

## Supporting Information

### Well-Defined Chiral Dinuclear Copper-Catalyzed Tandem Asymmetric Propargylic Amination-Carboxylative Cyclization Sequence to Chiral 2-Oxazolidinone Derivatives

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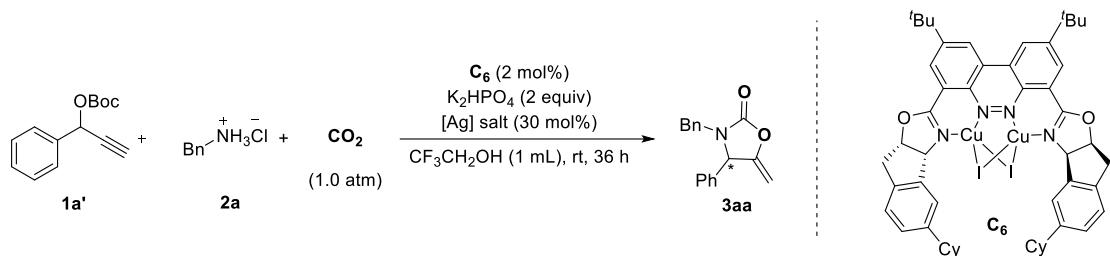
## **1. General Information and Materials**

Unless otherwise noted below, commercially available reagents were used throughout without further purification, and all reactions were performed using standard Schlenk techniques under an atmosphere of argon or in glovebox. Dry solvents were purchased and stored with molecular sieves in an atmosphere of argon. Flash column chromatography was performed using 200-300 mesh silica gel. Melting points were measured on a RY-I apparatus and uncorrected.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on Varian (400 MHz) or Agilent (400 MHz or 600 MHz) spectrometers. Chemical shifts were reported in parts per million (ppm) and refer to the appropriate residual solvent peak:  $^1\text{H}$  NMR were referenced to the central peak of  $\text{CDCl}_3$  (7.260 ppm); or to the internal standard TMS (0.000 ppm);  $^{13}\text{C}$  NMR were referenced to the central peak of 77.00 ppm for  $\text{CDCl}_3$ . Optical rotations were determined using a Perkin Elmer 341 MC polarimeter. HRMS(EI) was determined on a Waters Micromass GCT Premier instrument. HRMS(ESI) was determined on Bruker APEXIII 7.0 TESLA FTMS or Agilent Technologies 6224 TOF LC/MS. Single crystal X-ray diffraction data was collected on Bruker D<sub>8</sub> Venture diffractometer at 293(2) K or 173(0) K. Using Olex<sub>2</sub>, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. HPLC analyses were performed on a JASCO 2089 liquid chromatograph.

## 2. Experimental Data

### 2.1 Optimization of the reaction conditions

**Table S1.** Effects of the [Ag] salts<sup>a</sup>



Entry	Cat.	[Ag] salts	Yield [%] <sup>b</sup>	ee [%] <sup>c</sup>
1	<b>C<sub>6</sub></b>	AgBr	64	83
2	<b>C<sub>6</sub></b>	AgI	39	89
3	<b>C<sub>6</sub></b>	AgF	69	85
4	<b>C<sub>6</sub></b>	AgPF <sub>6</sub>	42	89
5	<b>C<sub>6</sub></b>	AgClO <sub>4</sub>	52	85
6	<b>C<sub>6</sub></b>	AgOTf	64	85
7	<b>C<sub>6</sub></b>	AgOTs	72	85
8	<b>C<sub>6</sub></b>	Ag <sub>2</sub> CO <sub>3</sub>	86	85
9	<b>C<sub>6</sub></b>	AgNO <sub>2</sub>	38	71
10	<b>C<sub>6</sub></b>	Ag <sub>2</sub> O	72	85
11	<b>C<sub>6</sub></b>	AgSCF <sub>3</sub>	trace	-
12	<b>C<sub>6</sub></b>	Ag <sub>3</sub> PO <sub>4</sub>	76	85

<sup>a</sup>Unless otherwise noted, reaction conditions are as follows: **1a'** (0.1 mmol), **2a** (0.15 mmol), K<sub>2</sub>HPO<sub>4</sub> (2.0 equiv), [Ag] salts (30 mol%) and **C<sub>6</sub>** (2 mol %) in CF<sub>3</sub>CH<sub>2</sub>OH (1.0 mL) at room temperature for 36 h. <sup>b</sup><sup>1</sup>H NMR yield using Mesitylene as the internal standard. <sup>c</sup>The ee value of **3aa** was determined by HPLC on a chiral column IA.

**Table S2.** Effects of leaving groups in propargylic<sup>a</sup>

Entry	Cat.	LG	Yield [%] <sup>b</sup>	ee [%] <sup>c</sup>
1	<b>C<sub>6</sub></b>	OBoc	86	85
2	<b>C<sub>6</sub></b>	OCOC <sub>6</sub> F <sub>5</sub>	65	91
3	<b>C<sub>6</sub></b>	OAc	64	89

<sup>a</sup>Unless otherwise noted, reaction conditions are as follows: **1** (0.1 mmol), **2a** (0.15 mmol), K<sub>2</sub>HPO<sub>4</sub> (2.0 equiv), Ag<sub>2</sub>CO<sub>3</sub> (30 mol%) and **C<sub>6</sub>** (2 mol %) in CF<sub>3</sub>CH<sub>2</sub>OH (1.0 mL) at room temperature for 36 h. <sup>b</sup><sup>1</sup>H NMR yield using mesitylene as the internal standard. <sup>c</sup>The ee value of **3aa** was determined by HPLC on a chiral column IA.

**Table S3.** Effects of the Base<sup>a</sup>

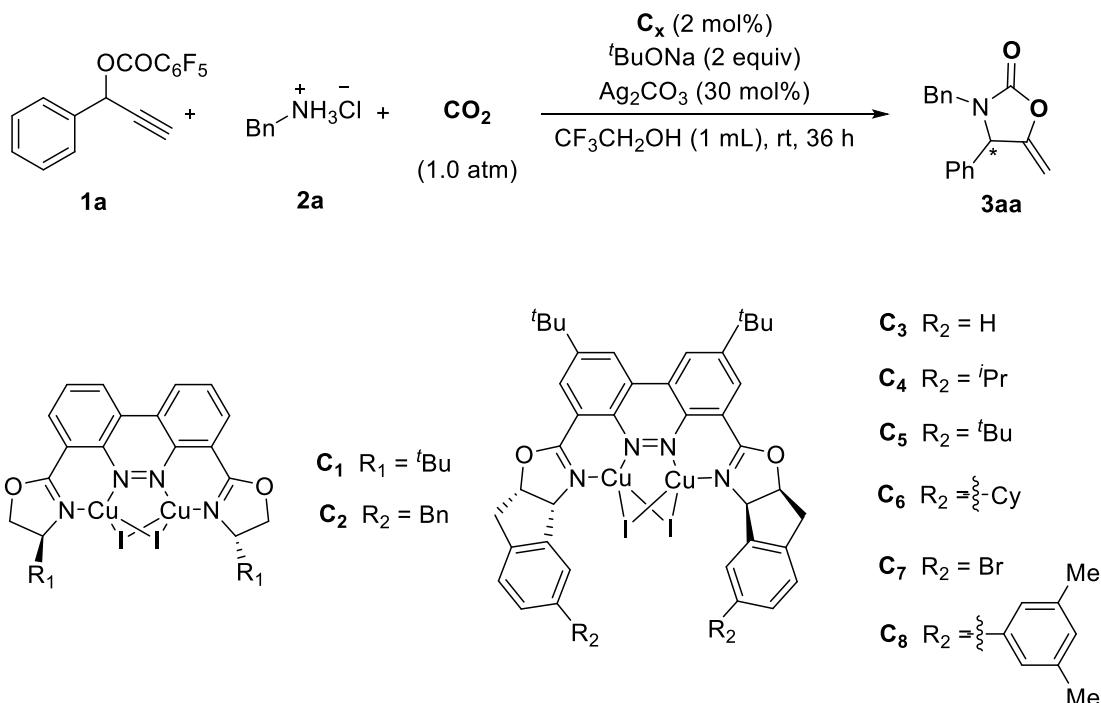
Entry	Cat.	Base	Yield [%] <sup>b</sup>	ee [%] <sup>c</sup>
1	<b>C<sub>6</sub></b>	CH <sub>3</sub> COOK	trace	-
2	<b>C<sub>6</sub></b>	'BuOLi	trace	-
3	<b>C<sub>6</sub></b>	K <sub>2</sub> CO <sub>3</sub>	76	87
4	<b>C<sub>6</sub></b>	'BuOK	65	91
5	<b>C<sub>6</sub></b>	'BuONa	70	91

6	<b>C<sub>6</sub></b>	CH <sub>3</sub> COOLi	trace	-
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<sup>a</sup>Unless otherwise noted, reaction conditions are as follows: **1a** (0.1 mmol), **2a** (0.15 mmol), Base (2.0 equiv), Ag<sub>2</sub>CO<sub>3</sub> (30 mol%) and **C<sub>6</sub>** (2 mol %) in CF<sub>3</sub>CH<sub>2</sub>OH (1.0 mL) at room temperature for 36 h. <sup>b</sup><sup>1</sup>H NMR yield using mesitylene as the internal standard.

<sup>c</sup>The *ee* value of **3aa** was determined by HPLC on a chiral column IA.

**Table S4.** Investigation of dinuclear copper-catalyzed asymmetric propargylic amination-carboxylative cyclization sequence<sup>a</sup>



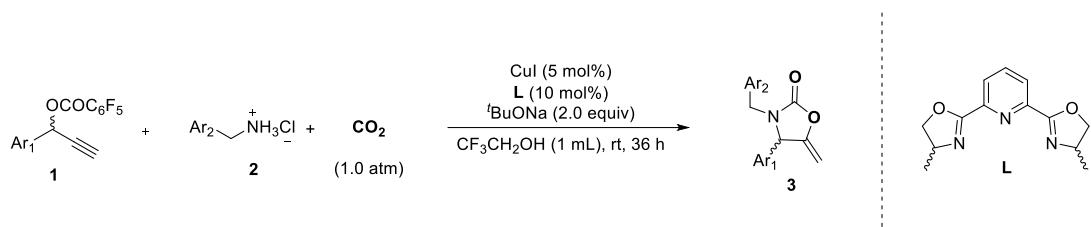
Entry	Cat.	Yield [%] <sup>b</sup>	<i>ee</i> [%] <sup>c</sup>
1	<b>C<sub>1</sub></b>	51	73
2	<b>C<sub>2</sub></b>	54	70
3	<b>C<sub>3</sub></b>	49	79
4	<b>C<sub>4</sub></b>	64	85
5	<b>C<sub>5</sub></b>	59	87
6	<b>C<sub>6</sub></b>	70 (64) <sup>d</sup>	91

7	<b>C<sub>7</sub></b>	54	65
8	<b>C<sub>8</sub></b>	47	70
9 <sup>e</sup>	<b>C<sub>6</sub></b>	74	88

<sup>a</sup>Unless otherwise noted, reaction conditions are as follows: **1a** (0.1 mmol), **2a** (0.15 mmol), <sup>t</sup>BuONa (2.0 equiv), Ag<sub>2</sub>CO<sub>3</sub> (30 mol%) and **C<sub>x</sub>** (2 mol %) in CF<sub>3</sub>CH<sub>2</sub>OH (1.0 mL) at room temperature for 36 h. <sup>b</sup><sup>1</sup>H NMR yield using mesitylene as the internal standard. <sup>c</sup>The *ee* value of **3aa** was determined by HPLC on a chiral column IA.

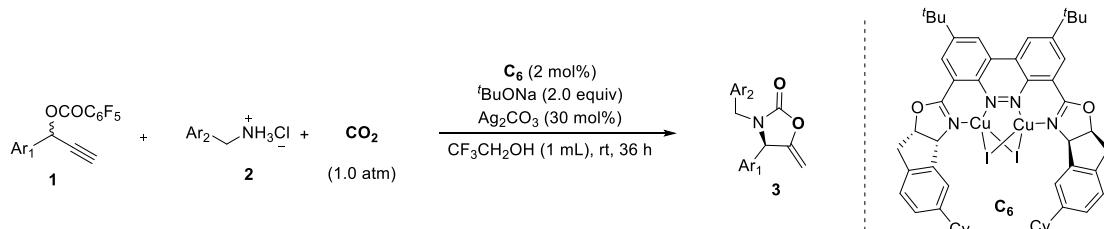
<sup>d</sup>Isolated yield. <sup>e</sup>**2a** was replaced by BnNH<sub>2</sub>.

## 2.2. General procedure for the preparation of racemic products



A typical experimental procedure for the preparation of (*rac*)-3-benzyl-5-methylene-4-phenyloxazolidin-2-one (*rac*-**3aa**) is described below. **1a** (32.6 mg, 0.1 mmol, 1.0 equiv), **2a** (21.46 mg, 0.15 mmol, 1.5 equiv), *'*BuONa (19.22 mg, 0.2 mmol, 2.0 equiv), CuI (0.95 mg, 0.005 mmol, 5 mol%) and **L** (2.45 mg, 0.01 mmol, 10 mol%) was added in a 10 mL Schlenk flask and a dry CO<sub>2</sub> atmosphere was established by a balloon filled with CO<sub>2</sub>. Then, CF<sub>3</sub>CH<sub>2</sub>OH (1.0 mL) was added. After stirring at room temperature for 36 h, the mixture was concentrated under reduced pressure. The residue was purified by silica gel chromatography with n-hexane and EtOAc (n-hexane/EtOAc = 10/1-5/1) as eluent to give *rac*-**3aa** as a yellow solid.

## 2.3 Representative experimental procedure and Substrate scope

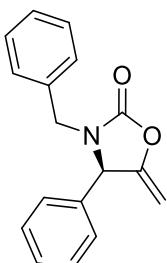


A typical experimental procedure for the preparation of (*R*)-3-benzyl-5-methylene-4-phenyloxazolidin-2-one (**3aa**) is described below. **1a** (32.6 mg, 0.1 mmol, 1.0 equiv), **2a** (21.46 mg, 0.15 mmol, 1.5 equiv), *'*BuONa (19.22 mg, 0.2 mmol, 2.0 equiv), Ag<sub>2</sub>CO<sub>3</sub> (8.27 mg, 0.03 mmol, 30 mol%) and **C<sub>6</sub>** (2.30 mg, 0.002 mmol, 2 mol%) was added in a 10 mL Schlenk flask and a dry CO<sub>2</sub> atmosphere was established by a balloon filled with CO<sub>2</sub>. Then, CF<sub>3</sub>CH<sub>2</sub>OH (1.0 mL) was added. After stirring at room temperature for 36 h, the mixture was concentrated under reduced pressure. The residue was purified by silica gel chromatography with n-hexane and EtOAc (n-hexane/EtOAc = 10/1-5/1) as eluent to give **3aa** as a yellow solid.

Spectroscopic datas are as follows.

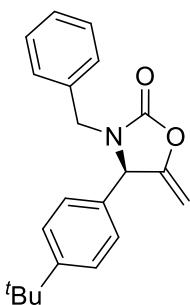
Preparations of chiral dinuclear copper complexes are in accordance with the literature<sup>1</sup>.

**(R)-3-benzyl-5-methylene-4-phenyloxazolidin-2-one (3aa)**



Yellow solid, 17.0 mg, 64% yield, 91% *ee*. M. P. 77-79 °C.  $[\alpha]_D^{20} = -21.50$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.39 (m, 3H), 7.36 – 7.28 (m, 3H), 7.24 – 7.19 (m, 2H), 7.18 – 7.12 (m, 2H), 5.02 (t, *J* = 2.4 Hz, 1H), 4.90 (d, *J* = 14.9 Hz, 1H), 4.75 (t, *J* = 3.0 Hz, 1H), 4.02 (t, *J* = 2.2 Hz, 1H), 3.64 (d, *J* = 14.9 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.23, 154.78, 136.80, 134.90, 129.38, 129.34, 128.95, 128.65, 128.26, 127.90, 88.43, 61.94, 45.57 ppm. IR (neat) ν 3061, 3028, 2959, 2925, 2126, 1953 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>17</sub>H<sub>15</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 288.0995, Found: 288.0994. The enantiomeric excess was determined by HPLC on Chiralcel IA column, *n*-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at  $\lambda$  = 214 nm, t<sub>R</sub> = 9.3 min (minor), t<sub>R</sub> = 9.9 min (major).

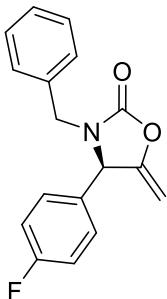
**(R)-3-benzyl-4-(4-(tert-butyl)phenyl)-5-methyleneoxazolidin-2-one (3ba)**



White solid, 13.7 mg, 42% yield, 91% *ee*. M. P. 83-85 °C.  $[\alpha]_D^{20} = -27.60$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.15 (t, *J* = 8.7 Hz, 4H), 5.00 (s, 1H), 4.86 (d, *J* = 15.0 Hz, 1H), 4.75 (s, 1H), 4.03 (s, 1H), 3.66

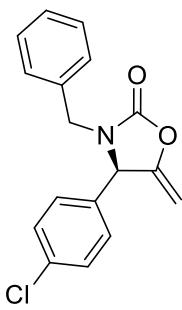
(d,  $J = 14.9$  Hz, 1H), 1.34 (s, 9H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.32, 154.97, 152.51, 135.15, 133.71, 128.95, 128.73, 128.23, 127.66, 126.26, 88.35, 61.73, 45.54, 34.85, 31.42 ppm. IR (neat)  $\nu$  3062, 3032, 2960, 2929, 2866, 2117, 1950, 1782  $\text{cm}^{-1}$ ; HRMS (ESI) m/z: calcd. for  $\text{C}_{21}\text{H}_{23}\text{NO}_2\text{Na}^+ [\text{M}+\text{Na}]^+$ : 344.1621, Found: 344.1613. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at  $\lambda = 214$  nm,  $t_R = 6.9$  min (minor),  $t_R = 7.6$  min (major).

**(R)-3-benzyl-4-(4-fluorophenyl)-5-methyleneoxazolidin-2-one (3ca)**



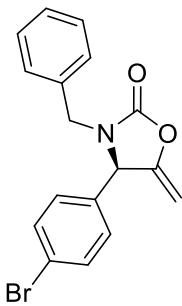
Yellow solid, 17.43 mg, 61% yield, 91% ee. M. P. 79-81 °C.  $[\alpha]_D^{20} = -11.70$  (c 0.2,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.28 (m, 3H), 7.24 – 7.16 (m, 2H), 7.16 – 7.05 (m, 4H), 5.01 (s, 1H), 4.88 (d,  $J = 15.0$  Hz, 1H), 4.78 (s, 1H), 4.01 (s, 1H), 3.63 (d,  $J = 15.0$  Hz, 1H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.28 (d,  $J = 250.0$  Hz), 155.13, 154.67, 134.77, 132.68 (d,  $J = 3.4$  Hz), 129.86 (d,  $J = 8.5$  Hz), 129.05, 128.67, 128.40, 116.43 (d,  $J = 22.0$  Hz), 88.74, 61.32, 45.69 ppm.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.83 ppm. IR (neat)  $\nu$  3300, 3065, 3030, 2962, 2926, 2854, 2445, 2351, 1950, 1884  $\text{cm}^{-1}$ ; HRMS (ESI) m/z: calcd. for  $\text{C}_{17}\text{H}_{14}\text{NO}_2\text{FNa}^+ [\text{M}+\text{Na}]^+$ : 306.0901, Found: 306.0894. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at  $\lambda = 214$  nm,  $t_R = 9.8$  min (minor),  $t_R = 10.7$  min (major).

**(R)-3-benzyl-4-(4-chlorophenyl)-5-methyleneoxazolidin-2-one (3da)**



Yellow oil, 17.6 mg, 58% yield, 92% *ee*.  $[\alpha]_D^{20} = -35.10$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.36 (m, 2H), 7.36 – 7.27 (m, 3H), 7.18 – 7.09 (m, 4H), 4.98 (t, *J* = 2.4 Hz, 1H), 4.89 (d, *J* = 15.0 Hz, 1H), 4.77 (dd, *J* = 3.3, 2.6 Hz, 1H), 4.00 (dd, *J* = 3.4, 2.1 Hz, 1H), 3.63 (d, *J* = 15.0 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.13, 154.40, 135.46, 135.40, 134.69, 129.66, 129.36, 129.08, 128.68, 128.44, 88.83, 61.34, 45.75 ppm. IR (neat) ν 3047, 3031, 2962, 2835, 2350, 1948 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub>NaCl<sup>+</sup> [M+Na]<sup>+</sup>: 322.0605, Found: 322.0607. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 0.5 mL/min, UV detection at λ = 214 nm, t<sub>R</sub> = 19.9 min (minor), t<sub>R</sub> = 22.0 min (major).

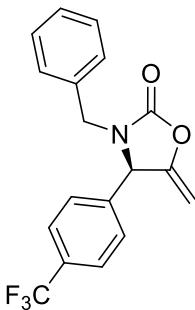
#### (*R*)-3-benzyl-4-(4-bromophenyl)-5-methyleneoxazolidin-2-one (3ea)



Yellow oil, 16.2 mg, 47% yield, 92% *ee*.  $[\alpha]_D^{20} = -49.00$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.52 (m, 2H), 7.37 – 7.30 (m, 3H), 7.16 – 7.06 (m, 4H), 4.97 (t, *J* = 2.4 Hz, 1H), 4.89 (d, *J* = 15.0 Hz, 1H), 4.77 (dd, *J* = 3.4, 2.6 Hz, 1H), 4.00 (dd, *J* = 3.4, 2.1 Hz, 1H), 3.63 (d, *J* = 15.0 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.13, 154.30, 135.93, 134.67, 132.62, 129.64, 129.08, 128.68, 128.45, 123.61, 88.86, 61.41, 45.75 ppm. IR (neat) ν 3027, 2924, 2347, 2128, 2070, 1954, 1910, 1887 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub>NaBr<sup>+</sup> [M+Na]<sup>+</sup>: 366.0100, Found: 366.0101. The

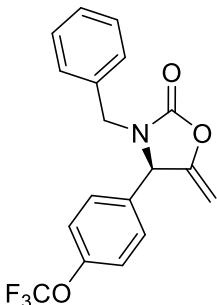
enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 0.5 mL/min, UV detection at  $\lambda$  = 214 nm,  $t_R$  = 20.7 min (minor),  $t_R$  = 23.2 min (major).

**(R)-3-benzyl-5-methylene-4-(4-(trifluoromethyl)phenyl)oxazolidin-2-one (3fa)**



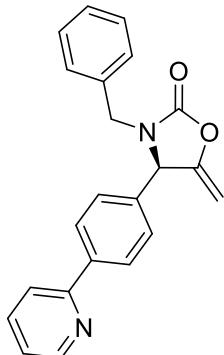
Yellow solid, 19.6 mg, 59% yield, 91% *ee*. M. P. 89-91 °C.  $[\alpha]_D^{20} = -32.20$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.29 (m, 5H), 7.16 – 7.09 (m, 2H), 5.07 (t, *J* = 2.4 Hz, 1H), 4.90 (d, *J* = 15.0 Hz, 1H), 4.80 (t, *J* = 2.6 Hz, 1H), 4.01 (dd, *J* = 3.5, 2.2 Hz, 1H), 3.66 (d, *J* = 15.0 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  155.14, 153.92, 140.90 (q, *J* = 1.4 Hz), 134.53, 131.70 (q, *J* = 32.9 Hz), 129.13, 128.67, 128.51, 128.35, 126.43 (q, *J* = 3.8 Hz), 123.85 (q, *J* = 273.3 Hz) 89.14, 61.49, 45.95 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.80 ppm. IR (neat)  $\nu$  3031, 2959, 2925, 2853, 2642, 2350, 2090, 1932 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>18</sub>H<sub>14</sub>NO<sub>2</sub>F<sub>3</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 356.0869, Found: 356.0876. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at  $\lambda$  = 214 nm,  $t_R$  = 9.2 min (minor),  $t_R$  = 10.4 min (major).

**(R)-3-benzyl-5-methylene-4-(4-(trifluoromethoxy)phenyl)oxazolidin-2-one (3ga)**



Yellow oil, 23.0 mg, 66% yield, 90% *ee*.  $[\alpha]_D^{20} = -19.70$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 (t, *J* = 8.0 Hz, 1H), 7.25 (dd, *J* = 4.9, 2.0 Hz, 3H), 7.21 – 7.17 (m, 1H), 7.12 – 7.08 (m, 1H), 7.07 – 7.03 (m, 2H), 6.99 – 6.97 (m, 1H), 4.94 (t, *J* = 2.3 Hz, 1H), 4.83 (d, *J* = 14.9 Hz, 1H), 4.73 (dd, *J* = 3.4, 2.6 Hz, 1H), 3.96 (dd, *J* = 3.4, 2.1 Hz, 1H), 3.60 (d, *J* = 14.9 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.10, 153.97, 149.88 (q, *J* = 1.9 Hz), 139.27, 134.53, 130.97, 129.10, 128.70, 128.51, 126.21, 121.84, 120.66, 120.5 (q, *J* = 259.0 Hz) 89.11, 61.48, 45.95 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -57.90 ppm. IR (neat) ν 3066, 3032, 2927, 2859, 2470, 1958 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>18</sub>H<sub>14</sub>NO<sub>3</sub>F<sub>3</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 372.0818, Found: 372.0811. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at λ = 214 nm, t<sub>R</sub> = 7.7 min (minor), t<sub>R</sub> = 8.7 min (major).

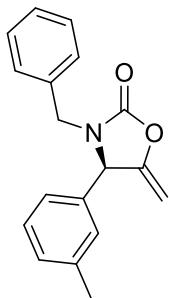
**(R)-3-benzyl-5-methylene-4-(4-(pyridin-2-yl)phenyl)oxazolidin-2-one (3ha)**



Yellow oil, 18.5 mg, 54% yield, 90% *ee*.  $[\alpha]_D^{20} = -88.50$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.72 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.07 – 7.98 (m, 2H), 7.83 – 7.72 (m, 2H), 7.36 – 7.23 (m, 6H), 7.18 – 7.12 (m, 2H), 5.06 (d, *J* = 2.4 Hz, 1H), 4.93 (d, *J* = 14.9 Hz, 1H), 4.78 (t, *J* = 2.9 Hz, 1H), 4.05 (dd, *J* = 3.3, 2.1 Hz, 1H), 3.67 (d, *J* = 15.0 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.58, 155.22, 154.59, 149.92, 140.59, 137.37, 137.06, 134.80, 128.99, 128.71, 128.38, 128.32, 127.92, 122.68, 120.77, 88.61, 61.63, 45.63 ppm. IR (neat) ν 3297, 3062, 3030, 3011, 2925, 2111, 1956, 1924 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>22</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 343.1441, Found: 343.1441. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane :

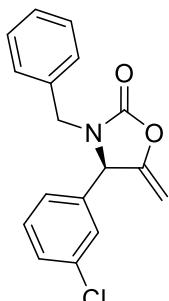
isopropanol = 90 : 10, flow rate = 1.0 mL/min, UV detection at  $\lambda$  = 254 nm,  $t_R$  = 18.1 min (minor),  $t_R$  = 20.7 min (major).

**(R)-3-benzyl-5-methylene-4-(m-tolyl)oxazolidin-2-one (3ia)**



White solid, 15.4 mg, 55% yield, 89% *ee*. M. P. 82-84 °C.  $[\alpha]_D^{20} = -16.10$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 – 7.30 (m, 3H), 7.30 – 7.27 (m, 1H), 7.20 (d,  $J$  = 7.6 Hz, 1H), 7.17 – 7.13 (m, 2H), 7.00 (d,  $J$  = 8.0 Hz, 2H), 4.98 (t,  $J$  = 2.3 Hz, 1H), 4.88 (d,  $J$  = 14.9 Hz, 1H), 4.75 (t,  $J$  = 2.9 Hz, 1H), 4.02 (dd,  $J$  = 3.2, 2.1 Hz, 1H), 3.65 (d,  $J$  = 15.0 Hz, 1H), 2.37 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  155.33, 154.90, 139.31, 136.83, 135.07, 130.18, 129.18, 128.97, 128.72, 128.34, 128.28, 125.11, 88.36, 62.01, 45.63, 21.53 ppm. IR (neat)  $\nu$  3024, 2923, 2854, 2738, 2632, 2459, 1957, 1902 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 302.1152, Found: 302.1154. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at  $\lambda$  = 214 nm,  $t_R$  = 8.0 min (minor),  $t_R$  = 9.0 min (major).

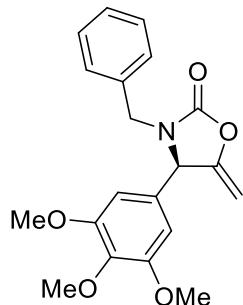
**(R)-3-benzyl-4-(3-chlorophenyl)-5-methyleneoxazolidin-2-one (3ja)**



Yellow solid, 12.1 mg, 40% yield, 91% *ee*. M. P. 77-79 °C.  $[\alpha]_D^{20} = -33.80$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 – 7.30 (m, 5H), 7.20 (t,  $J$  = 1.9 Hz, 1H),

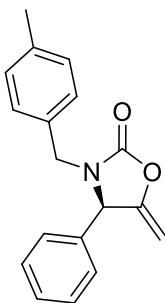
7.16 – 7.08 (m, 3H), 4.98 (t,  $J$  = 2.4 Hz, 1H), 4.90 (d,  $J$  = 15.0 Hz, 1H), 4.78 (dd,  $J$  = 3.4, 2.5 Hz, 1H), 4.03 (dd,  $J$  = 3.4, 2.1 Hz, 1H), 3.67 (d,  $J$  = 14.9 Hz, 1H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.12, 154.05, 138.95, 135.37, 134.65, 130.69, 129.68, 129.08, 128.68, 128.46, 128.01, 126.07, 88.99, 61.45, 45.85 ppm. IR (neat)  $\nu$  3542, 3186, 3030, 2959, 2923, 2853, 2636, 2457, 2328, 1956, 1891  $\text{cm}^{-1}$ ; HRMS (ESI) m/z: calcd. for  $\text{C}_{17}\text{H}_{14}\text{NO}_2\text{ClNa}^+$  [M+Na] $^+$ : 322.0605, Found: 322.0599. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 90 : 10, flow rate = 1.0 mL/min, UV detection at  $\lambda$  = 214 nm,  $t_R$  = 9.3 min (minor),  $t_R$  = 9.9 min (major).

**(R)-3-benzyl-5-methylene-4-(3,4,5-trimethoxyphenyl)oxazolidin-2-one (3ka)**



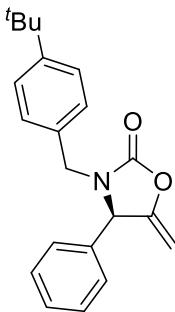
Red oil, 25.6 mg, 72% yield, 80% ee.  $[\alpha]_D^{20} = -4.70$  (c 0.2,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.30 (m, 3H), 7.19 – 7.14 (m, 2H), 6.37 (s, 2H), 4.95 (t,  $J$  = 2.4 Hz, 1H), 4.84 (d,  $J$  = 15.0 Hz, 1H), 4.80 – 4.76 (m, 1H), 4.09 (dd,  $J$  = 3.2, 2.1 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 6H), 3.77 (d,  $J$  = 14.9 Hz, 1H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.19, 154.47, 153.85, 138.60, 135.02, 132.11, 128.86, 128.67, 128.26, 104.78, 88.50, 62.45, 60.94, 56.31, 45.81 ppm. IR (neat)  $\nu$  3508, 3290, 3065, 3011, 2937, 2837, 2329, 2116, 1959  $\text{cm}^{-1}$ ; HRMS (ESI) m/z: calcd. for  $\text{C}_{20}\text{H}_{21}\text{NO}_5\text{Na}^+$  [M+Na] $^+$ : 378.1312, Found: 378.1311. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 90 : 10, flow rate = 1.0 mL/min, UV detection at  $\lambda$  = 254 nm,  $t_R$  = 16.0 min (minor),  $t_R$  = 13.3 min (major).

**(R)-3-(4-methylbenzyl)-5-methylene-4-phenyloxazolidin-2-one (3ab)**



Yellow oil, 14.1 mg, 50% yield, 92% *ee*.  $[\alpha]_D^{20} = -49.50$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.24 – 7.20 (m, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 4.99 (t, *J* = 2.4 Hz, 1H), 4.87 (d, *J* = 14.9 Hz, 1H), 4.74 (t, *J* = 2.9 Hz, 1H), 4.00 (dd, *J* = 3.2, 2.1 Hz, 1H), 3.58 (d, *J* = 14.8 Hz, 1H), 2.35 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.27, 154.90, 138.12, 136.95, 131.87, 129.66, 129.38, 128.73, 127.97, 88.39, 61.87, 45.33, 21.29 ppm. IR (neat) ν 3028, 2922, 2859, 2332, 2118, 1911, 1778 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 302.1152, Found: 302.1148. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 99 : 1, flow rate = 1.0 mL/min, UV detection at λ = 214 nm, t<sub>R</sub> = 21.0 min (minor), t<sub>R</sub> = 22.5 min (major).

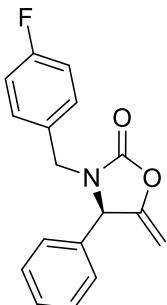
### (*R*)-3-(4-(tert-butyl)benzyl)-5-methylene-4-phenyloxazolidin-2-one (3ac)



Yellow oil, 15.1 mg, 47% yield, 87% *ee*.  $[\alpha]_D^{20} = -58.80$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.39 (m, 3H), 7.36 – 7.31 (m, 2H), 7.25 – 7.22 (m, 2H), 7.10 – 7.05 (m, 2H), 5.04 (t, *J* = 2.4 Hz, 1H), 4.85 (d, *J* = 14.9 Hz, 1H), 4.75 (t, *J* = 2.9 Hz, 1H), 4.01 (dd, *J* = 3.2, 2.1 Hz, 1H), 3.61 (d, *J* = 14.9 Hz, 1H), 1.32 (s, 9H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.28, 154.93, 151.34, 137.02, 131.90, 129.36, 128.51, 127.98, 125.89, 88.38, 61.97, 45.24, 34.72, 31.44 ppm. IR (neat) ν 3061, 3030, 2960, 2867, 2332, 2118, 1916, 1781 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>21</sub>H<sub>23</sub>NO<sub>2</sub>Na<sup>+</sup>

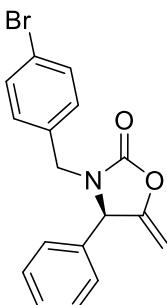
$[M+Na]^+$ : 344.1621, Found: 344.1616. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at  $\lambda$  = 214 nm,  $t_R$  = 8.8 min (minor),  $t_R$  = 7.7 min (major).

**(R)-3-(4-fluorobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3ad)**



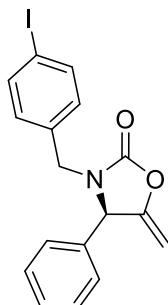
White solid, 18.9 mg, 67% yield, 91% *ee*. M. P. 99–101 °C.  $[\alpha]_D^{20} = -19.50$  (c 0.2,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.38 (m, 3H), 7.25 – 7.16 (m, 2H), 7.16 – 7.07 (m, 2H), 7.04 – 6.96 (m, 2H), 5.00 (t,  $J$  = 2.4 Hz, 1H), 4.82 (d,  $J$  = 15.0 Hz, 1H), 4.77 (t,  $J$  = 2.9 Hz, 1H), 4.03 (dd,  $J$  = 3.3, 2.2 Hz, 1H), 3.66 (d,  $J$  = 15.0 Hz, 1H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7 (d,  $J$  = 247.0 Hz), 155.23, 154.70, 136.72, 130.83 (d,  $J$  = 3.3 Hz), 130.5 (d,  $J$  = 8.2 Hz), 129.51, 129.44, 127.95, 115.92 (d,  $J$  = 21.6 Hz), 88.69, 62.10, 44.99 ppm.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.72 ppm. IR (neat)  $\nu$  3189, 3067, 3031, 2961, 2926, 2852, 2667, 1953 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for  $\text{C}_{17}\text{H}_{14}\text{NO}_2\text{NaF}^+$   $[M+\text{Na}]^+$ : 306.0901, Found: 306.0902. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at  $\lambda$  = 214 nm,  $t_R$  = 9.7 min (minor),  $t_R$  = 10.4 min (major).

**(R)-3-(4-bromobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3ae)**



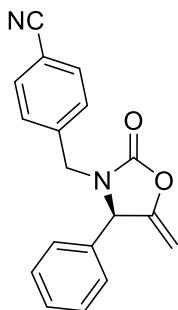
Yellow oil, 21.0 mg, 61% yield, 96% *ee*.  $[\alpha]_D^{20} = -76.30$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 – 7.38 (m, 5H), 7.23 – 7.17 (m, 2H), 7.01 (d, J = 8.3 Hz, 2H), 4.99 (t, J = 2.4 Hz, 1H), 4.83 – 4.75 (m, 2H), 4.03 (dd, J = 3.3, 2.2 Hz, 1H), 3.63 (d, J = 15.1 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.24, 154.61, 136.62, 134.02, 132.16, 130.41, 129.56, 129.47, 127.96, 122.41, 88.80, 62.12, 45.09 ppm. IR (neat) ν 3063, 3031, 2924, 2855, 2120, 1905 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub>NaBr<sup>+</sup> [M+Na]<sup>+</sup>: 366.0100, Found: 366.0099. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at λ = 214 nm, t<sub>R</sub> = 12.8 min (minor), t<sub>R</sub> = 13.8 min (major).

**(R)-3-(4-iodobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3af)**



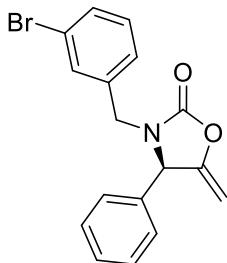
Colorless oil, 19.1 mg, 48% yield, 96% *ee*.  $[\alpha]_D^{20} = -66.50$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68 – 7.62 (m, 2H), 7.44 – 7.37 (m, 3H), 7.20 (dd, J = 6.5, 2.9 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 4.99 (t, J = 2.4 Hz, 1H), 4.84 – 4.74 (m, 2H), 4.03 (dd, J = 3.3, 2.1 Hz, 1H), 3.61 (d, J = 15.1 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.24, 154.60, 138.13, 136.61, 134.66, 130.61, 129.55, 129.46, 127.95, 94.00, 88.81, 62.11, 45.19 ppm. IR (neat) ν 3031, 2922, 2853, 2333, 2118, 1908, 1777 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub>NaI<sup>+</sup> [M+Na]<sup>+</sup>: 413.9961, Found: 413.9966. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 99 : 1, flow rate = 1.0 mL/min, UV detection at λ = 214 nm, t<sub>R</sub> = 29.4 min (minor), t<sub>R</sub> = 31.2 min (major).

**(R)-4-((5-methylene-2-oxo-4-phenyloxazolidin-3-yl)methyl)benzonitrile (3ag)**



White solid, 12.7 mg, 44% yield, 90% *ee*. M. P. 94–96 °C.  $[\alpha]_D^{20} = -68.40$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.51 (m, 2H), 7.36 – 7.31 (m, 3H), 7.21 – 7.15 (m, 2H), 7.15 – 7.10 (m, 2H), 4.96 (t, *J* = 2.4 Hz, 1H), 4.78 – 4.69 (m, 2H), 4.01 (dd, *J* = 3.4, 2.1 Hz, 1H), 3.76 (d, *J* = 15.4 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.26, 154.33, 140.52, 136.32, 132.76, 129.74, 129.52, 129.20, 127.96, 118.49, 112.29, 89.21, 62.60, 45.44 ppm. IR (neat) ν 3065, 3030, 2861, 2923, 2853, 2351, 2229, 2089, 1923 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 313.0948, Found: 313.0942. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at λ = 214 nm, t<sub>R</sub> = 27.9 min (minor), t<sub>R</sub> = 32.0 min (major).

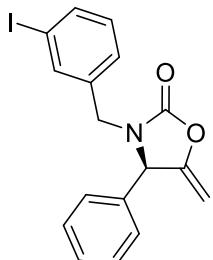
#### (*R*)-3-(3-bromobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3ah)



White solid, 20.0 mg, 58% yield, 92% *ee*. M. P. 72–74 °C.  $[\alpha]_D^{20} = -30.50$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.35 (m, 4H), 7.29 – 7.15 (m, 4H), 7.08 (d, *J* = 7.6 Hz, 1H), 5.03 (s, 1H), 4.86 – 4.72 (m, 2H), 4.06 (t, *J* = 2.8 Hz, 1H), 3.66 (d, *J* = 15.1 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.21, 154.58, 137.30, 136.57, 131.64, 131.49, 130.58, 129.61, 129.48, 127.98, 127.27, 123.01, 88.88, 62.25, 45.14 ppm. IR (neat) ν 3061, 3028, 2960, 2924, 2852, 2132, 1944, 1877 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub>NaBr<sup>+</sup> [M+Na]<sup>+</sup>: 366.0100, Found: 366.0099. The

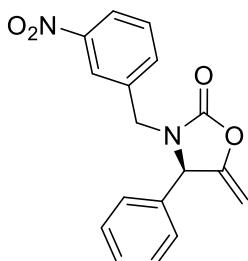
enantiomeric excess was determined by HPLC on Chiralcel IC column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at  $\lambda$  = 214 nm,  $t_R$  = 22.6 min (minor),  $t_R$  = 20.1 min (major).

**(R)-3-(3-iodobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3ai)**



Yellow solid, 20.8 mg, 53% yield, 92% *ee*. M. P. 94-96 °C.  $[\alpha]_D^{20} = -33.30$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.43 (dd, *J* = 7.8, 3.7 Hz, 4H), 7.21 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.7 Hz, 1H), 5.02 (s, 1H), 4.77 (d, *J* = 15.1 Hz, 2H), 4.05 (t, *J* = 2.8 Hz, 1H), 3.63 (d, *J* = 15.0 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.14, 154.57, 137.53, 137.39, 137.29, 136.54, 130.65, 129.58, 129.43, 127.94, 127.89, 94.73, 88.80, 62.24, 45.02 ppm. IR (neat) ν 3131, 3057, 3026, 2961, 2924, 2853, 2086, 1946, 1877 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub>NaI<sup>+</sup> [M+Na]<sup>+</sup>: 413.9961, Found: 413.9964. The enantiomeric excess was determined by HPLC on Chiralcel IC column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at  $\lambda$  = 214 nm,  $t_R$  = 23.7 min (minor),  $t_R$  = 21.1 min (major).

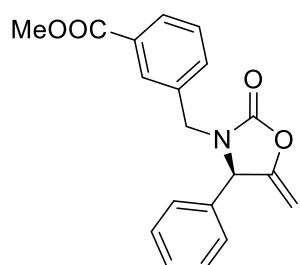
**(R)-5-methylene-3-(3-nitrobenzyl)-4-phenyloxazolidin-2-one (3aj)**



Brown solid, 14.2 mg, 45% yield, 86% *ee*. M. P. 97-99 °C.  $[\alpha]_D^{20} = -18.30$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 – 8.12 (m, 1H), 7.88 (t, *J* = 2.0 Hz, 1H),

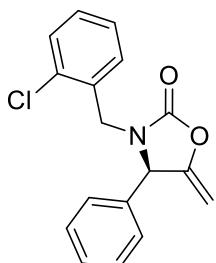
7.59 – 7.46 (m, 2H), 7.41 – 7.38 (m, 3H), 7.25 – 7.16 (m, 2H), 5.07 (t,  $J$  = 2.3 Hz, 1H), 4.85 – 4.75 (m, 2H), 4.08 (dd,  $J$  = 3.4, 2.1 Hz, 1H), 3.96 (d,  $J$  = 15.3 Hz, 1H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.22, 154.34, 148.48, 137.36, 136.34, 134.70, 130.12, 129.79, 129.58, 128.01, 123.41, 123.31, 89.26, 62.82, 45.29 ppm. IR (neat)  $\nu$  3084, 3029, 2959, 2922, 2853, 2333, 2118, 1970, 1921, 1765  $\text{cm}^{-1}$ ; HRMS (ESI) m/z: calcd. for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_4\text{Na}^+$  [M+Na] $^+$ : 333.0846, Found: 333.0843. The enantiomeric excess was determined by HPLC on Chiralcel IB column, n-hexane : isopropanol = 90 : 10, flow rate = 1.0 mL/min, UV detection at  $\lambda$  = 214 nm,  $t_R$  = 14.5 min (minor),  $t_R$  = 16.2 min (major).

**(R)-methyl 3-((5-methylene-2-oxo-4-phenyloxazolidin-3-yl)methyl)benzoate (3ak)**



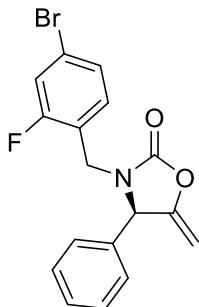
White solid, 18.6 mg, 57% yield, 91% ee. M. P. 99–101 °C.  $[\alpha]_D^{20} = -18.00$  (c 0.2,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 – 7.96 (m, 1H), 7.77 (d,  $J$  = 1.8 Hz, 1H), 7.44 – 7.34 (m, 5H), 7.23 – 7.17 (m, 2H), 5.02 (t,  $J$  = 2.3 Hz, 1H), 4.87 (d,  $J$  = 15.1 Hz, 1H), 4.78 (t,  $J$  = 2.9 Hz, 1H), 4.04 (dd,  $J$  = 3.3, 2.2 Hz, 1H), 3.92 (s, 3H), 3.76 (d,  $J$  = 15.1 Hz, 1H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.73, 155.24, 154.64, 136.62, 135.46, 133.14, 130.90, 129.65, 129.55, 129.54, 129.46, 129.19, 127.97, 88.79, 62.26, 52.39, 45.40 ppm. IR (neat)  $\nu$  3410, 3081, 3007, 2957, 2851, 2082, 1911  $\text{cm}^{-1}$ ; HRMS (ESI) m/z: calcd. for  $\text{C}_{19}\text{H}_{17}\text{NO}_4\text{Na}^+$  [M+Na] $^+$ : 346.1050, Found: 346.1049. The enantiomeric excess was determined by HPLC on Chiralcel IB-3 column, n-hexane : isopropanol = 90 : 10, flow rate = 1.0 mL/min, UV detection at  $\lambda$  = 214 nm,  $t_R$  = 9.1 min (minor),  $t_R$  = 9.5 min (major).

**(R)-3-(2-chlorobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3al)**



White solid, 20.7 mg, 69% yield, 91% *ee*. M. P. 91-93 °C.  $[\alpha]_D^{20} = 15.10$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.23 (m, 4H), 7.21 – 7.08 (m, 5H), 5.01 (t, *J* = 2.3 Hz, 1H), 4.77 (d, *J* = 15.4 Hz, 1H), 4.70 (dd, *J* = 3.3, 2.5 Hz, 1H), 4.01 – 3.93 (m, 2H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.27, 154.71, 137.05, 133.96, 132.63, 130.84, 129.95, 129.67, 129.37, 129.31, 127.68, 127.25, 88.55, 62.61, 43.39 ppm. IR (neat) ν 3189, 3069, 3012, 2959, 2924, 2853, 2640, 2328 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub>NaCl<sup>+</sup> [M+Na]<sup>+</sup>: 322.0605, Found: 322.0603. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at λ = 214 nm, t<sub>R</sub> = 10.0 min (minor), t<sub>R</sub> = 11.0 min (major).

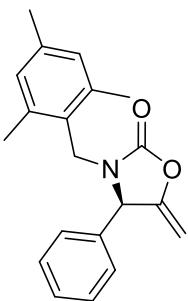
**(R)-3-(4-bromo-2-fluorobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3am)**



White solid, 16.0 mg, 44% yield, 92% *ee*. M. P. 89-91 °C.  $[\alpha]_D^{20} = -85.0$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.38 (m, 3H), 7.26 – 7.21 (m, 3H), 7.20 – 7.13 (m, 2H), 5.08 (t, *J* = 2.3 Hz, 1H), 4.78 (dd, *J* = 3.3, 2.5 Hz, 1H), 4.65 (d, *J* = 15.2 Hz, 1H), 4.06 (dd, *J* = 3.3, 2.1 Hz, 1H), 3.92 (d, *J* = 15.3 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.72 (d, J = 253.1 Hz), 155.17, 154.59, 136.77, 132.37 (d, J = 4.5 Hz), 129.53, 129.38, 128.07 (d, J = 3.7 Hz), 127.86, 122.72 (d, J = 9.4 Hz), 121.50 (d, J = 15.4 Hz), 119.42 (d, J = 24.9 Hz), 88.86, 62.74, 39.05 (d, J = 3.0 Hz) ppm. <sup>19</sup>F NMR

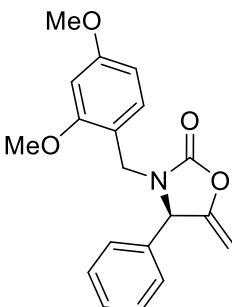
(376 MHz, CDCl<sub>3</sub>) δ -114.85 (t, *J* = 8.6 Hz) ppm. IR (neat) ν 3190, 3116, 3074, 3011, 2959, 2923, 2853, 2117, 1948 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>17</sub>H<sub>13</sub>NO<sub>2</sub>NaFBr<sup>+</sup> [M+Na]<sup>+</sup>: 384.0006, Found: 384.0009. The enantiomeric excess was determined by HPLC on Chiralcel IB column, n-hexane : isopropanol = 99 : 1, flow rate = 1.0 mL/min, UV detection at λ = 214 nm, t<sub>R</sub> = 15.0 min (minor), t<sub>R</sub> = 16.2 min (major).

**(R)-5-methylene-4-phenyl-3-(2,4,6-trimethylbenzyl)oxazolidin-2-one (3an)**



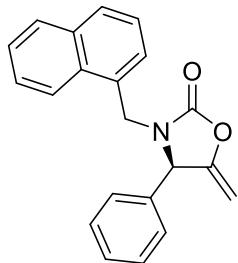
White solid, 17.0 mg, 55% yield, 80% *ee*. M. P. 77-79 °C. [α]<sub>D</sub><sup>20</sup> = 3.50 (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.33 (m, 3H), 7.07 – 7.00 (m, 2H), 6.76 (s, 2H), 4.82 (d, *J* = 14.6 Hz, 1H), 4.71 – 4.66 (m, 2H), 4.11 (d, *J* = 14.6 Hz, 1H), 3.95 (dd, *J* = 3.1, 2.1 Hz, 1H), 2.25 (s, 3H), 1.86 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.00, 138.09, 137.91, 137.85, 129.51, 129.32, 129.13, 127.27, 127.04, 88.06, 61.54, 40.36, 21.02, 19.52 ppm. IR (neat) ν 3064, 2959, 2921, 2853, 2097, 1950, 1771 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>20</sub>H<sub>21</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 330.1465, Found: 330.1470. The enantiomeric excess was determined by HPLC on Chiralcel IB column, n-hexane : isopropanol = 99 : 1, flow rate = 1.0 mL/min, UV detection at λ = 214 nm, t<sub>R</sub> = 12.3 min (minor), t<sub>R</sub> = 10.9 min (major).

**(R)-3-(2,4-dimethoxybenzyl)-5-methylene-4-phenyloxazolidin-2-one (3ao)**



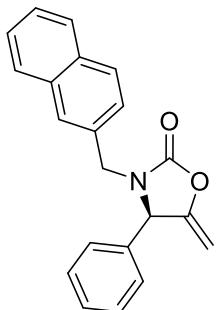
Yellow oil, 14.9 mg, 44% yield, 95% ee.  $[\alpha]_D^{20} = -49.00$  (c 0.2,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.35 (m, 3H), 7.23 – 7.19 (m, 2H), 7.05 – 7.01 (m, 1H), 6.43 – 6.39 (m, 2H), 5.03 (t,  $J = 2.3$  Hz, 1H), 4.71 (d,  $J = 10.0$  Hz, 1H), 4.69 – 4.68 (m, 1H). 3.97 (dd,  $J = 3.1, 2.1$  Hz, 1H), 3.82 (d,  $J = 13.5$  Hz, 1H), 3.82(s, 3H), 3.71 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.18, 158.85, 155.27, 155.23, 137.83, 131.88, 129.09, 129.01, 127.65, 115.59, 104.23, 98.51, 87.79, 62.42, 55.54, 55.32, 40.68 ppm. IR (neat)  $\nu$  3062, 3004, 2933, 2838, 2331, 1776  $\text{cm}^{-1}$ ; HRMS (ESI) m/z: calcd. for  $\text{C}_{19}\text{H}_{19}\text{NO}_4\text{Na}^+$   $[\text{M}+\text{Na}]^+$ : 348.1206, Found: 348.12053. The enantiomeric excess was determined by HPLC on Chiralcel IC column, n-hexane : isopropanol = 85 : 15, flow rate = 1.0 mL/min, UV detection at  $\lambda = 214$  nm,  $t_R = 25.0$  min (minor),  $t_R = 20.6$  min (major).

**(R)-5-methylene-3-(naphthalen-1-ylmethyl)-4-phenyloxazolidin-2-one (3ap)**



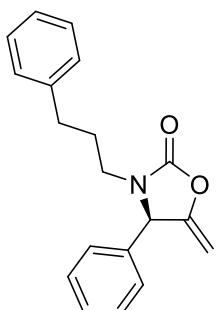
Colorless oil, 27.4 mg, 88% yield, 96% ee.  $[\alpha]_D^{20} = 9.40$  (c 0.2,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 – 8.06 (m, 1H), 7.92 – 7.80 (m, 2H), 7.60 – 7.50 (m, 2H), 7.43 – 7.40 (m, 3H), 7.34 (dd,  $J = 8.3, 7.0$  Hz, 1H), 7.17 (dd,  $J = 6.5, 2.9$  Hz, 2H), 7.00 (d,  $J = 6.9$  Hz, 1H), 5.44 (d,  $J = 14.8$  Hz, 1H), 4.81 (t,  $J = 2.3$  Hz, 1H), 4.69 (t,  $J = 2.8$  Hz, 1H), 4.11 (d,  $J = 14.8$  Hz, 1H), 3.94 (dd,  $J = 3.3, 2.1$  Hz, 1H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.95, 154.76, 137.13, 134.01, 131.70, 130.14, 129.49, 129.35, 129.32, 128.88, 128.41, 127.66, 127.20, 126.35, 125.01, 123.73, 88.37, 62.06, 43.86 ppm. IR (neat)  $\nu$  3058, 3028, 2929, 2925, 2855, 2634, 2332, 2122  $\text{cm}^{-1}$ ; HRMS (ESI) m/z: calcd. for  $\text{C}_{21}\text{H}_{17}\text{NO}_2\text{Na}^+$   $[\text{M}+\text{Na}]^+$ : 338.1152, Found: 338.1154. The enantiomeric excess was determined by HPLC on Chiralcel IC column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at  $\lambda = 214$  nm,  $t_R = 26.2$  min (minor),  $t_R = 23.4$  min (major).

**(R)-5-methylene-3-(naphthalen-2-ylmethyl)-4-phenyloxazolidin-2-one (3aq)**



Yellow oil, 26.6 mg, 83% yield, 93% *ee*.  $[\alpha]_D^{20} = -76.60$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87 – 7.81 (m, 2H), 7.80 – 7.76 (m, 1H), 7.54 – 7.47 (m, 3H), 7.44 – 7.39 (m, 3H), 7.32 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.25 – 7.19 (m, 2H), 5.07 (d, *J* = 14.9 Hz, 1H), 5.02 (t, *J* = 2.4 Hz, 1H), 4.77 (t, *J* = 3.0 Hz, 1H), 4.01 (dd, *J* = 3.3, 2.1 Hz, 1H), 3.80 (d, *J* = 14.9 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.35, 154.78, 136.85, 133.32, 133.15, 132.32, 129.44, 129.39, 129.02, 127.96, 127.92, 127.86, 127.78, 126.59, 126.47, 126.22, 88.56, 62.02, 45.81 ppm. IR (neat) ν 3055, 3022, 2929, 2925, 2855, 2651, 2331, 2120, 1954 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>21</sub>H<sub>17</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 338.1152, Found: 338.1154. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at λ = 214 nm, t<sub>R</sub> = 15.2 min (minor), t<sub>R</sub> = 13.0 min (major).

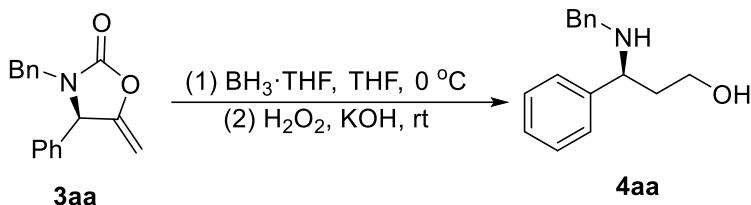
**(R)-5-methylene-4-phenyl-3-(3-phenylpropyl)oxazolidin-2-one (3ar)**



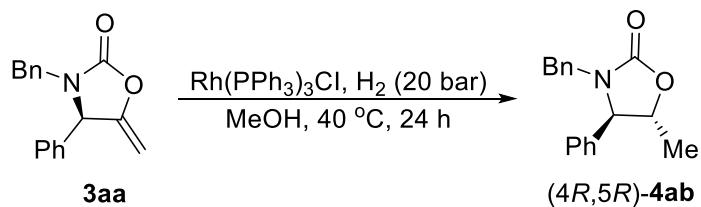
Yellow oil, 11.8 mg, 40% yield, 80% *ee*.  $[\alpha]_D^{20} = -10.00$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 (dd, *J* = 4.9, 1.9 Hz, 3H), 7.21 – 7.14 (m, 4H), 7.12 – 7.06 (m, 1H), 7.03 – 6.99 (m, 2H), 5.11 (t, *J* = 2.3 Hz, 1H), 4.67 (dd, *J* = 3.2, 2.5 Hz, 1H), 3.97 (dd, *J* = 3.2, 2.1 Hz, 1H), 3.46 – 3.33 (m, 1H), 2.83 – 2.73 (m, 1H), 2.56 – 2.41 (m, 2H),

1.78 – 1.61 (m, 2H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.17, 154.82, 140.97, 137.29, 129.39, 129.35, 128.55, 128.29, 127.73, 126.17, 88.22, 63.11, 41.76, 32.91, 28.52 ppm. IR (neat)  $\nu$  3297, 3062, 3028, 2926, 2857, 2120  $\text{cm}^{-1}$ ; HRMS (ESI) m/z: calcd. for  $\text{C}_{19}\text{H}_{19}\text{NO}_2\text{Na}^+$  [M+Na] $^+$ : 316.1308, Found: 316.1303. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at  $\lambda$  = 214 nm,  $t_R$  = 18.2 min (minor),  $t_R$  = 12.8 min (major).

## 2.4 The transformations of products<sup>2-4</sup>



(*R*)-**3aa** (26.5 mg, 0.1 mmol),  $\text{BH}_3\cdot\text{THF}$  (2.0 mL, 2 mmol), and anhydrous THF (2.0 mL) were added to a 10 mL Schlenk tube under a nitrogen atmosphere and reacted for 3 hours at 0°C until the reaction was complete, as confirmed by TLC. After cooling to room temperature, 1.0 mL of potassium hydroxide aqueous solution (2.0 M) and 1.0 mL of hydrogen peroxide were added. After stirring at room temperature for 30 minutes, the reaction was quenched by saturated  $\text{NH}_4\text{Cl}$  solution (10 mL), and organic materials were extracted with EA (15 mL×3). The combined extracts were washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was concentrated under reduced pressure and the residue was purified by column chromatography ( $\text{SiO}_2$ ) with n-hexane and ethyl acetate (5/1 - 1/1) as eluent to the compound **4aa** as a yellow oil (10.8mg, 45% yield, 90% ee).  $[\alpha]_D^{20} = -47.10$  (c 0.2,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 – 7.35 (m, 2H), 7.33 – 7.28 (m, 5H), 7.27 – 7.22 (m, 3H), 3.89 (dd,  $J = 9.4, 3.6$  Hz, 1H), 3.80 – 3.75 (m, 2H), 3.71 (d,  $J = 12.9$  Hz, 1H), 3.56 (d,  $J = 12.9$  Hz, 1H), 3.36 (brs, 2H), 2.08 – 1.97 (m, 1H), 1.87 – 1.78 (m, 1H) ppm. HRMS (ESI) m/z: calcd. for  $\text{C}_{16}\text{H}_{20}\text{NO}^+$  [ $\text{M}+\text{H}]^+$ : 242.1539, Found: 242.1539. The enantiomeric excess was determined by HPLC on Chiralcel AD-3 column, n-hexane : isopropanol = 70 : 30, flow rate = 0.5 mL/min, UV detection at  $\lambda = 214$  nm,  $t_R = 5.9$  min (minor),  $t_R = 6.3$  min (major).

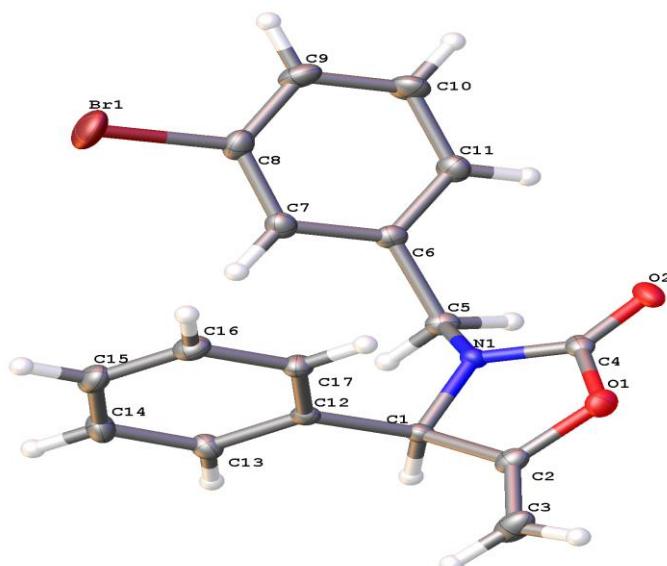


$\text{Rh}(\text{PPh}_3)_3\text{Cl}$  (4.6 mg, 0.005 mmol) and (*R*)-**3aa** (26.5 mg, 0.1 mmol) in 2 mL of anhydrous methanol was placed in an autoclave. The hydrogenation was performed at

room temperature under 20 bar of H<sub>2</sub> pressure for 3h. After concentration of the reaction mixture under reduced pressure, the residue was purified by silica gel chromatography (hexanes/AcOEt, 5/1) to afford (*4R, 5R*)-**4ab** (20.9 mg, 78% yield, 90% ee, >95:5 dr) as a yellow oil.  $[\alpha]_D^{20} = -72.00$  (c 0.2, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41 (d, *J* = 6.3 Hz, 3H), 7.32 – 7.28 (m, 3H), 7.17 – 7.07 (m, 4H), 4.96 (d, *J* = 14.8 Hz, 1H), 4.86 – 4.77 (m, 1H), 4.50 (d, *J* = 8.2 Hz, 1H), 3.66 (d, *J* = 14.7 Hz, 1H), 0.94 (d, *J* = 6.5 Hz, 3H). ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.48, 135.97, 134.30, 129.11, 129.02, 128.86, 128.59, 128.03, 74.56, 62.52, 46.35, 16.66 ppm. IR (neat) ν 3654, 3474, 3313, 3062, 3029, 2960, 2926, 2872, 2855, 2253, 1957, 1887 cm<sup>-1</sup>; HRMS (ESI) m/z: calcd. for C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub>Na<sup>+</sup>[M+Na]<sup>+</sup>: 290.1152, Found: 290.1158. The enantiomeric excess was determined by HPLC on Chiralcel IA column, n-hexane : isopropanol = 95 : 5, flow rate = 1.0 mL/min, UV detection at λ = 214 nm, t<sub>R</sub> = 19.8 min (minor), t<sub>R</sub> = 16.6 min (major).

### 3. X-ray Crystallographic Data for the **3ah**

Crystals suitable for X-ray single-crystal diffraction analysis was obtained through slowly evaporating the mixture solution of DCM and n-hexane at room temperature. CIF file for the product **3ah** has been deposited at the Cambridge Crystallographic Data Centre with deposition number 2356244. Copies of these data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].



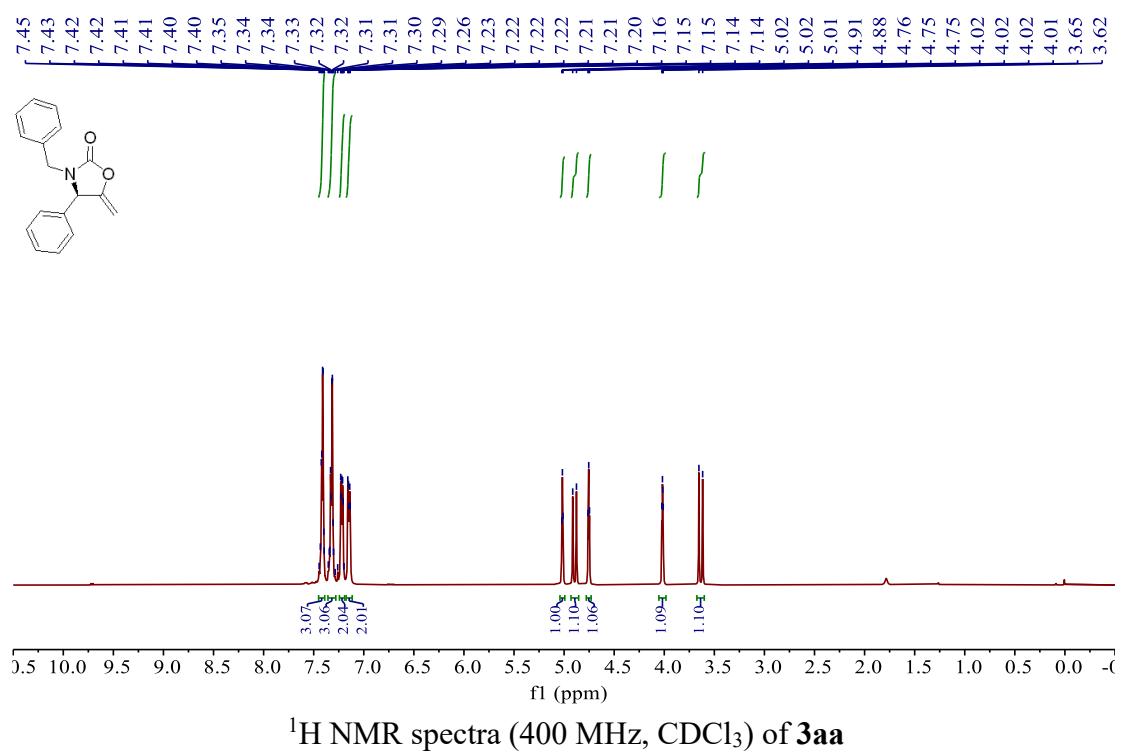
**Table 4.** Crystal data and structure refinement

Identification code	<b>3ah</b>
Empirical formula	C17 H14 Br N O2
Formula weight	344.20
Temperature	170.00 K
Wavelength	1.34139 Å
Crystal system	Monoclinic
Space group	C 1 2 1
Unit cell dimensions	a = 33.0990(7) Å $\alpha$ = 90°. b = 5.83420(10) Å $\beta$ = 91.5400(10)°.
	c = 7.8722(2) Å $\gamma$ = 90°.
Volume	1519.62(6) Å <sup>3</sup>
Z	4
Density (calculated)	1.504 Mg/m <sup>3</sup>
Absorption coefficient	2.452 mm <sup>-1</sup>
F(000)	696
Crystal size	0.17 x 0.17 x 0.05 mm <sup>3</sup>
Theta range for data collection	4.651 to 54.900°.
Index ranges	-40≤h≤40, -6≤k≤7, -9≤l≤9
Reflections collected	8082
Independent reflections	2603 [R(int) = 0.0423]
Completeness to theta = 53.594°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.5475
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2603 / 1 / 190
Goodness-of-fit on F <sup>2</sup>	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0278, wR2 = 0.0770
R indices (all data)	R1 = 0.0299, wR2 = 0.0804
Absolute structure parameter	-0.016(15)
Extinction coefficient	n/a
Largest diff. peak and hole	0.243 and -0.397 e.Å <sup>-3</sup>

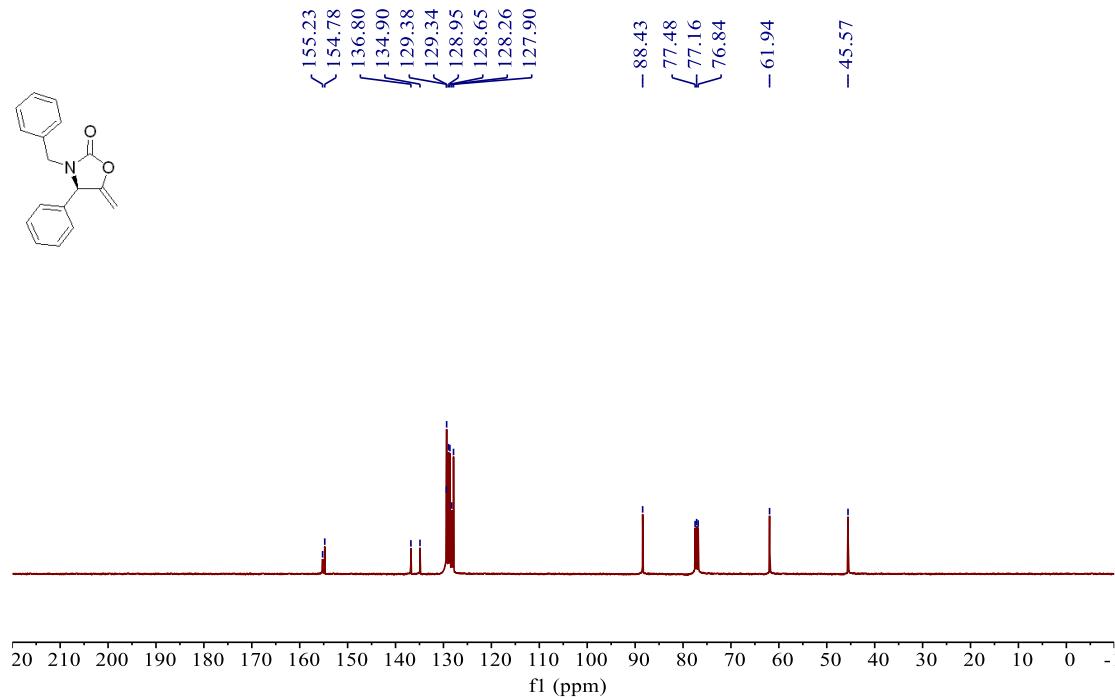
#### 4. References

- [1] Q. L. Cai, H. Q. Rao, S. J. Li, Y. Lan, K. L. Ding and X. M. Wang, Well-defined chiral dinuclear copper complexes in enantioselective propargylic substitution: For a long-standing supposition on binuclear mechanism, *Chem.*, 2024, **10**, 265 – 282.
- [2] M. P. Sibi, Mei Liu, Enantioselective Conjugate Addition of Hydroxylamines to Pyrazolidinone Acrylamides, *Org. Lett.*, 2001, **3**, 4181 – 4184.
- [3] L. Shao, Y. H. Wang, D. Y. Zhang, J. Xu, and X. P. Hu, Desilylation-Activated Propargylic Transformation: Enantioselective Copper-Catalyzed [3+2] Cycloaddition of Propargylic Esters with  $\beta$ -Naphthol or Phenol Derivatives, *Angew. Chem. Int. Ed.*, 2016, **55**, 5014 – 5018.
- [4] C. Miniejew, F. Outurquin and X. Pannecoucke, New phenylselanyl group activation: synthesis of aziridines and oxazolidin-2-ones, *Org. Biomol. Chem.* 2004, **2**, 1575 – 1576.

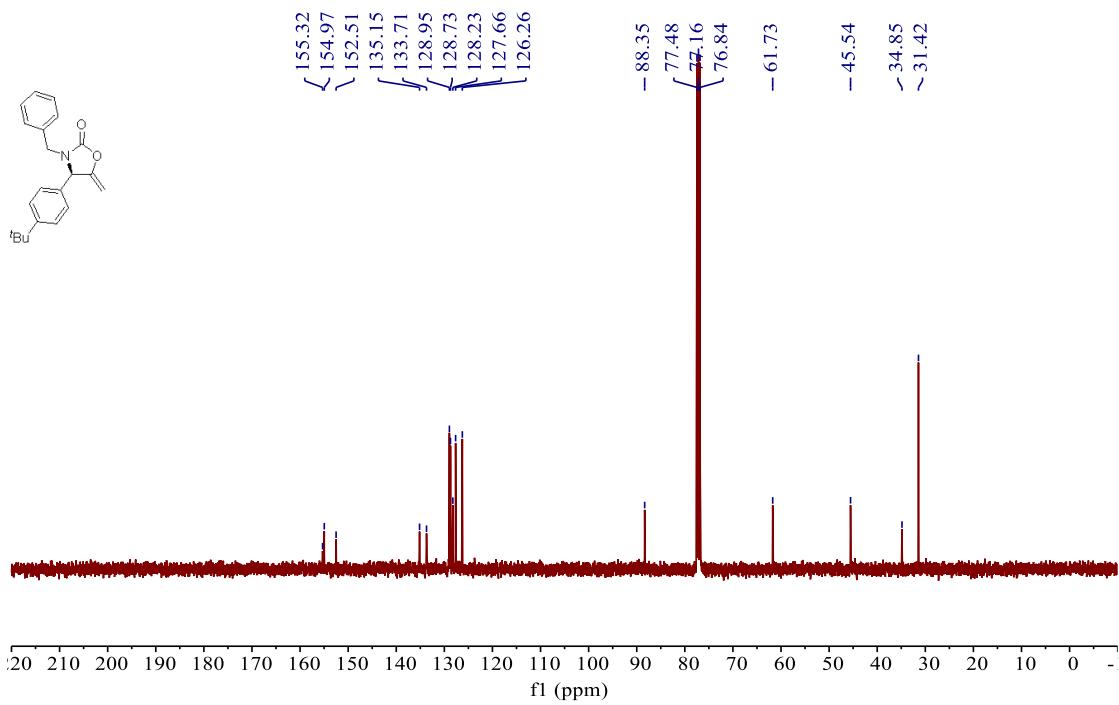
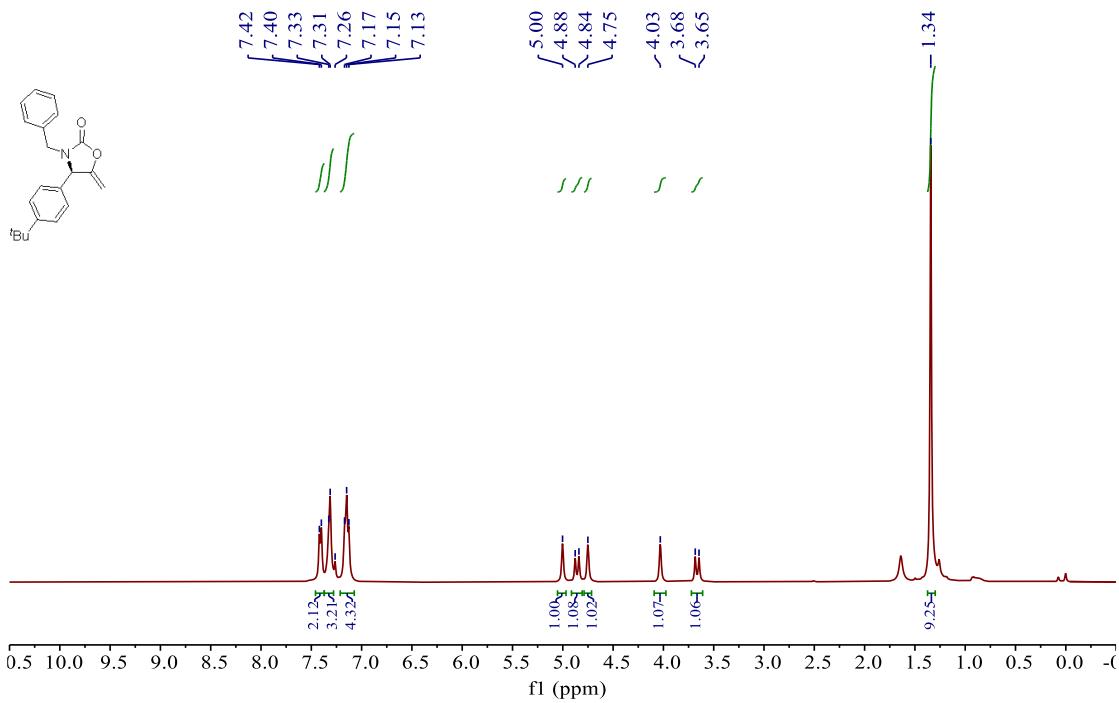
## 5. Copies of NMR Spectra

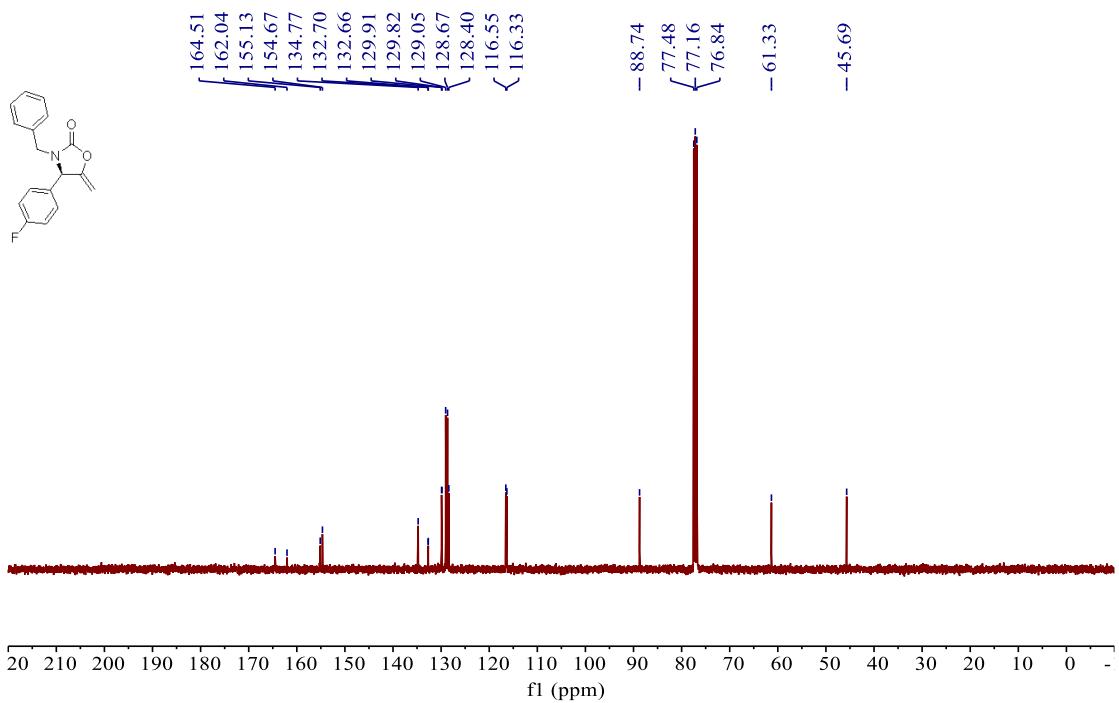
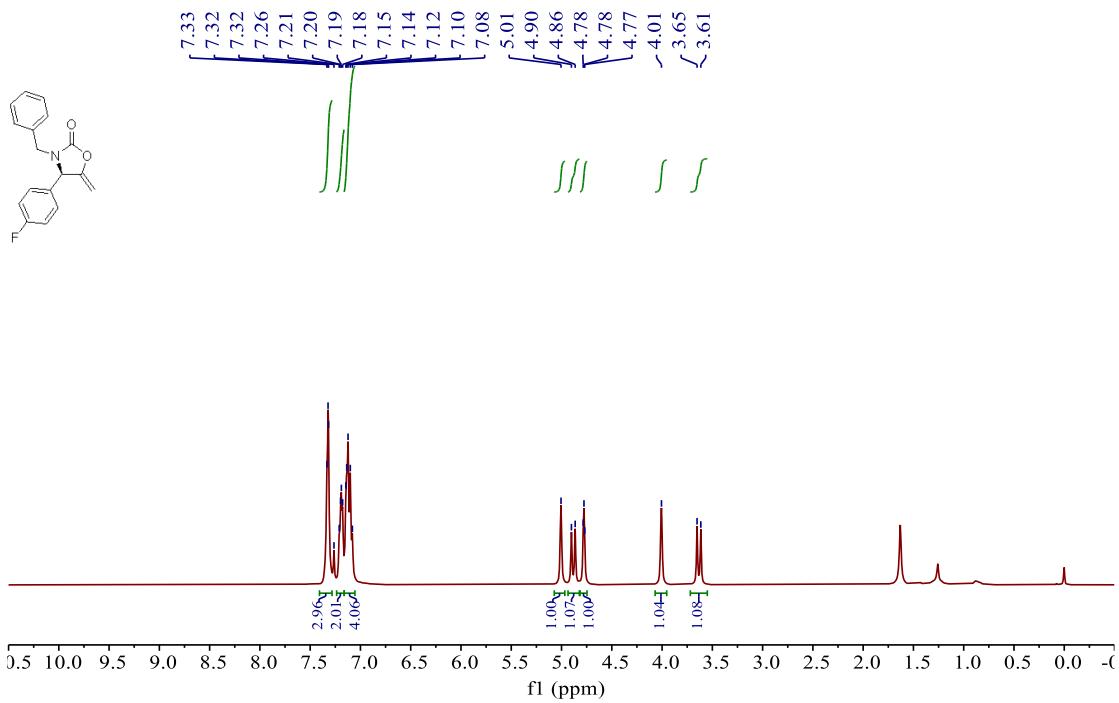


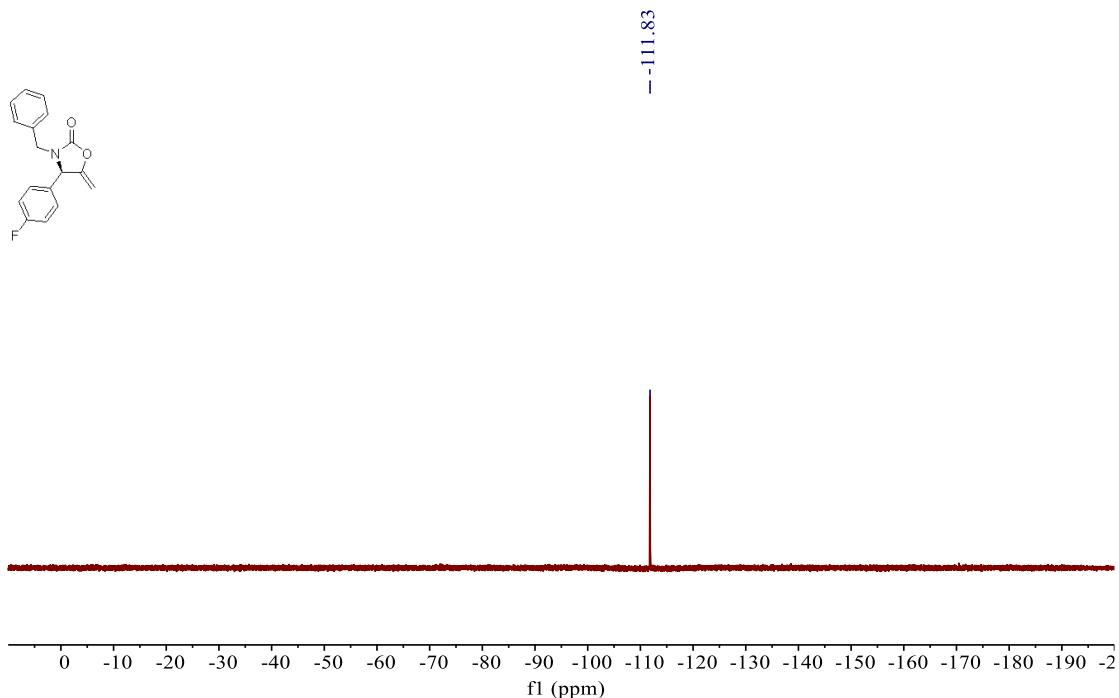
<sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of 3aa



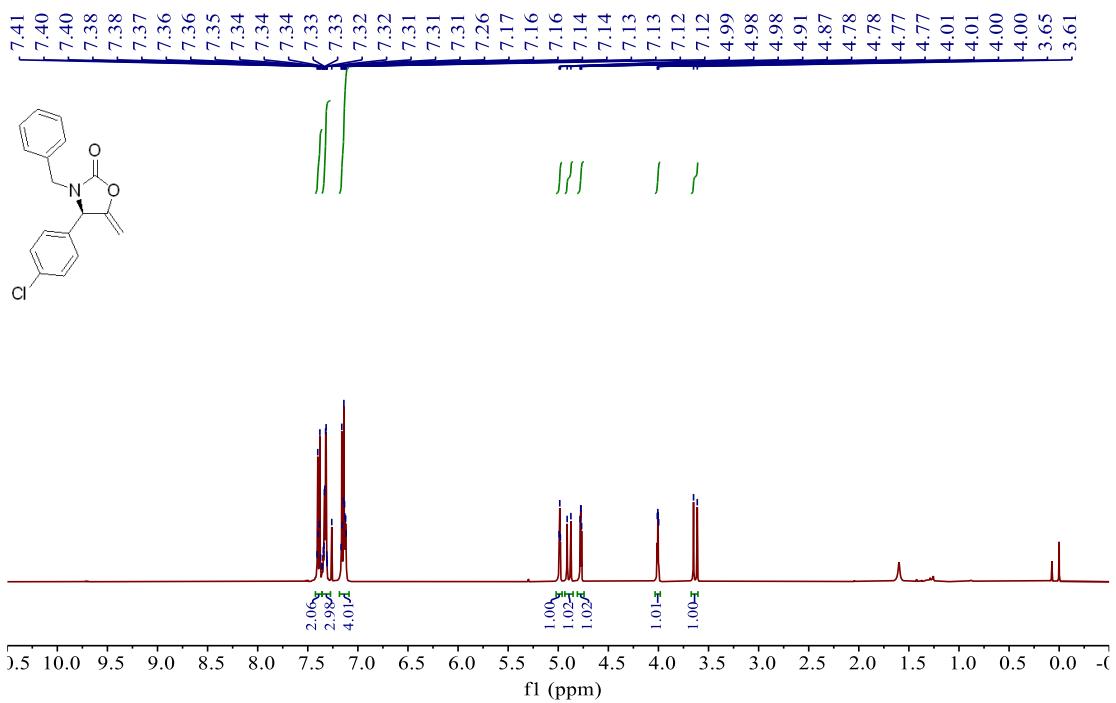
<sup>13</sup>C NMR spectra (101 MHz, CDCl<sub>3</sub>) of 3aa



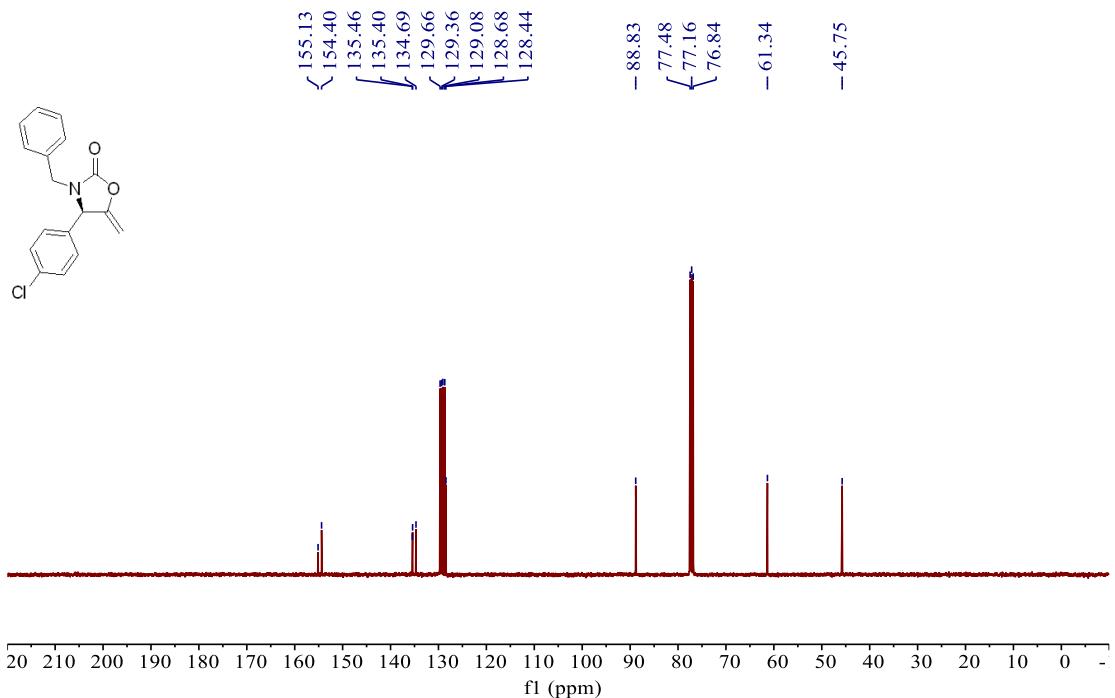




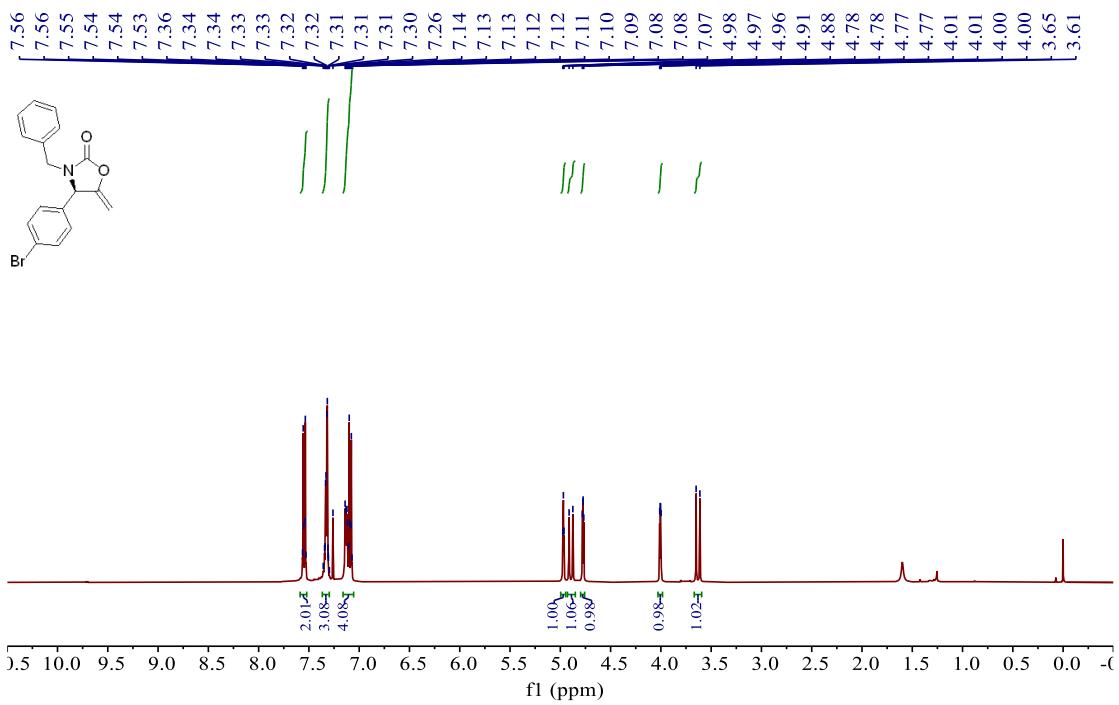
$^{19}\text{F}$  NMR spectra (376 MHz,  $\text{CDCl}_3$ ) of **3ca**



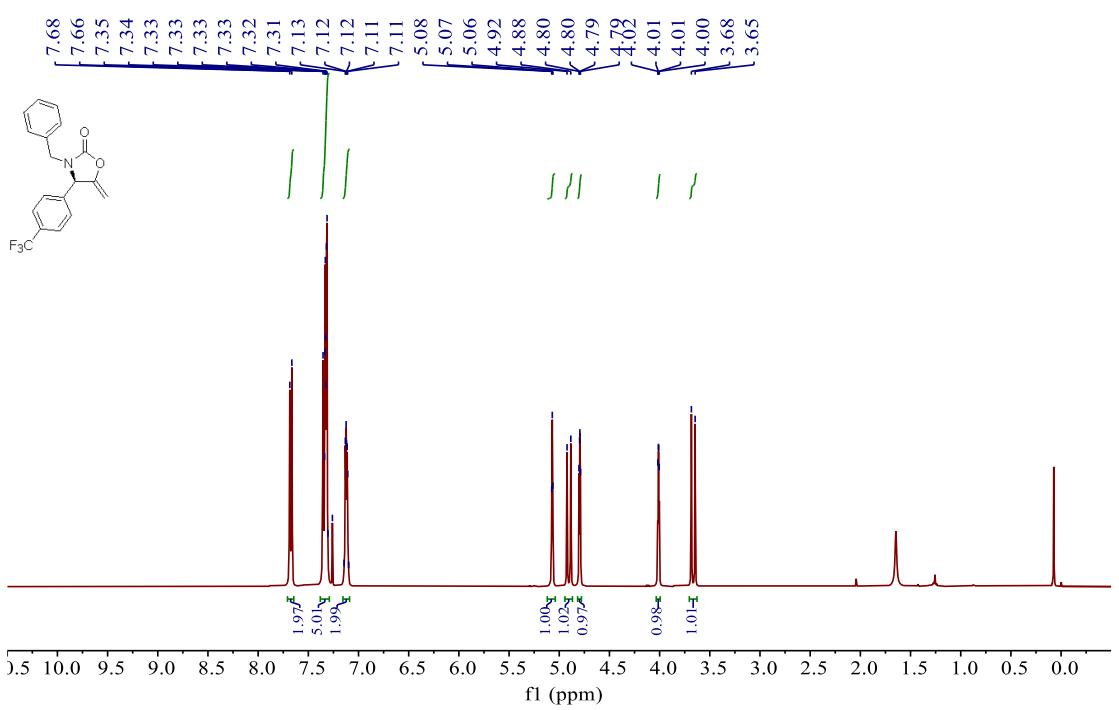
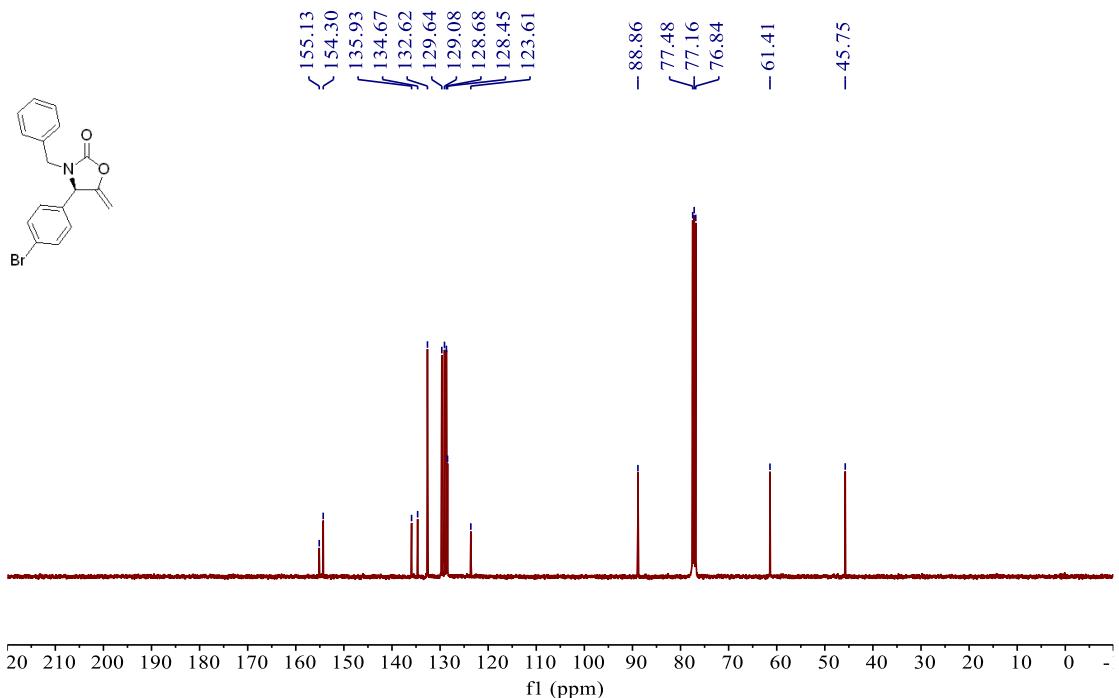
$^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of **3da**

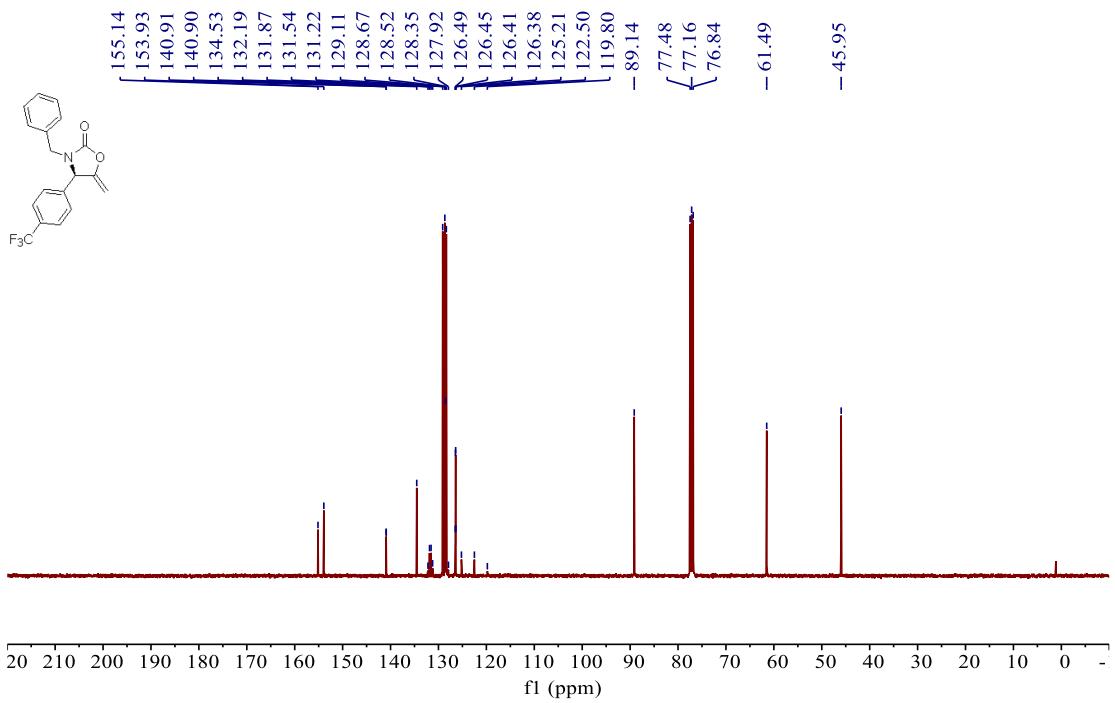


$^{13}\text{C}$  NMR spectra (101 MHz,  $\text{CDCl}_3$ ) of **3da**

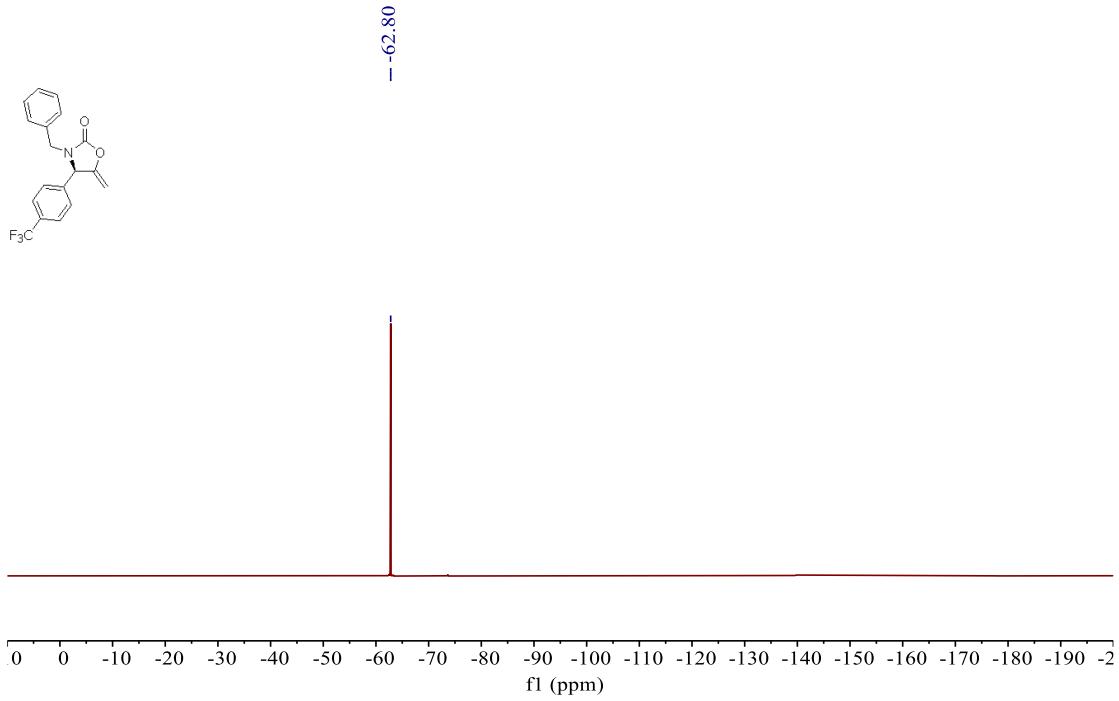


$^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of **3ea**

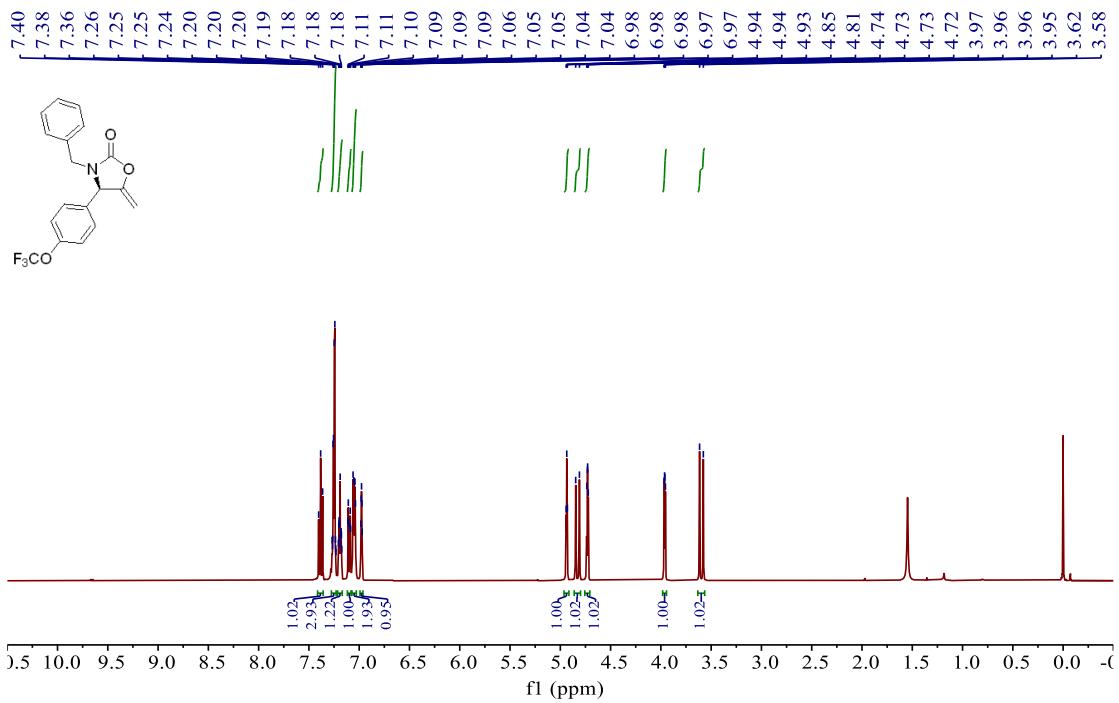




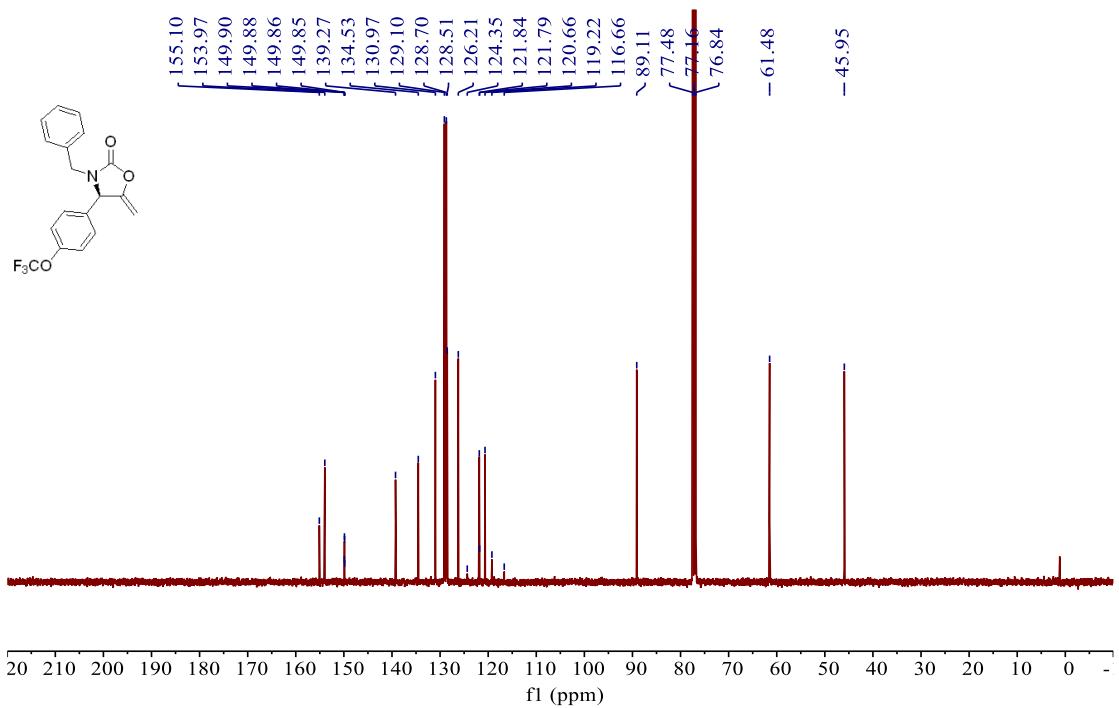
<sup>13</sup>C NMR spectra (101 MHz, CDCl<sub>3</sub>) of **3fa**



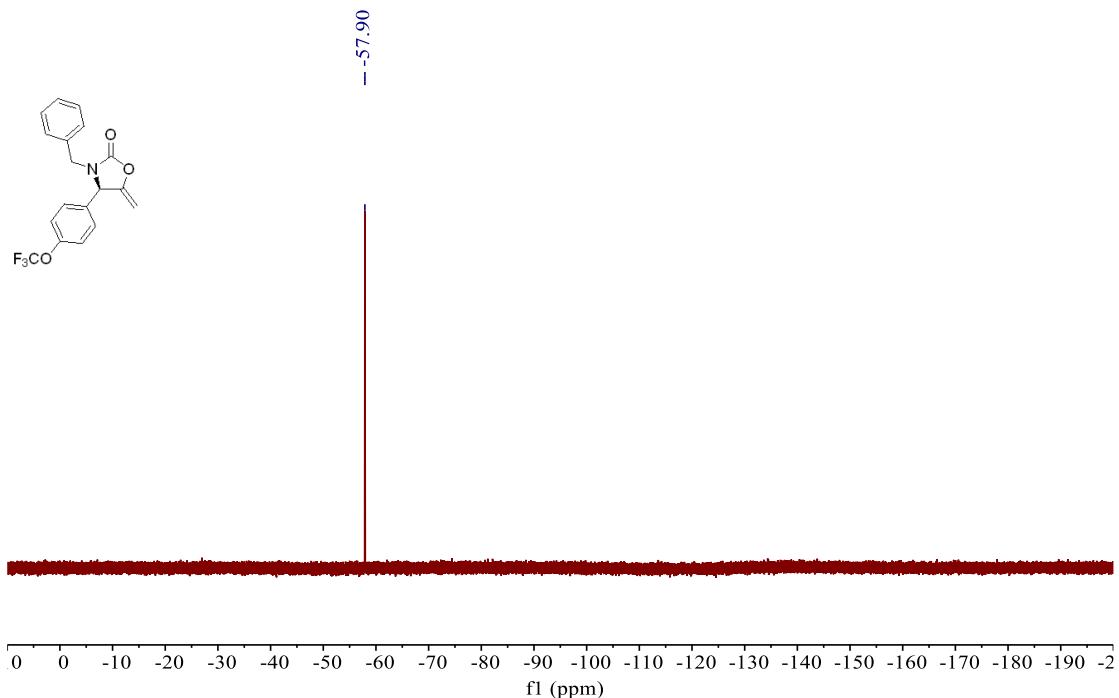
<sup>19</sup>F NMR spectra (376 MHz, CDCl<sub>3</sub>) of **3fa**



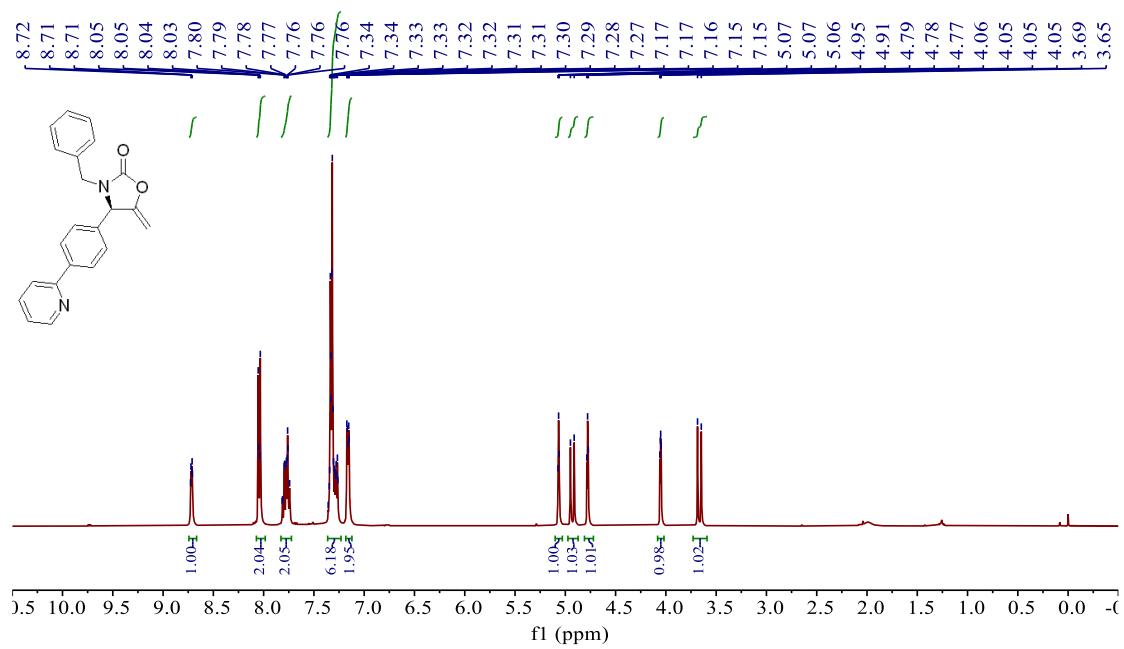
<sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of **3ga**



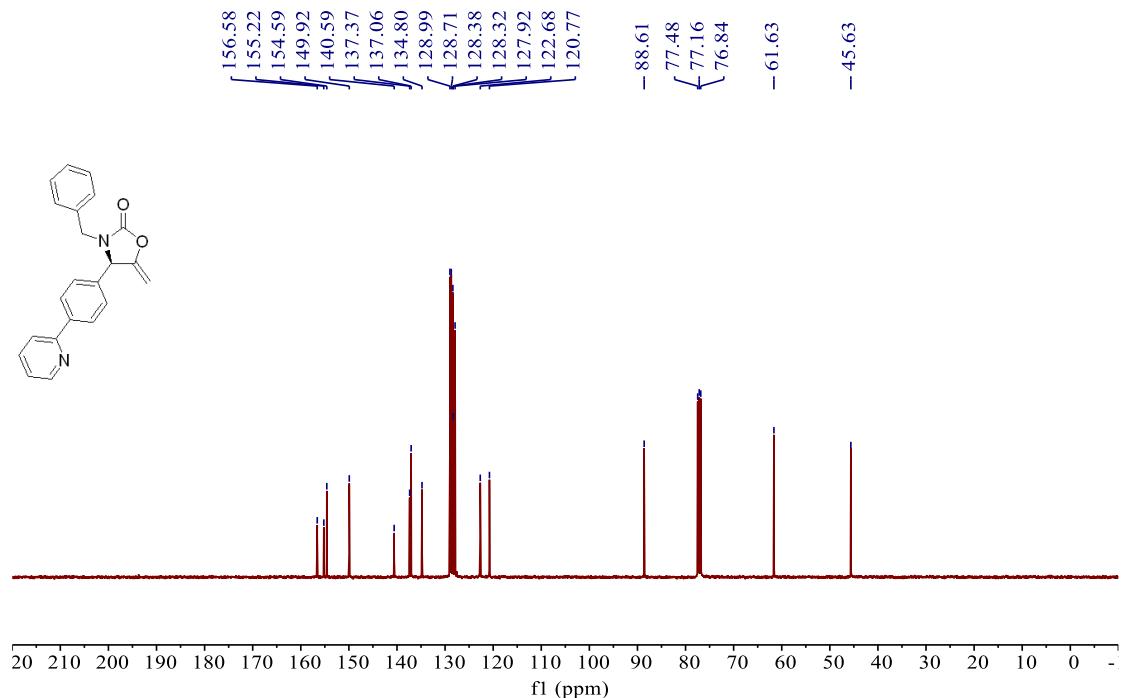
<sup>13</sup>C NMR spectra (101 MHz, CDCl<sub>3</sub>) of **3ga**



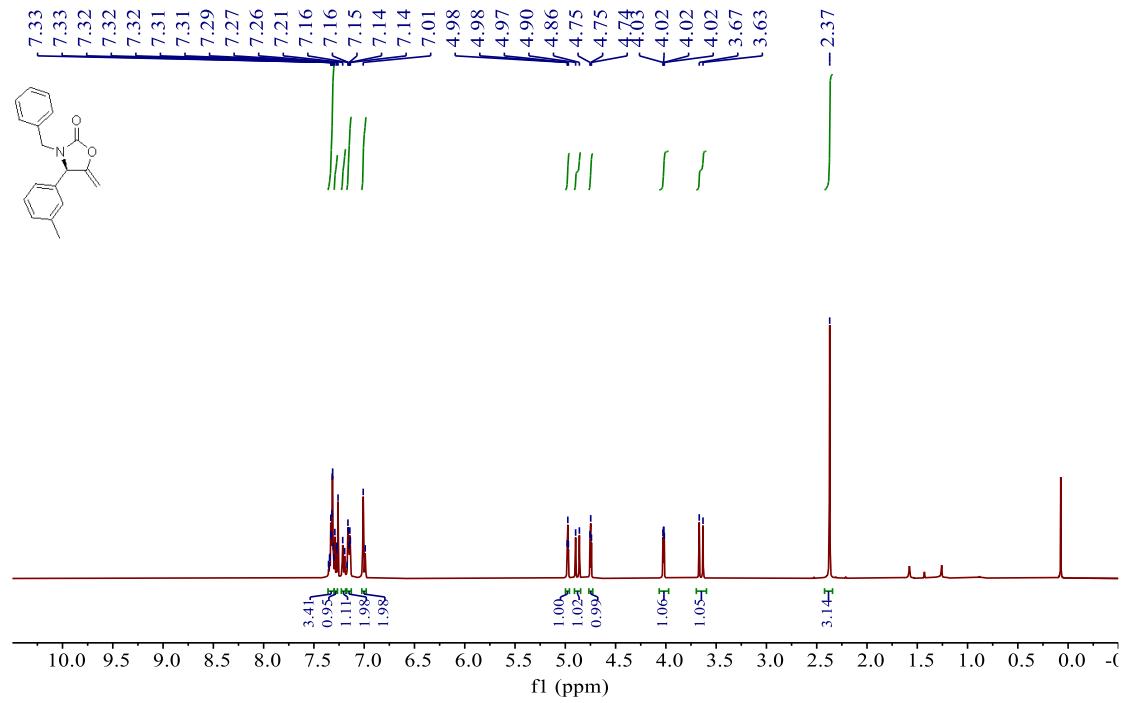
$^{19}\text{F}$  NMR spectra (376 MHz,  $\text{CDCl}_3$ ) of **3ga**



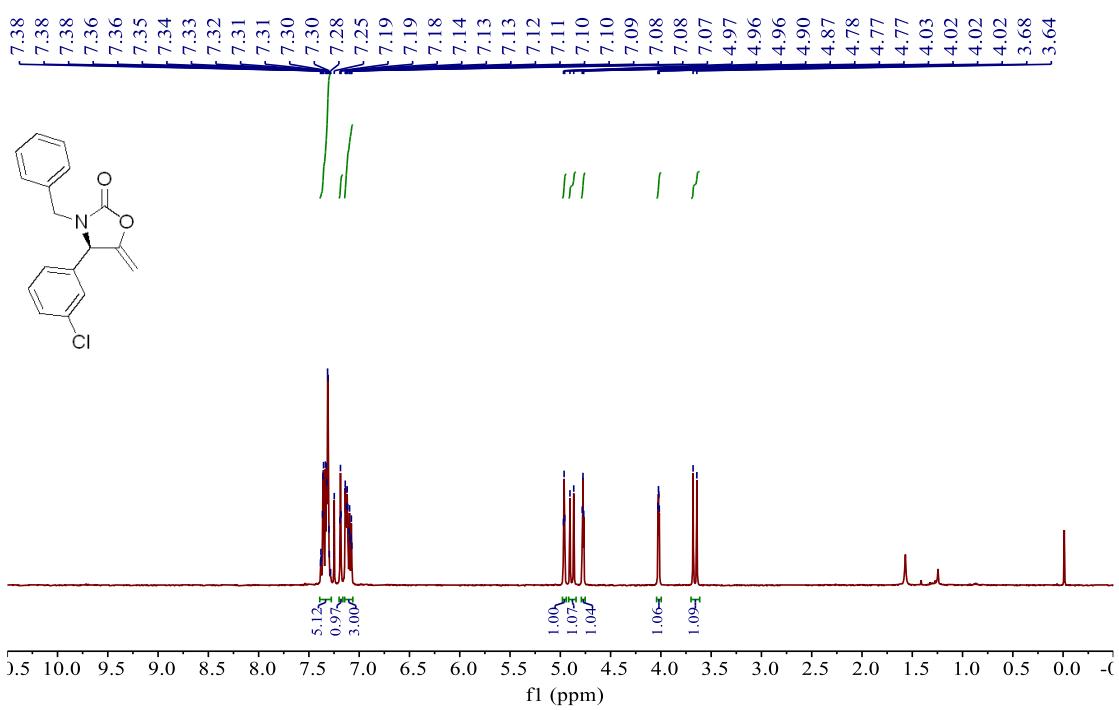
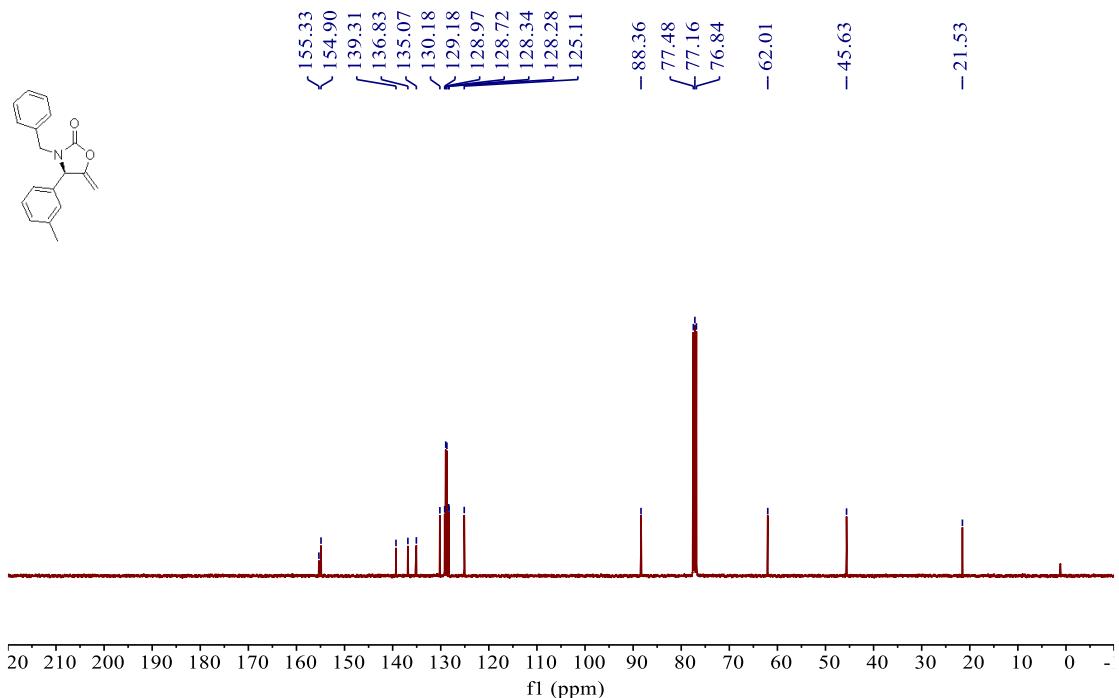
$^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of **3ha**

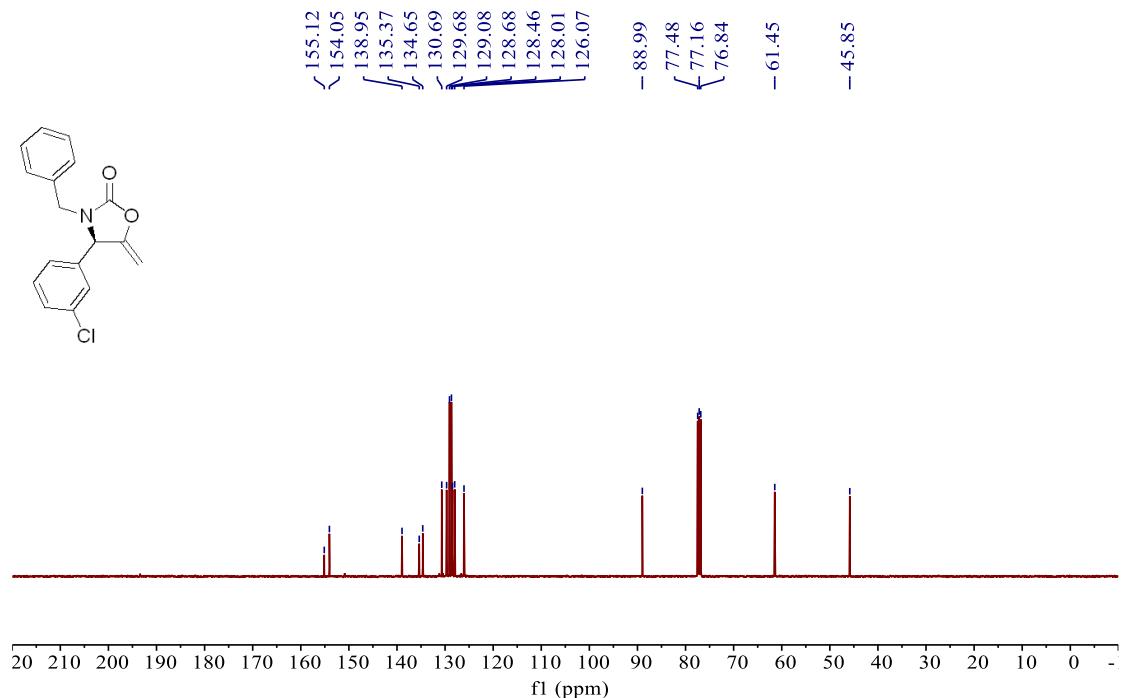


$^{13}\text{C}$  NMR spectra (101 MHz,  $\text{CDCl}_3$ ) of **3ha**

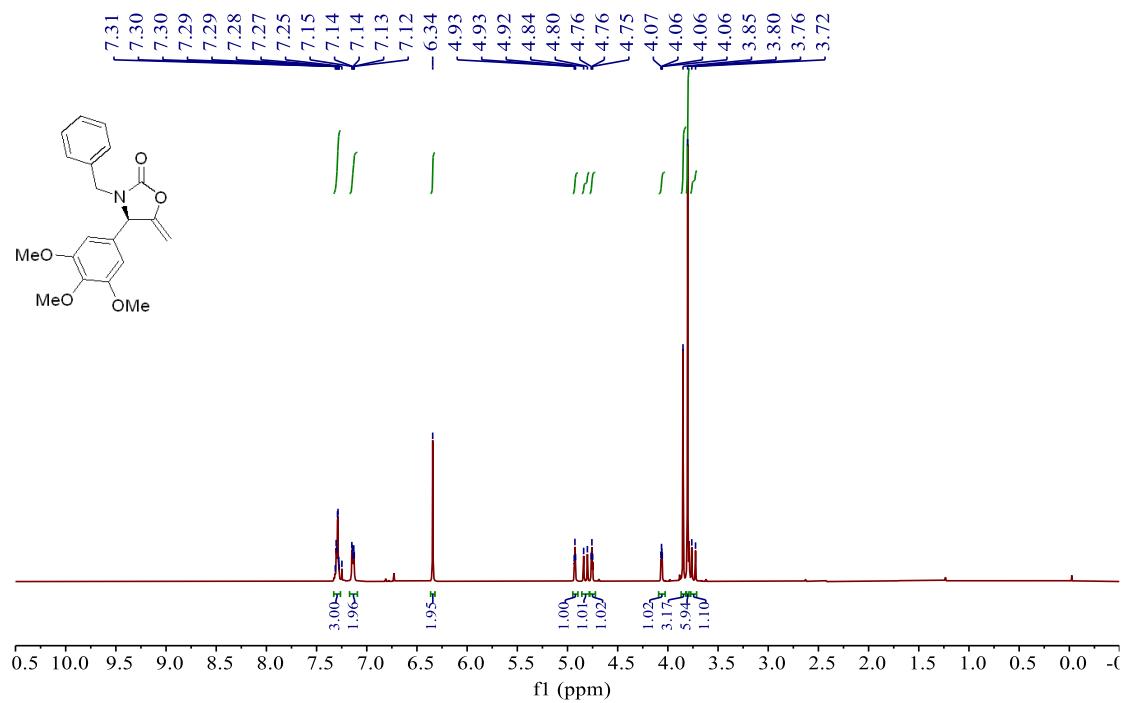


$^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of **3ia**

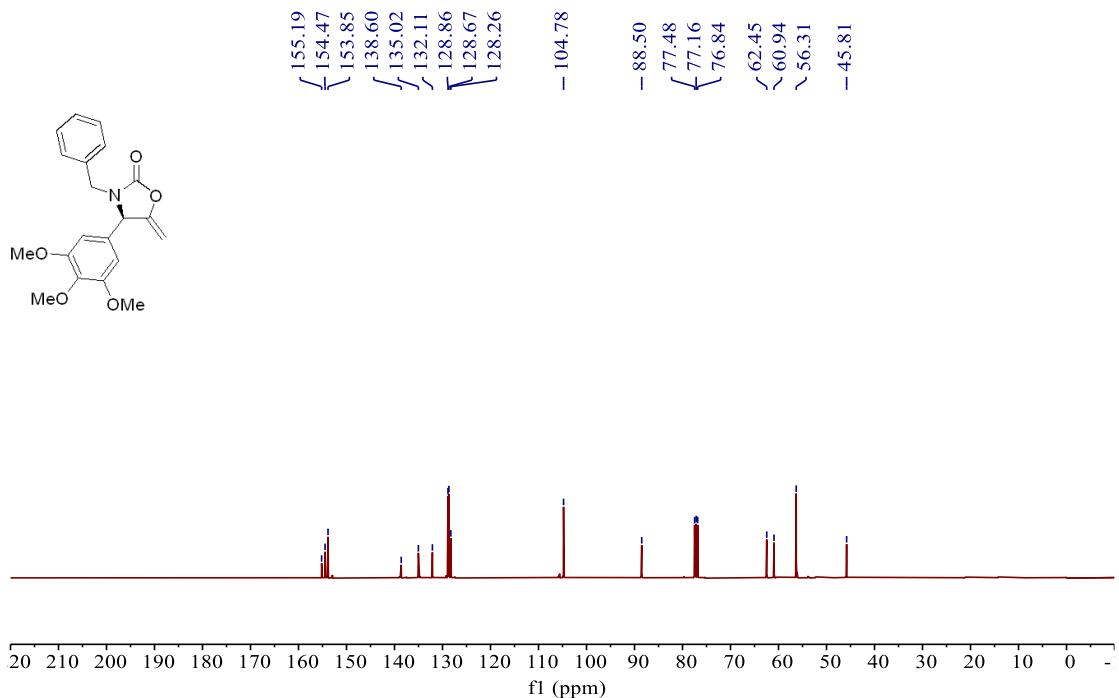




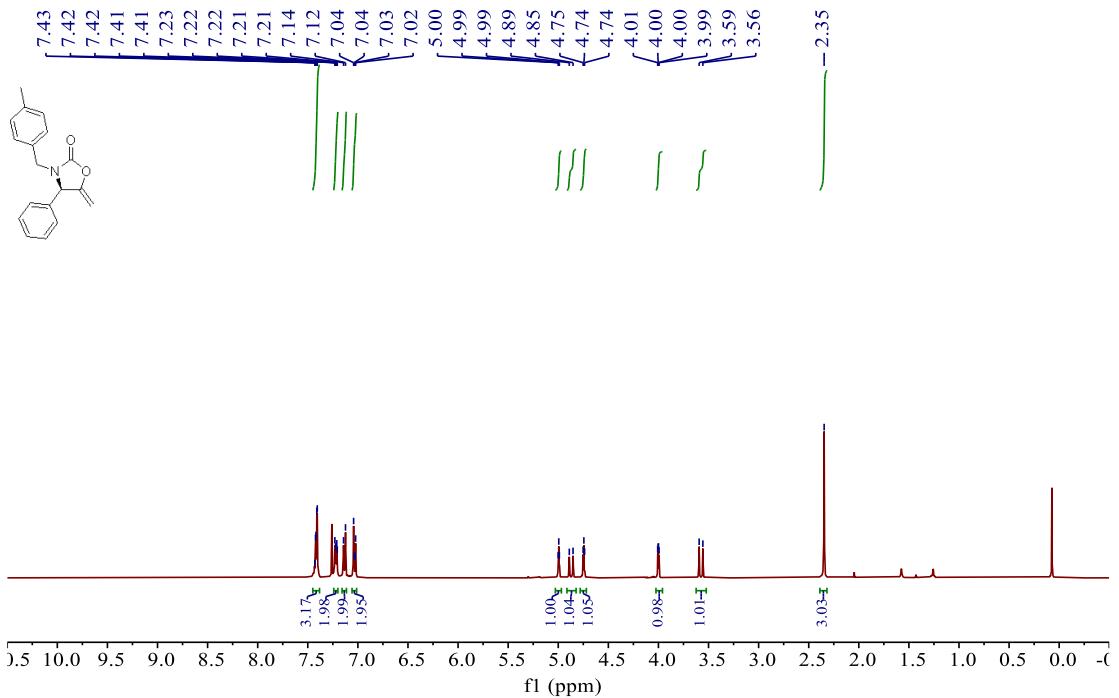
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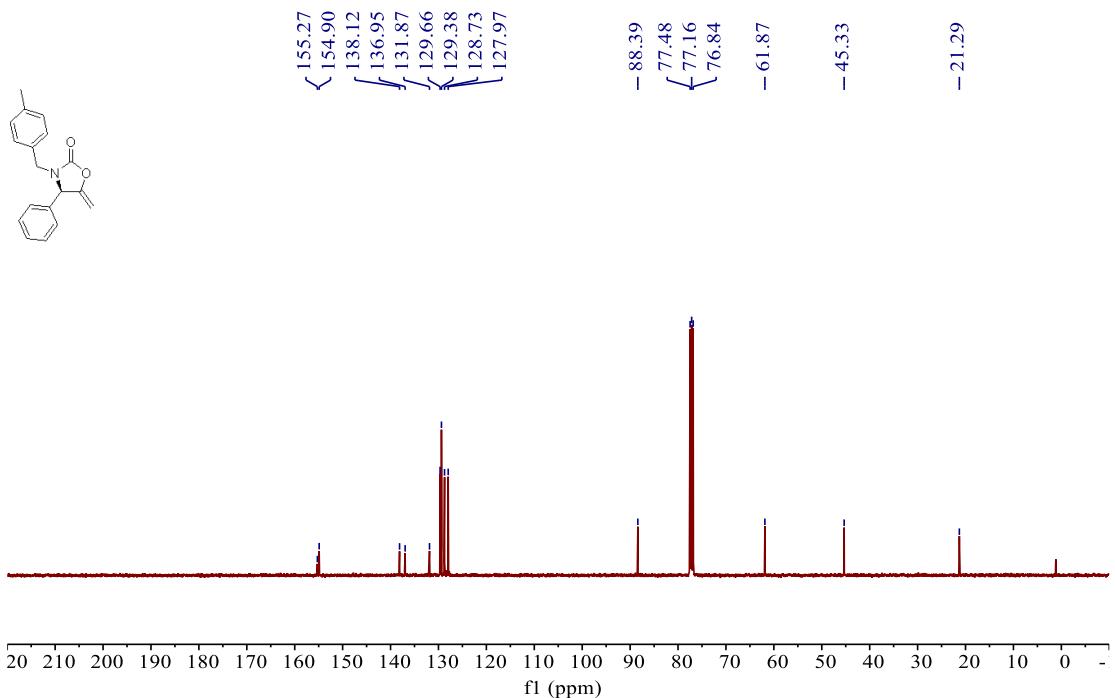
$^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of **3ka**



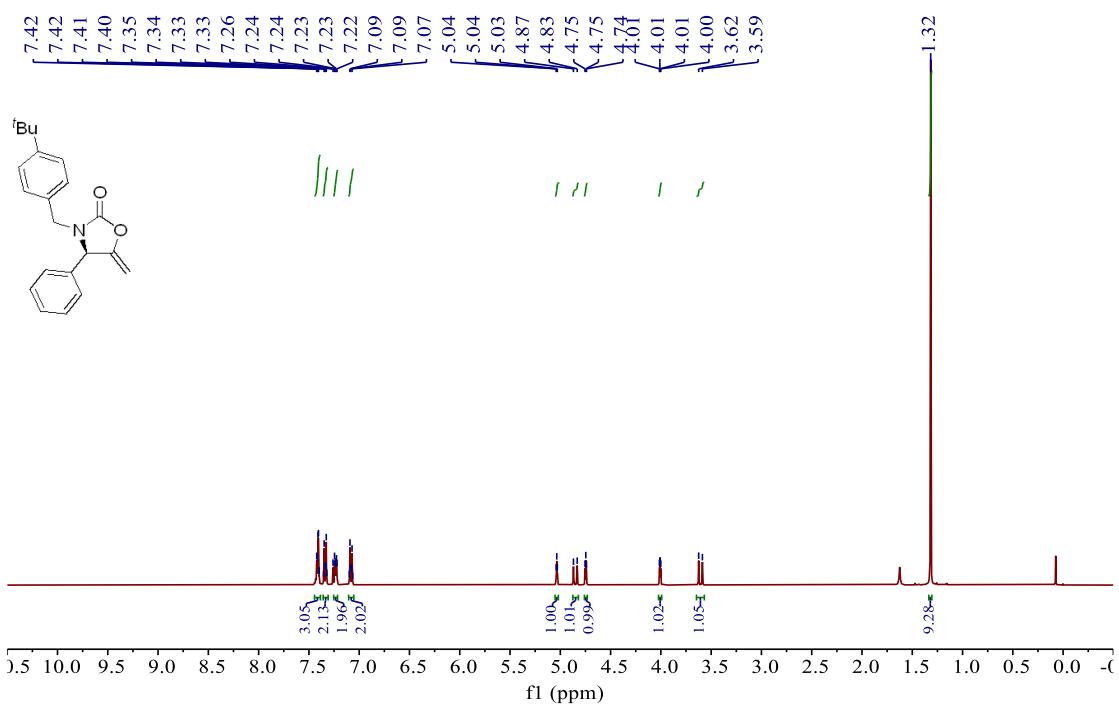
<sup>13</sup>C NMR spectra (101 MHz, CDCl<sub>3</sub>) of **3ka**



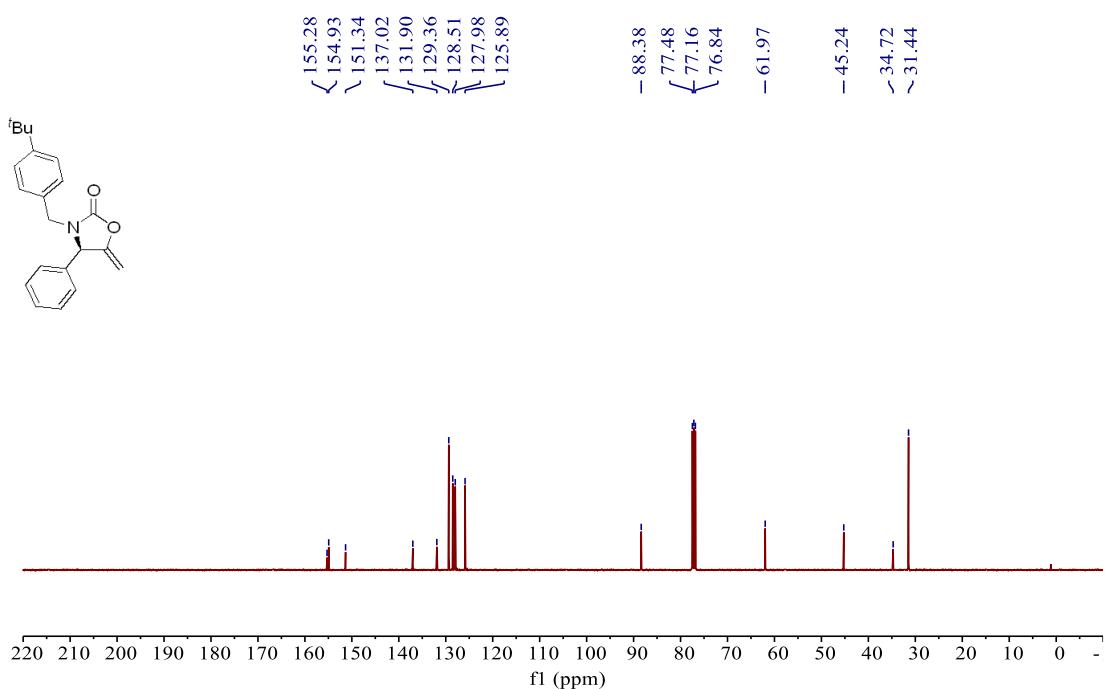
<sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of **3ab**



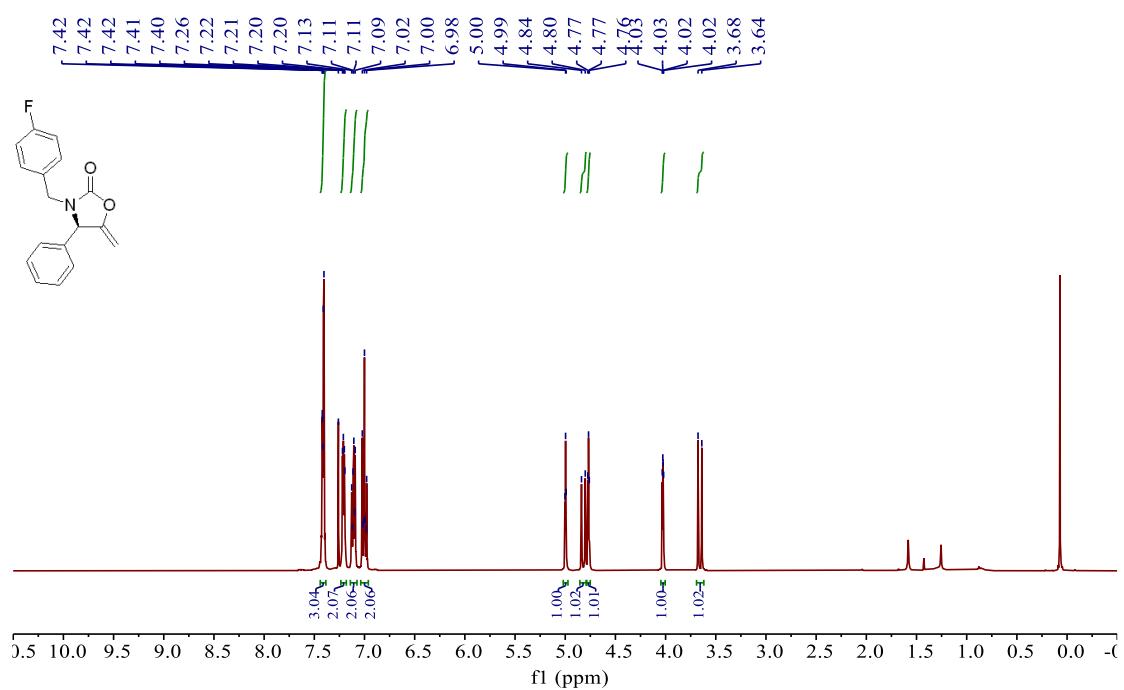
$^{13}\text{C}$  NMR spectra (101 MHz,  $\text{CDCl}_3$ ) of **3ab**



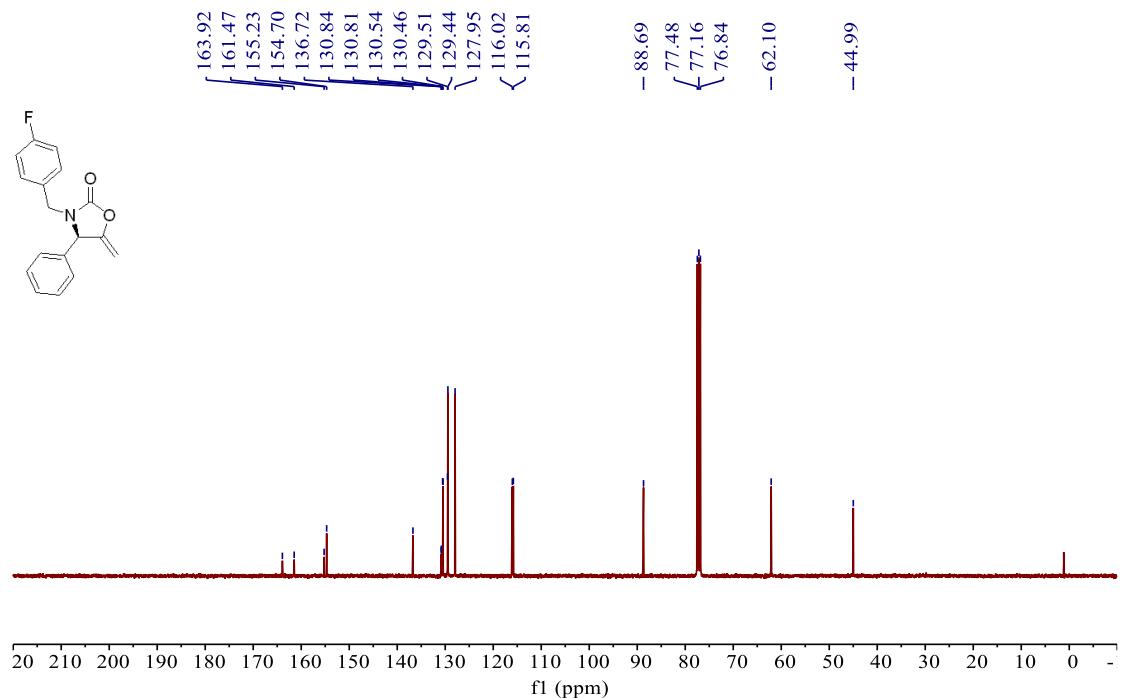
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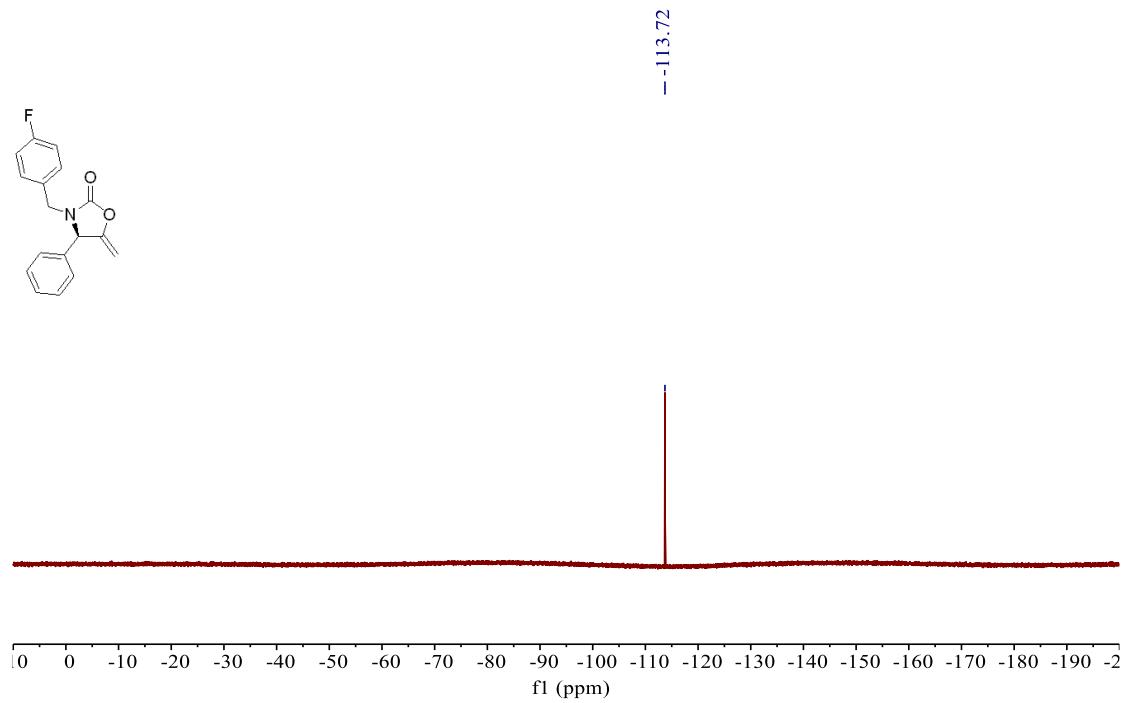
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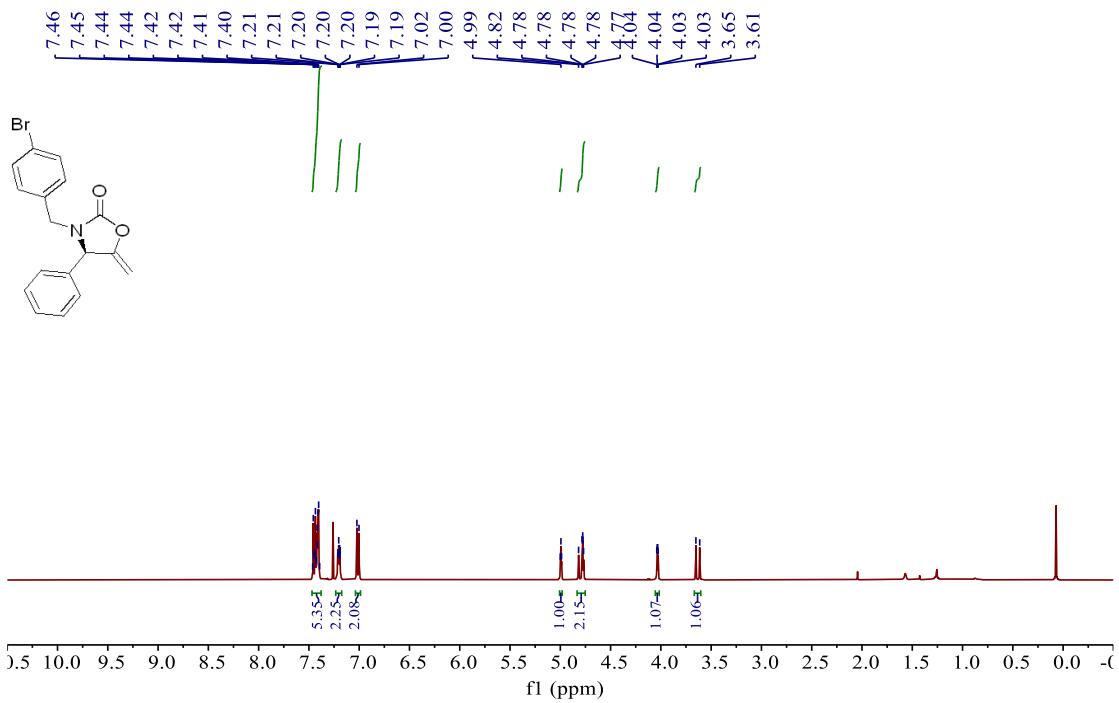
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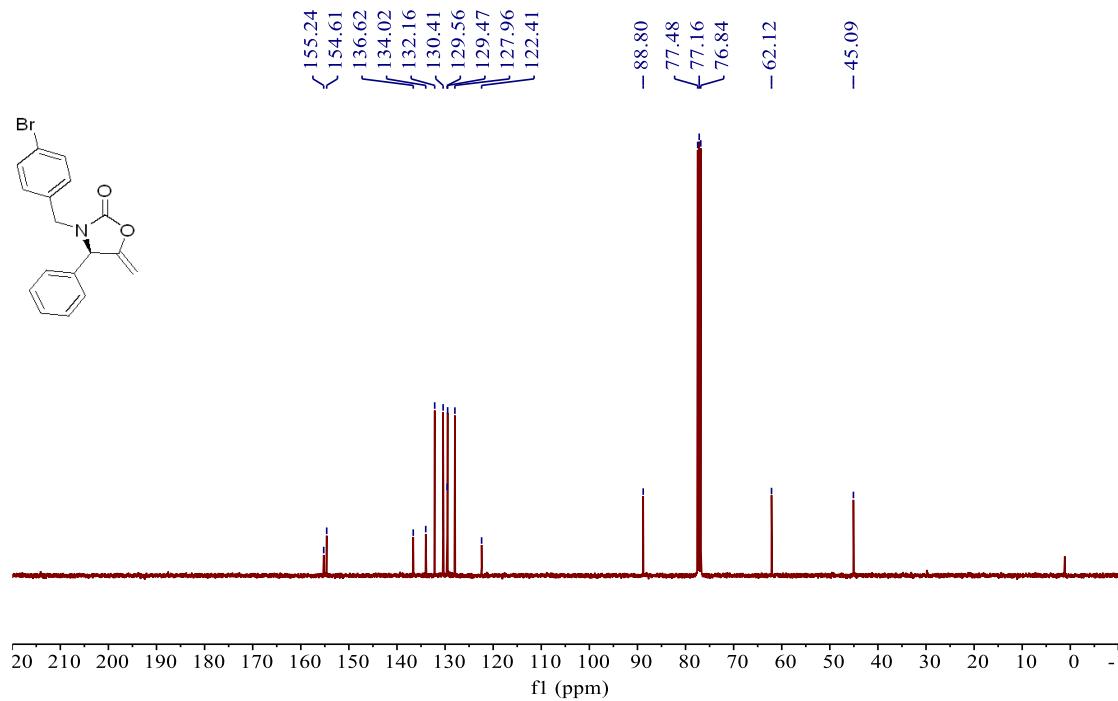
<sup>13</sup>C NMR spectra (101 MHz, CDCl<sub>3</sub>) of **3ad**



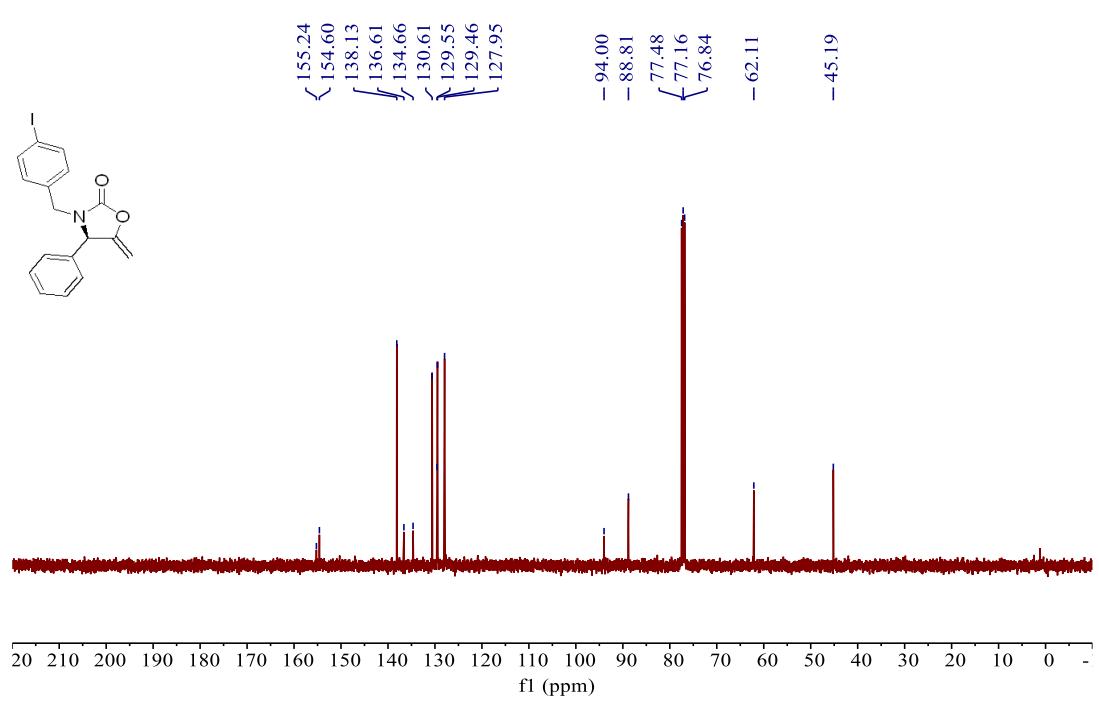
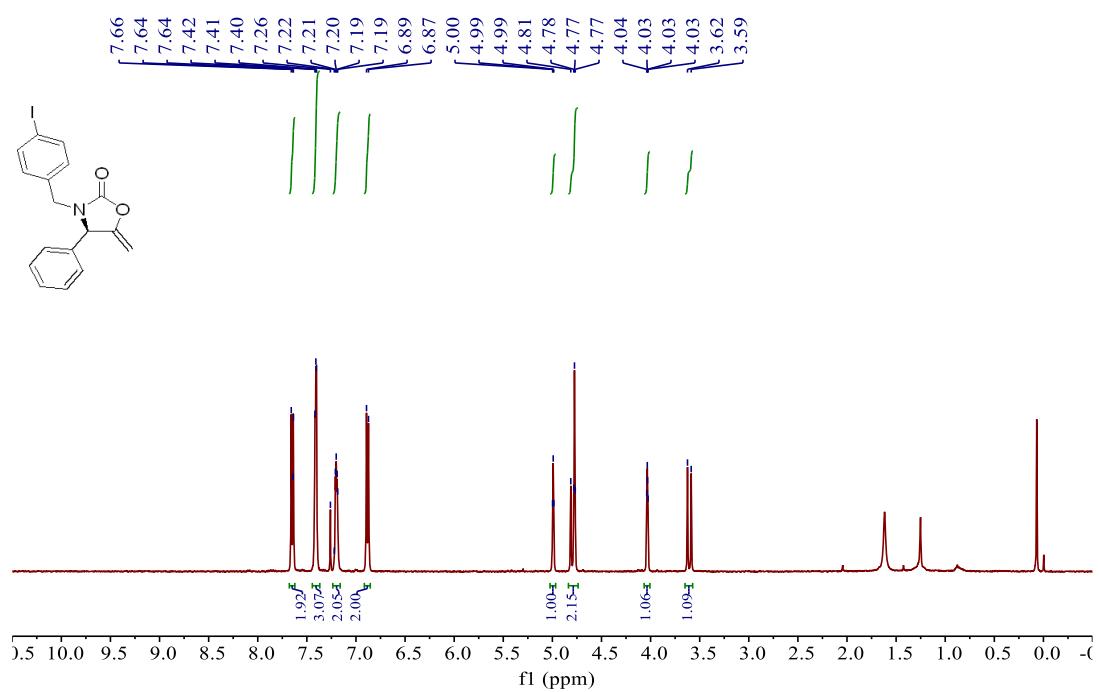
<sup>19</sup>F NMR spectra (376 MHz, CDCl<sub>3</sub>) of **3ad**

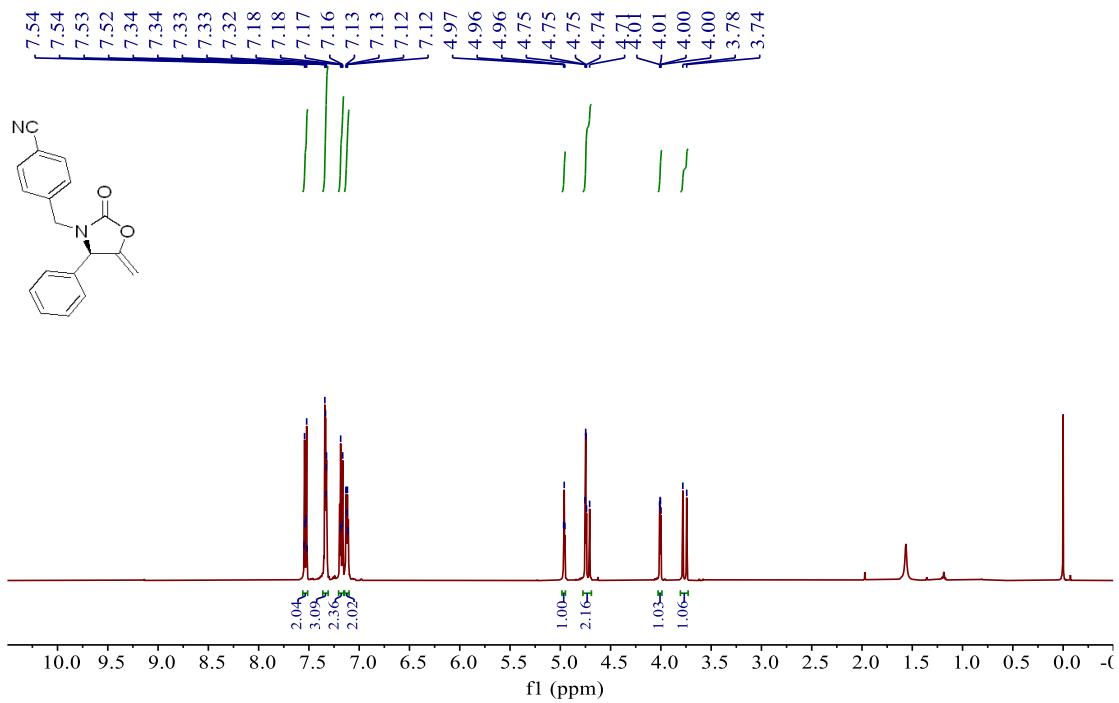


$^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of **3ae**

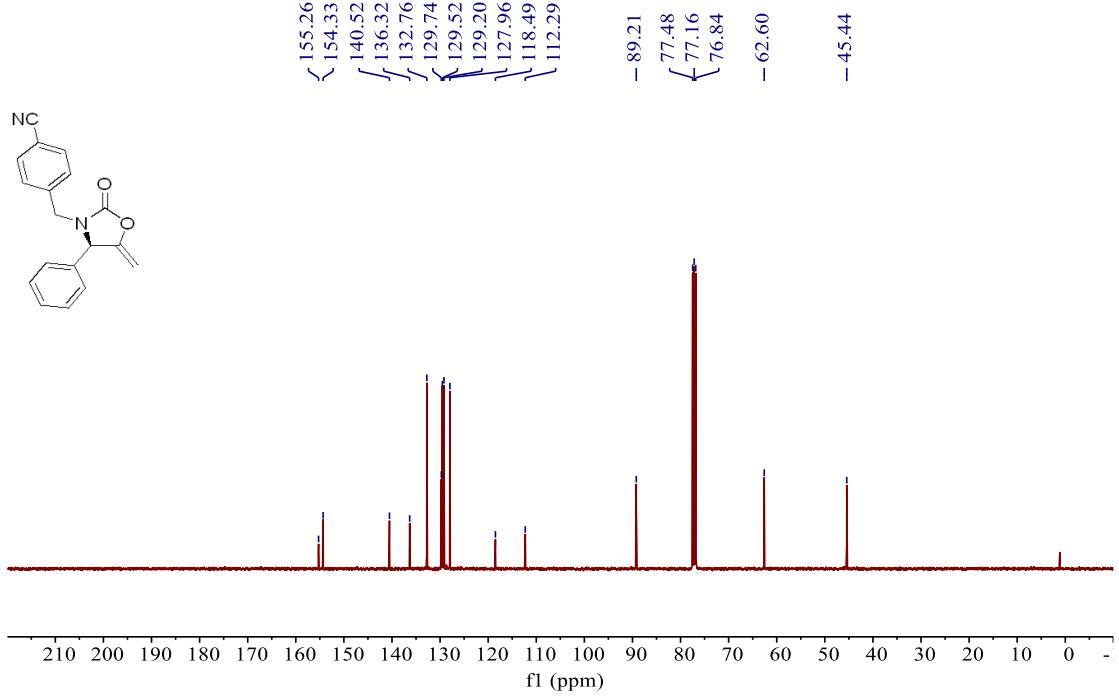


$^{13}\text{C}$  NMR spectra (101 MHz,  $\text{CDCl}_3$ ) of **3ae**

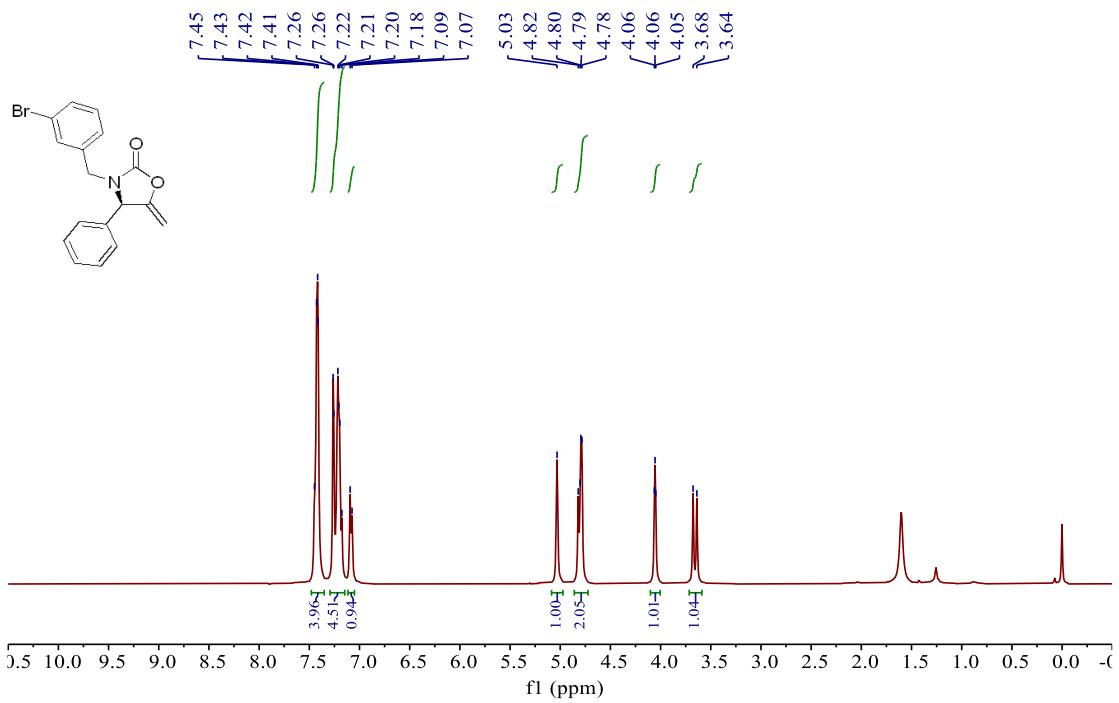




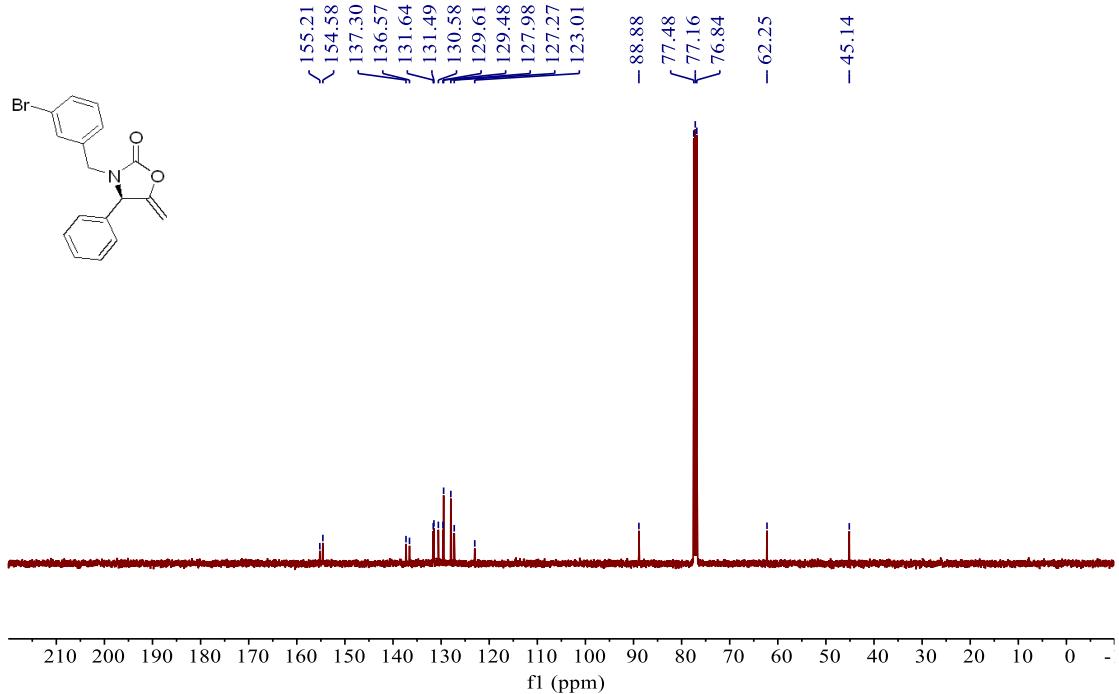
<sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of **3ag**



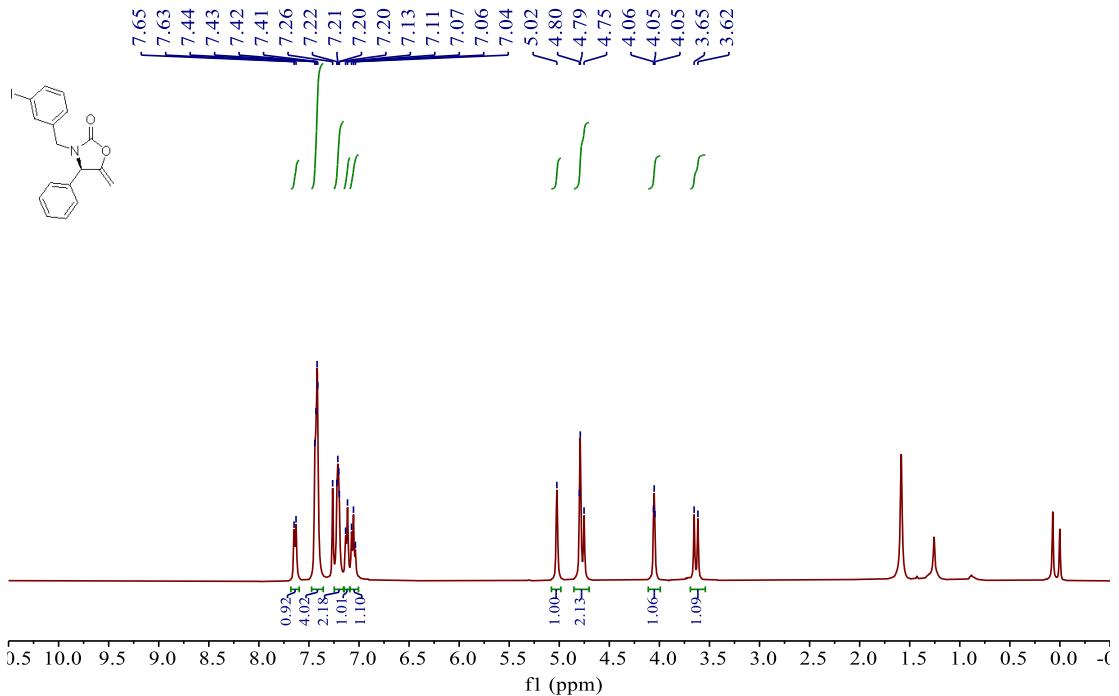
<sup>13</sup>C NMR spectra (101 MHz, CDCl<sub>3</sub>) of **3ag**



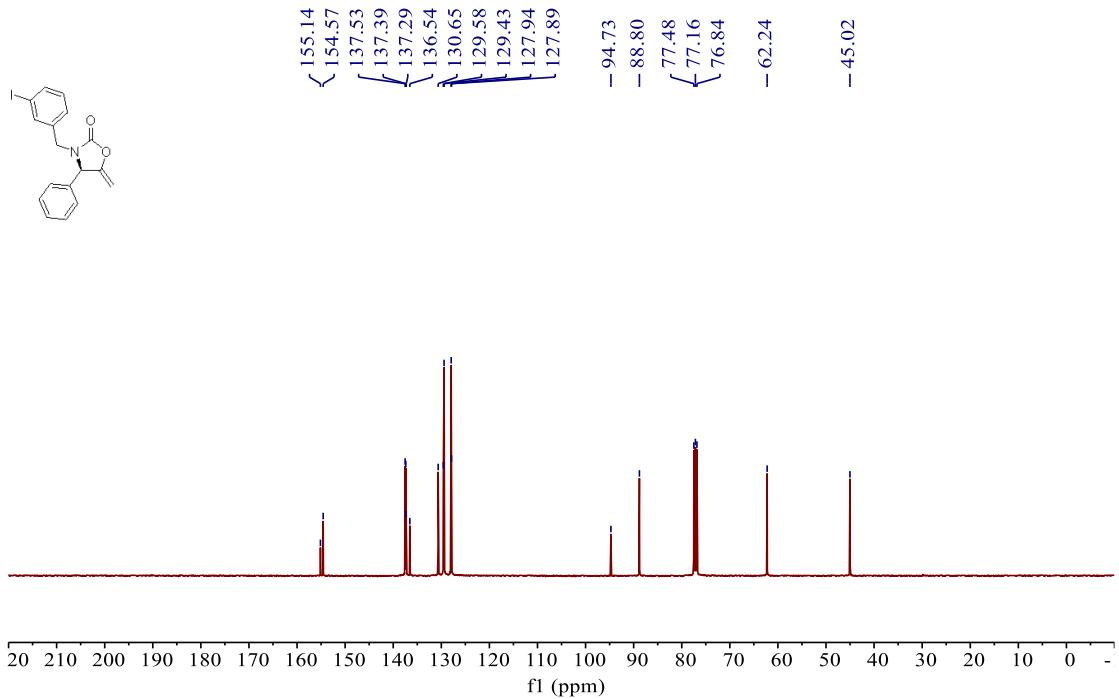
$^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of **3ah**



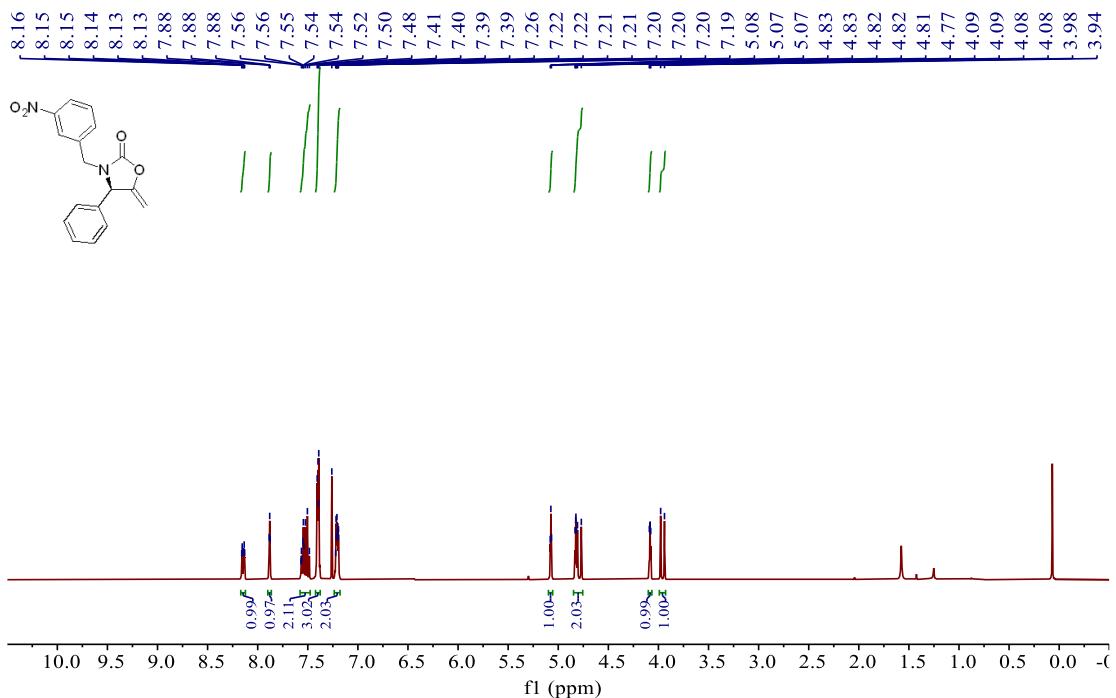
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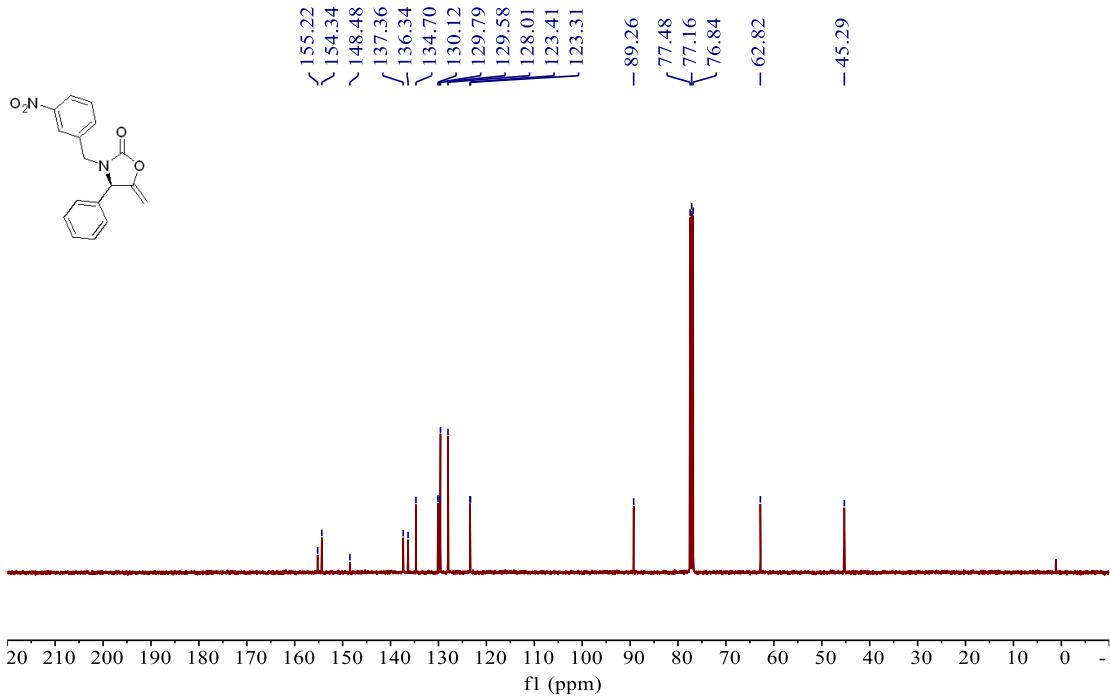
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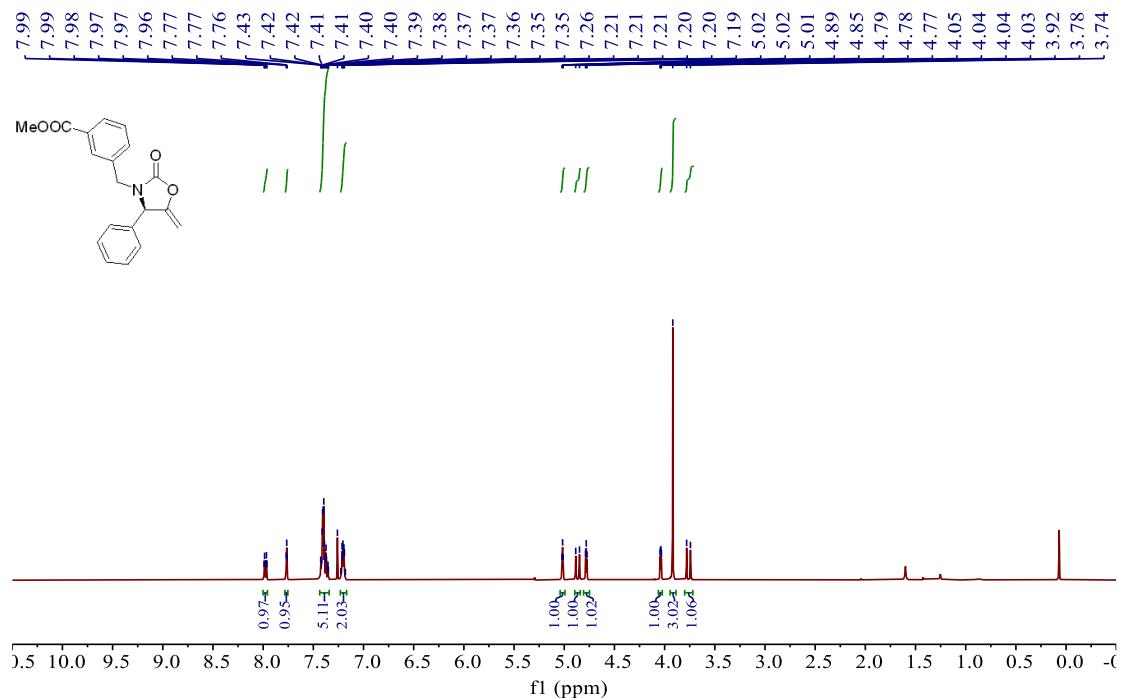
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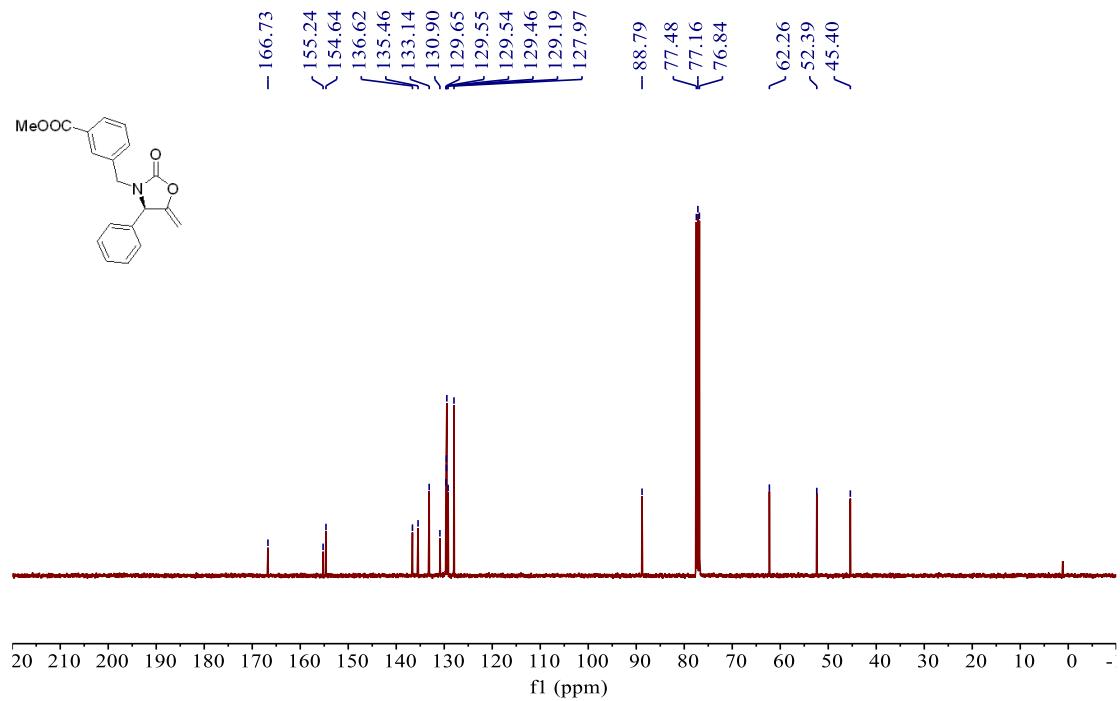
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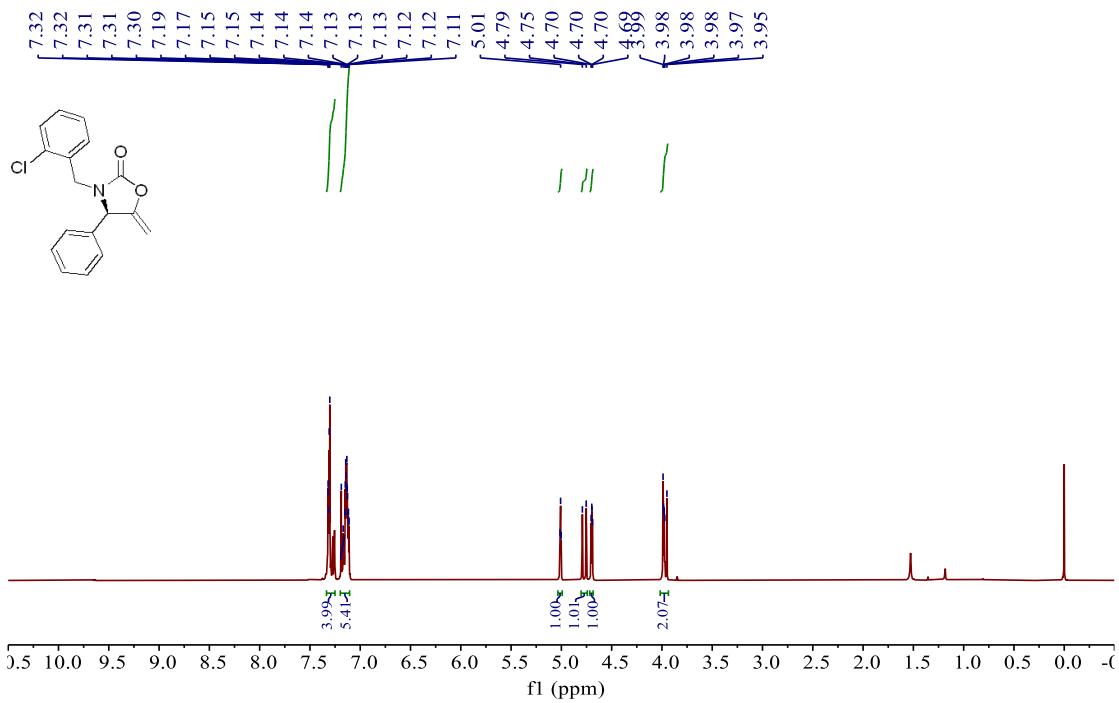
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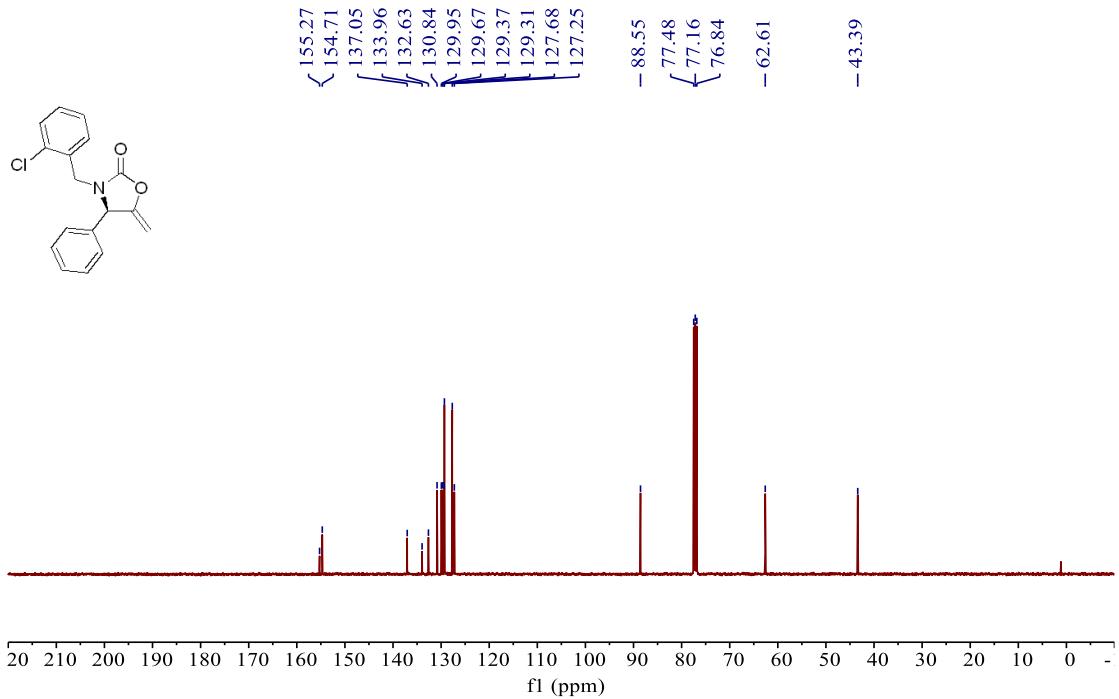
<sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of **3ak**



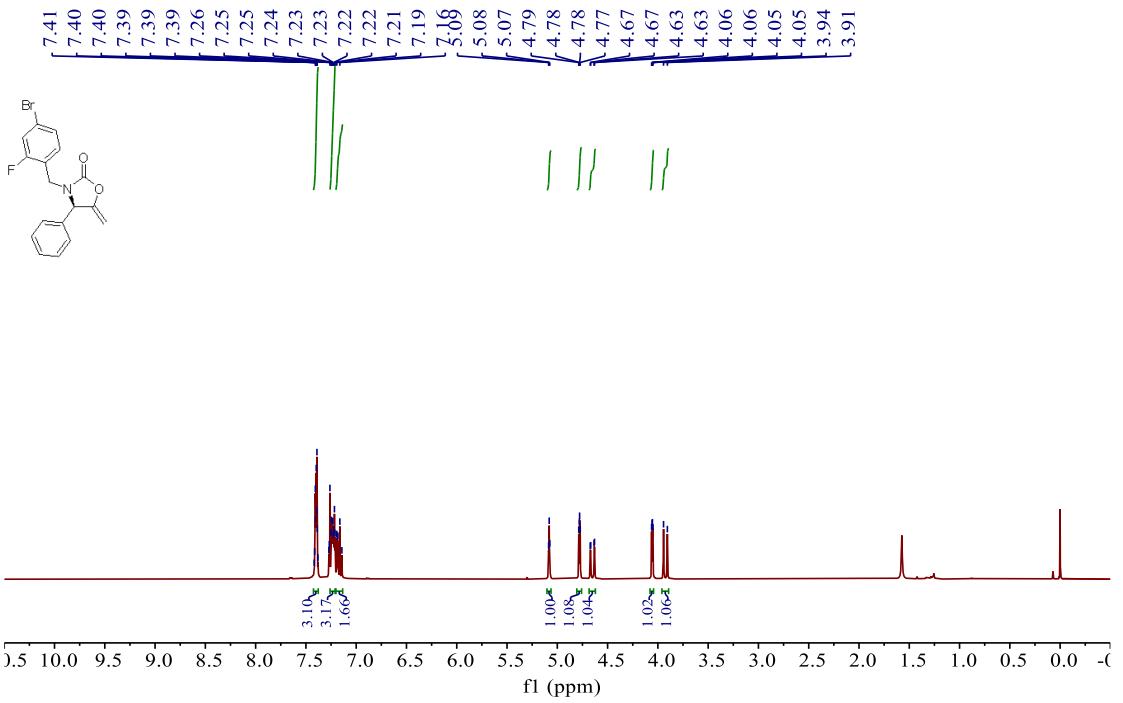
<sup>13</sup>C NMR spectra (101 MHz, CDCl<sub>3</sub>) of **3ak**



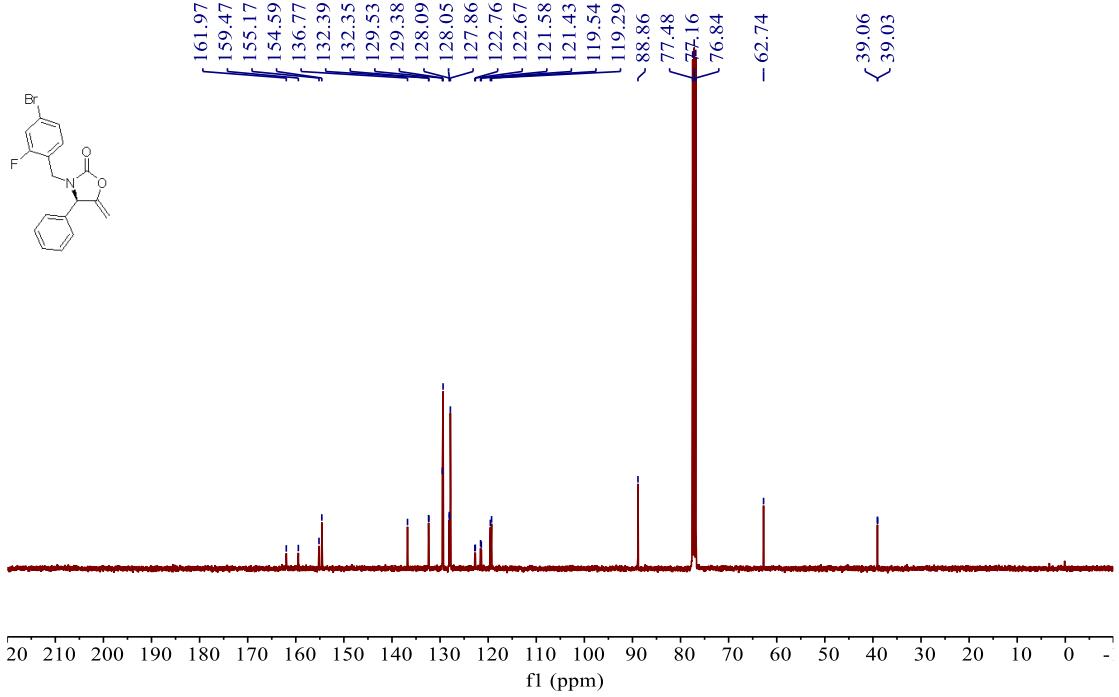
<sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of **3al**



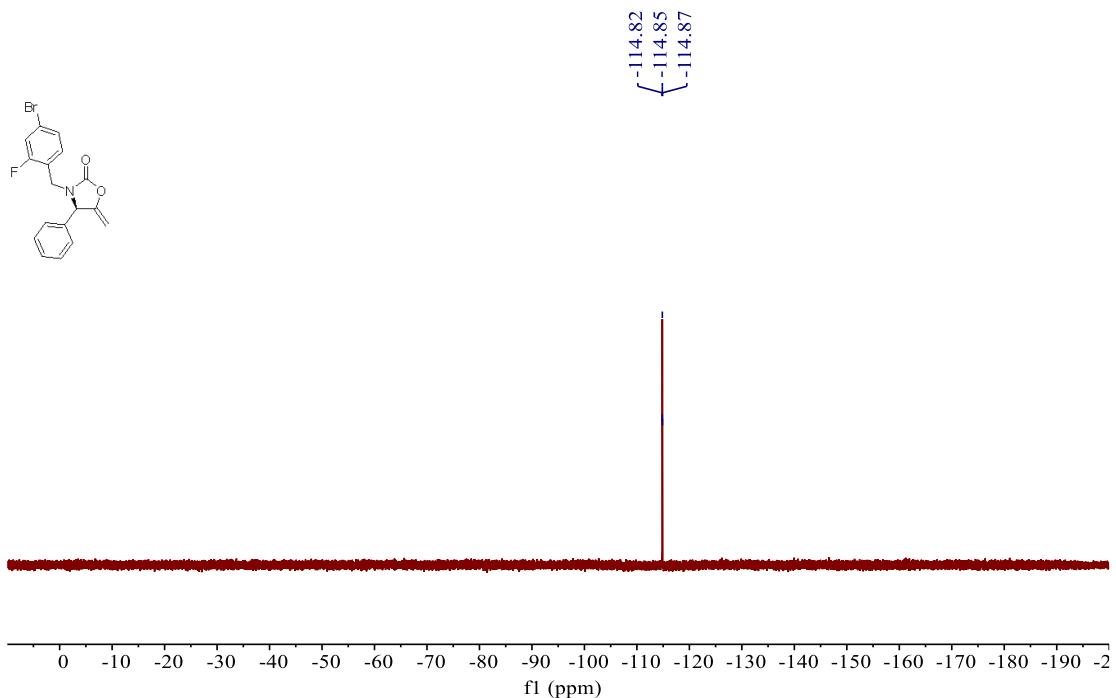
<sup>13</sup>C NMR spectra (101 MHz, CDCl<sub>3</sub>) of **3al**



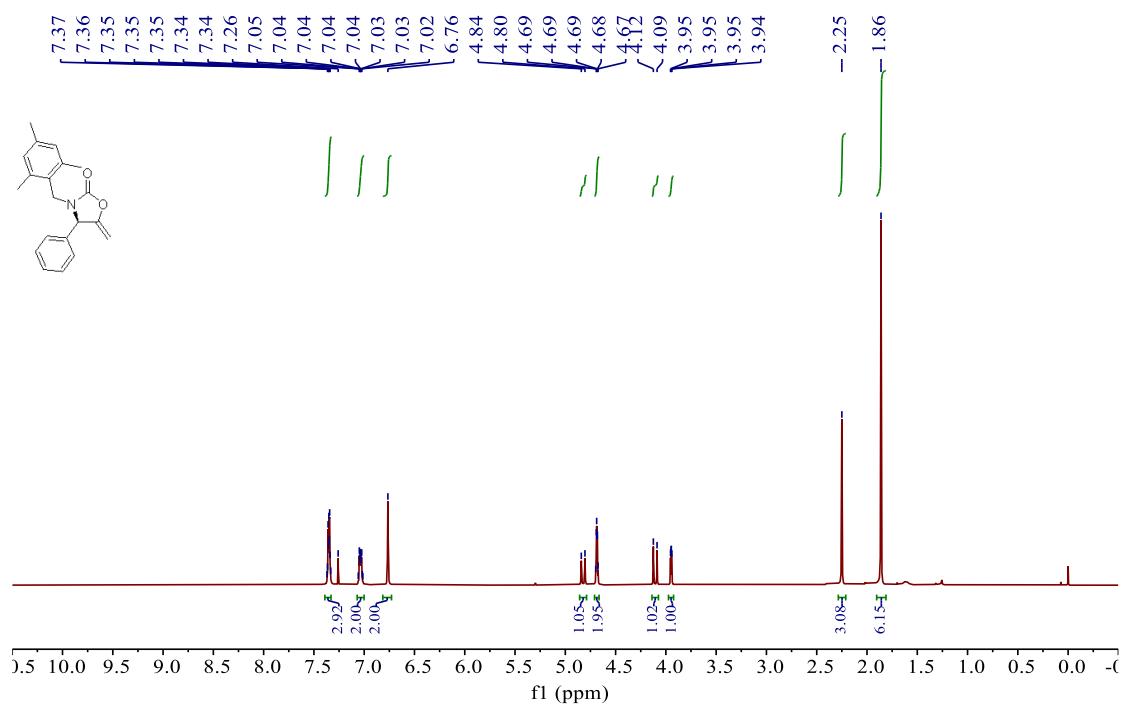
<sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of **3am**



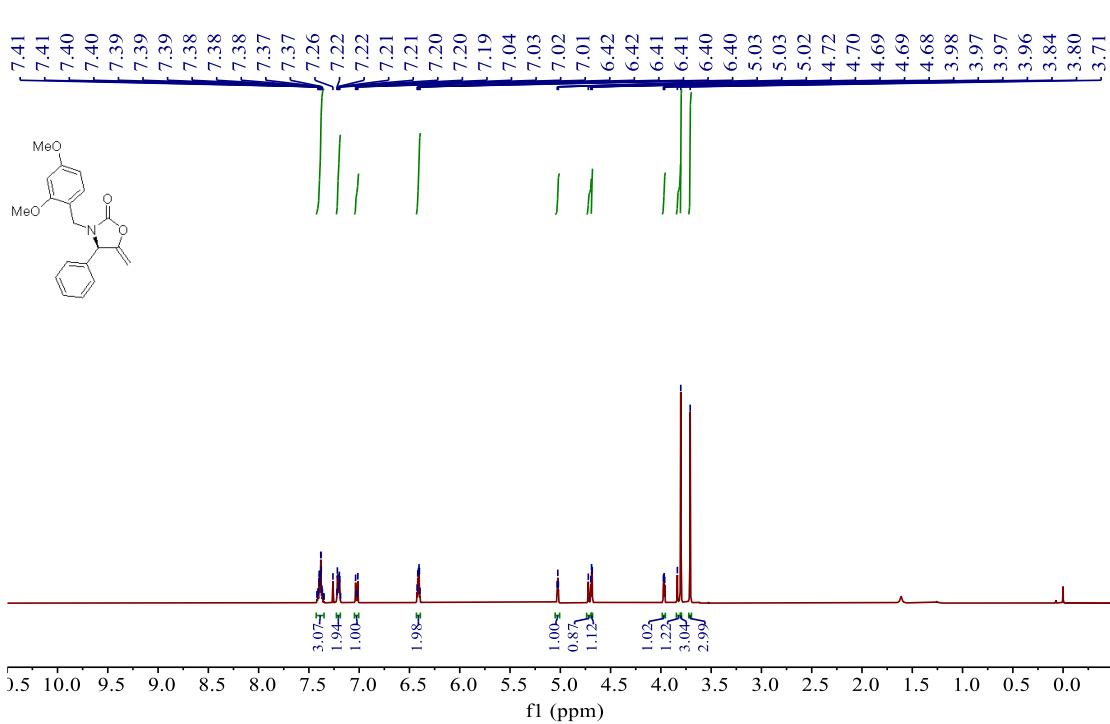
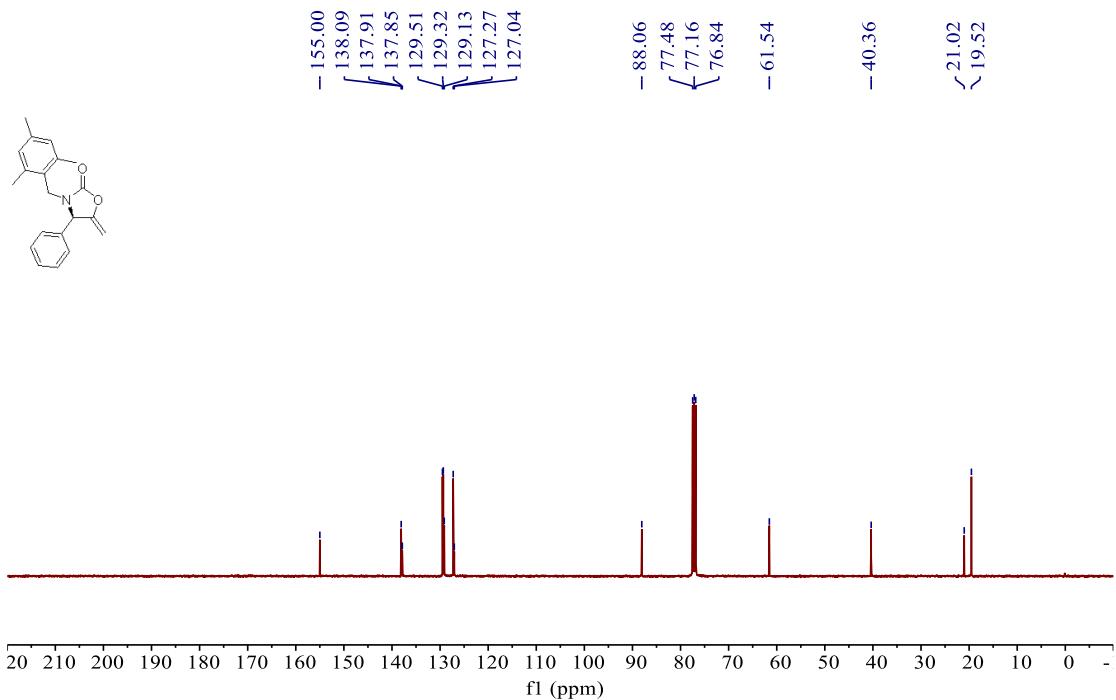
<sup>13</sup>C NMR spectra (101 MHz, CDCl<sub>3</sub>) of **3am**

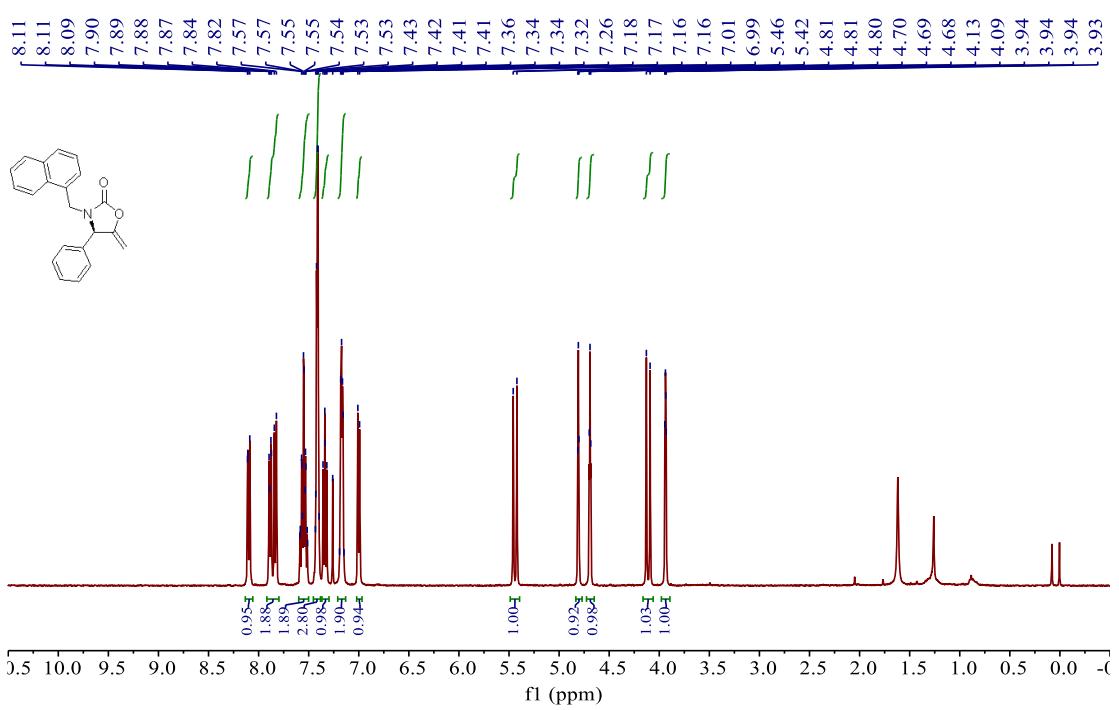
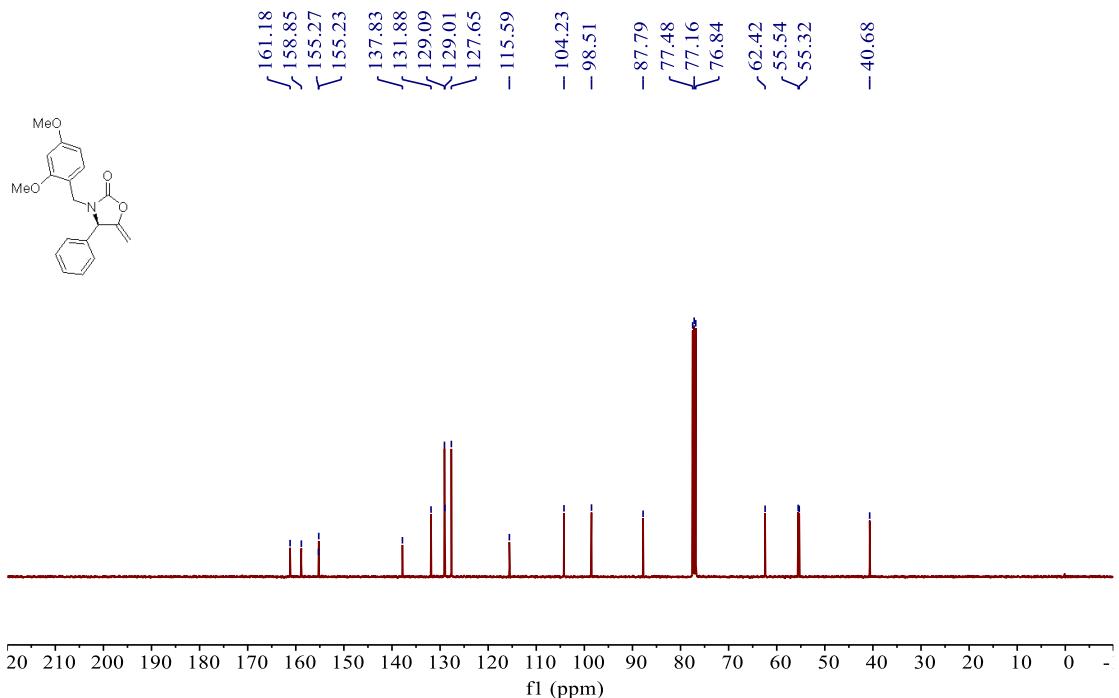


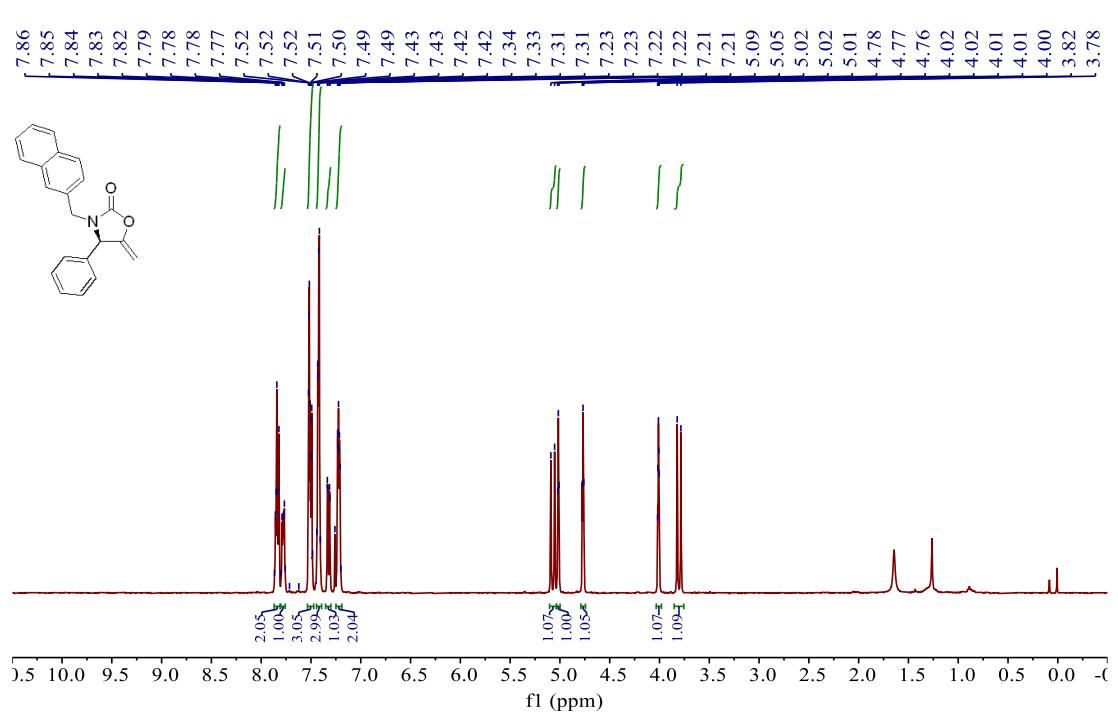
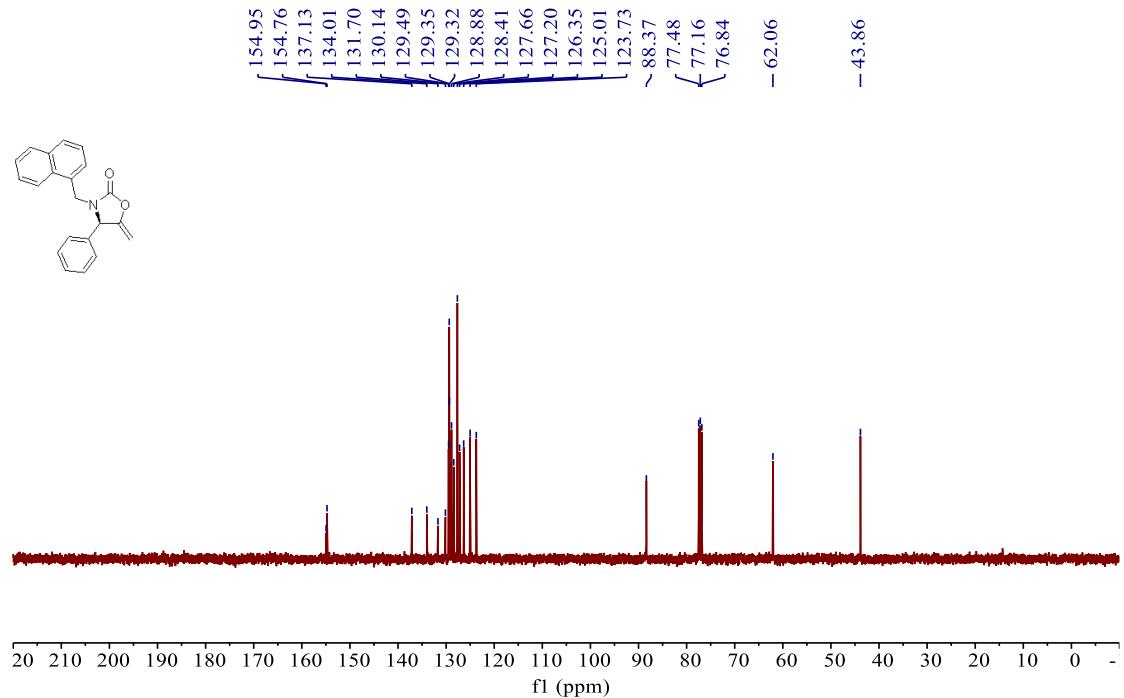
$^{19}\text{F}$  NMR spectra (376 MHz,  $\text{CDCl}_3$ ) of **3am**

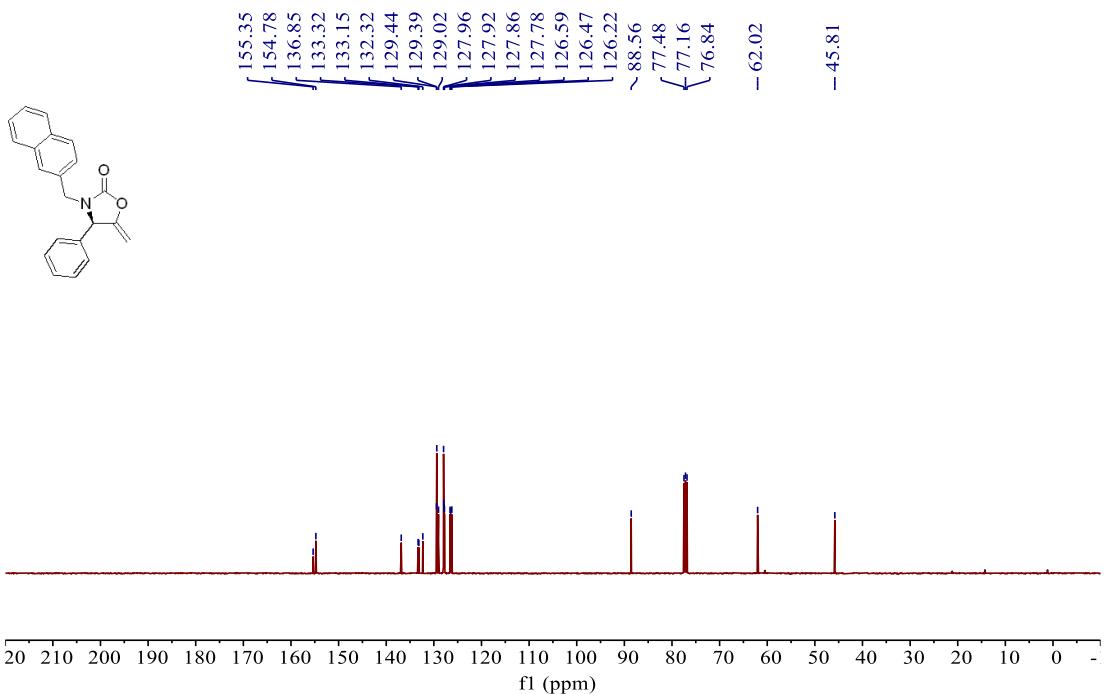


$^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of **3an**

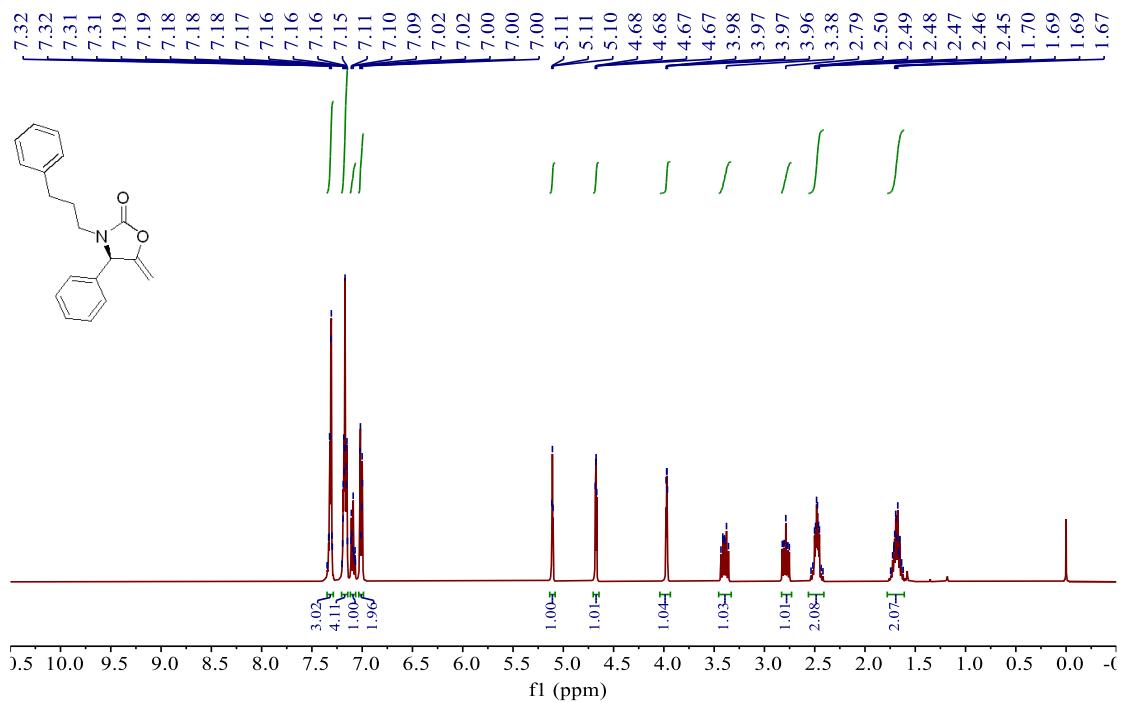




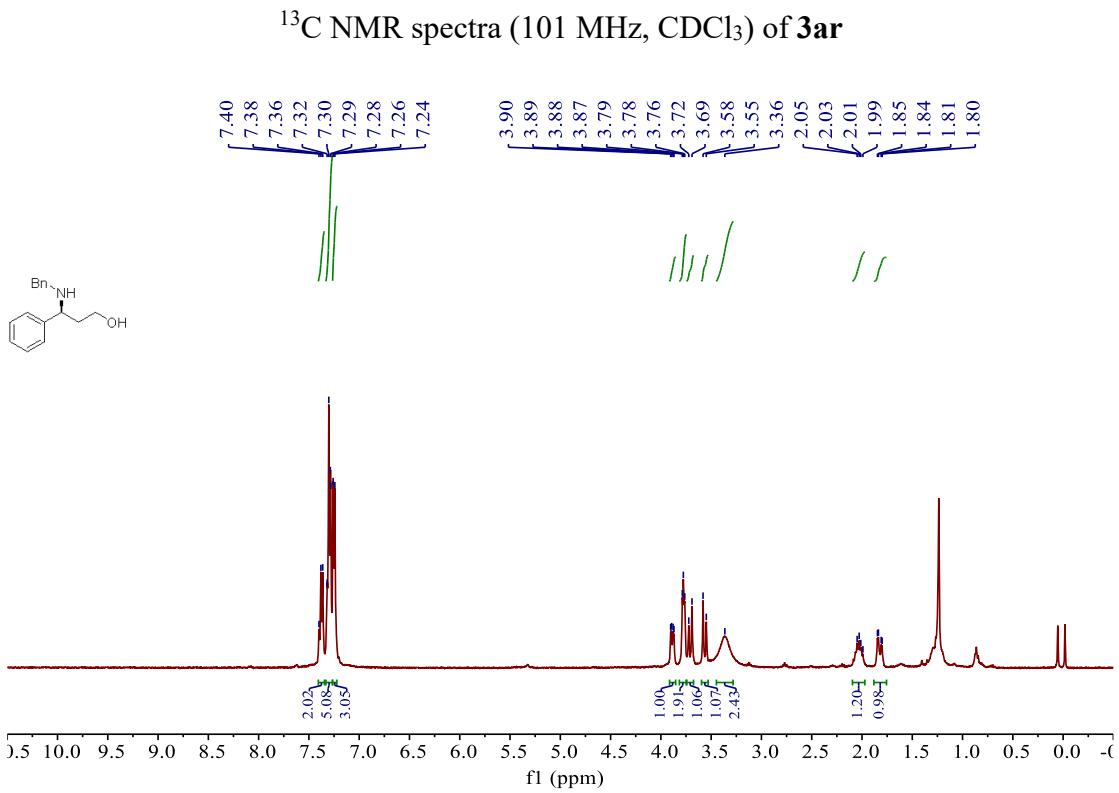
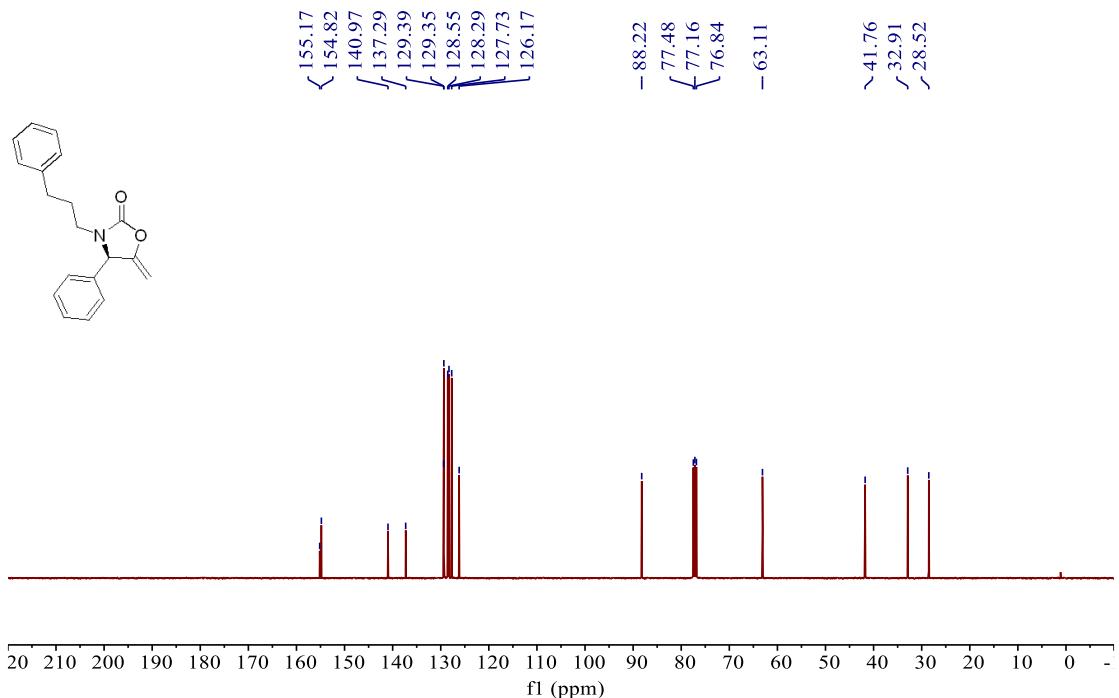


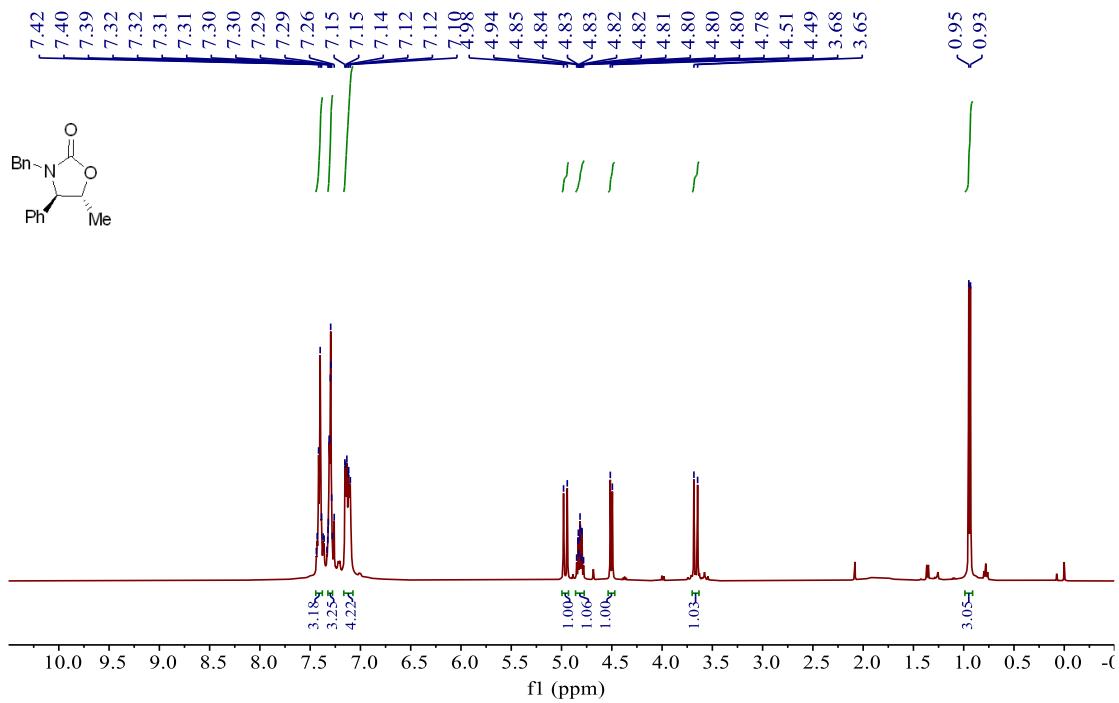


<sup>13</sup>C NMR spectra (101 MHz, CDCl<sub>3</sub>) of **3aq**

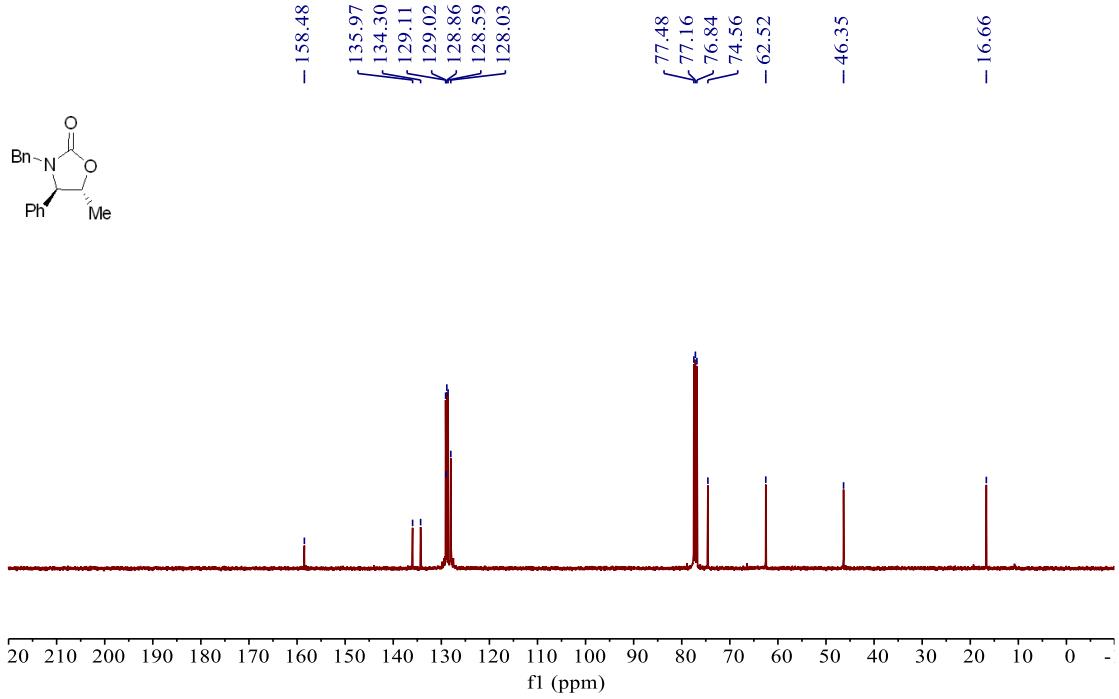


<sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of **3ar**





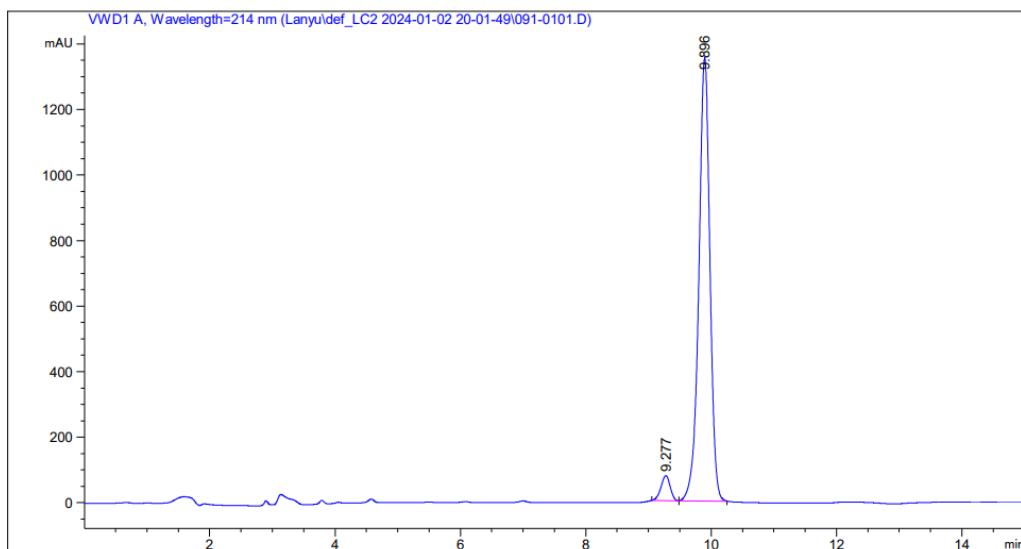
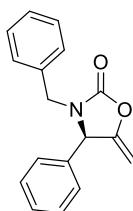
<sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of **4ab**



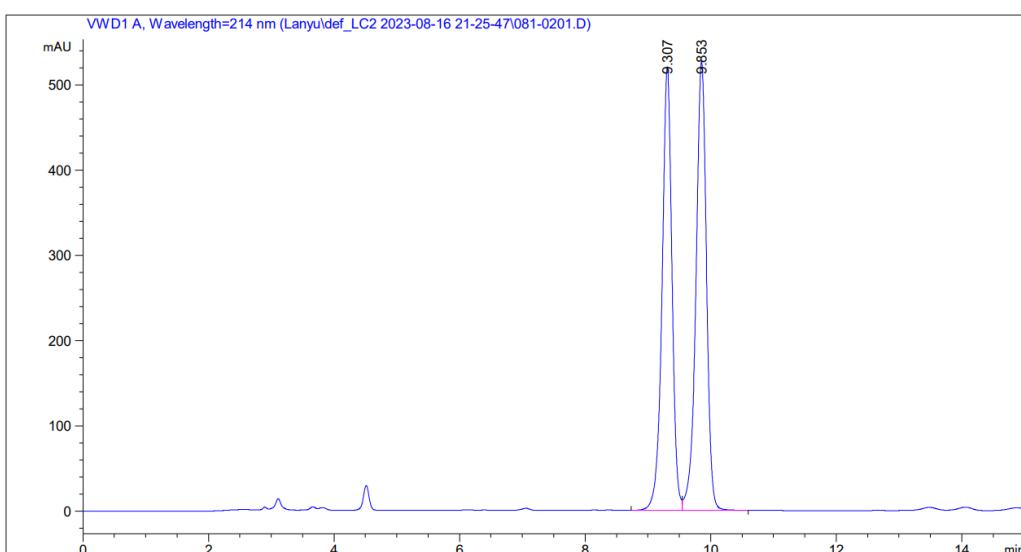
<sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of **4ab**

## 6. HPLC Chromatograms

### (R)-3-benzyl-5-methylene-4-phenyloxazolidin-2-one (3aa)

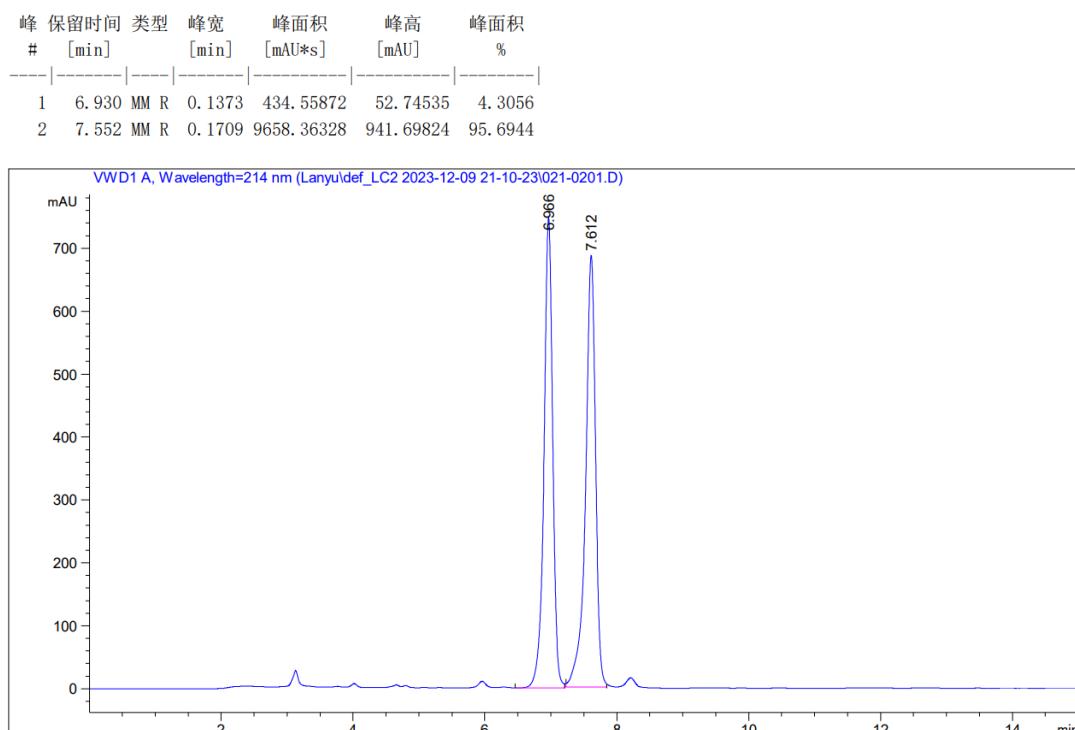
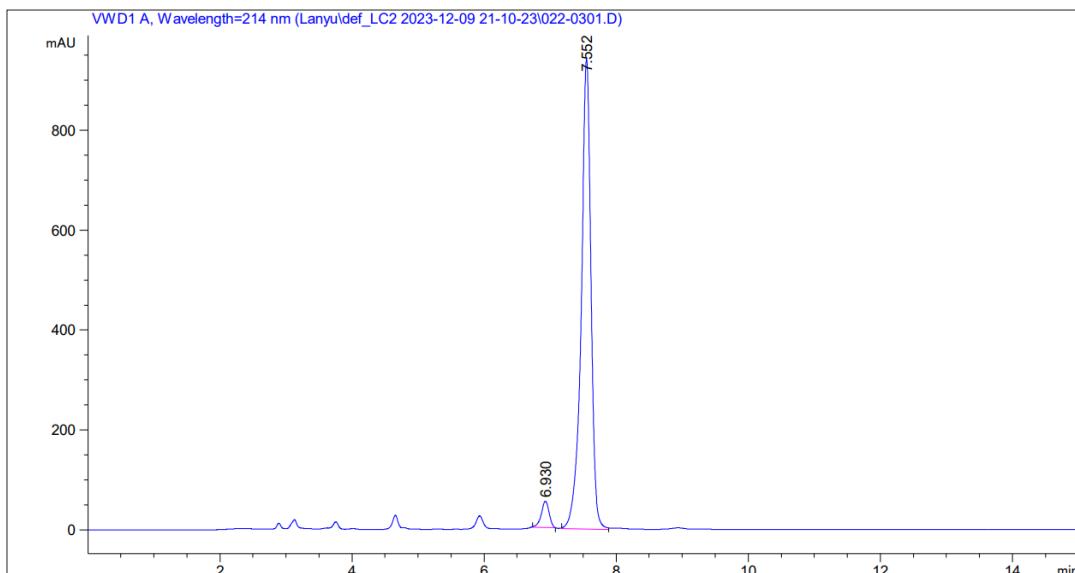
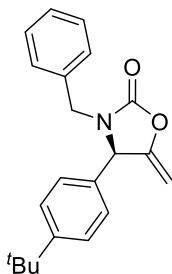


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.277	MF R	0.1690	770.71777	75.99125	4.4334
2	9.896	FM R	0.2046	1.66138e4	1353.11865	95.5666

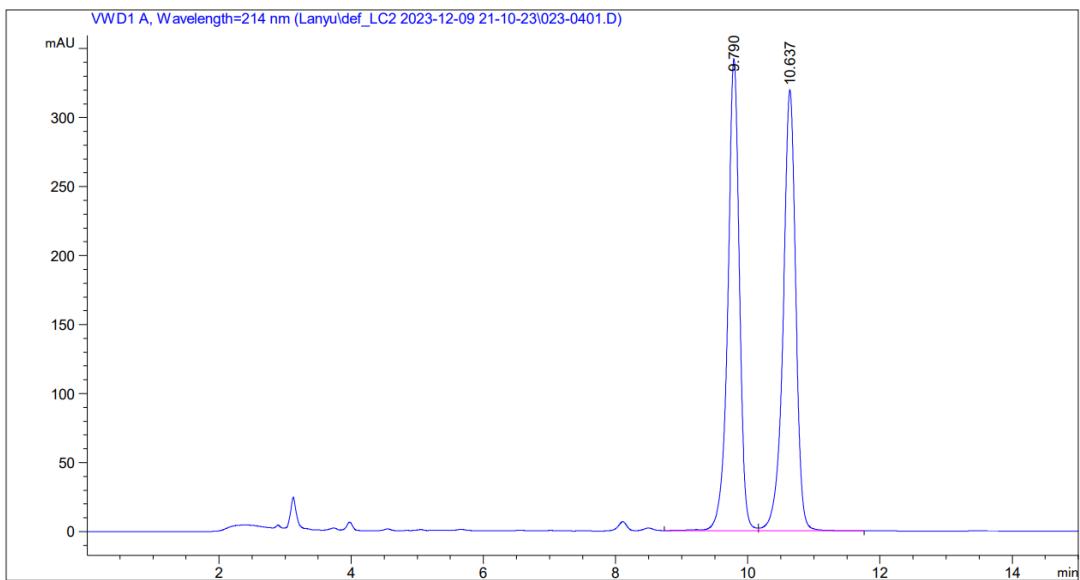
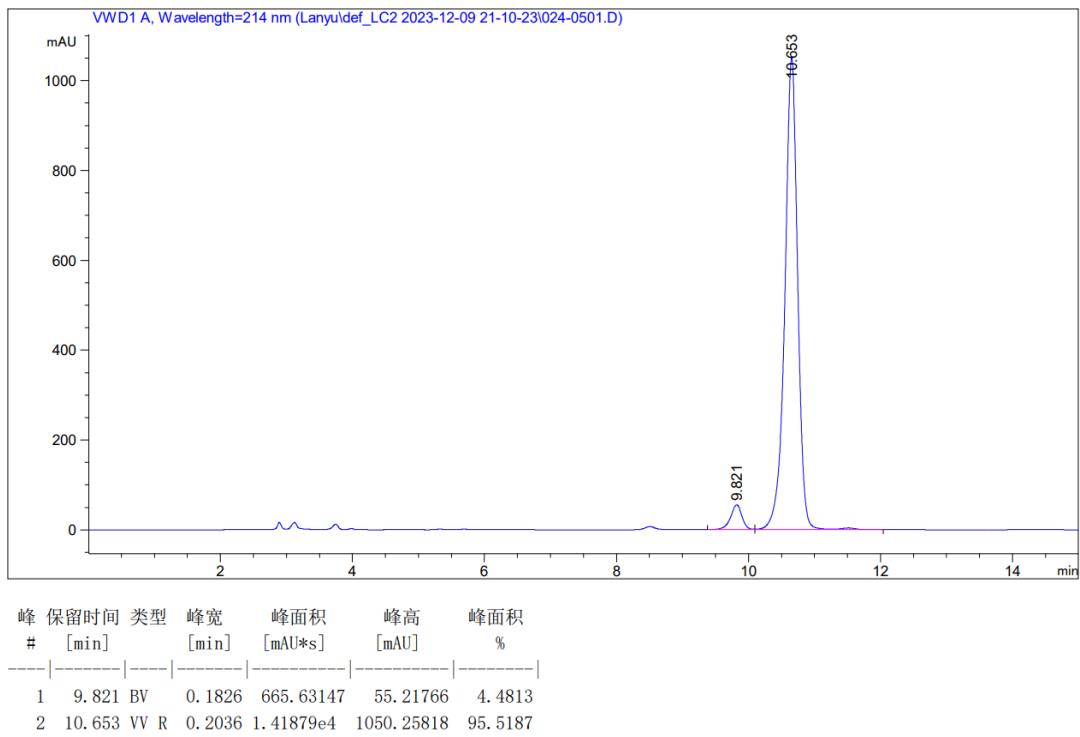
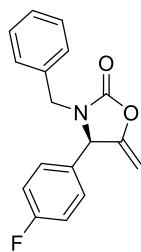


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.307	BV	0.1676	5737.67188	520.49817	48.3709
2	9.853	VB	0.1777	6124.15186	526.53735	51.6291

**(R)-3-benzyl-4-(4-(tert-butyl)phenyl)-5-methyleneoxazolidin-2-one (3ba)**

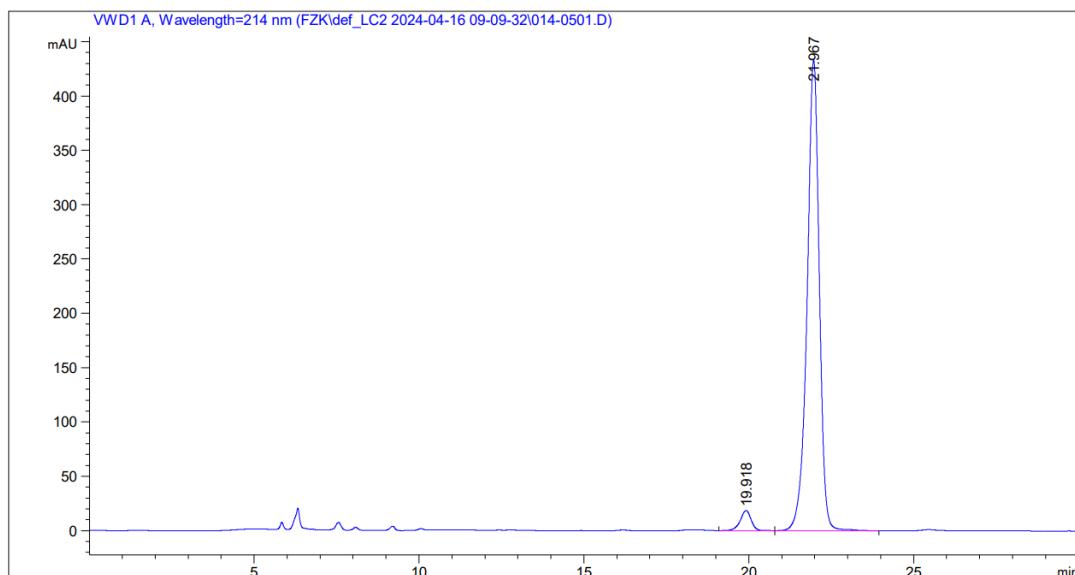
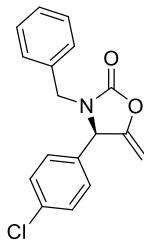


**(R)-3-benzyl-4-(4-fluorophenyl)-5-methyleneoxazolidin-2-one (3ca)**

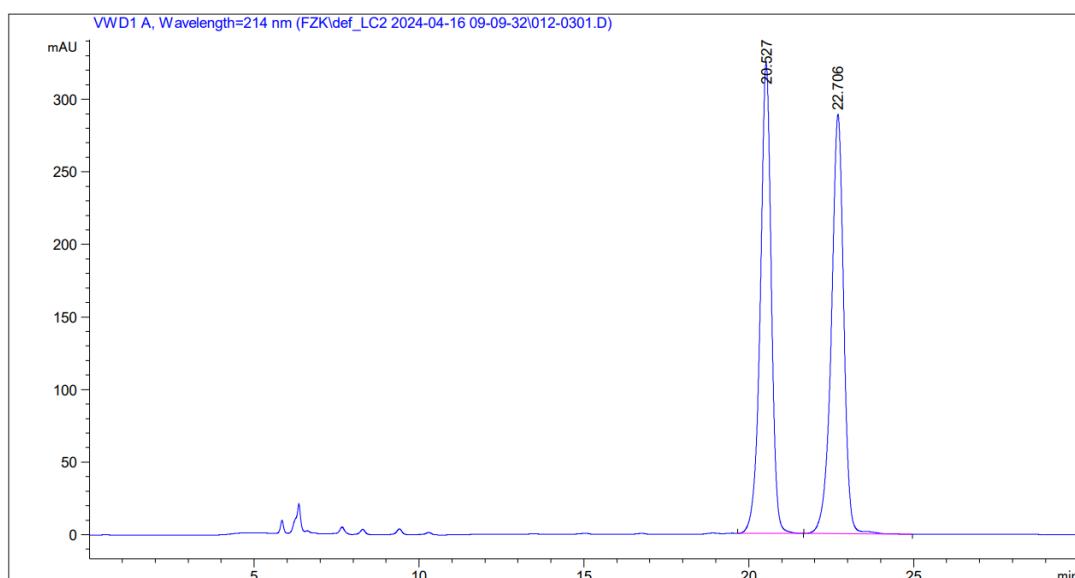


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.790	VV R	0.1837	4154.29443	341.93188	49.5275
2	10.637	VB	0.2006	4233.55566	319.53448	50.4725

**(R)-3-benzyl-4-(4-chlorophenyl)-5-methyleneoxazolidin-2-one (3da)**

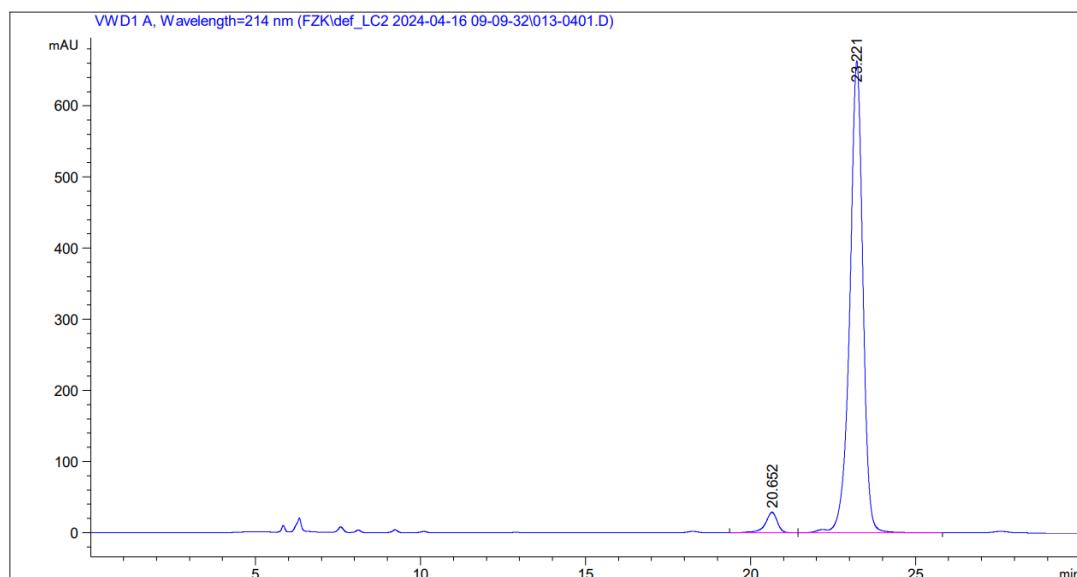
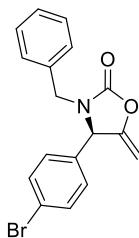


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.918	BB	0.3493	425.53543	18.50423	3.6910
2	21.967	BB	0.3881	1.11036e4	433.04745	96.3090

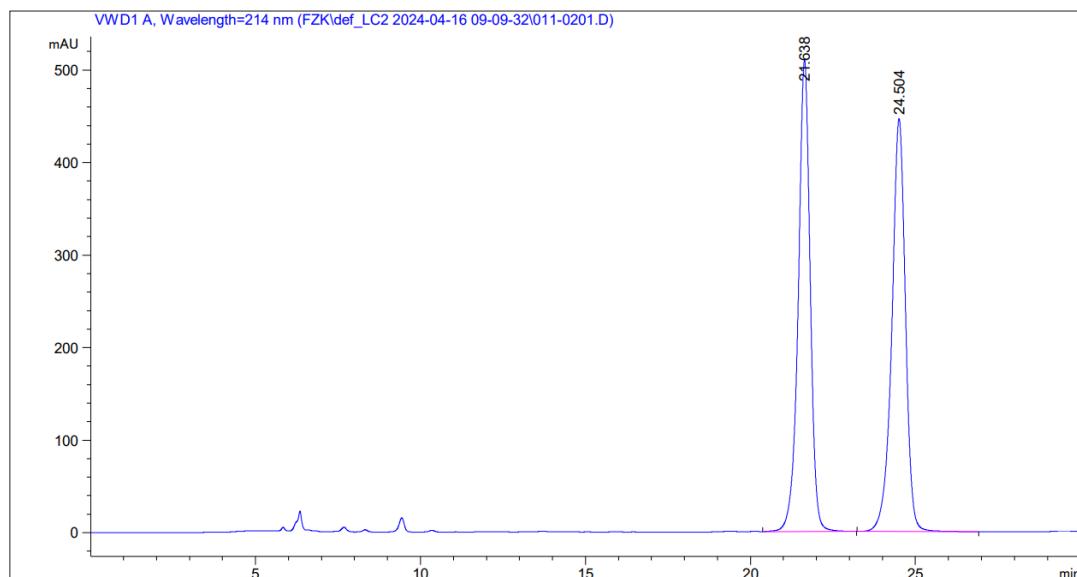


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.527	BB	0.3496	7490.35156	324.08426	49.8186
2	22.706	BB	0.3955	7544.89111	289.04489	50.1814

**(R)-3-benzyl-4-(4-bromophenyl)-5-methyleneoxazolidin-2-one (3ea)**

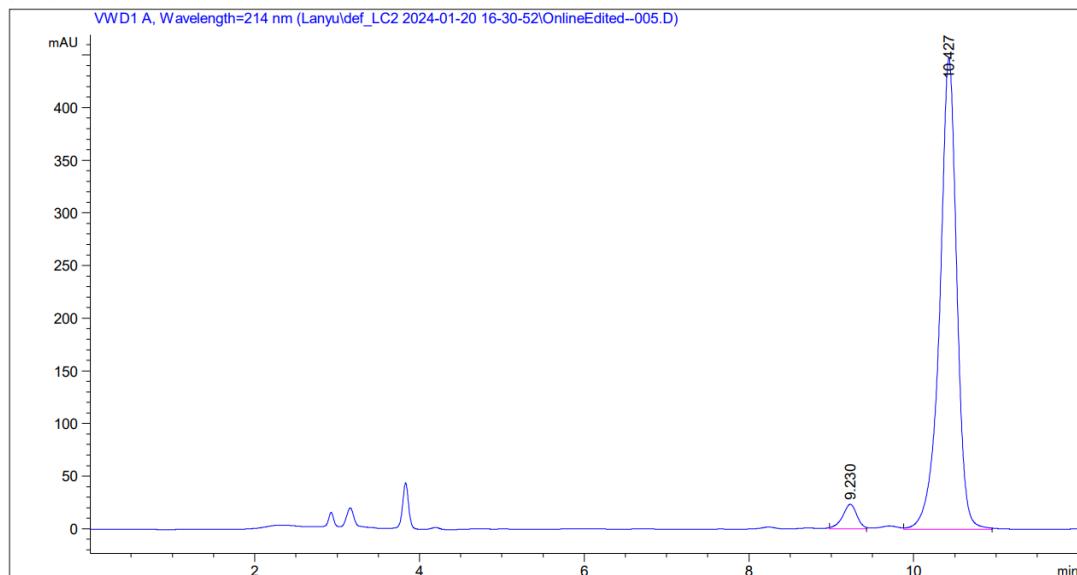
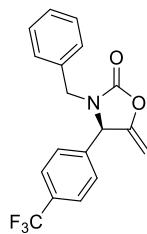


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.652	BB	0.3793	737.45264	28.93831	3.8867
2	23.221	VB R	0.4122	1.82362e4	663.18140	96.1133

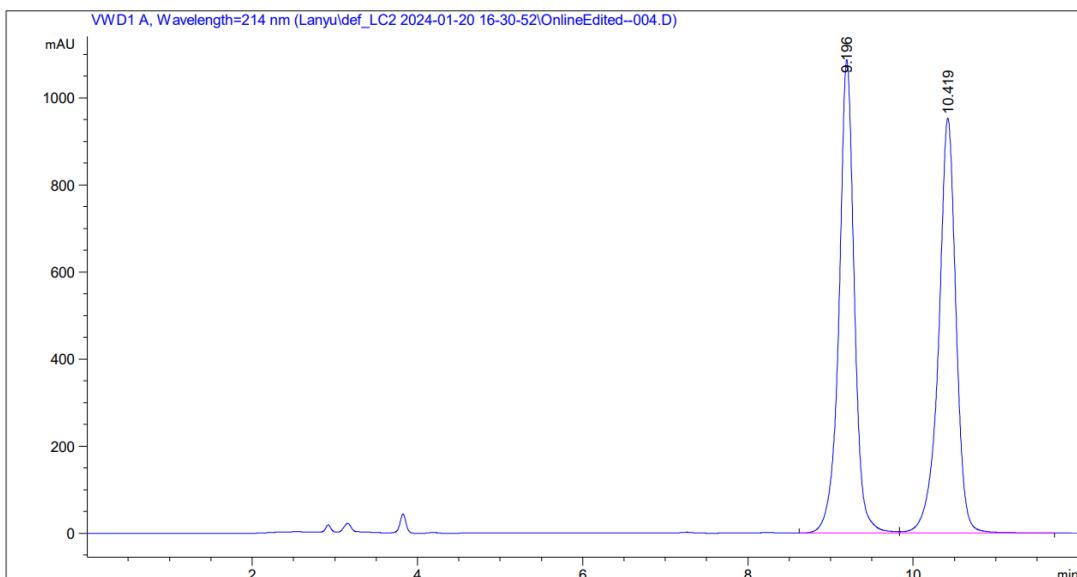


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	21.638	BB	0.3809	1.28388e4	509.67560	50.0174
2	24.504	BB	0.4345	1.28299e4	446.13266	49.9826

**(R)-3-benzyl-5-methylene-4-(trifluoromethyl)phenyl)oxazolidin-2-one (3fa)**

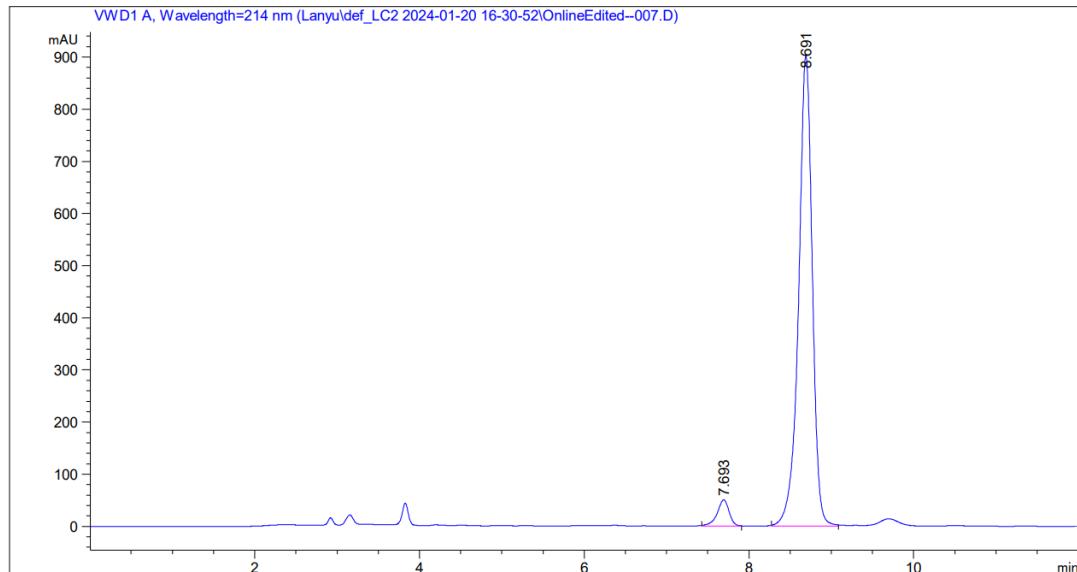
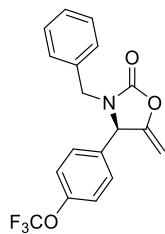


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.230	FM R	0.2049	288.74786	23.48664	4.2894
2	10.427	MM R	0.2400	6442.95801	447.47797	95.7106

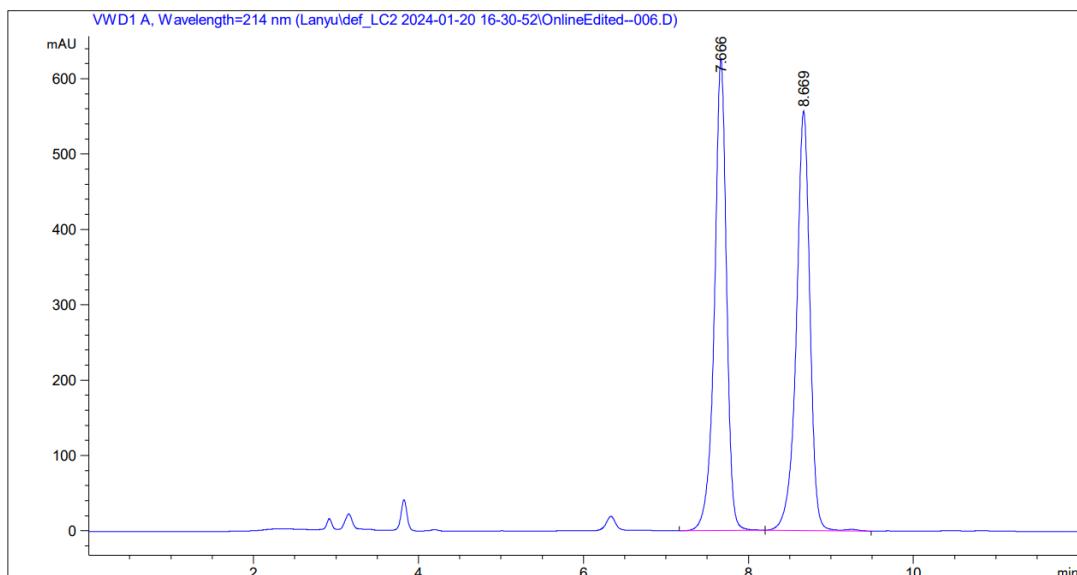


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.196	BV	0.1920	1.39791e4	1087.08887	50.1103
2	10.419	VB	0.2184	1.39175e4	953.14789	49.8897

**(R)-3-benzyl-5-methylene-4-(4-(trifluoromethoxy)phenyl)oxazolidin-2-one (3ga)**

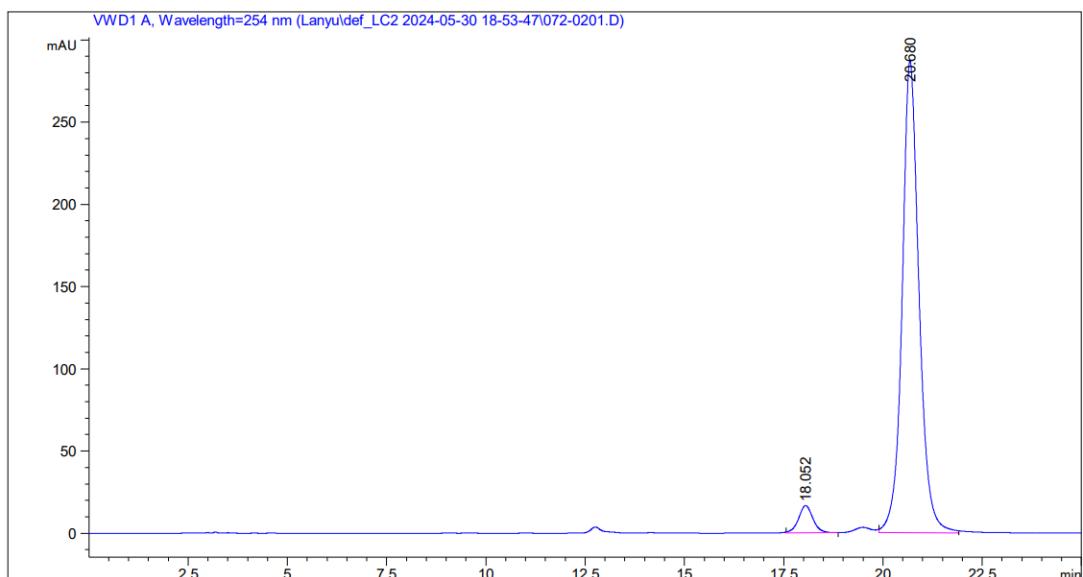
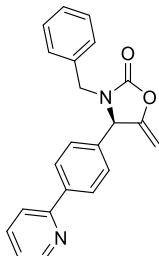


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.693	FM R	0.1692	511.99911	50.42985	4.6777
2	8.691	MF R	0.1926	1.04336e4	902.96021	95.3223

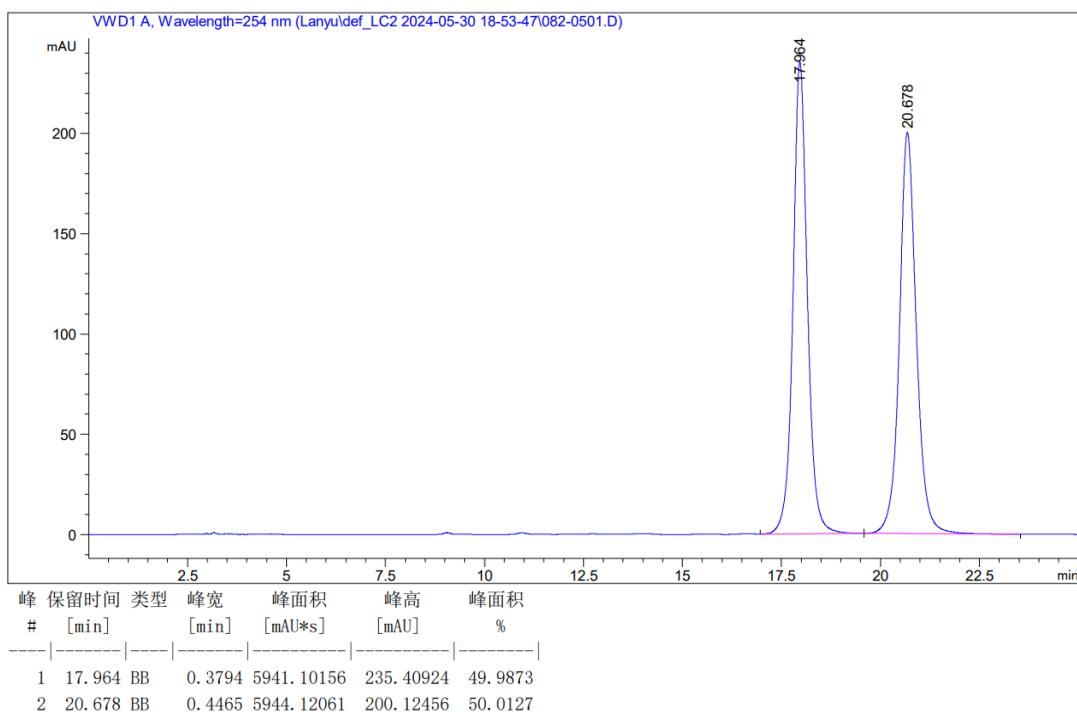


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.666	BB	0.1534	6344.62988	625.07703	49.9455
2	8.669	BV R	0.1717	6358.47412	556.62085	50.0545

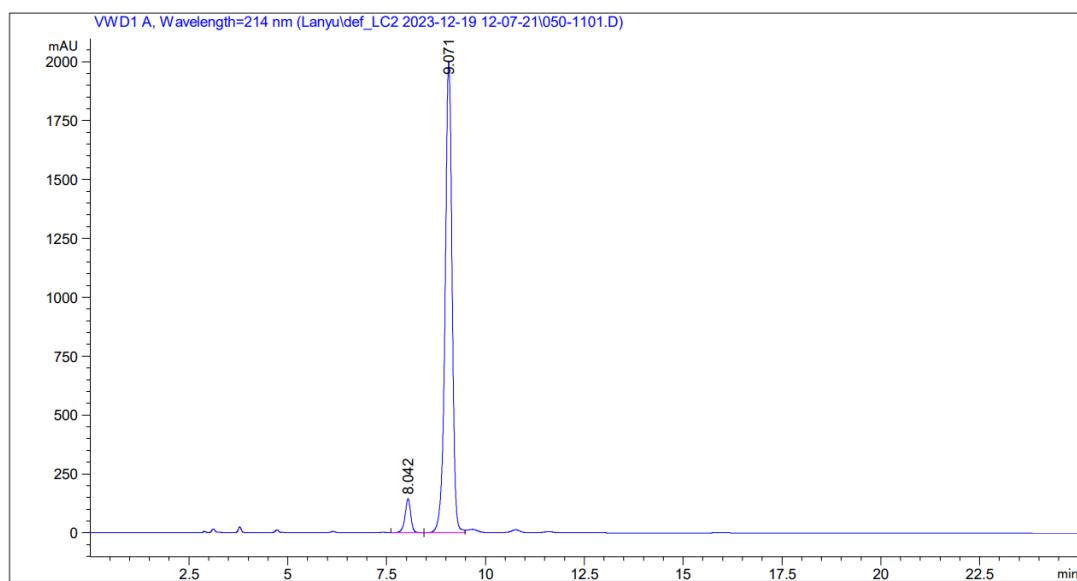
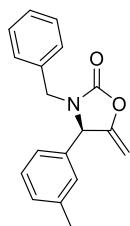
**(R)-3-benzyl-5-methylene-4-(4-(pyridin-2-yl)phenyl)oxazolidin-2-one (3ha)**



峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.052	FM R	0.4192	416.81735	16.57242	4.6862
2	20.680	MM R	0.4923	8477.68750	286.98917	95.3138

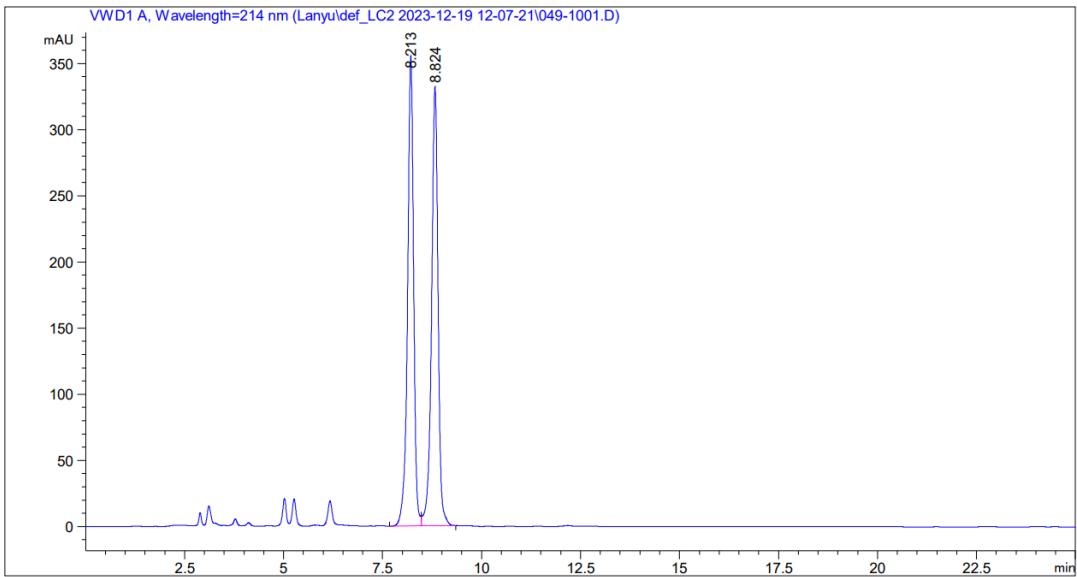


**(R)-3-benzyl-5-methylene-4-(m-tolyl)oxazolidin-2-one (3ia)**

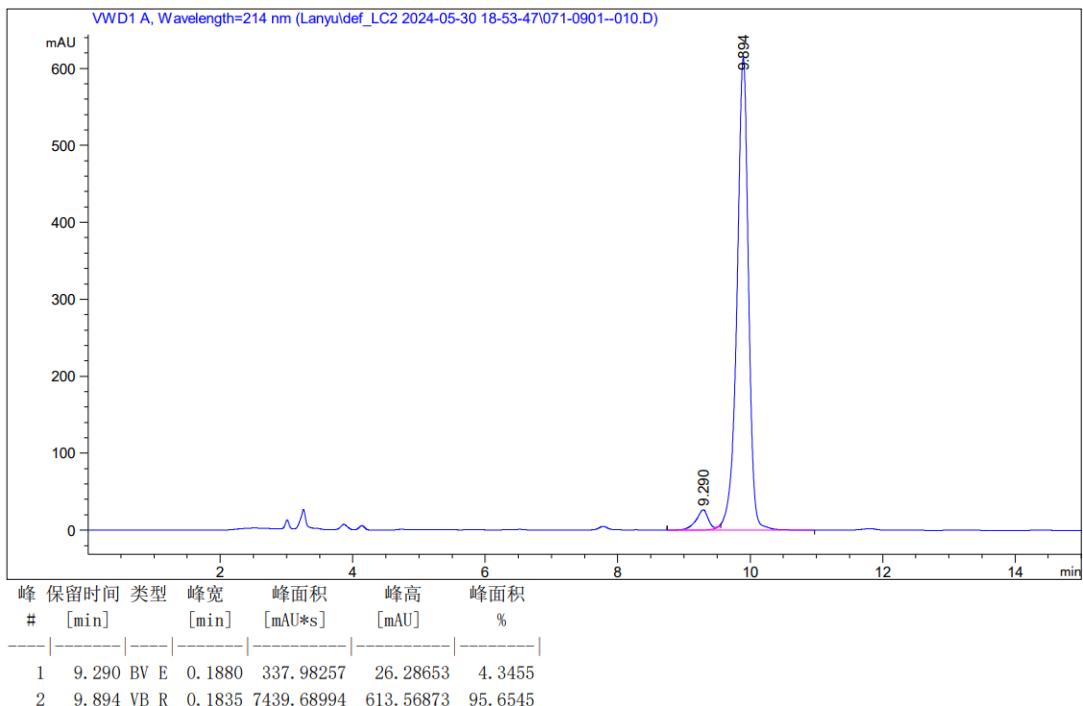
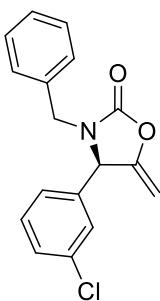


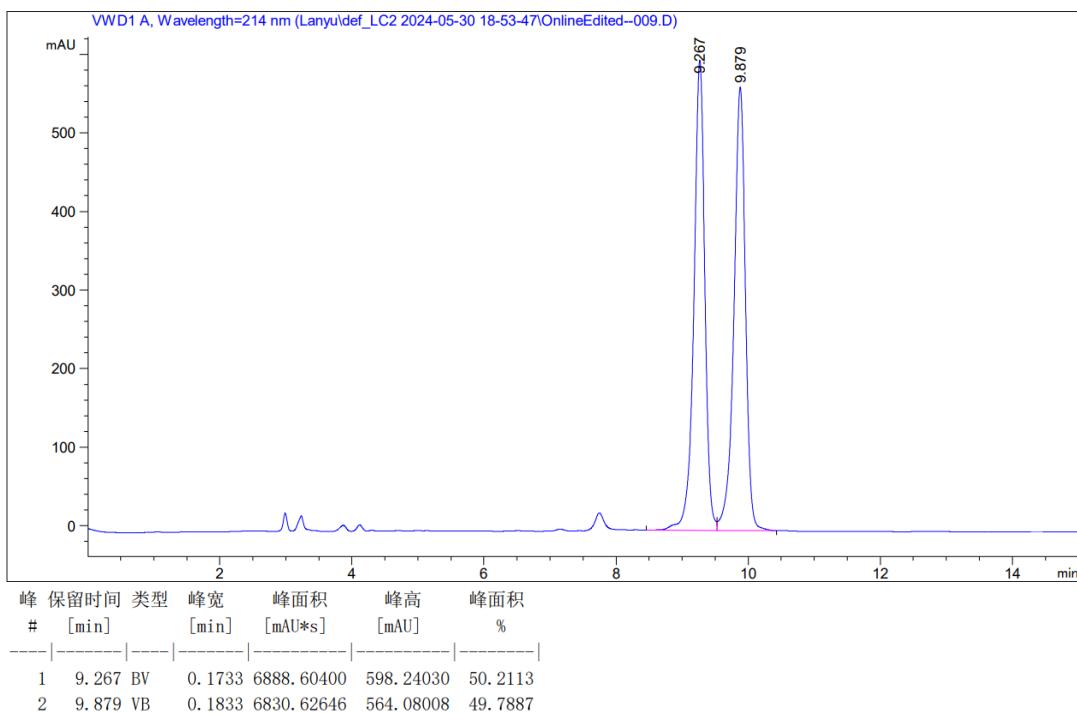
峰 保留时间 类型 峰宽 峰面积 峰高 峰面积  
# [min] [min] [mAU\*s] [mAU] %

#	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.042	BB	0.1532	1457.87207	143.84801	5.6040
2	9.071	MF R	0.2048	2.45569e4	1998.23279	94.3960

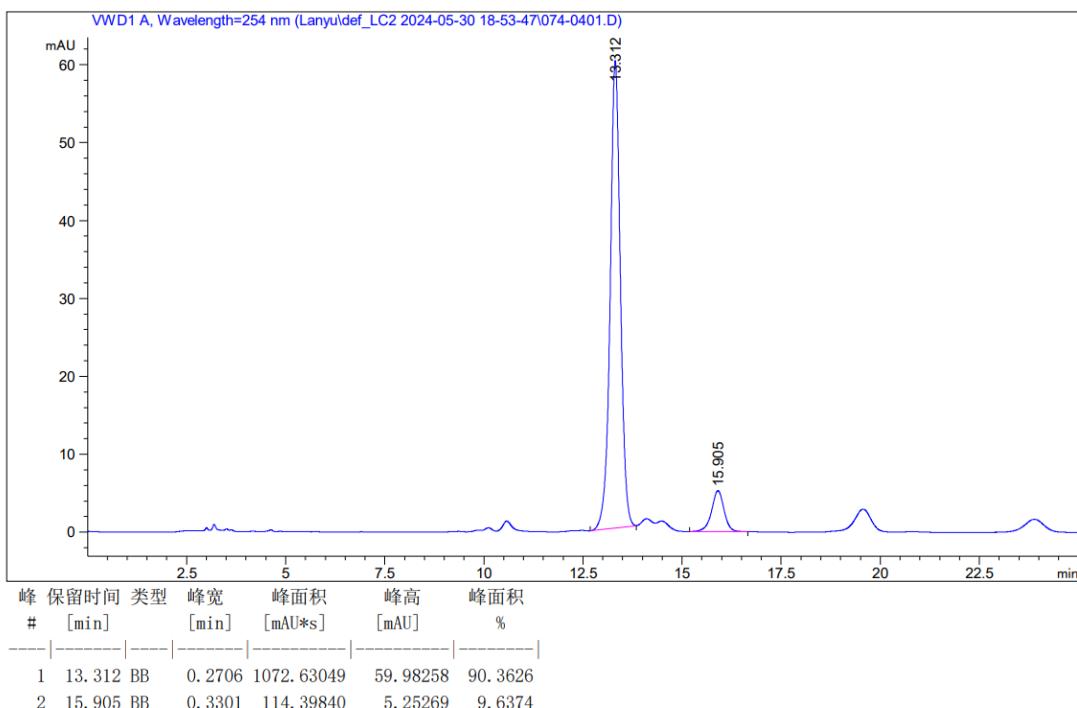
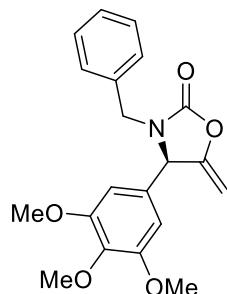


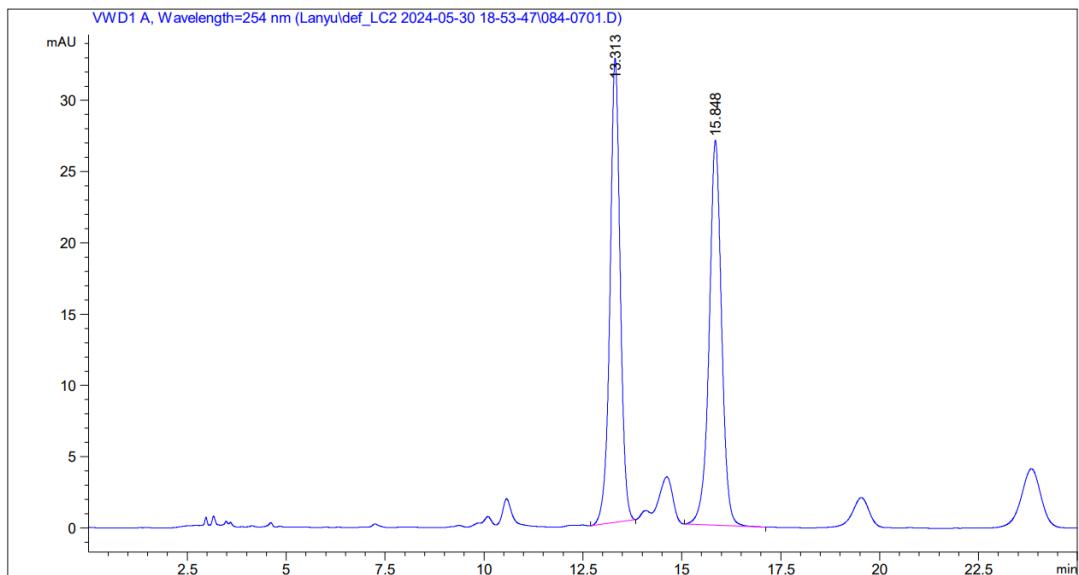
**(R)-3-benzyl-4-(3-chlorophenyl)-5-methyleneoxazolidin-2-one (3ja)**





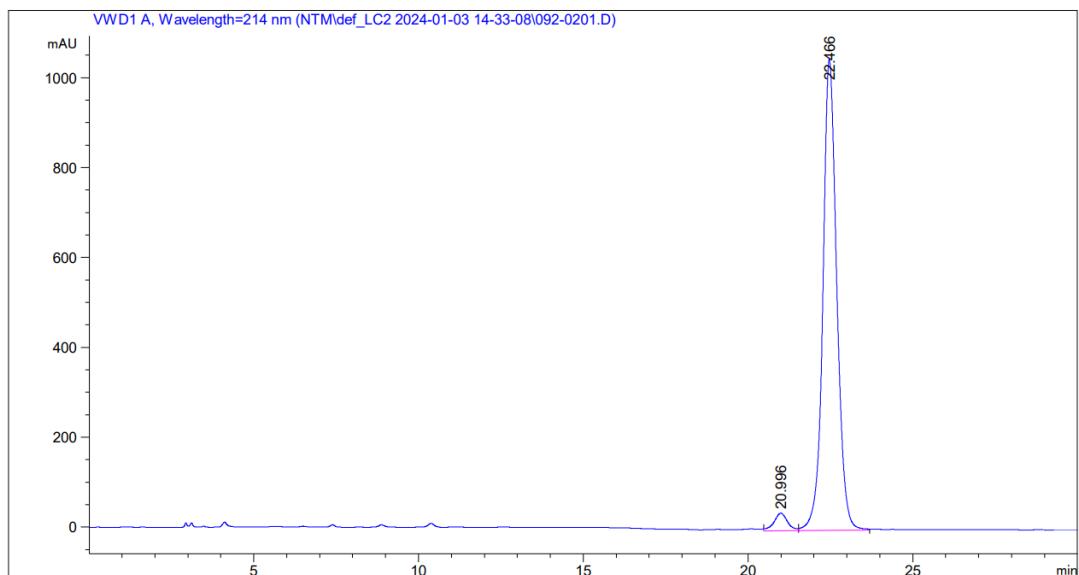
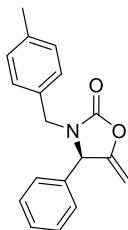
**(R)-3-benzyl-5-methylene-4-(3,4,5-trimethoxyphenyl)oxazolidin-2-one (3ka)**



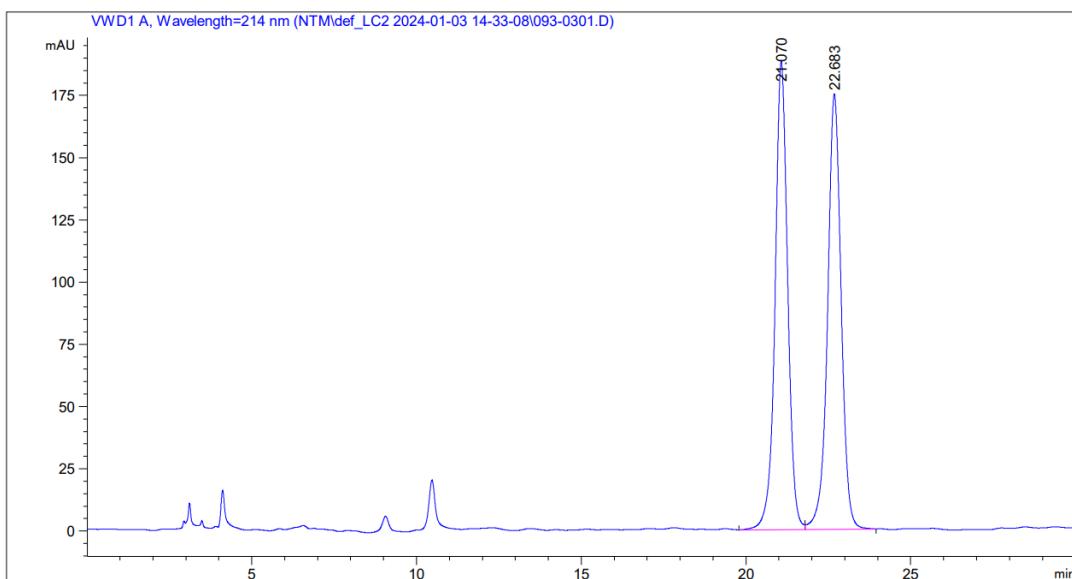


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.313	BB	0.2710	583.93384	32.59280	49.8085
2	15.848	BB	0.3302	588.42401	27.00689	50.1915

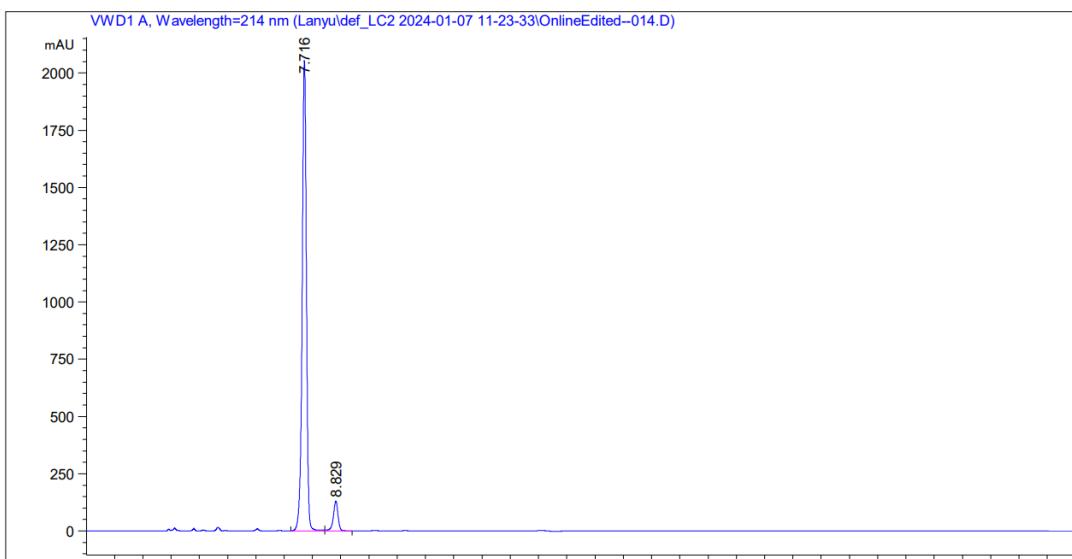
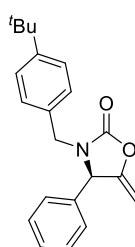
**(R)-3-(4-methylbenzyl)-5-methylene-4-phenyloxazolidin-2-one (3ab)**

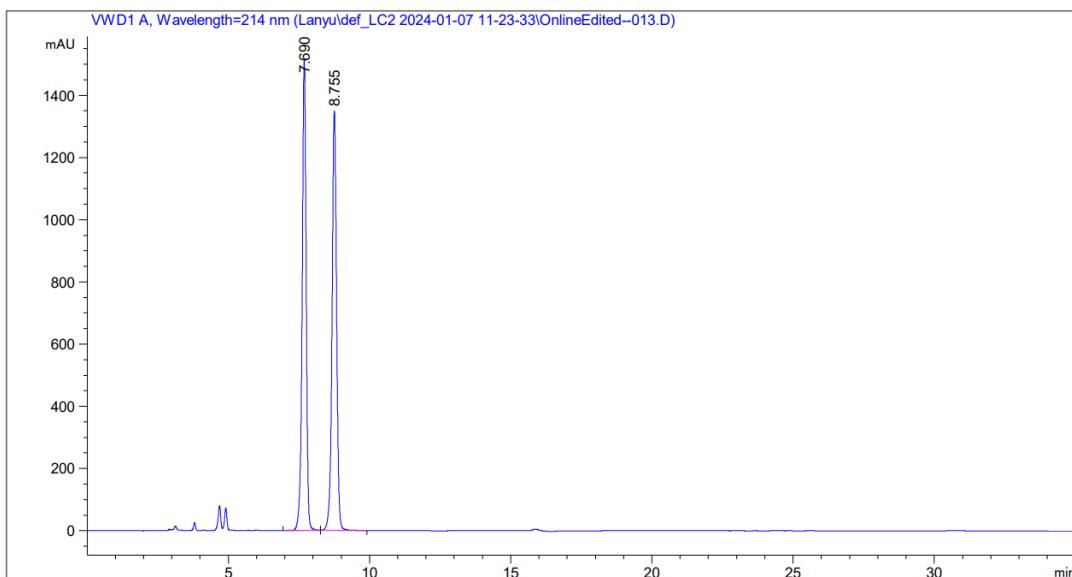


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.996	MF R	0.4787	1126.14514	39.21156	3.5460
2	22.466	FM R	0.4871	3.06320e4	1048.18481	96.4540

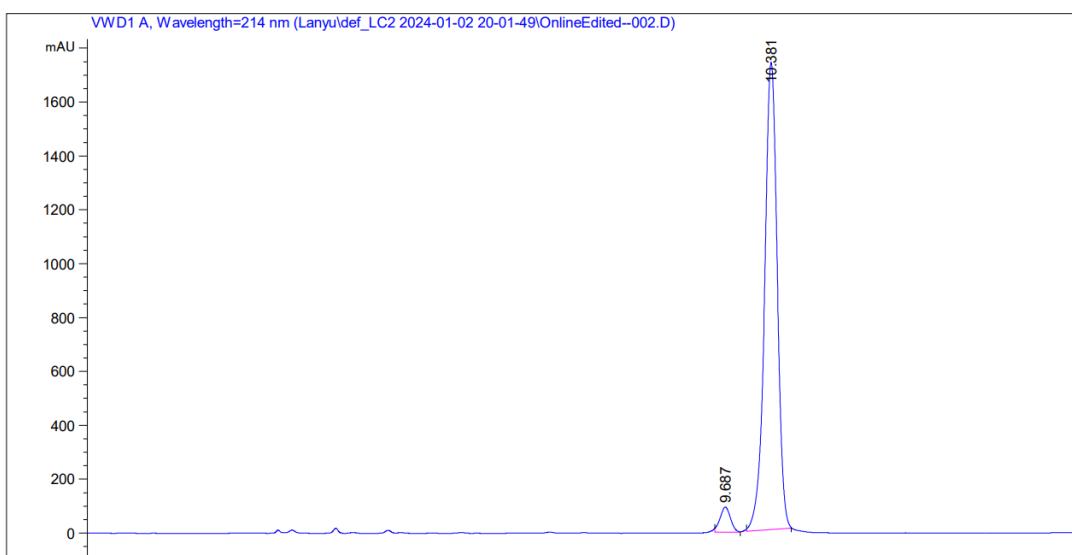
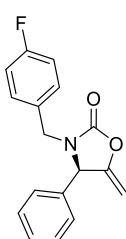


**(R)-3-(4-(tert-butyl)benzyl)-5-methylene-4-phenyloxazolidin-2-one (3ac)**

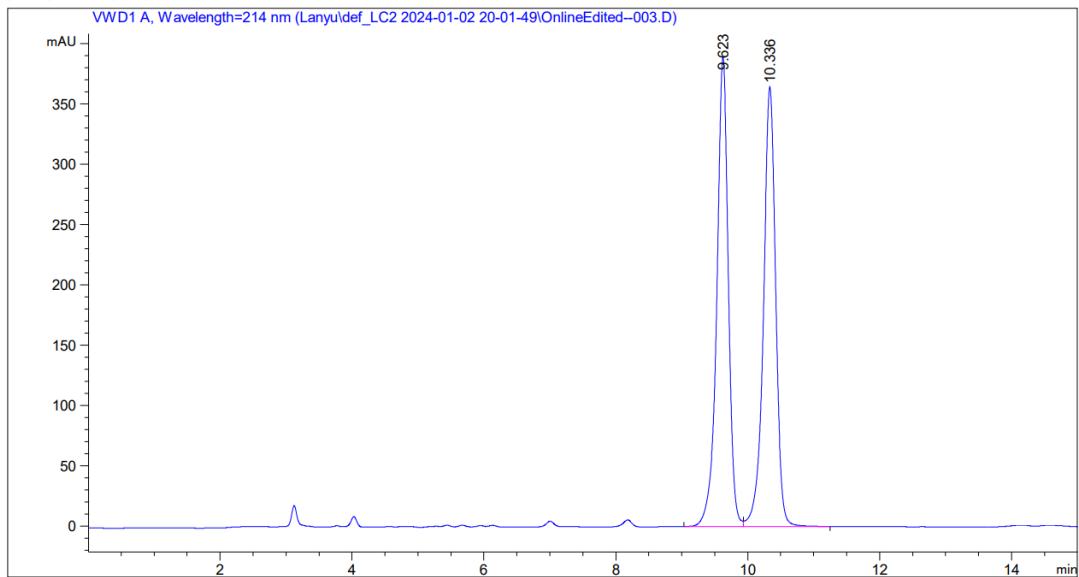




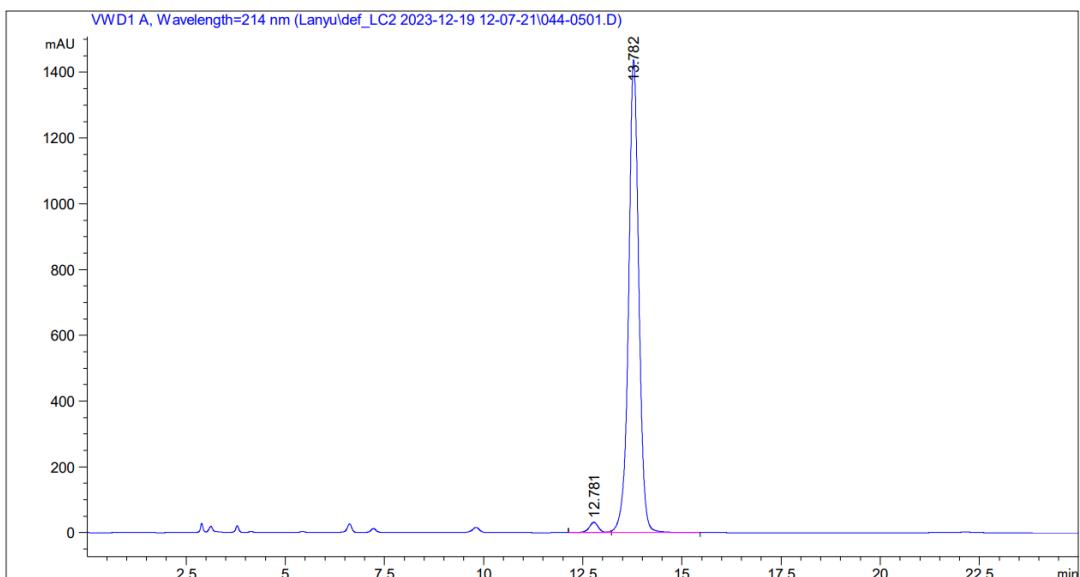
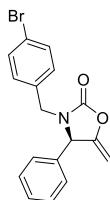
**(R)-3-(4-fluorobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3ad)**



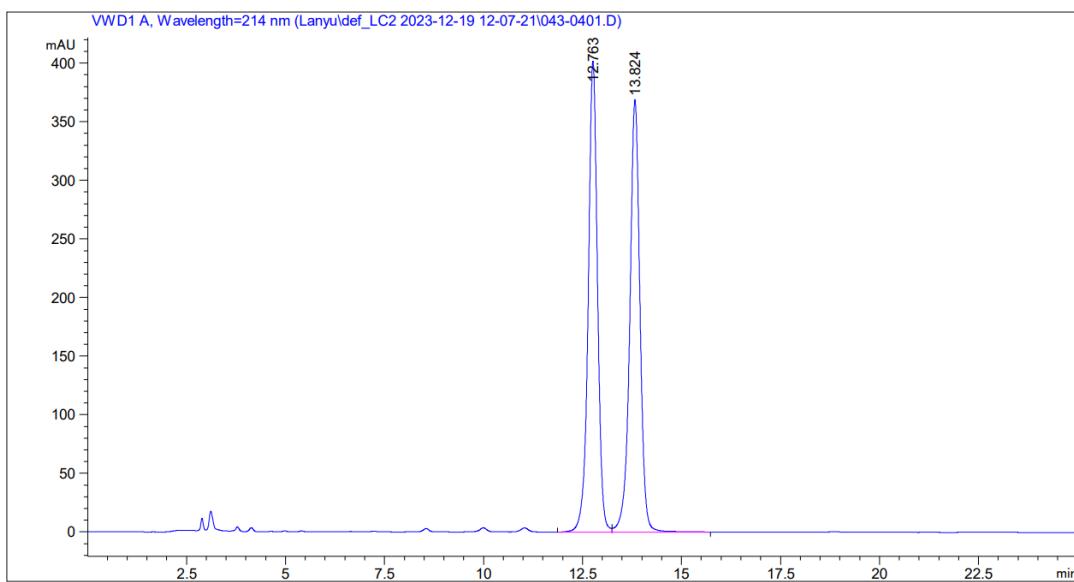
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.687	MM R	0.1830	1016.01324	92.54243	4.2305
2	10.381	MM R	0.2211	2.30003e4	1734.13989	95.7695



**(R)-3-(4-bromobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3ae)**

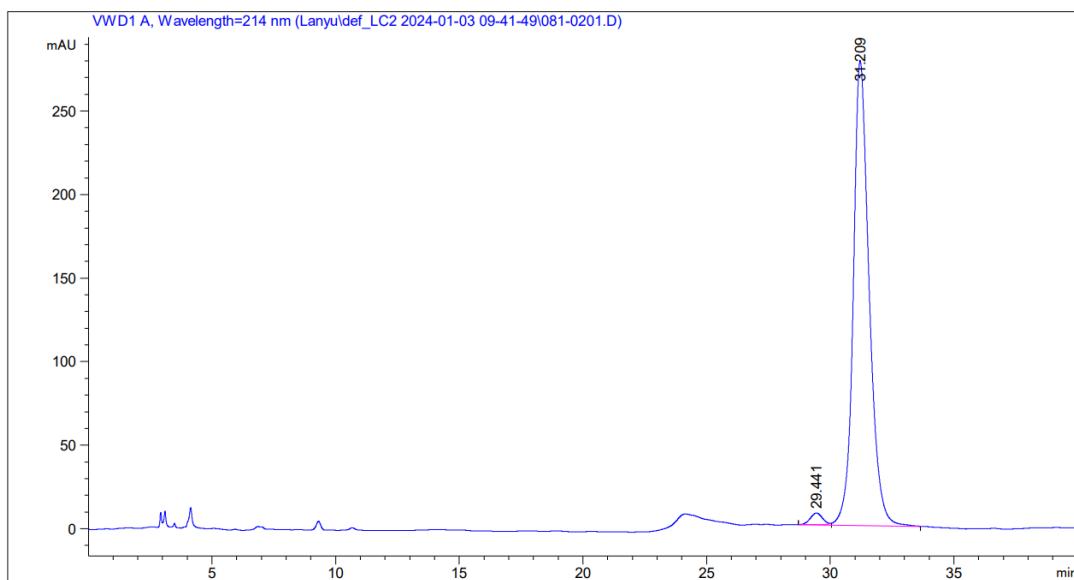
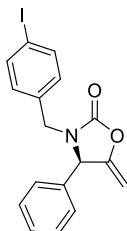


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.781	BV E	0.2471	511.35703	31.38836	1.9448
2	13.782	VB R	0.2713	2.57822e4	1437.10278	98.0552

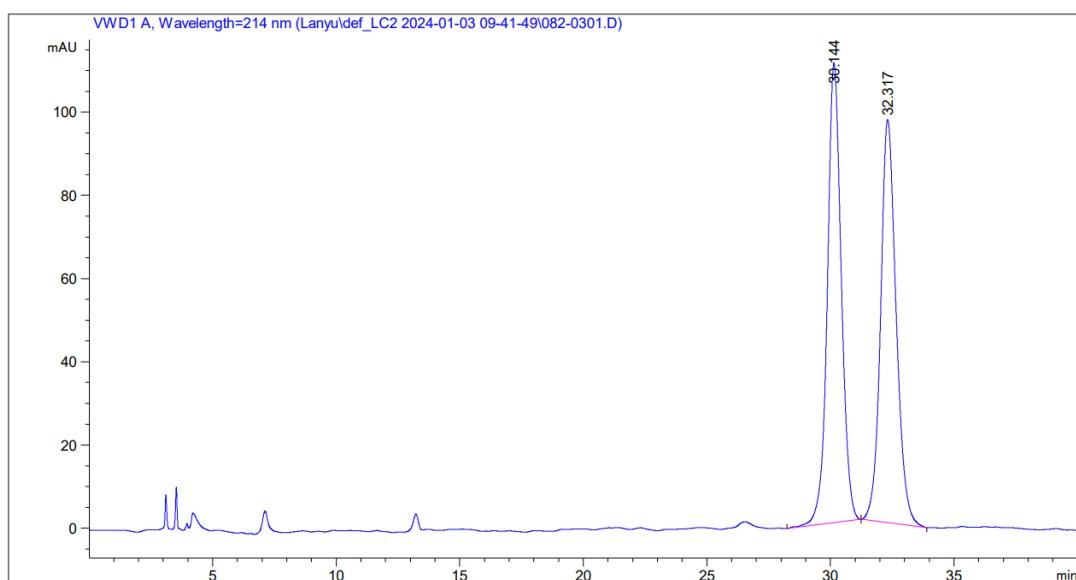


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.763	BV	0.2472	6551.87891	401.98462	49.8397
2	13.824	VB	0.2705	6594.01904	368.88678	50.1603

**(R)-3-(4-iodobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3af)**

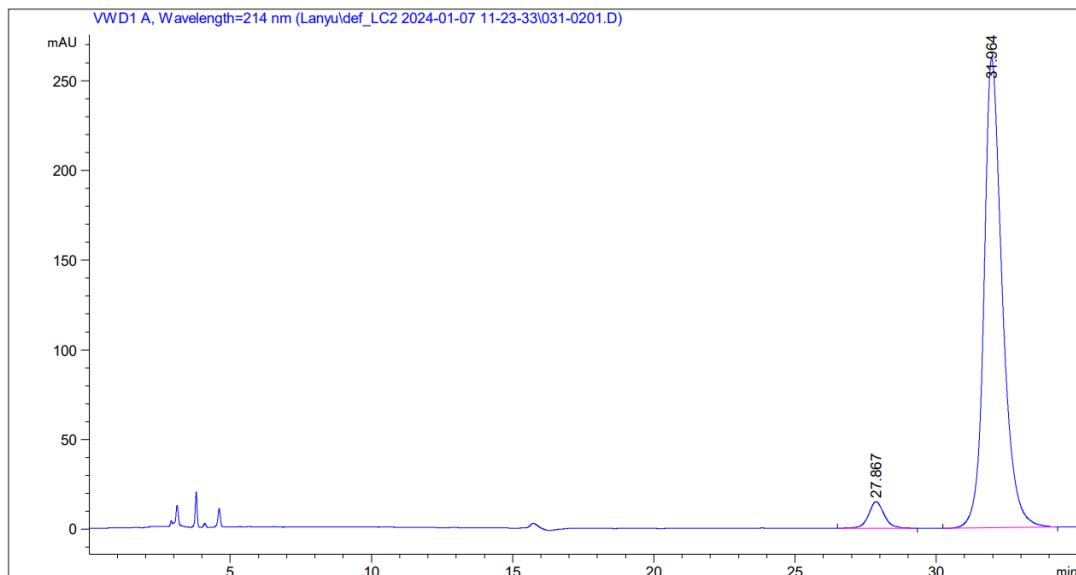
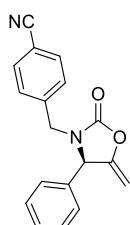


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	29.441	BV E	0.5206	237.53252	7.07749	1.8813
2	31.209	VB R	0.6664	1.23882e4	278.23956	98.1187

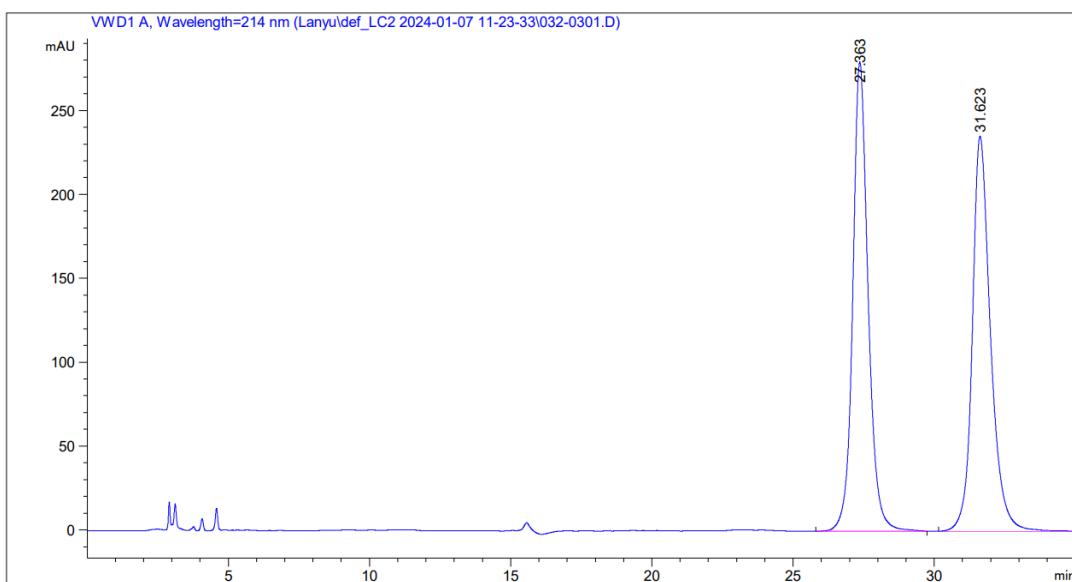


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	30.144	BB	0.5952	4329.61084	110.47592	50.6211
2	32.317	BB	0.6575	4223.36865	96.89544	49.3789

**(R)-4-((5-methylene-2-oxo-4-phenyloxazolidin-3-yl)methyl)benzonitrile (3ag)**

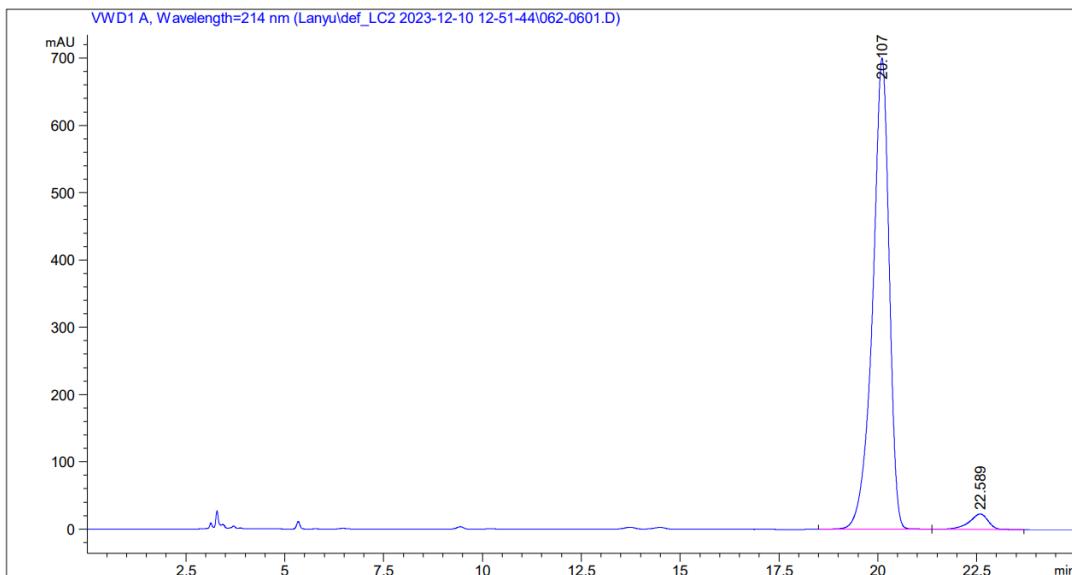
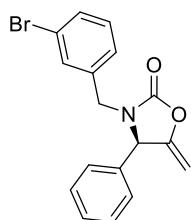


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	27.867	BB	0.5806	575.77472	14.80778	4.6406
2	31.964	BB	0.6774	1.18315e4	261.73975	95.3594

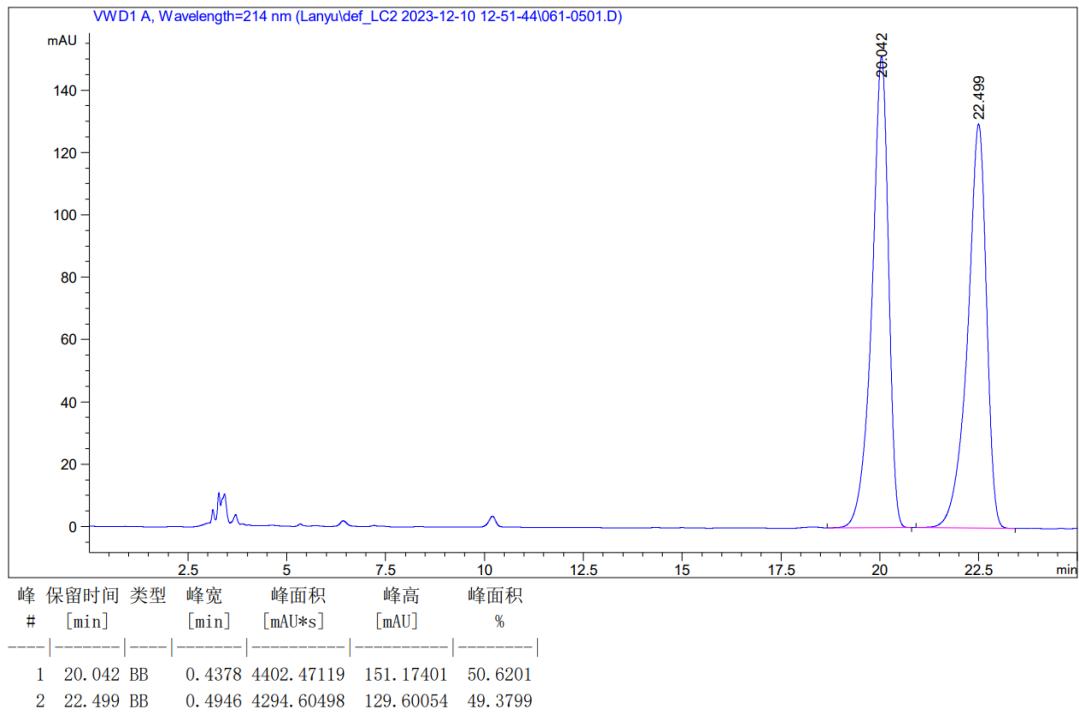


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	27.363	BB	0.5649	1.05433e4	279.64755	49.9882
2	31.623	BBA	0.6688	1.05483e4	235.40474	50.0118

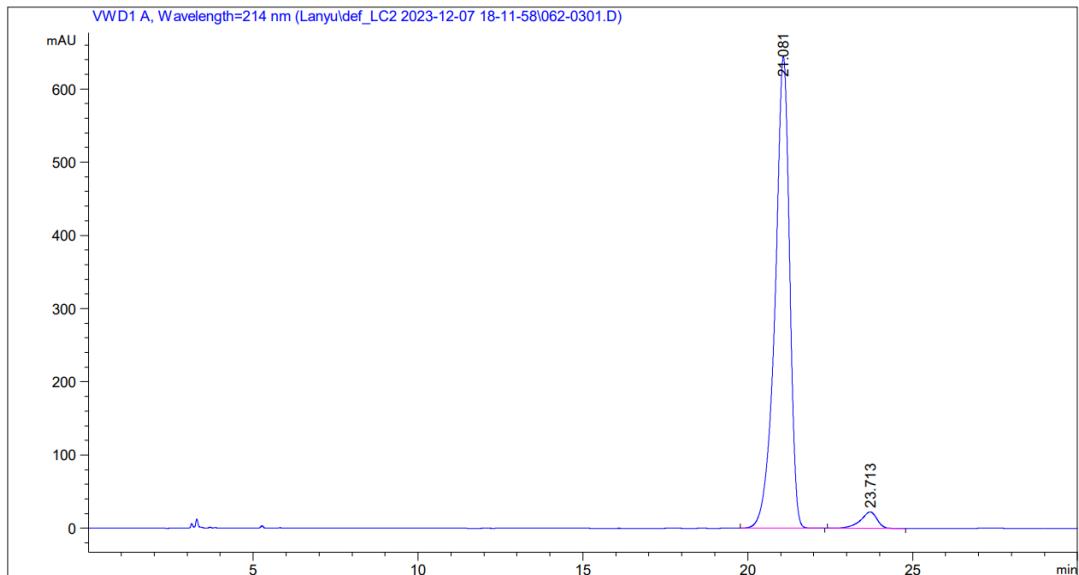
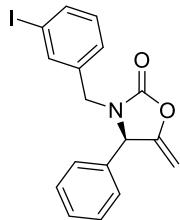
### (R)-3-(3-bromobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3ah)



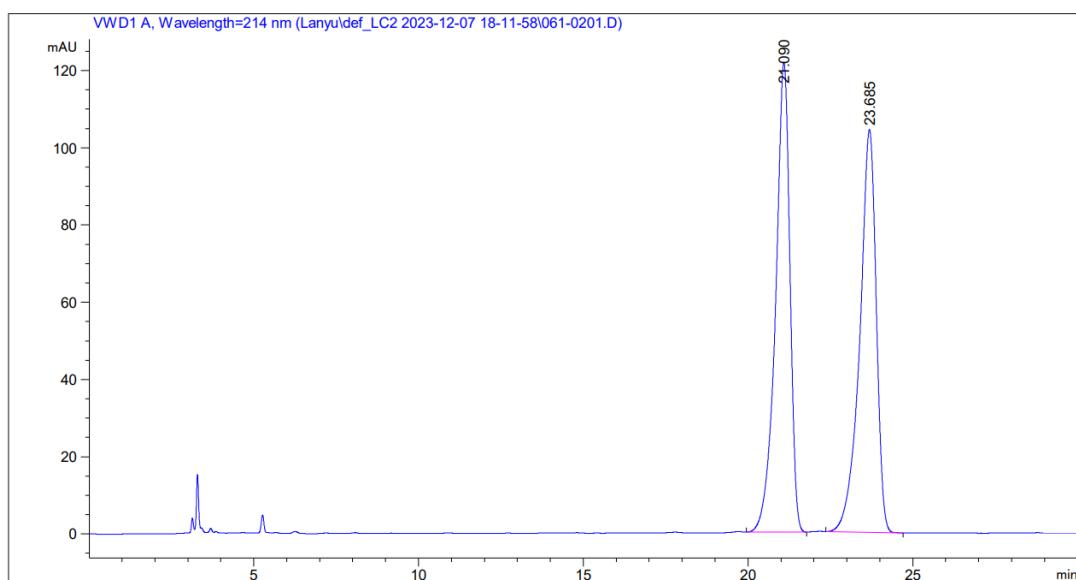
峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.107	BB	0.4350	2.03459e4	700.22131	96.4444
2	22.589	BB	0.4896	750.09082	22.87080	3.5556



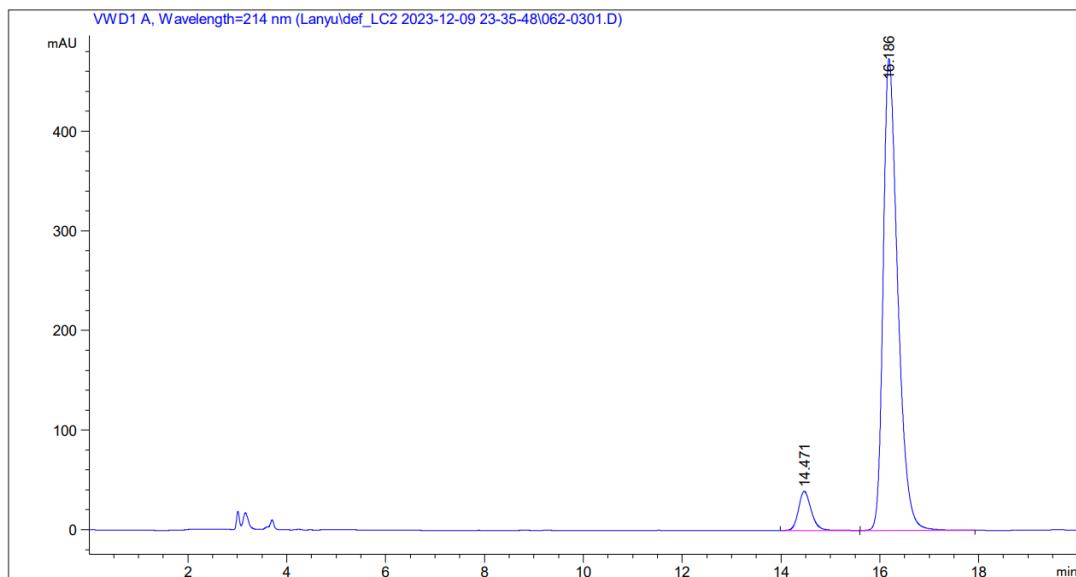
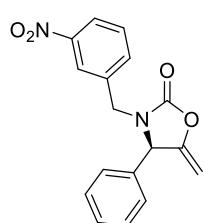
### (R)-3-(3-iodobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3ai)



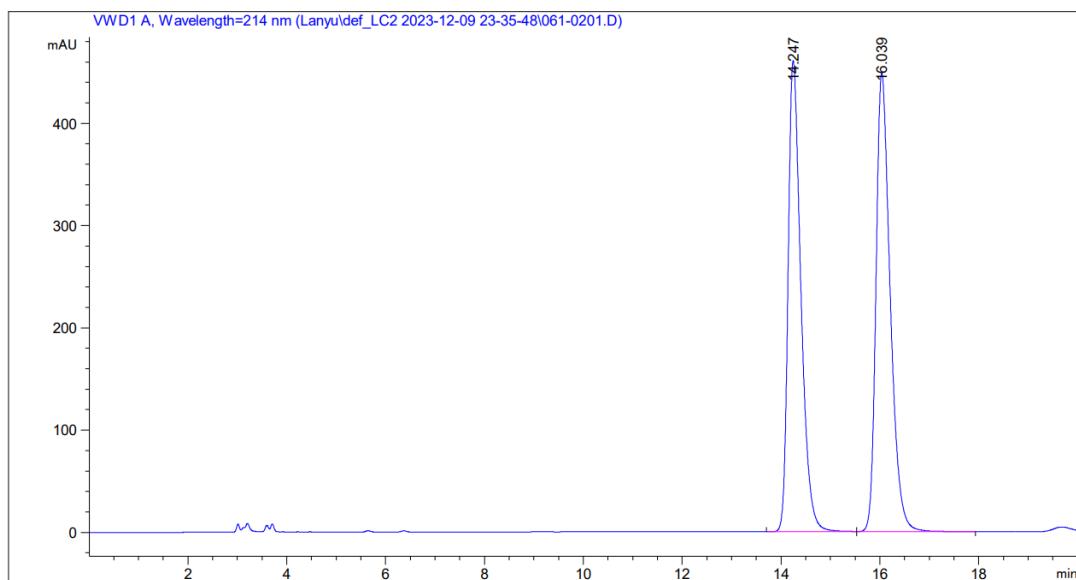
峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	21.081	BB	0.4570	1.96741e4	644.75323	96.2050
2	23.713	BB	0.5188	776.07581	22.31061	3.7950



**(R)-5-methylene-3-(3-nitrobenzyl)-4-phenyloxazolidin-2-one (3aj)**

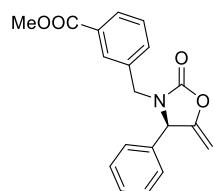


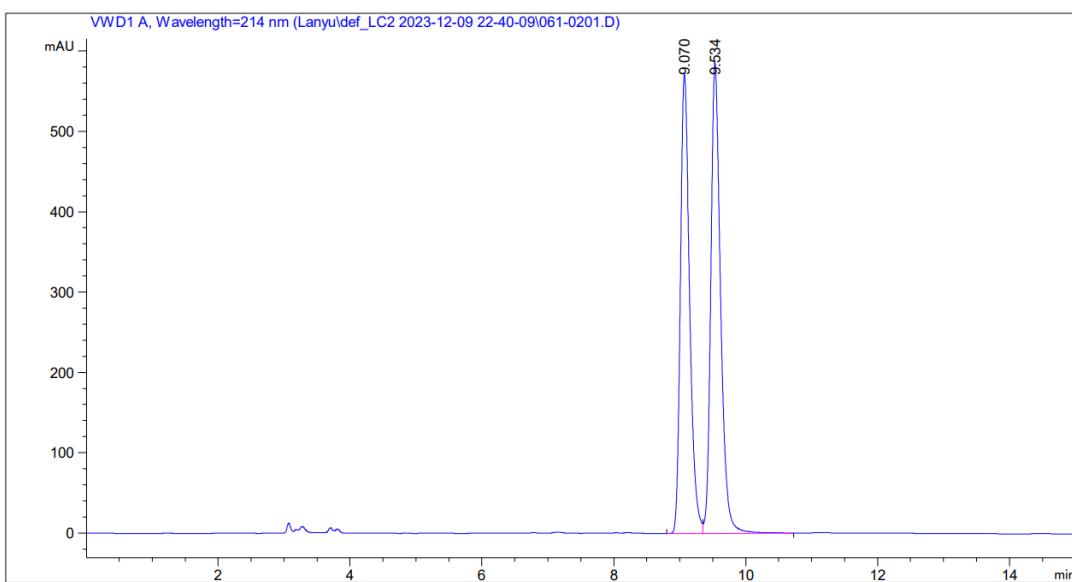
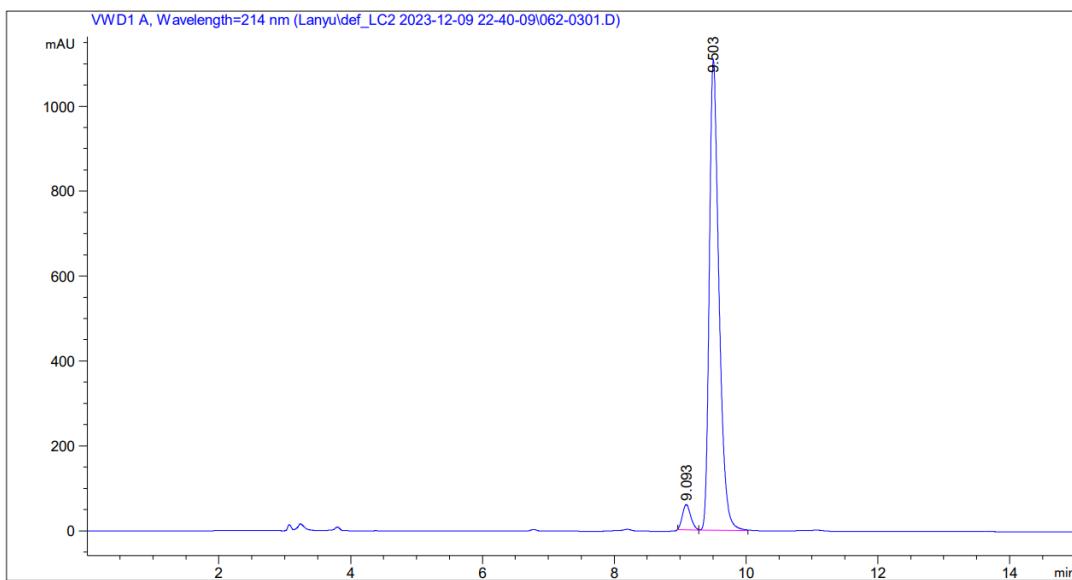
峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.471	BB	0.2724	702.37628	39.32718	6.7620
2	16.186	BB	0.3107	9684.80176	473.29517	93.2380



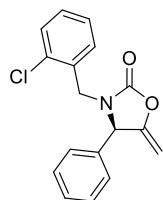
峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.247	BB	0.2739	8289.07422	460.76013	48.1429
2	16.039	BB	0.3023	8928.58887	448.48407	51.8571

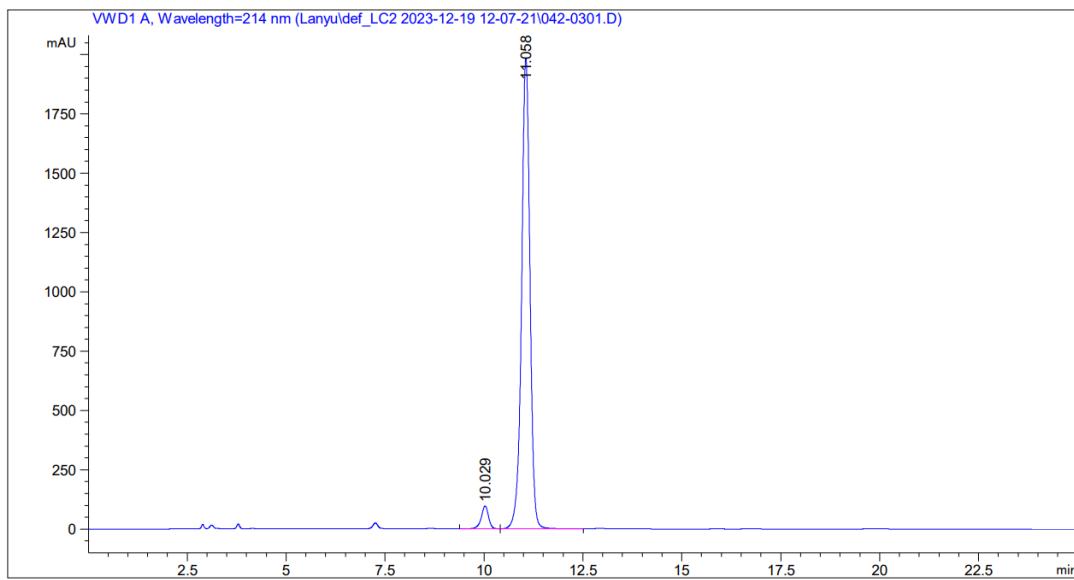
### (R)-methyl 3-((5-methylene-2-oxo-4-phenyloxazolidin-3-yl)methyl)benzoate (3ak)



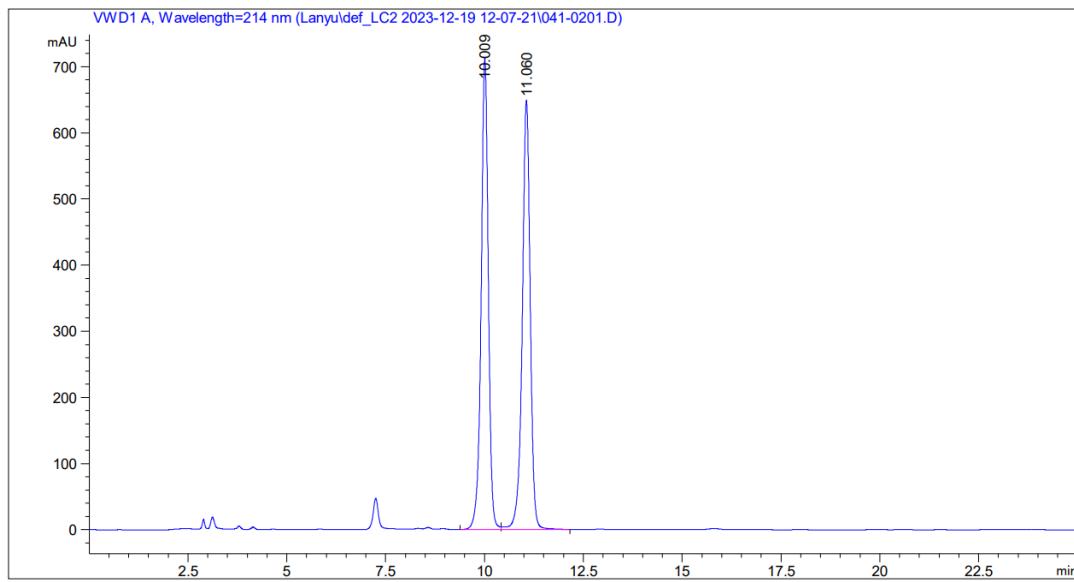


### (R)-3-(2-chlorobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3al)



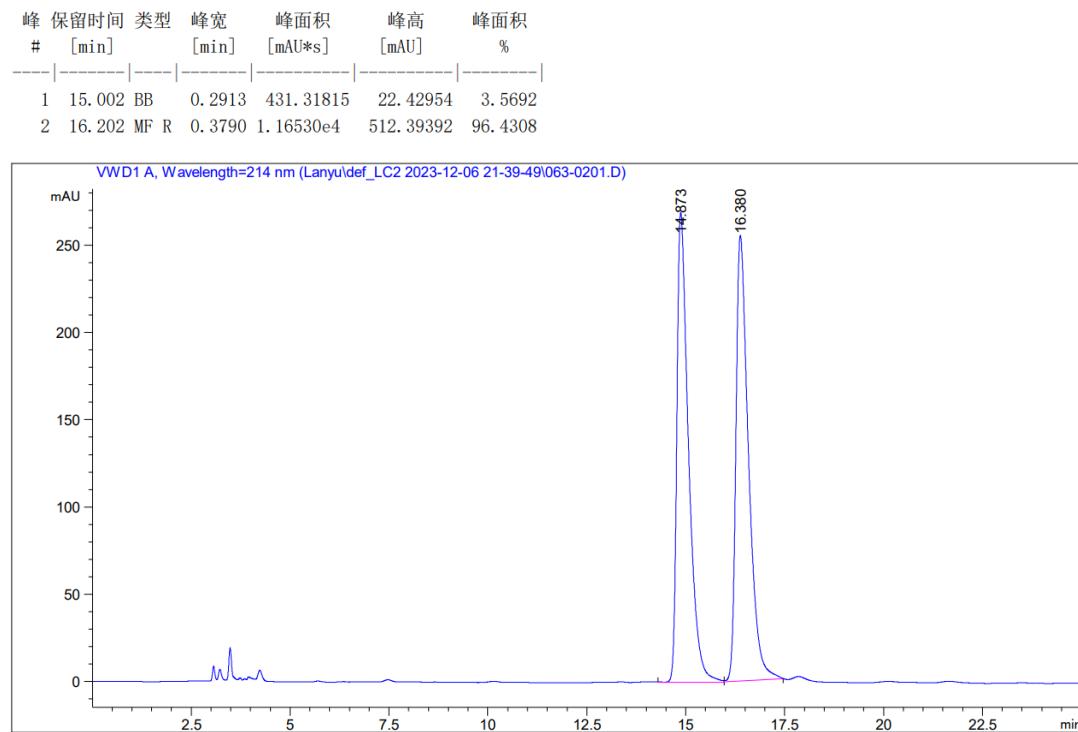
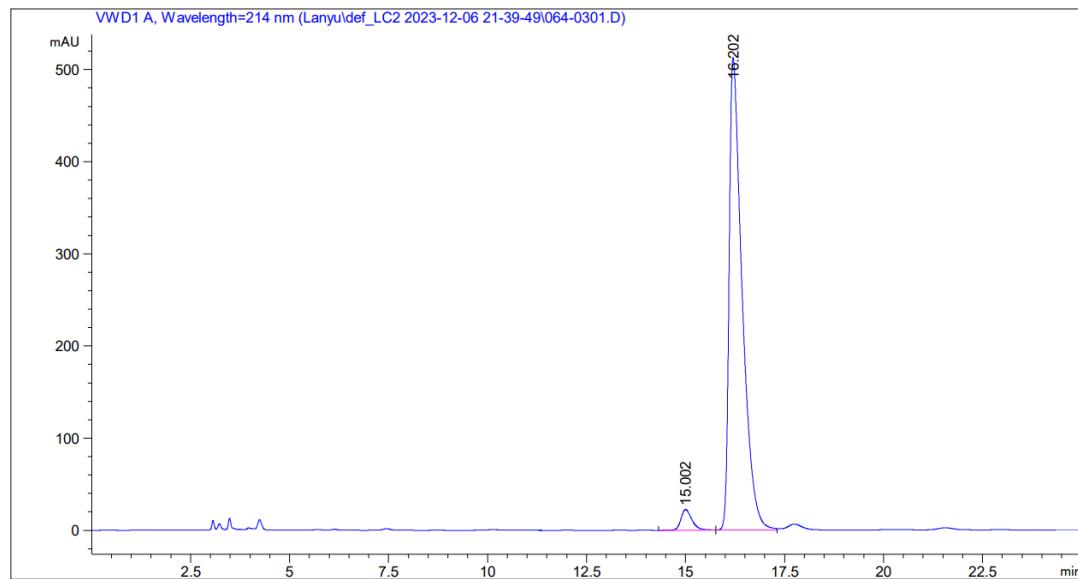
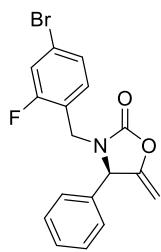


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.029	BV	0.1948	1256.00537	97.18166	4.1132
2	11.058	VB	0.2263	2.92801e4	1982.40100	95.8868

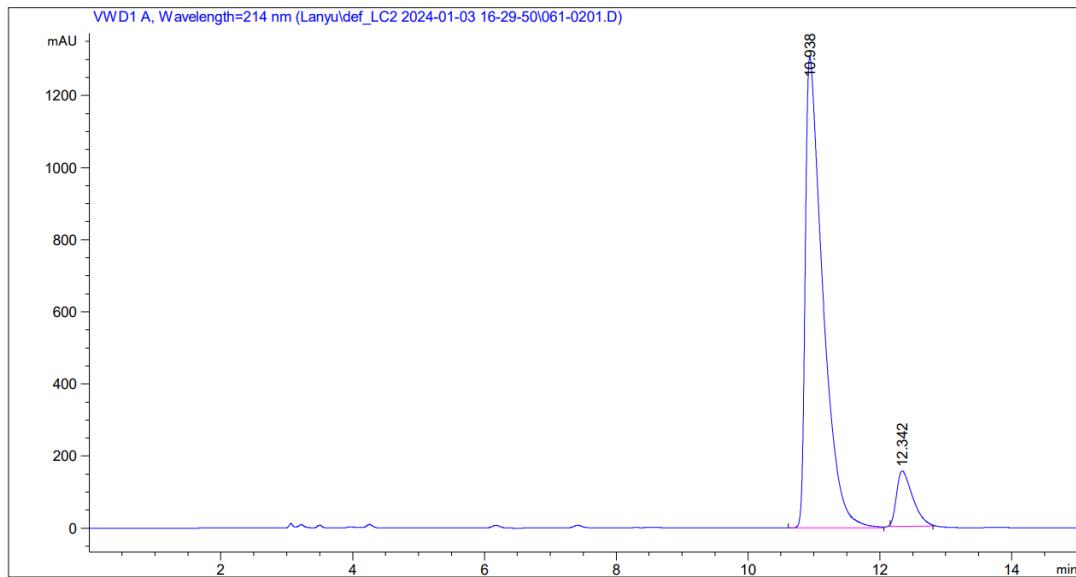
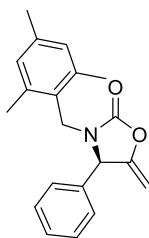


峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.009	BV	0.1914	9008.46582	713.01178	49.7543
2	11.060	VB	0.2126	9097.45020	648.87683	50.2457

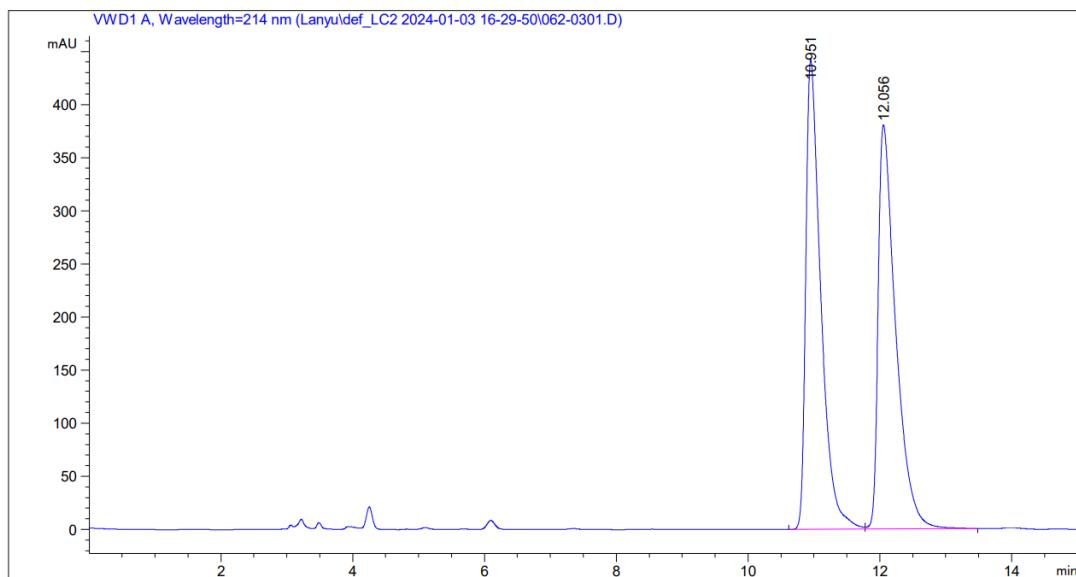
**(R)-3-(4-bromo-2-fluorobenzyl)-5-methylene-4-phenyloxazolidin-2-one (3am)**



### (R)-5-methylene-4-phenyl-3-(2,4,6-trimethylbenzyl)oxazolidin-2-one (3an)

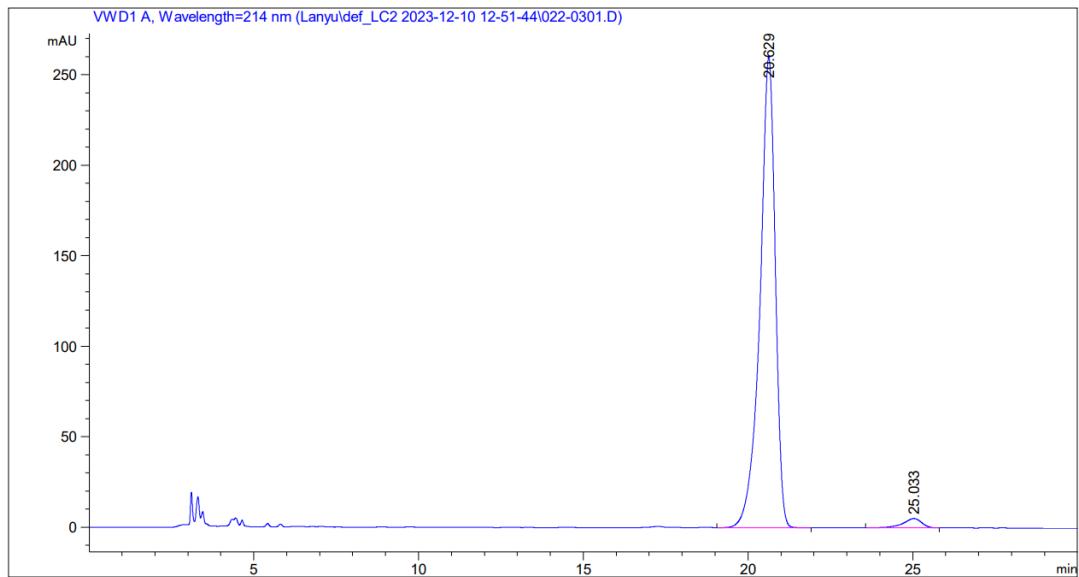
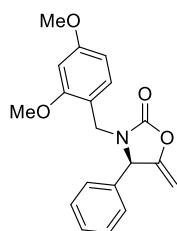


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.938	BV	0.2696	2.41694e4	1307.65393	90.3091
2	12.342	MM R	0.2812	2593.57422	153.69717	9.6909

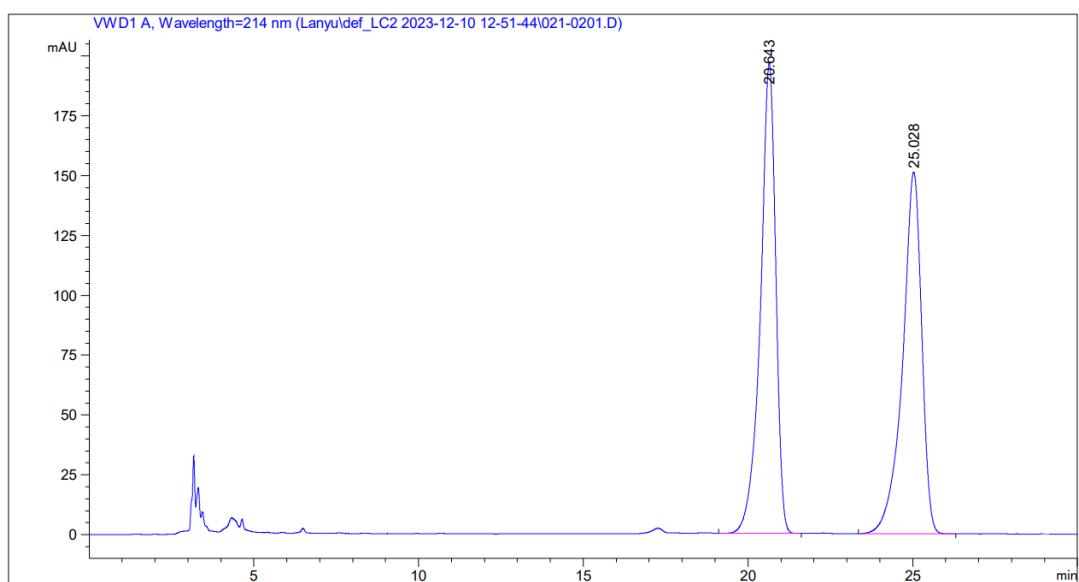


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.951	BV	0.2360	7019.07422	442.56430	49.9387
2	12.056	VB	0.2707	7036.29492	380.57446	50.0613

### (R)-3-(2,4-dimethoxybenzyl)-5-methylene-4-phenyloxazolidin-2-one (3ao)

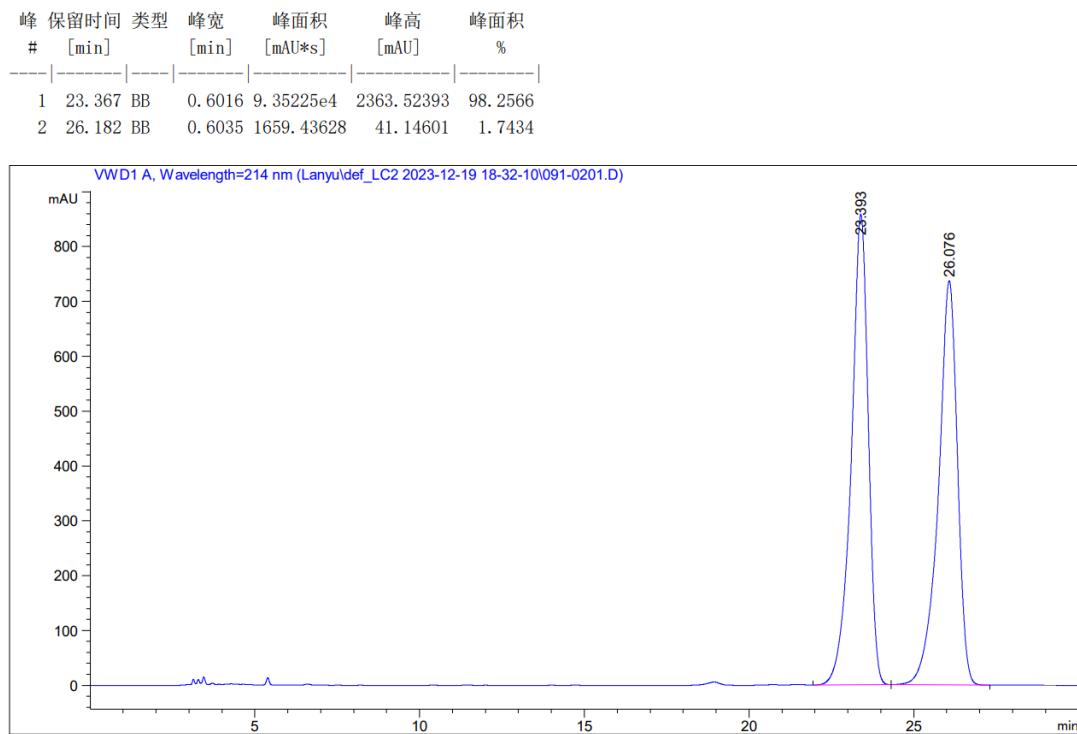
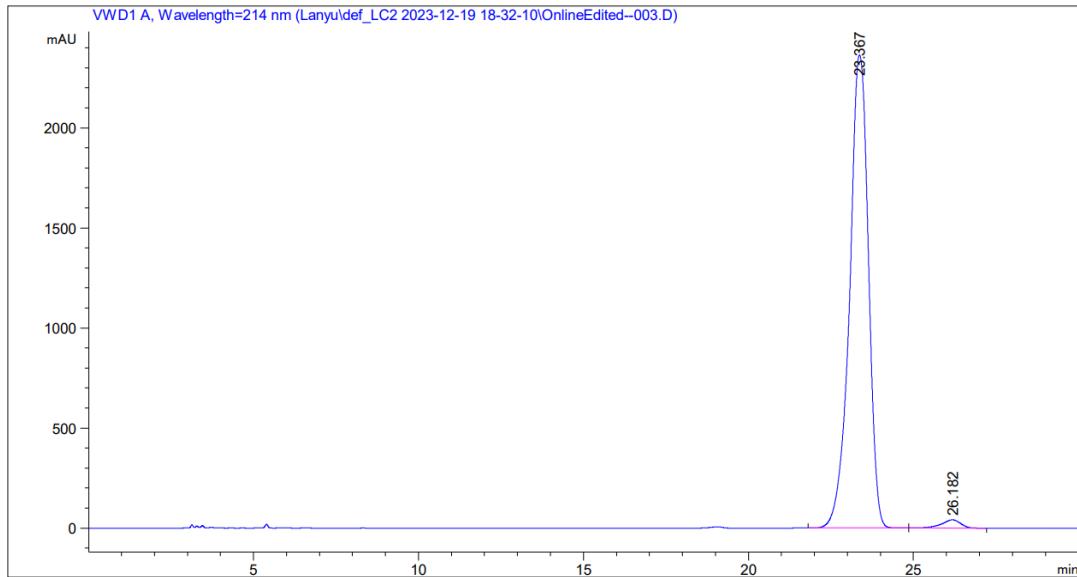
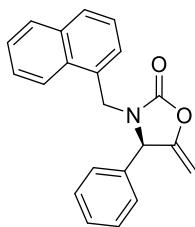


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.629	BB	0.4823	8414.57227	260.16025	97.5748
2	25.033	BB	0.5941	209.13828	5.19030	2.4252

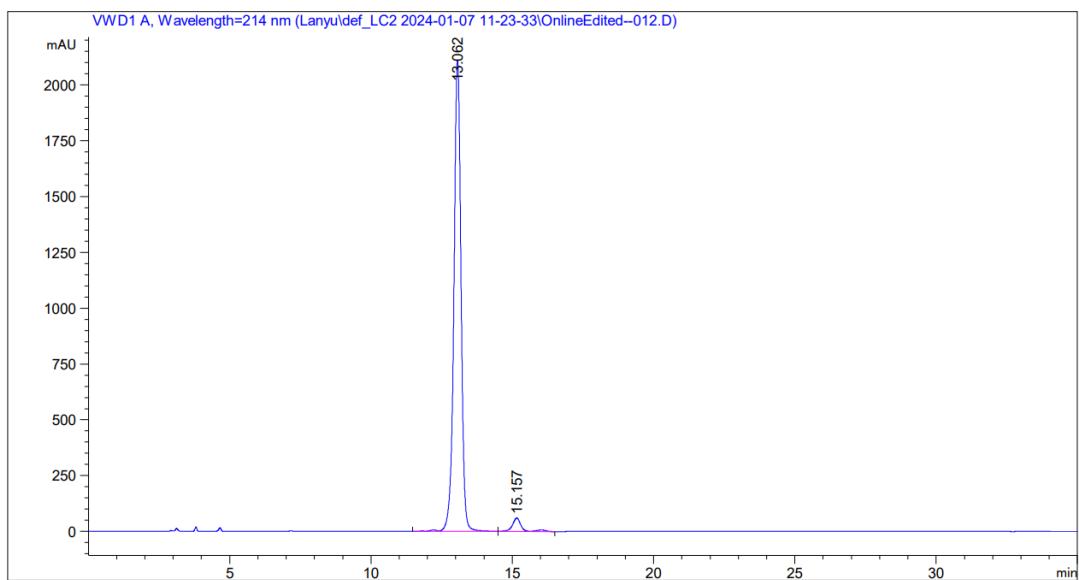
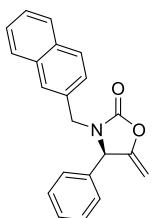


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.643	BB	0.4845	6356.66455	196.44385	51.0715
2	25.028	BB	0.6012	6089.93799	151.09442	48.9285

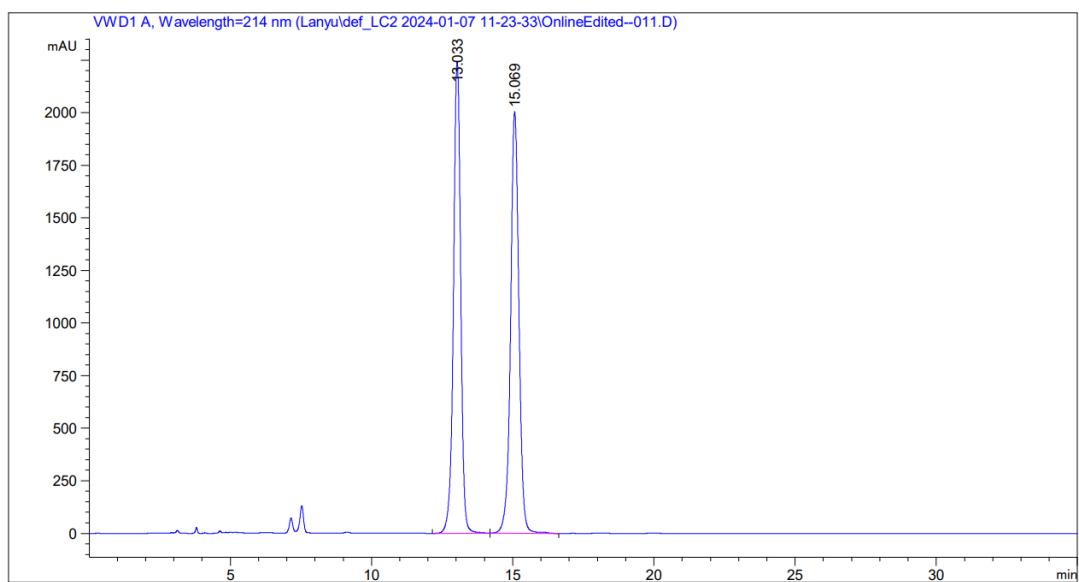
### (R)-5-methylene-3-(naphthalen-1-ylmethyl)-4-phenyloxazolidin-2-one (3ap)



**(R)-5-methylene-3-(naphthalen-2-ylmethyl)-4-phenyloxazolidin-2-one (3aq)**

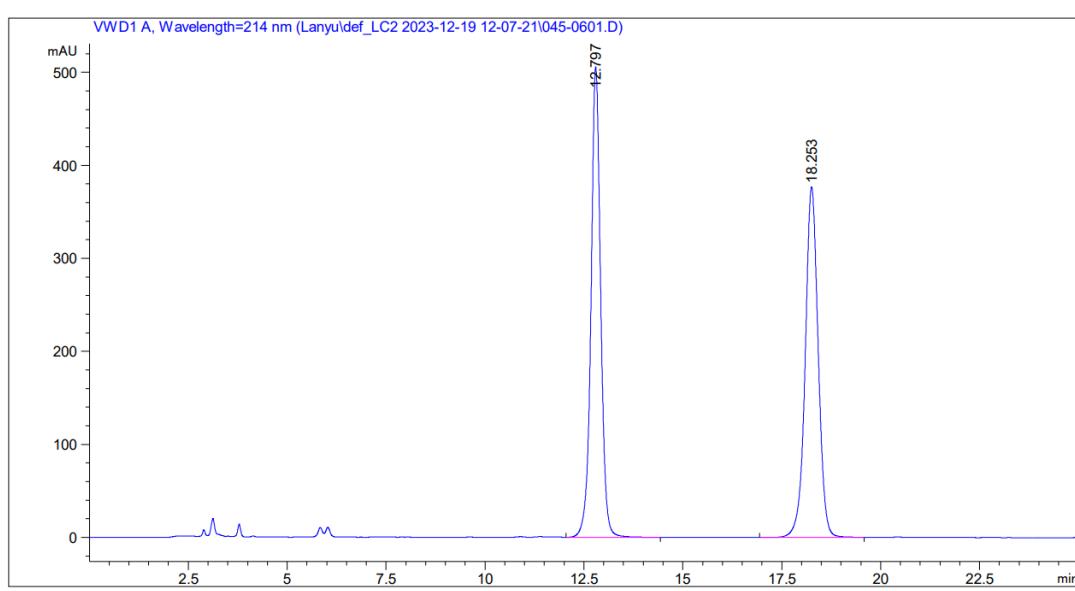
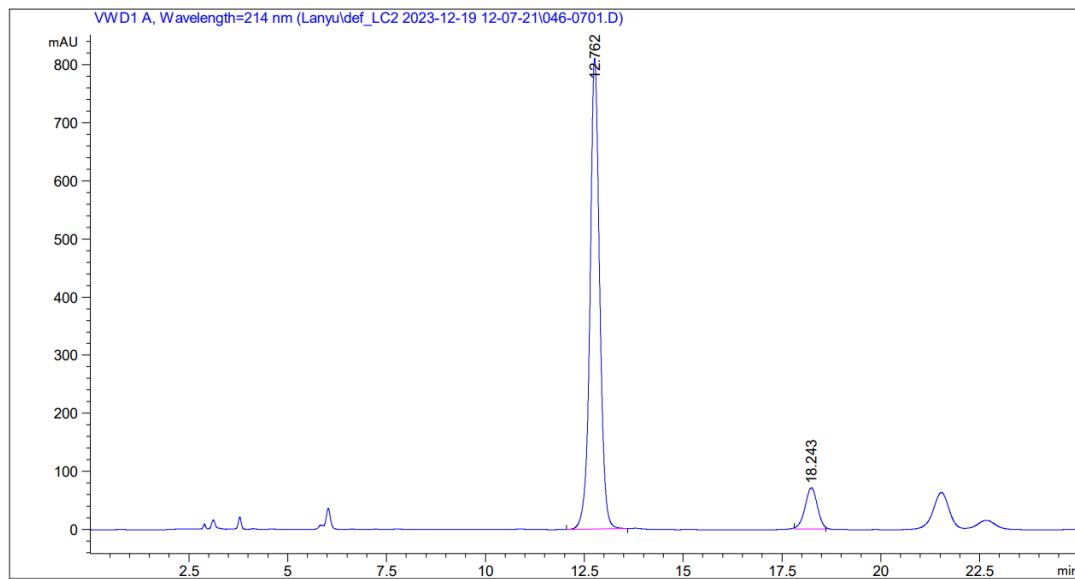
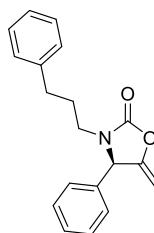


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.062	VB R	0.2684	3.70858e4	2109.12183	96.5330
2	15.157	BV R	0.2942	1331.94995	59.70985	3.4670

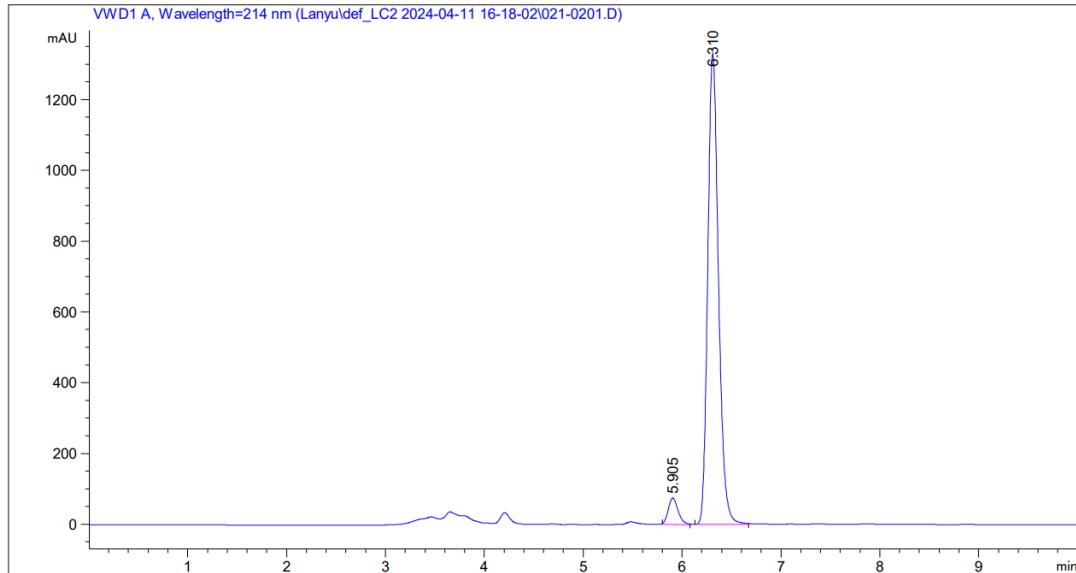
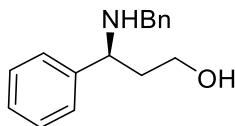


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.033	BB	0.2745	4.00639e4	2242.06665	49.3507
2	15.069	BV R	0.3130	4.11181e4	2004.08582	50.6493

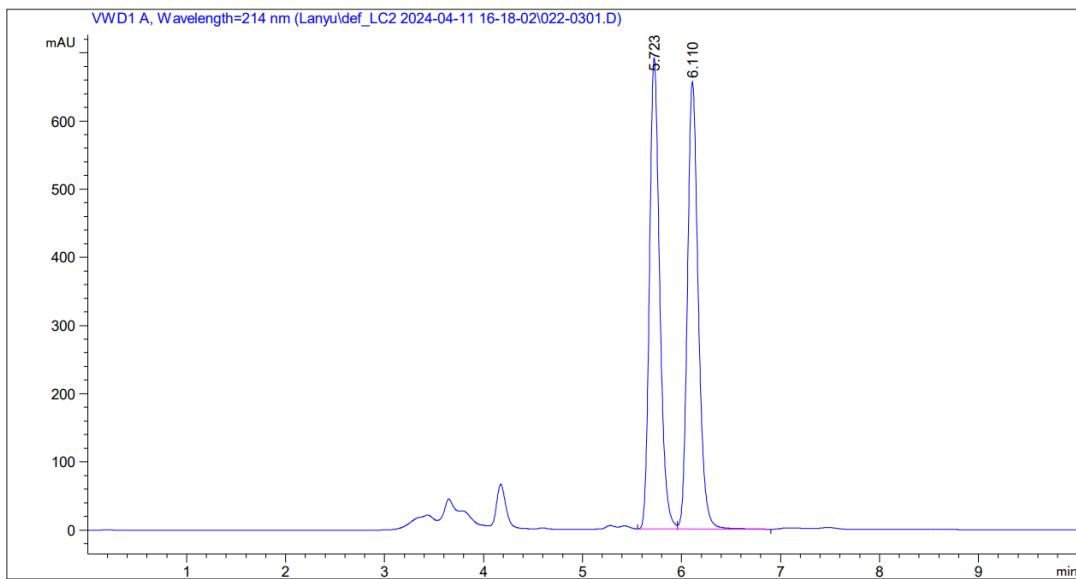
### (R)-5-methylene-4-phenyl-3-(3-phenylpropyl)oxazolidin-2-one (3ar)



### (R)-3-(benzylamino)-3-phenylpropan-1-ol (4aa)



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.905	MM	R	0.1158	516.09229	74.25692
2	6.310	MF	R	0.1254	1.00037e4	1330.09644



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %	
1	5.723	BV		0.1093	4931.73633	690.43823	49.6928
2	6.110	VB		0.1168	4992.70996	656.02411	50.3072

### (4*R*,5*R*)-3-benzyl-5-methyl-4-phenyloxazolidin-2-one (4ab)

