

Supporting Information

Synthesis of Optically Active Dihydropyrans from Asymmetric [4+2] Cycloaddition of β,γ -Unsaturated α -Ketoesters with Allenic Esters

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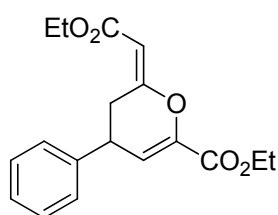
CONTENTS

1. General Remarks	S2
2. General Procedure and Data of Adducts	S3
3. Chiral HPLC traces of the products 3	S26
4. X-ray Crystal Data of 3na	S62
5. Reference	S63

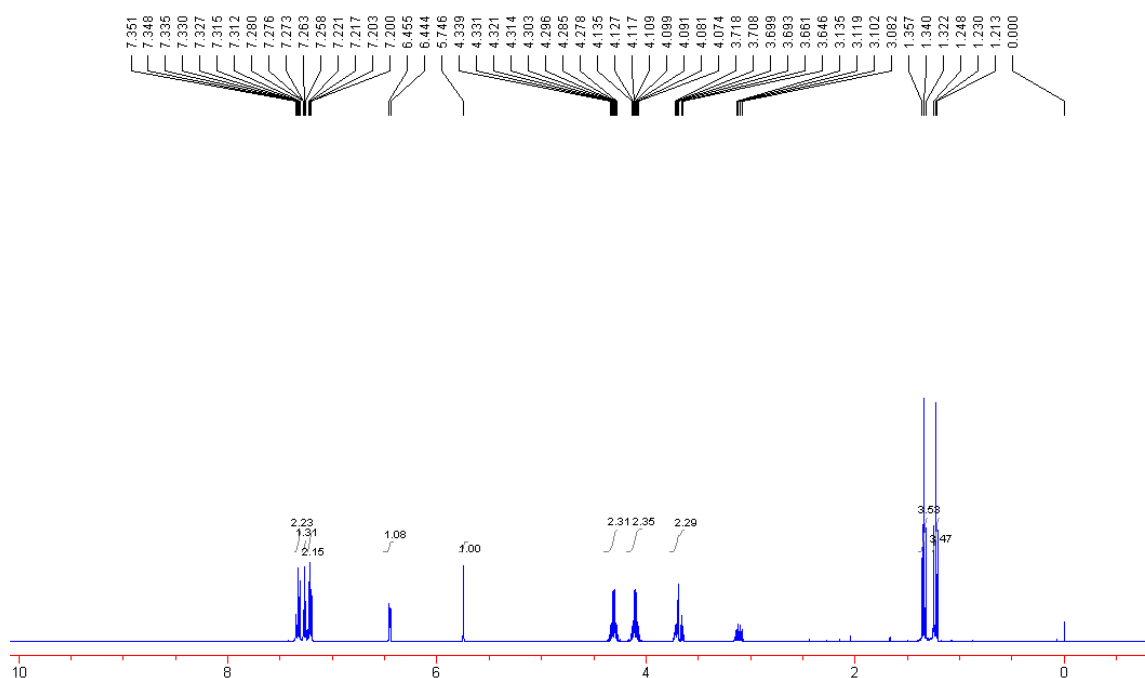
General Remarks: ^1H NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer for solution in CDCl_3 with tetramethylsilane (TMS) as internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1} . Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_{\text{D}}$ -values are given in unit of $10 \text{ deg}^{-1} \text{ cm}^2 \text{ g}^{-1}$. Chiral HPLC was performed on a SHIMADZU SPD-10A vp series with chiral columns (Chiralpak AD-H, IC-H columns $4.6 \times 250 \text{ mm}$, (Daicel Chemical Ind., Ltd.)). THF, toluene and Et_2O were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN , 1,2-dichloroethane and dichloromethane were distilled from CaH_2 under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All β,γ -unsaturated α -ketoesters were prepared according to the literature.¹ The cinchona alkaloid derivatives catalysts were prepared according to the literature.²

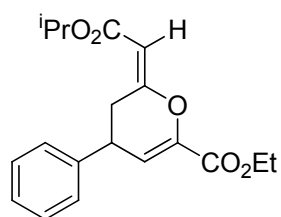
General Procedure and Data of Adducts 3

Under argon atmosphere, allenates **2** (0.12 mmol) was added to a solution of β,γ -unsaturated α -ketoesters **1** (0.1 mmol), β -ICD (0.02 mmol) in flourobenezene (3.0 mL) and stirred at -15 °C or room temperature for 24 h. The solvent was removed under reduced pressure and residue was chromatographed on silica gel (elution with petroleum ether/EtOAc = 8:1-4:1) to provide compound **3**.



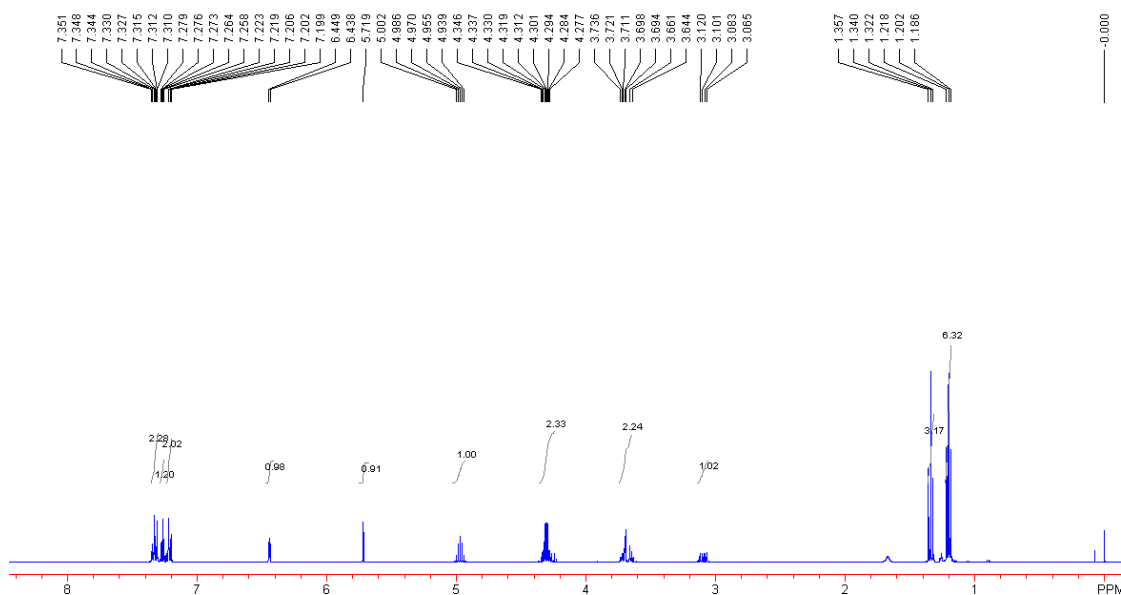
(*E*)-Ethyl 2-(2-ethoxy-2-oxoethylidene)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate **3aa**: a slight yellow liquid (28.4 mg, 90%); This is a known compound;³ ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.23 (t, $J = 7.2$ Hz, 3H), 1.34 (t, $J = 7.2$ Hz, 3H), 3.11 (dd, $J = 8.0$ Hz, 4.8 Hz, 1H), 3.68-3.72 (m, 2H), 4.07-4.14 (m, 2H), 4.28-4.34 (m, 2H), 5.75 (s, 1H), 6.45 (d, $J = 4.8$ Hz, 1H), 7.20-7.22 (m, 2H), 7.26-7.28 (m, 1H), 7.31-7.35 (m, 2H); $[\alpha]_D^{20} = -76.5$ (c 1.00, CH_2Cl_2) (85% ee); Chiralcel AD-H, hexane/ $^i\text{PrOH}$ = 80/20, 0.6 mL/min, 254 nm, $t_{\text{major}} = 7.97$ min, $t_{\text{minor}} = 7.35$ min.

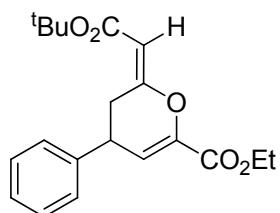
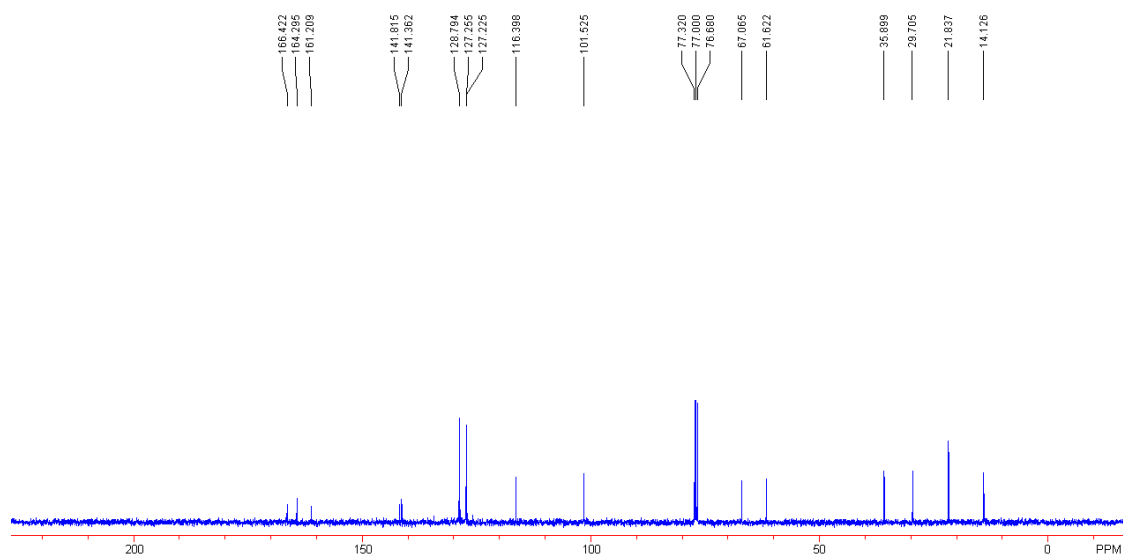




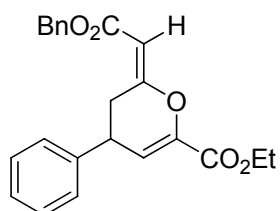
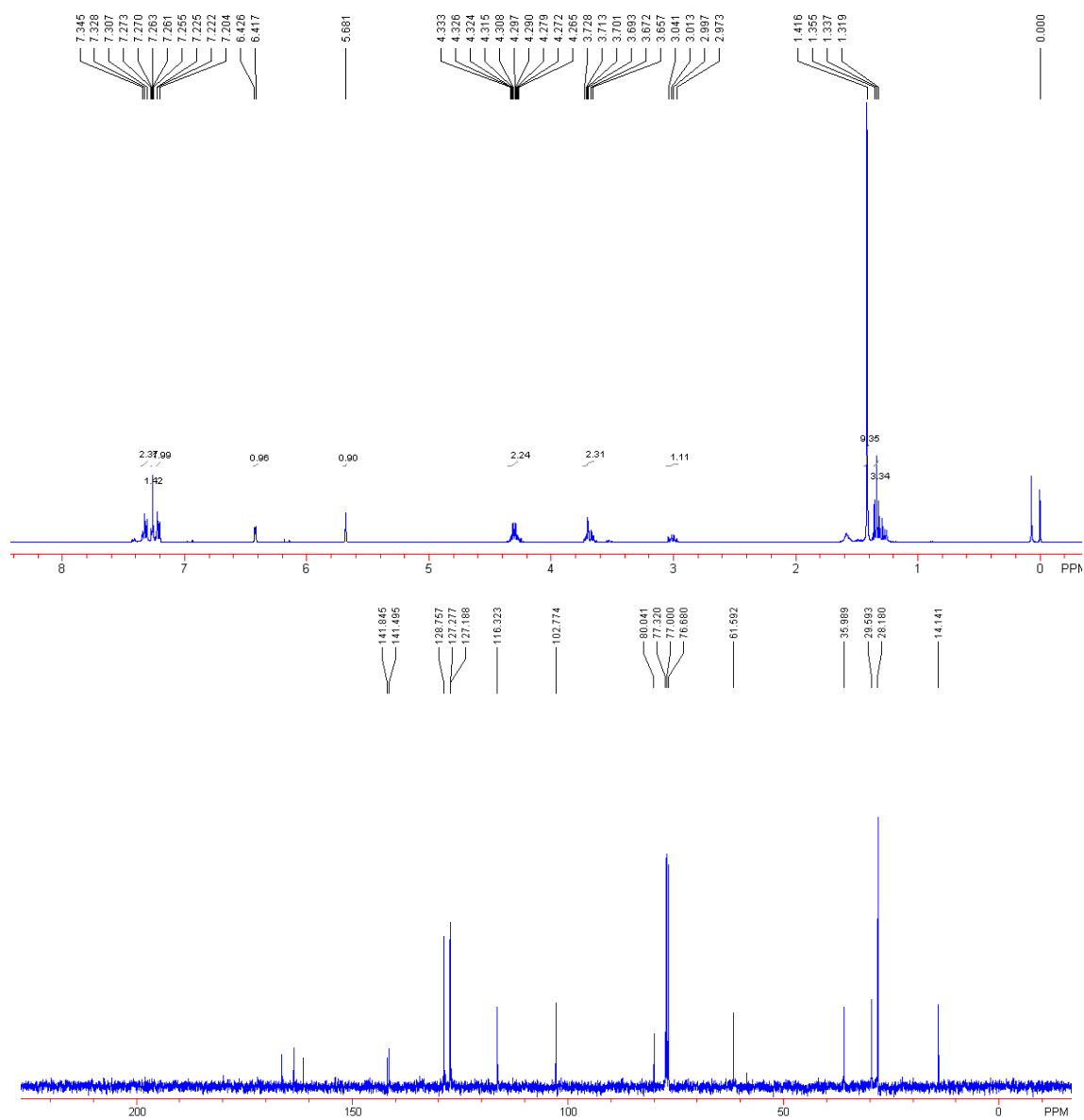
(*E*)-ethyl 2-(2-isopropoxy-2-oxoethylidene)-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate

3ab: a slight yellow liquid (26.4 mg, 80%); ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.19 (d, $J = 6.4$ Hz, 3H), 1.21 (d, $J = 6.4$ Hz, 3H), 1.34 (t, $J = 7.2$ Hz, 3H), 3.09 (dd, $J = 14.4$ Hz, 7.2 Hz, 1H), 3.64-3.74 (m, 2H), 4.28-4.35 (m, 2H), 4.97 (sept, $J = 6.4$ Hz, 1H), 5.72 (s, 1H), 6.46 (d, $J = 4.4$ Hz, 1H), 7.20-7.22 (m, 2H), 7.26-7.28 (m, 1H), 7.31-7.35 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.1, 21.8, 29.7, 35.9, 61.6, 67.1, 101.5, 116.4, 127.2, 127.3, 128.8, 141.4, 141.8, 161.2, 164.3, 166.4; IR (CH_2Cl_2) ν 3063, 3029, 2984, 2937, 1727, 1694, 1667, 1607, 1576, 1496, 1450, 1376, 1261, 1078, 982, 917, 848, 820, 742, 688, 636, 570 cm^{-1} ; MS (ESI) m/z 353.0 ($\text{M}+\text{Na}^+$); HRMS (ESI) Calcd. for $\text{C}_{19}\text{H}_{22}\text{O}_5\text{Na}$ requires ($\text{M}+\text{Na}^+$): 353.1359, Found: 353.1360; $[\alpha]_D^{20} = -57$ (c 0.30, CH_2Cl_2) (77% ee); Chiralcel AD-H, hexane/*i*PrOH = 90/10, 0.6 mL/min, 254 nm, $t_{\text{major}} = 10.06$ min, $t_{\text{minor}} = 8.98$ min.



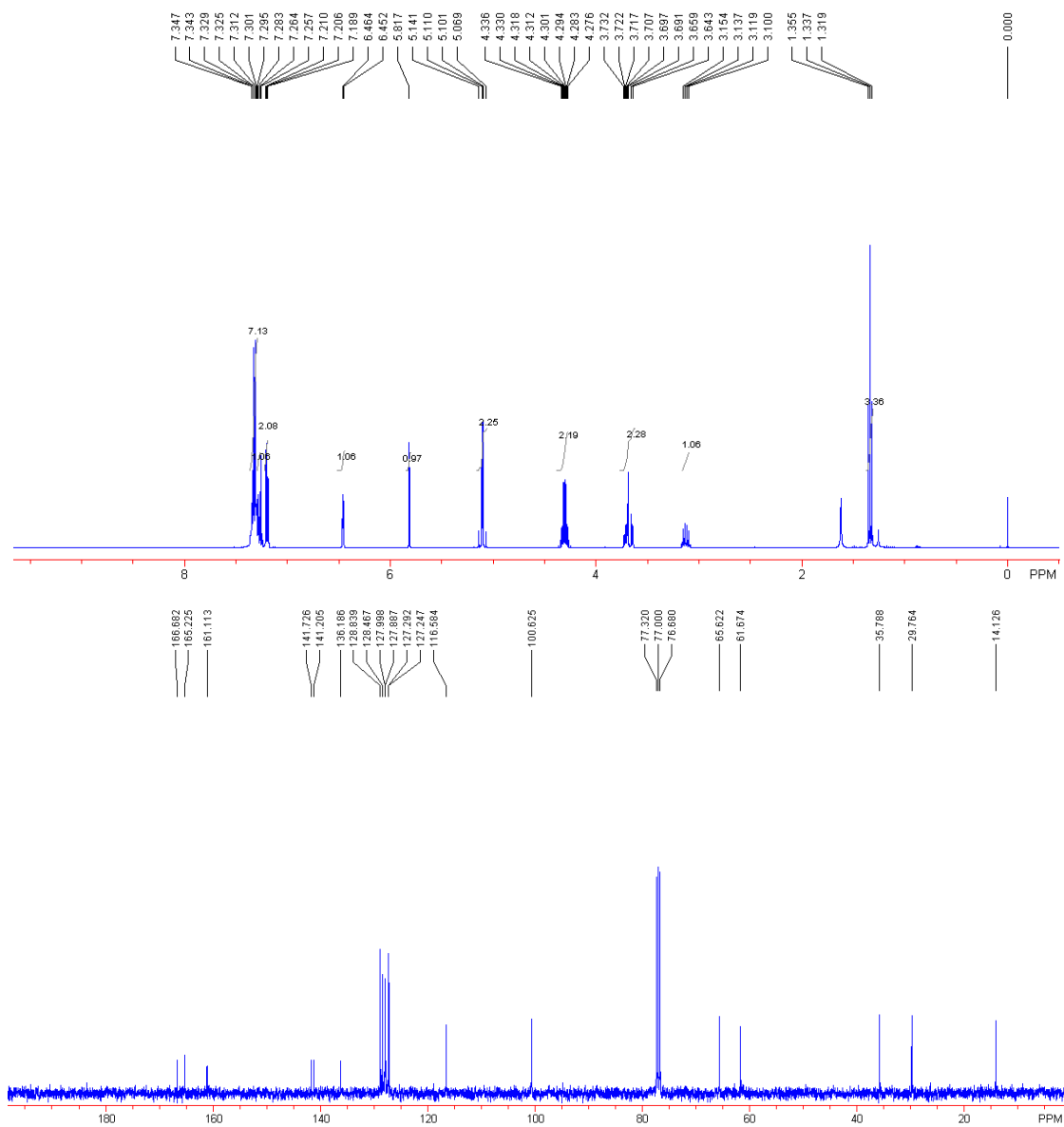


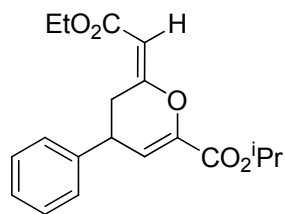
(*E*)-ethyl 2-(2-(tert-butoxy)-2-oxoethylidene)-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate **3ac**: a slight yellow liquid (26.8 mg, 78%); ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.34 (t, *J* = 7.2 Hz, 3H), 1.42 (s, 9H), 3.01 (dd, *J* = 17.6 Hz, 11.2 Hz, 1H), 3.65-3.73 (m, 2H), 4.25-4.33 (m, 2H), 5.68 (s, 1H), 6.42 (d, *J* = 3.6 Hz, 1H), 7.20-7.23 (m, 2H), 7.26-7.27 (m, 1H), 7.31-7.35 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 14.1, 28.2, 29.6, 36.0, 61.6, 80.0, 102.8, 116.3, 127.2, 127.3, 128.8, 141.5, 141.8, 161.3, 163.5, 166.3; IR (CH₂Cl₂) ν 2979, 2932, 2359, 2342, 1736, 1702, 1655, 1455, 1393, 1370, 1255, 1159, 1114, 862, 759, 700 cm⁻¹; MS (ESI) *m/z* 367.1 (M+Na⁺); HRMS (ESI) Calcd. for C₂₀H₂₄O₅Na requires (M+Na⁺): 367.1516, Found: 367.1516; [α]_D²⁰ = -114.5 (c 0.90, CH₂Cl₂) (83% ee); Chiralcel AD-H, hexane/ⁱPrOH = 90/10, 0.6 mL/min, 254 nm, *t*_{major} = 12.96 min, *t*_{minor} = 11.77 min.



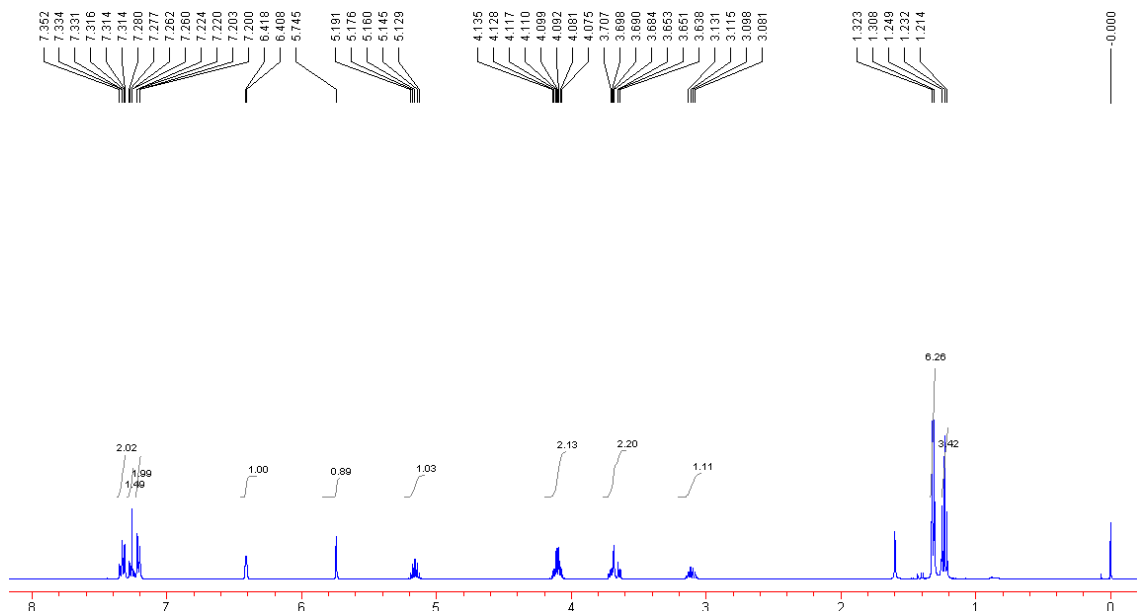
(*E*)-ethyl 2-(2-(benzyloxy)-2-oxoethylidene)-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate **3ad**: a slight yellow liquid (28.7 mg, 76%); ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.34 (t, *J* = 7.2 Hz, 3H), 3.13 (dd, *J* = 14.8 Hz, 7.6 Hz, 1H), 3.64-3.73 (m, 2H), 4.28-4.34 (m, 2H), 5.09 (d, *J* = 12.8 Hz, 1H), 5.13 (d, *J* = 12.8 Hz, 1H), 5.82 (s, 1H), 6.46 (d, *J* = 4.8 Hz, 1H), 7.19-7.21 (m, 2H), 7.26-7.28 (m, 1H), 7.30-7.35 (m, 7H); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 14.1,

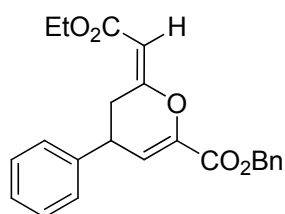
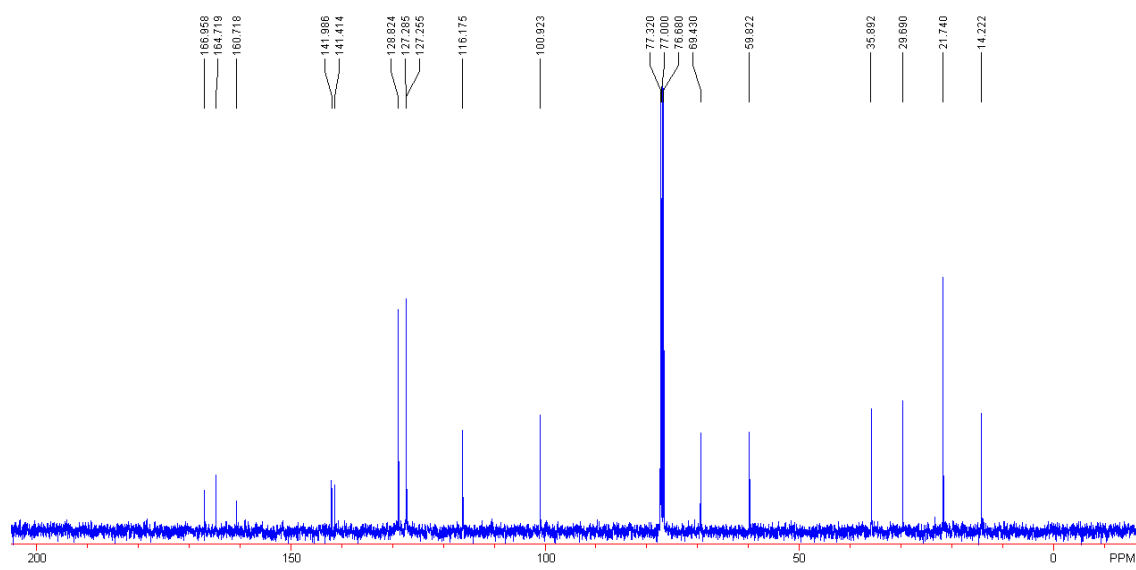
29.8, 35.8, 61.7, 65.6, 100.6, 116.6, 127.2, 127.3, 127.9, 128.0, 128.5, 128.8, 136.2, 141.2, 141.7, 161.1, 165.2, 166.7; IR (CH₂Cl₂) ν 3060, 3035, 1732, 1694, 1612, 1575, 1450, 1320, 1307, 1261, 1205, 1089, 996, 904, 746, 697 cm⁻¹; MS (ESI) m/z 401.0 (M+Na⁺); HRMS (ESI) Calcd. for C₂₃H₂₂O₅Na requires (M+Na⁺): 401.1359, Found: 401.1353; $[\alpha]_D^{20} = -131.0$ (c 1.70, CH₂Cl₂) (83% ee); Chiralcel AD-H, hexane/ⁱPrOH = 98/2, 0.6 mL/min, 254 nm, $t_{\text{major}} = 21.53$ min, $t_{\text{minor}} = 17.49$ min.



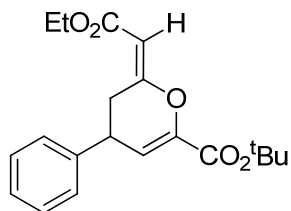
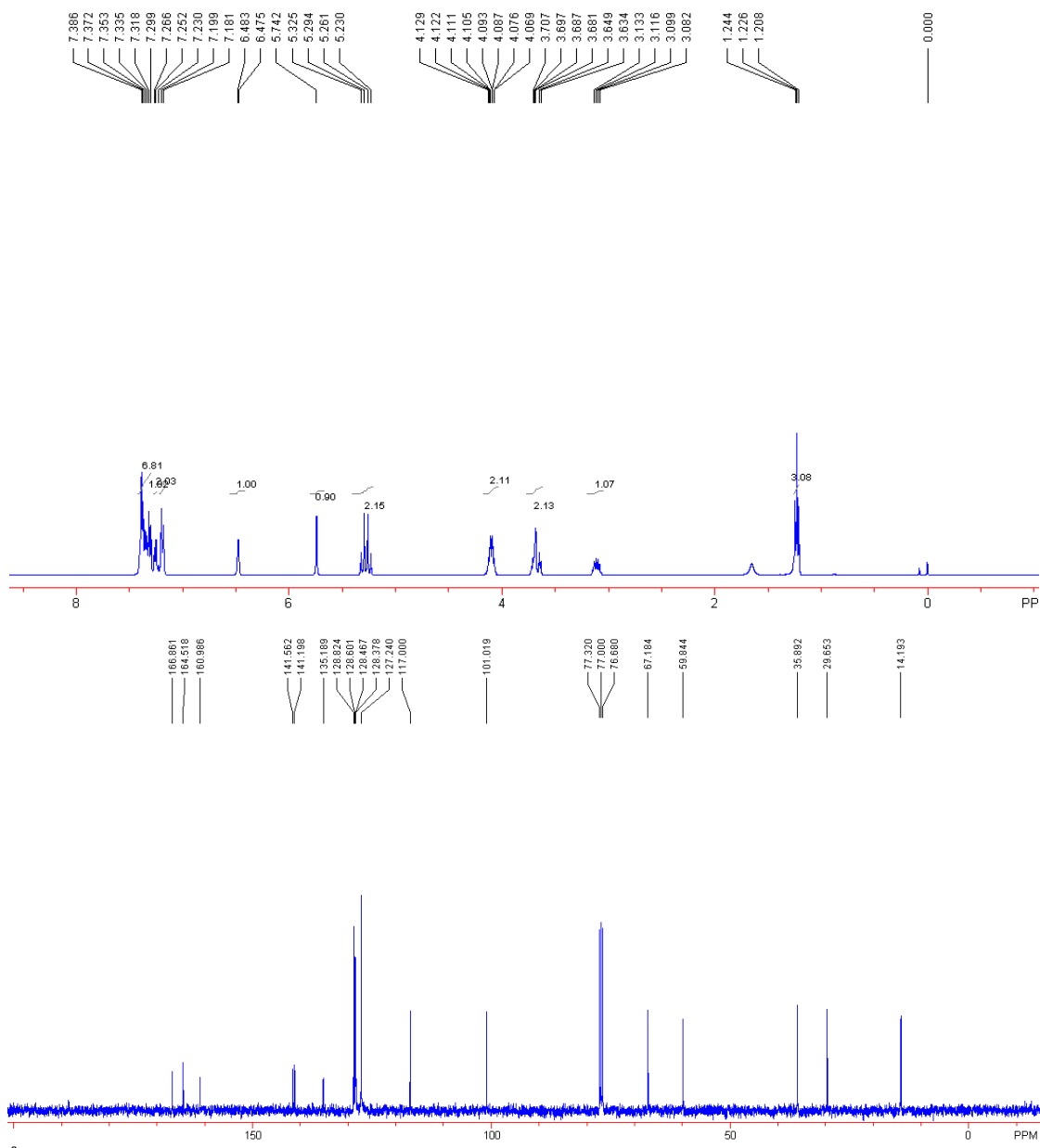


(*E*)-isopropyl 2-(2-ethoxy-2-oxoethylidene)-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate
3ba: a slight yellow liquid (37.0 mg, 90%); ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.23 (t, *J* = 7.2 Hz, 3H), 1.32 (d, *J* = 6.0 Hz, 6H), 3.11 (dd, *J* = 13.6 Hz, 6.8 Hz, 1H), 3.64-3.71 (m, 2H), 4.08-4.14 (m, 2H), 5.16 (sept, *J* = 6.0 Hz, 1H), 5.75 (s, 1H), 6.41 (d, *J* = 4.0 Hz, 1H), 7.20-7.22 (m, 2H), 7.26-7.28 (m, 1H), 7.31-7.33 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 14.2, 21.7, 29.7, 35.9, 59.8, 69.4, 100.9, 116.2, 127.25, 127.29, 128.8, 141.4, 142.0, 160.7, 164.7, 167.0; IR (CH₂Cl₂) ν 2984, 2937, 1727, 1694, 1667, 1607, 1576, 1496, 1450, 1376, 1261, 1078, 982, 917, 848, 820, 742, 688, 636, 570 cm⁻¹; MS (ESI) *m/z* 331.0 (M+H⁺); HRMS (MALDI) Calcd. for C₁₉H₂₂O₅Na requires (M+Na⁺): 353.1360, Found: 353.1371; [α]_D²⁰ = -205.1 (c 1.35, CH₂Cl₂) (86% ee); Chiralcel AD-H, hexane/ⁱPrOH = 95/5, 0.6 mL/min, 254 nm, *t*_{major} = 12.14 min, *t*_{minor} = 11.38 min.



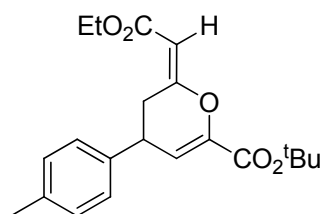
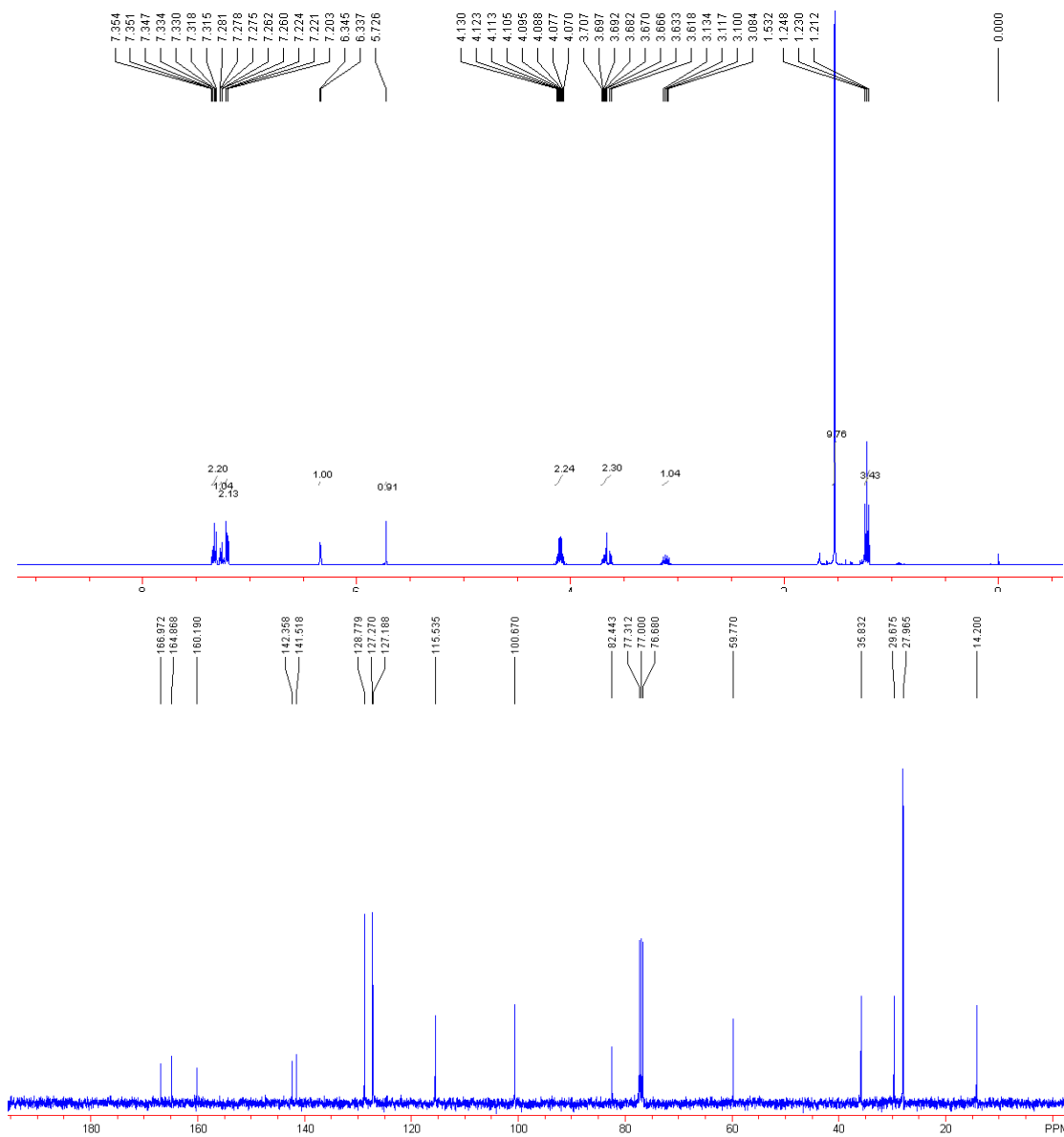


(*E*)-benzyl 2-(2-ethoxy-2-oxoethylidene)-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate **3ca**: a slight yellow liquid (34.0 mg, 90%); ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.23 (t, $J = 7.2$ Hz, 3H), 3.11 (dd, $J = 13.6$ Hz, 6.8 Hz, 1H), 3.63-3.71 (m, 2H), 4.07-4.13 (m, 2H), 5.25 (d, $J = 12.4$ Hz, 1H), 5.31 (d, $J = 12.4$ Hz, 1H), 5.74 (s, 1H), 6.48 (d, $J = 3.2$ Hz, 1H), 7.18-7.20 (m, 2H), 7.23-7.27 (m, 1H), 7.30-7.39 (m, 7H); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.2, 29.7, 35.9, 59.8, 67.2, 101.0, 117.0, 127.2, 128.4, 128.5, 128.6, 128.8, 135.2, 141.2, 141.6, 161.0, 164.5, 166.9; IR (CH_2Cl_2) ν 2359, 2342, 1734, 1716, 1654, 1276, 1260, 1168, 1116, 750, 668 cm^{-1} ; MS (ESI) m/z 401.0 ($\text{M}+\text{Na}^+$); HRMS (ESI) Calcd. for $\text{C}_{23}\text{H}_{22}\text{O}_5\text{Na}$ requires ($\text{M}+\text{Na}^+$): 401.1359, Found: 401.1353; $[\alpha]_{\text{D}}^{20} = -112.3$ (c 0.40, CH_2Cl_2) (84% ee); Chiralcel AD-H, hexane/ $^i\text{PrOH} = 90/10$, 0.7 mL/min, 254 nm, $t_{\text{major}} = 14.58$ min, $t_{\text{minor}} = 13.68$ min.

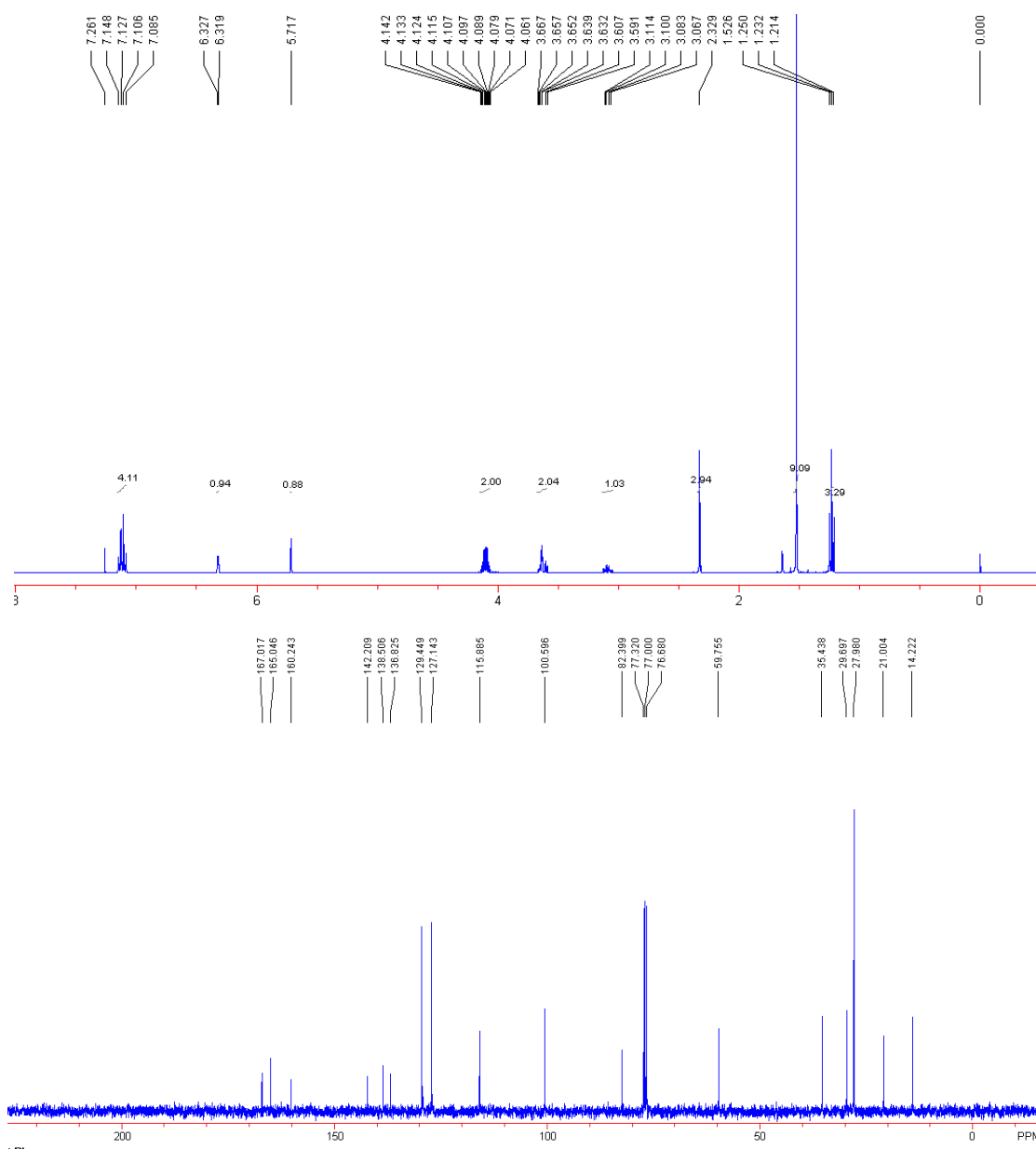


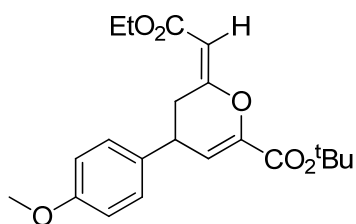
(*E*)-*tert*-butyl 2-(2-ethoxy-2-oxoethylidene)-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate
3da: a slight yellow liquid (29.2 mg, 85%); ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.23 (t, *J* = 7.2 Hz, 3H), 1.53 (s, 9H), 3.11 (dd, *J* = 13.2 Hz, 6.4 Hz, 1H), 3.62-3.71 (m, 2H), 4.07-4.13 (m, 2H), 5.73 (s, 1H), 6.34 (d, *J* = 3.2 Hz, 1H), 7.10-7.22 (m, 2H), 7.26-7.28 (m, 1H), 7.32-7.35 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 14.2, 28.0, 29.7, 35.8, 59.8, 82.4, 100.7, 115.5,

127.2, 127.3, 128.8, 141.5, 142.4, 161.2, 164.9, 167.0; IR (CH₂Cl₂) v 2928, 2360, 2342, 1792, 1772, 1733, 1716, 1647, 1541, 1473, 1373, 1339, 1259, 1164, 1116, 750, 669 cm⁻¹; MS (ESI) *m/z* 345.1 (M+H⁺); HRMS (MALDI) Calcd. for C₂₀H₂₄O₅Na requires (M+Na⁺): 367.1516, Found: 367.1515; [α]_D²⁰ = -214.4 (c 1.50, CH₂Cl₂) (90% ee); Chiralcel IC, hexane/*i*PrOH = 95/5, 0.6 mL/min, 254 nm, *t*_{major} = 18.45 min, *t*_{minor} = 18.42 min.



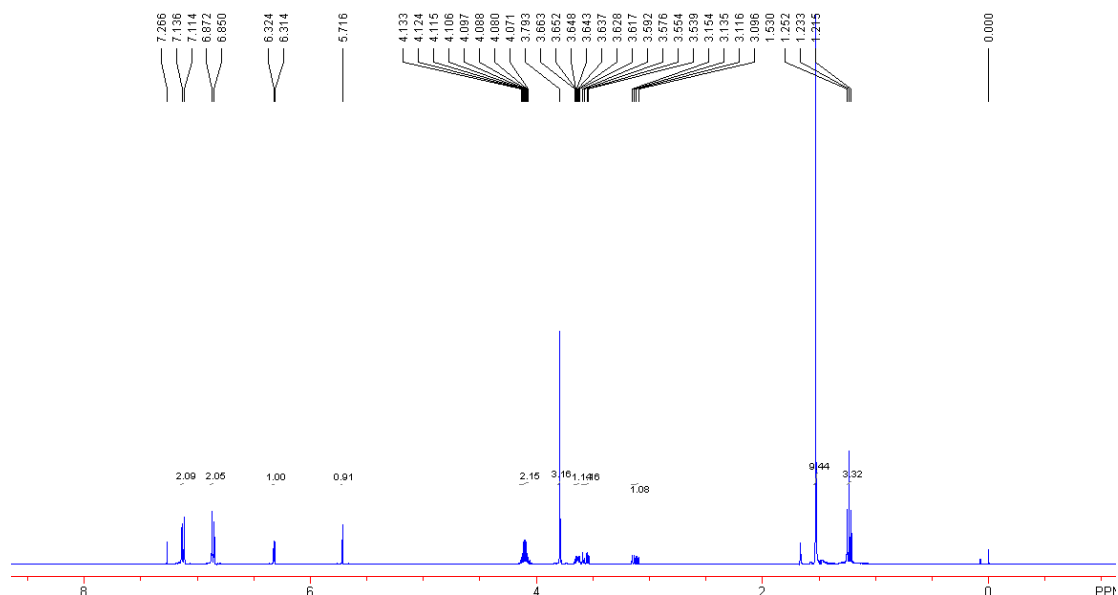
(*E*)-*tert*-butyl 2-(2-ethoxy-2-oxoethylidene)-4-(*p*-tolyl)-3,4-dihydro-2*H*-pyran-6-carboxylate
3ea: a slight yellow liquid (32.4 mg, 90%); ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.23 (t, *J* = 7.2 Hz, 3H), 1.53 (s, 9H), 2.33 (s, 3H), 3.08 (dd, *J* = 13.2 Hz, 6.4 Hz, 1H), 3.59-3.67 (m, 2H), 4.06-4.14 (m, 2H), 5.72 (s, 1H), 6.32 (d, *J* = 3.2 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 14.2, 21.0, 28.0, 29.7, 35.4, 59.8, 82.4, 100.6, 115.9, 127.1, 129.4, 136.8, 138.5, 142.2, 160.2, 165.0, 167.0; IR (CH₂Cl₂) ν 2980, 2932, 2359, 1732, 1716, 1659, 1515, 1394, 1371, 1259, 1165, 1117, 1046, 848, 758, 750 cm⁻¹; MS (ESI) *m/z* 359.1 (M+H⁺); HRMS (MALDI) Calcd. for C₂₁H₂₆O₅Na requires (M+Na⁺): 381.1673, Found: 381.1671; [α]_D²⁰ = -228.0 (c 1.65, CH₂Cl₂) (90% ee); Chiralcel IC, hexane/ⁱPrOH = 95/5, 0.6 mL/min, 254 nm, *t*_{major} = 15.77 min, *t*_{minor} = 14.80 min.

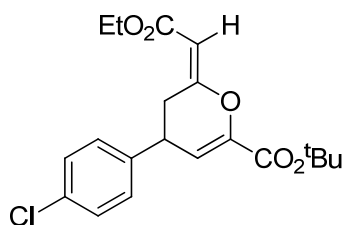
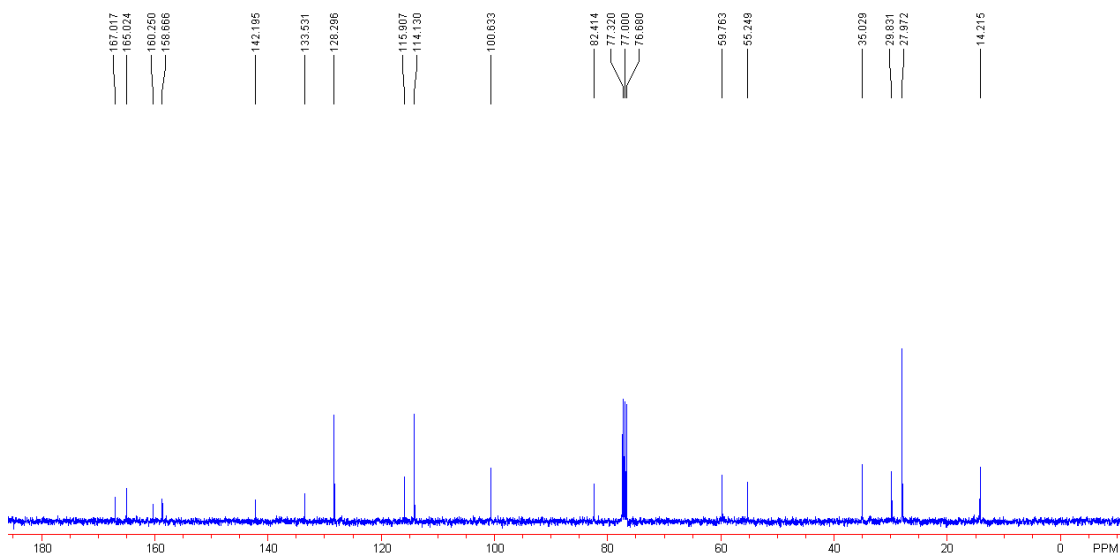




(*E*)-*tert*-butyl

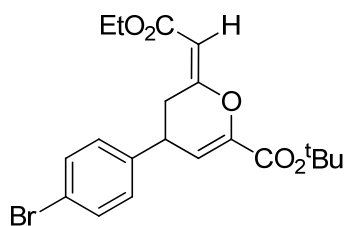
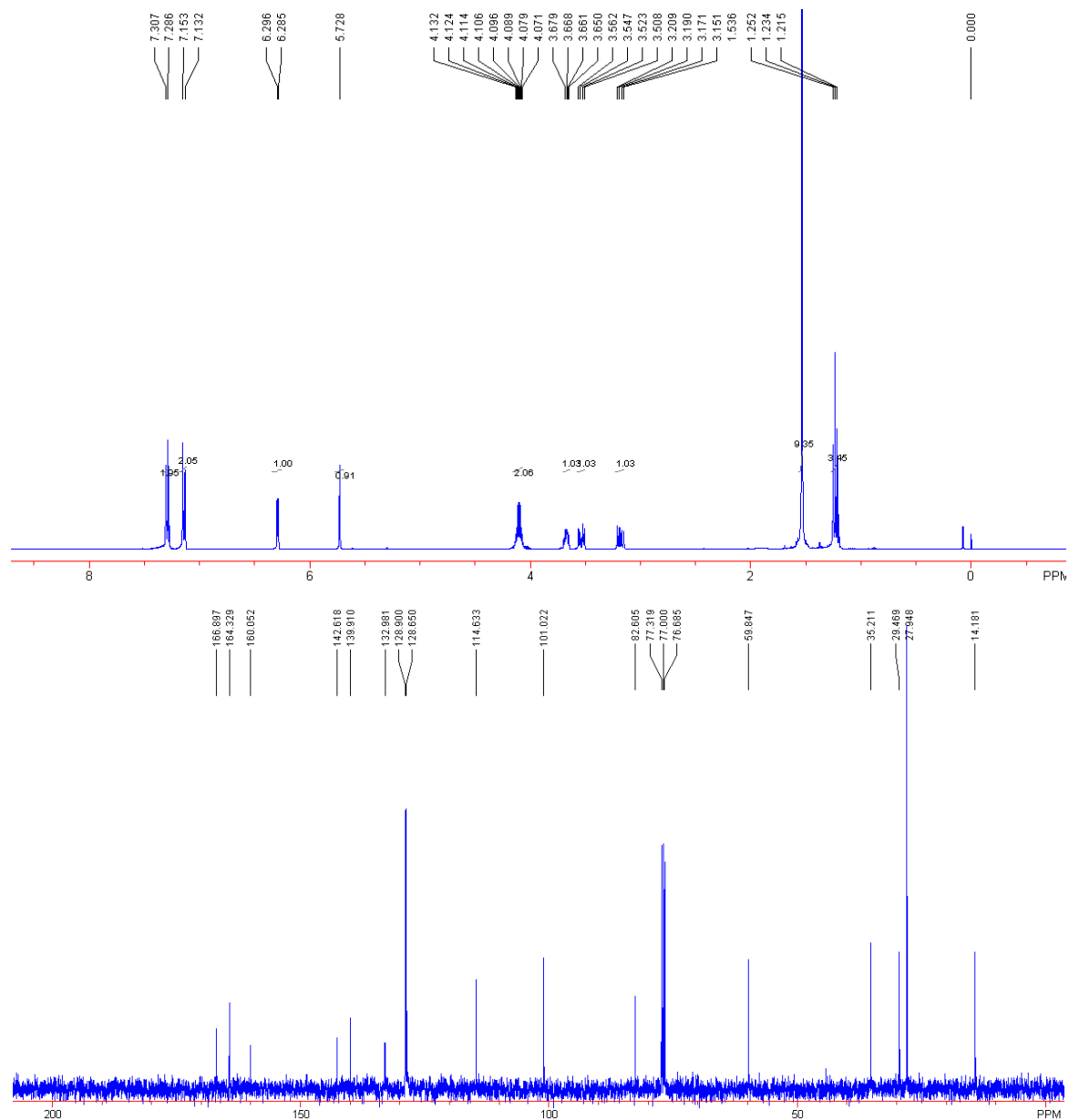
2-(2-ethoxy-2-oxoethylidene)-4-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyran-6-carboxylate **3fa**: a slight yellow liquid (33.1 mg, 89%); ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.23 (t, $J = 7.2$ Hz, 3H), 1.53 (s, 9H), 3.13 (dd, $J = 14.8$ Hz, 8.0 Hz, 1H), 3.57 (dd, $J = 14.8$ Hz, 6.4 Hz, 1H), 3.62-3.66 (m, 1H), 3.79 (s, 3H), 4.07-4.13 (m, 2H), 5.72 (s, 1H), 6.32 (d, $J = 4.0$ Hz, 1H), 6.86 (d, $J = 8.8$ Hz, 2H), 7.13 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.2, 28.0, 29.8, 35.0, 55.2, 59.8, 82.4, 100.6, 114.1, 115.9, 128.3, 133.5, 142.2, 158.7, 160.3, 165.0, 167.0; IR (CH_2Cl_2) ν 2978, 2359, 2342, 1733, 1716, 1654, 1647, 1509, 1457, 1370, 1258, 1164, 1114, 1039, 750, 669 cm^{-1} ; MS (ESI) m/z 375.1 ($\text{M}+\text{H}^+$); HRMS (MALDI) Calcd. for $\text{C}_{21}\text{H}_{26}\text{O}_6\text{Na}$ requires ($\text{M}+\text{Na}^+$): 397.1622, Found: 397.1627; $[\alpha]_D^{20} = -184.4$ (c 1.45, CH_2Cl_2) (87% ee); Chiralcel AS-H, hexane/ $^i\text{PrOH} = 95/5$, 0.6 mL/min, 254 nm, $t_{\text{major}} = 10.79$ min, $t_{\text{minor}} = 9.49$ min.





(E)-tert-butyl

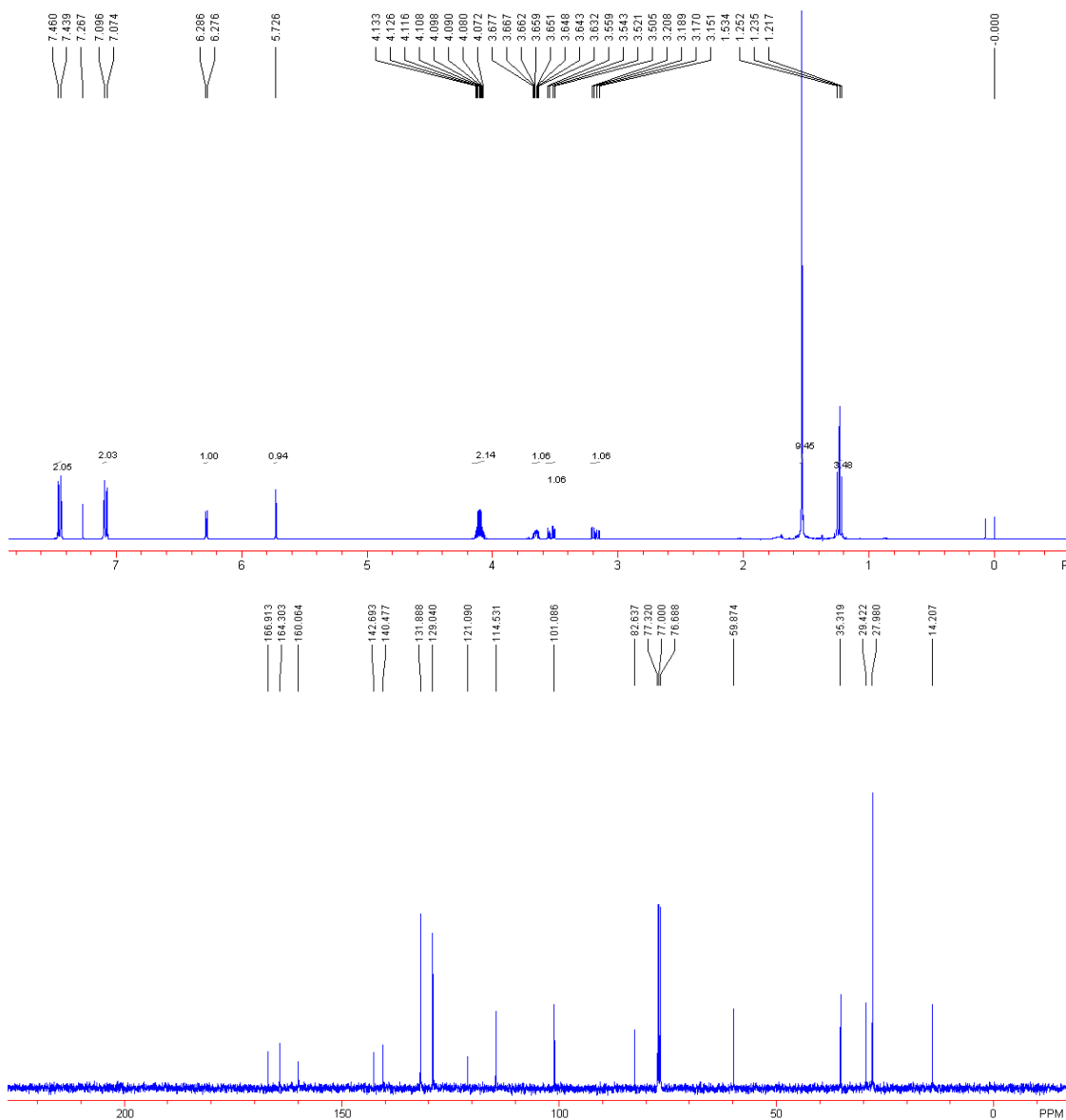
4-(4-chlorophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2*H*-pyran-6-carboxylate **3ga**: a slight yellow liquid (44.8 mg, 92%); ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.23 (t, $J = 7.2$ Hz, 3H), 1.54 (s, 9H), 3.18 (dd, $J = 15.6$ Hz, 8.0 Hz, 1H), 3.54 (dd, $J = 15.6$ Hz, 6.0 Hz, 1H), 3.65-3.68 (m, 1H), 4.07-4.13 (m, 2H), 5.73 (s, 1H), 6.29 (d, $J = 4.4$ Hz, 1H), 7.14 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.2, 27.9, 29.5, 35.2, 59.8, 82.6, 101.0, 114.6, 128.7, 128.9, 133.0, 139.9, 142.6, 160.1, 164.3, 166.9; IR (CH_2Cl_2) ν 2980, 2359, 2341, 1716, 1655, 1492, 1371, 1347, 1258, 1164, 1117, 1015, 848, 764 cm^{-1} ; MS (ESI) m/z 379.0 ($\text{M}+\text{H}^+$); HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{24}\text{ClO}_5$ requires ($\text{M}+\text{H}^+$): 379.1307, Found: 379.1322; $[\alpha]_D^{20} = -162.4$ (c 1.95, CH_2Cl_2) (90% ee); Chiralcel IC, hexane/*i*PrOH = 95/5, 0.6 mL/min, 254 nm, $t_{\text{major}} = 24.55$ min, $t_{\text{minor}} = 23.06$ min.

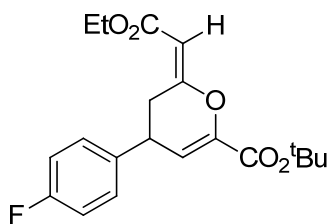


(*E*)-*tert*-butyl

4-(4-bromophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2*H*-pyran-6-carboxylate **3ha**: a slight yellow liquid (36.8 mg, 92%); ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.53 (s, 9H), 3.18 (dd, *J* = 15.2 Hz, 7.6 Hz, 1H), 3.53 (dd, *J* = 15.2 Hz, 6.4 Hz, 1H), 3.64-3.68 (m, 1H), 4.07-4.13 (m, 2H), 5.73 (s, 1H), 6.28 (d, *J* = 4.0 Hz, 1H), 7.09 (d, *J* = 8.8

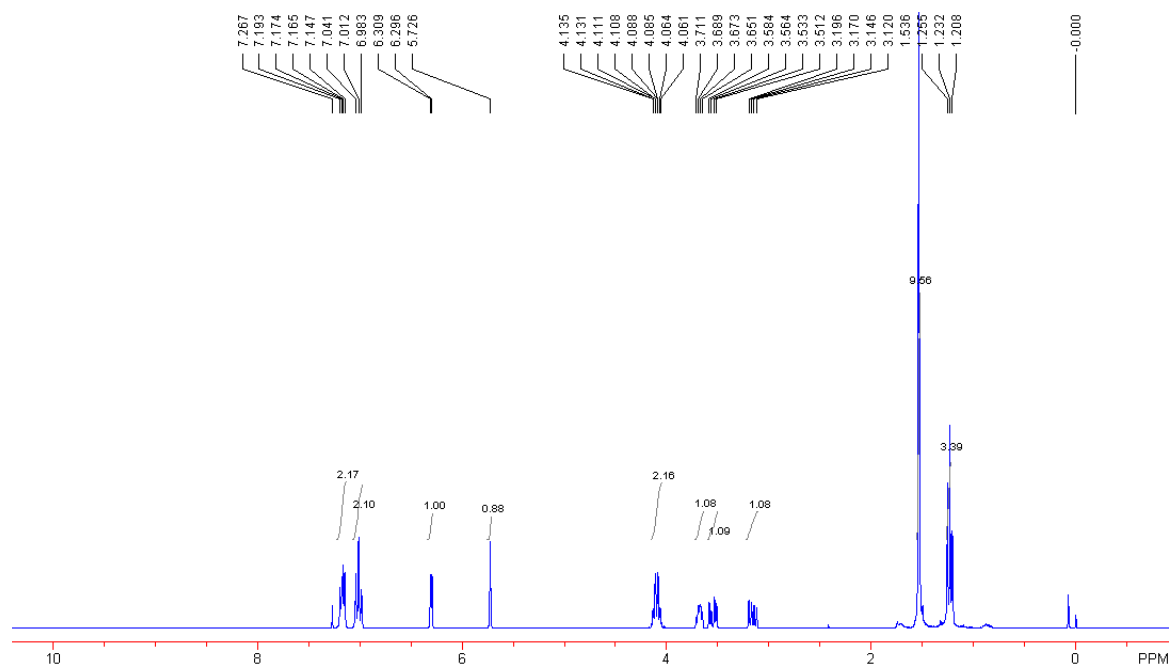
Hz, 2H), 7.45 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.2, 28.0, 29.4, 35.3, 59.9, 82.6, 101.1, 114.5, 121.1, 129.0, 131.9, 140.5, 142.7, 160.1, 164.3, 166.9; IR (CH_2Cl_2) ν 2359, 2342, 1734, 1716, 1370, 1275, 1260, 1114, 750, 640, 605, 576 cm^{-1} ; MS (ESI) m/z 423.0 ($\text{M}+\text{H}^+$); HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{24}\text{BrO}_5$ requires ($\text{M}+\text{H}^+$): 423.0802, Found: 423.0814; $[\alpha]_D^{20} = -186.8$ (c 0.45, CH_2Cl_2) (90% ee); Chiralcel IC, hexane/ i PrOH = 98/2, 0.6 mL/min, 254 nm, $t_{\text{major}} = 15.08$ min, $t_{\text{minor}} = 14.21$ min.

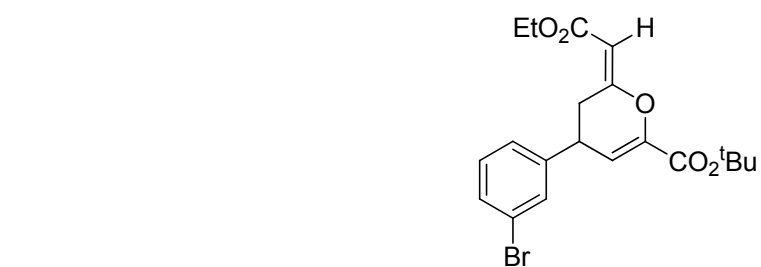
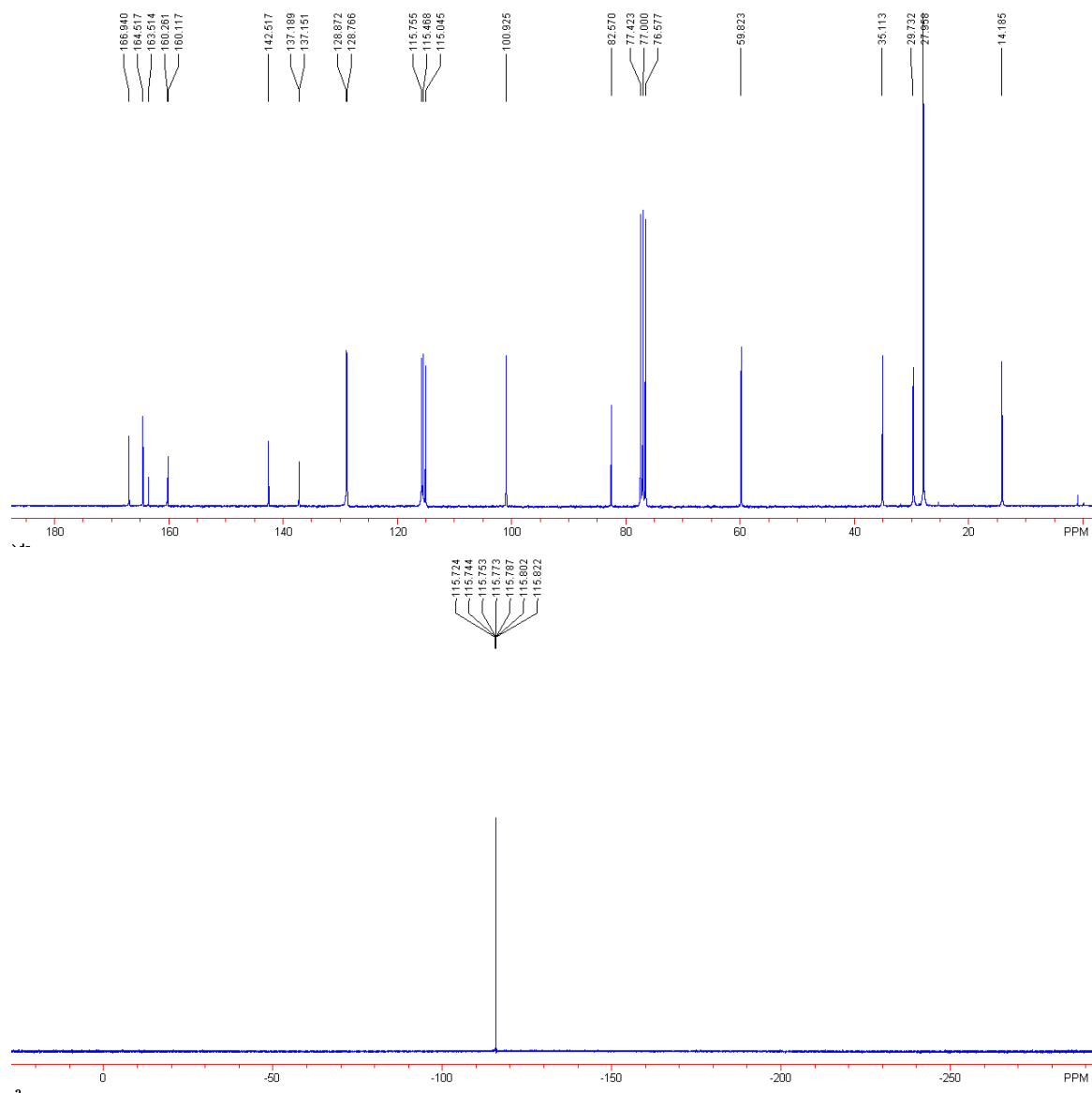




(*E*)-*tert*-butyl

2-(2-ethoxy-2-oxoethylidene)-4-(4-fluorophenyl)-3,4-dihydro-2*H*-pyran-6-carboxylate **3ia**: a slight yellow liquid (32.1 mg, 89%); ^1H NMR (CDCl_3 , 300 MHz, TMS) δ 1.23 (t, $J = 7.2$ Hz, 3H), 1.54 (s, 9H), 3.16 (dd, $J = 15.0$ Hz, 7.8 Hz, 1H), 3.55 (dd, $J = 15.0$ Hz, 6.3 Hz, 1H), 3.65-3.71 (m, 1H), 4.10 (dq, $J = 7.2$ Hz, 0.9 Hz, 2H), 5.73 (s, 1H), 6.30 (d, $J = 3.9$ Hz, 1H), 7.01 (t, $J = 8.4$ Hz, 2H), 7.17 (dd, $J = 8.4$ Hz, 5.4 Hz, 2H); ^{13}C NMR (CDCl_3 , 75 MHz, TMS) δ 14.2, 28.0, 29.7, 35.1, 59.8, 82.6, 100.0, 115.0, 115.6 (d, $J_{\text{C-F}} = 21.5$ Hz), 128.8 (d, $J_{\text{C-F}} = 8.0$ Hz), 137.2 (d, $J_{\text{C-F}} = 2.9$ Hz), 142.5, 160.1, 161.9 (d, $J_{\text{C-F}} = 244.0$ Hz), 164.5, 166.9; ^{19}F NMR (CDCl_3 , 282 MHz, CFCl_3): δ -115.822 ~ -115.724 (m, 1F); IR (CH_2Cl_2) ν 2359, 2342, 1734, 1716, 1653, 1558, 1541, 1507, 1276, 1108, 750, 669 cm^{-1} ; MS (ESI) m/z 385.1 ($\text{M}+\text{Na}^+$); HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{23}\text{FO}_5\text{Na}$ requires ($\text{M}+\text{Na}^+$): 385.1422, Found: 385.1421; $[\alpha]_{\text{D}}^{20} = -183.1$ (c 1.40, CH_2Cl_2) (90% ee); Chiralcel AS-H, hexane/*i*PrOH = 98/2, 0.6 mL/min, 254 nm, $t_{\text{major}} = 12.00$ min, $t_{\text{minor}} = 11.22$ min.

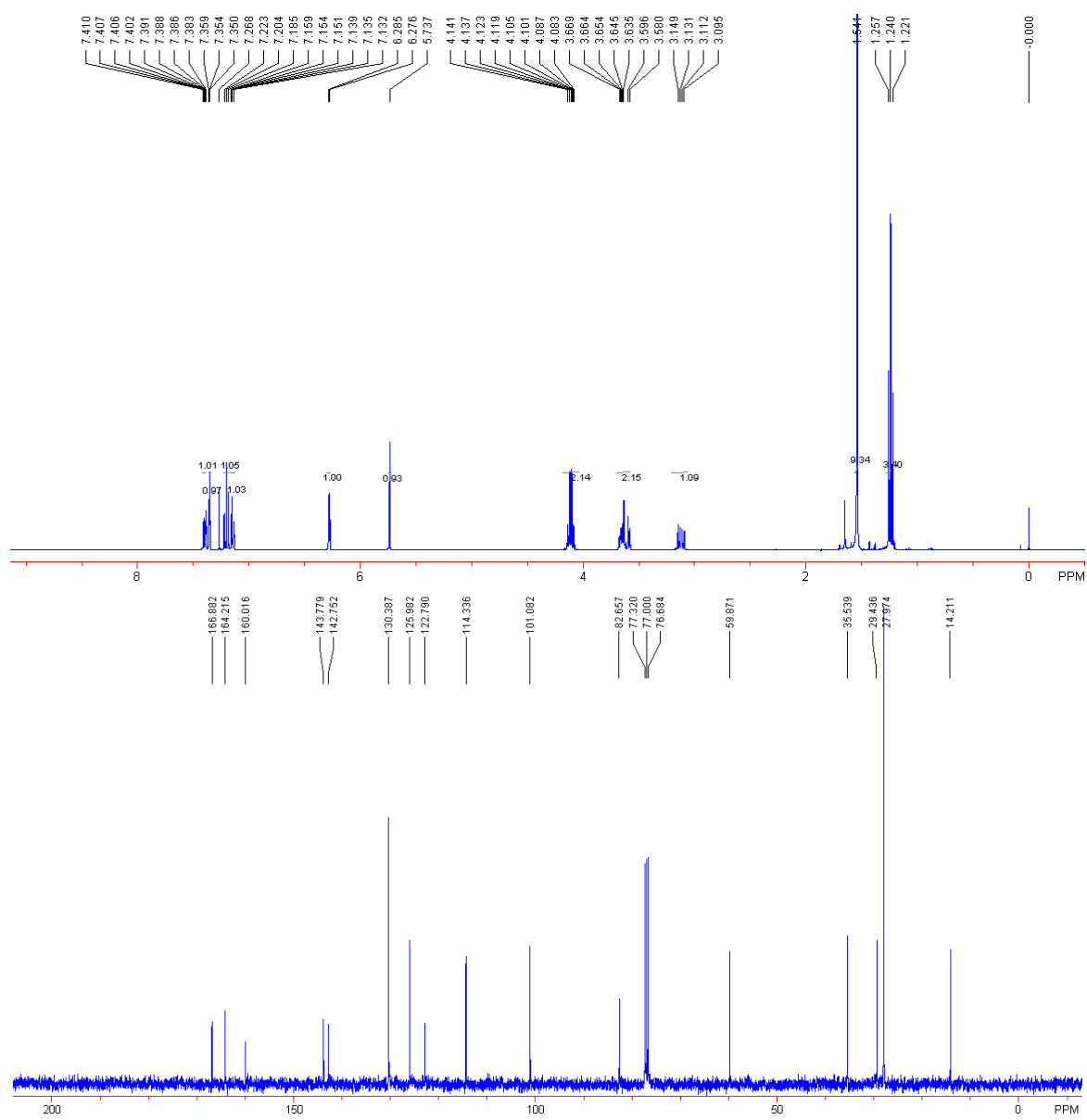


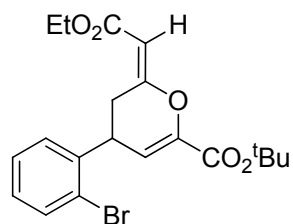


(E)-*tert*-butyl

4-(3-bromophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2*H*-pyran-6-carboxylate **3ja**: a slight yellow liquid (35.8 mg, 85%); ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.54 (s, 9H), 3.12 (dd, *J* = 14.8 Hz, 7.2 Hz, 1H), 3.58-3.67 (m, 2H), 4.11 (dq, *J* = 7.2 Hz, 1.6 Hz, 2H), 5.74 (s, 1H), 6.28 (d, *J* = 3.6 Hz, 1H), 7.13-7.16 (m, 1H), 7.20 (t, *J* = 7.6 Hz, 1H),

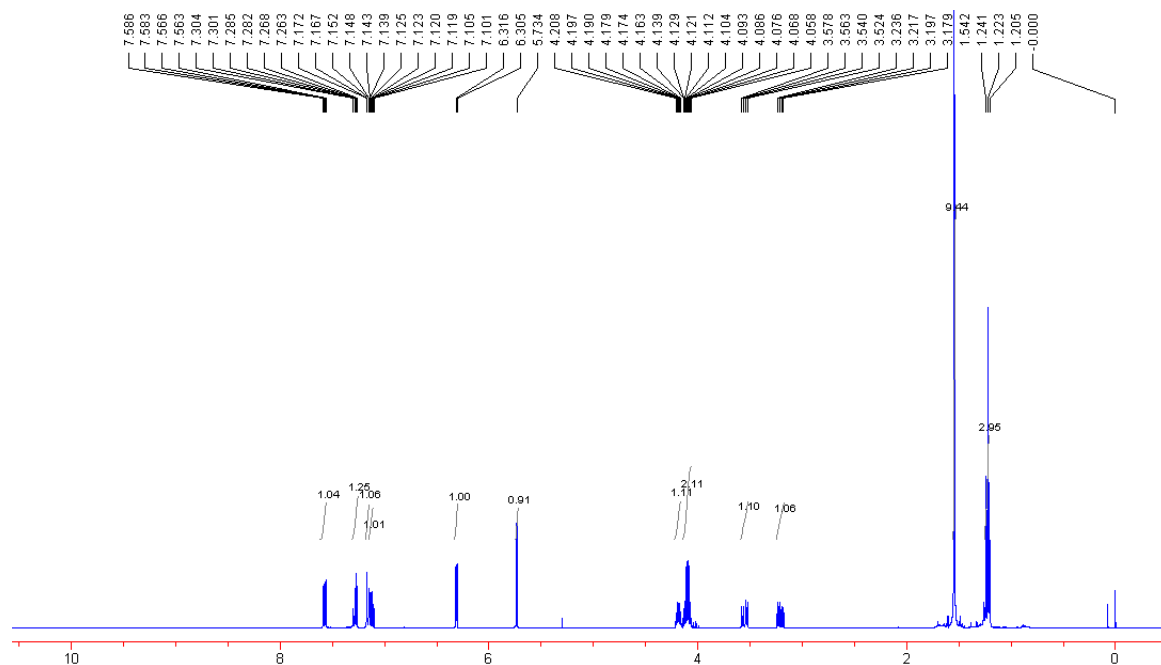
7.35 (t, $J = 7.6$ Hz, 1H), 7.38-7.41 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.2, 28.0, 29.4, 35.5, 59.8, 82.7, 101.1, 114.3, 122.8, 126.0, 130.4, 142.8, 143.8, 160.0, 164.2, 166.9; IR (CH_2Cl_2) ν 2979, 2932, 2360, 2342, 1733, 1716, 1655, 1593, 1568, 1475, 1394, 1371, 1347, 1257, 1164, 1115, 1045, 848, 764 cm^{-1} ; MS (ESI) m/z 445.0 ($\text{M}+\text{Na}^+$); HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{23}\text{BrO}_5\text{Na}$ requires ($\text{M}+\text{Na}^+$): 445.0621, Found: 445.0619; $[\alpha]_{\text{D}}^{20} = -195.7$ (c 1.65, CHCl_3) (88% ee); Chiralcel IC, hexane/ i PrOH = 98/2, 0.6 mL/min, 254 nm, $t_{\text{major}} = 26.85$ min, $t_{\text{minor}} = 23.17$ min.

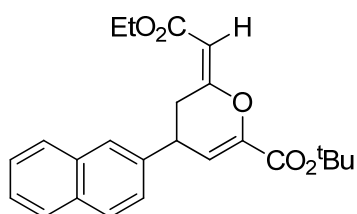
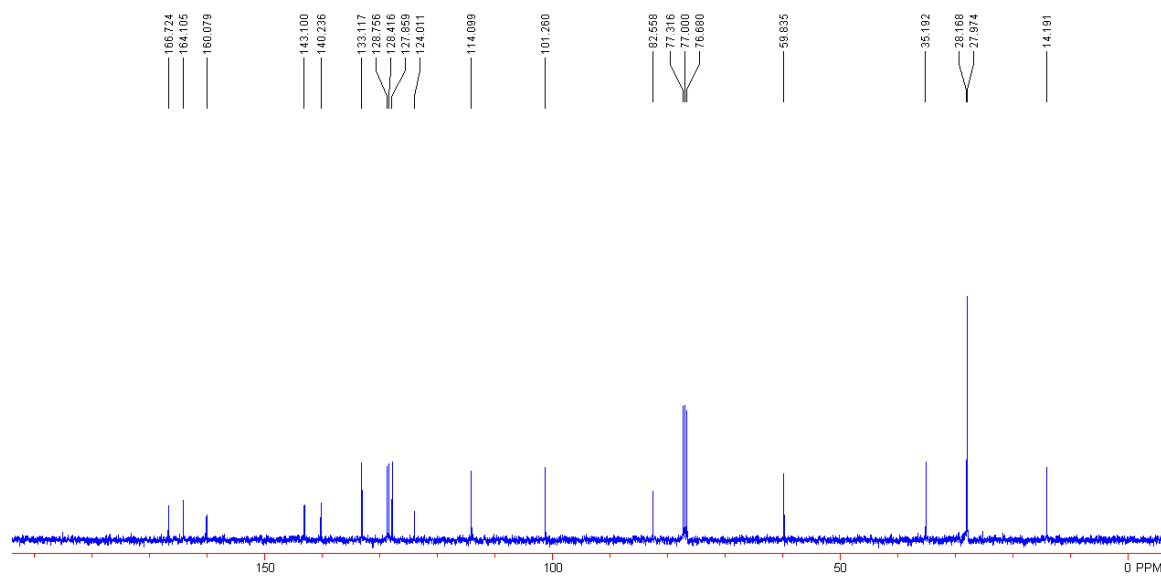




(*E*)-*tert*-butyl

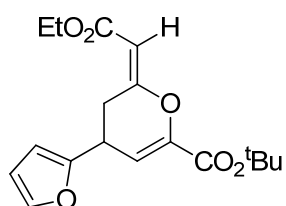
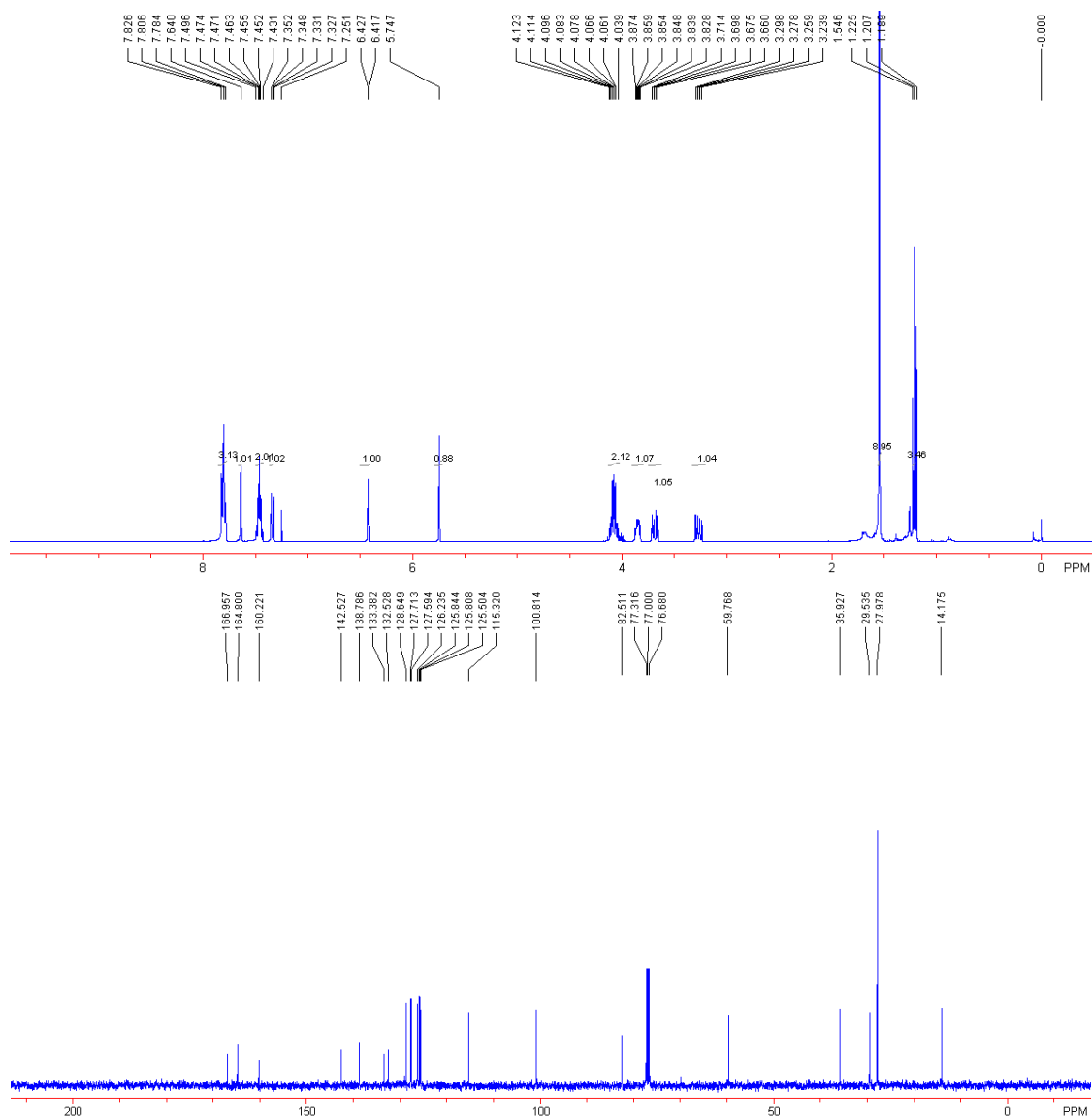
4-(2-bromophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2*H*-pyran-6-carboxylate **3ka**: a slight yellow liquid (36.4 mg, 91%); ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.22 (t, $J = 7.2$ Hz, 3H), 1.54 (s, 9H), 3.23 (dd, $J = 15.2$ Hz, 7.2 Hz, 1H), 3.55 (dd, $J = 15.2$ Hz, 6.4 Hz, 1H), 4.06-4.14 (m, 2H), 4.16-4.21 (m, 1H), 5.73 (s, 1H), 6.31 (d, $J = 4.4$ Hz, 1H), 7.10-7.14 (m, 1H), 7.16 (dd, $J = 7.6$ Hz, 1.6 Hz, 1H), 7.26-7.30 (m, 1H), 7.57 (dd, $J = 7.6$ Hz, 1.6 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.2, 28.0, 28.2, 35.2, 59.8, 82.6, 101.3, 114.1, 124.0, 127.9, 128.4, 128.8, 133.1, 140.2, 143.1, 160.1, 164.1, 166.7; IR (CH_2Cl_2) ν 2980, 2360, 2342, 1734, 1717, 1654, 1472, 1372, 1275, 1260, 1165, 1113, 848, 750, 669 cm^{-1} ; MS (ESI) m/z 423.0 ($\text{M}+\text{H}^+$); HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{24}\text{BrO}_5$ requires ($\text{M}+\text{H}^+$): 423.0802, Found: 423.0810; $[\alpha]_D^{20} = -52.9$ (c 2.00, CH_2Cl_2) (80% ee); Chiralcel IC, hexane/*i*PrOH = 98/2, 0.6 mL/min, 254 nm, $t_{\text{major}} = 29.29$ min, $t_{\text{minor}} = 25.58$ min.





(E)-*tert*-butyl

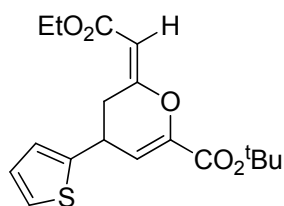
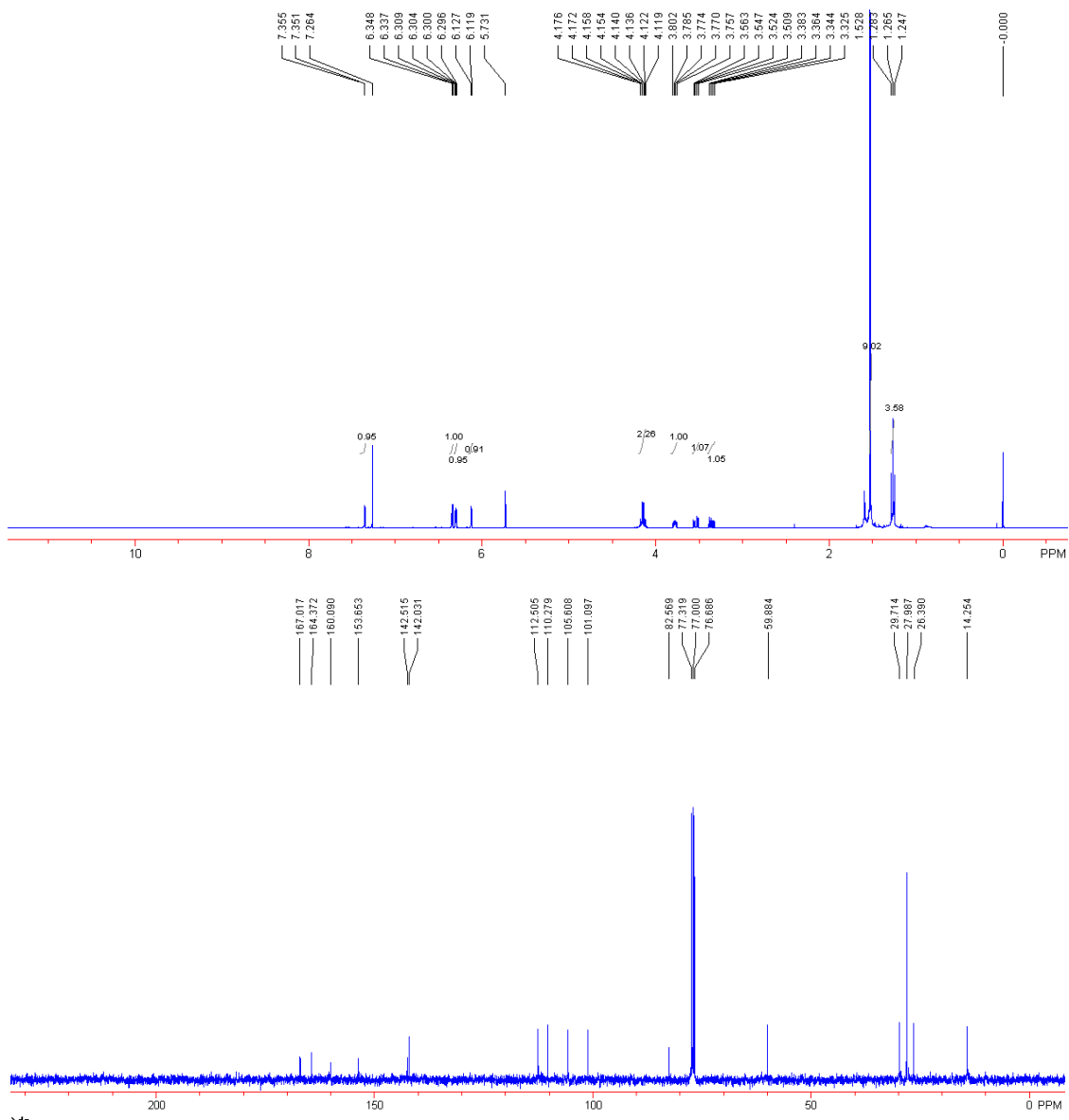
2-(2-ethoxy-2-oxoethylidene)-4-(naphthalen-2-yl)-3,4-dihydro-2*H*-pyran-6-carboxylate **3a**: a slight yellow liquid (46.2 mg, 90%); ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.21 (t, *J* = 7.2 Hz, 3H), 1.55 (s, 9H), 3.27 (dd, *J* = 15.6 Hz, 8.0 Hz, 1H), 3.69 (dd, *J* = 15.6 Hz, 6.0 Hz, 1H), 3.83-3.87 (m, 1H), 4.04-4.12 (m, 2H), 5.75 (s, 1H), 6.42 (d, *J* = 4.0 Hz, 1H), 7.34 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.43-7.50 (m, 2H), 7.64 (s, 1H), 7.78-7.83 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 14.2, 28.0, 29.5, 35.9, 59.8, 82.5, 100.8, 115.3, 125.5, 125.80, 125.84, 126.2, 127.6, 127.7, 128.6, 132.5, 133.4, 138.8, 142.5, 160.2, 164.8, 167.0; IR (CH₂Cl₂) ν 2979, 2931, 2359, 2341, 1733, 1717, 1654, 1508, 1457, 1394, 1373, 1260, 1163, 1113, 847, 749 cm⁻¹; MS (ESI) *m/z* 395.1 (M+H⁺); HRMS (ESI) Calcd. for C₂₄H₂₇O₅ requires (M+H⁺): 395.1853, Found: 395.1865; [α]_D²⁰ = -301.6 (c 1.50, CH₂Cl₂) (91% ee); Chiralcel IC, hexane/*i*PrOH = 98/2, 0.6 mL/min, 254 nm, *t*_{major} = 34.00 min, *t*_{minor} = 30.70 min.



(*E*)-*tert*-butyl

2-(2-ethoxy-2-oxoethylidene)-4-(furan-2-yl)-3,4-dihydro-2*H*-pyran-6-carboxylate **3ma**: a slight yellow liquid (24.0 mg, 72%); ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.27 (t, *J* = 7.2 Hz, 3H), 1.52 (s, 9H), 3.35 (dd, *J* = 15.6 Hz, 7.6 Hz, 1H), 3.52 (dd, *J* = 15.6 Hz, 6.0 Hz, 1H), 3.76-3.80 (m, 1H), 4.15 (dq, *J* = 7.2 Hz, 1.6 Hz, 2H), 5.73 (s, 1H), 6.12 (d, *J* = 3.2 Hz, 1H), 6.30 (dd, *J* = 3.2 Hz, 1.6 Hz, 1H), 6.34 (d, *J* = 4.4 Hz, 1H), 7.35 (d, *J* = 1.6 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 14.3, 26.4, 28.0, 29.7, 59.9, 82.6, 101.1, 105.6, 110.3, 112.5, 142.0,

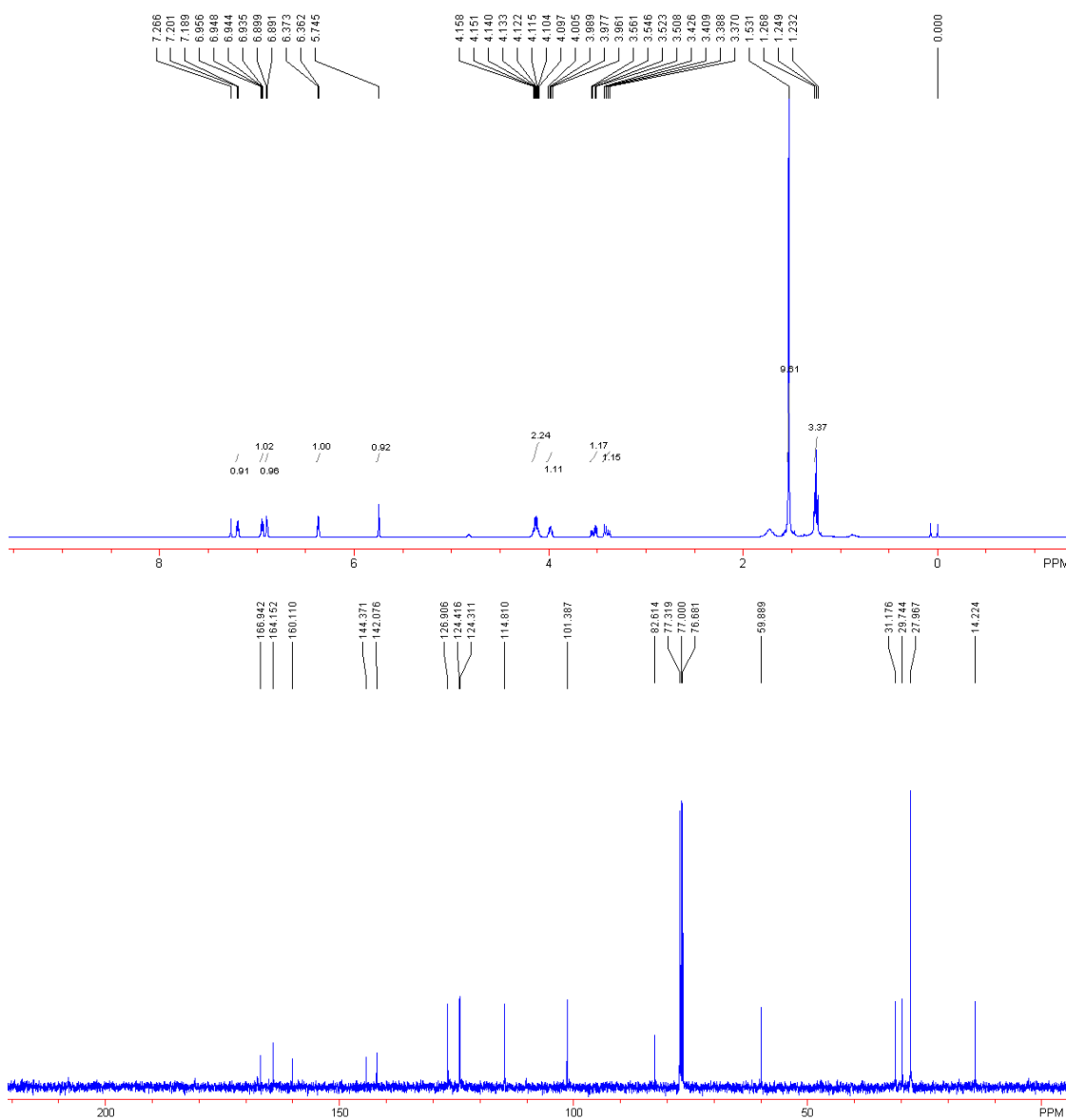
142.5, 153.7, 160.1, 164.4, 167.0; IR (CH₂Cl₂) v 2360, 2342, 1733, 1716, 1275, 1260, 1116, 846, 750, 669, cm⁻¹; MS (ESI) *m/z* 357.1 (M+Na⁺); HRMS (ESI) Calcd. for C₁₈H₂₂O₆Na requires (M+Na⁺): 357.1309, Found: 357.1322; [α]²⁰_D = -42.0 (c 0.30, CH₂Cl₂) (90% ee); Chiralcel IC, hexane/ⁱPrOH = 98/2, 0.6 mL/min, 254 nm, *t*_{major} = 23.11 min, *t*_{minor} = 26.68 min.

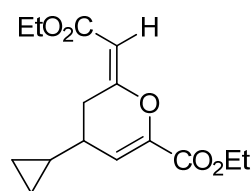


(*E*)-*tert*-butyl

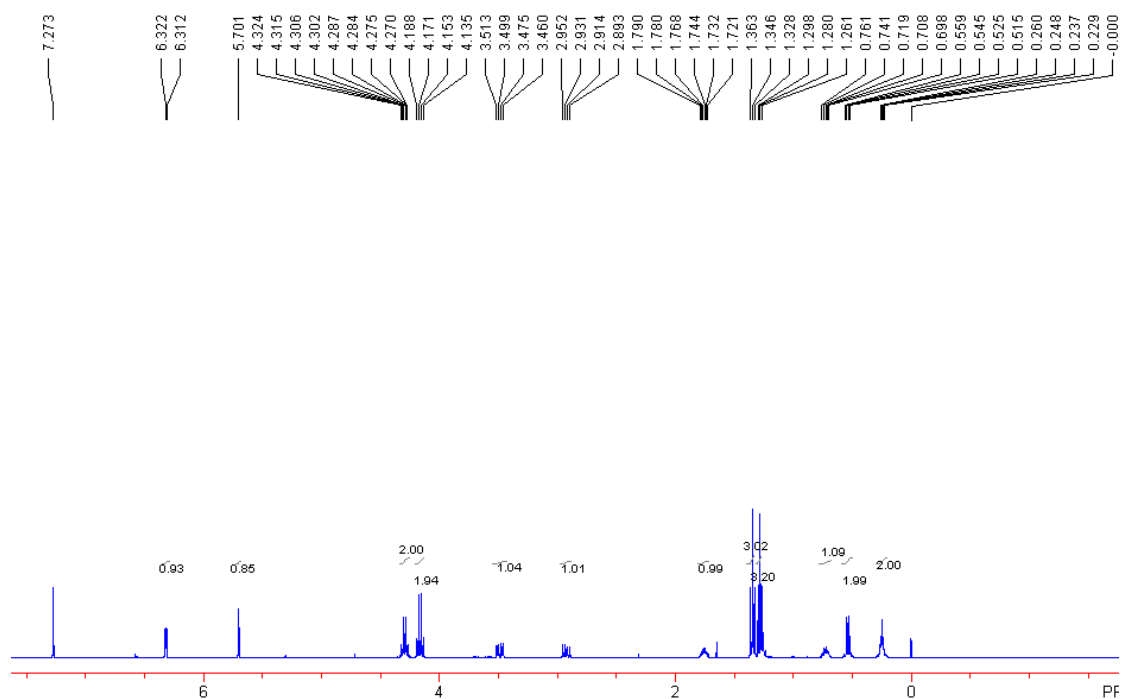
2-(2-ethoxy-2-oxoethylidene)-4-(thiophen-2-yl)-3,4-dihydro-2*H*-pyran-6-carboxylate **3na**: a

slight yellow liquid (26.3 mg, 75%); ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.25 (t, $J = 7.2$ Hz, 3H), 1.53 (s, 9H), 3.40 (dd, $J = 15.6$ Hz, 7.2 Hz, 1H), 3.54 (dd, $J = 15.6$ Hz, 6.0 Hz, 1H), 3.96-4.00 (m, 1H), 4.13 (dq, $J = 7.2$ Hz, 2.4 Hz, 2H), 5.75 (s, 1H), 6.37 (d, $J = 4.4$ Hz, 1H), 6.90 (d, $J = 3.2$ Hz, 1H), 6.95 (dd, $J = 5.2$ Hz, 3.2 Hz, 1H), 7.20 (d, $J = 5.2$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.2, 28.0, 29.7, 31.2, 59.9, 82.6, 101.4, 114.8, 124.3, 124.4, 126.9, 142.1, 144.4, 160.1, 164.2, 166.9; IR (CH_2Cl_2) ν 2983, 2360, 2342, 1733, 1715, 1659, 1507, 1372, 1276, 1260, 1115, 848, 750, 668 cm^{-1} ; MS (ESI) m/z 351.1 ($\text{M}+\text{H}^+$); HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{23}\text{SO}_5$ requires ($\text{M}+\text{H}^+$): 351.1261, Found: 351.1275; $[\alpha]_D^{20} = -178.8$ (c 0.50, CH_2Cl_2) (91% ee); Chiralcel IC, hexane/ $^i\text{PrOH} = 98/2$, 0.6 mL/min, 254 nm, $t_{\text{major}} = 26.81$ min, $t_{\text{minor}} = 30.47$ min.





(*E*)-ethyl 4-cyclopropyl-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-carboxylate
7ka: a slight yellow liquid (26.0 mg, 83%); This is a known compound;³ ¹H NMR (CDCl₃, 400 MHz, TMS) δ 0.23-0.26 (m, 2H), 0.52-0.56 (m, 2H), 0.70-0.76 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.72-1.79 (m, 1H), 2.92 (dd, *J* = 15.2 Hz, 8.4 Hz, 1H), 3.48 (dd, *J* = 15.2 Hz, 5.6 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.27-4.32 (m, 2H), 5.70 (s, 1H), 6.32 (d, *J* = 4.0 Hz, 1H); [α]_D²⁰ = -69.1 (c 1.00, CH₂Cl₂) (86% ee); Chiralcel OJ-H, hexane/^{*i*}PrOH = 98/2, 0.6 mL/min, 254 nm, *t*_{major} = 17.47 min, *t*_{minor} = 22.76 min.



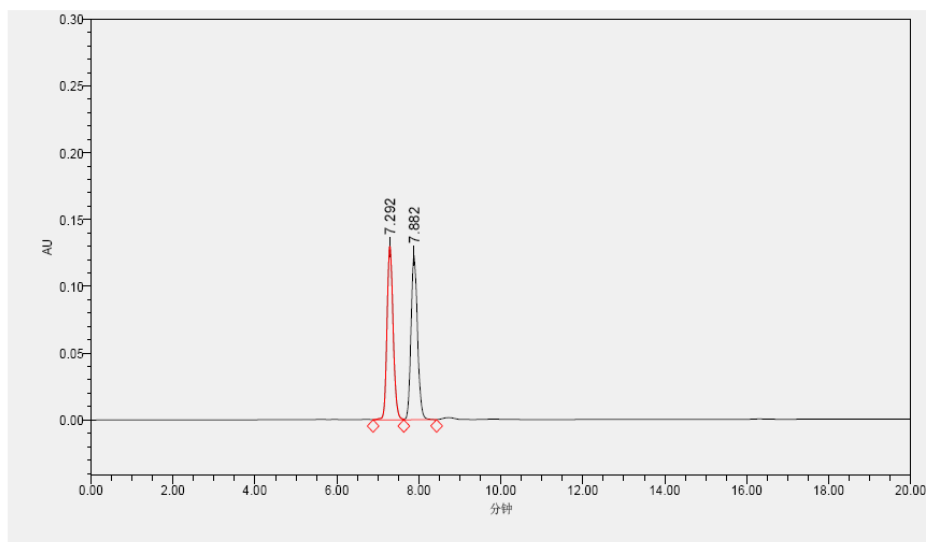
Chiral HPLC traces of the products 3

Column: AD-H

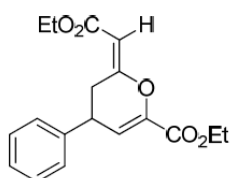
Velocity(ml/min): 0.7 ml/min

Mobile Phase: hexane/PrOH = 80/20

Detection Wavelength(nm): 254 nm



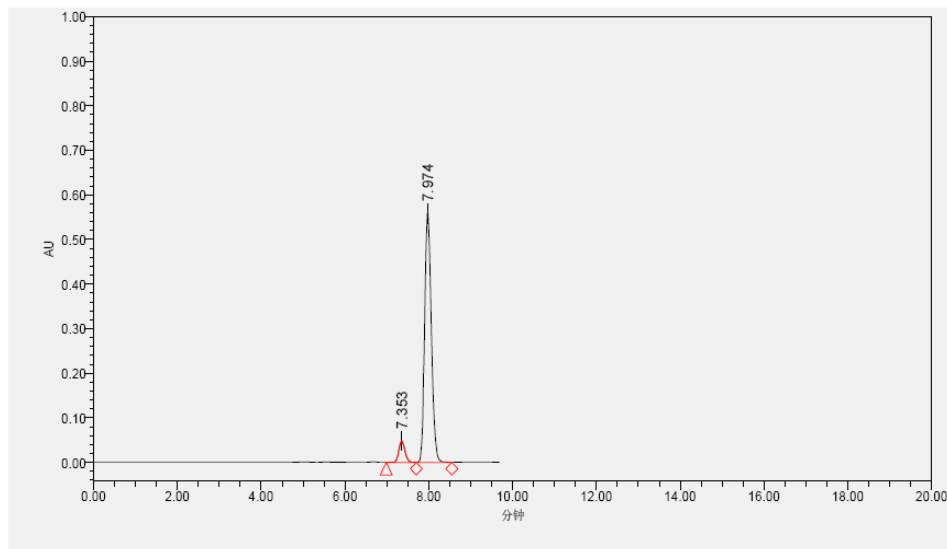
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
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2	7.882	1354580	49.93	122728	VV



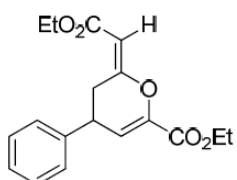
Chiralcel AD-H,
hexane/PrOH = 80/20,
0.6 mL/min, 254nm

Column: AD-H
Velocity(ml/min): 0.7 ml/min

Mobile Phase: hexane/iPrOH = 80/20
Detection Wavelength(nm): 254 nm



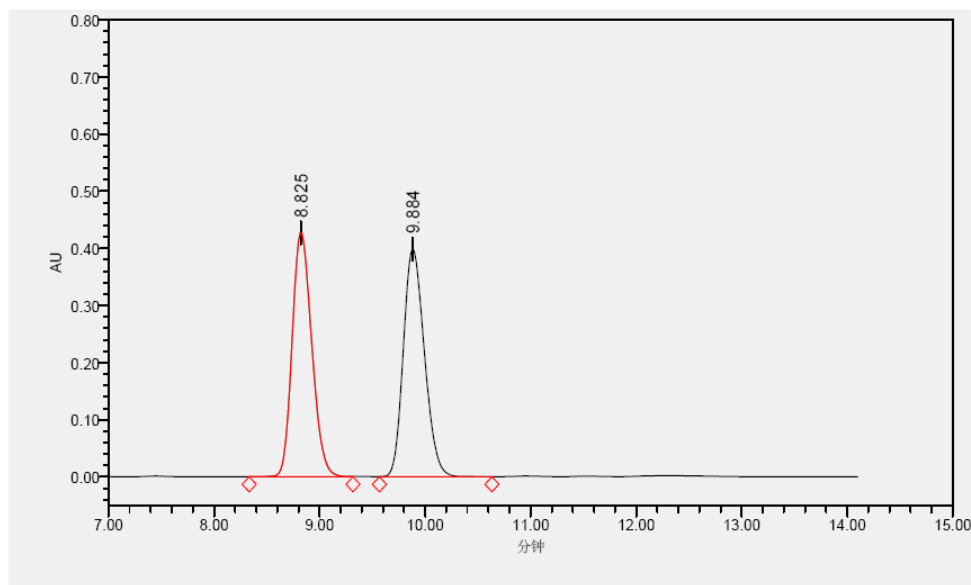
	保留时间	面积 (微伏 * 秒)	% 面积	高度 (微伏)	积分类型
1	7.353	489174	7.31	48061	bV
2	7.974	6205075	92.69	560739	VV



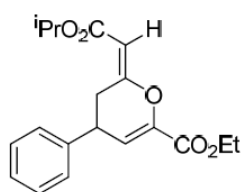
Chiralcel AD-H,
hexane/iPrOH = 80/20,
0.6 mL/min, 254nm

Column: AD-H
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/*i*PrOH = 90/10
Detection Wavelength(nm): 254 nm



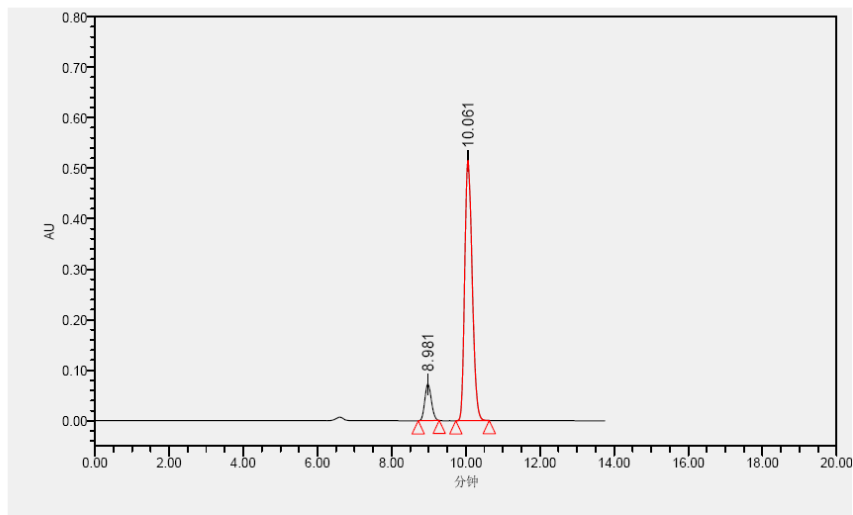
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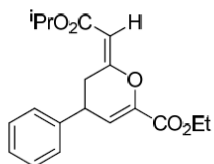
Chiralcel AD-H,
hexane/*i*PrOH = 90/10,
0.6 mL/min, 254nm

Column: AD-H
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/iPrOH = 90/10
Detection Wavelength(nm): 254 nm



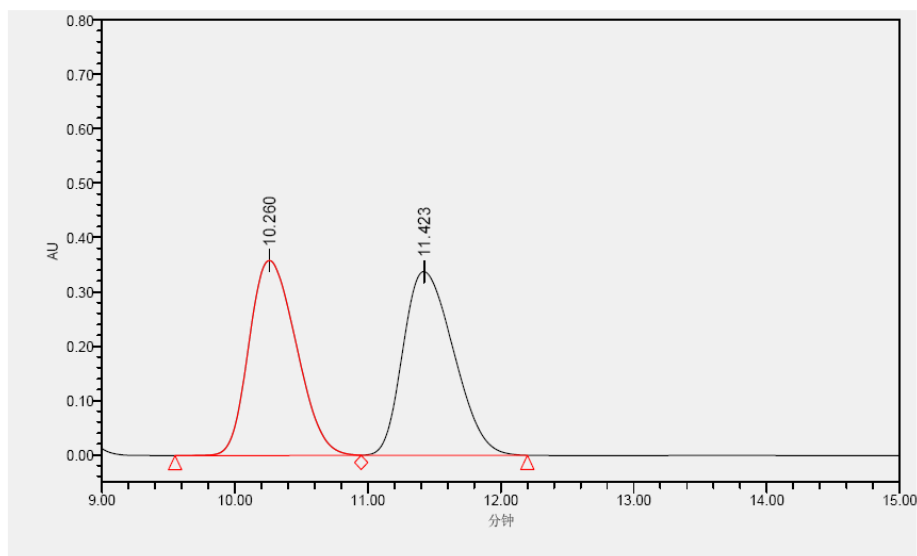
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2	10.061	7183824	88.90	516214	bb



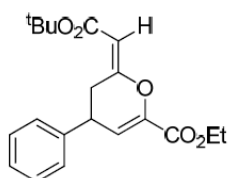
Chiralcel AD-H,
hexane/iPrOH = 90/10,
0.6 mL/min, 254nm

Column: AD-H
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/PrOH = 90/10
Detection Wavelength(nm): 254 nm



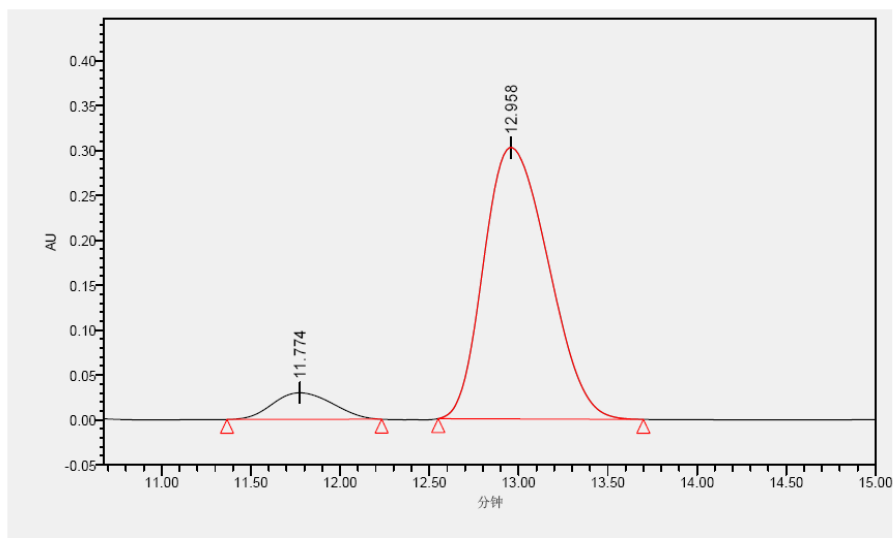
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	10.260	8874599	49.78	358983	BV
2	11.423	8953679	50.22	338264	Vb



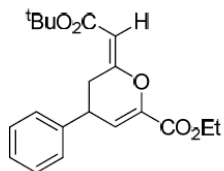
Chiralcel AD-H,
hexane/PrOH = 90/10,
0.6 mL/min, 254nm

Column: AD-H
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/iPrOH = 90/10
Detection Wavelength(nm): 254 nm



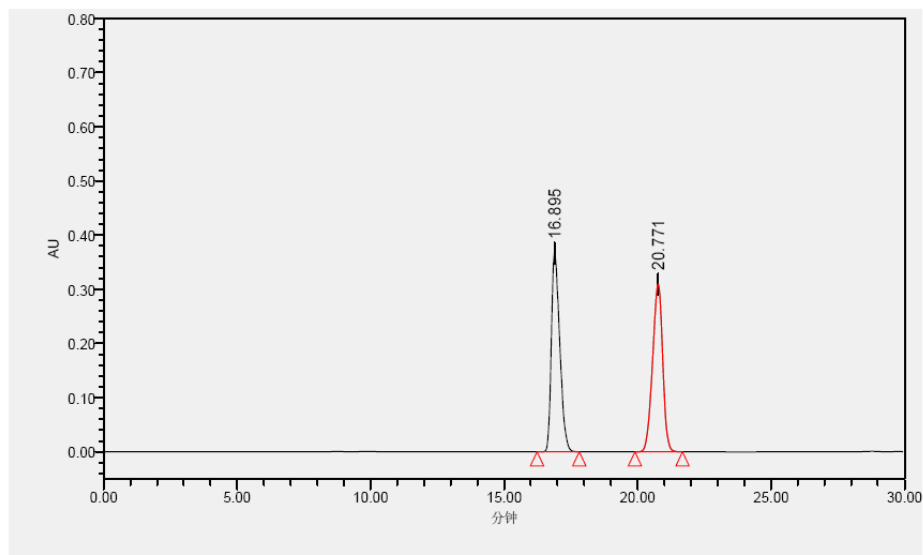
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	11.774	691204	8.34	29627	bb
2	12.958	7600066	91.66	302582	bb



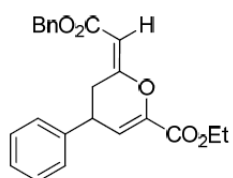
Chiralcel AD-H,
hexane/iPrOH = 90/10,
0.6 mL/min, 254nm

Column: AD-H
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/PrOH = 98/2
Detection Wavelength(nm): 254 nm



	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	16.895	8099227	49.81	366757	bb
2	20.771	8161505	50.19	309255	bb



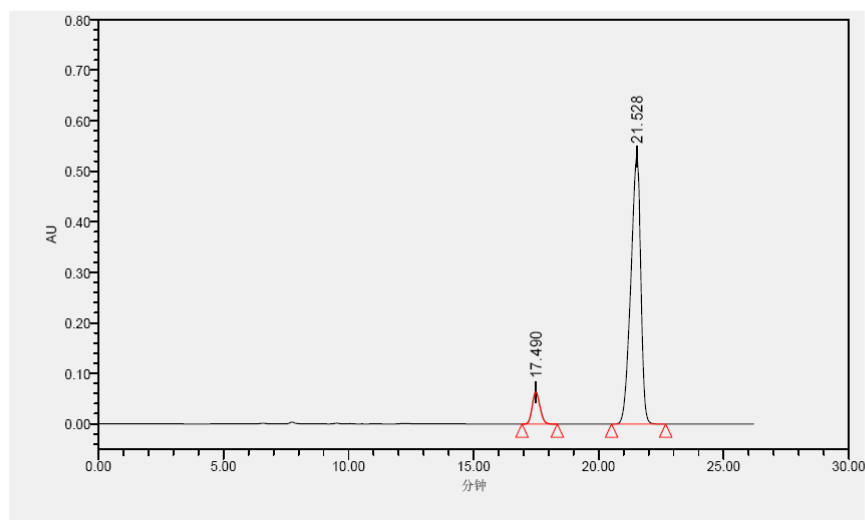
Chiralcel AD-H,
hexane/PrOH = 98/2,
0.6 mL/min, 254nm

Column: AD-H

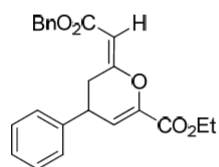
Mobile Phase: hexane/iPrOH = 98/2

Velocity(ml/min): 0.6 ml/min

Detection Wavelength(nm): 254 nm



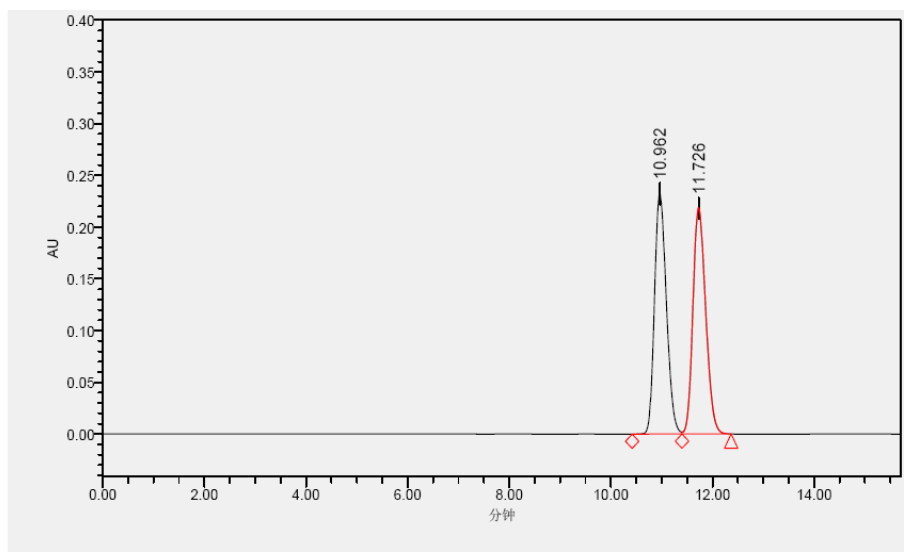
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	17.490	1373281	8.56	63437	BB
2	21.528	14675893	91.44	529736	BB



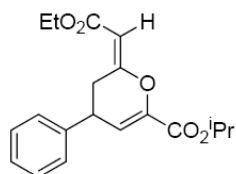
Chiralcel AD-H,
hexane/iPrOH = 98/2,
0.6 mL/min, 254nm

Column: AD-H
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/iPrOH = 95/5
Detection Wavelength(nm): 254 nm



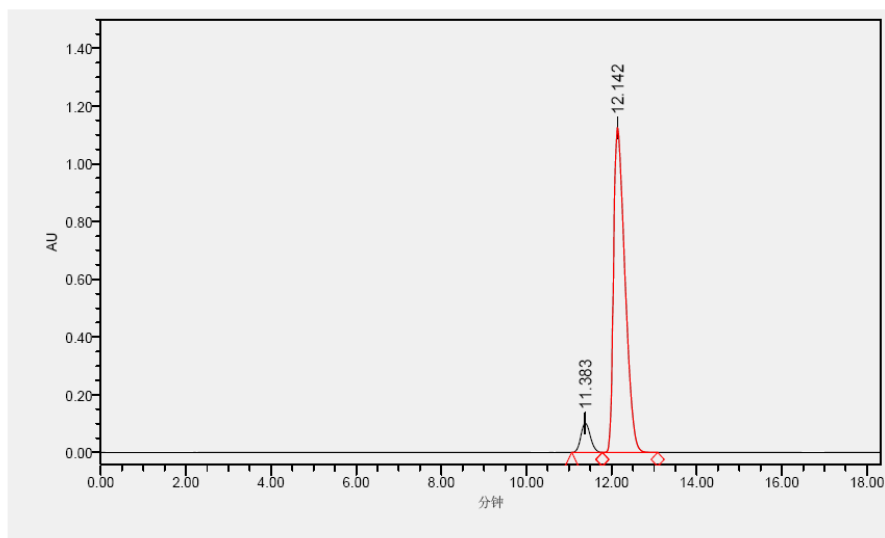
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	10.962	3789081	49.79	232824	VV
2	11.726	3821766	50.21	218664	Vb



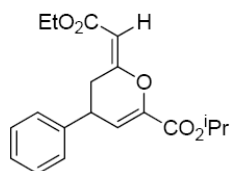
Chiralcel AD-H,
hexane/iPrOH = 95/5,
0.6 mL/min, 254nm

Column: AD-H
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/PrOH = 95/5
Detection Wavelength(nm): 254 nm



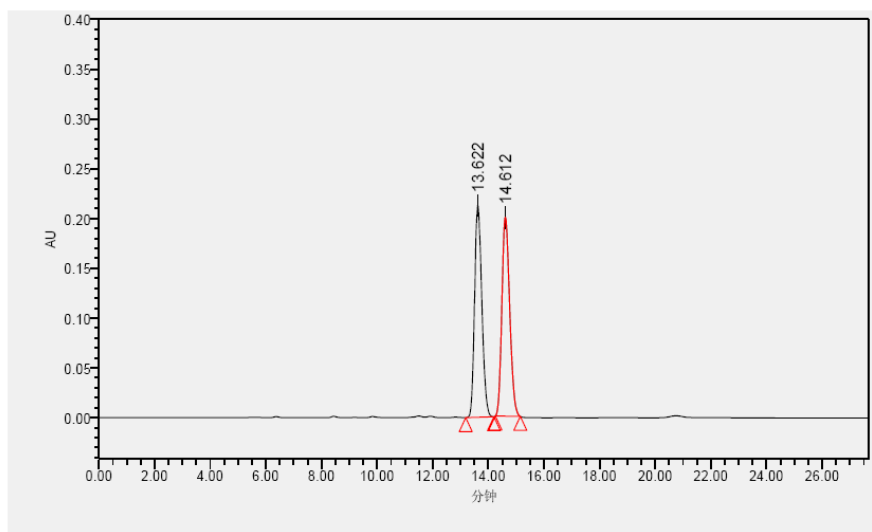
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	11.383	1572401	7.00	101620	bv
2	12.142	20882048	93.00	1127223	vV



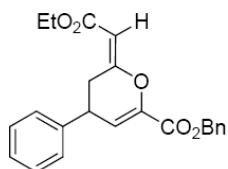
Chiralcel AD-H,
hexane/PrOH = 95/5,
0.6 mL/min, 254nm

Column: AD-H
Velocity(ml/min): 0.7 ml/min

Mobile Phase: hexane/PrOH = 90/10
Detection Wavelength(nm): 254 nm



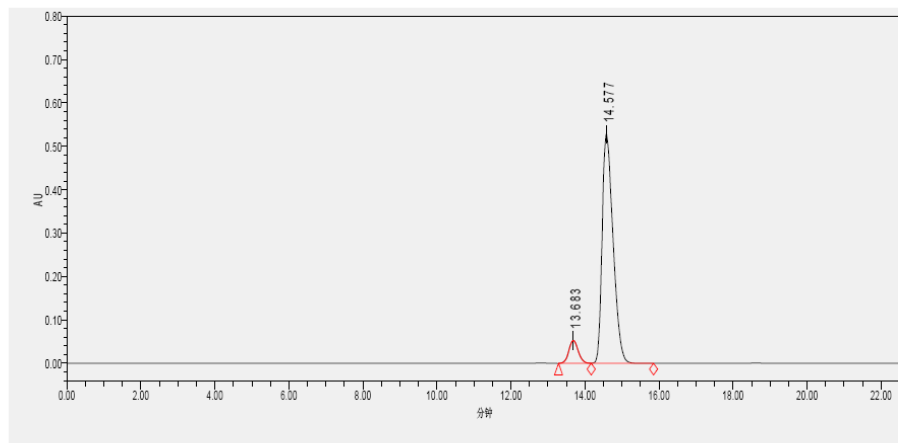
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	13.622	3857696	49.73	212963	bb
2	14.612	3898903	50.27	199795	bb



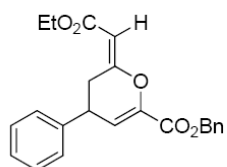
Chiralcel AD-H,
hexane/PrOH = 90/10,
0.7 mL/min, 254nm

Column: AD-H
Velocity(ml/min): 0.7 ml/min

Mobile Phase: hexane/ⁱPrOH = 90/10
Detection Wavelength(nm): 254 nm



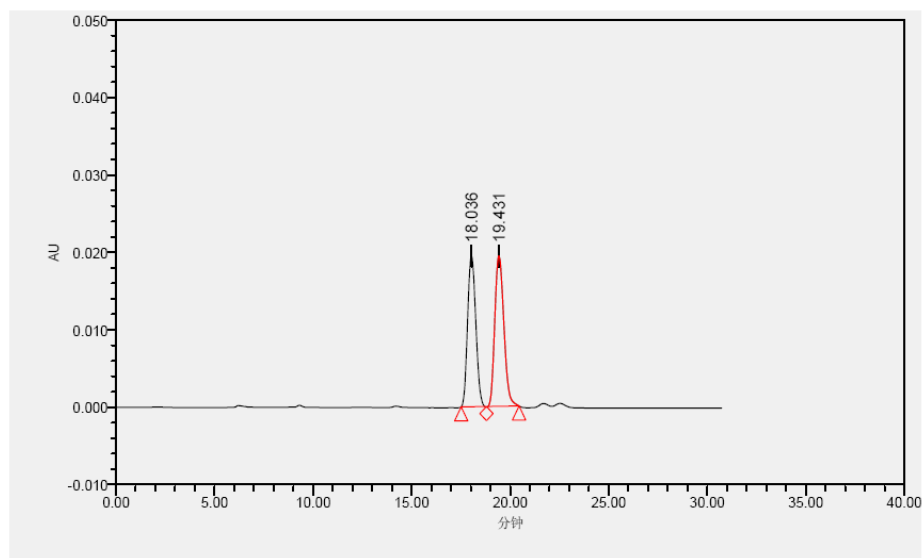
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	13.683	903727	7.71	52207	bV
2	14.577	10810450	92.29	527954	VV



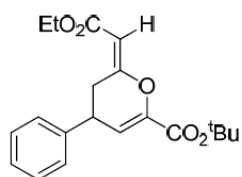
Chiralcel AD-H,
hexane/ⁱPrOH = 90/10,
0.7 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/PrOH = 95/5
Detection Wavelength(nm): 254 nm



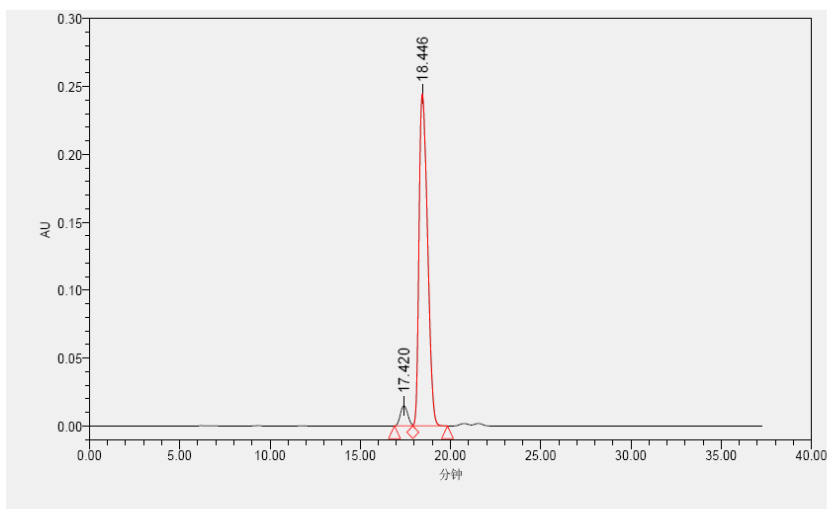
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	18.036	573150	49.91	19582	bb
2	19.431	575158	50.09	18828	bb



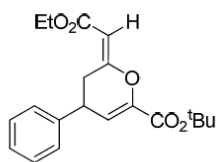
Chiralcel IC,
hexane/PrOH = 95/5,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/iPrOH = 95/5
Detection Wavelength(nm): 254 nm



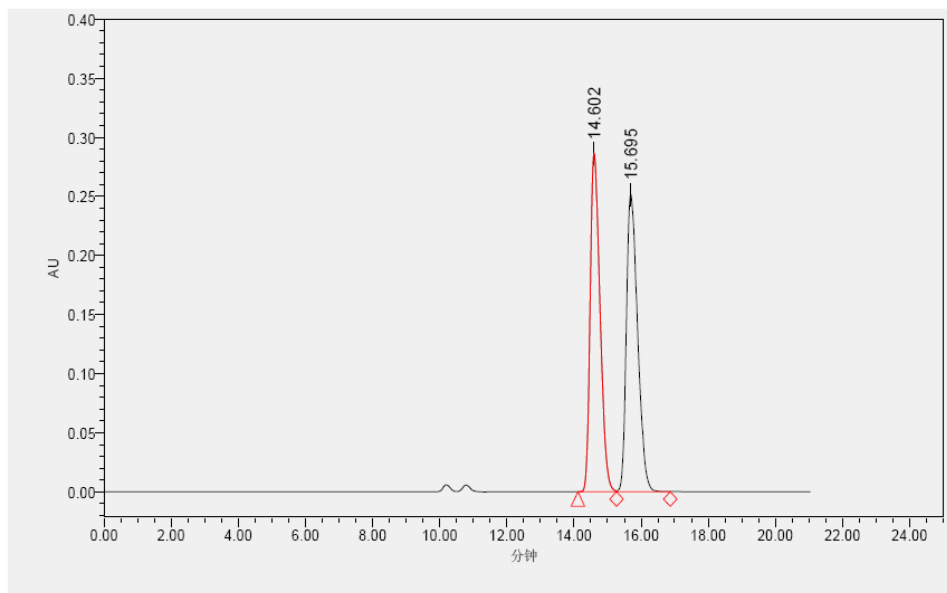
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	17.420	422007	5.06	14819	bV
2	18.446	7916837	94.94	244484	Vb



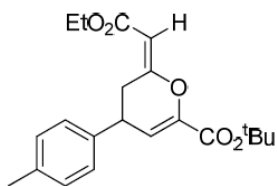
Chiralcel IC,
hexane/iPrOH = 95/5,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/*i*PrOH = 95/5
Detection Wavelength(nm): 254 nm



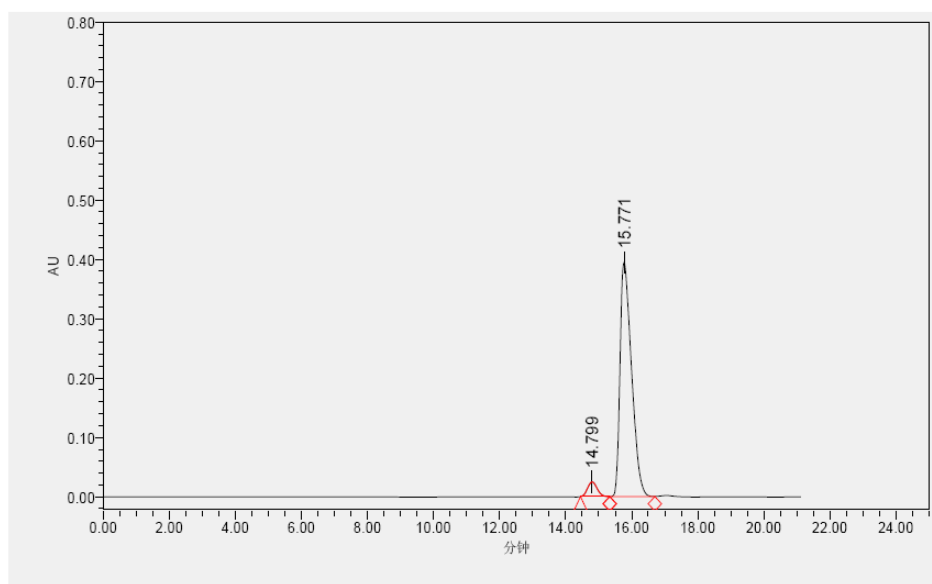
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	14.602	5850549	49.90	286740	BV
2	15.695	5873938	50.10	251662	VV



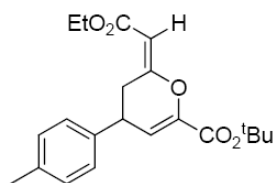
Chiralcel IC,
hexane/*i*PrOH = 95/5,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/*i*PrOH = 95/5
Detection Wavelength(nm): 254 nm



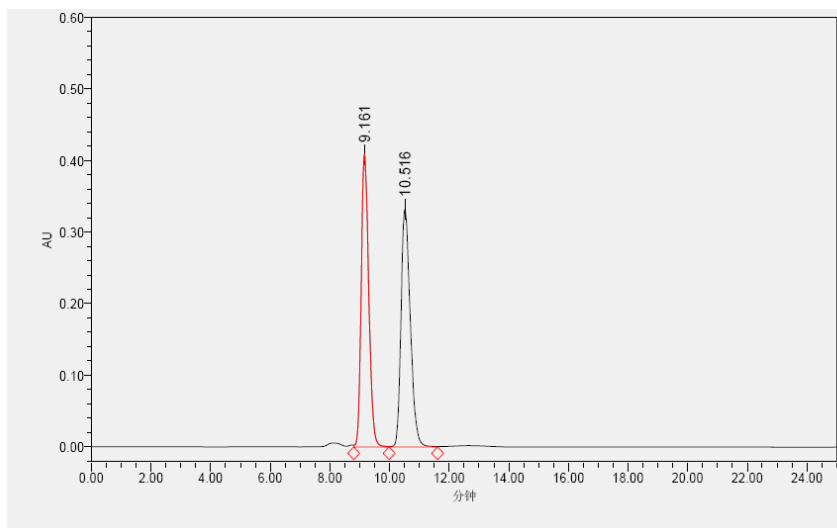
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	14.799	498280	4.96	24698	bV
2	15.771	9549895	95.04	394995	VV



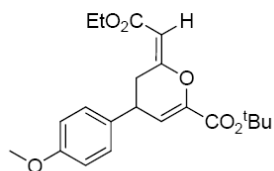
Chiralcel IC,
hexane/*i*PrOH = 95/5,
0.6 mL/min, 254nm

Column: AS-H
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/PrOH = 95/5
Detection Wavelength(nm): 254 nm



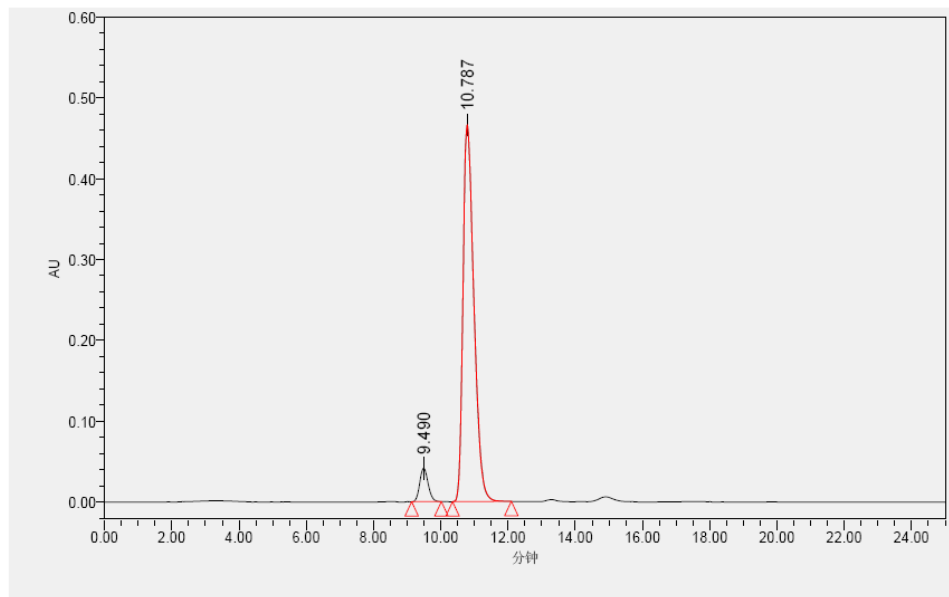
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	9.161	7180283	49.93	409037	VV
2	10.516	7201257	50.07	332433	VV



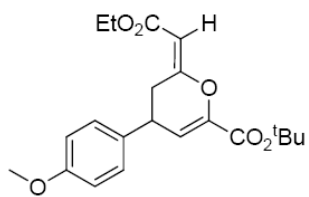
Chiralcel AS-H,
hexane/PrOH = 95/5,
0.6 mL/min, 254nm

Column: AS-H
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/PrOH = 95/5
Detection Wavelength(nm): 254 nm



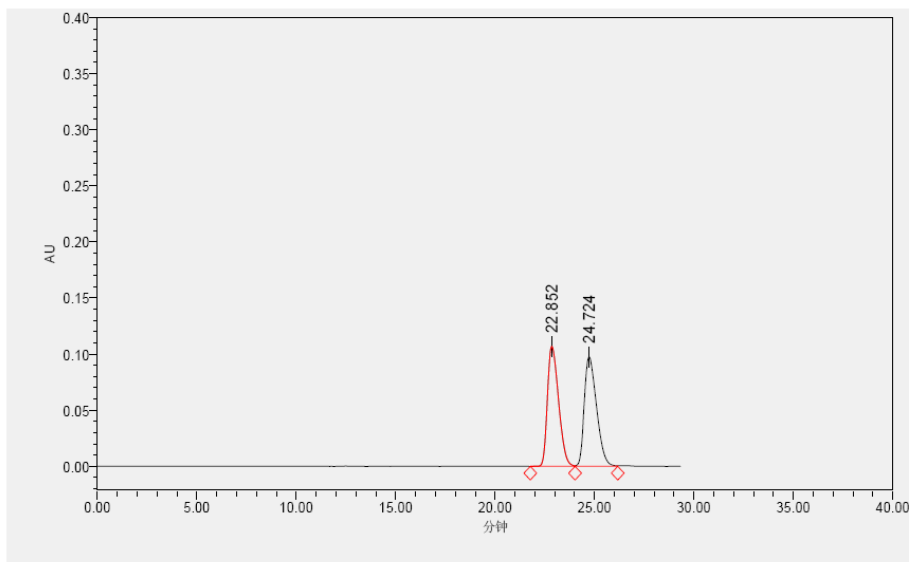
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	9.490	721007	6.43	41472	bb
2	10.787	10500874	93.57	466230	bb



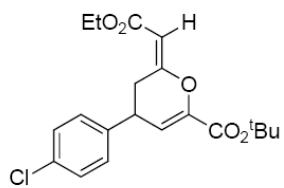
Chiralcel AS-H,
hexane/PrOH = 95/5,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/PrOH = 95/5
Detection Wavelength(nm): 254 nm



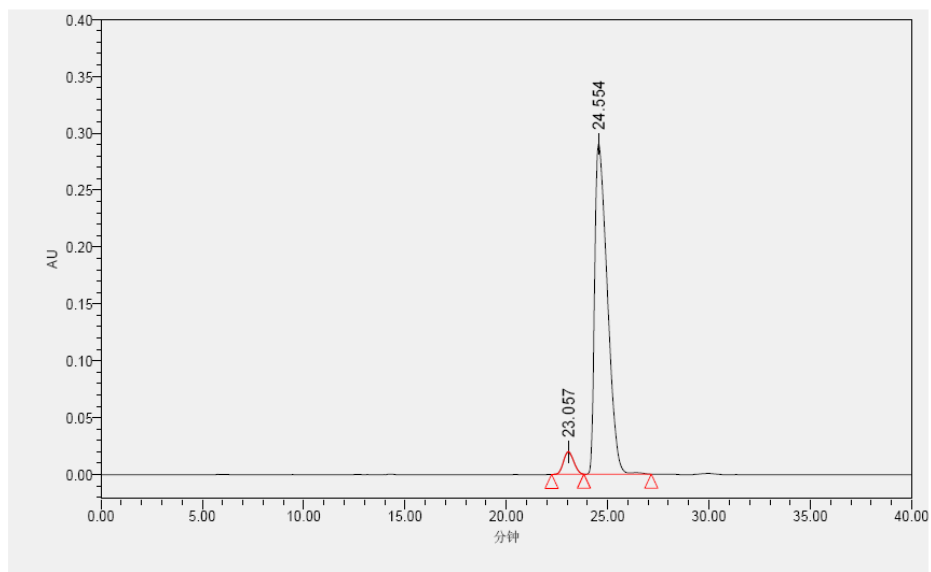
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	22.852	4168646	49.86	106815	VV
2	24.724	4191492	50.14	97523	VV



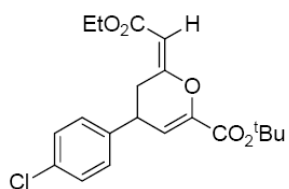
Chiralcel IC,
hexane/PrOH = 95/5,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/ⁱPrOH = 95/5
Detection Wavelength(nm): 254 nm



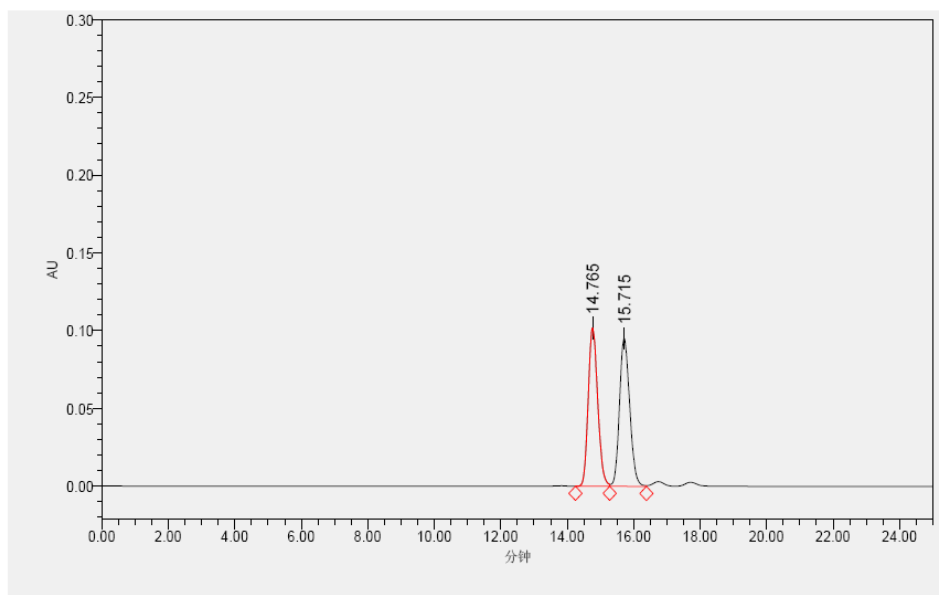
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	23.057	665351	5.01	19365	bb
2	24.554	12608500	94.99	290272	bb



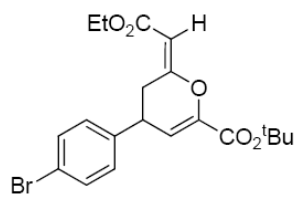
Chiralcel IC,
hexane/ⁱPrOH = 95/5,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/iPrOH = 98/2
Detection Wavelength(nm): 254 nm



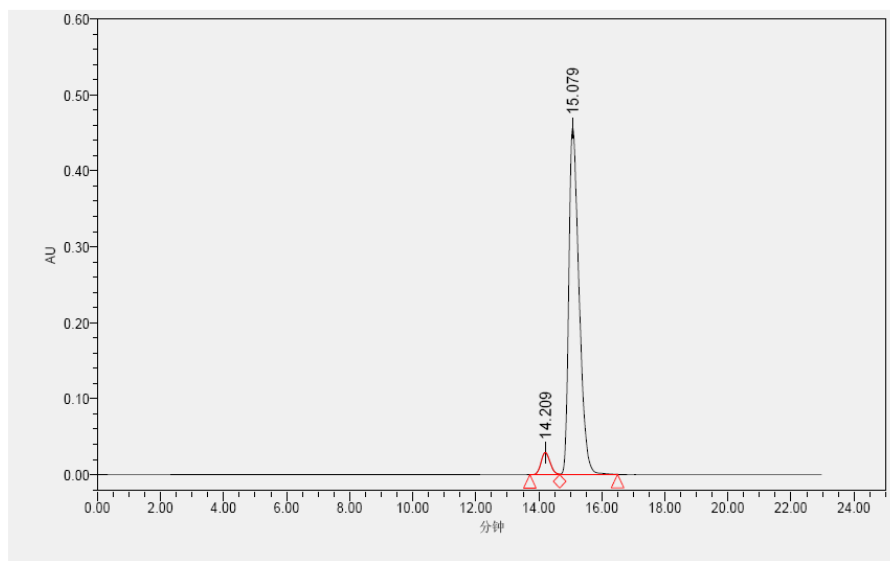
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	14.765	2023897	49.86	101967	Vv
2	15.715	2035441	50.14	95095	vV



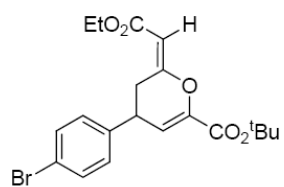
Chiralcel IC,
hexane/iPrOH = 98/2,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/*i*PrOH = 98/2
Detection Wavelength(nm): 254 nm



	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	14.209	526670	4.88	27867	bv
2	15.079	10256857	95.12	455466	vb



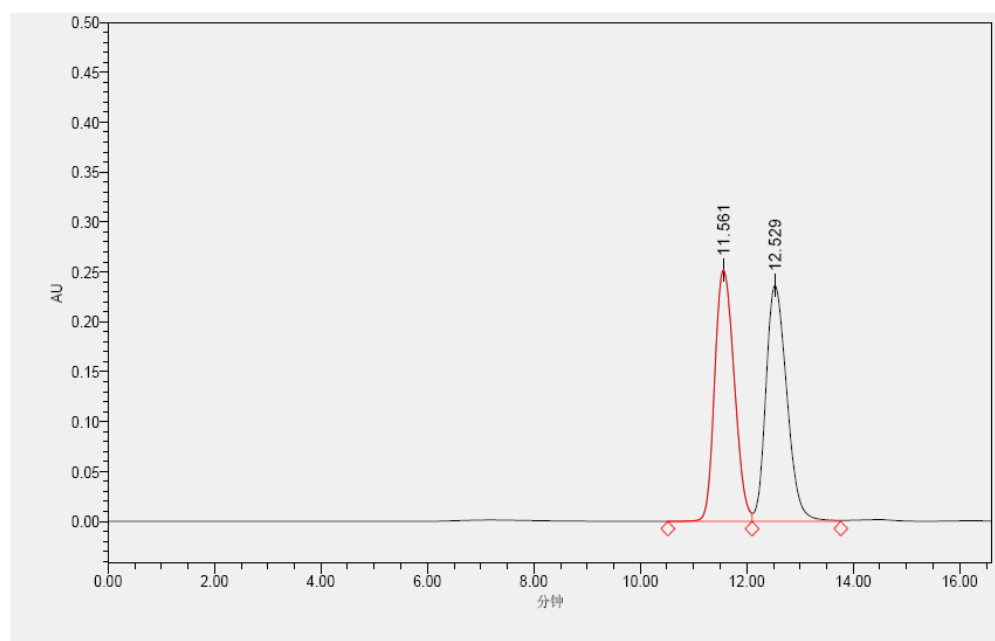
Chiralcel IC,
hexane/*i*PrOH = 98/2,
0.6 mL/min, 254 nm

Column: AS-H

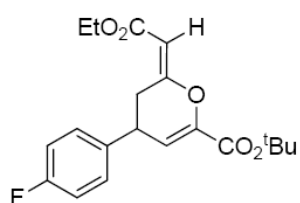
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/ⁱPrOH = 98/2

Detection Wavelength(nm): 254 nm



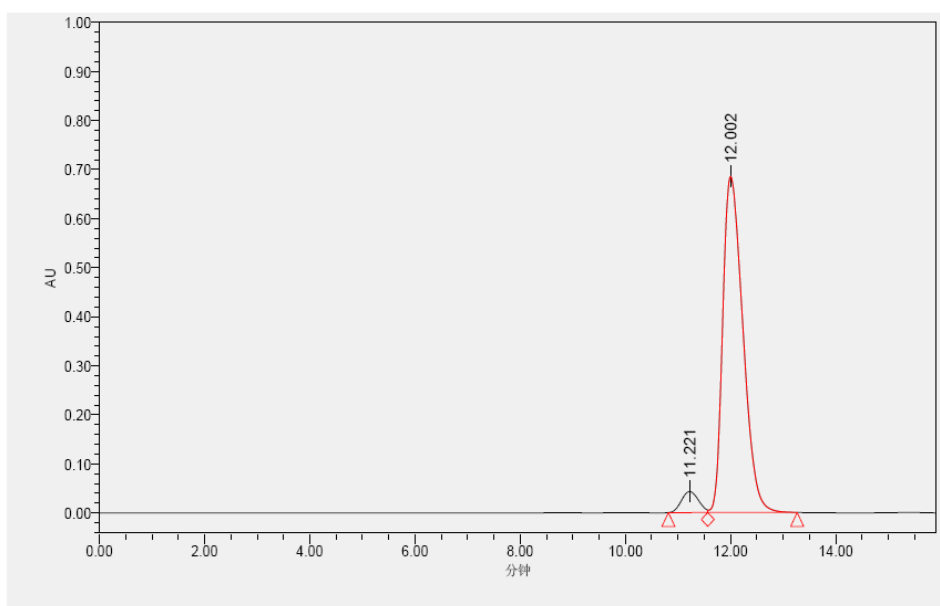
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	11.561	6420633	49.83	251812	VV
2	12.529	6464925	50.17	236265	VV



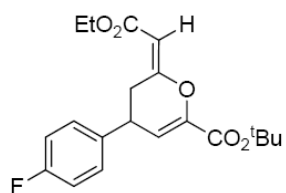
Chiralcel AS-H,
hexane/ⁱPrOH = 98/2,
0.6 mL/min, 254nm

Column: AS-H
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/PrOH = 98/2
Detection Wavelength(nm): 254 nm



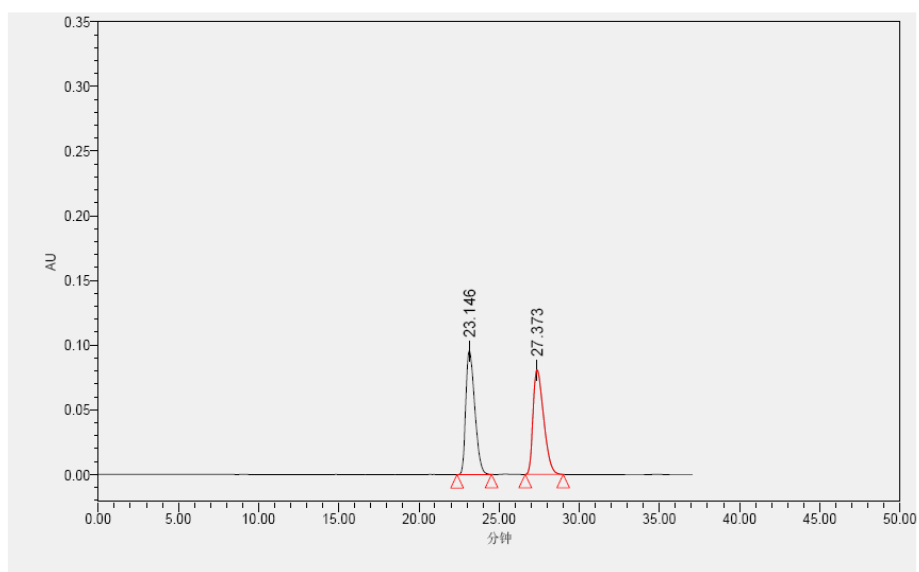
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	11.221	963656	5.02	42871	bv
2	12.002	18240354	94.98	685110	vb



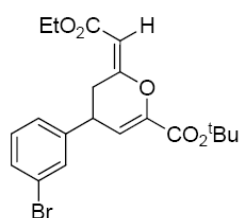
Chiralcel AS-H,
hexane/PrOH = 98/2,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/*i*PrOH = 98/2
Detection Wavelength(nm): 254 nm



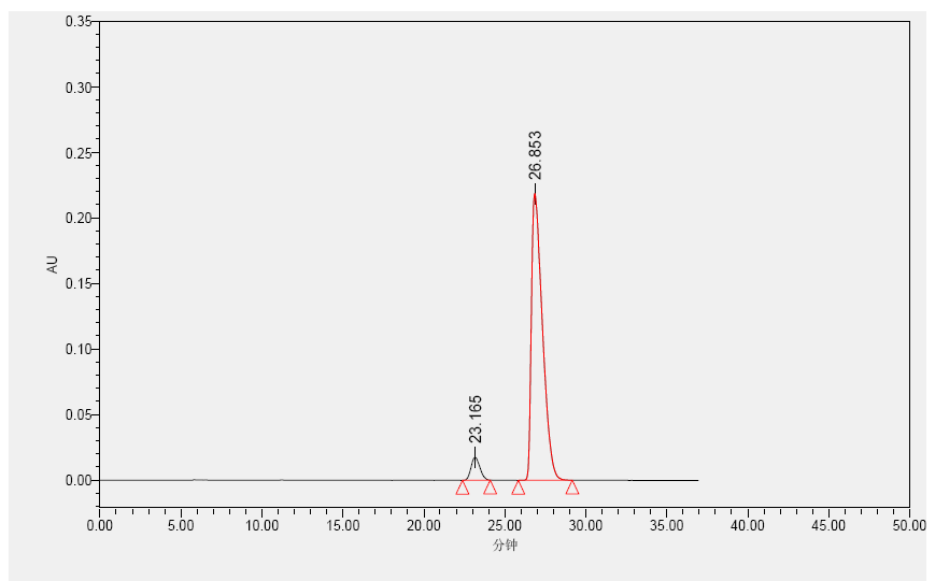
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	23.146	3723269	49.98	95706	bb
2	27.373	3725652	50.02	80835	bb



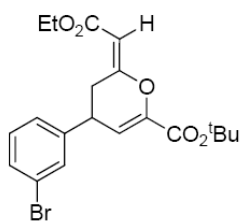
Chiralcel IC,
hexane/*i*PrOH = 98/2,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/iPrOH = 98/2
Detection Wavelength(nm): 254 nm



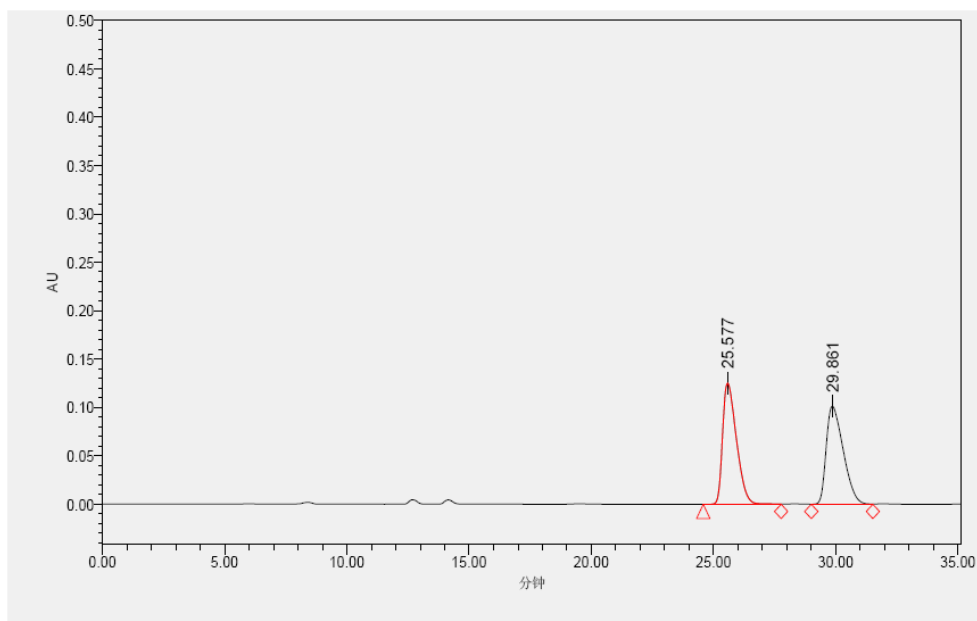
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	23.165	657598	5.99	17356	bb
2	26.853	10329126	94.01	218505	bb



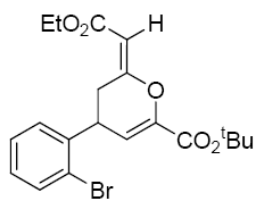
Chiralcel IC,
hexane/iPrOH = 98/2,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/iPrOH = 98/2
Detection Wavelength(nm): 254 nm



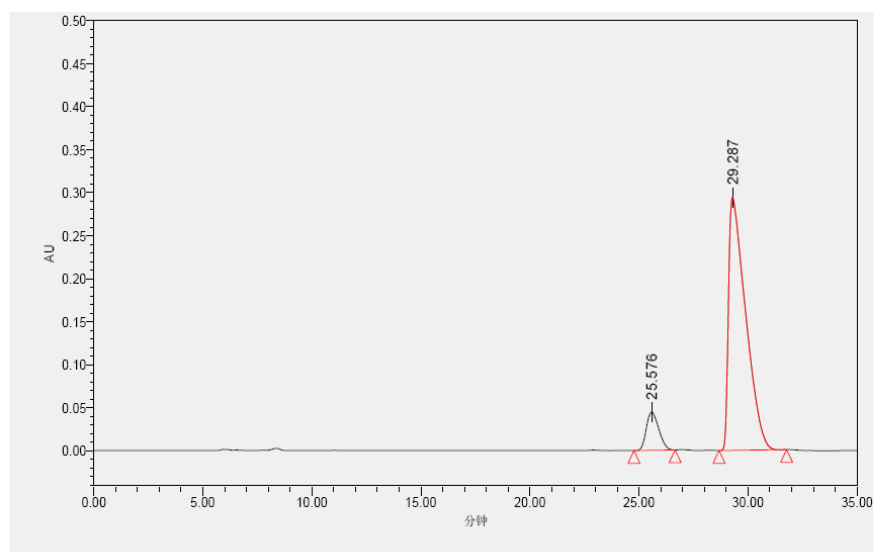
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	25.577	4924180	50.08	125090	BV
2	29.861	4908031	49.92	101349	VV



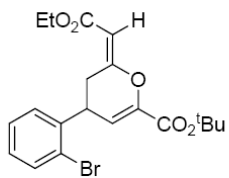
Chiralcel IC,
hexane/iPrOH = 98/2,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/PrOH = 98/2
Detection Wavelength(nm): 254 nm



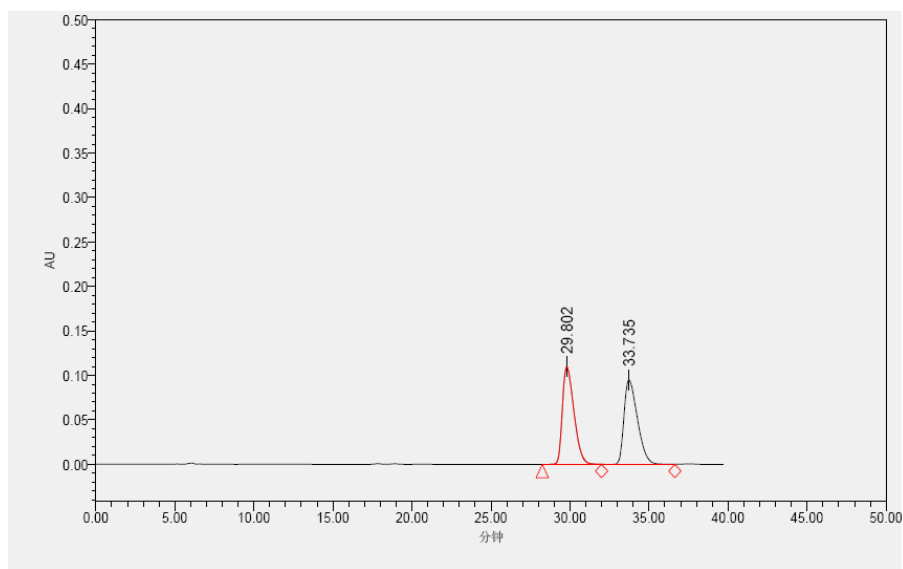
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	25.576	1764572	9.92	44449	bb
2	29.287	16019850	90.08	294229	bb



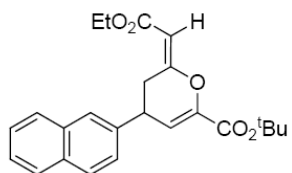
Chiralcel IC,
hexane/PrOH = 98/2,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/PrOH = 98/2
Detection Wavelength(nm): 254 nm



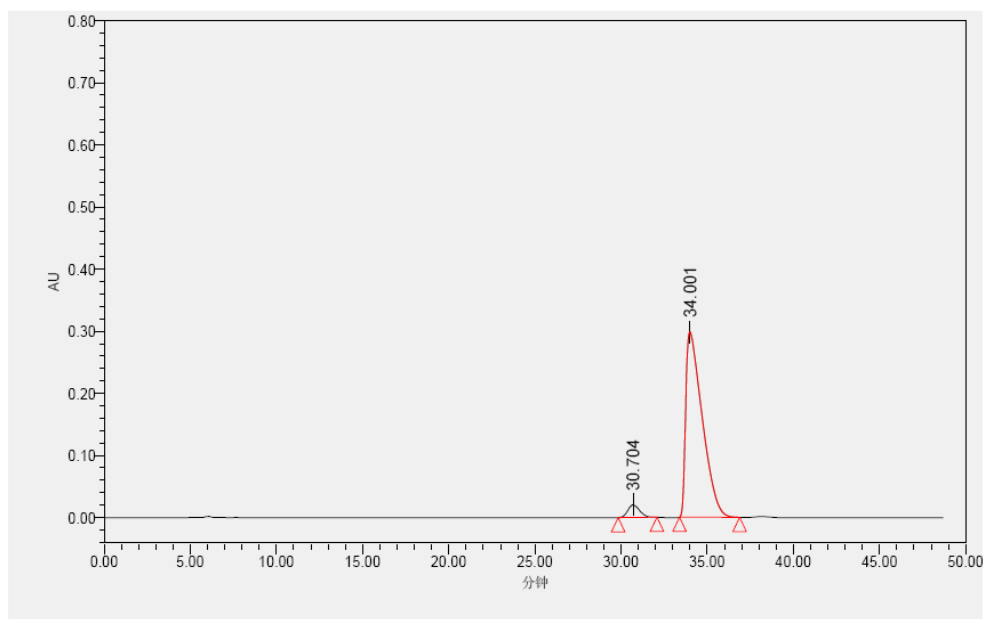
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	29.802	5590029	49.82	109643	Bv
2	33.735	5630792	50.18	94989	vV



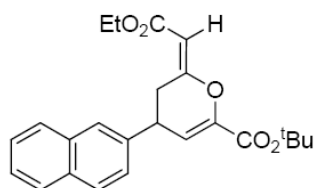
Chiralcel IC,
hexane/PrOH = 98/2,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/iPrOH = 98/2
Detection Wavelength(nm): 254 nm



	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	30.704	953895	4.59	20143	bb
2	34.001	19809469	95.41	298417	bb



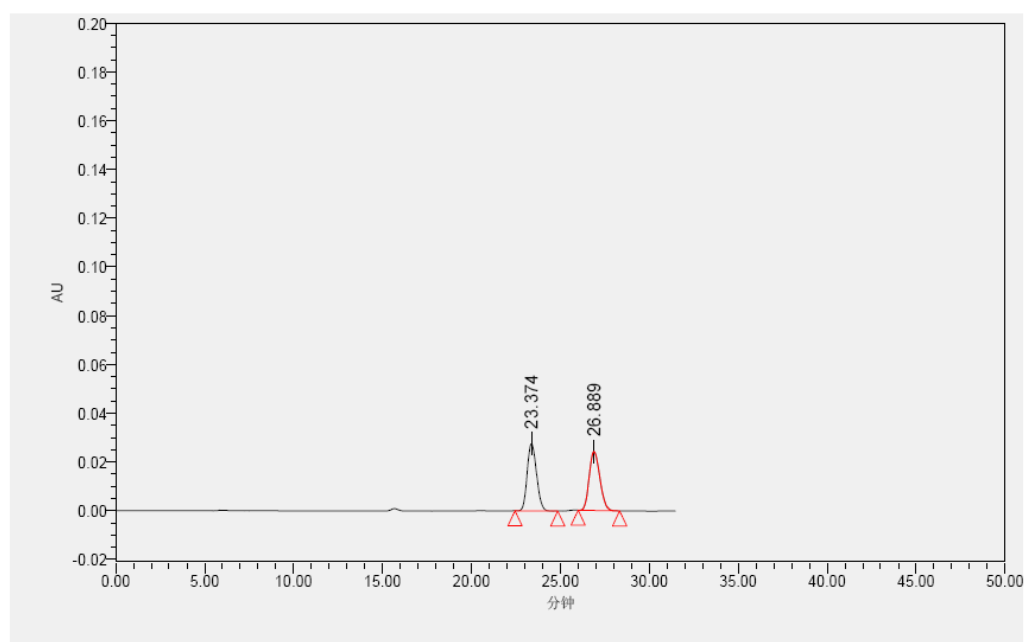
Chiralcel IC,
hexane/iPrOH = 98/2,
0.6 mL/min, 254nm

Column: IC

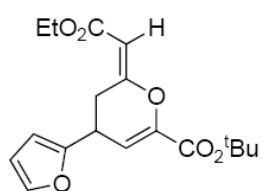
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/*i*PrOH = 98/2

Detection Wavelength(nm): 254 nm



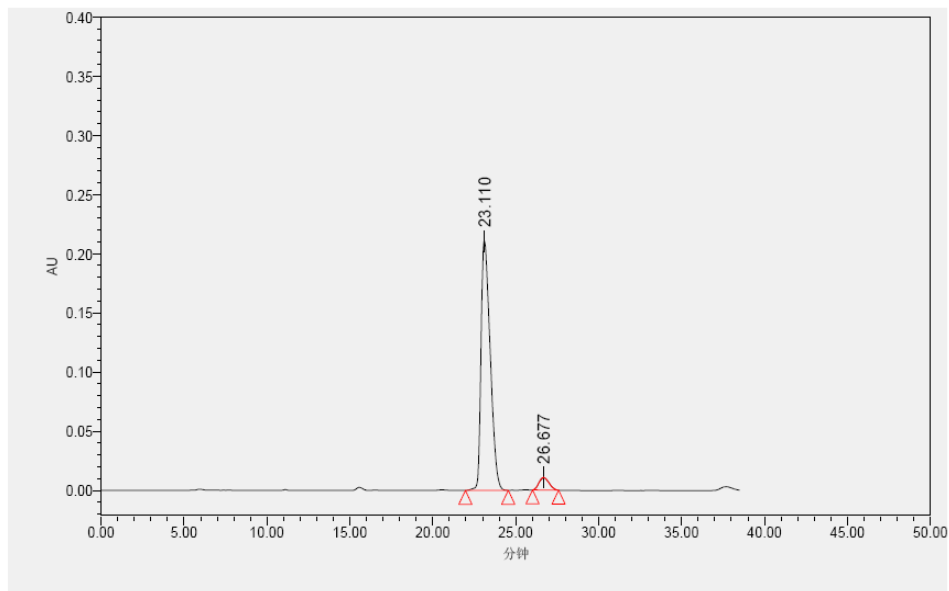
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	23.374	1008256	50.03	27633	bb
2	26.889	1007099	49.97	24112	bb



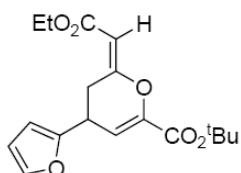
Chiralcel IC,
hexane/*i*PrOH = 98/2,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/iPrOH = 98/2
Detection Wavelength(nm): 254 nm



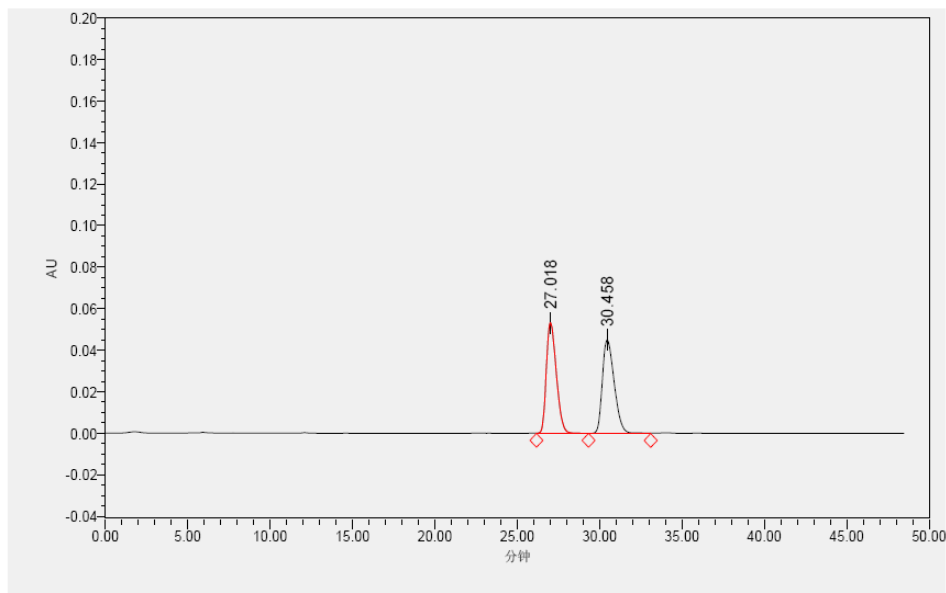
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	23.110	8120045	94.81	210832	bb
2	26.677	444430	5.19	10564	bb



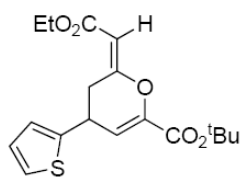
Chiralcel IC,
hexane/iPrOH = 98/2,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/ⁱPrOH = 98/2
Detection Wavelength(nm): 254 nm



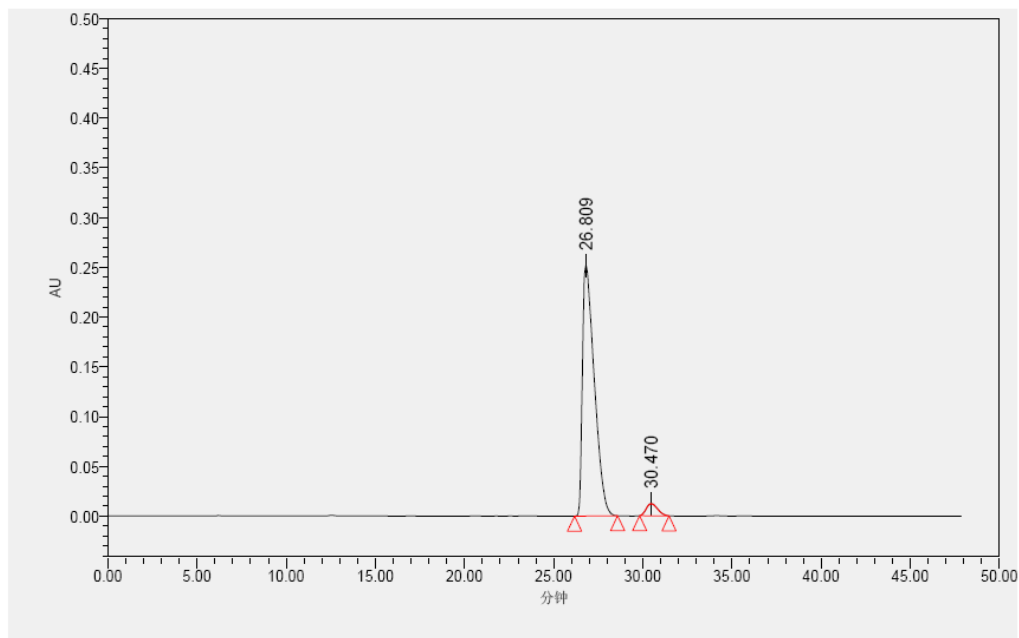
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	27.018	2254744	49.88	53349	VV
2	30.458	2265615	50.12	45053	VV



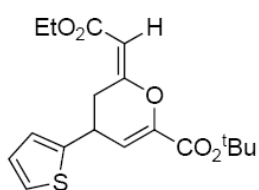
Chiralcel IC,
hexane/ⁱPrOH = 98/2,
0.6 mL/min, 254nm

Column: IC
Velocity(ml/min): 0.6 ml/min

Mobile Phase: hexane/*i*PrOH = 98/2
Detection Wavelength(nm): 254 nm



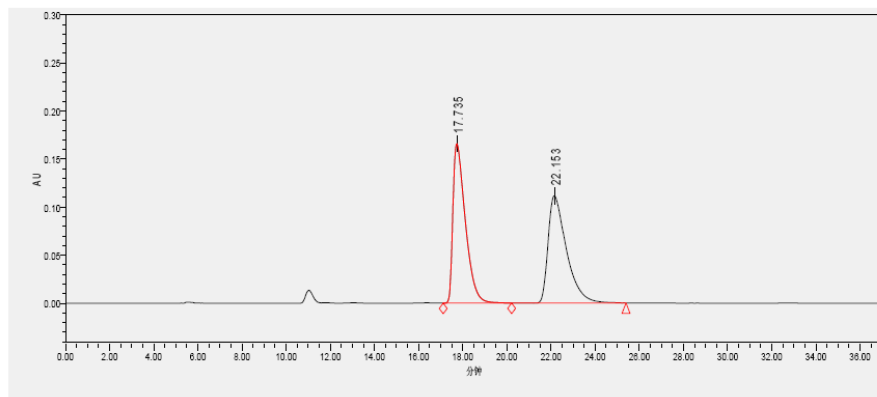
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	26.809	11662078	95.57	251889	bb
2	30.470	540826	4.43	12247	bb



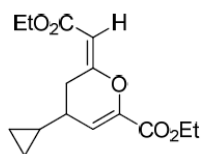
Chiralcel IC,
hexane/*i*PrOH = 98/2,
0.6 mL/min, 254nm

Column: OJ-H
Velocity (ml/min): 0.6 ml/min

Mobile Phase: hexane/ⁱPrOH = 98/2
Detection Wavelength (nm): 254 nm



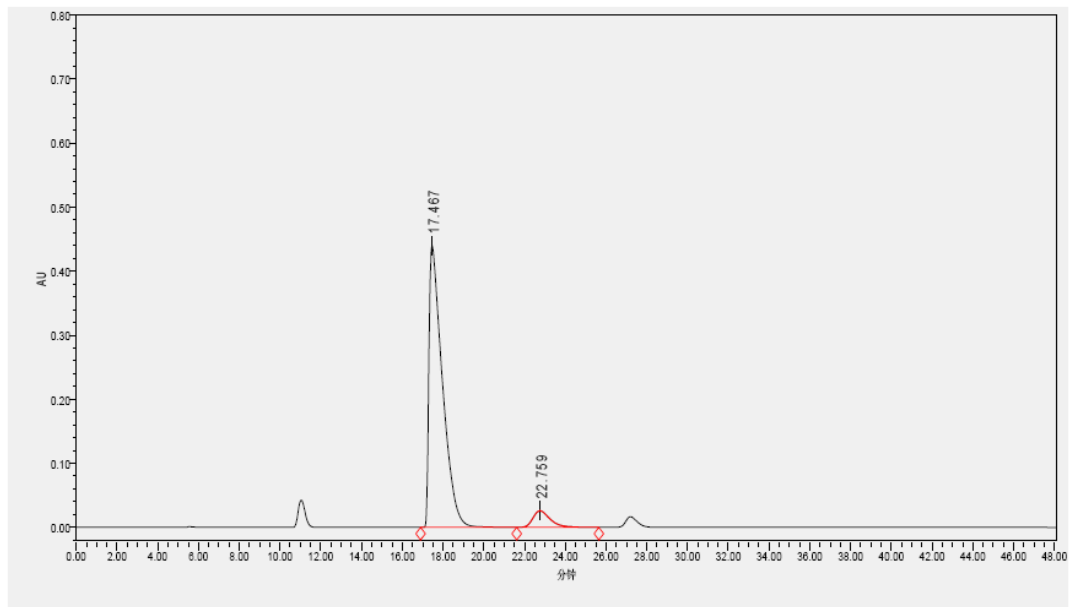
	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	17.735	6483301	50.23	165758	Vv
2	22.153	6424843	49.77	111461	vb



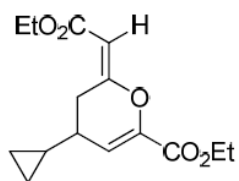
Chiralcel OJ-H,
hexane/ⁱPrOH = 98/2,
0.6 mL/min, 254 nm

Column: OJ-H
Velocity (ml/min): 0.6 ml/min

Mobile Phase: hexane/ⁿPrOH = 98/2
Detection Wavelength (nm): 254 nm

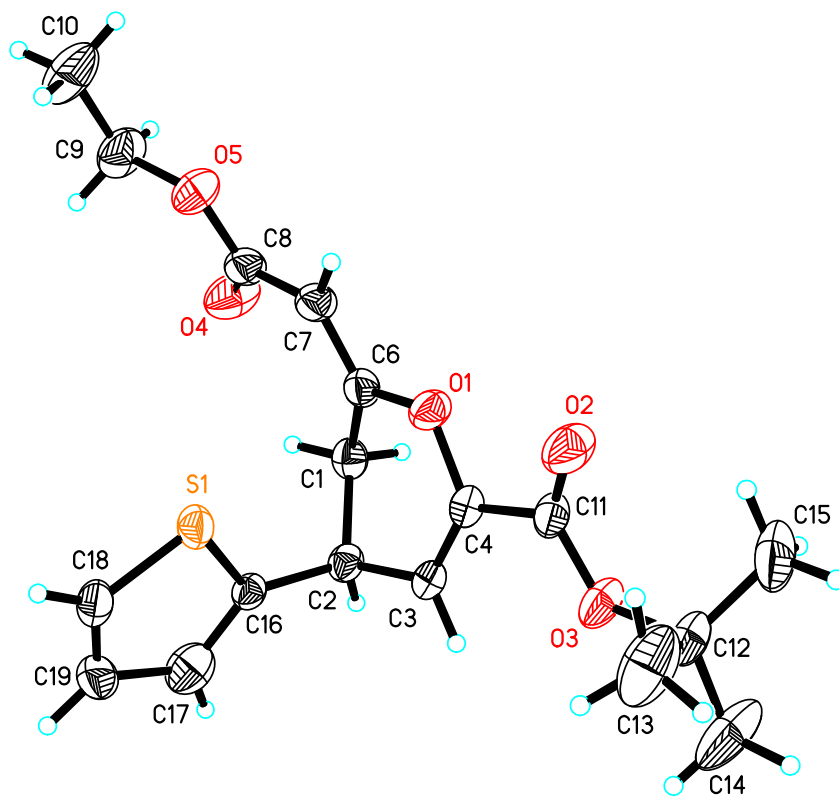


	保留时间	面积(微伏* 秒)	% 面积	高度(微 伏)	积分类型
1	17.467	20219988	92.91	439973	VV
2	22.759	1543677	7.09	25938	VV



Chiralcel OJ-H,
hexane/ⁿPrOH = 98/2,
0.6 mL/min, 254 nm

X-ray Crystal Data of 3na



The crystal data of compound **3na** have been deposited in CCDC with number 850472. Empirical Formula: $C_{18}H_{22}O_5S$; Formula Weight: 350.42; Crystal Color, Habit: colorless; Crystal Dimensions: 0.269 x 0.215 x 0.097 mm; Crystal System: Orthorhombic; Lattice Type: Primitive; Lattice Parameters: $a = 5.5779(5)\text{\AA}$, $b = 10.4276(10)\text{\AA}$, $c = 31.686(3)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 1843.0(3)\text{\AA}^3$; Space group: $P2(1)2(1)2(1)$; $Z = 4$; $D_{calc} = 1.263\text{ g/cm}^3$; $F_{000} = 744$; Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0447$; $wR2 = 0.1151$.

Reference:

1. A. Kumar, S. Sharma, V. D. Tripathi, R. A. Maurya, S. P. Srivastava, G. Bhatia, A. K. Tamrakar and A. K. Srivastava, *Bioorg. Med. Chem.*, 2010, **18**, 4138.
2. (a) Y. Liu, B. Sun, B. Wang, M. Wakem and L. Deng, *J. Am. Chem. Soc.*, 2009, **131**, 418; (b) J.-B. Denis, G. Masson, P. Retailleau and J. Zhu, *Angew. Chem., Int. Ed.*, 2011, **50**, 5356; (c) N. Abermil, G. Masson and J. Zhu, *J. Am. Chem. Soc.*, 2008, **130**, 12596. (d) J. Song, Y. Wang and L. Deng, *J. Am. Chem. Soc.*, 2006, **128**, 6048. (e) C.-K. Pei, X.-C. Zhang and M. Shi, *Eur. J. Org. Chem.*, 2011, 4479; (f) C.-K. Pei and M. Shi, *Tetrahedron: Asymmetry*, 2011, **22** 1239.
3. C.-K. Pei, L. Wu, Z. Lian and M. Shi, *Org. Biomol. Chem.*, 2012, **10**, 171.