Supporting Information

Iridium Catalysts with Modular Axial-Unfixed Biphenyl Phosphine-Oxazoline Ligands: Asymmetric Hydrogenation of α,β-Unsaturated Carboxylic Acids

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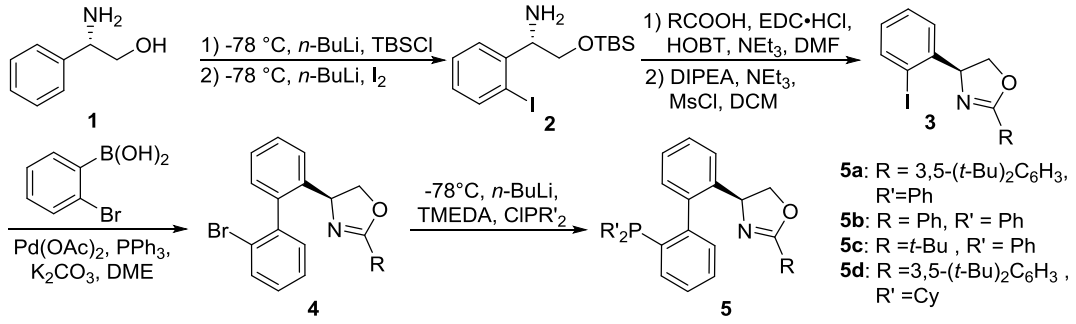
I. General Remarks

All reactions and manipulations which are sensitive to moisture or air were performed in an argon-filled glove box or using standard Schlenk techniques. Hydrogen gas (99.999%) was purchased from Shanghai Regulator Factory Co., Ltd. α-alkyl cinnamic acid derivatives were synthesized according to the literature.[1-2] Anhydrous THF, 1,4-dioxane and toluene was distilled from sodium benzophenone ketyl. Anhydrous *i*-PrOH, EA, CH_2Cl_2 were freshly distilled from calcium hydride. Anhydrous MeOH and EtOH were freshly distilled from Mg. Anhydrous CF_3CH_2OH were purchased from Sigma-Aldrich. Solvents were transferred by syringe. $[Ir(COD)Cl]_2$ was prepared according to the literature.[3-4] The synthesis of Ir complexs **6a-6d** were based on the article.[5] ^1H, ^{13}C and ^{31}P NMR spectra were recorded with a Bruker ADVANCE III (400 MHz, 500 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.26 ppm (for ^1H NMR) or 77.3 ppm (for ^{13}C NMR). Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz) and signal area integration in natural numbers. ^{13}C NMR and ^{31}P NMR analyses were run with decoupling. Optical rotations $[\alpha]_D$ were determined using a PERKIN ELMER polarimeter 343 instrument. The absolute configuration was assigned by comparison of the corresponding chiral carboxylic acids (**8a-8c**, **8e-8h**, **8l-8n**, **8p-8r**) with the optical rotation datas that reported in the literature,[6] the absolute configuration of others were assigned by analogy. GC analyses were performed using SHIMADZU Lab Solution instrument. HPLC analyses were performed using Daicel chiral column.

Ⅱ. General procedure for synthesis of Ligands.



(*S*)-4-(2'-bromo-[1,1'-biphenyl]-2-yl)-2-(3,5-di-tert-butylphenyl)-4,5-dihydrooxazole (4a)

2-(tert-Butyl-dimethyl-silanyloxy)-(1*R*)-(2-iodo-phenyl)-ethylamine **2** and various 2-iodophenyl oxazole compounds **3** were prepared according to the procedure of literature.[7] To a solution of (2-bromophenyl)boronic acid (0.11 g, 0.6 mmol), (*S*)-2-(3,5-di-tert-butylphenyl)-4-(2-iodophenyl)-4,5-dihydrooxazole **3a** (0.23 g, 0.5 mmol), PPh_3 (11.1 mg, 0.0425 mmol) and 0.625 mL K_2CO_3 (2 M in deionized water) in 0.6 mL DME (dimethoxyethane)was added $Pd(OAc)_2$ (2.25 mg). The resulting mixture was purged with argon and refluxed for overnight. The reaction was cooled to room temperature and diluted with CH_2Cl_2/H_2O (10 mL/10 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. After a flash chromatography on silica-gel column (Ethyl acetate/petroleum ether = 1/100 to 1/50), (*S*)-4-(2'-bromo-[1,1'-biphenyl]-2-yl)-2-(3,5-di-tert-butyl

phenyl)-4,5-dihydrooxazole (**4a**) was obtained with 75% yield. **4b**-**4d** were obtained in the procedure with moderate yields as white solid. **4a**: $[\alpha]_D^{25}$ = -9.9 (c = 1.0, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.85 (m, 2H), 7.68-7.66 (m, 1H), 7.58-7.26 (m, 6H), 7.26-7.24 (m, 1H), 7.17-7.15 (m, 1H), 5.26-5.18 (m, 1H), 4.54-4.49 (m, 0.7H), 4.27 (t, *J* = 8.8 Hz, 1H), 3.99-3.95 (m, 0.3H), 1.36 (s, 9H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 151.22, 151.19, 141.84, 141.79, 141.3, 140.97, 140.01, 139.8, 133.2, 132.8, 131.7, 131.6, 129.7, 129.50, 129.45, 129.1, 128.9, 127.7, 127.4, 127.3, 127.1, 126.9, 126.6, 126.02, 125.96, 124.2, 124.0, 122.98, 122.94, 75.2, 74.6, 67.9, 67.2, 35.2, 31.7. HRMS (ESI) Calcd for $C_{29}H_{33}ON^{81}Br$ = 492.17196, Found: 492.17111.

(*S*)-4-(2'-bromo-[1,1'-biphenyl]-2-yl)-2-phenyl-4,5-dihydrooxazole (4b)

This compound was produced by the same method used for **4a** as white oil, 70% yield, $[\alpha]_D^{25}$ = -18.0 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.99 (m, 2H), 7.68-7.65 (m, 1H), 7.54-7.13 (m, 11H), 5.28-5.18 (m, 1H), 4.57-4.52 (m, 0.6H), 4.30-4.26 (m, 1H), 4.00-3.95 (m, 0.4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 165.1, 141.8, 141.7, 141.1, 140.8, 140.1, 139.8, 133.1, 132.7, 131.7, 131.6, 129.71, 129.66, 129.52, 129.46, 129.2, 129.0, 128.9, 128.67, 128.64, 128.60, 128.58, 127.81, 127.78, 127.75, 127.43, 127.39, 127.37, 127.0, 126.8, 126.5, 124.2, 124.0, 75.4, 75.1, 74.8, 70.4, 67.8, 67.1.

(*S*)-4-(2'-bromo-[1,1'-biphenyl]-2-yl)-2-(tert-butyl)-4,5-dihydrooxazole (4c)

This compound was produced by the same method used for **4a** as a white oil, 72% yield, $[\alpha]_D^{25}$ = 5.1 (c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.67-7.63 (m, 1H), 7.45-7.27 (m, 5H), 7.26-7.10 (m, 2H), 5.06-4.95 (m, 1H), 4.35-4.30 (m, 0.7H), 4.09-4.03 (m, 1H), 3.77-3.73 (m, 0.3H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 175.6, 141.9, 141.8, 141.5, 141.2, 139.9, 139.7, 133.1, 132.7, 131.7, 131.6, 129.6, 129.43, 129.39, 129.1, 128.8, 127.7, 127.3, 127.22, 127.17, 126.3, 125.9, 124.2, 123.9, 75.4, 74.8, 67.0, 66.4, 33.7, 33.6, 28.2.

(*S*)-4-(2'-benzhydryl-[1,1'-biphenyl]-2-yl)-2-(3,5-di-tert-butylphenyl)-4,5-dihydrooxazole (5a)

To a suspension of (*S*)-4-(2'-bromo-[1,1'-biphenyl]-2-yl)-2-(3,5-di-tert-butylphenyl)- 4,5-di-hydrooxazole (**4a**) (98 mg, 0.2 mmol) and Tetramethylethylenediamine (34.8 mg, 0.3 mmol) in 1.5mL Et_2O at -78˚C was added *n*-BuLi (2 M solution in hexane, 0.2ml) dropwise. The resulting deep blue solution was stirred at -78 ˚C for 1.5 hour before $ClPPh_2$ (88 mg, 0.4 mmol) was added at the same temperature. The reaction mixture was allowed to warm to rt naturally and stirred overnight. After removing the solvent under reduced pressure, the product **5a** was isolated by flash column chromatography (hexane:EtOAc = 100:1) as a white solid (71.8 mg, 60%). **5a**: $[\alpha]_D^{25}$ = -37.0 (c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.90-7.85 (m, 2H), 7.57-7.56 (m, 1H), 7.46-7.26 (m, 11H), 7.25-7.15 (m, 6H), 6.74-6.69 (m, 1H), 5.46-5.41 (m, 0.3H), 5.30-5.25 (m, 0.7H), 4.33- 4.23 (m, 1.7H), 4.04-4.00 (m, 0.3H), 1.37 (s, 9H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 151.2, 146.6, 140.9, 137.4, 137.1, 134.4, 134.3, 134.2, 134.1, 133.9, 130.9, 130.8, 129.2, 129.0, 128.83, 128.79, 128.7, 128.64, 128.57, 128.5, 128.3, 128.0, 127.3, 126.6, 126.5, 125.9, 123.03, 122.95, 67.1, 35.2, 31.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ -14.1, -14.9. HRMS (ESI) Calcd for $C_{41}H_{43}ONP$ = 596.30768, Found: 596.30634.

(*S*)-4-(2'-(diphenylphosphanyl)-[1,1'-biphenyl]-2-yl)-2-phenyl-4,5-dihydrooxazole (5b)

White solid, 65% yield, $[\alpha]_D^{25}$ = -40.7 (c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.04-7.98 (m, 2H), 7.50-7.29 (m, 14H), 7.19-7.11 (m, 6H), 6.80-6.70 (m, 1H), 5.43-5.40 (m, 0.3H), 5.29-5.23 (m, 0.7H), 4.32-4.23 (m, 1.7H), 4.05-4.01 (m, 0.3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 146.8, 146.5, 140.8, 140.7, 140.0, 139.9, 137.4, 137.3, 137.2, 137.0, 136.0, 134.5, 134.4, 134.3, 134.2, 134.12, 134.06, 133.92, 133.87, 131.7, 131.6, 130.9, 130.8, 129.2, 129.0, 128.9, 128.8, 128.73, 128.66, 128.59, 128.57, 128.5, 128.4, 128.1, 128.0, 127.9, 126.6, 126.5, 126.2, 100.2, 75.2,

75.1, 75.0, 68.3, 67.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ -13.9, -14.8. HRMS (ESI) Calcd for $C_{33}H_{27}ONP$ = 484.18248, Found: 484.18137.

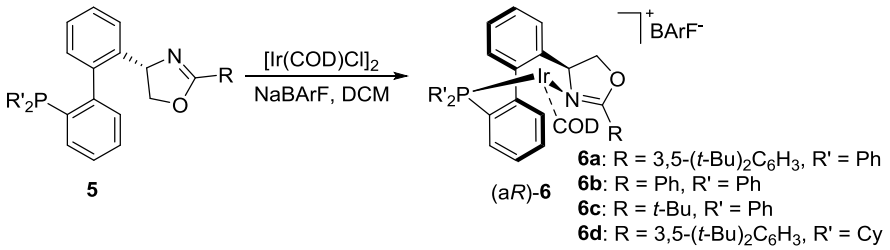
(*S*)-2-(tert-butyl)-4-(2'-(diphenylphosphanyl)-[1,1'-biphenyl]-2-yl)-4,5-dihydrooxazole (5c)

White solid, 60% yield, $[\alpha]_D^{25}$ = -7.4 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.20 (m, 11H), 7.20-7.03 (m, 5H), 7.00-6.90 (m, 1H), 6.65-6.60 (m, 1H), 5.22-5.07 (m, 1H), 4.16-4.07 (m, 1.8H), 3.83-3.79 (m, 0.2H), 1.29-1.28 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 146.9, 146.5, 141.2, 141.0, 139.8, 139.7, 137.6, 137.5, 137.1, 137.0, 136.9, 134.4, 134.3, 134.2, 134.1, 134.0, 133.9, 133.8, 130.8, 130.8, 130.7, 130.6, 129.1, 129.0, 128.8, 128.75, 128.7, 128.66, 128.6, 128.5, 128.42, 128.35, 128.3, 128.0, 127.94, 126.3, 126.0, 125.7, 75.2, 75.1, 75.0, 67.5, 66.4, 33.7, 33.6, 28.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ -14.2, -14.9. HRMS (ESI) Calcd for $C_{31}H_{31}ONP$ = 464.21378, Found: 464.21285.

(*S*)-2-(3,5-di-tert-butylphenyl)-4-(2'-(dicyclohexylphosphanyl)-[1,1'-biphenyl]-2-yl)-4,5-dihydrooxazole (5d)

White solid, 64% yield, $[\alpha]_D^{25}$ = -21.3 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.87 (m, 2H), 7.66 -7.30 (m, 7H), 7.28-7.09 (m, 2H), 5.37-5.19 (m, 1H), 4.61-4.43 (m, 1H), 4.18-3.93 (m, 1H), 1.75-1.65 (m, 10H), 1.38 (s, 9H), 1.37 (m, 9H), 1.26-0.86 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 165.0, 151.1, 148.5, 141.2, 135.2, 135.0, 133.1, 133.0, 132.8, 131.8, 130.7, 129.3, 129.24, 129.17, 128.7, 128.6, 128.4, 128.1, 127.5, 127.3, 127.1, 126.9, 126.4, 126.3, 126.2, 125.9, 125.7, 123.01, 122.97, 68.3, 68.2, 66.9, 35.9, 35.7, 35.6, 35.4, 35.2, 33.8, 33.7, 33.3, 33.2, 31.7, 30.4, 29.8, 27.9, 27.8, 27.5, 26.8, 26.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ -12.2, -12.9. HRMS (ESI) Calcd for $C_{41}H_{55}ONP$ = 608.40158, Found: 608.40021.

Synthesis of [Ir(L)COD]BArF complex 6a-6d



5 (*aR*)-**6**

6a: R = 3,5-(*t*-Bu)$_2$C$_6$H$_3$, R' = Ph
6b: R = Ph, R' = Ph
6c: R = *t*-Bu, R' = Ph
6d: R = 3,5-(*t*-Bu)$_2$C$_6$H$_3$, R' = Cy

Under N_2 atmosphere, ligand **5a** (110.8 mg, 0.186 mmol) and $[Ir(COD)Cl]_2$ (62.5 mg, 0.093 mmol) were dissolved in CH_2Cl_2. After stirring at rt for 1h, when TLC indicated that ligand was consumed completely, NaBArF (247.3 mg, 0.279 mmol) and H_2O (1.0 mL) were added successively. After vigorously stirring at the same temperature for 30 minutes, the mixture was diluted with DCM (30 mL) and washed with brine. The organic layer was dried with anhydrous Na_2SO_4 and concentrated in vacuo to afford the crude product. After chromatography on silica-gel column (hexane: CH_2Cl_2 = 1:1), the corresponding Ir complex **6a-6d** were obtained.

[Ir(L)COD]BArF complex 6a

Orange solid, 50% yield, $[\alpha]_D^{25}$ = -104.1 (c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.72 (s, 7H), 7.59-7.57 (m, 1H), 7.52 (s, 6H), 7.45-7.00 (m, 12H), 6.79 (s, 1H), 6.44-6.40 (m, 2H), 5.75-5.74 (m, 1H), 5.61 (s, 1H), 5.43-5.41 (m, 1H), 4.79-4.75 (m, 1H), 4.55 (s, 1H), 4.45-4.42 (m, 1H), 3.25 (s, 1H), 2.96 (s, 1H), 2.45 (s, 1H), 2.23-2.21 (m, 2H), 2.17-2.07 (m, 1H), 1.98 (s, 1H), 1.71-1.57 (m, 6H), 1.39 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 162.6, 162.2, 161.8, 161.4, 152.4, 143.6, 143.5, 139.6, 136.1, 136.0, 135.1, 135.0, 134.5, 133.6, 133.5, 132.6, 132.5, 131.8, 131.7, 131.6, 131.5, 131.4, 130.4, 130.2, 130.0, 129.5, 129.3, 129.2, 129.1, 128.8, 128.7, 128.6, 128.1, 127.5, 127.1, 125.9, 124.6, 123.8, 123.6, 121.6, 117.7, 91.4, 91.3, 83.1, 83.0, 75.2, 73.6, 73.1, 61.8, 35.4, 33.3, 31.6, 31.5, 30.4, 29.6, 28.6. ^{31}P NMR (202 MHz, $CDCl_3$) δ 20.0. HRMS (ESI) Calcd for $C_{49}H_{54}ONIrP$ $[M\text{-}BArF]^+$ = 896.35668, Found: 896.35588.

[Ir(L)COD]BArF complex 6b

Orange solid, 45% yield, $[\alpha]_D^{25}$ = -62.1 (c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 -8.25 (m, 2H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.72 (s, 7H), 7.60-7.45 (m, 6H), 7.44-7.33 (m, 2H), 7.31-7.28 (m, 2H), 7.26 (s, 1H), 7.25-7.17 (m, 6H), 7.14-7.10 (m, 1H), 7.04-7.00 (m, 1H), 6.69-6.62 (m, 3H), 5.75 (d, *J* = 7.3 Hz, 1H), 5.57-5.45 (m, 1H), 5.37-5.35 (m, 1H), 4.85-4.80 (m, 1H), 4.45-4.40 (m, 1H), 4.39-4.22 (m, 1H), 3.25-3.08 (m, 1H), 2.95-2.91 (m, 1H), 2.30 – 2.15 (m, 4H), 1.87-1.82 (m, 3H), 1.77-1.65 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 162.2, 161.7, 161.2, 143.2, 139.2, 136.0, 135.9, 135.1, 134.8, 134.1, 133.8, 133.7, 132.0, 131.6, 131.5, 131.3, 130.3, 129.9, 129.4, 129.3, 129.0, 128.9, 128.8, 128.3, 127.8, 126.2, 124.0, 123.5, 120.9, 117.7, 91.5, 91.4, 84.2, 77.6, 75.5, 74.3, 73.3, 60.8, 33.96, 32.0, 30.3, 30.0, 28.1, 27.2, 23.0, 14.4. ^{31}P NMR (162 MHz, $CDCl_3$)

δ 17.7. HRMS (ESI) Calcd for $C_{41}H_{38}ONIrP$ $[M\text{-}BArF]^+$ = 784.23257, Found: 784.23046.

[Ir(L)COD]BArF complex 6c

Orange solid, 47% yield, $[\alpha]_D^{25}$ = -13.9 (c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 7H), 7.68 – 7.59 (m, 1H), 7.60 – 7.38 (m, 9H), 7.36 – 7.06 (m, 9H), 6.62 (d, *J* = 6.6 Hz, 1H), 5.85 (d, *J* = 7.4 Hz, 1H), 5.32 (s, 1H), 5.14 (t, *J* = 11.3 Hz, 1H), 4.66 (t, *J* = 10.1 Hz, 1H), 4.08 (t, *J* = 10.0 Hz, 2H), 3.05-2.97 (m, 2H), 2.30-2.20 (m, 2H), 2.07-2.04 (m, 2H), 1.86-1.77 (m, 2H), 1.67-1.46 (m, 6H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.4, 162.6, 162.2, 161.8, 138.6, 135.7, 135.6, 135.1, 134.9, 134.1, 134.0, 133.3, 132.2, 131.8, 131.6, 131.4, 130.9, 130.5, 130.1, 129.9, 129.4, 129.3, 129.0, 128.7, 128.5, 126.9, 126.5, 125.9, 123.8, 121.6, 117.7, 92.2, 83.8, 75.2, 74.2, 71.9, 59.9, 34.6, 32.9, 32.2, 30.7, 30.0, 28.7, 28.0. ^{31}P NMR (202 MHz, $CDCl_3$) δ 17.2. HRMS (ESI) Calcd for $C_{39}H_{42}ONIrP$ $[M\text{-}BArF]^+$ = 764.26387, Found: 764.26172.

[Ir(L)COD]BArF complex 6d

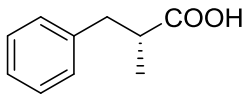
Orange solid, 43% yield, $[\alpha]_D^{25}$ = -50.9 (c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.75-7.70 (m, 8H), 7.62-7.51 (m, 8H), 7.31-7.30 (m, 1H), 7.18-7.14 (m, 2H), 5.60-5.55 (m, 1H), 5.29 (s, 3H), 5.00 (s, 1H), 4.59-4.50 (m, 2H), 4.14-4.05 (m, 4H), 3.97 (s, 1H), 3.63 (s, 1H), 2.36 (brs, 1H), 2.22 (brs, 1H), 2.19-1.89 (m, 2H), 1.64-1.48 (m, 14H), 1.46 – 1.33 (m, 18H), 1.27-0.75 (m, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 171.5, 162.6, 162.2, 161.8, 161.4, 152.2, 135.1, 133.1, 133.0, 132.6, 132.3, 131.3, 130.5, 130.0, 129.6, 129.3, 129.0, 128.7, 128.3, 128.2, 128.1, 125.9, 124.5, 123.9, 123.8, 117.7, 86.7, 74.2, 73.1, 66.0, 60.7, 58.9, 53.7, 39.3, 35.4, 33.1, 31.6, 31.5, 31.1, 31.05, 30.0, 29.6, 29.1, 29.0, 28.0, 27.95, 27.9, 27.8, 27.5, 27.1, 26.0, 21.3, 14.5. ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.6. HRMS (ESI) Calcd for $C_{49}H_{66}ONIrP$ $[M\text{-}BArF]^+$ = 908.45167, Found: 908.45001.

Ⅲ. General procedure for asymmetric hydrogenation.

α-substituted cinnamic acid (0.2 mmol) and Ir-complex **6** (0.2 μmol) was dissolved in EtOH (1 mL). This solution was then transferred into an autoclave. The hydrogenation was performed at room temperature under 30 bar of H_2 (or under reaction conditions described in Table 1 and Table 2). After carefully releasing the hydrogen, the reaction mixture was directly passed through a short silica gel column and flashed with EA. And then, the hydrogenation product in MeOH was slowly

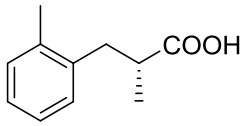
added (Trimethylsilyl)diazomethane. Half an hour later, the reaction system was concentrated in vacuo to afford the corresponding methyl ester was directly used for chiral HPLC or GC analysis to measure the enantiomeric excess and for NMR to measure the conversion.

(*R*)-2-methyl-3-phenylpropanoic acid **8a** [6a]



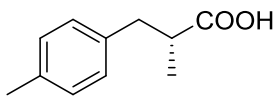
Colorless oil, 98% yield; 97% ee, $[\alpha]_D^{25}$ = -12.6 (c = 1, $CHCl_3$).[6] HPLC condition for corresponding methyl ester: Chiralpak OJ-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 18.9 min (major), 21.3 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 7.23-7.18 (m, 3H), 3.10-3.05 (m, 1H), 2.79-2.73 (m, 1H), 2.69-2.64 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.5, 139.3, 129.3, 128.7, 126.7, 41.5, 39.6, 16.7.

(*R*)-2-methyl-3-(o-tolyl)propanoic acid **8b** [6a]



Colorless oil, 96% yield, 94% ee, $[\alpha]_D^{25}$ = -11.2 (c = 0.5, acetone). HPLC condition for corresponding methyl ester: Chiralpak IB column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 205 nm; t_R = 9.7 min (major), 11.4 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (brs, 1H), 7.13 (s, 4H), 3.13-3.08 (m, 1H), 2.77-2.72 (m, 1H), 2.67-2.32 (m, 1H), 2.32 (s, 3H), 1.19 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.2, 137.6, 136.6, 130.7, 129.9, 126.8, 126.2, 40.3, 36.8, 19.7, 16.9.

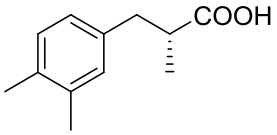
(*R*)-2-methyl-3-(p-tolyl)propanoic acid **8c** [6a]



Colorless oil, 96% yield, 95% ee, $[\alpha]_D^{25}$ = - 4.2 (c = 1.0, acetone). HPLC condition for corresponding methyl ester: Chiralpak OJ-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 17.5 min (major), 18.2 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-6.98 (m, 4H), 3.05-3.01 (m, 1H), 2.76-2.69 (m, 1H), 2.68-2.58 (m, 1H), 2.31 (s, 3H), 1.15 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.9, 136.3, 136.1, 129.4, 129.2,

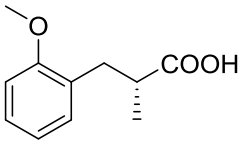
41.7, 39.2, 21.3, 16.7.

(*R*)-3-(3,4-dimethylphenyl)-2-methylpropanoic acid **8d**



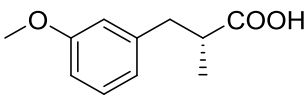
Colorless oil, 95% yield; 94% ee, $[\alpha]_D^{25}$ = -6.5 (c = 1.0, acetone). HPLC condition for corresponding methyl ester: Chiralpak OD-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 9.6 min (minor), 10.2 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05-7.03 (m, 1H), 6.95-6.90 (m, 2H), 3.04-2.99 (m, 1H), 2.75-2.69 (m, 1H), 2.60-2.54 (m, 1H), 2.22 (s, 6H), 1.15 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.7, 136.79, 136.75, 134.8, 130.6, 129.9, 126.6, 39.2, 30.0, 20.0, 19.6, 16.8.

(*R*)-3-(2-methoxyphenyl)-2-methylpropanoic acid **8e** [6a]



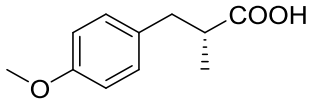
Colorless oil, 97% yield; 95% ee; $[\alpha]_D^{25}$ = -20.1 (c = 1.0, acetone), HPLC condition for corresponding methyl ester: Chiralpak OD-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 35.5 min (minor), 37.3 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.18 (m, 1H), 7.12 (d, *J* = 6.5 Hz, 1H), 6.89-6.83 (m, 2H), 3.80 (s, 3H), 3.07-3.02 (m, 1H), 2.88-2.81 (m, 1H), 2.72-2.67 (m, 1H), 1.16 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 183.2, 157.9, 131.2, 128.0, 127.7, 120.5, 110.4, 55.4, 39.6, 34.5, 17.1.

(*R*)-3-(3-methoxyphenyl)-2-methylpropanoic acid **8f** [6a]



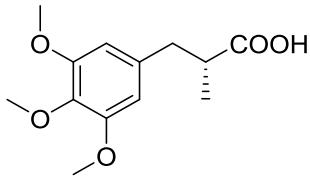
Colorless oil, 96% yield, 94% ee, $[\alpha]_D^{25}$ = -5.4 (c = 1.0, acetone). HPLC condition for corresponding methyl ester: Chiralpak OJ-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 21.7 min (major), 22.8 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.19 (m, 1H), 6.79-6.74 (m, 3H), 3.79 (s, 3H), 3.08-3.04 (m, 1H), 2.80-2.75 (m, 1H), 2.67-2.62 (m, 1H), 1.18 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 140.9, 129.7, 121.7, 115.0, 112.0, 55.4, 39.6, 16.8.

(*R*)-3-(4-methoxyphenyl)-2-methylpropanoic acid **8g** [6a]



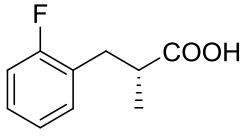
Colorless oil, 95% yield, 96% ee, $[\alpha]_D^{25}$ = -4.7 (c = 1.0, acetone). HPLC condition for corresponding methyl ester: Chiralpak OJ-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 29.9 min (minor), 31.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 3.03-2.98 (m, 1H), 2.75-2.68 (m, 1H), 2.65-2.59 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.7, 158.4, 131.4, 130.2, 114.0, 55.5, 41.9, 38.8, 16.7.

(*R*)-2-methyl-3-(3,4,5-trimethoxyphenyl)propanoic acid **8h** [6b]



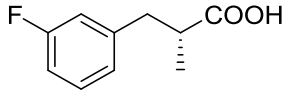
White solid, mp 116−118 °C, 98% yield, 93% ee, $[\alpha]_D^{25}$ = -11.8 (c = 1.0, acetone). HPLC condition for corresponding methyl ester: Chiralpak AD-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 205 nm; t_R = 37.2 min (major), 40.5 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (s, 2H), 3.84-3.83 (m, 9H), 3.05-3.00 (m, 1H), 2.78-2.73 (m, 1H), 2.62-2.57 (m, 1H), 1.19 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.4, 153.3, 136.7, 135.1, 106.1, 61.1, 56.3, 41.7, 40.0, 16.9.

(*R*)-3-(2-fluorophenyl)-2-methylpropanoic acid **8i**



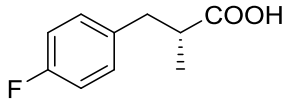
Colorless oil, 94% yield, 94% ee, $[\alpha]_D^{25}$ = -20.8 (c = 1.0, acetone). HPLC condition for corresponding methyl ester: Chiralpak AS-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 9.1 min (minor), 10.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.18 (m, 2H), 7.08-7.00 (m, 2H), 3.09-3.04 (m, 1H), 2.85-2.74 (m, 2H), 1.20 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6 (d, *J* = 243.8 Hz), 131.6 (d, *J* = 4.7 Hz), 128.6 (d, *J* = 8.1 Hz), 126.2 (d, *J* = 15.6 Hz), 124.2 (d, *J* = 3.5 Hz), 115.6 (d, *J* = 21.9 Hz), 40.1, 32.8, 16.9.

(*R*)-3-(3-fluorophenyl)-2-methylpropanoic acid **8j**



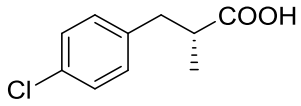
Colorless oil, 97% yield, 93% ee, $[\alpha]_D^{25}$ = -5.3 (c = 1.0, acetone). HPLC condition for corresponding methyl ester: Chiralpak AS-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 9.6 min (minor), 10.8 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (brs, 1H), 7.27-7.21 (m, 1H), 7.96-6.88 (m, 3H), 3.08-3.03 (m, 1H), 2.879-2.63 (m, 2H), 1.17 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.6, 163.1 (d, *J* = 244.0 Hz), 141.8 (d, *J* = 7.3 Hz), 130.1 (d, *J* = 8.3 Hz), 124.9 (d, *J* = 2.7 Hz), 116.1 (d, *J* = 20.9 Hz), 113.6 (d, *J* = 20.9 Hz), 41.4, 39.2, 16.8.

(*R*)-3-(4-fluorophenyl)-2-methylpropanoic acid **8k**



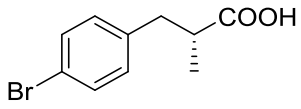
Colorless oil, 96% yield, 94% ee, $[\alpha]_D^{25}$ = -11.9 (c = 1.0, acetone). HPLC condition for corresponding methyl ester: Chiralpak AS-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 9.8 min (minor), 10.8 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.12 (m, 2H), 7.00-6.95 (m, 3H), 3.05-3.00 (m, 1H), 2.76-2.63 (m, 2H), 1.18 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.9, 161.7 (d, *J* = 242.8 Hz), 134.9, 130.7 (d, *J* = 7.8 Hz), 115.5 (d, *J* = 21.1 Hz), 41.6, 38.7, 16.8.

(*R*)-3-(4-chlorophenyl)-2-methylpropanoic acid **8l** [6a]



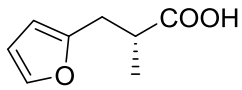
Colorless oil, 96% yield, 90% ee, $[\alpha]_D^{25}$ = -18.7 (c = 1.0, acetone). HPLC condition for corresponding methyl ester: Chiralpak AS-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 10.1 min (minor), 11.7 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.05-3.00 (m, 1H), 2.76-2.63 (m, 2H), 1.18 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 132.4, 130.6, 128.8, 41.8, 39.0, 16.9.

(*R*)-3-(4-bromophenyl)-2-methylpropanoic acid **8m** [6a]



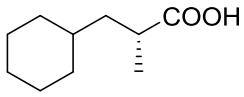
Colorless oil, 95% yield; 90% ee; $[\alpha]_D^{25}$ = -10.9 (c = 1.0, $CHCl_3$). HPLC condition for corresponding methyl ester: Chiralpak OJ-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 16.9 min (major), 17.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 3.03-2.98 (m, 1H), 2.76-2.61 (m, 2H), 1.18 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 131.8, 131.0, 120.6, 41.3, 39.0, 16.9.

(*R*)-3-(furan-2-yl)-2-methylpropanoic acid **8n** [6a]



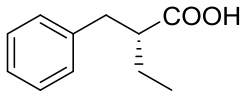
Colorless oil, 94% yield; 90% ee; $[\alpha]_D^{25}$ = -4.3 (c = 1.0, acetone), HPLC condition for corresponding methyl ester: Chiralpak OD-H column, hexane/ isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 9.5 min (major), 9.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 6.29 (s, 1H), 6.07 (d, *J* = 2.4 Hz, 1H), 3.10-3.05 (m, 1H), 2.87-2.71 (m, 2H), 1.21 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 181.5, 153.9, 141.5, 110.4, 106.6, 39.5, 32.0, 17.1.

(*R*)-3-cyclohexyl-2-methylpropanoic acid **8o**



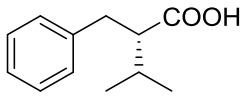
Colorless oil, 93% yield, 88% ee, $[\alpha]_D^{25}$ = -11.0 (c = 1.0, $CHCl_3$). GC (Supelco β-DEX^{TM}120, df = 0.25 μm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas, N_2 (flow 1.2 mL/min); injection temp, 250 °C; initial column temperature, 80 °C; progress rate, 0.5 °C/min; final column temperature, 150 °C; this temperature is held for 10 min; detector temp, 260 °C; t_R(*R*) = 73.5 min (major), t_S(*S*) = 74.9 min (minor).^{1}H NMR (400 MHz, $CDCl_3$) δ 3.08-3.02 (m, 1H), 2.52-2.49 (m, 1H), 1.85-1.48 (m, 5H), 1.30-1.15 (m, 5H), 1.13 (d, *J* = 6.9 Hz, 3H), 0.93-0.79 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.6, 41.8, 37.5, 35.5, 33.7, 33.3, 26.9, 26.6, 26.5, 17.8.

(*R*)-2-benzylbutanoic acid **8p** [6b]



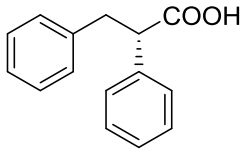
Colorless oil, 96% yield, 97% ee, $[\alpha]_D^{25}$ = -11.1 (c = 1.0, $CHCl_3$). HPLC condition for corresponding methyl ester: Chiralpak OJ-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 17.1 min (major), 19.8 min (minor), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.23-7.17 (m, 3H), 3.01-2.95 (m, 1H), 2.78-2.73 (m, 1H), 2.65-2.58 (m, 1H), 1.64-1.59 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.8, 139.4, 129.2, 128.7, 126.7, 49.1, 38.0, 25.0, 11.9.

(*S*)-2-benzyl-3-methylbutanoic acid **8q** [6a]



Colorless oil, 96% yield, 95% ee, $[\alpha]_D^{25}$ = -14.2 (c = 1.0, acetone). HPLC condition for corresponding methyl ester: Chiralpak OJ-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 13.1 min (major), 15.2 min (minor), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 7.24-7.20 (t, *J* = 8.6 Hz, 3H), 2.90-2.88 (m, 2H), 2.55-2.50 (m, 1H), 2.04-1.95 (m, 1H), 1.08-1.04 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 129.1, 128.7, 126.5, 54.6, 35.6, 30.7, 20.6, 20.3.

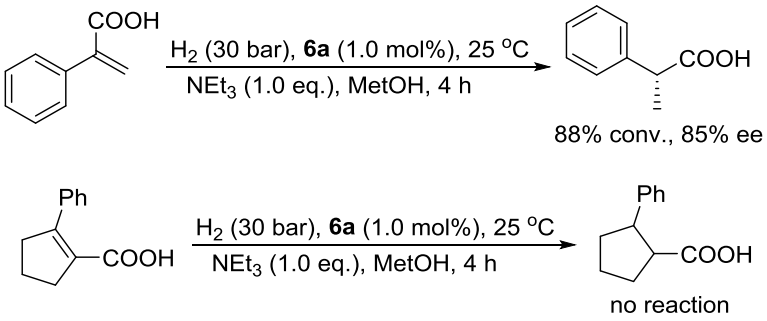
(*S*)-2,3-diphenylpropanoic acid **8r** [6a]



White solid, 95% yield, mp 79−81 °C, 94% ee, $[\alpha]_D^{25}$ =49.8 (c = 0.5, acetone). HPLC condition for corresponding methyl ester: Chiralpak OD-H column, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 12.9 min (minor), 14.2 min (major), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.03 (m, 10H), 3.78 (t, *J* =7.3, 1H), 3.33 (m, 1H), 2.97 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 139.1, 138.5, 129.2, 128.9, 128.7, 128.4, 127.7, 126.6, 77.6, 77.3, 77.0, 54.0, 39.6.

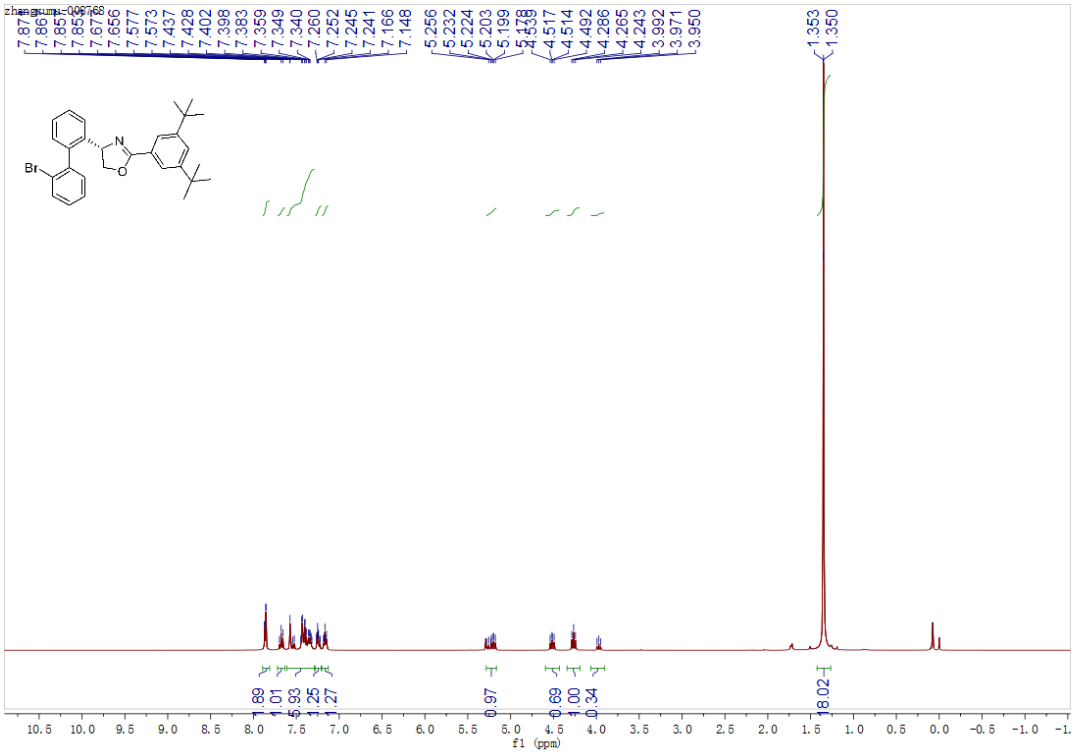
In addition, we applied our catalytic system to promote the asymmetric hydrogenation of two other types of unsaturated acids such as α-phenyl substituted acrylic acid and the unsaturated cyclic acid with tetra-substituted olefin. For α-phenyl substituted acrylic acid substrate, we can obtain the

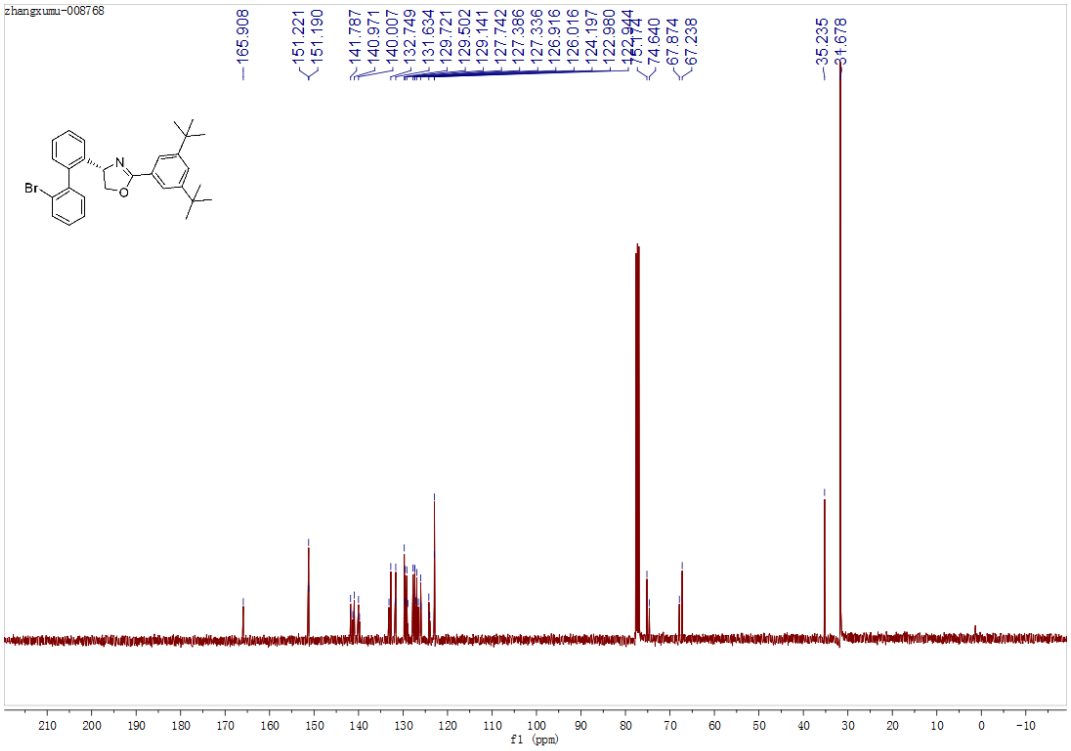
hydrogenation product with moderate result (85% ee, 88% conversion). For unsaturated cyclic acid with *tetra*-substituted olefin substrate, no product was observed in this transformation, it was mainly owing to the substrate with bulky steric hindrance.



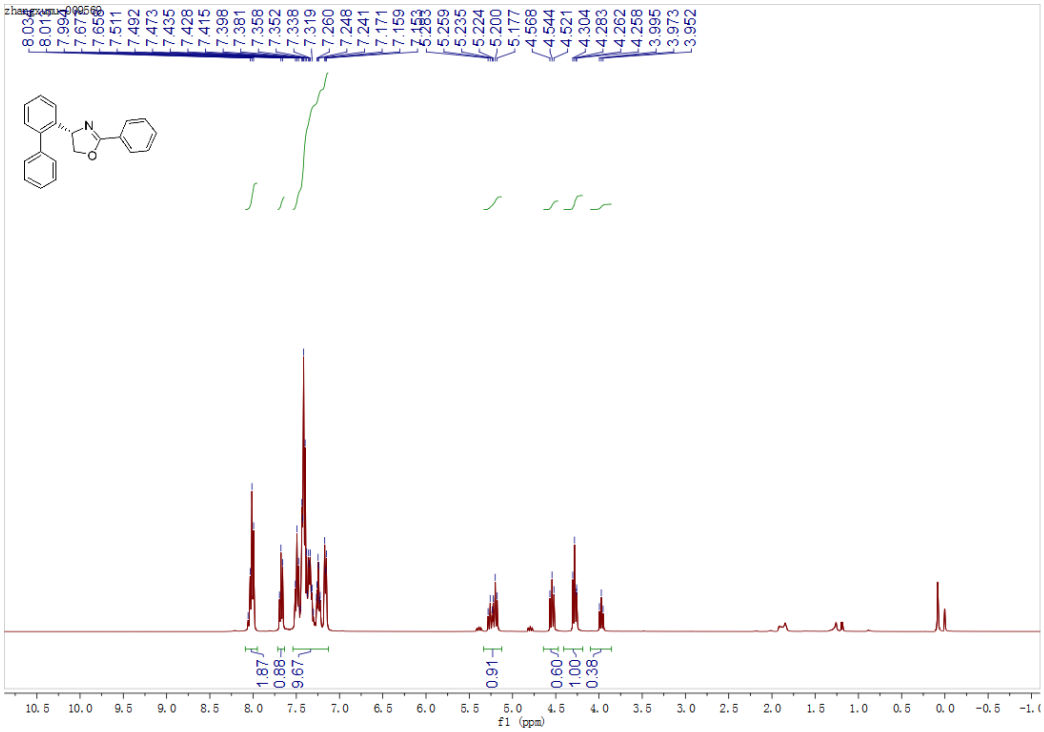
IV. NMR Spectra

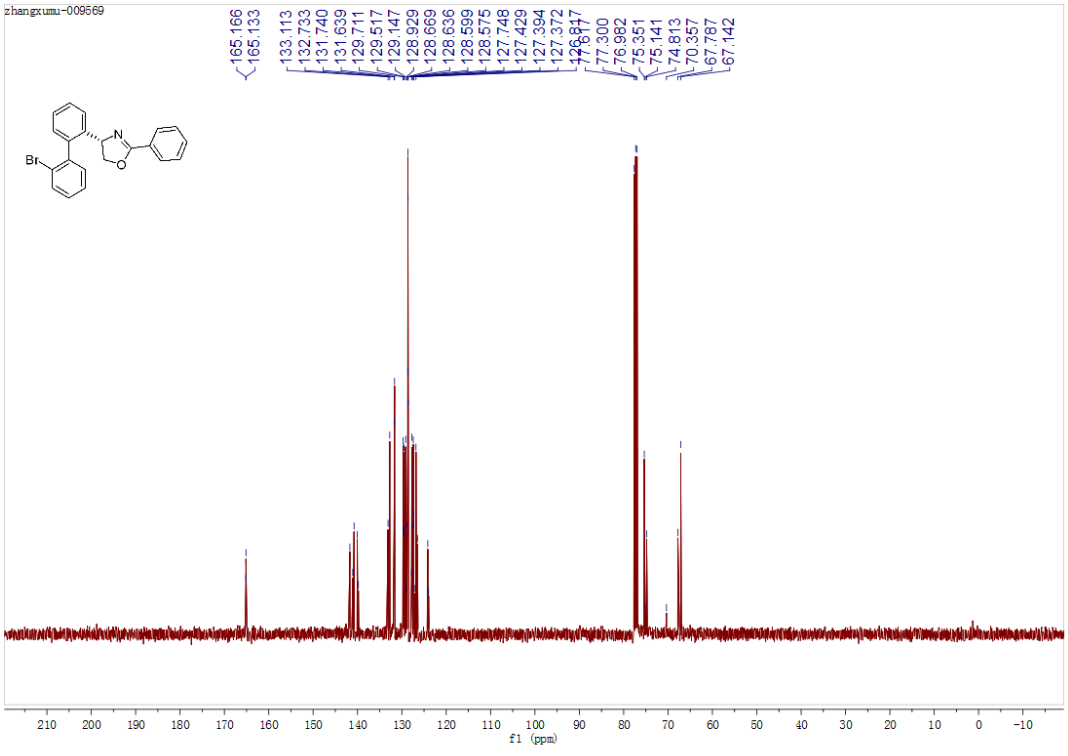
(*S*)-4-(2'-bromo-[1,1'-biphenyl]-2-yl)-2-(3,5-di-tert-butylphenyl)-4,5-dihydrooxazole (**4a**)



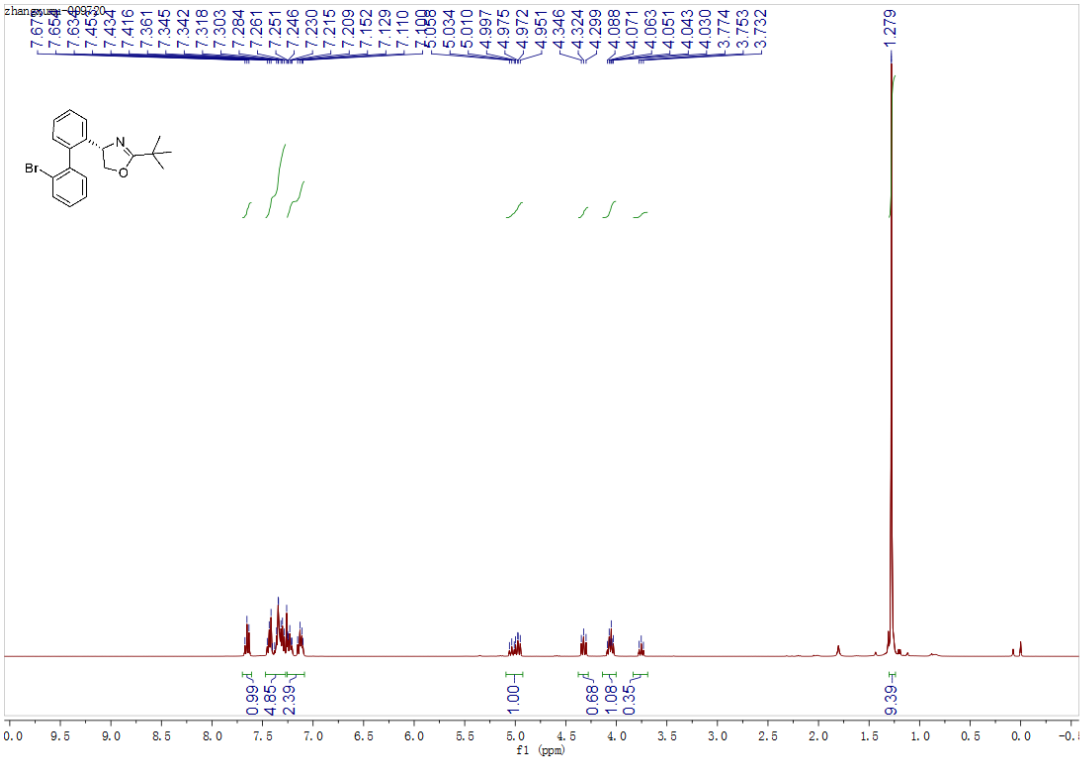


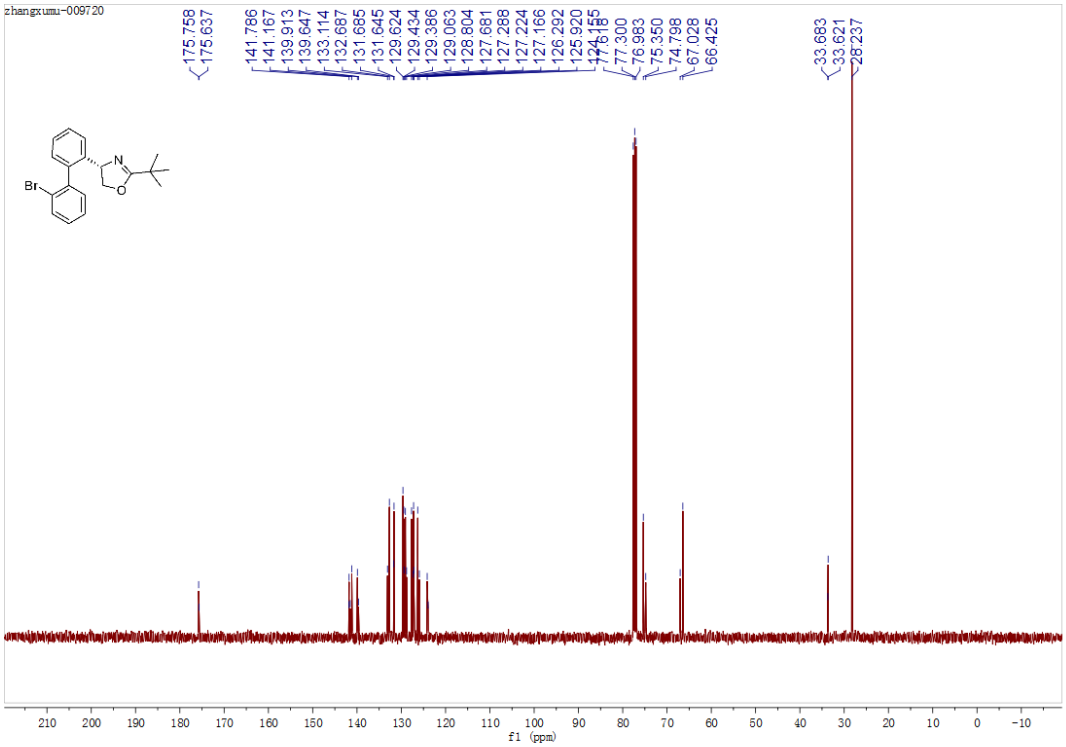
(*S*)-4-(2'-bromo-[1,1'-biphenyl]-2-yl)-2-phenyl-4,5-dihydrooxazole (**4b**)



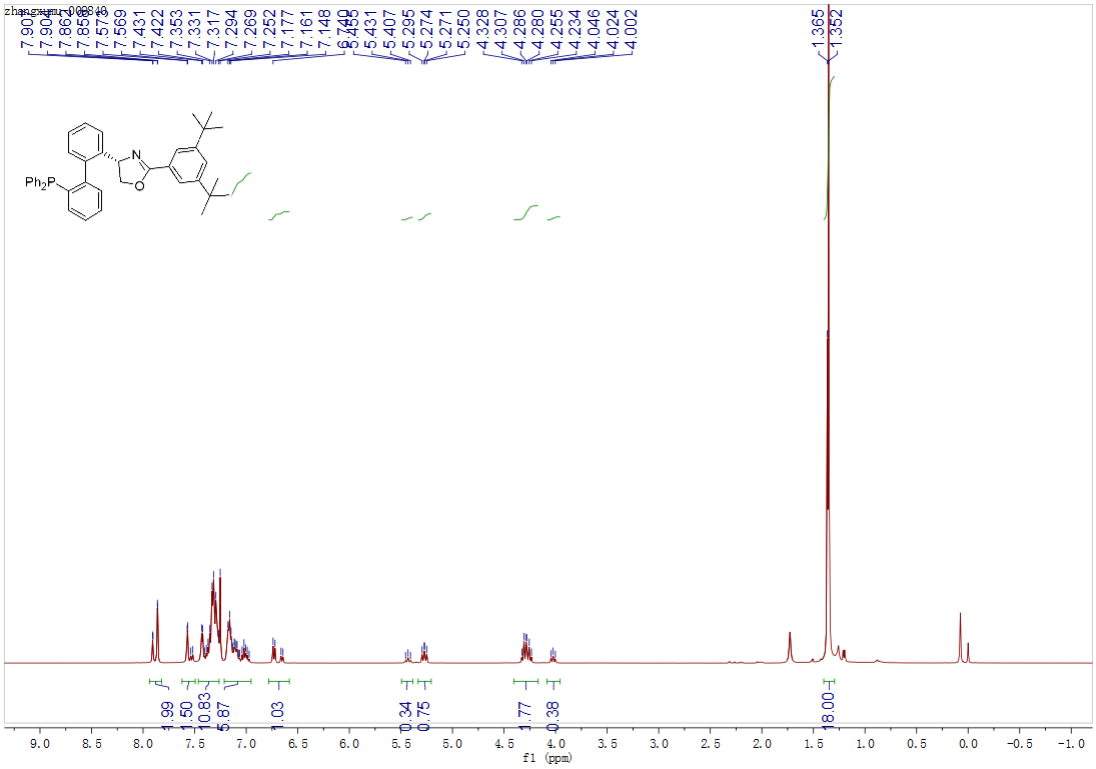


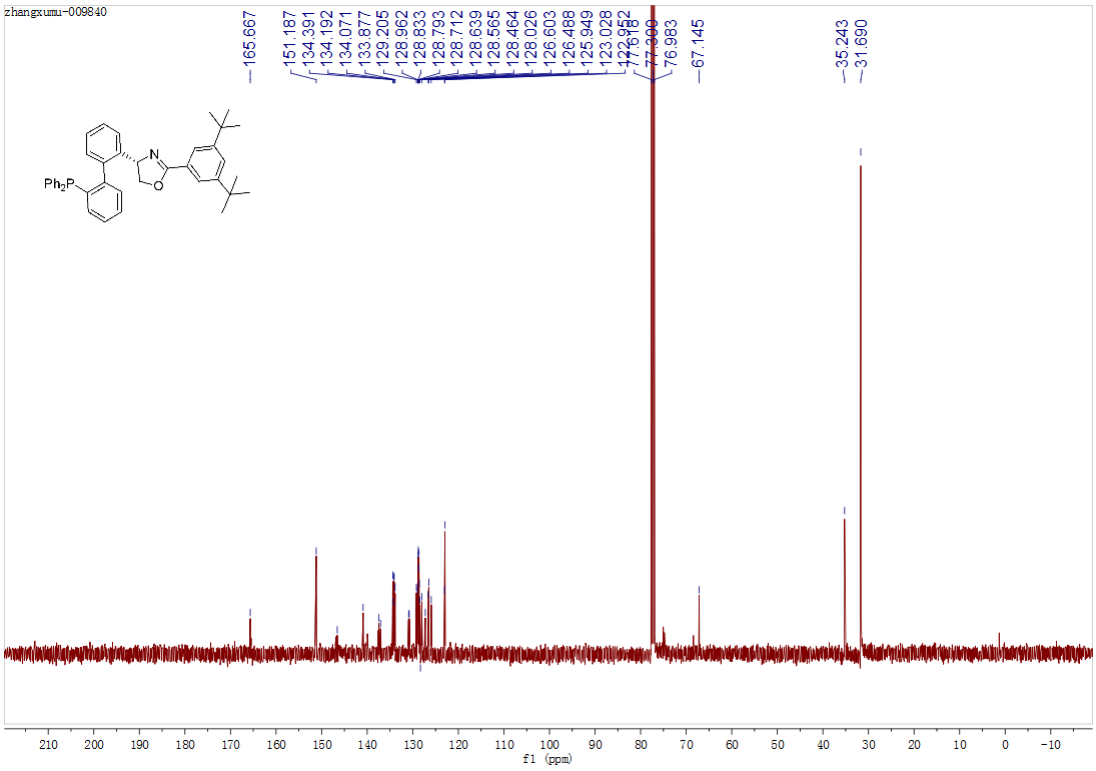
(*S*)-4-(2'-bromo-[1,1'-biphenyl]-2-yl)-2-(tert-butyl)-4,5-dihydrooxazole (**4c**)

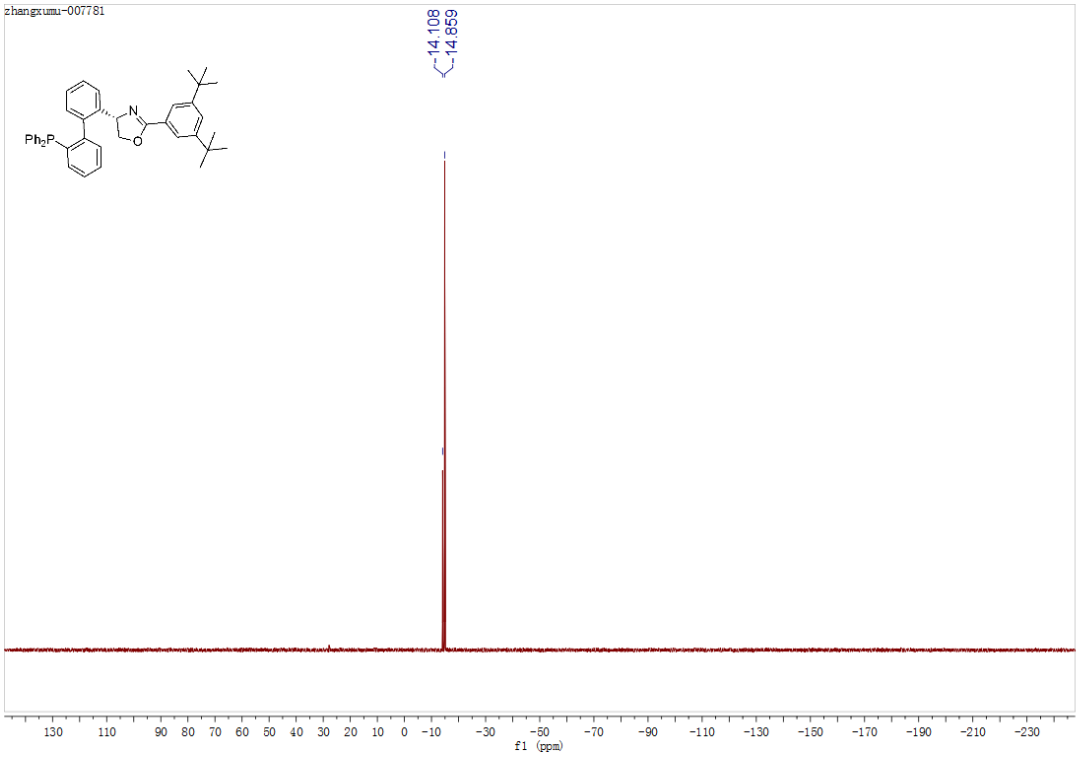




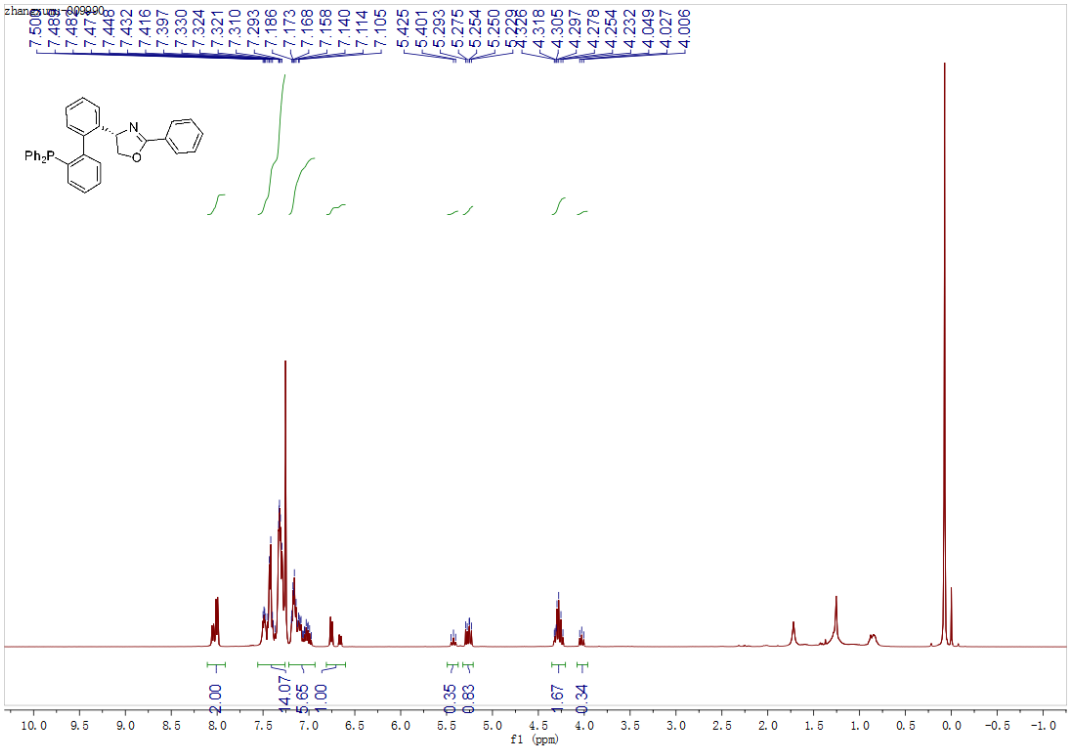
(*S*)-4-(2'-benzhydryl-[1,1'-biphenyl]-2-yl)-2-(3,5-di-tert-butylphenyl)-4,5-dihydrooxazole (**5a**)

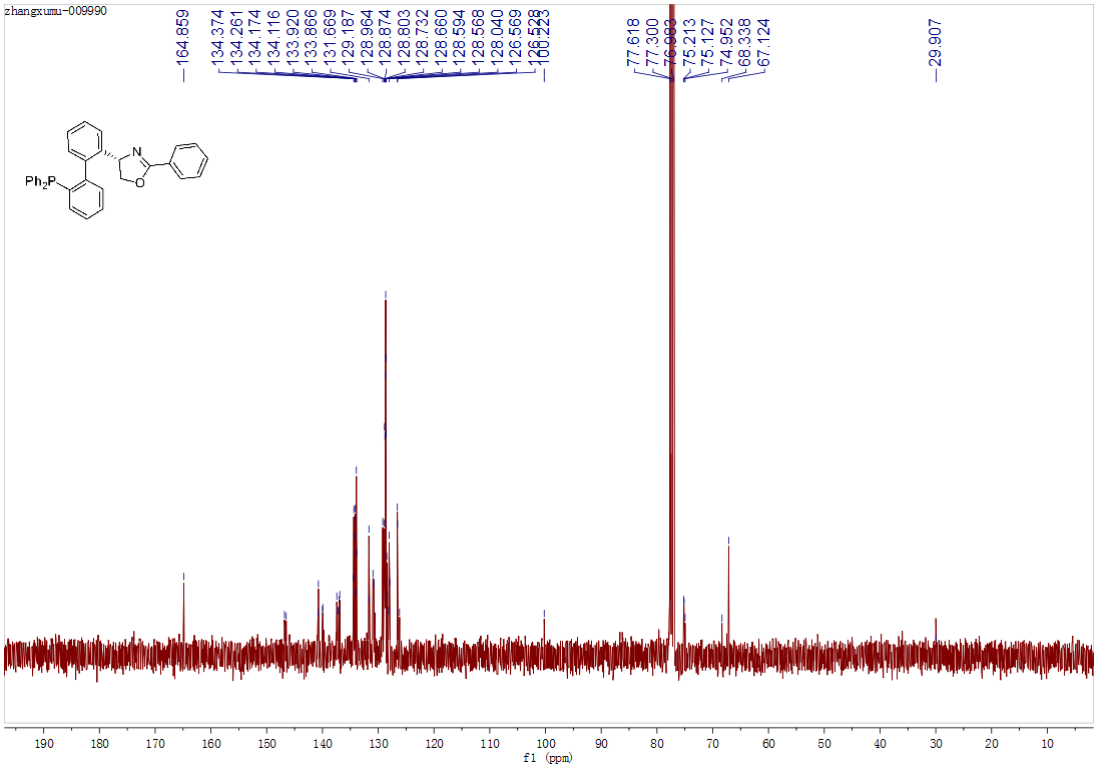


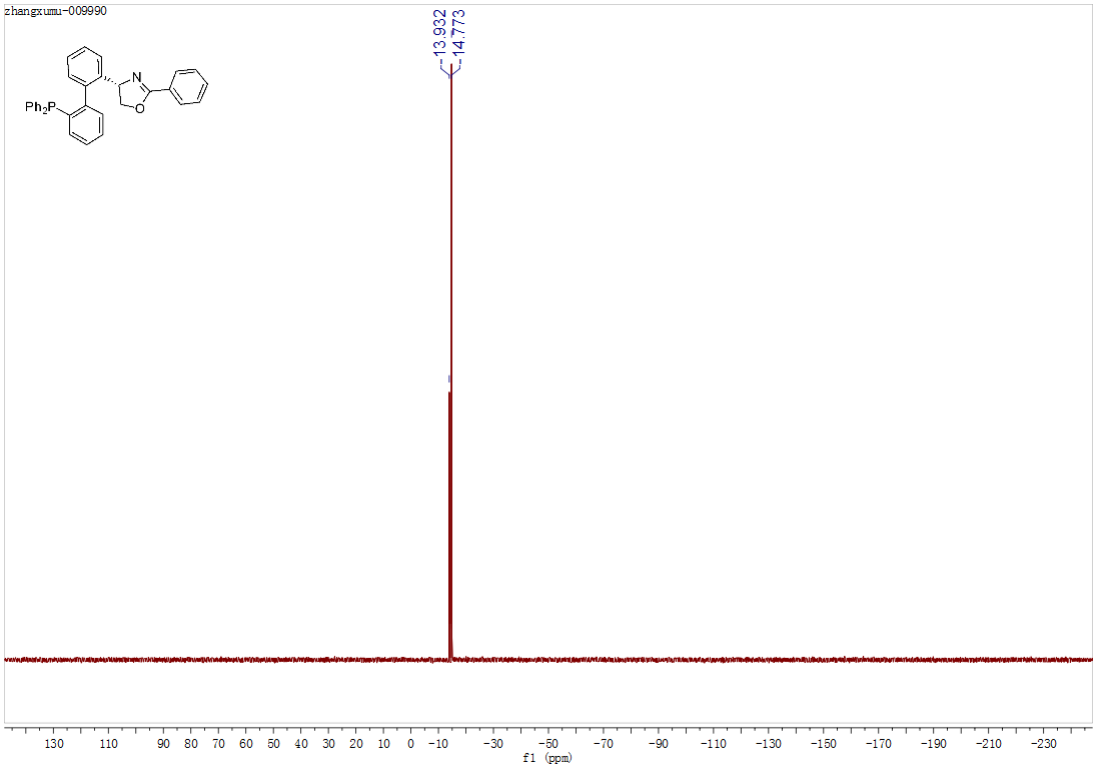




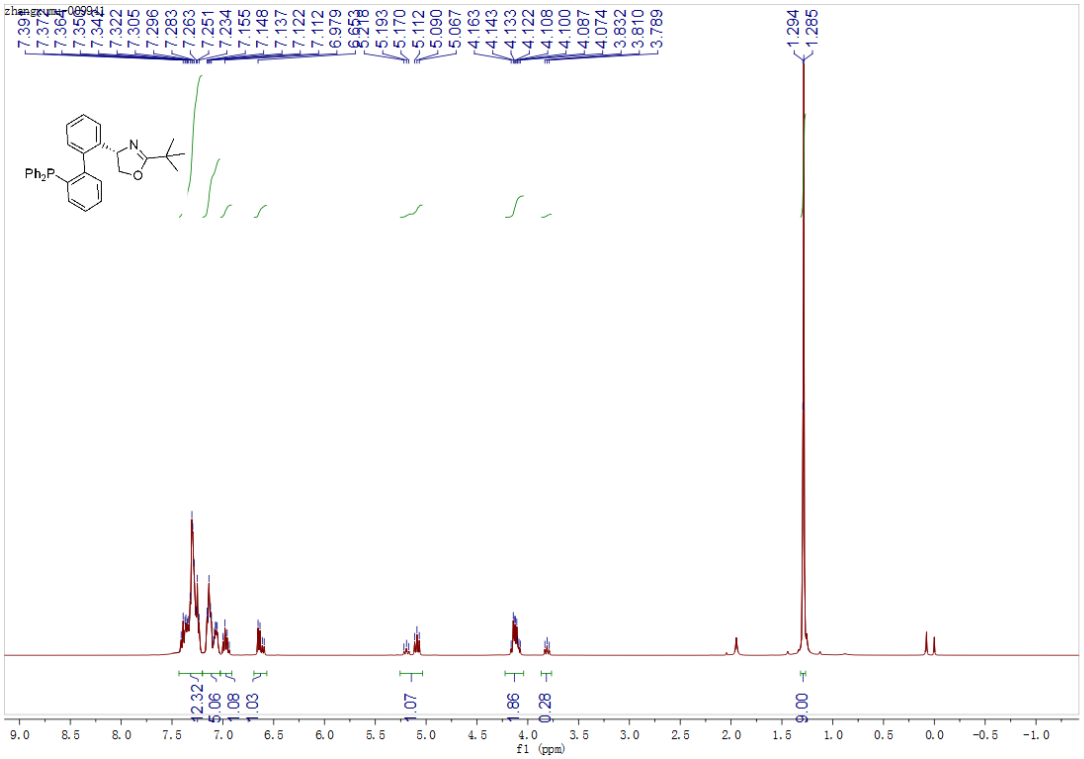
(*S*)-4-(2'-(diphenylphosphanyl)-[1,1'-biphenyl]-2-yl)-2-phenyl-4,5-dihydrooxazole (**5b**)

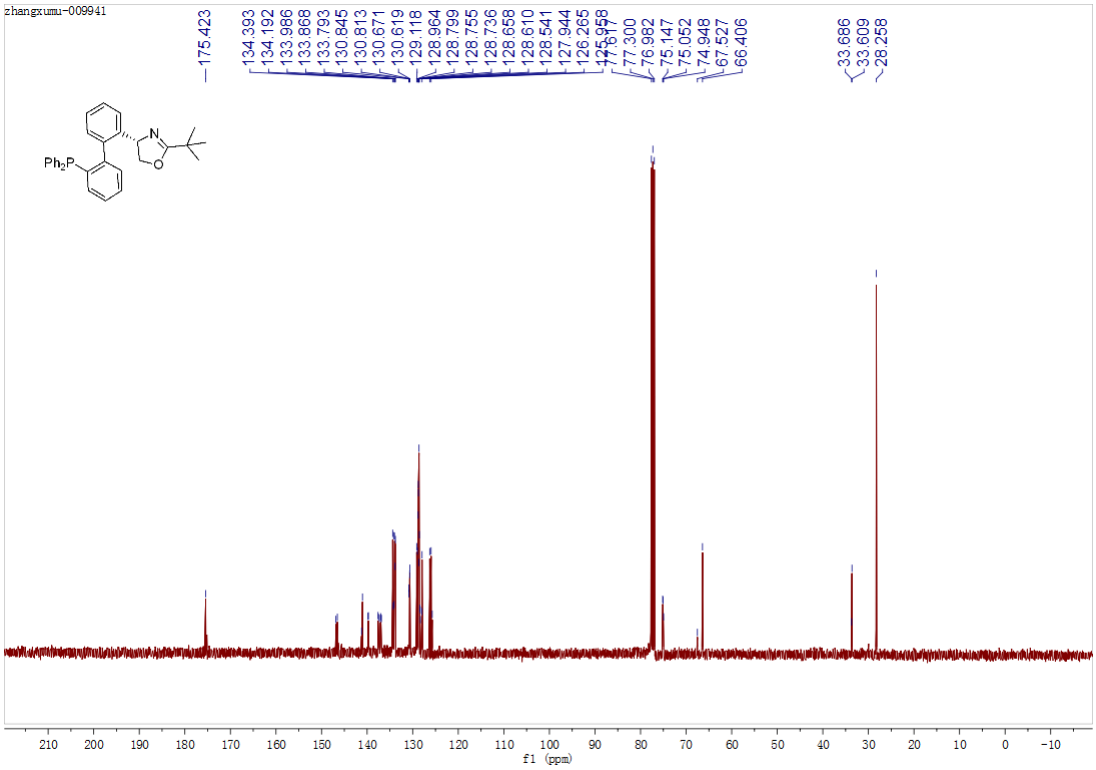


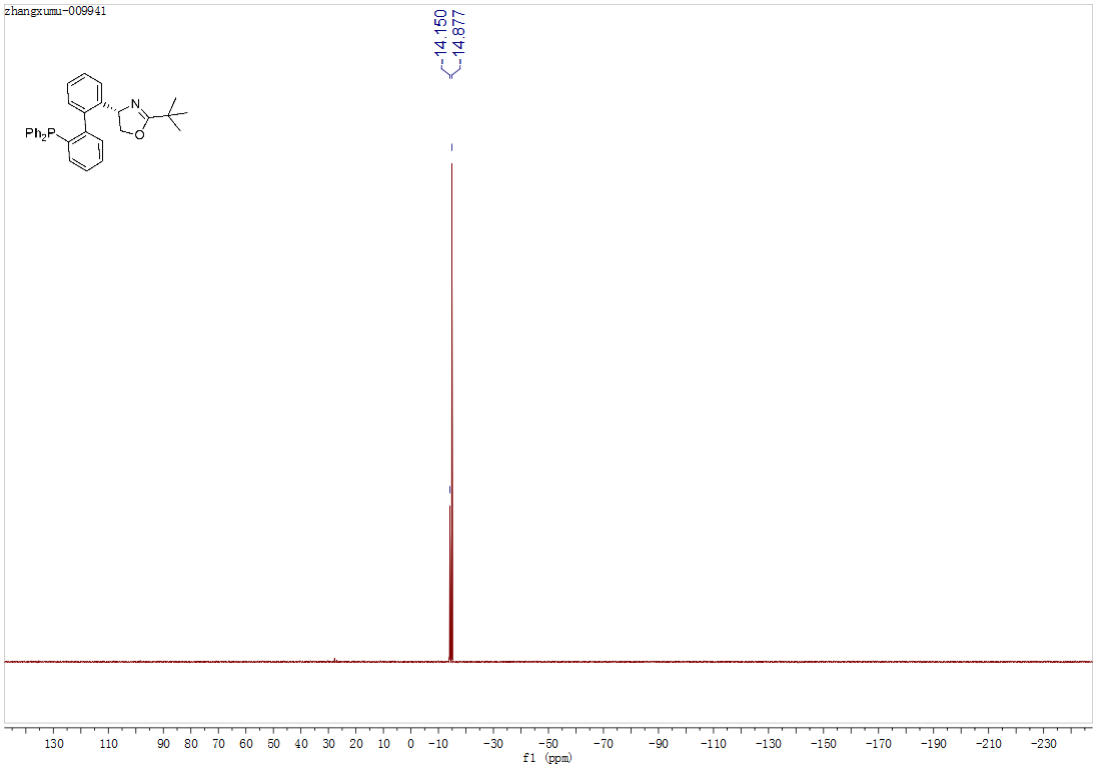

zhangxumu-009990
164.859
134.374
134.261
134.174
134.116
133.920
133.866
131.669
129.187
128.964
128.874
128.803
128.732
128.660
128.594
128.568
128.040
126.569
77.618
77.300
76.983
75.213
75.127
74.952
68.338
67.124
29.907
Ph2P
f1 (ppm)


zhangxumu-009990
13.932
14.773
Ph2P
f1 (ppm)

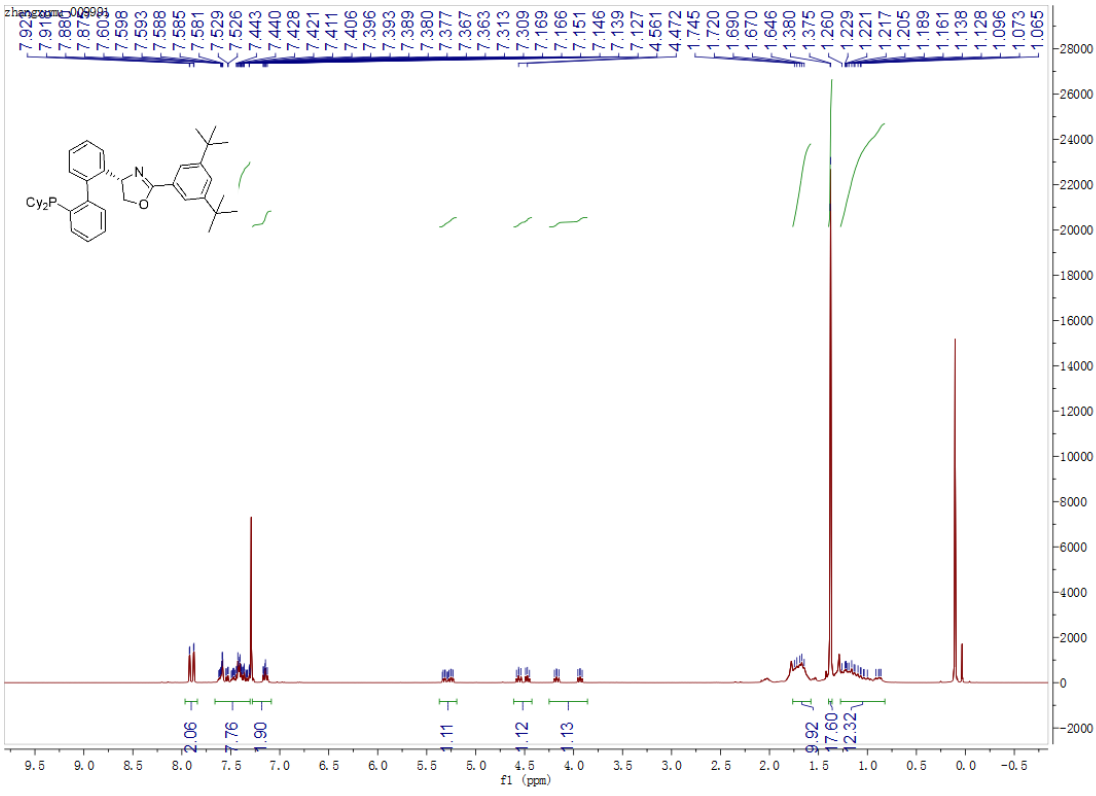
(*S*)-2-(tert-butyl)-4-(2'-(diphenylphosphanyl)-[1,1'-biphenyl]-2-yl)-4,5-dihydrooxazole (**5c**)

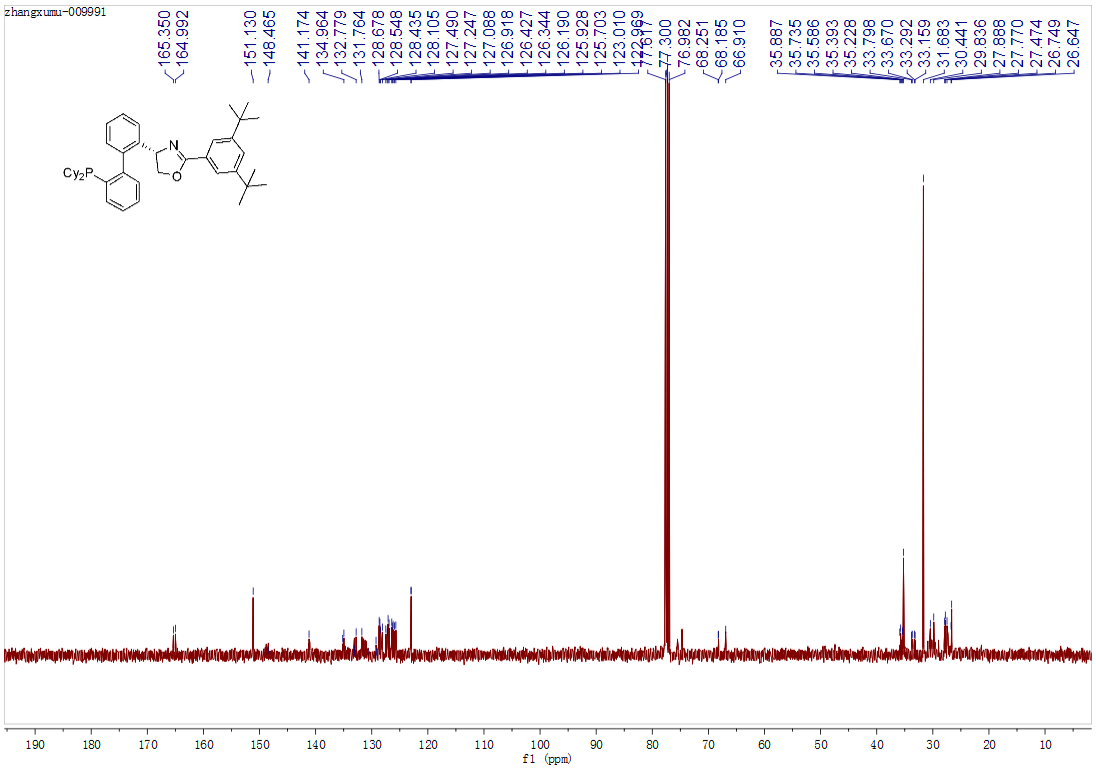






(*S*)-2-(3,5-di-tert-butylphenyl)-4-(2'-(dicyclohexylphosphanyl)-[1,1'-biphenyl]-2-yl)-4,5-dihydrooxazole (**5d**)

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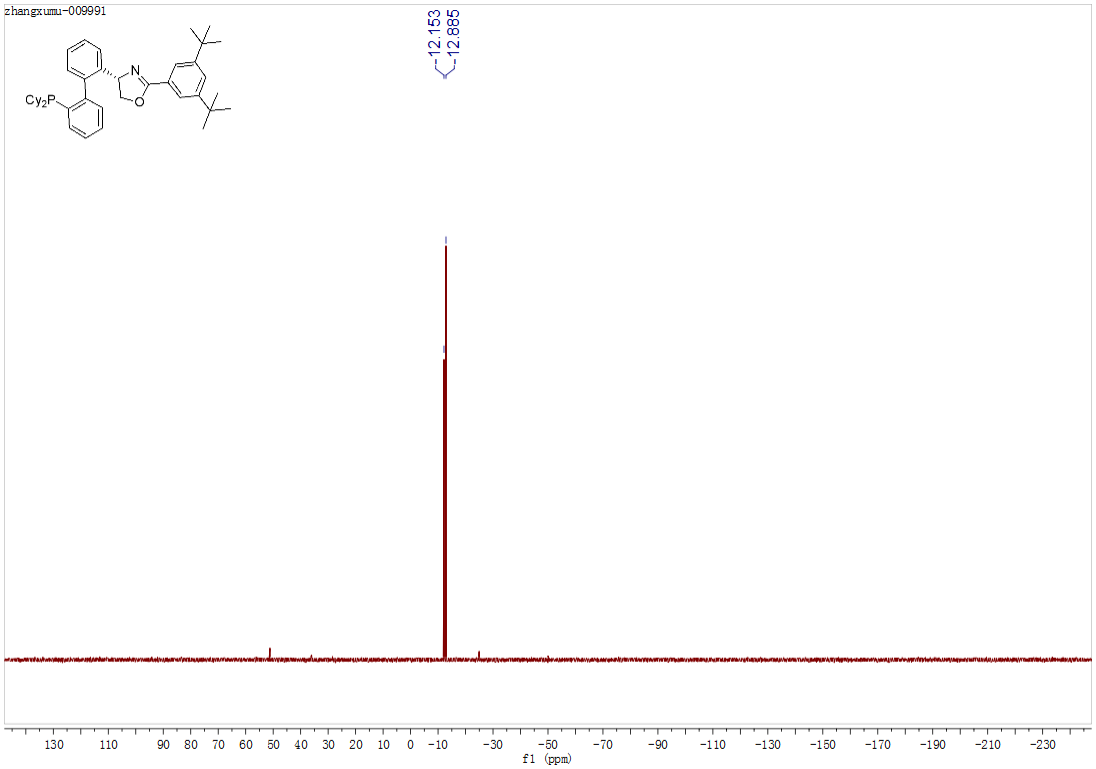
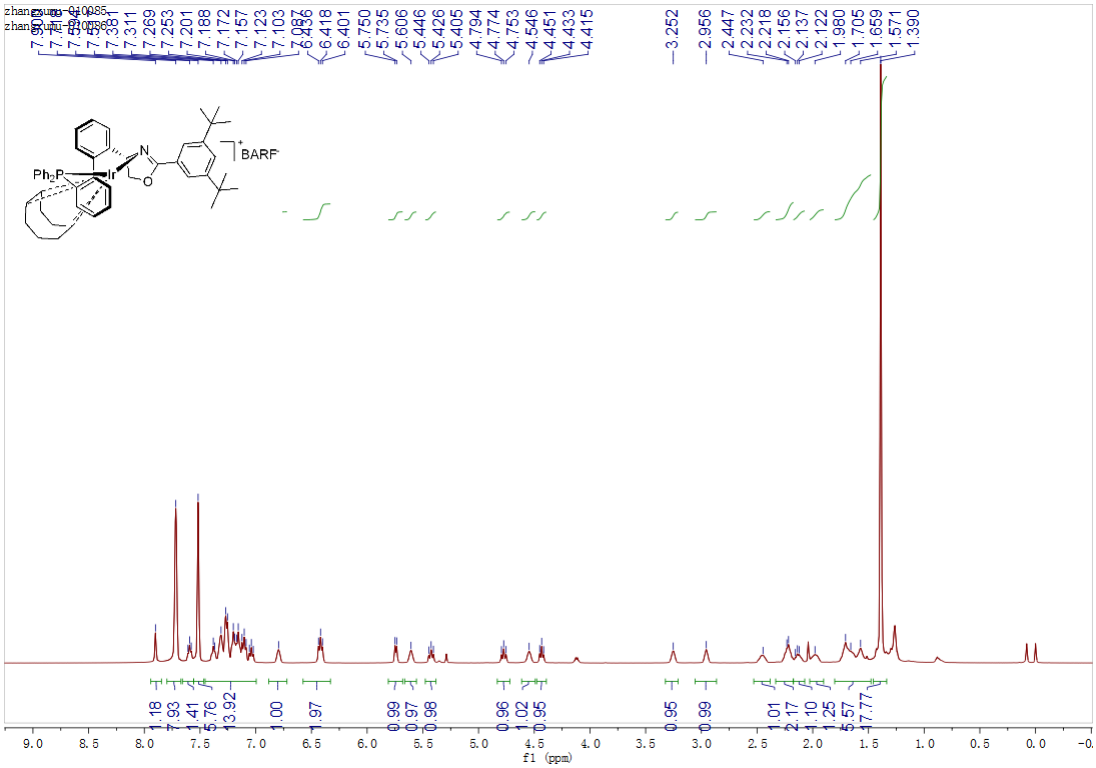
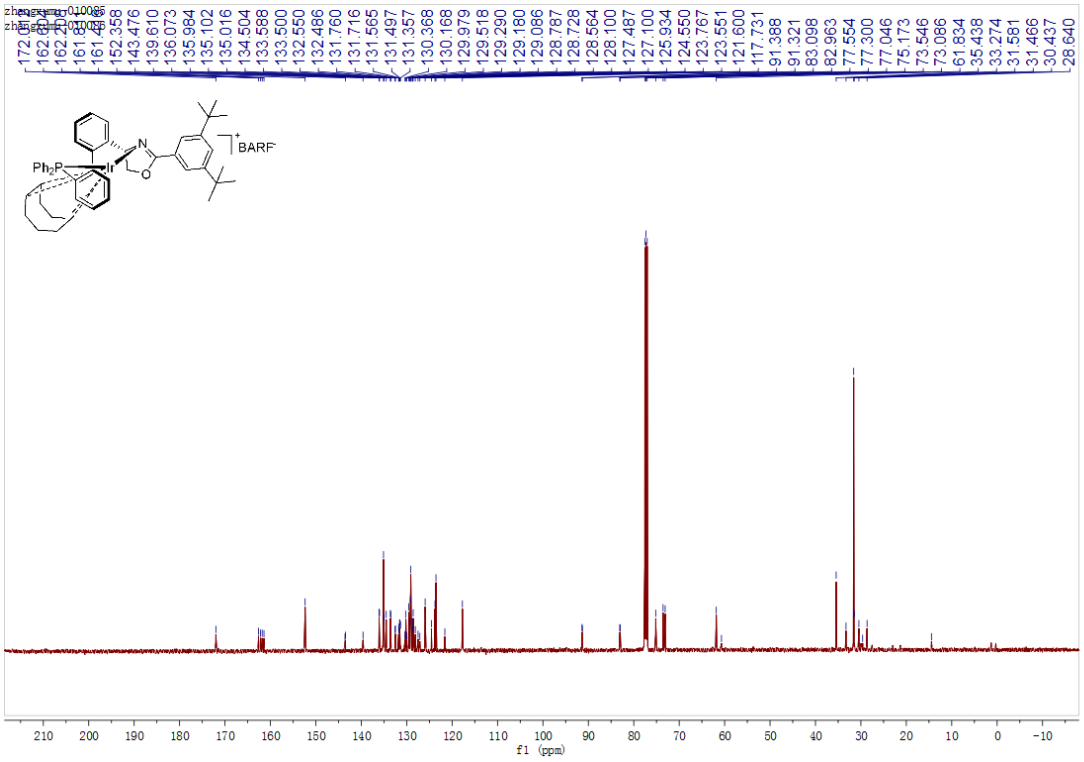
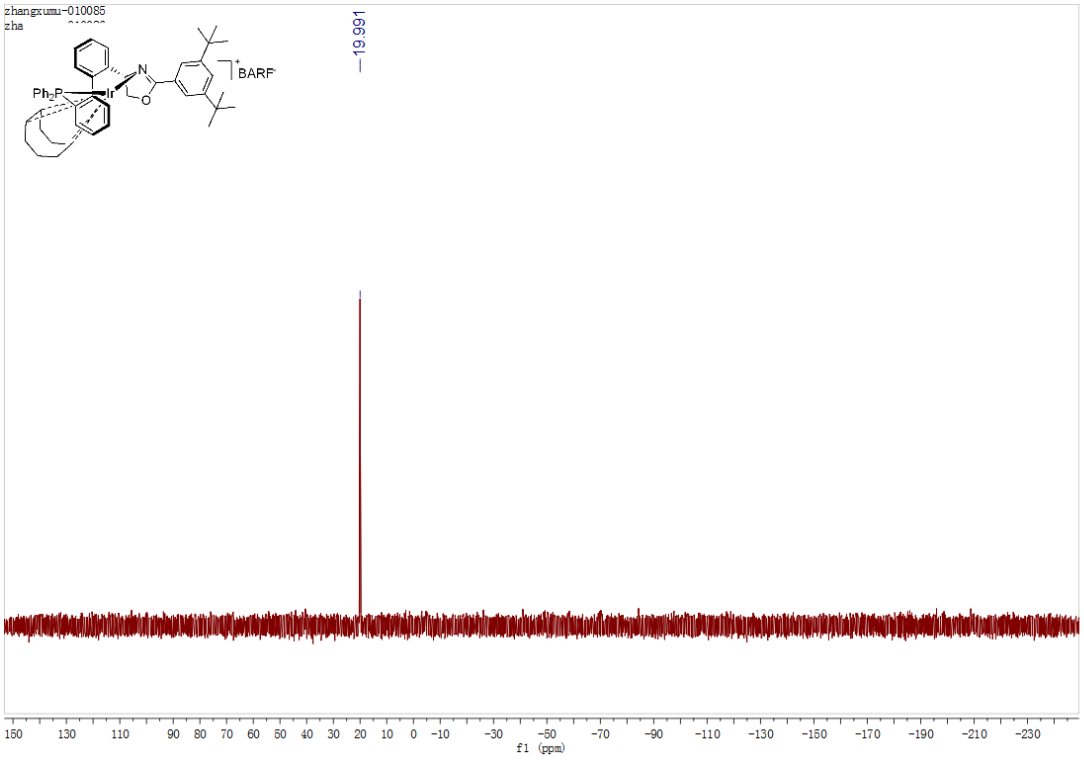
164.992
151.130
148.465
141.174
134.964
132.779
131.764
128.678
128.548
128.435
128.105
127.490
127.247
127.088
126.918
126.427
126.344
126.190
125.928
125.703
123.010
77.300
76.982
68.251
68.185
66.910
35.887
35.735
35.586
35.393
35.228
33.798
33.670
33.292
33.159
31.683
30.441
29.836
27.888
27.770
27.474
26.749
26.647
Cy_2P
N
O
f1 (ppm)


zhangxumu-009991
12.153
12.885
Cy_2P
N
O
f1 (ppm)

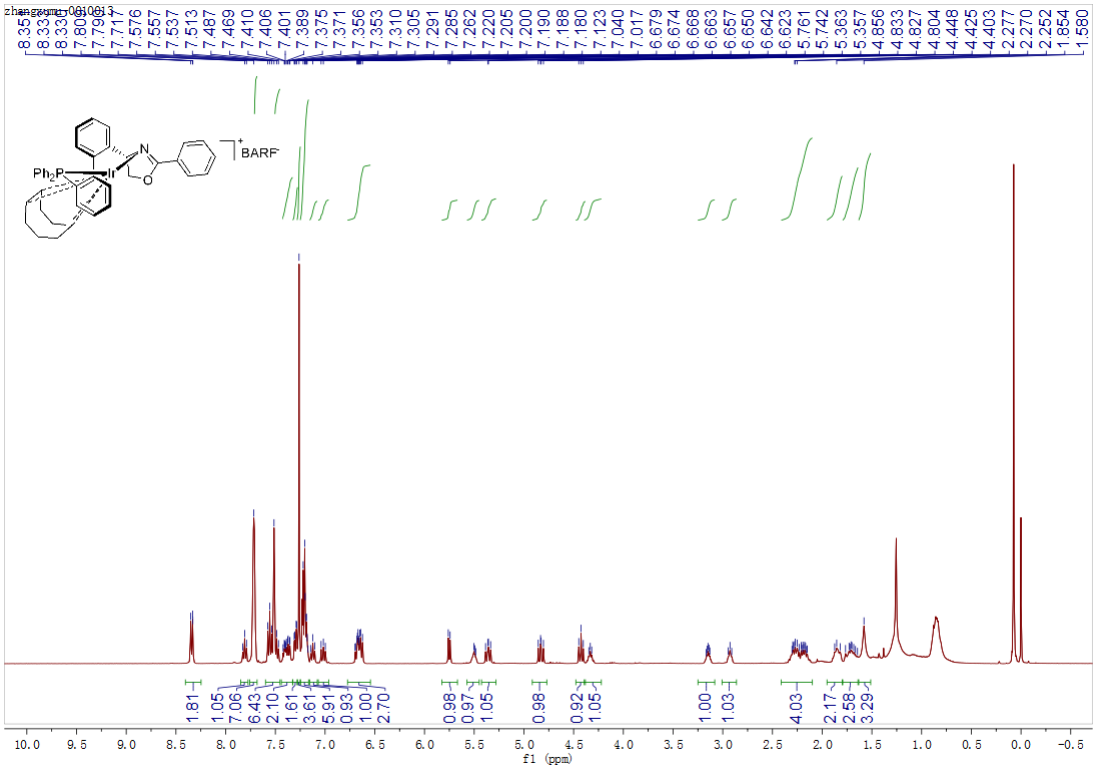
[Ir(L)COD]BArF complex **6a**

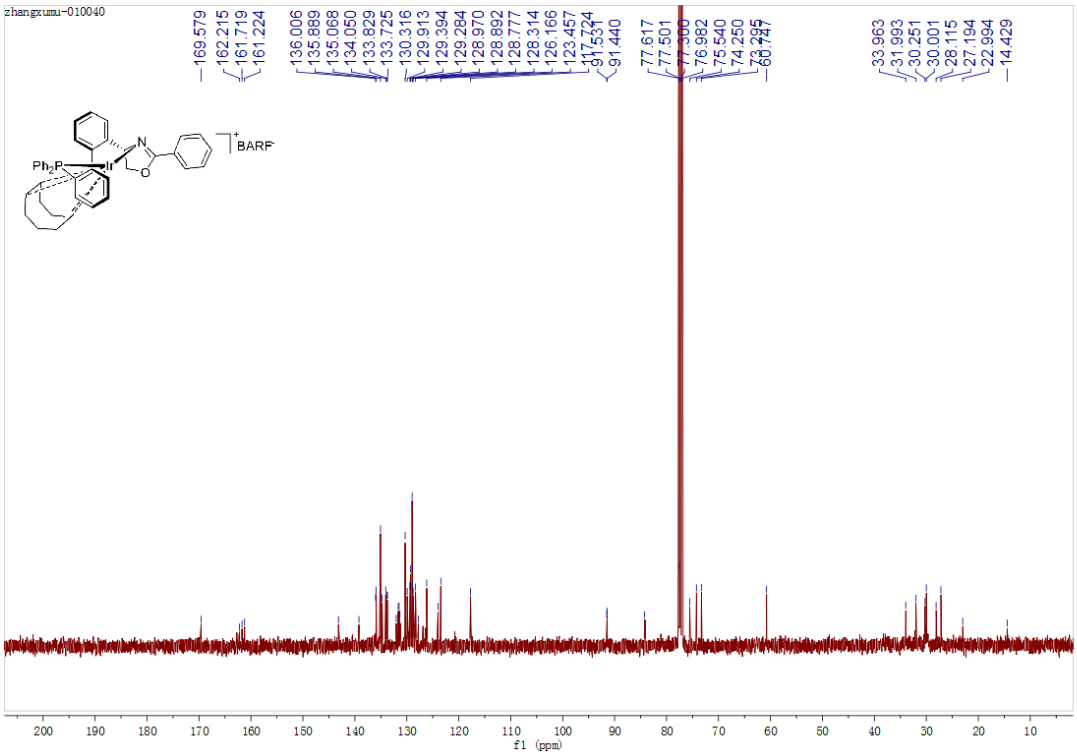


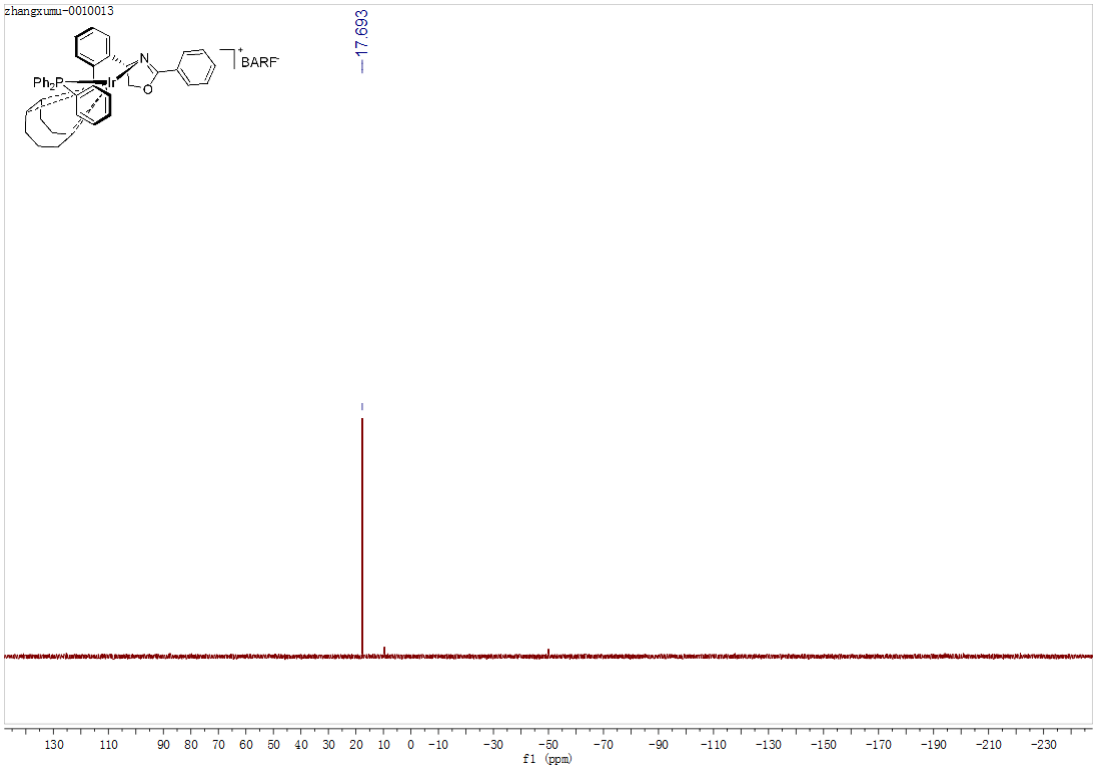




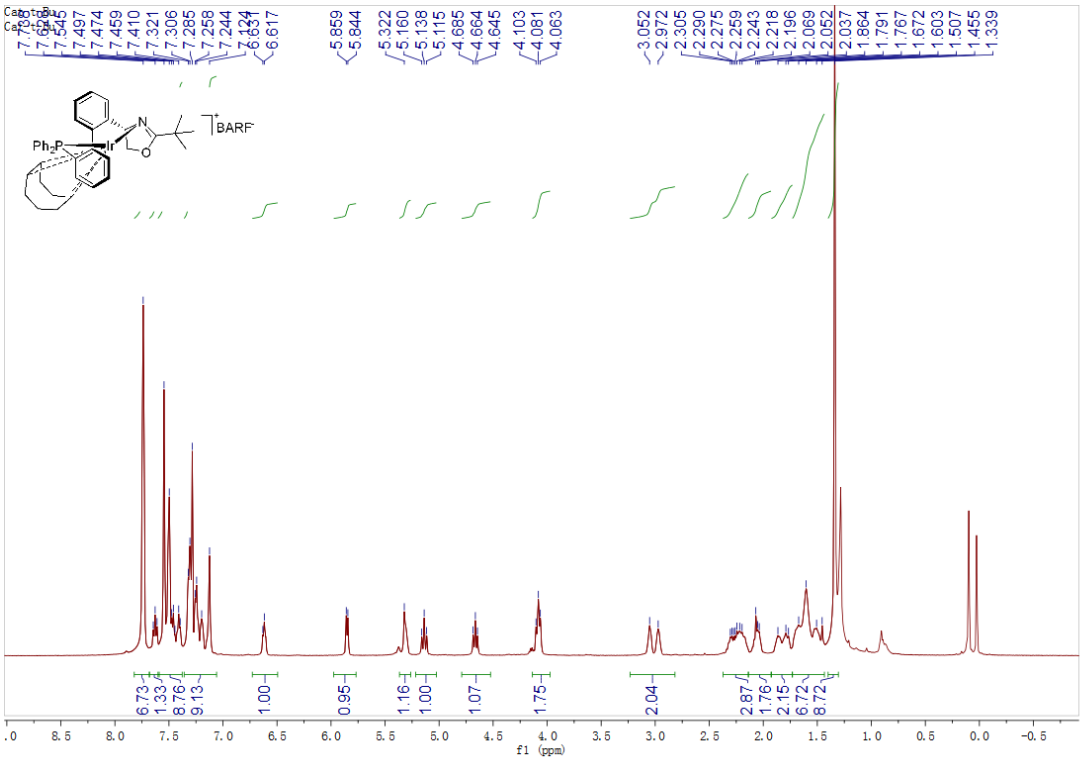
[Ir(L)COD]BArF complex **6b**

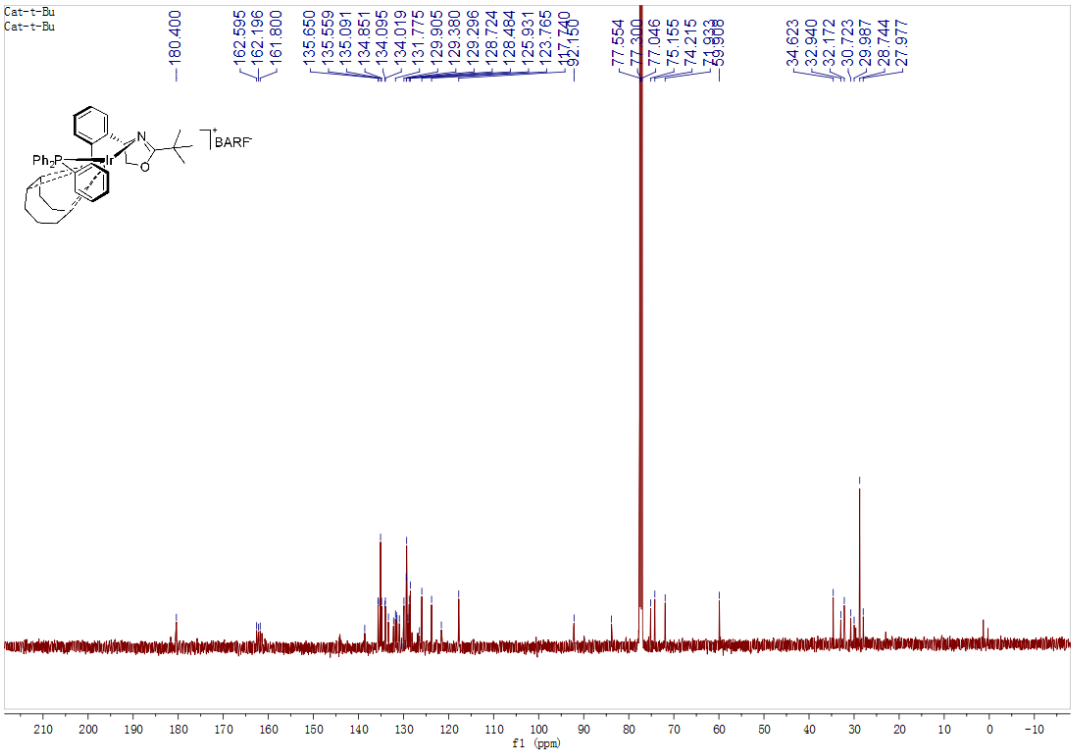


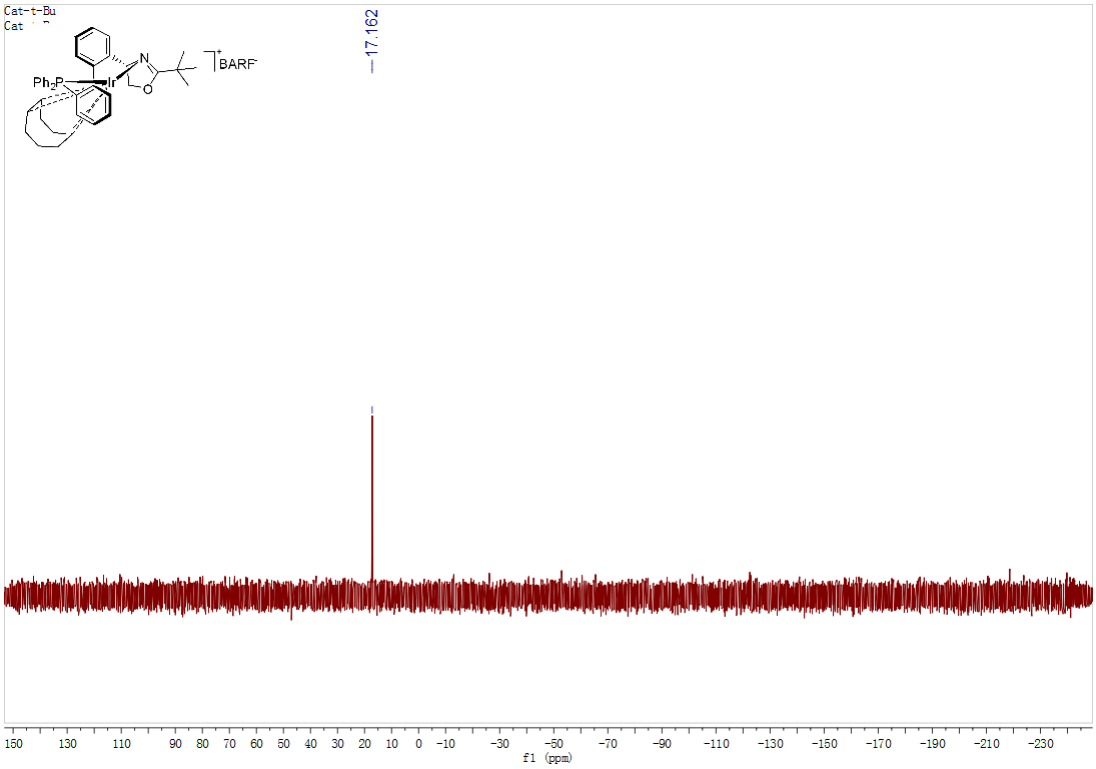

zhangxumu-010040
169.579
162.215
161.719
161.224
136.006
135.889
135.068
134.050
133.829
133.725
130.316
129.913
129.394
129.284
128.970
128.892
128.777
128.314
126.166
123.457
117.724
91.531
91.440
77.617
77.501
77.300
76.982
75.540
74.250
73.295
60.747
33.963
31.993
30.251
30.001
28.115
27.194
22.994
14.429
Ph2P
Ir
N
O
BARF
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


zhangxumu-0010013
17.693
Ph2P
Ir
N
O
BARF
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

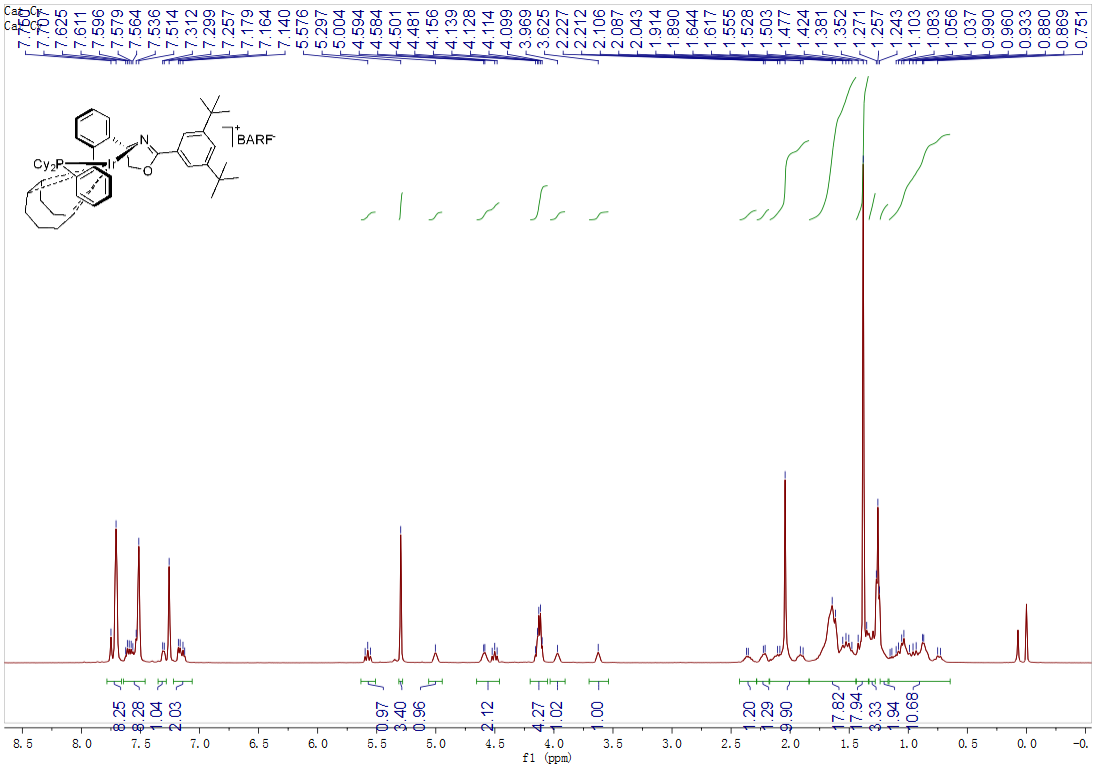
[Ir(L)COD]BArF complex **6c**

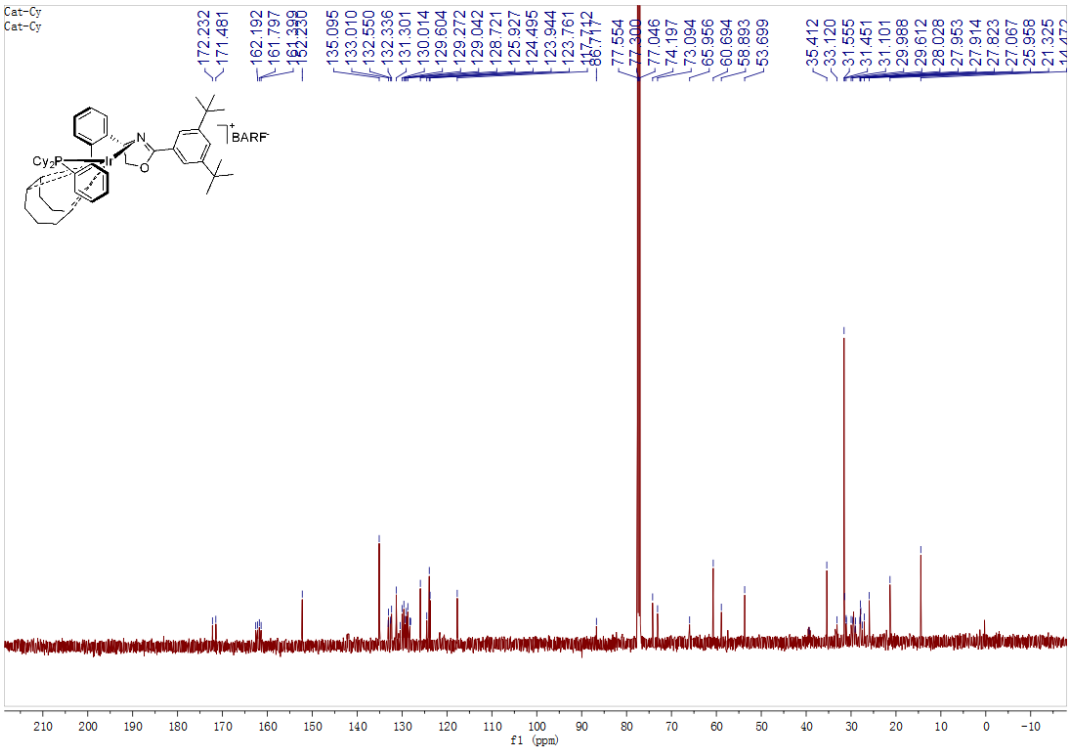


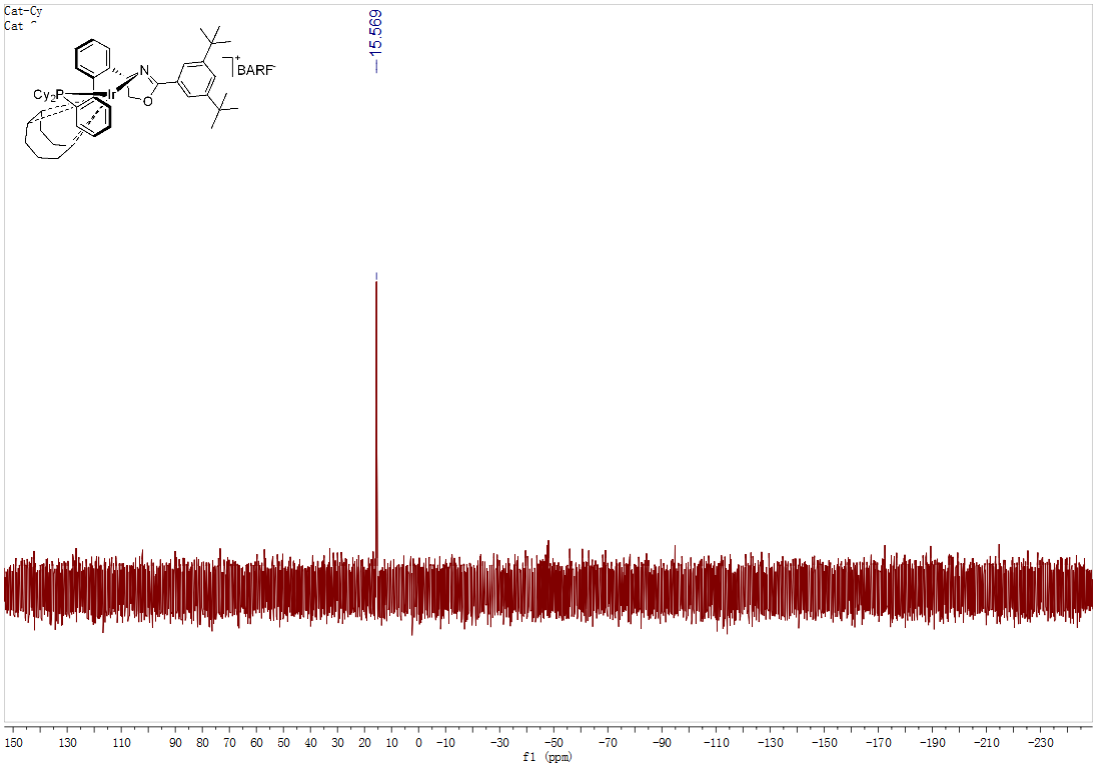




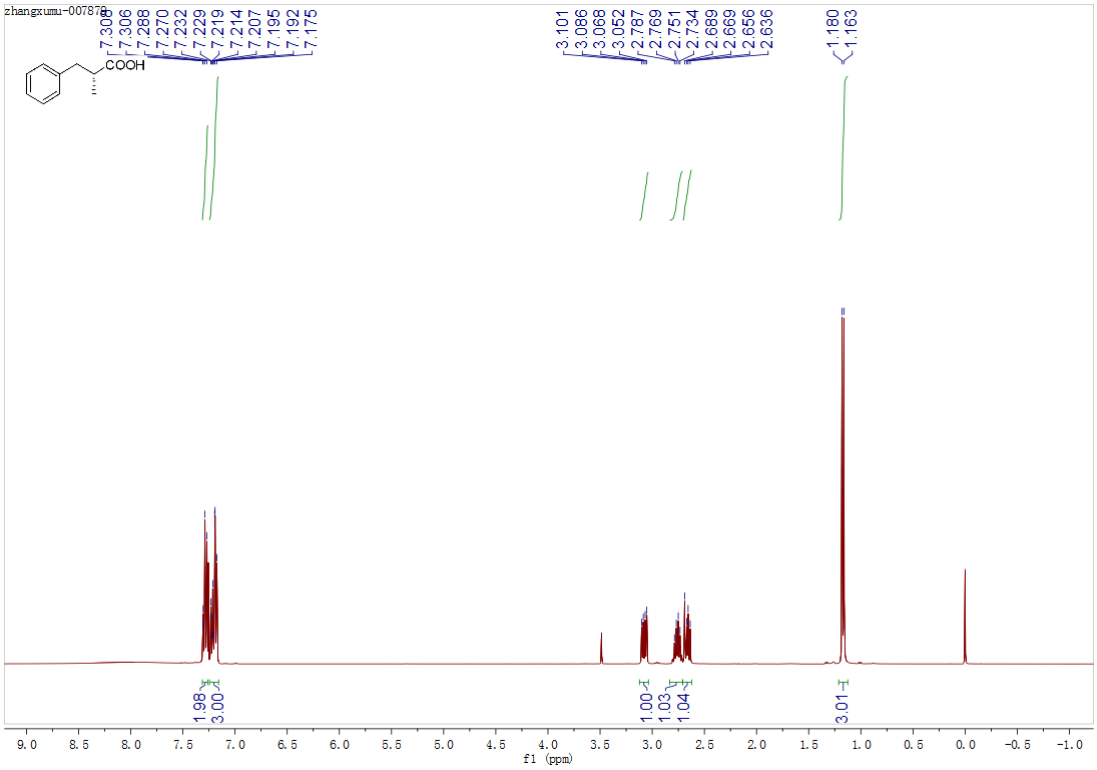
[Ir(L)COD]BArF complex 6d

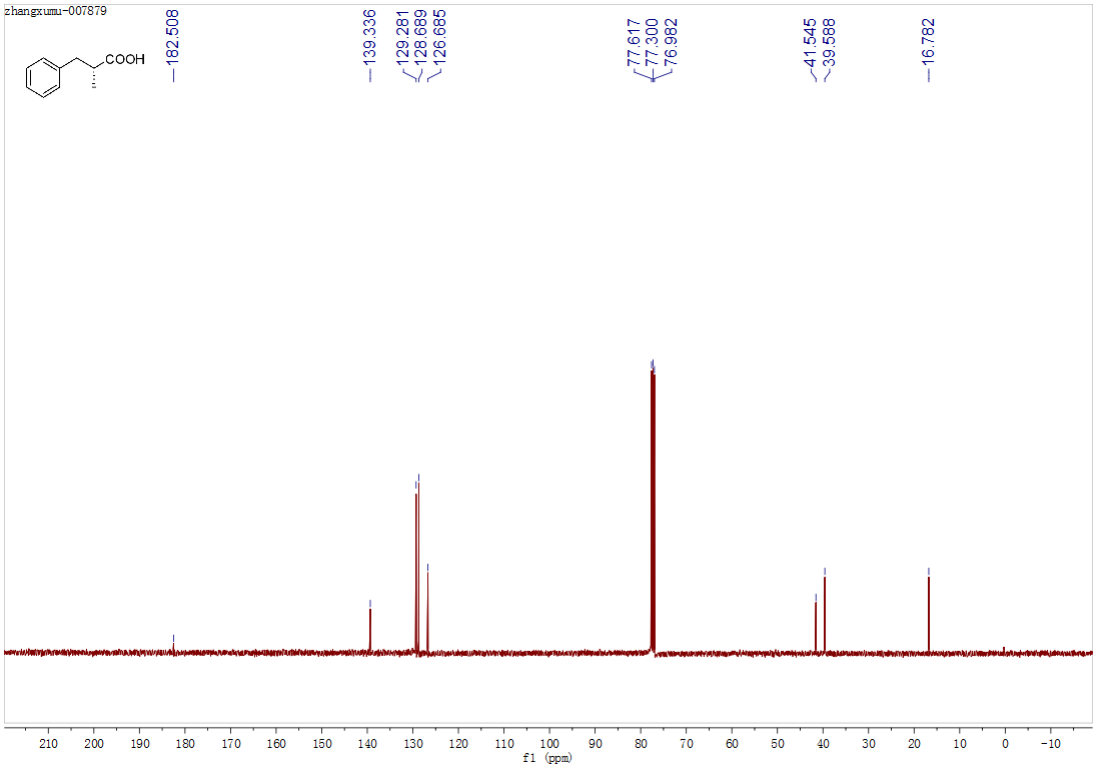



Cat-Cy
Cat-Cy
172.232
171.481
162.192
161.797
135.095
133.010
132.550
132.336
131.301
130.014
129.604
129.272
129.042
128.721
125.927
124.495
123.944
123.761
117.712
86.717
77.554
77.300
77.046
74.197
73.094
65.956
60.694
58.893
53.699
35.412
33.120
31.555
31.451
31.101
29.988
29.612
28.028
27.953
27.914
27.823
27.067
25.958
21.325
BARF
Cy2P
Ir
N
O
f1 (ppm)

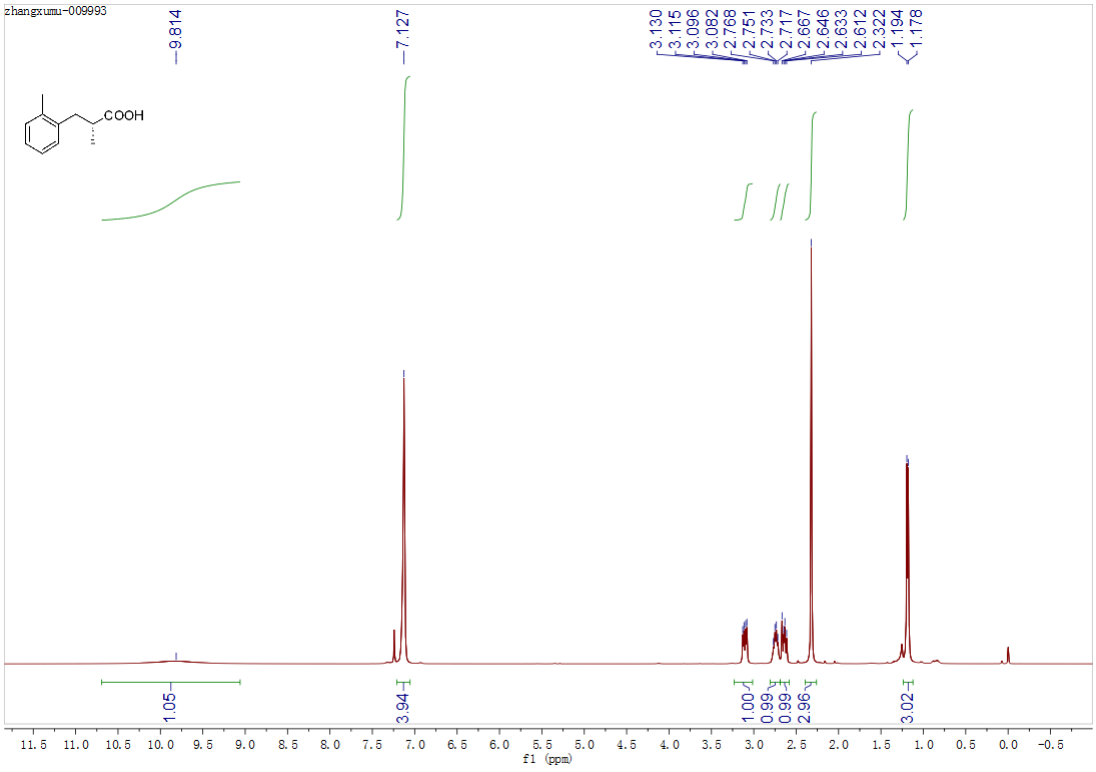

Cat-Cy
15.569
BARF
Cy2P
Ir
N
O
f1 (ppm)

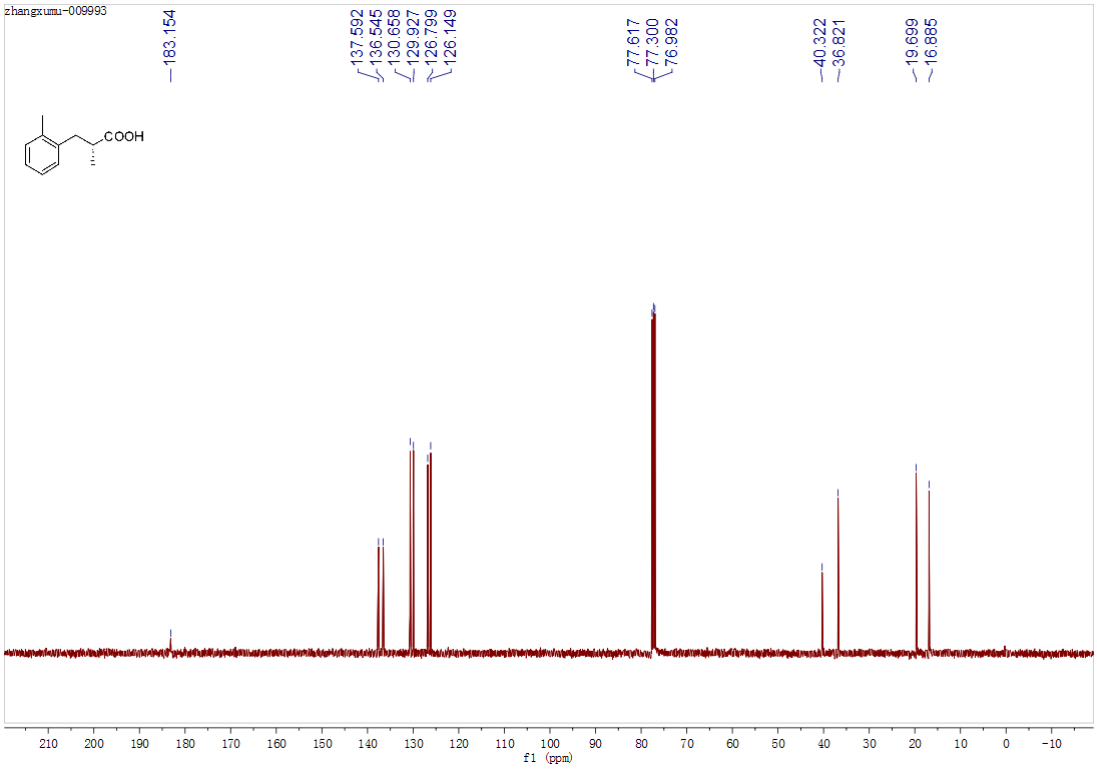
(*R*)-2-methyl-3-phenylpropanoic acid **8a**



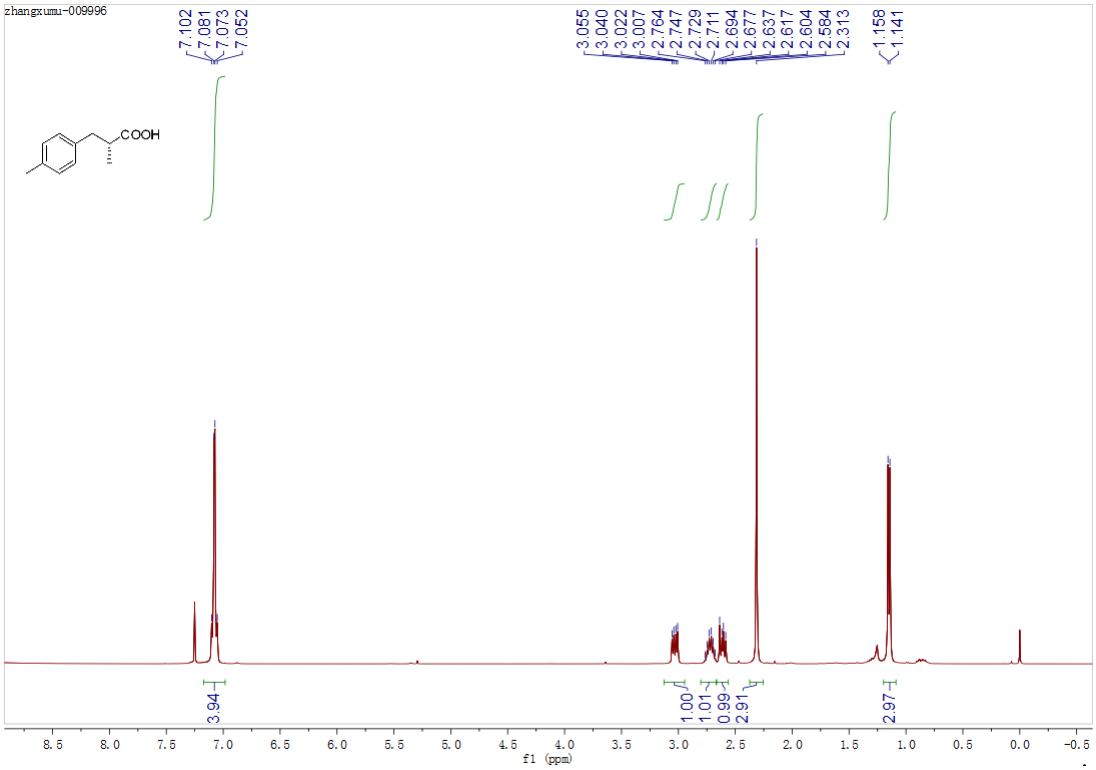


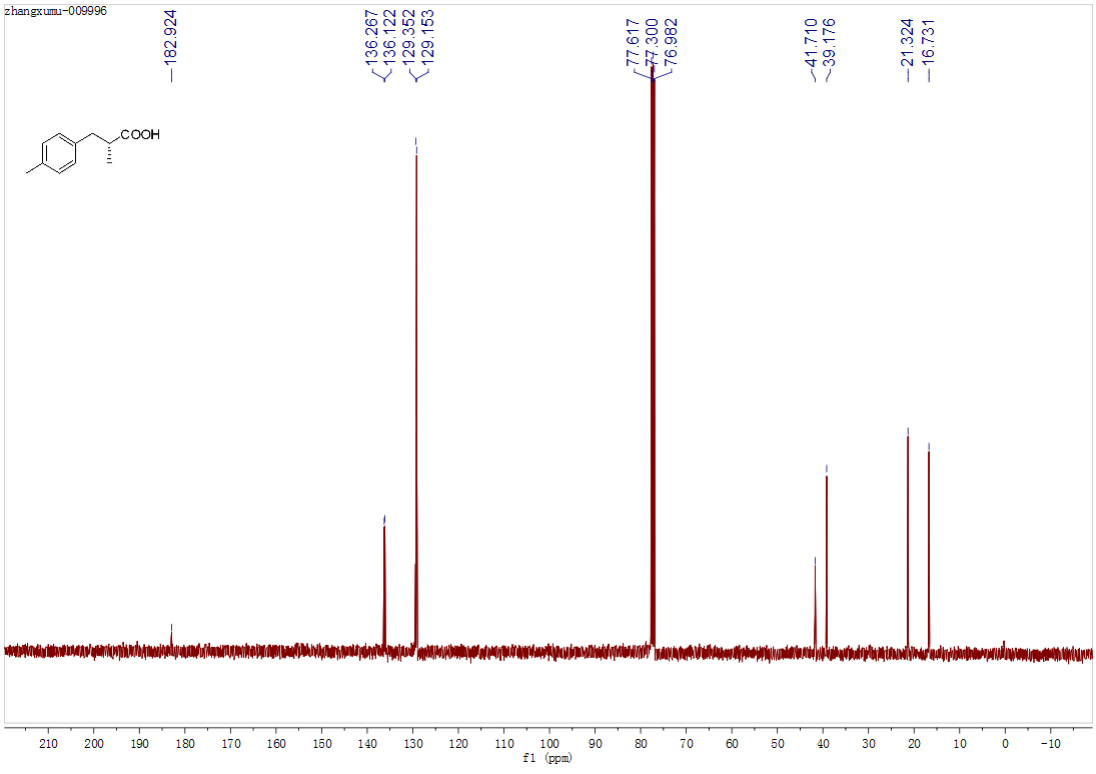
(*R*)-2-methyl-3-(o-tolyl)propanoic acid **8b**



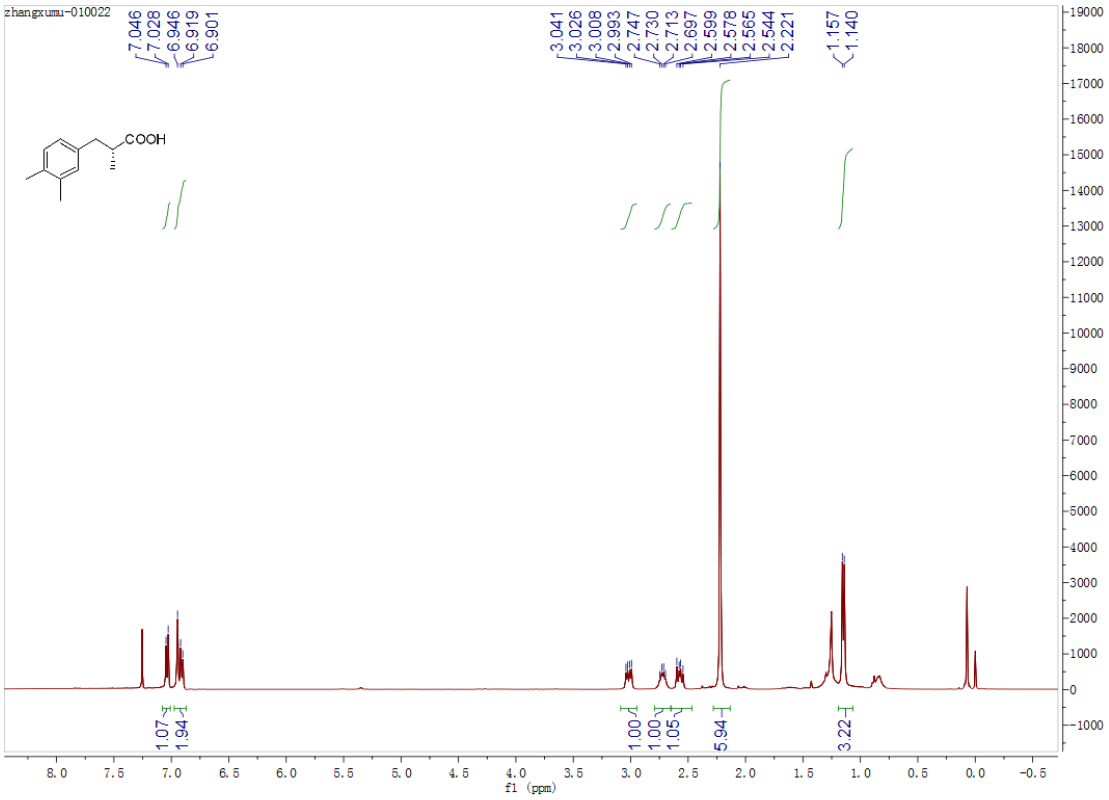


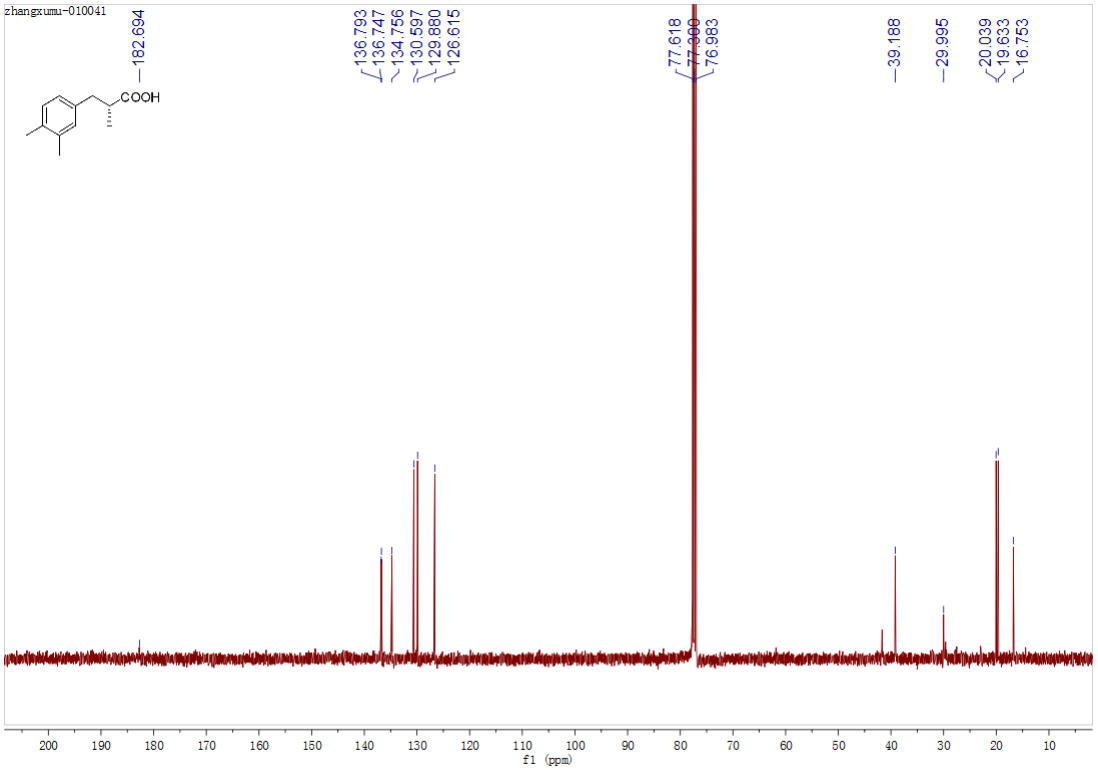
(*R*)-2-methyl-3-(p-tolyl)propanoic acid **8c**



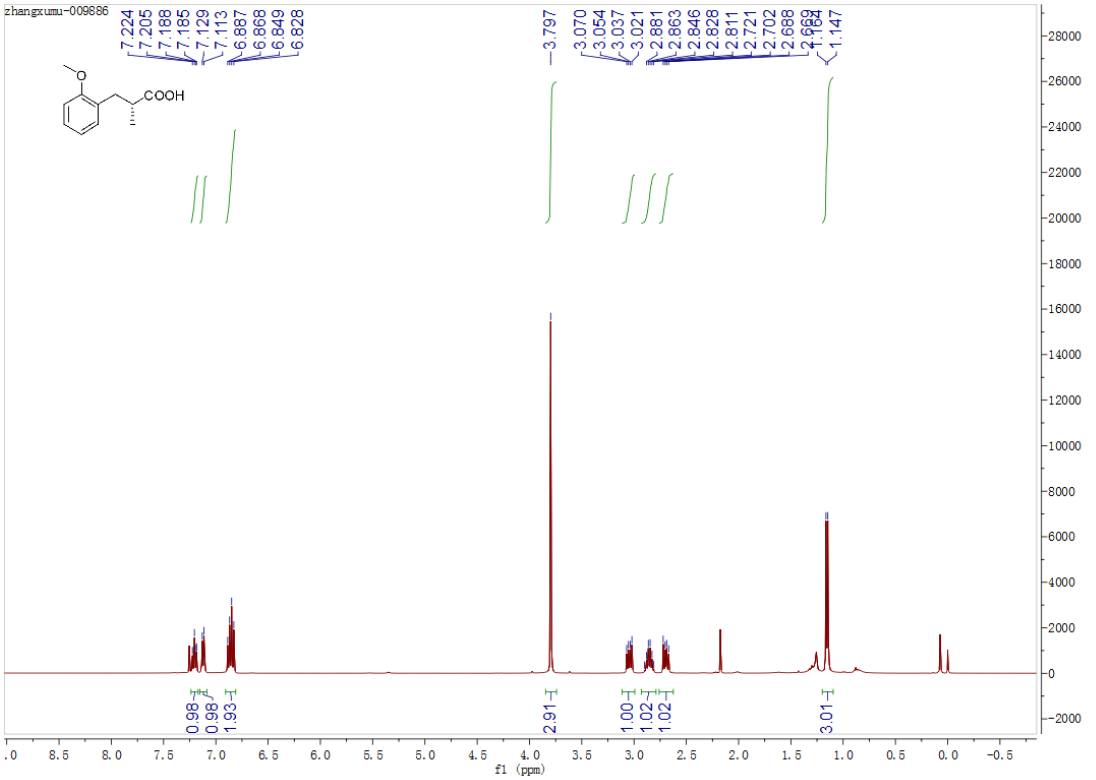


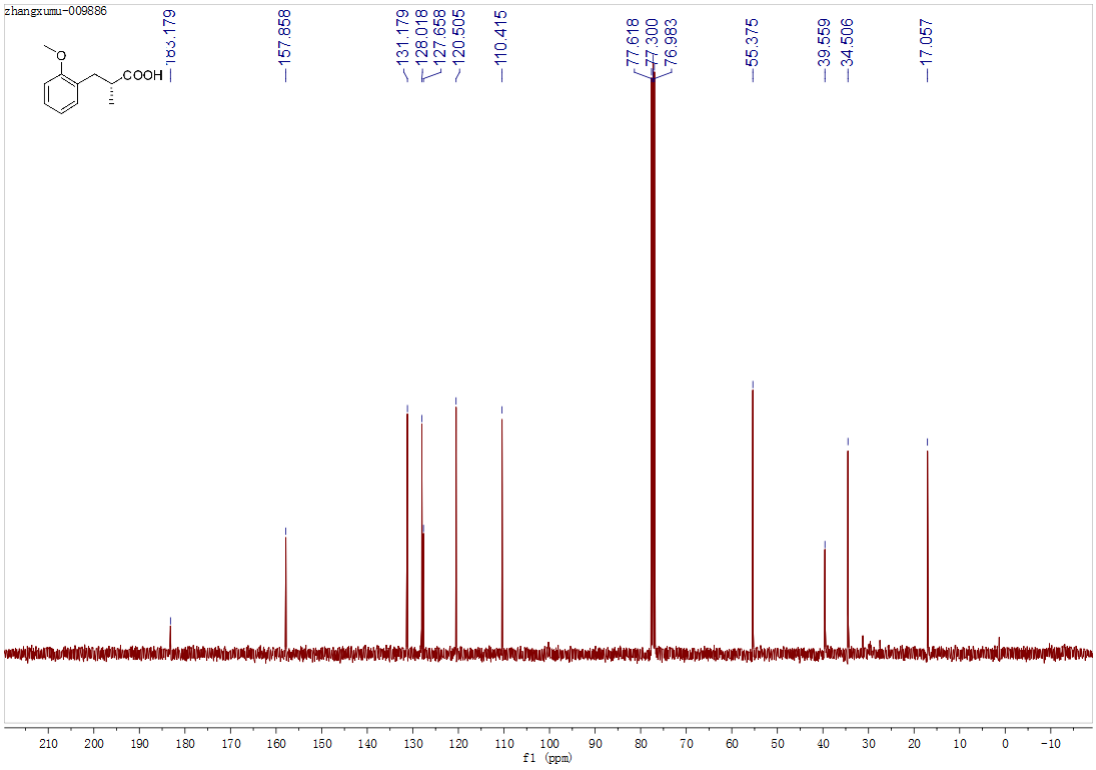
(*R*)-3-(3,4-dimethylphenyl)-2-methylpropanoic acid **8d**



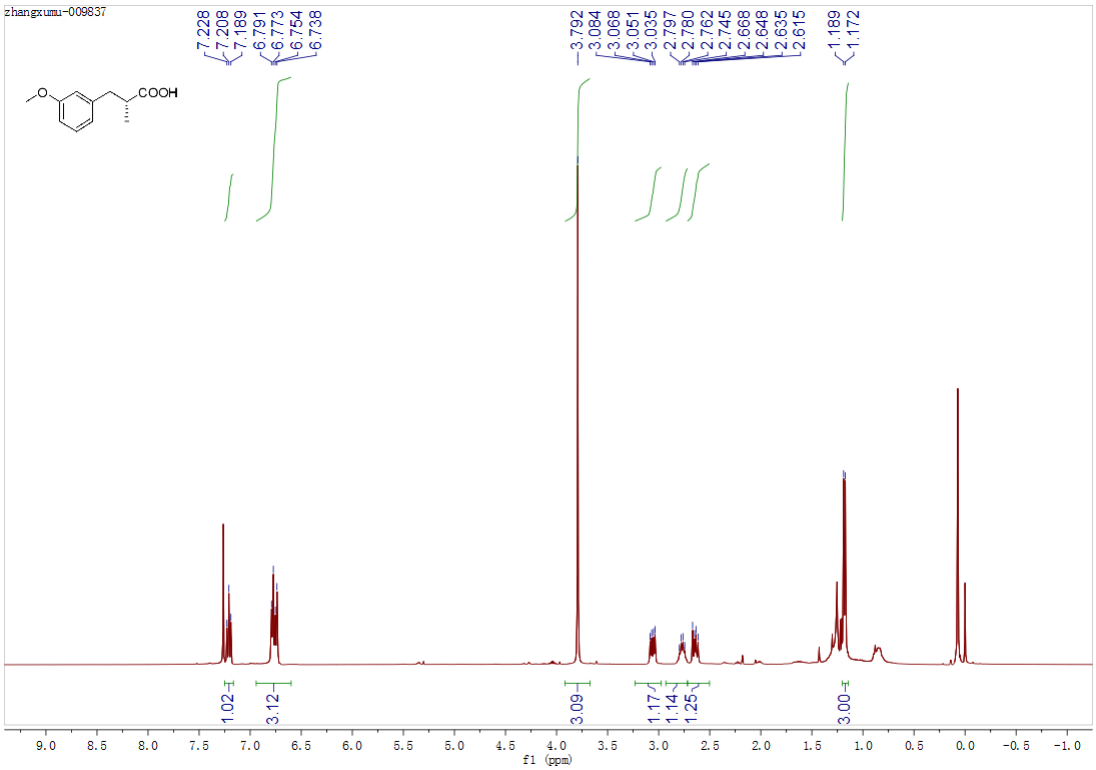


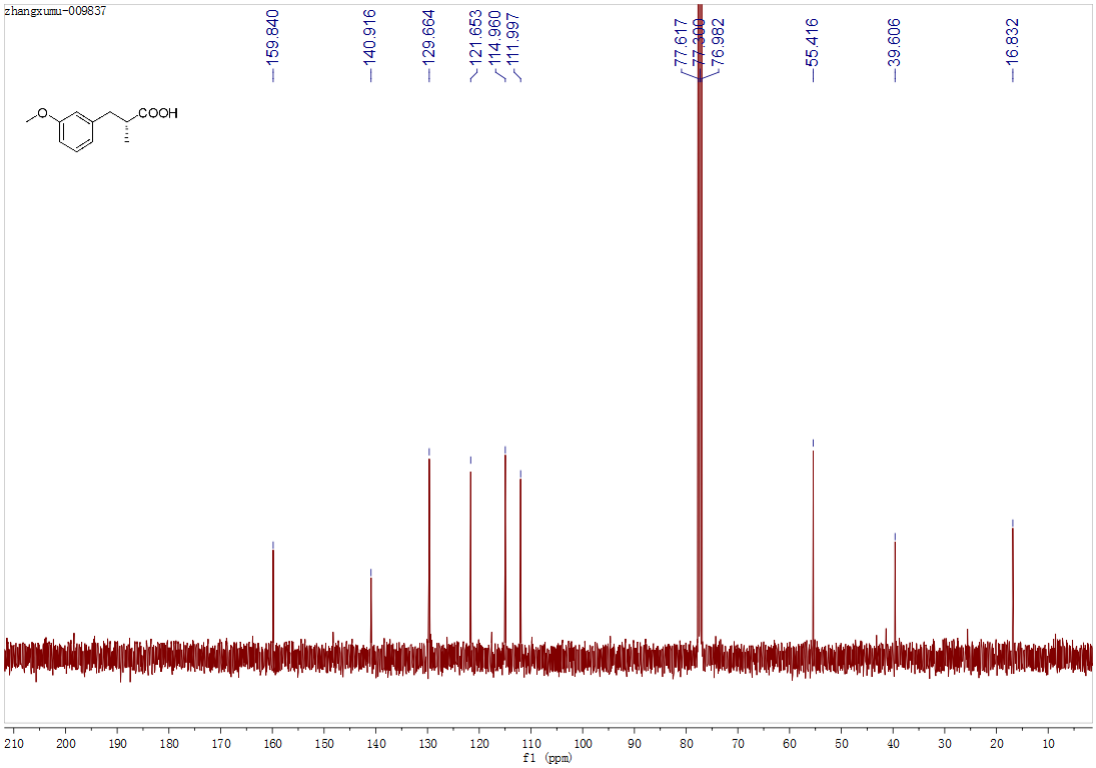
(*R*)-3-(2-methoxyphenyl)-2-methylpropanoic acid **8e**



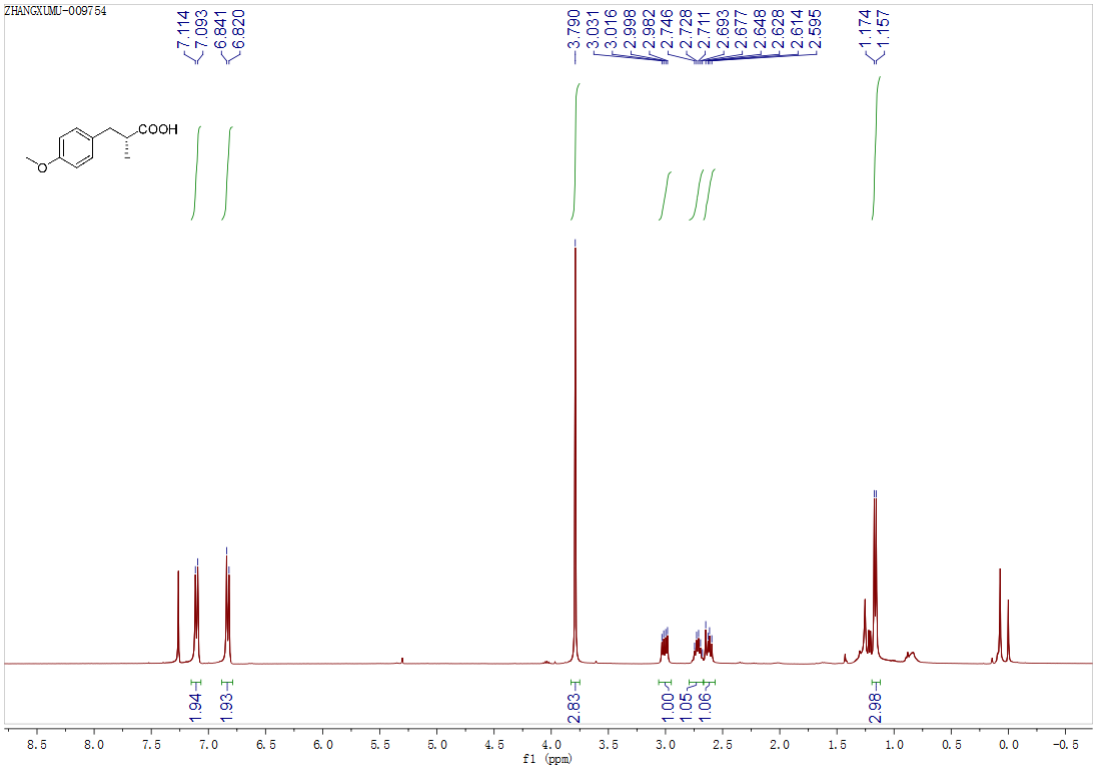


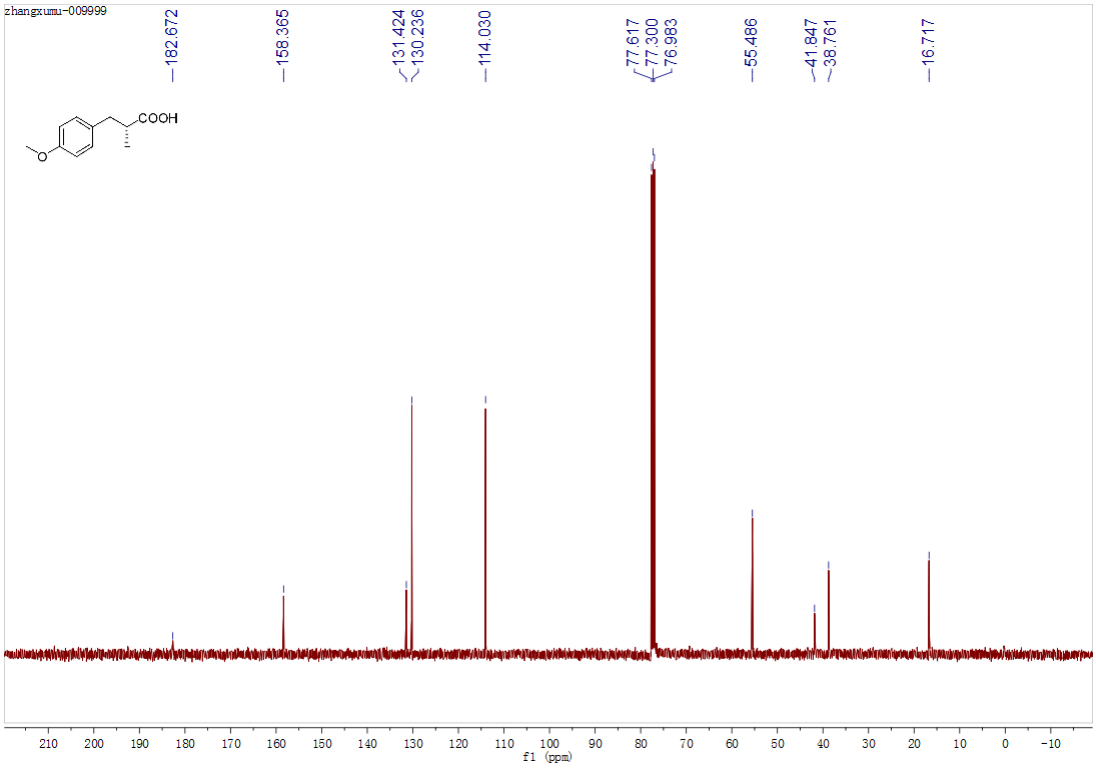
(*R*)-3-(3-methoxyphenyl)-2-methylpropanoic acid **8f**



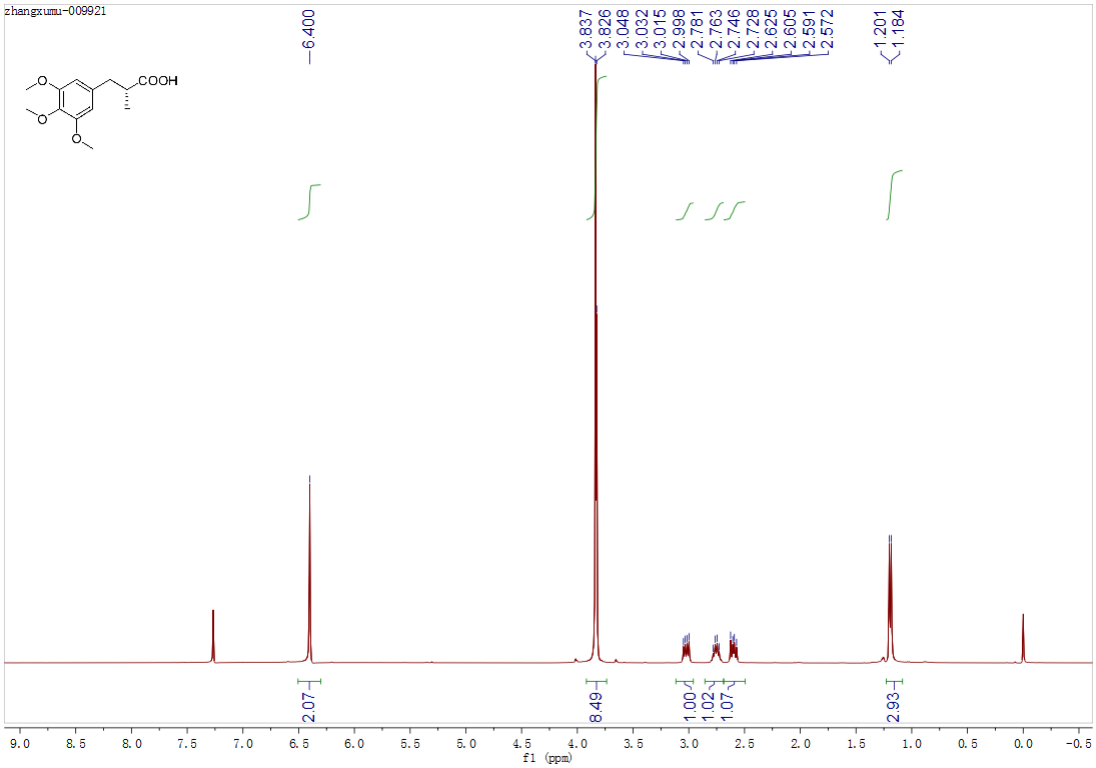


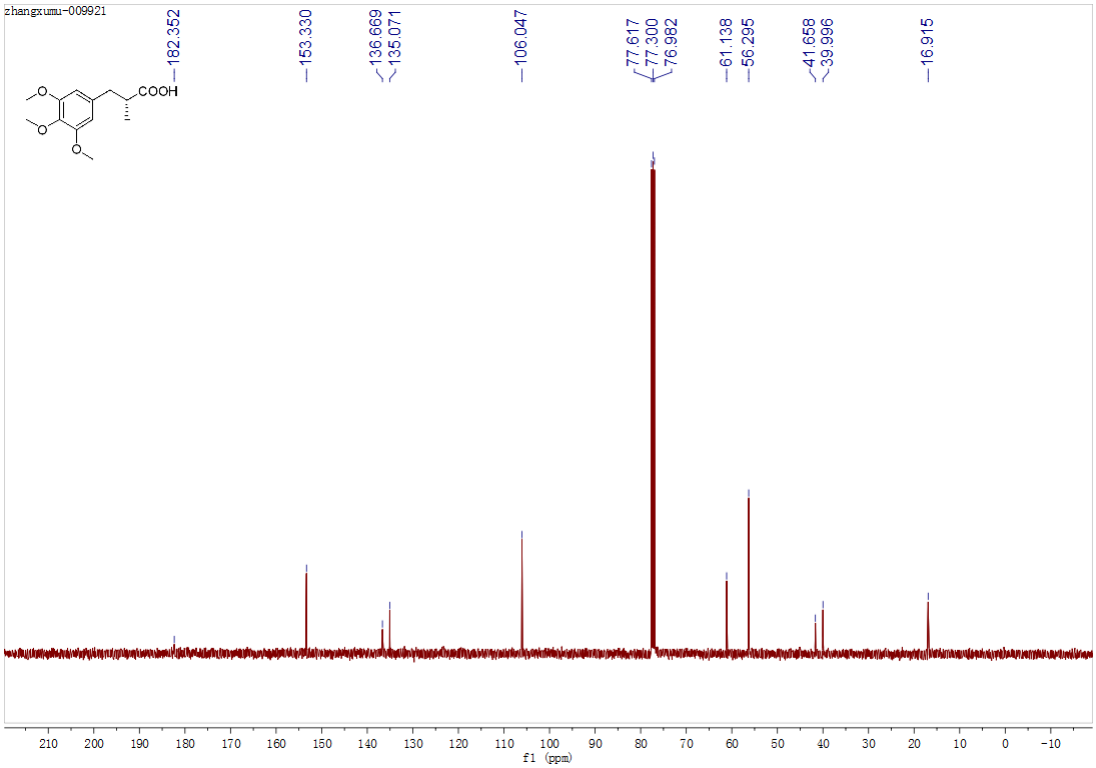
(*R*)-3-(4-methoxyphenyl)-2-methylpropanoic acid **8g**



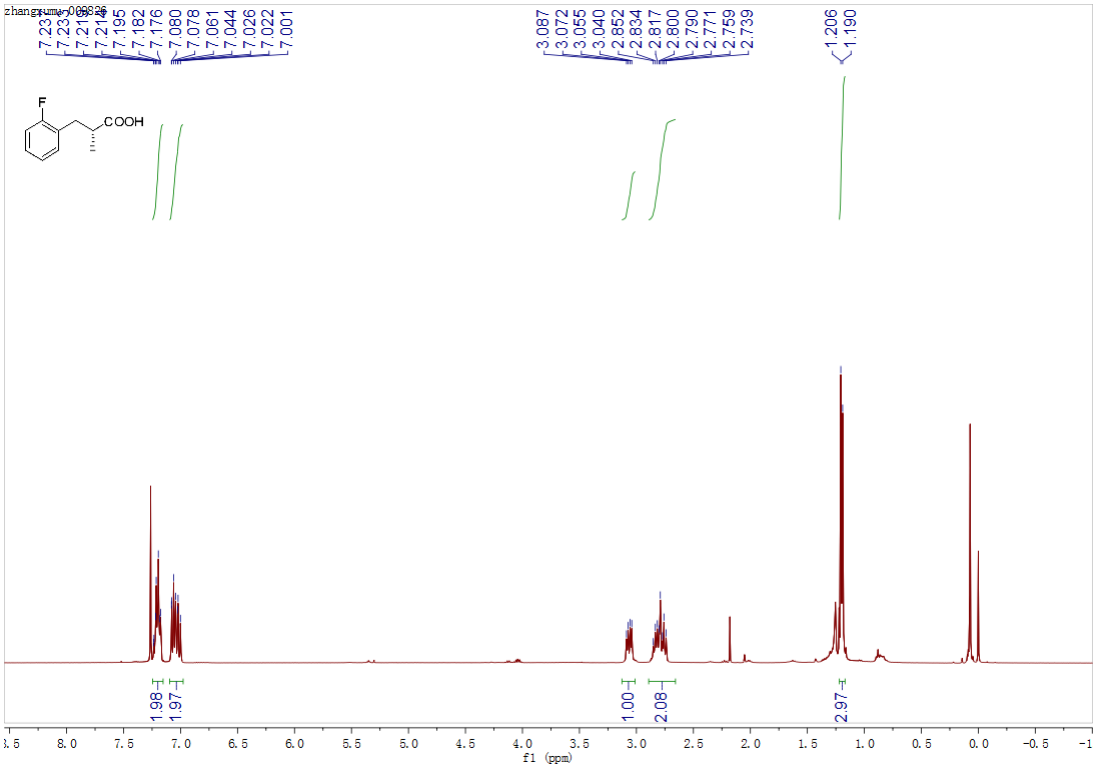


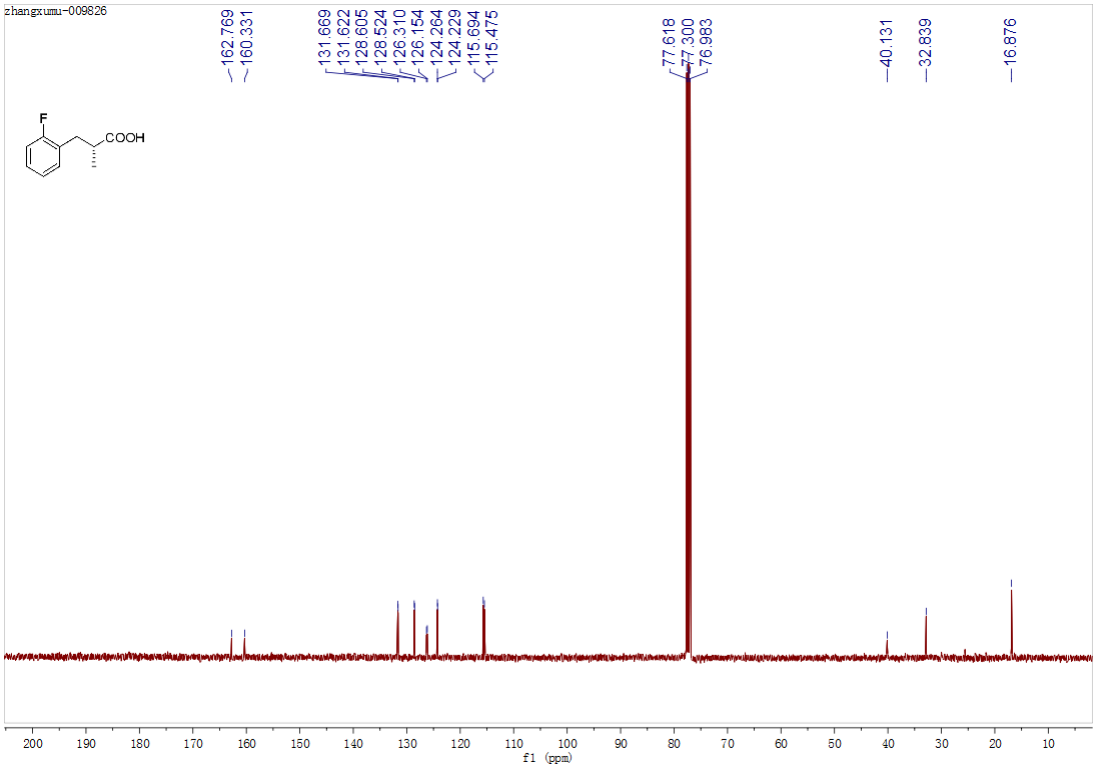
(*R*)-2-methyl-3-(3,4,5-trimethoxyphenyl)propanoic acid **8h**



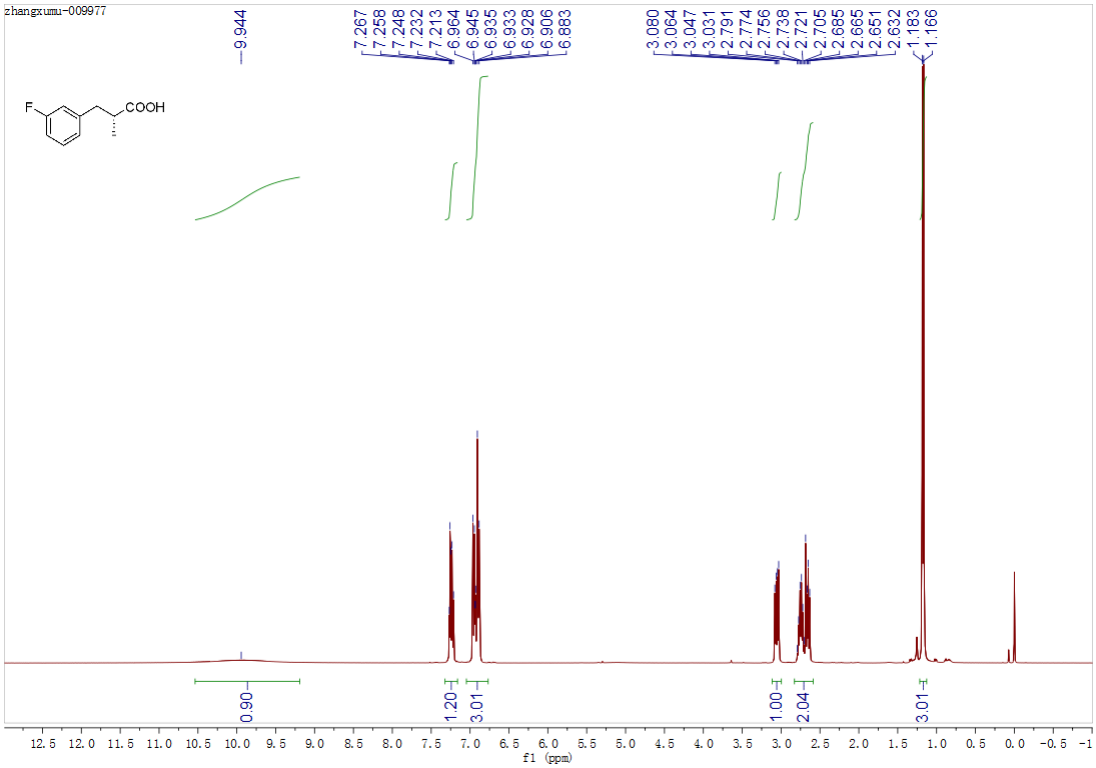


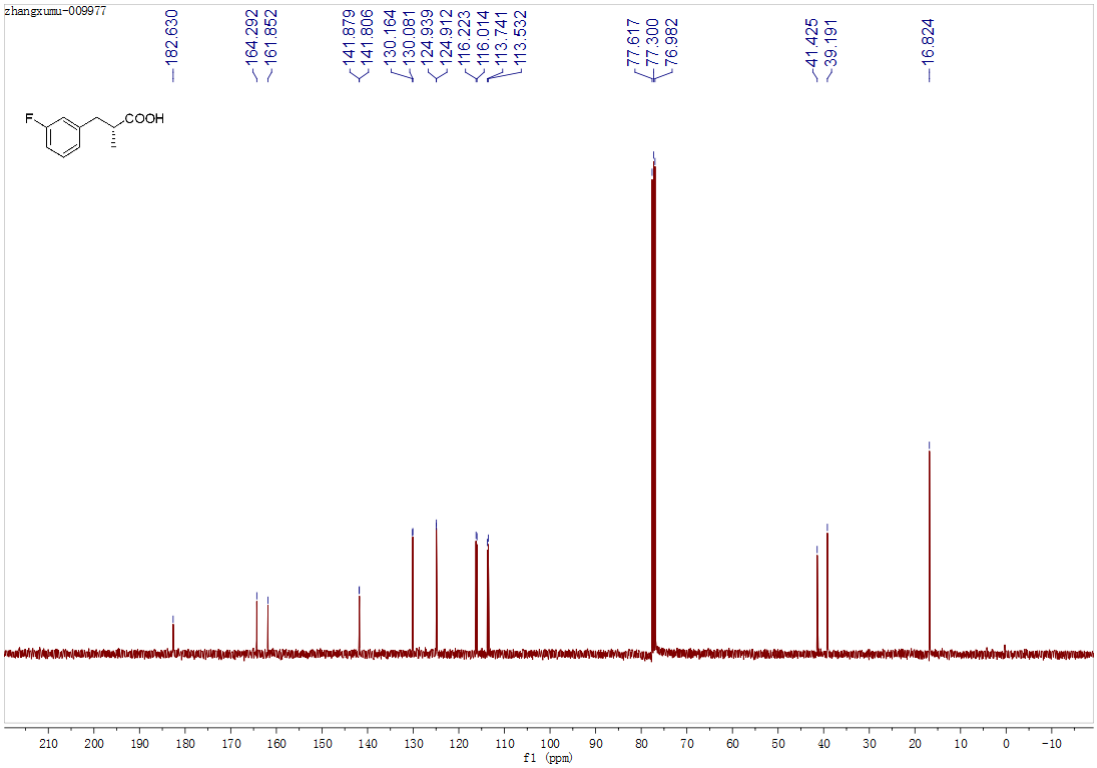
(*R*)-3-(2-fluorophenyl)-2-methylpropanoic acid **8i**



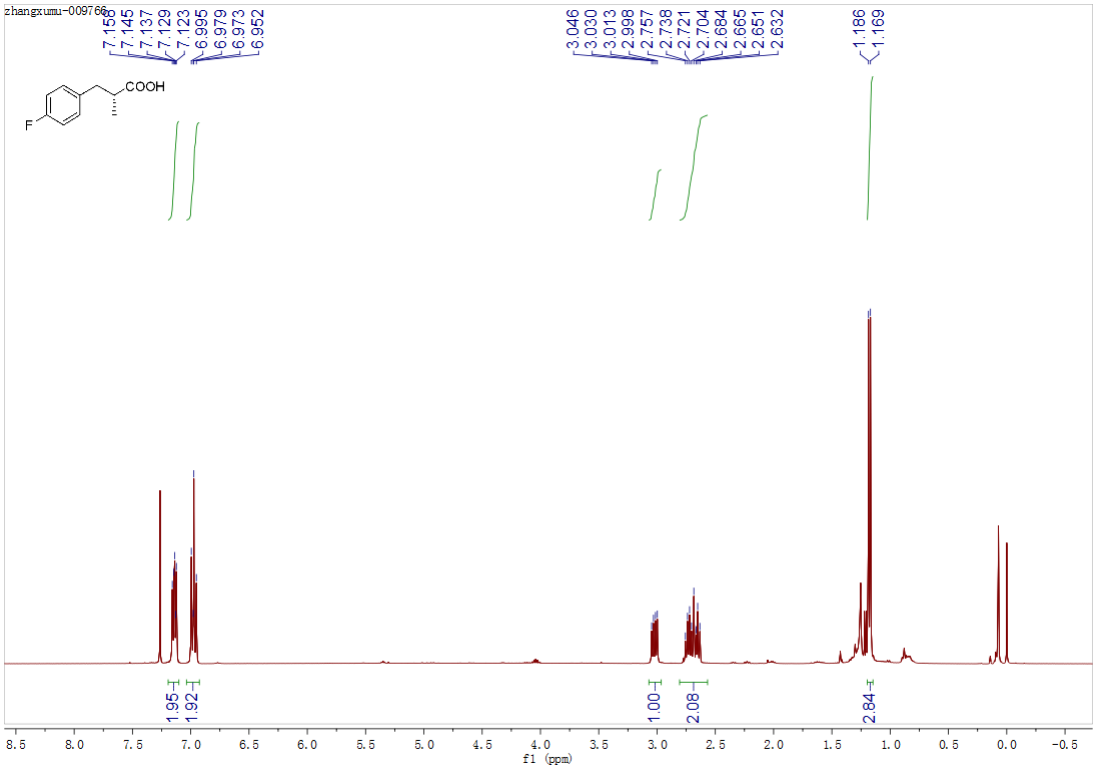


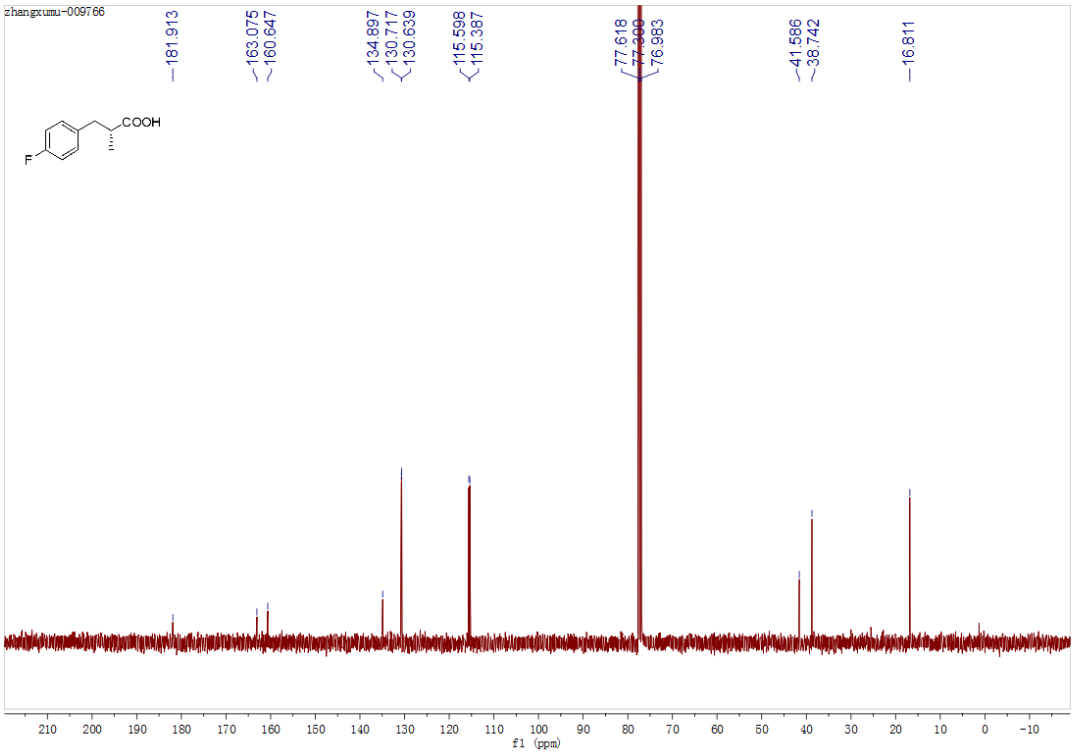
(*R*)-3-(3-fluorophenyl)-2-methylpropanoic acid **8j**



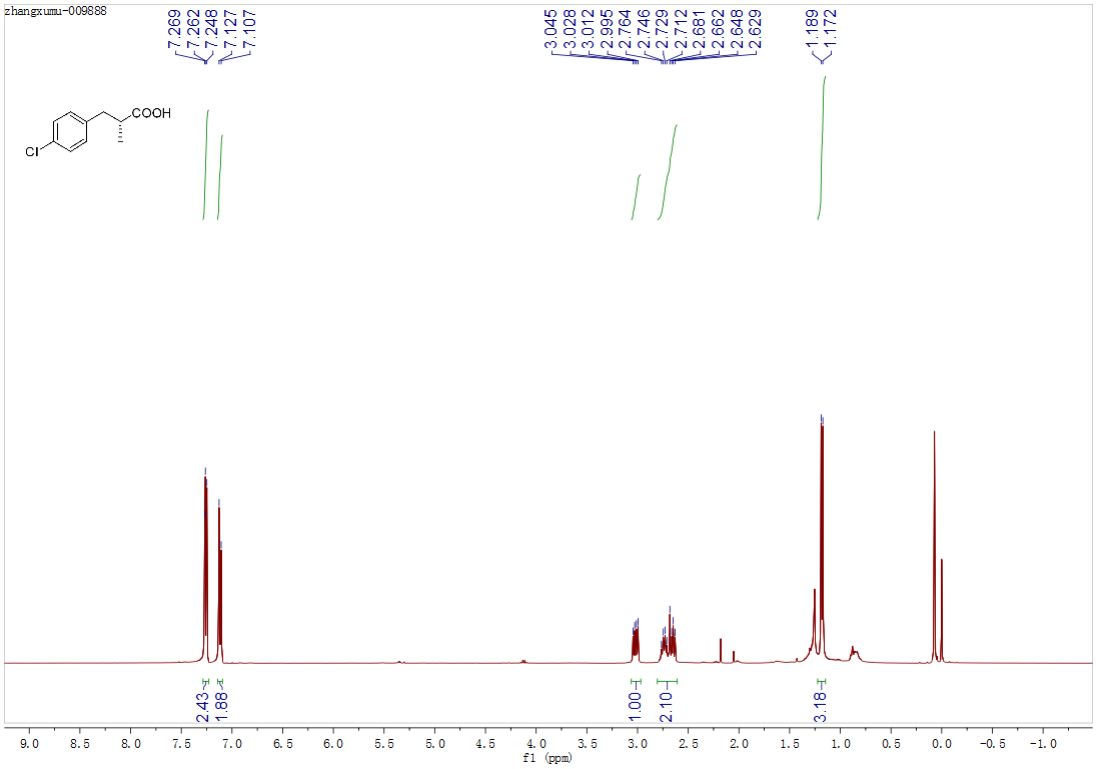


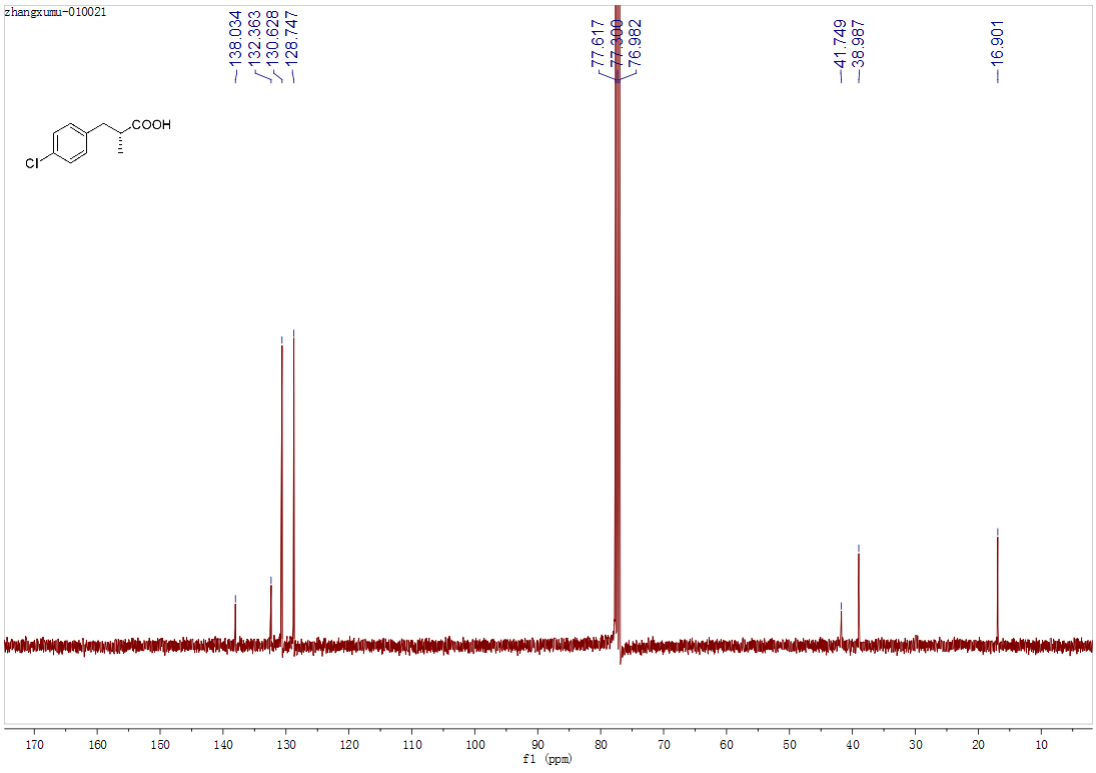
(*R*)-3-(4-fluorophenyl)-2-methylpropanoic acid **8k**



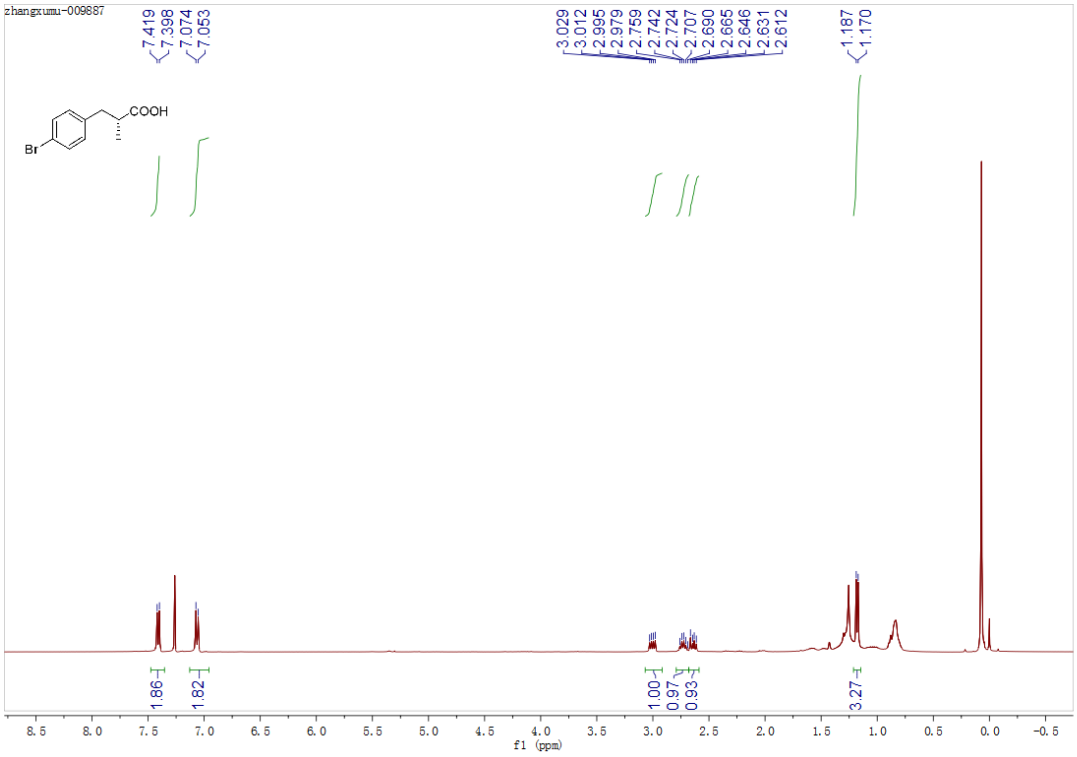


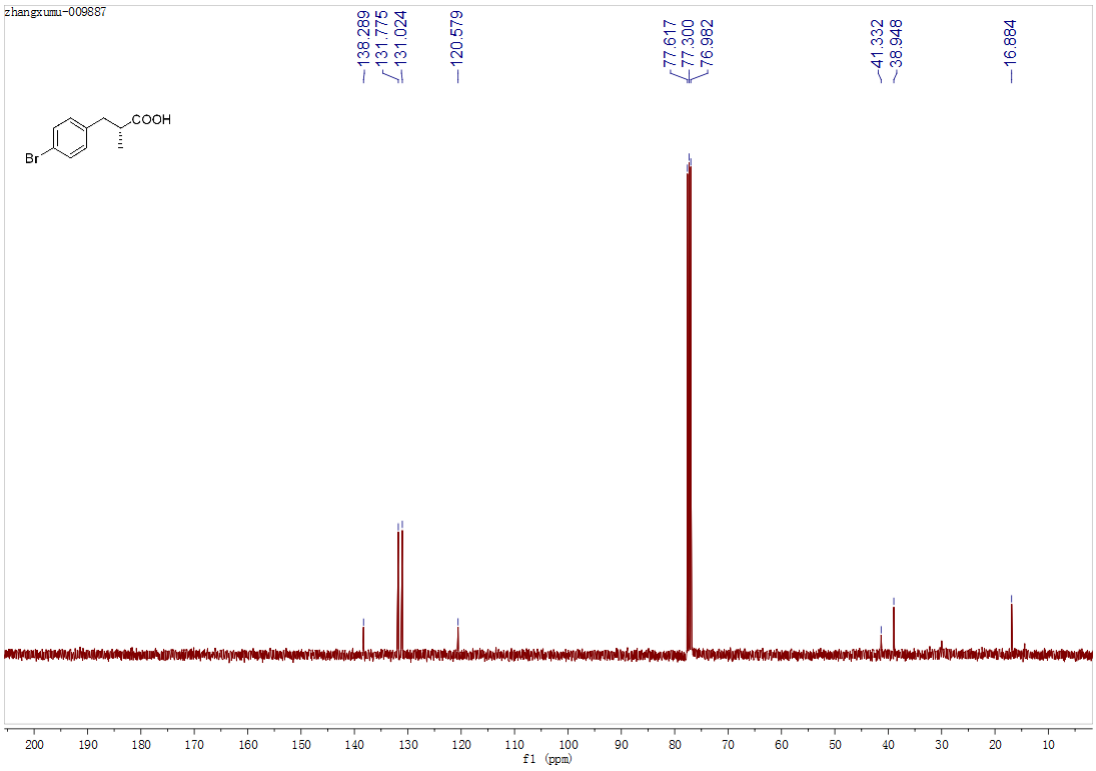
(*R*)-3-(4-chlorophenyl)-2-methylpropanoic acid **8l**



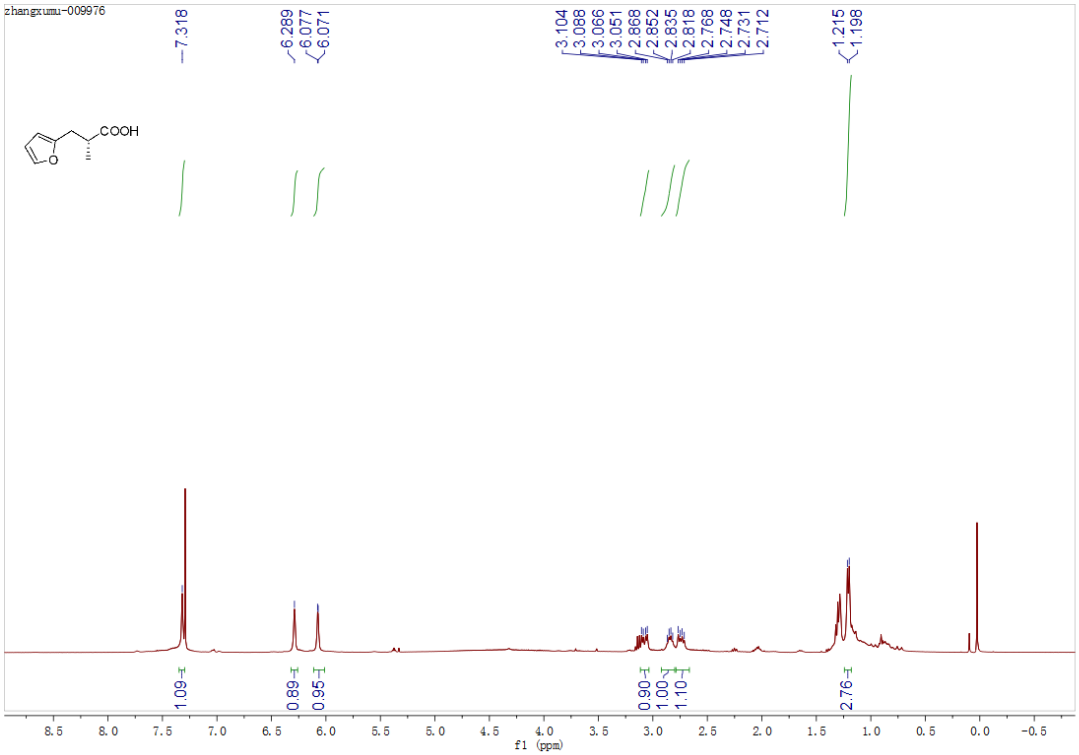


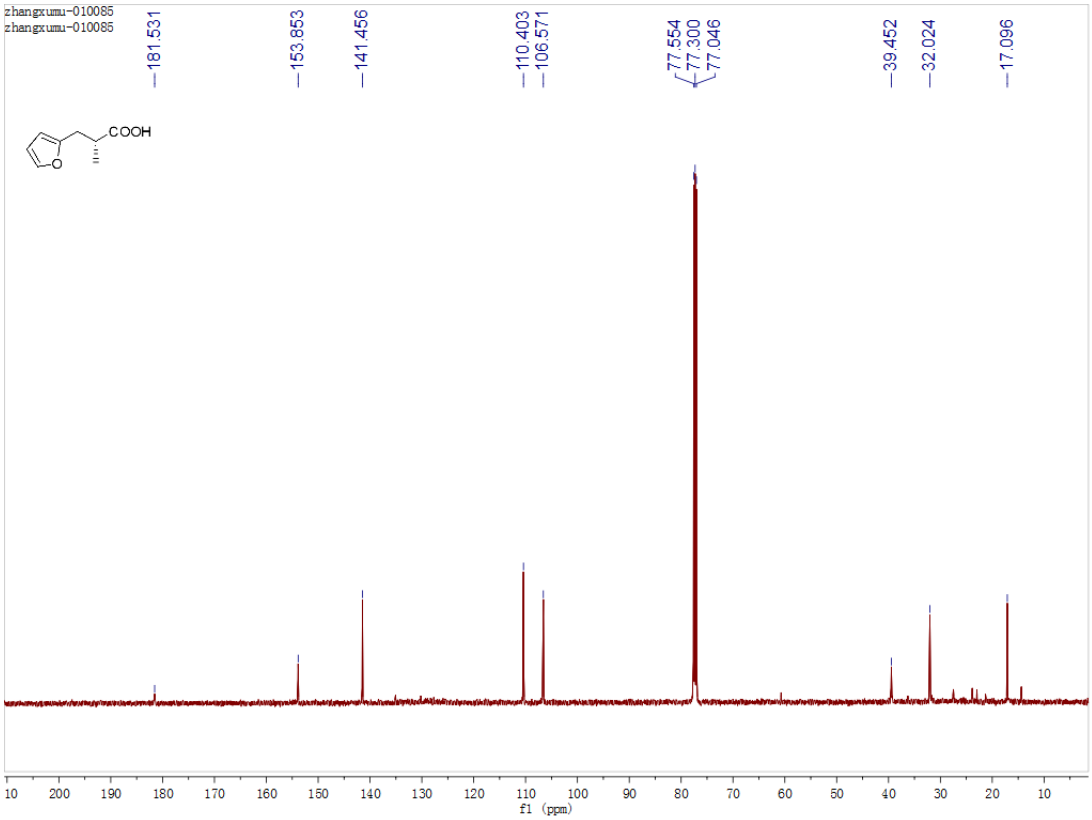
(*R*)-3-(4-bromophenyl)-2-methylpropanoic acid **8m**



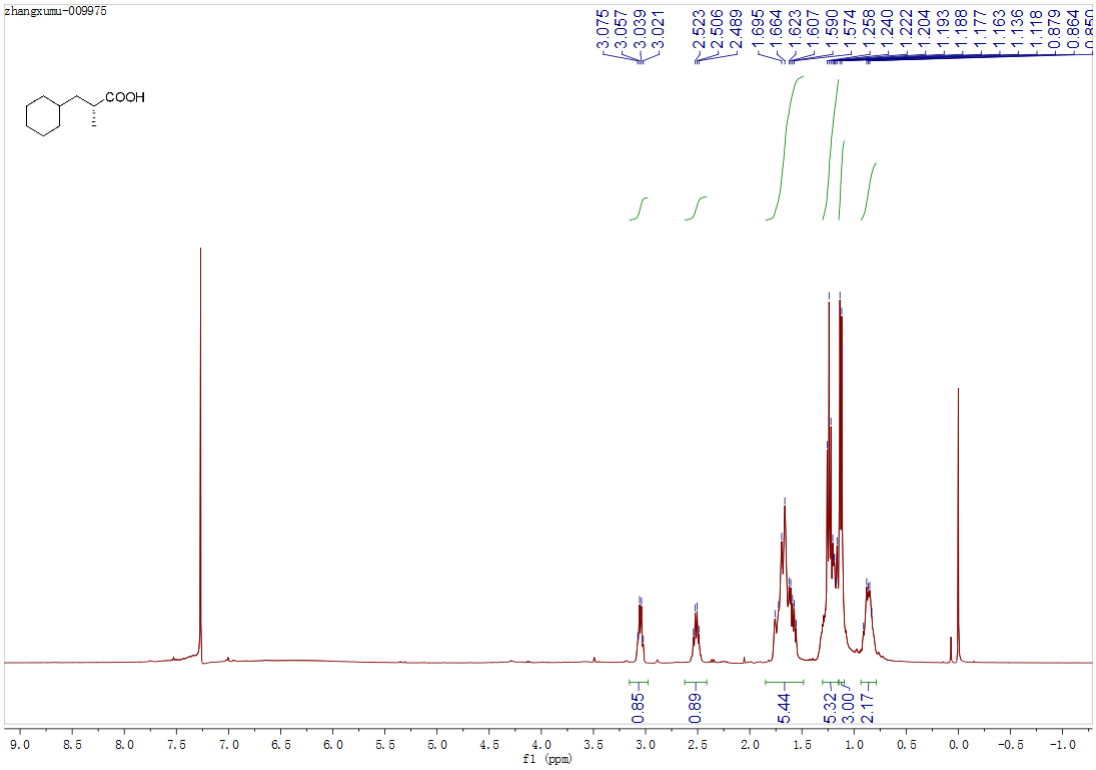


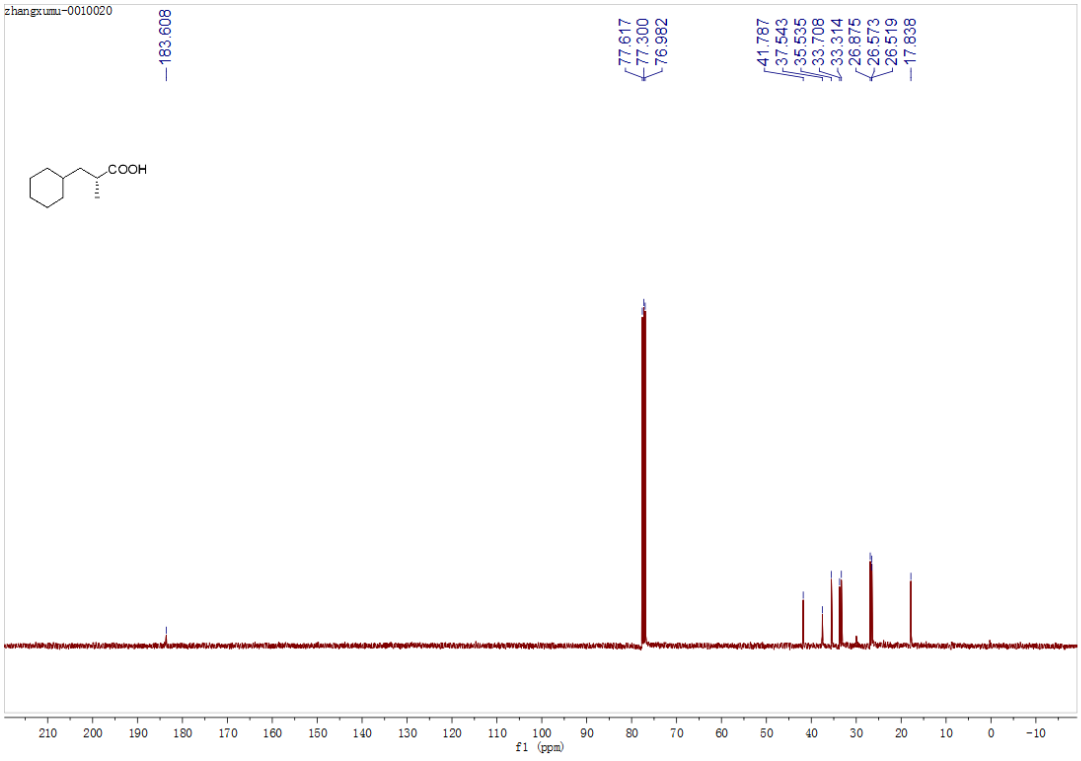
(*R*)-3-(furan-2-yl)-2-methylpropanoic acid **8n**



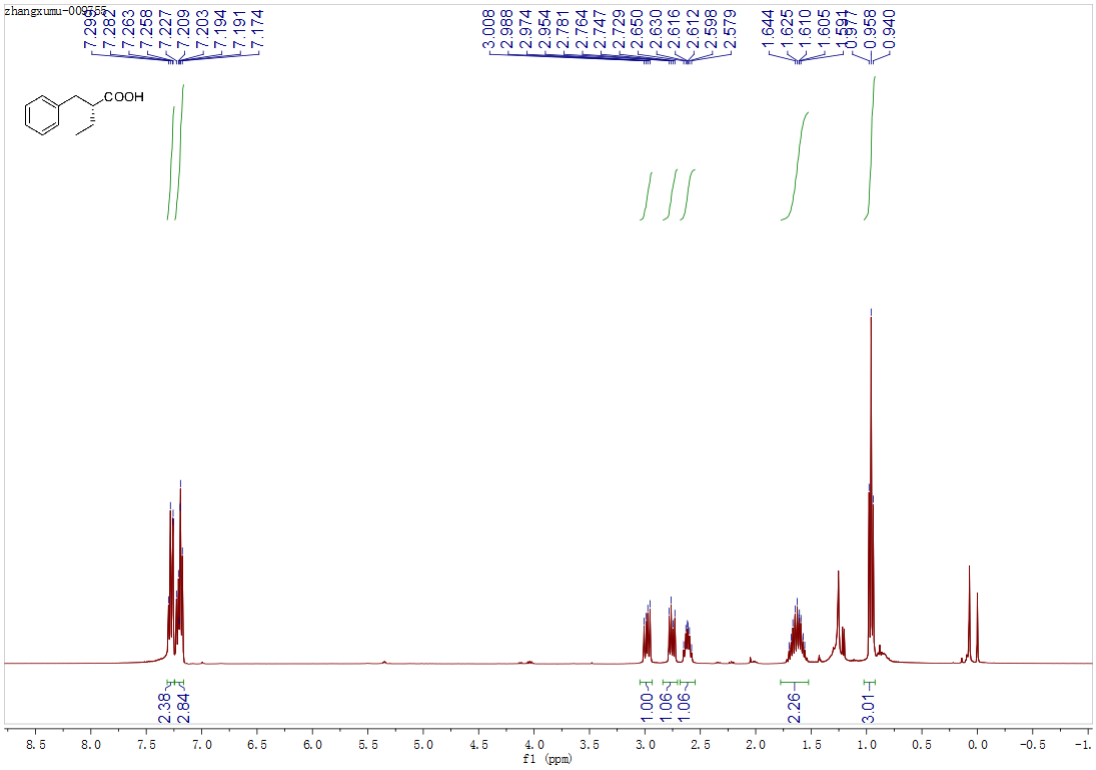


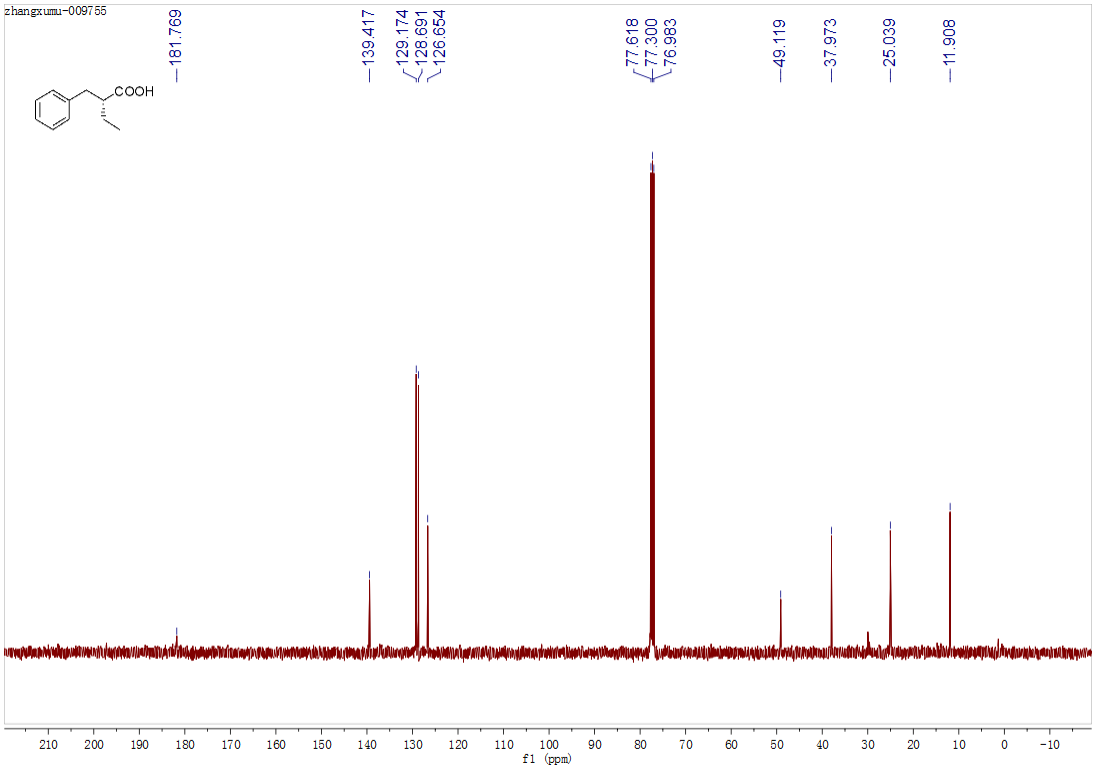
(*R*)-3-cyclohexyl-2-methylpropanoic acid **8o**



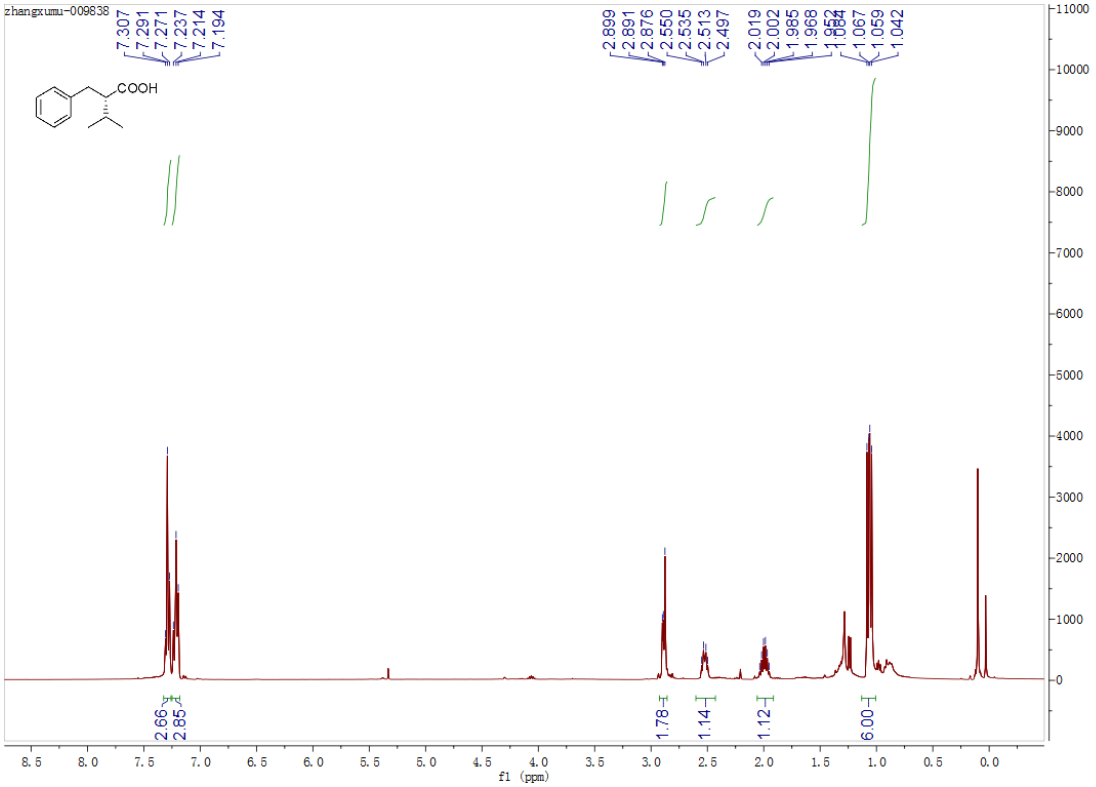


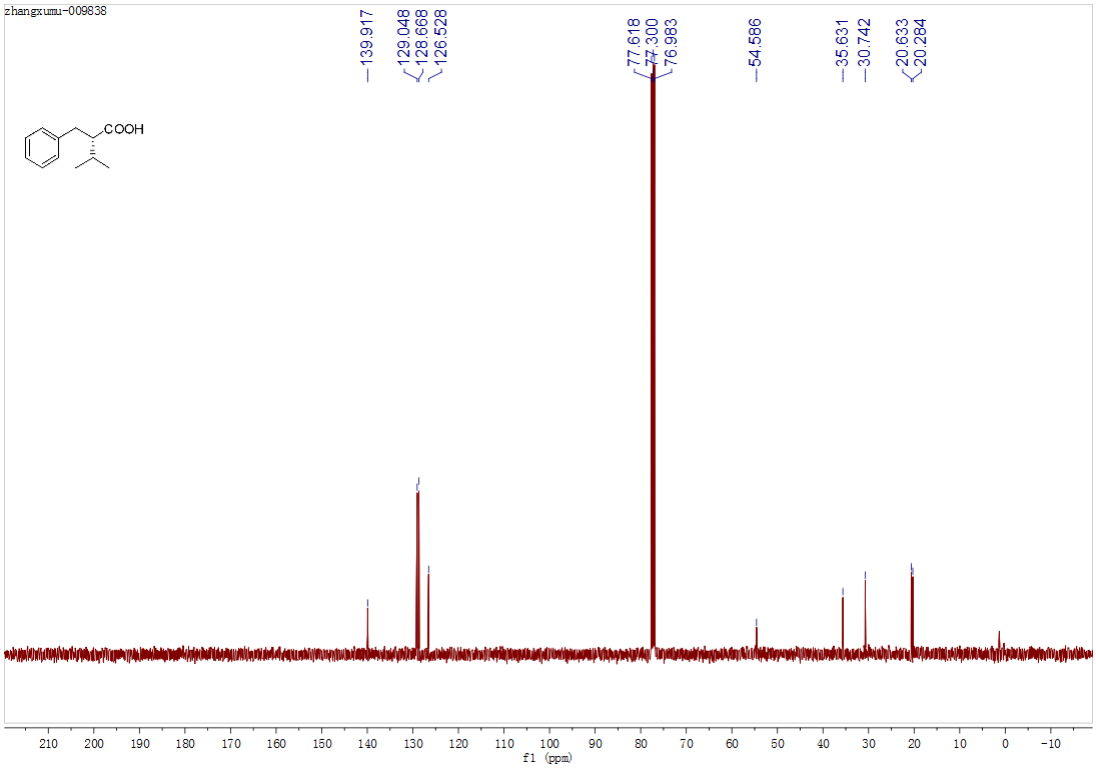
(*R*)-2-benzylbutanoic acid **8p**



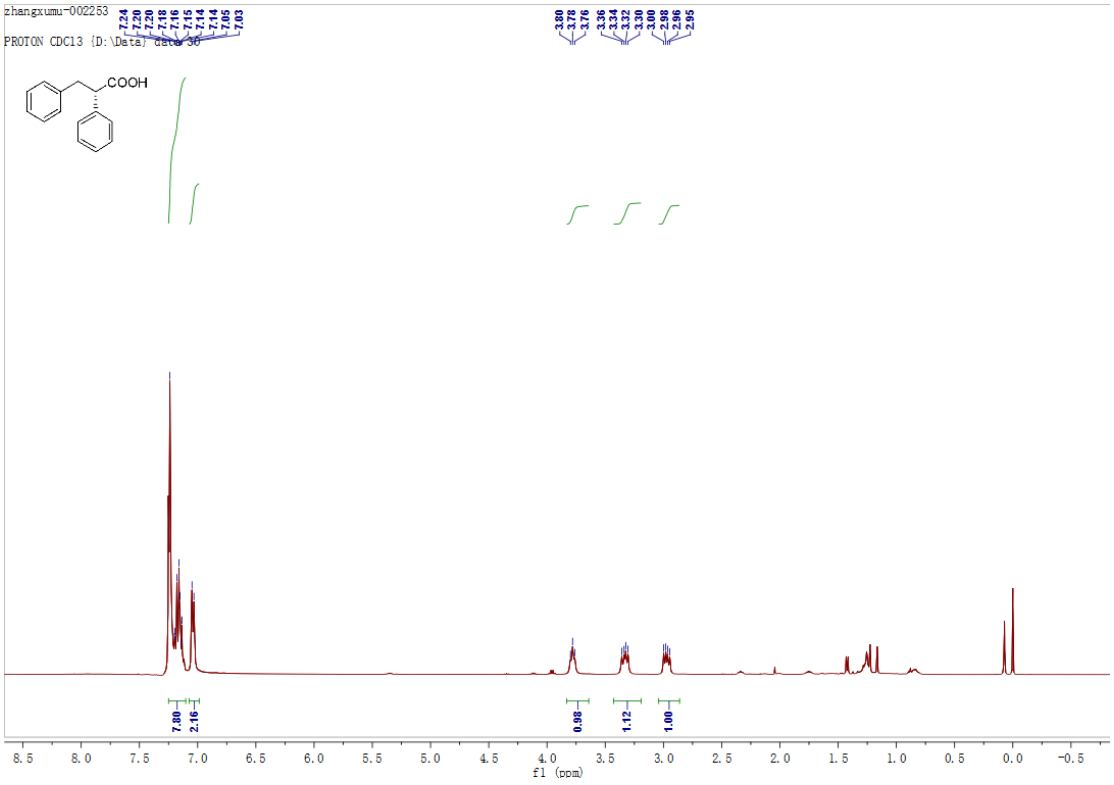


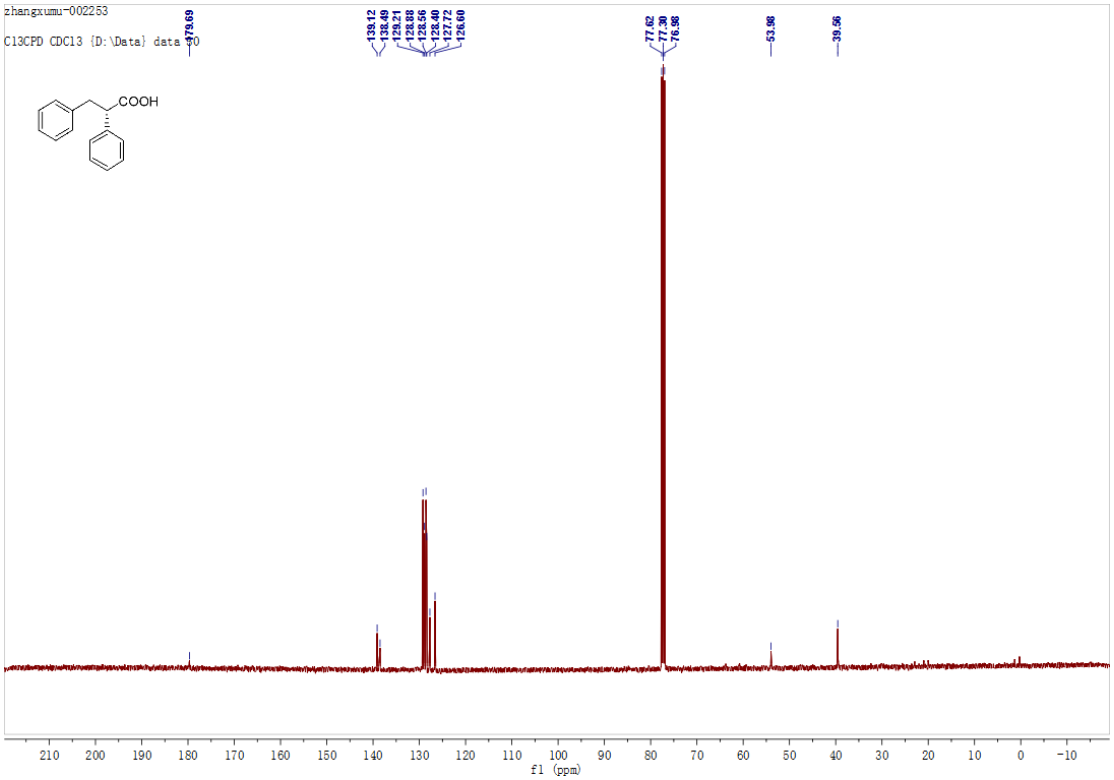
(*S*)-2-benzyl-3-methylbutanoic acid **8q**





(*S*)-2,3-diphenylpropanoic acid **8r**

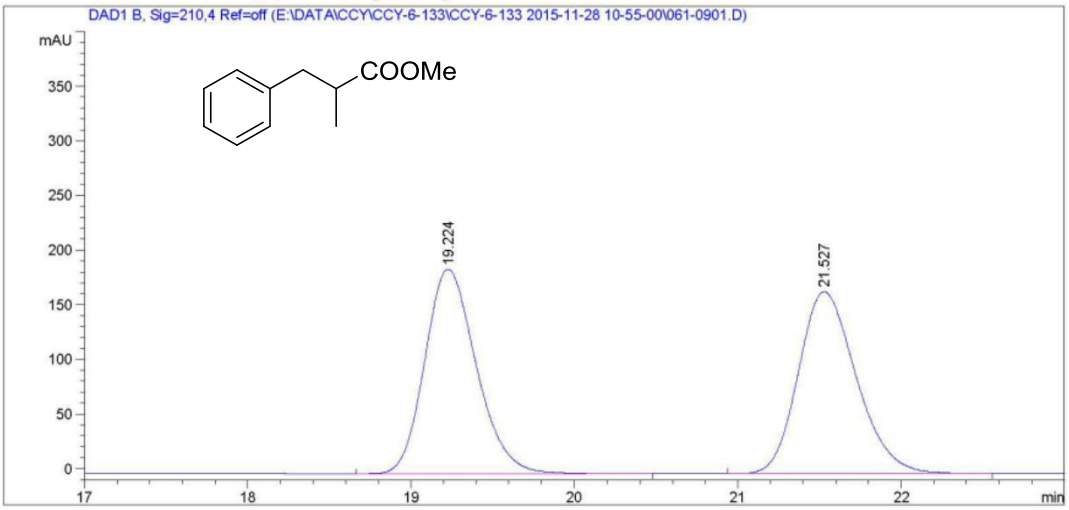




Ⅴ. HPLC and GC of hydrogenation product ester derivatives.

(*R*)-2-methyl-3-phenylpropanoic acid **8a**

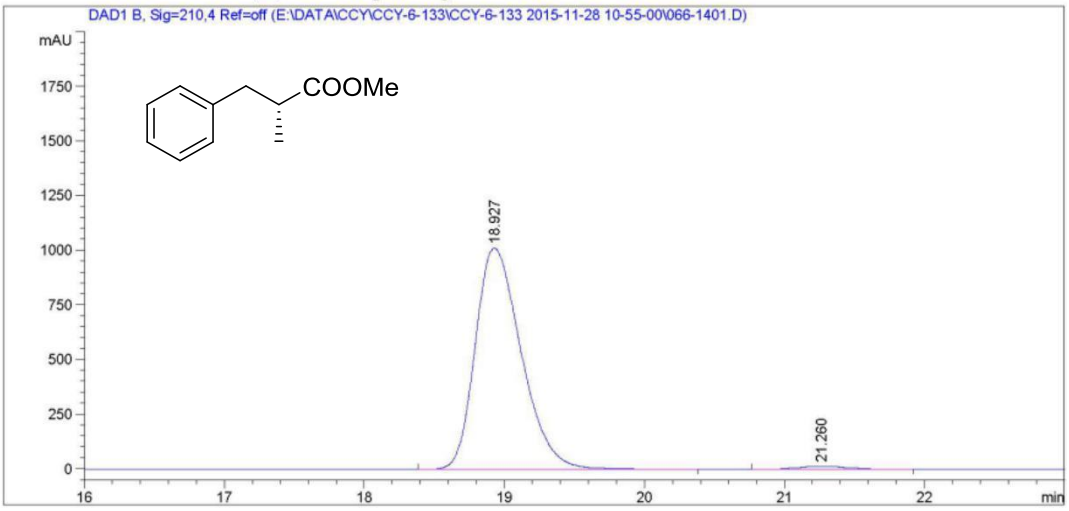
```
Data File E:\DATA\CCY\CCY-6-133\CCY-6-133 2015-11-28 10-55-00\061-0901.D
Sample Name: wq-s7-rac

    ==================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   9
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 61
    Injection Date  : 11/28/2015 2:53:43 PM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\CCY\CCY-6-133\CCY-6-133 2015-11-28 10-55-00\DAD-OJ(1-6)-99-1-0.5ML-
                      ALL-40MIN.M
    Last changed    : 11/28/2015 11:26:43 AM by SYSTEM
    Analysis Method : E:\DATA\CCY\CCY-6-133\CCY-6-133 2015-11-28 10-55-00\DAD-OJ(1-6)-99-1-0.5ML-
                      ALL-40MIN.M (Sequence Method)
    Last changed    : 5/29/2016 8:03:52 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                            Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 B, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  19.224 BB    0.3374 4095.74658  187.09590  50.0797
       2  21.527 BB    0.3784 4082.70752  166.29533  49.9203

    Totals :                  8178.45410  353.39124


    ==================================================================
                            *** End of Report ***

1260HPLC-DAD 5/29/2016 8:03:58 PM SYSTEM                        Page   1 of 1
```

Data File E:\DATA\CCY\CCY-6-133\CCY-6-133 2015-11-28 10-55-00\066-1401.D
Sample Name: wq-2-42-2

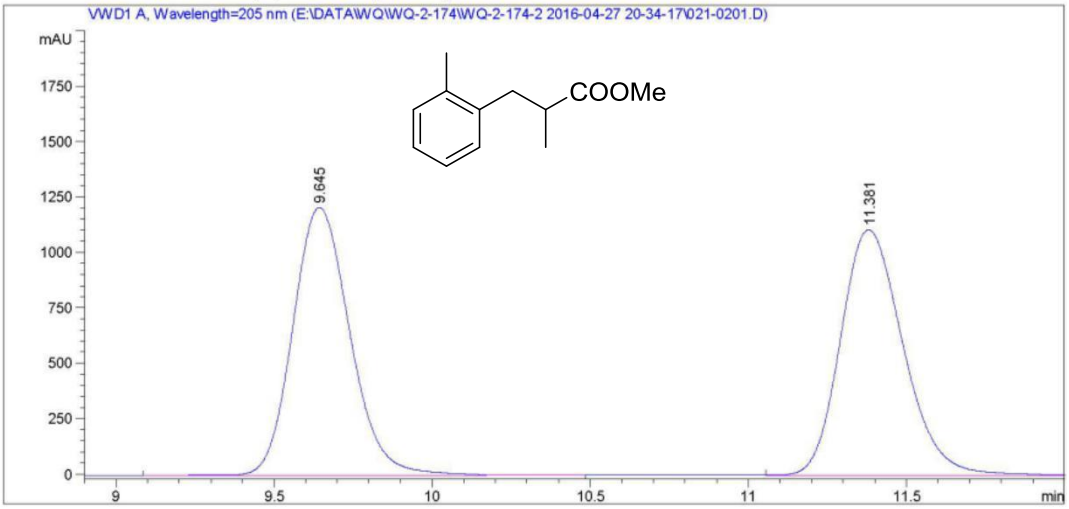
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  14
Acq. Instrument : 1260HPLC-DAD                    Location : Vial 66
Injection Date  : 11/28/2015 6:18:23 PM               Inj :   1
                                                  Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\CCY\CCY-6-133\CCY-6-133 2015-11-28 10-55-00\DAD-OJ(1-6)-99-1-0.5ML-
                  ALL-40MIN.M
Last changed    : 11/28/2015 11:26:43 AM by SYSTEM
Analysis Method : E:\DATA\CCY\CCY-6-133\CCY-6-133 2015-11-28 10-55-00\DAD-OJ(1-6)-99-1-0.5ML-
                  ALL-40MIN.M (Sequence Method)
Last changed    : 5/29/2016 7:59:34 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.927 BB    0.3525 2.29393e4  1011.94232  98.6494
   2  21.260 BB    0.3627  314.04916   13.14562   1.3506

Totals :                  2.32533e4  1025.08794


==========================================================================
                        *** End of Report ***
```

(*R*)-2-methyl-3-(o-tolyl)propanoic acid **8b**

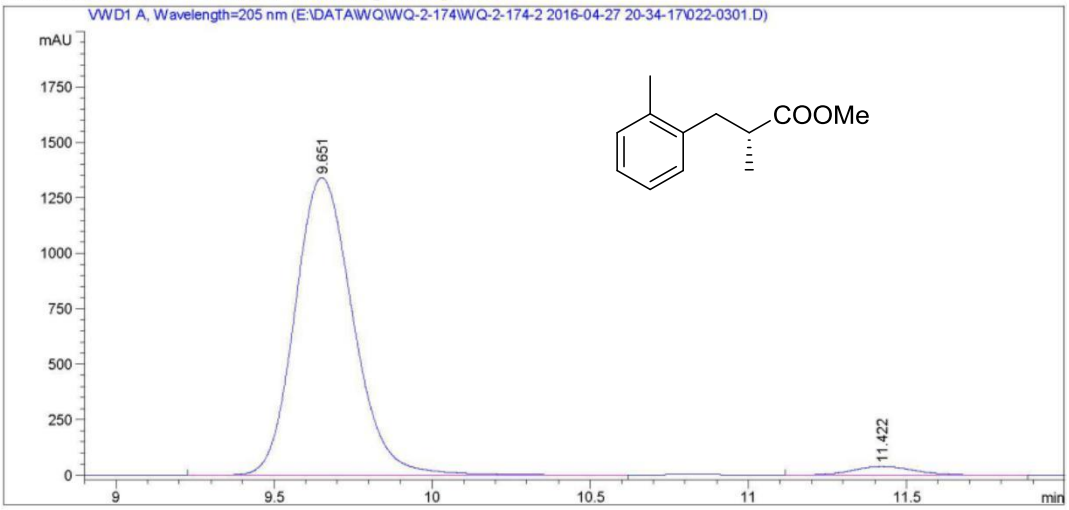
```
Data File E:\DATA\WQ\WQ-2-174\WQ-2-174-2 2016-04-27 20-34-17\021-0201.D
Sample Name: WQ-2-174-1-RAC

=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   2
Acq. Instrument : 1260HPLC-VWD                  Location : Vial 21
Injection Date  : 4/27/2016 8:45:53 PM             Inj :   1
                                               Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-174\WQ-2-174-2 2016-04-27 20-34-17\VWD-IB(1-6)-99-1-0.5ML-
                  205NM-25MIN.M
Last changed    : 4/27/2016 8:34:17 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-174\WQ-2-174-2 2016-04-27 20-34-17\VWD-IB(1-6)-99-1-0.5ML-
                  205NM-25MIN.M (Sequence Method)
Last changed    : 5/29/2016 8:38:19 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=205 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.645 BB    0.1953 1.51485e4  1207.81519  49.8559
   2  11.381 VB    0.2134 1.52361e4  1108.50342  50.1441

Totals :                  3.03845e4  2316.31860

=====================================================================
                        *** End of Report ***

1260HPLC-DAD 5/29/2016 8:38:39 PM SYSTEM                    Page   1 of 1
```

Data File E:\DATA\WQ\WQ-2-174\WQ-2-174-2 2016-04-27 20-34-17\022-0301.D
Sample Name: WQ-2-174-1

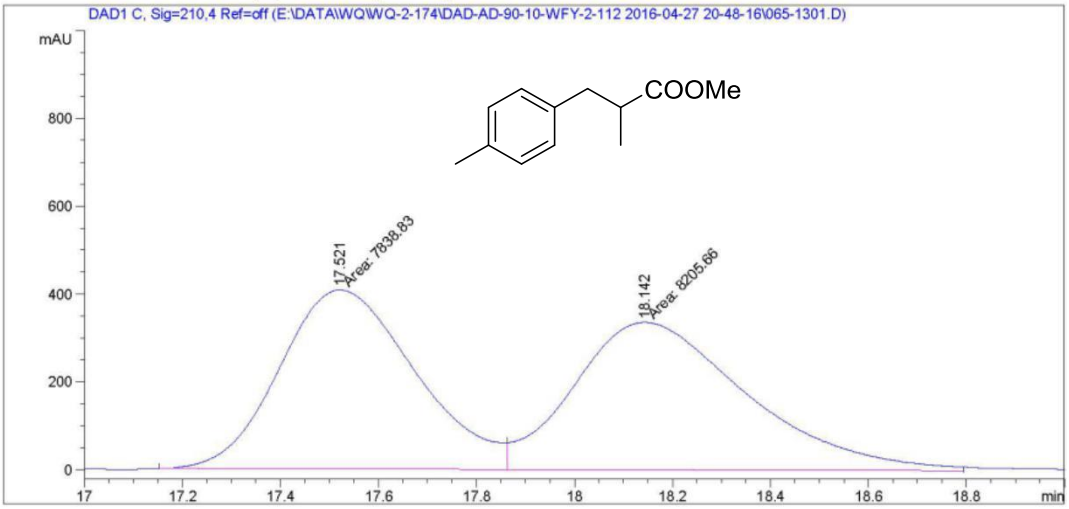
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   3
Acq. Instrument : 1260HPLC-VWD                    Location : Vial 22
Injection Date  : 4/27/2016 9:11:38 PM                 Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-174\WQ-2-174-2 2016-04-27 20-34-17\VWD-IB(1-6)-99-1-0.5ML-
                  205NM-25MIN.M
Last changed    : 4/27/2016 9:27:51 PM by SYSTEM
                  (modified after loading)
Analysis Method : E:\DATA\WQ\WQ-2-174\WQ-2-174-2 2016-04-27 20-34-17\VWD-IB(1-6)-99-1-0.5ML-
                  205NM-25MIN.M (Sequence Method)
Last changed    : 5/29/2016 8:40:05 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=205 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.651 BV    0.1982 1.70221e4  1339.85925  97.1191
   2  11.422 VB    0.2067  504.94086   37.83417   2.8809

Totals :                  1.75270e4  1377.69342

==========================================================================
```

(*R*)-2-methyl-3-(p-tolyl)propanoic acid **8c**

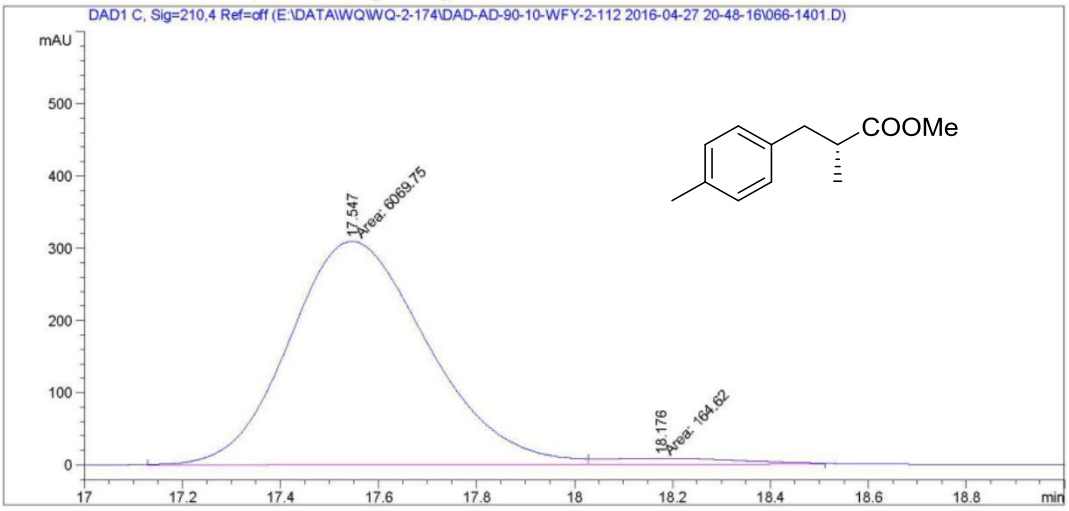
```
Data File E:\DATA\WQ\WQ-2-174\DAD-AD-90-10-WFY-2-112 2016-04-27 20-48-16\065-1301.D
Sample Name: WQ-2-174-9-RAC

=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  13
Acq. Instrument : 1260HPLC-DAD                  Location : Vial 65
Injection Date  : 4/28/2016 3:21:41 AM               Inj :  1
                                               Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-174\DAD-AD-90-10-WFY-2-112 2016-04-27 20-48-16\DAD-OJ(1-6)-
                  99-1-0.5ML-40MIN.M
Last changed    : 4/27/2016 8:49:49 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-174\DAD-AD-90-10-WFY-2-112 2016-04-27 20-48-16\DAD-OJ(1-6)-
                  99-1-0.5ML-40MIN.M (Sequence Method)
Last changed    : 5/29/2016 8:57:54 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.521 MF    0.3205 7838.83350  407.65817  48.8569
   2  18.142 FM    0.4079 8205.65820  335.30875  51.1431

Totals :                 1.60445e4   742.96692


=====================================================================
                        *** End of Report ***

1260HPLC-DAD 5/29/2016 9:00:21 PM SYSTEM                    Page   1 of 1
```

Data File E:\DATA\WQ\WQ-2-174\DAD-AD-90-10-WFY-2-112 2016-04-27 20-48-16\066-1401.D
Sample Name: WQ-2-174-9

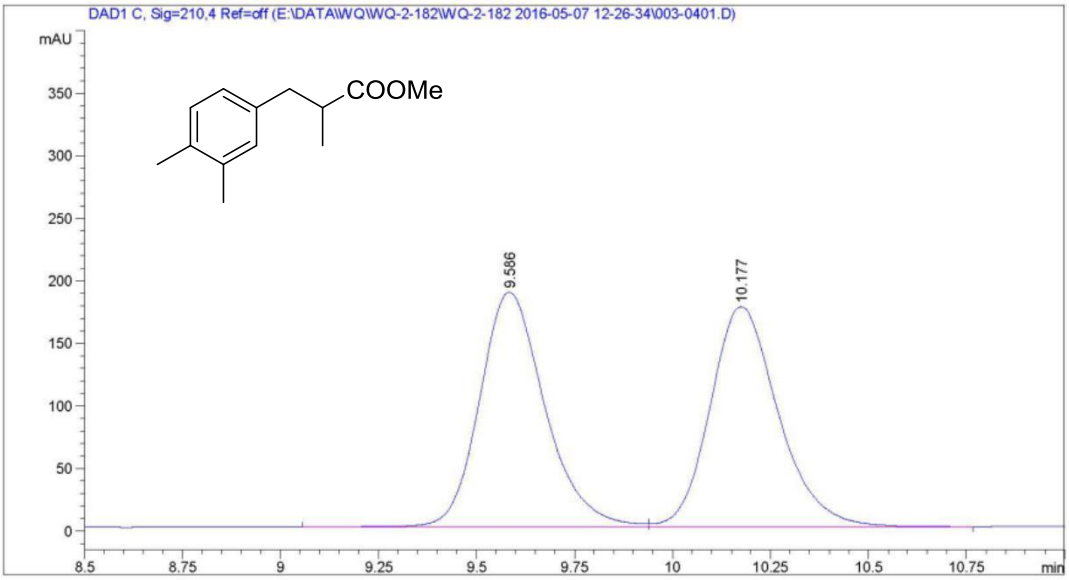
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  14
Acq. Instrument : 1260HPLC-DAD                    Location : Vial 66
Injection Date  : 4/28/2016 4:02:39 AM                 Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-174\DAD-AD-90-10-WFY-2-112 2016-04-27 20-48-16\DAD-OJ(1-6)-
                  99-1-0.5ML-40MIN.M
Last changed    : 4/27/2016 8:49:49 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-174\DAD-AD-90-10-WFY-2-112 2016-04-27 20-48-16\DAD-OJ(1-6)-
                  99-1-0.5ML-40MIN.M (Sequence Method)
Last changed    : 5/29/2016 9:03:22 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.547 MF    0.3273 6069.75488  309.09094  97.3595
   2  18.176 FM    0.3345  164.61998    8.20196   2.6405

Totals :                  6234.37486  317.29291


==========================================================================
                        *** End of Report ***
```

(*R*)-3-(3,4-dimethylphenyl)-2-methylpropanoic acid **8d**

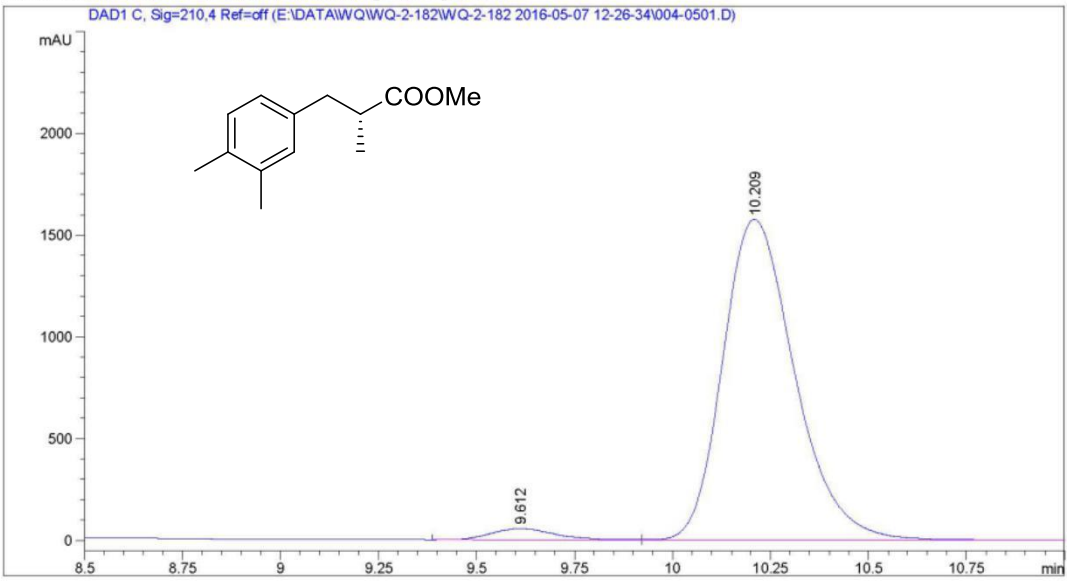
```
Data File E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\003-0401.D
Sample Name: WQ-2-182-4-RAC

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   4
    Acq. Instrument : 1260HPLC-DAD                    Location : Vial 3
    Injection Date  : 5/7/2016 2:22:15 PM                  Inj :   1
                                                    Inj Volume : 3.000 µl
    Acq. Method     : E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\DAD-OD(1-2)-99-1-0.5ML-3UL
                      -50MIN.M
    Last changed    : 5/7/2016 3:06:01 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\DAD-OD(1-2)-99-1-0.5ML-3UL
                      -50MIN.M (Sequence Method)
    Last changed    : 5/29/2016 9:11:23 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.586 BV    0.1750 2173.64331  187.85251  50.5599
       2  10.177 VB    0.1847 2125.50244  176.19662  49.4401

    Totals :                  4299.14575  364.04913

1260HPLC-DAD 5/29/2016 9:11:32 PM SYSTEM                          Page   1 of 2
```

Data File E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\004-0501.D
Sample Name: WQ-2-182-4

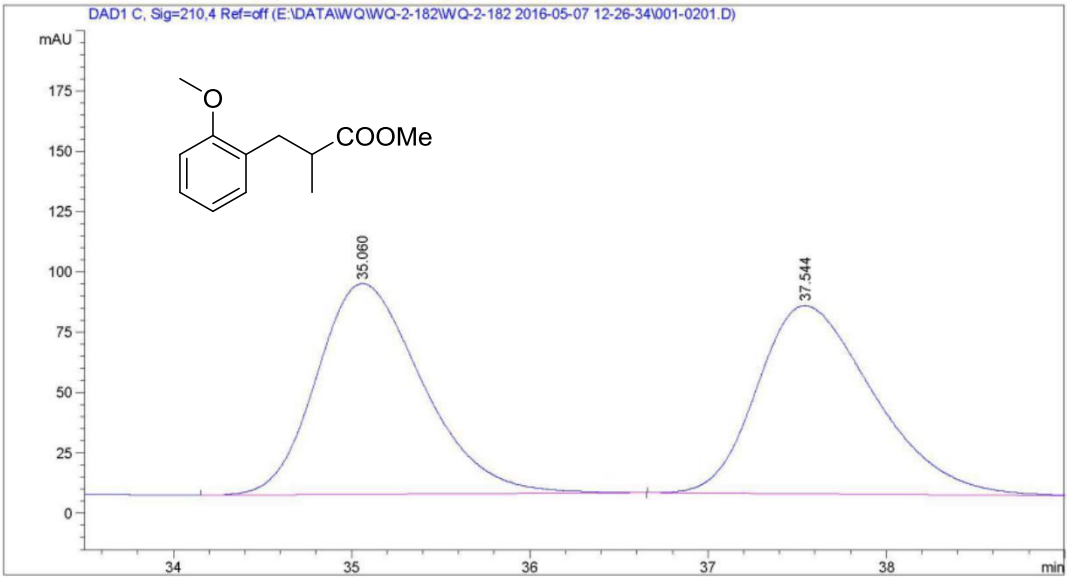
```
==================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   5
Acq. Instrument : 1260HPLC-DAD                   Location : Vial 4
Injection Date  : 5/7/2016 3:06:55 PM                 Inj :   1
                                                Inj Volume : 3.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\DAD-OD(1-2)-99-1-0.5ML-3UL
                  -50MIN.M
Last changed    : 5/7/2016 3:09:56 PM by SYSTEM
                  (modified after loading)
Analysis Method : E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\DAD-OD(1-2)-99-1-0.5ML-3UL
                  -50MIN.M (Sequence Method)
Last changed    : 5/29/2016 9:12:29 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.612 BV    0.1728  628.67419   55.23700   3.0329
   2  10.209 VB    0.1969 2.00997e4  1575.29175  96.9671

Totals :                  2.07284e4  1630.52874
```

(*R*)-3-(2-methoxyphenyl)-2-methylpropanoic acid **8e**

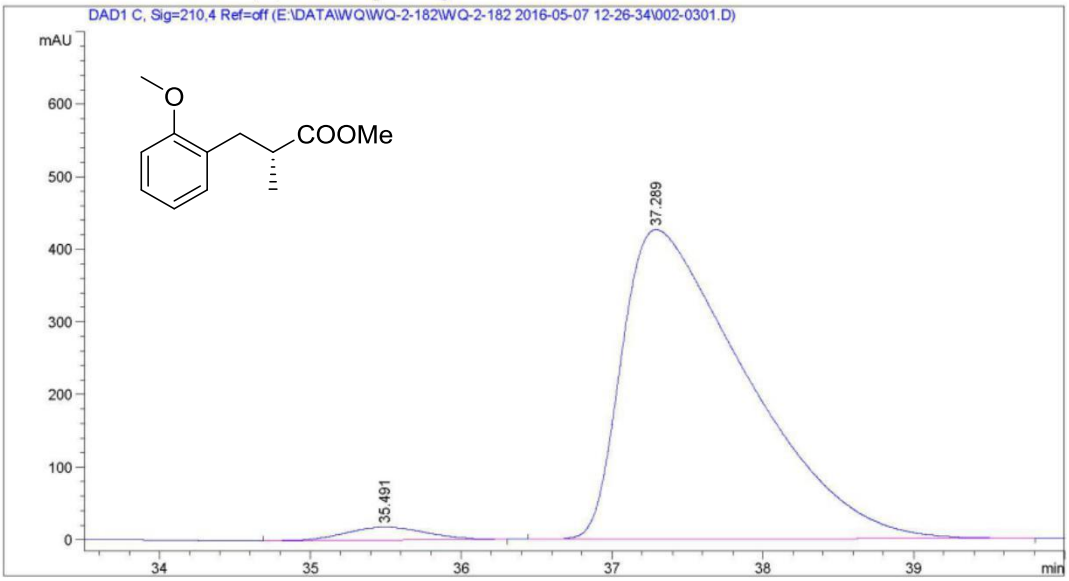
```
Data File E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\001-0201.D
Sample Name: WQ-2-182-1-RAC

=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   2
Acq. Instrument : 1260HPLC-DAD                  Location : Vial 1
Injection Date  : 5/7/2016 12:40:30 PM             Inj :   1
                                               Inj Volume : 3.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\DAD-OD(1-2)-99-1-0.5ML-3UL
                  -50MIN.M
Last changed    : 5/7/2016 12:26:35 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\DAD-OD(1-2)-99-1-0.5ML-3UL
                  -50MIN.M (Sequence Method)
Last changed    : 5/29/2016 9:06:08 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  35.060 BB    0.6392 3599.51636   87.27083  50.3794
   2  37.544 BB    0.7006 3545.30029   77.95901  49.6206

Totals :                  7144.81665  165.22984

1260HPLC-DAD 5/29/2016 9:06:17 PM SYSTEM                    Page   1 of 2
```

Data File E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\002-0301.D
Sample Name: WQ-2-182-1

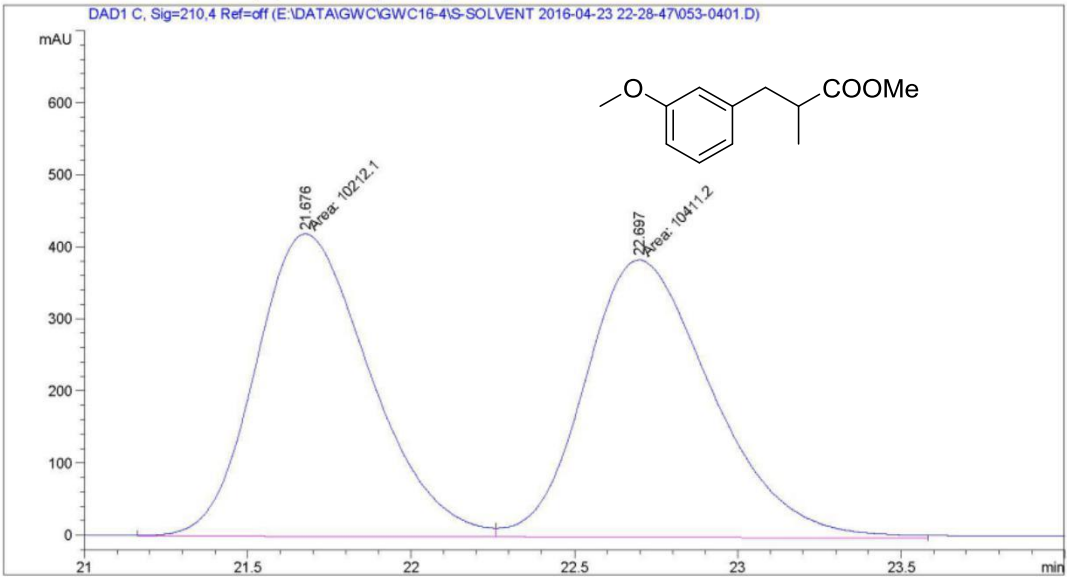
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   3
Acq. Instrument : 1260HPLC-DAD                    Location : Vial 2
Injection Date  : 5/7/2016 1:31:22 PM                  Inj :   1
                                                  Inj Volume : 3.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\DAD-OD(1-2)-99-1-0.5ML-3UL
                  -50MIN.M
Last changed    : 5/7/2016 12:26:35 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\DAD-OD(1-2)-99-1-0.5ML-3UL
                  -50MIN.M (Sequence Method)
Last changed    : 5/29/2016 9:08:50 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  35.491 BB    0.5739  648.52295   17.76537   2.5904
   2  37.289 BB    0.8401 2.43871e4   425.84824  97.4096

Totals :                  2.50356e4   443.61360
```

(*R*)-3-(3-methoxyphenyl)-2-methylpropanoic acid **8f**

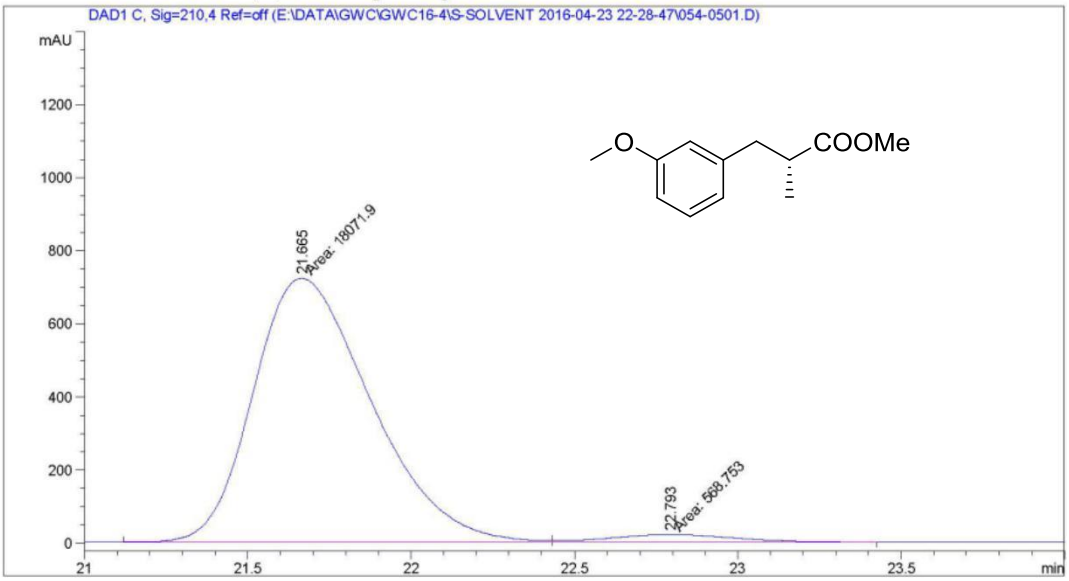
```
Data File E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 22-28-47\053-0401.D
Sample Name: WQ-2-172-2-RAC

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   4
    Acq. Instrument : 1260HPLC-DAD                    Location : Vial 53
    Injection Date  : 4/23/2016 11:42:40 PM              Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 22-28-47\DAD-OJ(1-6)-99-1-0.5ML-
                      210NM--30MIN.M
    Last changed    : 4/23/2016 10:28:48 PM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 22-28-47\DAD-OJ(1-6)-99-1-0.5ML-
                      210NM--30MIN.M (Sequence Method)
    Last changed    : 5/29/2016 8:51:24 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  21.676 MF    0.4058 1.02121e4   419.39774  49.5173
       2  22.697 FM    0.4513 1.04112e4   384.49316  50.4827

    Totals :                  2.06234e4   803.89090

1260HPLC-DAD 5/29/2016 8:51:53 PM SYSTEM                    Page   1 of 2
```

Data File E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 22-28-47\054-0501.D
Sample Name: WQ-2-172-2

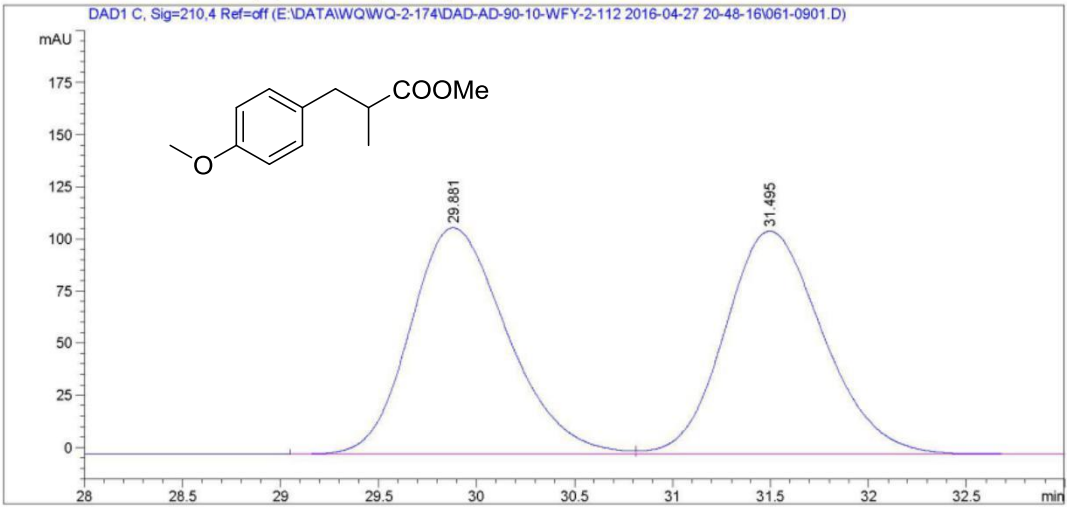
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   5
Acq. Instrument : 1260HPLC-DAD                    Location : Vial 54
Injection Date  : 4/24/2016 12:13:37 AM               Inj :   1
                                                  Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 22-28-47\DAD-OJ(1-6)-99-1-0.5ML-
                  210NM--30MIN.M
Last changed    : 4/23/2016 10:28:48 PM by SYSTEM
Analysis Method : E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 22-28-47\DAD-OJ(1-6)-99-1-0.5ML-
                  210NM--30MIN.M (Sequence Method)
Last changed    : 5/29/2016 8:53:34 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  21.665 MF    0.4174 1.80719e4   721.63135  96.9489
   2  22.793 FM    0.4560  568.75299   20.78808   3.0511

Totals :                  1.86407e4   742.41943
```

(*R*)-3-(4-methoxyphenyl)-2-methylpropanoic acid **8g**

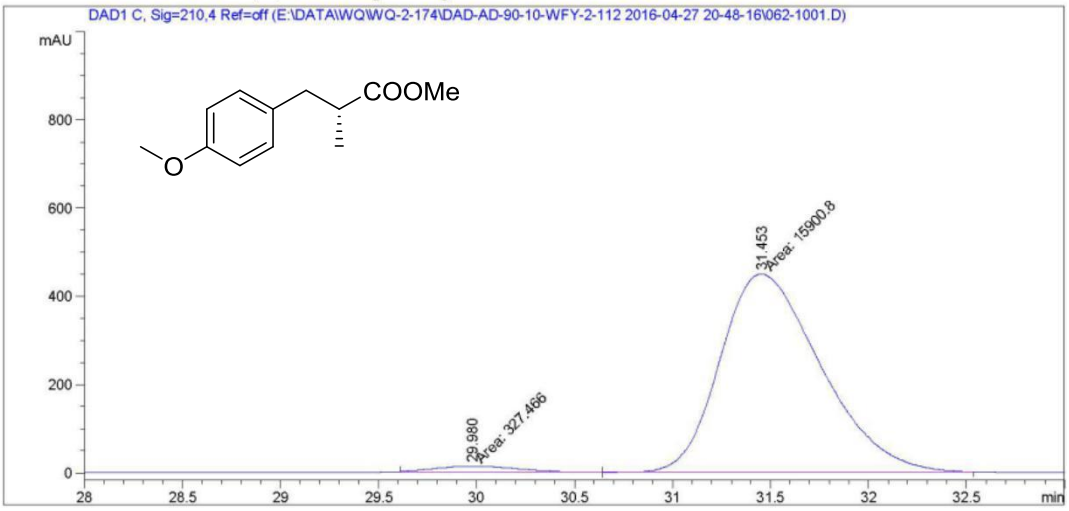
```
Data File E:\DATA\WQ\WQ-2-174\DAD-AD-90-10-WFY-2-112 2016-04-27 20-48-16\061-0901.D
Sample Name: WQ-2-174-6-RAC

    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   9
    Acq. Instrument : 1260HPLC-DAD                  Location : Vial 61
    Injection Date  : 4/28/2016 12:57:48 AM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\WQ\WQ-2-174\DAD-AD-90-10-WFY-2-112 2016-04-27 20-48-16\DAD-OJ(1-6)-
                      99-1-0.5ML-40MIN.M
    Last changed    : 4/27/2016 8:49:49 PM by SYSTEM
    Analysis Method : E:\DATA\WQ\WQ-2-174\DAD-AD-90-10-WFY-2-112 2016-04-27 20-48-16\DAD-OJ(1-6)-
                      99-1-0.5ML-40MIN.M (Sequence Method)
    Last changed    : 5/29/2016 8:31:38 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]    [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  29.881 BV    0.5308 3754.36743  108.73714  50.0339
       2  31.495 VB    0.5402 3749.27979  107.16940  49.9661

    Totals :                  7503.64722  215.90655


    ======================================================================
                               *** End of Report ***

1260HPLC-DAD 5/29/2016 8:31:50 PM SYSTEM                        Page   1 of 1
```

Data File E:\DATA\WQ\WQ-2-174\DAD-AD-90-10-WFY-2-112 2016-04-27 20-48-16\062-1001.D
Sample Name: WQ-2-174-6

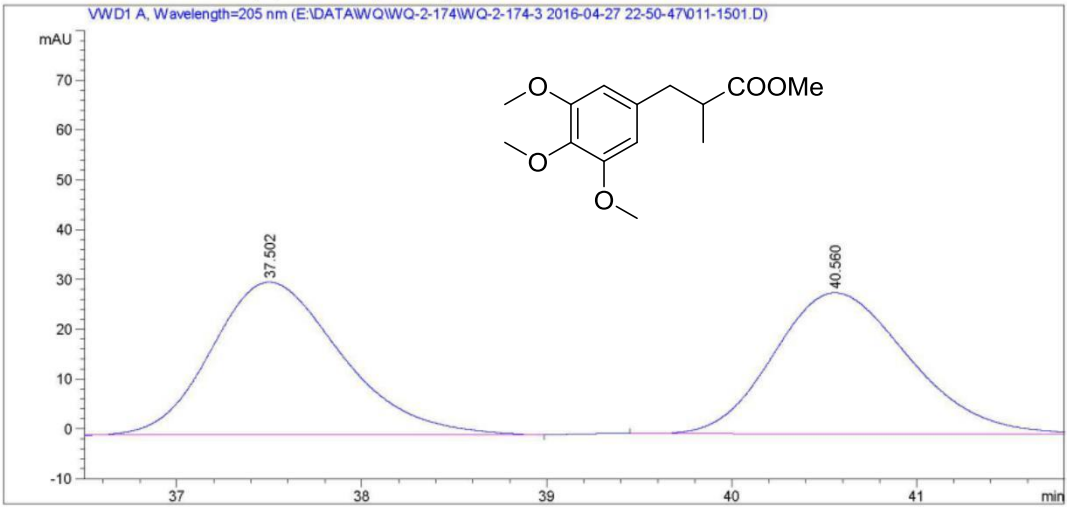
```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  10
Acq. Instrument : 1260HPLC-DAD                  Location : Vial 62
Injection Date  : 4/28/2016 1:38:45 AM               Inj :   1
                                               Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-174\DAD-AD-90-10-WFY-2-112 2016-04-27 20-48-16\DAD-OJ(1-6)-
                  99-1-0.5ML-40MIN.M
Last changed    : 4/27/2016 8:49:49 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-174\DAD-AD-90-10-WFY-2-112 2016-04-27 20-48-16\DAD-OJ(1-6)-
                  99-1-0.5ML-40MIN.M (Sequence Method)
Last changed    : 5/29/2016 8:33:52 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  29.980 MF    0.4523  327.46609   12.06774   2.0179
   2  31.453 FM    0.5923 1.59008e4   447.42841  97.9821

Totals :                  1.62282e4   459.49614


=====================================================================
                          *** End of Report ***
```

(*R*)-2-methyl-3-(3,4,5-trimethoxyphenyl)propanoic acid **8h**

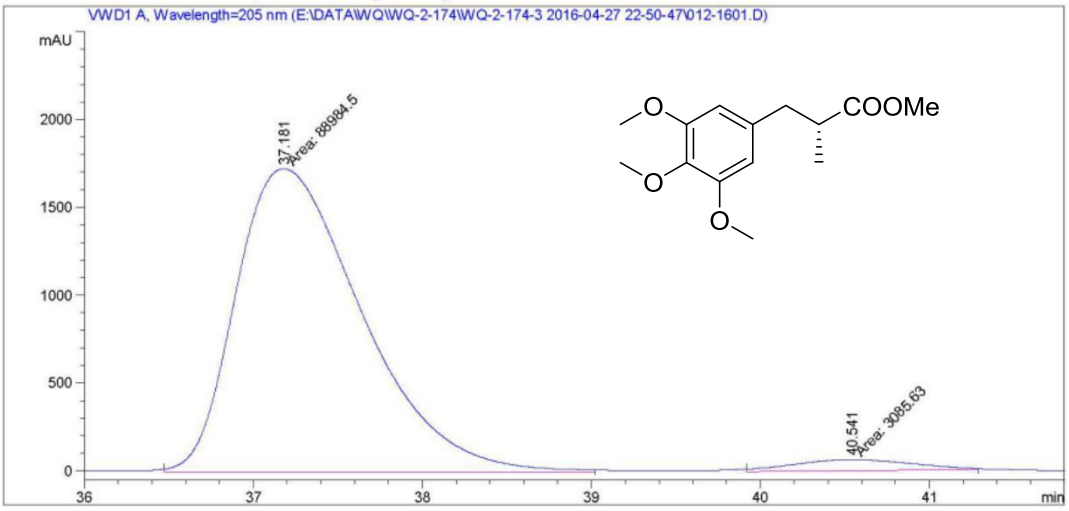
```
Data File E:\DATA\WQ\WQ-2-174\WQ-2-174-3 2016-04-27 22-50-47\011-1501.D
Sample Name: WQ-2-174-1O-RAC

=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  15
Acq. Instrument : 1260HPLC-VWD                  Location : Vial 11
Injection Date  : 4/28/2016 4:02:09 AM             Inj :   1
                                               Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-174\WQ-2-174-3 2016-04-27 22-50-47\VWD-AD(1-6)-99-1-0.5ML-
                  205NM-50MIN.M
Last changed    : 4/27/2016 10:50:47 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-174\WQ-2-174-3 2016-04-27 22-50-47\VWD-AD(1-6)-99-1-0.5ML-
                  205NM-50MIN.M (Sequence Method)
Last changed    : 5/29/2016 8:42:27 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=205 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  37.502 BB    0.7512 1501.69165   30.72799  50.8595
   2  40.560 BB    0.7937 1450.93335   28.36941  49.1405

Totals :                  2952.62500   59.09740


=====================================================================
                        *** End of Report ***

1260HPLC-DAD 5/29/2016 8:42:54 PM SYSTEM                    Page   1 of 1
```

Data File E:\DATA\WQ\WQ-2-174\WQ-2-174-3 2016-04-27 22-50-47\012-1601.D
Sample Name: WQ-2-174-10

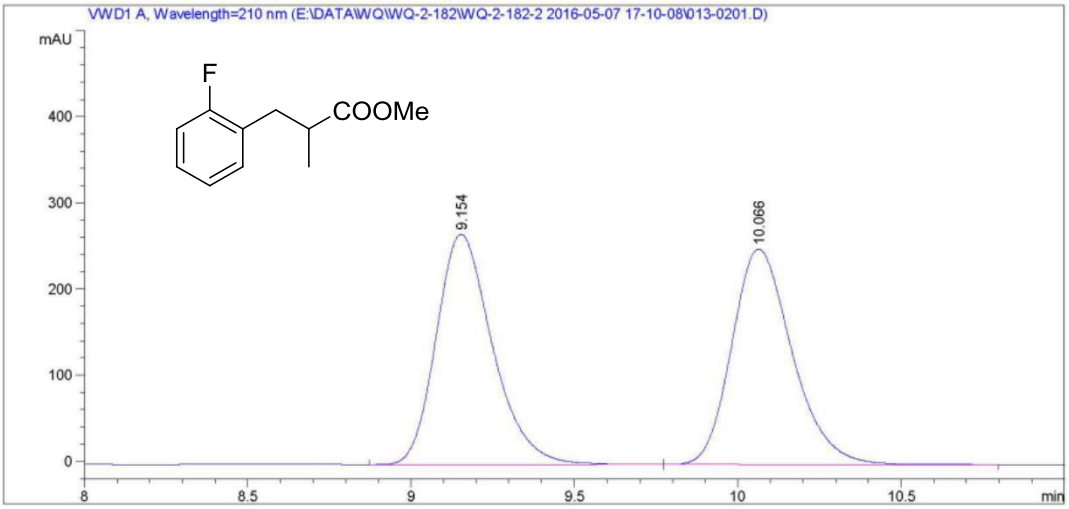
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  16
Acq. Instrument : 1260HPLC-VWD                    Location : Vial 12
Injection Date  : 4/28/2016 4:52:55 AM                 Inj :  1
                                                  Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-174\WQ-2-174-3 2016-04-27 22-50-47\VWD-AD(1-6)-99-1-0.5ML-
                  205NM-50MIN.M
Last changed    : 4/27/2016 10:50:47 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-174\WQ-2-174-3 2016-04-27 22-50-47\VWD-AD(1-6)-99-1-0.5ML-
                  205NM-50MIN.M (Sequence Method)
Last changed    : 5/29/2016 8:45:02 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=205 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  37.181 MM    0.8603 8.89845e4  1724.00012  96.6486
   2  40.541 MM    0.8230 3085.63428   62.48996   3.3514

Totals :                  9.20701e4  1786.49008

==========================================================================
                        *** End of Report ***
```

(*R*)-3-(2-fluorophenyl)-2-methylpropanoic acid **8i**

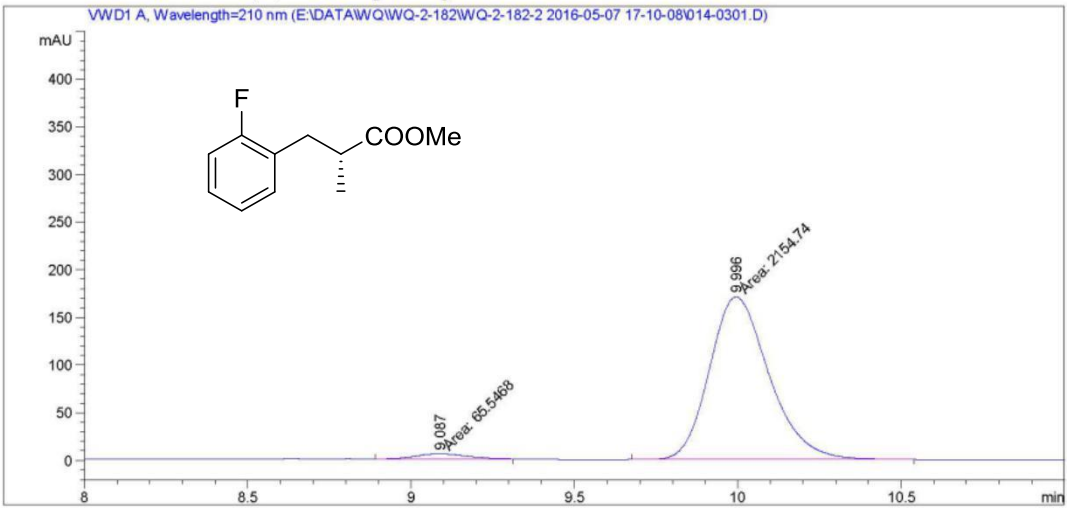
```
Data File E:\DATA\WQ\WQ-2-182\WQ-2-182-2 2016-05-07 17-10-08\013-0201.D
Sample Name: WQ-2-182-5-RAC

=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   2
Acq. Instrument : 1260HPLC-VWD                  Location : Vial 13
Injection Date  : 5/7/2016 5:21:52 PM              Inj :   1
                                               Inj Volume : 3.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-182\WQ-2-182-2 2016-05-07 17-10-08\VWD-AS(1-2)-99-1-0.50ML-
                  210NM-30MIN.M
Last changed    : 5/7/2016 5:10:08 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-182\WQ-2-182-2 2016-05-07 17-10-08\VWD-AS(1-2)-99-1-0.50ML-
                  210NM-30MIN.M (Sequence Method)
Last changed    : 5/29/2016 9:14:21 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.154 BB    0.1835 3193.89624  267.14471  49.9402
   2  10.066 BB    0.1964 3201.54761  249.94551  50.0598

Totals :                  6395.44385  517.09023


=====================================================================
                        *** End of Report ***

1260HPLC-DAD 5/29/2016 9:14:31 PM SYSTEM                    Page   1 of 1
```

Data File E:\DATA\WQ\WQ-2-182\WQ-2-182-2 2016-05-07 17-10-08\014-0301.D
Sample Name: WQ-2-182-5

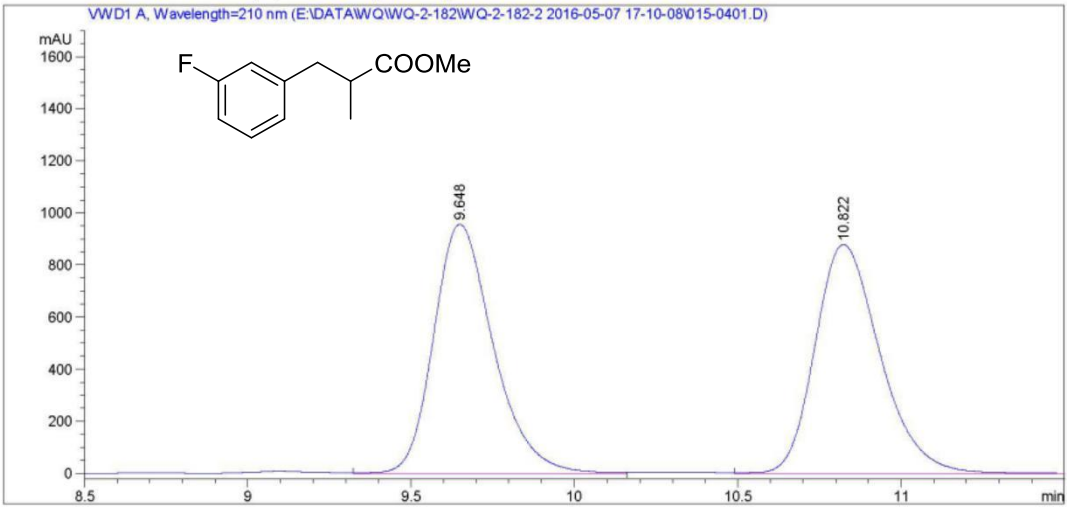
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   3
Acq. Instrument : 1260HPLC-VWD                    Location : Vial 14
Injection Date  : 5/7/2016 5:52:37 PM                  Inj :   1
                                                 Inj Volume : 3.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-182\WQ-2-182-2 2016-05-07 17-10-08\VWD-AS(1-2)-99-1-0.50ML-
                  210NM-30MIN.M
Last changed    : 5/7/2016 5:10:08 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-182\WQ-2-182-2 2016-05-07 17-10-08\VWD-AS(1-2)-99-1-0.50ML-
                  210NM-30MIN.M (Sequence Method)
Last changed    : 5/29/2016 9:17:26 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.087 MM    0.1885   65.54678    5.79515   2.9522
   2   9.996 MM    0.2107 2154.74170  170.42198  97.0478

Totals :                  2220.28848  176.21713


==========================================================================
                        *** End of Report ***
```

(*R*)-3-(3-fluorophenyl)-2-methylpropanoic acid **8j**

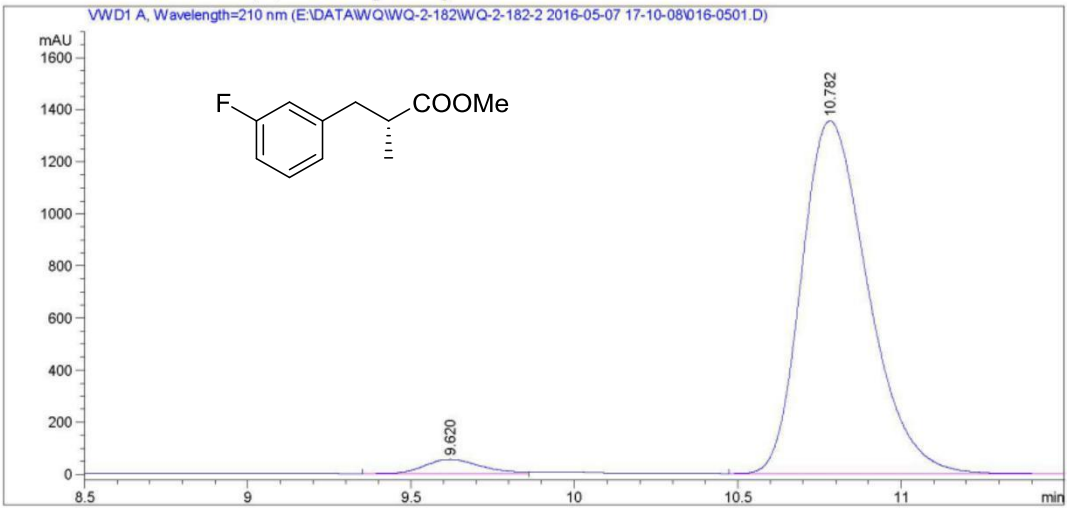
```
Data File E:\DATA\WQ\WQ-2-182\WQ-2-182-2 2016-05-07 17-10-08\015-0401.D
Sample Name: WQ-2-182-6-RAC

=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   4
Acq. Instrument : 1260HPLC-VWD                  Location : Vial 15
Injection Date  : 5/7/2016 6:23:22 PM              Inj :   1
                                               Inj Volume : 3.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-182\WQ-2-182-2 2016-05-07 17-10-08\VWD-AS(1-2)-99-1-0.50ML-
                  210NM-30MIN.M
Last changed    : 5/7/2016 5:10:08 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-182\WQ-2-182-2 2016-05-07 17-10-08\VWD-AS(1-2)-99-1-0.50ML-
                  210NM-30MIN.M (Sequence Method)
Last changed    : 5/29/2016 9:20:25 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.648 VV    0.1938 1.21032e4   955.40259  50.0189
   2  10.822 VB    0.2128 1.20940e4   877.66675  49.9811

Totals :                  2.41972e4  1833.06934


=====================================================================
                        *** End of Report ***

1260HPLC-DAD 5/29/2016 9:20:30 PM SYSTEM                    Page   1 of 1
```

Data File E:\DATA\WQ\WQ-2-182\WQ-2-182-2 2016-05-07 17-10-08\016-0501.D
Sample Name: WQ-2-182-6

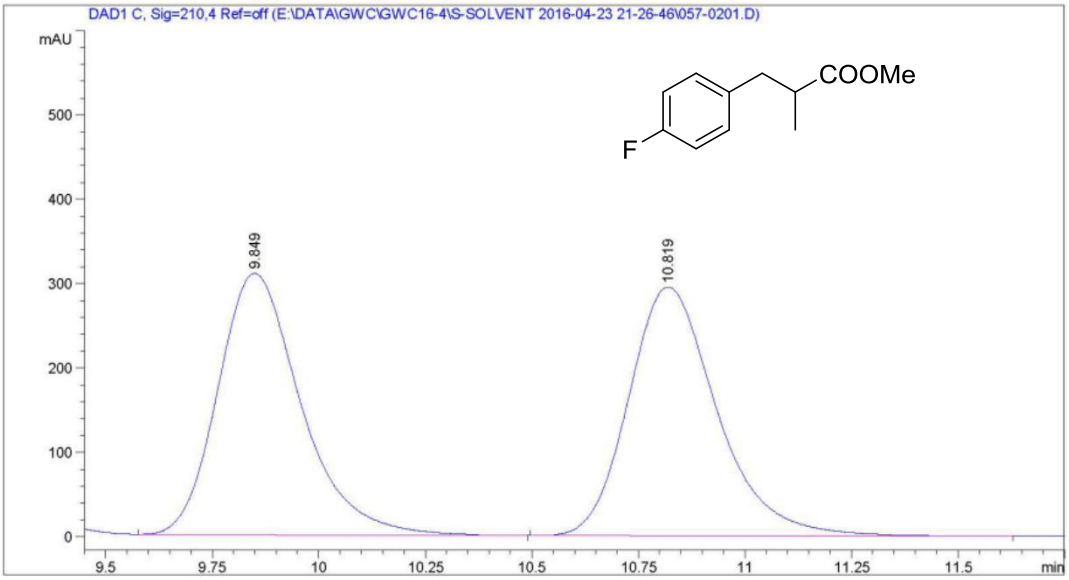
```
==================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   5
Acq. Instrument : 1260HPLC-VWD                   Location : Vial 16
Injection Date  : 5/7/2016 6:54:06 PM                 Inj :   1
                                                Inj Volume : 3.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-182\WQ-2-182-2 2016-05-07 17-10-08\VWD-AS(1-2)-99-1-0.50ML-
                  210NM-30MIN.M
Last changed    : 5/7/2016 5:10:08 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-182\WQ-2-182-2 2016-05-07 17-10-08\VWD-AS(1-2)-99-1-0.50ML-
                  210NM-30MIN.M (Sequence Method)
Last changed    : 5/29/2016 9:21:07 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.620 BV    0.1859  670.47961   55.12567   3.3845
   2  10.782 VB    0.2187 1.91398e4  1355.52502  96.6155

Totals :                  1.98103e4  1410.65070

==================================================================
                        *** End of Report ***
```

(*R*)-3-(4-fluorophenyl)-2-methylpropanoic acid **8k**

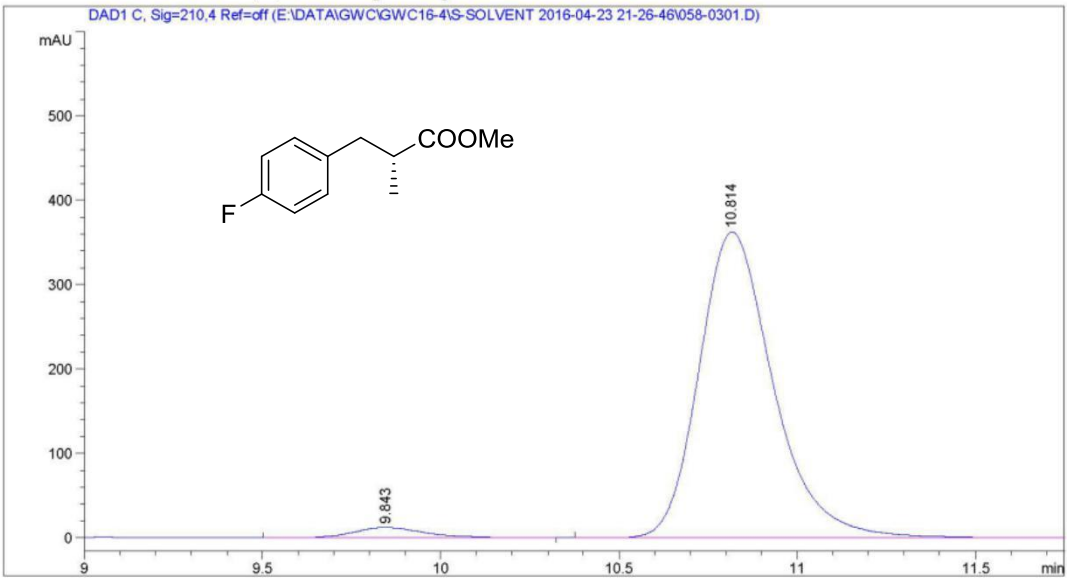
```
Data File E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 21-26-46\057-0201.D
Sample Name: WQ-2-172-4-RAC

==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   2
Acq. Instrument : 1260HPLC-DAD                    Location : Vial 57
Injection Date  : 4/23/2016 9:38:46 PM                 Inj :   1
                                                  Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 21-26-46\DAD-AS(1-2)-99-1-0.5ML-
                  210NM--20MIN.M
Last changed    : 4/23/2016 9:26:47 PM by SYSTEM
Analysis Method : E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 21-26-46\DAD-AS(1-2)-99-1-0.5ML-
                  210NM--20MIN.M (Sequence Method)
Last changed    : 5/29/2016 8:13:13 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.849 BB    0.2055 4182.33057  309.82227  49.7090
   2  10.819 BB    0.2195 4231.29590  294.73523  50.2910

Totals :                  8413.62646  604.55750

1260HPLC-DAD 5/29/2016 8:13:28 PM SYSTEM                    Page   1 of 2
```

Data File E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 21-26-46\058-0301.D
Sample Name: WQ-2-172-4

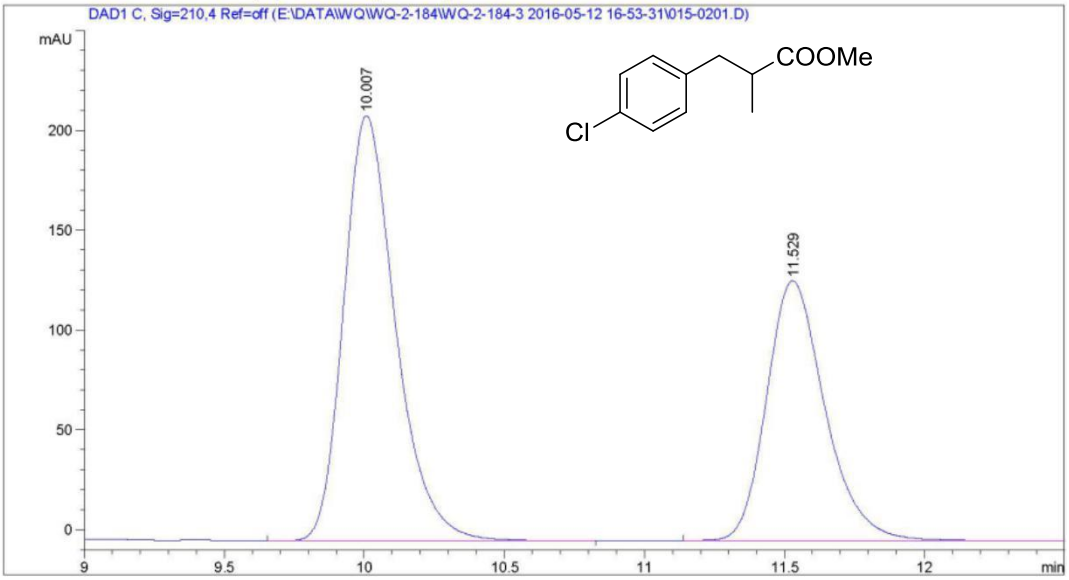
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   3
Acq. Instrument : 1260HPLC-DAD                    Location : Vial 58
Injection Date  : 4/23/2016 9:59:42 PM                 Inj :   1
                                                  Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 21-26-46\DAD-AS(1-2)-99-1-0.5ML-
                  210NM--20MIN.M
Last changed    : 4/23/2016 9:26:47 PM by SYSTEM
Analysis Method : E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 21-26-46\DAD-AS(1-2)-99-1-0.5ML-
                  210NM--20MIN.M (Sequence Method)
Last changed    : 5/29/2016 8:14:52 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.843 BB    0.2056  162.86629   12.05527   3.0265
   2  10.814 BB    0.2201 5218.46924  362.18933  96.9735

Totals :                  5381.33553  374.24461
```

(*R*)-3-(4-chlorophenyl)-2-methylpropanoic acid **8l**

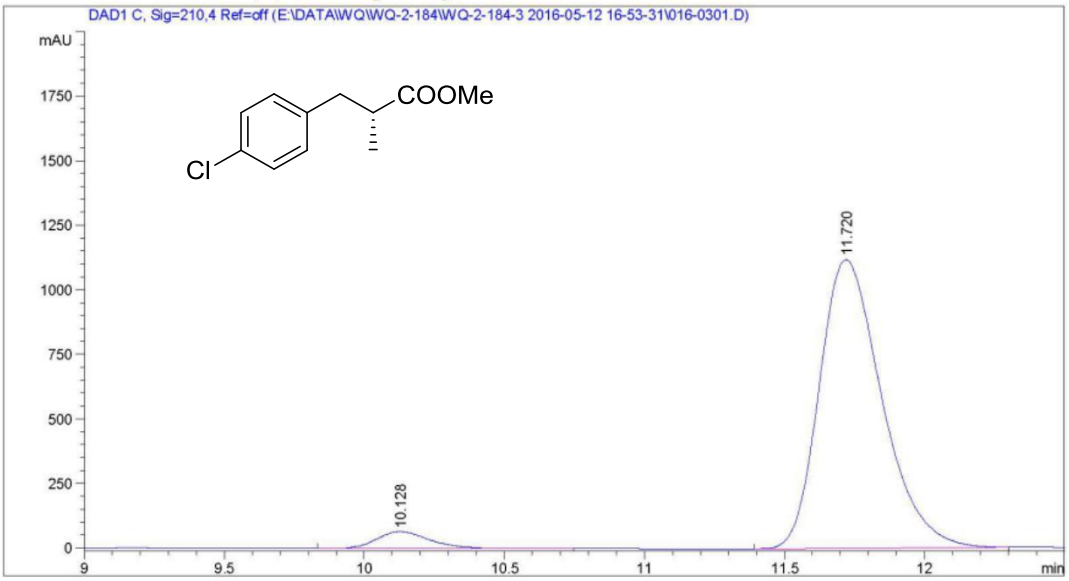
```
Data File E:\DATA\WQ\WQ-2-184\WQ-2-184-3 2016-05-12 16-53-31\015-0201.D
Sample Name: wq-2-184-5-rac

======================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   2
Acq. Instrument : 1260HPLC-DAD                    Location : Vial 15
Injection Date  : 5/12/2016 5:05:23 PM                 Inj :   1
                                                  Inj Volume : 3.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-184\WQ-2-184-3 2016-05-12 16-53-31\DAD-AS(1-6)-99-1-0.5ML-
                  3UL-30MIN.M
Last changed    : 5/12/2016 4:53:31 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-184\WQ-2-184-3 2016-05-12 16-53-31\DAD-AS(1-6)-99-1-0.5ML-
                  3UL-30MIN.M (Sequence Method)
Last changed    : 5/29/2016 9:39:49 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.007 BB    0.1960 2736.16089  212.87825  59.2150
   2  11.529 BB    0.2211 1884.56213  130.05888  40.7850

Totals :                  4620.72302  342.93713

1260HPLC-DAD 5/29/2016 9:39:54 PM SYSTEM                    Page   1 of 2
```

Data File E:\DATA\WQ\WQ-2-184\WQ-2-184-3 2016-05-12 16-53-31\016-0301.D
Sample Name: wq-2-184-5

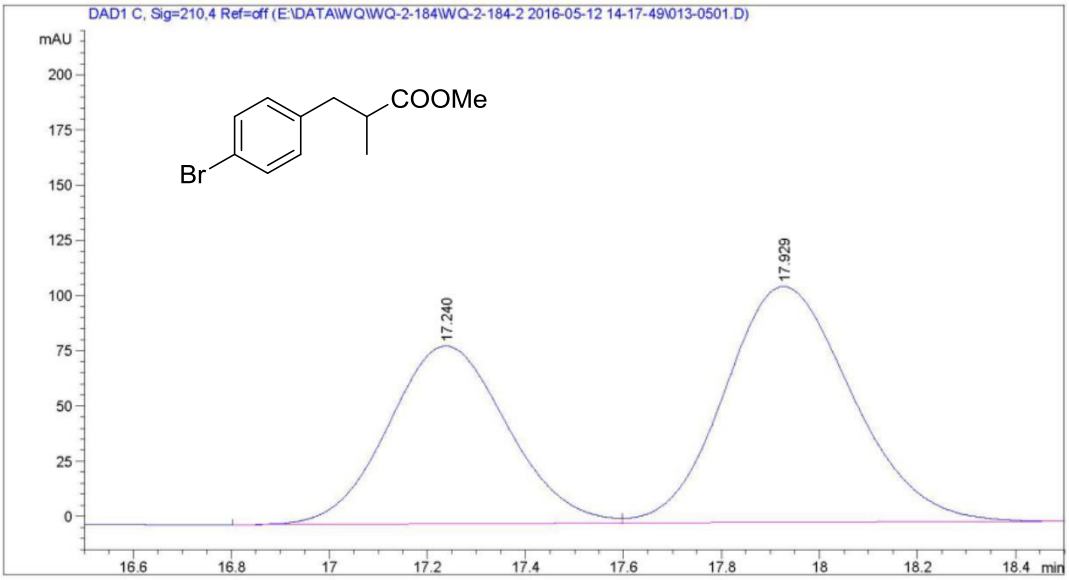
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   3
Acq. Instrument : 1260HPLC-DAD                    Location : Vial 16
Injection Date  : 5/12/2016 5:36:17 PM                 Inj :   1
                                                 Inj Volume : 3.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-184\WQ-2-184-3 2016-05-12 16-53-31\DAD-AS(1-6)-99-1-0.5ML-
                  3UL-30MIN.M
Last changed    : 5/12/2016 4:53:31 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-184\WQ-2-184-3 2016-05-12 16-53-31\DAD-AS(1-6)-99-1-0.5ML-
                  3UL-30MIN.M (Sequence Method)
Last changed    : 5/29/2016 9:41:10 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.128 BB    0.1994  855.14240   65.05398   4.7243
   2  11.720 BB    0.2380 1.72459e4  1117.64990  95.2757

Totals :                  1.81011e4  1182.70388
```

(*R*)-3-(4-bromophenyl)-2-methylpropanoic acid **8m**

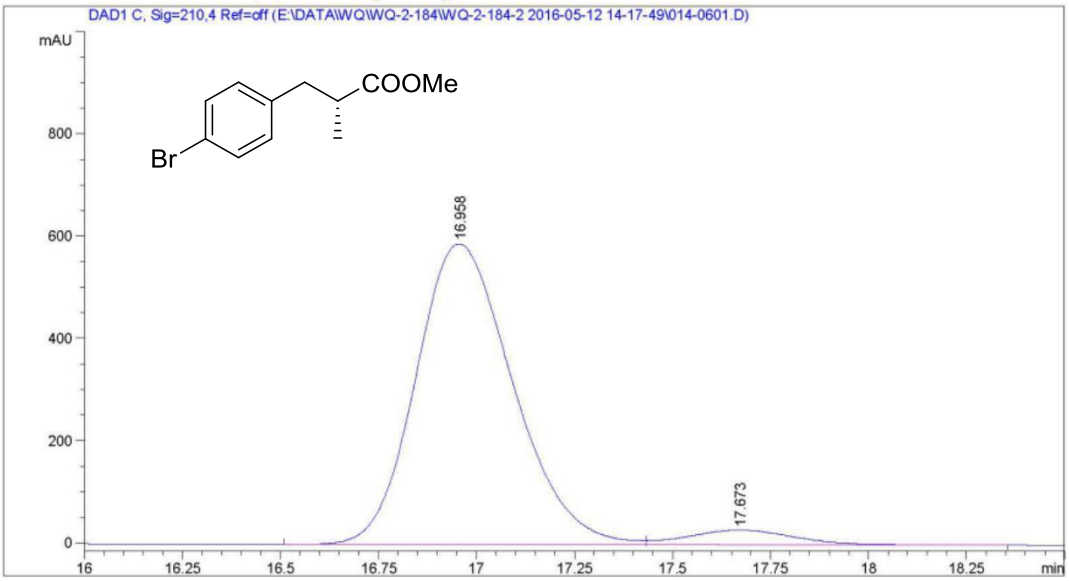
```
Data File E:\DATA\WQ\WQ-2-184\WQ-2-184-2 2016-05-12 14-17-49\013-0501.D
Sample Name: wq-2-184-4-rac

=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   5
Acq. Instrument : 1260HPLC-DAD                  Location : Vial 13
Injection Date  : 5/12/2016 3:43:26 PM               Inj :   1
                                               Inj Volume : 2.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-184\WQ-2-184-2 2016-05-12 14-17-49\DAD-OJ(1-6)-99-1-0.5ML-
                  2UL-205-35MIN.M
Last changed    : 5/12/2016 4:15:38 PM by SYSTEM
                  (modified after loading)
Analysis Method : E:\DATA\WQ\WQ-2-184\WQ-2-184-2 2016-05-12 14-17-49\DAD-OJ(1-6)-99-1-0.5ML-
                  2UL-205-35MIN.M (Sequence Method)
Last changed    : 5/29/2016 9:36:20 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.240 BV    0.2627 1357.95508   80.53570  41.2991
   2  17.929 VB    0.2807 1930.14392  106.89675  58.7009

Totals :                  3288.09900  187.43245
```

Data File E:\DATA\WQ\WQ-2-184\WQ-2-184-2 2016-05-12 14-17-49\014-0601.D
Sample Name: wq-2-184-4-rac

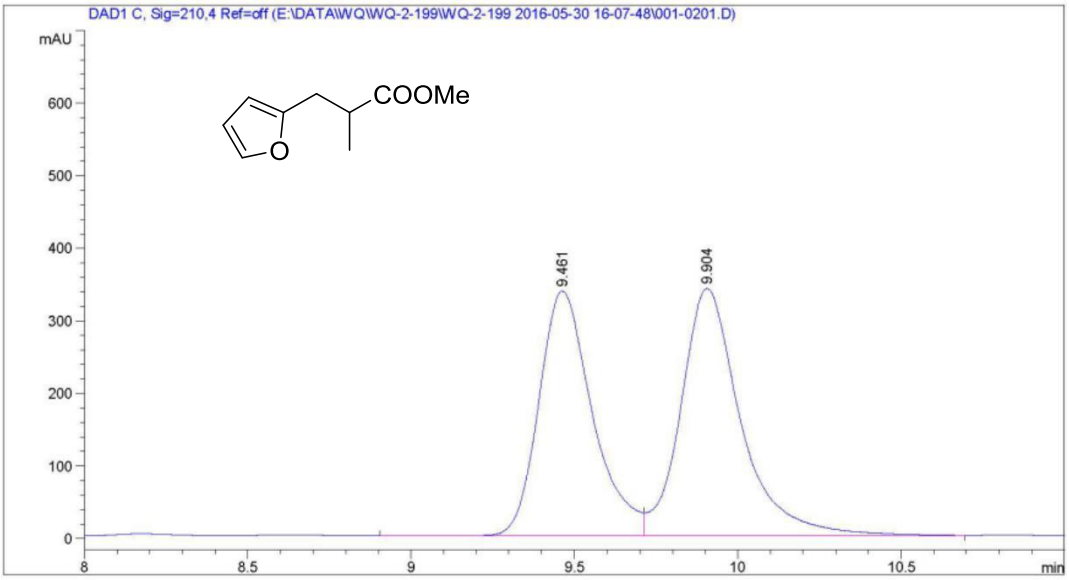
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   6
Acq. Instrument : 1260HPLC-DAD                    Location : Vial 14
Injection Date  : 5/12/2016 4:16:31 PM                 Inj :   1
                                                 Inj Volume : 2.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-184\WQ-2-184-2 2016-05-12 14-17-49\DAD-OJ(1-6)-99-1-0.5ML-
                  2UL-205-35MIN.M
Last changed    : 5/12/2016 4:15:38 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-184\WQ-2-184-2 2016-05-12 14-17-49\DAD-OJ(1-6)-99-1-0.5ML-
                  2UL-205-35MIN.M (Sequence Method)
Last changed    : 5/29/2016 9:37:49 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.958 BV    0.2663 1.00925e4   587.89148  94.9124
   2  17.673 VB    0.2878  540.98395   28.71175   5.0876

Totals :                  1.06335e4   616.60323
```

(*R*)-3-(furan-2-yl)-2-methylpropanoic acid **8n**

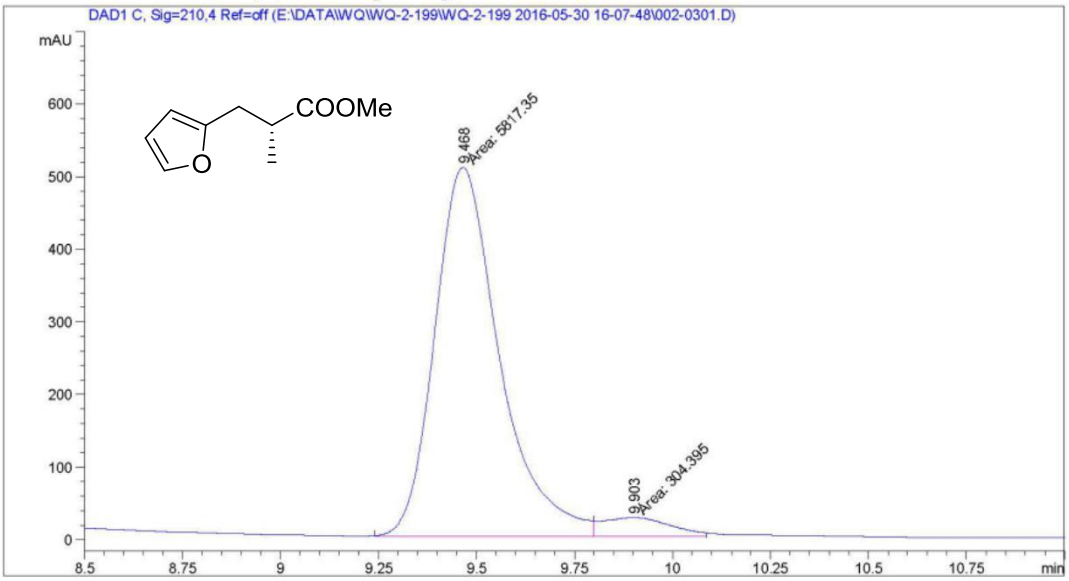
```
Data File E:\DATA\WQ\WQ-2-199\WQ-2-199 2016-05-30 16-07-48\001-0201.D
Sample Name: wq-2-199-2-rac

    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                  Location : Vial 1
    Injection Date  : 5/30/2016 4:24:40 PM             Inj :   1
                                                   Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\WQ\WQ-2-199\WQ-2-199 2016-05-30 16-07-48\DAD-OD(1-2)-99-1-0.5ML-2UL
                      -205-35MIN.M
    Last changed    : 5/30/2016 4:59:43 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\WQ\WQ-2-199\WQ-2-199 2016-05-30 16-07-48\DAD-OD(1-2)-99-1-0.5ML-2UL
                      -205-35MIN.M (Sequence Method)
    Last changed    : 6/7/2016 10:12:26 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.461 BV    0.1701 3815.09814  336.93869  47.0180
       2   9.904 VB    0.1875 4299.02002  340.02939  52.9820

    Totals :                   8114.11816  676.96808

1260HPLC-DAD 6/7/2016 10:12:39 AM SYSTEM                          Page   1 of 2
```

Data File E:\DATA\WQ\WQ-2-199\WQ-2-199 2016-05-30 16-07-48\002-0301.D
Sample Name: wq-2-199-2

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   3
Acq. Instrument : 1260HPLC-DAD                    Location : Vial 2
Injection Date  : 5/30/2016 5:00:34 PM                 Inj :   1
                                                  Inj Volume : 2.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-199\WQ-2-199 2016-05-30 16-07-48\DAD-OD(1-2)-99-1-0.5ML-2UL
                  -205-35MIN.M
Last changed    : 5/30/2016 4:59:43 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-199\WQ-2-199 2016-05-30 16-07-48\DAD-OD(1-2)-99-1-0.5ML-2UL
                  -205-35MIN.M (Sequence Method)
Last changed    : 6/7/2016 10:14:34 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.468 MF    0.1909 5817.34912  507.86591  95.0276
   2   9.903 FM    0.1997  304.39493   25.39856   4.9724

Totals :                  6121.74405  533.26447
```

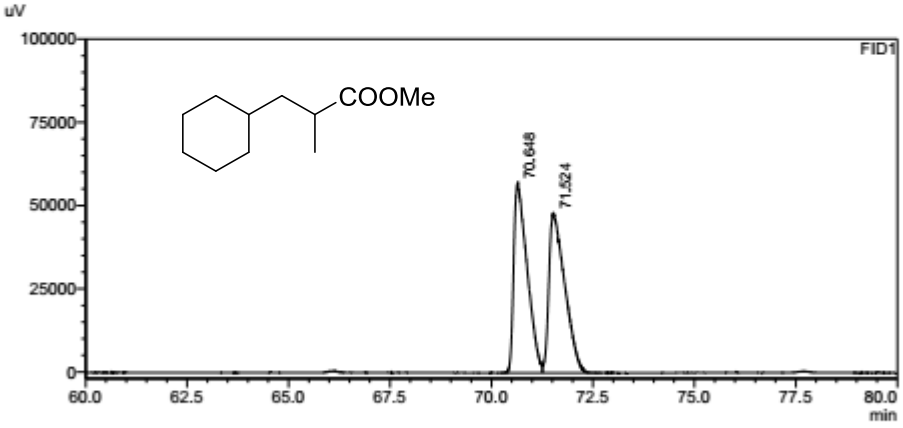
(*R*)-3-cyclohexyl-2-methylpropanoic acid **8o**

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: wq-cy-4		
Sample ID	:		
Data Filename	: wq-cy-4.gcd		
Method Filename	: bdex120-250-80-150-260-170min.gcm		
Batch Filename	: wq-cy-4.gcb		
Vial #	: 26	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 2016-5-14 10:56:38	Acquired by	: System Administrator
Date Processed	: 2016-5-23 21:08:23	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

FID1

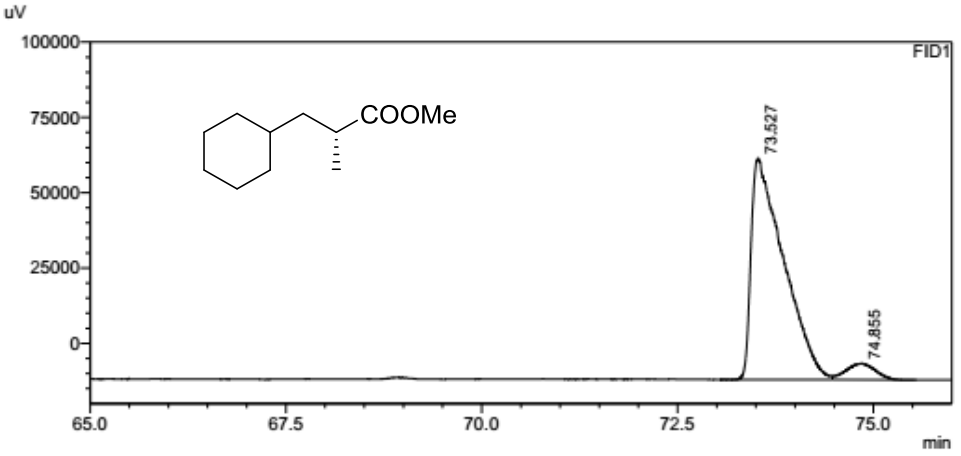
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	70.648	1314708	57141	50.093		M	
2	71.524	1309838	48019	49.907		V M	
Total		2624546	105160				

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: wq-cy-guanghuo		
Sample ID	:		
Data Filename	: wq-cy-guanghuo.gcd		
Method Filename	: bdex120-250-80-150-260-170min.gcm		
Batch Filename	: wq-cy-guanghuo.gcb		
Vial #	: 6	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 2016-5-23 19:51:24	Acquired by	: System Administrator
Date Processed	: 2016-5-23 22:55:58	Processed by	: System Administrator

<Chromatogram>



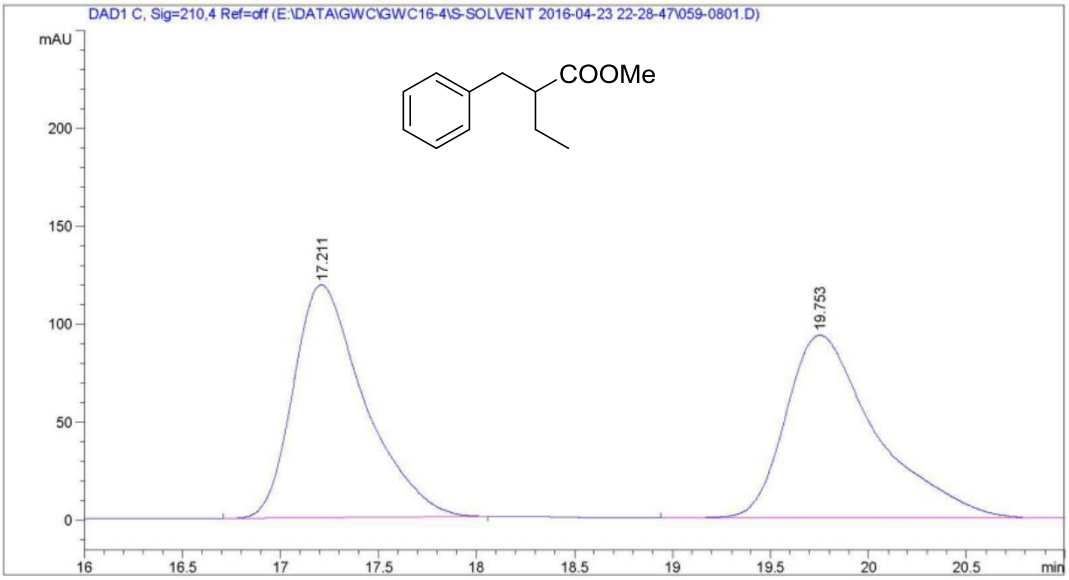
<Peak Table>

FID1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	73.527	2126550	73524	93.774		M	
2	74.855	141193	5411	6.226		V M	
Total		2267743	78935				

(*R*)-2-benzylbutanoic acid **8p**

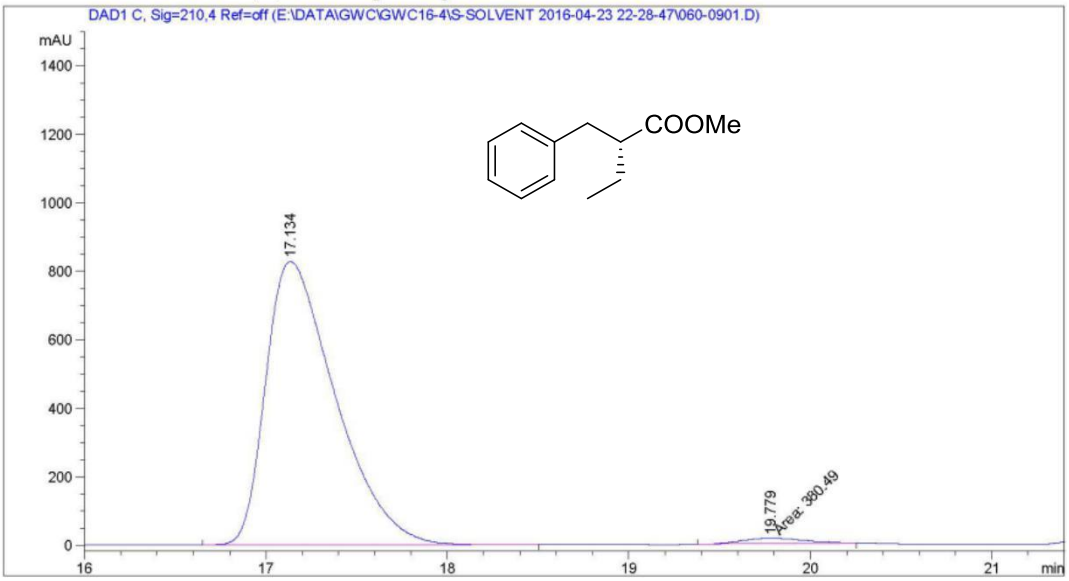
```
Data File E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 22-28-47\059-0801.D
Sample Name: WQ-2-172-5-RAC

    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   8
    Acq. Instrument : 1260HPLC-DAD                  Location : Vial 59
    Injection Date  : 4/24/2016 2:16:32 AM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 22-28-47\DAD-OJ(1-6)-99-1-0.5ML-
                      210NM--30MIN.M
    Last changed    : 4/23/2016 10:28:48 PM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 22-28-47\DAD-OJ(1-6)-99-1-0.5ML-
                      210NM--30MIN.M (Sequence Method)
    Last changed    : 5/29/2016 8:21:14 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  17.211 BB    0.3730 2986.34375  118.90550  50.0523
       2  19.753 BB    0.4682 2980.10596   93.39954  49.9477

    Totals :                  5966.44971  212.30505

1260HPLC-DAD 5/29/2016 8:21:30 PM SYSTEM                    Page   1 of 2
```

Data File E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 22-28-47\060-0901.D
Sample Name: WQ-2-172-5

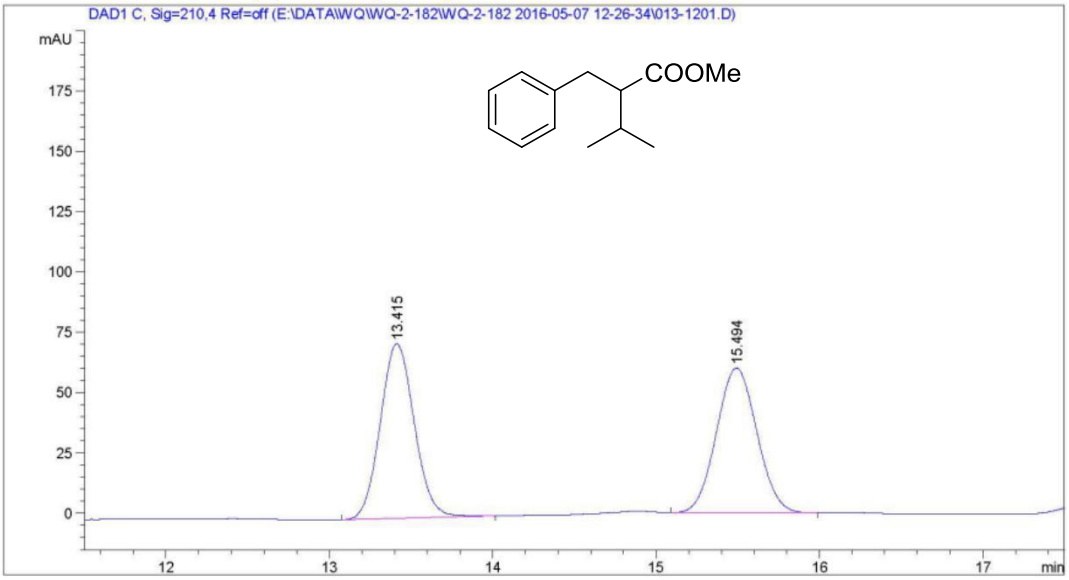
```
==================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   9
Acq. Instrument : 1260HPLC-DAD                   Location : Vial 60
Injection Date  : 4/24/2016 2:47:28 AM                Inj :   1
                                                Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 22-28-47\DAD-OJ(1-6)-99-1-0.5ML-
                  210NM--30MIN.M
Last changed    : 4/23/2016 10:28:48 PM by SYSTEM
Analysis Method : E:\DATA\GWC\GWC16-4\S-SOLVENT 2016-04-23 22-28-47\DAD-OJ(1-6)-99-1-0.5ML-
                  210NM--30MIN.M (Sequence Method)
Last changed    : 5/29/2016 8:26:45 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.134 BB    0.4026 2.20230e4   827.18225  98.3017
   2  19.779 MM    0.3977  380.48965   15.94494   1.6983

Totals :                  2.24035e4   843.12719
```

(*S*)-2-benzyl-3-methylbutanoic acid **8q**

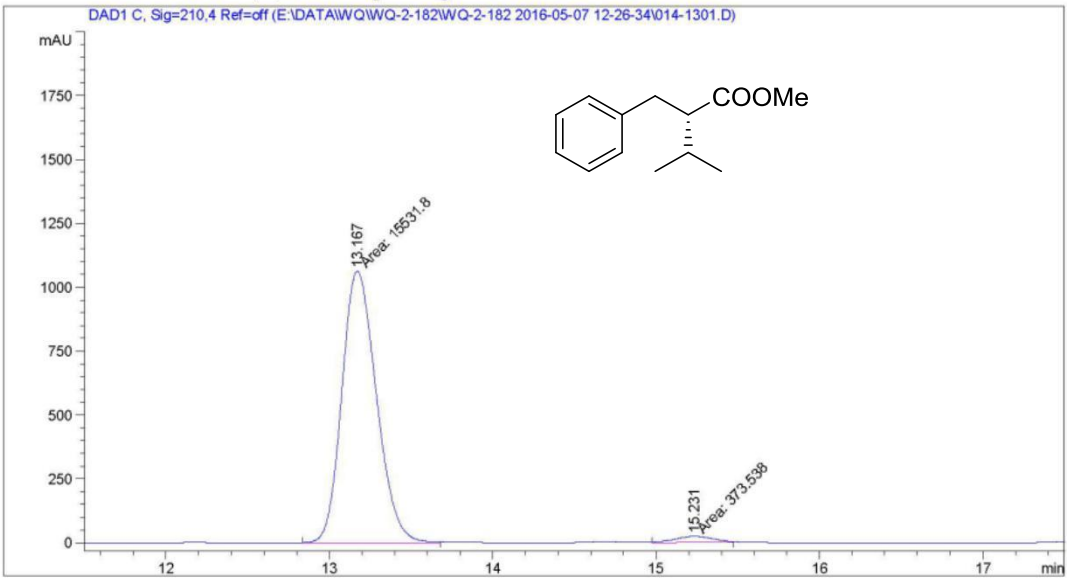
```
Data File E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\013-1201.D
Sample Name: WQ-2-182-7-RAC

    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  12
    Acq. Instrument : 1260HPLC-DAD                  Location : Vial 13
    Injection Date  : 5/7/2016 5:28:42 PM              Inj :   1
                                                   Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\DAD-OJ(1-6)-99-1-0.5ML-2UL
                      -205-35MIN.M
    Last changed    : 5/7/2016 12:44:53 PM by SYSTEM
    Analysis Method : E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\DAD-OJ(1-6)-99-1-0.5ML-2UL
                      -205-35MIN.M (Sequence Method)
    Last changed    : 5/29/2016 9:29:13 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  13.415 BB    0.2245 1046.47876   72.44518  50.5160
       2  15.494 BB    0.2699 1025.09985   59.83932  49.4840

    Totals :                  2071.57861  132.28451

1260HPLC-DAD 5/29/2016 9:29:22 PM SYSTEM                       Page   1 of 2
```

Data File E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\014-1301.D
Sample Name: WQ-2-182-7

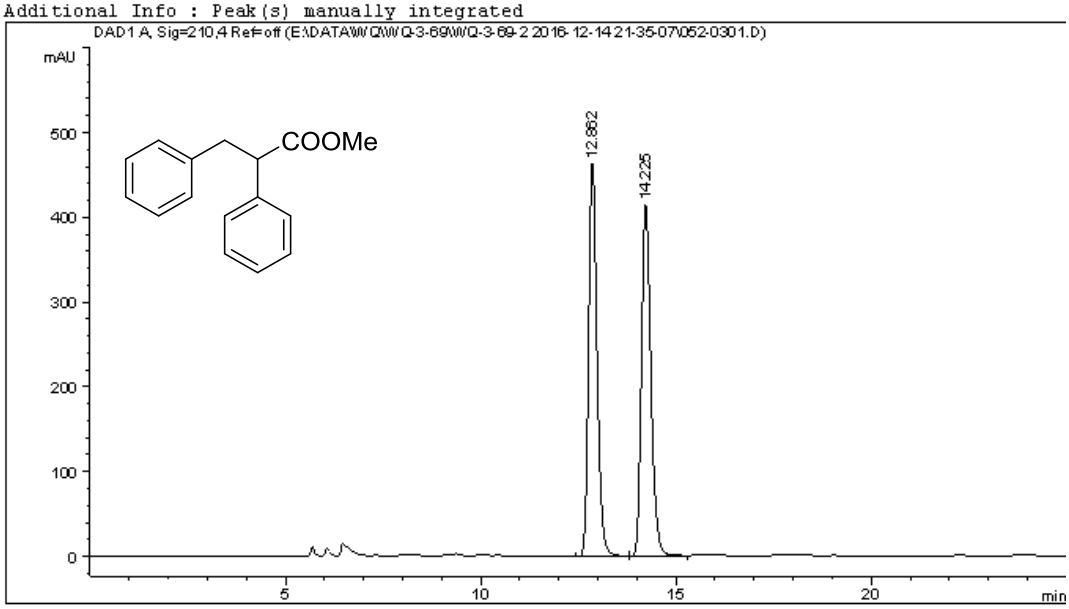
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  13
Acq. Instrument : 1260HPLC-DAD                    Location : Vial 14
Injection Date  : 5/7/2016 6:04:36 PM                 Inj :   1
                                                  Inj Volume : 2.000 µl
Acq. Method     : E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\DAD-OJ(1-6)-99-1-0.5ML-2UL
                  -205-35MIN.M
Last changed    : 5/7/2016 12:44:53 PM by SYSTEM
Analysis Method : E:\DATA\WQ\WQ-2-182\WQ-2-182 2016-05-07 12-26-34\DAD-OJ(1-6)-99-1-0.5ML-2UL
                  -205-35MIN.M (Sequence Method)
Last changed    : 5/29/2016 9:33:08 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.167 MM    0.2439 1.55318e4  1061.47192  97.6515
   2  15.231 MM    0.2697  373.53757   23.07980   2.3485

Totals :                  1.59053e4  1084.55173
```

(*S*)-2,3-diphenylpropanoic acid **8r**

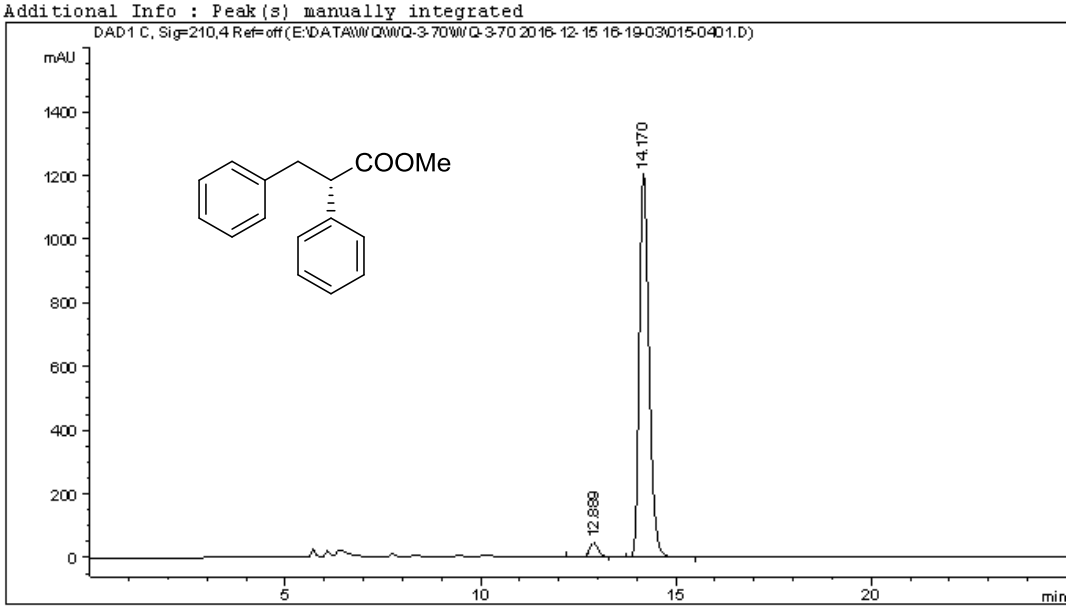
```
Data File E:\DATA\WQ\WQ-3-69\WQ-3-69-2 2016-12-14 21-35-07\052-0301.D
Sample Name: WQ-3-69-2

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-DAD                    Location : Vial 52
    Injection Date  : 12/14/2016 10:47:59 PM             Inj :   1
                                                    Inj Volume : 1.000 µl
    Acq. Method     : E:\DATA\WQ\WQ-3-69\WQ-3-69-2 2016-12-14 21-35-07\DAD-OD(1-2)-99-1-1UL-0.
                      5ML-210NM-60MIN.M
    Last changed    : 12/14/2016 9:35:07 PM by SYSTEM
    Analysis Method : E:\DATA\WQ\WQ-3-69\WQ-3-69-2 2016-12-14 21-35-07\DAD-OD(1-2)-99-1-1UL-0.
                      5ML-210NM-60MIN.M (Sequence Method)
    Last changed    : 12/19/2016 9:08:34 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  12.862 BB    0.2286 6941.72656  463.73779  50.0201
       2  14.225 BB    0.2555 6936.13574  413.99414  49.9799

    Totals :                  1.38779e4   877.73193


    ======================================================================
                            *** End of Report ***

1260HPLC-DAD 12/19/2016 9:08:43 AM SYSTEM                    Page 1 of 1
```

Data File E:\DATA\WQ\WQ-3-70\WQ-3-70 2016-12-15 16-19-03\015-0401.D
Sample Name: WQ-3-70-2

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 15
    Injection Date  : 12/15/2016 5:07:58 PM               Inj :   1
                                                   Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\WQ\WQ-3-70\WQ-3-70 2016-12-15 16-19-03\DAD-0D(1-2)-99-1-0.5ML-
                      2UL-25MIN.M
    Last changed    : 12/15/2016 4:19:03 PM by SYSTEM
    Analysis Method : E:\DATA\WQ\WQ-3-70\WQ-3-70 2016-12-15 16-19-03\DAD-0D(1-2)-99-1-0.5ML-
                      2UL-25MIN.M (Sequence Method)
    Last changed    : 12/19/2016 9:10:49 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  12.889 BB    0.2279  660.16901   44.29417   3.0872
       2  14.170 BB    0.2649 2.0724le4  1203.23914  96.9128

    Totals :                  2.13843e4  1247.53331


    ======================================================================
                              *** End of Report ***
```

Ⅵ. Reference

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