Supporting Information

Enantioselective Ir-Catalyzed Allylic Alkylation of Racemic Allylic Alcohols with Malonates

Chun-Yan Meng, Xiao Liang, Kun Wei,* and Yu-Rong Yang*

State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650201, China

E-mail: yangyurong@mail.kib.ac.cn

Table of Contents

General Information

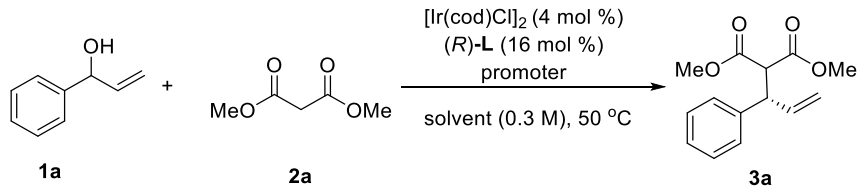
Unless otherwise stated, All solvents were purified and dried according to standard methods prior to use. The ligand (*R*)-**L** and (*rac*)-**L** were prepared according to the reported procedure.[1] Allylic alcohols were prepared by the reaction of the corresponding aldehydes with vinyl magnesium bromide. Reagents were purchased from commercial sources and were used without further purification.

Chromatographic purification of products was accomplished using forced-flow chromatography on 200-300 mesh silica gel. The TLC glass plates were performed on 0.20 mm or 1.0 mm (preparative) silica gel GF254 plates. Visualization was performed using ultraviolet light (254 nm), potassium permanganate ($KMnO_4$) in water.

^1H and ^{13}C NMR spectra were acquired on Bruker Avance III-400 spectrometer and Bruker Avance III 500MHz spectrometer (Bruker Corp., Germany), TMS was used as internal standard. Chemical shifts were given in parts per million (ppm) with reference to residual solvent signals [^1H NMR: $CDCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.0)]. Peak multiplicities were recorded as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br = broad singlet. Infrared (IR) spectra were recorded on a Bruker Tensor-27 Fourier-Transform Infrared spectrometer (Bruker Corp., Germany). High resolution mass spectral (HRMS) data were obtained at the mass spectrometry service operated at a Shimadzu UPLC-IT-TOF spectrometer (Shimadzu Corp., Japan) for electrospray ionization (ESI) and were reported as (m/z). Optical rotations were measured on Jasco P-1020 Polarimeter (Jasco Corp., Japan) and Rudolph Research Analytical Autopol VI Automatic Polarimeter (Rudolph Research Analytical., USA). Melting points were measured on a WRX-5A melting point apparatus. HPLC analysis was performed on an Agilent 1260 series system using Daicel chiralpak AD-H, Daicel chiralcel OD-H, AS-H and OJ-H with *n*-hexane and *i*-PrOH as solvents.

Optimization Studies

General Procedure for Optimization of Ir-Catalyzed Allylation of Dimethyl Malonate



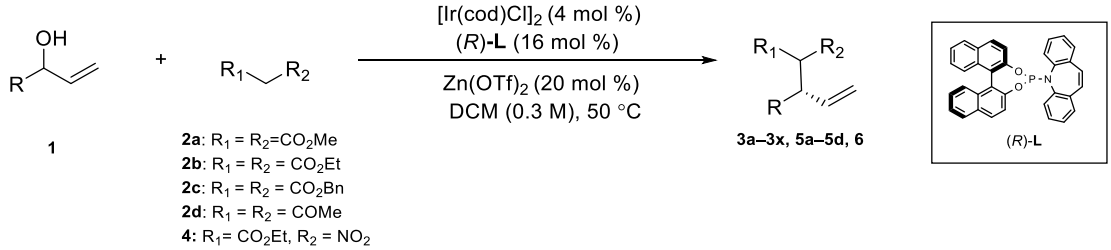
1a **2a** **3a**

$[Ir(cod)Cl]_2$ (2.7 mg, 4 μmol, 0.04 equiv) and (*R*)-**L** (8.1 mg, 16 μmol, 0.16 equiv) were added to a 4 mL nitrogen-filled pressure tube with solvent (200 μL) and stirred at room temperature for 30 min. To the resulting solution were added sequentially allylic alcohol **1a** (13.4 mg, 0.1 mmol, 1.0 equiv) in solvent (130 μL), dimethyl malonate **2a** (34.4 μL, 0.3 mmol, 3.0 equiv), and promoter (20 μmol, 0.2 equiv). The reaction was stirred at 50 °C and monitored by TLC. The crude reaction mixture was purified by flash chromatography (petroleum ether/ ethyl acetate 25/1) to give the desired product **3a**. Enantiomeric excess was determined by HPLC on chiral stationary phase (Chiralcel OJ-H).

Scale (5 mmol): $[Ir(cod)Cl]_2$ (134.2 mg, 0.2 mmol, 0.04 equiv) and (*R*)-**L** (407.2 mg, 0.8 mmol, 0.16 equiv) were added to a 100 mL nitrogen-filled pressure tube with DCM (10 mL) and stirred at room temperature for 30 min. To the resulting solution were added sequentially allylic alcohol **1a** (670 mg, 5 mmol, 1.0 equiv) in DCM (6 mL), dimethyl malonate **2a** (1.71 mL, 15 mmol, 3.0 equiv), and $Zn(OTf)_2$ (363 mg, 1 mmol, 0.2 equiv). The reaction was stirred at 50 °C and monitored by TLC. The crude reaction mixture was purified by flash chromatography (petroleum ether/ ethyl acetate 25/1) to give the desired product **3a**. Enantiomeric excess was determined by HPLC on chiral stationary phase (Chiralcel OJ-H).

Synthesis and Characterization of Products

General Procedure.



1

2a: $R_1 = R_2 = CO_2Me$
2b: $R_1 = R_2 = CO_2Et$
2c: $R_1 = R_2 = CO_2Bn$
2d: $R_1 = R_2 = COMe$
4: $R_1 = CO_2Et$, $R_2 = NO_2$

3a–3x, 5a–5d, 6

(*R*)-**L**

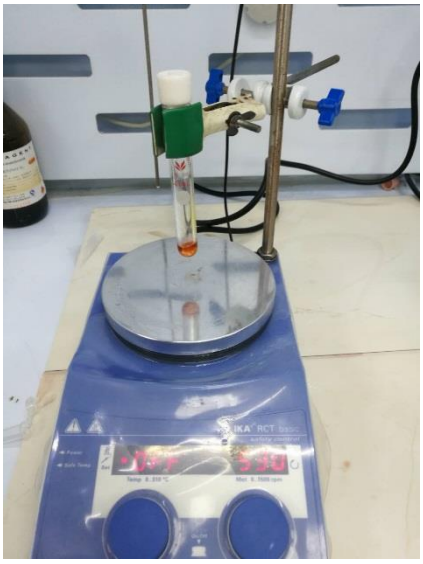
$[Ir(cod)Cl]_2$ (2.7 mg, 4 μmol, 0.04 equiv) and (*R*)-**L** (8.1 mg, 16 μmol, 0.16 equiv) were added to a 4 mL nitrogen-filled pressure tube with DCM (200 μL) and stirred at room temperature for 30 min. Then the allylic

alcohol **1** (0.1 mmol, 1.0 equiv) in DCM (130 µL), substrate **2** (or **4**) **(**0.3 mmol, 3.0 equiv), and $Zn(OTf)_2$ (7.3 mg, 20 µmol, 0.2 equiv) were sequentially added. The resulting orange mixture was stirred at 50 °C. The reaction progress was monitored by TLC. The crude reaction mixture was purified by flash chromatography to give the desired product (**3a-3x, 5a-5d, 6**).

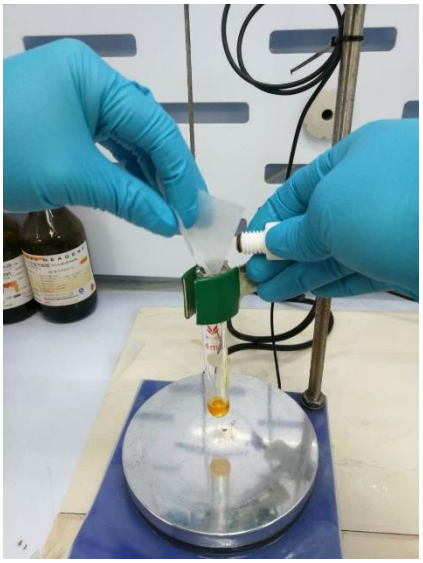
Graphical Procedure

a) Pressure Tube (4 mL)

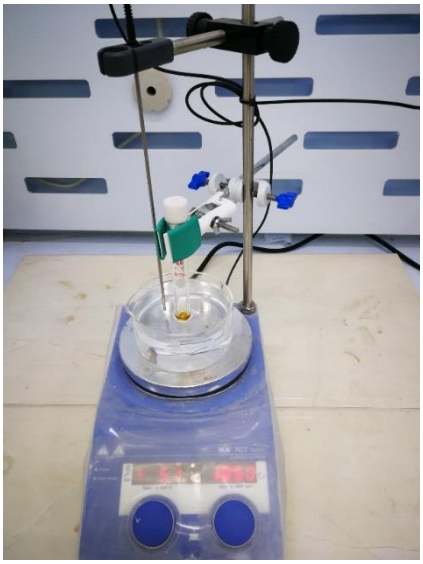
b) Backfilled with Nitrogen



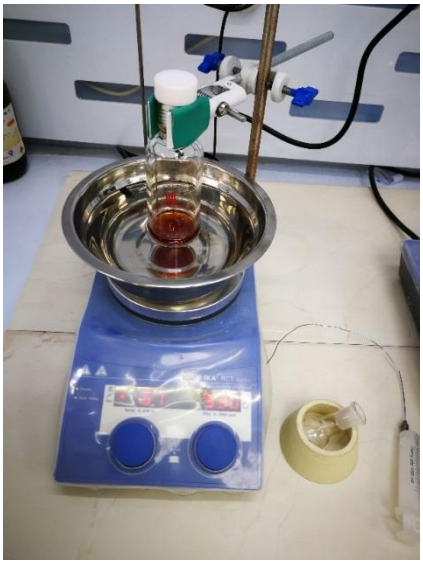
c) Addition of $[Ir(cod)Cl]_2$ and (*R*)-**L** to DCM



d) Addition of **1**, **2** (or **4**) and $Zn(OTf)_2$



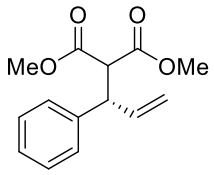
e) Stirring at 50 ^{o}C (scale: 0.1 mmol)



f) Scale: 5.0 mmol

Characterization of Products

Dimethyl (*S*)-2-(1-phenylallyl) malonate (**3a**)

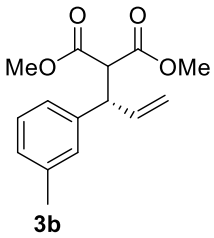


3a

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3a** as a colorless oil (22.0 mg, 90% yield). **HPLC:** 96% *ee* [(Chiralcel OJ-H) *n*-hexane/*i*-PrOH (210 nm, 25 °C) = 97/3, 0.5 mL/min, t (major) = 46.863 min, t (minor) = 55.466 min]. $[\alpha]_D^{21.5}$ = –36.5 (*c* = 0.83, $CHCl_3$). R_f = 0.51 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.22 (d, *J* = 7.2 Hz, 3H), 5.99 (ddd, *J* = 17.3, 10.2, 8.2 Hz, 1H), 5.24 – 4.99 (m, 2H), 4.11 (dd, *J* = 10.8, 8.4 Hz, 1H), 3.87 (d, *J* = 11.1 Hz, 1H), 3.74 (s, 3H), 3.49 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 167.8, 139.9, 137.8, 128.6, 127.9, 127.1, 116.6, 57.3, 52.6, 52.4, 49.7. **IR** (thin film): 3031, 2978, 1760, 1740, 1638, 1602, 1454, 1435, 1319, 1263, 1197, 1162, 1147, 1027, 926, 765, 702cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{14}H_{16}NaO_4$ $[M+Na]^+$: 271.0941. Found: 271.0942.

Characterization data of this compound were in accordance with previously reported values [2]. The absolute stereochemistry of the reported compound was determined (*R*) with specific rotation $[\alpha]_D^{22}$ = +34.1 (*c* = 1.08, $CHCl_3$) and optical purity of 98% *ee*.

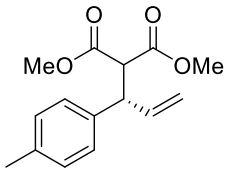
Dimethyl (*S*)-2-(1-(m-tolyl) allyl) malonate **3b**



3b

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3b** as a colorless oil (20.0 mg, 76% yield). **HPLC:** 96% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (210 nm, 25 °C) = 99/1, 1.0 mL/min, t (major) = 8.736 min, t (minor) = 8.118 min]. $[\alpha]_D^{21.3}$ = –45.7 (*c* = 0.99, $CHCl_3$). R_f = 0.48 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 9.7 Hz, 3H), 5.98 (ddd, *J* = 17.2, 10.1, 8.4 Hz, 1H), 5.17 – 5.00 (m, 2H), 4.06 (dd, *J* = 10.7, 8.6 Hz, 1H), 3.86 (d, *J* = 11.0 Hz, 1H), 3.74 (s, 3H), 3.51 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 167.9, 139.9, 138.2, 137.9, 128.6, 128.5, 127.9, 124.8, 116.5, 57.3, 52.6, 52.4, 49.7, 21.4. **IR** (thin film): 2954, 1760, 1740, 1607, 1435, 1262, 1193, 1162, 1028, 924, 786, 707cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{15}H_{18}NaO_4$ $[M+Na]^+$: 285.1097. Found: 285.1098.

Dimethyl (*S*)-2-(1-(p-tolyl) allyl) malonate **3c**

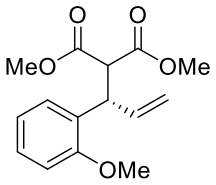


3c

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3c** as a colorless oil (16.5 mg, 63% yield). **HPLC:** 97% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 97/3, 1.0 mL/min, t (major) = 6.467 min, t (minor) = 6.064 min]; $[\alpha]_D^{21.2}$ = –43.1 (*c* = 1.07, $CHCl_3$). R_f = 0.49 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (s, 4H), 5.98 (ddd, *J* = 17.2, 10.1, 8.3 Hz, 1H), 5.17 – 5.01 (m, 2H), 4.07 (dd, *J* = 10.9, 8.4 Hz, 1H), 3.85 (d, *J* = 11.0 Hz, 1H), 3.74 (s, 3H), 3.51 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 167.9, 138.0, 136.9, 136.7, 129.3, 127.7, 116.4, 57.4, 52.6, 52.4, 49.4, 21.1. **IR** (thin film): 2954, 1758, 1740, 1639, 1513, 1513, 1435, 1318, 1260, 1159, 1147, 1026, 924, 814cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{15}H_{18}NaO_4$ $[M+Na]^+$: 285.1097. Found: 285.1094.

Characterization data of this compound were in accordance with previously reported values [3]. The absolute stereochemistry of the reported compound was determined (*S*) with specific rotation $[\alpha]_D^{20}$ = –35.8 (*c* = 1.02, $CHCl_3$) and optical purity of 94% *ee*.

Dimethyl (*S*)-2-(1-(2-methoxyphenyl) allyl) malonate **3d**

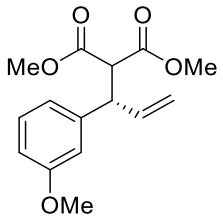


3d

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3d** as a colorless oil (18.0 mg, 65% yield). **HPLC:** 96% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 90/10, 1.0 mL/min, t (major) = 5.947 min, t (minor) = 5.49 min]; $[\alpha]_D^{21.1}$ = –53.3 (*c* = 1.01, $CHCl_3$). R_f = 0.41 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 16.9, 7.8 Hz, 2H), 6.93 – 6.80 (m, 2H), 6.21 – 6.07 (m, 1H), 5.17 – 4.98 (m, 2H), 4.40 – 4.27 (m, 1H), 4.19 (d, *J* = 10.7 Hz, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 3.48 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 168.2, 157.1, 136.9, 129.4, 128.3, 128.1, 120.7, 116.8, 111.1, 55.4, 55.3, 52.4, 52.3, 46.1. **IR** (thin film): 3003, 2954, 2840, 1759, 1739, 1638, 1600, 1586, 1494, 1463, 1436, 1323, 1291, 1247, 1195, 1163, 1127, 1052, 1028, 925, 756, 672cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{15}H_{18}NaO_5$ $[M+Na]^+$: 301.1046. Found: 301.1046.

Characterization data of this compound were in accordance with previously reported values [4]. The absolute stereochemistry of the reported compound was determined (*R*) with specific rotation $[\alpha]_D^{20}$ = +45.3 (*c* = 1.00, $CHCl_3$) and optical purity of 99% *ee*.

Dimethyl (*S*)-2-(1-(3-methoxyphenyl) allyl) malonate **3e**

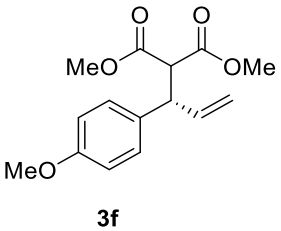


3e

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3e** as a colorless oil (22.0 mg, 79% yield). **HPLC:** 98% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 90/10, 1.0 mL/min, t (major) = 6.444 min, t (minor) = 6.036 min]; $[\alpha]_D^{21.7}$ = –42.3 (*c* = 0.99, $CHCl_3$). $\mathbf{R}_f$ = 0.40 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.7 Hz, 1H), 6.87 – 6.70 (m, 3H), 5.97 (dt, *J* = 17.7, 9.4 Hz, 1H), 5.22 – 5.01 (m, 2H), 4.17 – 4.00 (m, 1H), 3.86 (d, *J* = 11.0 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 167.8, 159.7, 141.5, 137.6, 129.6, 120.1, 116.7, 113.7, 112.4, 57.3, 55.2, 52.6, 52.5, 49.7. **IR** (thin film): 3004, 2954, 2839, 1760, 1739, 1601, 1585, 1491, 1455, 1435, 1263, 1195, 1157, 1045, 996, 926, 783, 703cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{15}H_{18}NaO_5$ $[M+Na]^+$: 301.1046. Found: 301.1049.

Characterization data of this compound were in accordance with previously reported values [4]. The absolute stereochemistry of the reported compound was determined (*R*) with specific rotation $[\alpha]_D^{20}$ = +45.6 (*c* = 1.00, $CHCl_3$) and optical purity of 96% *ee*.

Dimethyl (*S*)-2-(1-(4-methoxyphenyl) allyl) malonate **3f**



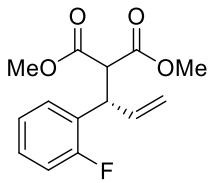
3f

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3f** as a colorless oil (13.0 mg, 46% yield). **HPLC:** 99% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 90/10, 1.0 mL/min, t (major) = 6.743 min, t (minor) = 6.07 min]; $[\alpha]_D^{22.6}$ = –29.6 (*c* = 0.81, $CHCl_3$). $\mathbf{R}_f$ = 0.39 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400

MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.97 (ddd, *J* = 17.9, 10.2, 8.1 Hz, 1H), 5.15 – 5.01 (m, 2H), 4.06 (dd, *J* = 10.7, 8.3 Hz, 1H), 3.81 (d, *J* = 11.1 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 167.9, 158.6, 138.0, 131.9, 128.9, 116.2, 114.0, 57.5, 55.2, 52.6, 52.4, 48.9. **IR** (thin film): 3004, 2954, 2839, 1760, 1739, 1638, 1611, 1514, 1457, 1435, 1305, 1250, 1179, 1163, 1034, 993, 925, 830, 785, 662, 542cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{15}H_{18}NaO_5$ $[M+Na]^+$: 301.1046. Found: 301.1044.

Characterization data of this compound were in accordance with previously reported values [4]. The absolute stereochemistry of the reported compound was determined (*R*) with specific rotation $[\alpha]_D^{20}$ = +23.6 (*c* = 1.00, $CHCl_3$) and optical purity of 95% *ee*.

Dimethyl (*S*)-2-(1-(2-fluorophenyl) allyl) malonate **3g**

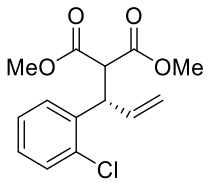


3g

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3g** as a colorless oil (23.4 mg, 88% yield). **HPLC:** 93% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (210 nm, 25 °C) = 90/10, 1.0 mL/min, t (major) = 5.145 min, t (minor) = 4.841 min]; $[\alpha]_D^{21.4}$ = –52.2 (*c* = 0.72, $CHCl_3$). R_f = 0.47 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (q, *J* = 7.2 Hz, 2H), 7.12 – 6.98 (m, 2H), 6.03 (dt, *J* = 17.4, 9.2 Hz, 1H), 5.21 – 5.07 (m, 2H), 4.39 – 4.27 (m, 1H), 4.02 (d, *J* = 11.1 Hz, 1H), 3.74 (s, 3H), 3.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 167.8, 161.9, 159.4, 136.0, 129.8, 129.8, 128.9, 128.8, 127.0, 126.9, 124.3, 124.3, 117.6, 116.0, 115.8, 55.8, 55.8, 52.6, 52.5, 44.8. **IR** (thin film): 2955, 1759, 1741, 1493, 1454, 1435, 1320, 1265, 1236, 1195, 1149, 1027, 993, 928, 807, 760, 670cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{14}H_{15}NaO_4F$ $[M+Na]^+$: 289.0847. Found: 289.0845.

Characterization data of this compound were in accordance with previously reported values [4]. The absolute stereochemistry of the reported compound was determined (*R*) with specific rotation $[\alpha]_D^{20}$ = +62.7 (*c* = 1.00, $CHCl_3$) and optical purity of 98% *ee*.

Dimethyl (*S*)-2-(1-(2-chlorophenyl) allyl) malonate **3h**

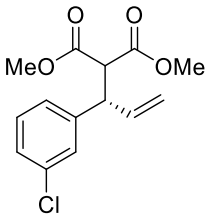


3h

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3h** as a colorless oil (20.0 mg, 71% yield). **HPLC:** 90% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (210 nm, 25 °C) = 90/10, 1.0 mL/min, t (major) = 5.818 min, t (minor) = 5.228 min]; $[\alpha]_D^{21.3}$ = –52.2 (*c* = 0.89, $CHCl_3$). R_f = 0.48 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.12 (m, 3H), 5.98 (ddd, *J* = 17.9, 10.1, 8.2 Hz, 1H), 5.21 – 5.05 (m, 2H), 4.72 – 4.63 (m, 1H), 4.03 (d, *J* = 10.7 Hz, 1H), 3.74 (s, 3H), 3.54 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 167.6, 137.5, 136.1, 134.0, 130.1, 128.6, 128.2, 127.0, 117.7, 56.0, 52.6, 52.6, 45.7. **IR** (thin film): 3006, 2954, 2845, 1759, 1740, 1638, 1476, 1435, 1351, 1314, 1263, 1224, 1164, 1036, 992, 928, 758, 732cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{14}H_{15}NaO_4Cl$ $[M+Na]^+$: 305.0551. Found: 305.0546.

Characterization data of this compound were in accordance with previously reported values [4]. The absolute stereochemistry of the reported compound was determined (*R*) with specific rotation $[\alpha]_D^{20}$ = +52.5 (*c* = 1.00, $CHCl_3$) and optical purity of 97% *ee*.

Dimethyl (*S*)-2-(1-(3-chlorophenyl) allyl) malonate **3i**

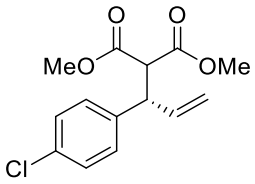


3i

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3i** as a colorless oil (23.0 mg, 80% yield). **HPLC:** 98% *ee* [(Chiralcel OJ-H) *n*-hexane/*i*-PrOH (210 nm, 25 °C) = 99/1, 1.0 mL/min, t (major) = 22.816 min, t (minor) = 19.485 min]; $[\alpha]_D^{23.0}$ = –34.8 (*c* = 1.17, $CHCl_3$). R_f = 0.38 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 3H), 7.11 (d, *J* = 7.0 Hz, 1H), 5.95 (ddd, *J* = 17.2, 10.2, 8.2 Hz, 1H), 5.19 – 5.06 (m, 2H), 4.08 (dd, *J* = 10.7, 8.4 Hz, 1H), 3.83 (d, *J* = 11.0 Hz, 1H), 3.74 (s, 3H), 3.53 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 167.6, 142.1, 137.0, 134.4, 129.9, 128.1, 127.4, 126.1, 117.3, 57.1, 52.7, 52.6, 49.3. **IR** (thin film): 2956, 2874, 1760, 1739, 1638, 1574, 1435, 1262, 1197, 1165, 1027, 997, 929, 788, 719, 699cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{14}H_{15}NaO_4Cl$ $[M+Na]^+$: 305.0551. Found: 305.0550.

Characterization data of this compound were in accordance with previously reported values [5]. The absolute stereochemistry of the reported compound was determined (*S*) with specific rotation $[\alpha]_D^{29.3}$ = –21.2 (*c* = 0.41, $CHCl_3$) and optical purity of 99% *ee*.

Dimethyl (*S*)-2-(1-(4-chlorophenyl) allyl) malonate **3j**

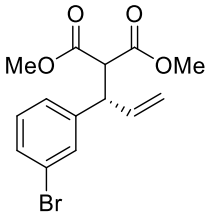


3j

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3j** as a colorless oil (22.0 mg, 78% yield). **HPLC:** 98% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 97/3, 1.0 mL/min, t (major) = 7.177 min, t (minor) = 6.767 min]; $[\alpha]_D^{22.7}$ = –53.3 (*c* = 0.83, $CHCl_3$). $\mathbf{R}_f$ = 0.42 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.02 – 5.89 (m, 1H), 5.18 – 5.04 (m, 2H), 4.14 – 4.04 (m, 1H), 3.82 (d, *J* = 11.0 Hz, 1H), 3.74 (s, 3H), 3.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 167.7, 138.5, 137.3, 133.0, 129.3, 128.8, 117.1, 57.2, 52.7, 52.5, 49.0. **IR** (thin film): 2954, 2846, 1759, 1739, 1639, 1493, 1435, 1409, 1314, 1262, 1164, 1148, 1092, 1015, 992, 927, 824, 652, 599, 525cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{14}H_{15}NaO_4Cl$ $[M+Na]^+$: 305.0551. Found: 305.0554.

Characterization data of this compound were in accordance with previously reported values [2]. The absolute stereochemistry of the reported compound was determined (*R*) with specific rotation $[\alpha]_D^{22}$ = +40.9 (*c* = 1.00, $CHCl_3$) and optical purity of 97% *ee*.

Dimethyl (*S*)-2-(1-(3-bromophenyl) allyl) malonate **3k**

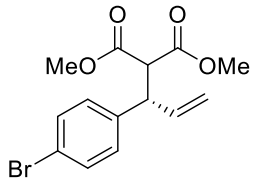


3k

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3k** as a colorless oil (26.0 mg, 79% yield). **HPLC:** >99% *ee* [(Chiralcel OJ-H) *n*-hexane/*i*-PrOH (210 nm, 25 °C) = 90/10, 1.0 mL/min, t (major) = 10.212 min]; $[\alpha]_D^{21.4}$ = –36.8 (*c* = 1.35, $CHCl_3$). $\mathbf{R}_f$ = 0.41 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 2H), 7.21 – 7.10 (m, 2H), 5.93 (dd, *J* = 8.5, 1.6 Hz, 1H), 5.19 – 5.06 (m, 2H),

4.07 (dd, *J* = 10.7, 8.4 Hz, 1H), 3.83 (d, *J* = 10.9 Hz, 1H), 3.74 (s, 3H), 3.54 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 167.6, 142.3, 137.0, 131.0, 130.3, 130.2, 126.6, 122.6, 117.3, 57.1, 52.7, 52.6, 49.2. **IR** (thin film): 2953, 1759, 1739, 1568, 1475, 1434, 1344, 1262, 1237, 1164, 1075, 1026, 954, 785, 699cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{14}H_{15}NaO_4Br$ $[M+Na]^+$: 349.0046 . Found: 349.0045.

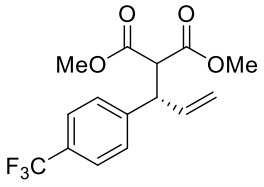
Dimethyl (*S*)-2-(1-(4-bromophenyl) allyl) malonate **3l**



3l

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3l** as a colorless oil (24.0 mg, 73% yield). **HPLC:** 96% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 90/10, 1.0 mL/min, t (major) = 5.326 min, t (minor) = 5.112 min]; **[α]**$_D^{23.1}$ = –46.0 (*c* = 1.28, $CHCl_3$). **R_f** = 0.39 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 5.94 (ddd, *J* = 17.2, 10.3, 8.2 Hz, 1H), 5.16 – 5.05 (m, 2H), 4.07 (dd, *J* = 10.7, 8.3 Hz, 1H), 3.82 (d, *J* = 11.0 Hz, 1H), 3.74 (s, 3H), 3.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 167.6, 139.0, 137.2, 131.8, 129.7, 121.0, 117.1, 57.1, 52.7, 52.6, 49.0. **IR** (thin film): 2953, 2848, 1759, 1740, 1639, 1489, 1435, 1405, 1313, 1263, 1198, 1155, 1074, 1011, 928, 820, 721, 545cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{14}H_{15}NaO_4Br$ $[M+Na]^+$: 349.0046. Found: 349.0048.

Dimethyl (*S*)-2-(1-(4-(trifluoromethyl) phenyl) allyl) malonate **3m**



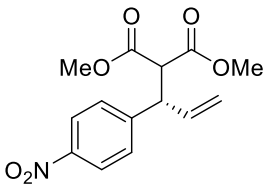
3m

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3m** as a colorless oil (25.0 mg, 79% yield). **HPLC:** 98% *ee* [(Chiralcel OJ-H) *n*-hexane/*i*-PrOH (210 nm, 25 °C) = 99.2/0.8, 1.0 mL/min, t (major) = 15.228 min, t (minor) = 14.231 min]; **[α]**$_D^{23.1}$ = –52.7 (*c* = 1.01, $CHCl_3$). **R_f** = 0.43 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.03 – 5.90 (m, 1H), 5.18 – 5.09 (m, 2H), 4.24 – 4.14 (m, 1H), 3.88 (d, *J* = 11.0 Hz, 1H), 3.75 (s, 3H), 3.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 167.5, 144.1, 136.9, 129.6, 129.3, 128.3, 125.7, 125.6, 125.6, 125.6, 125.4, 122.7, 117.6, 57.0, 52.7, 52.6, 49.4. **IR** (thin film): 3008, 2957, 2847, 1760, 1741, 1640, 1618, 1436, 1418, 1328, 1264, 1196, 1166, 1125, 1069, 1019, 992, 929, 835, 680, 604cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{15}H_{15}NaO_4F_3$ $[M+Na]^+$:

339.0815. Found: 339.0814.

Characterization data of this compound were in accordance with previously reported values [2]. The absolute stereochemistry of the reported compound was determined (*R*) with specific rotation $[\alpha]_D^{22}$ = +40.1 (*c* = 0.81, $CHCl_3$) and optical purity of 94% *ee*.

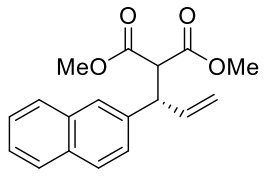
Dimethyl (*S*)-2-(1-(4-nitrophenyl) allyl) malonate **3n**



3n

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 10/1) to afford **3n** as a colorless oil (24.0 mg, 81% yield). m.p. 49 – 51 °C, **HPLC:** 92% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 90/10, 1.0 mL/min, t (major) = 11.305 min, t (minor) = 10.041 min]; $[\alpha]_D^{23.2}$ = –63.7 (*c* = 0.82, $CHCl_3$). R_f = 0.40 (petroleum ether/ ethyl acetate 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 5.95 (ddd, *J* = 17.7, 9.8, 8.3 Hz, 1H), 5.22 – 5.10 (m, 2H), 4.29 – 4.18 (m, 1H), 3.89 (d, *J* = 10.9 Hz, 1H), 3.75 (s, 3H), 3.53 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 167.4, 147.7, 147.0, 136.3, 128.9, 123.9, 118.2, 56.8, 52.8, 52.7, 49.3. **IR** (thin film): 2956, 1757, 1739, 1606, 1523, 1436, 1349, 1265, 1220, 1151, 1025, 931, 855, 705cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{14}H_{15}NNaO_6$ $[M+Na]^+$: 316.0792 . Found: 316.0795.

Dimethyl (*S*)-2-(1-(naphthalen-2-yl) allyl) malonate **3o**



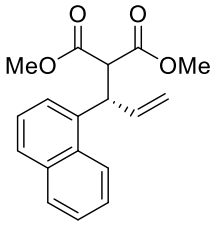
3o

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3o** as a colorless oil (25.0mg, 83% yield). **HPLC:** 97% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 90/10, 1.0 mL/min, t (major) = 6.074 min, t (minor) = 5.755 min]; $[\alpha]_D^{22.5}$ = –52.2 (*c* = 1.10, $CHCl_3$). R_f = 0.51 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 3H), 7.69 (s, 1H), 7.52 – 7.41 (m, 2H), 7.41 – 7.32 (m, 1H), 6.08 (ddd, *J* = 17.9, 10.1, 8.2 Hz, 1H), 5.24 – 5.07 (m, 2H), 4.36 – 4.24 (m, 1H), 4.01 (d, *J* = 11.0 Hz, 1H), 3.77 (s, 3H), 3.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 167.8, 137.7, 137.4, 133.5, 132.6, 128.4, 127.8, 127.6, 126.7, 126.1, 126.1, 125.8, 116.9, 57.3, 52.7, 52.5, 49.8. **IR** (thin film): 3055, 3006, 2953, 2844, 1759, 1738, 1637,

1600, 1508, 1434, 1317, 1262, 1193, 1154, 1025, 992, 926, 821, 750, 679, 479cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{18}H_{18}NaO_4$ $[M+Na]^+$: 321.1097. Found: 321.1096.

Characterization data of this compound were in accordance with previously reported values [2]. The absolute stereochemistry of the reported compound was determined (*R*) with specific rotation $\mathbf{[\alpha]}_D^{22}$ = +39.3 (*c* = 0.93, $CHCl_3$) and optical purity of 96% *ee*.

Dimethyl (*S*)-2-(1-(naphthalen-1-yl) allyl) malonate **3p**

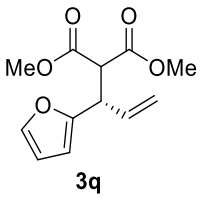


3p

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3p** as a colorless oil (22.6 mg, 76% yield). **HPLC:** 98% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (254 nm, 25 °C) = 90/10, 1.0 mL/min, t (major) = 6.822 min, t (minor) = 6.19 min]; $\mathbf{[\alpha]}_D^{22.7}$ = –48.1 (*c* = 1.03, $CHCl_3$). $\mathbf{R}_f$ = 0.50 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.46 – 7.35 (m, 2H), 6.08 (ddd, *J* = 17.6, 10.1, 8.0 Hz, 1H), 5.23 – 5.07 (m, 2H), 5.04 (dd, *J* = 10.5, 8.3 Hz, 1H), 4.17 (d, *J* = 10.8 Hz, 1H), 3.79 (s, 3H), 3.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 167.8, 137.6, 136.1, 134.1, 131.4, 128.9, 127.8, 126.2, 125.7, 125.3, 124.3, 123.3, 117.1, 57.0, 52.7, 52.5, 44.1. **IR** (thin film): 3007, 2953, 2844, 1759, 1739, 1637, 1598, 1511, 1435, 1287, 1260, 1195, 1163, 1027, 991, 926, 800, 780, 679cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{18}H_{18}NaO_4$ $[M+Na]^+$: 321.1097. Found: 321.1098.

Characterization data of this compound were in accordance with previously reported values [5]. The absolute stereochemistry of the reported compound was determined (*S*) with specific rotation $\mathbf{[\alpha]}_D^{28.3}$ = –35.8 (*c* = 0.80, $CHCl_3$) and optical purity of 96% *ee*.

Dimethyl (*S*)-2-(1-(furan-2-yl) allyl) malonate **3q**



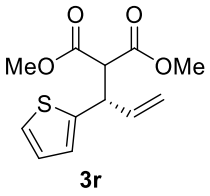
3q

The compound was prepared according to the general procedure. The crude reaction mixture was purified on

silica gel (petroleum ether/ ethyl acetate 15/1) to afford **3q** as a colorless oil (14.0 mg, 59% yield). **HPLC:** 98% *ee* [(Chiralcel OJ-H) *n*-hexane/*i*-PrOH (220 nm, 25 °C) = 90/10, 1.0 mL/min, t (major) = 11.09 min, t (minor) = 11.604 min]; $[\alpha]_D^{21.3}$ = –57.2 (*c* = 0.50, $CHCl_3$). R_f = 0.35 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.28 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.10 (d, *J* = 3.2 Hz, 1H), 5.96 (ddd, *J* = 17.1, 10.1, 8.5 Hz, 1H), 5.27 – 5.05 (m, 2H), 4.22 (t, *J* = 9.2 Hz, 1H), 3.88 (d, *J* = 10.0 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.9, 167.8, 153.0, 141.9, 134.7, 118.2, 110.3, 106.5, 55.5, 52.7, 52.6, 43.3. **IR** (thin film): 3004, 2955, 2848, 1759, 1741, 1640, 1591, 1505, 1436, 1258, 1198, 1164, 1148, 1073, 1013, 994, 926, 885, 809, 739, 599cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{12}H_{14}NaO_5$ $[M+Na]^+$: 261.0733. Found: 261.0733.

Characterization data of this compound were in accordance with previously reported values [6]. The absolute stereochemistry of the reported compound was determined (*S*) with specific rotation $[\alpha]_D^{23}$ = –39.7 (*c* = 0.17, $CHCl_3$) and optical purity of 88% *ee*.

Dimethyl (*S*)-2-(1-(thiophen-2-yl) allyl) malonate **3r**

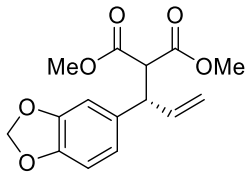


3r

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 20/1) to afford **3r** as a colorless oil (14.0 mg, 54% yield). **HPLC:** >99% *ee* [(Chiralcel OJ-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 98/2, 1.0 mL/min, t (major) = 21.642 min]; $[\alpha]_D^{23.2}$ = –27.7 (*c* = 0.69, $CHCl_3$). R_f = 0.45 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 5.0 Hz, 1H), 6.97 – 6.90 (m, 1H), 6.88 (d, *J* = 3.2 Hz, 1H), 6.02 (ddd, *J* = 17.1, 10.0, 8.5 Hz, 1H), 5.24 – 5.10 (m, 2H), 4.42 (t, *J* = 9.3 Hz, 1H), 3.84 (d, *J* = 10.2 Hz, 1H), 3.73 (s, 3H), 3.61 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 167.7, 143.1, 137.1, 126.8, 124.9, 124.4, 117.2, 58.3, 52.6, 44.8. **IR** (thin film): 3083, 2954, 2846, 1759, 1740, 1640, 1555, 1435, 1258, 1194, 1169, 1149, 1091, 1025, 991, 930, 855, 703, 676, 581, 544cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{12}H_{14}NaO_4S$ $[M+Na]^+$: 277.0505. Found: 277.0503.

Characterization data of this compound were in accordance with previously reported values [4]. The absolute stereochemistry of the reported compound was determined (*R*) with specific rotation $[\alpha]_D^{20}$ = +34.2 (*c* = 1.00, $CHCl_3$) and optical purity of 93% *ee*.

Dimethyl (*S*)-2-(1-(benzo[d] [1, 3] dioxol-5-yl) allyl) malonate **3s**

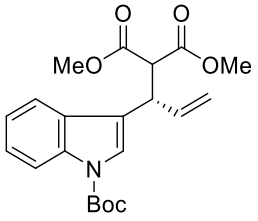


3s

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 20/1) to afford **3s** as a colorless oil (21.3 mg, 73% yield). **HPLC:** 98% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (210 nm, 25 °C) = 90/10, 1.0 mL/min, t (major) = 8.481 min, t (minor) = 7.059 min]; $[\alpha]_D^{22.5}$ = –27.5 (*c* = 0.91, $CHCl_3$). R_f = 0.42 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.76 – 6.64 (m, 3H), 5.93 (d, *J* = 4.1 Hz, 3H), 5.16 – 5.01 (m, 2H), 4.03 (dd, *J* = 10.8, 8.3 Hz, 1H), 3.79 (d, *J* = 11.1 Hz, 1H), 3.73 (s, 3H), 3.54 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 167.8, 147.8, 146.6, 137.8, 133.7, 121.1, 116.5, 108.4, 108.3, 101.0, 57.4, 52.6, 52.5, 49.3. **IR** (thin film): 3003, 2955, 2901, 2780, 1759, 1738, 1505, 1490, 1441, 1341, 1248, 1164, 1099, 1039, 994, 934, 863, 810, 682cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{15}H_{16}NaO_6$ $[M+Na]^+$: 315.0839. Found: 315.0839.

Characterization data of this compound were in accordance with previously reported values [2]. The absolute stereochemistry of the reported compound was determined (*R*) with specific rotation $[\alpha]_D^{22}$ = +22.0 (*c* = 1.13, $CHCl_3$) and optical purity of 97% *ee*.

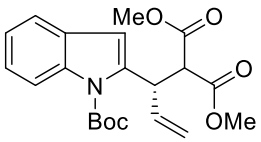
Dimethyl (*S*)-2-(1-(1-(tert-butoxycarbonyl)-1H-indol-3-yl) allyl) malonate **3t**



3t

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 20/1) to afford **3t** as a colorless oil (15.5 mg, 40% yield). **HPLC:** >99% *ee* [(Chiralcel OD-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 99.2/0.8, 0.5 mL/min, t (major) = 24.422 min]; $[\alpha]_D^{24.9}$ = –44.5 (*c* = 1.22, $CHCl_3$). R_f = 0.42 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz,$CDCl_3$) δ 8.07 – 7.80 (m, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.17 – 6.99 (m, 3H), 5.90 – 5.77 (m, 1H), 5.09 – 4.88 (m, 2H), 4.25 – 4.15 (m, 1H), 3.80 (d, *J* = 10.5 Hz, 1H), 3.57 (s, 3H), 3.37 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 168.0, 149.6, 136.5, 129.3, 124.6, 122.9, 122.5, 119.5, 119.4, 117.4, 115.3, 83.8, 56.4, 52.6, 40.9, 28.2. **IR** (thin film): 2979, 2953, 2932, 1737, 1608, 1454, 1371, 1309, 1257, 1158, 1087, 1022, 766, 747cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{21}H_{25}NNaO_6$ $[M+Na]^+$: 410.1574 . Found: 410.1572.

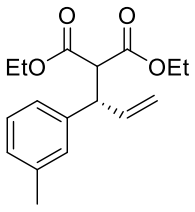
Dimethyl (*S*)-2-(1-(1-(tert-butoxycarbonyl) -1H-indol-2-yl) allyl) malonate **3u**



3u

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to afford **3u** as a colorless oil (29.5 mg, 76% yield). **HPLC:** 99% *ee* [(Chiralcel AD-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 97/3, 1.0 mL/min, t (major) = 7.399 min, t (minor) = 7.835 min]; $[\alpha]_D^{22.5}$ = –45.4 (*c* = 1.06, $CHCl_3$). $\mathbf{R}_f$ = 0.51 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.12 (m, 2H), 6.46 (s, 1H), 6.06 (ddd, *J* = 17.5, 10.2, 7.7 Hz, 1H), 5.28 – 5.16 (m, 1H), 5.15 – 5.02 (m, 2H), 4.02 (d, *J* = 10.4 Hz, 1H), 3.72 (s, 3H), 3.62 (s, 3H), 1.70 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 168.0, 150.2, 139.9, 136.7, 136.6, 128.7, 124.0, 122.7, 120.3, 117.7, 115.6, 107.6, 84.4, 56.6, 52.8, 52.6, 41.9, 28.2. **IR** (thin film): 2980, 2954, 1759, 1738, 1454, 1327, 1255, 1158, 1118, 1084, 929, 749cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{21}H_{25}NNaO_6$ $[M+Na]^+$: 410.1574 . Found: 410.1572.

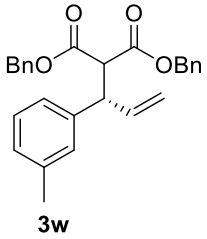
Diethyl (*S*)-2-(1-(m-tolyl) allyl) malonate **3v**



3v

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 15/1) to afford **3v** as a colorless oil (25.3 mg, 87% yield). **HPLC:** 95% *ee* [(Chiralcel AD-H) *n*-hexane/*i*-PrOH (210 nm, 25 °C) = 95/5, 1.0 mL/min, t (major) = 6.787 min, t (minor) = 7.214 min]; $[\alpha]_D^{18.8}$ = –41.1 (*c* = 0.35, $CHCl_3$). $\mathbf{R}_f$ = 0.42 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 9.7 Hz, 3H), 5.98 (ddd, *J* = 17.5, 10.1, 8.3 Hz, 1H), 5.20 – 4.99 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.06 (dd, *J* = 10.8, 8.5 Hz, 1H), 3.99 – 3.90 (m, 2H), 3.82 (d, *J* = 11.1 Hz, 1H), 2.31 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 167.5, 140.0, 138.1, 138.1, 128.8, 128.4, 127.8, 124.9, 116.3, 61.5, 61.3, 57.4, 49.7, 21.4, 14.1, 13.8. **IR** (KBr): 2982, 2937, 2908, 2873, 1758, 1735, 1639, 1607, 1465, 1446, 1391, 1369, 1304, 1258, 1179, 1156, 1035, 923, 859, 786, 707, 443cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{17}H_{22}NaO_4$ $[M+Na]^+$: 313.1410. Found: 313.1413.

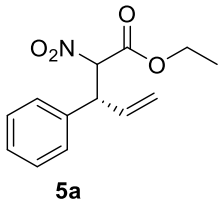
Dibenzyl (*S*)-2-(1-(m-tolyl) allyl) malonate **3w**



3w

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 15/1) to afford **3w** as a colorless oil (34.3 mg, 83% yield). **HPLC:** 97% *ee* [(Chiralcel AD-H) *n*-hexane/*i*-PrOH (210 nm, 25 °C) = 85/15, 1.0 mL/min, t (major) = 8.843 min, t (minor) = 10.588 min]; $[\alpha]_D^{19.5}$ = –32.1 (*c* = 0.26, $CHCl_3$). $\mathbf{R_f}$ = 0.42 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.20 (m, 8H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.01 (q, *J* = 7.6, 6.3 Hz, 5H), 5.96 (ddd, *J* = 17.3, 10.1, 8.3 Hz, 1H), 5.15 (s, 2H), 5.11 – 4.95 (m, 2H), 4.90 (s, 2H), 4.10 (dd, *J* = 10.7, 8.4 Hz, 1H), 3.96 (d, *J* = 11.1 Hz, 1H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 167.3, 139.8, 138.2, 137.8, 135.3, 135.1, 128.7, 128.6, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 128.0, 124.9, 116.6, 67.3, 67.1, 57.4, 49.8, 21.4. **IR** (KBr): 3065, 3034, 2953, 1758, 1737, 1638, 1607, 1589, 1498, 1456, 1378, 1302, 1265, 1215, 1152, 1002, 992, 924, 784, 751, 698, 582cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{27}H_{26}NaO_4$ $[M+Na]^+$: 437.1723. Found: 437.1721.

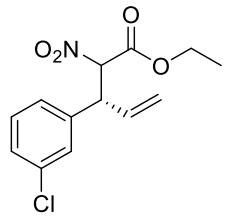
Ethyl (3*R*)-2-nitro-3-phenylpent-4-enoate **5a**



5a

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to give the crude product, purification of the crude product was performed by preparative TLC (petroleum ether/ ethyl acetate 8/1) to afford **5a** as a colorless oil (18.0 mg, 73% yield). **HPLC:** >99% *ee* [(Chiralcel OJ-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 91/9, 0.5 mL/min, t (major) = 31.556 min,]; $[\alpha]_D^{21.3}$ = –54.2 (*c* = 0.71, $CHCl_3$). $\mathbf{R_f}$ = 0.64 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.31 – 7.22 (m, 3H), 6.06 (ddd, *J* = 17.0, 10.2, 8.3 Hz, 1H), 5.45 (d, *J* = 10.5 Hz, 1H), 5.29 – 5.18 (m, 2H), 4.45 – 4.22 (m, 2H), 4.09 – 3.96 (m, 1H), 1.01 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.2, 162.9, 137.2, 136.3, 134.6, 134.1, 129.1, 129.0, 128.3, 128.1, 128.0, 127.8, 119.2, 119.0, 91.5, 91.2, 63.1, 62.9, 51.1, 50.9, 13.9, 13.6. **IR** (thin film): 2985, 1752, 1640, 1563, 1455, 1393, 1373, 1312, 1196, 1182, 1020, 764, 702, 669cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{13}H_{15}NNaO_4$ $[M+Na]^+$: 272.0893 .Found: 272.0891.

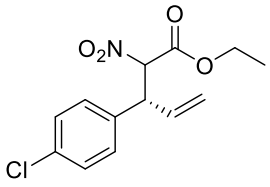
Ethyl (3*R*)-3-(3-chlorophenyl)-2-nitropent-4-enoate **5b**



5b

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to give the crude product, purification of the crude product was performed by preparative TLC (petroleum ether/ ethyl acetate 8/1) to afford **5b** as a colorless oil (14.4 mg, 51% yield). **HPLC:** >99% *ee* [(Chiralcel AS-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 99.3/0.7, 1.0 mL/min, t (major) = 11.764 min]; $[\alpha]_D^{22.4}$ = –48.3 (*c* = 0.89, $CHCl_3$). R_f = 0.59 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 3H), 7.19 – 7.10 (m, 1H), 6.08 – 5.97 (m, 1H), 5.42 (d, *J* = 10.5 Hz, 1H), 5.24 (ddt, *J* = 11.5, 9.2, 3.8 Hz, 2H), 4.41 – 4.25 (m, 2H), 4.07 (tq, *J* = 7.1, 3.9 Hz, 1H), 1.07 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 162.6, 139.2, 138.4, 134.9, 134.8, 133.9, 133.4, 130.3, 130.3, 128.5, 128.3, 128.1, 126.5, 126.0, 119.8, 119.7, 91.1 , 90.8, 63.3, 63.1, 50.6, 50.4, 13.9, 13.6. **IR** (thin film): 2986, 1752, 1596, 1564, 1477, 1434, 1373, 1360, 1307, 1259, 1185, 1020, 935, 788, 697cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{13}H_{13}NO_4Cl$ $[M–H]^-$: 282.0539. Found: 282.0539.

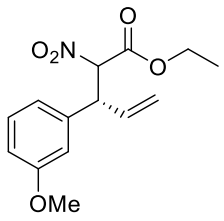
Ethyl (3*R*)-3-(4-chlorophenyl)-2-nitropent-4-enoate **5c**



5c

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to give the crude product, purification of the crude product was performed by preparative TLC (petroleum ether/ ethyl acetate 8/1) to afford **5c** as a colorless oil (20.0 mg, 70% yield). **HPLC:** >99% *ee* [(Chiralcel OJ-H) *n*-hexane/*i*-PrOH (230 nm, 25 °C) = 80/20, 1.0 mL/min, t (major) = 9.149 min]; $[\alpha]_D^{27.4}$ = –52.7 (*c* = 1.34, $CHCl_3$). R_f = 0.51 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.5, 2.9 Hz, 2H), 7.19 (d, *J* = 8.5, 3.1 Hz, 2H), 6.06 – 5.97 (m, 1H), 5.41 (d, *J* = 10.5 Hz, 1H), 5.28 – 5.17 (m, 2H), 4.42 – 4.24 (m, 2H), 4.06 (dd, *J* = 7.1, 6.1 Hz, 1H), 1.07 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 162.7, 135.6, 134.9, 134.1, 134.0, 134.0, 133.6, 129.7, 129.3, 129.2, 119.6, 119.4, 91.2, 91.0, 63.3, 63.1, 50.3, 50.1, 13.9, 13.6. **IR** (thin film): 2986, 1752, 1686, 1493, 1373, 1313, 1259, 1182, 1094, 1016, 935, 824cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{13}H_{14}NNaO_4Cl$ $[M+Na]^+$: 306.0504. Found: 306.0504.

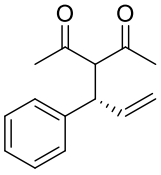
Ethyl (3*R*)-3-(3-methoxyphenyl)-2-nitropent-4-enoate **5d**



5d

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 25/1) to give the crude product, purification of the crude product was performed by preparative TLC (petroleum ether/ ethyl acetate 8/1) to afford **5d** as a colorless oil (19.0 mg, 68% yield). **HPLC:** >99% *ee* [(Chiralcel OJ-H) *n*-hexane/*i*-PrOH (210 nm, 25 °C) = 95/5, 0.5 mL/min, t (major) = 47.37 min]; $[\alpha]_D^{21.3}$ = –56.1 (*c* = 1.01, $CHCl_3$). R_f = 0.54 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 1H), 6.87 – 6.76 (m, 3H), 6.04 (ddd, *J* = 17.0, 10.2, 8.3 Hz, 1H), 5.44 (d, *J* = 10.6 Hz, 1H), 5.29 – 5.16 (m, 2H), 4.38 – 4.24 (m, 2H), 4.05 (qd, *J* = 7.1, 5.3 Hz, 1H), 3.79 (d, *J* = 2.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.1, 162.8, 160.0, 159.9, 138.7, 137.8, 134.4, 134.0, 130.1, 130.0, 120.4, 119.8, 119.2, 119.1, 114.2, 113.9, 113.2, 113.1, 91.4, 91.1, 63.1, 62.9, 55.3, 55.3, 51.1, 50.9, 13.9, 13.6. **IR** (thin film): 2985, 1752, 1602, 1563, 1492, 1313, 1265, 1186, 1043, 933, 858, 782, 702cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{14}H_{17}NNaO_5$ $[M+Na]^+$: 302.0999, Found: 302.0999.

(*S*)-3-(1-phenylallyl) pentane-2, 4-dione **6**



6

The compound was prepared according to the general procedure. The crude reaction mixture was purified on silica gel (petroleum ether/ ethyl acetate 15/1) to afford **6** as a colorless oil (19.0 mg, 88% yield). **HPLC:** 77% *ee* [(Chiralcel OJ-H) *n*-hexane/*i*-PrOH (210 nm, 25 °C) = 80/20, 1.0 mL/min, t (major) = 10.04 min, t (minor) = 12.38 min]; $[\alpha]_D^{23.3}$ = –22.6 (*c* = 0.48, $CHCl_3$). R_f = 0.39 (petroleum ether/ ethyl acetate 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.17 (m, 3H), 5.86 (ddd, *J* = 17.8, 10.2, 7.8 Hz, 1H), 5.12 – 5.04 (m, 2H), 4.26 (d, *J* = 11.7 Hz, 1H), 4.17 (dd, *J* = 11.7, 7.8 Hz, 1H), 2.25 (s, 3H), 1.88 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.0, 202.8, 139.8, 138.0, 129.0, 127.9, 127.2, 116.6, 74.3, 49.8, 30.1, 29.6. **IR** (KBr): 3004, 2918, 2850, 1727, 1699, 1601, 1453, 1419, 1357, 1262, 1189, 1155, 1028, 925, 757, 703cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{14}H_{16}NaO_2$ $[M+Na]^+$: 239.1043. Found: 239.1045.

Characterization data of this compound were in accordance with previously reported values[7] . The absolute stereochemistry of the reported compound was determined (*S*) with specific rotation $[\alpha]_D^{29}$ = –31.7 (*c* = 1.00, $CHCl_3$) and optical purity of 95% *ee*.

References

[1] Defieber, C.; Ariger, M. A.; Moriel, P.; Carreira, E. M. *Angew. Chem., Int. Ed*. **2007**, *46*, 3139.

[2] Alexakis, A.; Polet, D. *Org. Lett*. **2004**, 6, 3529.

[3] Hayashi, T.; Okada, A.; suzuka, T.; Kawatsura, M. *Org. Lett*. **2003**, 5, 1713.

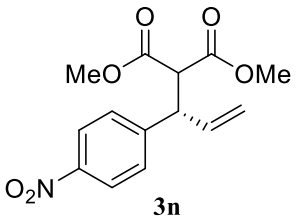
[4] Liu, W.-B.; Zheng, C.; Zhou, C.-X.; Dai, L.-X.; You, S.-L. *J. Am. Chem. Soc*. **2012**, 134, 4812.

[5] Hu, Z.-J.; Li, Y.-G.; Liu, K.; Shen, Q.-L. *J. Org. Chem*. **2012**, 77, 7957.

[6] Nemoto, T.; Sakamoto, T.; Fukuyama, T.; Hamada, Y. T*etrahedron Lett*. **2007**, 48, 4977.

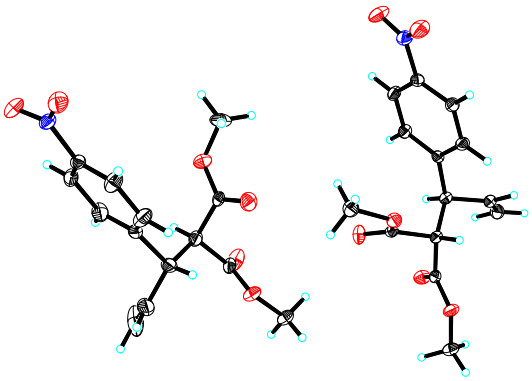
[7] Tang, S.-B.; Zhang, X.; Tu, H.-F.; You, S.-L. *J. Am. Chem. Soc*. **2018**, 140, 7737.

X-ray Crystallographic Data of 3n

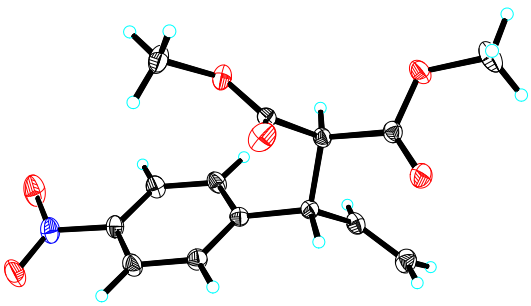


3n

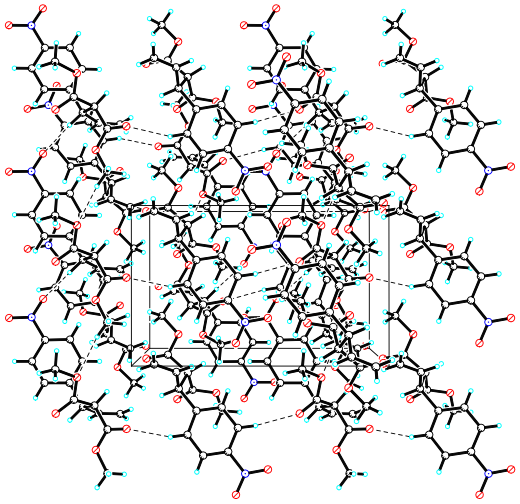
Crystal data for **3n**: $C_{14}H_{15}NO_6$, M = 293.27, a = 8.0639(6) Å, b = 13.7293(10) Å, c = 12.9037(10) Å, α = 90 °, β = 90.043(3) °, γ = 90 °, V = 1428.59(19) Å^3, T = 100(2) K, space group $P21$, Z = 4, μ(CuKα) = 0.914 mm^{-1}, 15151 reflections measured, 4734 independent reflections (R_{int} = 0.0451). The final R_1 values were 0.0506 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1287 ($I > 2\sigma(I)$). The final R_1 values were 0.0510 (all data). The final $wR(F^2)$ values were 0.1292 (all data). The goodness of fit on F^2 was 1.044. Flack parameter = -0.01(7).



View of the molecules in an asymmetric unit.
Displacement ellipsoids are drawn at the 30% probability level.



View of a molecule of amo3063 with the atom-labelling scheme.
Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of **3n**.
Hydrogen-bonds are shown as dashed lines.

Table 1. Crystal data and structure refinement for **3n**.

Identification code	**3n**
Empirical formula	$C_{14}H_{15}NO_6$
Formula weight	293.27
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a = 8.0639(6) Å	α= 90 °.
b = 13.7293(10) Å	β= 90.043(3) °.
c = 12.9037(10) Å	γ = 90 °.
Volume	1428.59(19) $Å^3$
Z	4
Density (calculated)	1.364 Mg/m^3
Absorption coefficient	0.914 mm^{-1}
F(000)	616
Crystal size	0.900 x 0.260 x 0.120 mm^3
Theta range for data collection	4.703 to 70.412 °.
Index ranges	$-9 \leqslant h \leqslant 9, -16 \leqslant k \leqslant 16, -15 \leqslant l \leqslant 15$
Reflections collected	15151
Independent reflections	4734 [R(int) = 0.0451]
Completeness to theta = 67.679 °	92.1 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4734 / 1 / 384

Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0506, wR2 = 0.1287
R indices (all data)	R1 = 0.0510, wR2 = 0.1292
Absolute structure parameter	-0.01(7)
Extinction coefficient	0.0052(7)
Largest diff. peak and hole	0.672 and -0.421 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3n**. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

x	y	z	U(eq)
O(1)	1085(4)	6683(3)	4007(3)	53(1)
O(2)	11454(3)	4397(2)	1531(2)	37(1)
O(3)	2726(4)	6559(3)	5323(3)	57(1)
O(4)	9844(4)	4863(2)	200(2)	39(1)
O(5)	7395(3)	4146(2)	3133(2)	35(1)
O(6)	6926(4)	3895(2)	1455(2)	41(1)
O(7)	1165(4)	1839(3)	2493(3)	53(1)
O(8)	-2563(4)	-567(3)	5669(3)	53(1)
O(9)	-3837(4)	-1021(3)	4287(3)	51(1)
O(10)	6118(3)	963(2)	1818(3)	43(1)
O(11)	4605(4)	1511(3)	498(2)	56(1)
O(12)	3540(4)	1793(3)	3372(3)	47(1)
C(1)	7985(4)	6059(3)	1632(3)	26(1)
N(2)	-2597(4)	-762(3)	4741(3)	37(1)
N(1)	2460(4)	6603(3)	4389(3)	40(1)
C(2)	3889(5)	6509(3)	3686(3)	30(1)
C(3)	5472(5)	6579(3)	4088(3)	33(1)
C(4)	6807(5)	6466(3)	3417(3)	32(1)
C(5)	6550(4)	6261(2)	2374(3)	26(1)
C(6)	8908(4)	5111(3)	1968(3)	26(1)
C(7)	10094(4)	4788(3)	1109(3)	28(1)
C(8)	12679(5)	4037(4)	805(4)	48(1)
C(9)	9209(5)	6890(3)	1579(3)	31(1)
C(10)	9758(5)	7248(3)	695(4)	39(1)
C(11)	7638(4)	4308(3)	2133(3)	26(1)
C(12)	6056(6)	3465(3)	3375(4)	41(1)
C(13)	4947(5)	6203(3)	1999(3)	31(1)
C(14)	3594(5)	6333(3)	2649(3)	34(1)
C(15)	543(8)	2507(4)	3292(6)	72(2)
C(16)	2675(4)	1524(3)	2659(3)	27(1)

C(17)	3192(5)	756(3)	1899(4)	36(1)
C(18)	3456(6)	-213(3)	2488(5)	53(1)
C(19)	1856(5)	-442(3)	3084(4)	44(1)
C(20)	1846(5)	-377(4)	4141(4)	48(1)
C(21)	393(5)	-498(4)	4684(4)	46(1)
C(22)	-1047(5)	-679(3)	4156(3)	30(1)
C(23)	409(6)	-657(4)	2571(4)	50(1)
C(24)	-1076(5)	-777(3)	3103(4)	41(1)
C(25)	4721(5)	1107(3)	1318(3)	34(1)
C(26)	7584(5)	1339(4)	1300(5)	57(1)
C(27)	4049(7)	-1059(4)	1909(6)	69(2)
C(28)	4114(10)	-1263(6)	1008(5)	91(3)

Table 3. Bond lengths [Å] and angles [°] for **3n**.

O(1)-N(1)	1.218(5)
O(2)-C(7)	1.337(5)
O(2)-C(8)	1.450(5)
O(3)-N(1)	1.225(5)
O(4)-C(7)	1.194(5)
O(5)-C(11)	1.324(5)
O(5)-C(12)	1.462(5)
O(6)-C(11)	1.191(5)
O(7)-C(16)	1.309(5)
O(7)-C(15)	1.469(7)
O(8)-N(2)	1.227(5)
O(9)-N(2)	1.211(5)
O(10)-C(25)	1.312(5)
O(10)-C(26)	1.453(5)
O(11)-C(25)	1.199(6)
O(12)-C(16)	1.211(5)
C(1)-C(9)	1.511(5)
C(1)-C(5)	1.528(5)
C(1)-C(6)	1.561(5)
C(1)-H(7)	1.0000
N(2)-C(22)	1.465(4)
N(1)-C(2)	1.473(4)
C(2)-C(14)	1.380(6)
C(2)-C(3)	1.381(5)
C(3)-C(4)	1.392(5)
C(3)-H(2)	0.9500
C(4)-C(5)	1.389(5)
C(4)-H(3)	0.9500

C(5)-C(13)	1.383(5)
C(6)-C(11)	1.519(5)
C(6)-C(7)	1.530(5)
C(6)-H(13)	1.0000
C(8)-H(1)	0.9800
C(8)-H(8)	0.9800
C(8)-H(9)	0.9800
C(9)-C(10)	1.318(6)
C(9)-H(6)	0.9500
C(10)-H(5)	0.9500
C(10)-H(4)	0.9500
C(12)-H(11)	0.9800
C(12)-H(12)	0.9800
C(12)-H(10)	0.9800
C(13)-C(14)	1.388(5)
C(13)-H(15)	0.9500
C(14)-H(14)	0.9500
C(15)-H(16)	0.9800
C(15)-H(24)	0.9800
C(15)-H(23)	0.9800
C(16)-C(17)	1.500(6)
C(17)-C(25)	1.522(5)
C(17)-C(18)	1.546(7)
C(17)-H(25)	1.0000
C(18)-C(27)	1.462(7)
C(18)-C(19)	1.535(5)
C(18)-H(19)	1.0000
C(19)-C(20)	1.367(8)
C(19)-C(23)	1.373(7)
C(20)-C(21)	1.376(6)
C(20)-H(29)	0.9500
C(21)-C(22)	1.369(6)
C(21)-H(30)	0.9500
C(22)-C(24)	1.364(6)
C(23)-C(24)	1.391(6)
C(23)-H(18)	0.9500
C(24)-H(17)	0.9500
C(26)-H(22)	0.9800
C(26)-H(20)	0.9800
C(26)-H(21)	0.9800
C(27)-C(28)	1.197(9)
C(27)-H(26)	0.9500
C(28)-H(27)	0.9500
C(28)-H(28)	0.9500

C(7)-O(2)-C(8)	115.7(3)
C(11)-O(5)-C(12)	115.2(3)
C(16)-O(7)-C(15)	114.1(4)
C(25)-O(10)-C(26)	114.8(4)
C(9)-C(1)-C(5)	112.7(3)
C(9)-C(1)-C(6)	109.3(3)
C(5)-C(1)-C(6)	109.8(3)
C(9)-C(1)-H(7)	108.3
C(5)-C(1)-H(7)	108.3
C(6)-C(1)-H(7)	108.3
O(9)-N(2)-O(8)	123.6(3)
O(9)-N(2)-C(22)	118.5(4)
O(8)-N(2)-C(22)	117.9(4)
O(1)-N(1)-O(3)	124.1(3)
O(1)-N(1)-C(2)	118.1(4)
O(3)-N(1)-C(2)	117.7(3)
C(14)-C(2)-C(3)	122.4(3)
C(14)-C(2)-N(1)	118.6(3)
C(3)-C(2)-N(1)	119.1(3)
C(2)-C(3)-C(4)	118.3(4)
C(2)-C(3)-H(2)	120.9
C(4)-C(3)-H(2)	120.9
C(5)-C(4)-C(3)	120.7(4)
C(5)-C(4)-H(3)	119.7
C(3)-C(4)-H(3)	119.7
C(13)-C(5)-C(4)	119.3(3)
C(13)-C(5)-C(1)	118.6(3)
C(4)-C(5)-C(1)	122.1(3)
C(11)-C(6)-C(7)	108.3(3)
C(11)-C(6)-C(1)	108.8(3)
C(7)-C(6)-C(1)	109.8(3)
C(11)-C(6)-H(13)	110.0
C(7)-C(6)-H(13)	110.0
C(1)-C(6)-H(13)	110.0
O(4)-C(7)-O(2)	124.9(3)
O(4)-C(7)-C(6)	125.6(4)
O(2)-C(7)-C(6)	109.5(3)
O(2)-C(8)-H(1)	109.5
O(2)-C(8)-H(8)	109.5
H(1)-C(8)-H(8)	109.5
O(2)-C(8)-H(9)	109.5
H(1)-C(8)-H(9)	109.5
H(8)-C(8)-H(9)	109.5
C(10)-C(9)-C(1)	122.8(4)

C(10)-C(9)-H(6)	118.6
C(1)-C(9)-H(6)	118.6
C(9)-C(10)-H(5)	120.0
C(9)-C(10)-H(4)	120.0
H(5)-C(10)-H(4)	120.0
O(6)-C(11)-O(5)	124.4(3)
O(6)-C(11)-C(6)	124.6(3)
O(5)-C(11)-C(6)	111.0(3)
O(5)-C(12)-H(11)	109.5
O(5)-C(12)-H(12)	109.5
H(11)-C(12)-H(12)	109.5
O(5)-C(12)-H(10)	109.5
H(11)-C(12)-H(10)	109.5
H(12)-C(12)-H(10)	109.5
C(5)-C(13)-C(14)	121.1(4)
C(5)-C(13)-H(15)	119.5
C(14)-C(13)-H(15)	119.5
C(2)-C(14)-C(13)	118.2(4)
C(2)-C(14)-H(14)	120.9
C(13)-C(14)-H(14)	120.9
O(7)-C(15)-H(16)	109.5
O(7)-C(15)-H(24)	109.5
H(16)-C(15)-H(24)	109.5
O(7)-C(15)-H(23)	109.5
H(16)-C(15)-H(23)	109.5
H(24)-C(15)-H(23)	109.5
O(12)-C(16)-O(7)	124.0(4)
O(12)-C(16)-C(17)	123.4(4)
O(7)-C(16)-C(17)	112.5(4)
C(16)-C(17)-C(25)	108.9(3)
C(16)-C(17)-C(18)	108.8(4)
C(25)-C(17)-C(18)	113.8(4)
C(16)-C(17)-H(25)	108.4
C(25)-C(17)-H(25)	108.4
C(18)-C(17)-H(25)	108.4
C(27)-C(18)-C(19)	111.6(4)
C(27)-C(18)-C(17)	118.5(5)
C(19)-C(18)-C(17)	107.9(4)
C(27)-C(18)-H(19)	106.0
C(19)-C(18)-H(19)	106.0
C(17)-C(18)-H(19)	106.0
C(20)-C(19)-C(23)	119.3(4)
C(20)-C(19)-C(18)	119.4(4)
C(23)-C(19)-C(18)	121.1(5)

C(19)-C(20)-C(21)	120.4(5)
C(19)-C(20)-H(29)	119.8
C(21)-C(20)-H(29)	119.8
C(22)-C(21)-C(20)	119.4(5)
C(22)-C(21)-H(30)	120.3
C(20)-C(21)-H(30)	120.3
C(24)-C(22)-C(21)	121.8(4)
C(24)-C(22)-N(2)	119.4(4)
C(21)-C(22)-N(2)	118.7(4)
C(19)-C(23)-C(24)	121.3(4)
C(19)-C(23)-H(18)	119.4
C(24)-C(23)-H(18)	119.4
C(22)-C(24)-C(23)	117.7(4)
C(22)-C(24)-H(17)	121.1
C(23)-C(24)-H(17)	121.1
O(11)-C(25)-O(10)	124.7(4)
O(11)-C(25)-C(17)	121.3(4)
O(10)-C(25)-C(17)	113.9(4)
O(10)-C(26)-H(22)	109.5
O(10)-C(26)-H(20)	109.5
H(22)-C(26)-H(20)	109.5
O(10)-C(26)-H(21)	109.5
H(22)-C(26)-H(21)	109.5
H(20)-C(26)-H(21)	109.5
C(28)-C(27)-C(18)	134.2(8)
C(28)-C(27)-H(26)	112.9
C(18)-C(27)-H(26)	112.9
C(27)-C(28)-H(27)	120.0
C(27)-C(28)-H(28)	120.0
H(27)-C(28)-H(28)	120.0

Symmetry transformations used to generate equivalent atoms.

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3n**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	26(1)	89(3)	45(2)	-3(2)	3(1)	5(2)
O(2)	24(1)	45(2)	43(2)	-1(1)	0(1)	7(1)
O(3)	42(2)	95(3)	34(2)	-20(2)	9(2)	-6(2)
O(4)	38(2)	52(2)	27(2)	0(1)	5(1)	7(1)
O(5)	34(1)	36(2)	34(2)	0(1)	10(1)	-4(1)

O(6)	46(2)	43(2)	35(2)	-2(1)	-6(1)	-17(1)
O(7)	31(2)	50(2)	78(3)	-3(2)	-6(2)	10(1)
O(8)	58(2)	61(2)	40(2)	-5(2)	20(2)	-12(2)
O(9)	27(1)	71(2)	56(2)	5(2)	4(2)	-7(2)
O(10)	26(1)	54(2)	49(2)	2(1)	6(1)	3(1)
O(11)	49(2)	92(3)	28(2)	2(2)	2(2)	-23(2)
O(12)	47(2)	54(2)	40(2)	-12(2)	-4(2)	-5(2)
C(1)	23(2)	31(2)	25(2)	2(1)	0(2)	1(2)
N(2)	29(2)	40(2)	43(2)	4(2)	10(2)	-1(2)
N(1)	33(2)	50(2)	36(2)	-9(2)	8(2)	-3(2)
C(2)	29(2)	32(2)	30(2)	-5(2)	7(2)	-2(2)
C(3)	30(2)	40(2)	30(2)	-9(2)	0(2)	-1(2)
C(4)	26(2)	40(2)	30(2)	-7(2)	-2(2)	2(2)
C(5)	27(2)	21(2)	29(2)	-1(1)	2(2)	1(1)
C(6)	21(2)	30(2)	27(2)	0(1)	0(2)	-1(1)
C(7)	24(2)	27(2)	32(2)	0(2)	2(2)	-3(1)
C(8)	27(2)	53(3)	63(3)	-12(2)	6(2)	6(2)
C(9)	25(2)	30(2)	39(2)	-4(2)	2(2)	-1(2)
C(10)	38(2)	33(2)	47(3)	3(2)	7(2)	-5(2)
C(11)	22(2)	26(2)	30(2)	3(2)	1(2)	2(1)
C(12)	41(2)	38(2)	45(3)	3(2)	15(2)	-9(2)
C(13)	29(2)	38(2)	26(2)	-1(2)	-1(2)	-2(2)
C(14)	24(2)	43(2)	35(2)	-2(2)	-3(2)	-4(2)
C(15)	56(3)	49(3)	110(5)	-10(3)	35(4)	15(2)
C(16)	25(2)	28(2)	30(2)	5(2)	4(2)	-7(1)
C(17)	31(2)	41(2)	35(2)	-7(2)	4(2)	-8(2)
C(18)	42(2)	29(2)	89(4)	-2(2)	32(3)	-2(2)
C(19)	34(2)	26(2)	74(4)	-3(2)	18(2)	-2(2)
C(20)	29(2)	52(3)	63(4)	24(2)	-1(2)	-1(2)
C(21)	37(2)	55(3)	45(3)	18(2)	-2(2)	-6(2)
C(22)	29(2)	30(2)	33(2)	4(2)	8(2)	1(2)
C(23)	61(3)	47(3)	42(3)	-15(2)	27(2)	-15(2)
C(24)	38(2)	42(2)	43(3)	-8(2)	7(2)	-13(2)
C(25)	33(2)	40(2)	29(2)	-9(2)	8(2)	-11(2)
C(26)	27(2)	57(3)	86(4)	-13(3)	19(2)	-5(2)
C(27)	56(3)	45(3)	105(5)	-21(3)	38(3)	-9(2)
C(28)	126(6)	84(5)	62(4)	-31(4)	41(4)	-64(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **3n**.

x	y	z	U(eq)
H(7)	7516	5953	924	31

H(2)	5644	6702	4805	40
H(3)	7906	6528	3674	39
H(13)	9539	5229	2624	31
H(1)	12215	3487	416	72
H(8)	13667	3822	1184	72
H(9)	12984	4558	322	72
H(6)	9599	7167	2208	38
H(5)	9384	6982	57	47
H(4)	10528	7772	697	47
H(11)	5014	3706	3080	62
H(12)	5944	3406	4129	62
H(10)	6314	2825	3079	62
H(15)	4768	6071	1285	37
H(14)	2494	6301	2387	41
H(16)	822	2251	3980	108
H(24)	-664	2567	3229	108
H(23)	1056	3148	3202	108
H(25)	2273	662	1388	43
H(19)	4319	-77	3026	64
H(29)	2849	-247	4503	58
H(30)	389	-457	5419	55
H(18)	423	-726	1838	60
H(17)	-2077	-922	2747	49
H(22)	7729	1005	636	85
H(20)	8560	1227	1737	85
H(21)	7452	2040	1180	85
H(26)	4476	-1558	2344	82
H(27)	3719	-816	503	109
H(28)	4561	-1872	797	109

Table 6. Torsion angles [°] for **3n**.

O(1)-N(1)-C(2)-C(14)	-11.9(6)
O(3)-N(1)-C(2)-C(14)	165.4(4)
O(1)-N(1)-C(2)-C(3)	169.4(4)
O(3)-N(1)-C(2)-C(3)	-13.3(6)
C(14)-C(2)-C(3)-C(4)	-0.1(6)
N(1)-C(2)-C(3)-C(4)	178.5(4)
C(2)-C(3)-C(4)-C(5)	-1.7(6)
C(3)-C(4)-C(5)-C(13)	2.1(6)
C(3)-C(4)-C(5)-C(1)	-175.4(4)
C(9)-C(1)-C(5)-C(13)	124.1(4)
C(6)-C(1)-C(5)-C(13)	-113.7(4)

C(9)-C(1)-C(5)-C(4)	-58.4(5)
C(6)-C(1)-C(5)-C(4)	63.8(4)
C(9)-C(1)-C(6)-C(11)	173.9(3)
C(5)-C(1)-C(6)-C(11)	49.7(4)
C(9)-C(1)-C(6)-C(7)	-67.8(4)
C(5)-C(1)-C(6)-C(7)	168.0(3)
C(8)-O(2)-C(7)-O(4)	-0.6(6)
C(8)-O(2)-C(7)-C(6)	178.7(3)
C(11)-C(6)-C(7)-O(4)	82.8(5)
C(1)-C(6)-C(7)-O(4)	-35.8(5)
C(11)-C(6)-C(7)-O(2)	-96.4(4)
C(1)-C(6)-C(7)-O(2)	145.0(3)
C(5)-C(1)-C(9)-C(10)	-132.1(4)
C(6)-C(1)-C(9)-C(10)	105.4(4)
C(12)-O(5)-C(11)-O(6)	-5.1(5)
C(12)-O(5)-C(11)-C(6)	173.3(3)
C(7)-C(6)-C(11)-O(6)	-45.6(5)
C(1)-C(6)-C(11)-O(6)	73.7(5)
C(7)-C(6)-C(11)-O(5)	136.1(3)
C(1)-C(6)-C(11)-O(5)	-104.7(3)
C(4)-C(5)-C(13)-C(14)	-0.8(6)
C(1)-C(5)-C(13)-C(14)	176.8(4)
C(3)-C(2)-C(14)-C(13)	1.4(6)
N(1)-C(2)-C(14)-C(13)	-177.3(4)
C(5)-C(13)-C(14)-C(2)	-0.9(6)
C(15)-O(7)-C(16)-O(12)	-4.1(6)
C(15)-O(7)-C(16)-C(17)	173.2(4)
O(12)-C(16)-C(17)-C(25)	-62.2(5)
O(7)-C(16)-C(17)-C(25)	120.5(4)
O(12)-C(16)-C(17)-C(18)	62.3(5)
O(7)-C(16)-C(17)-C(18)	-115.0(4)
C(16)-C(17)-C(18)-C(27)	-177.0(4)
C(25)-C(17)-C(18)-C(27)	-55.4(6)
C(16)-C(17)-C(18)-C(19)	55.1(5)
C(25)-C(17)-C(18)-C(19)	176.7(4)
C(27)-C(18)-C(19)-C(20)	118.3(6)
C(17)-C(18)-C(19)-C(20)	-109.9(5)
C(27)-C(18)-C(19)-C(23)	-65.5(7)
C(17)-C(18)-C(19)-C(23)	66.3(5)
C(23)-C(19)-C(20)-C(21)	-1.8(7)
C(18)-C(19)-C(20)-C(21)	174.5(4)
C(19)-C(20)-C(21)-C(22)	-0.4(7)
C(20)-C(21)-C(22)-C(24)	2.4(7)
C(20)-C(21)-C(22)-N(2)	-177.3(4)

O(9)-N(2)-C(22)-C(24)	7.9(6)
O(8)-N(2)-C(22)-C(24)	-172.2(4)
O(9)-N(2)-C(22)-C(21)	-172.5(4)
O(8)-N(2)-C(22)-C(21)	7.4(6)
C(20)-C(19)-C(23)-C(24)	2.3(7)
C(18)-C(19)-C(23)-C(24)	-174.0(4)
C(21)-C(22)-C(24)-C(23)	-1.9(7)
N(2)-C(22)-C(24)-C(23)	177.7(4)
C(19)-C(23)-C(24)-C(22)	-0.4(7)
C(26)-O(10)-C(25)-O(11)	0.2(6)
C(26)-O(10)-C(25)-C(17)	-177.0(4)
C(16)-C(17)-C(25)-O(11)	-94.4(5)
C(18)-C(17)-C(25)-O(11)	144.1(5)
C(16)-C(17)-C(25)-O(10)	82.8(5)
C(18)-C(17)-C(25)-O(10)	-38.7(5)
C(19)-C(18)-C(27)-C(28)	109.2(8)
C(17)-C(18)-C(27)-C(28)	-16.9(10)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **3n** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1
C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(8)-H(8)...O(6)#1	0.98	2.65	3.530(6)	149.2
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1
C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(8)-H(8)...O(6)#1	0.98	2.65	3.530(6)	149.2
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1
C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(8)-H(8)...O(6)#1	0.98	2.65	3.530(6)	149.2
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1

C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(8)-H(8)...O(6)#1	0.98	2.65	3.530(6)	149.2
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1
C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(8)-H(8)...O(6)#1	0.98	2.65	3.530(6)	149.2
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1
C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(8)-H(8)...O(6)#1	0.98	2.65	3.530(6)	149.2
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1
C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(8)-H(8)...O(6)#1	0.98	2.65	3.530(6)	149.2
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(8)-H(8)...O(6)#1	0.98	2.65	3.530(6)	149.2
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(8)-H(8)...O(6)#1	0.98	2.65	3.530(6)	149.2
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(8)-H(8)...O(6)#1	0.98	2.65	3.530(6)	149.2
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1

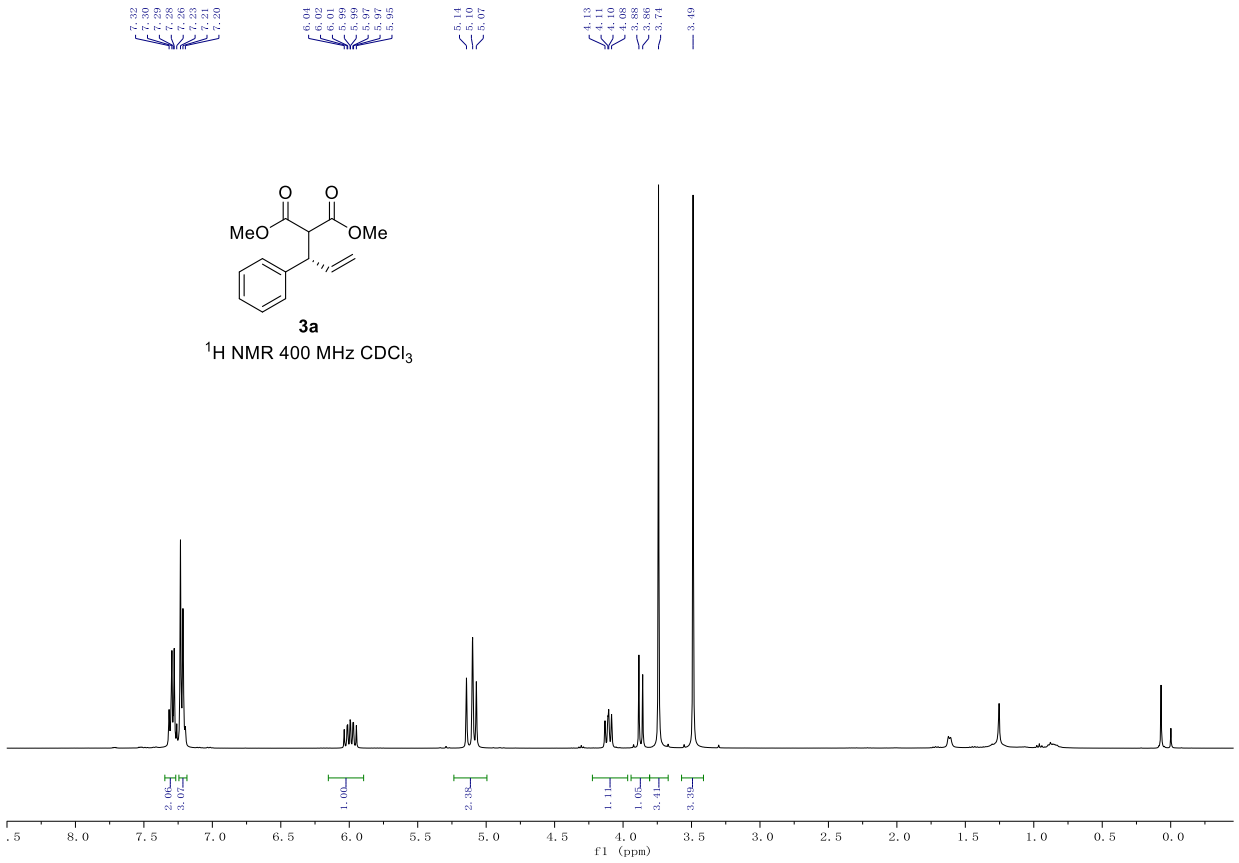
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(8)-H(8)...O(6)#1	0.98	2.65	3.530(6)	149.2
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(8)-H(8)...O(6)#1	0.98	2.65	3.530(6)	149.2
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7
C(3)-H(2)...O(12)#4	0.95	2.45	3.385(5)	169.9
C(8)-H(8)...O(6)#1	0.98	2.65	3.530(6)	149.2
C(15)-H(23)...O(8)#3	0.98	2.59	3.383(8)	138.0
C(21)-H(30)...O(5)#2	0.95	2.64	3.368(6)	133.7
C(26)-H(20)...O(7)#1	0.98	2.46	3.342(6)	149.1
C(26)-H(21)...O(6)	0.98	2.61	3.554(6)	162.7

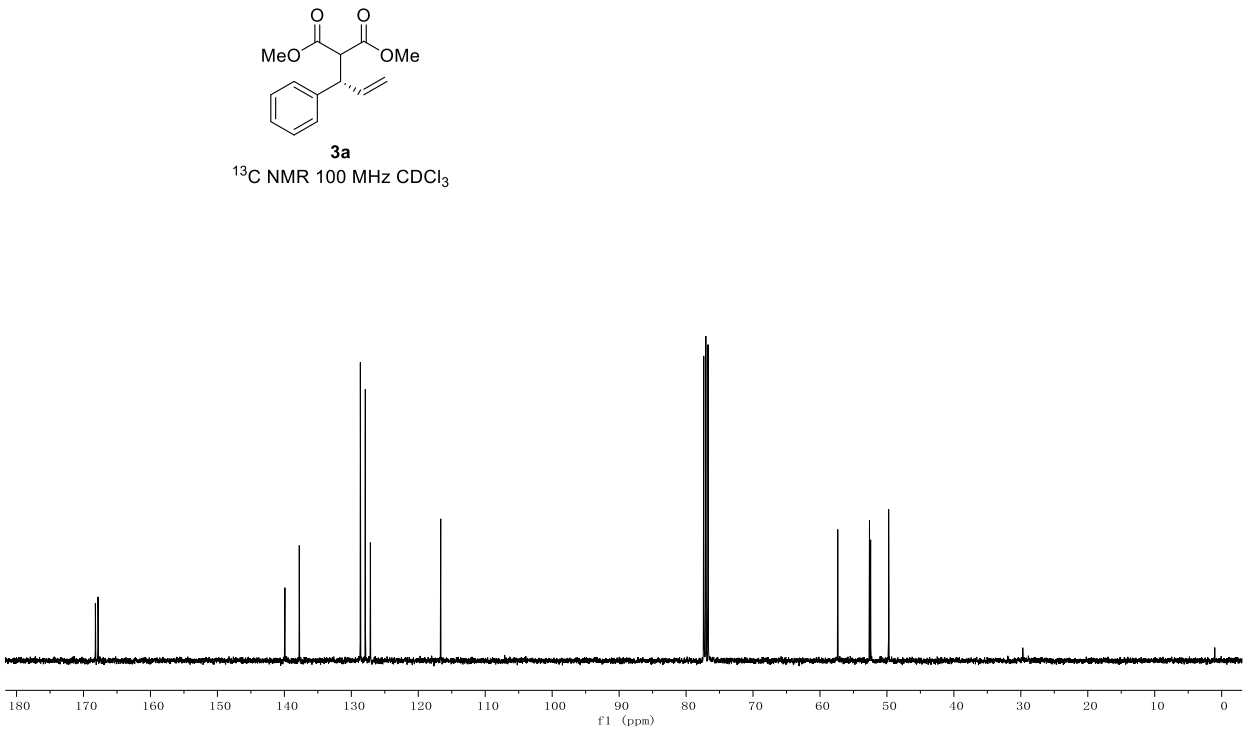
Symmetry transformations used to generate equivalent atoms:

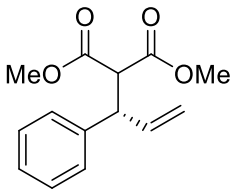
#1 x+1,y,z #2 -x+1,y-1/2,-z+1 #3 -x,y+1/2,-z+1

#4 -x+1,y+1/2,-z+1

NMR Spectral and HPLC Data.

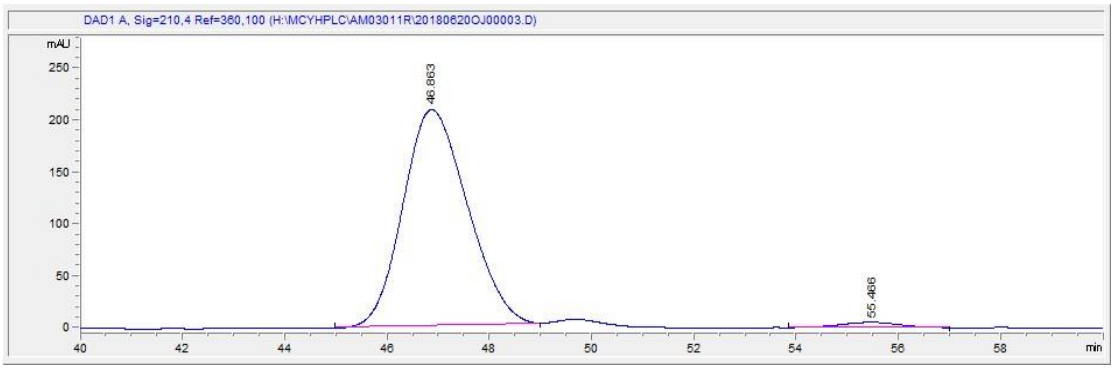






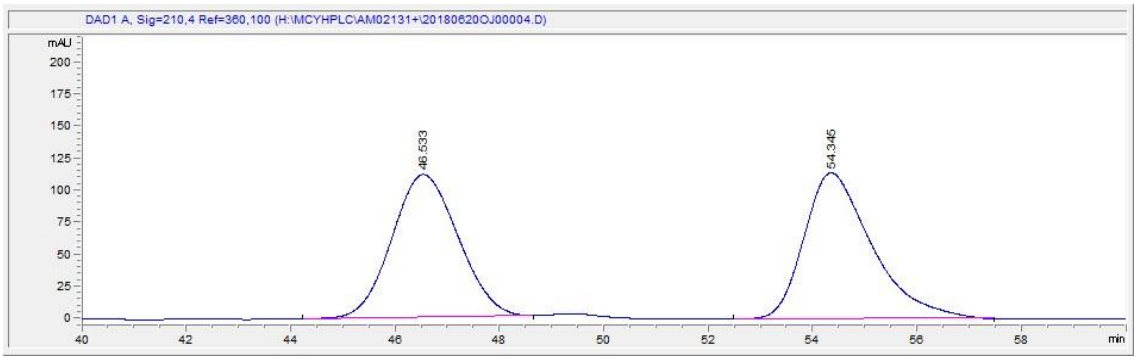
3a

Enantioenriched mixture of compound **3a**

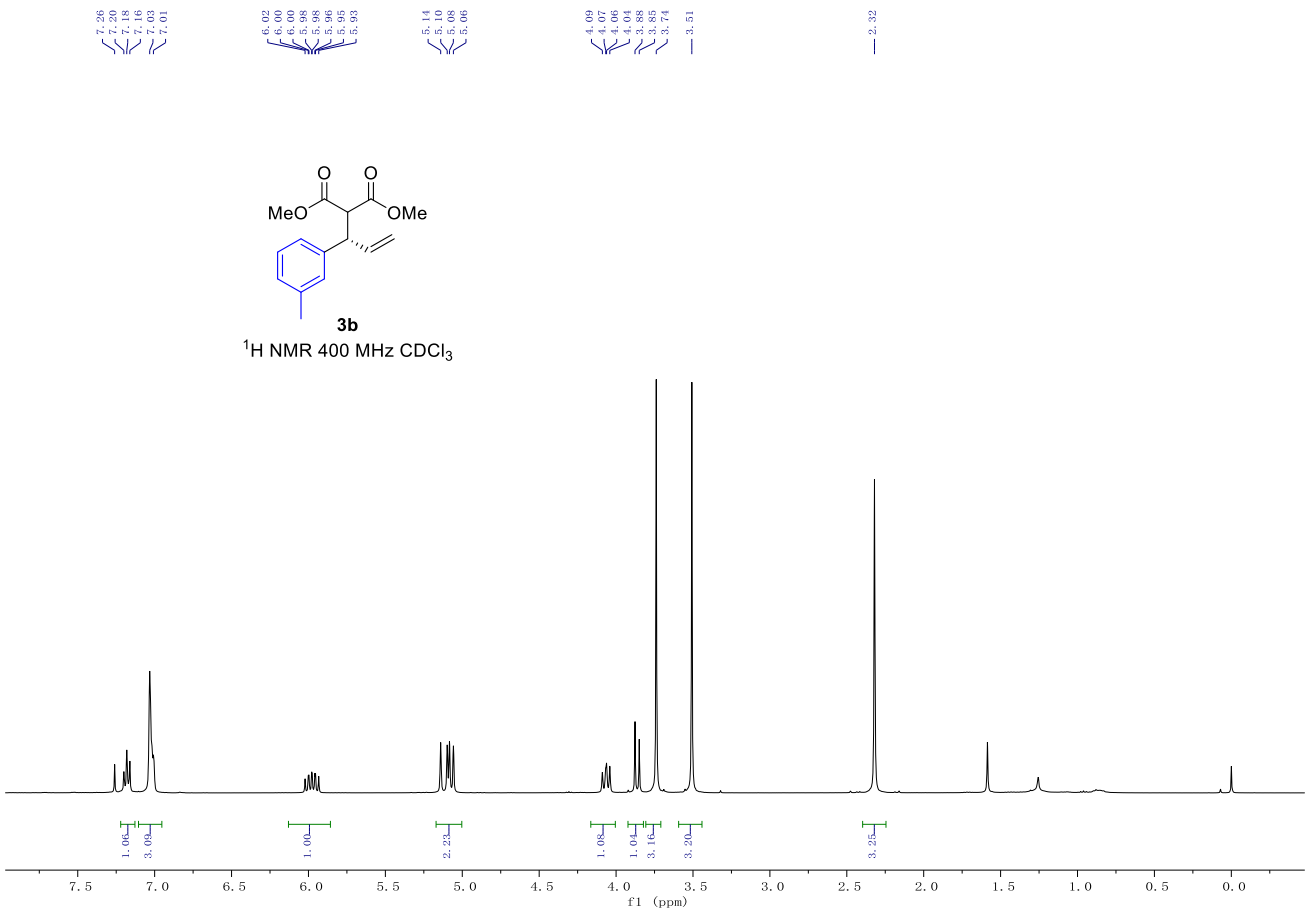


#	Time	Area	Height	Width	Area%	Symmetry
1	46.863	18263.5	208.4	1.3384	97.816	0.783
2	55.466	407.9	5.1	0.9583	2.184	1.098

Racemate of compond **3a**

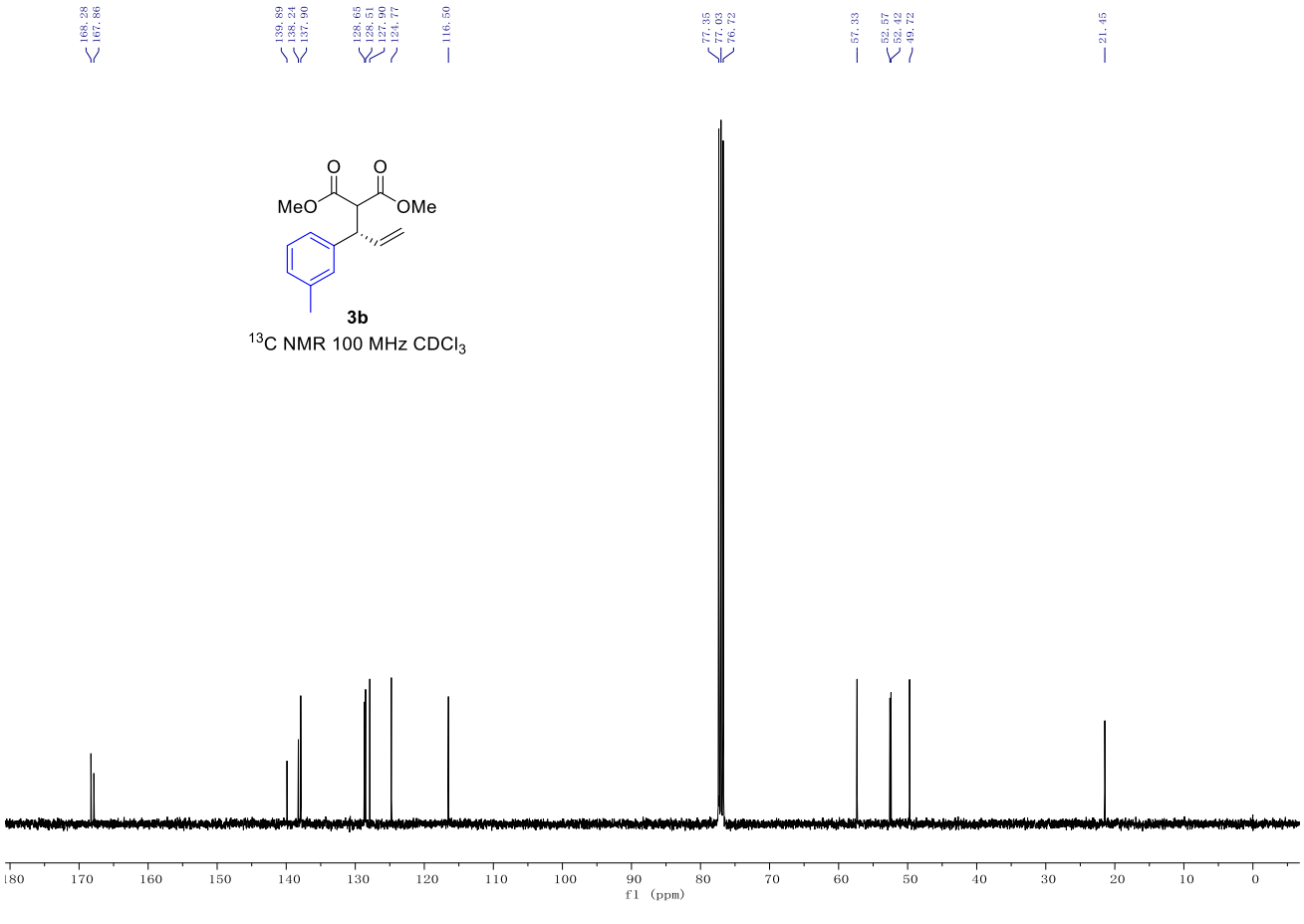


#	Time	Area	Height	Width	Area%	Symmetry
1	46.533	9840.2	111.4	1.3269	48.822	0.886
2	54.345	10315	113.9	1.3343	51.178	0.626



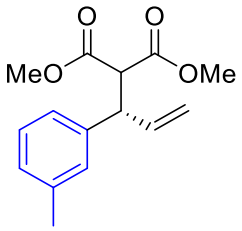
3b

^{1}H NMR 400 MHz $CDCl_3$



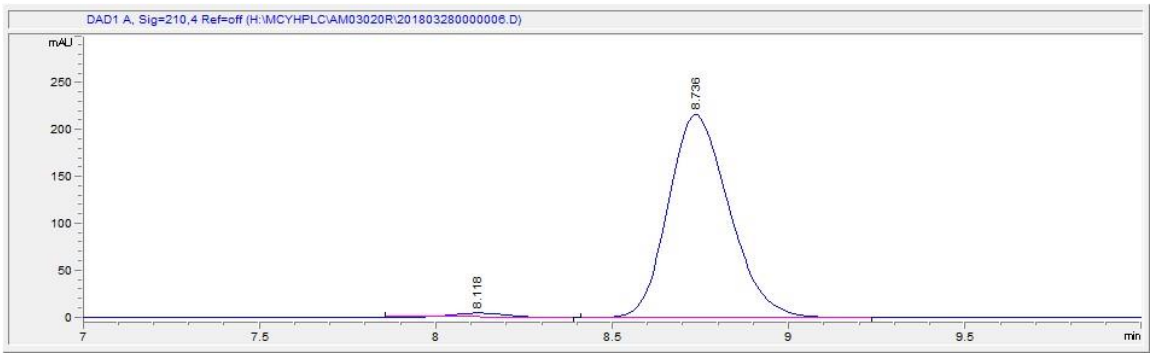
3b

^{13}C NMR 100 MHz $CDCl_3$



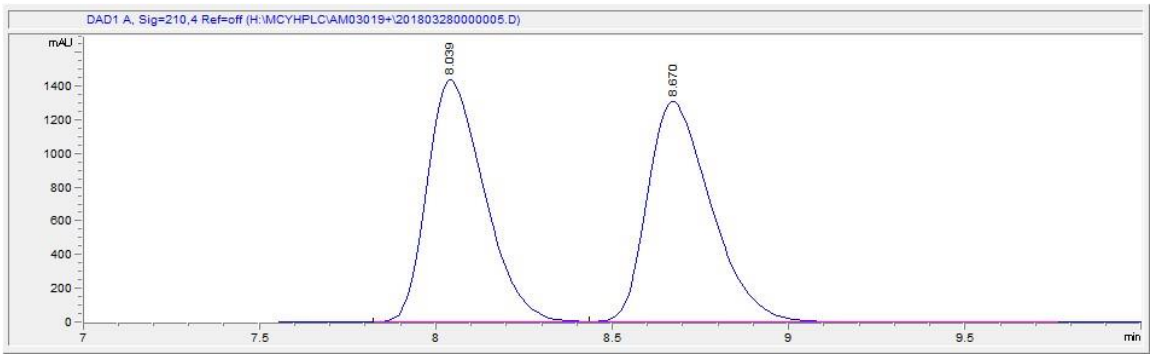
3b

Enantioenriched mixture of compound **3b**

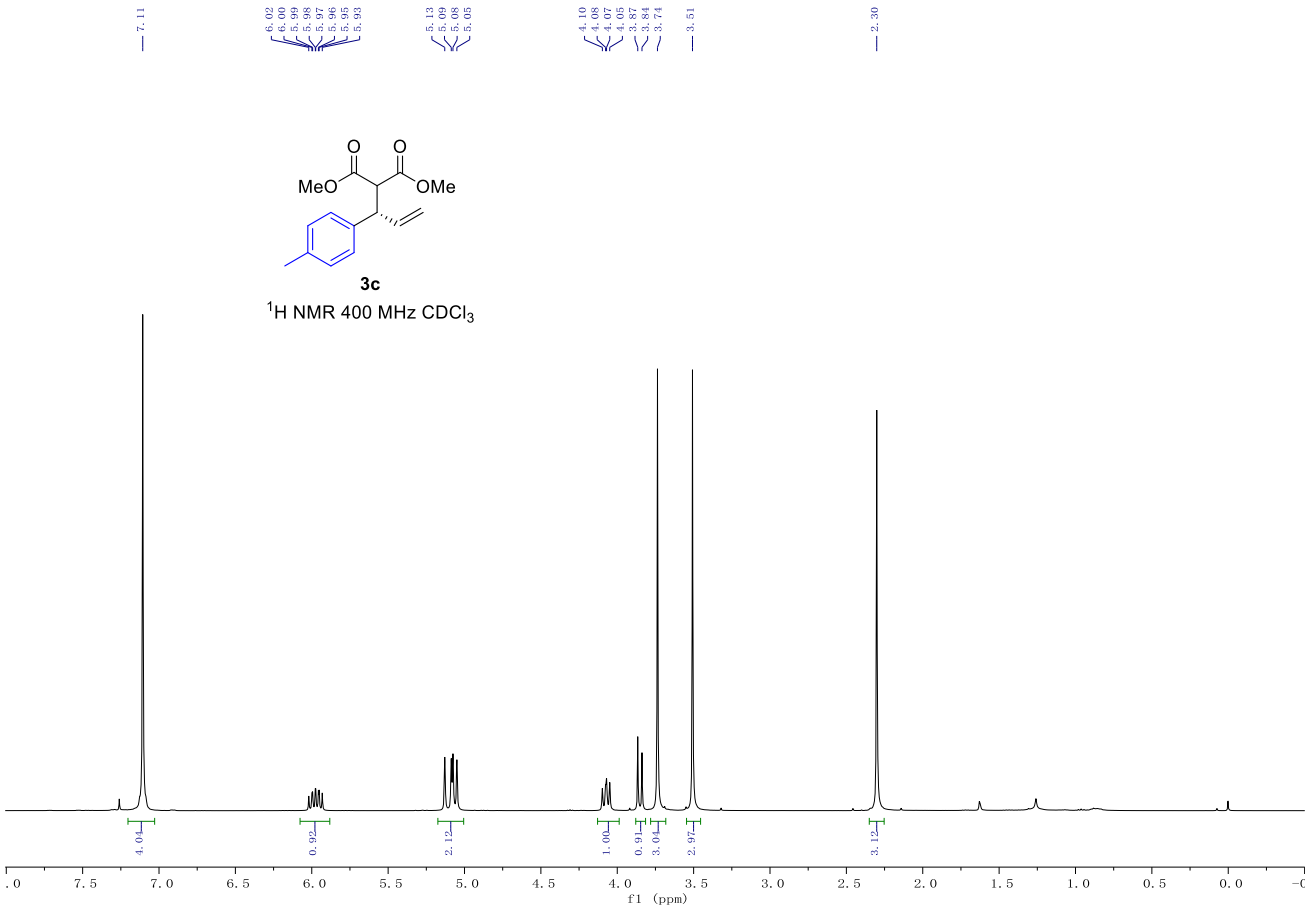


#	Time	Area	Height	Width	Area%	Symmetry
1	8.118	47.9	4.5	0.1633	1.815	0.93
2	8.736	2590	216.6	0.1855	98.185	0.789

Racemate of compond **3b**

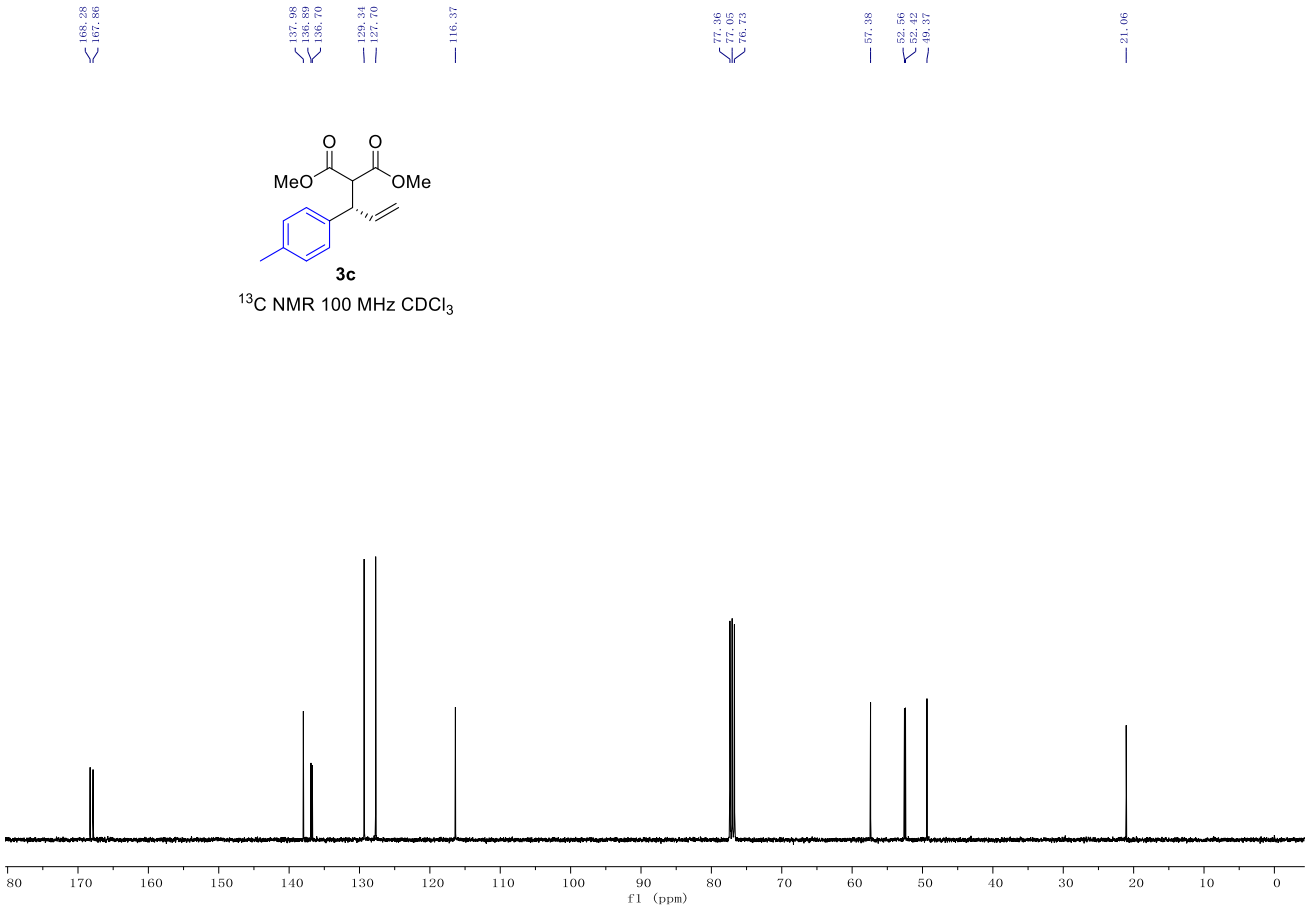


#	Time	Area	Height	Width	Area%	Symmetry
1	8.039	16127.4	1439.6	0.1727	49.731	0.647
2	8.67	16302.1	1310.9	0.1931	50.269	0.623



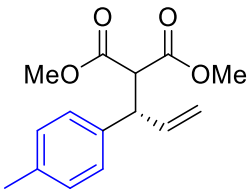
3c

^{1}H NMR 400 MHz $CDCl_3$



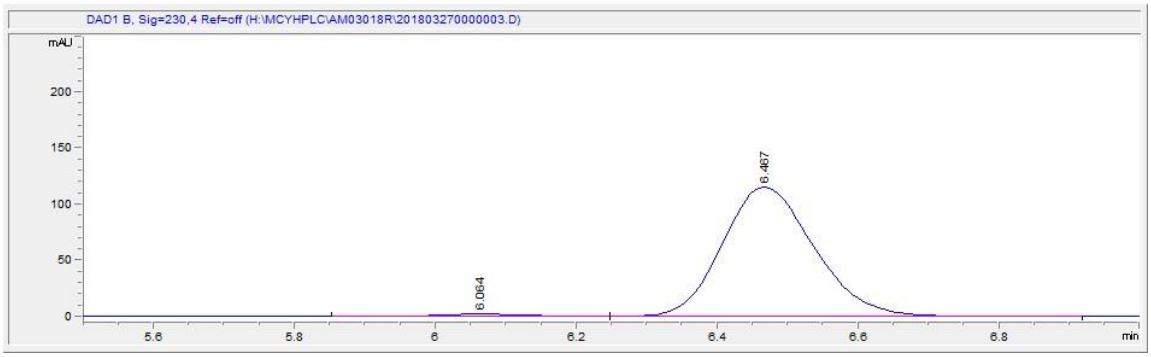
3c

^{13}C NMR 100 MHz $CDCl_3$



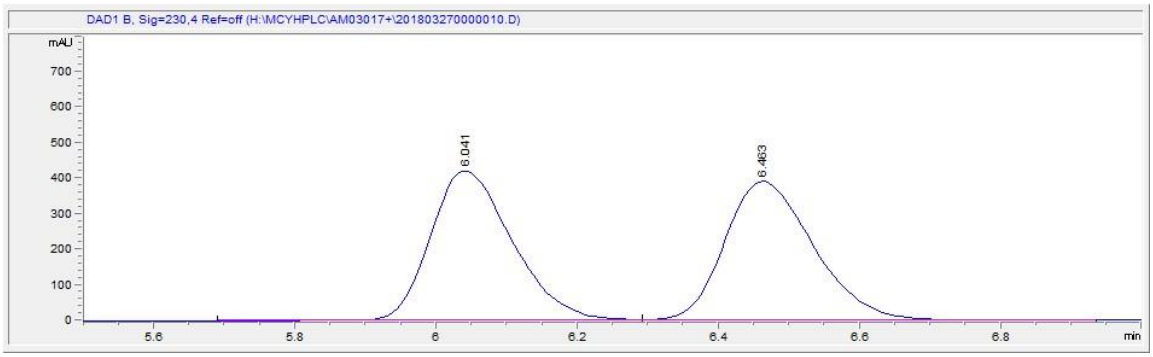
3c

Enantioenriched mixture of compound **3c**

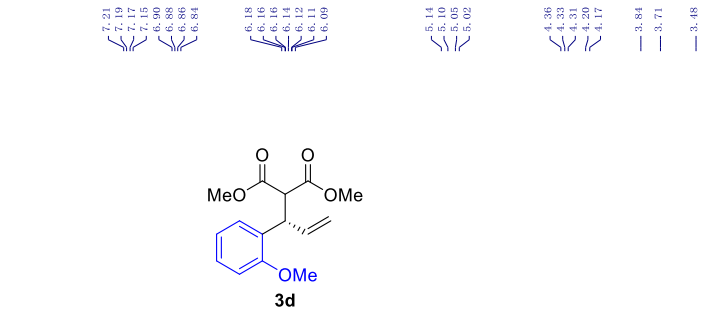


#	Time	Area	Height	Width	Area%	Symmetry
1	6.064	15.7	1.9	0.125	1.493	0.925
2	6.467	1038.6	115.1	0.1393	98.507	0.813

Racemate of compound **3c**

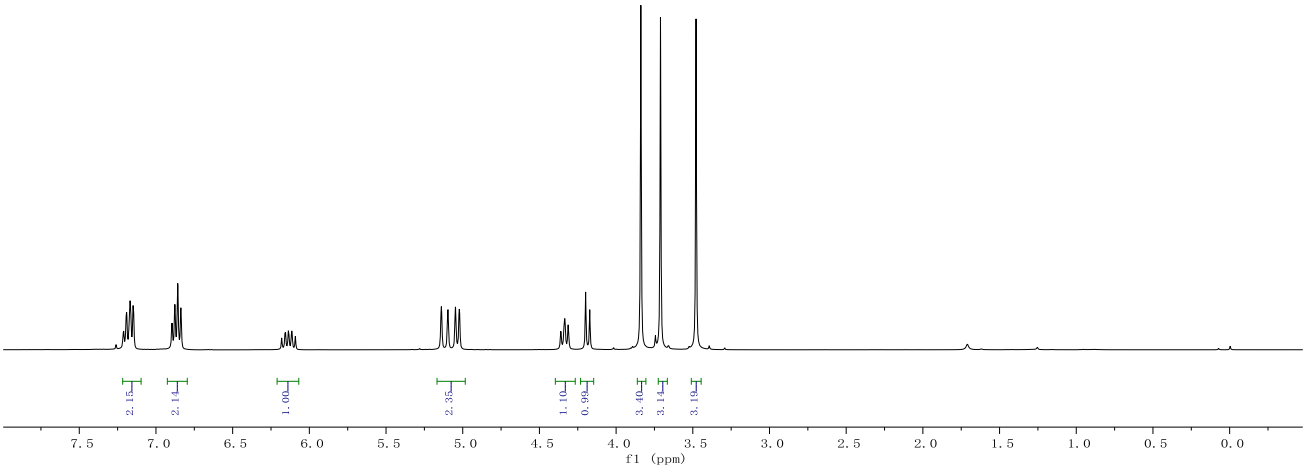


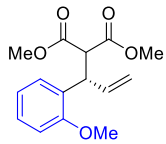
#	Time	Area	Height	Width	Area%	Symmetry
1	6.041	3342.8	419.3	0.123	49.756	0.703
2	6.463	3375.6	389.2	0.1352	50.244	0.717



3d

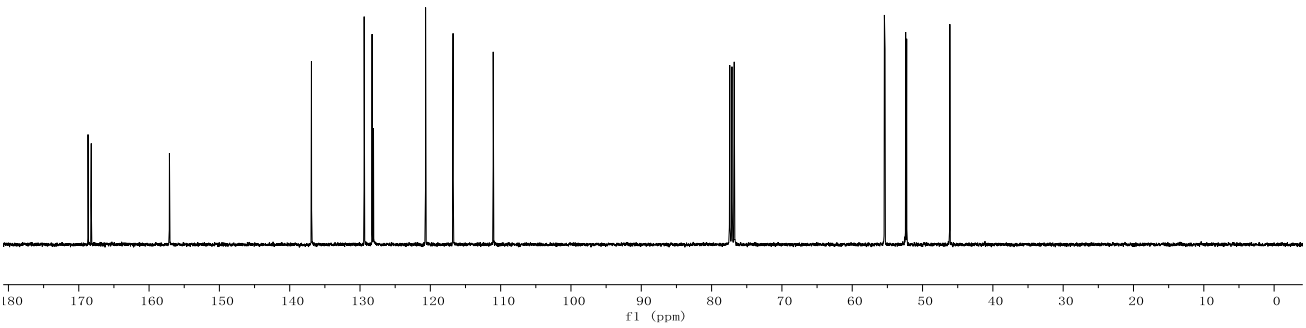
^{1}H NMR 400 MHz $CDCl_3$

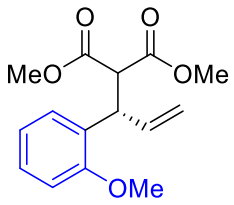




3d

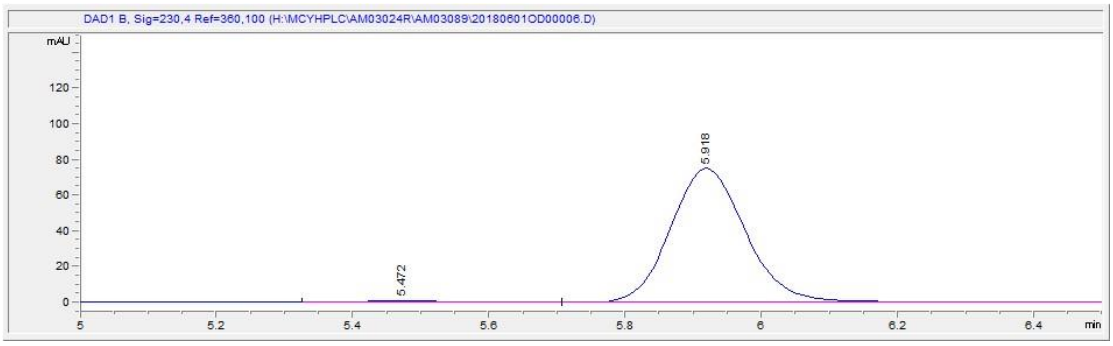
^{13}C NMR 100 MHz $CDCl_3$





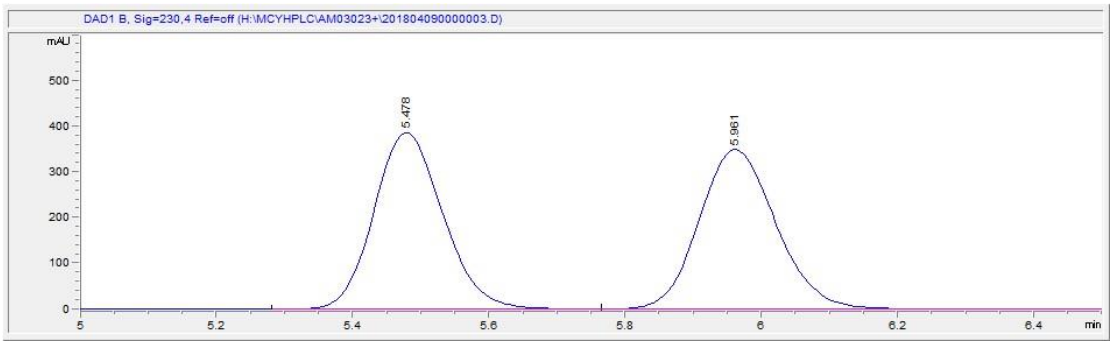
3d

Enantioenriched mixture of compound **3d**

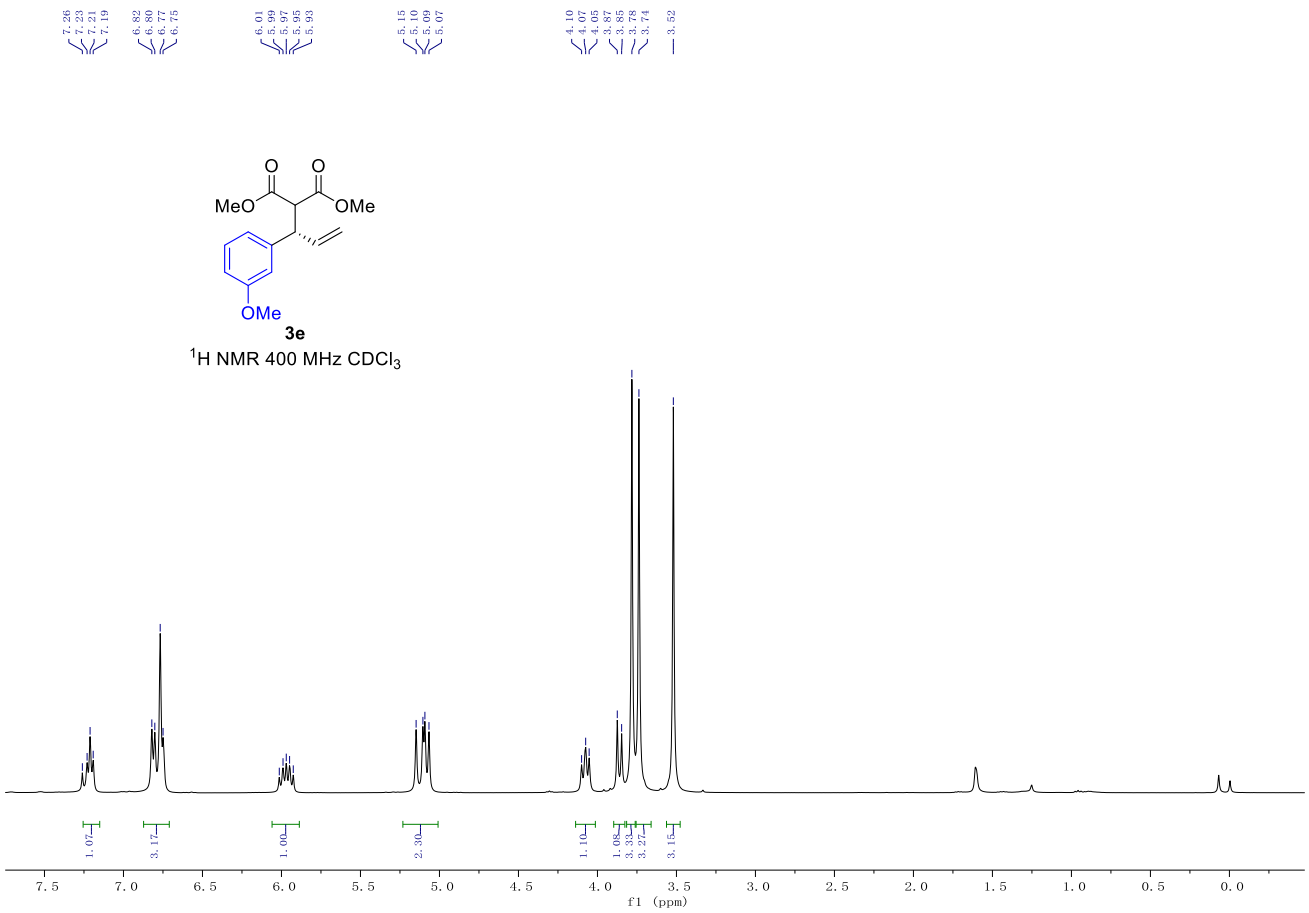


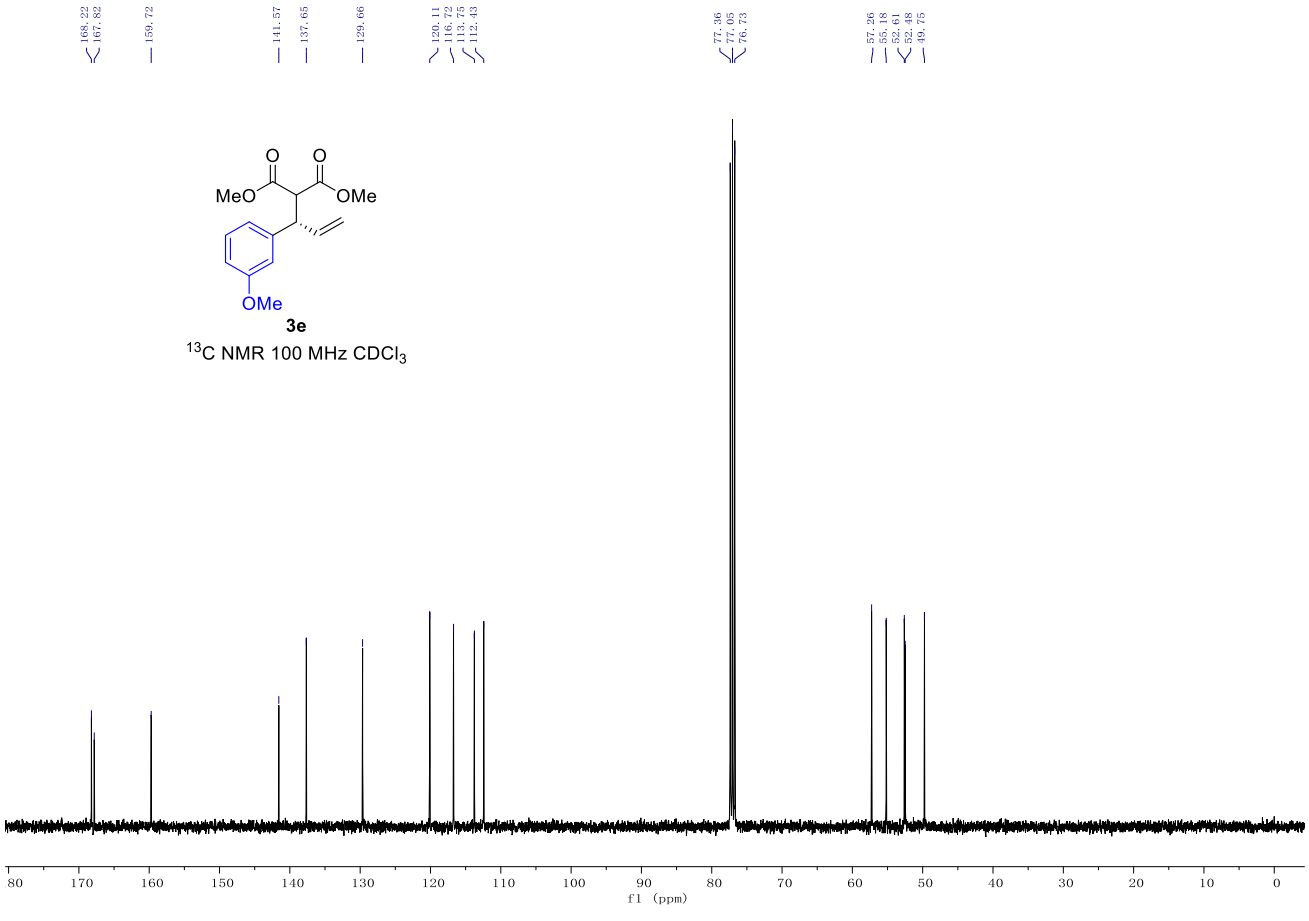
#	Time	Area	Height	Width	Area%	Symmetry
1	5.49	116.9	16.6	0.1082	1.895	0.873
2	5.947	6052.7	758.1	0.1252	98.105	0.786

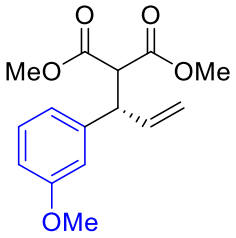
Racemate of compond **3d**



#	Time	Area	Height	Width	Area%	Symmetry
1	5.478	2709.8	386.4	0.1098	49.896	0.84
2	5.961	2721.1	349.4	0.1208	50.104	0.837

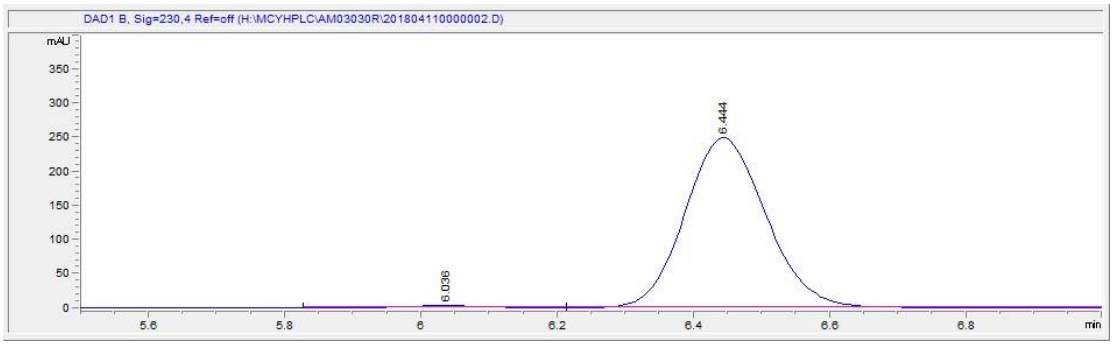

7.26
7.23
7.21
7.19
6.82
6.80
6.77
6.75
6.01
5.99
5.97
5.95
5.93
5.15
5.10
5.09
5.07
4.10
4.07
4.05
3.87
3.85
3.78
3.74
3.52
MeO
OMe
OMe
3e
1H NMR 400 MHz CDCl3
1.07
3.17
1.00
2.30
1.10
1.08
3.33
3.27
3.15
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.22
167.82
159.72
141.57
137.65
129.66
120.11
116.72
113.75
112.43
77.36
77.05
76.73
57.26
55.48
52.61
52.48
49.75
MeO
OMe
OMe
3e
13C NMR 100 MHz CDCl3
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



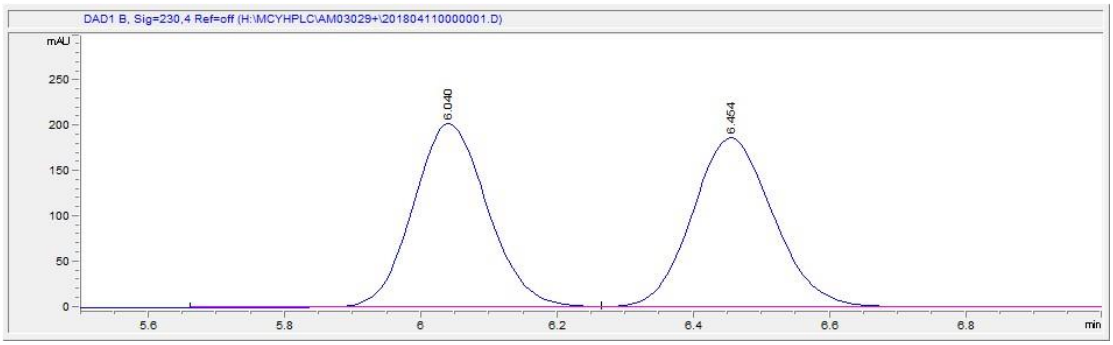
3e

Enantioenriched mixture of compound **3e**

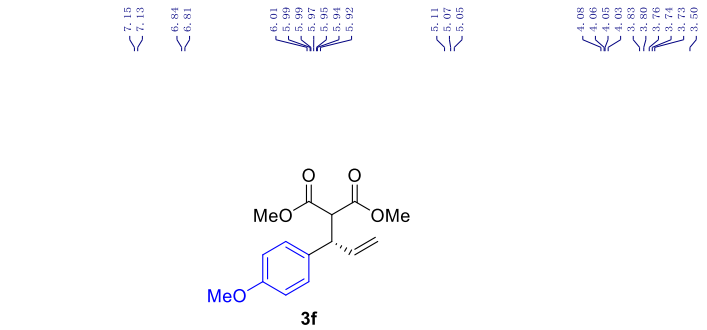


#	Time	Area	Height	Width	Area%	Symmetry
1	6.036	20.5	2.8	0.1141	0.987	0.957
2	6.444	2061.8	249.2	0.1285	99.013	0.862

Racemate of compond **3e**

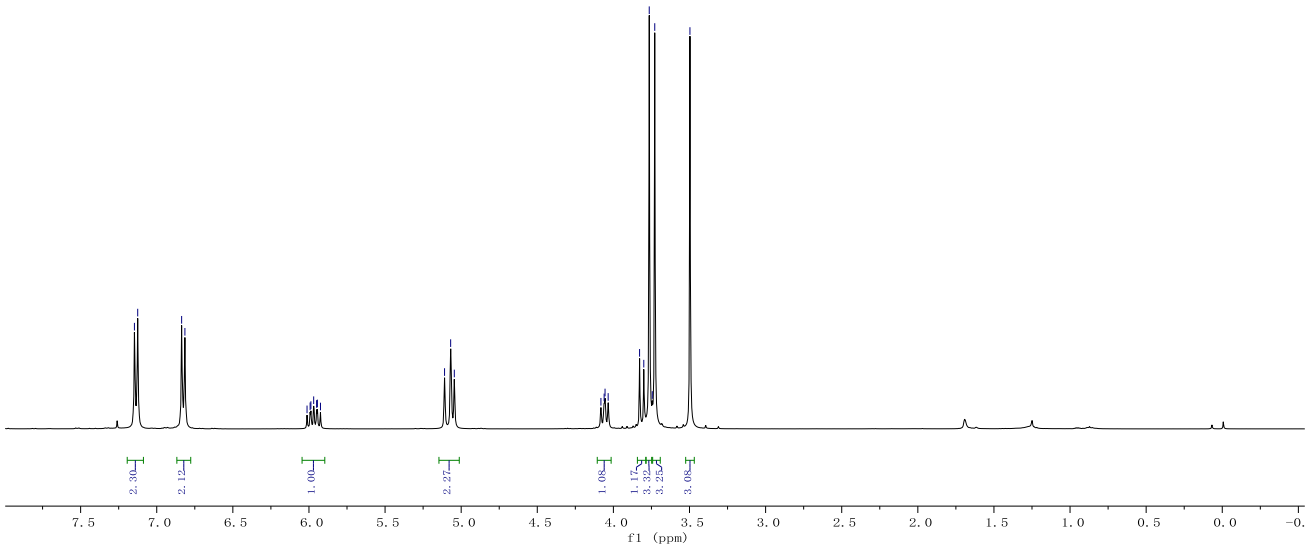


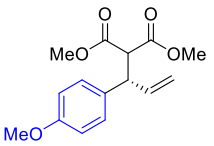
#	Time	Area	Height	Width	Area%	Symmetry
1	6.04	1526.4	202.2	0.1181	49.926	0.891
2	6.454	1531	186.1	0.128	50.074	0.869



3f

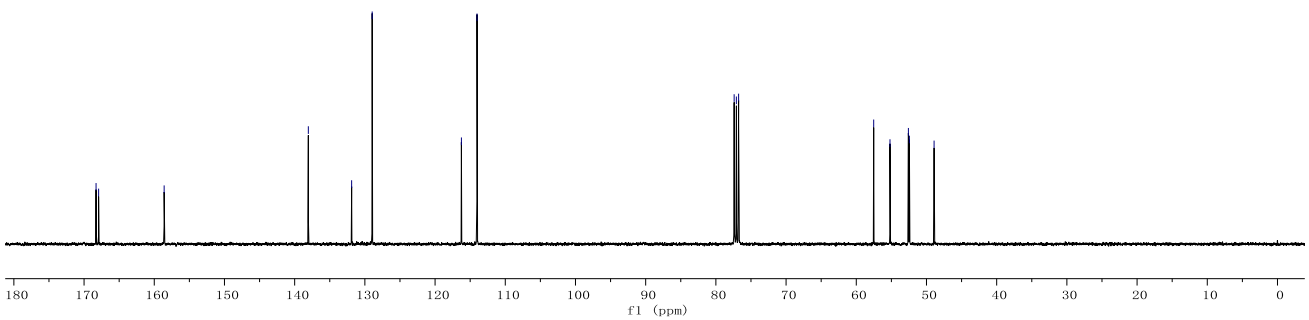
^{1}H NMR 400 MHz $CDCl_3$

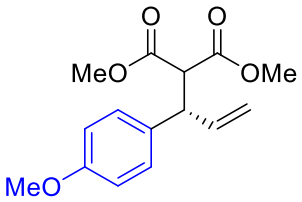




3f

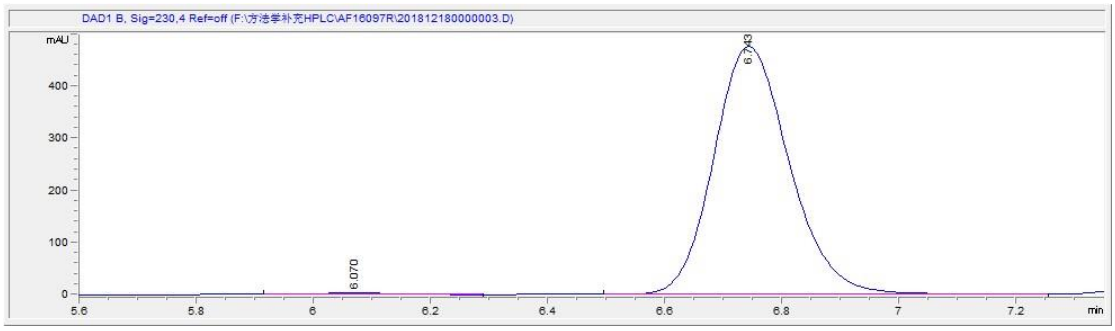
^{13}C NMR 100 MHz $CDCl_3$





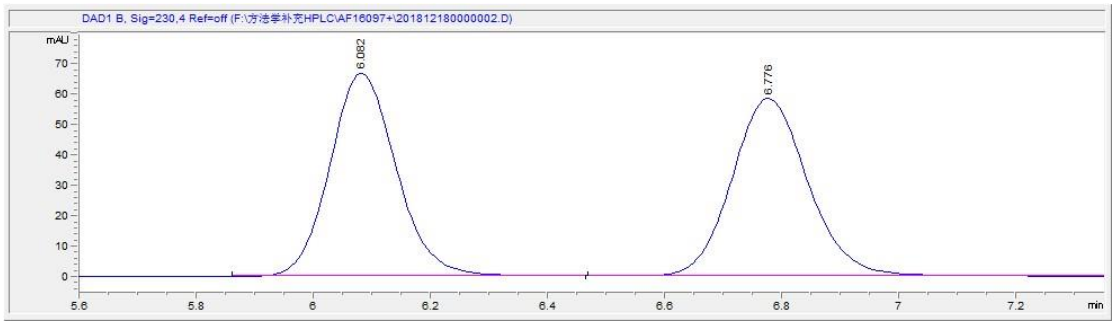
3f

Enantioenriched mixture of compound **3f**

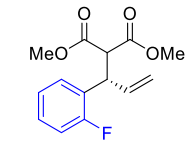


#	Time	Area	Height	Width	Area%	Symmetry
1	6.07	24	3.2	0.1182	0.559	0.903
2	6.743	4267.1	476.3	0.1385	99.441	0.812

Racemate of compond **3f**

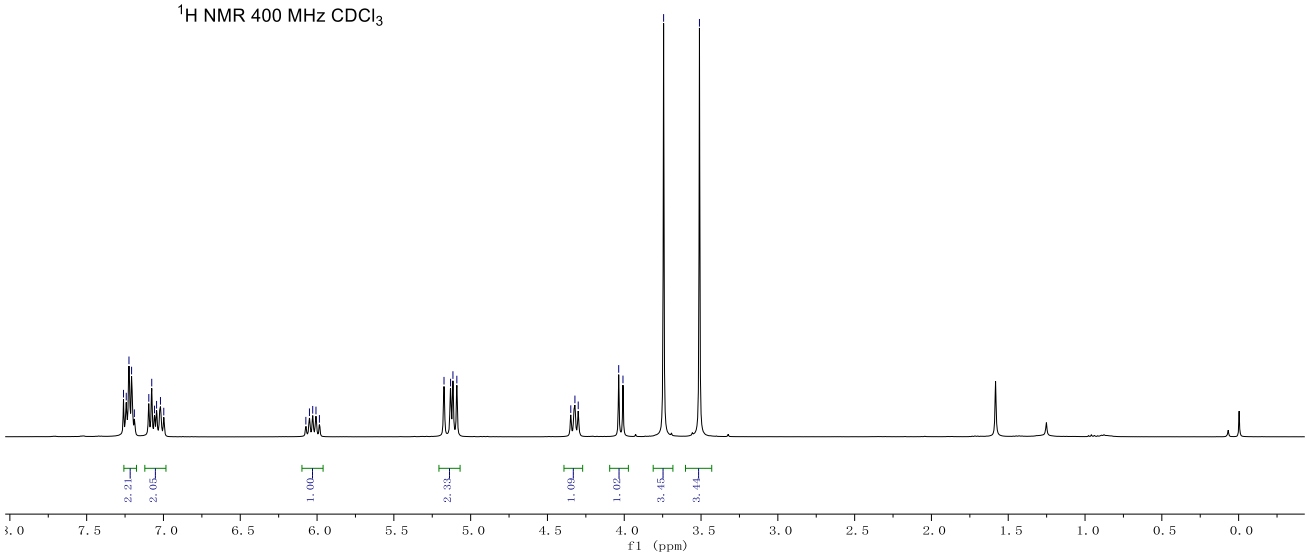


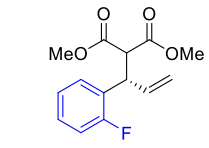
#	Time	Area	Height	Width	Area%	Symmetry
1	6.082	526	66.8	0.1218	49.951	0.869
2	6.776	527	58.4	0.1392	50.049	0.87



3g

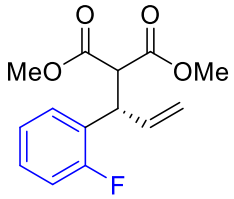
^{1}H NMR 400 MHz $CDCl_3$





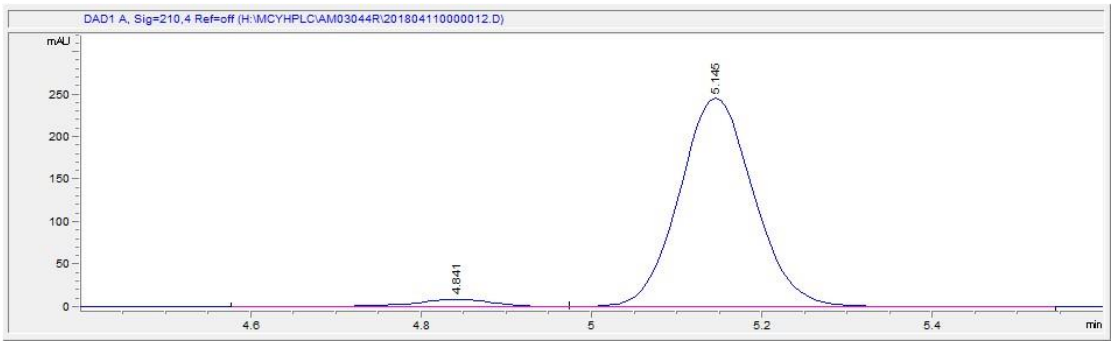
3g

^{13}C NMR 100 MHz $CDCl_3$



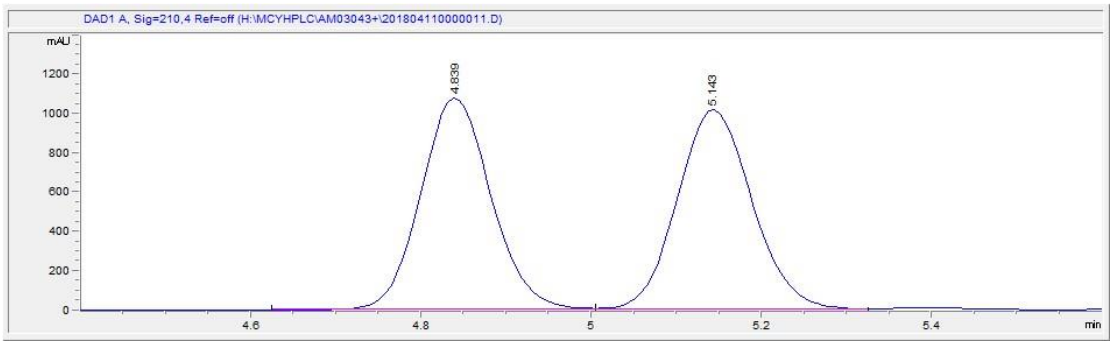
3g

Enantioenriched mixture of compound **3g**

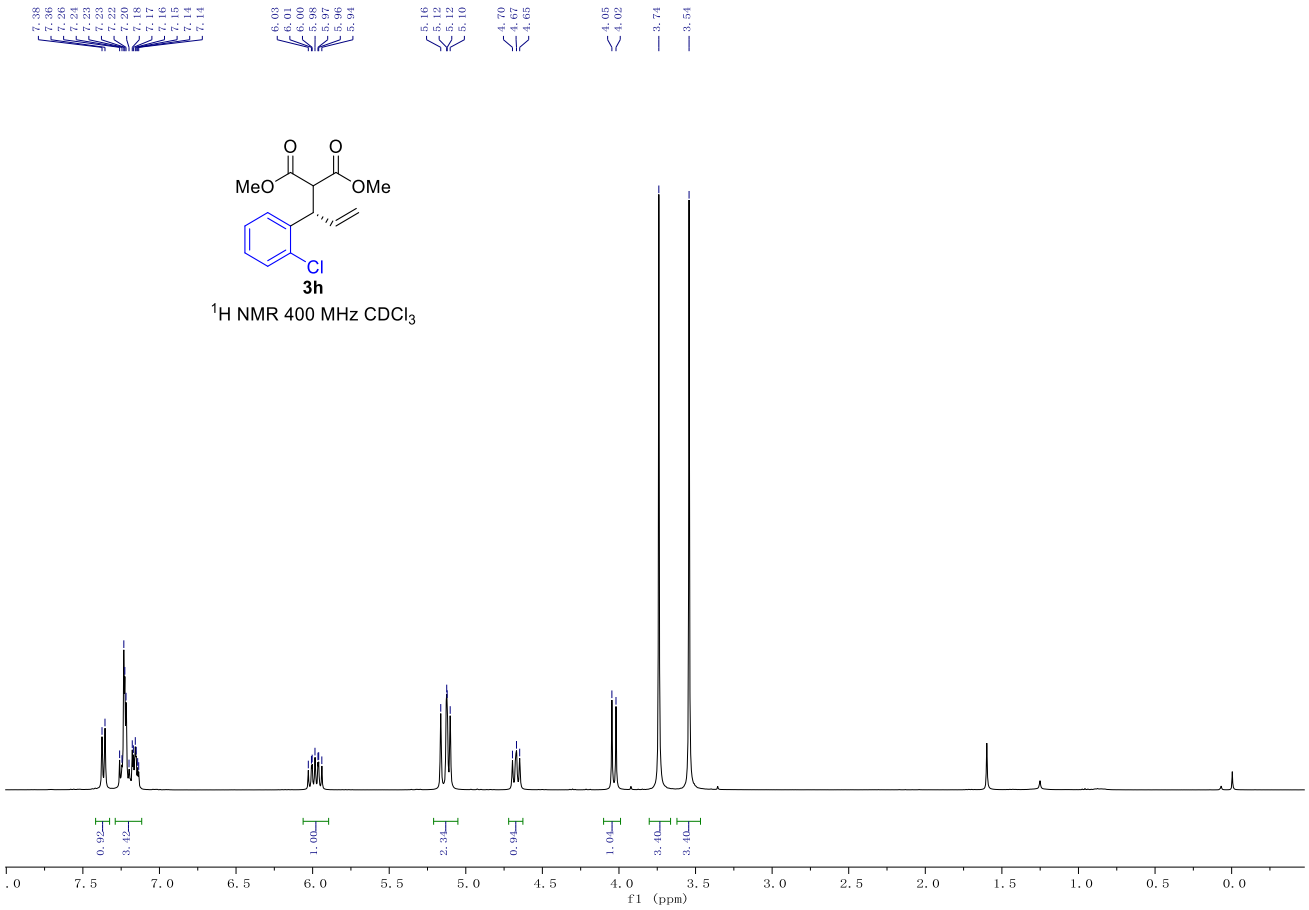


#	Time	Area	Height	Width	Area%	Symmetry
1	4.841	55.6	8.7	0.0965	3.601	1.243
2	5.145	1487.5	245.4	0.0927	96.399	0.907

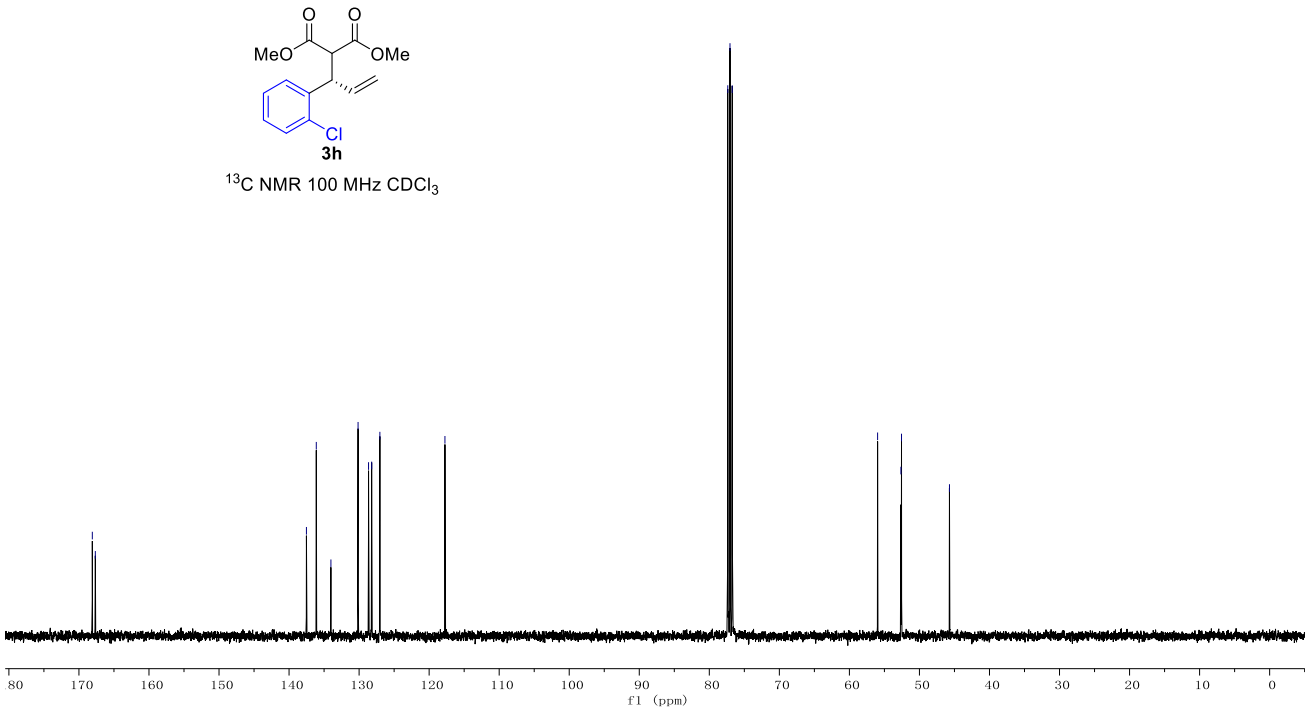
Racemate of compond **3g**



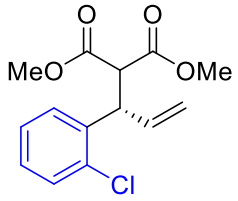
#	Time	Area	Height	Width	Area%	Symmetry
1	4.839	6117.6	1073.9	0.0885	49.986	0.904
2	5.143	6121.1	1010.7	0.0947	50.014	0.888



^{1}H NMR 400 MHz $CDCl_3$

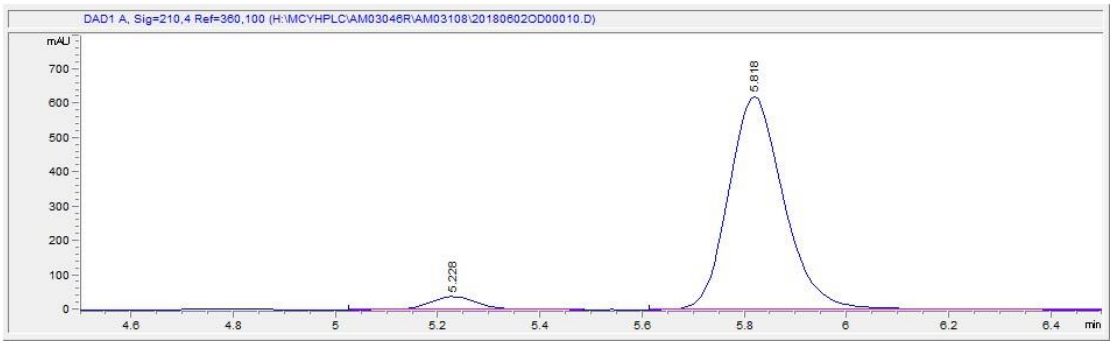


^{13}C NMR 100 MHz $CDCl_3$



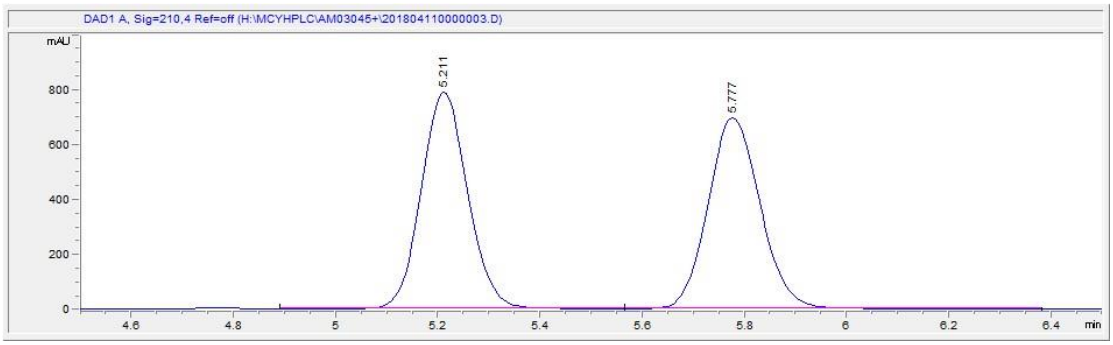
3h

Enantioenriched mixture of compound **3h**

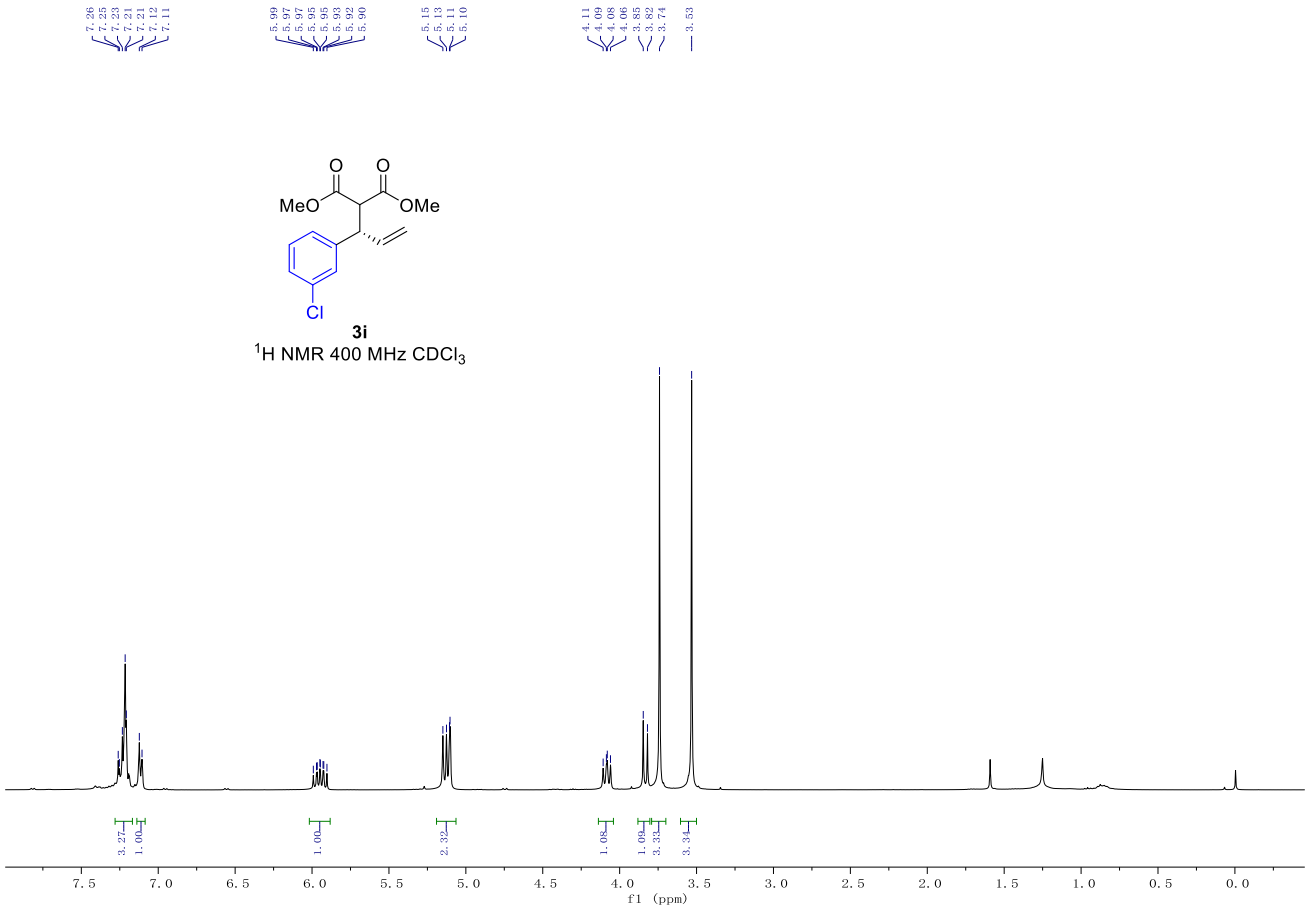


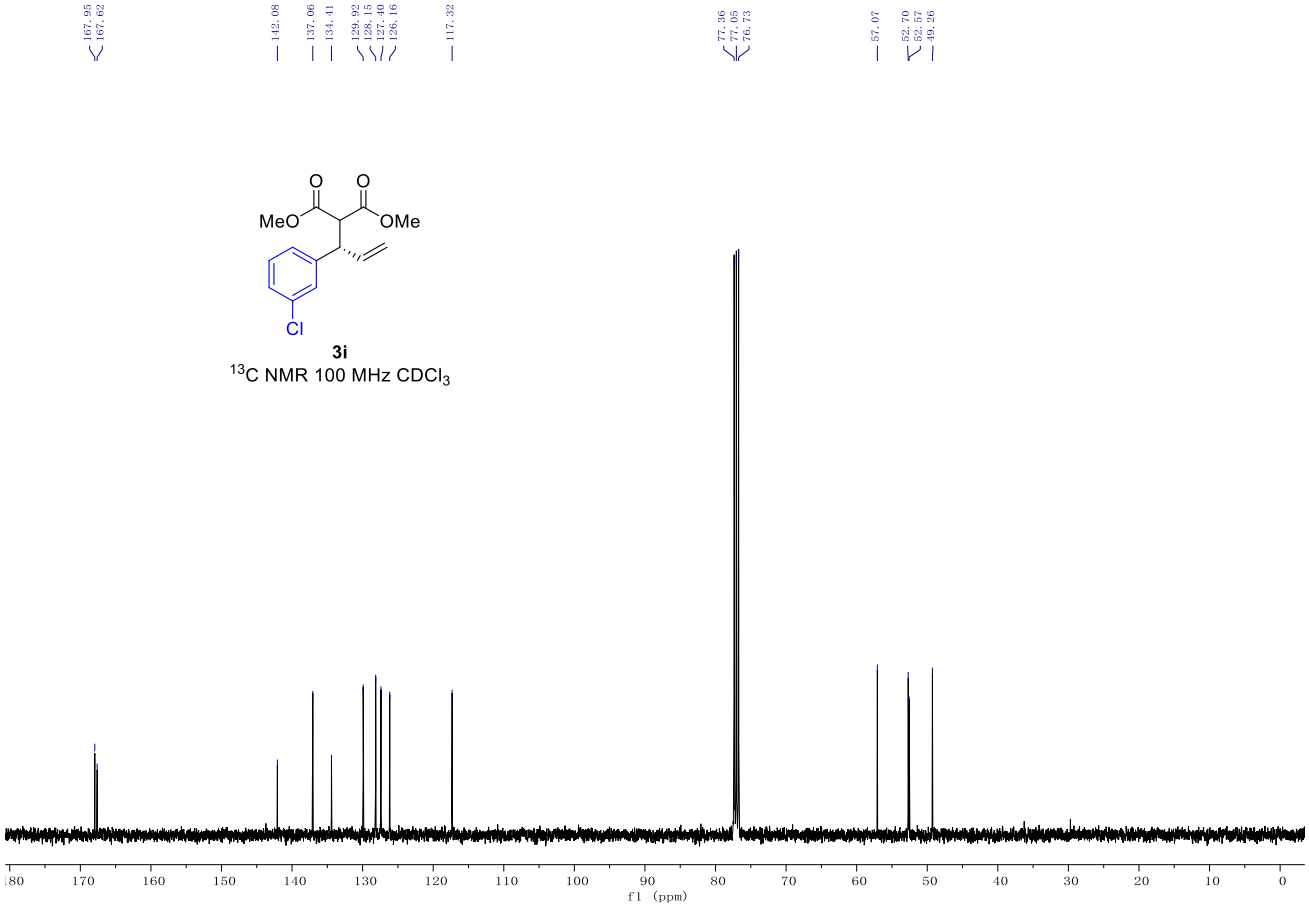
#	Time	Area	Height	Width	Area%	Symmetry
1	5.228	237.8	37.6	0.0978	4.854	0.889
2	5.818	4660.3	620.3	0.1156	95.146	0.8

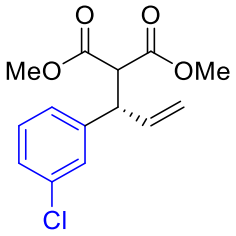
Racemate of compond **3h**



#	Time	Area	Height	Width	Area%	Symmetry
1	5.211	4965.6	788.6	0.0975	50.218	0.897
2	5.777	4922.5	696.1	0.1105	49.782	0.867

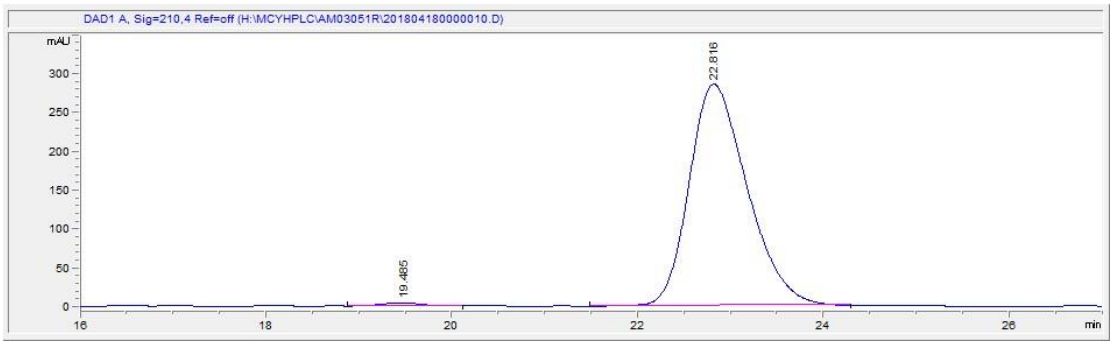

7.26
7.25
7.23
7.21
7.13
7.11
5.99
5.97
5.97
5.95
5.95
5.93
5.92
5.90
5.15
5.13
5.11
5.10
4.11
4.09
4.08
4.06
3.85
3.82
3.74
3.53
MeO
OMe
Cl
3i
1H NMR 400 MHz CDCl3
3.27
1.00
1.00
2.32
1.08
1.09
3.33
3.34
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.95
167.62
142.08
137.06
134.41
129.92
128.15
127.40
126.16
117.32
77.36
77.05
76.73
57.07
52.70
52.57
49.26
MeO
OMe
Cl
3i
13C NMR 100 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



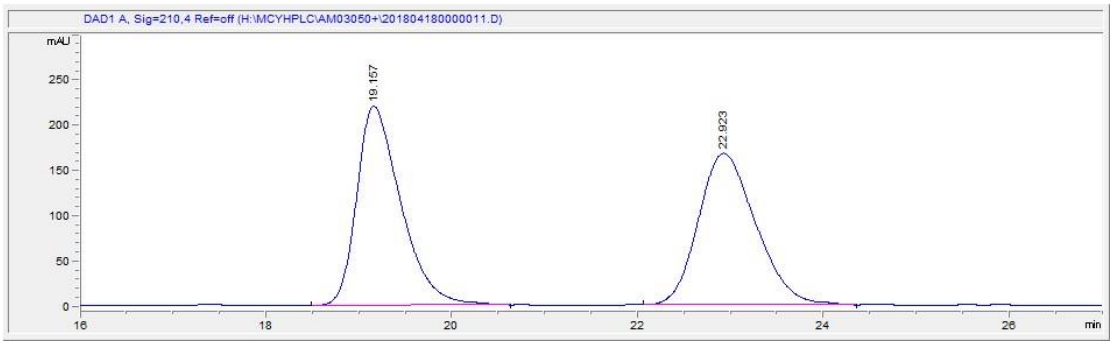
3i

Enantioenriched mixture of compound **3i**

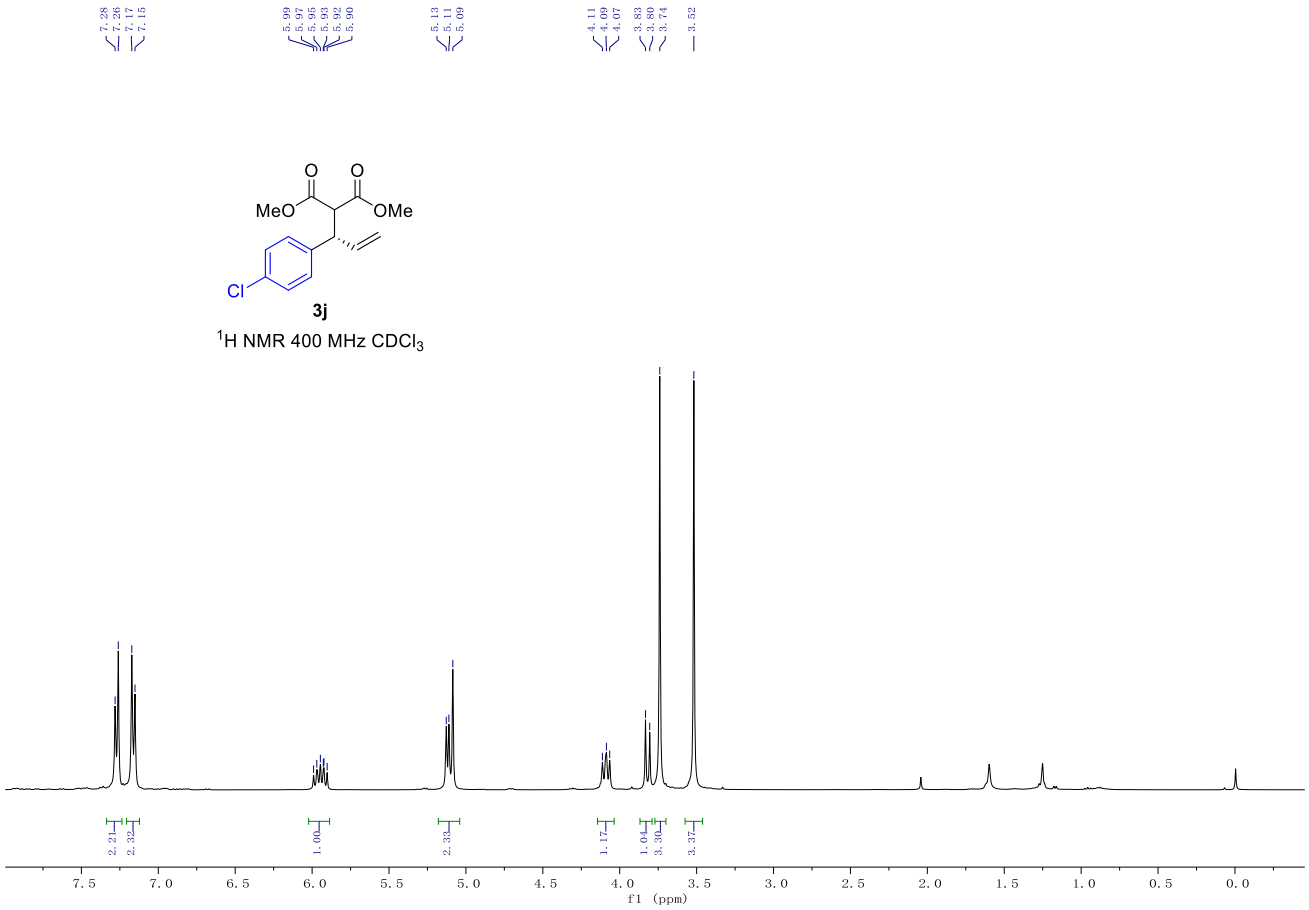


#	Time	Area	Height	Width	Area%	Symmetry
1	19.485	117.5	3.8	0.4184	0.937	1.274
2	22.816	12422.7	285.1	0.6704	99.063	0.7

Racemate of compond **3i**

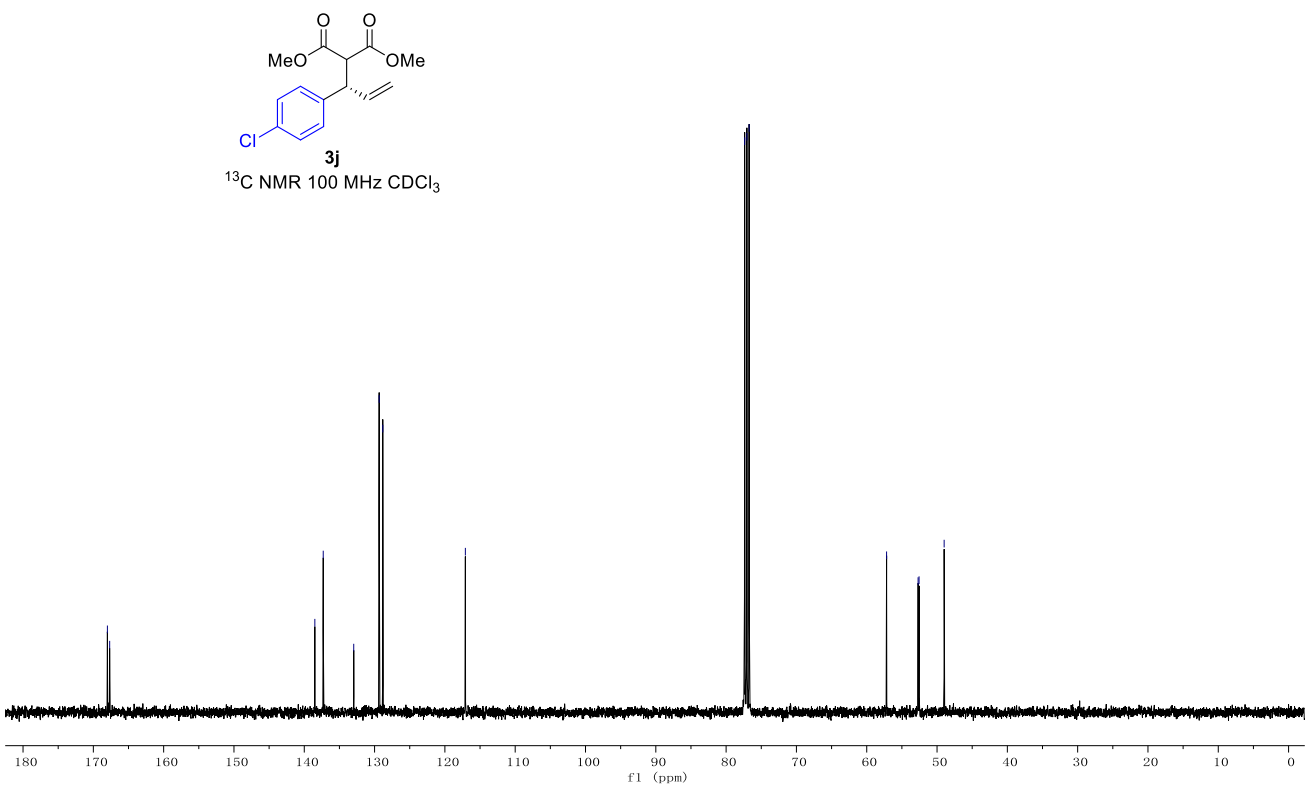


#	Time	Area	Height	Width	Area%	Symmetry
1	19.157	7257.5	219.9	0.493	50.270	0.596
2	22.923	7179.6	167.4	0.6524	49.730	0.754



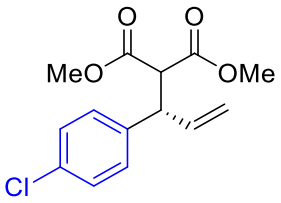
3j

^{1}H NMR 400 MHz $CDCl_3$



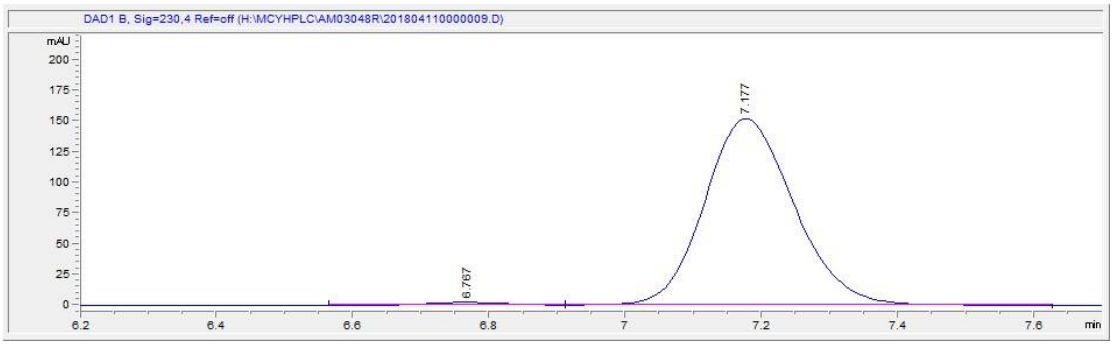
3j

^{13}C NMR 100 MHz $CDCl_3$



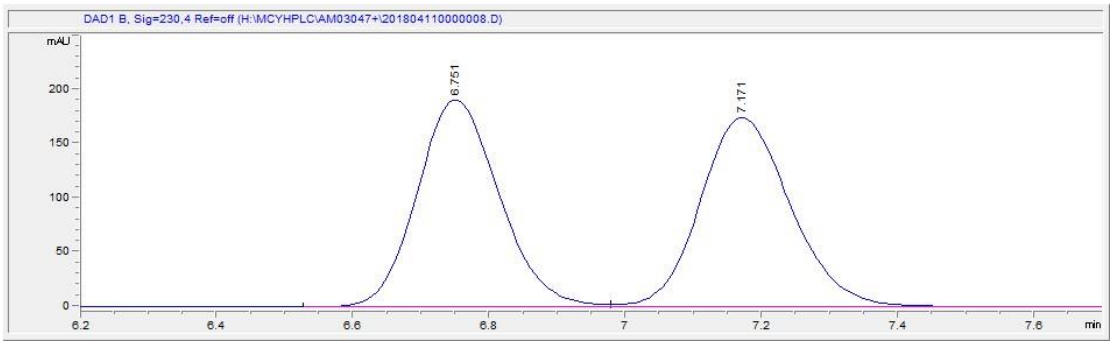
3j

Enantioenriched mixture of compound **3j**

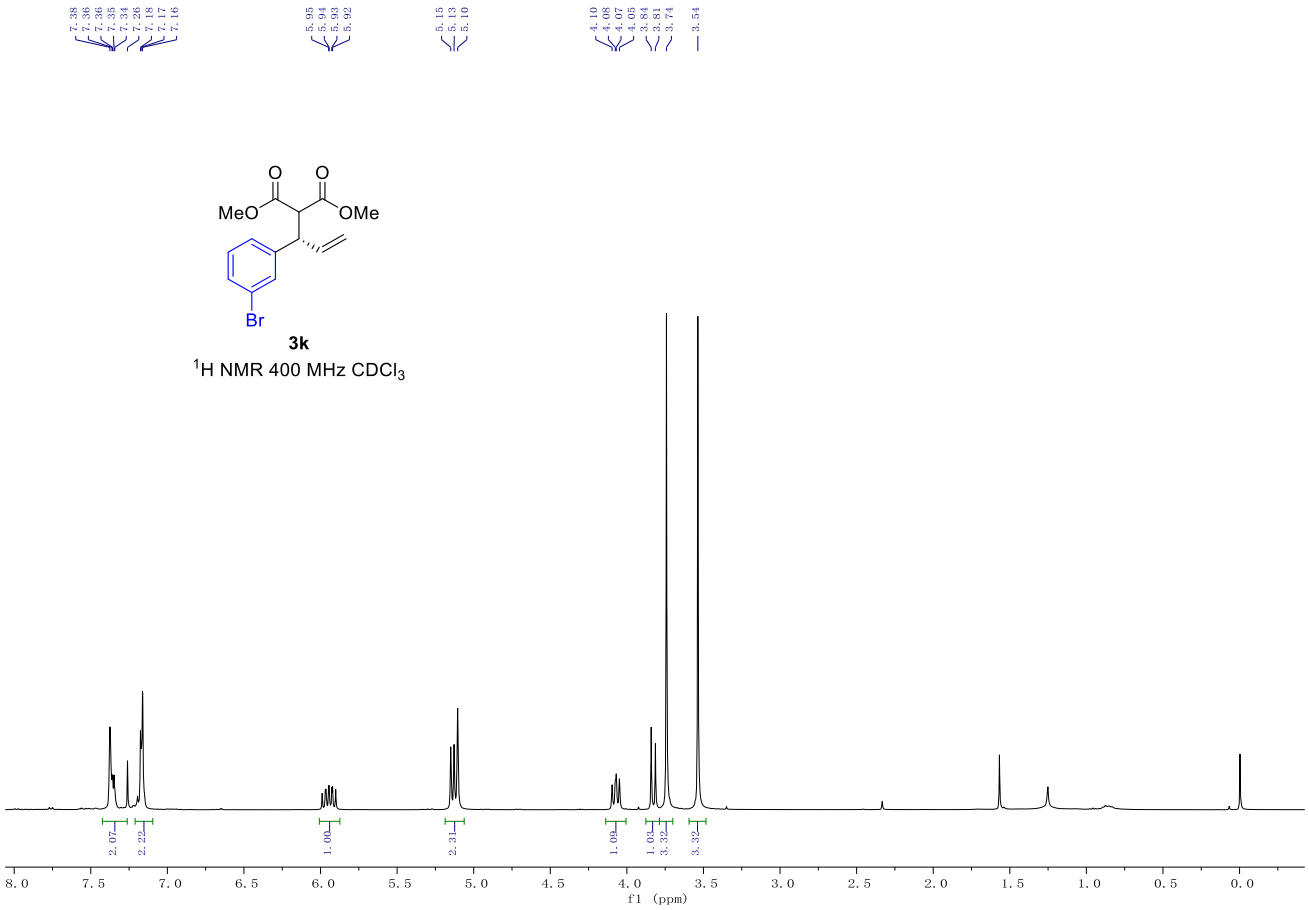


#	Time	Area	Height	Width	Area%	Symmetry
1	6.767	17.5	2.3	0.1219	1.249	1.023
2	7.177	1385.8	151.8	0.1405	98.751	0.826

Racemate of compond **3j**

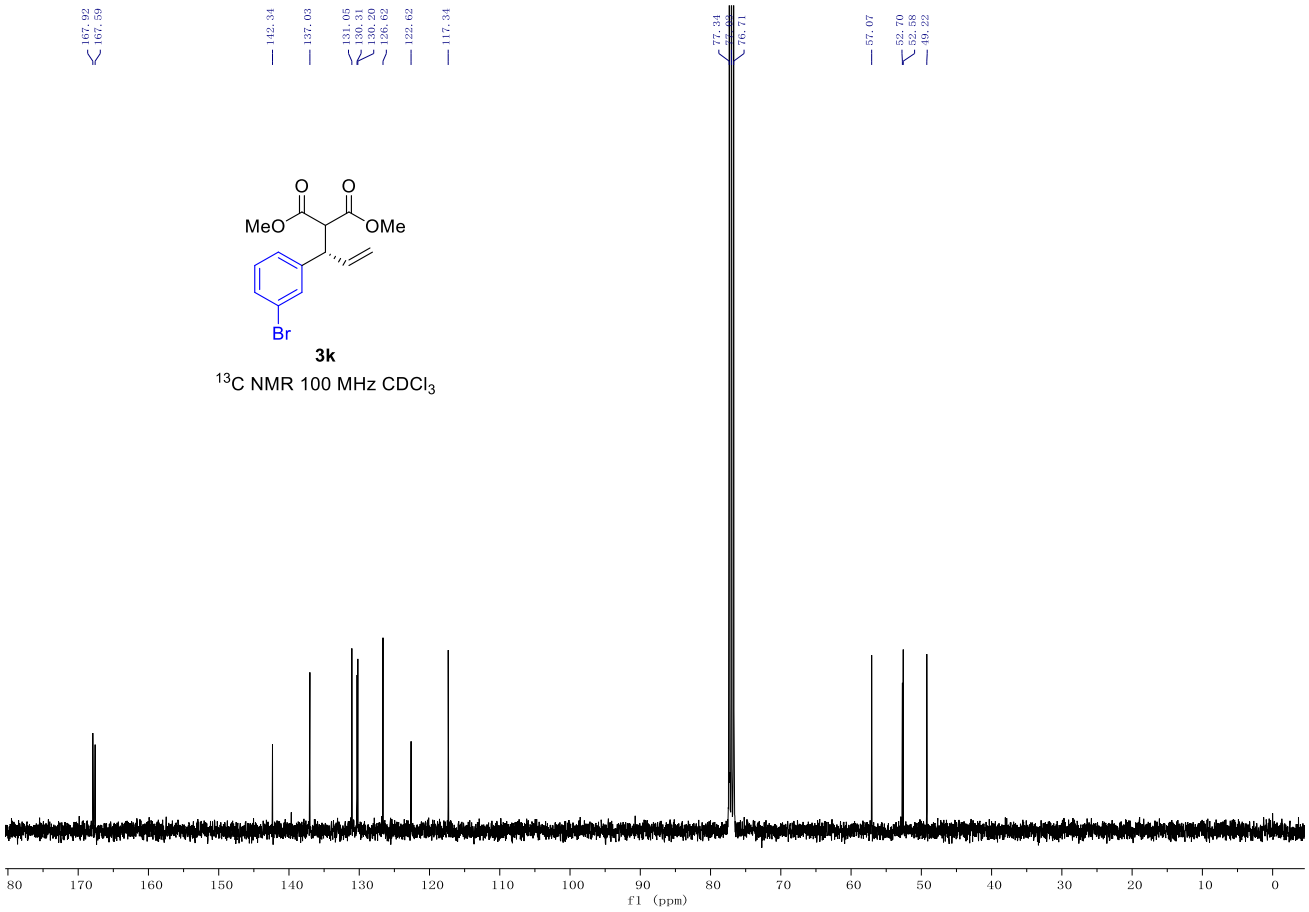


#	Time	Area	Height	Width	Area%	Symmetry
1	6.751	1573	190.2	0.1285	49.971	0.861
2	7.171	1574.8	173.7	0.1418	50.029	0.815



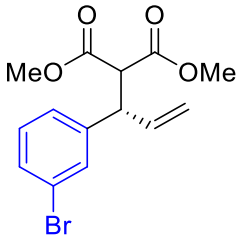
3k

^{1}H NMR 400 MHz $CDCl_3$



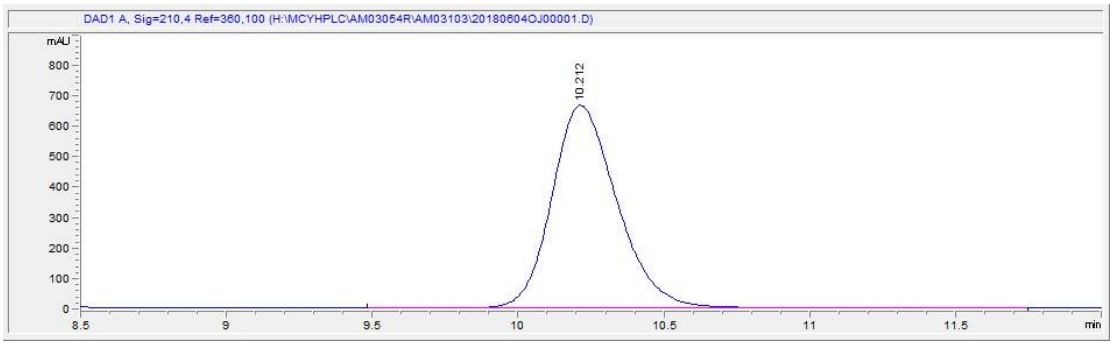
3k

^{13}C NMR 100 MHz $CDCl_3$



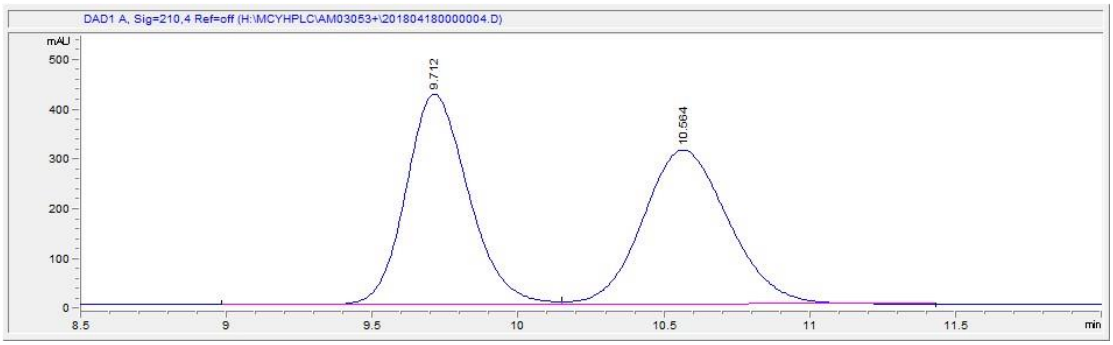
3k

Enantioenriched mixture of compound **3k**

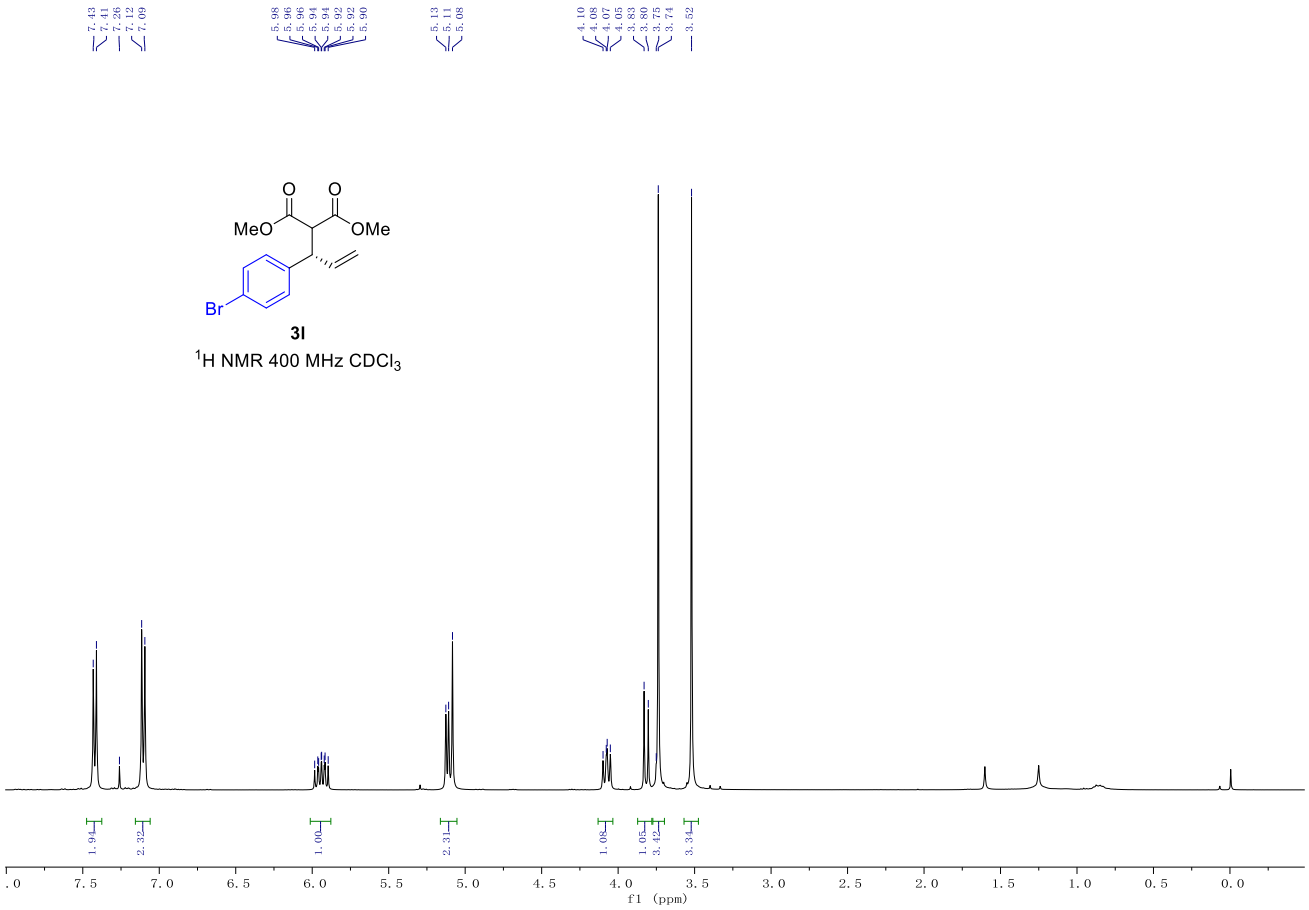


#	Time	Area	Height	Width	Area%	Symmetry
1	10.212	10388	664.4	0.2404	100.000	0.741

Racemate of compond **3k**

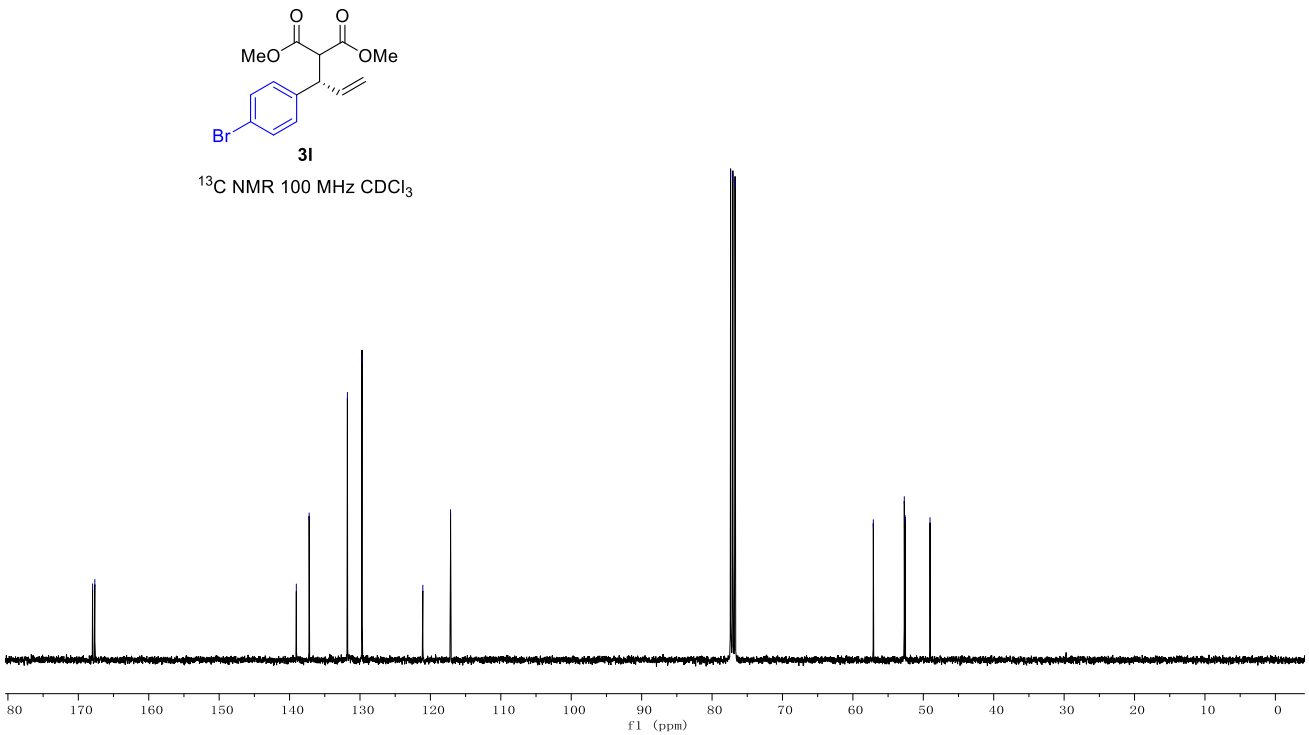


#	Time	Area	Height	Width	Area%	Symmetry
1	9.712	6140.3	420.2	0.2265	49.909	0.818
2	10.564	6162.5	306.4	0.3126	50.091	0.844



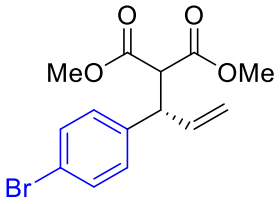
3l

^{1}H NMR 400 MHz $CDCl_3$



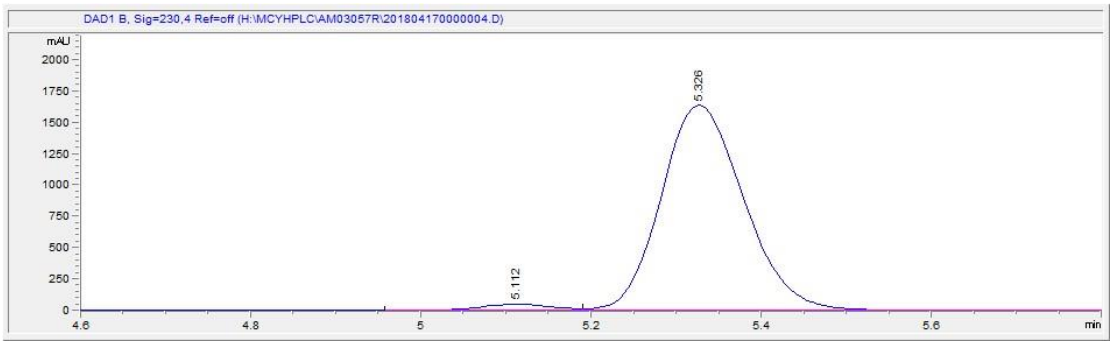
3l

^{13}C NMR 100 MHz $CDCl_3$



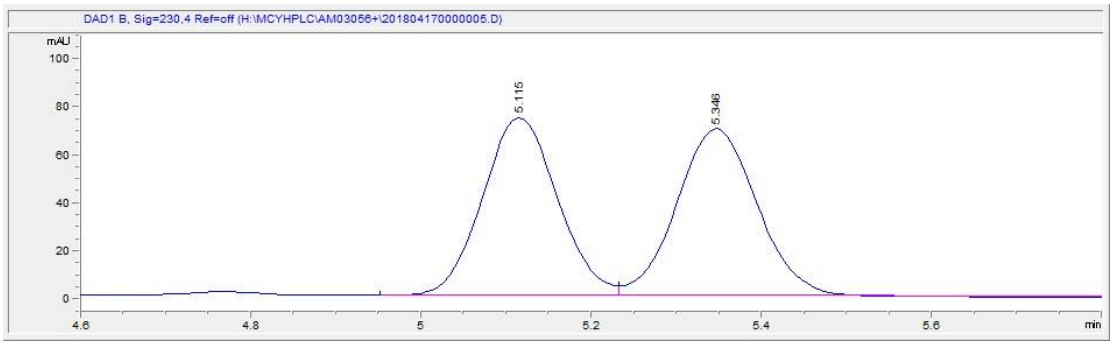
3l

Enantioenriched mixture of compound **3l**

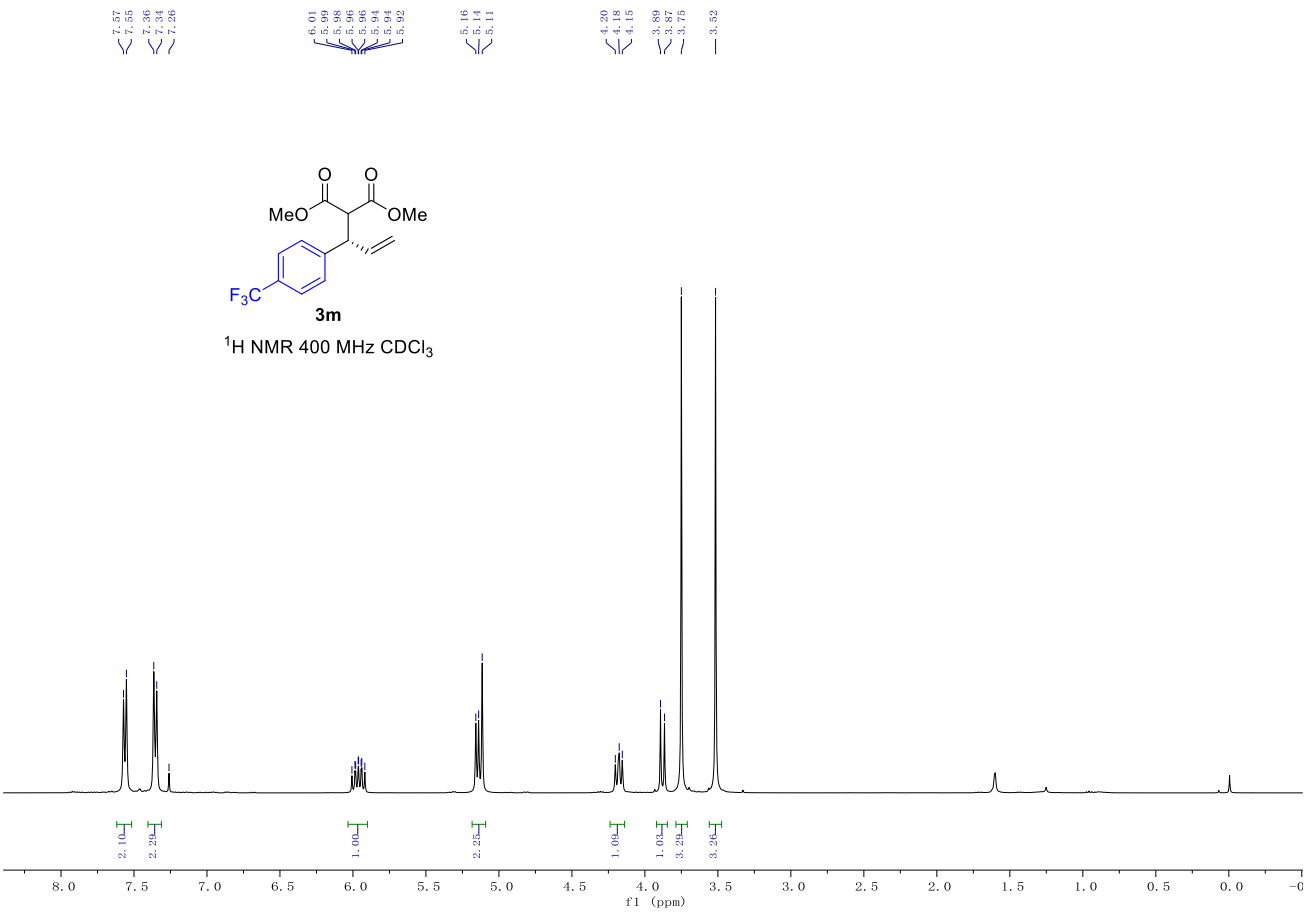


#	Time	Area	Height	Width	Area%	Symmetry
1	5.112	213.4	41.3	0.0843	1.927	1.164
2	5.326	10863.3	1629.3	0.1038	98.073	0.808

Racemate of compond **3l**

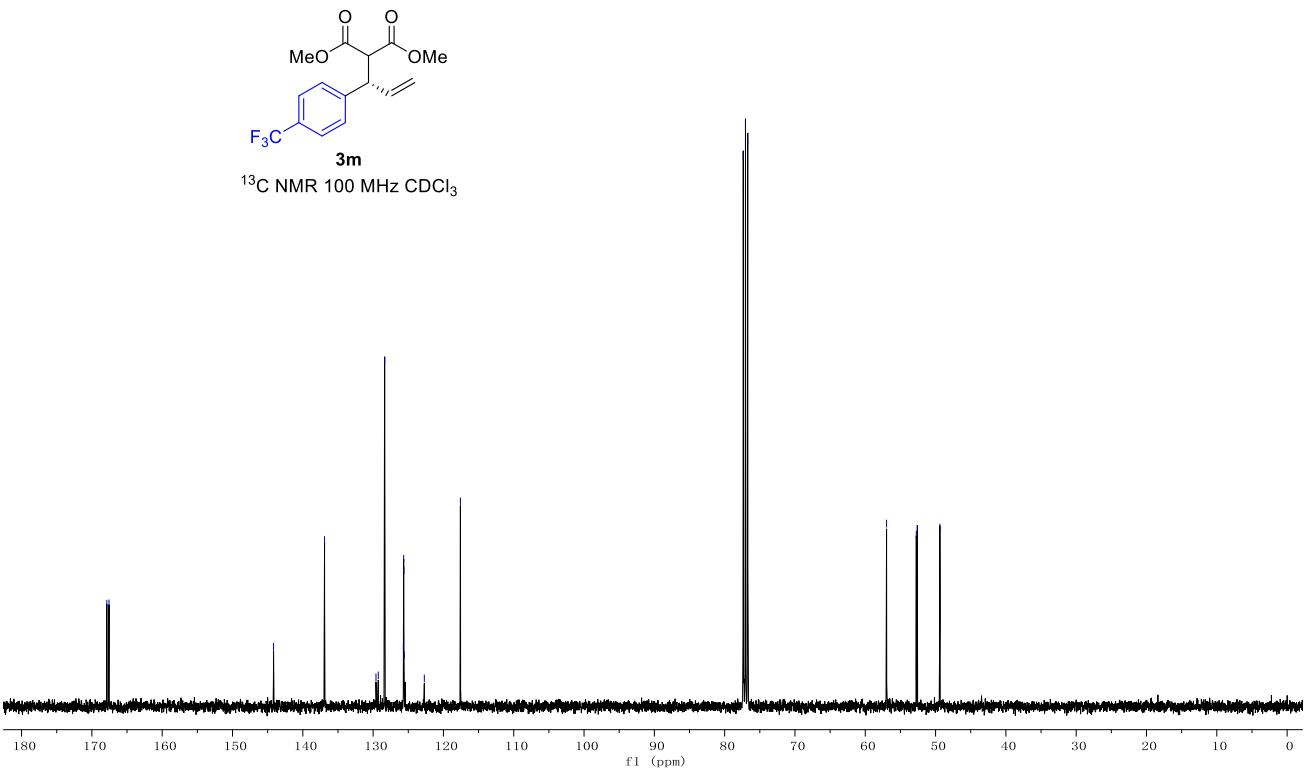


#	Time	Area	Height	Width	Area%	Symmetry
1	5.115	421.7	71.9	0.0924	50.086	0.974
2	5.346	420.3	67.2	0.099	49.914	0.878



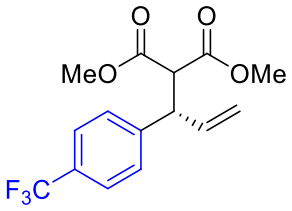
3m

^{1}H NMR 400 MHz $CDCl_3$



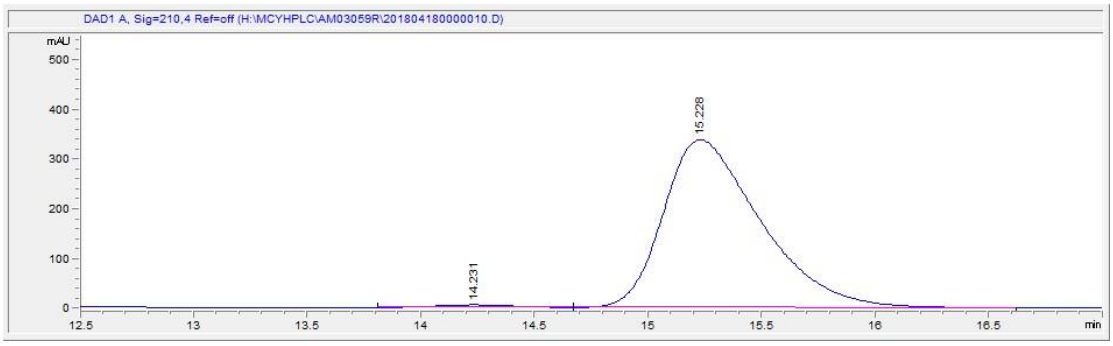
3m

^{13}C NMR 100 MHz $CDCl_3$



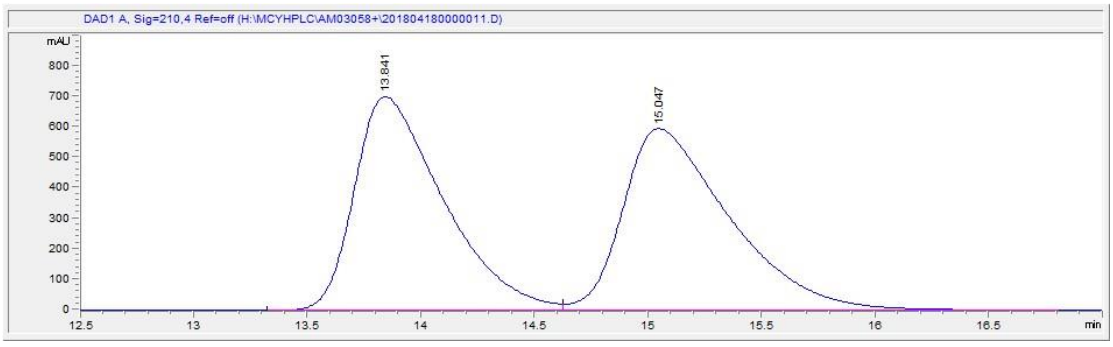
3m

Enantioenriched mixture of compound **3m**

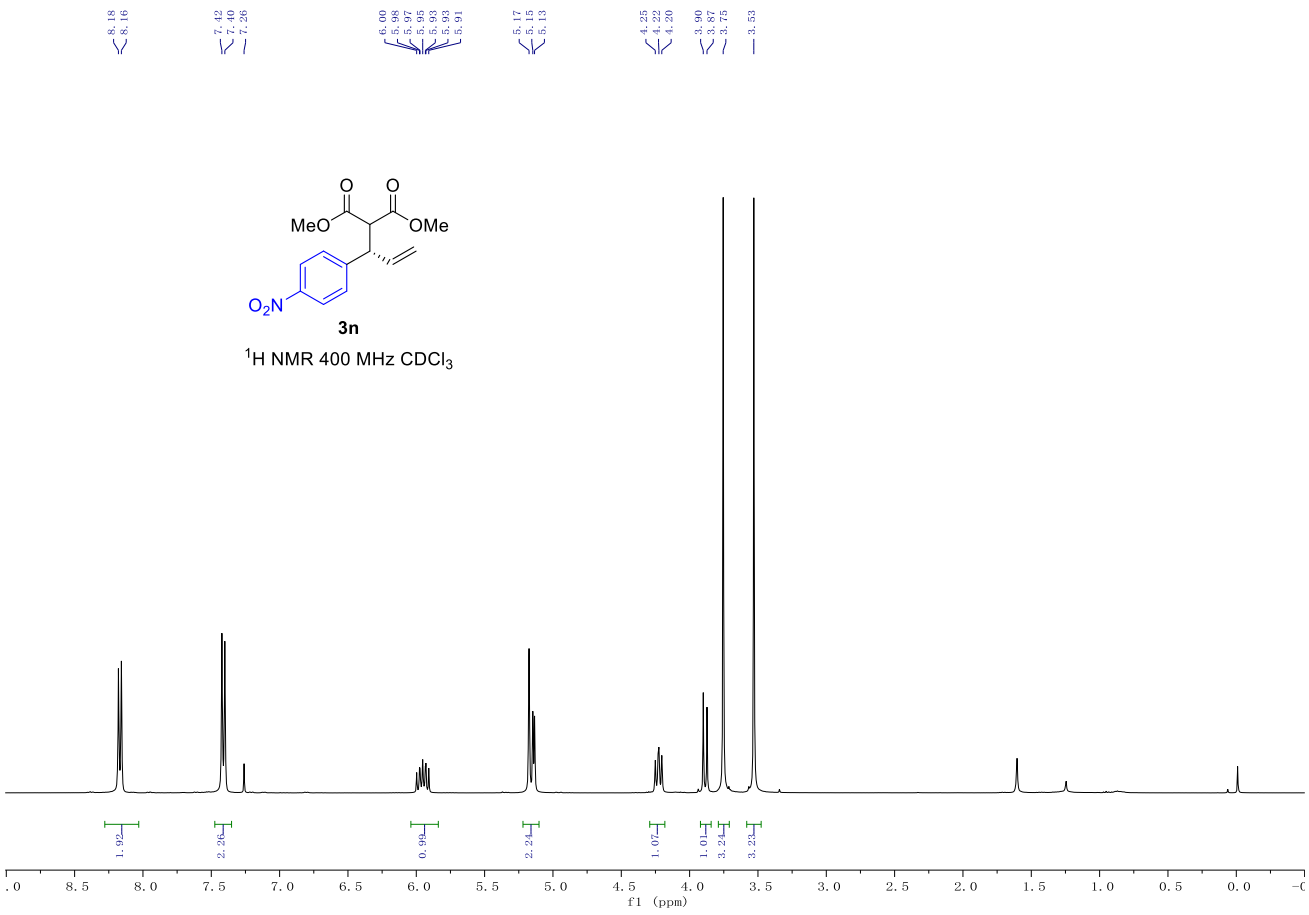


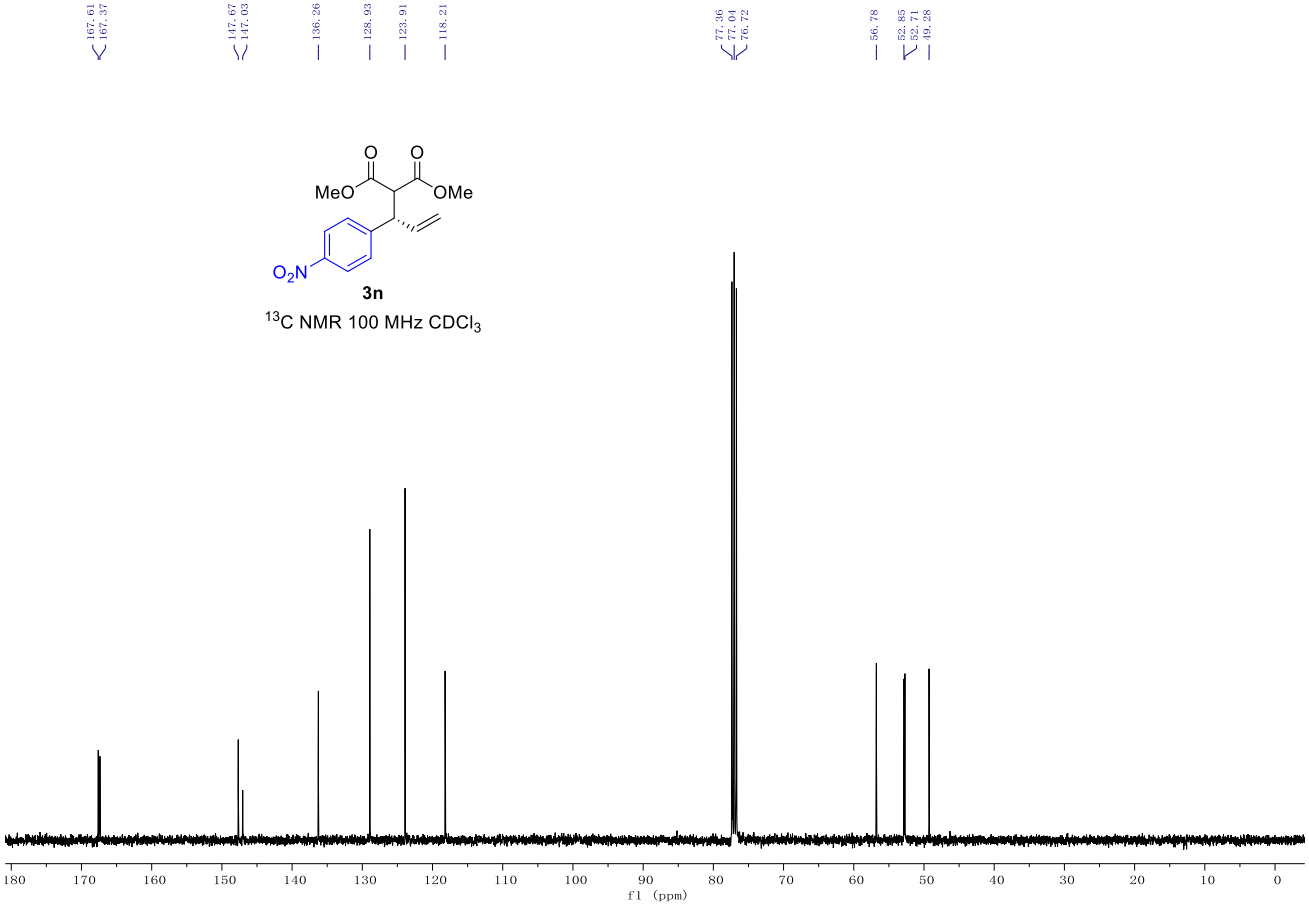
#	Time	Area	Height	Width	Area%	Symmetry
1	14.231	115.2	5.2	0.3526	1.130	0.916
2	15.228	10074.5	337.1	0.4507	98.870	0.57

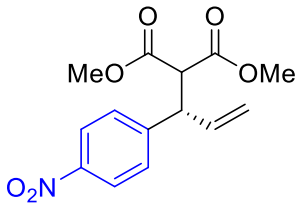
Racemate of compond **3m**



#	Time	Area	Height	Width	Area%	Symmetry
1	13.841	18313.1	692.1	0.3967	50.106	0.521
2	15.047	18235.3	579	0.4674	49.894	0.476

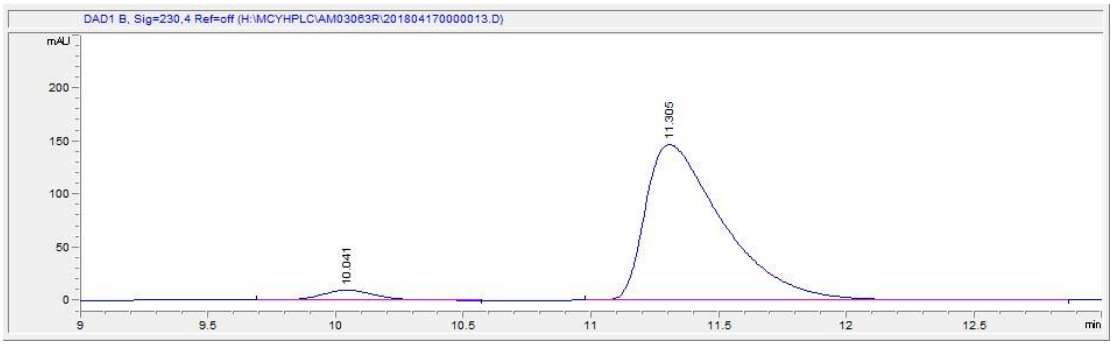

8.18
8.16
7.42
7.40
7.26
6.00
5.98
5.97
5.95
5.93
5.93
5.91
5.17
5.15
5.13
4.25
4.22
4.20
3.90
3.87
3.75
3.53
MeO
O
O
OMe
O2N
3n
1H NMR 400 MHz CDCl3
1.92
2.26
0.99
2.24
1.07
1.01
3.24
3.23
f1 (ppm)


167.61
167.37
147.67
147.03
136.26
128.93
123.91
118.21
77.36
77.04
76.72
56.78
52.85
52.71
49.28
MeO
O
O
OMe
O2N
3n
13C NMR 100 MHz CDCl3
f1 (ppm)



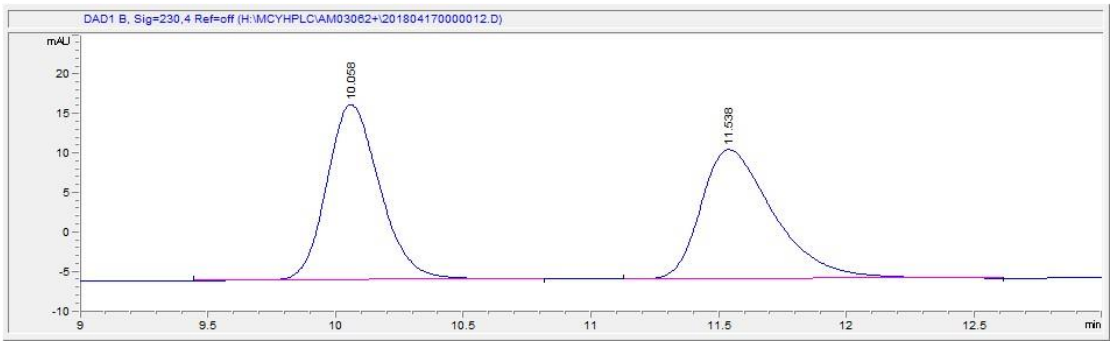
3n

Enantioenriched mixture of compound **3n**

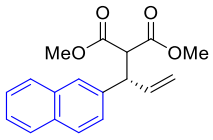


#	Time	Area	Height	Width	Area%	Symmetry
1	10.041	132.7	9.3	0.2224	4.122	0.83
2	11.305	3087.2	146.7	0.3135	95.878	0.413

Racemate of compond **3n**

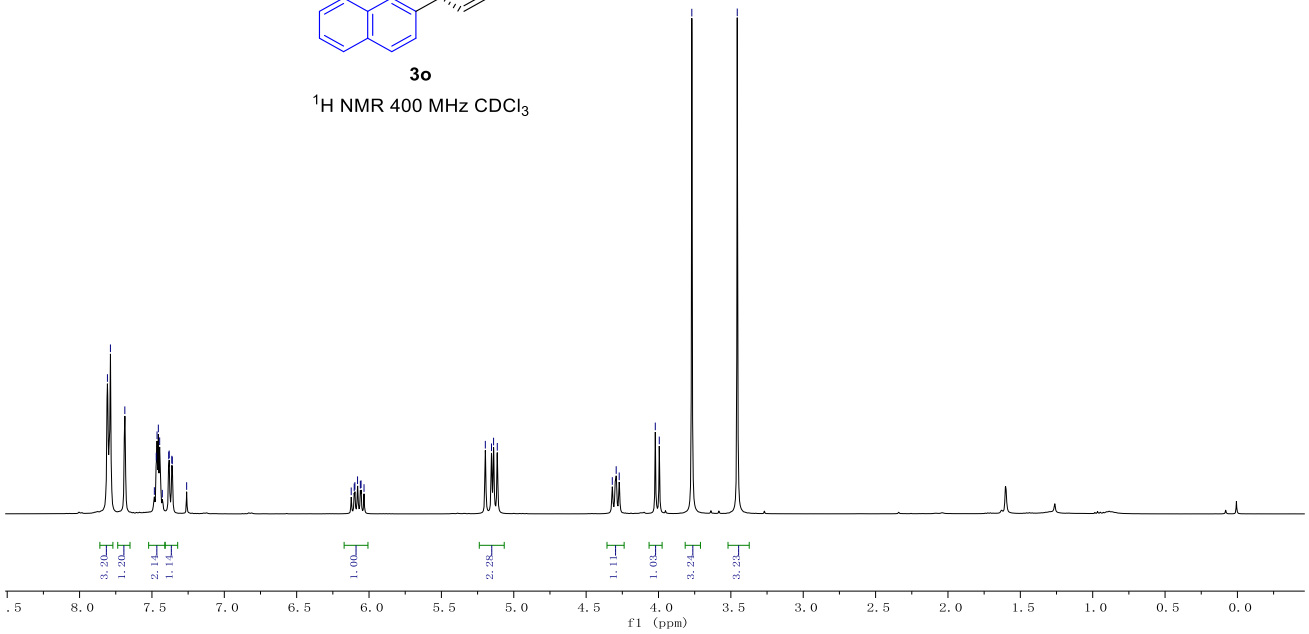


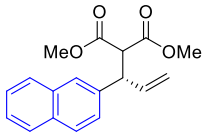
#	Time	Area	Height	Width	Area%	Symmetry
1	10.058	321.5	22.2	0.2228	49.826	0.791
2	11.538	323.7	16.4	0.3009	50.174	0.581



3o

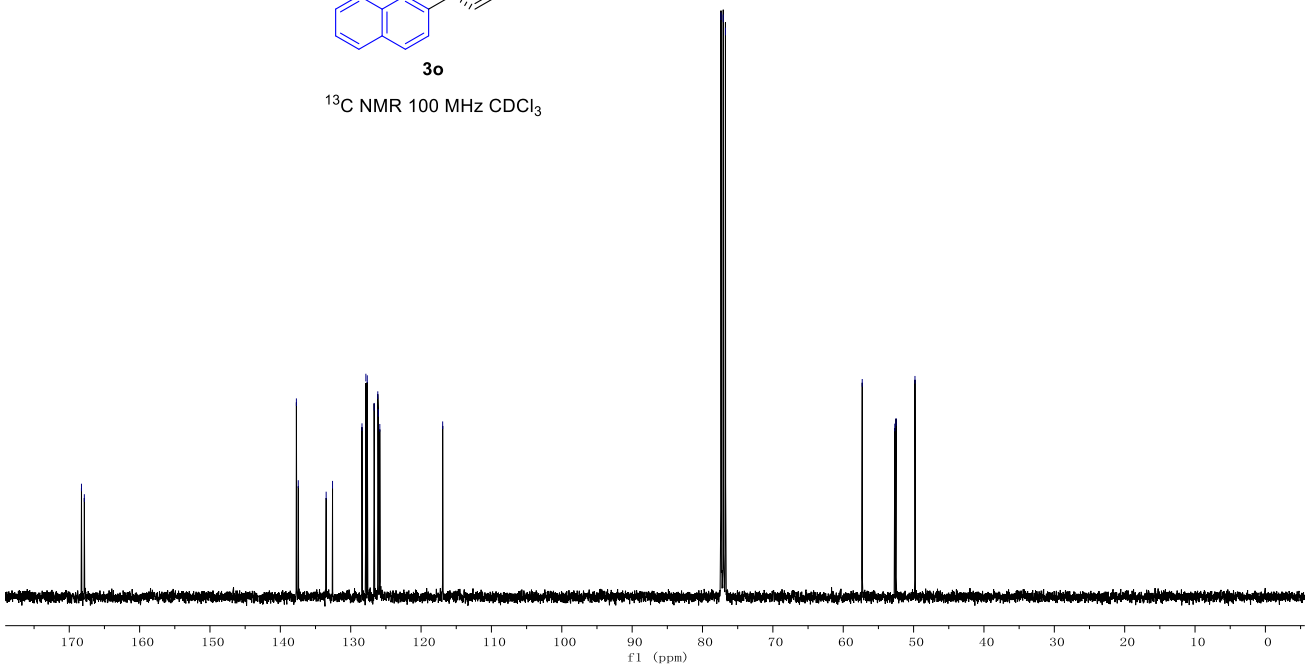
^{1}H NMR 400 MHz $CDCl_3$

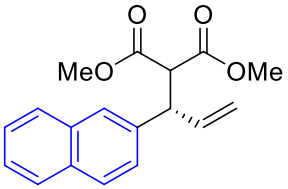




3o

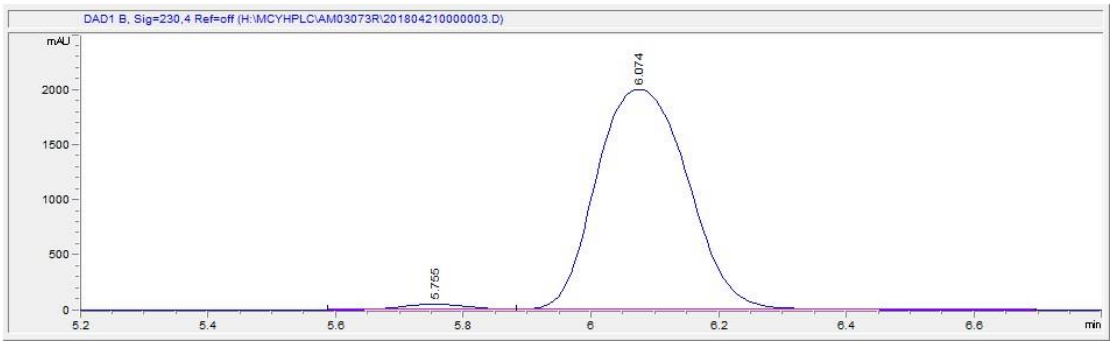
^{13}C NMR 100 MHz $CDCl_3$





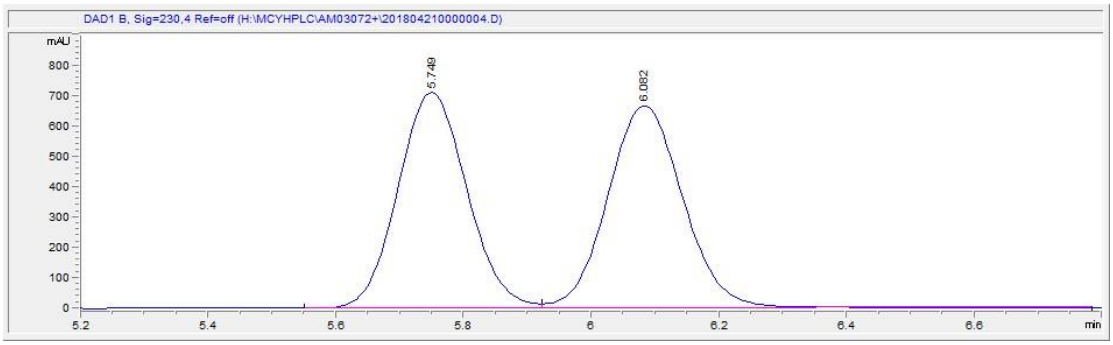
3o

Enantioenriched mixture of compound **3o**

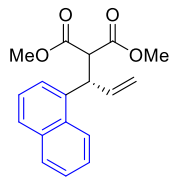


#	Time	Area	Height	Width	Area%	Symmetry
1	5.755	339.4	49.6	0.1078	1.680	1.01
2	6.074	19866.5	1998.3	0.164	98.320	0.826

Racemate of compond **3o**

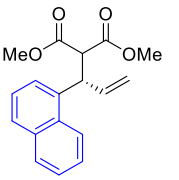


#	Time	Area	Height	Width	Area%	Symmetry
1	5.749	5185	704	0.1159	49.810	0.925
2	6.082	5224.5	657.8	0.1247	50.190	0.891



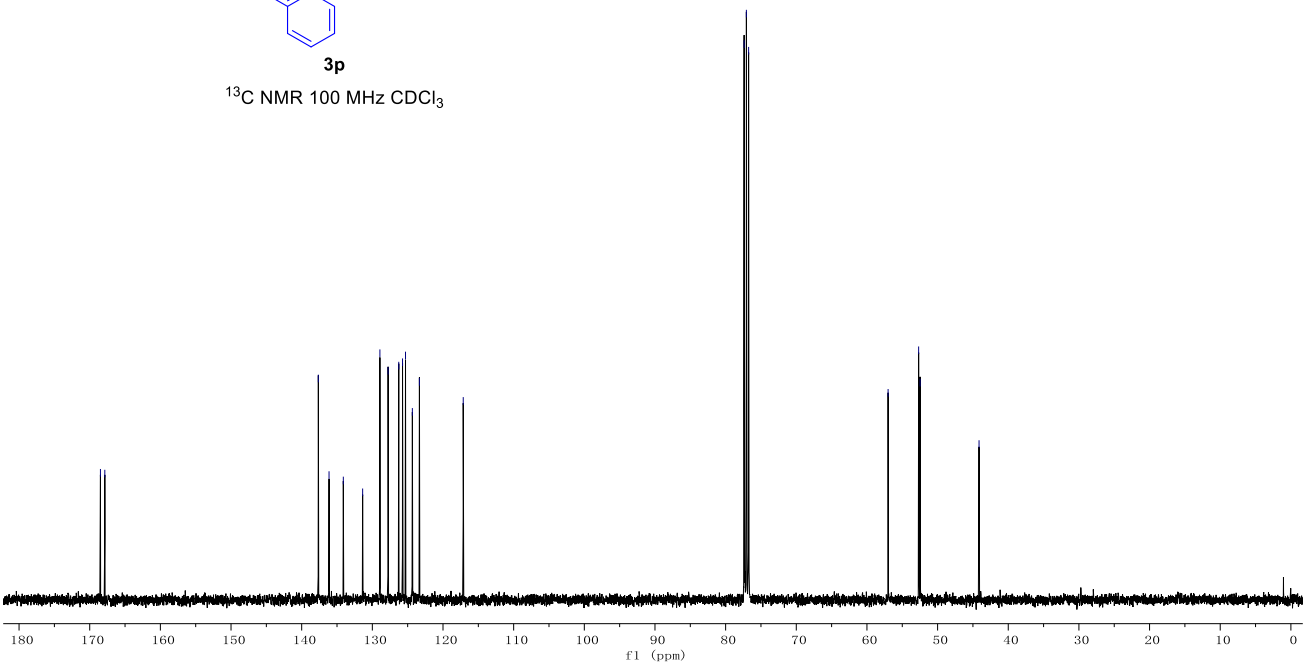
3p

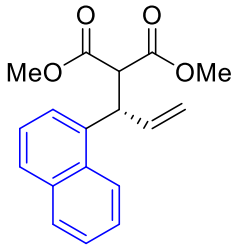
^{1}H NMR 400 MHz $CDCl_3$



3p

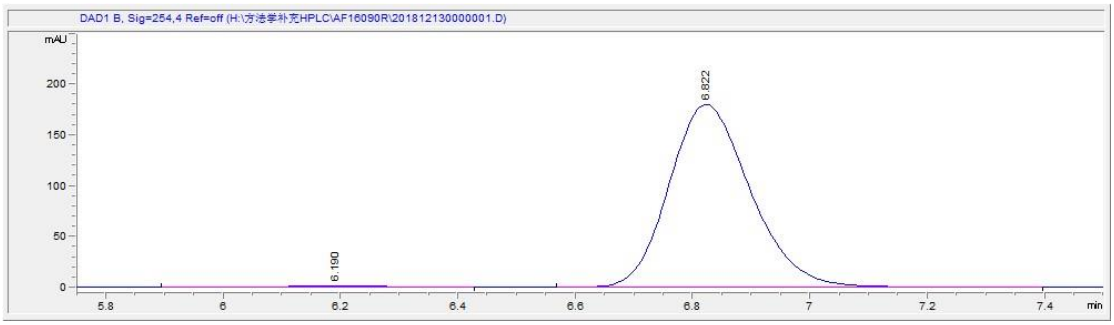
^{13}C NMR 100 MHz $CDCl_3$





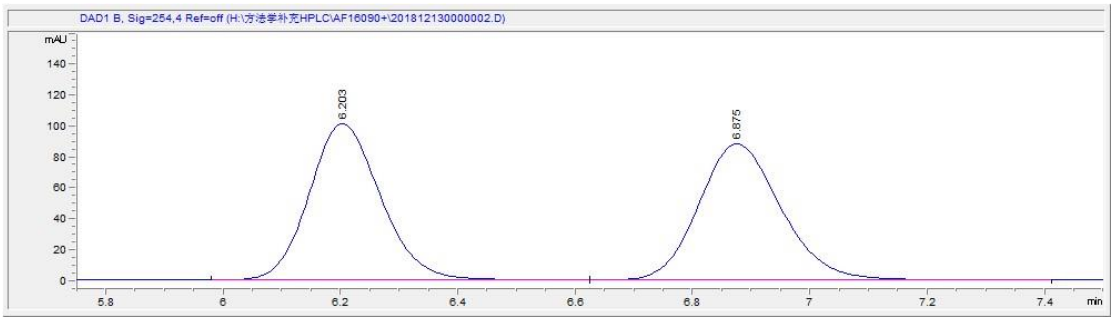
3p

Enantioenriched mixture of compound **3p**

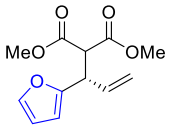


#	Time	Area	Height	Width	Area%	Symmetry
1	6.19	18.7	1.7	0.1618	1.067	0.976
2	6.822	1736.6	180	0.1486	98.933	0.784

Racemate of compond **3p**

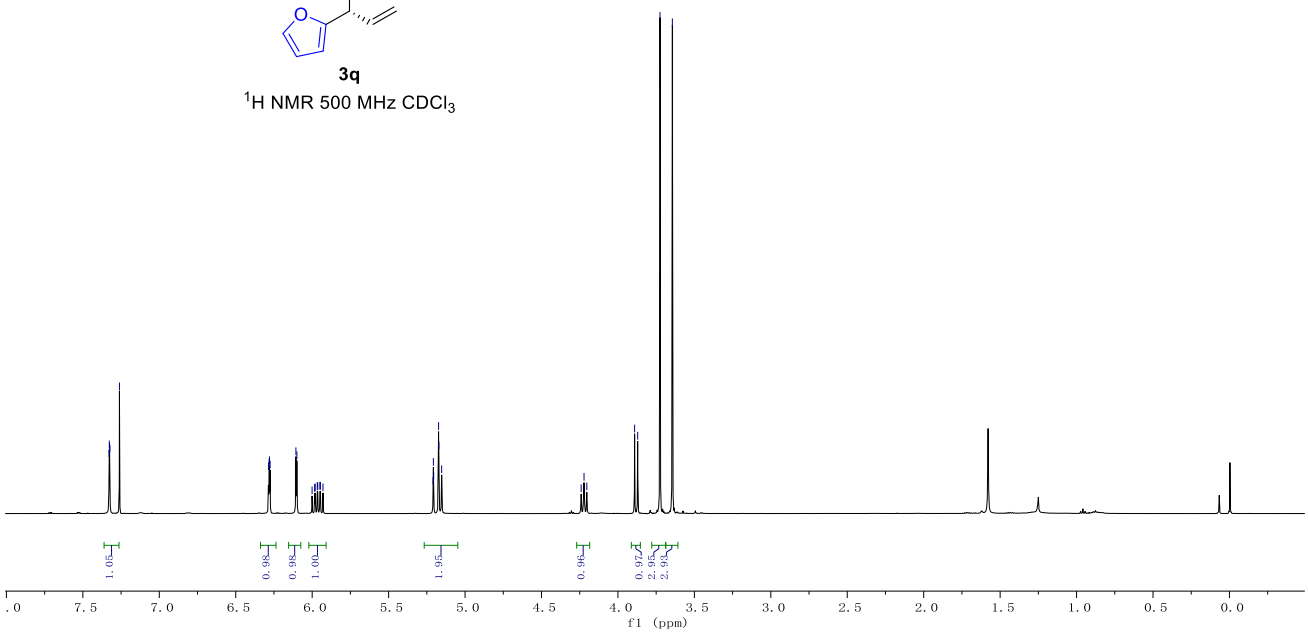


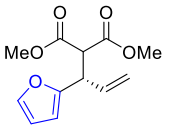
#	Time	Area	Height	Width	Area%	Symmetry
1	6.203	853.2	101.1	0.1305	49.950	0.843
2	6.875	854.9	88.2	0.1491	50.050	0.819



3q

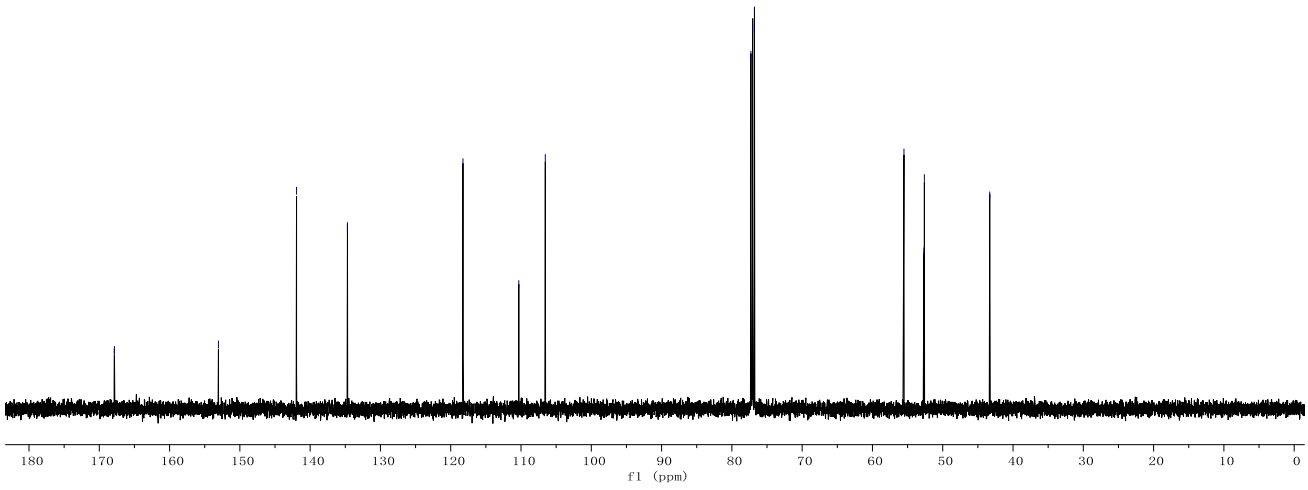
^{1}H NMR 500 MHz $CDCl_3$

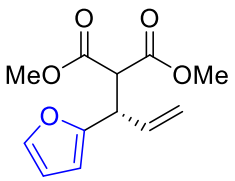




3q

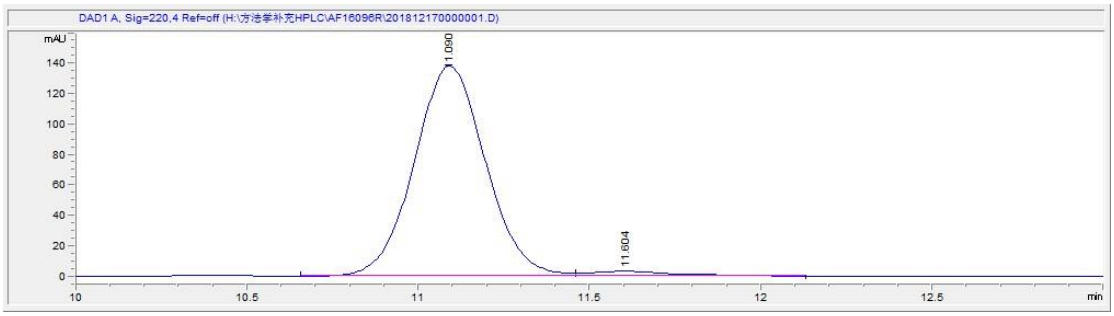
^{13}C NMR 125 MHz $CDCl_3$





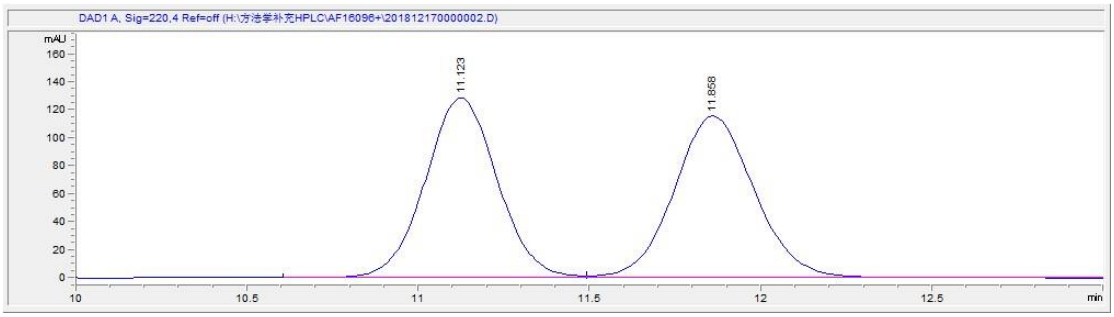
3q

Enantioenriched mixture of compound **3q**

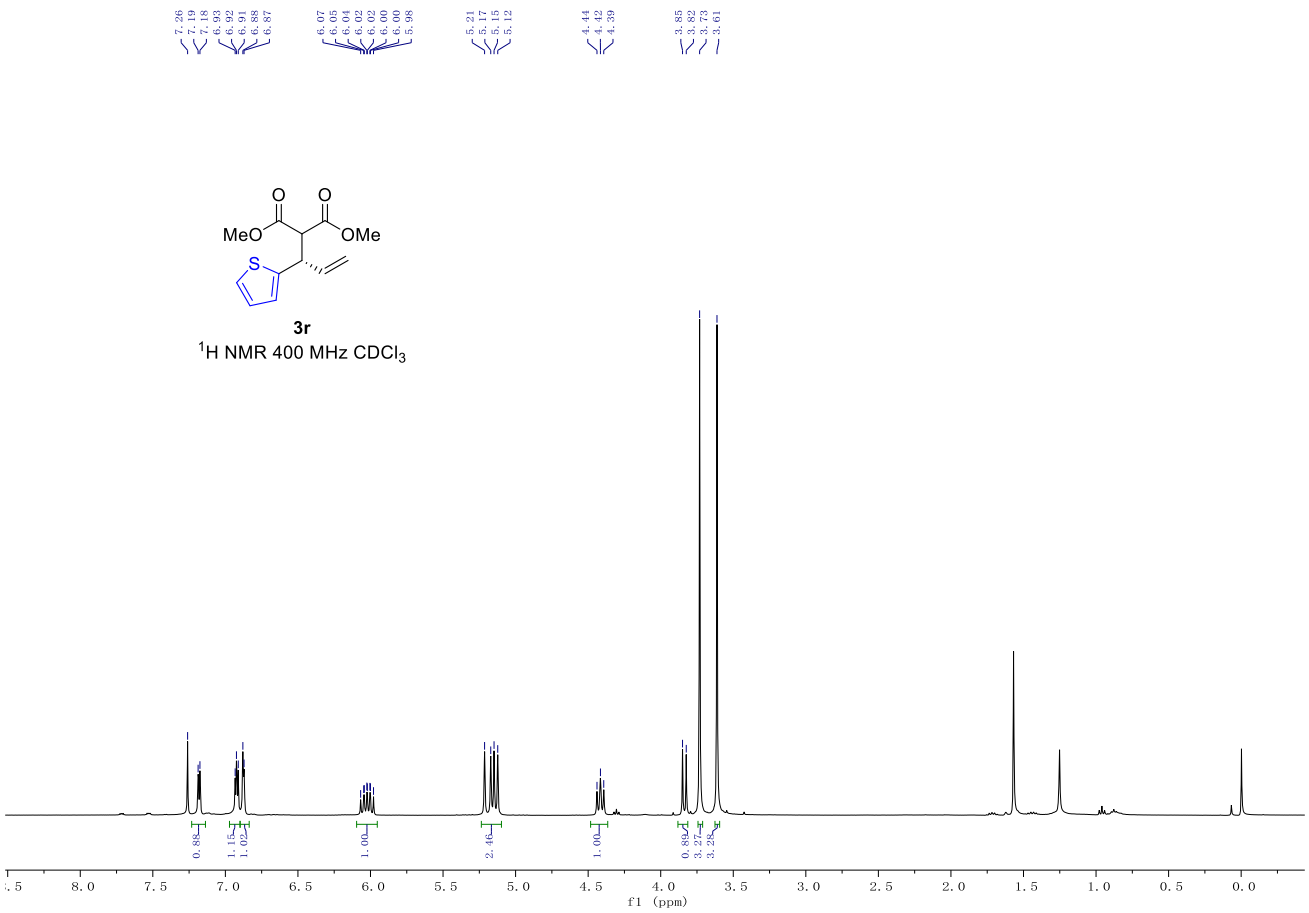


#	Time	Area	Height	Width	Area%	Symmetry
1	11.09	1956.4	137.3	0.2203	99.003	0.959
2	11.604	19.7	1.7	0.1789	0.997	0.576

Racemate of compond **3q**

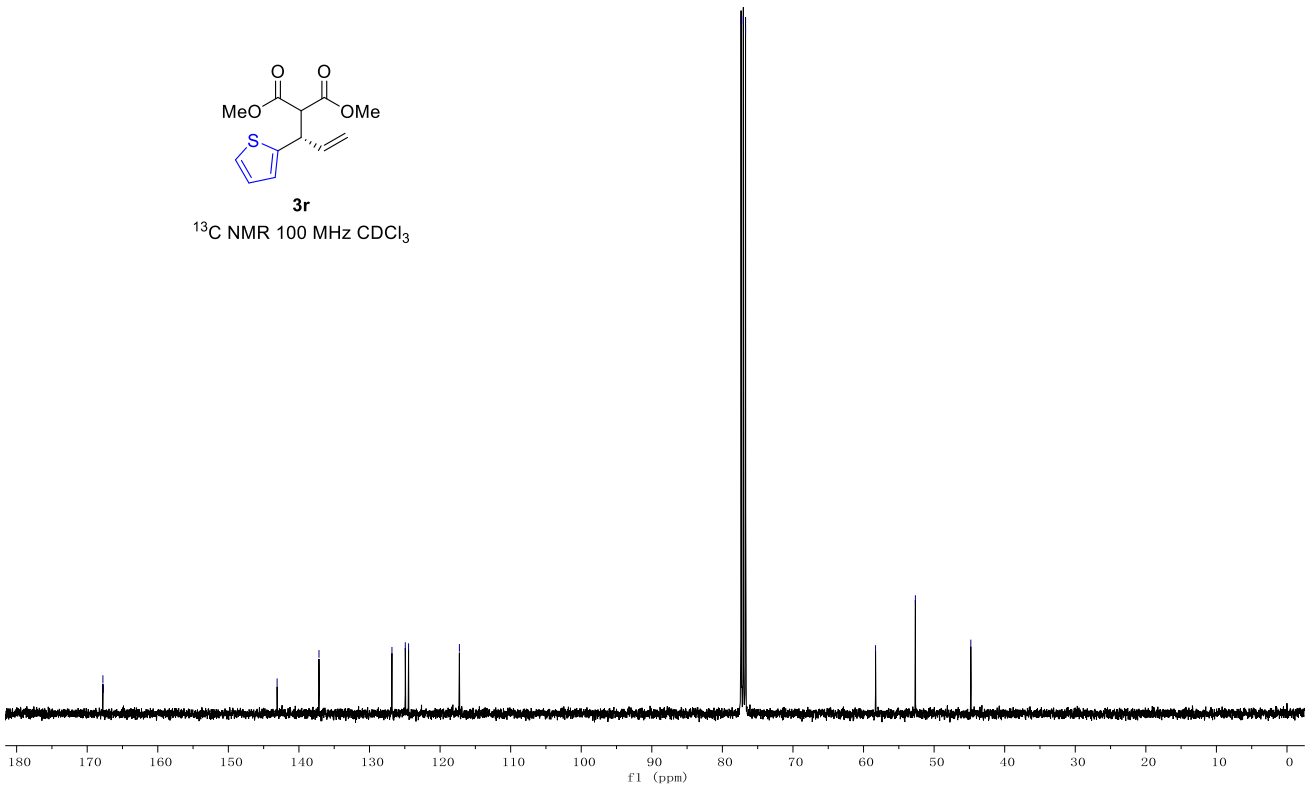


#	Time	Area	Height	Width	Area%	Symmetry
1	11.123	1847	128	0.2243	50.036	0.969
2	11.858	1844.4	114.7	0.2495	49.964	0.887



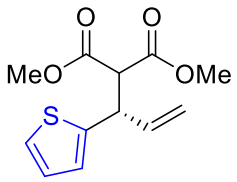
3r

^{1}H NMR 400 MHz $CDCl_3$



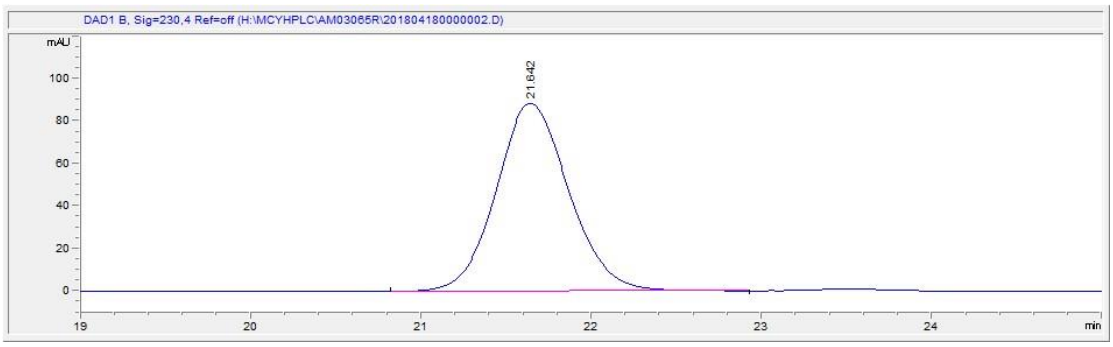
3r

^{13}C NMR 100 MHz $CDCl_3$



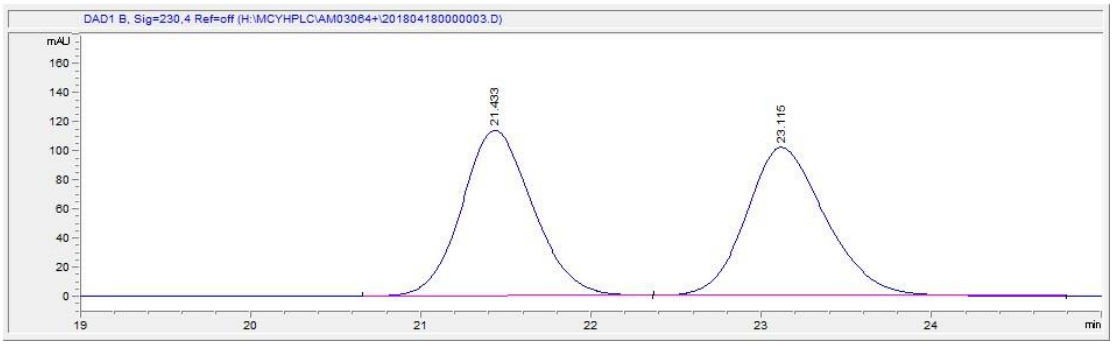
3r

Enantioenriched mixture of compound **3r**

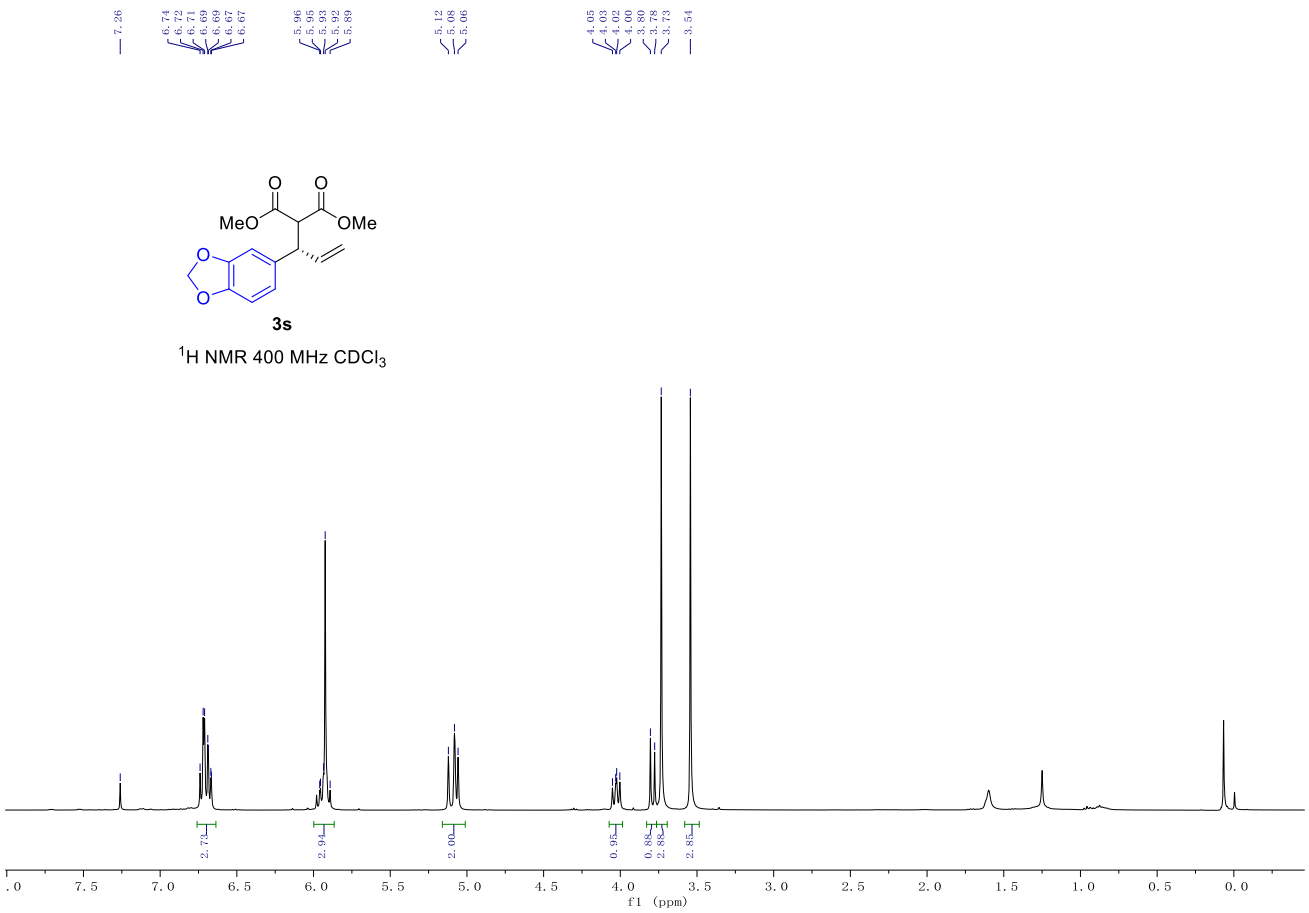


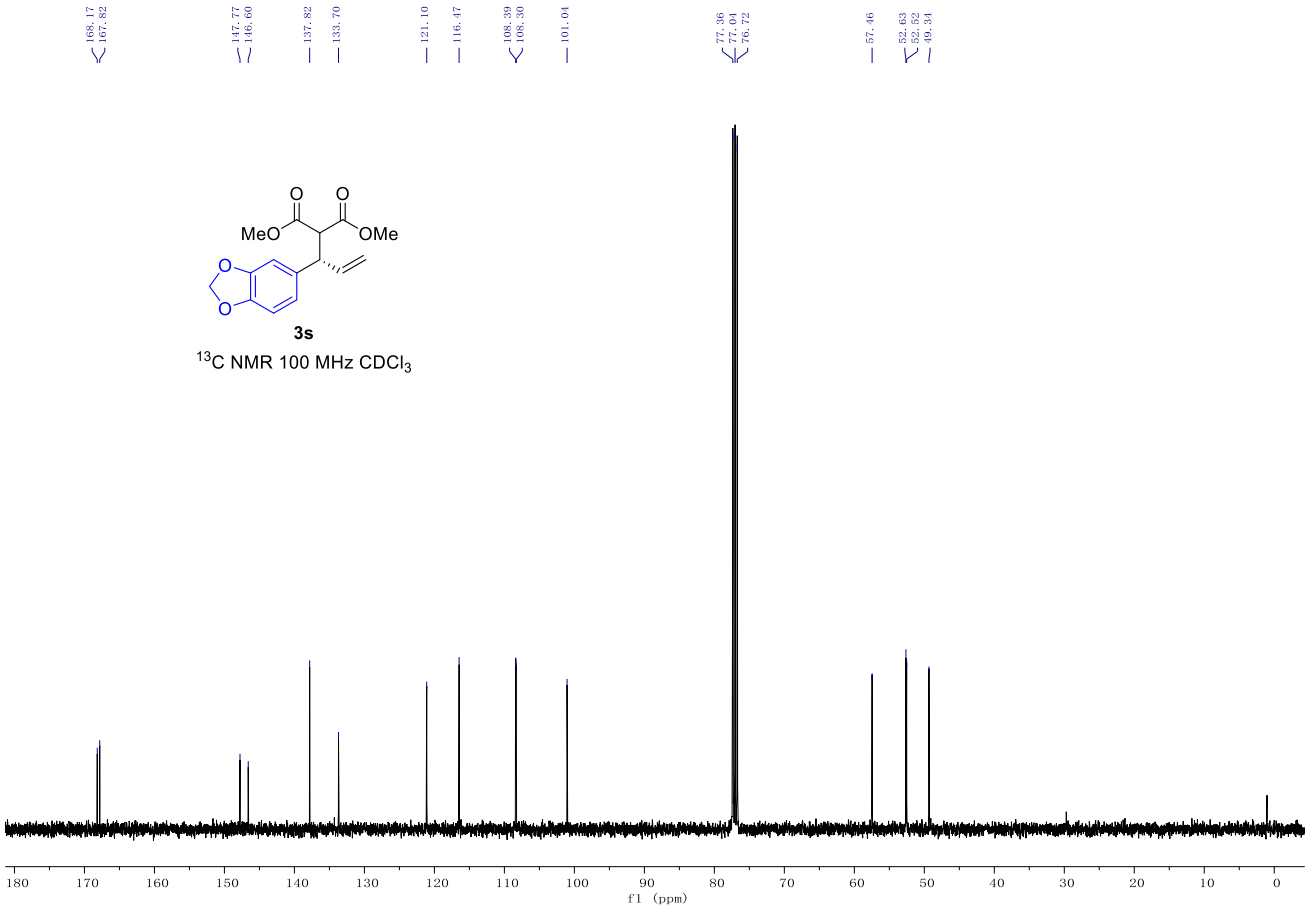
#	Time	Area	Height	Width	Area%	Symmetry
1	21.642	2616.5	88.4	0.4534	100.000	0.861

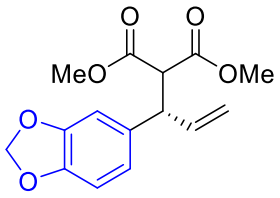
Racemate of compond **3r**



#	Time	Area	Height	Width	Area%	Symmetry
1	21.433	3303.3	113.8	0.4447	49.993	0.844
2	23.115	3304.2	101.9	0.4944	50.007	0.763

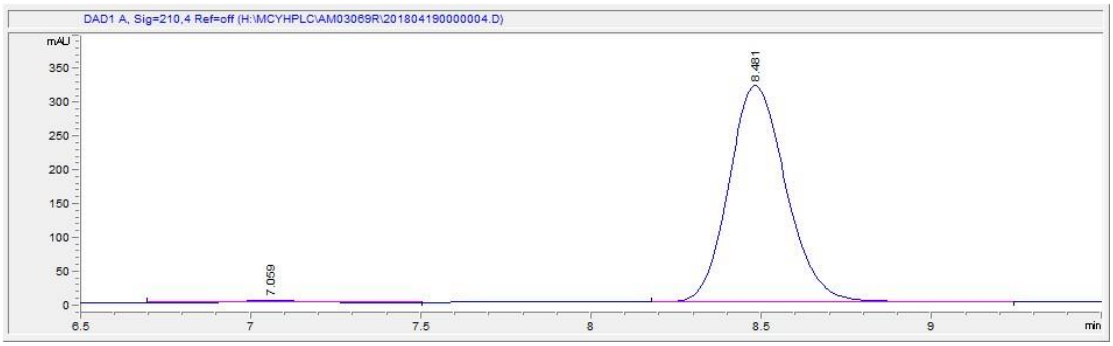

7.26
6.74
6.72
6.71
6.69
6.69
6.67
6.67
5.96
5.95
5.93
5.92
5.89
5.12
5.08
5.06
4.05
4.03
4.02
4.00
3.80
3.78
3.73
3.54
MeO
OMe
O
O
O
O
3s
1H NMR 400 MHz CDCl3
2.73
2.94
2.00
0.95
0.88
2.88
2.85
f1 (ppm)


168.17
167.82
147.77
146.60
137.82
133.70
121.10
116.47
108.39
108.30
101.04
77.36
77.04
76.72
57.46
52.63
52.52
49.34
MeO
OMe
O
O
O
O
3s
13C NMR 100 MHz CDCl3
f1 (ppm)



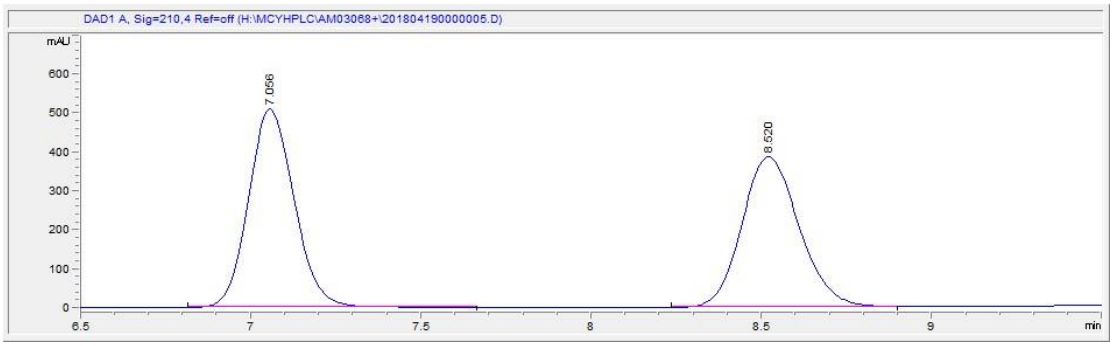
3s

Enantioenriched mixture of compound **3s**

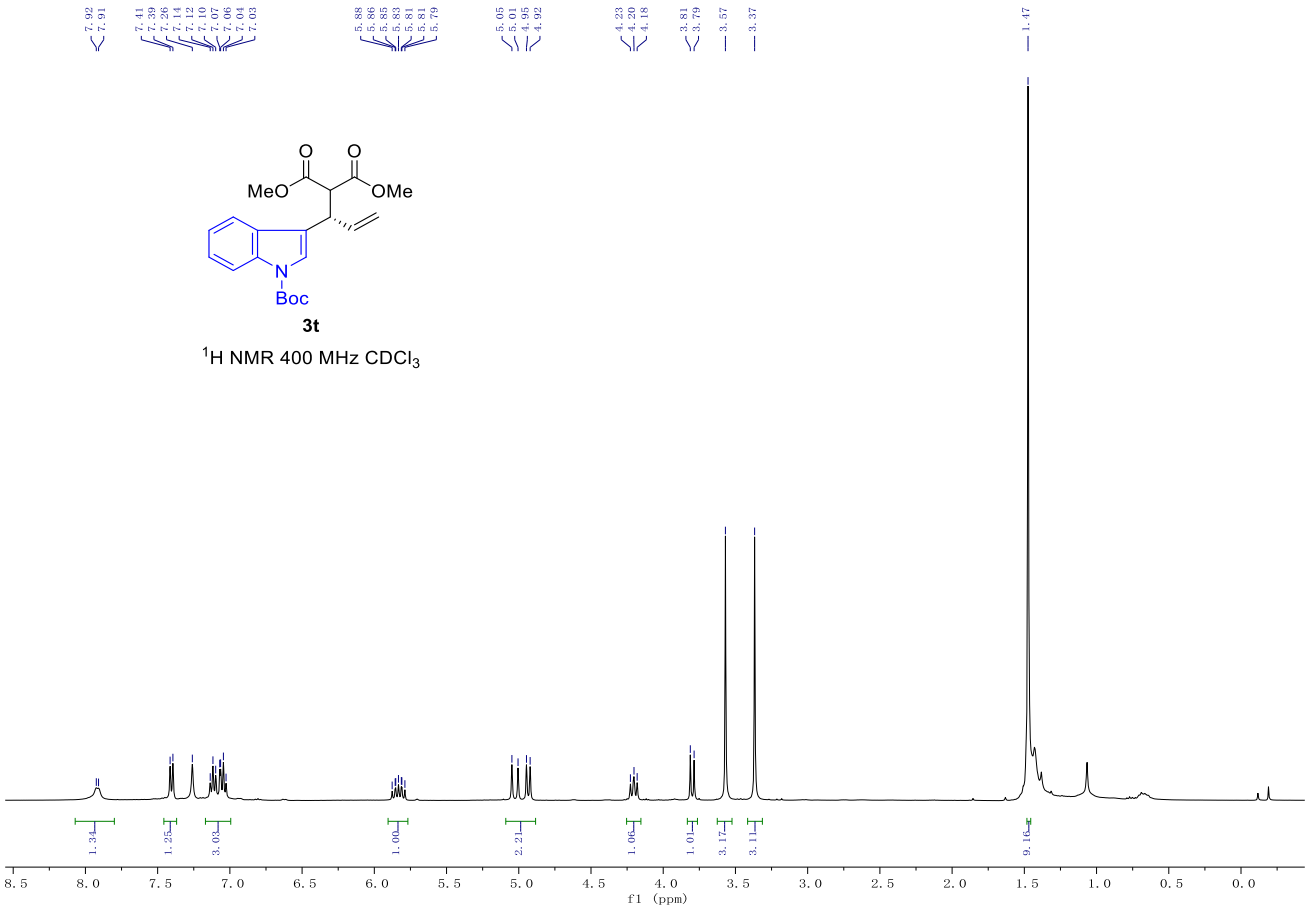


#	Time	Area	Height	Width	Area%	Symmetry
1	7.059	38.2	3.6	0.16	1.013	0.961
2	8.481	3730.6	319.9	0.18	98.987	0.821

Racemate of compond **3s**

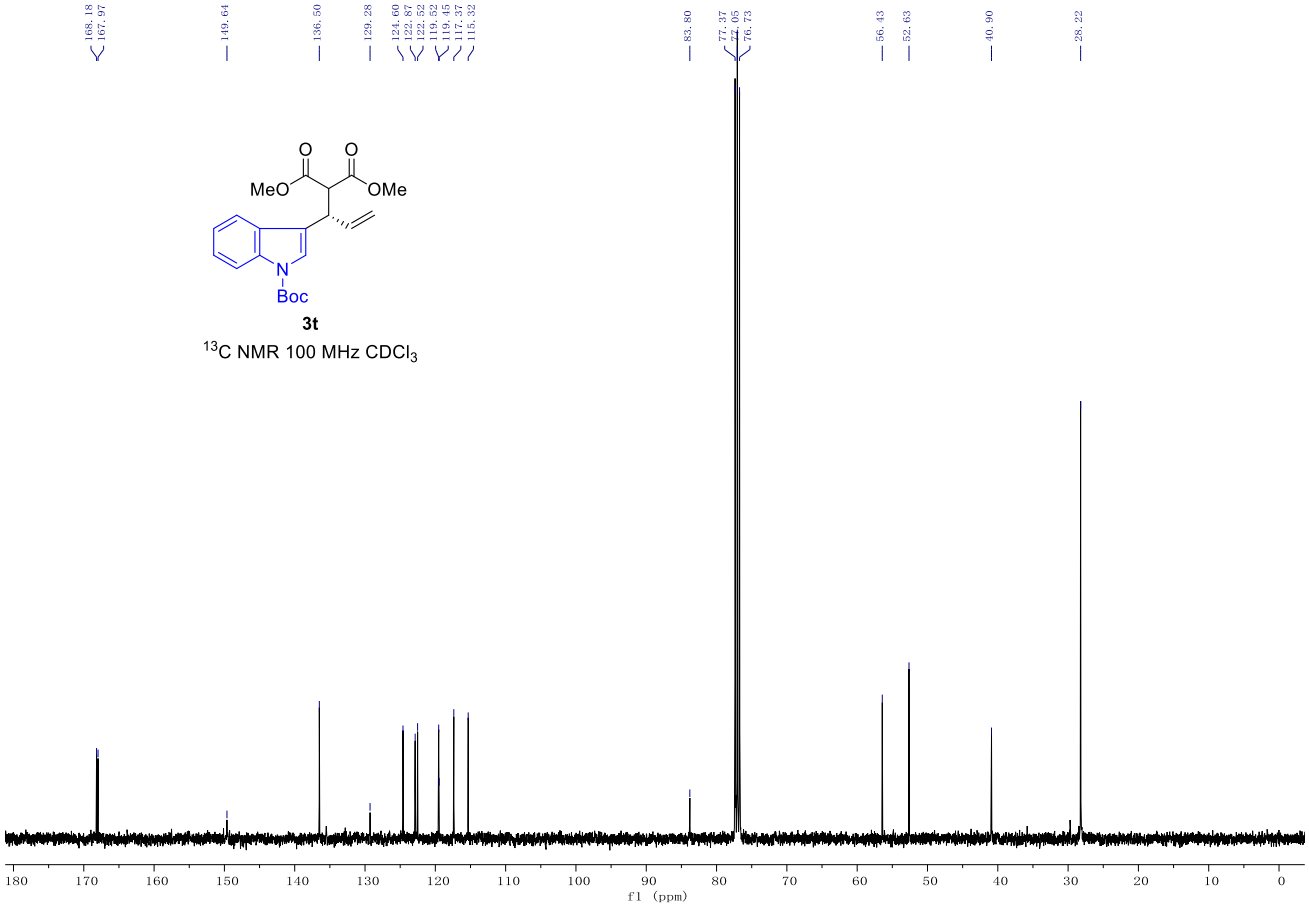


#	Time	Area	Height	Width	Area%	Symmetry
1	7.056	4717.8	507.3	0.1445	51.282	0.848
2	8.52	4482	384.3	0.1821	48.718	0.826



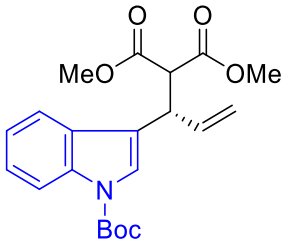
3t

^{1}H NMR 400 MHz $CDCl_3$



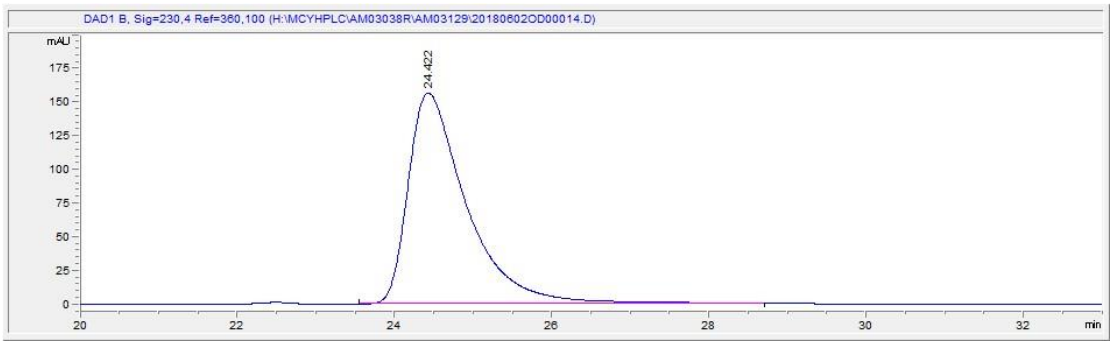
3t

^{13}C NMR 100 MHz $CDCl_3$



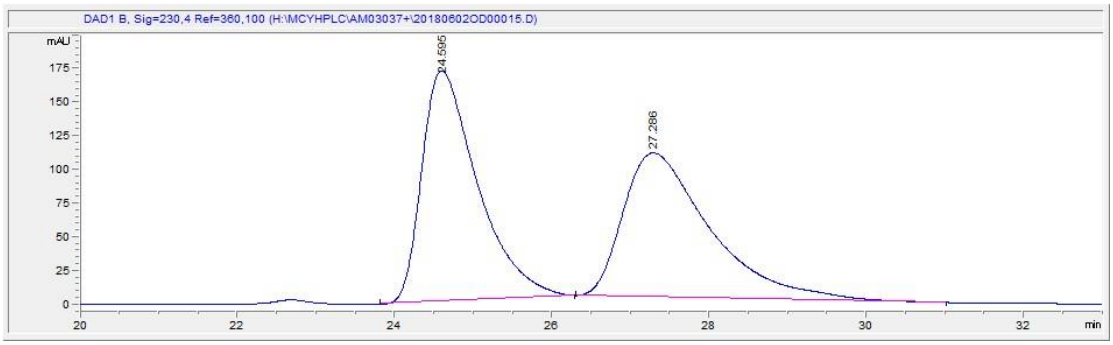
3t

Enantioenriched mixture of compound **3t**

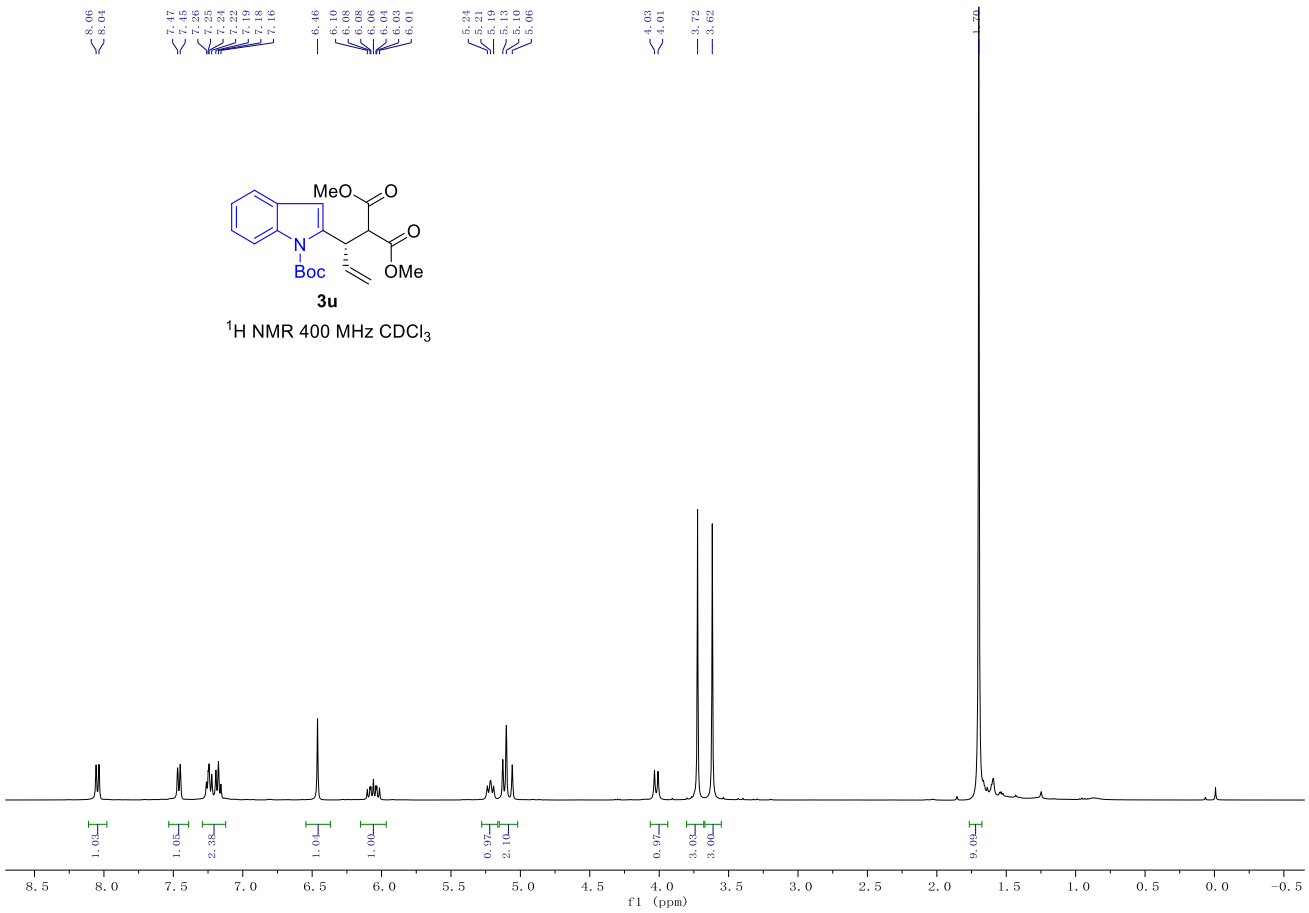


#	Time	Area	Height	Width	Area%	Symmetry
1	24.422	8115.4	156.6	0.7666	100.000	0.474

Racemate of compond **3t**

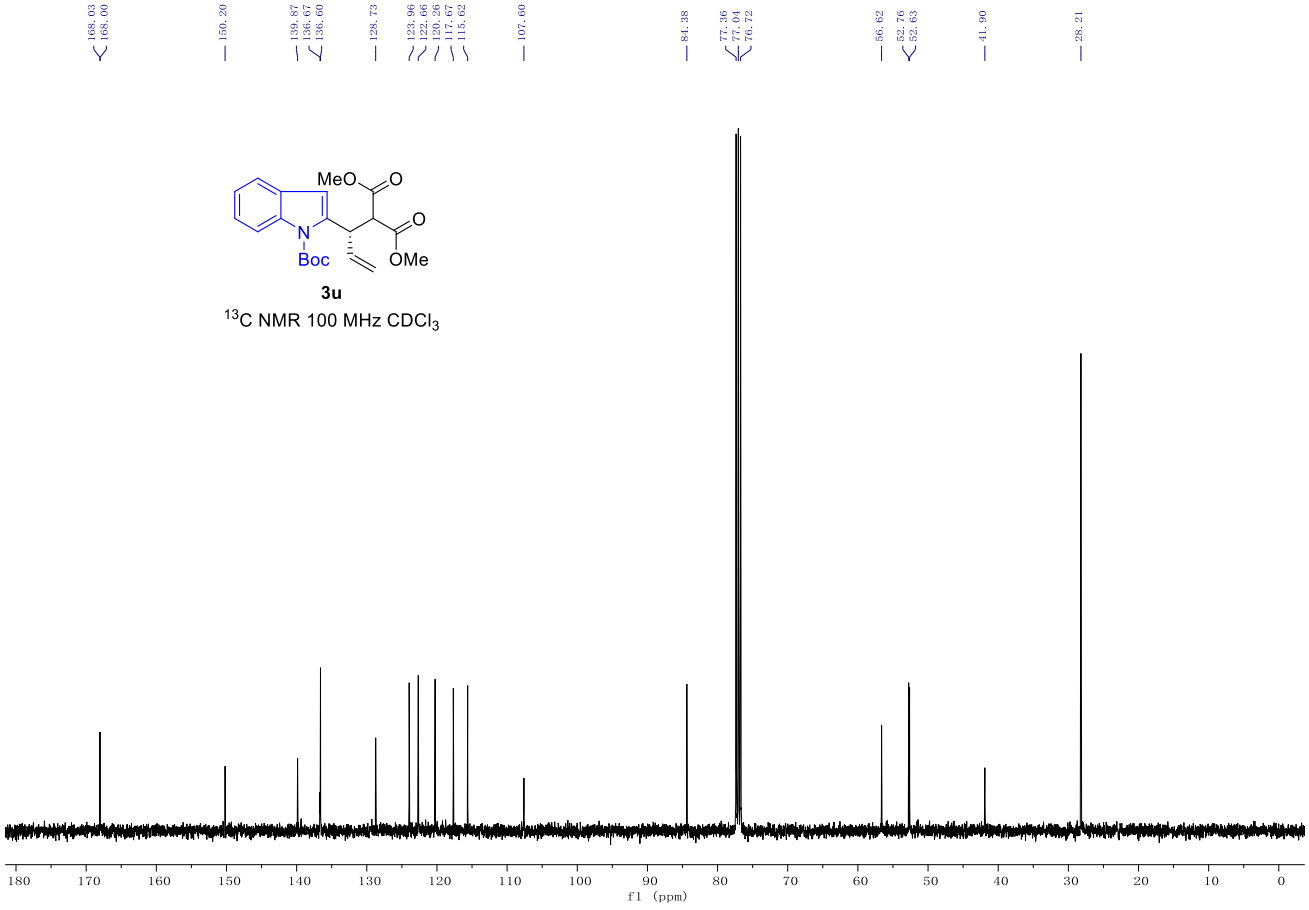


#	Time	Area	Height	Width	Area%	Symmetry
1	24.595	8442.2	171.3	0.7408	50.681	0.517
2	27.286	8215.4	106.9	1.1405	49.319	0.493



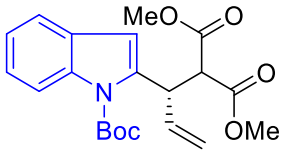
3u

^{1}H NMR 400 MHz $CDCl_3$



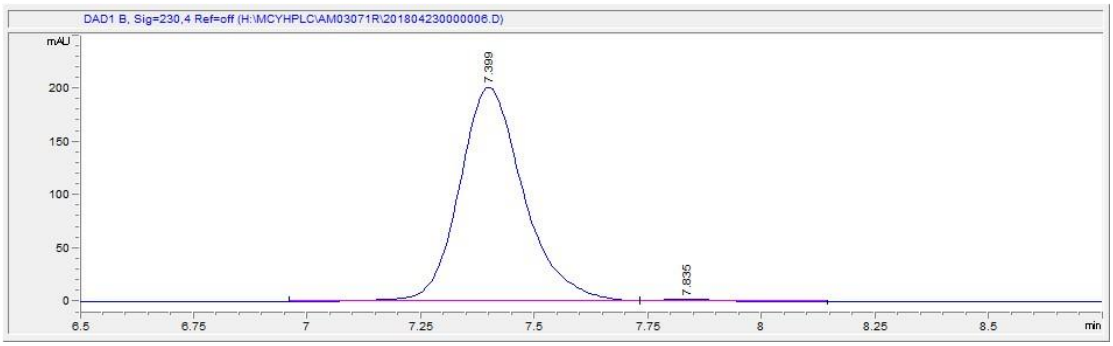
3u

^{13}C NMR 100 MHz $CDCl_3$



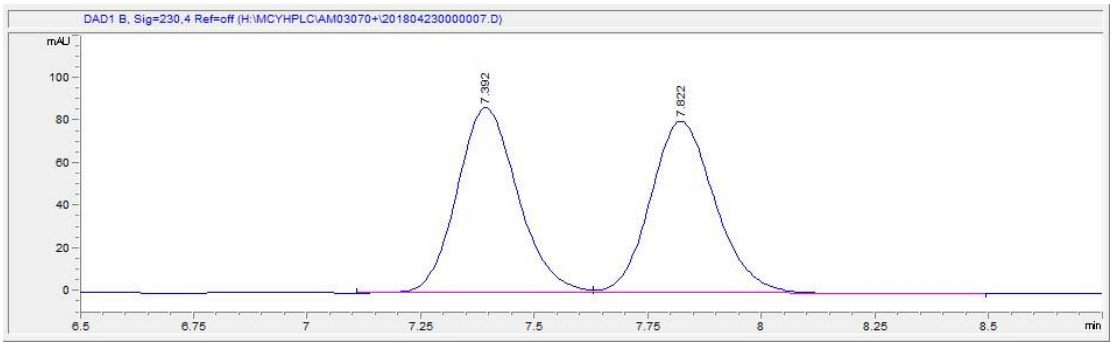
3u

Enantioenriched mixture of compound **3u**

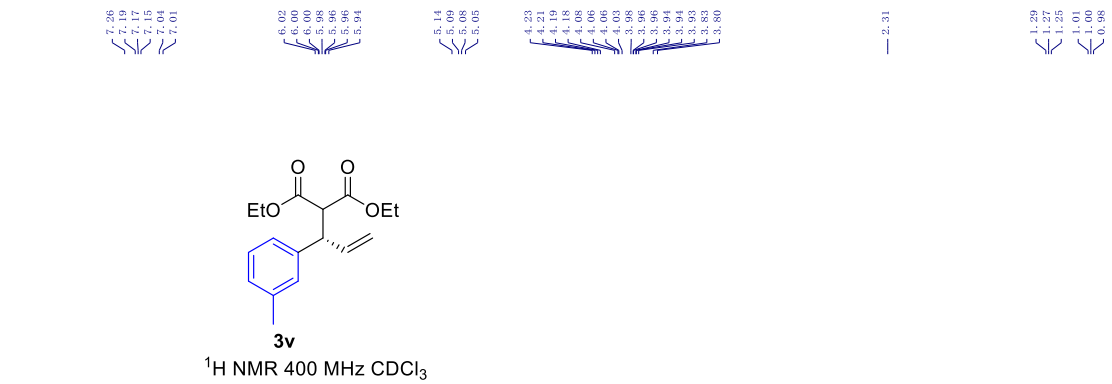


#	Time	Area	Height	Width	Area%	Symmetry
1	7.399	1961	200.7	0.15	99.452	0.813
2	7.835	10.8	1.5	0.1179	0.548	0.721

Racemate of compond **3u**

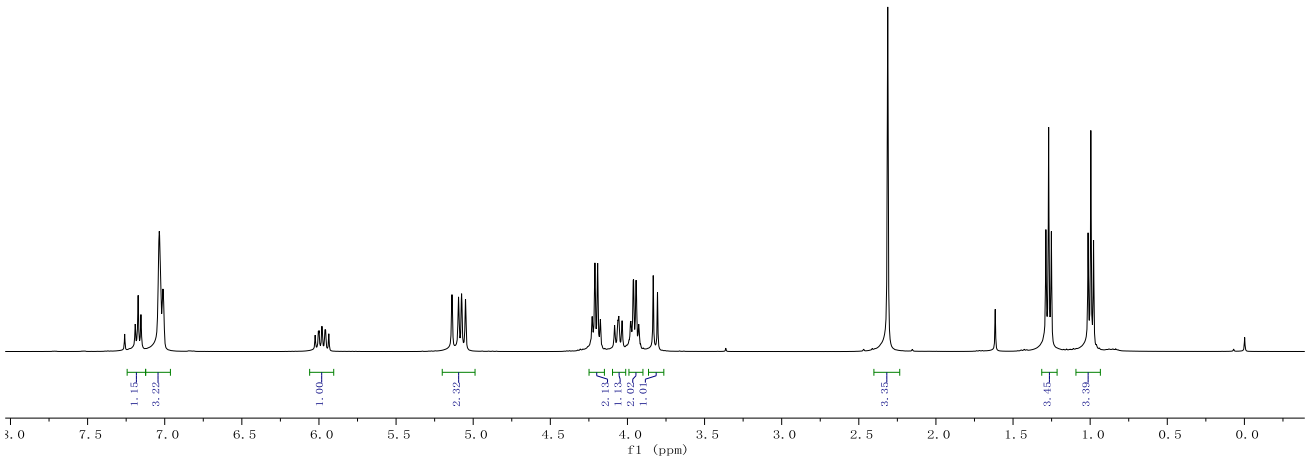


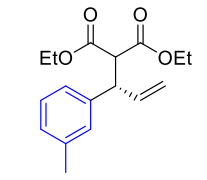
#	Time	Area	Height	Width	Area%	Symmetry
1	7.392	792.6	86.3	0.1432	50.519	0.866
2	7.822	776.3	79.9	0.1514	49.481	0.831



3v

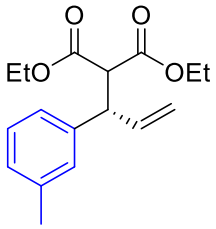
^{1}H NMR 400 MHz $CDCl_3$





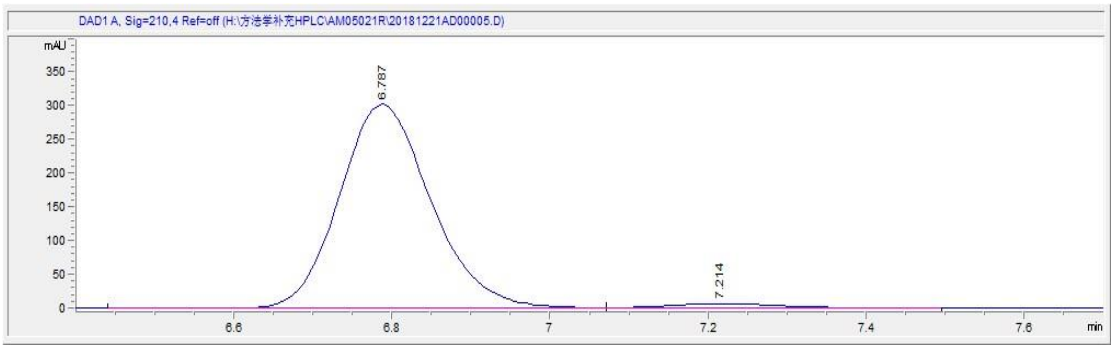
3v

^{13}C NMR 100 MHz $CDCl_3$



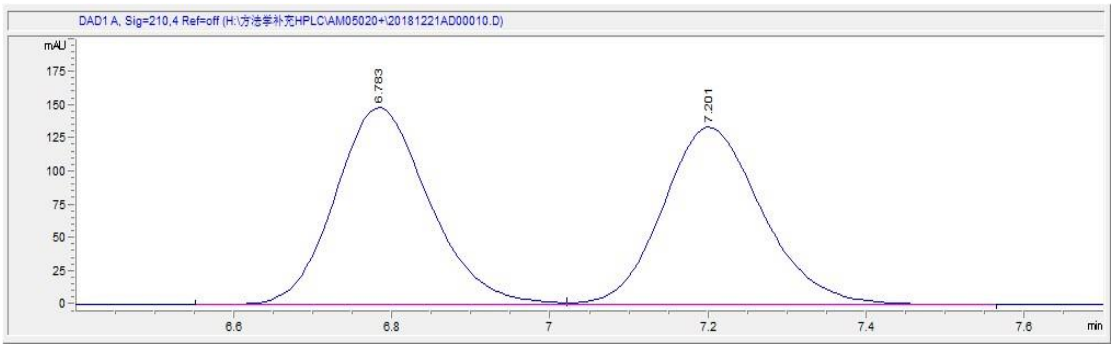
3v

Enantioenriched mixture of compound **3v**

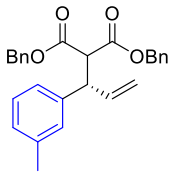


#	Time	Area	Height	Width	Area%	Symmetry
1	6.787	2417.7	302	0.1234	97.734	0.835
2	7.214	56	6.3	0.1399	2.266	0.757

Racemate of compound **3v**

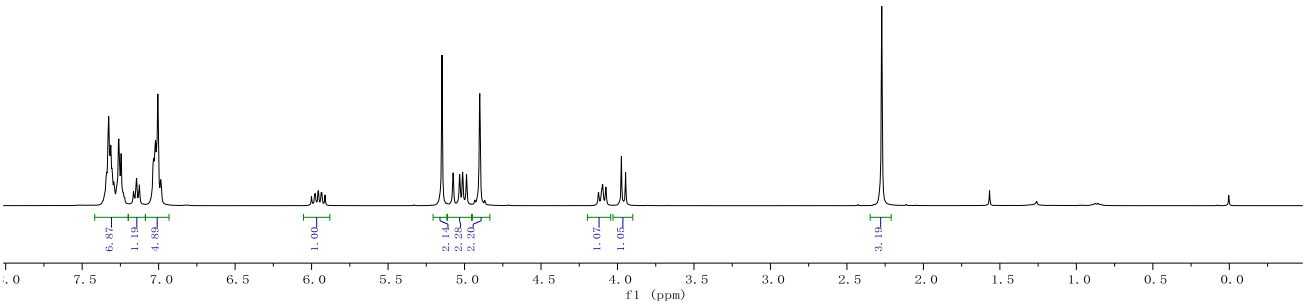


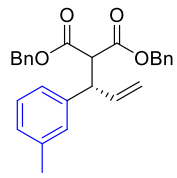
#	Time	Area	Height	Width	Area%	Symmetry
1	6.783	1207.5	147.8	0.1273	51.299	0.852
2	7.201	1146.4	132.7	0.1328	48.701	0.828



3w

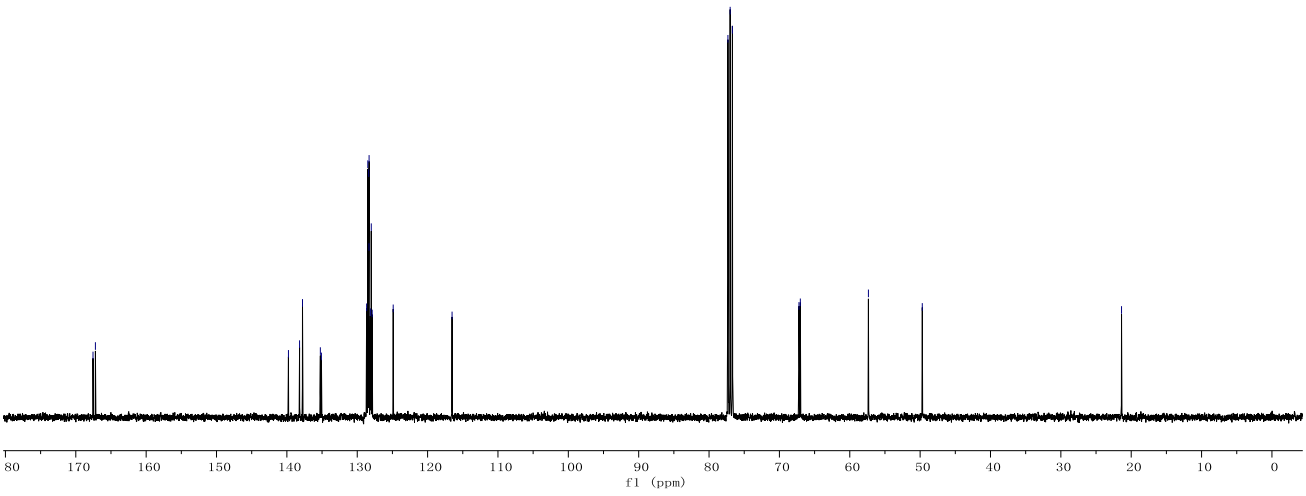
^{1}H NMR 400 MHz $CDCl_3$

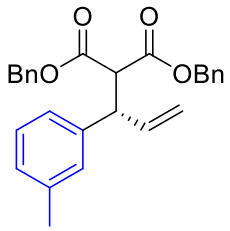




3w

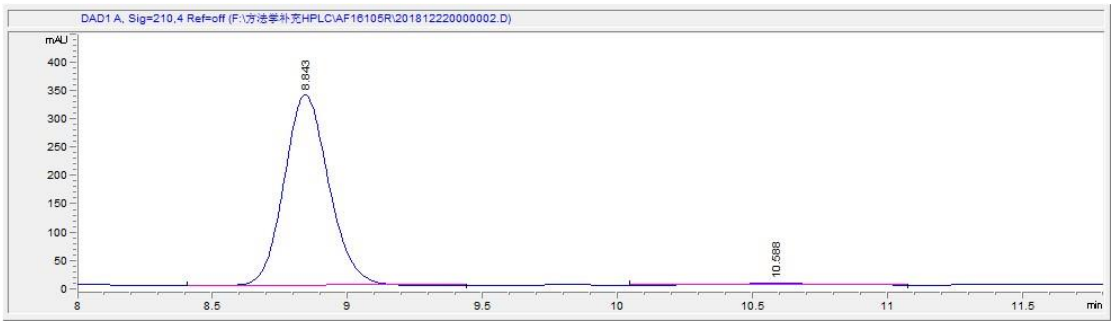
^{13}C NMR 100 MHz $CDCl_3$





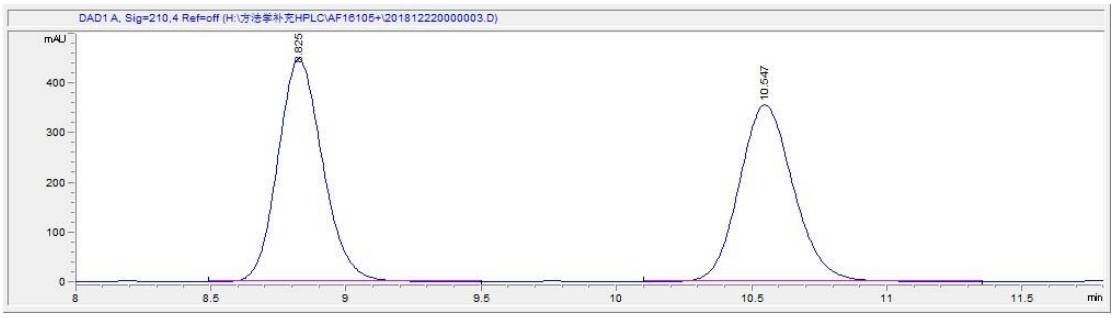
3w

Enantioenriched mixture of compound **3w**

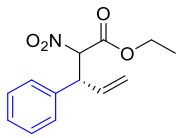


#	Time	Area	Height	Width	Area%	Symmetry
1	8.843	3871.1	336	0.1784	98.429	0.855
2	10.588	61.8	3.5	0.2558	1.571	1.15

Racemate of compound **3w**

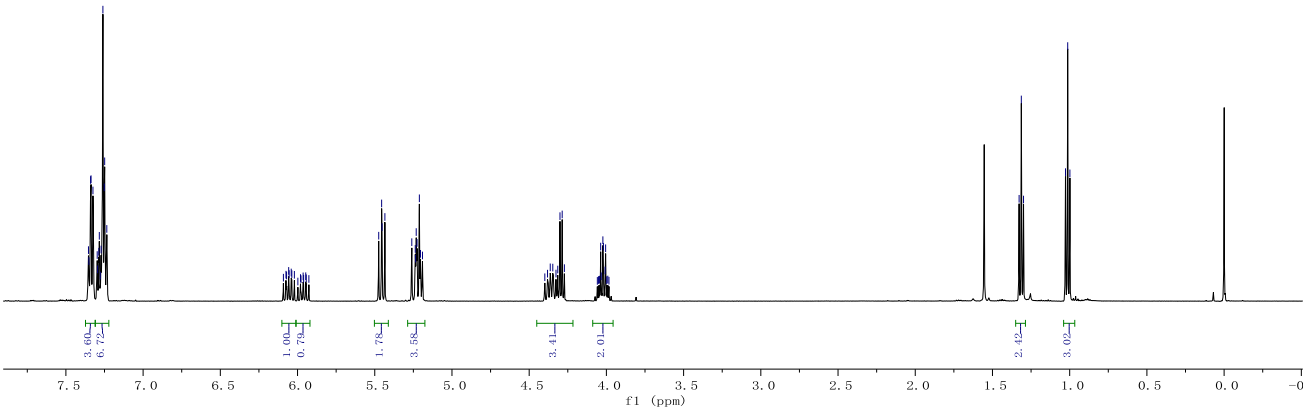


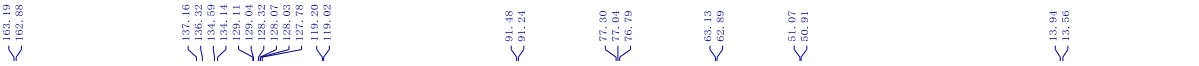
#	Time	Area	Height	Width	Area%	Symmetry
1	8.825	5130.7	447.1	0.1779	50.955	0.843
2	10.547	4938.4	354.6	0.2165	49.045	0.857

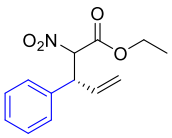


5a

^{1}H NMR 500 MHz $CDCl_3$

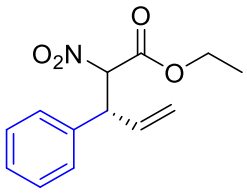






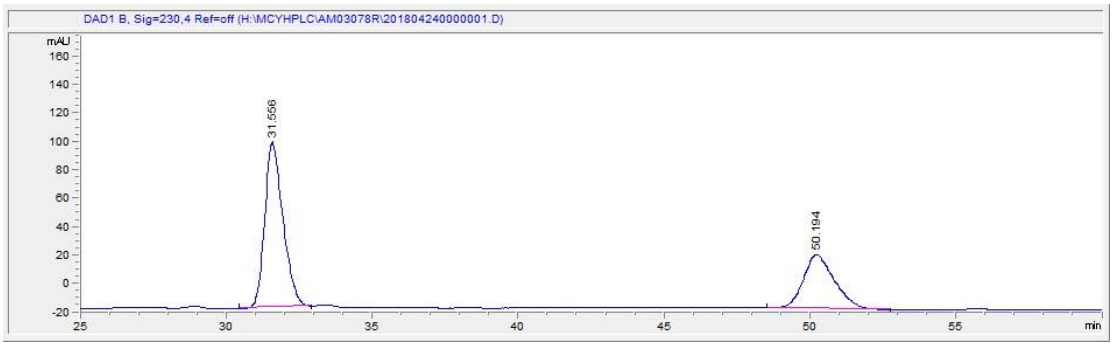
5a

^{13}C NMR 125 MHz $CDCl_3$



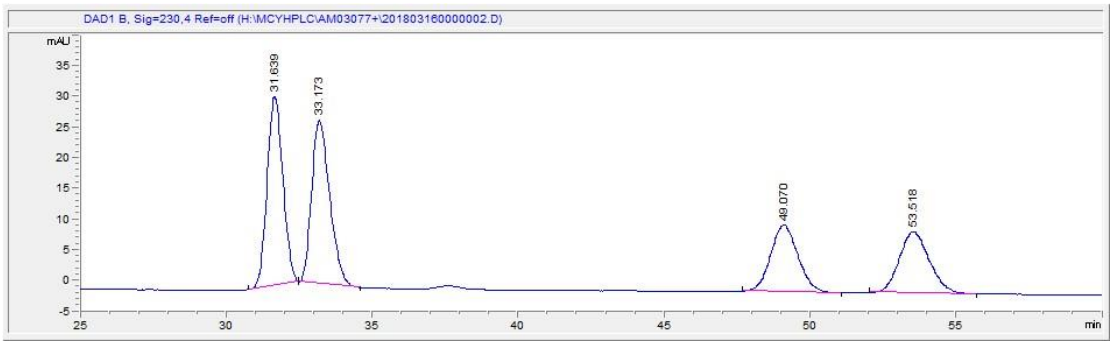
5a

Enantioenriched mixture of compound **5a**

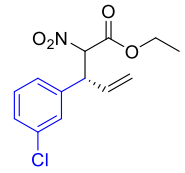


#	Time	Area	Height	Width	Area%	Symmetry
1	31.556	5048.9	116.5	0.6455	64.412	0.668
2	50.194	2789.6	37.9	1.0247	35.588	0.702

Racemate of compond **5a**

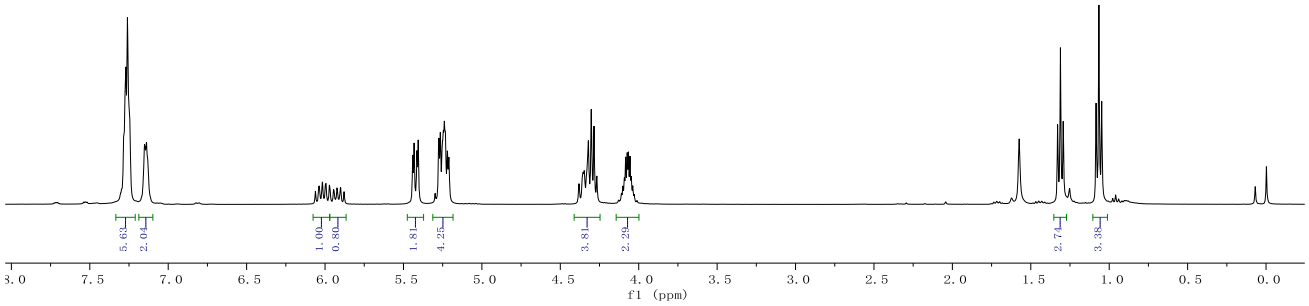


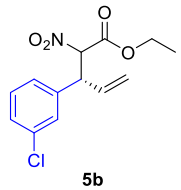
#	Time	Area	Height	Width	Area%	Symmetry
1	31.639	1155.9	30.8	0.5805	31.117	0.876
2	33.173	1142.8	26.7	0.6499	30.765	0.702
3	49.07	701.6	10.8	0.9146	18.889	0.868
4	53.518	714.3	10	0.9706	19.229	0.852



5b

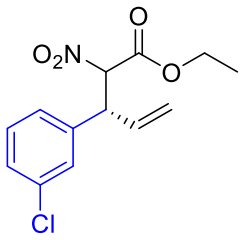
^{1}H NMR 400 MHz $CDCl_3$





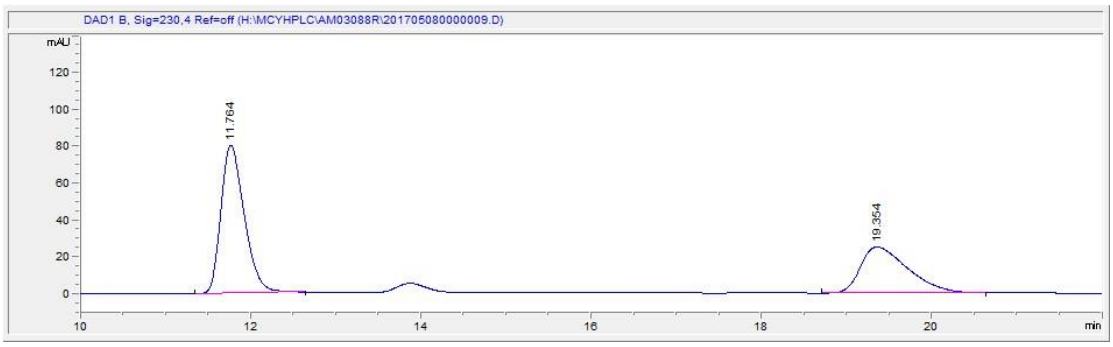
5b

^{13}C NMR 100 MHz $CDCl_3$



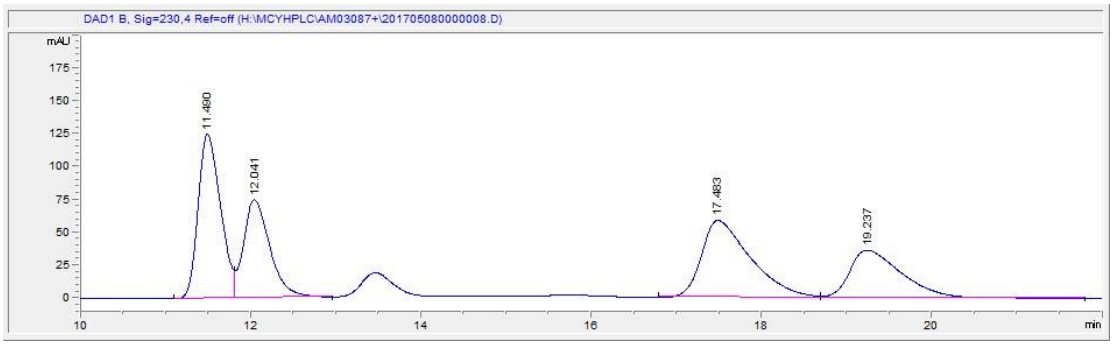
5b

Enantioenriched mixture of compound **5b**

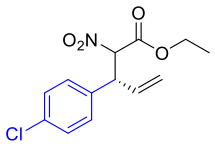


#	Time	Area	Height	Width	Area%	Symmetry
1	11.764	1534.3	80.4	0.2946	61.295	0.671
2	19.354	968.9	25.1	0.5745	38.705	0.512

Racemate of compond **5b**

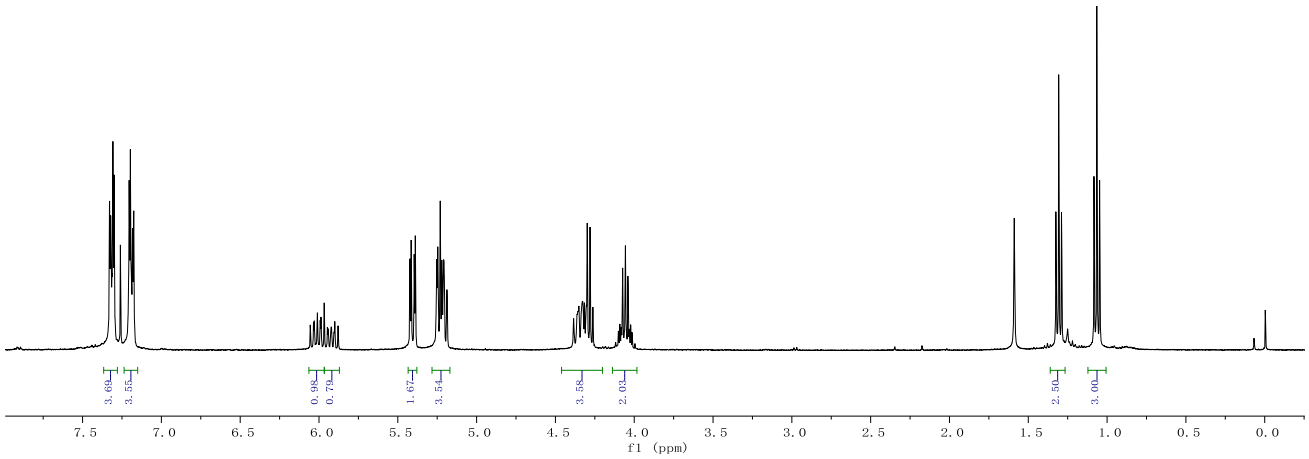


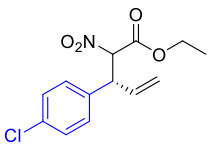
#	Time	Area	Height	Width	Area%	Symmetry
1	11.49	1884.7	114.4	0.2622	28.330	0.794
2	12.041	1050.6	59.1	0.2834	15.792	0.6
3	17.483	2276.8	58.3	0.5655	34.224	0.483
4	19.237	1440.5	35.3	0.616	21.653	0.479



5c

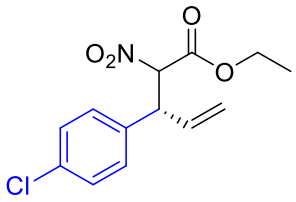
^{1}H NMR 400 MHz $CDCl_3$





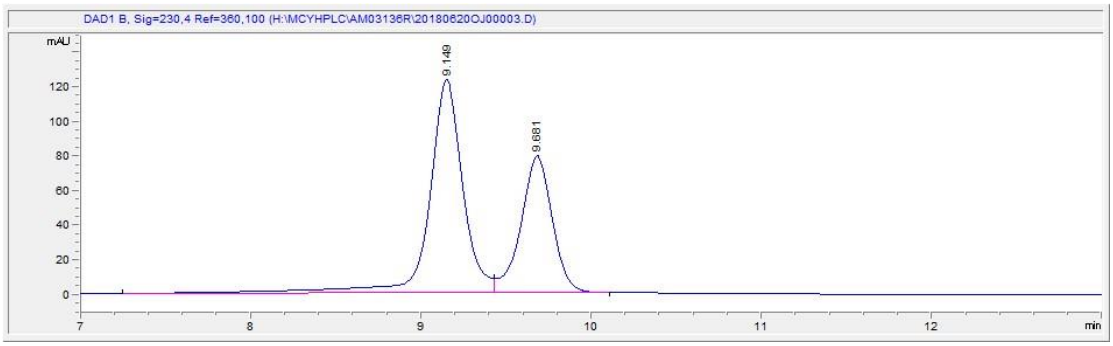
5c

^{13}C NMR 100 MHz $CDCl_3$



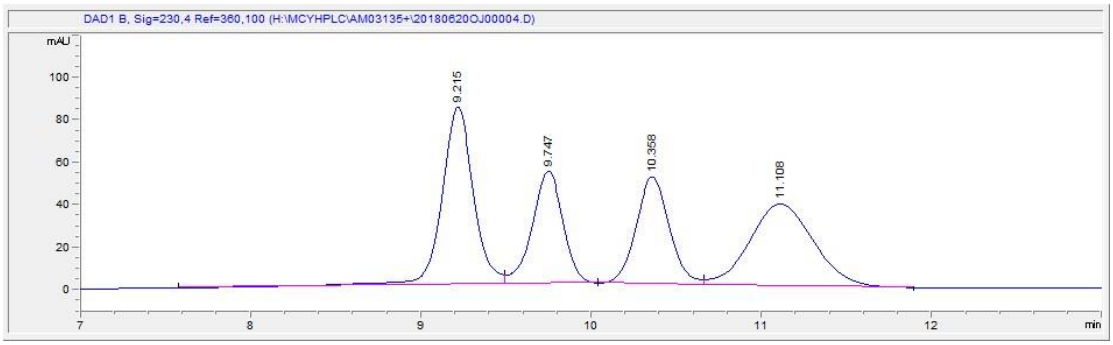
5c

Enantioenriched mixture of compound **5c**

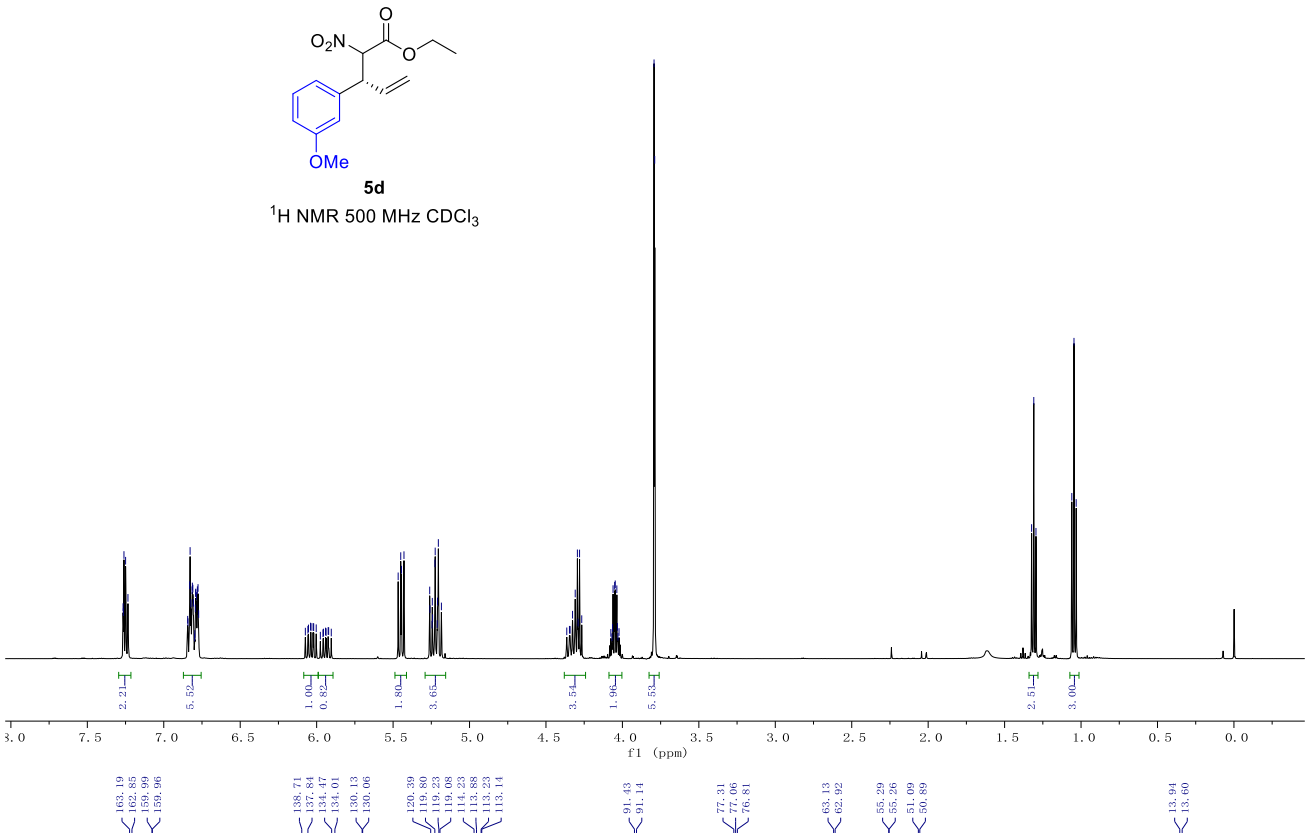


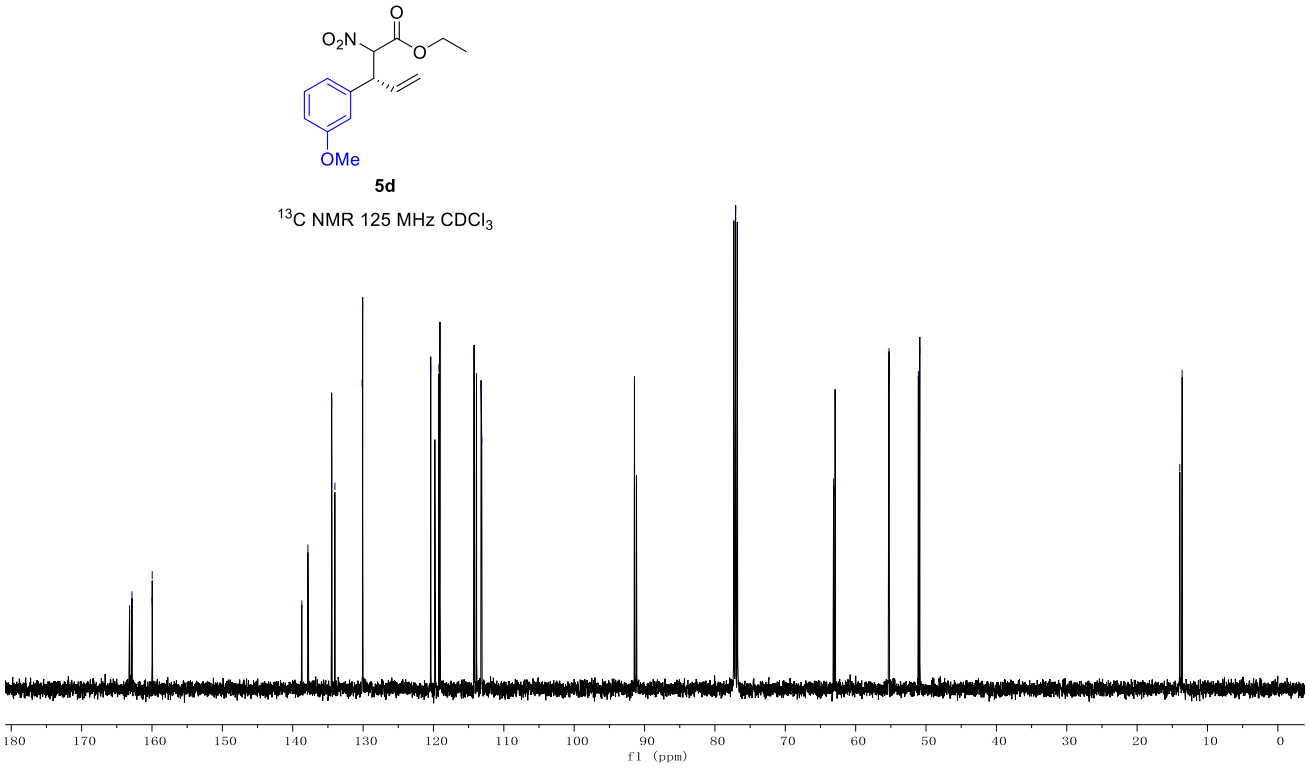
#	Time	Area	Height	Width	Area%	Symmetry
1	9.149	1364.8	117	0.1802	61.031	0.948
2	9.681	871.4	74.4	0.1827	38.969	0.943

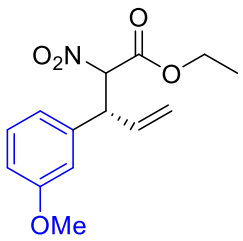
Racemate of compond **5c**



#	Time	Area	Height	Width	Area%	Symmetry
1	9.215	946.5	80.5	0.1832	30.533	0.965
2	9.747	596.3	50.8	0.183	19.236	0.965
3	10.358	641.4	49.3	0.2038	20.690	0.993
4	11.108	915.8	37.1	0.3858	29.541	0.833

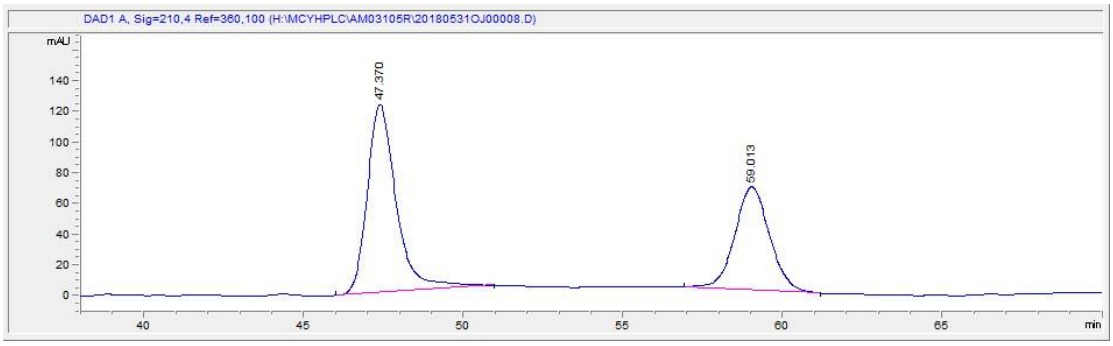

O2N
O
O
OMe
5d
1H NMR 500 MHz CDCl3
f1 (ppm)


O2N
O
O
OMe
5d
13C NMR 125 MHz CDCl3
f1 (ppm)



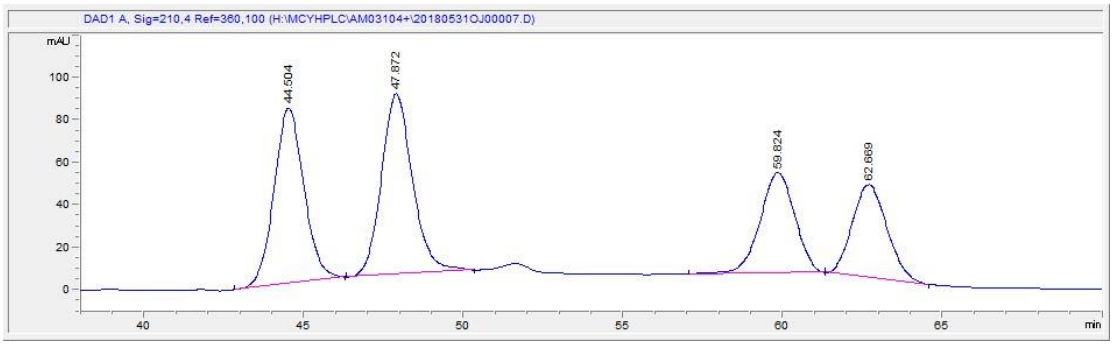
5d

Enantioenriched mixture of compound **5d**

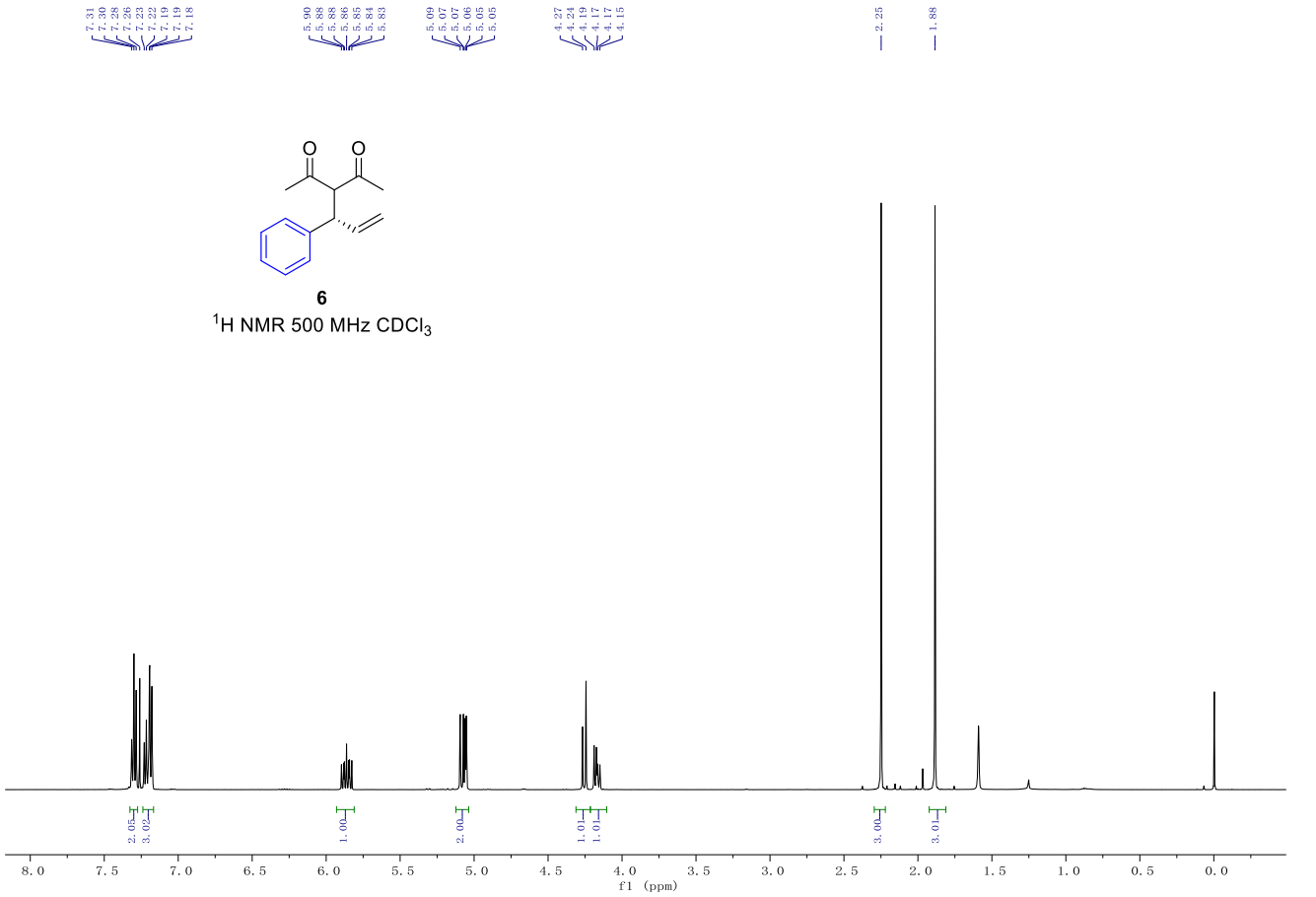


#	Time	Area	Height	Width	Area%	Symmetry
1	47.37	7764.6	122.6	0.9447	60.347	0.712
2	59.013	5102.1	67.3	1.1425	39.653	0.932

Racemate of compond **5d**

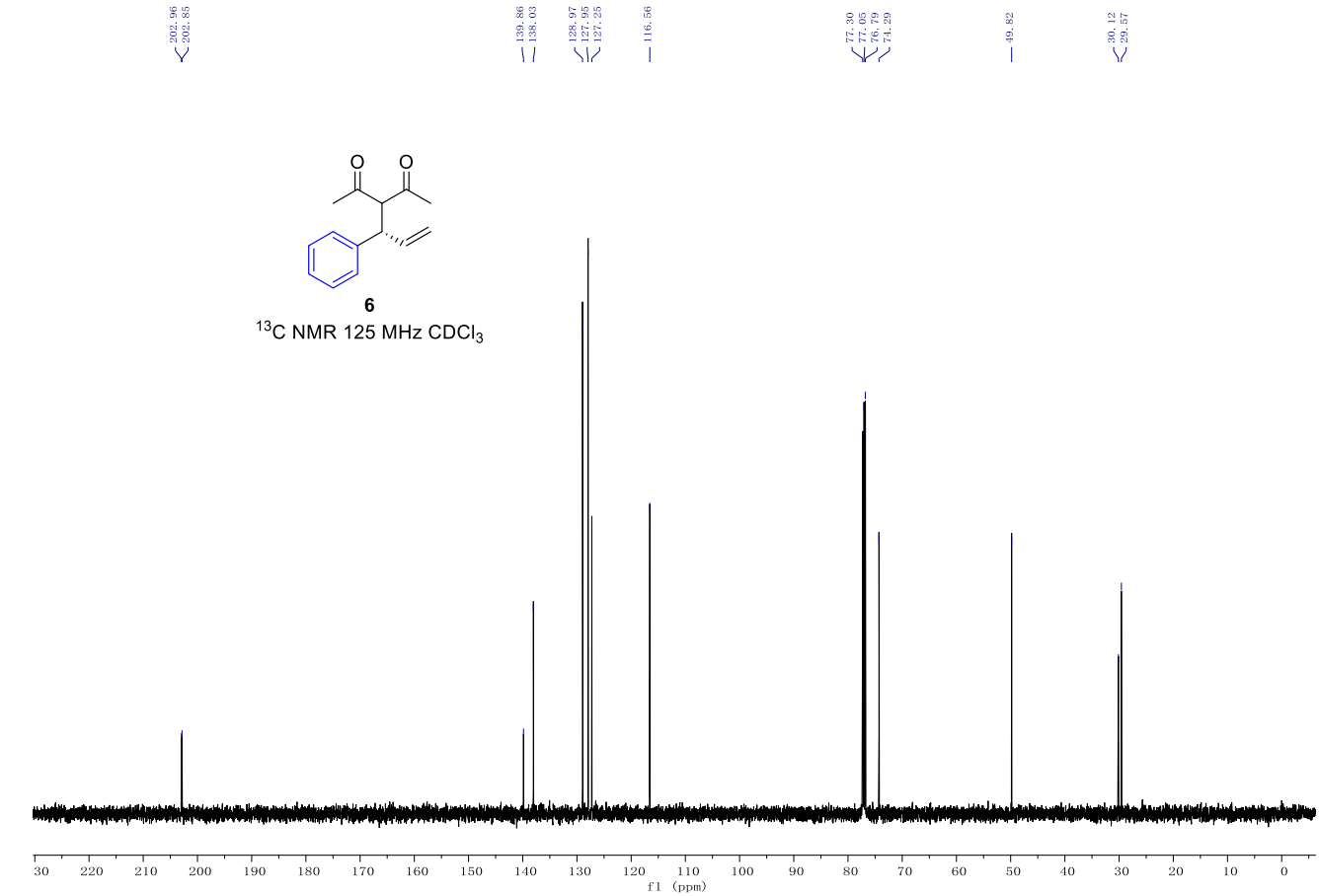


#	Time	Area	Height	Width	Area%	Symmetry
1	44.504	5377.9	82.4	0.9913	29.744	0.909
2	47.872	5765.7	85	1.0293	31.889	0.841
3	59.824	3615.2	47.4	1.1484	19.995	1.037
4	62.669	3321.5	43.7	1.1461	18.371	0.852



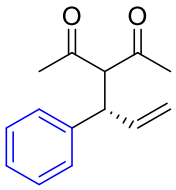
6

^{1}H NMR 500 MHz $CDCl_3$



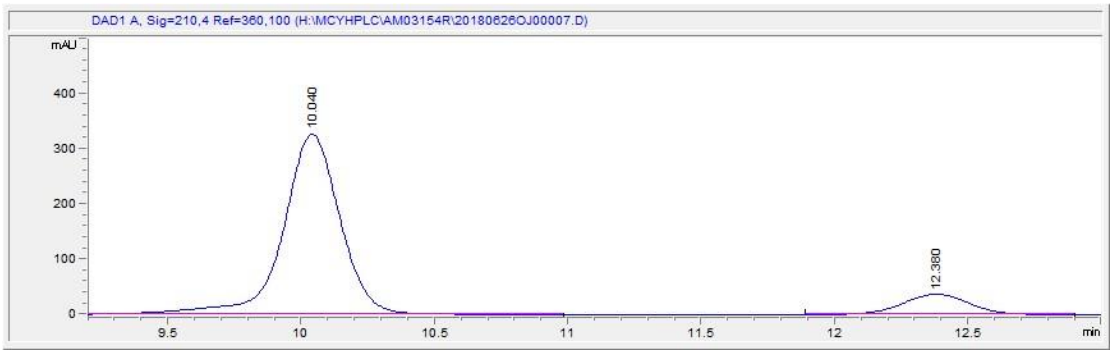
6

^{13}C NMR 125 MHz $CDCl_3$



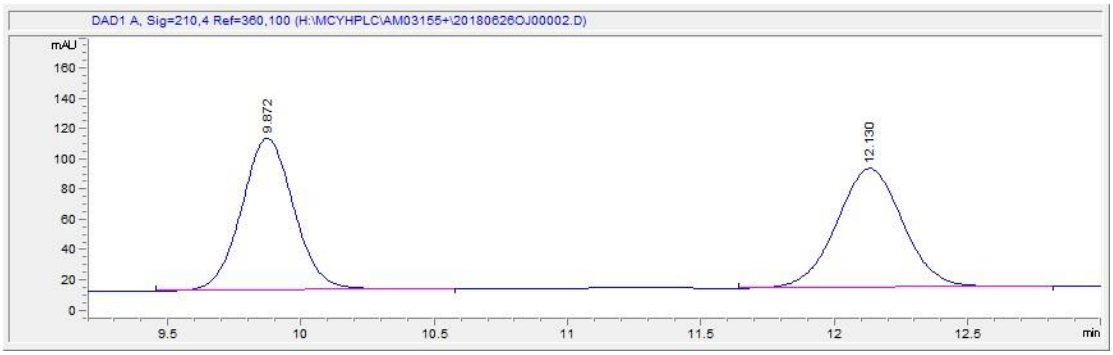
6

Enantioenriched mixture of compound **6**



#	Time	Area	Height	Width	Area%	Symmetry
1	10.04	4872.4	326.1	0.2243	88.546	1.044
2	12.38	630.3	36.5	0.2695	11.454	0.999

Racemate of compond **6**



#	Time	Area	Height	Width	Area%	Symmetry
1	9.872	1378.9	100.5	0.2121	50.336	0.925
2	12.13	1360.5	78.7	0.2677	49.664	0.967