M + H]^+$) 578.2722, found 578.2724.

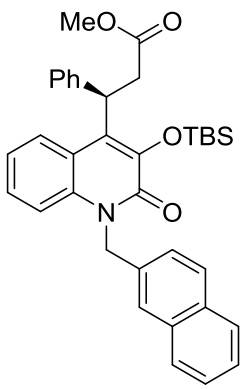




Racemic			
	Retention Time	Area	%Area
1	28.495	2978235	50.343
2	31.128	2937660	49.657

Enantioenriched			
	Retention Time	Area	%Area
1	28.335	1007895	4.549
2	30.381	21146895	95.451

Methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(naphthalen-2-ylmethyl)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4b)

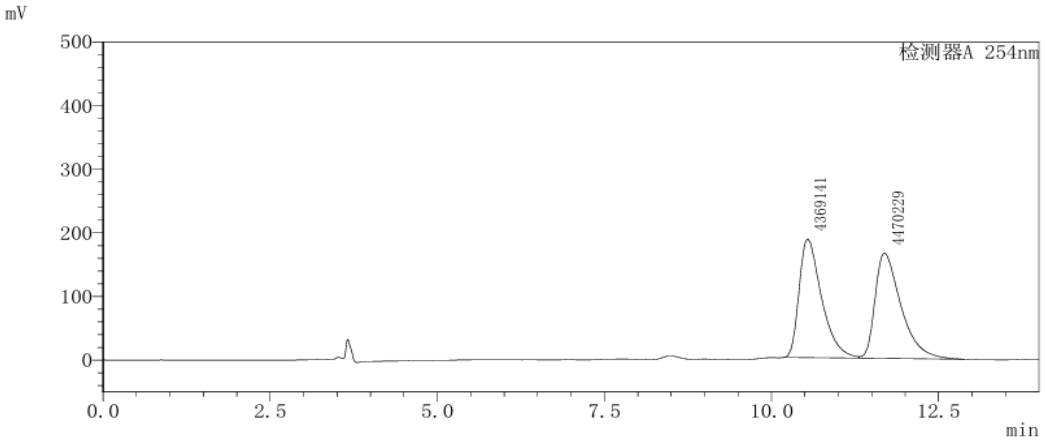


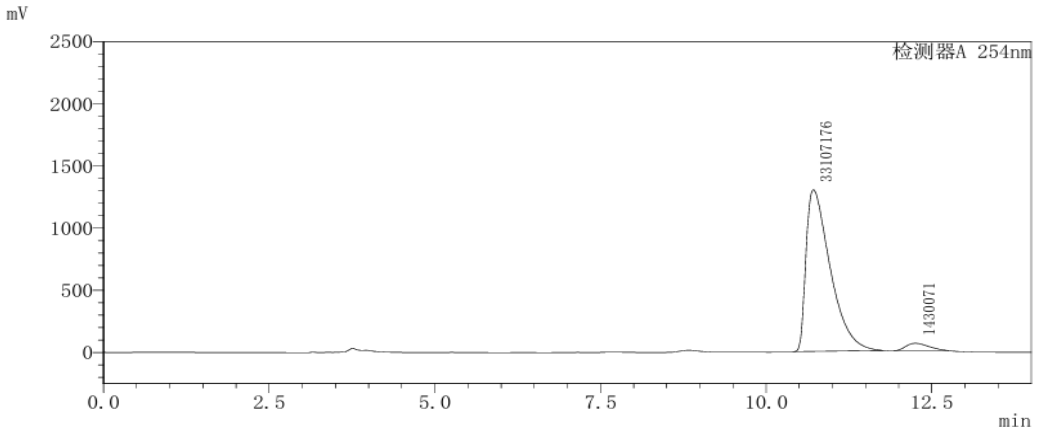
Compound **4b**: Prepared in 0.1 mmol scale at 0 ℃ for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. yellow solid, 59% yield (34.1 mg), 92% *ee*, m.p. = 110.8 – 111.4 ℃. HPLC (chiral IB column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 10.72 min, *tr* (minor) = 12.25 min. $[\alpha]^{25}_{D}$ = -152.8 (c = 0.09, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.61 (m, 3H),7.62 (s, 1H), 7.39 - 7.33 (m, 2H), 7.33 - 7.30 (m, 2H), 7.30 - 7.26 (m, 4H), 7.28 – 7.24 (m, 1H), 7.23 - 7.20 (m, 1H), 7.19 – 7.10 (m, 1H), 7.17 – 7.09 (m, 1H),5.87-5.84 (m, 1H), 5.71 (s, 2H), 3.70 (s, 3H), 3.57 (dd, *J* = 15.9, 8.9 Hz, 1H), 3.08 (dd, *J* = 15.9, 5.8 Hz, 1H), 1.00 (s, 9H), 0.49 (s, 3H), 0.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 159.4, 142.9, 141.5, 135.4, 133.9, 133.5, 132.8, 131.0, 128.9, 128.8, 127.8, 127.2, 126.8, 126.4, 126.4, 126.0, 125.3, 124.8, 122.2, 120.4, 115.3, 52.1, 47.1, 37.7, 37.0, 26.2, 19.3, -2.6, -3.1.

HRMS (ESI-TOF), m/z calcd for $C_{36}H_{40}NO_4Si^+$ ($[M + H]^+$) 578.2722, found 578.2733.

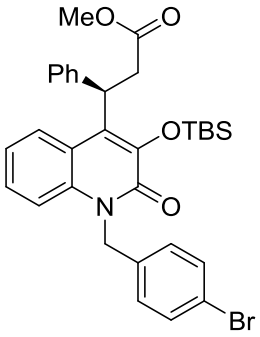




Racemic			
	Retention Time	Area	%Area
1	10.542	4369141	49.441
2	11.691	4470229	50.559

Enantioenriched			
	Retention Time	Area	%Area
1	10.715	33107176	95.859
2	12.252	1430071	4.141

methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydro quinolin-4-yl)-3-phenylpropanoate (4c)

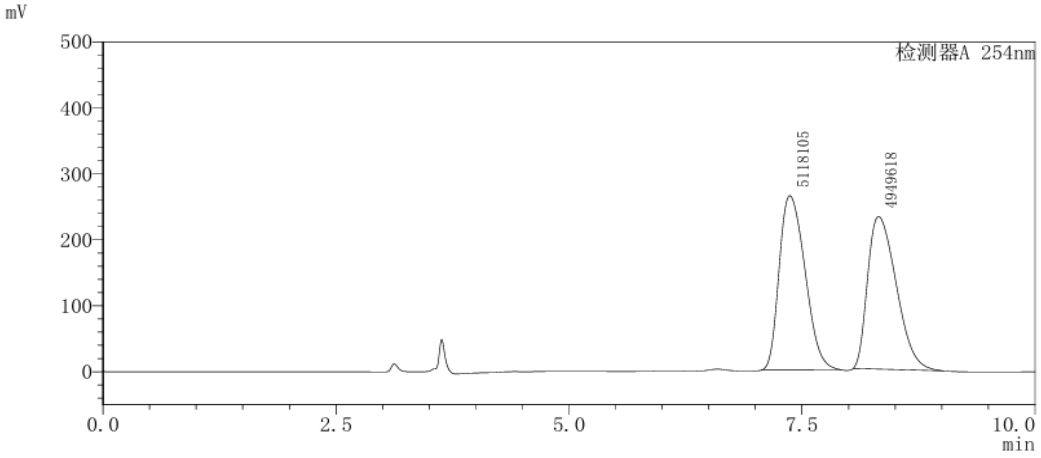


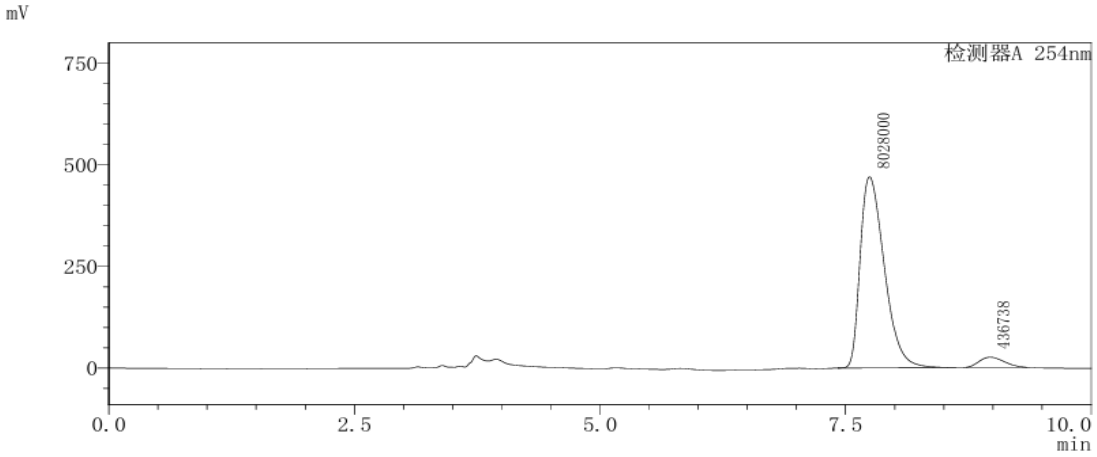
Compound **4c**: Prepared in 0.1 mmol scale at 0 °C for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. yellow solid, 77% yield (46.7 mg), 90% *ee*, m.p. = 119.5 – 120.4 ℃. HPLC (chiral IB column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 7.75 min, *tr* (minor) = 8.97 min. $[\alpha]^{25}_{D}$ = -124.0 (c = 0.09, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.28 (dd, *J* = 9.6, 6.4 Hz, 4H), 7.21-7.09 (m, 5H), (m, 5H), 6.94 (t, *J* = 7.6 Hz, 1H), 5.81 (t, *J* = 7.3 Hz, 1H), 5.62 – 5.41 (m, 2H), 3.68 (s, 3H), 3.54 (dd, *J* = 15.9, 8.8 Hz, 1H), 3.04 (dd, *J* = 15.8, 5.8 Hz, 1H), 0.97 (s, 9H), 0.44 (s, 3H), 0.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 159.2, 142.8, 141.4, 135.4, 135.1, 132.1, 131.1, 128.8, 128.4, 127.2, 126.8, 126.4, 126.1, 122.4, 121.3, 120.4, 115.0, 52.1, 46.4, 37.6, 36.9, 26.2, 19.3, -2.6, -3.1.

HRMS (ESI-TOF), m/z calcd for $C_{32}H_{37}BrNO_4Si^+$ ($[M + H]^+$) 606.1670 (608.1650 for ^{81}Br), found 606.1685 (608.1666 for ^{81}Br).

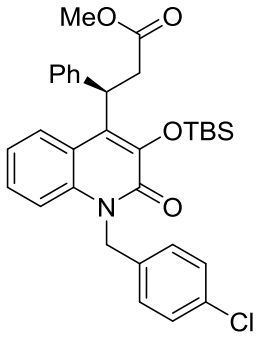




Racemic			
	Retention Time	Area	%Area
1	7.370	5118105	50.837
2	7.370	4949618	49.163

Enantioenriched			
	Retention Time	Area	%Area
1	7.745	8028000	94.841
2	8.971	436738	5.159

methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(4-chlorobenzyl)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4d)

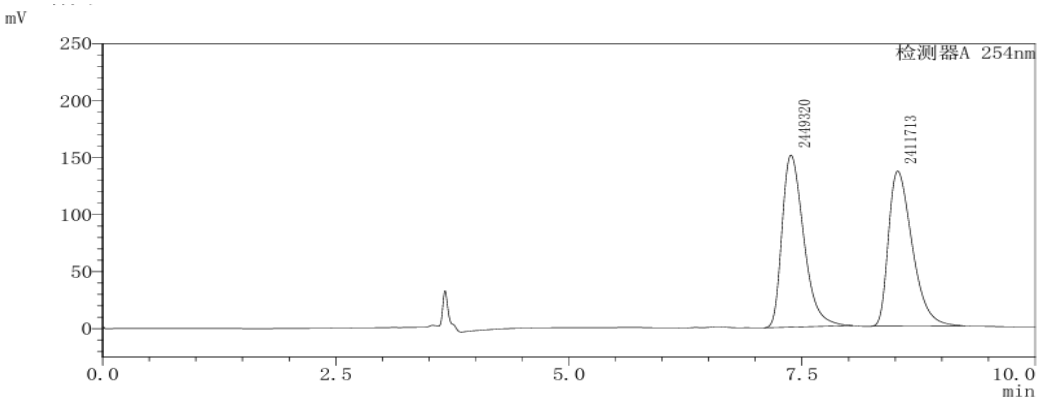


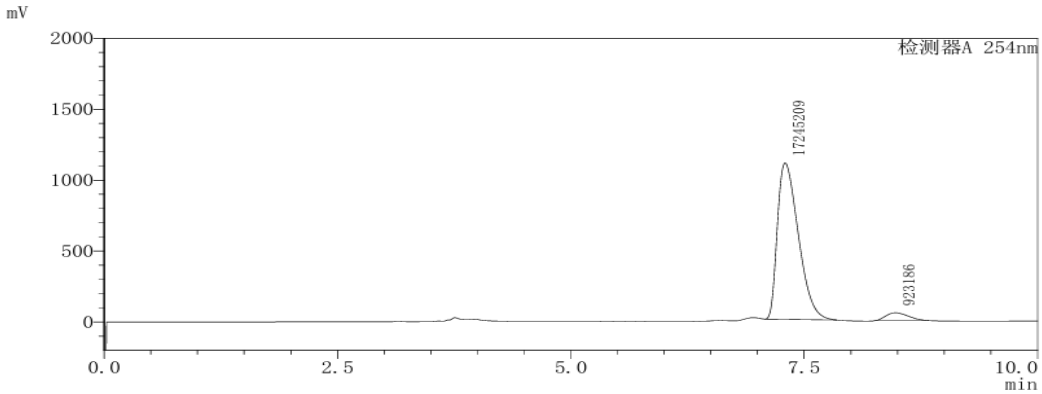
Compound **4d**: Prepared in 0.1 mmol scale at 0 ℃ for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. yellow solid, 74% yield (41.6 mg), 90% *ee*, m.p. = 120.7 – 121.4 ℃. HPLC (chiral IB column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 7.30 min, *tr* (minor) = 8.48 min. $[\alpha]^{25}_{D}$ = -155.1 (c = 0.07, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 1H), 7.28 (dd, *J* = 9.4, 7.0 Hz, 6H), 7.16 (dd, *J* = 16.3, 8.8 Hz, 5H), 6.94 (t, *J* = 7.5 Hz, 1H), 5.82 (dd, *J* = 8.8, 5.8 Hz, 1H), 5.55 (d, *J* = 25.7 Hz, 2H), 3.68 (s, 3H), 3.55 (dd, *J* = 15.9, 8.8 Hz, 1H), 3.04 (dd, *J* = 15.9, 5.8 Hz, 1H), 0.98 (s, 9H), 0.45 (s, 3H), 0.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 159.2, 142.8, 141.4, 135.1, 134.8, 133.2, 131.1, 129.1, 128.8, 128.1, 127.2, 126.8, 126.4, 126.0, 122.4, 120.4, 115.0, 52.1, 46.3, 37.6, 36.9, 26.2, 19.3, -2.6, -3.1.

HRMS (ESI-TOF), m/z calcd for $C_{32}H_{37}ClNO_4Si^+$ ($[M + H]^+$) 562.2175 (563.2209 for ^{37}Cl), found 562.2192 (563.2223 for ^{37}Cl).

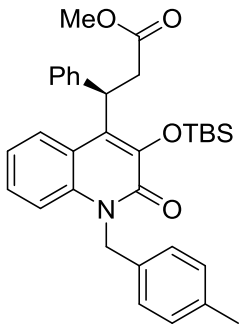




Racemic			
	Retention Time	Area	%Area
1	7.383	2449320	50.387
2	8.527	2411713	49.613

Enantioenriched			
	Retention Time	Area	%Area
1	7.297	17245209	94.919
2	8.477	923186	5.081

methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(4-methylbenzyl)-2-oxo-1,2-dihydro quinolin-4-yl)-3-phenylpropanoate (4e)

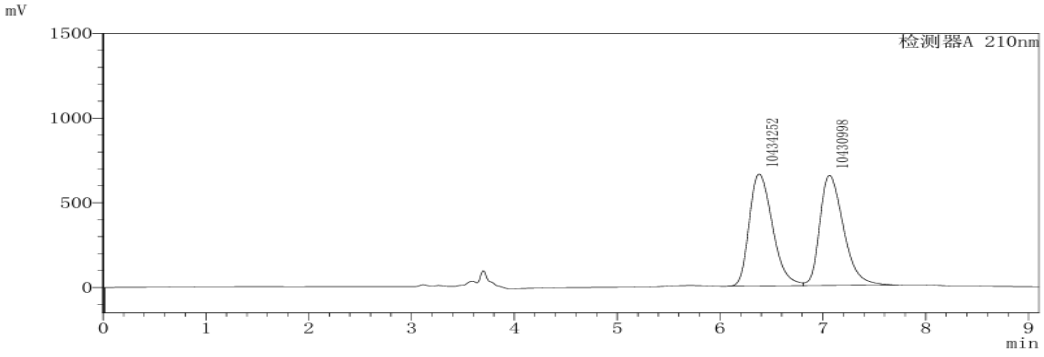


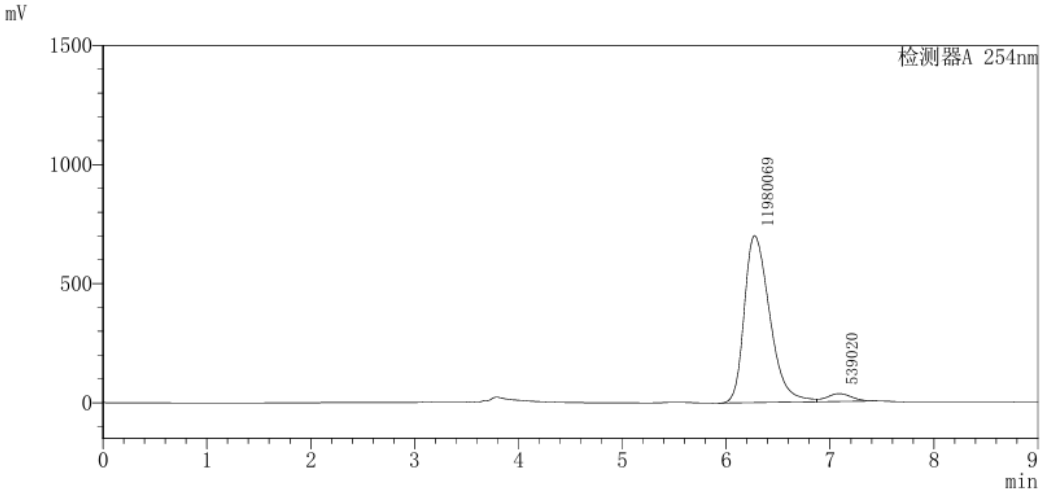
Compound **4e**: Prepared in 0.1 mmol scale at 0 ℃ for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. white solid, 60% yield (32.5 mg), 91% *ee*, m.p. = 89.8 – 90.9 ℃. HPLC (chiral IB column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 6.27 min, *tr* (minor) = 7.09 min. $[\alpha]^{25}_{D}$ = -147.8 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.23 (m, 4H), 7.24 – 7.15 (m, 4H), 7.14 – 7.05 (m, 4H), 6.92 (t, *J* = 7.7 Hz, 1H), 5.82 (dd, *J* = 8.8, 5.8 Hz, 1H), 5.54 (s, 2H), 3.69 (s, 3H), 3.54 (dd, *J* = 15.9, 8.9 Hz, 1H), 3.04 (dd, *J* = 15.9, 5.7 Hz, 1H), 2.31 (s, 3H), 0.98 (s, 9H), 0.46 (s, 3H), 0.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 159.2, 142.9, 141.5, 137.0, 135.4, 133.3, 130.8, 129.6, 128.8, 127.1, 126.8, 126.6, 126.4, 125.9, 122.1, 120.4, 115.3, 52.0, 46.6, 37.7, 36.9, 26.2, 21.2, 19.3, -2.6, -3.1.

HRMS (ESI-TOF), m/z calcd for $C_{33}H_{40}NO_4Si^+$ ($[M + H]^+$) 542.2722, found 542.2729.

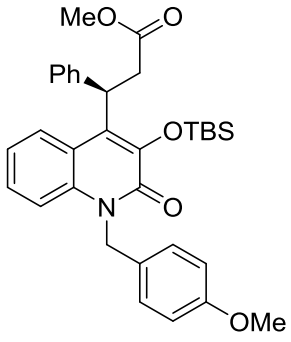




Racemic			
	Retention Time	Area	%Area
1	6.380	10434252	50.008
2	7.065	10430998	49.992

Enantioenriched			
	Retention Time	Area	%Area
1	6.274	11980069	95.694
2	7.086	539020	4.306

Methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(4-methoxybenzyl)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4f)

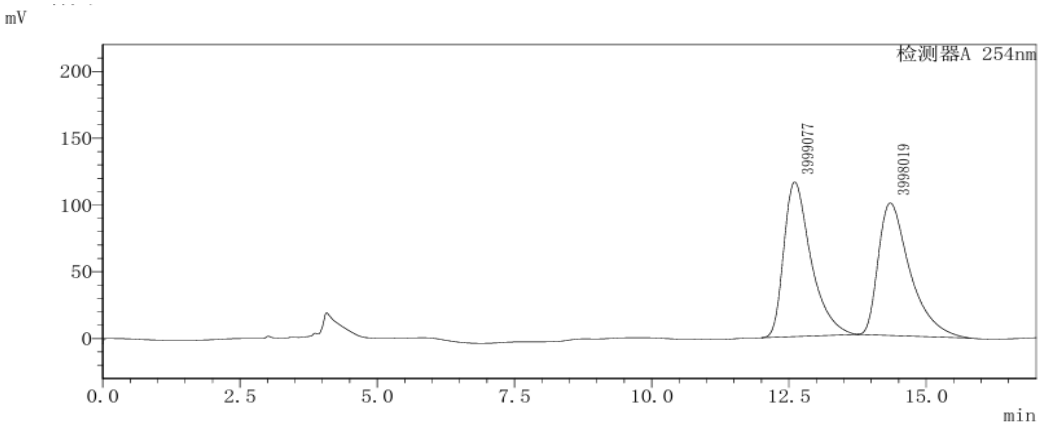


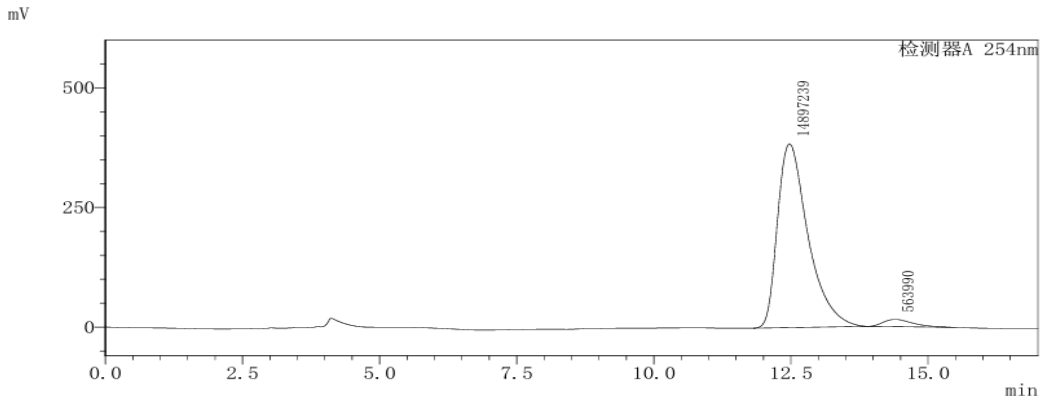
Compound **4f**: Prepared in 0.1 mmol scale at 0 ℃ for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. yellow oil, 58% yield (32.4 mg), 93% *ee*. HPLC (chiral IA column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 12.47 min, *tr* (minor) = 14.40 min. $[\alpha]^{25}_{D}$ = -139.0 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$**)** δ 7.35 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.12 (m, 9H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.82 (dd, *J* = 9.0, 5.8 Hz, 1H), 5.52 (s, 2H), 3.77 (s, 3H), 3.68 (s, 3H), 3.55 (dd, *J* = 15.9, 8.9 Hz, 1H), 3.04 (dd, *J* = 15.9, 5.7 Hz, 1H), 0.98 (s, 9H), 0.47 (s, 3H), 0.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$**)** δ 172.6, 159.2, 158.9, 142.9, 141.5, 135.3, 130.8, 128.8, 128.4, 128.0, 127.1, 126.8, 126.4, 125.9, 122.1, 120.4, 115.2, 114.3, 55.4, 52.1, 46.3, 37.7, 36.9, 26.2, 19.3, -2.6, -3.1.

HRMS (ESI-TOF), m/z calcd for $C_{33}H_{40}NO_5Si^+$ ($[M + H]^+$) 558.2671, found 558.2676.

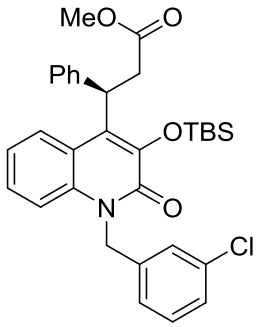




Racemic			
	Retention Time	Area	%Area
1	12.604	3999077	50.007
2	14.345	3998019	49.993

Enantioenriched			
	Retention Time	Area	%Area
1	12.473	14897239	96.352
2	14.398	563990	3.648

methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(3-chlorobenzyl)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4g)

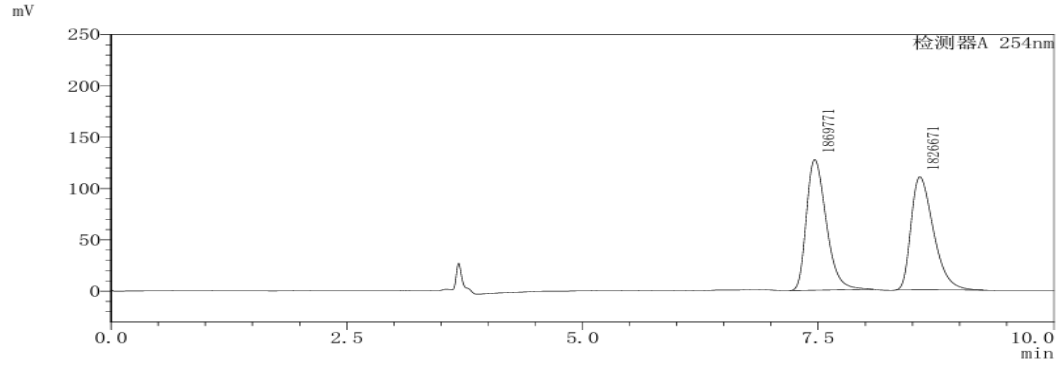


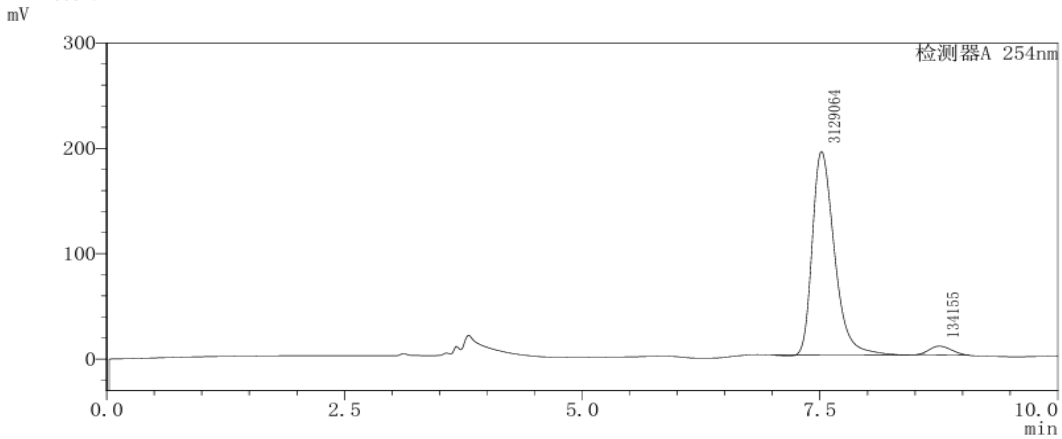
Compound **4g**: Prepared in 0.1 mmol scale at 0 ℃ for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. white solid, 55% yield (31.0 mg), 92% *ee*, m.p. = 102.8 – 103.4 ℃. HPLC (chiral IB column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 7.52 min, *tr* (minor) = 8.76 min. $[\alpha]^{25}_{D}$ = -167.7 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.14 (m, 9H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 6.4 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 5.89 – 5.78 (m, 1H), 5.55 (d, *J* = 36.3 Hz, 2H), 3.69 (s, 3H), 3.55 (dd, *J* = 15.9, 8.9 Hz, 1H), 3.05 (dd, *J* = 15.9, 5.8 Hz, 1H), 0.98 (s, 9H), 0.46 (s, 3H), 0.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 159.2, 142.8, 141.4, 138.4, 135.1, 134.9, 131.2, 130.3, 128.8, 127.7, 127.3, 126.8, 126.8, 126.4, 126.1, 124.8, 122.4, 120.4, 115.0, 52.1, 52.1, 46.5, 37.6, 36.9, 26.2, 19.3, -2.6, -3.2.

HRMS (ESI-TOF), m/z calcd for $C_{32}H_{37}ClNO_4Si^+$ ($[M + H]^+$) 562.2175 (563.2209 for ^{37}Cl), found 562.2188 (563.2213 for ^{37}Cl).

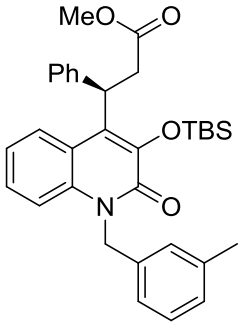




Racemic			
	Retention Time	Area	%Area
1	7.464	1869771	50.583
2	8.578	1826671	49.417

Enantioenriched			
	Retention Time	Area	%Area
1	7.517	3129064	95.889
2	8.756	134155	4.111

methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(3-methylbenzyl)-2-oxo-1,2-dihydro quinolin-4-yl)-3-phenylpropanoate (4h)

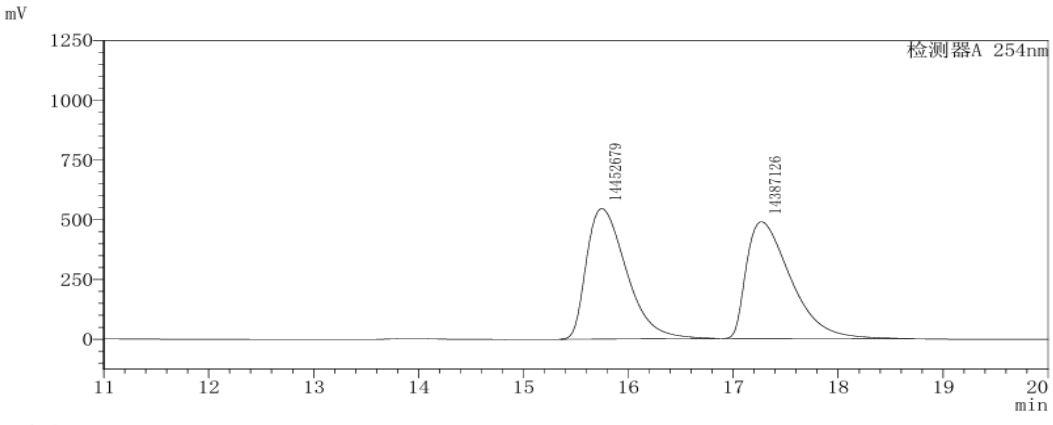


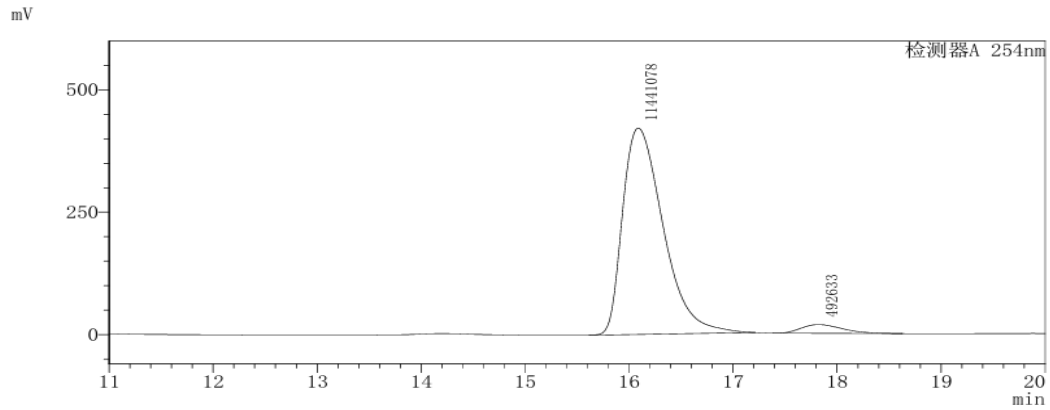
Compound **4h**: Prepared in 0.1 mmol scale at 0 °C for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. white solid, 53% yield (28.7 mg), 92% *ee*, m.p. = 115.8 – 116.9 ℃. HPLC (chiral IB column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 16.09 min, *tr* (minor) = 17.82 min. $[\alpha]^{25}_{D}$ = -161.8 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.25 (m, 4H), 7.24 – 7.13 (m, 4H), 7.05 (d, *J* = 6.7 Hz, 2H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.93 (t, *J* = 7.8 Hz, 1H), 5.82 (dd, *J* = 8.9, 5.7 Hz, 1H), 5.70 – 5.41 (m, 2H), 3.69 (s, 3H), 3.55 (dd, *J* = 15.9, 8.9 Hz, 1H), 3.05 (dd, *J* = 15.9, 5.8 Hz, 1H), 2.31 (s, 3H), 0.98 (s, 9H), 0.47 (s, 3H), 0.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 159.3, 142.9, 141.5, 138.6, 136.2, 135.4, 130.9, 128.8, 128.8, 128.2, 127.4, 127.2, 126.8, 126.4, 125.9, 123.6, 122.2, 120.4, 115.3, 52.0, 46.9, 37.7, 36.9, 26.2, 21.6, 19.3, -2.6, -3.1.

HRMS (ESI-TOF), m/z calcd for $C_{33}H_{40}NO_4Si^+$ ($[M + H]^+$) 542.2722, found 542.2735.

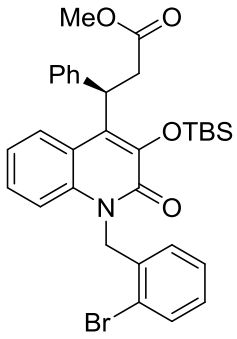




Racemic			
	Retention Time	Area	%Area
1	15.747	14452679	50.114
2	17.269	14387126	49.886

Enantioenriched			
	Retention Time	Area	%Area
1	16.088	11441078	95.872
2	17.822	492633	4.128

methyl 3-(1-(2-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydro quinolin-4-yl)-3-phenylpropanoate (4i)

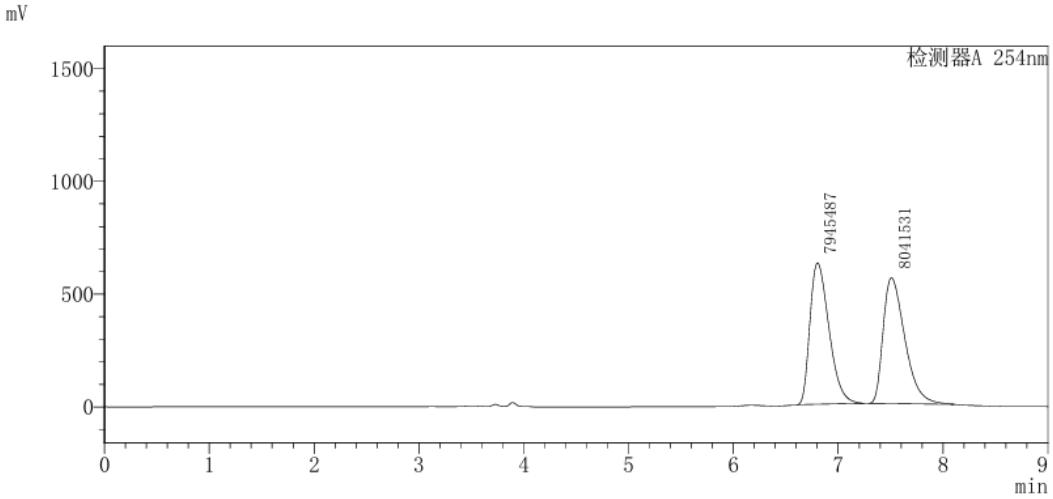


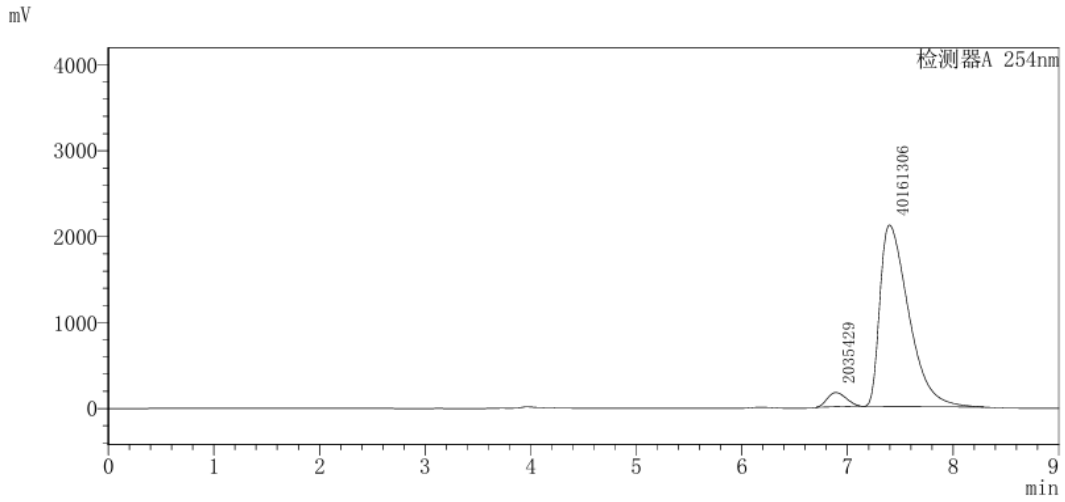
Compound **4i**: Prepared in 0.1 mmol scale at 0 °C for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. yellow solid, 46% yield (27.9 mg), 90% *ee*, m.p. = 106.8 – 107.6 ℃. HPLC (chiral IB column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (minor) = 6.89 min, *tr* (major) = 7.40 min. $[\alpha]^{25}_{D}$ = -146.5 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.34 – 7.25 (m, 4H), 7.24 – 7.07 (m, 4H), 6.95 (t, *J* = 7.9 Hz, 2H), 6.66 (dd, *J* = 7.4, 2.0 Hz, 1H), 5.83 (dd, *J* = 8.8, 6.0 Hz, 1H), 5.72 – 5.50 (m, 2H), 3.69 (d, *J* = 1.4 Hz, 3H), 3.56 (dd, *J* = 15.9, 8.8 Hz, 1H), 3.07 (dd, *J* = 15.9, 5.9 Hz, 1H), 0.97 (s, 9H), 0.43 (s, 3H), 0.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 159.2, 142.8, 141.4, 135.1, 134.7, 133.0, 131.2, 128.9, 128.9, 128.0, 126.9, 126.8, 126.5, 126.0, 122.6, 122.4, 120.4, 115.2, 52.1, 47.5, 37.7, 36.9, 26.2, 19.3, -2.7, -3.2.

HRMS (ESI-TOF), m/z calcd for $C_{32}H_{37}BrNO_4Si^+$ ($[M + H]^+$) 606.1670 (608.1650 for ^{81}Br), found 606.1675 (608.1661 for ^{81}Br).

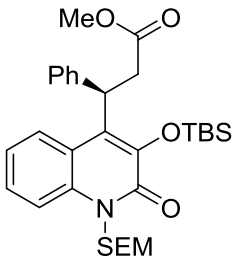




Racemic			
	Retention Time	Area	%Area
1	6.803	7945487	49.700
2	7.508	8041531	50.300

Enantioenriched			
	Retention Time	Area	%Area
1	6.890	2035429	4.824
2	7.398	40161306	95.176

Methyl 3-(3-((tert-butyldimethylsilyl)oxy)-2-oxo-1-((2-(trimethylsilyl)ethoxy)methyl)-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4j)

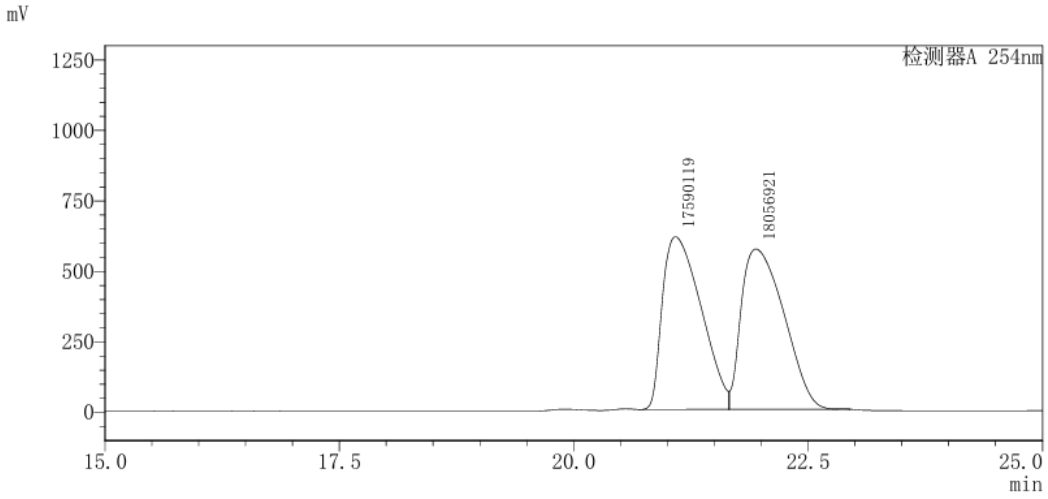


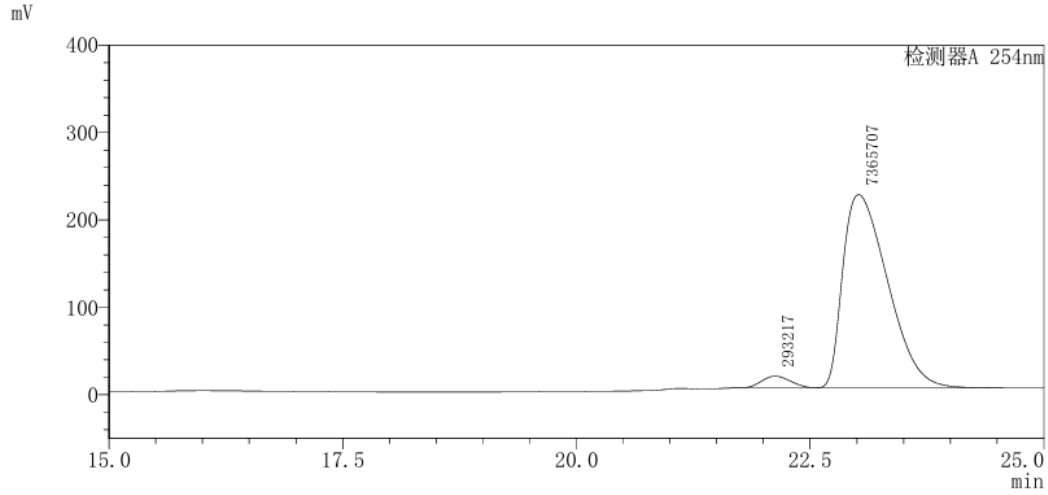
Compound **4j**: Prepared in 0.1 mmol scale at 0 °C for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. white oil, 53% yield (30.0 mg), 92% *ee*. HPLC (chiral IF column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (minor) = 22.13 min, *tr* (major) = 23.02 min. $[\alpha]^{25}_{D}$ = -156.0 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$**)** δ 7.59 – 7.50 (m, 1H), 7.37 – 7.25 (m, 3H), 7.29 – 7.13 (m, 4H), 7.06 – 6.93 (m, 1H), 5.80 (s, 2H), 5.80 – 5.71 (m, 1H), 3.77 – 3.67 (m, 2H), 3.67 (s, 3H), 3.52 (dd, *J* = 16.0, 8.8 Hz, 1H), 3.02 (dd, *J* = 16.0, 5.8 Hz, 1H), 1.0 - 0.91 (m, 11H), 0.42 (s, 3H), 0.33 (s, 3H), -0.03 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$**)** δ 172.5, 159.5, 142.5, 141.4, 135.1, 131.3, 128.8, 127.2, 126.8, 126.4, 125.7, 122.5, 120.2, 115.7, 72.3, 66.7, 52.0, 37.6, 36.9, 26.2, 19.3, 18.2, -1.3, -2.6, -3.1.

HRMS (ESI-TOF), m/z calcd for $C_{31}H_{46}NO_5Si_2^+$ ($[M + H]^+$) 568.2910, found 558.2917.

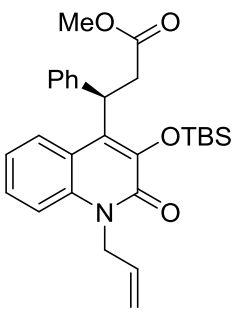




Racemic			
	Retention Time	Area	%Area
1	21.085	17590119	49.345
2	21.944	18056921	50.655

Enantioenriched			
	Retention Time	Area	%Area
1	22.125	293217	3.828
2	23.018	7365707	96.172

methyl 3-(1-allyl-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4k)

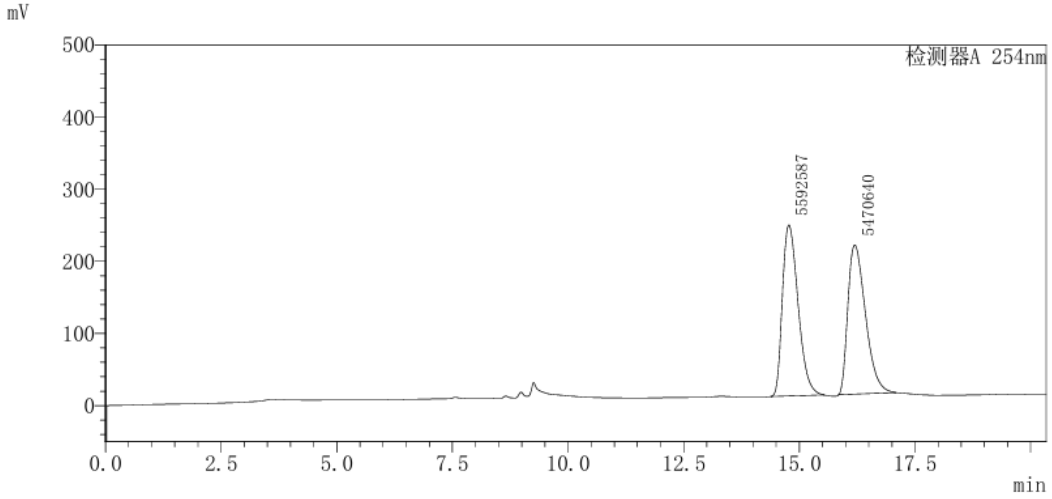


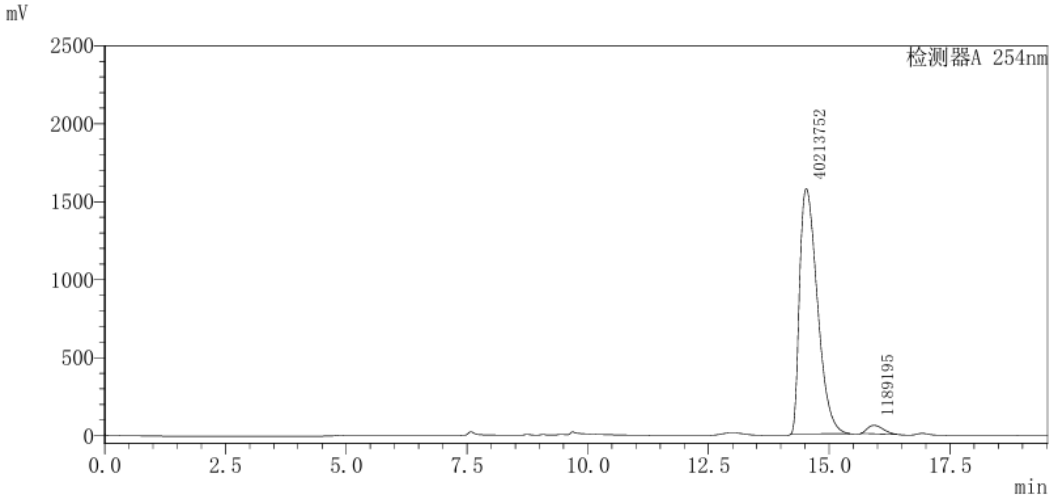
Compound **4k**: Prepared in 0.1 mmol scale at 0 °C for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. white oil, 50% yield (23.9 mg), 94% *ee*. HPLC (chiral IB column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 14.52 min, *tr* (minor) = 15.93 min. $[\alpha]^{25}_{D}$ = -185.6 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.22 (m, 6H), 7.19 (t, *J* = 7.0 Hz, 1H), 6.99-6.95 (m, 1H), 6.04-6.0 (m, 1H), 5.86 – 5.72 (m, 1H), 5.23 (d, *J* = 10.5 Hz, 1H), 5.09 (d, *J* = 17.3 Hz, 1H), 4.99 (dd, *J* = 9.7, 4.7 Hz, 2H), 3.67 (s, 3H), 3.54 (dd, *J* = 15.9, 8.8 Hz, 1H), 3.05 (s,1H), 0.96 (s, 9H), 0.44 (s, 3H), 0.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 158.7, 142.8, 141.5, 135.3, 131.9, 130.6, 128.8, 127.1, 126.8, 126.4, 125.9, 122.1, 120.3, 117.0, 115.0, 52.0, 45.5, 37.6, 36.9, 26.2, 19.3, -2.6, -3.2.

HRMS (ESI-TOF), m/z calcd for $C_{28}H_{35}NNaO_4Si^+$ ($[M + Na]^+$) 500.2228, found 500.2236.

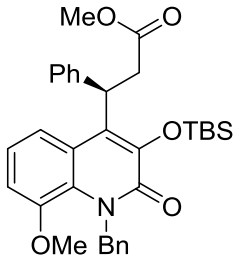




Racemic			
	Retention Time	Area	%Area
1	14.773	5592587	50.551
2	16.197	5470640	49.449

Enantioenriched			
	Retention Time	Area	%Area
1	14.524	40213752	97.128
2	15.926	1189195	2.872

methyl 3-(1-benzyl-3-((tert-butyldimethylsilyl)oxy)-8-methoxy-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4l)

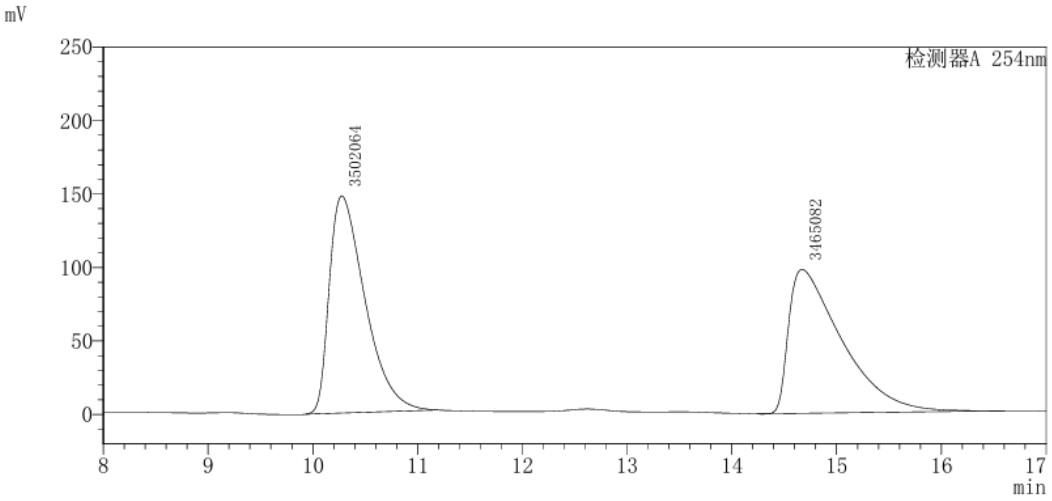


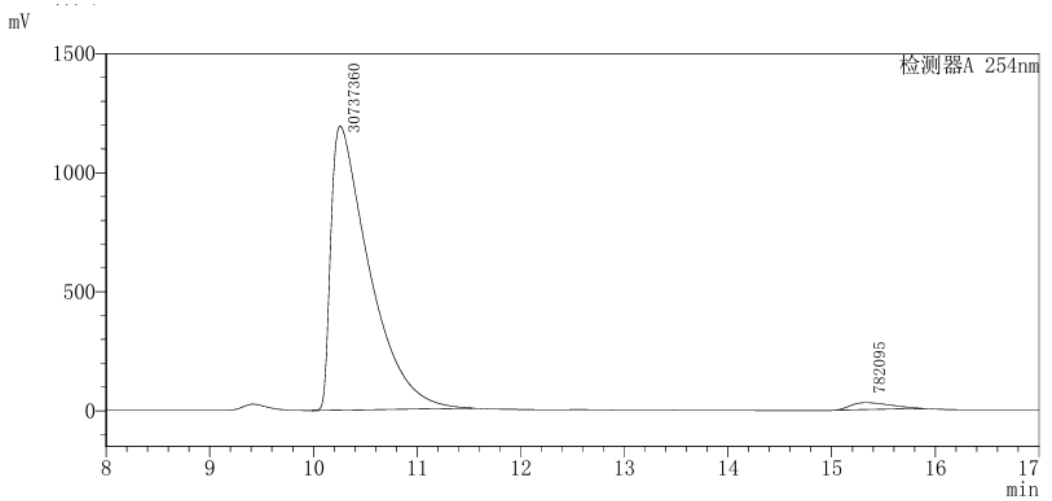
Compound **4l**: Prepared in 0.1 mmol scale at 0 °C for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. yellow oil, 21% yield (11.7 mg), 95% *ee*. HPLC (chiral IB column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 10.26 min, *tr* (minor) = 15.33 min. $[\alpha]^{25}_{D}$ = -129.2 (c = 0.09, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.15 (m,, 11H), 6.67 (d, *J* = 2.4 Hz, 1H), 6.52 (dd, *J* = 9.0, 2.4 Hz, 1H), 5.78 (t, *J* = 7.3 Hz, 1H), 5.55 (d, *J* = 12.2 Hz, 2H), 3.68 (s, 3H), 3.64 (s, 3H), 3.50 (dd, *J* = 15.9, 8.9 Hz, 1H), 3.01 (dd, *J* = 15.8, 5.7 Hz, 1H), 0.97 (s, 9H), 0.45 (s, 3H), 0.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.6, 159.7, 158.8, 141.6, 140.9, 136.9, 136.4, 131.3, 129.0, 128.8, 127.4, 127.1, 126.8, 126.7, 126.4, 114.0, 109.4, 100.3, 55.3, 52.0, 47.1, 37.8, 37.0, 26.3, 19.3, -2.6, -3.2.

HRMS (ESI-TOF), m/z calcd for $C_{33}H_{40}NO_5Si^+$ ($[M + H]^+$) 558.2671, found 558.2678.

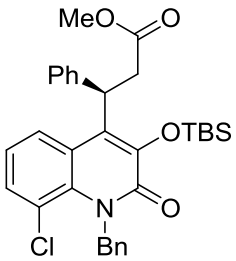




Racemic			
	Retention Time	Area	%Area
1	10.277	3502064	50.265
2	14.670	3465082	49.735

Enantioenriched			
	Retention Time	Area	%Area
1	10.259	30737360	97.519
2	15.331	29208	2.481

methyl 3-(1-benzyl-3-((tert-butyldimethylsilyl)oxy)-8-chloro-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4m)

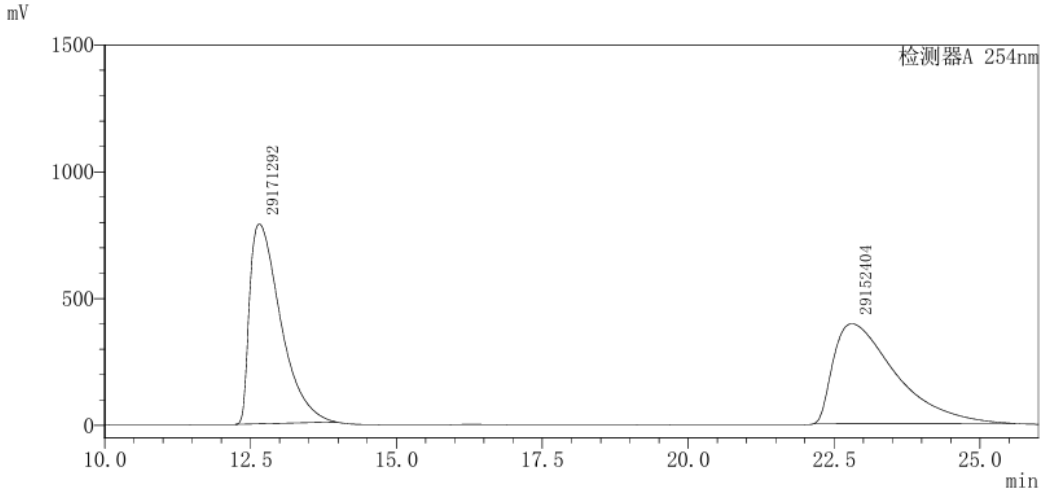


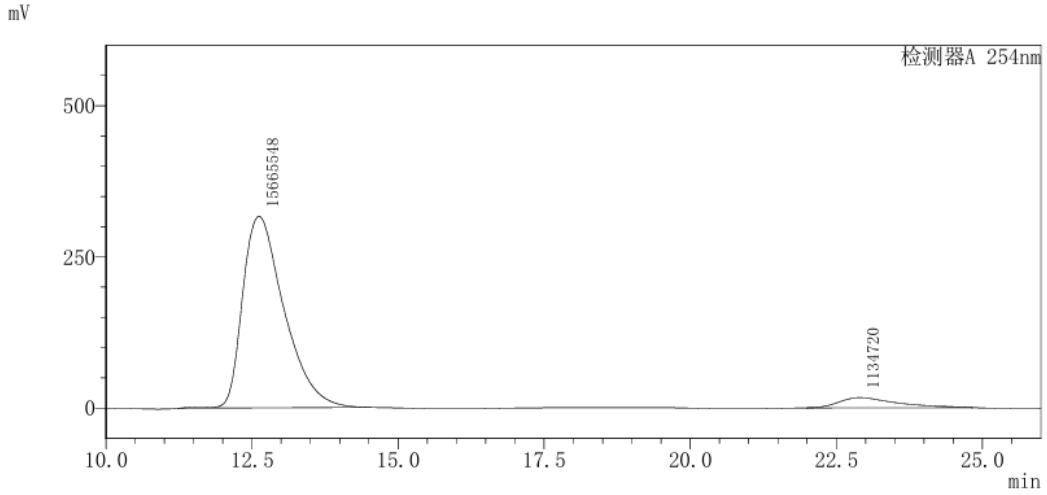
Compound **4m**: Prepared in 0.1 mmol scale at 0 ℃ for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. white solid, 56% yield (31.5 mg), 91% *ee*, m.p. = 146.8 – 147.4 ℃. HPLC (chiral IA column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 12.62 min, *tr* (minor) = 22.90 min. $[\alpha]^{25}_{D}$ = -131.0 (c = 0.06, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.15 (m, 10H), 7.09 – 7.02 (m, 2H), 6.85 (t, *J* = 8.0 Hz, 1H), 5.92 (d, *J* = 3.6 Hz, 2H), 5.78 (t, *J* = 7.5 Hz, 1H), 3.67 (s, 3H), 3.51 (dd, *J* = 15.8, 8.4 Hz, 1H), 3.07 (dd, *J* = 15.7, 6.4 Hz, 1H), 0.94 (s, 9H), 0.38 (s, 3H), 0.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 161.0, 143.5, 141.1, 138.2, 133.8, 130.8, 129.8, 128.9, 128.3, 126.7, 126.6, 126.6, 126.2, 124.8, 124.3, 123.0, 121.0, 52.1, 51.3, 37.5, 37.1, 26.1, 19.2, -2.7, -3.2.

HRMS (ESI-TOF), m/z calcd for $C_{32}H_{37}ClNO_4Si^+$ ($[M + H]^+$) 562.2175 (563.2209 for ^{37}Cl), found 562.2181 (563.2213 for ^{37}Cl).

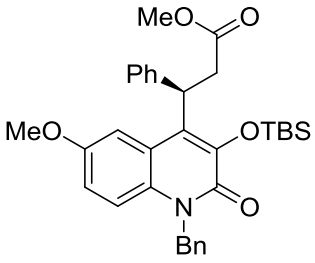




Racemic			
	Retention Time	Area	%Area
1	12.651	29171292	50.016
2	22.805	29152404	49.984

Enantioenriched			
	Retention Time	Area	%Area
1	12.621	15665548	95.596
2	22.904	721709	4.404

methyl 3-(1-benzyl-3-((tert-butyldimethylsilyl)oxy)-6-methoxy-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4n)

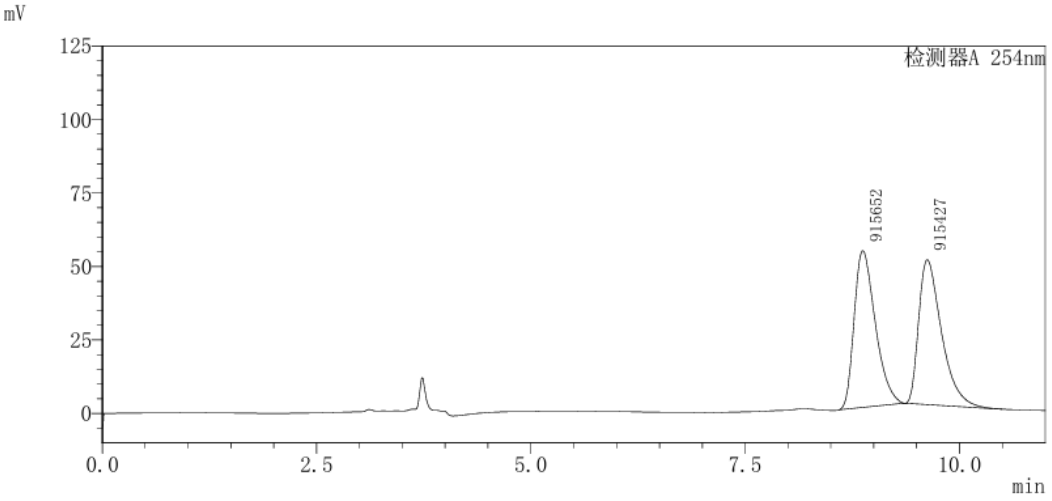


Compound **4n**: Prepared in 0.1 mmol scale at 0 ℃ for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. white solid, 38% yield (21.2 mg), 84% *ee*, m.p. = 124.8 – 125.4 ℃. HPLC (chiral IB column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 9.11 min, *tr* (minor) = 10.04 min. $[\alpha]^{25}_{D}$ = -130.0 (c = 0.09, CH_2Cl_2)

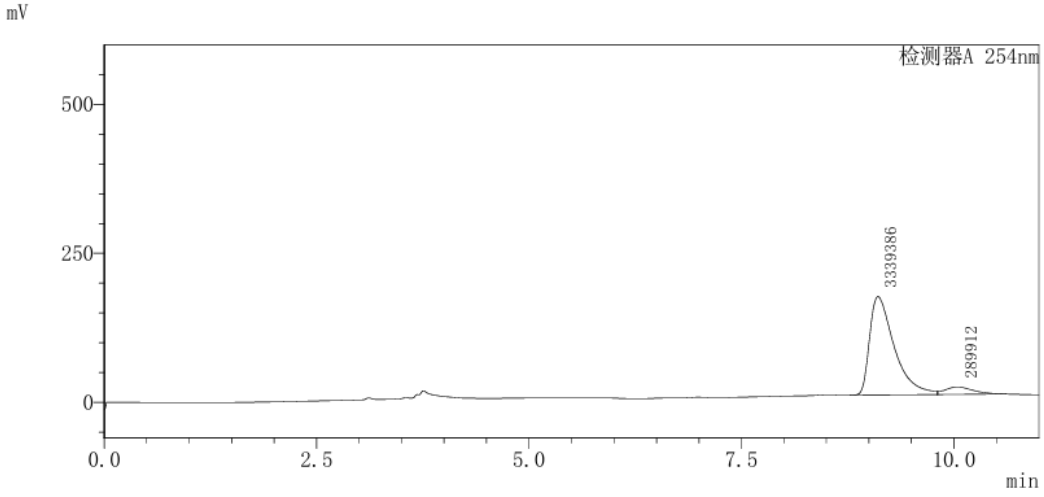
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.14 (m, 10H), 7.07 (d, *J* = 9.1 Hz, 1H), 6.83 – 6.67 (m, 2H), 5.84 (dd, *J* = 9.3, 5.7 Hz, 1H), 5.56 (s, 2H), 3.69 (s, 3H), 3.54 (dd, *J* = 15.7, 9.3 Hz, 1H), 3.47 (s, 3H), 3.02 (dd, *J* = 15.8, 5.7 Hz, 1H), 1.00 (s, 9H), 0.47 (s, 3H), 0.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 158.7, 154.4, 143.3, 141.6, 136.4, 130.5, 129.6, 128.9, 128.9, 127.4, 126.7, 126.5, 126.5, 121.2, 116.4, 115.6, 108.4, 55.4, 52.1, 47.0, 37.3, 37.0, 26.2, 19.3, -2.6, -3.2.

HRMS (ESI-TOF), m/z calcd for $C_{33}H_{40}NO_5Si^+$ ($[M + H]^+$) 558.2671, found 558.2679.



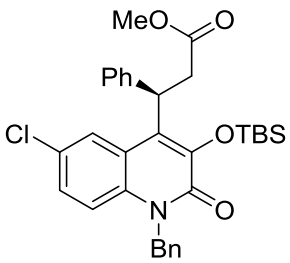
〈色谱图〉



Racemic			
	Retention Time	Area	%Area
1	8.872	915652	50.006
2	9.625	915427	49.994

Enantioenriched			
	Retention Time	Area	%Area
1	9.108	3339386	92.012
2	10.040	289912	7.988

methyl 3-(1-benzyl-3-((tert-butyldimethylsilyl)oxy)-6-chloro-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4o)

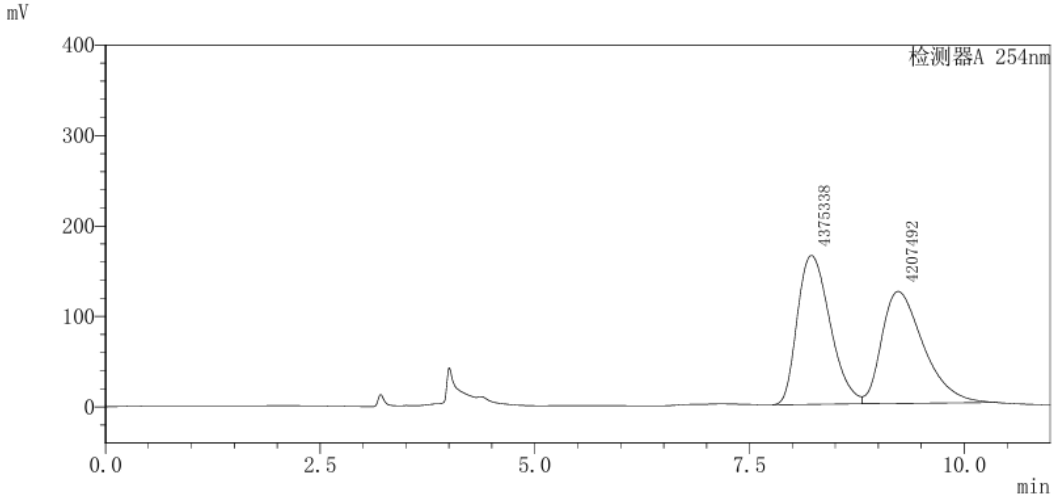


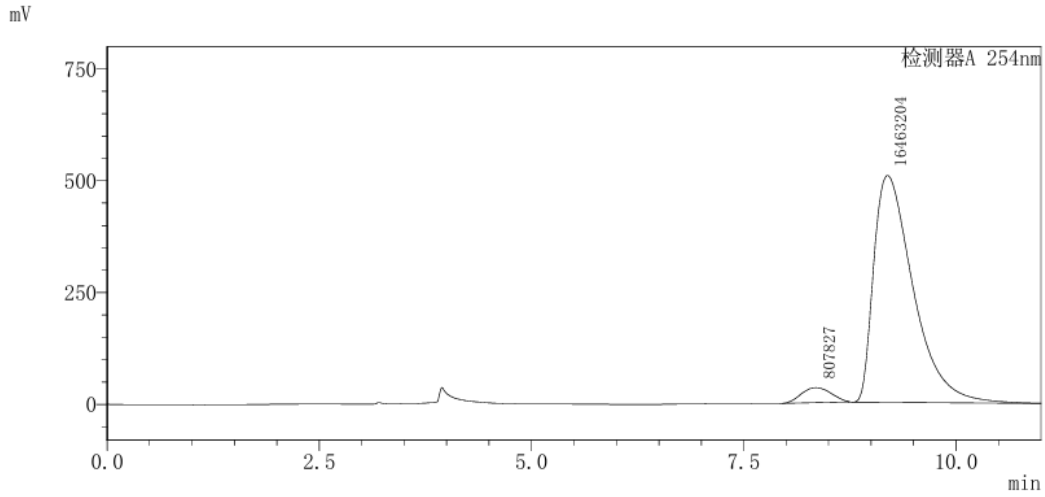
Compound **4o**: Prepared in 0.1 mmol scale at 0 °C for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. yellow oil, 41% yield (23.0 mg), 91% *ee*. HPLC (chiral IE column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (minor) = 8.35 min, *tr* (major) = 9.19 min. $[\alpha]^{25}_{D}$ = -119.4 (c = 0.09, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.20 (m, 9H), 7.16 (d, *J* = 7.5 Hz, 2H), 7.09 (s, 2H), 5.76 (t, *J* = 7.4 Hz, 1H), 5.55 (d, *J* = 15.5 Hz, 2H), 3.68 (s, 3H), 3.52 (dd, *J* = 15.8, 8.7 Hz, 1H), 3.05 (dd, *J* = 15.8, 6.2 Hz, 1H), 0.97 (s, 9H), 0.44 (s, 3H), 0.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 159.0, 143.7, 140.9, 135.9, 133.8, 129.7, 129.0, 129.0, 127.8, 127.6, 127.1, 126.8, 126.7, 126.5, 125.1, 121.9, 116.5, 52.0, 47.1, 37.4, 37.0, 26.3, 19.3, -2.6, -3.0.

HRMS (ESI-TOF), m/z calcd for $C_{32}H_{37}ClNO_4Si^+$ ($[M + H]^+$) 562.2175 (563.2209 for ^{37}Cl), found 562.2183 (563.2214 for ^{37}Cl).

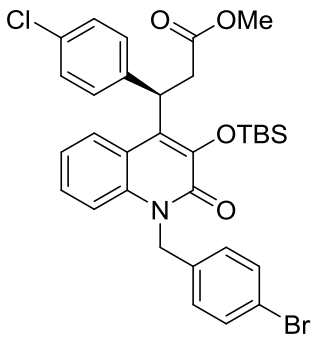




Racemic			
	Retention Time	Area	%Area
1	8.221	4375338	50.978
2	9.232	4207492	49.022

Enantioenriched			
	Retention Time	Area	%Area
1	8.351	807827	4.677
2	9.194	16463204	95.323

methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydroquinolin-4-yl)-3-(4-chlorophenyl)propanoate (4p)

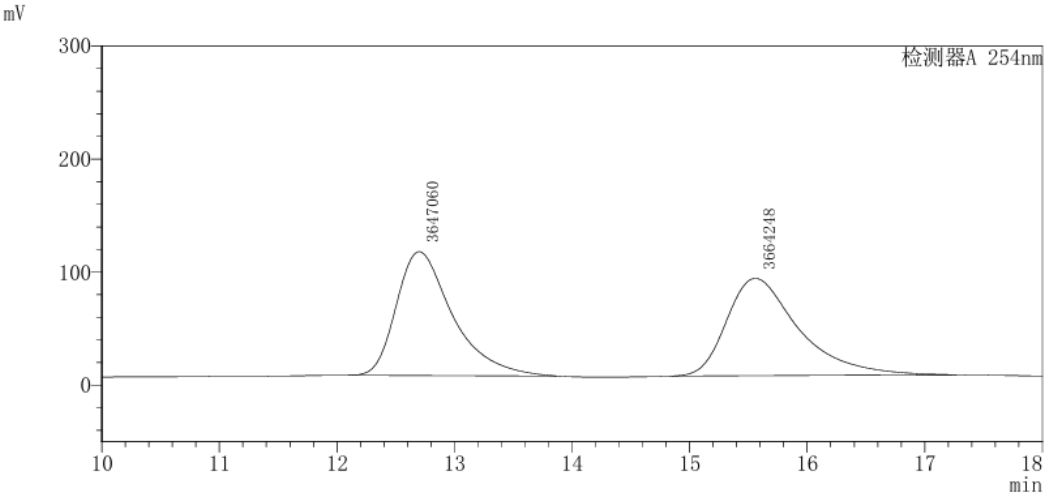


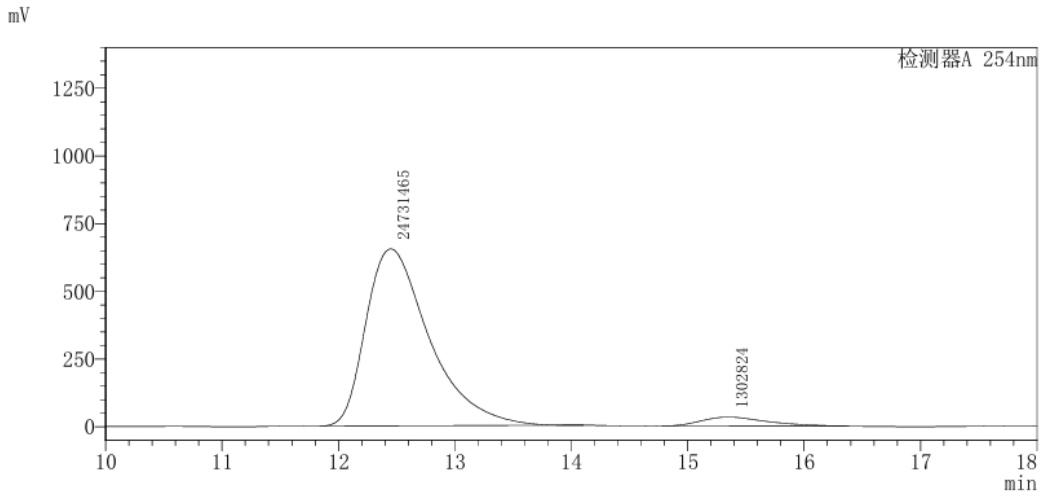
Compound **4p**: Prepared in 0.1 mmol scale at 0 ℃ for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. yellow solid, 70% yield (44.9 mg), 90% *ee*, m.p. = 119.8 – 120.4 ℃. HPLC (chiral IB column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 12.45 min, *tr* (minor) = 15.35 min. $[\alpha]^{25}_{D}$ = -119.2 (c = 0.1, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.25 (m, 3H), 7.22 – 7.17 (m,3H), 7.11 (dd, *J* = 18.0, 8.3 Hz, 3H), 6.97 (t, *J* = 7.6 Hz,1H), 5.89 – 5.70 (m, 1H), 5.53 (d, *J* = 36.7 Hz, 2H), 3.69 (s,3H), 3.51 (dd, *J* = 16.0, 9.1 Hz, 1H), 3.02 (dd, *J* = 16.0, 5.5 Hz, 1H), 0.97 (s, 9H), 0.44 (s, 3H), 0.36 (s,3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 159.1, 142.8, 140.0, 135.3, 135.1, 132.3, 132.1, 130.5, 129.0, 128.4, 128.2, 127.4, 125.8, 122.5, 121.3, 120.2, 115.1, 52.2, 46.4, 37.6, 36.4, 26.2, 19.3, -2.6, -3.1.

HRMS (ESI-TOF), m/z calcd for $C_{32}H_{36}BrClNO_4Si^+$ ($[M + H]^+$) 640.1281, found 640.1292.

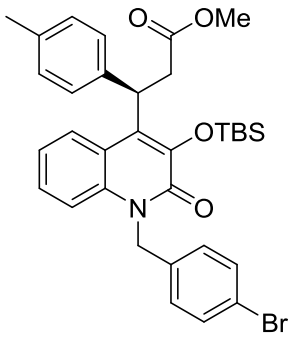




Racemic			
	Retention Time	Area	%Area
1	12.700	3647060	49.882
2	15.560	3664248	50.118

Enantioenriched			
	Retention Time	Area	%Area
1	12.449	24731465	94.996
2	15.350	1302824	5.004

methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydro quinolin-4-yl)-3-(p-tolyl)propanoate (4q)

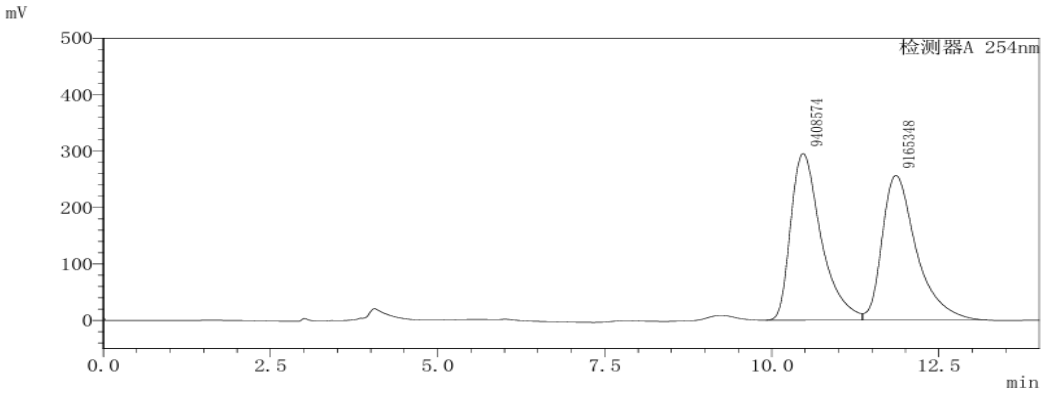


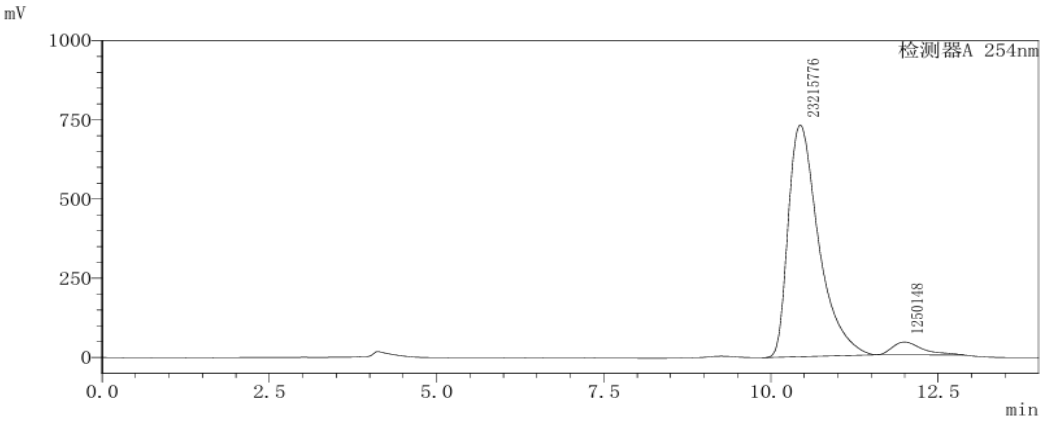
Compound **4q**: Prepared in 0.1 mmol scale at 0 ℃ for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. red solid, 55% yield (34.1 mg), 90% *ee*, m.p. = 126.8 – 128.4 ℃. HPLC (chiral IA column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 10.44 min, *tr* (minor) = 12.00 min. $[\alpha]^{25}_{D}$ = -138.6 (c = 0.1, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 14.1, 8.1 Hz, 3H), 7.28 – 7.04 (m, 8H), 6.94 (t, *J* = 7.9 Hz, 1H), 5.77 (t, *J* = 7.4 Hz, 1H), 5.66 – 5.42 (m, 2H), 3.68 (s, 3H), 3.52 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.02 (dd, *J* = 15.8, 5.8 Hz, 1H), 2.29 (s, 3H), 0.98 (s, 9H), 0.44 (s, 3H), 0.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 159.2, 142.7, 138.3, 135.9, 135.4, 135.1, 132.1, 131.3, 129.5, 128.4, 127.2, 126.6, 126.1, 122.3, 121.3, 120.5, 115.0, 52.0, 46.3, 37.7, 36.6, 26.2, 21.1, 19.3, -2.6, -3.1.

HRMS (ESI-TOF), m/z calcd for $C_{33}H_{39}BrNO_4Si^+$ ($[M + H]^+$) 620.1827, found 620.1833.

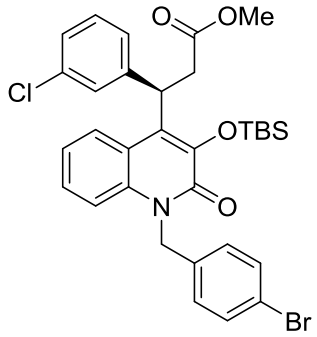




Racemic			
	Retention Time	Area	%Area
1	10.470	8786587	50.926
2	11.859	8466888	49.074

Enantioenriched			
	Retention Time	Area	%Area
1	10.438	23215776	94.890
2	11.997	1250148	5.110

methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydro quinolin-4-yl)-3-(3-chlorophenyl)propanoate (4r)

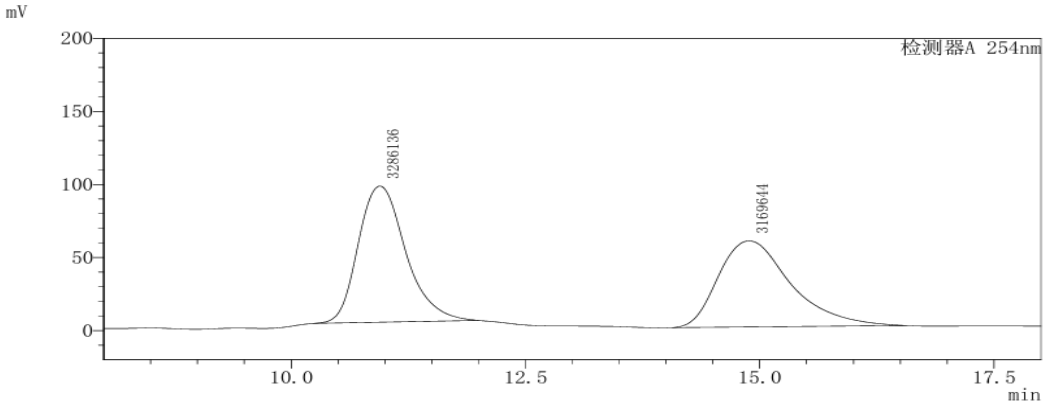


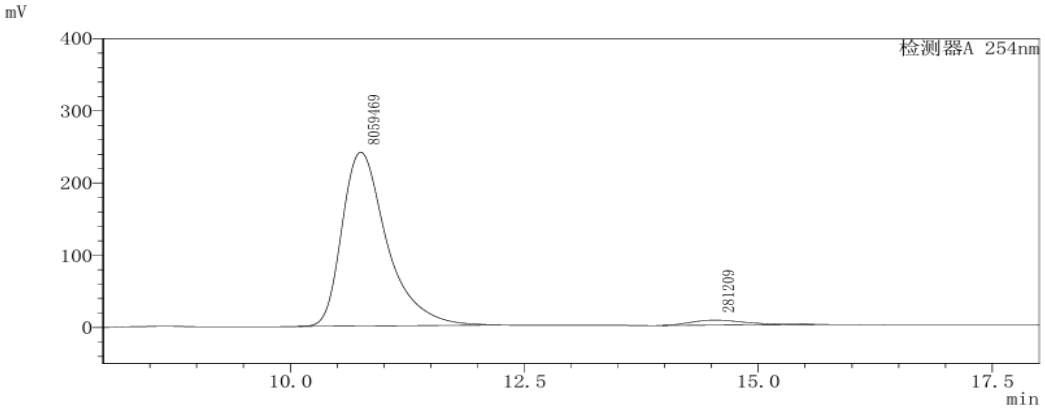
Compound **4r**: Prepared in 0.1 mmol scale at 0 °C for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. yellow solid, 40% yield (25.6 mg), 94% *ee*, m.p. = 136.8 – 137.9 ℃. HPLC (chiral IA column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 10.75 min, *tr* (minor) = 14.54 min. $[\alpha]^{25}_{D}$ = -144.0 (c = 0.1, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.05 (m, 8H), 6.99 (t, *J* = 7.6 Hz, 1H), 5.75 (t, *J* = 6.8 Hz, 1H), 5.53 (d, *J* = 45.9 Hz, 2H), 3.69 (s, 3H), 3.50 (dd, *J* = 16.1, 8.8 Hz, 1H), 3.04 (dd, *J* = 16.3, 5.6 Hz, 1H), 0.96 (s, 9H), 0.44 (s, 3H), 0.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 159.1, 143.6, 143.0, 135.3, 135.2, 134.8, 132.1, 130.2, 130.1, 128.4, 127.4, 127.1, 126.8, 125.7, 125.0, 122.5, 121.3, 120.3, 115.1, 52.1, 46.4, 37.5, 36.8, 26.2, 19.3, -2.6, -3.0.

HRMS (ESI-TOF), m/z calcd for $C_{32}H_{36}BrClNO_4Si^+$ ($[M + H]^+$) 640.1281, found 620.1288.

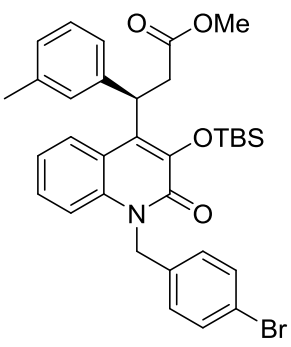




Racemic			
	Retention Time	Area	%Area
1	10.947	3286136	50.902
2	14.887	3169644	49.098

Enantioenriched			
	Retention Time	Area	%Area
1	10.753	8059469	96.802
2	14.541	266234	3.198

methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydro quinolin-4-yl)-3-(m-tolyl)propanoate (4s)

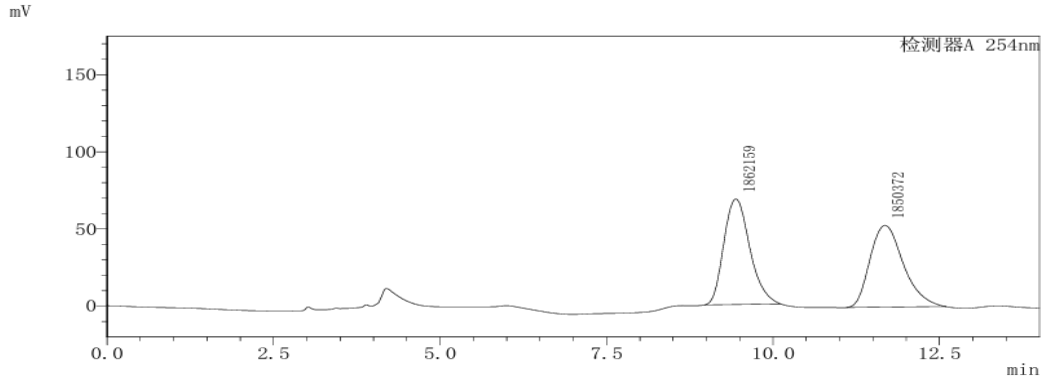


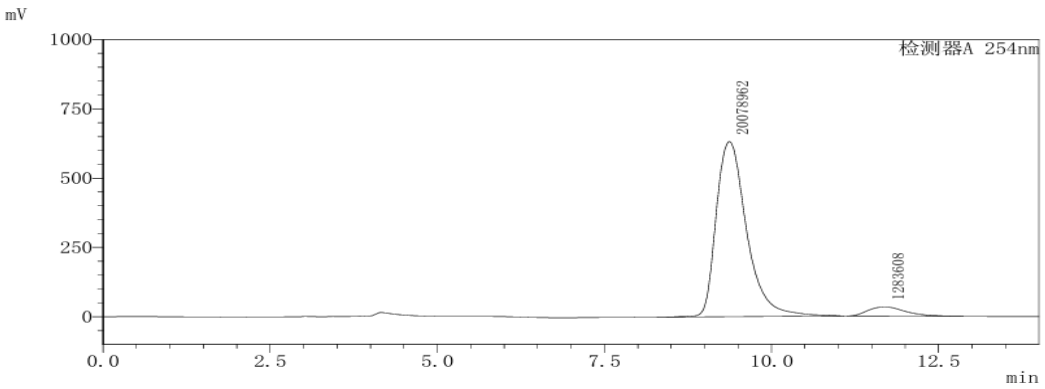
Compound 4s: Prepared in 0.1 mmol scale at 0 °C for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. yellow oil, 50% yield (31.0 mg), 88% *ee*. HPLC (chiral IA column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 9.37 min, *tr* (minor) = 11.69 min. $[\alpha]^{25}_{D}$ = -124.0 (c = 0.09, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.8 Hz, 3H), 7.29 – 7.14 (m, 2H), 7.14-7.05 (q, *J* = 8.5, 6.7 Hz, 5H), 7.02 – 6.92 (m,2H), 5.76 (t, *J* = 7.4 Hz, 1H), 5.53 (d, *J* = 50.0 Hz, 2H), 3.67 (s, 3H), 3.53 (dd, *J* = 15.9, 8.8 Hz, 1H), 3.04 (dd, *J* = 16.0, 5.9 Hz, 1H), 2.30 (s, 3H), 0.98 (s, 9H), 0.45 (s, 3H), 0.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 159.2, 142.7, 141.2, 138.3, 135.4, 135.1, 132.1, 131.2, 128.6, 128.4, 127.6, 127.2, 127.2, 126.0, 123.8, 122.4, 121.3, 120.5, 115.0, 52.0, 46.4, 37.6, 36.9, 26.2, 21.8, 19.3, -2.6, -3.1.

HRMS (ESI-TOF), m/z calcd for $C_{33}H_{39}BrNO_4Si^+$ ($[M + H]^+$) 620.1827, found 620.1831.

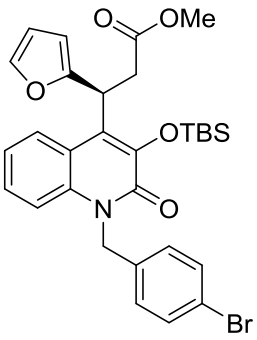




Racemic			
	Retention Time	Area	%Area
1	9.443	1862159	50.159
2	11.683	1850372	49.841

Enantioenriched			
	Retention Time	Area	%Area
1	9.371	20078962	93.991
2	11.693	1283608	6.009

methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydro quinolin-4-yl)-3-(furan-2-yl)propanoate (4t)

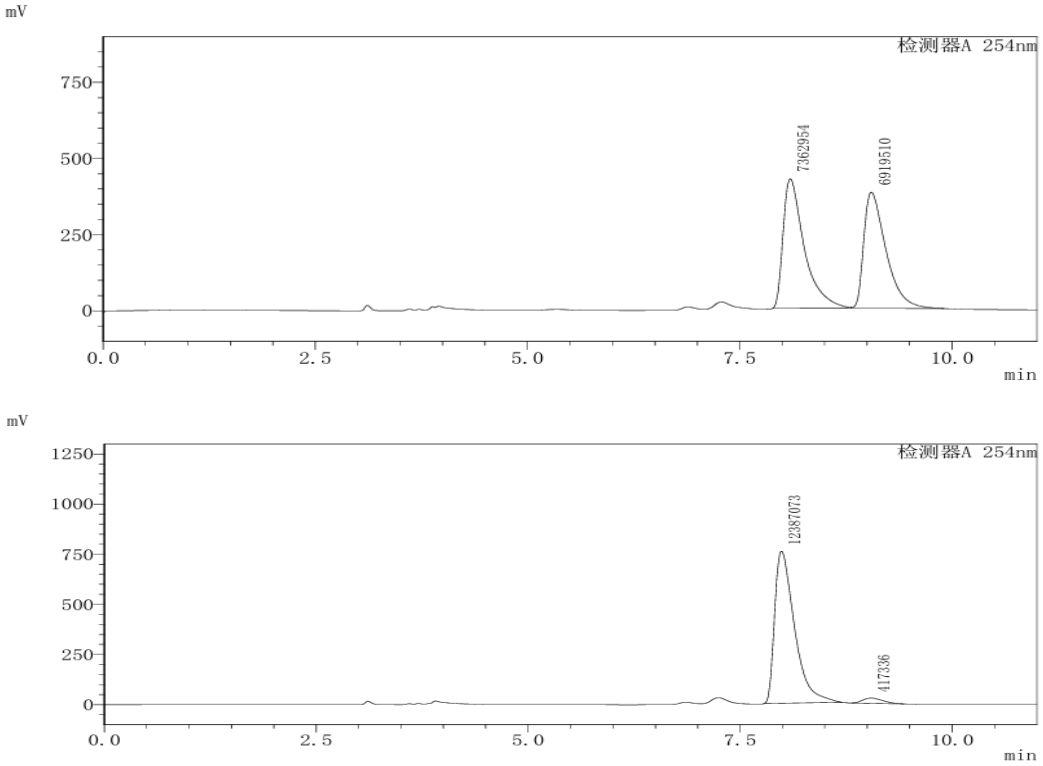


Compound 4t: Prepared in 0.1 mmol scale at 0 °C for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. yellow oil, 47% yield (28.0 mg), 94% *ee*. HPLC (chiral IB column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 7.99 min, *tr* (minor) = 9.05 min. $[\alpha]^{25}_{D}$ = -87.5.0 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.34 – 7.16 (m, 2H), 7.17 – 6.98 (m, 4H), 6.34 – 6.26 (m, 1H), 6.09 (d, *J* = 3.1 Hz, 1H), 5.83 – 5.72 (m, 1H), 5.51 (s, 2H), 3.70 (d, *J* = 1.5 Hz, 3H), 3.47 (dd, *J* = 15.9, 9.1 Hz, 1H), 2.95 (dd, *J* = 15.9, 5.6 Hz, 1H), 1.00 (s, 9H), 0.43 (s, 3H), 0.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 159.2, 154.5, 142.8, 141.5, 135.3, 135.0, 132.1, 128.6, 128.4, 127.4, 125.2, 122.5, 121.3, 120.6, 115.0, 110.7, 106.0, 52.1, 46.4, 36.7, 32.8, 26.1, 19.3, -2.8, -3.4.

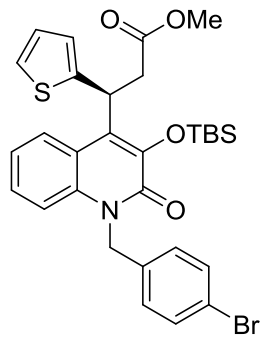
HRMS (ESI-TOF), m/z calcd for $C_{30}H_{35}BrNO_4Si^+$ ($[M + H]^+$) 596.1463, found 596.1469.



Racemic			
	Retention Time	Area	%Area
1	8.095	7362954	51.552
2	9.050	6919510	48.448

Enantioenriched			
	Retention Time	Area	%Area
1	7.988	12387073	96.741
2	9.045	417336	3.259

methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydroquinolin-4-yl)-3-(thiophen-2-yl)propanoate (4u)

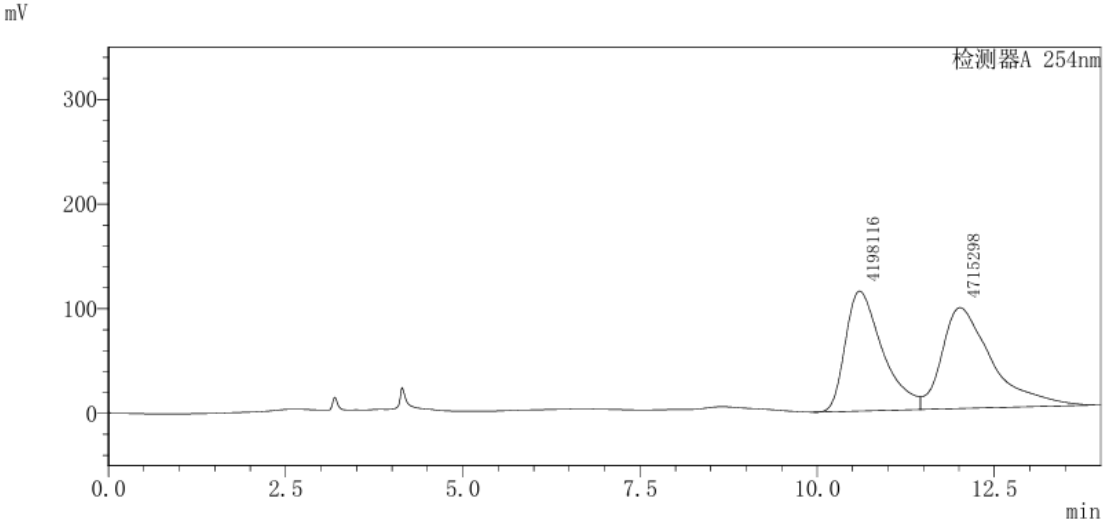


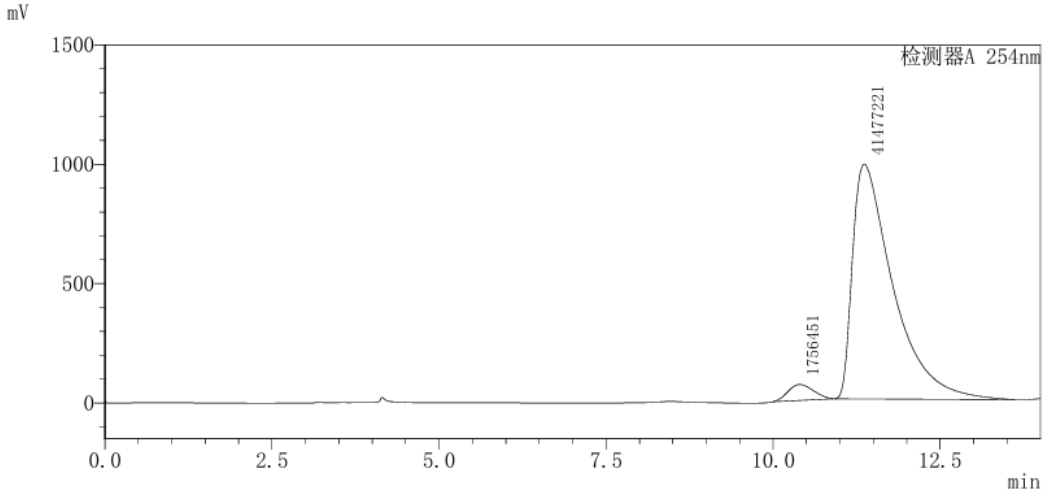
Compound **4u**: Prepared in 0.1 mmol scale at 0 °C for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. yellow oil, 57% yield (34.92 mg), 92% *ee*. HPLC (chiral IE column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (minor) = 10.40 min, *tr* (major) = 11.37 min. $[\alpha]^{25}_{D}$ = -80.0 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.18 (m, 2H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.11 – 6.99 (m, 3H), 6.87 (d, *J* = 3.8 Hz, 1H), 6.64 (dd, *J* = 3.9, 1.6 Hz, 1H), 5.81 (t, *J* = 20.6 Hz, 1H), 5.51 (s, 2H), 3.70 (s, 3H), 3.47 (dd, *J* = 16.0, 8.6 Hz, 1H), 3.07 (d, *J* = 16.1 Hz, 1H), 0.98 (s, 9H), 0.43 (s, 3H), 0.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 159.0, 147.5, 142.7, 135.2, 135.1, 132.1, 129.7, 129.2, 128.4, 127.5, 125.6, 124.2, 122.6, 121.3, 120.1, 115.2, 110.5, 52.2, 46.4, 38.7, 34.3, 26.2, 19.3, -2.6, -3.3.

HRMS (ESI-TOF), m/z calcd for $C_{30}H_{35}BrNO_4SSi^+$ ($[M + H]^+$) 612.1234 (614.1214 for ^{81}Br), found 612.1232 (614.1223 for ^{81}Br).

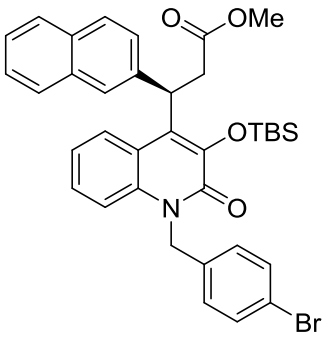




Racemic			
	Retention Time	Area	%Area
1	10.599	4198116	47.009
2	12.015	4715298	52.901

Enantioenriched			
	Retention Time	Area	%Area
1	10.400	1756451	4.063
2	11.366	41477221	95.937

methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydroquinolin-4-yl)-3-(naphthalen-2-yl)propanoate (4v)

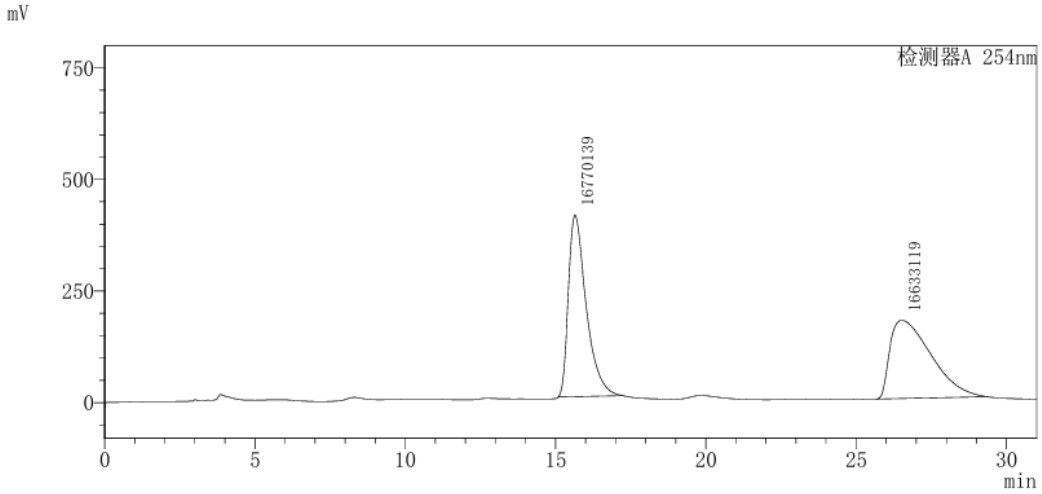


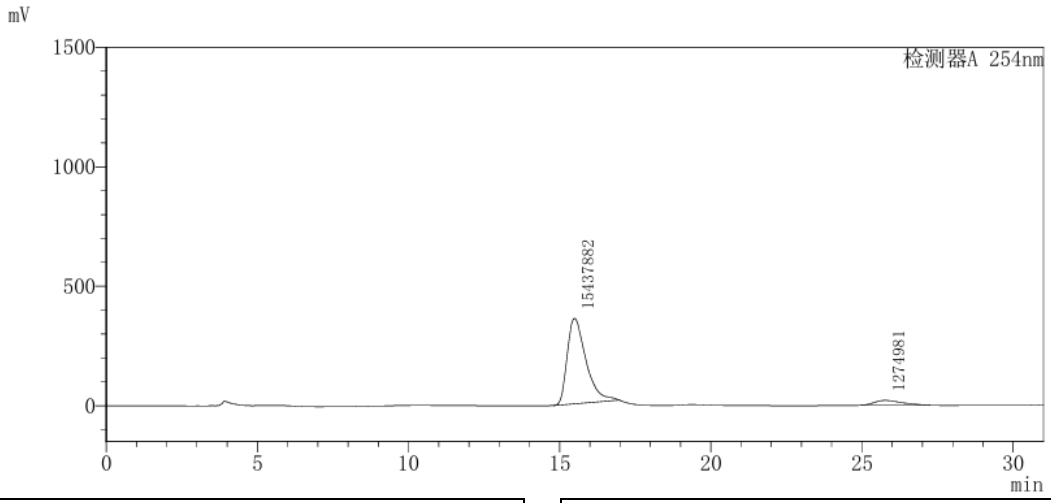
Compound 4v: Prepared in 0.1 mmol scale at 0 °C for 24 h**.** Purified by silica gel chromatography and eluted with PE/EA 30:1. white oil, 30% yield (19.7 mg), 85% *ee*. HPLC (chiral IA column), hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 15.49 min, *tr* (minor) = 25.77 min. $[\alpha]^{25}_{D}$ = -135.0 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (td, *J* = 15.0, 8.2 Hz, 4H), 7.57 – 7.39 (m, 5H), 7.34 (s, 1H), 7.13 (dt, *J* = 13.0, 8.1 Hz, 4H), 6.88 (t, *J* = 7.5 Hz, 1H), 5.96 (t, *J* = 7.2 Hz, 1H), 5.55 (d, *J* = 47.4 Hz, 2H), 3.70 (m, 4H), 3.14 (dd, *J* = 15.9, 5.8 Hz, 1H), 0.98 (s, 9H), 0.48 (s, 3H), 0.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 159.2, 142.9, 139.1, 135.4, 135.1, 133.6, 132.2, 132.1, 130.8, 128.6, 128.4, 128.0, 127.7, 127.3, 126.3, 125.9, 125.9, 125.8, 124.6, 122.5, 121.3, 120.5, 115.0, 52.1, 46.4, 37.7, 37.2, 26.2, 19.3, -2.6, -3.1.

HRMS (ESI-TOF), m/z calcd for $C_{36}H_{39}BrNO_4Si^+$ ($[M + H]^+$) 656.1827 (658.1806 for ^{81}Br), found 656.1829 (658.1818 for ^{81}Br).

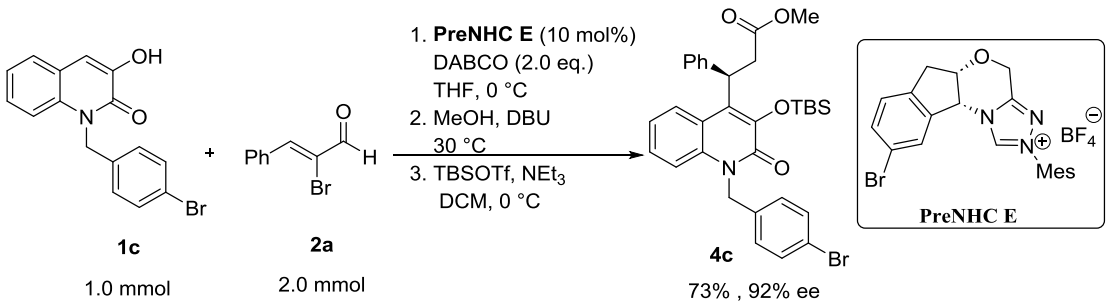




Racemic			
	Retention Time	Area	%Area
1	15.648	16770139	50.205
2	26.519	16633119	49.795

Enantioenriched			
	Retention Time	Area	%Area
1	15.492	15437882	92.371
2	25.769	1274981	7.629

6 Scale-up Experiments



To a dried round-bottom flask equipped with a magnetic stir bar were added 10 mol% of **pre NHC E** (50.0 mg), **1c** (1.0 mmol, 1.0 equiv.), and DABCO (0.2 mmol, 2.0 equiv.), followed by the addition of 10 mL of solvent. The mixture was cooled to

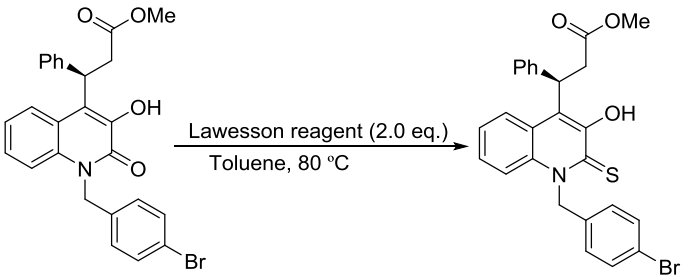
0 ℃ and stirred for several minutes, after which **2a** (2 mmol, 2.0 equiv.) was added slowly. The reaction was stirred at 0 ℃ for 24 hours, then purified by column chromatography on silica gel (PE/EA = 2:1) to afford the ring-closed product.

Subsequently, the cyclization product was transferred to a reaction round-bottom flask equipped with a stir bar. DBU (1.0 mmol, 1.0 equiv.) and methanol (10.0 mL) were added to the reaction mixture. The reaction was stirred at 30 ℃ until complete conversion of the cyclization substrate (monitored by TLC).

After concentration under reduced pressure, TBSOTf (2.0 mmol, 2.0 equiv.) was added to the residue followed by DCM (10.0 mL). The mixture was cooled to 0 ℃ and allowed to stir for several minutes before dropwise addition of Et_3N (3.0 mmol, 3.0 equiv.) at this temperature. The reaction was maintained at 0 ℃ for 2 hours, then purified by column chromatography on silica gel (PE/EA = 30:1) to afford product **4c** (442.84 mg, 73% yield, 90% ee).

7 Procedure for synthesis of product 5, 6, 7, 8 and 9

7.1 Procedure for synthesis of 5



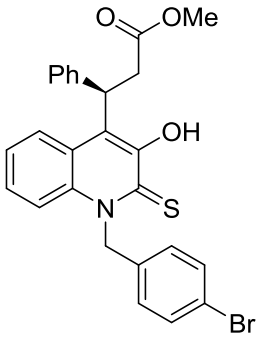
4c, 92% ee, 0.08 mmol

5: 59%, 93% ee

To a solution of compound **4c** (0.08 mmol, 49.2 mg, 93% ee) in toluene (1.0 mL) was added Lawesson reagent (64.7 mg, 0.16 mmol). The mixture was stirred at 80 ℃ for 48 h. After cooling to room temperature, the crude product was purified by flash column chromatography on silica gel (PE/EA = 10:1) to afford **5** as a yellow solid (24.0 mg, 59% yield, 92% ee).

7.2 Characterization of product 5

methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-thioxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (5)

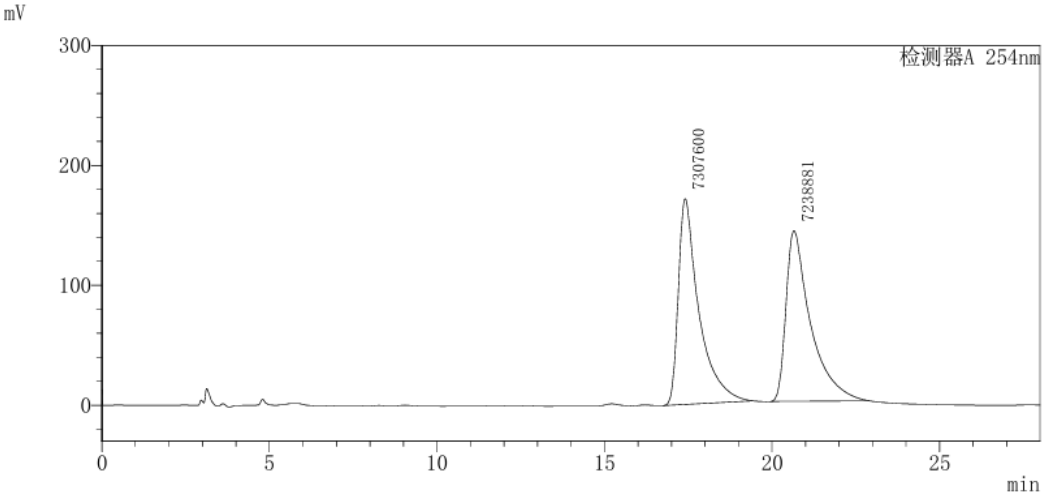


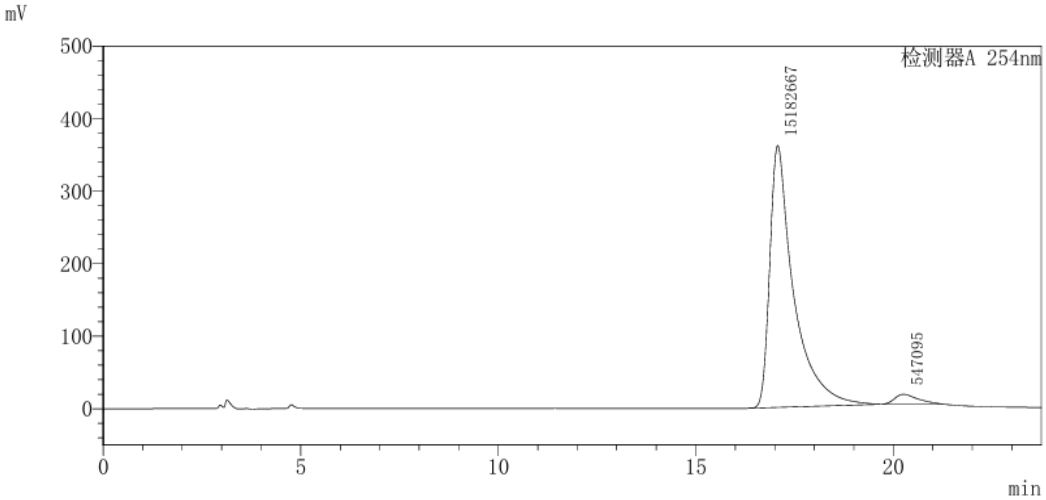
Compound **5**: yellow solid, 59% yield (24.0 mg), 93% *ee*, m.p. = 67.8 – 68.9 ℃. HPLC (chiral IA column), hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, *tr* (major) = 17.07 min, *tr* (minor) = 20.26 min. $[\alpha]^{25}_{D}$ = -135.0 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.25 – 8.10 (m, 1H), 7.54 – 7.36 (m, 8H), 7.35 – 7.16 (m, 2H), 7.21 (s, 1H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.26 (s, 2H), 5.37 (t, *J* = 7.5 Hz, 1H), 3.69 – 3.57 (m, 4H), 3.45 (dd, *J* = 16.8, 6.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 173.1, 148.1, 141.2, 135.6, 133.5, 132.3, 128.7, 128.2, 128.0, 127.8, 127.0, 125.6, 125.0, 124.4, 122.2, 121.7, 116.9, 55.7, 52.0, 39.2, 37.4.

HRMS (ESI-TOF), m/z calcd for $C_{26}H_{23}BrNO_3S^+$ ($[M + H]^+$) 508.0577 (510.0557 for ^{81}Br), found 508.0580 (510.0562 for ^{81}Br).

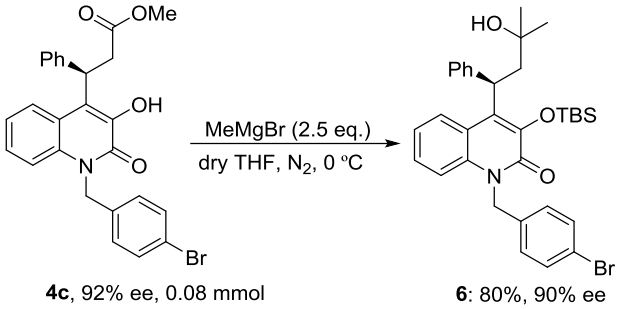




Racemic			
	Retention Time	Area	%Area
1	17.408	7307600	50.236
2	20.655	7238881	49.764

Enantioenriched			
	Retention Time	Area	%Area
1	17.072	15182667	96.522
2	20.257	547095	3.478

7.3 Procedure for synthesis of 6

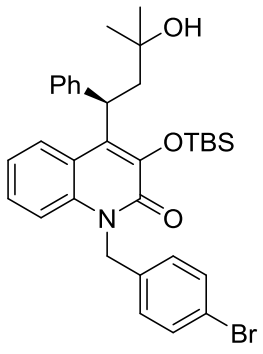


4c, 92% ee, 0.08 mmol — **6**: 80%, 90% ee

A dried tube equipped with a magnetic stir bar was charged with compound **4c** (0.08 mmol, 49.2 mg, 93% ee). The system was evacuated and purged with nitrogen (three cycles). Dry THF (1.0 mL) was injected via syringe, followed by dropwise addition of methylmagnesium bromide solution (3.0 M in THF, 0.66 mL, 0.20 mmol) at 0 ℃ under N_2 atmosphere (balloon pressure). The reaction mixture was stirred at 0 ℃ for 24 h, then quenched with ice-water. The aqueous layer was extracted with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography silica gel (PE/EA = 5:1) afforded product **6** as a white crystalline solid (39.0 mg, 80% yield, 90% ee).

7.4 Characterization of product 6

1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-4-(3-hydroxy-3-methyl-1-phenylbutyl)quinolin-2(1*H*)-one (6)

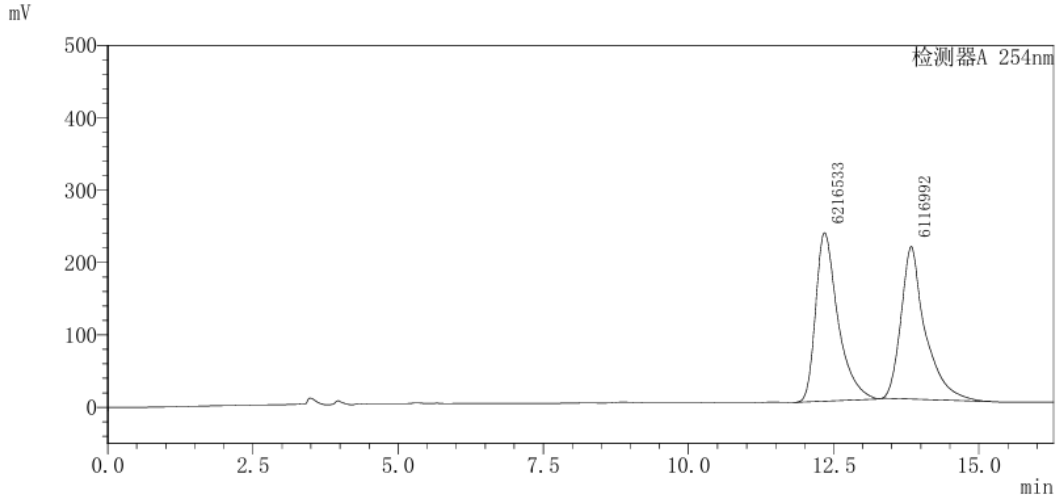


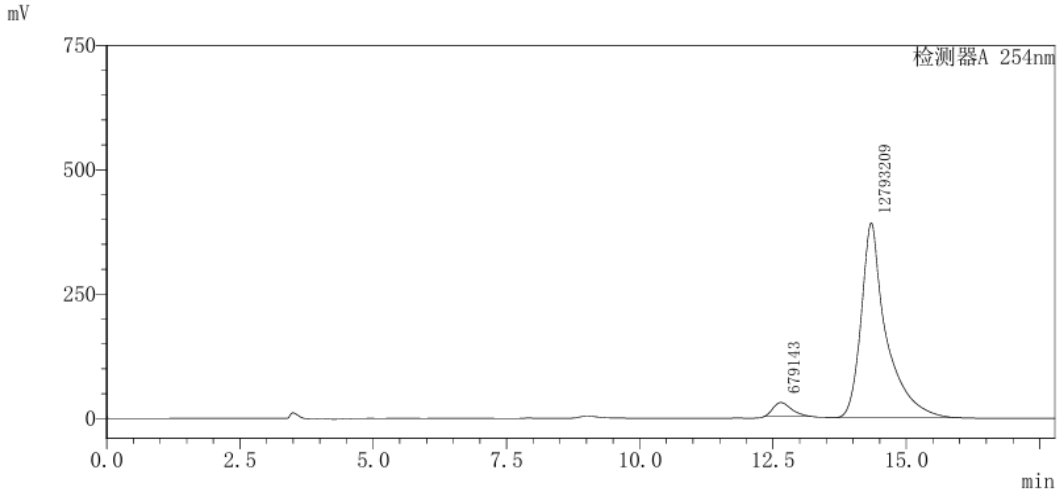
Compound **6**: white solid, 80% yield (39.0 mg), 90% *ee*, m.p. = 132.8 – 133.7 ℃. HPLC (chiral IA column), hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, *tr* (minor) = 12.65 min, *tr* (major) = 14.34 min. $[\alpha]^{25}_D$ = -114.6 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 2H), 7.38 – 7.22 (m, 5H), 7.24 – 7.05 (m, 5H), 6.95 (t, *J* = 7.6 Hz, 1H), 5.54 (d, *J* = 40.7 Hz, 2H), 5.25 - 5.32 (m, 1H), 2.84 – 2.62 (m, 1H), 2.45 - 2.3 (s, 1H), 1.32 (s, 3H), 1.24 (s, 3H), 0.91 (s, 9H), 0.49 (s, 3H), 0.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 143.1, 142.4, 135.6, 135.4, 134.2, 132.1, 128.5, 128.4, 127.6, 127.4, 127.1, 126.0, 122.1, 121.3, 120.1, 115.0, 71.6, 47.0, 46.3, 36.3, 30.2, 29.6, 26.3, 19.2, -2.5, -3.7.

HRMS (ESI-TOF), m/z calcd for $C_{33}H_{41}BrNO_3Si^+$ ($[M + H]^+$) 606.2034 (608.2014 for ^{81}Br), found 606.2043 (608.2031 for ^{81}Br).

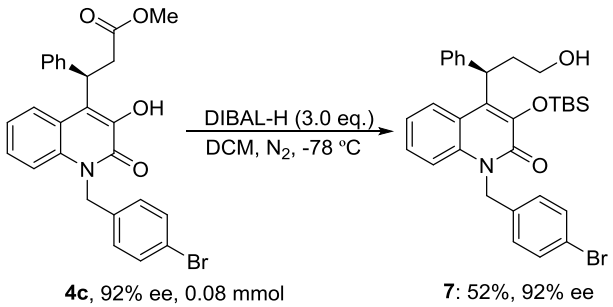




Racemic			
	Retention Time	Area	%Area
1	12.343	6216533	50.404
2	13.834	6116992	49.596

Enantioenriched			
	Retention Time	Area	%Area
1	12.647	679143	5.041
2	14.342	12793209	94.959

7.5 Procedure for synthesis of 7



4c, 92% ee, 0.08 mmol

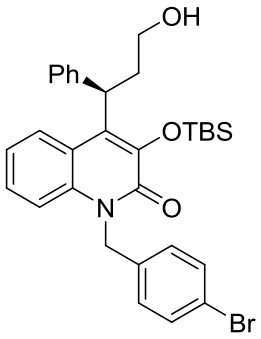
7: 52%, 92% ee

A dried tube equipped with a magnetic stir bar was charged with compound **4c** (0.08 mmol, 49.2 mg, 93% ee). The system was evacuated and purged with nitrogen

(three cycles) to establish an inert atmosphere. DCM (1.0 mL) was injected via syringe, followed by dropwise addition of DABAL-H solution (1.0 M in hexanes, 0.24 mL, 0.24 mmol) at -78 ℃ under a N_2 balloon. The reaction mixture was maintained at -78 ℃ for 12 h with vigorous stirring, then carefully quenched with 1 M HCl (5.0 mL) at low temperature. The aqueous phase was extracted with DCM , and the combined organic layers were dried over anhydrous Na_2 SO_4 . After filtration and solvent removal under reduced pressure, the residue was purified by flash column chromatography silica gel (PE/EA = 10:1) to afford **7** as a yellow solid (24.0 mg, 52% yield, 92% ee).

7.6 Characterization of product 7

1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-4-(3-hydroxy-1-phenylpropyl)quinolin-2(1*H*)-one (7)

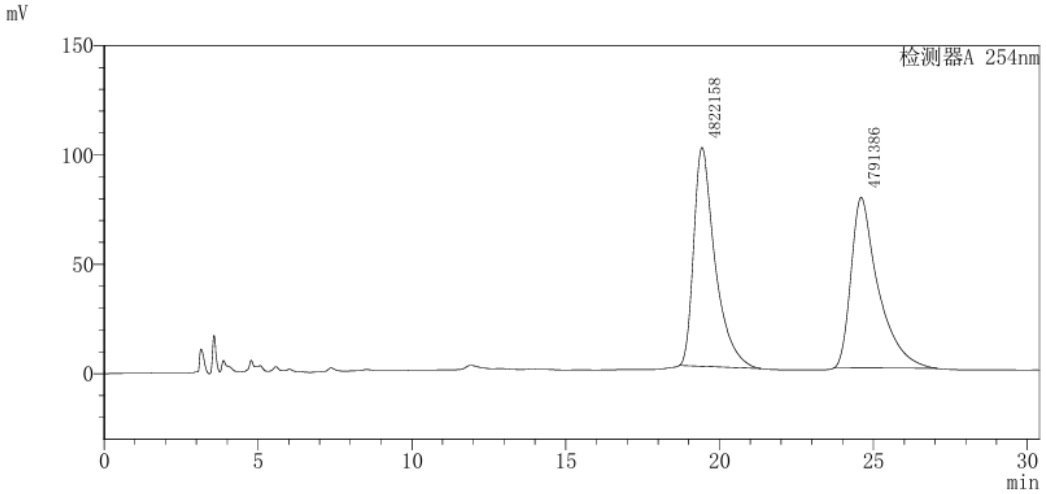


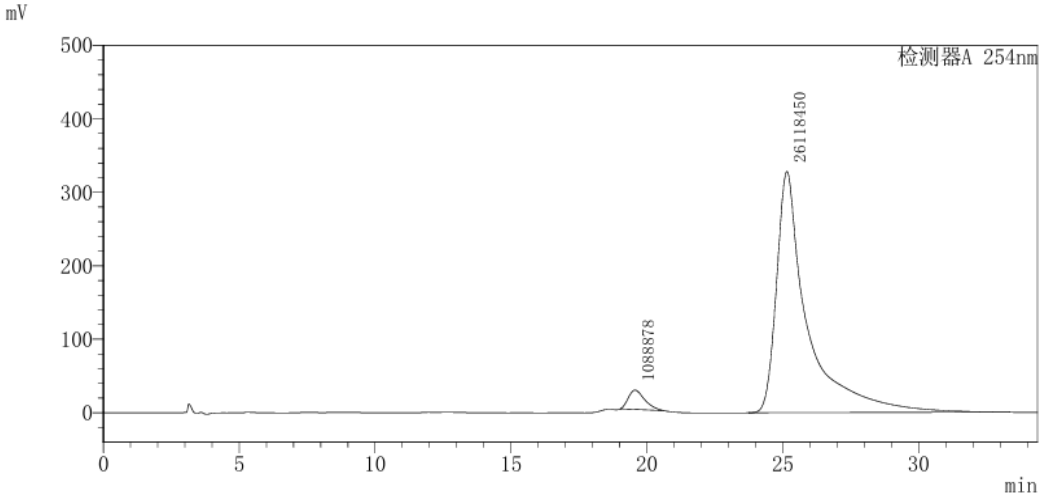
Compound **7**: yellow solid, 52% yield (24.0 mg), 92% *ee*, m.p. = 78.8 – 79.9 ℃. HPLC (chiral IA column), hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, *tr* (minor) = 19.56 min, *tr* (major) = 25.15 min. $[\alpha]^{25}_D$ = -136.7 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.41 – 7.29 (m, 5H), 7.23 – 7.04 (m, 5H), 6.90 (m, 1H), 5.54 (s, 2H), 5.38 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.76 – 3.47 (m, 1H), 2.91 – 2.72 (m, 1H), 2.53 – 2.36 (m, 1H), 1.98 (s, 1H), 0.97 (s, 9H), 0.51 (s, 3H), 0.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 143.3, 142.3, 135.4, 135.3, 132.1, 131.6, 128.8, 128.4, 127.5, 126.9, 126.8, 126.3, 122.2, 121.3, 119.9, 115.0, 61.4, 46.4, 36.8, 36.7, 34.0, 26.3, 26.3, 19.3, -2.7, -3.6.

HRMS (ESI-TOF), m/z calcd for $C_{31}H_{37}BrNO_3Si^+$ ($[M + H]^+$) 578.1721 (580.1701 for ^{81}Br), found 578.1739 (580.1721 for ^{81}Br).

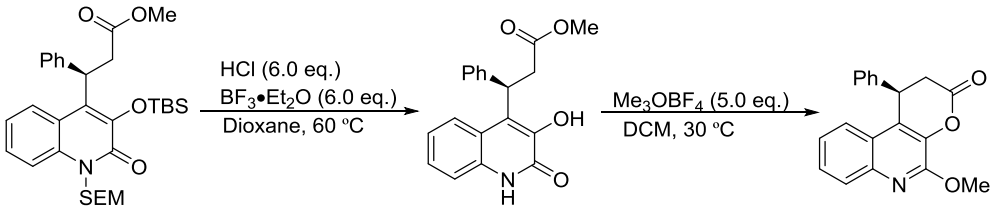




Racemic			
	Retention Time	Area	%Area
1	19.427	4822158	50.160
2	24.601	4791386	49.840

Enantioenriched			
	Retention Time	Area	%Area
1	19.564	1088878	4.002
2	25.152	26118450	95.998

7.7 Procedure for synthesis of 8 and 9



4j, 93% ee, 0.12 mmol

8: 83% yield, 0.1 mmol

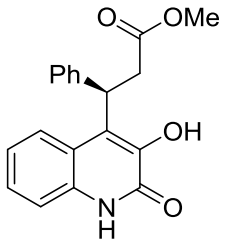
9: 33% , 92% ee

To a solution of compound **4j** (0.12 mmol, 68.1 mg, 93% ee) in 1,4-dioxane was added HCl (0.72 mmol, 22.2 μL) and BF_3 Et_2 O (0.72 mmol, 88.9 uL) sequentially via microliter syringe. The reaction mixture was stirred at 60 ℃ for 18 h under nitrogen atmosphere (balloon pressure) until complete consumption of starting material. The crude product was purified by flash column chromatography silica gel (PE/EA = 1:1) to give **8** as a white crystalline solid (32.3 mg, 83% yield).

A dried tube containing **8** (0.10 mmol, 32.3 mg) was charged with Me_3 OBF_4 (0.50 mmol, 126 mg) and DCM (1.0 mL). The mixture was stirred at 30 ℃ for 48 h. After cooling to ambient temperature, purification by flash column chromatography (silica gel, PE/EA = 10:1) afforded **9** as a white solid (10 mg, 33% yield, 92% ee).

7.8 Characterization of product 8 and 9

methyl (R)-3-(3-hydroxy-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (8)

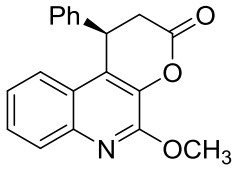


Compound **8**: white solid, 83% yield (10.0 mg), m.p. = 122.8 – 123.7 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.00 (m, 10H), 5.21 (d, *J* = 7.9 Hz, 1H), 3.55-3.62 (m, 4H), 3.41 (dd, *J* = 16.8, 6.6 Hz, 1H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 159.7, 142.3, 141.5, 132.6, 128.7, 127.7, 127.3, 126.9, 125.7, 124.0, 123.7, 121.1, 116.7, 51.9, 39.2, 37.8.

HRMS (ESI-TOF), m/z calcd for $C_{19}H_{18}NO_4^+$ ([M + H]$^+$) 324.1231, found 324.1232.

5-methoxy-1-phenyl-1,2-dihydro-3H-pyrano[2,3-c]quinolin-3-one (9)

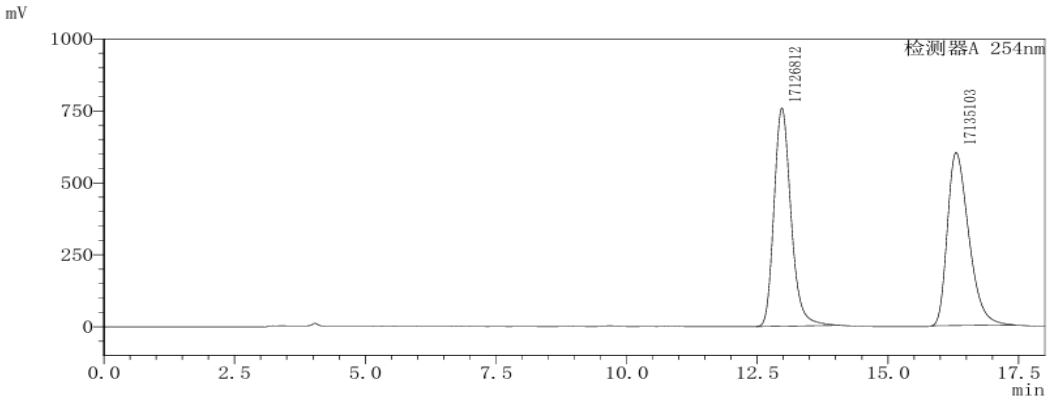


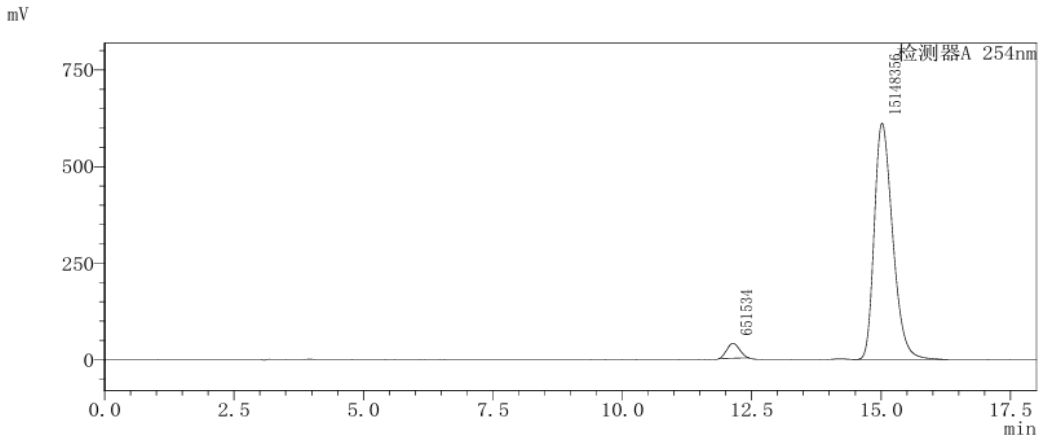
Compound **9**: white solid, 33% yield (10.0 mg), 92% *ee*, m.p. = 148.3 – 149.7 ℃. HPLC (chiral IA column), hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, *tr* (minor) = 12.14 min, *tr* (major) = 15.02 min. $[\alpha]^{25}_D$ = -138.7 (c = 0.1, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.66 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.57 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.36 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.33 – 7.19 (m, 3H), 7.18 – 7.09 (m, 2H), 4.89 (dd, *J* = 6.6, 2.5 Hz, 1H), 4.21 (s, 3H), 3.24 – 3.13 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 152.7, 143.1, 139.2, 136.5, 129.6, 128.8, 128.1, 128.0, 127.3, 127.0, 125.3, 123.0, 54.2, 37.8, 37.0.

HRMS (ESI-TOF), m/z calcd for $C_{19}H_{16}NO_3^+$ ([M + H]$^+$) 306.1125, found 306.1128.





Racemic			
	Retention Time	Area	%Area
1	12.971	17126812	49.988
2	16.305	17135103	50.012

Enantioenriched			
	Retention Time	Area	%Area
1	12.138	651534	4.124
2	15.019	15148356	95.876

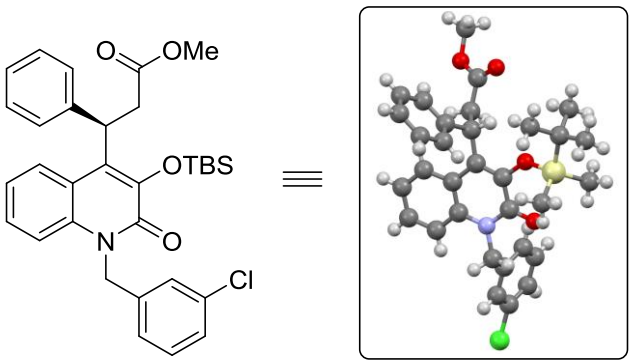
8 X-ray crystal structure

8.1 X-ray crystal Structure of Product 4g

Sample preparation Compound **4g** was recrystallized from mixture solvent of ethyl acetate, petroleum and dichloromethane ether by slowly evaporating the solvent at room temperature.

8.2 Experimental section

A suitable crystal was selected and on a Bruker APEX-II CCD diffractometer. The crystal was kept at 273.15 K during data collection. Using Olex2[11], the structure was solved with the SHELXS[12] structure solution program using Direct Methods and refined with the SHELXL[13] refinement package using Least Squares minimization.



CCDC: 2448156

Crystallographic Data of **4g**

Empirical formula	$C_{32}H_{36}ClNO_4Si$
Formula weight	562.16
Temperature/K	273.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.5508(7)
b/Å	11.5289(7)
c/Å	28.804(2)
α/°	90
β/°	90
γ/°	90

Volume/Å^3	3171.6(4)
Z	4
ρ_{calc}g/cm^3	1.177
μ/mm$^-$ 1	0.193
F(000)	1192.0
Crystal size/mm^3	0.4 × 0.4 × 0.35
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.494 to 55.068
Index ranges	-12 ⩽ h ⩽ 12, -14 ⩽ k ⩽ 14, -37 ⩽ l ⩽ 37
Reflections collected	91502
Independent reflections	7276 [R_{int} = 0.1176, R_{sigma} = 0.0479]
Data/restraints/parameters	7276/0/358
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0517, wR_2 = 0.1162
Final R indexes [all data]	R_1 = 0.0912, wR_2 = 0.1400
Largest diff. peak/hole / e Å^{-3}	0.35/-0.46
Flack parameter	-0.02(4)

9 Reference

[1] D. Zhang, Y. Fan, Z. Yan, Y. Nie, X. Xiong and L. Gao, *Green Chem.*, 2019, **21**, 4211–4216.

[2] S. K. Mal, A. Sharma, P. R. Maulik and I. Das, *Chem. – Eur. J.*, 2014, **20**, 662 —667.

[3] Z. Zheng, Q. Liu, X. Peng, Z. Jin and J. Wu, *Org. Lett.*, 2024, **26**, 917–921.

[4] I. Piel, M. Steinmetz, K. Hirano, R. Fröhlich, S. Grimme and F. Glorius, *Angew. Chem. Int. Ed.*, 2011, **50**, 4983–4987.

[5] C. D. Campbell, C. J. Collett, J. E. Thomson, A. M. Z. Slawin and A. D. Smith, *Org. Biomol. Chem.*, 2011, **9**, 4205.

[6] E. Sánchez-Larios, K. Thai, F. Bilodeau and M. Gravel, *Org. Lett.*, 2011, **13**, 4942–4945.

[7] Y. Wei, G. Bai, J. Wu, Y. Hua, T. Zhang, C. Yue, H. Wang and X. Bao, *Org. Chem. Front.*, 2025, **12**, 497–502.

[8] J. Wu, F. Hu, G. Bai, Y. Yang, D. Bonne, J. Rodriguez, C. Yue, H. Wang and X. Bao, *Eur. J. Org. Chem.*, 2023, **26**, e202300218.

[10] K. L. Skubi, J. B. Kidd, H. Jung, I. A. Guzei, M.-H. Baik and T. P. Yoon, *J. Am. Chem. Soc.*, 2017, **139**, 17186–17192.

[11] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

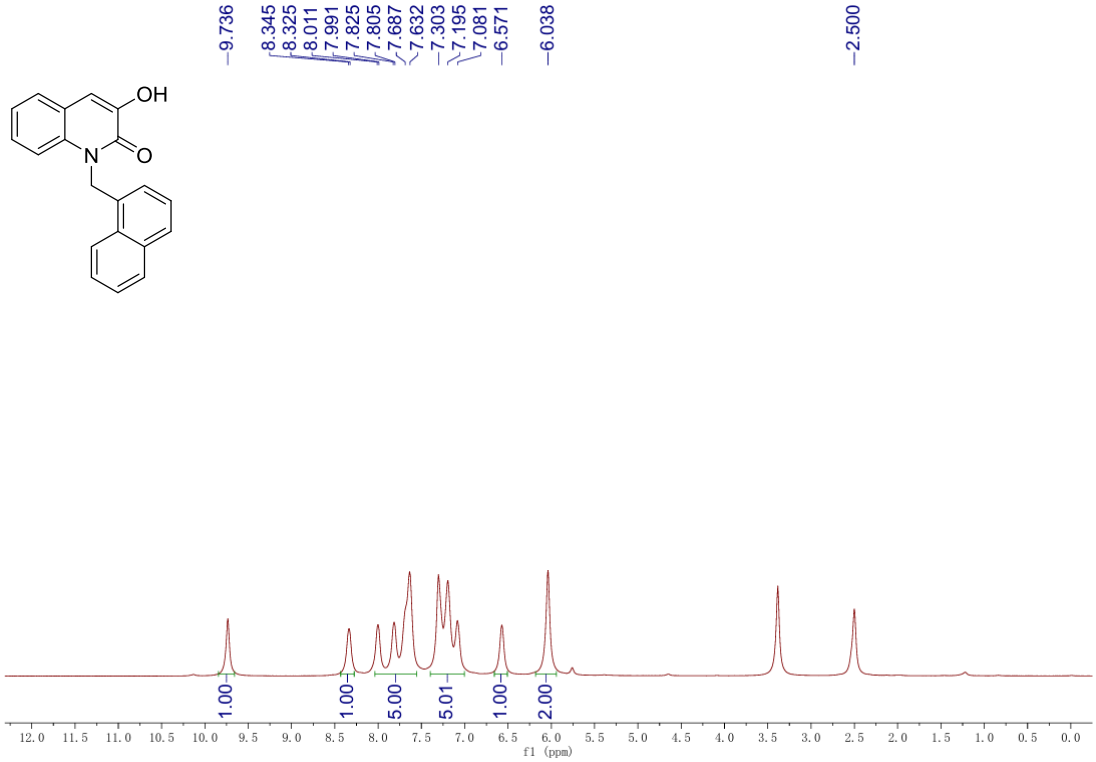
[12] G. M. Sheldrick, *Acta. Cryst.*, 2008, **A64**, 112-122.

[13] G. M. Sheldrick, *Acta. Cryst.*, 2015, **A71** , 3-8.

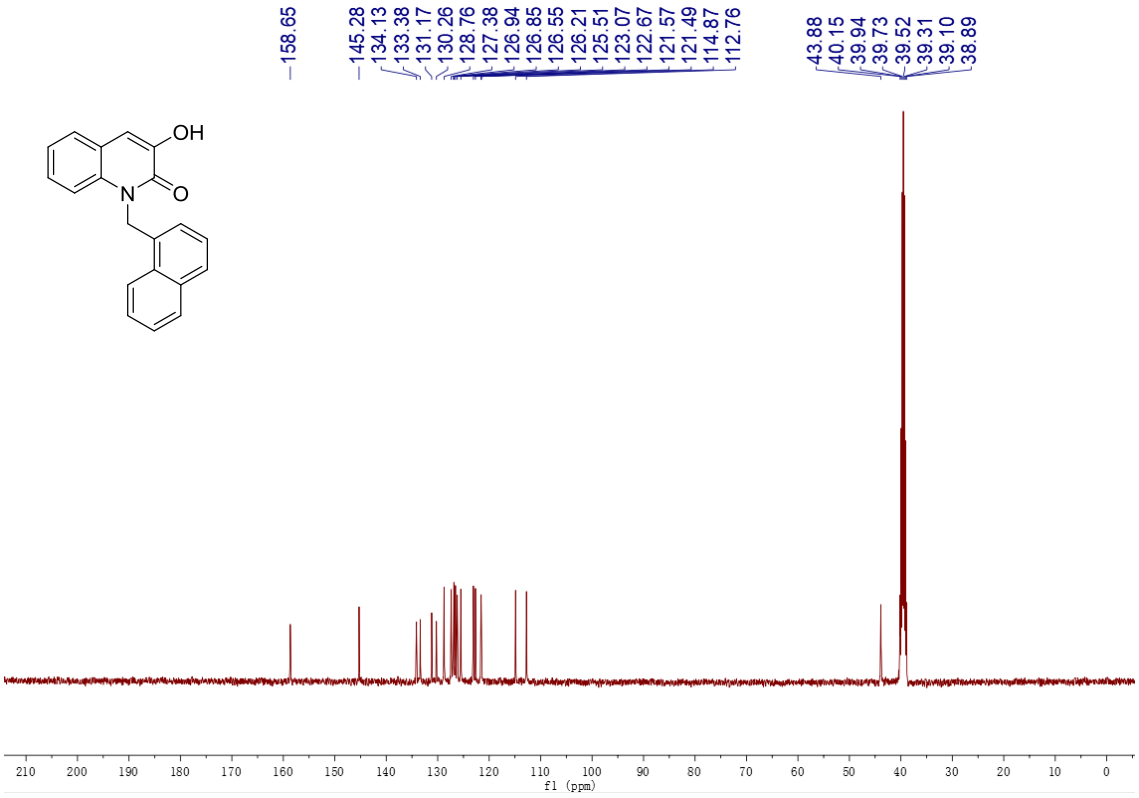
10 NMR spectra of substrates and catalytic products

3-hydroxy-1-(naphthalen-1-ylmethyl)quinolin-2(1*H*)-one (1a)

NMR (400 MHz, DMSO-d_6)

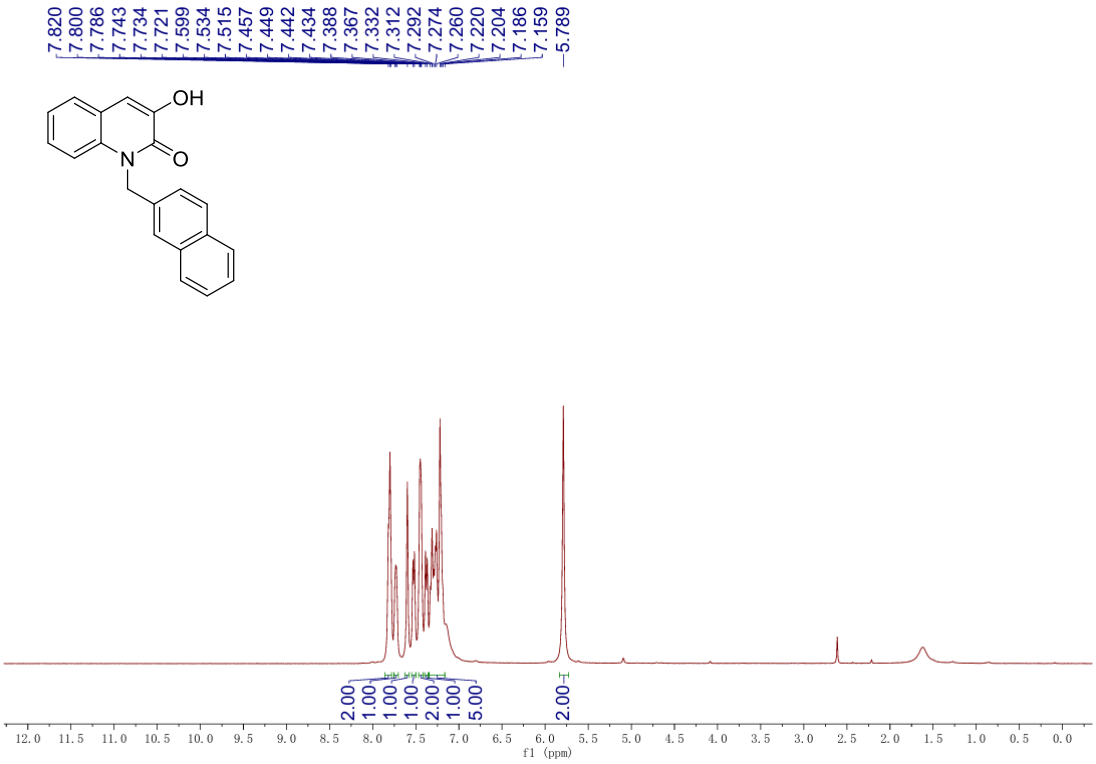


$^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6)

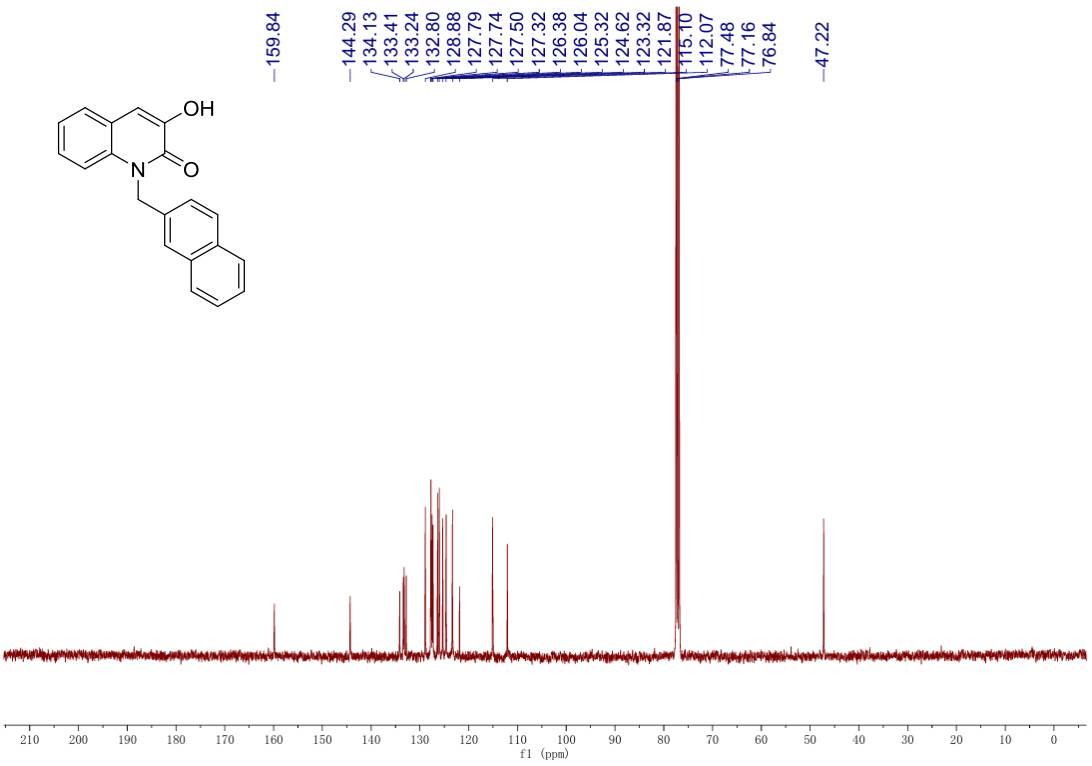


3-hydroxy-1-(naphthalen-2-ylmethyl) quinolin-2(1*H*)-one (1b)

NMR (400 MHz, $CDCl_3$)

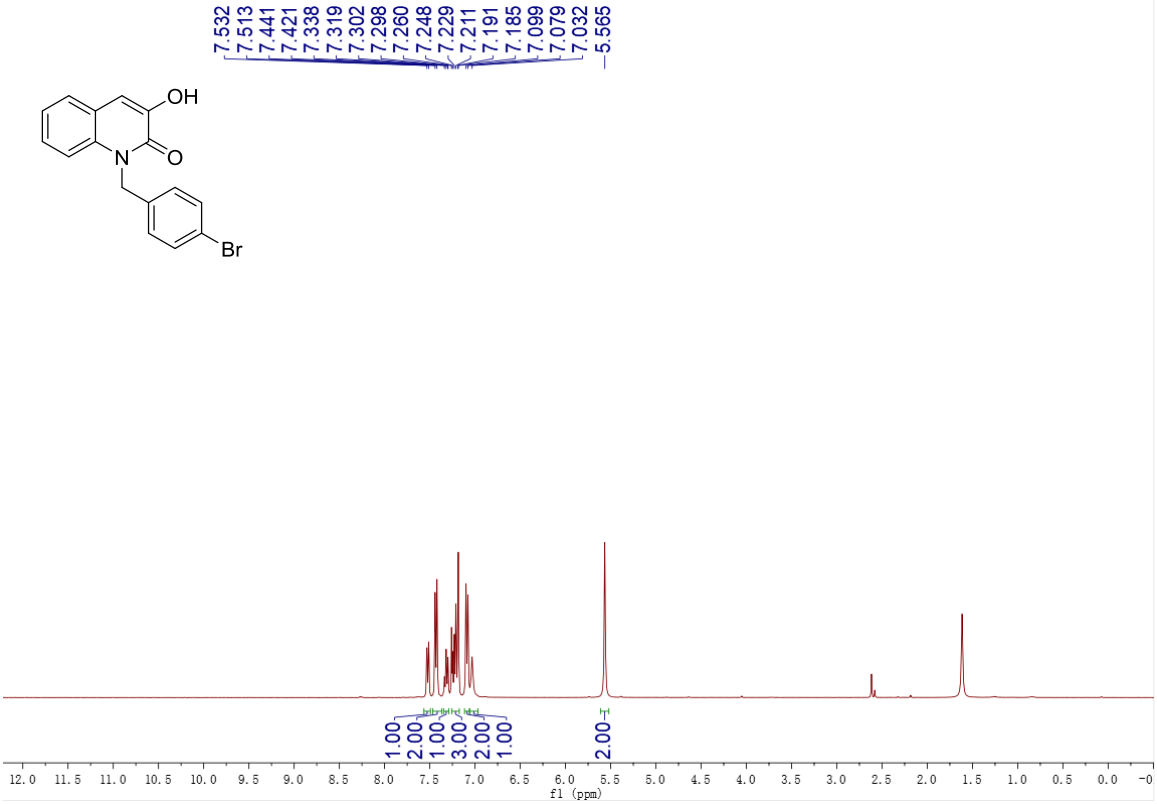


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

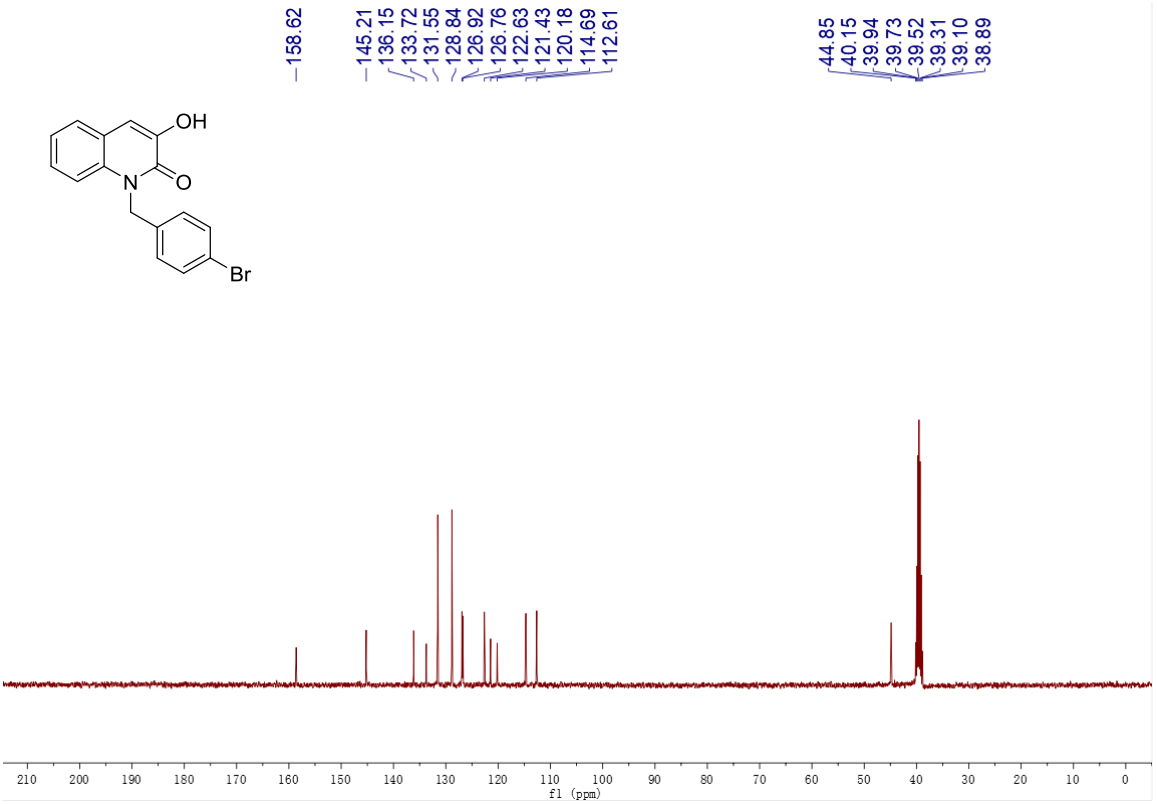


1-(4-bromobenzyl)-3-hydroxyquinolin-2(1*H*)-one (1c)

NMR (400 MHz, $CDCl_3$)

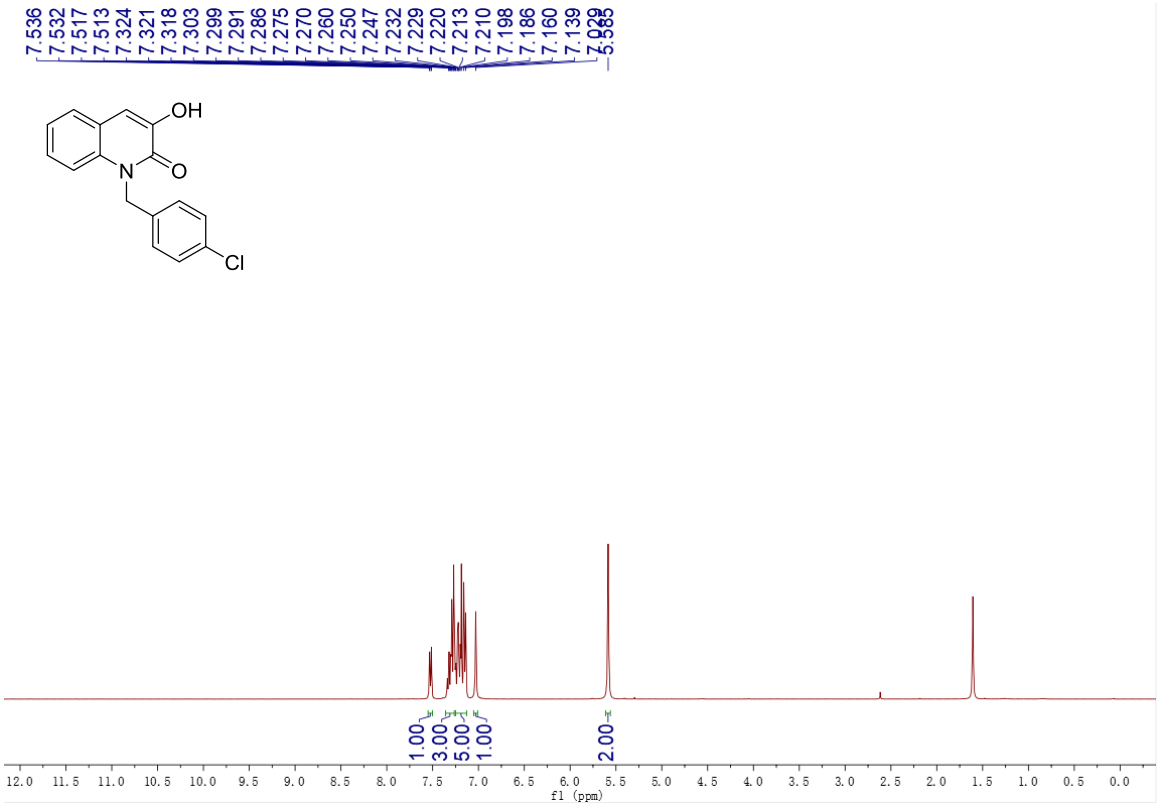


$^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6)

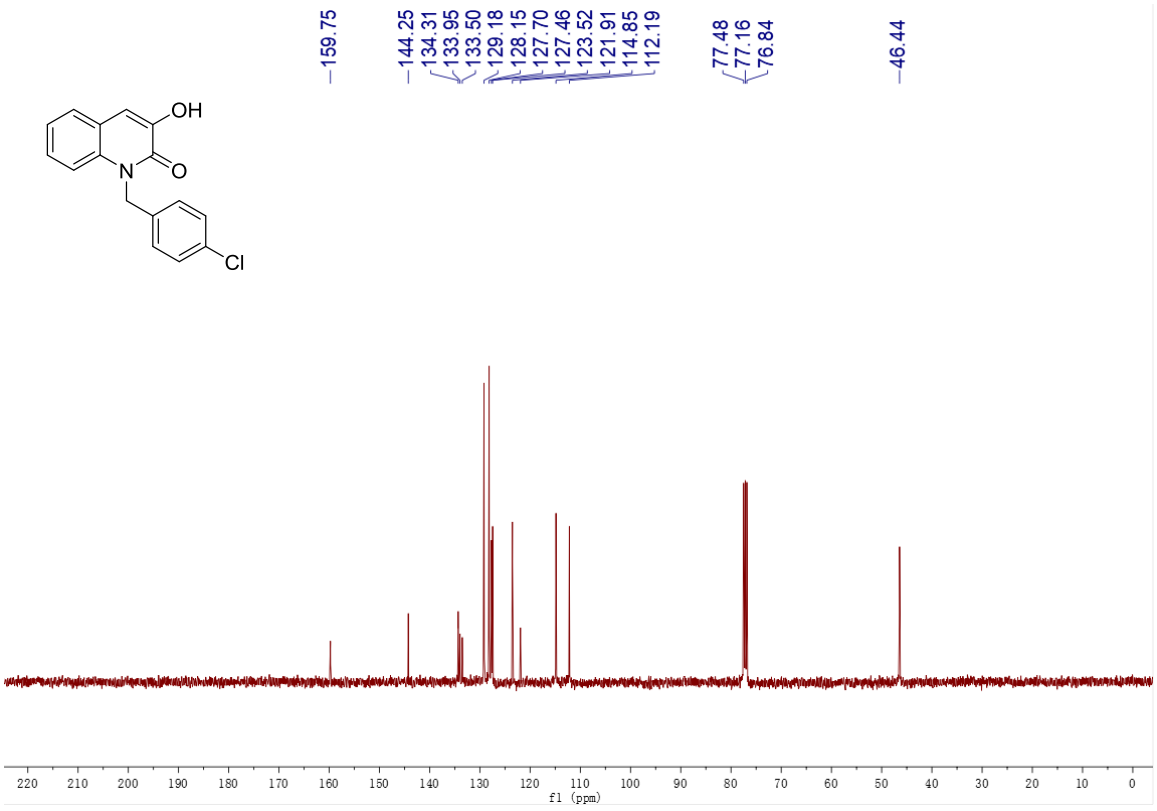


1-(4-chlorobenzyl)-3-hydroxyquinolin-2(1*H*)-one (1d)

NMR (400 MHz, $CDCl_3$)

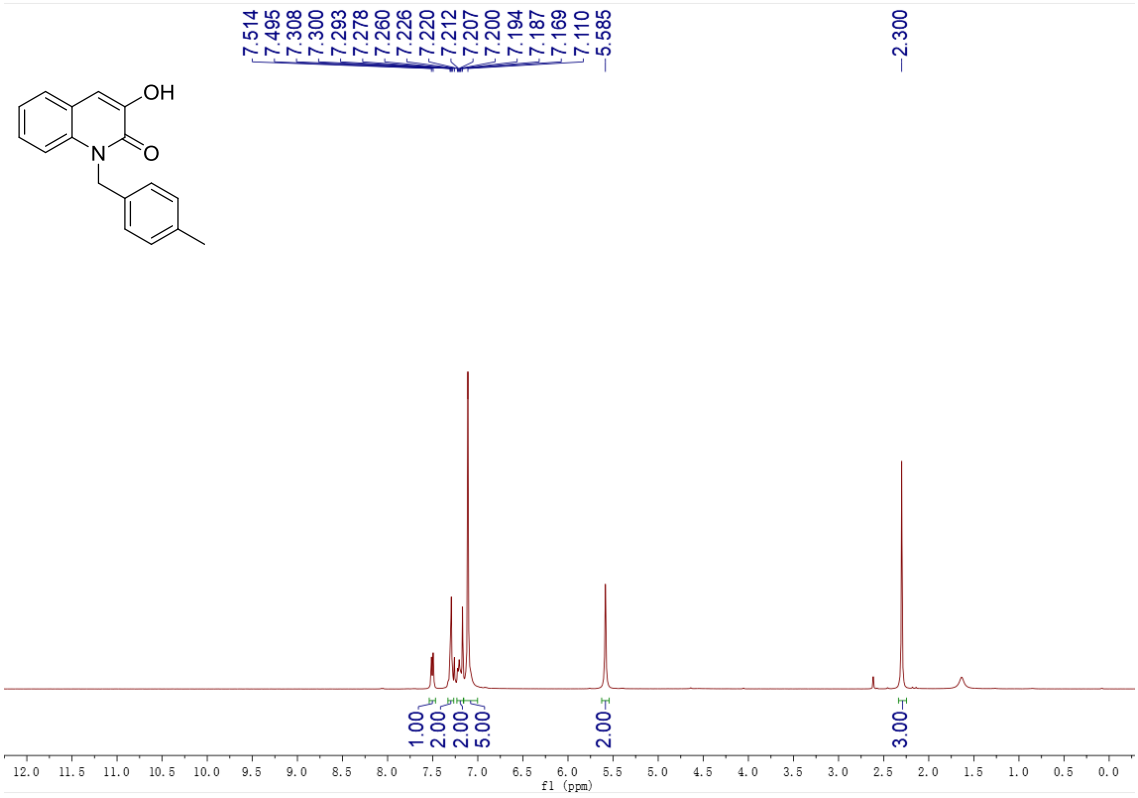


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

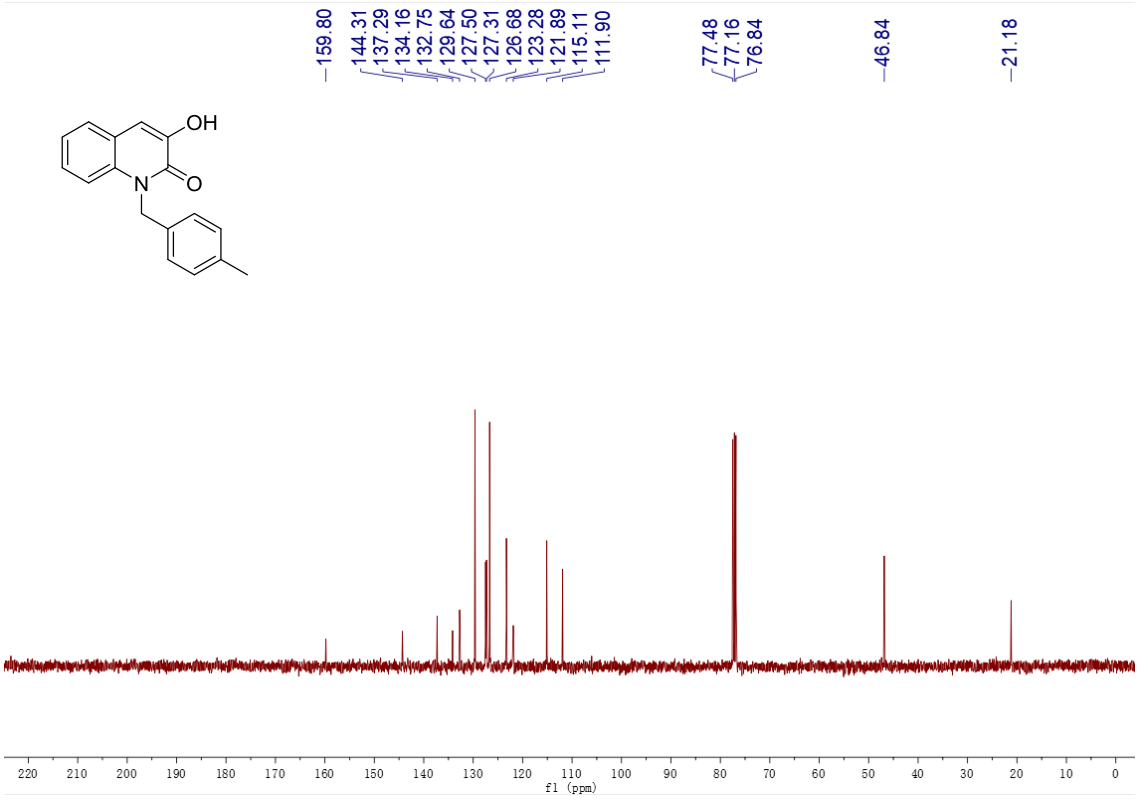


3-hydroxy-1-(4-methylbenzyl)quinolin-2(1*H*)-one (1e)

NMR (400 MHz, $CDCl_3$)

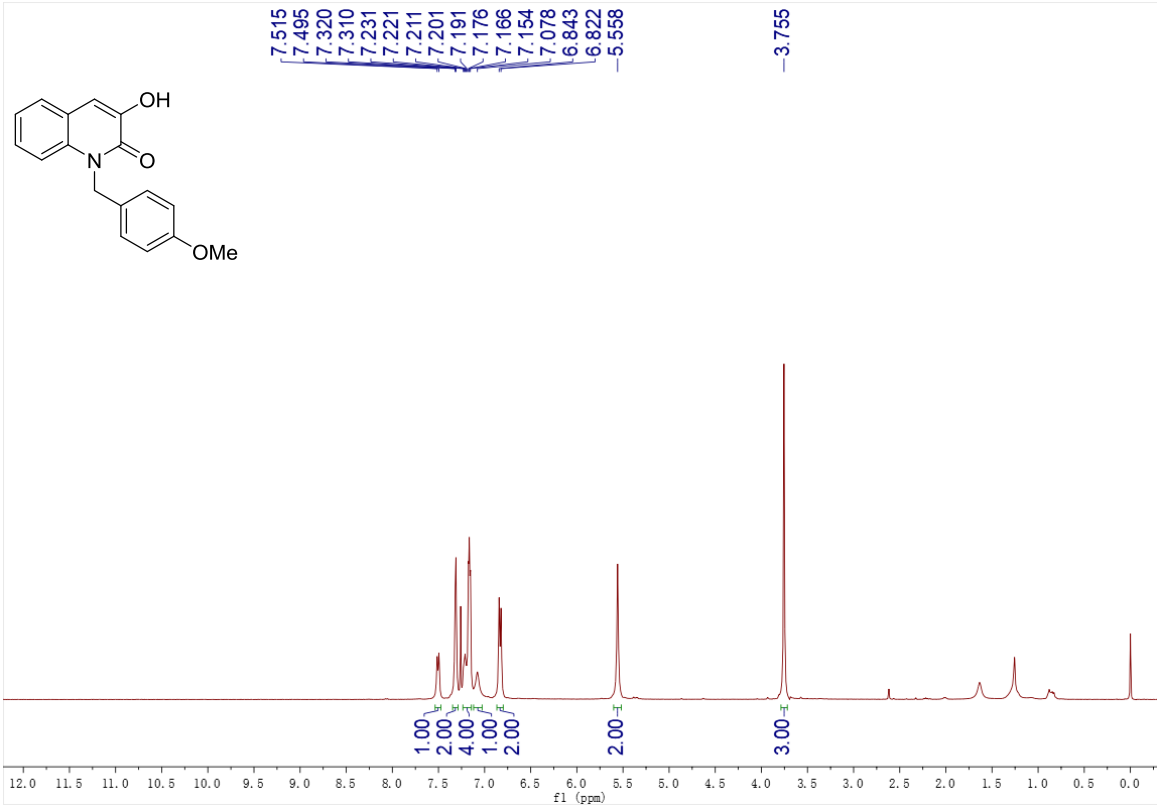


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

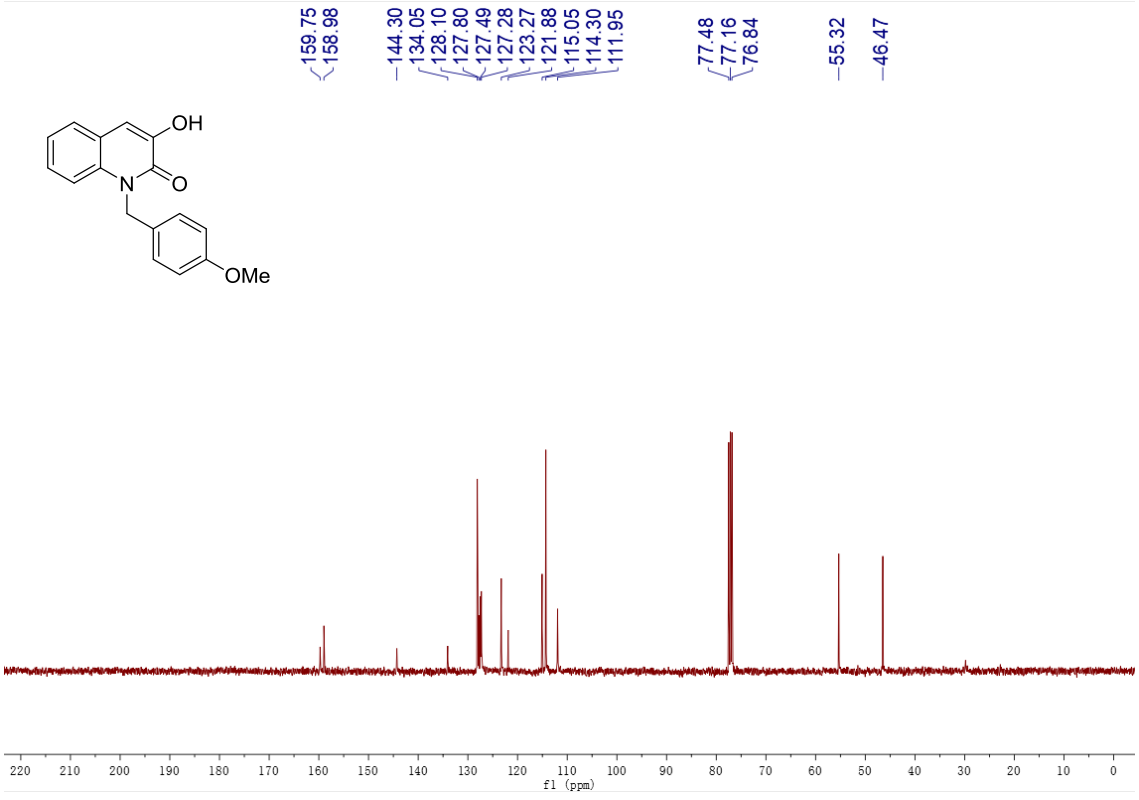


3-hydroxy-1-(4-methoxybenzyl)quinolin-2(1*H*)-one (1f)

NMR (400 MHz, $CDCl_3$)

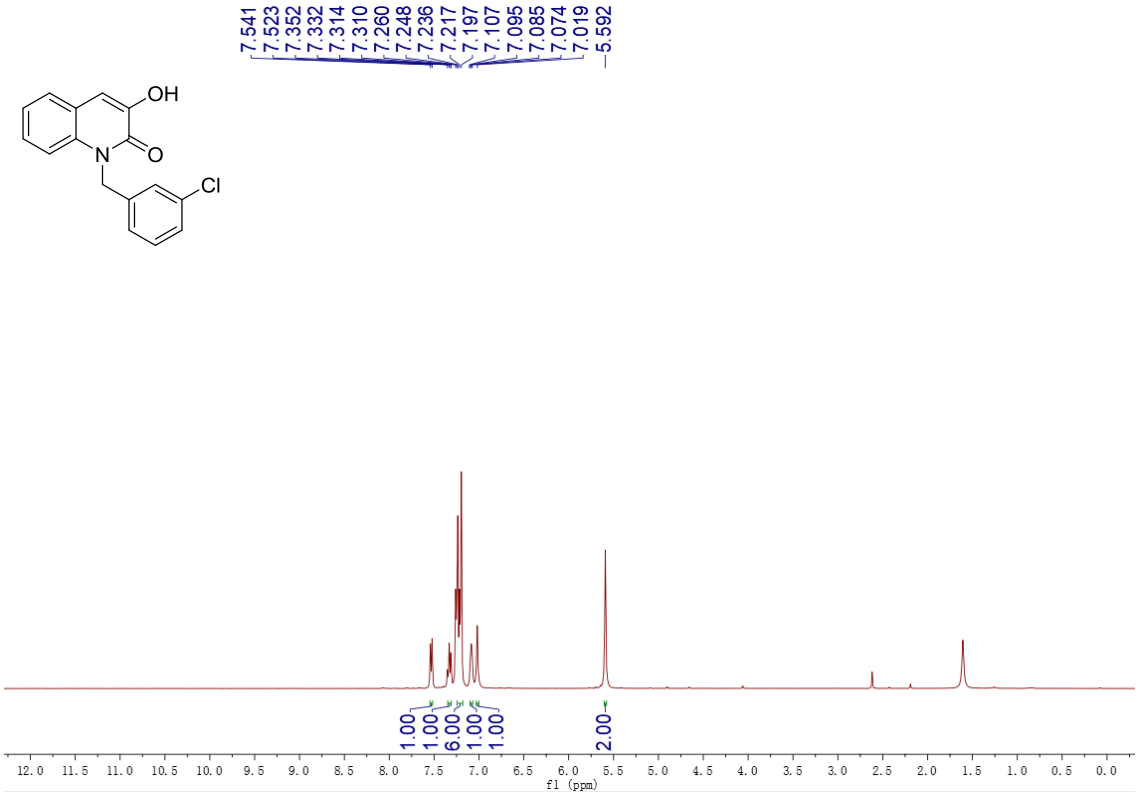


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

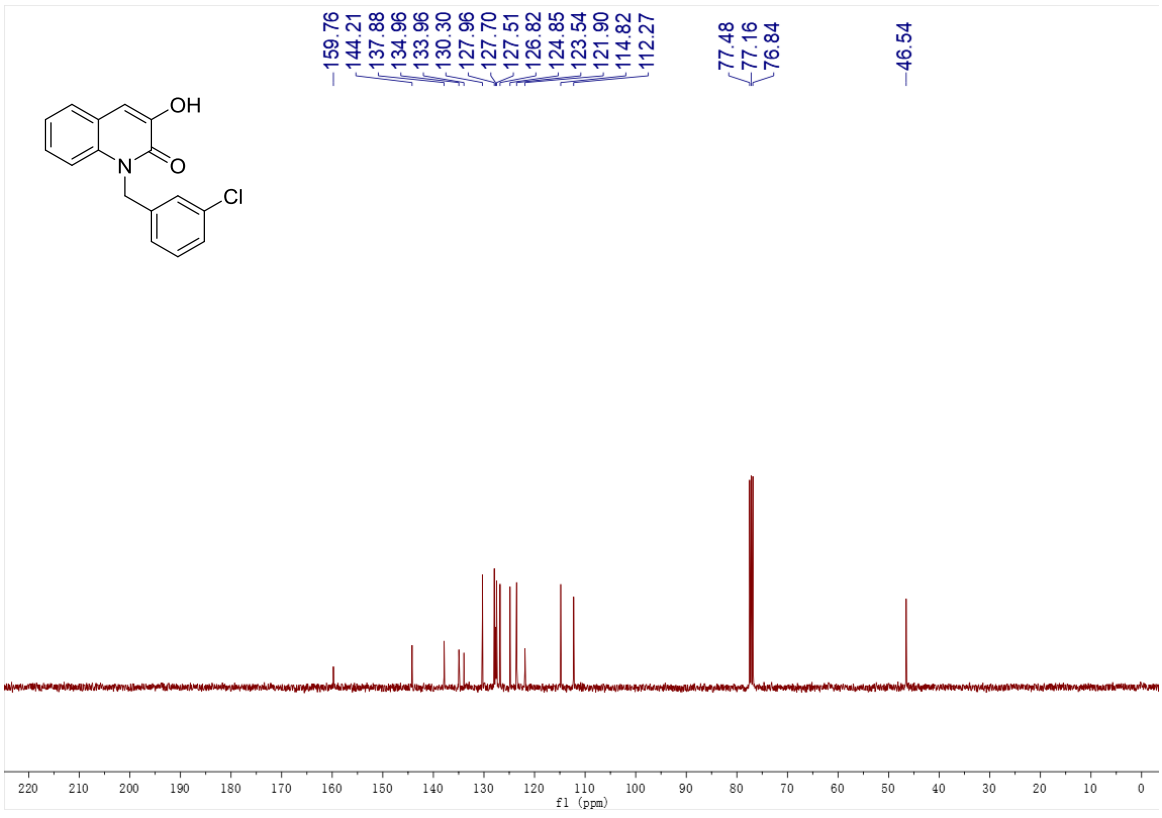


1-(3-chlorobenzyl)-3-hydroxyquinolin-2(1*H*)-one (1g)

NMR (400 MHz, $CDCl_3$)

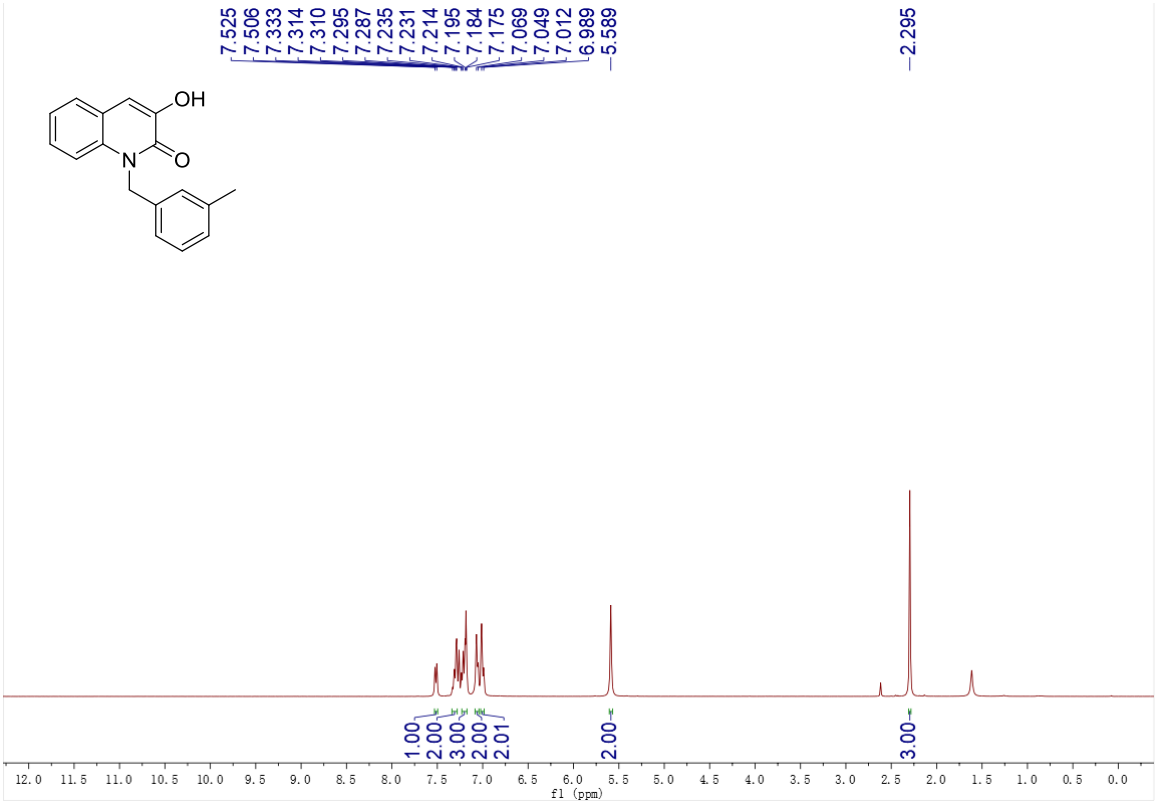


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

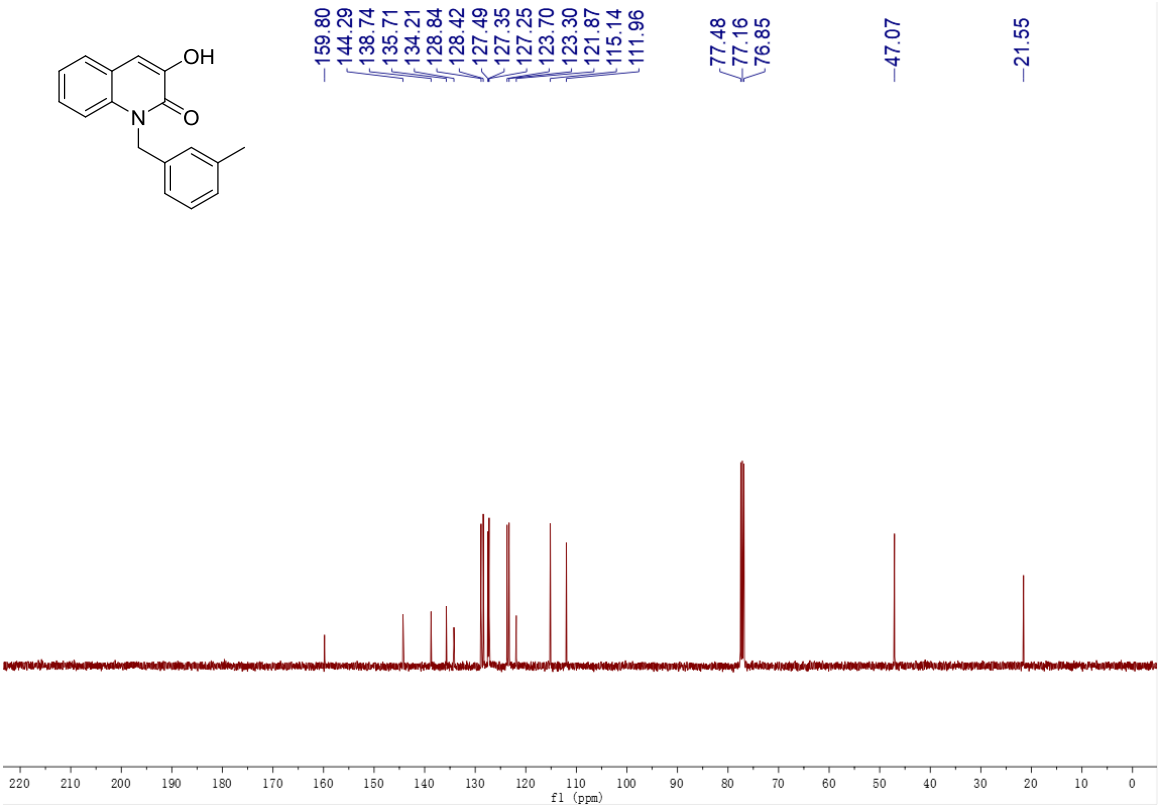


3-hydroxy-1-(3-methylbenzyl)quinolin-2(1*H*)-one (1h)

NMR (400 MHz, $CDCl_3$)

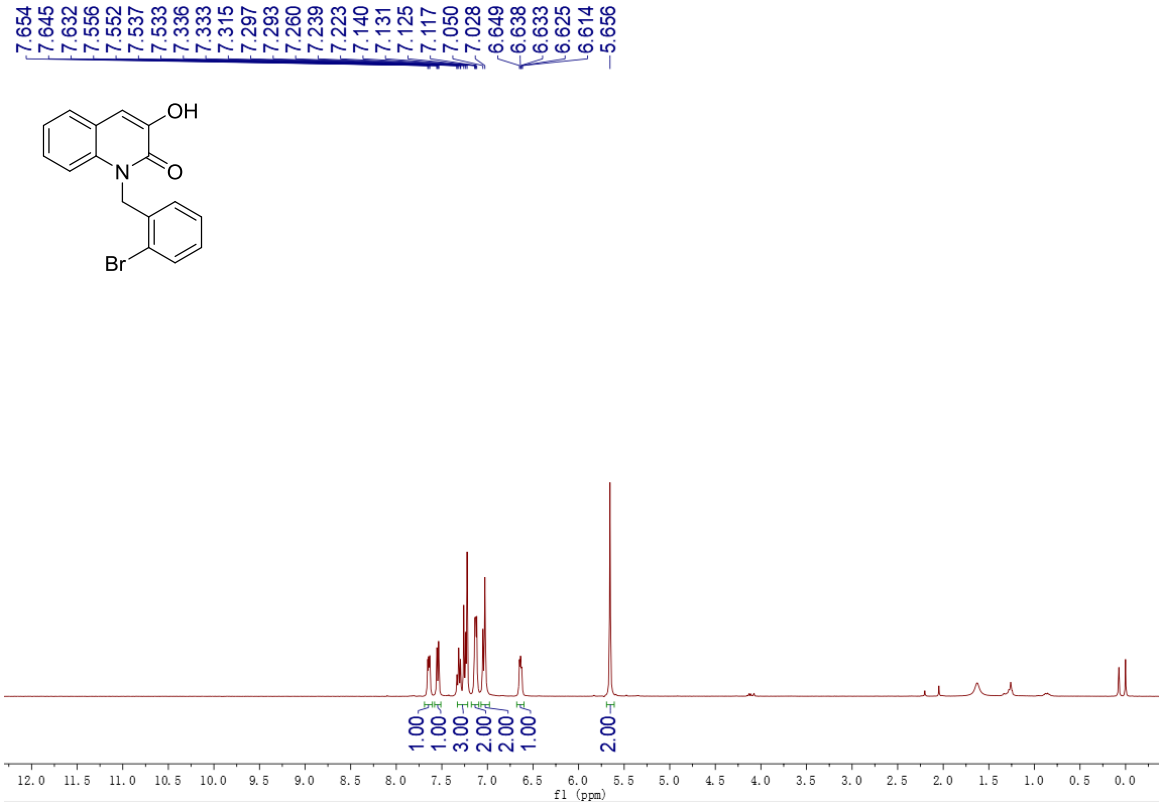


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

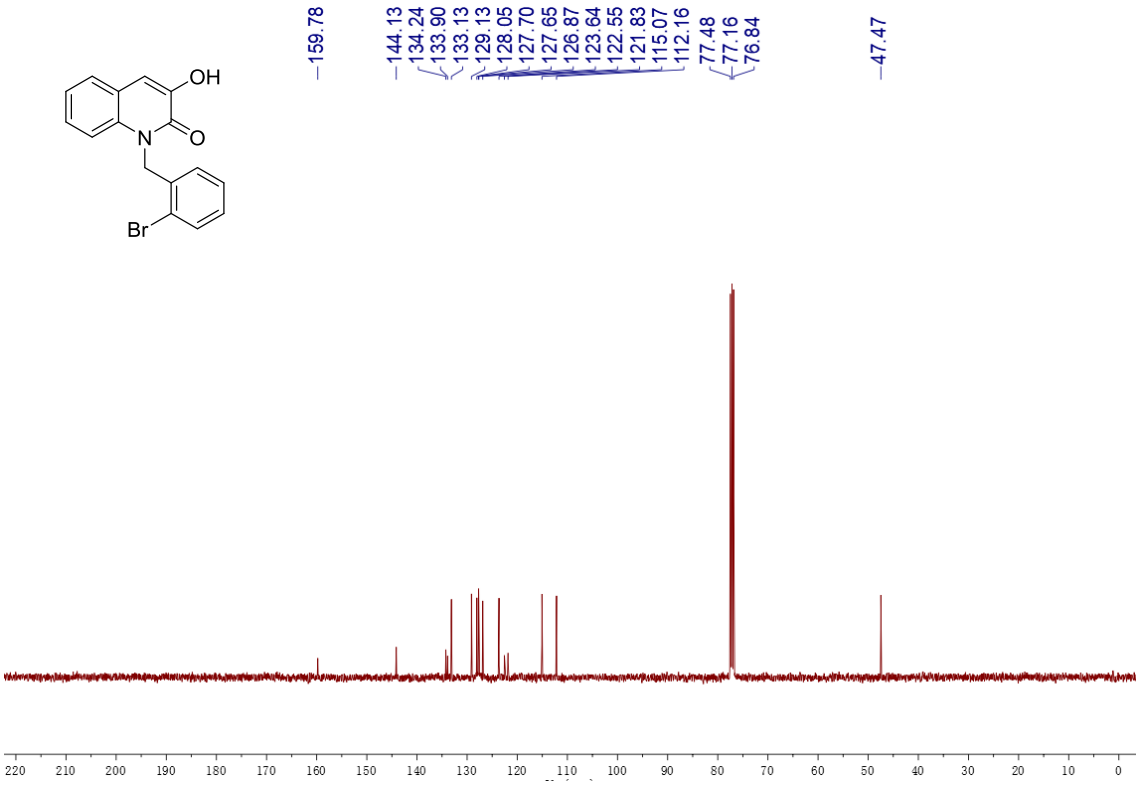


1-(2-bromobenzyl)-3-hydroxyquinolin-2(1*H*)-one (1i)

NMR (400 MHz, $CDCl_3$)

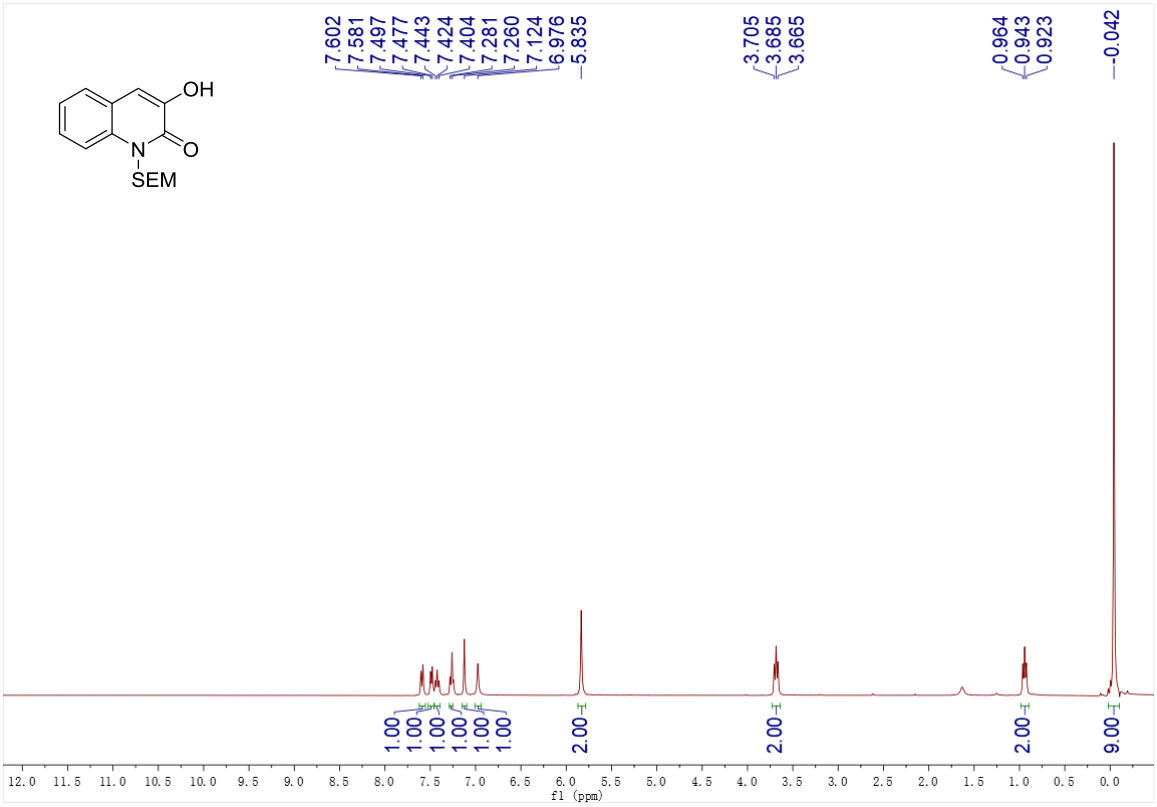


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

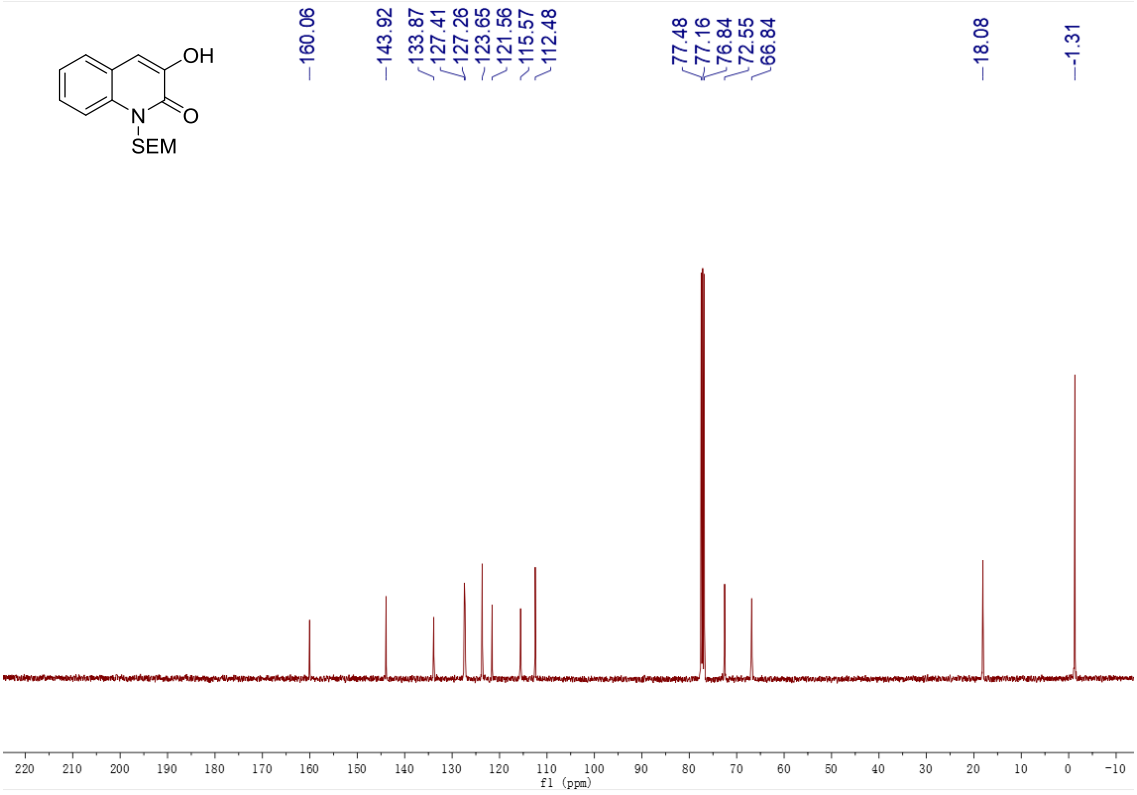


3-hydroxy-1-((2-(trimethylsilyl) ethoxy) methyl) quinolin-2(1*H*)-one (1j)

NMR (400 MHz, $CDCl_3$)

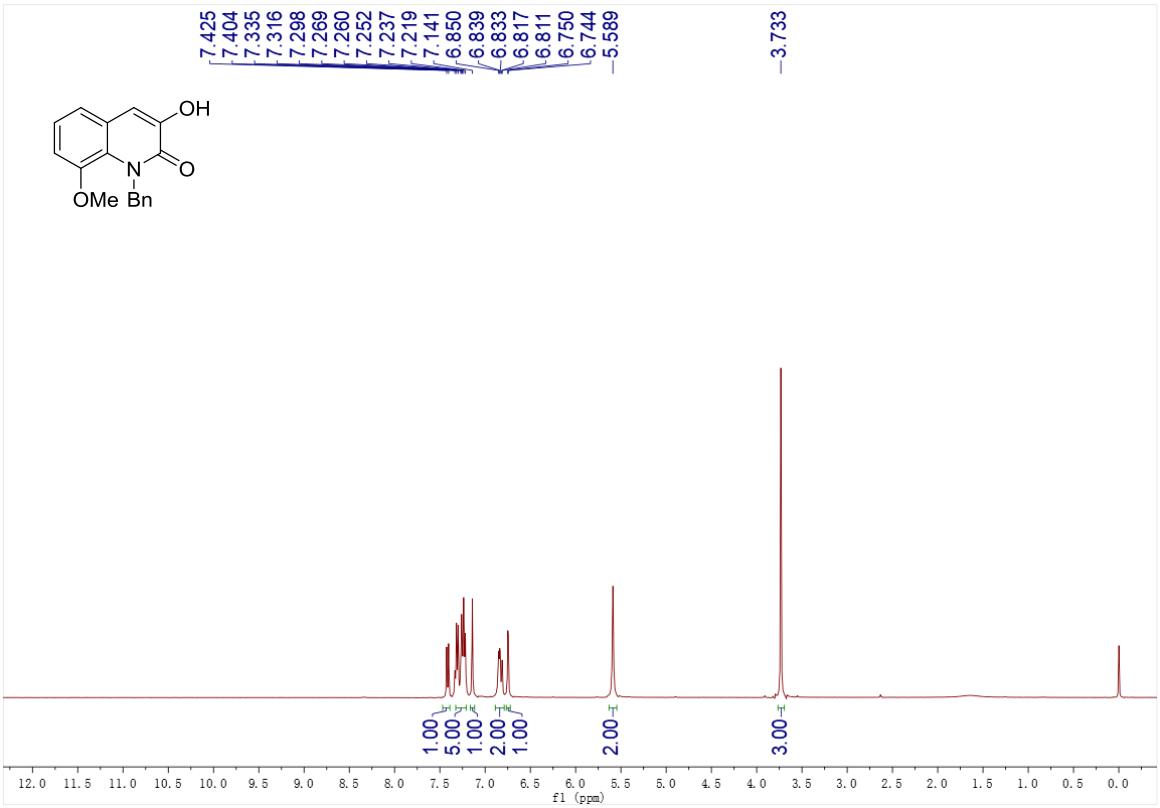


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

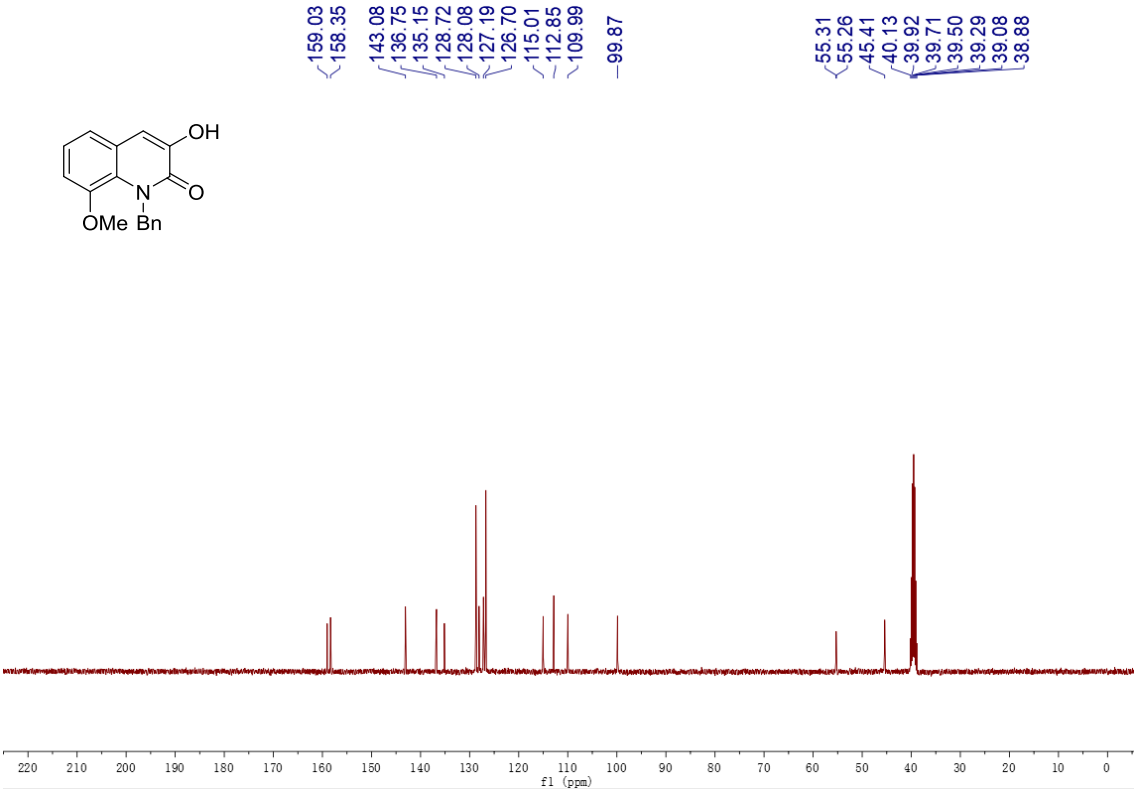


1-benzyl-3-hydroxy-8-methoxyquinolin-2(1*H*)-one (1l)

NMR (400 MHz, $CDCl_3$)

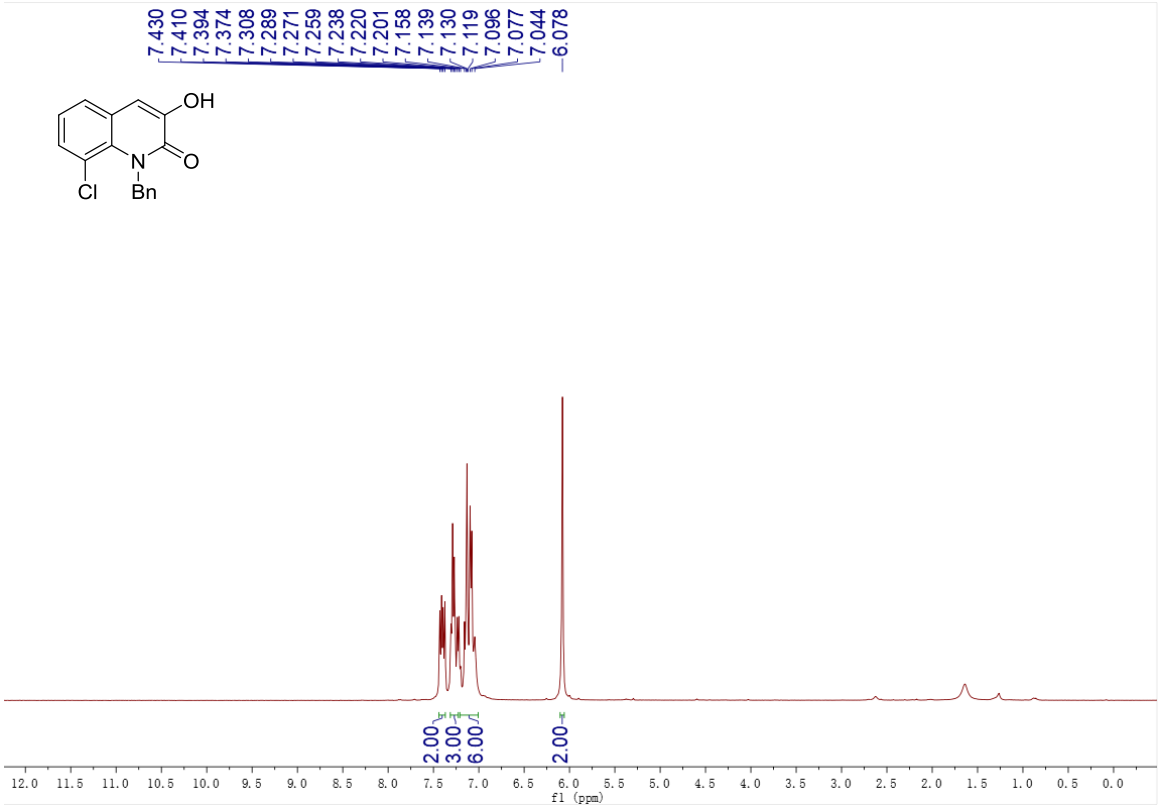


$^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6)

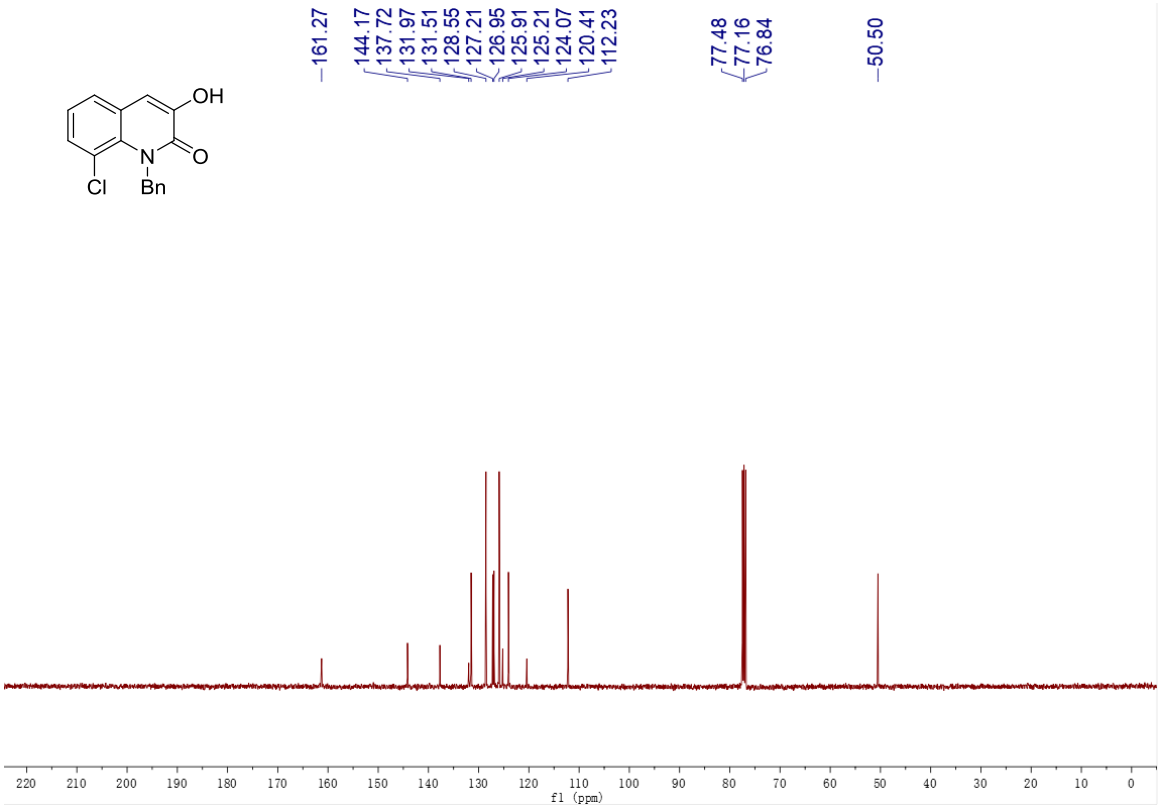


1-benzyl-8-chloro-3-hydroxyquinolin-2(1*H*)-one (1m)

NMR (400 MHz, $CDCl_3$)

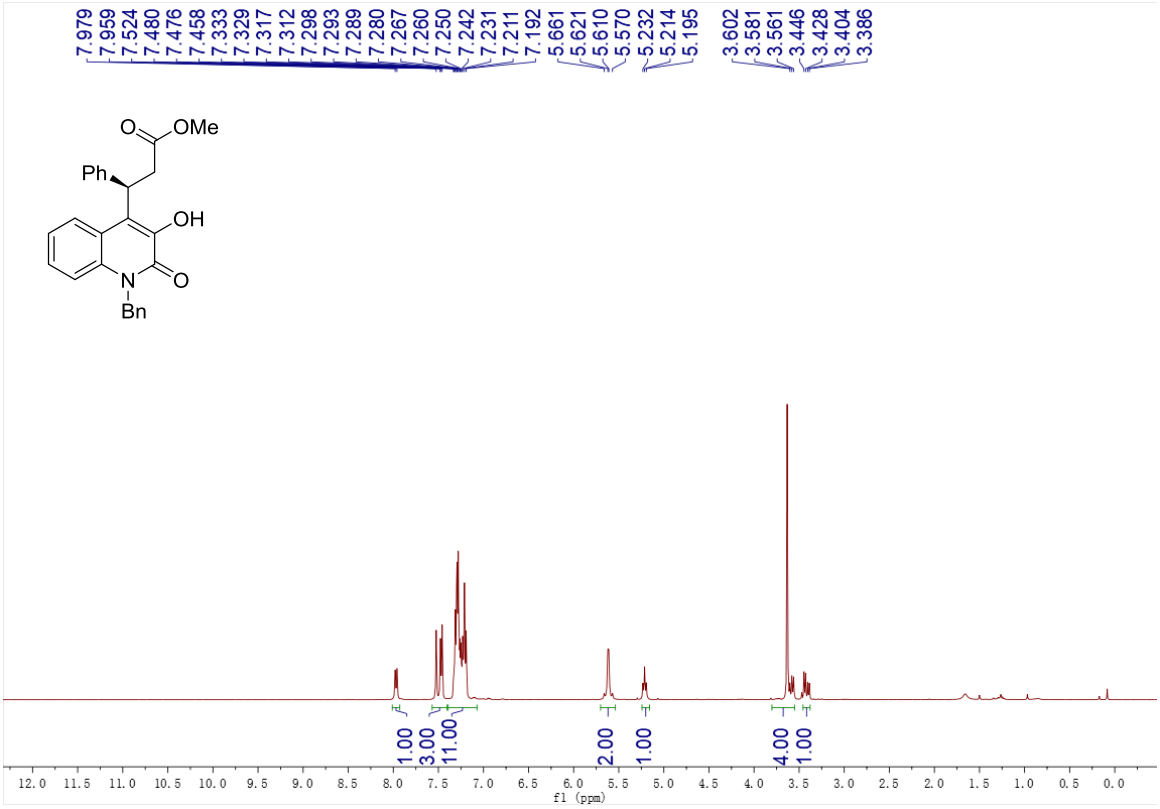


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

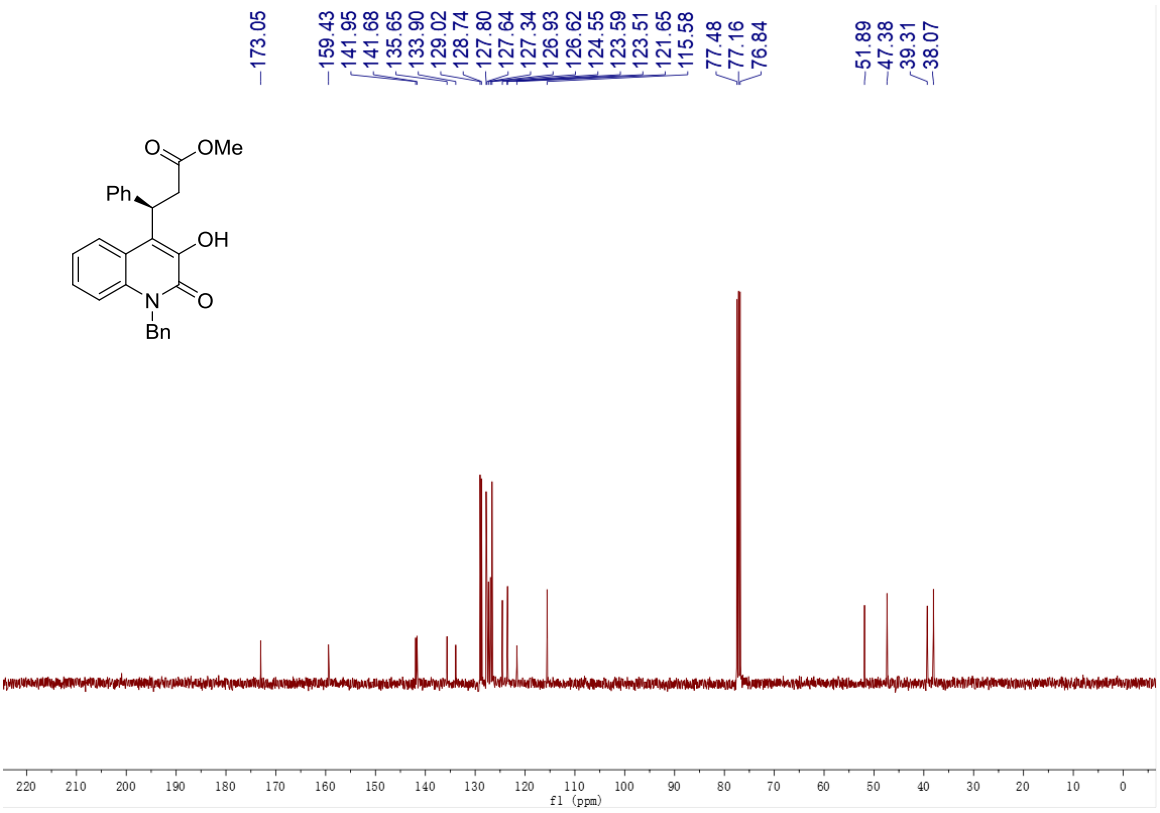


Methyl (R)-3-(1-benzyl-3-hydroxy-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (3a)

NMR (400 MHz, $CDCl_3$)

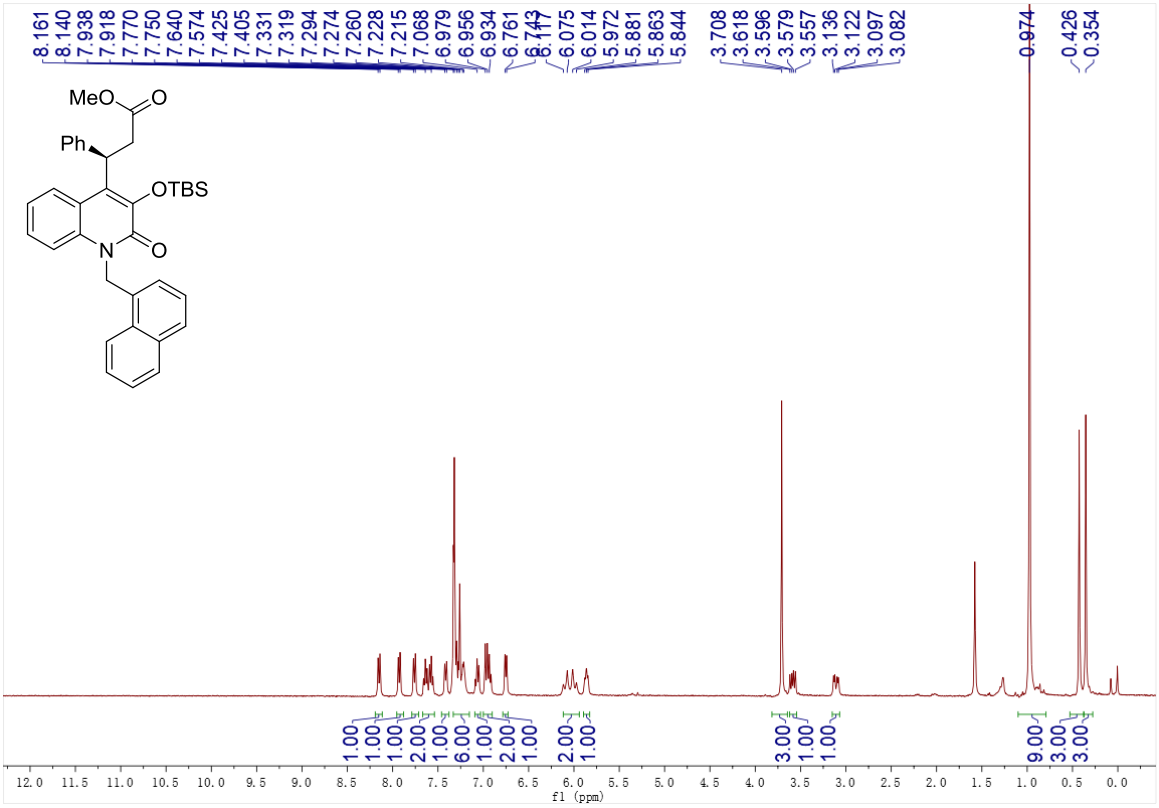


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

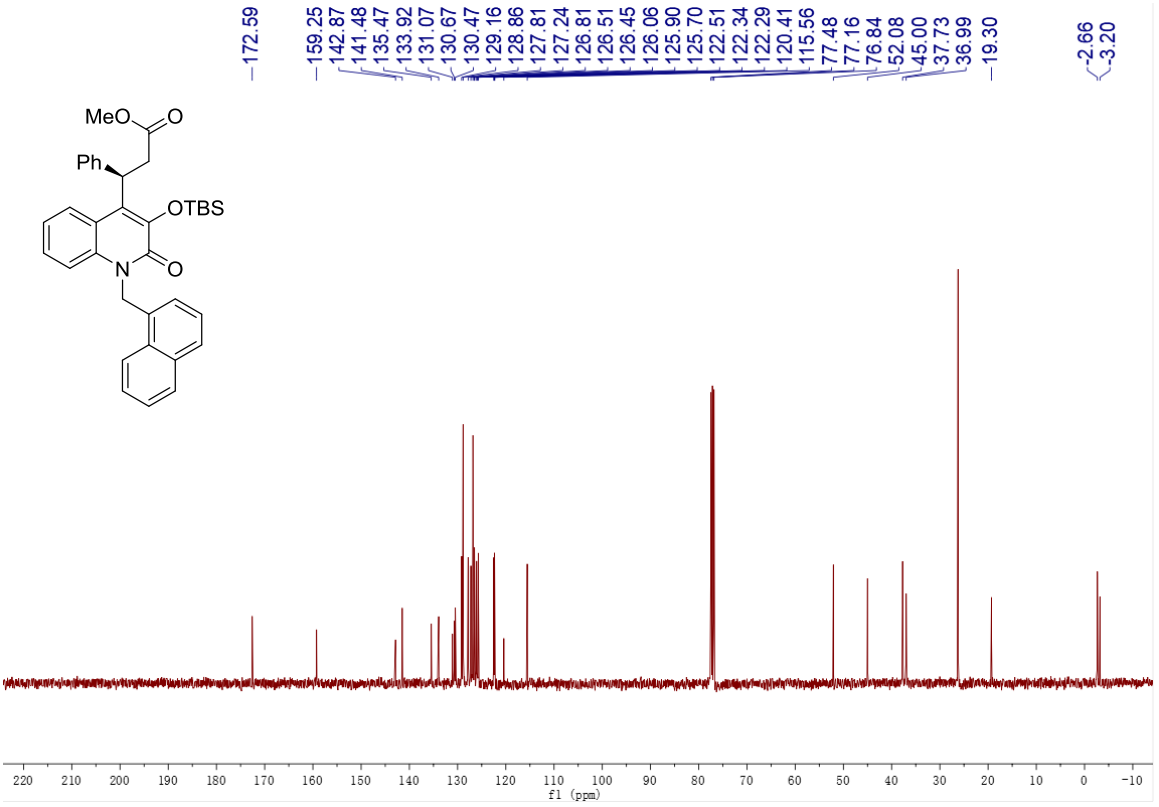


Methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(naphthalen-1-ylmethyl)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4a)

NMR (400 MHz, $CDCl_3$)

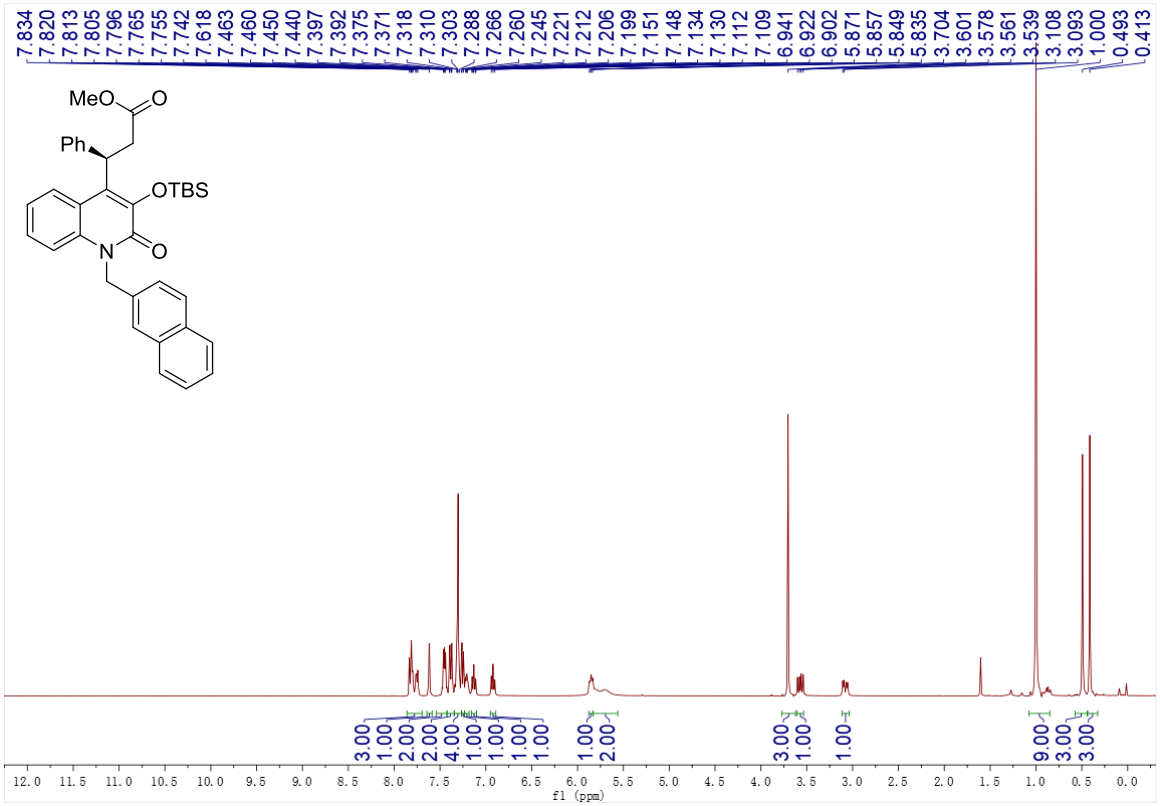


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

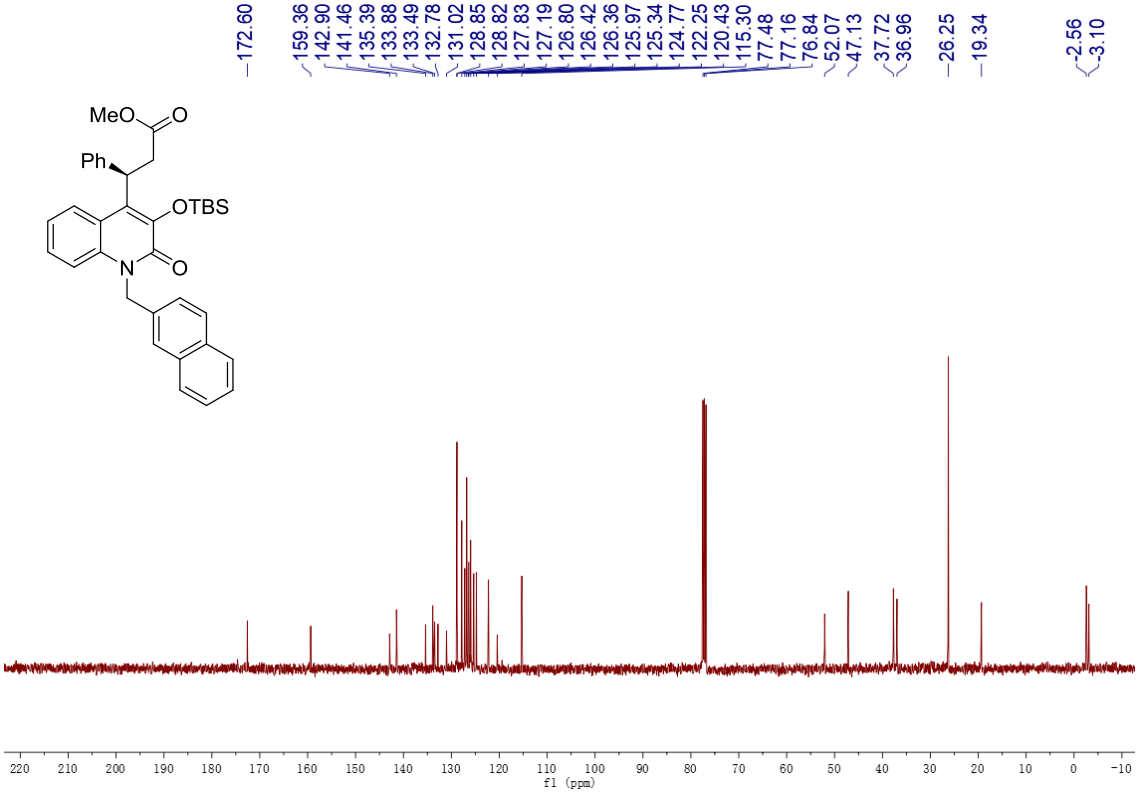


Methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(naphthalen-2-ylmethyl)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4b)

NMR (400 MHz, $CDCl_3$)

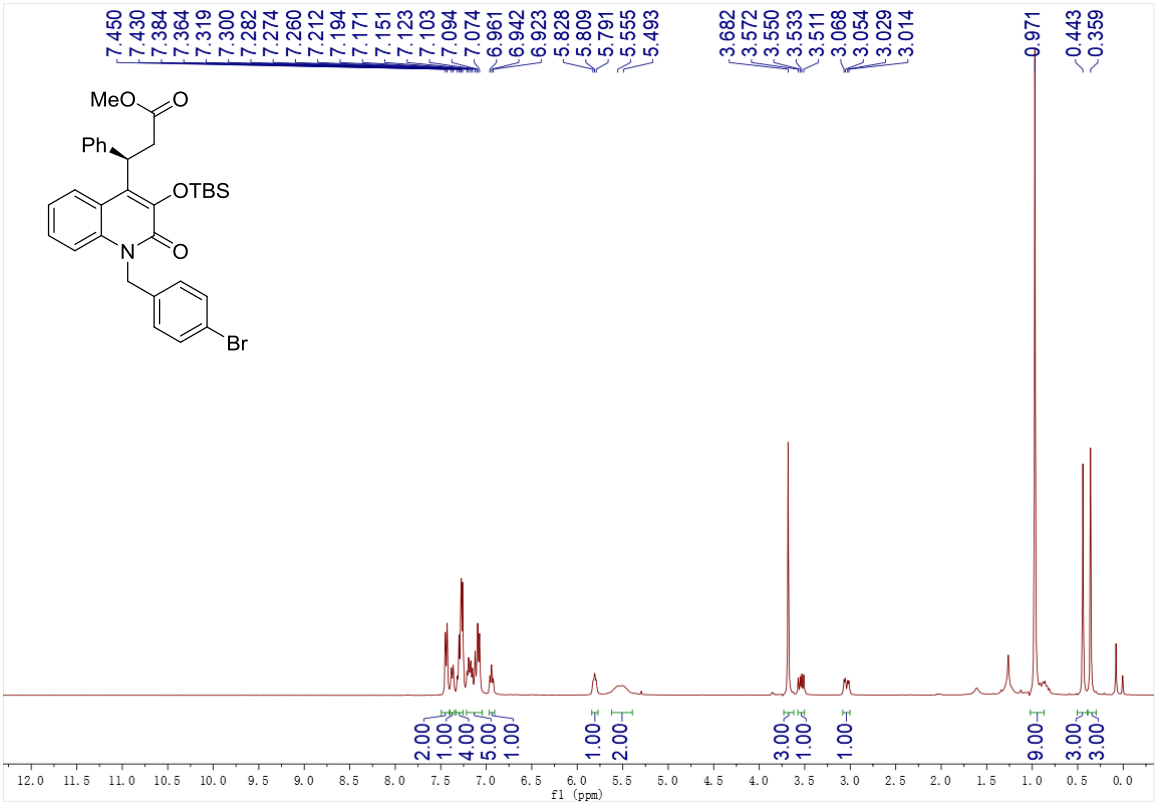


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

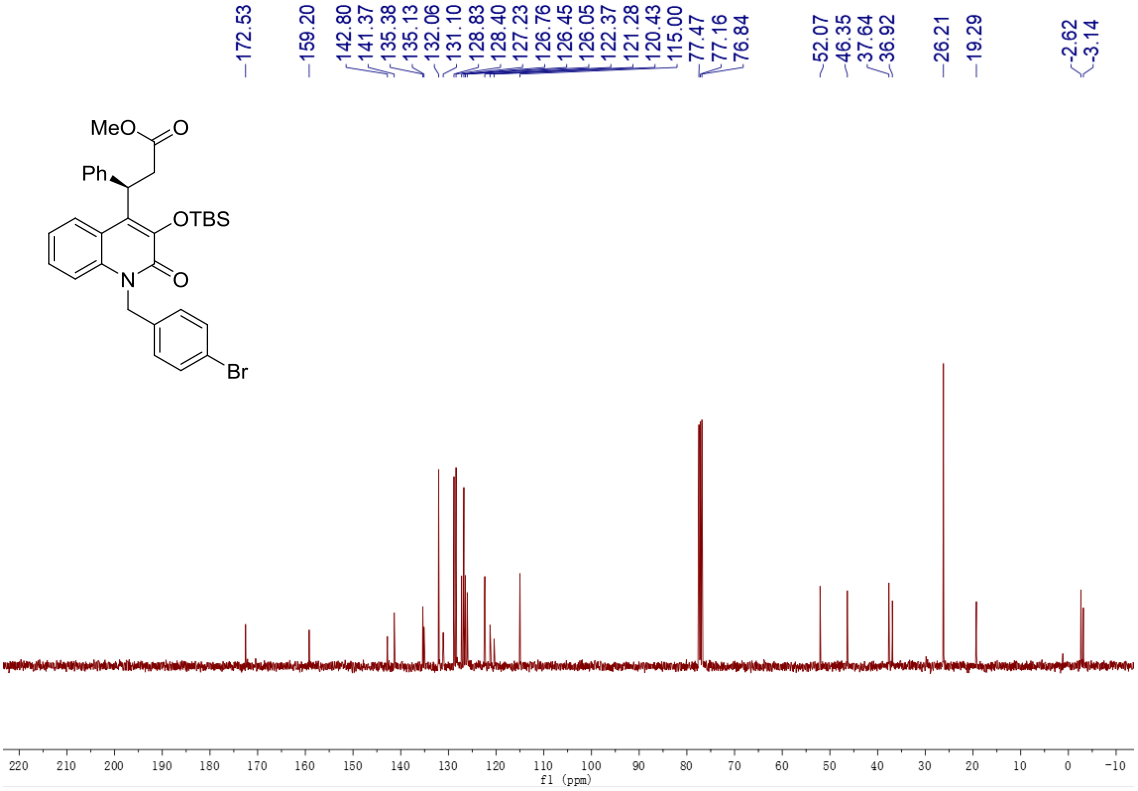


methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydro quinolin-4-yl)-3-phenylpropanoate (4c)

NMR (400 MHz, $CDCl_3$)

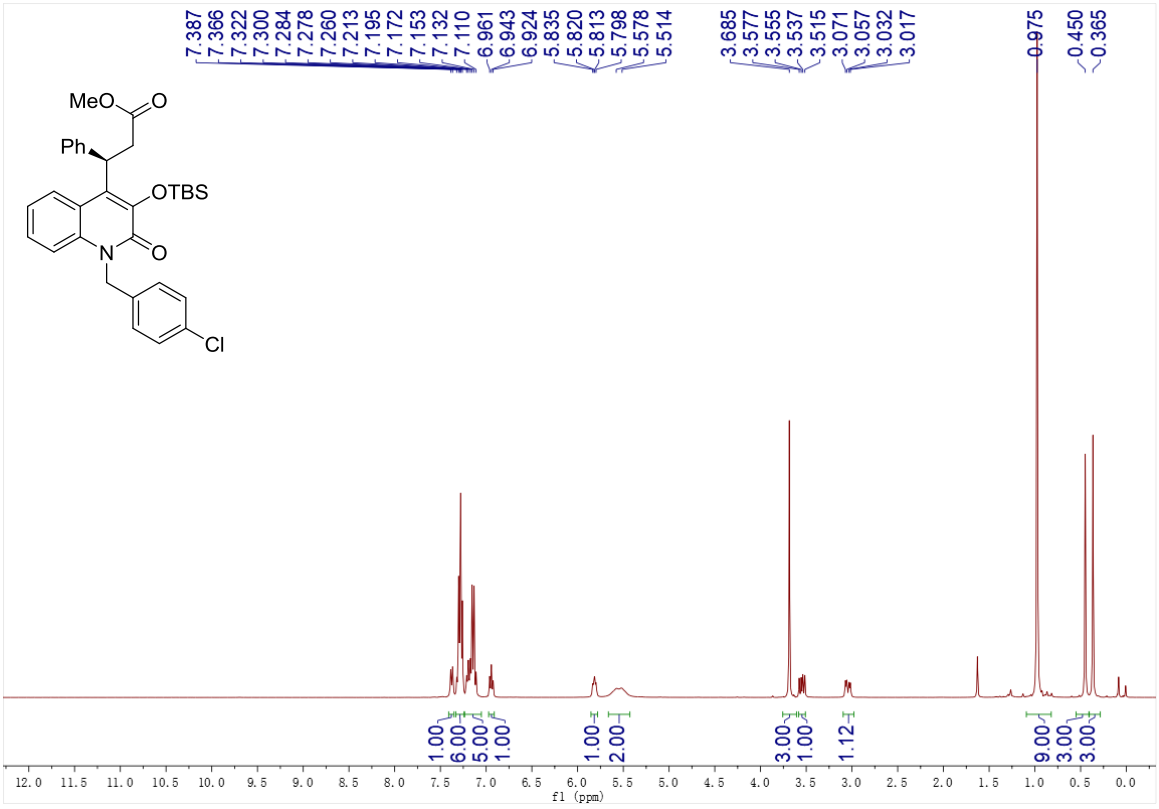


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

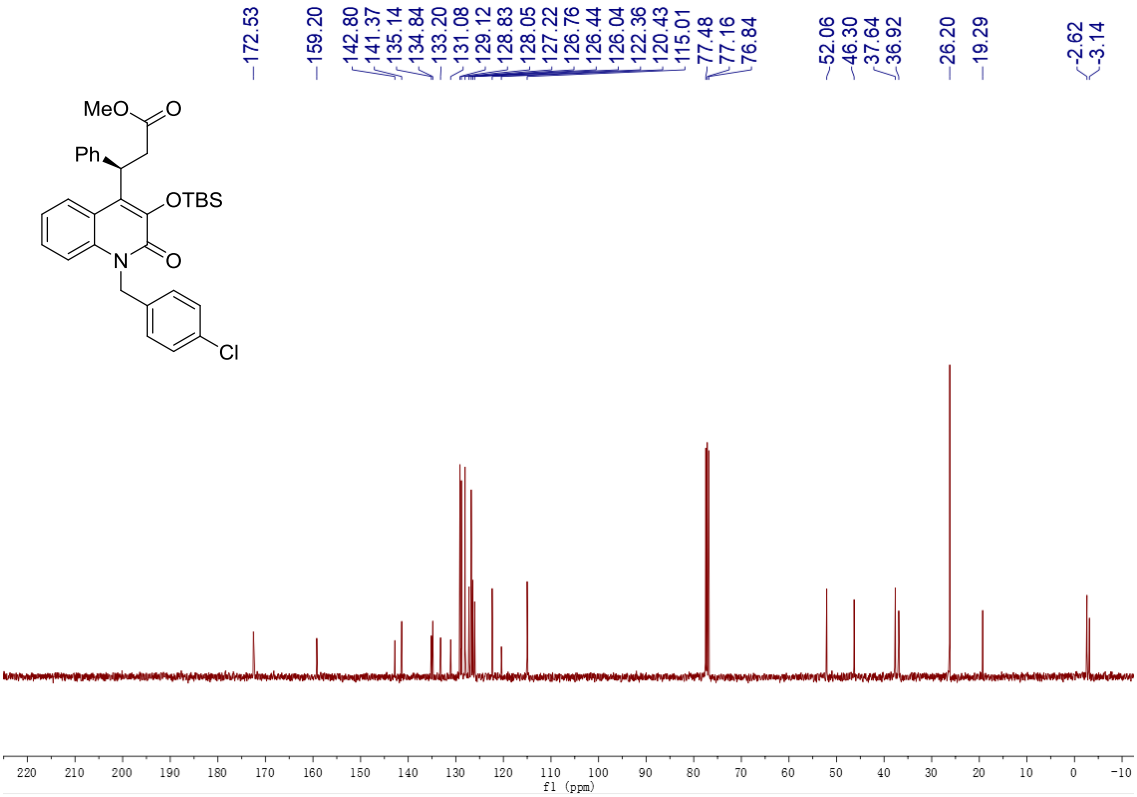


methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(4-chlorobenzyl)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4d)

NMR (400 MHz, $CDCl_3$)

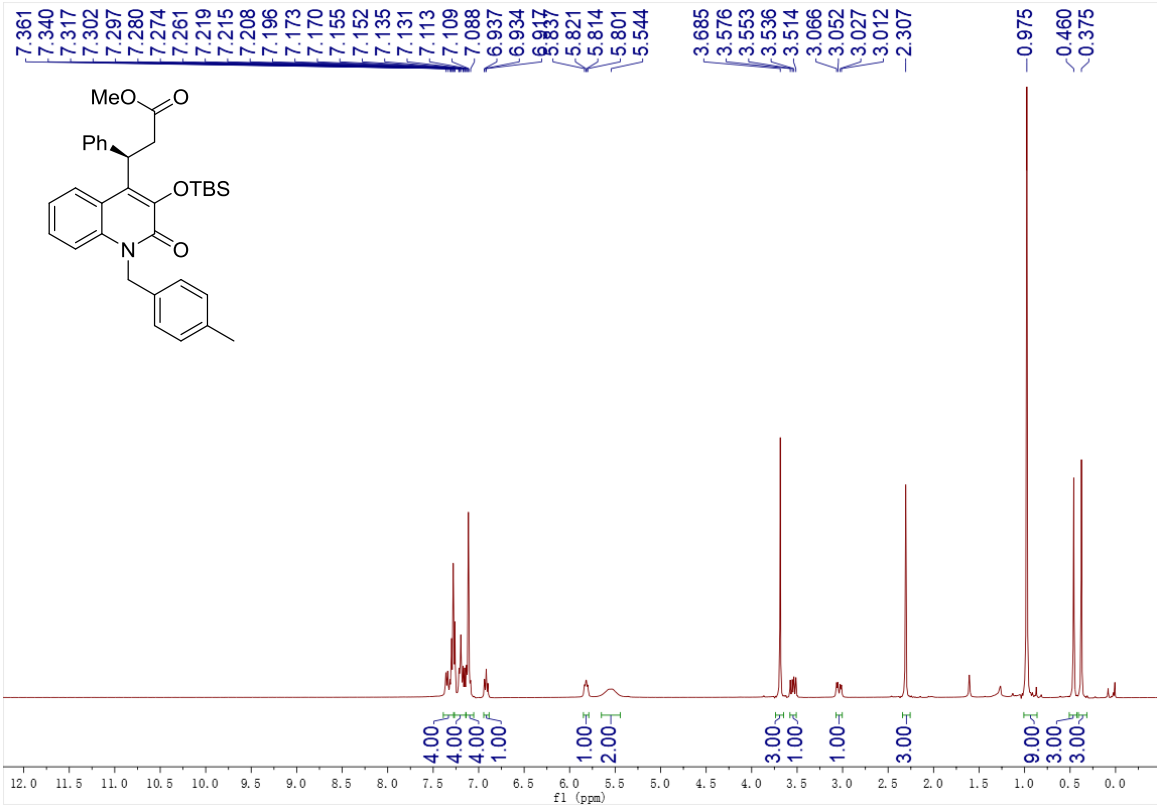


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

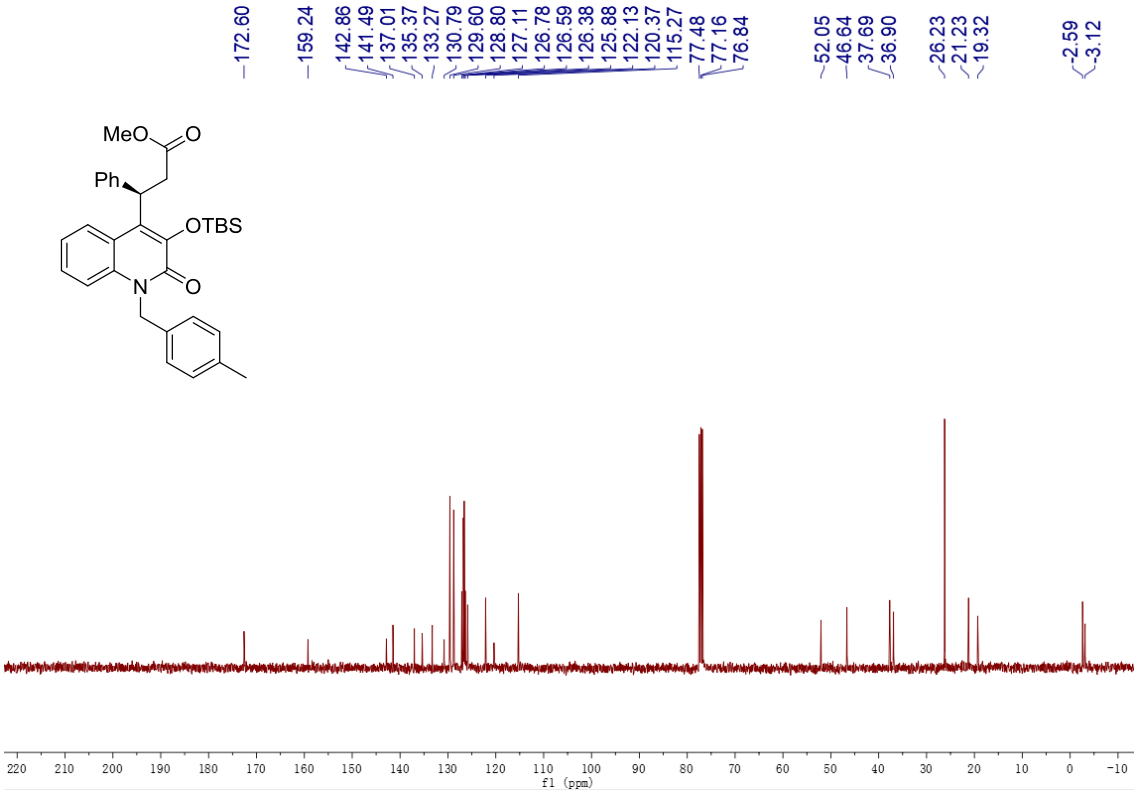


methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(4-methylbenzyl)-2-oxo-1,2-dihydro quinolin-4-yl)-3-phenylpropanoate (4e)

NMR (400 MHz, $CDCl_3$)

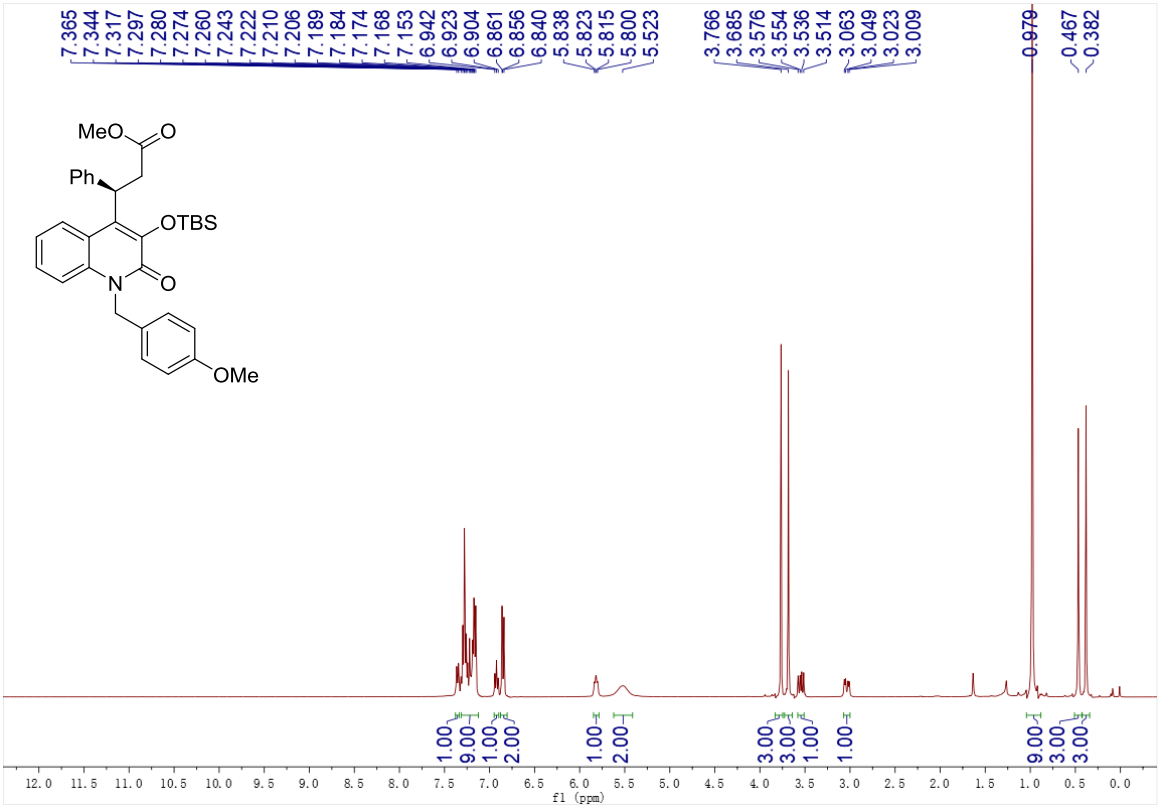


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

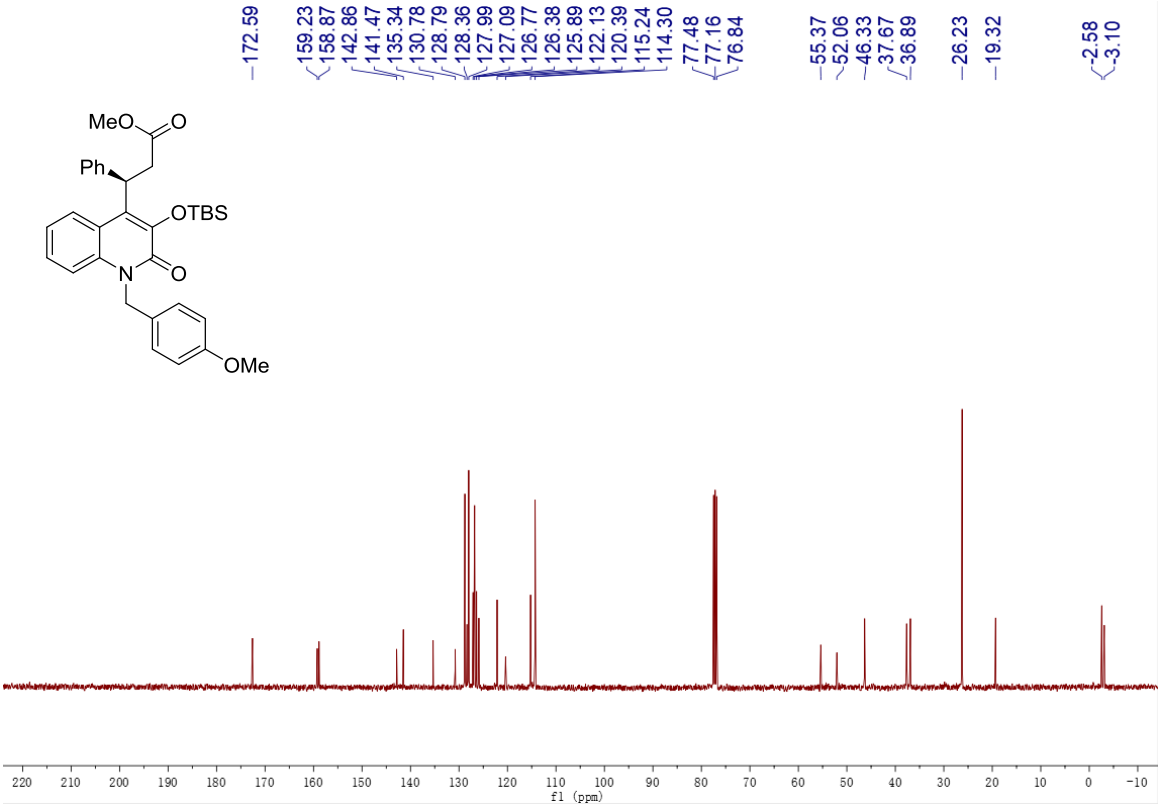


Methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(4-methoxybenzyl)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4f)

NMR (400 MHz, $CDCl_3$)

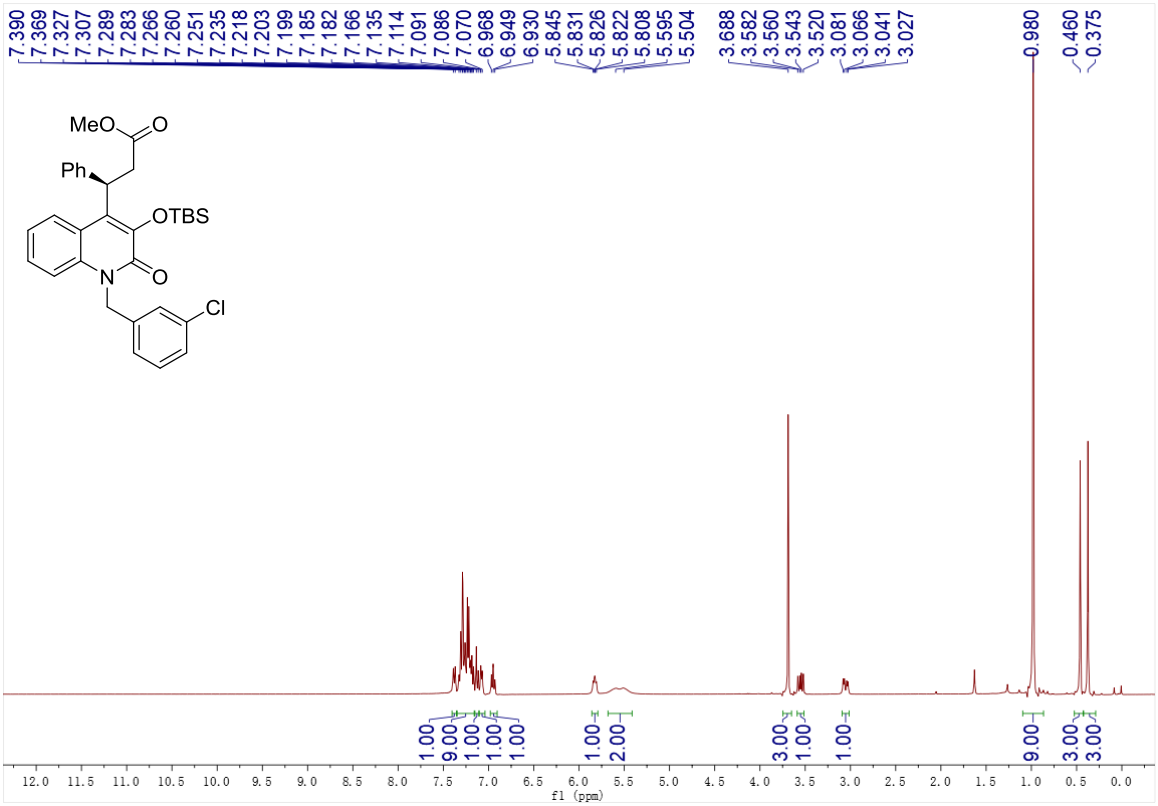


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

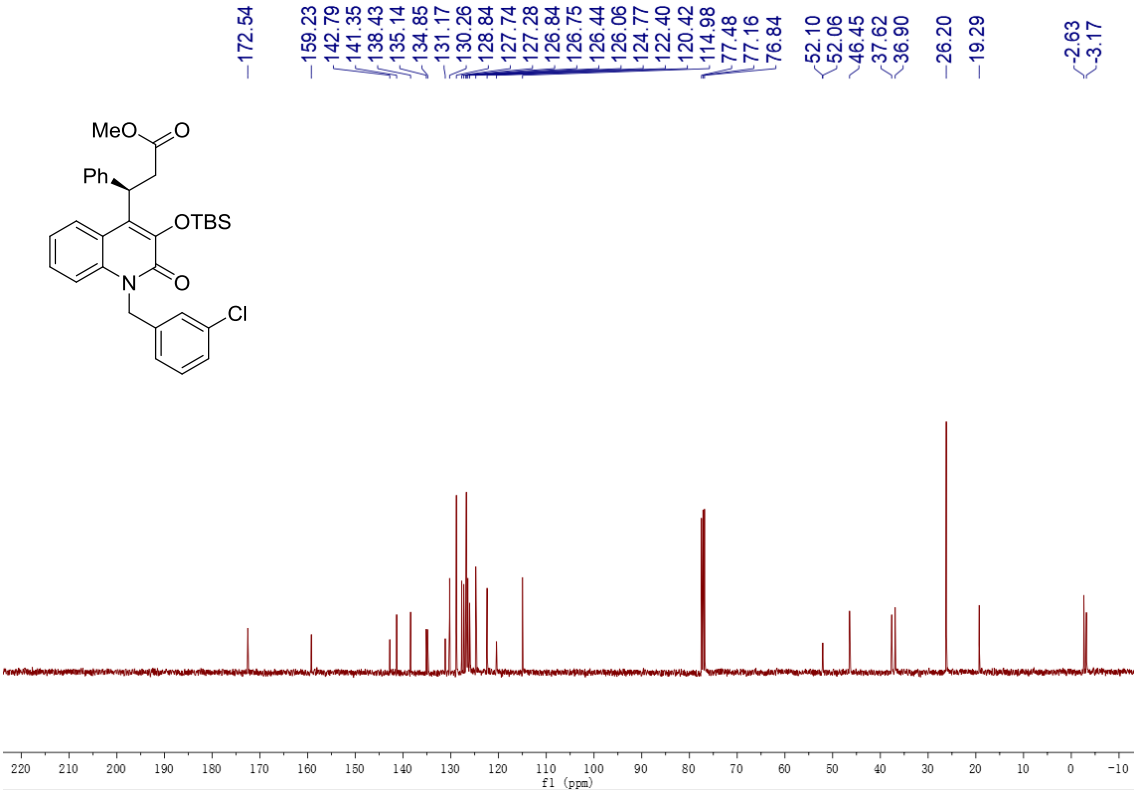


methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(3-chlorobenzyl)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4g)

NMR (400 MHz, $CDCl_3$)

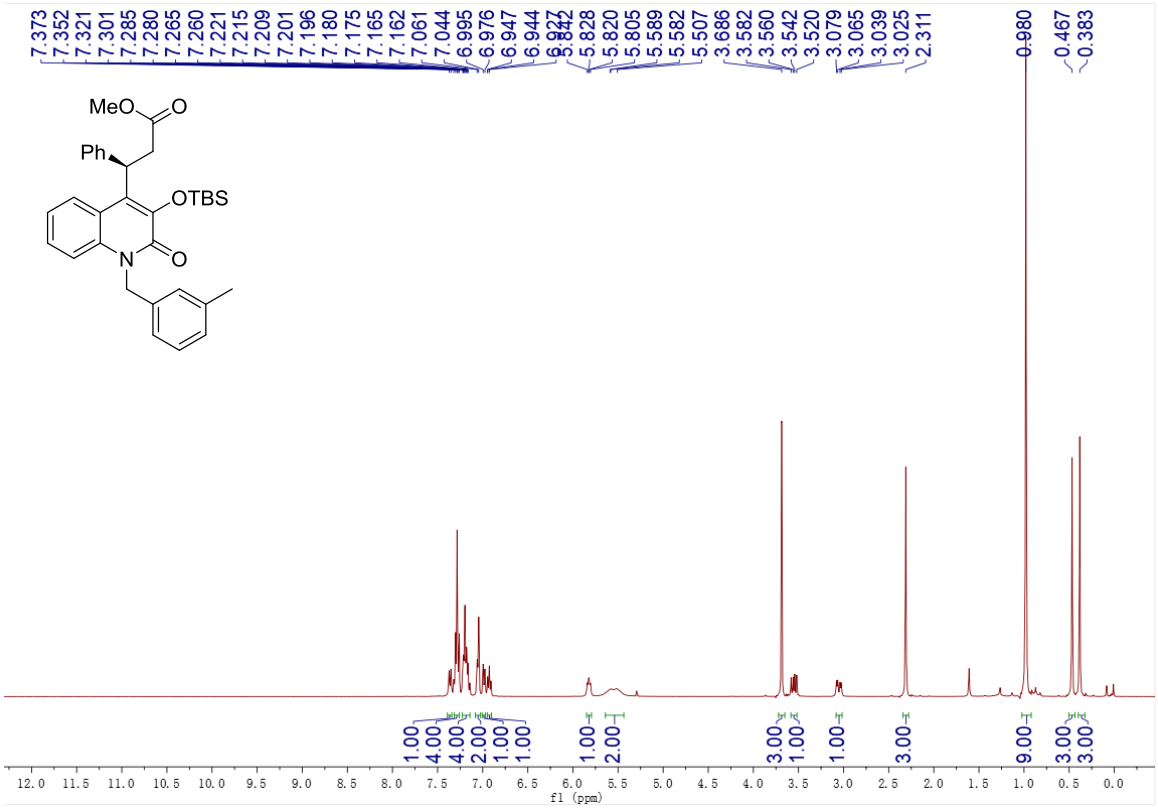


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

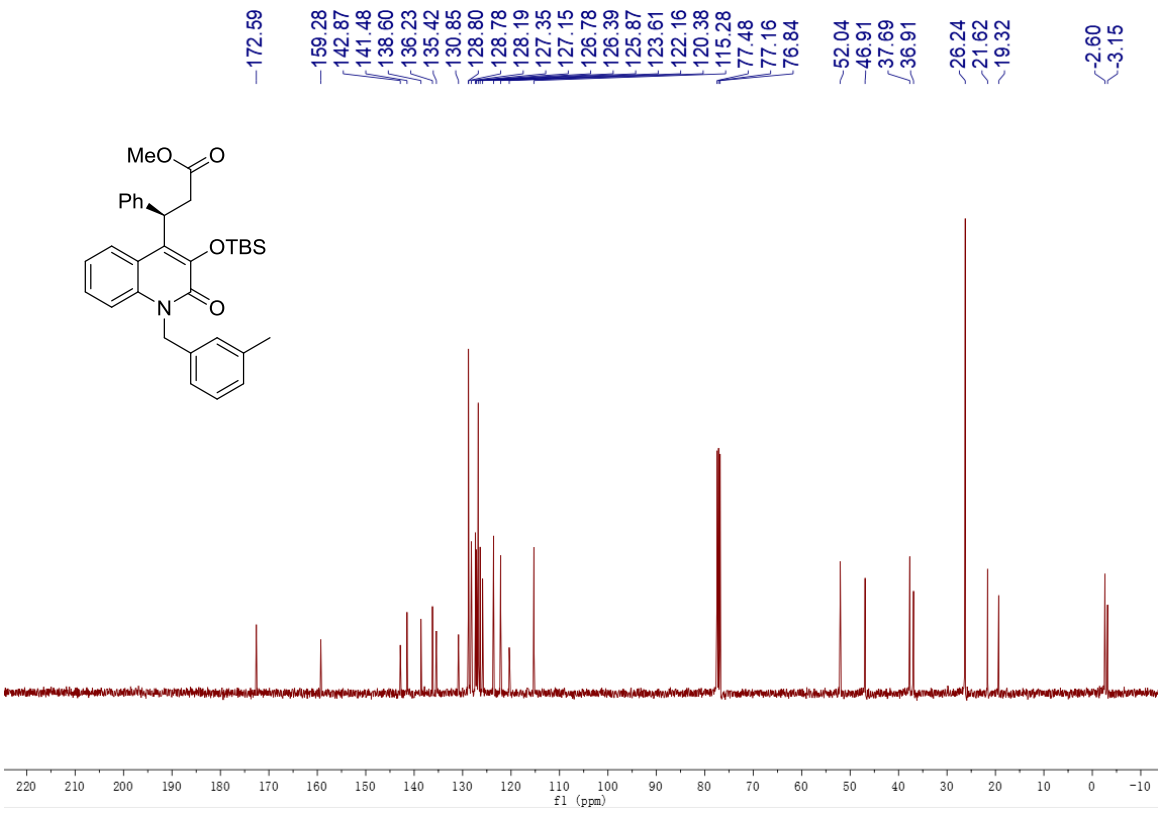


methyl 3-(3-((tert-butyldimethylsilyl)oxy)-1-(3-methylbenzyl)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4h)

NMR (400 MHz, $CDCl_3$)

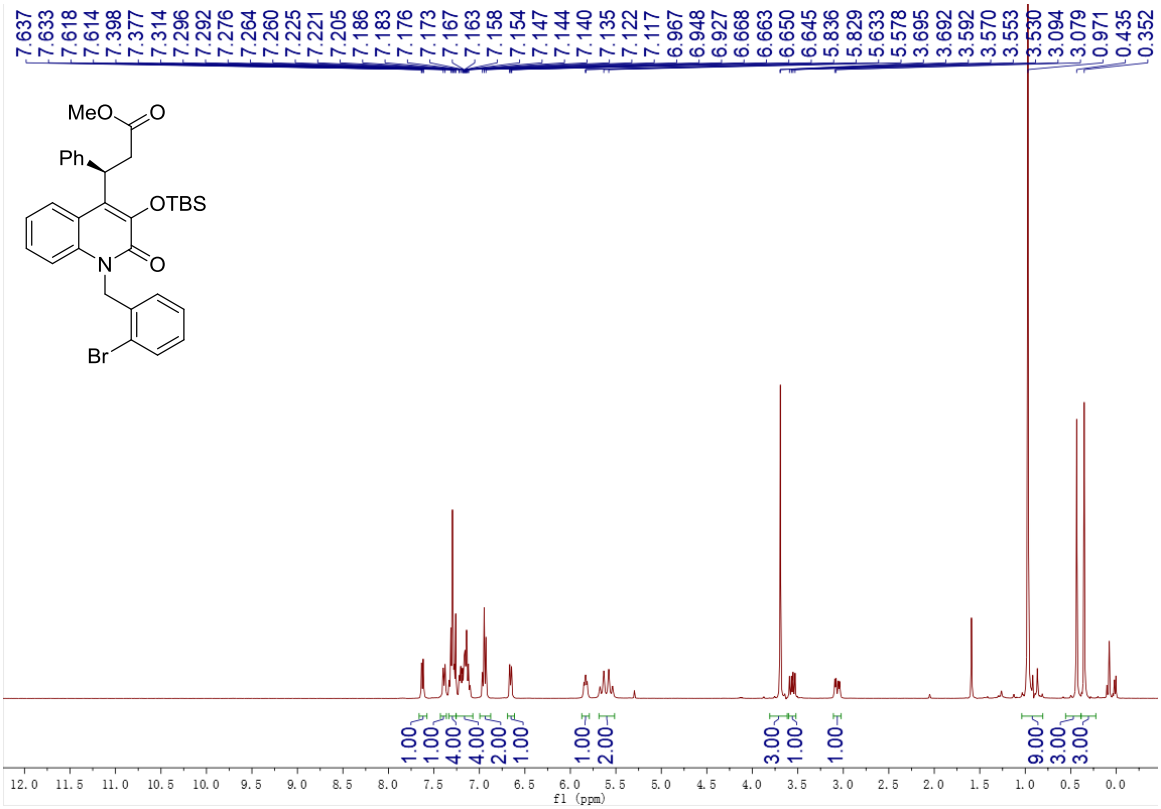


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

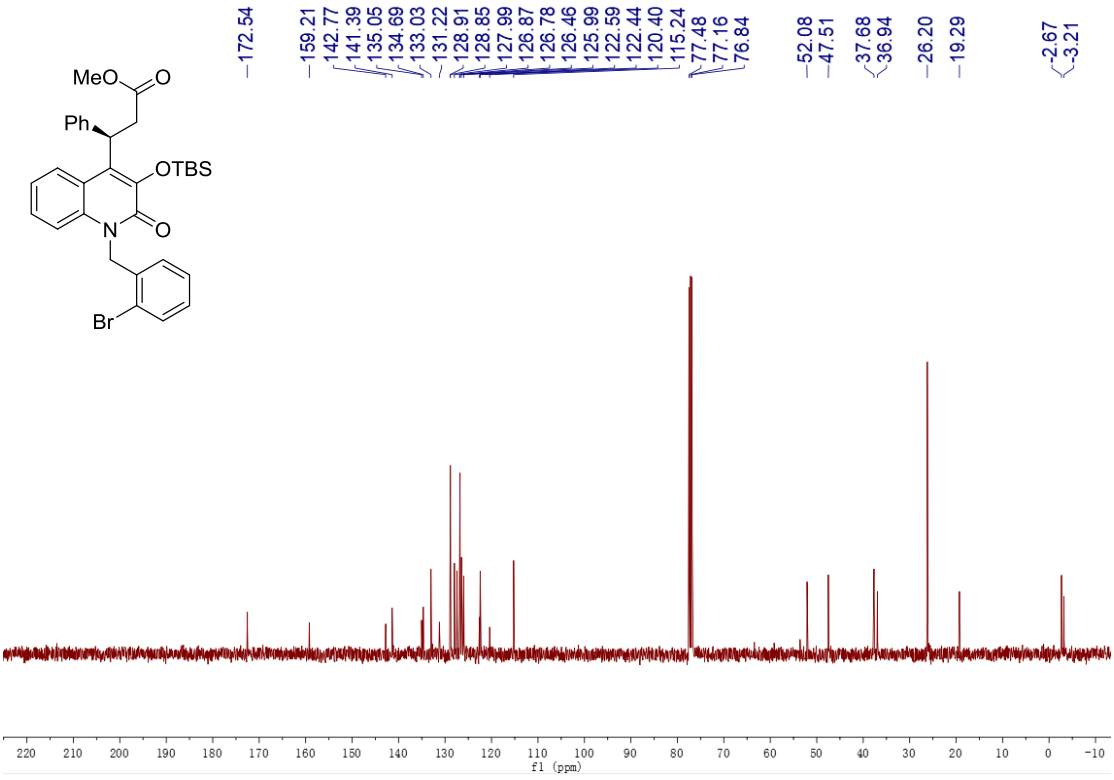


methyl 3-(1-(2-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4i)

NMR (400 MHz, $CDCl_3$)

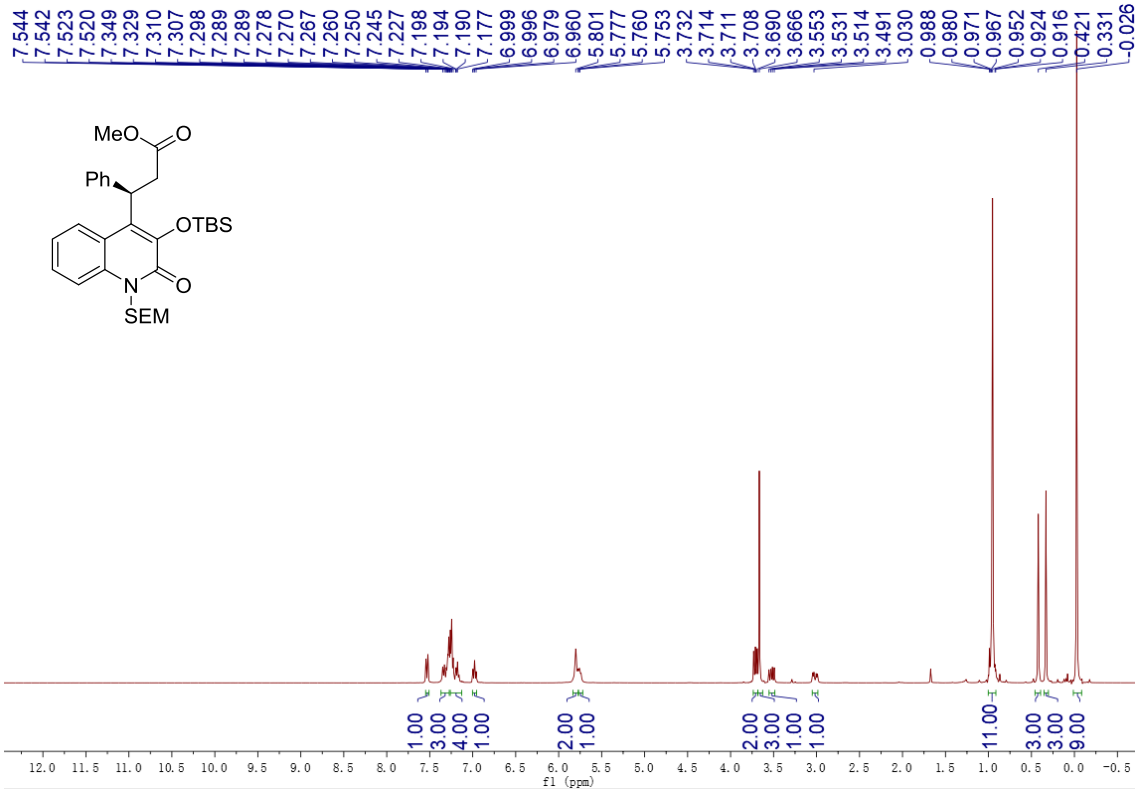


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

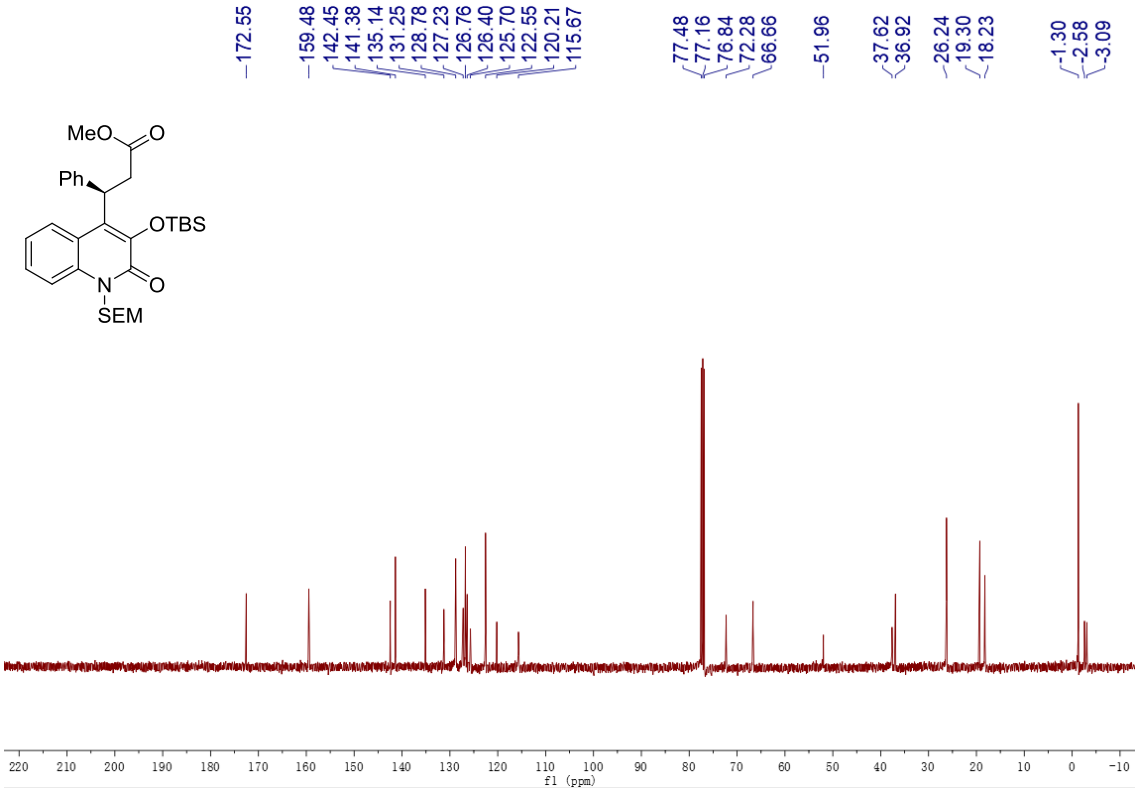


Methyl 3-(3-((tert-butyldimethylsilyl)oxy)-2-oxo-1-((2-(trimethylsilyl)ethoxy)methyl)-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4j)

NMR (400 MHz, $CDCl_3$)

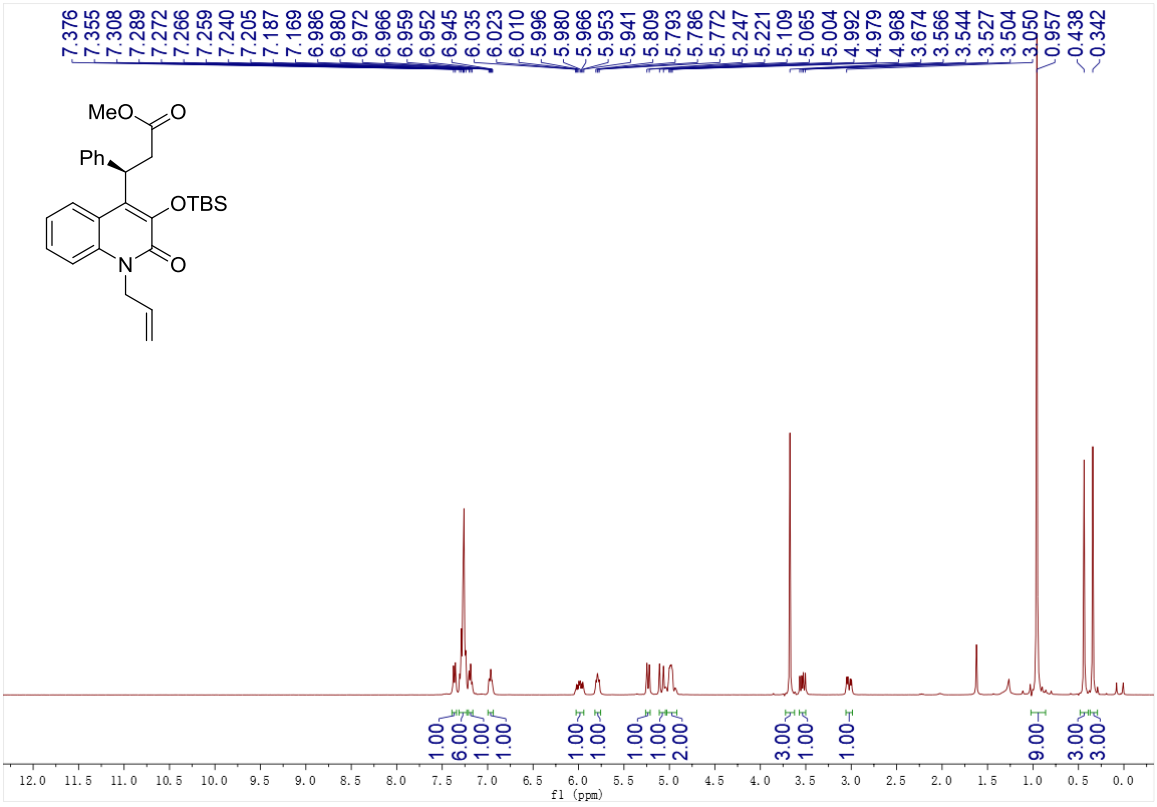


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

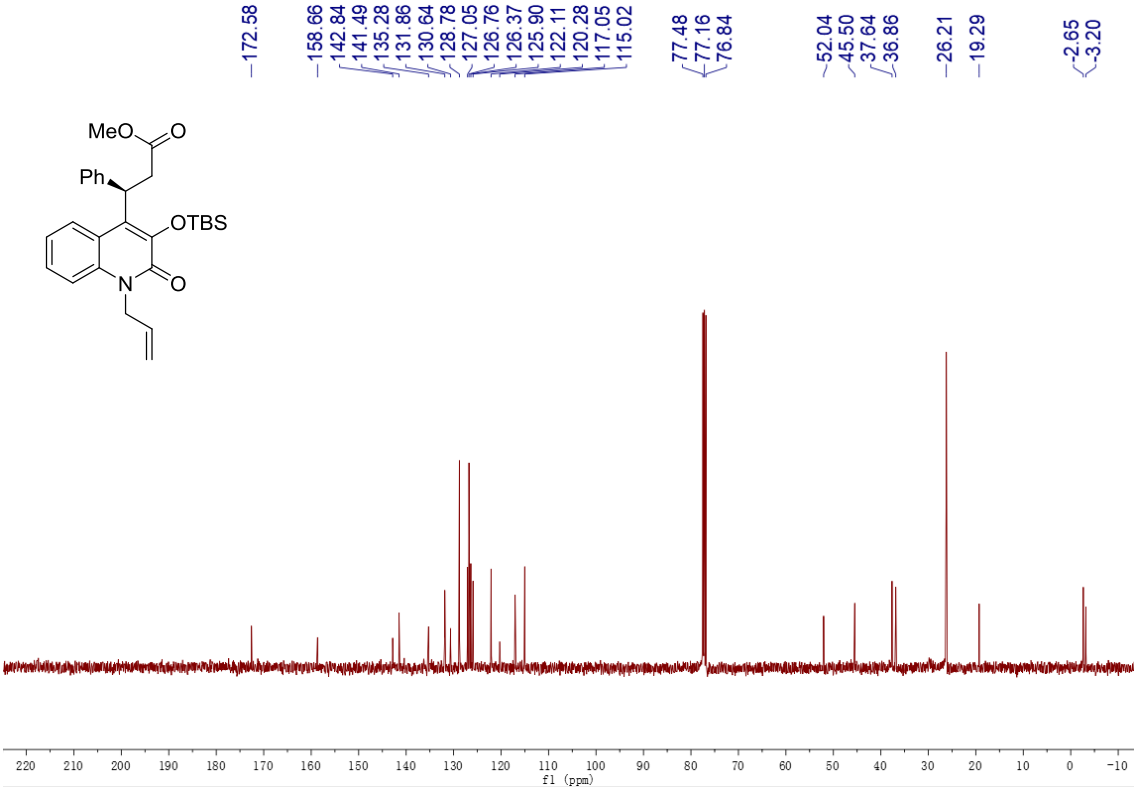


methyl 3-(1-allyl-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4k)

NMR (400 MHz, $CDCl_3$)

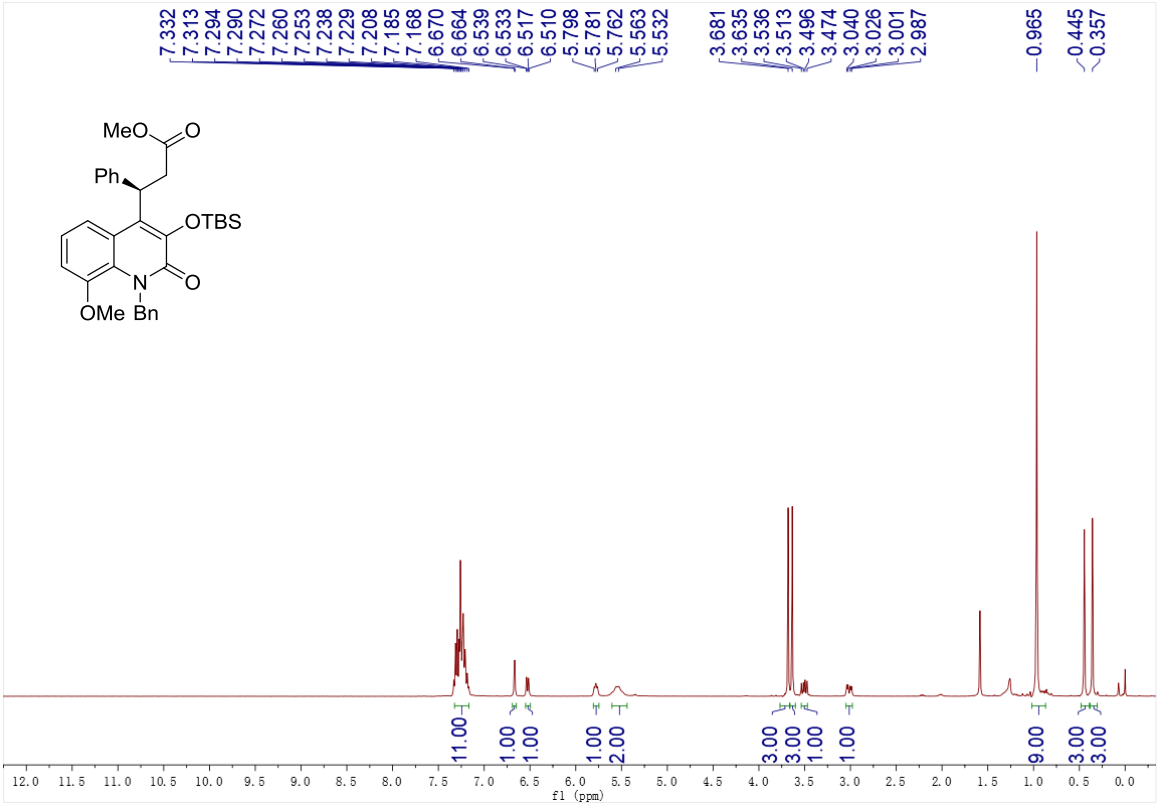


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

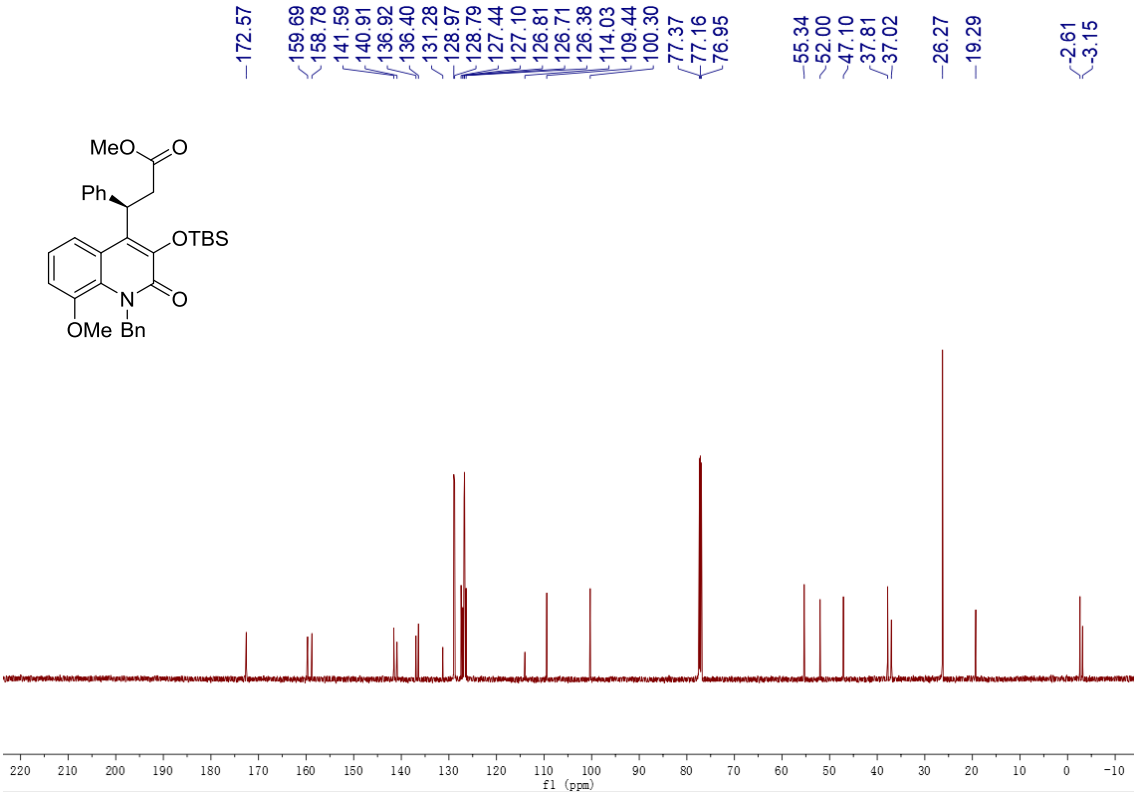


methyl 3-(1-benzyl-3-((tert-butyldimethylsilyl)oxy)-8-methoxy-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4l)

NMR (400 MHz, $CDCl_3$)

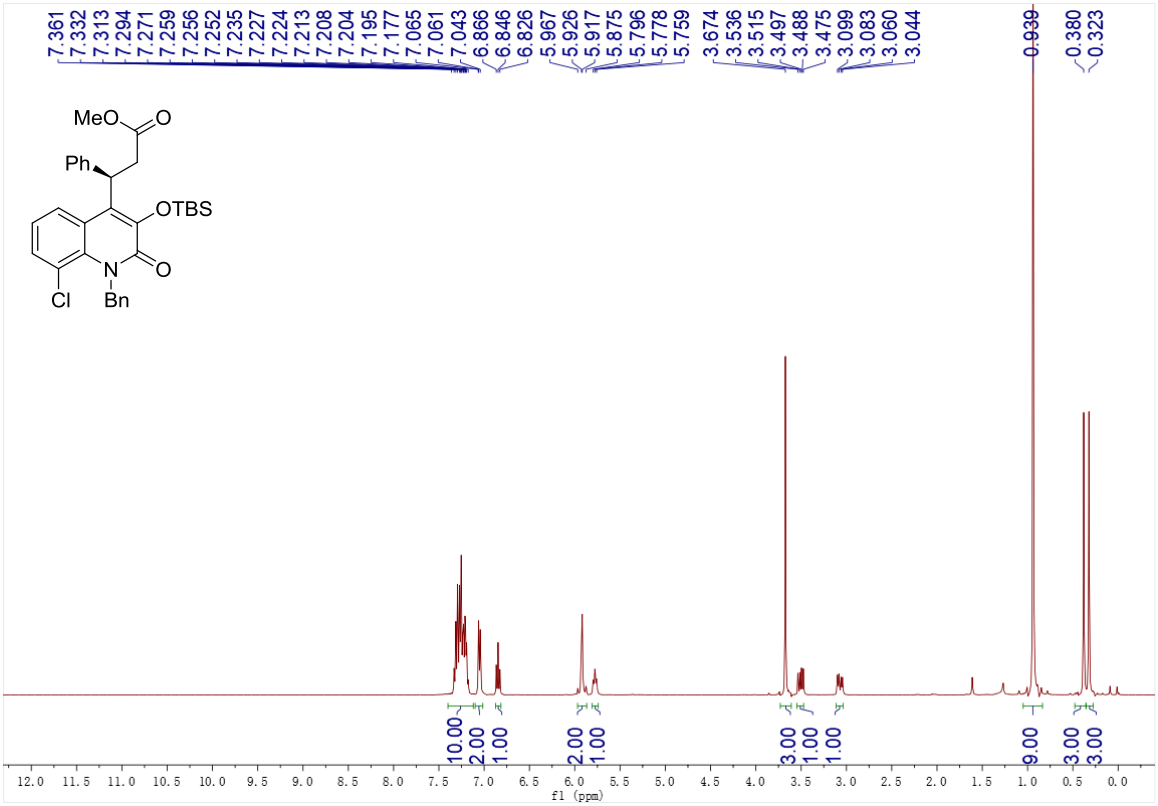


$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$)

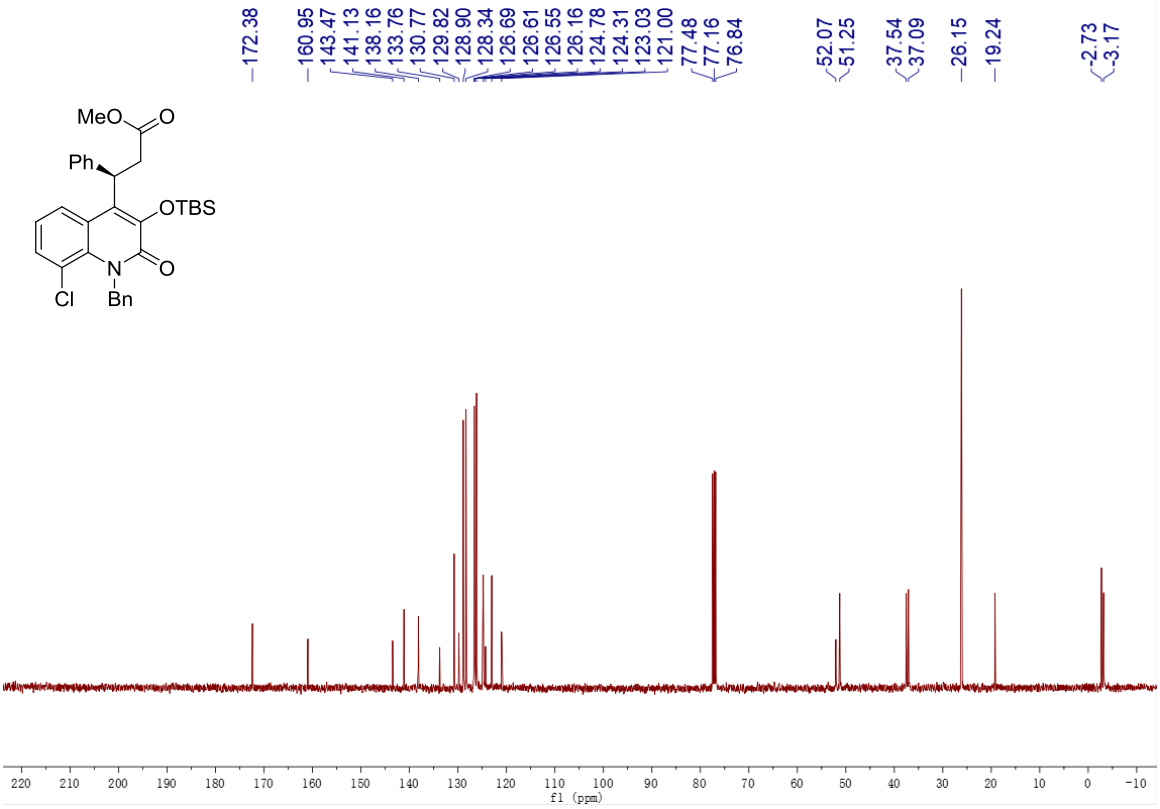


methyl 3-(1-benzyl-3-((tert-butyldimethylsilyl)oxy)-8-chloro-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4m)

NMR (400 MHz, $CDCl_3$)

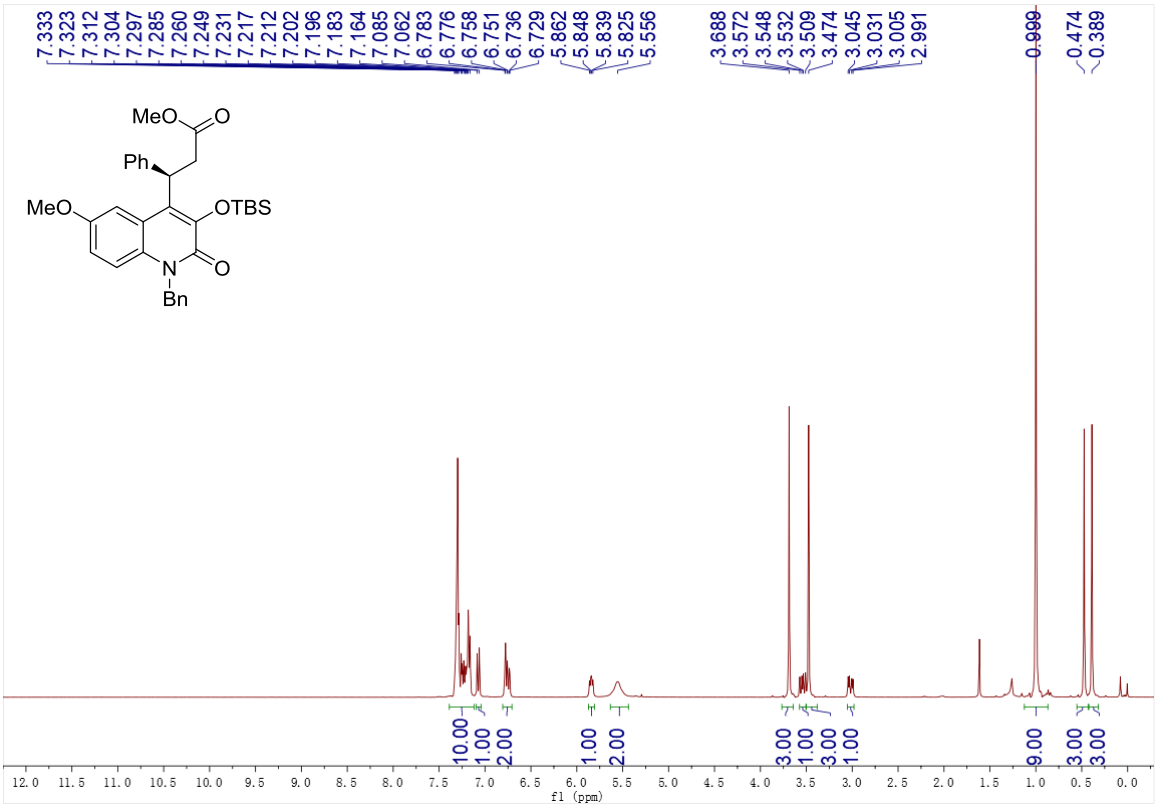


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

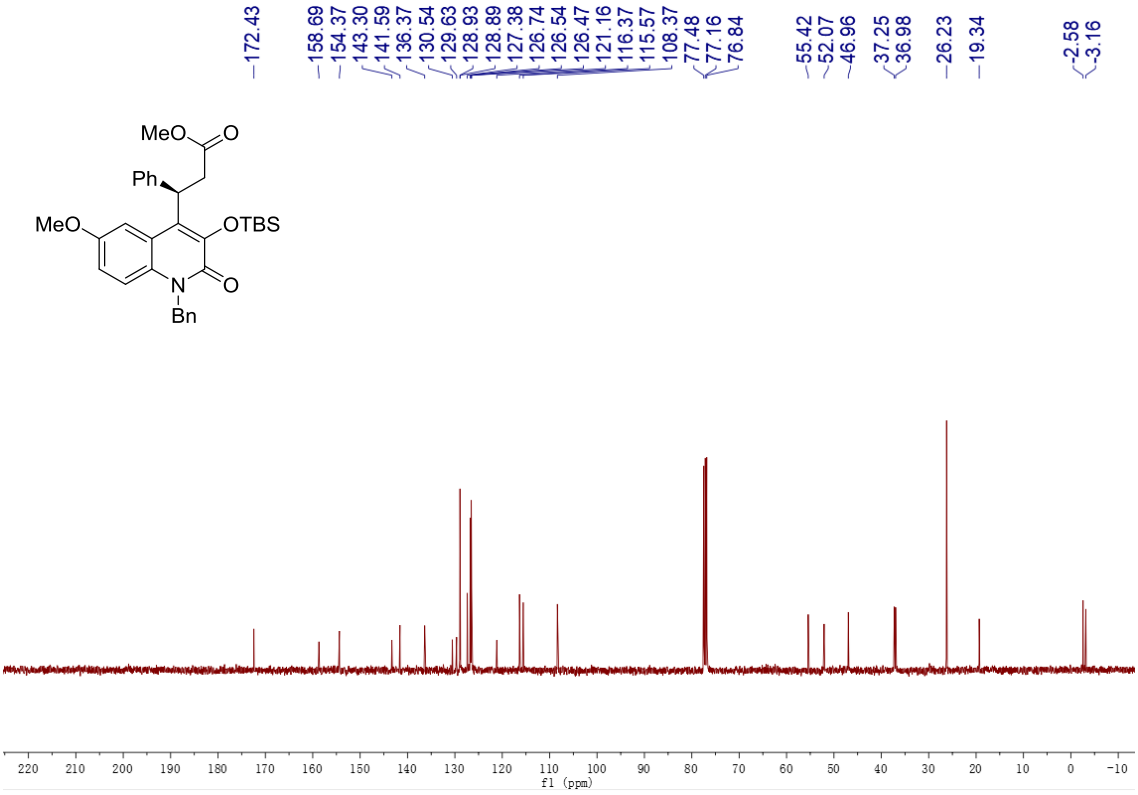


methyl 3-(1-benzyl-3-((tert-butyldimethylsilyl)oxy)-6-methoxy-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4n)

NMR (400 MHz, $CDCl_3$)

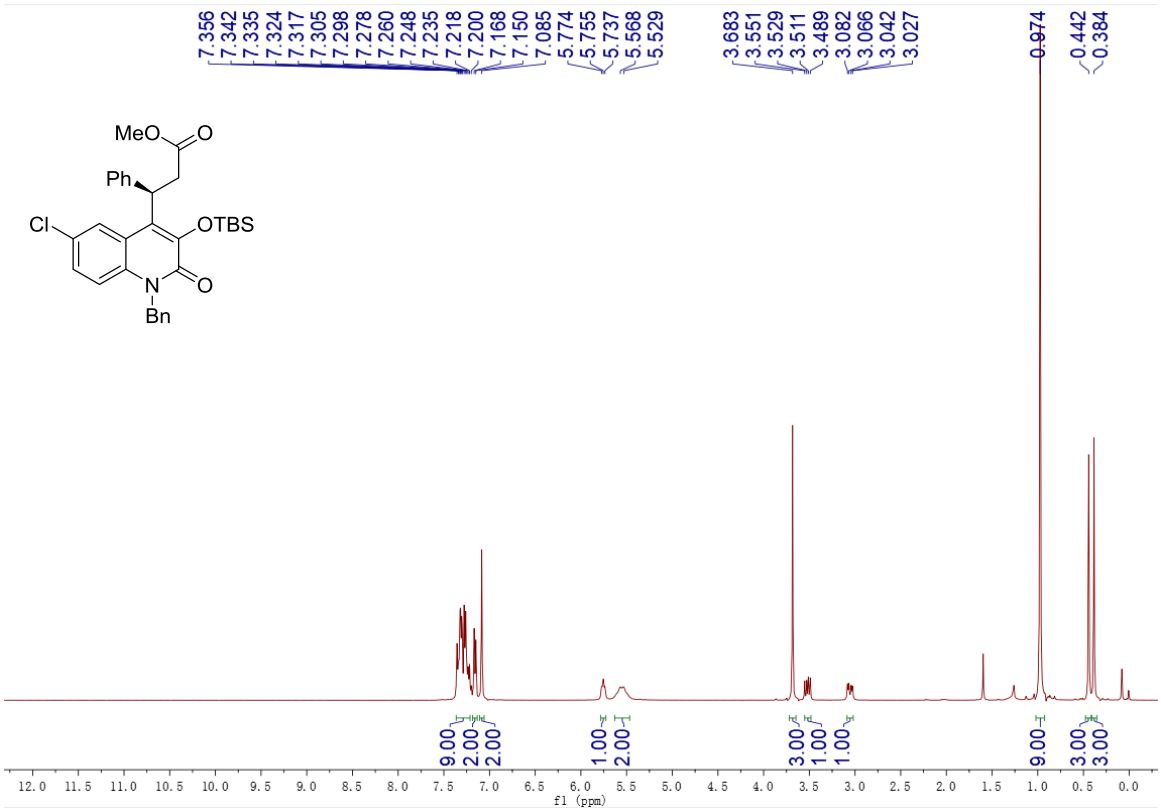


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

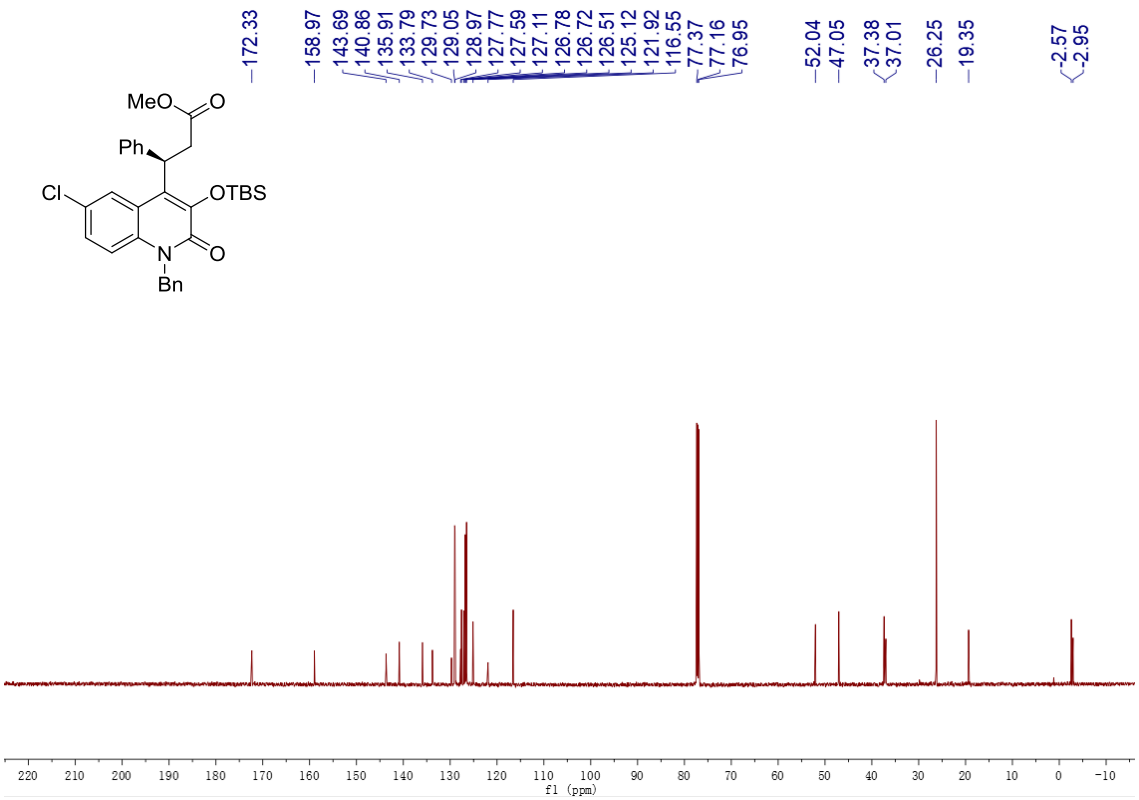


methyl 3-(1-benzyl-3-((tert-butyldimethylsilyl)oxy)-6-chloro-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (4o)

NMR (400 MHz, $CDCl_3$)

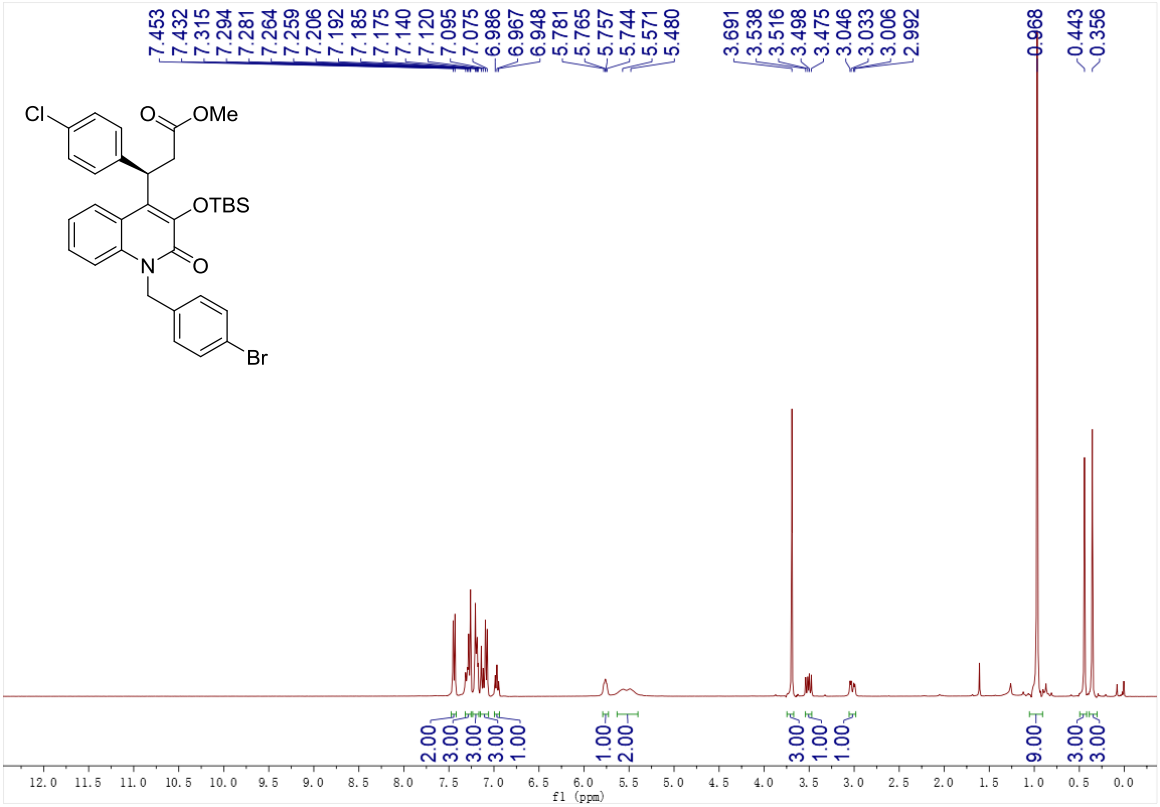


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

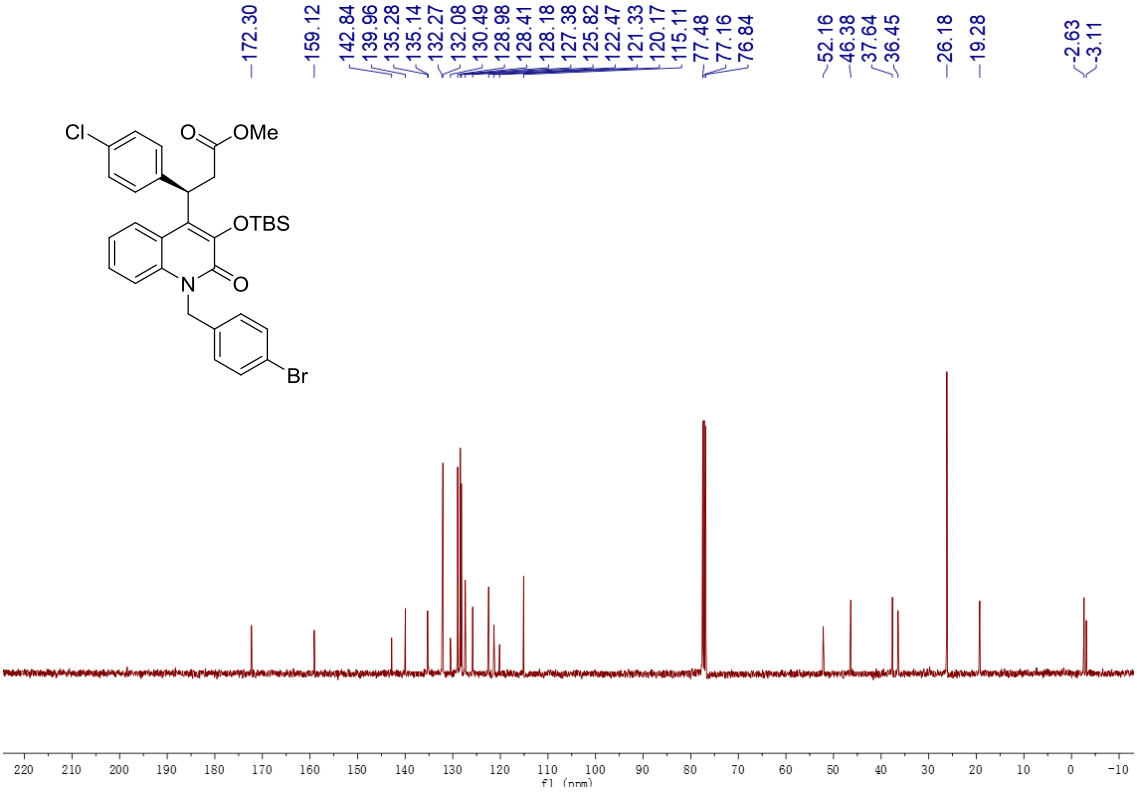


methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydroquinolin-4-yl)-3-(4-chlorophenyl)propanoate (4p)

NMR (400 MHz, $CDCl_3$)

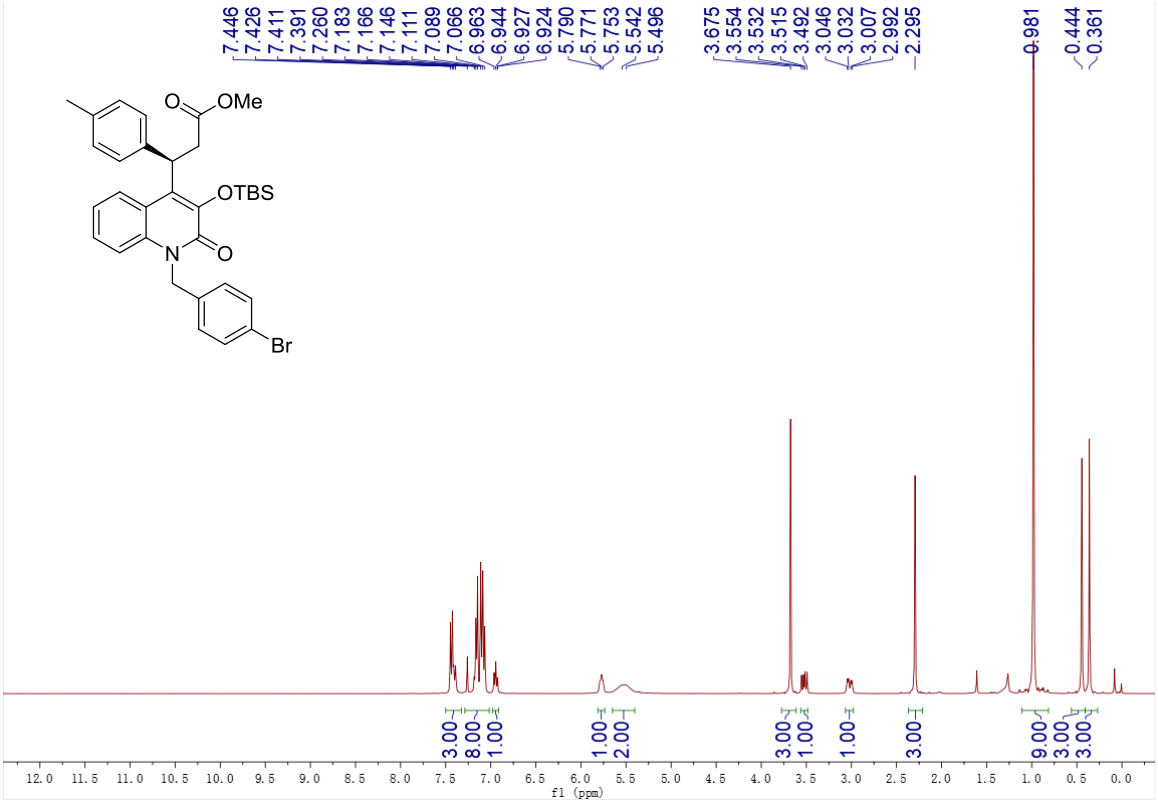


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

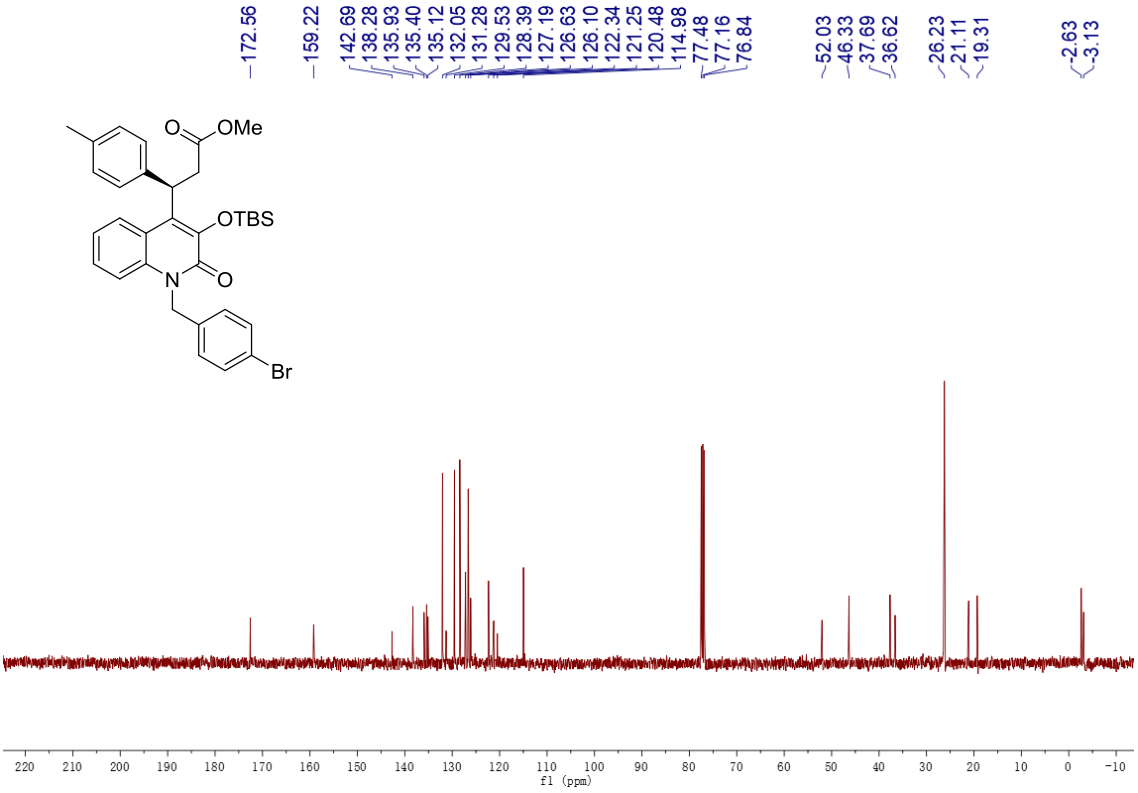


methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydro quinolin-4-yl)-3-(p-tolyl)propanoate (4q)

NMR (400 MHz, $CDCl_3$)

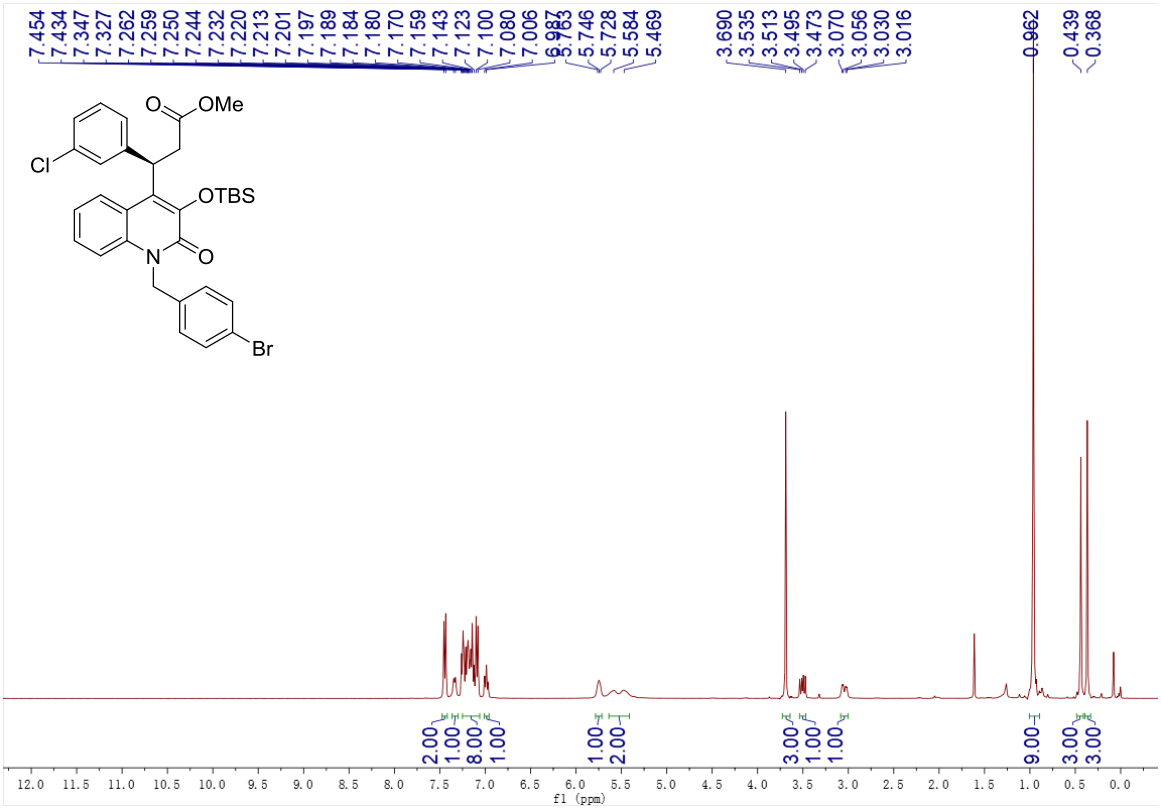


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

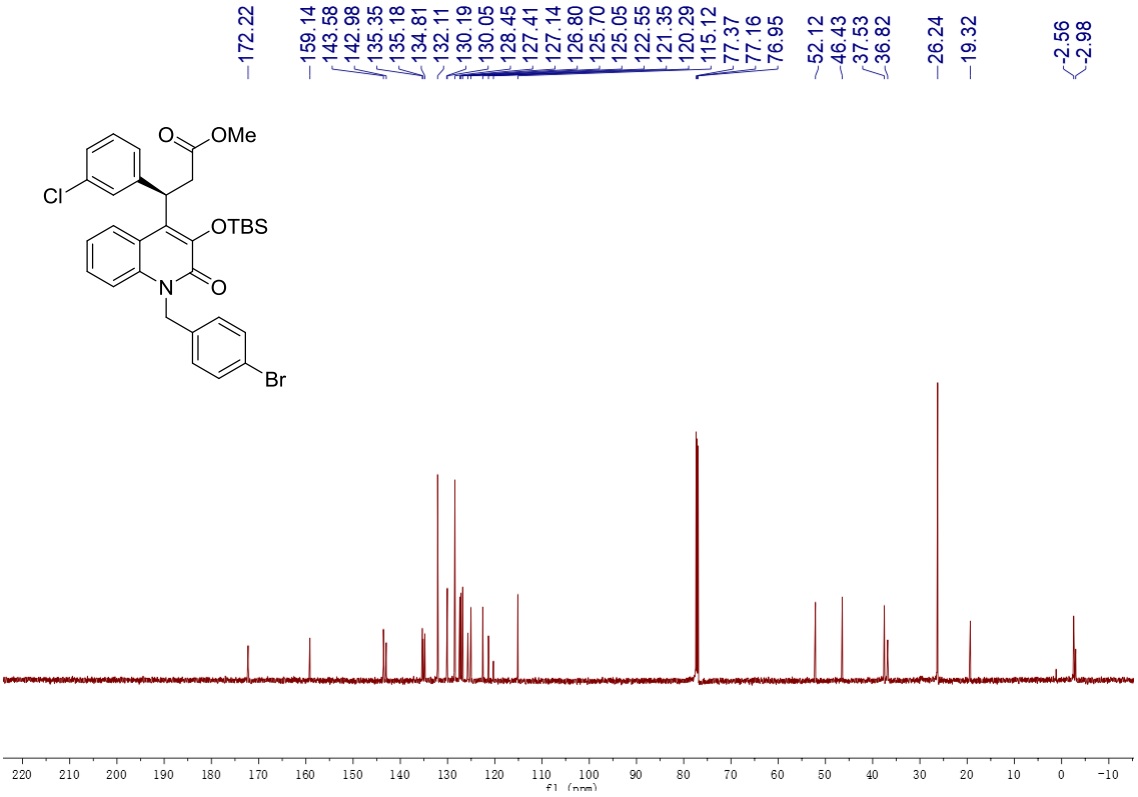


methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydro quinolin-4-yl)-3-(3-chlorophenyl)propanoate (4r)

NMR (400 MHz, $CDCl_3$)

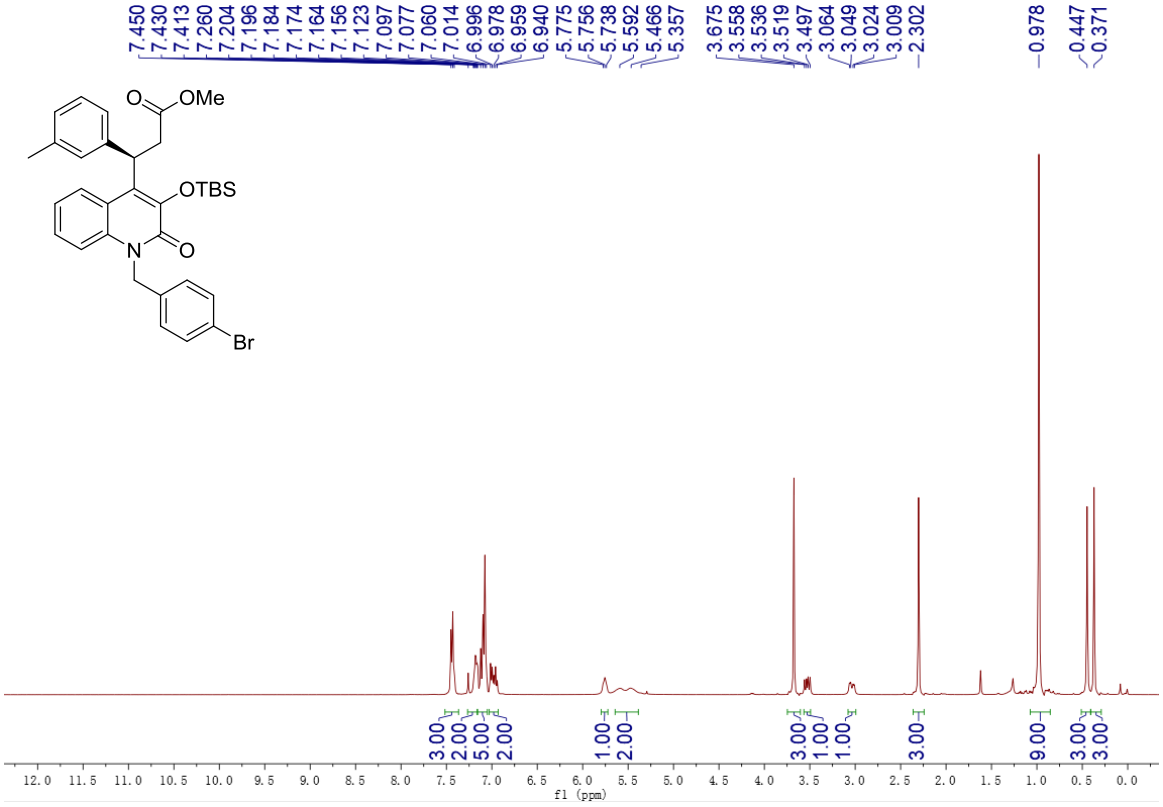


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

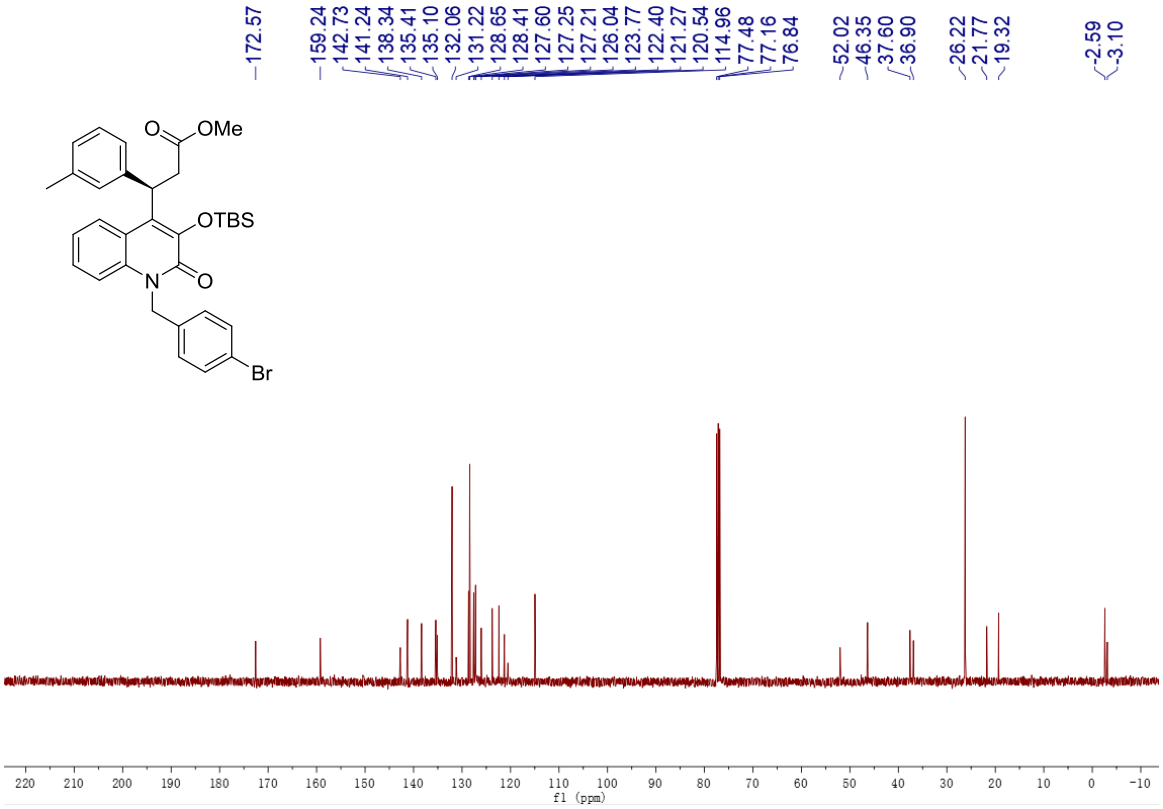


methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydro quinolin-4-yl)-3-(m-tolyl)propanoate (4s)

NMR (400 MHz, $CDCl_3$)

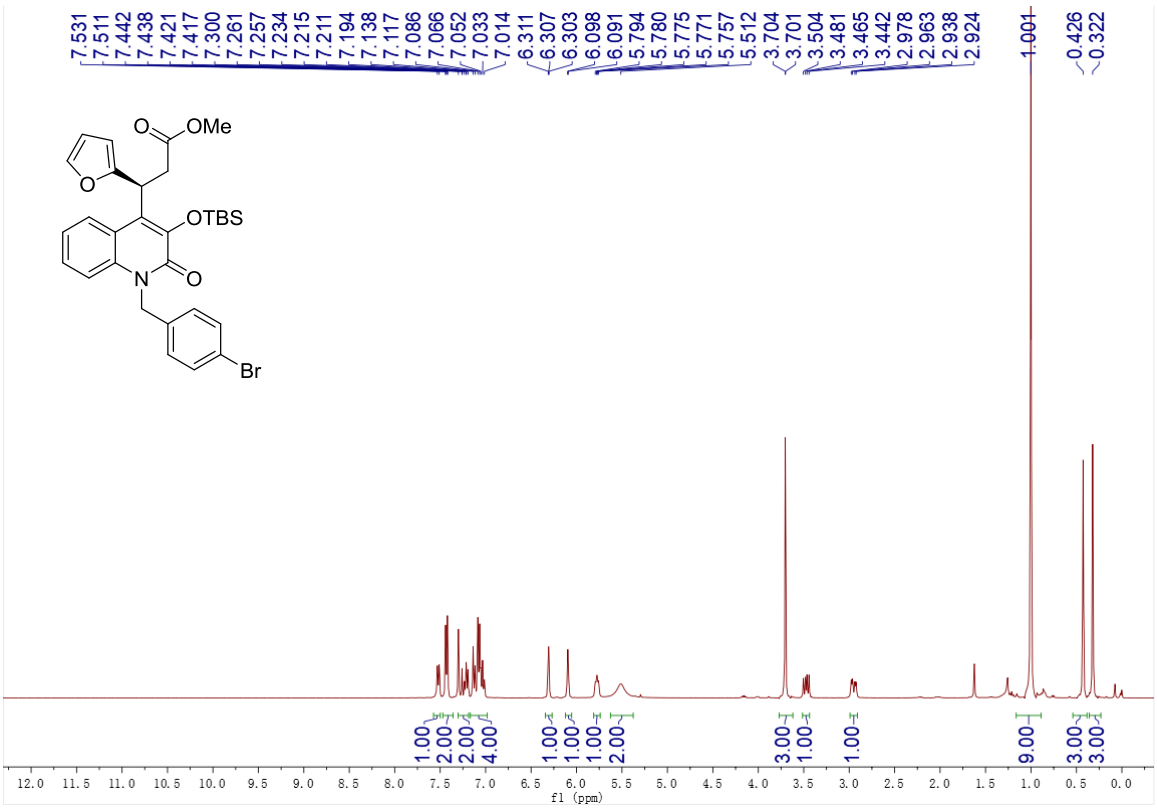


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

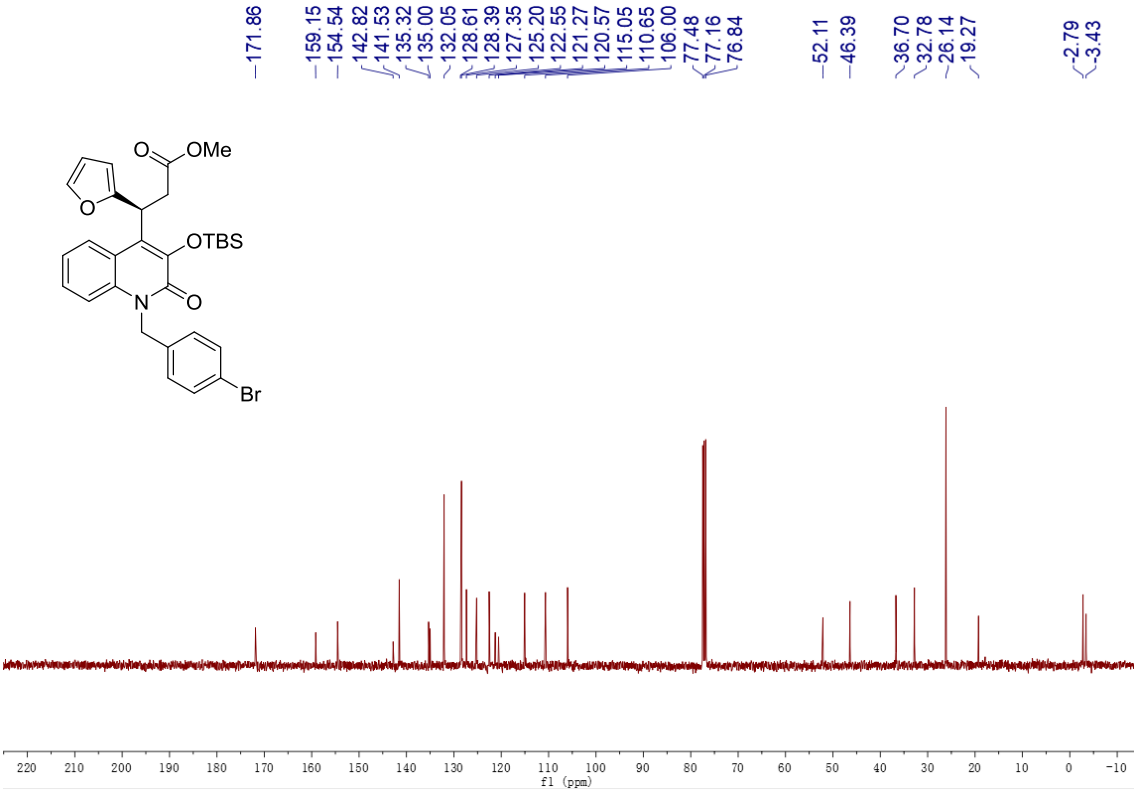


methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydroquinolin-4-yl)-3-(furan-2-yl)propanoate (4t)

NMR (400 MHz, $CDCl_3$)

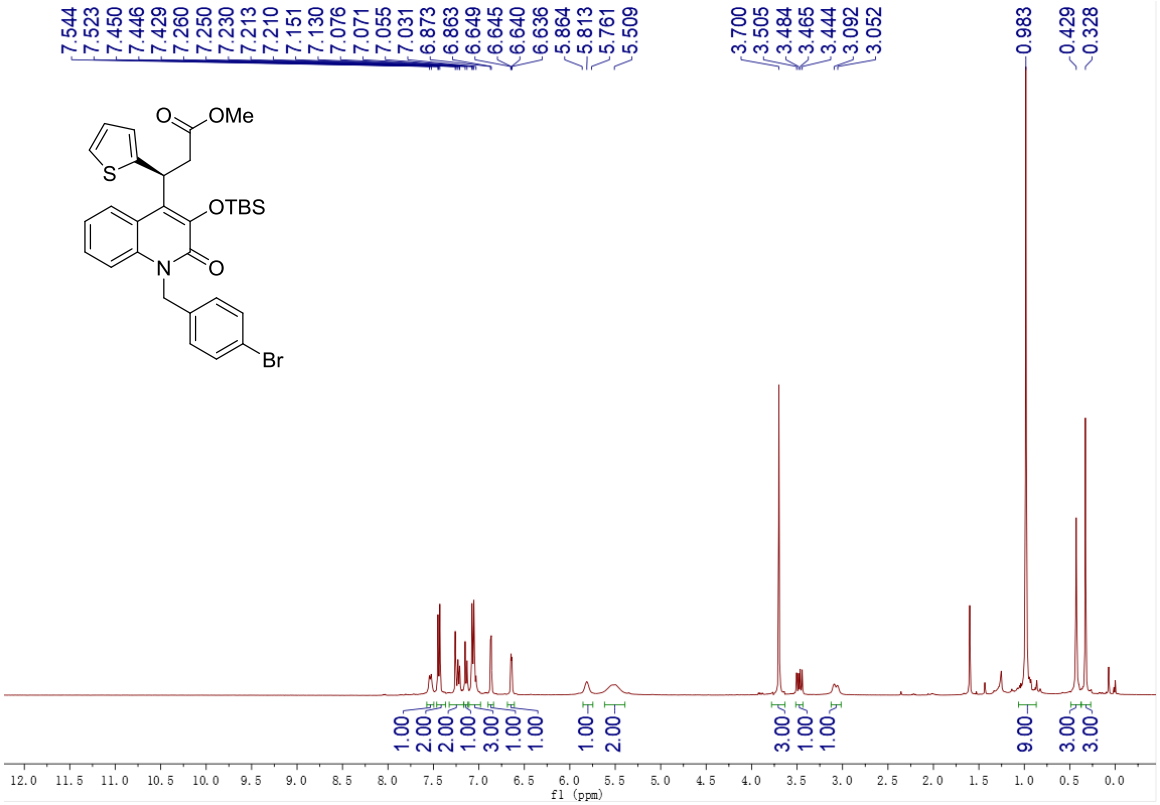


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

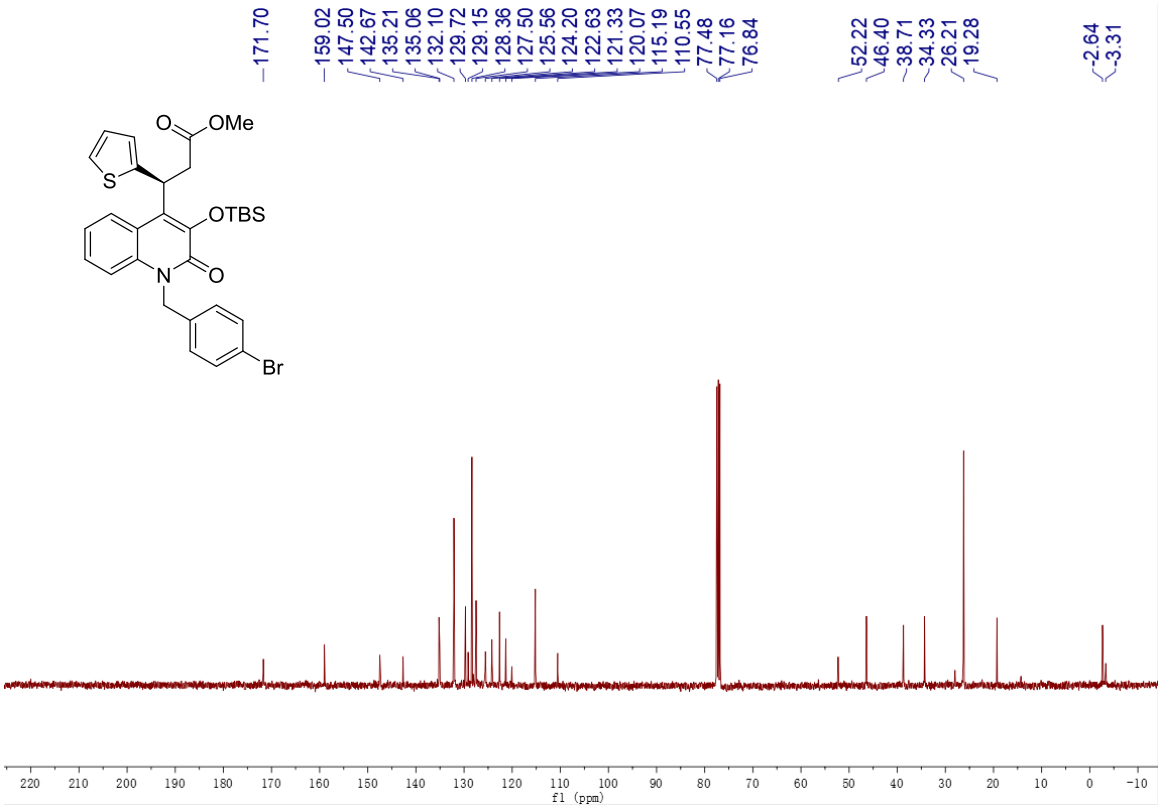


methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydro quinolin-4-yl)-3-(thiophen-2-yl)propanoate (4u)

NMR (400 MHz, $CDCl_3$)

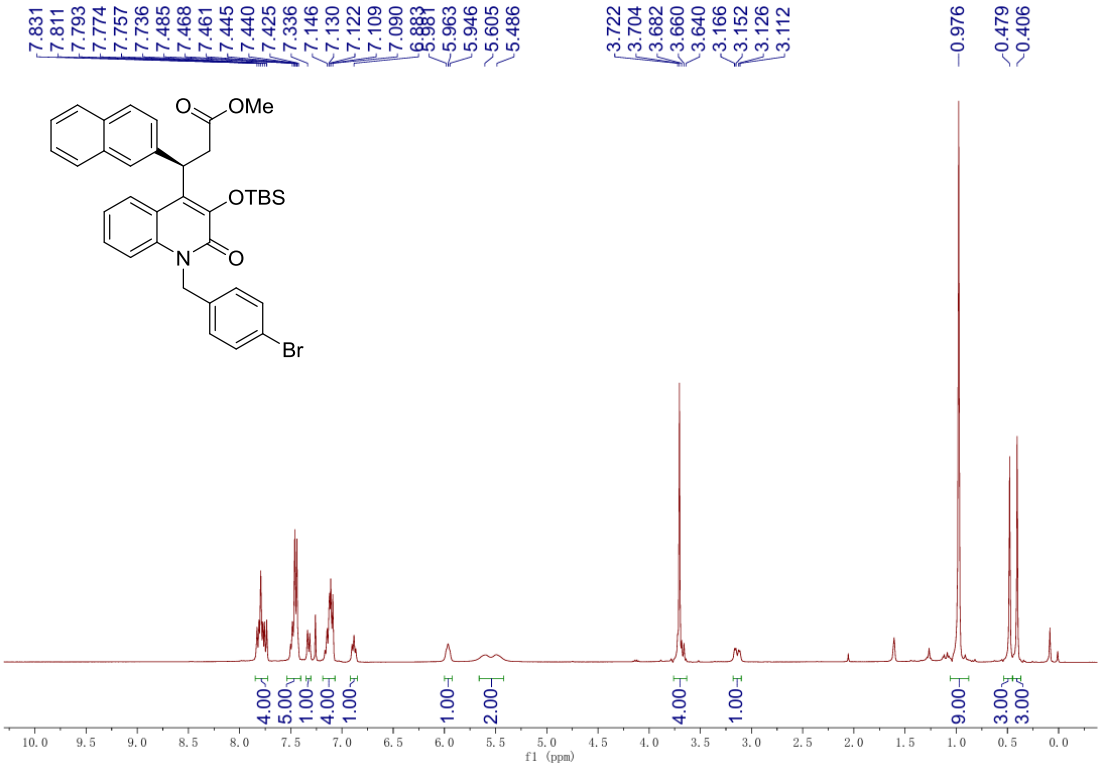


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

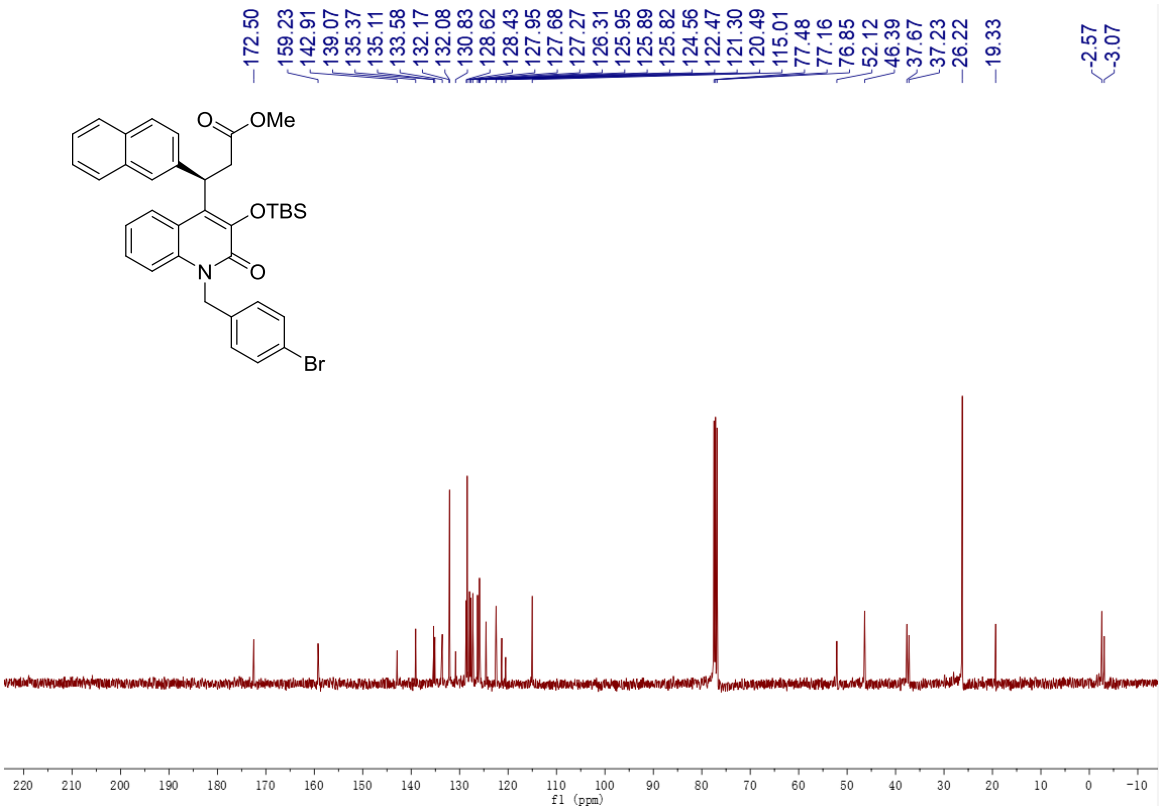


methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-oxo-1,2-dihydro quinolin-4-yl)-3-(naphthalen-2-yl)propanoate (4v)

NMR (400 MHz, $CDCl_3$)

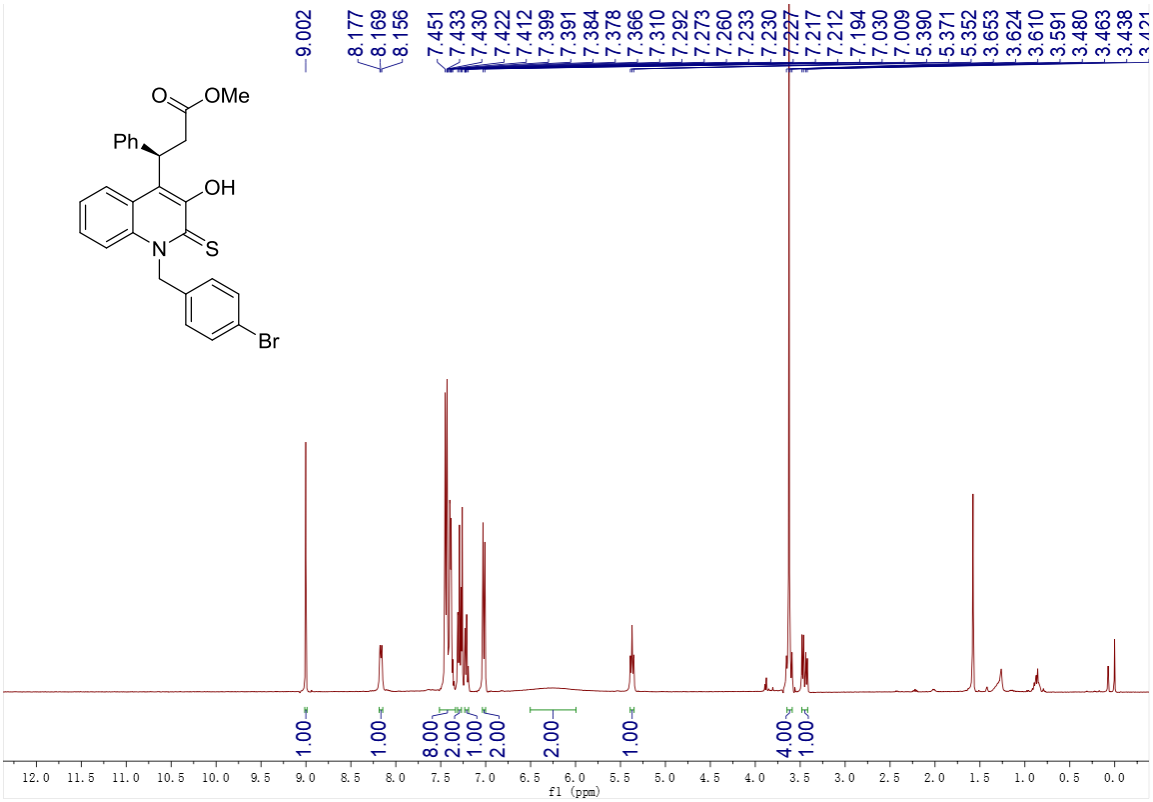


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

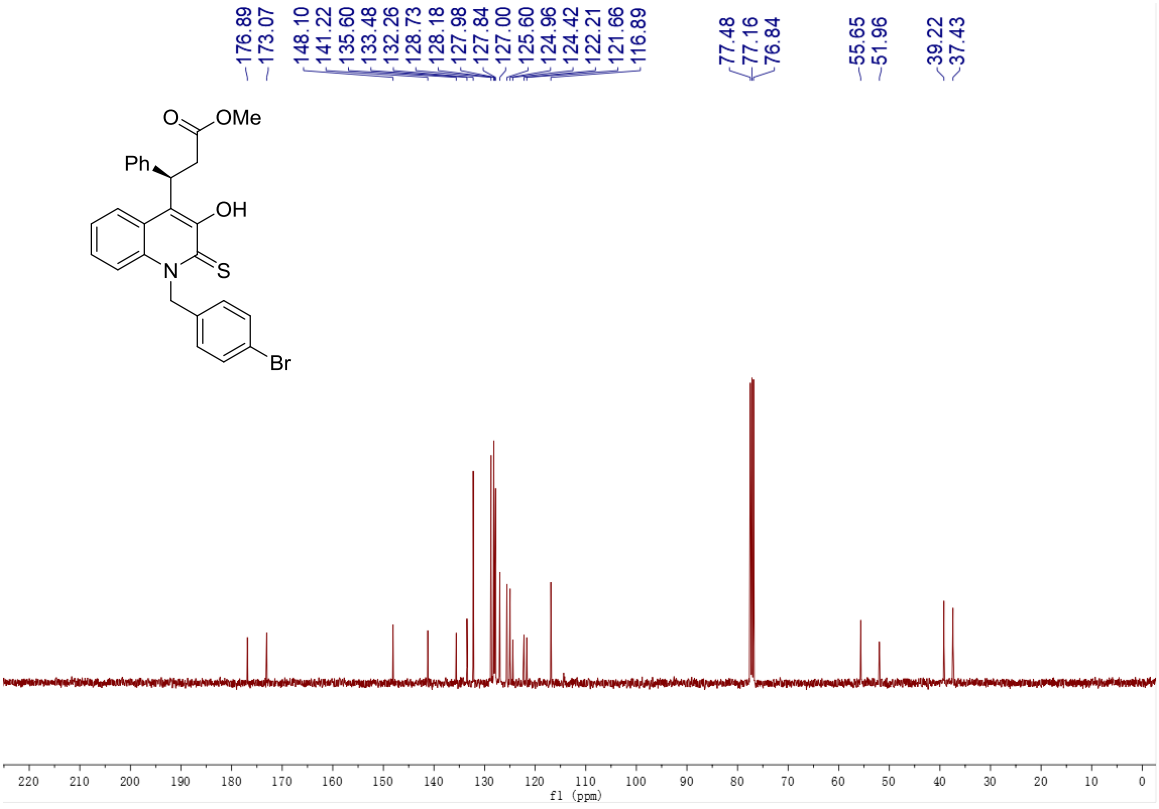


methyl 3-(1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-2-thioxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (5)

NMR (400 MHz, $CDCl_3$)

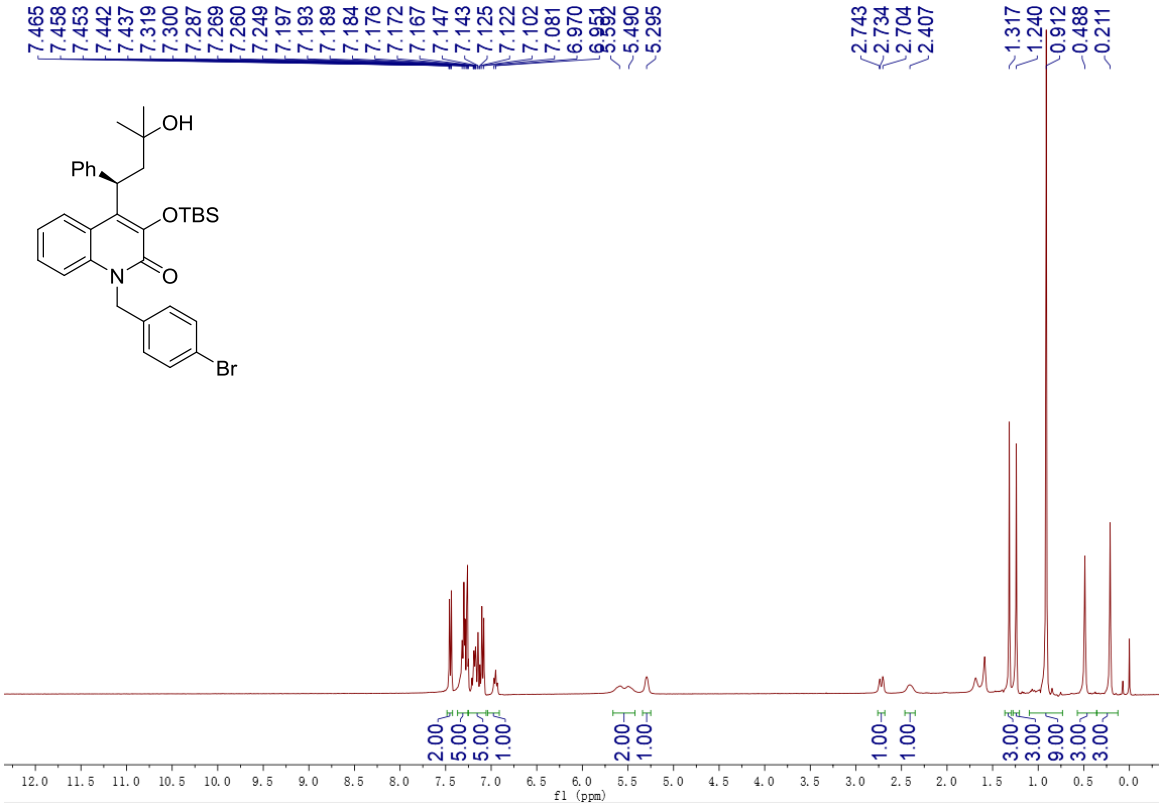


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

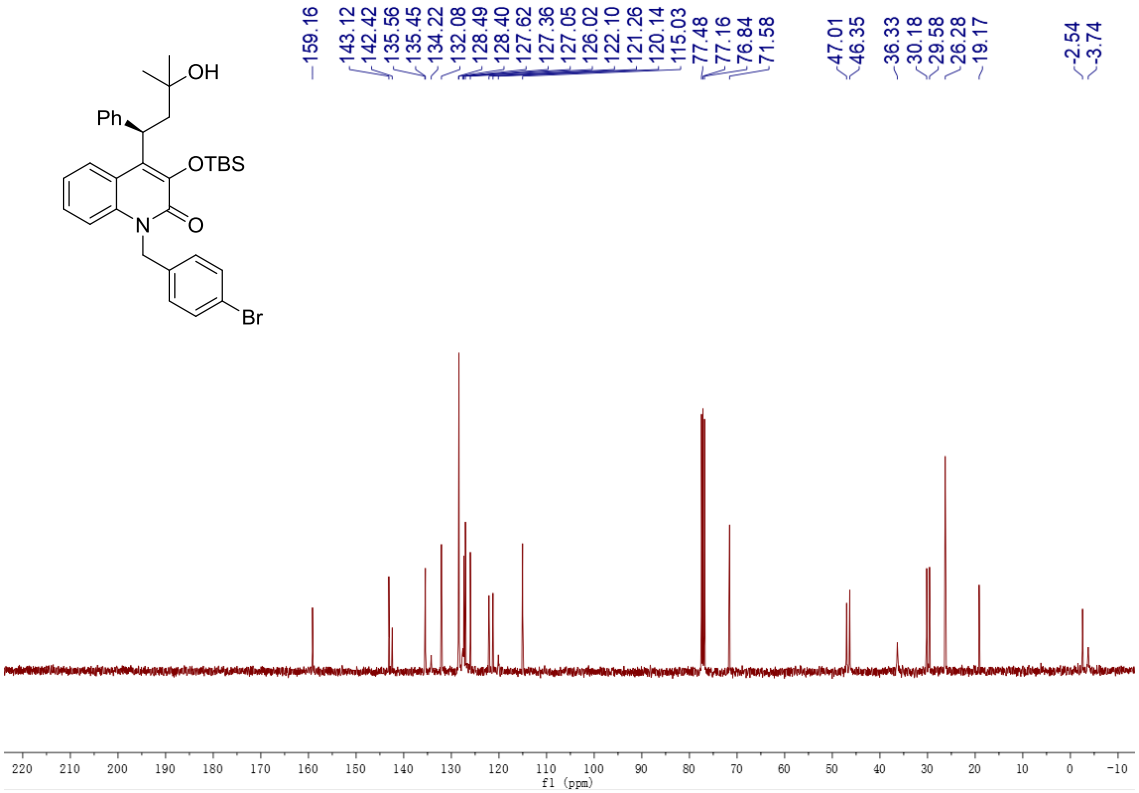


1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-4-(3-hydroxy-3-methyl-1-phenylbutyl)quinolin-2(1H)-one (6)

NMR (400 MHz, $CDCl_3$)

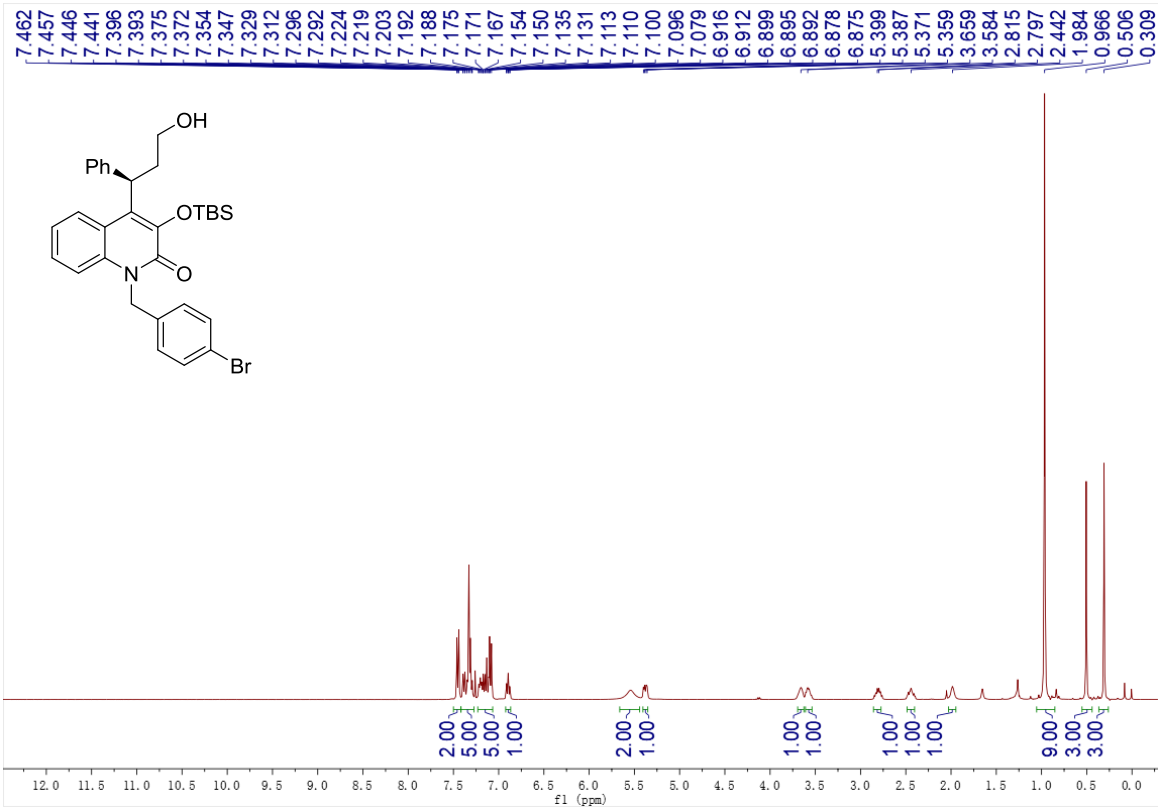


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

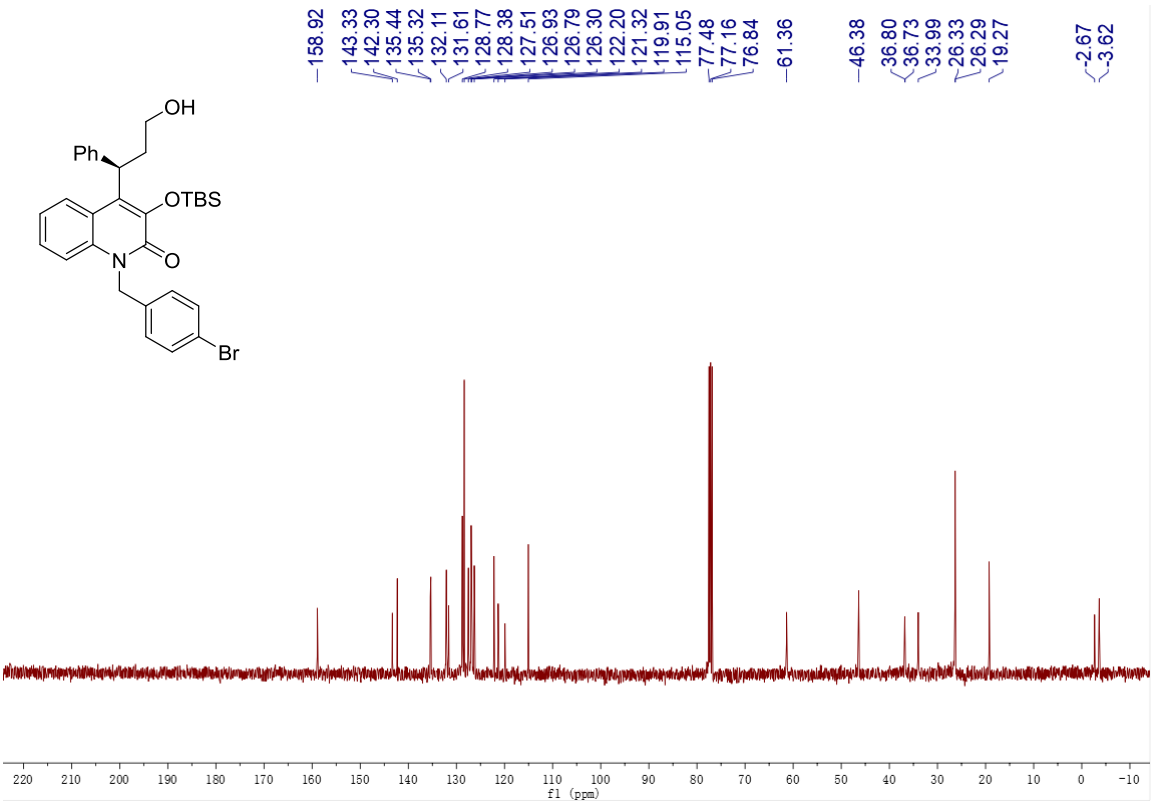


1-(4-bromobenzyl)-3-((tert-butyldimethylsilyl)oxy)-4-(3-hydroxy-1-phenylpropyl)quinolin-2(1H)-one (7)

NMR (400 MHz, $CDCl_3$)

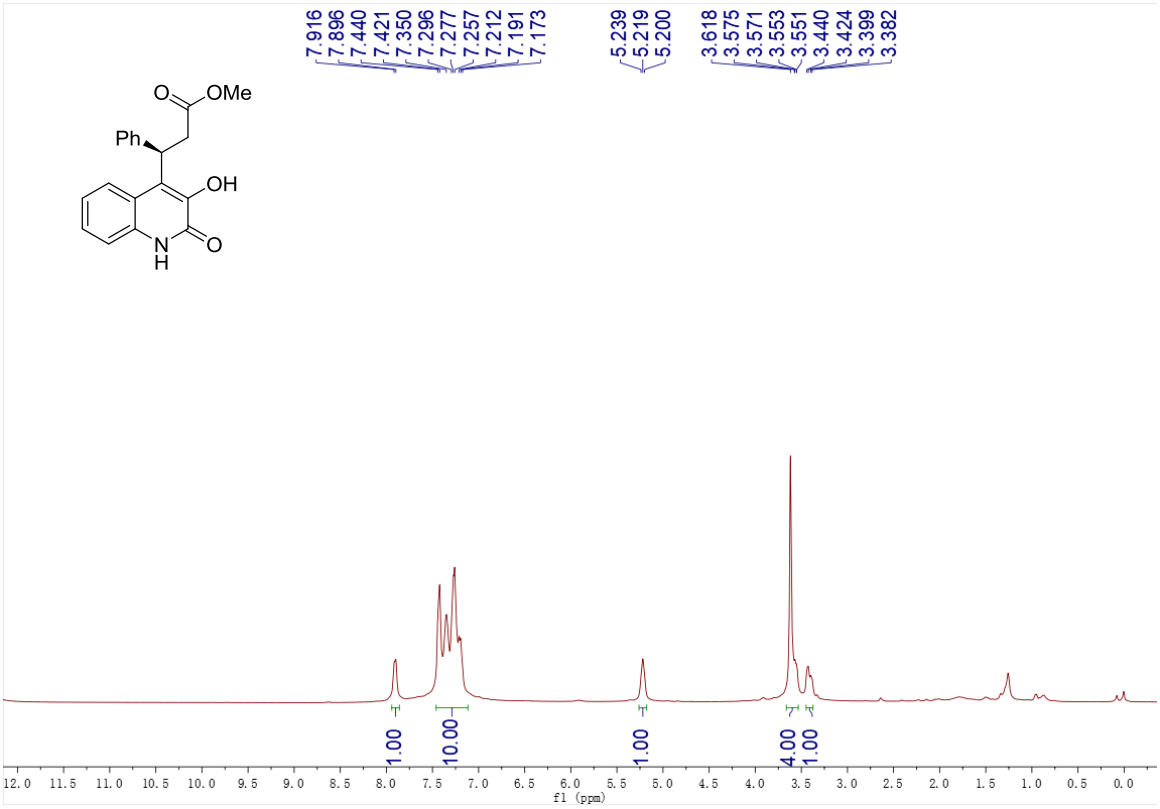


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

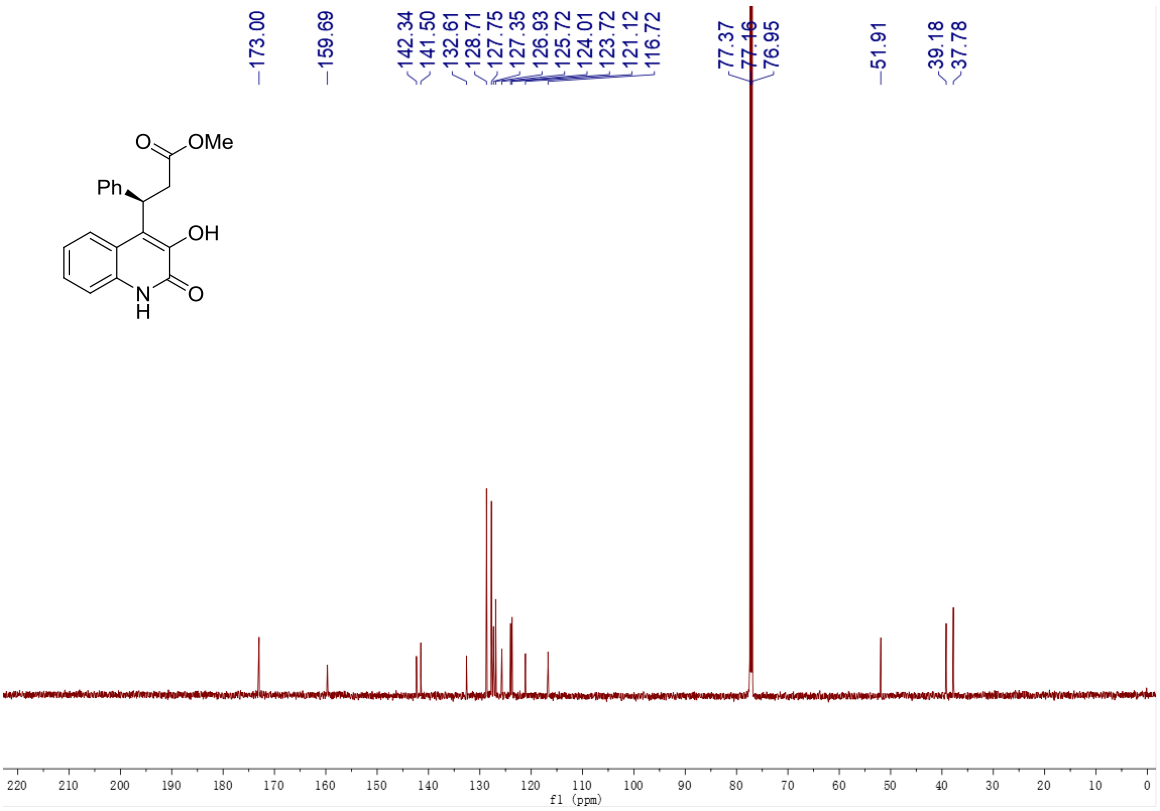


methyl (R)-3-(3-hydroxy-2-oxo-1,2-dihydroquinolin-4-yl)-3-phenylpropanoate (8)

NMR (400 MHz, $CDCl_3$)

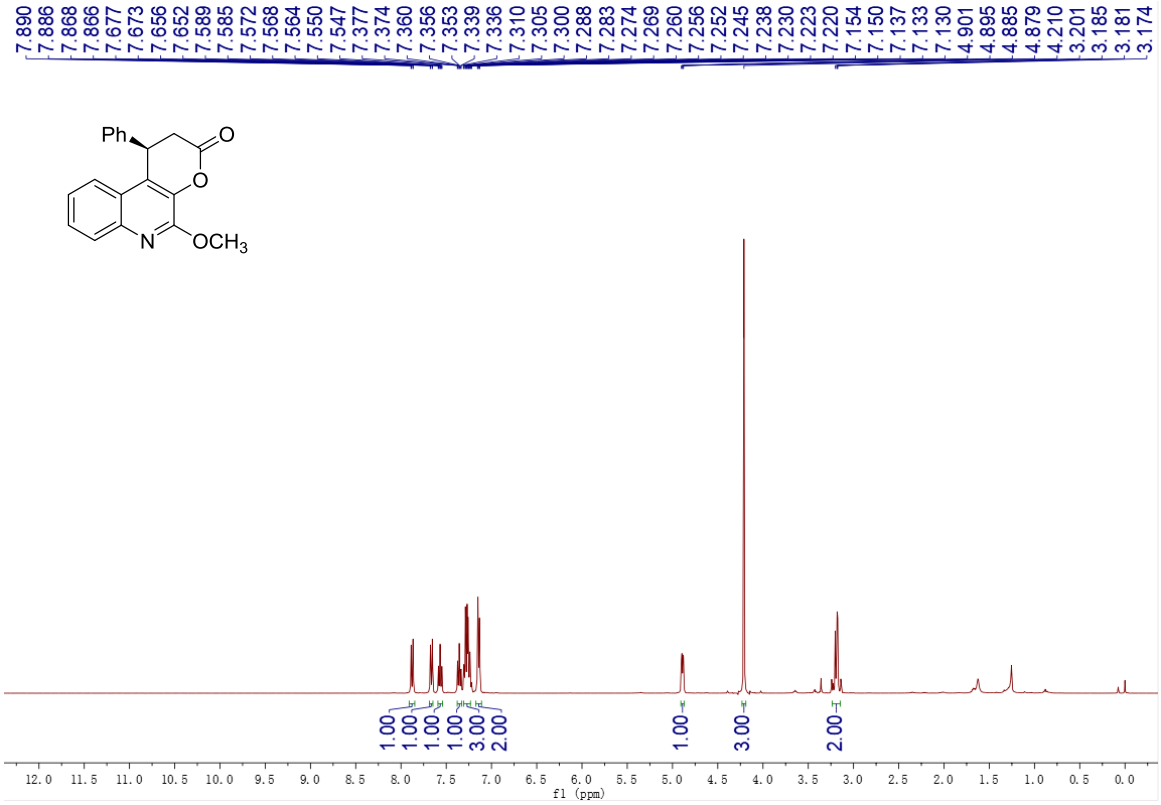


$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$)

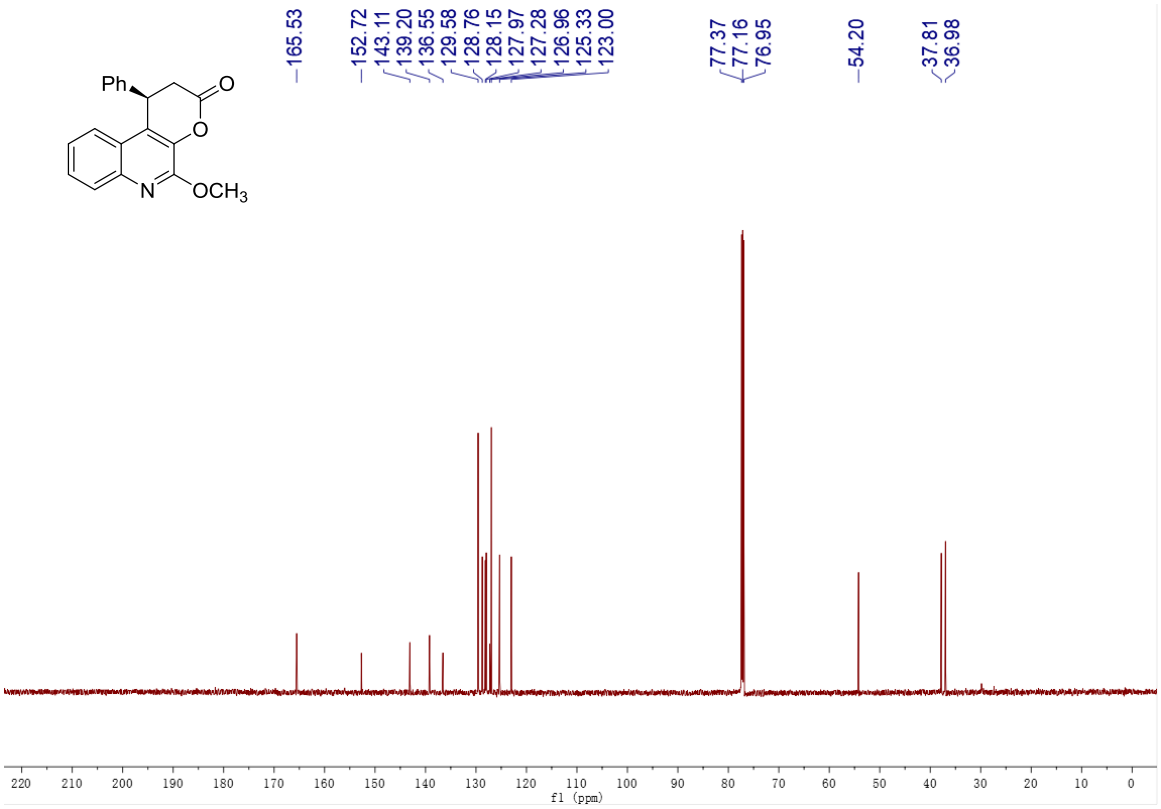


5-methoxy-1-phenyl-1,2-dihydro-3H-pyrano[2,3-c]quinolin-3-one (9)

NMR (400 MHz, $CDCl_3$)

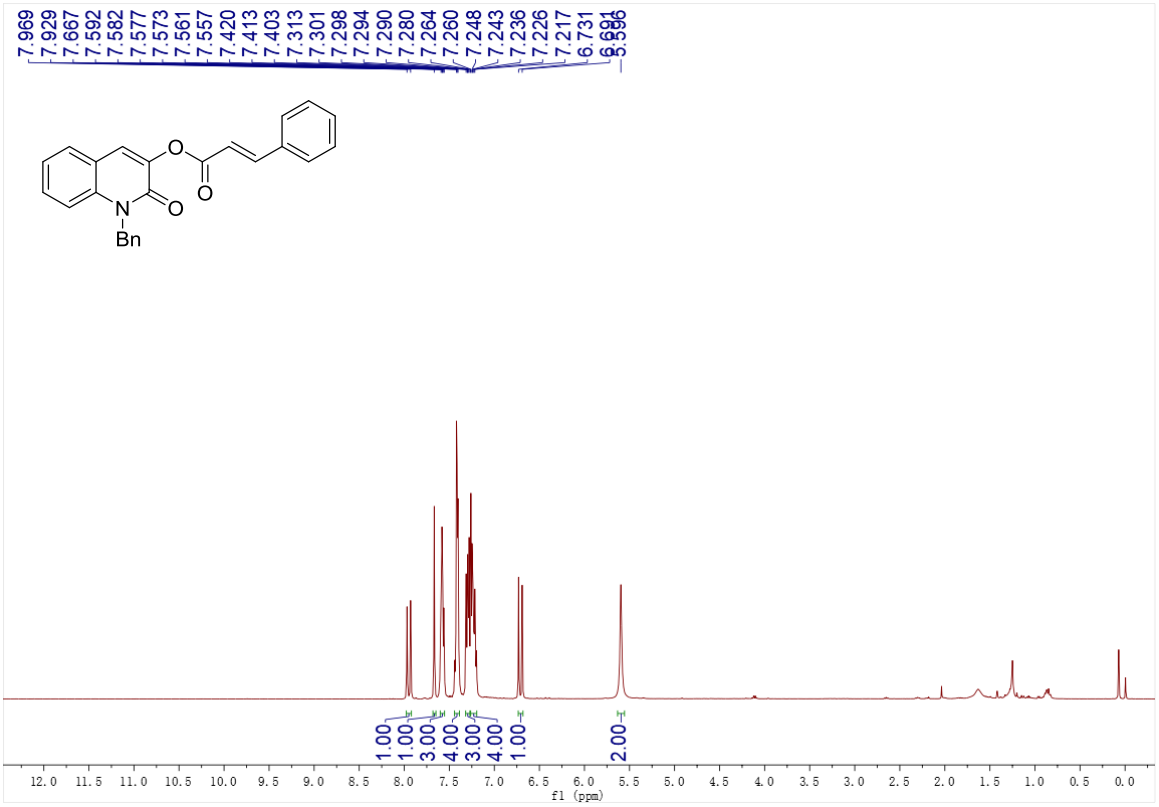


$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$)

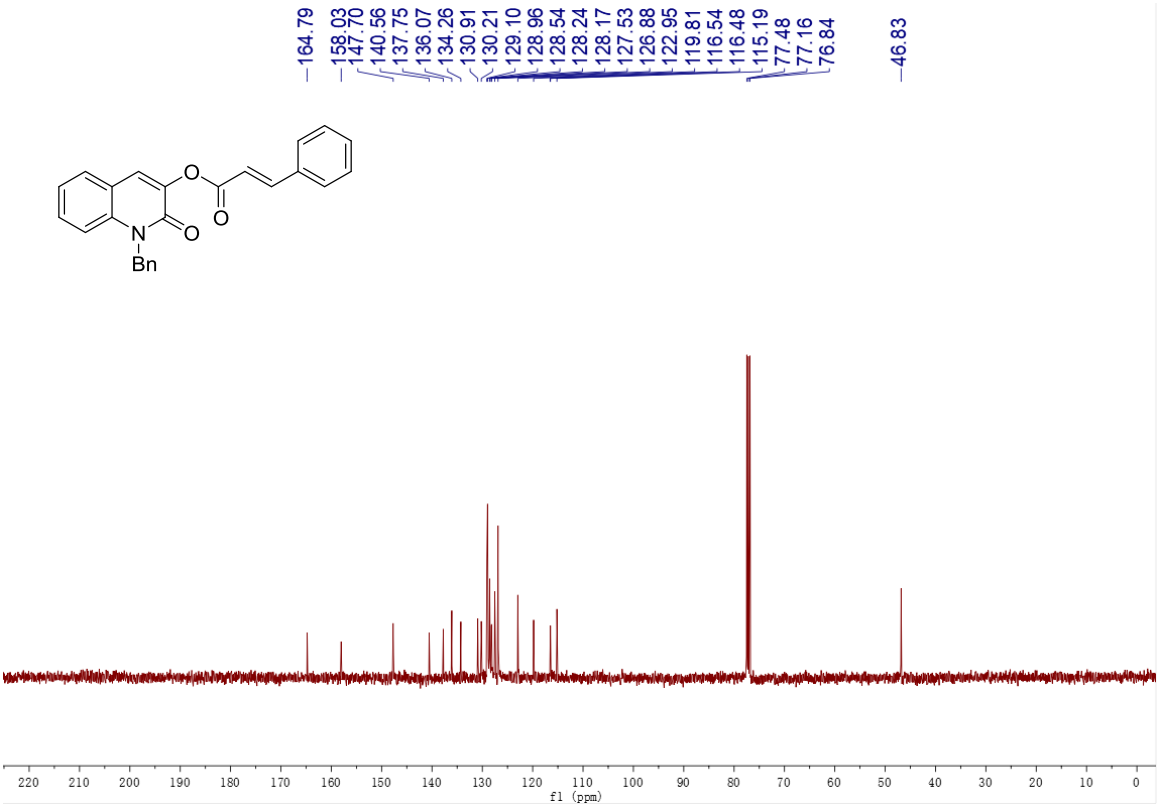


1-benzyl-2-oxo-1,2-dihydroquinolin-3-yl cinnamate (10)

NMR (400 MHz, $CDCl_3$)

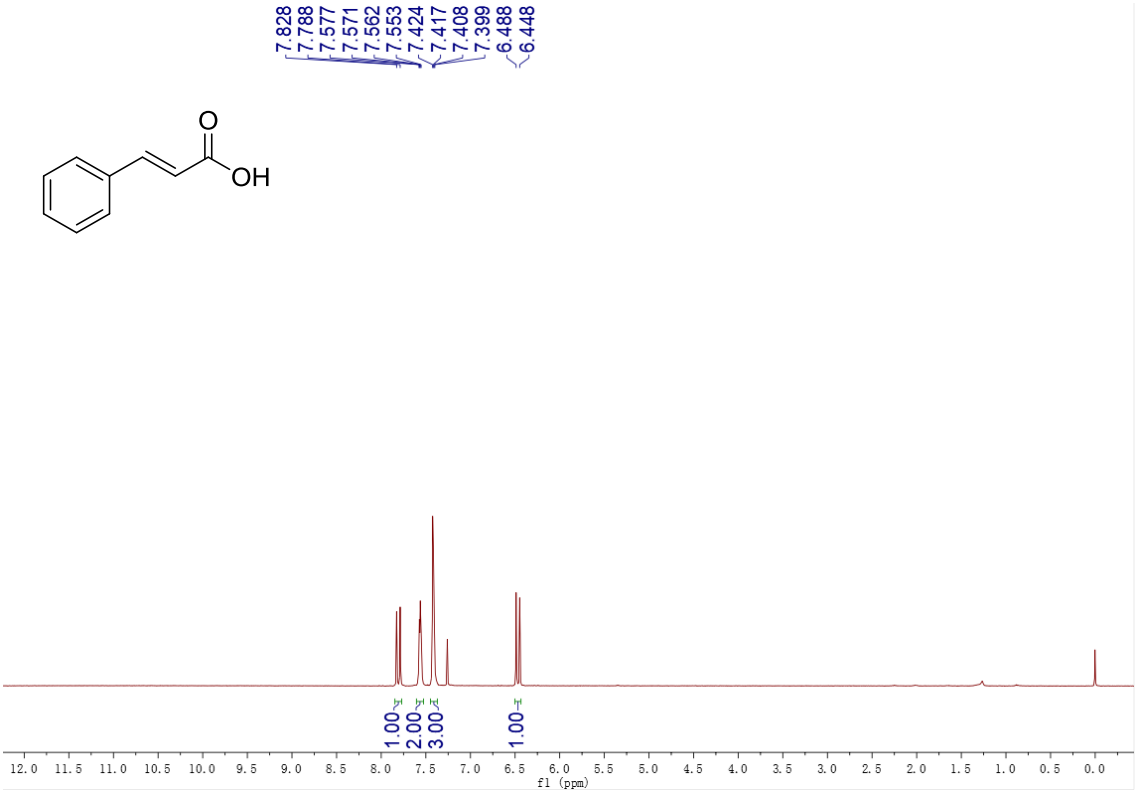


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



cinnamic acid (12)

NMR (400 MHz, $CDCl_3$)



3-(naphthalen-2-yl)acrylic acid (13)

NMR (400 MHz, DMSO-d_6)