## Electronic Supplementary Information

# Ni-Catalyzed Chemoselective Alcoholysis of *N*-Acyloxazolidinones

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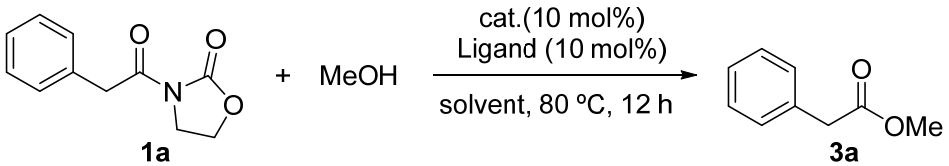
## General Information

Unless otherwise stated, reactions were run under an Argon atmosphere with rigid exclusion of moisture from reagents and glassware. All glassware was dried in Infrared rapid drying box prior to use. $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker 400 or Bruker 500 ($^{1}H$/400 or 500 MHz, $^{13}C$/100 or 125 MHz) spectrometer. Chemical shifts are expressed in parts per million (δ) relative to an internal standard of tetramethylsilane (TMS). Optical rotations were measured with an Anton Paar MCP 500 polarimeter. Melting points were uncorrected. Infrared spectra were recorded with a Nicolet Avatar 330 FT-IR spectrometer using film KBr pellet technique. HRMS spectra were recorded on a Bruker En Apex ultra 7.0T FT-MS apparatus. Unless otherwise stated, commercial reagents were purchased from the reagent supplier (Adamas-beta®, Alfa Aesar, Sigma-Aldrich) and used without purification. $Ni(COD)_2$ was obtained from Strem Chemicals. Silica gel (300–400 mesh) was used for flash column chromatography. All solvents were anhydrous and oxygen-excluded prior to use.

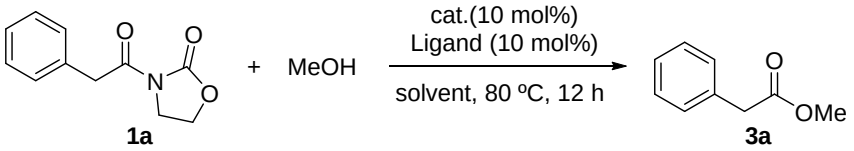
## Reaction optimization and Control experiments

### 1. Optimization of catalyst and ligand




**Typical procedure for the esterification of *N*-acyloxazolidinone (Table S1)(General procedure A).** A vial packaged with tin foil was charged with *N*-acyloxazolidinone **1a** (25.0 mg, 0.12 mmol, 1.0 equiv) and a magnetic stir bar. Then the vial was taken into a glove box and charged with **cat.** (0.024 mmol, 10 mol%) and **ligand** (0.024 mmol, 10 mol%). Subsequently, solvent (0.48 mL, 0.25 M) and then methanol (5.83 uL, 0.144 mmol, 1.2 equiv) were added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 80 °C for 12 h. After cooling to room temperature, the mixture was diluted with $CH_2Cl_2$ (1 mL). The volatiles were removed under reduced pressure, and the yield of **3a** was determined by $^{1}H$ NMR analysis with 1,3,5-trimethoxybenzene as an internal standard.

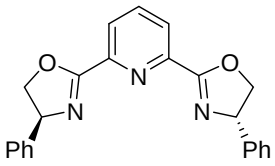
**Table S1.** Optimization of the catalyst and ligand.[a]



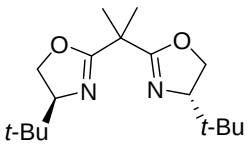

**1a** **3a**

| Entry | Cat.(mol%) | Ligand (mol%) | solvent (0.25 M) | Yield (%)[b] | |
|---|---|---|---|---|---|
| | | | | **3a** | **1a** |
| 1 | 0 | 0 | toluene | 0 | 100 |
| 2 | $PdCl_2$ (10) | $PCy_3$ (20) | toluene | 0 | 100 |
| 3 | $PdCl_2$ (10) | $PPh_3$ (20) | toluene | 0 | 100 |
| 4 | $Pd(PCy_3)_2Cl_2$ (10) | $PCy_3$ (20) | toluene | 0 | 100 |
| 5 | $NiCl_2$•$6H_2O$ (10) | di-$^t$Bubipy (10) | toluene | 0 | 100 |
| 6 | $Ni(PPh_3)_2Cl_2$ (10) | $PPh_3$ (20) | toluene | 0 | 100 |
| 7 | $Ni(PCy_3)_2Cl_2$ (10) | $PCy_3$ (20) | toluene | 0 | 100 |
| 8 | $Ni(cod)_2$ (10) | $PCy_3$ (10) | toluene | 27 | 65 |
| 9 | $Ni(cod)_2$ (10) | $PPh_3$ (10) | toluene | 17 | 77 |
| 10 | $Ni(cod)_2$ (10) | P$^n$Bu$_3$ (10) | toluene | 34 | 56 |
| 11 | $Ni(cod)_2$ (10) | Box**1** (10) | toluene | 24 | 75 |
| 12 | $Ni(cod)_2$ (10) | Box**2** (10) | toluene | 34 | 62 |
| 13 | $Ni(cod)_2$ (10) | SIPr (10) | toluene | 94 | trace |
| 14 | $Ni(cod)_2$ (10) | IPr (10) | toluene | 87 | 10 |
| 15 | $Ni(cod)_2$ (10) | SIMes (10) | toluene | 86 | 10 |
| 16 | $Ni(cod)_2$ (10) | IMes (10) | toluene | 95 | trace |
| **17** | **$Ni(cod)_2$ (10)** | **2,2'-bipyr. (10)** | **toluene** | **95** | **trace** |
| 18 | $Ni(cod)_2$ (10) | di-$^t$Bubipy (10) | toluene | 67 | 32 |
| 19 | $Ni(cod)_2$ (10) | 1,10-phenanthroline (10) | toluene | 54 | 38 |
| 20 | $NiCl_2$•glyme (10) | 2,2'-bipyr. (10) | toluene : DMF = 1:1 | 0 | 100 |
| 21 | $NiCl_2$•$6H_2O$ (10) | 2,2'-bipyr. (10) | toluene : DMF = 1:1 | 0 | 100 |
| 22 | $Ni(PPh_3)_2Cl_2$ (10) | 2,2'-bipyr. (10) | toluene | 0 | 100 |
| 23 | $Ni(PCy_3)_2Cl_2$ (10) | 2,2'-bipyr. (10) | toluene | 0 | 100 |
| 24 | $NiCl_2$ (10) | 2,2'-bipyr. (10) | toluene | 0 | 100 |
| 25 | $NiI_2$ (10) | 2,2'-bipyr. (10) | toluene | 0 | 100 |
| 26 | $NiCp_2$ (10) | 2,2'-bipyr. (10) | toluene | 88 | trace |

[a]Reaction conditions: **1a**, 0.12 mmol; MeOH, 0.144 mmol (1.2 equiv.);[b] Yield determined by $^1$H NMR spectroscpy using 1,3,5-trimethoxybenzene as an internal standard.

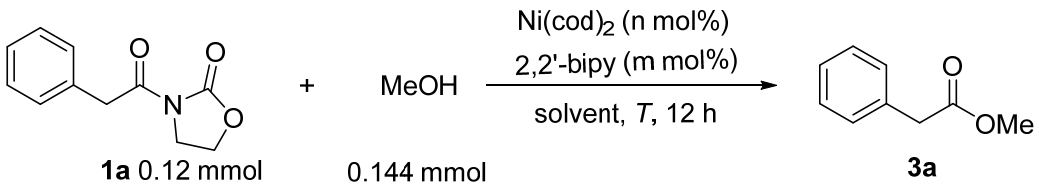



Box**1**



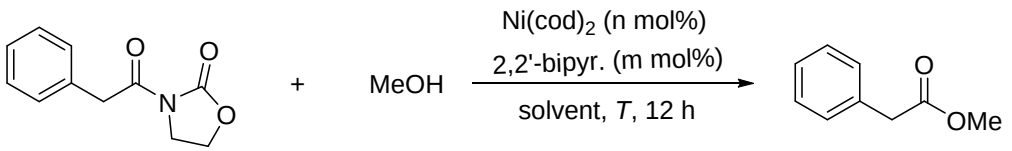

Box**2**

## 2. Optimization of the amount of catalytic system, the temperature, the solvent and the concentration.




**General procedure B for the esterification of *N*-acyloxazolidinone from Table S2 (1a is used as an example).** A vial packaged with tin foil was charged with *N*-Acyloxazolidinone **1a** (25.0 mg, 0.12 mmol, 1.0 equiv) and a magnetic stir bar. Then the vial was taken into a glove box and charged with **Ni(cod)$_2$ (n mol%)** and and **2,2'-bipyr. m mol%)**. Subsequently, solvent **(x M)** and then methanol (5.83 uL, 0.144 mmol, 1.2 equiv) were added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at ***T*** for 12 h. After cooling to room temperature, the mixture was diluted with $CH_2Cl_2$ (1 mL). The volatiles were removed under reduced pressure, and the yield of **3a** was determined by $^1$H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard or purified by flash column chromatography.

**Table S2.** The reaction conditions of screening for the esterification of *N*-acyloxazolidinone.

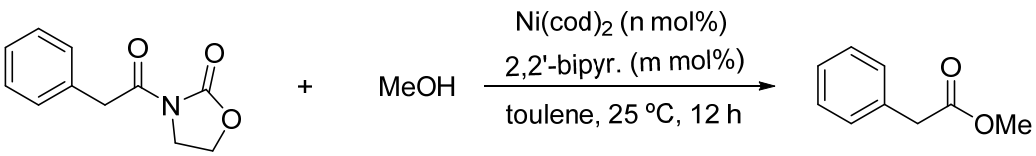



**1a** 0.12 mmol 0.144 mmol **3a**

| entry | $Ni(cod)_2$ (n mol%) | 2,2'-bipy (m mol%) | reaction condition | results (%)[b] | |
|---|---|---|---|---|---|
| | | | | **3a** | **1a** |
| 1 | 5 mol% | 5 mol% | 80 ºC, toluene (0.25 M),12 h | 56 | 33 |
| **2** | **5 mol%** | **10 mol%** | **80 ºC, toluene (0.25 M),12 h** | **96 (92)[c]** | **0** |
| 3 | 5 mol% | 15 mol% | 80 ºC, toluene (0.25 M),12 h | 94 (91)[c] | 0 |
| 4 | 5 mol% | 20 mol% | 80 ºC, toluene (0.25 M),12 h | 55 | 37 |
| 5 | 10 mol% | 5 mol% | 80 ºC, toluene (0.25 M),12 h | 53 | 45 |
| 6 | 10 mol% | 10 mol% | 80 ºC, toluene (0.25 M),12 h | 95 (91)[c] | 0 |
| 7 | 10 mol% | 20 mol% | 80 ºC, toluene (0.25 M),12 h | 95 | 0 |
| **8** | **5 mol%** | **10 mol%** | **25 ºC, toluene (0.25 M),12 h** | **95 (93)[b]** | **0** |
| 9 | 5 mol% | 15 mol% | 25ºC, toluene (0.25 M),12 h | 91 | 0 |
| 10 | 10 mol% | 10 mol% | 25 ºC, toluene (0.25 M),12 h | 93 | 0 |
| 11 | 10 mol% | 10 mol% | 66 ºC, THF (0.25 M),12 h | 63 | 36 |
| 12 | 10 mol% | 10 mol% | 80 ºC, 1,4-Dioxane (0.25 M),12 h | 75 | 17 |
| 13 | 10 mol% | 10 mol% | 80 ºC, DMF (0.25 M),12 h | 72 | 15 |
| 14 | 5 mol% | 10 mol% | 25 ºC, toluene (0.10 M),12 h | 46 | 45 |
| 15 | 5 mol% | 10 mol% | 25 ºC, toluene (0.20 M),12 h | 94 | 0 |
| 16 | 5 mol% | 10 mol% | 25 ºC, toluene (0.50 M),12 h | 92 | 0 |
| **17** | **5 mol%** | **10 mol%** | **25 ºC, toluene (0.80 M),12 h** | **94** | **0** |
| 18 | 5 mol% | 10 mol% | 25 ºC, toluene (1.00 M),12 h | 91 | 0 |

[a] Reaction conditions: **1a**, 0.12 mmol; MeOH, 0.144 mmol (1.2 equiv.);[b] Yield determined by $^1H$ NMR spectroscpy using 1,3,5-trimethoxybenzene as an internal standard; [c] Isolated yield.

## 3. Further optimization of the amount of $Ni(cod)_2$ and 2,2'-bipyr..

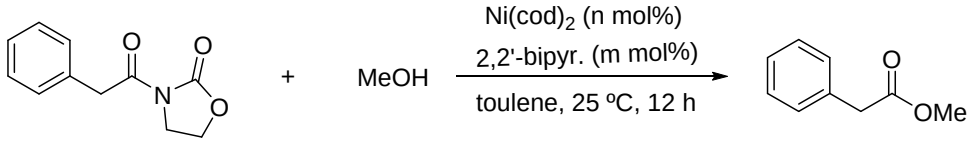



**1a** 0.50 mmol 0.60 mmol **3a**

**General procedure C for the esterification of *N*-acyloxazolidinone from Table S3 (1a is used as an example).** A vial packaged with tin foil was charged with *N*-Acyloxazolidinone **1a** (103 mg, 0.50 mmol, 1.0 equiv) and a magnetic stir bar. Then the vial was taken into a glove box and charged with **$Ni(cod)_2$ (n mol%)** and and **2,2'-bipyr. m mol%)**. Subsequently, toluene (0.25 M or 0.80 M) and then methanol (24.3 uL, 0.60 mmol, 1.2 equiv) were added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 25 ºC for 12 h. After cooling to room temperature, the mixture was diluted with $CH_2Cl_2$ (1 mL). The

volatiles were removed under reduced pressure, and the yield of **3a** was determined by $^1$H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard or purified by flash column chromatography.

**Table S3.** Screening for the amount of the catalytic system.[a]

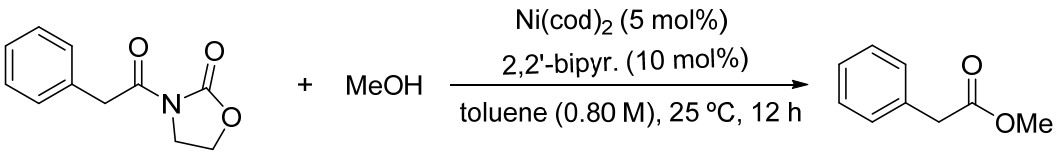



**1a** 0.50 mmol 0.60 mmol **3a**

| entry | $Ni(cod)_2$ (n mol%) | 2,2'-bipy (m mol%) | reaction condition | results (%)[b] | |
|---|---|---|---|---|---|
| | | | | **3a** | **1a** |
| 1 | 1 mol% | 2mol% | 25 ºC, toluene (0.25 M),12 h | 0 | 100 |
| 2 | 2 mol% | 3 mol% | 25 ºC, toluene (0.25 M),12 h | 0 | 100 |
| 3 | 2 mol% | 4 mol% | 25 ºC, toluene (0.25 M),12 h | 39 | 57 |
| 4 | 3 mol% | 5 mol% | 25 ºC, toluene (0.25 M),12 h | 48 | 46 |
| 5 | 5 mol% | 10 mol% | 25 ºC, toluene (0.25 M),12 h | 96 (92)[c] | 0 |
| **6** | **5 mol%** | **10 mol%** | **25 ºC, toluene (0.80 M),12 h** | **95 (92)[c]** | **0** |
| 7 | 4 mol% | 10 mol% | 25 ºC, toluene (0.80 M),12 h | 90 | trace |
| 8 | 4 mol% | 8 mol% | 25 ºC, toluene (0.80 M),12 h | 88 | trace |
| 9 | 4 mol% | 6 mol% | 25 ºC, toluene (0.80 M),12 h | 39 | 53 |
| 10 | 4 mol% | 12 mol% | 25 ºC, toluene (0.80 M),12 h | 85 | < 5 |

[a]Reaction conditions: **1a**, 0.50 mmol; MeOH, 0.60 mmol (1.2 equiv.); [b] Yield determined by $^1$H NMR spectroscpy using 1,3,5-trimethoxybenzene as an internal standard; [c] Isolated yield.

## 4. Optimization of the amount of MeOH added.

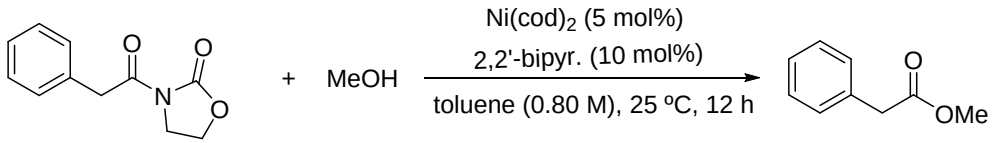



**1a** 0.12 mmol n equiv **3a**

**General procedure C for the esterification of *N*-acyloxazolidinone from Table S4 (1a is used as an example).** A vial packaged with tin foil was charged with *N*-Acyloxazolidinone **1a** (25.0 mg, 0.12 mmol, 1.0 equiv) and a magnetic stir bar. Then the vial was taken into a glove box and charged with $Ni(cod)_2$ (5 mol%) and and 2,2'-bipyr. (10 mol%). Subsequently, toluene (0.48 uL, 0.25 M) and then **methanol (n equiv)** were added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 25 ºC for 12 h. After cooling to room temperature, the mixture was diluted with $CH_2Cl_2$ (1 mL). The volatiles were removed under reduced pressure, and the yield of **3a** was determined by $^1$H NMR analysis with

1,3,5-trimethoxybenzene as an internal standard or purified by flash column chromatography.

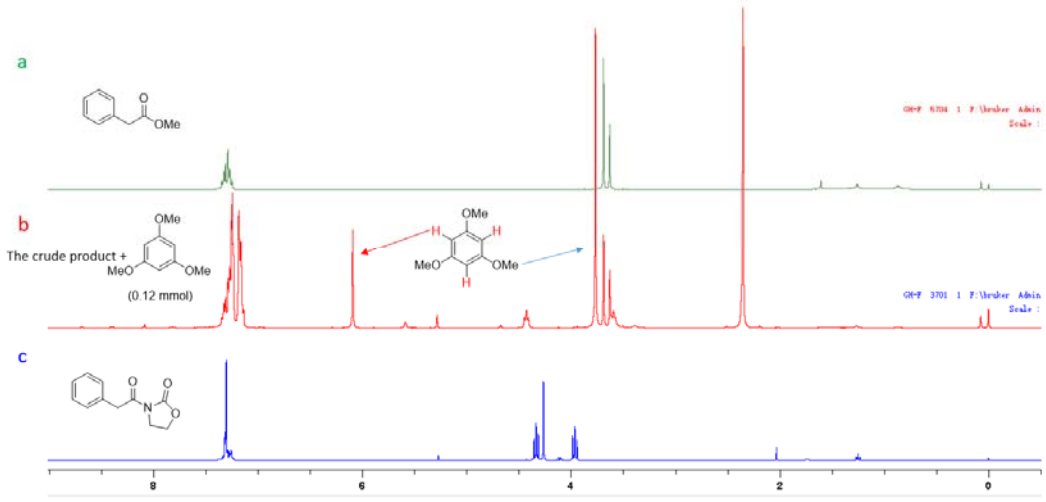
**Table S4.** Screening for the amount of MeOH added.[a]




**1a** 0.12 mmol  n equiv  **3a**

| entry | MeOH ( n equiv) | results (%)[b] | |
|---|---|---|---|
| | | **3a** | **1a** |
| 1 | 1.0 | 87 | trace |
| 2 | 1.1 | 91 | 0 |
| 3 | 1.2 | 94 | 0 |
| **4** | **1.5** | **97 (92)** | **0** |
| 5 | 1.8 | 92 | 0 |
| 6 | 2.0 | 90 | 0 |

[a] Reaction conditions: **1a**, 0.12 mmol; MeOH (n equiv.); [b] Yield determined by $^1$H NMR spectroscpy using 1,3,5-trimethoxybenzene as an internal standard.




**d.**

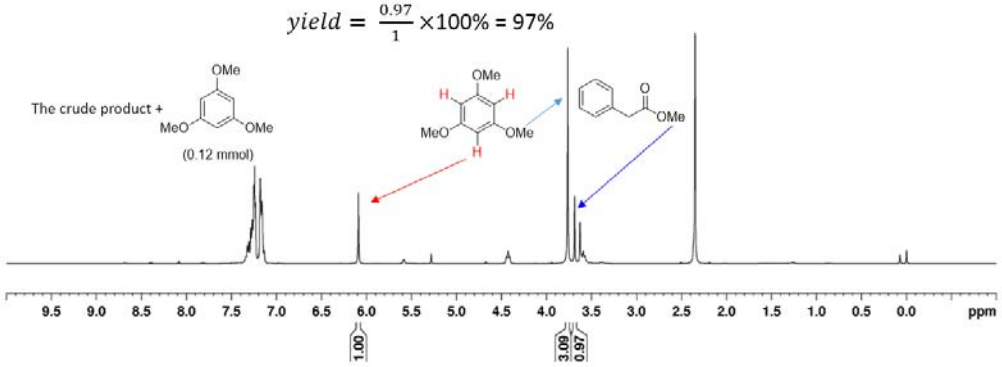



**Figure S1**. (a) The $^{1}$H-NMR spectra (400 MHz, $CDCl_3$) of purified product **3a**; (b) The $^{1}$H-NMR spectra (400 MHz, $CDCl_3$) of the mixture after reaction with 1,3,5-trimethoxybenzene as an internal standard; (c) The $^{1}$H-NMR spectra (400 MHz, $CDCl_3$) of the substrate **1a**; (d) The calculation formula of the yield of **3a** determined by $^{1}$H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard (entry 4, Table S4).

## Scope of methodology

### 1. Substrates 1a–1k, 2a-p, 5a, 5b.

The known *N*-Acyloxazolidinones **1a–1k** were synthesized according to literature procedure,[1] and **2a–2m** were synthesized according to the literature.[2] **2o**-**2p** were synthesized according to literature procedure.[3] The imide-type compound **5a** and **5b** were synthesized according to the literature.[4]

### 2. General procedure D for the catalytic methanolysis of *N*-acyloxazolidinones.

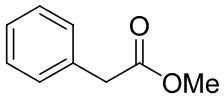
A vial packaged with tin foil was charged with *N*-acyloxazolidinones **1** (0.40 mmol, 1.0 equiv) and a magnetic stir bar. Then the vial was taken into a glove box and charged with $Ni(cod)_2$ (5.50 mg, 0.02 mmol, 5 mol%) and and 2,2'-bipyr. (6.24 mg, 0.04 mmol, 10 mol%). Subsequently, toluene (0.50 mL, 0.25 M) and then methanol (24.3 uL, 0.60 mmol, 1.5 equiv) were added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 25 $^{o}$C for 12 h. After cooling to room temperature, the mixture was diluted with $CH_2Cl_2$ (1 mL). The residue was purified by flash column chromatography to yield the desired methyl esters **3**.

### 3. General procedure E for the catalytic alcoholysis of chiral *N*-acyloxazolidinones.

A vial packaged with tin foil was charged with *N*-acyloxazolidinones **1 or 2** (0.30 mmol, 1.0 equiv) and a magnetic stir bar. Then the vial was taken into a glove box and charged with $Ni(cod)_2$ (4.13 mg, 0.015 mmol, 5 mol%) and and 2,2'-bipyr. (4.69 mg, 0.03 mmol, 10 mol%). Subsequently, toluene (0.38 mL, 0.25 M) and then methanol (18.2 uL, 0.45 mmol, 1.5 equiv) or EtOH (26.2 uL, 0.45 mmol, 1.5 equiv) or BnOH (46.6 uL, 0.45 mmol, 1.5 equiv) were added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 25$^{o}$C or 80 $^{o}$C for 12 h. After cooling to room temperature, the mixture was diluted with $CH_2Cl_2$ (1 mL). The residue was purified by flash column chromatography to yield the desired methyl esters **3**.

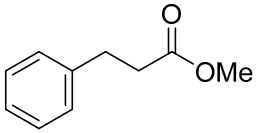
## Compound characterizations

### Methyl 2-phenylacetate (3a)



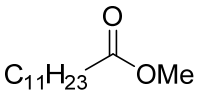

Following **general procedure D**, the reaction of *N*-acyloxazolidinone **1a** (82.0 mg, 0.40 mmol) with methanol (24.3 uL, 0.60 mmol), afforded the commercial available ester **3a** as a clear oil (55.2 mg, 92% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 50). Spectral data match those previously reported.[5a]

### Methyl 3-phenylpropanoate (3b)



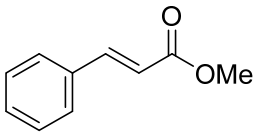

Following **general procedure D**, the reaction of *N*-acyloxazolidinone **1b** (87.6 mg, 0.40 mmol) with methanol (24.3 uL, 0.60 mmol), afforded the commercial available ester **3b** as a clear oil (57.8 mg, 88% Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 50). Spectral data match those previously reported.[5c]

### Methyl dodecanoate (3c)



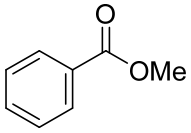

Following **general procedure D**, the reaction of *N*-acyloxazolidinone **1c** (107.7 mg, 0.40 mmol) with methanol (24.3 uL, 0.60 mmol), afforded the commercial available ester **3c** as a clear oil (77.2 mg, 90% Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 50). Spectral data match those previously reported.[5a]

### Methyl cinnamate (3d)



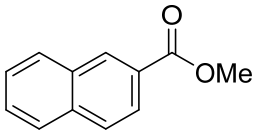

Following **general procedure D**, the reaction of *N*-acyloxazolidinone **1d** (86.8 mg, 0.40 mmol) with methanol (24.3 uL, 0.60 mmol), afforded the commercial available ester **3d** as a colorless oil (55.1 mg, 85% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 20). Spectral data match those previously reported.[5c]

### Methyl benzoate (3e)



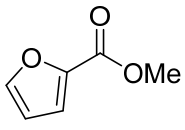

Following **general procedure D**, the reaction of *N*-acyloxazolidinone **1e** (76.4 mg, 0.40 mmol) with methanol (24.3 uL, 0.60 mmol), afforded the commercial available ester **3e** as a clear oil (49.5 mg, 91% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 20). Spectral data match those previously reported.[5a]

### Methyl 2-naphthoate (3f)




Following **general procedure D**, the reaction of *N*-acyloxazolidinone **1f** (96.4 mg, 0.40 mmol) with methanol (24.3 uL, 0.60 mmol), afforded the commercial available ester **3f** as a white solid (67.0 mg, 90% Yield). $R_f$: 0.6 (EtOAc/Hexane = 1/ 20). Spectral data match those previously reported.[5d]

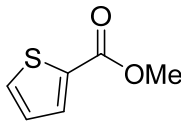
### Methyl 2-furoate (3g)




Following **general procedure D**, the reaction of *N*-acyloxazolidinone **1g** (72.4 mg, 0.40 mmol)

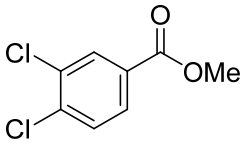
with methanol (24.3 uL, 0.60 mmol), afforded the commercial available ester **3g** as a clear oil (44.4 mg, 88% Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 20). Spectral data match those previously reported.[5i]

**Methyl thiophene-2-carboxylate (3h)**



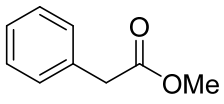

Following **general procedure D**, the reaction of *N*-acyloxazolidinone **1h** (78.8 mg, 0.40 mmol) with methanol (24.3 uL, 0.60 mmol), afforded the commercial available ester **3h** as a clear oil (50.6 mg, 89% Yield). $R_f$: 0.6 (EtOAc/Hexane = 1/ 20). Spectral data match those previously reported. [5j]

**Methyl 3,4-dichlorobenzoate (3i)**



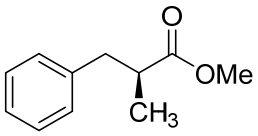

Following **general procedure D**, the reaction of *N*-acyloxazolidinone **1i** (103.6 mg, 0.40 mmol) with methanol (24.3 uL, 0.60 mmol), afforded the commercial available ester **3i** as a pale yellow solid (73.4 mg, 90% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 20). Spectral data match those previously reported.[5k]

**Methyl 2-phenylacetate (3a)**



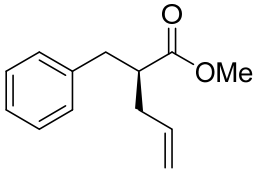

Following **general procedure D**, the reaction of *N*-acyloxazolidinone **1j** (112.4 mg, 0.40 mmol) with methanol (24.3 uL, 0.60 mmol), afforded the commercial available ester **3a** as a clear oil (54.6 mg, 91% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 50). Spectral data match those previously reported.[5a]

**Methyl (*S*)-2-methyl-3-phenylpropanoate (3j)**



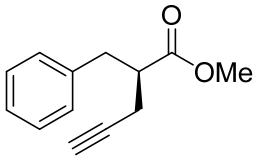

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2a** (92.7 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3j** [5e]as a colorless oil (45.4 mg, 85% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 20); $[\alpha]_D^{20}$ + 37.4 (*c* 1.0, $CHCl_3$); IR (film): 3033, 2917, 2849, 1720, 1451, 1271, 1109, 1026, 711, 697 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.15 (d, *J* = 6.9 Hz, 3H), 2.66 (dd, *J* = 13.2, 7.8 Hz, 1H), 2.70–2.78 (m, 1H), 3.03 (dd, *J* = 13.2, 6.7 Hz, 1H), 3.63 (s, 3H), 7.12–7.18 (m, 2H), 7.18–7.23 (m, 1H), 7.24–7.30 (m, 2H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 16.7, 39.7, 41.4, 51.5, 126.3, 128.3, 128.9, 139.3, 176.5 ppm; HRMS calcd for $[C_{11}H_{14}NaO_2]^+$ ($M+Na^+$): 201.0886; found: 201.0889; Conditions for the chiral HPLC analysis: Chiralpak OJ-H (*n*-hexane/ *i*-PrOH, 95: 5), flow rate = 0.5 mL·$min^{-1}$, $R_t$ = 14.613, 15.328 min, respectively. The enantiomeric excess was determined to be 94.3%.

## Methyl (*S*)-2-benzylpent-4-enoate (3k)



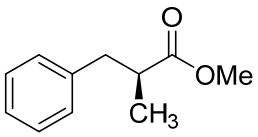

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2b** (100.5 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3k** [5l] as a colorless oil (53.9 mg, 88% Yield). $R_f$: 0.6 (EtOAc/Hexane = 1/ 20); $[\alpha]_D^{20}$ + 30.4 (*c* 0.8, EtOH); IR (film): 3064, 3028, 2950, 2849, 1736, 1642, 1604, 1496, 1454, 1436, 1370, 1164, 1031, 918, 744, 701 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 2.22–2.32 (m, 1H), 2.33–2.42 (m, 1H), 2.71–2.82 (m, 2H), 2.89–2.97 (m, 1H), 3.59 (s, 3H), 5.02–2.10 (m, 2H), 5.69–5.81 (m, 1H), 7.12–7.18 (m, 2H), 7.18–7.23 (m, 1H), 7.24–7.30 (m, 2H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 36.0, 37.8, 47.2, 51.4, 117.1, 126.4, 128.4, 128.9, 135.1, 139.1, 175.3 ppm; HRMS calcd for $[C_{13}H_{16}NaO_2]^+$ ($M+Na^+$): 227.1043; found: 227.1046; Conditions for the chiral HPLC analysis: Chiralpak AD-H (*n*-hexane/ EtOH, 98: 2), flow rate = 1.0 mL·$min^{-1}$, $R_t$ = 4.523, 4.832 min, respectively. The enantiomeric excess was determined to be 97.9%.

**Methyl (*S*)-2-benzylpent-4-ynoate (3l)**



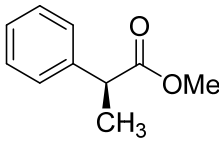

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2c** (99.9 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3l** [5l] as a colorless oil (49.7 mg, 88% Yield). $R_f$: 0.6 (EtOAc/Hexane = 1/ 20); $[\alpha]_D^{20}$ + 10.7(*c* 0.35, EtOH); IR (film): 2953, 2917, 2849, 1738, 1579, 1537, 1432, 1196, 1180, 1142, 1133, 1076, 1033, 636 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 2.05 (t, *J* = 2.7 Hz, 1H), 2.37–2.51 (m, 2H), 2.86 (td, *J* = 13.7, 6.7 Hz, 1H), 2.94 (dd, *J* = 13.7, 6.7 Hz, 1H), 3.05 (dd, *J* = 13.7, 6.7 Hz, 1H), 3.67 (s, 3H), 7.15–7.24 (m, 3H), 7.26–7.31 (m, 2H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 20.4, 36.8, 46.1, 51.8, 70.4, 81.1, 126.6, 128.5, 129.0, 138.3, 174.1 ppm; HRMS calcd for $[C_{13}H_{14}NaO_2]^+$ ($M+Na^+$): 225.0886; found: 225.0890; Conditions for the chiral HPLC analysis: Chiralpak AD-H (*n*-hexane/ EtOH, 98: 2), flow rate = 1.0 mL·$min^{-1}$, $R_t$ = 6.197, 6.688 min, respectively. The enantiomeric excess was determined to be 95.6%.

**Methyl (*S*)-2-methyl-3-phenylpropanoate (3j)**



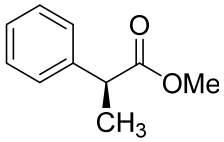

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2d** (96.3 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3j**[5e] as a colorless oil (47.6 mg, 89% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 20); $[\alpha]_D^{20}$ + 36.6 (*c* 1.0, $CHCl_3$); IR (film): 3033, 2917, 2849, 1720, 1451, 1271, 1109, 1026, 711, 697 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.15 (d, *J* = 6.9 Hz, 3H), 2.66 (dd, *J* = 13.2, 7.8 Hz, 1H), 2.70–2.78 (m, 1H), 3.03 (dd, *J* = 13.2, 6.7 Hz, 1H), 3.63 (s, 3H), 7.12–7.18 (m, 2H), 7.18–7.23 (m, 1H), 7.24–7.30 (m, 2H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 16.7, 39.7, 41.4, 51.5, 126.3, 128.3, 128.9, 139.3, 176.5 ppm; HRMS calcd for $[C_{11}H_{14}NaO_2]^+$ ($M+Na^+$): 201.0886; found: 201.0889; Conditions for the chiral HPLC analysis: Chiralpak OJ-H (*n*-hexane/ *i*-PrOH, 95: 5), flow rate = 0.5 mL·$min^{-1}$, $R_t$ = 14.741, 15.776 min, respectively. The enantiomeric excess was determined to be 93.8%.

**Methyl (*S*)-2-phenylpropanoate (3m)**



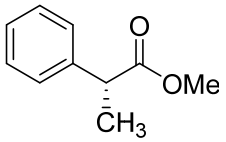

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2e** (92.7 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the chiral auxiliary **4c** (85%, $[\alpha]_D^{20}$ + 5.1 (*c* 1.05, EtOH; lit.[5n] $\alpha$] D + 4.9 (*c* 1.1, EtOH)) and the ester **3m**[5f] as a colorless oil (44.3 mg, 90% Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 20); $[\alpha]_D^{20}$ + 90.6 (*c* 1.0, EtOH); IR (film): 3033, 2917, 2849, 1738, 1461, 1180, 1142, 1076, 697 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.50 (d, *J* = 7.2 Hz, 3H), 3.66 (s, 3H), 3.73 (q, *J* = 7.2 Hz, 1H), 7.22–7.27 (m, 1H), 7.27–7.35 (m, 4H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 18.6, 45.4, 52.0, 127.1, 127.4, 128.6, 140.5, 175.0 ppm; HRMS calcd for $[C_{10}H_{12}NaO_2]^+$ ($M+Na^+$): 187.0730; found: 187.0726; Conditions for the chiral HPLC analysis: Chiralpak OJ-H (*n*-hexane/EtOH, 95: 5), flow rate = 1.0 mL·$min^{-1}$, $R_t$ = 8.757, 9.749 min, respectively. The enantiomeric excess was determined to be 92.3%.

**Methyl (*S*)-2-phenylpropanoate (3m)**



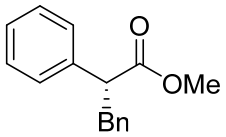

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2f** (78.3 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3m**[5f] as a colorless oil (43.3 mg, 88% Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 20); $[\alpha]_D^{20}$ + 95.6 (*c* 1.0, EtOH); IR (film): 3029, 2917, 1739, 1453, 1207, 1165, 699 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.50 (d, *J* = 7.2 Hz, 3H), 3.66 (s, 3H), 3.73 (q, *J* = 7.2 Hz, 1H), 7.23–7.27 (m, 1H), 7.27–7.35 (m, 4H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 18.6, 45.4, 52.0, 127.1, 127.4, 128.6, 140.5, 175.0 ppm; HRMS calcd for $[C_{10}H_{12}NaO_2]^+$ ($M+Na^+$): 187.0730; found: 187.0726; Conditions for the chiral HPLC analysis: Chiralpak OJ-H (*n*-hexane/EtOH, 97: 3), flow rate = 1.0 mL·$min^{-1}$, $R_t$ = 10.268, 11.434 min, respectively. The enantiomeric excess was determined to be 97.4%.

**Methyl (*R*)-2-phenylpropanoate (3n)**



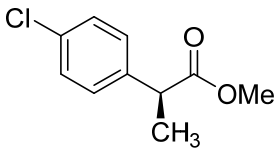
Following **general procedure E**, the reaction of *N*-Acyloxazolidinone **2g** (88.5 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3n** [5f] as a colorless oil (43.3 mg, 88% Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 20); $[\alpha]_D^{20}$ –83.7 (*c* 0.9, EtOH); IR (film): 3033, 2917, 2849, 1738, 1461, 1180, 1142, 1076, 697 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.50 (d, *J* = 7.2 Hz, 3H), 3.66 (s, 3H), 3.73 (q, *J* = 7.2 Hz, 1H), 7.23–7.27 (m, 1H), 7.27–7.35 (m, 4H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 18.6, 45.4, 52.0, 127.1, 127.4, 128.6, 140.5, 175.0 ppm; HRMS calcd for $[C_{10}H_{12}NaO_2]^+$ ($M+Na^+$): 187.0730; found: 187.0727; Conditions for the chiral HPLC analysis: Chiralpak OJ-H (*n*-hexane/EtOH, 95: 5), flow rate = 1.0 mL·$min^{-1}$, $R_t$ = 8.875, 9.525 min, respectively. The enantiomeric excess was determined to be 86.5%.

## Methyl (*R*)-2,3-diphenylpropanoate (3o)



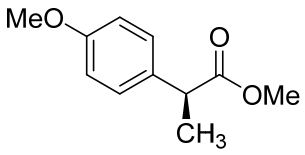
Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2h** (100.5 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3o**[5m] as a colorless oil (59.8 mg, 88% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 20); $[\alpha]_D^{20}$ –87.0 (*c* 1.0, $CHCl_3$); IR (film): 3029, 2917, 2849, 1737, 1620, 1433, 1261, 1196, 1142, 1076, 698 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 3.02 (dd, *J* = 13.8, 7.2 Hz, 1H), 3.41 (dd, *J* = 13.8, 8.8 Hz, 1H), 3.60 (s, 3H), 3.85 (dd, *J* = 8.8, 6.7 Hz, 1H), 7.09–7.13 (m, 2H), 7.15–7.19 (m, 1H), 7.21–7.27 (m, 3H), 7.28–7.33 (m, 4H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 39.8, 52.0, 53.6, 126.3, 127.4, 127.9, 128.3, 128.6, 128.9, 138.6, 139.0, 173.8 ppm; HRMS calcd for $[C_{16}H_{16}NaO_2]^+$ ($M+Na^+$): 263.1043; found: 263.1043; Conditions for the chiral HPLC analysis: Chiralpak OJ-H (*n*-hexane/*i*-PrOH, 90: 10), flow rate = 1.0 mL·$min^{-1}$, $R_t$ = 9.685, 16.939 min, respectively. The enantiomeric excess was determined to be 74.4%.

## Methyl (*S*)-2-(4-chlorophenyl)propanoate (3p)



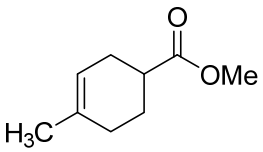

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2i** (102.9 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3p** as a colorless oil (52.3 mg, 88% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 20); $[\alpha]_D^{20}$ + 63.9 (*c* 1.0, $CHCl_3$); IR (film): 3030, 2958, 2917, 2849, 1738, 1641, 1580, 1409, 1180, 1141, 1092, 1076, 1016, 857, 801 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.48 (d, *J* = 7.2 Hz, 3H), 3.66 (s, 3H), 3.70 (q, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 18.5, 44.8, 52.1, 128.8, 128.9, 133.0, 138.9, 174.6 ppm; HRMS calcd for $[C_{10}H_{11}ClNaO_2]^+$ ($M+Na^+$): 221.0340; found: 221.0343; Conditions for the chiral HPLC analysis: Chiralpak OJ-H (*n*-hexane/ *i*-PrOH, 99: 1), flow rate = 1.0 mL·$min^{-1}$, $R_t$ = 10.389 min, respectively. The enantiomeric excess was determined to be >99.0%.

**Methyl (*S*)-2-(4-methoxyphenyl)propanoate (3q)**



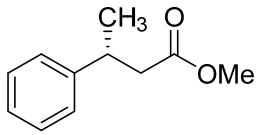

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2j** (101.7 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3q** as a colorless oil (41.9 mg, 72% Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 20); $[\alpha]_D^{20}$ + 74.0 (*c* 0.40, $CHCl_3$); IR (film): 3027, 2960, 2917, 2849, 1738, 1620, 1580, 1513, 1382, 1180, 1142, 1076, 1035, 865, 802 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.47 (d, *J* = 7.2 Hz, 3H), 3.65 (s, 3H), 3.68 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 6.82–6.89 (m, 2H), 7.19–7.25 (m, 2H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 18.6, 44.5, 52.0, 55.2, 114.0, 128.4, 132.6, 158.7, 175.3 ppm; HRMS calcd for $[C_{10}H_{11}ClNaO_2]^+$ ($M+Na^+$): 221.0340; found: 221.0343; Conditions for the chiral HPLC analysis: Chiralpak OJ-H (*n*-hexane/ *i*-PrOH, 99.2: 0.8), flow rate = 1.0 mL·$min^{-1}$, $R_t$ = 28.116, 30.974 min, respectively. The enantiomeric excess was determined to be 95.1%.

**Methyl 4-methylcyclohex-3-ene-1-carboxylate (3r)**



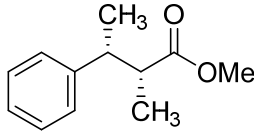

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2k** (62.7 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3r** as a colorless oil (38.8 mg, 84% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 20); IR (film): 2958, 2849, 1738, 1461, 1180, 1142, 1076, 724 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.65 (br s, 3H), 1.68-1.75 (m, 1H), 1.96-2.04 (m, 3H), 2.19- 2.25 (m, 2H), 2.45-2.52 (m, 1H), 3.68 (s, 3H), 5.37 (br s, 1H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 23.4, 25.5, 27.7, 29.3, 39.1, 51.6, 119.2, 133.7, 176.5 ppm; HRMS calcd for $[C_9H_{14}NaO_2]^+$ ($M+Na^+$): 177.0886; found: 177.0887.

## Methyl (*R*)-3-phenylbutanoate (3s)




Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2l** (92.7 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3s** as a colorless oil (40.4 mg, 83% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 20); $[\alpha]_D^{20}$ –16.8 (*c* 0.25, $CHCl_3$); IR (film): 3029, 2964, 2920, 2847, 1739, 1603, 1495, 1453, 1436, 1268, 1167, 1085, 1022, 763, 700 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.30 (d, *J* = 7.0 Hz, 3H), 2.55 (dd, *J* = 15.2, 8.3 Hz, 1H), 2.63 (dd, *J* = 15.2, 6.8 Hz, 1H), 3.24–3.33 (m, 1H), 3.62 (s, 3H), 7.17–7.25 (m, 3H), 7.27–7.33 (m, 2H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 21.8, 36.4, 42.7, 51.5, 126.4, 126.7, 128.5, 145.7, 172.8 ppm; HRMS calcd for $[C_{11}H_{14}NaO_2]^+$ ($M+Na^+$): 201.0886; found: 201.0890.

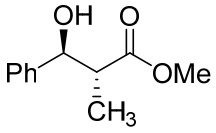
## Methyl (2*R*,3*R*)-2-methyl-3-phenylbutanoate (3t)




Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2m** (96.9 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3t** as a colorless oil (32.9 mg, 57%

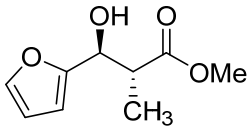
Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 20); $[\alpha]_D^{20}$ –13.0 (*c* 0.20, $CHCl_3$); IR (film): 3027, 2959, 2917, 2849, 1736, 1579, 1261, 1196, 1142, 1093, 1076, 1021, 801 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.17 (d, *J* = 7.0 Hz, 3H), 1.27 (d, *J* = 7.0 Hz, 3H), 2.63–2.71 (m, 1H), 3.02–3.10 (m, 1H), 3.48 (s, 3H), 7.16–7.22 (m, 3H), 7.26–7.30 (m, 2H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 14.1, 17.5, 42.3, 46.7, 51.3, 126.3, 127.3, 128.2, 144.9, 176.1 ppm; HRMS calcd for $[C_{12}H_{16}NaO_2]^+$ ($M+Na^+$): 215.1043; found: 215.1046.

**Methyl (2*R*,3*S*)-3-hydroxy-2-methyl-3-phenylpropanoate (3u)**




Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2n** (101.7 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3u** as a colorless oil (53.6 mg, 92% Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 2); $[\alpha]_D^{20}$ –45.6 (*c* 0.90, $CHCl_3$); IR (film): 3400, 2957, 2917, 2849, 1738, 1726, 1579, 1433, 1261, 1196, 1180, 1142, 1076, 1022, 801 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.01 (d, *J* = 7.2 Hz, 3H), 2.78–2.86 (m, 1H), 2.95 (d, *J* = 4.2 Hz, 1H), 3.73 (s, 3H), 4.75 (dd, *J* = 8.6, 4.2 Hz, 1H), 7.29–7.38 (m, 5H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 14.5, 47.1, 51.9, 76.4, 126.7, 128.1, 128.5, 141.5, 176.3 ppm; HRMS calcd for $[C_{11}H_{14}NaO_3]^+$ ($M+Na^+$): 217.0835; found: 217.0838.

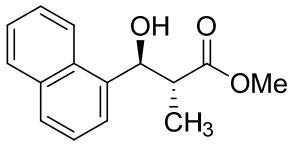
**Methyl (2*R*,3*S*)-3-(furan-2-yl)-3-hydroxy-2-methylpropanoate (3v)**




Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2o** (98.7 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3v** as a colorless oil (46.9 mg, 85% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 3); $[\alpha]_D^{20}$ –36.7 (*c* 1.0, $CHCl_3$); IR (film): 3457, 2952, 2917, 2849, 1738, 1723, 1461, 1434, 1196, 1180, 1142, 1076, 1013, 743 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.09 (d, *J* = 7.2 Hz, 3H), 2.98–3.07 (m, 1H), 3.11 (d, *J* = 6.0 Hz, 1H), 3.73 (s, 3H), 4.28 (dd, *J* = 8.4, 6.0 Hz, 1H), 6.26–6.31 (m, 1H), 6.31–6.36 (m, 1H), 7.34–7.41 (m, 1H) ppm; $^{13}C$

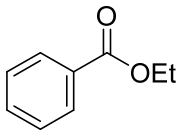
NMR (100 MHz, $CDCl_3$) $\delta$ 14.1, 44.6, 51.9, 69.7, 107.5, 110.2, 142.3, 154.1, 175.8 ppm; HRMS calcd for $[C_9H_{12}NaO_4]^+$ (M+$Na^+$): 207.0628; found: 207.0631.

**Methyl (2*R*,3*S*)-3-hydroxy-2-methyl-3-(naphthalen-1-yl)propanoate (3w)**



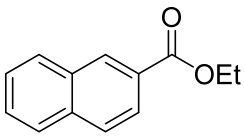

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2p** (116.7 mg, 0.30 mmol) with methanol (18.2 uL, 0.45 mmol), afforded the ester **3w** as a colorless oil (46.1 mg, 63% Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 3); $[\alpha]_D^{20}$ −54.9 (*c* 1.3, $CHCl_3$); IR (film): 3471, 3048, 2951, 2918, 2849, 1736, 1459, 1435, 1196, 1167, 1077, 1043, 803, 779 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.00 (d, *J* = 7.2 Hz, 3H), 3.11–3.20 (m, 1H), 3.35 (d, *J* = 3.3 Hz, 1H), 3.69 (s, 3H), 5.48 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.40–7.54 (m, 4H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.82–7.87 (m, 1H), 8.21 (d, *J* = 8.1 Hz, 1H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 14.9, 46.6, 51.8, 73.7, 123.5, 124.6, 125.2, 125.5, 126.1, 128.5, 128.9, 130.9, 133.8, 137.2, 176.4 ppm; HRMS calcd for $[C_{15}H_{16}NaO_3]^+$ (M+$Na^+$): 267.0992; found: 267.0988.

**Ethyl benzoate (3x)**




Following **general procedure E**, the reaction of *N*-acyloxazolidinone **1e** (57.3 mg, 0.30 mmol) with EtOH (26.2 uL, 0.45 mmol), afforded the commercial available ester **3x** as a clear oil (38.3 mg, 85% Yield). $R_f$: 0.6 (EtOAc/Hexane = 1/ 20). Spectral data match those previously reported.[5a]

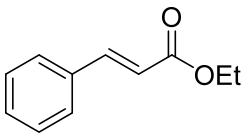
**Ethyl 2-naphthoate (3y)**




Following **general procedure E**, the reaction of *N*-acyloxazolidinone **1f** (72.3 mg, 0.30 mmol)

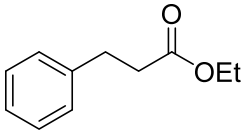
with EtOH (26.2 uL, 0.45 mmol), afforded the commercial available ester **3y** as a clear oil (49.2 mg, 82% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 50). Spectral data match those previously reported.[5h]

**Ethyl cinnamate (3z)**



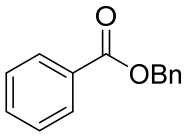

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **1d** (65.1 mg, 0.30 mmol) with EtOH (26.2 uL, 0.45 mmol), afforded the commercial available ester **3z** as a clear oil (42.3 mg, 80% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 50). Spectral data match those previously reported.[5c]

**Ethyl 3-phenylpropanoate (3aa)**



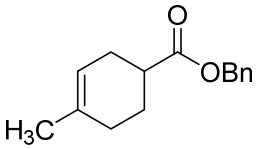

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **1b** (65.7 mg, 0.30 mmol) with EtOH (26.2 uL, 0.45 mmol), afforded the commercial available ester **(3aa)** as a clear oil (43.3 mg, 81% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 50). Spectral data match those previously reported.[5h]

**Benzyl benzoate (3ab)**



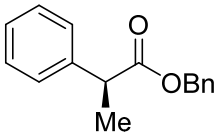

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **1e** (57.3 mg, 0.30 mmol) with BnOH (46.6 uL, 0.45 mmol), afforded the commercial available ester **3ab** as a clear oil (48.4 mg, 76% Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 20). Spectral data match those previously reported.[5a]

**Benzyl 4-methylcyclohex-3-ene-1-carboxylate (3ac)**



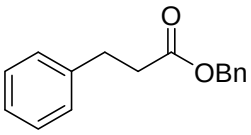

Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2k** (62.7 mg, 0.30 mmol) with BnOH (46.6 uL, 0.45 mmol), afforded the ester **(3ac)** as a clear oil (52.5 mg, 76% Yield). $R_f$: 0.5 (EtOAc/Hexane = 1/ 20); IR (film): 3033, 2917, 2849, 1737, 1455, 1168, 1157, 1142, 1076, 697 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.64 (br s, 3H), 1.69-1.77 (m, 1H), 1.96-2.05 (m, 3H), 2.21- 2.28 (m, 2H), 2.51-2.58 (m, 1H), 5.12 (s, 2H), 5.37 (s, 1H), 7.29-7.39 (m, 5H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 23.4, 25.4, 27.6, 29.2, 39.2, 66.0, 119.2, 127.9, 128.1, 128.5, 133.7, 136.3, 175.7 ppm; HRMS calcd for $[C_{15}H_{14}NaO_2]^+$ ($M+Na^+$): 253.1199; found: 253.1201.

**Benzyl (*S*)-2-phenylpropanoate (3ad)**




Following **general procedure E**, the reaction of *N*-acyloxazolidinone **2k** (92.7 mg, 0.30 mmol) with BnOH (46.6 uL, 0.45 mmol), afforded the ester **(3ad)**[5a] as a clear oil (54.0 mg, 75% Yield). $R_f$: 0.6 (EtOAc/Hexane = 1/ 20); IR (film): 3028, 2957, 2846, 1737, 1453, 1207, 1165, 696 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.52 (d, *J* = 7.2 Hz, 3H), 3.77 (q, *J* = 7.2 Hz, 1H), 5.10 (AB quart, *J* = 12.5 Hz, 2H), 7.19–7.34 (m, 10H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 18.4, 45.5, 66.4, 127.1, 127.5, 127.8, 128.0, 128.4, 128.6, 136.0, 140.4, 174.3 ppm; HRMS calcd for $[C_{16}H_{16}NaO_2]^+$ ($M+Na^+$): 263.1043; found: 263.1045.

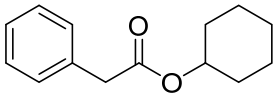
**Benzyl 3-phenylpropanoate (3ae)**




Following **general procedure E**, the reaction of *N*-acyloxazolidinone **1k** (88.5 mg, 0.30 mmol) with BnOH (46.6 uL, 0.45 mmol), afforded the ester **(3ae)**[5g] as a clear oil (67.0 mg, 93% Yield).

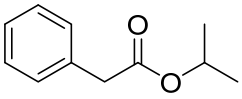
$R_f$: 0.6 (EtOAc/Hexane = 1/ 20); IR (film): 3029, 2918, 2846, 1735, 1501, 1453, 1207, 1165, 735, 696 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 2.67 (t, *J* = 7.7 Hz, 2H), 2.96 (t, *J* = 7.7 Hz, 2H), 5.10 (s, 2H), 7.13–7.38 (m, 10H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 30.9, 35.8, 66.2, 126.2, 128.2, 128.3, 128.4, 128.5, 135.9, 140.4, 172.7 ppm; HRMS calcd for $[C_{16}H_{16}NaO_2]^+$ ($M+Na^+$): 263.1043; found: 263.1043.

**Cyclohexyl 2-phenylacetate (3af)**



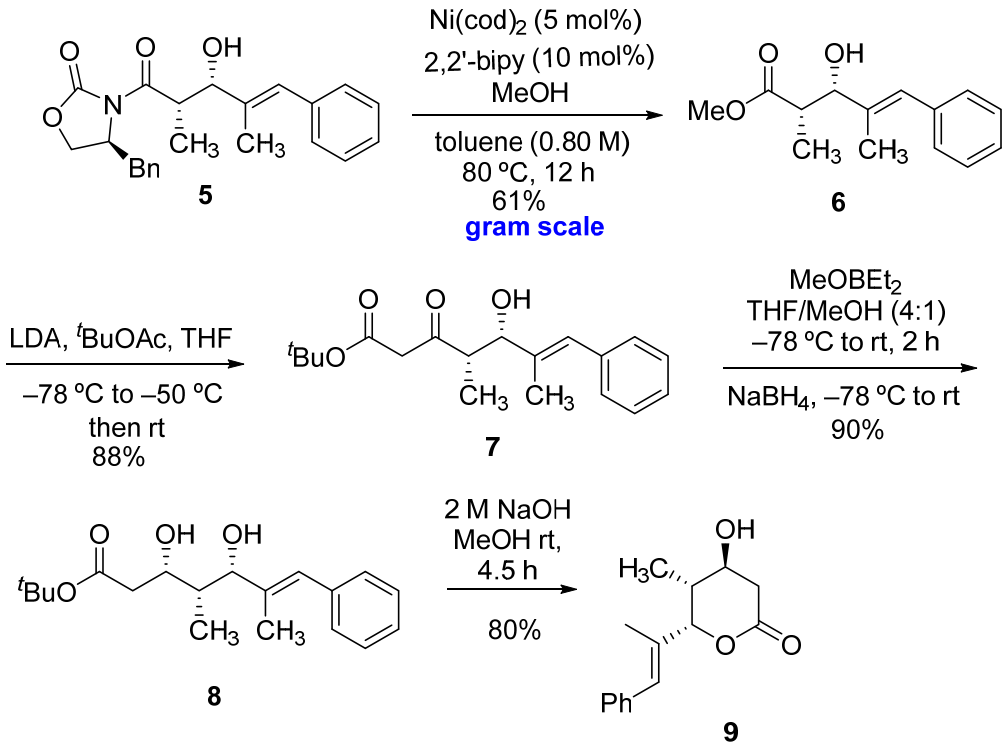
Following **general procedure E**, the reaction of *N*-acyloxazolidinone **1a** (62mg, 0.30 mmol) with cyclohexanol (34.5 uL, 0.45 mmol), afforded the ester **(3af)** as a clear oil (36.1 mg, 55% Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 20); IR (film): 3031, 2937, 2859, 1732, 1454, 1257, 1161, 1039, 1017, 723, 695 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.23–1.29 (m, 1H), 1.30–1.45 (m, 4H), 1.47–1.55 (m, 1H), 1.63–1.72 (m, 2H), 1.76–1.86 (m, 2H), 3.59 (s, 2H), 4.77 (m, 1H), 7.22–7.34 (m, 5H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 23.6, 25.4, 31.5, 41.8, 73.0, 126.9, 128.5, 129.2, 134.5, 171.0 ppm; HRMS calcd for $[C_{14}H_{18}NaO_2]^+$ ($M+Na^+$): 241.1199; found: 241.1201.

**Isopropyl 2-phenylacetate (3ag)**

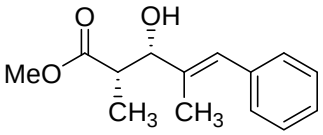


Following **general procedure E**, the reaction of *N*-acyloxazolidinone **1a** (62mg, 0.30 mmol) with *i*-PrOH (34.5 uL, 0.45 mmol), afforded the ester **(3ag)** as a clear oil (33.2 mg, 62% Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 20); IR (film): 3031, 2980, 2924, 2852, 1733, 1455, 1261, 1107, 1031, 696 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.22 (d, *J* = 6.3 Hz, 6H), 3.58 (s, 2H), 5.01 (hept, *J* = 6.3 Hz, 1H), 7.23-7.34 (m, 5H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 21.7, 41.7, 68.1, 126.9, 128.5, 129.2, 134.3, 171.1 ppm; HRMS calcd for $[C_{11}H_{14}NaO_2]^+$ ($M+Na^+$): 201.0886; found: 201.0888.

## Short synthesis of δ-lactone 9.

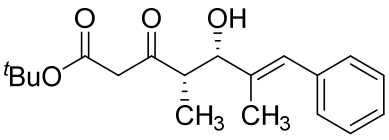



**Methyl (2*S*,3*S*,*E*)-3-hydroxy-2,4-dimethyl-5-phenylpent-4-enoate 6**



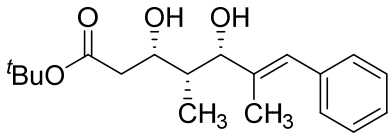
Following **general procedure E**, the reaction of *N*-acyloxazolidinone **5**[6] (1.33 g, 3.5 mmol) with methanol (213 uL, 5.25 mmol), afforded the ester **6** as a colorless oil (500.1 mg, 61% Yield). $R_f$: 0.4 (EtOAc/Hexane = 1/ 3); $[\alpha]_D^{20}$ –17.2 (*c* 1.0, $CHCl_3$); IR (film) $\nu_{max}$: 3400, 2950, 2917, 2849, 1738, 1726, 1642, 1601, 1385, 1260, 1196, 1180, 1142, 1076, 800 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$1.24 (d, *J* = 7.2 Hz, 3H), 1.87 (s, 3H), 2.62–2.69 (m, 1H), 2.79–2.87 (m, 1H), 3.73 (s, 3H), 4.46–4.53 (m, 1H), 6.63 (s, 1H), 7.21–7.31 (m, 3H), 7.32–7.38 (m, 2H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$10.9, 14.5, 42.9, 51.9, 76.8, 126.4, 126.5, 128.1, 128.9, 136.8, 137.5, 176.0 ppm; HRMS calcd for $[C_{14}H_{18}NaO_3]^+$ ($M+Na^+$): 257.1148; found: 257.1151.

***tert*-Butyl (4*S*,5*S*,*E*)-5-hydroxy-4,6-dimethyl-3-oxo-7-phenylhept-6-enoate 7**



To a solution of LDA (4.01 ml, 8.03 mmol, 2.0 M in THF/*n*-heptane/ethylbenzene), *tert*-butyl acetate (777 mg, 6.69 mmol) in anhydrous THF (10 mL) was added at –78 °C. The mixture was was stirred at –78 °C for 1.0 h. Then, the hydroxyester **6** (522 mg, 2.23 mmol) in anhydrous THF (3.0 mL) was added dropwise at –78 °C. The mixture was stirred at –50 °C for 1.5 h, and, then, at –15 °C for 15 min. Ice-water (10 mL) was added to quench the reaction, and the aqueous layer was extracted with ether (2 × 25 mL). The combined organic layer was washed with saturated $NaHCO_3$ (20 mL) and water (2 × 15 mL), and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (EtOAc/hexane, 1:5) to afford **7** (624 mg, 88%). $R_f$: 0.4 (EtOAc/Hexane = 1/ 5); $[\alpha]_D^{20}$ –34.8 (*c* 1.0, $CHCl_3$); IR (film) $\nu_{max}$: 3470, 2978, 2930, 1732, 1710, 1643, 1455, 1369, 1259, 1145, 1076, 750, 700 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.16 (d, *J* = 7.2 Hz, 3H), 1.48 (s, 9H), 1.83 (s, 3H), 2.78 (d, *J* = 2.3 Hz, 1H), 2.94–3.02 (m, 1H), 3.45–3.54 (m, 2H), 4.53–4.60 (m, 1H), 6.63 (s, 1H), 7.19–7.24 (m, 1H), 7.25–7.29 (m, 2H), 7.31–7.36 (m, 2H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 9.5, 15.2, 28.0, 48.9, 49.5, 75.2, 82.3, 126.1, 126.5, 128.1, 129.0, 136.3, 137.5, 166.4, 207.4 ppm; HRMS calcd for $[C_{19}H_{26}NaO_4]^+$ ($M+Na^+$): 341.1723; found: 341.1724.

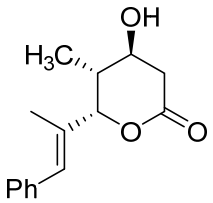
**_tert_-Butyl (3*S*,4*R*,5*S*,*E*)-3,5-dihydroxy-4,6-dimethyl-7-phenylhept-6-enoate 8**




A solution of diethylmethoxyborane (1.38 mL, 1 M in THF) in anhydrous THF-MeOH (25 mL; 4:1) was stirred for 1 h at room temperature under nitrogen then cooled to –78 °C before a solution of the hydroxyketone **7**[7a] (366 mg, 1.15 mmol) in THF (5.0 ml) was added. The mixture was kept at –78 °C for 1h. Then the $NaBH_4$ (52 mg, 1.38 mmol) was added in one portion. The mixture was stirred for 2 h at –78 °C, then quenched by the dropwise addition of saturated aqueous $NH_4Cl$ (2.0 ml). When the effervescence had stopped a 30% aqueous solution of $H_2O_2$ (5.0 ml) was added, followed by washed with $H_2O$ (10 ml). The mixture was extracted with ethyl acetate (2 × 25 mL). The combined organic layer was washed with water (10 mL) and brine (20 mL), and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography

(EtOAc/hexane, 1:3) to afford **8** (331 mg, 90%).$R_f$: 0.5 (EtOAc/Hexane = 1/ 2); $[\alpha]_D^{20}$ –50.2 (*c* 1.0, $CHCl_3$); IR (film) $\nu_{max}$: 3430, 2977, 2919, 1726, 1600, 1393, 1368, 1259, 1154, 1076, 750, 700 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 0.93 (d, *J* = 7.0 Hz, 3H), 1.47 (s, 9H), 1.76–1.83 (m, 4H), 2.37 (dd, *J* = 16.4, 3.3 Hz, 1H), 2.58 (dd, *J* = 16.4, 9.6 Hz, 1H), 3.33 (br s, 1H), 3.68 (br s, 1H), 4.30–4.37 (m, 1H), 4.41 (s, 1H), 6.65 (s, 1H), 7.17–7.24 (m, 1H), 7.24–7.35 (m, 4H), ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 5.2, 15.5, 28.1, 39.2, 40.6, 72.3, 79.8, 81.5, 124.9, 126.2, 128.0, 129.0, 137.8, 137.9, 172.5 ppm; HRMS calcd for $[C_{19}H_{28}NaO_4]^+$ ($M+Na^+$): 343.1880; found: 343.1881.

**(4*S*,5*R*,6*S*)-4-hydroxy-5-methyl-6-((*E*)-1-phenylprop-1-en-2-yl)tetrahydro-2*H*-pyran-2-one 9**




2 M NaOH (0.42 ml, 0.84 mmol) was added to a stirred solution of the ester **8**[7b] (90.0 mg, 0.28 mmol) in methanol (2.0 ml). The mixture was stirred at room temperature for 4.5 h before the most pare of methanol was removed under vacuum. The residue was diluted with water (0.5 ml), cooled to 0 ºC, and acidified with 2 M $H_2SO_4$. The mixture was extracted with ether (3 × 10 mL). The combined organic layer was washed with water (10 mL) and brine (20 mL), and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (EtOAc/hexane, 1:1) to afford **9** as a pale yellow solid (54.5 mg, 80%). $R_f$: 0.3 (EtOAc/Hexane = 1/ 1); Mp: 96–98 ºC; $[\alpha]_D^{20}$ –110.7 (*c* 0.67, $CHCl_3$); IR (film) $\nu_{max}$: 3430, 2977, 2919, 1726, 1600, 1393, 1368, 1259, 1154, 1076, 750, 700 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 0.91 (d, *J* = 7.2 Hz, 3H), 1.85 (s, 3H), 2.05 (br s, 1H), 2.21–2.28 (m, 1H), 2.65 (dd, *J* = 18.1, 2.7 Hz, 1H), 2.87 (dd, *J* = 18.1, 5.1 Hz, 1H), 4.17–4.22 (m, 1H), 5.27 (s, 1H), 6.71 (s, 1H), 7.21–7.26 (m, 1H), 7.26–7.29 (m, 2H), 7.32–7.36 (m, 2H), ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 10.3, 15.4, 35.5, 36.5, 68.3, 80.0, 125.9, 126.6, 128.1, 129.0, 132.5, 137.2, 170.3 ppm; HRMS calcd for $[C_{15}H_{18}NaO_3]^+$ ($M+Na^+$): 269.1148; found: 269.1150.

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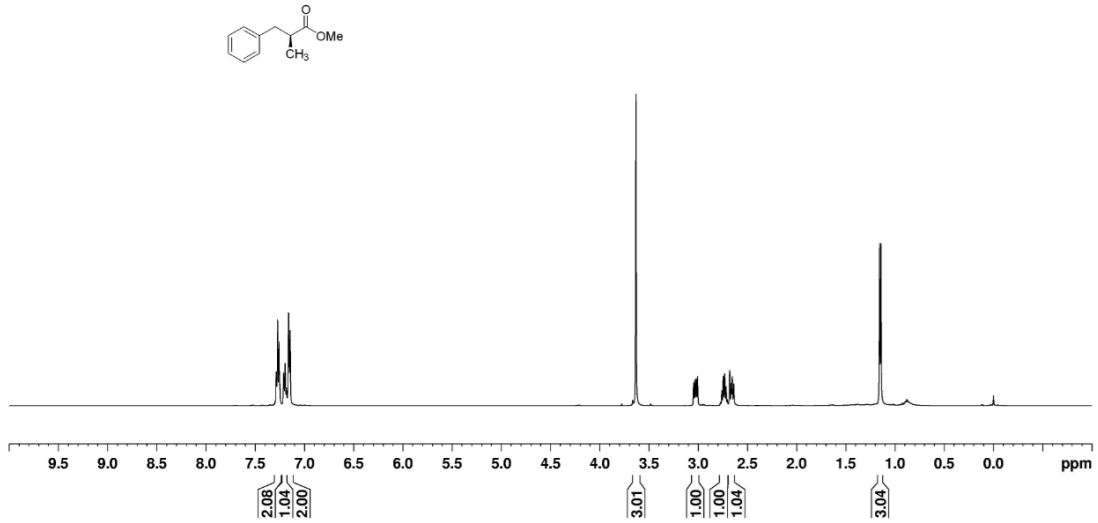
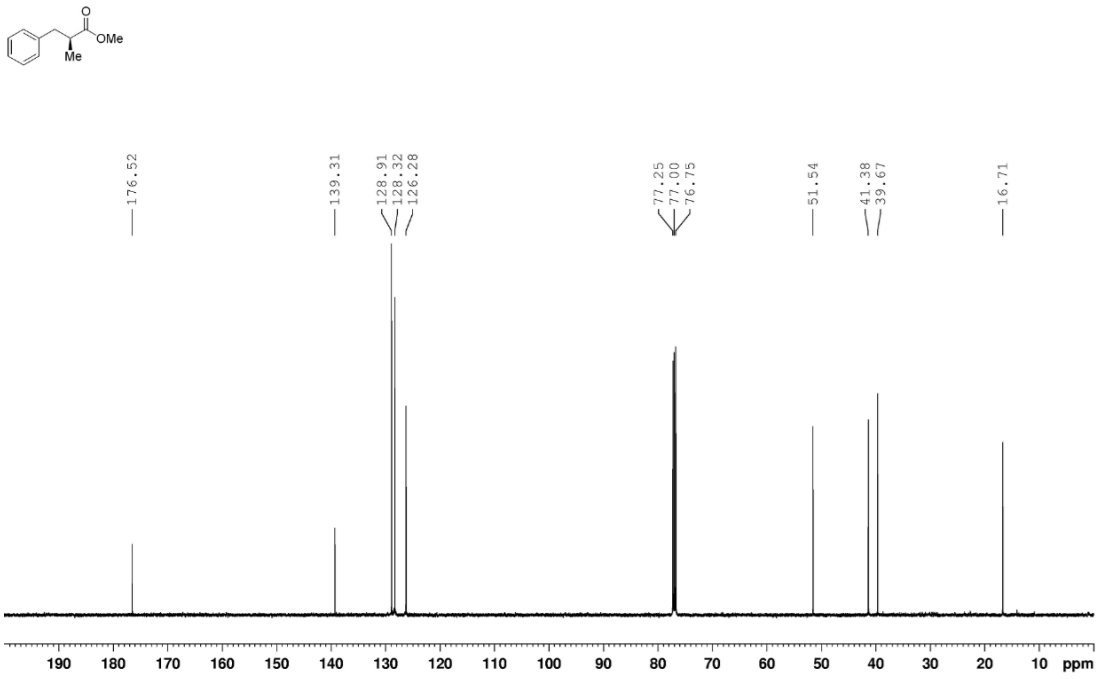
$^{1}H$ and $^{13}C$ NMR spectra of compound **3j** ($CDCl_3$)



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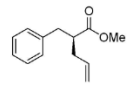


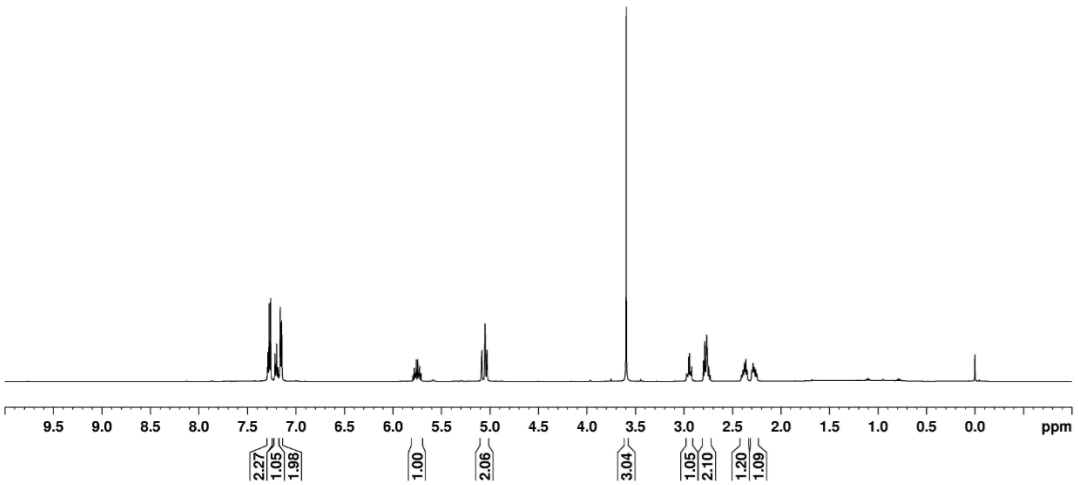


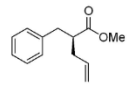


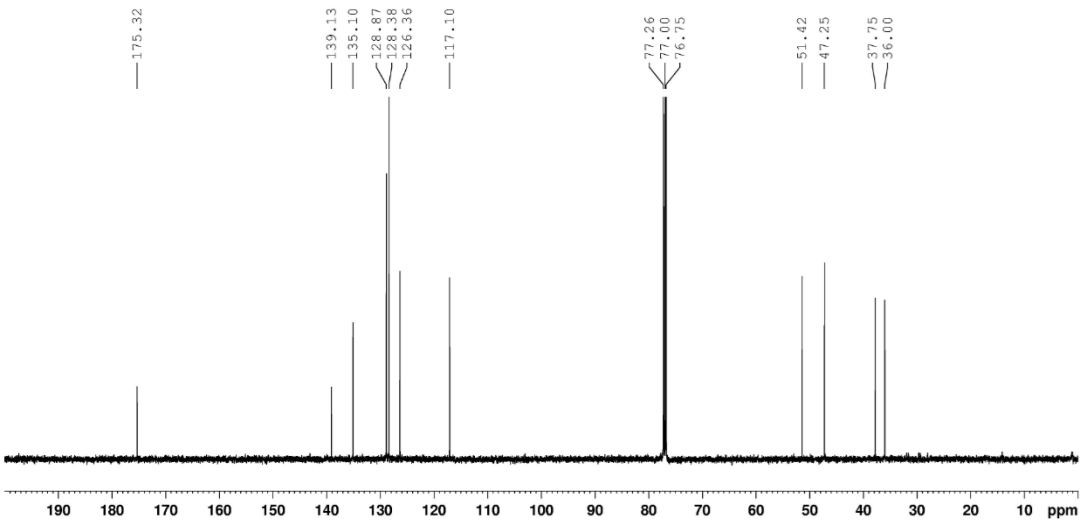

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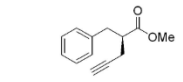


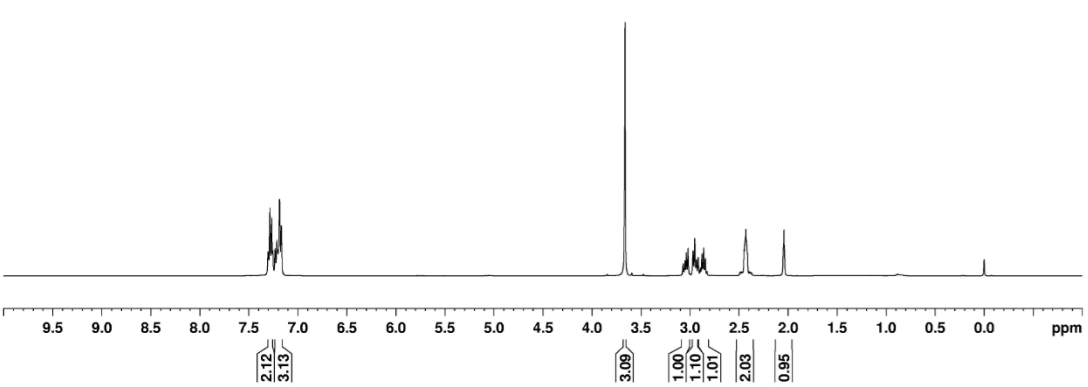


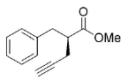


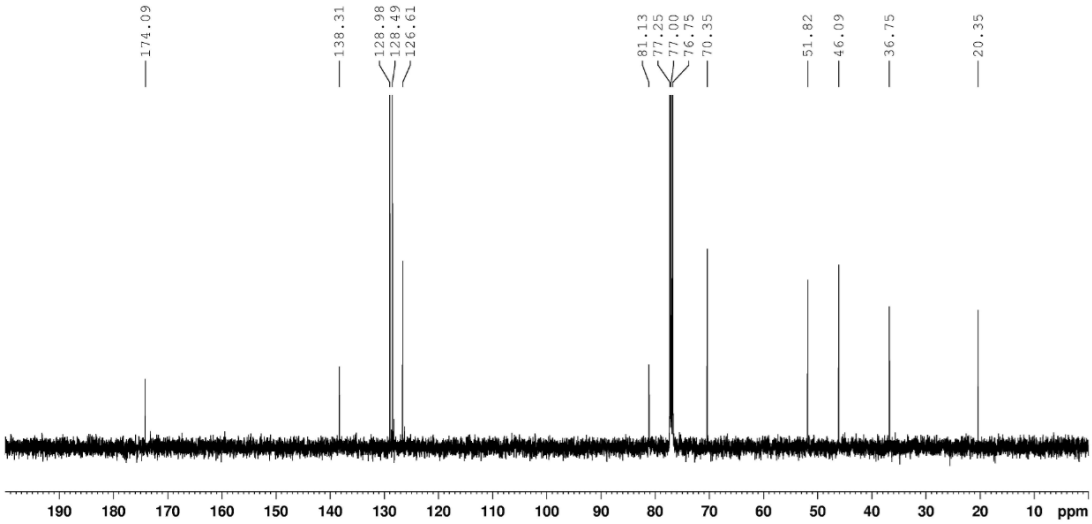

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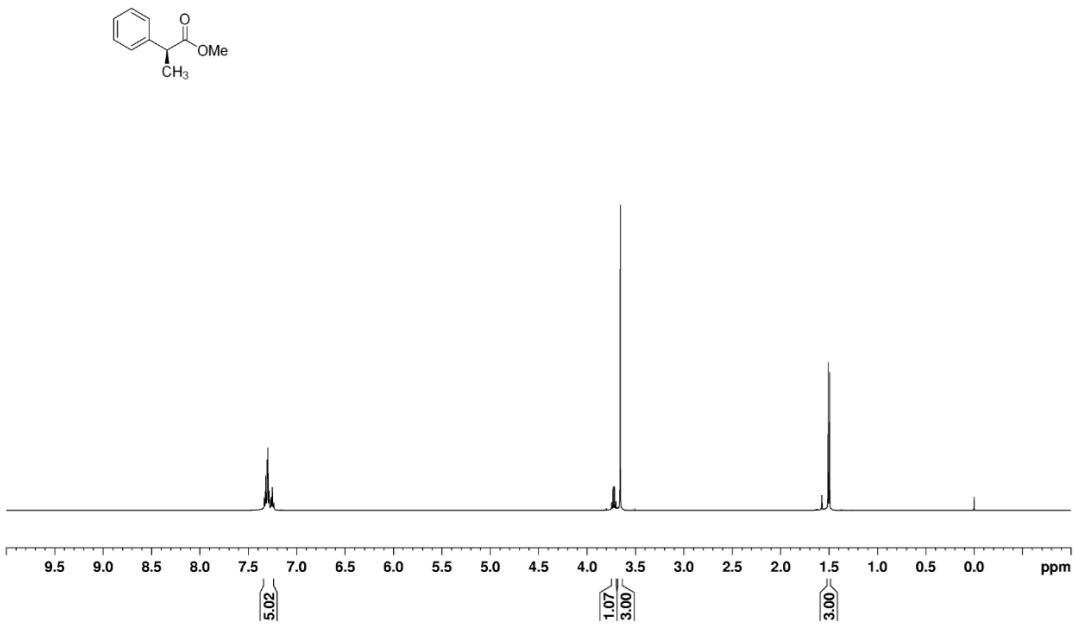


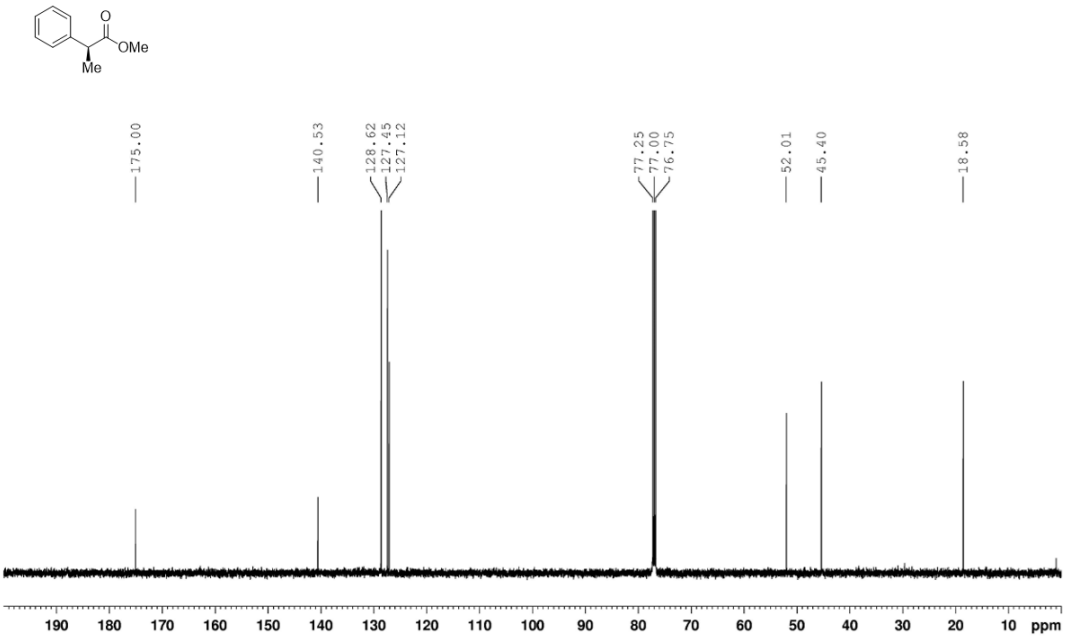

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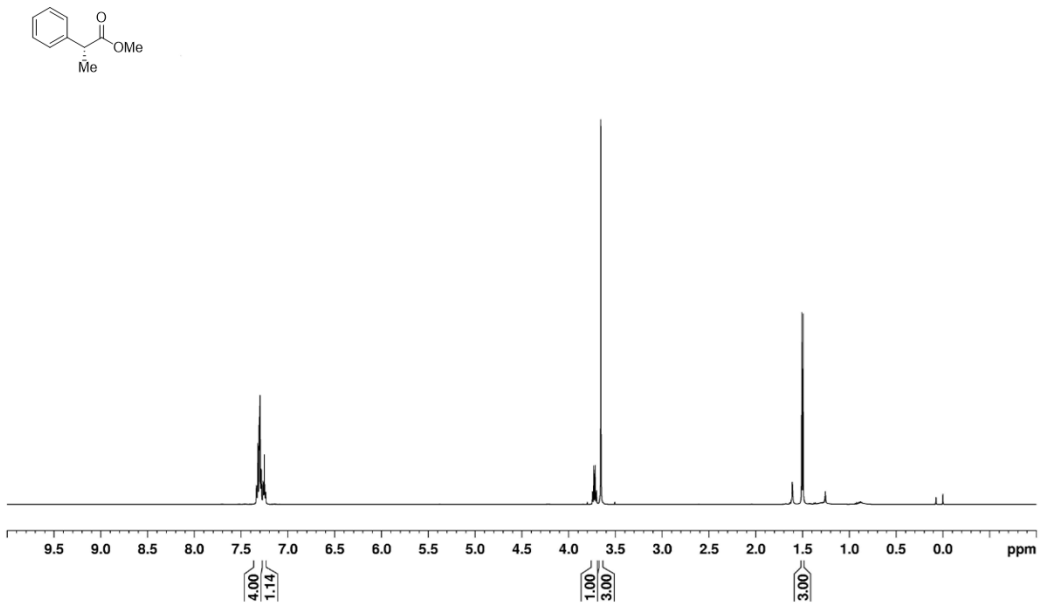


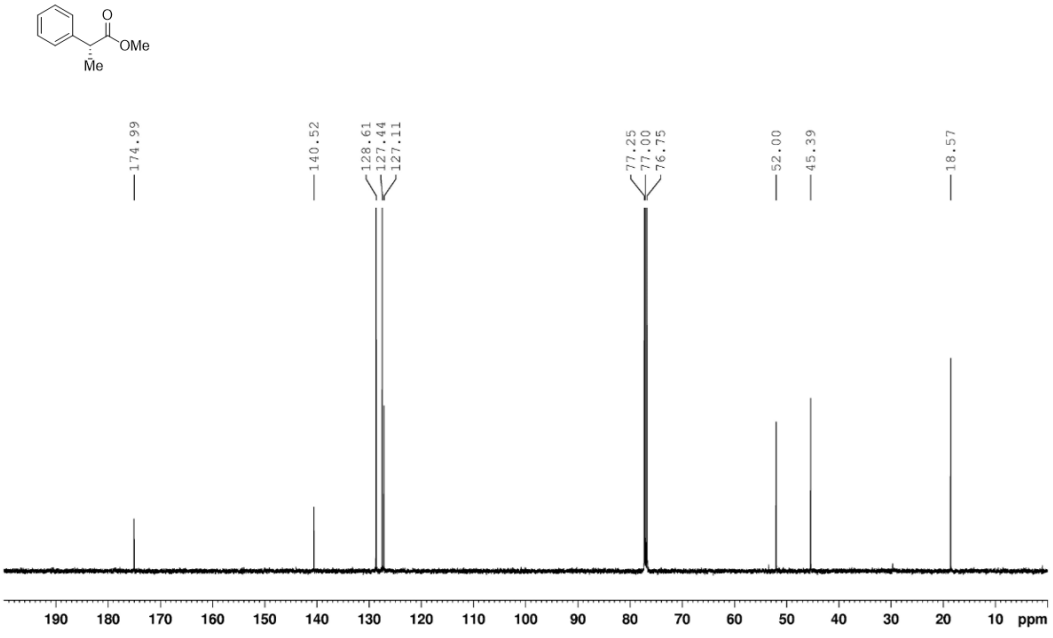

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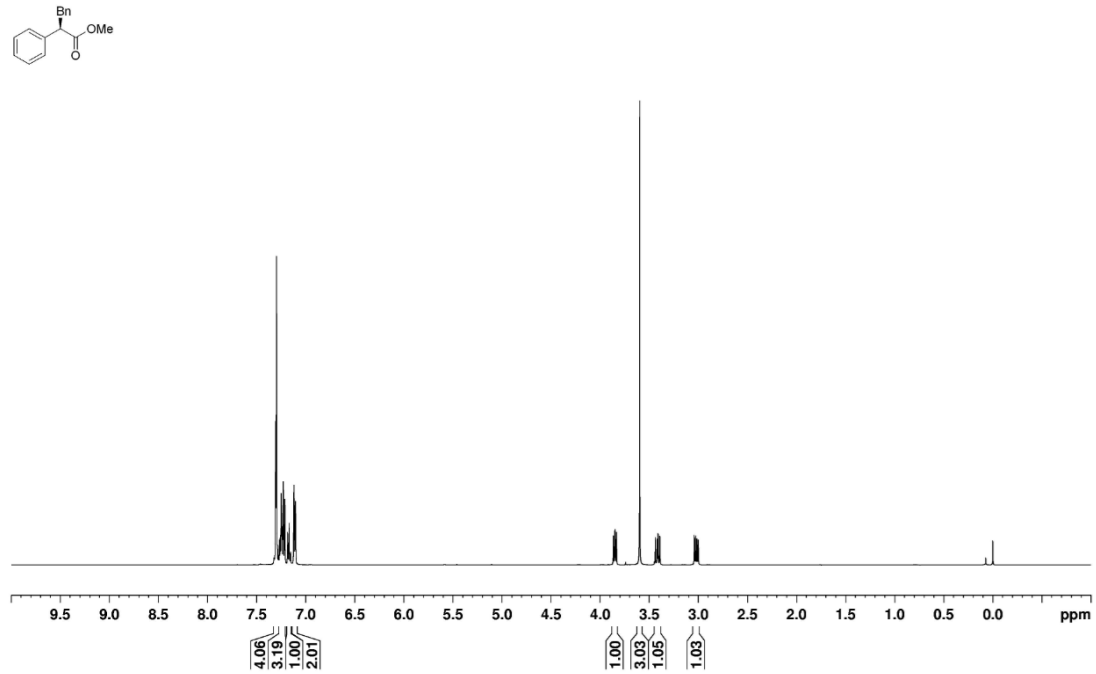


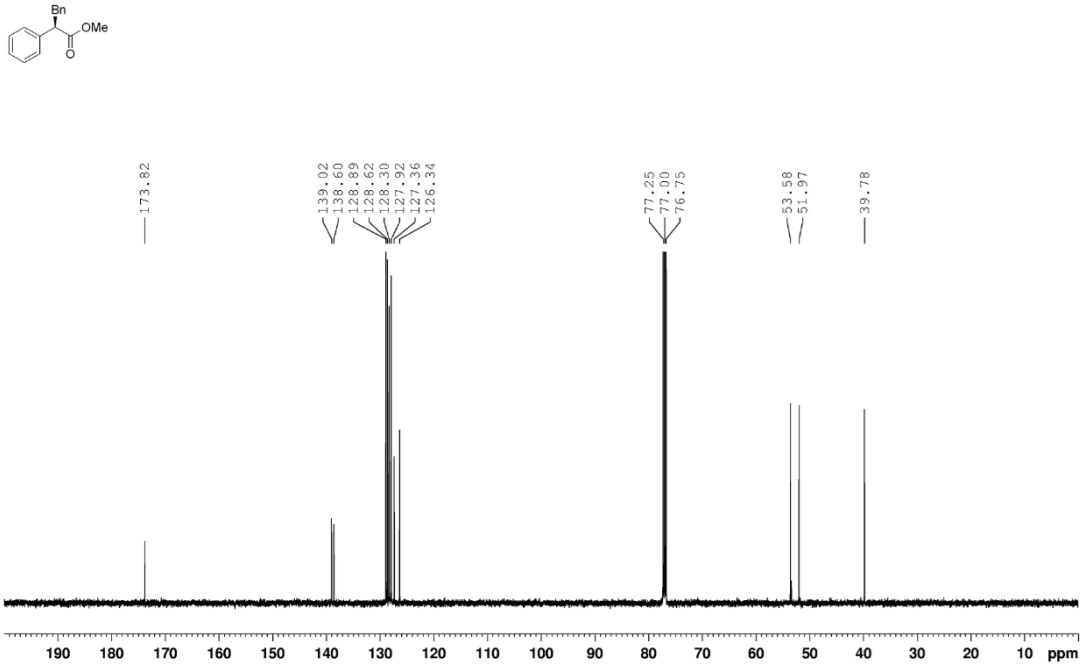

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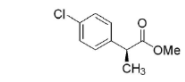


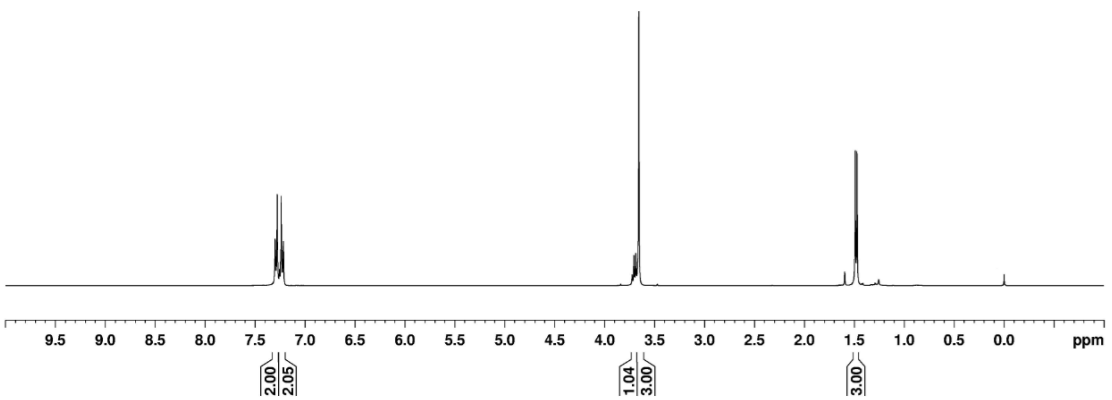


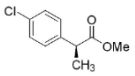


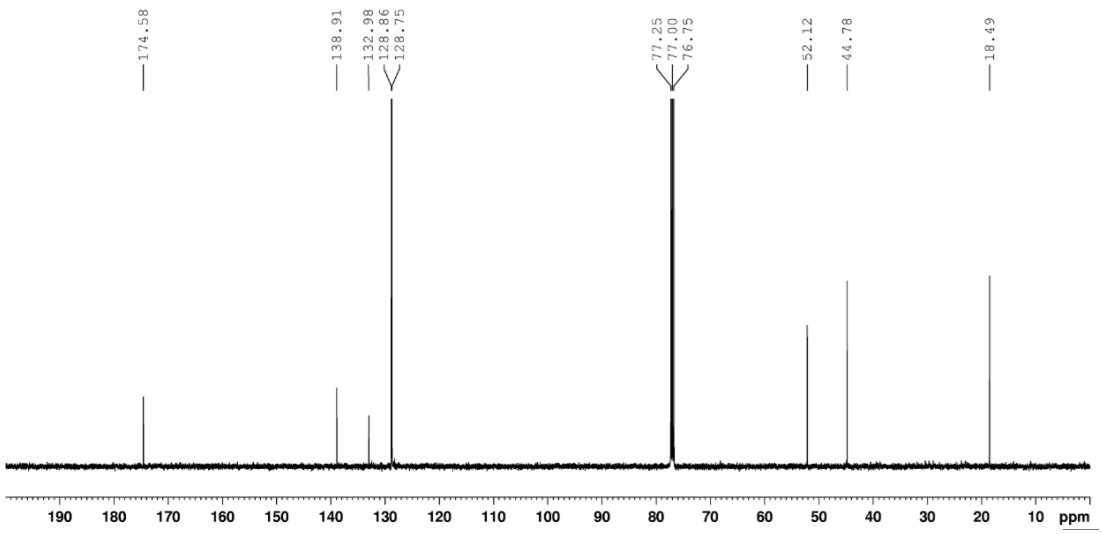

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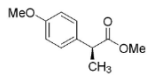
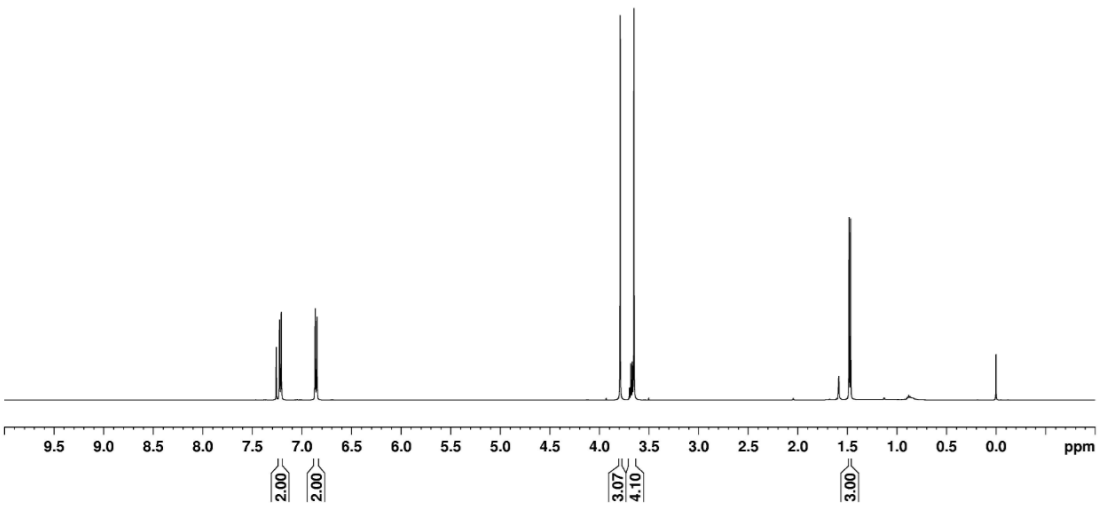
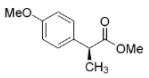
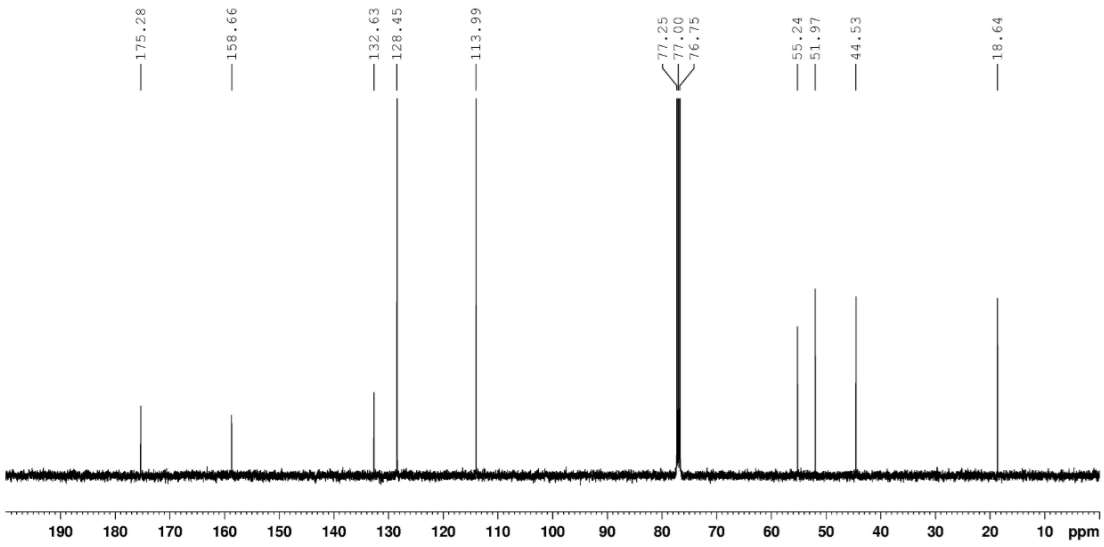
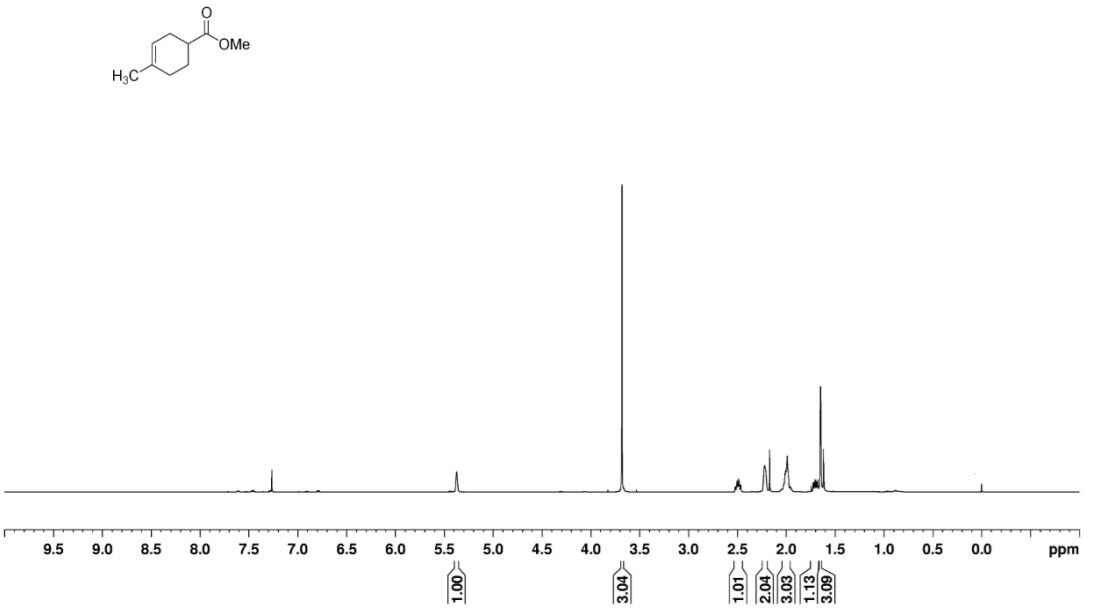


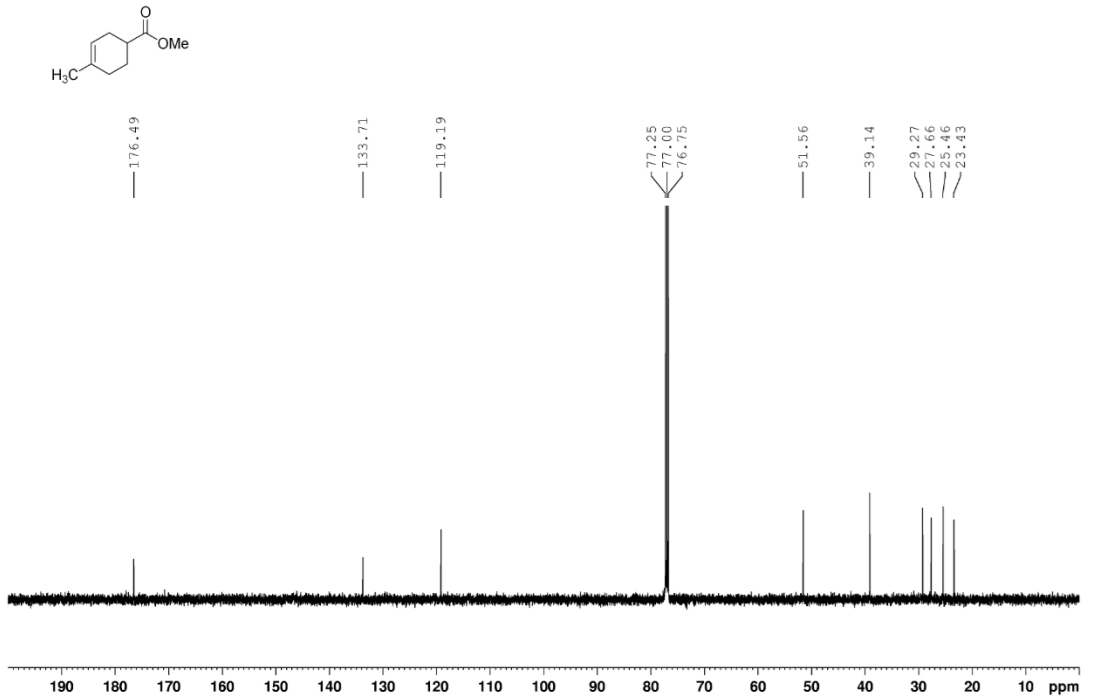



$^{1}H$ and $^{13}C$ NMR spectra of compound **3r** ($CDCl_3$)



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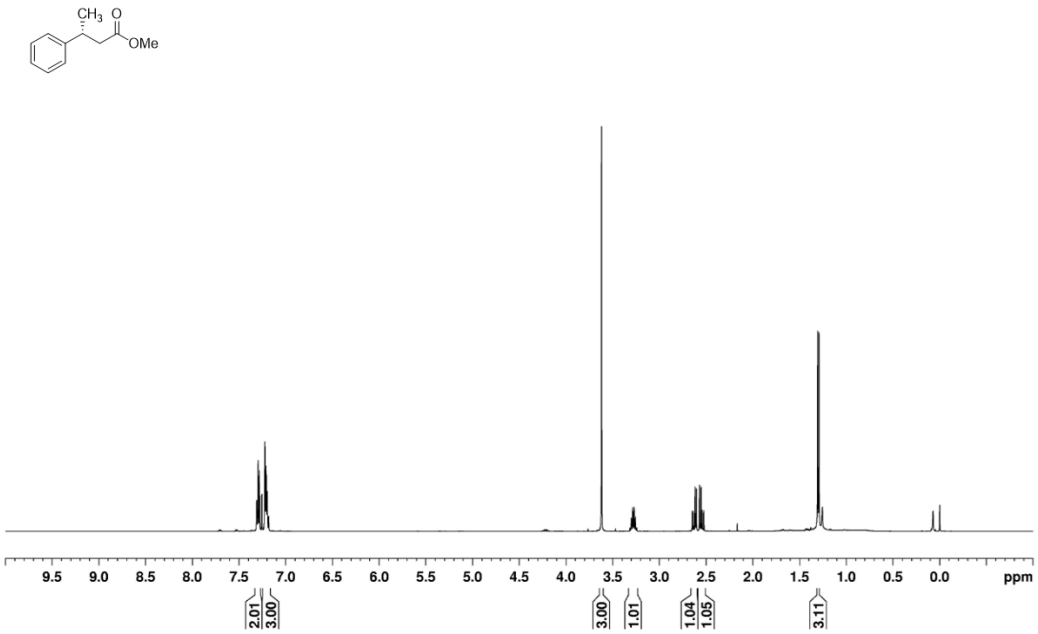
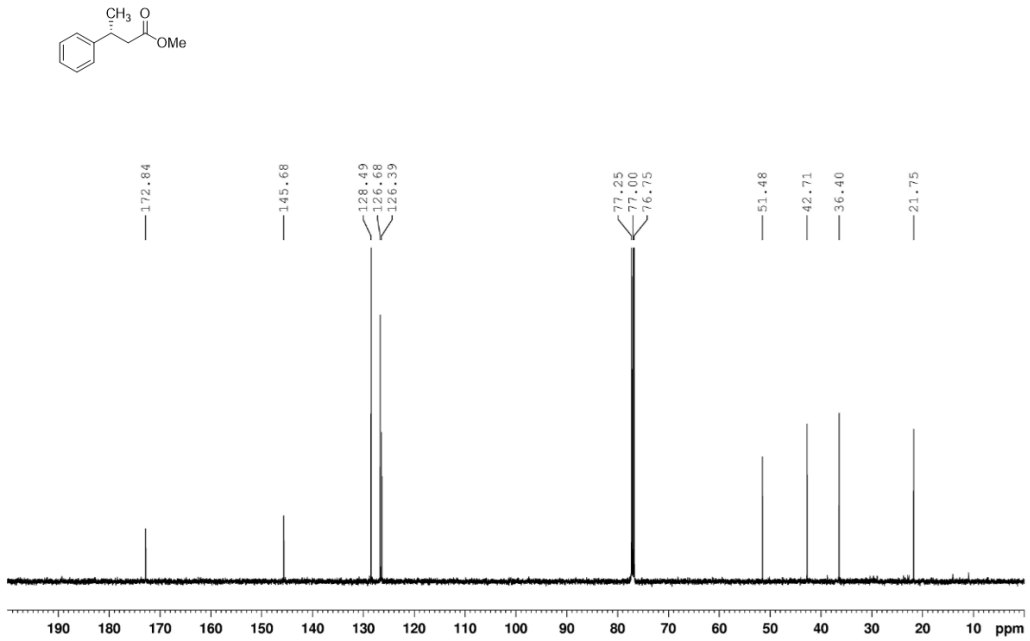
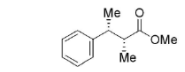
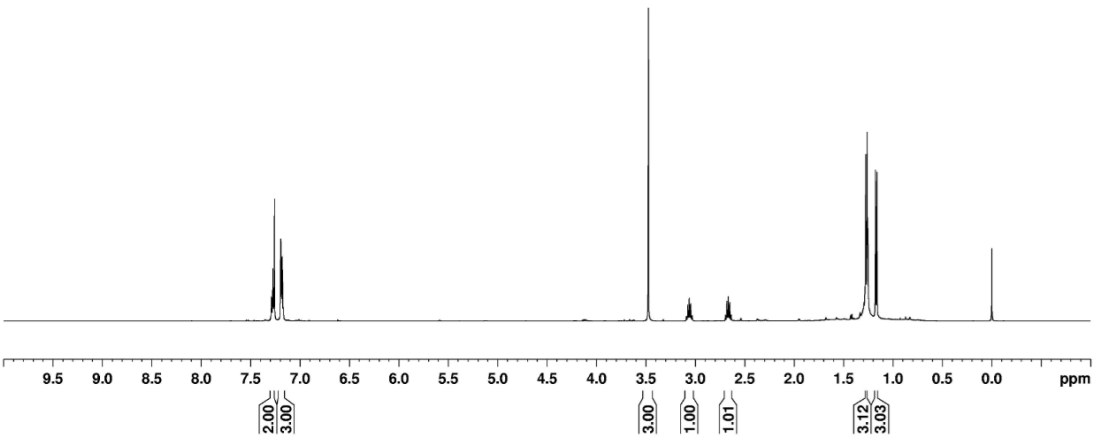
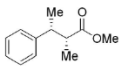


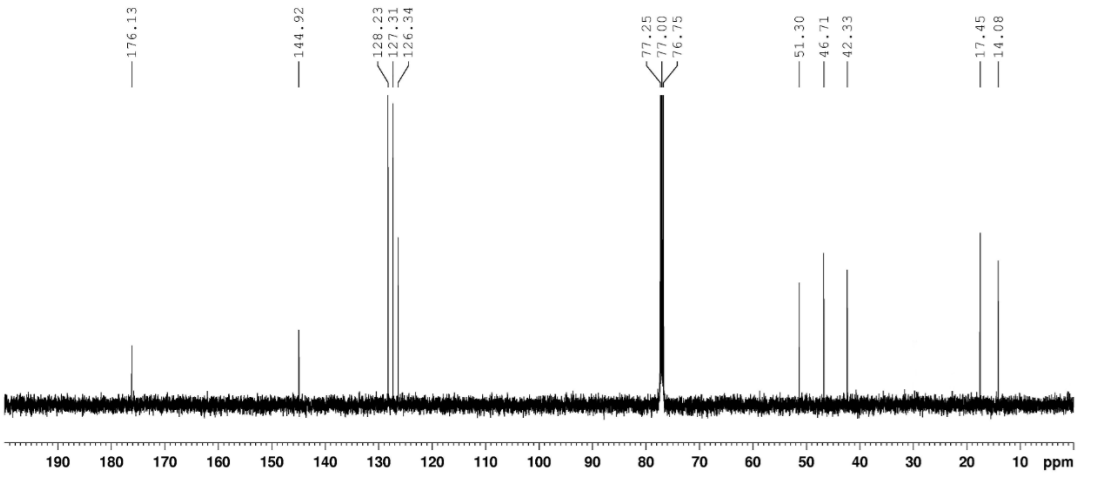



$^{1}H$ and $^{13}C$ NMR spectra of compound **3t** ($CDCl_3$)

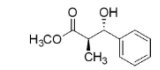


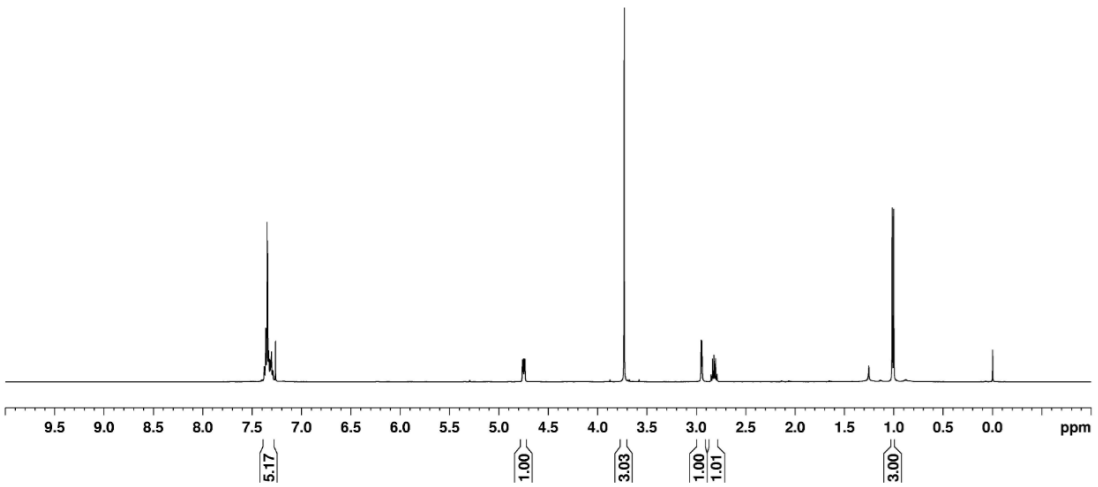



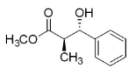



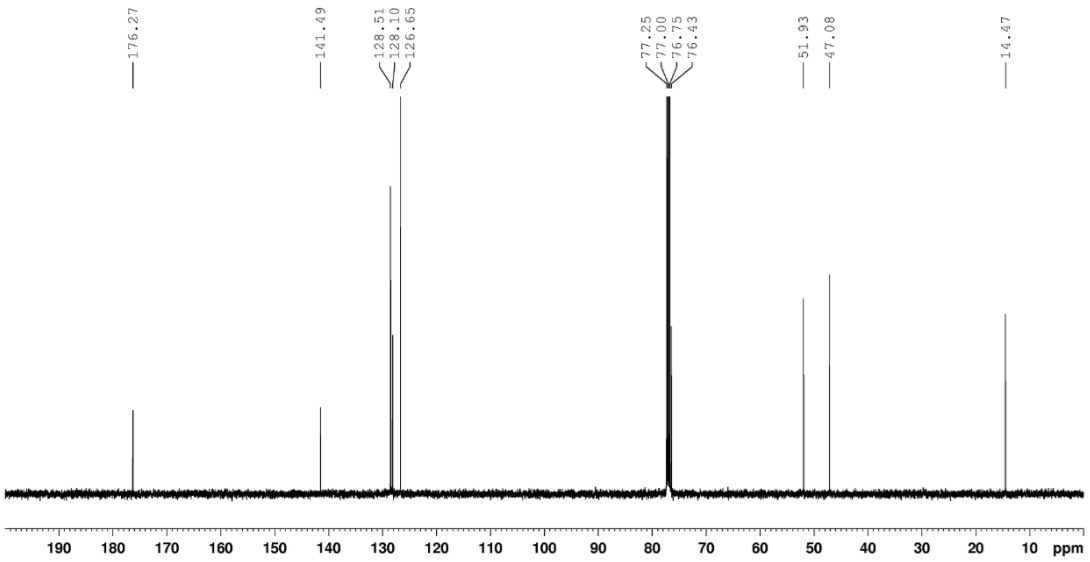



$^{1}H$ and $^{13}C$ NMR spectra of compound **3u** ($CDCl_3$)

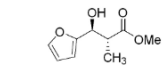


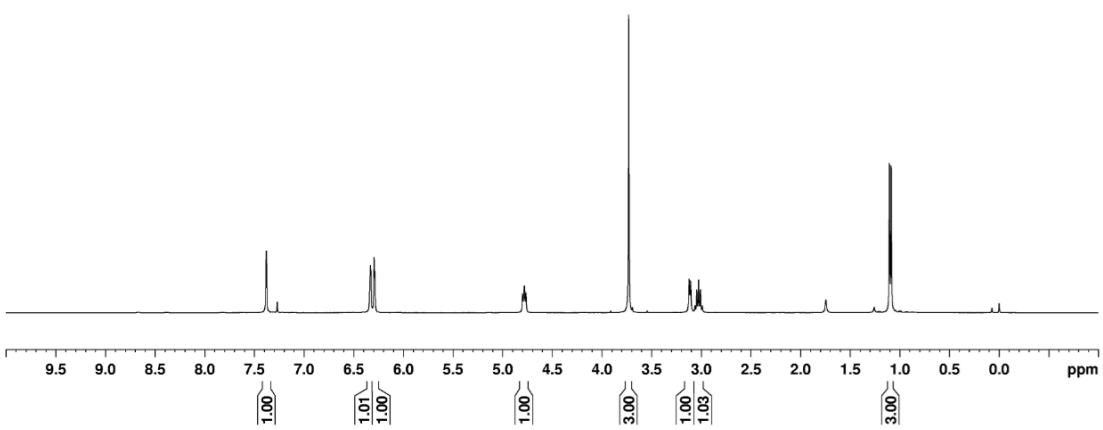


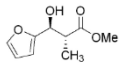



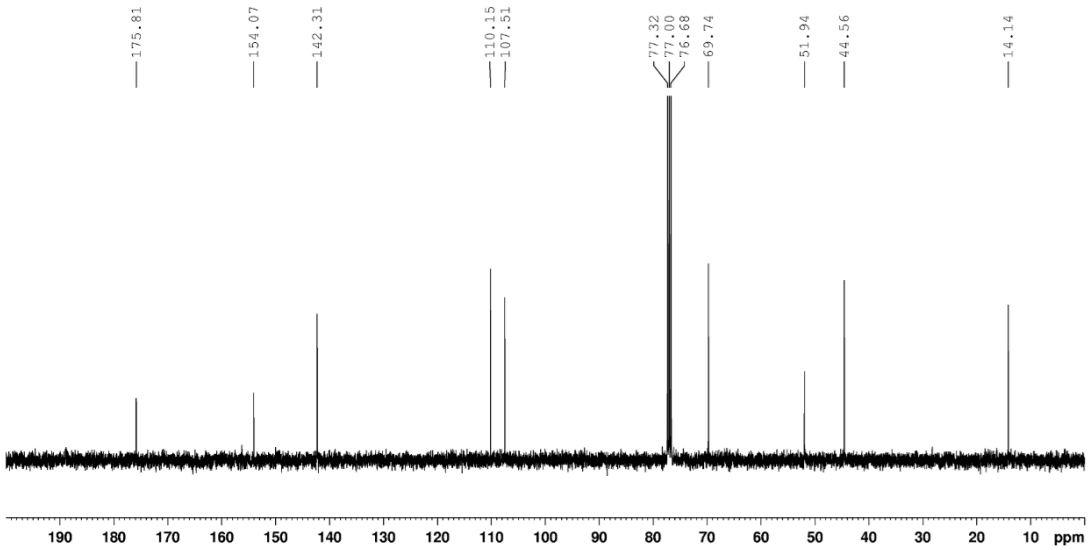


$^{1}H$ and $^{13}C$ NMR spectra of compound **3v** ($CDCl_3$)

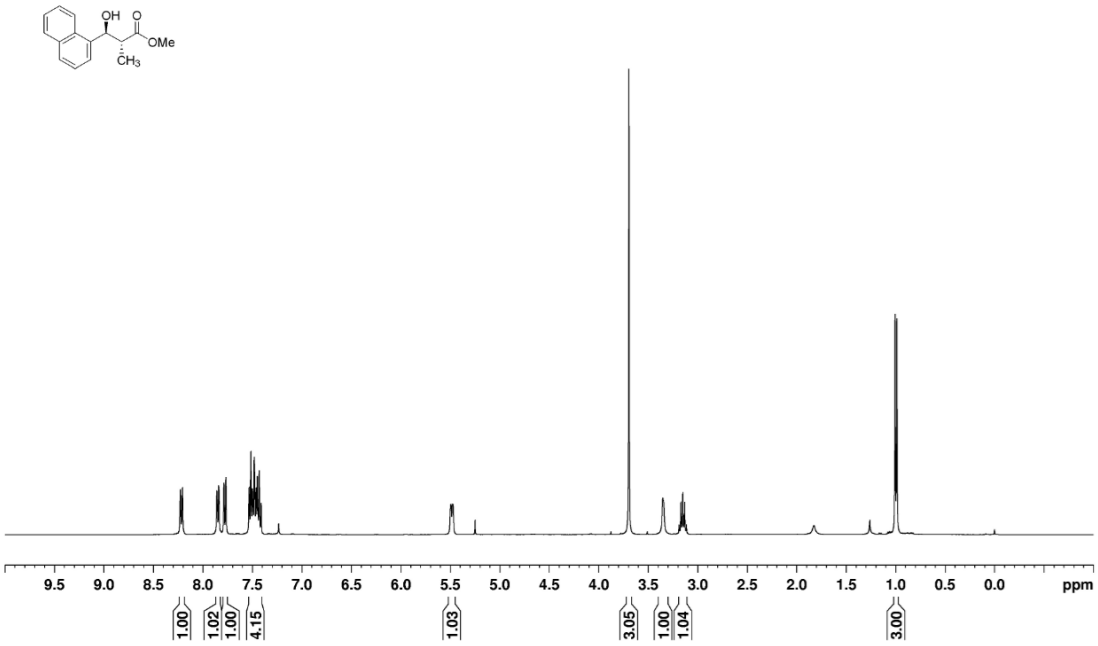


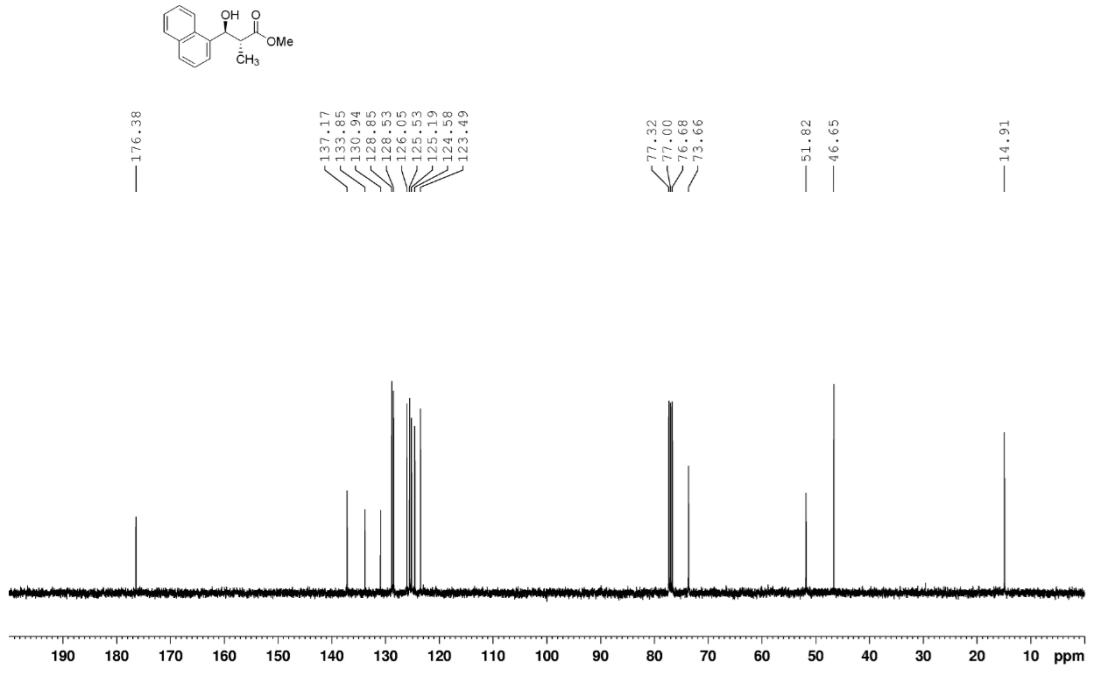



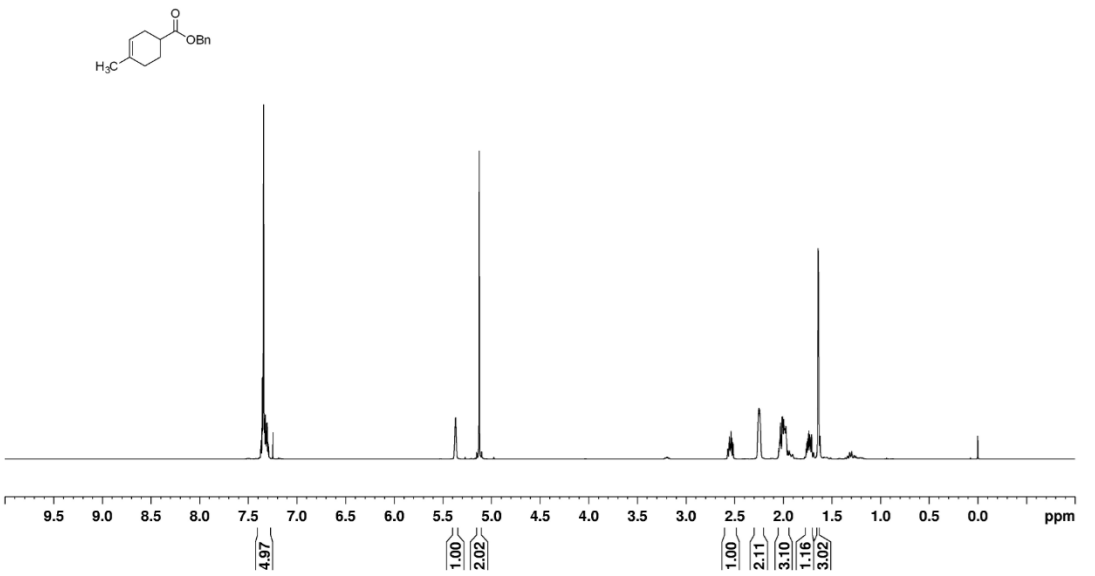



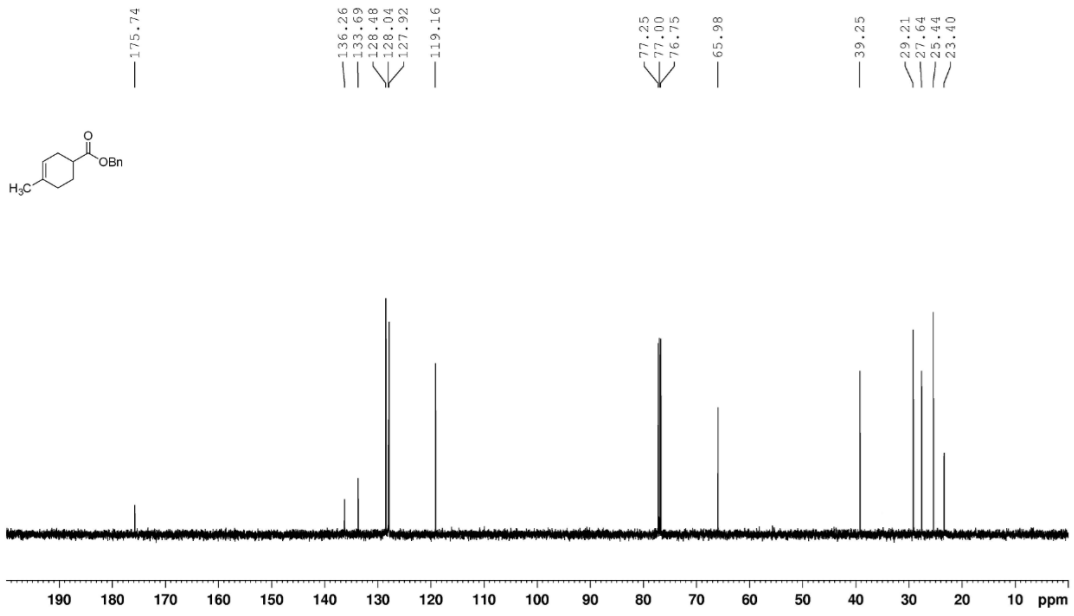
$^{1}H$ and $^{13}C$ NMR spectra of compound **3w** ($CDCl_3$)



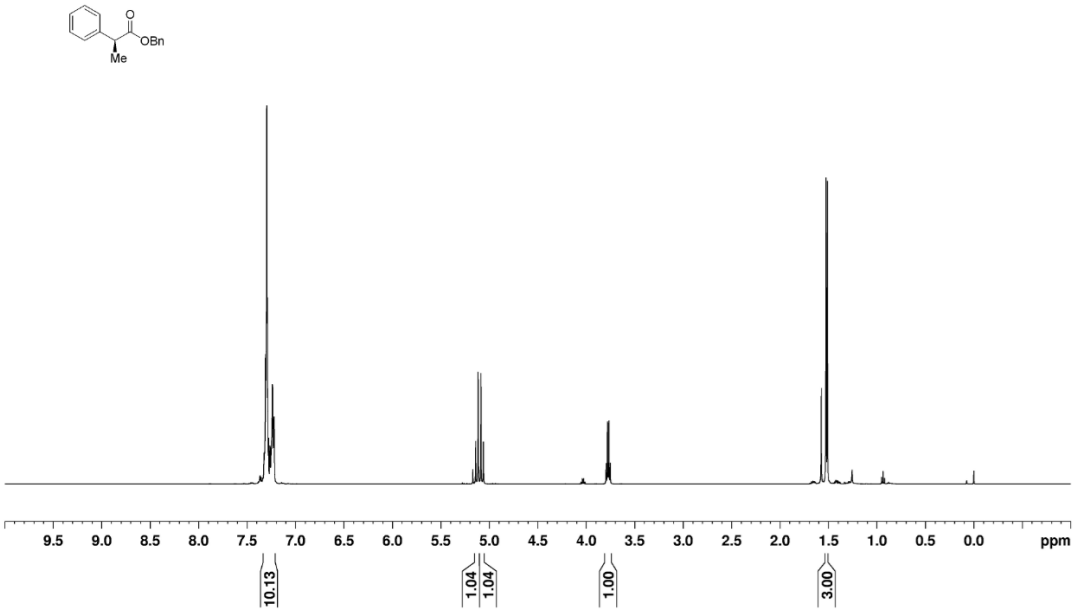



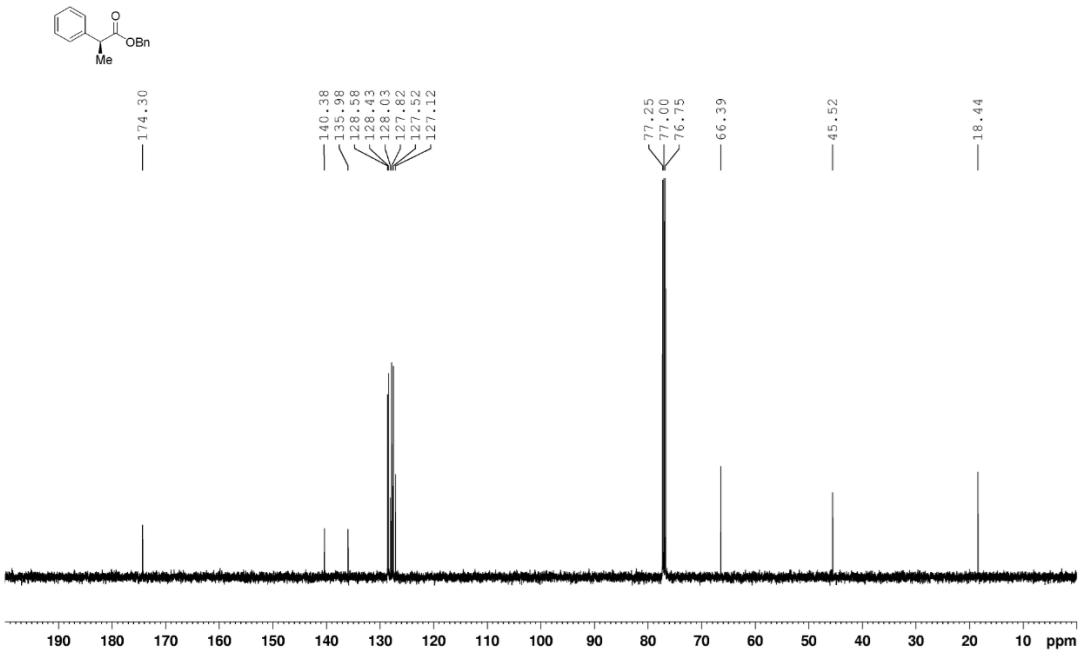
$^{1}H$ and $^{13}C$ NMR spectra of compound **3ac** ($CDCl_3$)



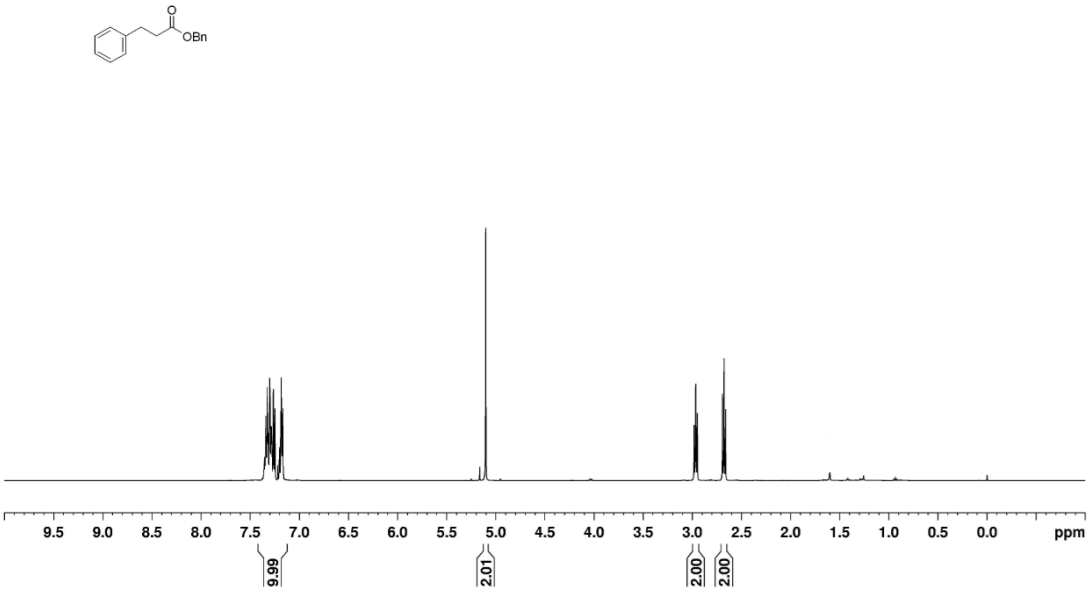



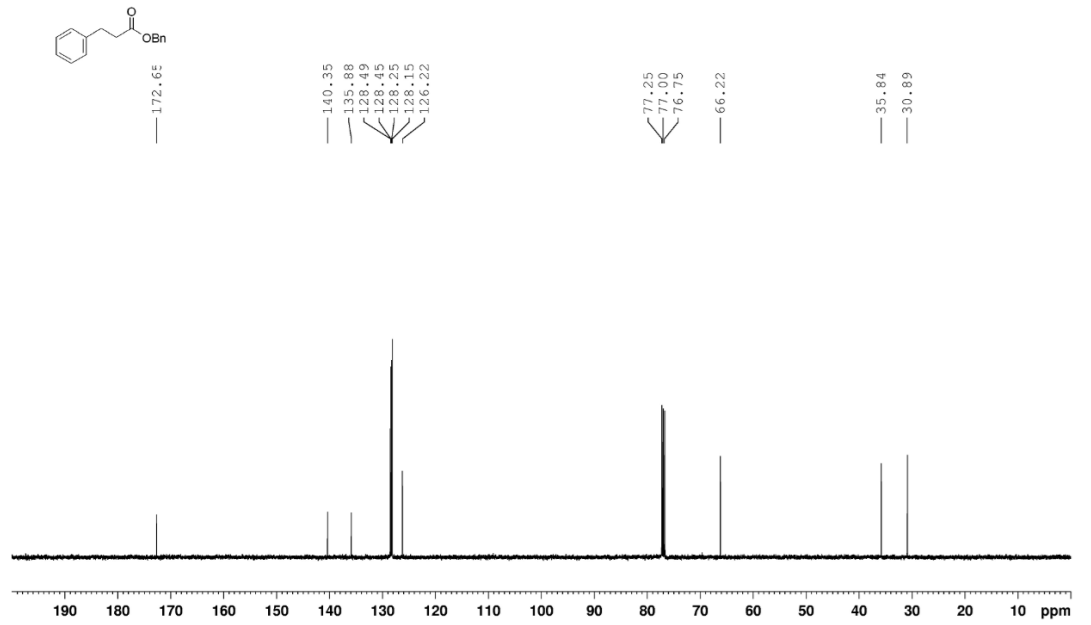
$^{1}H$ and $^{13}C$ NMR spectra of compound **3ad** ($CDCl_3$)



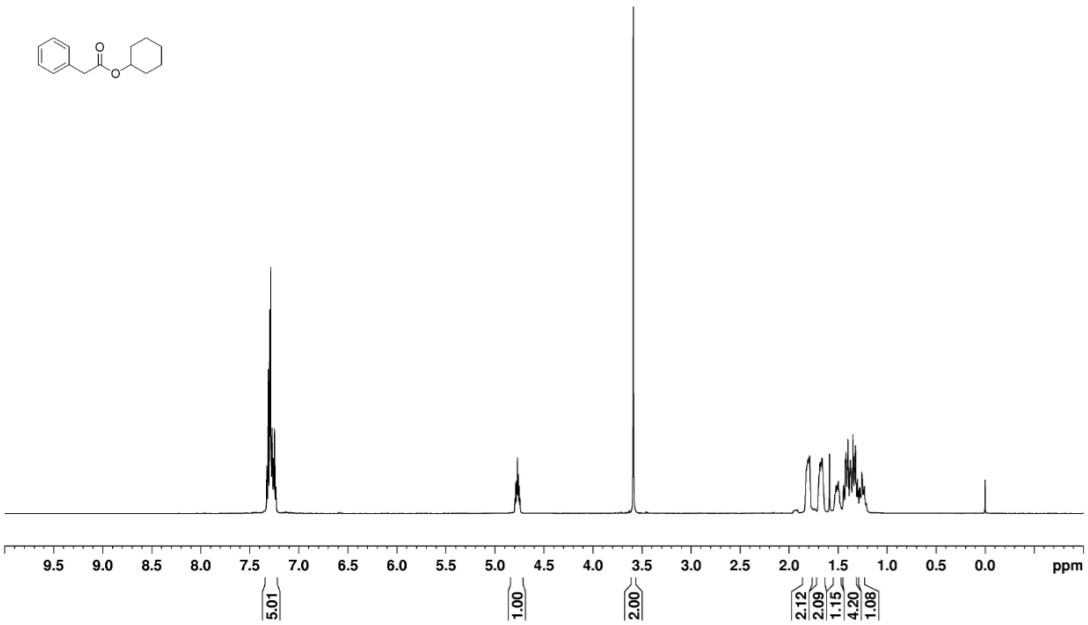



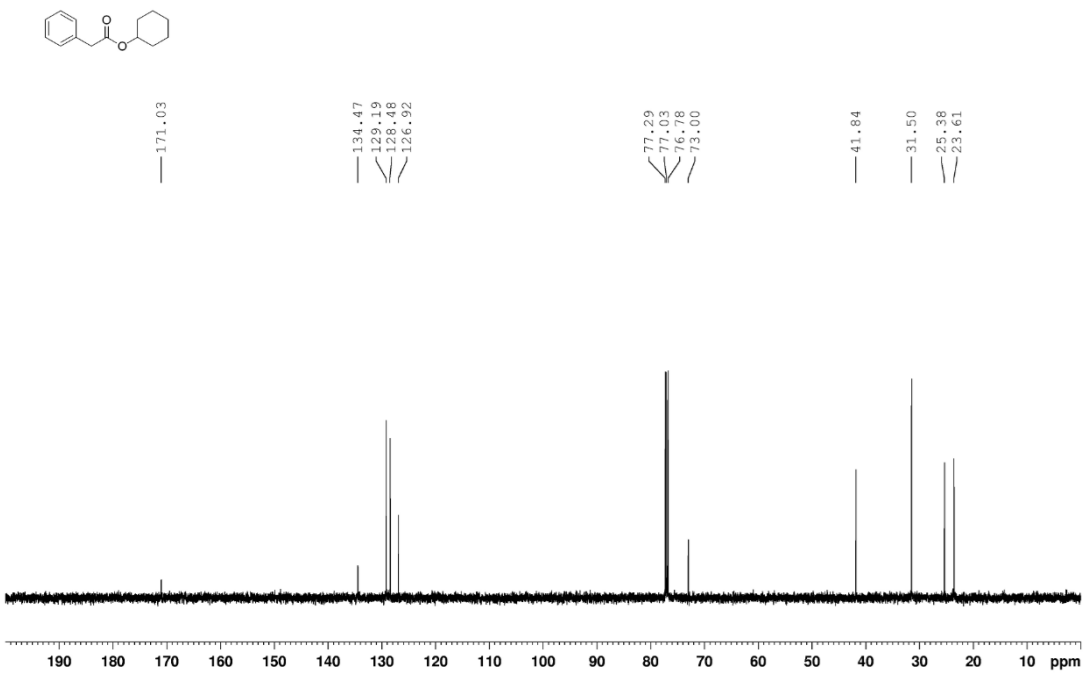
$^{1}H$ and $^{13}C$ NMR spectra of compound **3ae** ($CDCl_3$)



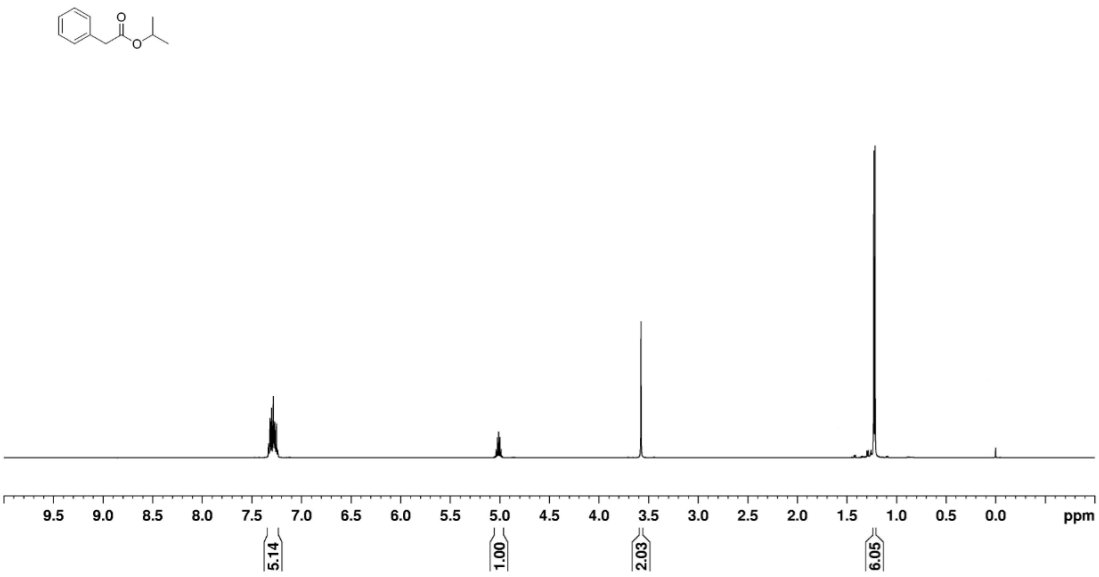



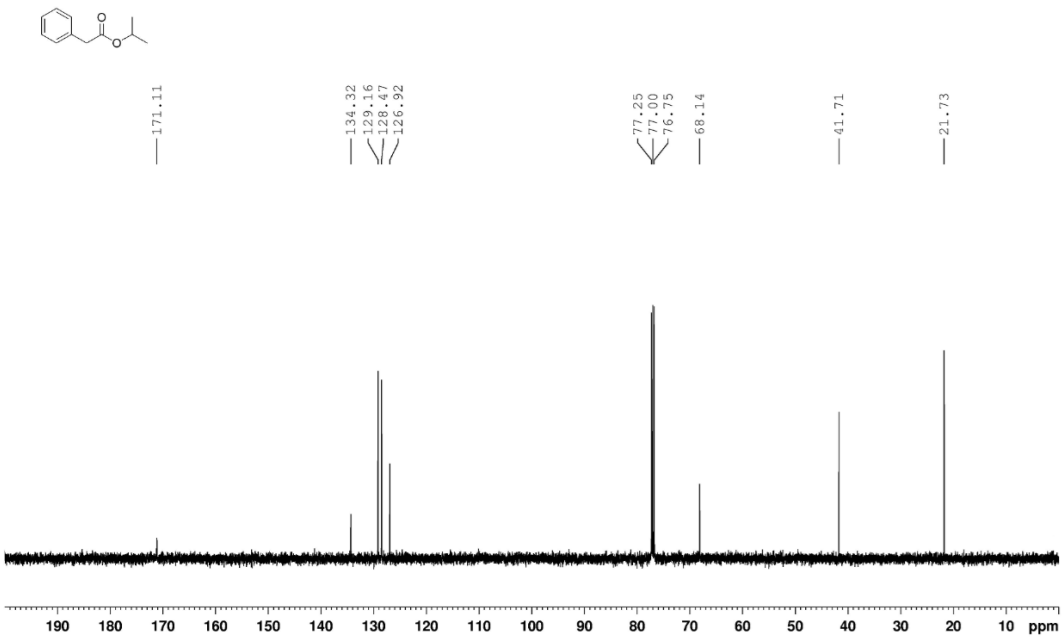
$^{1}H$ and $^{13}C$ NMR spectra of compound **3af** ($CDCl_3$)



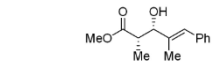



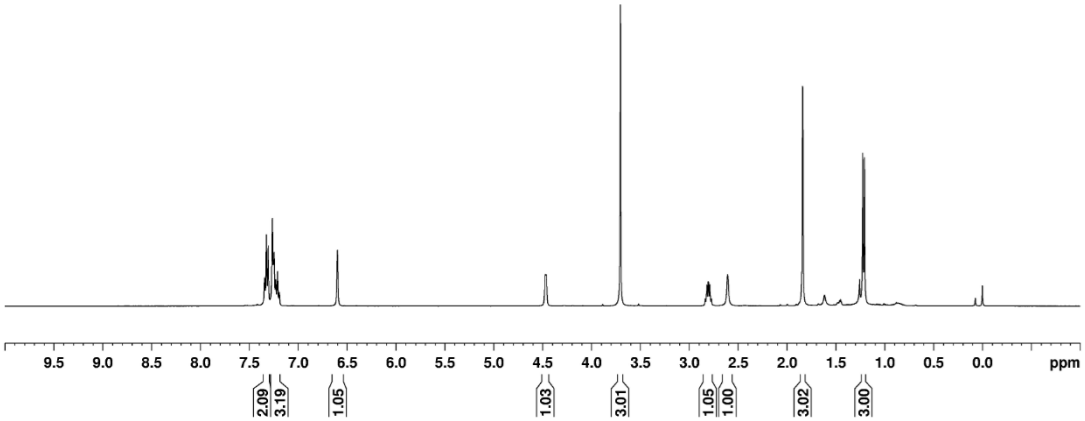
$^{1}H$ and $^{13}C$ NMR spectra of compound **3ag** ($CDCl_3$)

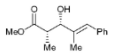


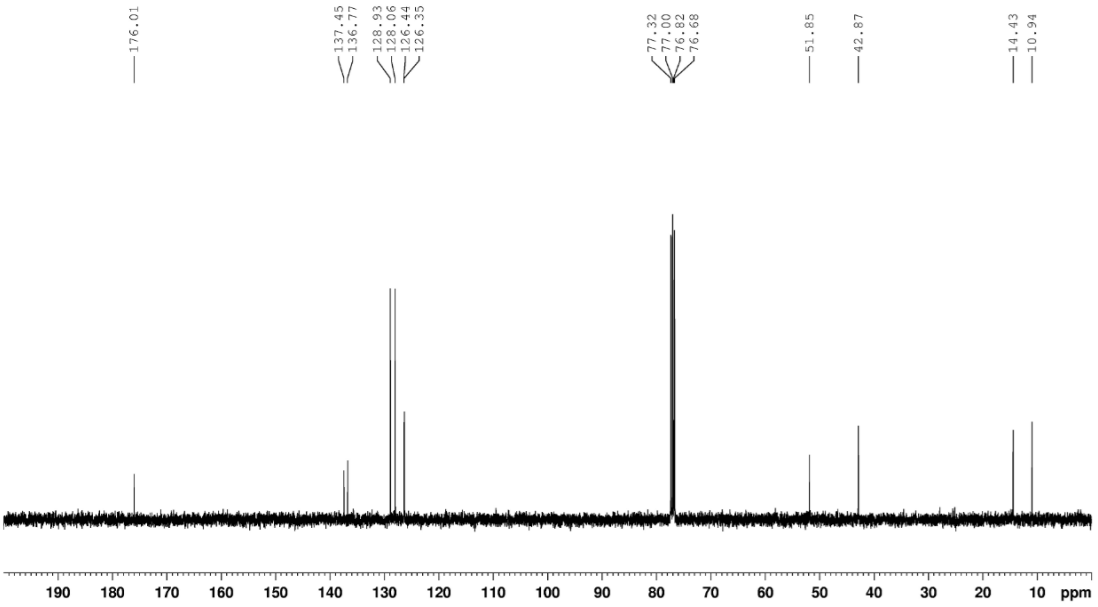



$^{1}H$ and $^{13}C$ NMR spectra of compound **6** ($CDCl_3$)

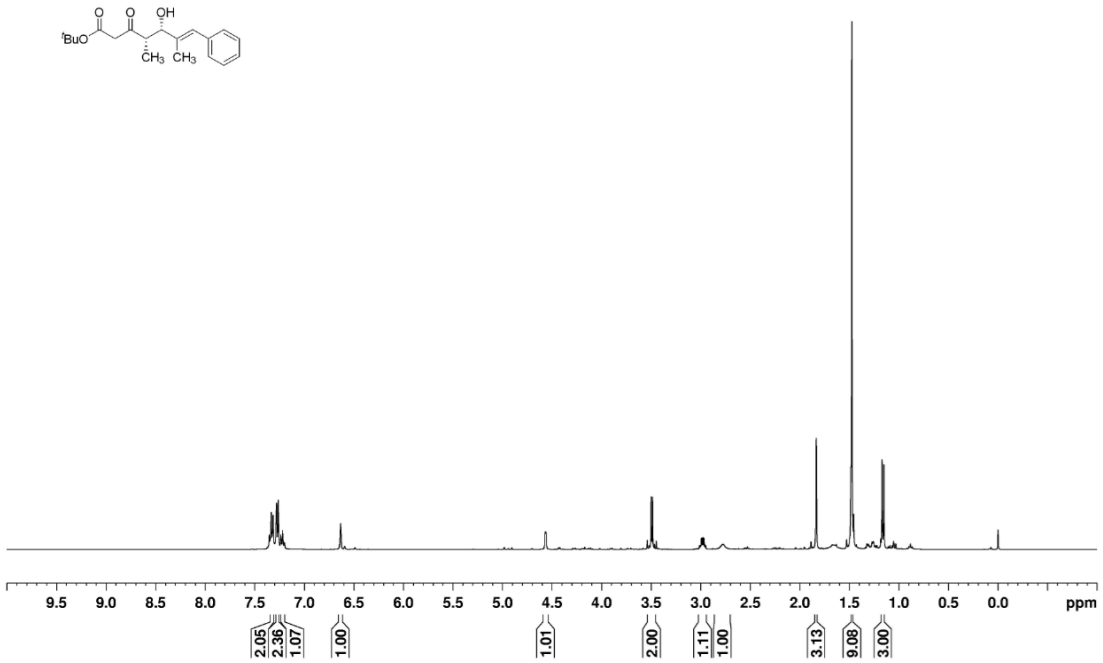


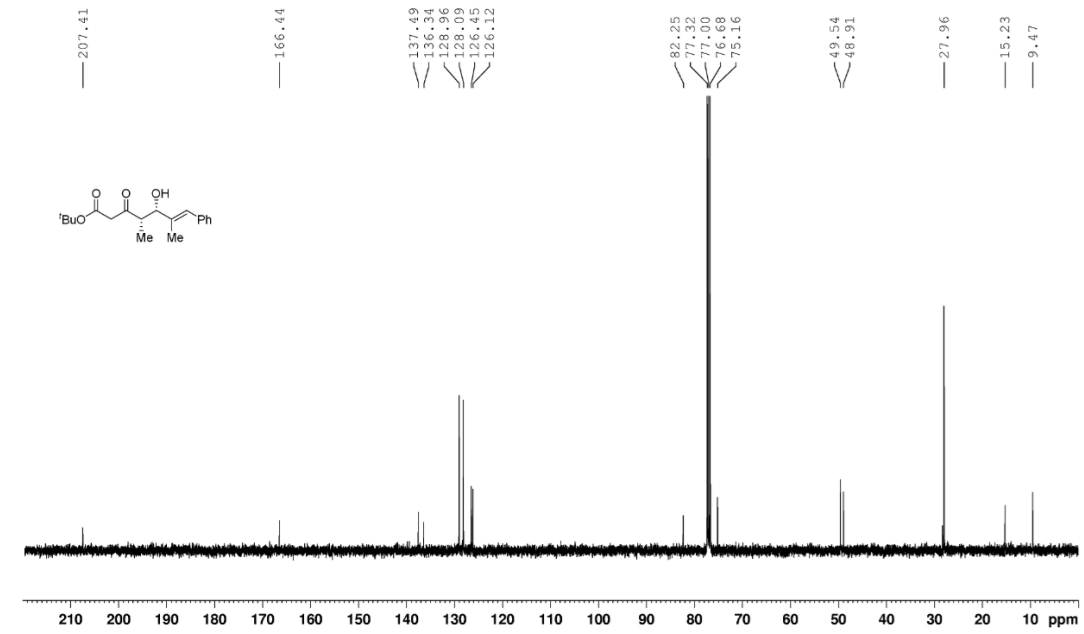



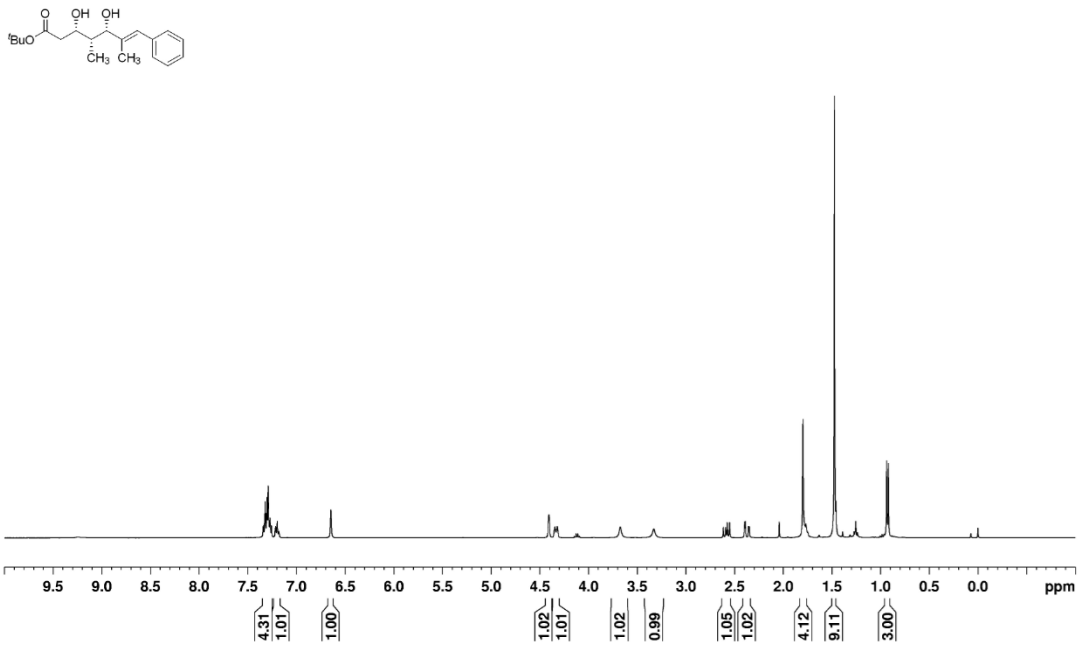



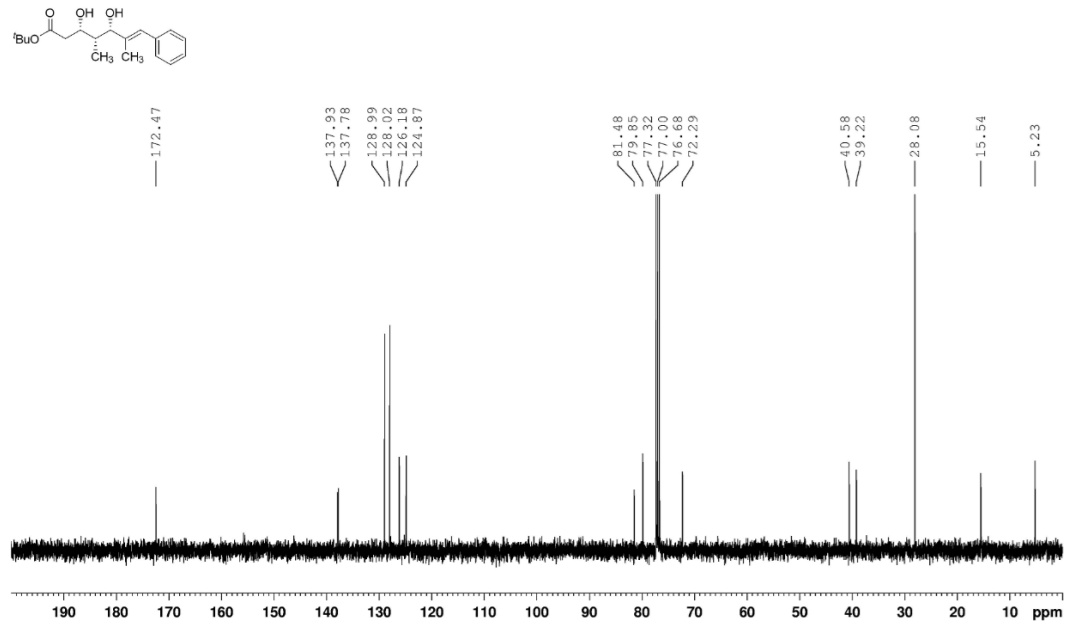
$^{1}H$ and $^{13}C$ NMR spectra of compound **7** ($CDCl_3$)



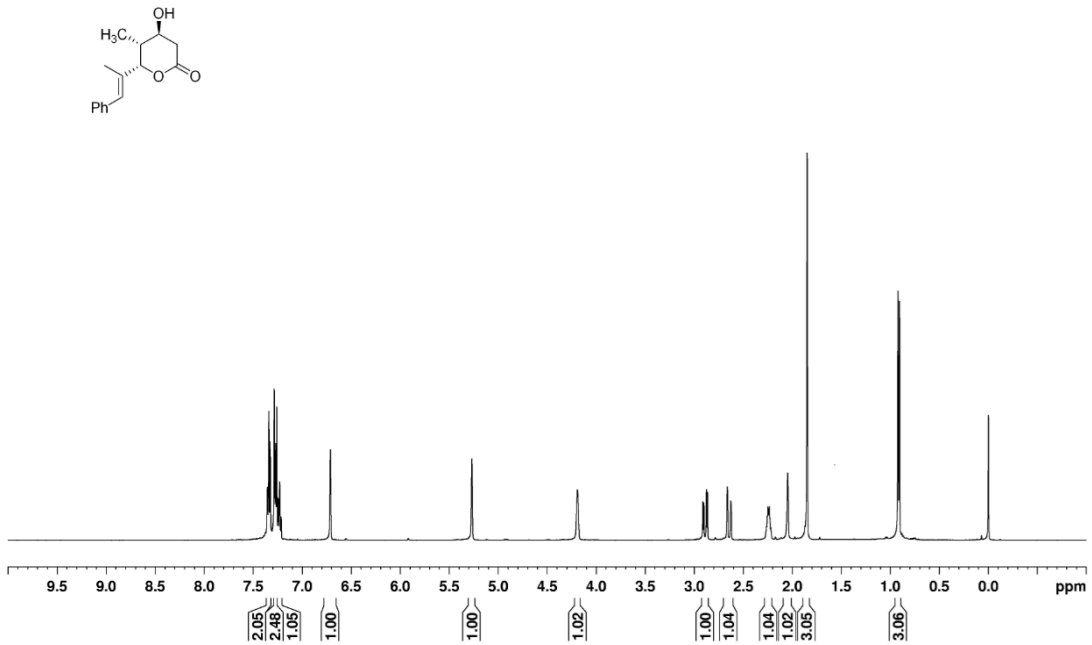



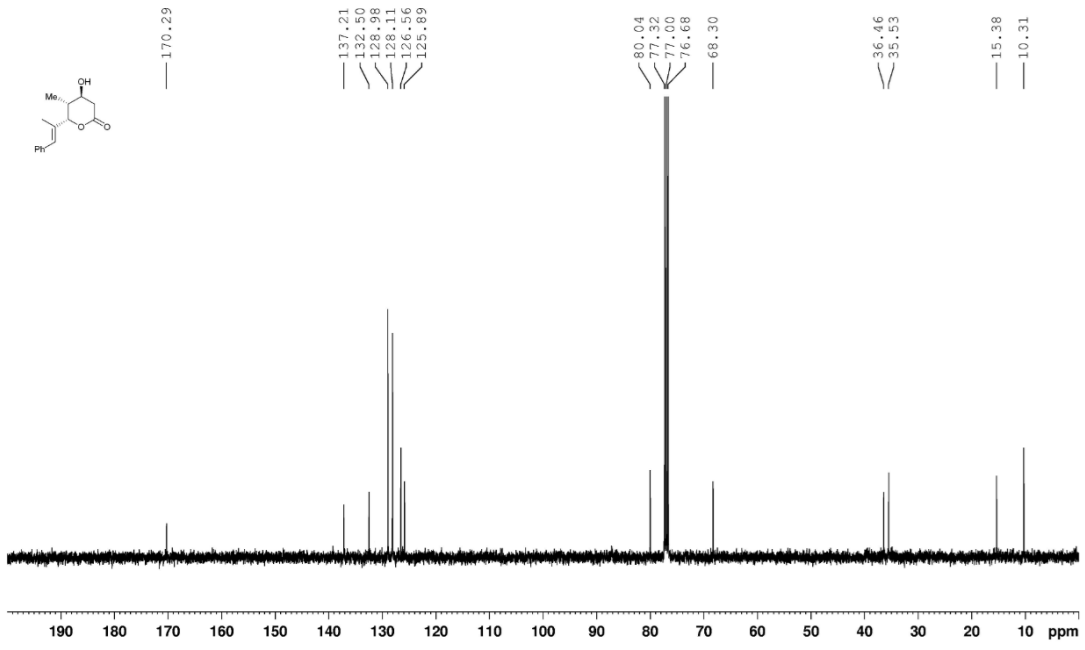
$^{1}H$ and $^{13}C$ NMR spectra of compound **8** ($CDCl_3$)



$^{1}H$ and $^{13}C$ NMR spectra of compound **9** ($CDCl_3$)

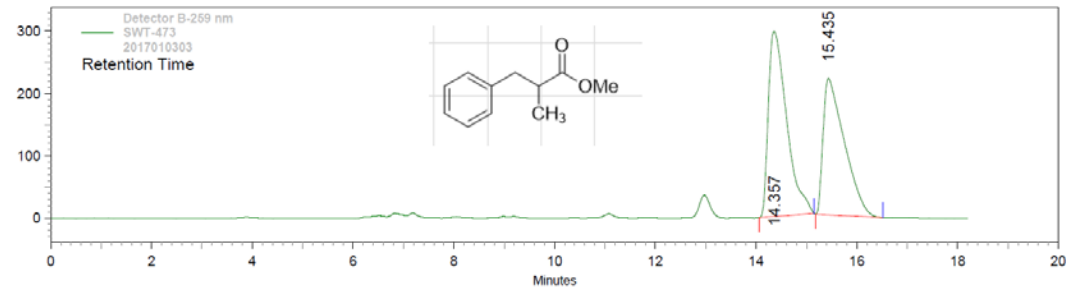


## Chiral HPLC diagrams of compounds (3j-3q)

## HPLC analysis of *racemic* 3j and (*S*)-3j from 2a

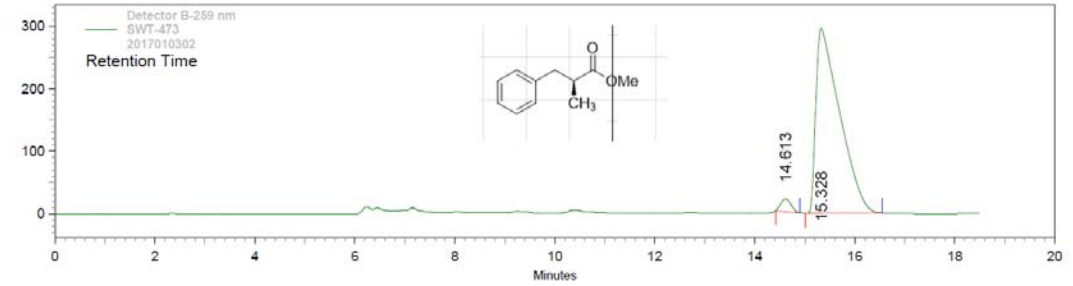
**Column: Chiral OJ-H**
**Mobile Phase:Hex/i-PrOH (95/5, v/v)**
**Flow Rate: 0.5mL/min**
**CT:30℃**




Detector B-259 nm

| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 14.357 | 7531282 | 53.97 | 0.00 |
| 2 | 15.435 | 6423007 | 46.03 | 0.00 |
| Totals | | 13954289 | 100.00 | |

**Shimadzu CLASS-VP V6.13 SP2** *Area % Report*
**Method Name: E:\科研数据\郑啸手性HPLC\121226.met**
**Data Name: E:\科研数据\耿辉\20170103\2017010302**
**Column: Chiral OJ-H**
**Mobile Phase:Hex/i-PrOH (95/5, v/v)**
**Flow Rate: 0.5mL/min**
**CT:30℃**




Detector B-259 nm

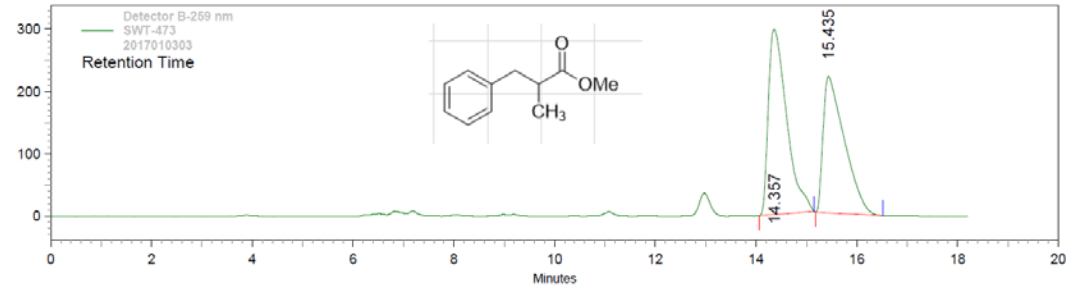
| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 14.613 | 288974 | 2.88 | 0.00 |
| 2 | 15.328 | 9761087 | 97.12 | 0.00 |
| Totals | | 10050061 | 100.00 | |

Conditions: Columnmon: Chiralpak OJ-H; Moblile phase: Hex/ *i*-PrOH (95:5, v/v); Flow Rate: 1.0 mL/ min; CT: 30 ºC; Detector wave: 259 nm.

**Figure S2** HPLC analysis of *racemic* **3j** and (***S***)**-3j** from **2a**

## HPLC analysis of *racemic* 3j and (*S*)-3j from 2d

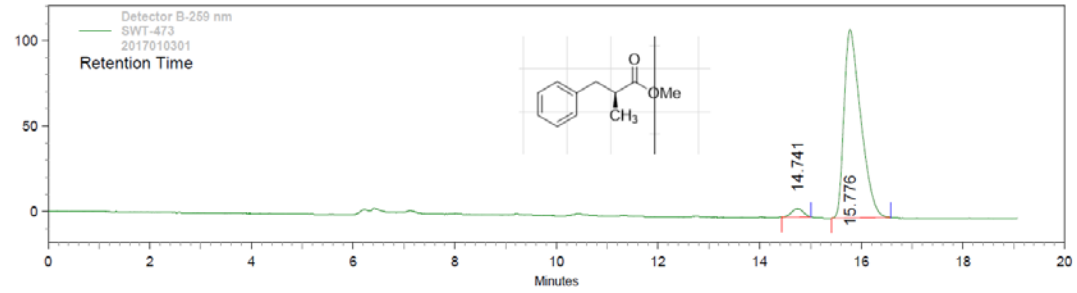
**Column: Chiral OJ-H**
**Mobile Phase:Hex/i-PrOH (95/5, v/v)**
**Flow Rate: 0.5mL/min**
**CT:30℃**




Detector B-259 nm

| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 14.357 | 7531282 | 53.97 | 0.00 |
| 2 | 15.435 | 6423007 | 46.03 | 0.00 |
| Totals | | 13954289 | 100.00 | |

**Column: Chiral OJ-H**
**Mobile Phase:Hex/i-PrOH (95/5, v/v)**
**Flow Rate: 0.5mL/min**
**CT:30℃**




Detector B-259 nm

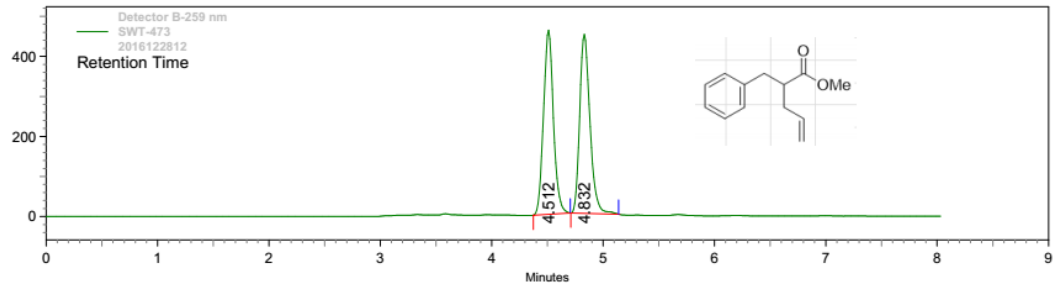
| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 14.741 | 80028 | 3.08 | 0.00 |
| 2 | 15.776 | 2521870 | 96.92 | 1.93 |
| Totals | | 2601898 | 100.00 | |

Conditions: Columnmon: Chiralpak OJ-H; Moblile phase: Hex/ *i*-PrOH (95:5, v/v); Flow Rate: 1.0 mL/ min; CT: 30 ºC; Detector wave: 259 nm.

**Figure S3** HPLC analysis of *racemic* **3j** and (***S***)-**3j** from **2d**

## HPLC analysis of *racemic* 3k and (*S*)-3k

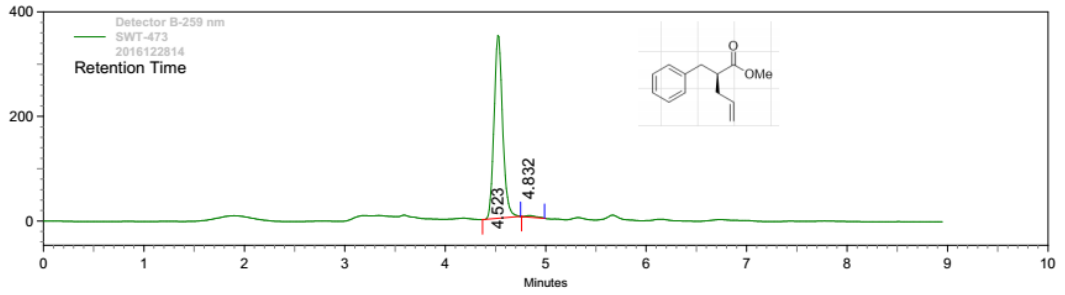
**Column: Chiral AD-H**
**Mobile Phase:Hex/EtOH (98/2, v/v)**
**Flow Rate: 1.0mL/min**
**CT:30℃ Sample Name: GHH-21**




Detector B-259 nm

| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 4.512 | 2847156 | 49.81 | 0.00 |
| 2 | 4.832 | 2868588 | 50.19 | 0.00 |
| Totals | | 5715744 | 100.00 | |

**Column: Chiral AD-H**
**Mobile Phase:Hex/EtOH (98/2, v/v)**
**Flow Rate: 1.0mL/min**
**CT:30℃ Sample Name: GHF-133**




Detector B-259 nm

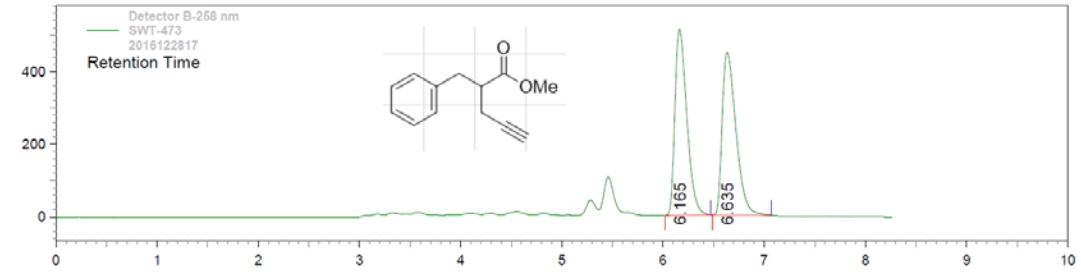
| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 4.523 | 2081789 | 98.93 | 0.00 |
| 2 | 4.832 | 22608 | 1.07 | 0.00 |
| Totals | | 2104397 | 100.00 | |

Conditions: Columnmon: Chiralpak AD-H; Moblile phase: Hex/ EtOH (98:2, v/v); Flow Rate: 1.0 mL/ min; CT: 30 ºC; Detector wave: 259 nm.

**Figure S4** HPLC analysis of *racemic* **3k** and (***S***)-**3k**

## HPLC analysis of *racemic* 3l and (*S*)-3l

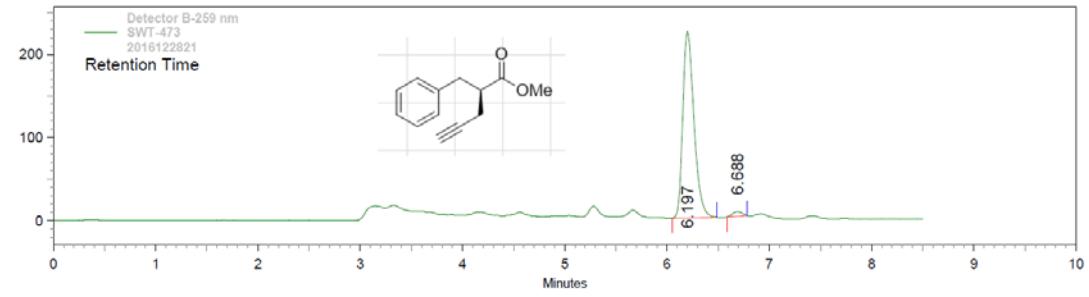
**Column: Chiral AD-H**
**Mobile Phase:Hex/EtOH (98/2, v/v)**
**Flow Rate: 1.0mL/min**
**CT:30℃** **Sample Name: GHH-22**




Detector B-258 nm

| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 6.165 | 4197167 | 49.76 | 0.00 |
| 2 | 6.635 | 4237445 | 50.24 | 0.00 |
| Totals | | 8434612 | 100.00 | |

**Column: Chiral AD-H**
**Mobile Phase:Hex/EtOH (98/2, v/v)**
**Flow Rate: 1.0mL/min**
**CT:30℃**




Detector B-259 nm

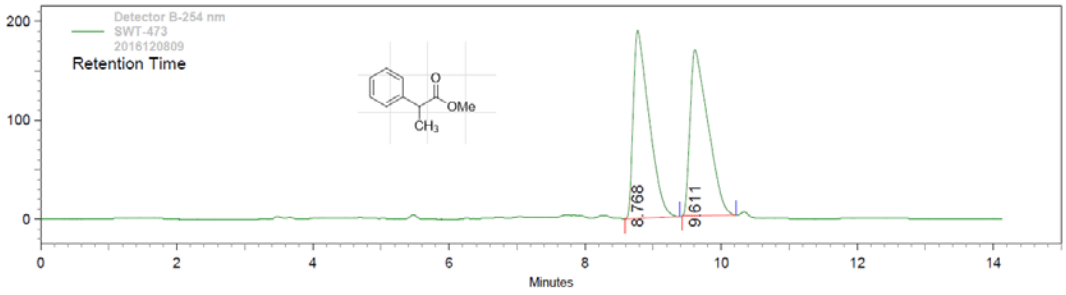
| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 6.197 | 1705634 | 97.80 | 0.00 |
| 2 | 6.688 | 38407 | 2.20 | 0.00 |
| Totals | | 1744041 | 100.00 | |

Conditions: Columnmon: Chiralpak AD-H; Moblile phase: Hex/ EtOH (98:2, v/v); Flow Rate: 1.0 mL/ min; CT: 30 ºC; Detector wave: 259 nm.

**Figure S5** HPLC analysis of *racemic* **3l** and (***S***)-**3l**

## HPLC analysis of *racemic* 3m and (*S*)-3m from 2e

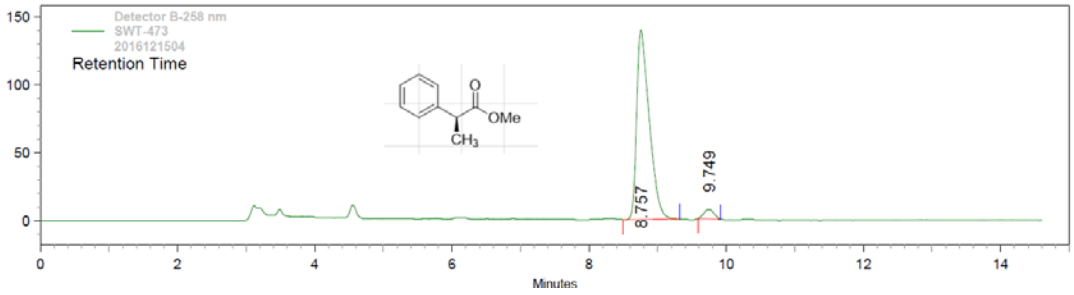
**Column: Chiralcel OJ-H**
**Mobile Phase: n-Hex/EtOH (95/5, v/v)**
**Flow Rate: 1.0 mL/min**
**CT: 30℃**




Detector B-254 nm

| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 8.768 | 3075208 | 50.02 | 0.00 |
| 2 | 9.611 | 3072719 | 49.98 | 0.00 |
| Totals | | 6147927 | 100.00 | |

**Column: Chiralpak OJ-H**
**Mobile Phase:n-Hex/EtOH (95/5, v/v)**
**Flow Rate: 1.0mL/min**
**CT:30℃** **Sample Name: GHH-5**




Detector B-258 nm

| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 8.757 | 1773505 | 96.15 | 0.00 |
| 2 | 9.749 | 70939 | 3.85 | 0.00 |
| Totals | | 1844444 | 100.00 | |

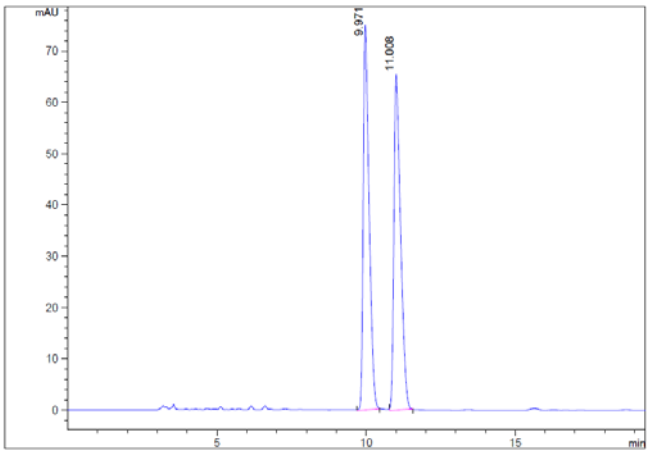
Conditions: Columnmon: Chiralpak OJ-H; Moblile phase: Hex/ EtOH (95:5, v/v); Flow Rate: 1.0 mL/ min; CT: 30 ºC; Detector wave: 254 nm.

**Figure S6** HPLC analysis of *racemic* **3m** and (***S***)-**3m** from **2e**

**HPLC analysis of *racemic* 3m and (*S*)-3m from 2f**

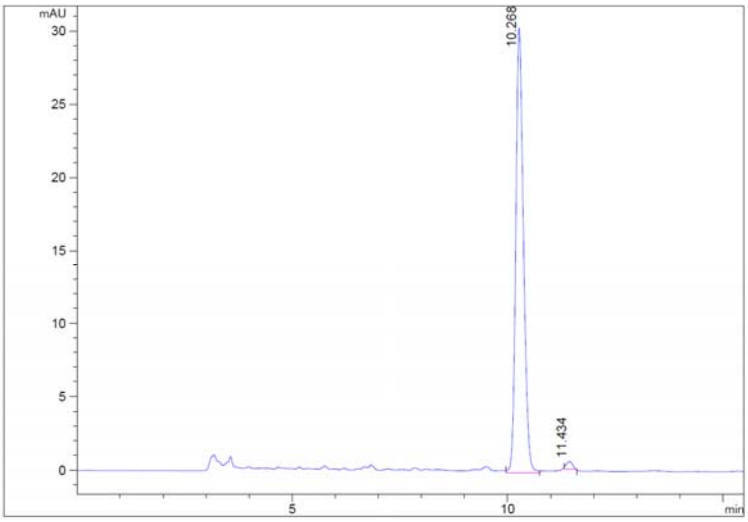
仪器名称: Agilent 1260 GH
色谱柱: Chiral OJ-H
流动相: Hex/EtOH=97/3 V/V
柱温: 26℃
流速: 1.000 mL/min

Nano pump test method




信号 1: VWD1 A, Wavelength=254 nm

| 峰面积 % | 峰面积 | 保留时间 [min] | 峰高 [min] | 化合物名称 |
|---|---|---|---|---|
| 50.101 | 1.019e3 | 9.971 | 74.985 | |
| 49.899 | 1.015e3 | 11.008 | 65.440 | |




信号 1: VWD1 A, Wavelength=254 nm

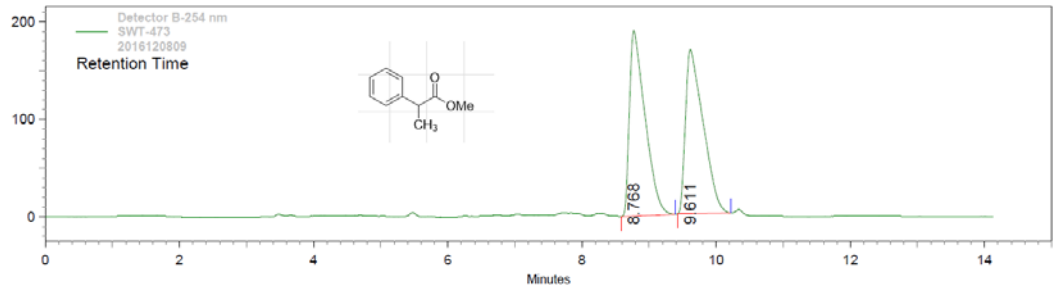
| 峰面积 % | 峰面积 | 保留时间 [min] | 峰高 [min] | 化合物名称 |
|---|---|---|---|---|
| 98.685 | 375.307 | 10.268 | 30.377 | |
| 1.315 | 5.003 | 11.434 | 0.504 | |

Conditions: Columnmon: Chiralpak OJ-H; Moblile phase: Hex/ EtOH (97:3, v/v); Flow Rate: 1.0 mL/ min; CT: 26 ºC; Detector wave: 254 nm.

**Figure S7** HPLC analysis of *racemic* **3m** and (***S***)-**3m** from **2f**

## HPLC analysis of *racemic* 3n and (*R*)-3n

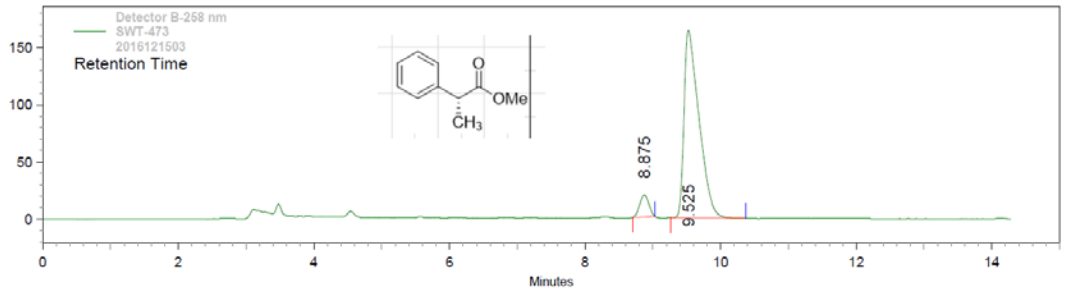
**Column: Chiralcel OJ-H**
**Mobile Phase: n-Hex/EtOH (95/5, v/v)**
**Flow Rate: 1.0 mL/min**
**CT: 30℃**




Detector B-254 nm

| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 8.768 | 3075208 | 50.02 | 0.00 |
| 2 | 9.611 | 3072719 | 49.98 | 0.00 |
| Totals | | 6147927 | 100.00 | |

**Column: Chiralpak OJ-H**
**Mobile Phase:n-Hex/EtOH (95/5, v/v)**
**Flow Rate: 1.0mL/min**
**CT:30℃**




Detector B-258 nm

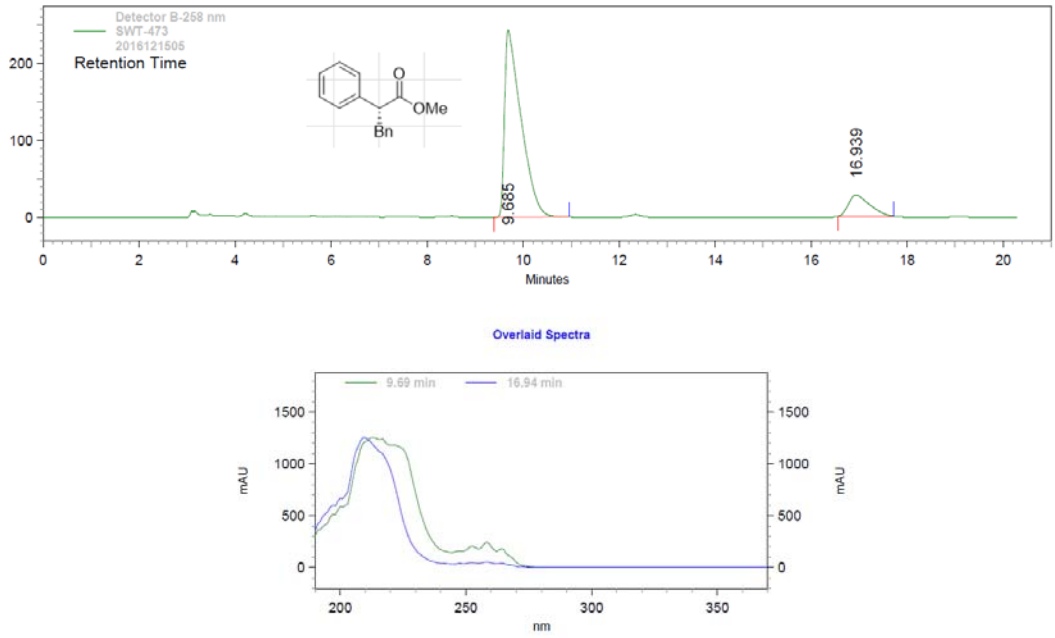
| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 8.875 | 181806 | 6.75 | 0.00 |
| 2 | 9.525 | 2513178 | 93.25 | 0.00 |
| Totals | | 2694984 | 100.00 | |

Conditions: Columnmon: Chiralpak OJ-H; Moblile phase: Hex/ EtOH (95:5, v/v); Flow Rate: 1.0 mL/ min; CT: 30 ºC; Detector wave: 254 nm.

**Figure S8** HPLC analysis of *racemic* **3n** and (***R***)-**3n**

## HPLC analysis of (*R*)-3o

**Column: Chiralpak OJ-H**
**Mobile Phase:n-Hex/i-PrOH (90/10, v/v)**
**Flow Rate: 1.0mL/min**
**CT:30℃**




Detector B-258 nm

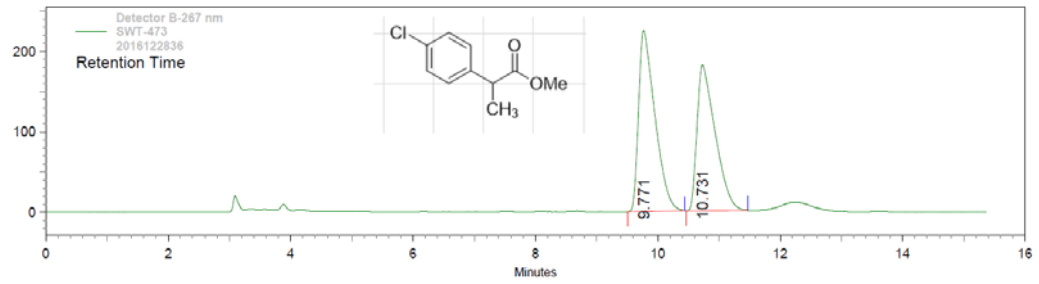
| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 9.685 | 5786082 | 87.21 | 0.00 |
| 2 | 16.939 | 848851 | 12.79 | 0.00 |
| Totals | | 6634933 | 100.00 | |

Conditions: Columnmon: Chiralpak OJ-H; Moblile phase: Hex/ i-PrOH (90:10, v/v); Flow Rate: 1.0 mL/ min; CT: 30 ºC; Detector wave: 258 nm.

**Figure S9** HPLC analysis of (***R***)-**3o**

## HPLC analysis of *racemic* 3p and (*S*)-3p

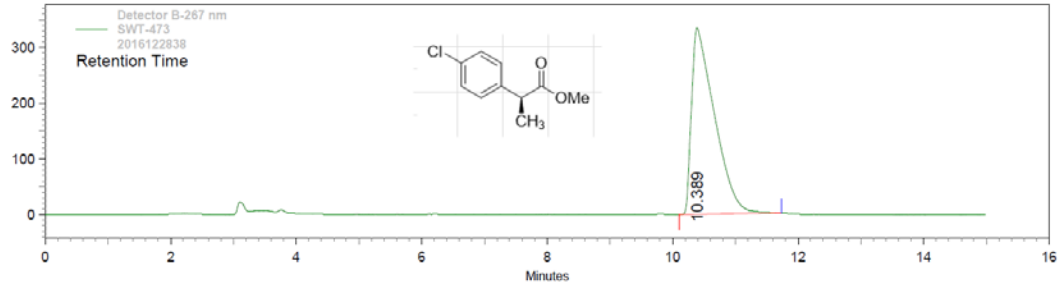
**Column: Chiral OJ-H**
**Mobile Phase:Hex/i-PrOH (99/1, v/v)**
**Flow Rate:1.0mL/min**
**CT:30℃**




Detector B-267 nm

| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 9.771 | 4170861 | 52.82 | 0.00 |
| 2 | 10.731 | 3724954 | 47.18 | 0.00 |
| Totals | | 7895815 | 100.00 | |

**Column: Chiral OJ-H**
**Mobile Phase:Hex/i-PrOH (99/1, v/v)**
**Flow Rate:1.0mL/min**
**CT:30℃**




Detector B-267 nm

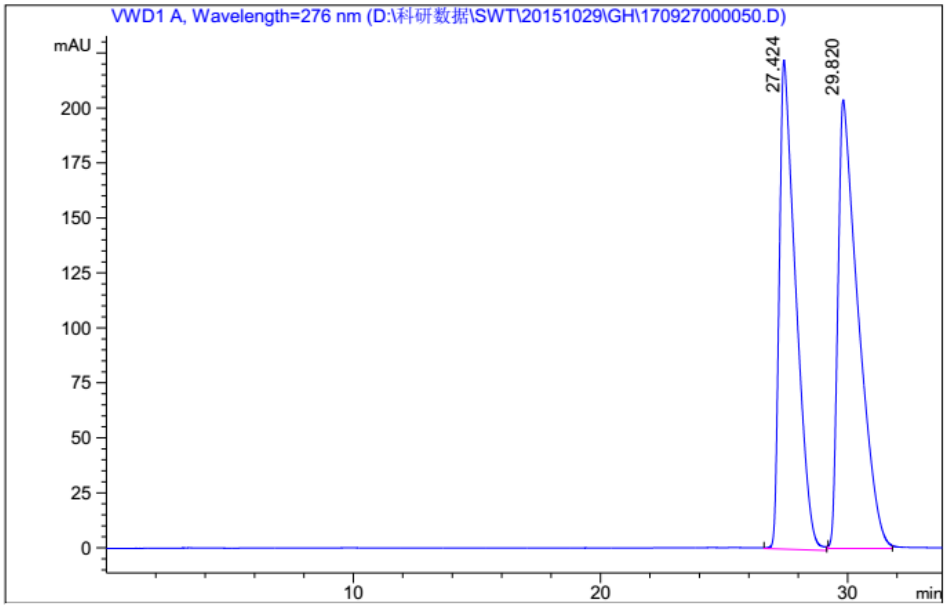
| Pk # | Retention Time | Area | Area Percent | Resolution |
|---|---|---|---|---|
| 1 | 10.389 | 8500544 | 100.00 | 0.00 |
| Totals | | 8500544 | 100.00 | |

Conditions: Columnmon: Chiralpak OJ-H; Moblile phase: Hex/ i-PrOH (99:1, v/v); Flow Rate: 1.0 mL/ min; CT: 30 ºC; Detector wave: 267 nm.

**Figure S10** HPLC analysis ***racemic* 3p** and (*S*)-**3p.**

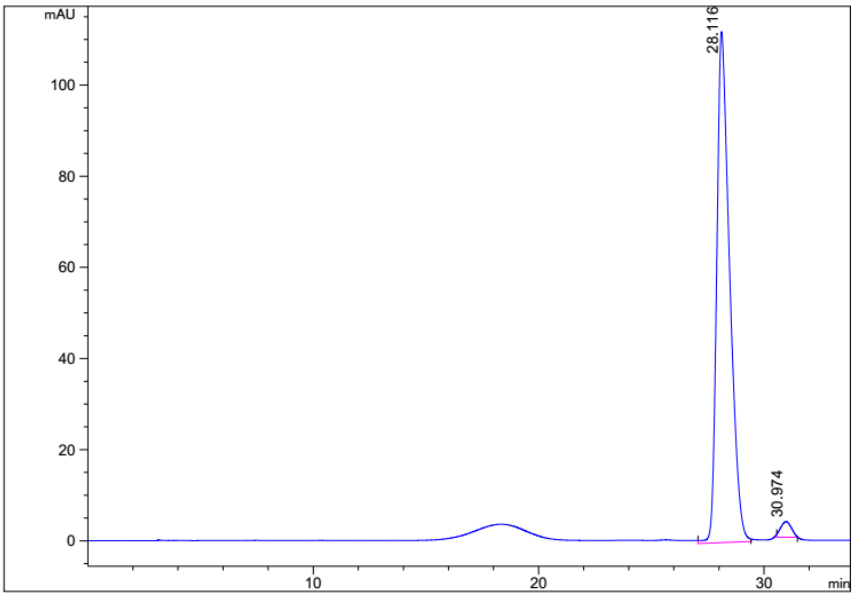
**HPLC analysis of *racemic* 3q and (*S*)-3q**

固定相: Chiralpak OJ-H
流动相: Hex/IPROH : 99.2/0.8, v/v
流速: 1.0 mL/min
柱温: 26℃




1信号 VWD1 A, Wavelength=276 nm

| 峰编号 | 保留时间 [min] | 峰面积 | 峰面积 % | 峰高 |
|---|---|---|---|---|
| 1 | 27.424 | 1.028e4 | 46.824 | 222.344 |
| 2 | 29.820 | 1.167e4 | 53.176 | 203.984 |




| 峰编号 | 峰面积 % | 峰面积 | 峰高 | 保留时间 [min] |
|---|---|---|---|---|
| 1 | 97.523 | 4.461e3 | 112.118 | 28.116 |
| 2 | 2.477 | 113.333 | 3.441 | 30.974 |

Conditions: Columnmon: Chiralpak OJ-H; Moblile phase: Hex/ i-PrOH (99.2:0.8, v/v); Flow Rate: 1.0 mL/ min; CT: 26 ºC; Detector wave: 276 nm.

**Figure S11** HPLC analysis *racemic* **3q** and (*S*)**-3q.**