

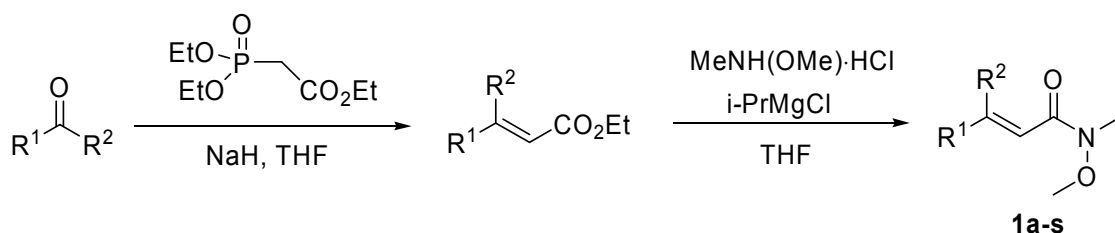
1. General

All air- and moisture-sensitive manipulations and reactions were performed using standard Schlenk techniques under argon or in a glove box under nitrogen. All reactions were carried out with anhydrous solvents unless otherwise noted. All reagents and starting materials, unless otherwise noted, were purchased from commercial vendors and were used without further purification. All solvents were dried and distilled before use by following standard procedures. Melting points were measured on a XT-4 or SGWX apparatus and uncorrected. ^1H , ^{13}C , ^{31}P and ^{19}F NMR spectra were recorded on a Varian Mercury VX300 or a Varian 400-MR spectrometer. Chemical shifts (δ values) were reported in ppm downfield from internal TMS (^1H NMR) or CDCl_3 (^{13}C NMR), external 85% H_3PO_4 (^{31}P NMR) and external $\text{CF}_3\text{CO}_2\text{H}$ (^{19}F NMR), respectively. The IR spectra were measured on a Bio-Rad FIS-185 or NICOLET AVARTAR 330FT-IR spectrometer. EI (70 eV) mass spectra were obtained on an Agilent 5973N spectrometer, and HRMS (EI, 70 eV) were determined on Waters Micromass GCT CA176 spectrometer. Optical rotations were determined using a Perkin Elmer 341 MC polarimeter. Chiral HPLC analyses were performed on a JASCO 2089 or JASCO 1580 liquid chromatography. The chiral iridium complexes (*R,S*)-**3a-e**, (*S,S*)-**3b-e** were synthesized by following our previously published procedure.^[1]

2 Synthesis of the α,β -unsaturated Weinreb amide substrates

2.1 General procedure for the preparation of α,β -unsaturated Weinreb amide substrates

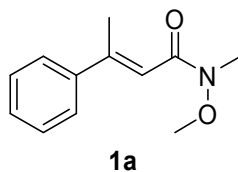
The α,β -unsaturated Weinreb amide substrates **1a-s** were synthesized by using a procedure analogous to that reported by Nishiyama et al.^[2]



To a suspension of NaH (60 % dispersion in oil, 26.0 mmol) in THF (10 mL) was slowly added a solution of triethyl phosphonoacetate (26.0 mmol) in THF (2 mL) under an argon atmosphere. After being stirred at room temperature for 30 min, a solution of a corresponding ketone (20 mmol) in THF (2 mL) was added to the reaction mixture. The resulting mixture was heated to reflux and stirred for 12 h. The reaction was quenched by adding sat. aq. NaHCO₃, and the mixture was extracted with ethyl acetate (3 × 50 mL). The organic layer was separated and washed with brine, dried over Na₂SO₄, filtered, and concentrated at reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate as the eluent to afford the corresponding (*E*)- and (*Z*)-α,β-unsaturated esters.

To a solution of the (*E*)-ester (15 mmol) and *N,O*-dimethylhydroxyamine hydrochloride (2.93 g, 30 mmol) in THF (20 mL) was added dropwise a solution of *i*PrMgCl in THF (3.58 M, 64.5 mmol) at – 5 °C. After being stirred for 0.5 h, the mixture was treated with saturated aq. NH₄Cl, followed by extraction with ethyl acetate (3 × 50 mL). The combined organic phase was washed with brine, dried over Na₂SO₄, filtered, and concentrated at reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate as the eluent to give the corresponding α,β-unsaturated *N*-methoxy amide **1**.

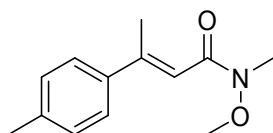
(*E*)-*N*-methoxy-*N*-methyl-3-phenylbut-2-enamide (1a**)**^[2]



Pale yellow liquid, 80% yield for two steps. ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.47

(m, 2H), 7.40-7.34 (m, 3H), 6.58 (s, 1H), 3.70 (s, 3H), 3.26 (s, 3H), 2.53 (d, $J = 1.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.8, 151.4, 142.9, 128.5, 128.3, 126.2, 115.9, 61.5, 32.2, 17.9 ppm.

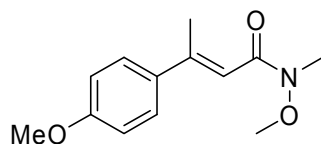
(*E*)-*N*-methoxy-*N*-methyl-3-*p*-tolylbut-2-enamide (1b)



1b

Pale yellow liquid, 87% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.35 (m, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 6.58 (s, 1H), 3.65 (s, 3H), 3.22 (s, 3H), 2.52 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.3, 151.4, 139.2, 137.9, 128.5, 125.5, 114.5, 60.7, 31.5, 20.4, 17.1 ppm; IR (film) ν 2935, 1644, 1616, 1513, 1439, 1413, 1366, 1323, 1178, 1102, 1075, 1017, 977, 871, 812, 623 cm^{-1} ; EI-MS (70 eV) m/z : 219 (M^+ , 1.6), 179 (2.4), 159 (100.0), 131 (14.7), 115 (19.6), 91 (16.8), 77 (2.5); HRMS (EI) m/z : Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_2$: 219.1259, Found: 219.1257 [M] $^+$.

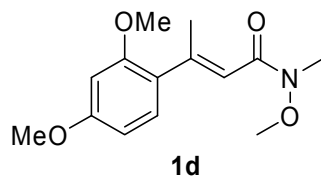
(*E*)-*N*-methoxy-3-(4-methoxyphenyl)-*N*-methylbut-2-enamide (1c)



1c

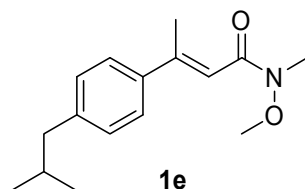
Pale yellow liquid, 89% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ 7.45 (dd, $J = 6.4, 1.6$ Hz, 2H), 6.90 (dd, $J = 6.4, 1.6$ Hz, 2H), 6.55 (s, 1H), 3.83 (s, 3H), 3.71 (s, 3H), 3.26 (s, 3H), 2.52 (d, $J = 1.2$ Hz, 3H) ppm; ^{13}C NMR (100MHz, CDCl_3) δ 168.1, 160.0, 151.7, 135.0, 127.5, 114.1, 113.7, 61.5, 55.2, 32.1, 17.7 ppm; IR (film) ν 2936, 2838, 1648, 1603, 1513, 1441, 1368, 1290, 1248, 1181, 1031, 979, 829, 562 cm^{-1} ; EI-MS (70 eV) m/z : 235 (M^+ , 3.3), 223 (2.0), 204 (4.7), 175 (100.0), 159 (7.7), 115 (13.0), 91 (11.2), 44 (16.0); HRMS (EI) m/z : Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: 235.1208, Found: 235.1214 [M] $^+$.

(*E*)-3-(2,4-dimethoxyphenyl)-*N*-methoxy-*N*-methylbut-2-enamide (1d)



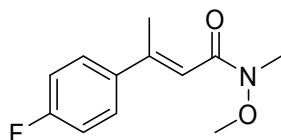
Pale yellow liquid, 49% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ 7.13-7.11 (m, 1H), 6.49-6.46 (m, 2H), 6.35 (s, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.69 (s, 3H), 3.25 (s, 3H), 2.44 (d, $J = 1.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 160.2, 157.0, 151.6, 128.9, 125.6, 116.7, 103.6, 98.2, 60.7, 54.7, 54.6, 31.5, 19.0 ppm; IR (film) ν 2998, 2937, 2837, 1610, 1577, 1502, 1462, 1440, 1413, 1301, 1267, 1208, 1160, 1034, 981, 836 cm^{-1} ; EI-MS (70 eV) m/z : 265 (M^+ , 1.38), 219 (1.4), 205 (100.0), 190 (5.2), 177 (6.5), 162 (15.4), 121 (4.5), 91 (4.8); HRMS (EI) m/z : Calcd. for $\text{C}_{14}\text{H}_{19}\text{NO}_4$: 265.1314, Found: 265.1309 [M] $^+$.

(*E*)-3-(4-isobutylphenyl)-*N*-methoxy-*N*-methylbut-2-enamide (1e)



Pale yellow liquid, 72% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.39 (m, 2H), 7.16-7.14 (m, 2H), 6.58 (s, 1H), 3.71 (s, 3H), 3.26 (s, 3H), 2.52 (d, $J = 1.2$ Hz, 3H), 2.49 (d, $J = 7.2$ Hz, 2H), 1.89-1.86 (m, 1H), 0.92 (d, $J = 5.6$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.5, 151.6, 141.9, 139.7, 128.7, 125.5, 114.6, 61.0, 44.6, 31.8, 30.0, 21.9, 17.3 ppm; IR (film) ν 2954, 2868, 1648, 1618, 1463, 1440, 1366, 1176, 1102, 1017, 978, 842, 797, 629 cm^{-1} ; EI-MS (70 eV) m/z : 261 (M^+ , 1.1), 246 (0.5), 231 (1.0), 201 (100.0), 145 (52.6), 129 (10.2), 115 (18.2), 91 (3.9); HRMS (EI) m/z : Calcd. for $\text{C}_{16}\text{H}_{23}\text{NO}_2$: 261.1729, Found: 261.1731 [M] $^+$.

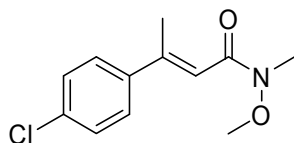
(*E*)-3-(4-fluorophenyl)-*N*-methoxy-*N*-methylbut-2-enamide (1f)



1f

Pale yellow liquid, 70% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ 7.48-7.44 (m, 2H), 7.08-7.03 (m, 2H), 6.53 (s, 1H), 3.71 (s, 3H), 3.27 (s, 3H), 2.51 (d, $J = 1.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.1, 162.3 (d, $J = 246.5$ Hz), 150.2, 138.3, 127.4 (d, $J = 8.8$ Hz), 115.4, 114.7 (d, $J = 21.5$ Hz), 60.9, 31.6, 17.3 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -113.3 (s) ppm; IR (film) ν 2937, 1644, 1619, 1600, 1509, 1439, 1368, 1231, 1161, 1103, 977, 828 cm^{-1} ; EI-MS (70 eV) m/z : 223 (M^+ , 2.0), 163 (100.0), 133 (21.1), 120 (3.0), 115 (16.6), 109 (12.9); HRMS (EI) m/z : Calcd. for $\text{C}_{12}\text{H}_{14}\text{NO}_2\text{F}$: 223.1009, Found: 223.1013 [M] $^+$.

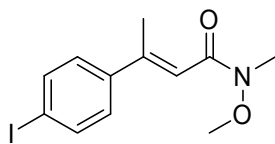
(E)-3-(4-chlororophenyl)-N-methoxy-N-methylbut-2-enamide (1g)^[3]



1g

Pale yellow liquid, 89% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.39 (m, 2H), 7.31-7.29 (m, 2H), 6.57 (s, 1H), 3.70 (s, 3H), 3.25 (s, 3H), 2.49 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 150.0, 140.6, 133.8, 128.0, 127.0, 115.8, 60.9, 31.6, 17.1 ppm; IR (film) ν 2963, 2936, 1649, 1621, 1490, 1441, 1370, 1178, 1092, 1012, 979, 824, 772 cm^{-1} ; EI-MS (70 eV) m/z : 239 (M^+ , 1.6), 209 (1.5), 179 (100.0), 151 (3.8), 115 (42.2), 89 (4.3), 75 (3.9), 63 (2.2); HRMS (EI) m/z : Calcd. for $\text{C}_{12}\text{H}_{14}\text{ClNO}_2$: 239.0713, Found: 239.0717 [M] $^+$.

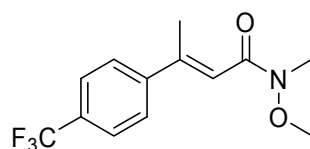
(E)-3-(4-iodophenyl)-N-methoxy-N-methylbut-2-enamide (1h)



1h

Pale yellow liquid, 72% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 6.55 (s, 1H), 3.70 (s, 3H), 3.26 (s, 3H), 2.48 (d, J = 1.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.3, 150.6, 142.1, 137.3, 127.8, 116.2, 94.2, 61.4, 32.1, 17.5 ppm; IR (film) ν 3058, 2962, 2934, 2815, 1642, 1581, 1483, 1440, 1411, 1370, 1178, 1112, 1076, 1003, 979, 817 cm^{-1} ; EI-MS (70 eV) m/z : 331 (M^+ , 5.4), 300 (1.8), 271 (100.0), 195 (20.9), 165 (6.1), 144 (75.7), 115 (65.5), 89 (6.5), 63 (4.7); HRMS (EI) m/z : Calcd. for $\text{C}_{12}\text{H}_{14}\text{INO}_2$: 331.0069, Found: 331.0070 $[\text{M}]^+$.

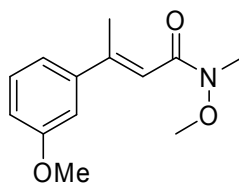
(*E*)-3-(4-trifluorophenyl)-*N*-methoxy-*N*-methylbut-2-enamide (1i)



1i

Pale yellow liquid, 82% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ 7.64-7.58 (m, 4H), 6.63 (s, 1H), 3.73 (s, 3H), 3.28 (s, 3H), 2.54 (d, J = 1.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.1, 150.0, 146.2, 130.0 (q, J_{CF} = 32.6 Hz), 126.3, 125.0 (q, J_{CF} = 3.8 Hz), 123.8 (q, J_{CF} = 270.0 Hz), 117.6, 61.2, 31.8, 17.5 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -62.8 (s) ppm; IR (film) ν 2939, 1650, 1624, 1575, 1443, 1406, 1371, 1327, 1168, 1119, 1079, 1015, 980, 833 cm^{-1} ; EI-MS (70 eV) m/z : 273 (M^+ , 1.6), 254 (2.5), 213 (100.0), 183 (2.9), 165 (25.1), 145 (5.8), 115 (14.4), 109 (1.7), 89 (0.9); HRMS (EI) m/z : Calcd. for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NO}_2$: 273.0977, Found: 273.0982 $[\text{M}]^+$.

(*E*)-*N*-methoxy-3-(3-methoxyphenyl)-*N*-methylbut-2-enamide (1j)

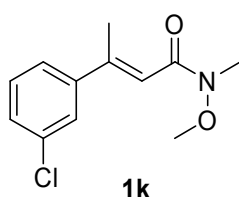


1j

Colorless liquid, 78% yield for two steps. ^1H NMR (300 MHz, CDCl_3) δ 7.30 (t, J =

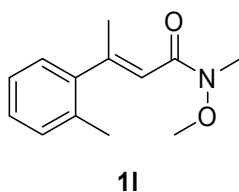
7.5 Hz, 1H), 7.07 (d, $J = 7.8$ Hz, 1H), 7.01 (t, $J = 1.8$ Hz, 1H), 6.89 (dd, $J = 8.4, 2.4$ Hz), 6.57 (s, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 3.27 (s, 3H), 2.51 (s, 3H) ppm, ^{13}C NMR (75 MHz, CDCl_3) δ 167.6, 159.3, 151.8, 144.2, 129.3, 118.6, 116.0, 113.4, 112.1, 61.3, 55.0, 32.0, 17.8 ppm; EI-MS (70 eV) m/z : 235 (M^+ , 2.3), 222 (20.4), 175 (100), 168 (6.8), 132 (10.0), 115 (17.9), 104 (9.0), 91 (16.2); HRMS (EI) m/z : Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: 235.1208, Found: 235.1207 [M] $^+$.

(*E*)-3-(3-chlorophenyl)-*N*-methoxy-*N*-methylbut-2-enamide (1k)



White solid, 62% yield for two steps, m.p. 64-66 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.45 (s, 1H), 7.35-7.30 (m, 3H), 6.55 (s, 1H), 3.72 (s, 3H), 3.28 (s, 3H), 2.50 (s, 3H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 167.3, 150.4, 144.5, 134.2, 129.5, 128.3, 126.2, 124.3, 116.7, 61.4, 32.0, 17.7 ppm; EI-MS (70 eV) m/z : 239 (M^+ , 2.6), 181 (32.7), 179 (100.0), 151 (5.8), 138 (6.6), 115 (74.1), 101 (4.2), 89 (6.7); HRMS (EI) m/z : Calcd. for $\text{C}_{12}\text{H}_{14}\text{ClNO}_2$: 239.0713, Found: 239.0711 [M] $^+$.

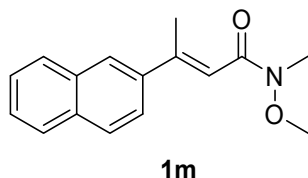
(*E*)-*N*-methoxy-*N*-methyl-3-*o*-tolylbut-2-enamide (1l)



Pale yellow liquid, 59% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ 7.18-7.14 (m, 3H), 7.10-7.09 (m, 1H), 6.22 (s, 1H), 3.65 (s, 3H), 3.24 (s, 3H), 2.42 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 154.6, 144.3, 133.7, 130.1, 127.2, 127.0, 125.5, 117.5, 61.2, 31.9, 20.3, 19.5 ppm; IR (film) ν 3060, 2935, 2817, 1655, 1486, 1441, 1409, 1366, 1319, 1178, 1101, 1015, 981, 762, 730 cm^{-1} ; EI-MS (70 eV) m/z : 219 (M^+ , 2.7), 189 (0.7), 159 (100.0), 131 (23.4), 115 (21.4), 103 (2.5), 91 (26.6),

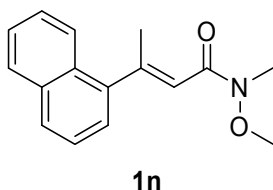
77 (3.5), 65 (3.7); HRMS (EI) m/z : Calcd. for $C_{13}H_{17}NO_2$: 219.1259, Found: 219.1264 $[M]^+$.

(*E*)-*N*-methoxy-*N*-methyl-3-(naphthalen-2-yl)but-2-enamide (1m)^[3]



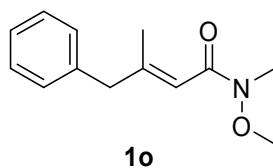
Pale yellow liquid, 81% yield for two steps. 1H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.85-7.78 (m, 3H), 7.59 (d, $J = 11.2$ Hz, 1H), 7.49-7.42 (m, 2H), 6.72 (s, 1H), 3.68 (s, 3H), 3.27 (s, 3H), 2.64 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 151.1, 139.3, 132.7, 132.5, 127.8, 127.5, 126.9, 125.8, 125.7, 125.0, 123.4, 115.8, 60.8, 31.7, 17.3 ppm; IR (film) ν 3056, 2963, 2934, 1648, 1440, 1408, 1370, 1345, 1178, 1103, 980, 817, 750, 629 cm^{-1} ; EI-MS (70 eV) m/z : 255 (M^+ , 3.5), 225 (2.1), 205 (0.7), 195 (100.0), 165 (26.0), 152 (21.9), 128 (3.3), 83 (6.3); HRMS (EI) m/z : Calcd. for $C_{16}H_{17}NO_2$: 255.1259, Found: 255.1261 $[M]^+$.

(*E*)-*N*-methoxy-*N*-methyl-3-(naphthalen-1-yl)but-2-enamide (1n)



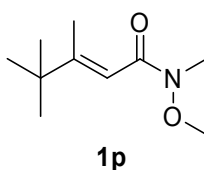
Pale yellow liquid, 61% yield for two steps. 1H NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (m, 1H), 7.85-7.83 (m, 1H), 7.79-7.76 (m, 1H), 7.48-7.41 (m, 3H), 7.31-7.29 (m, 1H), 6.42 (s, 1H), 3.63 (s, 3H), 3.27 (s, 3H), 2.60 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 153.6, 142.6, 133.6, 130.2, 128.3, 127.7, 126.0, 125.8, 125.3, 125.1, 124.1, 118.9, 61.4, 32.1, 21.4 ppm; IR (film) ν 3057, 2963, 2935, 1642, 1506, 1409, 1381, 1317, 1179, 1096, 1005, 974, 801, 779, 634 cm^{-1} ; EI-MS (70 eV) m/z : 255 (M^+ , 6.3), 195 (100.0), 165 (25.4), 152 (23.7), 139 (2.0), 126 (2.0), 115 (1.7), 105 (1.3), 83 (3.5); HRMS (EI) m/z : Calcd. for $C_{16}H_{17}NO_2$: 255.1259, Found: 255.1255 $[M]^+$.

(E)-N-methoxy-N-methyl-3-methyl-4-phenylbut-2-enamide (1o)



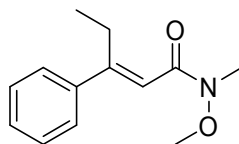
Pale yellow liquid, 74% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.16 (m, 5H), 6.11 (s, 1H), 3.59 (s, 3H), 3.43 (s, 2H), 3.17 (s, 3H), 2.08 (d, $J = 1.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.6, 154.4, 138.0, 128.8, 128.2, 126.2, 115.6, 61.1, 46.9, 31.9, 18.3 ppm; IR (film) ν 3027, 2963, 2935, 1656, 1494, 1412, 1369, 1327, 1261, 1177, 1099, 1076, 998, 701 cm^{-1} ; EI-MS (70 eV) m/z : 219 (M^+ , 1.8), 189 (3.1), 159 (100.0), 144 (23.6), 131 (20.3), 115 (12.2), 91 (29.5), 77 (3.3), 65 (6.6); HRMS (EI) m/z : Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_2$: 219.1259, Found: 219.1261 $[\text{M}]^+$.

(E)-N-methoxy-N-methyl-3,4,4-trimethylpent-2-enamide (1p)



Colorless liquid, 88% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ 6.16 (s, 1H), 3.66 (s, 3H), 3.19 (s, 3H), 2.08 (s, 3H), 1.12 (s, 9H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 161.1, 111.3, 60.4, 36.8, 31.5, 27.9, 14.1 ppm; IR (film) ν 2963, 1652, 1625, 1463, 1409, 1372, 1359, 1316, 1178, 1099, 1041, 1007, 981, 862, 835, 723, 620 cm^{-1} ; EI-MS (70 eV) m/z : 185 (M^+ , 1.1), 170 (1.6), 159 (4.5), 125 (100.0), 110 (2.8), 97 (6.5), 83 (4.7), 69 (7.9), 57 (13.6), 55 (21.5); HRMS (EI) m/z : Calcd. for $\text{C}_{10}\text{H}_{19}\text{NO}_2$: 185.1416, Found: 185.1415 $[\text{M}]^+$.

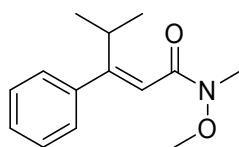
(E)-N-methoxy-N-methyl-3-phenylpent-2-enamide (1q)^[3]



1q

Pale yellow liquid, 70% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.41 (m, 2H), 7.36-7.27 (m, 3H), 6.46 (s, 1H), 3.63 (s, 3H), 3.22 (s, 3H), 3.06 (q, $J = 7.2$ Hz, 2H), 1.07 (t, $J = 7.6$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 158.0, 141.1, 127.9, 127.8, 126.1, 115.1, 60.8, 31.5, 23.7, 13.0 ppm; IR (film) ν 2967, 2935, 2874, 1642, 1619, 1575, 1461, 1446, 1409, 1381, 1334, 1178, 1112, 1094, 996, 766, 699 cm^{-1} ; EI-MS (70 eV) m/z : 219 (M^+ , 1.96), 189 (0.53), 159 (100.0), 144 (5.62), 131 (10.6), 115 (10.4), 91 (23.4), 77 (5.0); HRMS (EI) m/z : Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_2$: 219.1259, Found: 219.1263 $[\text{M}]^+$.

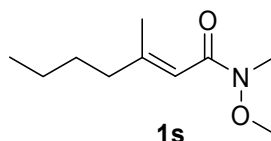
(E)-N-methoxy-N,4-dimethyl-3-phenylpent-2-enamide (1r)^[4]



1r

This compound was prepared by following a literature procedure.^[4]

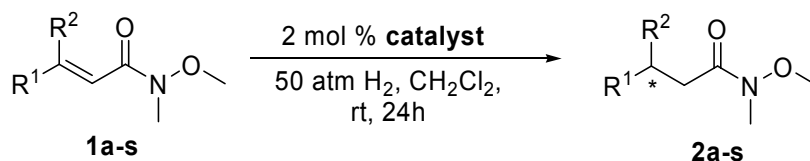
(E)-N-methoxy-N,3-dimethylhept-2-enamide (1s)



1s

Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.11 (s, 1H), 3.68 (s, 3H), 3.20 (s, 3H), 2.17-2.12 (m, 5H), 1.51-1.44 (m, 2H), 1.38-1.29 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.7, 156.2, 113.4, 60.9, 40.4, 31.7, 29.3, 21.9, 18.1, 13.4 ppm; IR (film) 2958, 2932, 2872, 1655, 1633, 1367, 1087, 1013, 629 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{19}\text{NO}_2$: m/z 185.1416, found 186.1408.

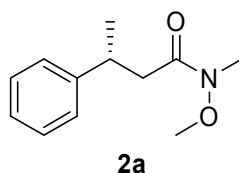
3 Catalytic asymmetric hydrogenation of 1a-s



General procedure

The catalyst **3** (0.002 mmol) and the α,β -unsaturated Weinreb amide **1** (0.1 mmol) were dissolved in solvent (dichloromethane) (1.0 mL) in a vial under argon atmosphere. The vial was transferred in a glove box into a Parr steel autoclave, which was purged three times with hydrogen and finally pressurized to 50 atm. The reaction mixture was stirred under rt for 24 h, before the hydrogen gas was released in a hood. The conversion was determined by ^1H NMR analysis of an aliquot of the crude reaction mixture. The reaction mixture was filtered through a short pad of silica and eluted with a mixture of petroleum ether and EtOAc (v/v = 5/1). The ee of the product **2** was determined by chiral HPLC analysis.

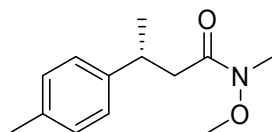
(*R*)-*N*-methoxy-*N*-methyl-3-phenylbutanamide (**2a**)^[5,6]



Colorless liquid, conversion >99%, 95% ee. $[\alpha]_{\text{D}}^{20} = +7.9$ (*c* 0.50, CH_2Cl_2), [lit.^[5] $[\alpha]_{\text{D}}^{20} = +2.9$ (*c* 1.13, CHCl_3), (*R*)-enantiomer]; ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.24 (m, 4H), 7.21-7.17 (m, 1H), 3.57 (s, 3H), 3.40-3.35 (m, 1H), 3.14 (s, 3H), 2.77-2.62 (m, 2H), 1.31 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 173.1, 146.4, 128.4, 126.8, 126.1, 61.1, 40.2, 35.7, 32.0, 21.6 ppm.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, *n*-hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at $\lambda = 220$ nm, $t_{\text{R}} = 9.9$ min (minor), $t_{\text{R}} = 11.2$ min (major).

(*R*)-*N*-methoxy-*N*-methyl-3-*p*-tolylbutanamide (2b)^[5,7,8]

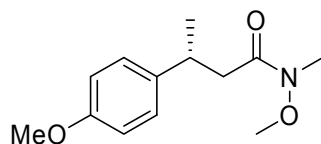


2b

Colorless liquid, conversion >99%, 97% ee. $[\alpha]_D^{20} = +4.8$ (*c* 0.50, CH₂Cl₂), [lit.^[5] $[\alpha]_D^{20} = +3.6$ (*c* 0.87, CHCl₃), lit.^[7] $[\alpha]_D^{28} = +6.4$ (*c* 3.6, *n*-hexane), both for the (*R*)-enantiomer]; ¹H NMR (400 MHz, CDCl₃) δ 7.15-7.13 (m, 2H), 7.10-7.07 (m, 2H), 3.55 (s, 3H), 3.36-3.30 (m, 1H), 3.11 (s, 3H), 2.72-2.59 (m, 2H), 2.29 (s, 3H), 1.29 (d, *J* = 7.2 Hz, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 172.9, 143.2, 135.3, 128.8, 126.7, 60.8, 40.1, 35.1, 31.7, 21.5, 20.7 ppm; IR (film) ν 2963, 2935, 1666, 1515, 1456, 1415, 1383, 1176, 1111, 999, 817, 545 cm⁻¹; EI-MS (70 eV) *m/z*: 221 (*M*⁺, 12.4), 190 (4.4), 161 (4.6), 119 (100.0), 105 (8.7), 91 (11.8), 77 (4.0).

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, *n*-hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at λ = 220 nm, *t*_R = 10.4 min (minor), *t*_R = 12.3 min (major).

(*R*)-*N*-methoxy-3-(4-methoxyphenyl)-*N*-methylbutanamide (2c)^[5]

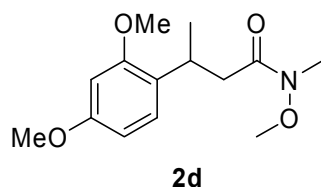


2c

Colorless liquid, conversion >99%, 96% ee. $[\alpha]_D^{20} = +2.4$ (*c* 0.50, CH₂Cl₂), [lit.^[5] $[\alpha]_D^{20} = +3.3$ (*c* 1.16, CHCl₃), (*R*)-enantiomer]; ¹H NMR (400 MHz, CDCl₃) δ 7.17 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 3.57 (s, 3H), 3.37-3.28 (m, 1H), 3.13 (s, 3H), 2.73-2.58 (m, 2H), 1.29 (d, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 173.0, 157.7, 138.4, 127.6, 113.6, 60.9, 55.0, 40.3, 34.8, 31.8, 21.7 ppm; IR (film) ν 2961, 2937, 2835, 1664, 1612, 1583, 1513, 1461, 1247, 1178, 1037, 998, 832, 554 cm⁻¹; EI-MS (70 eV) *m/z*: 237 (*M*⁺, 10.6), 206 (10.5), 149 (15.9), 135 (100.0), 105 (9.4), 91 (9.5), 77 (5.9).

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, *n*-hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at $\lambda = 220$ nm, $t_R = 15.2$ min (minor), $t_R = 18.5$ min (major).

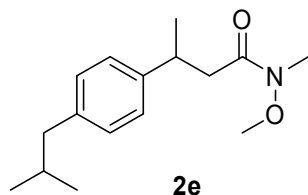
(+)-3-(2,4-dimethoxyphenyl)-*N*-methoxy-*N*-methylbutanamide (2d)



Colorless liquid, conversion >99%, 83% ee. $[\alpha]_D^{20} = +3.7$ (*c* 0.50, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.11-7.09 (m, 1H), 6.46-6.43 (m, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 3.64 (s, 3H), 3.63-3.58 (m, 1H), 3.16 (s, 3H), 2.78-2.72 (m, 1H), 2.64-2.54 (m, 1H), 1.26 (d, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 173.7, 158.8, 157.6, 127.2, 126.7, 103.6, 98.4, 60.9, 55.0, 38.6, 31.9, 28.9, 19.9 ppm; IR (film) ν 2961, 2937, 2836, 1657, 1611, 1586, 1505, 1456, 1416, 1384, 1206, 1180, 1032, 997, 935, 832, 797 cm⁻¹; EI-MS (70 eV) *m/z*: 267 (M⁺, 12.3), 236 (2.1), 179 (6.6), 165 (100.0), 149 (2.5), 103 (2.5), 77 (3.2); HRMS (EI) *m/z*: Calcd. for C₁₄H₂₁NO₄: 267.1471, Found: 267.1476 [M]⁺.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, *n*-hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at $\lambda = 220$ nm, $t_R = 19.2$ min (minor), $t_R = 21.5$ min (major).

(+)-3-(4-isobutylphenyl)-*N*-methoxy-*N*-methylbutanamide (2e)

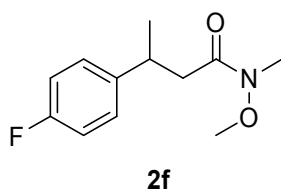


Colorless liquid, conversion >99%, 96% ee. $[\alpha]_D^{20} = +1.4$ (*c* 0.50, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.15 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.57 (s, 3H), 3.38-3.30 (m, 1H), 3.14 (s, 3H), 2.74-2.59 (m, 2H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.87-1.80

(m, 1H), 1.55 (s, 3H), 0.89 (d, $J = 6.4$ Hz, 6H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 172.8, 143.4, 139.1, 128.8, 126.3, 60.8, 44.7, 40.2, 35.1, 31.7, 29.9, 22.1, 21.4 ppm; IR (film) ν 2956, 2869, 1662, 1512, 1462, 1415, 1383, 1173, 1113, 1018, 997, 845, 798 cm^{-1} ; EI-MS (70 eV) m/z : 263 (M^+ , 10.9), 232 (3.0), 175 (7.9), 161 (100.0), 117 (14.0), 91 (8.1); HRMS (EI) m/z : Calcd. for $\text{C}_{16}\text{H}_{25}\text{NO}_2$: 263.1885, Found: 263.1883 [M] $^+$.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, n -hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at $\lambda = 220$ nm, $t_R = 8.3$ min (minor), $t_R = 9.8$ min (major).

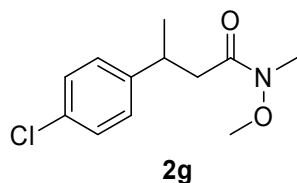
(+)-3-(4-fluorophenyl)-*N*-methoxy-*N*-methylbutanamide (2f)



Colorless liquid, conversion >99%, 96% ee. $[\alpha]_D^{20} = +1.9$ (c 0.50, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 7.23-7.19 (m, 2H), 7.00-6.95 (m, 2H), 3.59 (s, 3H), 3.41-3.32 (m, 1H), 3.13 (s, 3H), 2.74-2.59 (m, 2H), 1.29 (d, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 172.7, 161.1 (d, $^1J_{\text{F-C}} = 241.5$ Hz), 142.0, 128.1 (d, $^3J_{\text{F-C}} = 7.8$ Hz), 114.9 (d, $^2J_{\text{F-C}} = 21.3$ Hz), 61.0, 40.1, 34.9, 31.8, 21.7 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -62.39 (s) ppm; IR (film) ν 2964, 2937, 1658, 1604, 1509, 1384, 1220, 1160, 1118, 1098, 997, 834, 803 cm^{-1} ; EI-MS (70 eV) m/z : 225 (M^+ , 12.8), 194 (5.1), 165 (6.0), 137 (3.8), 123 (100.0), 109 (15.0), 103 (14.7), 61 (11.7); HRMS (EI) m/z : Calcd. for $\text{C}_{12}\text{H}_{16}\text{FNO}_2$: 225.1165, Found: 225.1171 [M] $^+$.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, n -hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at $\lambda = 220$ nm, $t_R = 11.1$ min (minor), $t_R = 12.7$ min (major).

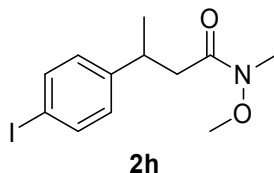
(+)-3-(4-chlorophenyl)-*N*-methoxy-*N*-methylbutanamide (2g)



Colorless liquid, conversion >99%, 94% ee. $[\alpha]_D^{20} = +5.6$ (c 0.50, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.25 (m, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 3.60 (s, 3H), 3.40-3.31 (m, 1H), 3.13 (s, 3H), 2.74-2.59 (m, 2H), 1.29 (d, $J = 6.8$ Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 172.5, 144.7, 131.5, 128.2, 128.0, 60.9, 39.8, 34.9, 31.7, 21.5 ppm; IR (film) ν 2964, 2936, 1656, 1493, 1459, 1412, 1384, 1176, 1093, 1013, 996, 827, 765 cm^{-1} ; EI-MS (70 eV) m/z : 241 (M^+ , 14.2), 210 (4.3), 181 (5.1), 139 (100.0), 125 (10.7), 105 (47.6), 77 (15.2), 61 (17.4); HRMS (EI) m/z : Calcd. for $\text{C}_{12}\text{H}_{16}\text{ClNO}_2$: 241.0870, Found: 241.0872 $[\text{M}]^+$.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, n -hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at $\lambda = 220$ nm, $t_R = 11.3$ min (minor), $t_R = 13.5$ min (major).

(+)-3-(4-iodophenyl)-N-methoxy-N-methylbutanamide (2h)

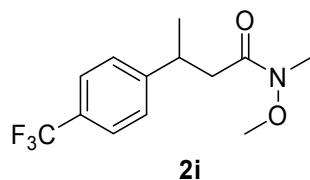


Colorless liquid, conversion >99%, 94% ee. $[\alpha]_D^{20} = +3.6$ (c 0.50, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 3.60 (s, 3H), 3.37-3.28 (m, 1H), 3.13 (s, 3H), 2.73-2.59 (m, 2H), 1.28 (d, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 146.2, 137.4, 129.0, 91.2, 61.2, 40.0, 35.3, 32.0, 21.7 ppm; IR (film) ν 2962, 2934, 1656, 1484, 1459, 1405, 1320, 1175, 1021, 1003, 819, 755, 730 cm^{-1} ; EI-MS (70 eV) m/z : 333 (M^+ , 23.0), 302 (8.1), 273 (11.4), 231 (100.0), 128 (22.9), 104 (30.9), 91 (7.7), 78 (11.9), 61 (17.2); HRMS (EI) m/z : Calcd. for $\text{C}_{12}\text{H}_{16}\text{INO}_2$: 333.0226, Found: 333.0222 $[\text{M}]^+$.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, n -hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at $\lambda = 220$

nm, t_R = 12.3 min (minor), t_R = 15.3 min (major).

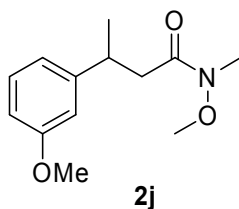
(+)-*N*-methoxy-*N*-methyl-3-(4-(trifluoromethyl)phenyl)butanamide (2i)



Colorless liquid, conversion >99%, 92% ee. $[\alpha]_D^{20}$ = +3.9 (c 0.50, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 3.61 (s, 3H), 3.49-3.40 (m, 1H), 3.14 (s, 3H), 2.79-2.64 (m, 2H), 1.32 (d, J = 6.8 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 172.4, 150.5, 128.3 (q, J = 31.7 Hz), 127.1, 125.1 (q, J = 3.8 Hz), 124.0 (q, J = 270 Hz), 60.9, 39.6, 35.4, 31.8, 21.5 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.00 (s) ppm; IR (film) ν 2967, 2940, 1660, 1619, 1420, 1386, 1324, 1162, 1115, 1067, 1016, 998, 840, 731 cm⁻¹; EI-MS (70 eV) m/z : 275 (M⁺, 15.9), 256 (4.2), 215 (9.9), 187 (8.0), 173 (100.0), 159 (23.3), 133 (12.4), 103 (5.0), 61 (24.3); HRMS (EI) m/z : Calcd. for C₁₃H₁₆F₃NO₂: 275.1133, Found: 275.1136 [M]⁺.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, *n*-hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at λ = 220 nm, t_R = 9.5 min (minor), t_R = 11.3 min (major).

(+)-*N*-methoxy-3-(3-methoxyphenyl)-*N*-methylbutanamide (2j)

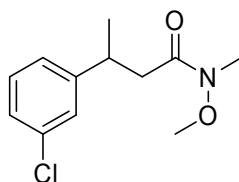


Colorless liquid, conversion >99%, 95% ee. $[\alpha]_D^{20}$ = +3.9 (c 0.50, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.81 (s, 1H), 6.74 (d, J = 8.0 Hz, 1H), 3.80 (s, 3H), 3.60 (s, 3H), 3.38-3.32 (m, 1H), 3.15 (s, 3H), 2.76-2.61 (m, 2H), 1.30 (d, J = 6.8 Hz, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 172.4, 159.1, 147.6, 128.8, 118.6, 112.3, 110.7, 60.5, 54.4, 39.5, 35.2, 31.4, 21.1 ppm; IR

(film) ν 2963, 2938, 1652, 1600, 1584, 1487, 1454, 1436, 1385, 1290, 1262, 1158, 1043, 1027, 996, 866, 780, 700 cm^{-1} ; EI-MS (70 eV) m/z : 237 (M^+ , 17.6), 205 (0.9), 177 (21.4), 149 (5.5), 135 (100.0), 121 (8.6), 91 (11.2); HRMS (EI) m/z : Calcd. for $\text{C}_{13}\text{H}_{19}\text{NO}_3$: 237.1365, Found: 237.1362 [M] $^+$.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, *n*-hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at λ = 220 nm, t_R = 13.2 min (minor), t_R = 15.0 min (major).

(+)-3-(3-chlorophenyl)-*N*-methoxy-*N*-methylbutanamide (2k)

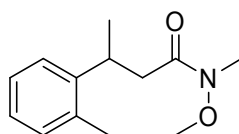


2k

Colorless liquid, conversion >99%, 95% ee. $[\alpha]_D^{20} = +5.0$ (*c* 0.50, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 7.24 (t, J = 2.0 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 7.18-7.15 (m, 1H), 7.14-7.12 (m, 1H), 3.61 (s, 3H), 3.40-3.31 (m, 1H), 3.14 (s, 3H), 2.76-2.60 (m, 2H), 1.30 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 148.6, 134.1, 129.7, 127.0, 126.4, 125.3, 61.2, 40.0, 35.5, 32.0, 21.6 ppm; IR (film) ν 2964, 2937, 1657, 1597, 1571, 1454, 1416, 1385, 1176, 1118, 1081, 1020, 997, 880, 783, 763, 698 cm^{-1} ; EI-MS (70 eV) m/z : 241 (M^+ , 8.9), 207 (16.0), 181 (4.8), 147 (11.7), 139 (43.4), 105 (100.0), 91 (16.2); HRMS (EI) m/z : Calcd. for $\text{C}_{12}\text{H}_{16}\text{ClNO}_2$: 241.0870, Found: 241.0874 [M] $^+$.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, *n*-hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at λ = 220 nm, t_R = 9.9 min (minor), t_R = 10.8 min (major).

(+)-*N*-methoxy-*N*-methyl-3-*o*-tolylbutanamide (2l)

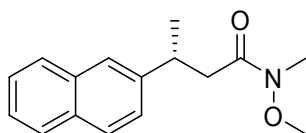


2l

Colorless liquid, conversion >99%, 82% ee. $[\alpha]_D^{20} = +10.5$ (*c* 0.50, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.07 (m, 4H), 3.65 (s, 3H), 3.67-3.58 (m, 1H), 3.16 (s, 3H), 2.75-2.61 (m, 2H), 2.39 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 172.8, 144.4, 135.0, 130.1, 125.8, 125.6, 124.8, 60.8, 39.2, 31.7, 30.4, 20.9, 19.1 ppm; IR (film) ν 2965, 1658, 1491, 1459, 1415, 1383, 1176, 1113, 996, 941, 758, 727 cm⁻¹; EI-MS (70 eV) *m/z*: 221 (M⁺, 0.9), 191 (1.1), 176 (0.9), 161 (4.0), 145 (1.9), 133 (2.0), 119 (100.0), 115 (8.6), 105 (9.9), 91 (13.3), 77 (4.4), 61 (23.8); HRMS (EI) *m/z*: Calcd. for C₁₃H₁₉NO₂: 221.1416, Found: 221.1413 [M]⁺.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, *n*-hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at λ = 220 nm, *t*_R = 8.3 min (minor), *t*_R = 9.0 min (major).

(*R*)-*N*-methoxy-*N*-methyl-3-(naphthalen-2-yl)butanamide (2m)^[5]



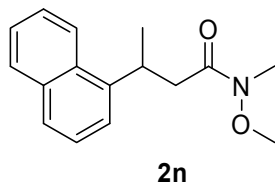
2m

Colorless liquid, conversion >99%, 95% ee. $[\alpha]_D^{20} = +5.2$ (*c* 0.50, CH₂Cl₂), [lit.^[5] $[\alpha]_D^{20} = +7.3$ (*c* 1.01, CHCl₃), (*R*)-enantiomer]; ¹H NMR (400 MHz, CDCl₃) δ 7.77-7.75 (m, 3H), 7.67 (s, 1H), 7.43-7.36 (m, 3H), 3.58-3.52 (m, 1H), 3.51 (s, 3H), 3.09 (s, 3H), 2.86-2.81 (m, 1H), 2.74-2.68 (m, 1H), 1.39 (d, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 172.8, 143.8, 133.4, 132.0, 127.8, 127.4, 127.3, 125.7, 125.6, 125.1, 124.8, 60.9, 40.0, 35.7, 31.8, 21.5 ppm; IR (film) ν 3052, 2963, 2935, 1664, 1600, 1460, 1414, 1384, 1176, 1115, 998, 820, 748 cm⁻¹; EI-MS (70 eV) *m/z*: 257 (M⁺, 18.0), 227 (4.1), 197 (9.1), 155 (100.0), 141 (10.3), 115 (7.8), 91 (20.1), 57 (13.7), 43 (6.9).

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, *n*-hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at λ = 220

nm, t_R = 13.9 min (minor), t_R = 16.8 min (major).

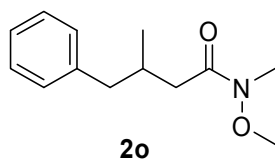
(+)-*N*-methoxy-*N*-methyl-3-(naphthalen-1-yl)butanamide (2n)



Colorless liquid, conversion >99%, 79% ee. $[\alpha]_D^{20}$ = +24.9 (*c* 0.50, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.73-7.71 (m, 1H), 7.55-7.42 (m, 4H), 4.29-4.23 (m, 1H), 3.63 (s, 3H), 3.19 (s, 3H), 2.85-2.77 (m, 2H), 1.46 (d, *J* = 7.2 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 173.2, 142.6, 133.9, 131.2, 128.8, 126.7, 126.0, 125.44, 125.43, 123.3, 122.4, 61.2, 40.1, 30.0, 29.6, 20.9 ppm; IR (film) ν 2965, 2932, 1659, 1597, 1510, 1458, 1415, 1385, 1175, 1117, 994, 796, 778 cm⁻¹; EI-MS (70 eV) *m/z*: 257 (M⁺, 21.1), 197 (18.7), 155 (100.0), 141 (8.0), 128 (21.9), 115 (4.8), 101 (3.6), 78 (3.9), 57 (3.1); HRMS (EI) *m/z*: Calcd. for C₁₆H₁₉NO₂: 257.1416, Found: 257.1418 [M]⁺.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, *n*-hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at λ = 220 nm, t_R = 12.6 min (minor), t_R = 14.1 min (major).

(+)-*N*-methoxy-*N*-methyl-3-methy-4-phenylbutanamide (2o)

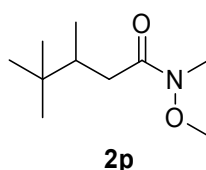


Colorless liquid, conversion >99%, 91% ee. $[\alpha]_D^{20}$ = +6.3 (*c* 0.50, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.26 (m, 2H), 7.20-7.17 (m, 3H), 3.60 (s, 3H), 3.16 (s, 3H), 2.65-2.63 (m, 1H), 2.53-2.47 (m, 1H), 2.44-2.25 (m, 3H), 0.95 (d, *J* = 6.0 Hz, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 173.7, 140.3, 129.0, 127.9, 125.6, 60.8, 43.0, 38.1, 31.8, 31.5, 19.6 ppm; IR (film) ν 2960, 2932, 1657, 1495, 1454, 1413, 1383, 1342, 1175, 1118, 1001, 741, 700 cm⁻¹; EI-MS (70 eV) *m/z*: 221 (M⁺, 9.2), 161 (59.1), 143 (10.8),

103 (30.8), 91 (100.0), 73 (15.1), 65 (9.6), 61 (7.5); HRMS (EI) m/z : Calcd. for $C_{13}H_{19}NO_2$: 221.1416, Found: 221.1420 $[M]^+$.

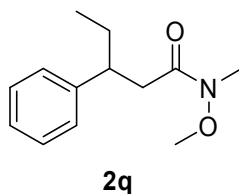
The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, *n*-hexane: isopropanol = 98 : 2, flowing rate = 1.0 mL/min, UV detection at $\lambda = 220$ nm, $t_R = 14.1$ min (minor), $t_R = 15.1$ min (major).

***N*-methoxy-*N*-methyl-3,4,4-trimethylpentanamide (2p)**



Colorless liquid, conversion 12%. 1H NMR (400 MHz, $CDCl_3$) δ 3.56 (s, 3H), 3.06 (s, 3H), 2.39-2.35 (m, 1H), 2.07-2.00 (m, 1H), 1.77-1.74 (m, 1H), 0.77-0.76 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 60.8, 38.9, 34.3, 32.4, 31.9, 26.9, 14.7 ppm; IR (film) ν 2961, 1663, 1465, 1413, 1380, 1333, 1177, 1119, 1003, 944, 798, 715 cm^{-1} ; EI-MS (70 eV) m/z : 187 (M^+ , 4.5), 172 (16.6), 157 (12.1), 142 (47.0), 127 (80.2), 100 (82.3), 85 (56.6), 73 (90.3), 57 (100.0), 41 (56.9); HRMS (EI) m/z : Calcd. for $C_{10}H_{21}NO_2$: 187.1572, Found: 187.1573 $[M]^+$.

(+)-*N*-methoxy-*N*-methyl-3-phenylpentanamide (2q)

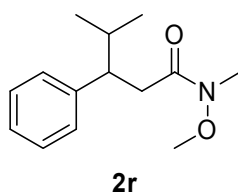


Colorless liquid, conversion >99%, 96% ee. $[\alpha]_D^{20} = +4.6$ (c 0.50, CH_2Cl_2); 1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.23-7.18 (m, 3H), 3.56 (s, 3H), 3.11-3.09 (m, 1H), 3.09 (s, 3H), 2.73-2.70 (m, 2H), 1.77-1.53 (m, 2H), 0.79 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 144.4, 128.1, 127.5, 126.0, 60.9, 43.1, 38.7, 31.8, 28.8, 11.9 ppm; IR (film) ν 2962, 2933, 2874, 1658, 1603, 1494, 1453, 1414, 1383, 1175, 1119, 994, 948, 757, 700 cm^{-1} ; EI-MS (70 eV) m/z : 221 (M^+ , 19.31), 191 (1.6),

161 (21.0), 119 (100.0), 103 (12.2), 91 (91.9), 77 (8.7), 61 (11.2); HRMS (EI) m/z : Calcd. for $C_{13}H_{19}NO_2$: 221.1416, Found: 221.1414 $[M]^+$.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, *n*-hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at λ = 220 nm, t_R = 9.8 min (minor), t_R = 11.6 min (major).

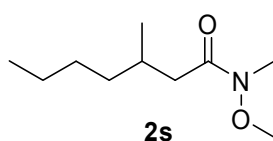
***N*-methoxy-*N*-methyl-4-methyl-3-phenylpentanamide (2r)^[5]**



Colorless liquid, conversion 94%, 90% ee. 1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2H), 7.19-7.15 (m, 3H), 3.57 (s, 3H), 3.05 (s, 3H), 3.01-2.98 (m, 1H), 2.81-2.79 (m, 2H), 1.93-1.86 (m, 1H), 0.97 (d, J = 6.4 Hz, 3H), 0.76 (d, J = 6.4 Hz, 3H) ppm.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column, *n*-hexane: isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at λ = 220 nm, t_R = 10.0 min (minor), t_R = 12.2 min (major).

***N*-methoxy-*N*,3-dimethylheptanamide (2s)**

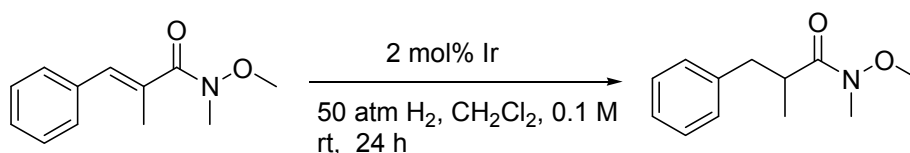


Colorless liquid, conversion >99%, 65% ee. $[\alpha]_D^{20}$ = +2.2 (c 0.9, CH_2Cl_2); 1H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 3.18 (s, 3H), 2.39 (dd, J = 14.8 Hz, 7.2 Hz, 1H), 2.34 (dd, J = 14.8 Hz, 7.2 Hz, 1H), 2.04-1.99 (m, 1H), 1.38-1.16 (m, 6H), 0.94 (d, J = 6.8 Hz, 3H), 0.91-0.87 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 61.0, 39.0, 36.6, 31.9, 29.6, 29.1, 22.7, 19.8, 13.9 ppm; IR (film) 2957, 2928, 2872, 2859, 1663, 1461, 1380, 1177, 1003, 732 cm^{-1} ; HRMS (ESI) calcd for $C_{10}H_{21}NO_2$: 187.1572, found 187.1569. The enantiomeric excess was determined by HPLC on a Chiralcel OJ-3 column, hexane : isopropanol = 99 : 1, flowing rate = 0.5 mL/min, UV detection

at $\lambda = 214$ nm, $t_R = 12.9$ min (minor), $t_R = 14.7$ min (major).

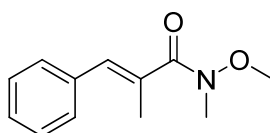
4. Preliminary studies on the AH of an β,β -diaryl α,β -unsaturated amide and an α,β -disubstituted α,β -unsaturated Weinreb amide

The complex **3** catalyzed AH of an α,β -disubstituted α,β -unsaturated Weinreb amide [(*E*)-*N*-methoxy-*N*,2-dimethyl-3-phenylacrylamide] and an β,β -disubstituted α,β -unsaturated Weinreb amide have been carried out by following a procedure similar to that described above, and the results have been summarized in the following Tables.



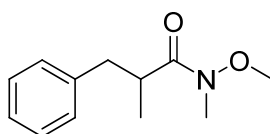
Entry	cat	Conv.%	Ee%	Configuration
1	(<i>R</i> , <i>S</i>)- 3b	9	2	/
2	(<i>S</i> , <i>S</i>)- 3b	45	56	<i>S</i>
3	(<i>S</i> , <i>S</i>)- 3c	>99	52	<i>S</i>
4	(<i>S</i> , <i>S</i>)- 3d	83	32	<i>S</i>
5	(<i>S</i> , <i>S</i>)- 3e	83	37	<i>S</i>

(*E*)-*N*-methoxy-*N*,2-dimethyl-3-phenylacrylamide



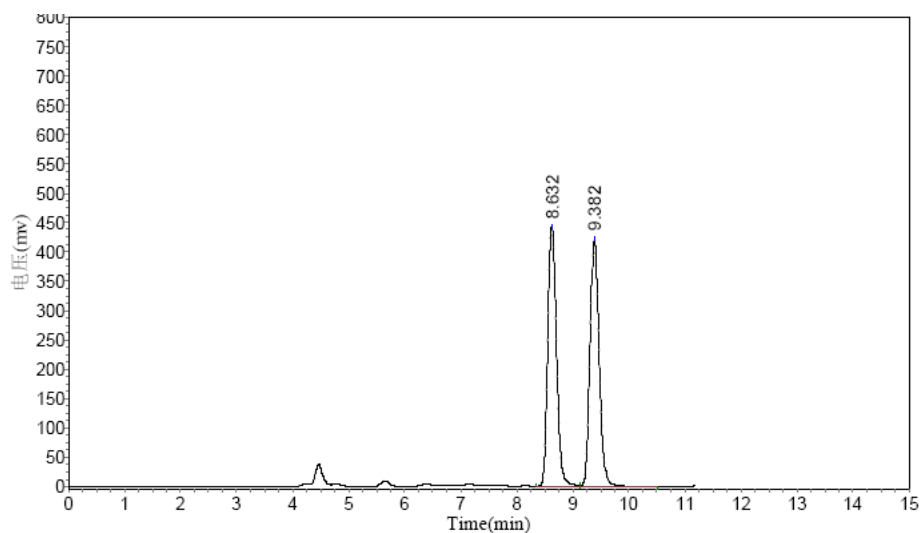
Colorless liquid.^[9] ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.21 (d, 4H), 7.16-7.12 (m, 1H), 6.70 (d, $J = 2$ Hz, 1H), 3.55 (s, 3H), 3.15 (s, 3H), 2.01 (d, $J = 2$ Hz, 3H).

N-methoxy-*N*-methyl-2-phenylmethylpropionamide



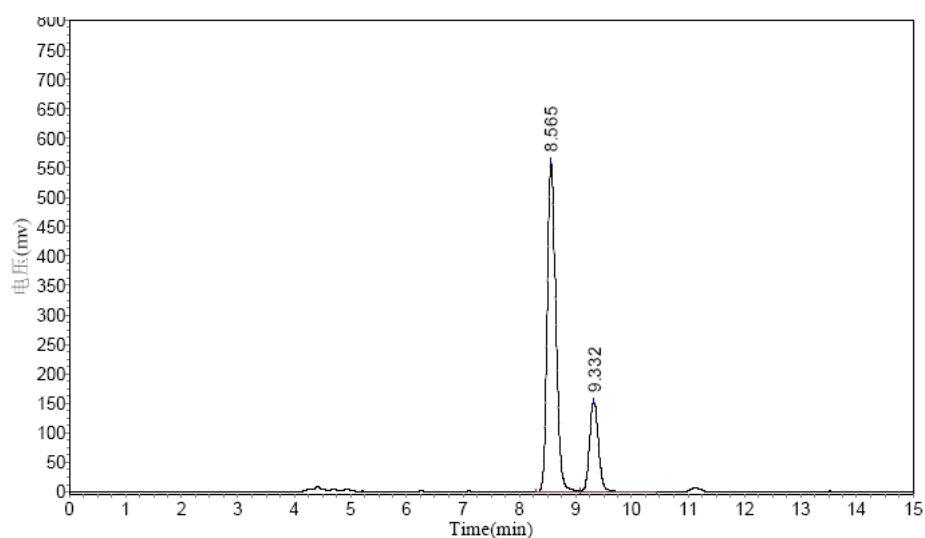
Colorless liquid.^[10] conversion >99%, 56% ee. $[\alpha]_D^{20} = +33.7$ (c 0.79, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.25 (m, 2H), 7.20-7.16 (m, 3H), 3.46 (s, 3H),

3.12-3.00 (m, 5H), 2.61 (dd, $J = 13.2$ Hz, 6.8 Hz, 1H), 1.15 (d, $J = 7.2$ Hz, 3H). The enantiomeric excess was determined by HPLC on a Chiralcel AS-H column, hexane : isopropanol = 95 : 5, flowing rate = 0.7 mL/min, UV detection at $\lambda = 220$ nm, $t_R = 8.5$ min (major), $t_R = 9.3$ min (minor).



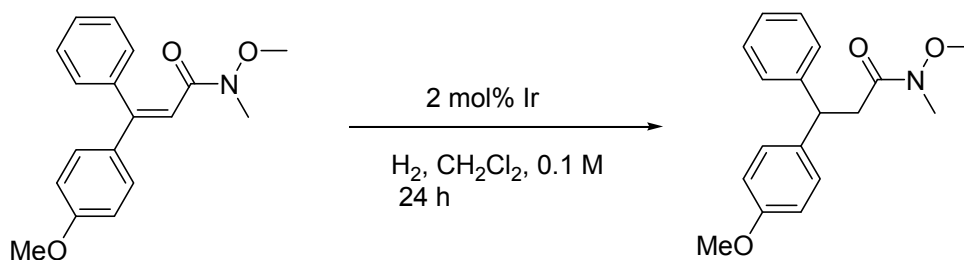
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.632	440634.000	4763650.000	49.8555
2		9.382	415885.156	4791259.500	50.1445
Total			856519.156	9554909.500	100.0000



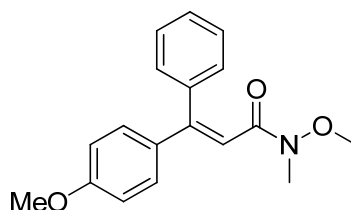
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.565	555911.813	5971661.000	78.0533
2		9.332	152578.203	1679085.500	21.9467
Total			708490.016	7650746.500	100.0000



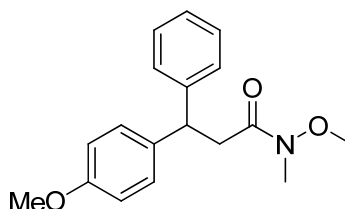
Entry	cat	P _{H2}	Temp (°C)	Conv.%	Ee%
1	(R, S)- 3a	70	40	67	10.7
2	(R, S)- 3b	50	rt	25	69.3
3	(R, S)- 3c	70	40	23	80.7
4	(R, S)- 3d	70	40	14	69.5

(E)-N-methoxy-3-(4-methoxyphenyl)-N-methyl-3-phenylacrylamide



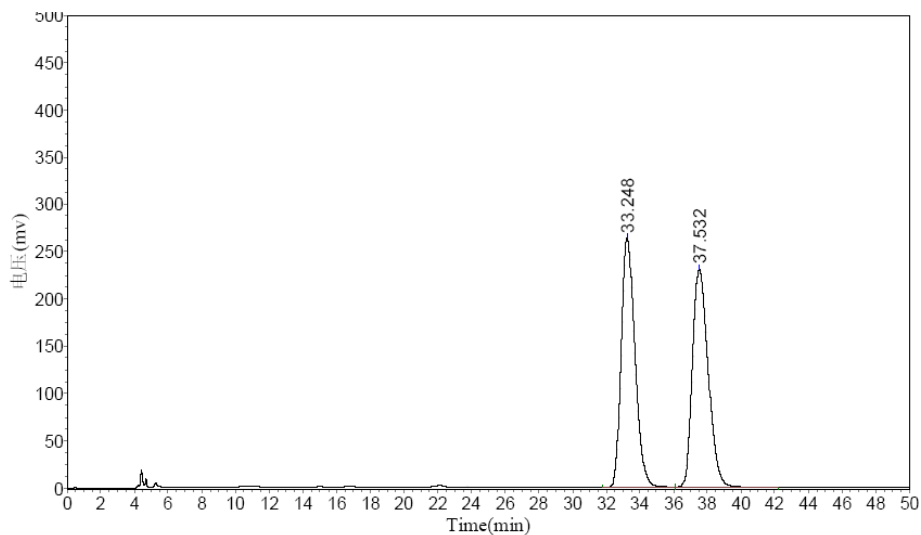
Colorless liquid and solidified to white solid on standing. ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.34 (m, 3H), 7.26-7.22 (m, 4H), 6.87-6.83 (m, 2H), 6.67(s, br, 1H), 3.82(s, 3H), 3.72 (s, 3H), 3.14(s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 166.7, 159.8, 152.4, 138.9, 133.2, 129.0, 128.6, 127.3, 127.2, 114.7, 113.1, 60.9, 54.6, 31.6 ppm; IR (film) 2963, 1648, 1602, 1509, 1442, 1378, 1256, 1176, 1094, 1029, 828, 808, 731, 698 cm⁻¹; HRMS (ESI) calcd for C₁₈H₁₉NO₃: *m/z* 297.1365, found 297.1360.

N-methoxy-3-(4-methoxyphenyl)-N-methyl-3-phenylpropanamide



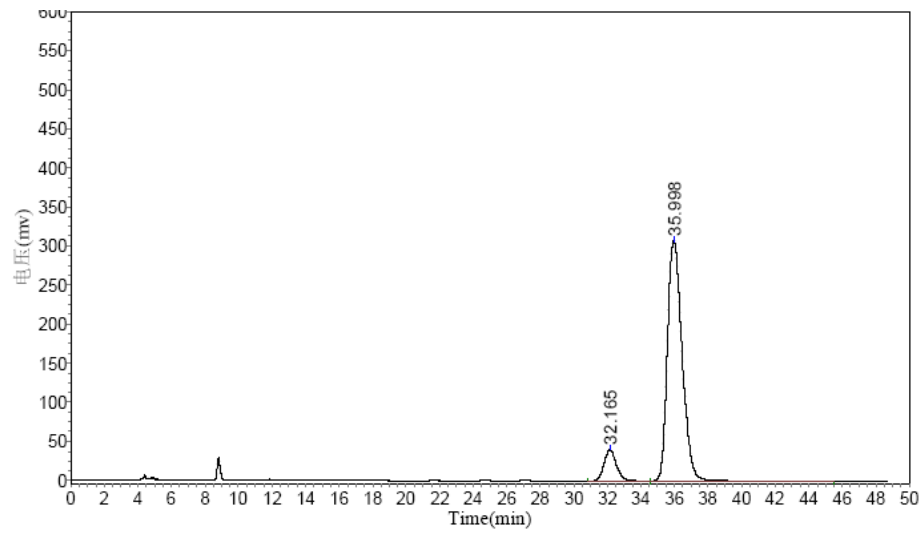
Colorless liquid.^[5] Conversion 23%, 80% ee. [α]_D²⁰ = +6.0 (*c* 0.52, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.23 (m, 4H), 7.19-7.14 (m, 3H), 6.82-6.80 (m, 2H), 4.64(t, *J* = 7.6 Hz, 1H), 3.74(s, 3H), 3.54 (s, 3H), 3.15 (d, *J* = 6.4 Hz, 2H), 3.09 (s, 3H). The

enantiomeric excess was determined by HPLC on a Chiralcel AS-H column, hexane : isopropanol = 90 :10, flowing rate = 0.7 mL/min, UV detection at $\lambda = 220$ nm, $t_R = 32.2$ min (minor), $t_R = 36.0$ min (major).



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		33.248	264116.094	14879146.000	49.9164
2		37.532	230967.578	14929000.000	50.0836
Total			495083.672	29808146.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		32.165	39637.027	1992955.750	9.6442
2		35.998	308409.969	18671862.000	90.3558
Total			348046.996	20664817.750	100.0000

5. Crystallographic data for catalysts (*R,S*)-**3a** and (*S,S*)-**3c**

Single crystals of the catalyst precursors (*R,S*)-**3a** and (*S,S*)-**3c** were obtained by crystallization from a solvent mixture of pentane and dichloromethane or petroleum ether and dichloromethane at -20 °C, respectively.

Table S1. Crystal data and structure refinement for (*R,S*)-**3a**.

Identification code	cd27555
Empirical formula	C ₆₈ H ₅₆ BF ₂₄ IrNOP
Formula weight	1593.12
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2
Unit cell dimensions	a = 18.957(2) Å alpha = 90 deg. b = 18.652(2) Å beta = 100.713(2) deg. c = 39.347(4) Å gamma = 90 deg.
Volume	13670(3) Å ³
Z, Calculated density	8, 1.548 Mg/m ³
Absorption coefficient	2.085 mm ⁻¹
F(000)	6336
Crystal size	0.287 x 0.268 x 0.235 mm
Theta range for data collection	1.05 to 26.00 deg.
Limiting indices	-23 ≤ h ≤ 21, -21 ≤ k ≤ 22, -44 ≤ l ≤ 48
Reflections collected / unique	37792 / 24351 [R(int) = 0.0631]
Completeness to theta = 26.00	99.6 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.7953
Refinement method	Full-matrix-block least-squares on F ²
Data / restraints / parameters	24351 / 61 / 1829

Goodness-of-fit on F^2	0.891
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0637$, $wR2 = 0.1497$
R indices (all data)	$R1 = 0.1136$, $wR2 = 0.1874$
Absolute structure parameter	-0.025(8)
Largest diff. peak and hole	1.472 and -0.567 e.Å ⁻³

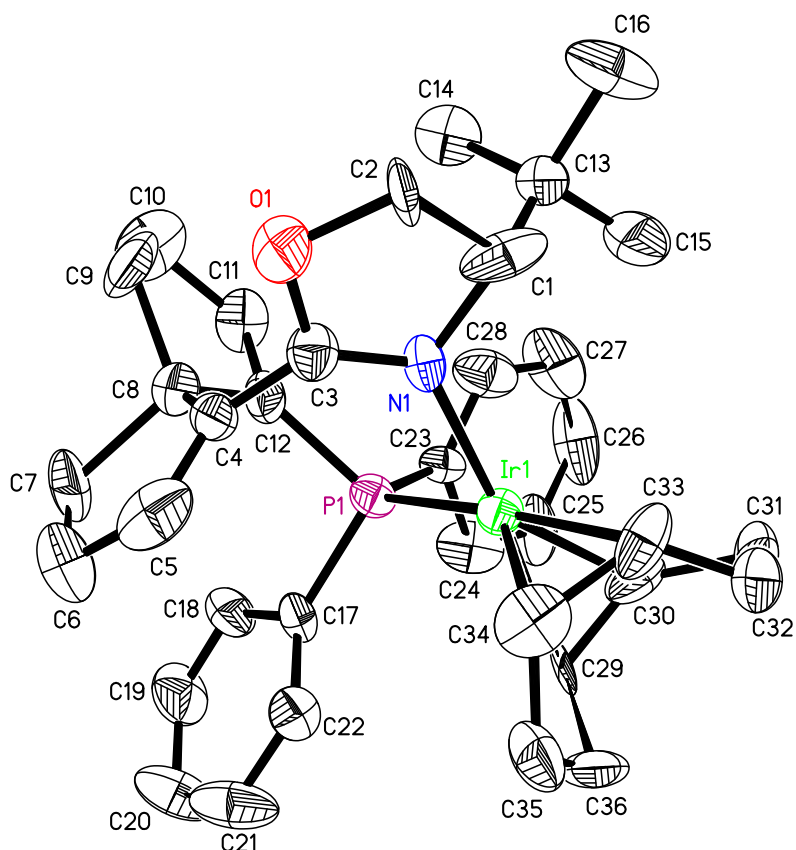


Figure S1. Crystal structures of the iridium complexes (*R, S*)-**3a**. Counteranion BAr_F^- and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)-P(1), 2.331(4); Ir(1)-N(1), 2.170(11); Ir(1)-C(29), 2.215(15); Ir(1)-C(30), 2.137(16); Ir(1)-C(33), 2.165(15); Ir(1)-C(34), 2.142(15); N(1)-Ir(1)-P(1), 94.8(3).

Table S2. X-ray crystal data and structure refinement for (*S,S*)-**3c**

Identification code	cu_dm11277_0m
Empirical formula	C ₇₂ H ₅₇ BF ₂₄ IrN _{1.50} P
Formula weight	1650.17
Temperature	133(2) K
Wavelength	1.54178 Å
Crystal system, space group	Tetragonal, P4(1)2(1)2
Unit cell dimensions	a = 13.1138(3) Å alpha = 90 deg.
	b = 13.1138(3) Å beta = 90 deg.
	c = 78.0725(18) Å gamma = 90 deg.
Volume	13426.3(5) Å ³
Z, Calculated density	8, 1.633 Mg/m ³
Absorption coefficient	5.089 mm ⁻¹
F(000)	6568
Crystal size	0.20 x 0.18 x 0.16 mm
Theta range for data collection	2.26 to 64.99 deg.
Limiting indices	-15 ≤ h ≤ 14, -15 ≤ k ≤ 13, -87 ≤ l ≤ 91
Reflections collected / unique	66313 / 11281 [R(int) = 0.0495]
Completeness to theta = 64.99	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4965 and 0.4293
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11281 / 158 / 1023
Goodness-of-fit on F ²	1.122
Final R indices [I > 2sigma(I)]	R1 = 0.0519, wR2 = 0.1244
R indices (all data)	R1 = 0.0526, wR2 = 0.1248
Absolute structure parameter	0.040(10)
Largest diff. peak and hole	1.561 and -1.658 e.Å ⁻³

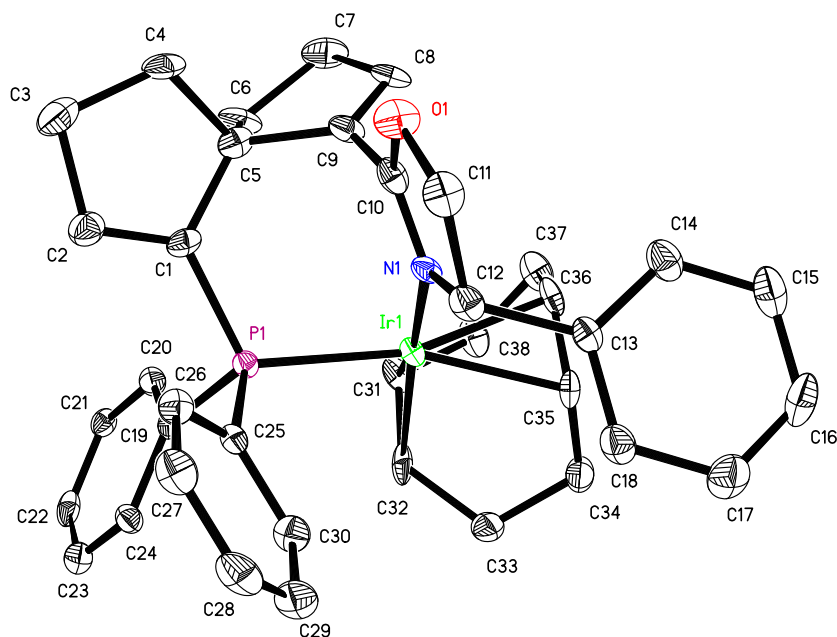


Figure S2. Crystal structures of the iridium complexes (*S,S*)-**3c**. Counteranion BArF[−] and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)-P(1), 2.3005(18); Ir(1)-N(1), 2.153(6); Ir(1)-C(31), 2.130(8); Ir(1)-C(32), 2.138(9); Ir(1)-C(35), 2.225(7); Ir(1)-C(36), 2.200(7); N(1)-Ir(1)-P(1), 85.28(17).

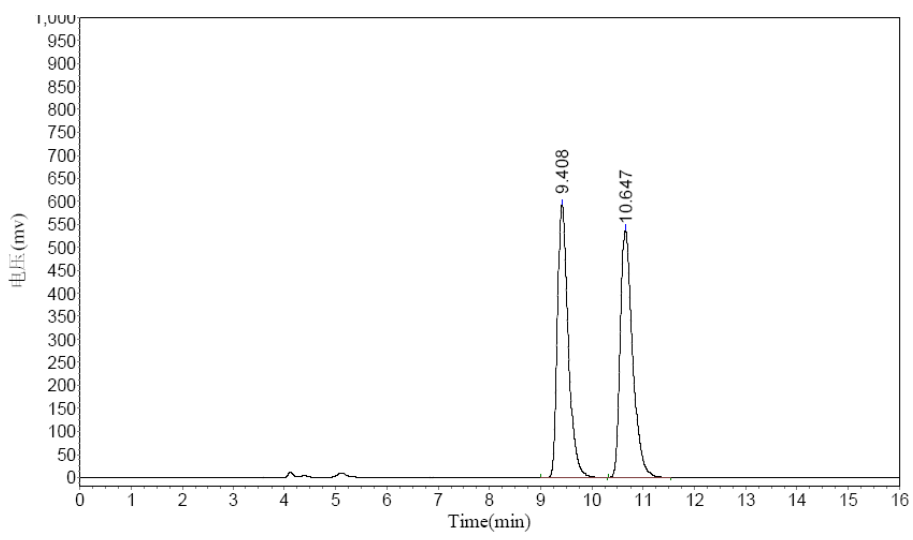
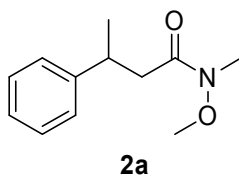
CIF files of (*R,S*)-**3a** and (*S,S*)-**3c** can be obtained from the Cambridge Crystallographic Data Centre using deposition numbers 822915 and 865426, respectively. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk].

56. References

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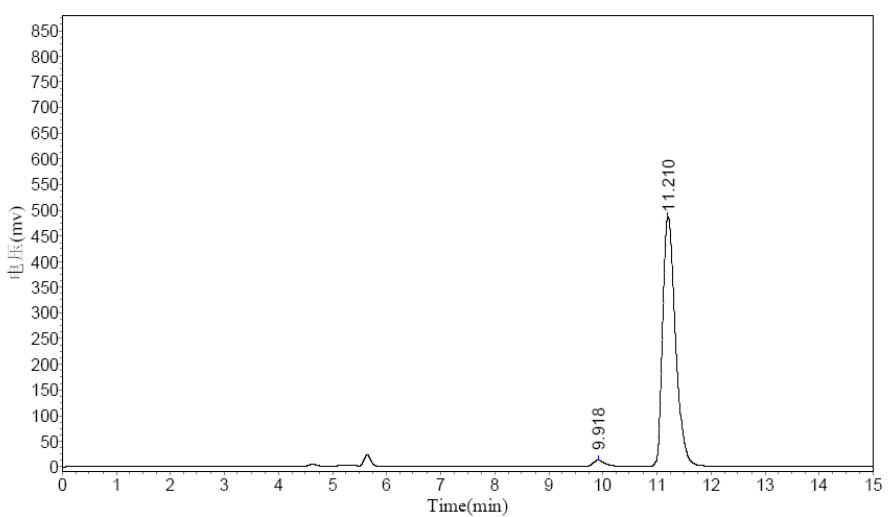
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7. HPLC spectra of chiral products



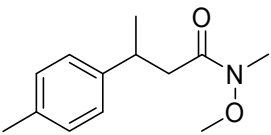
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.408	593755.938	8674512.000	49.5350
2		10.647	538466.500	8837369.000	50.4650
Total			1132222.438	17511881.000	100.0000

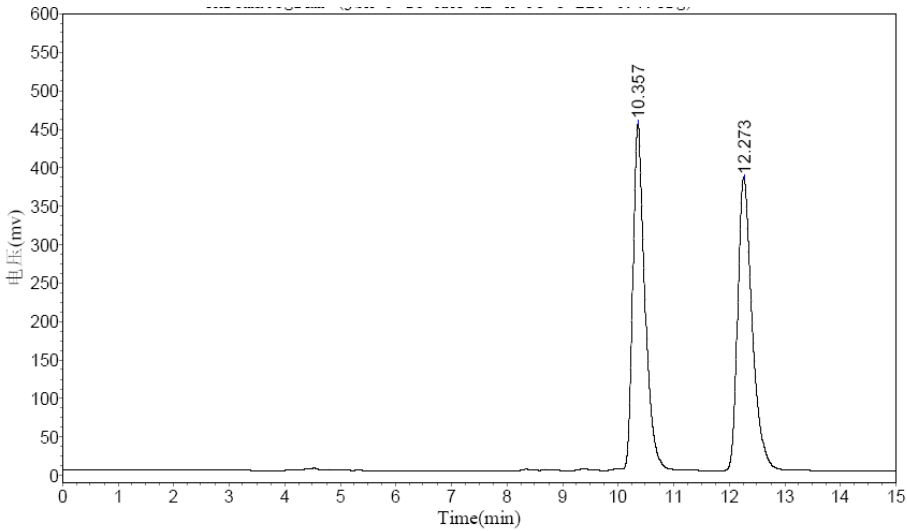


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.918	13251.553	180807.000	2.2332
2		11.210	485881.344	7915409.500	97.7668
Total			499132.896	8096216.500	100.0000

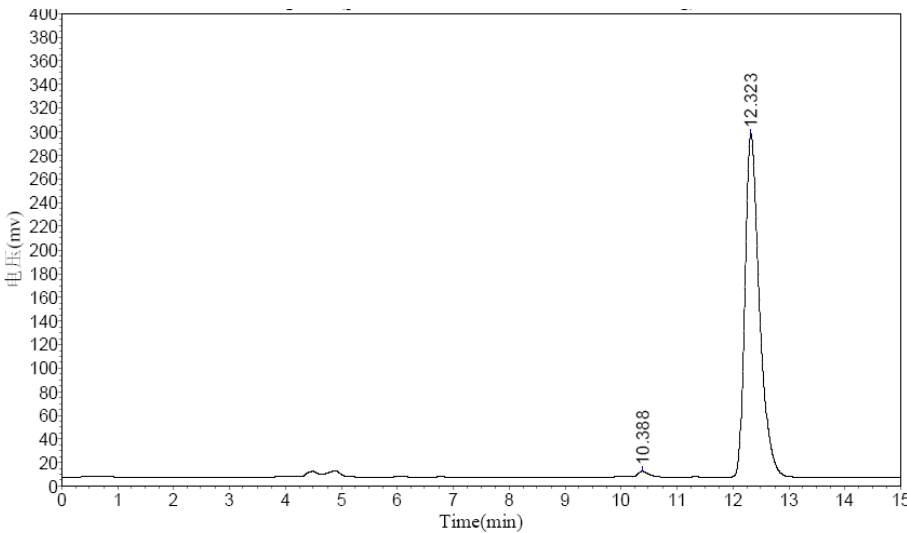


2b



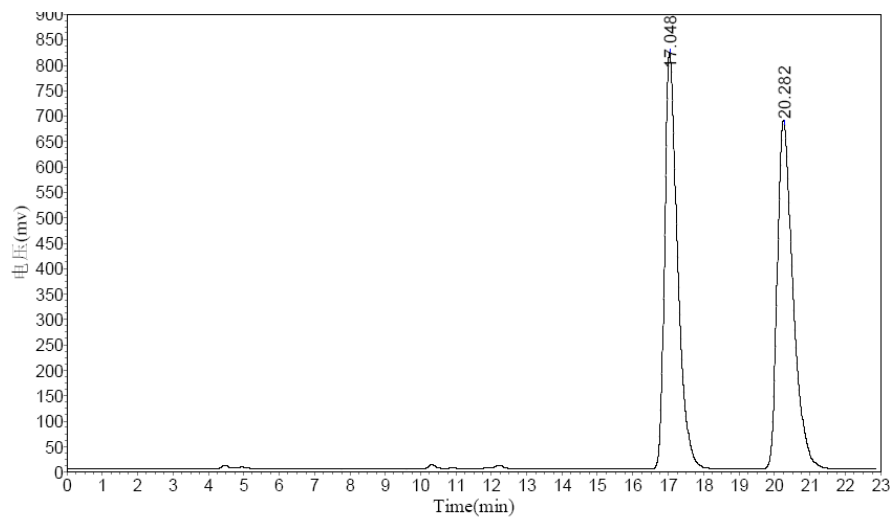
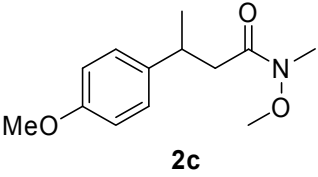
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.357	448496.438	6947139.000	50.0121
2		12.273	379896.844	6943767.500	49.9879
Total			828393.281	13890906.500	100.0000



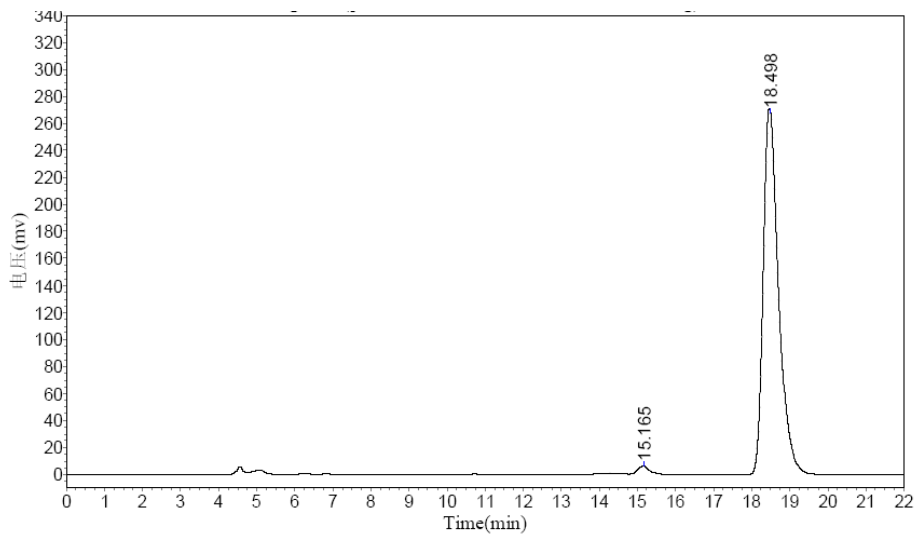
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.388	5277.378	72824.695	1.3547
2		12.323	291127.813	5302837.500	98.6453
Total			296405.191	5375662.195	100.0000



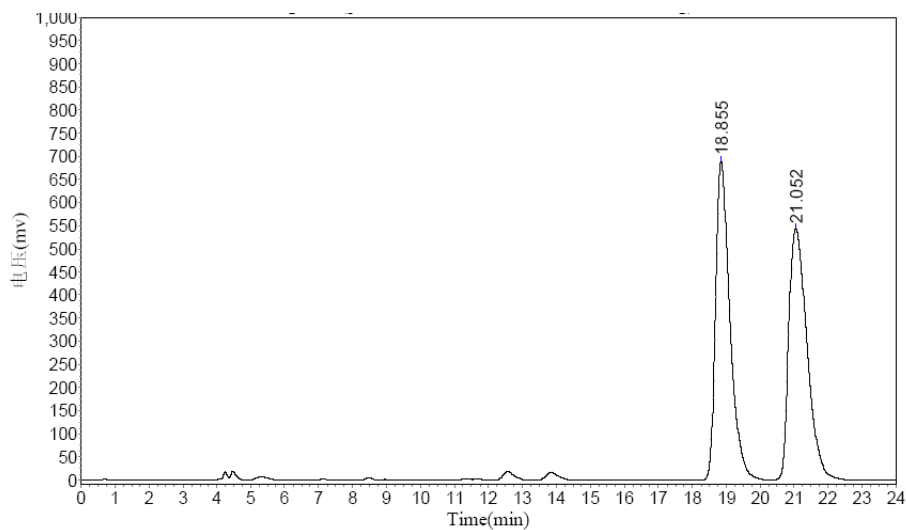
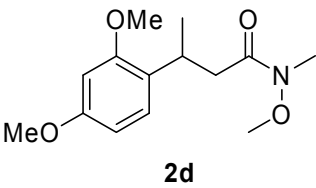
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.048	817355.438	20968090.000	49.9647
2		20.282	682322.125	20997692.000	50.0353
Total			1499677.563	41965782.000	100.0000



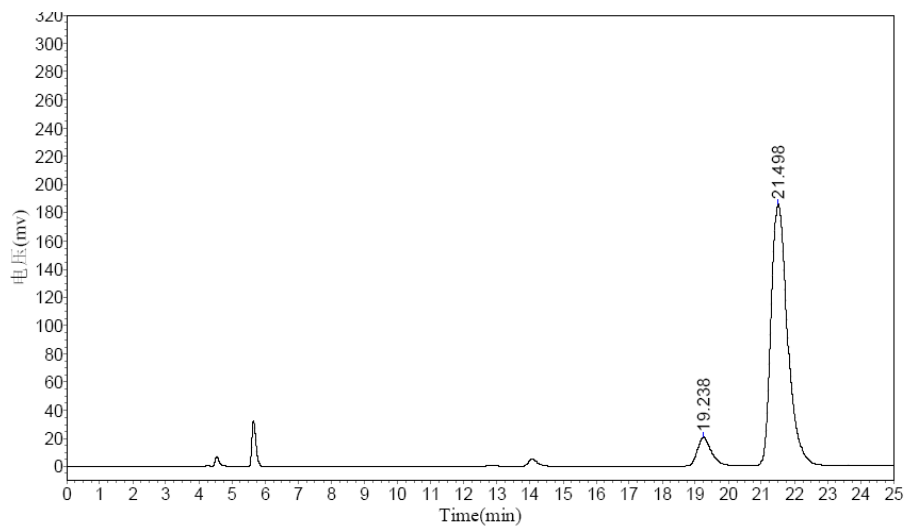
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.165	6005.664	138361.156	1.8128
2		18.498	270001.844	7494292.000	98.1872
Total			276007.507	7632653.156	100.0000



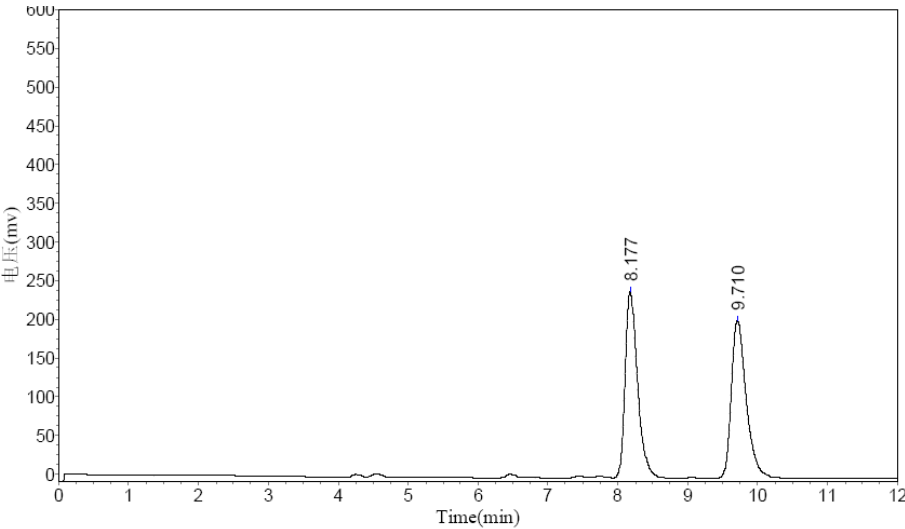
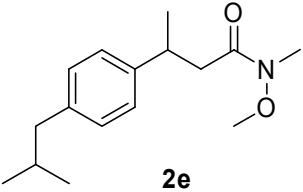
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.855	689940.625	20107194.000	49.9375
2		21.052	543514.563	20157552.000	50.0625
Total			1233455.188	40264746.000	100.0000



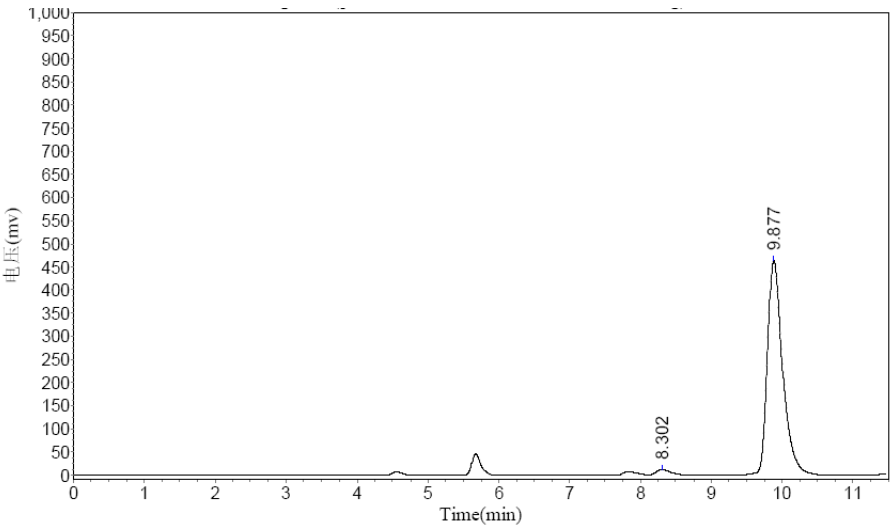
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.238	20209.852	587882.875	8.3803
2		21.498	185139.516	6427206.500	91.6197
Total			205349.367	7015089.375	100.0000



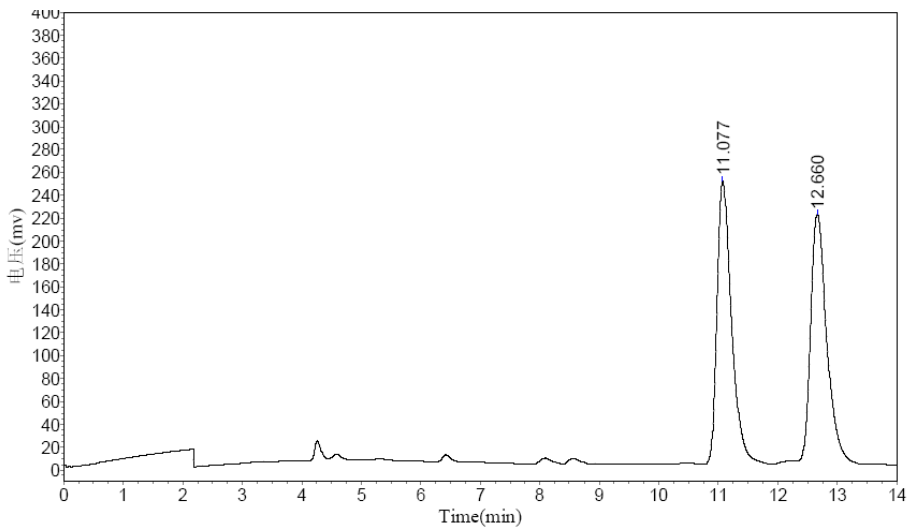
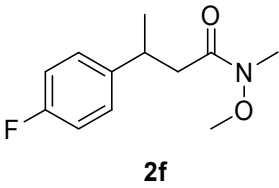
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.177	240577.547	2957568.250	49.8417
2		9.710	203012.719	2976360.250	50.1583
Total			443590.266	5933928.500	100.0000



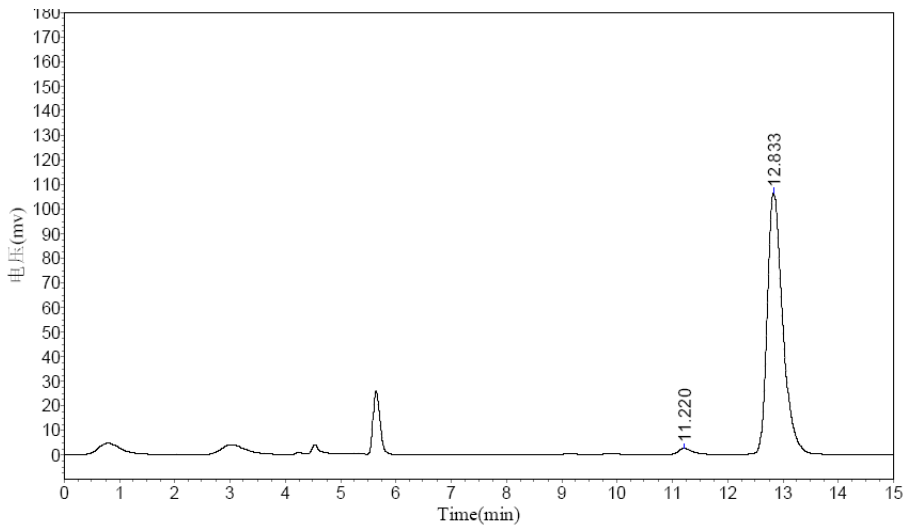
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.302	10949.730	131491.391	1.8610
2		9.877	462664.156	6934258.500	98.1390
Total			473613.887	7065749.891	100.0000



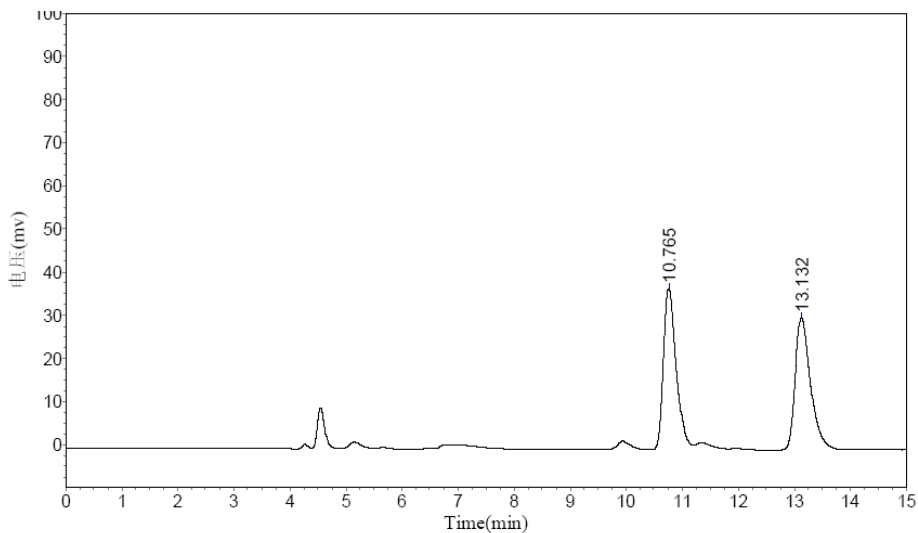
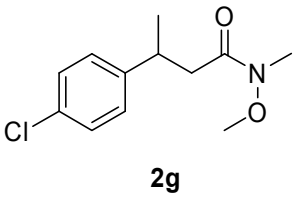
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.077	247175.344	4149967.750	50.0958
2		12.660	217778.906	4134099.500	49.9042
Total			464954.250	8284067.250	100.0000



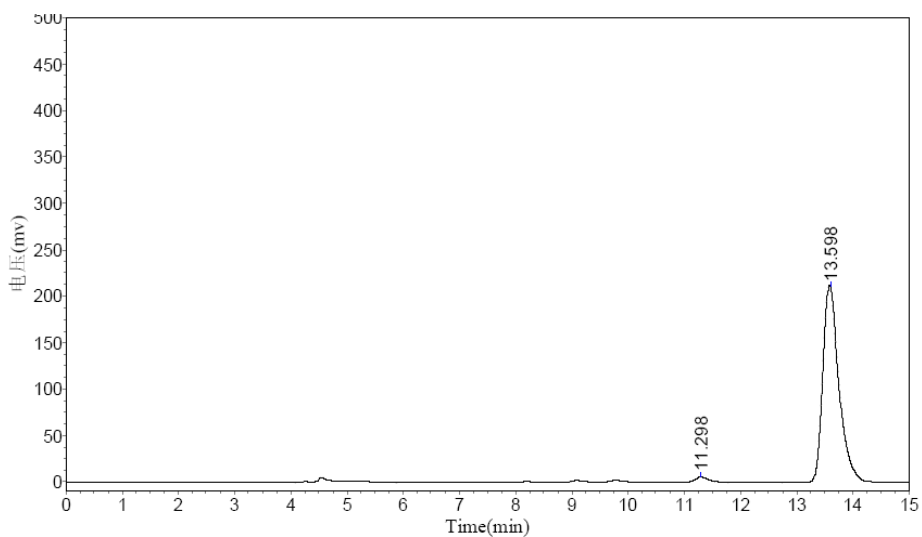
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.220	2488.117	40492.848	1.9321
2		12.833	106497.023	2055310.000	98.0679
Total			108985.140	2095802.848	100.0000



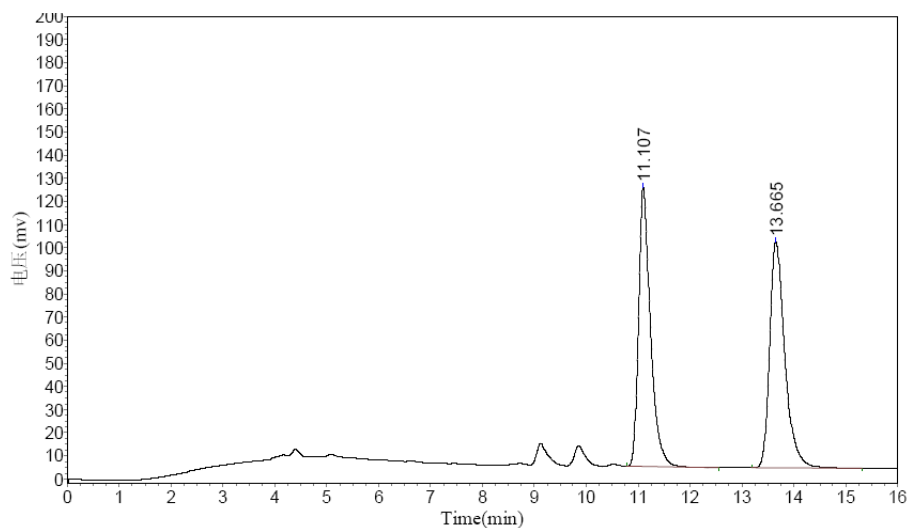
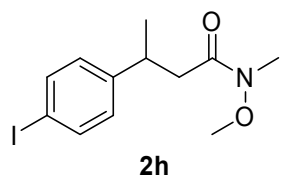
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.765	37152.742	589943.813	49.9596
2		13.132	30462.451	590896.813	50.0404
Total			67615.193	1180840.625	100.0000



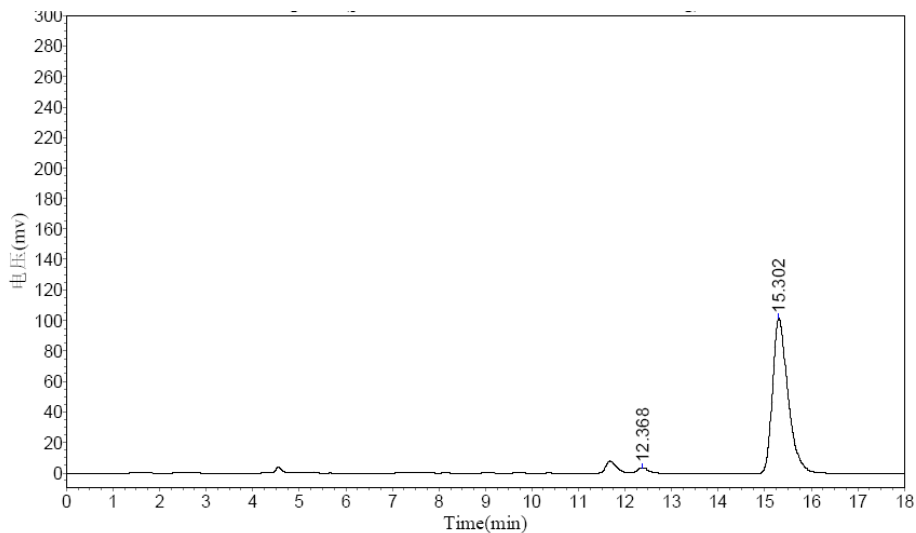
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.298	6553.955	111268.547	2.5343
2		13.598	212031.031	4279231.500	97.4657
Total			218584.986	4390500.047	100.0000



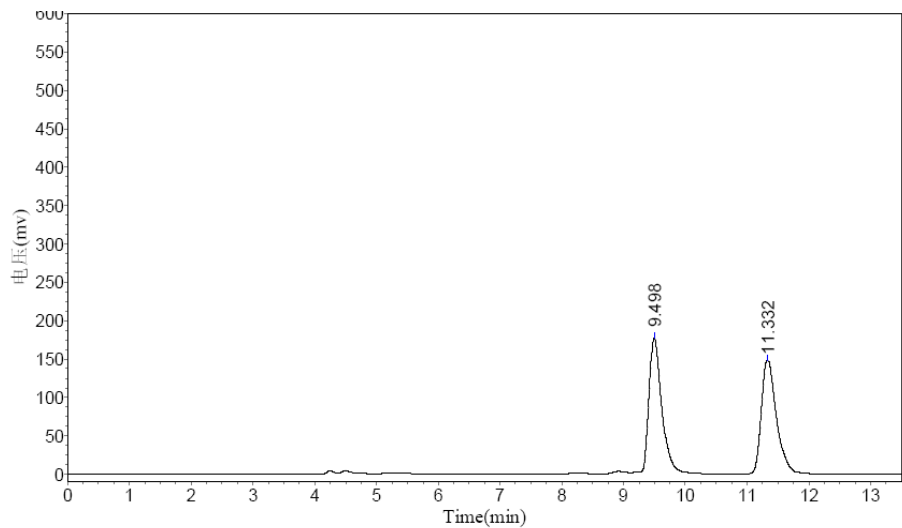
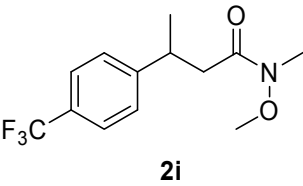
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.107	120794.398	1970038.125	49.7904
2		13.665	97951.164	1986625.250	50.2096
Total			218745.563	3956663.375	100.0000



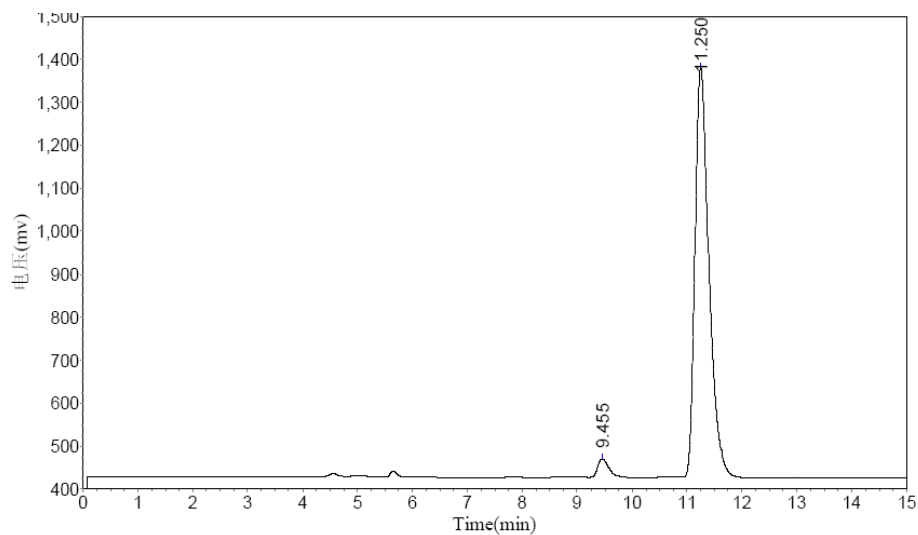
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.368	3499.166	63029.469	2.6446
2		15.302	101644.273	2320341.000	97.3554
Total			105143.439	2383370.469	100.0000



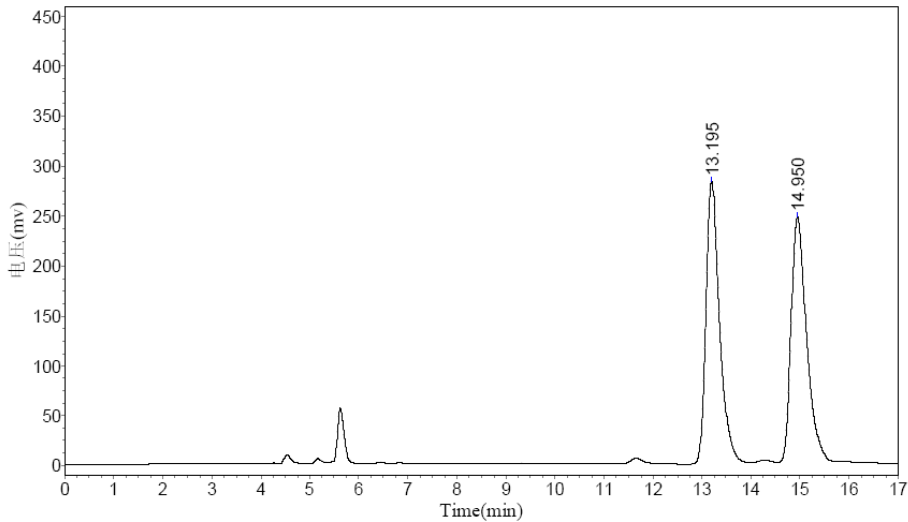
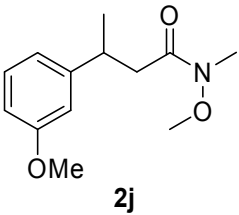
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.498	176856.969	2584654.000	50.7369
2		11.332	146904.781	2509575.000	49.2631
Total			323761.750	5094229.000	100.0000



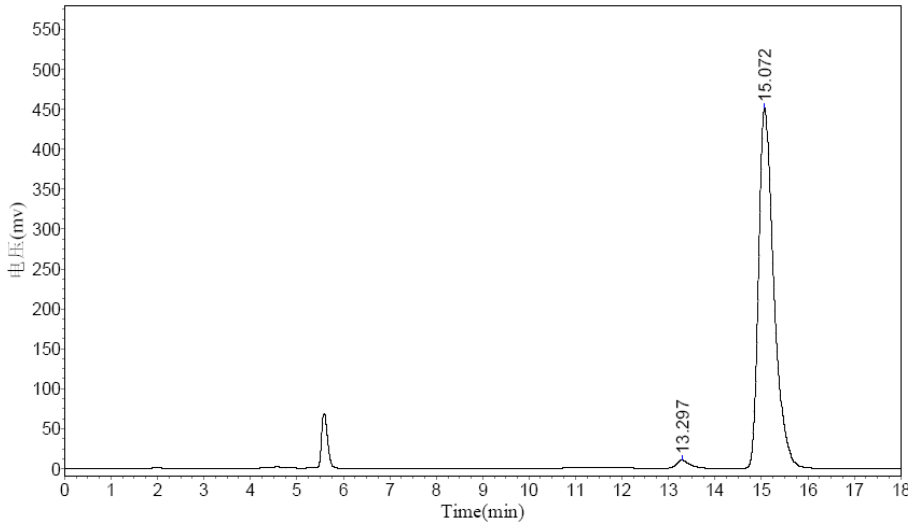
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.455	42942.309	608330.250	3.5417
2		11.250	953867.938	16567926.000	96.4583
Total			996810.246	17176256.250	100.0000



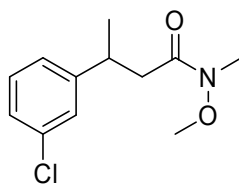
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.195	282541.688	5514727.000	49.9360
2		14.950	246931.125	5528863.000	50.0640
Total			529472.813	11043590.000	100.0000

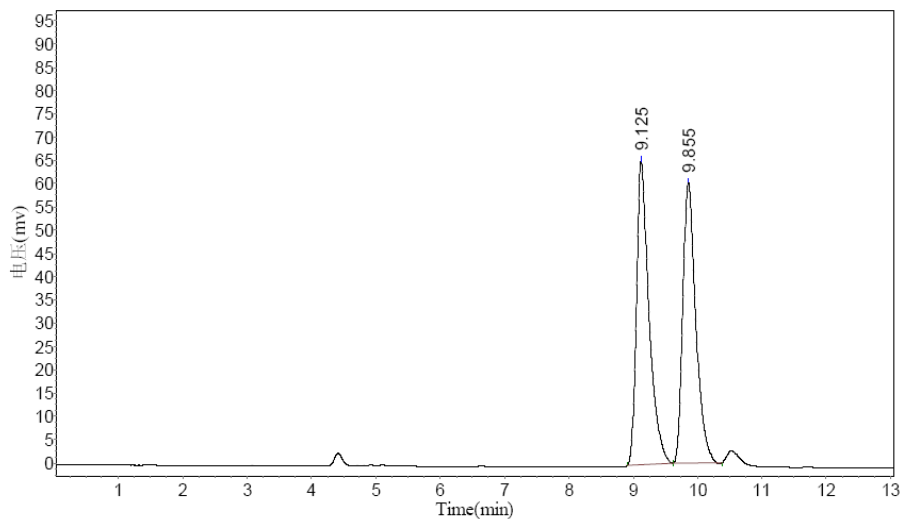


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.297	11237.215	230015.188	2.1920
2		15.072	451866.344	10263430.000	97.8080
Total			463103.559	10493445.188	100.0000

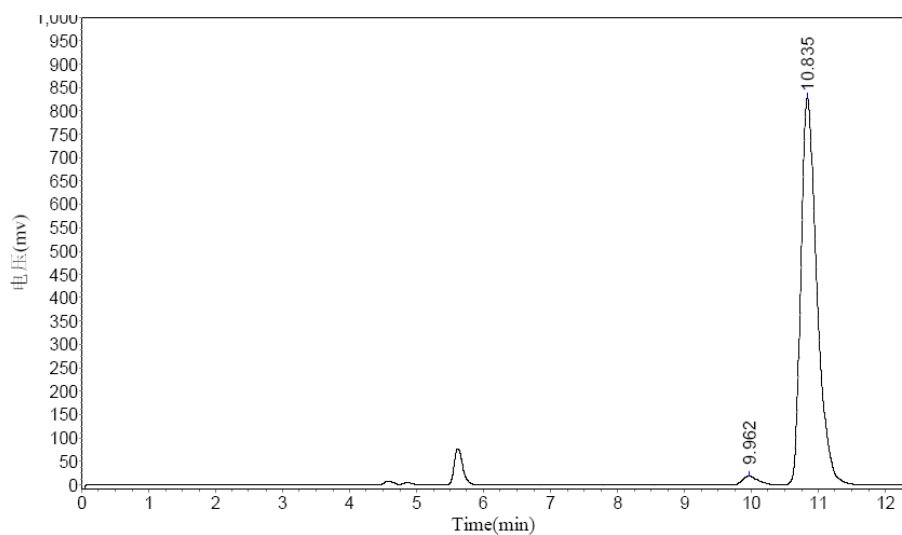


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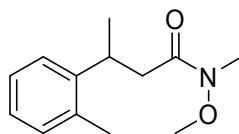
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.125	65217.641	893894.000	51.8117
2		9.855	60140.176	831381.813	48.1883
Total			125357.816	1725275.813	100.0000

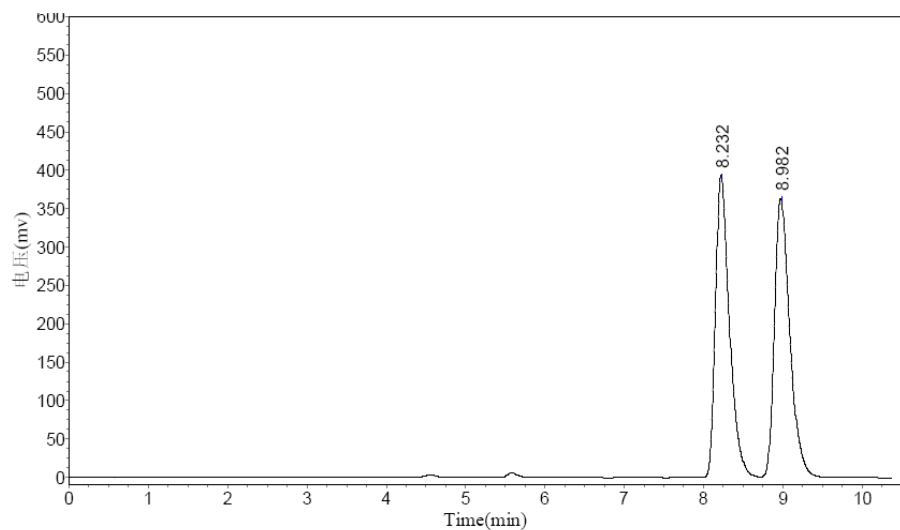


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.962	19398.420	284765.156	2.0540
2		10.835	828826.188	13579298.000	97.9460
Total			848224.607	13864063.156	100.0000

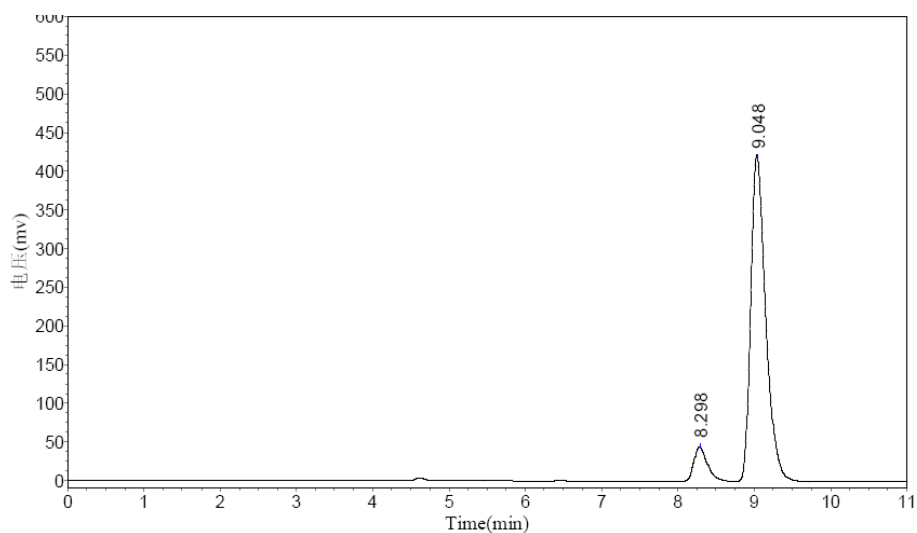


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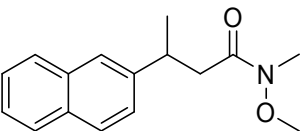
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.232	392663.250	4895441.500	49.8408
2		8.982	363084.156	4926710.500	50.1592
Total			755747.406	9822152.000	100.0000

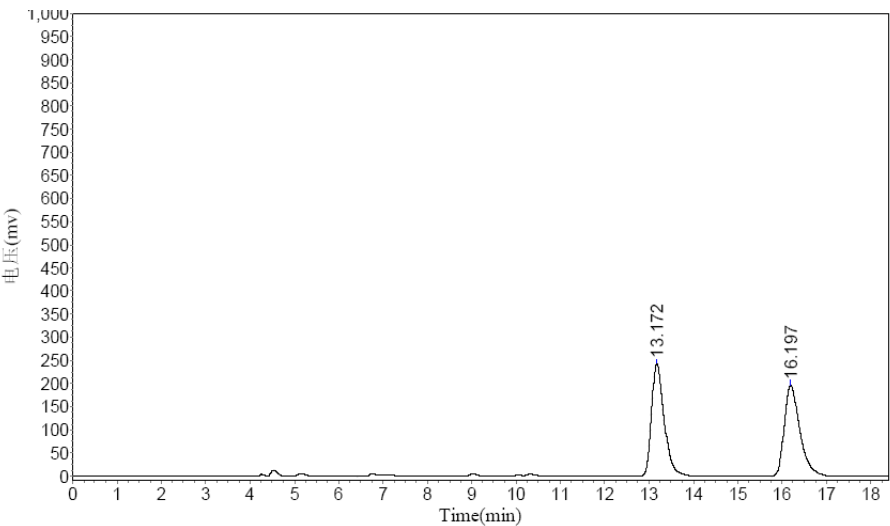


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.298	44694.555	564764.250	8.8371
2		9.048	420698.031	5826046.500	91.1629
Total			465392.586	6390810.750	100.0000

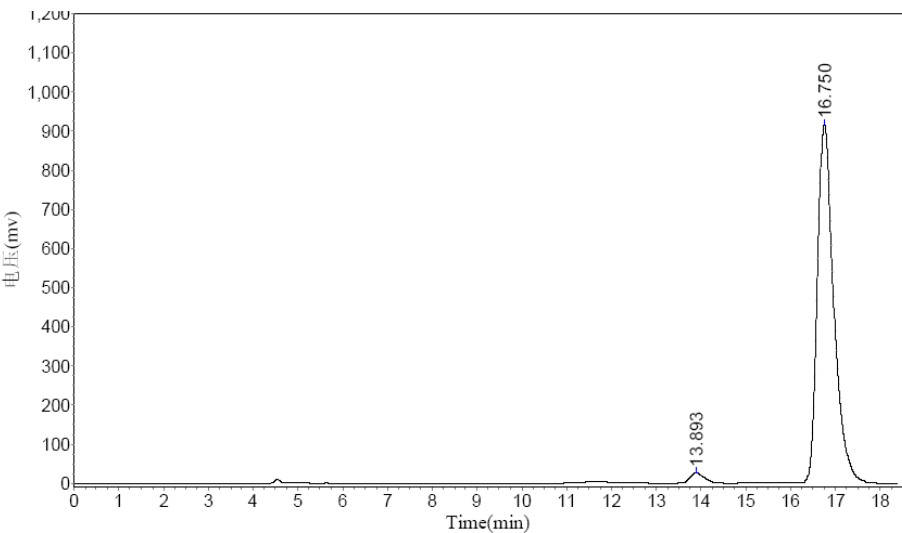


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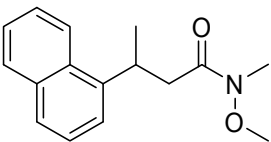
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.172	243648.078	4795755.000	50.2792
2		16.197	197341.016	4742493.000	49.7208
Total			440989.094	9538248.000	100.0000

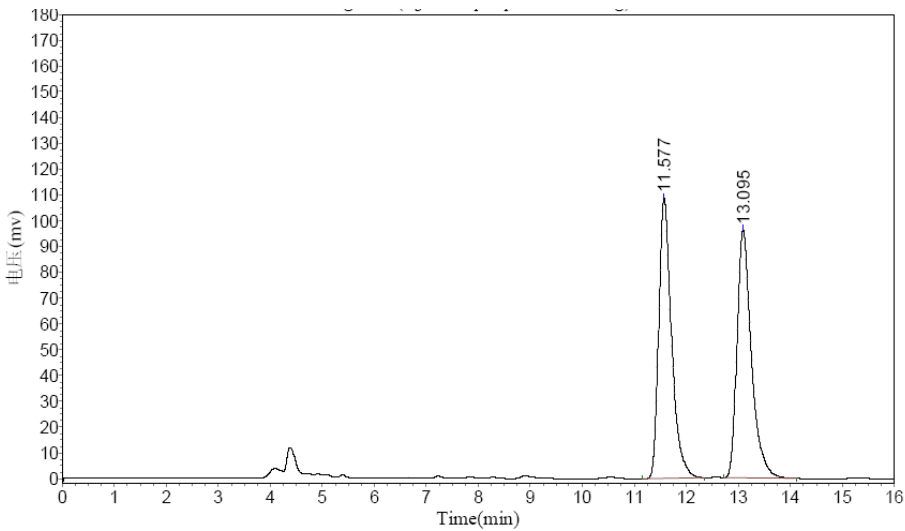


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.893	28628.170	585381.375	2.4297
2		16.750	916609.063	23507132.000	97.5703
Total			945237.232	24092513.375	100.0000

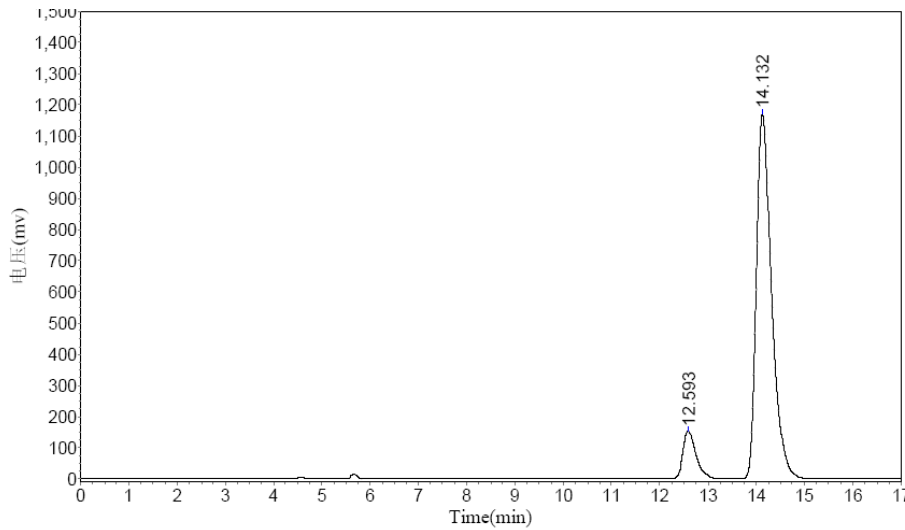


2n



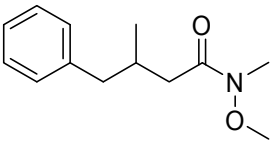
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.577	108846.820	1859830.750	49.9723
2		13.095	96241.547	1861891.625	50.0277
Total			205088.367	3721722.375	100.0000

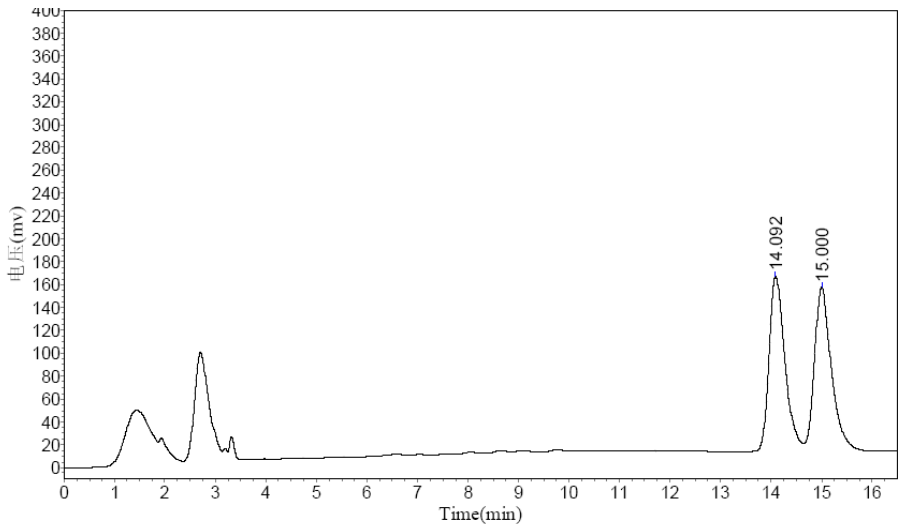


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.593	153420.297	2882575.250	10.1261
2		14.132	1170291.000	25584288.000	89.8739
Total			1323711.297	28466863.250	100.0000

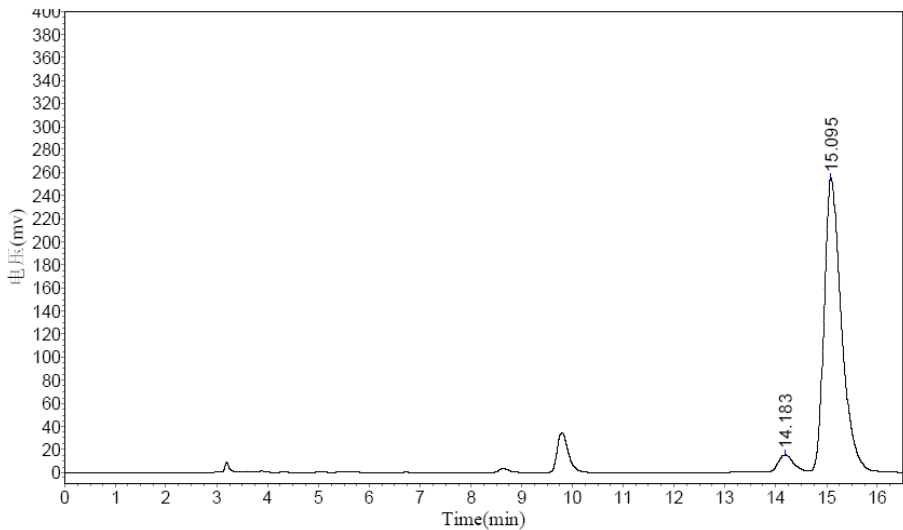


20



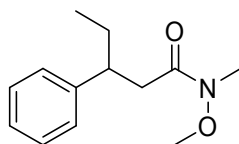
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.092	153415.969	3339604.750	49.6306
2		15.000	143546.047	3389318.750	50.3694
Total			296962.016	6728923.500	100.0000

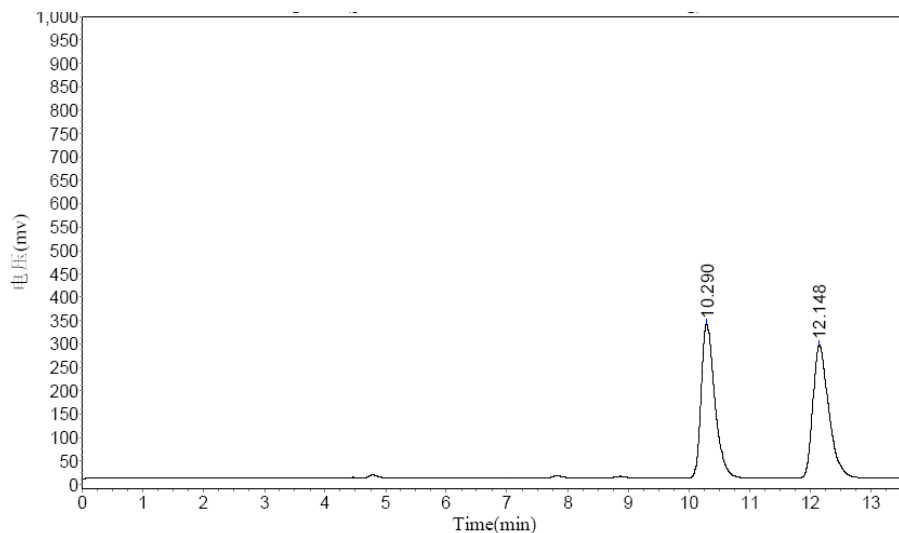


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.183	14337.490	288639.406	4.4959
2		15.095	255623.047	6131445.000	95.5041
Total			269960.537	6420084.406	100.0000

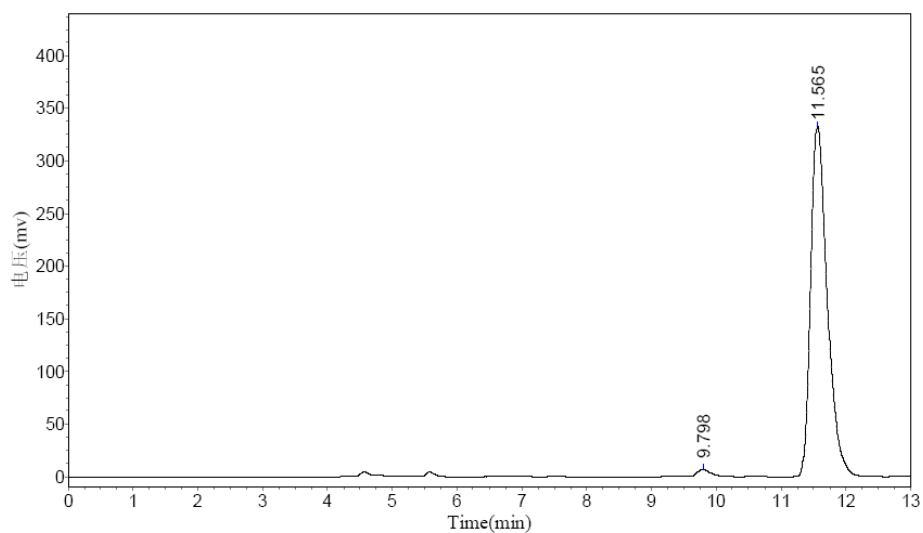


2q



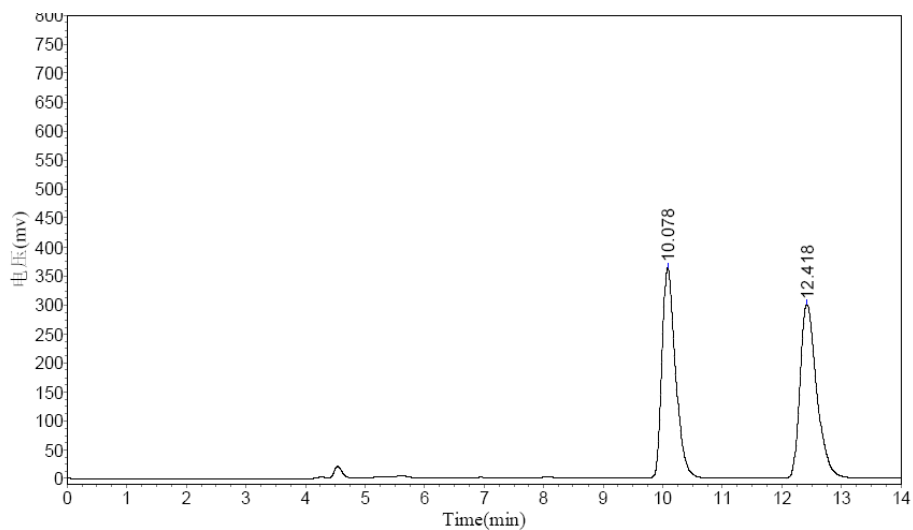
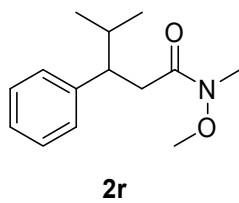
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.290	328724.375	5014107.500	49.5058
2		12.148	283859.094	5114209.000	50.4942
Total			612583.469	10128316.500	100.0000



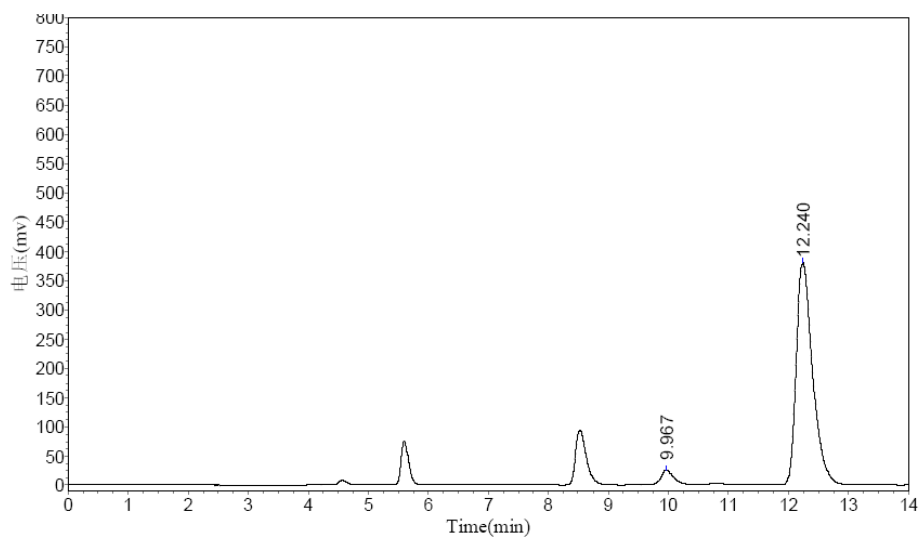
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.798	7098.204	106545.094	1.7848
2		11.565	328176.938	5863044.500	98.2152
Total			335275.142	5969589.594	100.0000



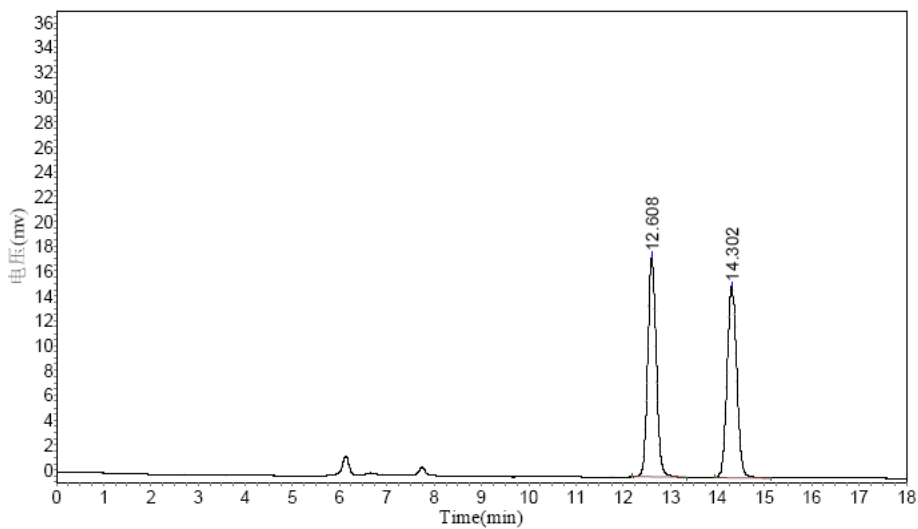
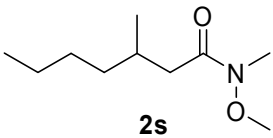
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.078	363928.813	5731834.500	49.6970
2		12.418	300595.750	5801738.500	50.3030
Total			664524.563	11533573.000	100.0000



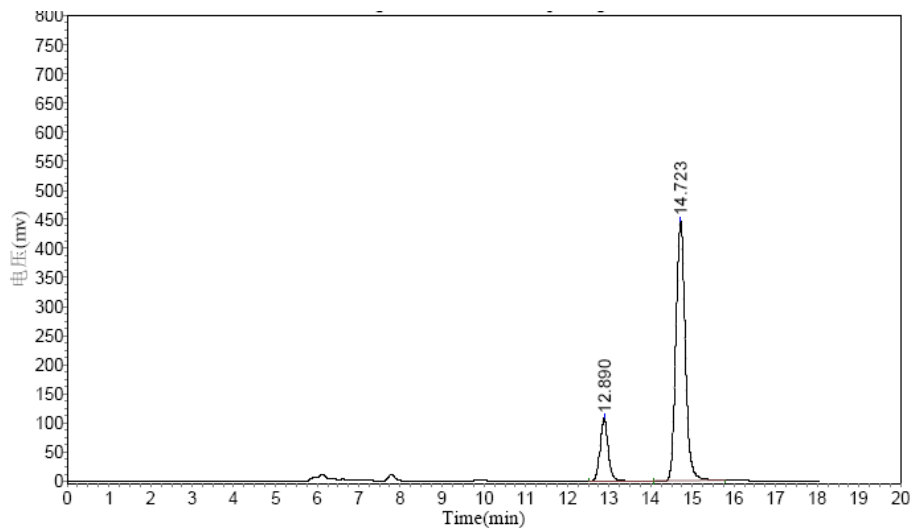
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.967	25209.189	366091.844	4.7990
2		12.240	380613.031	7262417.000	95.2010
Total			405822.221	7628508.844	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.608	17722.496	221379.000	50.0376
2		14.302	15397.696	221045.891	49.9624
Total			33120.192	442424.891	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.890	107303.688	1474240.250	17.4828
2		14.723	446485.375	6958275.000	82.5172
Total			553789.063	8432515.250	100.0000