

Supporting Information

Organocatalytic Enantioselective Decarboxylative Protonation of α -Alkyl- α -Aryl Malonate Monoesters

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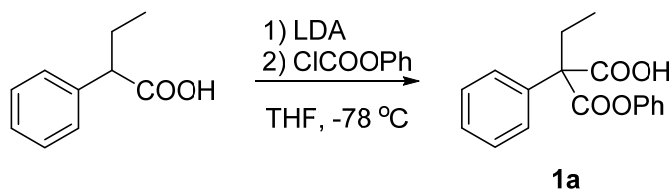
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1. General information

All reagents and organic solvents were purchased from TCI, Sigma-Aldrich, Adamas-beta and Energy Chemical of the highest purity grade and used without further purification unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on Bruker Avance or Joel 400 MHz spectrometers. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. HRMS-ESI spectra were recorded on Waters Micromass GCT Premier. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. Melting points were measured without correction. HPLC spectra were measured using a Thermo 3000. The **C1** and **C6** catalysts were purchased from Adamas-beta and used without further purification. The known Cinchona alkaloid catalysts **C2-C5** were prepared according to literature method.¹ The chiral 1,2-*trans*-diaminocyclohexane derived organocatalysts **C7-C14** were synthesized based on the literature method.²

2. The procedure of preparation and corresponding spectral characterizations of α -alkyl- α -aryl malonate monoesters **1**



LDA (23 mL, 45.8 mmol, 2 M in hexanes) was added to a flame-dried round bottom flask containing anhydrous THF (60 mL) at $-78\text{ }^{\circ}\text{C}$ under argon. A solution of 2-phenylbutanoic acid (3 g, 18.3 mmol) dissolved in THF (10 mL) was added dropwise to the LDA solution. The solution was allowed to warm to room temperature and stir for four hours. The solution was then cooled to $-78\text{ }^{\circ}\text{C}$ and the dianion was allowed to react with phenylchloroformate (3.4 g, 22 mmol). The reaction was stirred overnight and quenched with HCl (3 M). Diethyl ether (25 mL) was added to the reaction mixture and two resulting phases were separated. The aqueous phase was acidified with 3 M HCl to pH = 3 and extracted three times with diethyl ether (20 mL) and the combined organic phases were washed three times with brine, and dried over anhydrous sodium sulfate. The solvent was removed in vacuo at $-20\text{ }^{\circ}\text{C}$. The remaining residue was purified by silica gel column chromatography (hexane/ethyl acetate =10/1) to afford the desired product **1a** as a white solid (2.3 g, 44%). (Note: α -Alkyl- α -aryl substituted malonate phenyl monoesters demonstrate stability at $-30\text{ }^{\circ}\text{C}$ when stored in a refrigerator. However, after a period of three weeks, less than 5% of the decarboxylative protonation product was observed. The racemic decarboxylative protonation product could be removed by washing the crude mixture with petroleum ether.)

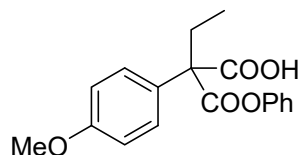
2-(phenoxycarbonyl)-2-phenylbutanoic acid (1a): white solid, Mp: $82\text{--}83\text{ }^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3): δ 7.56 – 7.53 (m, 2H), 7.43 – 7.33 (m, 5H), 7.26 – 7.22 (m, 1H), 7.04 – 7.01 (m, 2H), 2.68 – 2.52 (m, 2H), 1.09 (t, $J = 7.4\text{ Hz}$, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 175.3, 170.7, 150.5, 136.1, 129.7, 128.8, 128.4, 127.8, 126.5, 121.3, 63.2, 28.6, 9.7.

HRMS-ESI (m/z) Calcd for $\text{C}_{17}\text{H}_{17}\text{O}_4$ [(M + H) $^+$] 285.1121, Found: 285.1130.

IR (KBr): ν (cm^{-1}) 2980, 1744, 1618, 1592, 1492, 1457, 747, 589.



2-(4-methoxyphenyl)-2-(phenoxycarbonyl)butanoic acid (1d)

Compound **1d** was prepared according to the same procedure as the one used for **1a**.

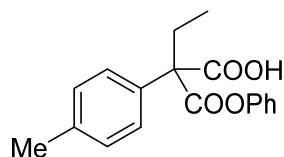
Yield: 81%, white solid, Mp: $81\text{--}83\text{ }^{\circ}\text{C}$.

^1H NMR (400MHz, CDCl_3): δ 7.46 – 7.43 (m, 2H), 7.38 (t, $J = 7.9\text{ Hz}$, 2H), 7.28 - 7.24 (m, 1H), 7.01 (d, $J = 7.8\text{ Hz}$, 2H), 6.95 – 6.92 (m, 2H), 3.82 (s, 3H), 2.71 – 2.51 (m, 2H), 1.11 (t, $J = 7.4\text{ Hz}$, 3H).

^{13}C NMR (100MHz, CDCl_3): δ 175.6, 170.8, 159.4, 150.5, 129.7, 129.2, 127.8, 126.4, 121.3, 114.1, 62.4, 55.4, 28.4, 9.7.

HRMS-ESI (m/z) Calcd for $\text{C}_{18}\text{H}_{19}\text{O}_5$ [(M + H) $^+$] 315.1227, Found: 315.1238.

IR (KBr): ν (cm^{-1}) 3474, 2938, 1742, 1713, 1591, 1254, 829, 799.



2-(phenoxycarbonyl)-2-(p-tolyl)butanoic acid (1e)

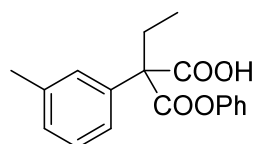
Compound **1e** was prepared according to the same procedure as the one used for **1a**. Yield: 78%, white solid, Mp: 90–91 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.42 – 7.36 (m, 4H), 7.28 – 7.21 (m, 3H), 7.03 – 7.00 (m, 2H), 2.71 – 2.51 (m, 2H), 2.36 (s, 3H), 1.11 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 175.3, 171.0, 150.5, 138.2, 133.0, 129.6, 129.5, 127.7, 126.5, 121.3, 62.8, 28.5, 21.2, 9.7.

HRMS-ESI (m/z) Calcd for $\text{C}_{18}\text{H}_{19}\text{O}_4$ [(M + H) $^+$] 299.1278, Found: 299.1284.

IR (KBr): ν (cm^{-1}) 3446, 1706, 1650, 1630, 1592, 815, 764, 749.



2-(phenoxycarbonyl)-2-(m-tolyl)butanoic acid (1f)

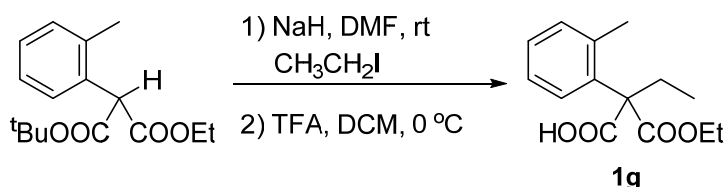
Compound **1f** was prepared according to the same procedure as the one used for **1a**. Yield: 57%, white solid, Mp: 66–67 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.37 – 7.21 (m, 6H), 7.15 (d, J = 7.3 Hz, 1H), 7.03 (d, J = 8.5 Hz, 2H), 2.63 – 2.52 (m, 2H), 2.37 (s, 3H), 1.08 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 175.1, 170.9, 150.5, 138.4, 136.0, 129.6, 129.1, 128.6, 128.4, 126.5, 124.8, 121.3, 63.1, 28.6, 21.8, 9.8.

HRMS-ESI (m/z) Calcd for $\text{C}_{18}\text{H}_{19}\text{O}_4$ [(M + H) $^+$] 299.1278, Found: 299.1283.

IR (KBr): ν (cm^{-1}) 3473, 2979, 1743, 1710, 1591, 1491, 782, 748.



1-(*tert*-butyl) 3-ethyl 2-(*o*-tolyl) malonate (583 mg, 3.1 mmol) was slowly added to a suspension of NaH (126 mg, 3.15 mmol) in 10 mL of DMF at 0 °C. After the solution was stirred for 0.5 h at room temperature, ethyl iodide (983 mg, 6.3 mmol) was added and the mixture was stirred at rt overnight. Then the solution was quenched with saturated NH_4Cl solution. Diethyl ether (25 mL) was added to the reaction mixture and extracted three times with diethyl ether (20 mL) and the combined organic phases were washed three times with brine, and dried over anhydrous sodium sulfate. The

solvent was removed in vacuo. The remaining residue was purified by silica gel column chromatography (hexane/ethyl acetate = 20/1) to afford the alkylated product. A solution of the alkylated product in dry CH₂Cl₂ (1.5 mL) was treated with TFA (0.98 mL, 12.7 mmol), and the reaction was stirred at 0 °C for 10 h. The reaction was concentrated in vacuo, the remaining residue was purified by column chromatography with 5% MeOH in CH₂Cl₂ to afford the desired product **1g** (180 mg, 34%, Colorless oil).

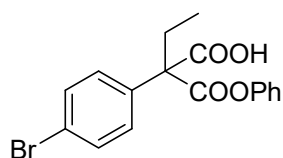
2-(ethoxycarbonyl)-2-(o-tolyl)butanoic acid (1g)

¹H NMR (400MHz, CDCl₃): δ 7.49 – 7.47 (m, 1H), 7.28 – 7.21 (m, 2H), 7.15 – 7.13 (m, 1H), 4.33 – 4.15 (m, 2H), 2.62 – 2.53 (m, 1H), 2.47 – 2.38 (m, 1H), 2.17 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100MHz, CDCl₃): δ 177.8, 172.1, 136.7, 136.0, 131.6, 128.1, 126.7, 126.5, 63.5, 60.1, 30.9, 20.0, 13.8, 9.6.

HRMS-ESI (m/z) Calcd for C₁₄H₁₉O₄ [(M + H)⁺] 251.1278, Found: 251.1285.

IR (KBr): ν (cm⁻¹) 3473, 2985, 1737, 1637, 1488, 1456, 765, 749.



2-(4-bromophenyl)-2-(phenoxycarbonyl)butanoic acid (1h)

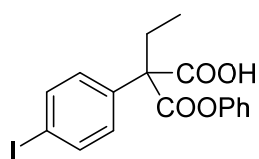
Compound **1h** was prepared according to the same procedure as the one used for **1a**. Yield: 53%, white solid, Mp: 87–89 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.55 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.44 – 7.37 (m, 4H), 7.29 – 7.25(m,1H), 7.01 – 7.00 (m, 2H), 2.65 – 2.50 (m, 2H), 1.10 – 1.06 (m, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 175.3, 169.7, 150.4, 134.8, 131.9, 129.8, 129.7, 126.6, 122.7, 121.2, 62.8, 28.5, 9.5.

HRMS-ESI (m/z) Calcd for C₁₇H₁₆BrO₄ [(M + H)⁺] 363.0226, Found: 363.0232.

IR (KBr): ν (cm⁻¹) 3063, 1744, 1713, 1592, 1492, 1457, 1387, 747, 689.



2-(4-iodophenyl)-2-(phenoxycarbonyl)butanoic acid (1i)

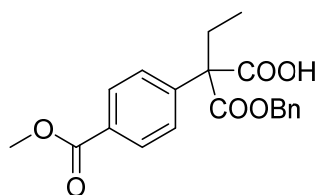
Compound **1i** was prepared according to the same procedure as the one used for **1a**. Yield: 65%, white solid, Mp: 92–94 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.76 – 7.72 (m, 2H), 7.40 – 7.35 (m, 2H), 7.31 – 7.24 (m, 3H), 7.03 – 7.01 (m, 2H), 2.63 – 2.48 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 175.1, 169.7, 150.4, 137.8, 135.6, 129.9, 129.7, 126.6, 121.2, 94.4, 62.9, 28.4, 9.5.

HRMS-ESI (m/z) Calcd for C₁₇H₁₆IO₄ [(M + H)⁺] 411.0088, Found: 411.0089.

IR (KBr): ν (cm⁻¹) 3447, 1739, 1713, 1592, 1489, 817, 745, 687.



2-((benzyloxy)carbonyl)-2-(4-(methoxycarbonyl)phenyl)butanoic acid (**1j**)

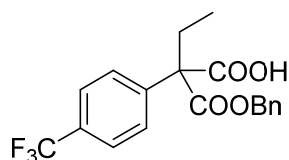
Compound **1j** was prepared according to the same procedure as the one used for **1g**.
Yield: 81%, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 8.02 – 7.96 (m, 2H), 7.45 – 7.39 (m, 2H), 7.32 (dd, J = 4.8, 2.0 Hz, 3H), 7.23 (dd, J = 6.5, 3.1 Hz, 2H), 5.28 – 5.18 (m, 2H), 3.92 (s, 3H), 2.60 – 2.48 (m, 1H), 2.45 – 2.36 (m, 1H), 0.91 (t, J = 7.3 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 173.7, 172.0, 166.7, 141.3, 134.4, 129.7, 129.6, 128.6, 128.6, 128.2, 127.6, 68.2, 62.8, 52.3, 28.5, 9.4.

HRMS-ESI (m/z) Calcd for C₂₀H₂₀O₆ [(M + Na)⁺] 379.1152, Found: 379.1152.

IR (KBr): ν (cm⁻¹) 3676, 2953 1725 1610, 1438, 1282, 745, 597.



2-((benzyloxy)carbonyl)-2-(4-(trifluoromethyl)phenyl)butanoic acid (**1k**)

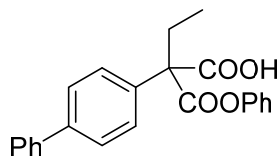
Compound **1k** was prepared according to the same procedure as the one used for **1g**.
Yield: 82%, white solid.

¹H NMR (400MHz, CDCl₃): δ 7.58 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.31 (dd, J = 5.0, 2.1 Hz, 3H), 7.22 (dd, J = 6.7, 2.9 Hz, 2H), 5.27 – 5.11 (m, 2H), 2.50 – 2.40 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H).

¹³C NMR (100MHz, CDCl₃): δ 173.9, 171.7, 140.2, 134.5, 130.2 (q, J = 32.8), 128.7, 128.6, 128.2, 128.1, 125.4, 125.4, 123.8 (q, J = 272.3), 68.1, 62.7, 28.5, 9.4.

HRMS-ESI (m/z) Calcd for C₁₉H₁₇F₃O₄ [(M + Na)⁺] 389.0971, Found: 389.0970.

IR (KBr): ν (cm⁻¹) 2979, 1741, 1705, 1327, 1218, 1126, 887, 749.



2-([1,1'-biphenyl]-4-yl)-2-(phenoxycarbonyl)butanoic acid (**1l**)

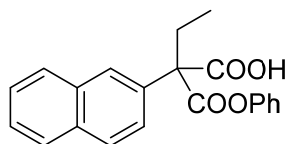
Compound **1l** was prepared according to the same procedure as the one used for **1a**.
Yield: 66%, white solid, Mp: 93–94 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.65 – 7.59 (m, 6H), 7.45 (t, J = 7.5 Hz, 2H), 7.37 (q, J = 8.1 Hz, 3H), 7.28 – 7.24 (m, 1H), 7.06 (d, J = 8.0 Hz, 2H), 2.74 – 2.57 (m, 2H), 1.14 (t, J = 4.0 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 175.0, 170.8, 150.5, 141.2, 140.4, 135.0, 129.7, 129.0, 128.3, 127.7, 127.5, 127.3, 126.6, 121.3, 62.9, 28.6, 9.8.

HRMS-ESI (m/z) Calcd for C₂₃H₂₁O₄ [(M + H)⁺] 361.1434, Found: 361.1446.

IR (KBr): ν (cm⁻¹) 3474, 2979, 1743, 1710, 1618, 1591, 1488, 834, 764, 749.



2-(naphthalen-2-yl)-2-(phenoxy-carbonyl)butanoic acid (1m)

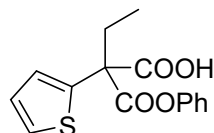
Compound **1m** was prepared according to the same procedure as the one used for **1a**. Yield: 73%, white solid, Mp: 79–81 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.02 (d, $J = 1.3$ Hz, 1H), 7.89 – 7.83 (m, 3H), 7.61 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.53 – 7.50 (m, 2H), 7.37 (t, $J = 7.9$ Hz, 2H), 7.25 (t, $J = 7.4$ Hz, 1H), 7.02 (d, $J = 7.9$ Hz, 2H), 2.82 – 2.65 (m, 2H), 1.16 (t, $J = 7.4$ Hz, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 174.6, 170.9, 150.5, 133.5, 133.2, 132.9, 129.7, 128.5, 128.4, 127.6, 127.0, 126.8, 126.6, 126.5, 125.6, 121.3, 63.2, 28.7, 9.8.

HRMS-ESI (m/z) Calcd for $\text{C}_{21}\text{H}_{19}\text{O}_4$ [(M + H) $^+$] 335.1278, Found: 335.1287.

IR (KBr): ν (cm^{-1}) 3454, 1647, 1632, 1492, 1457, 815, 745, 688.



2-(phenoxy-carbonyl)-2-(thiophen-2-yl)butanoic acid (1n)

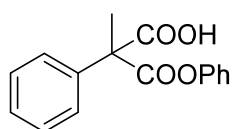
Compound **1n** was prepared according to the same procedure as the one used for **1a**. Yield: 59%, white solid, Mp: 72–73 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.40 – 7.35 (m, 3H), 7.27 – 7.24 (m, 2H), 7.09 – 7.04 (m, 3H), 2.68 – 2.53 (m, 2H), 1.05 (t, $J = 7.4$ Hz, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 174.3, 168.9, 150.5, 138.1, 129.6, 127.2, 126.6, 126.5, 126.5, 121.2, 60.7, 31.0, 9.4.

HRMS-ESI (m/z) Calcd for $\text{C}_{15}\text{H}_{15}\text{SO}_4$ [(M + H) $^+$] 291.0686, Found: 291.0688.

IR (KBr): ν (cm^{-1}) 3474, 2977, 1719, 1592, 1491, 1457, 747, 703.



2-methyl-3-oxo-3-phenoxy-2-phenylpropanoic acid (1o)

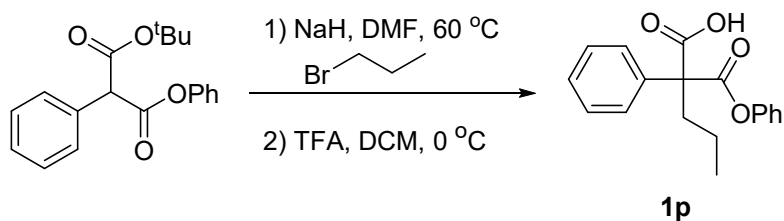
Compound **1o** was prepared according to the same procedure as the one used for **1a**. Yield: 75%, white solid, Mp: 76–77 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.54 – 7.51 (m, 2H), 7.42 – 7.33 (m, 5H), 7.24 – 7.20 (m, 1H), 7.08 – 7.06 (m, 2H), 2.06 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 177.3, 170.1, 150.7, 137.0, 129.6, 128.6, 128.4, 127.6, 126.4, 121.3, 58.9, 22.0.

HRMS-ESI (m/z) Calcd for $\text{C}_{16}\text{H}_{15}\text{O}_4$ [(M + H) $^+$] 271.0965, Found: 271.0973.

IR (KBr): ν (cm^{-1}) 3271, 1747, 1713, 1591, 1492, 1457, 745, 694.



2-(phenoxycarbonyl)-2-phenylpentanoic acid (**1p**)

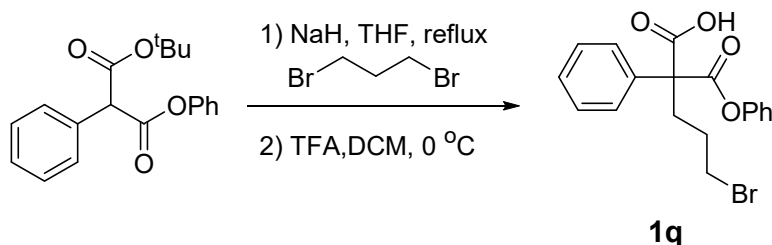
Compound **1p** was prepared according to the same procedure as the one used for **1g**.
Yield: 31%, white solid, Mp: 66–67 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.42 – 7.33 (m, 5H), 7.26 – 7.22 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.54 – 2.46 (m, 2H), 1.47 – 1.44 (m, 2H), 1.03 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 174.7, 171.2, 150.4, 136.4, 129.7, 128.8, 128.3, 127.6, 126.5, 121.2, 62.5, 37.5, 18.7, 14.5.

HRMS-ESI (m/z) Calcd for C₁₈H₁₉O₄ [(M + H)⁺] 299.1278, Found: 299.1284.

IR (KBr): ν (cm⁻¹) 3412, 2965, 1743, 1710, 1591, 1492, 1448, 744, 689.



5-bromo-2-(phenoxycarbonyl)-2-phenylpentanoic acid (**1q**)

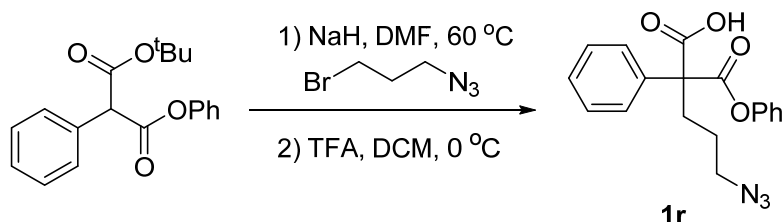
Compound **1q** was prepared according to the same procedure as the one used for **1g**.
Yield: 30%, white solid, Mp: 117–119 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.55 – 7.52 (m, 2H), 7.44 – 7.34 (m, 5H), 7.26 – 7.23 (m, 1H), 7.07 – 7.04 (m, 2H), 3.50 – 3.41 (m, 2H), 2.69 – 2.65 (m, 2H), 2.07 – 1.90 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 174.6, 170.1, 150.4, 135.8, 129.7, 128.9, 128.5, 127.7, 126.5, 121.2, 62.2, 34.3, 33.3, 28.3.

HRMS-ESI (m/z) Calcd for C₁₈H₁₈BrO₄ [(M + H)⁺] 377.0383, Found: 377.0390.

IR (KBr): ν (cm⁻¹) 3413, 3063, 1743, 1715, 1590, 1491, 1447, 766, 748.



5-azido-2-(phenoxycarbonyl)-2-phenylpentanoic acid (**1r**)

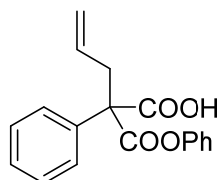
Compound **1r** was prepared according to the same procedure as the one used for **1g**.
Yield: 35%, white solid, Mp: 55–57 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.45 – 7.37 (m, 5H), 7.28 – 7.25 (m, 1H), 7.05 – 7.03 (m, 2H), 3.46 – 3.34 (m, 2H), 2.64 – 2.57 (m, 2H), 1.77 – 1.68 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 174.7, 170.2, 150.4, 135.7, 129.7, 128.9, 128.5, 127.6, 126.6, 121.2, 62.3, 51.4, 32.8, 24.8.

HRMS-ESI (m/z) Calcd for C₁₈H₁₈N₃O₄ [(M + H)⁺] 340.1292, Found: 340.1291.

IR (KBr): ν (cm⁻¹) 2936, 2098, 1744, 1591, 1492, 1448, 746, 689.



2-(4-isobutylphenyl)-2-phenylpent-4-enoic acid (1s)

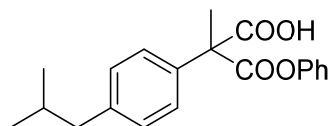
Compound **1s** was prepared according to the same procedure as the one used for **1g**. Yield: 44%, white solid, Mp: 76–77 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.55 – 7.53 (m, 2H), 7.44 – 7.35 (m, 5H), 7.27 – 7.23 (m, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 5.96 – 5.85 (m, 1H), 5.31 – 5.20 (m, 2H), 3.37 (dd, *J* = 14.1, 6.7 Hz, 1H), 3.25 (dd, *J* = 14.0, 7.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 173.4, 171.2, 150.4, 136.0, 132.2, 129.7, 128.9, 128.5, 127.5, 126.6, 121.2, 120.2, 62.4, 39.9.

HRMS-ESI (m/z) Calcd for C₁₈H₁₇O₄ [(M + H)⁺] 297.1121, Found: 297.1126.

IR (KBr): ν (cm⁻¹) 3063, 1747, 1713, 1629, 1591, 1492, 796, 746.



2-(4-isobutylphenyl)-2-methyl-3-oxo-3-phenoxypropanoic acid (1t)

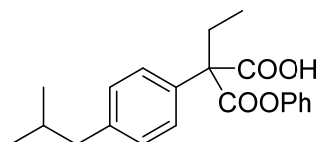
Compound **1t** was prepared according to the same procedure as the one used for **1a**. Yield: 53%, white solid, Mp: 60–62 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.24 – 7.16 (m, 3H), 7.07 (d, *J* = 7.6 Hz, 2H), 2.48 (d, *J* = 7.2 Hz, 2H), 2.05 (s, 3H), 1.92 – 1.82 (m, 1H), 0.91 (d, *J* = 7.6 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 177.2, 170.4, 150.8, 141.9, 134.2, 129.6, 129.4, 127.3, 126.3, 121.3, 58.6, 45.1, 30.2, 22.6, 22.1.

HRMS-ESI (m/z) Calcd for C₂₀H₂₃O₄ [(M + H)⁺] 327.1591, Found: 327.1604.

IR (KBr): ν (cm⁻¹) 3412, 2954, 1748, 1713, 1592, 1514, 1383, 739, 687.



2-(4-isobutylphenyl)-2-(phenoxycarbonyl)butanoic acid (1u)

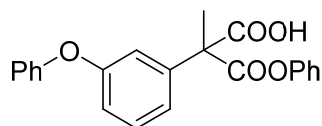
Compound **1u** was prepared according to the same procedure as the one used for **1a**. Yield: 56%, white solid, Mp: 68–70 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.25 – 7.22 (m, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 2.66 – 2.50 (m, 2H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.90 – 1.82 (m, 1H), 1.08 (t, *J* = 7.4 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 174.5, 171.4, 150.4, 141.9, 133.4, 129.6, 129.5, 127.3, 126.5, 121.2, 62.8, 45.1, 30.2, 28.6, 22.5, 9.8.

HRMS-ESI (m/z) Calcd for C₂₁H₂₅O₄ [(M + H)⁺] 341.1747, Found: 341.1758.

IR (KBr): ν (cm⁻¹) 3414, 1746, 1710, 1638, 1618, 1492, 764, 749.



2-methyl-3-oxo-3-phenoxy-2-(3-phenoxyphenyl)propanoic acid (1v)

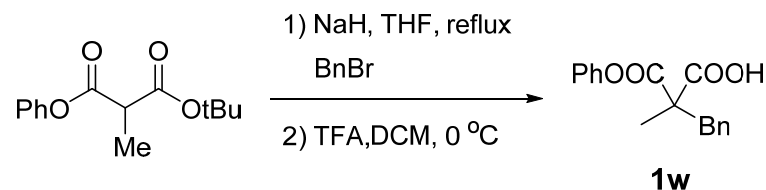
Compound **1v** was prepared according to the same procedure as the one used for **1a**. Yield: 56%, white solid, Mp: 116–117 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.30 (m, 5H), 7.27 – 7.20 (m, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 4H), 6.98 (dd, *J* = 8.0, 2.1 Hz, 1H), 2.04 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 176.7, 169.8, 157.4, 157.0, 150.6, 138.9, 130.0, 129.9, 129.6, 126.4, 123.6, 122.4, 121.3, 119.1, 118.5, 118.5, 58.8, 22.1.

HRMS-ESI (m/z) Calcd for C₂₂H₁₉O₅ [(M + H)⁺] 363.1227, Found: 363.1232.

IR (KBr): ν (cm⁻¹) 3451, 1747, 1714, 1592, 1488, 1223, 750, 689.



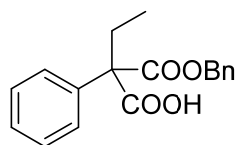
2-benzyl-2-methyl-3-oxo-3-phenoxypropanoic acid (1w)

Compound **1w** was prepared according to the same procedure as the one used for **1g**. Yield: 52%, white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.39 (t, *J* = 7.9 Hz, 2H), 7.33 – 7.26 (m, 6H), 7.06 (d, *J* = 7.8 Hz, 2H), 3.47 (d, *J* = 13.7 Hz, 1H), 3.32 (d, *J* = 13.7 Hz, 1H), 1.57 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 178.0, 170.2, 150.6, 135.5, 130.5, 129.6, 128.5, 127.4, 126.3, 121.4, 55.3, 41.2, 20.1.

HRMS-ESI (m/z) calcd for C₁₇H₁₆O₄Na [(M + Na)⁺] 309.0941, found 309.0947.



2-((benzyloxy)carbonyl)-2-phenylbutanoic acid (1b)

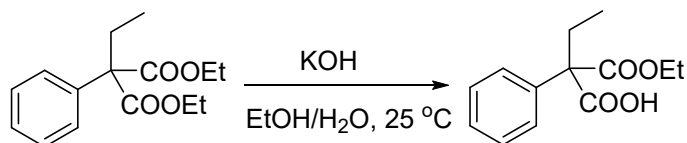
Compound **1b** was prepared according to the same procedure as the one used for **1a**. Yield: 88%, white solid, Mp: 79–80 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.30 (m, 8H), 7.23 – 7.21 (m, 2H), 5.22 (q, *J* = 12.3 Hz, 2H), 2.57 – 2.35 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 173.8, 173.4, 136.8, 134.7, 128.7, 128.7, 128.3, 128.2, 127.2, 68.2, 62.7, 28.6, 9.8.

HRMS-ESI (m/z) Calcd for C₁₈H₁₈O₄Na [(M + Na)⁺] 321.1097, Found: 321.1103.

IR (KBr): ν (cm⁻¹) 3446, 2977, 1735, 1711, 1601, 1498, 1455, 735, 696.



1c

A solution of 1.27 g (22.7 mmol) of KOH in 11 mL of H₂O is added dropwise to a solution of 3.0 g (11.4 mmol) of diethyl 2-ethyl-2-phenylmalonate in 26 mL of cold ethanol (0-5 °C). Agitation is continued for 24 hours at 25 °C and the solvent is evaporated off. The residue is separated with H₂O and diethylether. After decantation, the aqueous layer is acidified at 0 °C with 3N HCl and extracted with diethylether (50 mL × 2). The solution was evaporated in vacuo, the remaining residue was purified by recrystallization with PE and DCM to afford the desired product **1c** as a white solid (2 g, 74%).

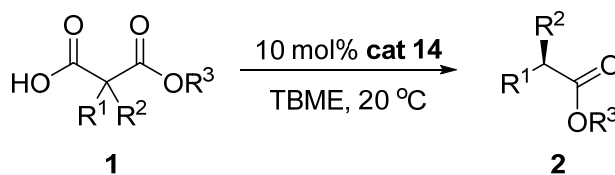
¹H NMR (400 MHz, CDCl₃): δ 7.40 – 7.31 (m, 5H), 4.36 – 4.22 (m, 2H), 2.61 – 2.52 (m, 1H), 2.43 – 2.34 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 174.8, 173.0, 137.2, 128.8, 128.2, 126.9, 62.9, 62.5, 28.7, 13.9, 9.9.

HRMS-ESI (m/z) Calcd for C₁₃H₁₇O₄ [(M + H)⁺] 237.1121, Found: 237.1123.

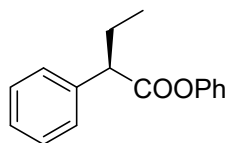
IR (KBr): ν (cm⁻¹) 3509, 2981, 1708, 1601, 1498, 1447, 760, 697.

3. Representative procedure for the enantioselective decarboxylative protonation and spectral characterizations of the products 2



To a mixture of catalyst **C14** (0.01 mmol), disubstituted malonic acid half-esters **1** (0.1 mmol) in a vial (4.0 mL) were added TBME (1.0 mL). Then the reaction mixture was stirred at 20 °C and was monitored by TLC. After completion, the reaction mixture was concentrated in vacuo, and the remaining residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product **2**.

(*R*)-phenyl-2-phenylbutanoate (**2a**):



Yield: 98%; ee: 91%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -68^{\circ}$ (0.44, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.42 – 7.28 (m, 7H), 7.19 (t, $J = 7.5$ Hz, 1H), 7.00 – 6.98 (m, 2H), 3.70 (t, $J = 7.7$ Hz, 1H), 2.28 – 2.17 (m, 1H), 1.96 – 1.85 (m, 1H), 1.00 (t, $J = 7.4$ Hz, 3H).

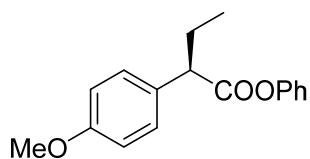
$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.7, 150.9, 138.7, 129.5, 128.9, 128.2, 127.5, 125.9, 121.6, 53.6, 26.9, 12.3.

HRMS-ESI (m/z) Calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2$ [$(\text{M} + \text{H})^+$] 241.1223, Found: 241.1229.

IR (KBr): ν (cm^{-1}) 3478, 2966, 1754, 1618, 1592, 1491, 764, 748.

HPLC: Chiralcel OJ-H (25 cm \times 0.46 cm), hexane/2-propanol = 90/10, 1.0 mL/min, 210 nm, 25 °C, $t_{\text{R}} = 8.72$ min (minor), 10.09 min (major).

(*R*)-phenyl-2-(4-methoxyphenyl) butanoate (**2d**):



Yield: 96%; ee: 91%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -65^{\circ}$ (0.23, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.35 – 7.31 (m, 4H), 7.21 – 7.17 (m, 1H), 6.99 – 6.97 (m, 2H), 6.91 – 6.89 (m, 2H), 3.81 (s, 3H), 3.64 (t, $J = 7.7$ Hz, 1H), 2.25 – 2.14 (m, 1H), 1.93 – 1.82 (m, 1H), 0.99 (t, $J = 7.4$ Hz, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.9, 159.0, 150.9, 130.7, 129.4, 129.1, 125.8, 121.6, 114.2, 55.4, 52.7, 26.8, 12.2.

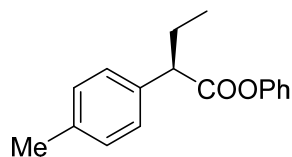
HRMS-ESI (m/z) Calcd for $\text{C}_{17}\text{H}_{19}\text{O}_3$ [$(\text{M} + \text{H})^+$] 271.1329, Found: 271.1338.

IR (KBr): ν (cm^{-1}) 3414, 2932, 1753, 1610, 1592, 1511, 1252, 816, 750.

HPLC: Chiralcel OJ-H (25 cm \times 0.46 cm), hexane/2-propanol = 90/10, 1.0 mL/min,

204 nm, 25 °C, t_R = 27.54 min (minor), 38.92 min (major).

(R)-phenyl -2-(p-tolyl) butanoate (2e):



Yield: 91%; ee: 91%.

Colorless oil, $[\alpha]_D^{20}$ = -74° (0.39, CHCl₃).

¹H NMR (400 MHz, CDCl₃): δ 7.34 – 7.27 (m, 4H), 7.20 – 7.16 (m, 3H), 7.00 – 6.97 (m, 2H), 3.66 (t, J = 7.7 Hz, 1H), 2.35 (s, 3H), 2.26 – 2.15 (m, 1H), 1.93 – 1.83 (m, 1H), 0.99 (t, J = 7.4 Hz, 3H).

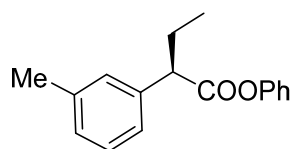
¹³C NMR (100 MHz, CDCl₃): δ 172.8, 151.0, 137.2, 135.7, 129.5, 129.4, 128.0, 125.8, 121.6, 53.2, 26.9, 21.2, 12.3.

HRMS-ESI (m/z) Calcd for C₁₇H₁₉O₂ [(M + H)⁺] 255.1380, Found: 255.1388.

IR (KBr): ν (cm⁻¹) 3450, 2964, 1754, 1646, 1513, 1491, 749, 687.

HPLC: Chiralcel OJ-H (25 cm × 0.46 cm), hexane/2-propanol = 90/10, 1.0 mL/min, 204 nm, 25 °C, t_R = 15.59 min (major), 18.64 min (minor).

(R)-phenyl -2-(m-tolyl) butanoate (2f):



Yield: 91%; ee: 90%.

Colorless oil, $[\alpha]_D^{20}$ = -65° (0.24, CHCl₃).

¹H NMR (400 MHz, CDCl₃): δ 7.35 – 7.31 (m, 2H), 7.27 – 7.23 (m, 1H), 7.20 – 7.16 (m, 3H), 7.10 (d, J = 7.2 Hz, 1H), 7.00 – 6.98 (m, 2H), 3.65 (t, J = 7.7 Hz, 1H), 2.36 (s, 3H), 2.26 – 2.16 (m, 1H), 1.94 – 1.83 (m, 1H), 0.99 (t, J = 7.4 Hz, 3H).

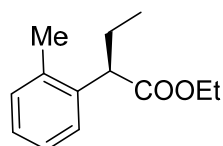
¹³C NMR (100 MHz, CDCl₃): δ 172.8, 150.9, 138.7, 138.5, 129.4, 128.9, 128.7, 128.3, 125.8, 125.1, 121.6, 53.6, 26.9, 21.6, 12.3.

HRMS-ESI (m/z) Calcd for C₁₇H₁₉O₂ [(M + H)⁺] 255.1380, Found: 255.1385.

IR (KBr): ν (cm⁻¹) 3451, 2965, 1755, 1630, 1592, 1491, 767, 749.

HPLC: Chiralcel OJ-H (25 cm × 0.46 cm), hexane/2-propanol = 90/10, 1.0 mL/min, 204 nm, 25 °C, t_R = 12.10 min (minor), 13.76 min (major).

(R)-ethyl-2-(o-tolyl) butanoate (2g):



Yield: 90%; ee: 89%.

Colorless oil, $[\alpha]_D^{20}$ = -60° (0.13, CHCl₃).

¹H NMR (400 MHz, CDCl₃): δ 7.32 (d, J = 7.2 Hz, 1H), 7.19 – 7.13 (m, 3H), 4.16 – 4.05 (m, 2H), 3.73 (t, J = 8 Hz, 1H), 2.38 (s, 3H), 2.17 – 2.06 (m, 1H), 1.81 – 1.70 (m, 1H), 1.20 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.4 Hz, 3H).

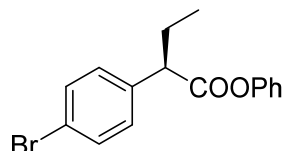
¹³C NMR (100 MHz, CDCl₃): δ 174.4, 137.9, 136.3, 130.5, 126.9, 126.8, 126.4, 60.7, 48.8, 26.4, 20.0, 14.3, 12.4.

HRMS-ESI (m/z) Calcd for C₁₃H₁₉O₂ [(M + H)⁺] 207.1380, Found: 207.1383.

IR (KBr): ν (cm⁻¹) 3415, 2965, 1733, 1636, 1490, 1463, 750, 732.

HPLC: Chiralcel OJ-H (25 cm × 0.46 cm), hexane/2-propanol = 99.8/0.2, 0.6 mL/min, 204 nm, 25 °C, t_R = 11.24 min (major), 12.21 min (minor).

(R)-phenyl-2-(4-bromophenyl) butanoate (2h):



Yield: 99%; ee: 86%.

Colorless oil, [α]_D²⁰ = -64° (0.18, CHCl₃).

¹H NMR (400 MHz, CDCl₃): 7.50 – 7.47 (m, 2H), 7.36 – 7.32 (m, 2H), 7.29 – 7.27 (m, 2H), 7.22 – 7.18 (m, 1H), 6.99 – 6.97 (m, 2H), 3.66 (t, *J* = 7.7 Hz, 1H), 2.26 – 2.15 (m, 1H), 1.93 – 1.82 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H).

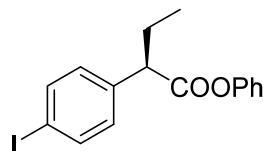
¹³C NMR (100 MHz, CDCl₃): δ 172.2, 150.7, 137.7, 132.0, 129.9, 129.5, 126.0, 121.5, 121.5, 53.0, 26.8, 12.2.

HRMS-ESI (m/z) Calcd for C₁₆H₁₆BrO₂ [(M + H)⁺] 319.0328, Found: 319.0337.

IR (KBr): ν (cm⁻¹) 3461, 2965, 1754, 1592, 1489, 1456, 815, 749.

HPLC: Chiralcel OJ-H (25 cm × 0.46 cm), hexane/2-propanol = 95/5, 1.0 mL/min, 204 nm, 25 °C, t_R = 16.46 min (minor), 23.39 min (major).

(R)-phenyl-2-(4-iodophenyl) butanoate (2i):



Yield: 94%; ee: 85%.

Colorless oil, [α]_D²⁰ = -59° (0.13, CHCl₃).

¹H NMR (400 MHz, CDCl₃): δ 7.71 – 7.68 (m, 2H), 7.36 – 7.32 (m, 2H), 7.22 – 7.18 (t, *J* = 7.7 Hz, 1H), 7.17 – 7.14 (m, 2H), 6.98 (d, *J* = 7.7 Hz, 2H), 3.64 (t, *J* = 7.7 Hz, 1H), 2.26 – 2.15 (m, 1H), 1.93 – 1.82 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H).

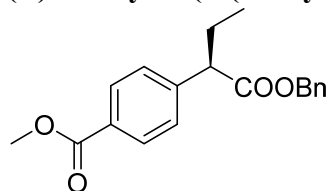
¹³C NMR (100 MHz, CDCl₃): δ 172.2, 150.8, 138.4, 137.9, 130.2, 129.5, 126.0, 121.5, 93.1, 53.1, 26.8, 12.2.

HRMS-ESI (m/z) Calcd for C₁₆H₁₆IO₂ [(M + H)⁺] 367.0189, Found: 367.0195.

IR (KBr): ν (cm⁻¹) 3477, 2964, 1755, 1638, 1592, 1485, 814, 750.

HPLC: Chiralcel OJ-H (25 cm × 0.46 cm), hexane/2-propanol = 95/5, 1.0 mL/min, 204 nm, 25 °C, t_R = 17.77 min (minor), 31.39 min (major).

(R)-methyl-4-(1-(benzyloxy)-1-oxobutan-2-yl)benzoate (2j):



Yield: 97%; ee: 84%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -6^{\circ}$ (0.21, CHCl_3).

^1H NMR (400 MHz, CDCl_3): δ 7.98 (d, $J = 8.2$ Hz, 2H), 7.38 (d, $J = 8.2$ Hz, 2H), 7.34 – 7.28 (m, 3H), 7.24 (m, 2H), 5.26 – 4.97 (m, 2H), 3.91 (s, 3H), 3.57 (t, $J = 7.7$ Hz, 1H), 2.19 – 2.08 (m, 1H), 1.88 – 1.77 (m, 1H), 0.88 (t, $J = 7.3$ Hz, 3H).

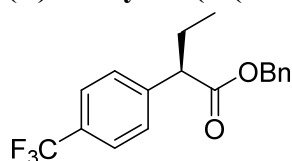
^{13}C NMR (100 MHz, CDCl_3): δ 173.2, 166.9, 144.0, 135.7, 129.8, 129.1, 128.5, 128.2, 128.1, 128.0, 66.6, 53.4, 52.1, 26.6, 12.0.

HRMS-ESI (m/z) Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_4$ $[(\text{M} + \text{H})^+]$ 313.1434, Found: 313.1437.

IR (KBr): ν (cm^{-1}) 2966, 2406, 1725, 1559, 1281, 1162, 921, 746.

HPLC: Chiralcel OJ-H (25 cm \times 0.46 cm), hexane/2-propanol = 80/20, 1.0 mL/min, 254 nm, 25 $^{\circ}\text{C}$, $t_{\text{R}} = 12.56$ min (minor), 17.99 min (major).

(R)-benzyl 2-(4-(trifluoromethyl)phenyl)butanoate (2k)



Yield: 99%; ee: 78%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -4^{\circ}$ (0.11, CHCl_3).

^1H NMR (400 MHz, CDCl_3): δ 7.57 (d, $J = 8.2$ Hz, 2H), 7.42 (d, $J = 8.1$ Hz, 2H), 7.36 – 7.29 (m, 3H), 7.26 – 7.22 (m, 2H), 5.46 – 4.85 (m, 2H), 3.57 (t, $J = 7.7$ Hz, 1H), 2.20 – 2.09 (m, 1H), 1.88 – 1.77 (m, 1H), 0.89 (t, $J = 7.3$ Hz, 3H).

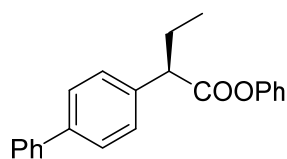
^{13}C NMR (100 MHz, CDCl_3): δ 173.1, 142.8, 135.7, 129.5 (q, $J = 32.8$), 128.5, 128.4, 128.2, 128.0, 125.5, 125.5, 122.8, 66.6, 53.2, 26.6, 12.0.

HRMS-ESI (m/z) Calcd for $\text{C}_{18}\text{H}_{17}\text{F}_3\text{O}_2$ $[(\text{M} + \text{Na})^+]$ 345.1073, Found: 345.1083.

IR (KBr): ν (cm^{-1}) 3662, 2966, 2235, 1736, 1261, 1123, 801, 751.

HPLC: Chiralcel OJ-H (25 cm \times 0.46 cm), hexane/2-propanol = 98/2, 1.0 mL/min, 210 nm, 25 $^{\circ}\text{C}$, $t_{\text{R}} = 9.08$ min (minor), 11.53 min (major).

(R)-phenyl 2-([1,1'-biphenyl]-4-yl) butanoate (2l):



Yield: 98%; ee: 90%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -69^{\circ}$ (0.44, CHCl_3).

^1H NMR (400 MHz, CDCl_3): δ 7.61 – 7.58 (m, 4H), 7.49 – 7.42 (m, 4H), 7.36 – 7.32 (m, 3H), 7.21 – 7.17 (m, 1H), 7.02 – 7.00 (m, 2H), 3.74 (t, $J = 7.7$ Hz, 1H), 2.32 – 2.21 (m, 1H), 2.00 – 1.89 (m, 1H), 1.03 (t, $J = 7.4$ Hz, 3H).

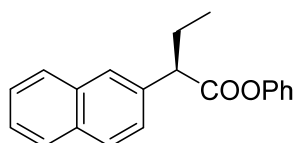
^{13}C NMR (100 MHz, CDCl_3): δ 172.7, 150.9, 140.8, 140.5, 137.8, 129.5, 128.9, 128.6, 127.6, 127.5, 127.2, 125.9, 121.6, 53.3, 26.9, 12.3.

HRMS-ESI (m/z) Calcd for $\text{C}_{22}\text{H}_{21}\text{O}_2$ $[(\text{M} + \text{H})^+]$ 317.1536, Found: 317.1539.

IR (KBr): ν (cm^{-1}) 3476, 2965, 1753, 1619, 1592, 1486, 816, 748.

HPLC: Chiralcel OJ-H (25 cm \times 0.46 cm), hexane/2-propanol = 85/15, 1.0 mL/min, 204 nm, 35 $^{\circ}\text{C}$, $t_{\text{R}} = 19.86$ min (minor), 23.97 min (major).

(R)-phenyl 2-(naphthalen-2-yl) butanoate (2m):



Yield: 99%; ee: 91%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -91^{\circ}$ (0.26, CHCl_3).

^1H NMR (400 MHz, CDCl_3): δ 7.87 – 7.83 (m, 4H), 7.56 – 7.47 (m, 3H), 7.34 – 7.30 (m, 2H), 7.20 – 7.16 (m, 1H), 6.99 – 6.97 (m, 2H), 3.87 (t, $J = 7.7$ Hz, 1H), 2.38 – 2.27 (m, 1H), 2.07 – 1.96 (m, 1H), 1.03 (t, $J = 7.4$ Hz, 3H).

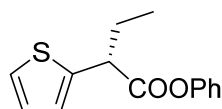
^{13}C NMR (100 MHz, CDCl_3): δ 172.7, 150.9, 136.1, 133.6, 132.8, 129.4, 128.6, 128.0, 127.8, 127.2, 126.3, 126.0, 126.0, 125.9, 121.5, 53.7, 26.8, 12.3.

HRMS-ESI (m/z) Calcd for $\text{C}_{20}\text{H}_{19}\text{O}_2$ [(M + H)⁺] 291.1380, Found: 291.1386.

IR (KBr): ν (cm^{-1}) 3472, 2965, 1752, 1630, 1592, 1491, 764, 749.

HPLC: Chiralcel OJ-H (25 cm \times 0.46 cm), hexane/2-propanol = 85/15, 1.0 mL/min, 204 nm, 25 $^{\circ}\text{C}$, $t_{\text{R}} = 20.06$ min (minor), 25.87 min (major).

(R)-phenyl-2-(thiophen-2-yl) butanoate (2n):



Yield: 99%; ee: 88%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -26^{\circ}$ (0.29, CHCl_3).

^1H NMR (400 MHz, CDCl_3): δ 7.37 – 7.33 (m, 2H), 7.25 – 7.19 (m, 2H), 7.05 – 7.03 (m, 3H), 7.00 – 6.98 (m, 1H), 4.01 (t, $J = 7.6$ Hz, 1H), 2.30 – 2.20 (m, 1H), 2.05 – 1.94 (m, 1H), 1.05 (t, $J = 7.4$ Hz, 3H).

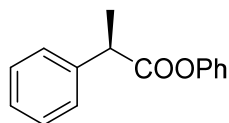
^{13}C NMR (100 MHz, CDCl_3): δ 171.7, 150.8, 140.9, 129.5, 126.9, 126.0, 125.8, 124.9, 121.5, 48.8, 28.1, 12.2.

HRMS-ESI (m/z) Calcd for $\text{C}_{14}\text{H}_{15}\text{SO}_2$ [(M + H)⁺] 247.0787, Found: 247.0788.

IR (KBr): ν (cm^{-1}) 3414, 2931, 1757, 1592, 1491, 1456, 750, 700.

HPLC: Chiralcel OJ-H (25 cm \times 0.46 cm), hexane/2-propanol = 85/15, 1.0 mL/min, 204 nm, 25 $^{\circ}\text{C}$, $t_{\text{R}} = 21.53$ min (major), 24.38 min (minor).

(R)-phenyl-2-phenylpropanoate (2o):



Yield: 92%; ee: 86%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -83^{\circ}$ (0.2, CHCl_3).

^1H NMR (400 MHz, CDCl_3): δ 7.42 – 7.28 (m, 7H), 7.21 – 7.17 (m, 1H), 7.00 – 6.97 (m, 2H), 3.96 (q, $J = 7.2$ Hz, 1H), 1.62 (d, $J = 7.2$ Hz, 3H).

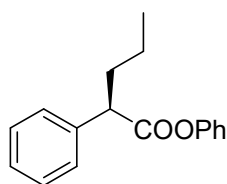
^{13}C NMR (100 MHz, CDCl_3): δ 173.2, 150.9, 140.2, 129.4, 128.9, 127.6, 127.5, 125.9, 121.5, 45.8, 18.6.

HRMS-ESI (m/z) Calcd for $\text{C}_{15}\text{H}_{15}\text{O}_2$ [(M + H)⁺] 227.1067, Found: 227.1078.

IR (KBr): ν (cm^{-1}) 3414, 2979, 1757, 1638, 1592, 1491, 749, 732.

HPLC: Chiralcel OJ-H (25 cm \times 0.46 cm), hexane/2-propanol = 90/10, 1.0 mL/min, 204 nm, 25 $^{\circ}\text{C}$, $t_{\text{R}} = 32.89$ min (major), 36.80 min (minor).

(R)-phenyl-2-phenylpentanoate (2p):



Yield: 91%; ee: 92%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -60^{\circ}$ (0.13, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.42 – 7.27 (m, 7H), 7.21 – 7.17 (m, 1H), 7.00 – 6.97 (m, 2H), 3.80 (t, $J = 7.7$ Hz, 1H), 2.20 – 2.13 (m, 1H), 1.89 – 1.81 (m, 1H), 1.39 (ddd, $J = 14.2, 9.3, 7.6$ Hz, 2H), 0.97 (t, $J = 7.4$ Hz, 3H).

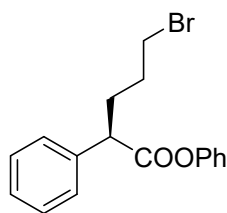
$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.8, 150.9, 138.9, 129.4, 128.8, 128.1, 127.5, 125.9, 121.5, 51.7, 35.7, 20.9, 14.0.

HRMS-ESI (m/z) Calcd for $\text{C}_{17}\text{H}_{19}\text{O}_2$ $[(\text{M} + \text{H})^+]$ 255.1380, Found: 255.1387.

IR (KBr): ν (cm^{-1}) 3415, 2929, 1755, 1618, 1592, 1491, 750, 697.

HPLC: Chiralcel OJ-H (25 cm \times 0.46 cm), hexane/2-propanol = 90/10, 1.0 mL/min, 204 nm, 25 $^{\circ}\text{C}$, $t_{\text{R}} = 12.84$ min (minor), 15.07 min (major).

(R)-phenyl-5-bromo-2-phenylpentanoate (2q):



Yield: 91%; ee: 91%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -46^{\circ}$ (0.14, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.41 – 7.25 (m, 7H), 7.22 – 7.18 (m, 1H), 6.99 – 6.96 (m, 2H), 3.81 (td, $J = 7.7, 1.8$ Hz, 1H), 3.43 (t, $J = 6.5$ Hz, 2H), 2.36 – 2.30 (m, 1H), 2.09 – 1.97 (m, 1H), 1.96 – 1.81 (m, 2H).

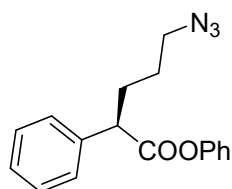
$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.2, 150.8, 138.1, 129.5, 129.1, 128.1, 127.8, 126.0, 121.5, 51.1, 33.1, 32.0, 30.7.

HRMS-ESI (m/z) Calcd for $\text{C}_{16}\text{H}_{16}\text{BrO}_2$ $[(\text{M} + \text{H})^+]$ 333.0485, Found: 333.0488.

IR (KBr): ν (cm^{-1}) 3451, 2921, 1752, 1630, 1491, 1454, 764, 749.

HPLC: Chiralcel OJ-H (25 cm \times 0.46 cm), hexane/2-propanol = 85/15, 1.0 mL/min, 204 nm, 25 $^{\circ}\text{C}$, $t_{\text{R}} = 29.49$ min (minor), 42.53 min (major).

(R)-phenyl-5-azido-2-phenylpentanoate (2r):



Yield: 99%; ee: 90%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -75^{\circ}$ (0.15, CHCl_3).

¹H NMR (400 MHz, CDCl₃): δ 7.41 – 7.30 (m, 7H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.98 (dd, *J* = 8.5, 0.9 Hz, 2H), 3.80 (t, *J* = 7.7 Hz, 1H), 3.34 – 3.30 (m, 2H), 2.27 – 2.23 (m, 1H), 1.99 – 1.96 (m, 1H), 1.69 – 1.60 (m, 2H).

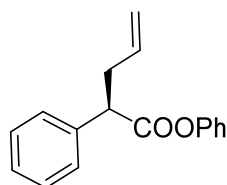
¹³C NMR (100 MHz, CDCl₃): δ 172.3, 150.7, 138.1, 129.5, 129.1, 128.0, 127.8, 126.0, 121.4, 51.4, 51.2, 30.6, 27.0.

HRMS-ESI (m/z) Calcd for C₁₇H₁₇N₃O₂ [(M + H)⁺] 296.1394, Found: 296.1398.

IR (KBr): ν (cm⁻¹) 2961, 2096, 1754, 1592, 1491, 1452, 729, 689.

HPLC: Chiralcel OJ-H (25 cm × 0.46 cm), hexane/2-propanol = 70/30, 1.0 mL/min, 204 nm, 35 °C, t_R = 14.00 min (minor), 21.90 min (major).

(*R*)-phenyl-2-phenylpent-4-enoate (2s):



Yield: 99%; ee: 90%.

Colorless oil, [α]_D²⁰ = -54° (0.13, CHCl₃).

¹H NMR (400 MHz, CDCl₃): δ 7.42 – 7.28 (m, 7H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 2H), 5.86 – 5.78 (m, 1H), 5.12 (dd, *J* = 33.8, 13.6 Hz, 2H), 3.96 – 3.79 (m, 1H), 2.98 – 2.91 (m, 1H), 2.65 – 2.58 (m, 1H).

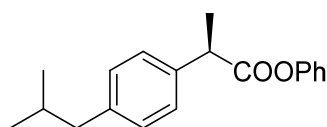
¹³C NMR (100 MHz, CDCl₃): δ 172.1, 150.9, 138.2, 135.1, 129.5, 128.9, 128.1, 127.7, 126.0, 121.5, 117.5, 51.6, 37.7.

HRMS-ESI (m/z) Calcd for C₁₇H₁₇O₂ [(M + H)⁺] 253.1223, Found: 253.1229.

IR (KBr): ν (cm⁻¹) 3472, 3078, 2921, 1756, 1644, 1592, 1491, 749.

HPLC: Chiralcel OJ-H (25 cm × 0.46 cm), hexane/2-propanol = 95/5, 1.0 mL/min, 204 nm, 25 °C, t_R = 17.61 min (major), 18.72 min (minor).

(*R*)-phenyl-2-(4-isobutylphenyl) propanoate (2t):



Yield: 92%; ee: 86%.

Colorless oil, [α]_D²⁰ = -67° (0.22, CHCl₃).

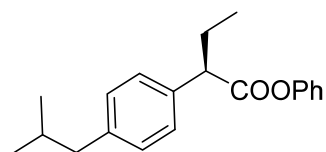
¹H NMR (400 MHz, CDCl₃): δ 7.34 – 7.29 (m, 4H), 7.20 – 7.13 (m, 3H), 7.00 – 6.98 (m, 2H), 3.93 (q, *J* = 7.1 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.91 – 1.81 (m, 1H), 1.60 (d, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 173.4, 151.0, 140.9, 137.4, 129.6, 129.4, 127.3, 125.8, 121.5, 45.4, 45.2, 30.3, 22.5, 18.7.

HRMS-ESI (m/z) Calcd for C₁₉H₂₃O₂ [(M + H)⁺] 283.1693, Found: 283.1701.

HPLC: Chiralcel OJ-H (25 cm × 0.46 cm), hexane/2-propanol = 99/1, 1.0 mL/min, 210 nm, 25 °C, t_R = 23.03 min (major), 35.55 min (minor).

(*R*)-phenyl-2-(4-isobutylphenyl) butanoate (2u):



Yield: 99%; ee: 90%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -44^{\circ}$ (0.11, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.35 – 7.28 (m, 4H), 7.21 – 7.17 (m, 1H), 7.13 (d, $J = 8.1$ Hz, 2H), 7.00 – 6.98 (m, 2H), 3.67 (t, $J = 7.7$ Hz, 1H), 2.47 (d, $J = 7.2$ Hz, 2H), 2.25 – 2.17 (m, 1H), 1.92 – 1.85 (m, 2H), 1.00 (t, $J = 7.4$ Hz, 3H), 0.91 (d, $J = 6.6$ Hz, 6H).

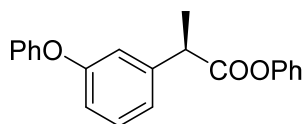
$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.9, 151.0, 141.0, 135.9, 129.5, 129.4, 127.8, 125.8, 121.6, 53.3, 45.2, 30.3, 26.9, 22.5, 12.3.

HRMS-ESI (m/z) Calcd for $\text{C}_{20}\text{H}_{25}\text{O}_2$ [(M + H)⁺] 297.1849, Found: 297.1854.

IR (KBr): ν (cm^{-1}) 3473, 2960, 1756, 1632, 1511, 1492, 1382, 749.

HPLC: Chiralcel OJ-H (25 cm \times 0.46 cm), hexane/2-propanol = 98/2, 1.0 mL/min, 204 nm, 25 $^{\circ}\text{C}$, $t_{\text{R}} = 11.39$ min (minor), 12.77 min (major).

(R)-phenyl 2-(3-phenoxyphenyl) propanoate (2v):



Yield: 99%; ee: 87%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -62^{\circ}$ (0.18, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.36 – 7.30 (m, 5H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.14 – 7.07 (m, 3H), 7.04 – 6.92 (m, 5H), 3.93 (q, $J = 7.1$ Hz, 1H), 1.60 (d, $J = 7.2$ Hz, 3H).

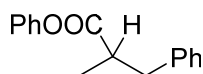
$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.8, 157.7, 157.1, 150.9, 142.1, 130.2, 129.9, 129.5, 125.9, 123.5, 122.5, 121.5, 119.1, 118.2, 117.8, 45.6, 18.5.

HRMS-ESI (m/z) Calcd for $\text{C}_{21}\text{H}_{19}\text{O}_3$ [(M + H)⁺] 319.1329, Found: 319.1332.

IR (KBr): ν (cm^{-1}) 3473, 2963, 1757, 1583, 1487, 1260, 764, 750.

HPLC: Chiralcel OJ-H (25 cm \times 0.46 cm), hexane/2-propanol = 80/20, 1.0 mL/min, 204 nm, 25 $^{\circ}\text{C}$, $t_{\text{R}} = 32.36$ min (major), 38.65 min (minor).

phenyl 2-methyl-3-phenylpropanoate (2w)



Yield: 30%; ee: 8%.

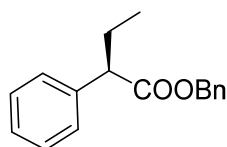
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 (dd, $J = 15.0, 7.1$ Hz, 4H), 7.24 (dd, $J = 7.6, 6.1$ Hz, 3H), 7.19 (t, $J = 7.4$ Hz, 1H), 6.92 (d, $J = 7.8$ Hz, 2H), 3.13 (dd, $J = 13.3, 7.6$ Hz, 1H), 3.05 – 2.94 (m, 1H), 2.83 (dd, $J = 13.3, 7.2$ Hz, 1H), 1.32 (d, $J = 6.9$ Hz, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.7, 150.8, 139.1, 129.5, 129.2, 128.6, 126.6, 125.8, 121.6, 41.8, 39.9, 17.1.

HRMS-ESI (m/z) calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{Na}$ [(M + Na)⁺] 263.1043, found 263.1053.

HPLC: Chiralcel OD-H (25 cm \times 0.46 cm), hexane/2-propanol = 98/2, 1.0 mL/min, 204 nm, 25 $^{\circ}\text{C}$, $t_{\text{R}} = 21.93$ min (major), 23.12 min (minor).

(R)-benzyl 2-phenylbutanoate (2b)³



Yield: 47%; ee: 88%.

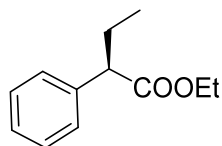
Colorless oil, $[\alpha]_{\text{D}}^{20} = -12^{\circ}$ (0.11, CHCl_3).

^1H NMR (400 MHz, CDCl_3): δ 7.31 – 7.28 (m, 7H), 7.26 – 7.23 (m, 3H), 5.10 (dd, $J = 33.2, 12.5$ Hz, 2H), 3.51 (t, $J = 7.7$ Hz, 1H), 2.18 – 2.07 (m, 1H), 1.87 – 1.77 (m, 1H), 0.88 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 174.0, 139.0, 136.1, 128.7, 128.6, 128.2, 128.1, 128.0, 127.3, 66.4, 53.6, 26.8, 12.3.

HPLC: Chiralcel OD-H (25 cm \times 0.46 cm), hexane/2-propanol = 98/2, 1.0 mL/min, 204 nm, 25 $^{\circ}\text{C}$, $t_{\text{R}} = 22.23$ min (major), 24.90 min (minor).

(*R*)-ethyl-2-phenylbutanoate (2c)⁴



Yield: 50%; ee: 90%.

Colorless oil, $[\alpha]_{\text{D}}^{20} = -56^{\circ}$ (0.05, CHCl_3).

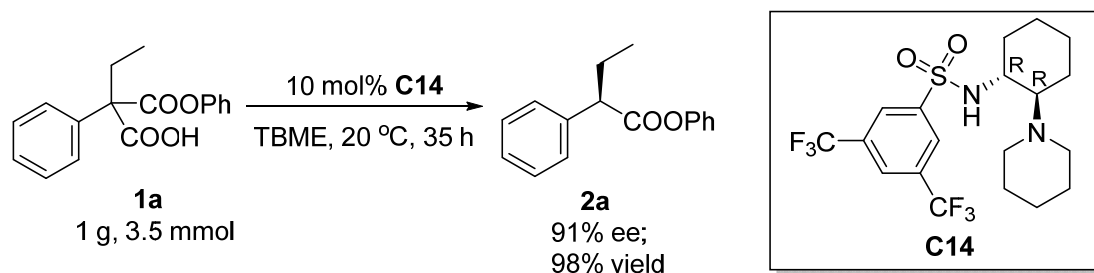
^1H NMR (400 MHz, CDCl_3): δ 7.35 – 7.24 (m, 5H), 4.18 – 4.06 (m, 2H), 3.43 (t, $J = 7.7$ Hz, 1H), 2.13 – 2.06 (m, 1H), 1.83 – 1.75 (m, 1H), 1.21 (t, $J = 7.1$ Hz, 3H), 0.89 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 174.2, 139.3, 128.6, 128.0, 127.2, 60.7, 53.6, 26.9, 14.3, 12.3.

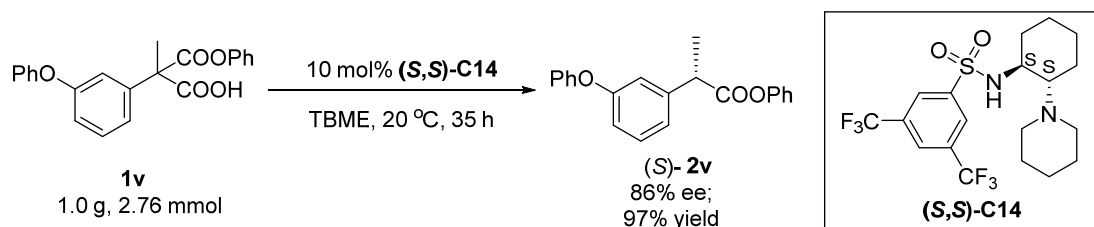
HPLC: Chiralcel OD-H (25 cm \times 0.46 cm), hexane/2-propanol = 99.8/0.2, 1.0 mL/min, 204 nm, 25 $^{\circ}\text{C}$, $t_{\text{R}} = 14.18$ min (major), 28.64 min (minor).

4. Synthetic Applications

4.1 Gram-Scale Synthesis of **2a** and (*S*)-**2v**

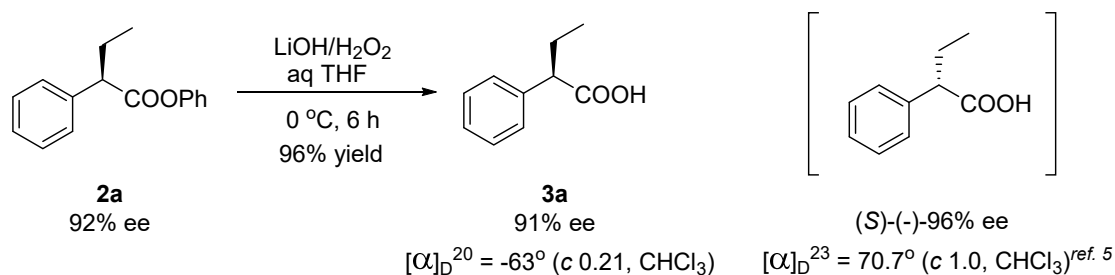


To a mixture of catalyst **C14** (10 mol%) and 2-(phenoxy-carbonyl)-2-phenylbutanoic acid **1a** (1.0 g, 3.5 mmol) in a vial were added TBME (35.0 mL), then the reaction mixture was stirred at 20 °C for 35 h. The mixture was concentrated in vacuo. The remaining residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product **2a** (828 mg, 98%) in 91% ee.



To a mixture of catalyst (*S,S*)-**C14** (10 mol%) and 2-methyl-3-oxo-3-phenoxy-2-(3-phenoxyphenyl) propanoic acid **1v** (1.0 g, 2.76 mmol) in a vial were added TBME (28.0 mL), then the reaction mixture was stirred at 20 °C for 35 h. The mixture was concentrated in vacuo, and the remaining residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product (*S*)-**2v** (878 mg, 97%) in 86% ee.

4.2 The Transformations of Compound **2a** and enantiomer (*S*)-**2v**



30% H_2O_2 (0.48 mL) and aq. LiOH (1.22 mL, 2.0 M) were added to a solution of **2a** (0.200 g, 0.83 mmol) in THF (4.88 mL) and water (0.73 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 6 h, quenched with $\text{Na}_2\text{S}_2\text{O}_3$ (4.9 mL, 0.7 M) and NaHCO_3 (9.8 mL, 0.5 M), stirred for another 15 min, acidified with 20% HCl , extracted with EtOAc (5 mL \times 3), dried over Na_2SO_4 , filtered, concentrated, and purified by flash chromatography (petroleum ether/ethyl acetate = 10/1) to give acid **3a** as a colorless oil (0.13 g, 96% yield, 91% ee).

(*R*)-2-phenylbutanoic acid (*R*)-**3a**⁵

$[\alpha]_{\text{D}}^{20} = -63^\circ$ (*c* 0.21, CHCl_3).

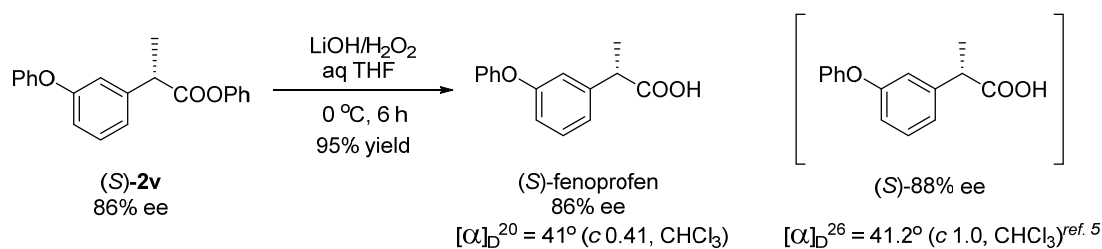
¹**H NMR** (400 MHz, CDCl_3): δ 7.35 – 7.28 (m, 5H), 3.50 – 3.45 (m, 1H), 2.15 – 2.08 (m, 1H), 1.88 – 1.80 (m, 1H), 0.96 – 0.90 (m, 3H).

¹³**C NMR** (100 MHz, CDCl_3): δ 180.9, 138.5, 128.8, 128.2, 127.6, 53.5, 26.4, 12.2.

IR (KBr): ν (cm^{-1}) 3468, 2966, 1706, 1601, 1495, 1455, 748, 697.

HPLC: Chiralcel OJ-H (25 cm \times 0.46 cm), hexane/2-propanol/ CF_3COOH = 95/4/1, 1.0 mL/min, 204 nm, 25 °C, t_{R} = 16.61 min (major), 17.74 min (minor).

The optical rotation of compound **3a** was $[\alpha]_{\text{D}}^{20} = -63^\circ$ (*c* 0.21, CHCl_3), and the absolute configuration of **3a** was determined to be *R* by comparing the reported optical rotation of (-)-(*S*)-**3a** $[\alpha]_{\text{D}}^{23} = 70.7$ (*c* 1.0 CHCl_3).⁵



30% H_2O_2 (0.36 mL) and aq. LiOH (0.93 mL, 2.0 M) were added to a solution of (*S*)-**2v** (0.200 g, 0.63 mmol) in THF (3.7 mL) and water (0.56 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 6 h, quenched with $\text{Na}_2\text{S}_2\text{O}_3$ (3.7 mL, 0.7 M) and NaHCO_3 (7.4 mL, 0.5 M), stirred for another 15 min, acidified with 20% HCl , extracted with EtOAc (5 mL \times 3), dried over Na_2SO_4 , filtered, concentrated, and purified by flash chromatography (petroleum ether/ethyl acetate = 10/1) to give (*s*)-fenpropfen⁵ as a colorless oil (0.14 g, 95% yield, 86% ee).

$[\alpha]_{\text{D}}^{20} = 41^\circ$ (0.41, CHCl_3).

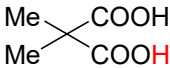

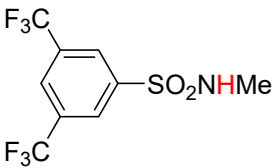
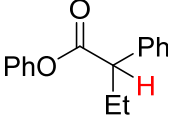
¹**H NMR** (400 MHz, CDCl_3): δ 7.36 – 7.25 (m, 3H), 7.13 – 7.03 (m, 2H), 7.02 – 7.01 (m, 3H), 6.89 (dd, *J* = 7.9, 2.2 Hz, 1H), 3.72 (q, *J* = 7.2 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl_3): δ 180.6, 157.6, 157.0, 141.8, 130.0, 129.9, 123.5, 122.5, 119.1, 118.3, 117.6, 45.3, 18.2.

IR (KBr): ν (cm^{-1}) 3473, 2930, 1708, 1583, 1488, 1245, 752, 691.

HPLC: Chiralcel AD-H (25 cm \times 0.46 cm), hexane/2-propanol/ CF_3COOH = 90/10/0.1, 1.0 mL/min, 204 nm, 25 $^\circ\text{C}$, t_{R} = 24.42 min (minor), 28.20 min (major).

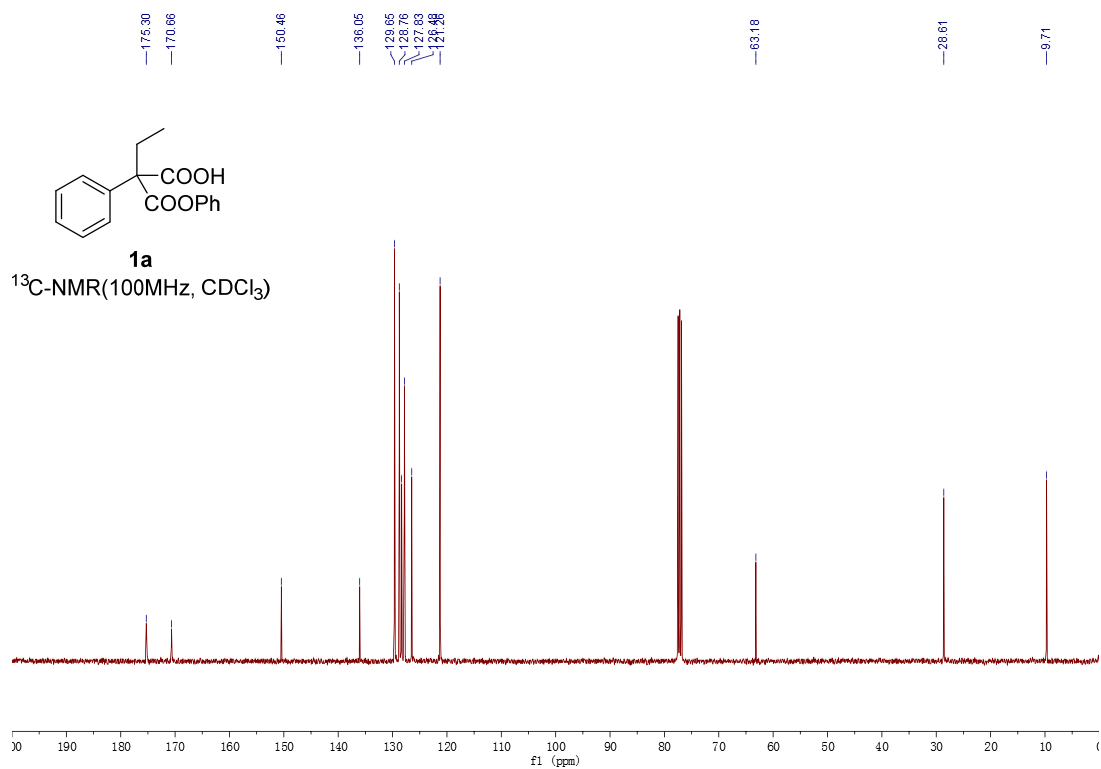
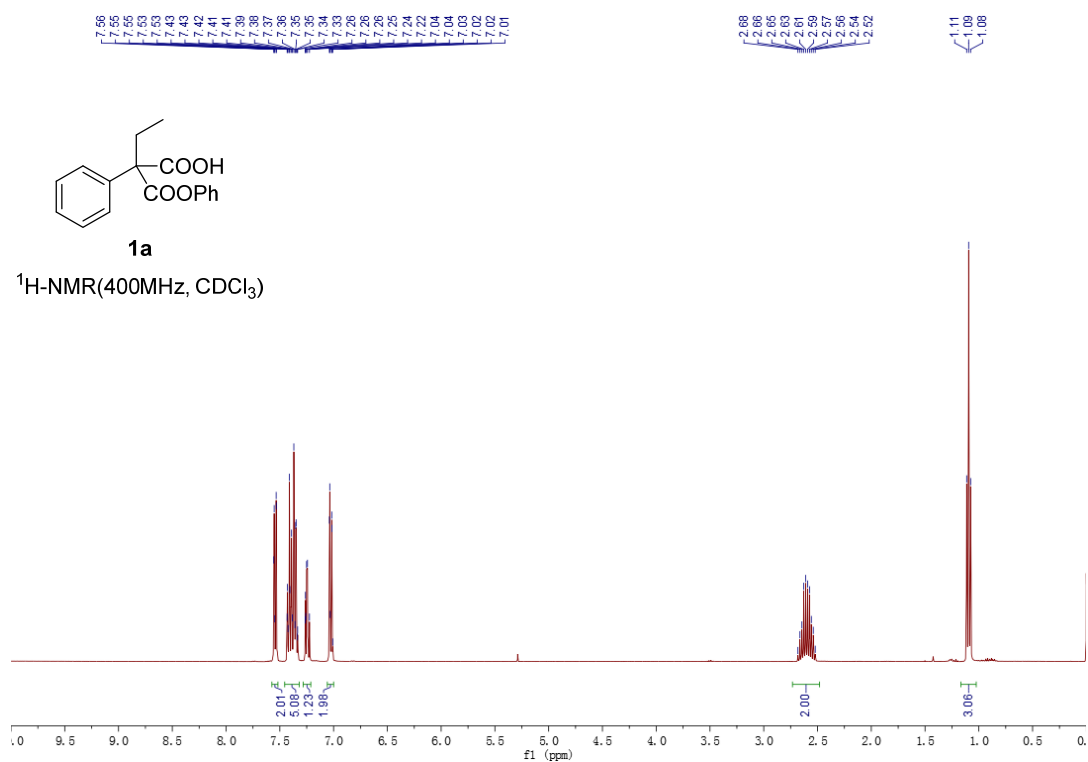
5. Some *pKa* values of our reaction related compounds

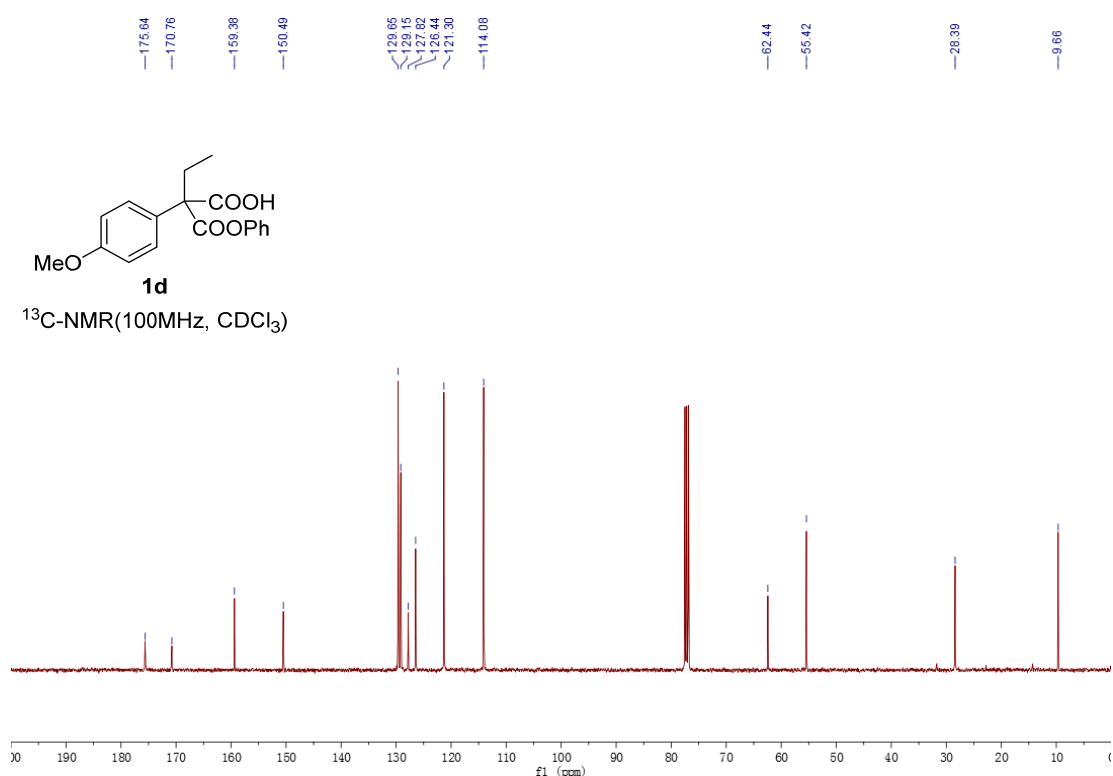
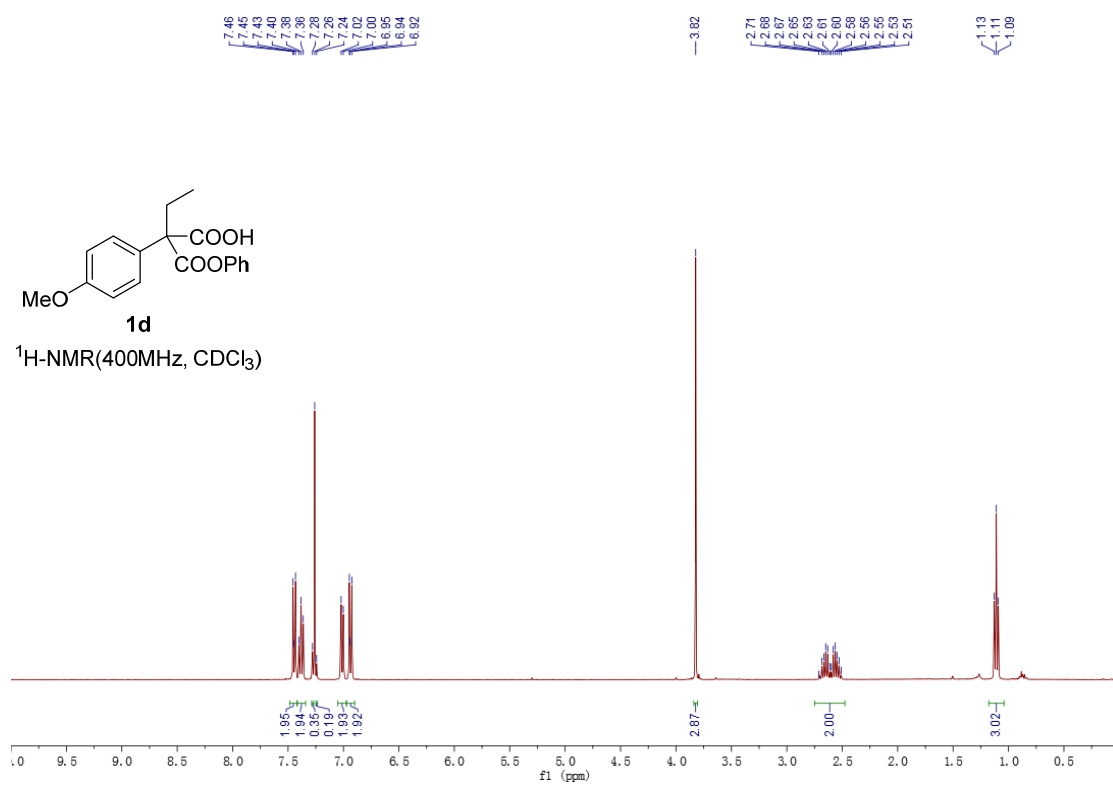
Entry	Compounds	<i>pKa</i> (H ₂ O)	<i>pKa</i> (DMSO)
1 ⁶		3.15	-
2 ⁷		10.72	9.07
3 ⁸		5.50	11.11
4 ⁸		9.14	17.96

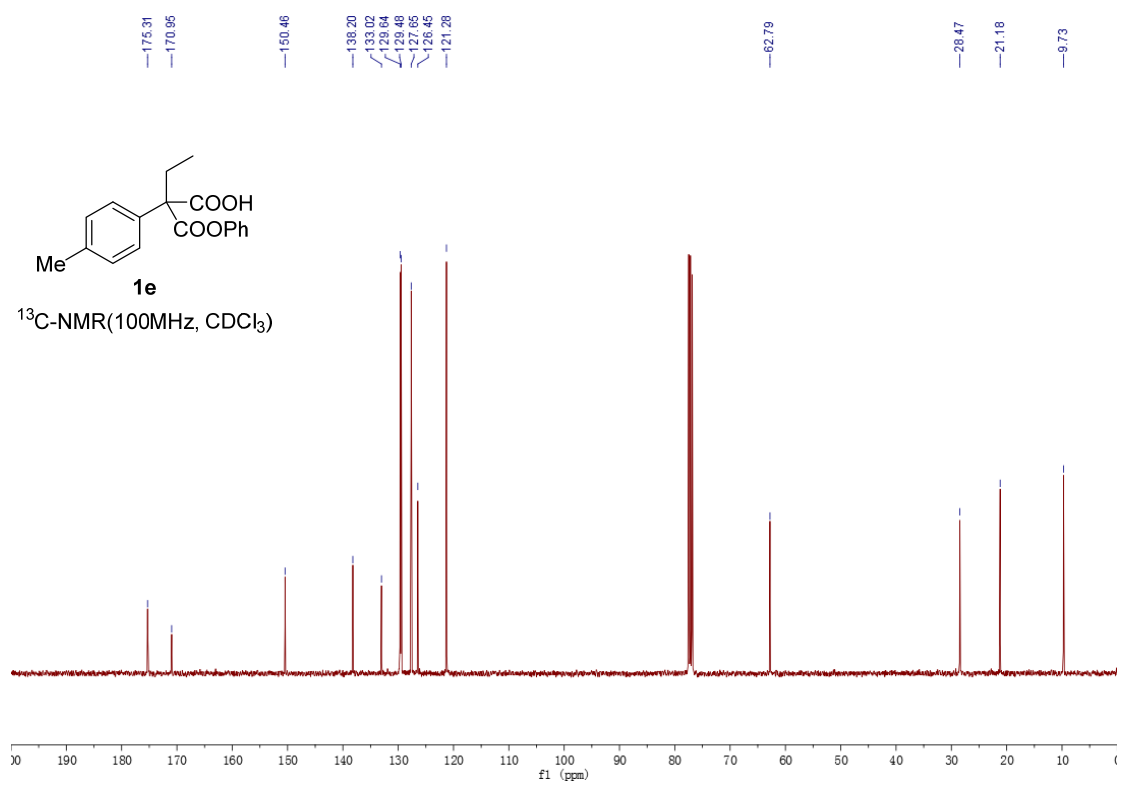
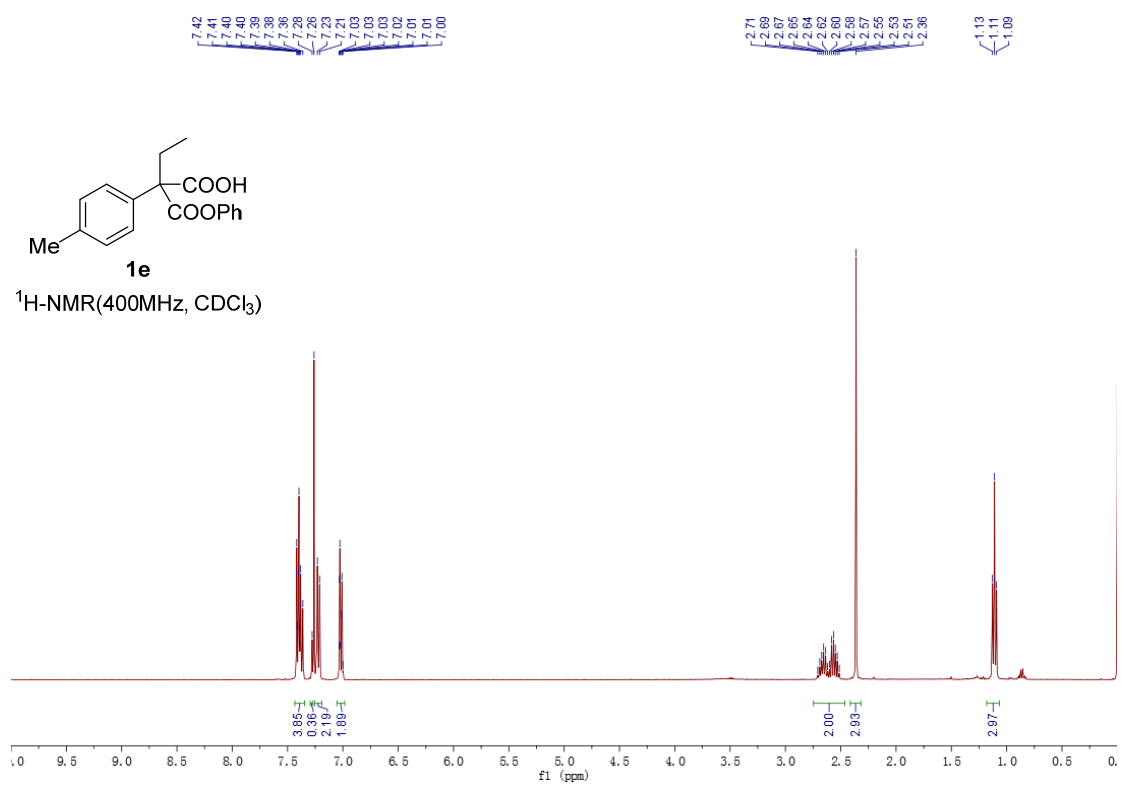
6. Reference

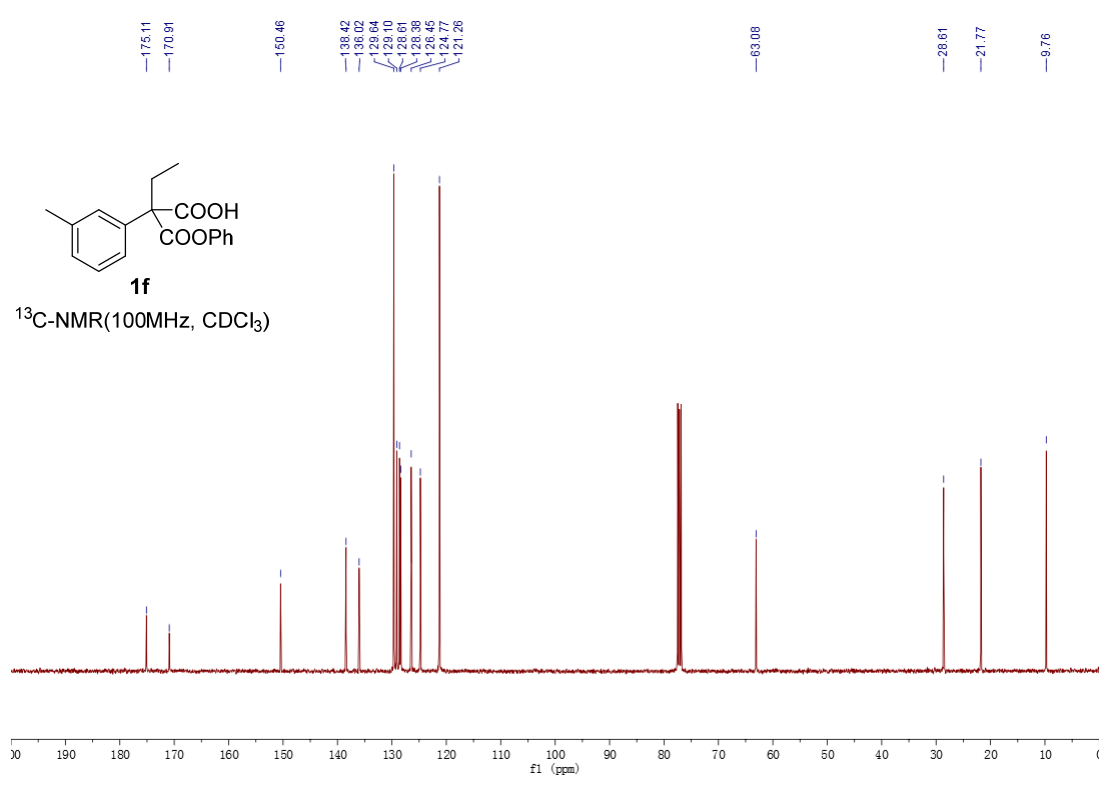
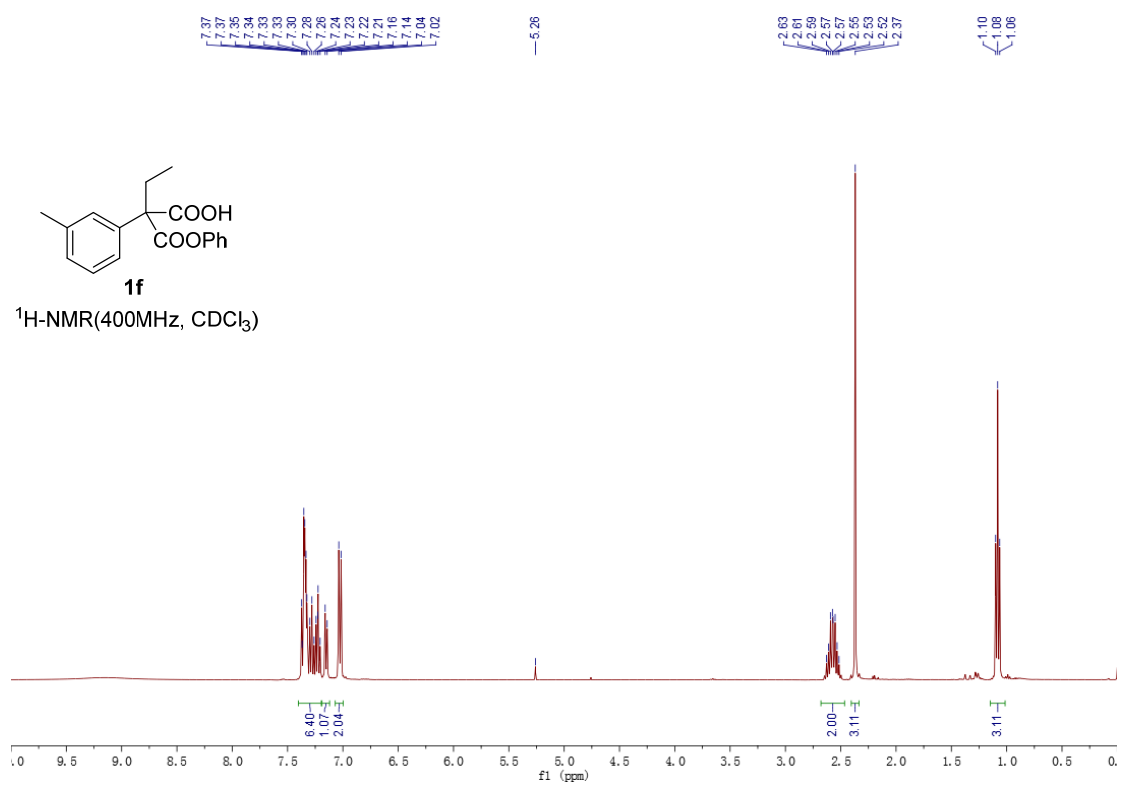
- 1). (a) A. Nakano, S. Kawahara, S. Akamatsu, K. Morokuma, M. Nakatani, Y. Iwabuchi, K. Takahashi, J. Ishihara and S. Hatakeyama, *Tetrahedron* 2006, **62**, 381; (b) B. Hu and L. Deng, *Angew. Chem. Int. Ed.* 2018, **57**, 2233; (c) J. Luo, L.-W. Xu, R. A. S. Hay and Y. Lu, *Org. Lett.* 2009, **11**, 437; (d) B. Vakulya, S. Varga, A. Csámpai and T. Soós, *Org. Lett.* 2005, **7**, 1967.
- 2). M. Dajek, R. Kowalczyk and P. J. Boratyński, *Catal. Sci. Technol.*, 2018, **8**, 4358.
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- 8). Corresponding p*K*_a value was predicted by the approach developed by Luo and Zhang, see: Q. Yang, Y. Li, J.-D. Yang, Y. Liu, L. Zhang, S. Luo and J.-P. Cheng, *Angew. Chem. Int. Ed.* 2020, **59**, 19282.

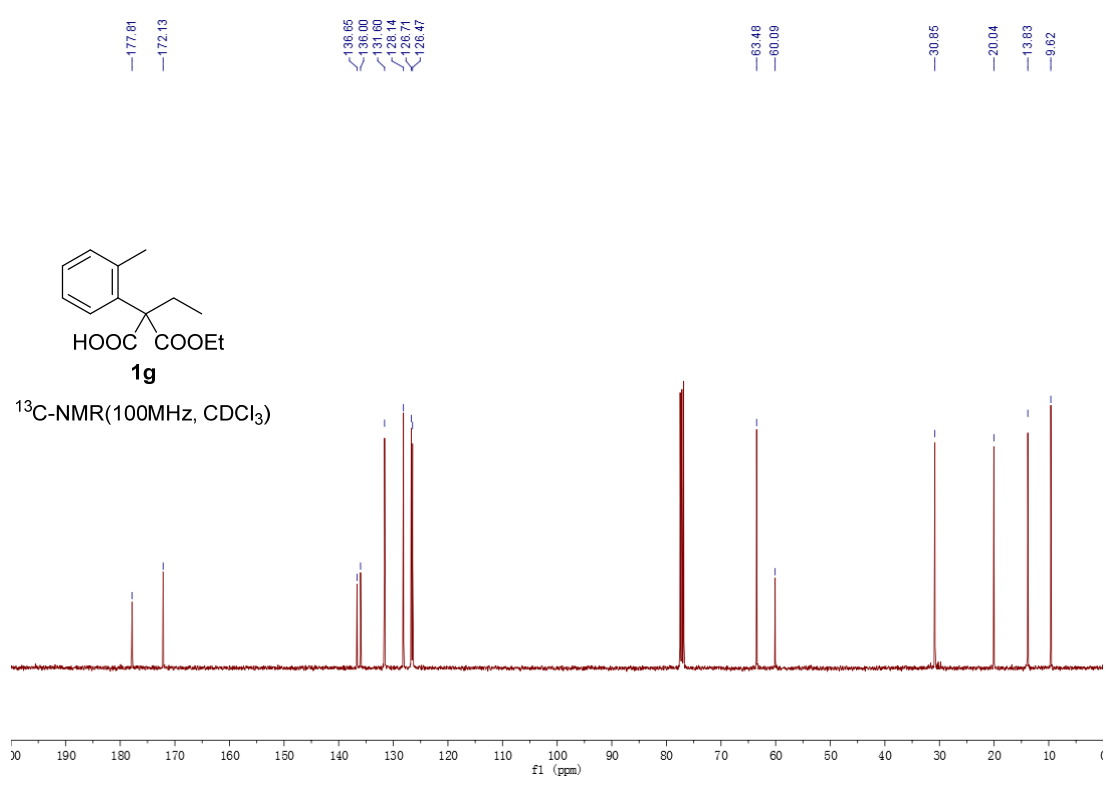
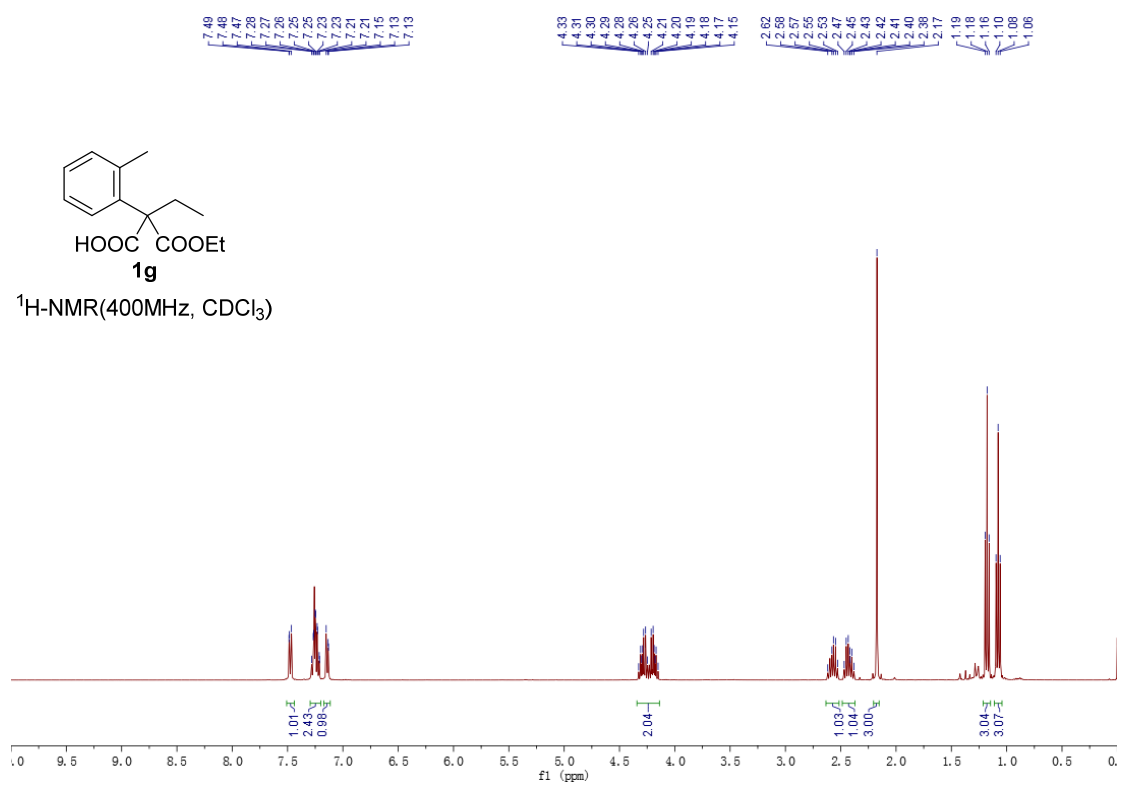
7. ¹H NMR, ¹³C NMR and HPLC Spectra Data

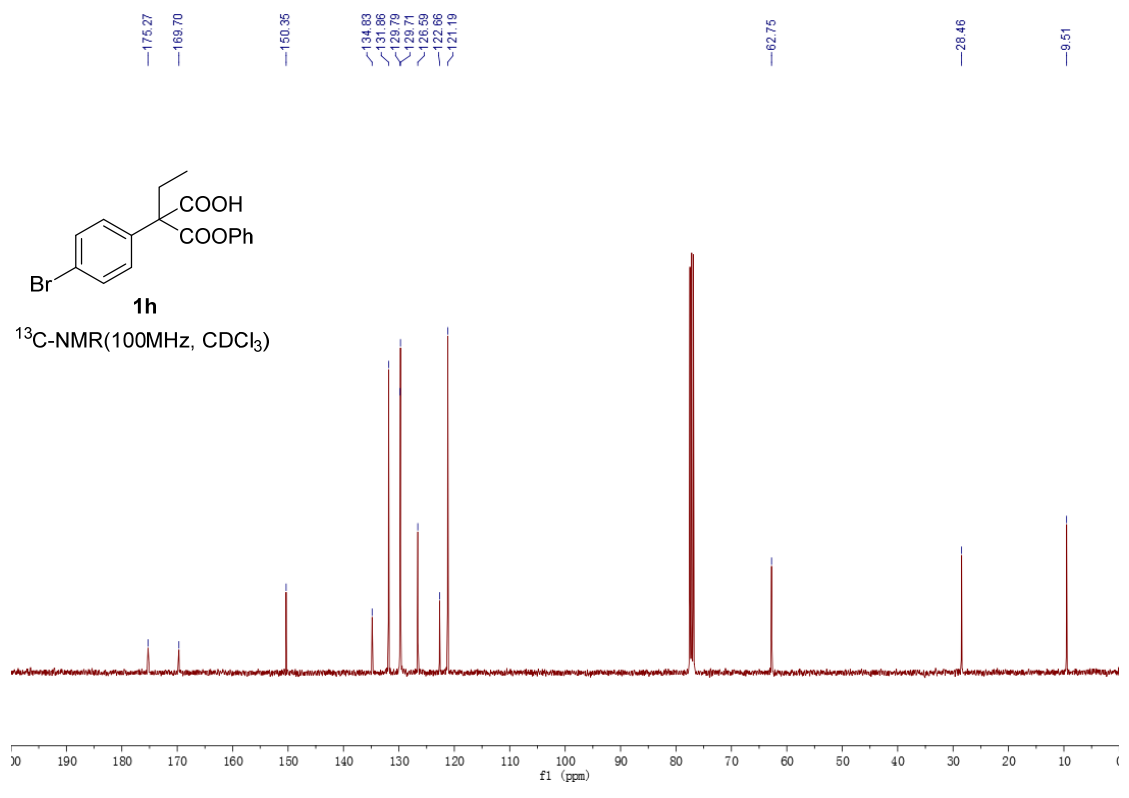
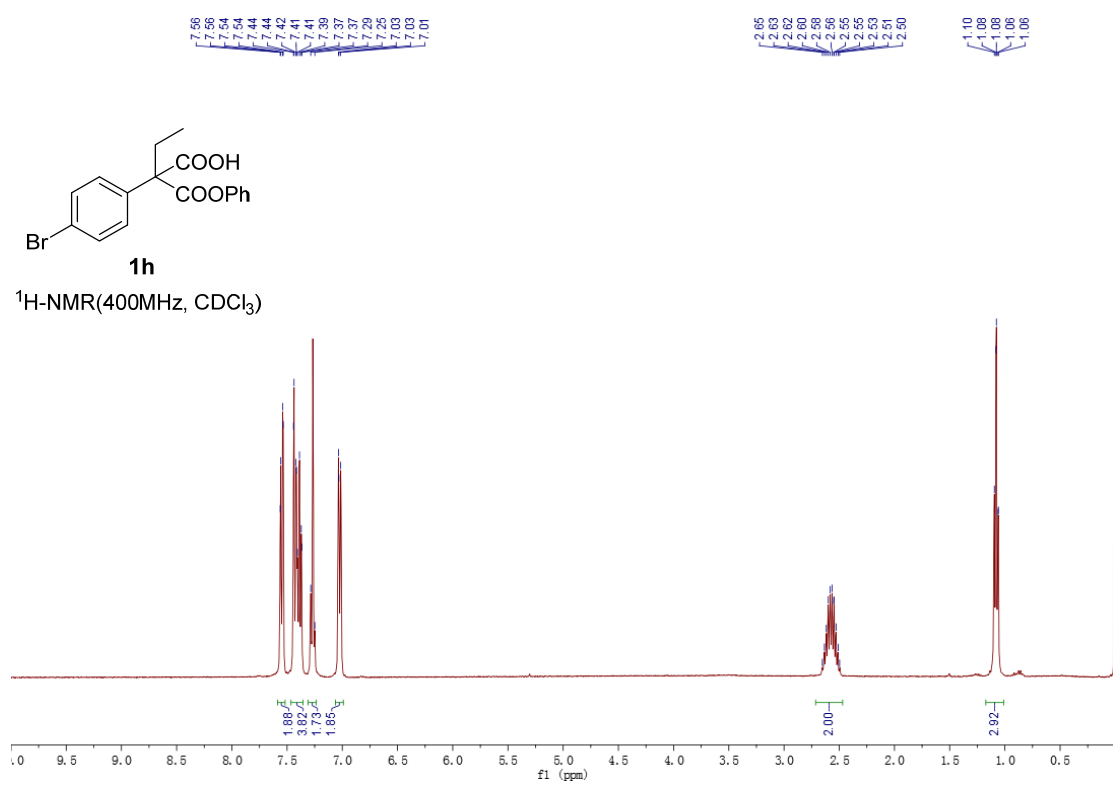


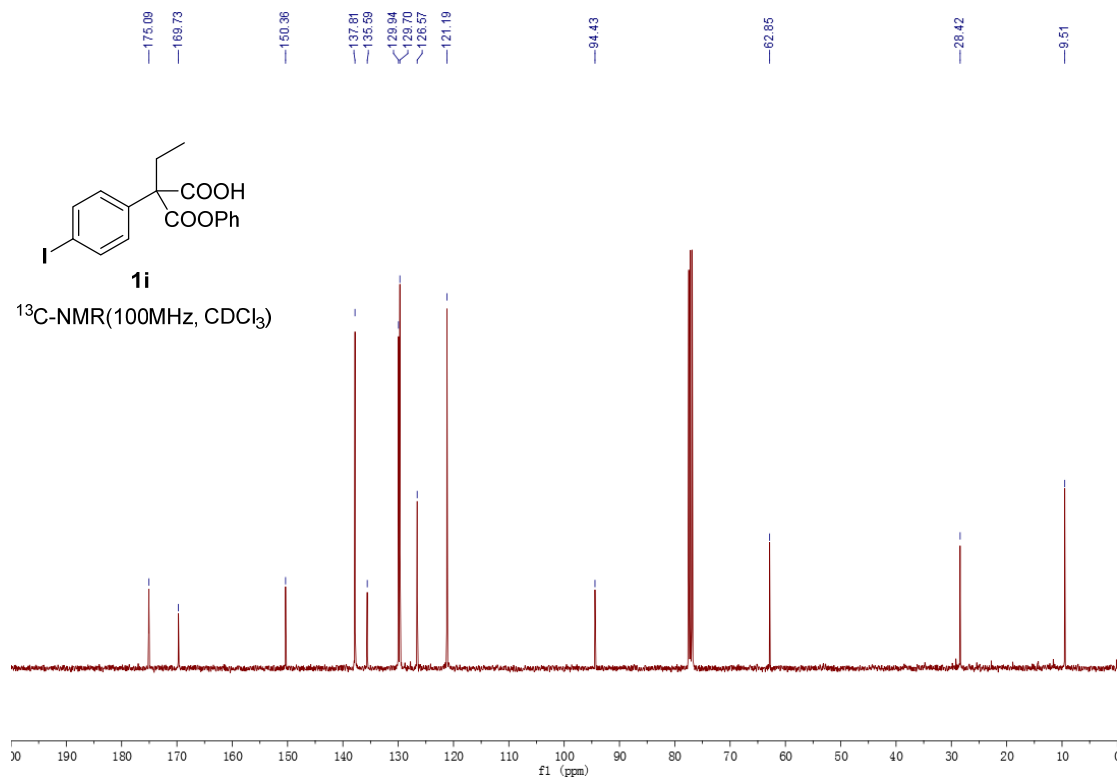
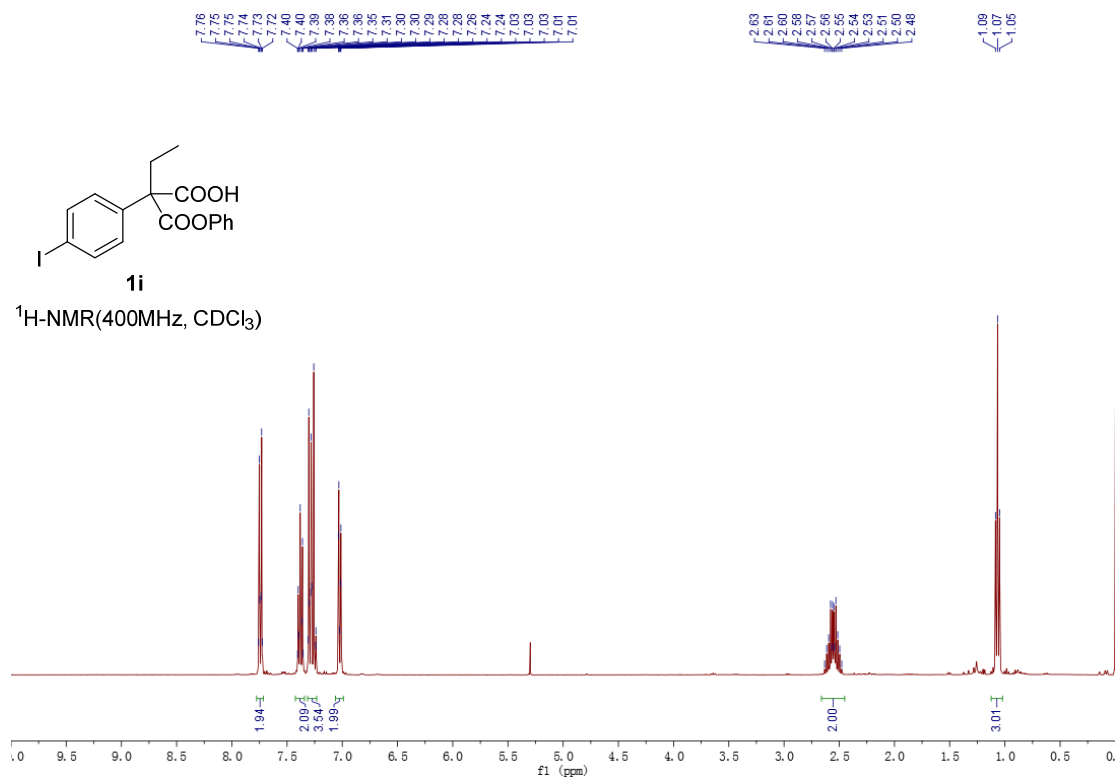




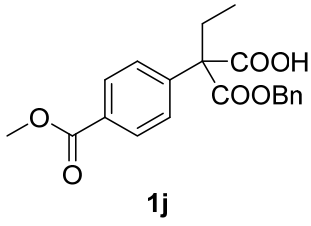




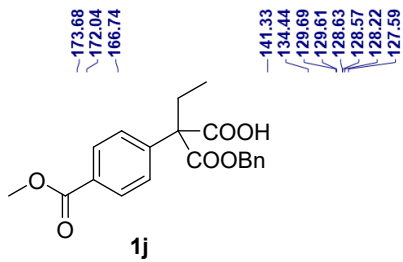
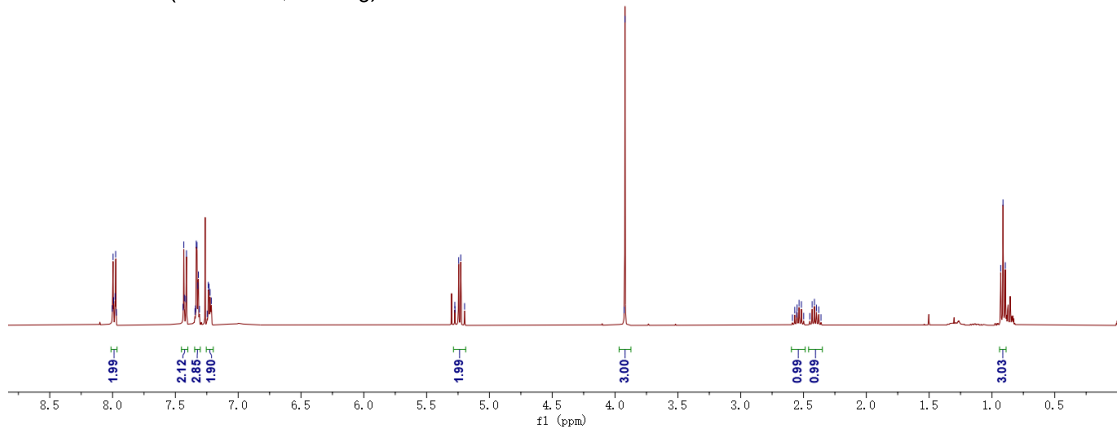




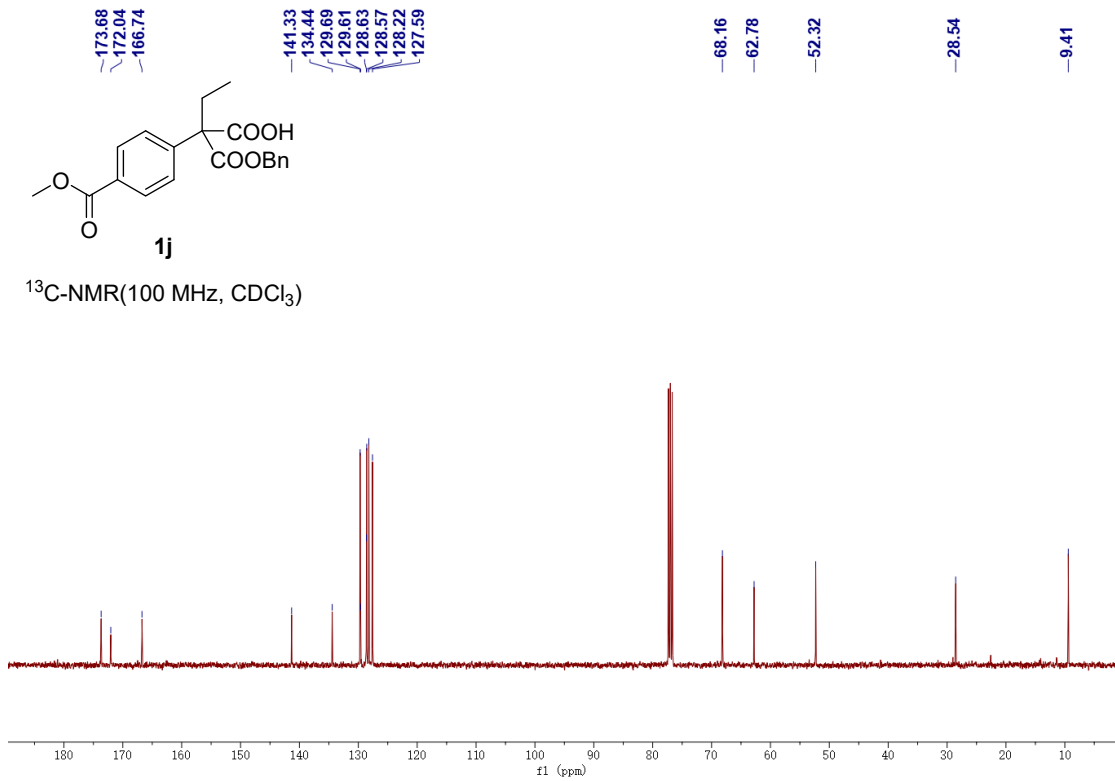
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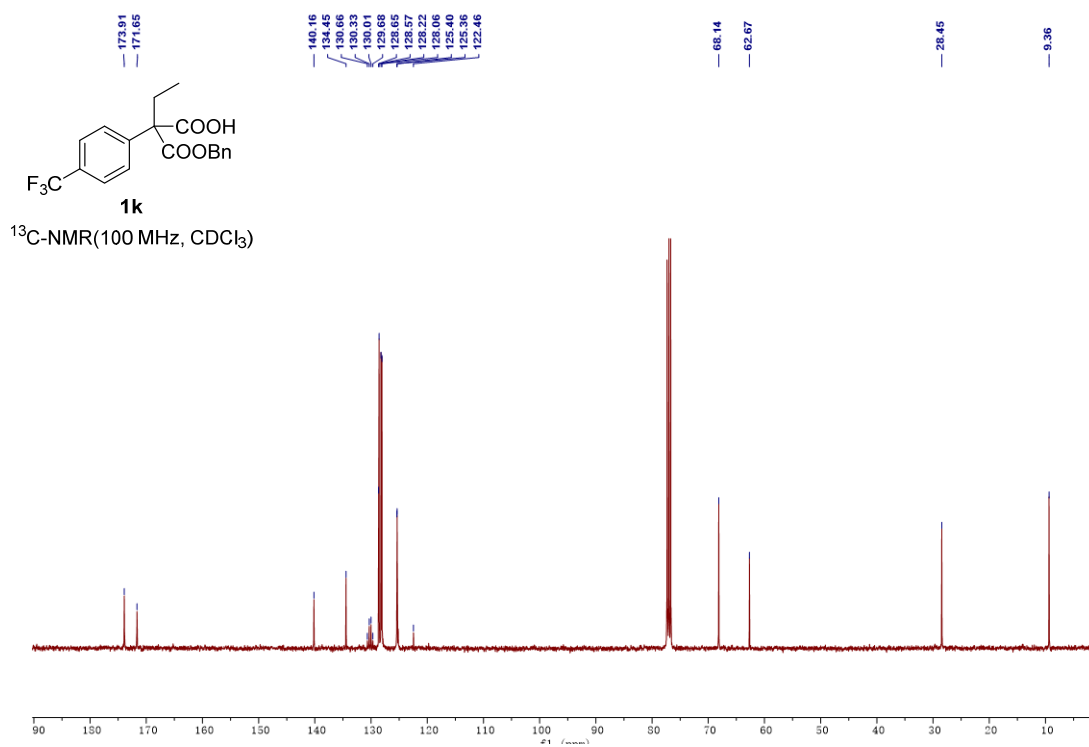
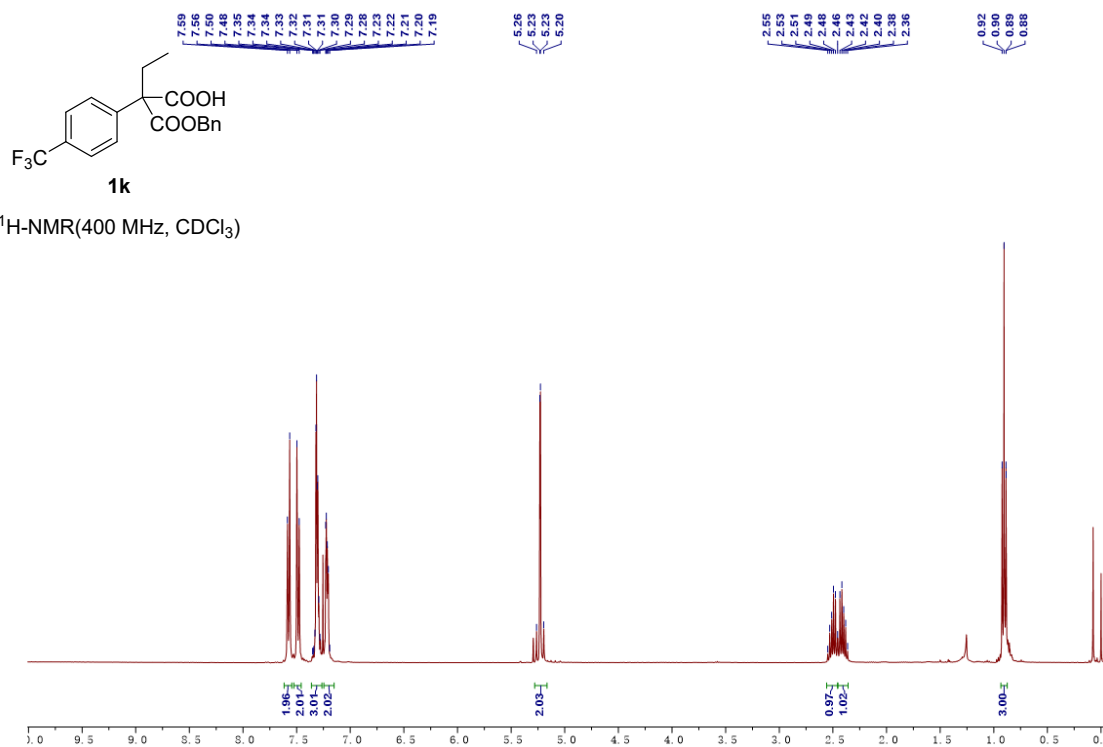


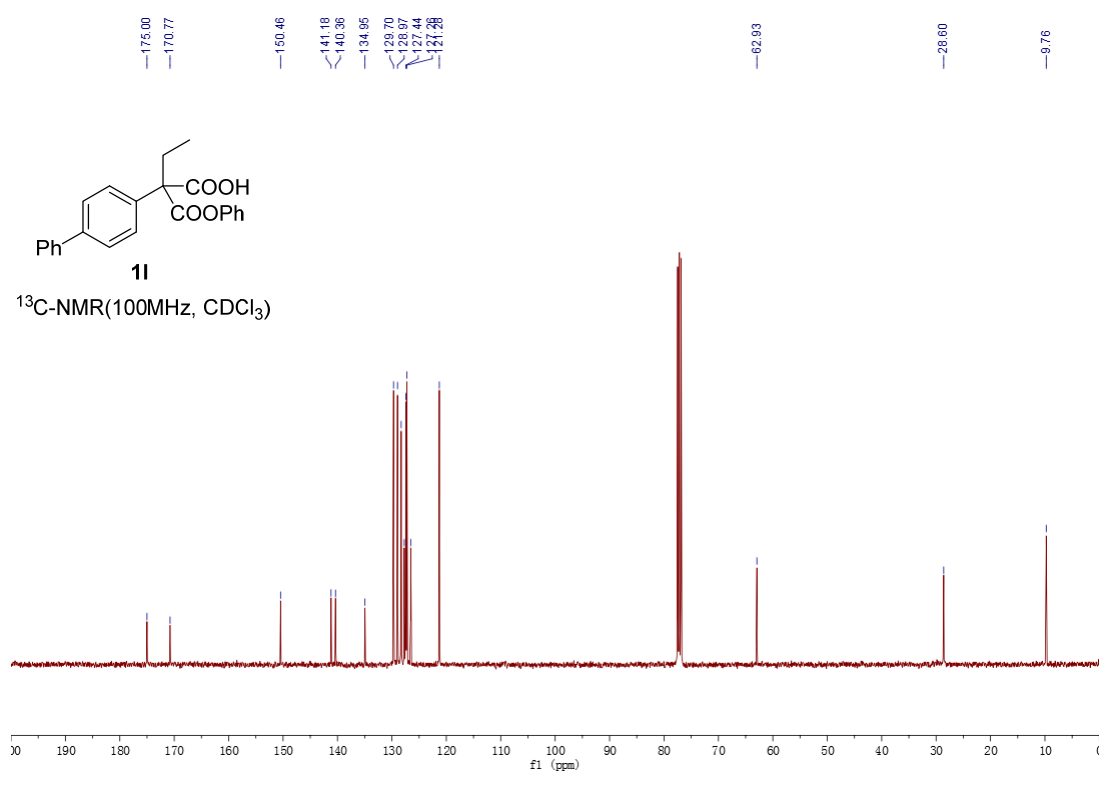
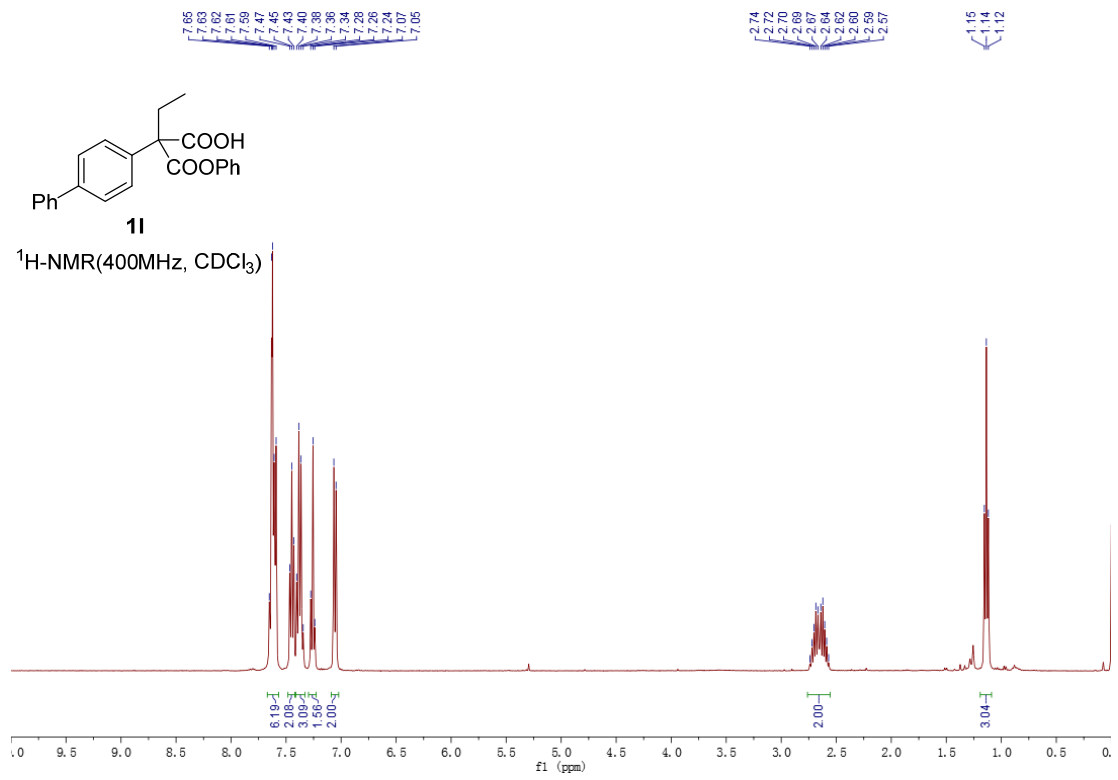
$^1\text{H-NMR}$ (400 MHz, CDCl_3)

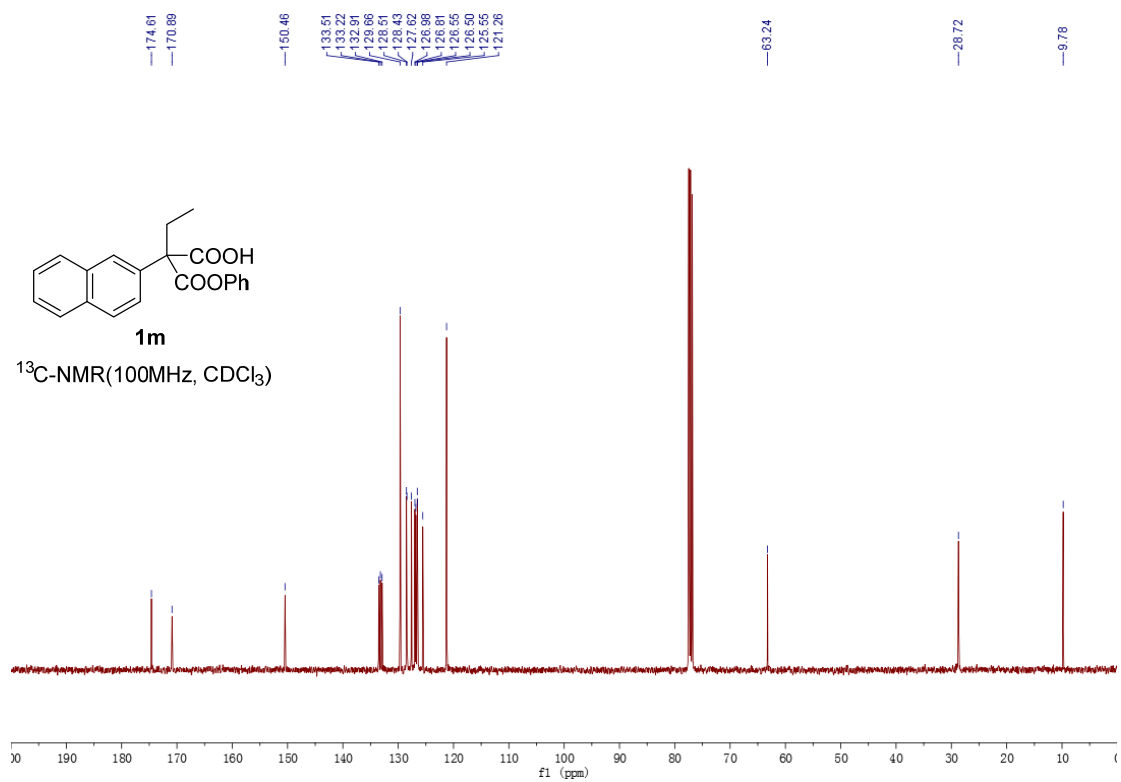
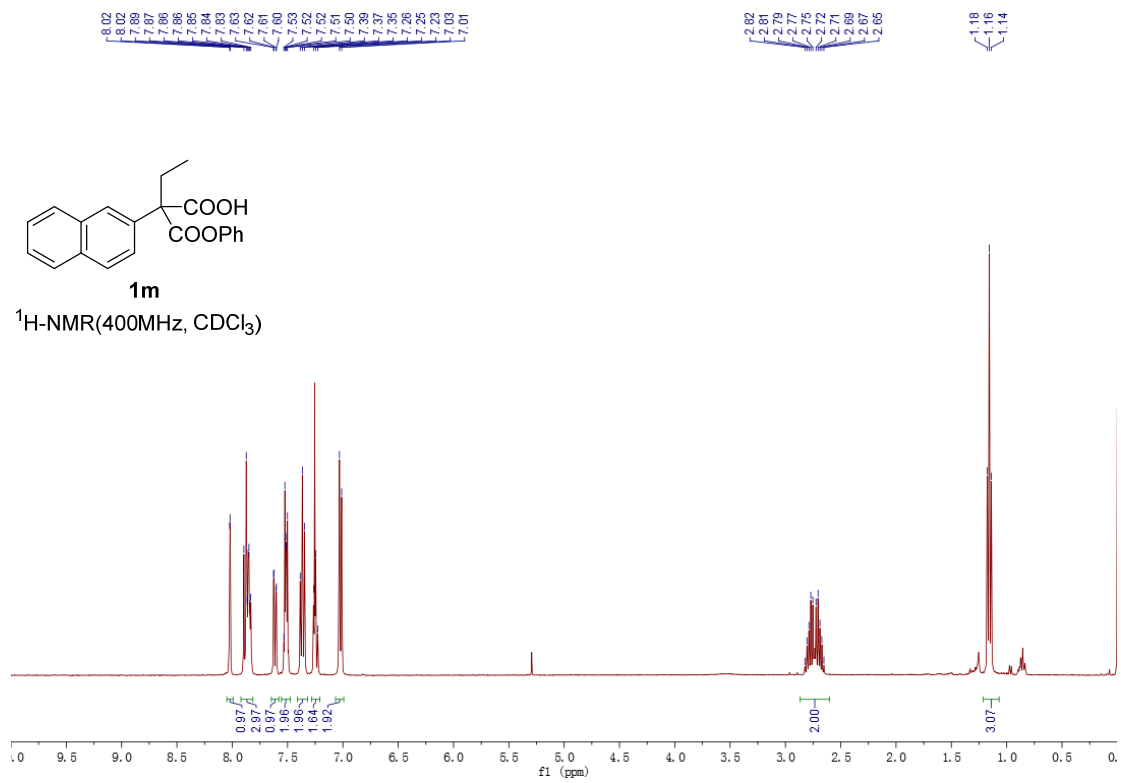


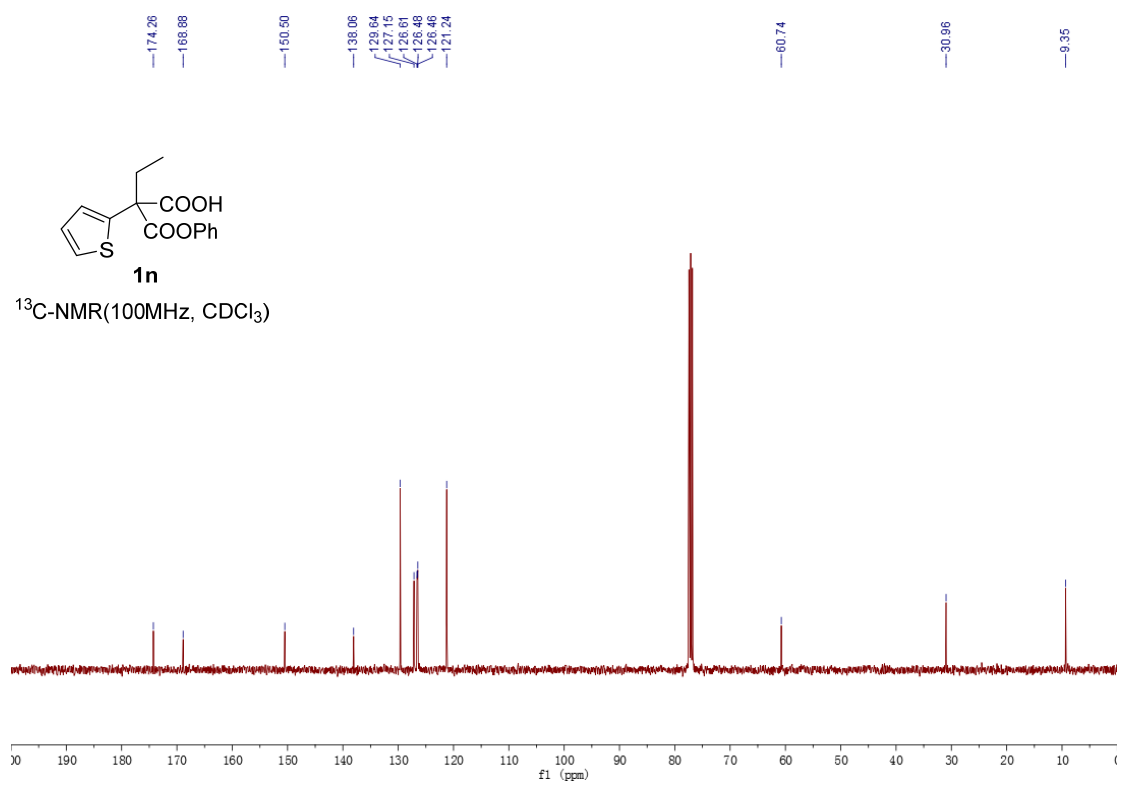
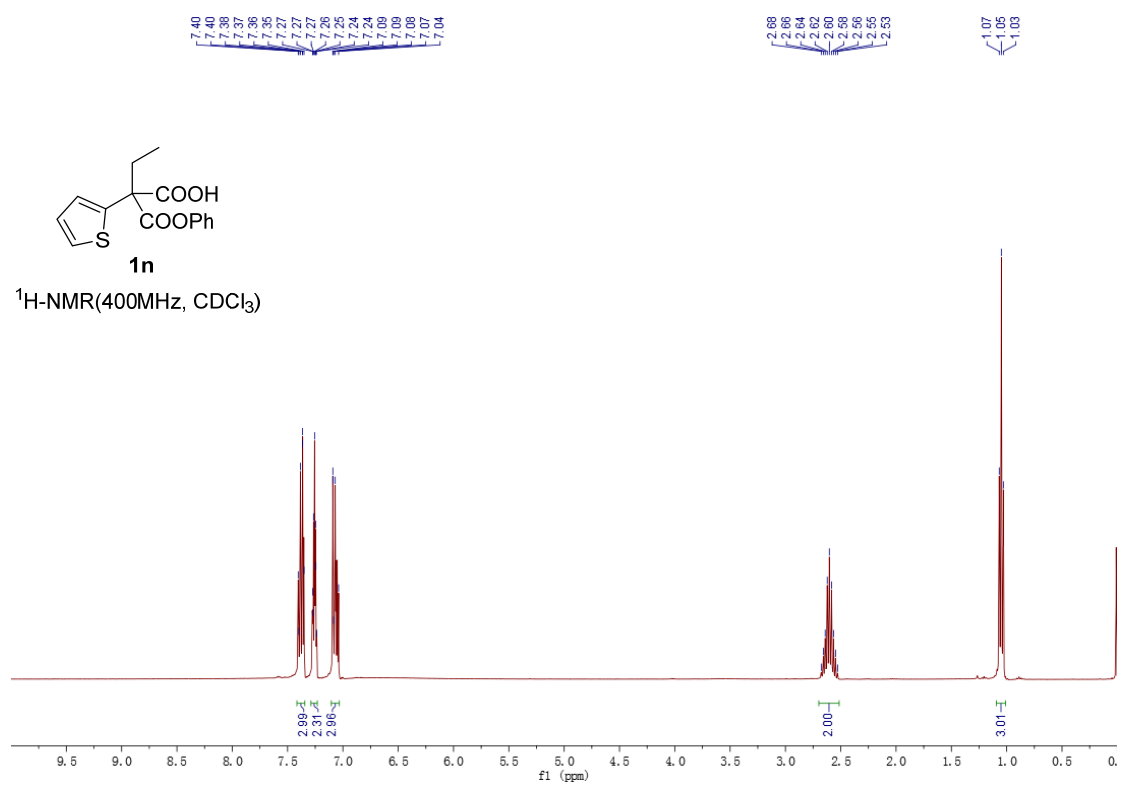
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3)

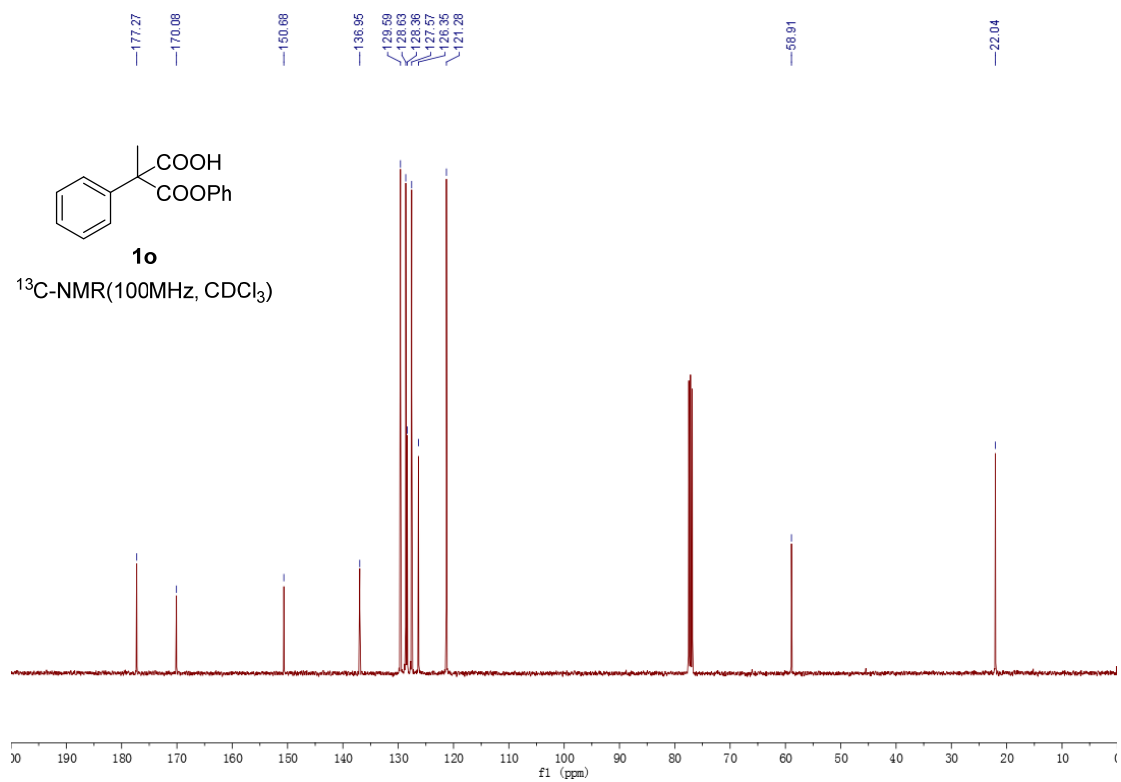
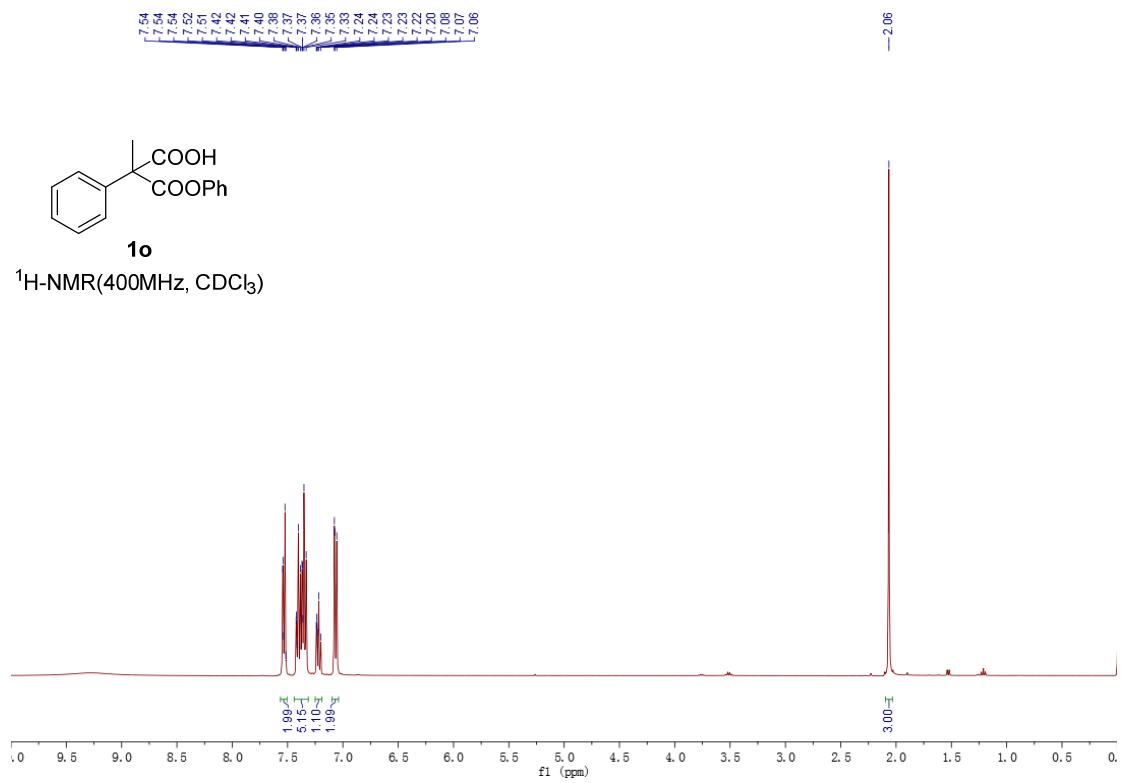


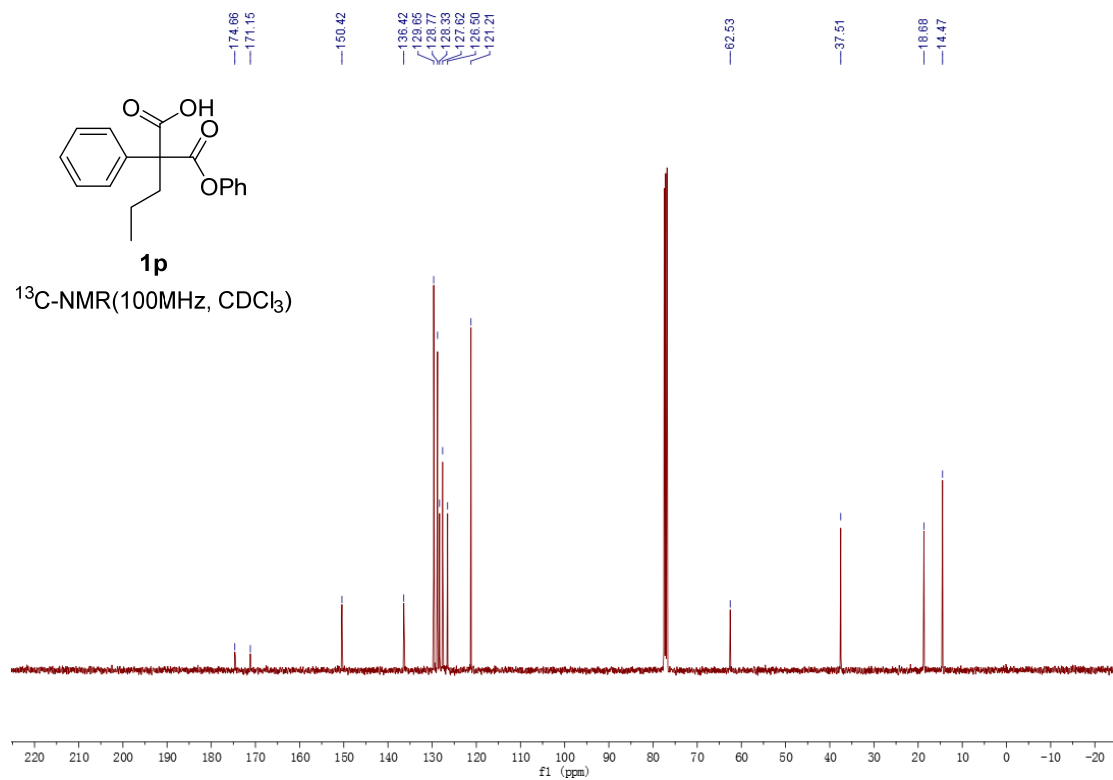
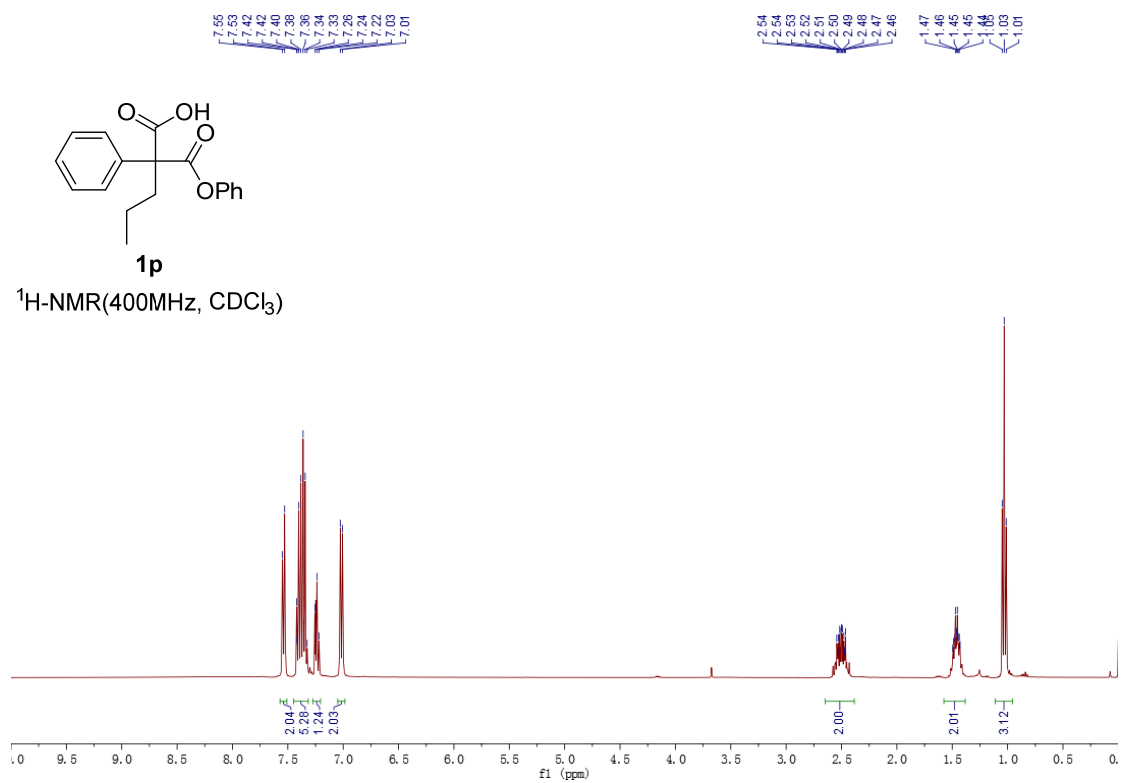


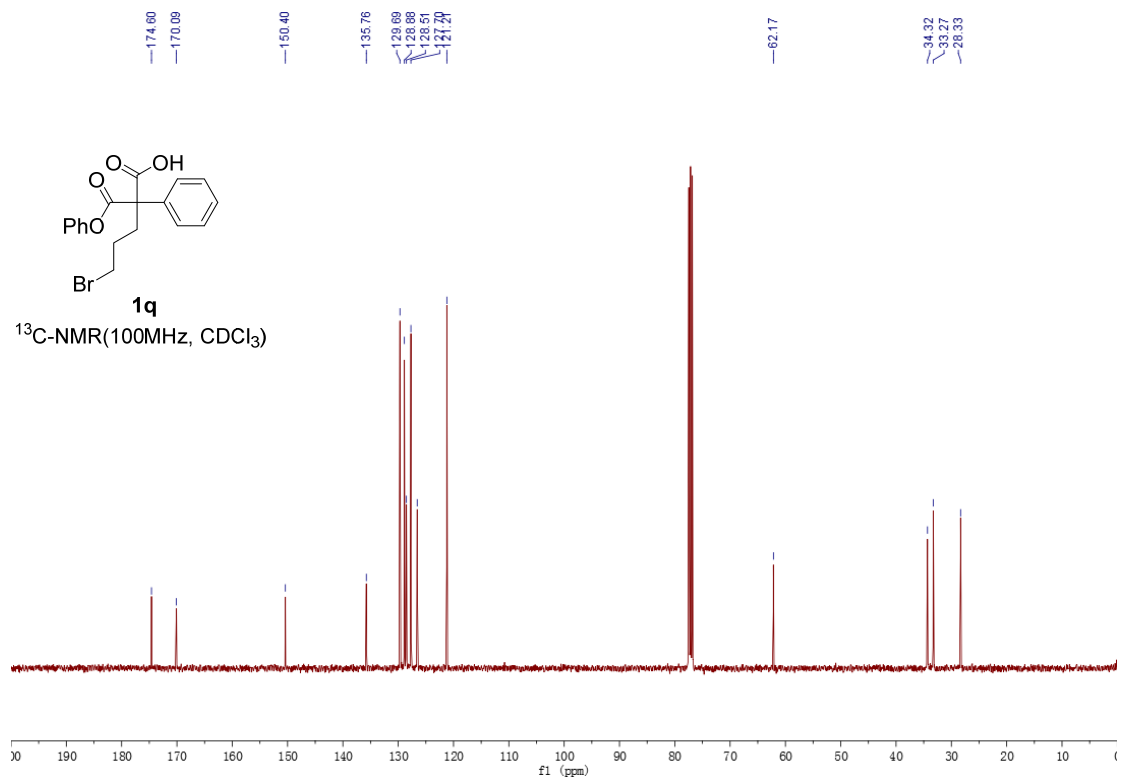
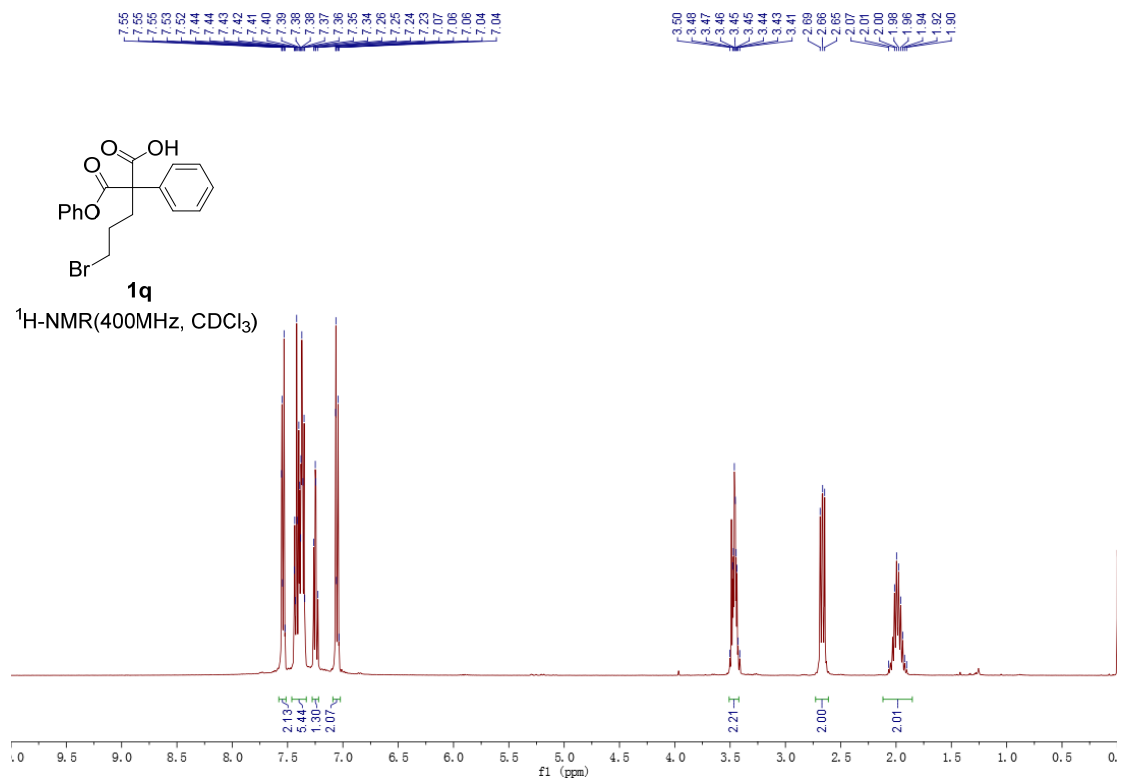


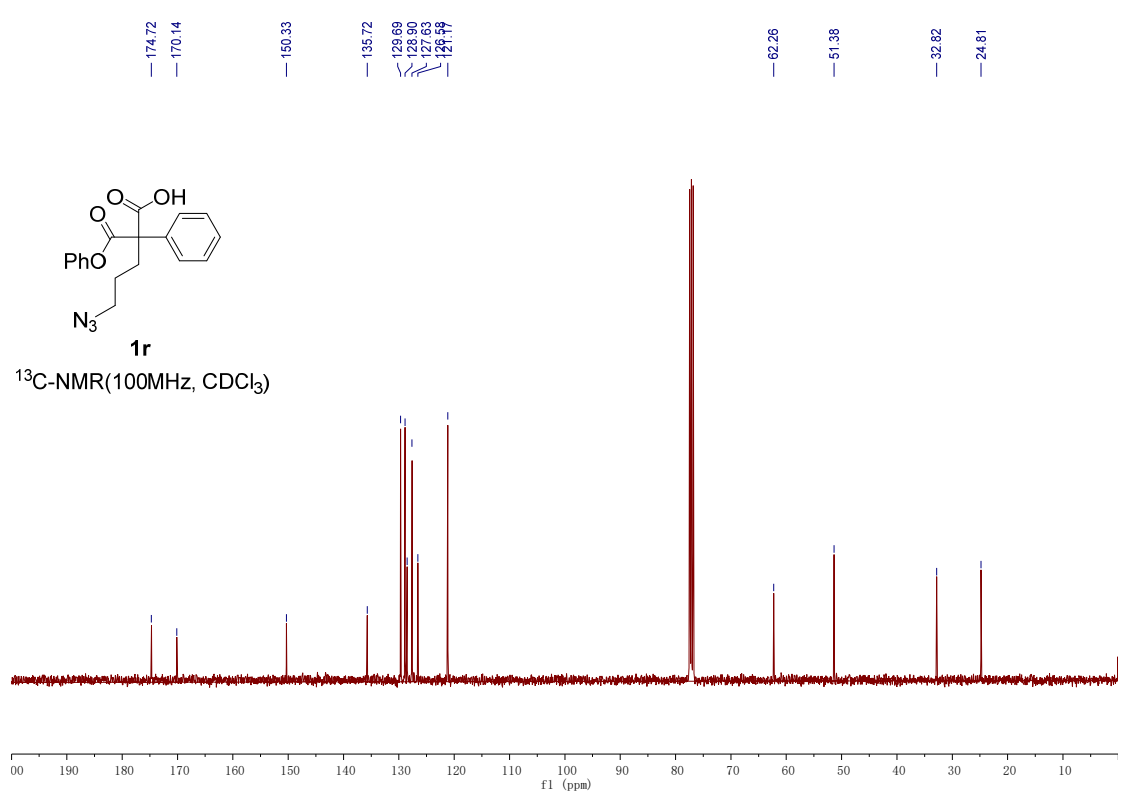
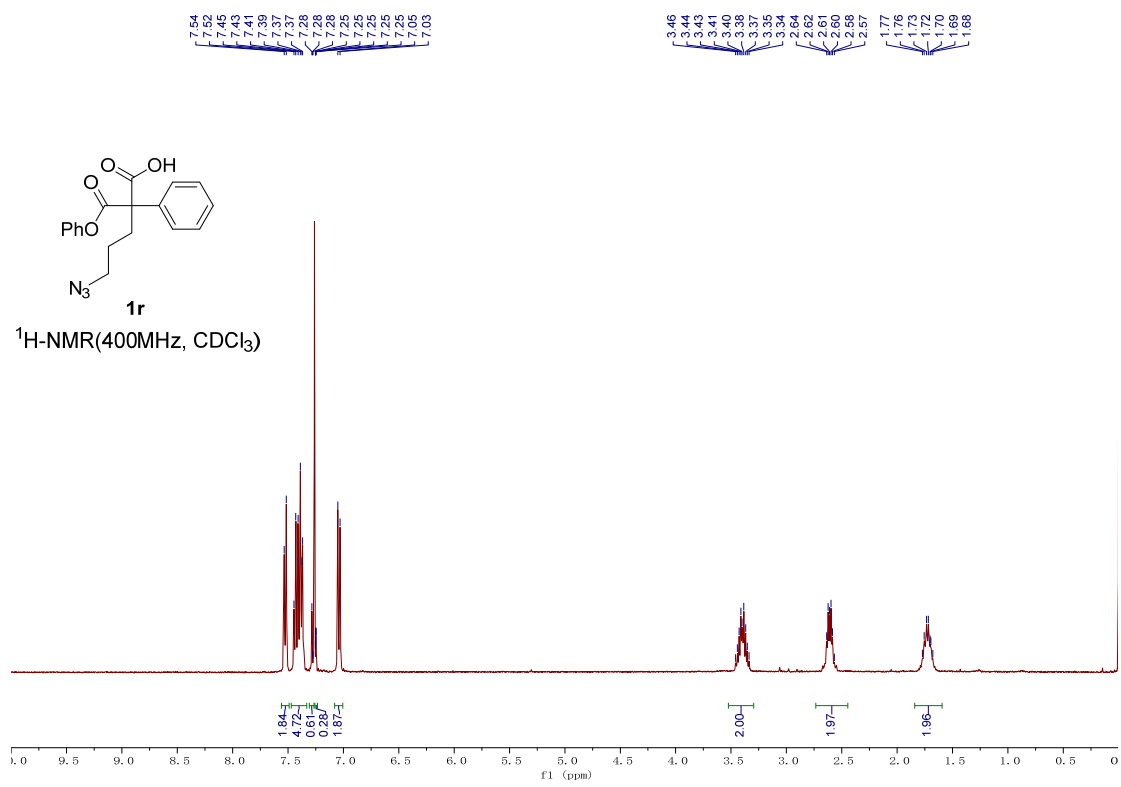


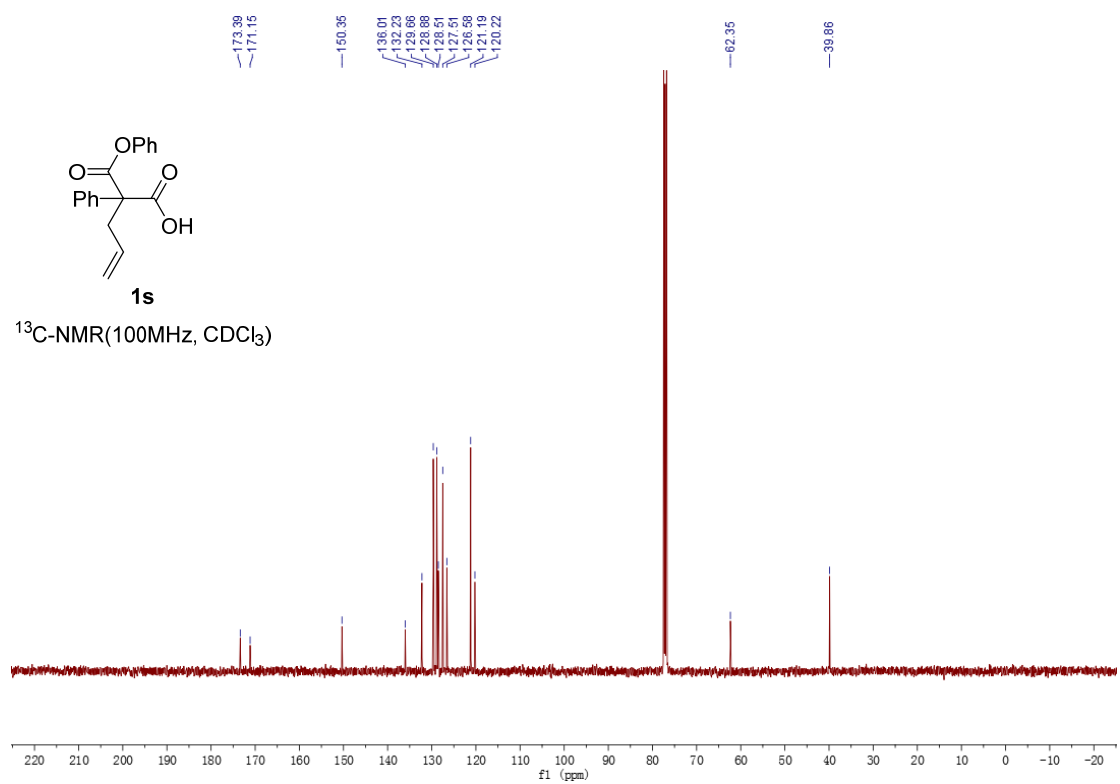
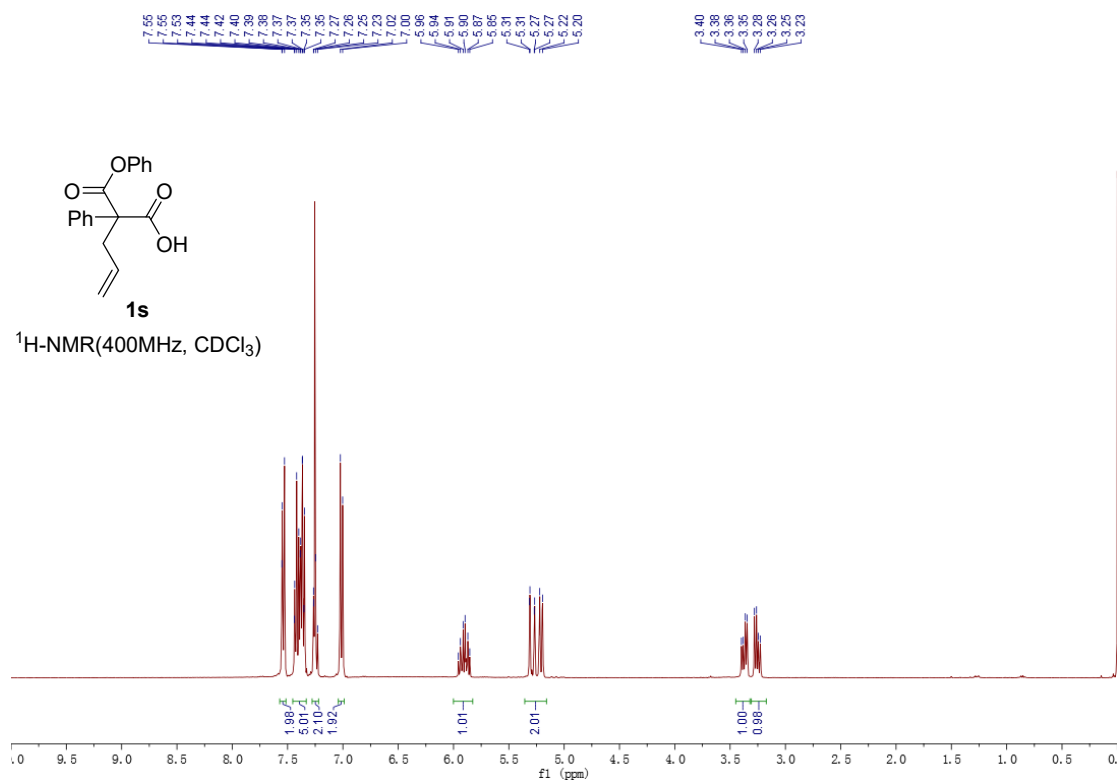


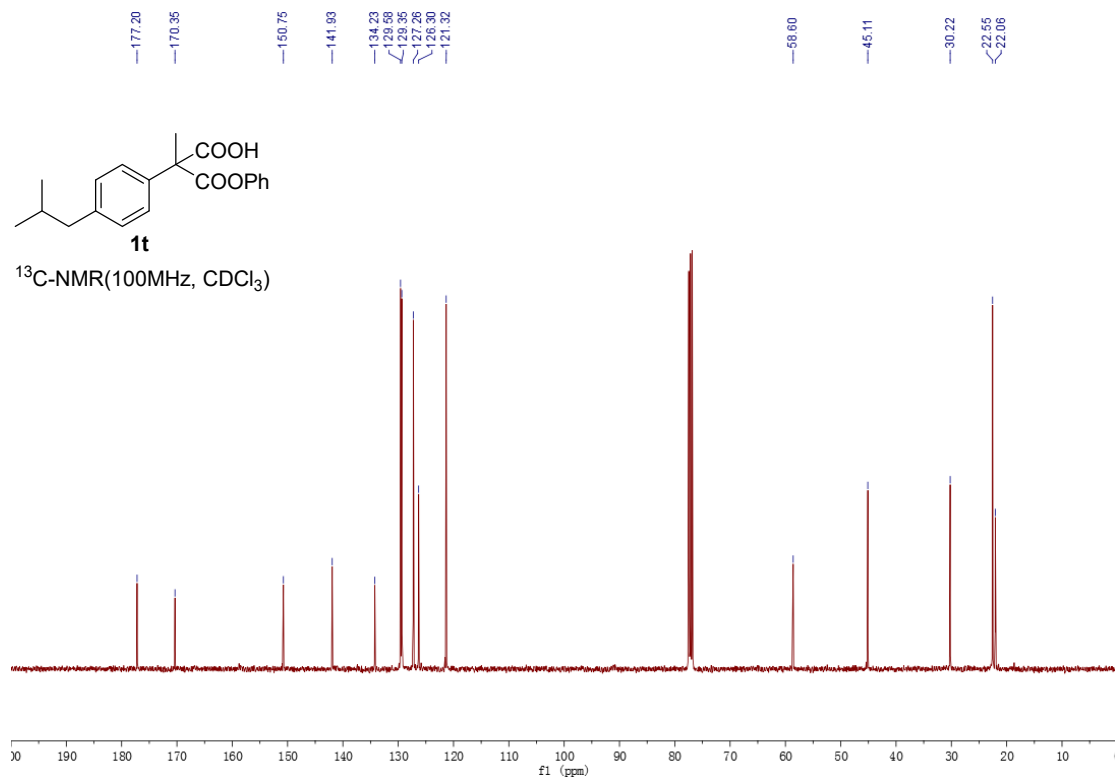
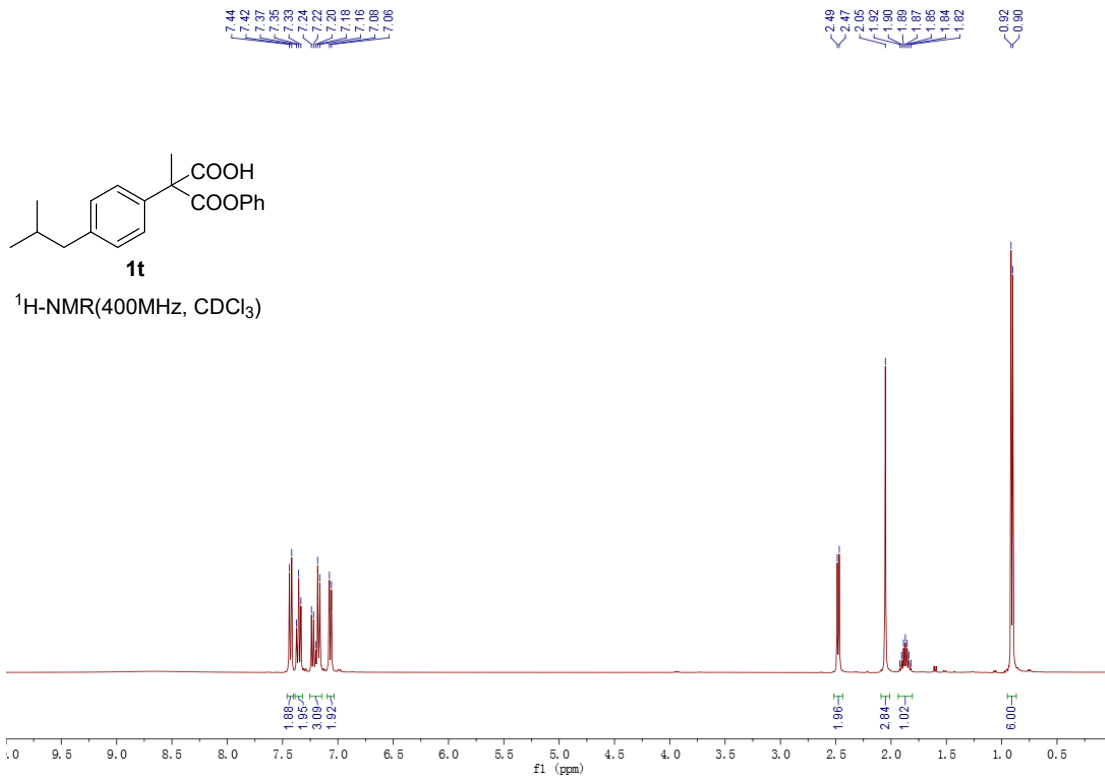


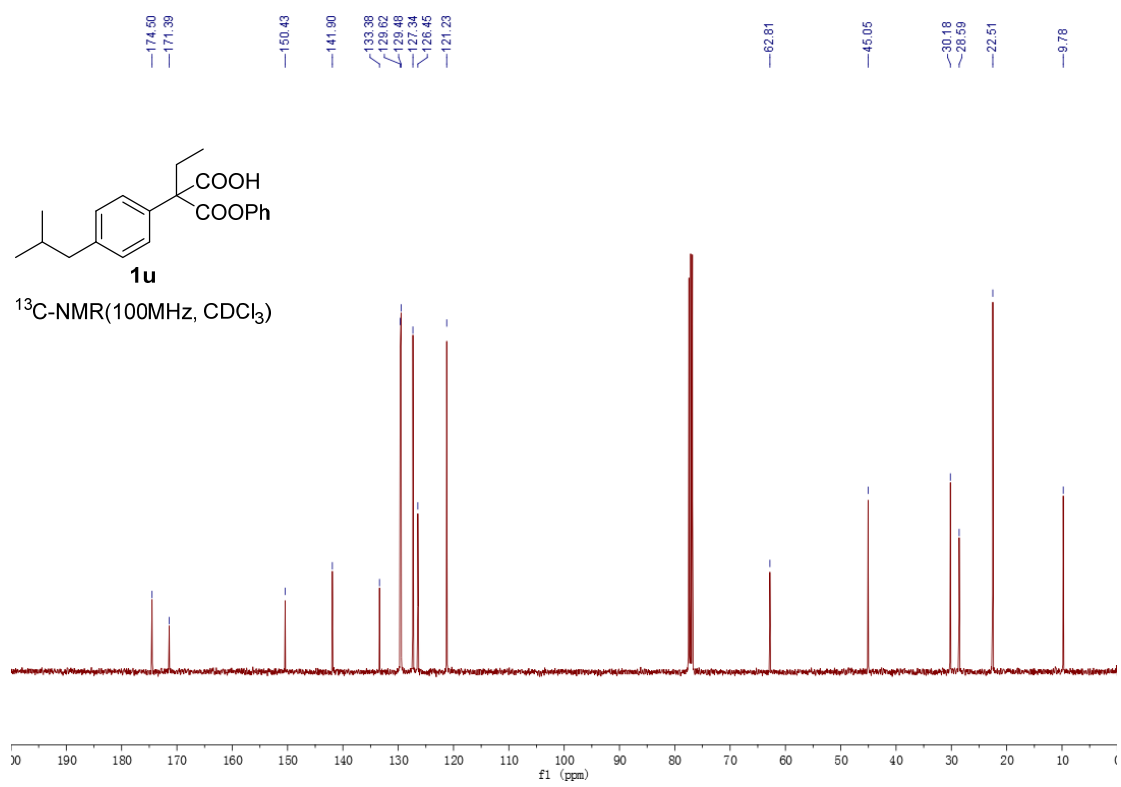
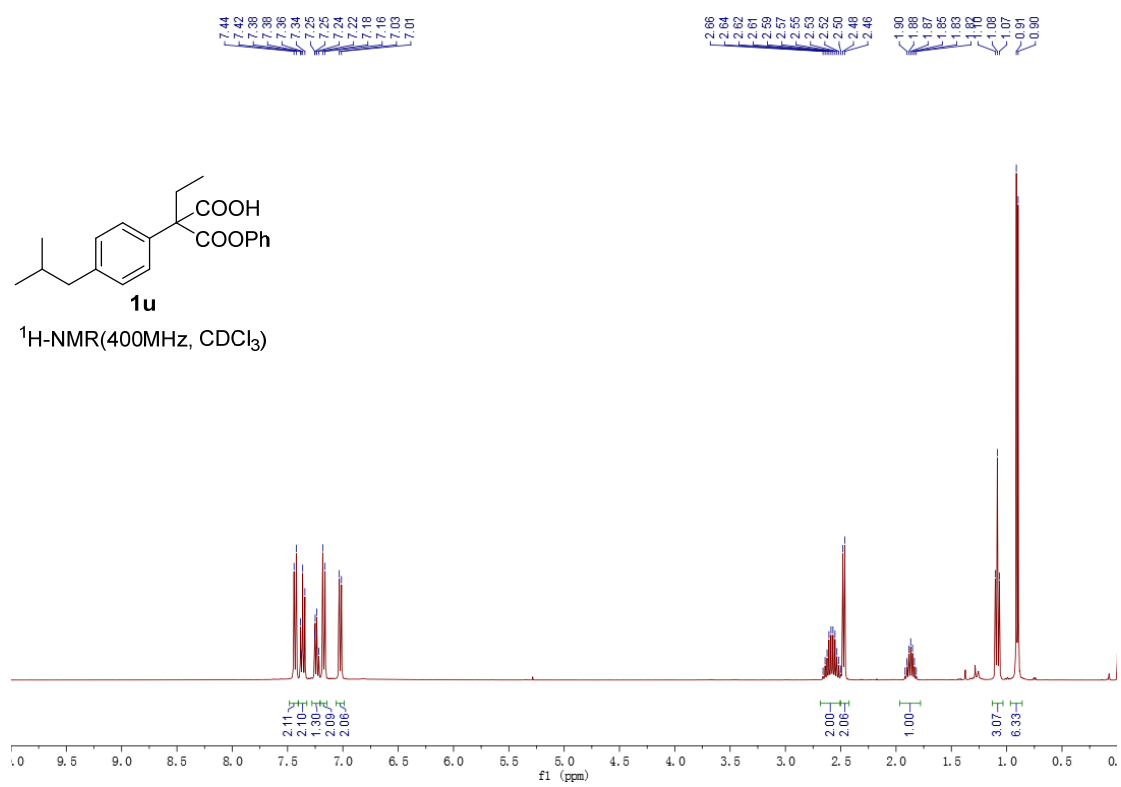


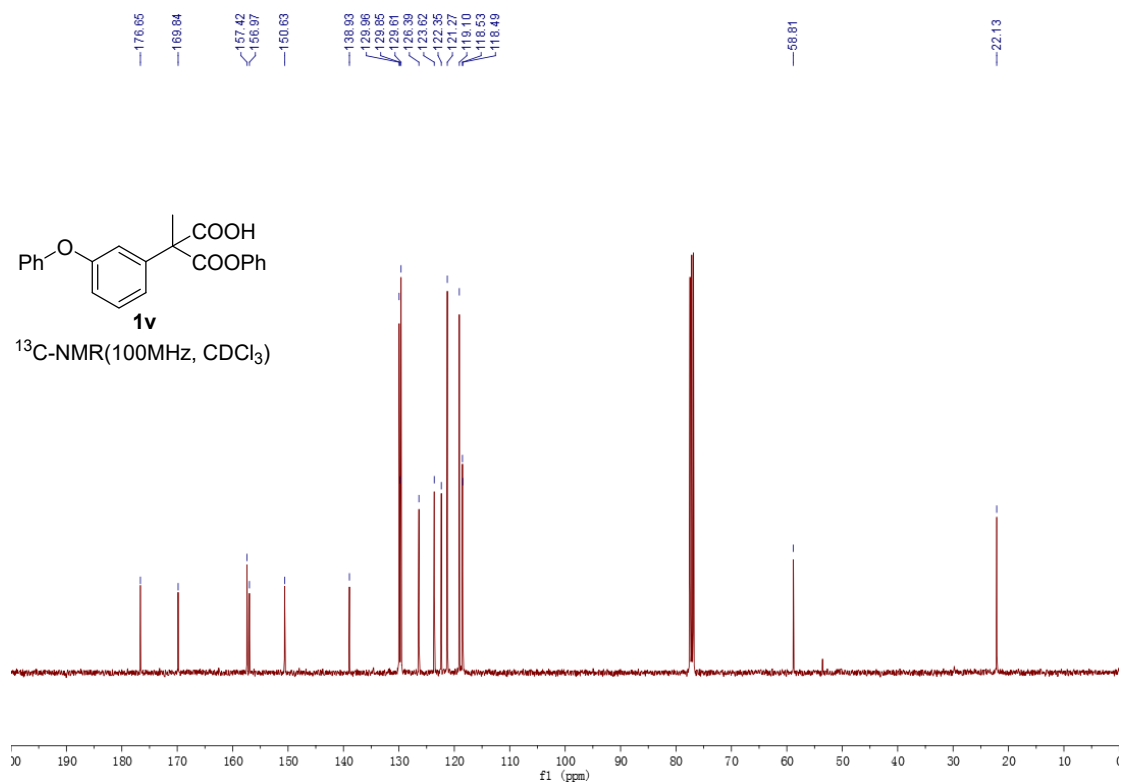
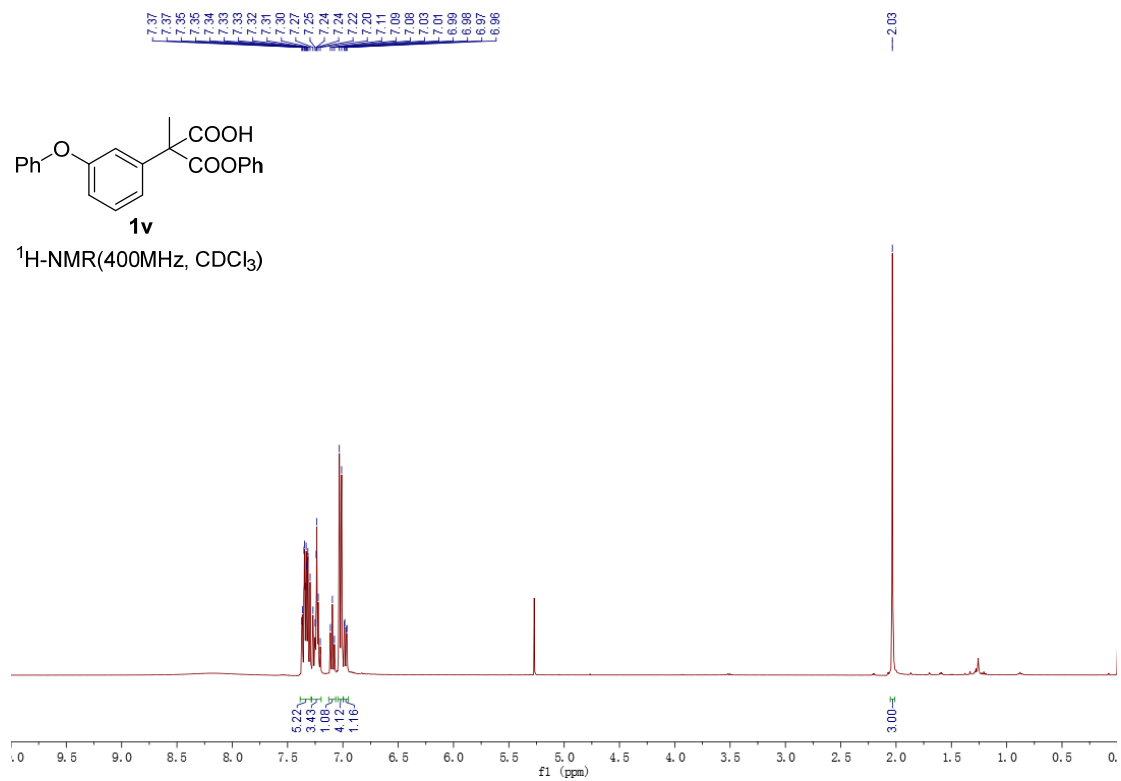


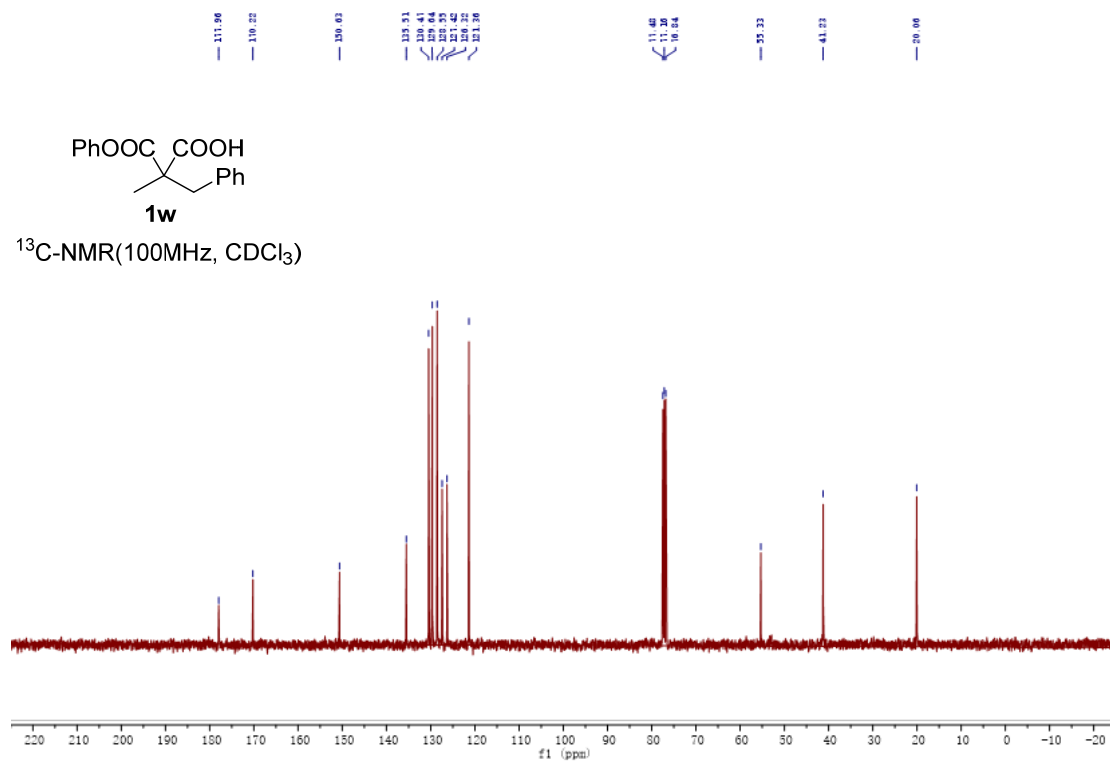
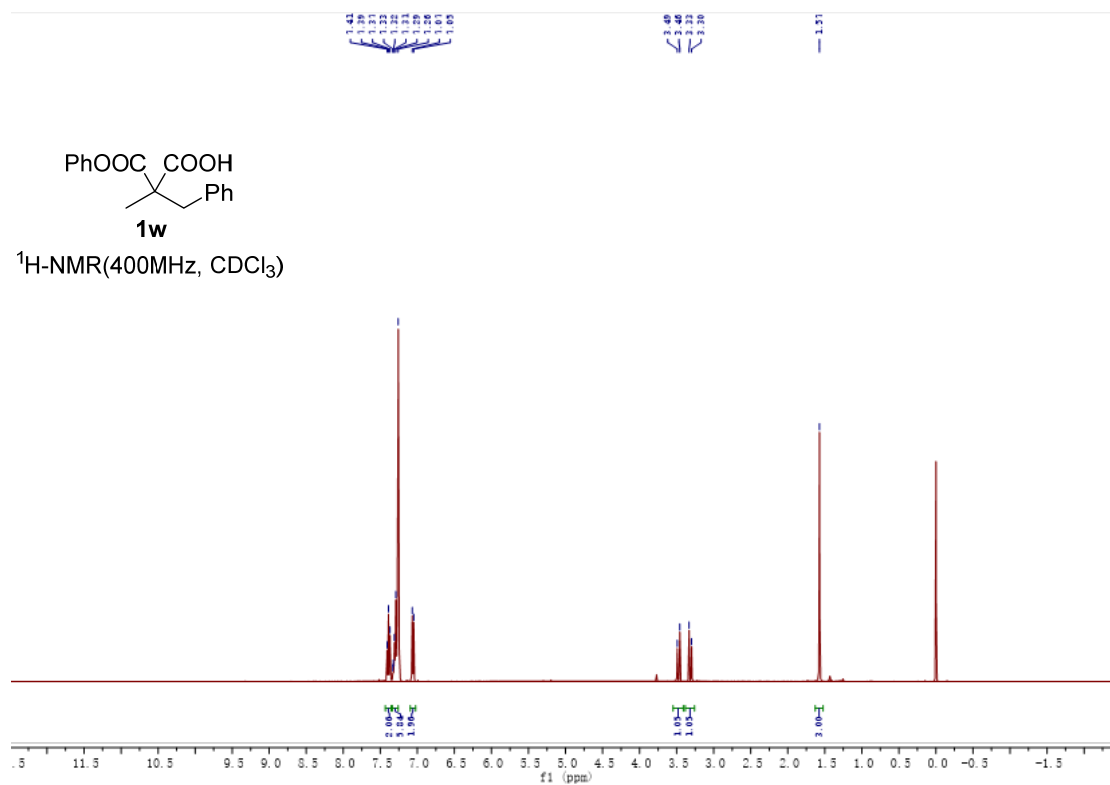


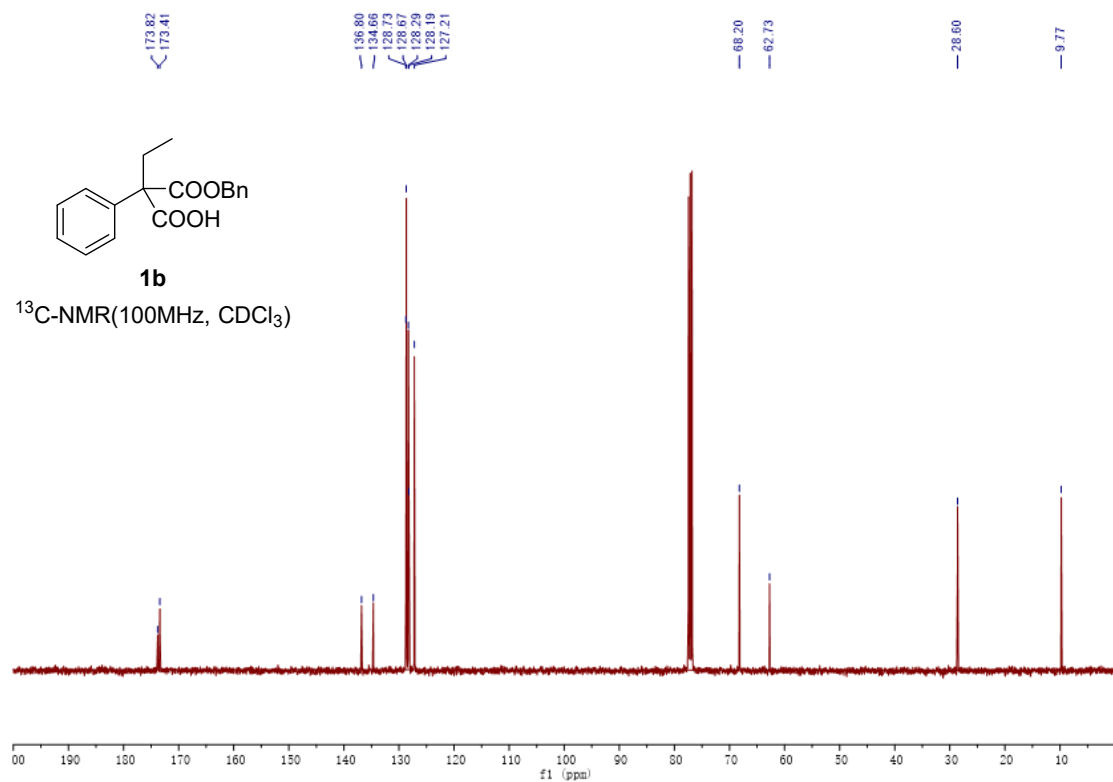
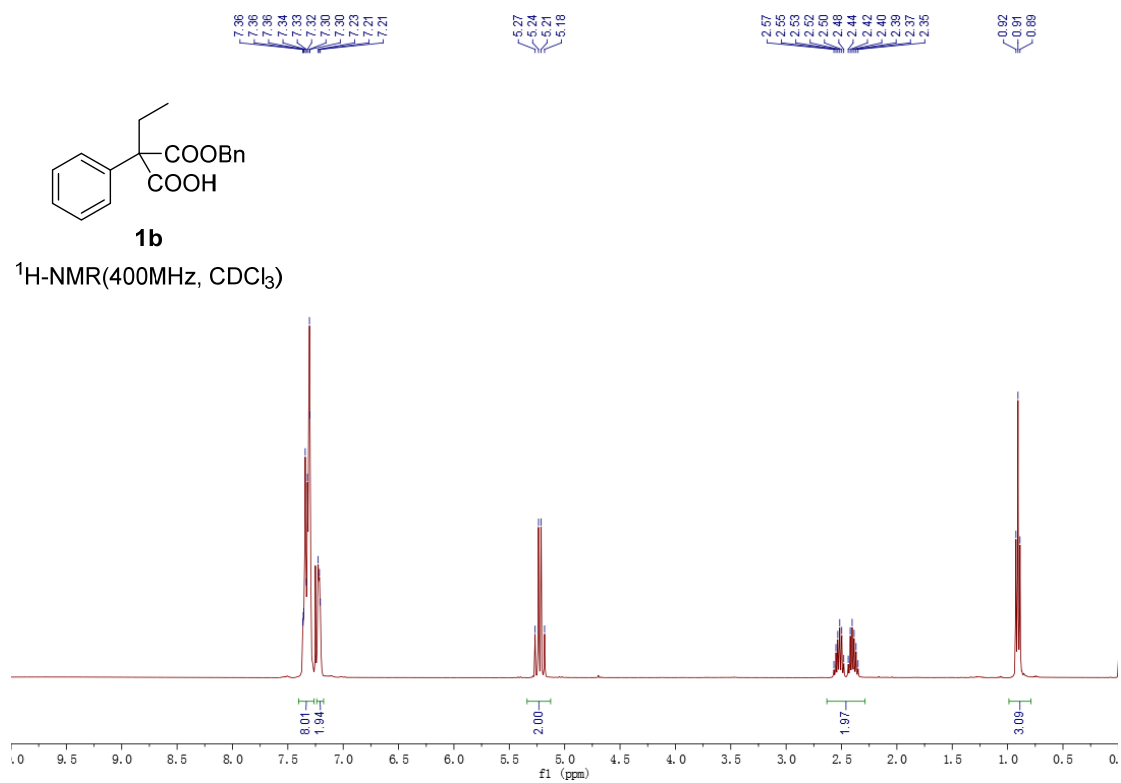


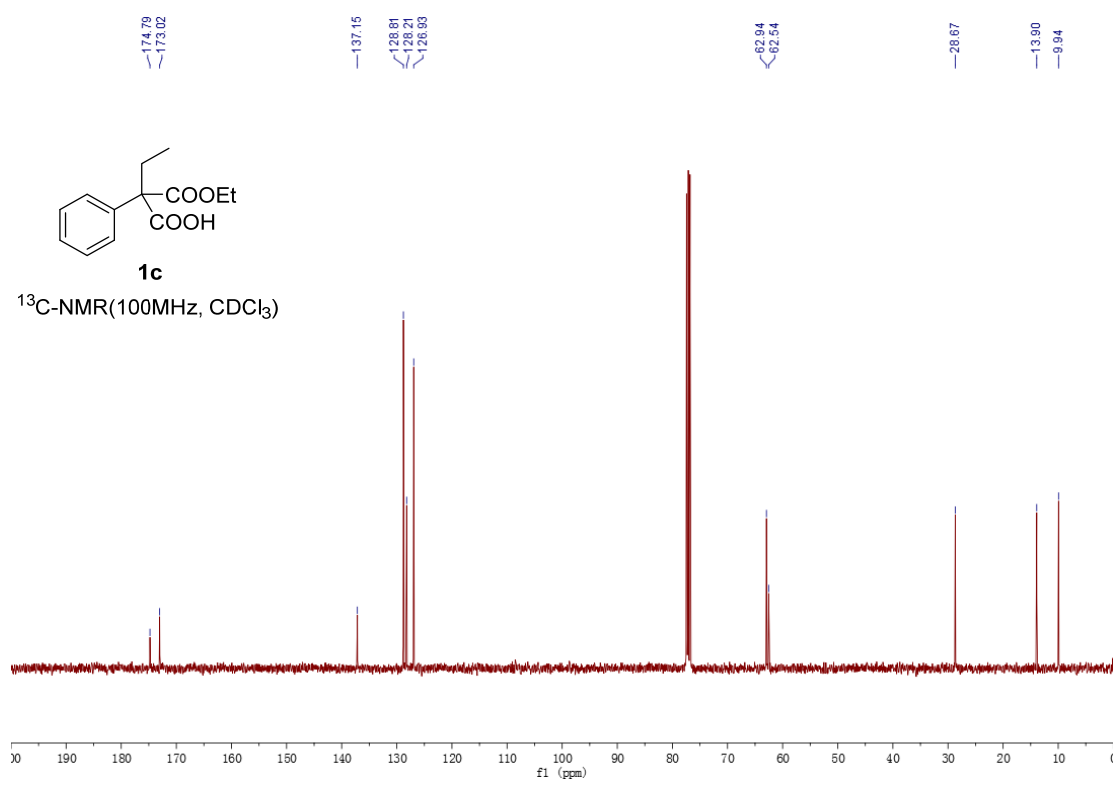
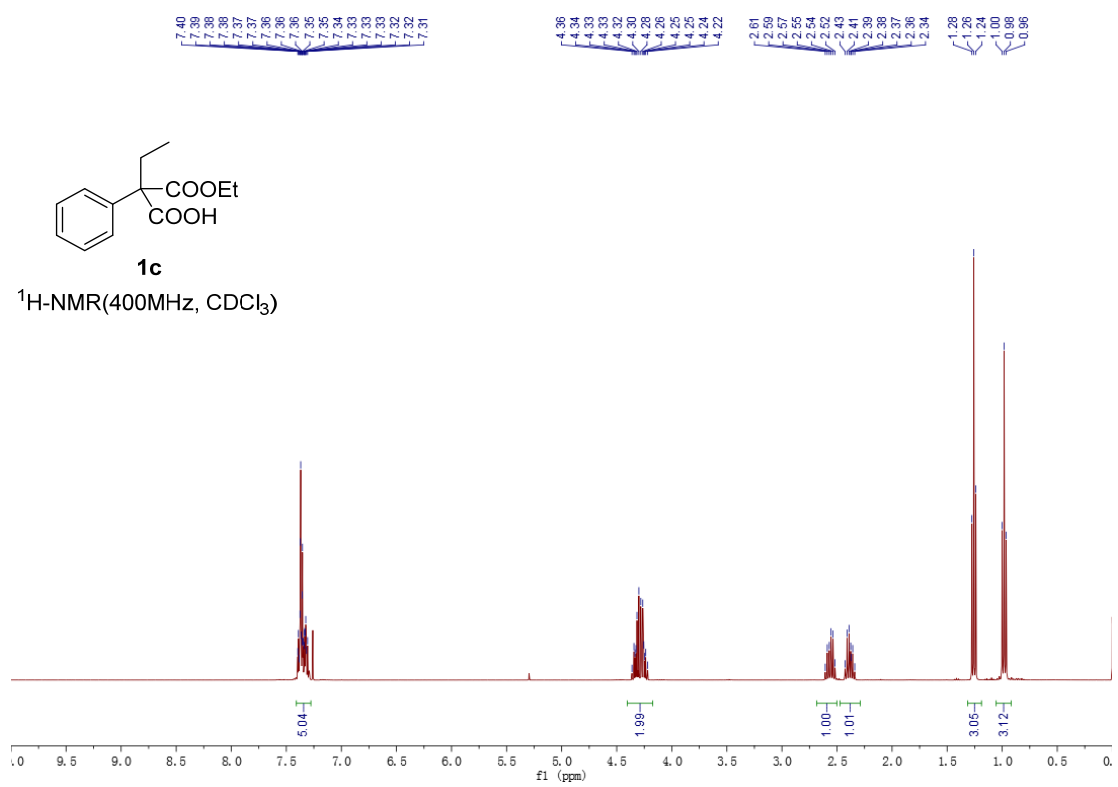


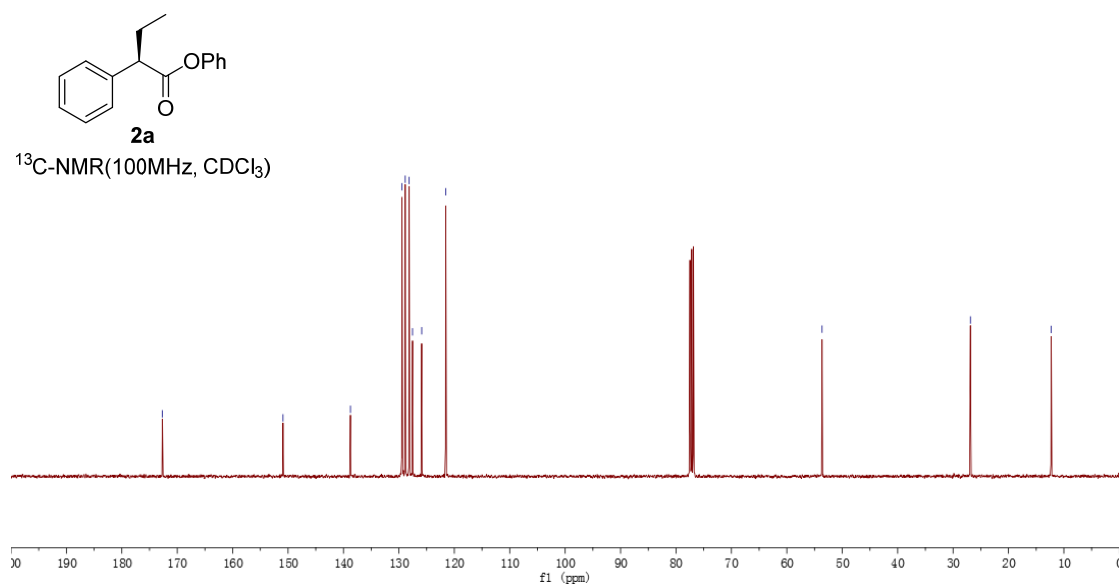
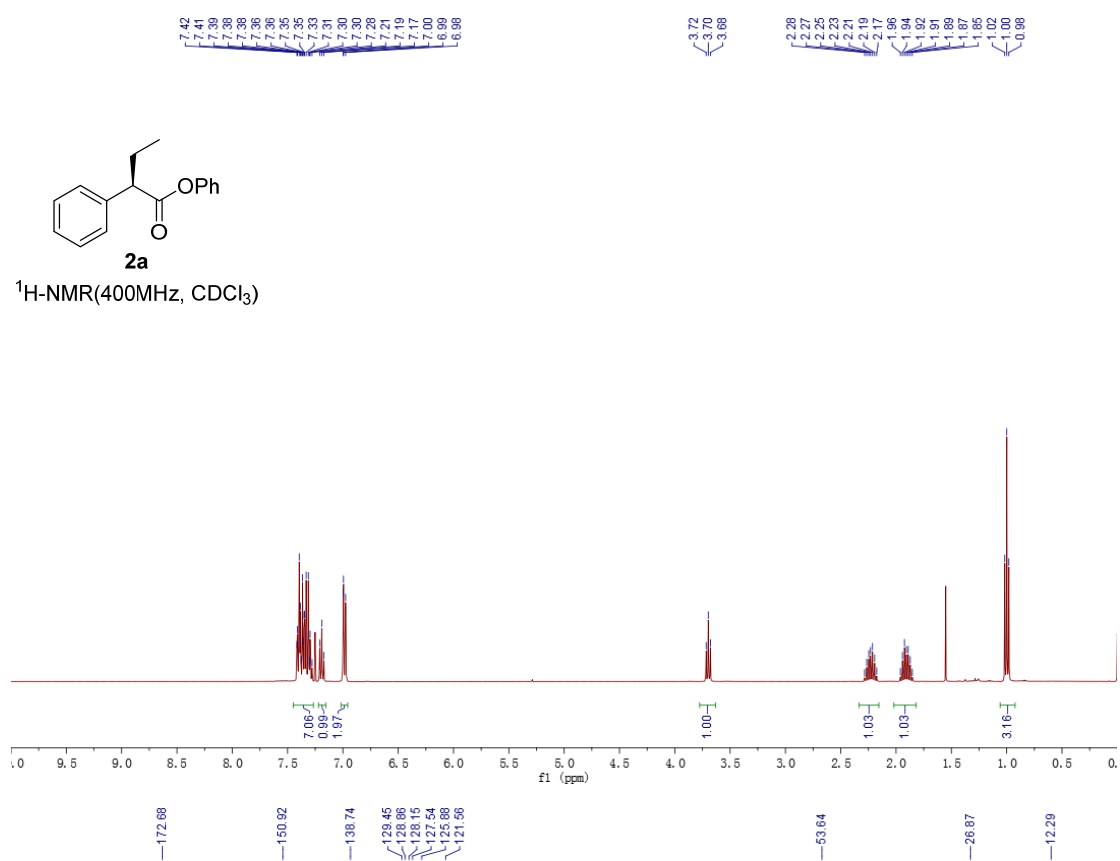


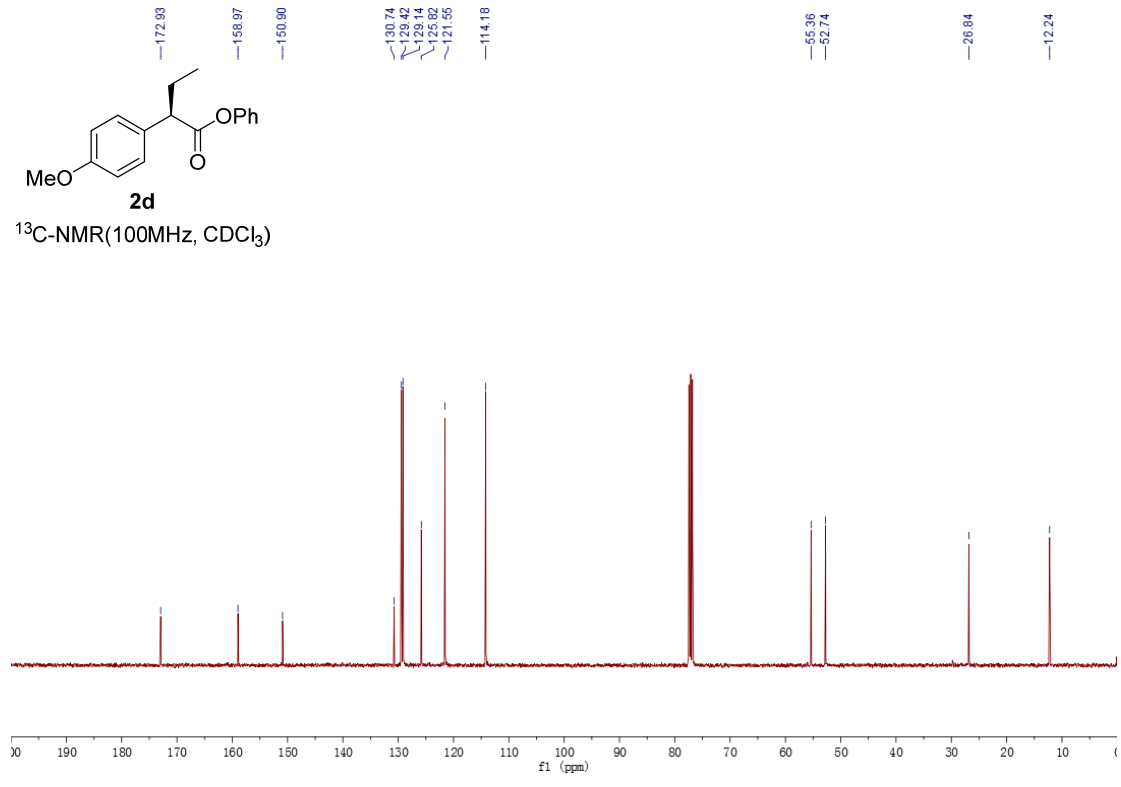
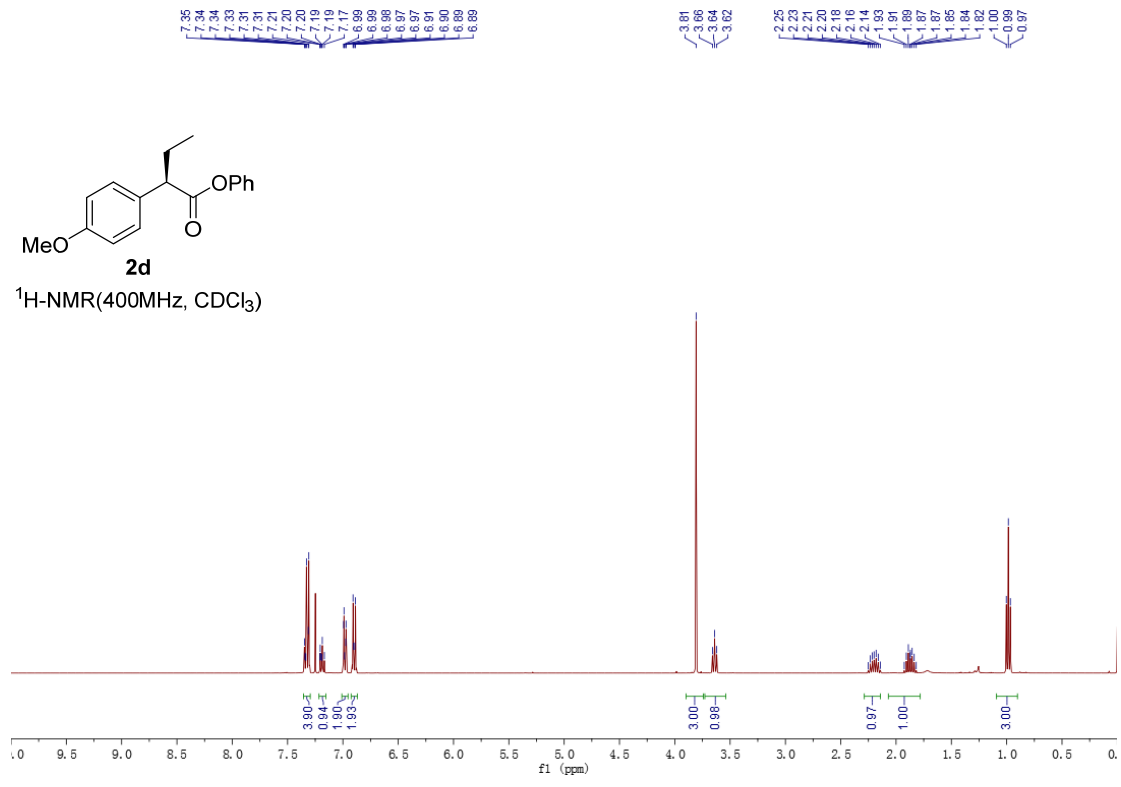


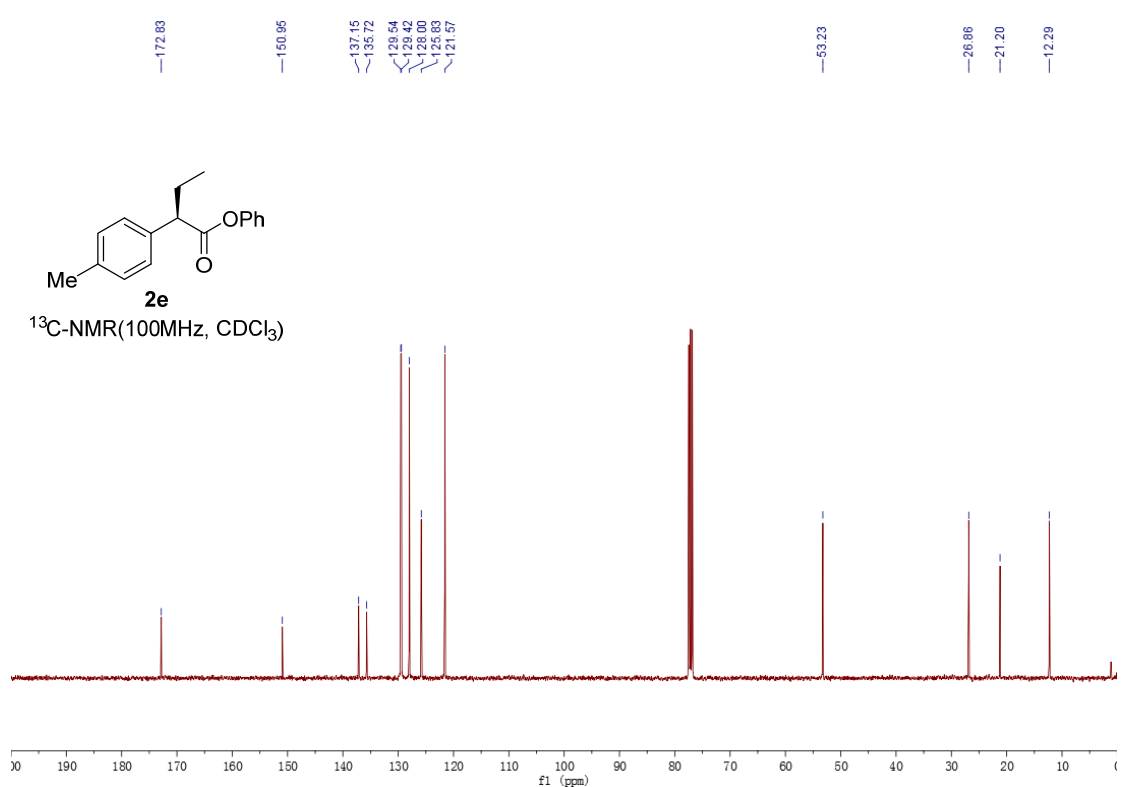
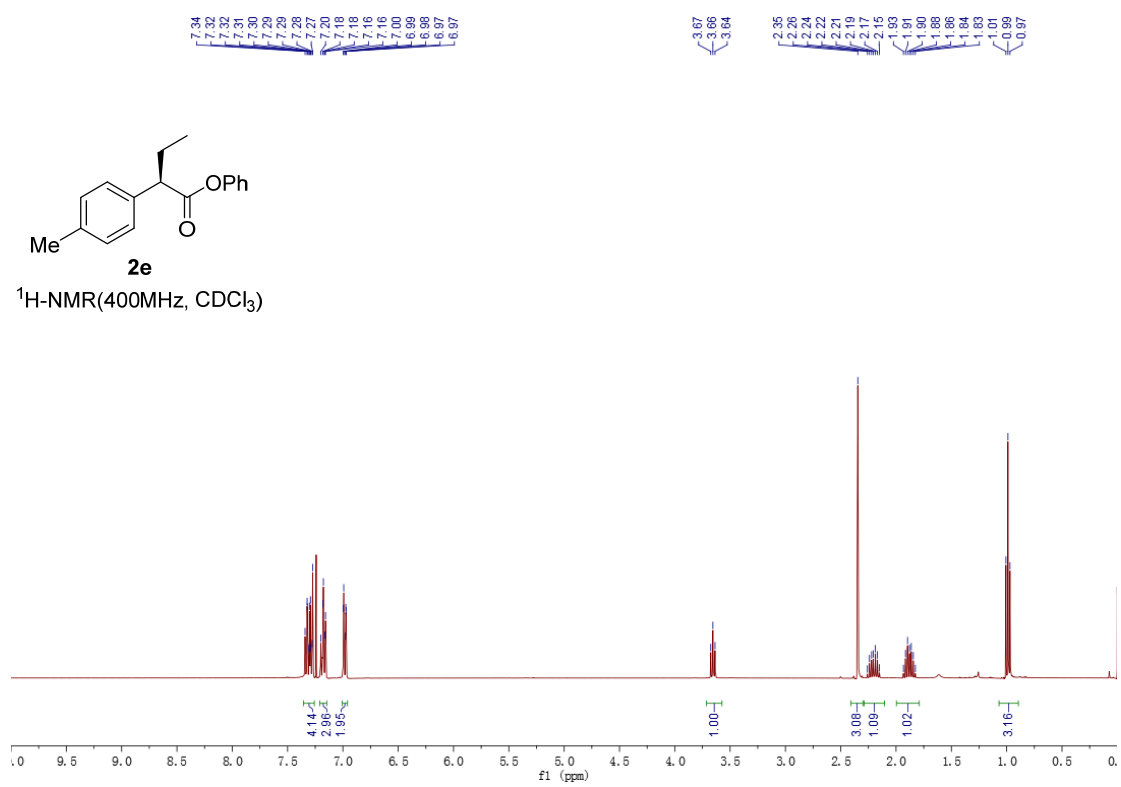


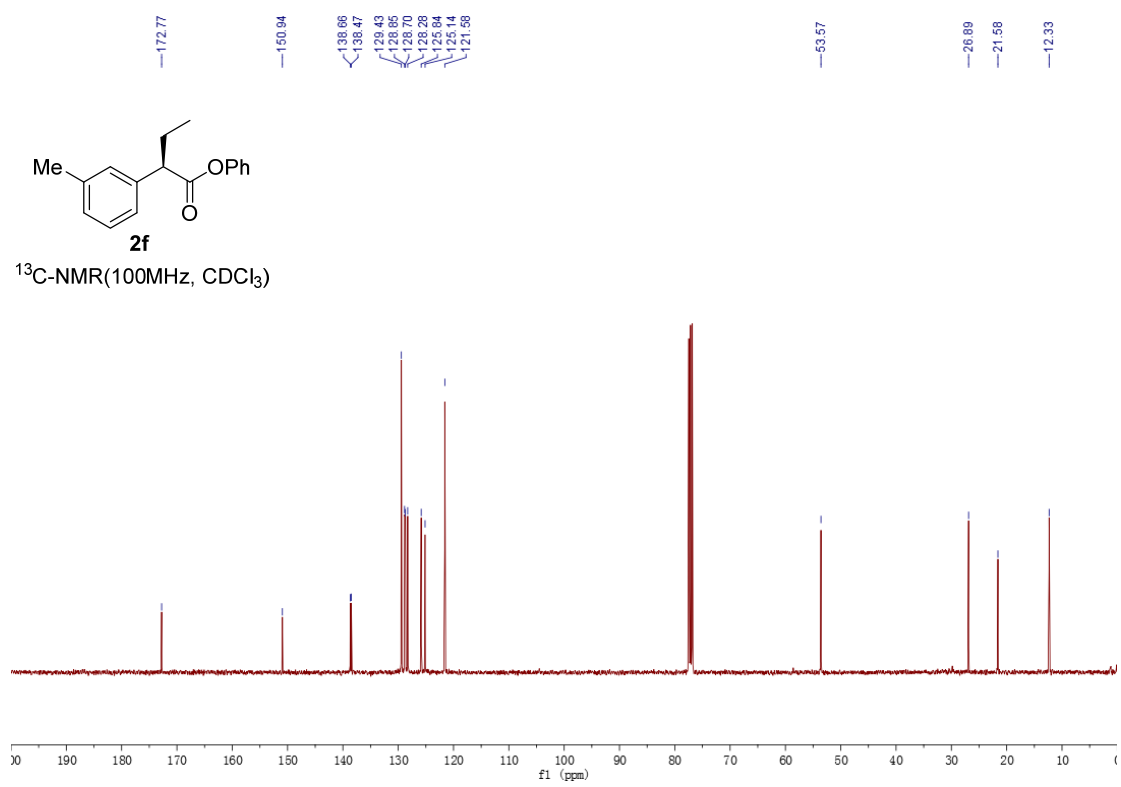
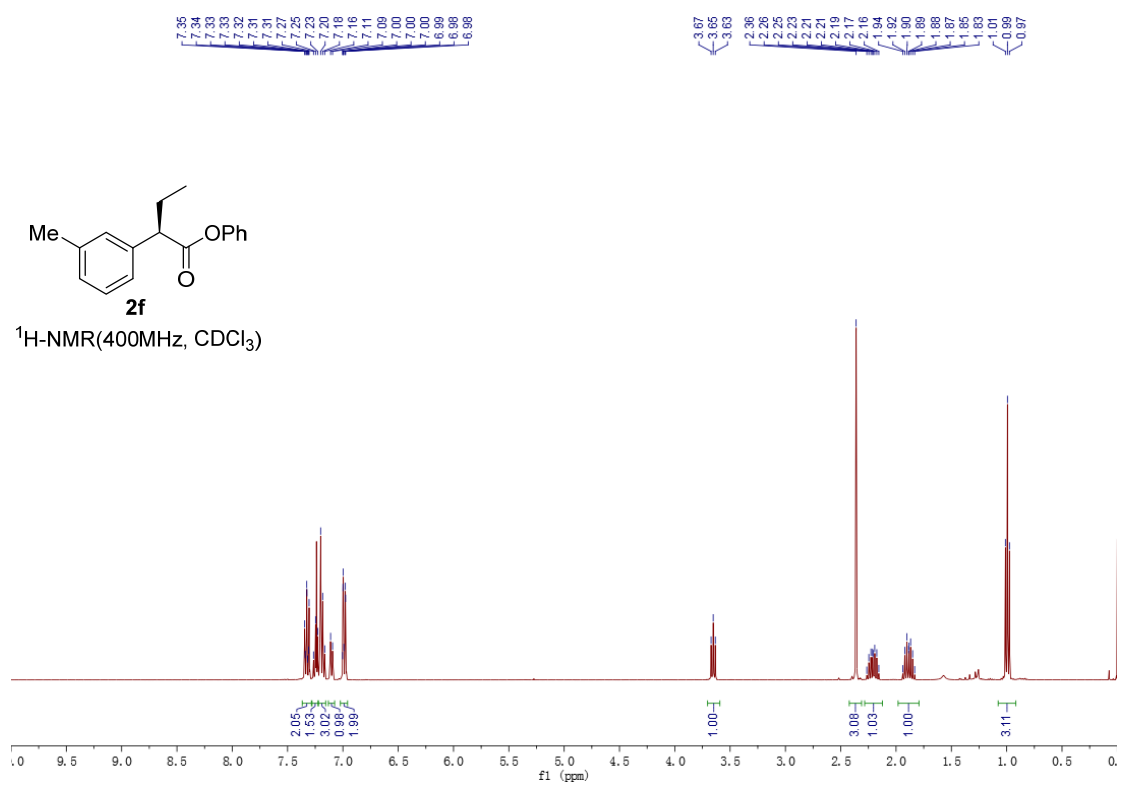


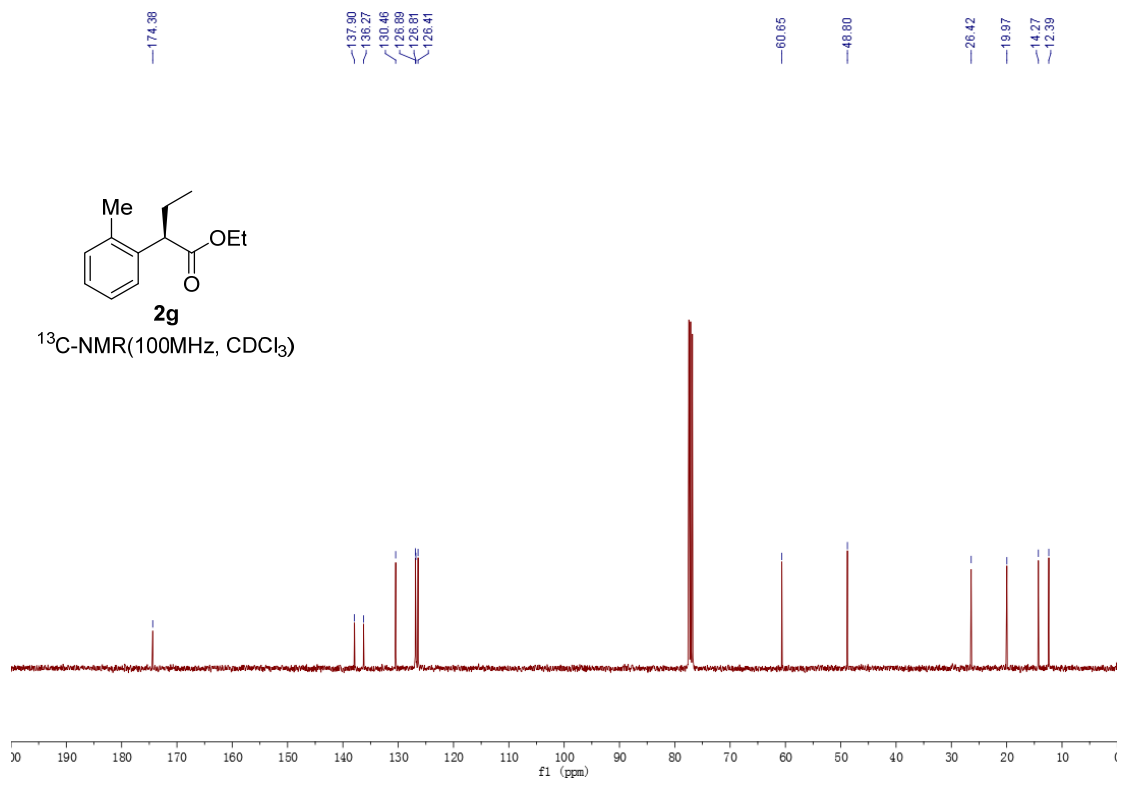
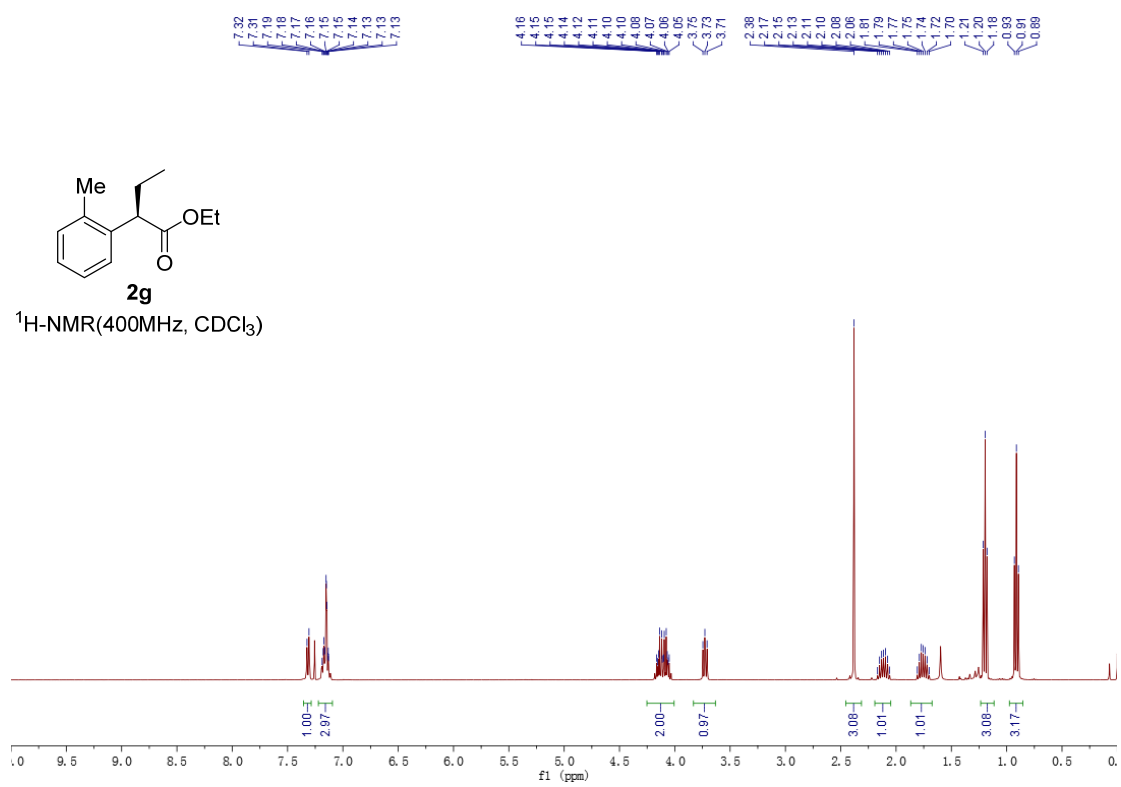


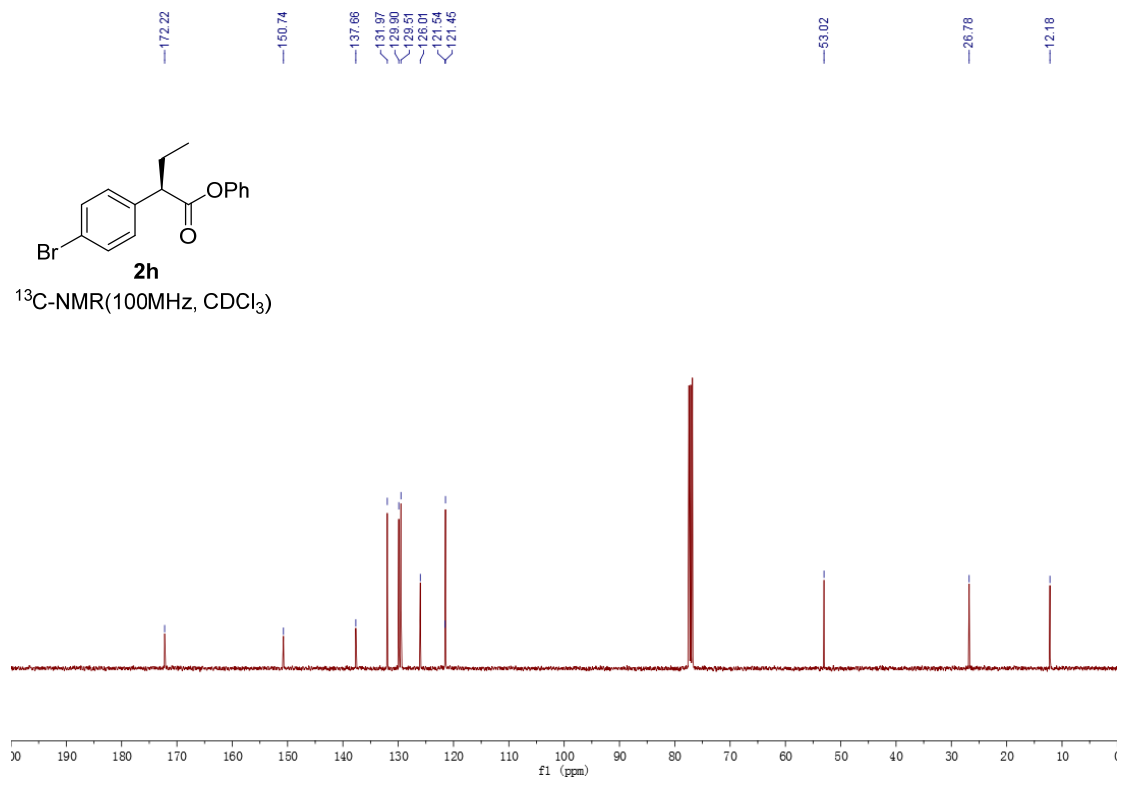
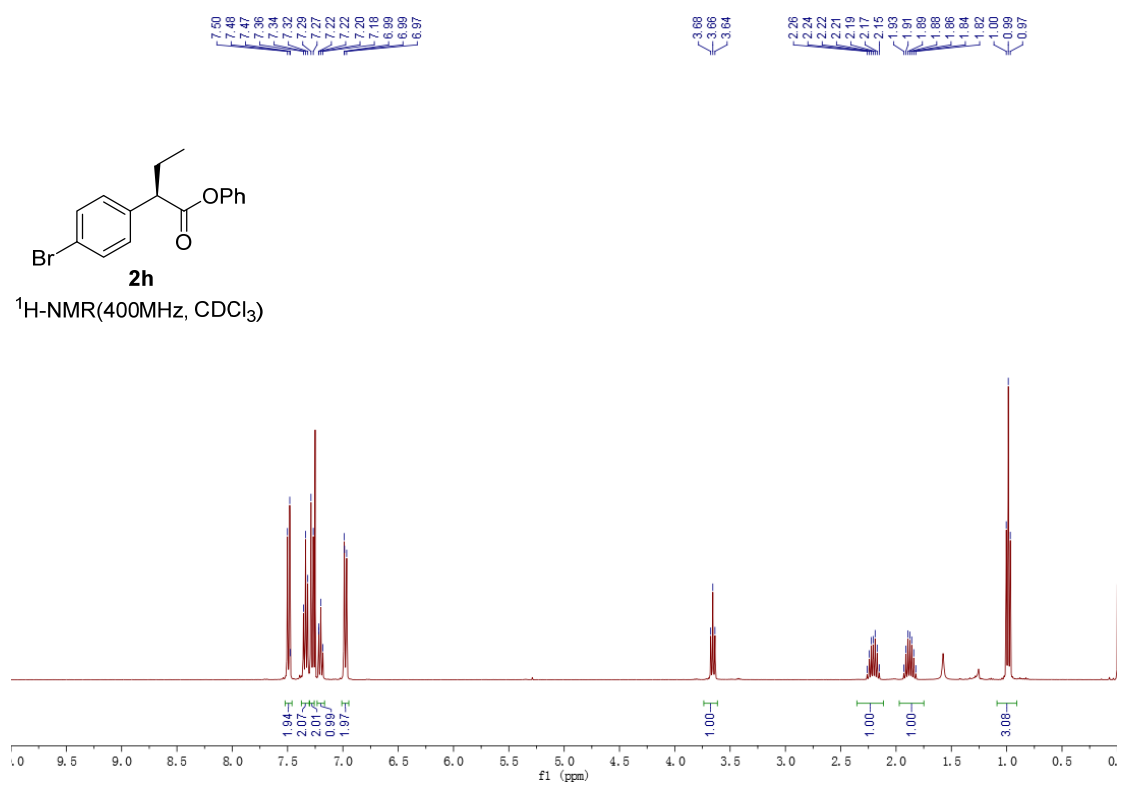


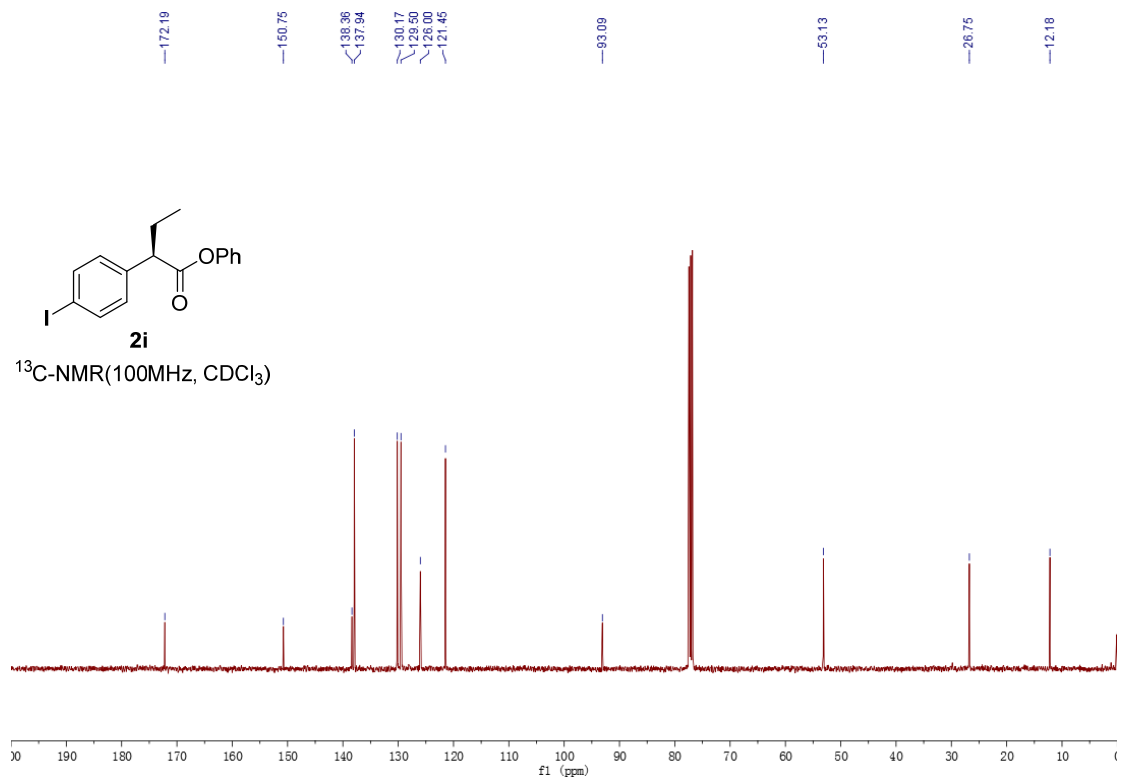
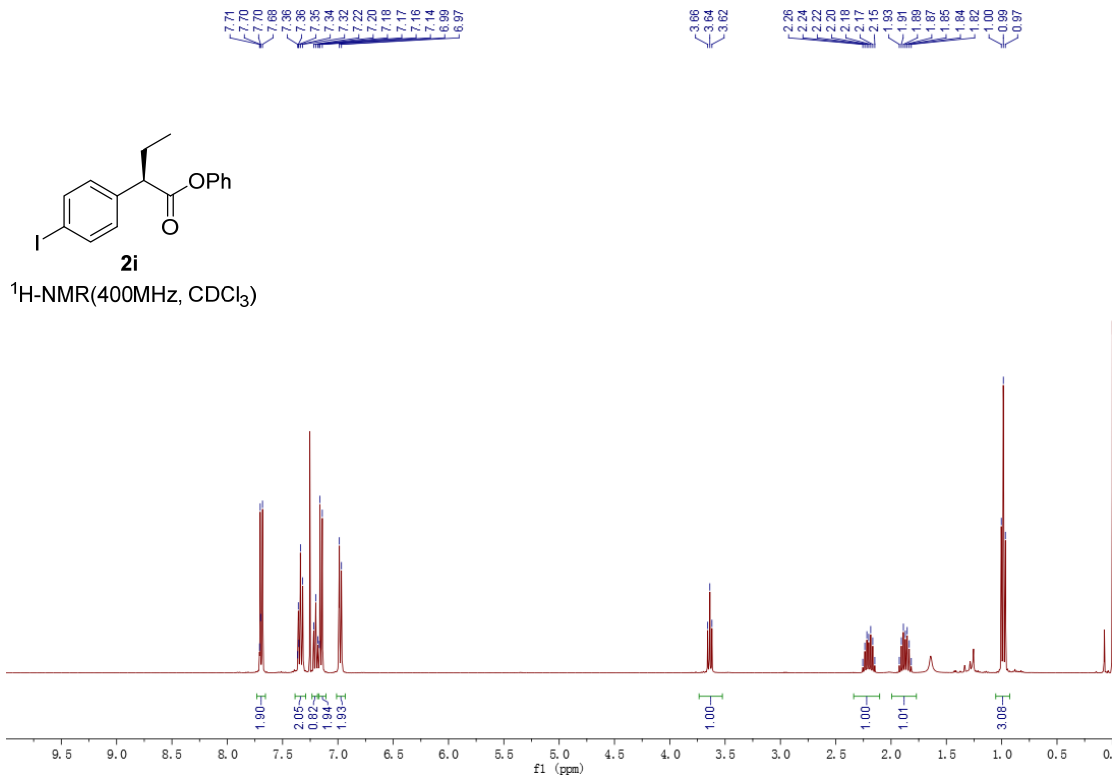


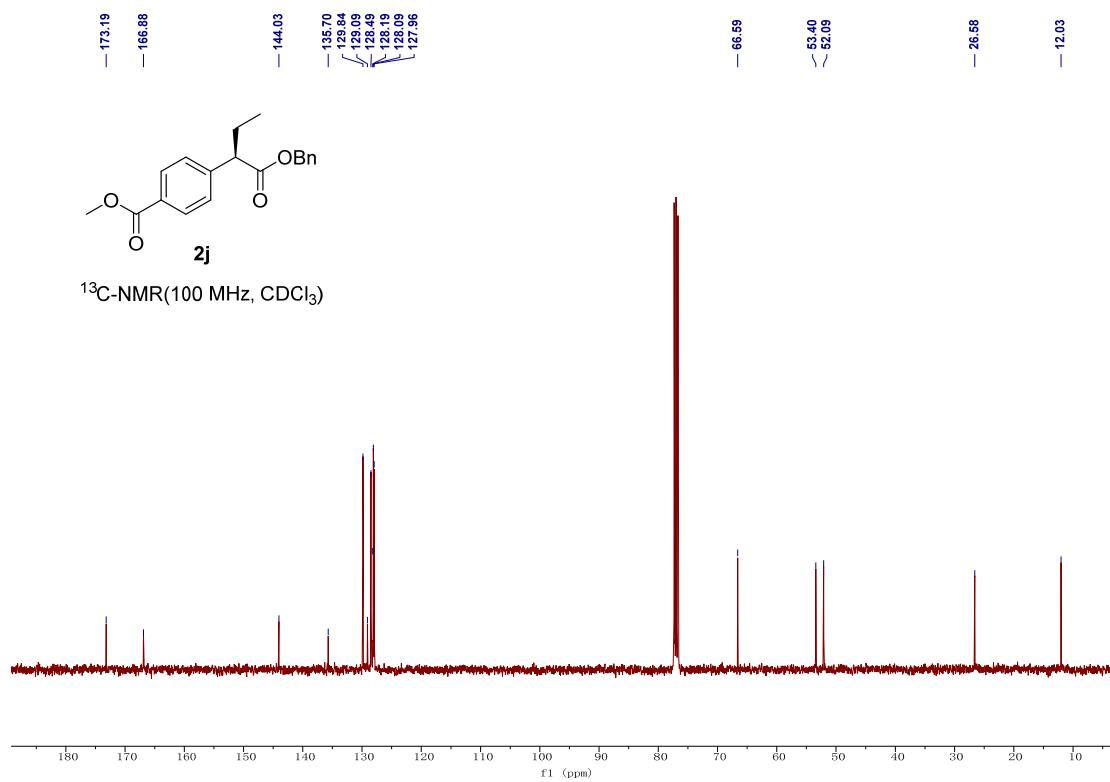
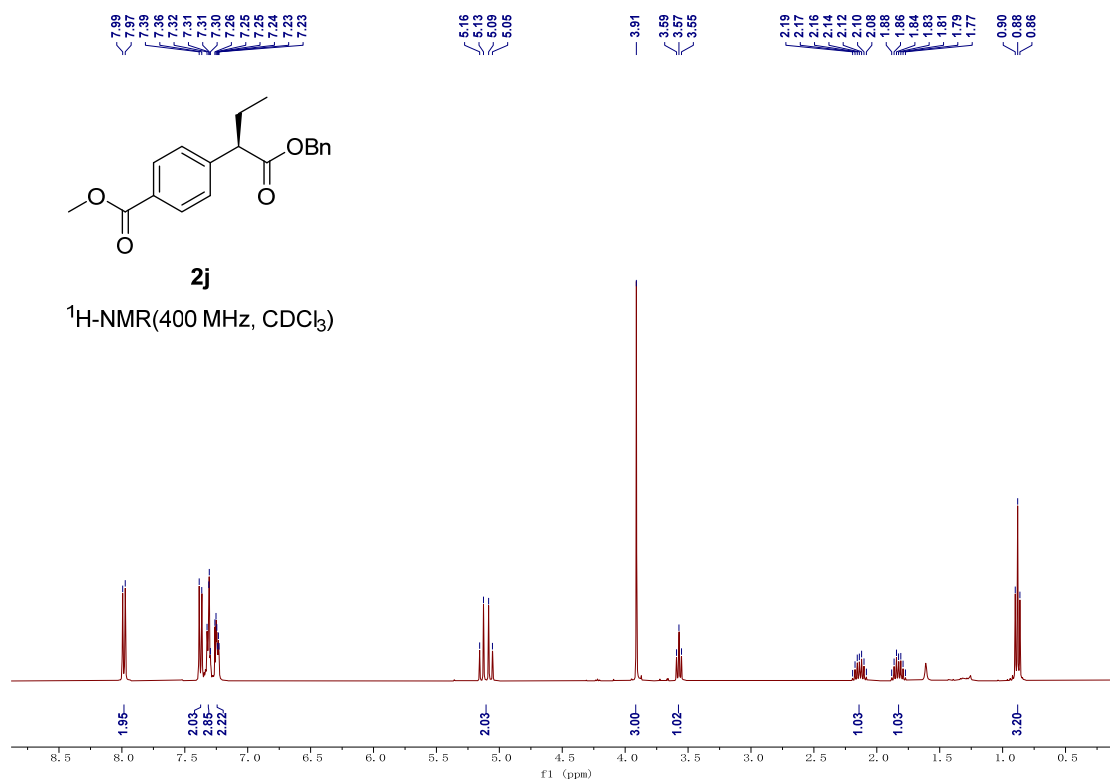


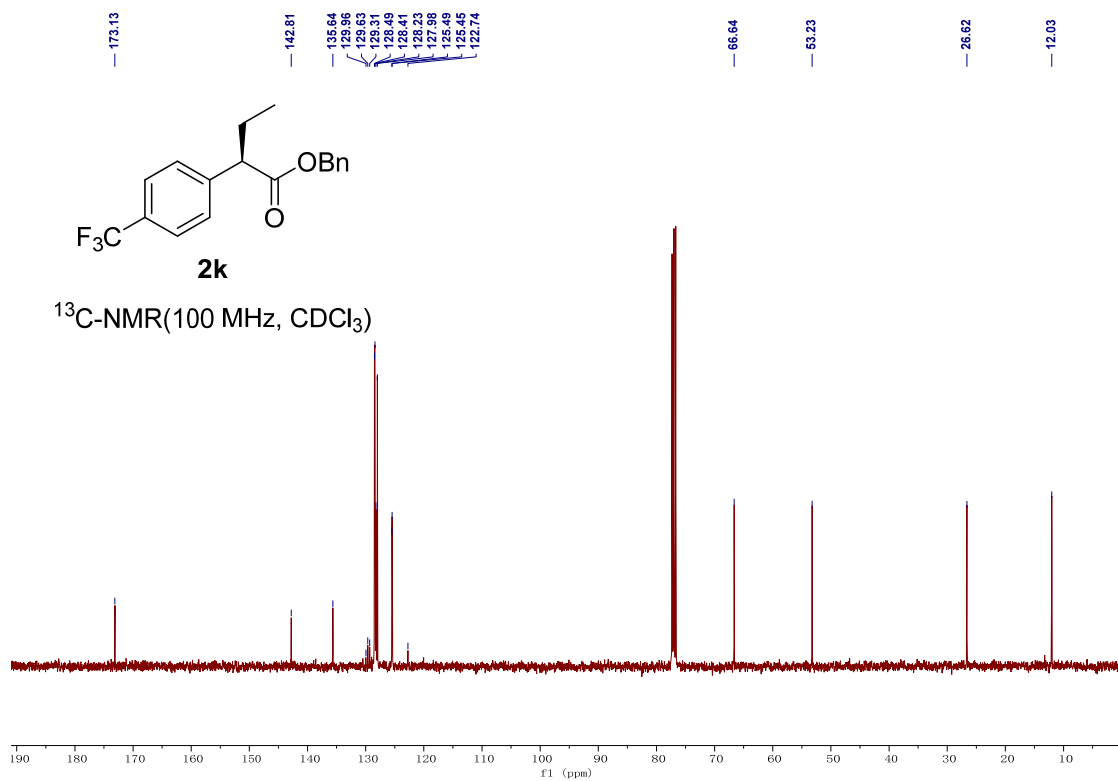
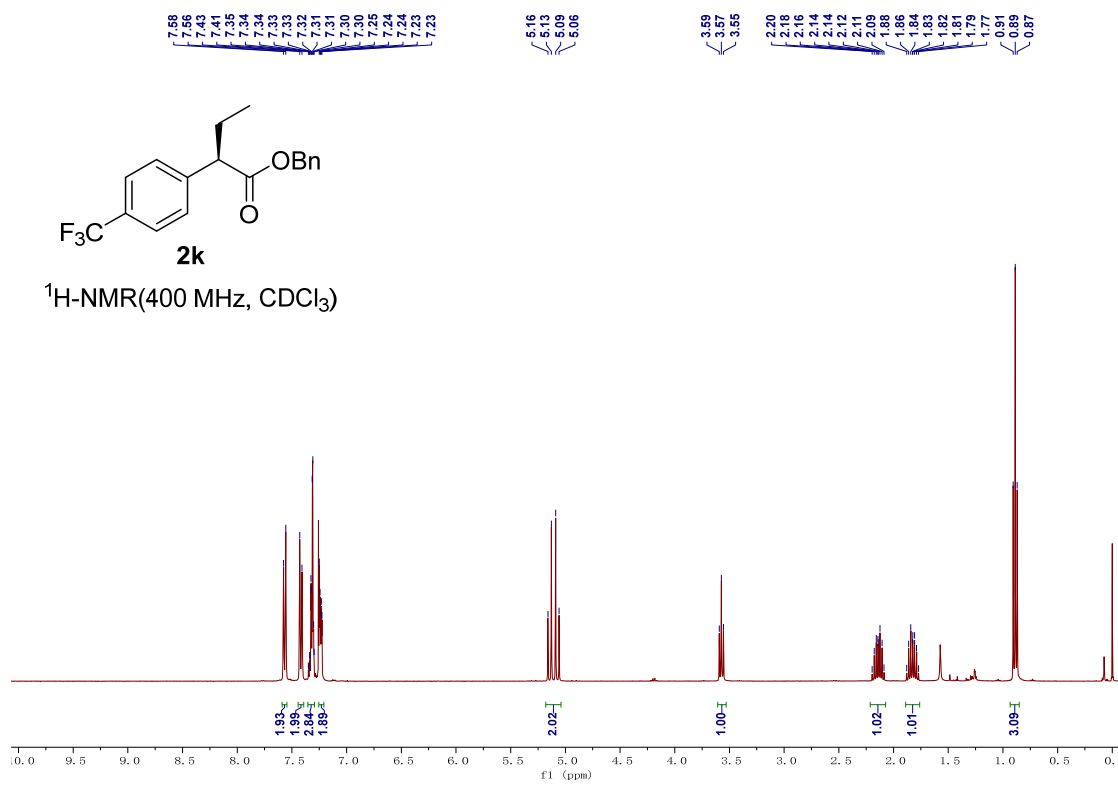


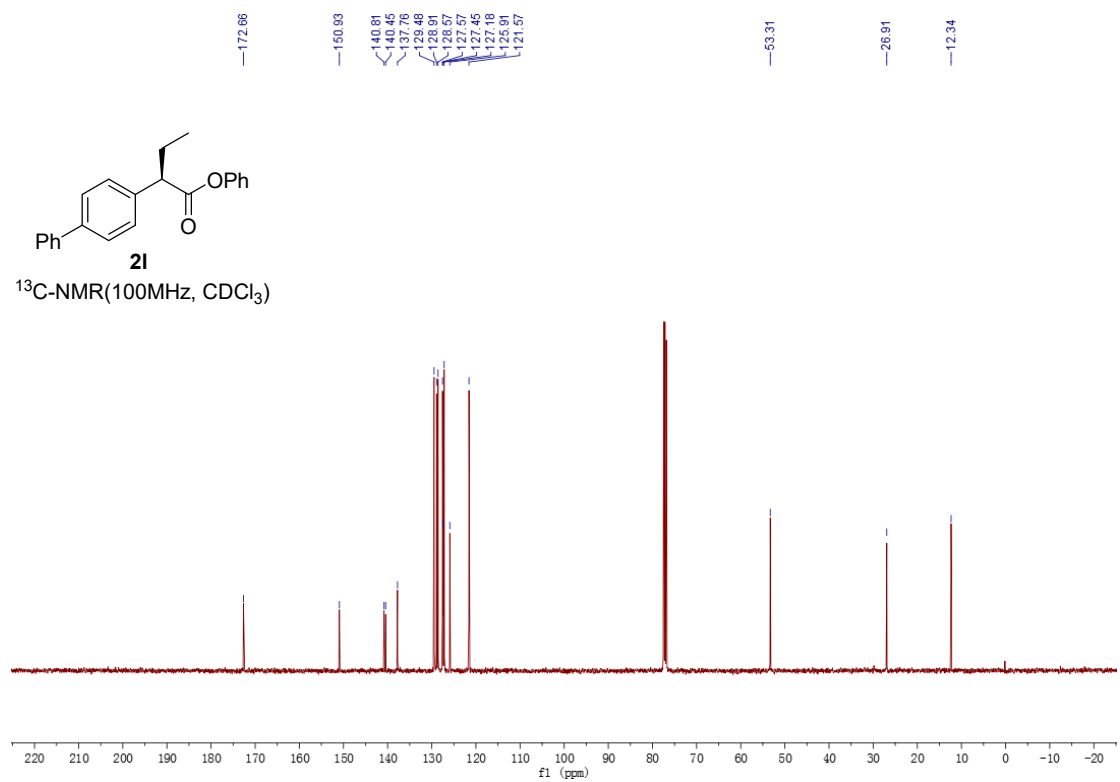
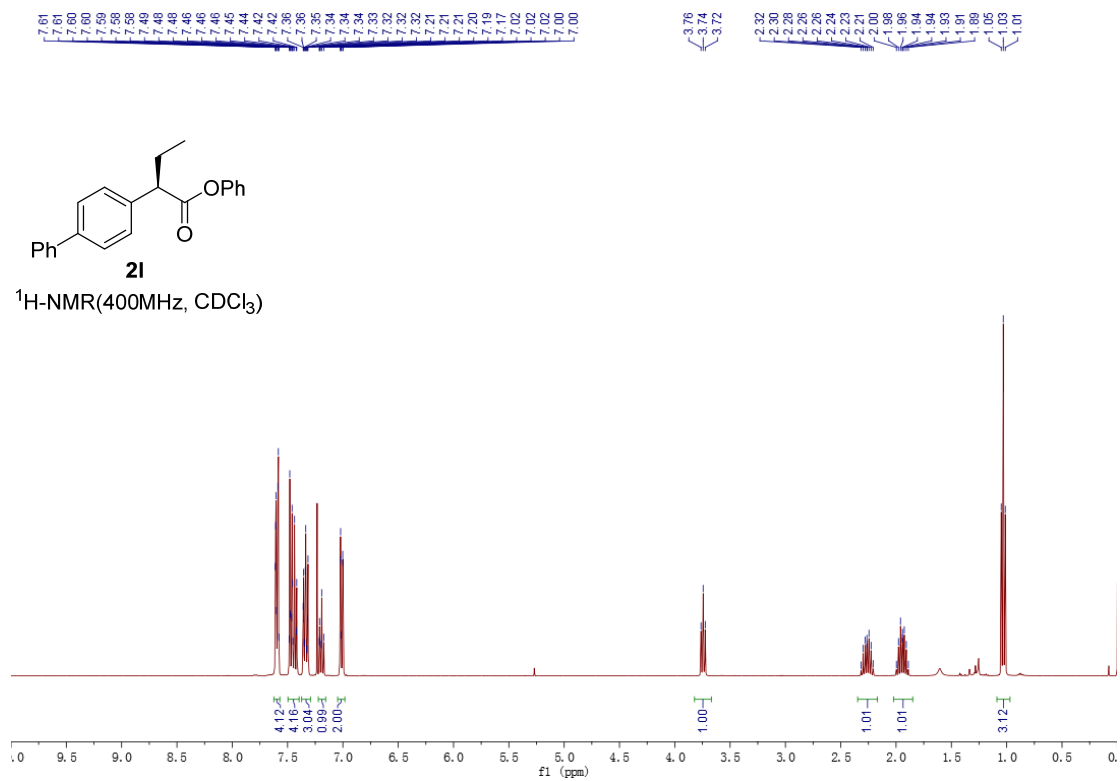


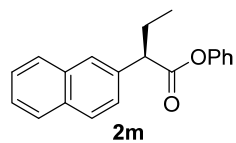




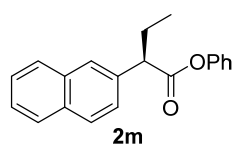
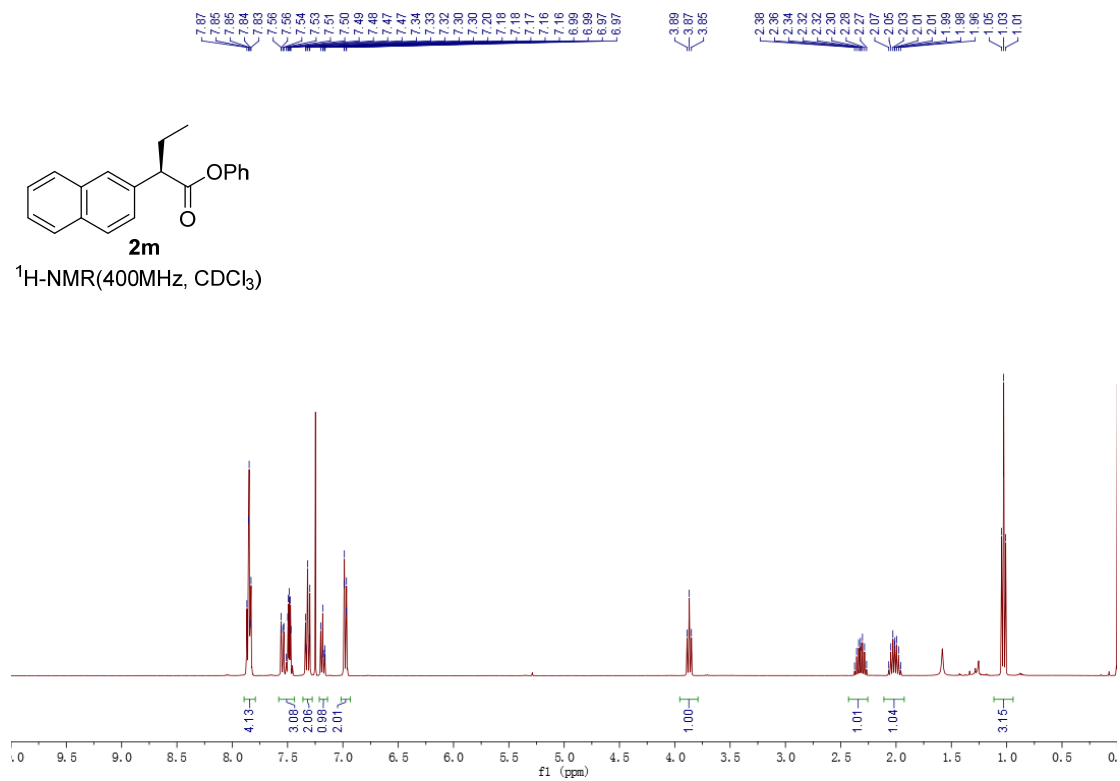




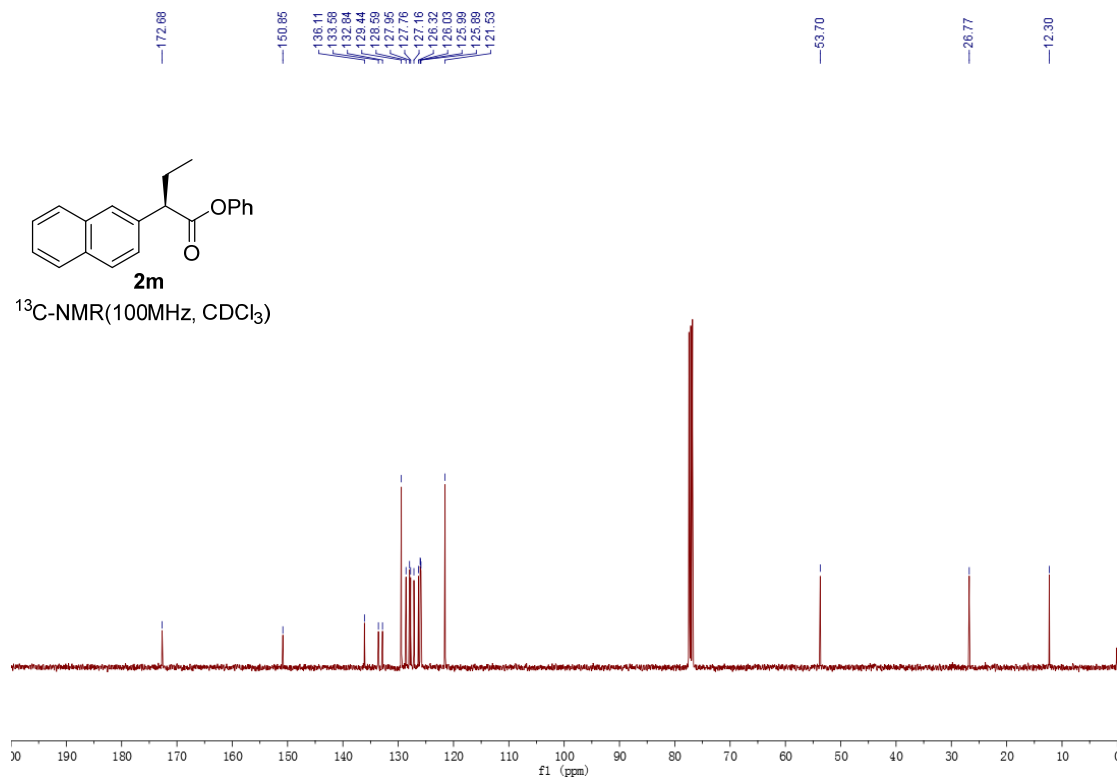


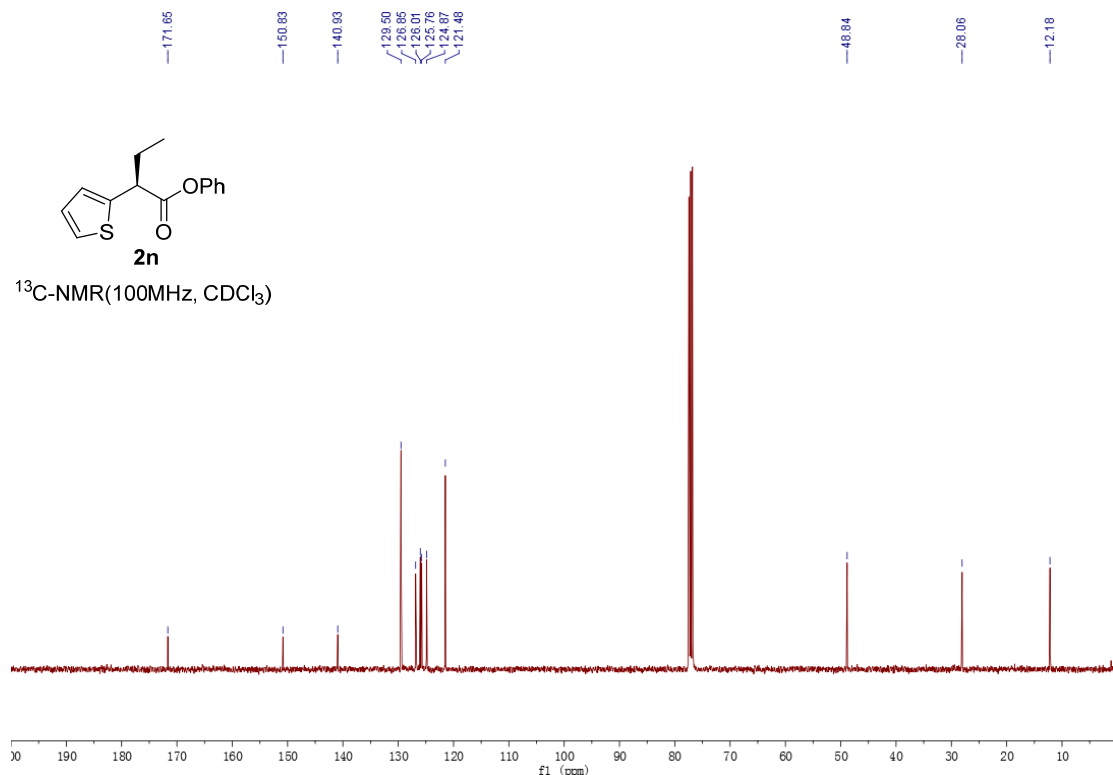
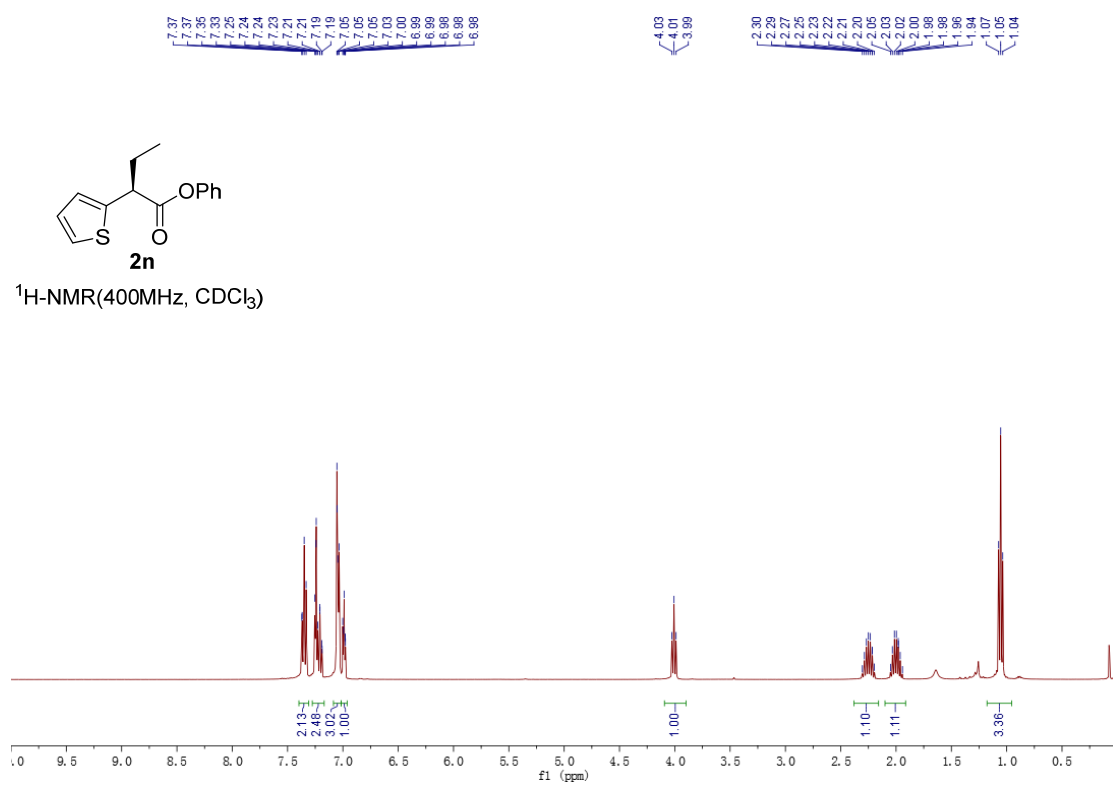


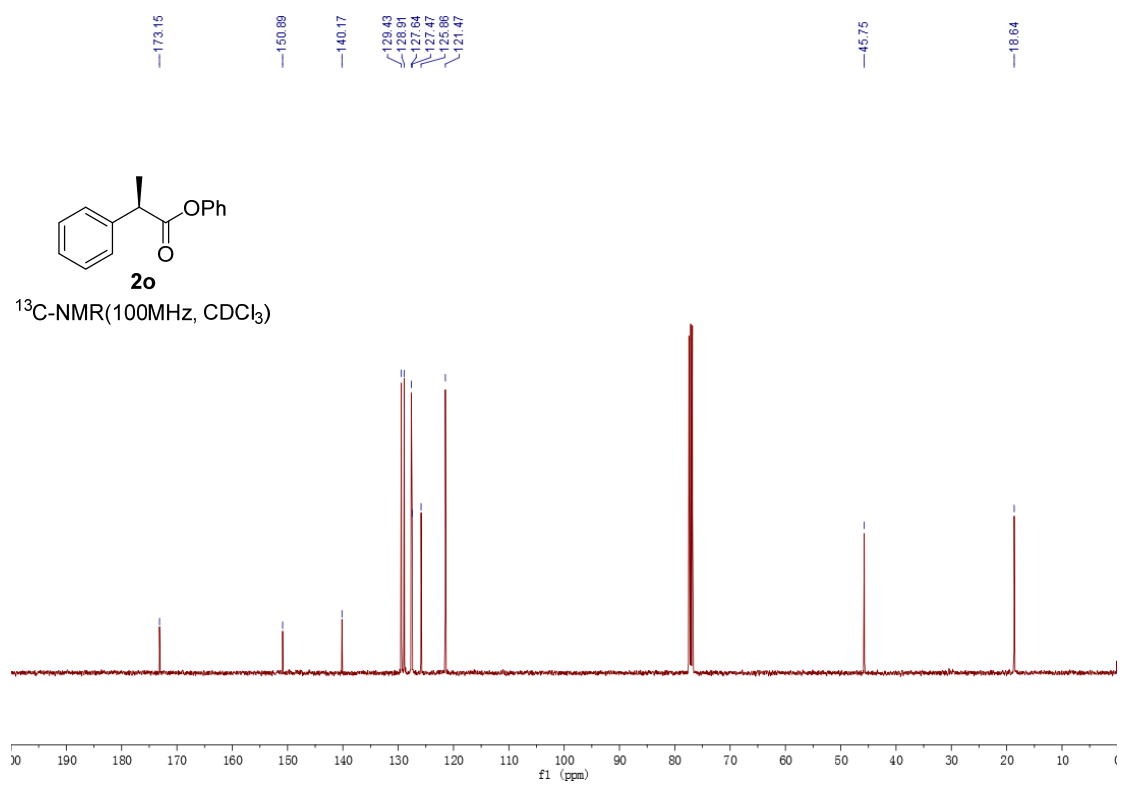
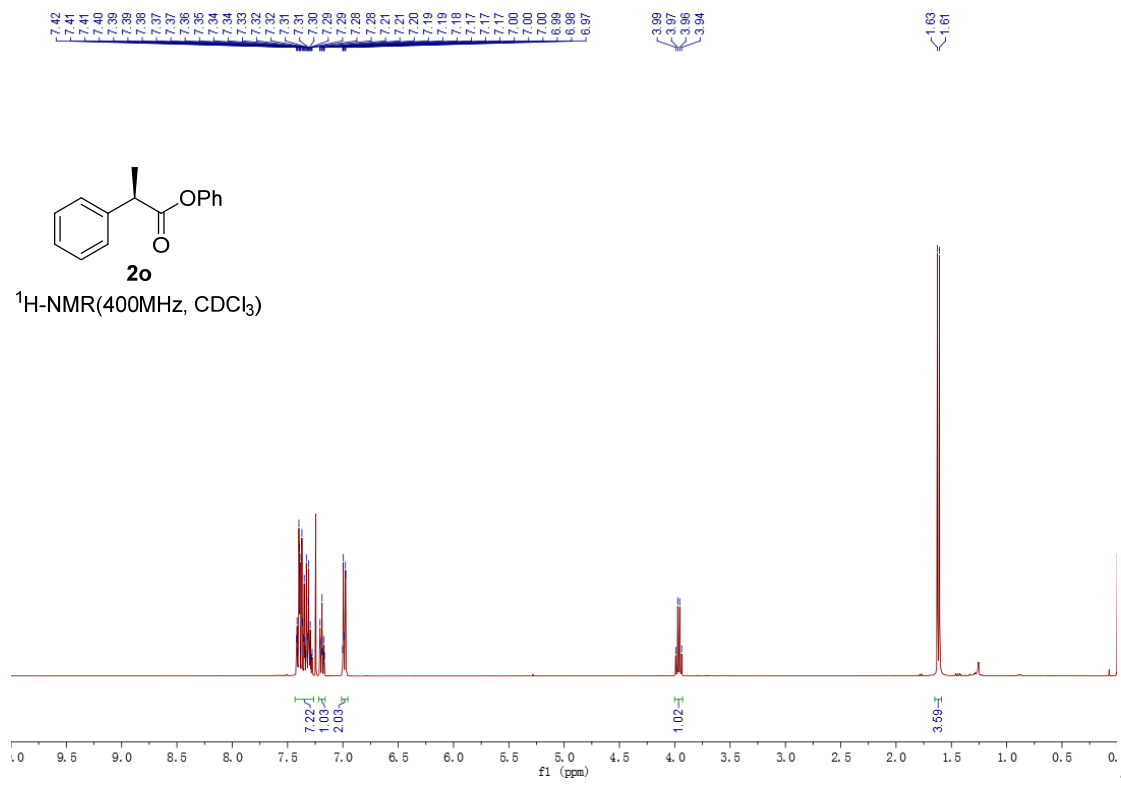
¹H-NMR(400MHz, CDCl₃)

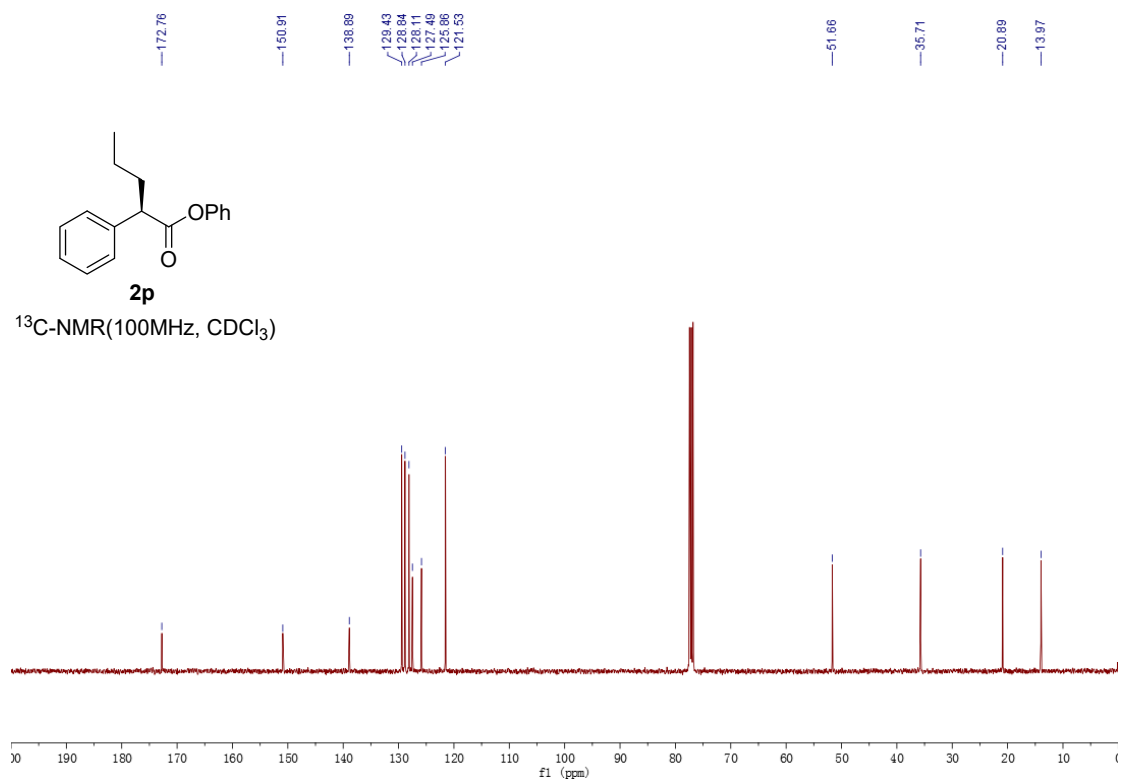
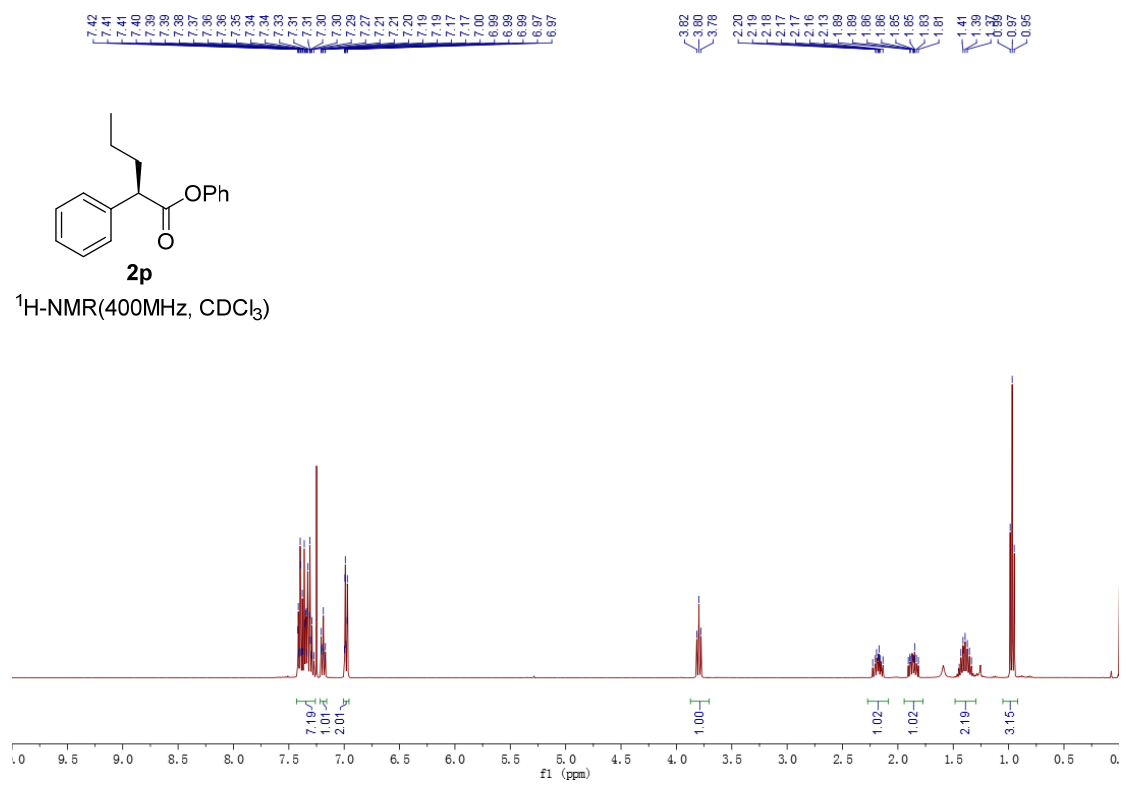


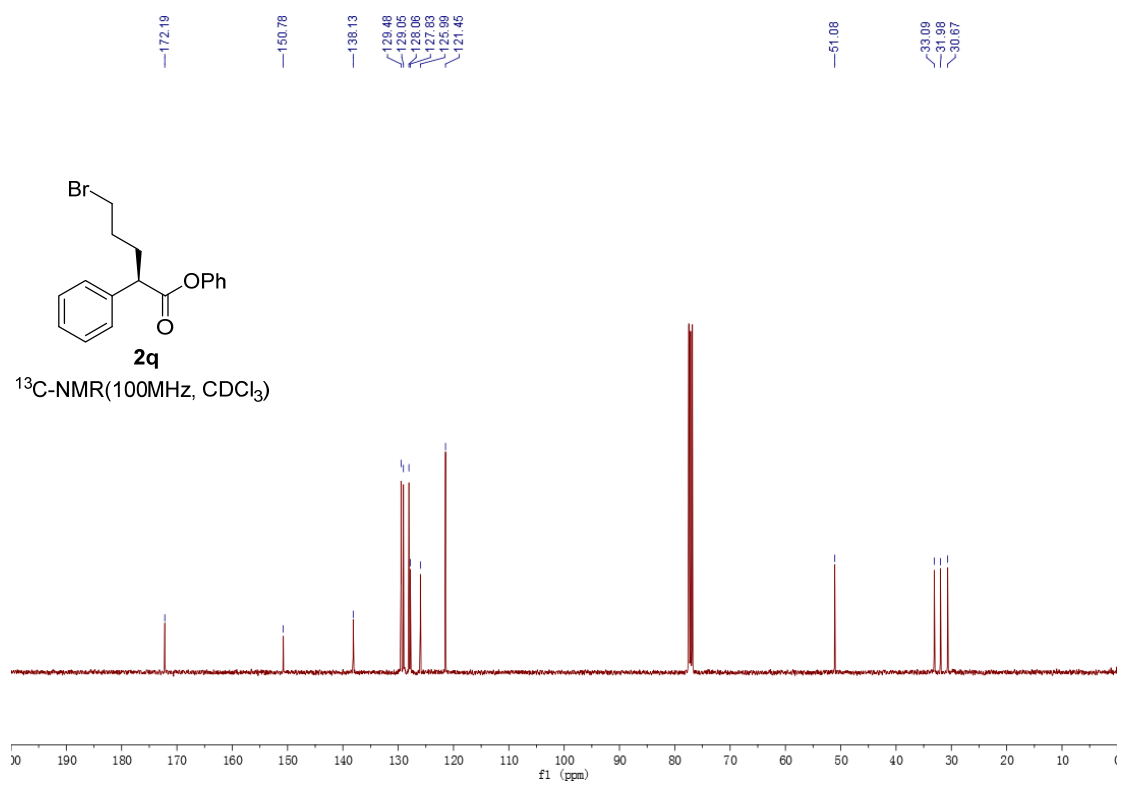
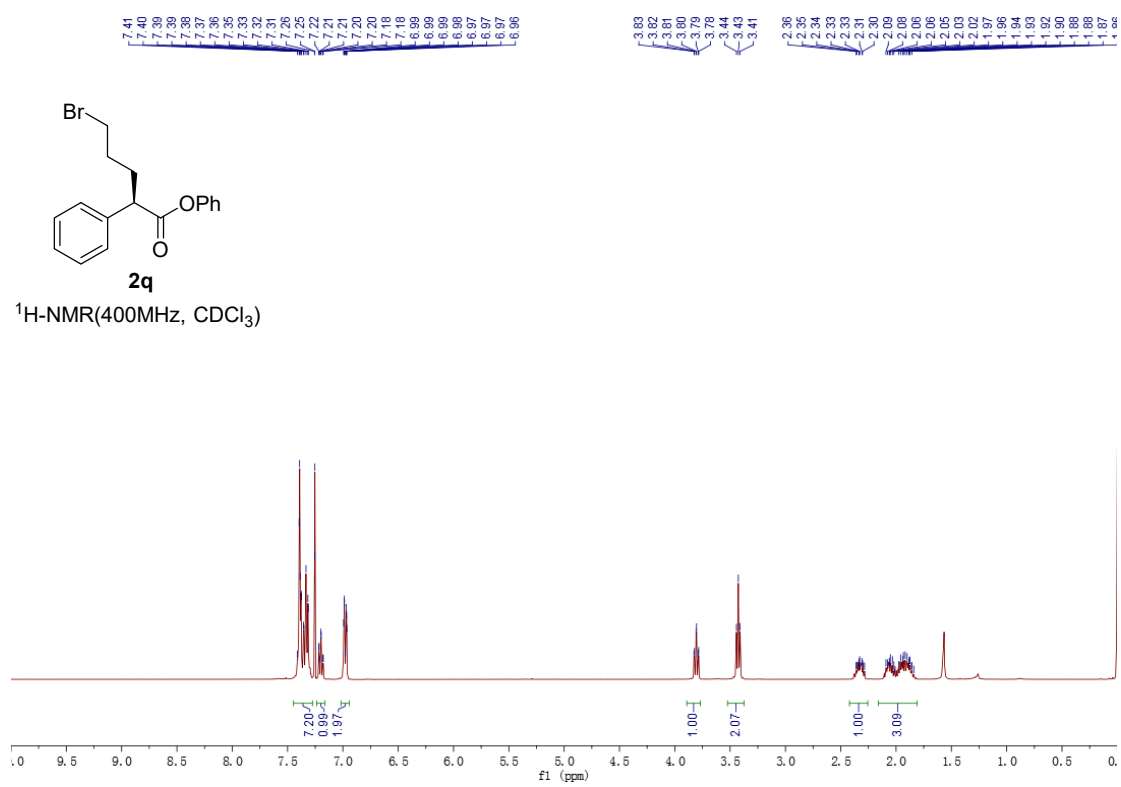
¹³C-NMR(100MHz, CDCl₃)

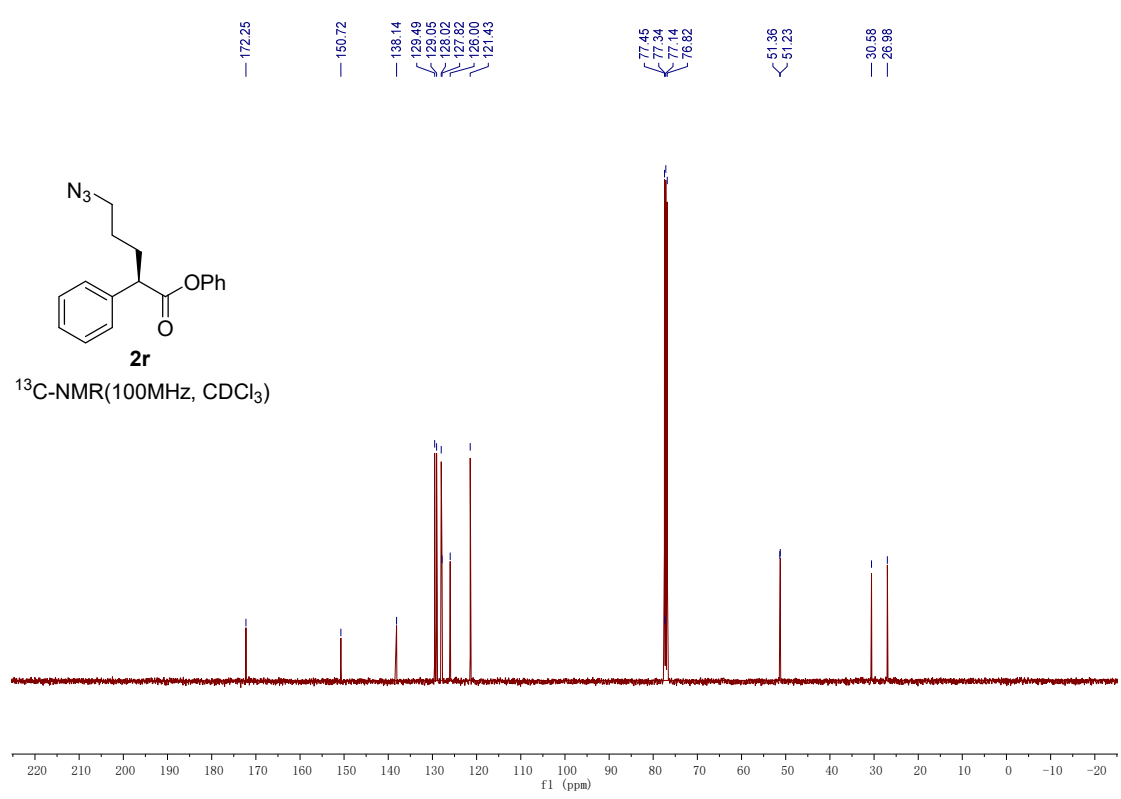
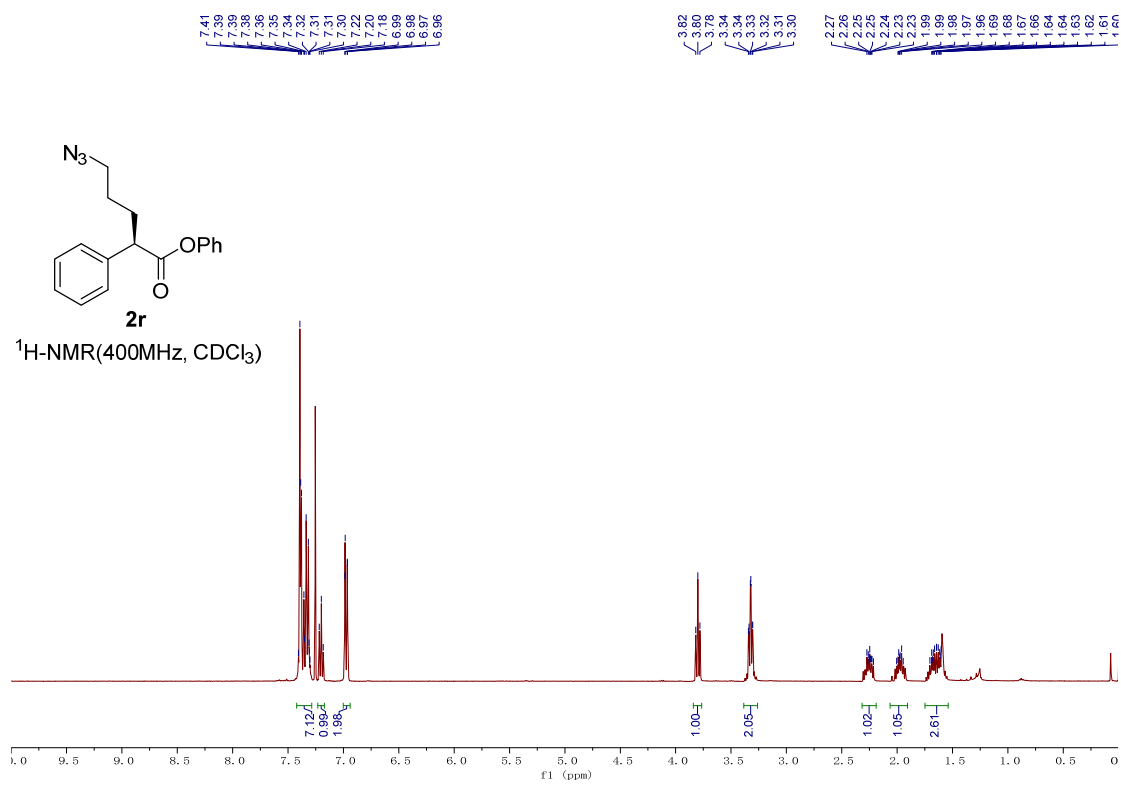


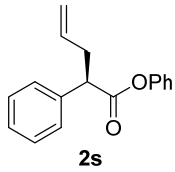




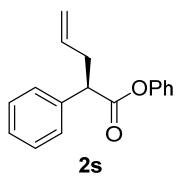
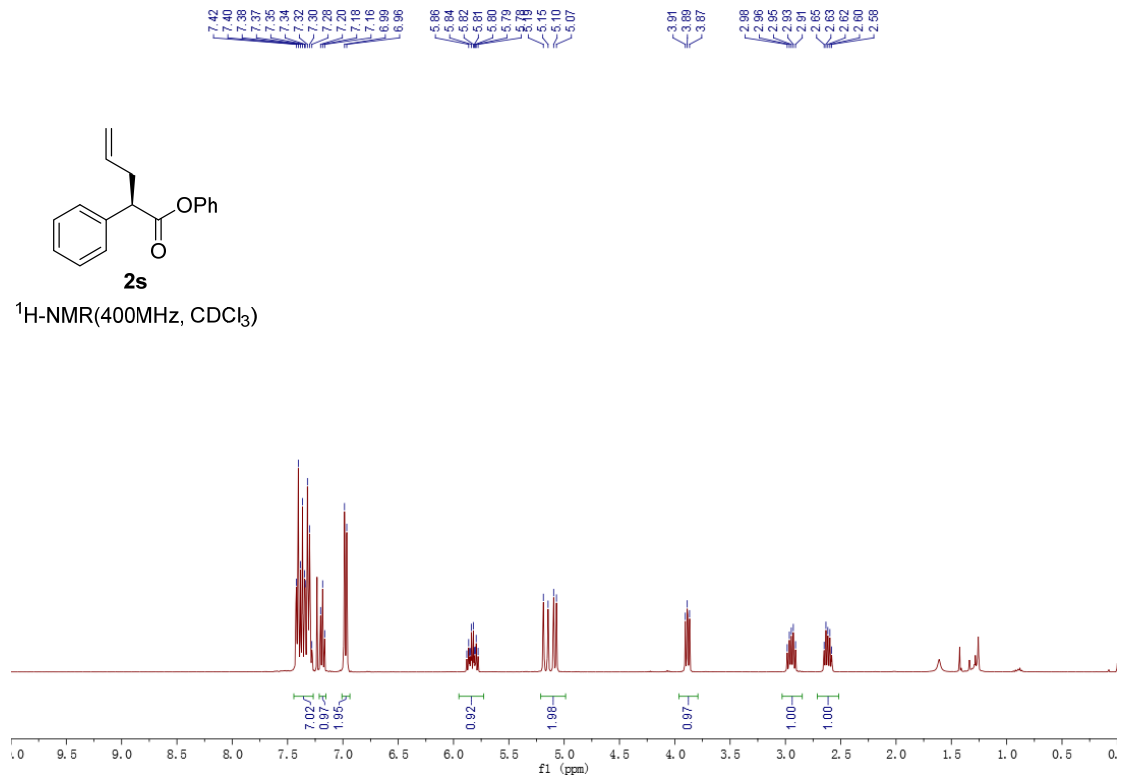




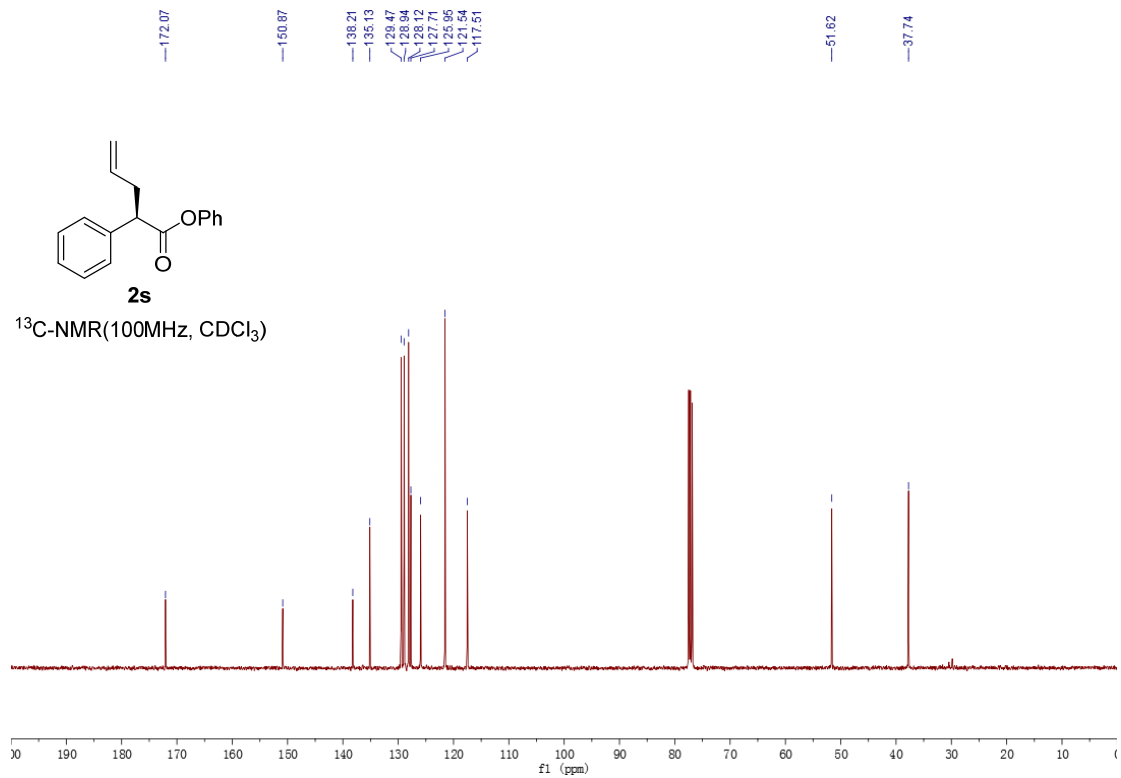


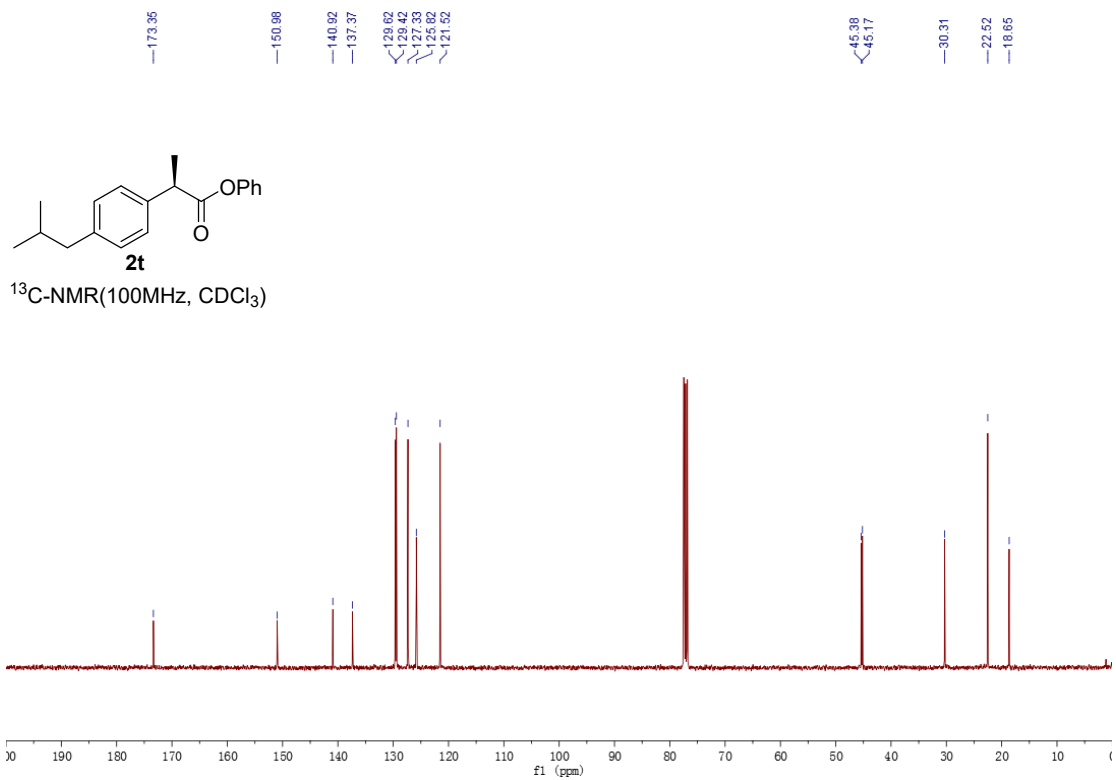
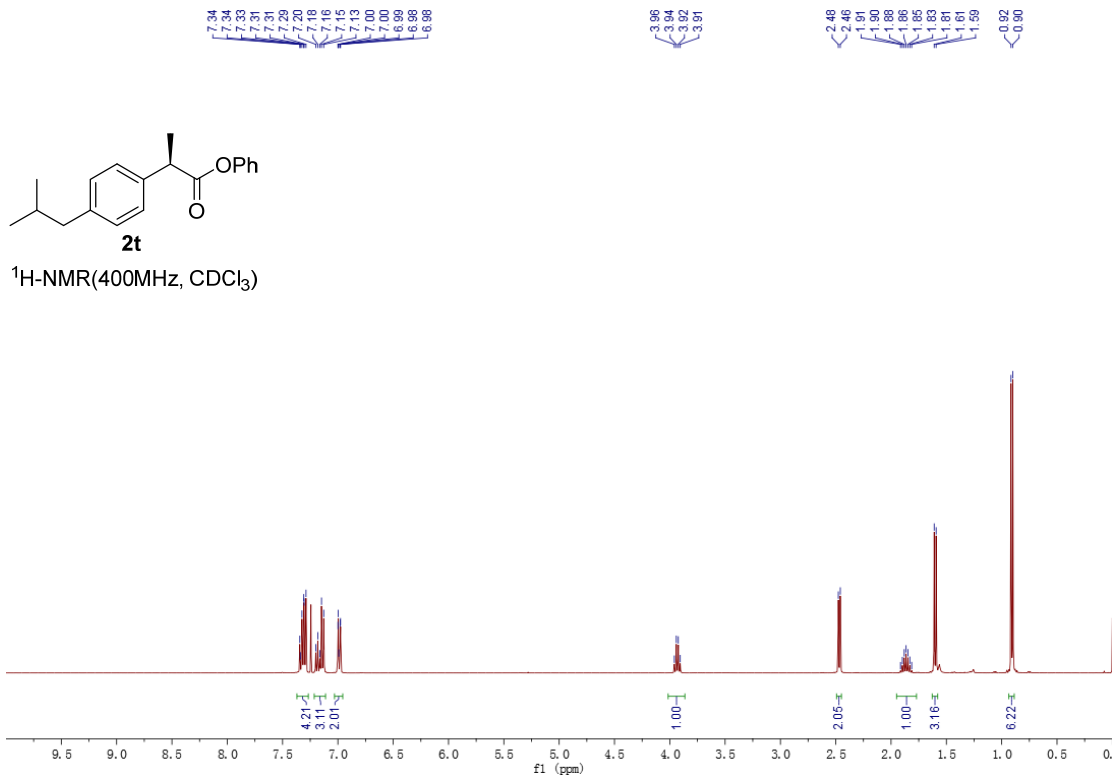


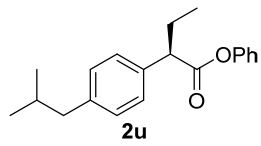
$^1\text{H-NMR}$ (400MHz, CDCl_3)



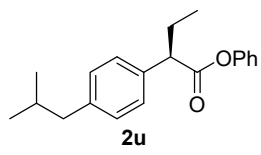
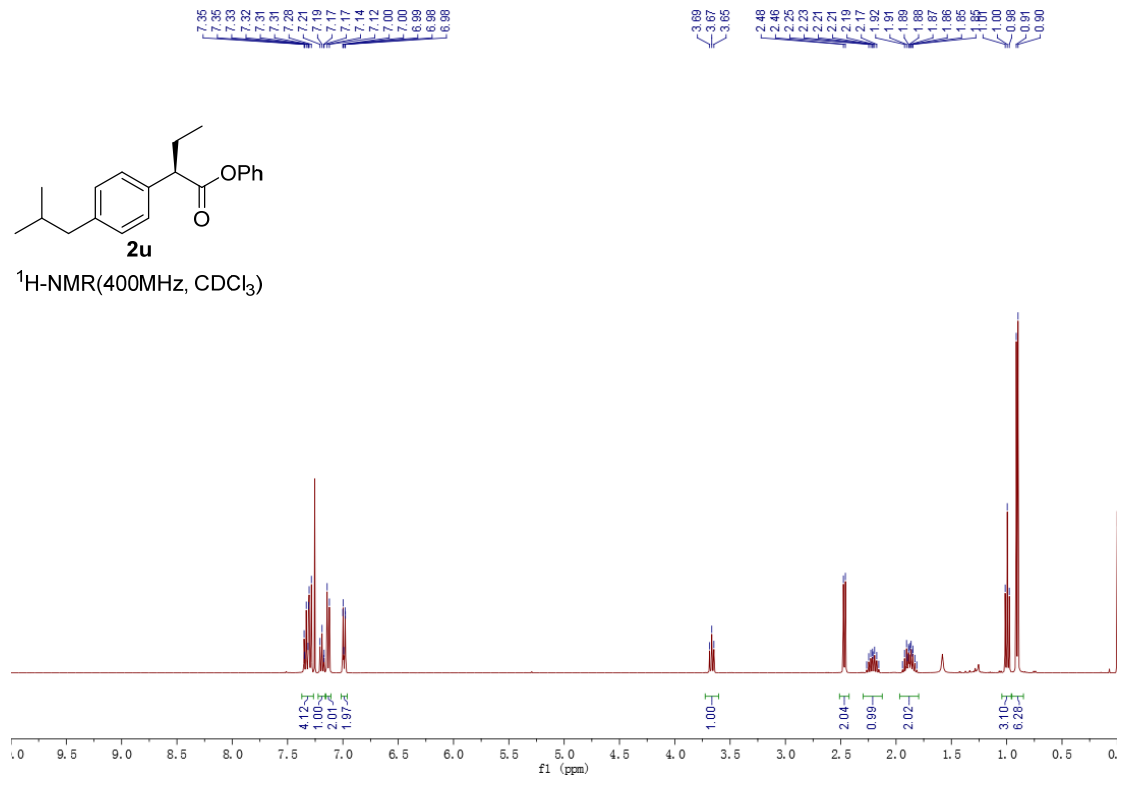
$^{13}\text{C-NMR}$ (100MHz, CDCl_3)



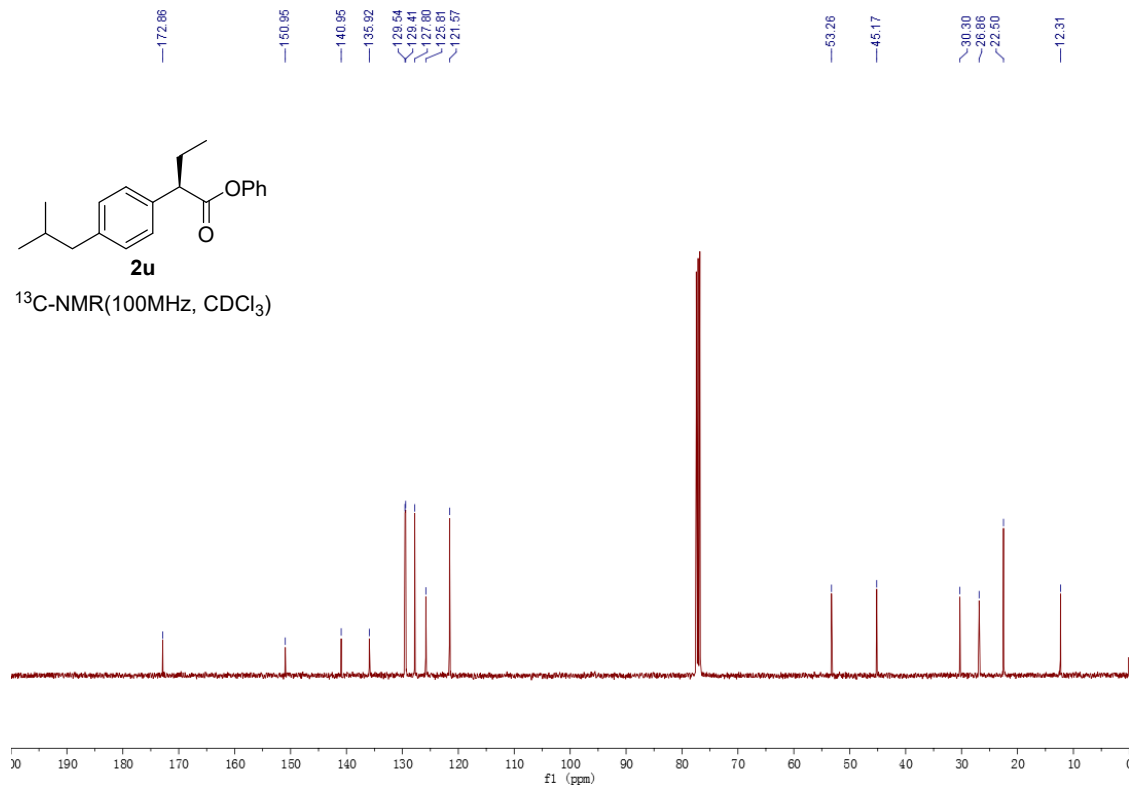


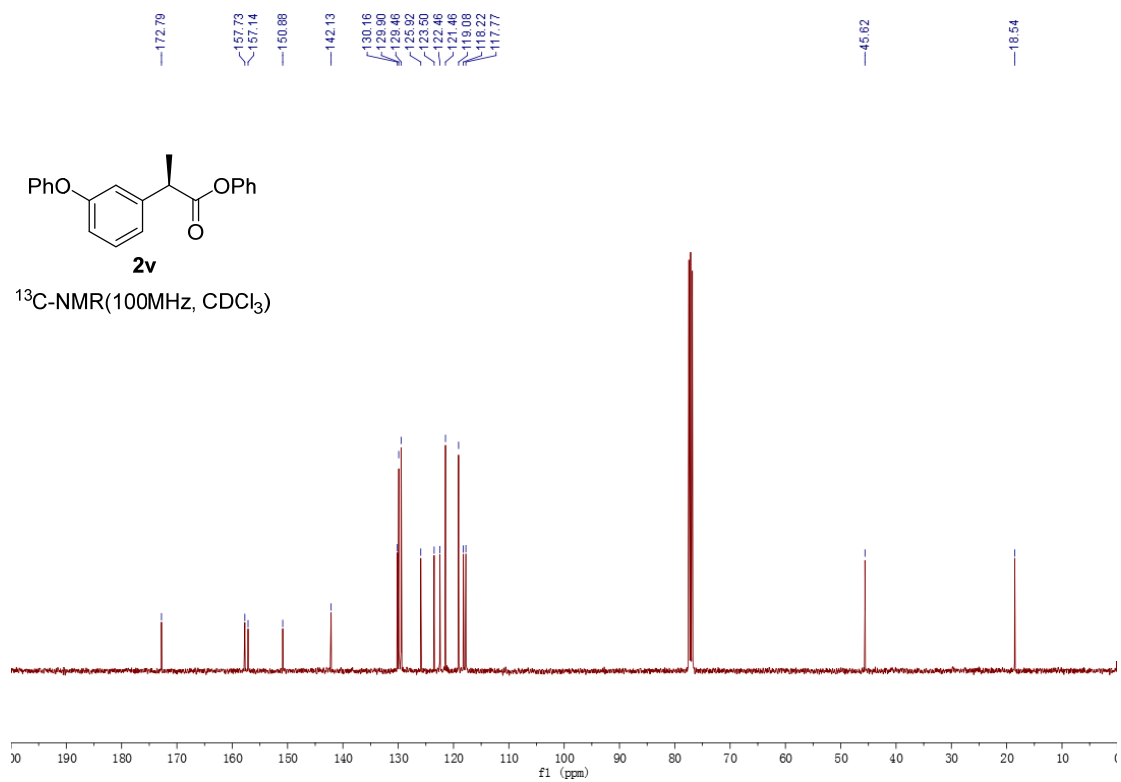
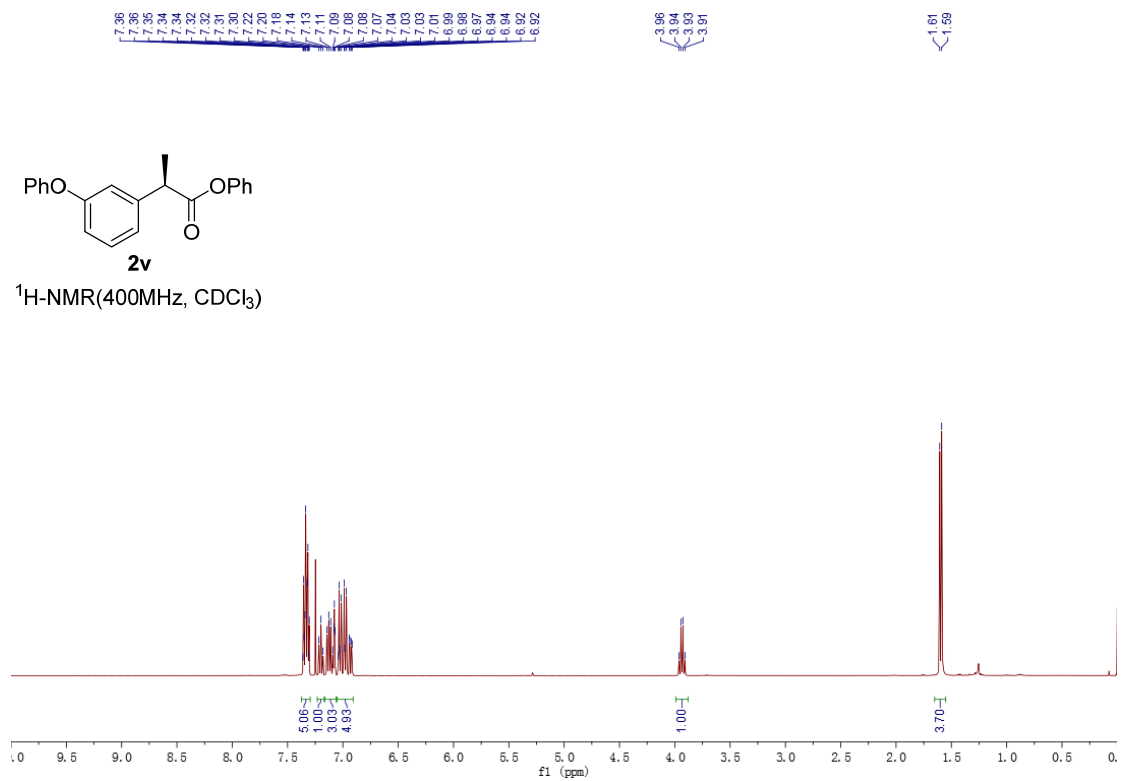


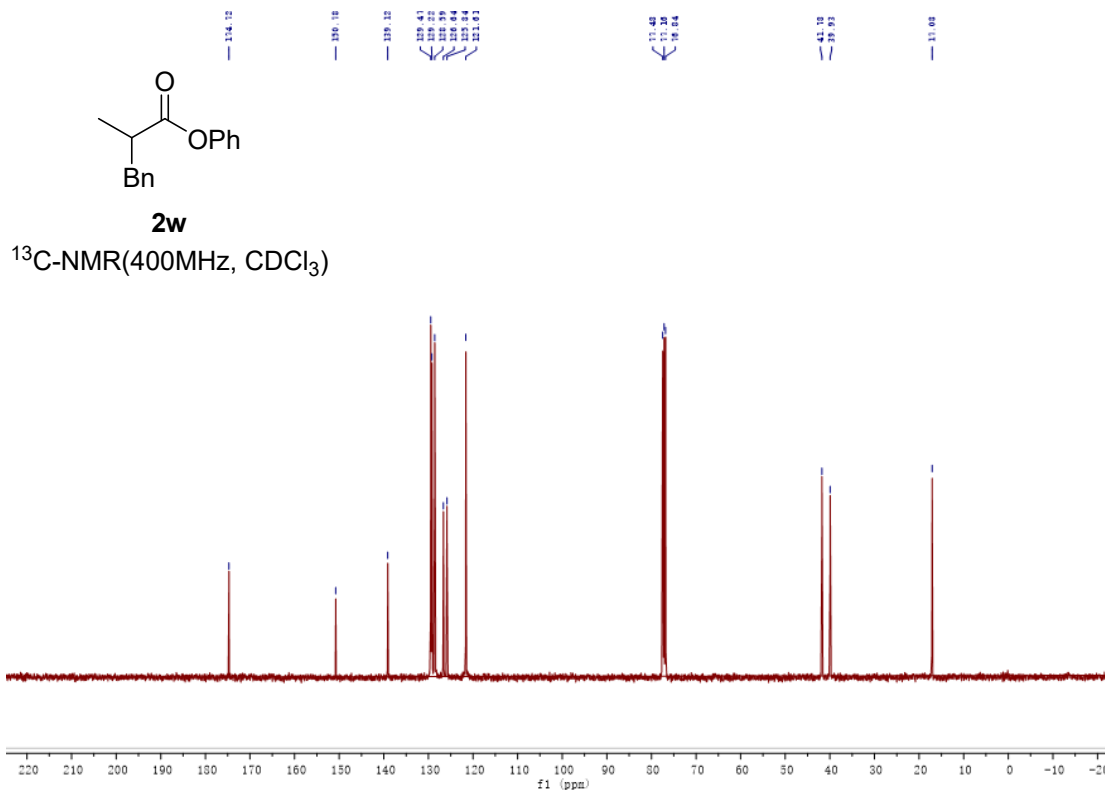
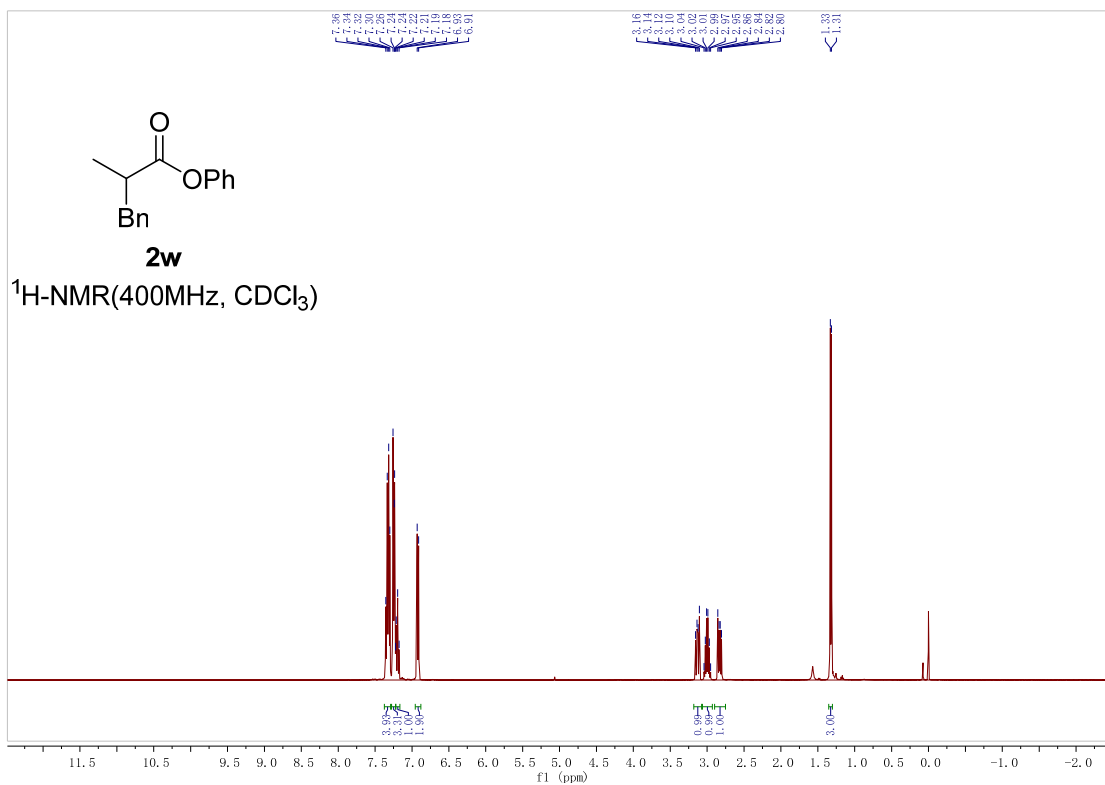
¹H-NMR(400MHz, CDCl₃)

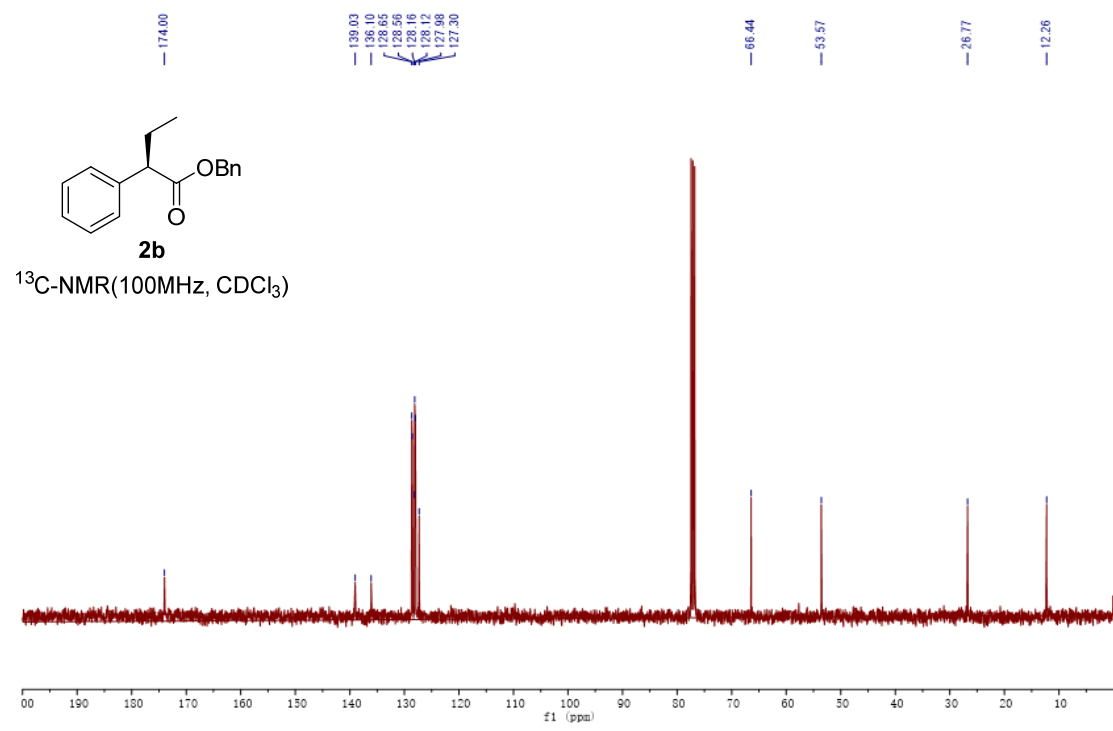
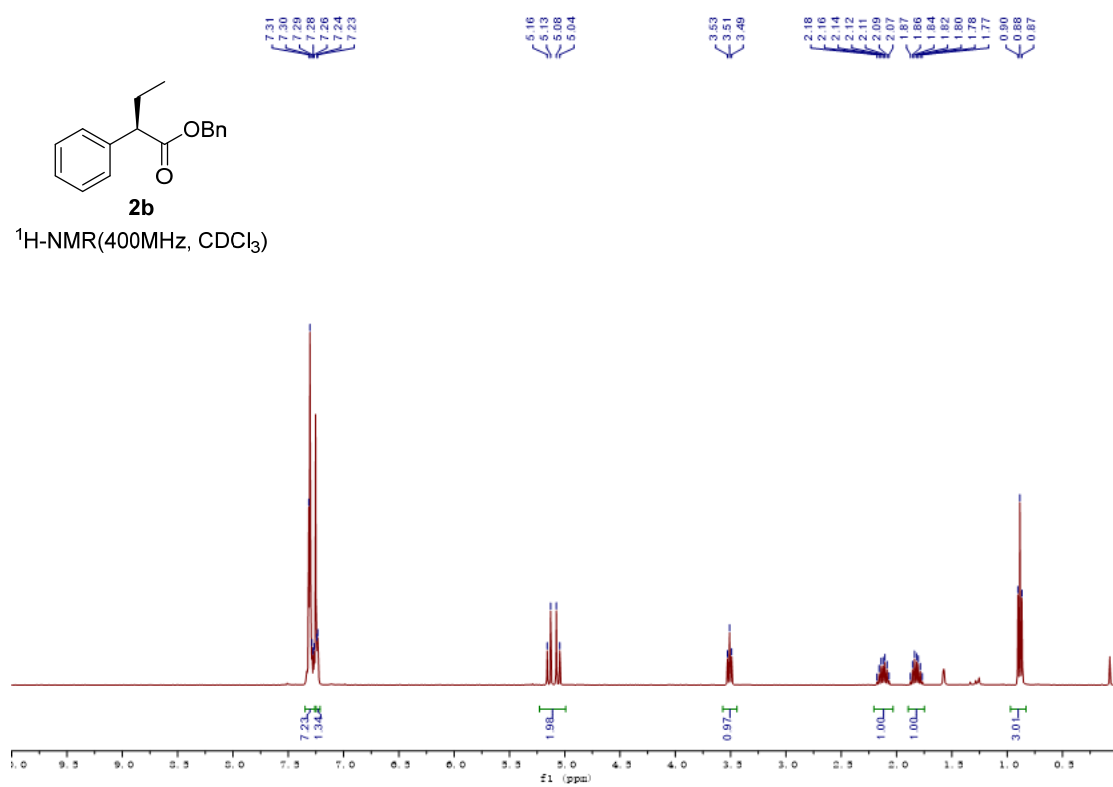


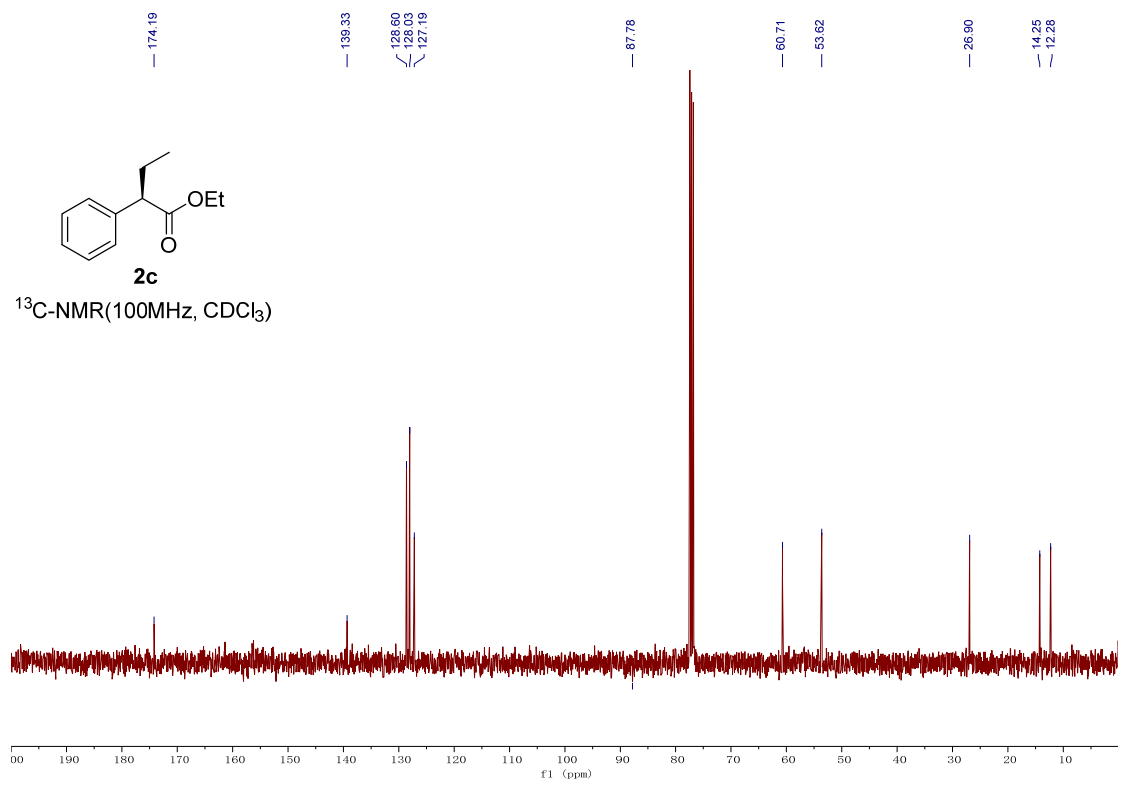
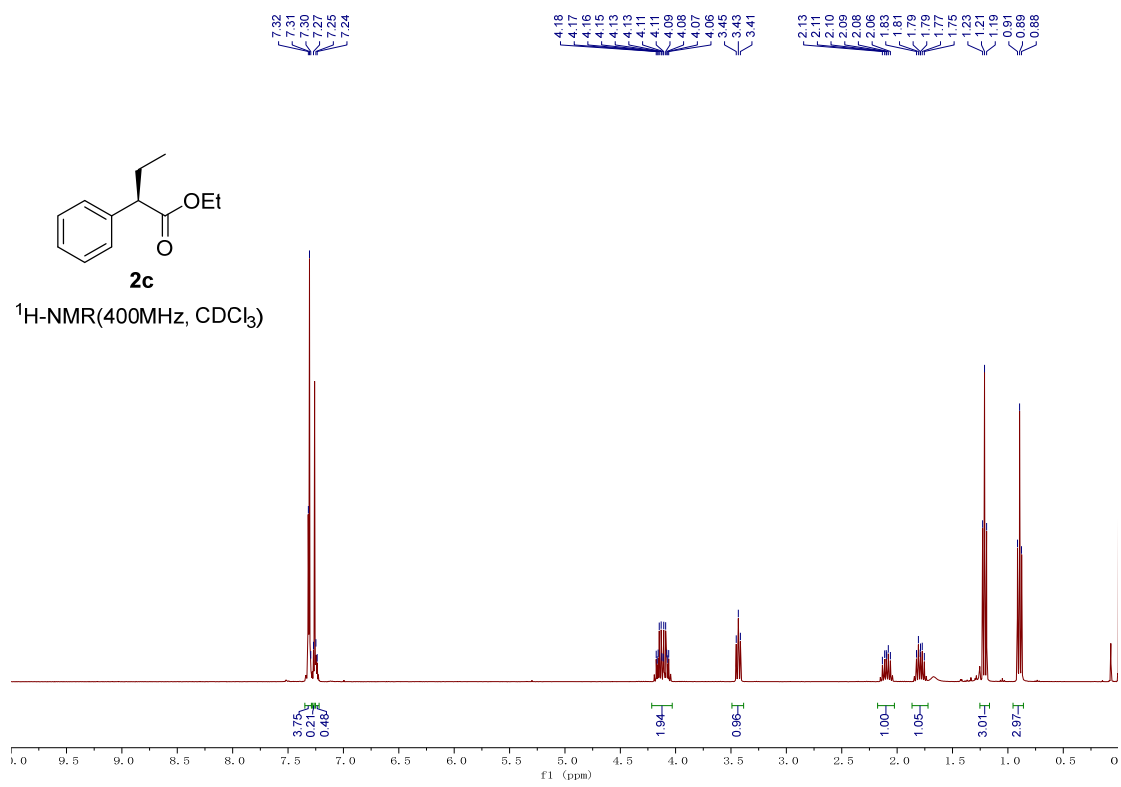
¹³C-NMR(100MHz, CDCl₃)

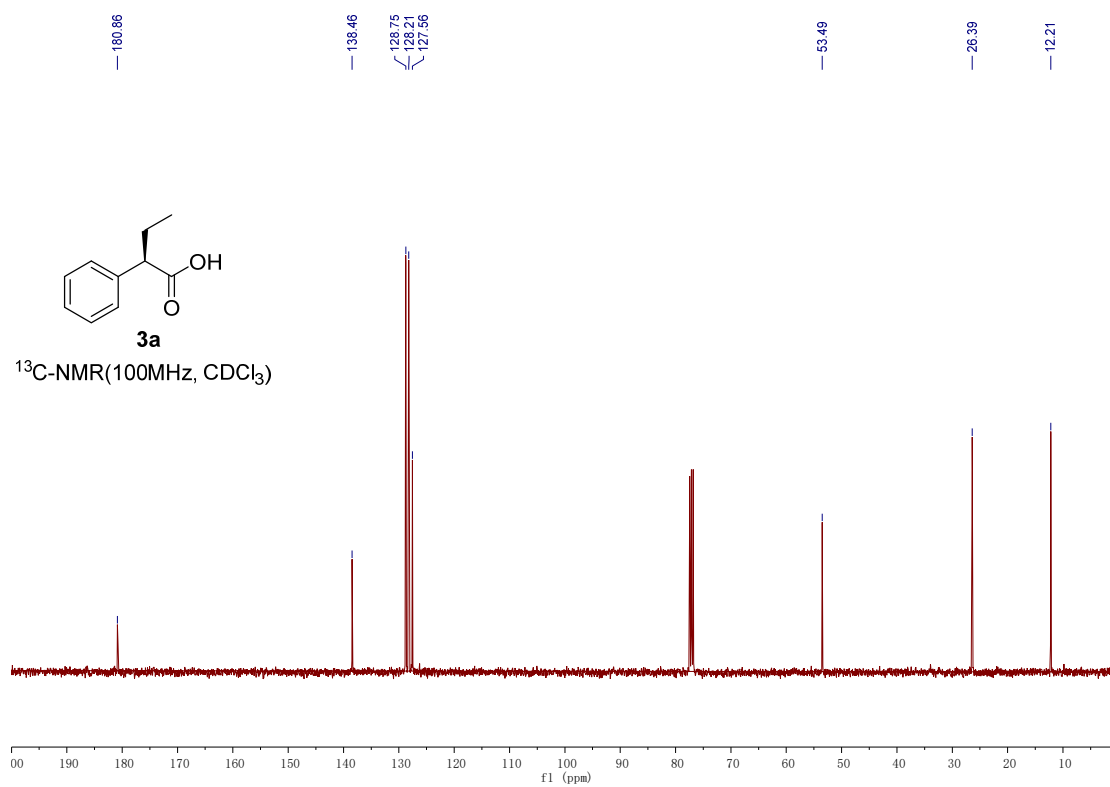
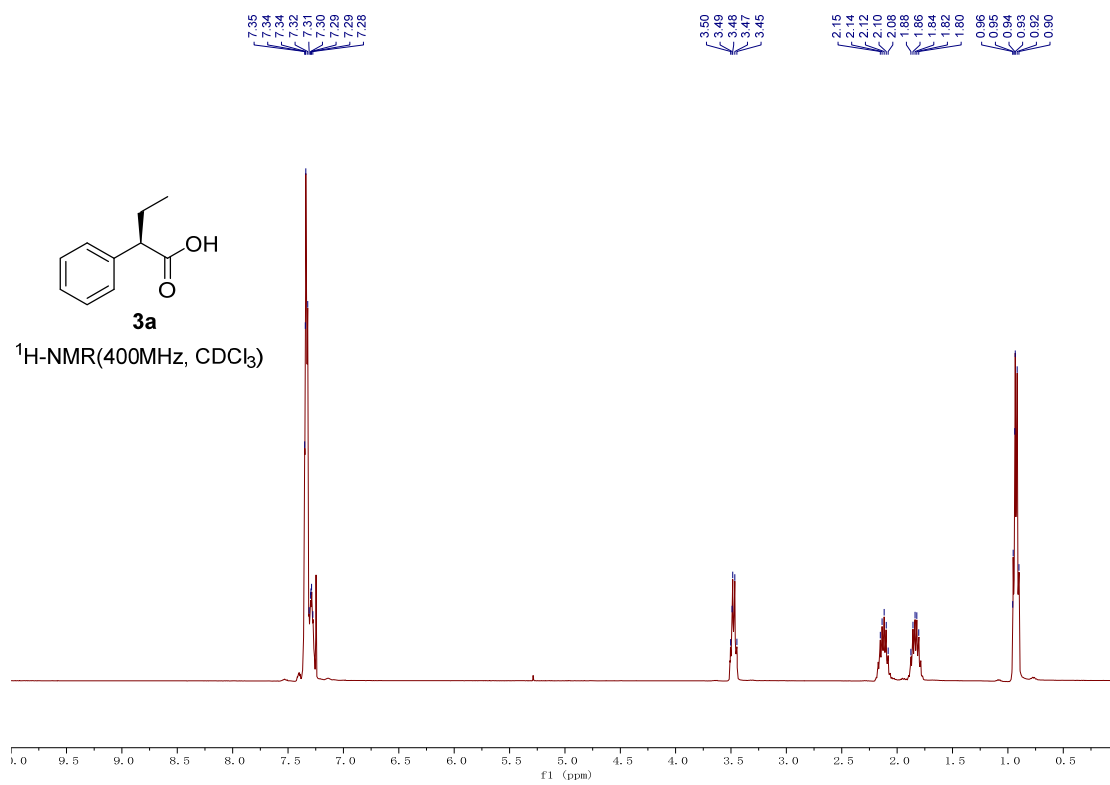


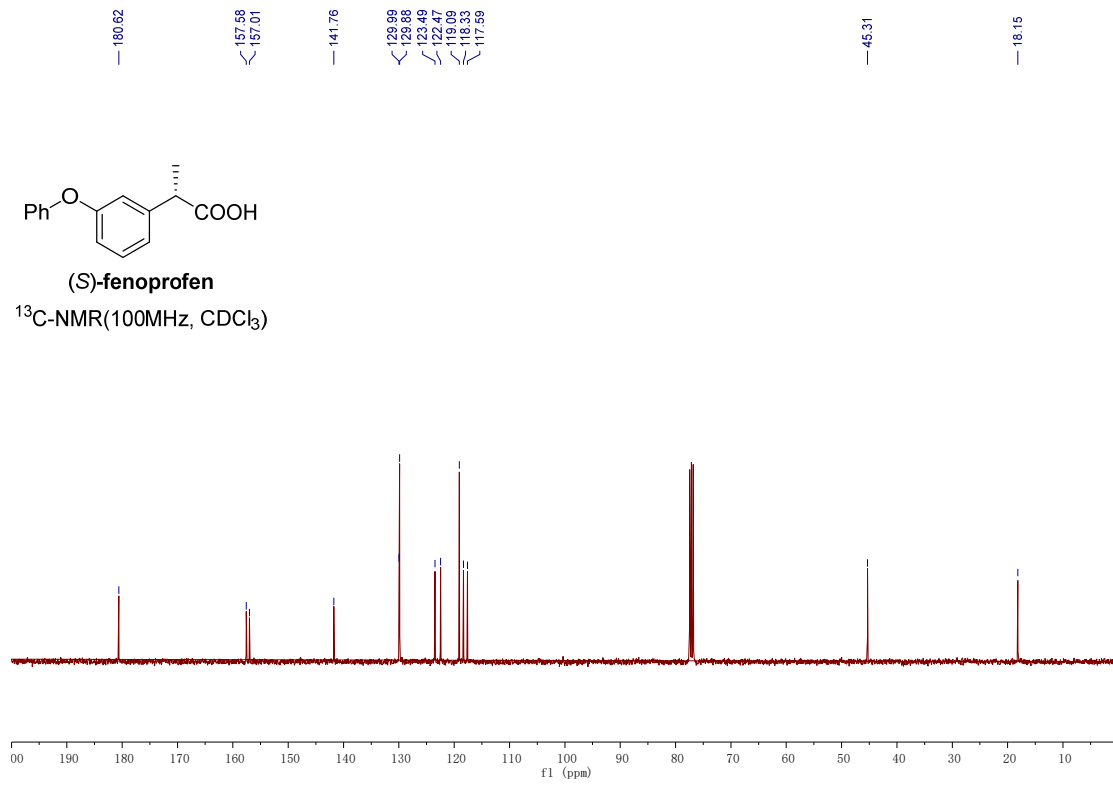
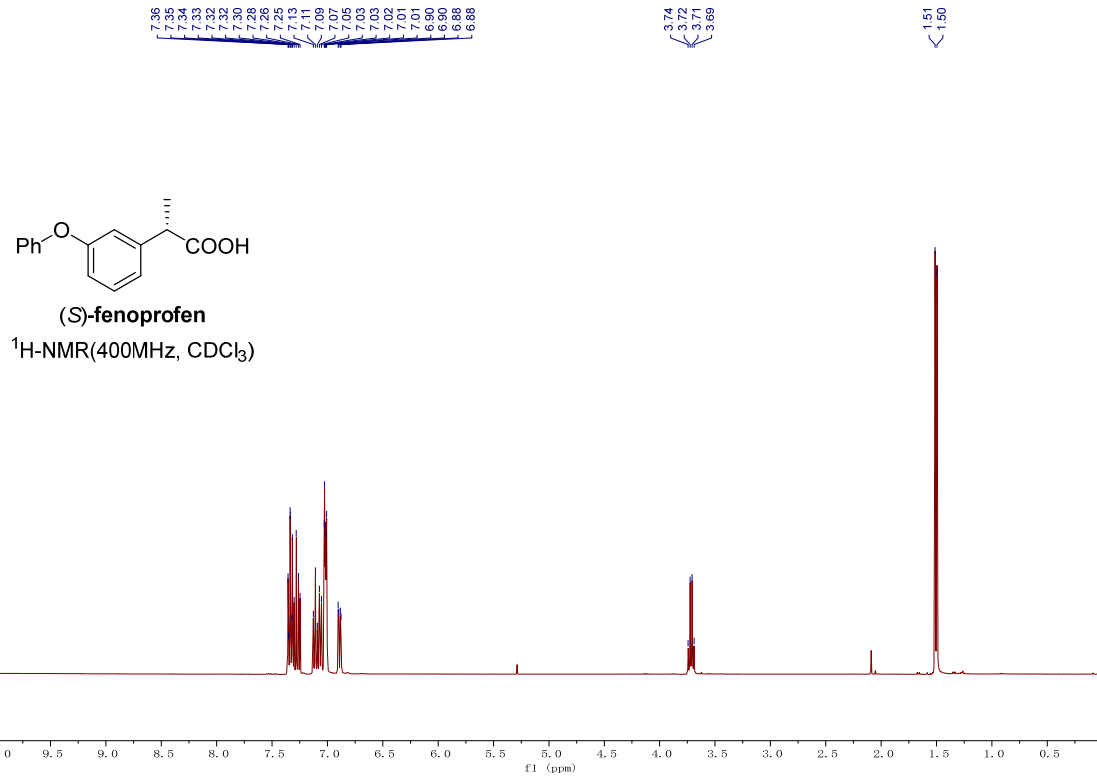






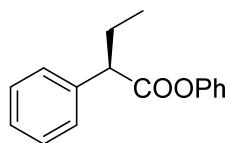




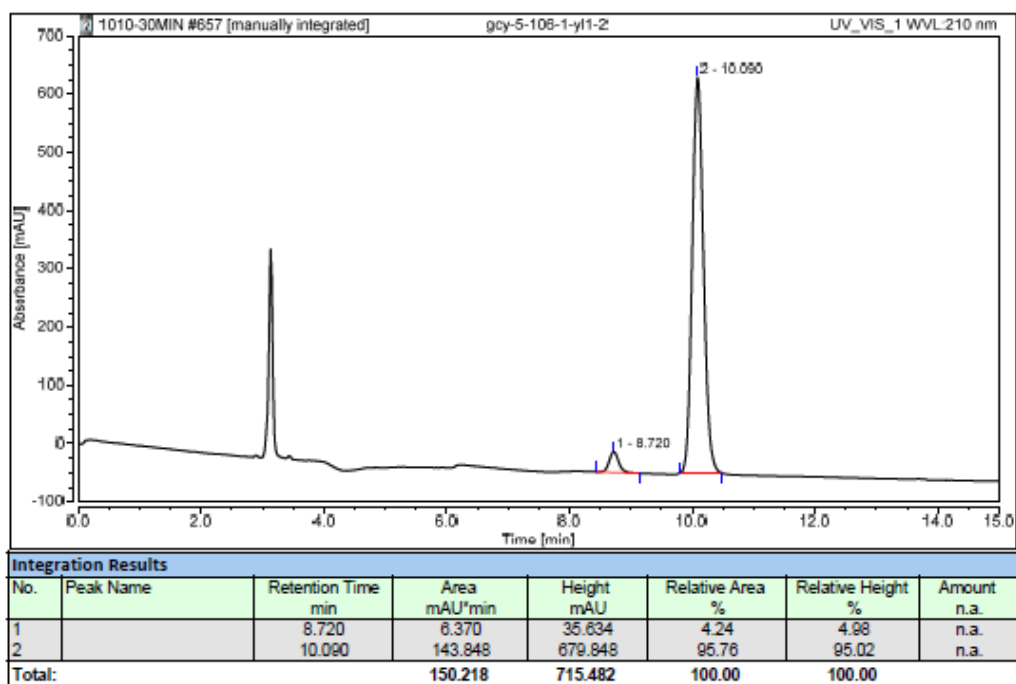
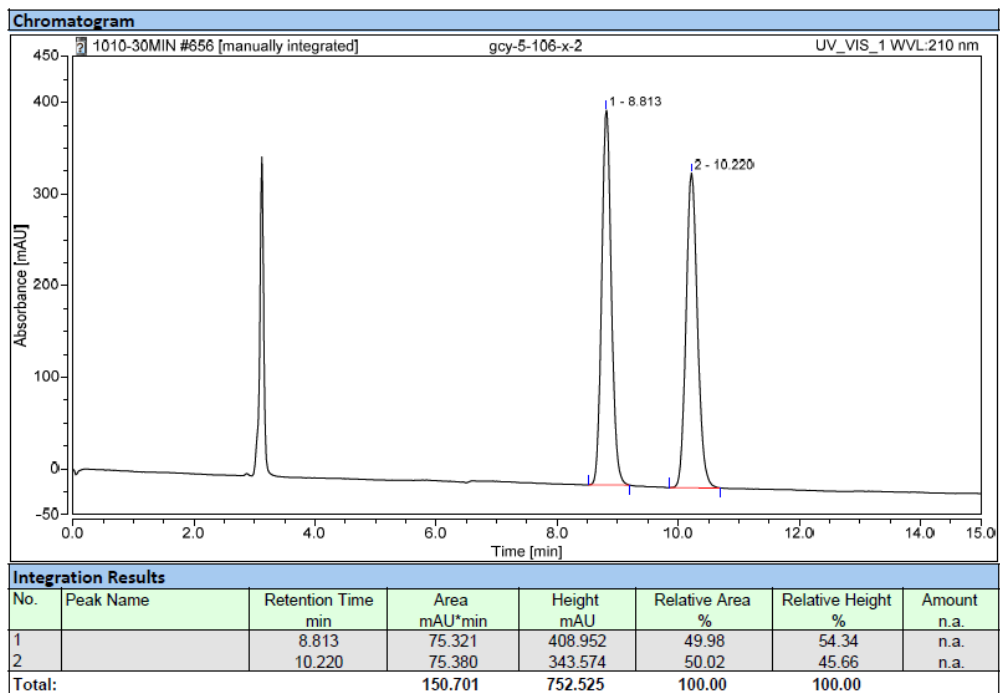


HPLC Spectra Data:

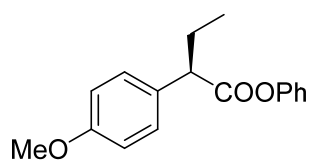
(R)-phenyl-2-phenylbutanoate (2a):



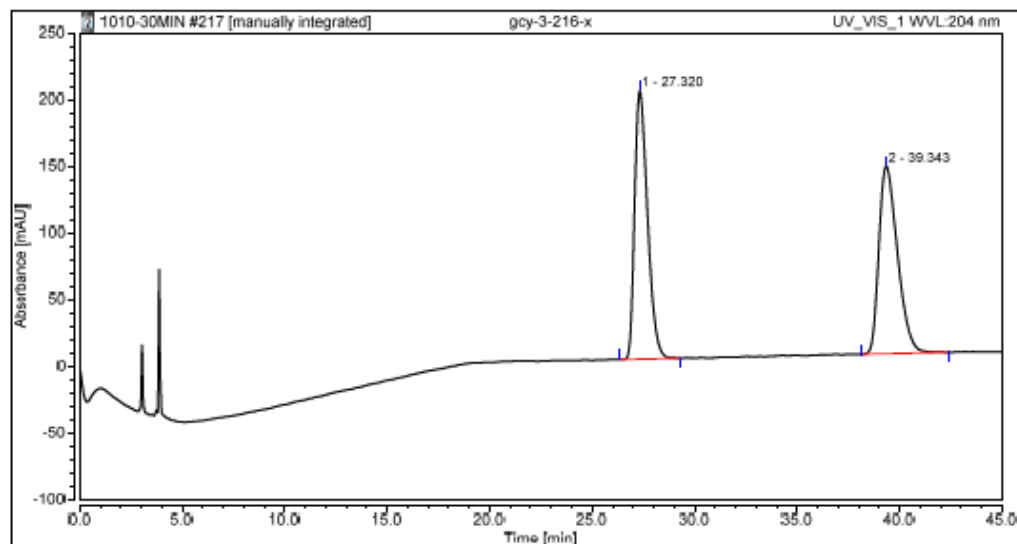
Column DAICEL Chiralcel OJ-H 5 μ m, heptane/*i*-PrOH 90:10, flow rate 1 mL/min, 25 °C, UV 210 nm



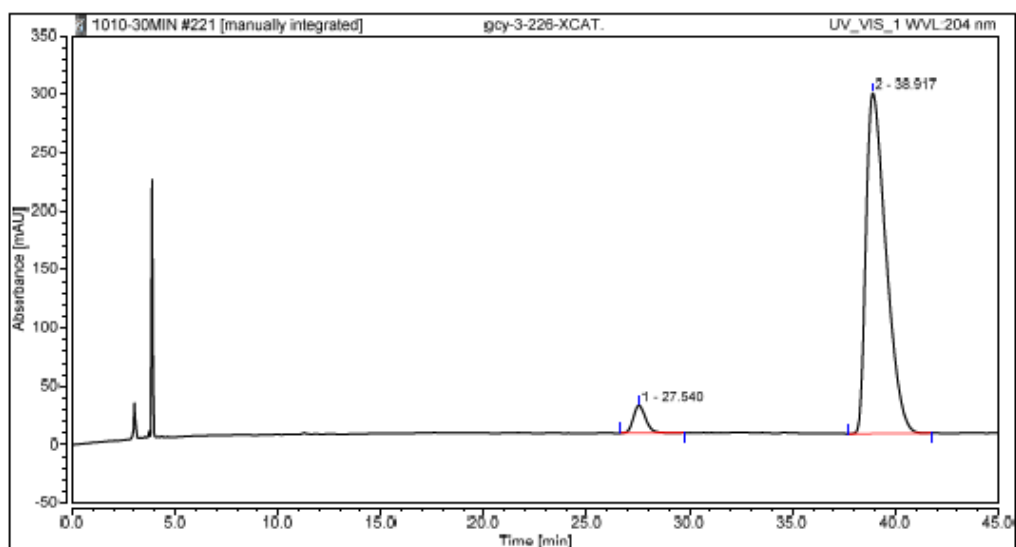
(R)-phenyl -2-(4-methoxyphenyl) butanoate (2d):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 90:10, flow rate 1 mL/min, 25 °C, UV 204 nm

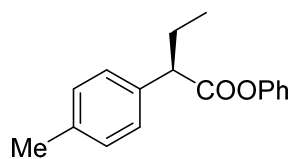


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.320	146.641	201.031	49.82	58.88	n.a.
2		39.343	147.689	140.369	50.18	41.12	n.a.
Total:			294.330	341.400	100.00	100.00	

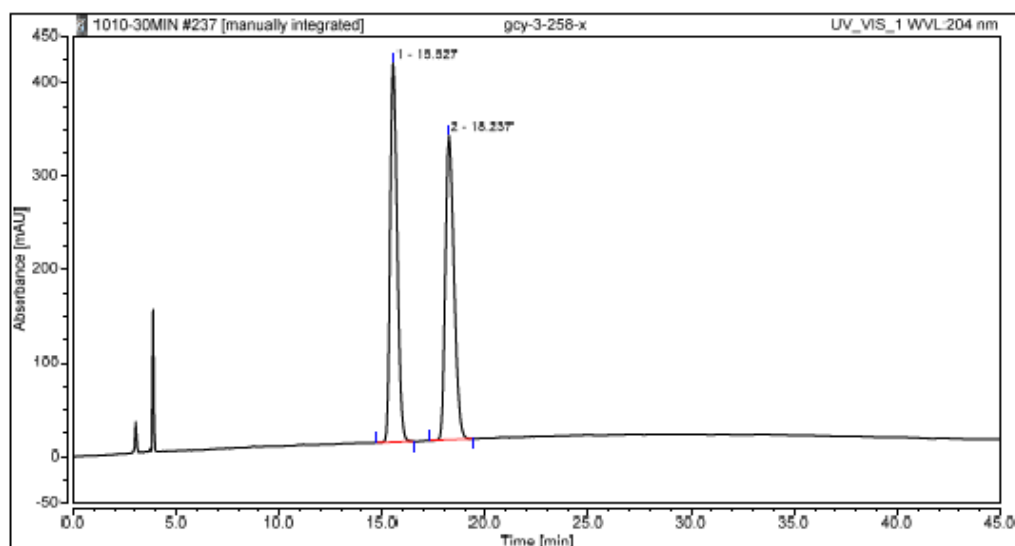


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.540	16.115	23.689	4.69	7.51	n.a.
2		38.917	327.580	291.953	95.31	92.49	n.a.
Total:			343.695	315.642	100.00	100.00	

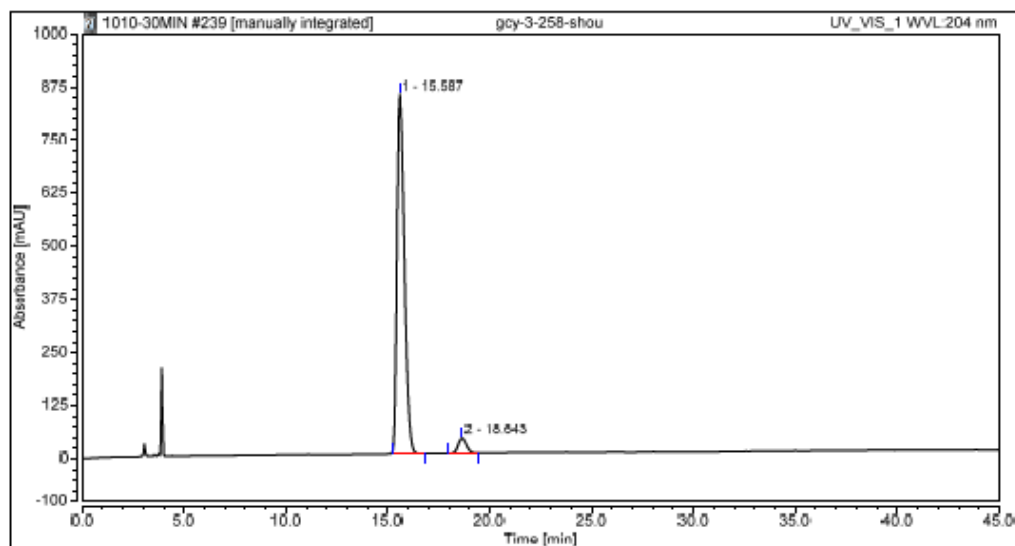
(R)-phenyl -2-(p-tolyl) butanoate (2e):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 90:10, flow rate 1 mL/min, 25 °C, UV 204 nm

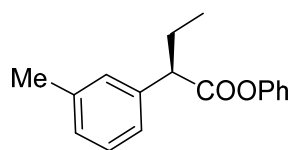


Integration Results							
No.	Peak Name	Retention Time min	Area mAU ² min	Height mAU	Relative Area %	Relative Height %	Amount
1		15.527	159.284	405.226	50.10	55.47	n.a.
2		18.237	158.655	325.326	49.90	44.53	n.a.
Total:			317.939	730.552	100.00	100.00	

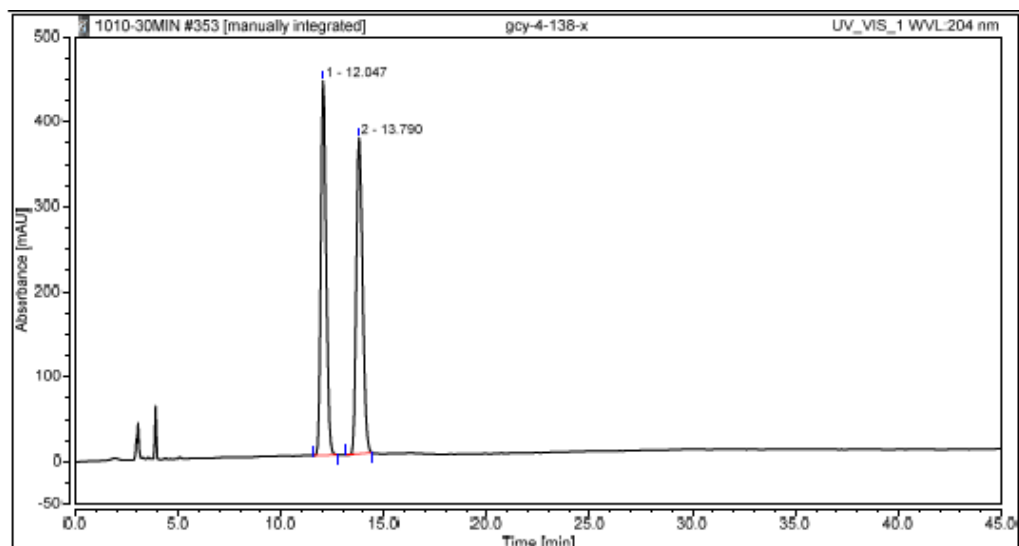


Integration Results							
No.	Peak Name	Retention Time min	Area mAU ² min	Height mAU	Relative Area %	Relative Height %	Amount
1		15.587	352.955	845.801	95.42	96.00	n.a.
2		18.643	16.940	35.228	4.58	4.00	n.a.
Total:			369.895	881.029	100.00	100.00	

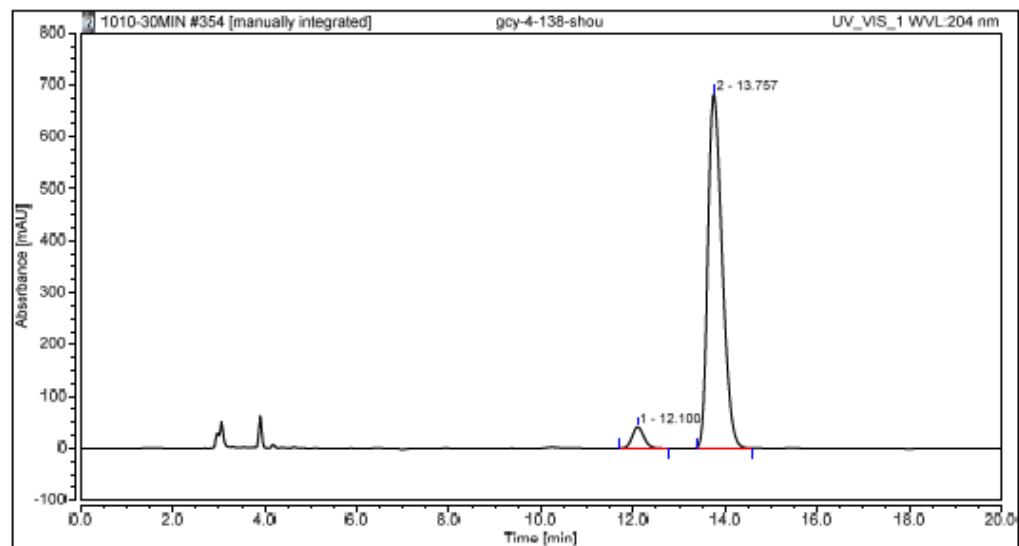
(R)-phenyl -2-(m-tolyl) butanoate (2f):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 90:10, flow rate 1 mL/min, 25 °C, UV 204 nm

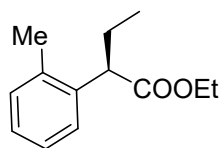


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		12.047	131.384	440.721	50.23	54.22	n.a.
2		13.790	130.188	372.094	49.77	45.78	n.a.
Total:			261.572	812.815	100.00	100.00	

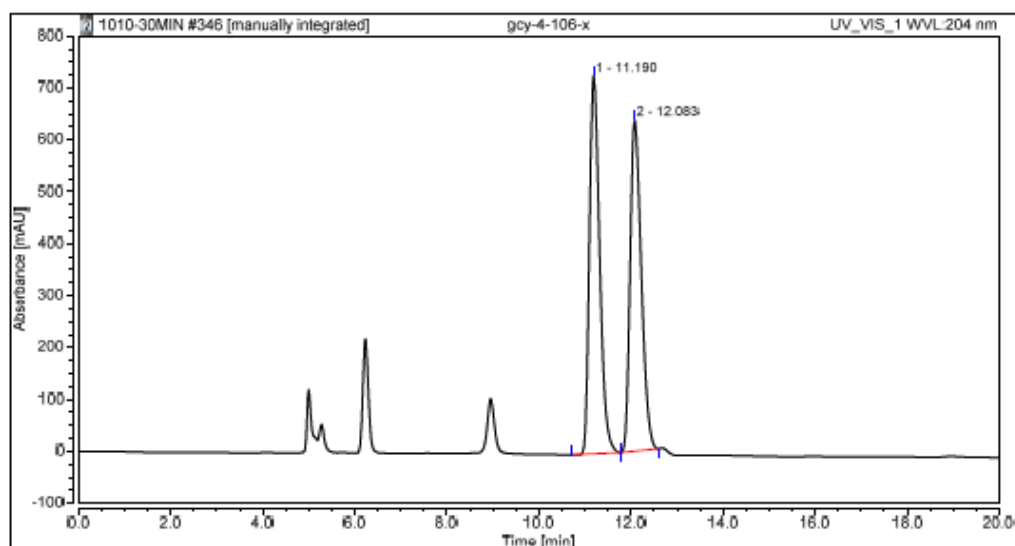


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		12.100	12.230	41.157	4.78	5.70	n.a.
2		13.757	243.751	681.531	95.22	94.30	n.a.
Total:			255.981	722.689	100.00	100.00	

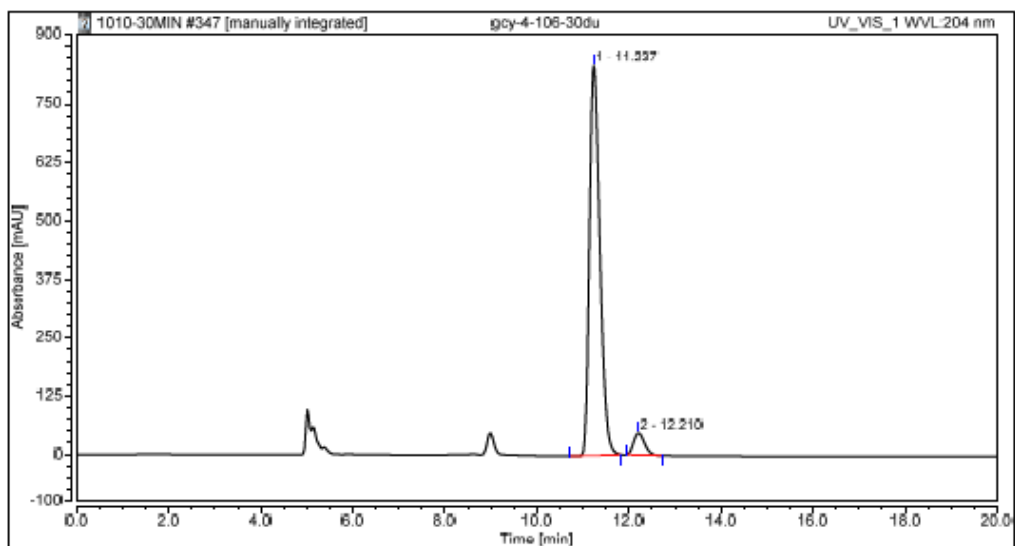
(R)-ethyl-2-(o-tolyl) butanoate (2g):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 99.8:0.2, flow rate 0.6 mL/min, 25 °C, UV 204 nm

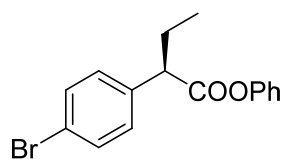


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		11.190	186.173	727.831	50.88	53.31	n.a.
2		12.083	179.908	637.523	49.14	46.69	n.a.
Total:			366.080	1365.354	100.00	100.00	

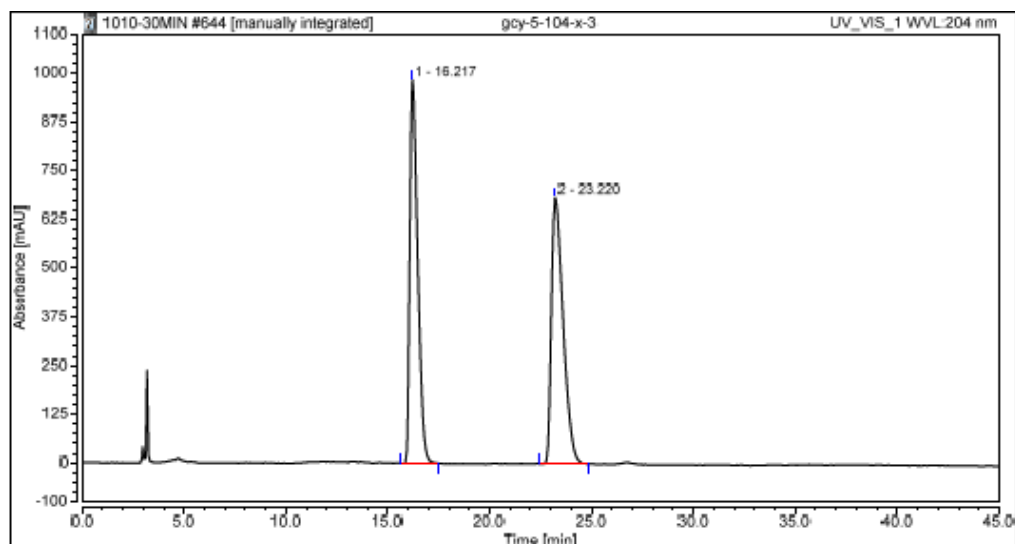


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		11.237	217.610	835.010	94.39	94.61	n.a.
2		12.210	12.925	47.588	5.61	5.39	n.a.
Total:			230.534	882.598	100.00	100.00	

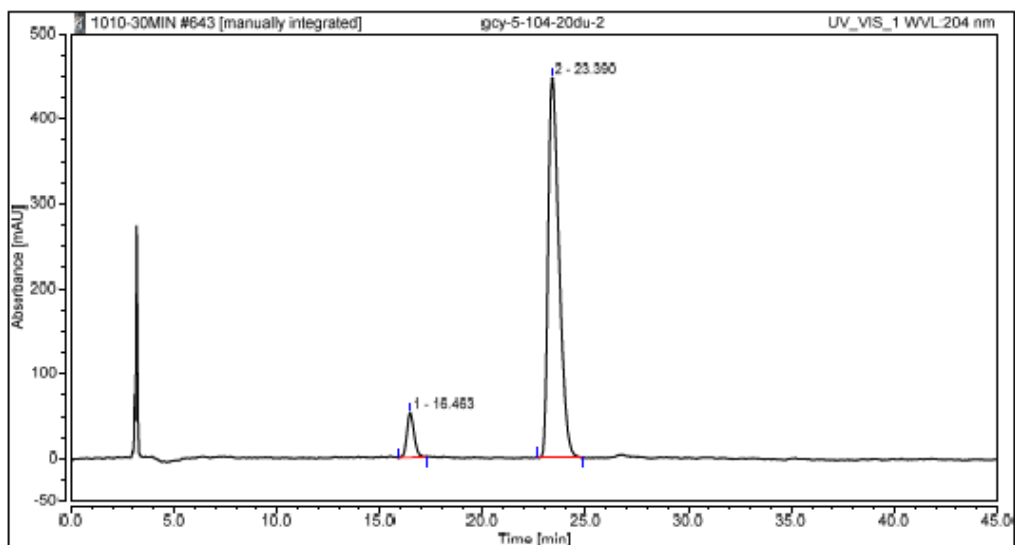
(R)-phenyl-2-(4-bromophenyl) butanoate (2h):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/*i*-PrOH 95:5, flow rate 1.0 mL/min, 25 °C, UV 204 nm

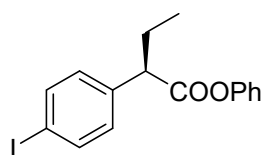


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		16.217	440.221	983.394	49.22	59.02	n.a.
2		23.220	454.202	682.753	50.78	40.98	n.a.
Total:			894.423	1666.146	100.00	100.00	

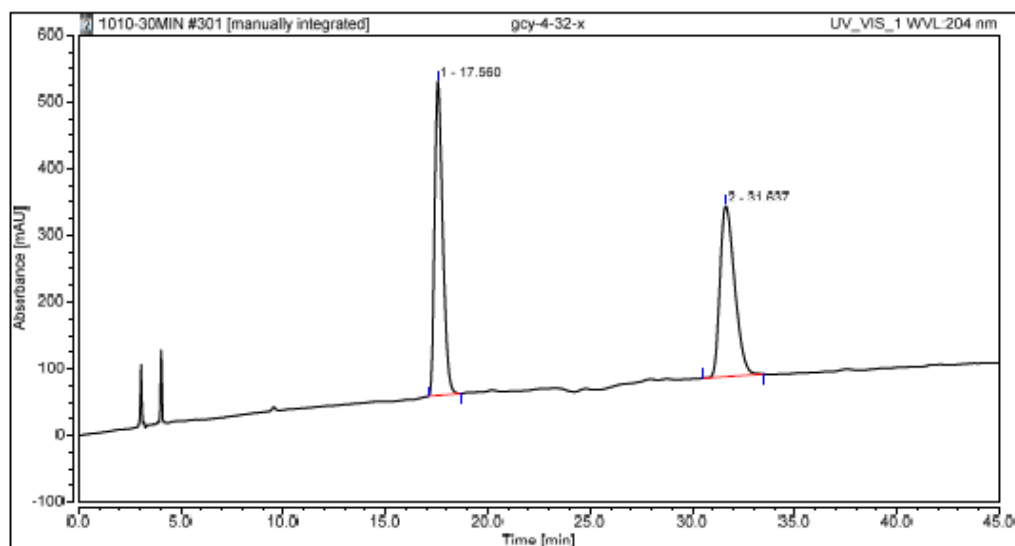


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		16.463	21.185	53.150	7.19	10.62	n.a.
2		23.390	273.313	447.246	92.81	89.38	n.a.
Total:			294.497	500.396	100.00	100.00	

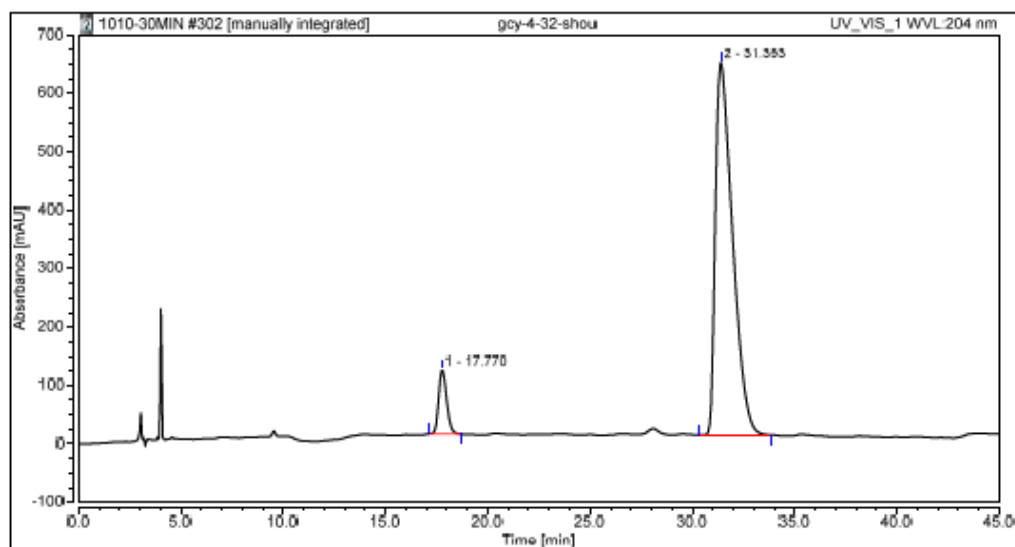
(R)-phenyl-2-(4-iodophenyl) butanoate (2i):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/*i*-PrOH 95:5, flow rate 1.0 mL/min, 25 °C, UV 204 nm

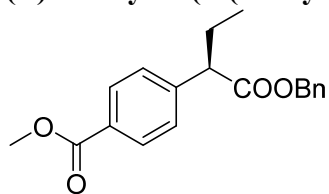


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		17.560	215.180	470.846	50.29	64.74	n.a.
2		31.637	212.736	256.459	49.71	35.26	n.a.
Total:			427.916	727.305	100.00	100.00	

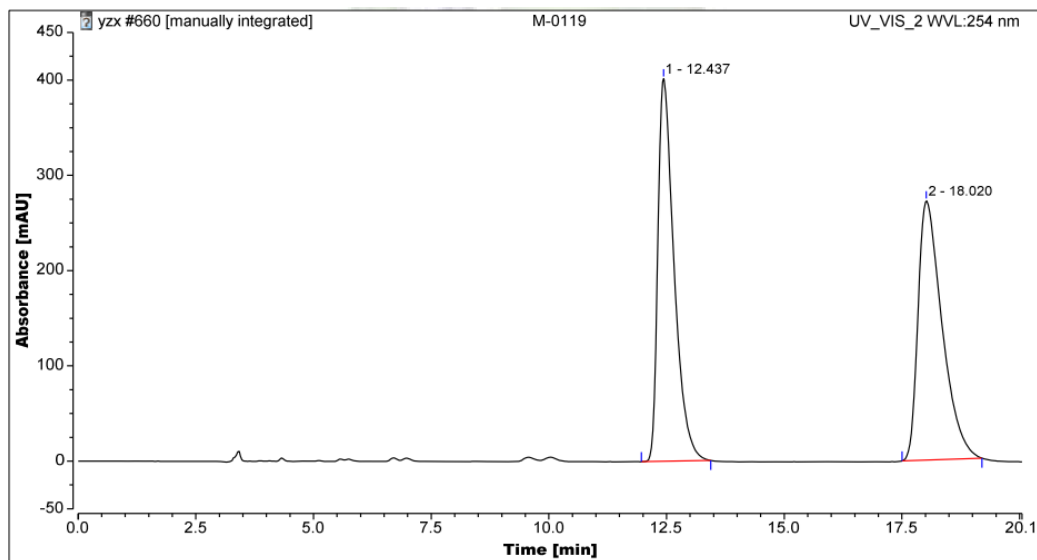


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		17.770	49.588	110.094	7.39	14.72	n.a.
2		31.393	621.022	637.648	92.61	85.28	n.a.
Total:			670.608	747.742	100.00	100.00	

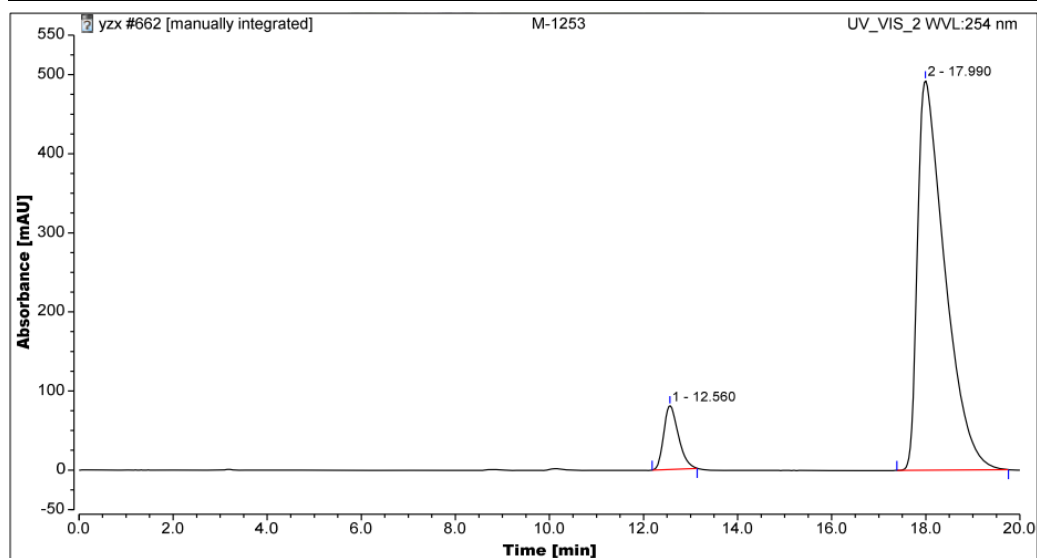
(R)-methyl-4-(1-(benzyloxy)-1-oxobutan-2-yl)benzoate (2j):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 80:20, flow rate 1.0 mL/min, 25 °C, UV 254 nm

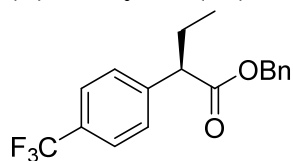


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		12.437	159.669	401.560	49.82	59.61	n.a.
2		18.020	160.803	272.089	50.18	40.39	n.a.
Total:			320.472	673.649	100.00	100.00	

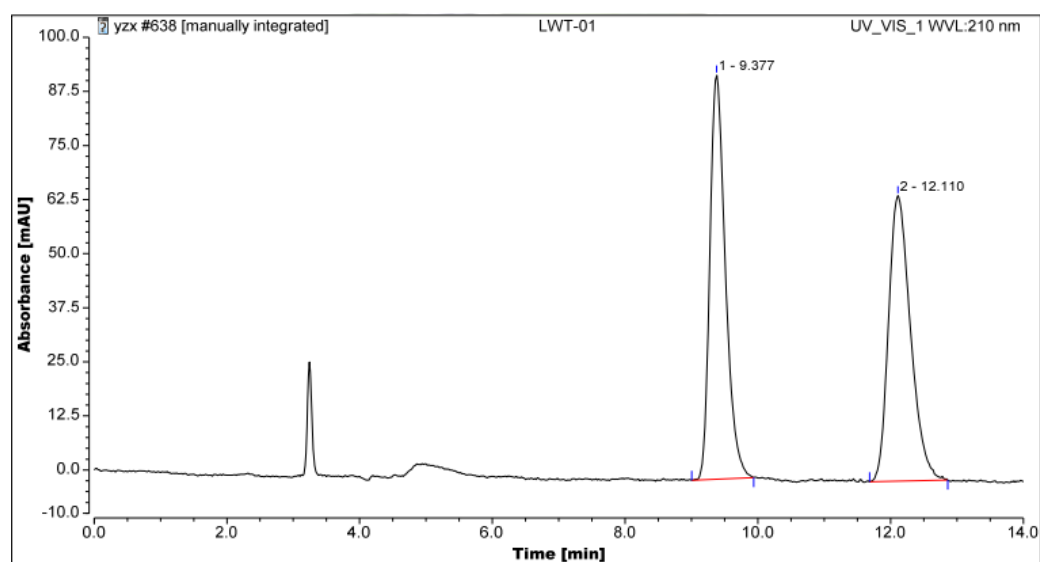


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		12.560	29.049	80.555	8.04	14.05	n.a.
2		17.990	332.370	492.770	91.96	85.95	n.a.
Total:			361.419	573.326	100.00	100.00	

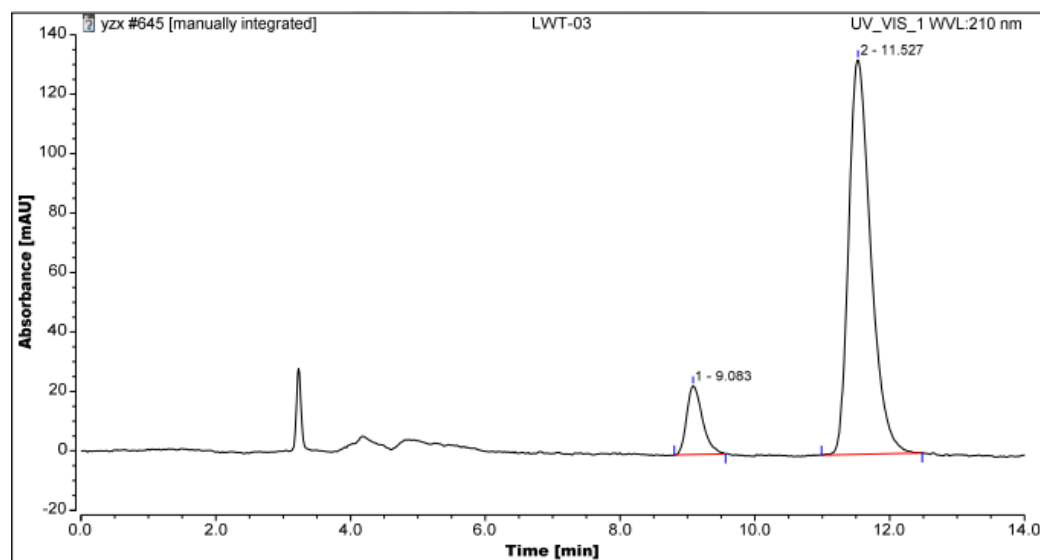
(R)-benzyl -2-(4-(trifluoromethyl)phenyl)butanoate (2k):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 98:2, flow rate 1.0 mL/min, 25 °C, UV 210 nm

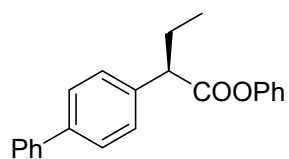


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.377	25.302	93.428	50.00	58.61	n.a.
2		12.110	25.302	65.983	50.00	41.39	n.a.
Total:			50.604	159.411	100.00	100.00	

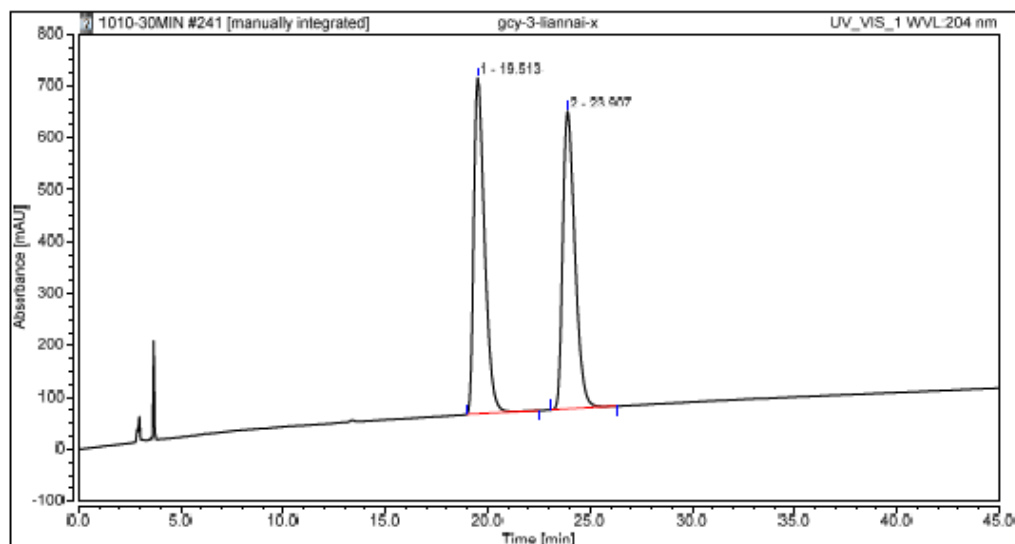


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.083	6.222	23.127	10.98	14.84	n.a.
2		11.527	50.451	132.761	89.02	85.16	n.a.
Total:			56.672	155.888	100.00	100.00	

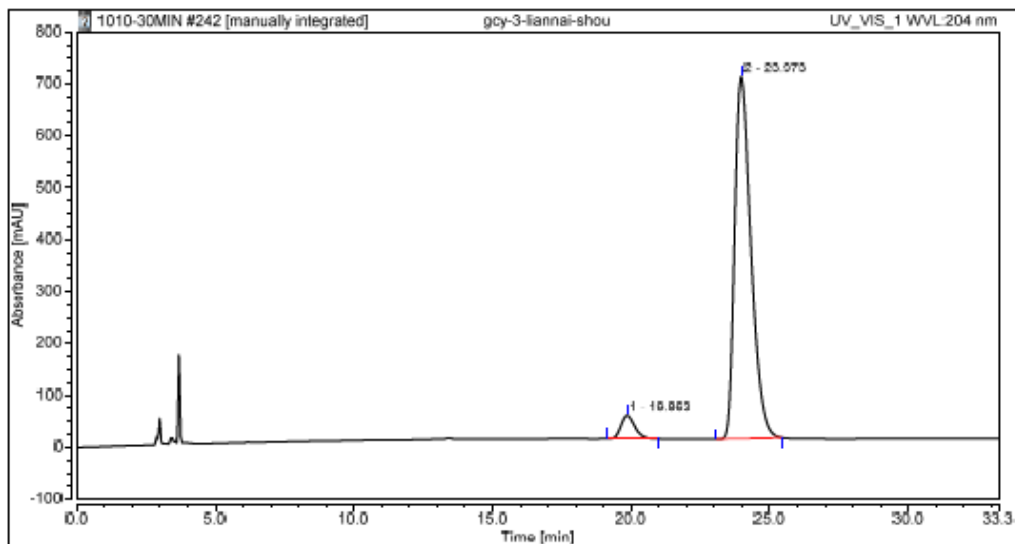
(R)-phenyl-2-([1,1'-biphenyl]-4-yl) butanoate (2l):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 85:15, flow rate 1.0 mL/min, 35 °C, UV 204 nm

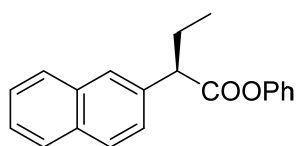


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		19.513	393.663	647.320	50.04	53.03	n.a.
2		23.907	392.956	573.395	49.96	46.97	n.a.
Total:			786.619	1220.715	100.00	100.00	

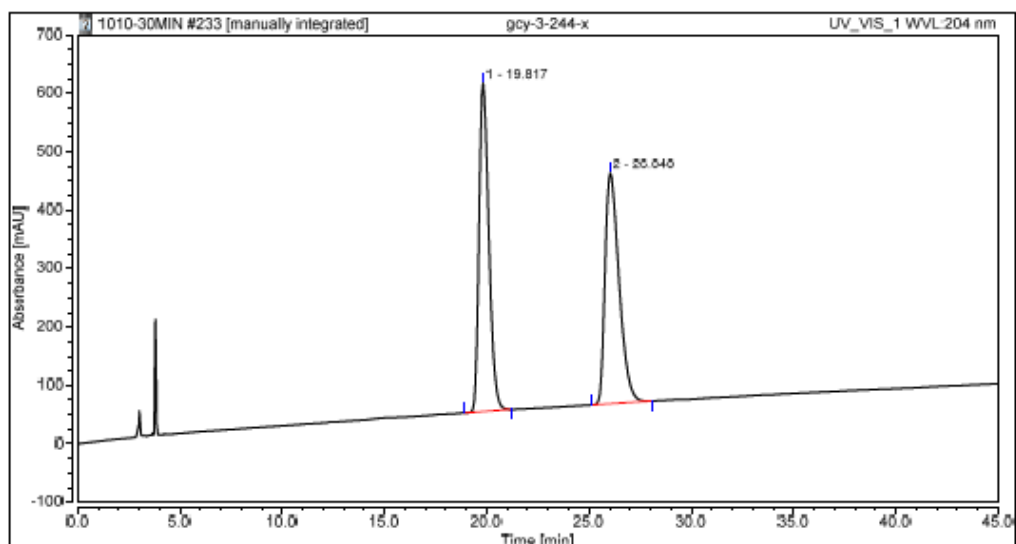


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		19.863	25.959	44.592	5.17	6.01	n.a.
2		23.973	476.373	697.155	94.83	93.99	n.a.
Total:			502.332	741.746	100.00	100.00	

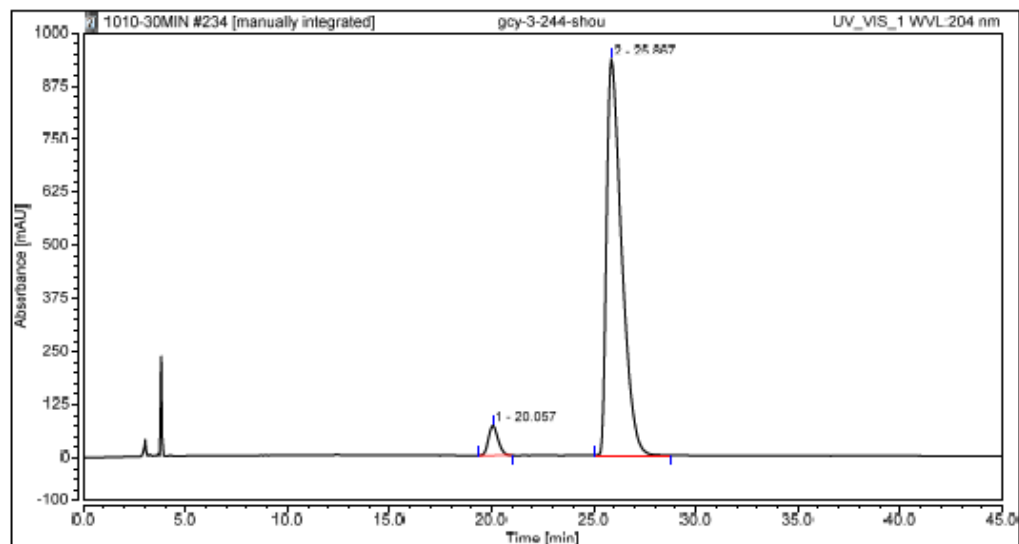
(R)-phenyl-2-(naphthalen-2-yl) butanoate (2m):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 85:15, flow rate 1.0 mL/min, 25 °C, UV 204 nm

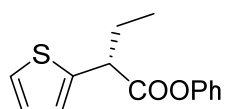


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		19.817	312.943	562.180	50.01	58.71	n.a.
2		26.040	312.787	395.434	49.99	41.29	n.a.
Total:			625.730	957.614	100.00	100.00	

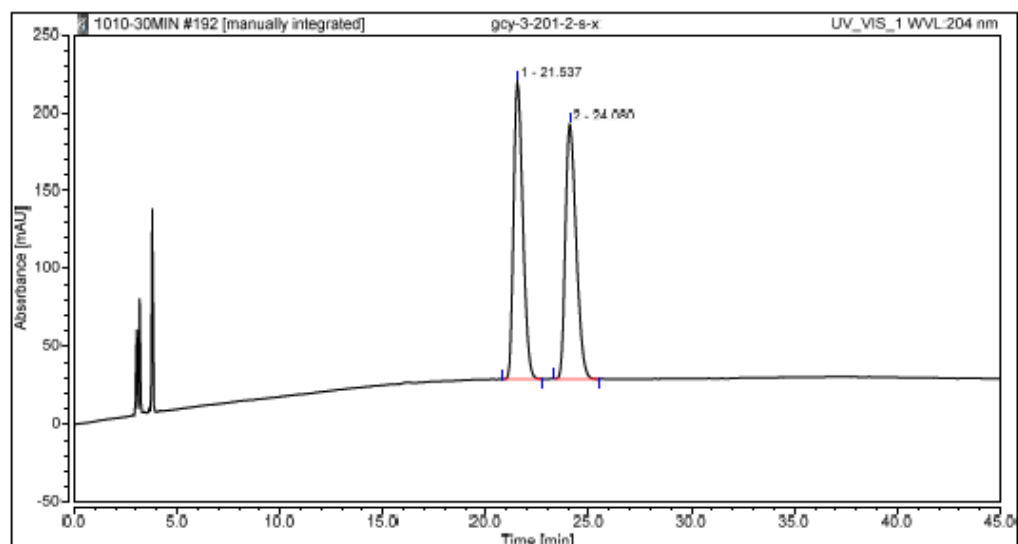


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		20.057	38.336	70.234	4.61	7.00	n.a.
2		26.867	793.563	933.324	95.39	93.00	n.a.
Total:			831.899	1003.558	100.00	100.00	

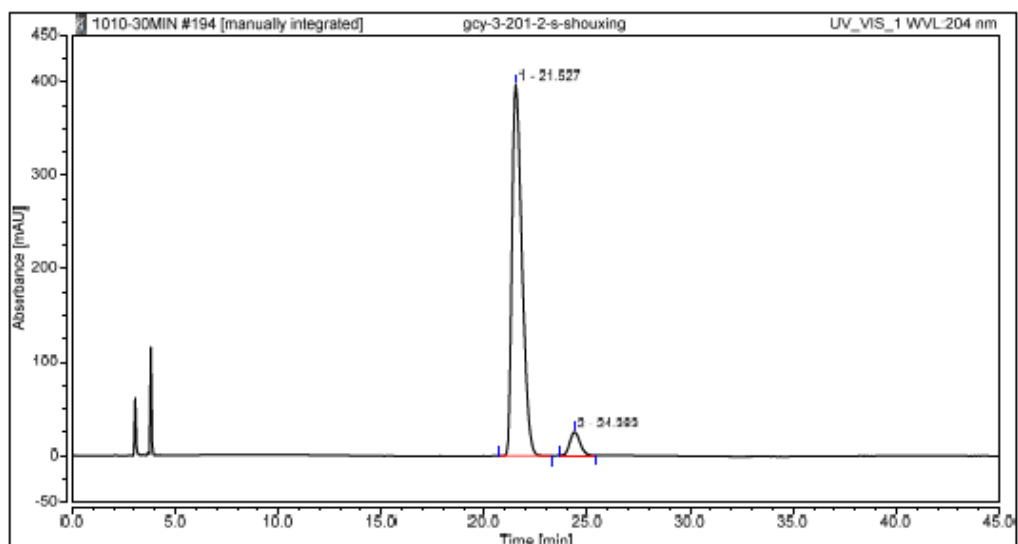
(R)-phenyl-2-(thiophen-2-yl) butanoate (2n):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 85:15, flow rate 1.0 mL/min, 25 °C, UV 204 nm

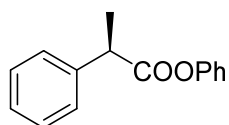


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		21.537	99.393	191.368	50.08	53.87	n.a.
2		24.080	99.057	163.887	49.92	46.13	n.a.
Total:			198.450	355.255	100.00	100.00	

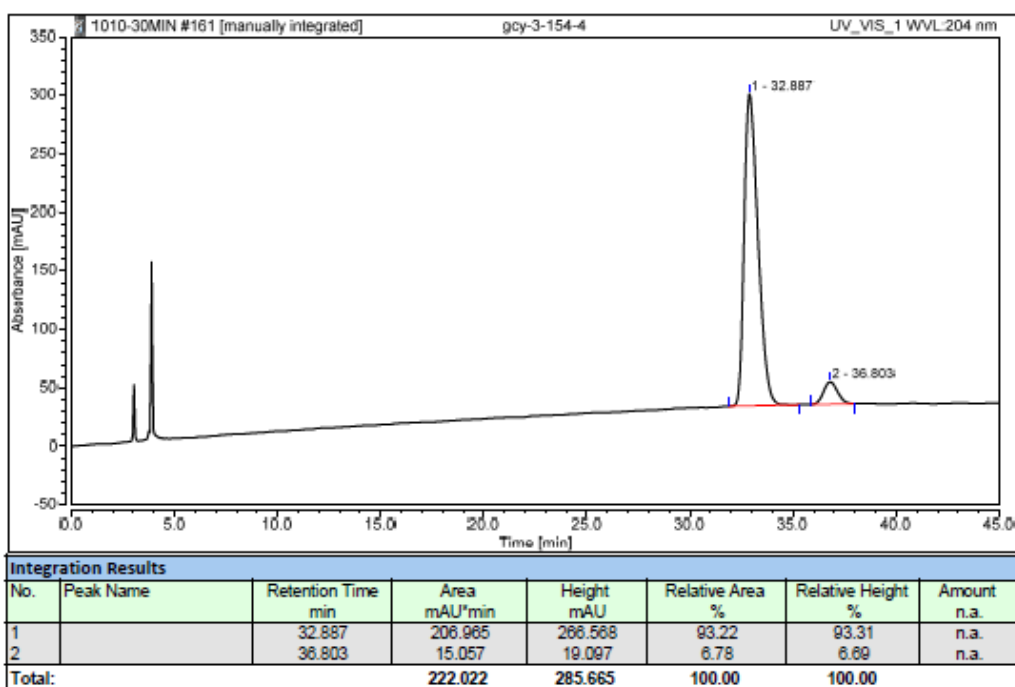
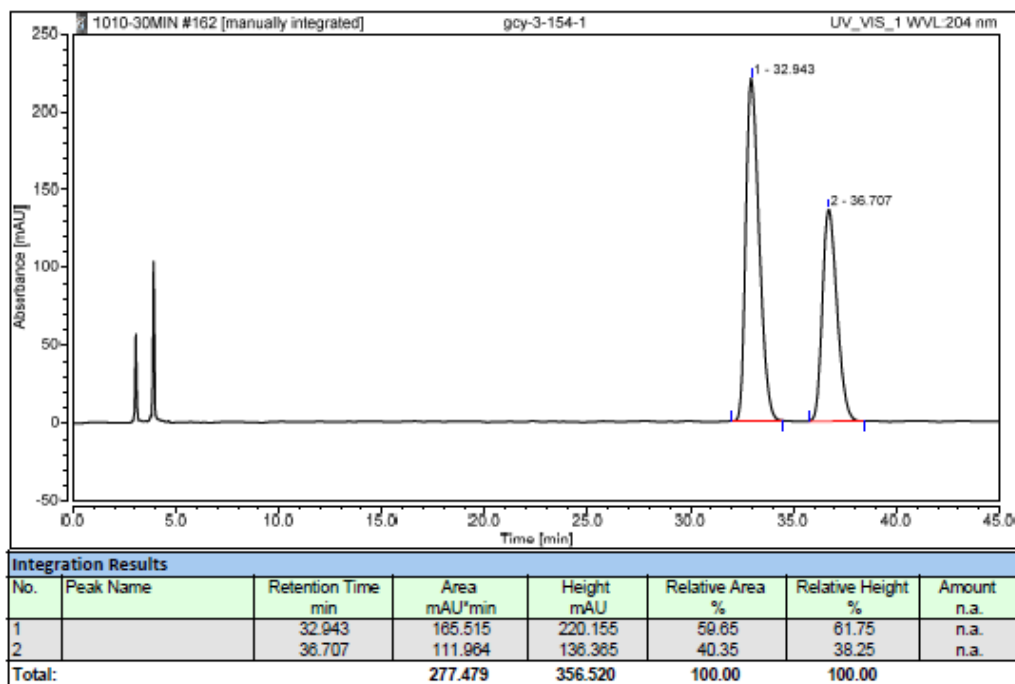


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		21.527	223.831	398.088	93.95	94.03	n.a.
2		24.383	14.413	25.267	6.05	5.97	n.a.
Total:			238.244	423.355	100.00	100.00	

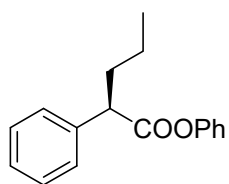
(R)-phenyl-2-phenylpropanoate (2o):



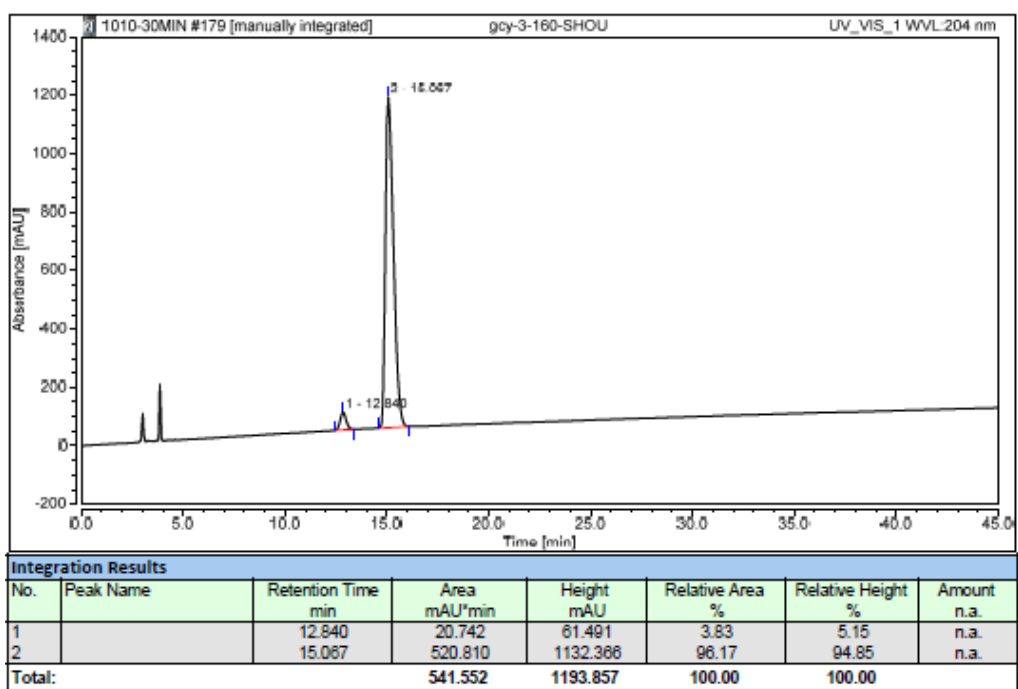
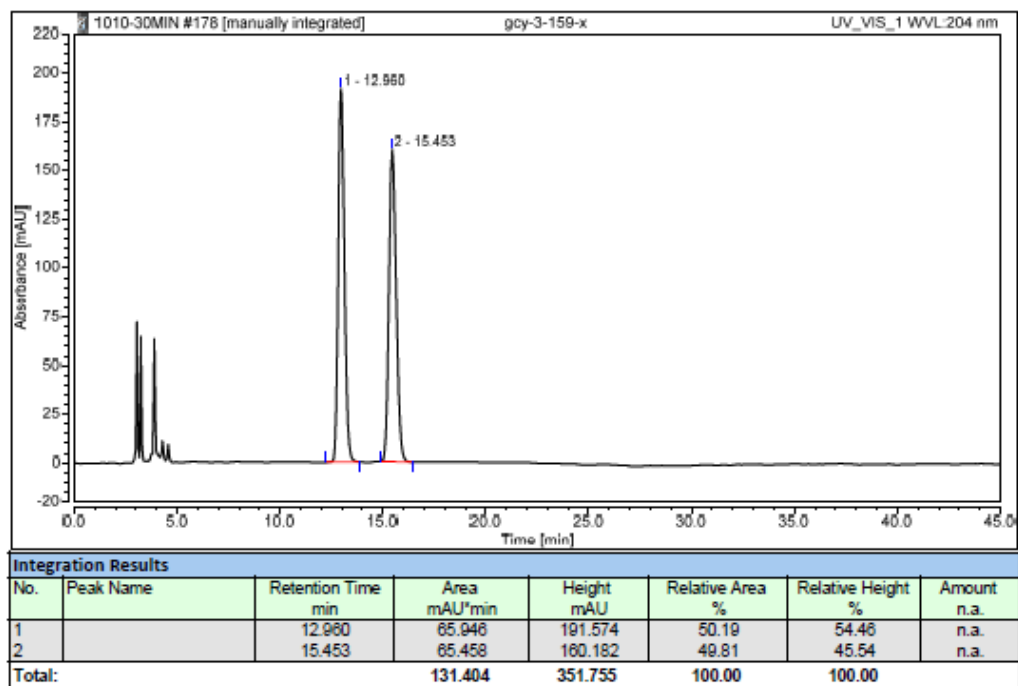
Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 90:10, flow rate 1.0 mL/min, 25 °C, UV 204 nm



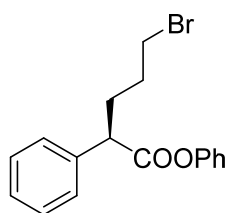
(R)-phenyl-2-phenylpentanoate (2p):



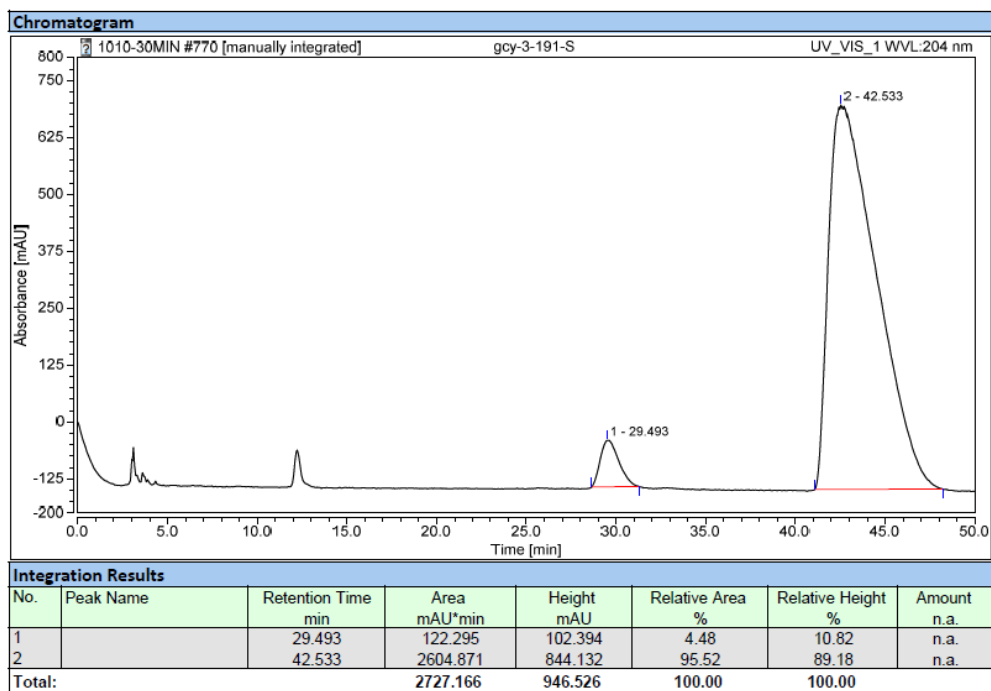
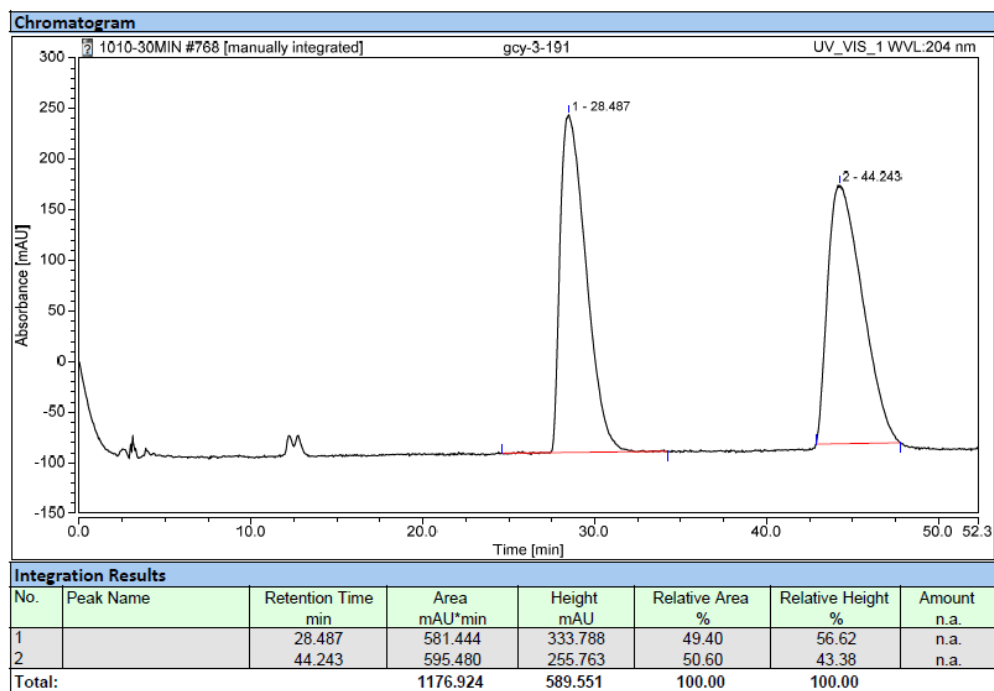
Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 90:10, flow rate 1.0 mL/min, 25 °C, UV 204 nm



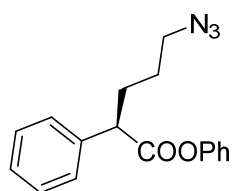
(R)-phenyl-5-bromo-2-phenylpentanoate (2q):



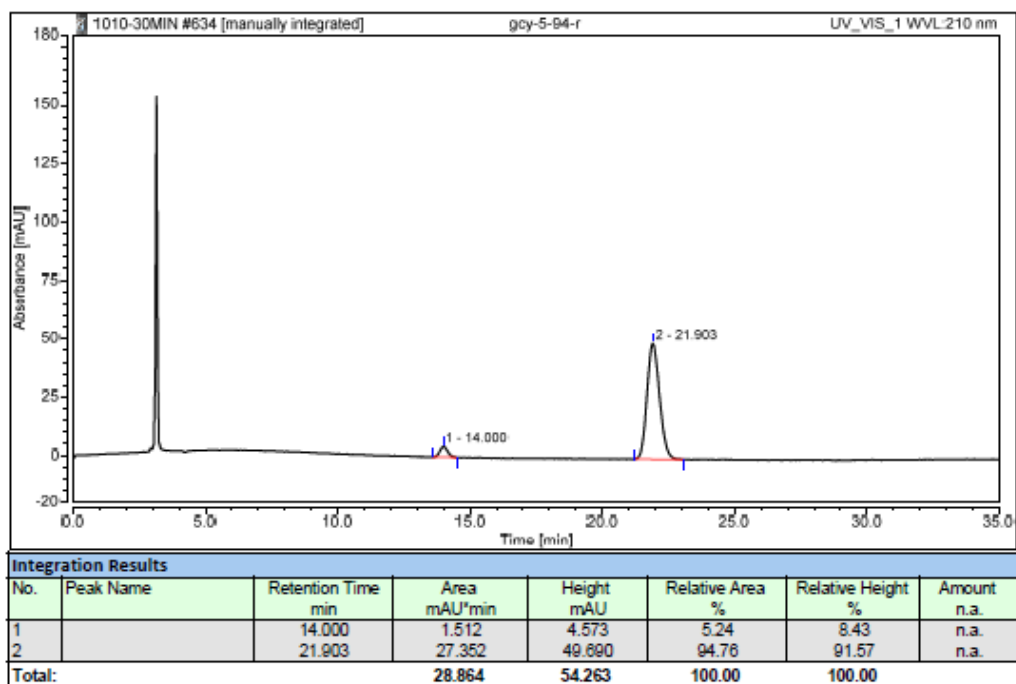
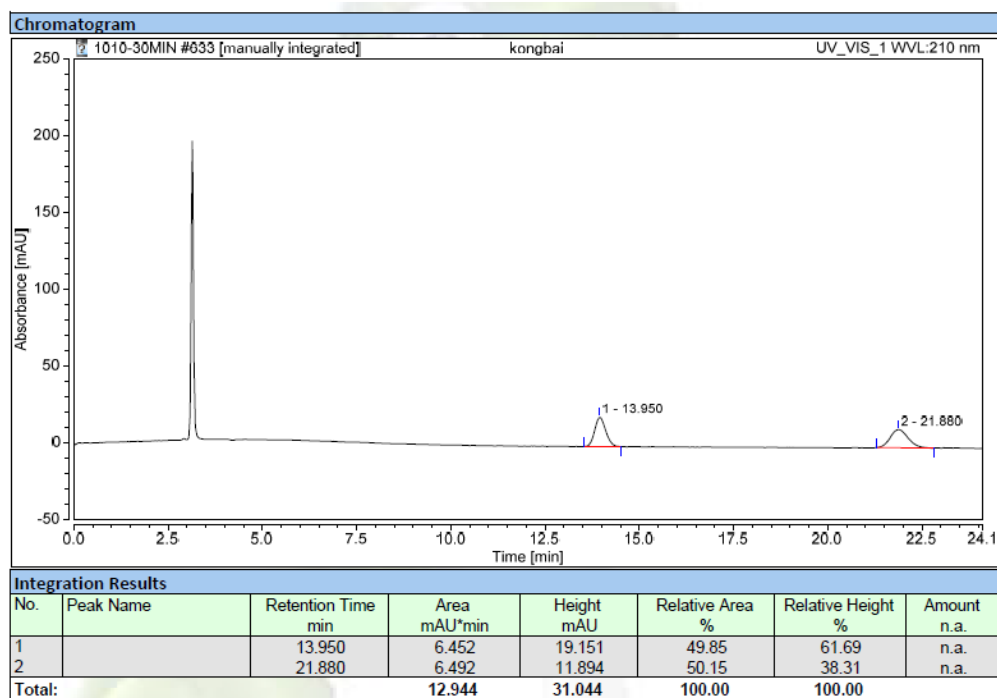
Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 85:15, flow rate 1.0 mL/min, 25 °C, UV 204 nm



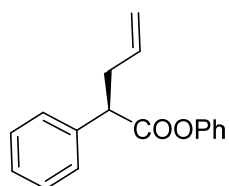
(R)-phenyl-5-azido-2-phenylpentanoate (2r):



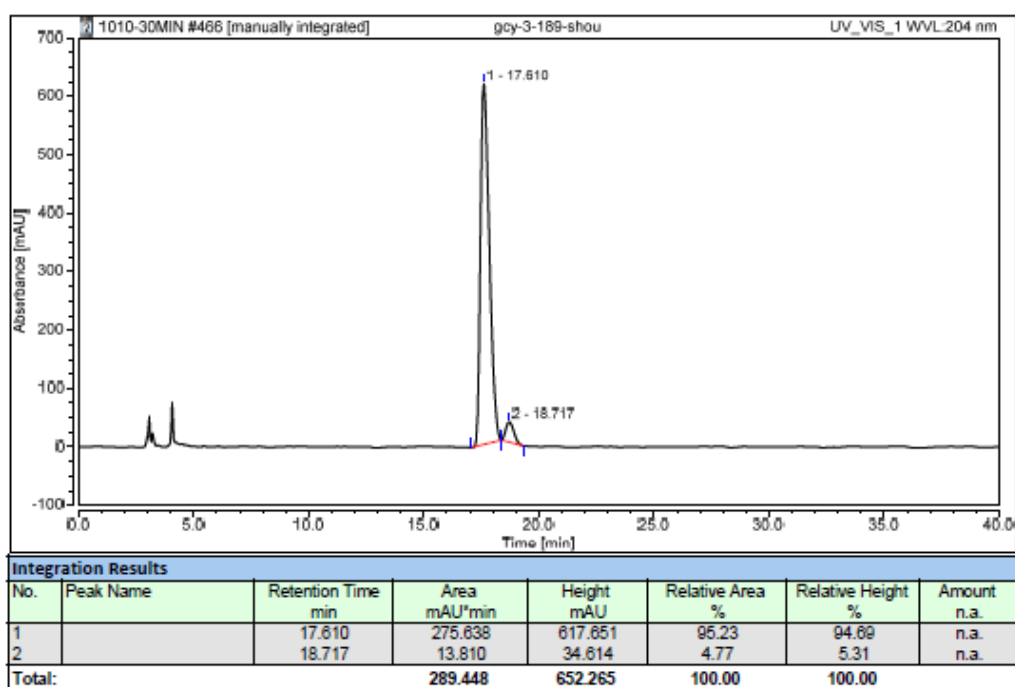
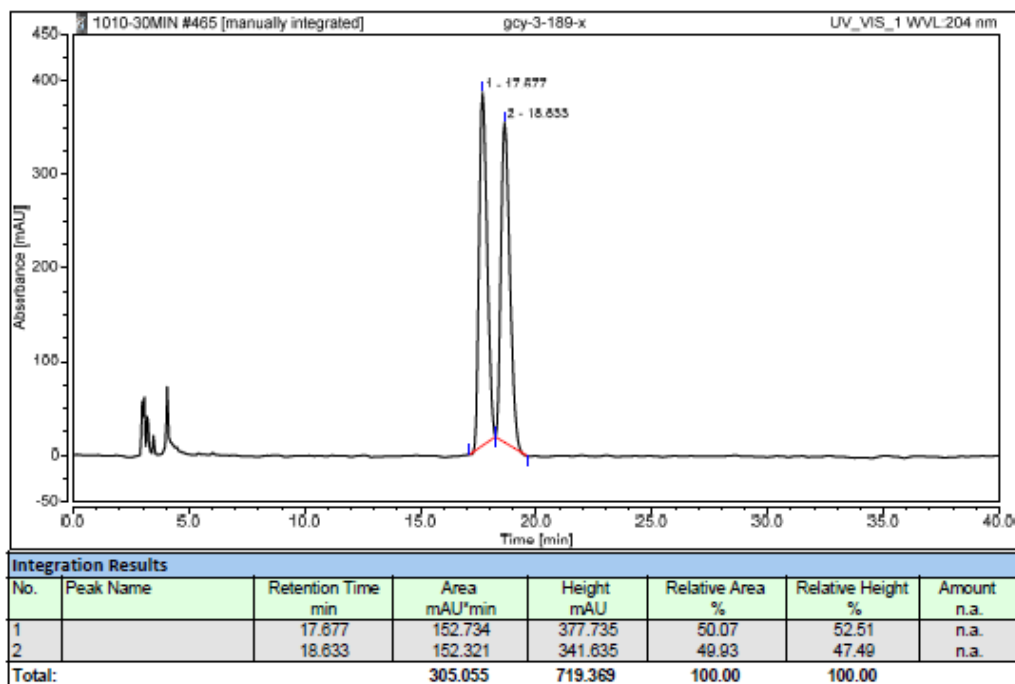
Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 70:30, flow rate 1.0 mL/min, 35 °C, UV 204 nm



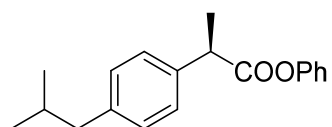
(R)-phenyl-2-phenylpent-4-enoate (2s):



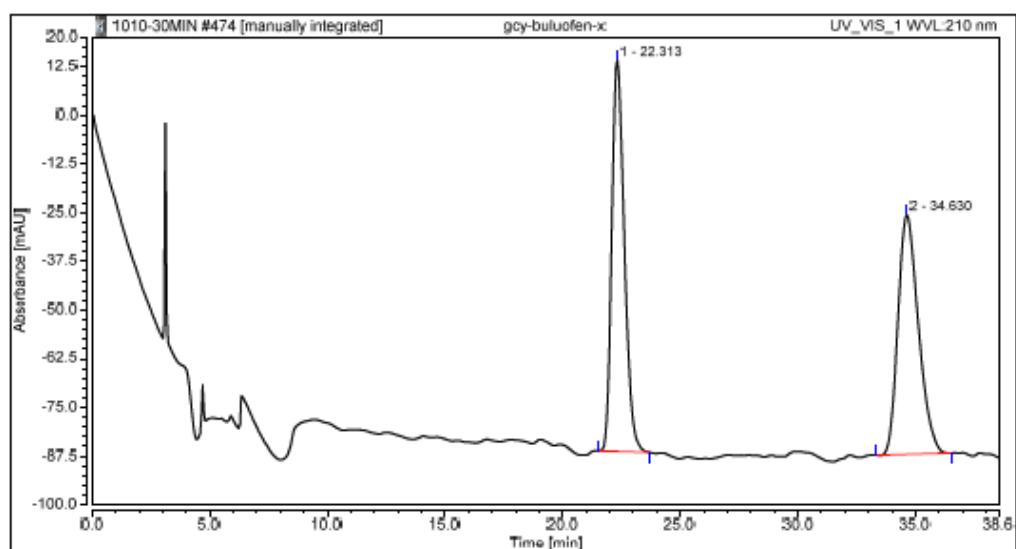
Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 95:5, flow rate 1.0 mL/min, 25 °C, UV 204 nm



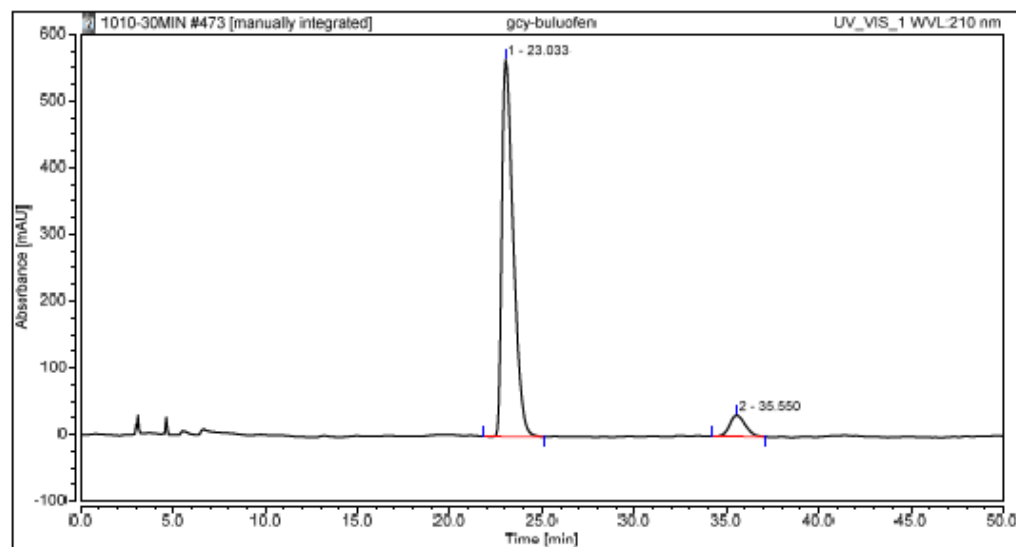
(R)-phenyl-2-(4-isobutylphenyl) propanoate (2t):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/*i*-PrOH 99:1, flow rate 1.0 mL/min, 25 °C, UV 210 nm

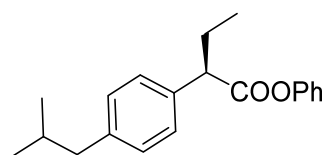


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.313	62.222	100.285	50.22	62.02	n.a.
2		34.630	61.669	61.412	49.78	37.98	n.a.
Total:			123.891	161.697	100.00	100.00	

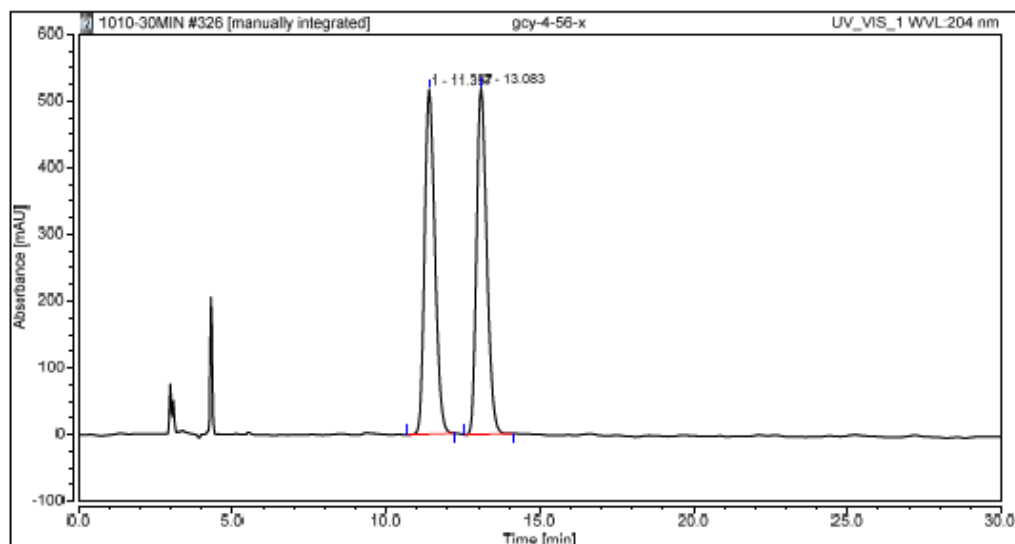


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.033	404.214	565.013	92.88	94.68	n.a.
2		35.550	30.975	31.747	7.12	5.32	n.a.
Total:			435.189	596.760	100.00	100.00	

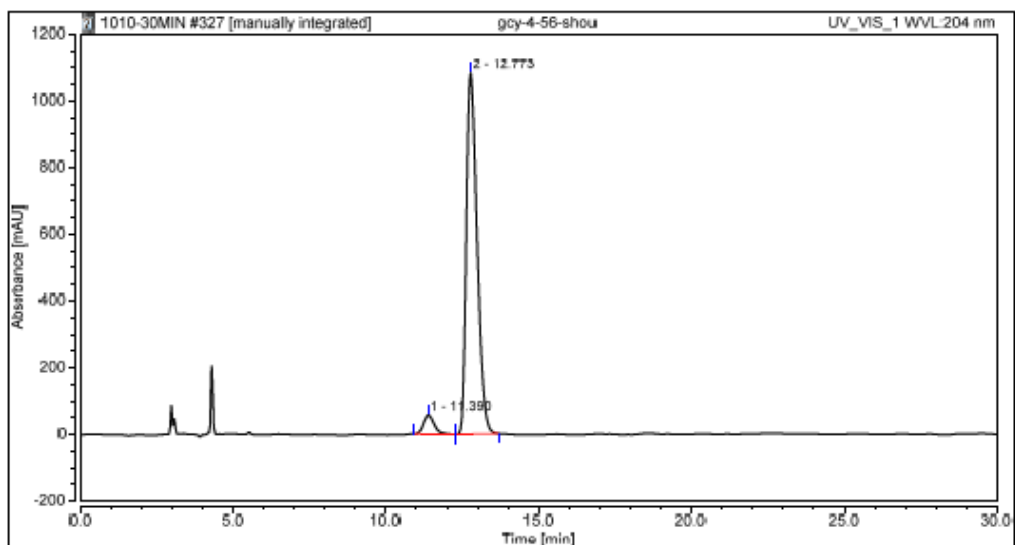
(R)-phenyl-2-(4-isobutylphenyl) butanoate (2u):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 98:2, flow rate 1.0 mL/min, 25 °C, UV 204 nm

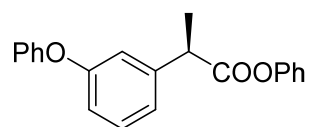


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		11.397	199.212	516.949	49.98	49.89	n.a.
		13.083	199.356	519.218	50.02	50.11	n.a.
Total:			398.567	1036.167	100.00	100.00	

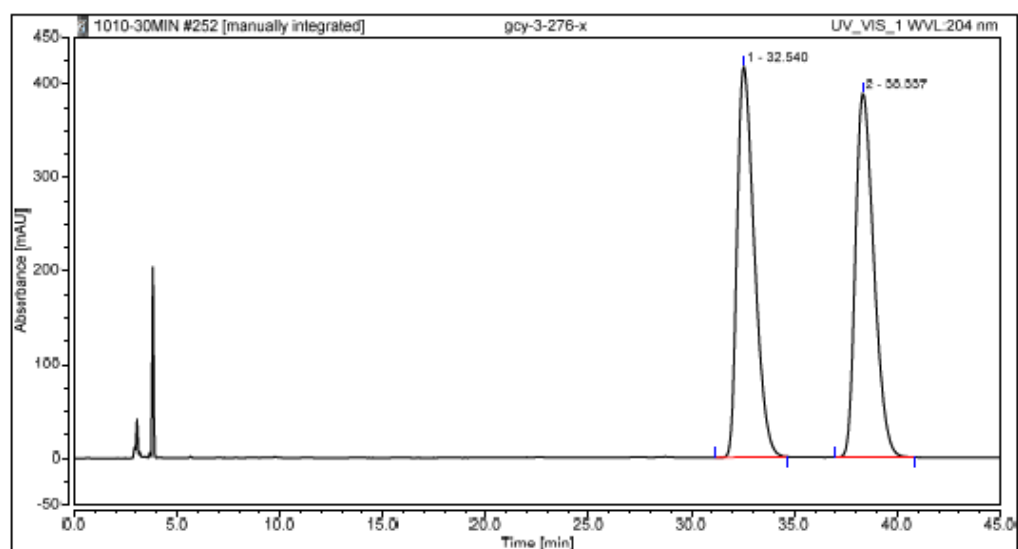


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		11.390	22.919	56.252	4.99	4.94	n.a.
2		12.773	436.432	1082.256	95.01	95.06	n.a.
Total:			459.351	1138.508	100.00	100.00	

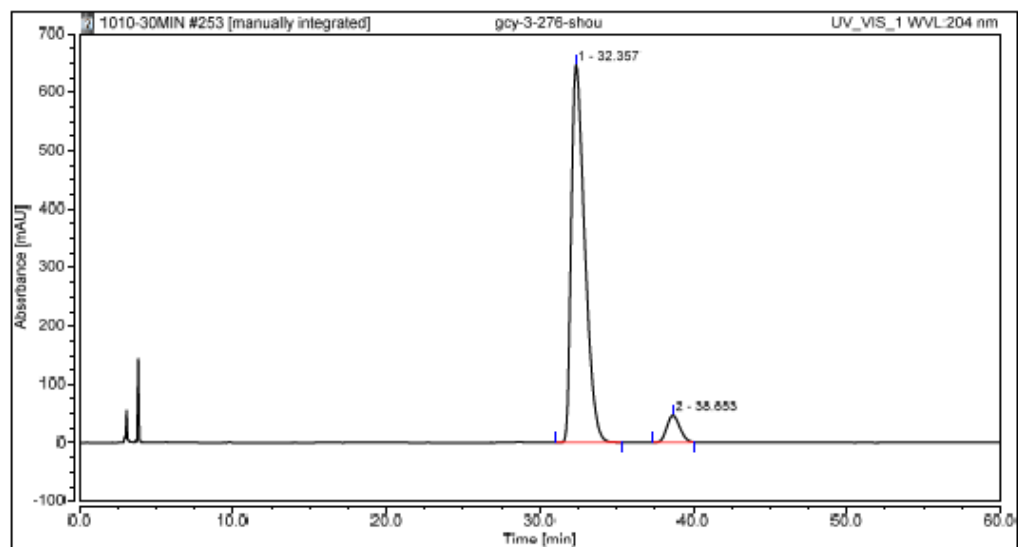
(R)-phenyl-2-(3-phenoxyphenyl) propanoate (2v):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH 80:20, flow rate 1.0 mL/min, 25 °C, UV 204 nm

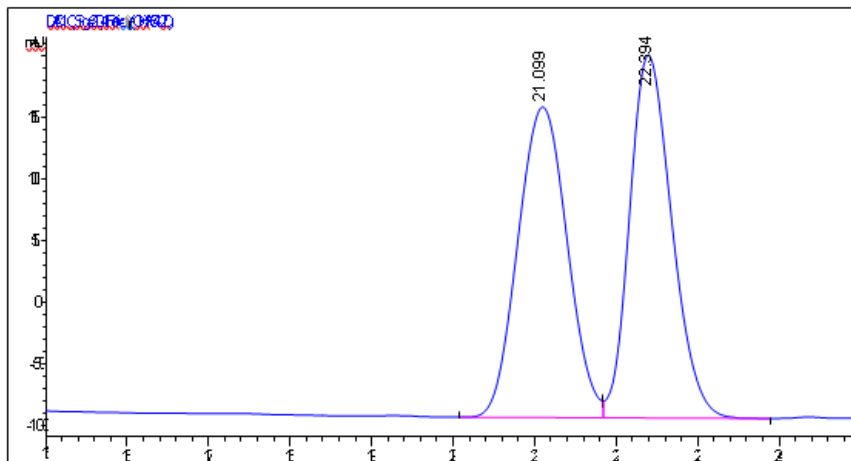
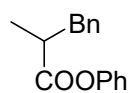


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		32.540	403.407	417.520	49.92	51.76	n.a.
2		38.337	404.647	389.095	50.08	48.24	n.a.
Total:			808.054	806.614	100.00	100.00	

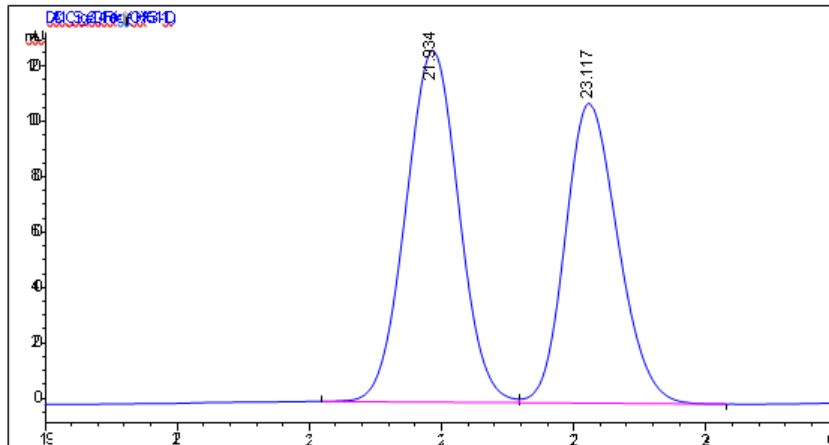


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		32.357	667.526	646.145	93.56	93.34	n.a.
2		38.653	45.260	46.094	6.44	6.66	n.a.
Total:			702.786	692.238	100.00	100.00	

phenyl 2-methyl-3-phenylpropanoate (2w):

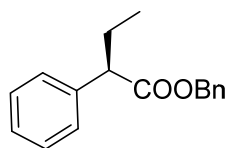


No	Peak Name	Retention Time min	Area mAU*mi	Height mAU	Relative Area %	Relative Height %	Amount n.a
1		21.099	501.5	251.9	49.971	49.971	n.a
2		22.394	473.1	294.6	50.029	50.029	n.a

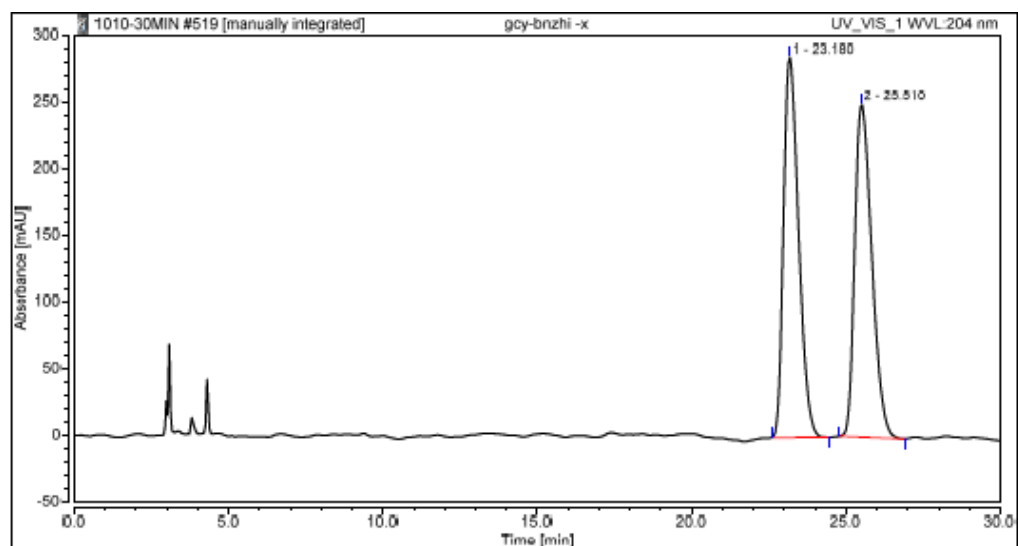


No	Peak Name	Retention Time min	Area mAU*mi	Height mAU	Relative Area %	Relative Height %	Amount n.a
1		21.934	161.6	127.1	54.117	54.117	n.a
2		23.117	130.1	108.4	45.883	45.883	n.a

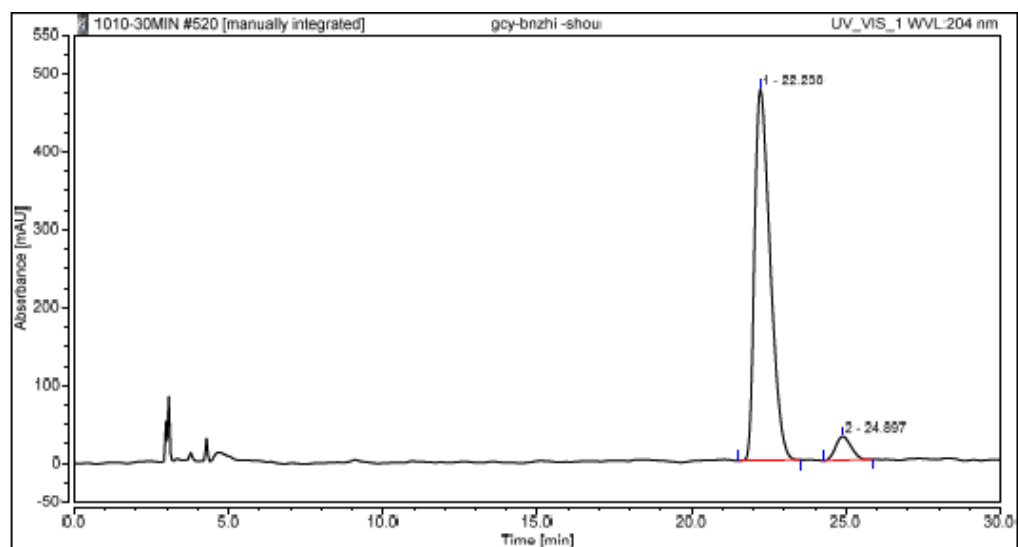
(R)-benzyl-2-phenylbutanoate (2b):



Column DAICEL Chiralcel OD-H 5 μ m, heptane/i-PrOH 98:2, flow rate 1.0 mL/min, 25 °C, UV 204 nm

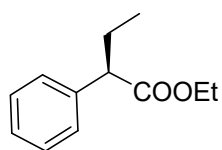


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.180	160.943	284.763	50.12	53.32	n.a.
2		25.510	160.143	249.306	49.88	46.68	n.a.
Total:			321.086	534.069	100.00	100.00	

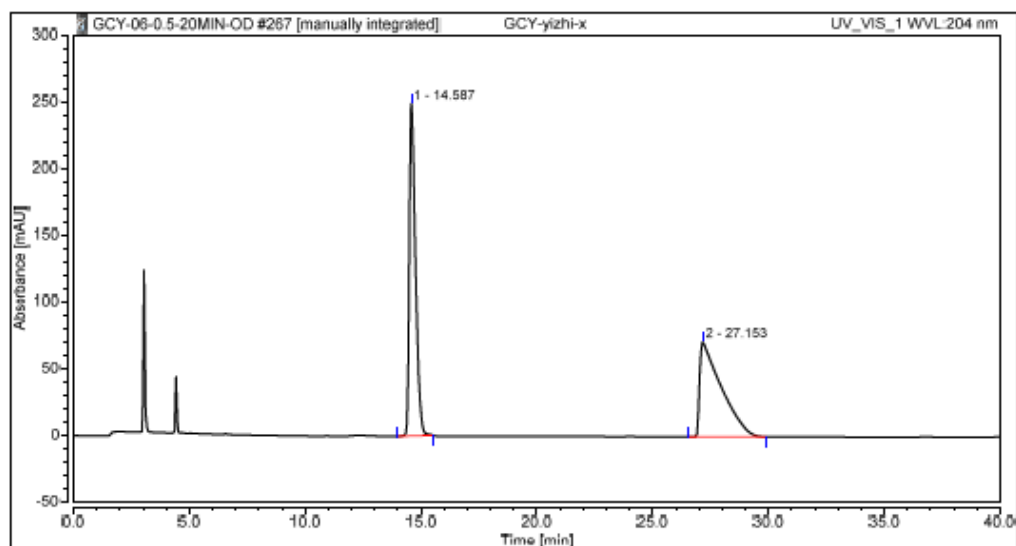


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.230	278.580	476.467	94.06	93.98	n.a.
2		24.897	17.600	30.530	5.94	6.02	n.a.
Total:			296.180	506.997	100.00	100.00	

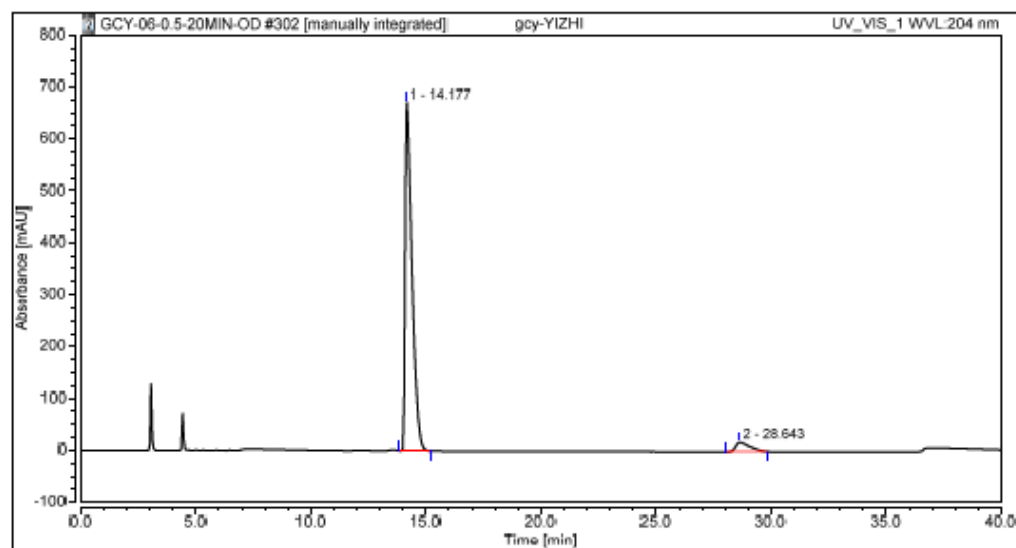
(R)-ethyl-2-phenylbutanoate (2c):



Column DAICEL Chiralcel OD-H 5 μ m, heptane/*i*-PrOH 99.8:0.2, flow rate 1.0 mL/min, 25 °C, UV 204 nm

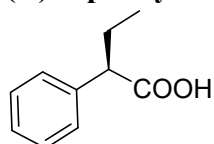


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		14.587	77.151	248.869	50.22	77.83	n.a.
2		27.153	76.475	70.894	49.78	22.17	n.a.
Total:			153.626	319.763	100.00	100.00	

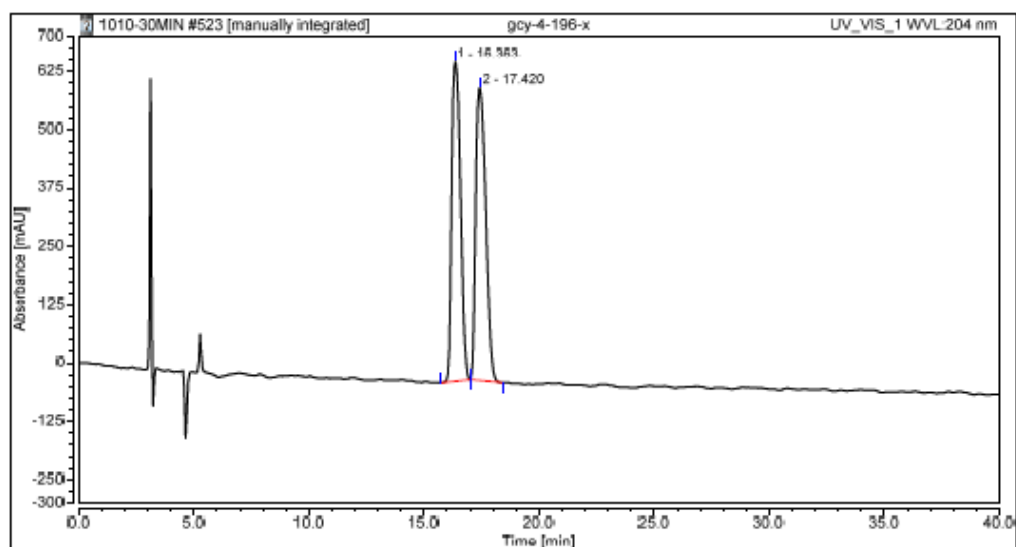


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		14.177	232.221	670.084	94.87	97.37	n.a.
2		28.643	12.550	18.087	5.13	2.63	n.a.
Total:			244.770	688.151	100.00	100.00	

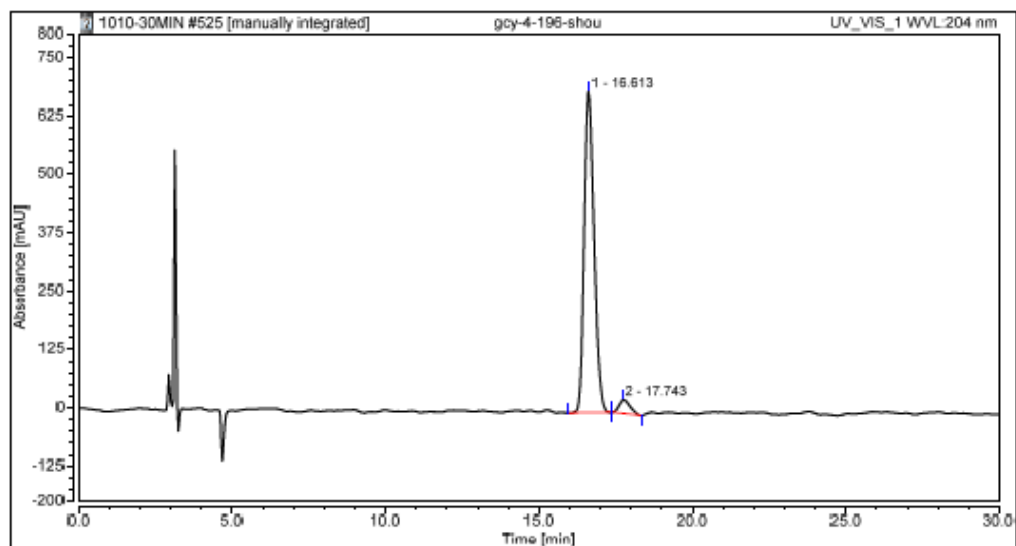
(R)-2-phenylbutanoic acid (3a):



Column DAICEL Chiralcel OJ-H 5 μ m, heptane/i-PrOH/CF₃COOH 95:4:1, flow rate 1.0 mL/min, 25 °C, UV 204 nm

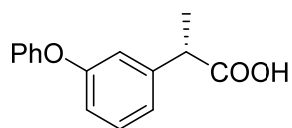


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		16.363	302.143	683.458	49.01	52.21	n.a.
2		17.420	314.412	625.622	50.99	47.79	n.a.
Total:			616.554	1309.080	100.00	100.00	

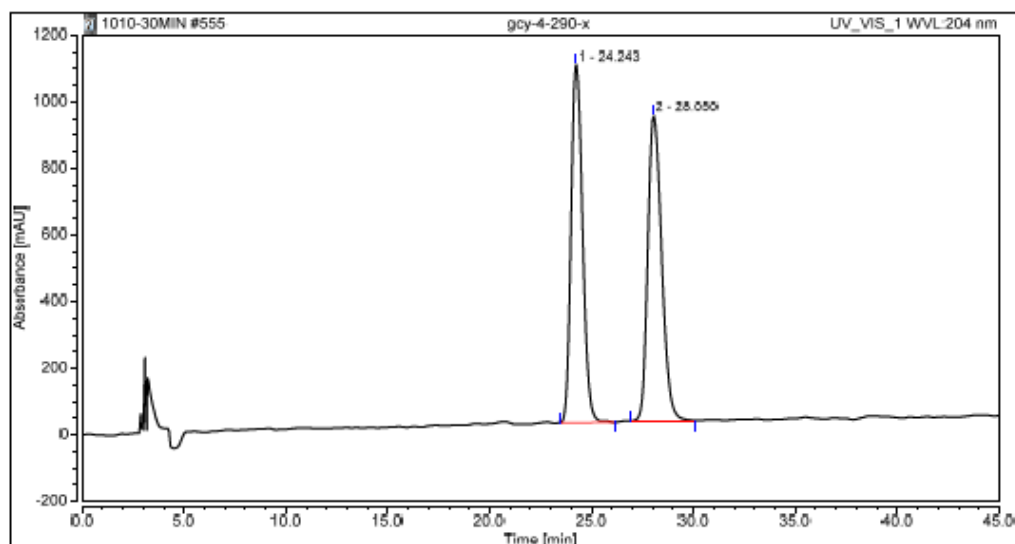


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		16.613	258.042	687.405	95.56	95.99	n.a.
2		17.743	12.002	28.702	4.44	4.01	n.a.
Total:			270.044	716.107	100.00	100.00	

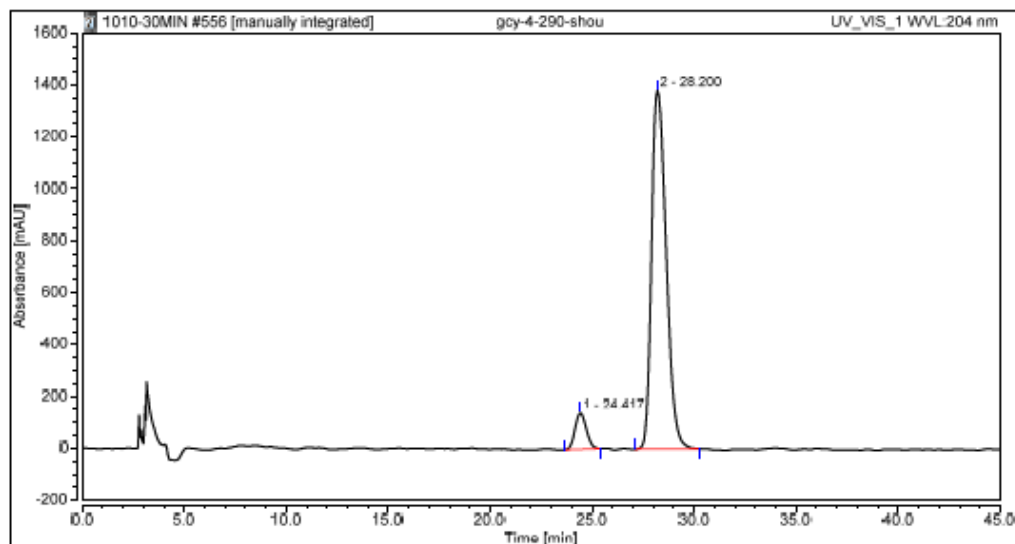
(S)-phenyl-2-(3-phenoxyphenyl)propanoate:



Column DAICEL Chiralcel AD-H 5 μ m, heptane/*i*-PrOH/CF₃COOH 90:10:0.1, flow rate 1.0 mL/min, 25 °C, UV 204 nm



No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		24.243	704.267	1074.526	49.39	53.97	n.a.
2		28.050	721.704	916.399	50.61	46.03	n.a.
Total:			1425.971	1990.925	100.00	100.00	



No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		24.417	89.259	140.355	7.22	9.22	n.a.
2		28.200	1146.745	1382.495	92.78	90.78	n.a.
Total:			1236.004	1522.850	100.00	100.00	