Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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General information

Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.27 ppm, for ^{13}C NMR: $CDCl_3$ = 77.23. Infrared spectra were recorded on a FT-IR spectrometer with KBr discs. Analytical TLC was performed on precoated silica gel GF254 plates. Column chromatography was carried out on silica gel or alumina (200–300 mesh). HRMS were carried out on an Orbitrap analyzer. Optical rotations were measured using a 1.0 mL cell with a 10 cm path length on ANTON PAAR MCP 200 polarimeter and concentrations (c) were reported in g×(100 mL)$^{-1}$. Enantiomeric excesses were determined by HPLC using a Daicel Chiralpak AD-H or OD-H column with hexane/*i*-PrOH as the eluent.

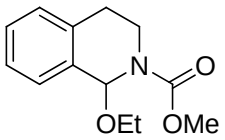
General procedure for the asymmetric coupling of aldehyde with carbamates

To a solution of **1a** (0.1 mmol, 1.0 eq) in dry Et_2O (1.0 mL) was added ligand **E** (0.02 mmol, 0.2 eq), **2a** (0.3 mmol, 3.0 eq), $Cu(OTf)_2$ (0.01 mmol, 0.1 eq), EtOH (0.1 mmol, 1.0 eq) at room temperature. The resulting mixture was stirred for 8 h until TLC indicated the completed consumption of **1a**. Then the reaction mixture was poured into the suspension of excess $NaBH_4$ (0.2 mmol, 2.0 eq) in EtOH (1 mL) at 0 °C, and after stirring for 10 min, the solution was treated with saturated aqueous $NaHCO_3$. The mixture was extracted with Et_2O (10 mL×3), organic layers were combined and dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography to give the desired product **3a** as oil (25.0 mg, 91% yield, syn/anti = 74:26). The anti- and syn- diastereoisomers can be separated using ethyl acetate/MeOH/petroleum ether (10:5:90) as eluent.

General procedure for the one-pot alkylation of quinolines

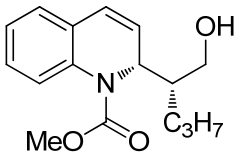
An oven-dried 5 mL flask was sequentially charged with $NaHCO_3$ (0.15 mmol, 1.5 eq), **5a** (0.1 mmol, 1.0 eq), EtOH (0.3 mmol, 3 eq) and dry toluene (1.0 mL). The reaction mixture was allowed to stir in an ice-bath for 15 min, and then methyl chloroformate (0.12 mmol, 1.2 eq) was added dropwise. It was allowed to warm to room temperature and stirred for 3h before the TLC showed the completed consumption of **5a** (NOTE: the TLC plate was saturated by Et_3N to avoid the decomposing of in situ **1a**). Solvent was removed under reduced pressure, EtOH and excess methyl chloroformate was removed via azeotropic distillation (1 mL×3, freshly distilled toluene). Et_2O (1 mL) was added and the mixture was stirred for 1 min. Then it was hold still and the supernatant was removed to another dry 5 mL flask. Ligand **E** (0.02 mmol, 0.2 eq), **2a** (0.3 mmol, 3.0 eq), $Cu(OTf)_2$ (0.01 mmol, 0.1 eq) and EtOH (0.1 mmol, 1.0 eq) were added sequentially at room temperature. The resulting mixture was stirred for 8 h until TLC indicated the completed reaction. Then the reaction mixture was poured into the suspension of excess $NaBH_4$ (0.2 mmol, 2.0 eq) in EtOH (1 mL) at 0 °C, and after stirring for 10 min, the solution was treated with saturated aqueous $NaHCO_3$. The mixture was extracted with Et_2O (10 mL×3), organic layers were combined and dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography to give the desired product **3a** as oil (19.8 mg, 72% yield, syn/anti = 63:37). The anti- and syn-diastereoisomers can be separated using ethyl acetate/MeOH/petroleum ether (10:5:90) as eluent.

Analytical data for products



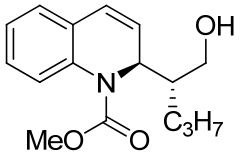
Methyl 1-ethoxy-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (6b)

^{1}H NMR (400 MHz, $CDCl_3$, rotamers seen) δ 7.32 (s, 1H), 7.26–7.22 (m, 2H), 7.14 (s, 1H), 6.29–6.05 (m, 1H), 4.26–3.96 (m, 1H), 3.77 (s, 3H), 3.75–3.60 (m, 2H), 3.55–3.36 (m, 1H), 3.03–2.70 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, rotamers seen) δ 156.7, 156.0, 135.1, 134.9, 134.5, 134.3, 128.8, 128.7, 128.4, 126.6, 81.6, 63.7, 63.2, 52.9, 37.9, 37.3, 28.4, 28.2, 15.4; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{13}H_{18}NO_3$: 236.1281, found 236.1279.



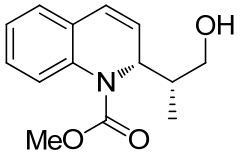
(*R*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (3a-*syn*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.25–7.19 (m, 1H), 7.15–7.07 (m, 2H), 6.54 (d, *J* = 9.6 Hz, 1H), 6.21 (dd, *J* = 9.4, 6.1 Hz, 1H), 4.86 (dd, *J* = 10.8, 6.0 Hz, 1H), 3.83 (s, 3H), 3.63 (d, *J* = 11.8 Hz, 1H), 3.49 (s, 1H), 3.22 (br, 1H), 1.67–1.57 (m, 1H), 1.51–1.39 (m, 2H), 1.36–1.26 (m, 1H), 1.22–1.12 (m, 1H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 133.8, 129.5, 127.7, 127.6, 126.5, 125.1, 125.0, 124.6, 59.8, 53.7, 53.4, 43.3, 28.5, 20.6, 14.5; IR ν_{max} 2958, 2923, 2169, 1704, 1475, 1438, 1322, 1261, 1141, 1077, 965 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{16}H_{22}NO_3$: 276.1594, found 276.1597; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 7.913 min, t_{minor} = 27.960 min, ee = 99%; $[\alpha]_D^{20}$ = 282.6 (c = 0.12, $CHCl_3$).



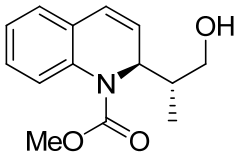
(*S*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (3a-*anti*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.24–7.13 (m, 1H), 7.13–7.01 (m, 2H), 6.57 (d, *J* = 9.7 Hz, 1H), 6.01 (dd, *J* = 9.5, 5.9 Hz, 1H), 5.23 (s, 1H), 3.81 (s, 3H), 3.66–3.59 (m, 1H), 3.53–3.39 (m, 1H), 1.67 (s, 1H), 1.41–1.20 (m, 2H), 1.18–1.01 (m, 2H), 0.71 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 135.4, 129.2, 128.0, 127.6, 126.3, 125.9, 124.9, 124.9, 61.6, 53.8, 53.7, 45.6, 27.5, 20.8, 14.2; IR ν_{max} 2958, 2923, 2169, 1704, 1475, 1438, 1322, 1261, 1141, 1077, 965 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{16}H_{22}NO_3$: 276.1594, found 276.1597; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 13.977 min, t_{minor} = 8.762 min, ee = 99%; $[\alpha]_D^{20}$ = –125.2 (c = 0.11, $CHCl_3$).



(*R*)-Methyl 2-((*R*)-1-hydroxypropan-2-yl)quinoline-1(2*H*)-carboxylate (3b-*syn*)

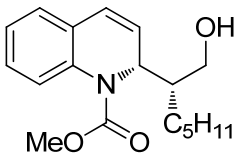
The reaction was performed following the general procedure. Yield: 21.0 mg, 85%, syn/anti = 72 : 28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.26–7.18 (m, 1H), 7.16–7.04 (m, 2H), 6.53 (d, *J* = 9.6 Hz, 1H), 6.16 (dd, *J* = 9.5, 6.0 Hz, 1H), 4.83 (dd, *J* = 10.6, 6.0 Hz, 1H), 3.83 (s, 3H), 3.70 (d, *J* = 11.1 Hz, 1H), 3.35 (s, 1H), 3.13 (br, 1H), 1.64 (s, 1H), 1.04 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 134.0, 129.2, 127.7, 127.6, 126.5, 125.2, 124.9, 124.6, 64.0, 54.2, 53.7, 38.4, 13.3; IR ν_{max} 2974, 2929, 2169, 1701, 1453, 1422, 1305, 1211, 1162, 1020, 768 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{14}H_{18}NO_3$: 248.1281, found 248.1283; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 8.648 min, t_{minor} = 13.725 min, ee = 85%; $[\alpha]_D^{20}$ = 183.0 (c = 0.15, $CHCl_3$).



(*S*)-Methyl 2-((*R*)-1-hydroxypropan-2-yl)quinoline-1(2*H*)-carboxylate (3b-*anti*)

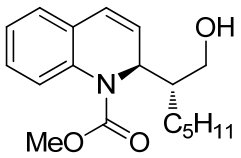
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.24–7.15 (m, 1H), 7.08 (t, *J* = 6.3 Hz, 2H), 6.57 (d, *J* = 9.7 Hz, 1H), 5.99 (dd, *J* = 9.3, 6.0 Hz, 1H), 5.20 (s, 1H), 3.82 (s, 3H), 3.47 (s, 2H), 1.91–1.80 (m, 1H), 0.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1,

135.7, 129.0, 127.9, 127.7, 126.4, 125.8, 124.8, 124.7, 64.0, 53.8, 53.7, 41.3, 10.8; IR ν_{max} 2974, 2929, 2169, 1701, 1453, 1422, 1305, 1211, 1162, 1020, 768 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{14}H_{18}NO_3$: 248.1281, found 248.1283; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 15/85, 1.0 mL/min, 236 nm), retention time: t_{major} = 17.003 min, t_{minor} = 12.867 min, ee = 94%; $[\alpha]_D^{20}$ = –119.2 (c = 0.12, $CHCl_3$).



(*R*)-Methyl 2-((*R*)-1-hydroxyheptan-2-yl)quinoline-1(2*H*)-carboxylate (3c-*syn*)

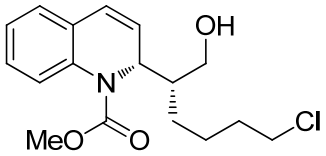
The reaction was performed following the general procedure. Yield: 24.8 mg, 82%, syn/anti = 70 : 30; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.26–7.18 (m, 1H), 7.14–7.03 (m, 2H), 6.53 (d, *J* = 9.6 Hz, 1H), 6.20 (dd, *J* = 9.5, 6.0 Hz, 1H), 4.86 (dd, *J* = 10.7, 6.0 Hz, 1H), 3.83 (s, 3H), 3.63 (d, *J* = 11.1 Hz, 1H), 3.49 (d, *J* = 12.0 Hz, 1H), 3.15 (br, 1H), 1.69–1.52 (m, 1H), 1.49–1.09 (m, 8H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 133.9, 129.5, 127.7, 127.6, 126.5, 125.1, 124.9, 124.6, 59.9, 53.7, 53.4, 43.5, 32.3, 27.1, 26.3, 22.7, 14.2; IR ν_{max} 2954, 2925, 2169, 1706, 1490, 1441, 1337, 1261, 1277, 1130, 1026, 770 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{18}H_{26}NO_3$: 304.1907, found 304.1903; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 7.252 min, t_{minor} = 21.264 min, ee = 95%; $[\alpha]_D^{20}$ = 46.2 (c = 0.21, $CHCl_3$).



(*S*)-Methyl 2-((*R*)-1-hydroxyheptan-2-yl)quinoline-1(2*H*)-carboxylate (3c-*anti*)

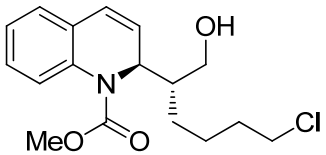
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.19–7.05 (m, 1H), 7.04–6.94 (m, 2H), 6.49 (d, *J* = 9.7 Hz, 1H), 5.94 (dd, *J* = 9.6, 5.8 Hz, 1H), 5.14 (s, 1H), 3.73 (s, 3H), 3.61–3.49 (m, 1H), 3.46–3.33 (m, 1H), 1.57 (s, 1H), 1.28–0.90 (m, 8H), 0.71 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 135.4, 129.3, 128.0, 127.6, 126.3, 125.9, 124.9, 124.9, 61.7, 53.8, 53.6, 46.0, 32.0, 27.4, 25.4, 22.6, 14.1; IR ν_{max} 2954,

2925, 2169, 1706, 1490, 1441, 1337, 1261, 1277, 1130, 1026, 770 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{18}H_{26}NO_3$: 304.1907, found 304.1903; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 12.058 min, t_{minor} = 7.809 min, ee = 90%; $[\alpha]_D^{20}$ = –12.5 (c = 0.19, $CHCl_3$).



(*R*)-Methyl 2-((*R*)-6-chloro-1-hydroxyhexan-2-yl)quinoline-1(2*H*)-carboxylate (3d-*syn*)

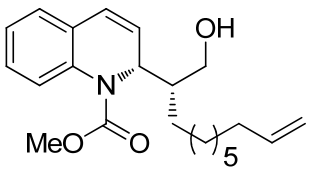
The reaction was performed following the general procedure. Yield: 29.1 mg, 90%, syn/anti = 72 : 28; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.25–7.18 (m, 1H), 7.17–7.08 (m, 2H), 6.55 (d, *J* = 9.6 Hz, 1H), 6.19 (dd, *J* = 9.5, 6.1 Hz, 1H), 4.86 (dd, *J* = 10.6, 6.0 Hz, 1H), 3.83 (s, 3H), 3.70–3.61 (m, 1H), 3.58–3.42 (m, 3H), 3.24 (br, 1H), 1.80–1.53 (m, 4H), 1.47–1.29 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 133.8, 129.1, 127.7, 127.6, 126.5, 125.4, 125.0, 124.6, 59.8, 53.7, 53.2, 45.0, 43.4, 33.0, 25.7, 24.8; IR ν_{max} 2926, 2851, 2170, 1702, 1676, 1571, 1490, 1441, 1384, 1339, 1304, 1278, 1256, 1209, 1192, 1129, 1025, 766 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{17}H_{23}ClNO_3$: 324.1361, found 324.1360; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 11.439 min, t_{minor} = 39.166 min, ee = 98%; $[\alpha]_D^{20}$ = 88.0 (c = 0.10, $CHCl_3$).



(*S*)-Methyl 2-((*R*)-6-chloro-1-hydroxyhexan-2-yl)quinoline-1(2*H*)-carboxylate (3d-*anti*)

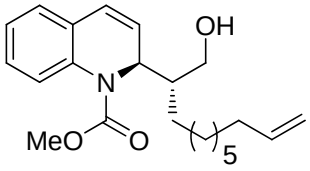
^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.25–7.15 (m, 1H), 7.13–6.99 (m, 2H), 6.58 (d, *J* = 9.7 Hz, 1H), 6.01 (dd, *J* = 9.5, 5.9 Hz, 1H), 5.23 (s, 1H), 3.81 (s, 3H), 3.63 (dd, *J* = 11.7, 4.1 Hz, 1H), 3.51–3.44 (m, 1H), 3.37 (t, *J* = 6.5 Hz, 2H), 1.70–1.47 (m, 4H), 1.43–1.35 (m, 1H), 1.28–1.13 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 135.3, 129.0, 127.9, 127.8, 126.4, 126.0, 125.0, 124.9, 61.5, 53.7, 53.6, 45.8, 44.9,

32.7, 25.0, 24.8; IR ν_{max} 2926, 2851, 2170, 1702, 1676, 1571, 1490, 1441, 1384, 1339, 1304, 1278, 1256, 1209, 1192, 1129, 1025, 766 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{17}H_{23}ClNO_3$: 324.1361, found 324.1360; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 20.869 min, t_{minor} = 14.017 min, ee = 93%; $[\alpha]_D^{20}$ = –68.3 (c = 0.16, $CHCl_3$).



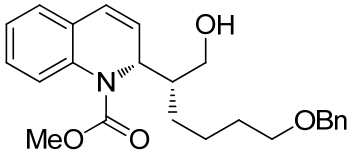
(*R*)-Methyl 2-((*R*)-1-hydroxyundec-10-en-2-yl)quinoline-1(2*H*)-carboxylate (3e-*syn*)

The reaction was performed following the general procedure. Yield: 27.8 mg, 78%, syn/anti = 64 : 36; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.25–7.19 (m, 1H), 7.16–7.09 (m, 2H), 6.54 (d, *J* = 9.6 Hz, 1H), 6.21 (dd, *J* = 9.5, 6.1 Hz, 1H), 5.80 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.04–4.78 (m, 3H), 3.84 (s, 3H), 3.63 (d, *J* = 11.8 Hz, 1H), 3.48 (t, *J* = 10.7 Hz, 1H), 3.19 (br, 1H), 2.02 (q, *J* = 7.0 Hz, 2H), 1.70–1.56 (m, 1H), 1.45–1.12 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 139.3, 129.5, 127.7, 127.6, 126.5, 125.1, 124.9, 124.6, 114.3, 59.9, 53.7, 53.4, 43.5, 33.9, 30.0, 29.7, 29.6, 29.5, 29.2, 29.1, 29.0, 27.4, 26.3; IR ν_{max} 2925, 2854, 1680, 1494, 1459, 1441, 1383, 1338, 1276, 1254, 1130, 1029, 909, 766 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{22}H_{32}NO_3$: 358.2377, found 358.2375; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 6.983 min, t_{minor} = 25.972 min, ee = 97%; $[\alpha]_D^{20}$ = 102.1 (c = 0.24, $CHCl_3$).



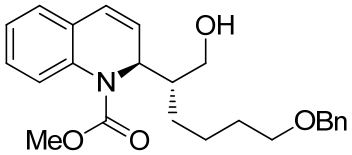
(*S*)-Methyl 2-((*R*)-1-hydroxyundec-10-en-2-yl)quinoline-1(2*H*)-carboxylate (3e-*anti*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.20 (dd, *J* = 10.1, 4.0 Hz, 1H), 7.15–7.05 (m, 2H), 6.57 (d, *J* = 9.7 Hz, 1H), 6.01 (dd, *J* = 9.5, 5.8 Hz, 1H), 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.23 (s, 1H), 5.07–4.89 (m, 2H), 3.81 (s, 3H), 3.62 (d, *J* = 10.9 Hz, 1H), 3.49–3.41 (m, 1H), 1.99 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.64 (s, 1H), 1.38–1.02 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 139.4, 135.4, 129.3, 128.0, 127.7, 126.3, 125.9, 124.9, 124.9, 114.3, 61.7, 53.8, 53.7, 46.0, 33.9, 29.7, 29.3, 29.1, 29.0, 27.7, 25.3; IR ν_{max} 2925, 2854, 1680, 1494, 1459, 1441, 1383, 1338, 1276, 1254, 1130, 1029, 909, 766 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{22}H_{32}NO_3$: 358.2377, found 358.2375; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 10.491 min, t_{minor} = 7.690 min, ee = 91%; $[\alpha]_D^{20}$ = –112.6 (c = 0.25, $CHCl_3$).



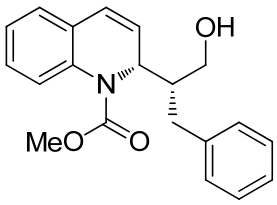
(*R*)-Methyl 2-((*R*)-6-(benzyloxy)-1-hydroxyhexan-2-yl)quinoline-1(2*H*)-carboxylate (3f-*syn*)

The reaction was performed following the general procedure. Yield: 33.6 mg, 85%, syn/anti = 60 : 40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.31 (m, 5H), 7.31–7.26 (m, 1H), 7.25–7.18 (m, 1H), 7.16–7.04 (m, 2H), 6.54 (d, *J* = 9.6 Hz, 1H), 6.21 (dd, *J* = 9.5, 6.0 Hz, 1H), 4.87 (dd, *J* = 10.6, 6.0 Hz, 1H), 4.50 (s, 2H), 3.84 (s, 3H), 3.64 (d, *J* = 11.0 Hz, 1H), 3.52–3.42 (m, 3H), 3.14 (br, 1H), 1.71–1.53 (m, 3H), 1.38–1.26 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 138.9, 133.8, 129.4, 128.5, 127.8, 127.7, 127.6, 126.5, 125.1, 124.9, 124.6, 73.0, 70.6, 59.9, 53.7, 53.4, 43.5, 29.9, 27.4, 26.3; IR ν_{max} 2963, 2842, 1700, 1532, 1492, 1461, 1440, 1357, 1332, 1259, 1204, 1027, 766 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{24}H_{30}NO_4$: 396.2169, found 396.2166; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 236 nm), retention time: t_{major} = 8.210 min, t_{minor} = 26.742 min, ee = 93%; $[\alpha]_D^{20}$ = 310.7 (c = 0.31, $CHCl_3$).



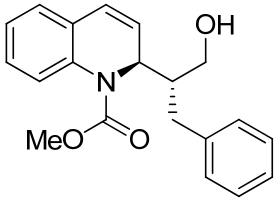
(*S*)-Methyl 2-((*R*)-6-(benzyloxy)-1-hydroxyhexan-2-yl)quinoline-1(2*H*)-carboxylate (3f-*anti*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.27 (m, 6H), 7.22–7.15 (m, 1H), 7.12–7.01 (m, 2H), 6.57 (d, *J* = 9.7 Hz, 1H), 6.00 (dd, *J* = 9.6, 5.8 Hz, 1H), 5.23 (s, 1H), 4.48 (s, 2H), 3.81 (s, 3H), 3.62 (dd, *J* = 11.8, 4.4 Hz, 1H), 3.50–3.36 (m, 3H), 1.65 (s, 1H), 1.56–1.46 (m, 2H), 1.21–1.06 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 138.9, 135.5, 129.3, 128.6, 128.0, 127.8, 127.7, 126.3, 126.0, 124.9, 73.0, 70.6, 61.8, 53.8, 53.7, 46.0, 29.6, 27.7, 26.1; IR ν_{max} 2963, 2842, 1700, 1532, 1492, 1461, 1440, 1357, 1332, 1259, 1204, 1027, 766 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{24}H_{30}NO_4$: 396.2169, found 396.2166; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 40/60, 1.0 mL/min, 236 nm), retention time: t_{major} = 8.805 min, t_{minor} = 7.269 min, ee = 80%; $[\alpha]_D^{20}$ = –132.6 (c = 0.09, $CHCl_3$).



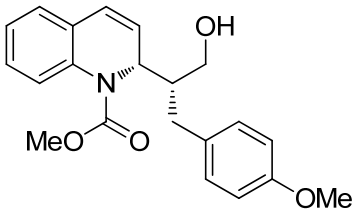
(*R*)-Methyl 2-((*R*)-1-hydroxy-3-phenylpropan-2-yl)quinoline-1(2*H*)-carboxylate (3g-*syn*)

The reaction was performed following the general procedure. Yield: 29.1 mg, 90%, syn/anti = 82 : 18; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.28–7.08 (m, 8H), 6.64 (d, *J* = 9.6 Hz, 1H), 6.31 (dd, *J* = 9.6, 6.0 Hz, 1H), 5.01 (dd, *J* = 10.8, 6.0 Hz, 1H), 3.86 (s, 3H), 3.54 (d, *J* = 10.9 Hz, 1H), 3.29–3.18 (m, 1H), 2.93–2.74 (m, 2H), 1.72 (t, *J* = 9.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 140.3, 133.8, 129.5, 129.0, 128.6, 128.6, 128.5, 127.8, 127.6, 126.6, 126.1, 125.5, 125.0, 124.6, 58.8, 53.8, 53.2, 46.1, 32.6; IR ν_{max} 3028, 2952, 2923, 2848, 2169, 1702, 1490, 1440, 1393, 1378, 1329, 1276, 1250, 1129, 1028, 766, 746 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{20}H_{22}NO_3$: 324.1594, found 324.1593; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 236 nm), retention time: t_{major} = 8.745 min, t_{minor} = 29.554 min, ee = 99%; $[\alpha]_D^{20}$ = 111.4 (c = 0.21, $CHCl_3$).



(*S*)-Methyl 2-((*R*)-1-hydroxy-3-phenylpropan-2-yl)quinoline-1(2*H*)-carboxylate (3g-*anti*)

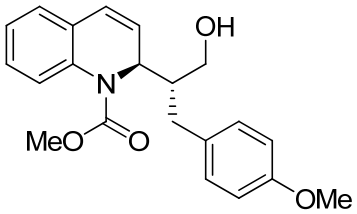
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.26–7.08 (m, 6H), 6.98 (d, *J* = 7.2 Hz, 2H), 6.63 (d, *J* = 9.6 Hz, 1H), 6.12 (dd, *J* = 9.6, 5.9 Hz, 1H), 5.33 (s, 1H), 3.84 (s, 3H), 3.63–3.38 (m, 2H), 2.62 (d, *J* = 11.2 Hz, 1H), 2.27–1.88 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 140.4, 135.3, 129.0, 128.5, 127.9, 126.5, 126.2, 126.1, 125.0, 61.0, 53.7, 53.5, 47.9, 32.5; IR ν_{max} 3028, 2952, 2923, 2848, 2169, 1702, 1490, 1440, 1393, 1378, 1329, 1276, 1250, 1129, 1028, 766, 746 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{20}H_{22}NO_3$: 324.1594, found 324.1593; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 236 nm), retention time: t_{major} = 13.087 min, t_{minor} = 8.622 min, ee = 95%; $[\alpha]_D^{20}$ = –43.3 (c = 0.22, $CHCl_3$).



(*R*)-Methyl 2-((*R*)-1-hydroxy-3-(4-methoxyphenyl)propan-2-yl)quinoline-1(2*H*)-carboxylate (3h-*syn*)

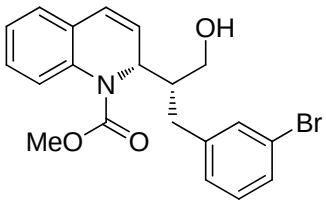
The reaction was performed following the general procedure. Yield: 26.7 mg, 76%, syn/anti = 79 : 21; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.25–7.11 (m, 3H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.79 (d, *J* = 8.3 Hz, 2H), 6.63 (d, *J* = 9.6 Hz, 1H), 6.30 (dd, *J* = 9.5, 6.1 Hz, 1H), 5.00 (dd, *J* = 10.6, 6.0 Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 3.55 (d, *J* = 10.3 Hz, 1H), 3.24 (t, *J* = 10.2 Hz, 1H), 2.86–2.71 (m, 2H), 1.69 (t, *J* = 9.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 156.4, 133.8, 132.2, 130.3, 129.4, 129.0, 127.6, 127.5, 126.5, 125.3, 124.9, 124.6, 113.9, 113.8, 58.8, 55.3, 53.7, 53.2, 46.2, 31.6; IR ν_{max} 3037, 2921, 2850, 2169, 1704, 1512, 1490, 1441, 1384, 1336, 1300, 1276, 1247, 1129, 1028, 766 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{21}H_{24}NO_4$: 354.1700, found 354.1701; HPLC: the ee value was determined by HPLC

analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 236 nm), retention time: t_{major} = 13.061 min, t_{minor} = 37.970 min, ee = 99%; $[\alpha]_D^{20}$ = 405.1 (c = 0.12, $CHCl_3$).



(*S*)-Methyl 2-((*R*)-1-hydroxy-3-(4-methoxyphenyl)propan-2-yl)quinoline-1(2*H*)-carboxylate (3h-*anti*)

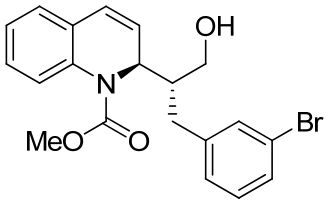
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.27–7.21 (m, 1H), 7.18–7.05 (m, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 2H), 6.62 (d, *J* = 9.7 Hz, 1H), 6.11 (dd, *J* = 9.6, 5.9 Hz, 1H), 5.31 (s, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.45 (dt, *J* = 11.7, 9.3 Hz, 2H), 2.55 (d, *J* = 11.0 Hz, 1H), 2.06–1.82 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 156.9, 135.3, 132.4, 129.8, 128.9, 127.9, 127.8, 126.5, 126.1, 125.0, 113.9, 60.9, 55.4, 53.7, 53.5, 48.0, 31.5; IR ν_{max} 3037, 2921, 2850, 2169, 1704, 1512, 1490, 1441, 1384, 1336, 1300, 1276, 1247, 1129, 1028, 766 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{21}H_{24}NO_4$: 354.1700, found 354.1701; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 236 nm), retention time: t_{major} = 15.698 min, t_{minor} = 11.812 min, ee = 93%; $[\alpha]_D^{20}$ = –367.1 (c = 0.17, $CHCl_3$).



(*R*)-Methyl 2-((*R*)-1-(3-bromophenyl)-3-hydroxypropan-2-yl)quinoline-1(2*H*)-carboxylate (3i-*syn*)

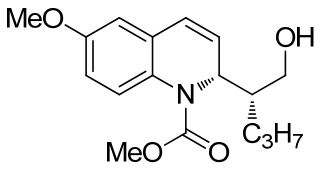
The reaction was performed following the general procedure. Yield: 35.3 mg, 88%, syn/anti = 81 : 19; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.31–7.26 (m, 2H), 7.25–7.13 (m, 3H), 7.12–7.06 (m, 2H), 6.63 (d, *J* = 9.6 Hz, 1H), 6.27 (dd, *J* = 9.5, 6.0 Hz, 1H), 4.98 (dd, *J* = 10.7, 6.1 Hz, 1H), 3.85 (s, 3H), 3.54 (d, *J* = 11.6 Hz, 1H), 3.37–3.03 (m, 2H), 2.88–2.64 (m, 2H), 1.68 (t, *J* = 10.0 Hz, 1H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ 156.6, 142.7, 133.7, 132.3, 130.0, 129.3, 128.6, 128.4, 127.9, 127.4, 126.7, 125.7, 125.1, 124.6, 122.5, 58.6, 53.9, 53.1, 45.9, 32.2; IR ν_{max} 2949, 2922, 2851, 2169, 1701, 1567, 1490, 1444, 1377, 1335, 1276, 1251, 1129, 1071, 1026, 845, 764 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{20}H_{21}BrNO_3$: 402.0699, found 402.0701; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 236 nm), retention time: t_{major} = 7.635 min, t_{minor} = 33.531 min, ee = 99%; $[\alpha]_D^{20}$ = 315.5 (c = 0.19, $CHCl_3$).



(*S*)-Methyl 2-((*R*)-1-(3-bromophenyl)-3-hydroxypropan-2-yl)quinoline-1(2*H*)-carboxylate (3i-*anti*)

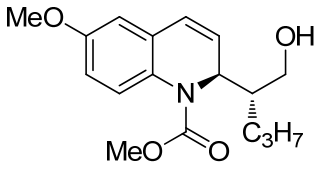
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.28–7.19 (m, 2H), 7.14–7.01 (m, 4H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 9.6 Hz, 1H), 6.09 (dd, *J* = 9.6, 5.9 Hz, 1H), 5.32 (s, 1H), 3.83 (s, 3H), 3.54–3.37 (m, 2H), 2.57 (d, *J* = 11.1 Hz, 1H), 2.25–1.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 142.9, 135.1, 132.0, 130.0, 129.3, 128.7, 127.9, 127.8, 127.6, 126.5, 126.3, 125.1, 125.0, 122.5, 60.9, 53.7, 53.4, 47.6, 32.3; IR ν_{max} 2949, 2922, 2851, 2169, 1701, 1567, 1490, 1444, 1377, 1335, 1276, 1251, 1129, 1071, 1026, 845, 764 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{20}H_{21}BrNO_3$: 402.0699, found 402.0701; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 22.329 min, t_{minor} = 16.499 min, ee = 89%; $[\alpha]_D^{20}$ = –62.5 (c = 0.14, $CHCl_3$).



(*R*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-6-methoxyquinoline-1(2*H*)-carboxylate (4a-*syn*)

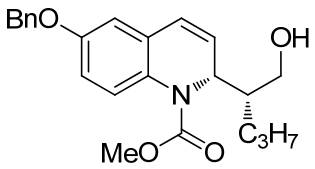
The reaction was performed following the general procedure. Yield: 26.2 mg, 86%, syn/anti = 77 : 23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 1H), 6.76 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.65 (d, *J* = 2.8 Hz, 1H), 6.49 (d, *J* = 9.7 Hz, 1H), 6.22 (dd, *J* = 9.2, 6.1 Hz, 1H), 4.84 (dd, *J* = 10.7, 6.0 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.61 (d, *J* = 12.0 Hz,

1H), 3.54–3.38 (m, 1H), 3.23 (s, 1H), 1.73–1.55 (m, 1H), 1.53–1.38 (m, 2H), 1.35–1.26 (m, 1H), 1.21–1.11 (m, 1H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 156.6, 130.2, 128.7, 126.8, 125.6, 125.1, 113.3, 111.1, 59.9, 55.6, 53.6, 53.4, 43.1, 28.6, 20.6, 14.5; IR ν_{max} 2956, 2928, 2871, 1726, 1500, 1442, 1351, 1319, 1298, 1265, 1237, 1219, 1134, 1059, 1033, 814, 763 cm^{-1}; HRMS (EI) *m/z* [M + H]$^+$ calculated for $C_{17}H_{24}NO_4$: 306.1700, found 306.1702; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 254 nm), retention time: t_{major} = 6.899 min, t_{minor} = 23.222 min, ee = 96%; $[\alpha]_D^{20}$ = 184.6 (c = 0.20, $CHCl_3$).



(*S*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-6-methoxyquinoline-1(2*H*)-carboxylate (4a-*anti*)

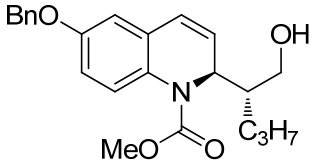
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 6.75 (dd, J = 8.8, 2.6 Hz, 1H), 6.61 (d, J = 2.8 Hz, 1H), 6.53 (d, J = 9.7 Hz, 1H), 6.19–5.90 (m, 1H), 5.23 (s, 1H), 3.80 (s, 3H), 3.80 (s, 3H), 3.62 (dd, J = 11.8, 4.2 Hz, 1H), 3.52–3.39 (m, 1H), 1.66 (s, 1H), 1.26 (s, 2H), 1.08 (s, 2H), 0.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 156.7, 130.0, 128.9, 128.5, 126.0, 125.9, 113.2, 111.0, 61.7, 55.6, 53.8, 53.6, 45.5, 27.4, 20.9, 14.2; IR ν_{max} 2956, 2928, 2871, 1726, 1500, 1442, 1351, 1319, 1298, 1265, 1237, 1219, 1134, 1059, 1033, 814, 763 cm^{-1}; HRMS (EI) *m/z* [M + H]$^+$ calculated for $C_{17}H_{24}NO_4$: 306.1700, found 306.1702; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 236 nm), retention time: t_{major} = 13.477 min, t_{minor} = 7.266 min, ee = 95%; $[\alpha]_D^{20}$ = –27.5 (c = 0.12, $CHCl_3$).



(*R*)-Methyl 6-(benzyloxy)-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4b-*syn*)

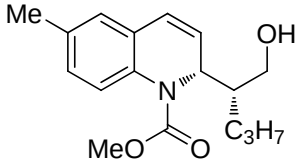
The reaction was performed following the general procedure. Yield: 27.4 mg, 72%, syn/anti = 75 : 25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.32 (m, 5H), 7.25 (s, 1H),

6.85 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.75 (d, *J* = 2.8 Hz, 1H), 6.49 (d, *J* = 9.7 Hz, 1H), 6.23 (dd, *J* = 9.2, 6.1 Hz, 1H), 5.06 (s, 2H), 4.85 (dd, *J* = 10.8, 6.0 Hz, 1H), 3.83 (s, 3H), 3.63 (d, *J* = 11.4 Hz, 1H), 3.49 (d, *J* = 11.7 Hz, 1H), 3.11 (br, 1H), 1.72–1.58 (m, 1H), 1.54–1.39 (m, 2H), 1.34–1.26 (m, 1H), 1.23–1.10 (m, 1H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 156.0, 137.1, 130.3, 128.8, 128.7, 128.2, 127.7, 127.0, 125.7, 125.1, 114.1, 112.2, 70.5, 59.9, 53.7, 53.5, 43.2, 28.6, 20.6, 14.5; IR ν_{max} 2955, 2925, 2853, 2170, 1724, 1674, 1605, 1498, 1453, 1384, 1349, 1266, 1133, 1026, 738, 694 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{23}H_{28}NO_4$: 382.2013, found 382.2011; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 15.412 min, t_{minor} = 22.368 min, ee = 94%; $[\alpha]_D^{20}$ = 26.7 (c = 0.18, $CHCl_3$).



(*S*)-Methyl 6-(benzyloxy)-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4b-*anti*)

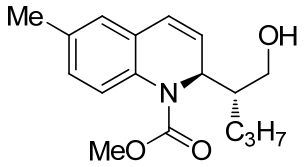
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.30 (m, 5H), 7.23 (s, 1H), 6.83 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.70 (d, *J* = 2.8 Hz, 1H), 6.53 (d, *J* = 9.7 Hz, 1H), 6.10–5.97 (m, 1H), 5.23 (s, 1H), 5.06 (s, 2H), 3.80 (s, 3H), 3.63 (dd, *J* = 11.8, 4.3 Hz, 1H), 3.54–3.38 (m, 1H), 1.67 (s, 1H), 1.27 (t, *J* = 7.0 Hz, 2H), 1.09 (s, 2H), 0.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 155.9, 137.1, 130.0, 129.0, 128.8, 128.7, 128.2, 127.7, 126.0, 114.1, 112.1, 70.5, 61.7, 53.8, 53.6, 45.5, 27.5, 20.9, 14.2; IR ν_{max} 2955, 2925, 2853, 2170, 1724, 1674, 1605, 1498, 1453, 1384, 1349, 1266, 1133, 1026, 738, 694 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{23}H_{28}NO_4$: 382.2013, found 382.2011; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 40/60, 1.0 mL/min, 236 nm), retention time: t_{major} = 20.739 min, t_{minor} = 8.220 min, ee = 94%; $[\alpha]_D^{20}$ = –33.5 (c = 0.22, $CHCl_3$).



(*R*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-6-methylquinoline-1(2*H*)-carboxylate

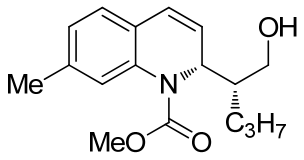
(4c-*syn*)

The reaction was performed following the general procedure. Yield: 21.7 mg, 75%, syn/anti = 71 : 29; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 1H), 7.03 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.94 (s, 1H), 6.49 (d, *J* = 9.6 Hz, 1H), 6.19 (dd, *J* = 9.5, 6.0 Hz, 1H), 4.84 (dd, *J* = 10.7, 6.0 Hz, 1H), 3.82 (s, 3H), 3.70–3.57 (m, 1H), 3.47 (d, *J* = 12.1 Hz, 1H), 3.21 (br, 1H), 2.32 (s, 3H), 1.71–1.57 (m, 1H), 1.52–1.39 (m, 2H), 1.34–1.08 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 134.6, 131.3, 129.4, 128.3, 127.5, 127.0, 125.1, 124.4, 59.9, 53.6, 53.4, 43.2, 28.6, 21.0, 20.6, 14.5; IR ν_{max} 2955, 2926, 2870, 2169, 1706, 1678, 1497, 1444, 1385, 1335, 1279, 1023, 871, 766, 706 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{17}H_{24}NO_3$: 290.1751, found 290.1749; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 7.622 min, t_{minor} = 22.992 min, ee = 98%; $[\alpha]_D^{20}$ = 176.5 (c = 0.23, $CHCl_3$).



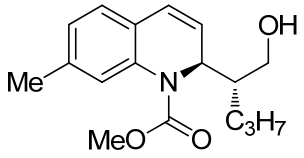
(*S*)-Methyl 6-chloro-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4c-*anti*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.88 (s, 1H), 6.52 (d, *J* = 9.7 Hz, 1H), 5.99 (dd, *J* = 9.5, 5.8 Hz, 1H), 5.20 (s, 1H), 3.80 (s, 3H), 3.66–3.57 (m, 1H), 3.45 (t, *J* = 9.4 Hz, 1H), 2.31 (s, 3H), 1.66 (s, 1H), 1.41–1.19 (m, 2H), 1.17–1.02 (m, 2H), 0.73 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 134.4, 132.8, 129.1, 128.3, 127.7, 126.8, 126.0, 124.7, 61.7, 53.8, 53.6, 45.6, 27.5, 21.0, 20.8, 14.2; IR ν_{max} 2955, 2926, 2870, 2169, 1706, 1678, 1497, 1444, 1385, 1335, 1279, 1023, 871, 766, 706 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{17}H_{24}NO_3$: 290.1751, found 290.1749; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 18.572 min, t_{minor} = 9.707 min, ee = 84%; $[\alpha]_D^{20}$ = –7.1 (c = 0.14, $CHCl_3$).



(*R*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-7-methylquinoline-1(2*H*)-carboxylate (4d-*syn*)

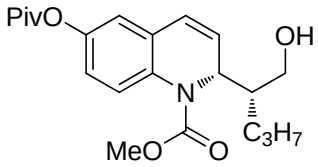
The reaction was performed following the general procedure. Yield: 22.5 mg, 78%, syn/anti = 66 : 34; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.50 (d, *J* = 9.6 Hz, 1H), 6.13 (dd, *J* = 9.5, 6.0 Hz, 1H), 4.84 (dd, *J* = 10.7, 6.0 Hz, 1H), 3.82 (s, 3H), 3.63 (dd, *J* = 12.1, 1.3 Hz, 1H), 3.47 (dd, *J* = 12.2, 1.5 Hz, 1H), 3.08 (br, 1H), 2.35 (s, 3H), 1.66–1.59 (m, 1H), 1.53–1.38 (m, 2H), 1.35–1.25 (m, 1H), 1.24–1.08 (m, 1H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 137.5, 133.7, 128.2, 126.2, 125.7, 125.1, 124.9, 59.8, 53.6, 53.4, 43.2, 28.5, 21.7, 20.5, 14.4; IR ν_{max} 2957, 2931, 2847, 2169, 1702, 1493, 1443, 1376, 1331, 1282, 1054, 903, 766 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{17}H_{24}NO_3$: 290.1751, found 290.1749; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 6.580 min, t_{minor} = 23.289 min, ee = 99%; $[\alpha]_D^{20}$ = 176.8 (c = 0.12, $CHCl_3$).



(*S*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-7-methylquinoline-1(2*H*)-carboxylate (4d-*anti*)

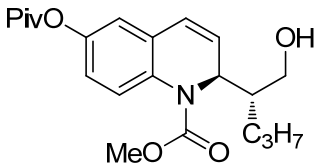
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 9.6 Hz, 1H), 5.94 (dd, *J* = 9.5, 5.9 Hz, 1H), 5.19 (s, 1H), 3.81 (s, 3H), 3.62 (dd, *J* = 11.8, 4.4 Hz, 1H), 3.51–3.37 (m, 1H), 2.35 (s, 3H), 1.72–1.61 (m, 1H), 1.33–1.23 (m, 1H), 1.16–1.04 (m, 2H), 0.93–0.79 (m, 1H), 0.73 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 137.6, 135.3, 127.9, 126.1, 125.8, 125.7, 125.4, 125.3, 61.7, 53.8, 53.6, 45.6, 27.6, 21.8, 20.8, 14.2; IR ν_{max} 2957, 2931, 2847, 2169, 1702, 1493, 1443, 1376, 1331, 1282, 1054, 903, 766 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{17}H_{24}NO_3$: 290.1751, found 290.1749; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min,

236 nm), retention time: t_{major} = 13.041 min, t_{minor} = 9.207 min, ee = 95%; $[\alpha]_D^{20}$ = –33.6 (c = 0.20, $CHCl_3$).



(*R*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-6-(pivaloyloxy)quinoline-1(2*H*)-carboxylate (4e-*syn*)

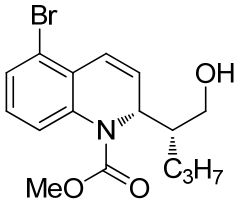
The reaction was performed following the general procedure. Yield: 30.4 mg, 81%, syn/anti = 80 : 20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 6.91 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.85 (d, *J* = 2.5 Hz, 1H), 6.49 (d, *J* = 9.7 Hz, 1H), 6.24 (dd, *J* = 9.5, 6.1 Hz, 1H), 4.87 (dd, *J* = 10.8, 6.0 Hz, 1H), 3.82 (s, 3H), 3.61 (d, *J* = 11.9 Hz, 1H), 3.47 (d, *J* = 12.1 Hz, 1H), 3.12 (br, 1H), 1.61 (d, *J* = 8.9 Hz, 1H), 1.52–1.39 (m, 2H), 1.35 (s, 9H), 1.30–1.24 (m, 1H), 1.21–1.10 (m, 1H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 156.6, 147.9, 131.1, 130.5, 128.7, 125.5, 124.7, 120.5, 119.1, 59.8, 53.8, 53.5, 43.2, 39.3, 28.5, 27.3, 20.6, 14.5; IR ν_{max} 2958, 2929, 2867, 2170, 1752, 1709, 1492, 1446, 1369, 1323, 1298, 1252, 1154, 1129, 1027, 903, 770 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{21}H_{30}NO_5$: 376.2118, found 376.2116; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 7.371 min, t_{minor} = 15.990 min, ee = 99%; $[\alpha]_D^{20}$ = 170.2 (c = 0.19, $CHCl_3$).



(*S*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-6-(pivaloyloxy)quinoline-1(2*H*)-carboxylate (4e-*anti*)

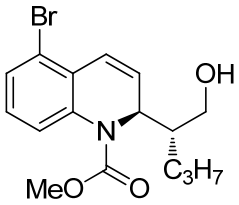
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 6.89 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.81 (d, *J* = 2.5 Hz, 1H), 6.52 (d, *J* = 9.7 Hz, 1H), 6.05 (dd, *J* = 9.3, 5.9 Hz, 1H), 5.23 (s, 1H), 3.80 (s, 3H), 3.62 (dd, *J* = 11.8, 4.3 Hz, 1H), 3.52–3.39 (m, 1H), 1.66 (s, 1H), 1.35 (s, 9H), 1.32–1.17 (m, 2H), 1.15–1.02 (m, 2H), 0.73 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 157.0, 147.8, 132.7, 130.2, 128.9, 125.8, 125.4, 120.4, 118.9, 61.6, 53.9, 53.7, 45.5, 39.3, 27.6, 27.3, 20.8, 14.2; IR ν_{max} 2958, 2929, 2867, 2170,

1752, 1709, 1492, 1446, 1369, 1323, 1298, 1252, 1154, 1129, 1027, 903, 770 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{21}H_{30}NO_5$: 376.2118, found 376.2116; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: t_{major} = 11.303 min, t_{minor} = 7.591 min, ee = 93%; $[\alpha]_D^{20}$ = –60.3 (c = 0.10, $CHCl_3$).



(*R*)-Methyl 5-bromo-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4f-*syn*)

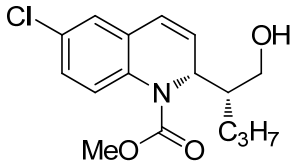
The reaction was performed following the general procedure. Yield: 26.7 mg, 76%, syn/anti = 52 : 48; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.27 (m, 2H), 7.10–7.00 (m, 1H), 6.87 (d, *J* = 9.9 Hz, 1H), 6.29 (dd, *J* = 9.8, 6.2 Hz, 1H), 4.86 (dd, *J* = 10.7, 6.2 Hz, 1H), 3.81 (s, 3H), 3.65–3.55 (m, 1H), 3.54–3.42 (m, 1H), 3.04 (br, 1H), 1.66–1.54 (m, 1H), 1.51–1.24 (m, 3H), 1.20–1.02 (m, 1H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 136.7, 131.3, 128.8, 128.0, 127.2, 124.5, 124.0, 121.1, 59.8, 53.7, 53.1, 43.1, 27.9, 20.5, 14.1; IR ν_{max} 2951, 2849, 2169, 1704, 1502, 1483, 1451, 1441, 1356, 1331, 1217, 1200, 1022, 764 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{16}H_{21}BrNO_3$: 354.0699, found 354.0701; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 9.847 min, t_{minor} = 15.710 min, ee = 75%; $[\alpha]_D^{20}$ = 106.1 (c = 0.21, $CHCl_3$).



(*S*)-Methyl 5-bromo-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4f-*anti*)

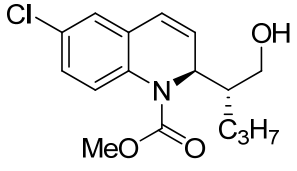
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.27 (m, 2H), 7.10–7.00 (m, 1H), 6.90 (d, *J* = 9.9 Hz, 1H), 6.17 (dd, *J* = 9.8, 6.0 Hz, 1H), 5.18 (s, 1H), 3.79 (s, 3H), 3.65–3.55 (m, 1H), 3.54–3.42 (m, 1H), 1.66–1.54 (m, 1H), 1.51–1.24 (m, 2H), 1.20–1.02 (m, 2H), 0.73 (t,

J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 135.3, 131.3, 128.9, 128.1, 127.5, 124.6, 124.1, 121.4, 61.2, 53.8, 53.5, 44.8, 28.4, 20.5, 14.5; IR ν_{max} 2951, 2849, 2169, 1704, 1502, 1483, 1451, 1441, 1356, 1331, 1217, 1200, 1022, 764 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{16}H_{21}BrNO_3$: 354.0699, found 354.0701; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: t_{major} = 13.466 min, t_{minor} = 10.533 min, ee = 64%; $[\alpha]_D^{20}$ = –19.5 (c = 0.16, $CHCl_3$).



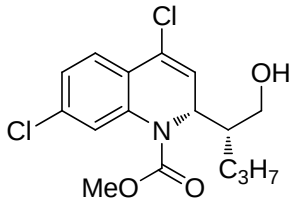
(*R*)-Methyl 6-chloro-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4g-*syn*)

The reaction was performed following the general procedure. Yield: 26.3 mg, 85%, syn/anti = 76 : 24; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.20–7.06 (m, 2H), 6.48 (d, *J* = 9.7 Hz, 1H), 6.26 (dd, *J* = 9.5, 6.1 Hz, 1H), 4.87 (dd, *J* = 10.7, 6.0 Hz, 1H), 3.83 (s, 3H), 3.59 (d, *J* = 12.1 Hz, 1H), 3.51–3.39 (m, 1H), 3.08 (br, 1H), 1.70–1.53 (m, 1H), 1.50–1.37 (m, 2H), 1.31–1.23 (m, 1H), 1.19–1.09 (m, 1H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 132.4, 131.0, 130.8, 130.2, 130.2, 130.1, 129.2, 127.5, 126.2, 125.9, 124.3, 59.9, 53.9, 53.5, 43.4, 28.5, 20.6, 14.5; IR ν_{max} 2956, 2929, 2871, 2169, 1710, 1682, 1486, 1444, 1386, 1370, 1332, 1250, 1204, 1091, 1049, 1025, 877, 820, 764, 710 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{16}H_{21}ClNO_3$: 310.1204, found 310.1207; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 236 nm), retention time: t_{major} = 9.129 min, t_{minor} = 20.663 min, ee = 94%; $[\alpha]_D^{20}$ = 151.6 (c = 0.12, $CHCl_3$).



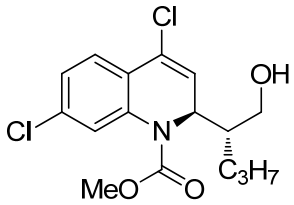
(*S*)-Methyl 6-chloro-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4g-*anti*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.15 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.05 (d, *J* = 1.9 Hz, 1H), 6.51 (d, *J* = 9.7 Hz, 1H), 6.07 (dd, *J* = 9.1, 5.9 Hz, 1H), 5.23 (s, 1H), 3.81 (s, 3H), 3.68–3.55 (m, 1H), 3.51–3.35 (m, 1H), 1.65 (s, 1H), 1.36–1.19 (m, 2H), 1.19–0.97 (m, 2H), 0.73 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 133.9, 130.7, 130.0, 129.4, 127.5, 126.2, 126.0, 125.0, 61.5, 53.9, 53.8, 45.6, 27.5, 20.8, 14.2; IR ν_{max} 2956, 2929, 2871, 2169, 1710, 1682, 1486, 1444, 1386, 1370, 1332, 1250, 1204, 1091, 1049, 1025, 877, 820, 764, 710 cm^{-1}; HRMS (EI) *m/z* [M + H]$^+$ calculated for $C_{16}H_{21}ClNO_3$: 310.1204, found 310.1207; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: t_{major} = 18.385 min, t_{minor} = 9.649 min, ee = 74%; $[\alpha]_D^{20}$ = –47.8 (c = 0.11, $CHCl_3$).



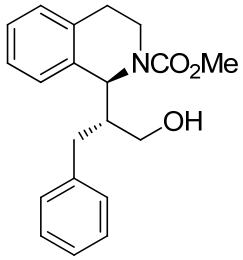
(*S*)-Methyl 4,7-dichloro-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4h-*syn*)

The reaction was performed following the general procedure. Yield: 28.5 mg, 83%, syn/anti = 79 : 21; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 1H), 7.38 (s, 1H), 7.16 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.31 (d, *J* = 6.7 Hz, 1H), 4.95 (dd, *J* = 10.6, 6.7 Hz, 1H), 3.86 (s, 3H), 3.60–3.42 (m, 2H), 2.76 (br, 1H), 1.65–1.52 (m, 1H), 1.52–1.37 (m, 2H), 1.30–1.08 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 135.4, 134.6, 127.5, 126.6, 125.9, 125.2, 124.7, 124.6, 59.7, 54.7, 54.2, 43.3, 28.5, 20.5, 14.4; IR ν_{max} 2965, 2924, 2847, 1705, 1507, 1483, 1441, 1358, 1332, 1261, 1214, 1015, 954, 766 cm^{-1}; HRMS (EI) *m/z* [M + H]$^+$ calculated for $C_{16}H_{20}Cl_2NO_3$: 344.0815, found 344.0814; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: t_{major} = 7.350 min, t_{minor} = 12.098 min, ee = 85%; $[\alpha]_D^{20}$ = 177.3 (c = 0.31, $CHCl_3$).



(*R*)-Methyl 4,7-dichloro-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4h-*anti*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 1H), 7.43 (s, 1H), 7.15 (dd, *J* = 8.4, 1.4 Hz, 1H), 6.20 (d, *J* = 6.4 Hz, 1H), 5.26 (s, 1H), 3.84 (s, 3H), 3.63 (dd, *J* = 11.7, 4.1 Hz, 1H), 3.46 (dd, *J* = 11.2, 7.6 Hz, 1H), 2.81 (br, 1H), 1.64 (s, 1H), 1.35–1.27 (m, 1H), 1.15–1.04 (m, 2H), 0.99–0.84 (m, 1H), 0.76 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 136.7, 134.5, 127.9, 126.7, 125.5, 125.2, 125.0, 124.8, 61.2, 55.0, 54.1, 45.4, 28.0, 20.6, 14.3; IR ν_{max} 2965, 2924, 2847, 1705, 1507, 1483, 1441, 1358, 1332, 1261, 1214, 1015, 954, 766 cm^{-1}; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{16}H_{20}Cl_2NO_3$: 344.0815, found 344.0814; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: t_{major} = 12.249 min, t_{minor} = 7.462 min, ee = 89%; $[\alpha]_D^{20}$ = –65.0 (c = 0.22, $CHCl_3$).

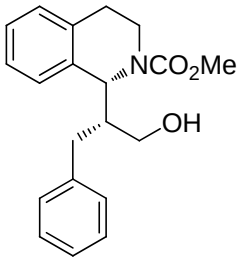


(*S*)-Methyl 1-((*R*)-1-hydroxy-3-phenylpropan-2-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (7b-*anti*)

The reaction was performed following the general procedure. Yield: 22.1 mg, 68%, anti/syn = 60 : 40.

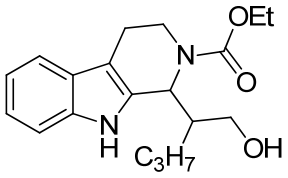
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.16 (m, 6H), 7.12 (t, *J* = 7.1 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 2H), 5.06 (d, *J* = 11.0 Hz, 1H), 4.02–3.85 (m, 1H), 3.76 (s, 3H), 3.76–3.68 (m, 1H), 3.58 (d, *J* = 12.3 Hz, 1H), 3.49 (td, *J* = 11.9, 5.6 Hz, 1H), 3.39–3.31 (m, 1H), 3.15–3.02 (m, 1H), 2.91–2.78 (m, 2H), 2.46 (d, *J* = 11.7 Hz, 1H), 1.79 (t, *J* = 10.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 140.8, 136.7, 135.0, 129.4, 129.1, 128.4, 128.3, 127.8, 126.4, 126.0, 59.0, 57.5, 53.5, 48.2, 42.2, 34.2, 27.7; HRMS (EI) *m/z* [M

+ H]$^+$ calculated for $C_{20}H_{24}NO_3$: 326.1751, found 326.1748; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 40/60, 1.0 mL/min, 213 nm), retention time: t_{major} = 7.301 min, t_{minor} = 22.274 min, ee = 95%; $[\alpha]_D^{20}$ = –20.2 (c = 0.15, $CHCl_3$).



(*R*)-Methyl 1-((*R*)-1-hydroxy-3-phenylpropan-2-yl)-3,4-dihydroisoquinoline-2(1*H*) - carboxylate (7b-*syn*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.26–7.13 (m, 5H), 6.98 (d, *J* = 7.3 Hz, 2H), 5.58 (d, *J* = 2.7 Hz, 1H), 4.42–4.26 (m, 1H), 3.81 (s, 3H), 3.64–3.43 (m, 2H), 3.27 (td, *J* = 13.4, 3.7 Hz, 1H), 3.03–2.85 (m, 1H), 2.84–2.74 (m, 1H), 2.68–2.56 (m, 2H), 2.17 (t, *J* = 12.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 140.6, 135.6, 135.1, 129.2, 128.8, 128.5, 127.0, 126.9, 126.6, 126.3, 61.8, 54.2, 53.6, 51.3, 40.6, 34.0, 29.2; HRMS (EI) *m/z* [M + H]$^+$ calculated for $C_{20}H_{24}NO_3$: 326.1751, found 326.1748; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 213 nm), retention time: t_{major} = 27.144 min, t_{minor} = 33.342 min, ee = 84%; $[\alpha]_D^{20}$ = –73.8 (c = 0.27, $CHCl_3$).



Ethyl 1-(1-hydroxypentan-2-yl)-3,4-dihydro-1H-pyrido[3,4-b]indole-2(9*H*)-carboxylate (7c)

The reaction was performed following the general procedure. Yield: 23.4 mg, 77%, major/minor = 64 : 36.

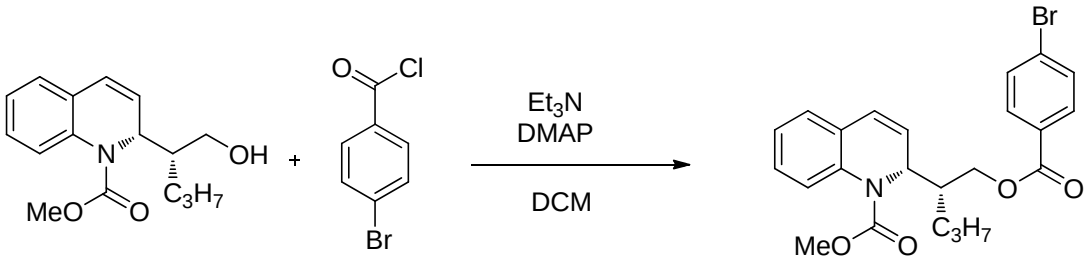
major: ^{1}H NMR (400 MHz, $CDCl_3$, rotamers seen) δ 9.35–8.98 (m, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.4 Hz,

1H), 5.62 (d, *J* = 2.8 Hz, 1H), 4.48 (dd, *J* = 13.5, 3.7 Hz, 1H), 4.35–4.19 (m, 2H), 3.95–3.78 (m, 1H), 3.60 (t, *J* = 10.8 Hz, 1H), 3.34–3.15 (m, 1H), 2.91–2.72 (m, 2H), 2.27 (s, 1H), 1.42–1.27 (m, 5H), 1.22–1.07 (m, 2H), 0.93–0.72 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 136.5, 132.7, 127.0, 121.7, 119.3, 117.9, 111.4, 109.5, 62.5, 52.0, 46.7, 41.3, 29.6, 21.6, 21.5, 14.8, 14.4; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{19}H_{27}N_2O_3$: 331.2016, found 331.2018; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 225 nm), retention time: t_{major} = 11.596 min, t_{minor} = 13.882 min, ee = 95%; $[\alpha]_D^{20}$ = –56.2 (c = 0.20, $CHCl_3$).

minor:

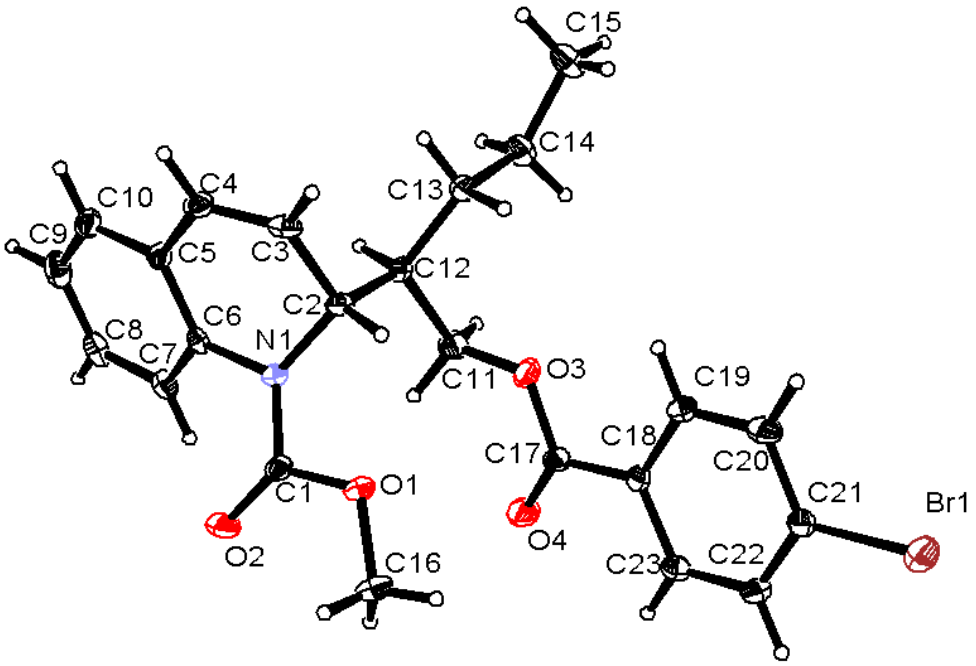
^{1}H NMR (400 MHz, $CDCl_3$, rotamers seen) δ 9.09–8.36 (m, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 5.26 (d, *J* = 5.0 Hz, 1H), 4.72–4.33 (m, 1H), 4.24 (d, *J* = 6.3 Hz, 2H), 3.97–3.69 (m, 2H), 3.29 (t, *J* = 10.5 Hz, 1H), 2.92–2.74 (m, 2H), 2.06–1.90 (m, 1H), 1.81–1.49 (m, 2H), 1.38–1.22 (m, 5H), 0.91–0.83 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 136.1, 132.8, 126.8, 122.0, 119.5, 118.2, 111.1, 109.1, 62.2, 61.1, 53.6, 44.6, 39.3, 29.7, 21.7, 20.8, 14.9, 14.5; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{19}H_{27}N_2O_3$: 331.2016, found 331.2018; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 40/60, 1.0 mL/min, 225 nm), retention time: t_{major} = 9.998 min, t_{minor} = 13.048 min, ee = 93%; $[\alpha]_D^{20}$ = 32.1 (c = 0.87, $CHCl_3$).

Absolute stereochemistry determination



3a-major **3a-p**

To a solution of **3a-major** (0.2 mmol, 55.2 mg), Et_3N (0.4 mmol, 55.6 μL), DMAP (0.02 mol, 2.5 mg) in DCM (1 mL) was added dropwise a solution of 4-bromobenzoyl chloride (0.3 mmol, 66 mg) in DCM at 0 °C. The resulted mixture was vigorously stirred at room temperature and the reaction was monitored by TLC. After the completion of the reaction, it was treated with saturated aqueous $NaHCO_3$ (2 mL). After stirring at room temperature for 20 min, the mixture was diluted with ethyl acetate, and the organic layer was separated and washed with water and brine, dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by flash chromatography to give the desired product **3a-p**. $[\alpha]_D^{20}$ = 76 (c = 0.43, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.49 (s, 1H), 7.23–7.15 (m, 1H), 7.18–7.03 (m, 2H), 6.57 (d, *J* = 9.6 Hz, 1H), 6.18 (dd, *J* = 9.4, 6.1 Hz, 1H), 5.12 (s, 1H), 4.34–4.16 (m, 2H), 3.66 (s, 3H), 1.90–1.80 (m, 1H), 1.55–1.39 (m, 3H), 1.34–1.24 (m, 1H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 155.3, 134.9, 131.9, 131.4, 129.6, 128.6, 128.2, 127.9, 127.8, 126.4, 125.9, 125.5, 124.9, 63.8, 53.3, 53.2, 41.3, 29.8, 20.3, 14.5; HRMS (EI) *m/z* $[M + H]^+$ calcd for $C_{23}H_{25}BrNO_4$: 458.0961, found 458.0960.

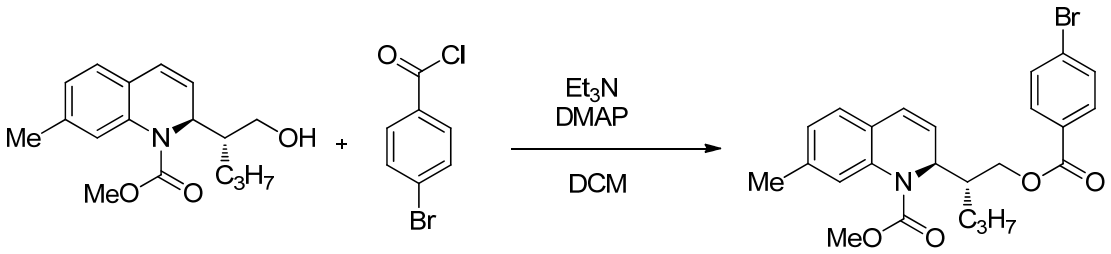


The absolute stereochemistry (the **major** diastereomer from the reaction) was determined by the X-ray diffraction. A suitable crystal was selected and analyzed on an Xcalibur, Eos, Gemini diffractometer. Further information is contained in the CCDC file 1400167.

CCDC file 1400167

Identification code	3a-major
Empirical formula	C23 H24 Br N O4
Formula weight	458.34
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 5.1792(4) A alpha = 90 deg.
	b = 11.1118(9) A beta = 90 deg.
	c = 36.240(3) A gamma = 90 deg.
Volume	2085.6(3) A^3
Z, Calculated density	4, 1.460 Mg/m^3
Absorption coefficient	2.000 mm^-1

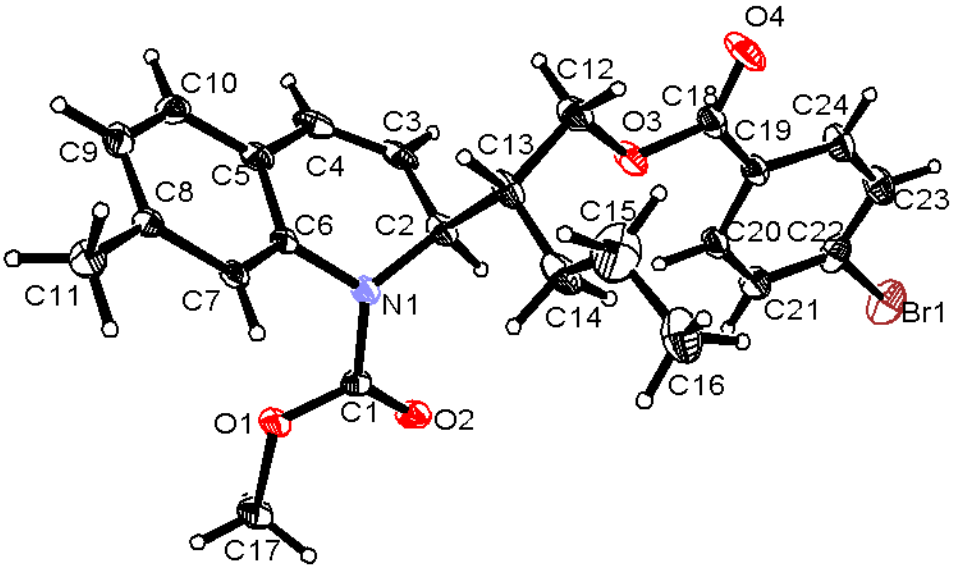
F(000)	944
Crystal size	0.37 x 0.15 x 0.10 mm
Theta range for data collection	2.49 to 25.02 deg.
Limiting indices	-6<=h<=6, -13<=k<=12, -33<=l<=43
Reflections collected / unique	10531 / 3655 [R(int) = 0.0750]
Completeness to theta = 25.02	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8250 and 0.5248
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3655 / 0 / 264
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0467, wR2 = 0.0666
R indices (all data)	R1 = 0.0941, wR2 = 0.0732
Absolute structure parameter	0.013(11)
Largest diff. peak and hole	0.494 and -0.312 e.A^-3.



4d-minor **4d-p**

To a solution of **4d-minor** (0.2 mmol, 58 mg), Et_3N (0.4 mmol, 55.6 μL), DMAP (0.02 mol, 2.5 mg) in DCM (1 mL) was added dropwise a solution of 4-bromobenzoyl chloride (0.3 mmol, 66 mg) in DCM at 0 °C. The resulted mixture was vigorously stirred at room temperature and the reaction was monitored by TLC. After the completion of the reaction, it was treated with saturated aqueous $NaHCO_3$ (2 mL). After stirring at room temperature for 20 min, the mixture was diluted with ethyl acetate, and the organic layer was separated and washed with water and brine, dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by flash chromatography to give the desired product **4d-p**. $[\alpha]_D^{20} = -112$ (c = 0.21, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.33 (s,

1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 9.6 Hz, 1H), 6.05 (dd, *J* = 9.5, 6.0 Hz, 1H), 5.25–5.02 (m, 1H), 4.29 (d, *J* = 4.2 Hz, 2H), 3.79 (s, 3H), 2.33 (s, 3H), 1.90–1.80 (m, 1H), 1.49–1.37 (m, 3H), 1.27–1.17 (m, 1H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 155.6, 137.8, 134.8, 132.0, 131.3, 129.4, 128.3, 127.0, 126.2, 126.0, 125.8, 125.7, 125.1, 64.2, 53.9, 53.3, 41.6, 29.8, 21.8, 20.1, 14.4; HRMS (EI) *m/z* $[M + H]^+$ calcd for $C_{24}H_{27}BrNO_4$: 472.1118, found 472.1121.



The absolute stereochemistry (the **minor** diastereomer from the reaction) was determined by the X-ray diffraction. A suitable crystal was selected and analyzed on an Xcalibur, Eos, Gemini diffractometer. Further information is contained in the CCDC file 1400005.

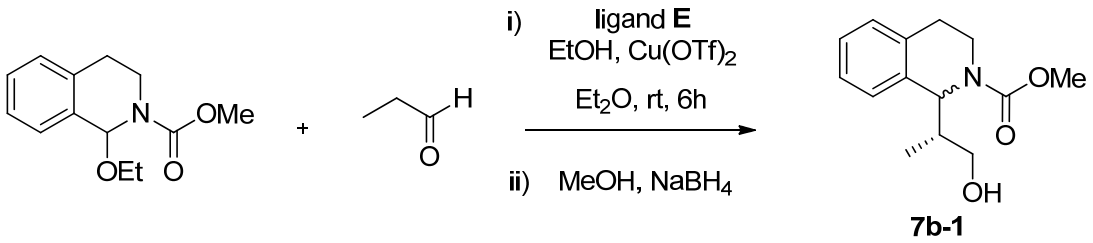
CCDC file 1400005

Identification code	4d-minor
Empirical formula	C24 H26 Br N O4
Formula weight	472.37
Temperature	298(2) K

Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 10.7238(9) A alpha = 90 deg.
	b = 7.4576(7) A beta = 93.5020(10) deg.
	c = 13.7590(11) A gamma = 90 deg.
Volume	1098.30(16) A^3
Z, Calculated density	2, 1.428 Mg/m^3
Absorption coefficient	1.901 mm^-1
F(000)	488
Crystal size	0.50 x 0.38 x 0.14 mm
Theta range for data collection	2.48 to 25.02 deg.
Limiting indices	-12<=h<=10, -8<=k<=8, -16<=l<=15
Reflections collected / unique	5473 / 3598 [R(int) = 0.0530]
Completeness to theta = 25.02	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7767 and 0.4499
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3598 / 1 / 274
Goodness-of-fit on F^2	0.999
Final R indices [I>2sigma(I)]	R1 = 0.0574, wR2 = 0.1164
R indices (all data)	R1 = 0.1096, wR2 = 0.1297
Absolute structure parameter	0.019(16)
Largest diff. peak and hole	0.691 and -0.553 e.A^-3

Absolute stereochemistry determination for 7b

The absolute stereochemistry of **7b** was determined by comparing **7b-1** with a compound whose stereochemistry can be easily assigned.

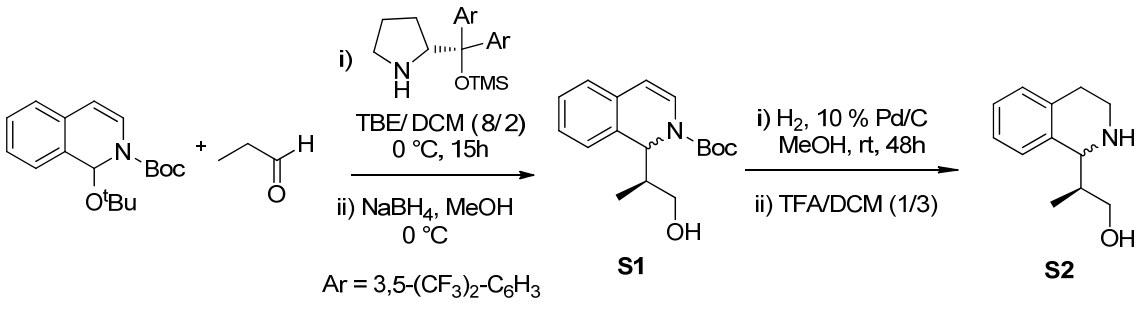


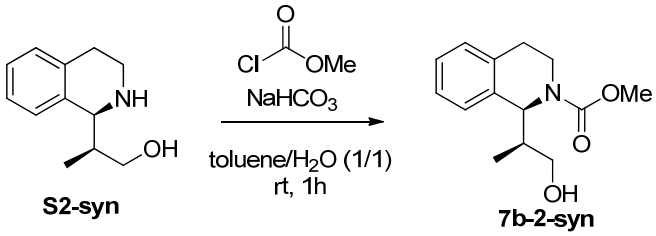
7b-1

The reaction was performed following the general procedure to afford **7b-1** as colorless oil (a mixture of two isomers, 15.5 mg, 62% yield, major/minor = 65/35)

Minor: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.27–7.11 (m, 4H), 5.44 (s, 1H), 4.62–4.42 (m, 1H), 4.33–4.20 (m, 1H), 3.83–3.74 (m, 3H), 3.56 (dd, *J* = 14.7, 6.9 Hz, 1H), 3.44 (t, *J* = 10.5 Hz, 1H), 3.24 (t, *J* = 12.4 Hz, 1H), 2.96–2.81 (m, 1H), 2.74 (d, *J* = 15.8 Hz, 1H), 2.47 (s, 1H), 0.70 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.4, 135.9, 134.9, 129.0, 126.8, 126.7, 126.6, 64.9, 53.9, 53.5, 43.7, 41.0, 29.2, 12.3; HRMS (EI) *m/z* $[M + H]^+$ calcd for $C_{14}H_{20}NO_3$: 250.1438, found 250.1441.

Major: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.27–7.10 (m, 4H), 4.89 (d, *J* = 11.0 Hz, 1H), 3.89–3.75 (m, 2H), 3.76 (s, 3H), 3.70 (dd, *J* = 10.8, 4.7 Hz, 1H), 3.54–3.43 (m, 2H), 3.11–2.97 (m, 1H), 2.88–2.75 (m, 1H), 1.82–1.70 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.6, 136.8, 134.8, 128.7, 128.1, 127.5, 126.2, 64.5, 58.0, 53.5, 42.0, 40.4, 27.7, 15.6; HRMS (EI) *m/z* $[M + H]^+$ calcd for $C_{14}H_{20}NO_3$: 250.1438, found 250.1441.





S2-syn **7b-2-syn**

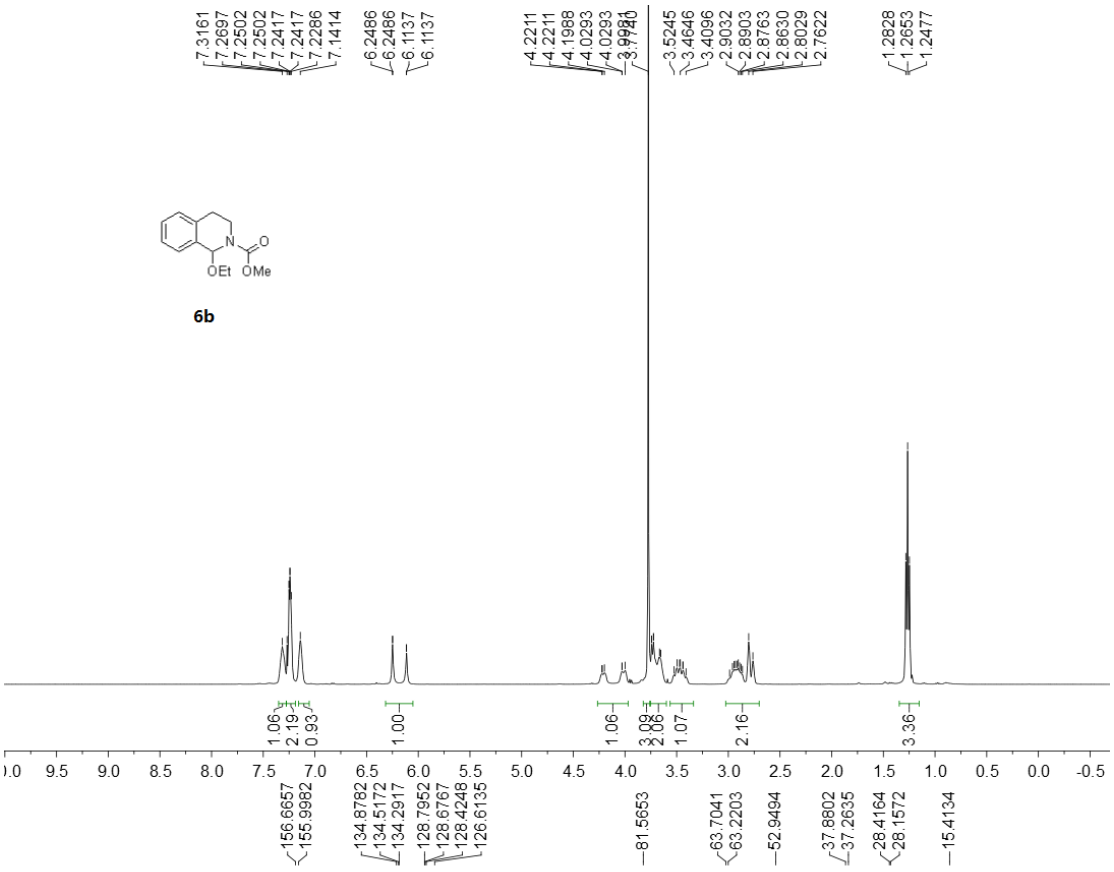
S1 and **S2** was prepared following Cozzi's method, and the analytical data are consistent with the literature reports.[1] The NMR data for major product **S1-*syn*** (1*S*,2'*S*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.19 (m, 2H), 7.16 (d, *J* = 3.8 Hz, 1H), 7.10–7.01 (m, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.78 (d, *J* = 7.8 Hz, 1H), 5.63 (d, *J* = 2.8 Hz, 1H), 4.26 (s, 1H), 3.42 (s, 1H), 3.37–3.29 (m, 1H), 2.03–1.95 (m, 1H), 1.56 (s, 9H), 0.71 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 132.3, 131.2, 127.6, 127.4, 126.7, 126.6, 124.4, 109.4, 82.5, 64.0, 54.3, 46.7, 28.4, 10.7.

The major diastereoisomer **S2-*syn*** (1*S*,2'*S*) (0.1 mmol, 1.0 eq) was placed in a 10 mL flask, then toluene (0.5 mL), H_2O (0.5 mL), $NaHCO_3$ (0.15 mmol, 1.5 eq), methyl chloroformate (0.12 mmol, 1.2 eq) was added subsequentially. The mixture was stirred at rt for 1h. After completion of the reaction, organic layer was seperated and aqueous layer was extacted twice with ethyl acetate (5 mL). Combined organic layers were dried and concentrated, purified by flash chromatography to afford **7b-2-*syn*** as colorless oil. It is obviously that the absolute configuration of **7b-2-*syn*** is **(**1*S*,2'*S***)**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.07 (m, 4H), 5.44 (d, *J* = 3.1 Hz, 1H), 4.33–4.16 (m, 1H), 3.80–3.72 (m, 3H), 3.63–3.55 (m, 1H), 3.49–3.40 (m, 1H), 3.32–3.19 (m, 1H), 2.94–2.83 (m, 1H), 2.80–2.69 (m, 1H), 2.55–2.38 (m, 1H), 0.71 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 136.0, 135.0, 129.0, 126.8, 126.6, 65.0, 54.1, 53.5, 43.8, 41.1, 29.2, 12.4. These data are consistent with **7b-1-minor**, which means **7b-2-*syn*** and **7b-1-minor** are the same isomer. Then we can assign the stereocenter of **7b-1-minor** by comparing the HPLC traces using: chiral column Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 211 nm.

The retention time of **7b-1-minor**: t_{major} = 7.677 min, t_{minor} = 8.177 min, ee = 80%. The retention time of **7b-2-*syn***: t_{major} = 8.228 min, t_{minor} = 7.696 min, ee = 96%. This can allow us to assign the absolute configuration of **7b-1-minor** as (1*R*,2'*R*). And so can we assign **7b-1-major** as (1*S*,2'*R*) using the same method. The stereo structure of **7b** is consistent with **7b-1**.

1. L. Mengozzi, A. Gualandi and P. G. Cozzi, *Chem. Sci.*, **2014**, 5, 3915-3921.

NMR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OEt OMe
6b
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2.19
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1.06
3.09
2.06
1.07
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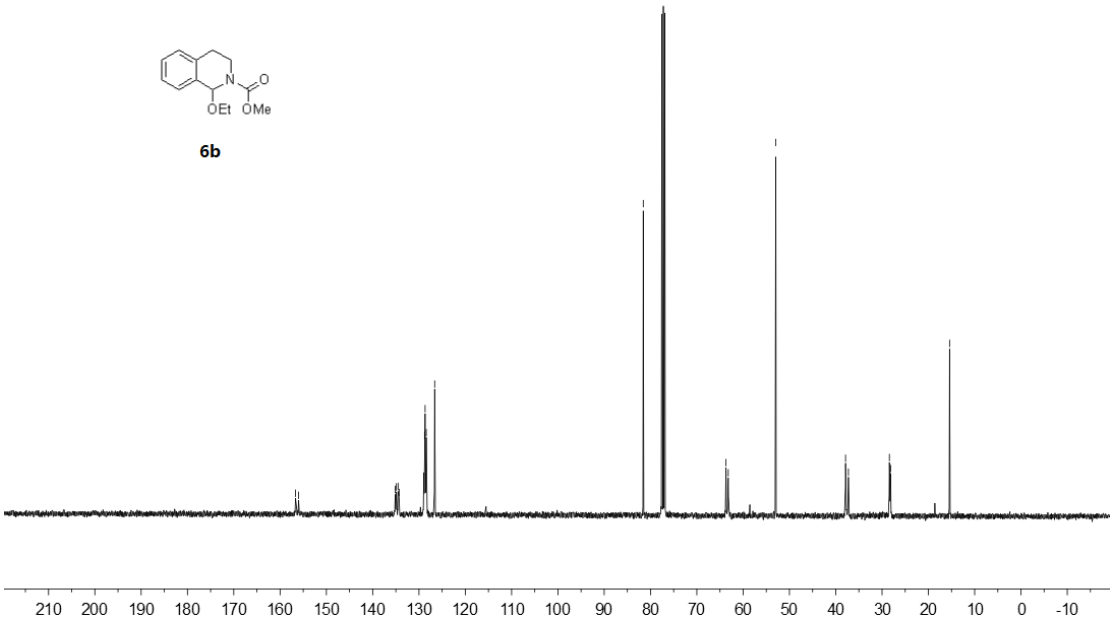
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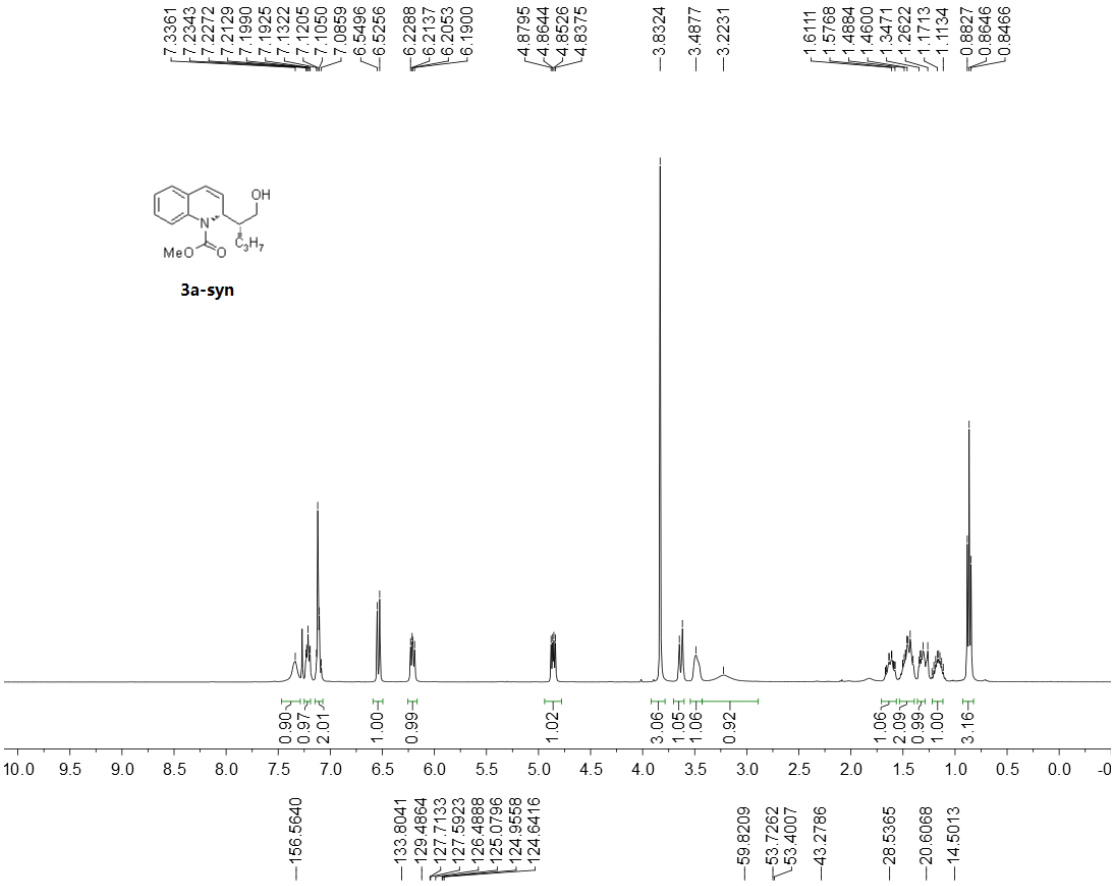
6b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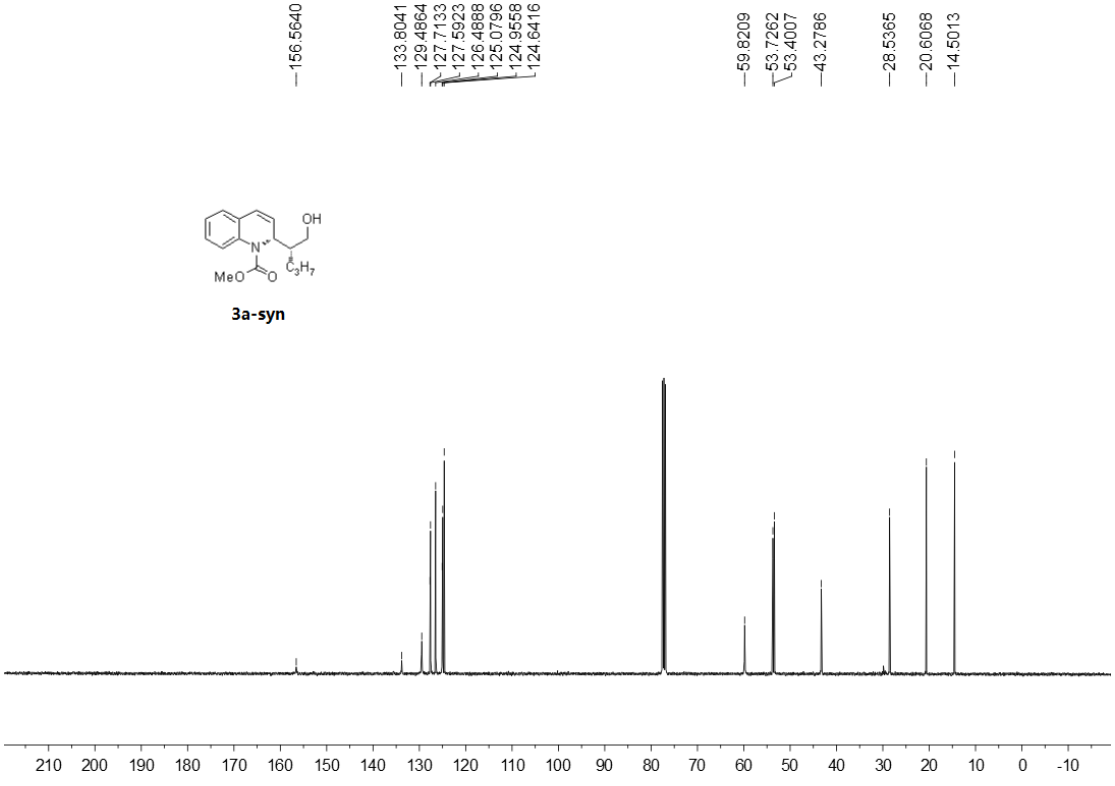
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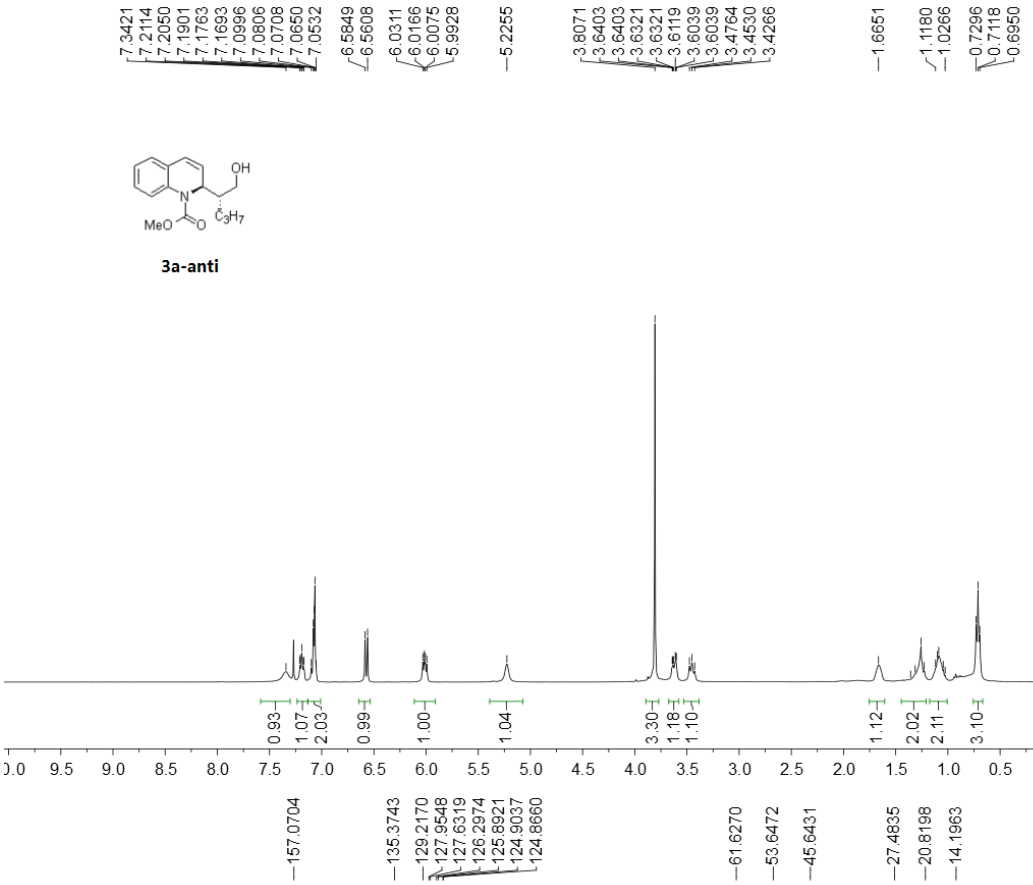
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1.10
1.12
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3.10
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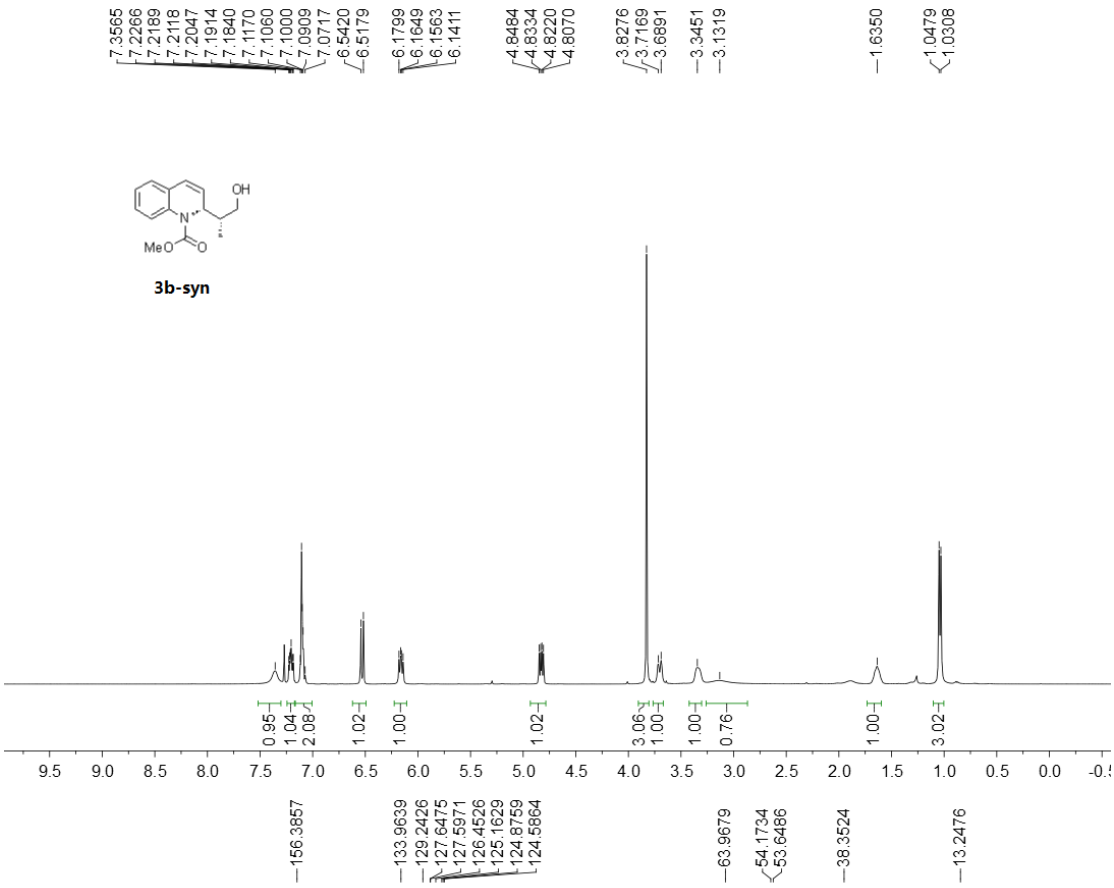
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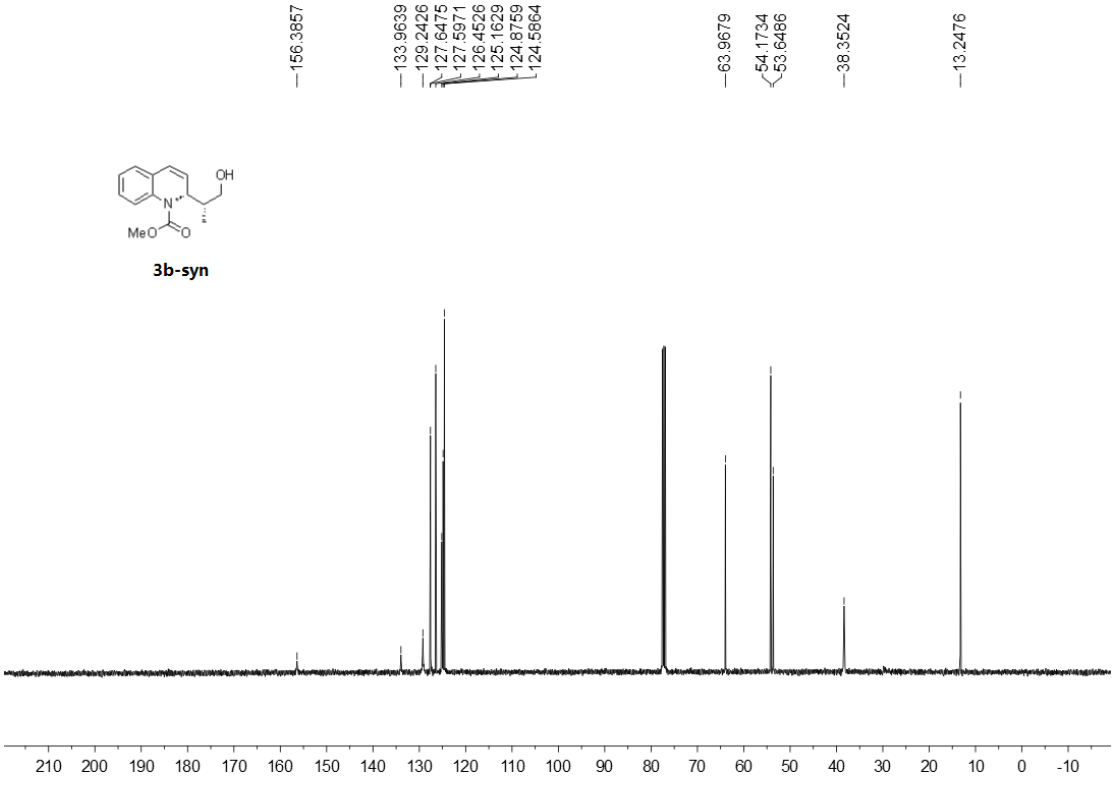
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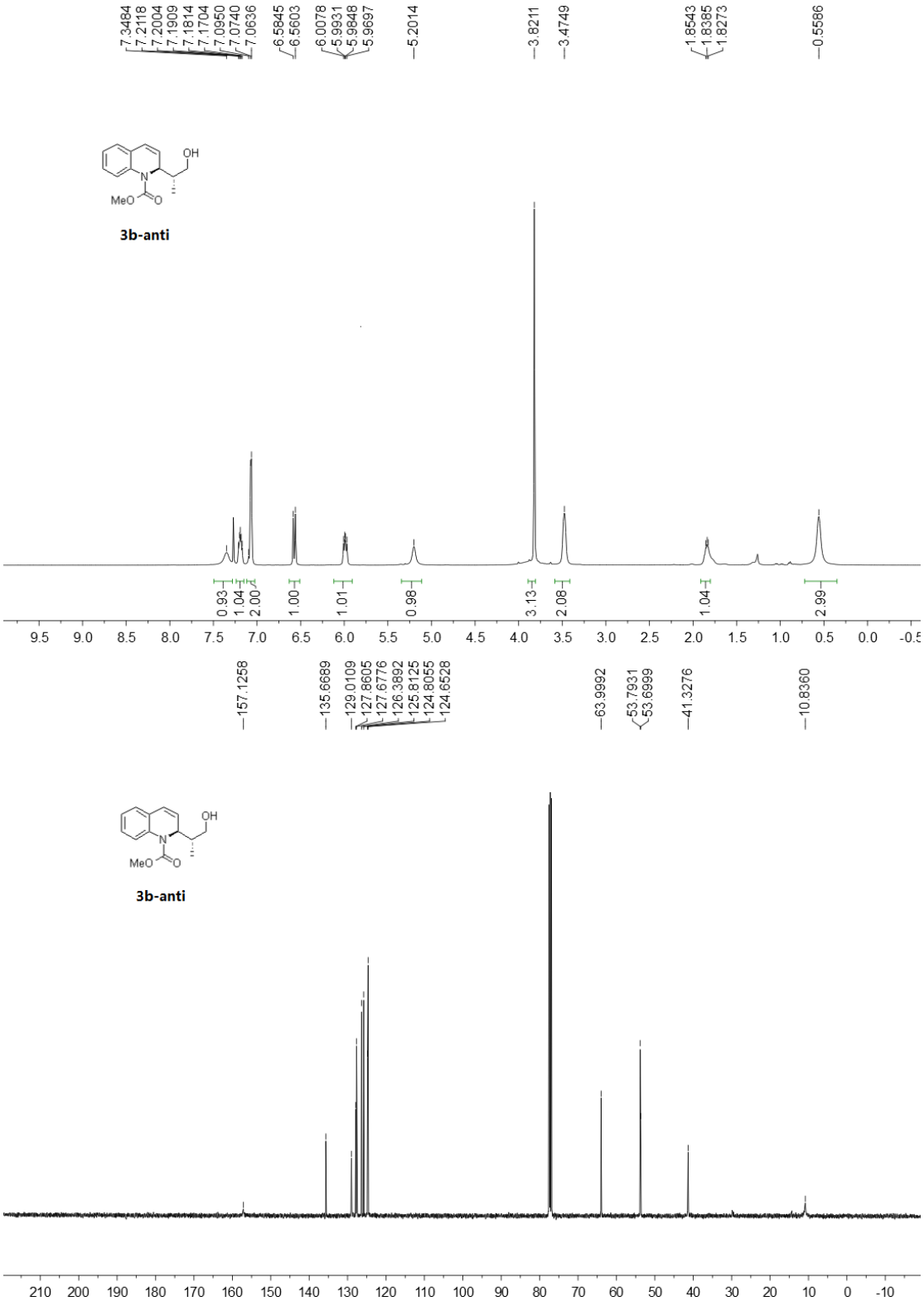
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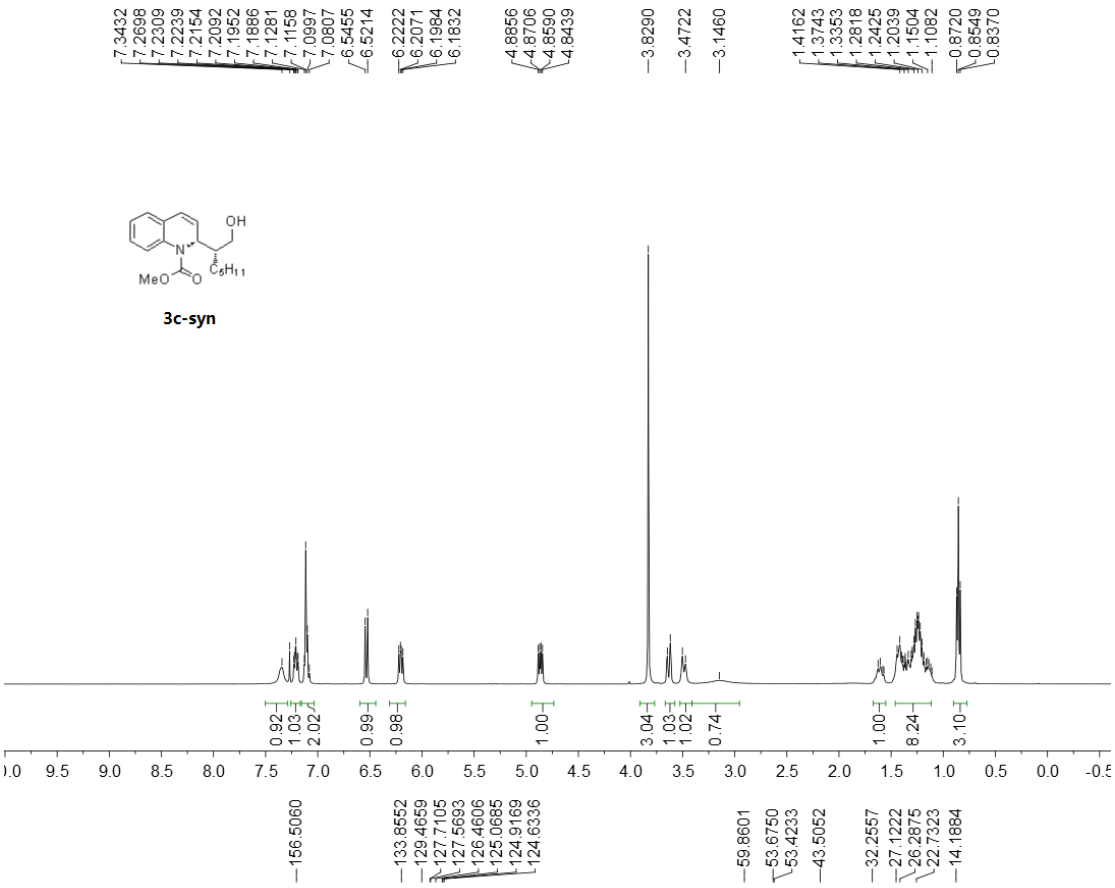
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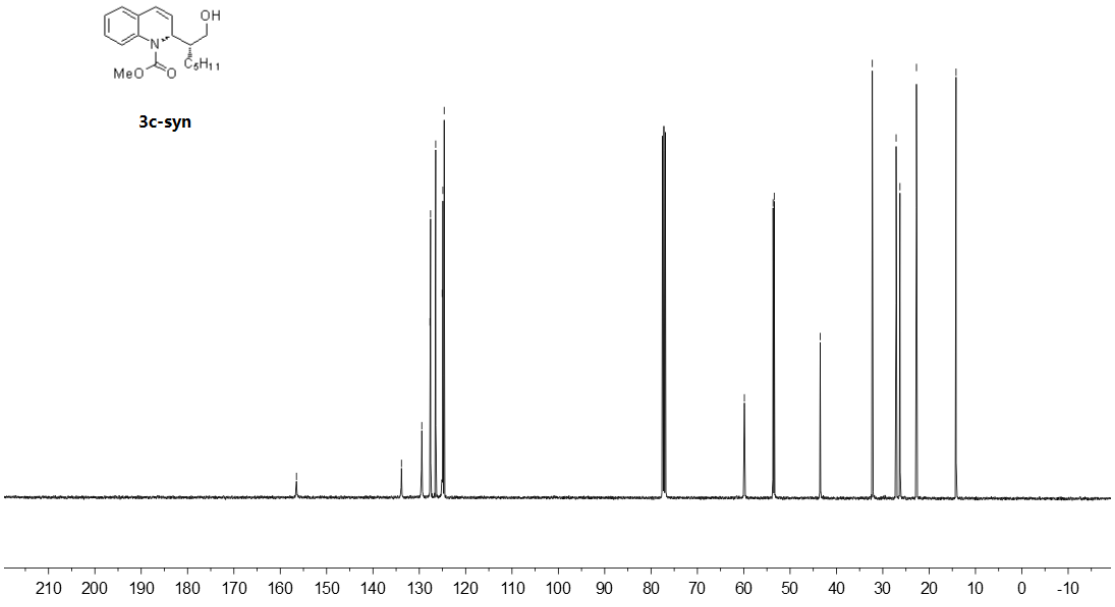
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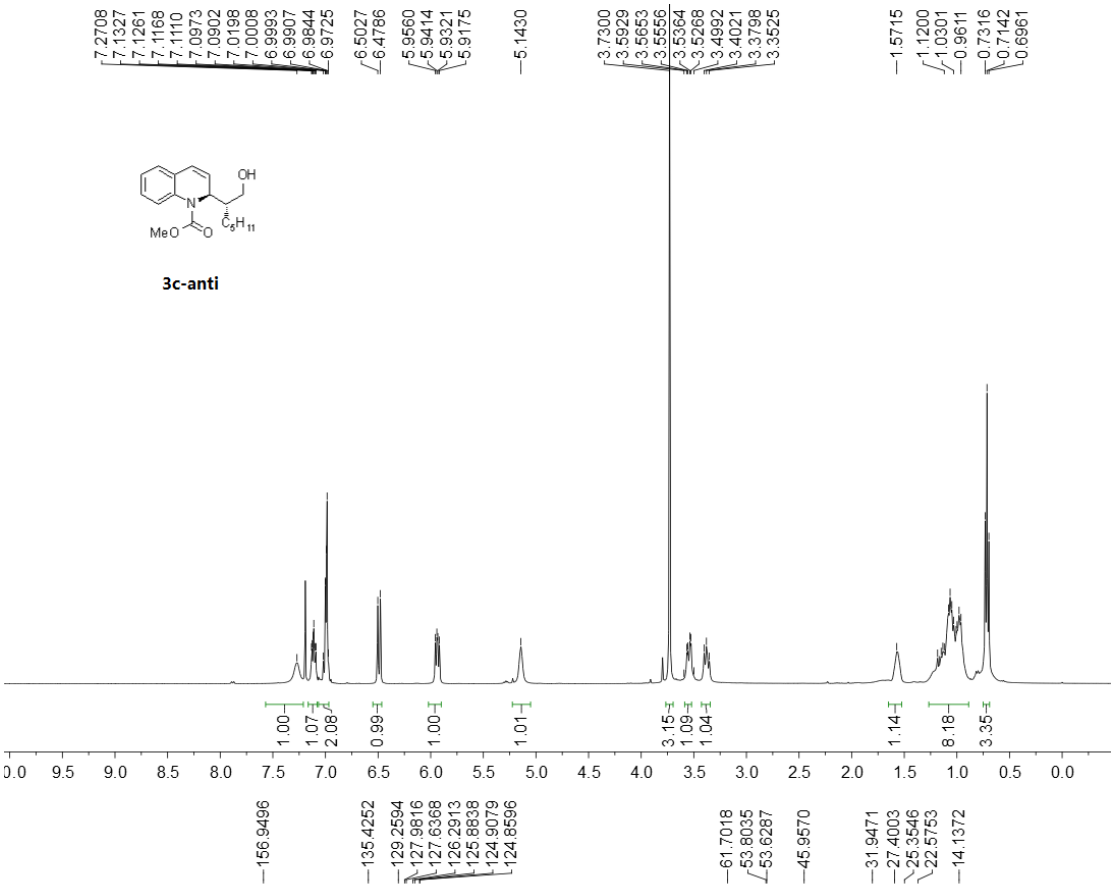
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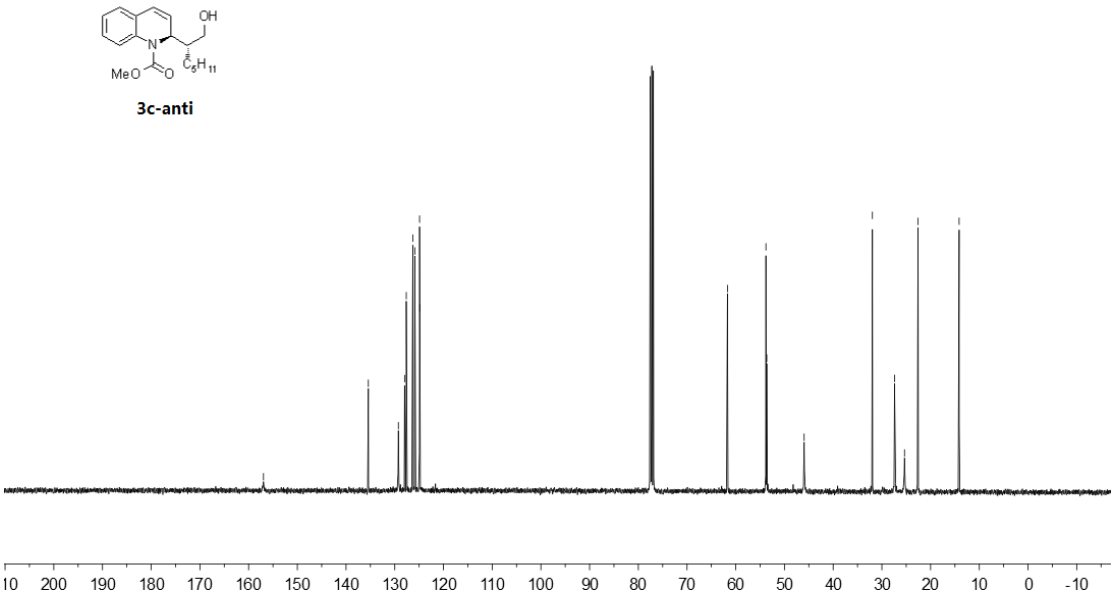
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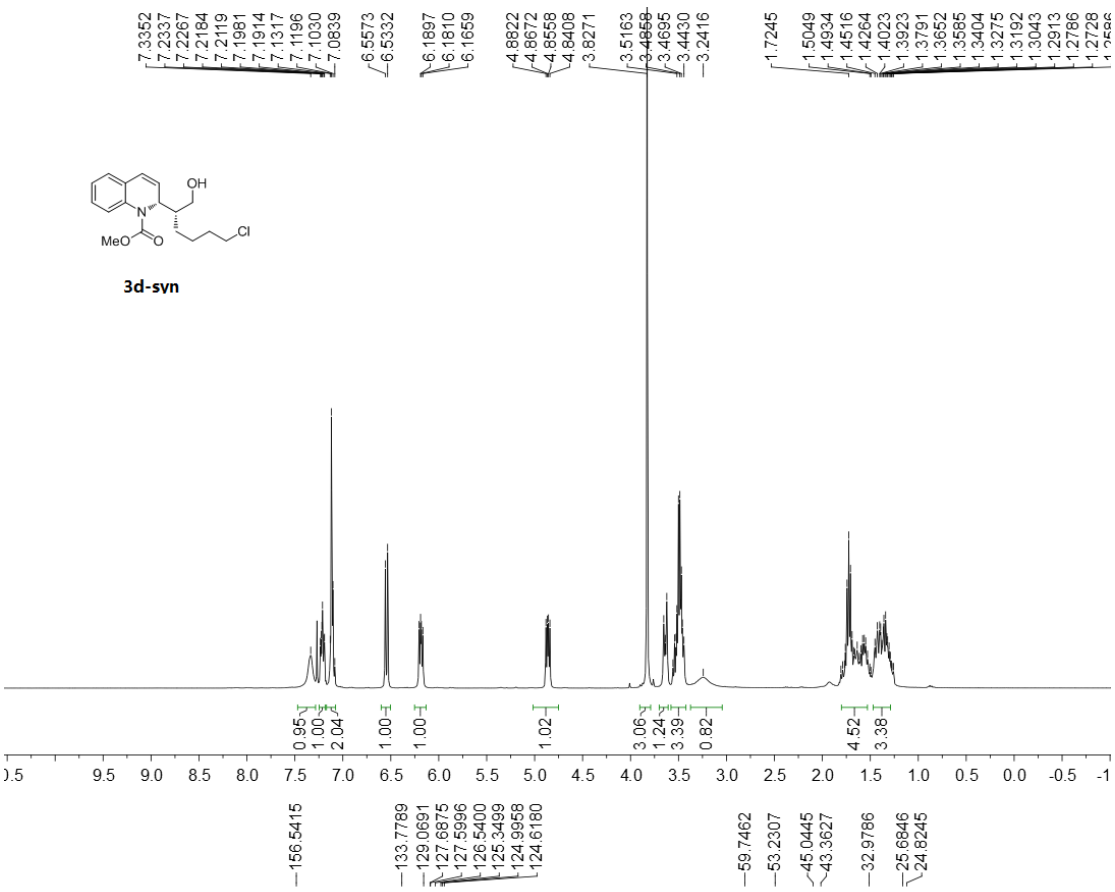
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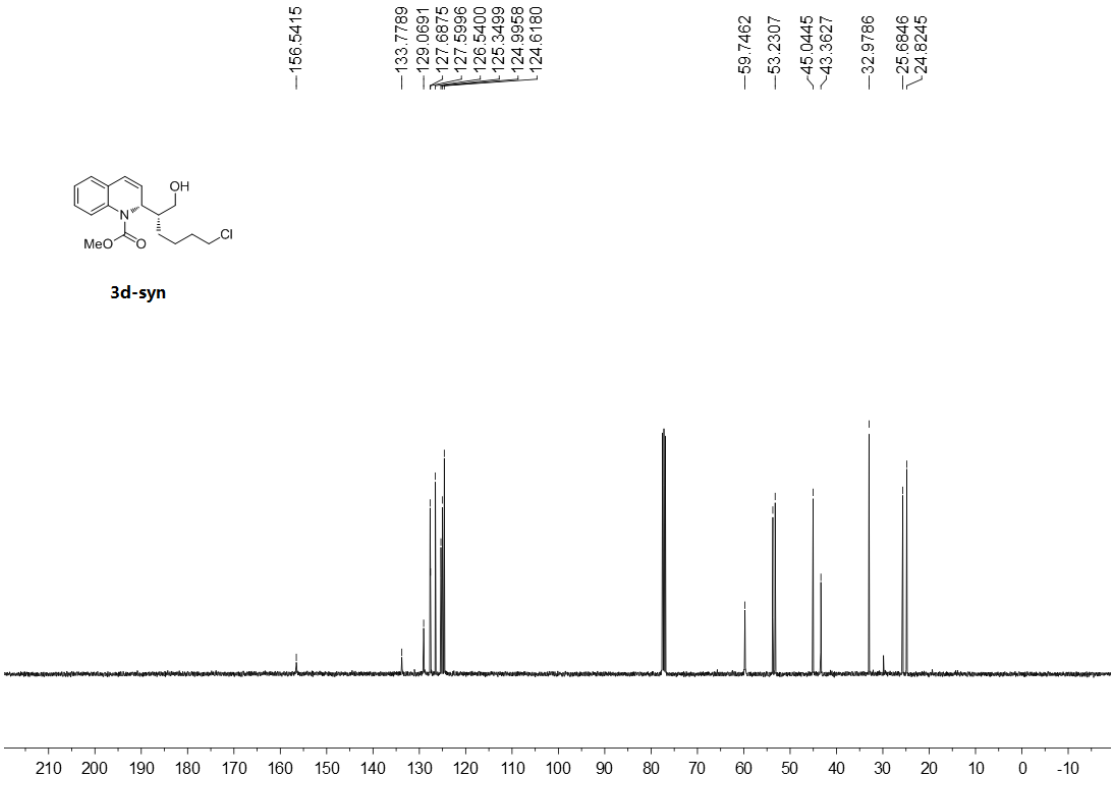
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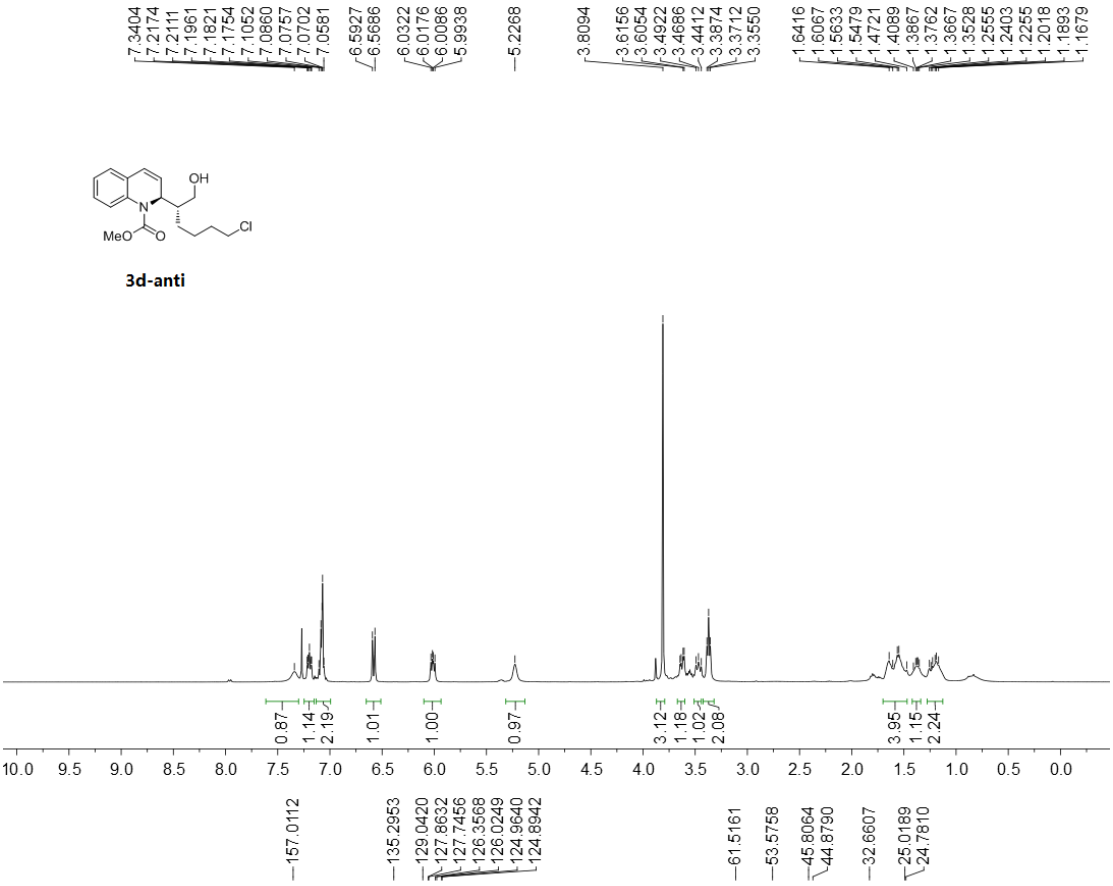
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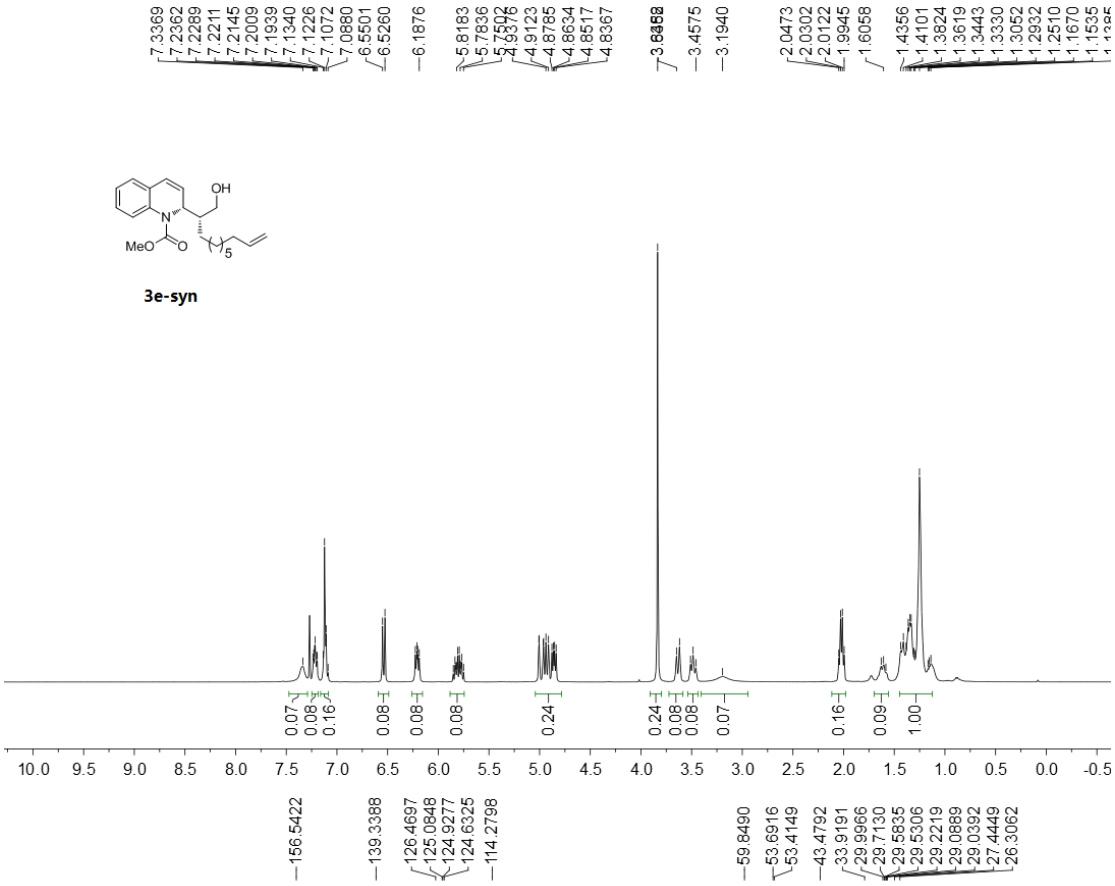
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6.5260
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5.7502
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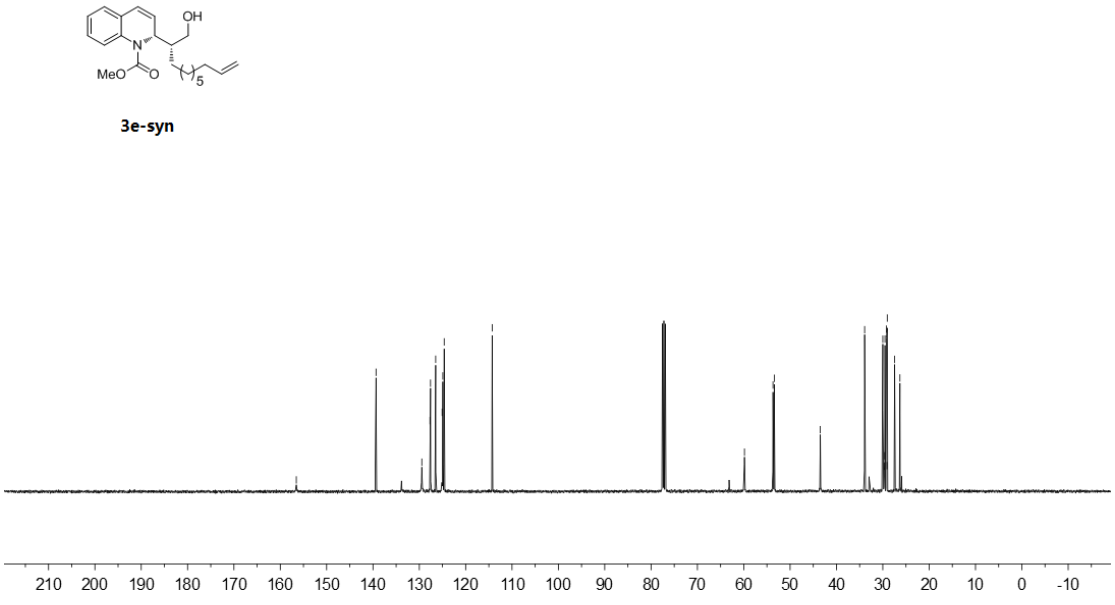
4.9123
4.8785
4.8634
4.8517
4.8367
3.4575
3.1940
2.0473
2.0302
2.0122
1.9945
1.6058
1.4356
1.4101
1.3824
1.3619
1.3443
1.3330
1.3052
1.2932
1.2510
1.1670
1.1535
OH
N
MeO
O
5
3e-syn
0.07
0.08
0.16
0.08
0.08
0.08
0.24
0.24
0.08
0.08
0.07
0.16
0.09
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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114.2798
59.8490
53.6916
53.4149
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33.9191
29.9966
29.7130
29.5835
29.5306
29.2219
29.0889
29.0392
27.4449
26.3062
OH
N
MeO
O
5
3e-syn
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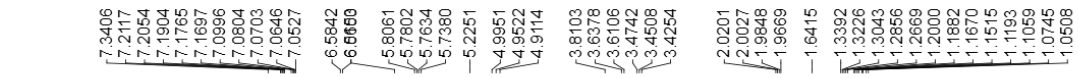

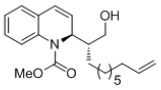

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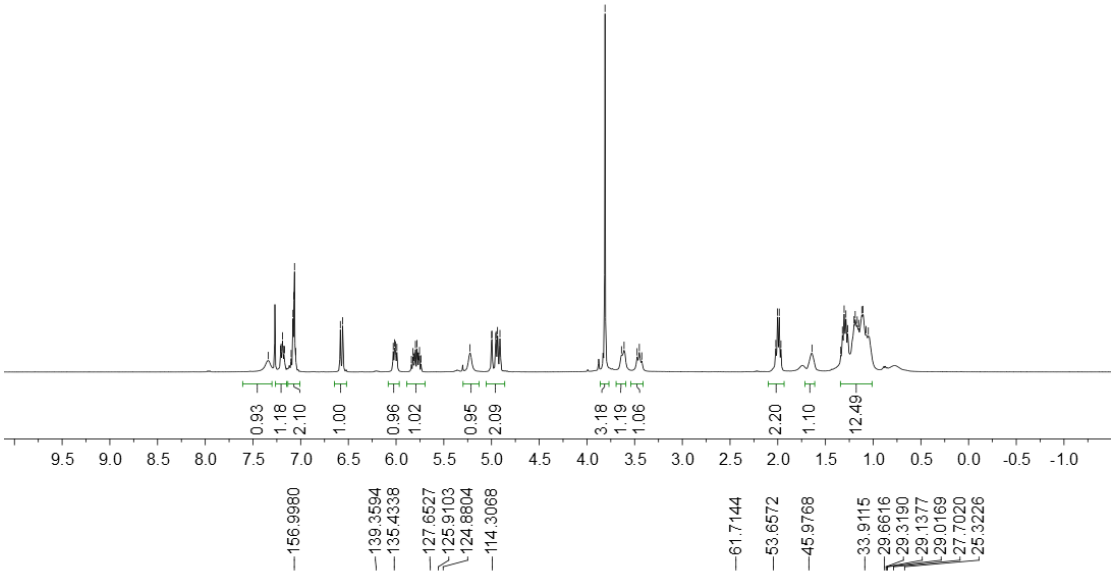

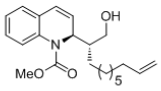

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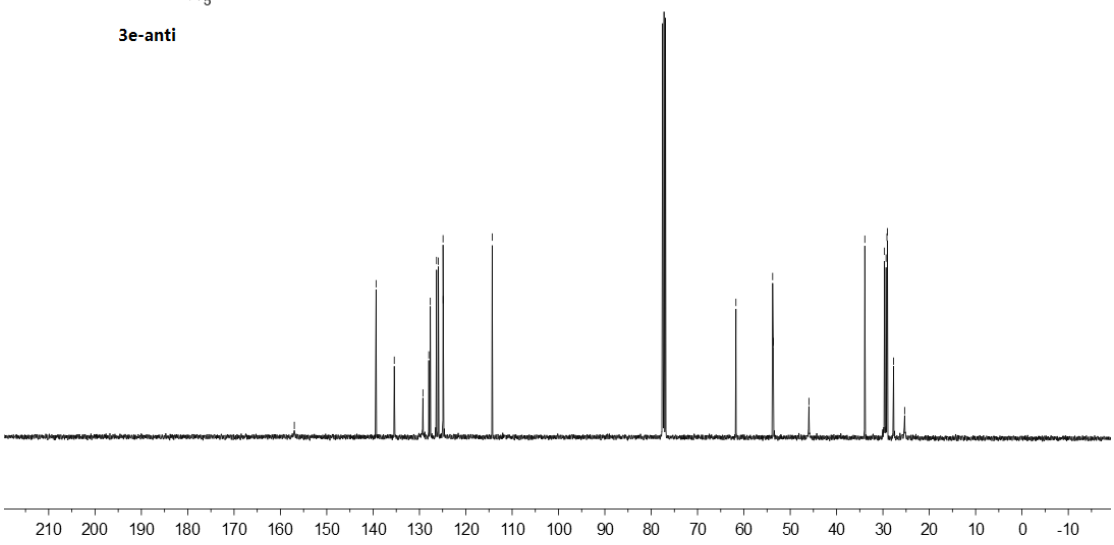

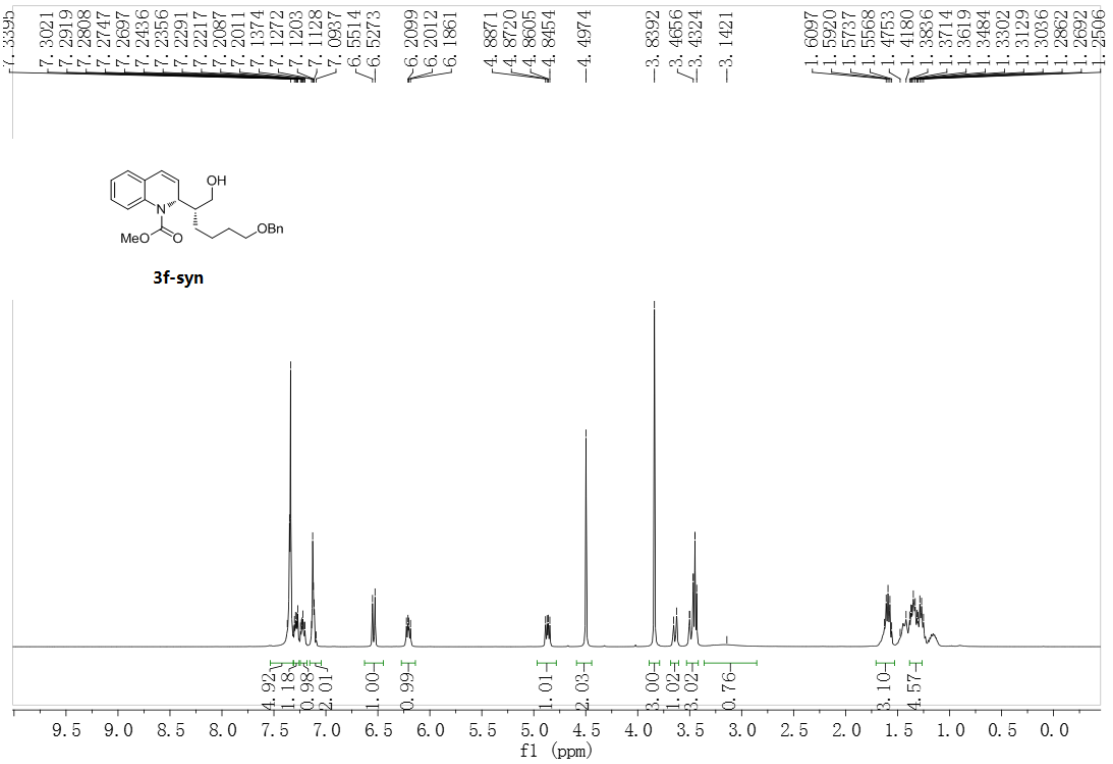
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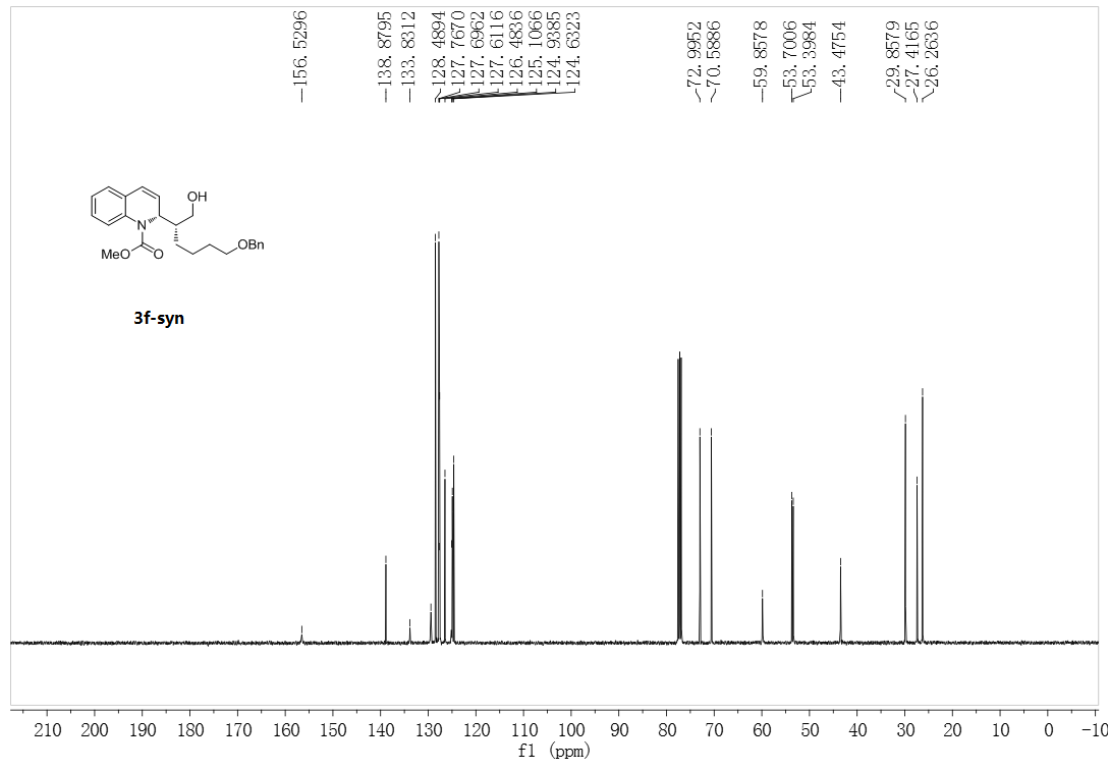
7.2087
7.2011
7.1374
7.1272
7.1203
7.1128
7.0937
6.5514
6.5273
6.2099
6.2012
6.1861
4.8871
4.8720
4.8605
4.8454
4.4974
3.8392
3.4656
3.4324
3.1421
1.6097
1.5920
1.5737
1.5568
1.4753
1.4180
1.3836
1.3714
1.3619
1.3484
1.3302
1.3129
1.3036
1.2862
1.2692
1.2506
OH
N
MeO
O
OBn
3f-syn
4.92
1.18
0.98
2.01
1.00
0.99
1.01
2.03
3.00
1.02
3.02
0.76
3.10
4.57
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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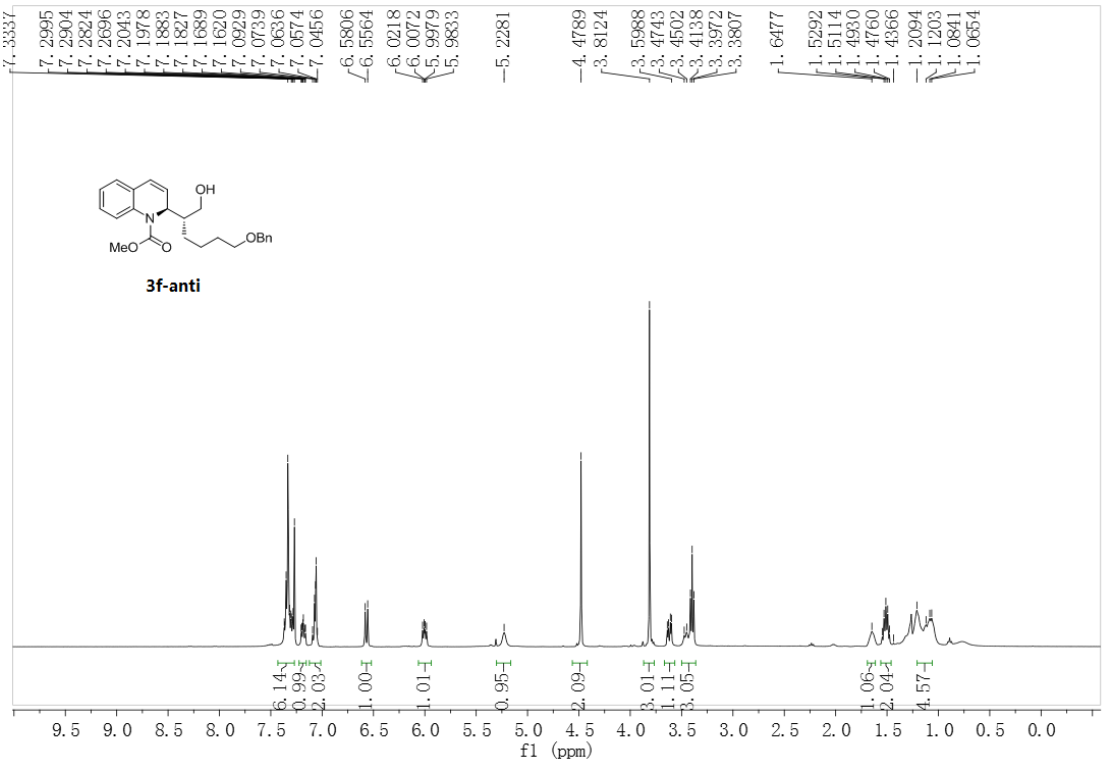
127.6962
127.6116
126.4836
125.1066
124.9385
124.6323
72.9952
70.5886
59.8578
53.7006
53.3984
43.4754
29.8579
27.4165
26.2636
OH
N
MeO
O
OBn
3f-syn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.2824
7.2696
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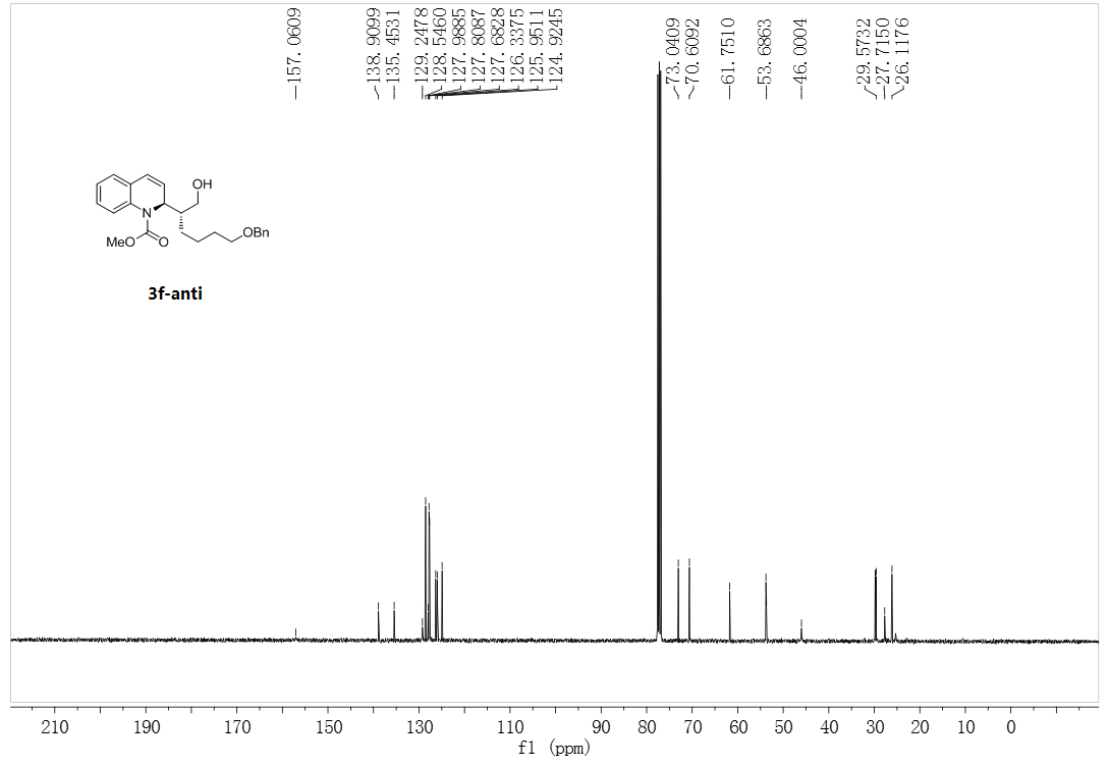
7.1978
7.1883
7.1827
7.1689
7.1620
7.0929
7.0739
7.0636
7.0574
7.0456
6.5806
6.5564
6.0218
6.0072
5.9979
5.9833
5.2281
4.4789
3.8124
3.5988
3.4743
3.4502
3.4138
3.3972
3.3807
1.6477
1.5292
1.5114
1.4930
1.4760
1.4366
1.2094
1.1203
1.0841
1.0654
OH
N
MeO
O
OBn
3f-anti
6.14
0.99
2.03
1.00
1.01
0.95
2.09
3.01
1.11
3.05
1.06
2.04
4.57
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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124.9245
73.0409
70.6092
61.7510
53.6863
46.0004
29.5732
27.7150
26.1176
OH
N
MeO
O
OBn
3f-anti
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.3391
7.2564
7.2528
7.2368
7.2190
7.2033
7.1976
7.1922
7.1735
7.1626
7.1575
7.1531
7.1499
7.1441
7.1340
7.1329
7.1135
6.6488
6.6247
6.3162
6.3073
6.2922
5.0333
5.0183
5.0064
4.9913
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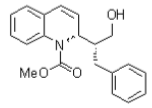
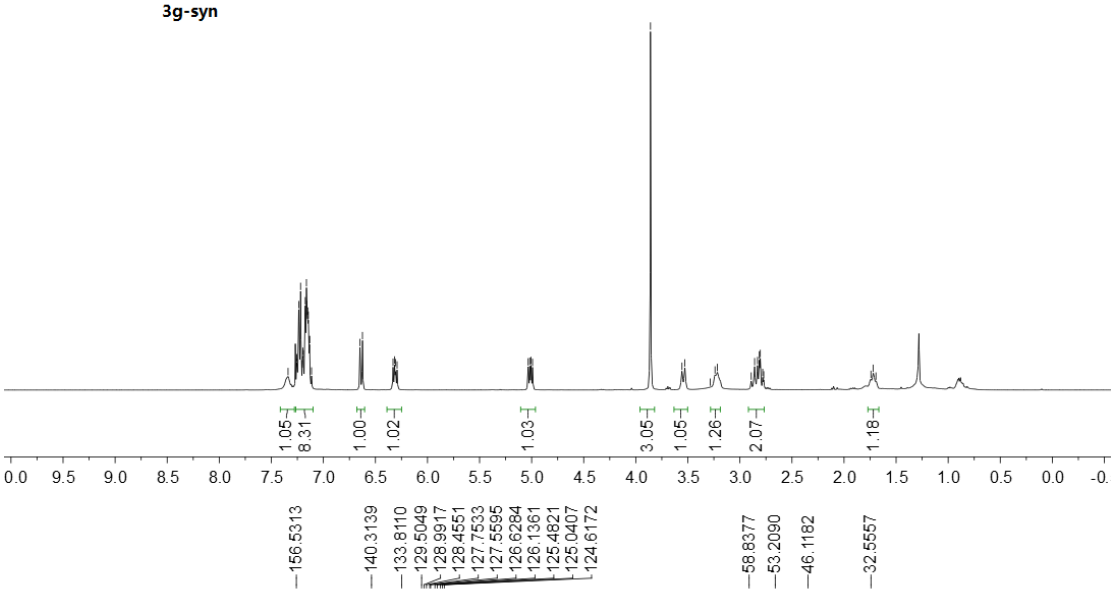
1.7195
1.6938


OH
MeO
O
N

3g-syn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8.31
1.00
1.02
1.03
3.05
1.05
1.26
2.07
1.18
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

156.5313
140.3139
133.8110
129.5049
128.9917
128.4551
127.7533
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126.1361
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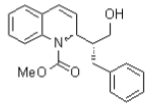
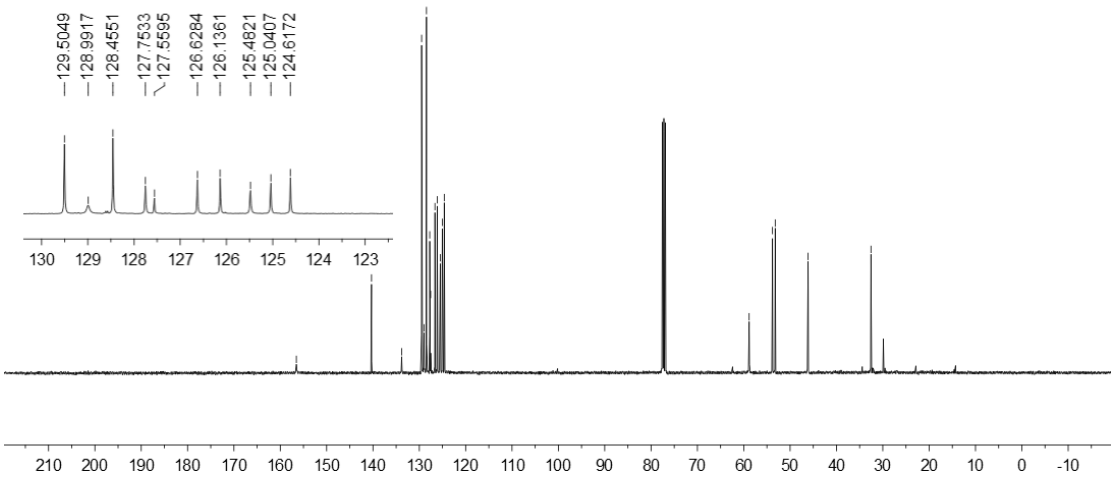
32.5557


OH
MeO
O
N

3g-syn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125.0407
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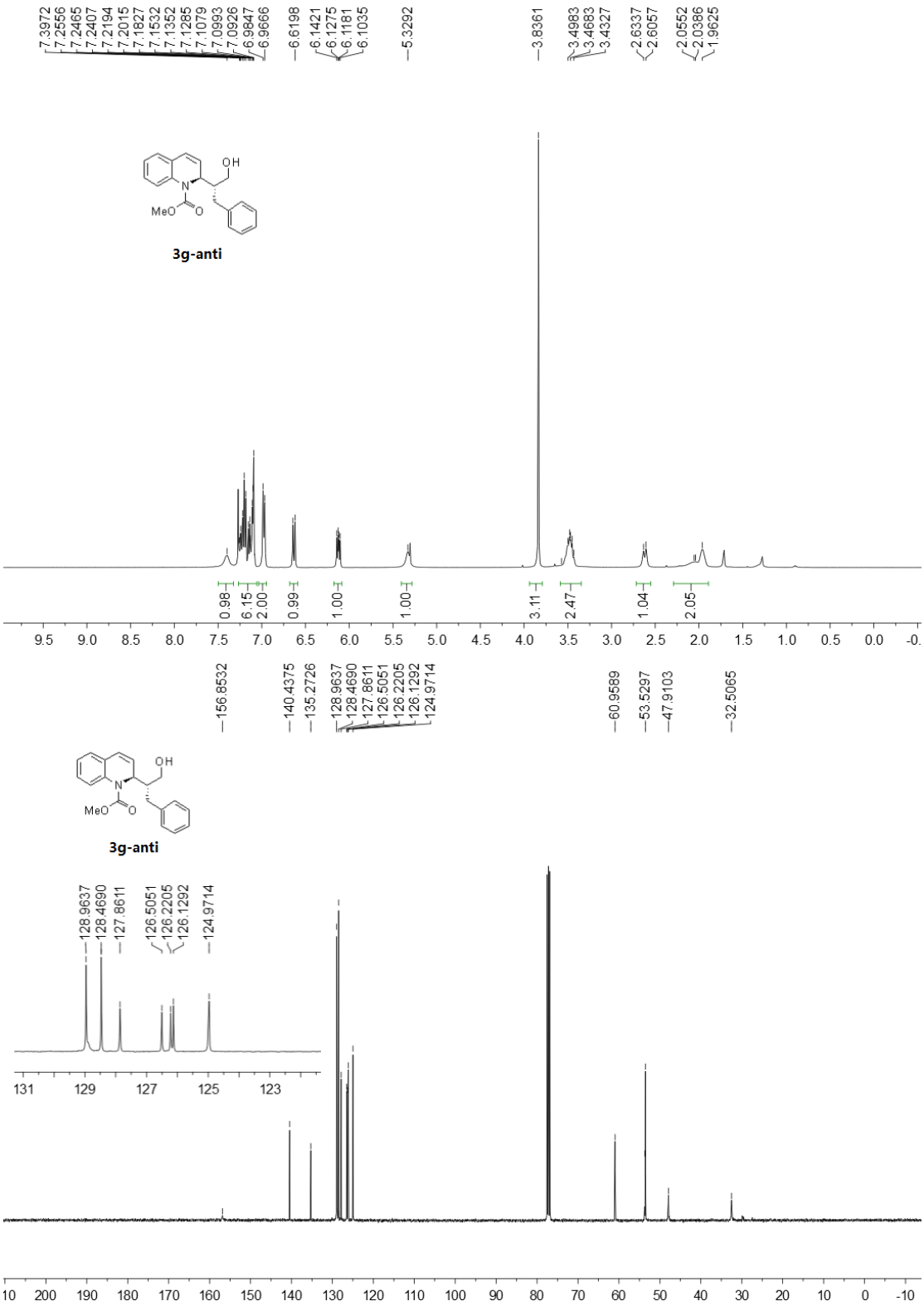
130 129 128 127 126 125 124 123
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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7.0993
7.0926
6.9847
6.9666
6.6198
6.1421
6.1275
6.1181
6.1035
5.3292
3.8361
3.4983
3.4683
3.4327
2.6337
2.6057
2.0552
2.0386
1.9625
OH
N
MeO
O
3g-anti
0.98
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2.00
0.99
1.00
1.00
3.11
2.47
1.04
2.05
156.8532
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128.4690
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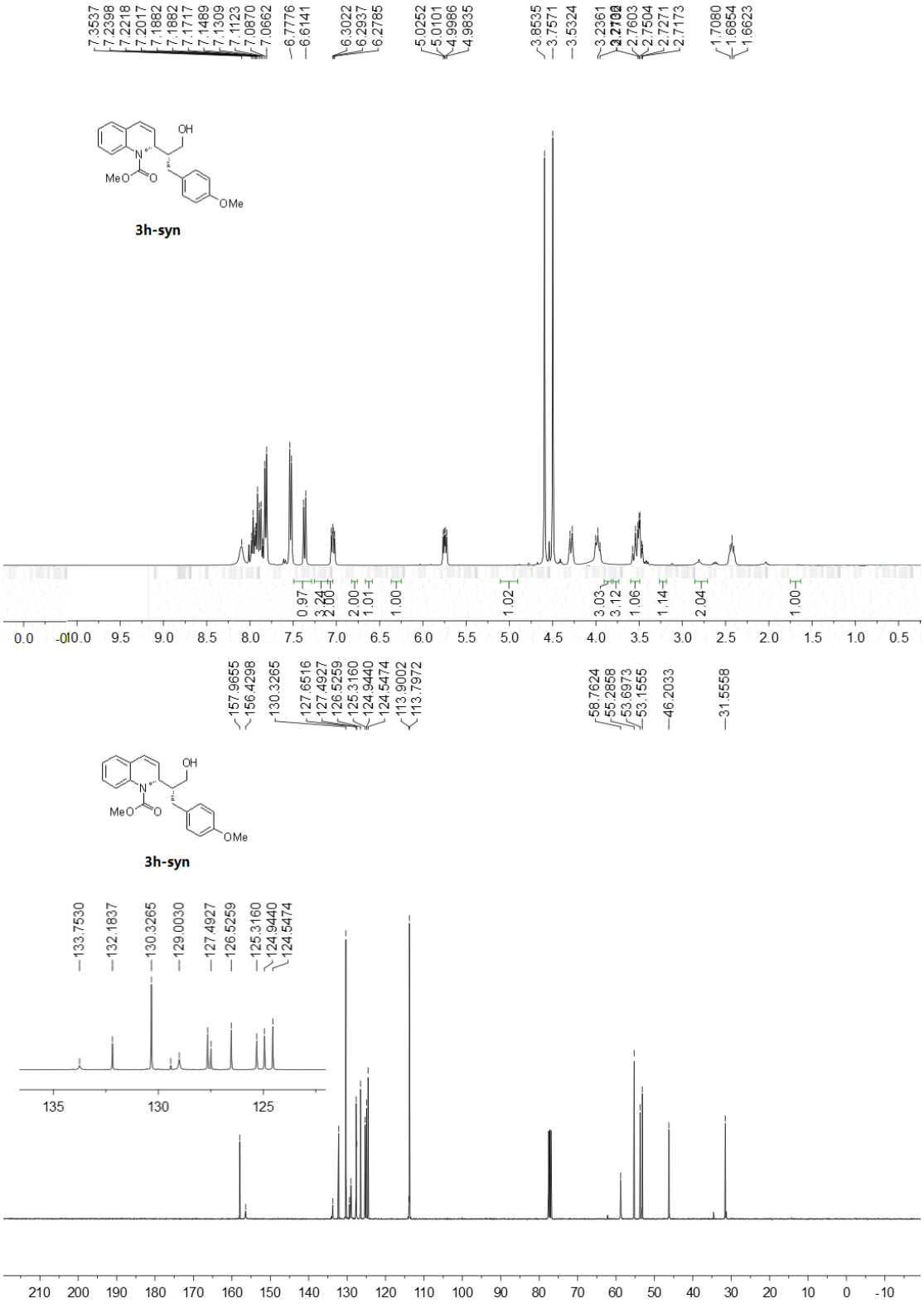
3g-anti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6.2785
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5.0101
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3.8535
3.7571
3.5324
3.2361
2.7603
2.7504
2.7271
2.7173
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1.6854
1.6623
OH
MeO
O
N
OMe
3h-syn
0.97
3.24
2.00
2.00
1.01
1.00
1.02
3.03
3.12
1.06
1.14
2.04
1.00
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113.7972
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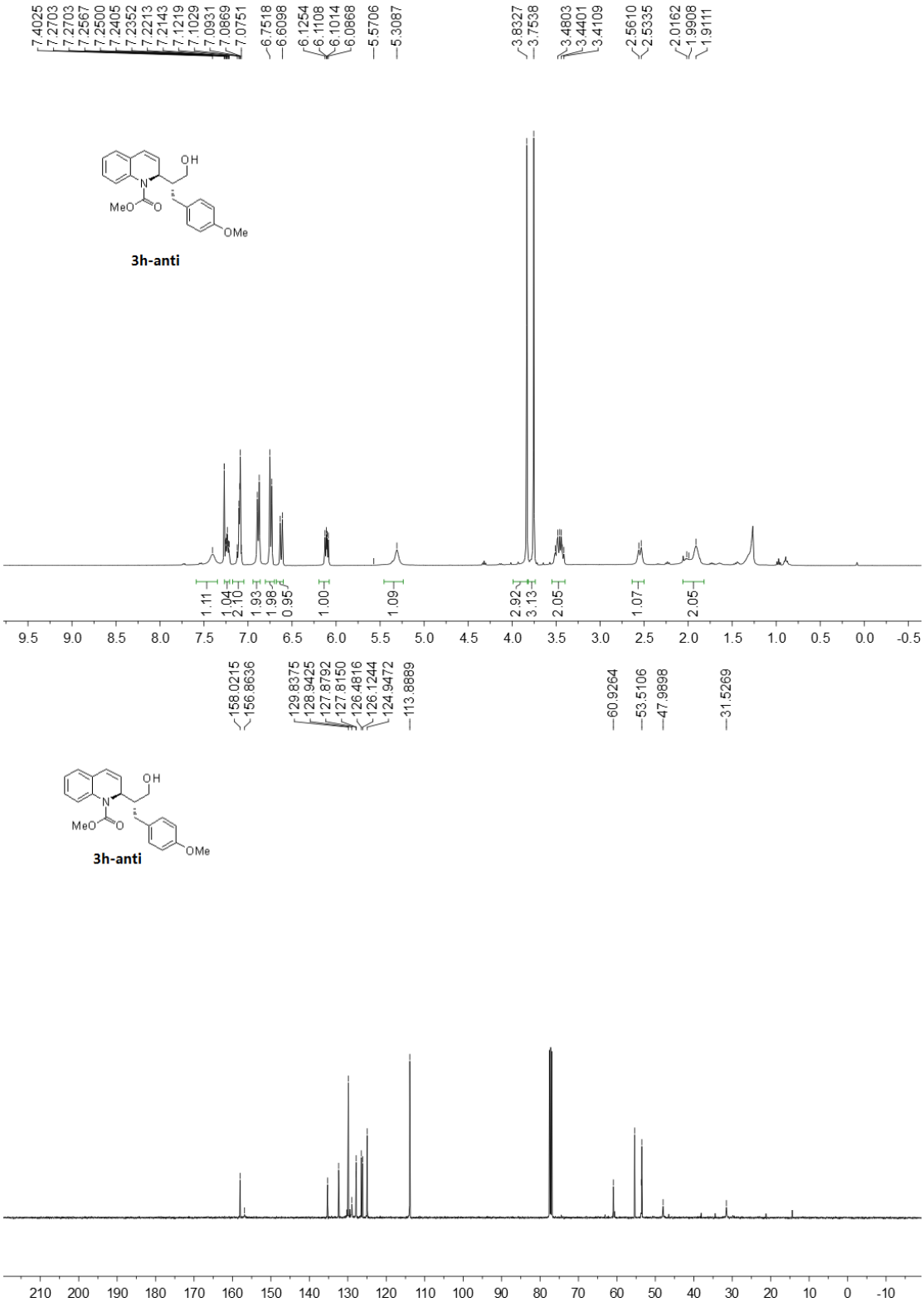
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7.0931
7.0869
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6.6098
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6.1108
6.1014
6.0868
5.5706
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3.7538
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3.4401
3.4109
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2.5335
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1.9908
1.9111
OH
MeO
O
N
OMe
3h-anti
1.11
1.04
2.10
1.93
1.98
0.95
1.00
1.09
2.92
3.13
2.05
1.07
2.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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128.9425
127.8792
127.8150
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126.1244
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60.9264
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O
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OMe
3h-anti
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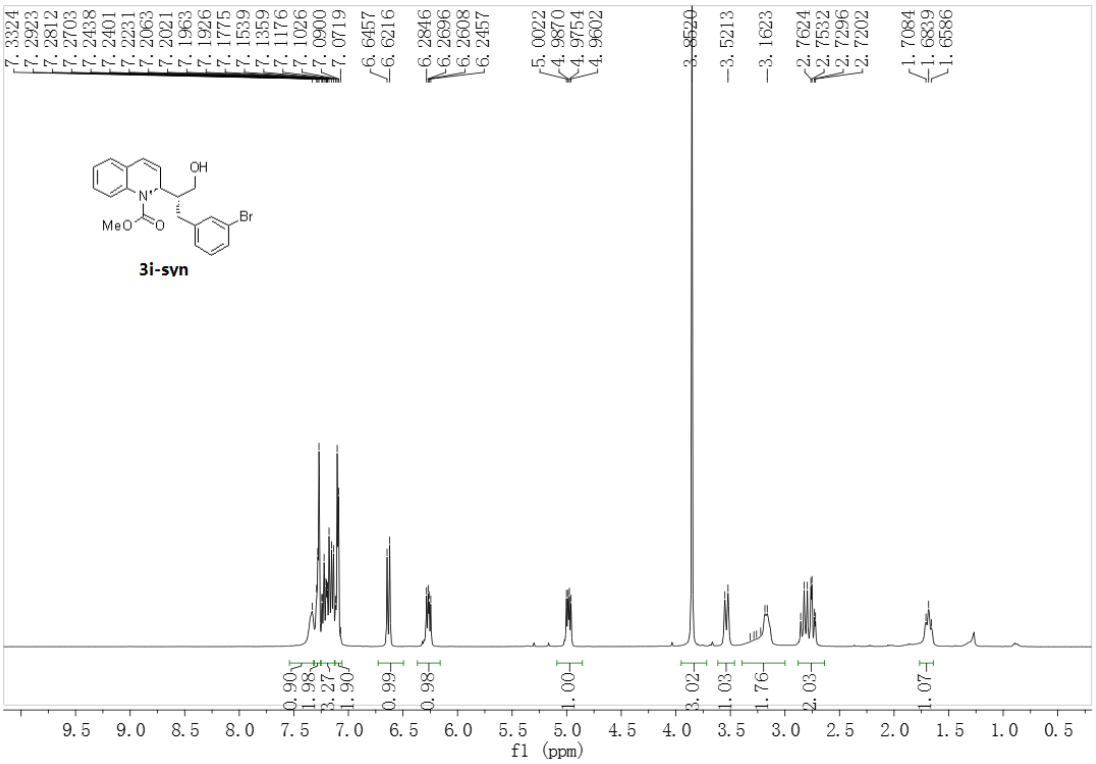
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7.2231
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7.2021
7.1963
7.1926
7.1775
7.1539
7.1359
7.1176
7.1026
7.0900
7.0719
6.6457
6.6216
6.2846
6.2696
6.2608
6.2457
5.0022
4.9870
4.9754
4.9602
3.8520
3.5213
3.1623
2.7624
2.7532
2.7296
2.7202
1.7084
1.6839
1.6586
OH
MeO
O
N
Br
3i-syn
0.90
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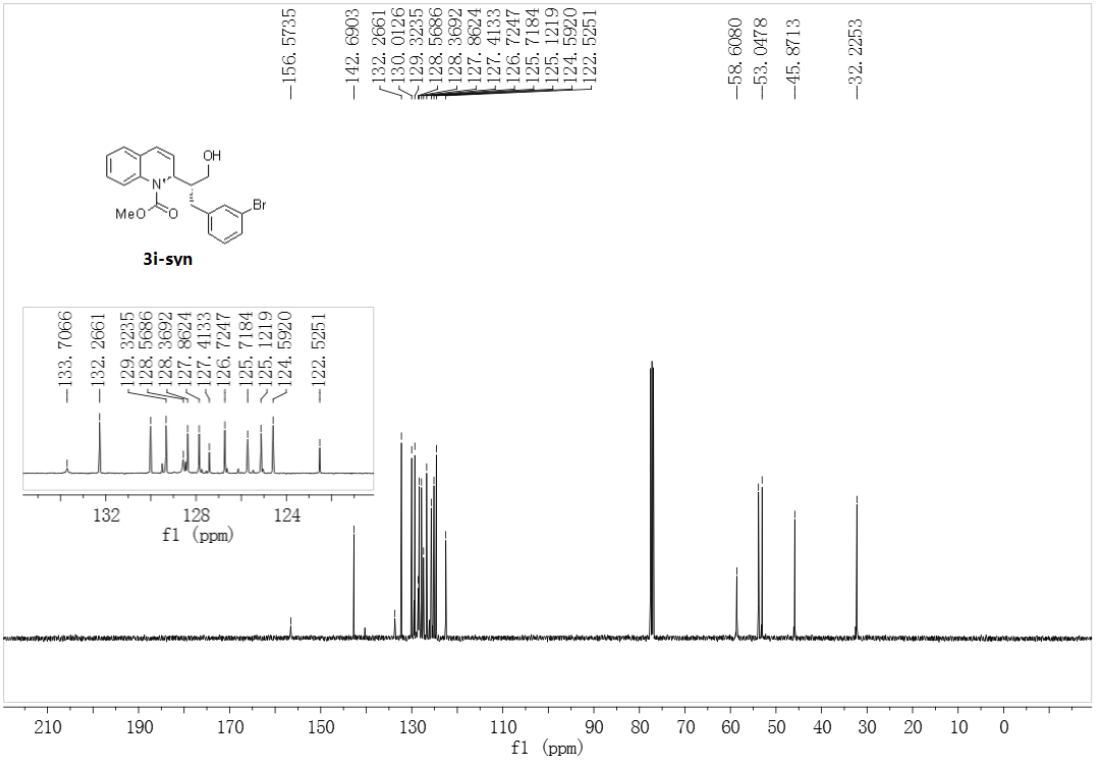
0.99
0.98
1.00
3.02
1.03
1.76
2.03
1.07
f1 (ppm)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125.7184
125.1219
124.5920
122.5251
58.6080
53.0478
45.8713
32.2253
OH
MeO
O
N
Br
3i-syn
133.7066
132.2661
129.3235
128.5686
128.3692
127.8624
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125.7184
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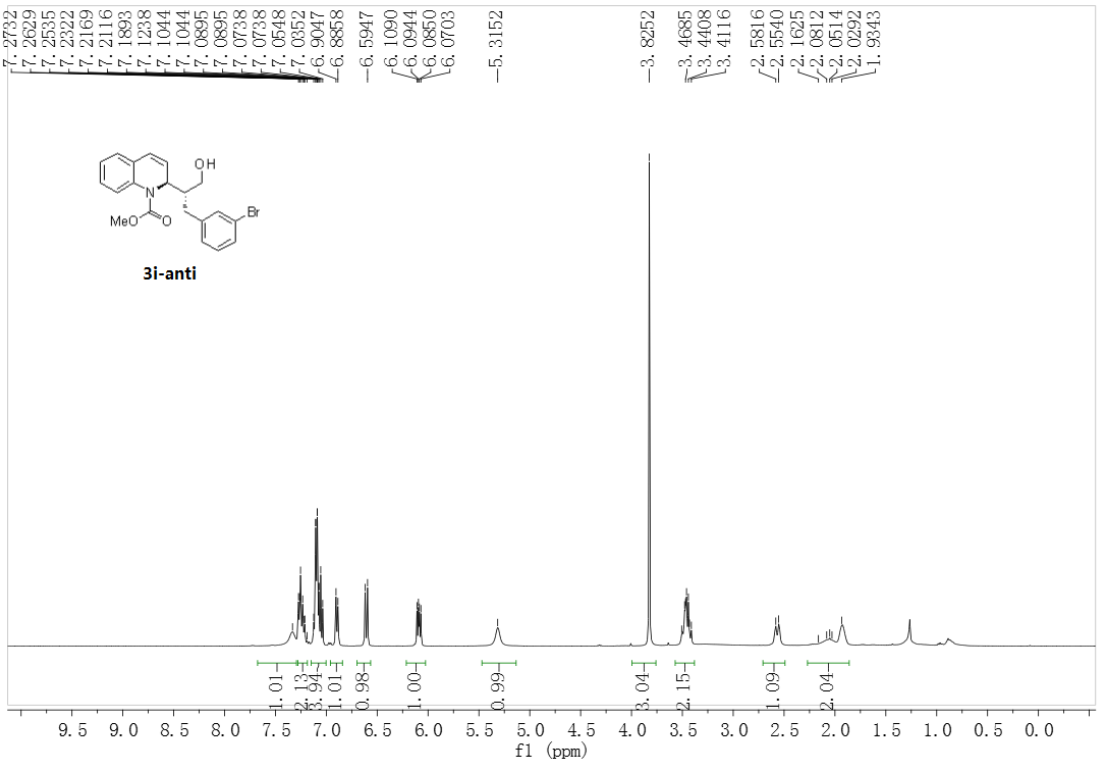
124.5920
122.5251
132
128
124
f1 (ppm)
f1 (ppm)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7.0895
7.0738
7.0738
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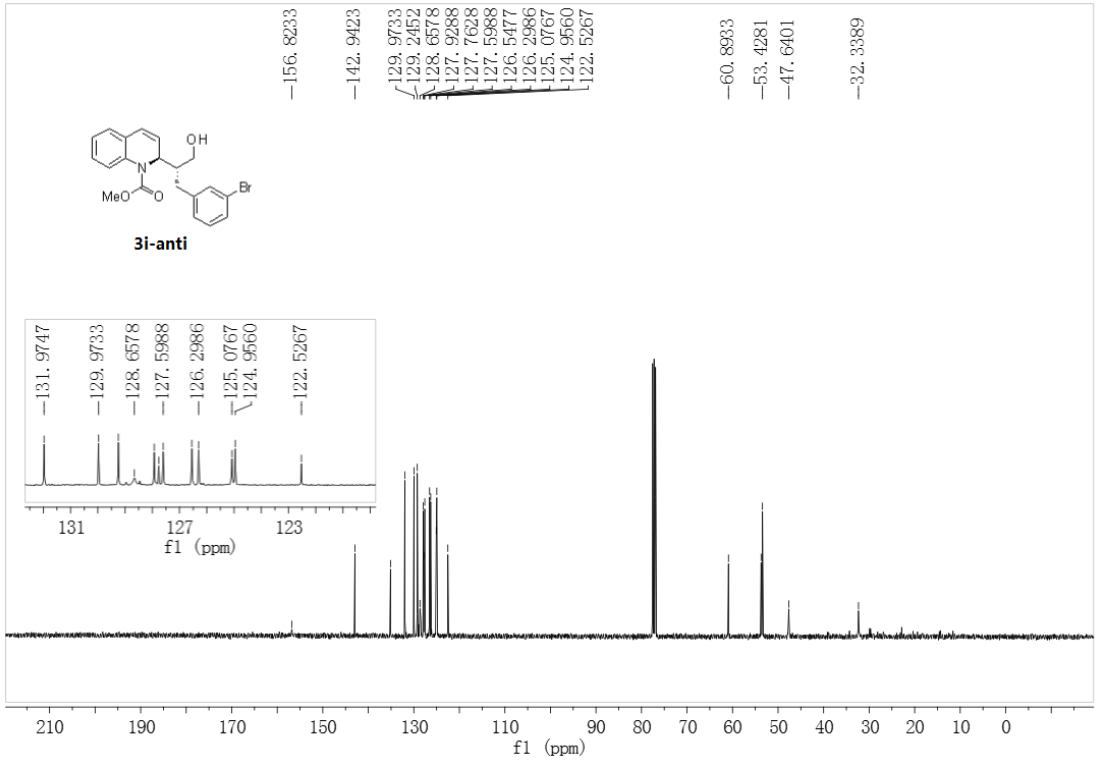
1.9343
OH
N
MeO
O
Br
3i-anti
1.01
2.13
3.94
1.01
0.98
1.00
0.99
3.04
2.15
1.09
2.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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125.0767
124.9560
122.5267
60.8933
53.4281
47.6401
32.3389
OH
N
MeO
O
Br
3i-anti
131.9747
129.9733
128.6578
127.5988
126.2986
125.0767
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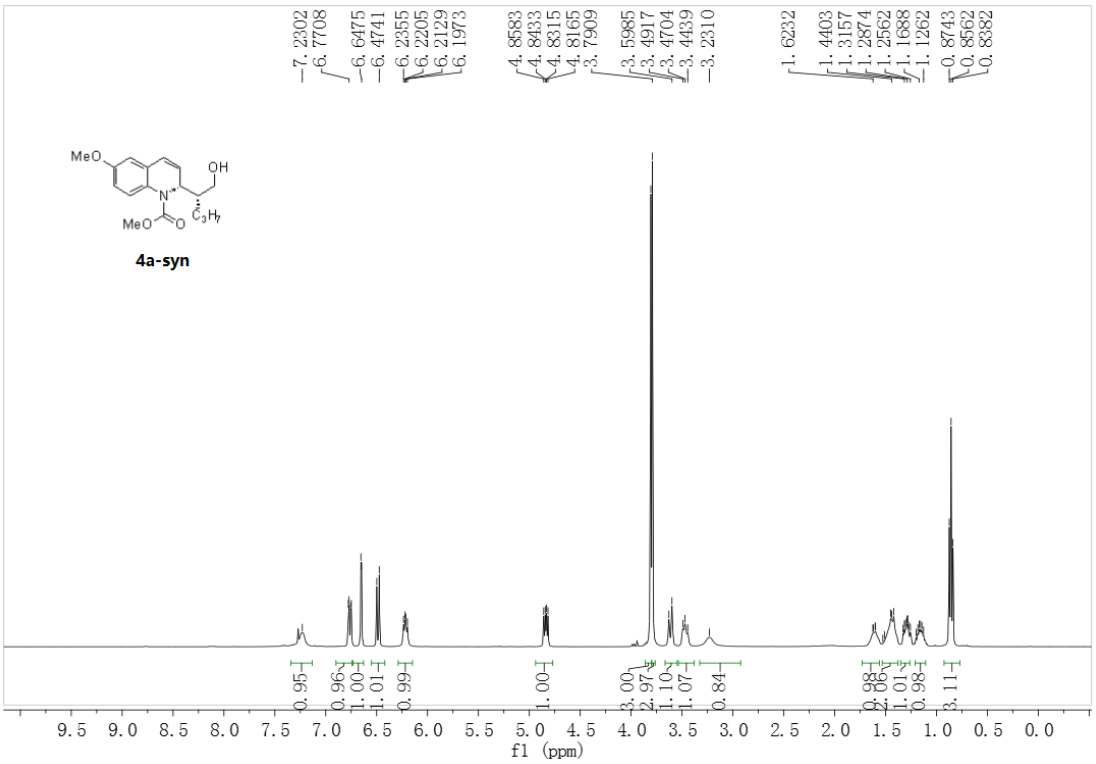
122.5267
131
127
123
f1 (ppm)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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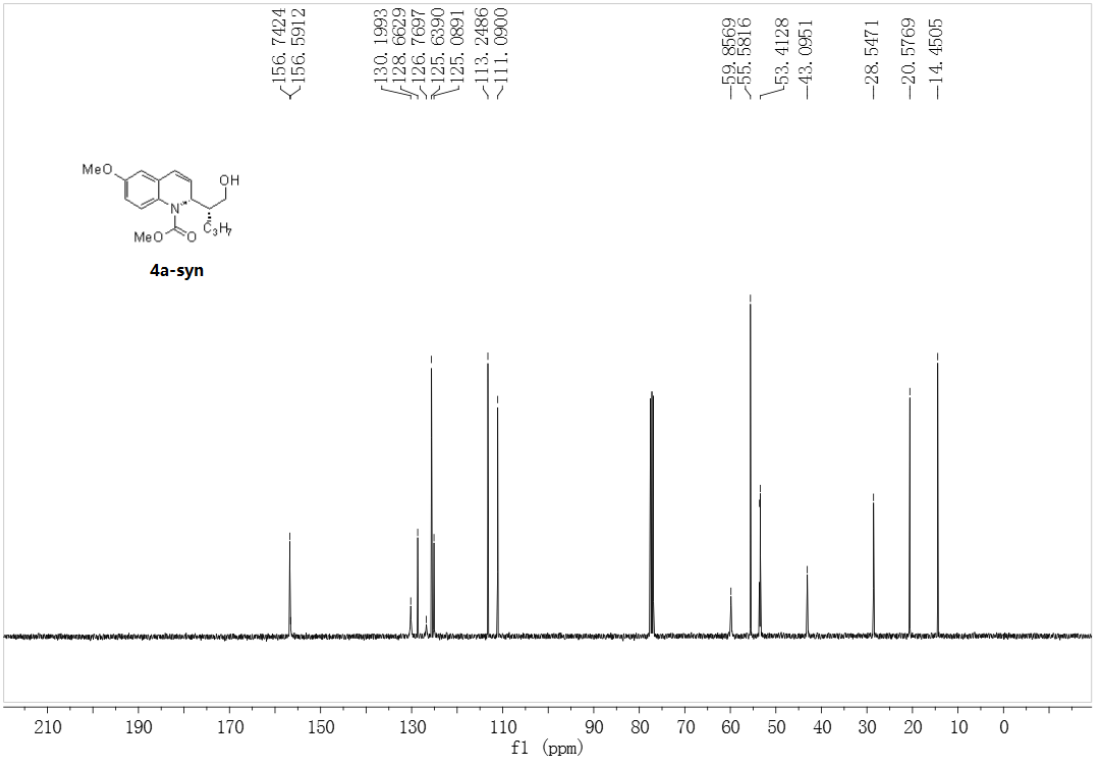
4.8315
4.8165
3.7909
3.5985
3.4917
3.4704
3.4439
3.2310
1.6232
1.4403
1.3157
1.2874
1.2562
1.1688
1.1262
0.8743
0.8562
0.8382
MeO
OH
N
MeO
O
C3H7
4a-syn
0.95
0.96
1.00
1.01
0.99
1.00
3.00
2.97
1.10
1.07
0.84
0.98
2.06
1.01
0.98
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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55.5816
53.4128
43.0951
28.5471
20.5769
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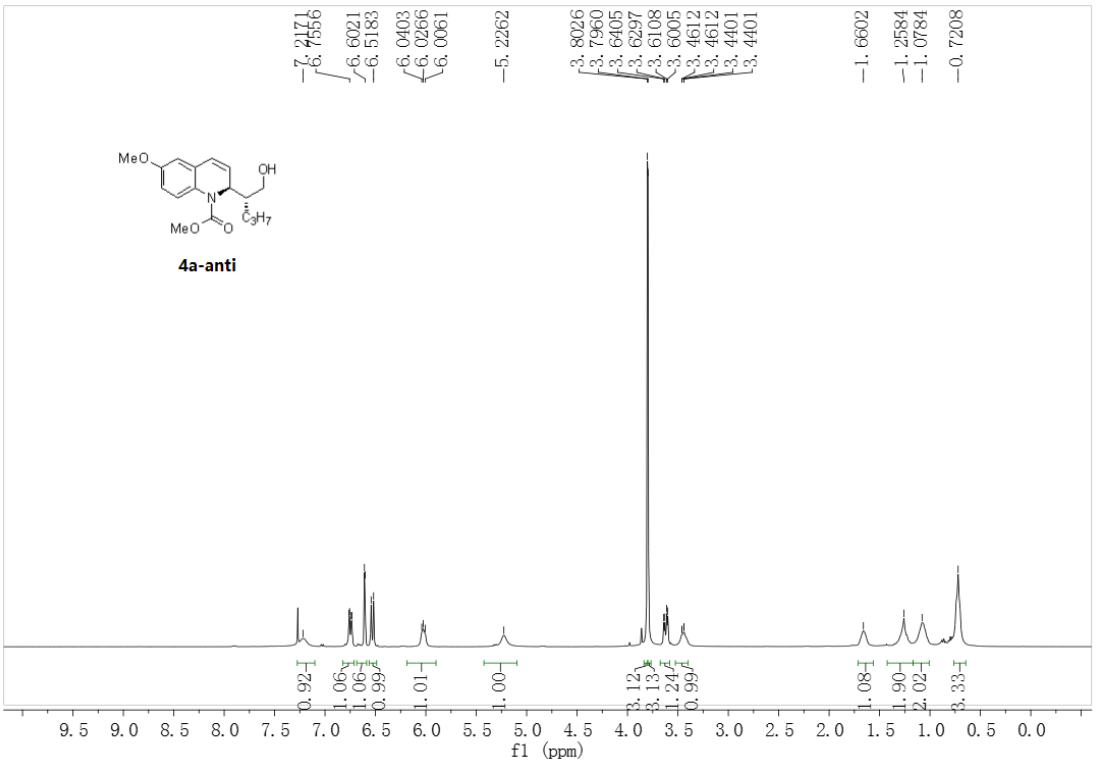
OH
N
MeO
O
C3H7
4a-syn
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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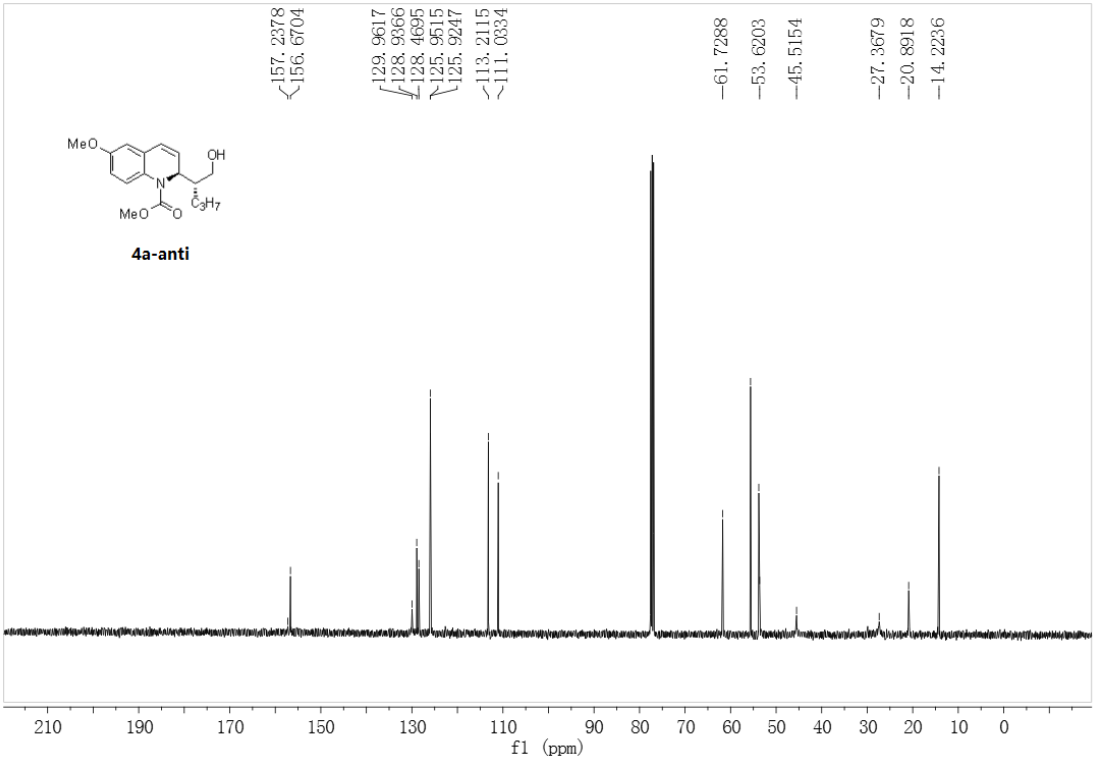
5.2262
3.8026
3.7960
3.6405
3.6297
3.6108
3.6005
3.4612
3.4612
3.4401
3.4401
1.6602
1.2584
1.0784
0.7208
MeO
OH
N
MeO
O
C3H7
4a-anti
0.92
1.06
1.06
0.99
1.01
1.00
3.12
3.13
1.24
0.99
1.08
1.90
2.02
3.33
f1 (ppm)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53.6203
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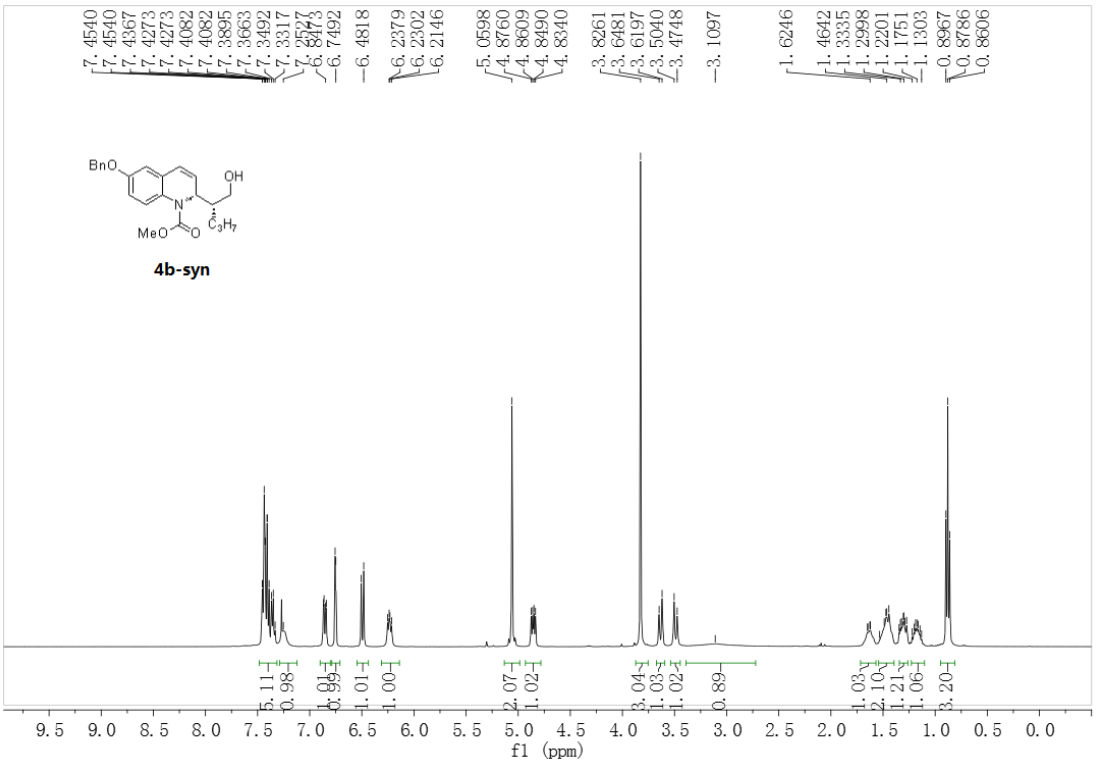
MeO
OH
N
MeO
O
C3H7
4a-anti
f1 (ppm)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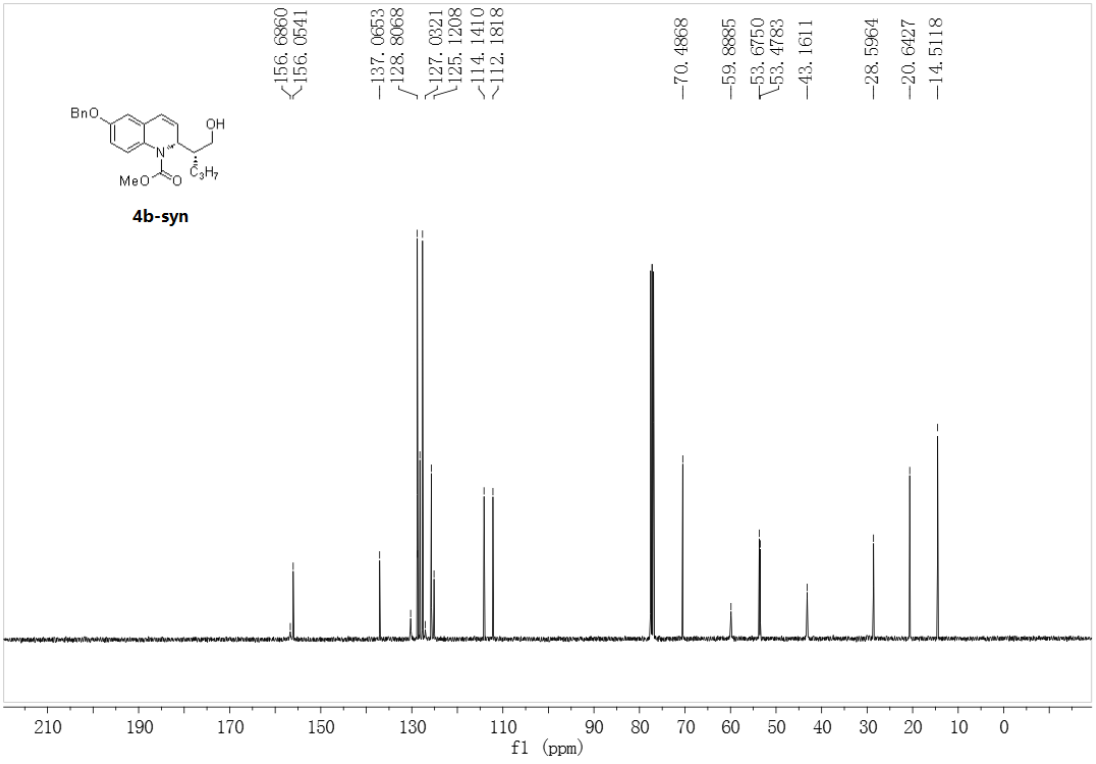
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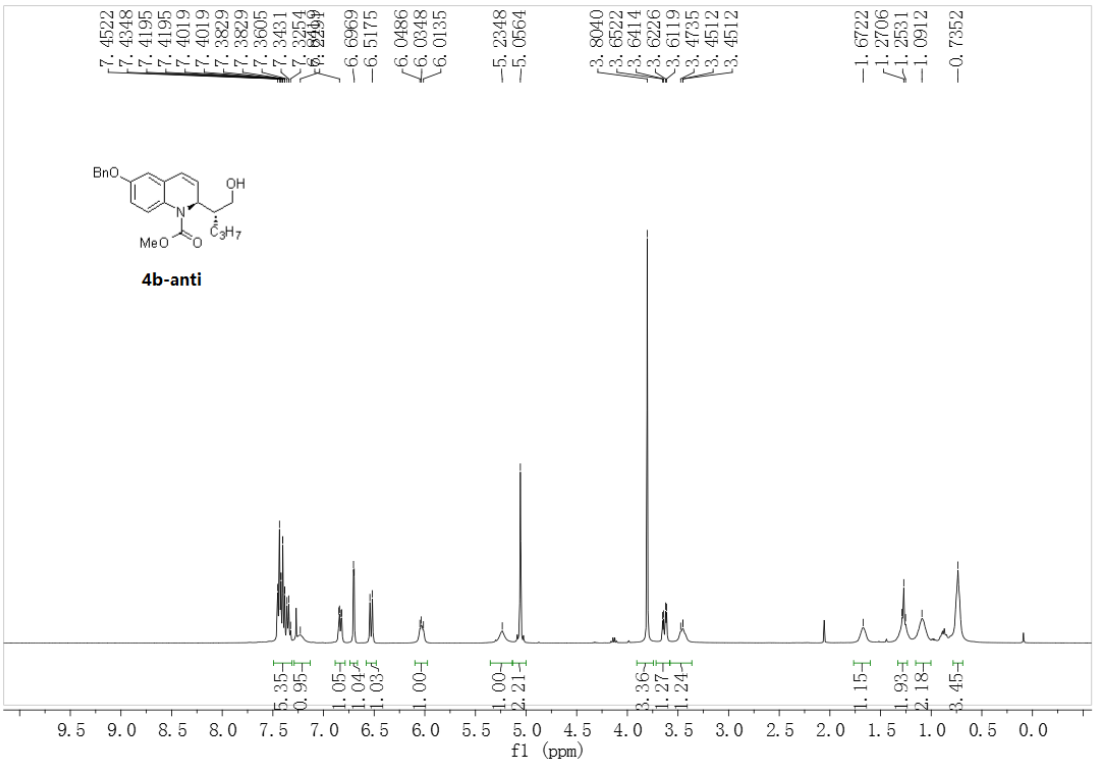
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7.3431
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6.5175
6.0486
6.0348
6.0135
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5.0564
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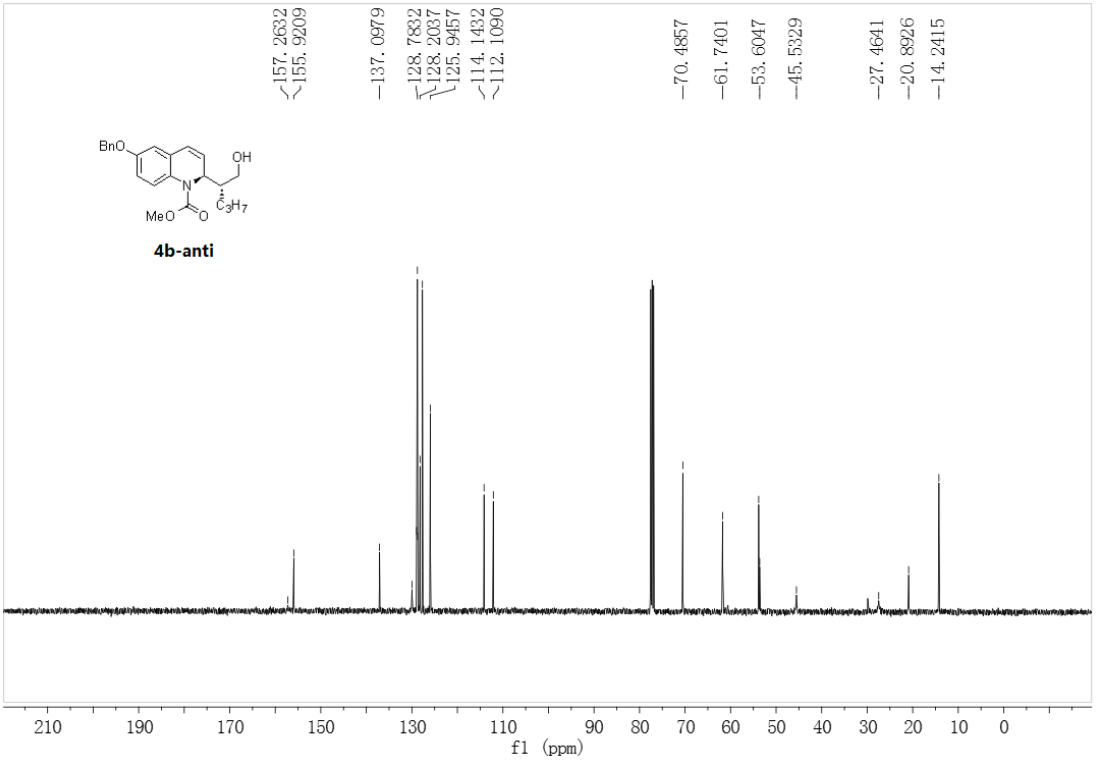
3.6522
3.6414
3.6226
3.6119
3.4735
3.4512
3.4512
1.6722
1.2706
1.2531
1.0912
0.7352
BnO
OH
N
MeO
O
C3H7
4b-anti
6.35
0.95
1.05
1.04
1.03
1.00
1.00
2.21
3.36
1.27
1.24
1.15
1.93
2.18
3.45
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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53.6047
45.5329
27.4641
20.8926
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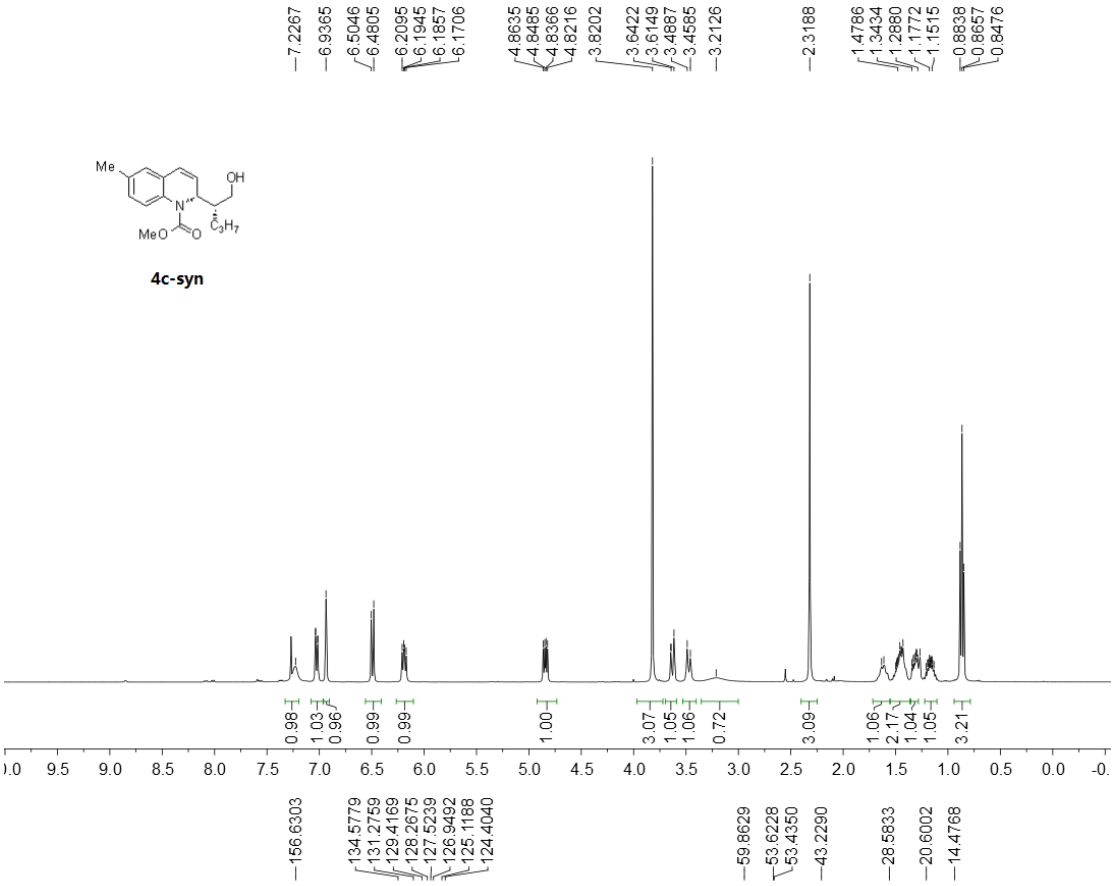
BnO
OH
N
MeO
O
C3H7
4b-anti
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.1857
6.1706
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4.8485
4.8366
4.8216
3.8202
3.6422
3.6149
3.4887
3.4585
3.2126
2.3188
1.4786
1.3434
1.2880
1.1772
1.1515
0.8838
0.8657
0.8476
Me
OH
N
MeO
O
C3H7
4c-syn
0.98
1.03
0.96
0.99
0.99
1.00
3.07
1.05
1.06
0.72
3.09
1.06
2.17
1.04
1.05
3.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
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2.0
1.5
1.0
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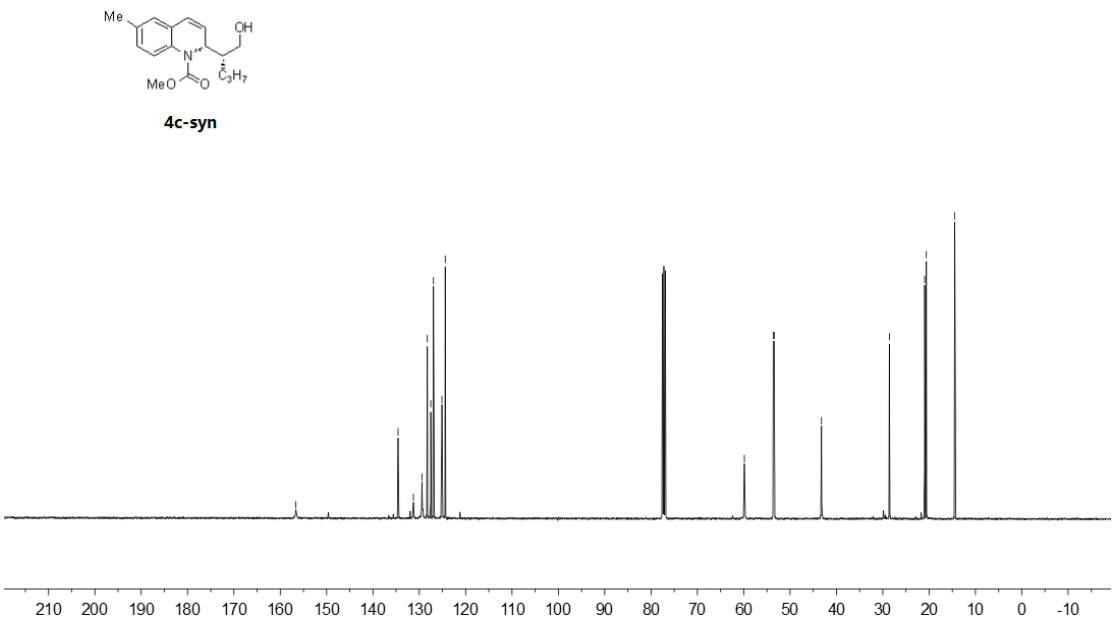
0.0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53.4350
43.2290
28.5833
20.6002
14.4768
Me
OH
N
MeO
O
C3H7
4c-syn
210
200
190
180
170
160
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140
130
120
110
100
90
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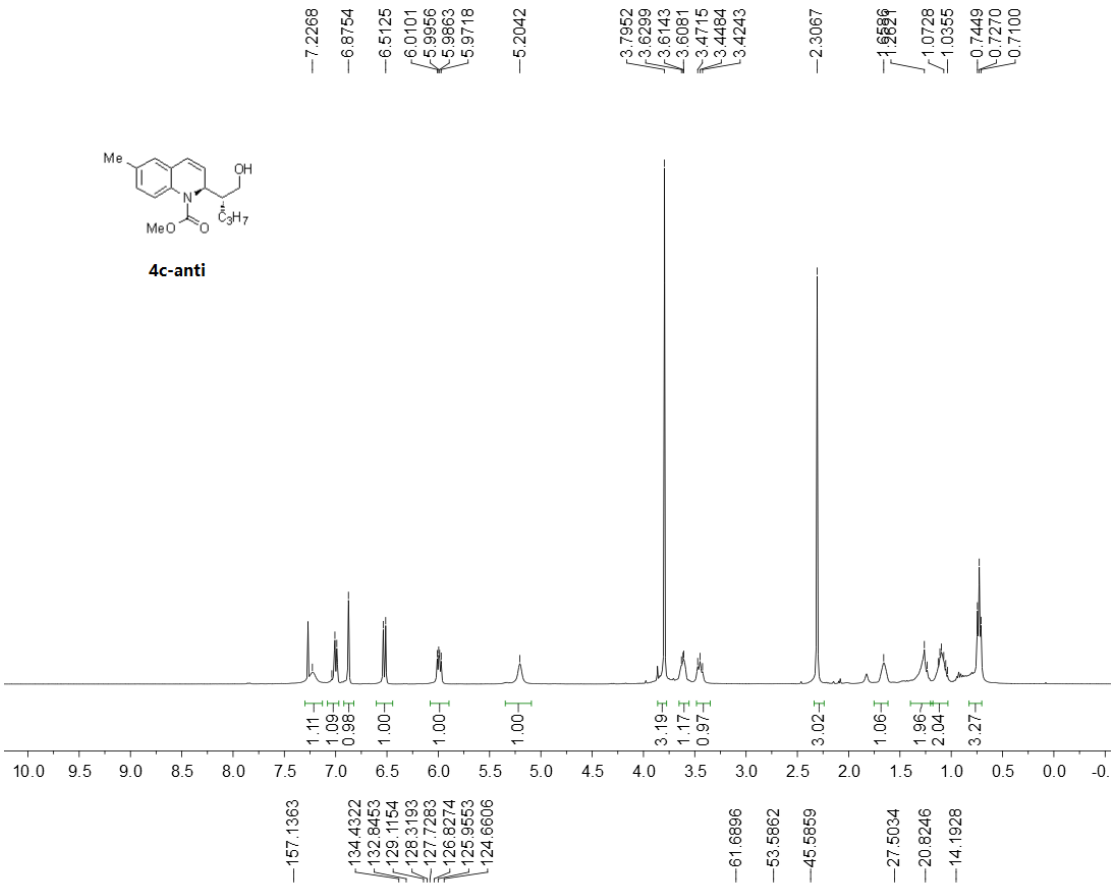
60
50
40
30
20
10
0
-10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3.6143
3.6081
3.4715
3.4484
3.4243
2.3067
1.6586
1.0728
1.0355
0.7449
0.7270
0.7100
Me
OH
N
MeO
O
C3H7
4c-anti
1.11
1.09
0.98
1.00
1.00
1.00
3.19
1.17
0.97
3.02
1.06
1.96
2.04
3.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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134.4322
132.8453
129.1154
128.3193
127.7283
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125.9553
124.6606
61.6896
53.5862
45.5859
27.5034
20.8246
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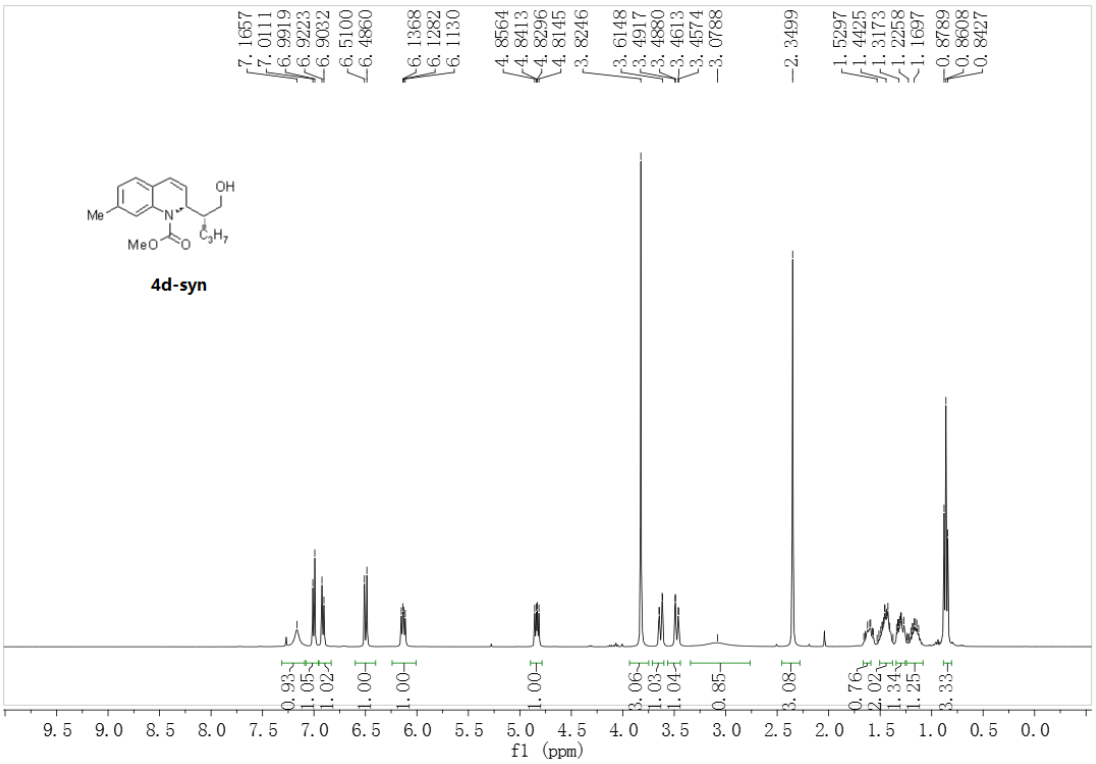
OH
N
MeO
O
C3H7
4c-anti
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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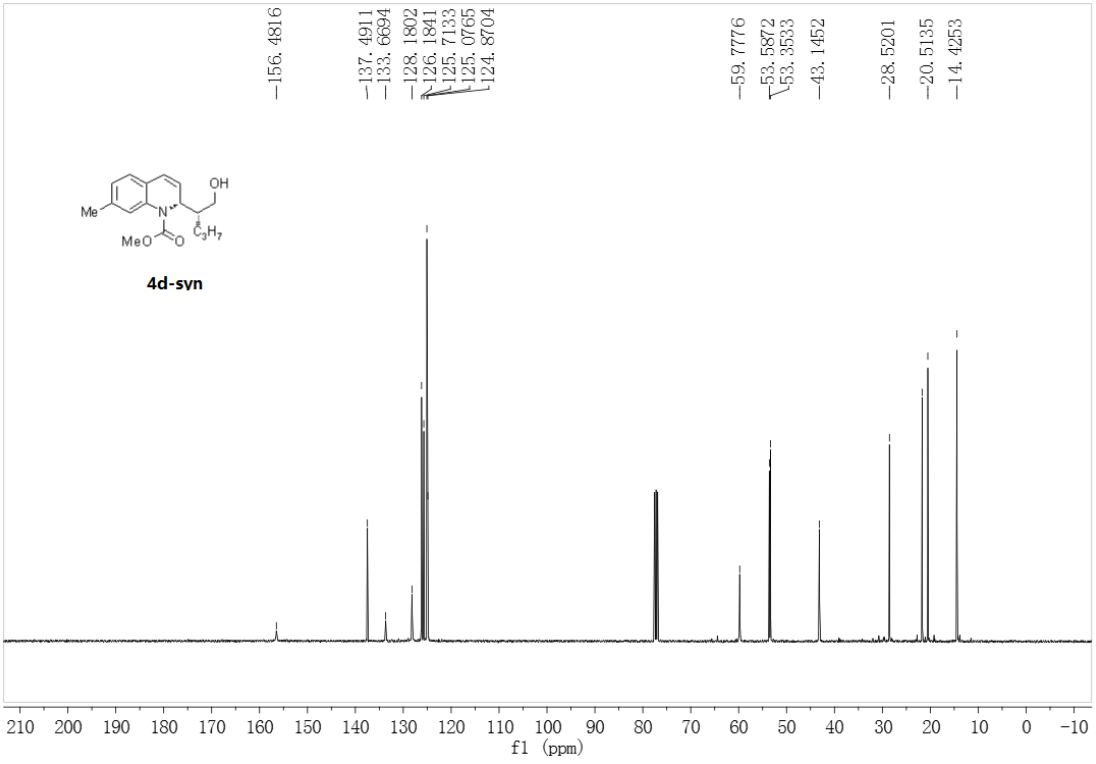
4.8564
4.8413
4.8296
4.8145
3.8246
3.6148
3.4917
3.4880
3.4613
3.4574
3.0788
2.3499
1.5297
1.4425
1.3173
1.2258
1.1697
0.8789
0.8608
0.8427
Me
OH
MeO
O
C_3H_7
4d-syn
0.93
1.05
1.02
1.00
1.00
1.00
3.06
1.03
1.04
0.85
3.08
0.76
2.02
1.34
1.25
3.33
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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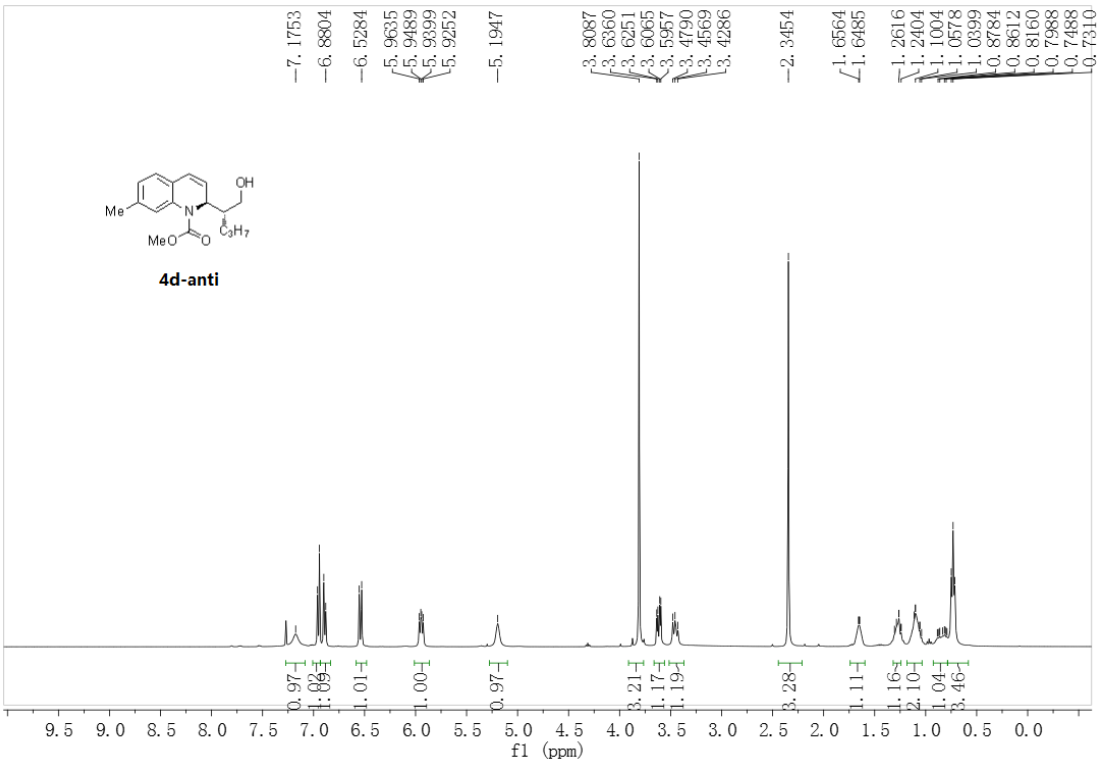
53.3533
43.1452
28.5201
20.5135
14.4253
Me
OH
MeO
O
C_3H_7
4d-syn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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3.4569
3.4286
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1.6564
1.6485
1.2616
1.2404
1.1004
1.0578
1.0399
0.8784
0.8612
0.8160
0.7988
0.7488
0.7310
0.97
1.02
1.01
1.00
0.97
3.21
1.17
1.19
3.28
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1.04
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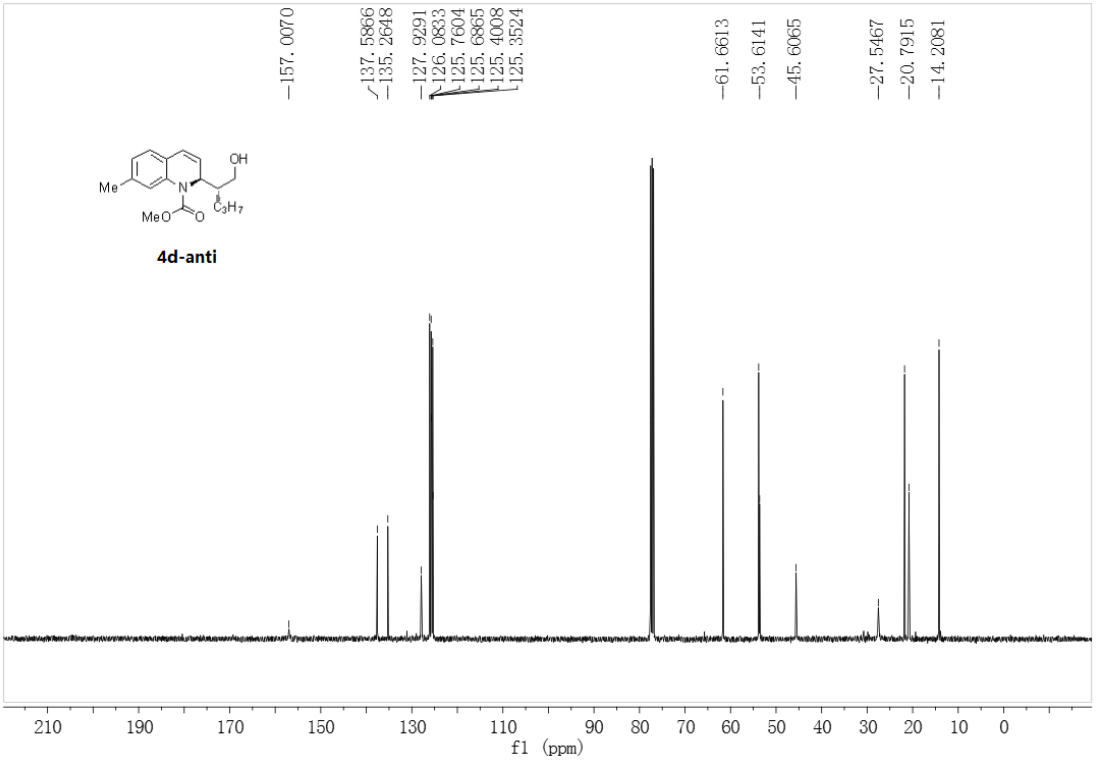
MeO
O
C3H7
4d-anti
f1 (ppm)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Me
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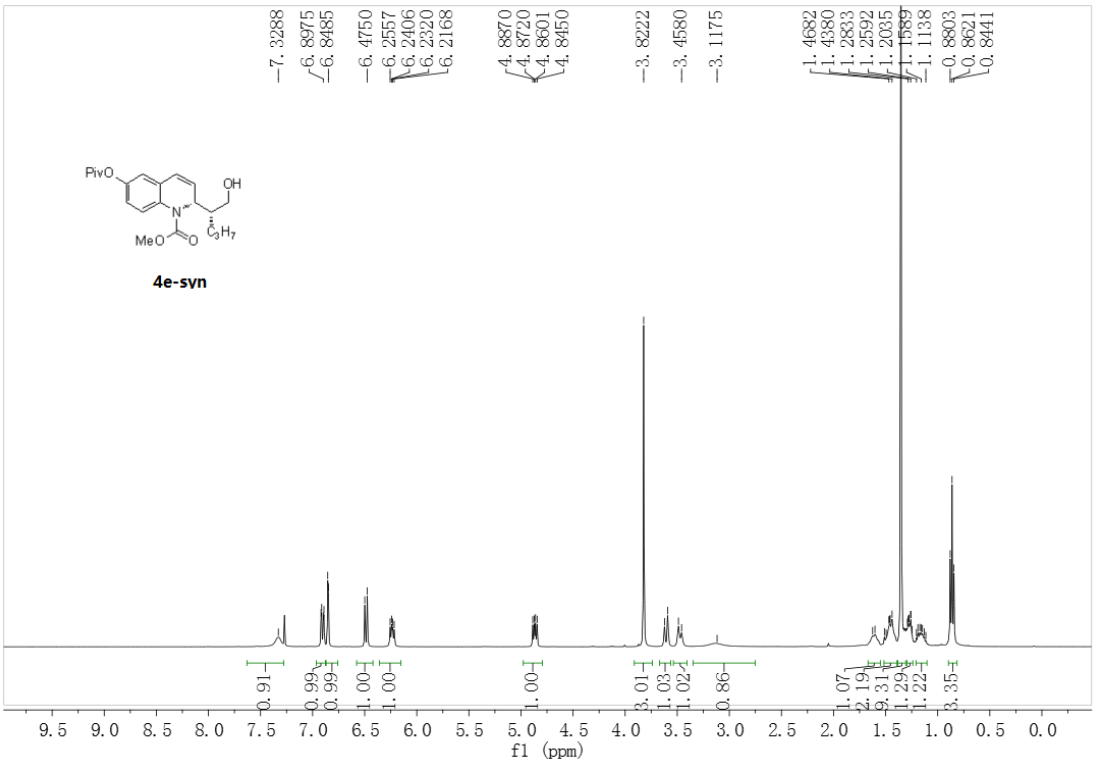
N
MeO
O
C3H7
4d-anti
f1 (ppm)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4.8450
3.8222
3.4580
3.1175
1.4682
1.4380
1.2833
1.2592
1.2035
1.1589
1.1138
0.8803
0.8621
0.8441
PivO
OH
MeO
4e-syn
0.91
0.99
0.99
1.00
1.00
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1.02
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1.07
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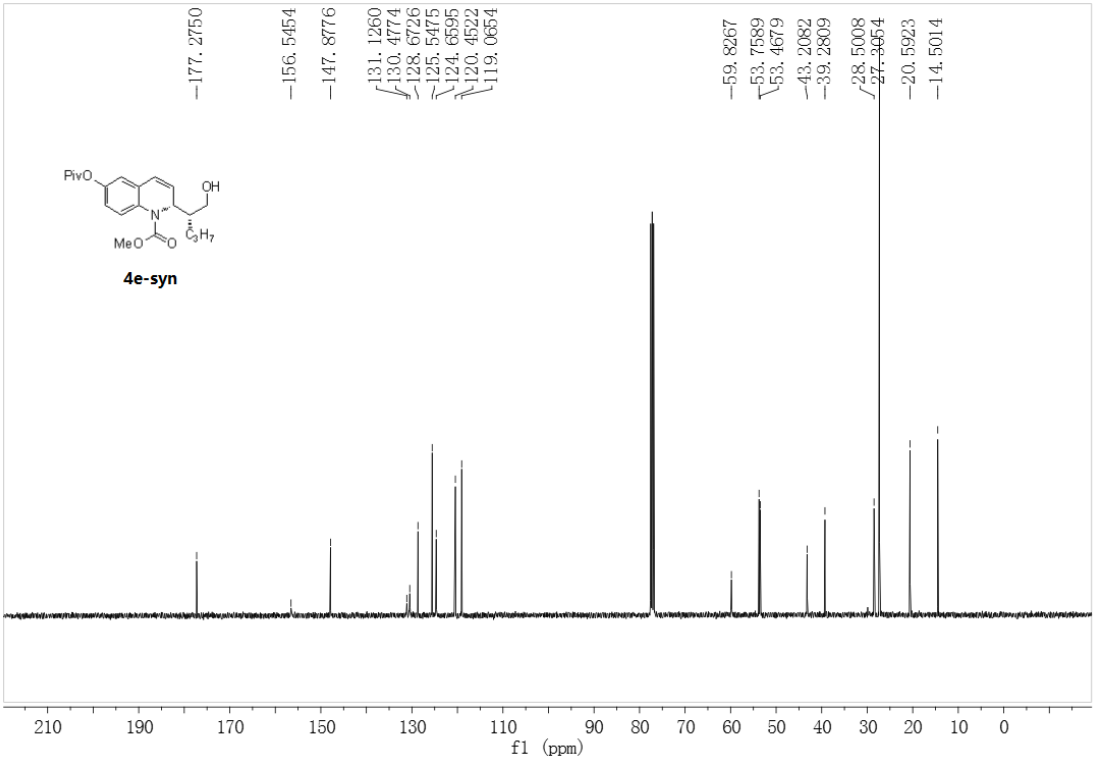
3.35
f1 (ppm)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53.4679
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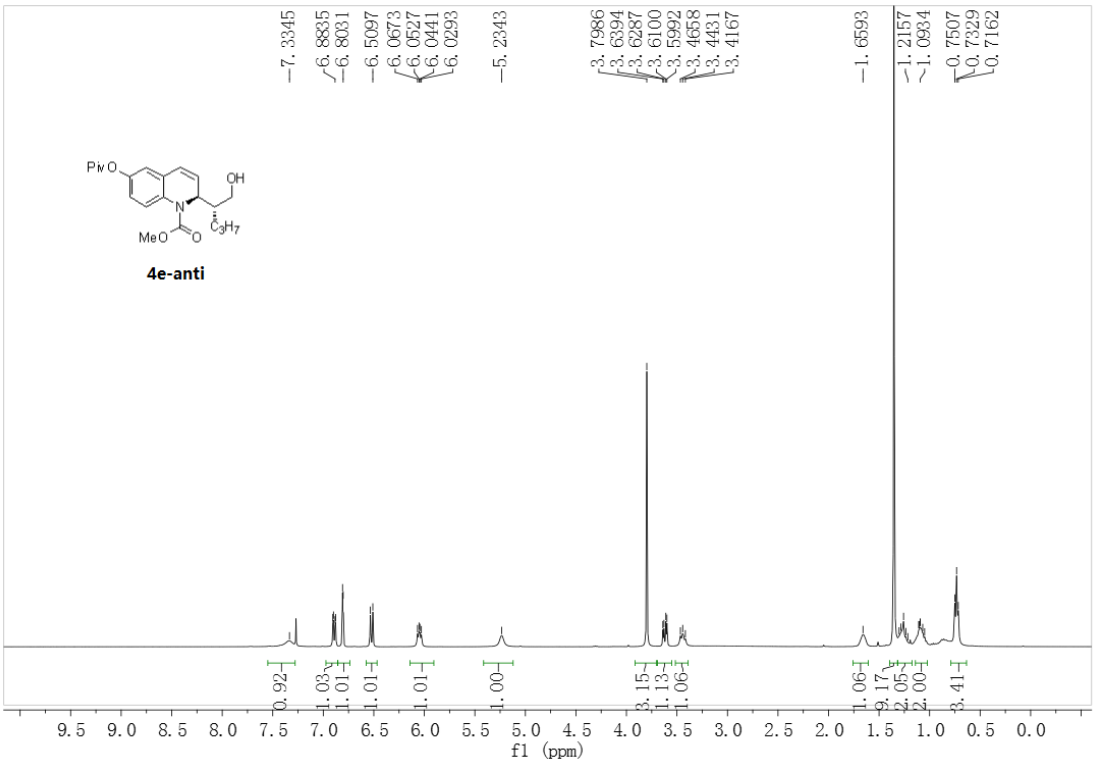
PivO
OH
MeO
4e-syn
f1 (ppm)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3.6100
3.5992
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3.4431
3.4167
1.6593
1.2157
1.0934
0.7507
0.7329
0.7162
PivO
OH
MeO
O
N
C3H7
4e-anti
0.92
1.03
1.01
1.01
1.01
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1.06
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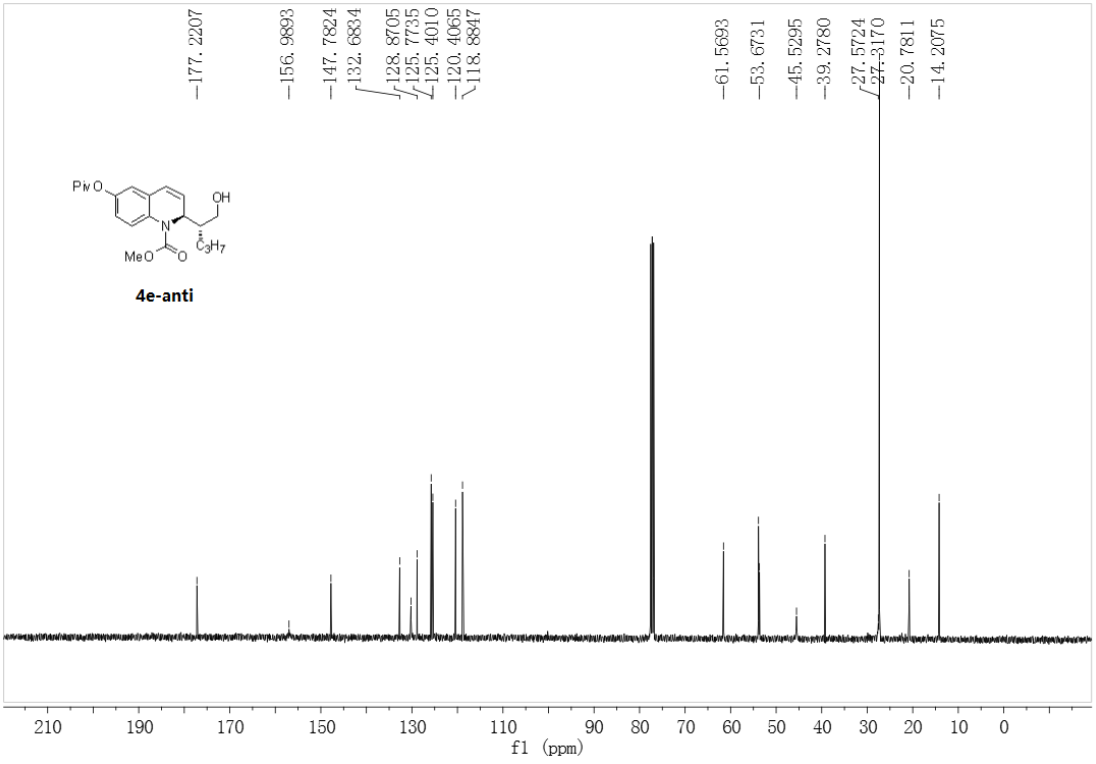
3.41
f1 (ppm)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45.5295
39.2780
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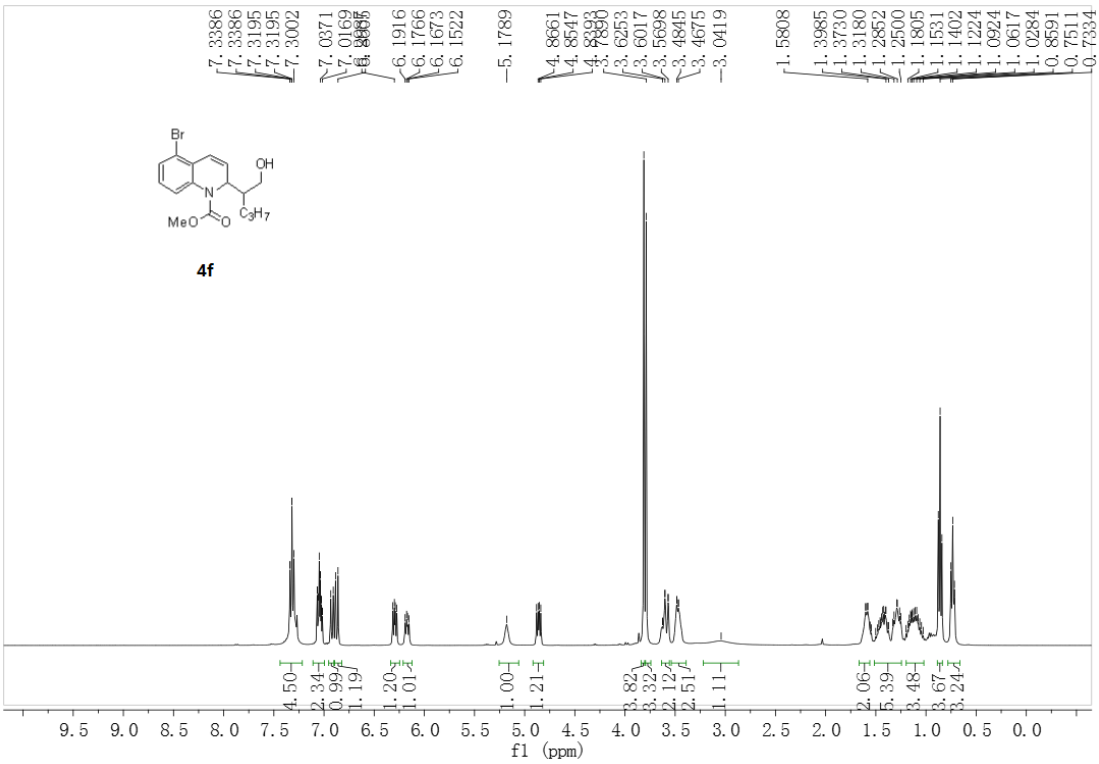
14.2075
PivO
OH
MeO
O
N
C3H7
4e-anti
f1 (ppm)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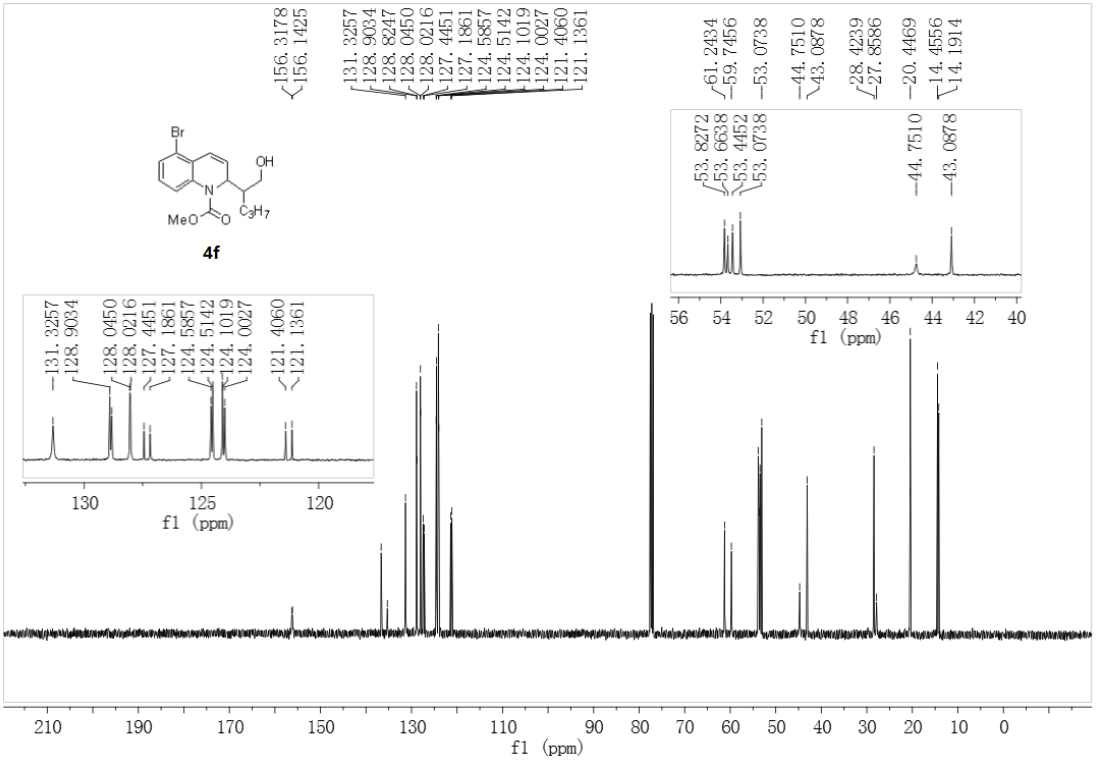
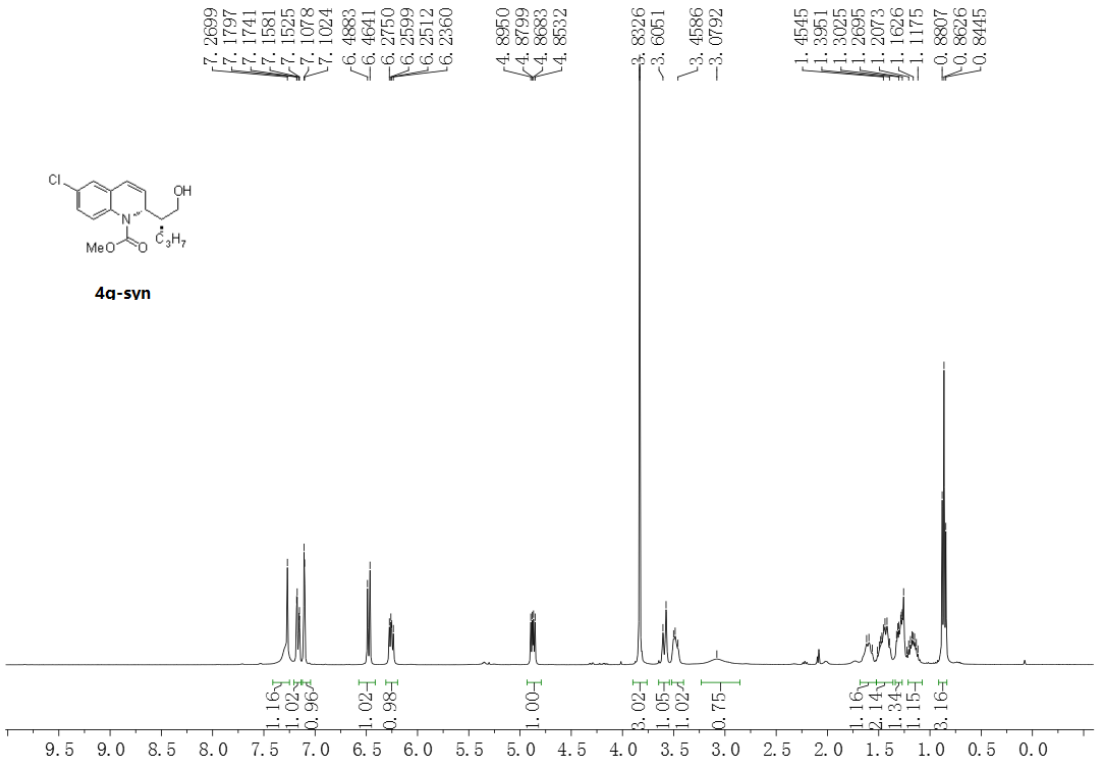

4f
f1 (ppm)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4.8950
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3.4586
3.0792
1.4545
1.3951
1.3025
1.2695
1.2073
1.1626
1.1175
0.8807
0.8626
0.8445
Cl
OH
N
MeO
O
C_3H_7
4a-syn
1.16
1.02
0.96
1.02
0.98
1.00
3.02
1.05
1.02
0.75
1.16
2.14
1.34
1.15
3.16
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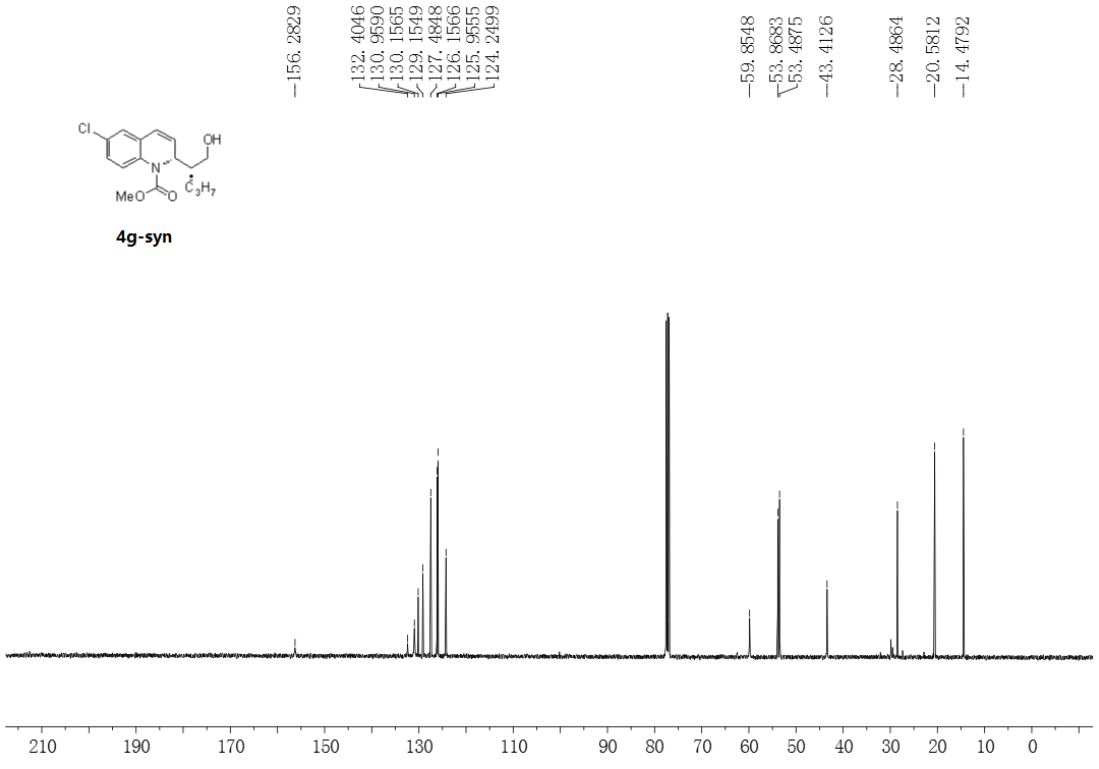
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53.4875
43.4126
28.4864
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Cl
OH
N
MeO
O
C_3H_7
4g-syn
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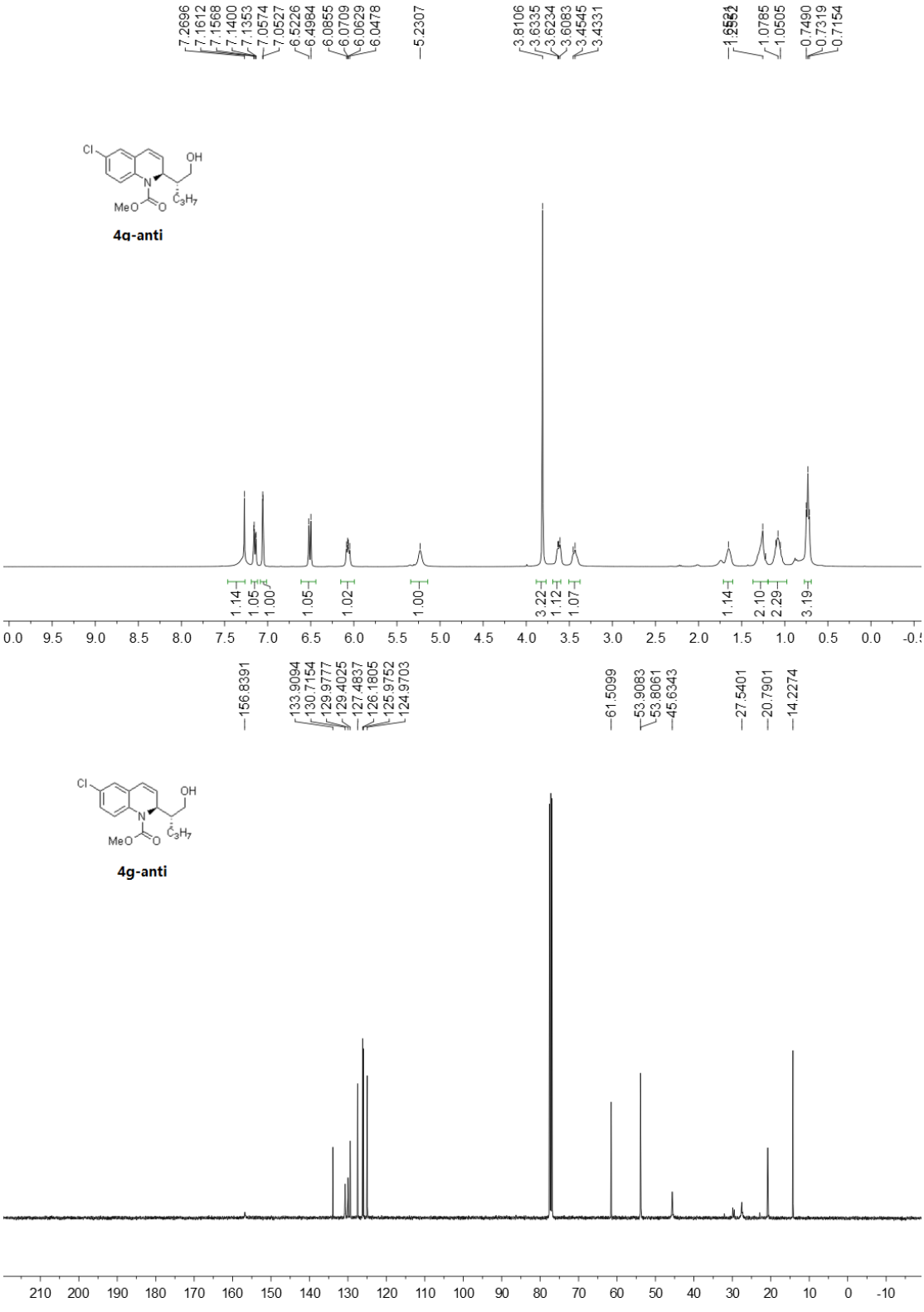
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6.0478
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3.4545
3.4331
1.0785
1.0505
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0.7154
Cl
OH
N
MeO
O
C_3H_7
4g-anti
1.14
1.05
1.00
1.05
1.02
1.00
3.22
1.12
1.07
1.14
2.10
2.29
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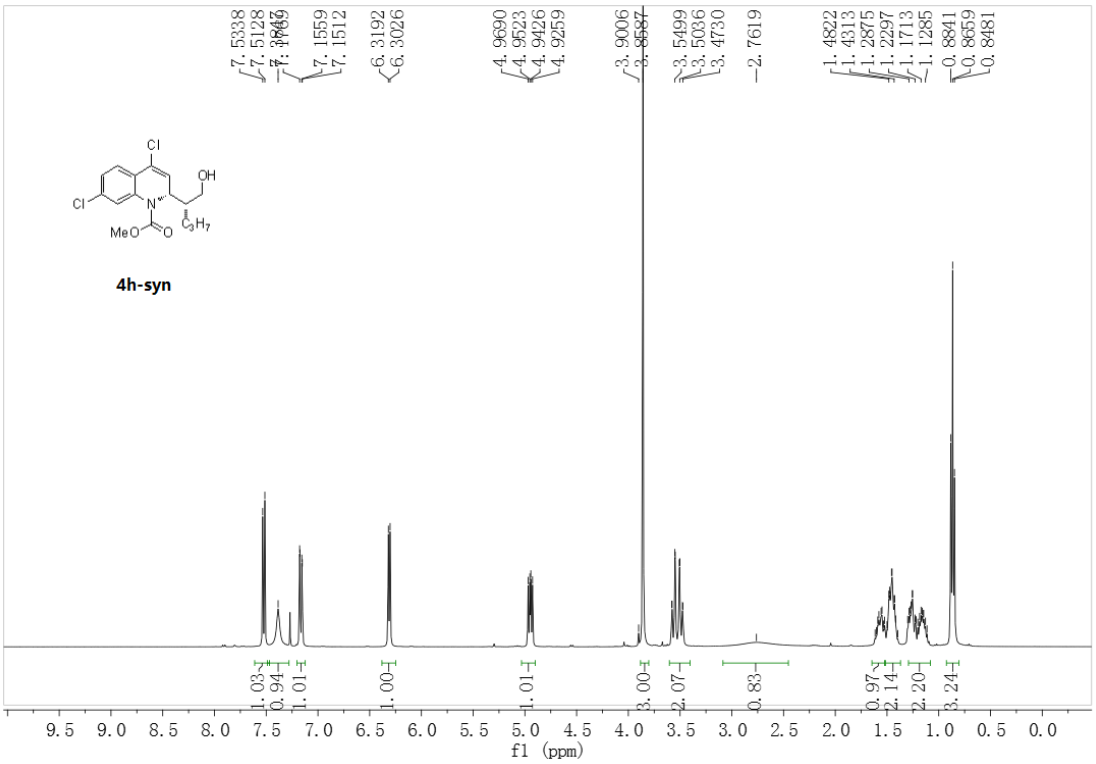
4g-anti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3.4730
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1.4822
1.4313
1.2875
1.2297
1.1713
1.1285
0.8841
0.8659
0.8481
1.03
0.94
1.01
1.00
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3.00
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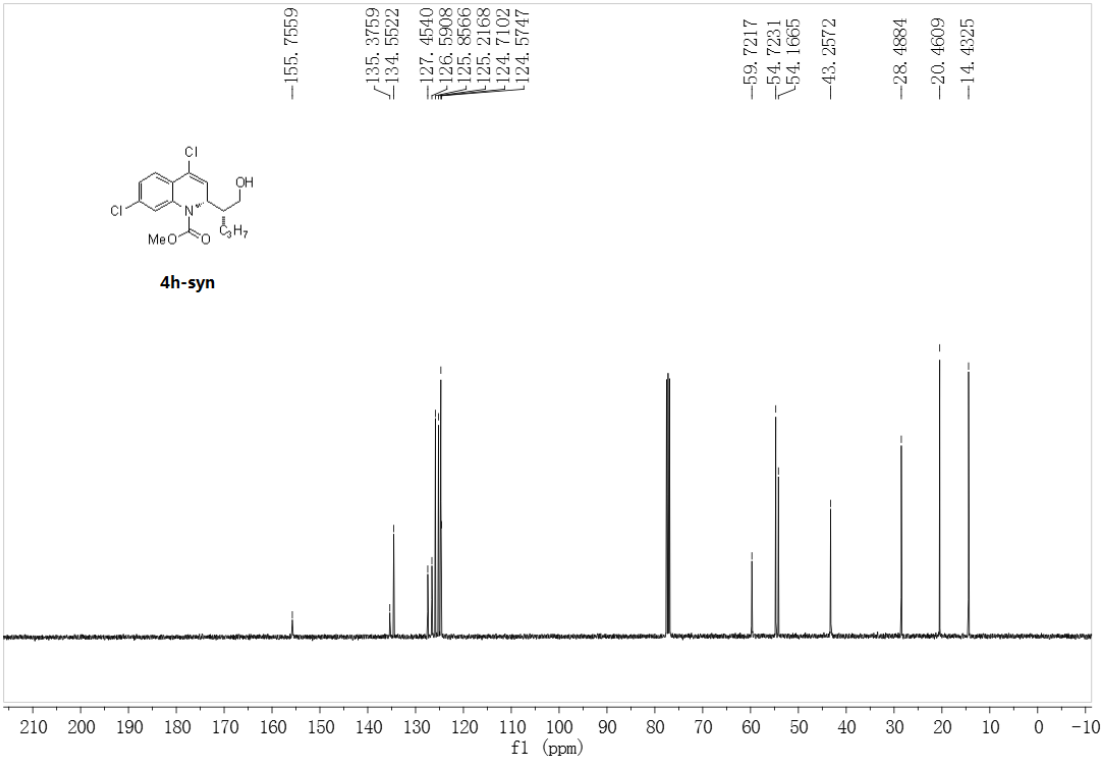
2.14
2.20
3.24
f1 (ppm)
4h-syn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125.2168
124.7102
124.5747
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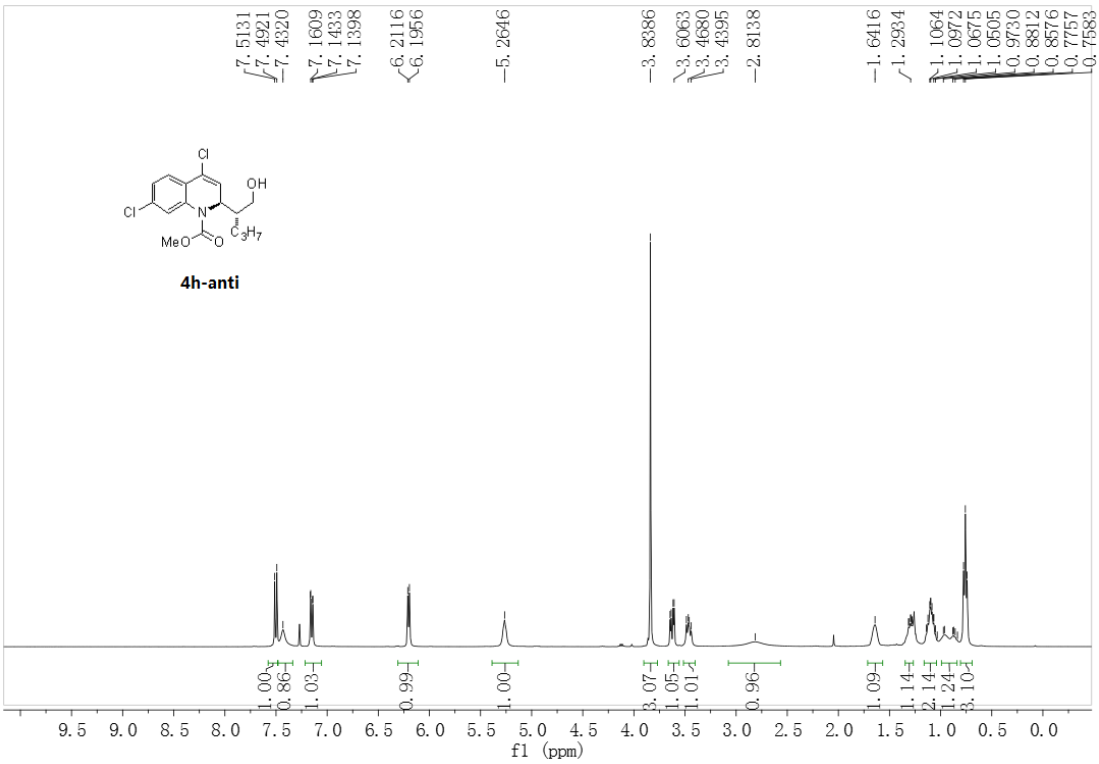
54.7231
54.1665
43.2572
28.4884
20.4609
14.4325
f1 (ppm)
4h-syn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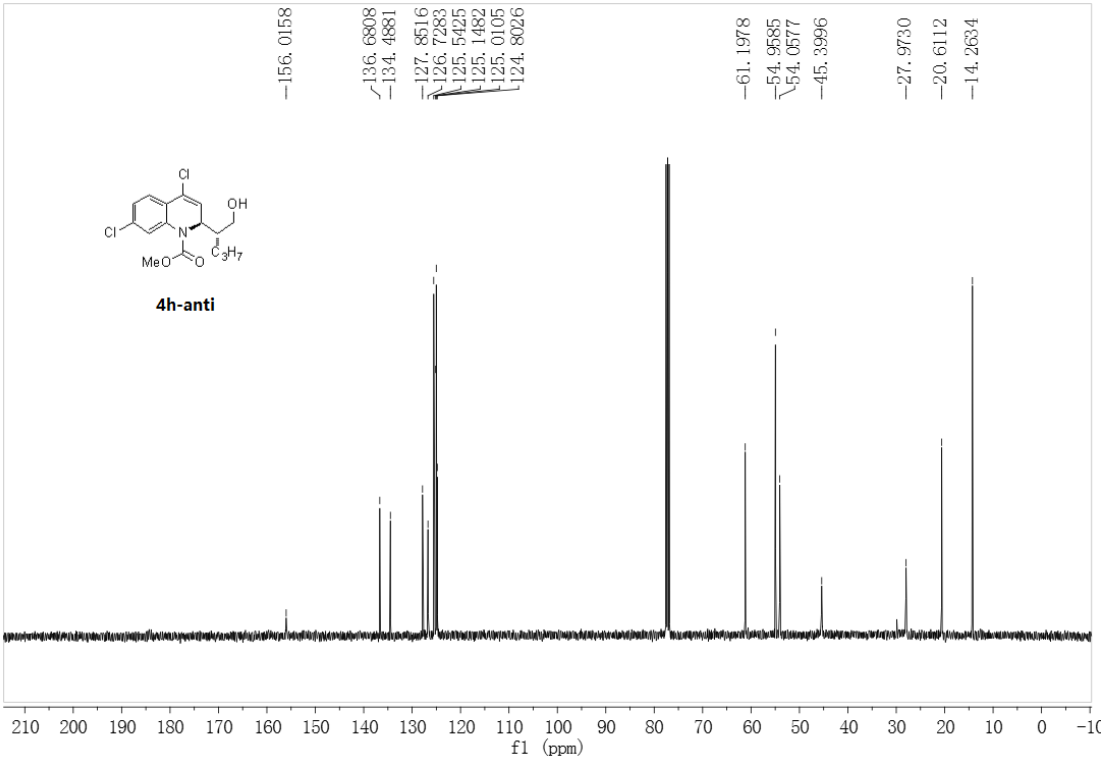
7.4320
7.1609
7.1433
7.1398
6.2116
6.1956
5.2646
3.8386
3.6063
3.4680
3.4395
2.8138
1.6416
1.2934
1.1064
1.0972
1.0675
1.0505
0.9730
0.8812
0.8576
0.7757
0.7583
Cl
OH
Cl
N
MeO
O
C3H7
4h-anti
1.00
0.86
1.03
0.99
1.00
3.07
1.05
1.01
0.96
1.09
1.14
2.14
1.24
3.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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125.1482
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124.8026
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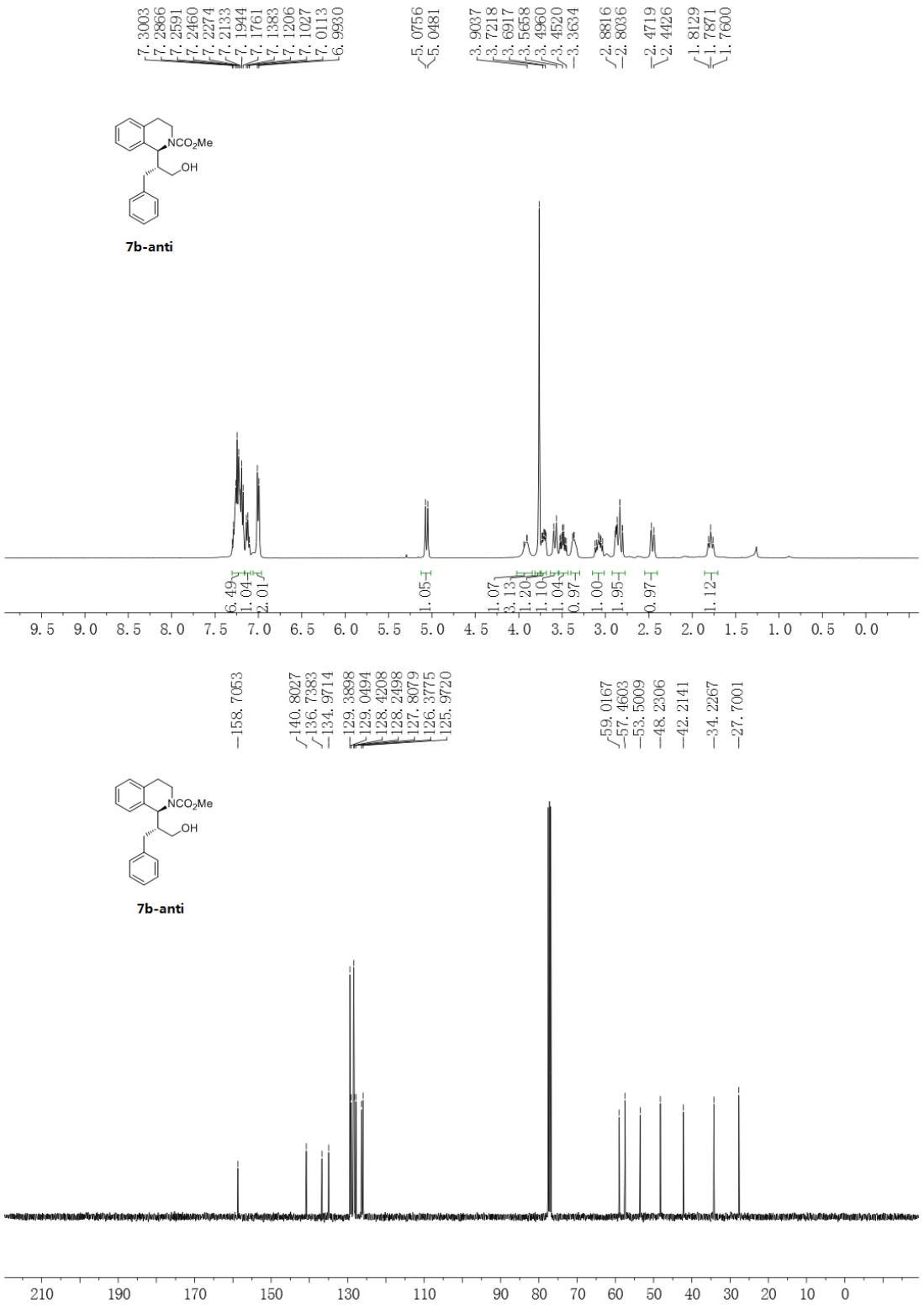
54.9585
54.0577
45.3996
27.9730
20.6112
14.2634
Cl
OH
Cl
N
MeO
O
C3H7
4h-anti
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.2274
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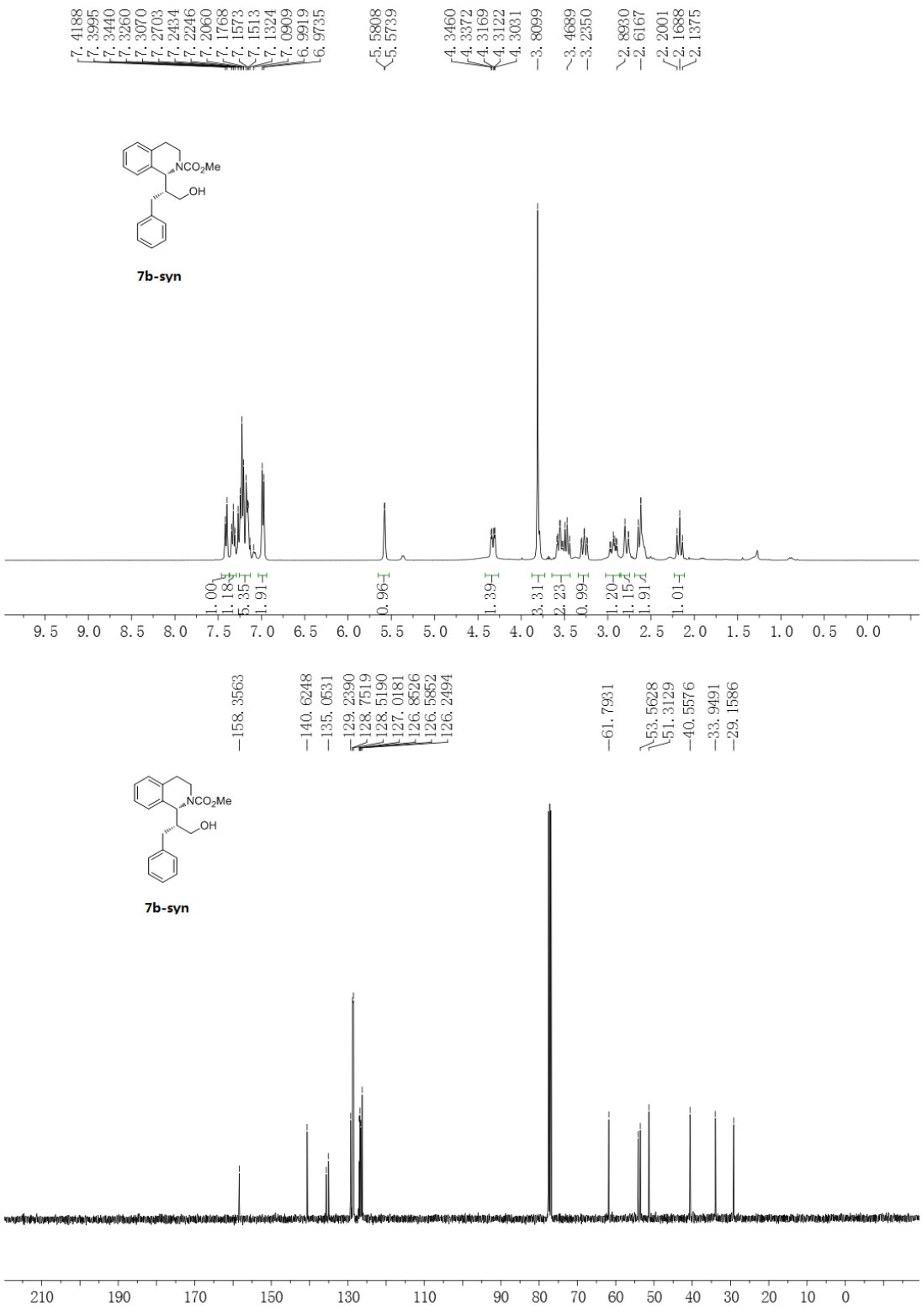
7.1206
7.1027
7.0113
6.9930
5.0756
5.0481
3.9037
3.7218
3.6917
3.5658
3.4960
3.4520
3.3634
2.8816
2.8036
2.4719
2.4426
1.8129
1.7871
1.7600
NCO2Me
OH
7b-anti
6.49
1.04
2.01
1.05
1.07
3.13
1.20
1.10
1.04
0.97
1.00
1.95
0.97
1.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
158.7053
140.8027
136.7383
134.9714
129.3898
129.0494
128.4208
128.2498
127.8079
126.3775
125.9720
59.0167
57.4603
53.5009
48.2306
42.2141
34.2267
27.7001
NCO2Me
OH
7b-anti
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0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7.3070
7.2703
7.2434
7.2246
7.2060
7.1768
7.1573
7.1513
7.1324
7.0909
6.9919
6.9735
5.5808
5.5739
4.3460
4.3372
4.3169
4.3122
4.3031
3.8099
3.4689
3.2350
2.8930
2.6167
2.2001
2.1688
2.1375
NCO2Me
OH
7b-syn
1.00
1.18
5.35
1.91
0.96
1.39
3.31
2.23
0.99
1.20
1.15
1.91
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
158.3563
140.6248
135.0531
129.2390
128.7519
128.5190
127.0181
126.8526
126.5852
126.2494
61.7931
53.5628
51.3129
40.5576
33.9491
29.1586
NCO2Me
OH
7b-syn
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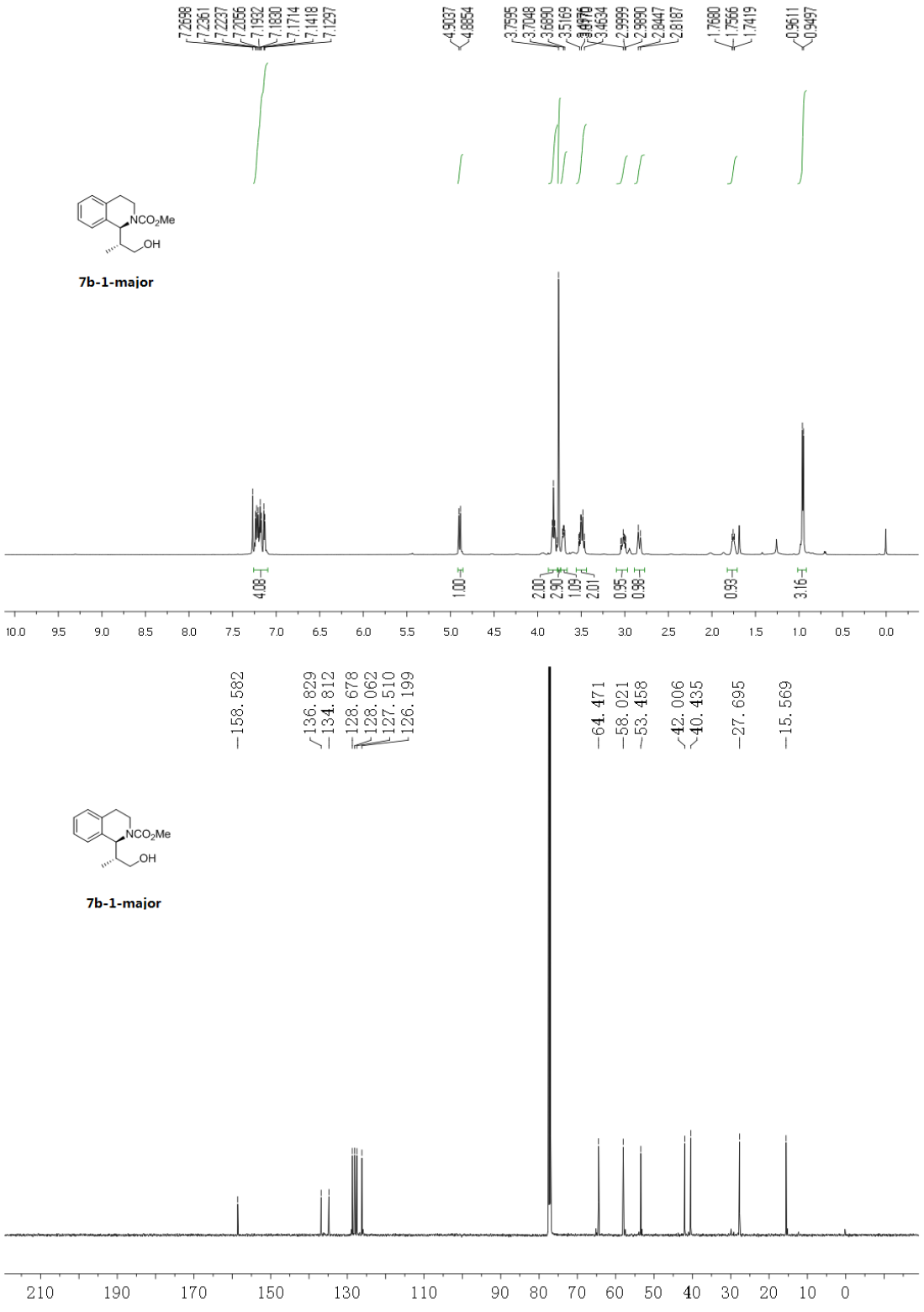
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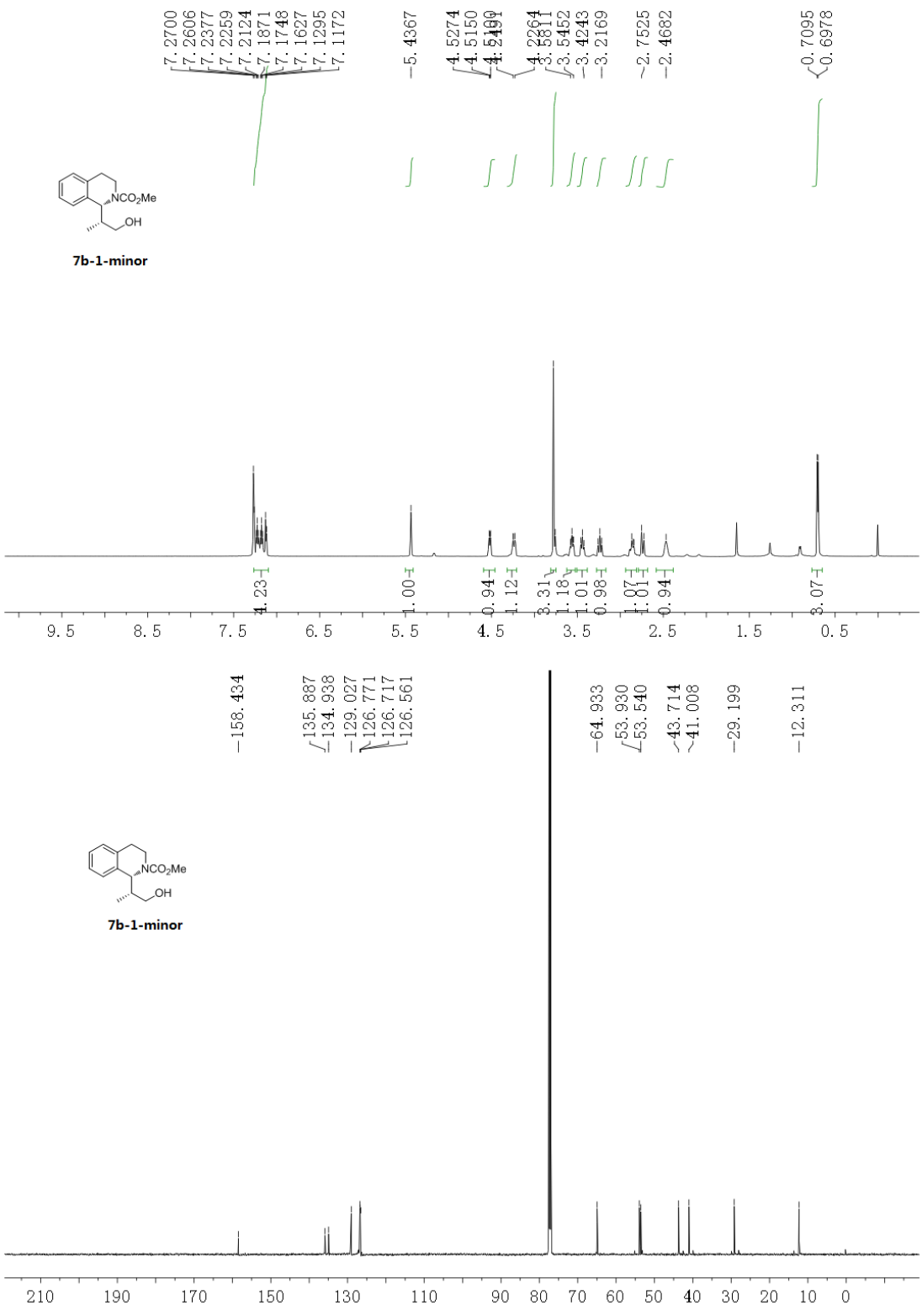
7.2361
7.2237
7.2056
7.1932
7.1830
7.1714
7.1418
7.1297
4.9037
4.8854
3.7595
3.7048
3.6890
3.5169
3.4634
2.9999
2.9890
2.8447
2.8187
1.7680
1.7566
1.7419
0.9611
0.9497
NCO2Me
OH
7b-1-major
4.08
1.00
2.00
2.90
1.09
2.01
0.95
0.98
0.93
3.16
158.582
136.829
134.812
128.678
128.062
127.510
126.199
64.471
58.021
53.458
42.006
40.435
27.695
15.569
NCO2Me
OH
7b-1-major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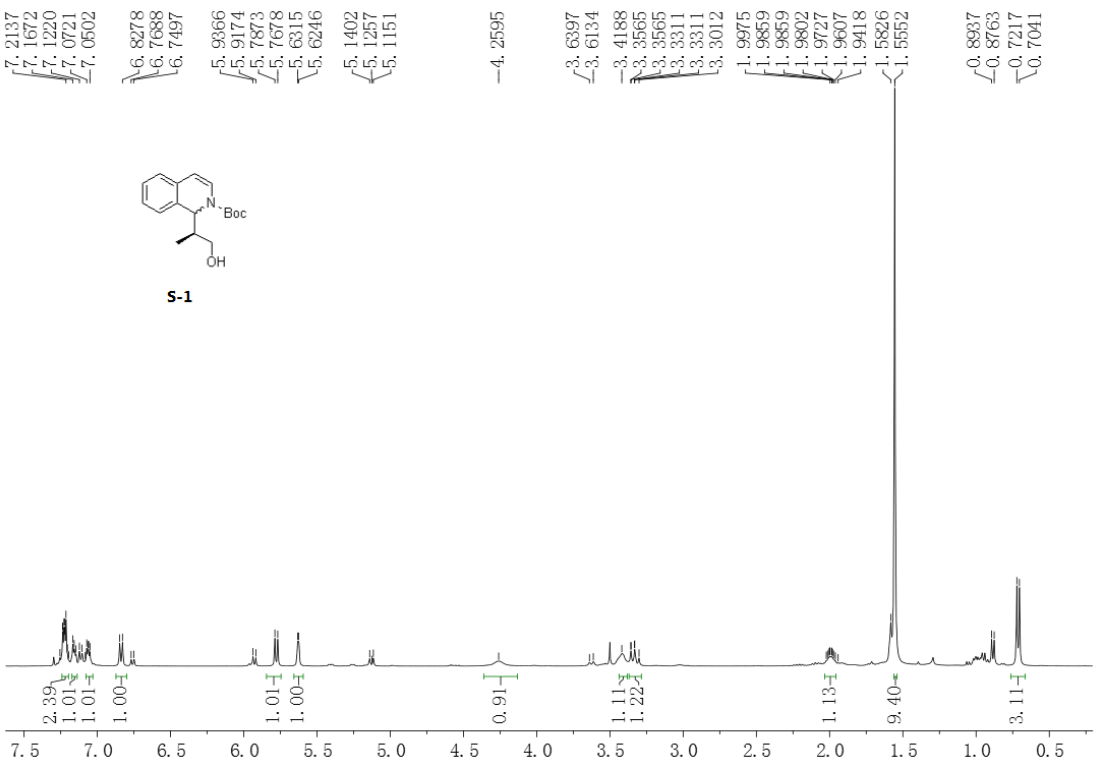
7.2124
7.1871
7.1748
7.1627
7.1295
7.1172
5.4367
4.5274
4.5150
4.2264
3.5811
3.5452
3.4243
3.2169
2.7525
2.4682
0.7095
0.6978
NCO2Me
OH
7b-1-minor
4.23
1.00
0.94
1.12
3.31
1.18
1.01
0.98
1.07
1.01
0.94
3.07
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
158.434
135.887
134.938
129.027
126.771
126.717
126.561
64.933
53.930
53.540
43.714
41.008
29.199
12.311
NCO2Me
OH
7b-1-minor
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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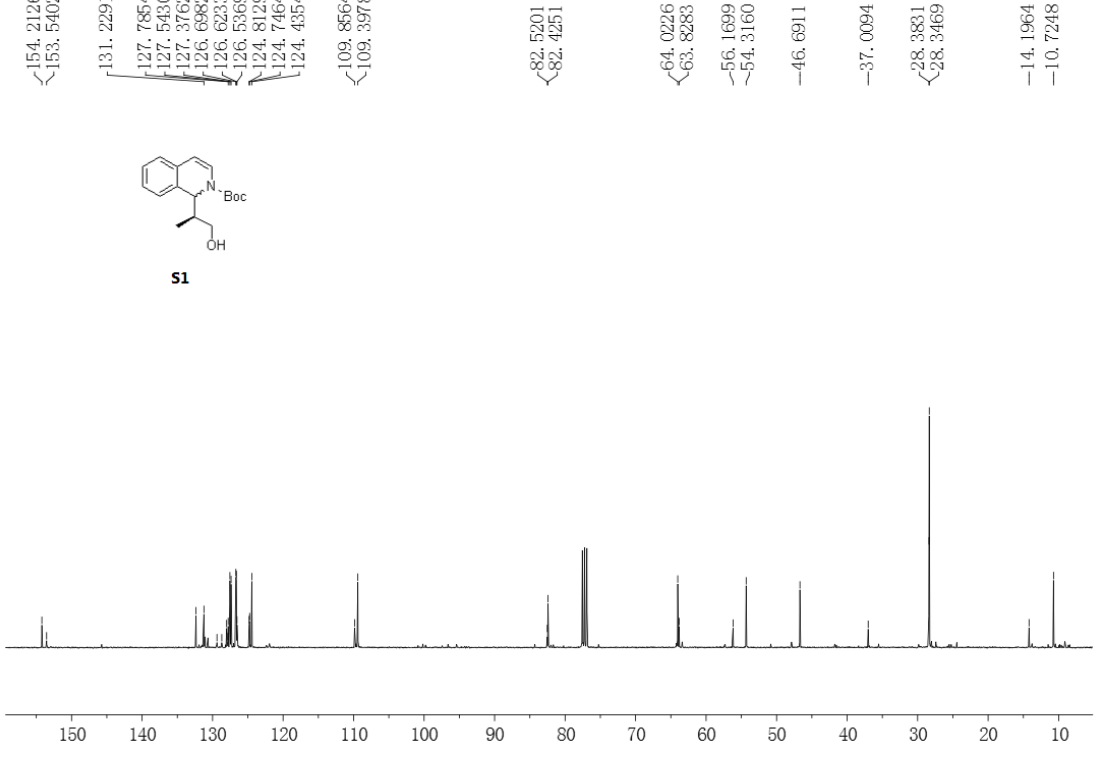
7.0721
7.0502
6.8278
6.7688
6.7497
5.9366
5.9174
5.7873
5.7678
5.6315
5.6246
5.1402
5.1257
5.1151
4.2595
3.6397
3.6134
3.4188
3.3565
3.3565
3.3311
3.3311
3.3012
1.9975
1.9859
1.9859
1.9802
1.9727
1.9607
1.9418
1.5826
1.5552
0.8937
0.8763
0.7217
0.7041
Boc
OH
2.39
1.01
1.01
1.00
1.01
1.00
0.91
1.11
1.22
1.13
9.40
3.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

S-1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127.5430
127.3762
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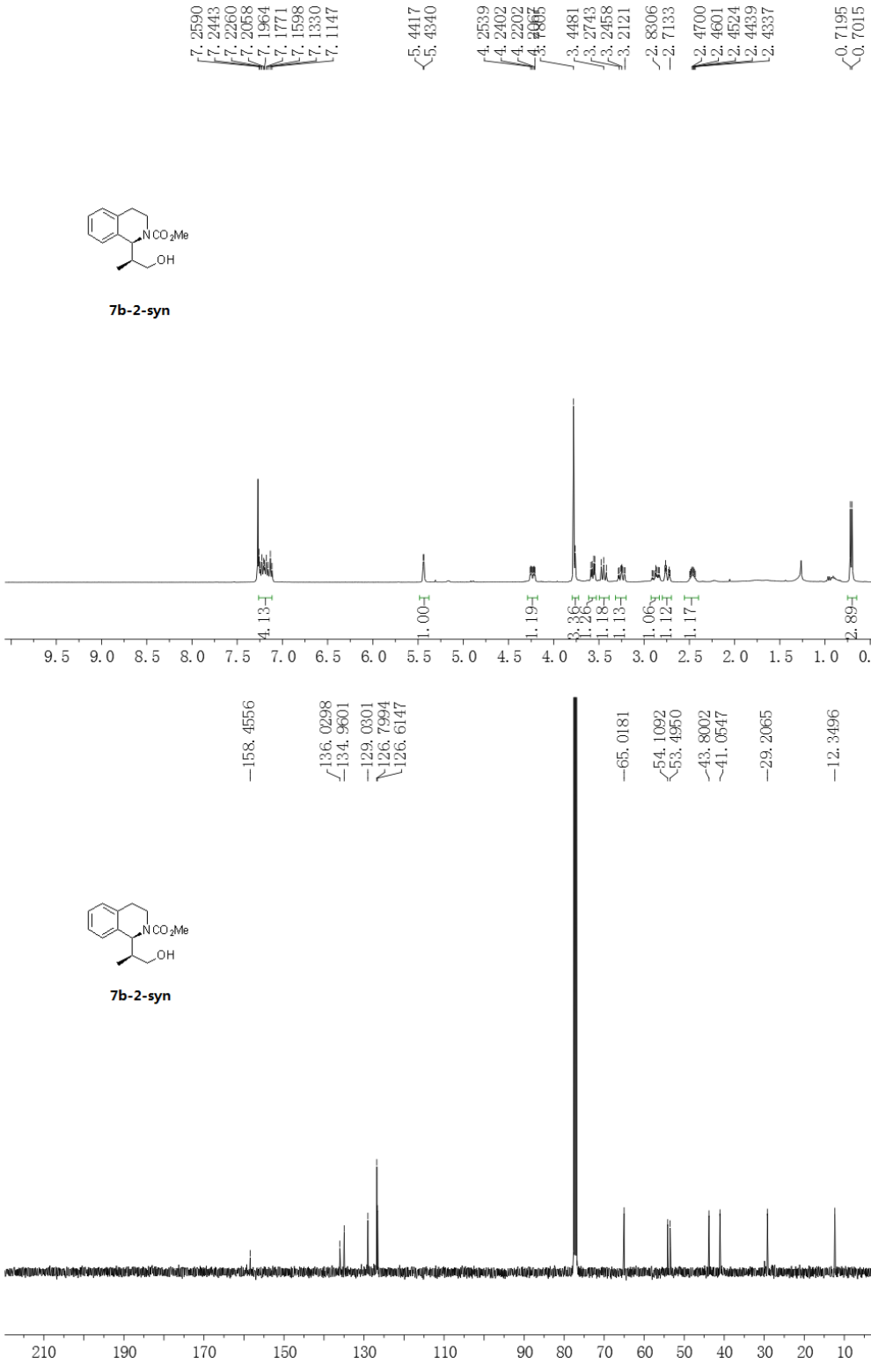
126.6233
126.5369
124.8129
124.7464
124.4354
109.8564
109.3978
82.5201
82.4251
64.0226
63.8283
56.1699
54.3160
46.6911
37.0094
28.3831
28.3469
14.1964
10.7248
Boc
OH
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

S1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7.1964
7.1771
7.1598
7.1330
7.1147
5.4417
5.4340
4.2539
4.2402
4.2202
3.4481
3.2743
3.2458
3.2121
2.8306
2.7133
2.4700
2.4601
2.4524
2.4439
2.4337
0.7195
0.7015
N
CO2Me
OH
7b-2-syn
4.13
1.00
1.19
3.36
1.26
1.18
1.13
1.06
1.12
1.17
2.89
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
158.4556
136.0298
134.9601
129.0301
126.7994
126.6147
65.0181
54.1092
53.4950
43.8002
41.0547
29.2065
12.3496
N
CO2Me
OH
7b-2-syn
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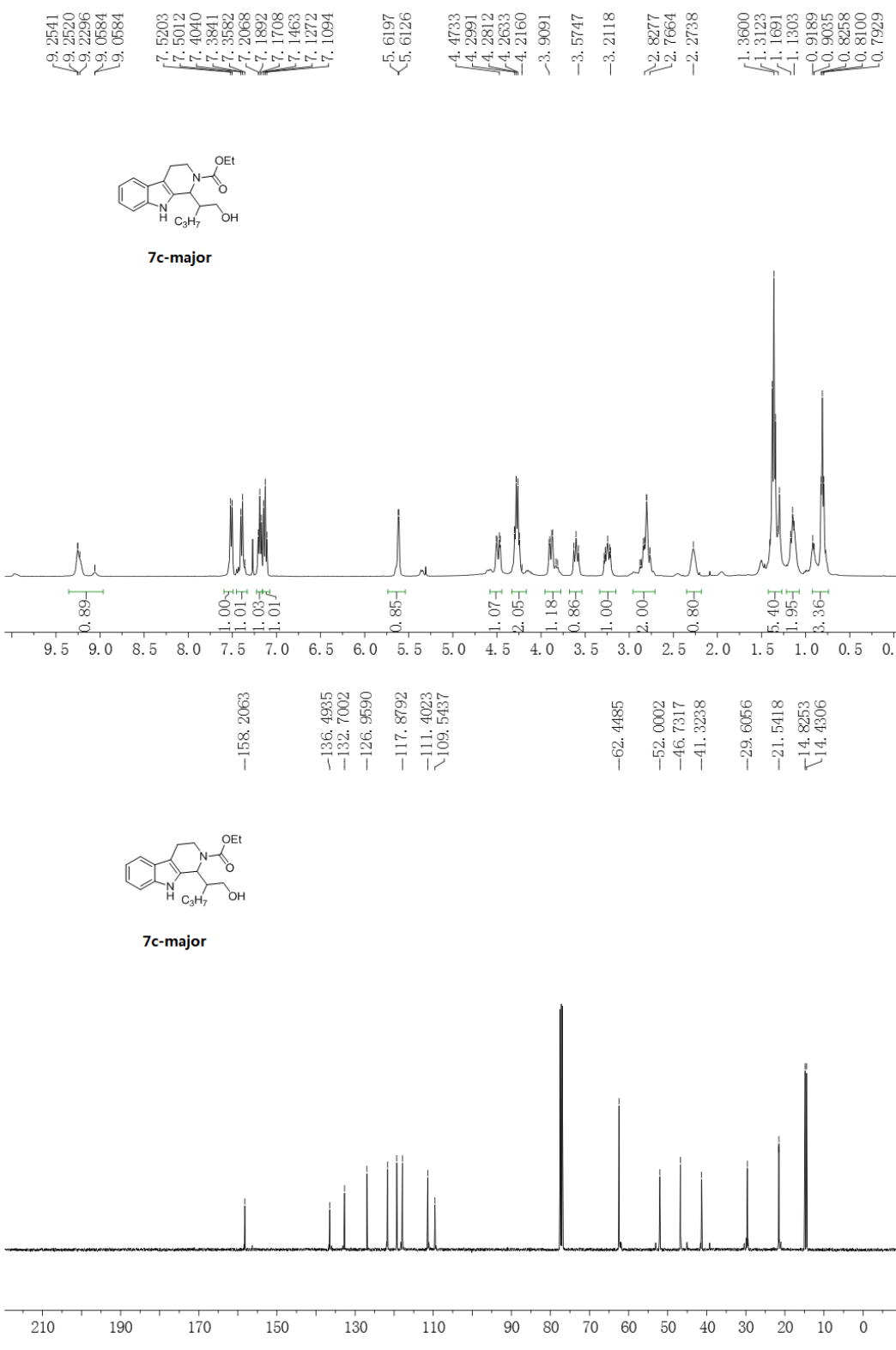
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9.2520
9.2296
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9.0584
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7.5012
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7.3841
7.3582
7.2068
7.1892
7.1708
7.1463
7.1272
7.1094
5.6197
5.6126
4.4733
4.2991
4.2812
4.2633
4.2160
3.9091
3.5747
3.2118
2.8277
2.7664
2.2738
1.3600
1.3123
1.1691
1.1303
0.9189
0.9035
0.8258
0.8100
0.7929
OEt
N
O
N
H
C3H7
OH
7c-major
0.89
1.00
1.01
1.03
1.01
0.85
1.07
2.05
1.18
0.86
1.00
2.00
0.80
5.40
1.95
3.36
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
158.2063
136.4935
132.7002
126.9590
117.8792
111.4023
109.5437
62.4485
52.0002
46.7317
41.3238
29.6056
21.5418
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OEt
N
O
N
H
C3H7
OH
7c-major
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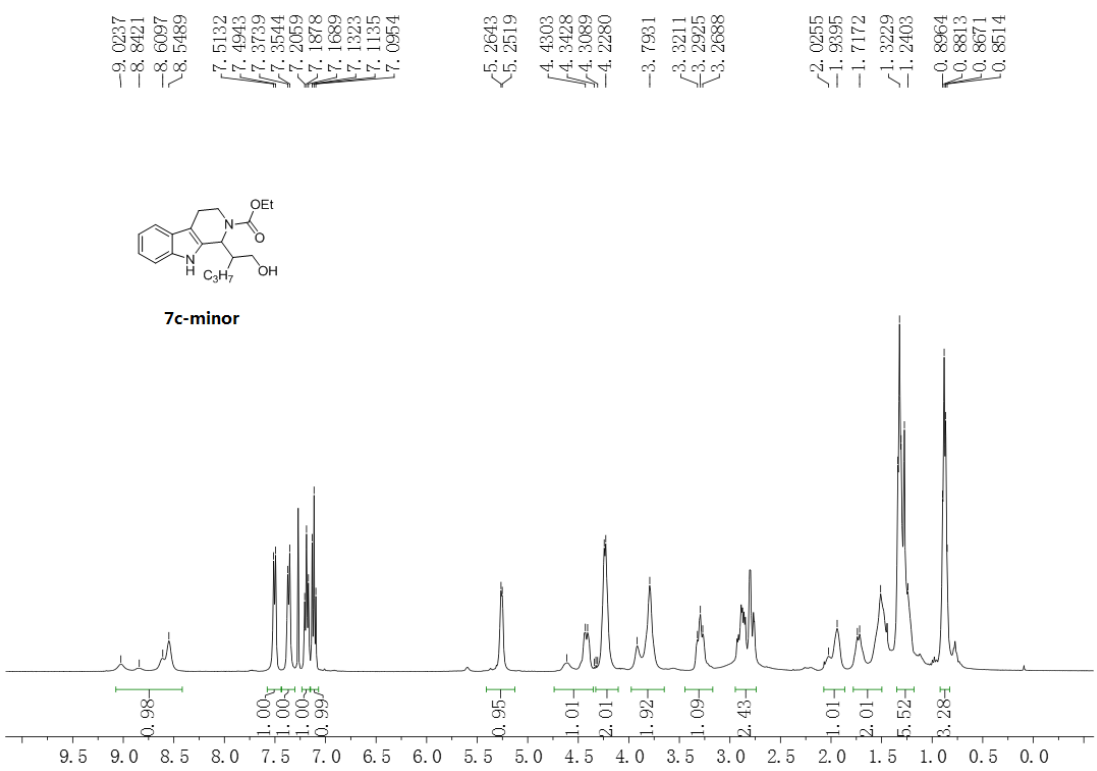
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7.3739
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7.2059
7.1878
7.1689
7.1323
7.1135
7.0954
5.2643
5.2519
4.4303
4.3428
4.3089
4.2280
3.7931
3.3211
3.2925
3.2688
2.0255
1.9395
1.7172
1.3229
1.2403
0.8964
0.8813
0.8671
0.8514
OEt
N
O
H
C3H7
OH
7c-minor
0.98
1.00
1.00
1.00
0.99
0.95
1.01
2.01
1.92
1.09
2.43
1.01
2.01
5.52
3.28
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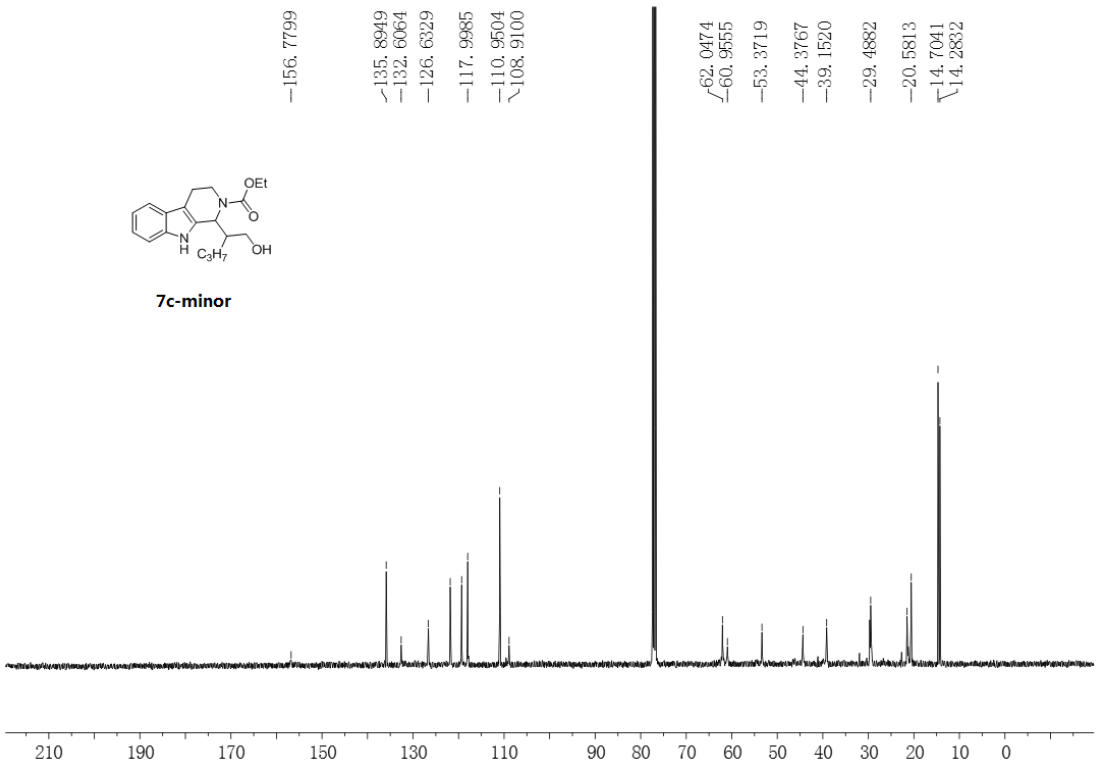
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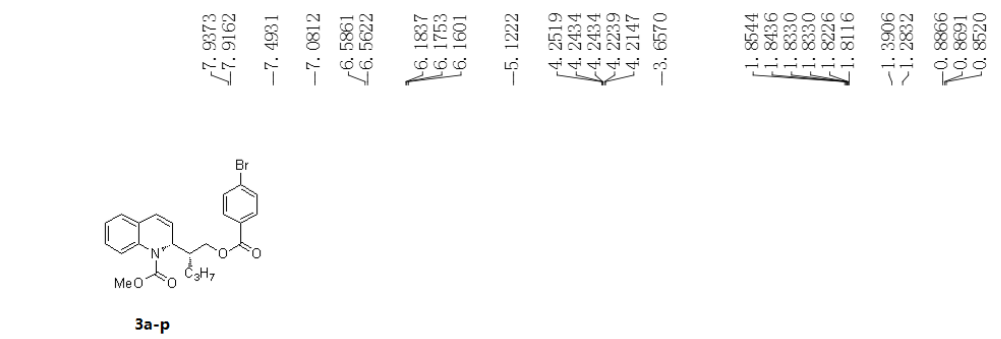
108.9100
62.0474
60.9555
53.3719
44.3767
39.1520
29.4882
20.5813
14.7041
14.2832
OEt
N
O
H
C3H7
OH
7c-minor
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0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6.5622
6.1837
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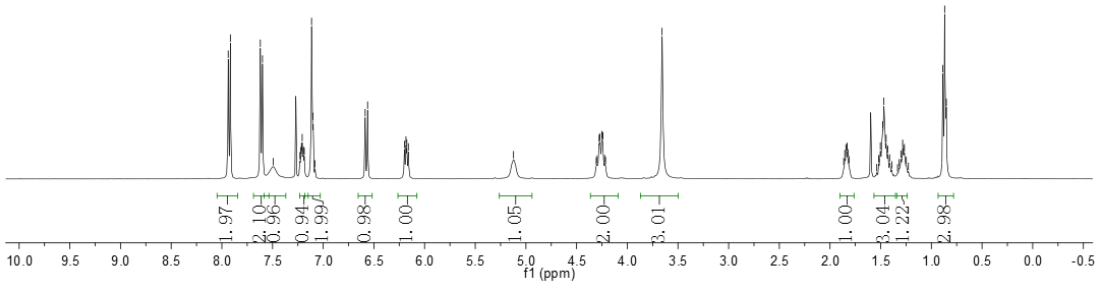
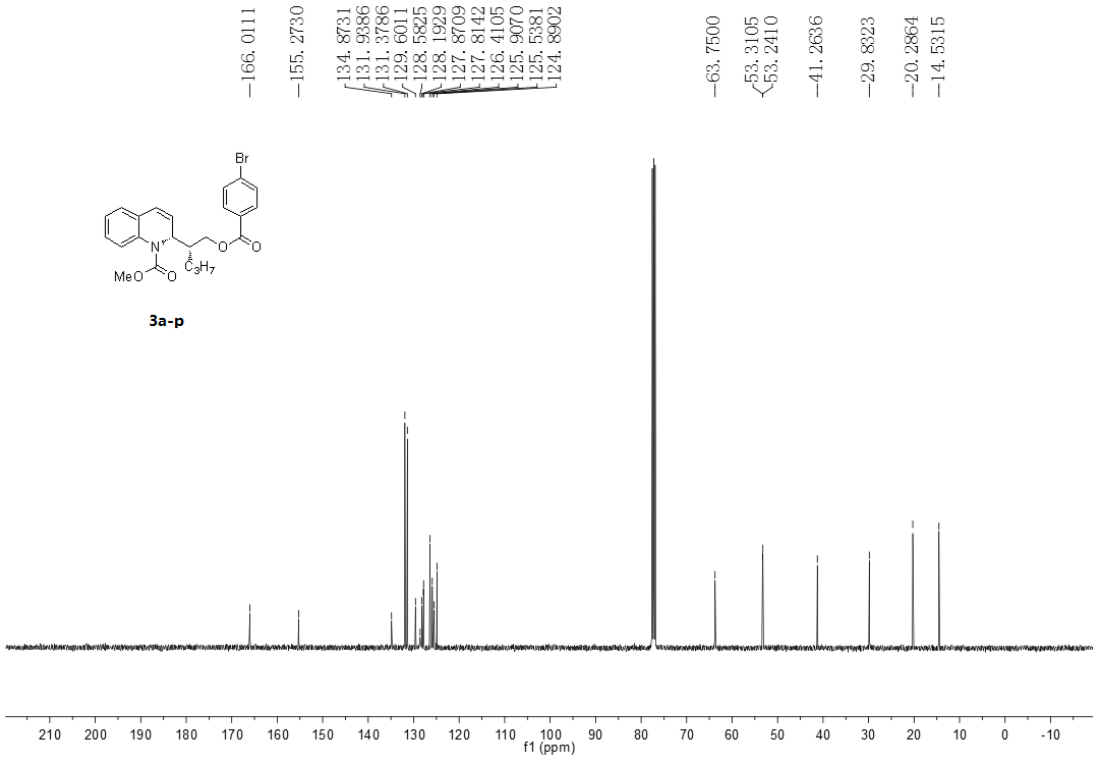
6.1601
5.1222
4.2519
4.2434
4.2434
4.2239
4.2147
3.6570
1.8544
1.8436
1.8330
1.8330
1.8226
1.8116
1.3906
1.2832
0.8866
0.8691
0.8520
Br
N
O
O
MeO
O
C3H7

3a-p


1.97
2.10
0.96
0.94
1.99
0.98
1.00
1.05
2.00
3.01
1.00
3.04
1.22
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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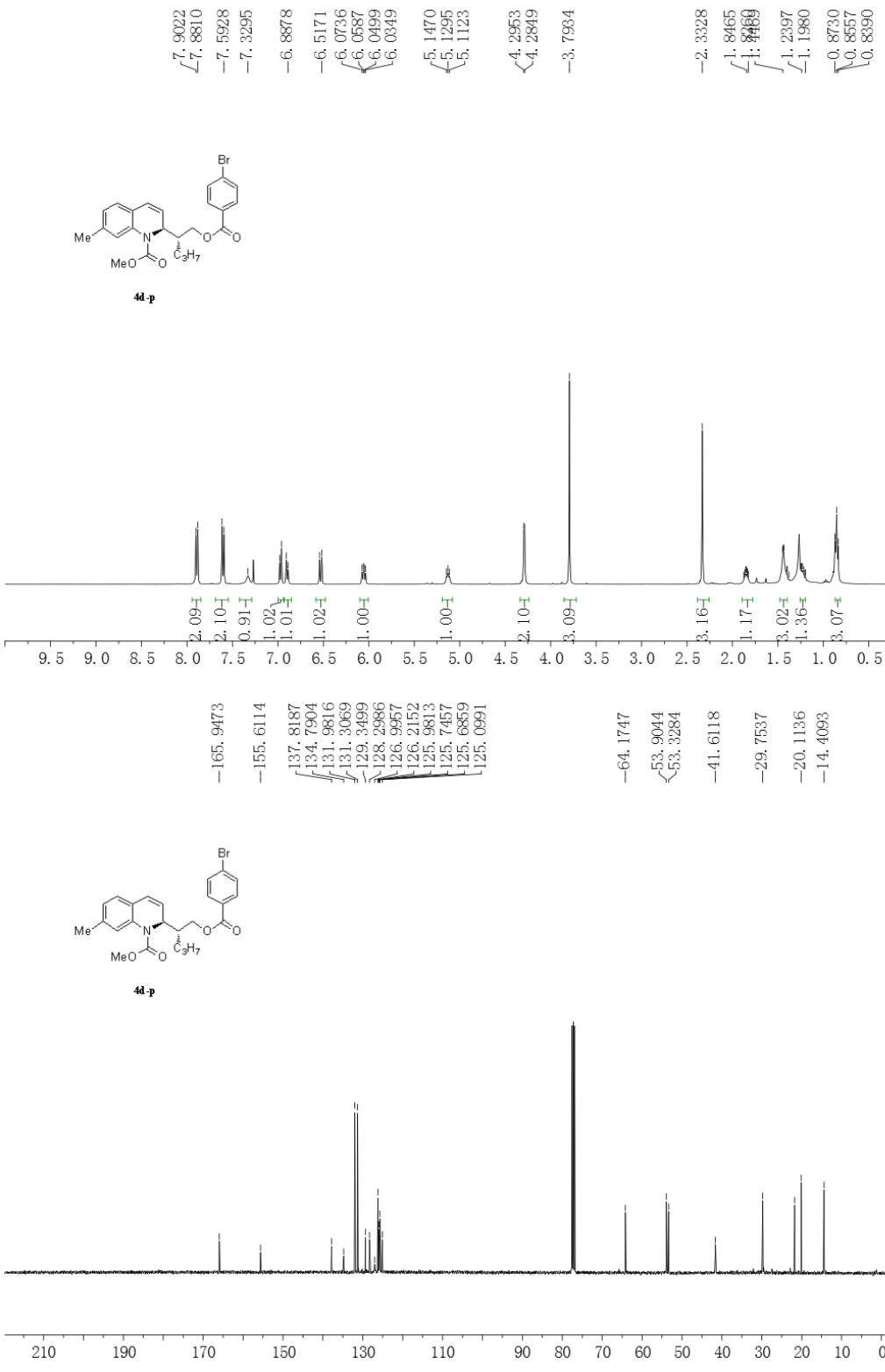
131.9386
131.3786
129.6011
128.5825
128.1929
127.8709
127.8142
126.4105
125.9070
125.5381
124.8902
63.7500
53.3105
53.2410
41.2636
29.8323
20.2864
14.5315
Br
N
O
O
MeO
O
C3H7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3a-p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6.0736
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6.0499
6.0349
5.1470
5.1295
5.1123
4.2953
4.2849
3.7934
2.3328
1.8465
1.2397
1.1980
0.8730
0.8557
0.8390
Br
Me
MeO
C3H7
4d-p
2.09
2.10
0.91
1.02
1.01
1.02
1.00
1.00
2.10
3.09
3.16
1.17
3.02
1.36
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
165.9473
155.6114
137.8187
134.7904
131.9816
131.3069
129.3499
128.2986
126.9957
126.2152
125.9813
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125.6859
125.0991
64.1747
53.9044
53.3284
41.6118
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Br
Me
MeO
C3H7
4d-p
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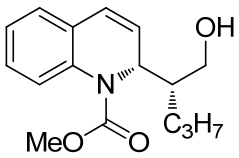
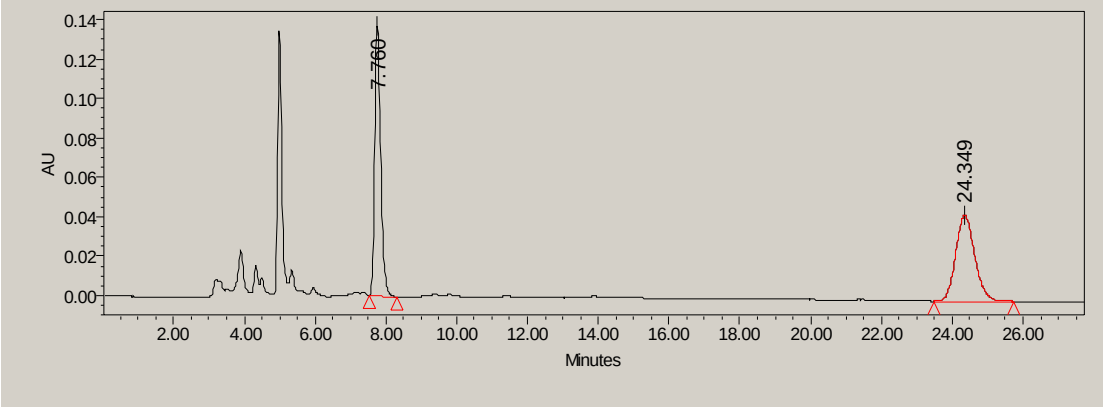
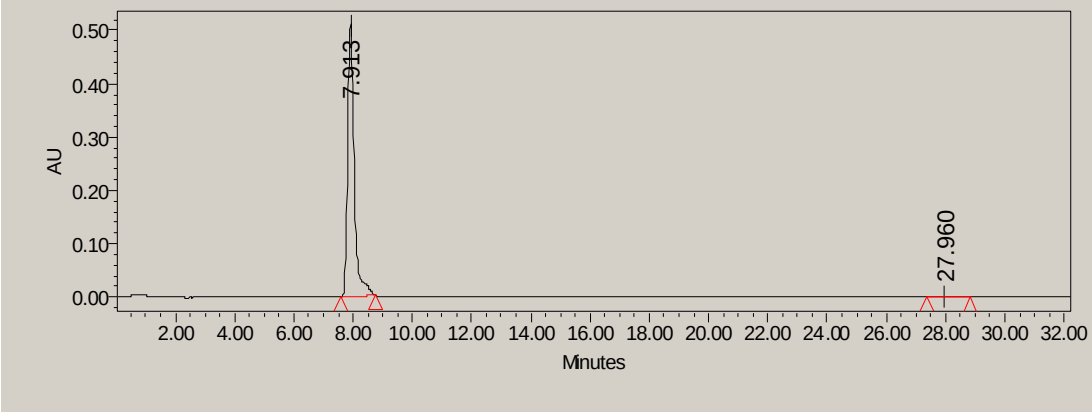
HPLC



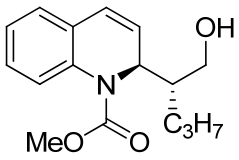
(*R*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (3a-*syn*)



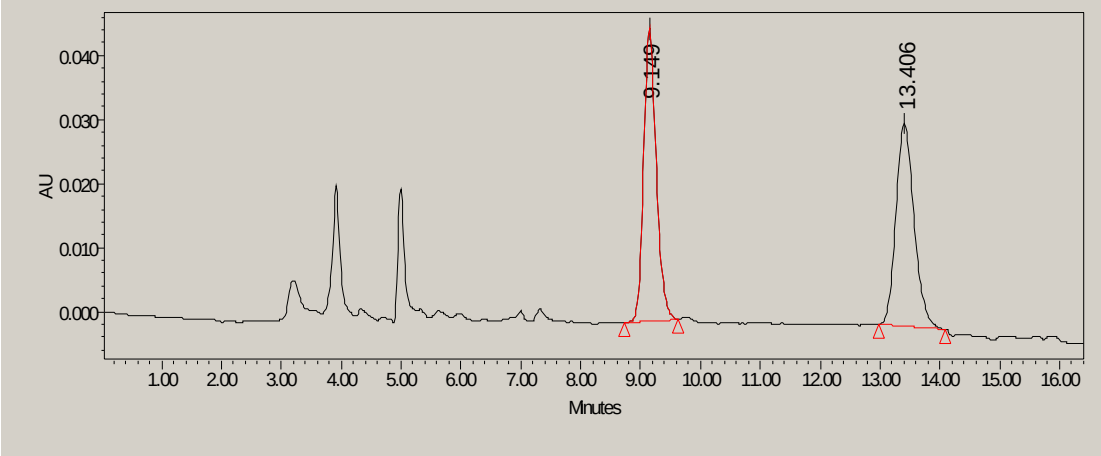
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.760	1613834	49.87	137513	bb	Unknown
2		24.349	1622120	50.13	43552	bb	Unknown



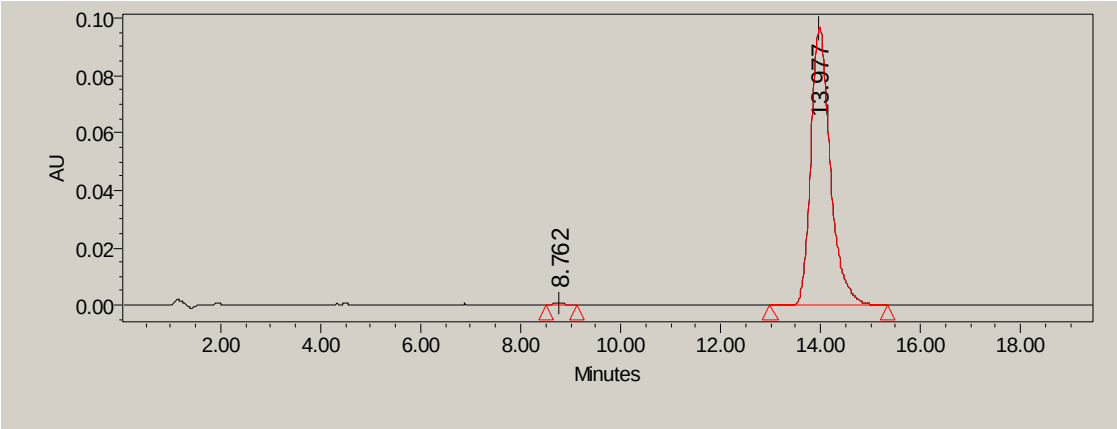
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.913	7900578	99.58	509360	bb	Unknown
2		27.960	33510	0.42	851	bb	Unknown



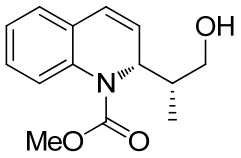
(*S*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (3a-*anti*)



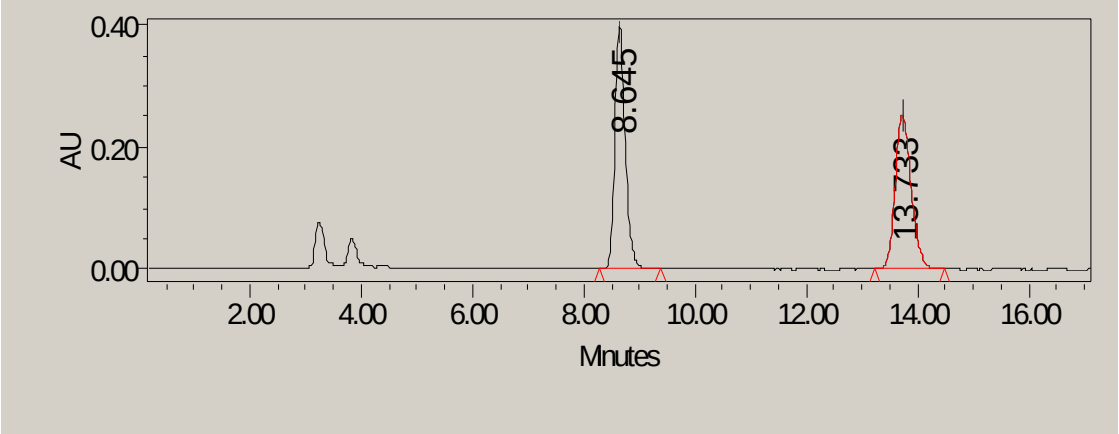
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		9.149	669928	50.10	45744	bb	Unknown
2		13.406	667327	49.90	31647	bb	Unknown



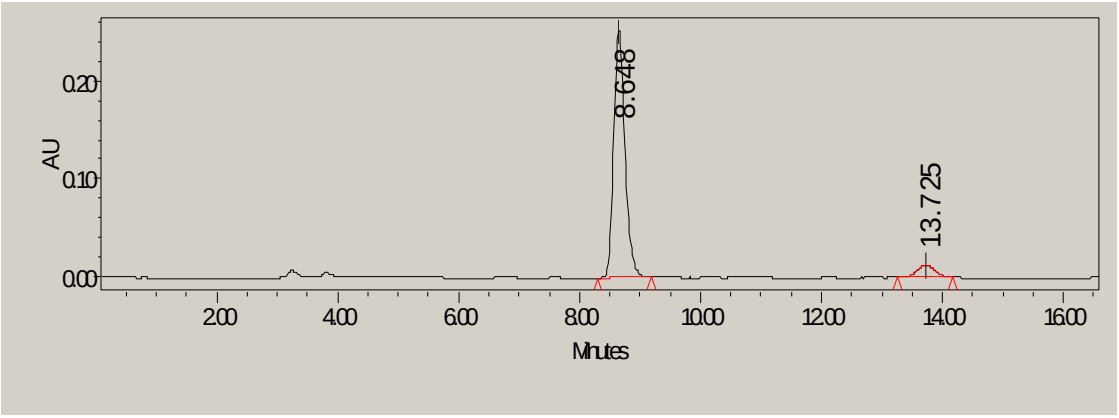
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.762	12895	0.49	823	bb	Unknown
2		13.977	2617196	99.51	96562	bb	Unknown



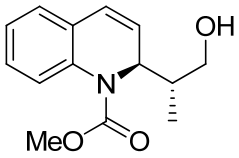
(*R*)-Methyl 2-((*R*)-1-hydroxypropan-2-yl)quinoline-1(2*H*)-carboxylate (3b-*syn*)



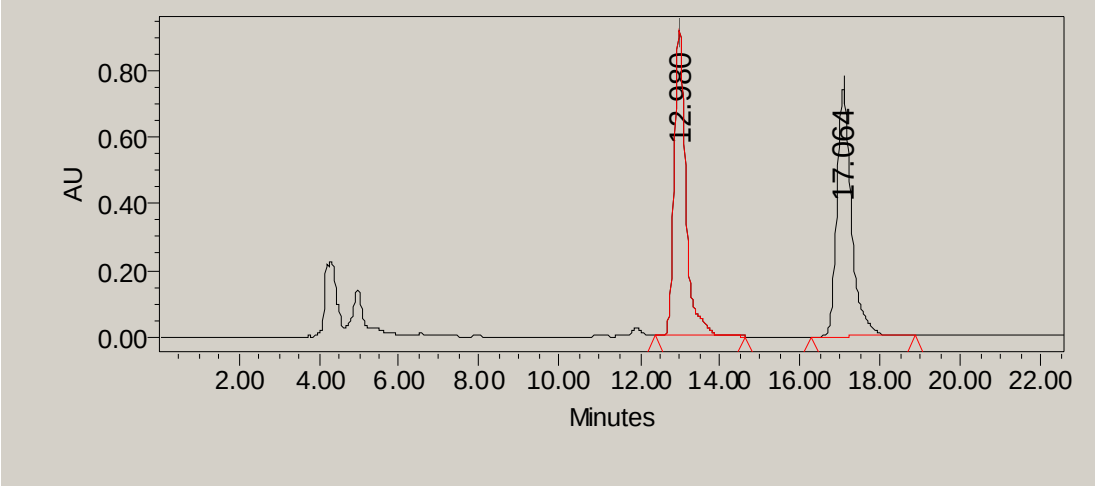
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.645	705589	50.38	55005	bb	Unknown
2		13.731	694831	49.62	34885	bb	Unknown



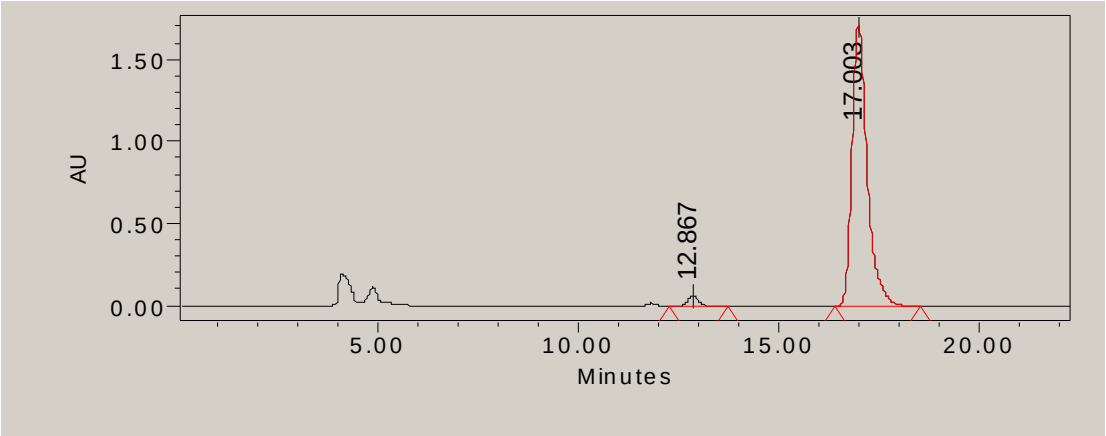
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.648	3201242	92.42	252969	bb	Unknown
2		13.725	262479	7.58	12781	bb	Unknown



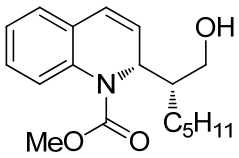
(*S*)-Methyl 2-((*R*)-1-hydroxypropan-2-yl)quinoline-1(2*H*)-carboxylate (3b-*anti*)



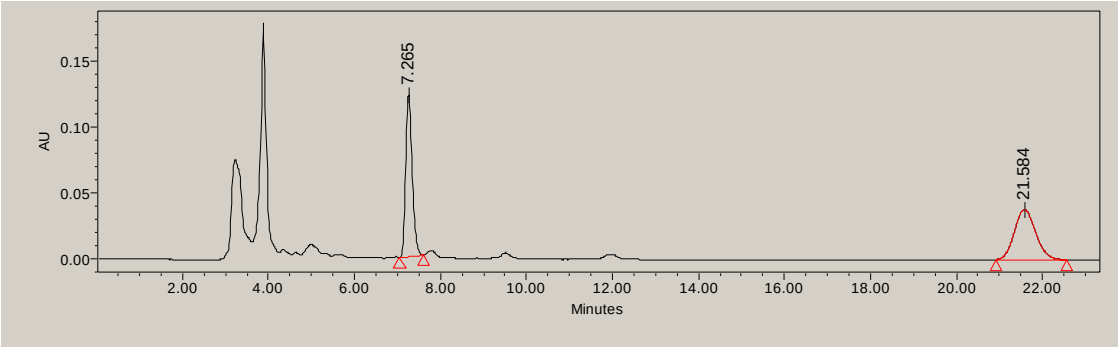
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		12.980	18810121	49.81	917371	bb	Unknown
2		17.064	18951645	50.19	745576	bb	Unknown



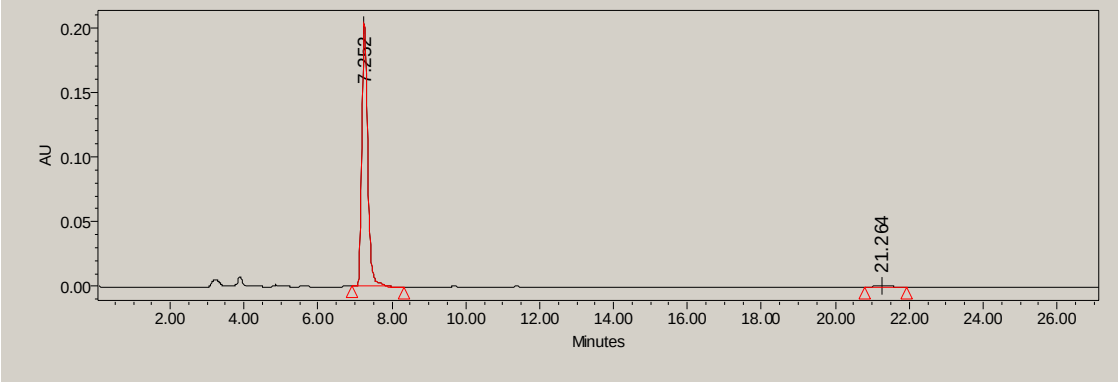
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		12.867	1301925	2.77	65651	bb	Unknown
2		17.003	45650666	97.23	1714935	bb	Unknown



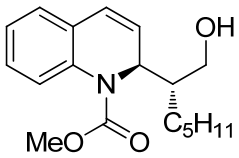
(*R*)-Methyl 2-((*R*)-1-hydroxyheptan-2-yl)quinoline-1(2*H*)-carboxylate (3c-*syn*)



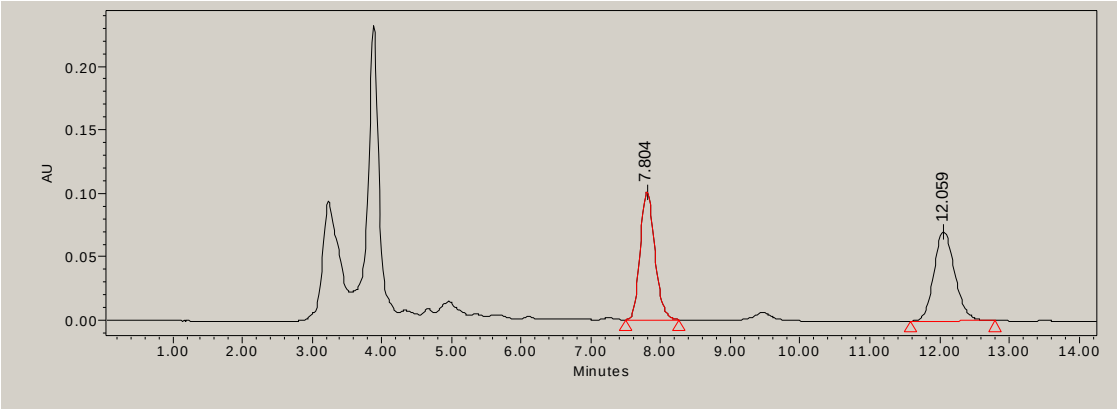
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.265	1290079	49.73	122997	bb	Unknown
2		21.584	1304051	50.27	38131	bb	Unknown



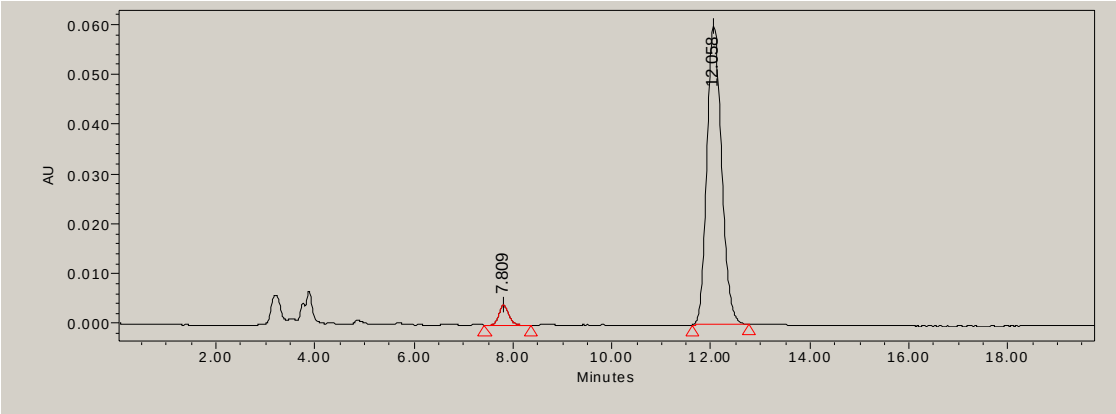
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.252	2214708	97.68	203035	bb	Unknown
2		21.264	52606	2.32	1676	bb	Unknown



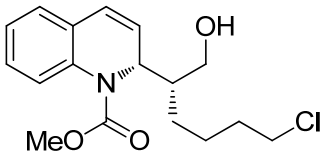
(*S*)-Methyl 2-((*R*)-1-hydroxyheptan-2-yl)quinoline-1(2*H*)-carboxylate (3c-*anti*)



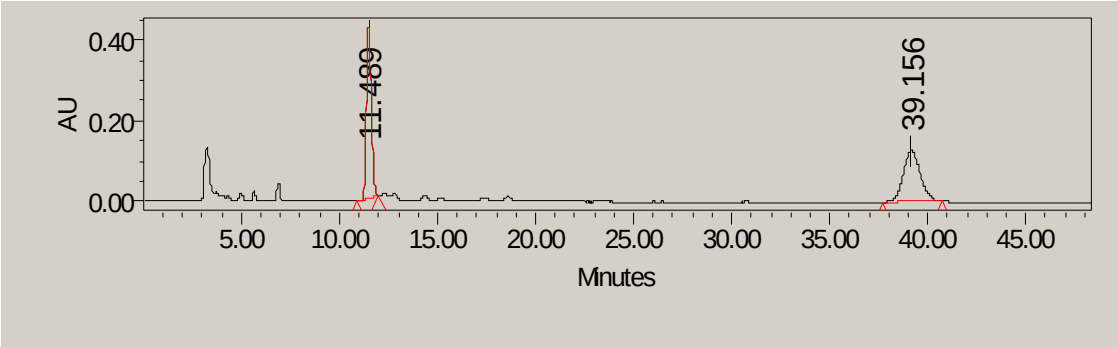
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.804	1456414	49.77	100715	bb	Unknown
2		12.059	1469723	50.23	70335	bb	Unknown



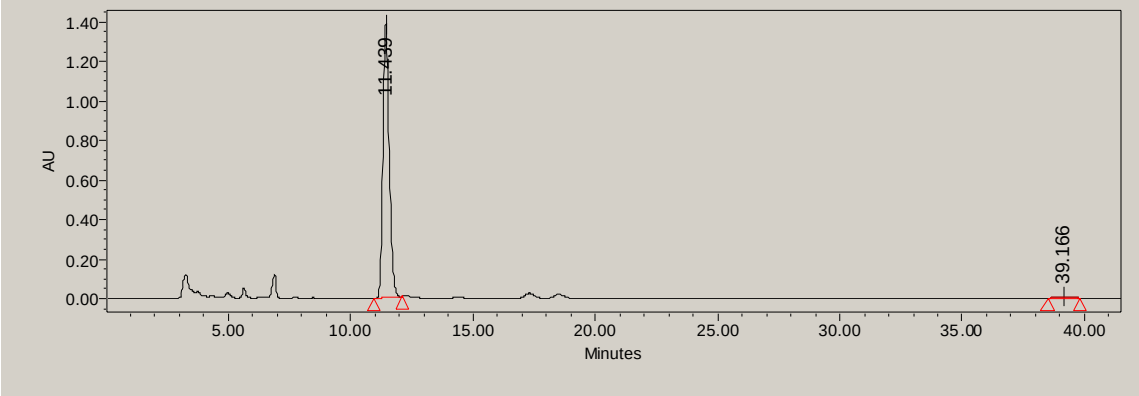
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.809	57096	4.77	4067	bb	Unknown
2		12.058	1140406	95.23	58703	bb	Unknown



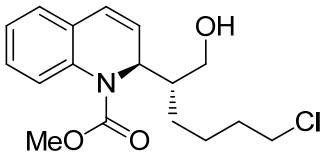
(*R*)-Methyl 2-((*R*)-6-chloro-1-hydroxyhexan-2-yl)quinoline-1(2*H*)-carboxylate (3d-*syn*)



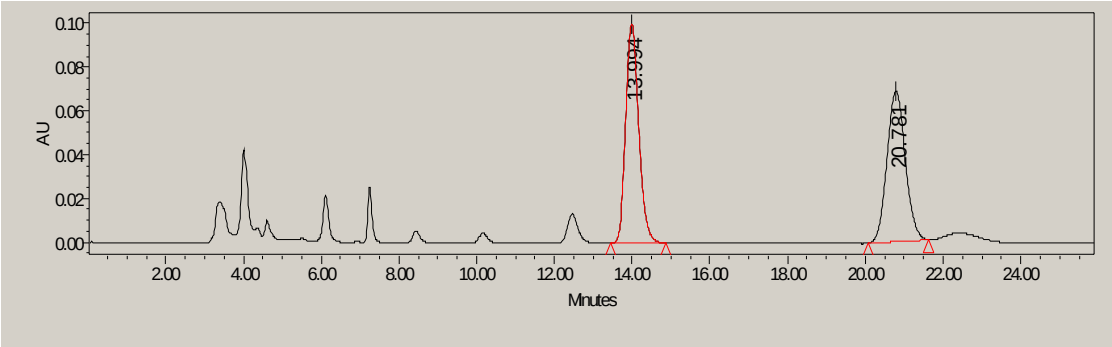
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		11.489	7401829	49.43	426611	bb	Unknown
2		39.156	7571678	50.57	125354	bb	Unknown



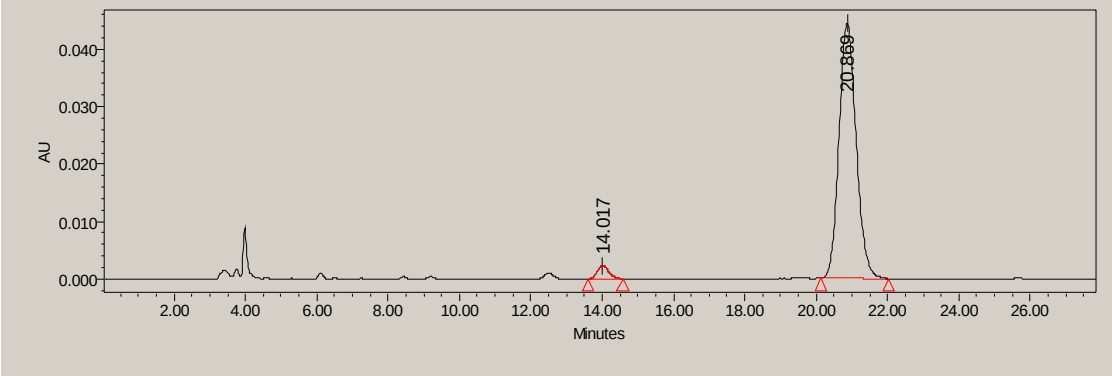
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		11.439	24985200	98.87	1384914	bb	Unknown
2		39.166	285827	1.13	7245	bb	Unknown



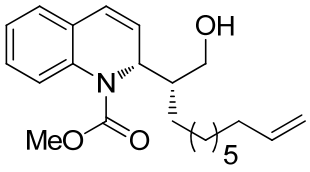
(*S*)-Methyl 2-((*R*)-6-chloro-1-hydroxyhexan-2-yl)quinoline-1(2*H*)-carboxylate (3d-*anti*)



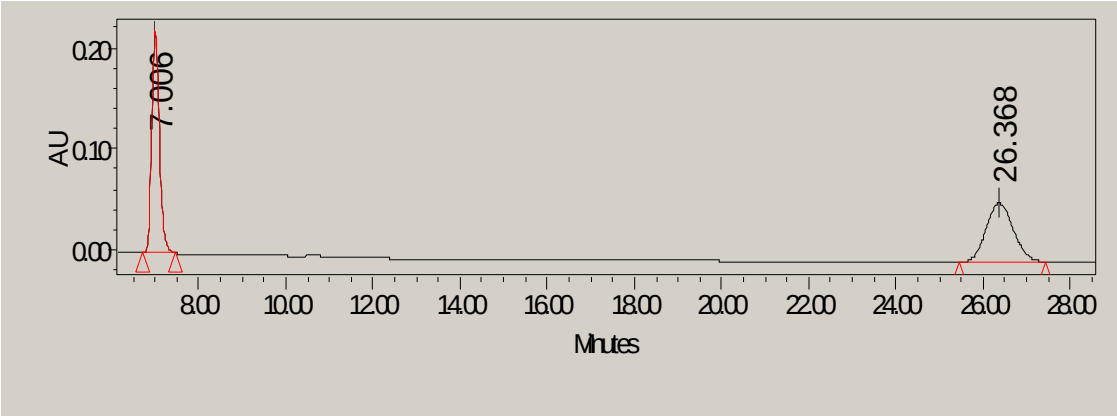
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		13.994	2325168	50.57	100393	bb	Unknown
2		20.781	2272771	49.43	68973	bb	Unknown



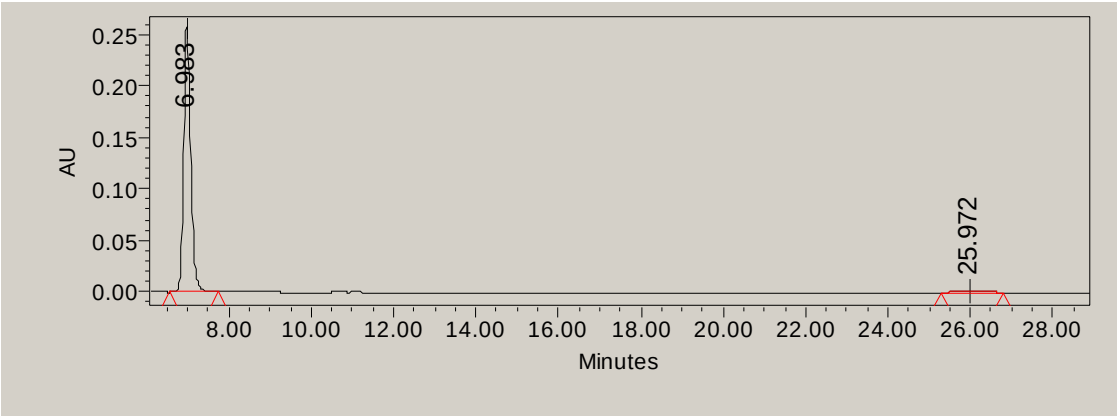
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		14.017	52461	3.42	2325	bb	Unknown
2		20.869	1482823	96.58	44486	bb	Unknown



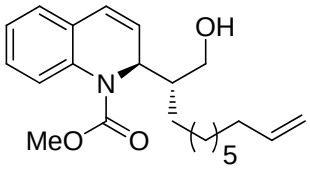
(*R*)-Methyl 2-((*R*)-1-hydroxyundec-10-en-2-yl)quinoline-1(2*H*)-carboxylate (3e-*syn*)



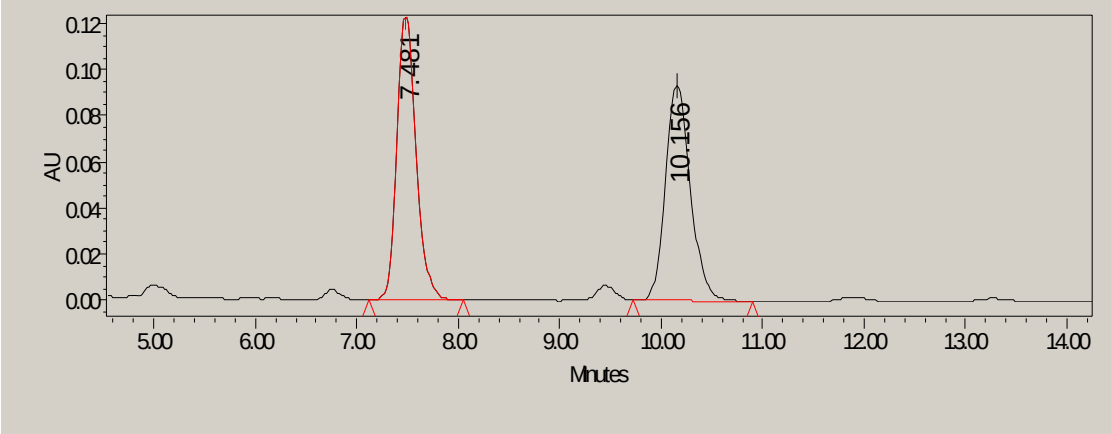
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.006	2656554	50.83	220153	bb	Unknown
2		26.368	2569686	49.17	58574	bb	Unknown



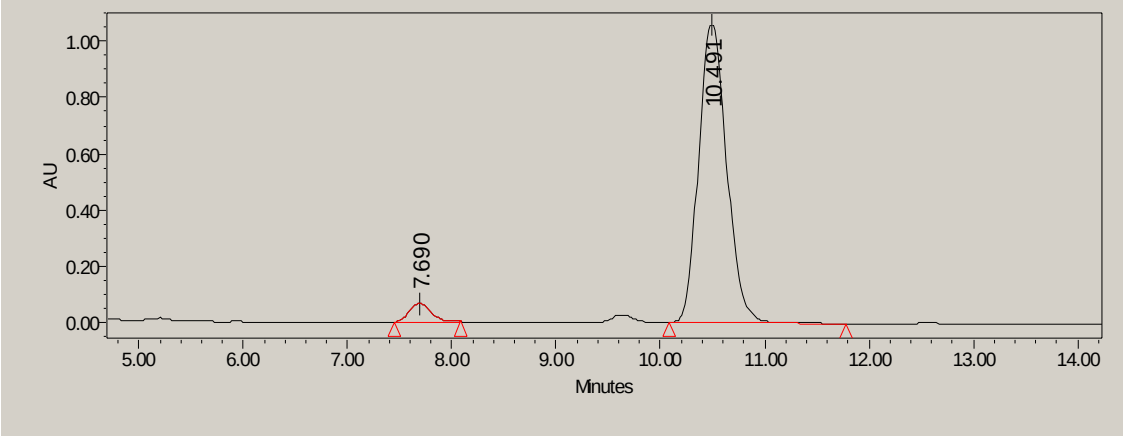
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		6.983	3139831	98.46	258646	bb	Unknown
2		25.972	49222	1.54	1201	bb	Unknown



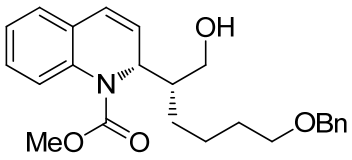
(*S*)-Methyl 2-((*R*)-1-hydroxyundec-10-en-2-yl)quinoline-1(2*H*)-carboxylate (3e-*anti*)



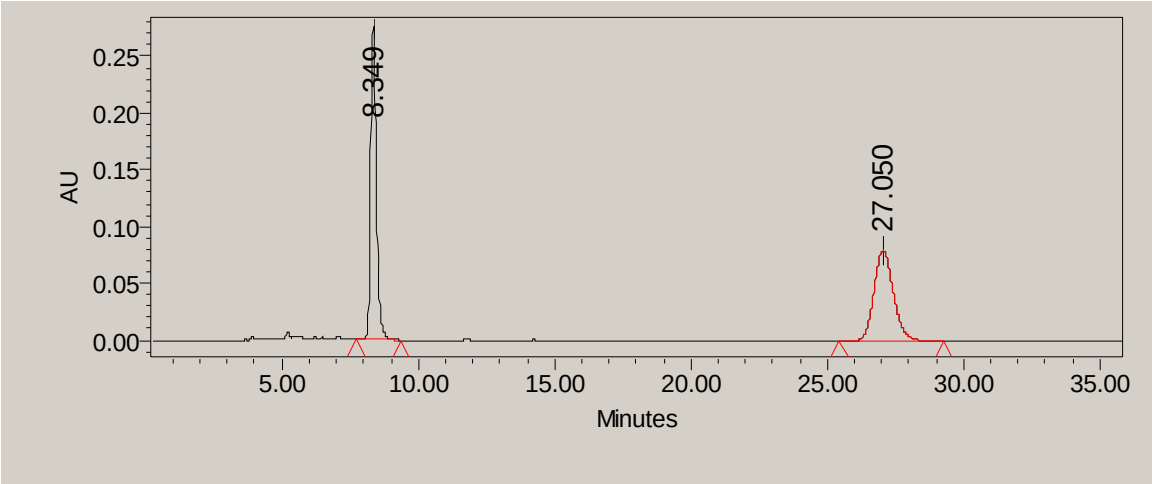
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.481	1586124	49.98	122582	bb	Unknown
2		10.156	1587187	50.02	93294	bb	Unknown



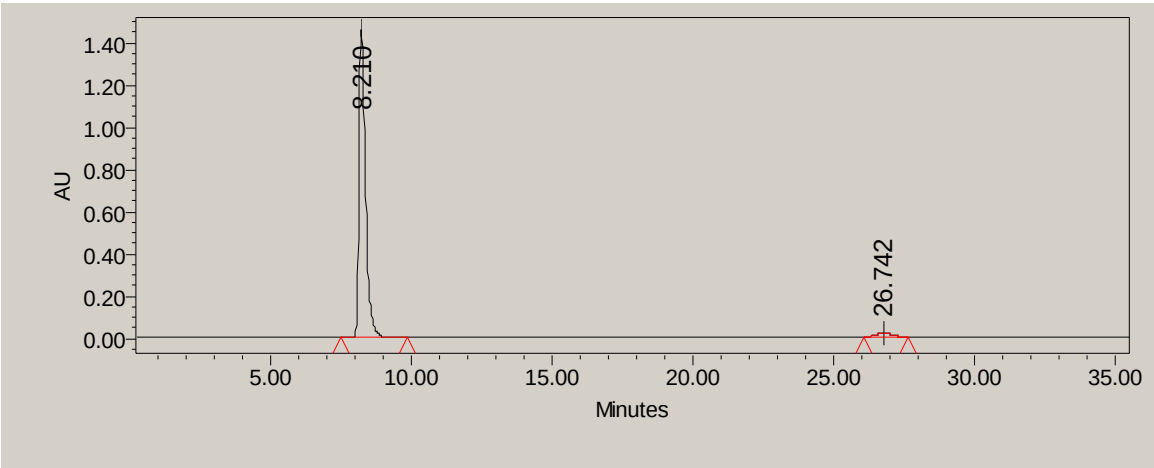
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.690	798270	4.48	55054	bb	Unknown
2		10.491	17019904	95.52	913666	bb	Unknown



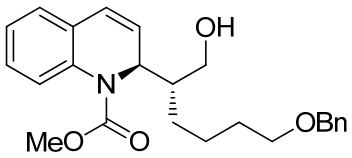
(*R*)-Methyl 2-((*R*)-6-(benzyloxy)-1-hydroxyhexan-2-yl)quinoline-1(2*H*)-carboxylate (3f-*syn*)



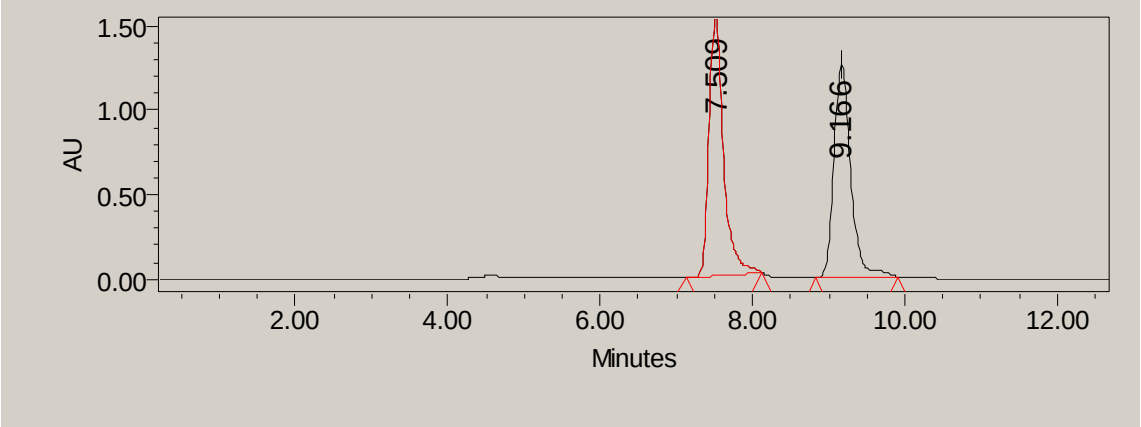
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.349	3995255	50.34	275936	bb	Unknown
2		27.050	3941018	49.66	79514	bb	Unknown



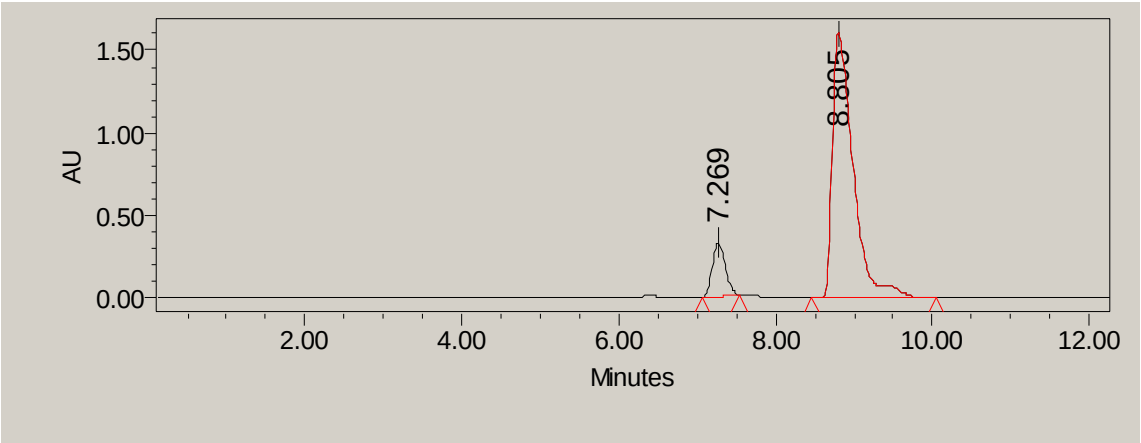
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.210	23218522	96.43	1460451	bb	Unknown
2		26.742	860035	3.57	18858	bb	Unknown



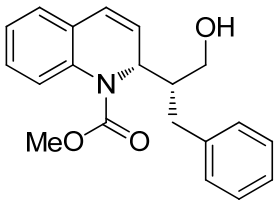
(*S*)-Methyl 2-((*R*)-6-(benzyloxy)-1-hydroxyhexan-2-yl)quinoline-1(2*H*)-carboxylate (3f-*anti*)



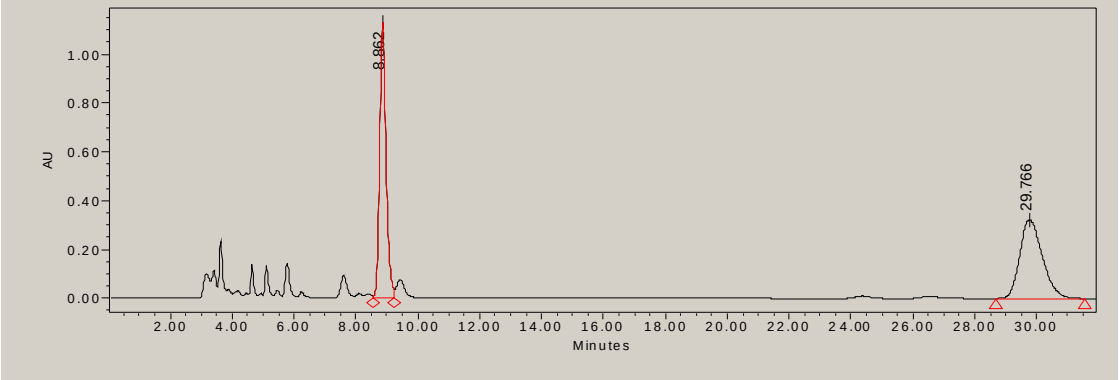
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.509	20385729	50.84	1535807	bb	Unknown
2		9.166	19712033	49.16	1272043	bb	Unknown



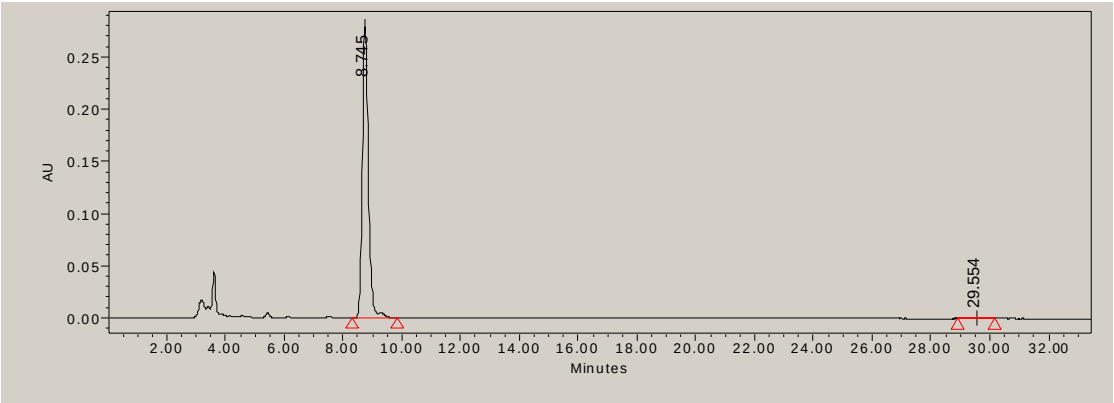
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.269	3258040	9.92	307469	bb	Unknown
2		8.805	29596156	90.08	1611282	bb	Unknown



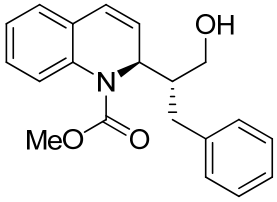
(*R*)-Methyl 2-((*R*)-1-hydroxy-3-phenylpropan-2-yl)quinoline-1(2*H*)-carboxylate (3g-*syn*)



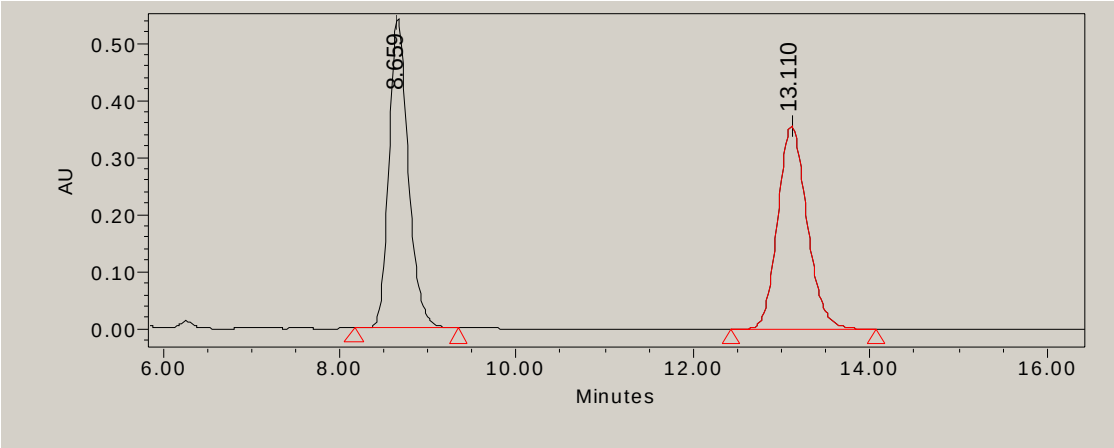
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.862	16412778	50.13	1130309	VV	Unknown
2		29.766	16329210	49.87	322895	BB	Unknown



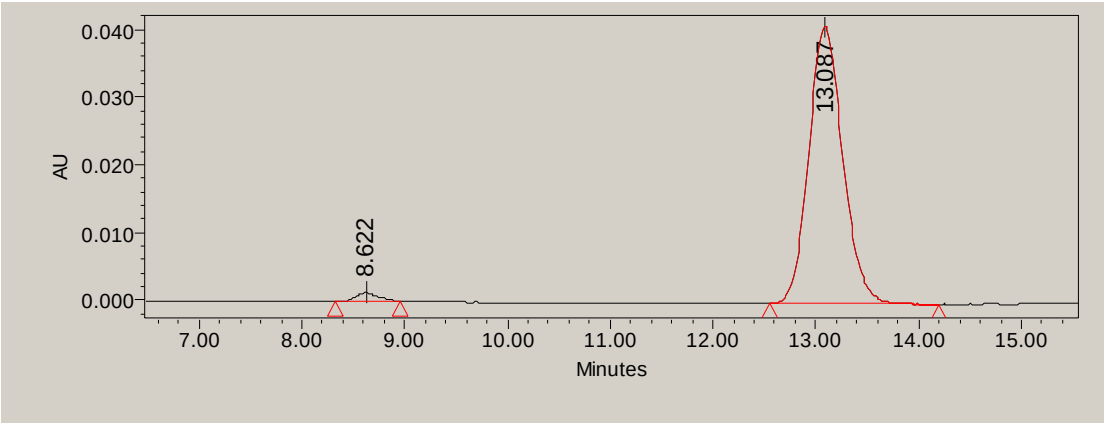
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.745	4016631	99.47	279745	bb	Unknown
2		29.554	21451	0.53	559	bb	Unknown



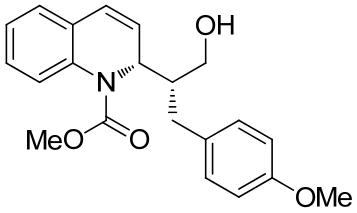
(*S*)-Methyl 2-((*R*)-1-hydroxy-3-phenylpropan-2-yl)quinoline-1(2*H*)-carboxylate (3g-*anti*)



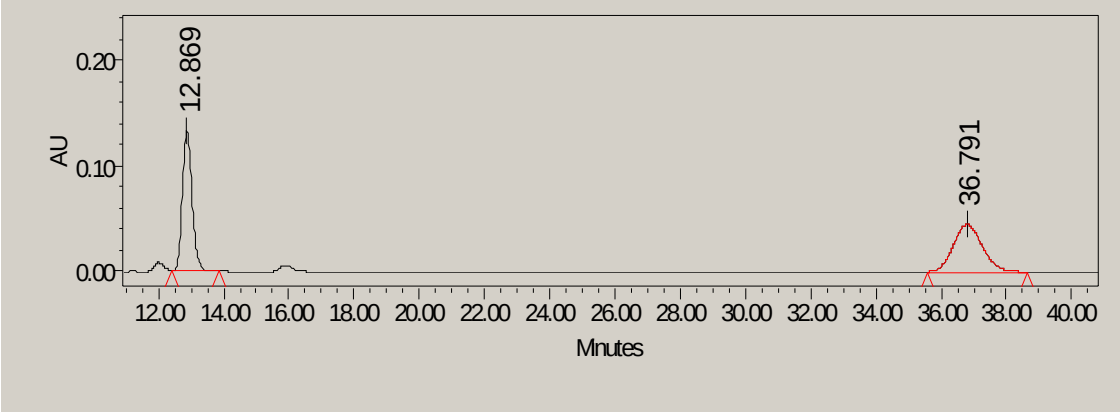
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.659	8280075	50.19	541852	bb	Unknown
2		13.110	8217096	49.81	354947	bb	Unknown



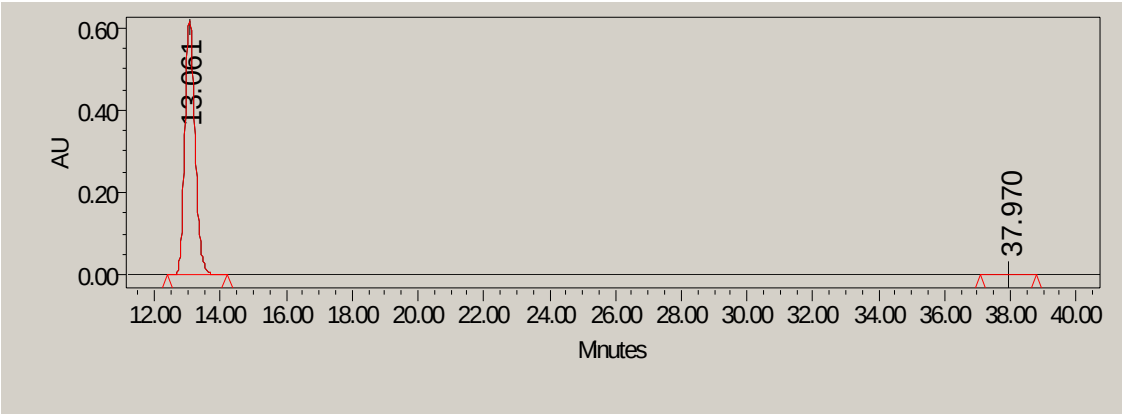
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.622	19197	2.30	1277	bb	Unknown
2		13.087	815746	97.70	38364	bb	Unknown



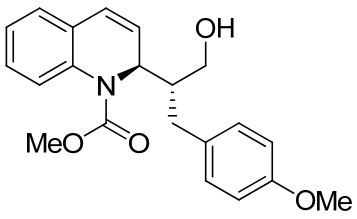
(*R*)-Methyl 2-((*R*)-1-hydroxy-3-(4-methoxyphenyl)propan-2-yl)quinoline-1(2*H*)-carboxylate (3h-*syn*)



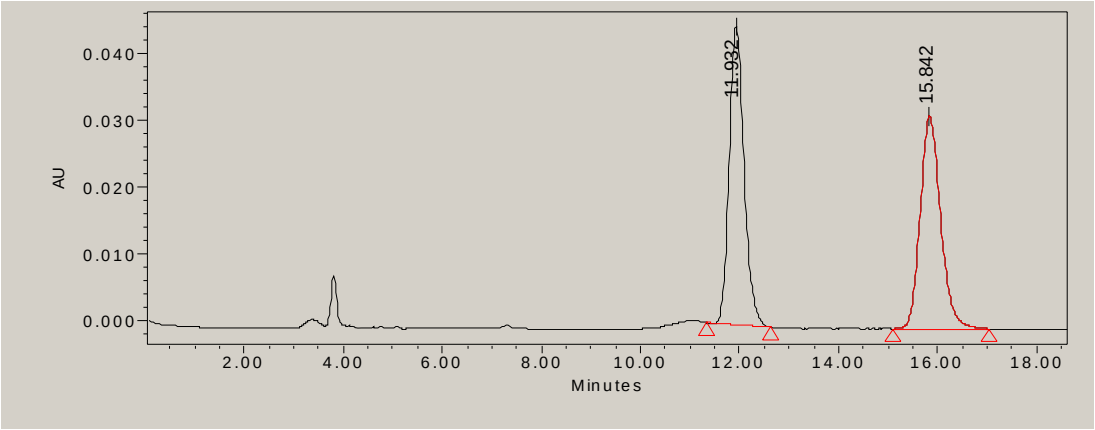
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		12.869	2742809	49.75	132914	bb	Unknown
2		36.791	2769874	50.25	44756	bb	Unknown



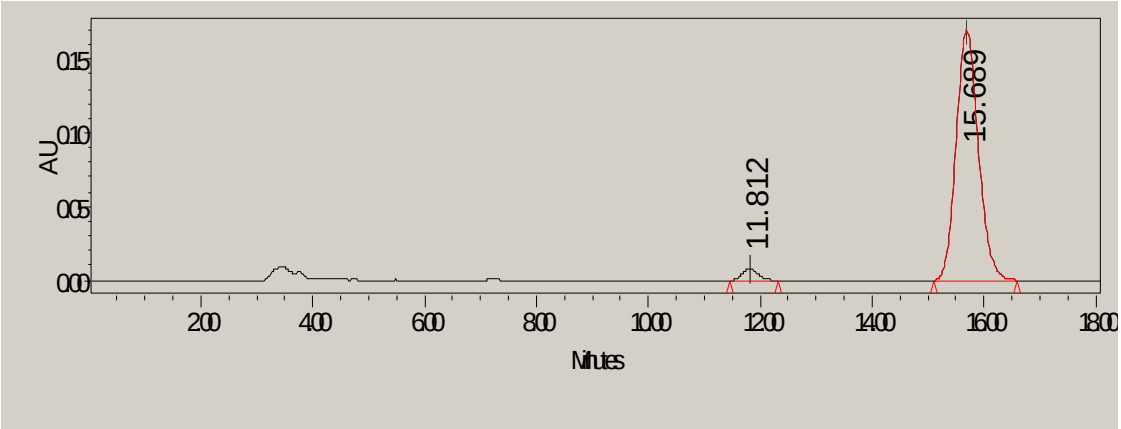
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		13.061	13260401	99.67	616266	bb	Unknown
2		37.970	43396	0.33	822	bb	Unknown



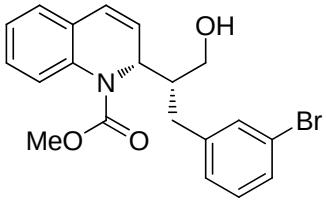
(*S*)-Methyl 2-((*R*)-1-hydroxy-3-(4-methoxyphenyl)propan-2-yl)quinoline-1(2*H*)-carboxylate (3h-*anti*)



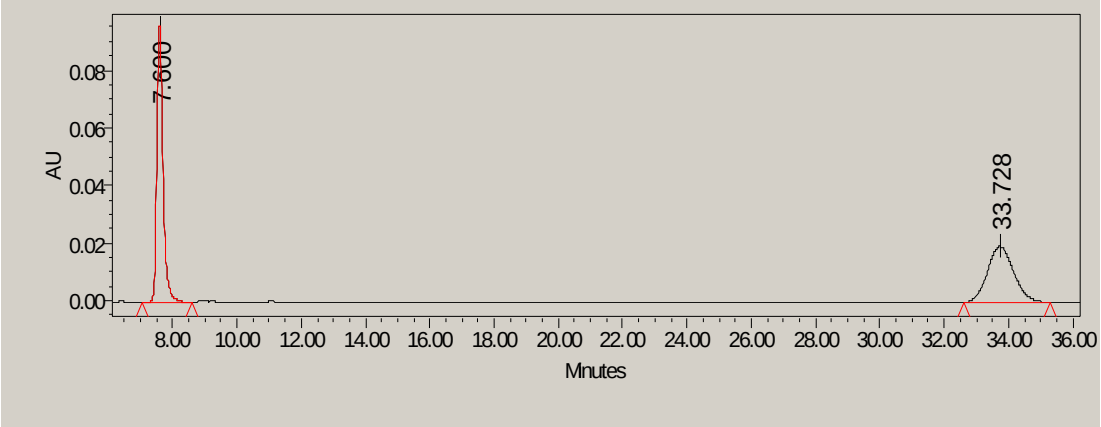
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		11.932	930451	50.52	44614	bb	Unknown
2		15.842	911311	49.48	31855	bb	Unknown



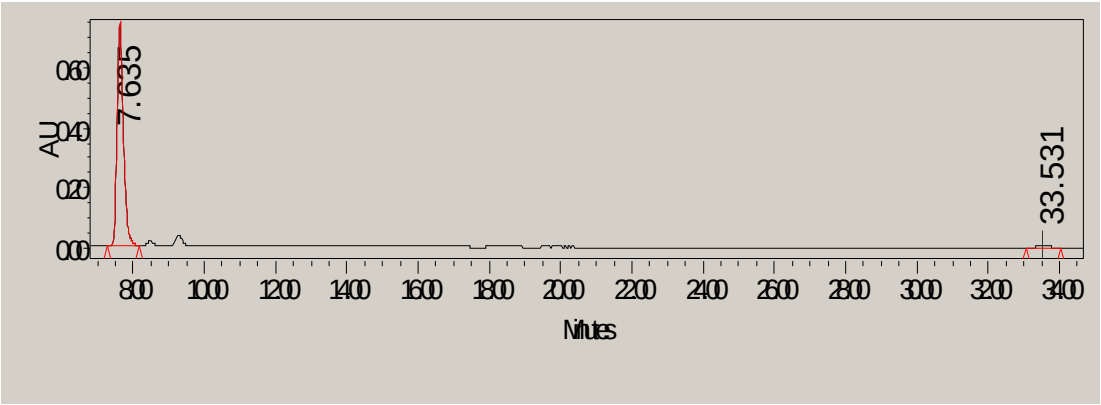
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		11.812	171887	3.52	8273	bb	Unknown
2		15.689	4704572	96.48	169742	bb	Unknown



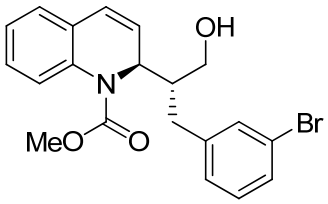
(*R*)-Methyl 2-((*R*)-1-(3-bromophenyl)-3-hydroxypropan-2-yl)quinoline-1(2*H*)-carboxylate (3i-*syn*)



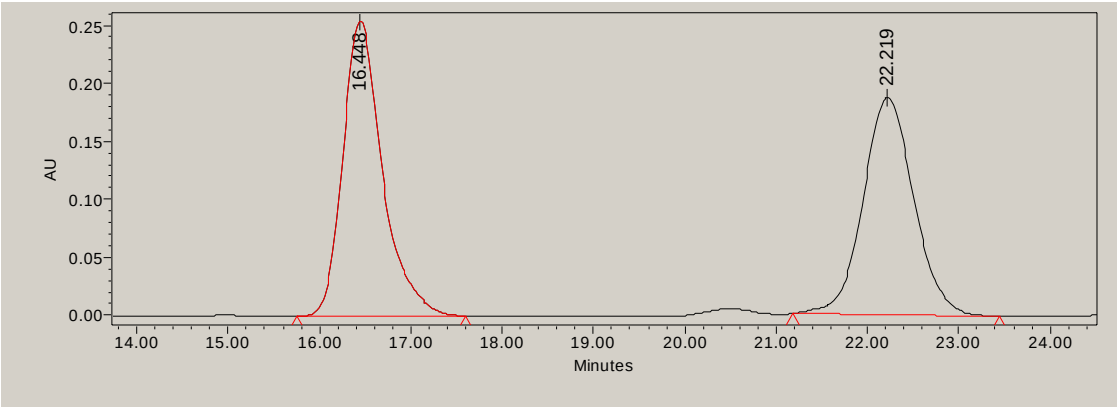
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.600	1191525	51.87	95038	bb	Unknown
2		33.728	1105733	48.13	19430	bb	Unknown



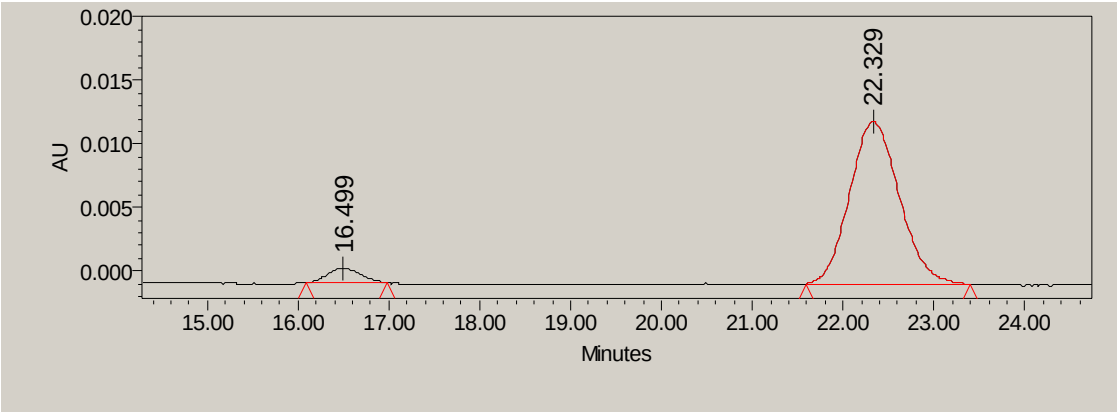
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.635	9137688	99.61	744953	bb	Unknown
2		33.531	35859	0.39	1185	bb	Unknown



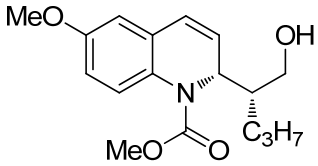
(*S*)-Methyl 2-((*R*)-1-(3-bromophenyl)-3-hydroxypropan-2-yl)quinoline-1(2*H*)-carboxylate (3i-*anti*)



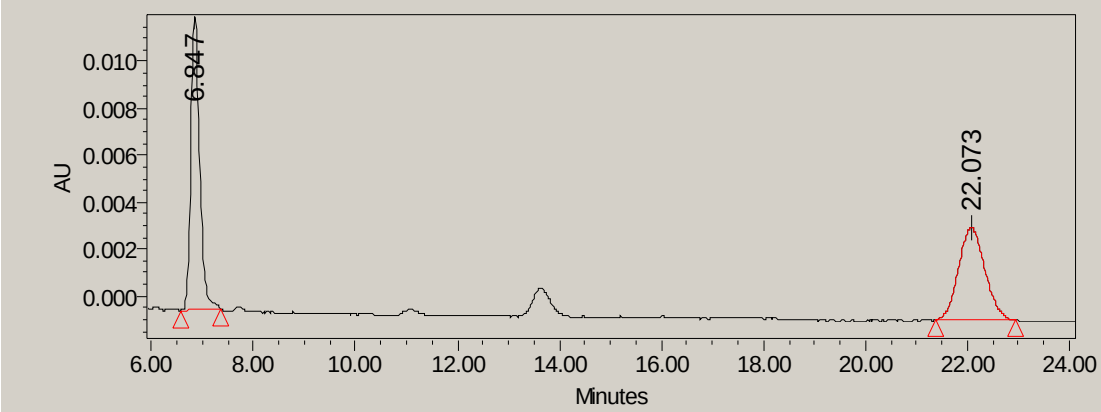
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		16.448	7668189	51.49	254372	bb	Unknown
2		22.219	7224261	48.51	187303	bb	Unknown



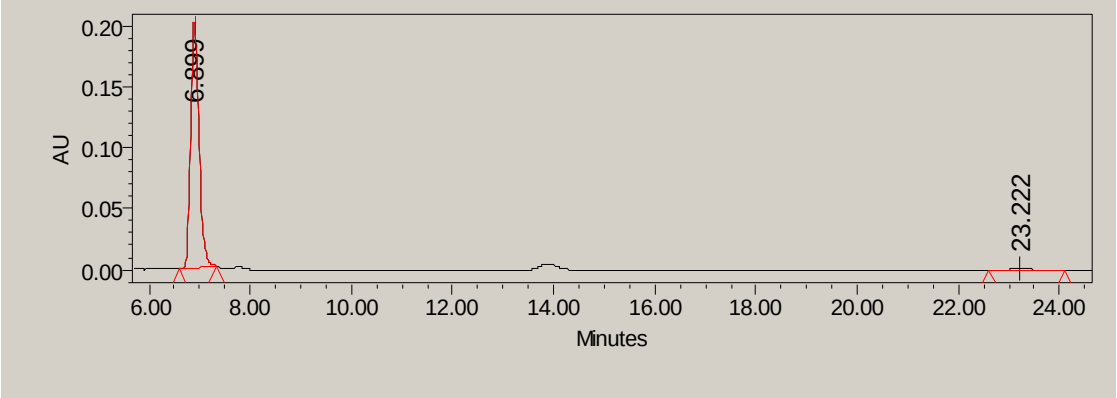
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		16.499	28616	5.57	1143	bb	Unknown
2		22.329	484955	94.43	12766	bb	Unknown



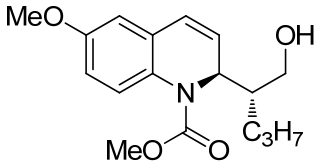
(*R*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-6-methoxyquinoline-1(2*H*)-carboxylate (4a-*syn*)



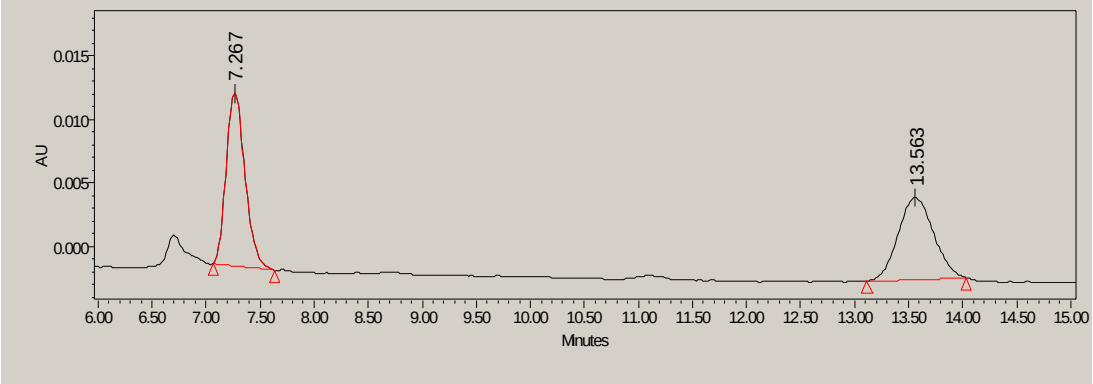
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		6.847	149372	51.21	12511	bb	Unknown
2		22.073	142342	48.79	3929	bb	Unknown



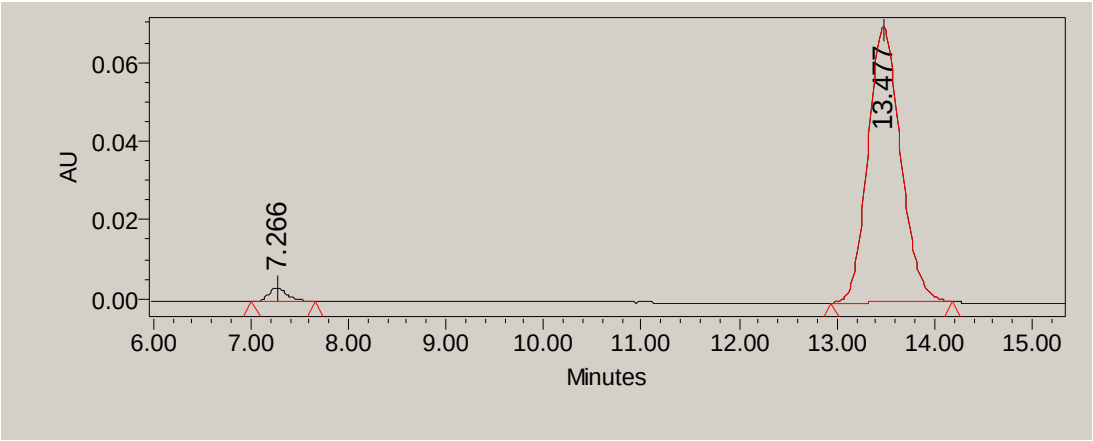
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		6.899	2281767	98.02	201949	bb	Unknown
2		23.222	46131	1.98	1207	bb	Unknown



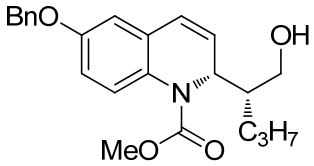
(*S*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-6-methoxyquinoline-1(2*H*)-carboxylate (4a-*anti*)



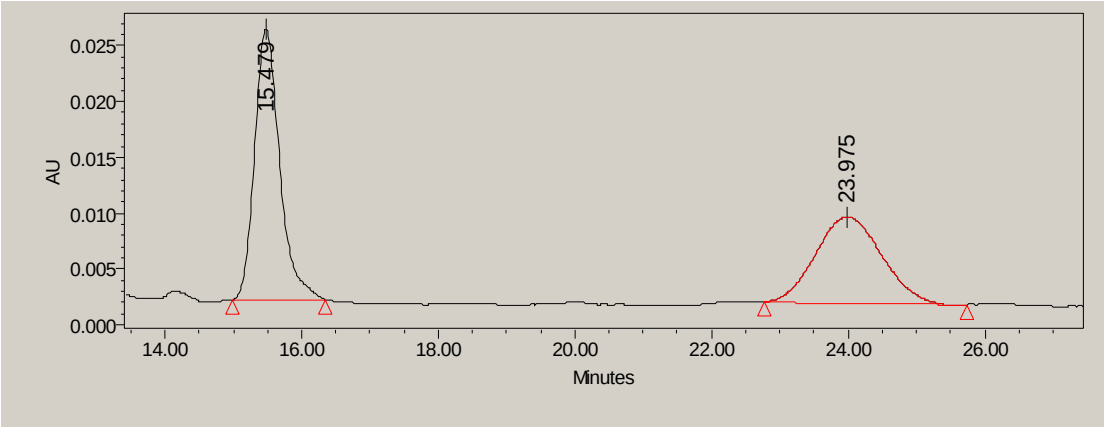
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.267	165227	52.85	13609	bb	Unknown
2		13.563	147421	47.15	6458	bb	Unknown



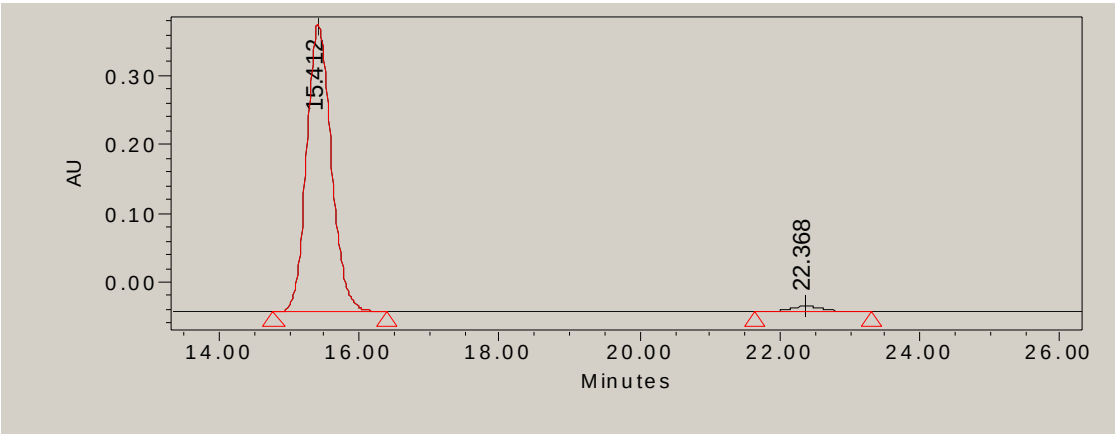
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.266	43431	2.60	3341	bb	Unknown
2		13.477	1629513	97.40	69934	bb	Unknown



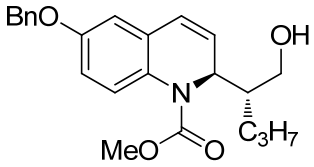
(*R*)-Methyl 6-(benzyloxy)-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4b-*syn*)



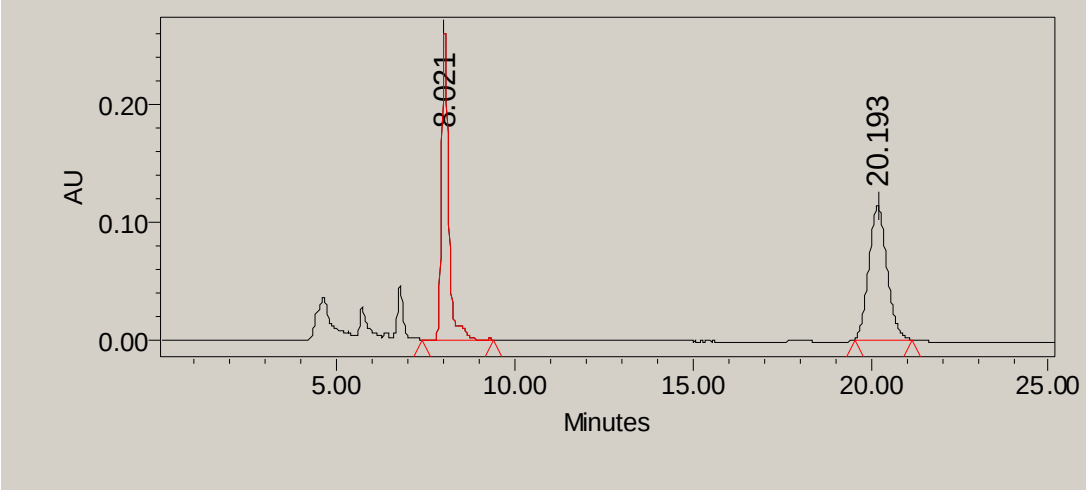
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		15.479	575149	52.49	23716	bb	Unknown
2		23.975	520493	47.51	7707	bb	Unknown



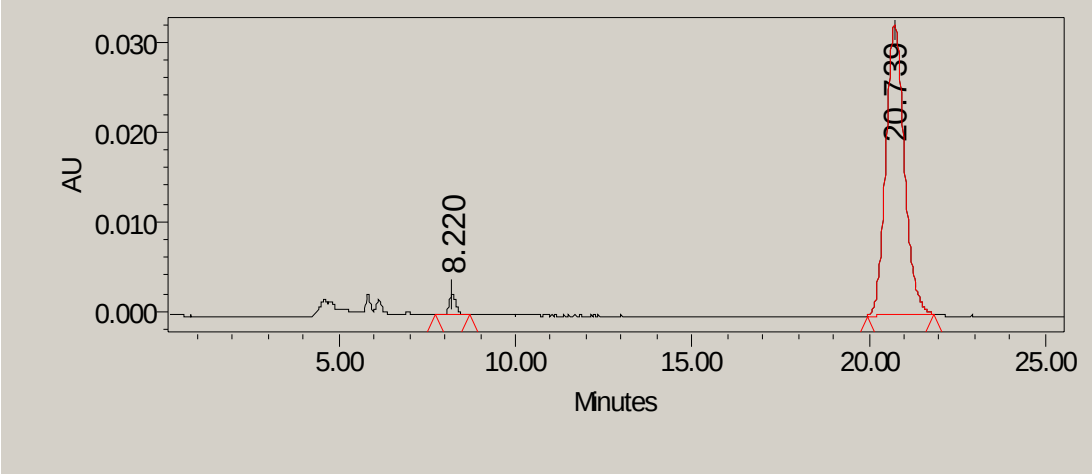
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		15.412	10272138	97.12	418521	bb	Unknown
2		22.368	304211	2.88	8400	bb	Unknown



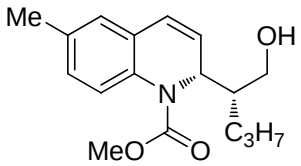
(*S*)-Methyl 6-(benzyloxy)-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4b-*anti*)



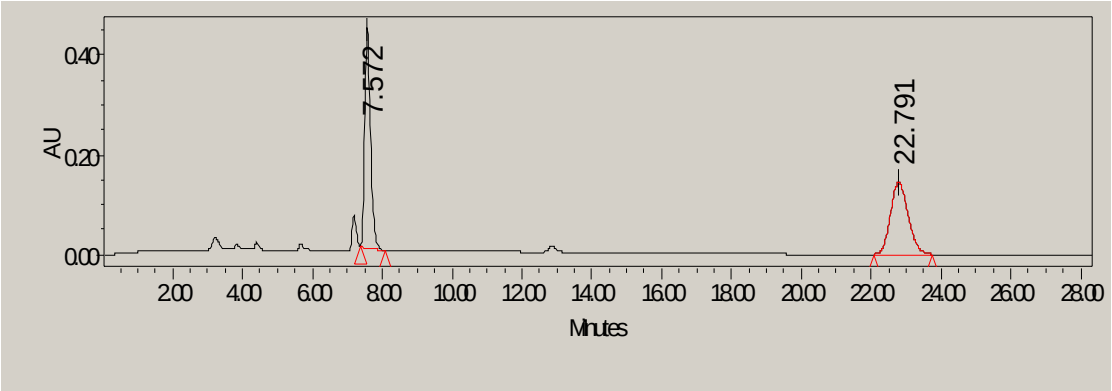
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.021	3596306	48.53	260962	bb	Unknown
2		20.193	3814833	51.47	110273	bb	Unknown



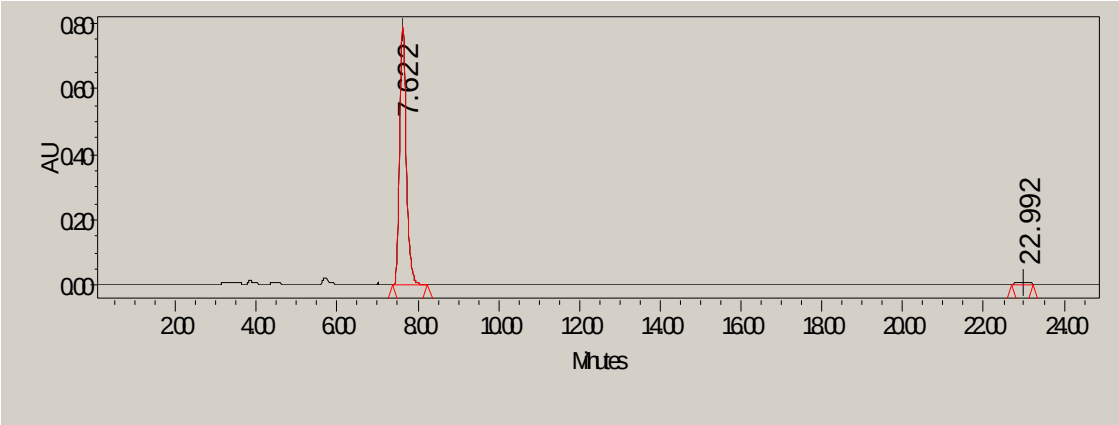
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.220	29754	2.71	2238	bb	Unknown
2		20.739	1067634	97.29	30959	bb	Unknown



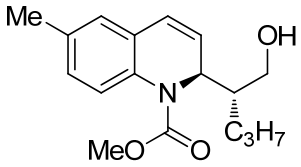
(*R*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-6-methylquinoline-1(2*H*)-carboxylate (4c-*syn*)



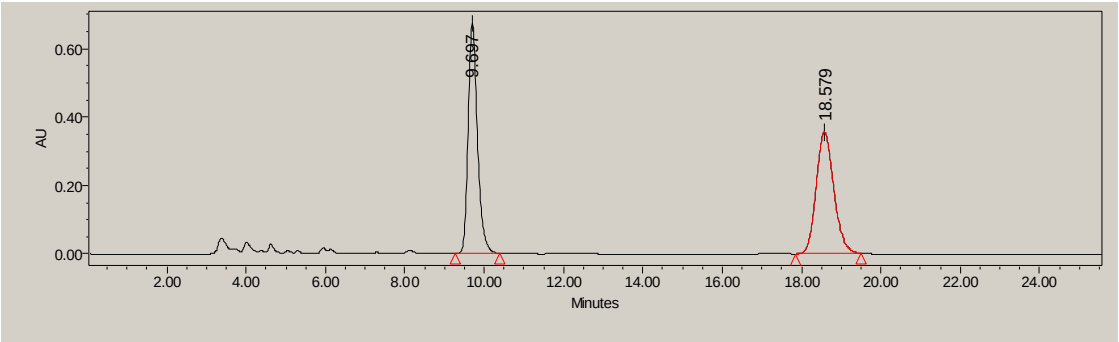
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.572	5054382	50.07	440533	bb	Unknown
2		22.791	5040672	49.93	143817	bb	Unknown



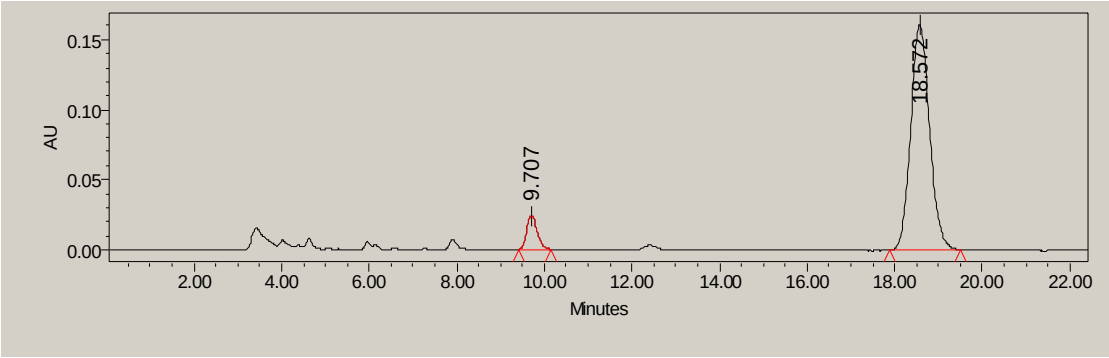
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.622	8994117	98.97	787971	bb	Unknown
2		22.992	93720	1.03	4827	bb	Unknown



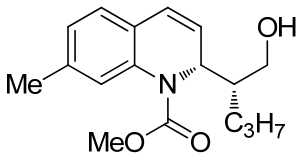
(*S*)-Methyl 6-chloro-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4c-*anti*)



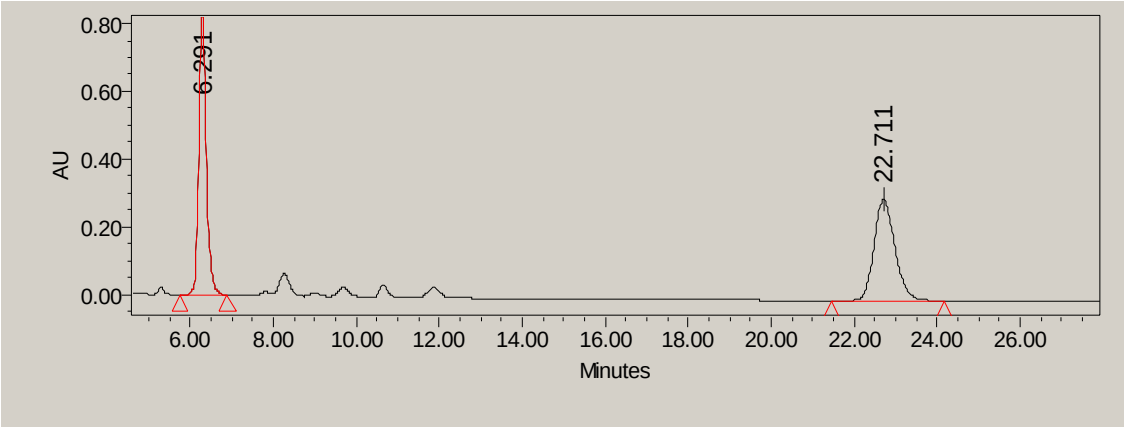
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		9.697	11009157	49.99	674052	bb	Unknown
2		18.579	11014103	50.01	355169	bb	Unknown



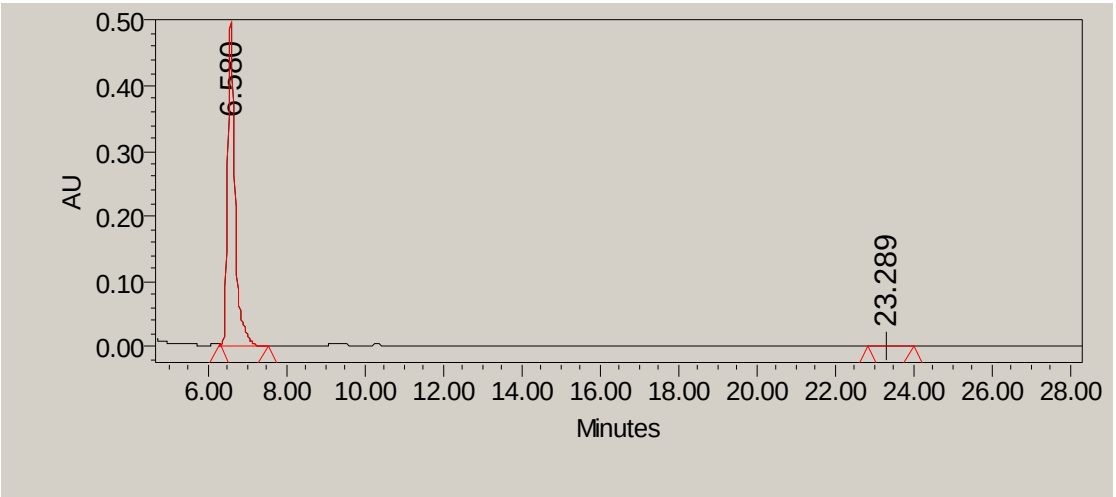
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		9.707	393589	7.95	24077	bb	Unknown
2		18.572	4558726	92.05	157825	bb	Unknown



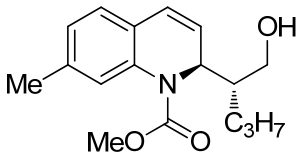
(*R*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-7-methylquinoline-1(2*H*)-carboxylate (4d-*syn*)



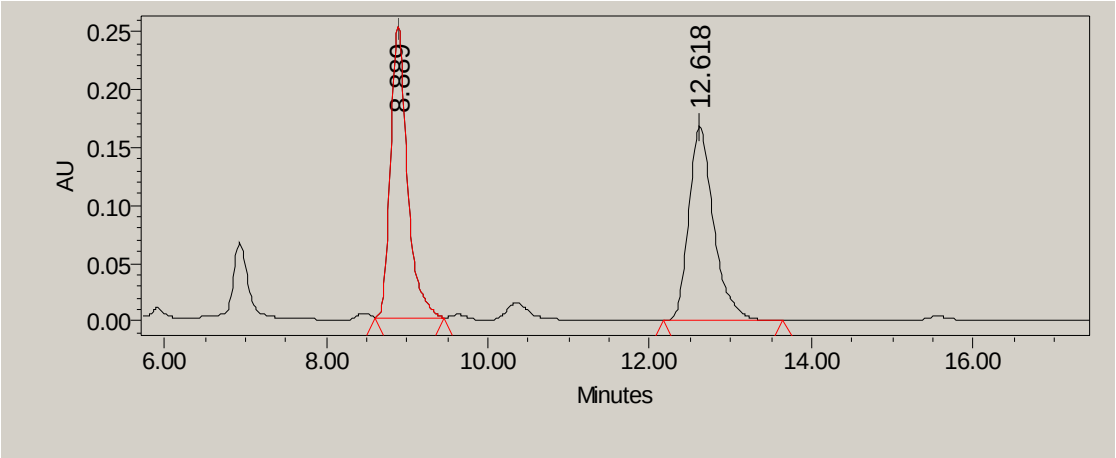
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		6.291	10616958	50.58	825924	bb	Unknown
2		22.711	10372415	49.42	297405	bb	Unknown



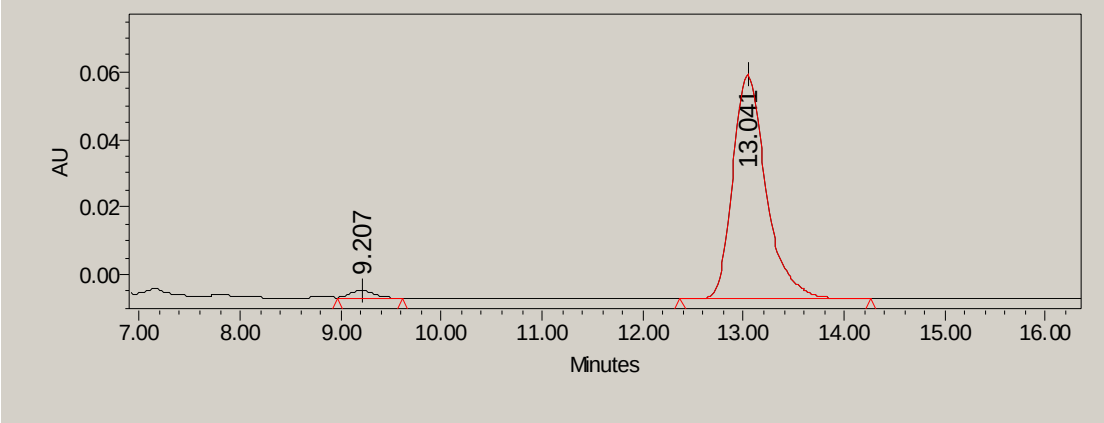
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		6.580	6685146	99.43	495550	bb	Unknown
2		23.289	38137	0.57	1133	bb	Unknown



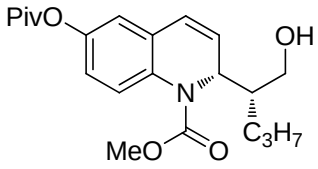
(*S*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-7-methylquinoline-1(2*H*)-carboxylate (4d-*anti*)



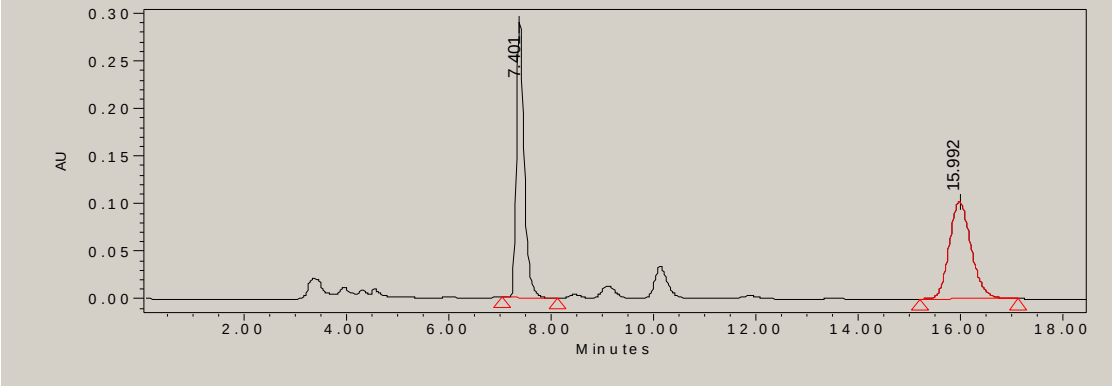
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.889	3661091	50.54	251377	bb	Unknown
2		12.618	3582494	49.46	167391	bb	Unknown



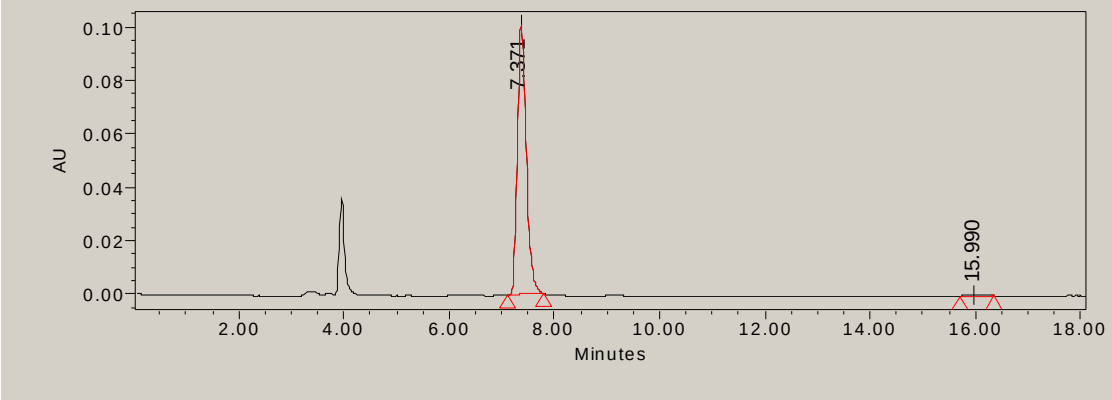
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		9.207	31394	2.39	2032	bb	Unknown
2		13.041	1280326	97.61	62230	bb	Unknown



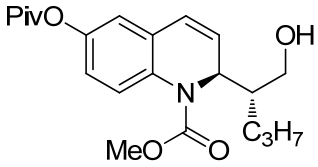
(*R*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-6-(pivaloyloxy)quinoline-1(2*H*)-carboxylate (4e-*syn*)



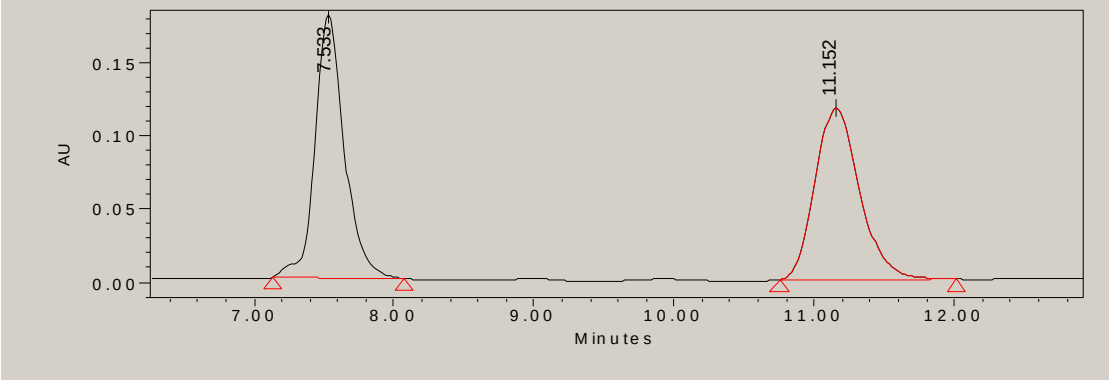
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.401	3766288	50.29	355737	bb	Unknown
2		15.992	3722318	49.71	125398	bb	Unknown



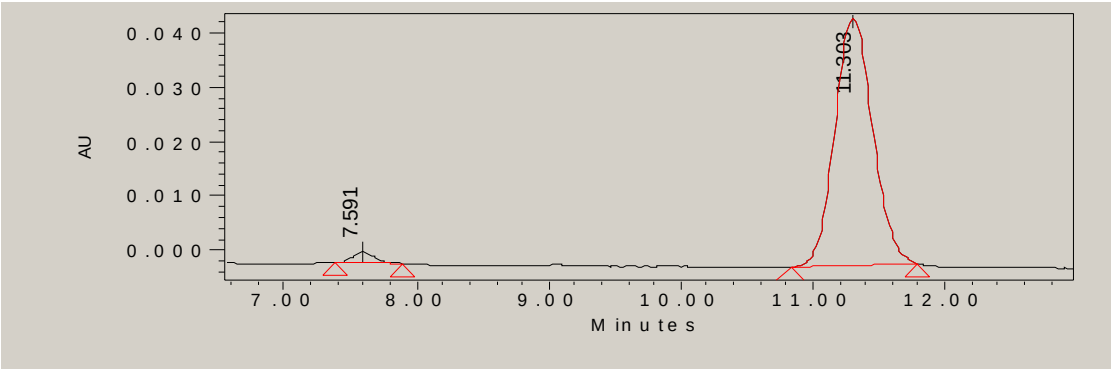
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.371	1181336	99.44	100697	bb	Unknown
2		15.990	6704	0.56	323	bb	Unknown



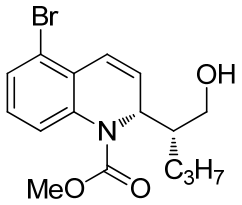
(*S*)-Methyl 2-((*R*)-1-hydroxypentan-2-yl)-6-(pivaloyloxy)quinoline-1(2*H*)-carboxylate (4e-*anti*)



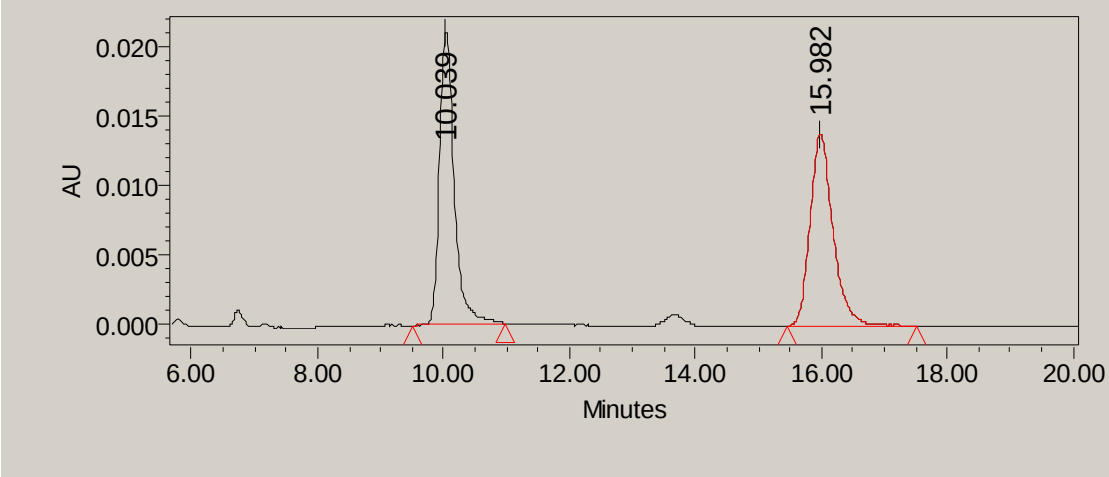
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.533	2656478	50.76	179189	bb	Unknown
2		11.152	2577053	49.24	116695	bb	Unknown



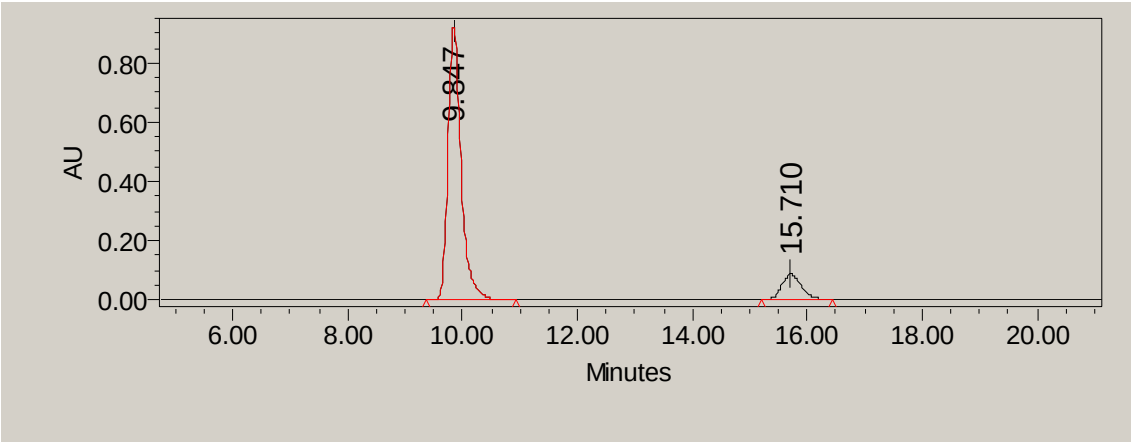
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.591	30701	3.43	2224	bb	Unknown
2		11.303	865278	96.57	44715	bb	Unknown



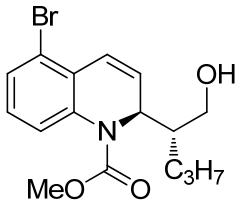
(*R*)-Methyl 5-bromo-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4f-*syn*)



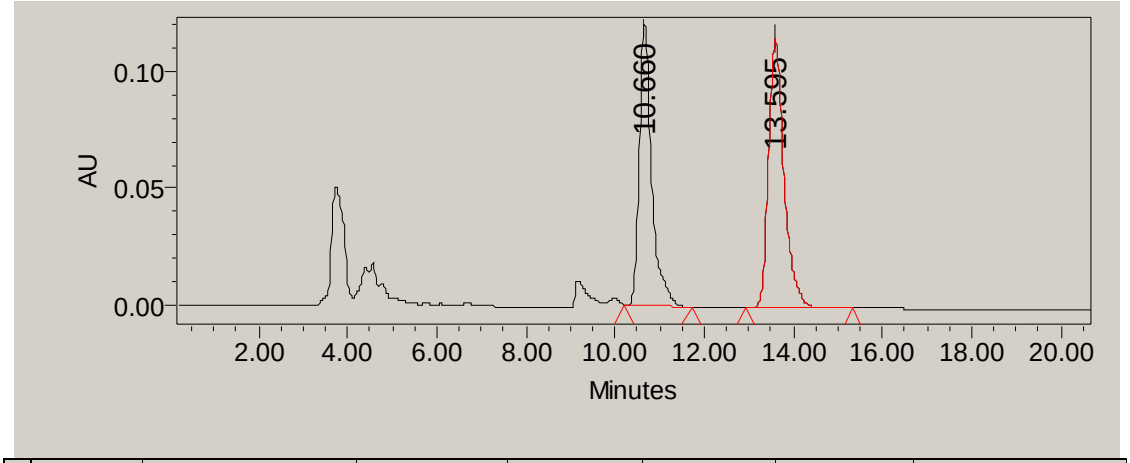
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		10.039	341081	49.18	21171	bb	Unknown
2		15.982	352410	50.82	13890	bb	Unknown



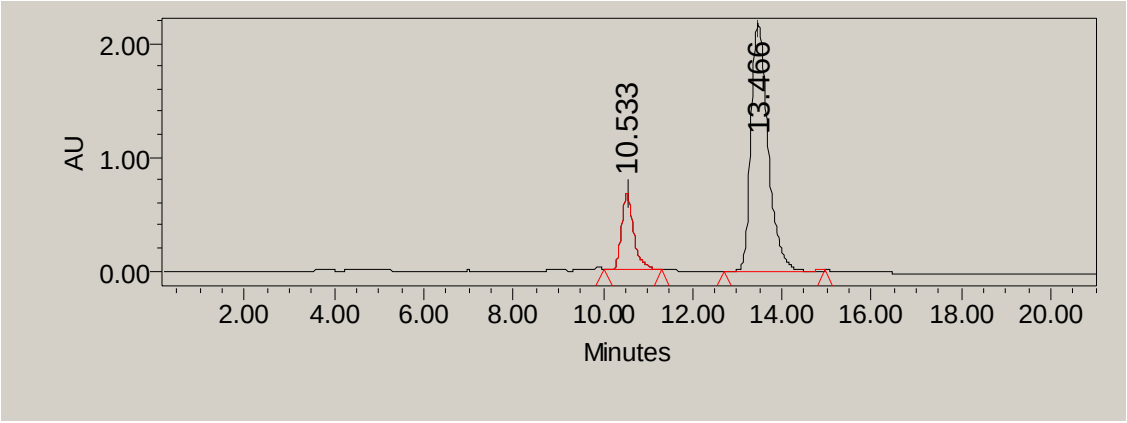
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		9.847	14743795	87.52	918252	bb	Unknown
2		15.710	2101996	12.48	86466	bb	Unknown



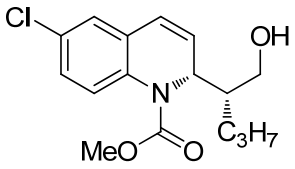
(*S*)-Methyl 5-bromo-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4f-*anti*)



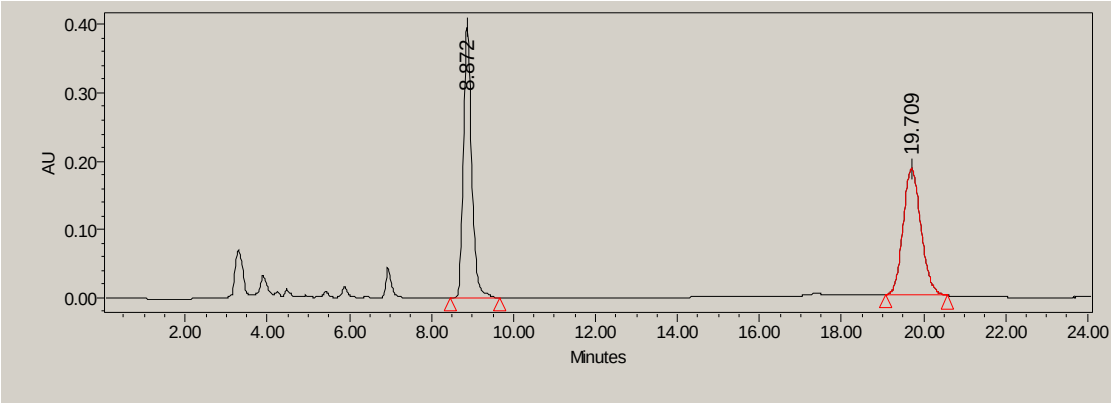
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		10.660	2367406	45.67	120634	bb	Unknown
2		13.595	2816680	54.33	115870	bb	Unknown



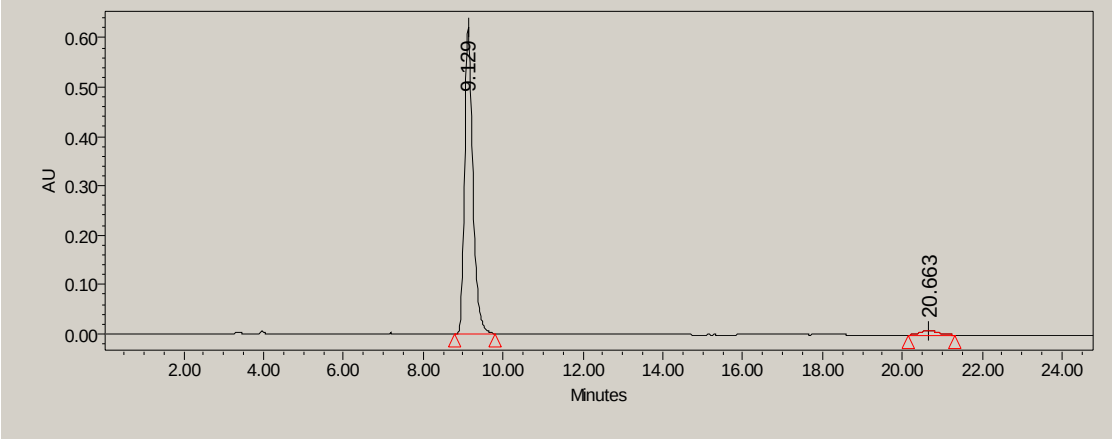
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		10.533	12712018	18.04	666726	bb	Unknown
2		13.466	57761195	81.96	2172626	bb	Unknown



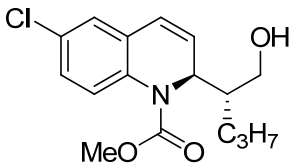
(*R*)-Methyl 6-chloro-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4g-*syn*)



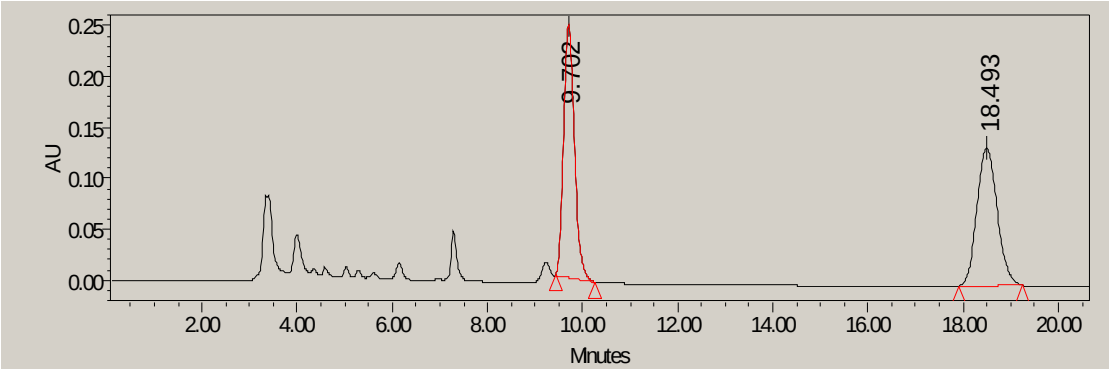
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.872	5713520	50.57	397655	bb	Unknown
2		19.709	5585578	49.43	184432	bb	Unknown



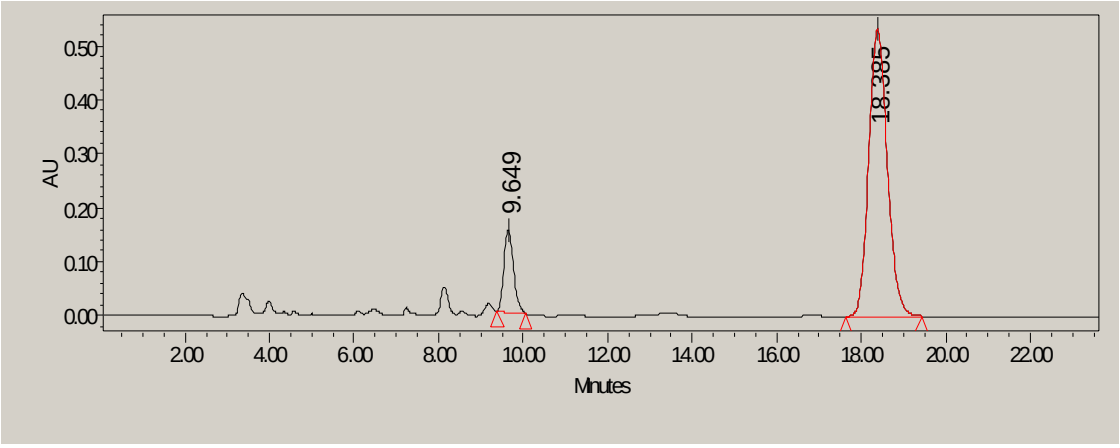
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		9.129	8597898	97.12	612198	bb	Unknown
2		20.663	255144	2.88	8436	bb	Unknown



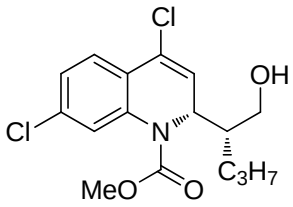
(*S*)-Methyl 6-chloro-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4g-*anti*)



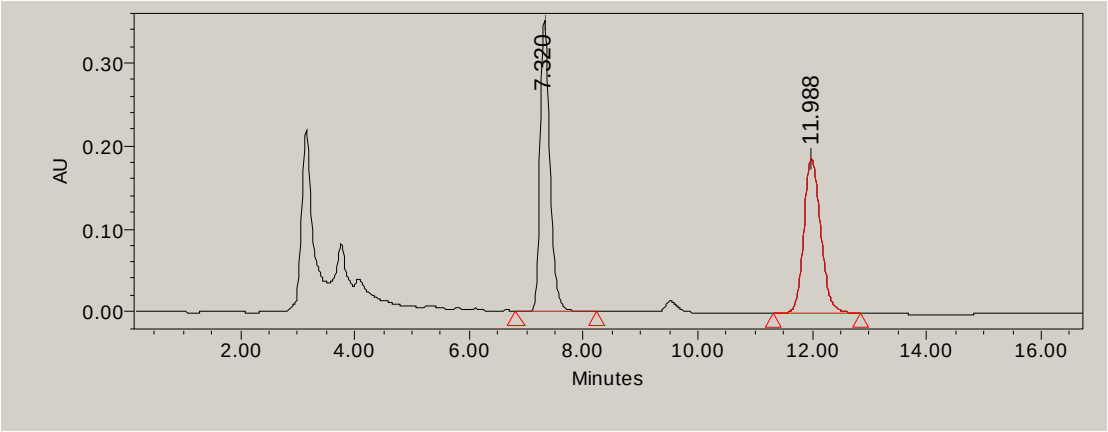
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		9.702	3897052	49.27	248263	bb	Unknown
2		18.493	4013074	50.73	135126	bb	Unknown



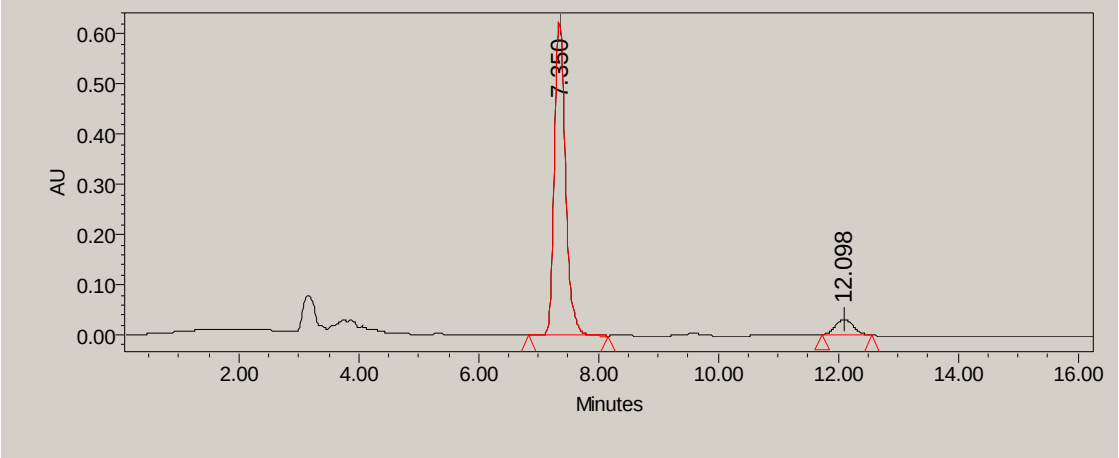
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		9.649	2405171	12.90	151682	bb	Unknown
2		18.385	16241822	87.10	532223	bb	Unknown



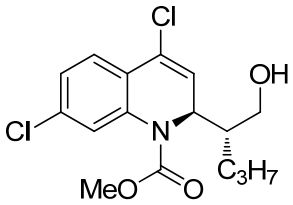
(*S*)-Methyl 4,7-dichloro-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4h-*syn*)



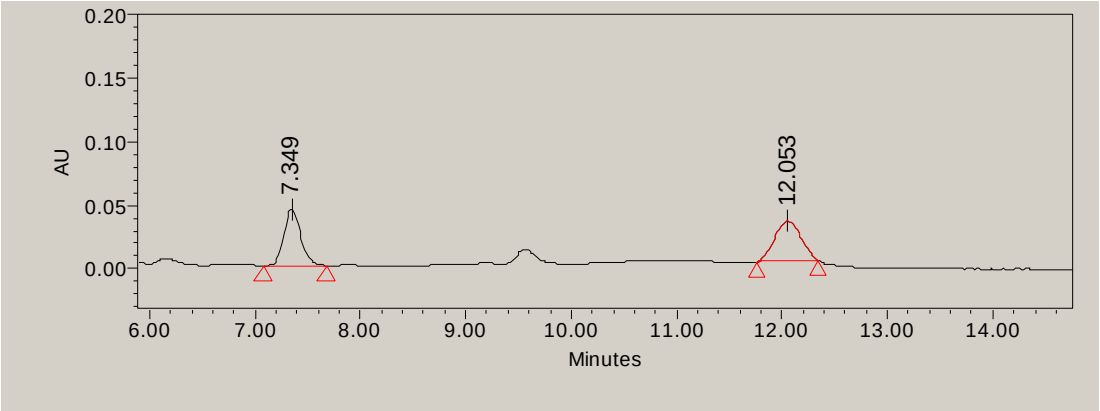
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.320	4032589	51.26	348023	bb	Unknown
2		11.988	3833590	48.74	186177	bb	Unknown



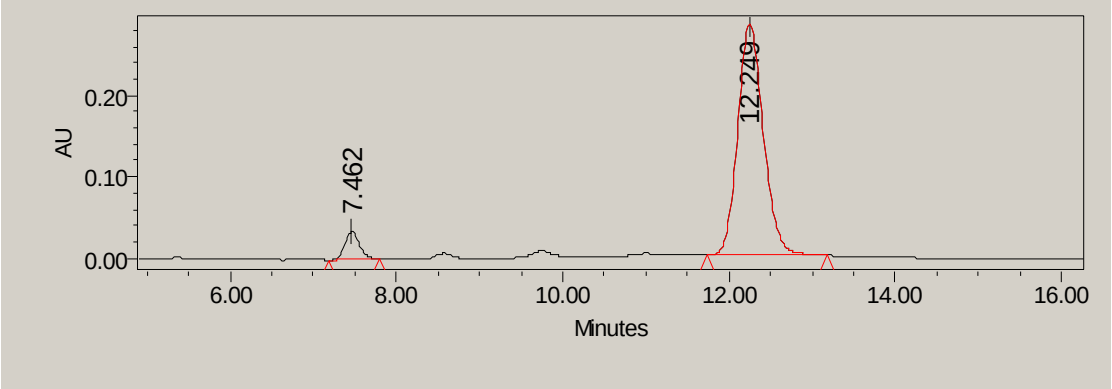
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.350	8150405	92.48	624187	bb	Unknown
2		12.098	663075	7.52	31638	bb	Unknown



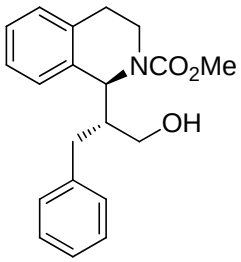
(*R*)-Methyl 4,7-dichloro-2-((*R*)-1-hydroxypentan-2-yl)quinoline-1(2*H*)-carboxylate (4h-*anti*)



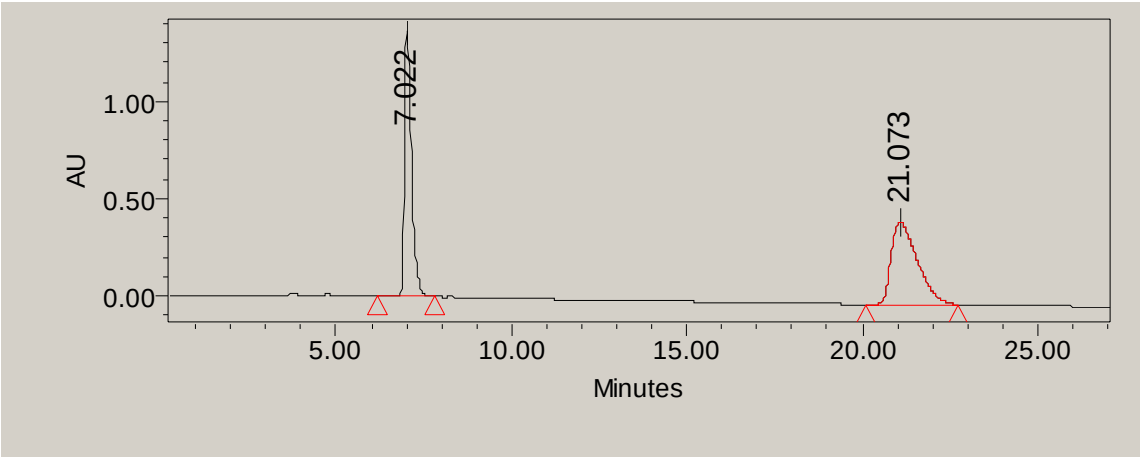
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.349	495819	48.09	44815	bb	Unknown
2		12.053	535257	51.91	31214	bb	Unknown



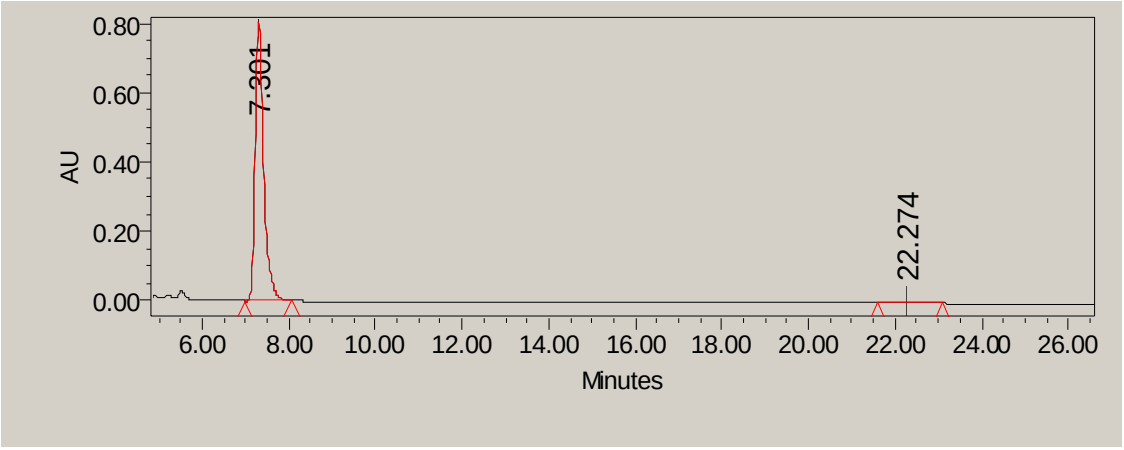
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.462	415328	5.52	35968	bb	Unknown
2		12.249	7104965	94.48	327691	bb	Unknown



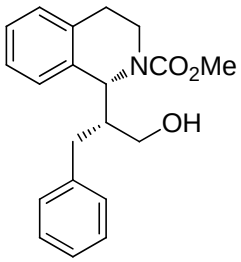
(*S*)-Methyl 1-((*R*)-1-hydroxy-3-phenylpropan-2-yl)-3,4-dihydroisoquinoline-2(1*H*) - carboxylate (7b-*anti*)



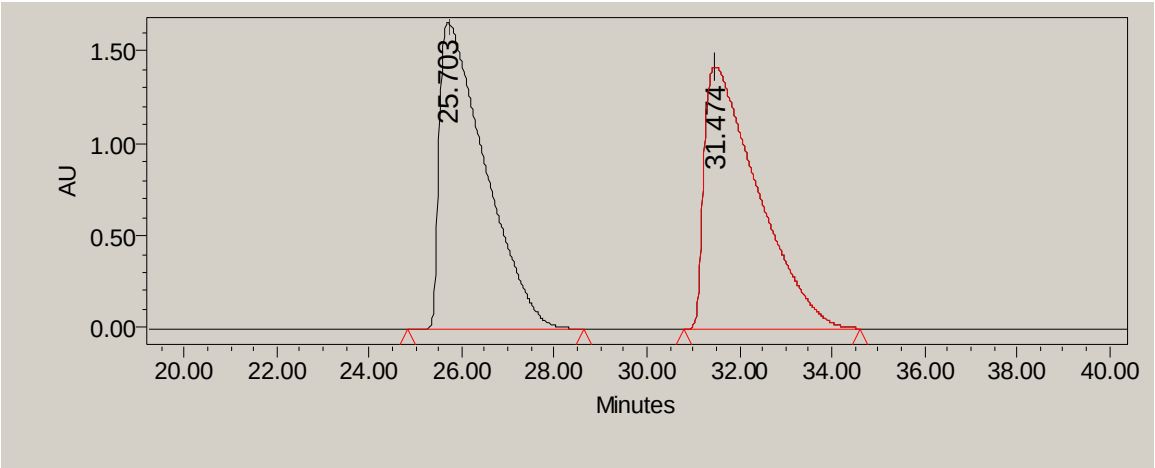
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.022	19640056	48.90	1367065	bb	Unknown
2		21.073	20520380	51.10	415331	bb	Unknown



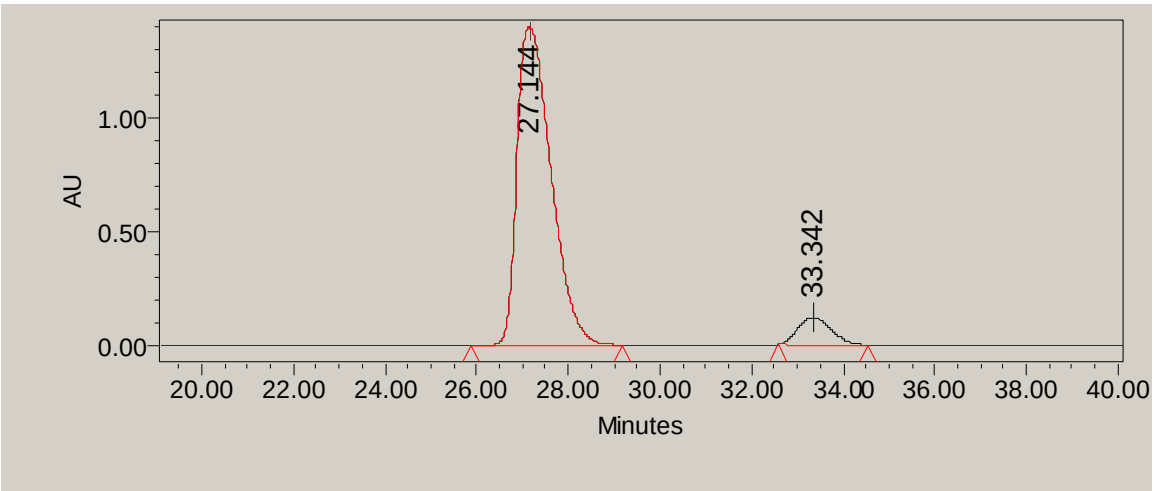
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.301	10827855	97.46	808041	bb	Unknown
2		22.274	282465	2.54	6296	bb	Unknown



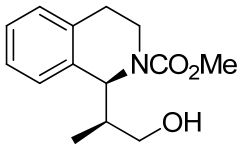
(*R*)-Methyl 1-((*R*)-1-hydroxy-3-phenylpropan-2-yl)-3,4-dihydroisoquinoline-2(1*H*) - carboxylate (7b-*syn*)



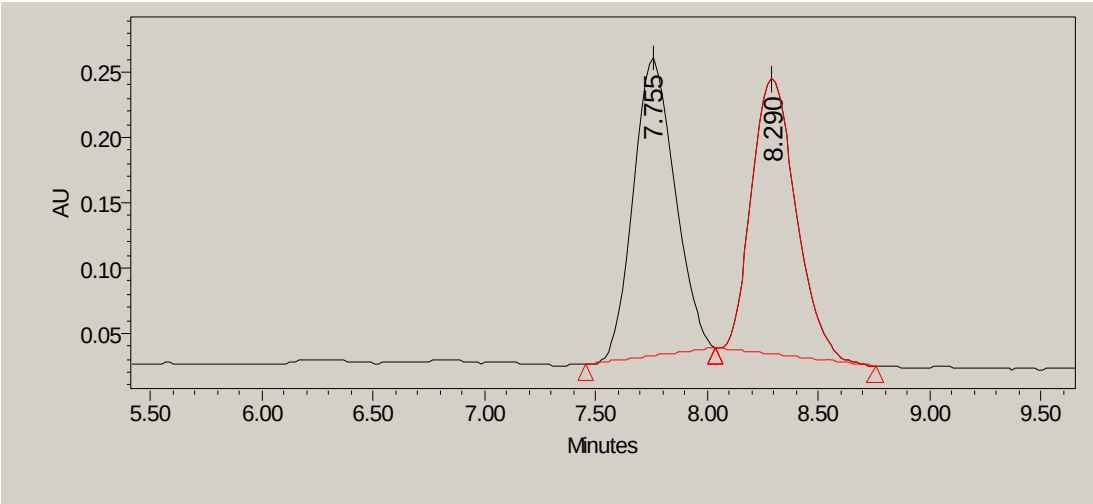
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		25.703	113904532	49.84	1657906	bb	Unknown
2		31.474	114630022	50.16	1420518	bb	Unknown



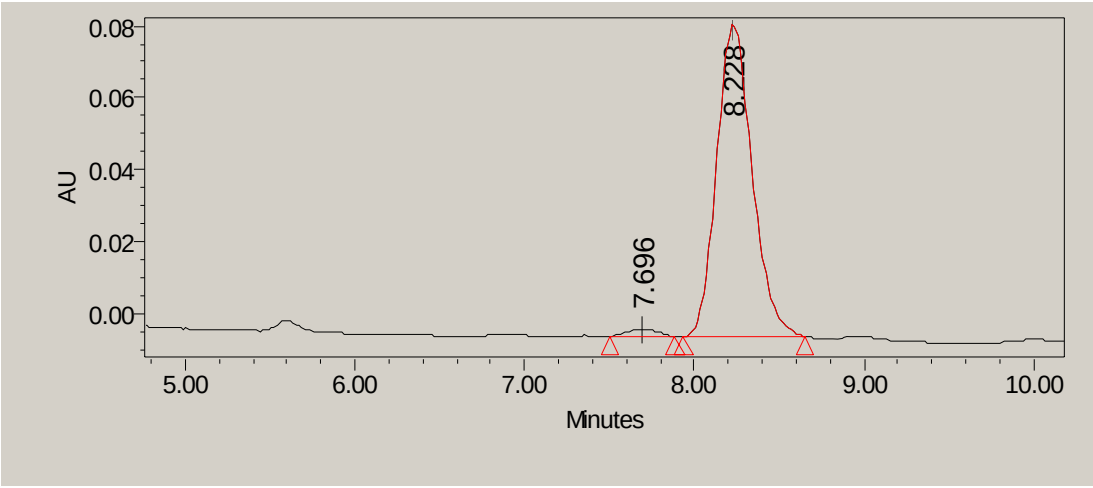
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		27.144	72521427	92.19	1401115	bb	Unknown
2		33.342	6144468	7.81	121312	bb	Unknown



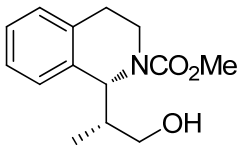
(*S*)-Methyl 1-((*S*)-1-hydroxypropan-2-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (7b-2-syn)



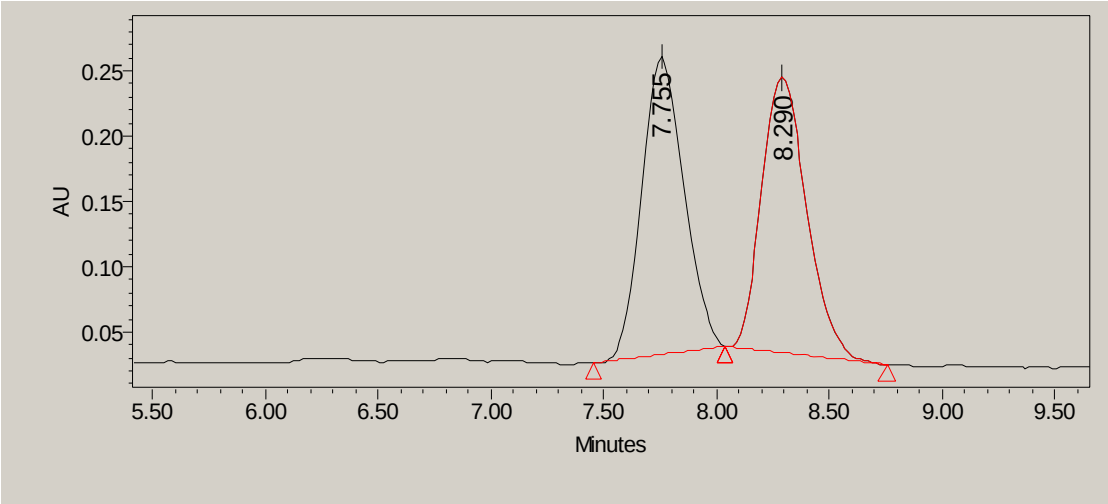
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.755	2962114	50.30	227917	bb	Unknown
2		8.290	2926451	49.70	210675	bb	Unknown



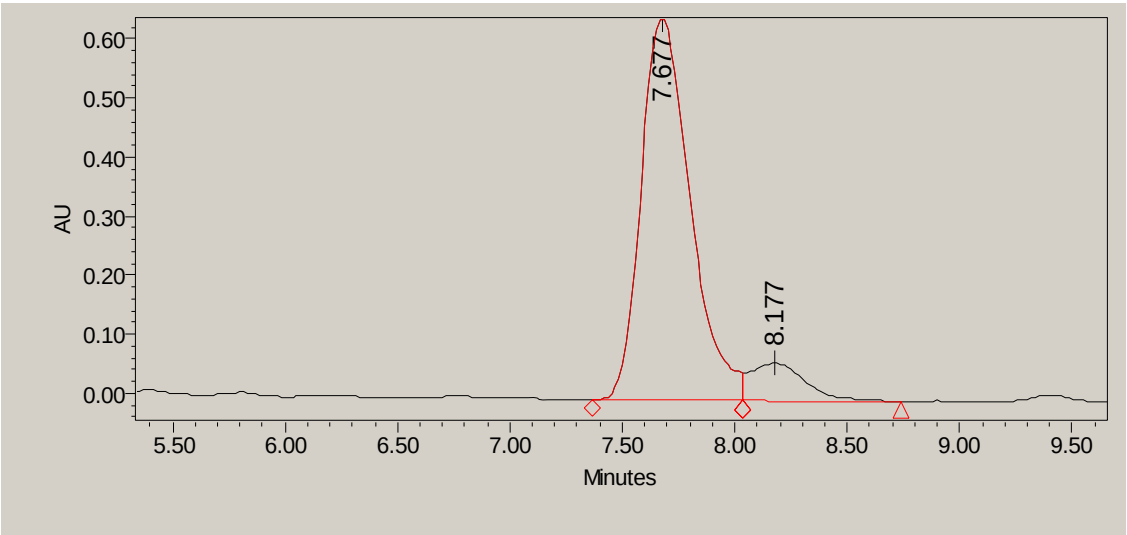
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.696	24724	1.91	2033	bb	Unknown
2		8.228	1267086	98.09	86722	bb	Unknown



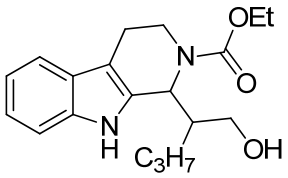
(*R*)-Methyl 1-((*R*)-1-hydroxypropan-2-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (7b-1-minor)



	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.755	2962114	50.30	227917	bb	Unknown
2		8.290	2926451	49.70	210675	bb	Unknown

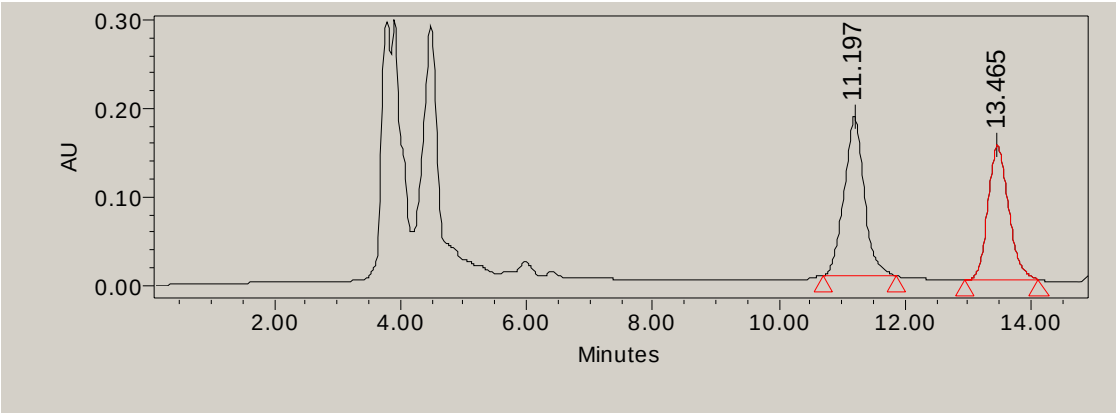


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		7.677	9857959	90.14	646610	VV	Unknown
2		8.177	1078878	9.86	63268	VB	Unknown

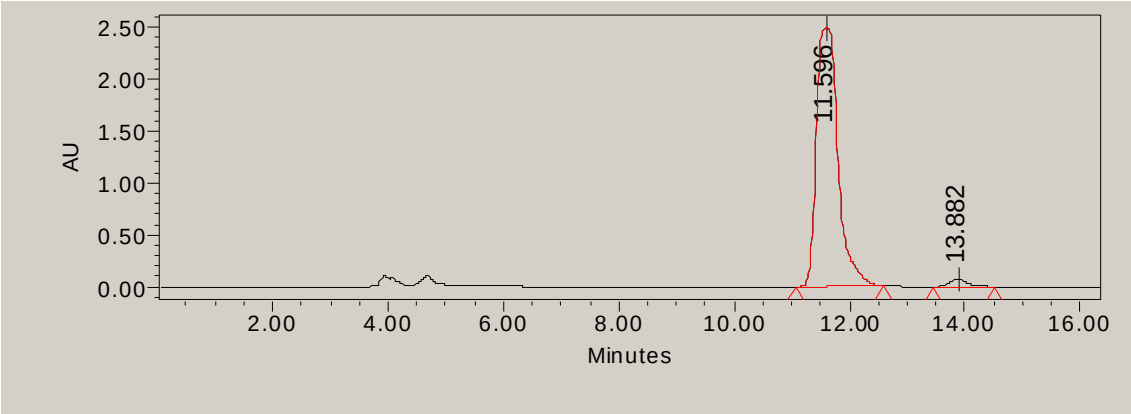


Ethyl 1-(1-hydroxypentan-2-yl)-3,4-dihydro-1H-pyrido[3,4-b]indole-2(9*H*)-carboxylate (7c)

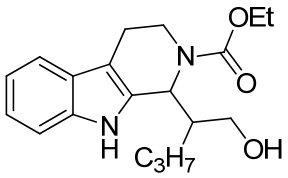
major:



	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		11.197	3672283	51.51	174170	bb	Unknown
2		13.465	3456751	48.49	153849	bb	Unknown



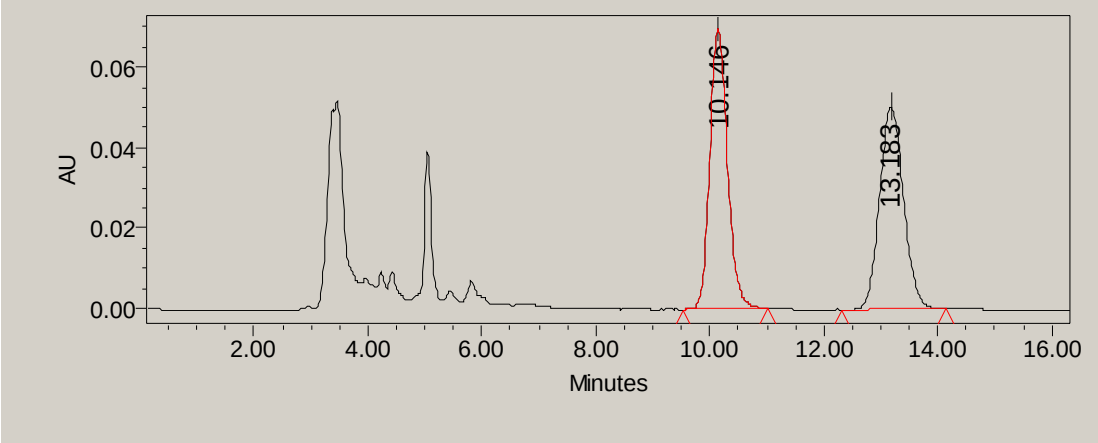
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		11.596	64610407	97.62	2488765	bb	Unknown
2		13.882	1578212	2.38	70334	bb	Unknown



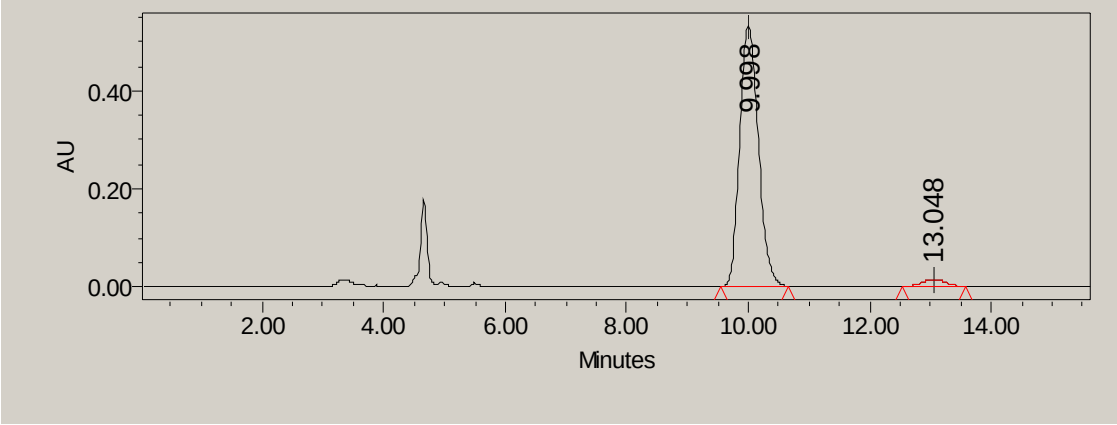
Ethyl 1-(1-hydroxypentan-2-yl)-3,4-dihydro-1H-pyrido[3,4-b]indole-2(9*H*)-carboxylate (7c)

minor:

,



	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		10.146	1498582	50.59	69781	bb	Unknown
2		13.183	1463635	49.41	50376	bb	Unknown



	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		9.998	11214357	96.54	531982	bb	Unknown
2		13.048	402263	3.46	15199	bb	Unknown