

## Supporting Information

For

### Facile Synthesis of Axially Chiral Styrene-Type Carboxyl Acid via Palladium-Catalyzed Asymmetric C-H Activation

Chi Yang, Tian-Rui Wu, Yan Li, Bing-Bing Wu, Ruo-Xing Jin, Duo-Duo Hu,

Yuan-Bo Li, Kang-Jie Bian and Xi-Sheng Wang \*

Hefei National Laboratory for Physical Sciences at the Microscale and Department of  
Chemistry, Center for Excellence in Molecular Synthesis of CAS

University of Science and Technology of China

96 Jinzhai Road, Hefei, Anhui 230026, China

### Table of Contents

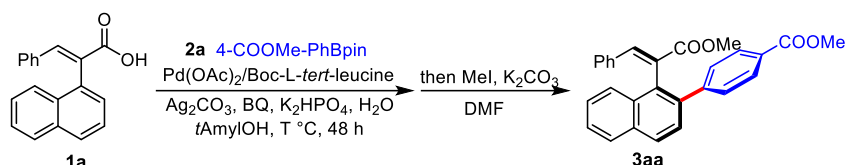
1. General Information .....	S2
2. Tables of the Optimization of Reaction Conditions .....	S3
3. Experimental Section .....	S8
3.1 General Procedure for Synthesis of Starting Materials.....	S8
3.2 General Procedure for Pd(II)-catalyzed Asymmetric C-H Arylation.....	S13
3.3 General Procedure for Pd(II)-catalyzed Asymmetric C-H Olefination.....	S26
3.4 Reduction of <b>CCA1</b> .....	S39
3.5 Transformation of <b>5aa</b> .....	S40
3.6 Co <sup>III</sup> -catalyzed Enantioselective C(sp <sup>3</sup> )-H Amidation of Thioamide.....	S41
3.7 Co <sup>III</sup> -catalyzed Enantioselective 1,4-addition of Indoles and Maleimides.....	S41
3.8 General Procedure for CCAs.....	S42
4. NMR Data .....	S49
5. HPLC Data .....	S123

## 1. General Information:

NMR spectra were recorded on Bruker-400 MHz NMR spectrometer (400 MHz for  $^1\text{H}$  and 101 MHz for  $^{13}\text{C}$  { $^1\text{H}$ ,  $^{13}\text{C}$  decoupled}). Or Bruker-500 MHz NMR spectrometer (500 MHz for  $^1\text{H}$  and 126 MHz for  $^{13}\text{C}$  { $^1\text{H}$ ,  $^{13}\text{C}$  decoupled}).  $^1\text{H}$  NMR chemical shifts were determined relative to internal  $(\text{CH}_3)_4\text{Si}$  (TMS) at  $\delta$  0.0 or at the signal of a residual protonated solvent:  $\text{CDCl}_3$   $\delta$  7.26.  $^{13}\text{C}$  NMR chemical shifts were determined relative to  $\text{CDCl}_3$   $\delta$  77.16. Data for  $^1\text{H}$ ,  $^{13}\text{C}$  NMR are recorded as follows: chemical shift ( $\delta$ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad). High resolution mass spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. using ESI-TOF (electrospray ionization-time of flight) or Micromass GCT using EI (electron impact). HPLC analysis was performed on Shimadzu LC-20AT. Chiral column ID, IB, IF, AD-H, AS-H, AD-3 and OD-H were purchased from Daicel Chemical Industries, LTD. Palladium acetate was purchased from Strem, and used as received. Silver carbonate, phenoborate borate alcohol ester, acrylic ester, potassium bicarbonate, p-benzoquinone, potassium hydroxide, iodomethane and N-protected amino acids were obtained from Adamas, Darui Finechemical, Energy Chemical, and Sinopharm, and used as received. Solvents were obtained from Sinopharm and Qinba Chemie, and used as received.

## 2. Tables of the Optimization of Reaction Conditions

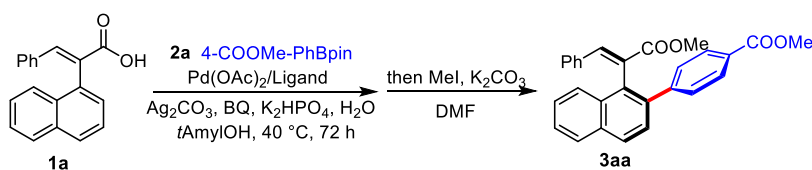
**Table S1.** Temperature Screening of Pd catalyzed C-H arylation<sup>a,b,c</sup>



entry	temperature	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	80 °C	80	25
2	60 °C	67	74
3	50 °C	62	84
4	45 °C	46	90
5	40 °C	43	95

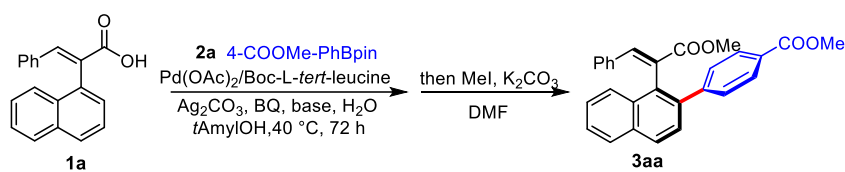
<sup>a</sup>Unless otherwise noted, the reaction conditions were as follows: *rac*-**1a** (0.2 mmol), **2a** (2.0 equiv), Pd(OAc)<sub>2</sub> (0.1 equiv), Boc-L-*tert*-leucine (0.2 equiv), BQ (0.5 equiv), Ag<sub>2</sub>CO<sub>3</sub> (1.5 equiv), K<sub>2</sub>HPO<sub>4</sub> (2.0 equiv), H<sub>2</sub>O (20.0 equiv) in *t*AmylOH under air for 48 h. To simplify separation and HPLC analysis, the crude mixture was methylated using MeI. <sup>b</sup> isolate yields. <sup>c</sup> The ee value was determined by HPLC.

**Table S2.** Ligand screening of Pd catalyzed C-H arylation<sup>a,b,c</sup>



entry	Ligand	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	Boc-L-Alanine	39	40
2	Boc-L-Phenylalanine	47	40
3	Boc-L-Ser(Bn)-OH	19	27
4	Boc-L-Thr- <i>t</i> Bu-OH	43	92
5	Boc-L-Thr-(Bn)-OH	38	75
6	Boc-L-Threonine	11	-
7	Boc-L-Leucine	20	59
8	Boc-L-Valine	56	87
9	Boc-L- <i>tert</i> -Leucine	52	95
10	Fmoc-L- <i>tert</i> -Leucine	42	92
11	Cbz-L- <i>tert</i> -Leucine	35	92
12	<i>tert</i> -Leucine	nr	-

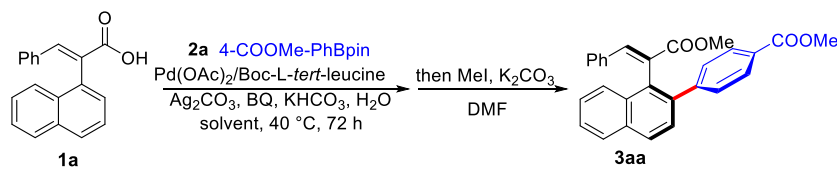
<sup>a</sup>Unless otherwise noted, the reaction conditions were as follows: *rac*-**1a** (0.2 mmol), **2a** (2.0 equiv), Pd(OAc)<sub>2</sub> (0.1 equiv), ligand (0.2 equiv), BQ (0.5 equiv), Ag<sub>2</sub>CO<sub>3</sub> (1.5 equiv), K<sub>2</sub>HPO<sub>4</sub> (2.0 equiv), H<sub>2</sub>O (20.0 equiv) in *t*AmylOH under air for 72 h. To simplify separation and HPLC analysis, the crude mixture was methylated using MeI. <sup>b</sup> isolate yields. <sup>c</sup> The ee value was determined by HPLC.

**Table S3.** Base Screening of Pd catalyzed C-H arylation <sup>a,b,c</sup>

entry	base	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	K <sub>3</sub> PO <sub>4</sub>	12	97
2	K <sub>2</sub> HPO <sub>4</sub>	52	95
3	KH <sub>2</sub> PO <sub>4</sub>	49	94
4	KOtBu	37	96
5	KOMe	trace	-
6	K <sub>2</sub> CO <sub>3</sub>	24	98
7	KHCO <sub>3</sub>	74	97
8	KOAc	44	89
9	KOH	30	96
10	Cs <sub>2</sub> CO <sub>3</sub>	trace	-
11	Na <sub>2</sub> CO <sub>3</sub>	54	96
12	Li <sub>2</sub> CO <sub>3</sub>	71	93
13	NaHCO <sub>3</sub>	79	78

<sup>a</sup>Unless otherwise noted, the reaction conditions were as follows: *rac*-**1a** (0.2 mmol), **2a** (2.0 equiv), Pd(OAc)<sub>2</sub> (0.1 equiv), Boc-L-*tert*-leucine (0.2 equiv), BQ (0.5 equiv), Ag<sub>2</sub>CO<sub>3</sub> (1.5 equiv), base (2.0 equiv), H<sub>2</sub>O (20.0 equiv) in *t*AmylOH under air for 72 h. To simplify separation and HPLC analysis, the crude mixture was methylated using MeI. <sup>b</sup> isolate yields.

<sup>c</sup> The ee value was determined by HPLC.

**Table S4.** Solvent Screening of Pd catalyzed C-H arylation <sup>a,b,c</sup>

entry	Solvent	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	toulene	trace	-
2	DME	52	95
3	DMF	71	94
4	dioxane	38	73
5	MeCN	trace	-
6	<i>t</i> AmylOH	74	97
7	<i>t</i> BuOH	17	91
8	<i>i</i> PrOH	34	96
9	EtOH	28	95
10	MeOH	trace	-
11	HFIP	trace	-
12 <sup>d</sup>	<i>t</i> AmylOH	41	67
13 <sup>e</sup>	<i>t</i> AmylOH	69	88
14 <sup>f</sup>	<i>t</i> AmylOH	52	96

<sup>a</sup>Unless otherwise noted, the reaction conditions were as follows: *rac*-**1a** (0.2 mmol), **2a** (2.0 equiv), Pd(OAc)<sub>2</sub> (0.1 equiv), Boc-L-*tert*-leucine (0.2 equiv), BQ (0.5 equiv), Ag<sub>2</sub>CO<sub>3</sub> (1.5 equiv), KHCO<sub>3</sub> (2.0 equiv), H<sub>2</sub>O (20.0 equiv) in solvent under air for 72 h. To simplify separation and HPLC analysis, the crude mixture was methylated using MeI. <sup>b</sup> isolate yields.

<sup>c</sup> The ee value was determined by HPLC. <sup>d</sup> no H<sub>2</sub>O. <sup>e</sup> 10 equiv H<sub>2</sub>O. <sup>f</sup> 30 equiv H<sub>2</sub>O.

**Table S5.** Oxidant Screening of Pd catalyzed C-H arylation <sup>a,b,c</sup>

entry	[Ag] sources	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	AgOAc	65	91
2	AgNO <sub>3</sub>	12	90
3	Ag <sub>2</sub> O	51	97
4	AgTFA	57	93
5	AgOTf	trace	-
6	AgBF <sub>4</sub>	trace	-
7	AgF	trace	-
8 <sup>d</sup>	Ag <sub>2</sub> CO <sub>3</sub>	51	90

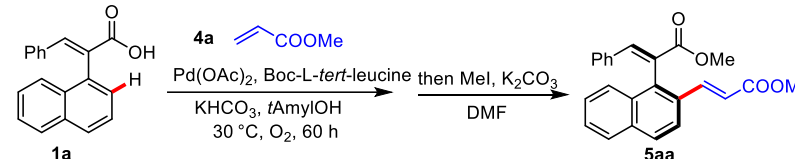
<sup>a</sup>Unless otherwise noted, the reaction conditions were as follows: *rac*-**1a** (0.2 mmol), **2a** (2.0 equiv), Pd(OAc)<sub>2</sub> (0.1 equiv), Boc-L-*tert*-leucine (0.2 equiv), BQ (0.5 equiv), [Ag] (1.5 equiv), KHCO<sub>3</sub> (2.0 equiv), H<sub>2</sub>O (20.0 equiv) in *t*AmylOH under air for 72 h. To simplify separation and HPLC analysis, the crude mixture was methylated using MeI. <sup>b</sup> isolate yields. <sup>c</sup> The ee value was determined by HPLC. <sup>d</sup> no BQ.

**Table S6.** Ligand Screening of Pd catalyzed C-H olefination <sup>a,b,c</sup>

Entry	ligand	yield	ee
1	Boc-L- <i>tert</i> -leucine	49 %	76 %
2	Ac-L-valine	54%	64 %
3	Fmoc-L-valine	41%	71 %
4	Cbz-L-leucine	47%	76 %
5 <sup>d</sup>	Fmoc-L-isoleucine	24 %	93 %
6 <sup>d</sup>	Boc-L-isoleucine	39 %	96 %
7 <sup>d</sup>	Fmoc-L-leucine	31 %	86 %
8 <sup>d</sup>	Boc-L-isoleucine	44%	94 %
9 <sup>d</sup>	Boc-L- <i>tert</i> -leucine	49 %	96 %
10 <sup>d</sup>	Boc-L-Thr(O- <i>t</i> Bu)-OH	72 %	87 %

<sup>a</sup>Unless otherwise noted, the reaction conditions were as follows: *rac*-**1a** (0.2 mmol), **4a** (3.0 equiv), Pd(OAc)<sub>2</sub> (0.1 equiv), ligand (0.3 equiv), KHCO<sub>3</sub> (2.0 equiv), in *t*AmylOH under 1 atm O<sub>2</sub> for 24 h. To simplify separation and HPLC analysis, the crude mixture was methylated using MeI. <sup>b</sup> isolate yields. <sup>c</sup> The ee value was determined by HPLC. <sup>d</sup> at 30 °C, 48 h.

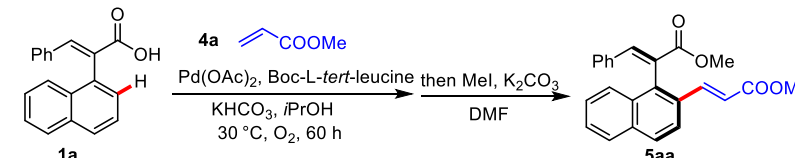
**Table S7.** Solvent Screening of Pd catalyzed C-H olefination <sup>a,b,c</sup>



Entry	solvent	yield	ee
1	<i>t</i> AmylOH	54%	96%
2	<i>t</i> BuOH	62%	91 %
3	<i>i</i> PrOH	69%	96 %
4	HFIP	39%	90 %
5	EtOH	21%	91 %
6	MeOH	55%	92 %
7	toulene	30%	61%
8	dioxane	trace	-
9	DCE	trace	-
10	DME	trace	-
11	DMF	trace	-

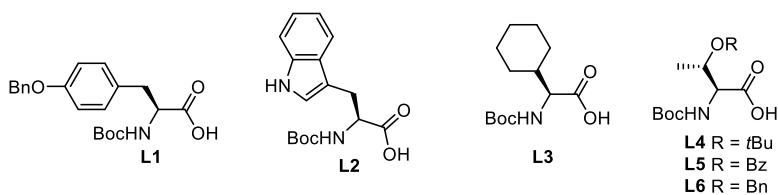
<sup>a</sup>Unless otherwise noted, the reaction conditions were as follows: *rac*-**1a** (0.2 mmol), **4a** (3.0 equiv), Pd(OAc)<sub>2</sub> (0.1 equiv), Boc-L-*tert*-leucine (0.3 equiv), KHCO<sub>3</sub> (2.0 equiv), in solvent under 1 atm O<sub>2</sub> for 60 h. To simplify separation and HPLC analysis, the crude mixture was methylated using MeI. <sup>b</sup> isolate yields. <sup>c</sup> The ee value was determined by HPLC.

**Table S8.** Ligand Screening of Pd catalyzed C-H olefination <sup>a,b,c</sup>



Entry	ligand	yield	ee
1	<b>L1</b> as ligand	89 %	85 %
2	<b>L2</b> as ligand	nr	-
3	<b>L3</b> as ligand	79 %	84 %
4	<b>L4</b> as ligand	72 %	87 %
5	<b>L5</b> as ligand	66 %	90 %
6 <sup>d</sup>	<b>L5</b> as ligand	32 %	90 %
7	<b>L6</b> as ligand	80 %	84%

<sup>a</sup>Unless otherwise noted, the reaction conditions were as follows: *rac*-**1a** (0.2 mmol), **4a** (3.0 equiv), Pd(OAc)<sub>2</sub> (0.1 equiv), ligand (0.3 equiv), KHCO<sub>3</sub> (2.0 equiv), in *i*PrOH under 1 atm O<sub>2</sub> for 60 h. To simplify separation and HPLC analysis, the crude mixture was methylated using MeI. <sup>b</sup> isolate yields. <sup>c</sup> The ee value was determined by HPLC. <sup>d</sup> *t*AmylOH as solvent.



**Table S9.** Base Screening of Pd catalyzed C-H olefination <sup>a,b,c</sup>

Entry	variations from standard conditions	yield	ee
1	K <sub>3</sub> PO <sub>4</sub> as base	89%	91 %
2	K <sub>2</sub> HPO <sub>4</sub> as base	52 %	88 %
3	KH <sub>2</sub> PO <sub>4</sub> as base	trace	-
4	KOtBu as base	38%	95%
5	KOMe as base	33%	95%
6	K <sub>2</sub> CO <sub>3</sub> as base	88 %	94 %
7	KHCO <sub>3</sub> as base	75 %	96 %
8	KOAc as base	20 %	89 %
9	KOH as base	89 %	98 %
10	NaHCO <sub>3</sub> as base	trace	-
11	Na <sub>3</sub> PO <sub>4</sub> as base	trace	-
12	NaOH as base	trace	-

<sup>a</sup>Unless otherwise noted, the reaction conditions were as follows: *rac*-**1a** (0.2 mmol), **4a** (3.0 equiv), Pd(OAc)<sub>2</sub> (0.1 equiv), Boc-L-*tert*-leucine (0.3 equiv), base (2.0 equiv), in *i*PrOH under 1 atm O<sub>2</sub> for 72 h. To simplify separation and HPLC analysis, the crude mixture was methylated using MeI. <sup>b</sup> isolate yields. <sup>c</sup> The ee value was determined by HPLC.

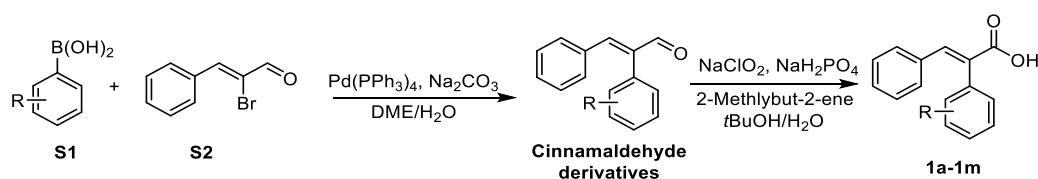
**Table S10.** Modification of the condition of Pd catalyzed C-H olefination <sup>a,b,c</sup>

Entry	variations from standard conditions	yield	ee
1	<i>n</i> PrOH as solvent	86 %	91 %
2	<i>i</i> PrOH 1 mL as solvent	62 %	93 %
3	<i>n</i> PrOH 1mL as solvent	68 %	95 %
4	KOH in 36 $\mu$ L H <sub>2</sub> O	97%	97%
5	KOH in 72 $\mu$ L H <sub>2</sub> O	98 %	88 %
6	KOH in 108 $\mu$ L H <sub>2</sub> O	98 %	88 %

<sup>a</sup>Unless otherwise noted, the reaction conditions were as follows: *rac*-**1a** (0.2 mmol), **4a** (3.0 equiv), Pd(OAc)<sub>2</sub> (0.1 equiv), Boc-L-*tert*-leucine (0.3 equiv), KOH (2.0 equiv, presolved in 36  $\mu$ L water) in *i*PrOH 2 mL under 1 atm O<sub>2</sub> for 72 h. To simplify separation and HPLC analysis, the crude mixture was methylated using MeI. <sup>b</sup> isolate yields. <sup>c</sup> The ee value was determined by HPLC.

### 3. Experimental Section

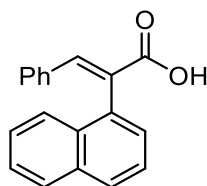
#### 3.1 General Procedure for Synthesis of Starting Materials <sup>[1], [2]</sup>



To a 100 mL dried round bottom flask was charged with **S1** (5.5 mmol, 1.1 equiv), **S2** (5 mmol, 1.0 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%), Na<sub>2</sub>CO<sub>3</sub> (10 mmol, 2.0 equiv), DME (30 mL), H<sub>2</sub>O (10 mL). The mixture was stirred at 110 °C overnight. After cooling to room temperature, the reaction was diluted with EtOAc, and quenched with H<sub>2</sub>O, then extracted with EtOAc for three times. The combined organic layer was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration, the solvent was then evaporated under reduced pressure and the cinnamaldehyde derivatives were obtained via flash column chromatography (petroleum ether/ethyl acetate = 20:1).

To a solution of cinnamaldehyde (4 mmol) in *t*BuOH (1.5 M) were added a solution of NaH<sub>2</sub>PO<sub>4</sub> (5.0 equiv) and NaClO<sub>2</sub> (3.7 equiv) in water, and followed by 2-methyl-2-butene (9.0 equiv). The reaction mixture was stirred at room temperature for 4 hours. After full conversion of aldehyde, monitored by TLC, saturated NH<sub>4</sub>Cl was added and the reaction mixture was extracted with EtOAc for three times. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration, the solvent was then evaporated under reduced pressure and **1a-1m** was afford via flash column chromatography (DCM/MeOH = 100:1).

#### (E)-2-(naphthalen-1-yl)-3-phenylacrylic acid (**1a**)

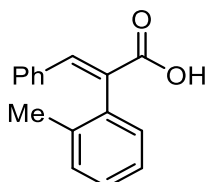


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.18 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.47 (m, 2H), 7.42 (m, 1H), 7.32 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.18 – 7.12 (m,



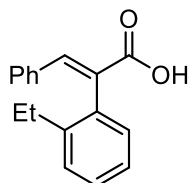
1H), 7.04 (t,  $J = 7.8$  Hz, 2H), 6.94 (d,  $J = 7.4$  Hz, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 144.1, 134.2, 133.9, 133.4, 131.9, 130.9, 129.92, 129.87, 128.8, 128.7, 128.5, 127.3, 126.7, 126.3, 125.9, 125.1. HRMS (ESI) calcd. for  $\text{C}_{19}\text{H}_{15}\text{O}_2[\text{M}+\text{H}]^+$ : 275.1072, found: 275.1074.

**(E)-3-phenyl-2-(o-tolyl) acrylic acid (1b)**



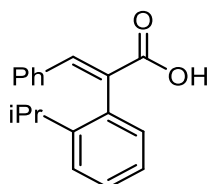
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (s, 1H), 7.35 – 7.26 (m, 2H), 7.25 – 7.14 (m, 4H), 7.10 (d,  $J = 7.7$  Hz, 1H), 7.02 (d,  $J = 7.4$  Hz, 2H), 2.16 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.2, 142.6, 136.6, 135.1, 134.4, 130.9, 130.6, 130.4, 129.8, 129.46, 128.5, 128.4, 126.4, 19.6. HRMS (ESI) calcd. for  $\text{C}_{16}\text{H}_{15}\text{O}_2[\text{M}+\text{H}]^+$ : 239.1072, found: 239.1082.

**(E)-2-(2-ethylphenyl)-3-phenylacrylic acid (1c)**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (s, 1H), 7.42 – 7.30 (m, 2H), 7.26 – 7.19 (m, 2H), 7.16 (t,  $J = 7.5$  Hz, 2H), 7.09 (d,  $J = 7.5$  Hz, 1H), 7.02 (d,  $J = 7.6$  Hz, 2H), 2.50 (ddq,  $J = 29.7, 14.9, 7.4$  Hz, 2H), 1.09 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 142.6, 142.4, 134.6, 134.3, 130.9, 130.8, 129.8, 129.6, 128.6, 128.6, 128.4, 126.5, 26.2, 14.6. HRMS (ESI) calcd. for  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Na}[\text{M}+\text{Na}]^+$ : 275.1048, found: 275.1037.

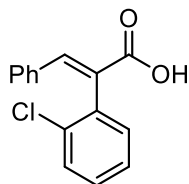
**(E)-2-(2-isopropylphenyl)-3-phenylacrylic acid (1d)**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (s, 1H), 7.41 (d,  $J = 4.2$  Hz, 2H), 7.27 – 7.19 (m,

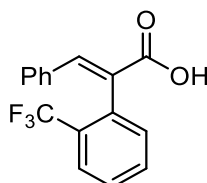
2H), 7.16 (t,  $J = 7.6$  Hz, 2H), 7.08 (d,  $J = 7.6$  Hz, 1H), 7.02 (d,  $J = 7.4$  Hz, 2H), 2.89 (hept,  $J = 6.8$  Hz, 1H), 1.20 (d,  $J = 6.8$  Hz, 3H), 0.97 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 147.2, 142.7, 134.3, 133.8, 131.0, 130.9, 129.7, 129.4, 128.8, 128.3, 126.4, 126.0, 30.8, 23.9, 23.8. HRMS (ESI) calcd. for  $\text{C}_{18}\text{H}_{19}\text{O}_2[\text{M}+\text{H}]^+$ : 267.1385, found: 267.1371.

**(E)-2-(2-chlorophenyl)-3-phenylacrylic acid (1e)**



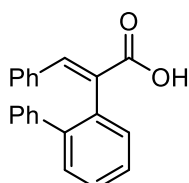
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (s, 1H), 7.49 (dd,  $J = 8.0, 1.1$  Hz, 1H), 7.34 (td,  $J = 7.7, 1.8$  Hz, 1H), 7.29 – 7.27 (m, 1H), 7.25 – 7.23 (m, 1H), 7.22 – 7.15 (m, 3H), 7.09 – 7.03 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.0, 143.6, 134.8, 134.3, 134.0, 131.2, 130.5, 129.9, 129.8, 129.7, 129.1, 128.5, 127.3. HRMS (ESI) calcd. for  $\text{C}_{15}\text{H}_{12}\text{ClO}_2[\text{M}+\text{H}]^+$ : 259.0526, found: 259.0522.

**(E)-3-phenyl-2-(2-(trifluoromethyl)phenyl)acrylic acid (1f)**



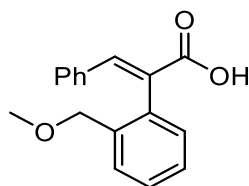
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (s, 1H), 7.78 (d,  $J = 7.7$  Hz, 1H), 7.58 (t,  $J = 7.3$  Hz, 1H), 7.52 (t,  $J = 7.6$  Hz, 1H), 7.32 – 7.21 (m, 2H), 7.16 (t,  $J = 7.6$  Hz, 2H), 6.96 (d,  $J = 7.5$  Hz, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 143.3, 134.6, 133.7, 132.4, 131.6, 130.9, 123.0, 129.4 (q,  $J = 30.2$  Hz), 128.8, 128.5, 128.4, 126.8 (q,  $J = 4.9$  Hz), 123.9 (q,  $J = 274.3$  Hz);  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -60.7; HRMS (ESI) calcd. for  $\text{C}_{16}\text{H}_{12}\text{F}_3\text{O}_2[\text{M}+\text{H}]^+$ : 293.0789, found: 293.0779.

**(E)-2-([1,1'-biphenyl]-2-yl)-3-phenylacrylic acid (1g)**



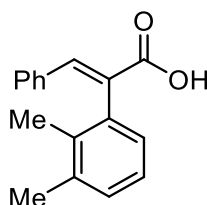
$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.59 (s, 1H), 7.48 (t,  $J = 7.5$  Hz, 1H), 7.44 – 7.35 (m, 2H), 7.28 – 7.21 (m, 4H), 7.19 (t,  $J = 7.4$  Hz, 3H), 7.17 – 7.11 (m, 2H), 7.00 (d,  $J = 7.6$  Hz, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  168.7, 141.5, 141.3, 139.8, 135.5, 134.9, 133.5, 130.7, 130.5, 129.7, 128.8, 128.6, 128.4, 128.3, 127.4. HRMS (ESI) calcd. for  $\text{C}_{21}\text{H}_{17}\text{O}_2[\text{M}+\text{H}]^+$ : 301.1229, found: 301.1238.

**(E)-2-(2-(methoxymethyl)phenyl)-3-phenylacrylic acid (1h)**



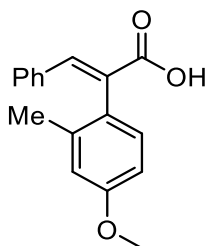
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (s, 1H), 7.52 (d,  $J = 7.6$  Hz, 1H), 7.41 (td,  $J = 7.5$ , 1.3 Hz, 1H), 7.33 (td,  $J = 7.5$ , 1.4 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.19 – 7.10 (m, 3H), 7.06 – 6.99 (m, 2H), 4.32 (dd,  $J = 86.9$ , 12.5 Hz, 2H), 3.25 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 142.3, 136.7, 134.4, 134.1, 130.7, 130.1, 129.8, 129.8, 128.4, 128.2, 72.6, 58.2. HRMS (ESI) calcd. for  $\text{C}_{17}\text{H}_{16}\text{O}_3\text{Na}[\text{M}+\text{Na}]^+$ : 291.0997, found: 291.0998.

**(E)-2-(2,3-dimethylphenyl)-3-phenylacrylic acid (1i)**



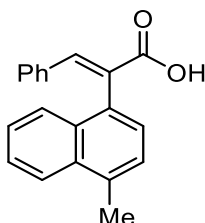
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (s, 1H), 7.22 (d,  $J = 7.2$  Hz, 1H), 7.17 (q,  $J = 7.2$  Hz, 3H), 7.11 (t,  $J = 7.5$  Hz, 1H), 7.03 (d,  $J = 7.7$  Hz, 2H), 6.94 (d,  $J = 7.5$  Hz, 1H), 2.31 (s, 3H), 2.09 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 142.3, 137.3, 135.2, 135.1, 134.5, 131.7, 130.8, 123.0, 129.7, 128.4, 127.1, 126.1, 20.6, 16.3. HRMS (ESI) calcd. for  $\text{C}_{17}\text{H}_{17}\text{O}_2[\text{M}+\text{H}]$ : 253.1229, found: 253.1230.

**(E)-2-(4-methoxy-2-methylphenyl)-3-phenylacrylic acid (1j)**



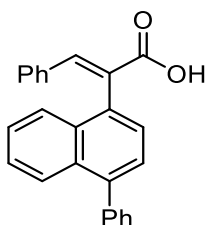
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (s, 1H), 7.27 – 7.22 (m, 1H), 7.18 (t,  $J = 7.6$  Hz, 2H), 7.06 (d,  $J = 7.8$  Hz, 2H), 7.01 (d,  $J = 8.3$  Hz, 1H), 6.83 (d,  $J = 2.6$  Hz, 1H), 6.77 (dd,  $J = 8.4, 2.7$  Hz, 1H), 3.83 (s, 3H), 2.13 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 159.5, 142.8, 138.2, 134.6, 130.63, 130.58, 129.7, 128.5, 127.3, 116.0, 111.8, 55.2, 19.9. HRMS (ESI) calcd. for  $\text{C}_{17}\text{H}_{17}\text{O}_3[\text{M}+\text{H}]^+$ : 269.1178, found: 269.1182.

**(E)-2-(4-methylnaphthalen-1-yl)-3-phenylacrylic acid (1k)**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (s, 1H), 8.04 (d,  $J = 8.4$  Hz, 1H), 7.79 (d,  $J = 8.3$  Hz, 1H), 7.54 – 7.48 (m, 1H), 7.46 – 7.38 (m, 1H), 7.31 (d,  $J = 7.2$  Hz, 1H), 7.20 (d,  $J = 7.1$  Hz, 1H), 7.14 (t,  $J = 7.3$  Hz, 1H), 7.04 (t,  $J = 7.7$  Hz, 2H), 6.96 (d,  $J = 7.6$  Hz, 2H), 2.73 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 143.8, 135.1, 134.2, 132.9, 131.8, 131.5, 130.8, 130.1, 129.7, 128.4, 126.9, 126.7, 126.2, 126.0, 125.5, 124.7, 19.7. HRMS (ESI) calcd. for  $\text{C}_{20}\text{H}_{17}\text{O}_2[\text{M}+\text{H}]^+$ : 289.1229, found: 289.1225.

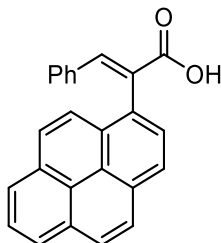
**(E)-3-phenyl-2-(4-phenylnaphthalen-1-yl)acrylic acid (1l)**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (s, 1H), 8.02 – 7.91 (m, 1H), 7.91 – 7.78 (m, 1H), 7.59 – 7.54 (m, 2H), 7.50 (t,  $J = 7.5$  Hz, 2H), 7.48 – 7.39 (m, 4H), 7.36 (d,  $J = 7.2$  Hz, 1H), 7.22 – 7.16 (m, 1H), 7.09 (t,  $J = 7.8$  Hz, 2H), 7.02 (d,  $J = 7.4$  Hz, 2H);  $^{13}\text{C}$  NMR

(126 MHz, CDCl<sub>3</sub>)  $\delta$  172.9, 144.1, 140.8, 140.6, 134.0, 132.8, 132.1, 131.9, 130.8, 130.2, 129.8, 129.8, 128.4, 128.3, 127.3, 126.9, 126.7, 126.7, 126.4, 126.2, 125.2. HRMS (ESI) calcd. for C<sub>25</sub>H<sub>19</sub>O<sub>2</sub>[M+H]<sup>+</sup>: 351.1385, found: 351.1375.

### (E)-3-phenyl-2-(pyren-1-yl)acrylic acid (1m)

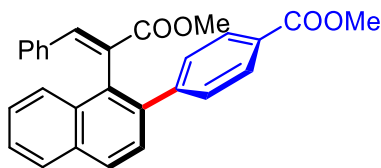


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 (s, 1H), 8.22 – 8.17 (m, 2H), 8.15 (d, *J* = 7.6 Hz, 1H), 8.13 – 8.06 (m, 2H), 8.00 (m, 3H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 7.6 Hz, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  172.9, 144.3, 134.1, 131.4, 131.3, 131.1, 130.9, 130.5, 130.1, 129.8, 129.4, 128.4, 128.2, 127.8, 127.5, 127.4, 126.1, 125.4, 125.3, 125.3, 125.0, 124.9, 124.4. HRMS (ESI) calcd. for C<sub>25</sub>H<sub>16</sub>O<sub>2</sub>Na[M+Na]<sup>+</sup>: 371.1048, found: 371.1036.

### 3.2 General Procedure for Pd(II)-catalyzed Asymmetric C-H Arylation

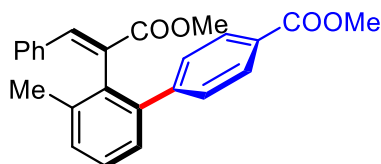
A sealed tube with magnetic stir bar was charged with substrate (0.2 mmol), phenylboronic acid pinacol ester (0.4 mmol), Pd(OAc)<sub>2</sub> (10 mol%, 4.5 mg), Boc-*L*-tert-leucine (0.04 mmol, 9.2 mg), Ag<sub>2</sub>CO<sub>3</sub> (0.3 mol, 82.7 mg), BQ (0.1 mmol, 10.8 mg), KHCO<sub>3</sub> (0.4 mmol, 40 mg), H<sub>2</sub>O 72  $\mu$ L and *t*AmylOH 1 mL as solvent in air. The reaction mixture was stirred at 40 °C for 72 hours. Upon completion, the reaction was diluted with ethyl acetate, and filtered through a plug of Celite. The solvent was concentrated *in vacuo* and then the obtained slurry was dissolved in DMF (5 mL), treated with MeI (0.3 mmol, 19  $\mu$ L) and K<sub>2</sub>CO<sub>3</sub> (0.4 mmol, 55.6 mg). The reaction mixture was stirred for 2 hours at room temperature. Then the mixture was diluted with ethyl acetate 20 (mL) and washed with water. The organic layer was concentrated *in vacuo* and purified by flash chromatography (petroleum ether/ethyl acetate = 60:1 to 40:1) to afford the product.

### methyl (E)-4-(1-(3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)naphthalene -2-yl)benzoate (3aa)



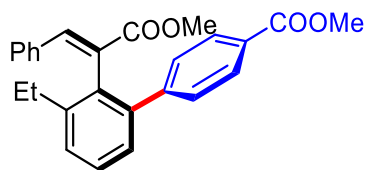
The product **3aa** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (74% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 – 7.92 (m, 2H), 7.91 – 7.85 (m, 3H), 7.83 (d,  $J = 8.4$  Hz, 1H), 7.55 – 7.50 (m, 1H), 7.49 – 7.41 (m, 2H), 7.14 (t,  $J = 7.4$  Hz, 1H), 7.12 – 7.06 (m, 2H), 7.02 (t,  $J = 7.7$  Hz, 2H), 6.78 – 6.71 (m, 2H), 3.90 (s, 3H), 3.64 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.4, 167.1, 146.5, 143.3, 138.1, 134.4, 133.1, 131.9, 131.4, 130.2, 129.4, 129.1, 129.0, 128.8, 128.7, 128.50, 128.46, 128.3, 127.8, 127.2, 126.4, 125.4, 52.4, 52.1. HRMS (ESI) calcd. for  $\text{C}_{28}\text{H}_{23}\text{O}_4[\text{M}+\text{H}]^+$ : 423.1596, found: 423.1606.  $[\alpha]_{\text{D}}^{20} = -42.3$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 12.8$  min (major), 10.7 min (minor), 97% ee.

**methyl (E)-2'-(3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)-3'-methyl-[1,1'-biphenyl]-4-carboxylate (3ba)**



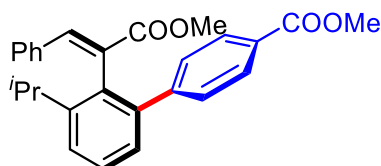
The product **3ba** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (57% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.80 (m, 2H), 7.64 (s, 1H), 7.38 (t,  $J = 7.6$  Hz, 1H), 7.35 – 7.30 (m, 1H), 7.26 – 7.21 (m, 1H), 7.19 – 7.12 (m, 3H), 7.05 – 7.00 (m, 2H), 6.90 – 6.83 (m, 2H), 3.88 (s, 3H), 3.69 (s, 3H), 2.18 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.1, 167.1, 146.5, 141.7, 141.0, 137.2, 134.7, 134.0, 130.1, 130.0, 129.9, 129.5, 128.9, 128.6, 128.5, 128.4, 128.2, 127.7, 52.4, 52.1, 20.1. HRMS (ESI) calcd. for  $\text{C}_{25}\text{H}_{22}\text{O}_4[\text{M}+\text{Na}]^+$ : 409.1416, found: 409.1407.  $[\alpha]_{\text{D}}^{20} = -124.6$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 9.5$  min (major), 7.2 min (minor), 94% ee.

**methyl (E)-2'-(3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)-3'-methyl-[1,1'-biphenyl]-4-carboxylate (3ca)**



The product **3ca** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (65% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 – 7.79 (m, 2H), 7.64 (s, 1H), 7.48 – 7.41 (m, 1H), 7.38 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.25 – 7.20 (m, 1H), 7.18 – 7.11 (m, 3H), 7.04 – 7.00 (m, 2H), 6.88 – 6.83 (m, 2H), 3.88 (s, 3H), 3.69 (s, 3H), 2.52 (ddt,  $J = 41.9, 14.8, 7.4$  Hz, 2H), 1.11 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 167.1, 146.6, 142.9, 141.9, 140.9, 134.7, 133.4, 130.2, 129.8, 129.5, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 127.7, 52.3, 52.1, 26.4, 14.6. HRMS (ESI) calcd. for  $\text{C}_{26}\text{H}_{24}\text{O}_4\text{Na}[\text{M}+\text{Na}]^+$ : 423.1572, found: 423.1567.  $[\alpha]_{\text{D}}^{20} = -47.6$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 7.8$  min (major), 6.9 min (minor), 98% ee.

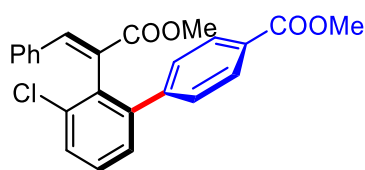
**methyl (E)-3'-isopropyl-2'-(3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)-[1,1'-biphenyl]-4-carboxylate (3da)**



The product **3da** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (81% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 – 7.75 (m, 2H), 7.62 (s, 1H), 7.51 – 7.41 (m, 2H), 7.23 – 7.18 (m, 1H), 7.17 – 7.10 (m, 3H), 7.06 – 6.97 (m, 2H), 6.87 – 6.78 (m, 2H), 3.87 (s, 3H), 3.71 (s, 3H), 2.92 (p,  $J = 6.8$  Hz, 1H), 1.19 (d,  $J = 6.9$  Hz, 3H), 1.02 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.4, 167.1, 147.8, 146.8, 141.9, 140.8, 134.7, 132.7, 130.4, 129.9, 129.5, 128.8, 128.6, 128.3, 128.3, 127.7, 125.6, 52.3, 52.1, 30.9, 24.0, 23.8. HRMS (ESI) calcd. for  $\text{C}_{27}\text{H}_{27}\text{O}_4[\text{M}+\text{H}]^+$ : 415.1909, found: 415.1906.  $[\alpha]_{\text{D}}^{20} = -77.6$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 6.3$  min (major), 6.0 min (minor), 98% ee.

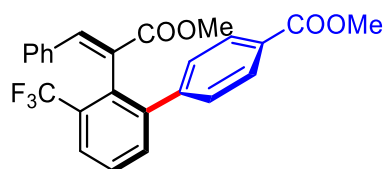
**methyl (E)-3'-chloro-2'-(3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)-[1,1'-biphenyl]**

### -4-carboxylate (**3ea**)



The product **3ea** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (61% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 – 7.78 (m, 2H), 7.62 (s, 1H), 7.54 (dd,  $J = 8.1, 1.2$  Hz, 1H), 7.41 (t,  $J = 7.9$  Hz, 1H), 7.26 – 7.21 (m, 1H), 7.18 (dd,  $J = 7.6, 1.2$  Hz, 1H), 7.15 – 7.10 (m, 2H), 6.94 – 6.88 (m, 2H), 6.79 – 6.74 (m, 2H), 3.90 (s, 3H), 3.78 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.5, 166.9, 145.0, 142.9, 142.5, 135.2, 134.3, 133.6, 129.6, 129.4, 129.3, 129.1, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 52.5, 52.1. HRMS (ESI) calcd. for  $\text{C}_{24}\text{H}_{19}\text{ClO}_4\text{Na}[\text{M}+\text{Na}]^+$ : 429.0870, found: 429.0882.  $[\alpha]_{\text{D}}^{20} = -74.6$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 9.1$  min (major), 7.4 min (minor), 90% ee.

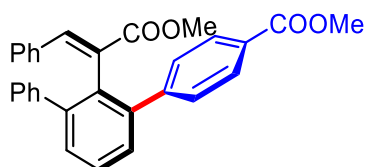
### methyl (E)-2'-(3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)-3'-(trifluoromethyl)-[1,1'-biphenyl]-4-carboxylate (**3fa**)



The product **3fa** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 30:1) as a white solid (22% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (dd,  $J = 8.0, 1.3$  Hz, 1H), 7.82 – 7.77 (m, 2H), 7.64 (s, 1H), 7.61 (td,  $J = 7.8, 0.9$  Hz, 1H), 7.49 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.25 – 7.22 (m, 1H), 7.15 (t,  $J = 7.8$  Hz, 2H), 7.00 – 6.91 (m, 2H), 6.77 (dd,  $J = 7.4, 1.5$  Hz, 2H), 3.89 (s, 3H), 3.73 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.5, 166.8, 144.7, 142.9, 142.7, 133.9 (q,  $J = 32.7$  Hz), 130.3, 130.0, 129.8, 129.7, 129.0, 128.9, 128.44, 128.43, 128.40, 127.4, 126.4 (q,  $J = 3.8$  Hz), 125.0, 122.8, 52.4, 52.1.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -60.4. HRMS (ESI) calcd. for  $\text{C}_{25}\text{H}_{19}\text{F}_3\text{O}_4\text{Na}[\text{M}+\text{Na}]^+$ : 463.1133, found: 463.1134.  $[\alpha]_{\text{D}}^{20} = -18.7$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 9.3$  min (major), 7.6 min (minor), 98% ee.

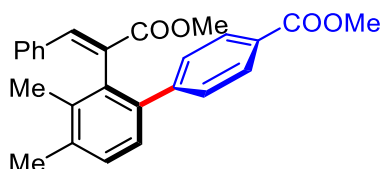


**methyl (E)-2'-(3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)-[1,1',3',1''-terphenyl]-4-carboxylate (3ga)**



The product **3fa** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (52% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 – 7.75 (m, 2H), 7.53 (t,  $J = 7.7$  Hz, 1H), 7.40 (dd,  $J = 7.7, 1.3$  Hz, 1H), 7.36 (s, 1H), 7.32 (dd,  $J = 7.7, 1.3$  Hz, 1H), 7.24 – 7.17 (m, 4H), 7.15 – 7.03 (m, 6H), 6.88 – 6.74 (m, 2H), 3.88 (s, 3H), 3.49 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.2, 167.1, 146.2, 142.6, 142.1, 141.3, 141.0, 134.9, 133.0, 130.5, 130.2, 129.9, 129.3, 129.2, 128.9, 128.82, 128.76, 128.44, 128.37, 128.3, 127.7, 127.0, 52.10, 52.06. HRMS (ESI) calcd. for  $\text{C}_{30}\text{H}_{25}\text{O}_4[\text{M}+\text{H}]^+$ : 449.1753, found: 449.1764.  $[\alpha]_{\text{D}}^{20} = -26.9$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 9.0$  min (major), 8.0 min (minor), 98% ee.

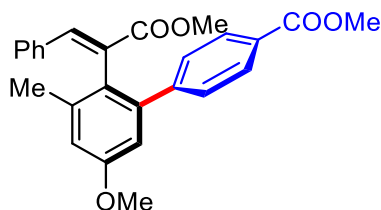
**methyl (E)-2'-(3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)-3',4'-dimethyl-[1,1'-biphenyl]-4-carboxylate (3ia)**



The product **3ia** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (65% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 8.3$  Hz, 2H), 7.63 (s, 1H), 7.27 (d,  $J = 7.8$  Hz, 1H), 7.22 (t,  $J = 7.4$  Hz, 1H), 7.14 (t,  $J = 7.7$  Hz, 2H), 7.06 (d,  $J = 7.7$  Hz, 1H), 6.99 (d,  $J = 8.3$  Hz, 2H), 6.84 (d,  $J = 7.5$  Hz, 2H), 3.88 (s, 3H), 3.69 (s, 3H), 2.37 (s, 3H), 2.11 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 167.2, 146.9, 141.6, 138.7, 137.0, 135.6, 134.8, 133.8, 130.8, 130.1, 129.9, 129.4, 128.9, 128.7, 128.4, 128.2, 127.3, 52.4, 52.1, 20.7, 16.4. HRMS (ESI) calcd. for  $\text{C}_{26}\text{H}_{24}\text{O}_4\text{Na}[\text{M}+\text{Na}]^+$ : 423.1572, found: 423.1564.  $[\alpha]_{\text{D}}^{20} = -36.2$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-3 column (5% isopropanol in hexanes, 0.5 mL/min,  $\lambda = 254$  nm),

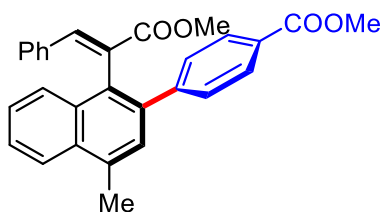
$t_R = 23.0$  min (major),  $22.4$  min (minor), 98% ee.

**methyl (E)-5'-methoxy-2'-(3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)-3'-methyl-[1,1'-biphenyl]-4-carboxylate (3ja)**



The product **3ja** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (72% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 7.9$  Hz, 2H), 7.63 (s, 1H), 7.23 (d,  $J = 7.3$  Hz, 1H), 7.17 (t,  $J = 7.6$  Hz, 2H), 7.04 (d,  $J = 7.9$  Hz, 2H), 6.96 – 6.85 (m, 3H), 6.71 (d,  $J = 2.7$  Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.68 (s, 3H), 2.15 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.4, 167.1, 159.1, 146.4, 142.2, 141.9, 138.8, 134.9, 123.0, 129.9, 129.4, 128.9, 128.53, 128.48, 128.45, 126.3, 115.7, 113.0, 55.3, 52.3, 52.1, 20.3. HRMS (ESI) calcd. for  $\text{C}_{26}\text{H}_{24}\text{O}_5\text{Na}[\text{M}+\text{Na}]^+$ :439.1521, found: 439.1516.  $[\alpha]_D^{20} = -61.9$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 14.3$  min (major), 9.0 min (minor), 91% ee.

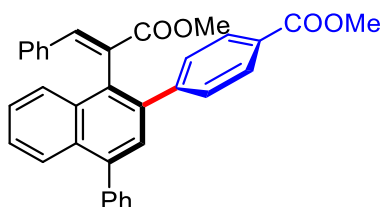
**methyl (E)-4-(1-(3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)-4-methylnaphthalen-2-yl)benzoate (3ka)**



The product **3ka** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (62% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 – 8.07 (m, 1H), 7.93 – 7.80 (m, 4H), 7.58 – 7.56 (m, 1H), 7.45 – 7.40 (m, 1H), 7.29 (s, 1H), 7.18 – 7.11 (m, 1H), 7.12 – 7.06 (m, 2H), 7.02 (t,  $J = 7.8$  Hz, 2H), 6.87 – 6.71 (m, 2H), 3.90 (s, 3H), 3.64 (s, 3H), 2.80 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 167.1, 146.6, 143.2, 137.6, 135.0, 134.5, 132.3, 131.9, 130.1, 129.5, 129.3, 129.2, 128.9, 128.7, 128.6, 128.34, 128.26, 126.8, 126.2, 125.9, 124.6, 52.4, 52.1, 19.7. HRMS (ESI) calcd.

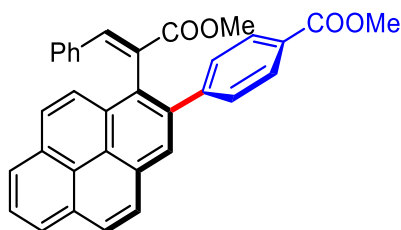
for  $C_{29}H_{24}O_4Na[M+Na]^+$ : 459.1572, found: 459.1559.  $[\alpha]_D^{20} = -42.6$  ( $c = 0.25$ ,  $CHCl_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 8.7$  min (major), 9.4 min (minor), 95% ee.

**methyl (E)-4-(1-(3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)-4-methylnaphthalen-2-yl)benzoate (3la)**



The product **3la** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (53% yield).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.06 – 8.00 (m, 1H), 7.95 – 7.88 (m, 2H), 7.88 – 7.78 (m, 2H), 7.64 – 7.58 (m, 2H), 7.56 – 7.50 (m, 2H), 7.50 – 7.43 (m, 3H), 7.40 (s, 1H), 7.22 – 7.15 (m, 1H), 7.15 – 7.11 (m, 2H), 7.06 (t,  $J = 7.8$  Hz, 2H), 6.90 – 6.78 (m, 2H), 3.90 (s, 3H), 3.69 (s, 3H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  168.4, 167.1, 146.4, 143.4, 140.8, 140.1, 137.6, 134.4, 132.3, 131.2, 130.7, 130.2, 130.1, 129.4, 129.1, 129.0, 128.8, 128.5, 128.33, 128.32, 127.6, 127.0, 126.6, 126.4, 125.7, 52.4, 52.1. HRMS (ESI) calcd. for  $C_{34}H_{27}O_4[M+H]^+$ : 499.1909, found: 499.1915.  $[\alpha]_D^{20} = -23.1$  ( $c = 0.25$ ,  $CHCl_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 9.7$  min (major), 15.6 min (minor), 97% ee.

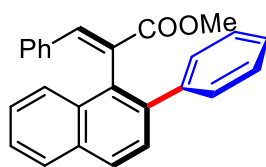
**methyl (E)-4-(1-(3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)pyren-2-yl)benzoate (3ma)**



The product **3ma** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (41% yield).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.22 (dd,  $J = 7.7, 1.1$  Hz, 1H), 8.18 (dd,  $J = 7.7, 1.1$  Hz, 1H), 8.16 – 8.12 (m, 2H), 8.10 (s, 1H), 8.05 (s, 2H), 8.04 – 7.99 (m, 2H), 7.96 – 7.87 (m, 2H), 7.31 – 7.23 (m, 2H), 7.13 – 7.06

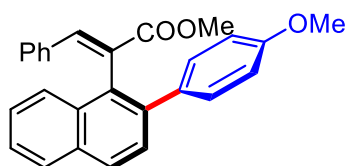
(m, 1H), 6.93 (t,  $J = 7.9$  Hz, 2H), 6.80 – 6.64 (m, 2H), 3.92 (s, 3H), 3.63 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 167.2, 146.7, 143.5, 138.7, 134.5, 131.3, 131.2, 131.0, 130.3, 129.7, 129.5, 129.4, 129.3, 129.0, 128.8, 128.6, 128.4, 128.3, 127.4, 126.4, 126.3, 125.63, 125.57, 124.73, 124.68, 124.5, 52.5, 52.2. HRMS (ESI) calcd. for  $\text{C}_{34}\text{H}_{24}\text{O}_4\text{Na}[\text{M}+\text{Na}]^+$ : 519.1572, found: 519.1567.  $[\alpha]_{\text{D}}^{20} = -42.6$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 11.5$  min (major), 18.6 min (minor), 97% ee.

### methyl (E)-3-phenyl-2-(2-phenylnaphthalen-1-yl)acrylate (3ab)



The product **3ab** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (81% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.87 (m, 3H), 7.84 – 7.76 (m, 1H), 7.54 – 7.37 (m, 3H), 7.21 – 7.16 (m, 3H), 7.14 – 7.09 (m, 1H), 7.08 – 7.04 (m, 2H), 7.03 – 6.96 (m, 2H), 6.85 – 6.71 (m, 2H), 3.61 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 142.9, 141.7, 139.2, 134.7, 132.9, 131.8, 131.3, 130.2, 129.5, 129.3, 128.7, 128.5, 128.4, 128.3, 127.7, 127.0, 126.9, 126.0, 125.4, 52.3. HRMS (ESI) calcd. for  $\text{C}_{26}\text{H}_{21}\text{O}_2[\text{M}+\text{H}]^+$ : 365.1542, found: 365.1548.  $[\alpha]_{\text{D}}^{20} = -29.7$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 11.6$  min (major), 8.2 min (minor), 94% ee.

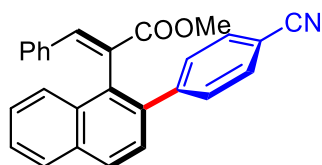
### methyl (E)-2-(2-(4-methoxyphenyl)naphthalen-1-yl)-3-phenylacrylate (3ac)



The product **3ac** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 30:1) as a white solid (66% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.89 (m, 3H), 7.79 (dd,  $J = 8.4, 1.1$  Hz, 1H), 7.54 – 7.45 (m, 2H), 7.43 – 7.38 (m, 1H), 7.17 – 7.10 (m, 1H), 7.08 – 6.97 (m, 4H), 6.95 – 6.81 (m, 2H), 6.79 – 6.70 (m, 2H), 3.78 (s, 3H), 3.61 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.7, 158.5, 142.8, 138.9, 134.6,

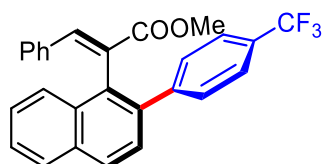
134.1, 132.7, 131.7, 131.2, 130.3, 129.8, 129.5, 129.3, 128.6, 128.42, 128.37, 128.3, 126.9, 125.9, 125.3, 113.2, 55.2, 52.4. HRMS (ESI) calcd. for  $C_{27}H_{22}O_3Na[M+Na]^+$ : 417.1467, found: 417.1464  $[\alpha]_D^{20} = -19.9$  ( $c = 0.25$ ,  $CHCl_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 17.3$  min (major), 13.1 min (minor), 89% ee.

**methyl (E)-2-(2-(4-cyanophenyl)naphthalen-1-yl)-3-phenylacrylate (3ad)**



The product **3ad** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 20:1) as a pale brown solid (53% yield).  $^1H$  NMR (500 MHz,  $CDCl_3$ ) 8.00 – 7.94 (m, 2H), 7.88 (s, 1H), 7.83 (d,  $J = 8.3$  Hz, 1H), 7.58 – 7.54 (m, 1H), 7.52 – 7.43 (m, 3H), 7.38 (d,  $J = 8.4$  Hz, 1H), 7.16 (t,  $J = 7.5$  Hz, 1H), 7.13 – 7.08 (m, 2H), 7.03 (t,  $J = 7.7$  Hz, 2H), 6.74 – 6.64 (m, 2H), 3.68 (s, 3H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  168.3, 146.5, 143.5, 137.1, 134.2, 133.2, 131.9, 131.5, 131.5, 130.1, 129.6, 129.5, 129.0, 128.9, 128.5, 128.4, 127.44, 127.37, 126.7, 125.4, 119.0, 110.6, 52.5. HRMS (ESI) calcd. for  $C_{27}H_{19}NO_3Na[M+Na]^+$ : 412.1313, found: 412.1309.  $[\alpha]_D^{20} = -25.5$  ( $c = 0.25$ ,  $CHCl_3$ ), HPLC chiralcel AS-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 12.0$  min (major), 13.1 min (minor), 96% ee.

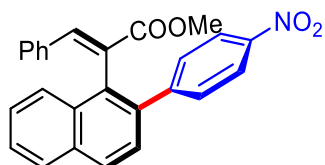
**methyl (E)-3-phenyl-2-(2-(4-(trifluoromethyl)phenyl)naphthalen-1-yl)acrylate (3ae)**



The product **3ae** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (66% yield).  $^1H$  NMR (500 MHz,  $CDCl_3$ ) 8.01 – 7.92 (m, 2H), 7.89 (s, 1H), 7.86 – 7.79 (m, 1H), 7.56 – 7.51 m, 1H), 7.50 – 7.35 (m, 4H), 7.18 – 7.07 (m, 3H), 7.01 (t,  $J = 7.8$  Hz, 2H), 6.73 (dd,  $J = 8.3, 1.4$  Hz, 2H), 3.66 (s, 3H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  168.4, 145.4, 143.4, 137.6, 134.4, 133.1, 132.0,

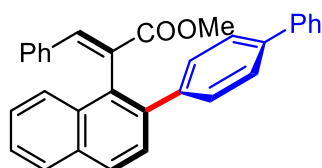
131.5, 130.1, 129.4, 129.1, 129.0, 128.1, 128.8, 128.5, 128.3, 127.8, 127.3, 126.5, 125.4, 124.6 (q,  $J = 3.9$  Hz), 124.2 (q,  $J = 279.3$  Hz), 52.4;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.4. HRMS (ESI) calcd. for  $\text{C}_{27}\text{H}_{19}\text{F}_3\text{O}_2\text{Na}[\text{M}+\text{Na}]^+$ : 455.1235, found: 455.1227.  $[\alpha]_{\text{D}}^{20} = -5.3$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel OD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 5.4$  min (major), 6.4 min (minor), 97% ee.

**methyl (E)-2-(2-(4-nitrophenyl)naphthalen-1-yl)-3-phenylacrylate (3af)**



The product **3af** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a yellow solid (56% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 – 8.01 (m, 2H), 8.02 – 7.95 (m, 2H), 7.88 (s, 1H), 7.87 – 7.81 (m, 1H), 7.56 (ddd,  $J = 8.1, 6.9, 1.3$  Hz, 1H), 7.53 – 7.47 (m, 1H), 7.40 (d,  $J = 8.4$  Hz, 1H), 7.24 – 7.11 (m, 3H), 7.03 (t,  $J = 7.8$  Hz, 2H), 6.79 – 6.66 (m, 2H), 3.69 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 148.6, 146.7, 143.6, 136.8, 134.2, 133.3, 132.0, 131.6, 130.1, 129.6, 129.0, 128.6, 128.44, 128.37, 127.5, 127.3, 126.8, 125.4, 124.4, 123.0, 52.6. HRMS (ESI) calcd. for  $\text{C}_{26}\text{H}_{19}\text{NO}_4\text{Na}[\text{M}+\text{Na}]^+$ : 432.1212, found: 432.1206.  $[\alpha]_{\text{D}}^{20} = -19.9$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 13.9$  min (major), 15.1 min (minor), 91% ee.

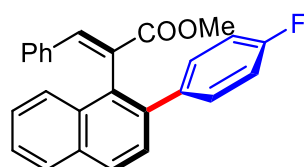
**methyl (E)-2-(2-([1,1'-biphenyl]-4-yl)naphthalen-1-yl)-3-phenylacrylate (3ag)**



The product **3ah** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a pale yellow solid (79% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 8.00 – 7.90 (m, 3H), 7.85 – 7.81 (m, 1H), 7.64 – 7.55 (m, 2H), 7.54 – 7.46 (m, 2H), 7.47 – 7.39 (m, 5H), 7.36 – 7.28 (m, 1H), 7.18 – 7.08 (m, 3H), 7.0 – 6.99 (m, 2H), 6.92 – 6.76 (m, 2H), 3.63 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 143.1, 140.8, 140.7, 139.5, 138.8, 134.7, 132.9, 131.9, 131.3, 130.2, 129.5, 129.3, 129.2, 128.8, 128.5, 128.4, 128.4,

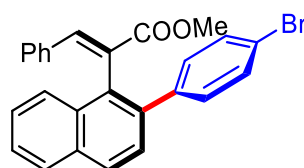
128.3, 127.3, 127.0, 127.0, 126.4, 126.1, 125.4, 52.4. HRMS (ESI) calcd. for  $C_{32}H_{24}O_2Na[M+Na]^+$ : 463.1674, found: 463.1670.  $[\alpha]_D^{20} = -28.0$  ( $c = 0.25$ ,  $CHCl_3$ ), HPLC chiralcel OD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 6.7$  min (major), 8.4 min (minor), 95% ee.

**methyl (E)-2-(2-(4-fluorophenyl)naphthalen-1-yl)-3-phenylacrylate (3ah)**



The product **3ag** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a white solid (79% yield).  $^1H$  NMR (500 MHz,  $CDCl_3$ ) 7.97 – 7.89 (m, 3H), 7.80 (d,  $J = 8.4$  Hz, 1H), 7.54 – 7.47 (m, 1H), 7.47 – 7.38 (m, 2H), 7.20 – 7.10 (m, 1H), 7.06 – 6.95 (m, 4H), 6.94 – 6.84 (m, 2H), 6.83 – 6.71 (m, 2H), 3.64 (s, 3H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  168.49, 161.93 (d,  $J = 245.5$  Hz), 142.97, 138.08, 137.61 (d,  $J = 2.9$  Hz), 134.5, 132.9, 131.9, 131.4, 130.3, 130.2, 130.1, 129.4, 128.5, 128.4, 128.3, 128.2, 127.1, 126.1, 125.3, 114.6 (d,  $J = 21.2$  Hz), 52.4;  $^{19}F$  NMR (471 MHz,  $CDCl_3$ )  $\delta$  -115.8. HRMS (ESI) calcd. for  $C_{26}H_{19}FO_2Na[M+Na]^+$ : 405.1267, found: 405.1264.  $[\alpha]_D^{20} = -39.9$  ( $c = 0.25$ ,  $CHCl_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 10.3$  min (major), 7.8 min (minor), 96% ee.

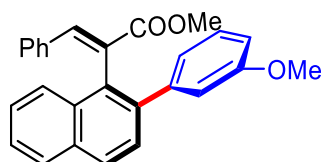
**methyl (E)-2-(2-(4-bromophenyl)naphthalen-1-yl)-3-phenylacrylate (3ai)**



The product **3ai** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 40:1) as a yellow solid (74% yield).  $^1H$  NMR (500 MHz,  $CDCl_3$ ) 7.98 – 7.92 (m, 3H), 7.82 (d,  $J = 8.4$  Hz, 1H), 7.56 – 7.50 (m, 1H), 7.46 (ddd,  $J = 8.2, 6.9, 1.3$  Hz, 1H), 7.41 (d,  $J = 8.4$  Hz, 1H), 7.36 – 7.29 (m, 2H), 7.21 – 7.10 (m, 1H), 7.03 (t,  $J = 7.8$  Hz, 2H), 6.94 – 6.84 (m, 2H), 6.78 (d,  $J = 7.4$  Hz, 2H), 3.66 (s, 3H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  168.4, 143.1, 140.6, 137.8, 134.4, 132.9, 131.9, 131.3, 130.8, 130.3,

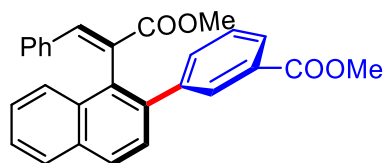
130.1, 129.4, 129.2, 128.6, 128.4, 128.2, 127.9, 127.1, 126.2, 125.3, 121.2, 52.3. HRMS (ESI) calcd. for  $C_{26}H_{19}BrO_2Na[M+Na]^+$ : 465.0466, found: 465.0457.  $[\alpha]_D^{20} = -25.7$  ( $c = 0.25$ ,  $CHCl_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 8.7$  min (major), 7.8 min (minor), 94% ee.

**methyl (E)-2-(2-(3-methoxyphenyl)naphthalen-1-yl)-3-phenylacrylate (3aj)**



The product **3aj** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 30:1) as a white solid (60% yield).  $^1H$  NMR (500 MHz,  $CDCl_3$ ) 8.01 – 7.91 (m, 3H), 7.82 (d,  $J = 8.4$  Hz, 1H), 7.63 – 7.38 (m, 3H), 7.16 – 7.09 (m, 2H), 7.02 (t,  $J = 7.7$  Hz, 2H), 6.88 – 6.72 (m, 3H), 6.68 – 6.64 (m, 1H), 6.55 (t,  $J = 2.0$  Hz, 1H), 3.64 (s, 3H), 3.57 (s, 3H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  168.6, 158.8, 143.1, 142.9, 139.0, 134.7, 132.9, 131.9, 131.2, 130.3, 129.4, 129.3, 128.8, 128.43, 128.41, 128.27, 128.25, 127.0, 126.1, 125.4, 121.1, 113.6, 113.3, 55.0, 52.4. HRMS (ESI) calcd. for  $C_{27}H_{22}O_3Na[M+Na]^+$ : 417.1467, found: 417.1462.  $[\alpha]_D^{20} = -13.3$  ( $c = 0.25$ ,  $CHCl_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 16.1$  min (major), 11.0 min (minor), 96% ee.

**methyl (E)-2-(2-(3-methoxyphenyl)naphthalen-1-yl)-3-phenylacrylate (3ak)**

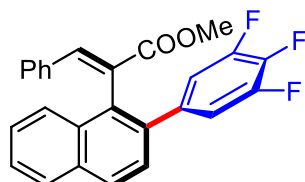


The product **3ak** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 30:1) as a white solid (73% yield).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.00 – 7.92 (m, 2H), 7.89 (d,  $J = 7.6$  Hz, 2H), 7.84 (dd,  $J = 8.4, 1.2$  Hz, 1H), 7.69 (t,  $J = 1.8$  Hz, 1H), 7.52 (ddd,  $J = 8.2, 6.9, 1.3$  Hz, 1H), 7.50 – 7.43 (m, 2H), 7.30 – 7.19 (m, 2H), 7.17 – 7.11 (m, 1H), 7.01 (t,  $J = 7.7$  Hz, 2H), 6.78 – 6.67 (m, 2H), 3.83 (s, 3H), 3.66 (s, 3H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  168.5, 166.9, 143.3, 141.9, 138.0, 134.4, 133.1, 133.0, 132.0, 131.5, 130.10, 130.05, 129.6, 129.4, 129.2, 128.7, 128.5, 128.3, 128.1, 128.0,



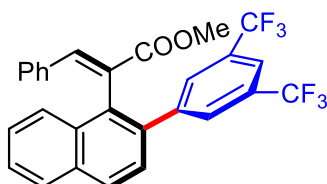
127.8, 127.2, 126.3, 125.4, 52.4, 52.1. HRMS (ESI) calcd. for  $C_{28}H_{22}O_4Na[M+Na]^+$ : 445.1416, found: 445.1410.  $[\alpha]_D^{20} = -23.6$  ( $c = 0.25$ ,  $CHCl_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 19.8$  min (major), 16.9 min (minor), 96% ee.

**methyl (E)-3-phenyl-2-(2-(3,4,5-trifluorophenyl)naphthalen-1-yl)acrylate (3al)**



The product **3ak** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 30:1) as a white solid (57% yield).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.99 – 7.90 (m, 3H), 7.82 (d,  $J = 8.3$  Hz, 1H), 7.55 (t,  $J = 7.0$  Hz, 1H), 7.52 – 7.46 (m, 1H), 7.33 (d,  $J = 8.4$  Hz, 1H), 7.17 (t,  $J = 7.4$  Hz, 1H), 7.04 (t,  $J = 7.7$  Hz, 2H), 6.72 (d,  $J = 7.6$  Hz, 2H), 6.61 – 6.51 (m, 2H), 3.71 (s, 3H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  168.3, 151.4, 149.4, 143.4, 137.6, 136.0, 134.3, 133.1, 132.0, 131.6, 130.6, 129.9, 129.6, 129.3, 129.0, 128.9, 128.5, 128.4, 128.3, 127.4 (d,  $J = 8.0$  Hz), 126.7, 125.4, 112.96 (d,  $J = 5.2$  Hz), 112.83 (d,  $J = 5.0$  Hz), 52.5;  $^{19}F$  NMR (471 MHz,  $CDCl_3$ )  $\delta$  -135.1 (d,  $J = 20.7$  Hz), -162.8 (t,  $J = 20.4$  Hz). HRMS (ESI) calcd. for  $C_{26}H_{17}F_3O_2Na[M+Na]^+$ : 441.1078, found: 441.1075.  $[\alpha]_D^{20} = -44.4$  ( $c = 0.25$ ,  $CHCl_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 6.8$  min (major), 5.7 min (minor), 95% ee.

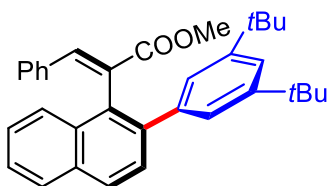
**methyl (E)-3-phenyl-2-(2-(3,4,5-trifluorophenyl)naphthalen-1-yl)acrylate (3am)**



The product **3am** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 30:1) as a white solid (49% yield).  $^1H$  NMR (400 MHz,  $CDCl_3$ ) 8.03 – 7.95 (m, 2H), 7.92 – 7.86 (m, 1H), 7.82 (s, 1H), 7.71 (s, 1H), 7.64 – 7.49 (m, 2H), 7.36 (d,  $J = 8.4$  Hz, 3H), 7.18 – 7.10 (m, 1H), 7.07 – 6.94 (m, 2H), 6.70 – 6.51 (m, 2H), 3.72 (s, 3H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  168.3, 143.7, 143.6, 135.9, 134.1, 133.3, 132.5,

132.1, 130.8 (q,  $J = 32.9$  Hz), 129.7, 129.6, 129.2, 129.1, 128.9, 128.6, 128.5, 128.4, 127.6, 127.1, 126.9, 125.5, 123.2 (q,  $J = 273.0$  Hz), 120.6 (sept = 4.0 Hz), 52.5.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.90. HRMS (ESI) calcd. for  $\text{C}_{28}\text{H}_{18}\text{F}_6\text{NaO}_2[\text{M}+\text{Na}]^+$ : 523.1109, found: 523.1107.  $[\alpha]_{\text{D}}^{20} = -36.9$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 4.4$  min (major), 4.0 min (minor), 94% ee.

### methyl (E)-3-phenyl-2-(2-(3,4,5-trifluorophenyl)naphthalen-1-yl)acrylate (3an)



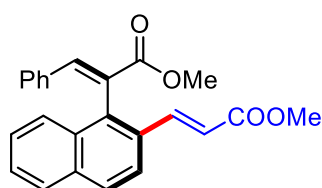
The product **3an** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 30:1) as a white solid (41% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (dd,  $J = 11.6, 8.4$  Hz, 2H), 7.87 – 7.79 (m, 2H), 7.57 – 7.48 (m, 2H), 7.47 – 7.40 (m, 1H), 7.25 – 7.24 (m, 1H), 7.15 – 7.07 (m, 1H), 7.00 (t,  $J = 7.7$  Hz, 2H), 6.89 (t,  $J = 1.7$  Hz, 2H), 6.75 (d,  $J = 8.0$  Hz, 2H), 3.65 (d,  $J = 1.0$  Hz, 3H), 1.17 (d,  $J = 1.6$  Hz, 18H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 149.8, 142.6, 140.7, 140.3, 134.7, 132.8, 132.1, 131.3, 130.2, 129.8, 129.2, 128.42, 128.35, 128.29, 128.2, 126.8, 125.8, 125.4, 123.1, 120.5, 52.2, 34.7, 31.3. HRMS (ESI) calcd. for  $\text{C}_{34}\text{H}_{36}\text{NaO}_2[\text{M}+\text{Na}]^+$ : 499.2613, found: 499.2619.  $[\alpha]_{\text{D}}^{20} = -59.5$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 4.7$  min (major), 4.1 min (minor), 97% ee.

### 3.3 General Procedure for Pd(II)-catalyzed Asymmetric C-H olefination

Substrate (0.2 mmol),  $\text{Pd}(\text{OAc})_2$  (10 mol%, 4.5 mg), Boc-L-*tert*-leucine (0.06 mmol, 13.9 mg) were placed in a Schlenk tube, which was filled with oxygen by using standard Schlenk techniques. After which, *i*PrOH (2 mL) was added using a syringe. Olefin (0.6 mmol) and a solution of KOH (22.4 mg in 36  $\mu\text{L}$   $\text{H}_2\text{O}$ ) was added via microsyringe, subsequently. The reaction mixture was vigorously stirred at 30  $^\circ\text{C}$  for 72 hours. Upon completion, the reaction was diluted with ethyl acetate, and filtered through a plug of Celite. The solvent was concentrated *in vacuo* and then the obtained

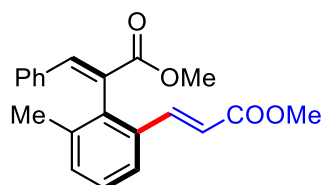
slurry was dissolved in DMF (5 mL), treated with MeI (0.3 mmol, 19  $\mu$ L) and  $K_2CO_3$  (0.4 mmol, 55.6 mg). The reaction mixture was stirred for another 2 hours at room temperature. Then the mixture was diluted with ethyl acetate 20 mL and washed with water. Organic layer was concentrated *in vacuo* and purified by flash chromatography (petroleum ether/ethyl acetate = 30:1 to 10:1) to afford the product.

**methyl (E)-2-(2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)naphthalen-1-yl)-3-phenylacrylate (5aa)**



The product **5aa** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (97% yield).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.29 (s, 1H), 7.96 – 7.68 (m, 5H), 7.49 (ddd,  $J$  = 8.1, 6.9, 1.2 Hz, 1H), 7.41 (ddd,  $J$  = 8.3, 6.9, 1.3 Hz, 1H), 7.16 – 7.07 (m, 1H), 7.05 – 6.99 (m, 2H), 6.94 – 6.78 (m, 2H), 6.41 (d,  $J$  = 15.9 Hz, 1H), 3.72 (s, 3H), 3.68 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  167.9, 167.2, 143.9, 142.2, 135.1, 134.2, 133.9, 131.8, 130.4, 130.4, 129.7, 128.9, 128.5, 128.4, 127.4, 127.31, 127.30, 125.7, 123.1, 119.6, 52.6, 51.7. HRMS (ESI) calcd. for  $C_{24}H_{20}O_4Na[M+Na]^+$ : 395.1259, found: 395.1264.  $[\alpha]_D^{20}$  = -51.9 ( $c$  = 0.25,  $CHCl_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  = 24.9 min (major), 23.1 min (minor), 97% ee.

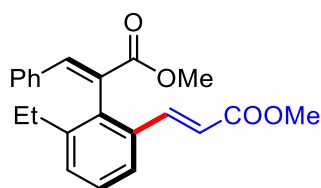
**methyl (E)-2-(2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)naphthalen-1-yl)-3-phenylacrylate (5ba)**



The product **5ba** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (68% yield).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.03 (s, 1H), 7.64 (d,  $J$  = 15.9 Hz, 1H), 7.54 (d,  $J$  = 7.3 Hz, 1H), 7.32 (dt,  $J$  = 13.7, 7.2 Hz, 2H), 7.21 (t,  $J$  = 7.4 Hz, 1H), 7.14 (t,  $J$  = 7.6 Hz, 2H), 7.01 – 6.87 (m, 2H), 6.28 (d,  $J$  = 15.9 Hz,

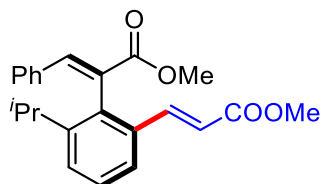
1H), 3.76 (s, 3H), 3.70 (s, 3H), 2.10 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 167.7, 167.1, 142.7, 142.3, 137.3, 136.3, 134.2, 133.5, 132.1, 130.1, 129.7, 128.6, 128.5, 128.4, 124.31, 119.4, 52.6, 51.60, 19.9. HRMS (ESI) calcd. for C<sub>21</sub>H<sub>20</sub>O<sub>4</sub>Na[M+Na]<sup>+</sup>: 359.1259, found: 359.1253. [α]<sub>D</sub><sup>20</sup> = -25.8 (c = 0.25, CHCl<sub>3</sub>), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm), t<sub>R</sub> = 9.8 min (major), 13.4 min (minor), 90% ee.

**methyl (E)-2-(2-ethyl-6-((E)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-3-phenylacrylate (5ca)**



The product **5ca** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (99% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.03 (s, 1H), 7.64 (d, *J* = 15.9 Hz, 1H), 7.59 – 7.48 (m, 1H), 7.46 – 7.33 (m, 2H), 7.24 – 7.17 (m, 1H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.07 – 6.79 (m, 2H), 6.27 (d, *J* = 15.9 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 2.45 (ddt, *J* = 40.7, 14.8, 7.4 Hz, 2H), 1.03 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.0, 167.1, 143.0, 142.8, 142.5, 135.7, 134.2, 133.6, 130.37, 130.35, 129.7, 128.6, 128.5, 128.3, 124.3, 119.4, 52.6, 51.6, 26.3, 14.4. HRMS (ESI) calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>4</sub>Na[M+Na]<sup>+</sup>: 373.1416, found: 373.1413. [α]<sub>D</sub><sup>20</sup> = -51.8 (c = 0.25, CHCl<sub>3</sub>), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm), t<sub>R</sub> = 8.7 min (major), 12.1 min (minor), 98% ee.

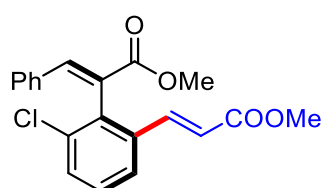
**methyl (E)-2-(2-isopropyl-6-((E)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-3-phenylacrylate (5da)**



The product **5da** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (99% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.04 (s, 1H), 7.65 (d, *J* = 15.8 Hz, 1H), 7.54 (m, *J* = 5.5, 3.5 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.22 –

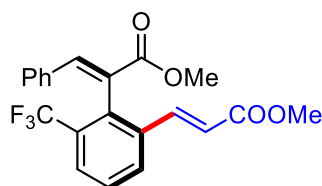
7.17 (m, 1H), 7.13 (t,  $J = 7.6$  Hz, 2H), 6.93 (d,  $J = 7.6$  Hz, 2H), 6.25 (d,  $J = 15.8$  Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 2.88 (hept,  $J = 6.9$  Hz, 1H), 1.13 (d,  $J = 6.8$  Hz, 3H), 0.92 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 167.1, 147.8, 143.0, 142.6, 134.8, 134.2, 133.4, 130.5, 129.7, 128.8, 128.4, 128.3, 127.8, 124.3, 119.4, 52.5, 51.6, 30.7, 23.7. HRMS (ESI) calcd. for  $\text{C}_{23}\text{H}_{25}\text{O}_4[\text{M}+\text{H}]^+$ : 365.1753, found: 365.1739.  $[\alpha]_{\text{D}}^{20} = -81.1$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 6.6$  min (major), 10.1 min (minor), >99% ee.

**methyl (E)-2-(2-chloro-6-((E)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-3-phenylacrylate (5ea)**



The product **5ea** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (55% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (s, 1H), 7.59 – 7.47 (m, 3H), 7.40 – 7.33 (m, 1H), 7.25 – 7.20 (m, 1H), 7.15 (t,  $J = 7.5$  Hz, 2H), 7.00 – 6.92 (m, 2H), 6.20 (d,  $J = 15.9$  Hz, 1H), 3.78 (d,  $J = 1.0$  Hz, 3H), 3.70 (d,  $J = 1.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 166.7, 143.5, 141.5, 135.6, 135.4, 135.2, 133.9, 130.9, 130.0, 129.8, 129.5, 128.6, 127.0, 125.1, 120.7, 52.7, 51.7. HRMS (ESI) calcd. for  $\text{C}_{20}\text{H}_{17}\text{ClO}_4\text{Na}[\text{M}+\text{Na}]^+$ : 379.0713, found: 379.0712.  $[\alpha]_{\text{D}}^{20} = -21.6$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 7.2$  min (major), 6.5 min (minor), 97% ee.

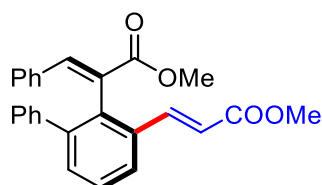
**methyl (E)-2-(2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-6-(trifluoromethyl)phenyl)-3-phenylacrylate (5fa)**



The product **5fa** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (47% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (s, 1H), 7.87 (d,  $J = 7.9$  Hz, 1H), 7.80 (d,  $J = 7.8$  Hz, 1H), 7.63 (d,  $J = 15.9$  Hz, 1H), 7.57 (t,  $J = 7.5$  Hz, 2H), 7.40 – 7.33 (m, 1H), 7.25 – 7.20 (m, 1H), 7.15 (t,  $J = 7.5$  Hz, 2H), 7.00 – 6.92 (m, 2H), 6.20 (d,  $J = 15.9$  Hz, 1H), 3.78 (d,  $J = 1.0$  Hz, 3H), 3.70 (d,  $J = 1.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 166.7, 143.5, 141.5, 135.6, 135.4, 135.2, 133.9, 130.9, 130.0, 129.8, 129.5, 128.6, 127.0, 125.1, 120.7, 52.7, 51.7. HRMS (ESI) calcd. for  $\text{C}_{21}\text{H}_{17}\text{F}_3\text{O}_4\text{Na}[\text{M}+\text{Na}]^+$ : 393.0713, found: 393.0712.  $[\alpha]_{\text{D}}^{20} = -21.6$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 7.2$  min (major), 6.5 min (minor), 97% ee.

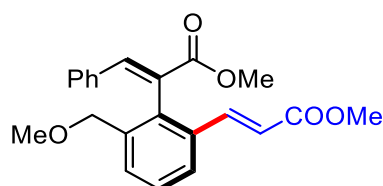
= 7.9 Hz, 1H), 7.22 (t,  $J = 7.4$  Hz, 1H), 7.14 (t,  $J = 7.7$  Hz, 2H), 6.88 (d,  $J = 7.5$  Hz, 2H), 6.31 (d,  $J = 15.9$  Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 166.5, 143.6, 140.8, 135.7, 135.2, 133.7, 130.4, 130.2, 130.1, 130.0, 128.7, 128.6, 128.1 (q,  $J = 5.3$  Hz), 125.8, 124.7, 123.6 (q,  $J = 274.2$  Hz), 121.5, 52.6, 51.8.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -60.9. HRMS (ESI) calcd. for  $\text{C}_{21}\text{H}_{17}\text{F}_3\text{O}_2\text{Na}[\text{M}+\text{Na}]^+$ : 413.0977, found: 413.0976.  $[\alpha]_{\text{D}}^{20} = -30.5$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 10.9$  min (major), 14.3 min (minor), >99% ee.

**methyl (E)-2-(3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl)-3-phenylacrylate (5ga)**



The product **5ga** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (72% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (s, 1H), 7.72 – 7.64 (m, 2H), 7.49 (t,  $J = 7.8$  Hz, 1H), 7.38 (dd,  $J = 7.5$ , 1.3 Hz, 1H), 7.24 – 7.17 (m, 4H), 7.14 (dd,  $J = 8.4$ , 7.0 Hz, 2H), 7.05 – 6.97 (m, 2H), 6.94 – 6.87 (m, 2H), 6.28 (d,  $J = 15.9$  Hz, 1H), 3.71 (s, 3H), 3.61 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.6, 167.0, 143.0, 142.8, 142.6, 140.6, 135.1, 134.4, 133.9, 132.0, 130.2, 129.5, 128.8, 128.5, 128.45, 128.37, 127.7, 127.1, 125.8, 119.8, 52.3, 51.6. HRMS (ESI) calcd. for  $\text{C}_{26}\text{H}_{23}\text{O}_4[\text{M}+\text{H}]^+$ : 399.1596, found: 399.1589.  $[\alpha]_{\text{D}}^{20} = -17.5$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 9.5$  min (major), 13.7 min (minor), 99% ee.

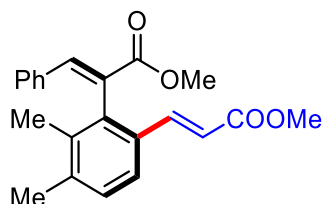
**methyl (E)-2-(2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-6-(methoxymethyl)phenyl)-3-phenylacrylate (5ha)**



The product **5ha** was purified with silica gel chromatography (petroleum ether/ethyl

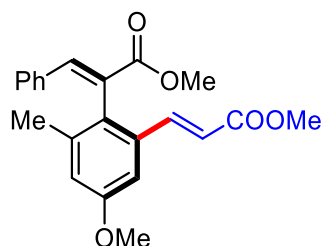
acetate = 10:1) as a white solid (45% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.01 (s, 1H), 7.71 – 7.61 (m, 2H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.4 Hz, 2H), 6.32 (d, *J* = 15.9 Hz, 1H), 4.21 (dd, *J* = 85.3, 12.5 Hz, 2H), 3.75 (s, 3H), 3.71 (s, 3H), 3.23 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 167.7, 167.1, 142.1, 142.0, 137.4, 135.6, 134.0, 133.8, 130.2, 129.9, 129.8, 128.64, 128.57, 127.6, 126.0, 119.7, 72.4, 58.4, 52.6, 51.7. HRMS (ESI) calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>5</sub>Na[M+Na]<sup>+</sup>: 389.1365, found: 389.1368. [α]<sub>D</sub><sup>20</sup> = -17.7 (c = 0.25, CHCl<sub>3</sub>), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm), t<sub>R</sub> = 13.0 min (major), 18.8 min (minor), 95% ee.

**methyl (E)-2-(6-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-2,3-dimethylphenyl)-3-phenylacrylate (5ia)**



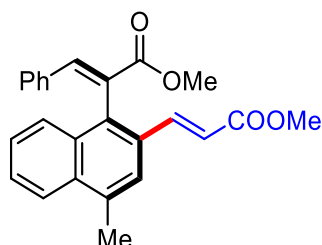
The product **5ia** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (87% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.03 (s, 1H), 7.60 (d, *J* = 15.9 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.7 Hz, 2H), 6.23 (d, *J* = 15.8 Hz, 1H), 3.76 (d, *J* = 0.9 Hz, 3H), 3.69 (d, *J* = 0.8 Hz, 3H), 2.33 (s, 3H), 2.04 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 167.9, 167.3, 143.0, 142.1, 139.6, 136.2, 135.6, 134.4, 131.2, 130.2, 130.1, 129.6, 129.2, 128.5, 124.0, 118.3, 52.6, 51.5, 20.8, 16.3. HRMS (ESI) calcd. for C<sub>22</sub>H<sub>23</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 351.1596, found: 351.1605. [α]<sub>D</sub><sup>20</sup> = -7.4 (c = 0.25, CHCl<sub>3</sub>), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm), t<sub>R</sub> = 10.4 min (major), 15.0 min (minor), 98% ee.

**methyl (E)-2-(4-methoxy-2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-6-methylphenyl)-3-phenylacrylate (5ja)**



The product **5ja** was purified with silica gel chromatography (petroleum ether/ethylacetate = 10:1) as a white solid (86% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (s, 1H), 7.59 (d,  $J = 15.9$  Hz, 1H), 7.24 – 7.18 (m, 1H), 7.16 (t,  $J = 8.4, 6.6$  Hz, 2H), 7.05 (d,  $J = 2.7$  Hz, 1H), 7.00 – 6.94 (m, 2H), 6.88 (d,  $J = 2.5$  Hz, 1H), 6.25 (d,  $J = 15.8$  Hz, 1H), 3.86 (s, 3H), 3.76 (s, 3H), 3.70 (s, 3H), 2.08 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 167.1, 159.2, 142.7, 142.6, 138.8, 134.6, 134.4, 130.2, 129.7, 128.9, 128.6, 128.4, 119.5, 118.4, 108.8, 55.3, 52.6, 51.6, 20.1. HRMS (ESI) calcd. for  $\text{C}_{22}\text{H}_{24}\text{O}_5[\text{M}+\text{H}]^+$ : 367.1545, found: 367.1540.  $[\alpha]_{\text{D}}^{20} = -31.7$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 12.3$  min (major), 16.1 min (minor), 83% ee.

**methyl (E)-2-(2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-4-methylnaphthalen-1-yl)-3-phenylacrylate (5ka)**

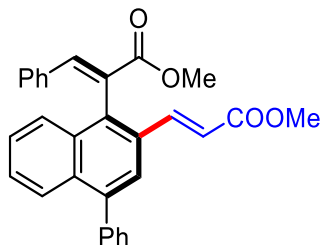


The product **5ka** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (79% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (s, 1H), 8.01 (d,  $J = 8.4$  Hz, 1H), 7.89 – 7.77 (m, 2H), 7.61 (s, 1H), 7.53 (dd,  $J = 8.3, 6.8$  Hz, 1H), 7.41 (dd,  $J = 8.3, 6.9$  Hz, 1H), 7.15 – 7.07 (m, 1H), 7.02 (t,  $J = 7.6$  Hz, 2H), 6.90 (d,  $J = 7.8$  Hz, 2H), 6.41 (d,  $J = 15.9$  Hz, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 2.75 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.1, 167.3, 143.8, 142.3, 135.2, 134.0, 133.7, 133.5, 131.9, 130.4, 129.9, 129.6, 128.5, 127.6, 127.2, 127.0, 126.3, 124.7, 123.7, 119.3, 52.6, 51.7, 19.8. HRMS (ESI) calcd. for  $\text{C}_{25}\text{H}_{23}\text{O}_4[\text{M}+\text{H}]^+$ : 387.1596, found: 387.1591.  $[\alpha]_{\text{D}}^{20} = -40.4$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in



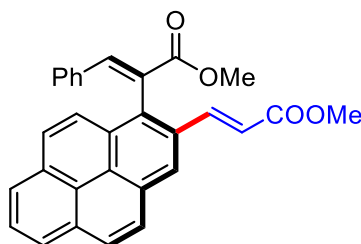
hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 16.9$  min (major), 22.7 min (minor), 89% ee.

**methyl (E)-2-(2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-4-phenylnaphthalen-1-yl)-3-phenylacrylate (5la)**



The product **5la** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (77% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (s, 1H), 8.01 – 7.91 (m, 1H), 7.91 – 7.82 (m, 2H), 7.71 (s, 1H), 7.57 (d,  $J = 6.8$  Hz, 2H), 7.53 (t,  $J = 7.5$  Hz, 2H), 7.50 – 7.37 (m, 3H), 7.21 – 7.11 (m, 1H), 7.06 (t,  $J = 7.6$  Hz, 2H), 6.95 (d,  $J = 7.6$  Hz, 2H), 6.42 (d,  $J = 15.9$  Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 167.2, 144.0, 142.1, 141.1, 140.1, 134.5, 134.0, 132.7, 132.3, 130.4, 130.1, 129.9, 129.8, 128.6, 128.5, 127.7, 127.5, 127.4, 127.2, 126.7, 126.1, 124.1, 119.8, 52.7, 51.7. HRMS (ESI) calcd. for  $\text{C}_{30}\text{H}_{24}\text{O}_4\text{Na}[\text{M}+\text{Na}]^+$ : 471.1572, found: 471.1569.  $[\alpha]_{\text{D}}^{20} = -59.4$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 10.3$  min (major), 21.1 min (minor), 93% ee.

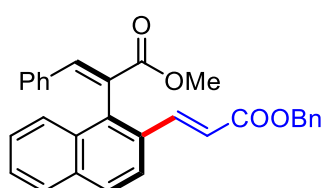
**methyl (E)-2-(2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)pyren-1-yl)-3-phenylacrylate (5ma)**



The product **5ma** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a yellow solid (54% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (s, 1H), 8.41 (s, 1H), 8.17 (ddd,  $J = 17.3, 7.6, 1.2$  Hz, 2H), 8.10 (d,  $J = 1.9$  Hz, 2H), 8.06 (d,  $J = 15.8$  Hz, 1H), 8.01 (d,  $J = 3.5$  Hz, 3H), 7.11 – 7.02 (m, 1H), 6.94 (t,  $J = 7.8$  Hz,

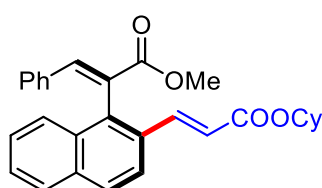
2H), 6.83 (dd,  $J = 8.2, 1.4$  Hz, 2H), 6.61 (d,  $J = 15.9$  Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.2, 167.1, 144.1, 143.1, 134.0, 131.5, 131.4, 131.24, 131.19, 131.0, 130.5, 129.7, 128.8, 128.5, 128.4, 127.9, 127.5, 126.7, 125.8, 125.69, 125.67, 124.6, 122.8, 120.5, 52.7, 51.8. HRMS (ESI) calcd. for  $\text{C}_{30}\text{H}_{22}\text{NaO}_4[\text{M}+\text{Na}]^+$ : 469.1416, found: 469.1416.  $[\alpha]_{\text{D}}^{20} = -33.6$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-3 column (5% isopropanol in hexanes, 0.5 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 72.7$  min (major), 46.4 min (minor), >99% ee.

**methyl (E)-2-(2-((E)-3-(benzyloxy)-3-oxoprop-1-en-1-yl)naphthalen-1-yl)-3-phenylacrylate (5ab)**



The product **5ab** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (79% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (s, 1H), 7.93 – 7.84 (m, 3H), 7.80 (d,  $J = 8.4$  Hz, 1H), 7.75 (d,  $J = 8.8$  Hz, 1H), 7.49 (t,  $J = 7.4$  Hz, 1H), 7.41 (t,  $J = 7.6$  Hz, 1H), 7.38 – 7.26 (m, 5H), 7.10 (t,  $J = 7.4$  Hz, 1H), 7.00 (t,  $J = 7.7$  Hz, 2H), 6.85 (d,  $J = 7.6$  Hz, 2H), 6.45 (d,  $J = 15.9$  Hz, 1H), 5.35 – 4.97 (m, 2H), 3.68 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 166.6, 143.9, 142.7, 136.1, 135.3, 134.3, 133.9, 131.9, 130.39, 130.36, 129.7, 129.0, 128.6, 128.51, 128.45, 128.22, 128.17, 127.5, 127.40, 127.36, 125.8, 123.1, 119.6, 66.2, 52.7. HRMS (ESI) calcd. for  $\text{C}_{30}\text{H}_{25}\text{O}_4[\text{M}+\text{H}]^+$ : 449.1753, found: 449.1760.  $[\alpha]_{\text{D}}^{20} = -25.7$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel ID column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 24.9$  min (major), 22.6 min (minor), 96% ee.

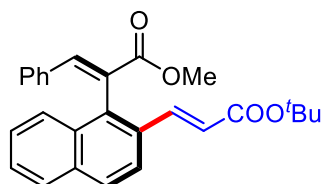
**methyl (E)-2-(2-((E)-3-(cyclohexyloxy)-3-oxoprop-1-en-1-yl)naphthalen-1-yl)-3-phenylacrylate (5ac)**



The product **5ac** was purified with silica gel chromatography (petroleum ether/ethyl

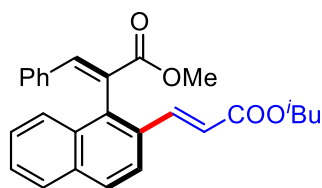
acetate = 10:1) as a white solid (88% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (s, 1H), 7.92 – 7.72 (m, 5H), 7.48 (t,  $J = 7.5$  Hz, 1H), 7.40 (t,  $J = 7.6$  Hz, 1H), 7.18 – 7.05 (m, 1H), 7.01 (t,  $J = 7.7$  Hz, 2H), 6.87 (d,  $J = 7.8$  Hz, 2H), 6.40 (d,  $J = 15.9$  Hz, 1H), 4.85 – 4.80 (m, 1H), 3.68 (s, 3H), 1.83 (m, 2H), 1.75 – 1.67 (m, 2H), 1.57 – 1.22 (m, 6H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 166.2, 143.8, 141.7, 135.0, 134.2, 134.0, 132.0, 130.5, 130.4, 129.6, 128.9, 128.5, 128.4, 127.6, 127.28, 127.25, 125.8, 123.2, 120.6, 72.6, 52.6, 31.7, 25.5, 23.7. HRMS (ESI) calcd. for  $\text{C}_{29}\text{H}_{28}\text{O}_4\text{Na}[\text{M}+\text{Na}]^+$ : 463.1885, found: 463.1896.  $[\alpha]_{\text{D}}^{20} = -70.2$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 10.5$  min (major), 14.7 min (minor), 95% ee.

**methyl (E)-2-(2-((E)-3-(tert-butoxy)-3-oxoprop-1-en-1-yl)naphthalen-1-yl)-3-phenylacrylate (5ad)**



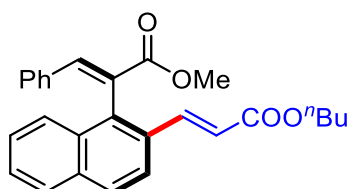
The product **5ad** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (99% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (s, 1H), 7.97 – 7.83 (m, 2H), 7.82 – 7.69 (m, 3H), 7.48 (m, 1H), 7.40 (m, 1H), 7.17 – 7.07 (m, 1H), 7.02 (dd,  $J = 8.5, 7.0$  Hz, 2H), 6.93 – 6.79 (m, 2H), 6.34 (d,  $J = 15.8$  Hz, 1H), 3.69 (s, 3H), 1.47 (s, 9H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 166.1, 143.7, 141.0, 134.8, 134.1, 134.1, 131.9, 130.7, 130.4, 129.6, 128.8, 128.44, 128.37, 127.6, 127.23, 127.15, 125.7, 123.2, 121.9, 80.4, 52.6, 28.2. HRMS (ESI) calcd. for  $\text{C}_{27}\text{H}_{26}\text{O}_4\text{Na}[\text{M}+\text{Na}]^+$ : 437.1729, found: 437.1733.  $[\alpha]_{\text{D}}^{20} = -63.1$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 11.4$  min (major), 9.0 min (minor), 99% ee.

**methyl (E)-2-(2-((E)-3-isobutoxy-3-oxoprop-1-en-1-yl)naphthalen-1-yl)-3-phenylacrylate (5ae)**



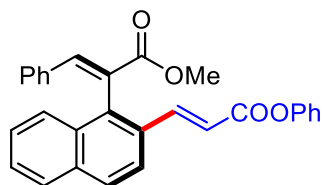
The product **5ae** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (84% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (s, 1H), 7.94 – 7.84 (m, 3H), 7.79 (dd,  $J = 14.0, 8.6$  Hz, 2H), 7.57 – 7.45 (m, 1H), 7.41 (ddd,  $J = 8.3, 6.9, 1.2$  Hz, 1H), 7.11 (t,  $J = 7.3$  Hz, 1H), 7.01 (t,  $J = 7.7$  Hz, 2H), 6.92 – 6.83 (m, 2H), 6.43 (d,  $J = 15.9$  Hz, 1H), 3.92 (dd,  $J = 6.6, 2.4$  Hz, 2H), 3.68 (s, 3H), 1.95 (dp,  $J = 13.4, 6.7$  Hz, 1H), 0.93 (dd,  $J = 6.8, 1.6$  Hz, 6H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 166.8, 143.8, 142.0, 135.1, 134.2, 133.9, 131.9, 130.43, 130.39, 129.7, 128.9, 128.5, 128.4, 127.5, 127.3, 125.8, 123.1, 120.0, 70.6, 52.7, 27.8, 19.2. HRMS (ESI) calcd. for  $\text{C}_{27}\text{H}_{26}\text{O}_4\text{Na}[\text{M}+\text{Na}]^+$ : 437.1729, found: 437.1729.  $[\alpha]_{\text{D}}^{20} = -59.6$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 11.3$  min (major), 16.1 min (minor), 94% ee.

**methyl (E)-2-(2-((E)-3-(tert-butoxy)-3-oxoprop-1-en-1-yl)naphthalen-1-yl)-3-phenylacrylate (5af)**



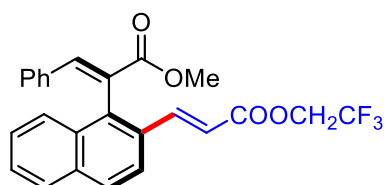
The product **5af** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (91% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (s, 1H), 7.95 – 7.65 (m, 5H), 7.49 (m, 1H), 7.40 (m, 1H), 7.18 – 7.06 (m, 1H), 7.01 (t,  $J = 7.7$  Hz, 2H), 6.91 – 6.80 (m, 2H), 6.41 (d,  $J = 15.9$  Hz, 1H), 4.13 (m, 2H), 3.68 (s, 3H), 1.75 – 1.50 (m, 2H), 1.47 – 1.31 (m, 2H), 0.93 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 166.9, 143.8, 142.0, 135.1, 134.2, 134.0, 131.9, 130.5, 130.4, 129.7, 128.9, 128.5, 128.4, 127.5, 127.3, 125.8, 123.1, 120.0, 64.4, 52.7, 30.7, 19.2, 13.8. HRMS (ESI) calcd. for  $\text{C}_{27}\text{H}_{26}\text{O}_4\text{Na}[\text{M}+\text{Na}]^+$ : 437.1729, found: 439.1727.  $[\alpha]_{\text{D}}^{20} = -70.2$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 15.0$  min (major), 20.0 min (minor), 91% ee.

**methyl (E)-2-(2-((E)-3-oxo-3-phenoxyprop-1-en-1-yl)naphthalen-1-yl)-3-phenylacrylate (5ag)**



The product **5ag** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (53% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (s, 1H), 8.01 (d,  $J = 15.9$  Hz, 1H), 7.98 – 7.88 (m, 2H), 7.83 (d,  $J = 8.7$  Hz, 2H), 7.53 (m, 1H), 7.44 (m, 1H), 7.41 – 7.34 (m, 2H), 7.29 – 7.19 (m, 1H), 7.18 – 7.12 (m, 1H), 7.12 – 7.07 (m, 2H), 7.04 (dd,  $J = 8.5, 7.1$  Hz, 2H), 6.89 (dd,  $J = 8.4, 1.4$  Hz, 2H), 6.59 (d,  $J = 15.8$  Hz, 1H), 3.71 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.9, 165.2, 150.8, 144.04, 144.0, 135.6, 134.4, 133.9, 132.0, 130.4, 130.1, 129.8, 129.4, 129.1, 128.54, 128.48, 127.6, 127.5, 127.4, 125.9, 125.8, 123.1, 121.6, 119.0, 52.7. HRMS (ESI) calcd. for  $\text{C}_{29}\text{H}_{22}\text{O}_4\text{Na}[\text{M}+\text{Na}]^+$ : 457.1416, found: 457.1422.  $[\alpha]_{\text{D}}^{20} = -31.0$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 16.8$  min (major), 21.0 min (minor), 92% ee.

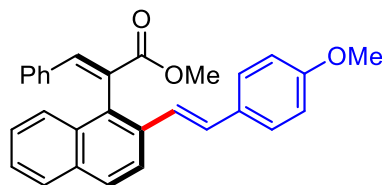
**methyl (E)-2-(2-((E)-3-oxo-3-(2,2,2-trifluoroethoxy)prop-1-en-1-yl)naphthalen-1-yl)-3-phenylacrylate (5ah)**



The product **5ah** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (76% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 (s, 1H), 7.99 – 7.84 (m, 3H), 7.82 (d,  $J = 8.4$  Hz, 1H), 7.76 (d,  $J = 8.7$  Hz, 1H), 7.52 (m, 1H), 7.43 (m, 1H), 7.12 (t,  $J = 7.3$  Hz, 1H), 7.02 (t,  $J = 7.7$  Hz, 2H), 6.91 – 6.81 (m, 2H), 6.43 (d,  $J = 15.8$  Hz, 1H), 4.51 (qd,  $J = 8.5, 3.1$  Hz, 2H), 3.70 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.9, 165.0, 144.6, 144.1, 135.9, 134.5, 133.9, 132.0, 130.3, 129.81, 129.75, 129.1, 128.52, 128.48, 127.7, 127.5, 127.3, 125.9, 123.1 (q,  $J = 277.83$  Hz), 123.0, 117.5, 60.3 (q,  $J = 36.7$  Hz), 52.7.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -73.7. HRMS (ESI) calcd. for  $\text{C}_{25}\text{H}_{29}\text{F}_3\text{O}_4\text{Na}[\text{M}+\text{Na}]^+$ : 463.1133, found: 463.1141.  $[\alpha]_{\text{D}}^{20} = -29.4$  ( $c$

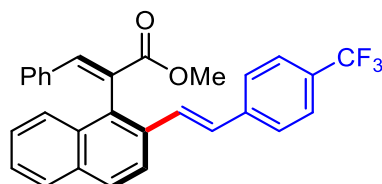
= 0.25, CHCl<sub>3</sub>), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm), t<sub>R</sub> = 14.0 min (major), 18.1 min (minor), 91% ee.

**methyl (E)-2-(2-((E)-4-methoxystyryl)naphthalen-1-yl)-3-phenylacrylate (5ai)**



The product **5ai** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (59% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.28 (s, 1H), 7.91 – 7.86 (m, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.46 – 7.38 (m, 1H), 7.38 – 7.29 (m, 3H), 7.16 – 7.06 (m, 3H), 7.02 (t, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.67 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.7, 159.4, 143.0, 134.3, 133.4, 133.0, 132.0, 131.3, 130.4, 130.3, 130.2, 129.5, 128.52, 128.45, 128.3, 128.0, 126.9, 125.9, 125.2, 124.1, 122.9, 114.1, 55.3, 52.6. HRMS (ESI) calcd. for C<sub>28</sub>H<sub>24</sub>O<sub>3</sub>Na[M+Na]<sup>+</sup>: 443.1623, found: 443.1622. [α]<sub>D</sub><sup>20</sup> = -18.9 (c = 0.25, CHCl<sub>3</sub>), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm), t<sub>R</sub> = 13.6 min (major), 23.3 min (minor), 98% ee.

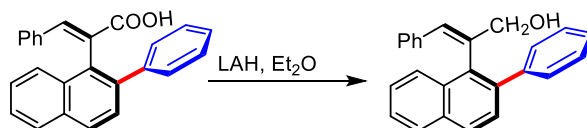
**methyl (E)-2-(2-((E)-4-(trifluoromethyl)styryl)naphthalen-1-yl)-3-phenylacrylate (5aj)**



The product **5aj** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1) as a white solid (60% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.30 (s, 1H), 7.95 – 7.84 (m, 3H), 7.77 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.51 – 7.45 (m, 3H), 7.41 (m, 1H), 7.33 (d, *J* = 16.2 Hz, 1H), 7.15 – 7.09 (m, 2H), 7.04 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.00 – 6.91 (m, 2H), 3.69 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.5, 143.3, 140.9, 134.1, 133.4, 132.6, 132.4, 132.0, 130.3, 129.7, 129.5, 129.0, 128.8, 128.5, 128.3, 128.2, 127.1, 126.8, 126.7, 126.5, 126.5, 125.6 (q, *J* = 3.8 Hz), 125.4, 122.9, 52.7; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -62.5. HRMS (ESI) calcd. for C<sub>29</sub>H<sub>21</sub>F<sub>3</sub>O<sub>2</sub>Na[M+Na]<sup>+</sup>: 481.1391, found: 481.1386. [α]<sub>D</sub><sup>20</sup> = -4.4 (c = 0.25, CHCl<sub>3</sub>),

HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 8.8$  min (major), 19.0 min (minor), 96% ee.

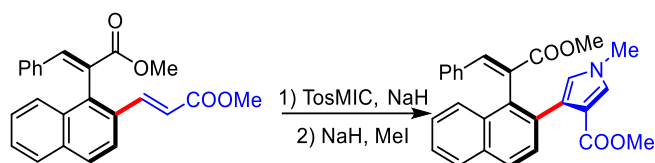
### 3.4 Reduction of CCA 1



To a stirred cold solution of **CCA 1** (0.2 mmol) in dry Et<sub>2</sub>O (5mL), which was placed in a 25mL round flask. The mixture was stirred at -78 °C. To this solution was added LAH (Lithium Aluminum Hydride) (0.6 mmol, 3 equiv) slowly. The resulting mixture was allowed to warm to room temperature and stirred for 2 hours until the substrate was consumed completely which was detected by TLC. Upon completion, the reaction was moved to 0 °C, and 1.3 mL water added dropwisely followed by 1.3 mL NaOH solution (15% in water), and then 1.3 mL water was added dropwisely, further stirred at room temperature for 15 minutes, after that, Na<sub>2</sub>SO<sub>4</sub> solid was added, then filtered. Then water 10mL was added, organic layers was separated. The aqueous layer was extracted with EA (10 mL) for two times, and the organic layers were combined. The solution was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography to afford **6**. The product **6** was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1:1) as a white solid (85% yield).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (d,  $J = 8.4$  Hz, 1H), 7.90 (t,  $J = 8.8$  Hz, 2H), 7.52 (d,  $J = 8.4$  Hz, 1H), 7.49 – 7.45 (m, 1H), 7.44 – 7.38 (m, 1H), 7.33 – 7.26 (m, 5H), 7.10 – 7.00 (m, 3H), 7.00 – 6.92 (m, 3H), 4.23 – 3.87 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  141.5, 138.2, 137.5, 136.3, 133.9, 133.0, 131.0, 129.3, 128.9, 128.7, 128.6, 128.32, 128.25, 128.04, 127.95, 127.2, 127.1, 127.0, 126.1, 125.8, 67.7. HRMS (ESI) calcd. for C<sub>25</sub>H<sub>20</sub>ONa[M+Na]<sup>+</sup>: 359.1412, found: 359.1410.  $[\alpha]_D^{20} = -40.1$  (c = 0.25, CHCl<sub>3</sub>), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 12.0$  min (major), 10.8 min (minor), 94% ee.

### 3.5 Transformation of **5aa** [3]

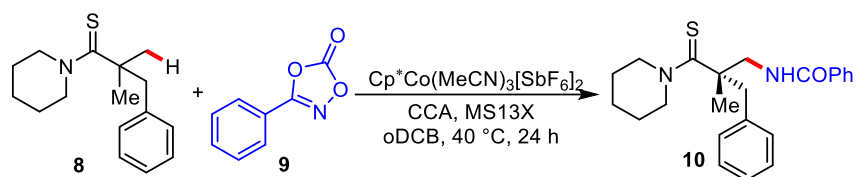


To a suspension of NaH (60% dispersion in mineral oil, 3 equiv.) in dry DMF (5 mL) was added a solution of **5aa** (0.2 mmol) and tosylmethylisocyanate (TosMIC) (1.2 equiv) in dry DMF (0.3 M final concentration) dropwise at 0 °C. Then the reaction mixture was stirred at 0 °C for 0.5 hours, diluted with ethyl acetate and brine. The organic layer was washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude product was dissolved in dry DMF and NaH (60% dispersion in mineral oil, 1.2 equiv.) was added. The mixture was stirred for 20 minutes and iodomethane (1.2 equiv.) were added dropwise at 0 °C. Then the reaction mixture was warmed to room temperature and stirred for 1 hours, diluted with ethyl acetate and brine. The organic layer was washed with water and, brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 2:1) on silica gel to afford **7** as a white solid in 77% yield and 93% ee.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.95 (s, 1H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.43 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.34 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.13 – 7.07 (m, 1H), 7.03 (t, *J* = 7.6 Hz, 2H), 7.00 – 6.92 (m, 2H), 6.20 (d, *J* = 2.4 Hz, 1H), 3.59 (s, 3H), 3.54 (s, 3H), 3.52 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 169.0, 164.4, 141.9, 134.6, 132.8, 132.6, 131.6, 131.5, 130.51, 130.48, 129.8, 129.1, 128.3, 128.2, 127.8, 126.8, 126.3, 125.6, 125.4, 125.0, 122.4, 113.8, 52.1, 50.5, 36.6. HRMS (ESI) calcd. for C<sub>27</sub>H<sub>23</sub>NO<sub>4</sub>Na[M+Na]<sup>+</sup>: 448.1525, found: 448.1520. [α]<sub>D</sub><sup>20</sup> = -24.5 (c = 0.25, CHCl<sub>3</sub>), HPLC chiralcel AS-H column (5% isopropanol in hexanes, 0.5 mL/min, λ = 254 nm), t<sub>R</sub> = 43.3 min (major), 50.0 min (minor), 93% ee.



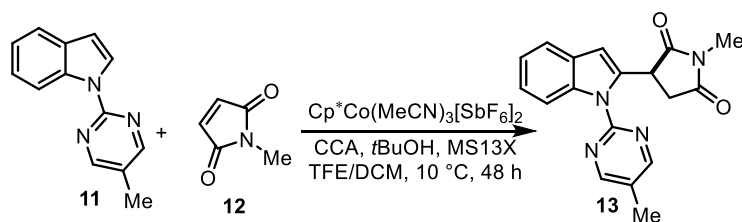
### 3.6 Co<sup>III</sup>-catalyzed enantioselective C(sp<sup>3</sup>)-H amidation of thioamide. <sup>[4]</sup>



To an oven-dried 25 mL Schlenk tube was added thioamide **8** (0.20 mmol, 1.0 equiv), dioxazolone **9** (0.24 mmol, 1.2 equiv), CCA (0.02 mmol, 10 mol %), [Cp\*Co(MeCN)<sub>3</sub>][SbF<sub>6</sub>]<sub>2</sub> (0.01 mmol), activated MS13X (40 mg), and *o*-dichlorobenzene (1 mL). The tube was then charged with N<sub>2</sub>. The reaction mixture was stirred for 24 hours at 40 °C, the reaction mixture was cooled to room temperature and purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), to afford **10**.

**10** is known compound. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.87 – 7.83 (m, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.55 – 7.44 (m, 1H), 7.43 – 7.38 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.19 (m, 3H), 4.12 (d, *J* = 12.6 Hz, 3H), 4.02 – 3.84 (m, 3H), 3.19 (d, *J* = 14.2 Hz, 1H), 2.97 (d, *J* = 14.2 Hz, 1H), 1.75 (s, 6H), 1.39 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 207.5, 167.27, 136.3, 134.8, 131.3, 130.3, 128.5, 128.4, 127.02, 126.98, 54.4, 53.0, 51.5, 43.5, 26.2, 24.2, 22.4. HPLC chiralcel IF column (10% isopropanol in hexanes, 1.0 mL/min, λ = 284 nm).

### 3.7 Co<sup>III</sup>-catalyzed enantioselective 1,4-addition of indole and maleimides<sup>[5]</sup>



To an oven-dried 25 mL Schlenk tube was added *N*-5-methyl-pyrimidyl indole **11** (0.20 mmol, 1.0 equiv), maleimide **12** (0.4 mmol, 2 equiv), CCA (0.02 mmol, 10 mol %), [Cp\*Co(MeCN)<sub>3</sub>][SbF<sub>6</sub>]<sub>2</sub> (0.01 mmol), activated MS13X (40 mg). To the mixture were added *t*BuOK in TFE (0.1 M, 240 μL, 0.024 mmol, 12 mol %), TFE (560 μL), and DCM (200 μL) at 4 °C, and the mixture was stirred at 10 °C. After 72 hours, the reaction mixture was filtered through a short pad of silica gel and purified by silica gel column

chromatography (petroleum ether/ethyl acetate = 4/1 to 1/1) to afford **13** as white solid..

**13** is known compound.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.56 (d,  $J = 8.5$  Hz, 1H), 8.42 (s, 2H), 7.56 (d,  $J = 7.7$  Hz, 1H), 7.31 (t,  $J = 7.8$  Hz, 1H), 7.22 (t,  $J = 7.4$  Hz, 1H), 6.68 (s, 1H), 4.76 (dd,  $J = 9.4, 5.8$  Hz, 1H), 3.31 – 3.00 (m, 4H), 2.89 (dd,  $J = 18.1, 5.8$  Hz, 1H), 2.29 (s, 3H). HPLC chiralcel IB column (50% isopropanol in hexanes, 0.5 mL/min,  $\lambda = 254$  nm).

### 3.8 General Procedure for CCAs

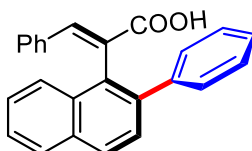
#### For CCA 1 – CCA 3.

A sealed tube with magnetic stir bar was charged with substrate (0.2 mmol), phenylboronic acid pinacol ester (0.4 mmol),  $\text{Pd}(\text{OAc})_2$  (10 mol%, 4.5 mg), Boc-*tert*-L-leucine (0.04 mmol, 9.2 mg),  $\text{Ag}_2\text{CO}_3$  (0.3 mol, 82.7 mg), BQ (0.1 mmol, 10.8 mg),  $\text{KHCO}_3$  (0.4 mmol, 40 mg),  $\text{H}_2\text{O}$  72  $\mu\text{L}$  and *t*AmylOH 1 mL as solvent in air. The reaction mixture was stirred at 40  $^\circ\text{C}$  for 72 hours. Upon completion, the reaction was diluted with ethyl acetate, and filtered through a plug of Celite. The solvent was concentrated *in vacuo* and purified by preparative TLC (DCM/MeOH = 30:1) to afford the product.

#### For CCA 4 – CCA 6.

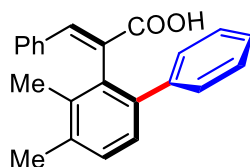
Substrate (0.2 mmol),  $\text{Pd}(\text{OAc})_2$  (10 mol%, 4.5 mg), Boc-*tert*-L-leucine (0.06 mmol, 14.0 mg) were placed in a Schlenk tube, which was filled with oxygen by using standard Schlenk techniques. After which, *i*PrOH (2mL) was added using a syringe. Olefin (0.6 mmol) and a solution of KOH (22.4 mg in 36  $\mu\text{L}$   $\text{H}_2\text{O}$ ) was added via microsyringe, subsequently. The reaction mixture was stirred at 30  $^\circ\text{C}$  for 72 hours. Upon completion, the reaction was diluted with ethyl acetate, and filtered through a plug of Celite. The solvent was concentrated *in vacuo* and purified by flash chromatography (DCM/MeOH = 100:1) to afford the product.

#### (*E*)-3-phenyl-2-(2-phenylnaphthalen-1-yl)acrylic acid (CCA 1)



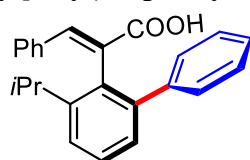
The product **CCA 1** was purified with preparative TLC (DCM/MeOH = 30:1) as a white solid (77 % yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 – 7.91 (m, 3H), 7.87 – 7.81 (m, 1H), 7.56 – 7.41 (m, 3H), 7.24 – 7.11 (m, 4H), 7.08 – 6.96 (m, 4H), 6.82 – 6.74 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 144.7, 141.6, 139.3, 134.3, 132.8, 131.8, 130.6, 130.4, 129.7, 128.8, 128.7, 128.6, 128.44, 128.39, 128.3, 127.7, 127.0, 126.9, 126.1, 125.3. HRMS (ESI) calcd. for  $\text{C}_{25}\text{H}_{18}\text{O}_2\text{Na}[\text{M}+\text{Na}]^+$ : 373.1204, found: 373.1207.  $[\alpha]_{\text{D}}^{20} = -16.9$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), The ee value determined by corresponding methyl ester (**3ab**), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 11.6$  min (major), 8.2 min (minor), 94% ee.

**(E)-2-(3,4-dimethyl-[1,1'-biphenyl]-2-yl)-3-phenylacrylic acid (CCA 2)**



The product **CCA 2** was purified with preparative TLC (DCM/MeOH = 30:1) as a white solid (59 % yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (s, 1H), 7.30 – 7.21 (m, 2H), 7.19 – 7.11 (m, 5H), 7.08 (d,  $J = 7.7$  Hz, 1H), 6.99 – 6.95 (m, 2H), 6.93 – 6.88 (m, 2H), 2.37 (s, 3H), 2.14 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.3, 142.8, 141.8, 139.7, 136.2, 135.2, 134.7, 133.4, 130.5, 130.3, 129.9, 129.6, 128.7, 128.3, 127.7, 127.5, 126.5, 20.6, 16.4. HRMS (ESI) calcd. for  $\text{C}_{23}\text{H}_{20}\text{O}_2\text{Na}[\text{M}+\text{Na}]^+$ : 351.1361, found: 351.1358.  $[\alpha]_{\text{D}}^{20} = -39.1$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), The ee value determined by corresponding methyl ester, HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 5.5$  min (major), 5.2 min (minor), 98% ee.

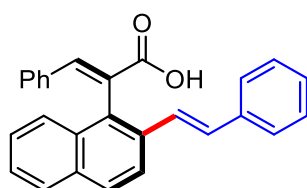
**(E)-2-(3-isopropyl-[1,1'-biphenyl]-2-yl)-3-phenylacrylic acid (CCA 3)**



The product **CCA 3** was purified with preparative TLC (DCM/MeOH = 30:1) as a white solid (71 % yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (s, 1H), 7.56 – 7.37 (m, 2H), 7.23 (d,  $J = 7.4$  Hz, 1H), 7.14 (dt,  $J = 17.6, 6.6$  Hz, 6H), 6.99 (d,  $J = 7.2$  Hz, 2H), 6.91

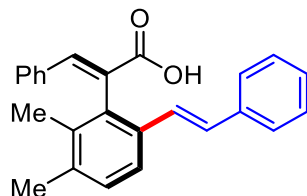
(d,  $J = 7.7$  Hz, 2H), 2.95 (p,  $J = 6.8$  Hz, 1H), 1.23 (d,  $J = 6.8$  Hz, 3H), 1.01 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 147.5, 143.2, 141.9, 134.6, 132.4, 130.6, 129.7, 128.7, 128.6, 128.3, 128.1, 127.5, 126.7, 126.6, 125.1, 30.9, 24.1, 23.9. HRMS (ESI) calcd. for  $\text{C}_{24}\text{H}_{22}\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 365.1517, found: 365.1513.  $[\alpha]_{\text{D}}^{20} = -25.4$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), The ee value determined by corresponding methyl ester, HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 5.1$  min (major), 6.0 min (minor), 99% ee.

**(E)-3-phenyl-2-(2-((E)-styryl)naphthalen-1-yl)acrylic acid (CCA 4)**



The product **CCA 4** was purified with silica gel chromatography (DCM/MeOH = 100:1) as a white solid (72 % yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (s, 1H), 7.90 - 7.86 (m, 2H), 7.82 (d,  $J = 8.0$  Hz, 1H), 7.75 (d,  $J = 8.3$  Hz, 1H), 7.43 - 7.31 (m, 4H), 7.31 - 7.24 (m, 3H), 7.21 (d,  $J = 17.7$  Hz, 1H), 7.14 - 7.08 (m, 2H), 7.01 (t,  $J = 7.7$  Hz, 2H), 6.97 (d,  $J = 7.7$  Hz, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 144.8, 137.3, 133.9, 133.12, 133.09, 131.9, 131.2, 130.8, 130.6, 123.0, 128.8, 128.6, 128.5, 128.3, 127.7, 127.0, 126.7, 126.1, 126.0, 125.2, 122.9.  $\text{C}_{27}\text{H}_{20}\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 399.1361 found: 399.1355.  $[\alpha]_{\text{D}}^{20} = -42.9$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ), HPLC chiralcel AS-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}} = 7.5$  min (major), 12.3 min (minor), 99% ee.

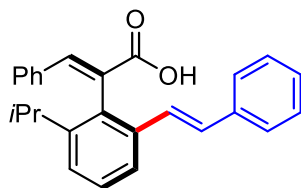
**(E)-2-(2,3-dimethyl-6-((E)-styryl)phenyl)-3-phenylacrylic acid (CCA 5)**



The product **CCA 5** was purified with silica gel chromatography (DCM/MeOH = 100:1) as a white solid (64 % yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (s, 1H), 7.52 (d,  $J = 8.0$  Hz, 1H), 7.32 (d,  $J = 7.6$  Hz, 2H), 7.22 (dt,  $J = 14.3, 7.4$  Hz, 4H), 7.14 (q,  $J = 7.1$  Hz, 3H), 7.07 - 6.99 (m, 3H), 6.91 (d,  $J = 16.1$  Hz, 1H), 2.29 (s, 3H), 2.04 (s, 3H);  $^{13}\text{C}$

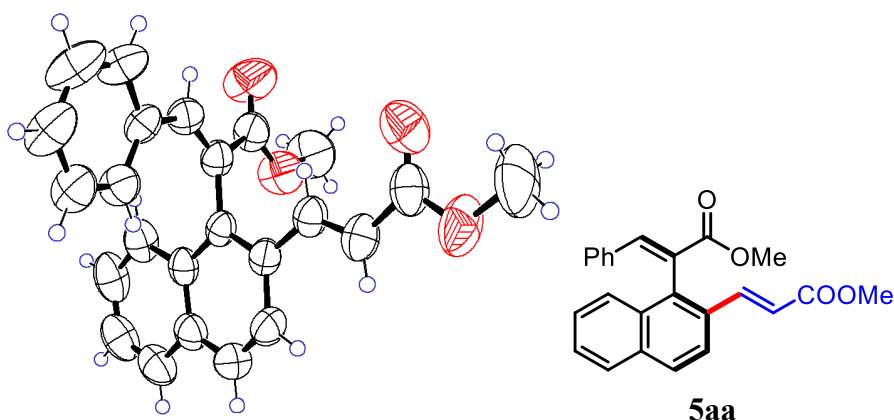
NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  172.9, 143.1, 137.7, 136.7, 135.1, 134.4, 134.0, 133.8, 130.5, 130.2, 129.9, 129.6, 129.4, 128.6, 128.5, 127.4, 126.6, 122.9, 20.7, 16.4. HRMS (ESI) calcd. for C<sub>25</sub>H<sub>22</sub>O<sub>2</sub>Na[M+Na]<sup>+</sup>: 377.1517, found: 377.1510.  $[\alpha]_D^{20} = -61.0$  (c = 0.25, CHCl<sub>3</sub>), HPLC chiralcel As-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 5.3$  min (major), 8.2 min (minor), 99% ee.

**(E)-2-(2-isopropyl-6-((E)-styryl)phenyl)-3-phenylacrylic acid (CCA 6)**



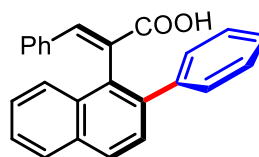
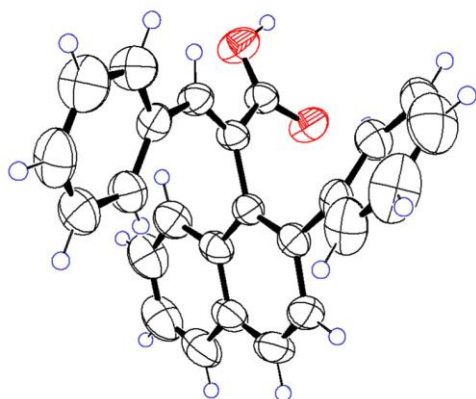
The product **CCA 6** was purified with silica gel chromatography (DCM/MeOH = 100:1) as a white solid (76 % yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.10 (s, 1H), 7.60 (dd,  $J = 7.7, 1.1$  Hz, 1H), 7.42 (t,  $J = 7.8$  Hz, 1H), 7.31 (td,  $J = 7.4, 1.4$  Hz, 3H), 7.28 – 7.17 (m, 2H), 7.20 – 7.05 (m, 5H), 7.02 (d,  $J = 7.3$  Hz, 2H), 6.94 (d,  $J = 16.1$  Hz, 1H), 2.89 (p,  $J = 6.8$  Hz, 1H), 1.14 (d,  $J = 6.8$  Hz, 3H), 0.87 (d,  $J = 6.8$  Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  173.1, 147.5, 143.6, 137.5, 136.2, 134.4, 132.7, 130.7, 130.5, 123.0, 128.90, 128.85, 128.6, 128.5, 127.5, 126.6, 125.4, 123.3, 30.9, 24.0, 23.9. HRMS (ESI) calcd. for C<sub>26</sub>H<sub>24</sub>O<sub>2</sub>Na[M+Na]<sup>+</sup>: 391.1674, found: 391.1670.  $[\alpha]_D^{20} = -33.6$  (c = 0.25, CHCl<sub>3</sub>), HPLC chiralcel AS-H column (10% isopropanol in hexanes, 1.0 mL/min,  $\lambda = 254$  nm),  $t_R = 5.5$  min (major), 6.5 min (minor), >99% ee.

## X-ray Crystallographic Data of 5aa



Empirical formula	C <sub>24</sub> H <sub>20</sub> O <sub>4</sub>
Formula weight	372.40
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	8.99240(10)
b/Å	19.5139(2)
c/Å	23.2425(2)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	4078.52(7)
Z	8
ρ <sub>calc</sub> /cm <sup>3</sup>	1.213
μ/mm <sup>-1</sup>	0.664
F(000)	1568.0
Crystal size/mm <sup>3</sup>	? × ? × ?
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.608 to 146.386
Index ranges	-11 ≤ h ≤ 10, -24 ≤ k ≤ 24, -28 ≤ l ≤ 28
Reflections collected	42944
Independent reflections	8078 [R <sub>int</sub> = 0.0341, R <sub>sigma</sub> = 0.0182]
Data/restraints/parameters	8078/10/509
Goodness-of-fit on F <sup>2</sup>	1.578
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0670, wR <sub>2</sub> = 0.1995
Final R indexes [all data]	R <sub>1</sub> = 0.0754, wR <sub>2</sub> = 0.2077
Largest diff. peak/hole / e Å <sup>-3</sup>	0.40/-0.24
Flack parameter	-0.07(8)

## X-ray Crystallographic Data of CCA 1



CCA1

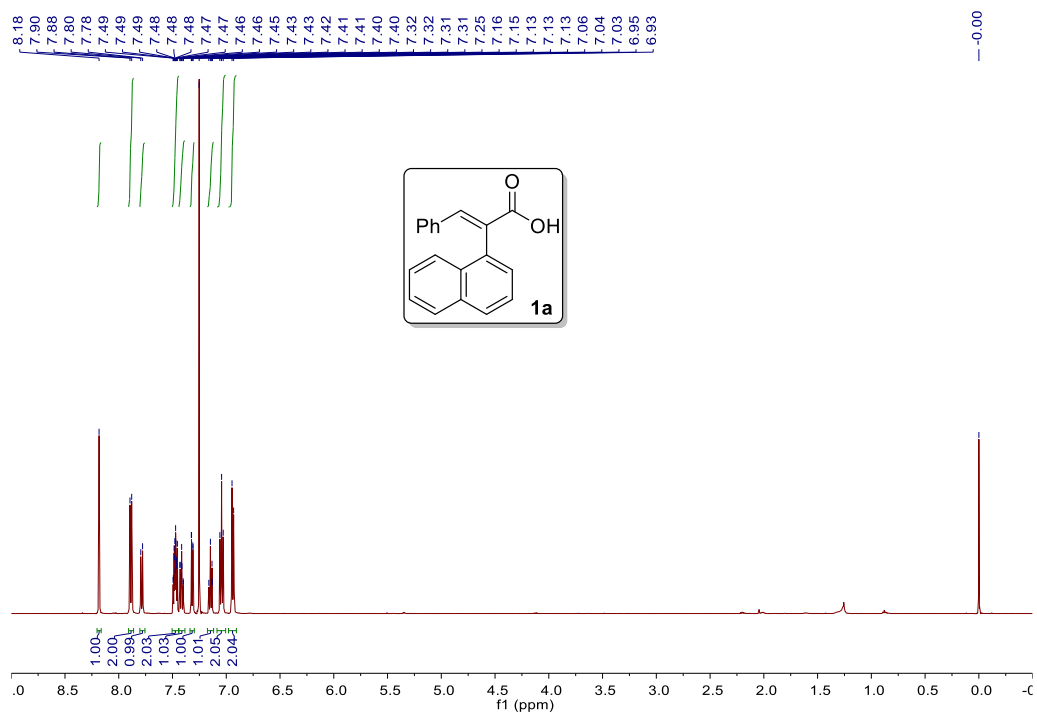
Empirical formula	C <sub>25</sub> H <sub>18</sub> O <sub>2</sub>
Formula weight	350.39
Temperature/K	293(2)
Crystal system	triclinic
Space group	P1
a/Å	8.6935(2)
b/Å	11.1218(2)
c/Å	12.2142(2)
α/°	87.3760(10)
β/°	70.785(2)
γ/°	81.6190(10)
Volume/Å <sup>3</sup>	1103.26(4)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.055
μ/mm <sup>-1</sup>	0.520
F(000)	368.0
Crystal size/mm <sup>3</sup>	0.4 × 0.4 × 0.2
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.666 to 139.896
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	36949
Independent reflections	7868 [R <sub>int</sub> = 0.0270, R <sub>sigma</sub> = 0.0128]
Data/restraints/parameters	7868/3/489
Goodness-of-fit on F <sup>2</sup>	1.079
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0603, wR <sub>2</sub> = 0.1552
Final R indexes [all data]	R <sub>1</sub> = 0.0607, wR <sub>2</sub> = 0.1562
Largest diff. peak/hole / e Å <sup>-3</sup>	0.27/-0.47
Flack parameter	0.11(6)

## References

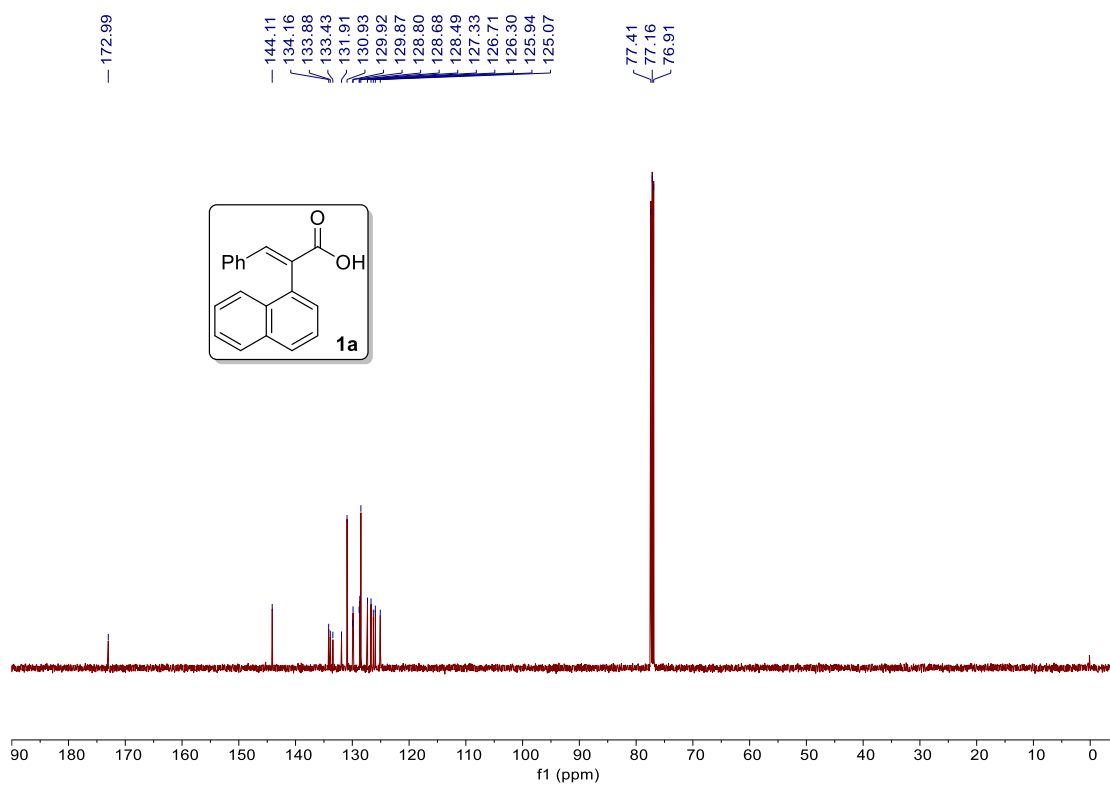
- (1) T. Matsuda, Y. Sakurai, *Eur. J. Org. Chem.*, 2013, **2013**, 4219.
- (2) S. Zhang, Q.-J. Yao, G. Liao, X. Li, H. Li, H.-M. Chen, X. Hong, B.-F. Shi, *ACS Catal.*, 2019, **9**, 1956.
- (3) Y. Su, H. Zhou, J. Chen, J. Xu, X. Wu, A. Lin, H. Yao, *Org. Lett.*, 2014, **16**, 4884.
- (4) S. Fukagawa, Y. Kato, R. Tanaka, M. Kojima, T. Yoshino, S. Matsunaga, *Angew. Chem. Int. Ed.*, 2019, **58**, 1153.
- (5) L.-T. Huang, S. Fukagawa, M. Kojima, T. Yoshino, S. Matsunaga, *Org. Lett.*, 2020, **22**, 8256.



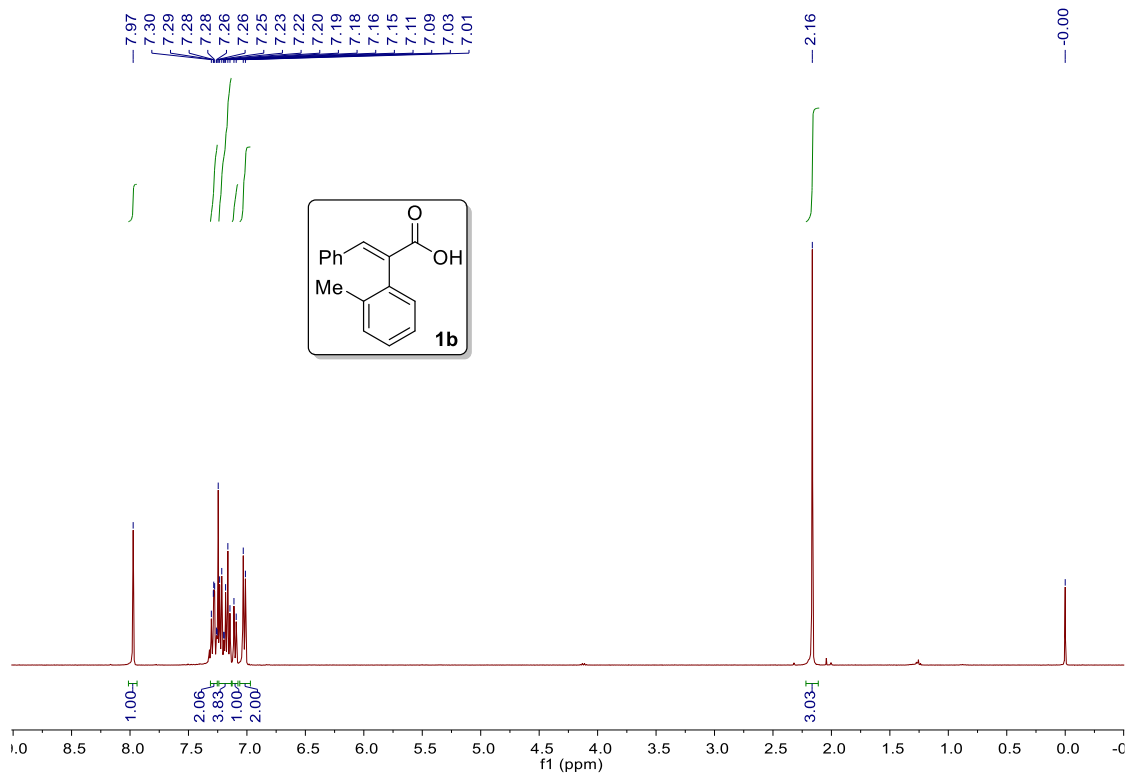
## 4. NMR Data



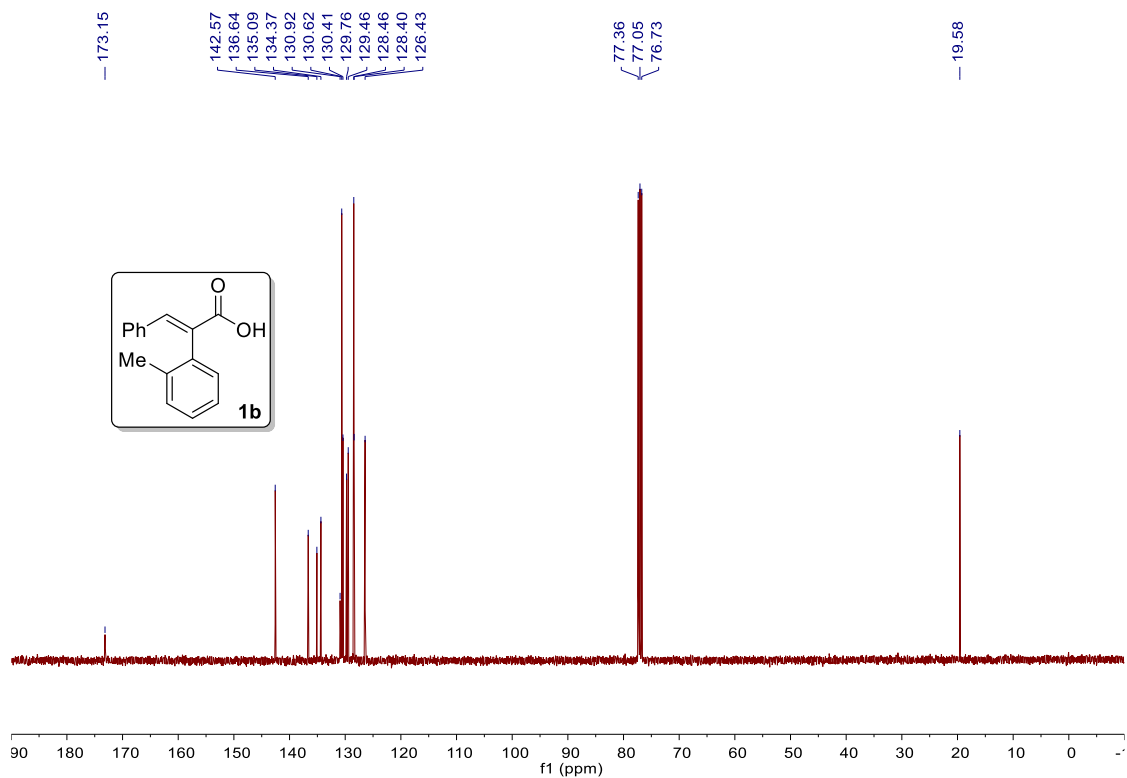
<sup>1</sup>H NMR Spectrum of **1a** (CDCl<sub>3</sub>, 500 MHz)



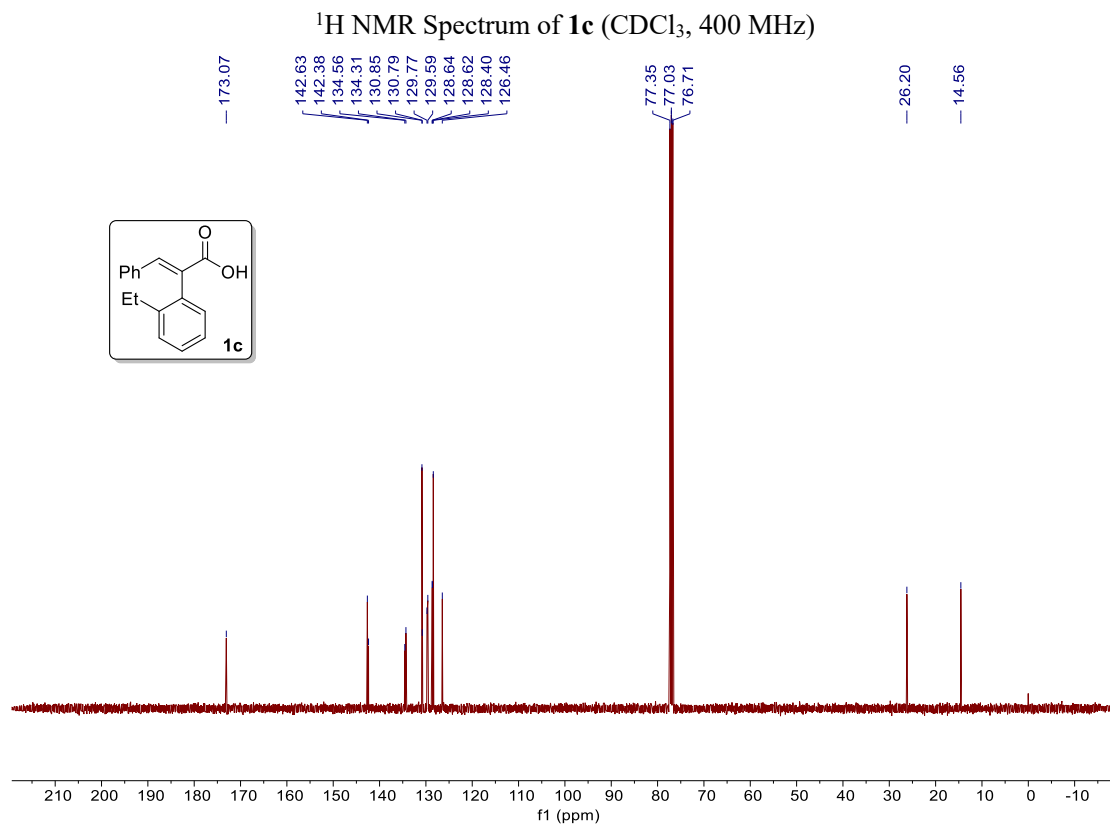
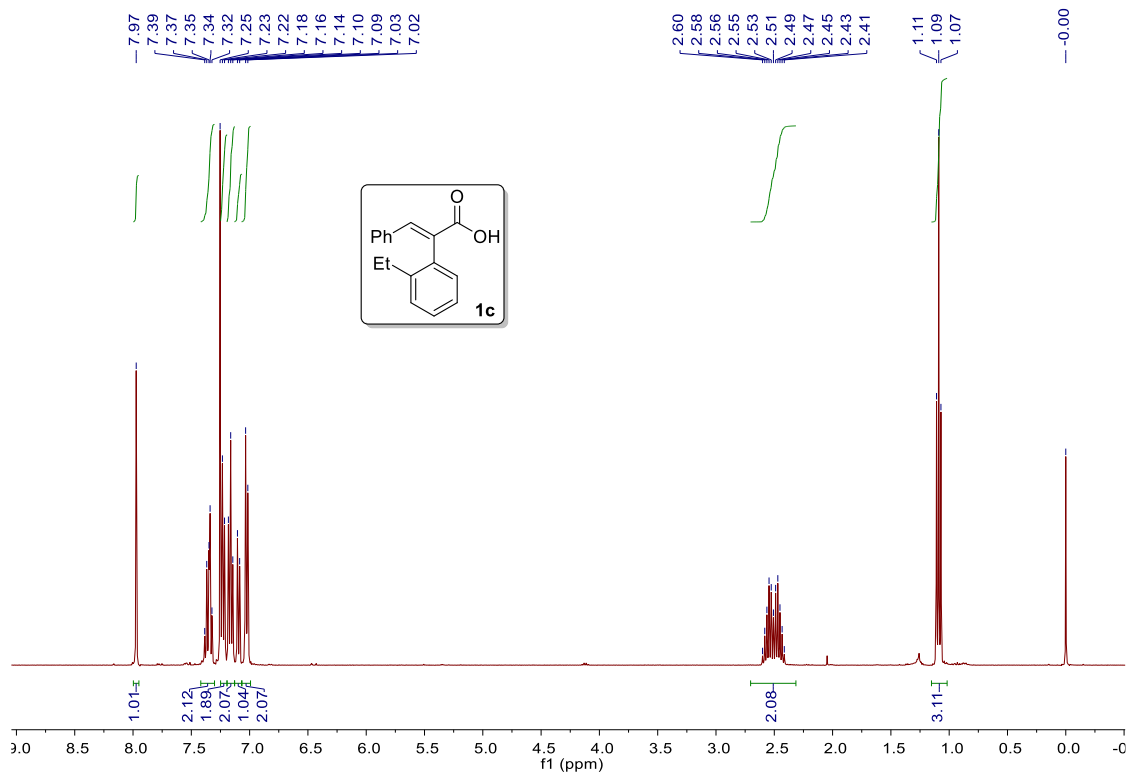
<sup>13</sup>C NMR Spectrum of **1a** (CDCl<sub>3</sub>, 126 MHz)

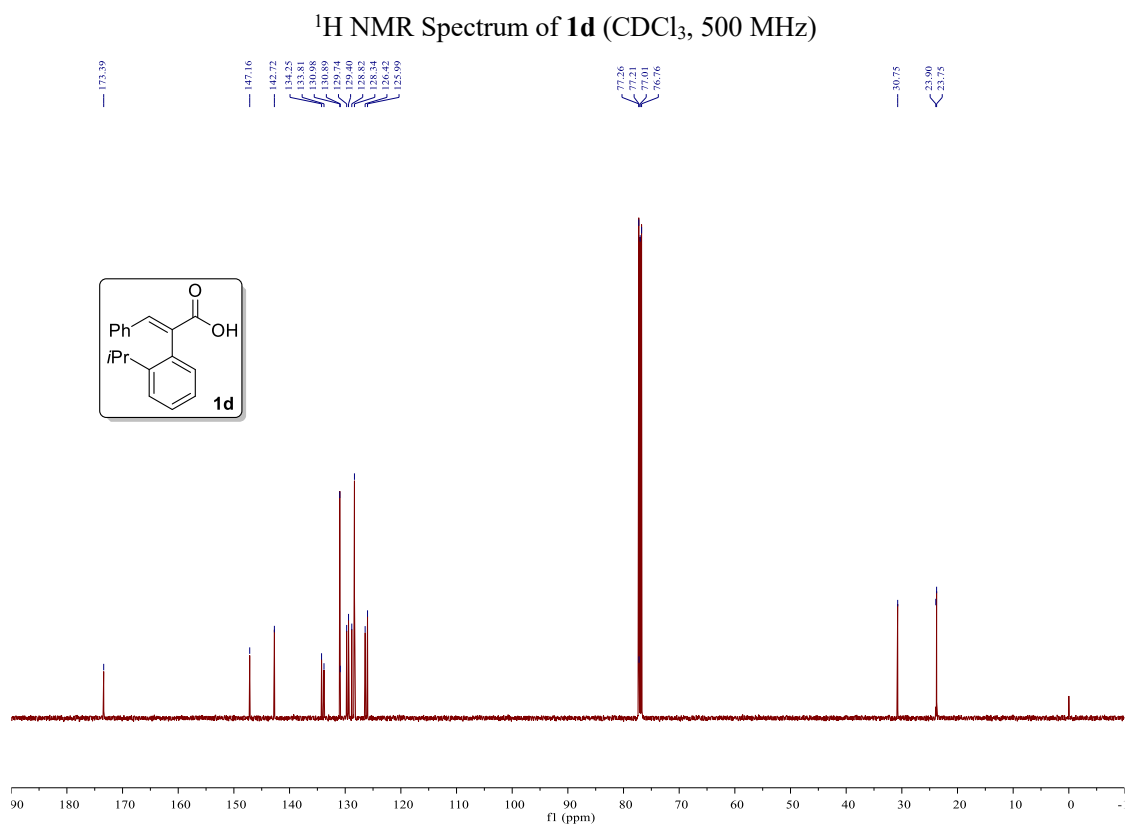
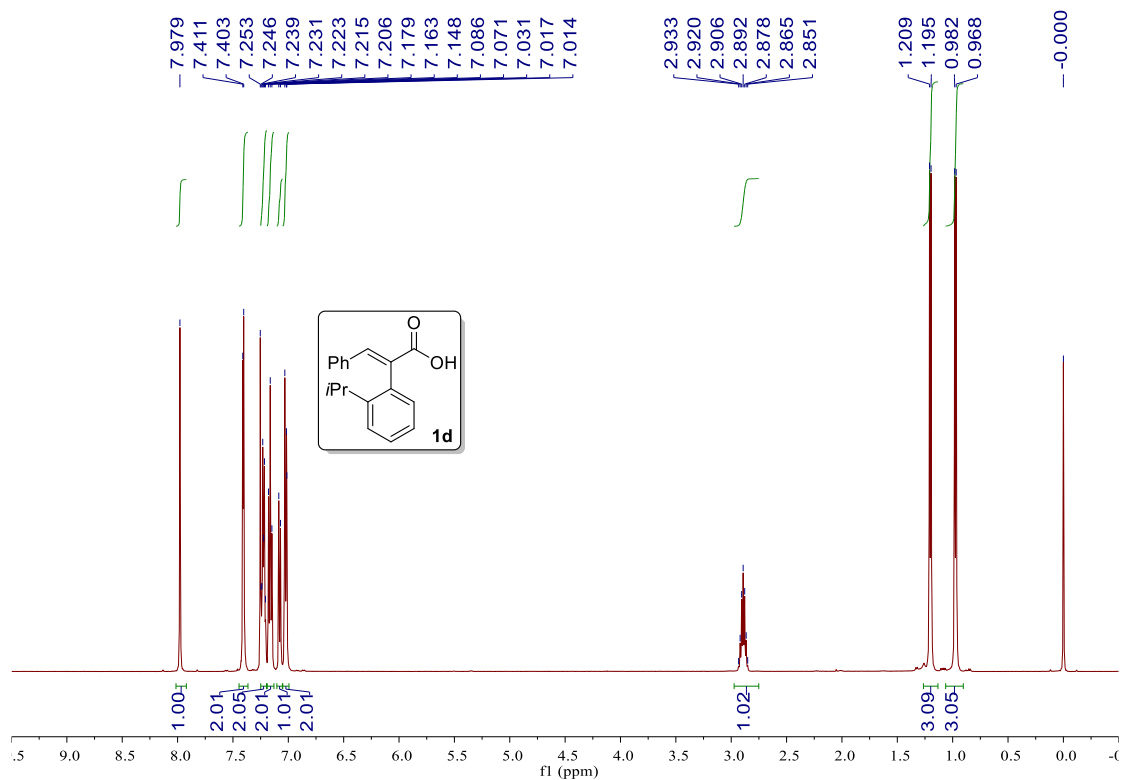


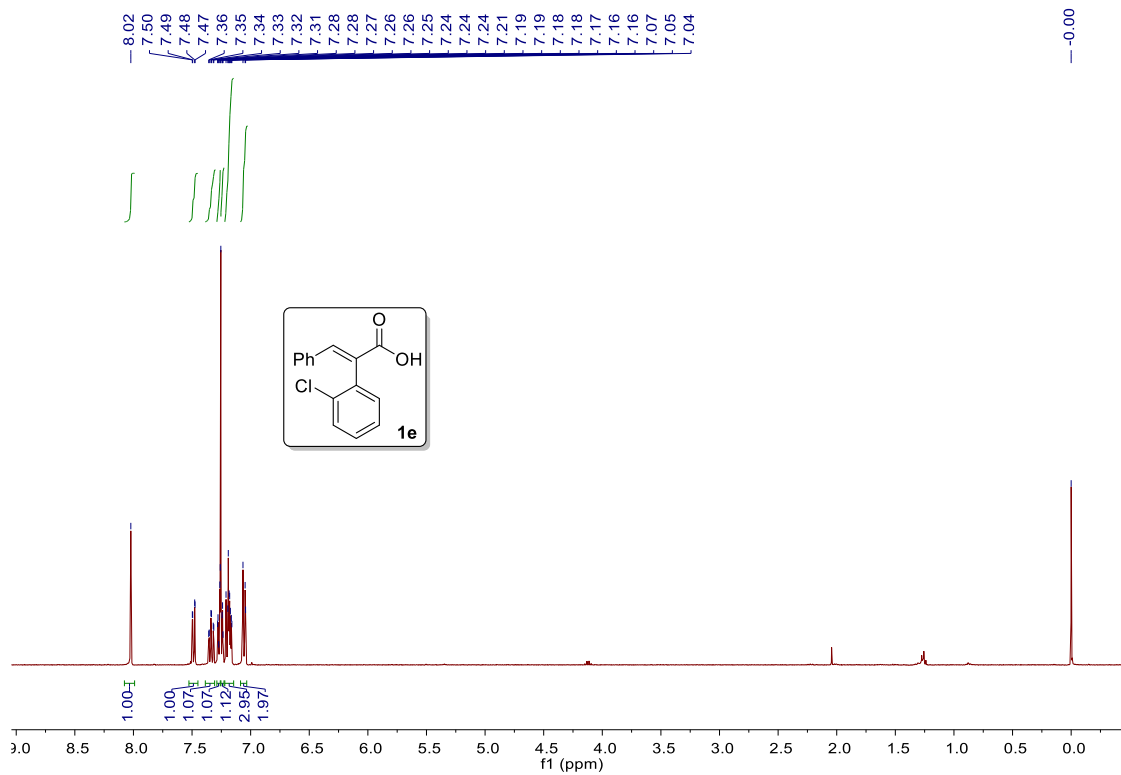
**<sup>1</sup>H NMR Spectrum of **1b** (CDCl<sub>3</sub>, 400 MHz)**



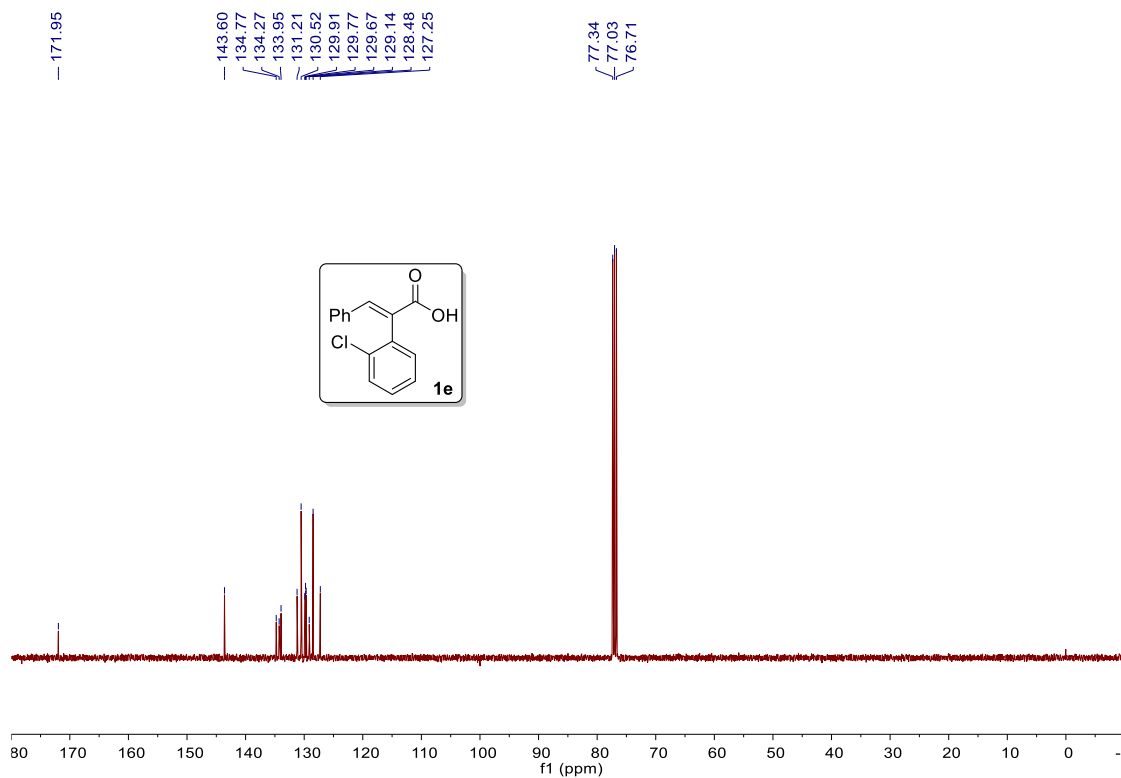
**<sup>13</sup>C NMR Spectrum of **1b** (CDCl<sub>3</sub>, 101 MHz)**



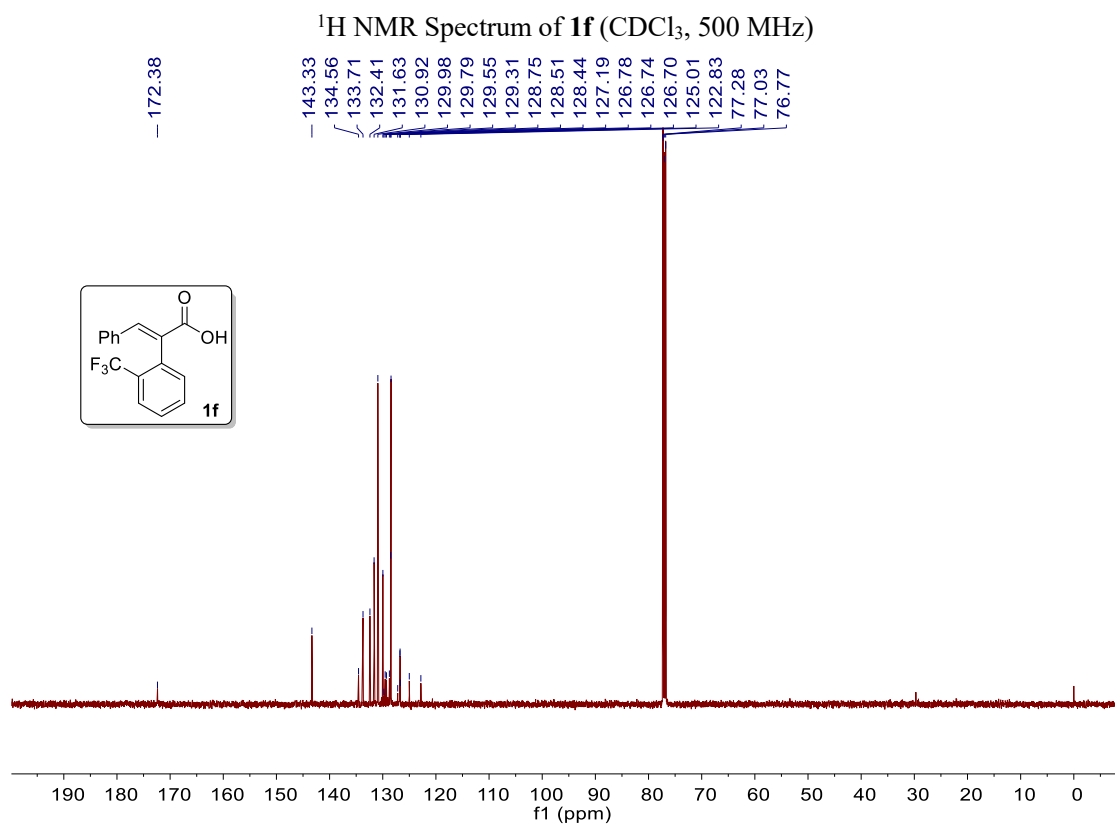
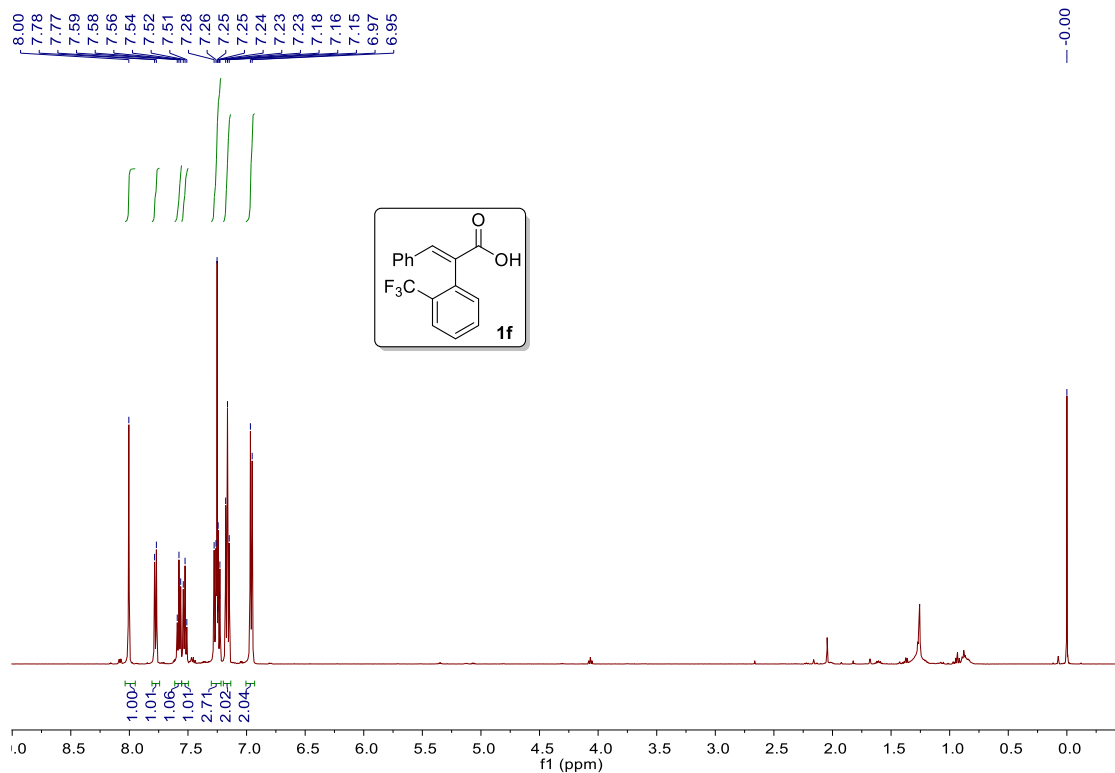


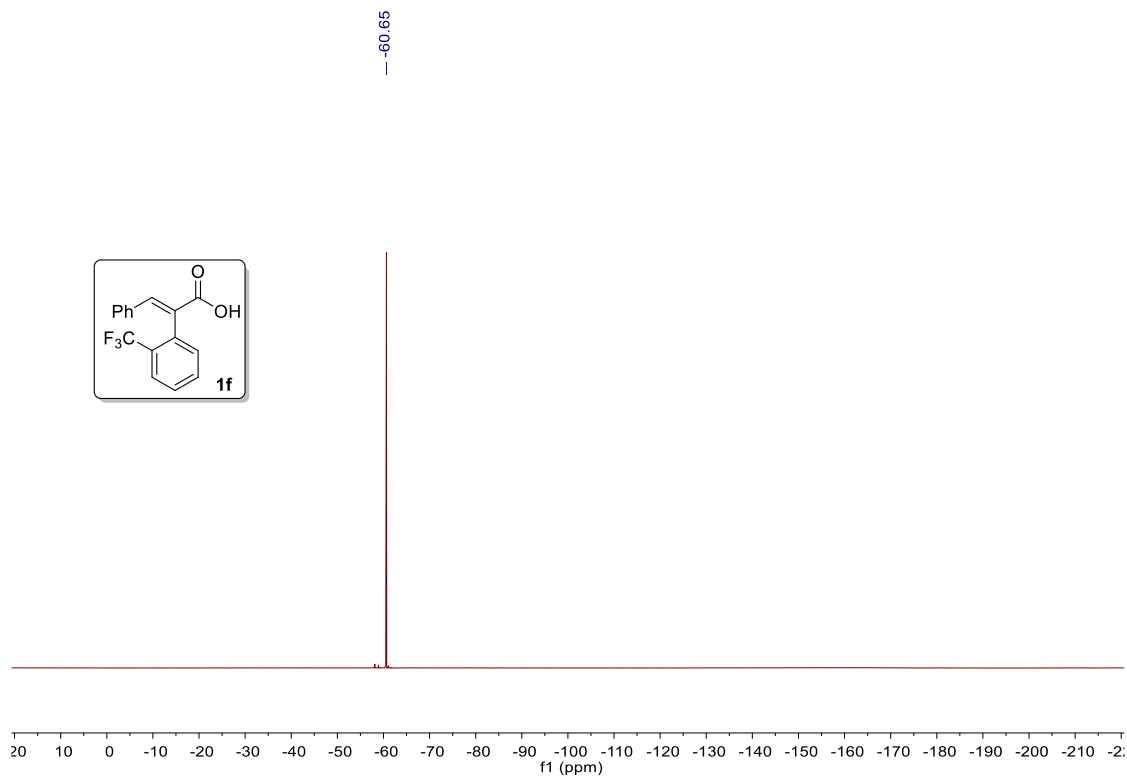


<sup>1</sup>H NMR Spectrum of **1e** (CDCl<sub>3</sub>, 400 MHz)

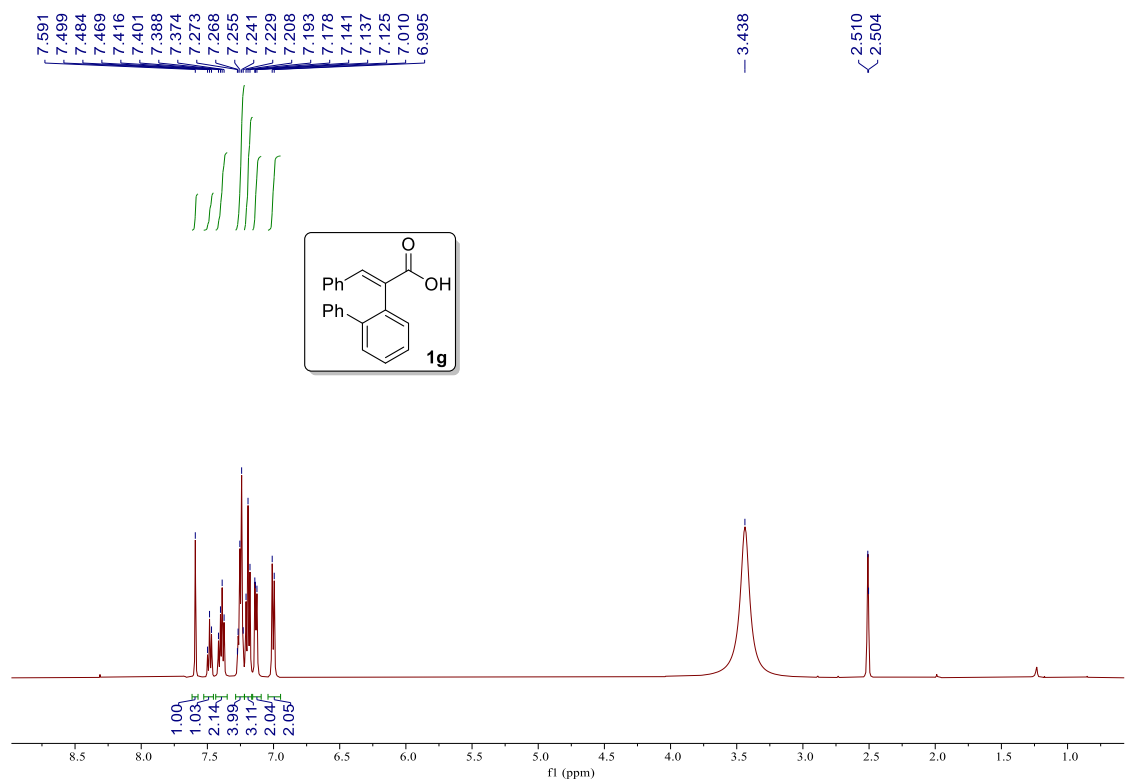


<sup>13</sup>C NMR Spectrum of **1e** (CDCl<sub>3</sub>, 101 MHz)

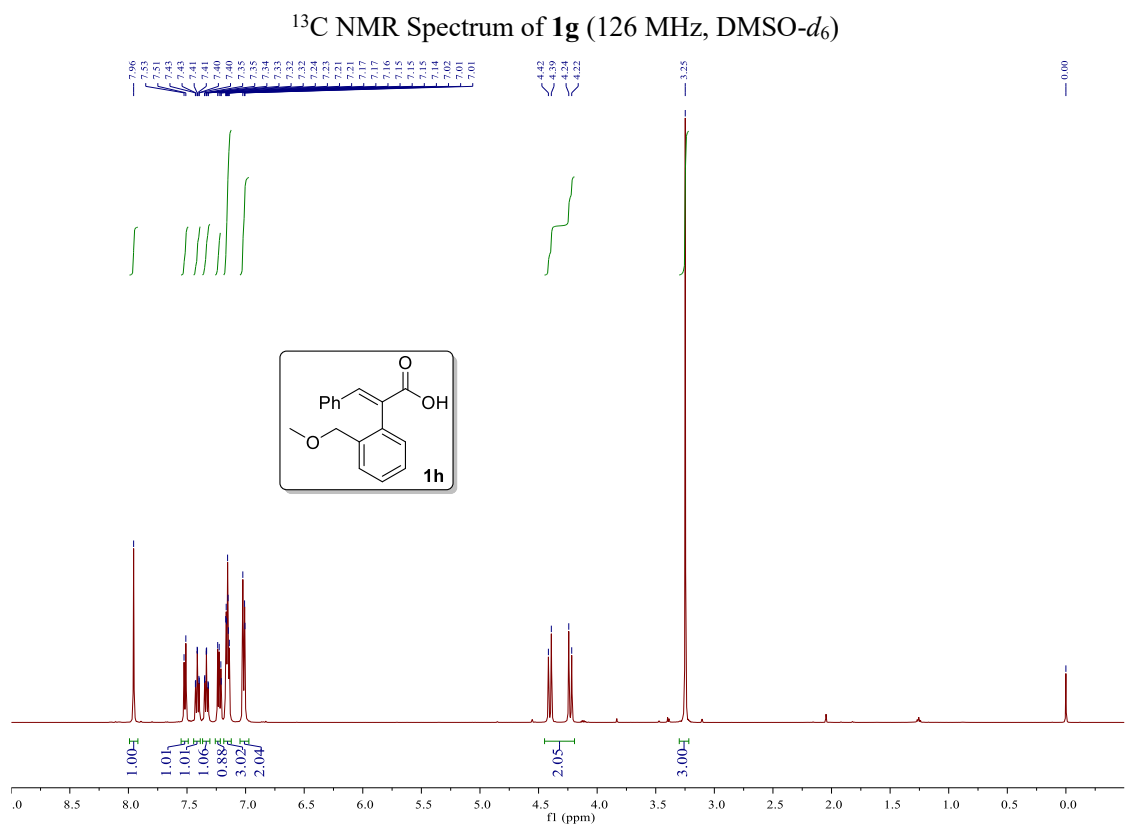
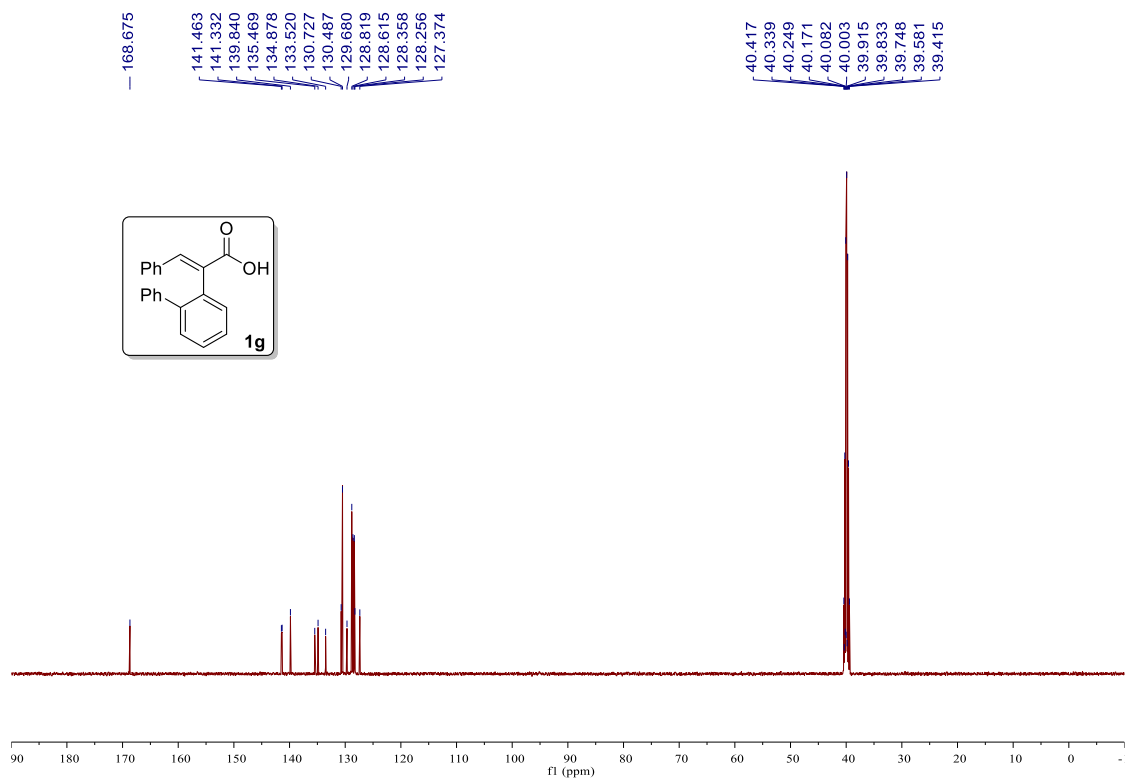




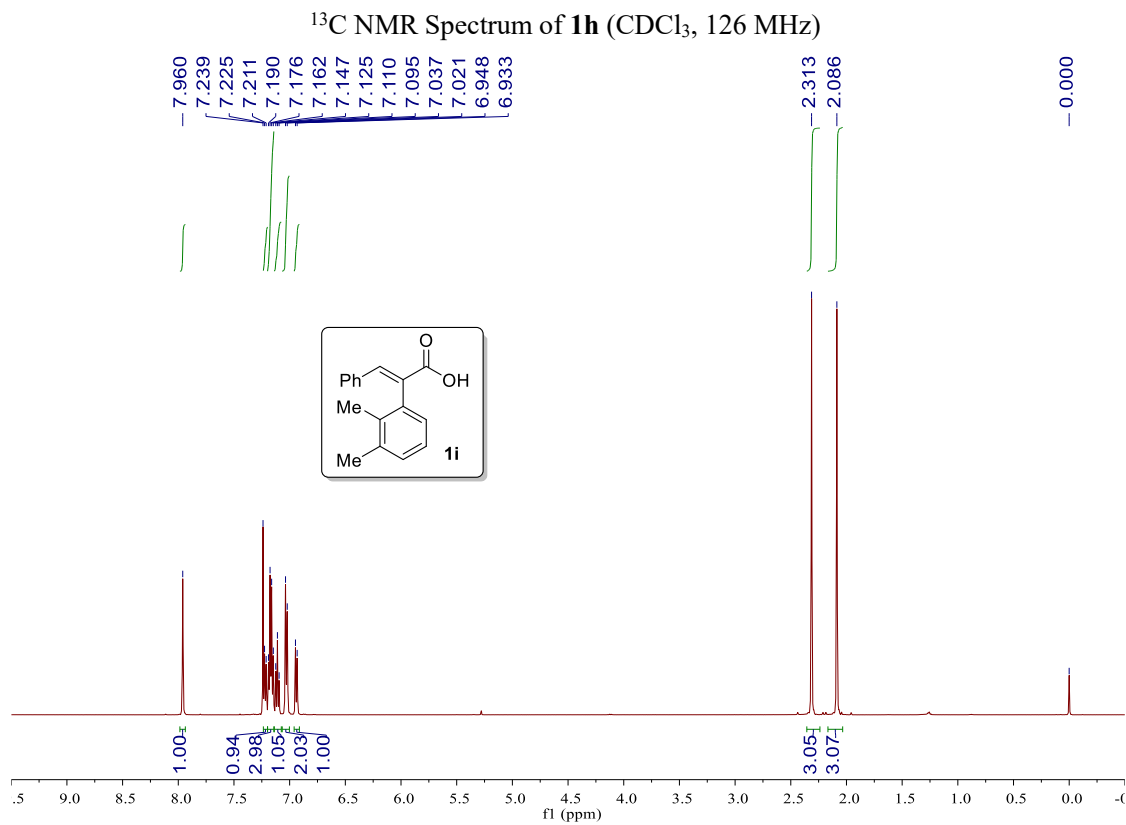
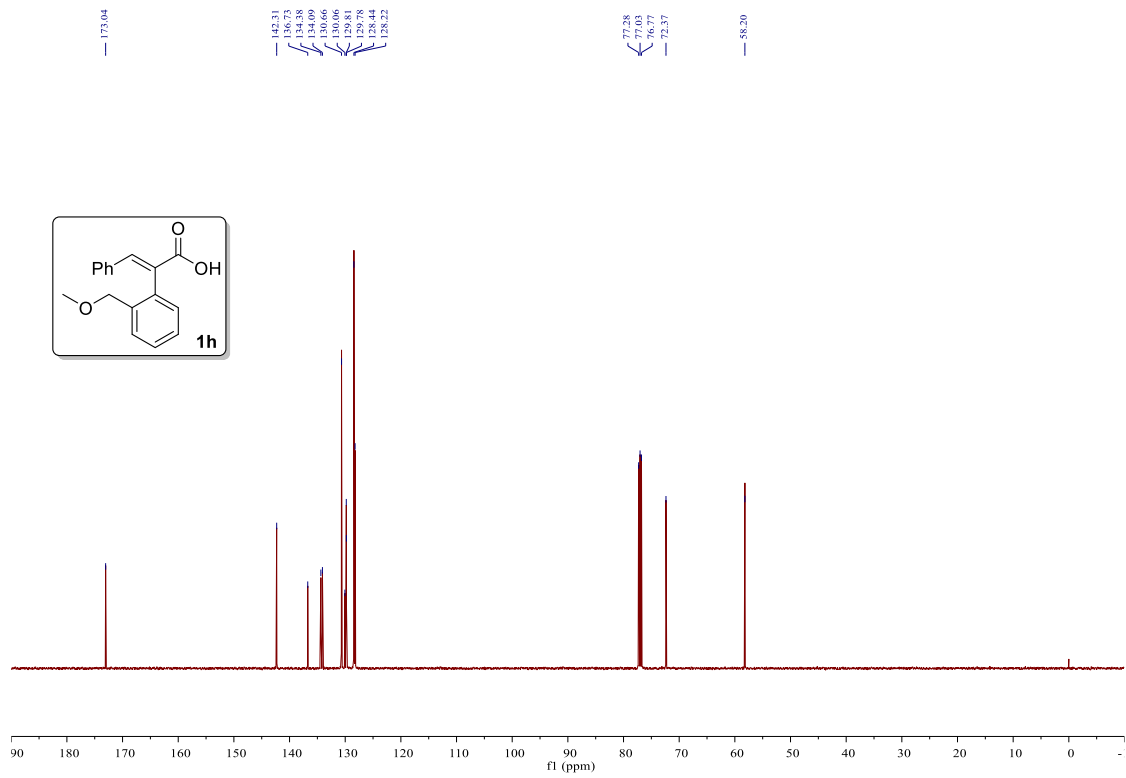
<sup>19</sup>F NMR Spectrum of **1f** (471 MHz, CDCl<sub>3</sub>)

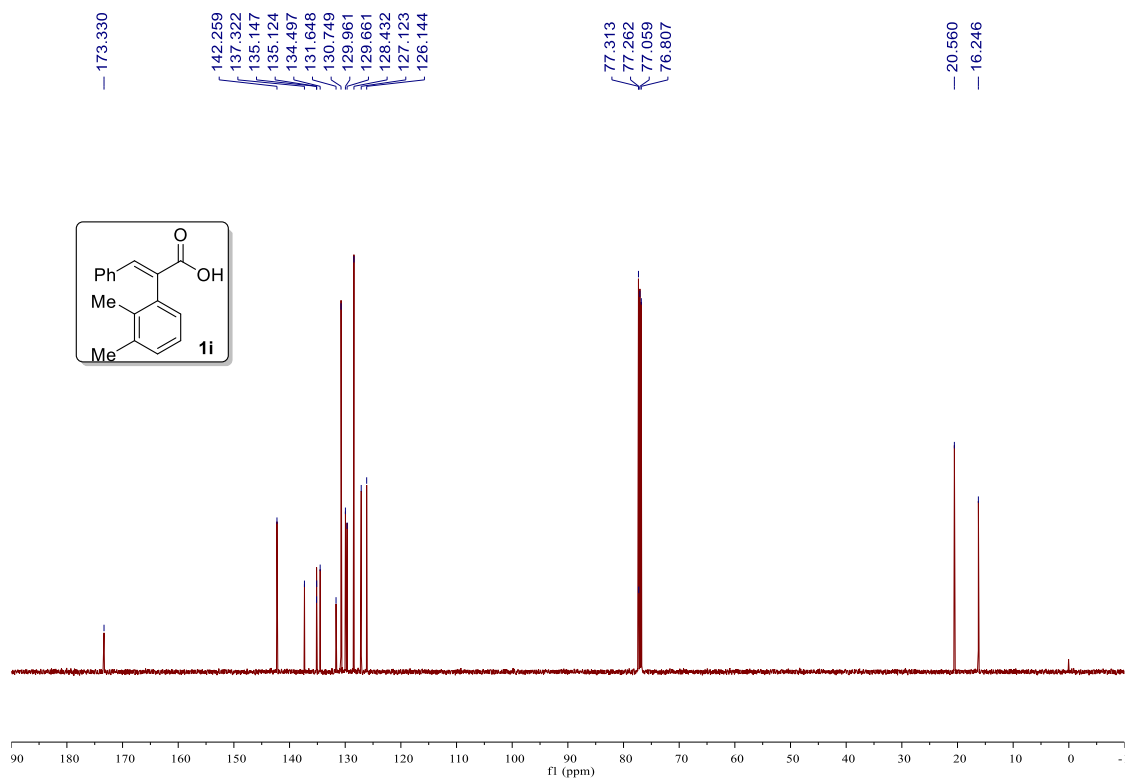


<sup>1</sup>H NMR Spectrum of **1g** (500 MHz, DMSO-*d*<sub>6</sub>)

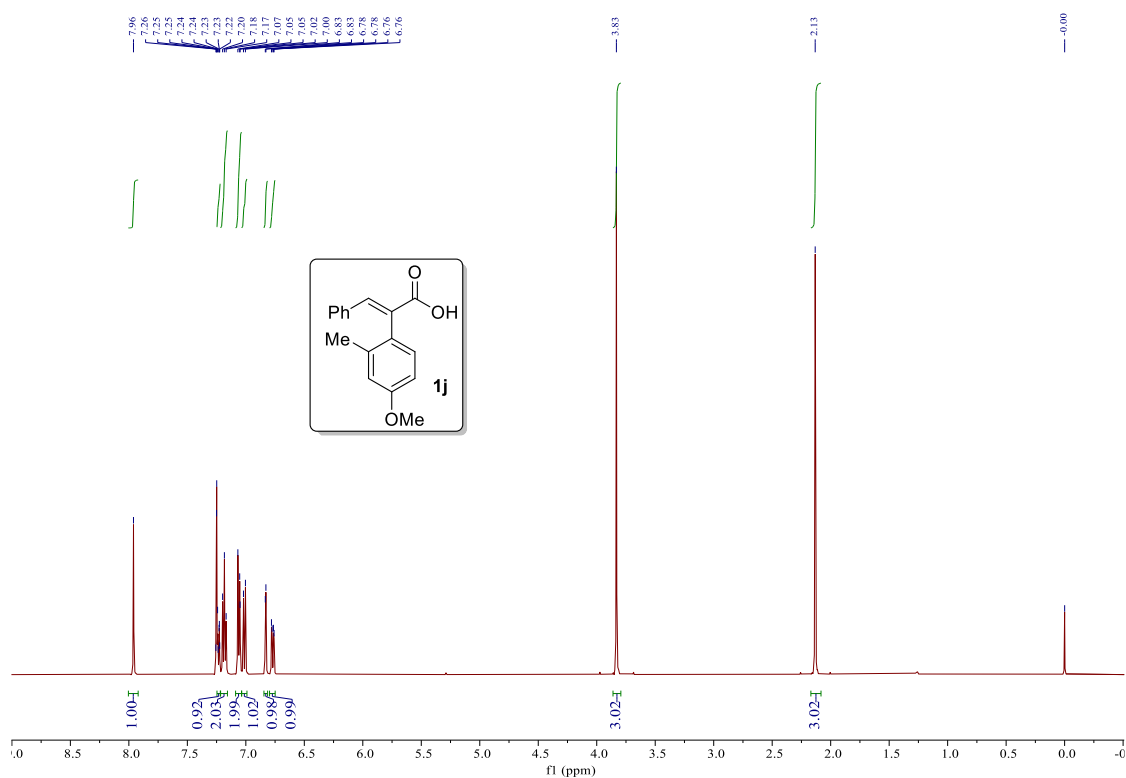




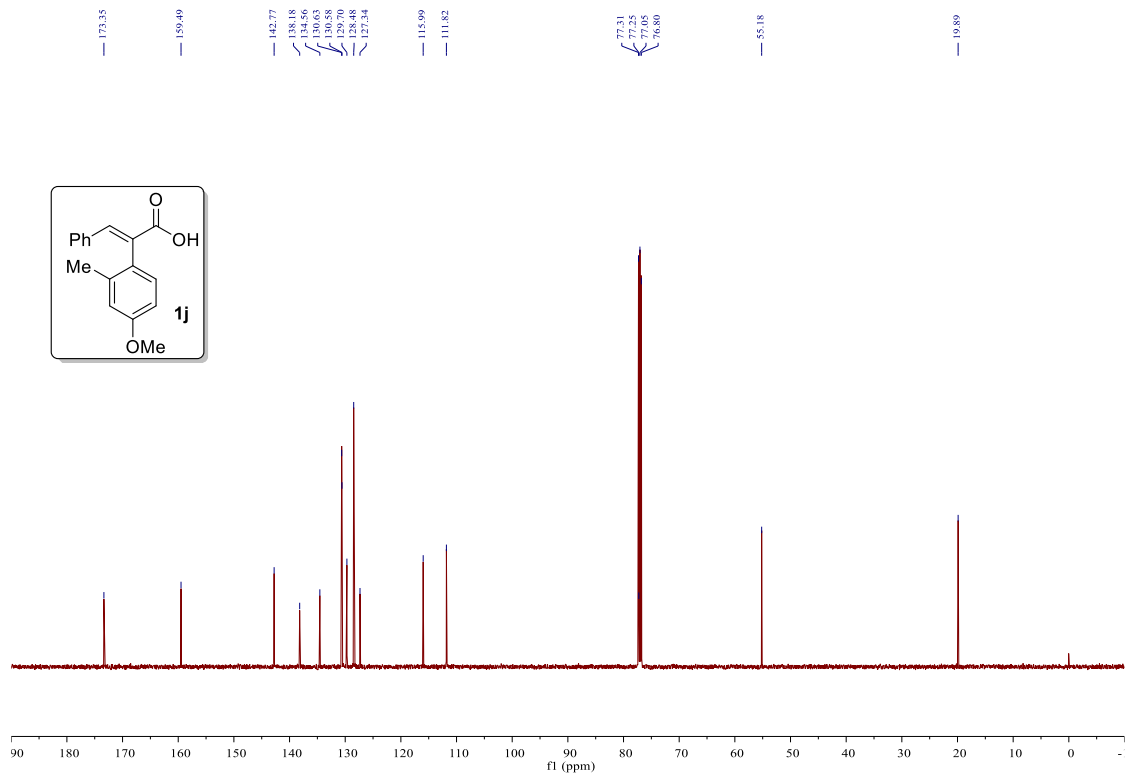




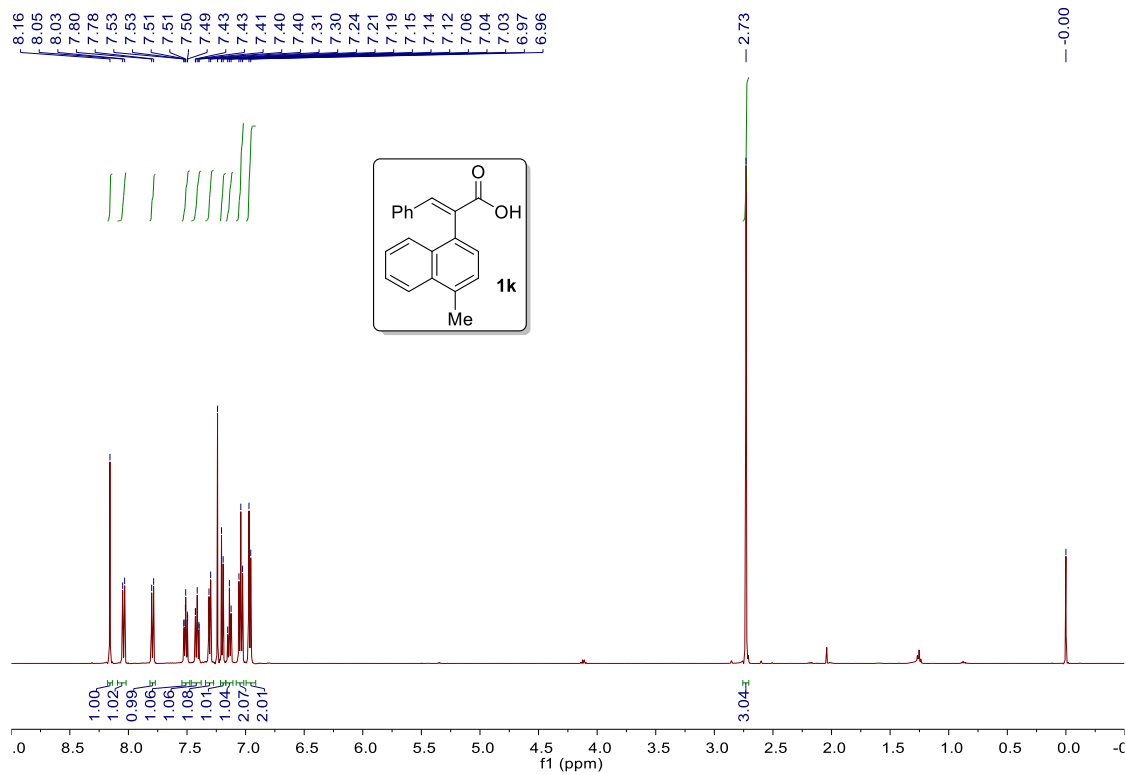
<sup>13</sup>C NMR Spectrum of **1i** (CDCl<sub>3</sub>, 126 MHz)



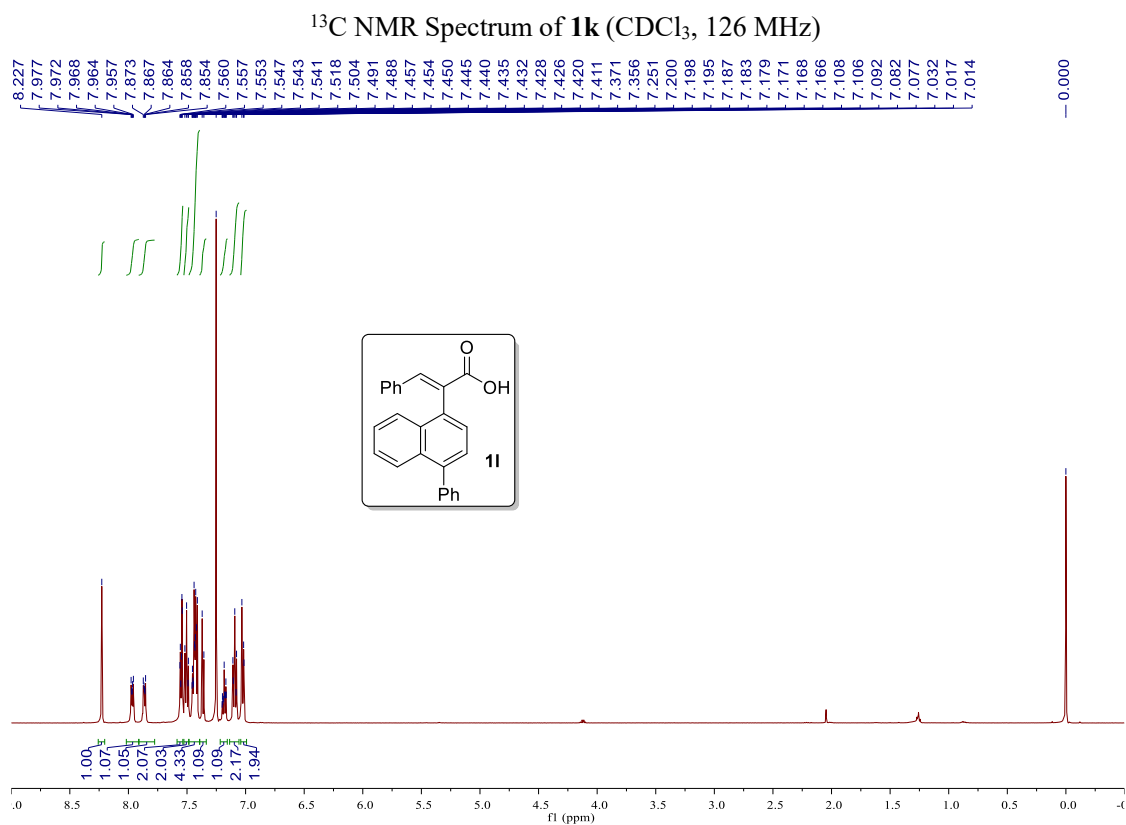
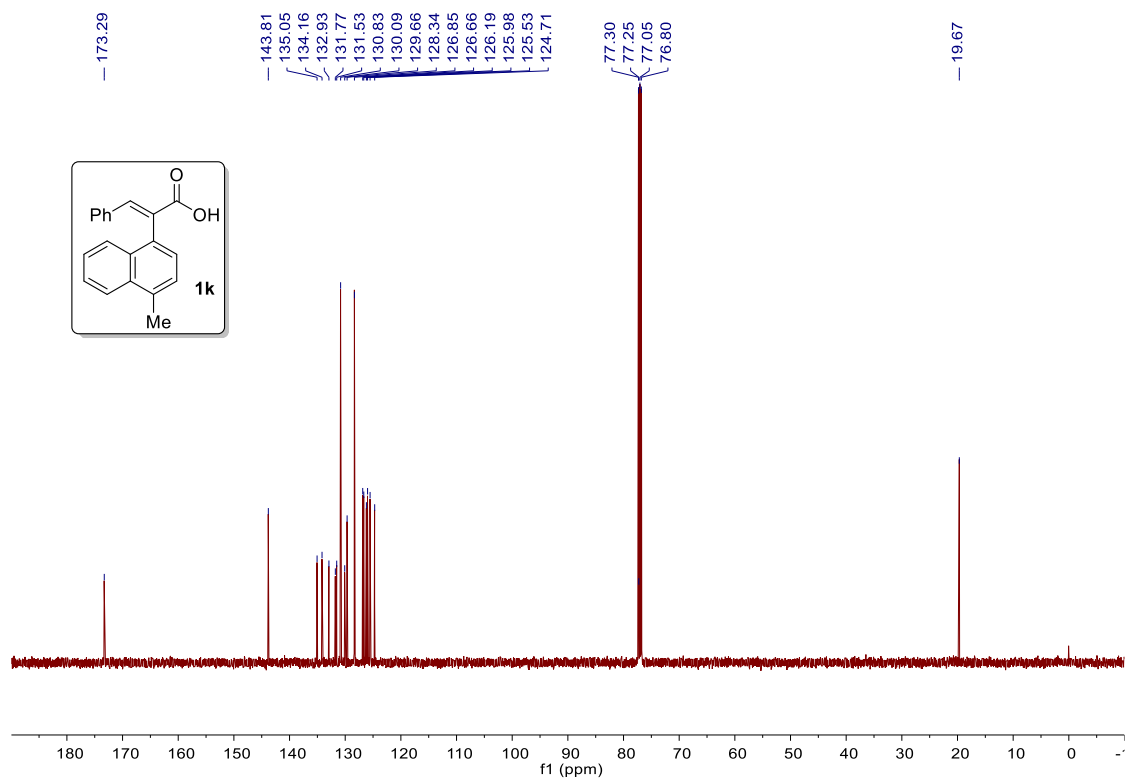
<sup>1</sup>H NMR Spectrum of **1j** (CDCl<sub>3</sub>, 500 MHz)

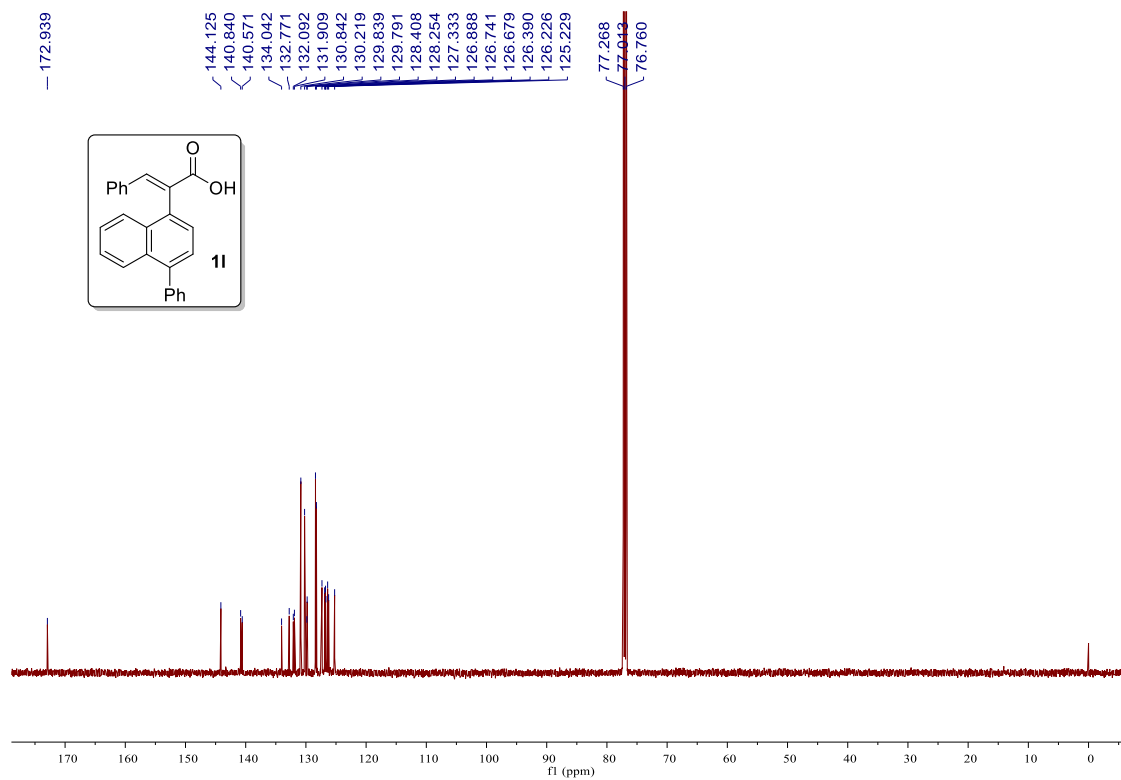


<sup>13</sup>C NMR Spectrum of **1j** (CDCl<sub>3</sub>, 126 MHz)

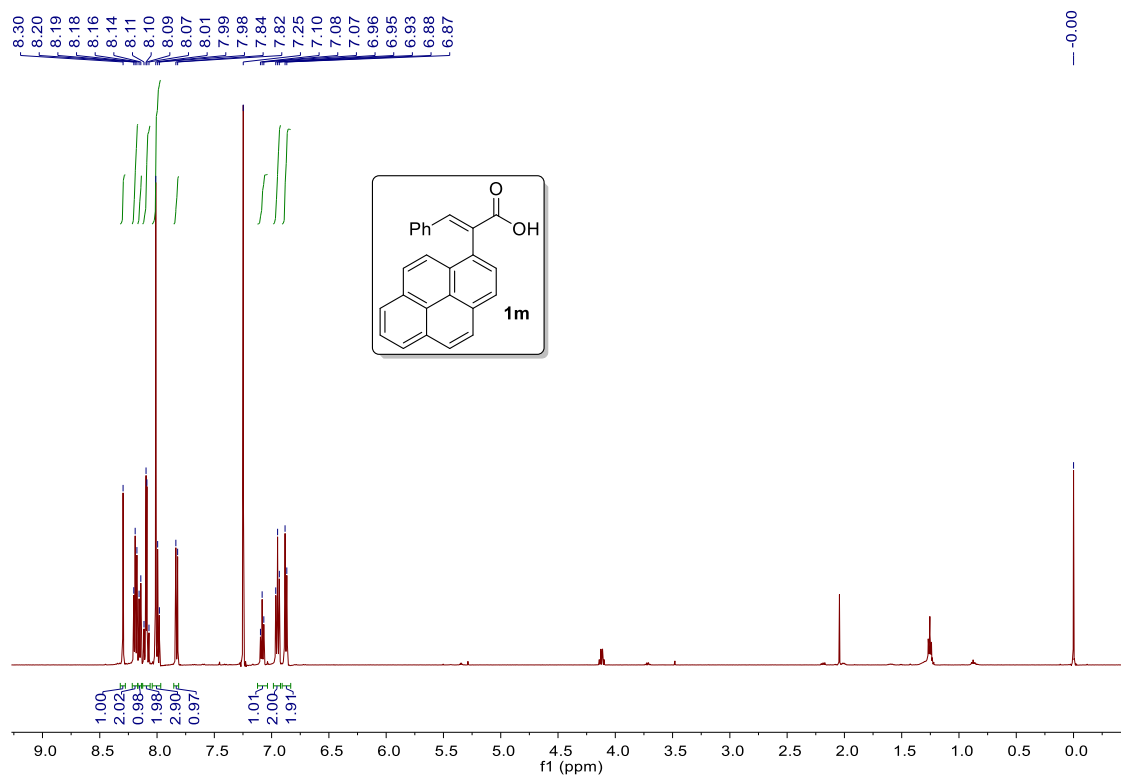


<sup>1</sup>H NMR Spectrum of **1k** (CDCl<sub>3</sub>, 500 MHz)

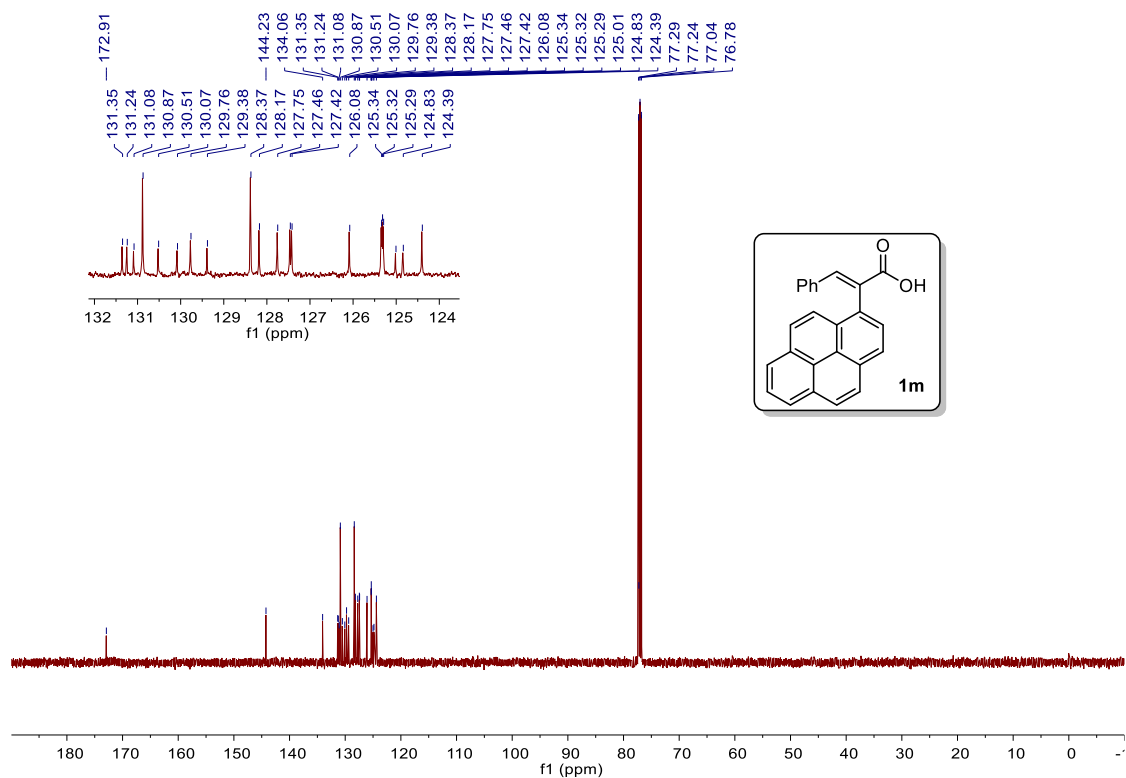




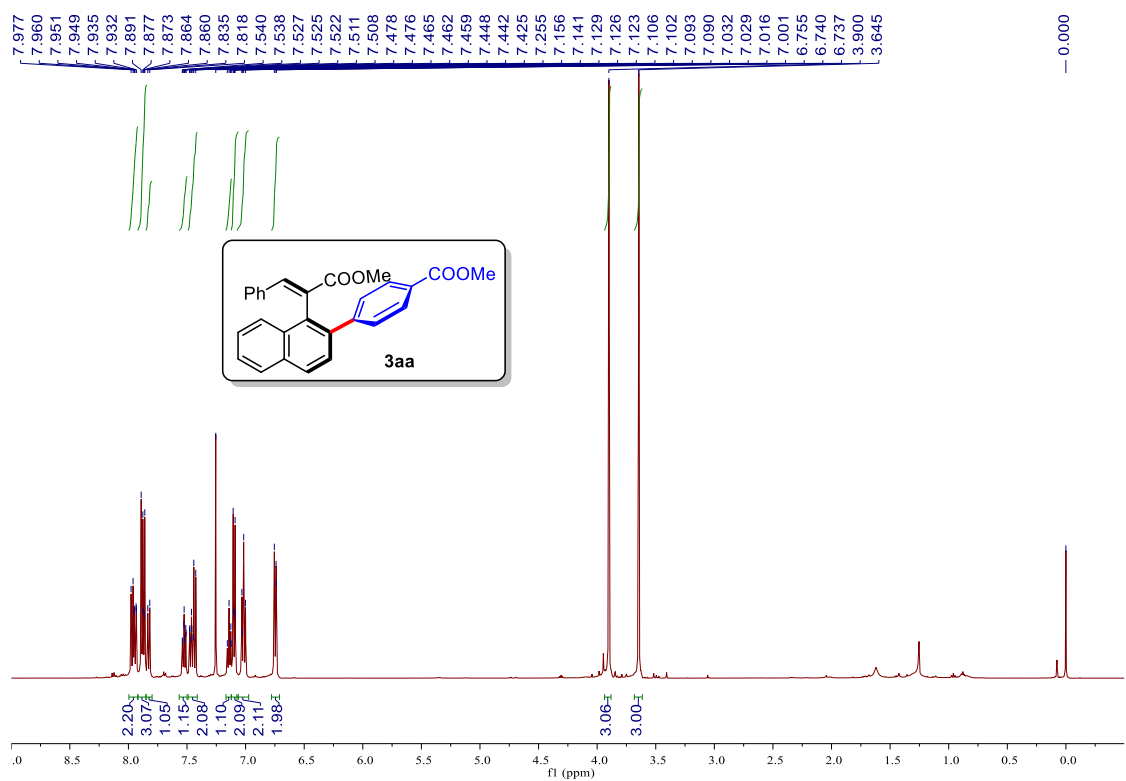
<sup>13</sup>C NMR Spectrum of **1l** (CDCl<sub>3</sub>, 126 MHz)



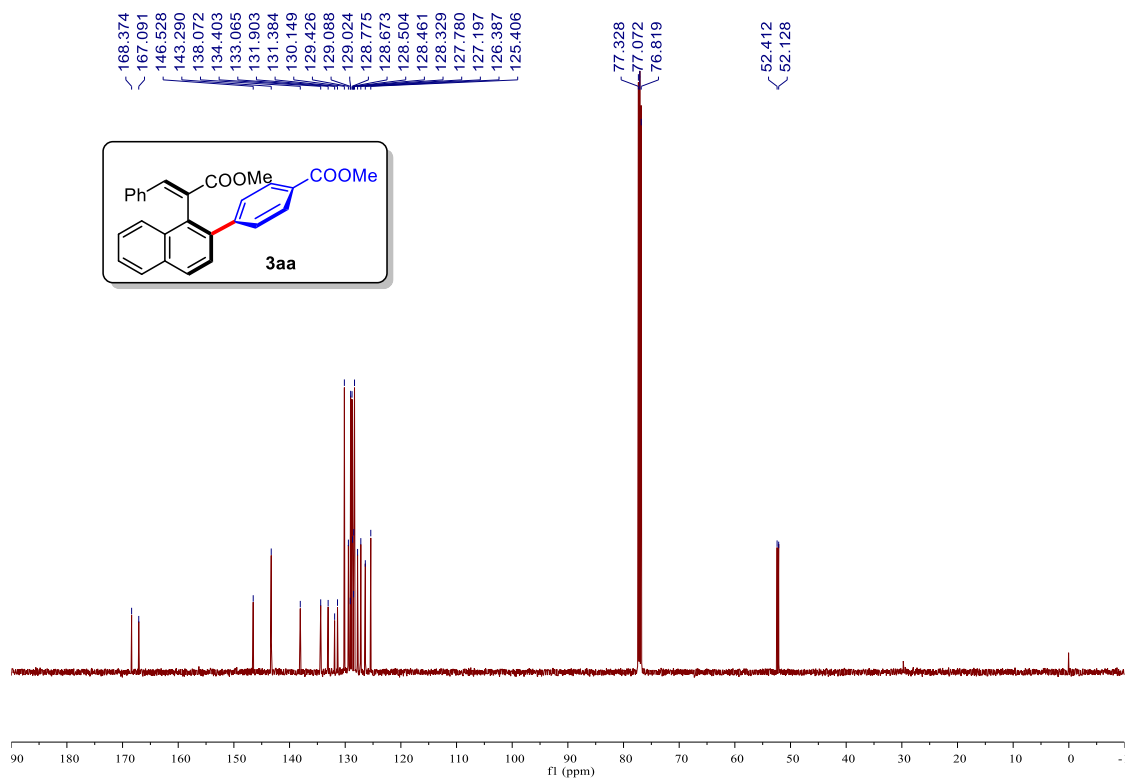
<sup>1</sup>H NMR Spectrum of **1m** (CDCl<sub>3</sub>, 500 MHz)



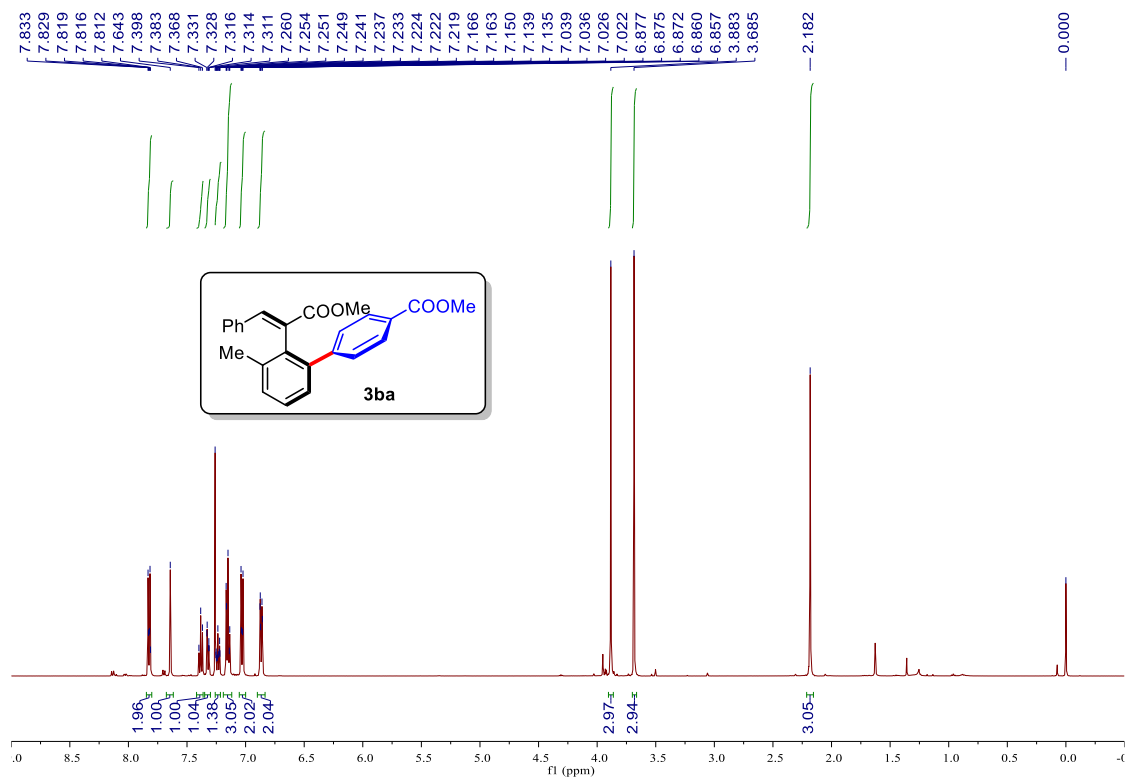
<sup>13</sup>C NMR Spectrum of **1m** (CDCl<sub>3</sub>, 126 MHz) <sup>1</sup>H NMR Spectrum of **1n** (CDCl<sub>3</sub>, 500 MHz) <sup>13</sup>C NMR Spectrum of **1n** (CDCl<sub>3</sub>, 126 MHz)



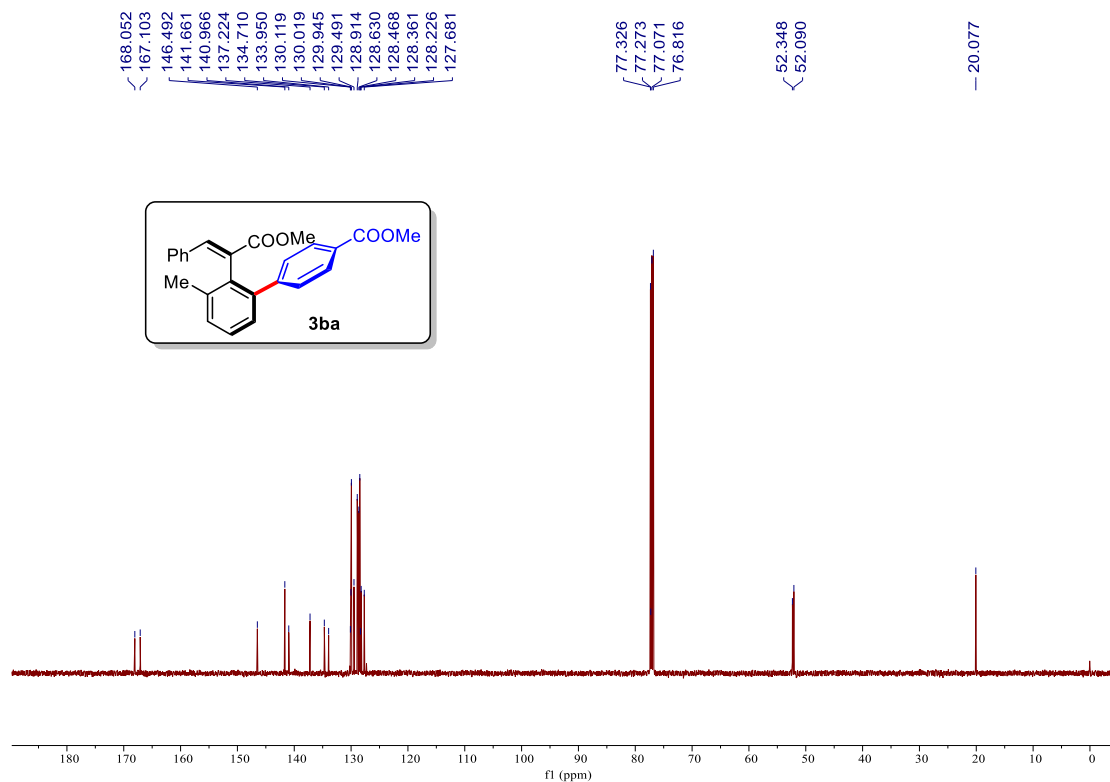
<sup>1</sup>H NMR Spectrum of **3aa** (CDCl<sub>3</sub>, 500 MHz)



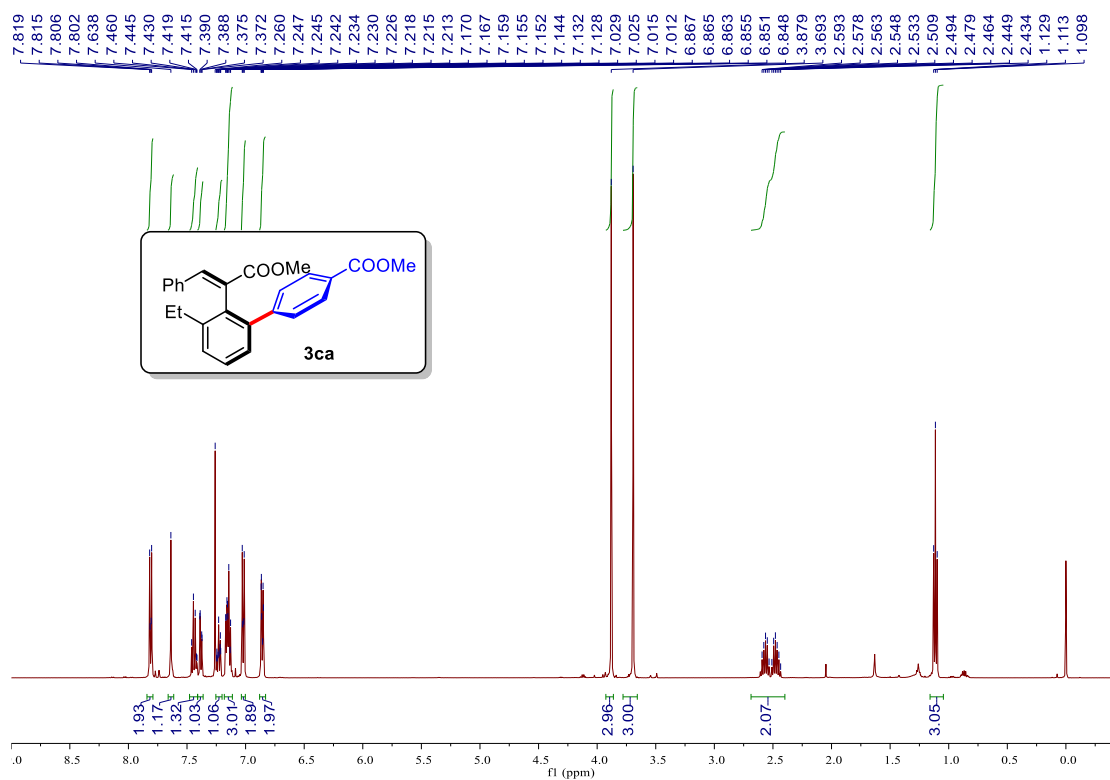
<sup>13</sup>C NMR Spectrum of **3aa** (CDCl<sub>3</sub>, 126 MHz)



<sup>1</sup>H NMR Spectrum of **3ba** (CDCl<sub>3</sub>, 500 MHz)

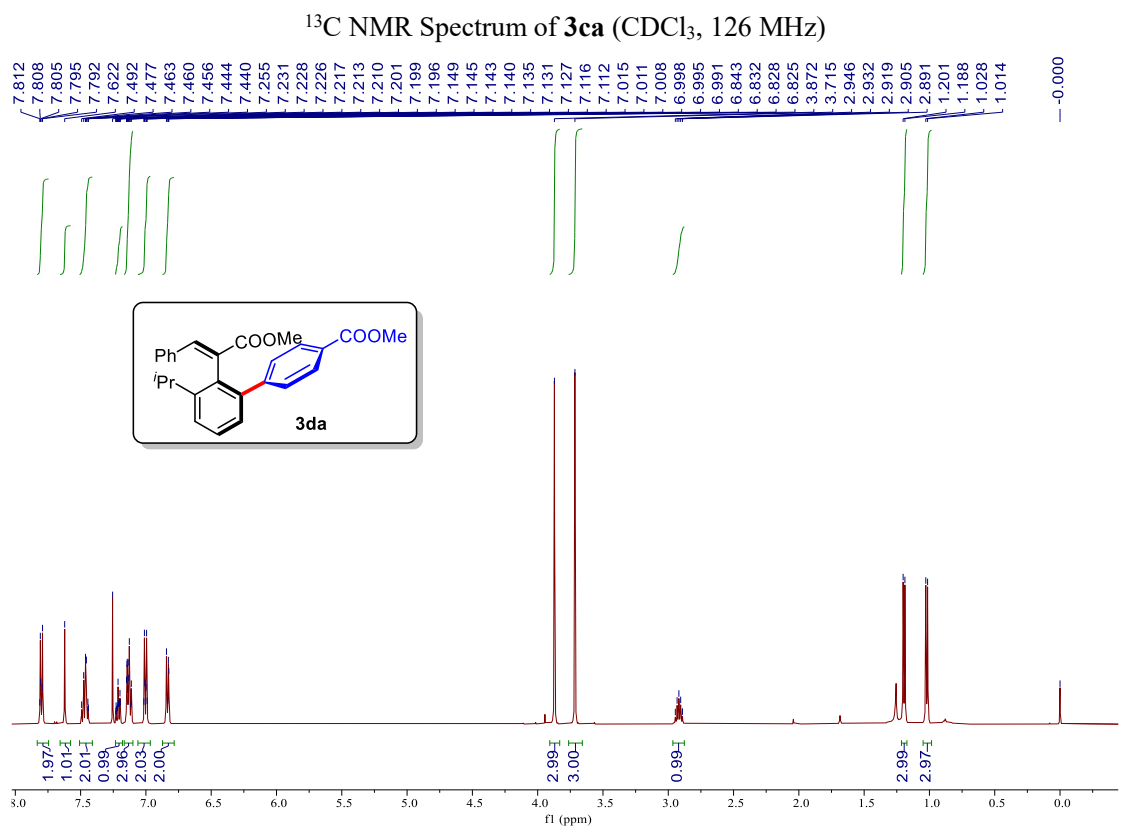
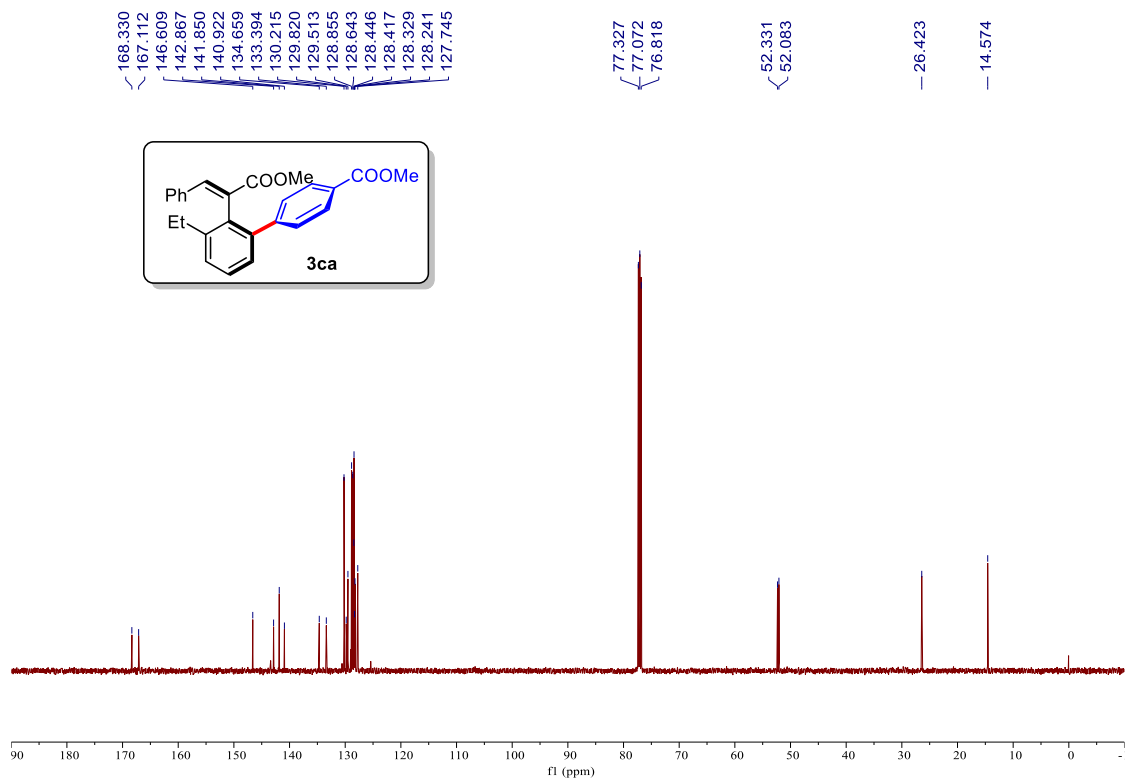


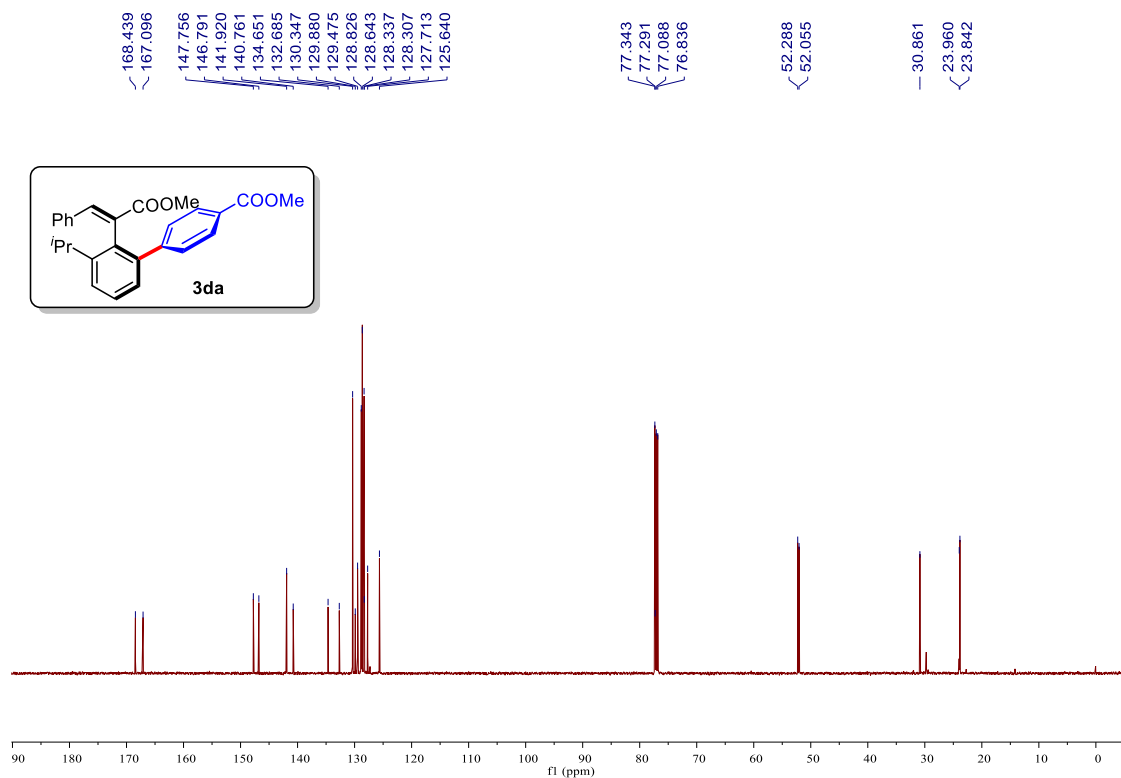
<sup>13</sup>C NMR Spectrum of **3ba** (CDCl<sub>3</sub>, 126 MHz)



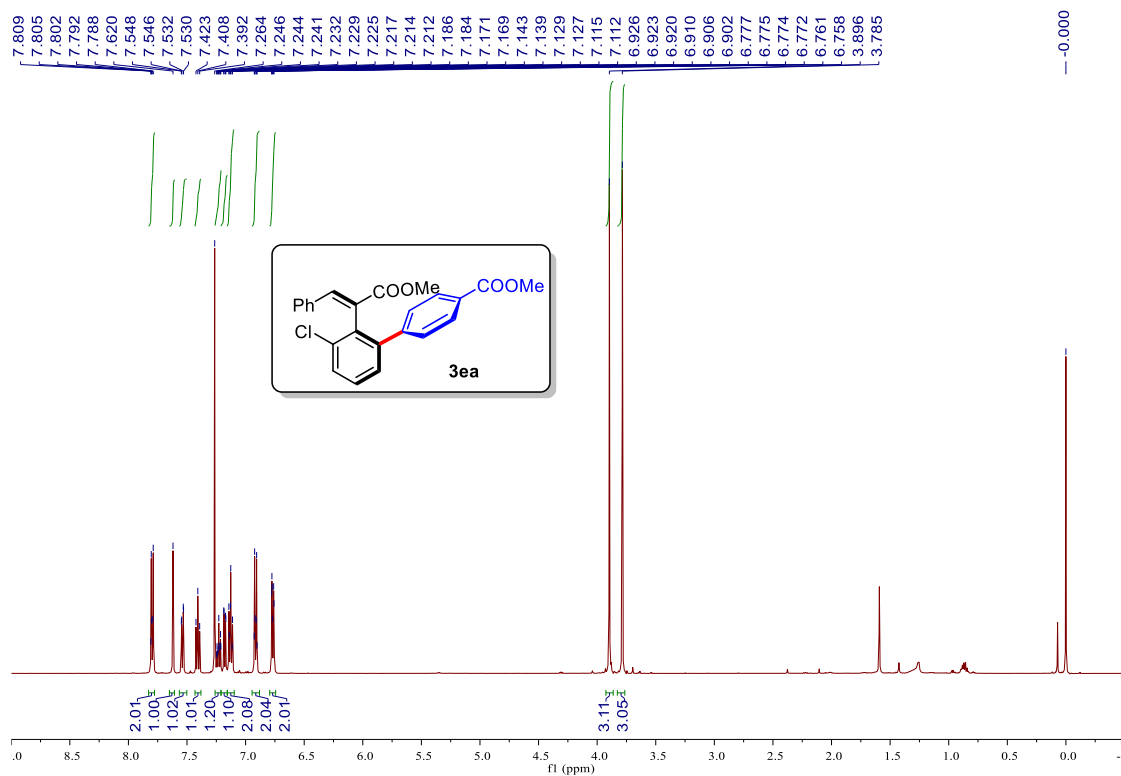
<sup>1</sup>H NMR Spectrum of **3ca** (CDCl<sub>3</sub>, 500 MHz)



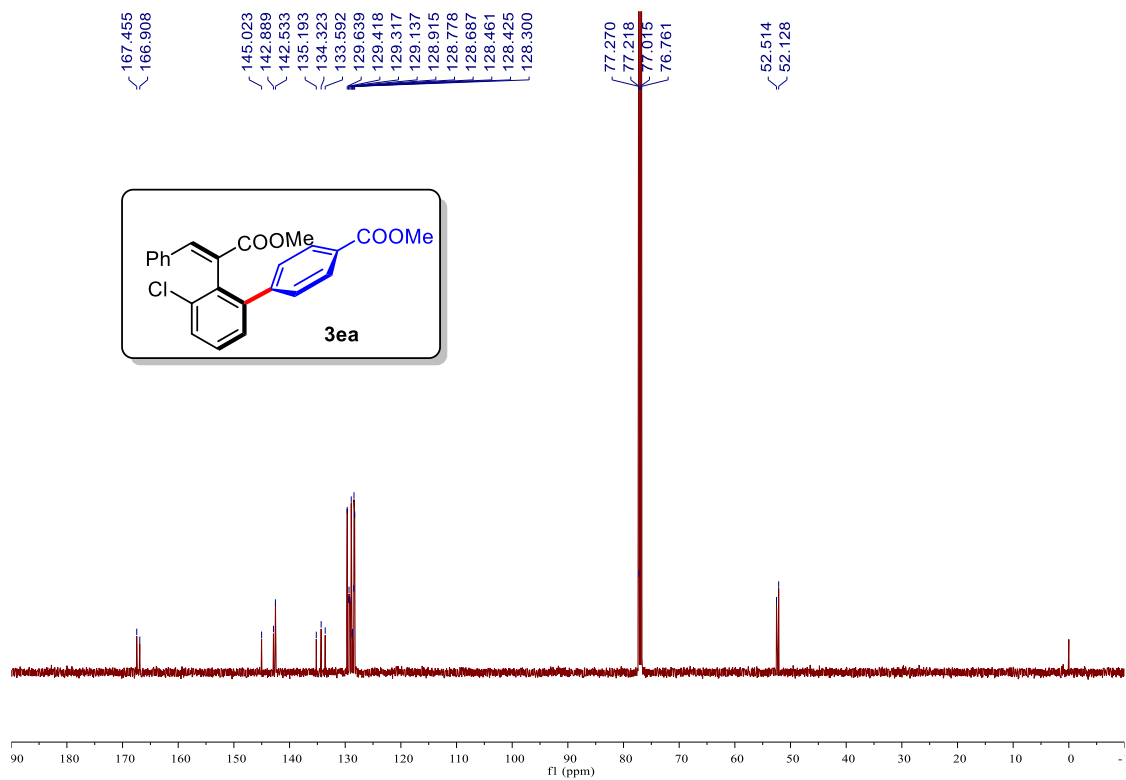




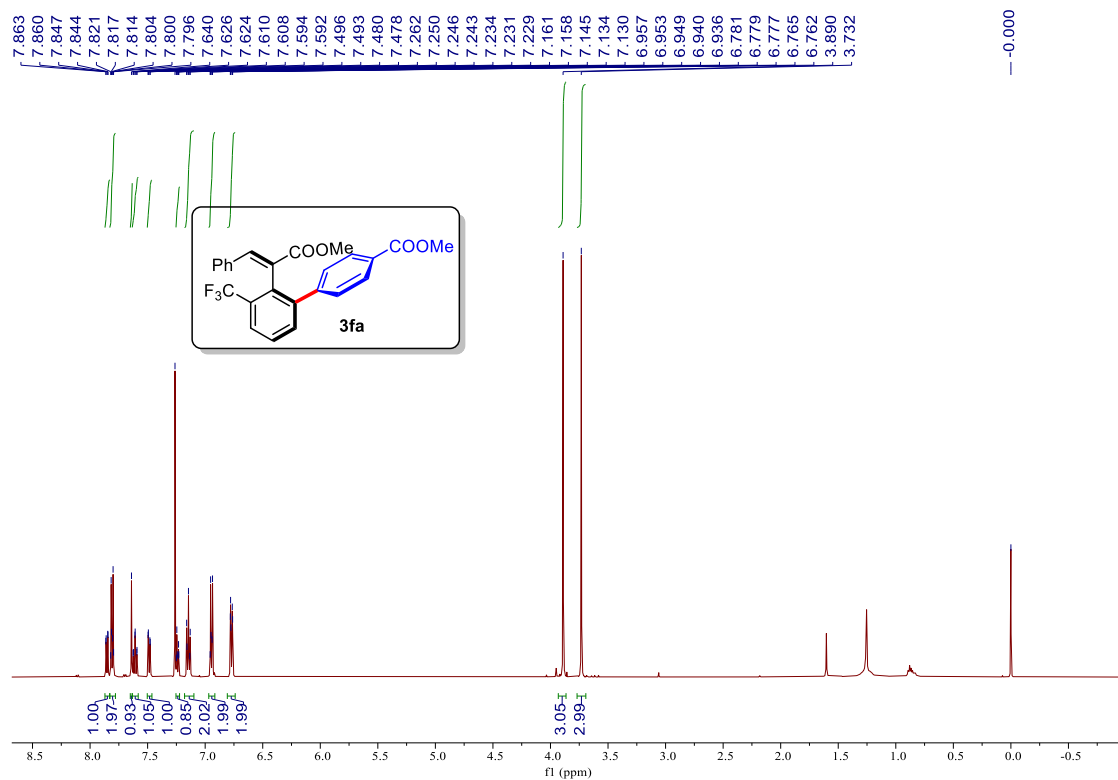
<sup>13</sup>C NMR Spectrum of **3da** (CDCl<sub>3</sub>, 126 MHz)



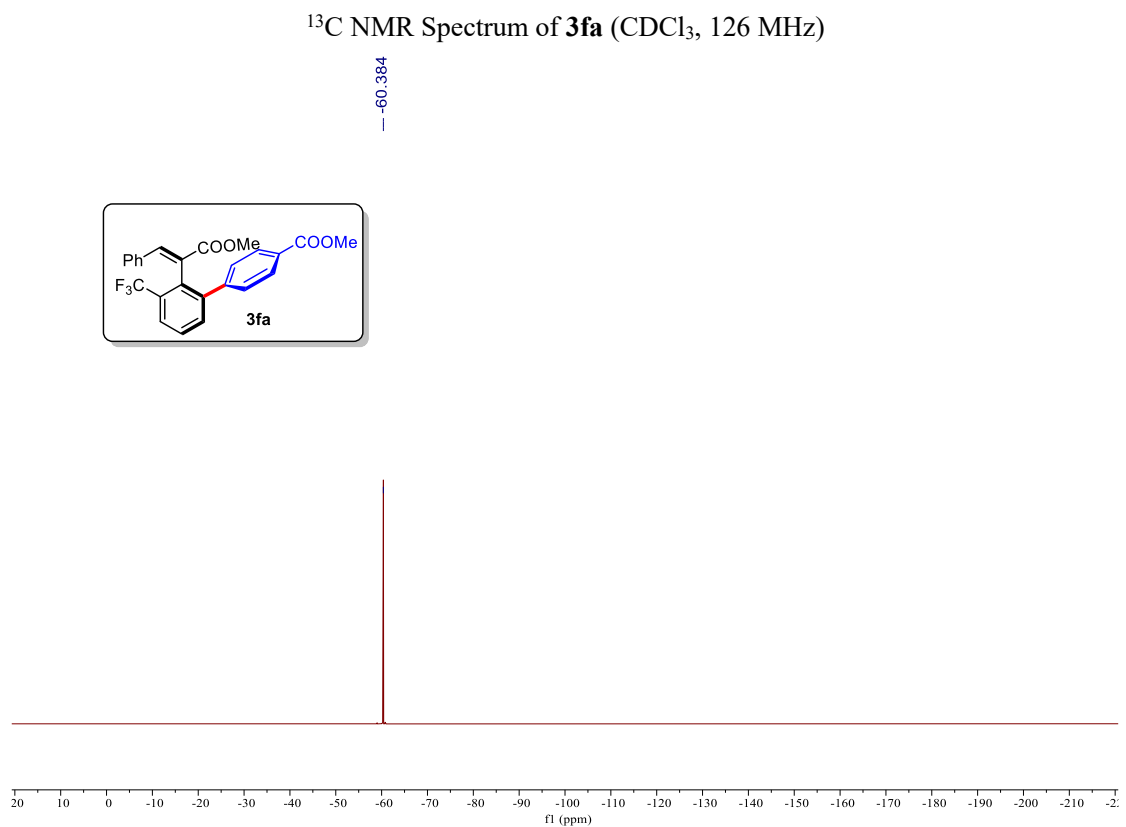
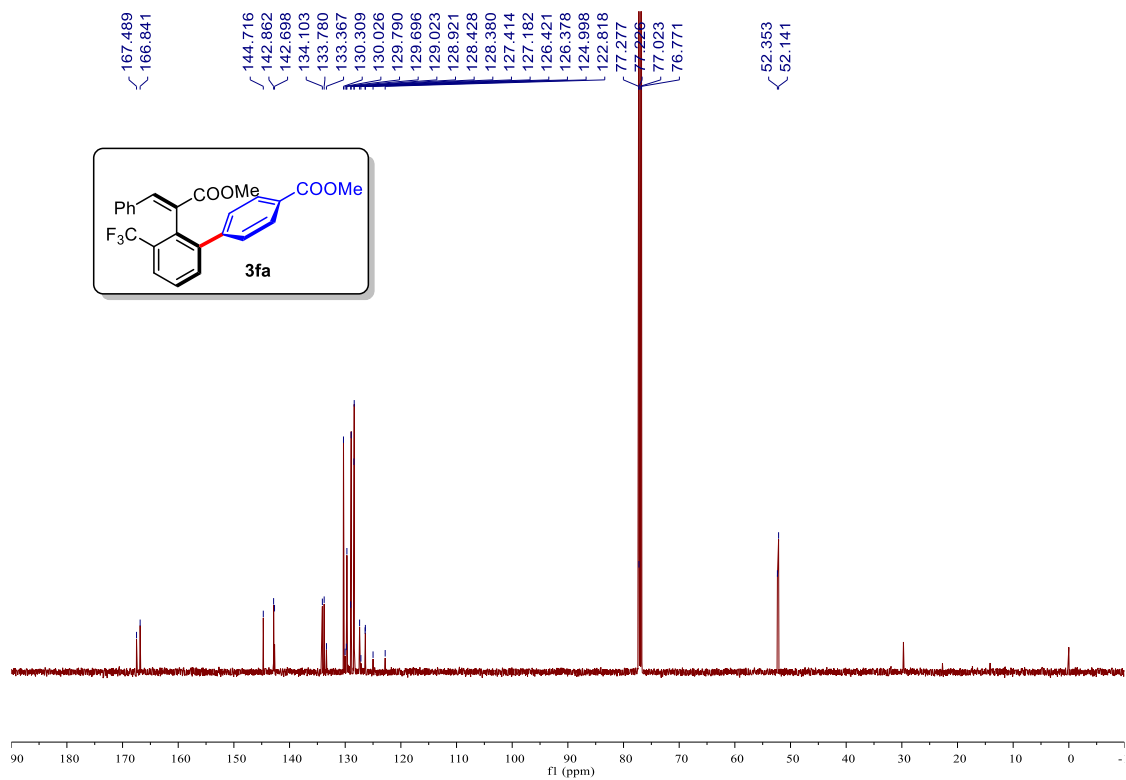
<sup>1</sup>H NMR Spectrum of **3ea** (CDCl<sub>3</sub>, 500 MHz)

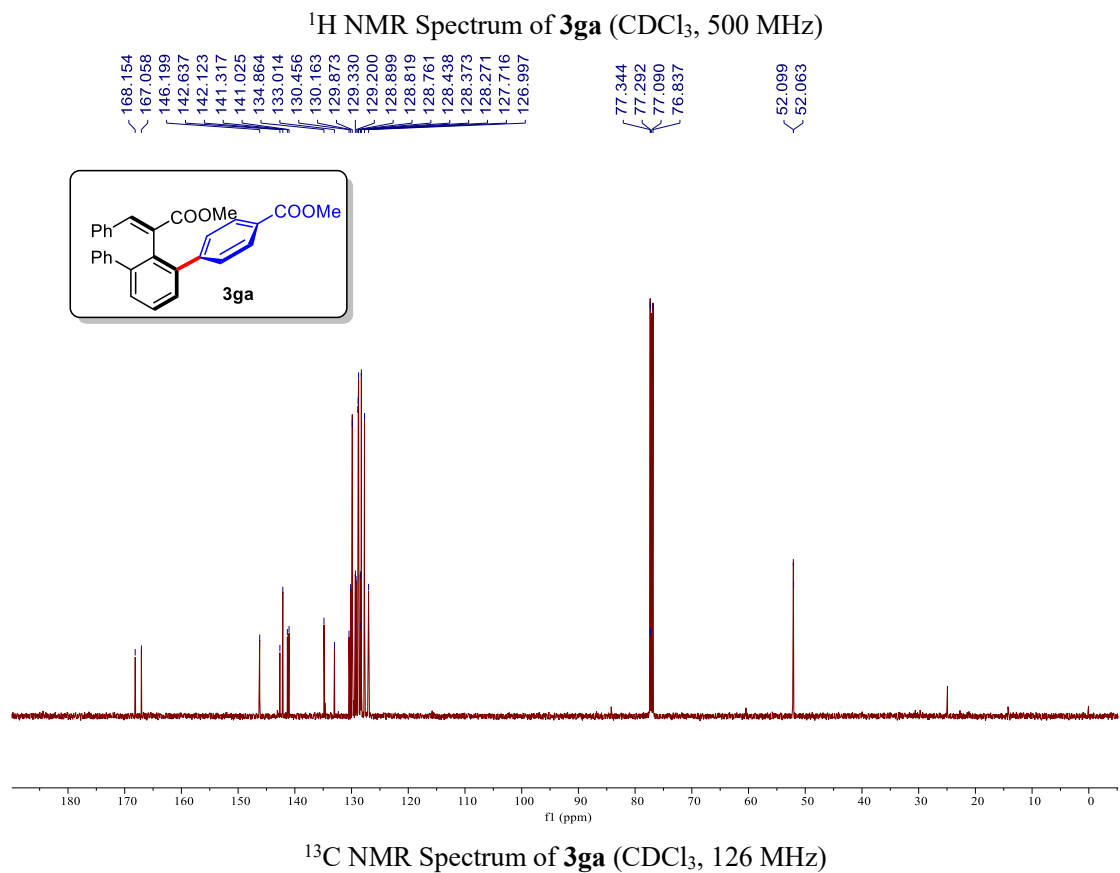
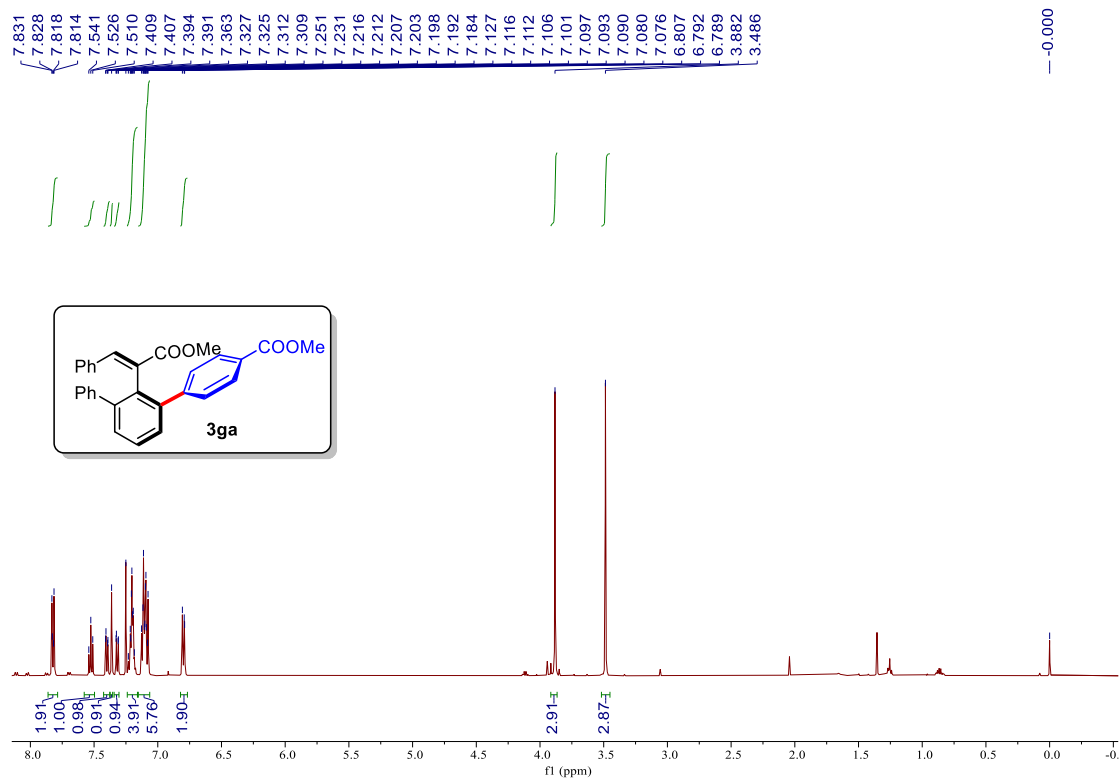


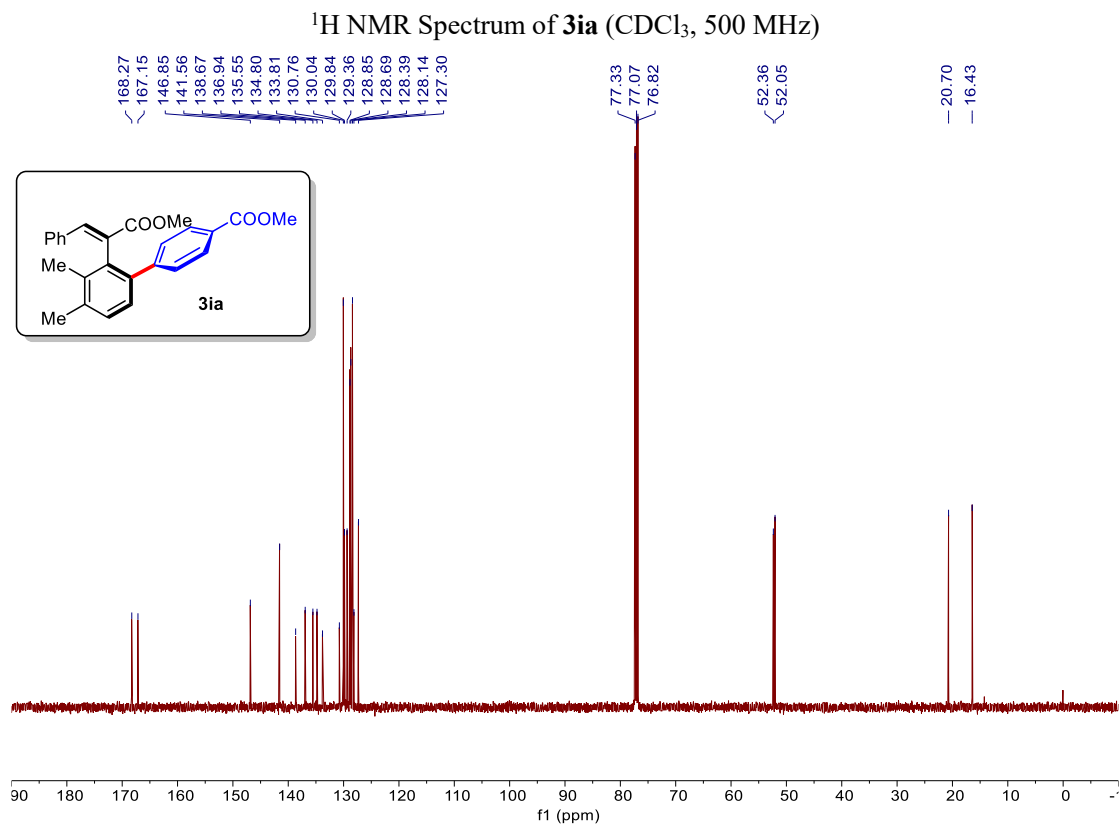
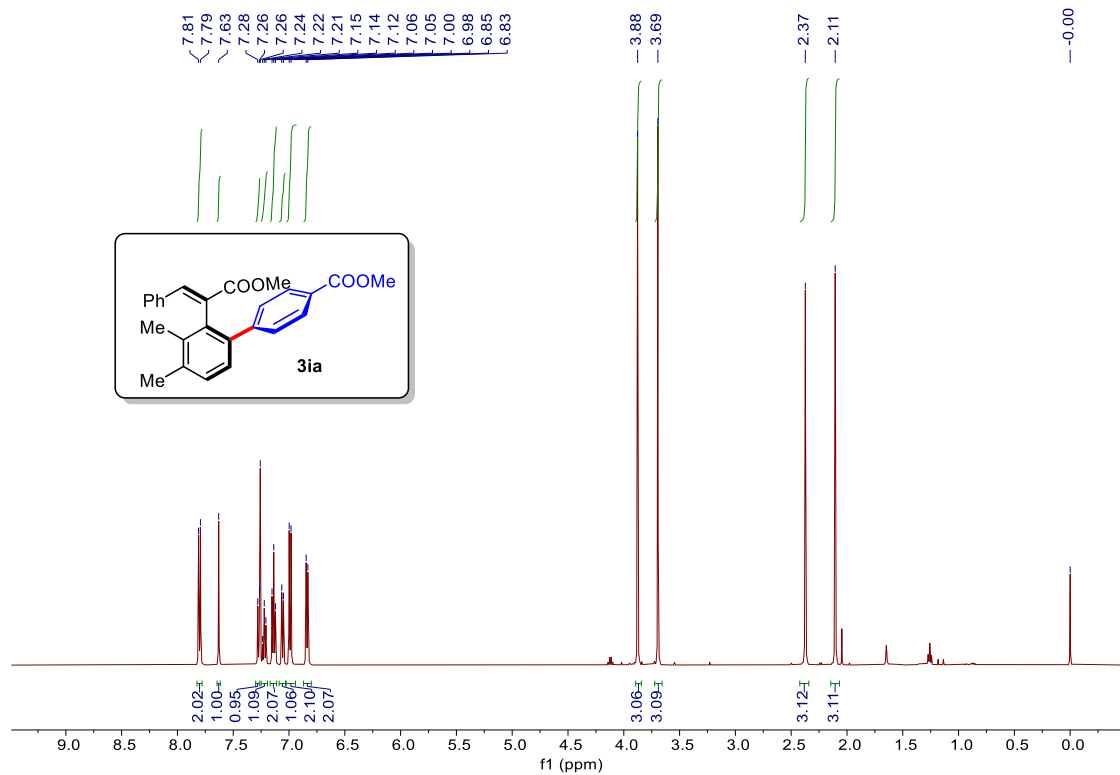
<sup>13</sup>C NMR Spectrum of **3ea** (CDCl<sub>3</sub>, 126 MHz)

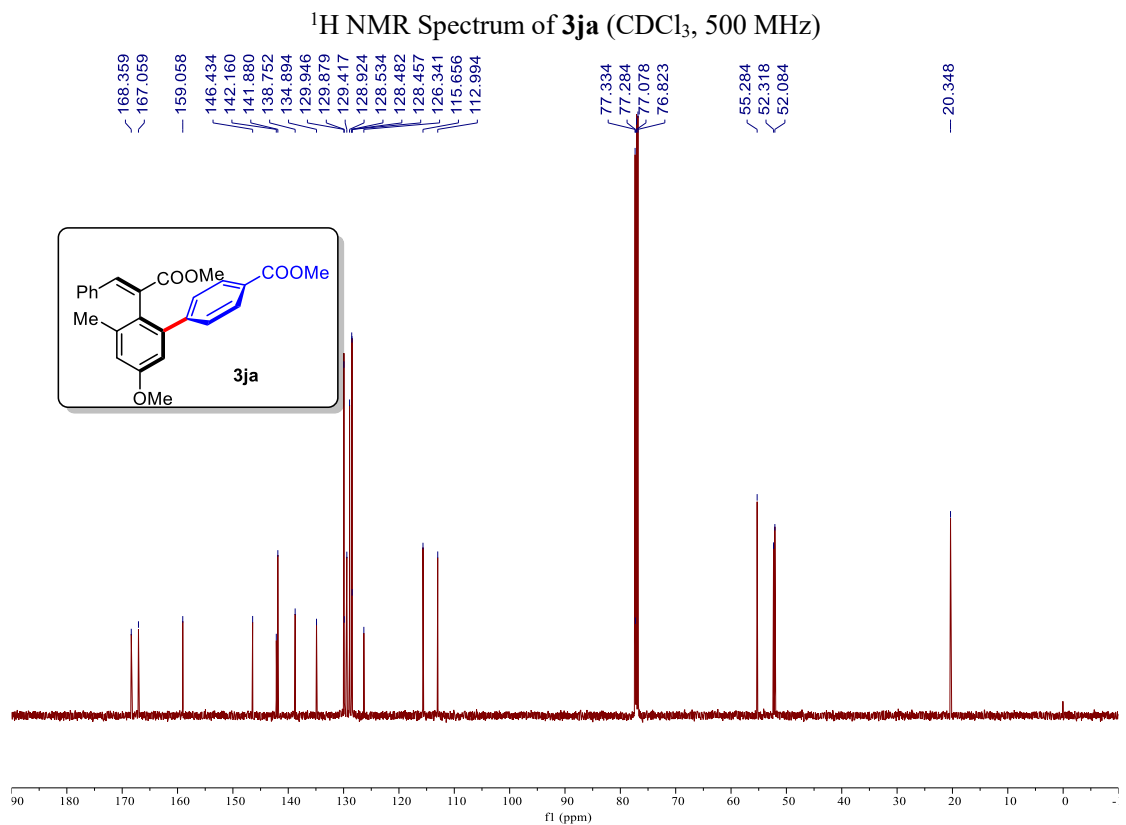
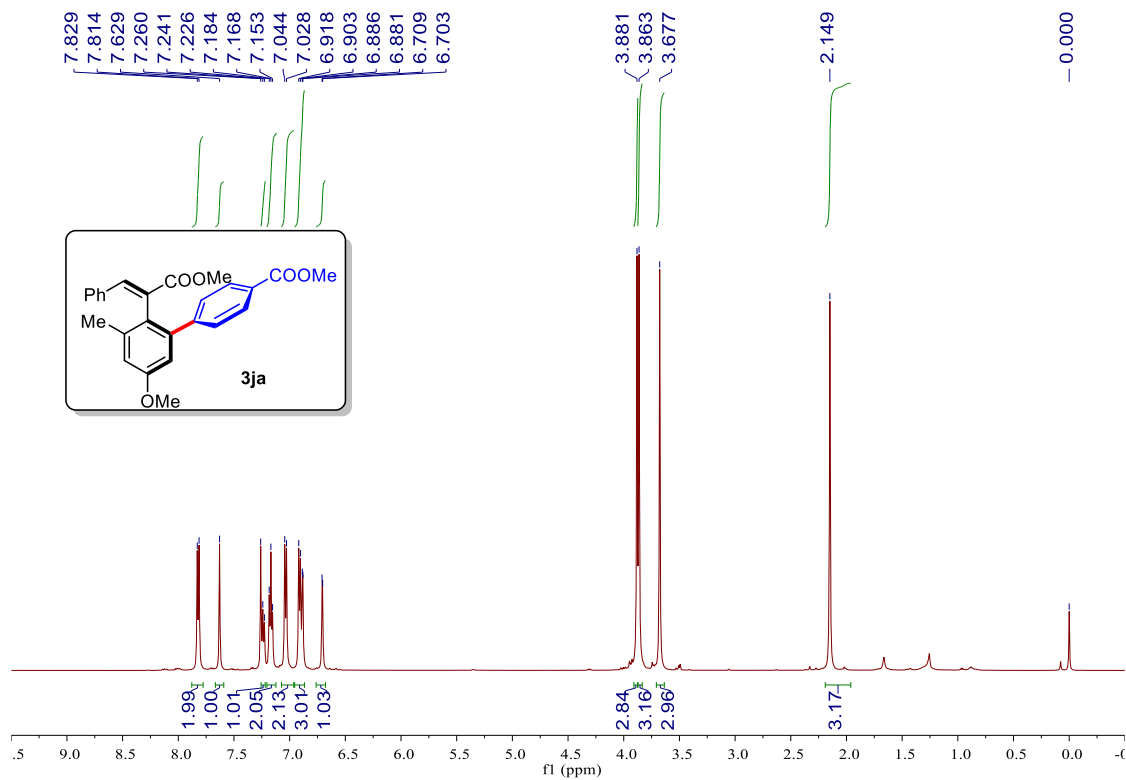


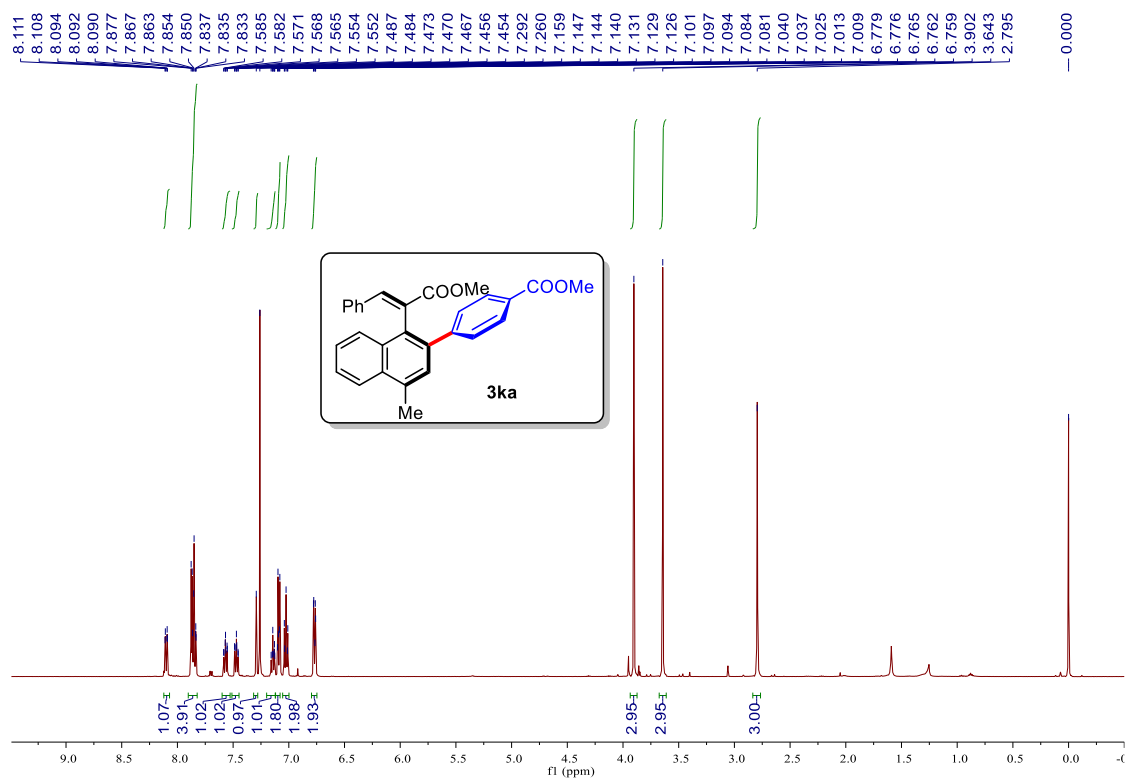
<sup>1</sup>H NMR Spectrum of **3fa** (CDCl<sub>3</sub>, 500 MHz)



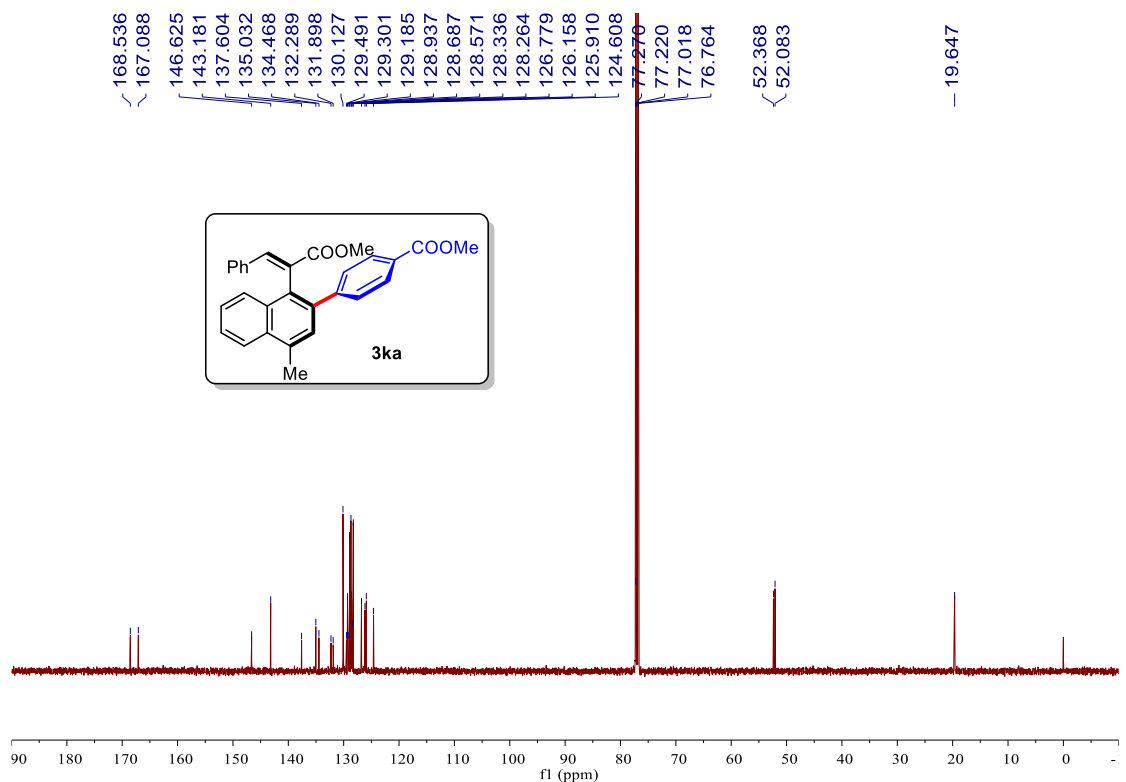






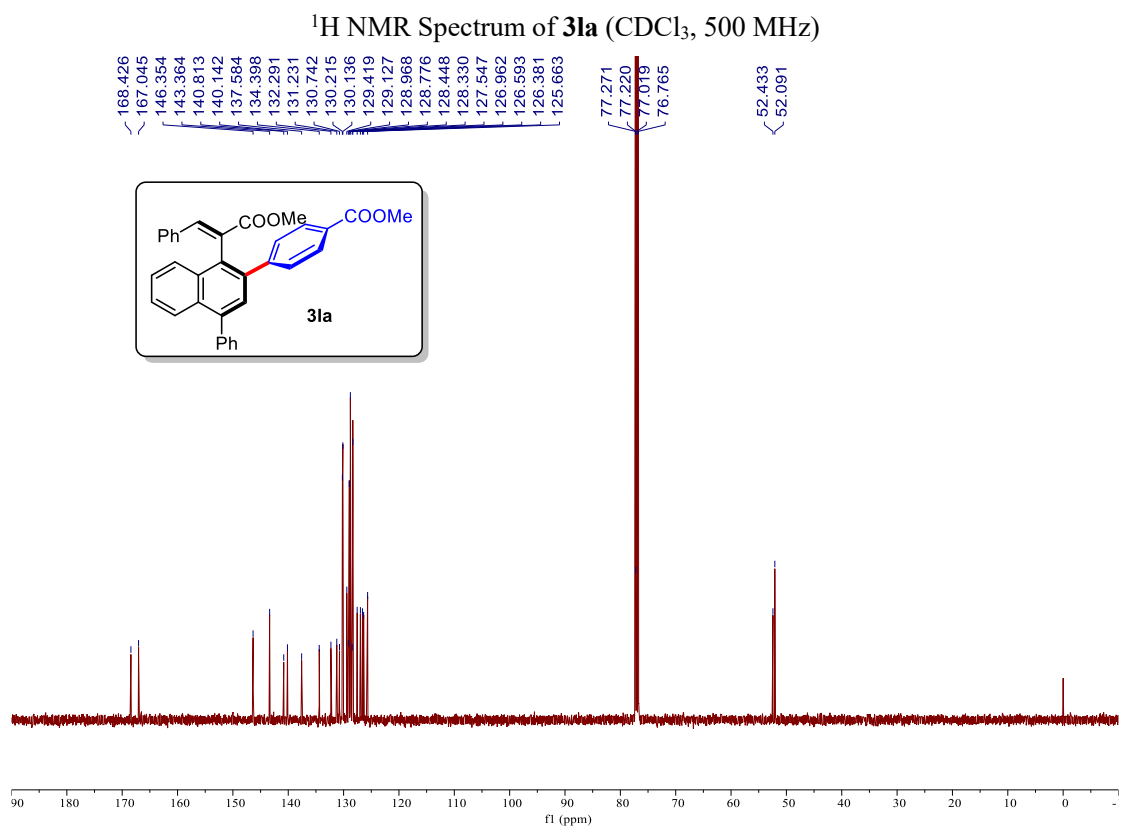
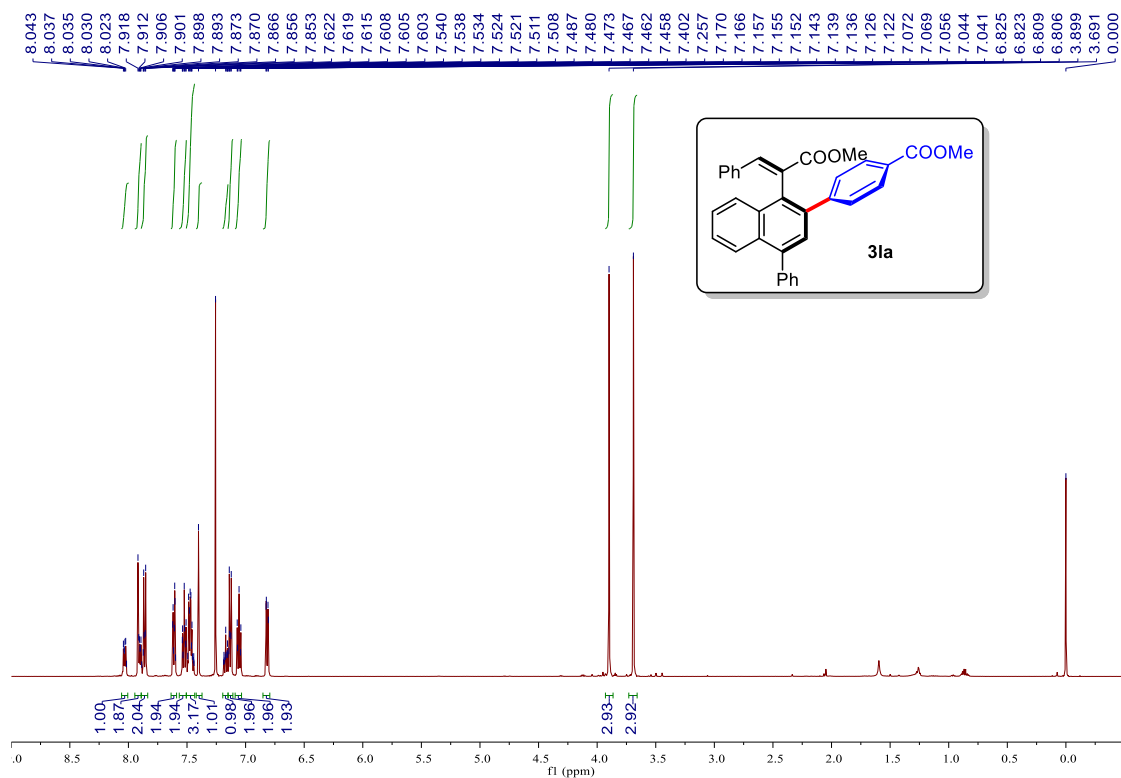


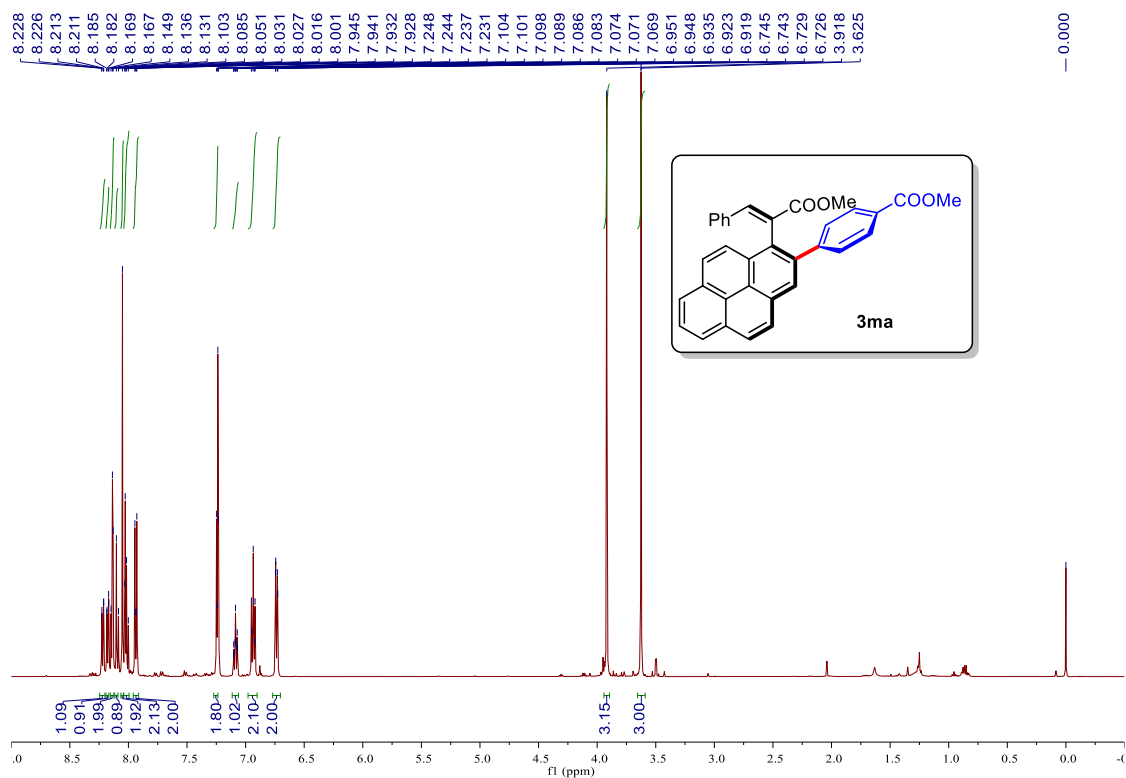
<sup>1</sup>H NMR Spectrum of **3ka** (CDCl<sub>3</sub>, 500 MHz)

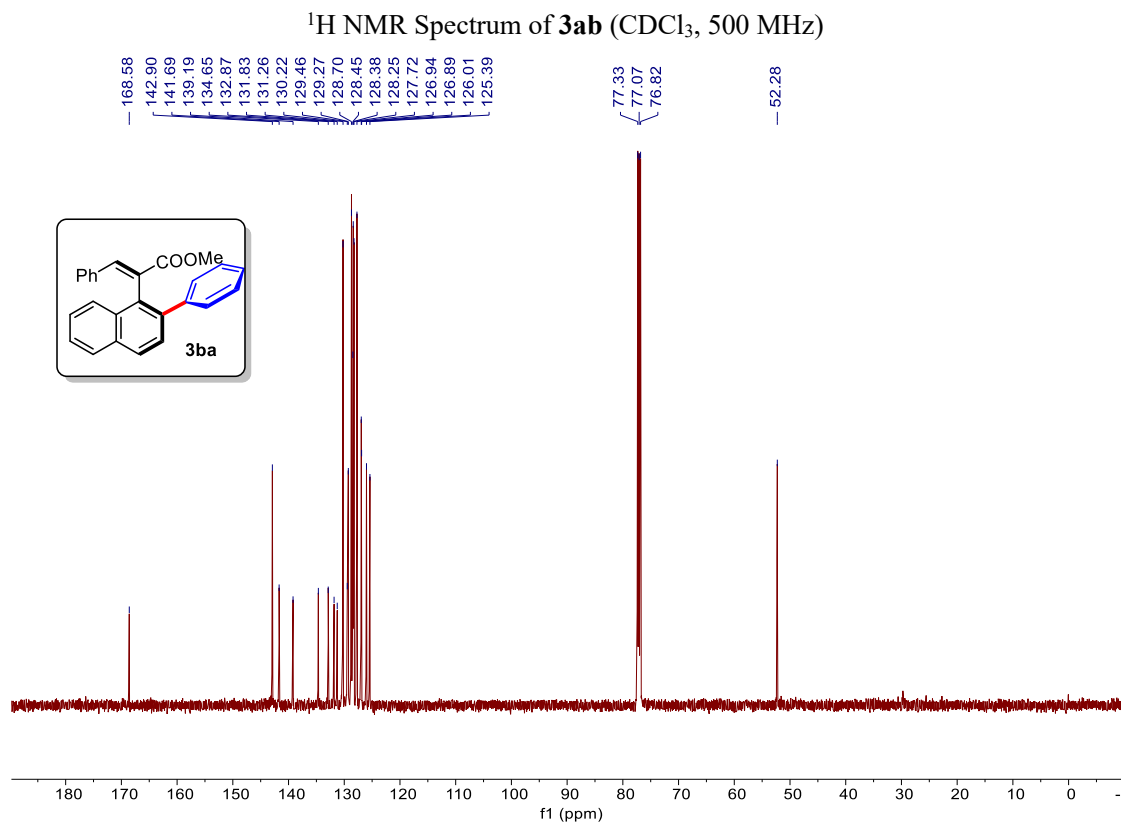
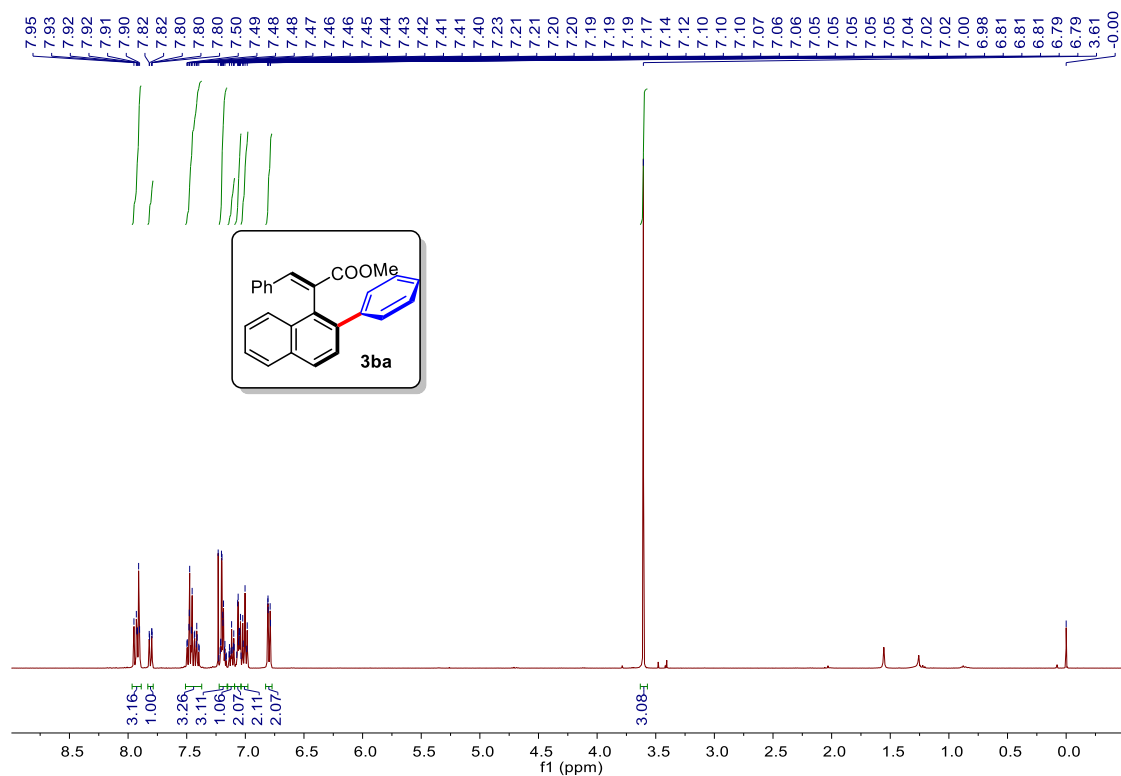


<sup>13</sup>C NMR Spectrum of **3ka** (CDCl<sub>3</sub>, 126 MHz)

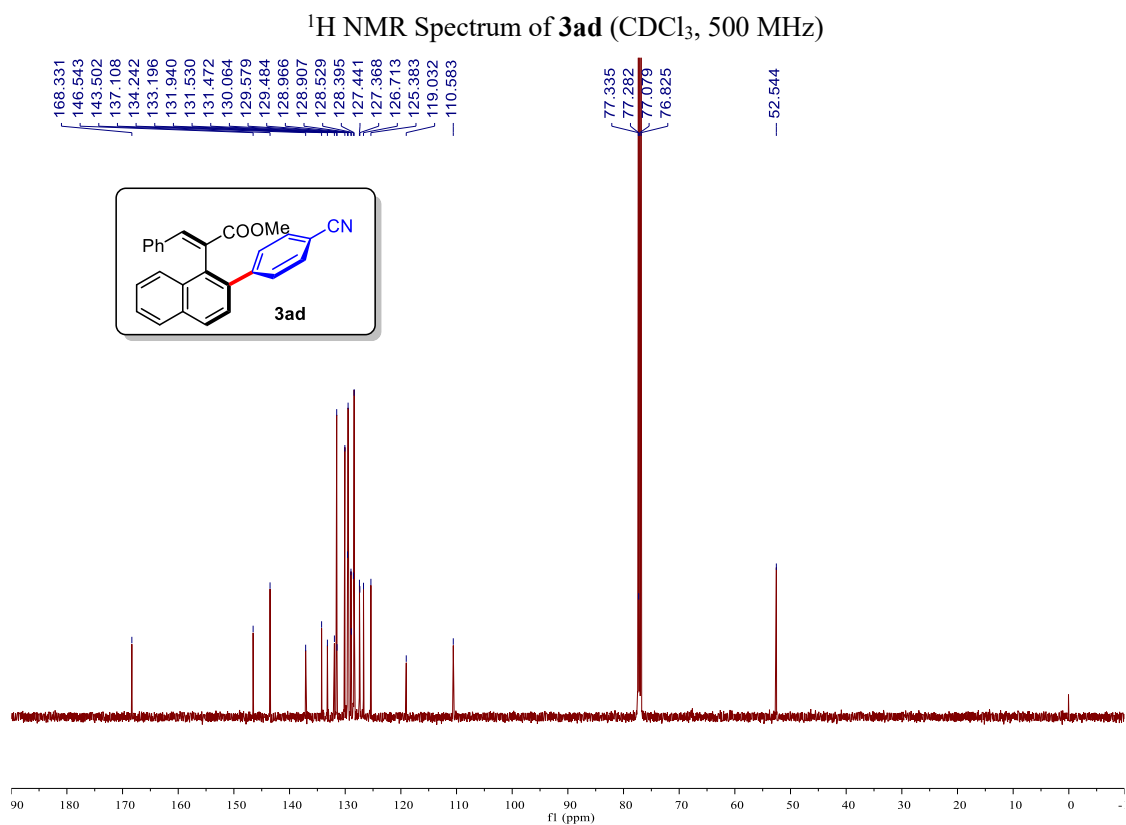
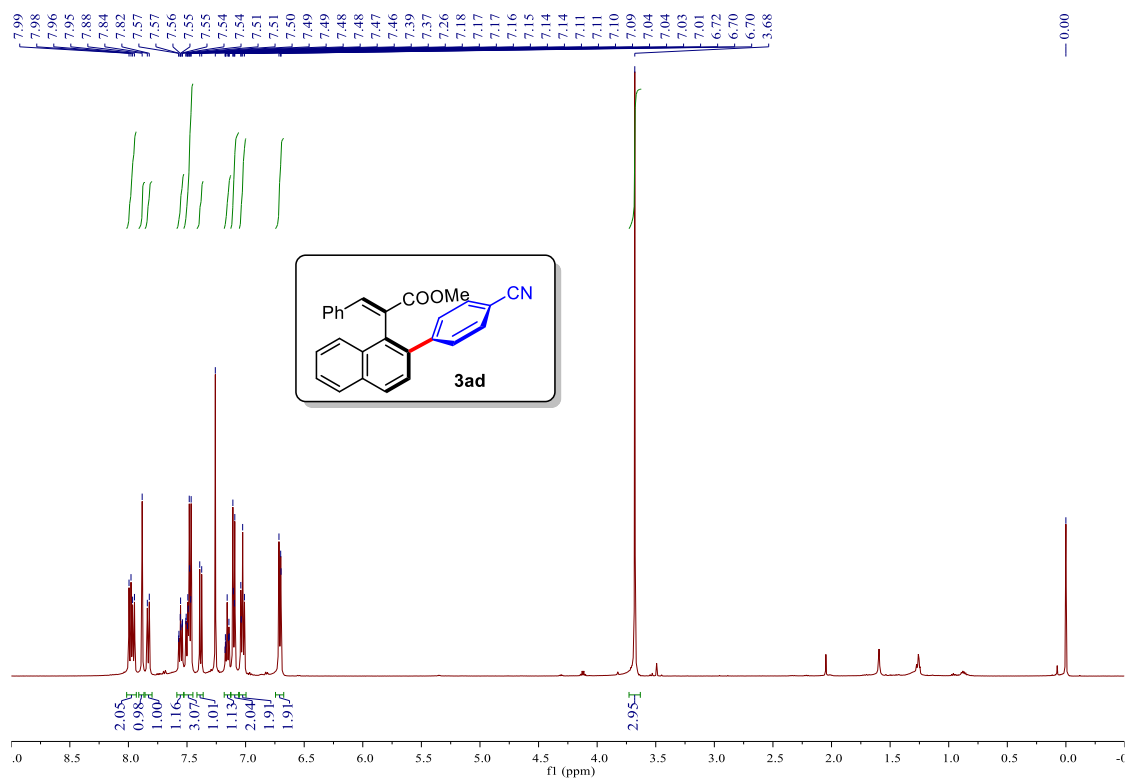


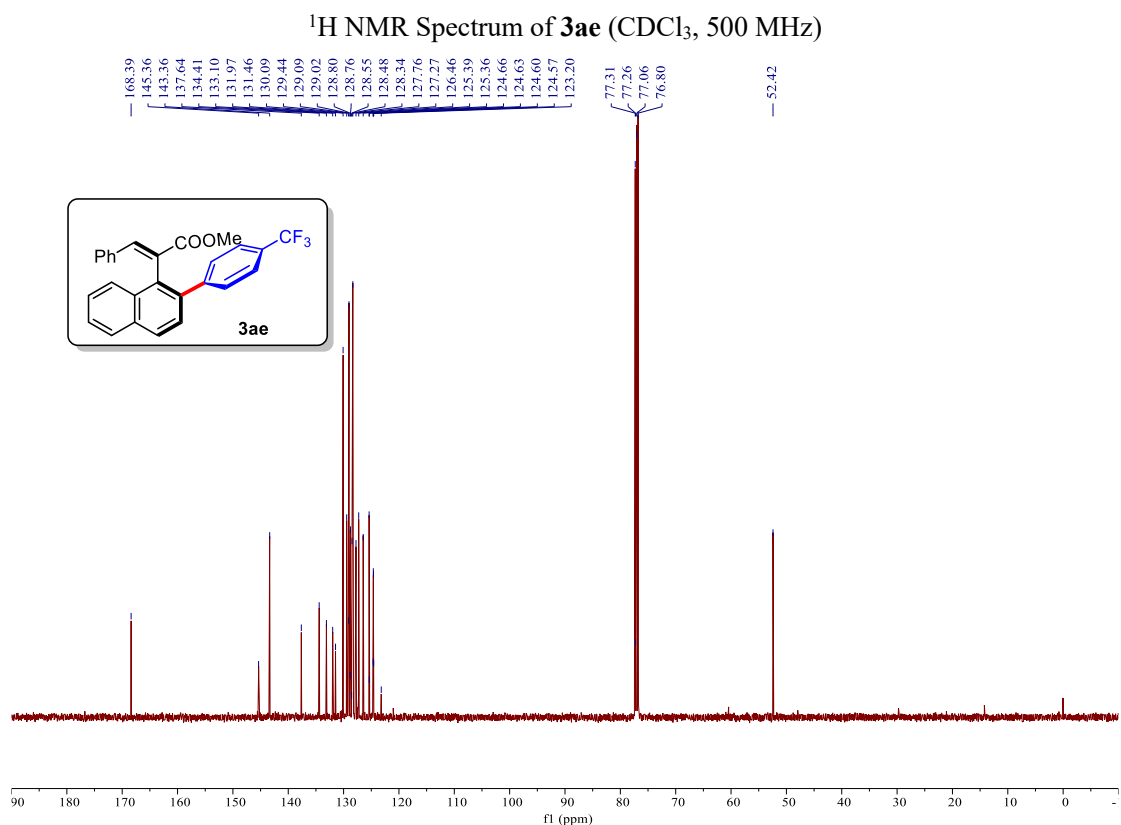
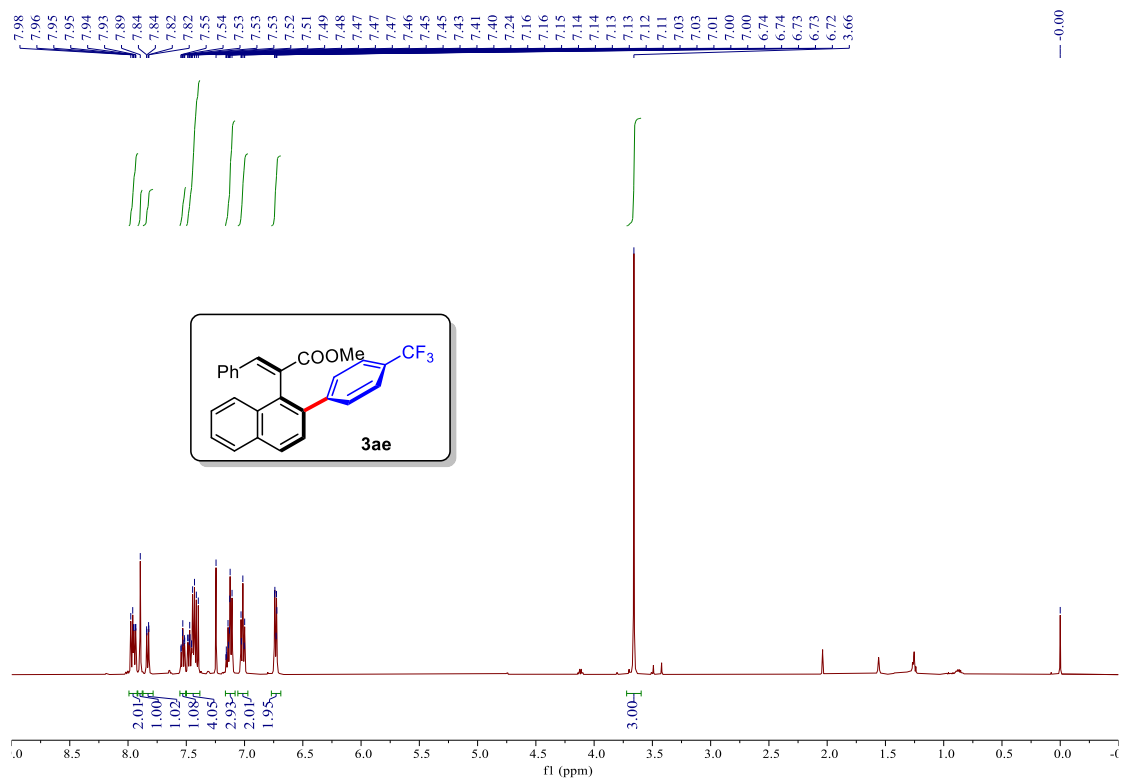


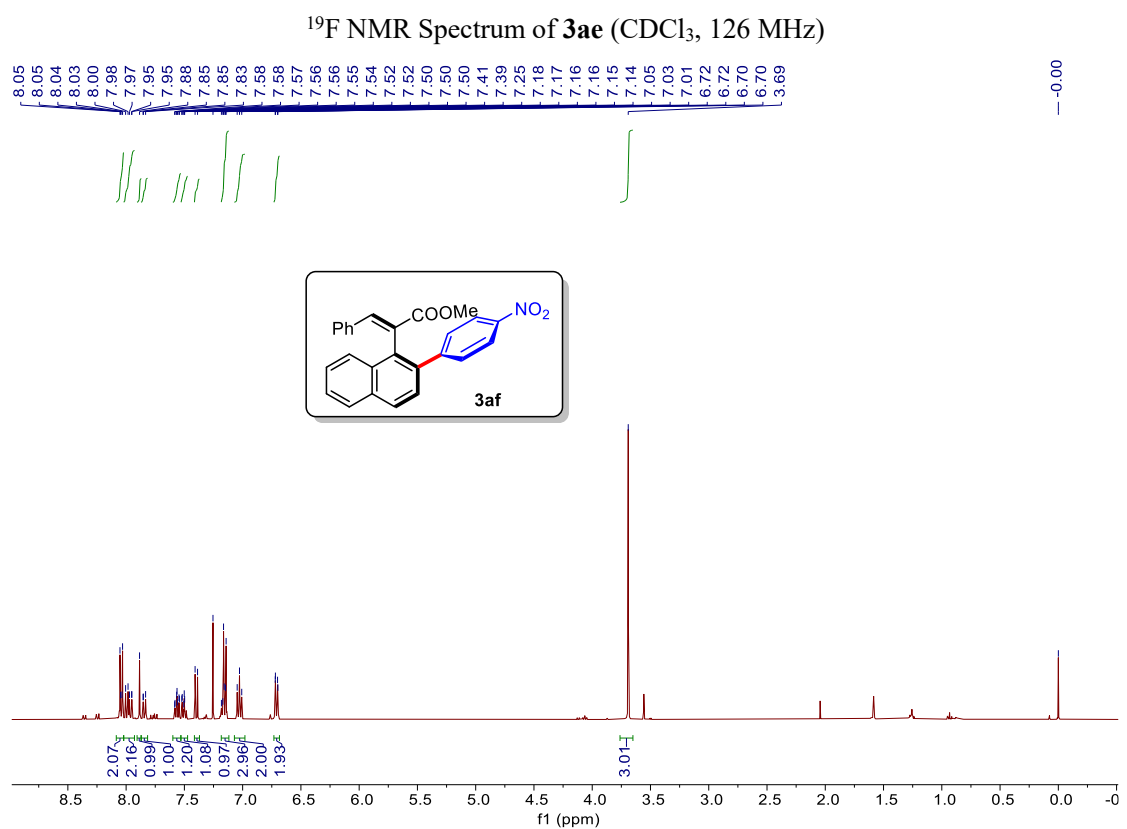
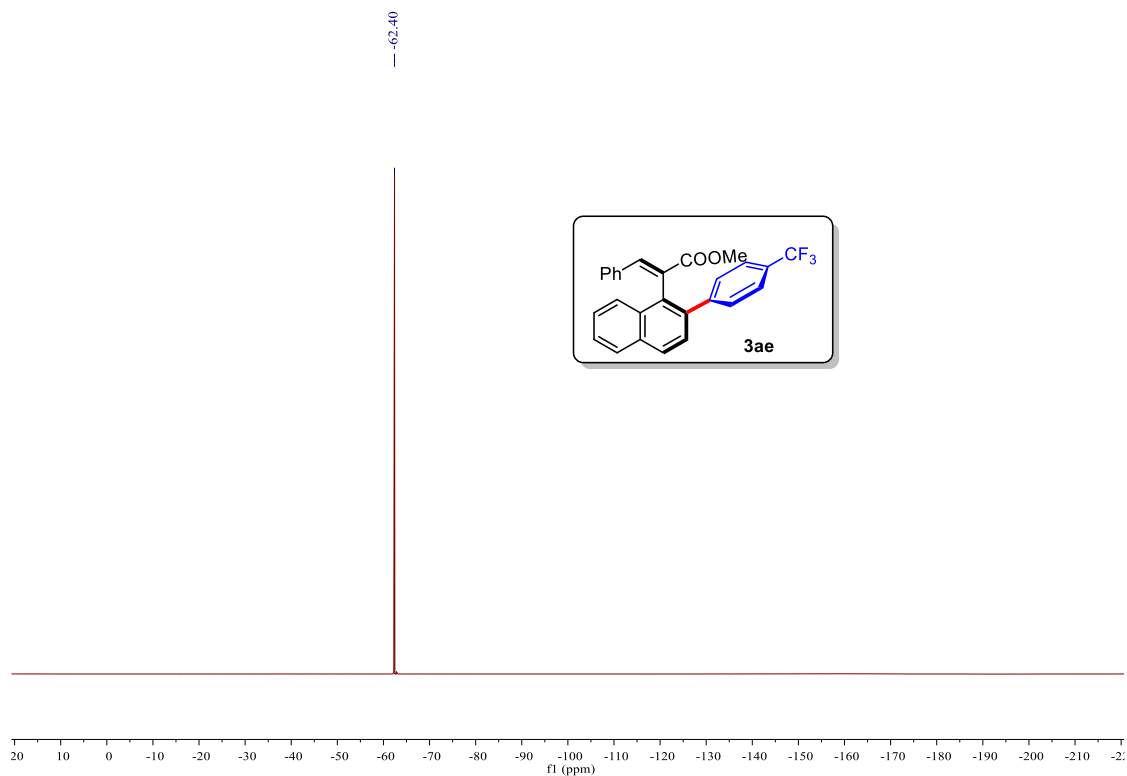


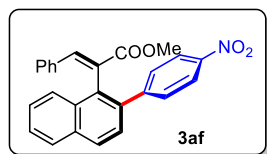
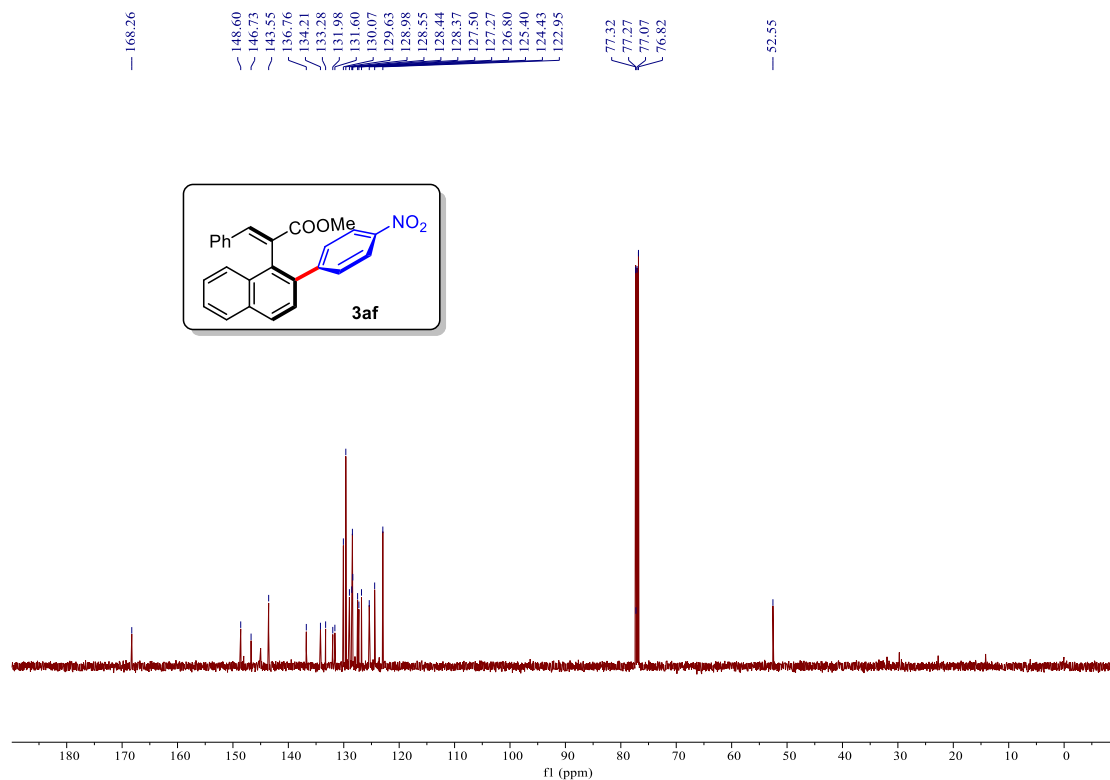




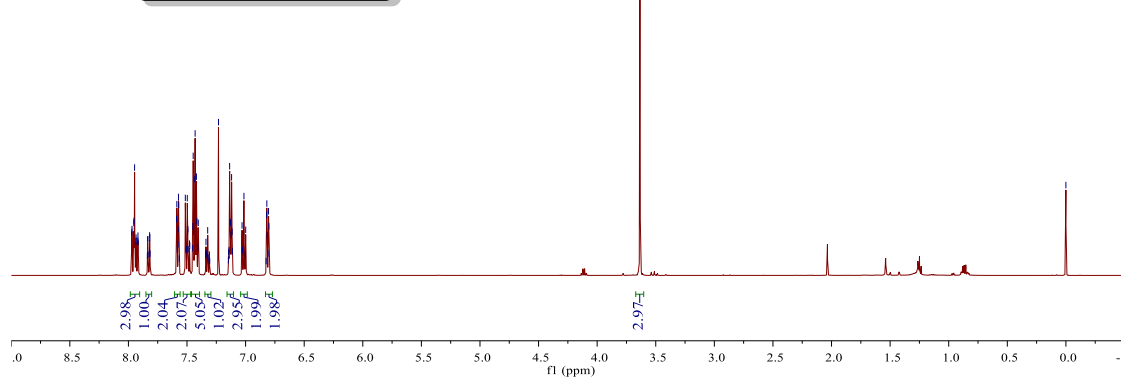
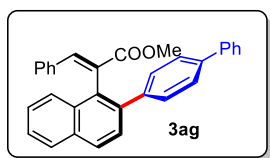
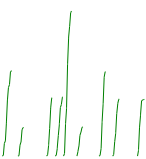
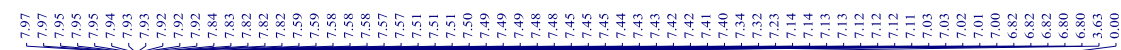






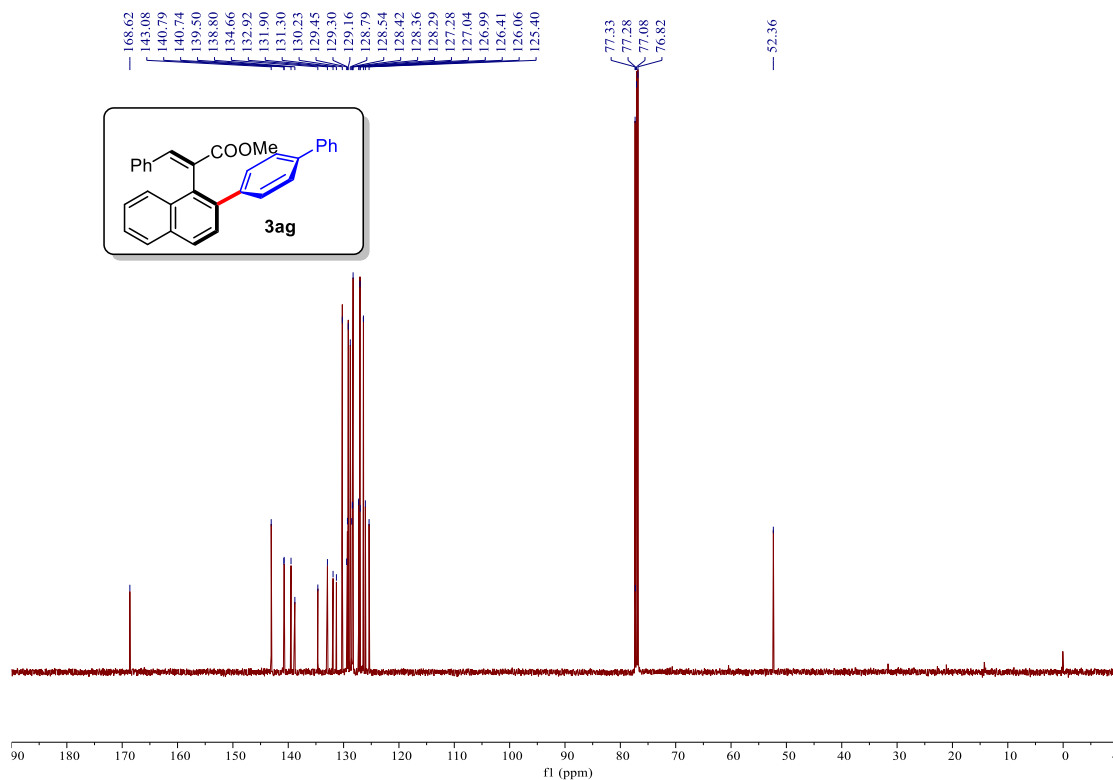


$^{13}\text{C}$  NMR Spectrum of **3af** ( $\text{CDCl}_3$ , 126 MHz)

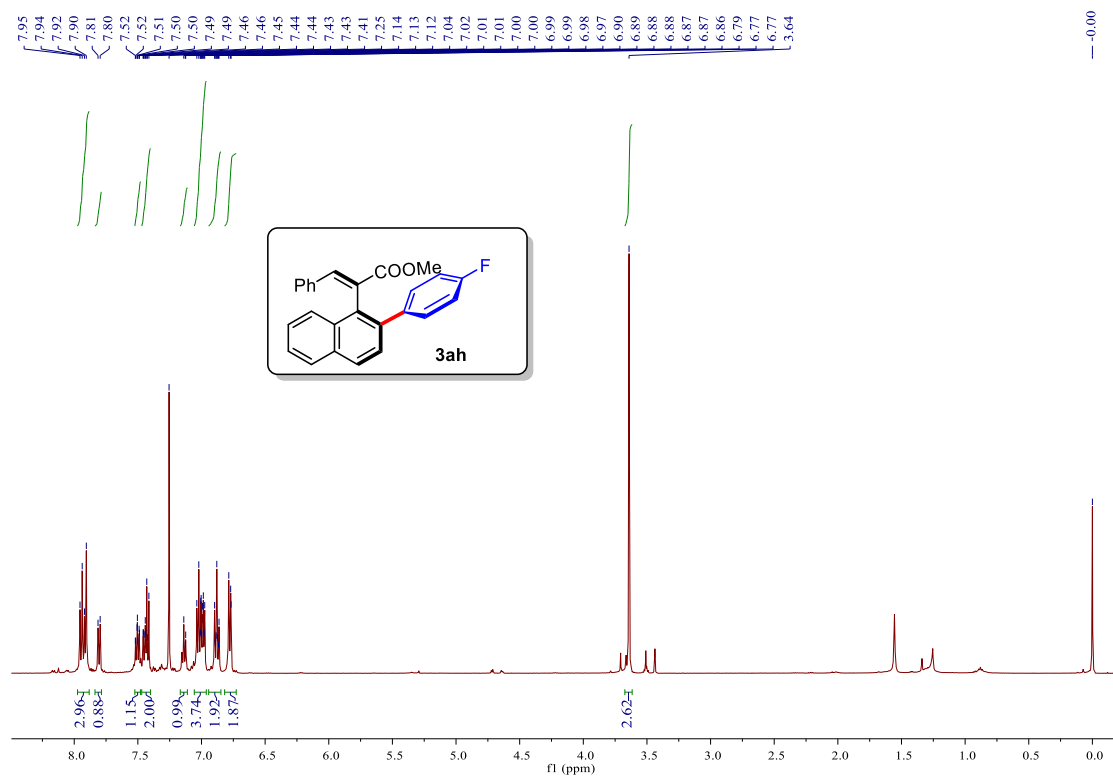


$^1\text{H}$  NMR Spectrum of **3ag** ( $\text{CDCl}_3$ , 500 MHz)

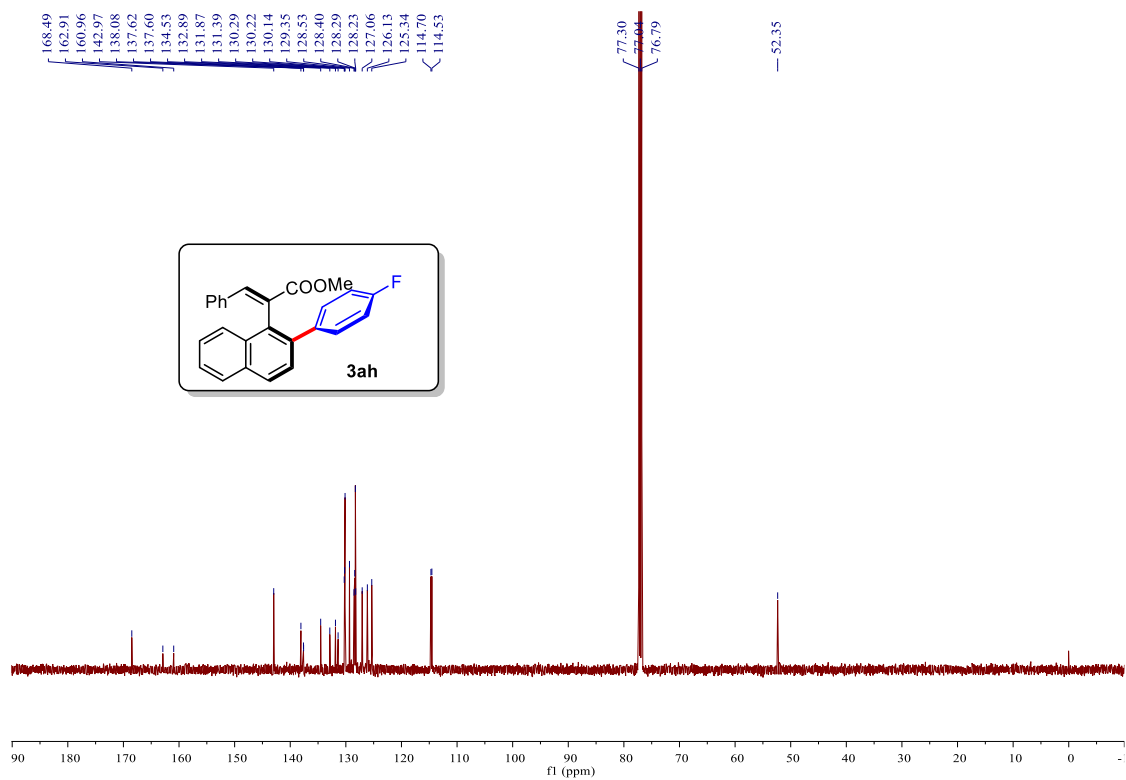




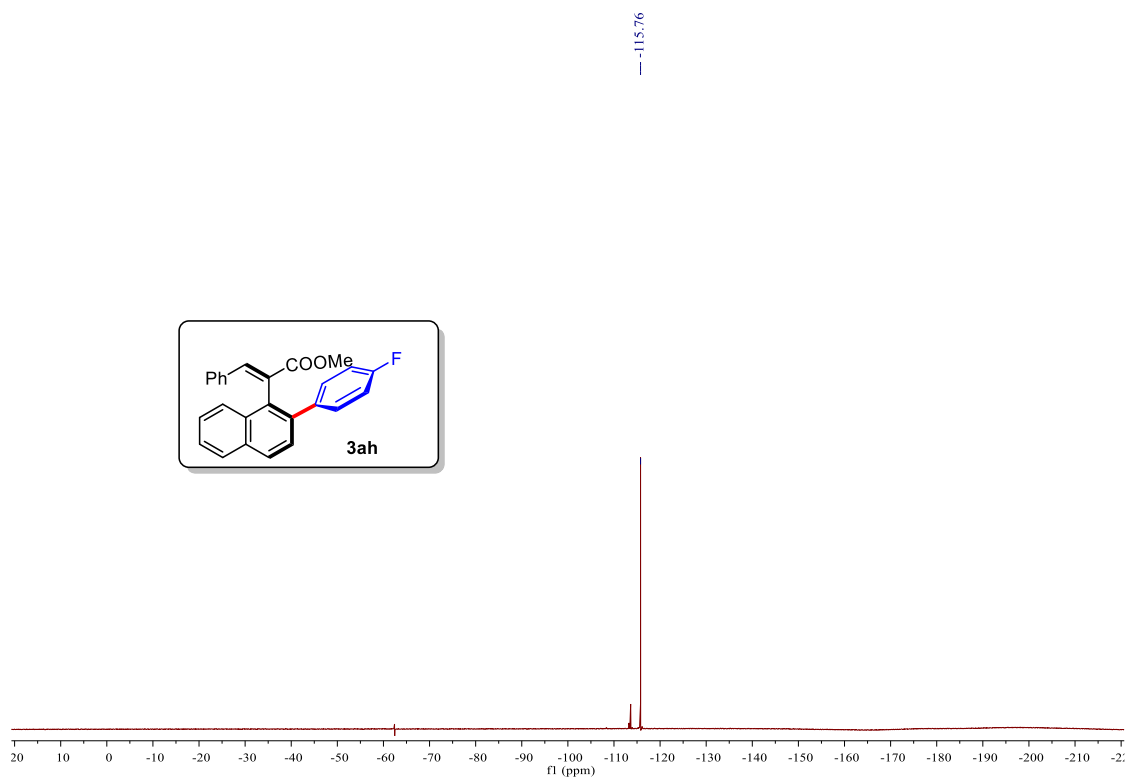
<sup>13</sup>C NMR Spectrum of **3ag** (CDCl<sub>3</sub>, 126 MHz)



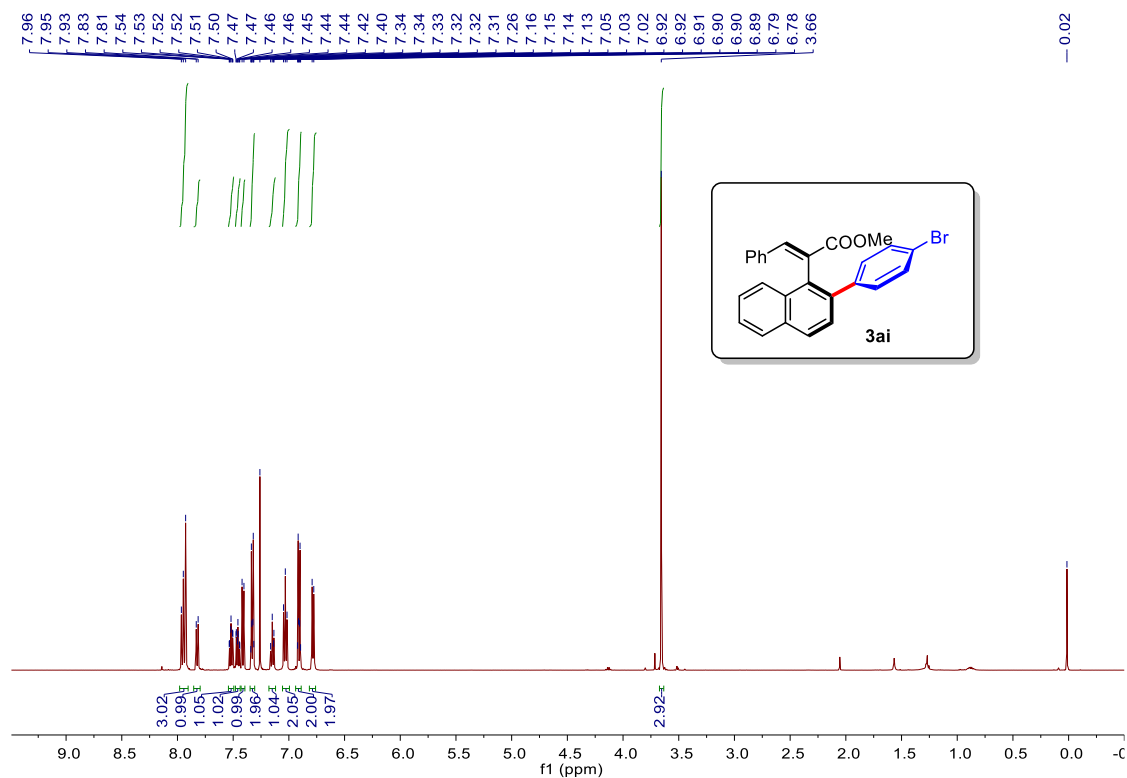
<sup>1</sup>H NMR Spectrum of **3ah** (CDCl<sub>3</sub>, 500 MHz)



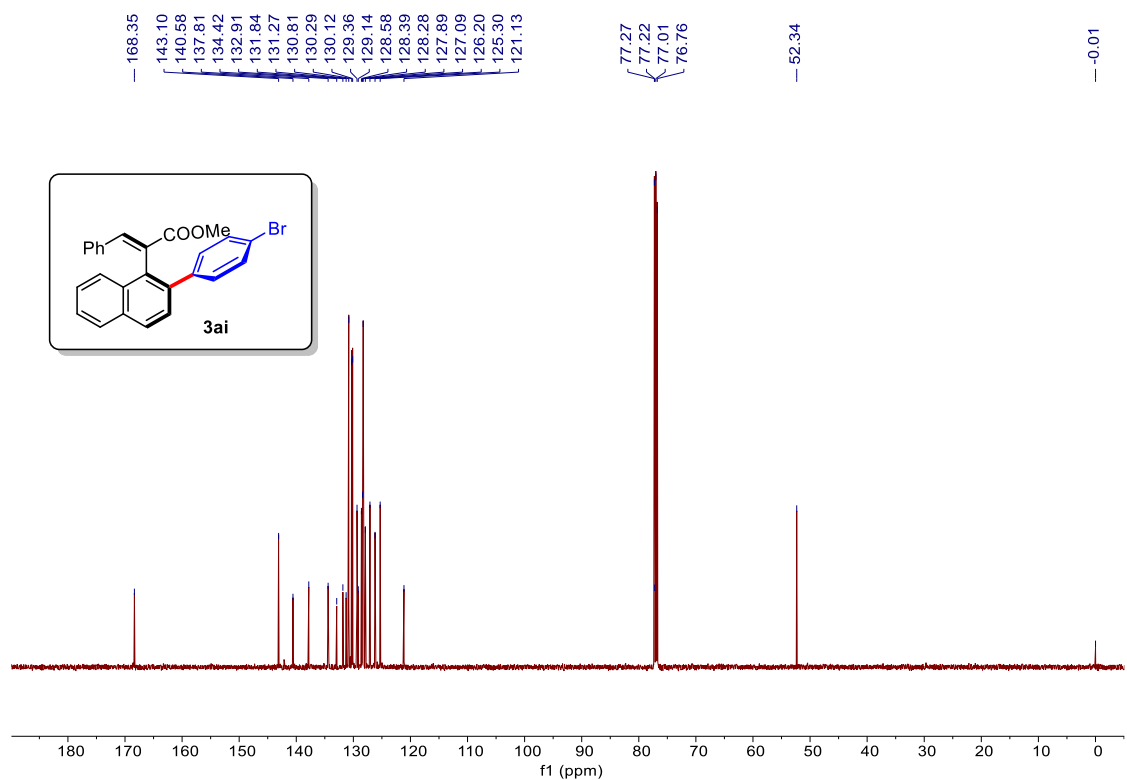
$^{13}\text{C}$  NMR Spectrum of **3ah** ( $\text{CDCl}_3$ , 126 MHz)



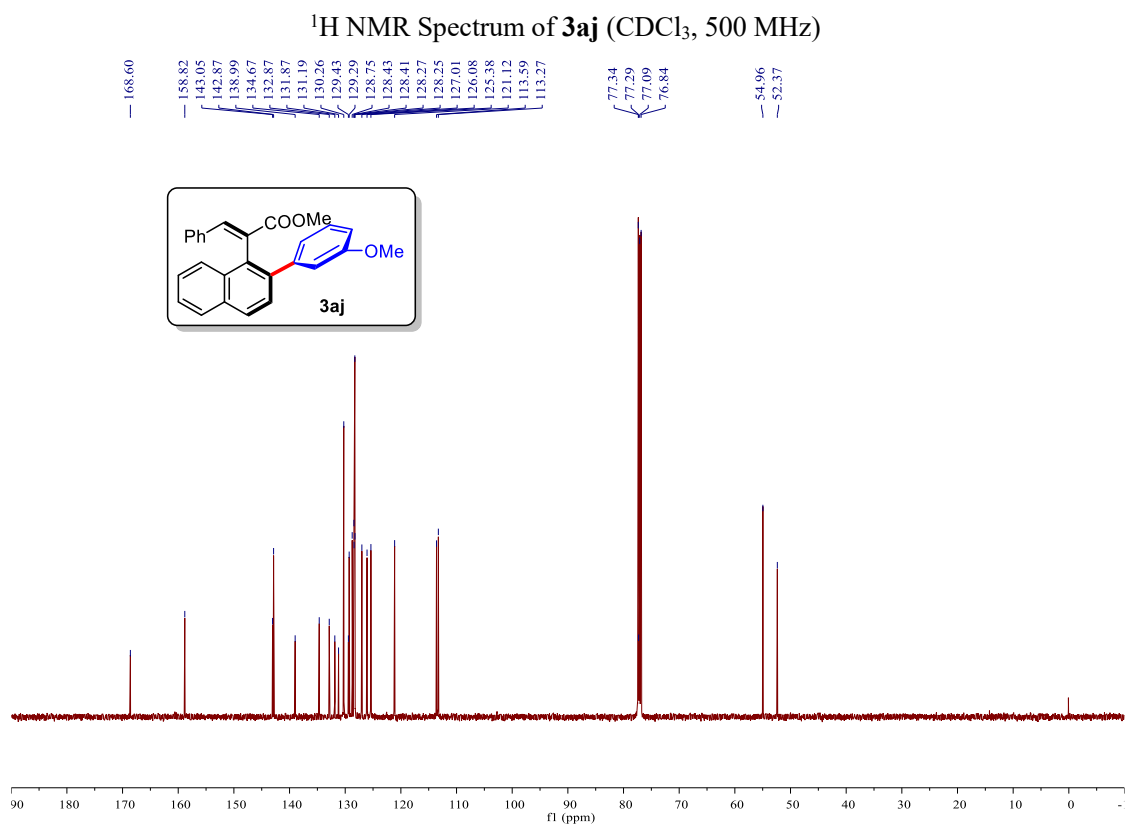
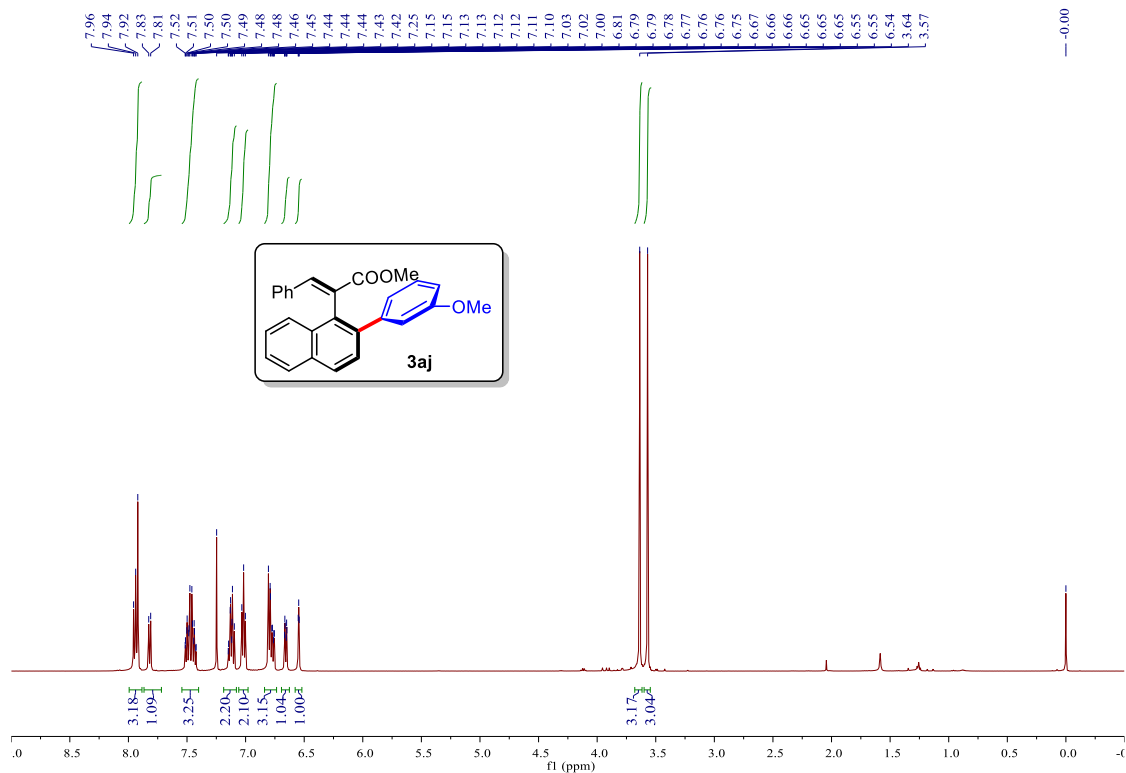
$^{19}\text{F}$  NMR Spectrum of **3ah** ( $\text{CDCl}_3$ , 126 MHz)



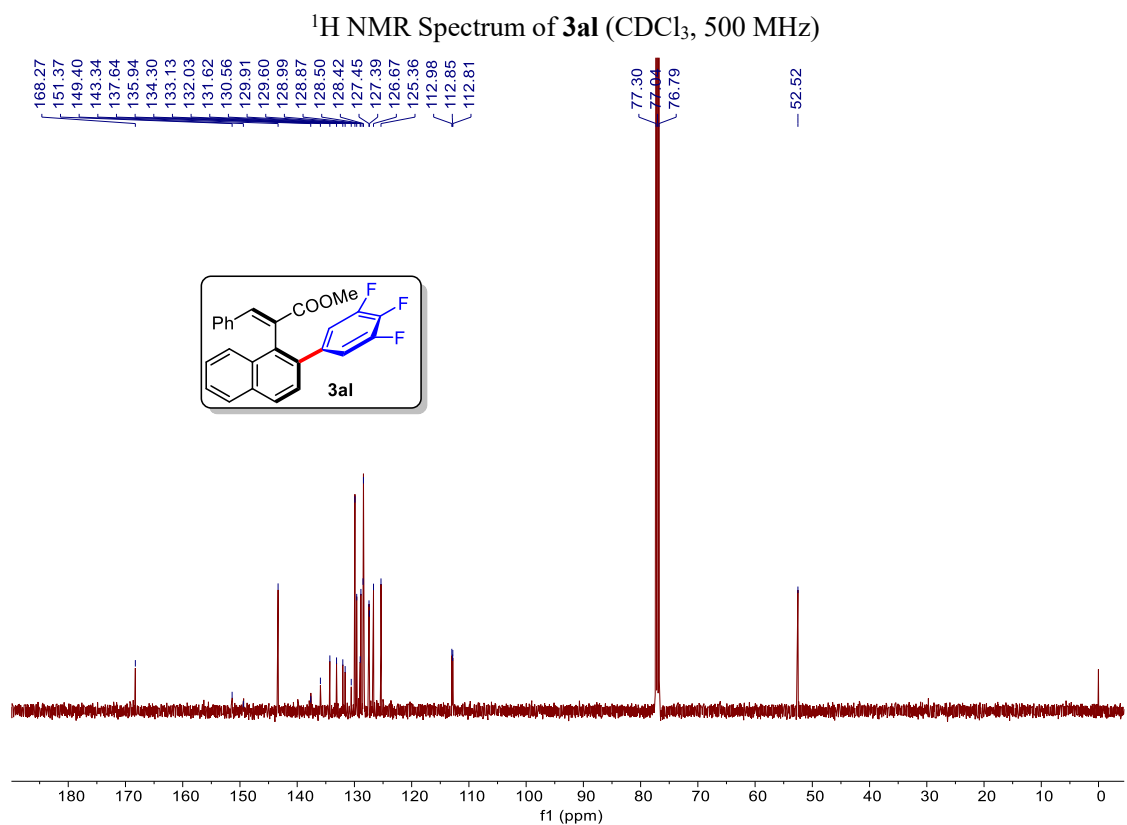
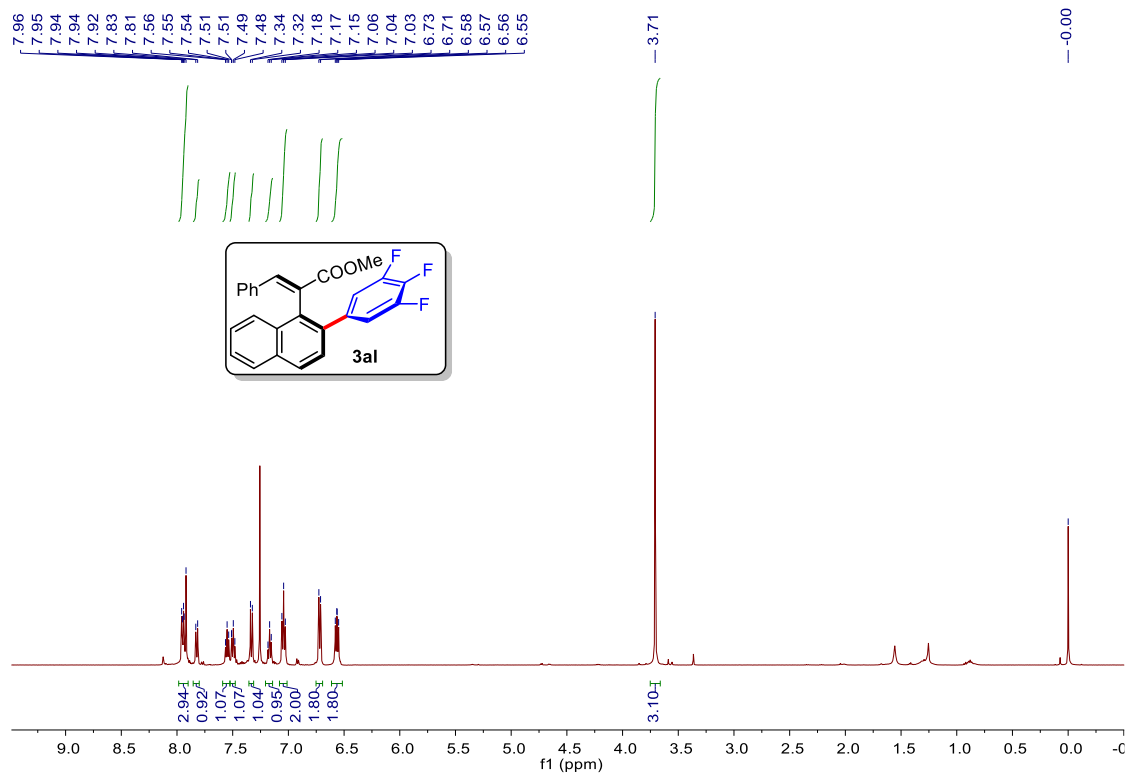
**<sup>1</sup>H NMR Spectrum of 3ai (CDCl<sub>3</sub>, 500 MHz)**

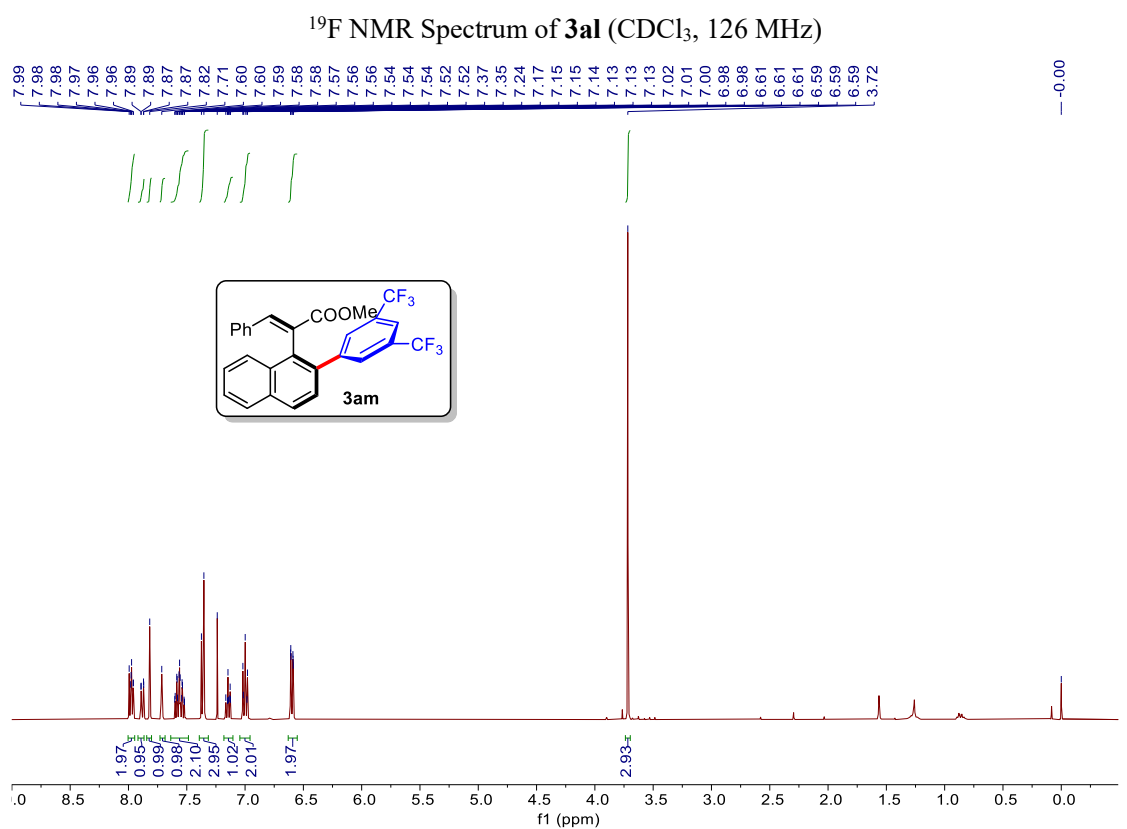
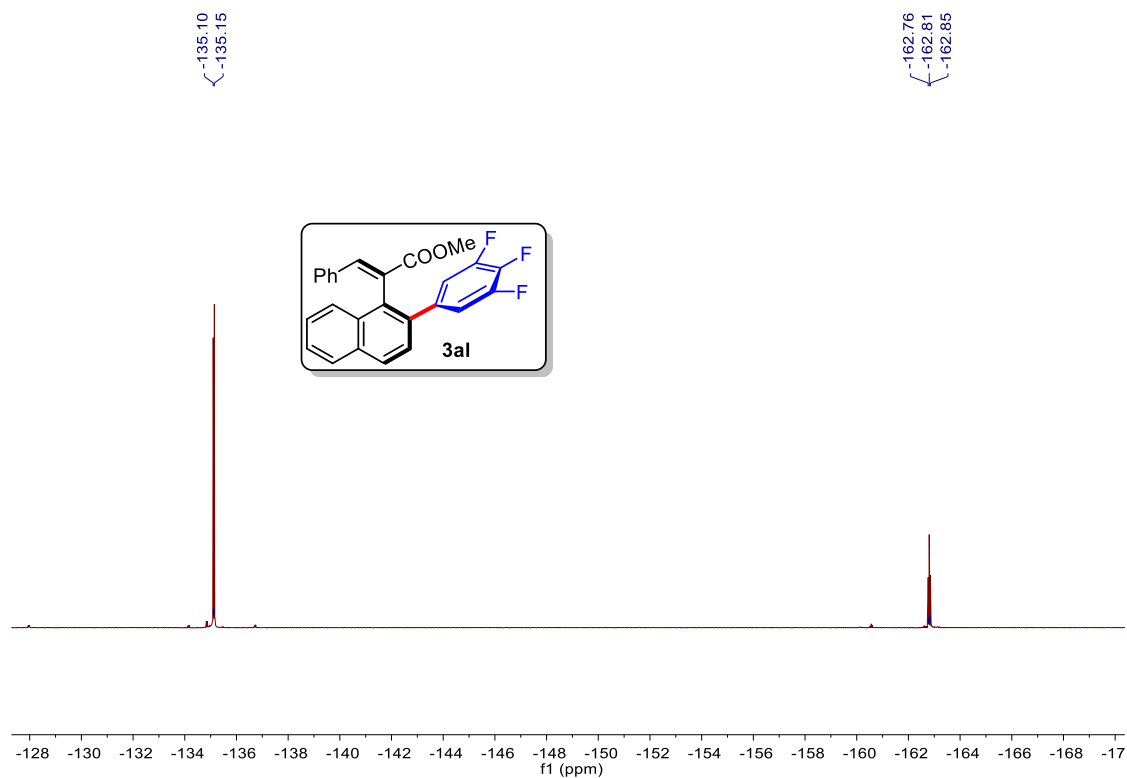


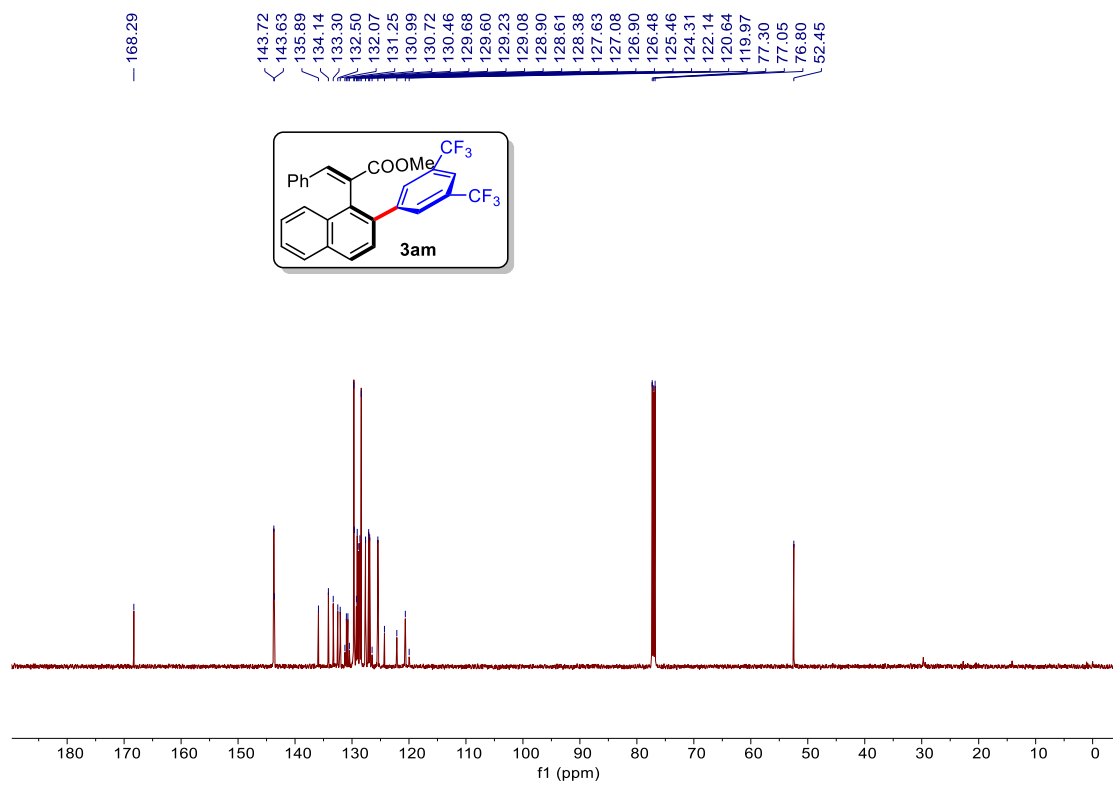
**<sup>13</sup>C NMR Spectrum of 3ai (CDCl<sub>3</sub>, 126 MHz)**



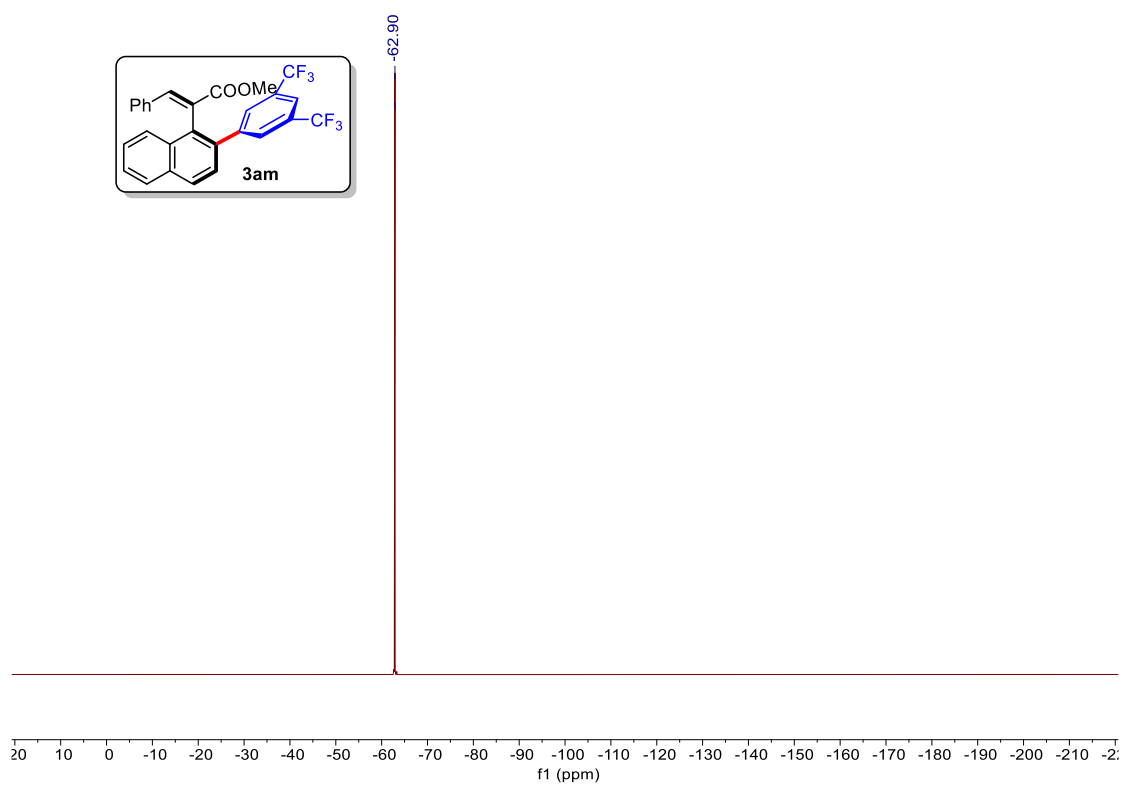






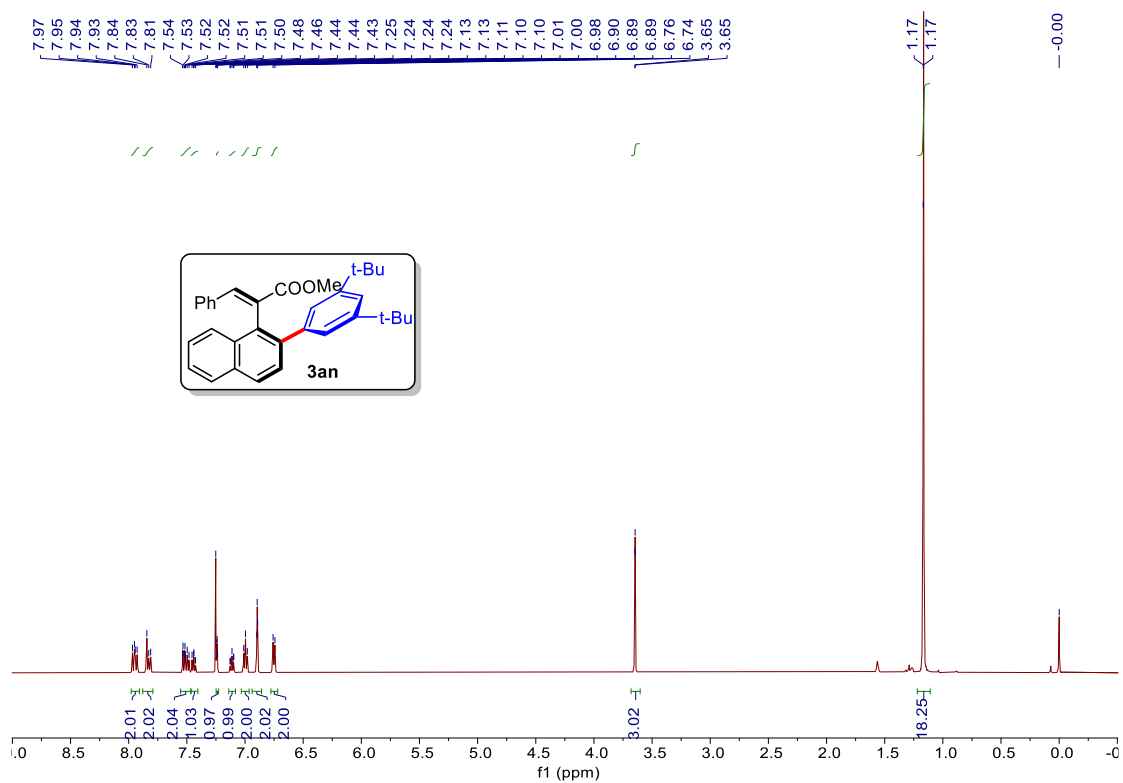


<sup>13</sup>C NMR Spectrum of **3am** (CDCl<sub>3</sub>, 126 MHz)

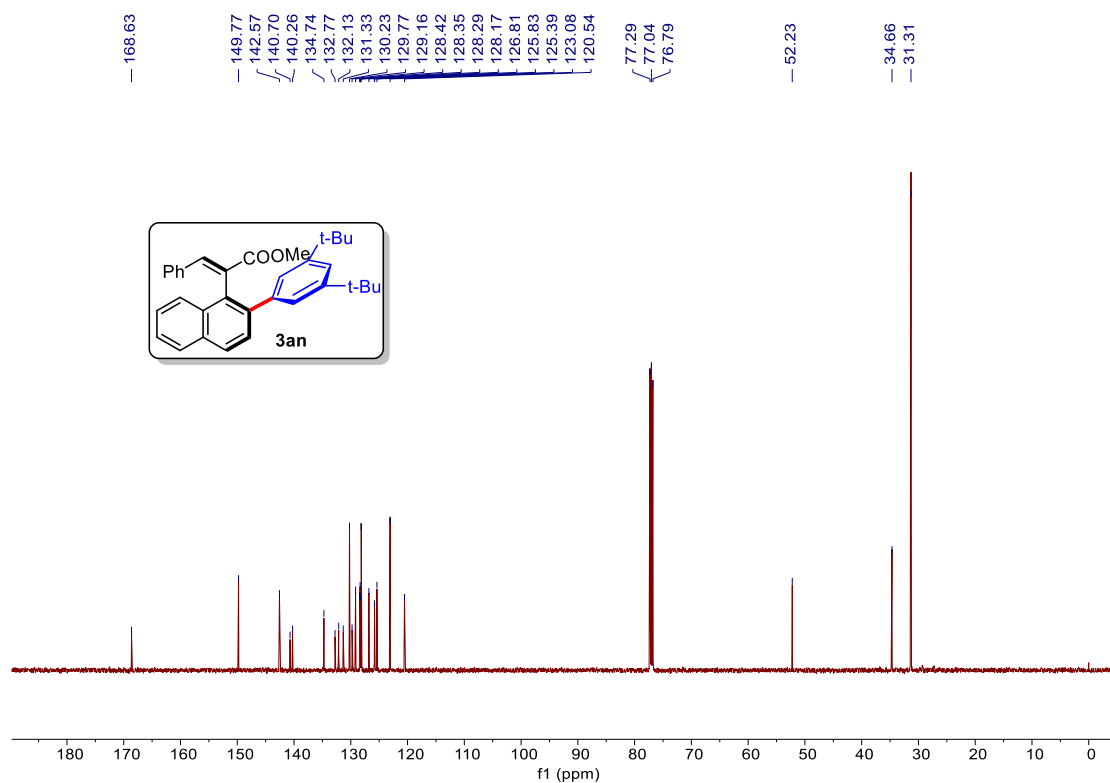


<sup>19</sup>F NMR Spectrum of **3am** (CDCl<sub>3</sub>, 126 MHz)

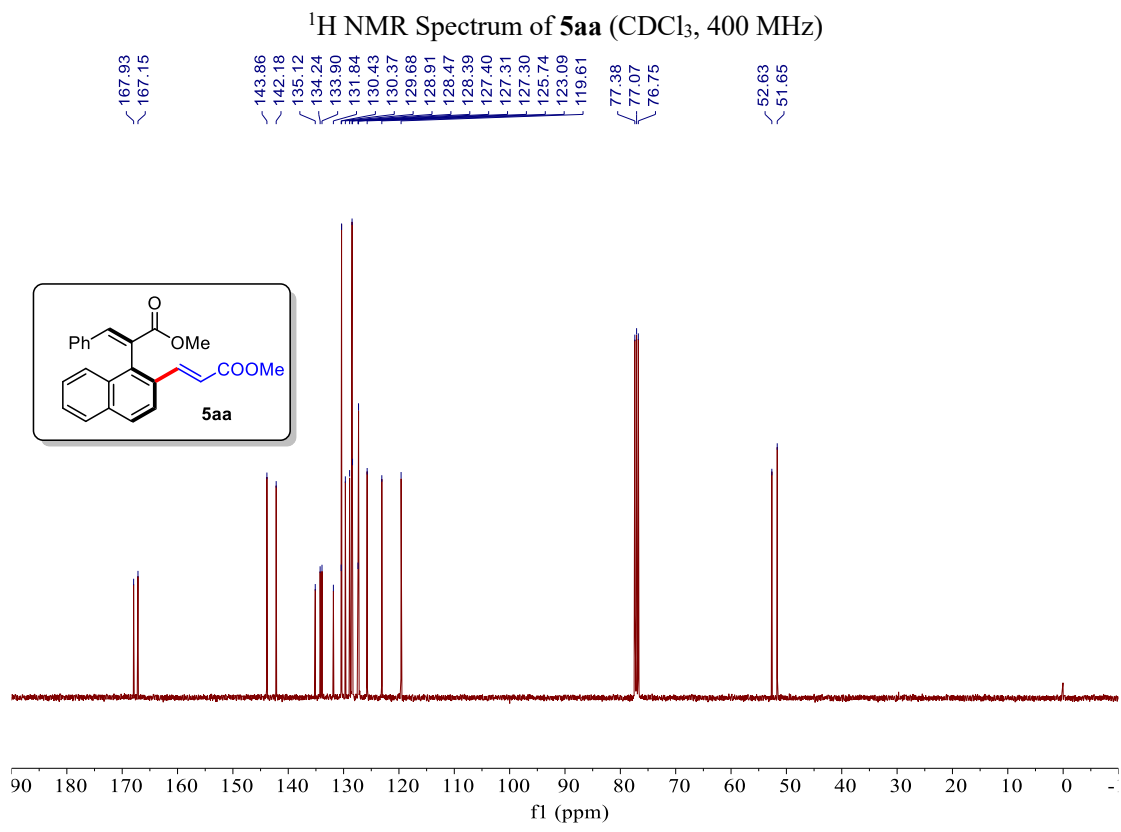
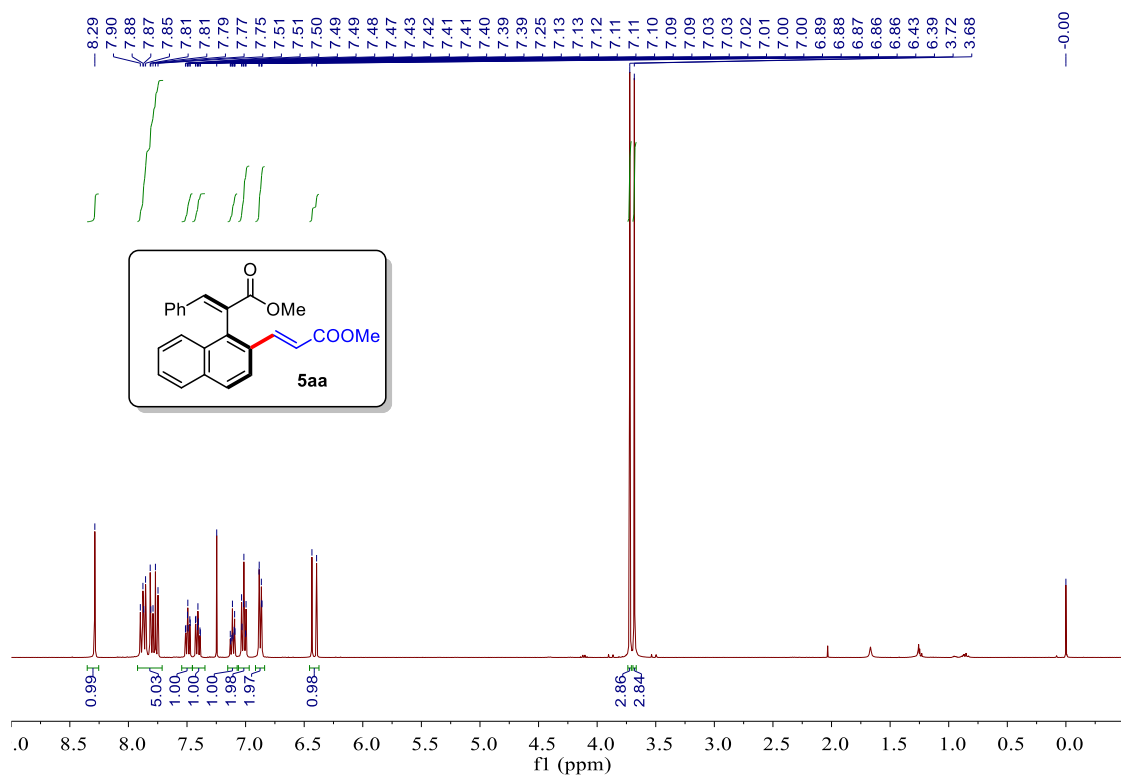


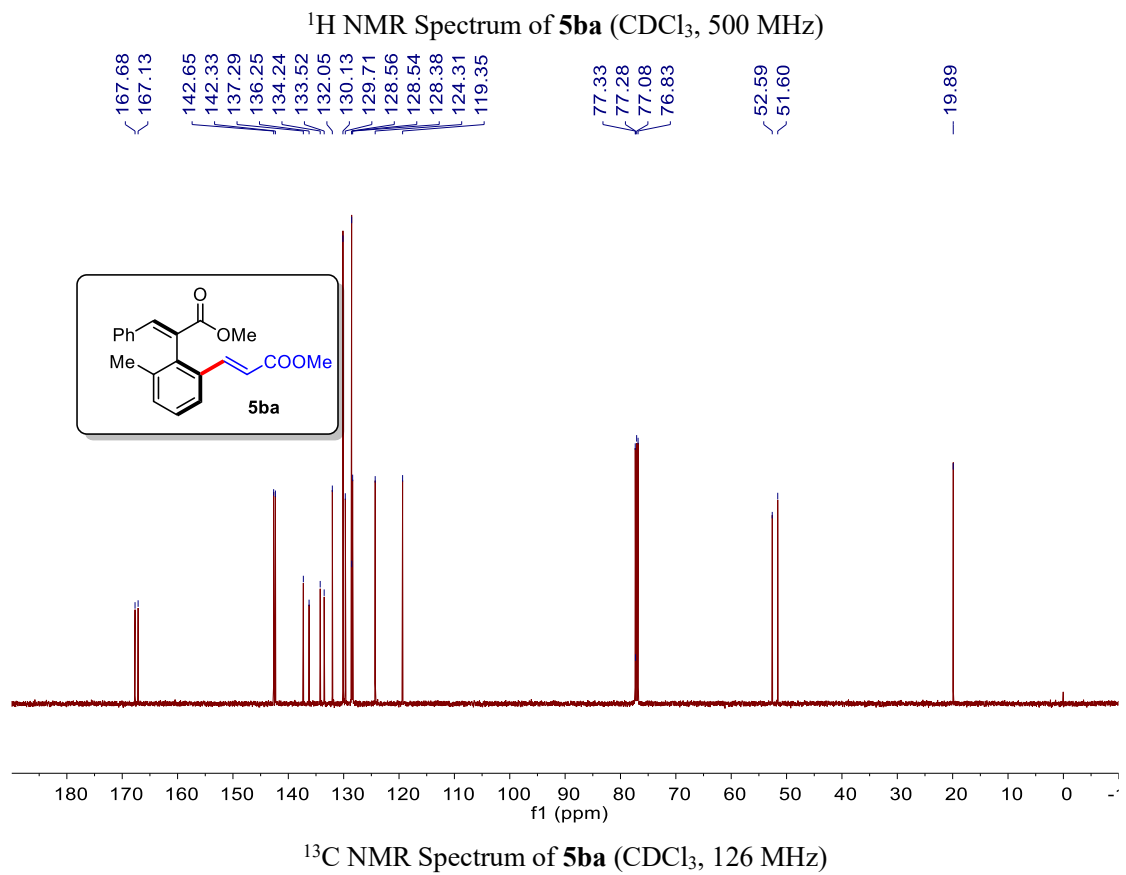
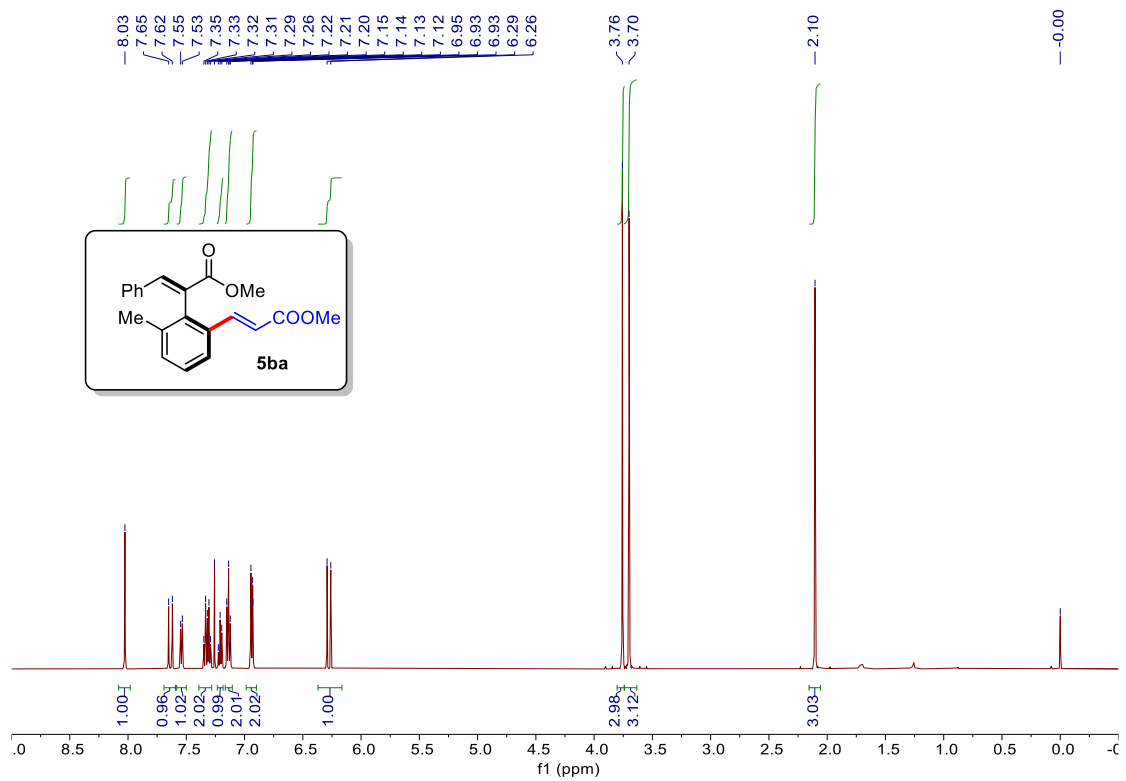


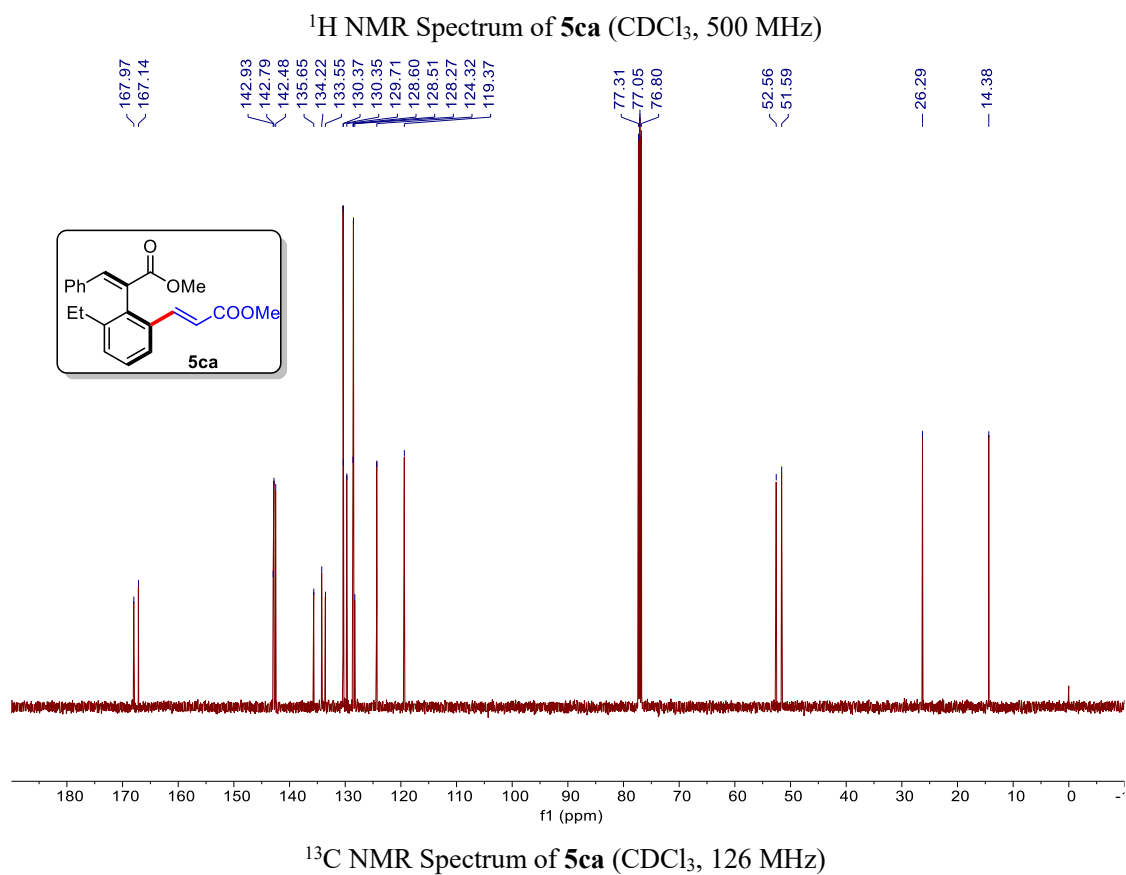
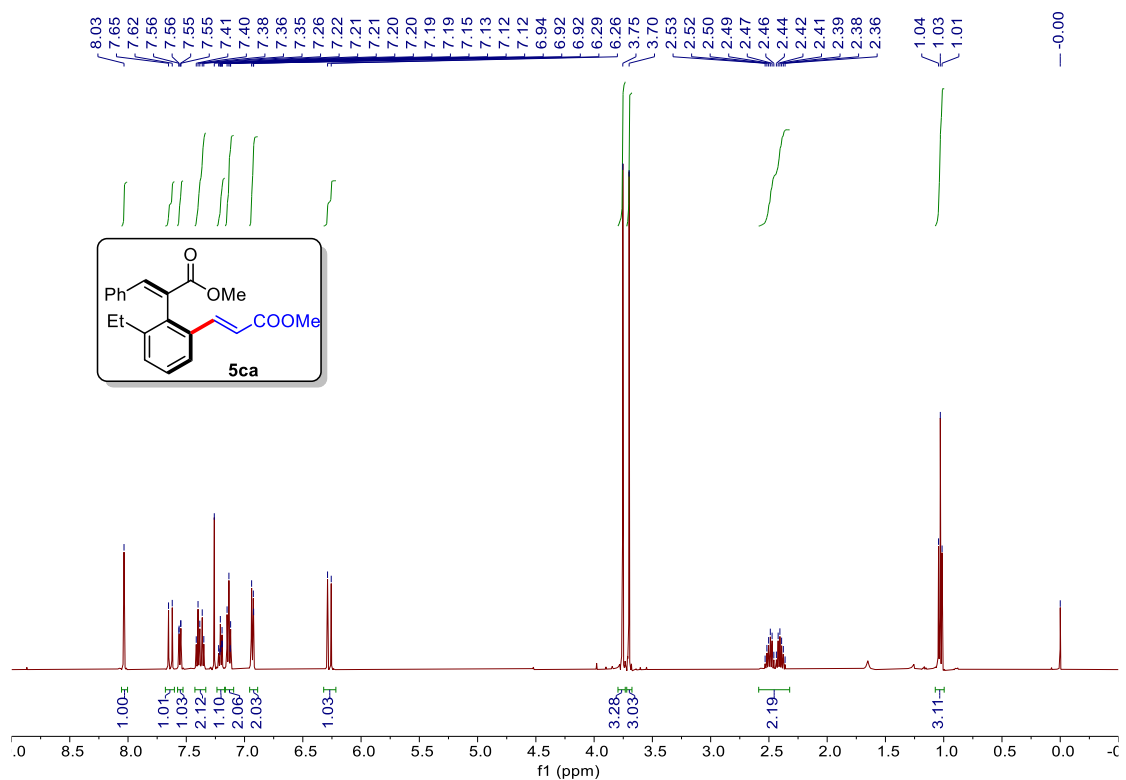
**<sup>1</sup>H NMR Spectrum of 3an (CDCl<sub>3</sub>, 500 MHz)**

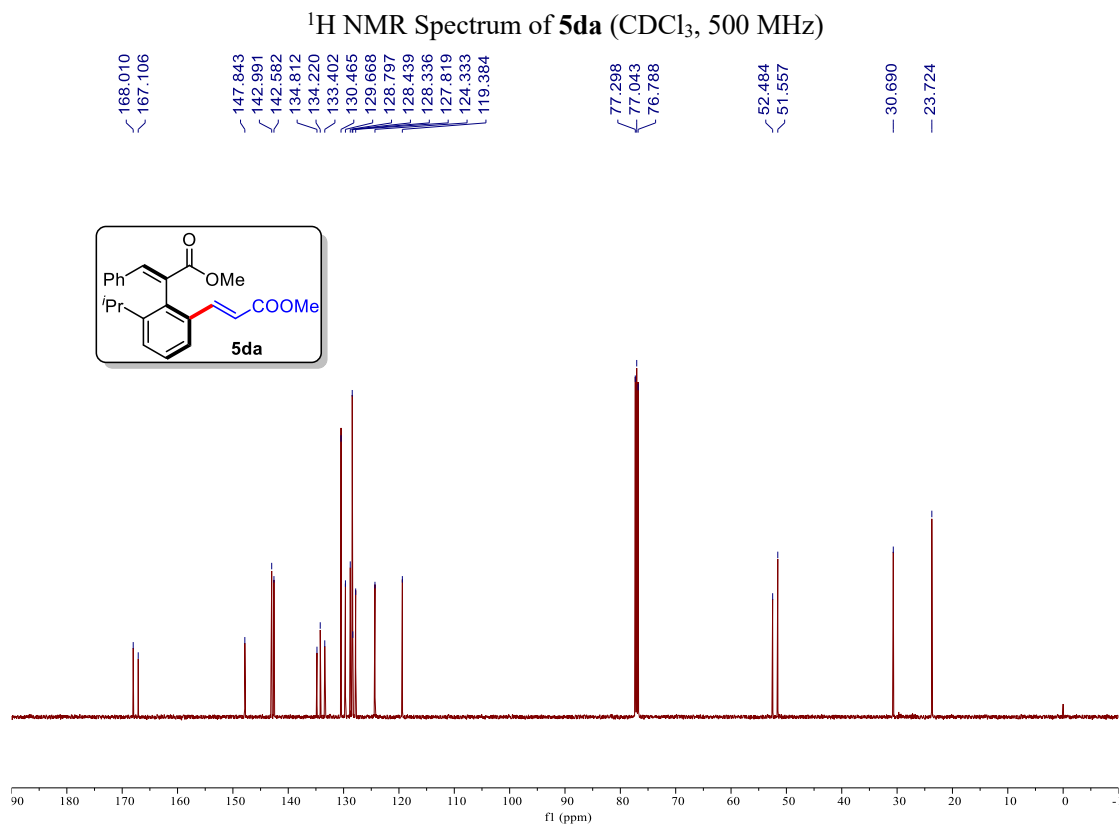
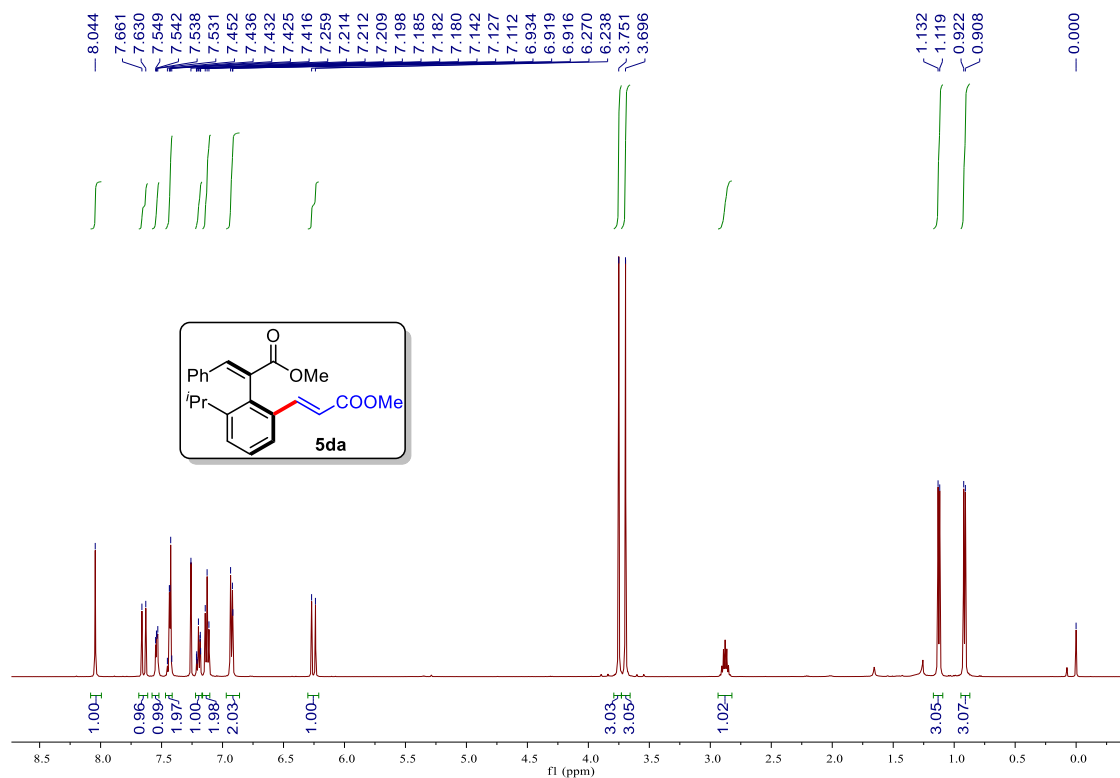


**<sup>13</sup>C NMR Spectrum of 3an (CDCl<sub>3</sub>, 126 MHz)**

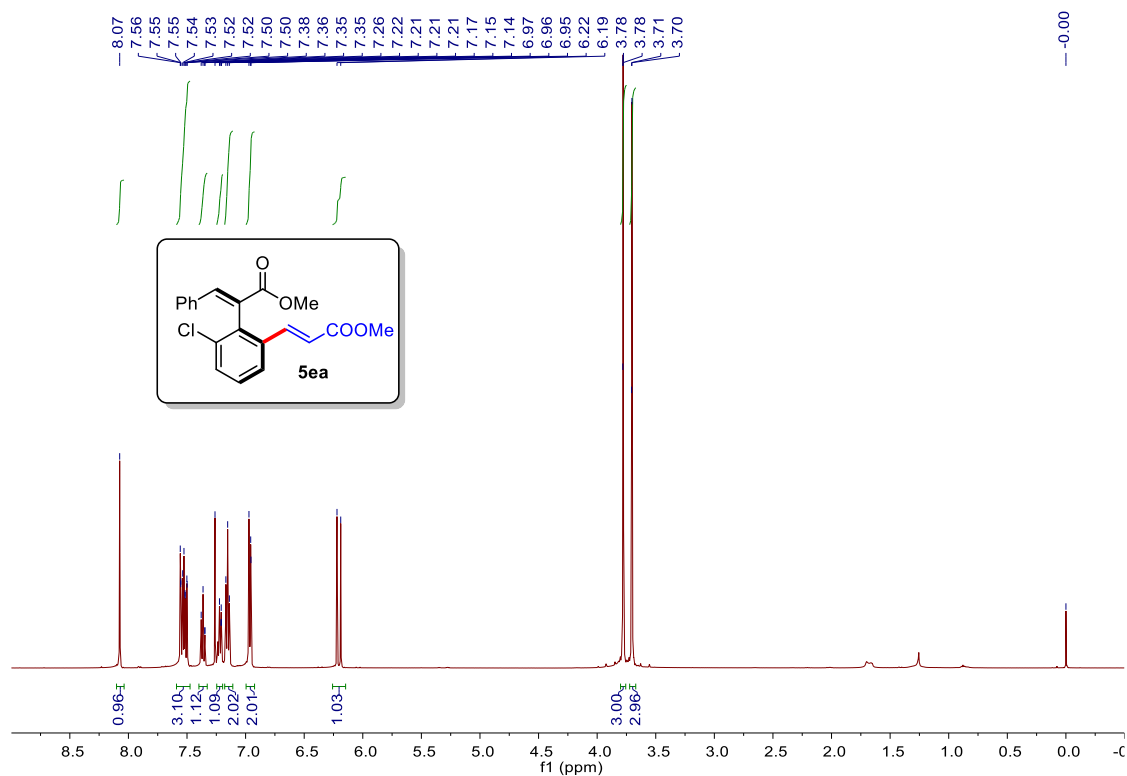




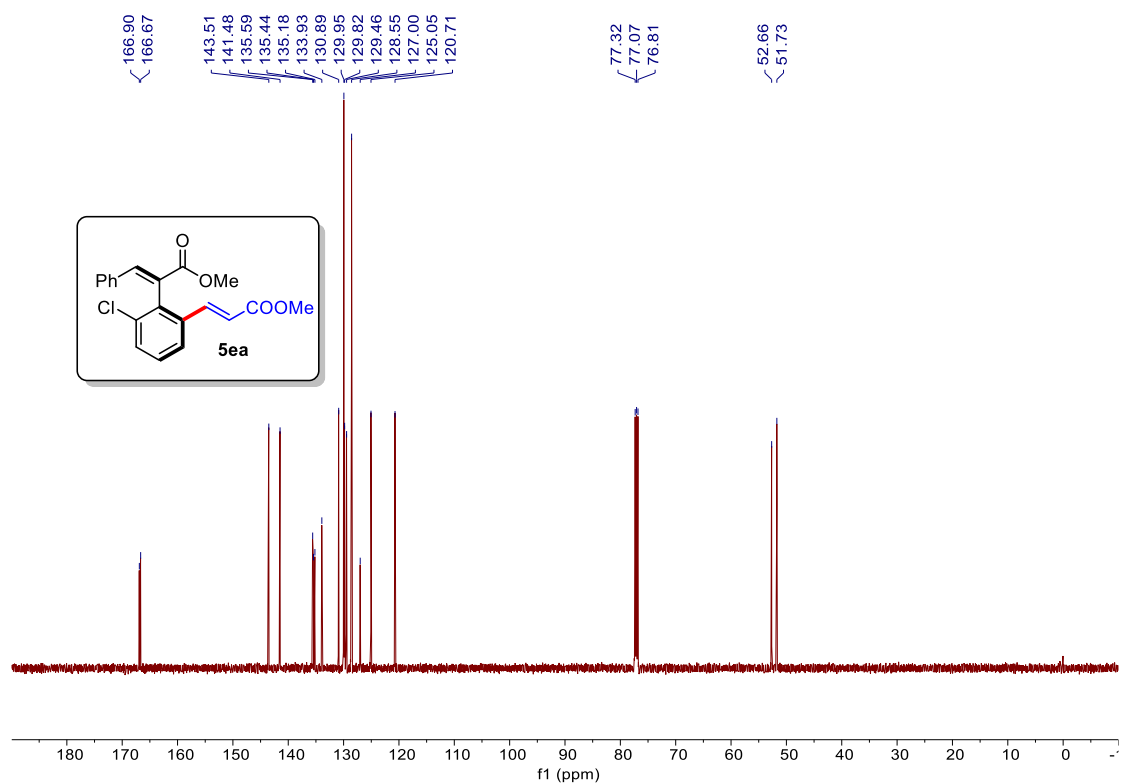




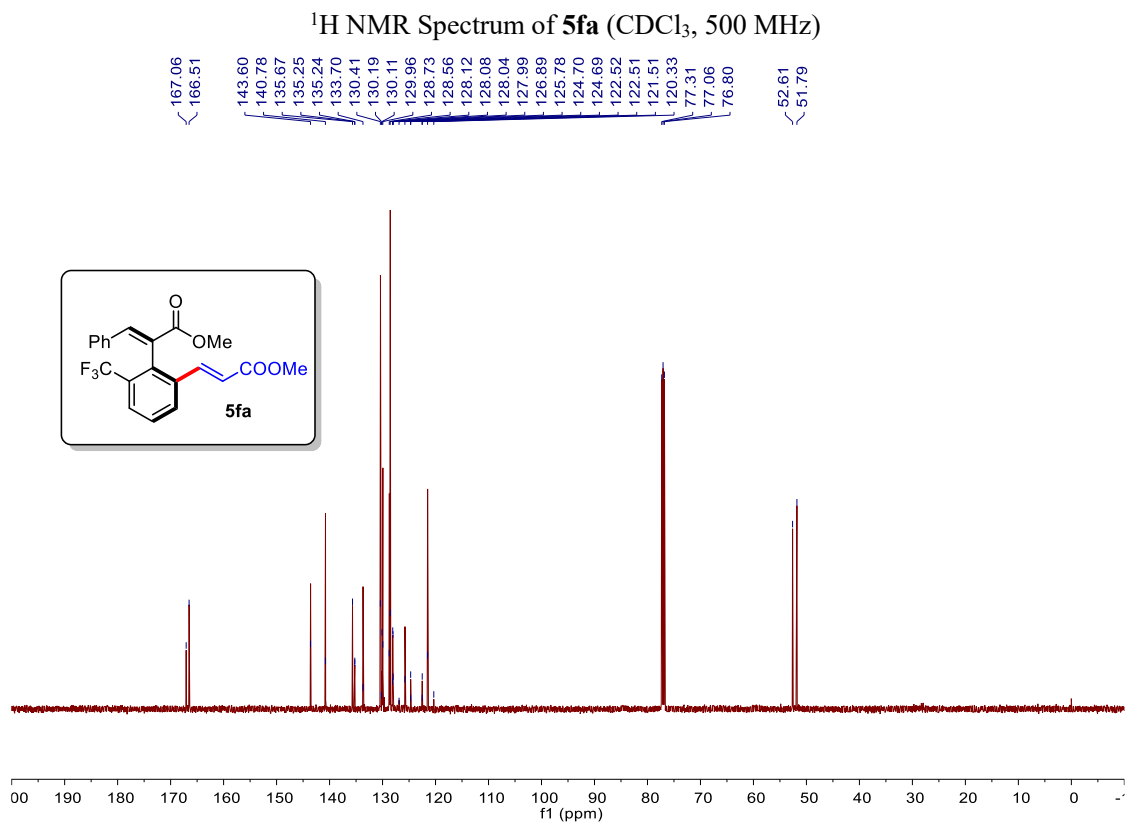
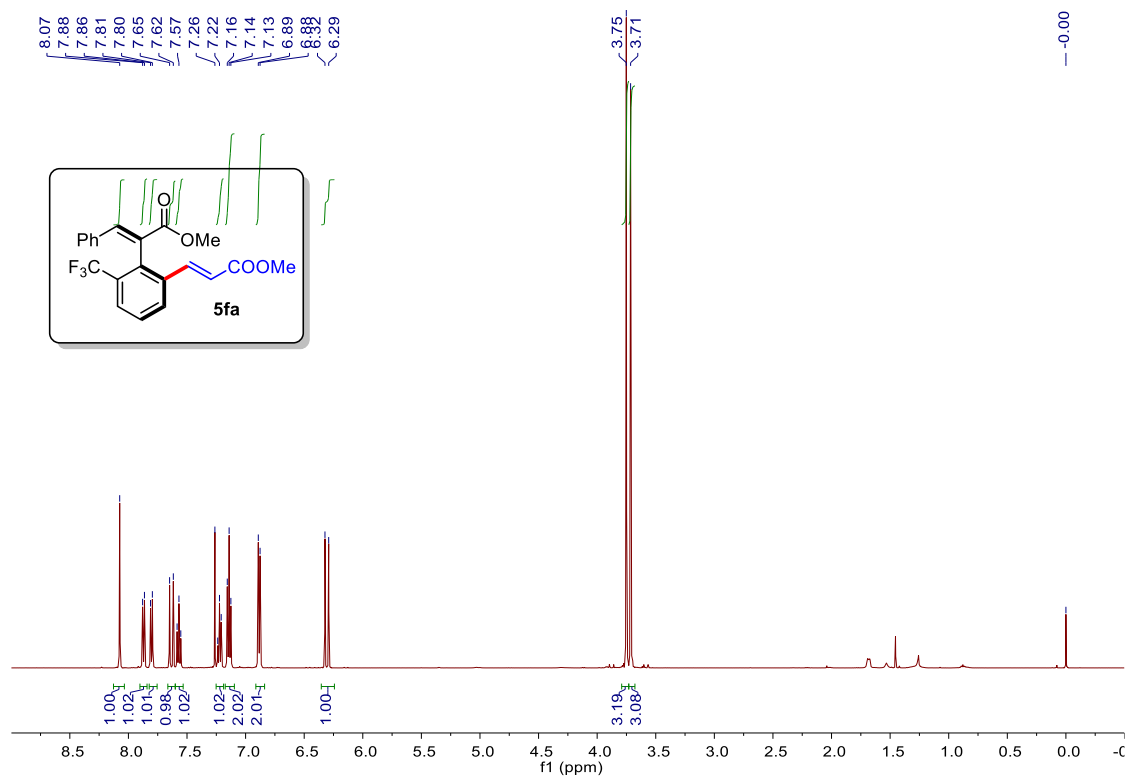
**<sup>13</sup>C NMR Spectrum of 5da (CDCl<sub>3</sub>, 126 MHz)**

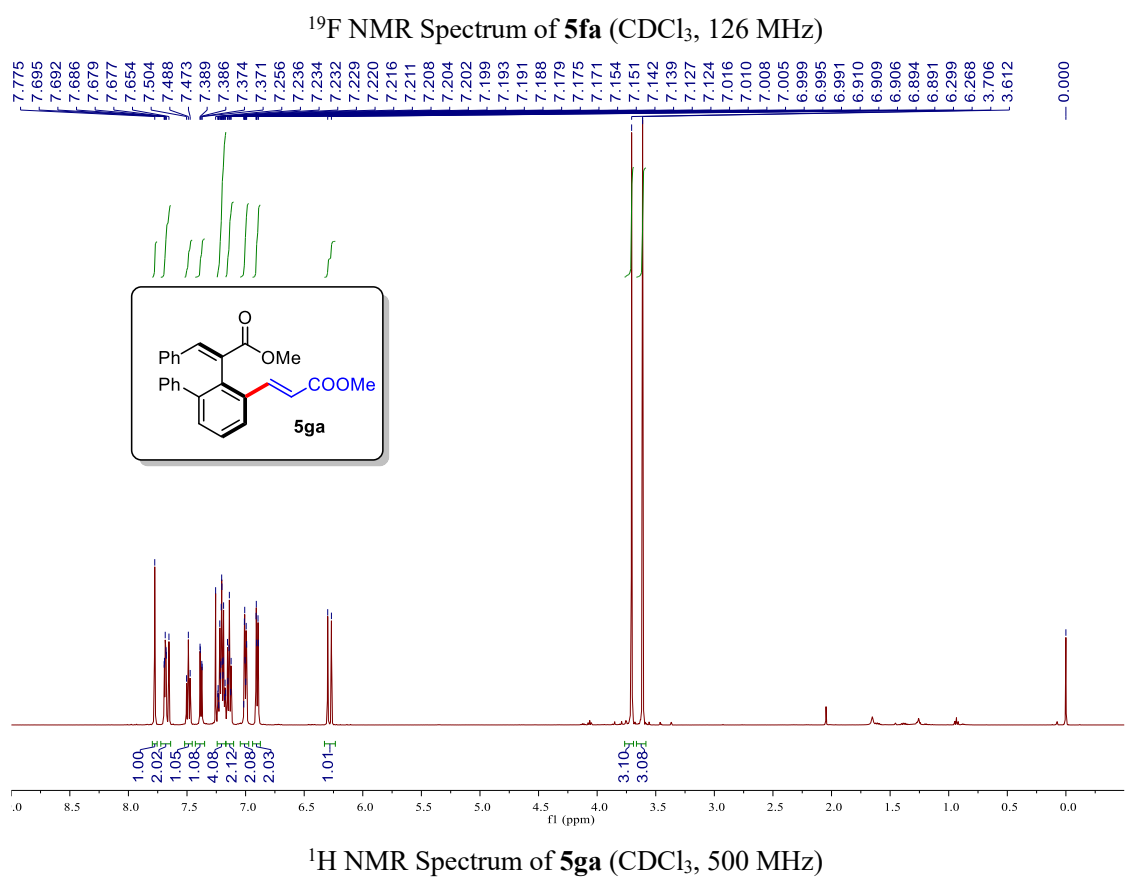
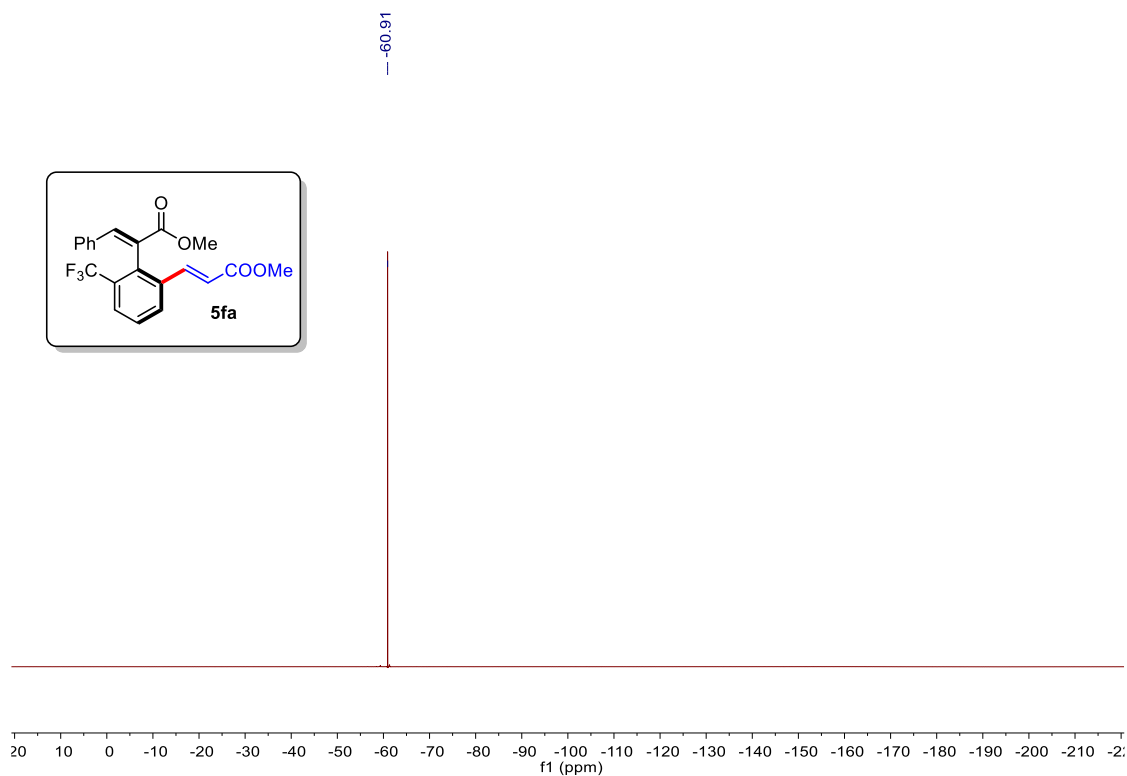


**<sup>1</sup>H NMR Spectrum of 5ea (CDCl<sub>3</sub>, 500 MHz)**

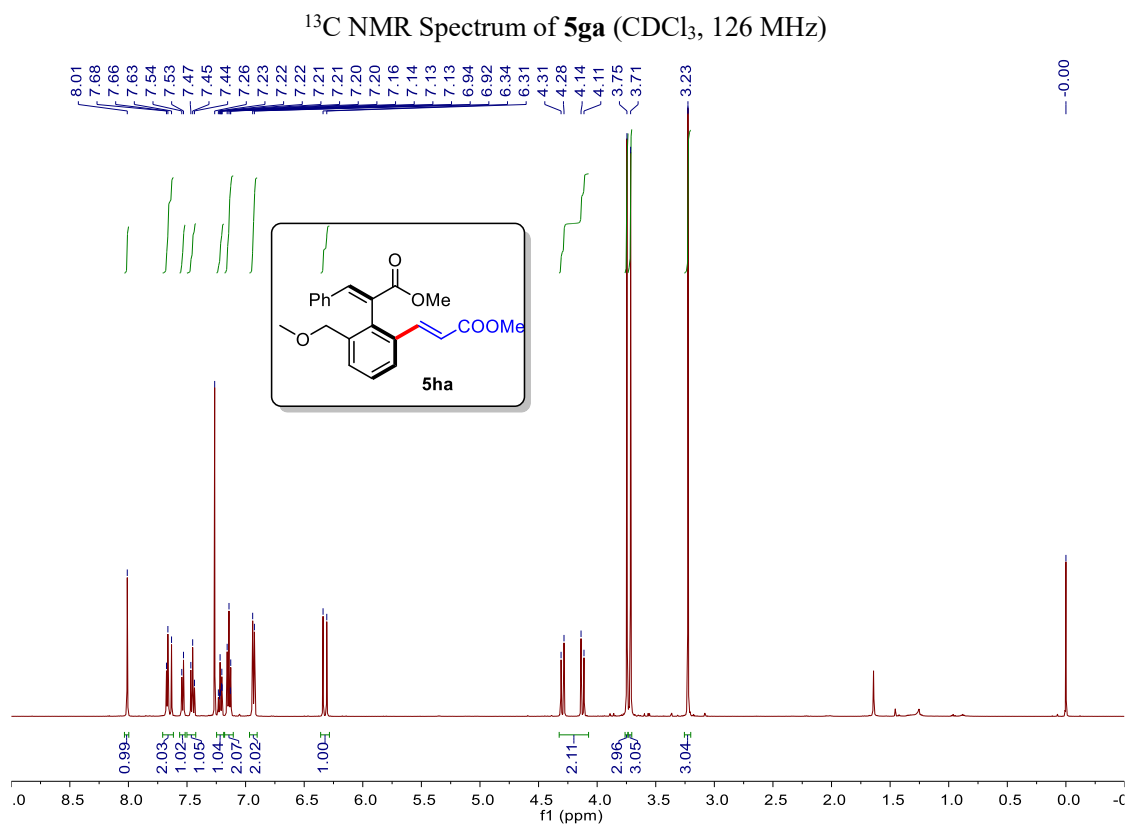
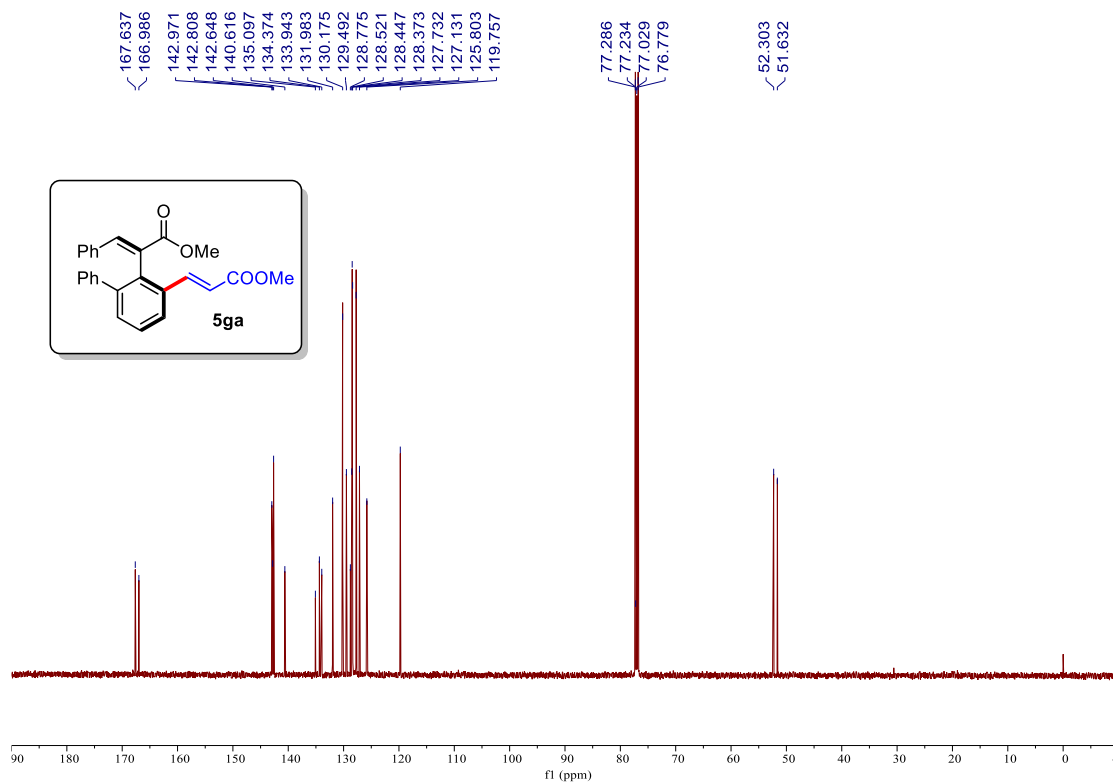


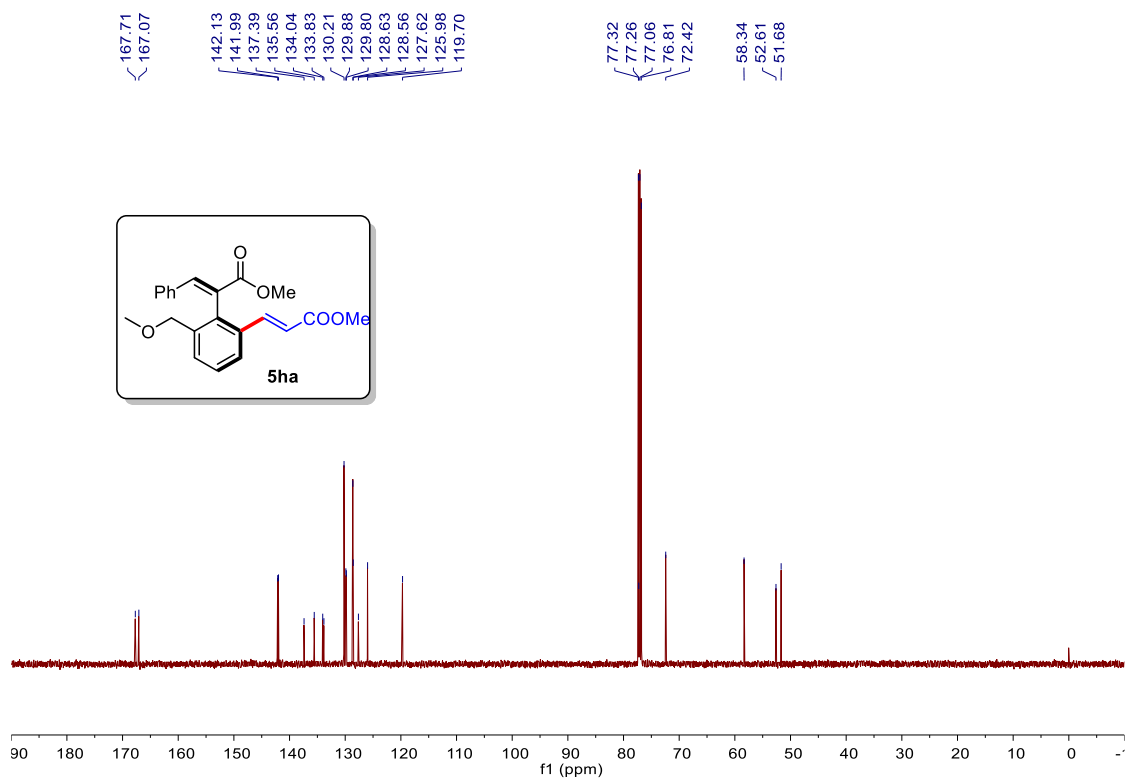
**<sup>13</sup>C NMR Spectrum of 5ea (CDCl<sub>3</sub>, 126 MHz)**



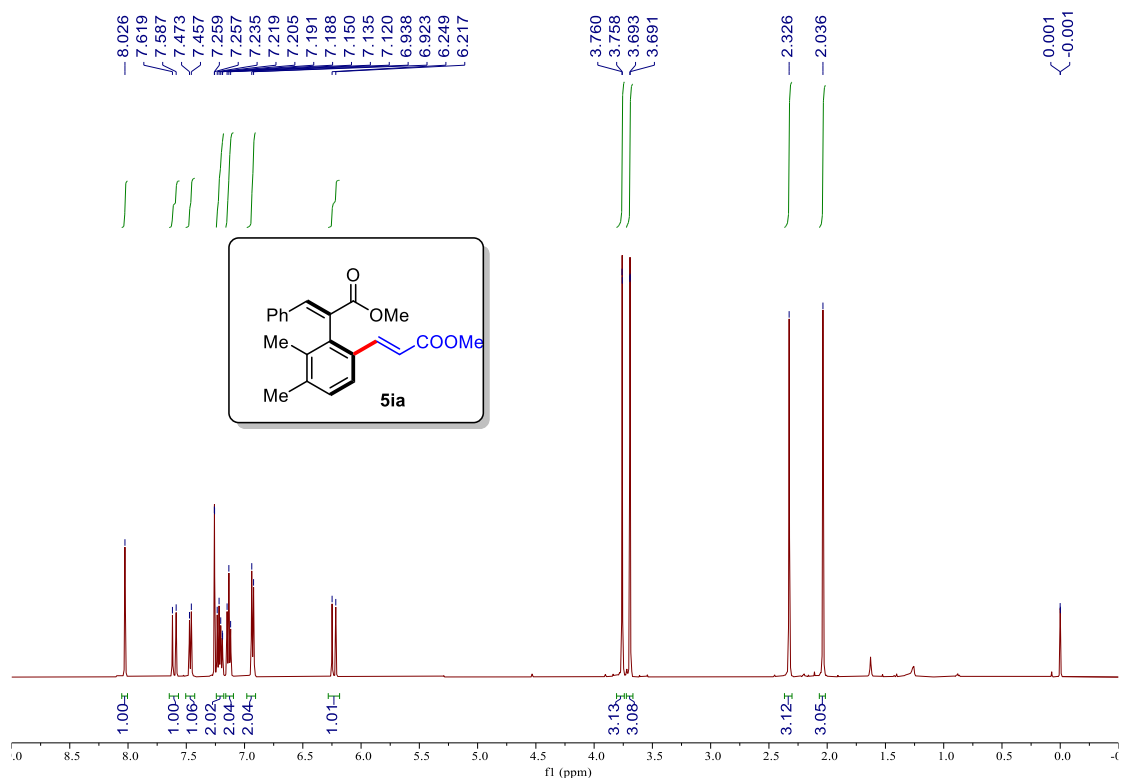




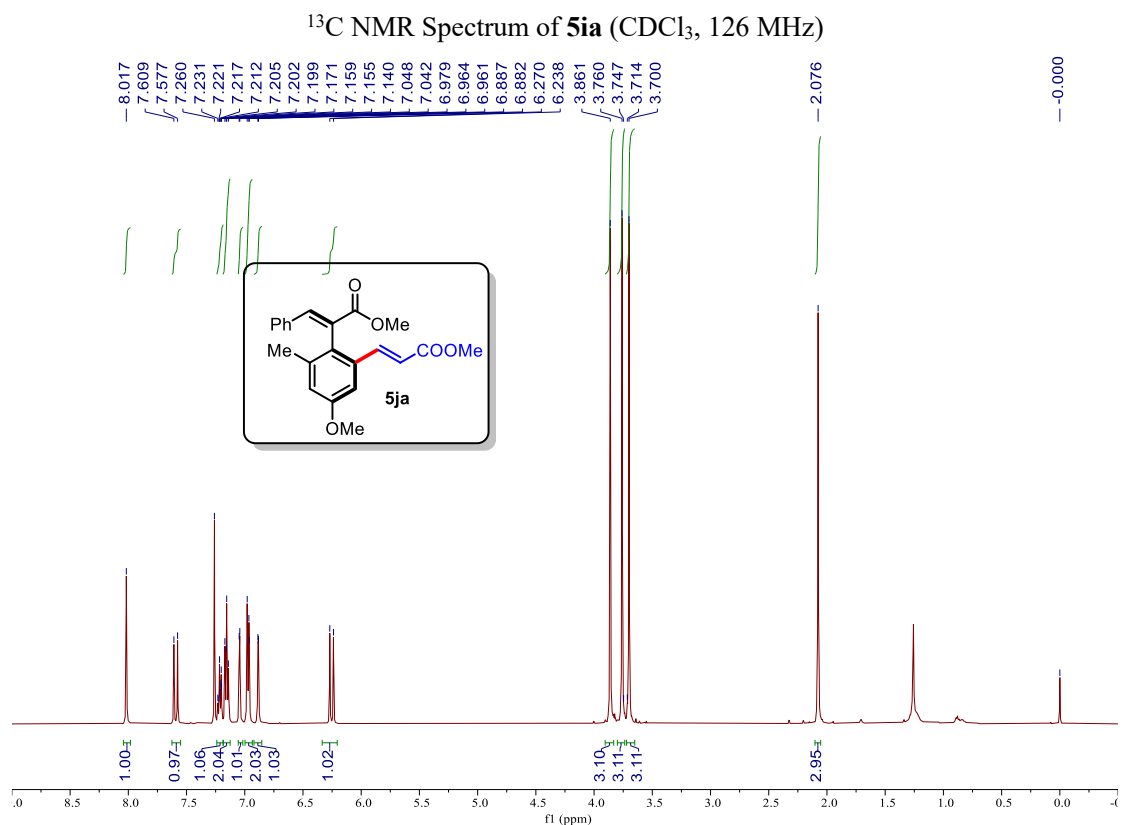
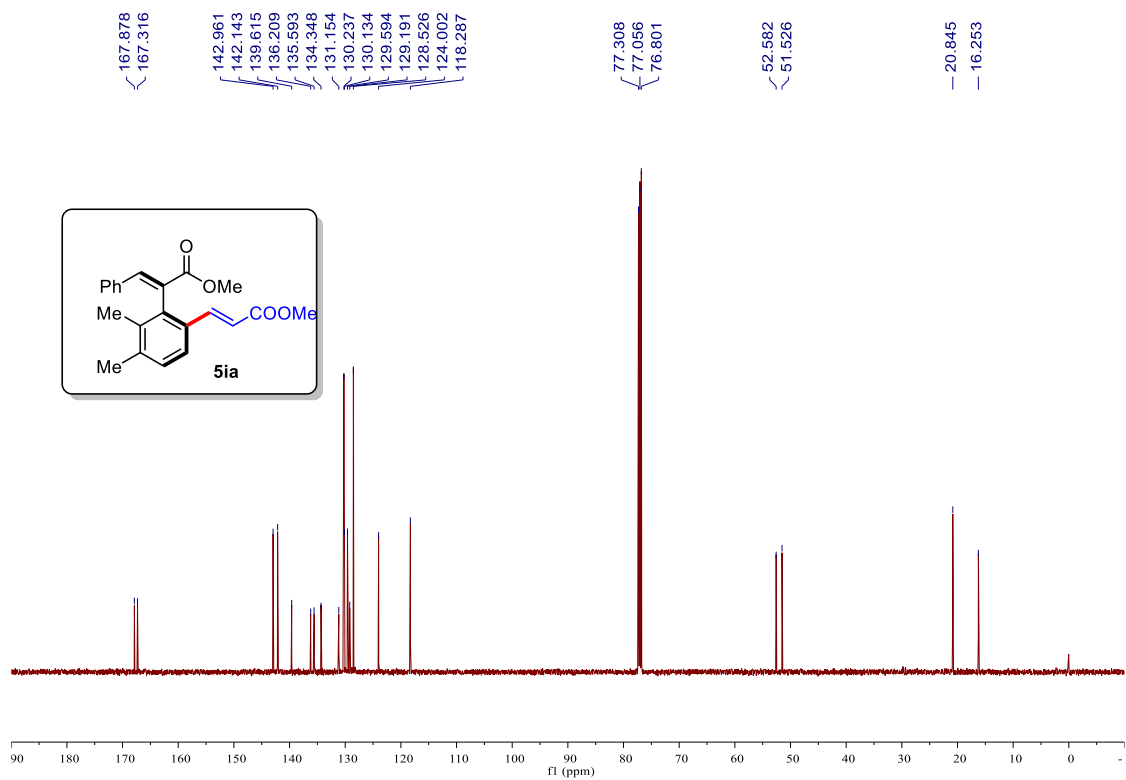


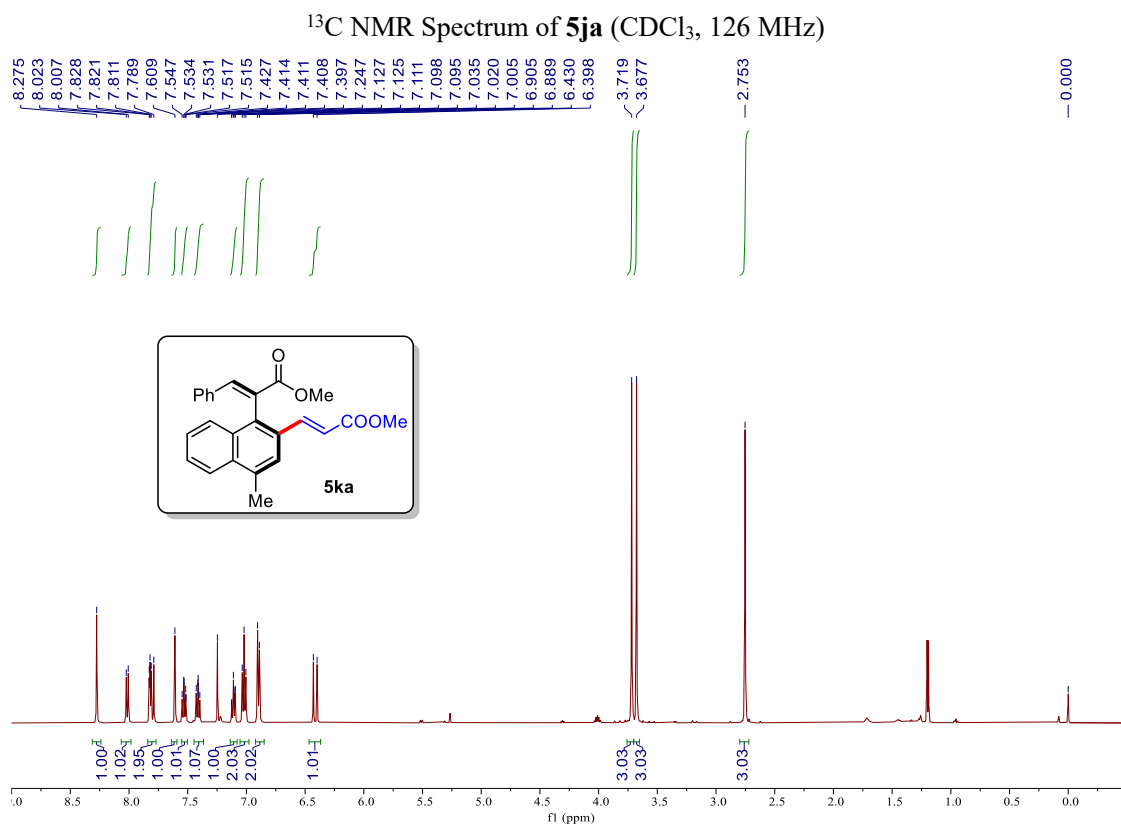
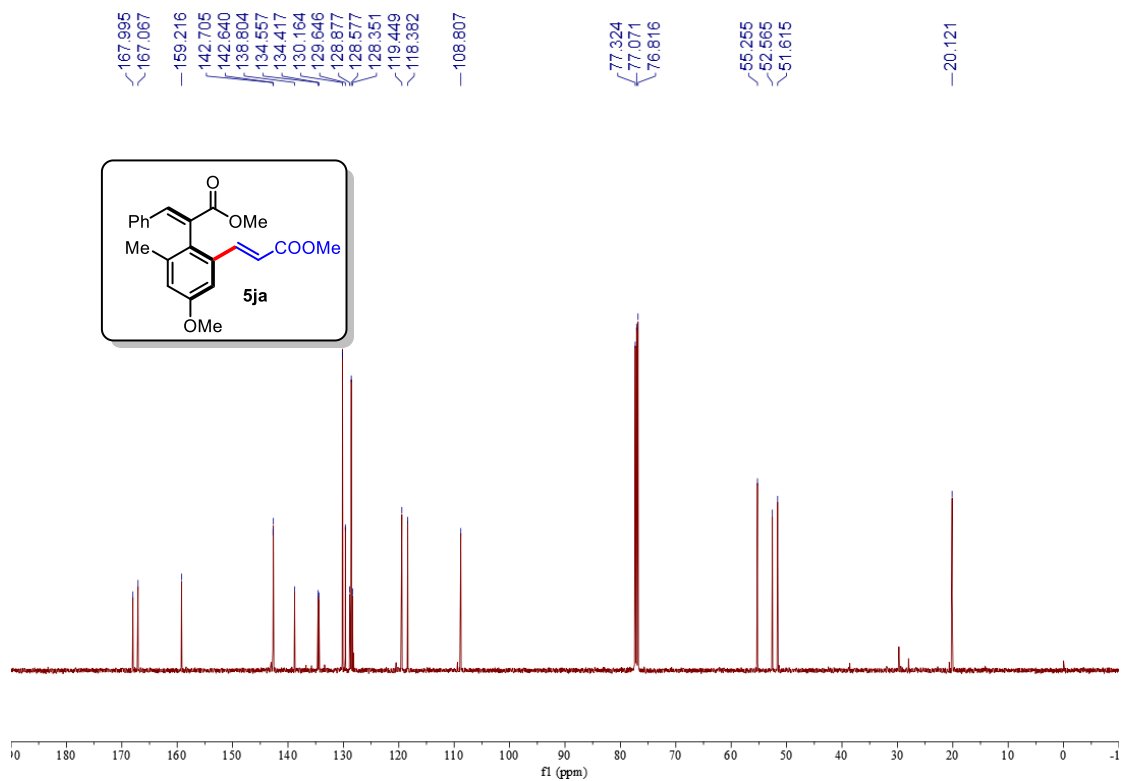


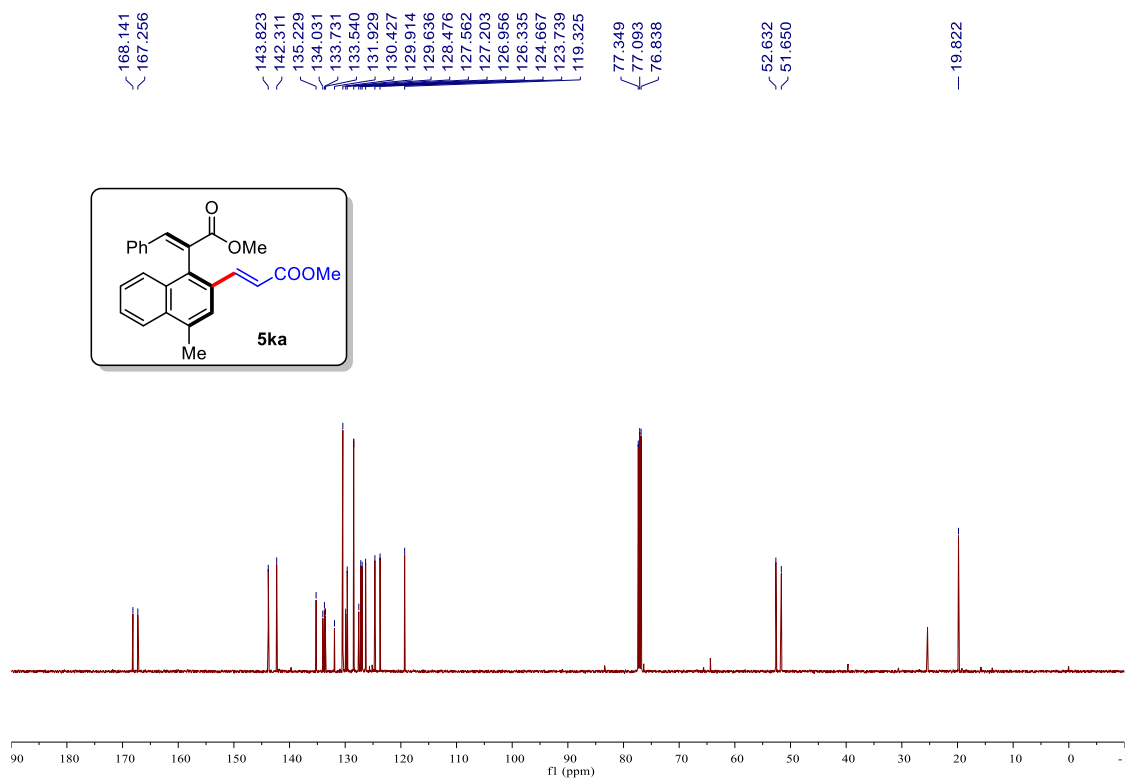
<sup>13</sup>C NMR Spectrum of **5ha** (CDCl<sub>3</sub>, 126 MHz)



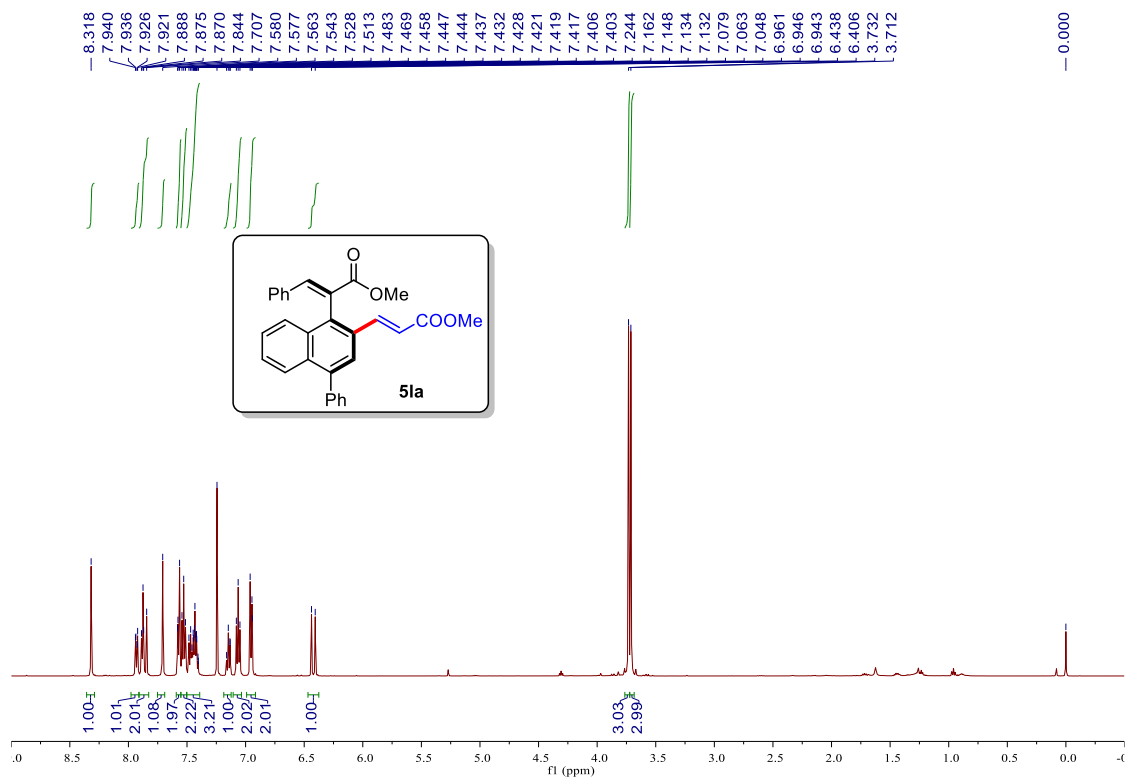
<sup>1</sup>H NMR Spectrum of **5ia** (CDCl<sub>3</sub>, 500 MHz)



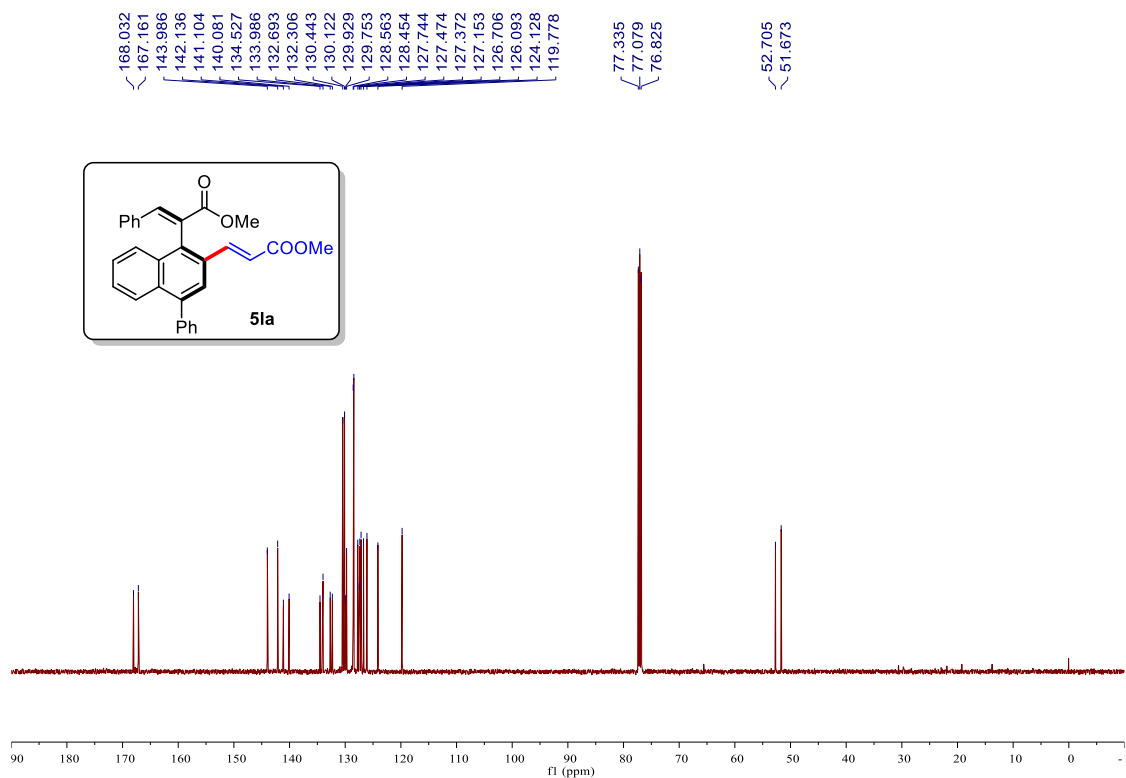




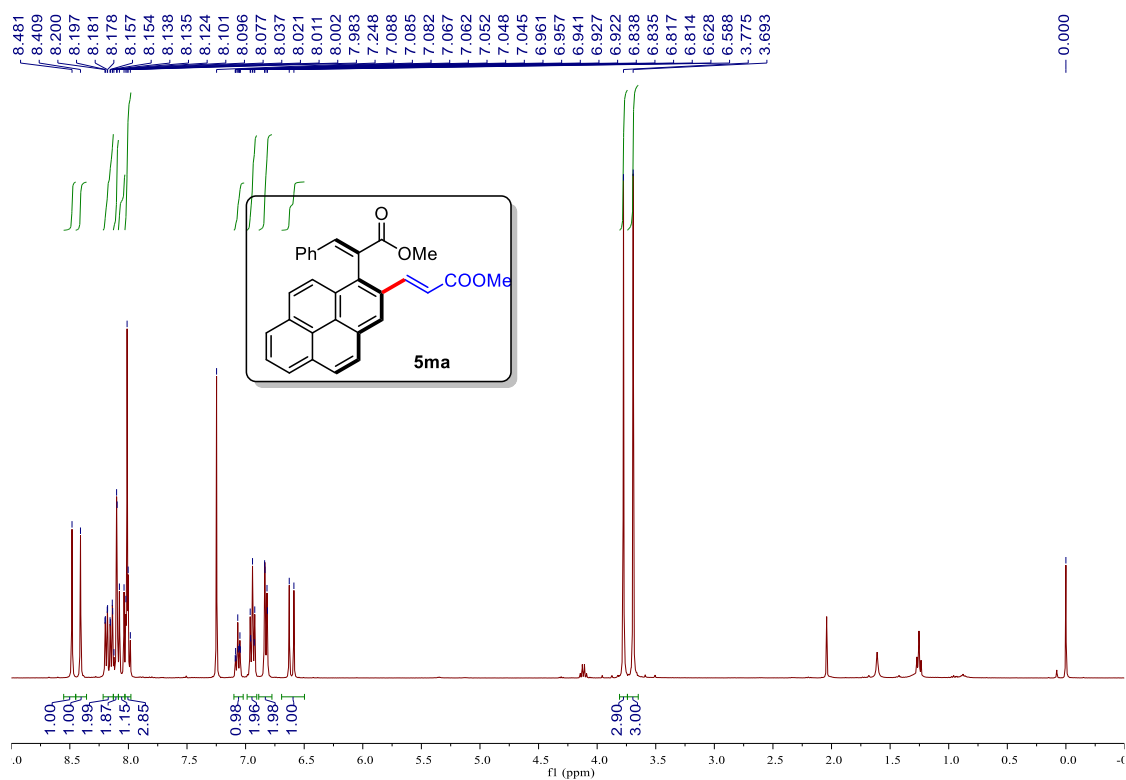
<sup>13</sup>C NMR Spectrum of **5ka** (CDCl<sub>3</sub>, 126 MHz)



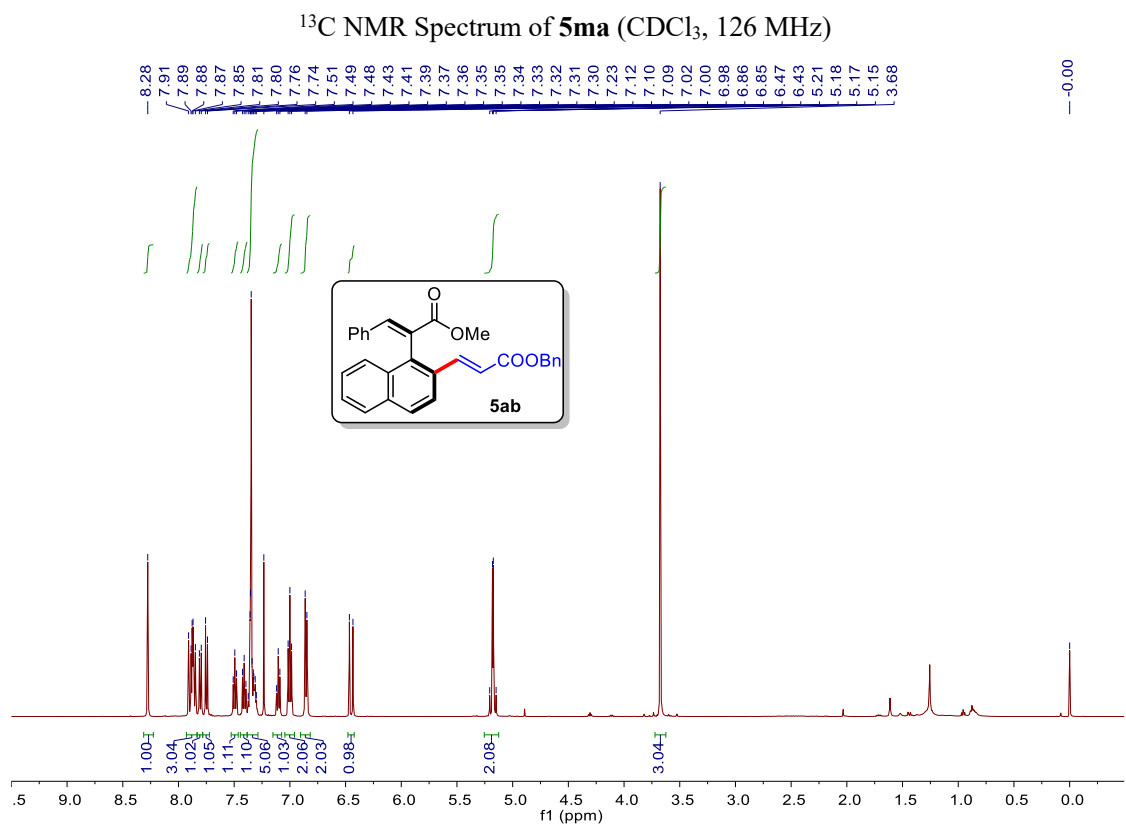
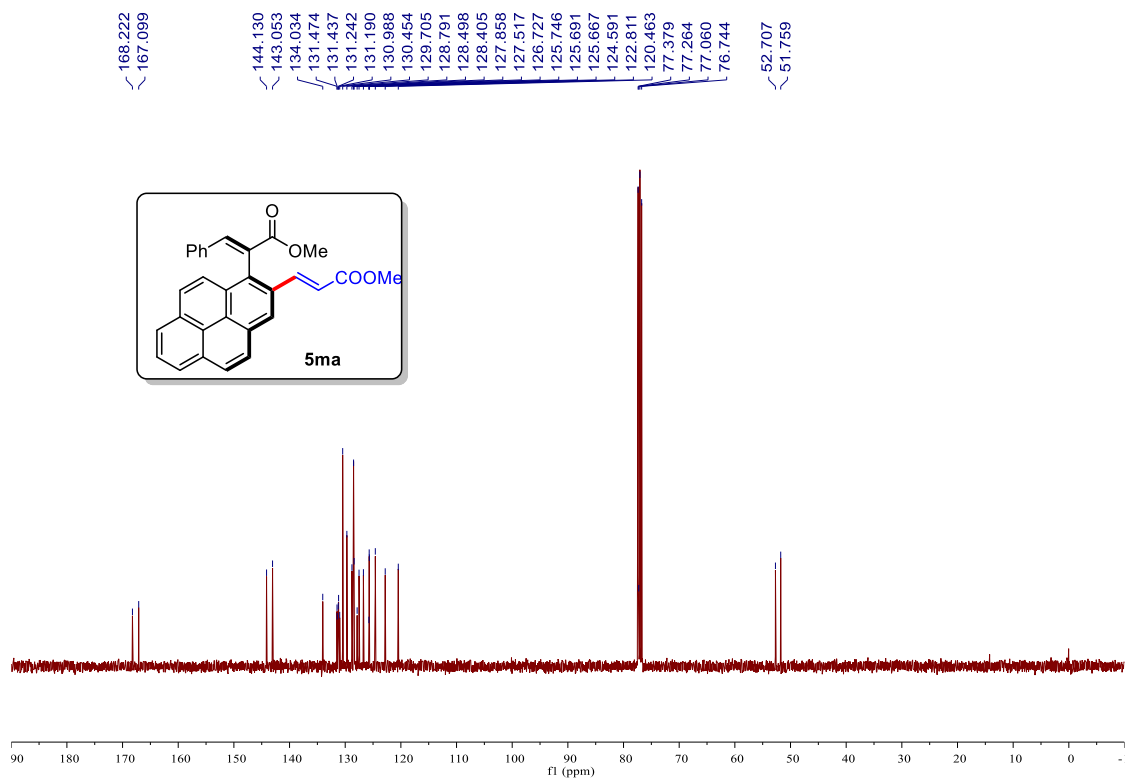
<sup>1</sup>H NMR Spectrum of **5la** (CDCl<sub>3</sub>, 500 MHz)

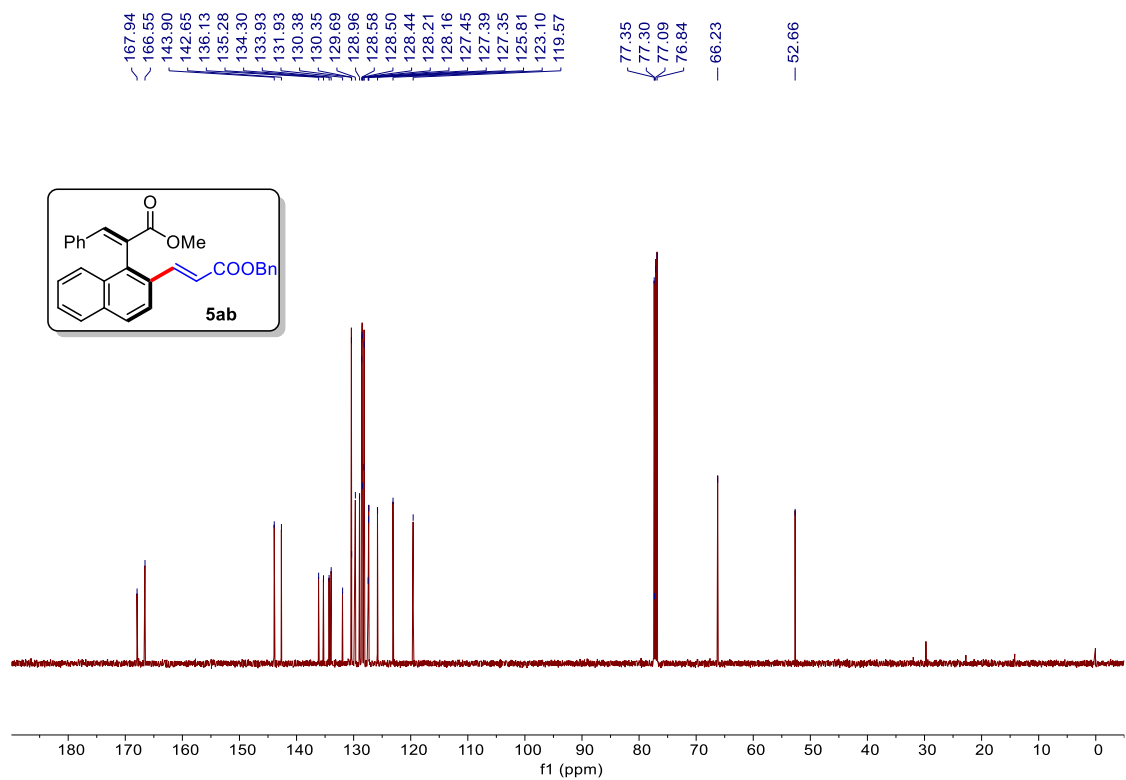


<sup>13</sup>C NMR Spectrum of **5la** (CDCl<sub>3</sub>, 126 MHz)

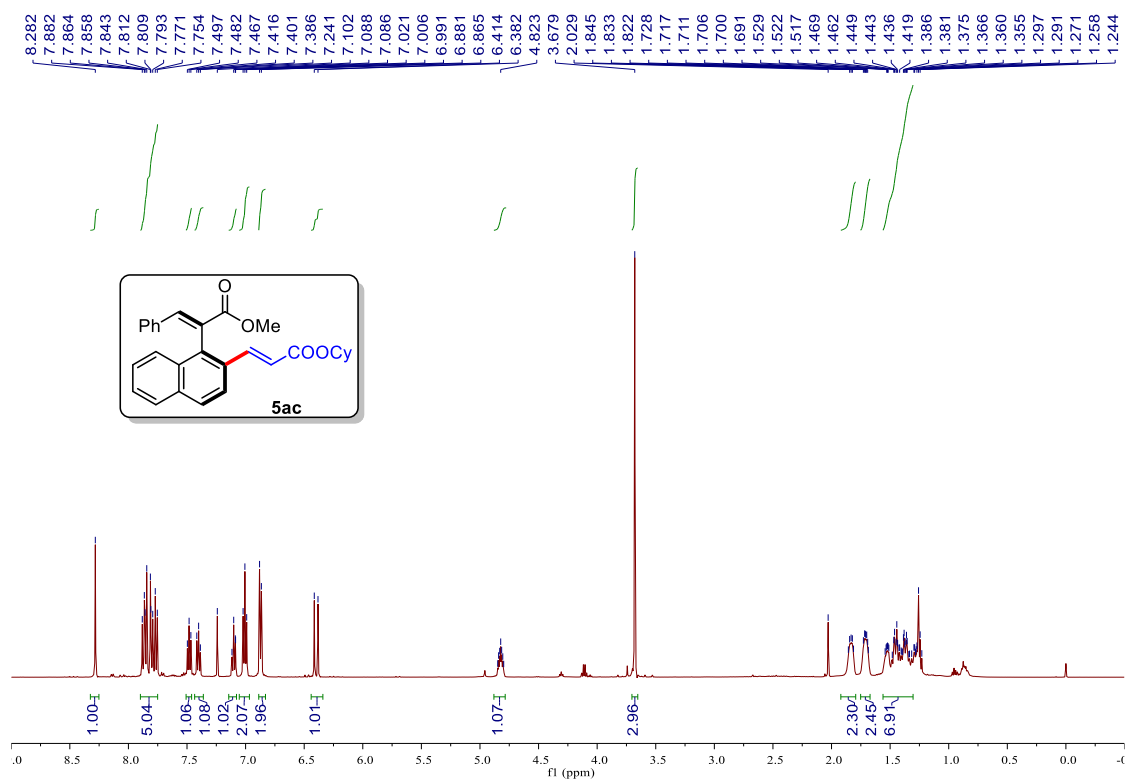


<sup>1</sup>H NMR Spectrum of **5ma** (CDCl<sub>3</sub>, 500 MHz)



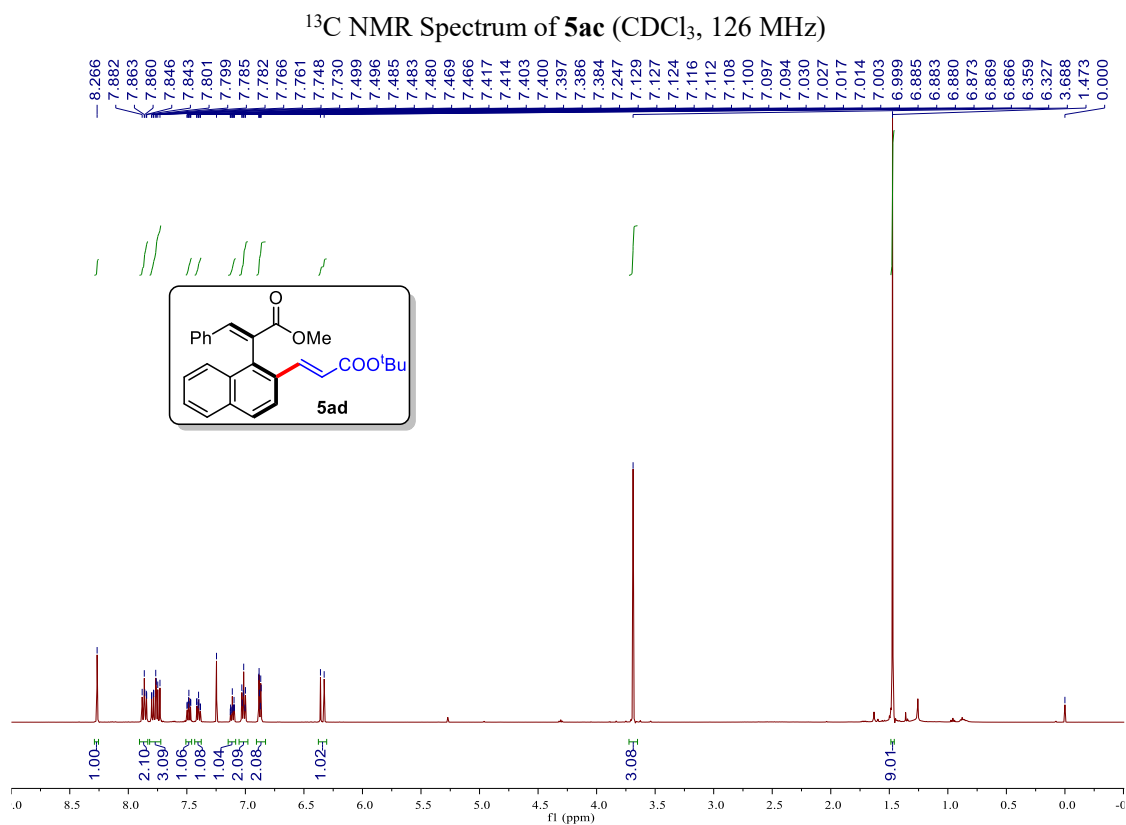
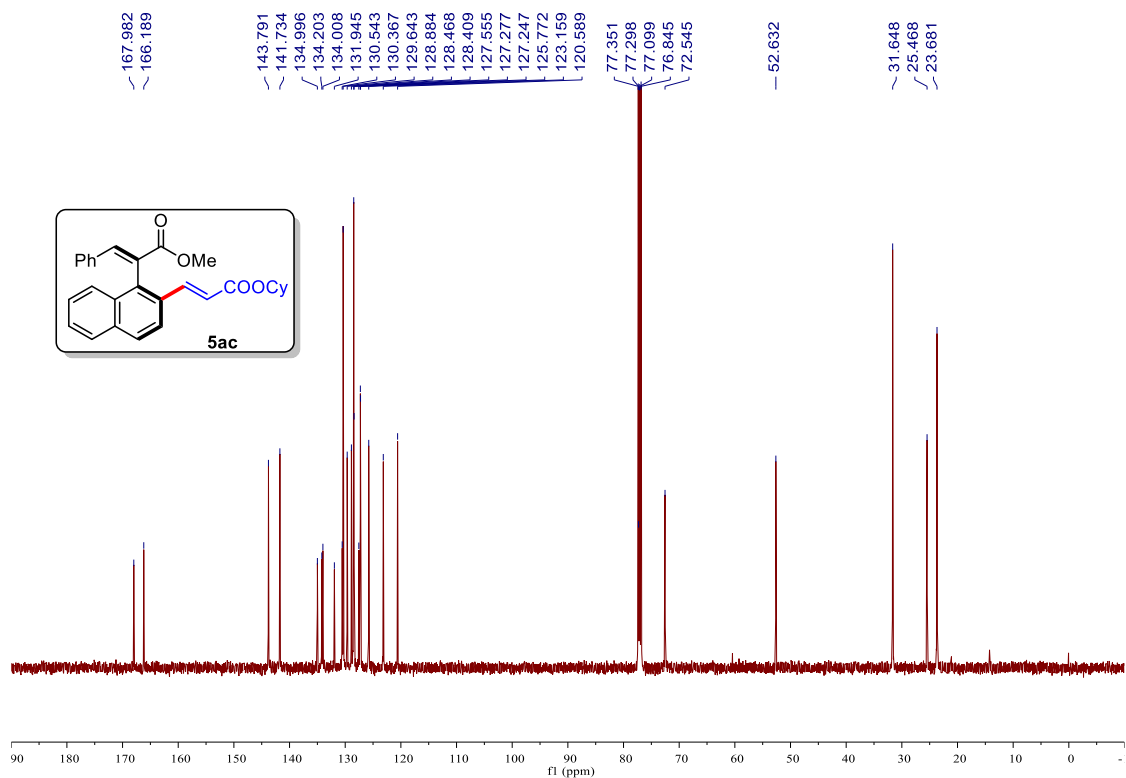


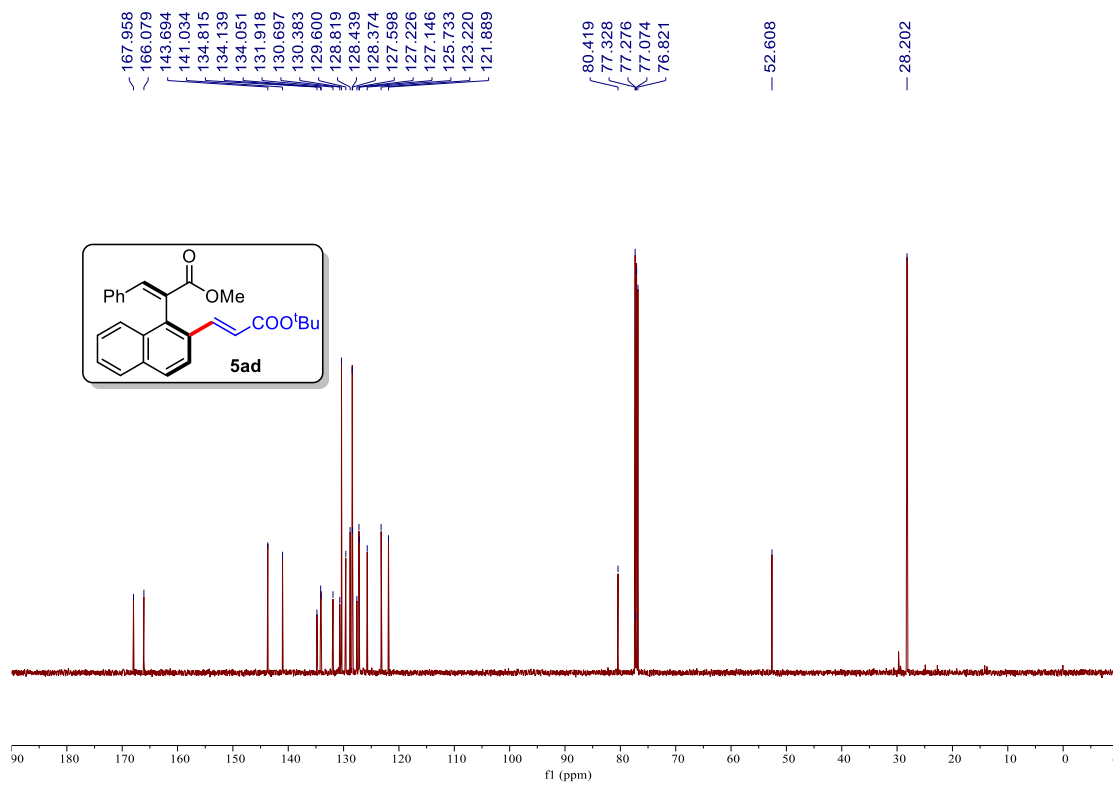
<sup>13</sup>C NMR Spectrum of **5ab** (CDCl<sub>3</sub>, 126 MHz)



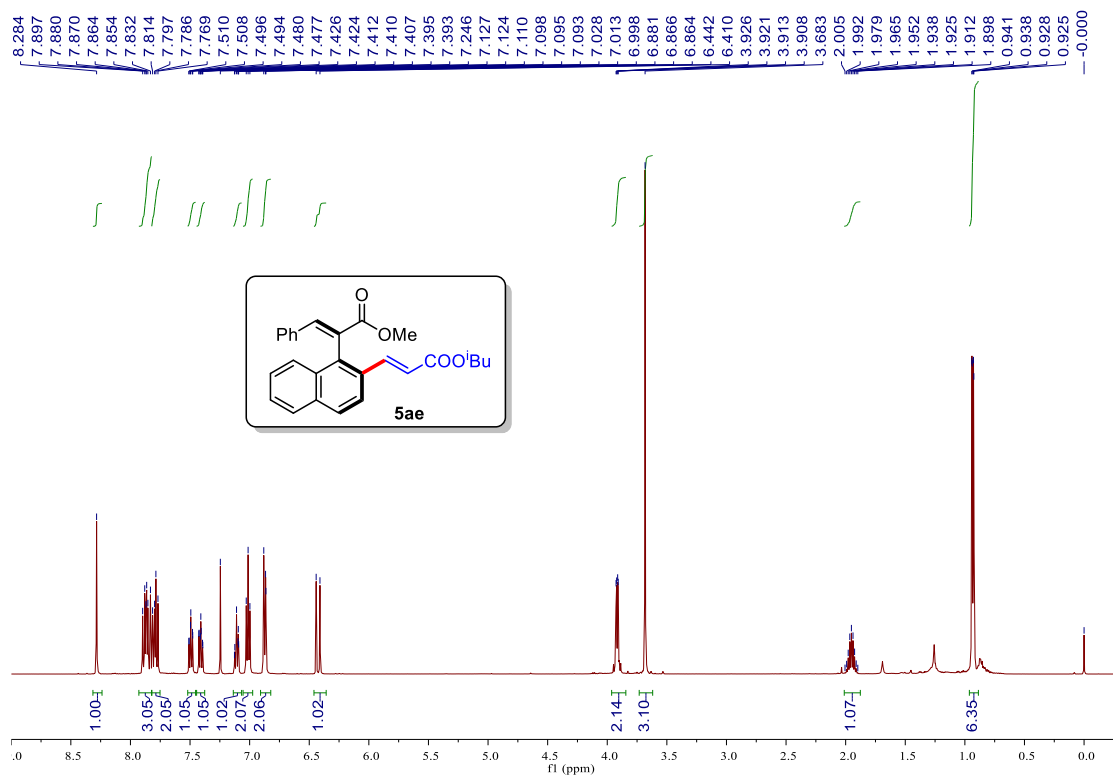
<sup>1</sup>H NMR Spectrum of **5ac** (CDCl<sub>3</sub>, 500 MHz)



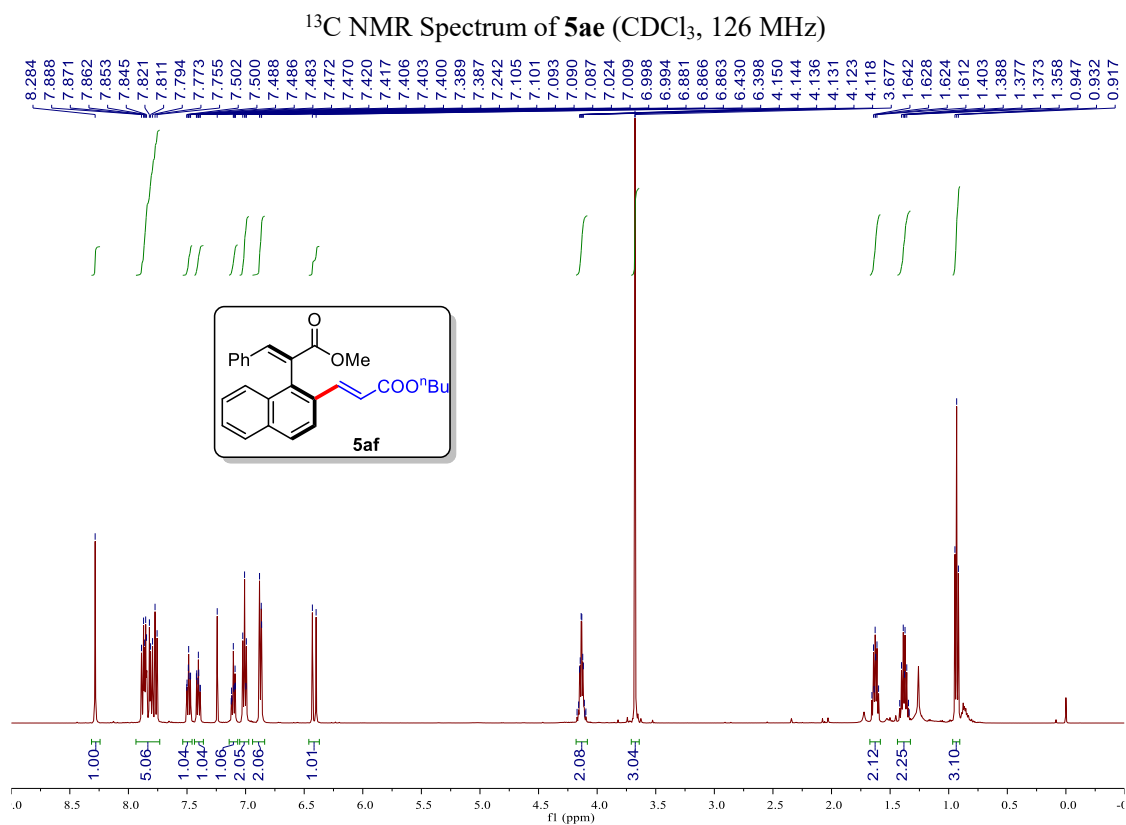
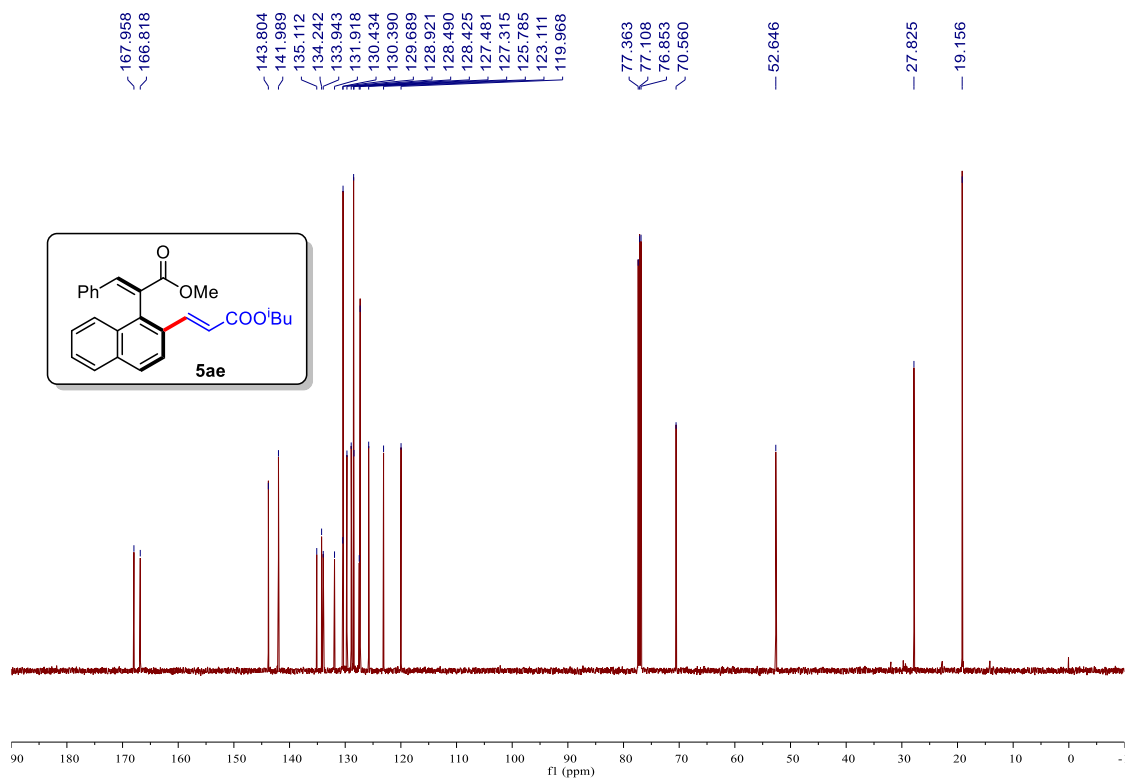


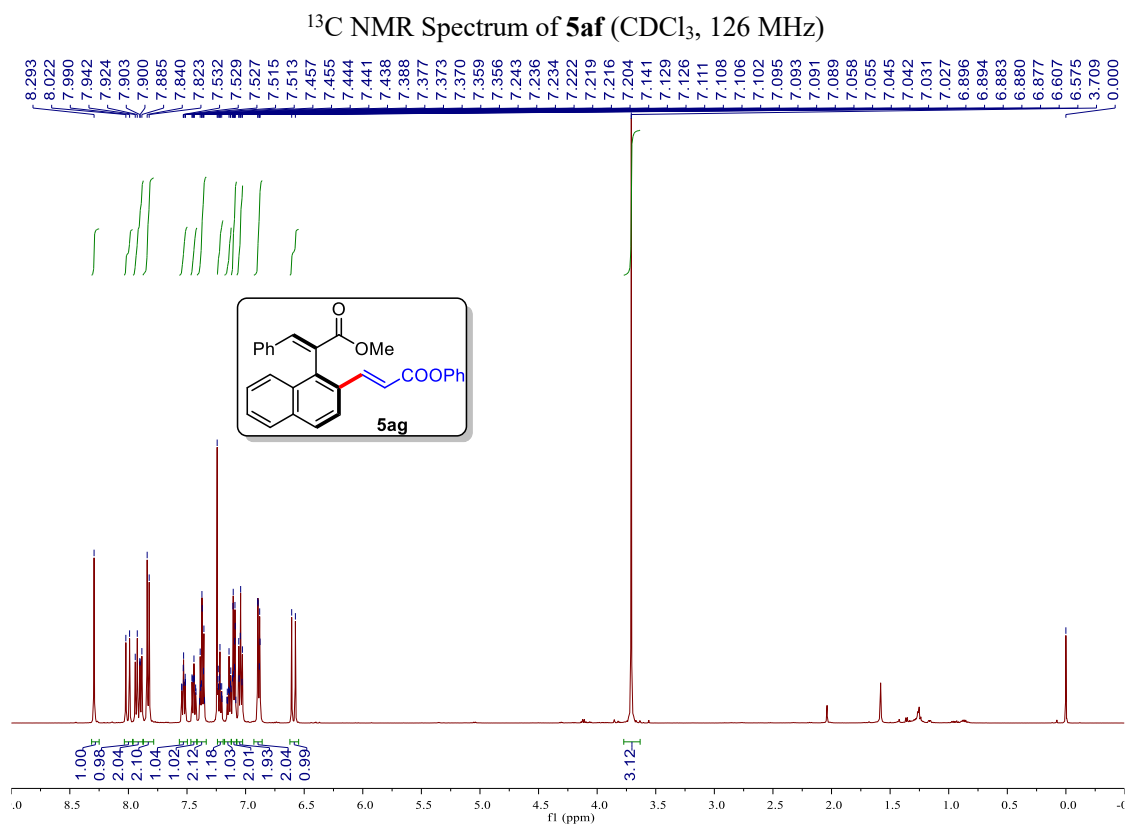
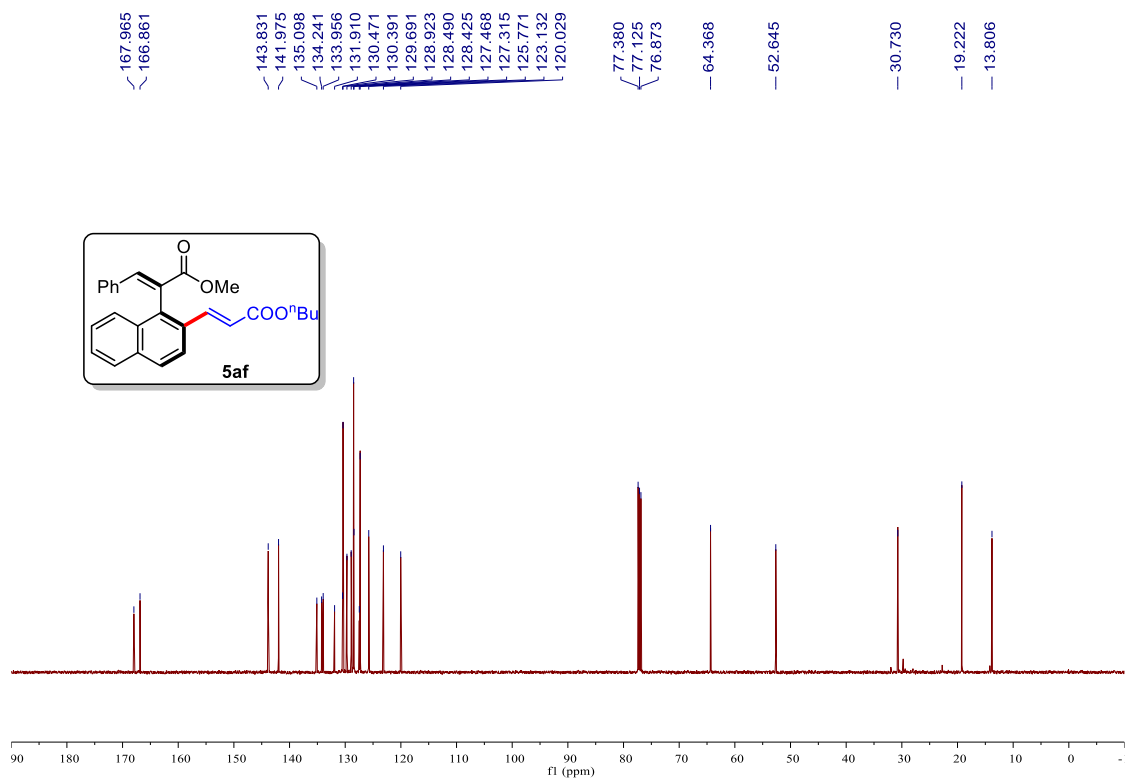


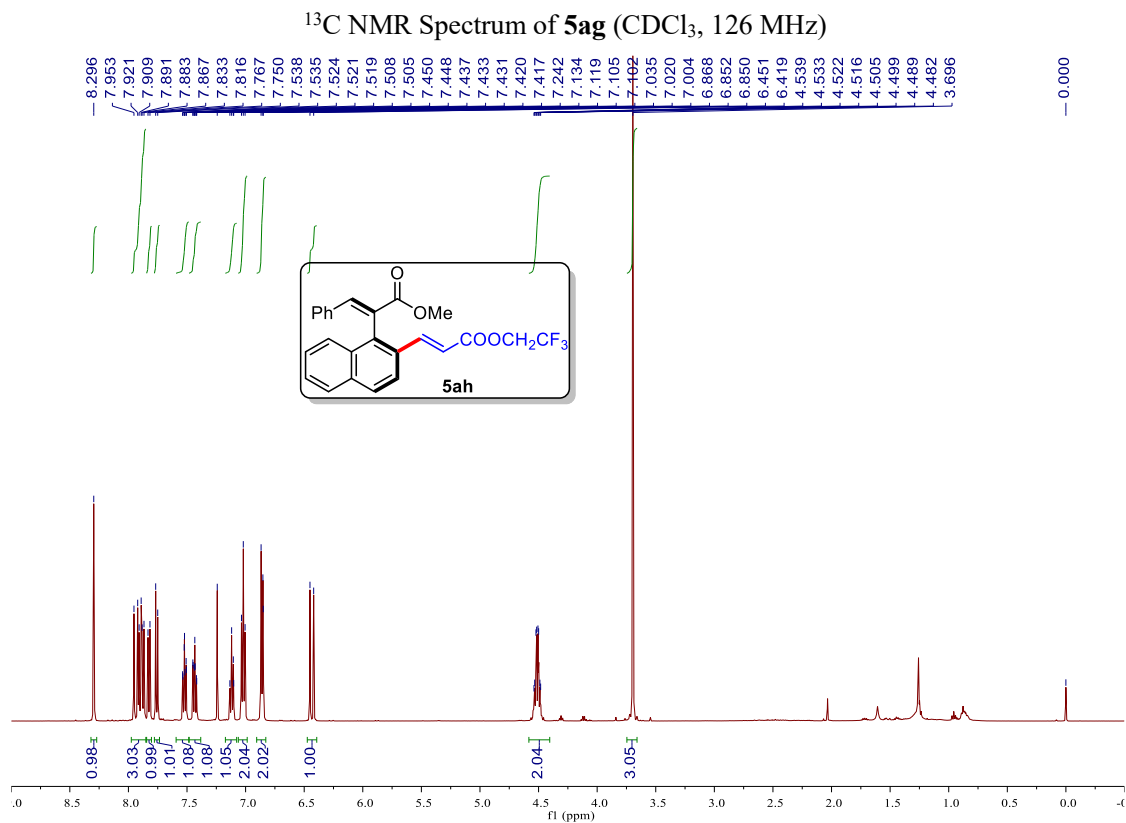
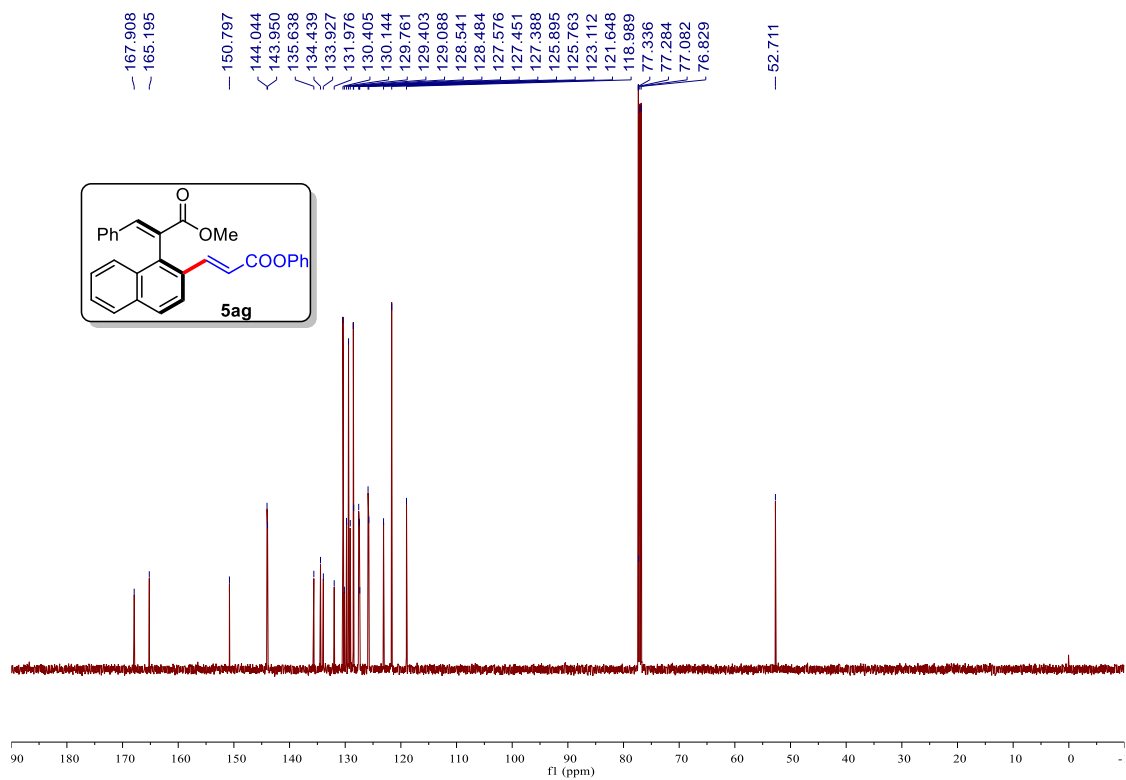
<sup>13</sup>C NMR Spectrum of **5ad** (CDCl<sub>3</sub>, 126 MHz)

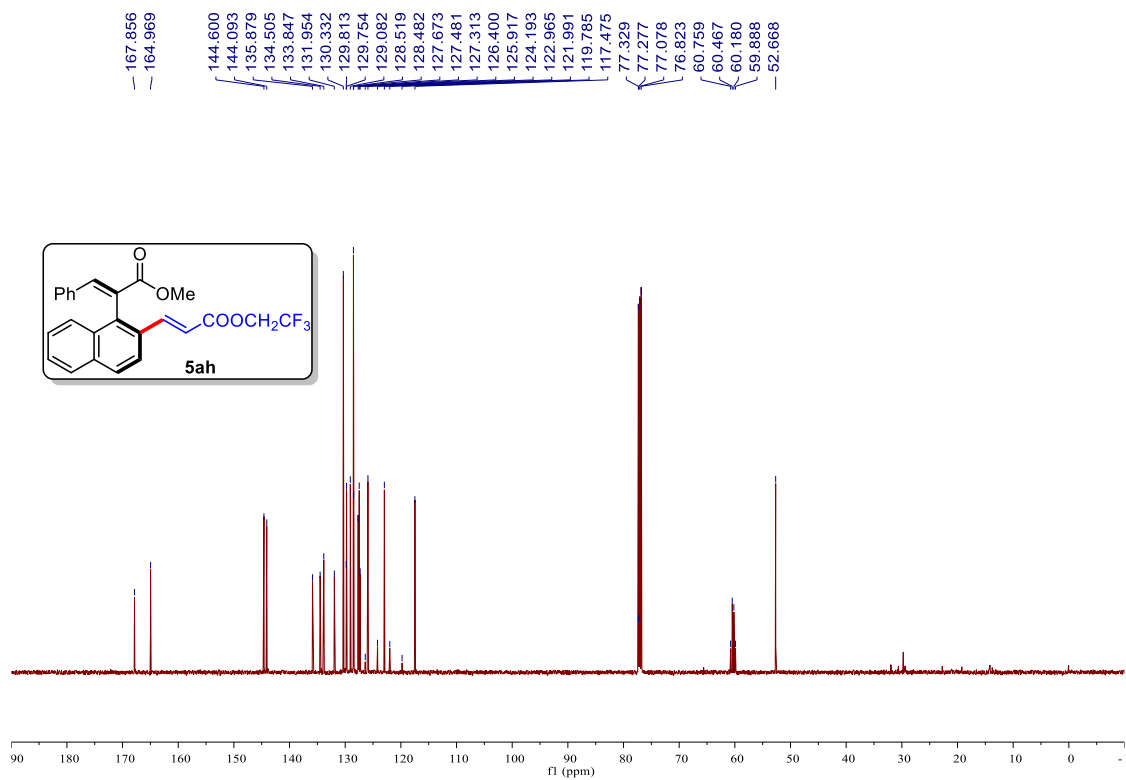


<sup>1</sup>H NMR Spectrum of **5ae** (CDCl<sub>3</sub>, 500 MHz)

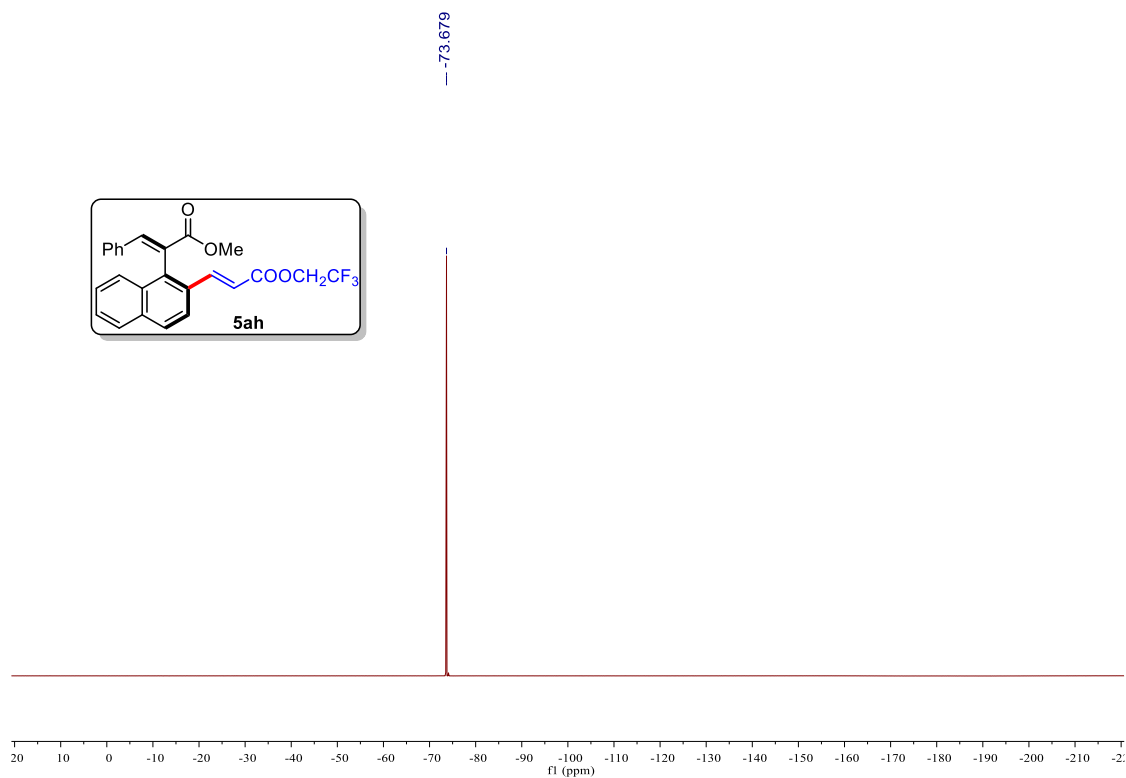




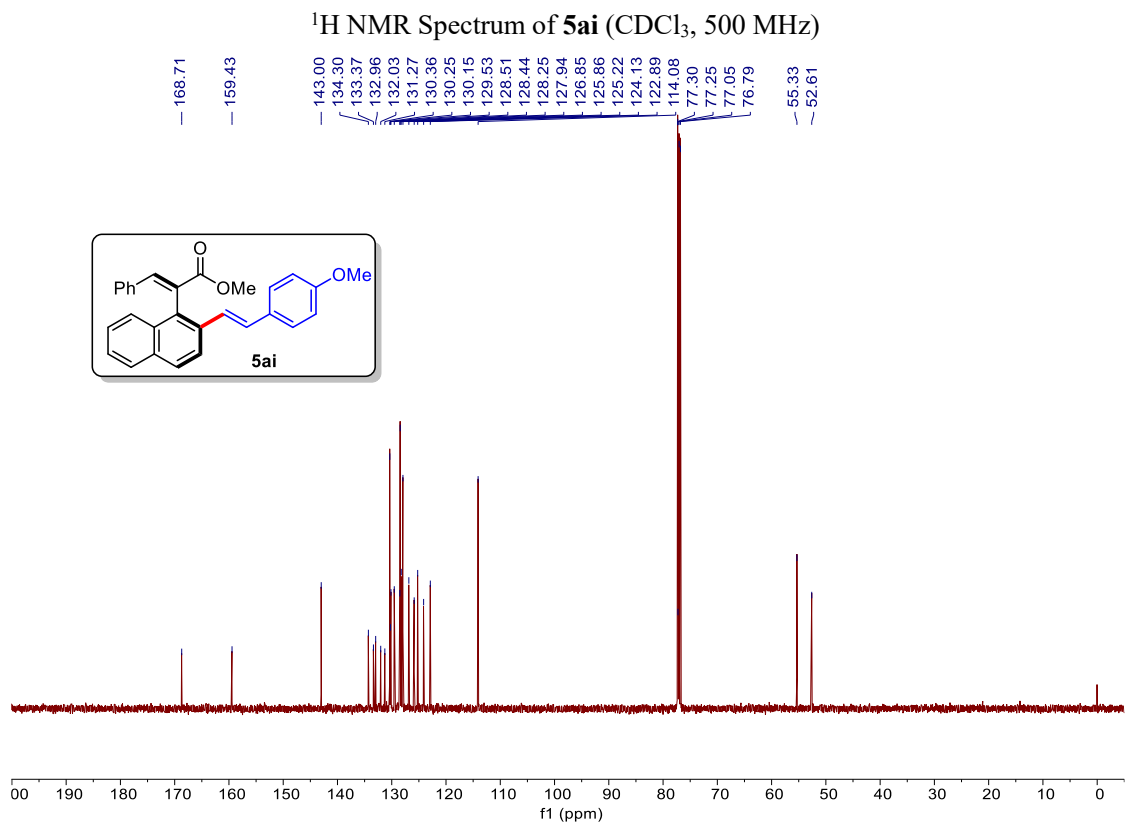
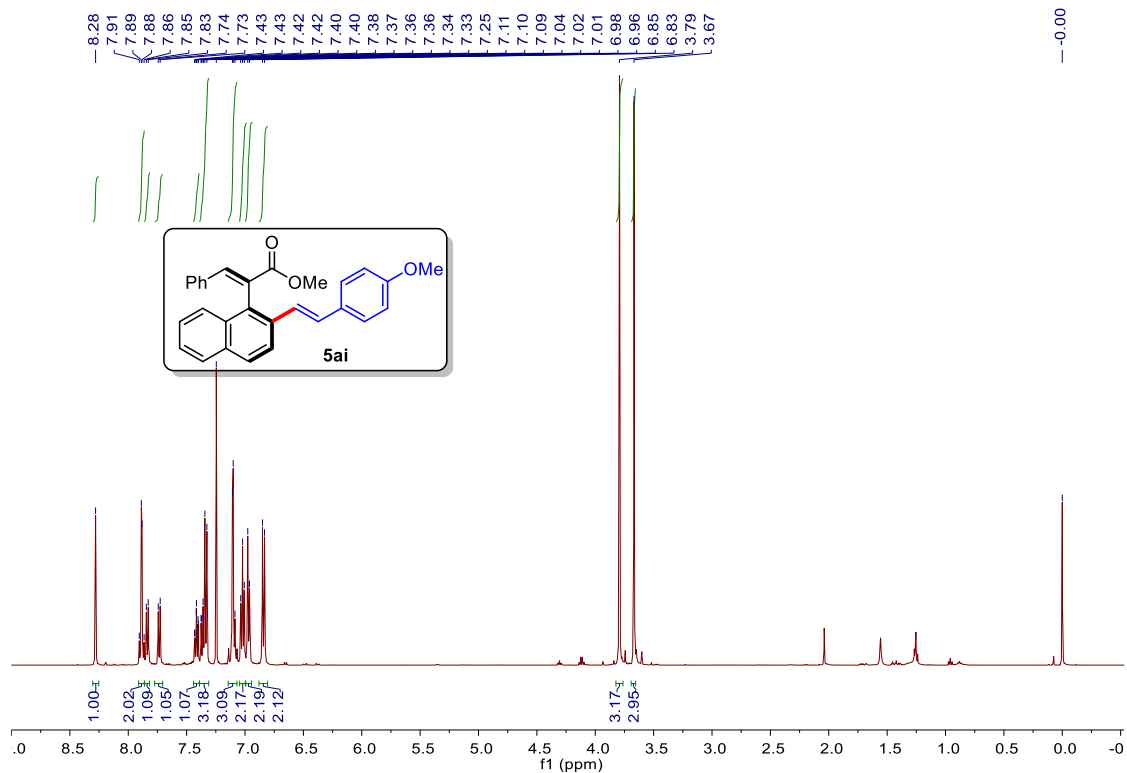


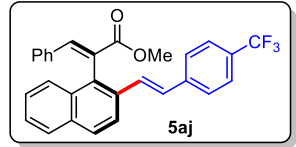
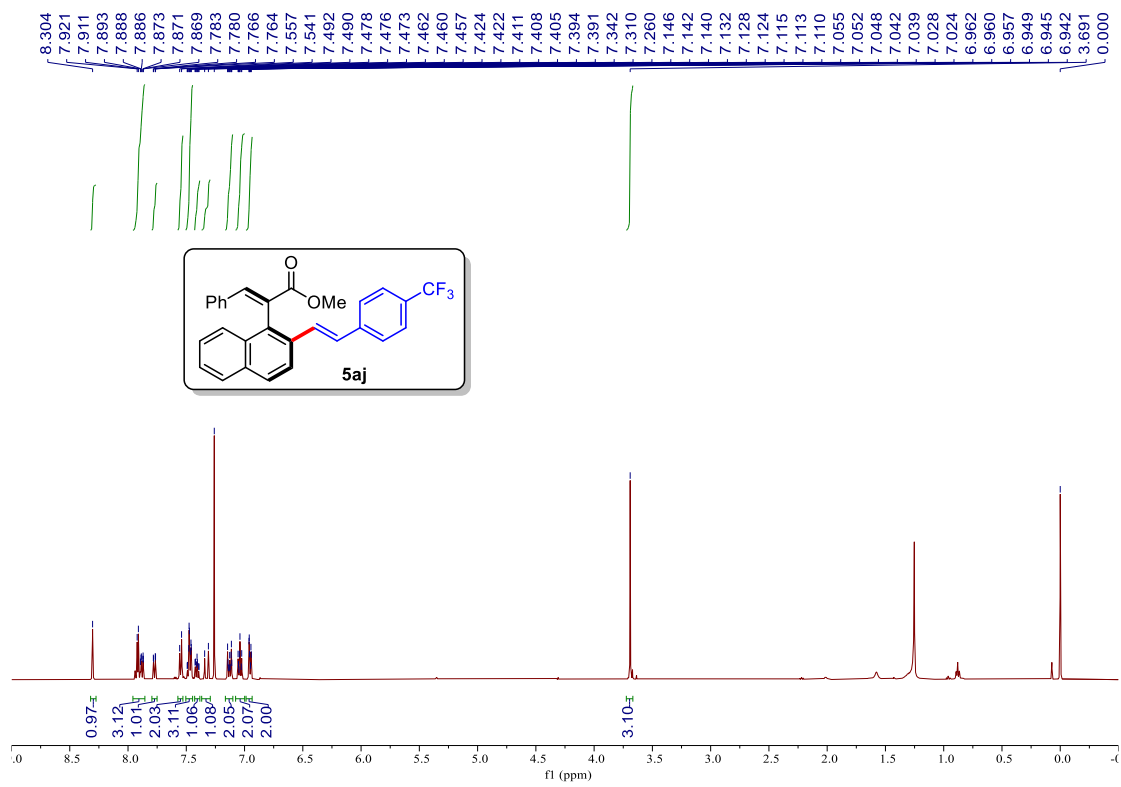


<sup>13</sup>C NMR Spectrum of **5ah** (CDCl<sub>3</sub>, 126 MHz)

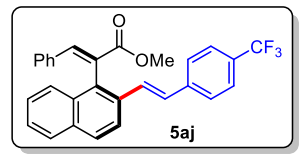
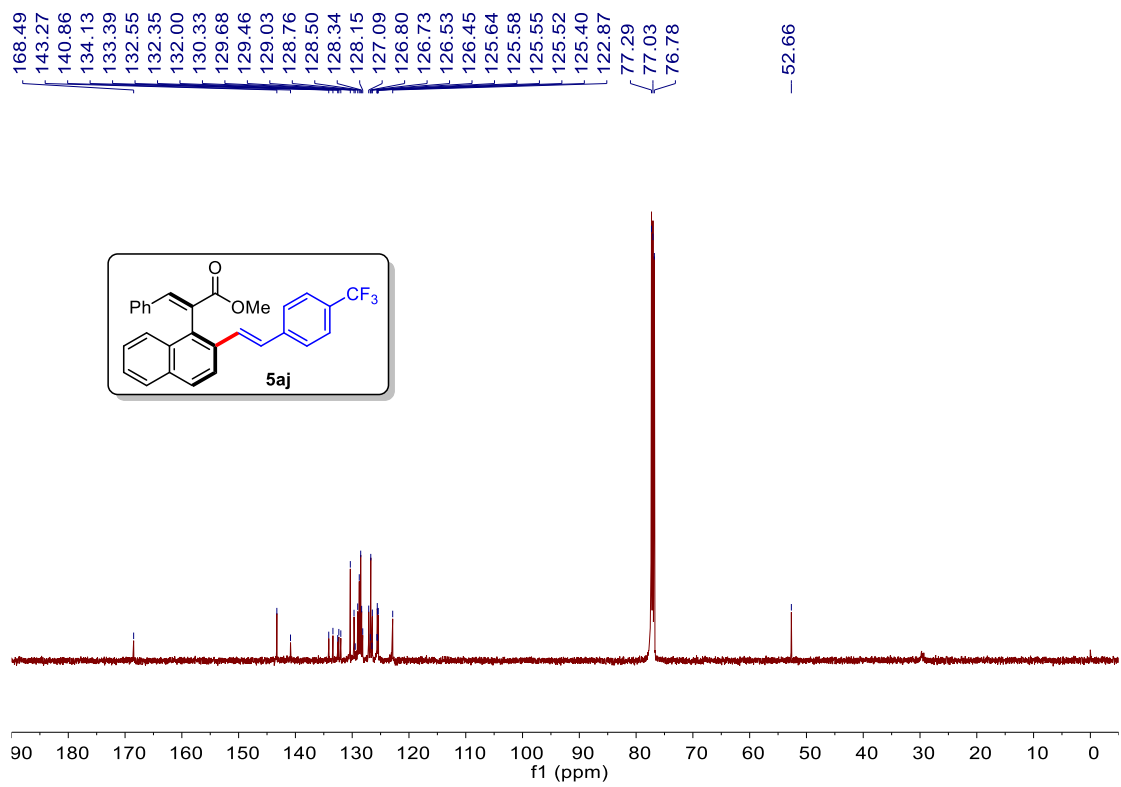


<sup>19</sup>F NMR Spectrum of **5ah** (CDCl<sub>3</sub>, 126 MHz)



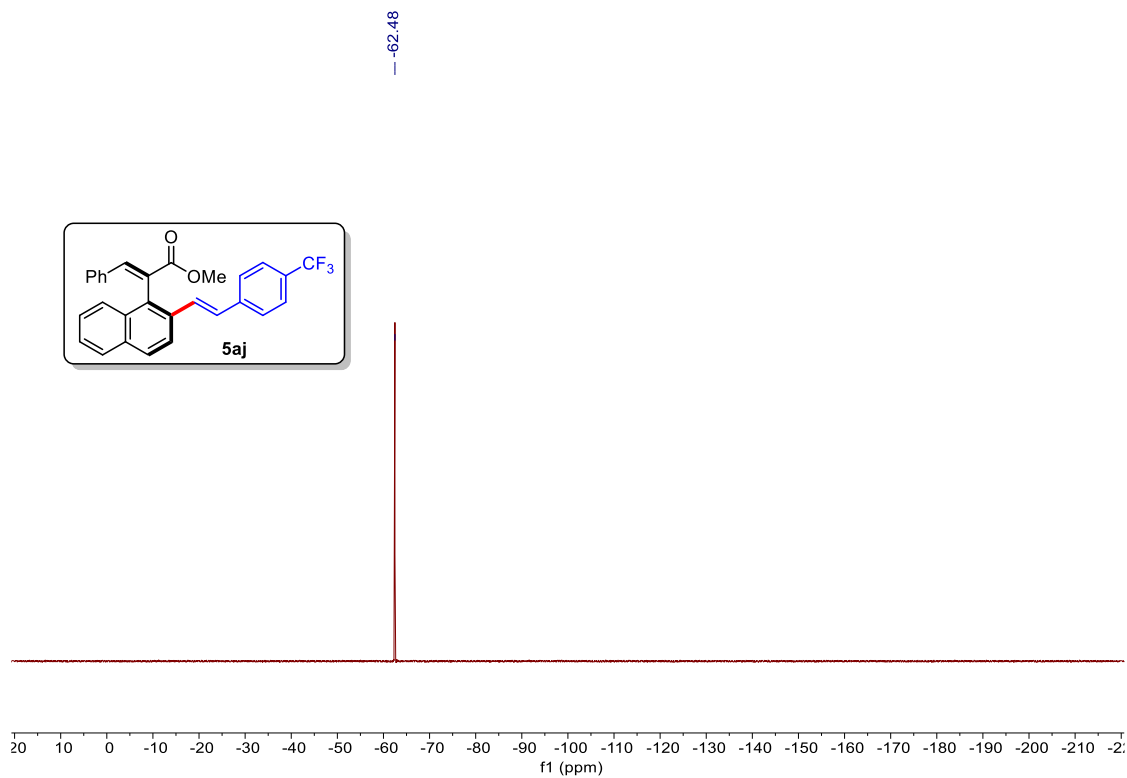


<sup>1</sup>H NMR Spectrum of **5aj** (CDCl<sub>3</sub>, 500 MHz)

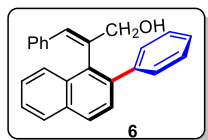
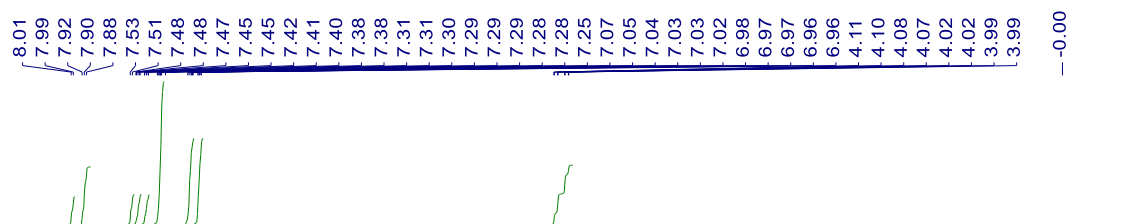


<sup>13</sup>C NMR Spectrum of **5aj** (CDCl<sub>3</sub>, 126 MHz)

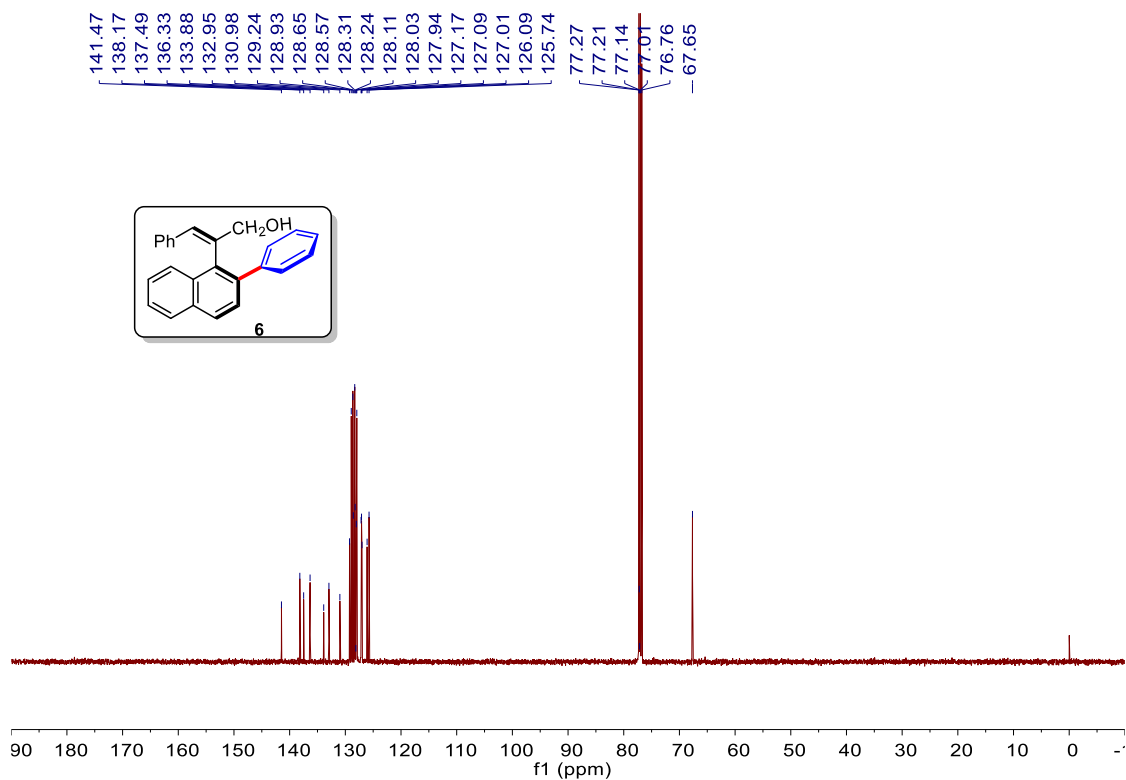




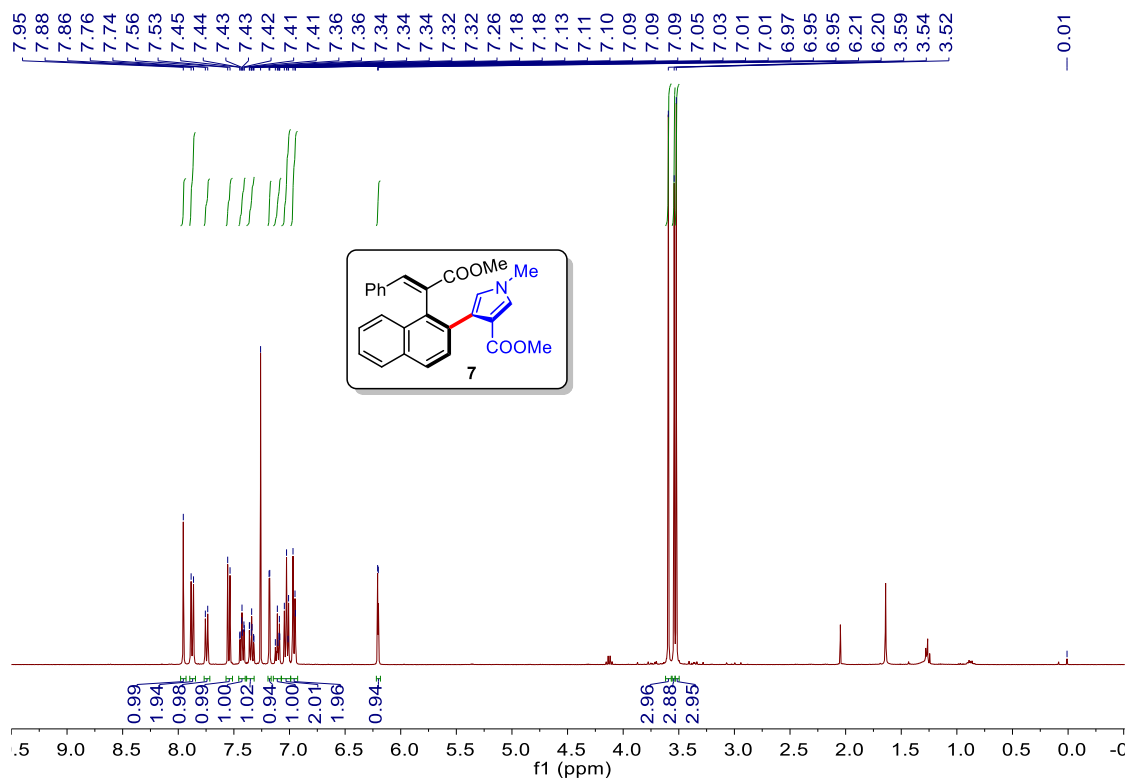
<sup>19</sup>F NMR Spectrum of **5aj** (CDCl<sub>3</sub>, 471 MHz)



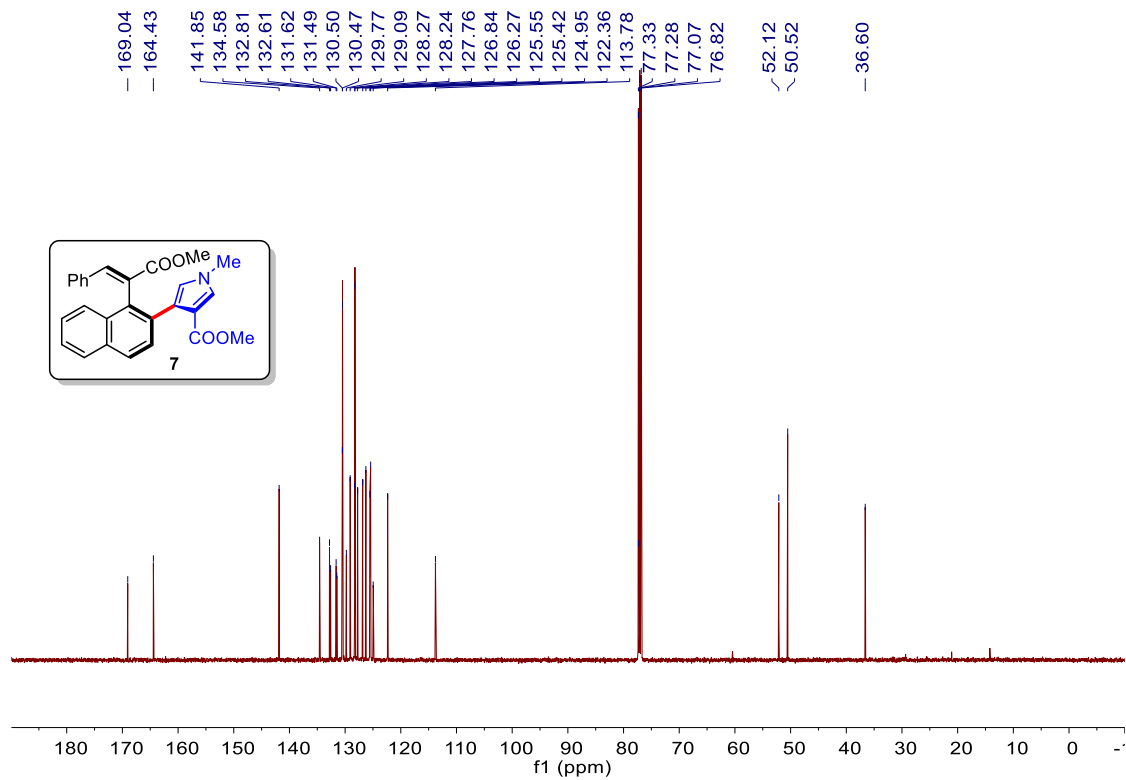
<sup>1</sup>H NMR Spectrum of **6** (CDCl<sub>3</sub>, 500 MHz)



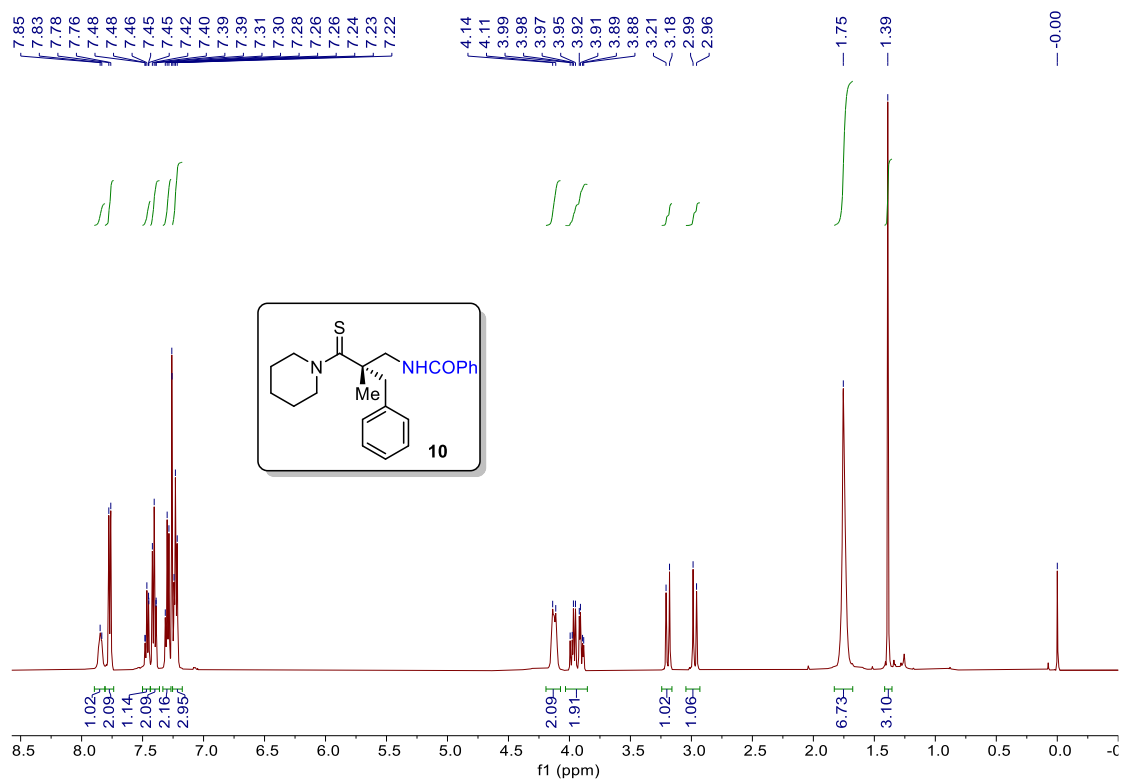
<sup>13</sup>C NMR Spectrum of 6 (CDCl<sub>3</sub>, 126 MHz)



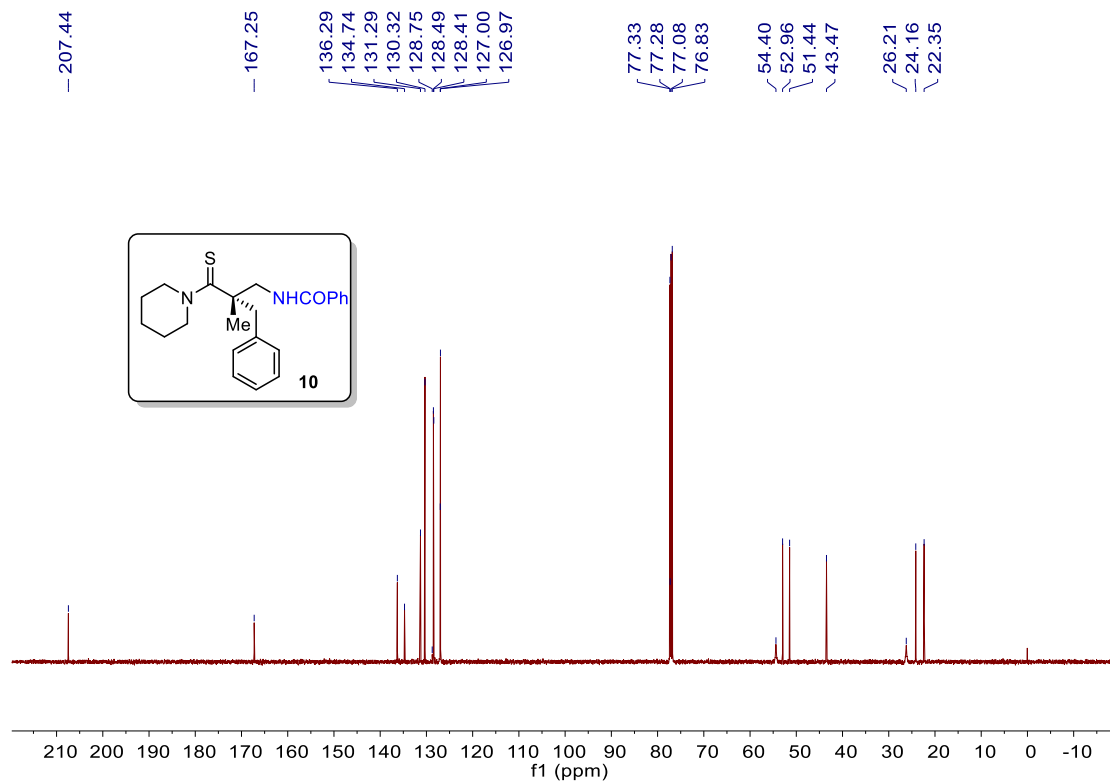
<sup>1</sup>H NMR Spectrum of 7 (CDCl<sub>3</sub>, 500 MHz)



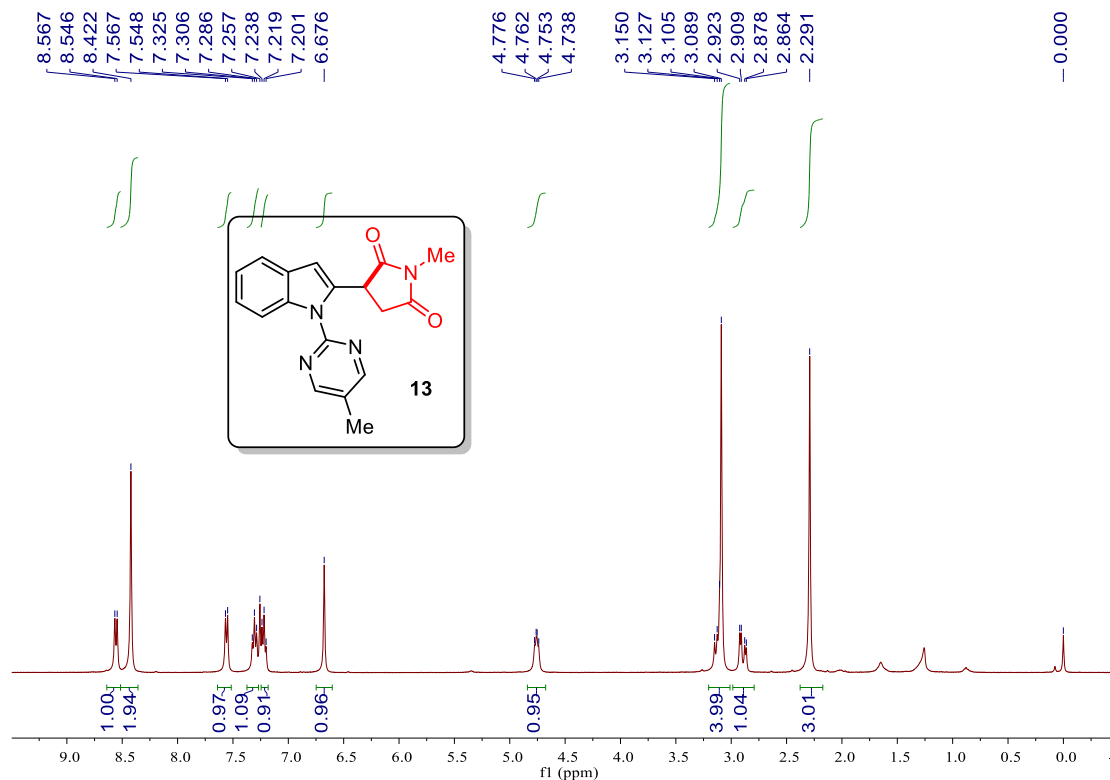
<sup>13</sup>C NMR Spectrum of **7** (CDCl<sub>3</sub>, 126 MHz)



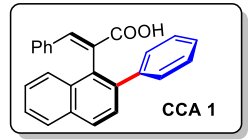
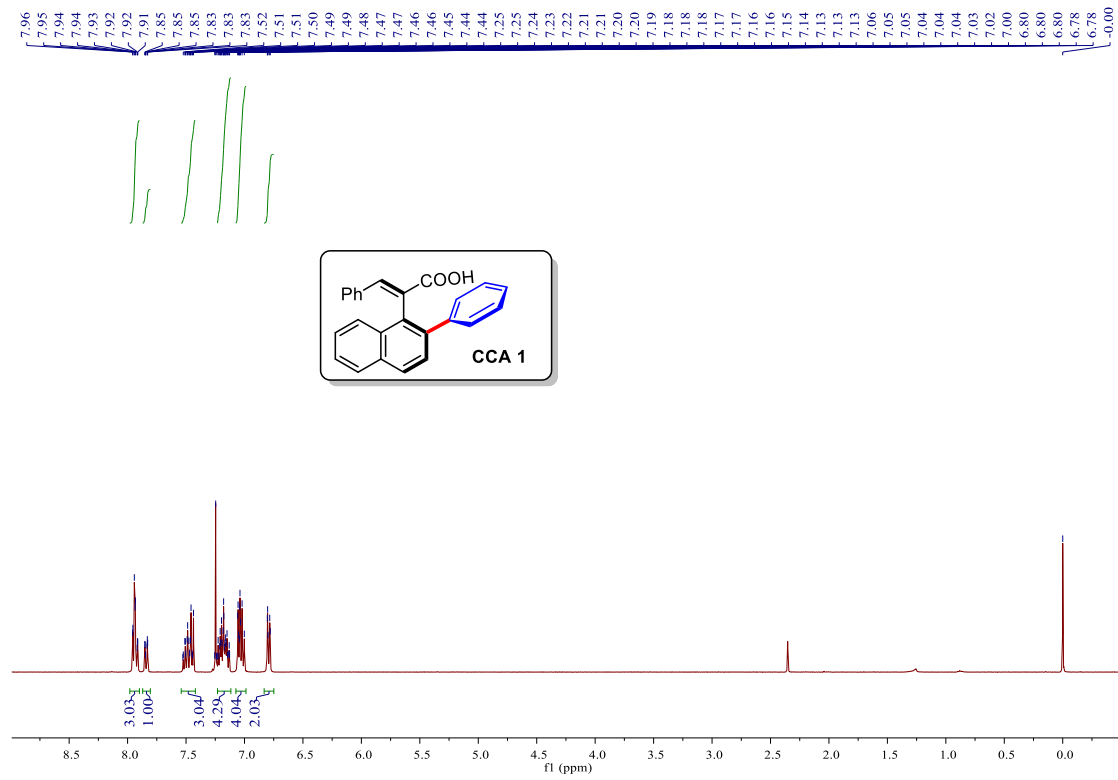
<sup>1</sup>H NMR Spectrum of **10** (CDCl<sub>3</sub>, 500 MHz)



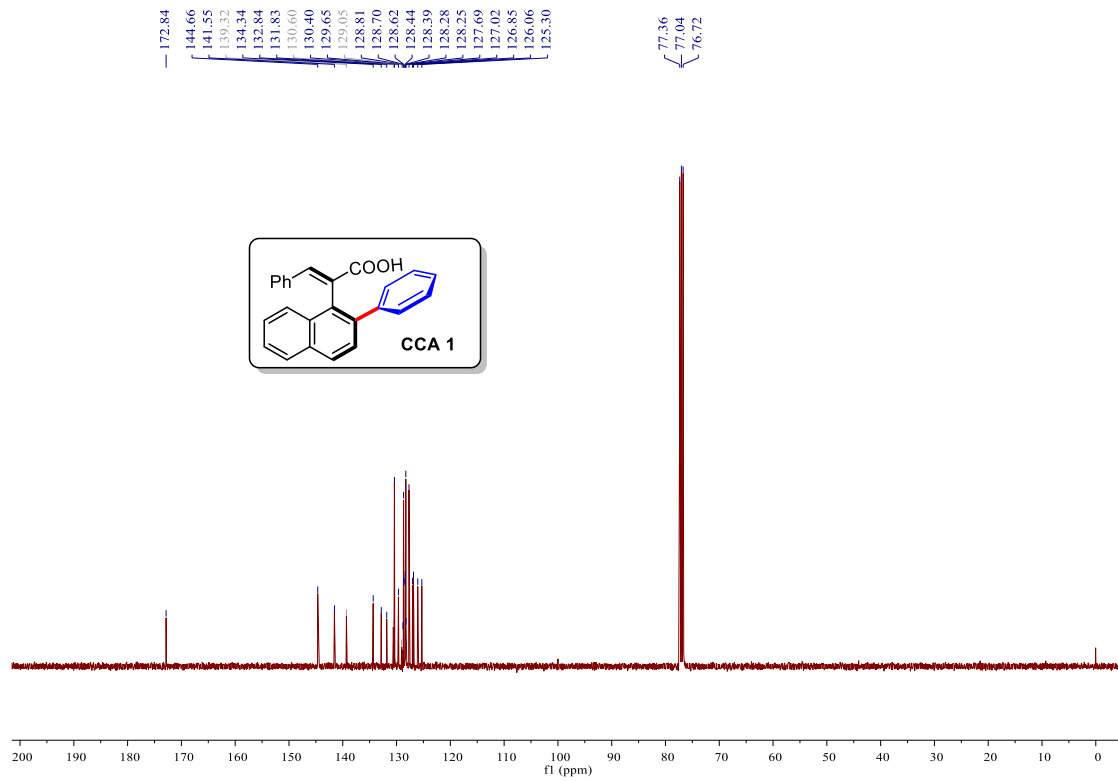
<sup>13</sup>C NMR Spectrum of **10** (CDCl<sub>3</sub>, 500 MHz)



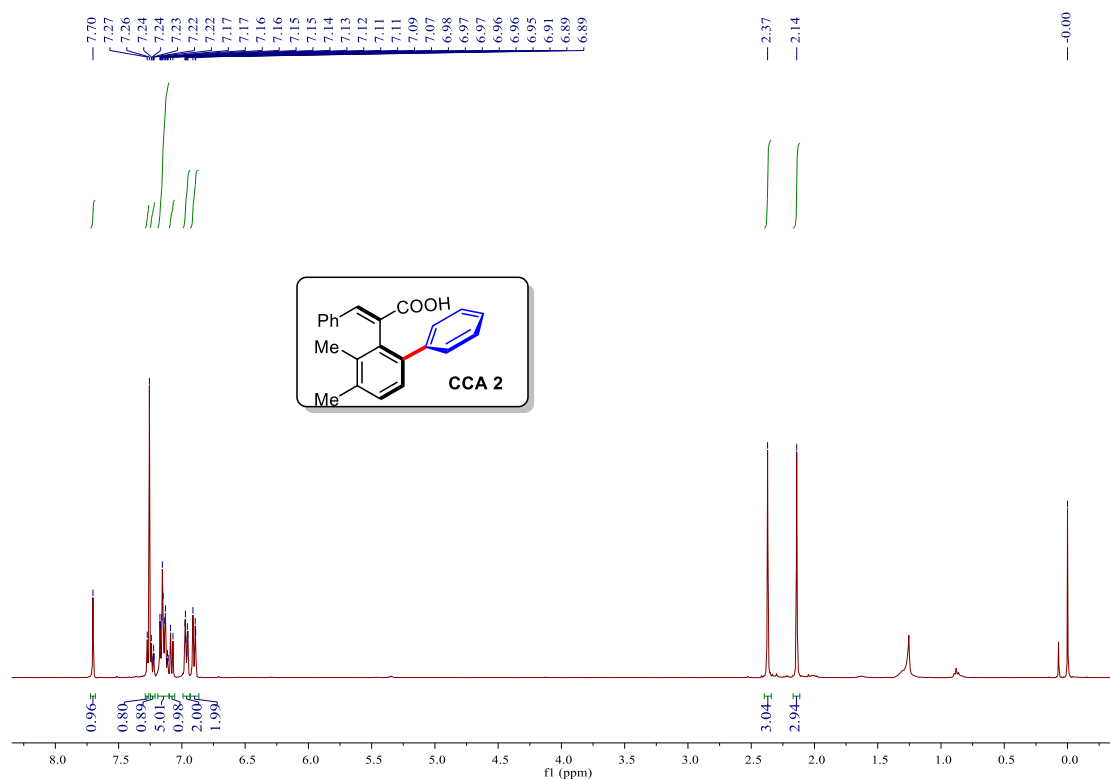
<sup>1</sup>H NMR Spectrum of **13** (CDCl<sub>3</sub>, 400 MHz)



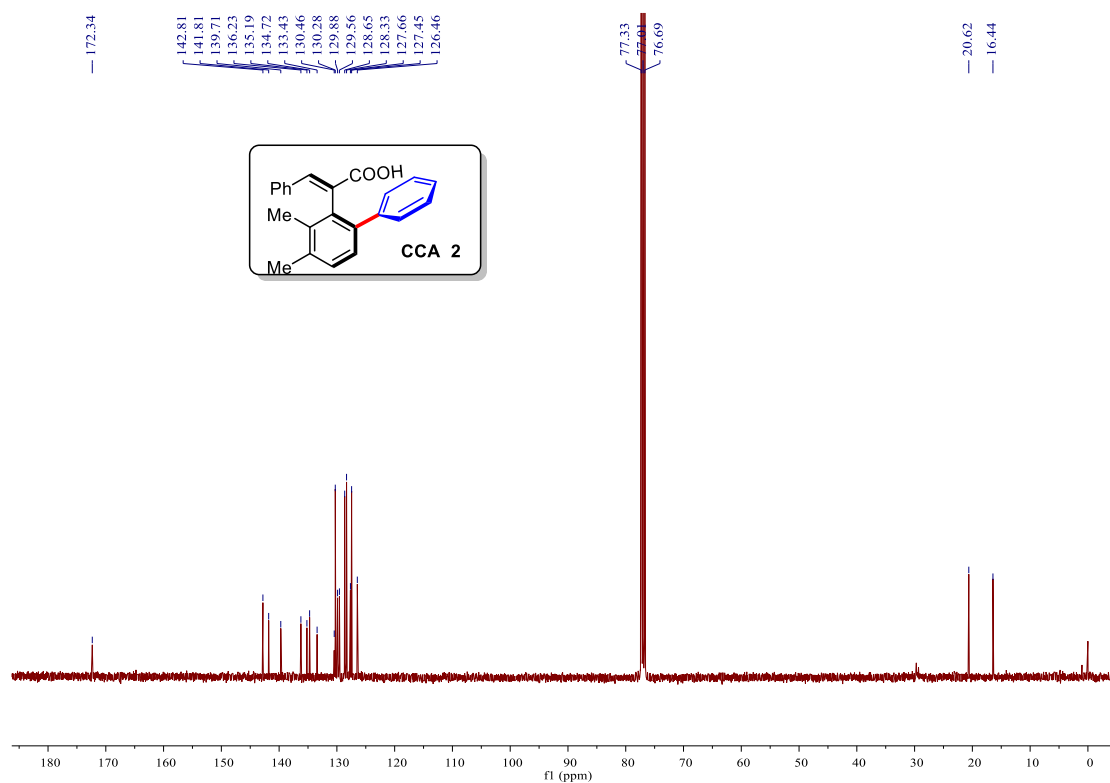
**<sup>1</sup>H NMR Spectrum of CCA 1 (CDCl<sub>3</sub>, 400 MHz)**



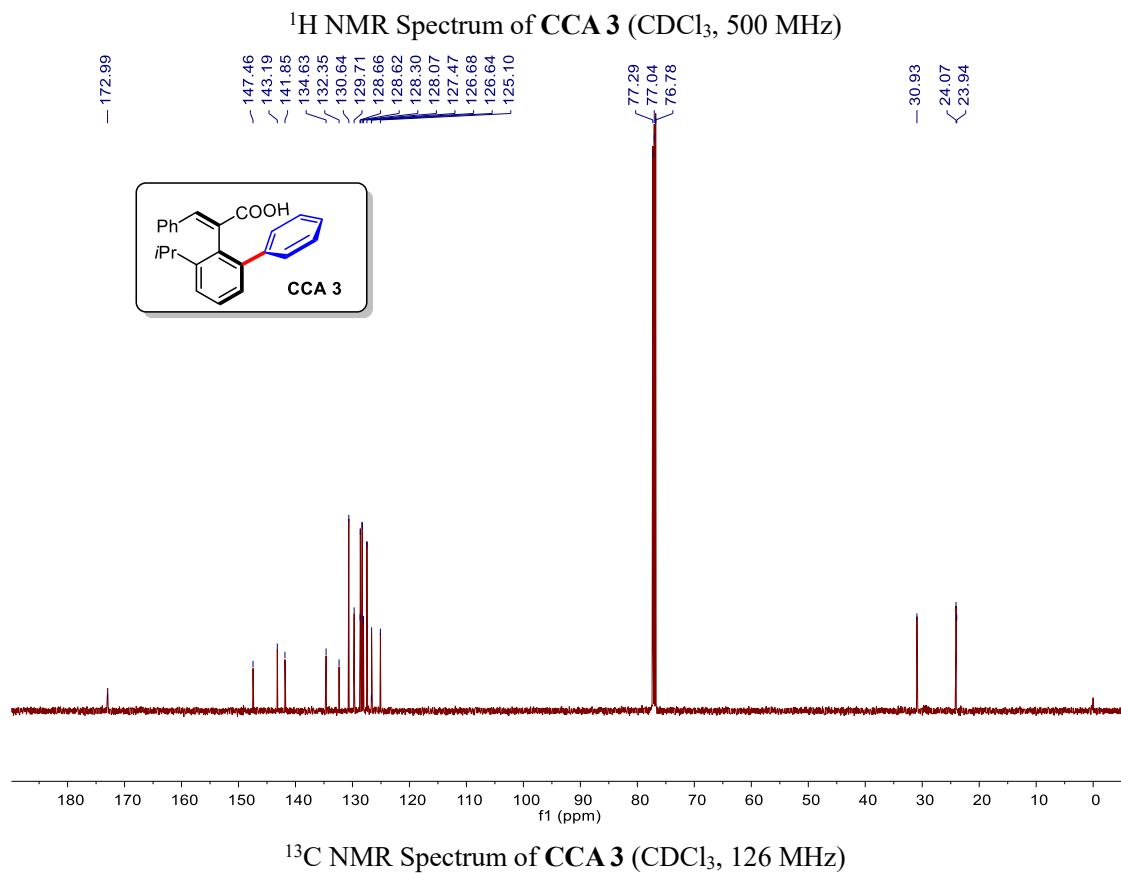
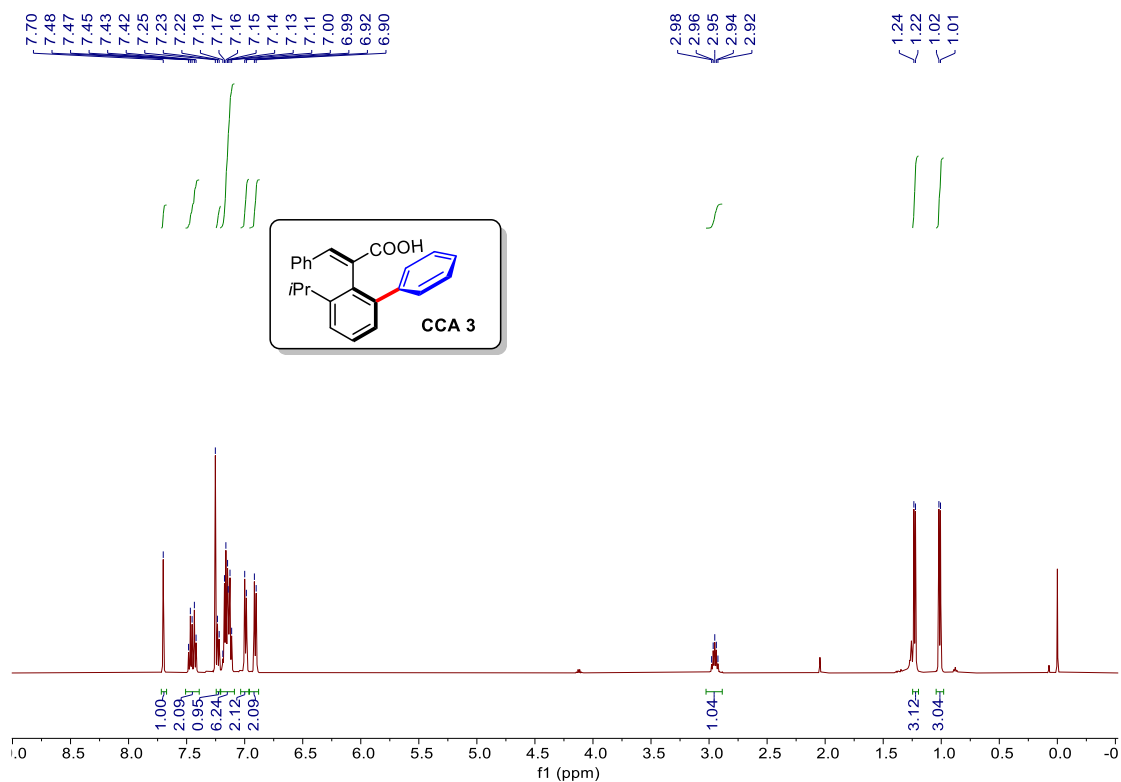
**<sup>13</sup>C NMR Spectrum of CCA 1 (CDCl<sub>3</sub>, 101 MHz)**

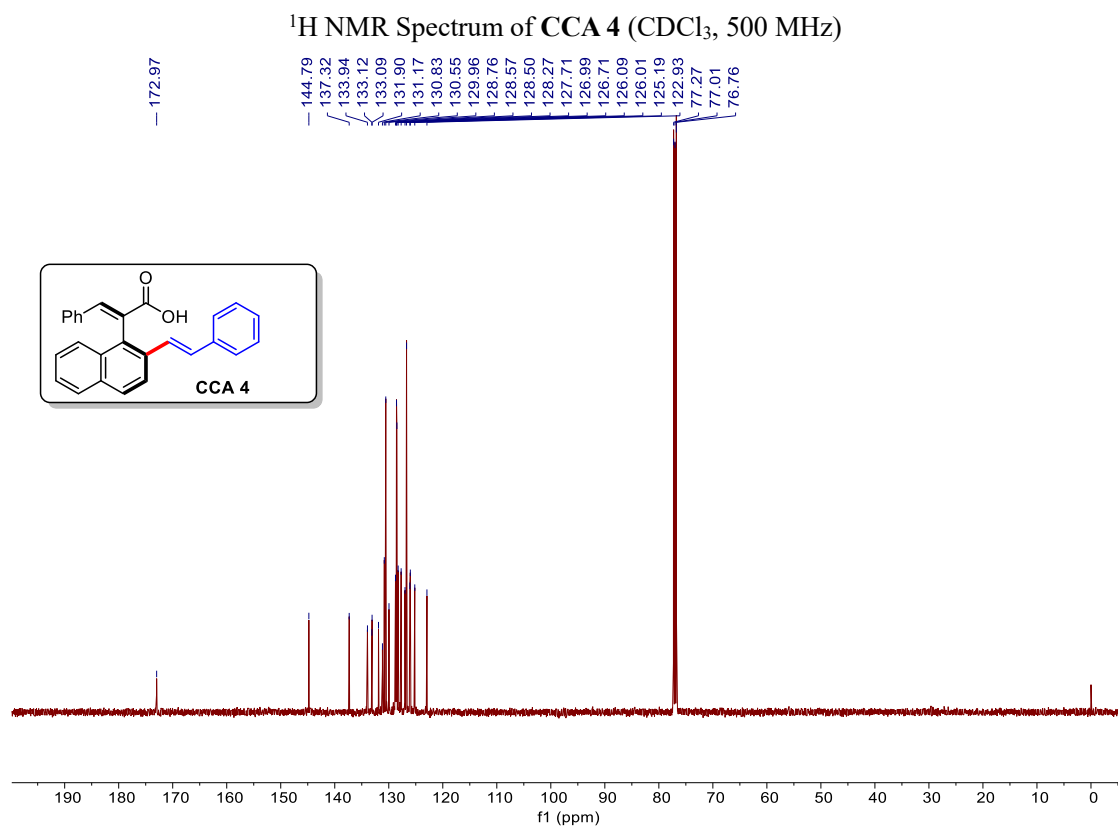
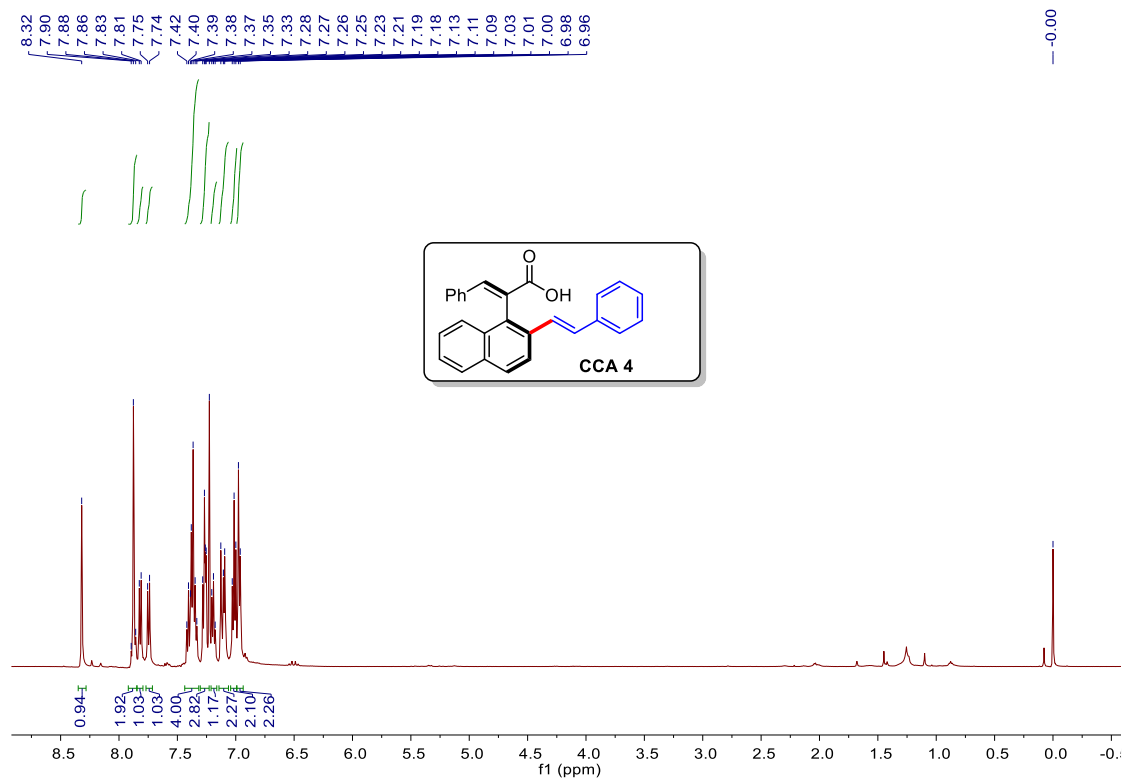


**<sup>1</sup>H NMR Spectrum of CCA 2 (CDCl<sub>3</sub>, 400 MHz)**

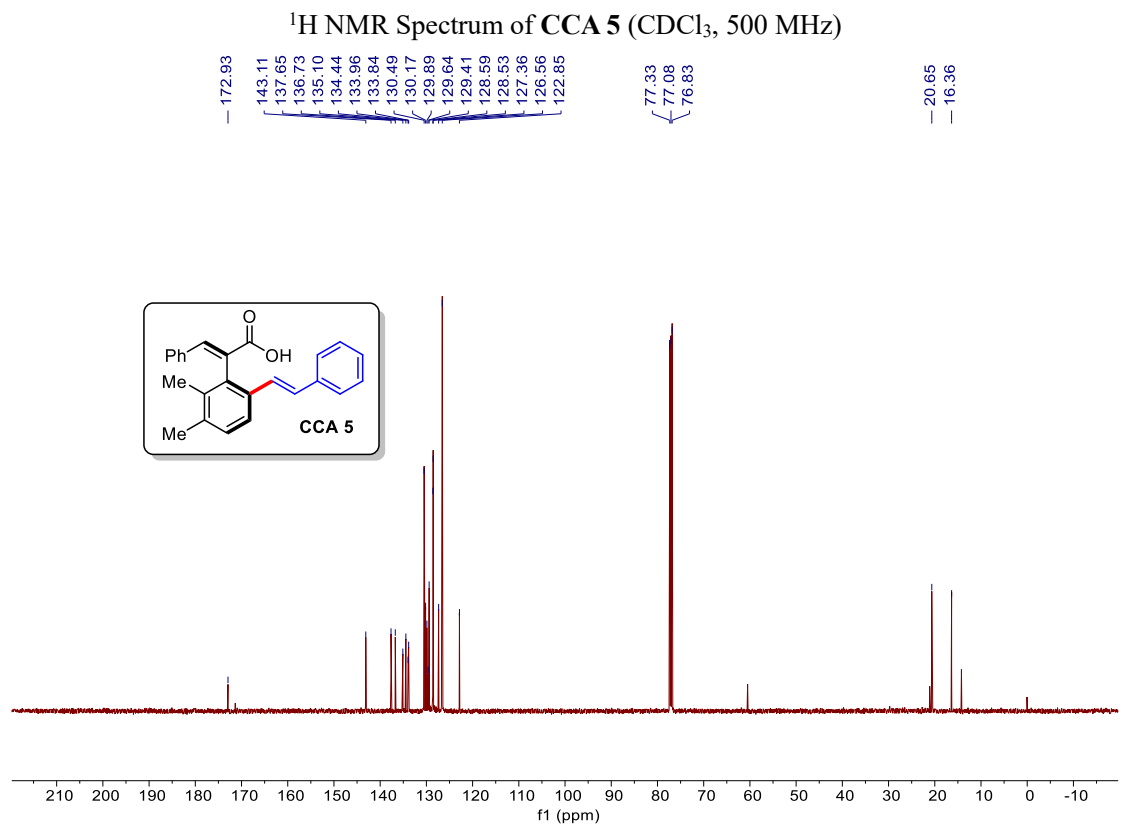
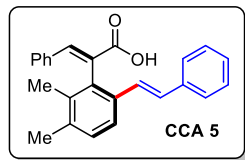
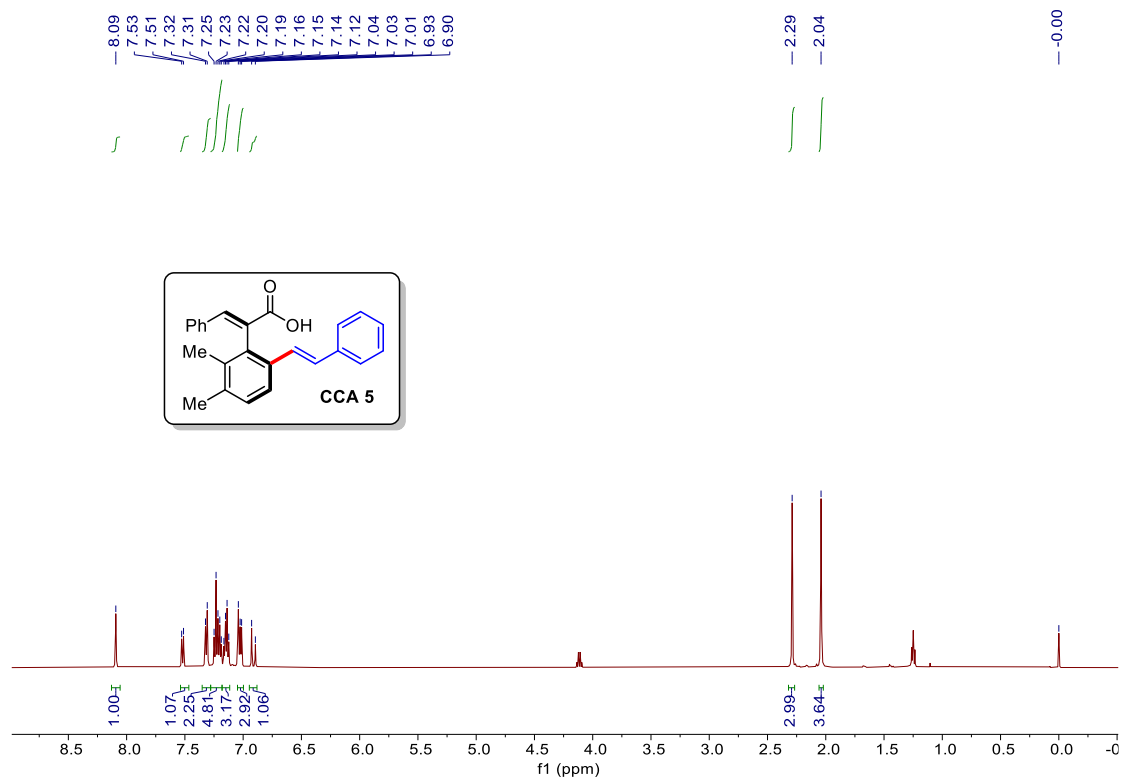


**<sup>13</sup>C NMR Spectrum of CCA 2 (CDCl<sub>3</sub>, 101 MHz)**

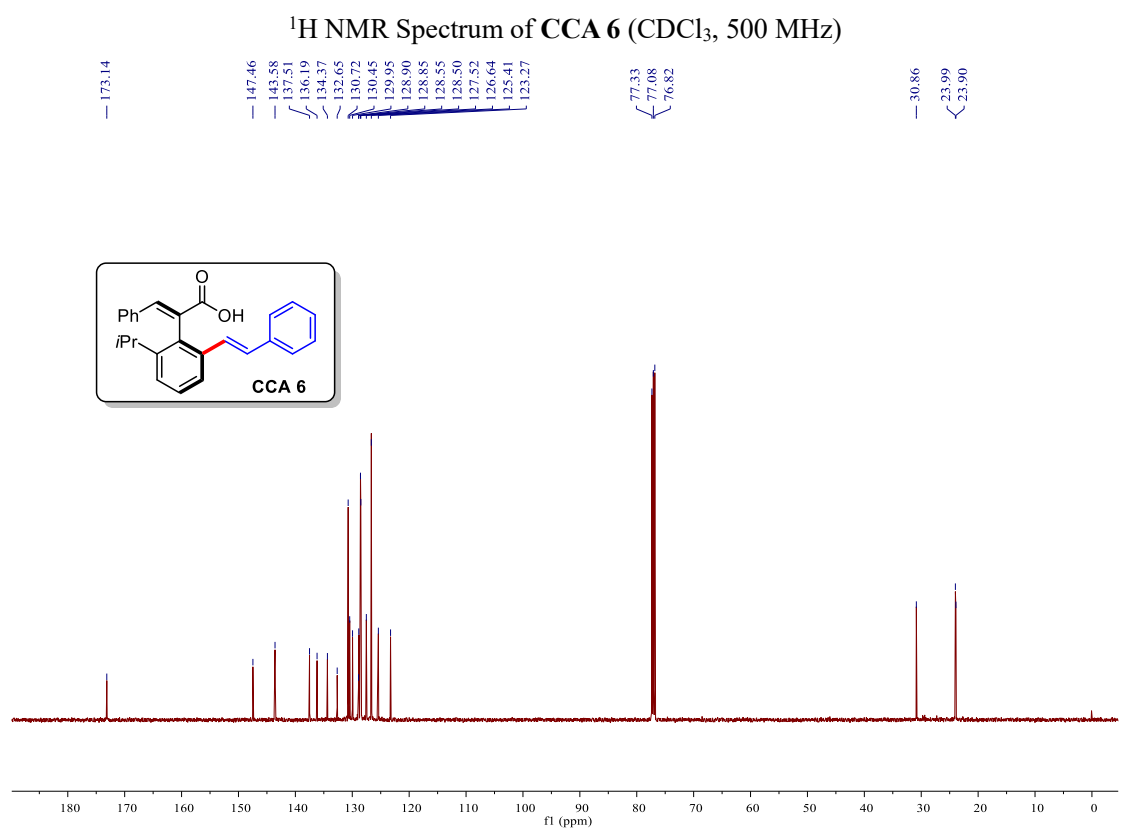
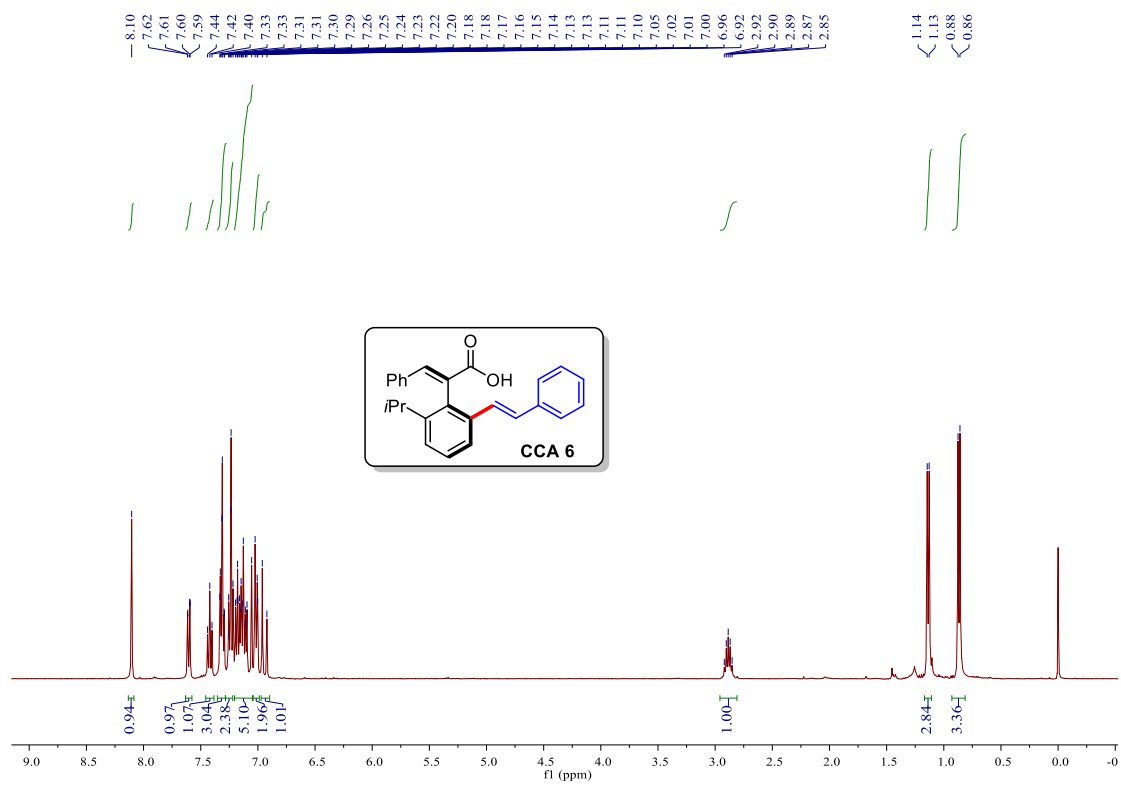








**<sup>13</sup>C NMR Spectrum of CCA 5 (CDCl<sub>3</sub>, 500 MHz)**



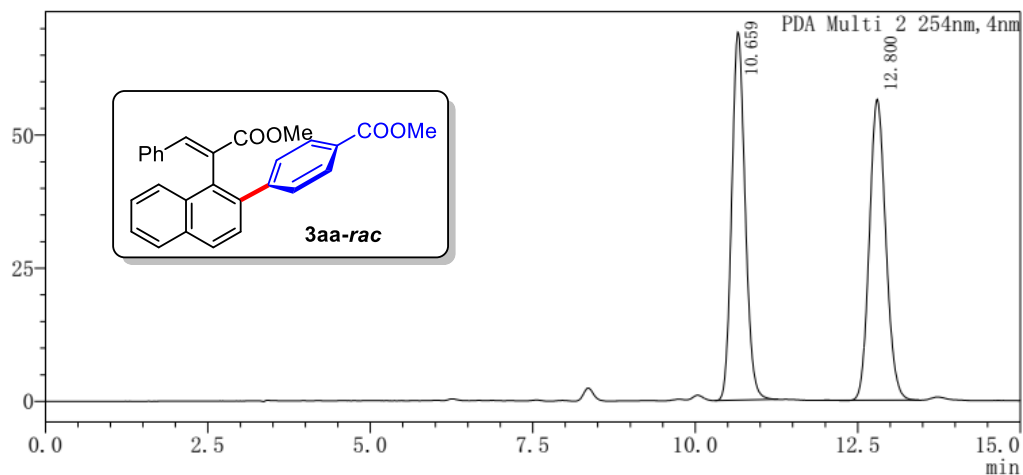
## 5. HPLC Data

### General Information:

The Chinese character “色谱图” means “Chromatogram”, “峰表” means “Peak Table”, “峰号” means “Peak Number”, “保留时间” means “Retention Time”, “面积” means “Peak Area”, “高度” means “Peak Height”, and “面积%” means “Peak Area%”.

<色谱图>

mAU



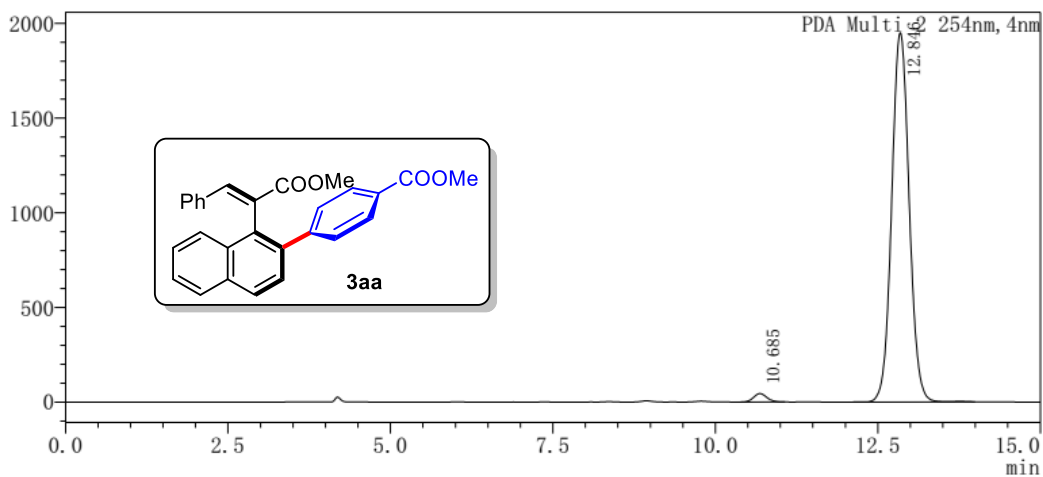
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	10.659	991669	69067	49.945
2	12.800	993854	56506	50.055
总计		1985523	125572	100.000

<色谱图>

mAU



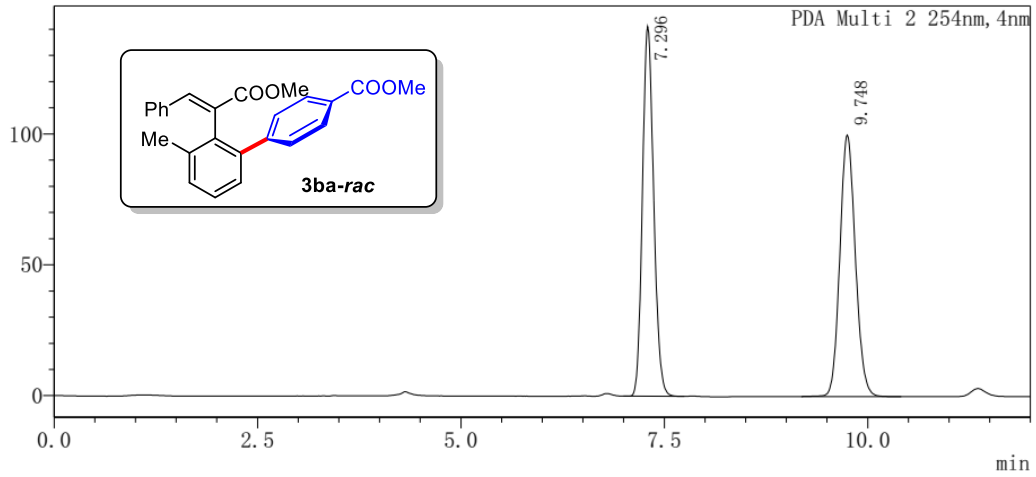
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	10.685	632626	44475	1.703
2	12.846	36513944	1948807	98.297
总计		37146570	1993282	100.000

<色谱图>

mAU



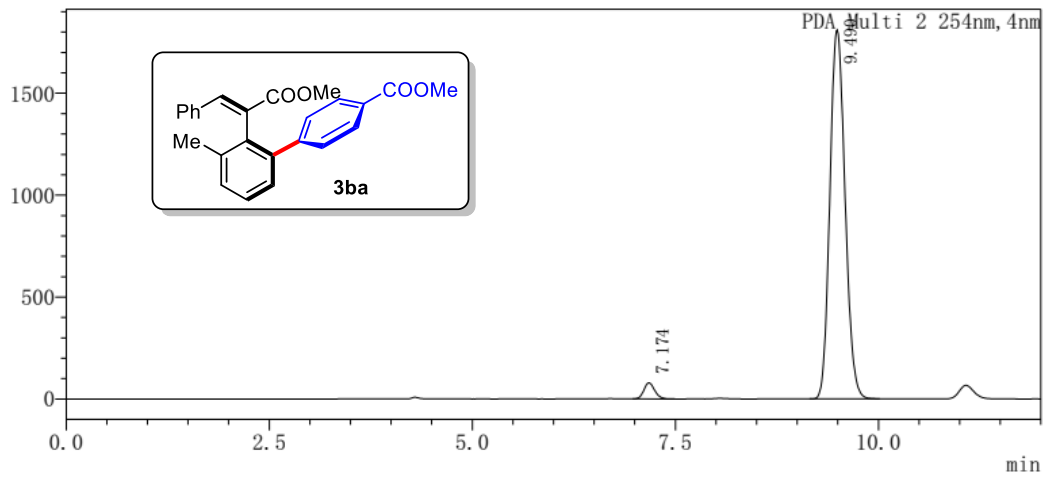
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	7.296	1359147	141217	50.619
2	9.748	1325905	99948	49.381
总计		2685051	241164	100.000

<色谱图>

mAU



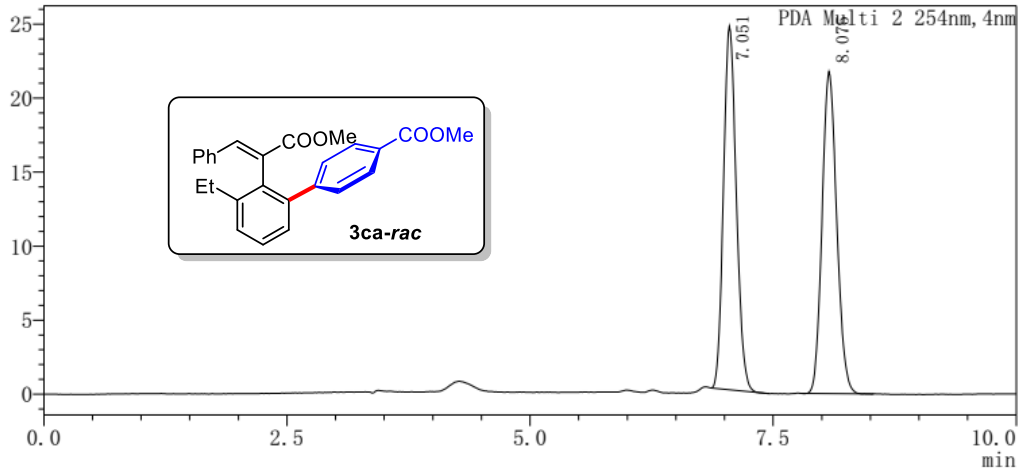
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	7.174	725083	78244	2.987
2	9.490	23549464	1810199	97.013
总计		24274548	1888444	100.000

<色谱图>

mAU



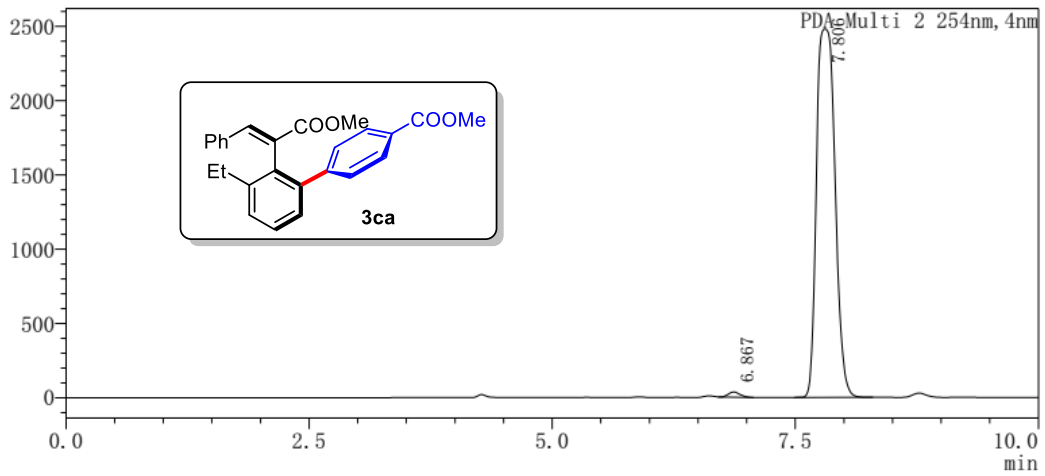
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	7.051	224929	24548	49.630
2	8.075	228281	21747	50.370
总计		453210	46296	100.000

<色谱图>

mAU



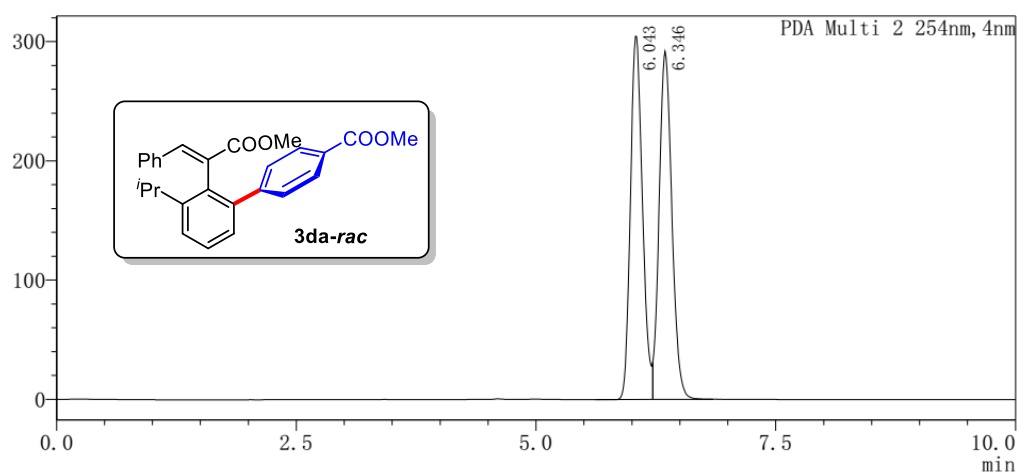
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	6.867	294522	35334	0.888
2	7.806	32872962	2478762	99.112
总计		33167484	2514097	100.000

<色谱图>

mAU



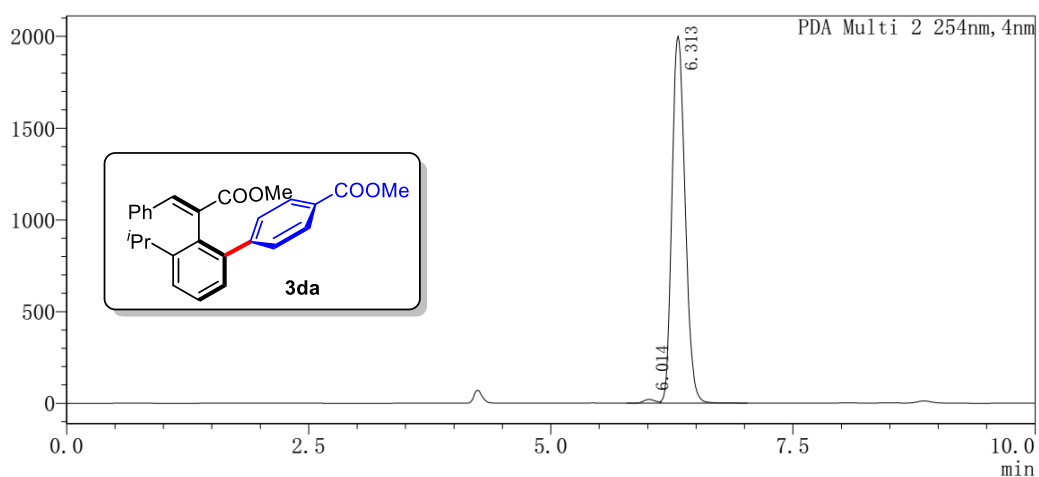
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	6.043	2679022	304684	49.940
2	6.346	2685510	291936	50.060
总计		5364532	596620	100.000

<色谱图>

mAU



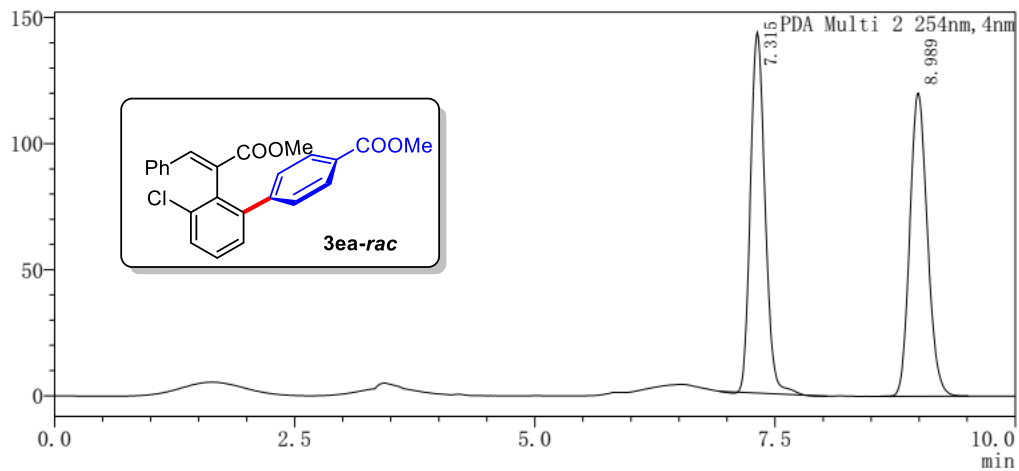
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	6.014	181481	20447	0.947
2	6.313	18986846	1999405	99.053
总计		19168327	2019852	100.000

<色谱图>

mAU



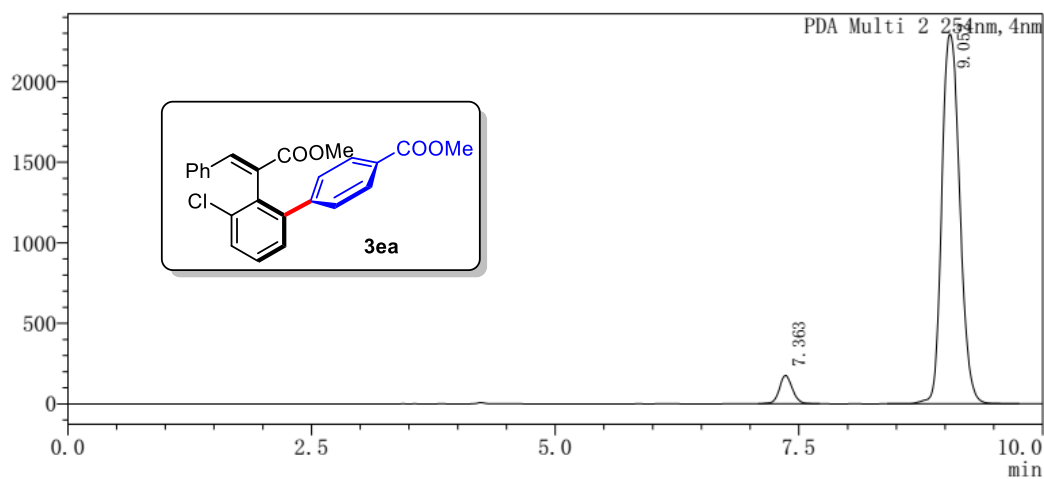
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	7.315	1514176	143021	49.701
2	8.989	1532404	120188	50.299
总计		3046580	263210	100.000

<色谱图>

mAU



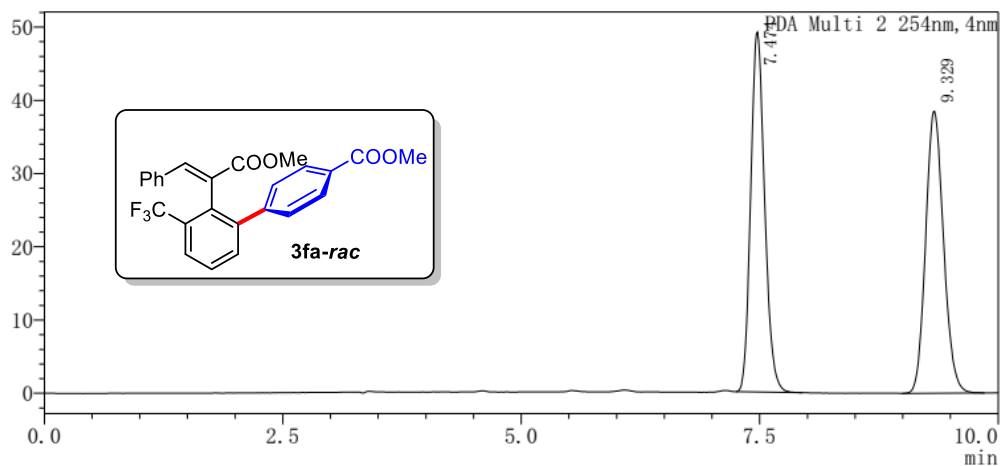
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	7.363	1640230	175987	5.280
2	9.052	29424735	2292293	94.720
总计		31064966	2468280	100.000

<色谱图>

mAU



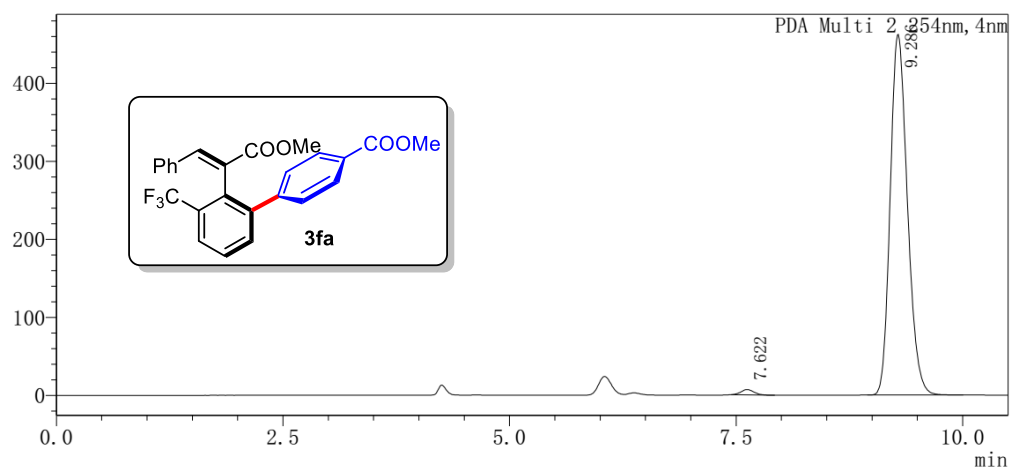
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	7.474	500533	49126	49.866
2	9.329	503214	38475	50.134
总计		1003747	87601	100.000

<色谱图>

mAU



<峰表>

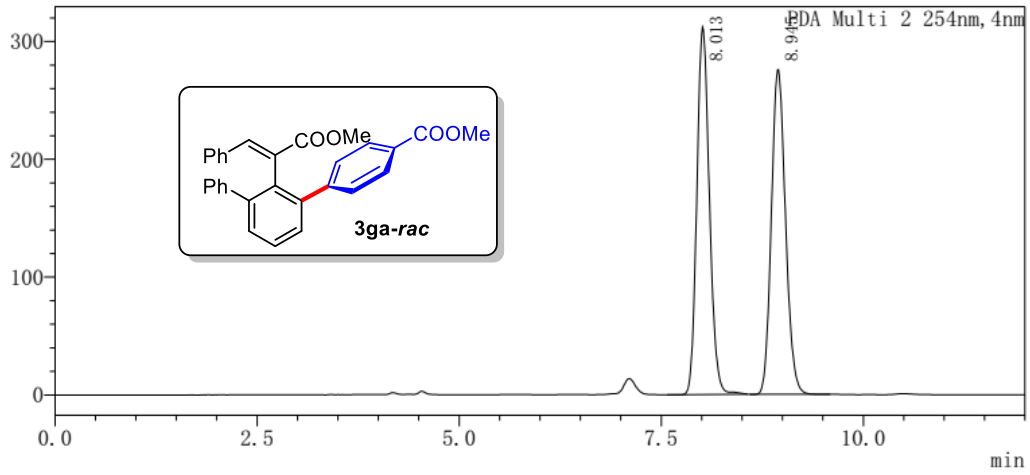
PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	7.622	66709	6753	1.082
2	9.286	6099946	462225	98.918
总计		6166655	468978	100.000



<色谱图>

mAU



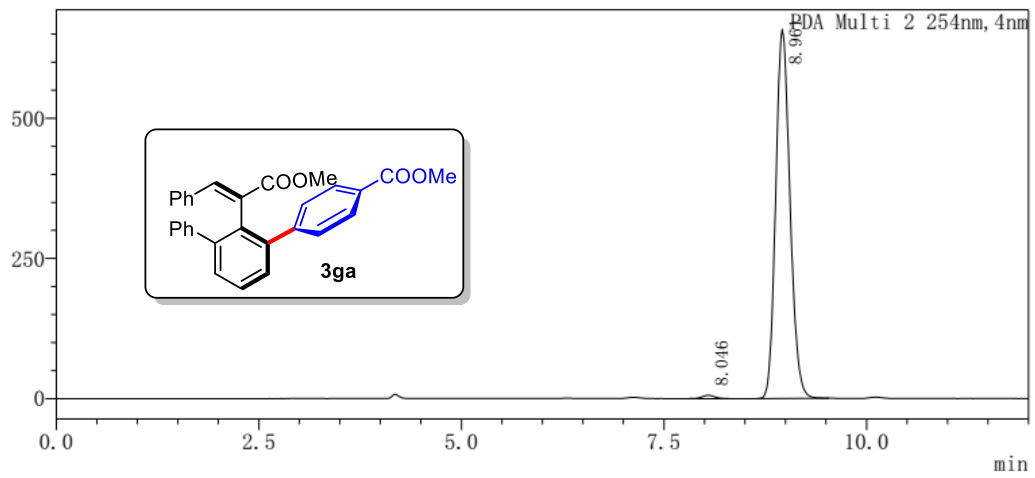
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	8.013	3374854	311788	50.081
2	8.945	3363878	275697	49.919
总计		6738733	587484	100.000

<色谱图>

mAU



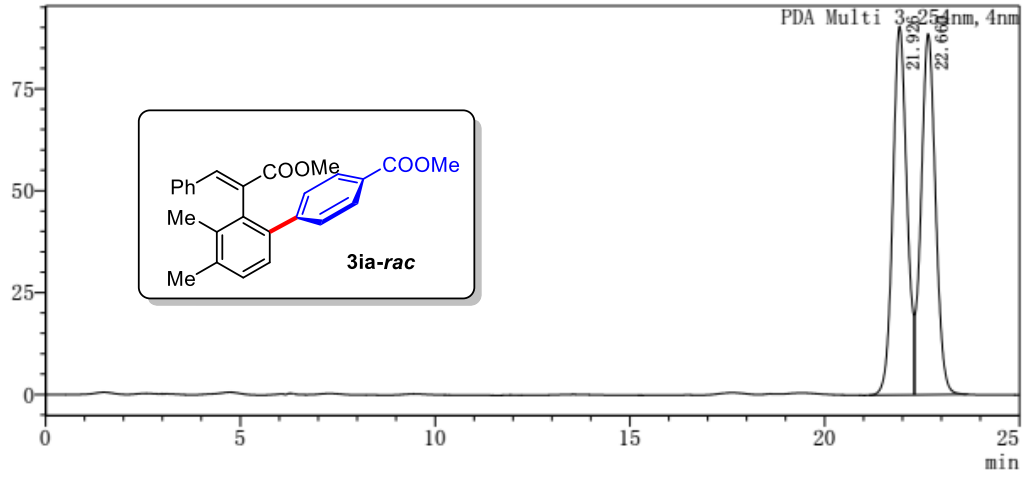
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	8.046	64323	5884	0.789
2	8.961	8087884	656511	99.211
总计		8152206	662395	100.000

<色谱图>

mAU



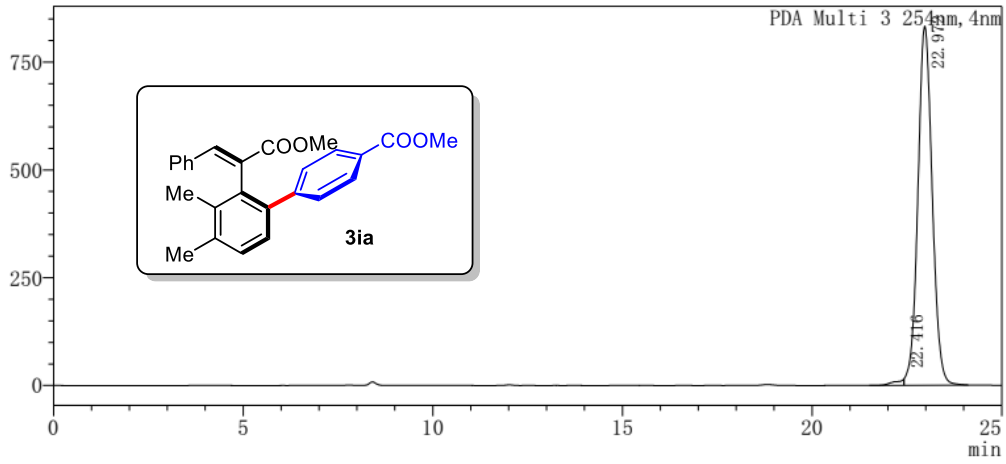
<峰表>

PDA Ch3 254nm

峰号	保留时间	面积	高度	面积%
1	21.926	2269496	90376	49.811
2	22.660	2286760	88470	50.189
总计		4556255	178846	100.000

<色谱图>

mAU



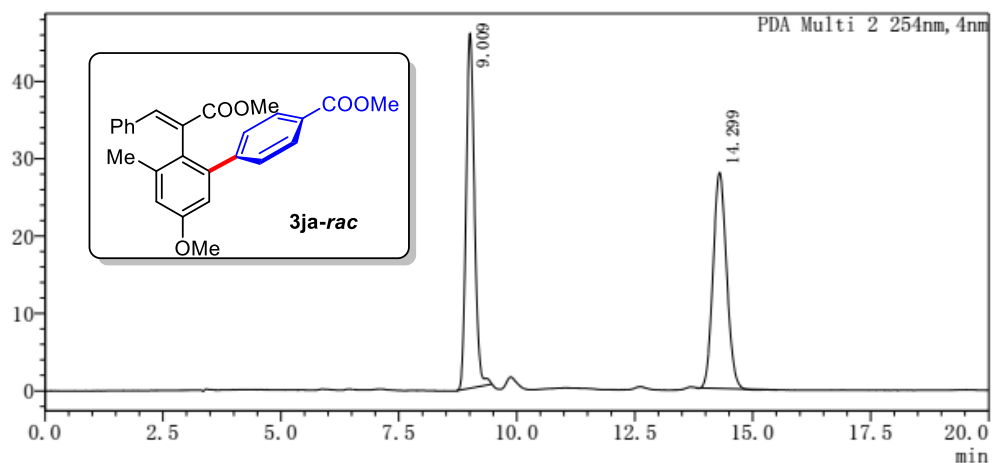
<峰表>

PDA Ch3 254nm

峰号	保留时间	面积	高度	面积%
1	22.416	236745	13720	1.071
2	22.972	21878587	832289	98.929
总计		22115332	846009	100.000

<色谱图>

mAU



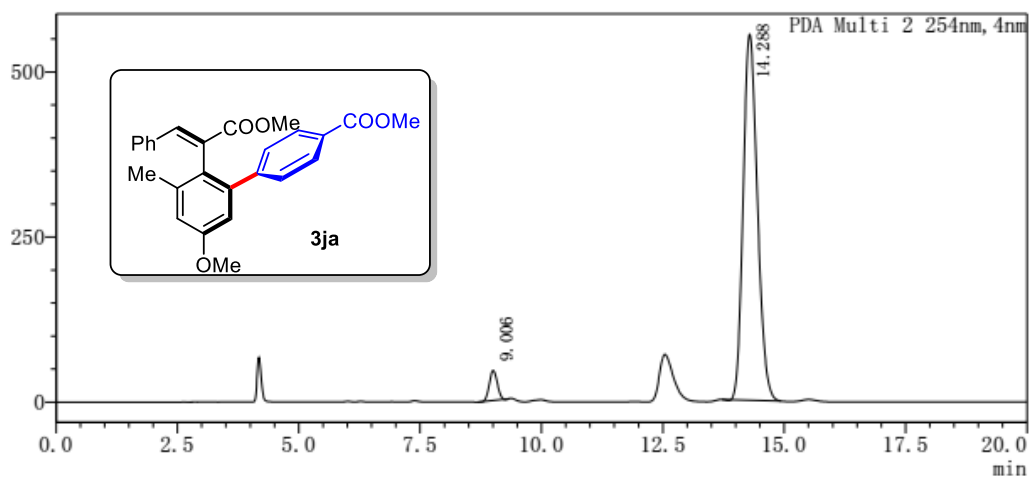
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	9.009	563353	45850	50.377
2	14.299	554919	27884	49.623
总计		1118272	73734	100.000

<色谱图>

mAU



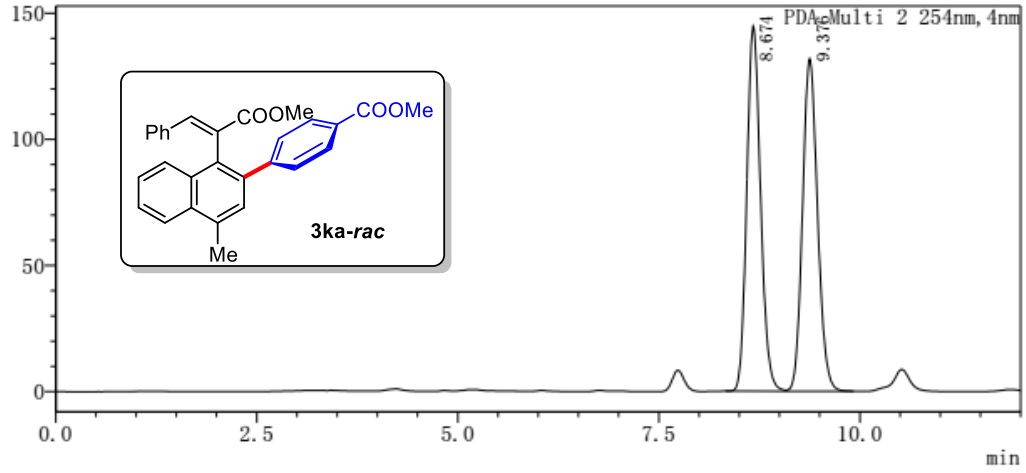
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	9.006	504688	45088	4.280
2	14.288	11287402	554202	95.720
总计		11792090	599290	100.000

<色谱图>

mAU



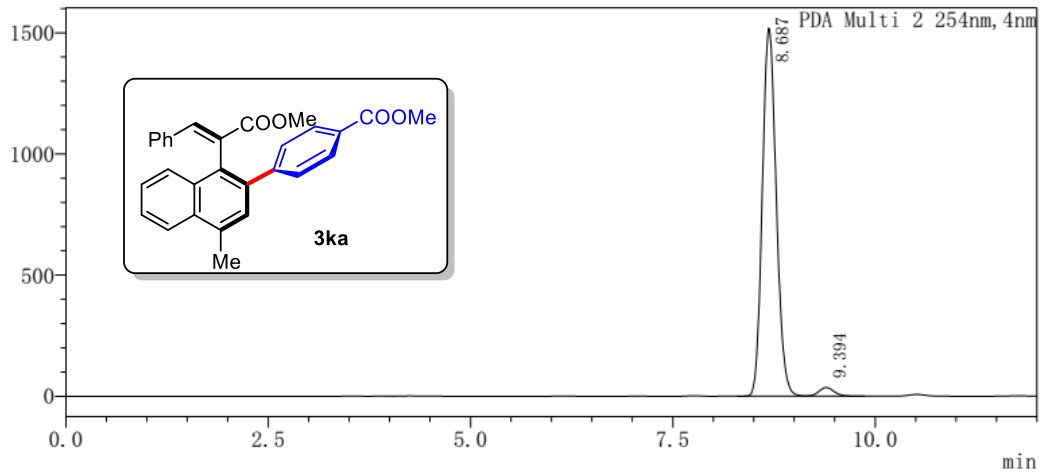
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	8.674	1726022	144539	50.150
2	9.376	1715727	131669	49.850
总计		3441749	276208	100.000

<色谱图>

mAU



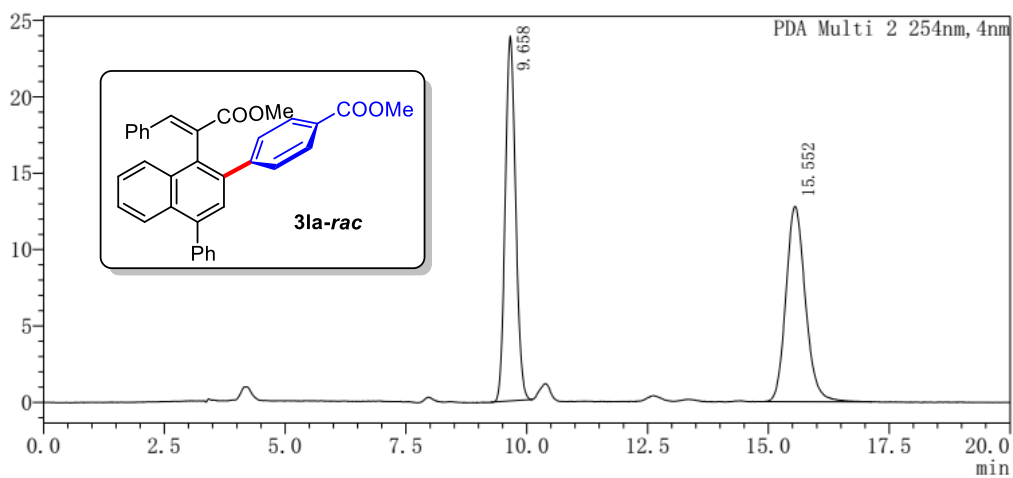
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	8.687	18182538	1517855	97.479
2	9.394	470249	35594	2.521
总计		18652788	1553449	100.000

<色谱图>

mAU



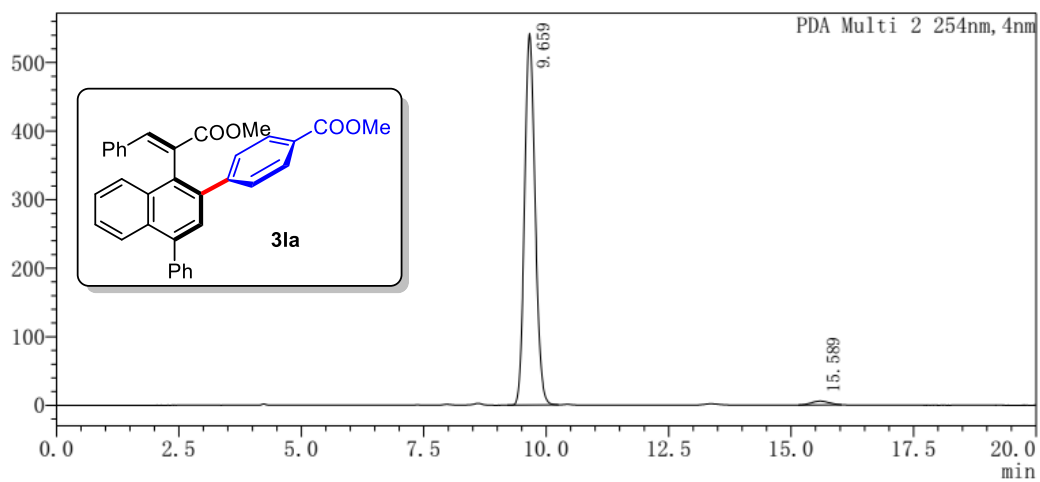
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	9.658	356889	23831	49.939
2	15.552	357761	12777	50.061
总计		714650	36608	100.000

<色谱图>

mAU



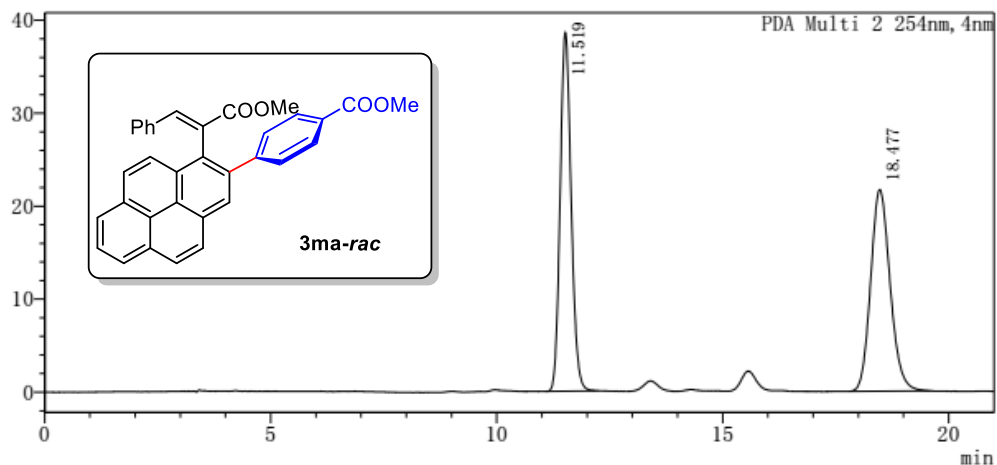
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	9.659	8131373	541384	98.330
2	15.589	138116	5496	1.670
总计		8269489	546880	100.000

<色谱图>

mAU



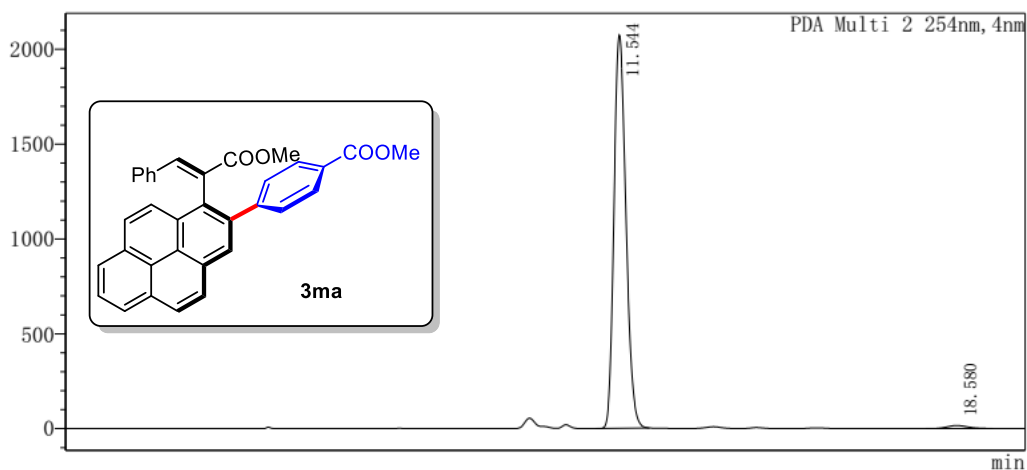
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	11.519	653454	38541	50.135
2	18.477	649922	21679	49.865
总计		1303376	60220	100.000

<色谱图>

mAU



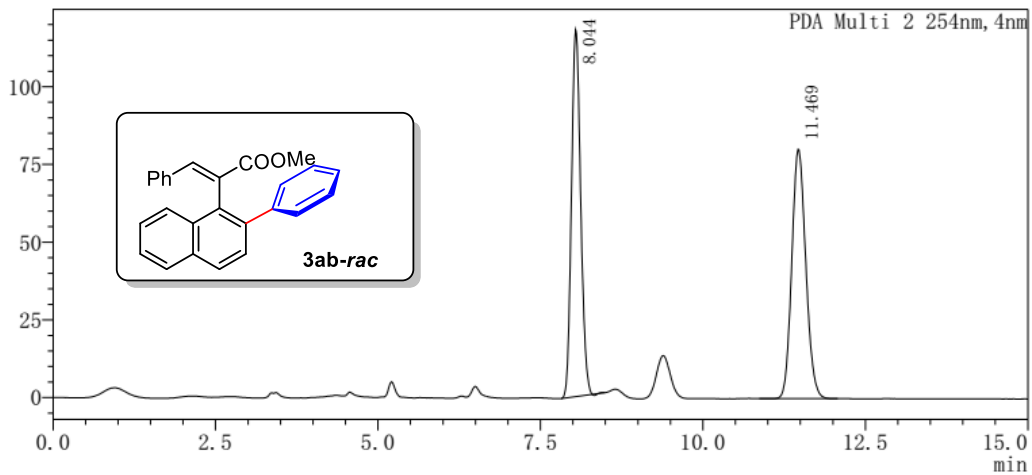
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	11.544	35952226	2072468	98.680
2	18.580	480800	16114	1.320
总计		36433026	2088582	100.000

<色谱图>

mAU



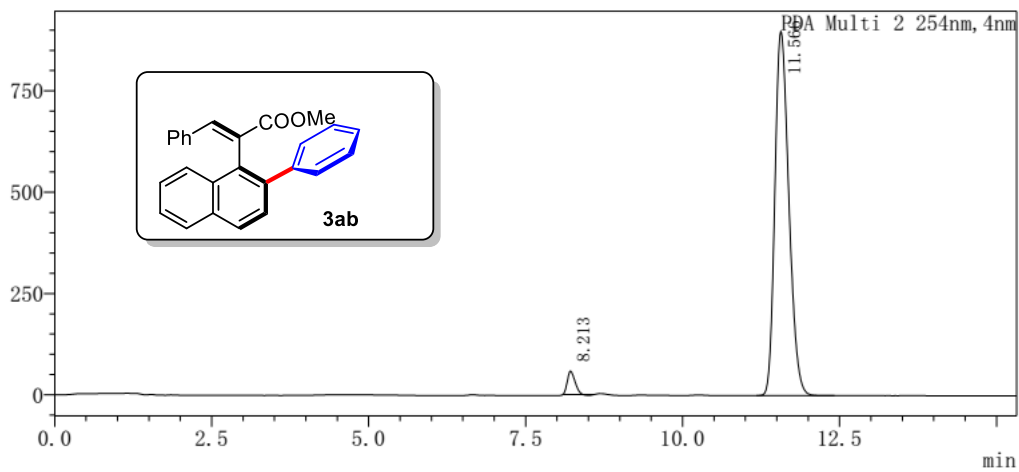
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	面积%
1	8.044	1158333	49.047
2	11.469	1203334	50.953
总计		2361667	100.000

<色谱图>

mAU



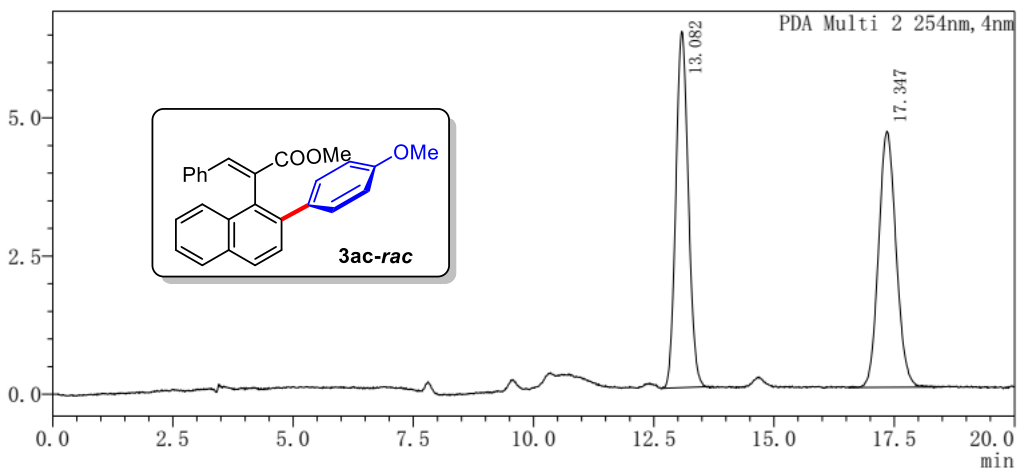
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	8.213	467989	57453	3.248
2	11.566	13940383	897994	96.752
总计		14408373	955448	100.000

<色谱图>

mAU



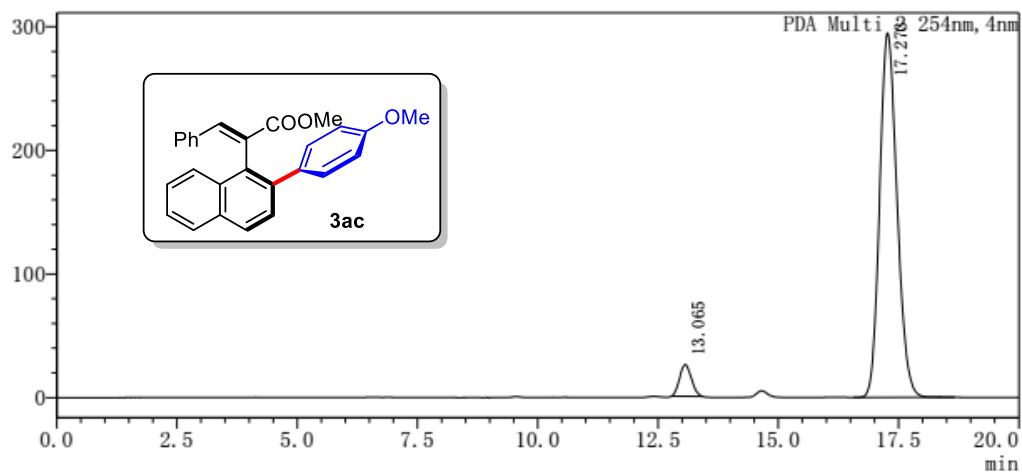
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	13.082	116621	6442	49.810
2	17.347	117509	4630	50.190
总计		234130	11072	100.000

<色谱图>

mAU



<峰表>

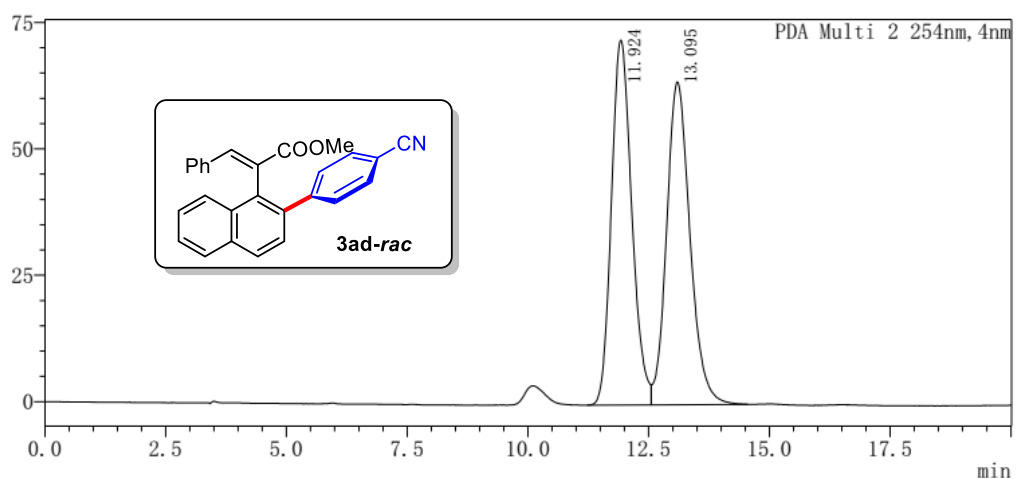
PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	13.065	439851	25616	5.600
2	17.273	7414111	294606	94.400
总计		7853961	320222	100.000



<色谱图>

mAU



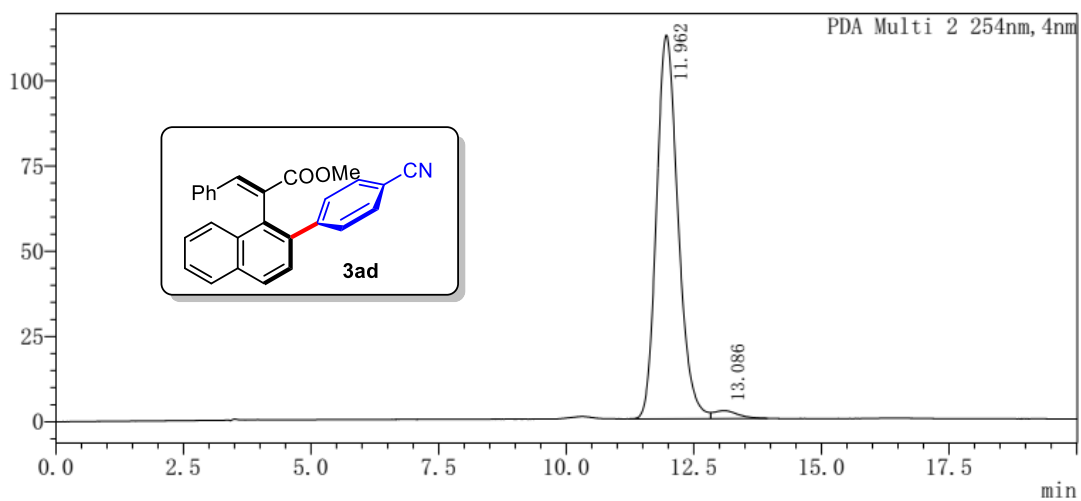
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	11.924	2119048	72187	49.583
2	13.095	2154729	63829	50.417
总计		4273777	136016	100.000

<色谱图>

mAU



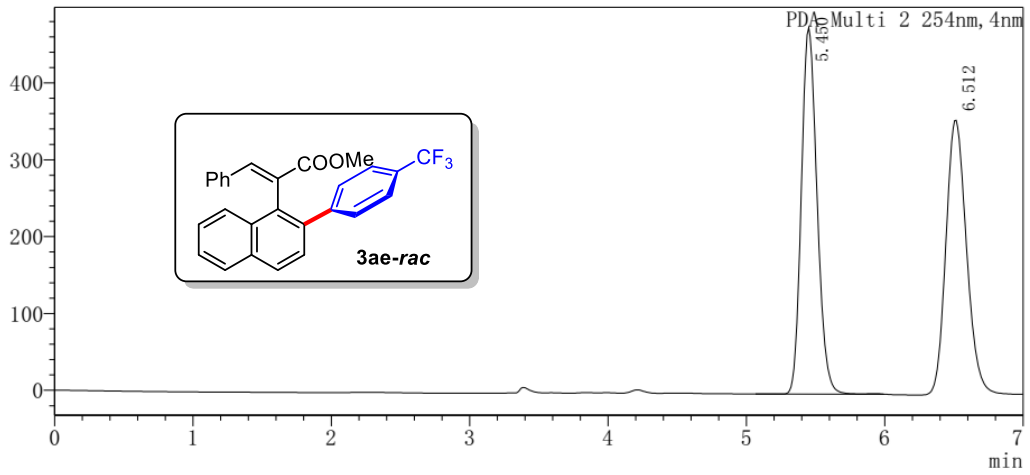
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	11.962	3301767	112452	97.778
2	13.086	75039	2299	2.222
总计		3376806	114751	100.000

<色谱图>

mAU



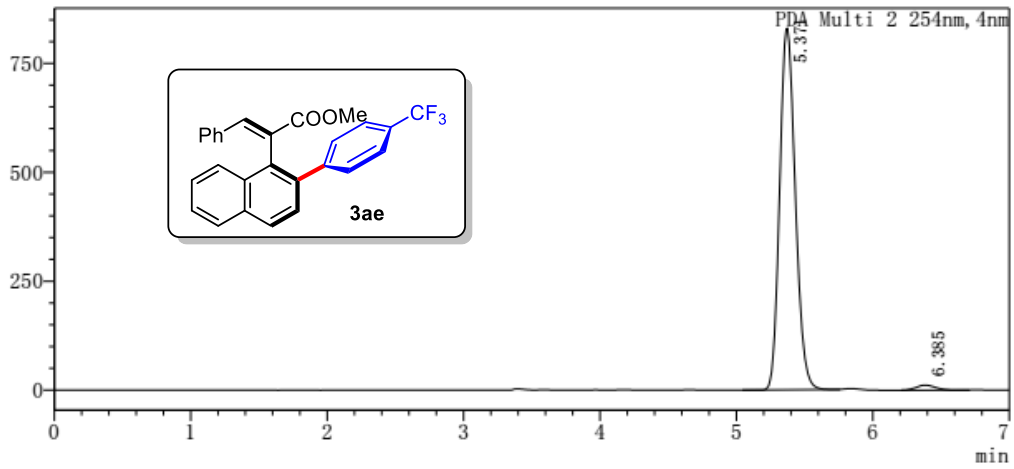
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	5.450	3763830	476521	50.564
2	6.512	3679893	356882	49.436
总计		7443723	833403	100.000

<色谱图>

mAU



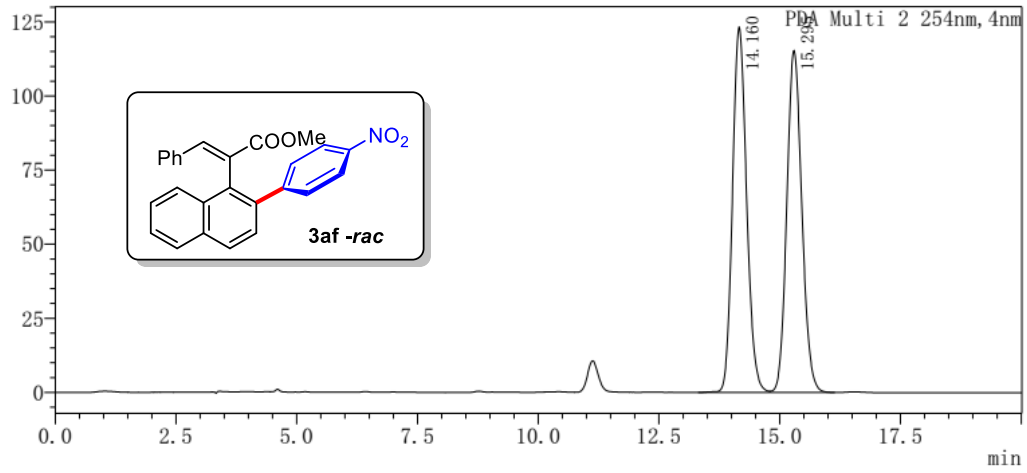
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	5.371	6610841	828311	98.417
2	6.385	106351	11200	1.583
总计		6717192	839511	100.000

<色谱图>

mAU



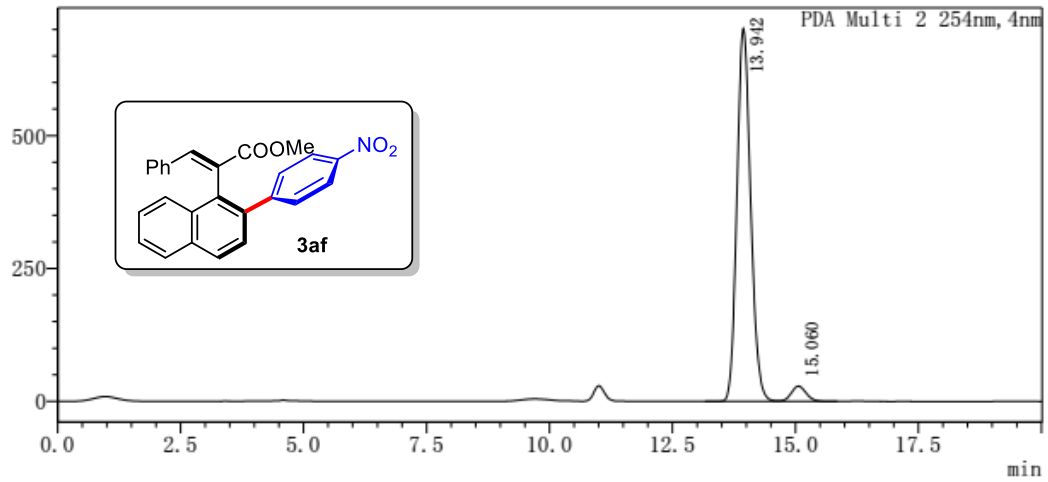
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	14.160	2504821	123275	50.070
2	15.295	2497794	115295	49.930
总计		5002615	238570	100.000

<色谱图>

mAU



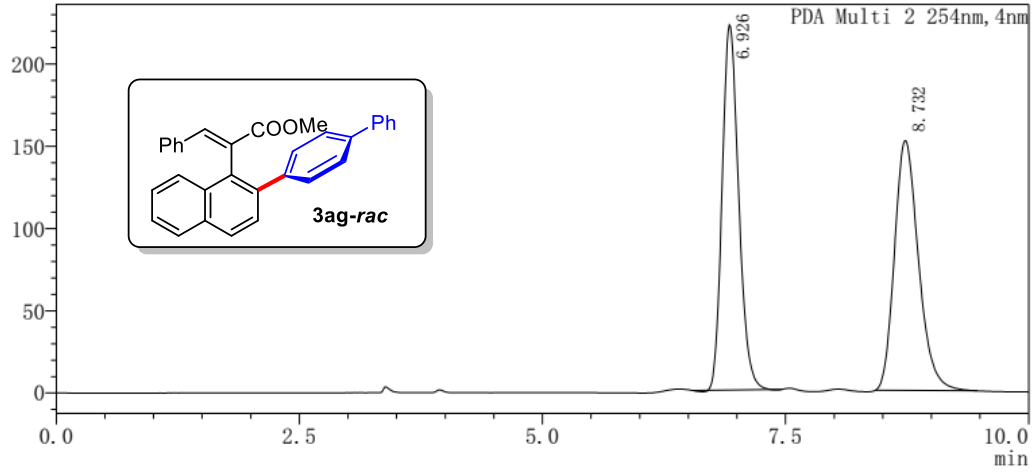
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	13.942	13613893	701233	95.728
2	15.060	607613	28714	4.272
总计		14221506	729947	100.000

<色谱图>

mAU



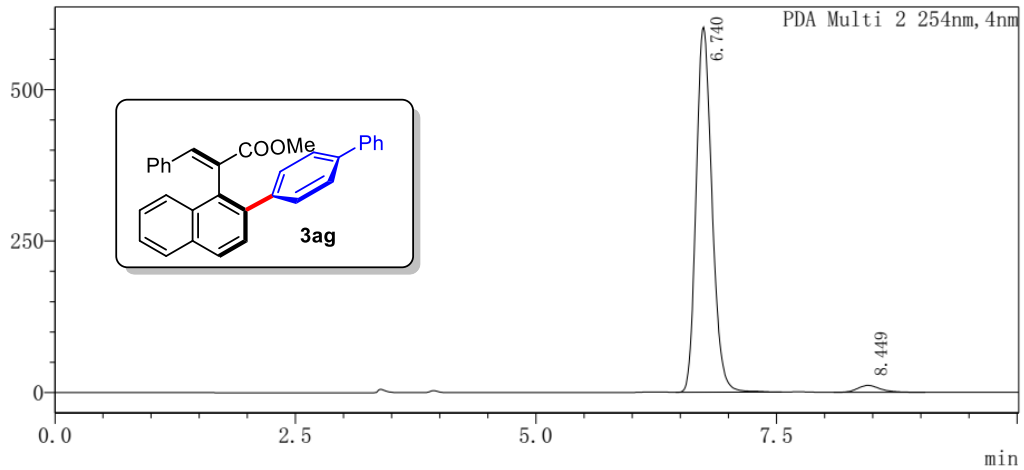
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	6.926	2620836	221892	50.093
2	8.732	2611140	151835	49.907
总计		5231975	373727	100.000

<色谱图>

mAU



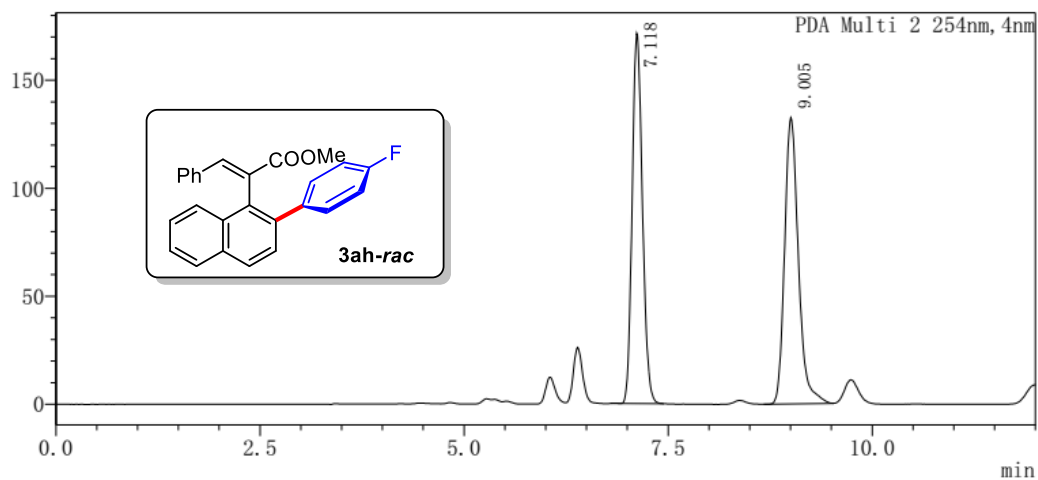
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	6.740	6920364	602365	97.333
2	8.449	189658	11420	2.667
总计		7110022	613785	100.000

<色谱图>

mAU



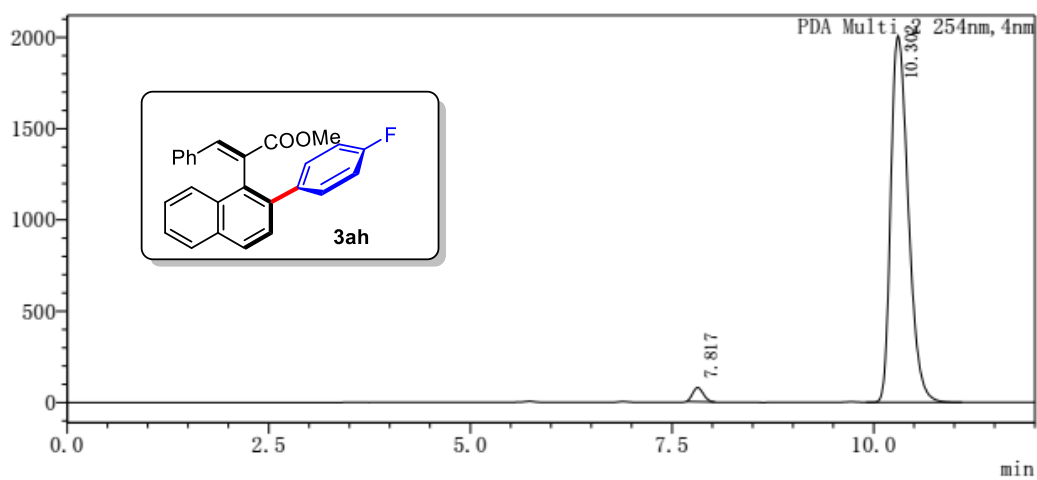
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	7.118	1495804	171211	49.016
2	9.005	1555887	132441	50.984
总计		3051691	303652	100.000

<色谱图>

mAU



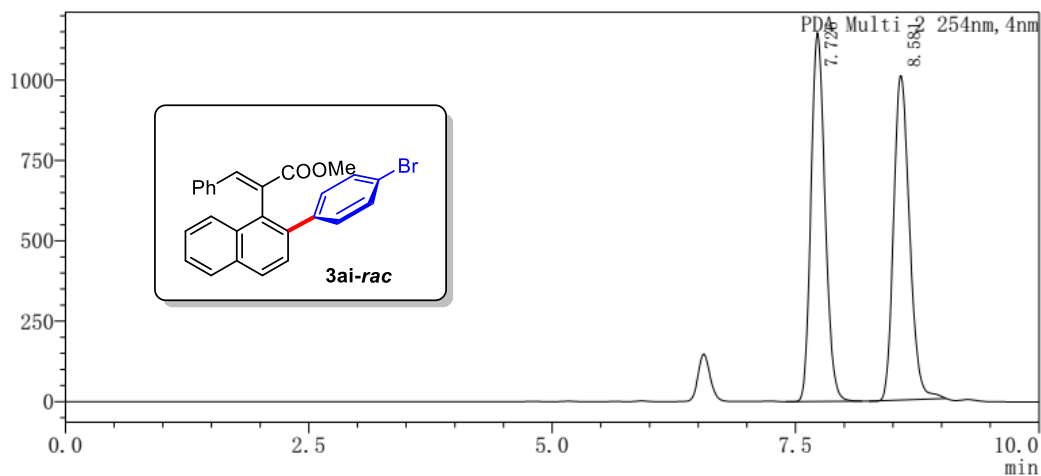
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	7.817	705638	77200	2.269
2	10.302	30396659	2007779	97.731
总计		31102296	2084979	100.000

<色谱图>

mAU



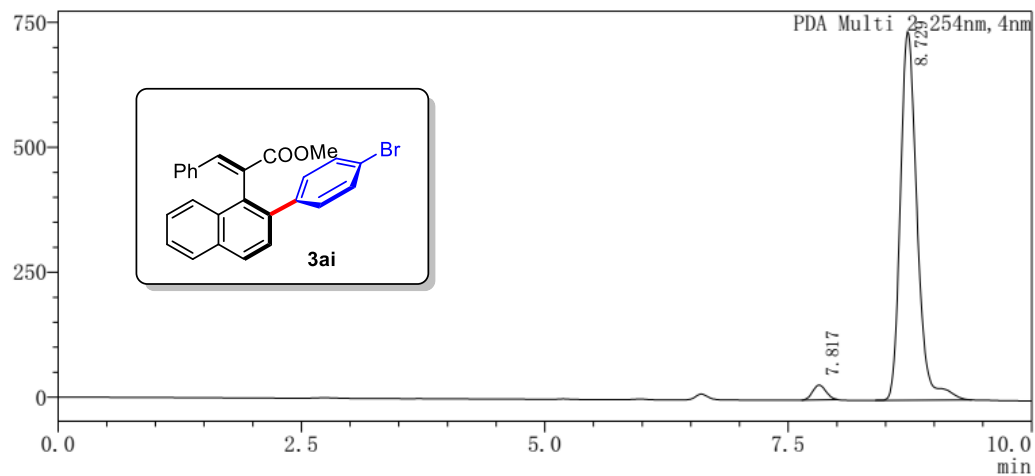
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	7.726	11515617	1146073	50.025
2	8.581	11504209	1007855	49.975
总计		23019826	2153928	100.000

<色谱图>

mAU



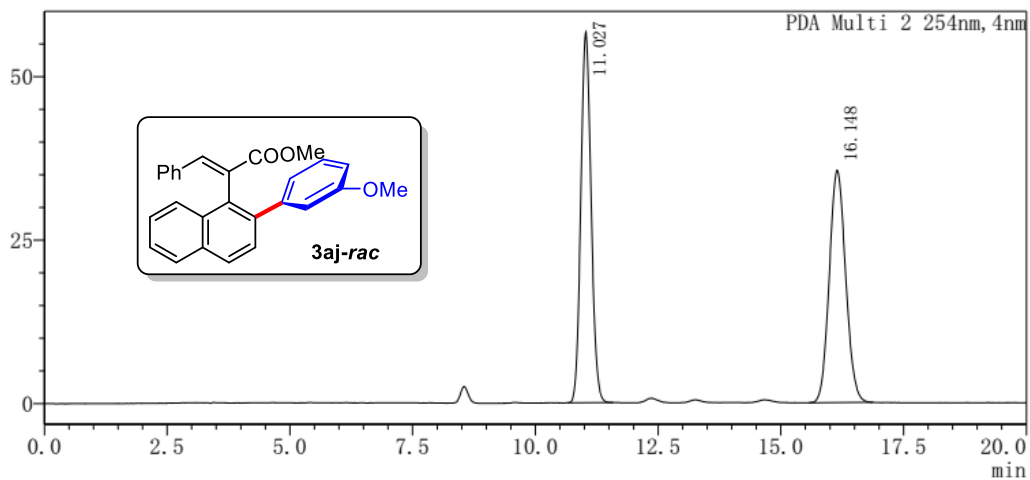
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	7.817	284109	29688	3.124
2	8.729	8809328	736971	96.876
总计		9093436	766659	100.000

<色谱图>

mAU



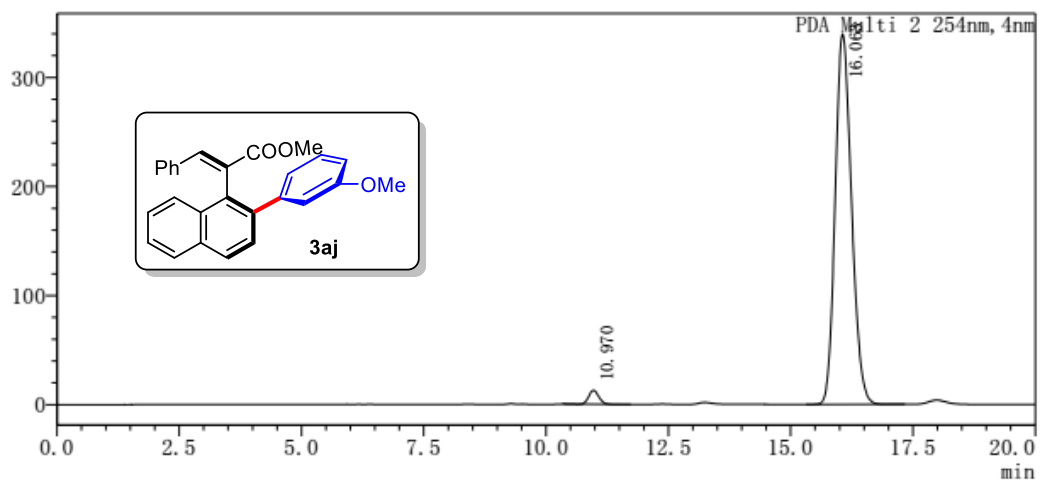
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	11.027	826593	56695	50.021
2	16.148	825905	35549	49.979
总计		1652498	92244	100.000

<色谱图>

mAU



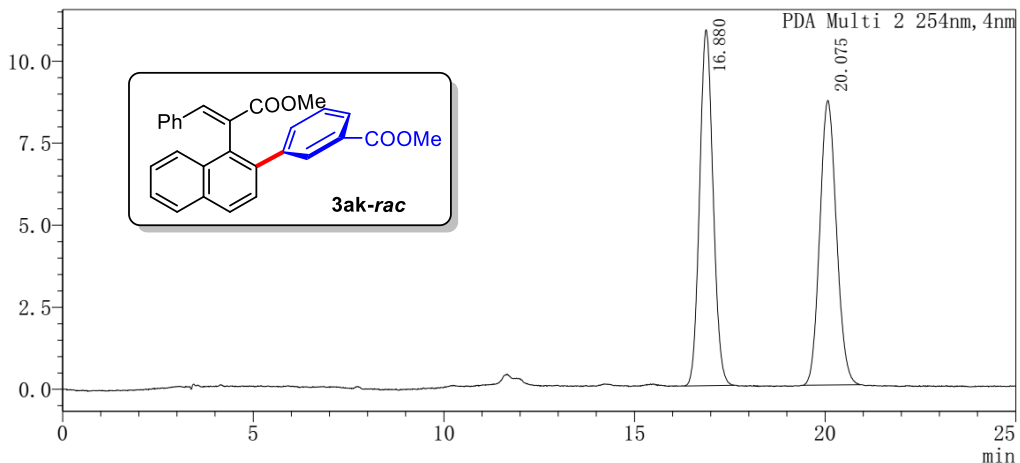
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	10.970	178560	12653	2.204
2	16.063	7922818	339446	97.796
总计		8101378	352099	100.000

<色谱图>

mAU



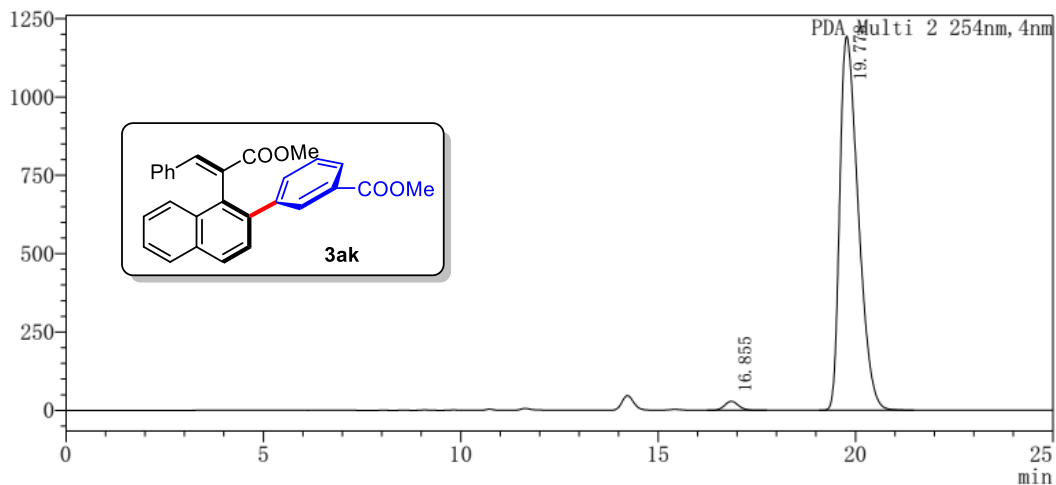
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	16.880	266855	10847	50.259
2	20.075	264101	8672	49.741
总计		530956	19519	100.000

<色谱图>

mAU



<峰表>

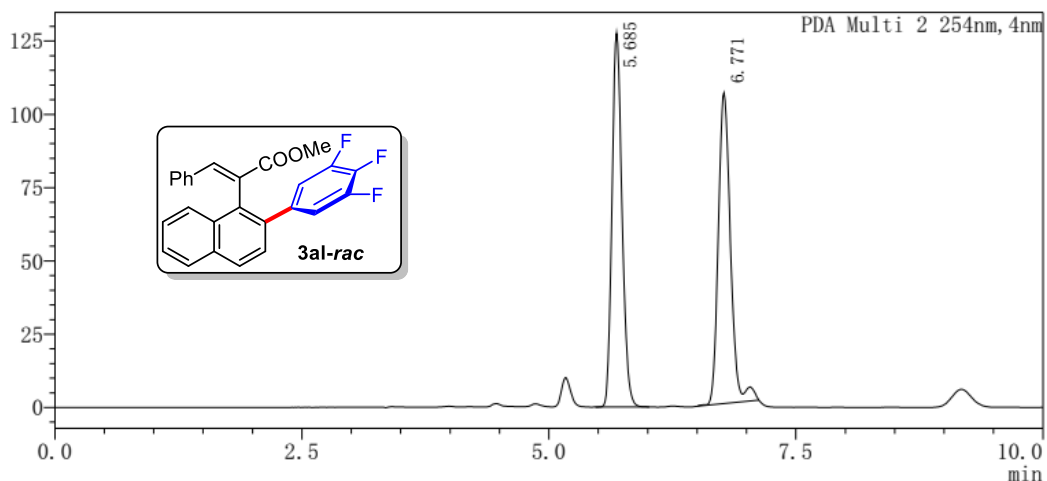
PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	16.855	702995	28689	1.776
2	19.778	38875196	1193327	98.224
总计		39578191	1222016	100.000



<色谱图>

mAU



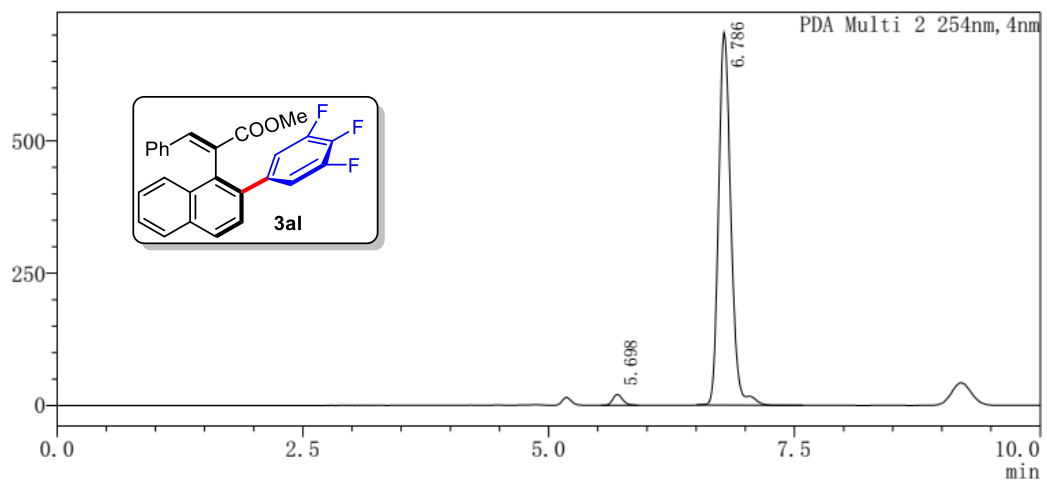
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	5.685	902374	127459	49.811
2	6.771	909232	105990	50.189
总计		1811607	233450	100.000

<色谱图>

mAU



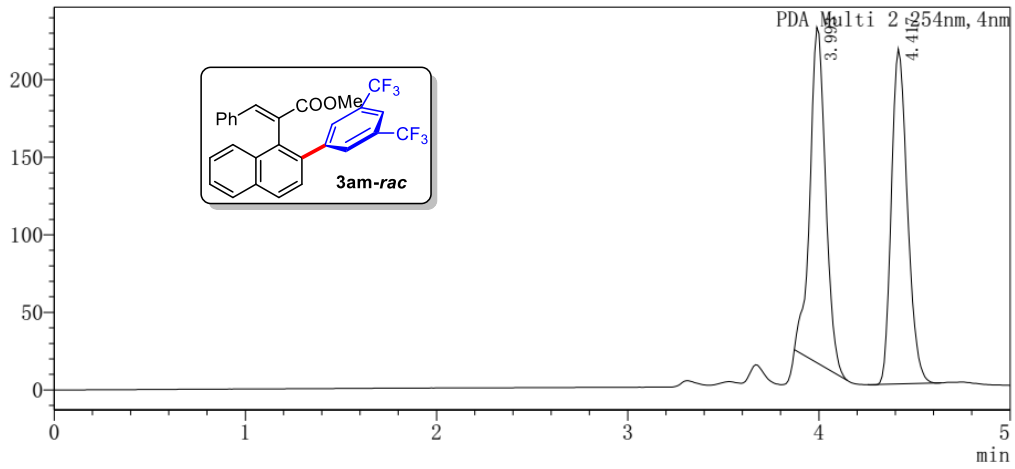
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	5.698	144286	20333	2.310
2	6.786	6101068	702674	97.690
总计		6245354	723007	100.000

<色谱图>

mAU



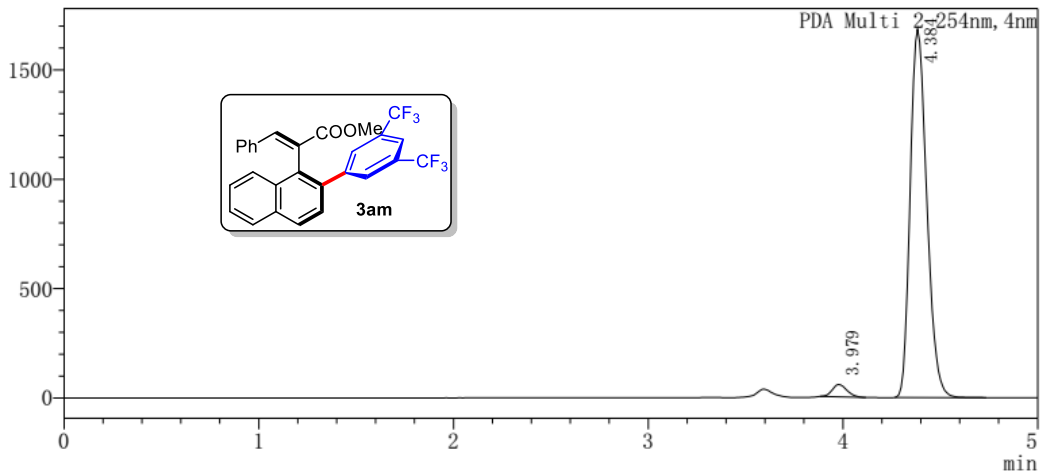
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	3.993	1229543	216391	49.384
2	4.417	1260231	216112	50.616
总计		2489774	432503	100.000

<色谱图>

mAU



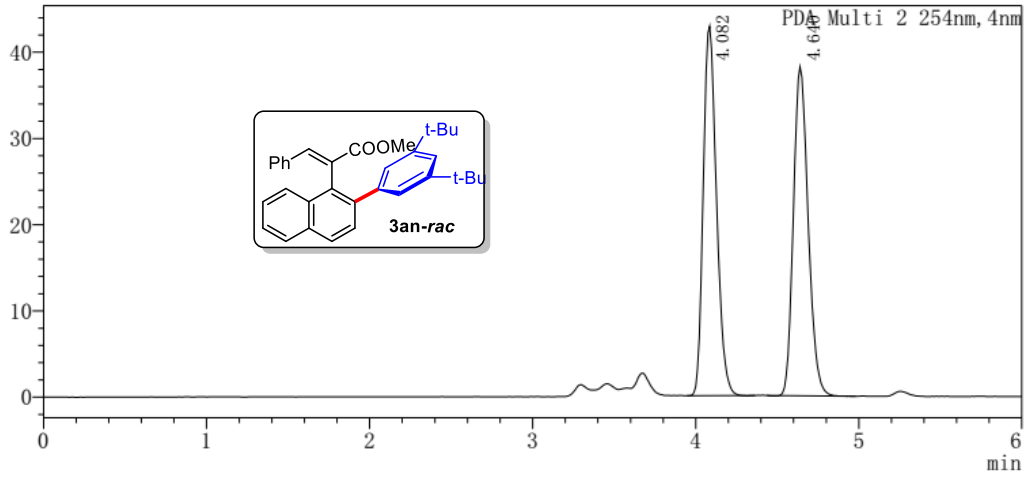
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	3.979	291438	56346	2.833
2	4.384	9995644	1684411	97.167
总计		10287082	1740757	100.000

<色谱图>

mAU



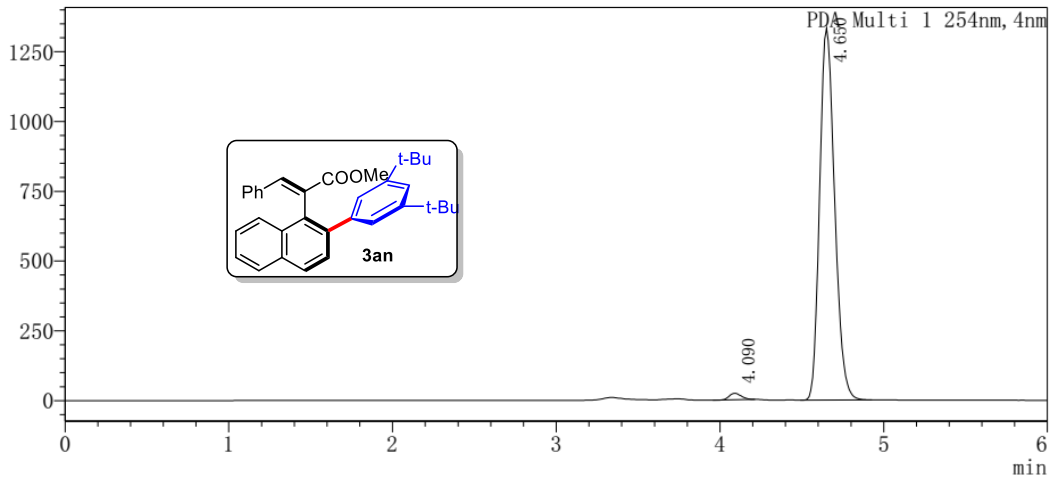
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	4.082	241064	42818	50.088
2	4.640	240218	38135	49.912
总计		481282	80952	100.000

<色谱图>

mAU



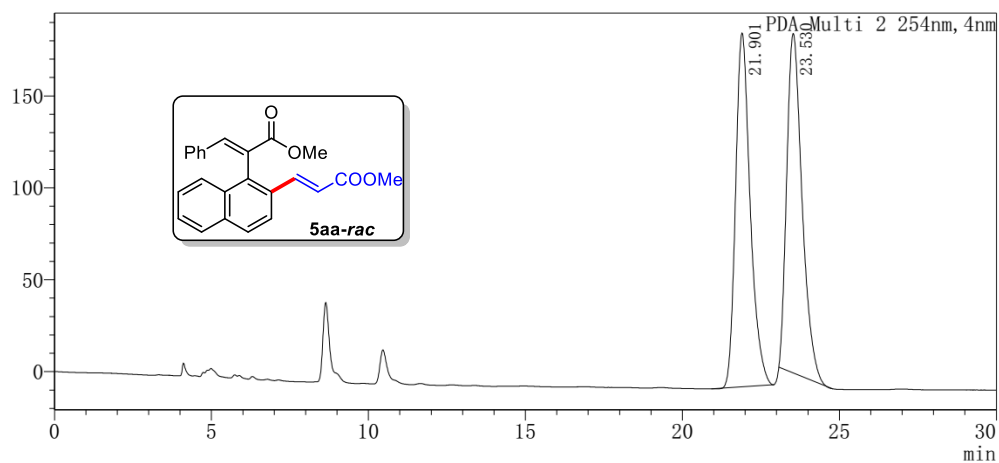
<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	面积%
1	4.090	117348	22599	0.000	1.360
2	4.650	8508210	1332122	0.000	98.640
总计		8625558	1354721		100.000

<色谱图>

mAU



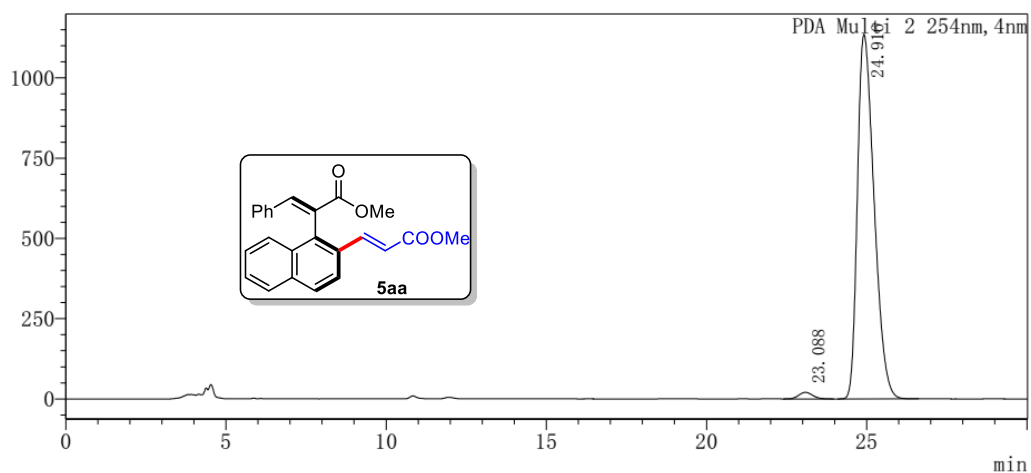
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	21.901	6239385	192415	49.944
2	23.530	6253478	184703	50.056
总计		12492863	377118	100.000

<色谱图>

mAU



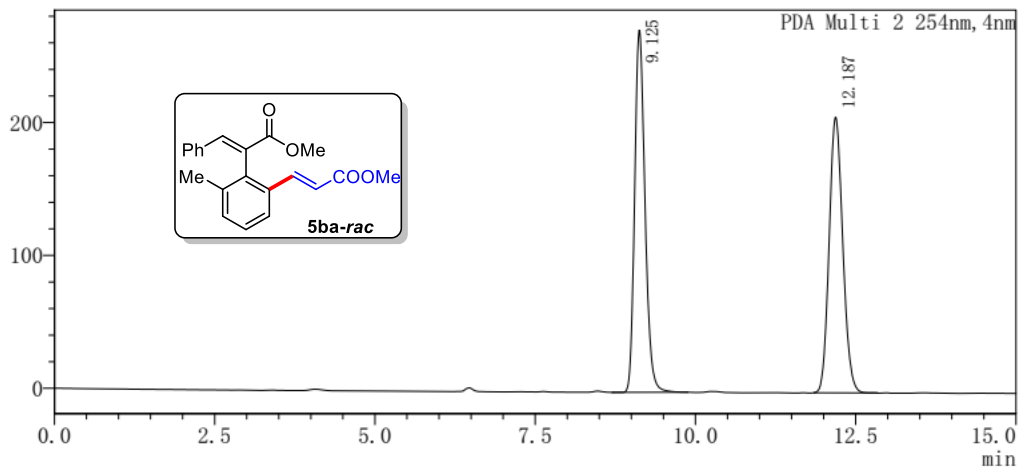
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	23.088	617452	20417	1.480
2	24.916	41089541	1135557	98.520
总计		41706993	1155974	100.000

<色谱图>

mAU



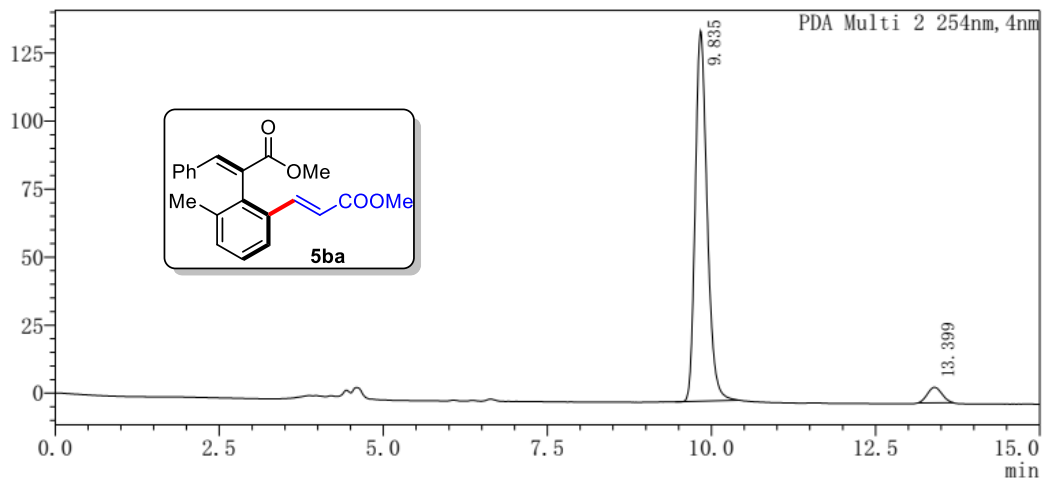
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	9.125	3068384	272482	49.998
2	12.187	3068652	207395	50.002
总计		6137036	479877	100.000

<色谱图>

mAU



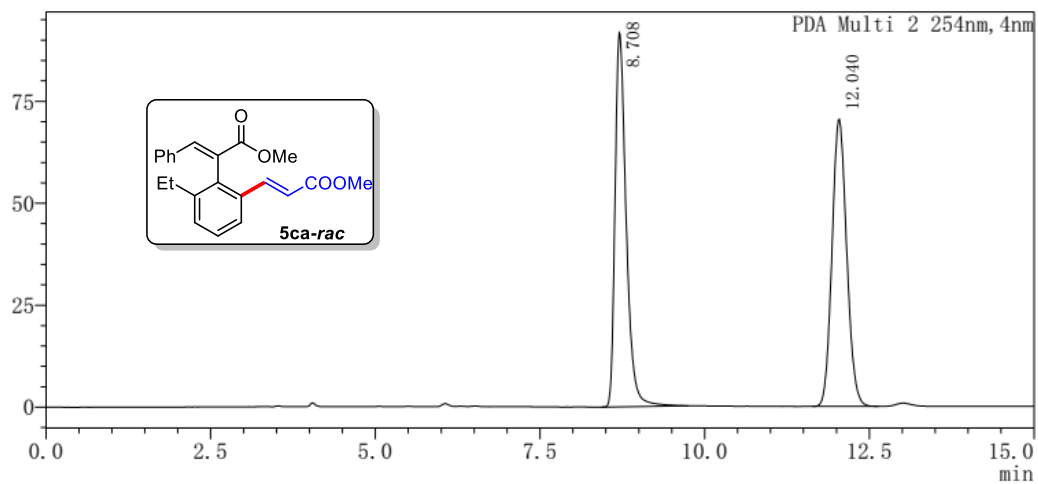
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	9.835	1718070	135961	95.190
2	13.399	86816	5680	4.810
总计		1804887	141641	100.000

<色谱图>

mAU



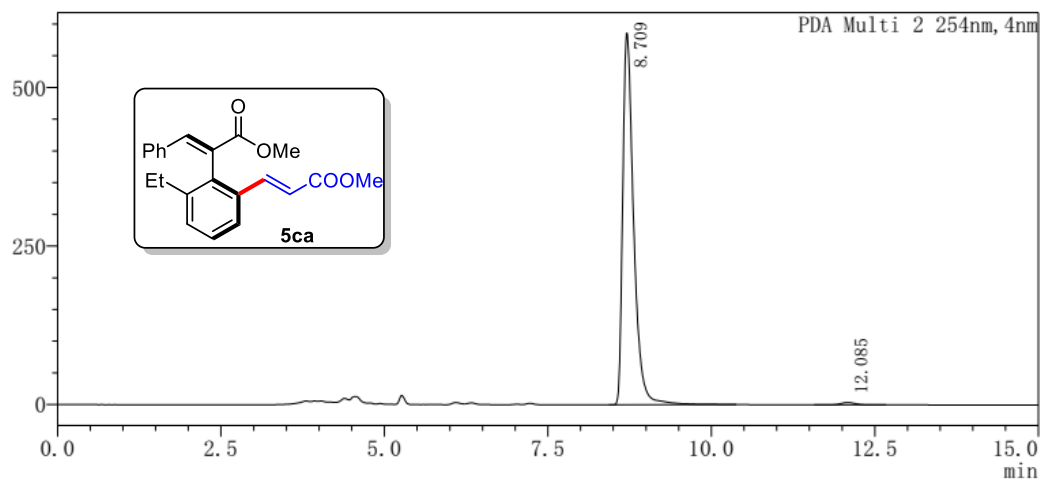
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	8.708	1078402	91688	49.656
2	12.040	1093324	70388	50.344
总计		2171726	162077	100.000

<色谱图>

mAU



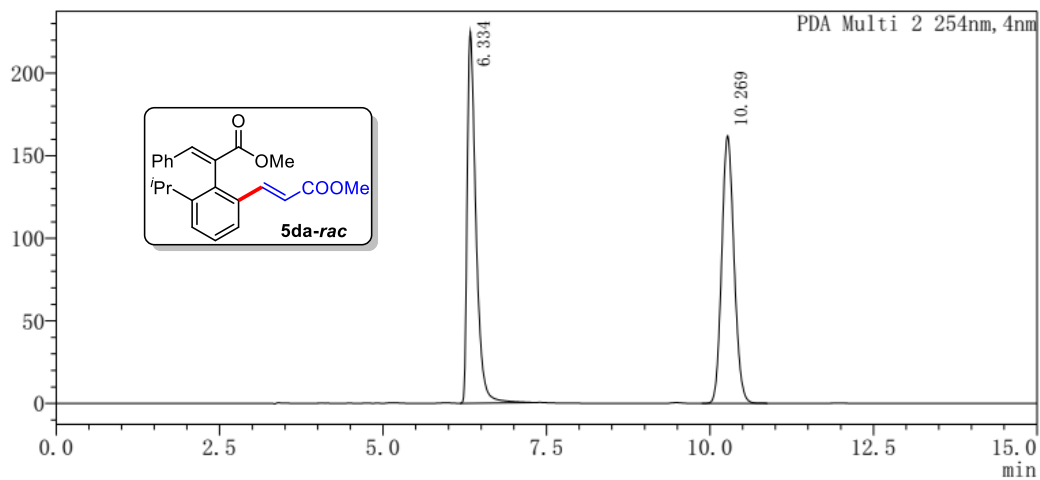
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	8.709	6828216	585628	99.180
2	12.085	56480	3692	0.820
总计		6884696	589319	100.000

<色谱图>

mAU



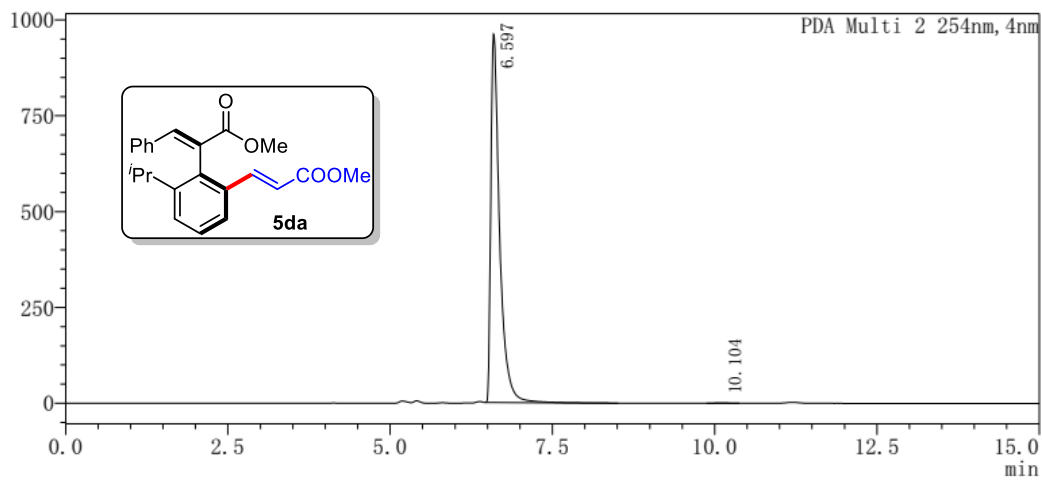
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	6.334	2090807	224734	49.589
2	10.269	2125475	162032	50.411
总计		4216282	386766	100.000

<色谱图>

mAU



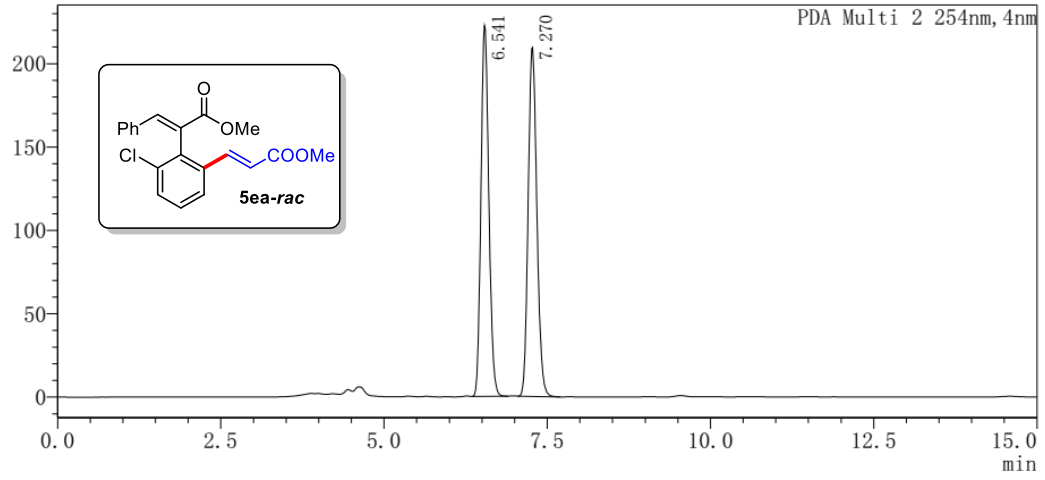
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	6.597	9126999	960675	99.838
2	10.104	14809	1201	0.162
总计		9141809	961876	100.000

<色谱图>

mAU



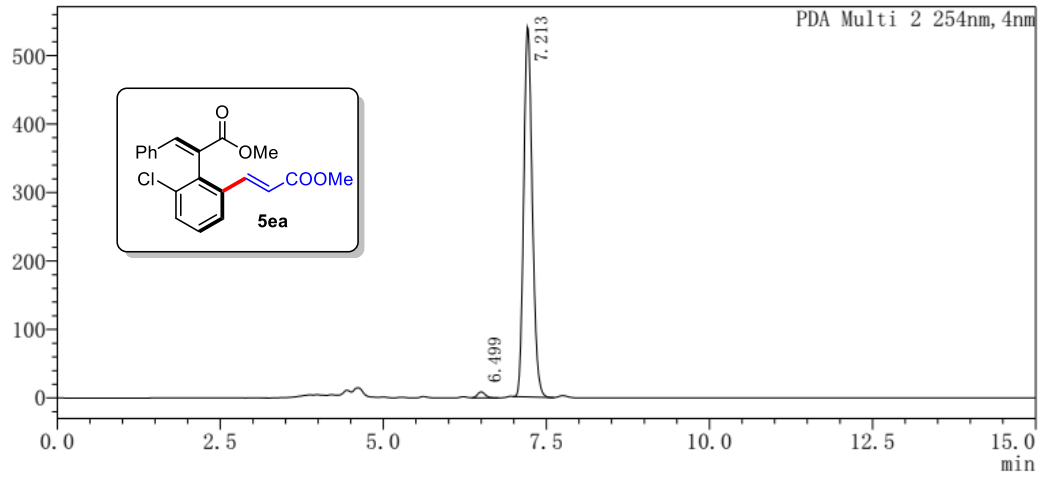
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	6.541	1866943	222274	49.137
2	7.270	1932491	209192	50.863
总计		3799434	431466	100.000

<色谱图>

mAU



<峰表>

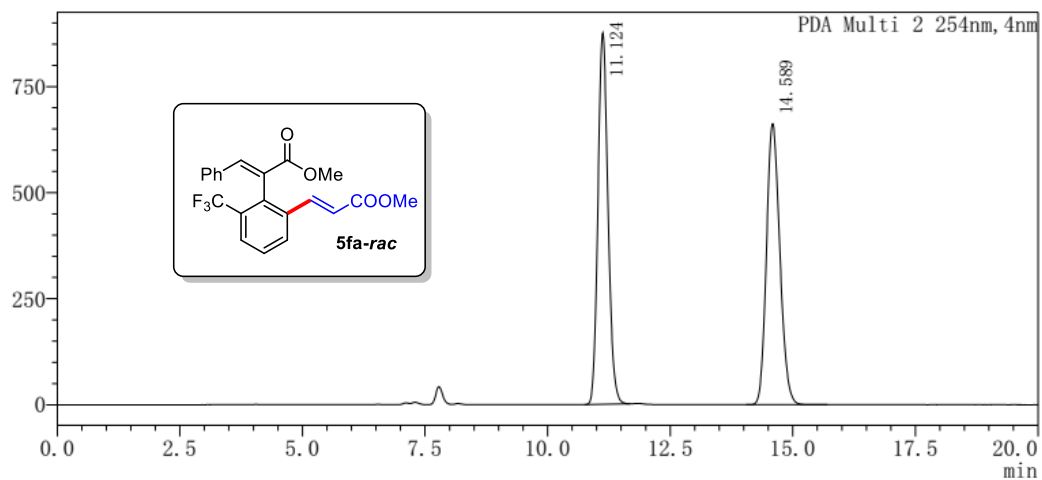
PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	6.499	69067	8570	1.370
2	7.213	4971105	539478	98.630
总计		5040172	548047	100.000



<色谱图>

mAU



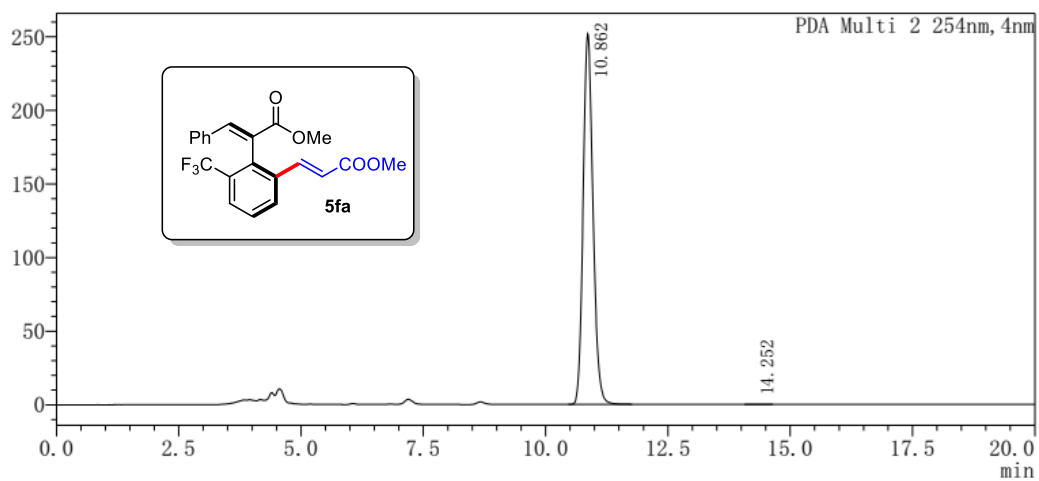
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	11.124	12476486	874973	49.824
2	14.589	12564381	662245	50.176
总计		25040867	1537218	100.000

<色谱图>

mAU



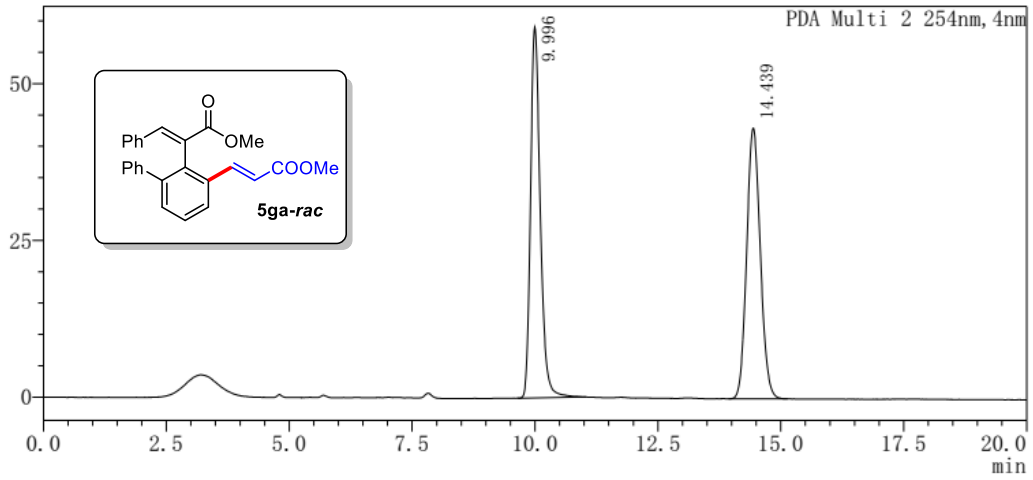
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	10.862	3530464	251438	99.961
2	14.252	1370	89	0.039
总计		3531834	251528	100.000

<色谱图>

mAU



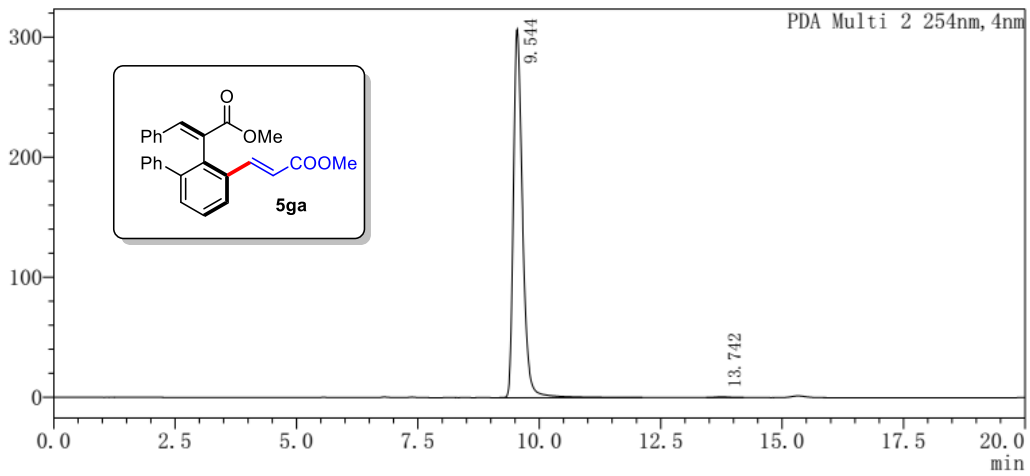
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	9.996	815892	59110	49.536
2	14.439	831165	43165	50.464
总计		1647057	102275	100.000

<色谱图>

mAU



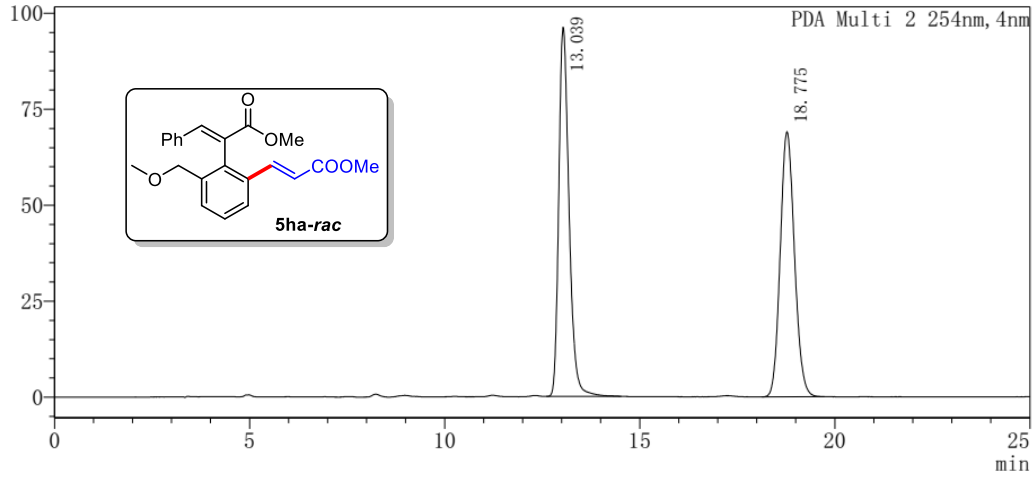
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	9.544	4021664	306451	99.745
2	13.742	10264	570	0.255
总计		4031928	307021	100.000

<色谱图>

mAU



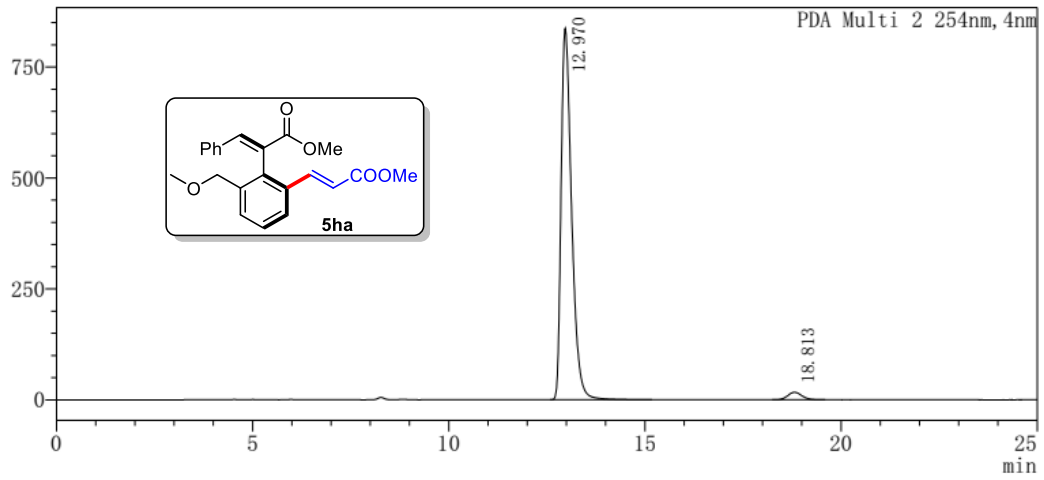
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	13.039	1761153	96121	50.140
2	18.775	1751287	69021	49.860
总计		3512440	165142	100.000

<色谱图>

mAU



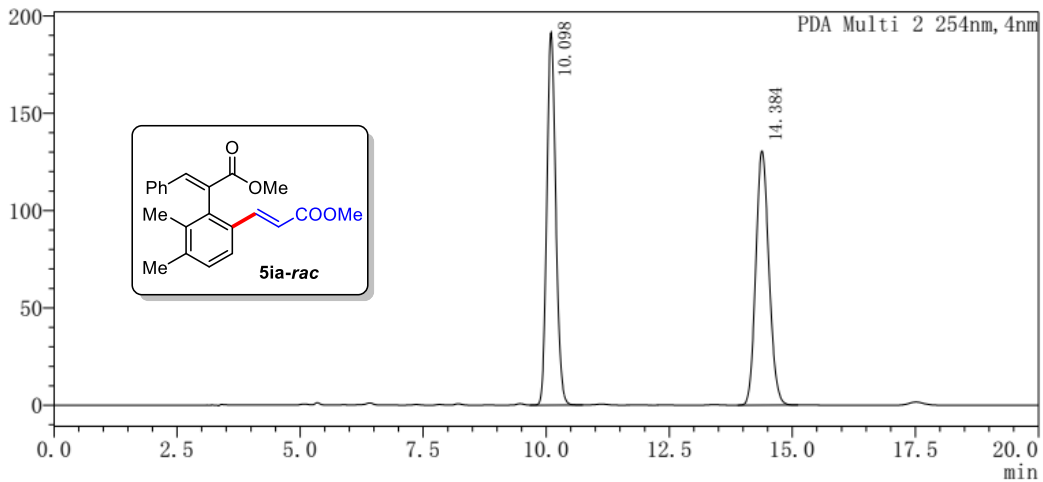
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	12.970	15614085	836880	97.364
2	18.813	422654	16781	2.636
总计		16036739	853661	100.000

<色谱图>

mAU



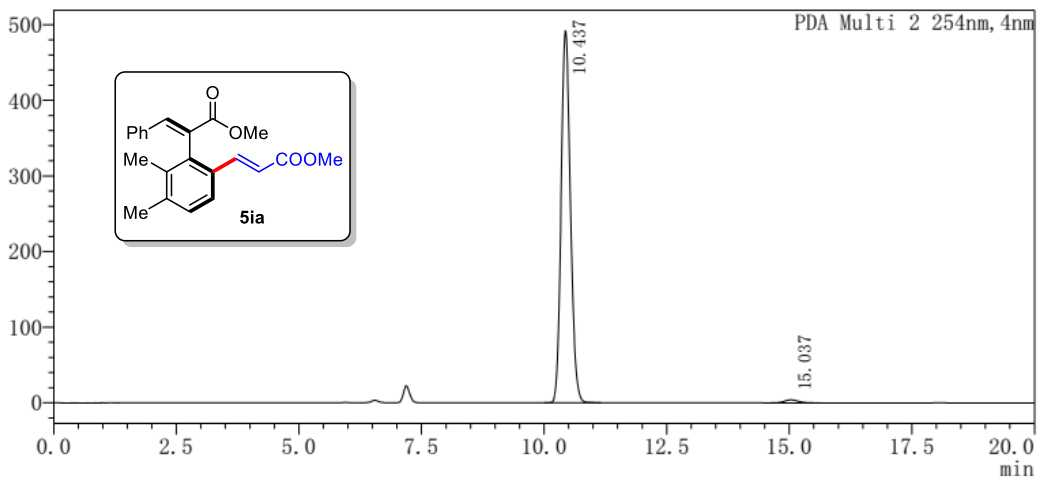
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	10.098	2435288	191242	50.122
2	14.384	2423478	130510	49.878
总计		4858766	321753	100.000

<色谱图>

mAU



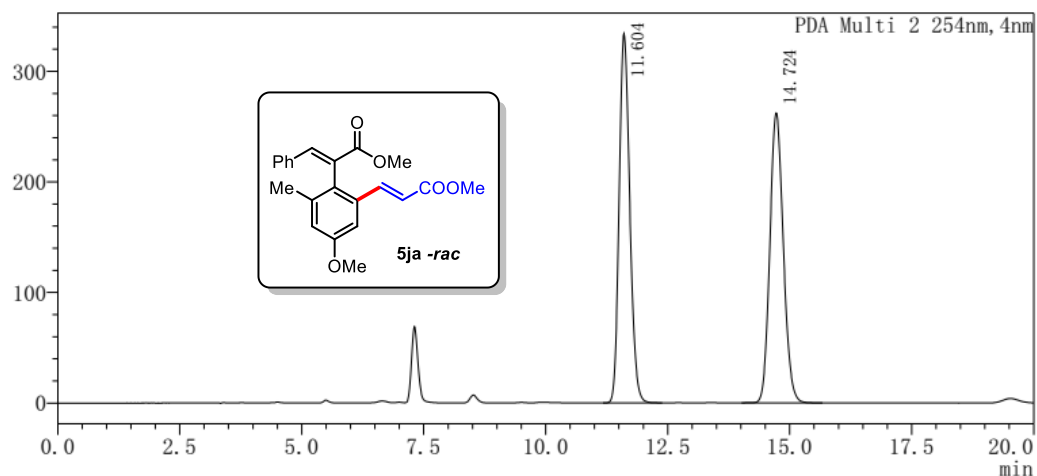
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	10.437	6501104	491363	98.816
2	15.037	77903	4012	1.184
总计		6579007	495376	100.000

<色谱图>

mAU



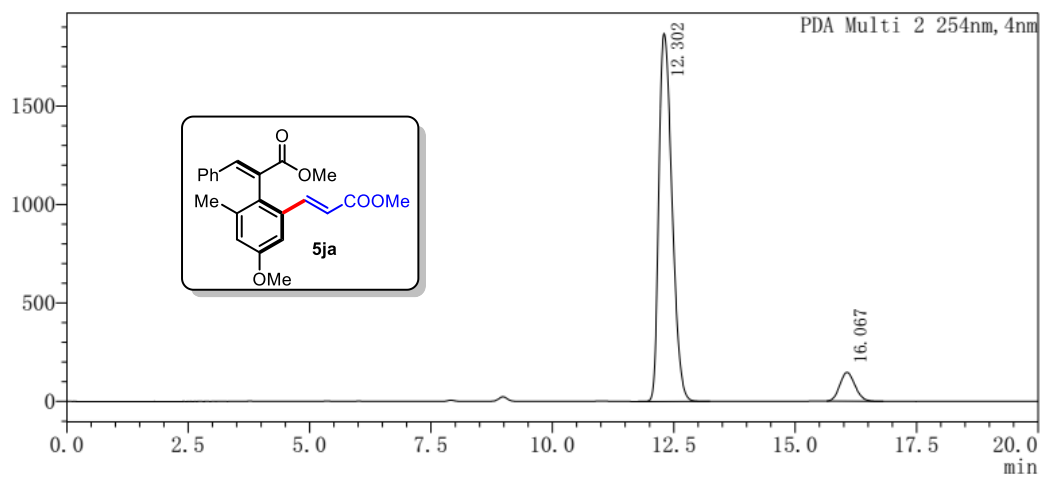
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	11.604	5053246	333798	50.055
2	14.724	5042187	262093	49.945
总计		10095433	595890	100.000

<色谱图>

mAU



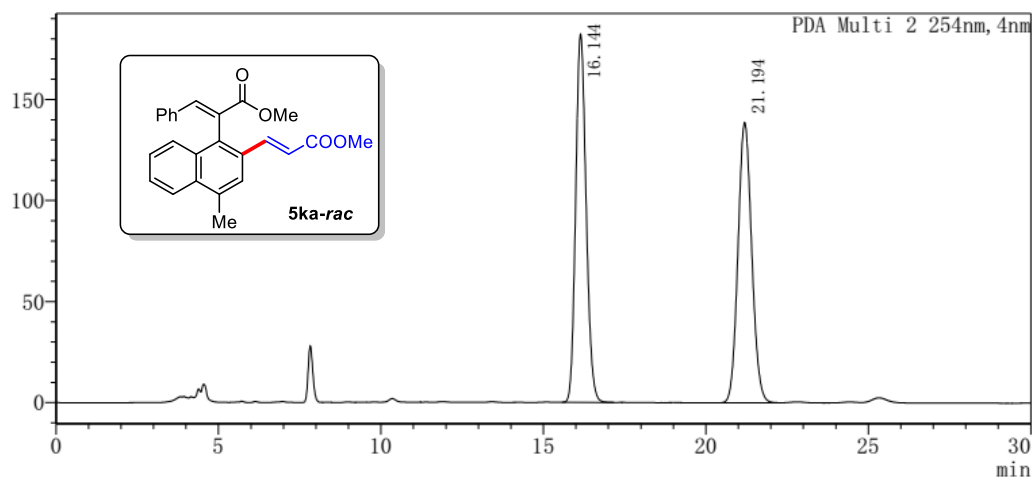
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	12.302	35291205	1866952	91.669
2	16.067	3207384	146448	8.331
总计		38498589	2013400	100.000

<色谱图>

mAU



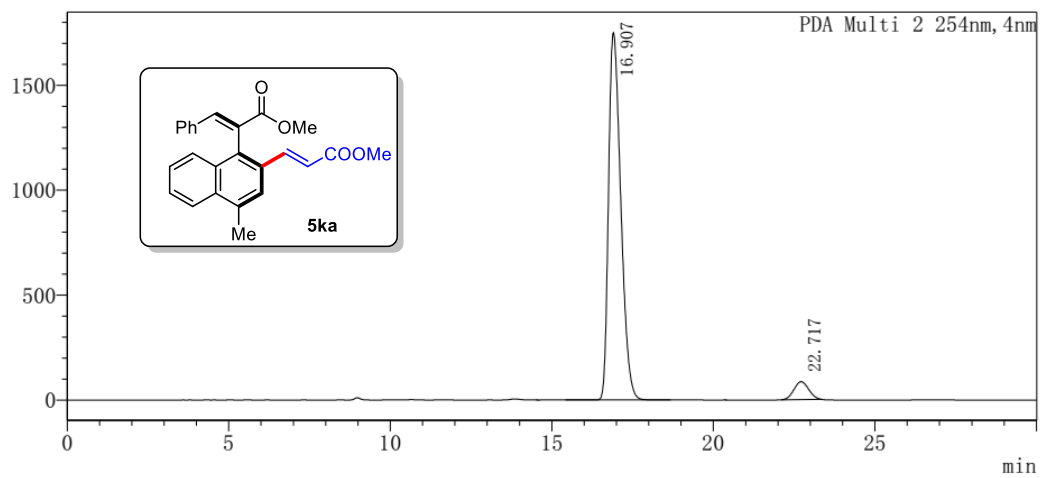
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	16.144	4075576	182156	49.994
2	21.194	4076620	138593	50.006
总计		8152196	320749	100.000

<色谱图>

mAU



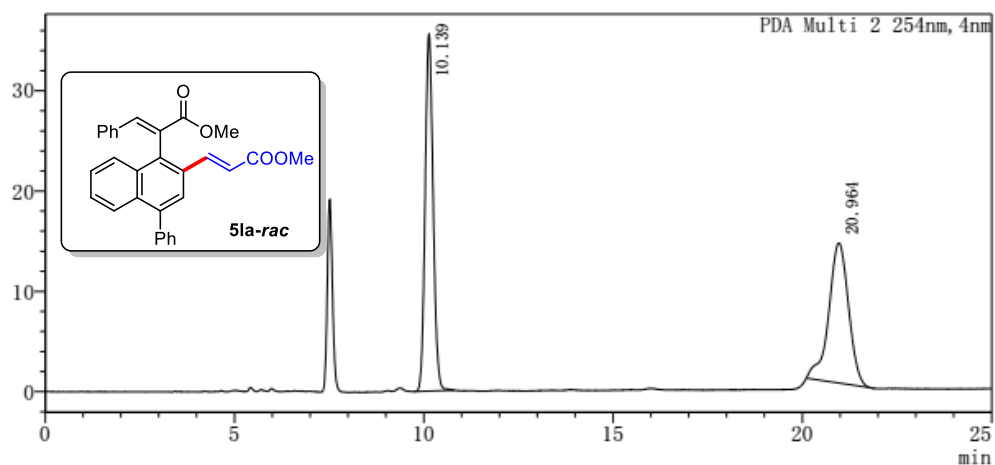
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	16.907	46172461	1750419	94.455
2	22.717	2710425	85457	5.545
总计		48882887	1835876	100.000

<色谱图>

mAU



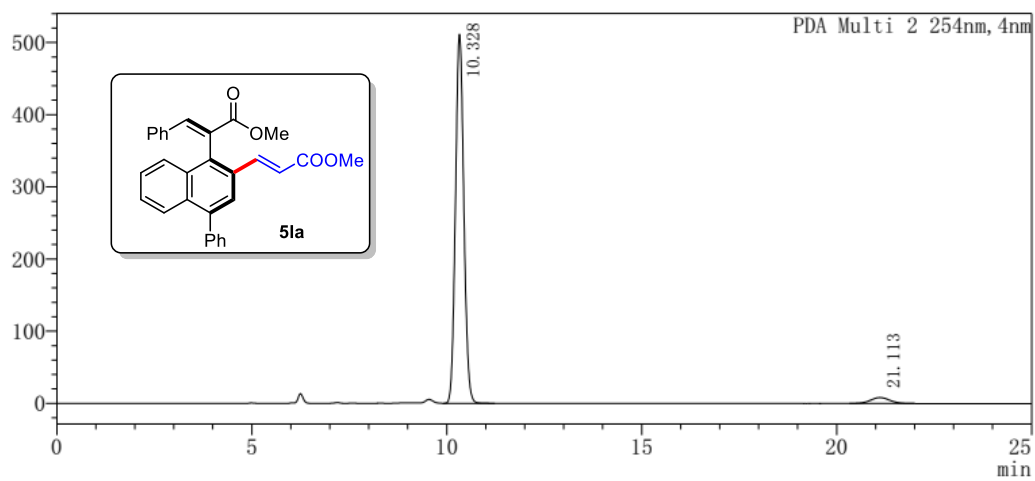
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	10.139	522214	35598	50.723
2	20.964	507319	13955	49.277
总计		1029534	49553	100.000

<色谱图>

mAU



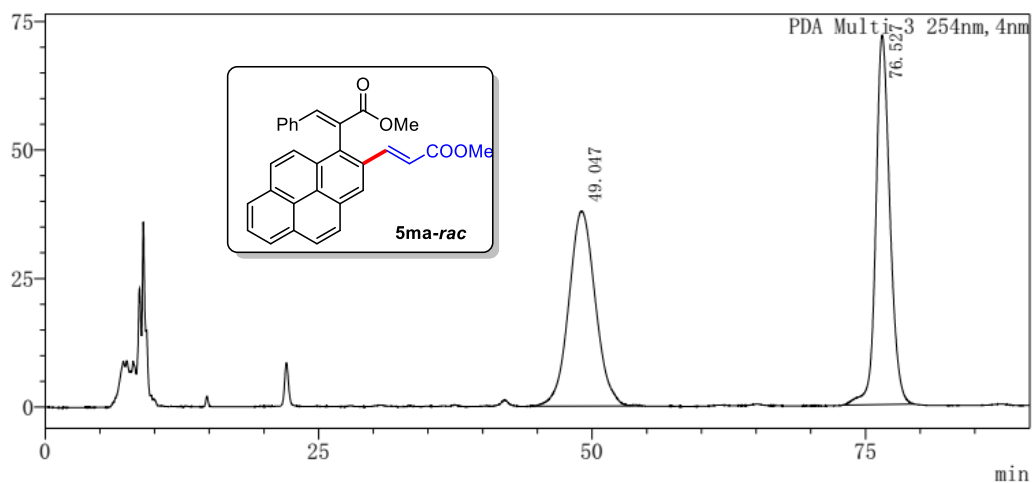
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	10.328	7623388	511602	96.422
2	21.113	282886	8184	3.578
总计		7906273	519786	100.000

<色谱图>

mAU



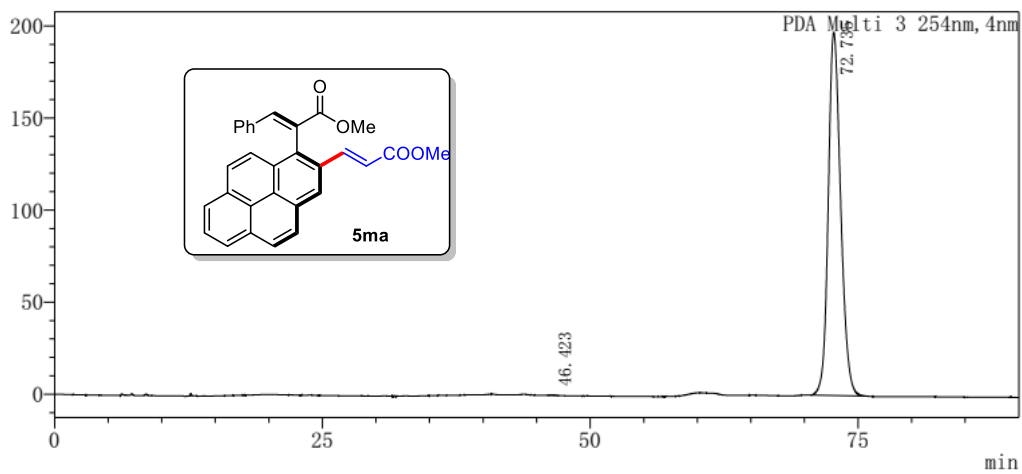
<峰表>

PDA Ch3 254nm

峰号	保留时间	面积	高度	面积%
1	49.047	6408715	37929	49.825
2	76.527	6453837	71905	50.175
总计		12862552	109834	100.000

<色谱图>

mAU



<峰表>

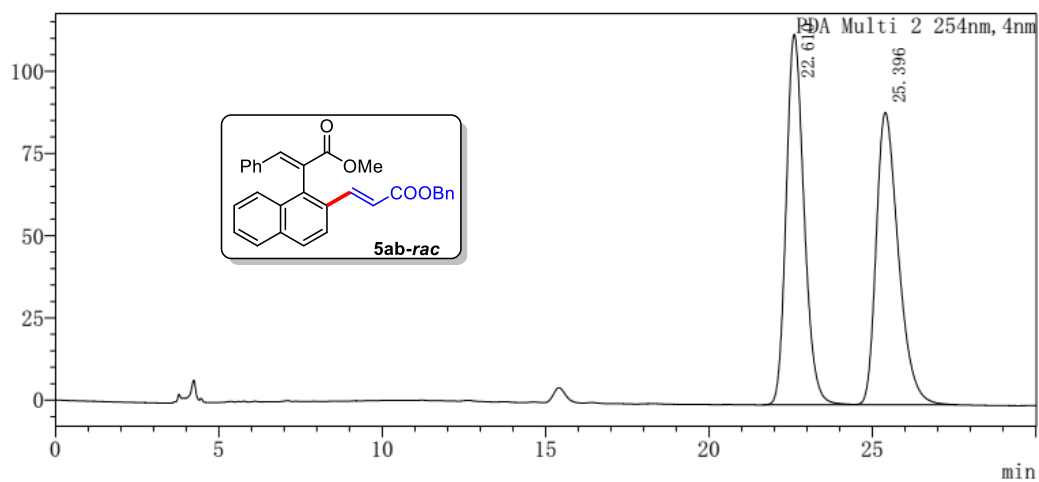
PDA Ch3 254nm

峰号	保留时间	面积	高度	面积%
1	46.423	9556	273	0.060
2	72.735	15868869	197324	99.940
总计		15878425	197598	100.000



<色谱图>

mAU



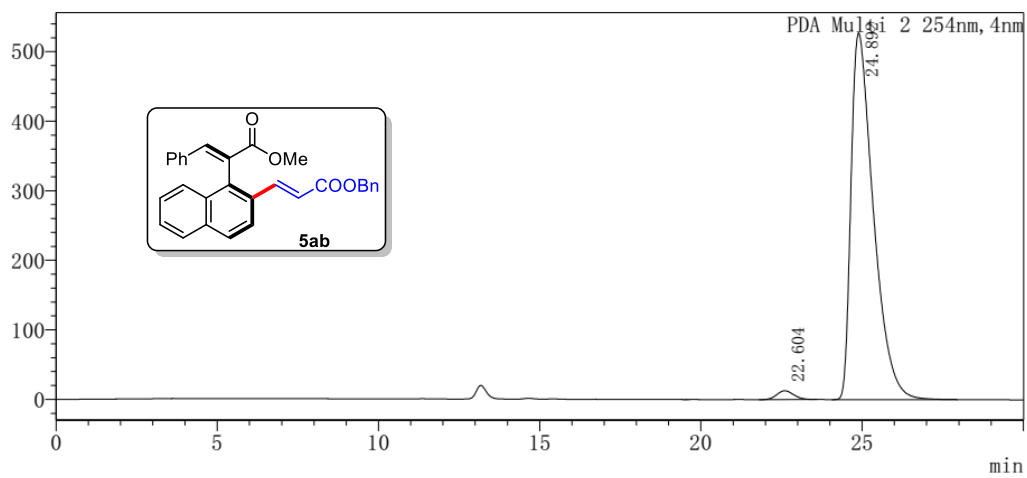
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	22.610	4282279	112629	50.419
2	25.396	4211174	88871	49.581
总计		8493453	201500	100.000

<色谱图>

mAU



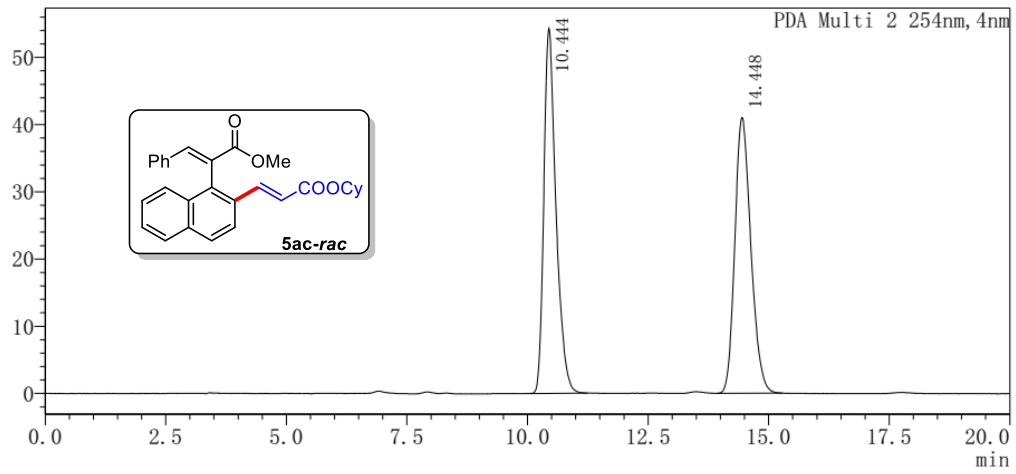
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	22.604	467051	12707	1.801
2	24.892	25462416	526964	98.199
总计		25929467	539671	100.000

<色谱图>

mAU



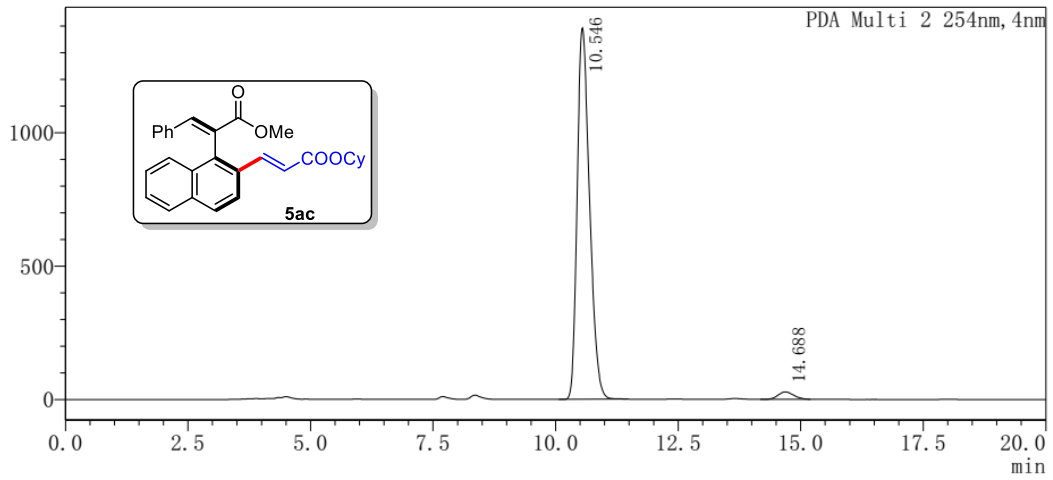
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	10.444	951180	54289	50.028
2	14.448	950130	41012	49.972
总计		1901310	95301	100.000

<色谱图>

mAU



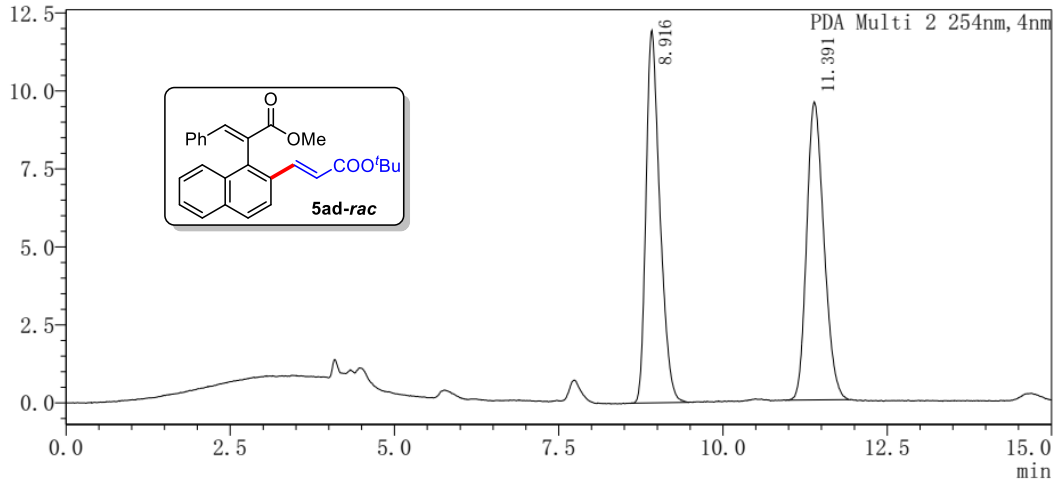
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	10.546	24449220	1391552	97.511
2	14.688	624071	27822	2.489
总计		25073291	1419374	100.000

<色谱图>

mAU



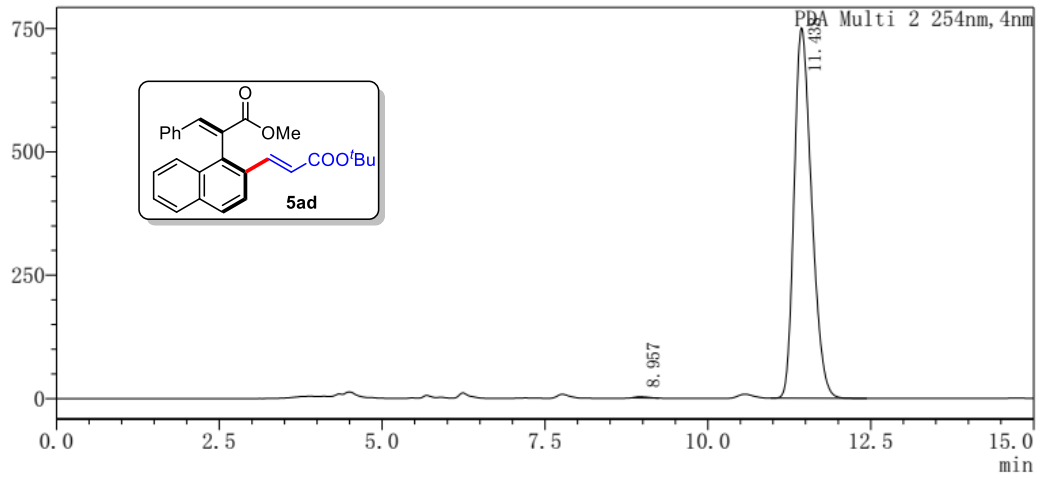
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	8.916	175802	11937	50.151
2	11.391	174745	9549	49.849
总计		350548	21486	100.000

<色谱图>

mAU



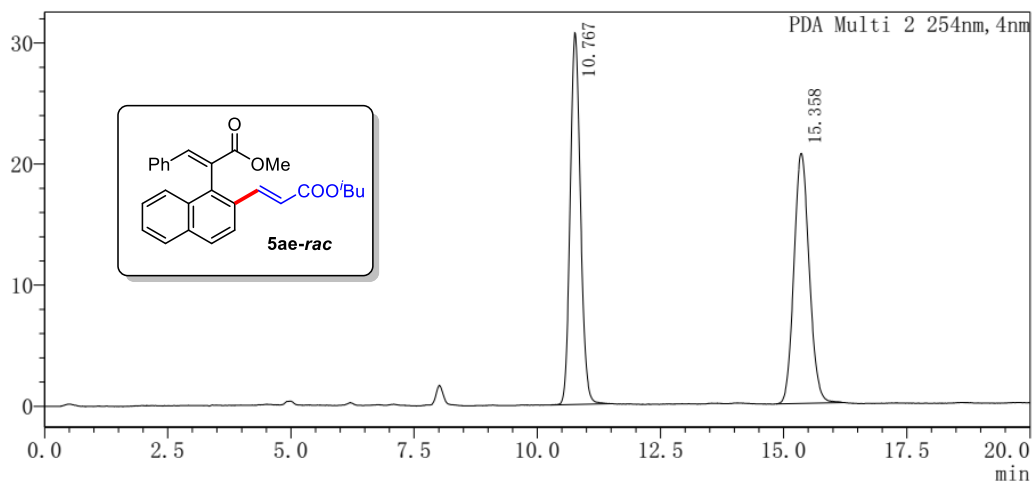
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	8.957	34085	2502	0.243
2	11.438	14005339	750058	99.757
总计		14039425	752560	100.000

<色谱图>

mAU



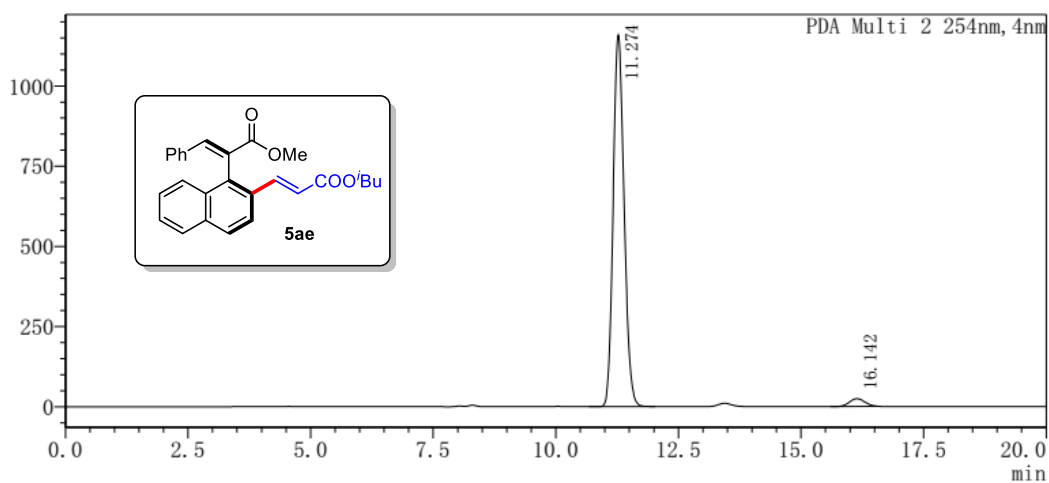
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	10.767	446545	30680	50.007
2	15.358	446423	20659	49.993
总计		892968	51339	100.000

<色谱图>

mAU



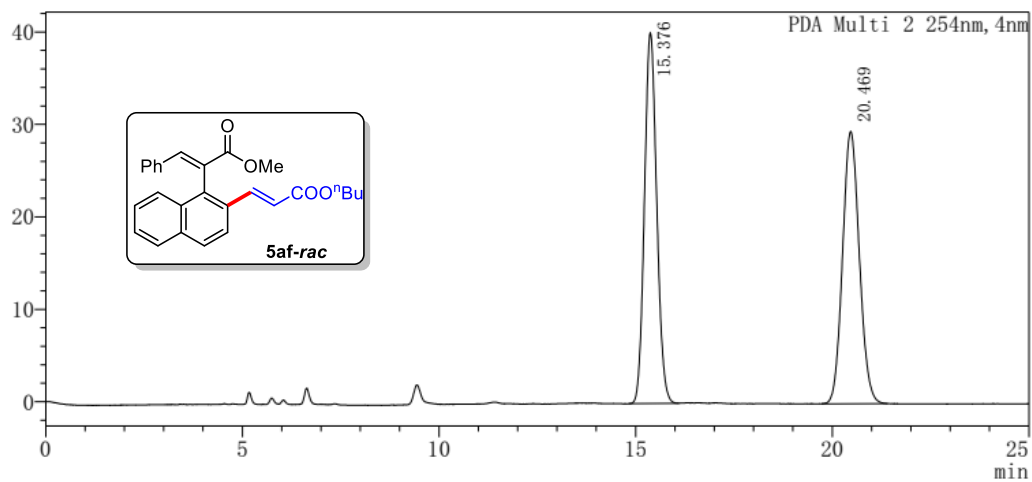
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	浓度	面积%
1	11.274	17987540	1157743	0.000	97.064
2	16.142	544161	24360	0.000	2.936
总计		18531702	1182102		100.000

<色谱图>

mAU



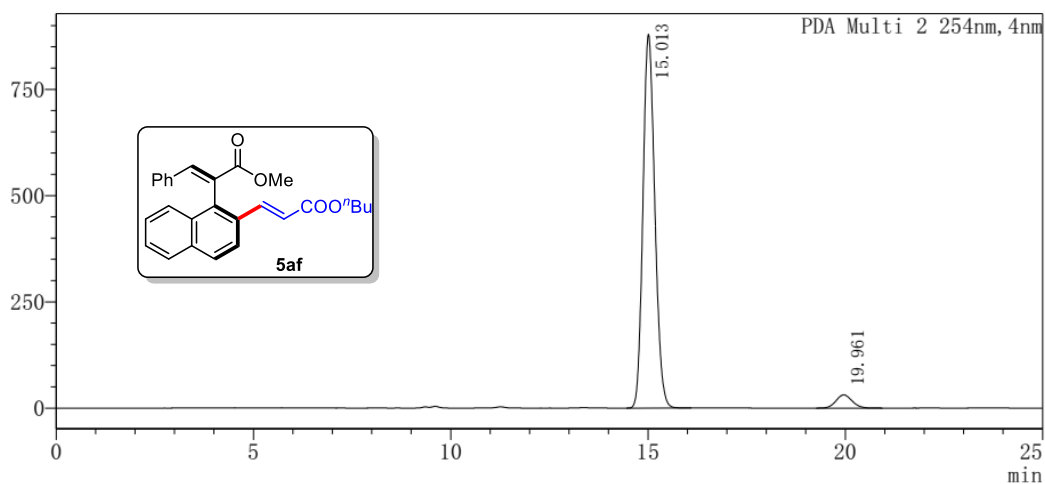
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	浓度	面积%
1	15.376	868911	40079	0.000	49.912
2	20.469	871958	29441	0.000	50.088
总计		1740869	69519		100.000

<色谱图>

mAU



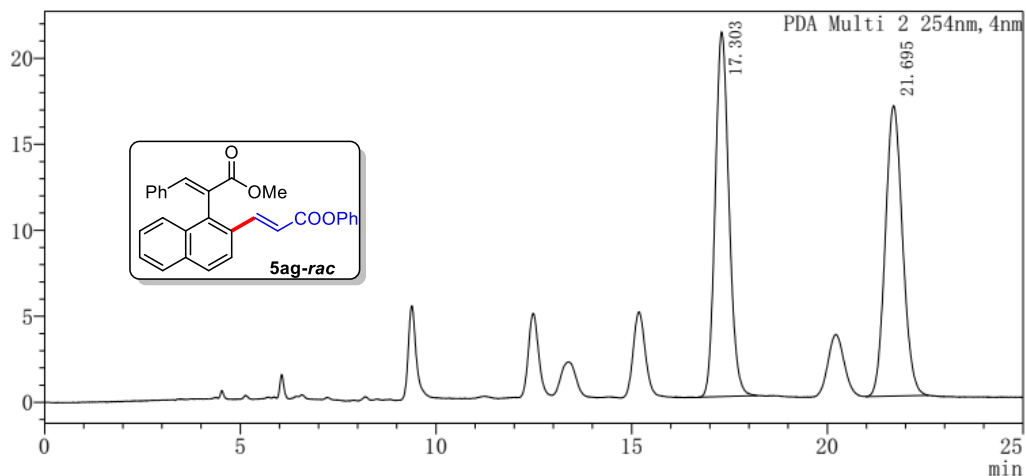
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	15.013	18393501	878911	95.410
2	19.961	884959	31101	4.590
总计		19278460	910012	100.000

<色谱图>

mAU



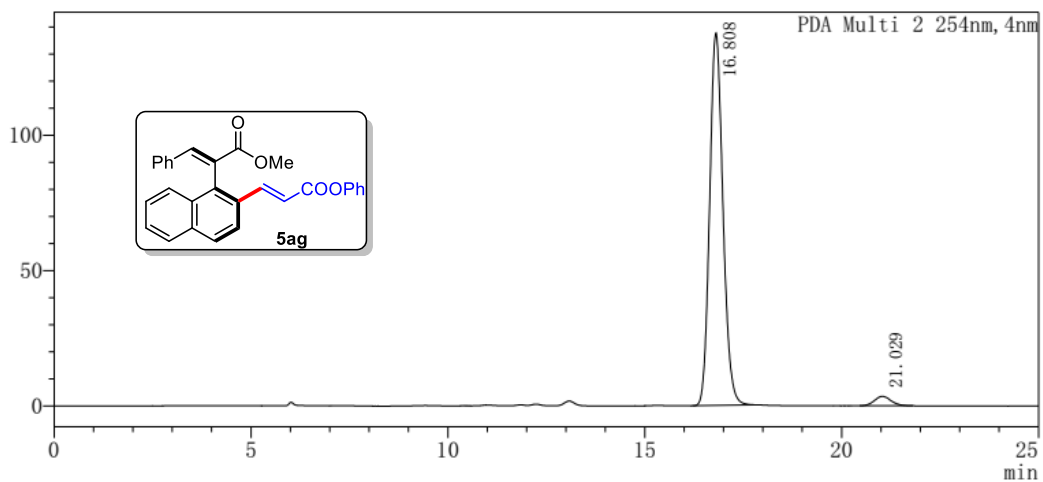
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	17.303	519765	21189	50.097
2	21.695	517748	16876	49.903
总计		1037513	38065	100.000

<色谱图>

mAU



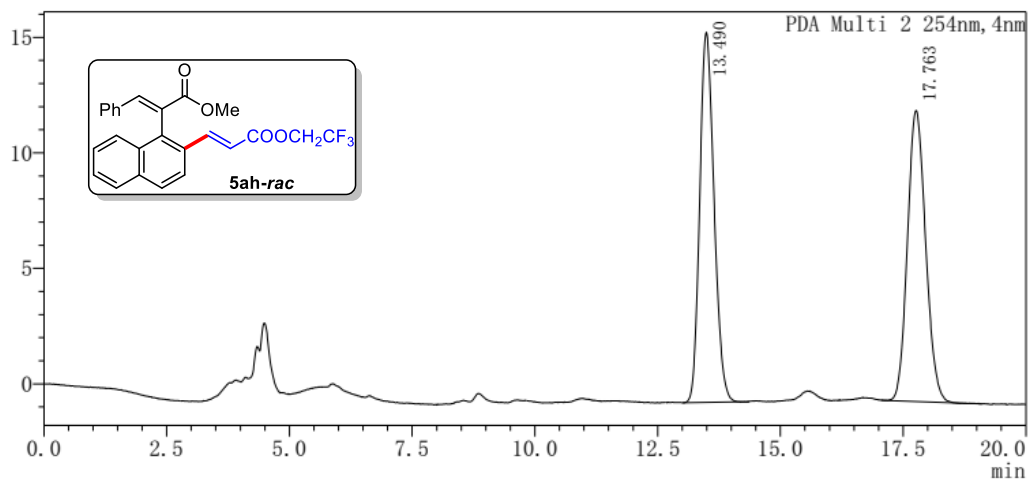
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	16.808	3228882	137542	96.936
2	21.029	102063	3481	3.064
总计		3330946	141023	100.000

<色谱图>

mAU



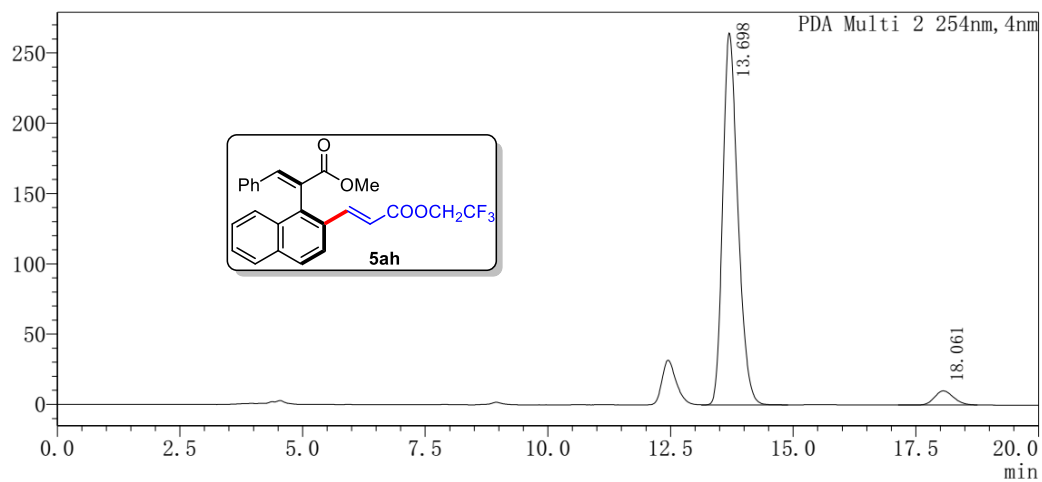
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	浓度	面积%
1	13.490	325278	16007	0.000	50.024
2	17.763	324968	12597	0.000	49.976
总计		650246	28604		100.000

<色谱图>

mAU



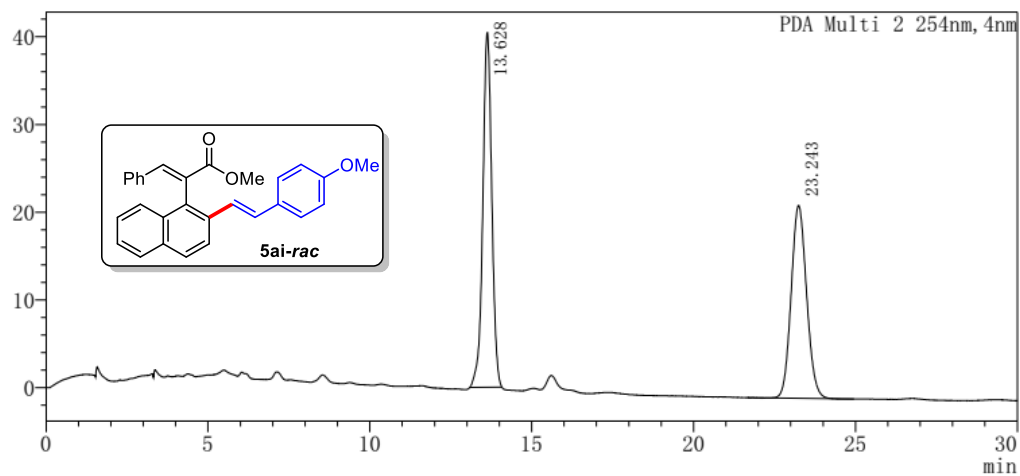
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	13.698	5692126	264474	95.474
2	18.061	269818	10055	4.526
总计		5961944	274529	100.000

<色谱图>

mAU



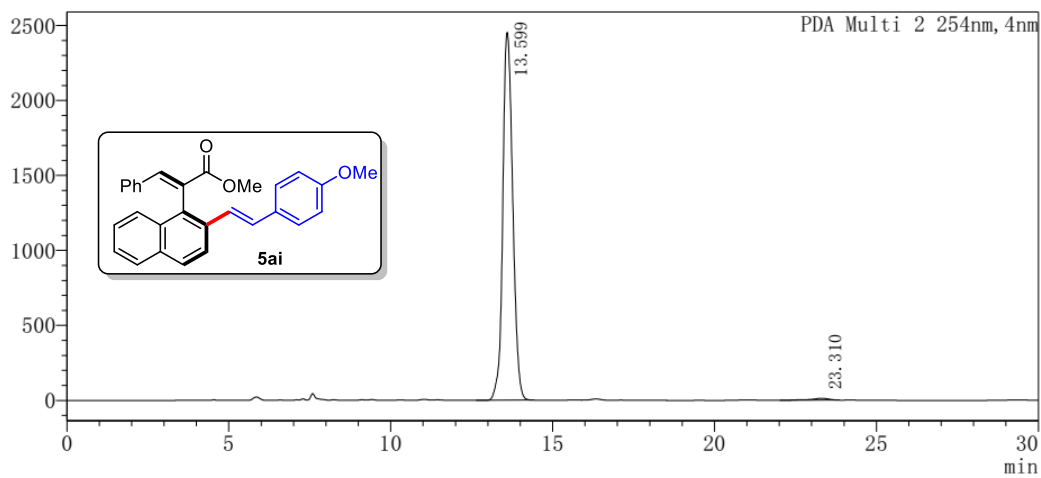
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	13.628	780133	40409	51.744
2	23.243	727537	21981	48.256
总计		1507670	62390	100.000

<色谱图>

mAU



<峰表>

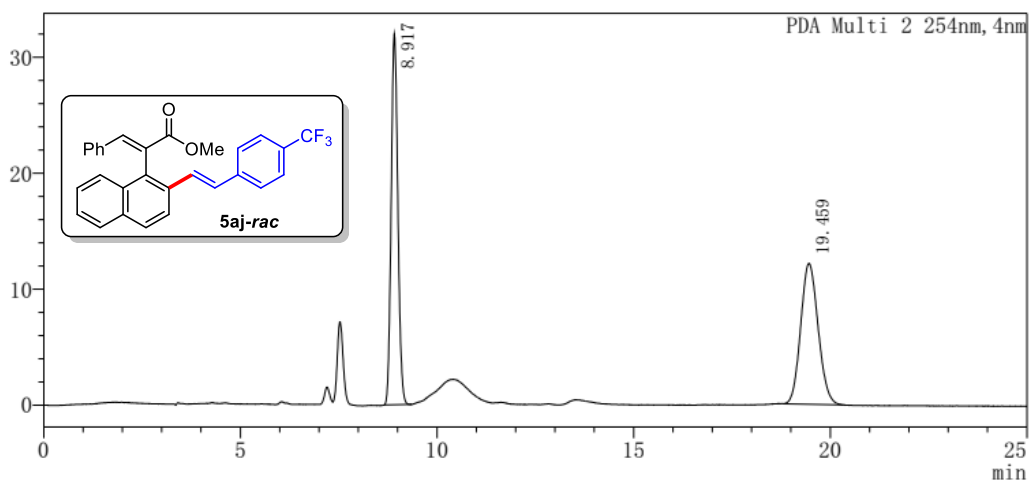
PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	13.599	52522725	2451410	99.037
2	23.310	510764	12706	0.963
总计		53033490	2464116	100.000



<色谱图>

mAU



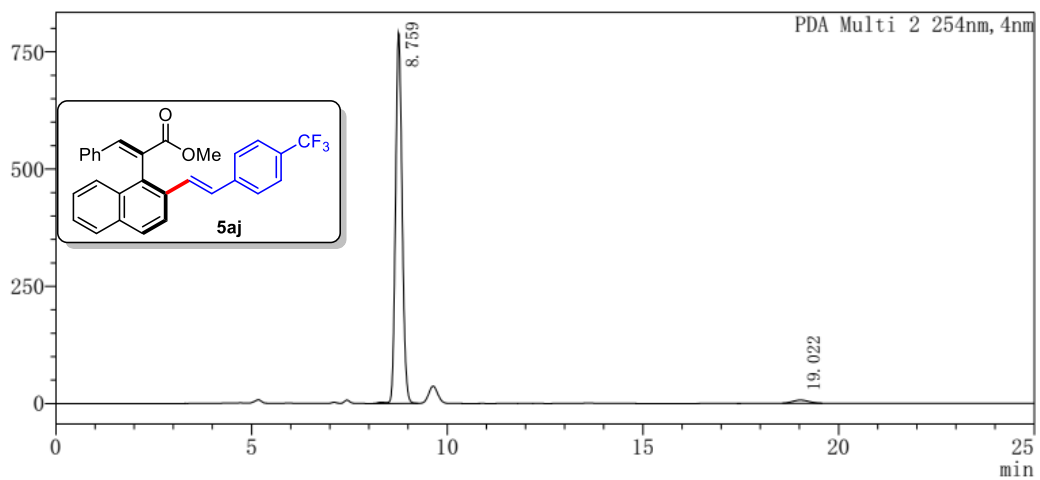
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	8.917	377247	31941	50.198
2	19.459	374264	12141	49.802
总计		751511	44082	100.000

<色谱图>

mAU



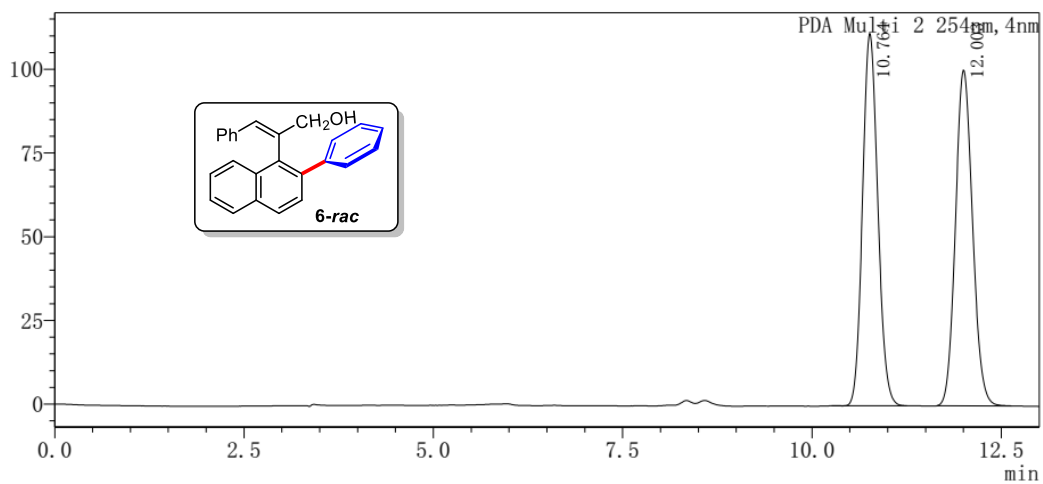
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	浓度	面积%
1	8.759	9272216	789779	0.000	97.972
2	19.022	191951	6728	0.000	2.028
总计		9464167	796508		100.000

<色谱图>

mAU



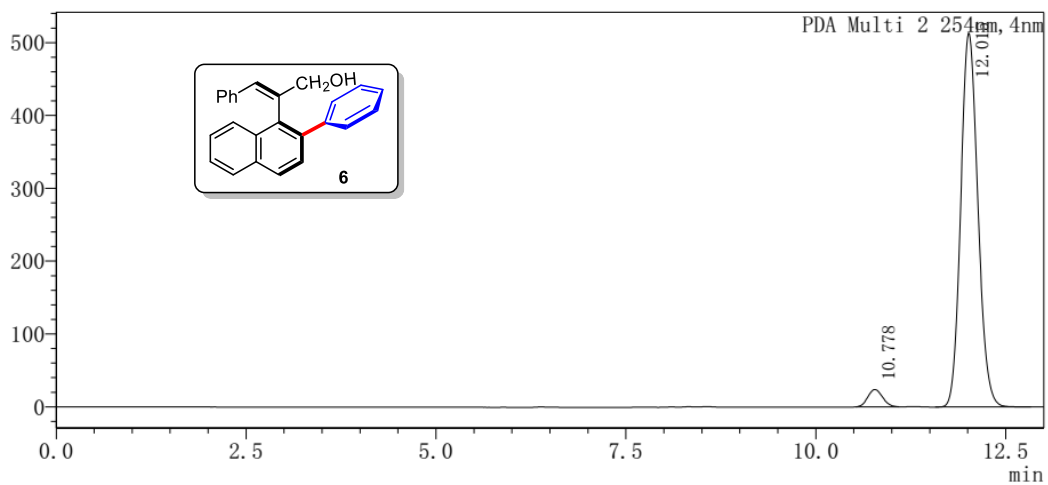
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	10.764	1553521	111163	49.662
2	12.003	1574670	100275	50.338
总计		3128190	211438	100.000

<色谱图>

mAU



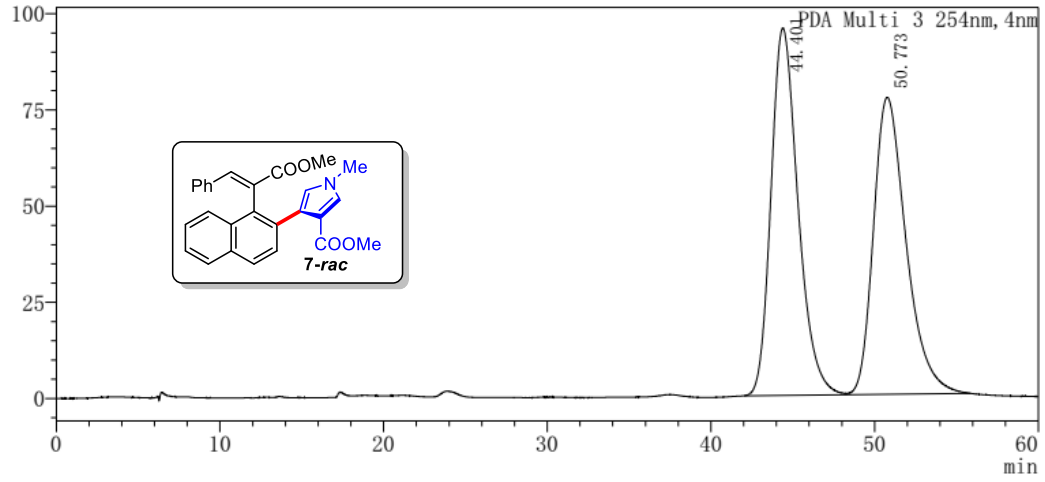
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	10.778	321711	23807	3.848
2	12.015	8038592	513064	96.152
总计		8360303	536871	100.000

<色谱图>

mAU



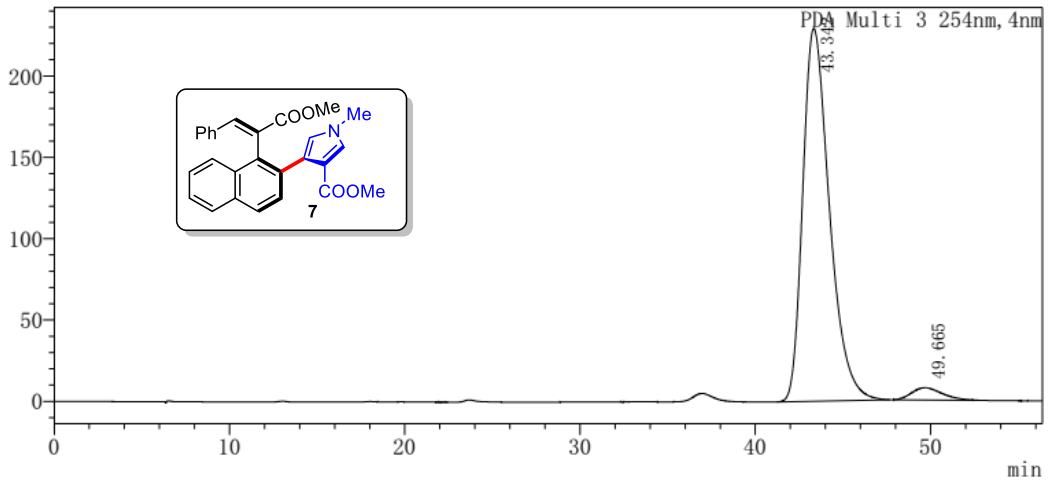
<峰表>

PDA Ch3 254nm

峰号	保留时间	面积	高度	面积%
1	44.401	10969186	95411	50.653
2	50.773	10686512	77178	49.347
总计		21655698	172589	100.000

<色谱图>

mAU



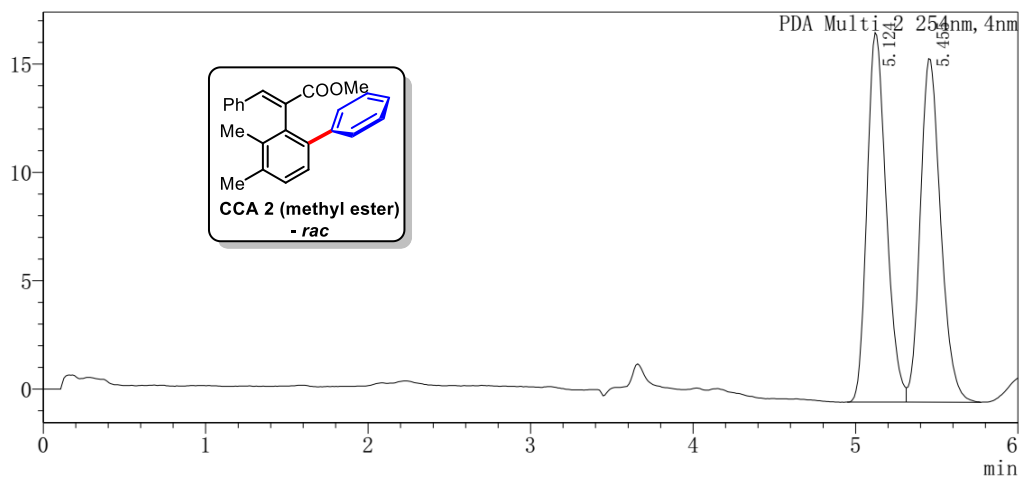
<峰表>

PDA Ch3 254nm

峰号	保留时间	面积	高度	面积%
1	43.342	24226859	229131	96.428
2	49.665	897398	7461	3.572
总计		25124257	236592	100.000

<色谱图>

mAU



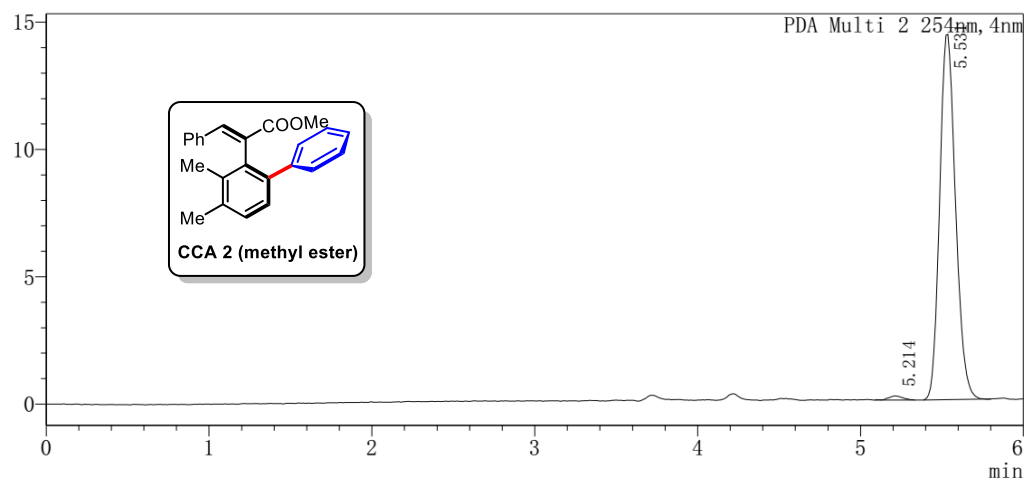
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	浓度	面积%
1	5.124	140682	17045	0.000	50.368
2	5.455	138628	15855	0.000	49.632
总计		279310	32900		100.000

<色谱图>

mAU



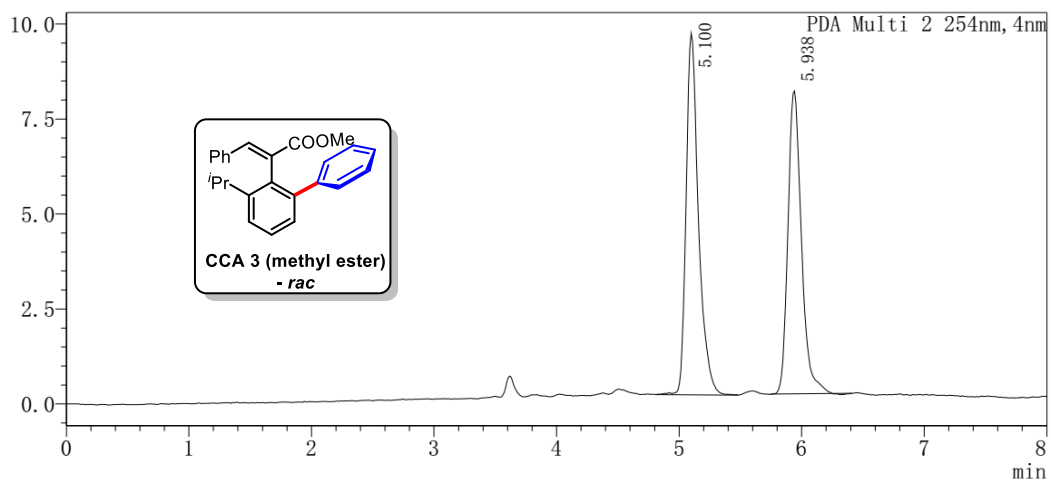
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	5.214	939	160	0.958
2	5.531	97140	14320	99.042
总计		98079	14480	100.000

<色谱图>

mAU



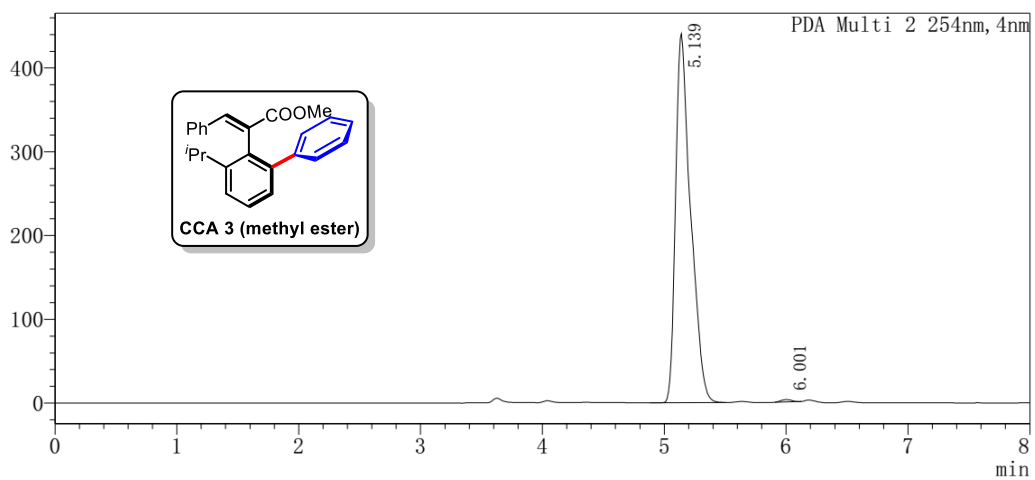
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	5.100	66747	9511	52.189
2	5.938	61147	7972	47.811
总计		127894	17483	100.000

<色谱图>

mAU



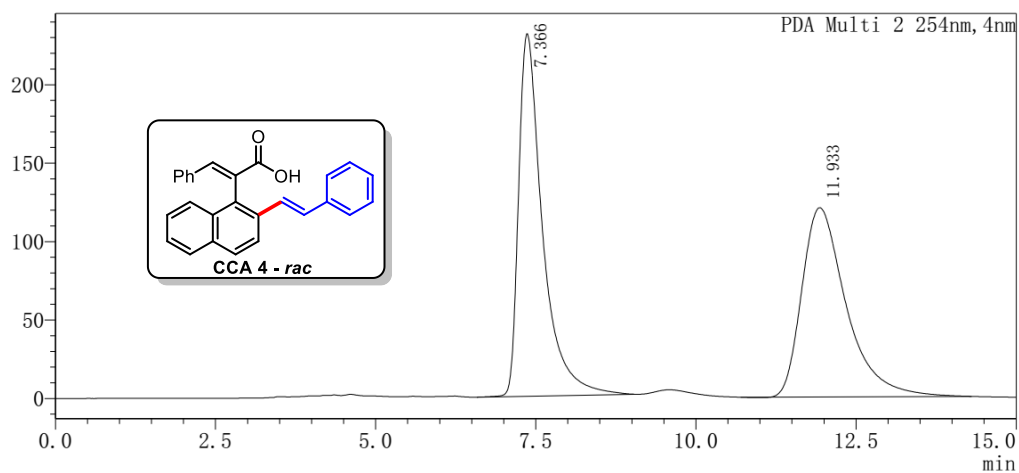
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	5.139	3768240	440241	99.554
2	6.001	16891	2705	0.446
总计		3785131	442946	100.000

<色谱图>

mAU



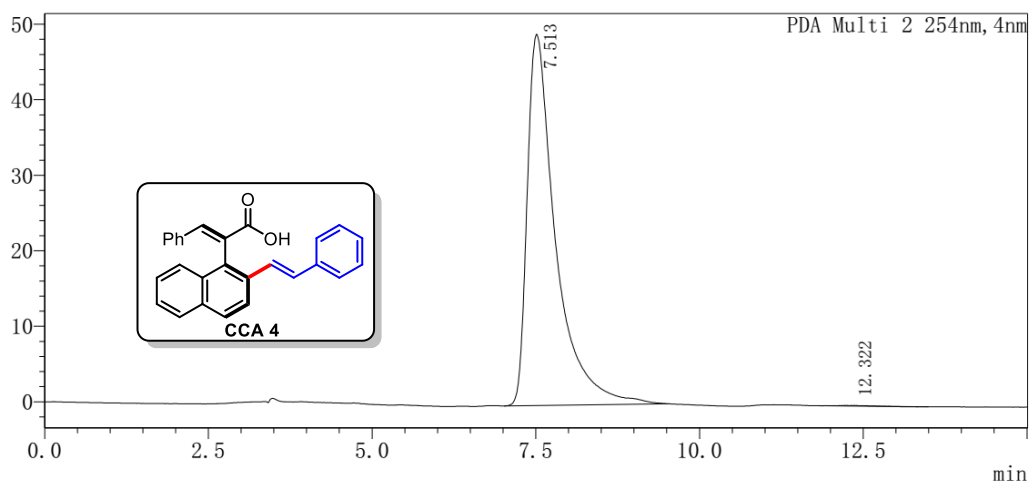
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	7.366	6014174	230911	50.859
2	11.933	5811059	120630	49.141
总计		11825233	351541	100.000

<色谱图>

mAU



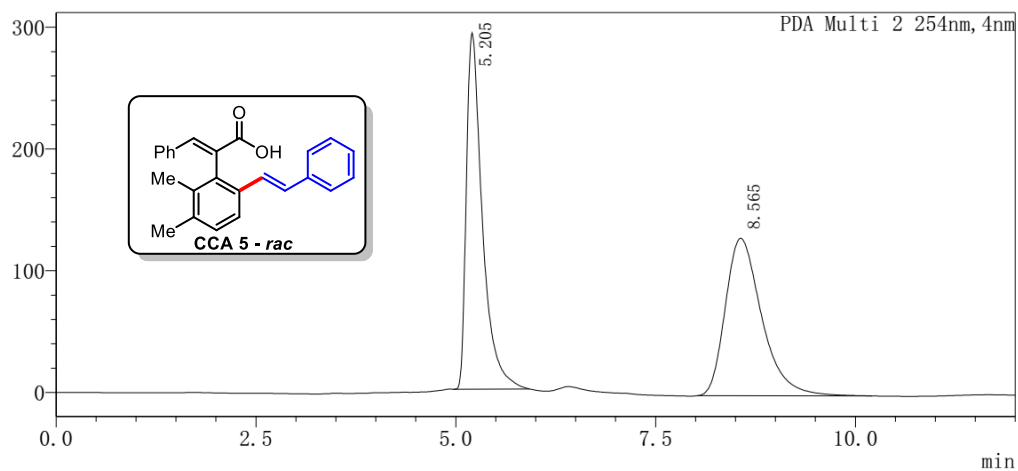
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	7.513	1484318	49156	99.882
2	12.322	1757	80	0.118
总计		1486075	49236	100.000

<色谱图>

mAU



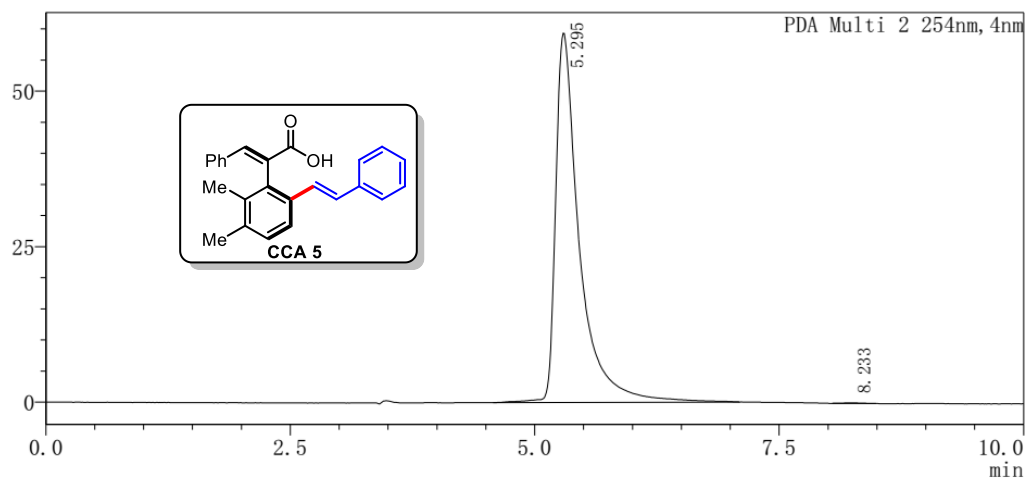
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	5.205	4075759	292671	49.814
2	8.565	4106214	129364	50.186
总计		8181973	422035	100.000

<色谱图>

mAU



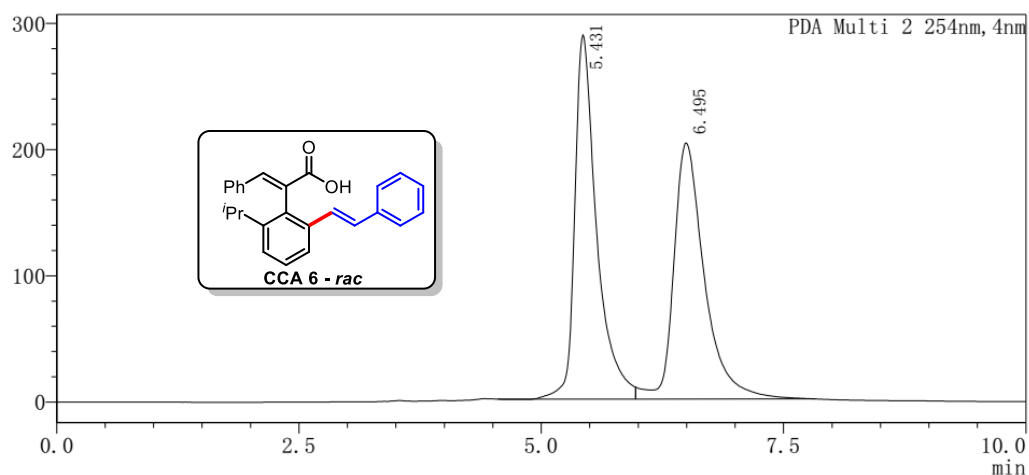
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	5.295	1003912	59355	99.886
2	8.233	1145	83	0.114
总计		1005056	59438	100.000

<色谱图>

mAU



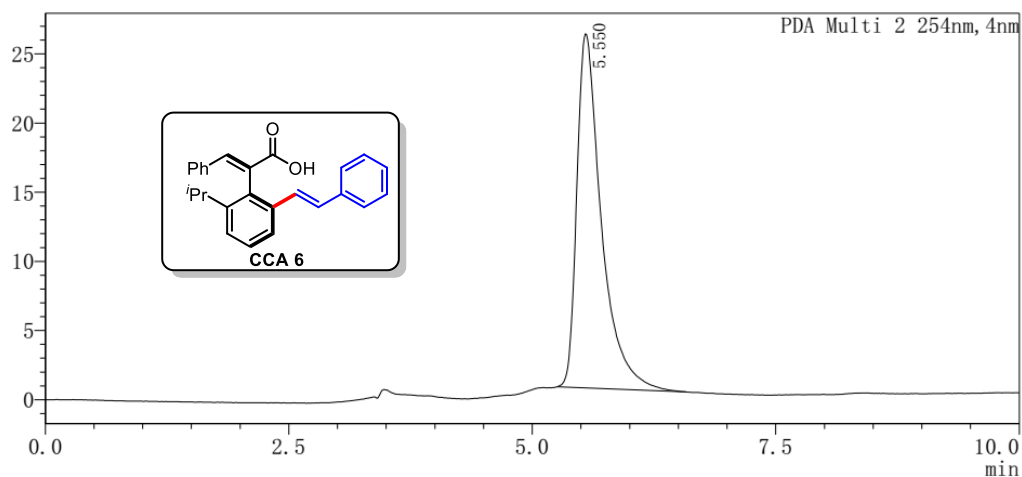
<峰表>

PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	5.431	4534641	288366	50.272
2	6.495	4485517	202982	49.728
总计		9020158	491348	100.000

<色谱图>

mAU



<峰表>

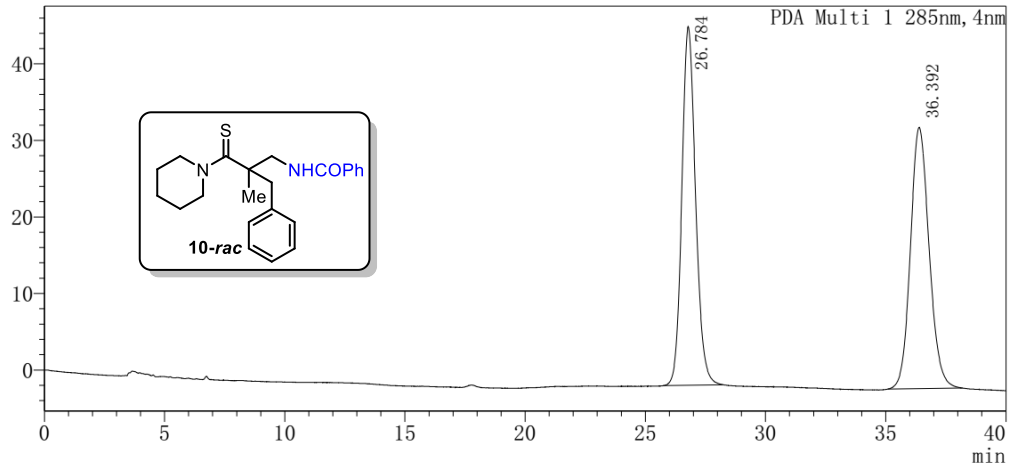
PDA Ch2 254nm

峰号	保留时间	面积	高度	面积%
1	5.550	448405	25583	100.000
总计		448405	25583	100.000



<色谱图>

mAU



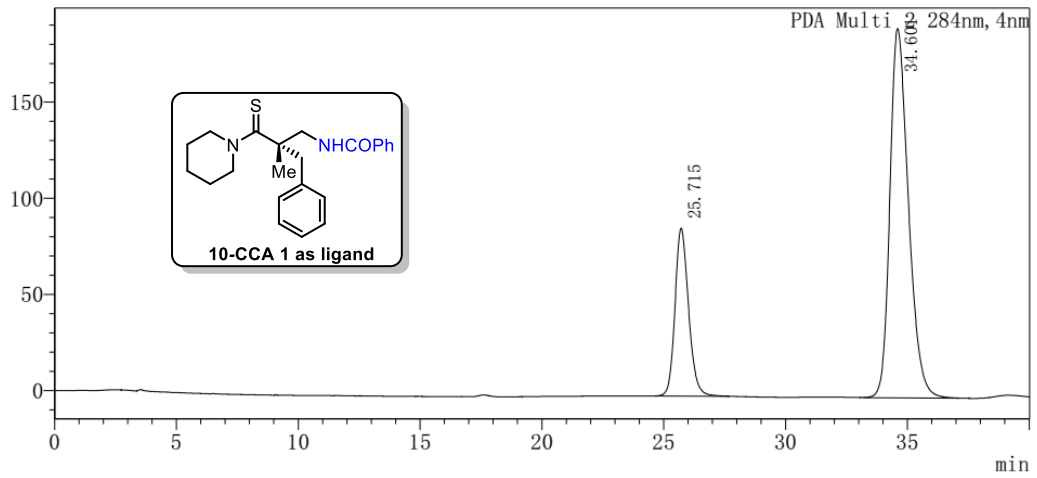
<峰表>

PDA Ch1 285nm

峰号	保留时间	面积	高度	面积%
1	26.784	1859743	46887	50.169
2	36.392	1847216	34160	49.831
总计		3706959	81047	100.000

<色谱图>

mAU



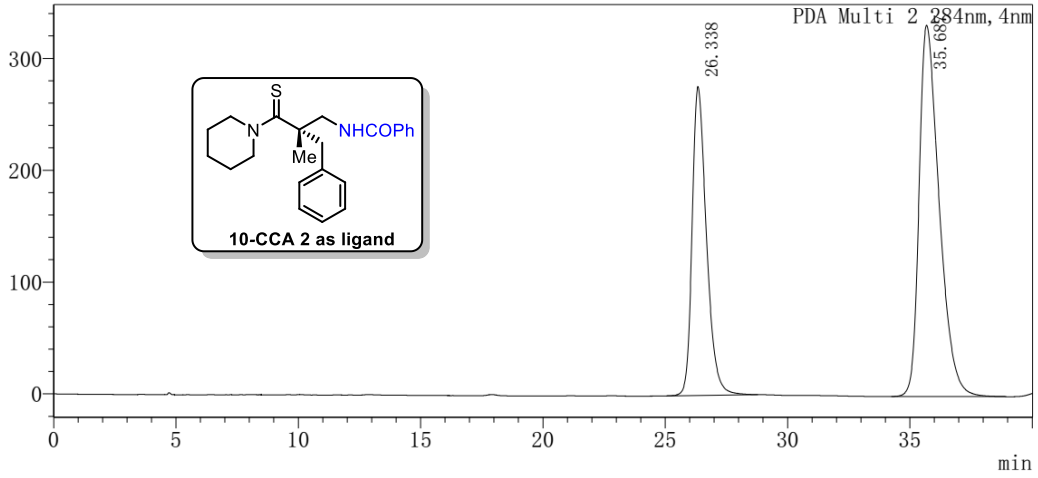
<峰表>

PDA Ch2 284nm

峰号	保留时间	面积	高度	面积%
1	25.715	3379411	87219	24.966
2	34.601	10156610	191793	75.034
总计		13536021	279012	100.000

<色谱图>

mAU



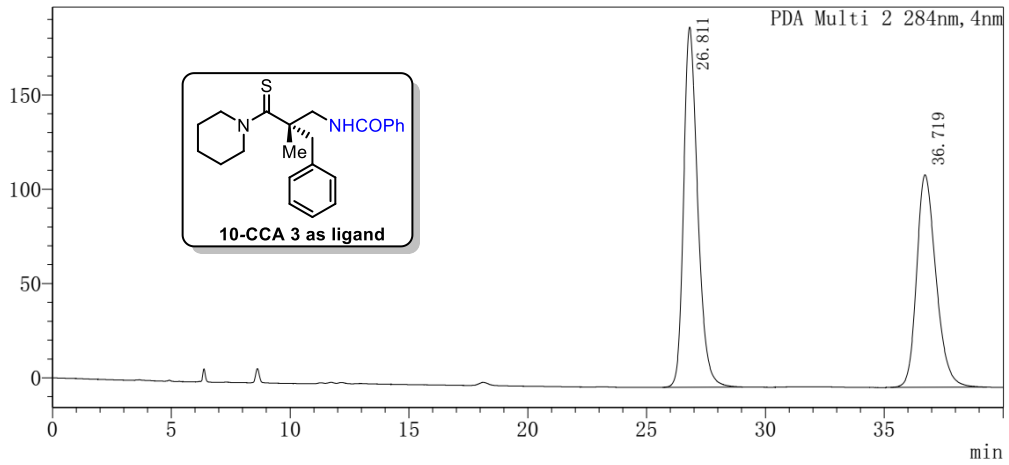
<峰表>

PDA Ch2 284nm

峰号	保留时间	面积	高度	面积%
1	26.338	11274272	276165	37.267
2	35.687	18978559	331880	62.733
总计		30252831	608045	100.000

<色谱图>

mAU



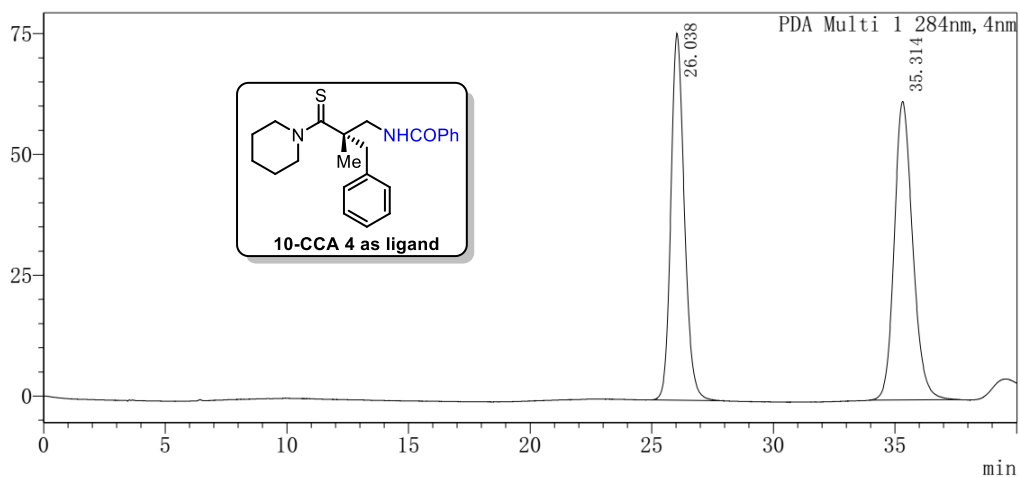
<峰表>

PDA Ch2 284nm

峰号	保留时间	面积	高度	面积%
1	26.811	7873536	190847	55.218
2	36.719	6385393	112719	44.782
总计		14258929	303566	100.000

<色谱图>

mAU



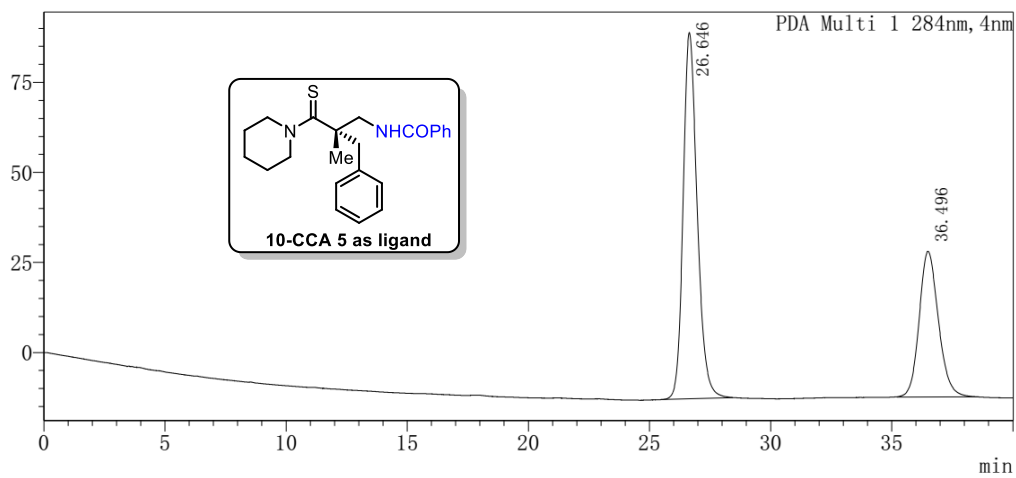
<峰表>

PDA Ch1 284nm

峰号	保留时间	面积	高度	面积%
1	26.038	2924040	75898	47.225
2	35.314	3267677	61810	52.775
总计		6191716	137708	100.000

<色谱图>

mAU



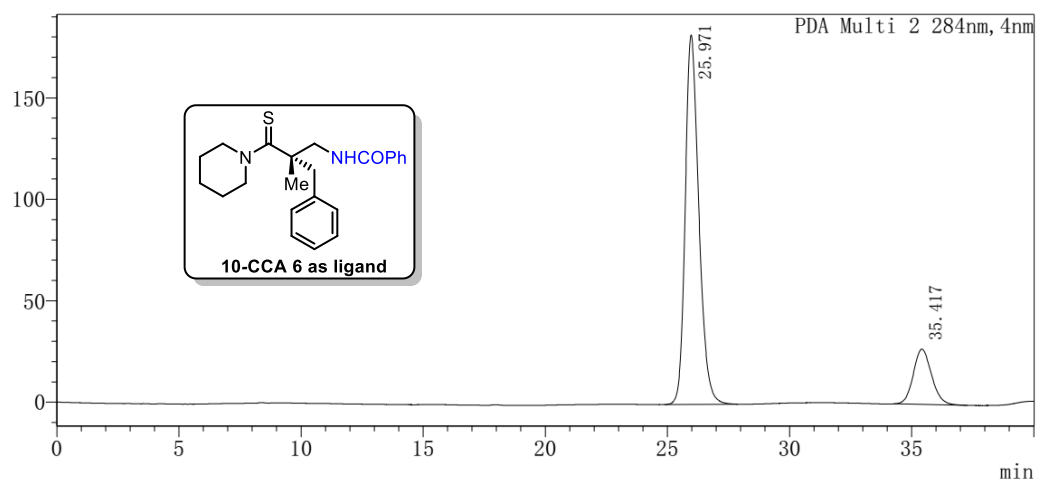
<峰表>

PDA Ch1 284nm

峰号	保留时间	面积	高度	面积%
1	26.646	4098143	101676	64.689
2	36.496	2237028	40489	35.311
总计		6335171	142164	100.000

<色谱图>

mAU



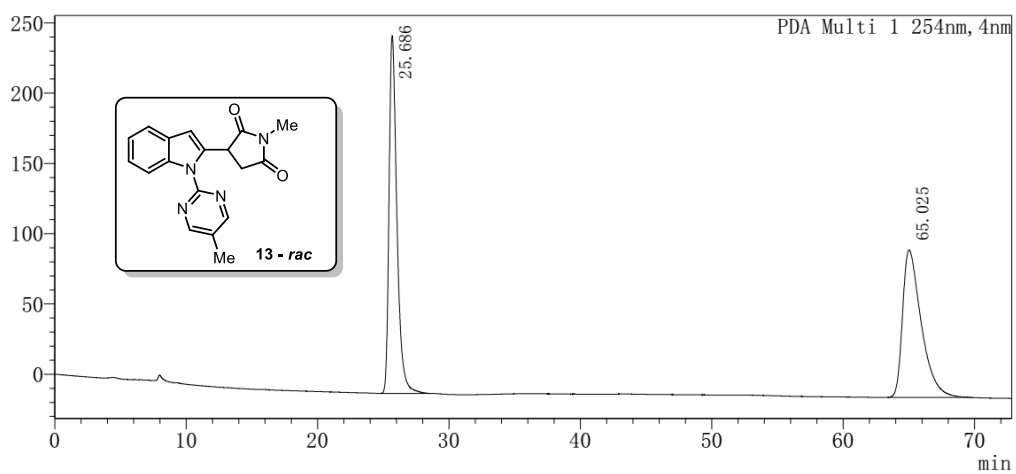
<峰表>

PDA Ch2 284nm

峰号	保留时间	面积	高度	面积%
1	25.971	7065159	182058	83.277
2	35.417	1418759	27268	16.723
总计		8483919	209327	100.000

<色谱图>

mAU



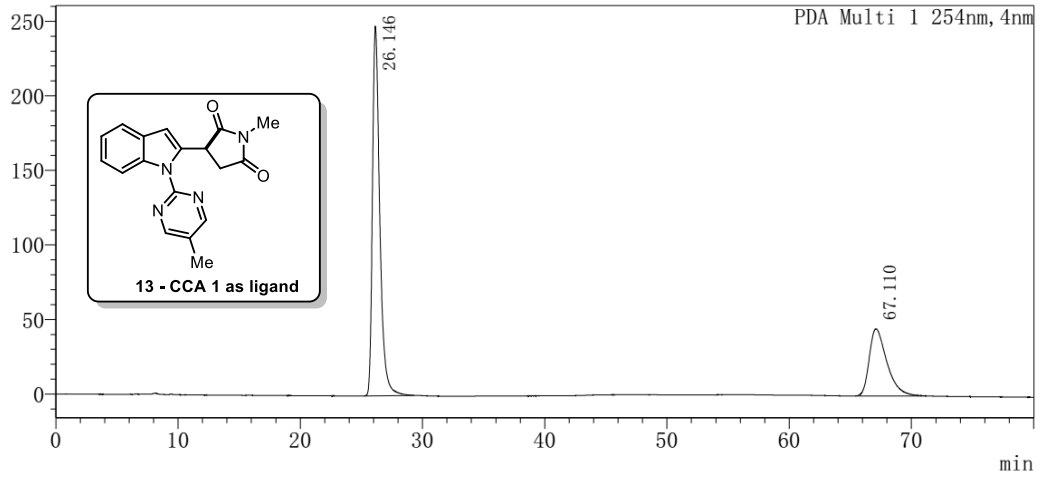
<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	25.686	10579989	254485	50.429
2	65.025	10400074	104906	49.571
总计		20980063	359391	100.000

<色谱图>

mAU



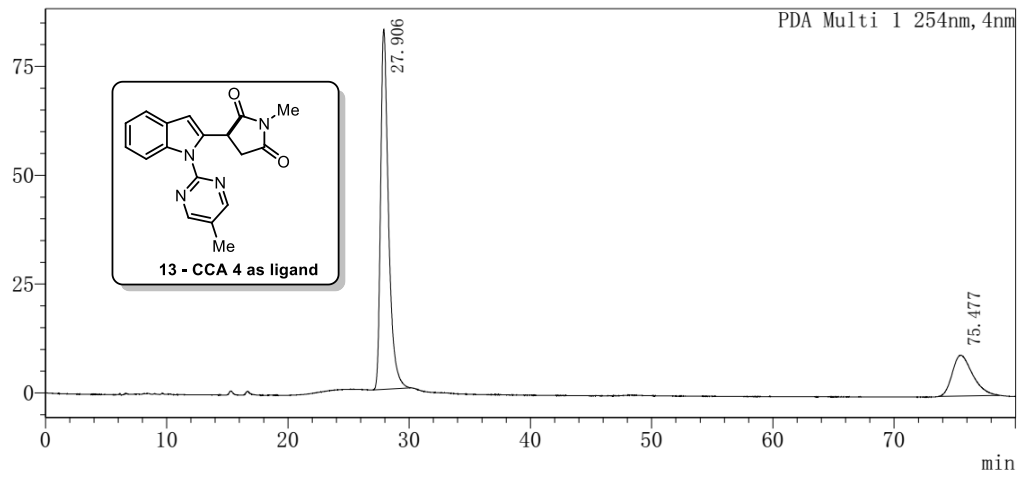
<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	26.146	10311815	247820	69.547
2	67.110	4515264	44966	30.453
总计		14827079	292786	100.000

<色谱图>

mAU



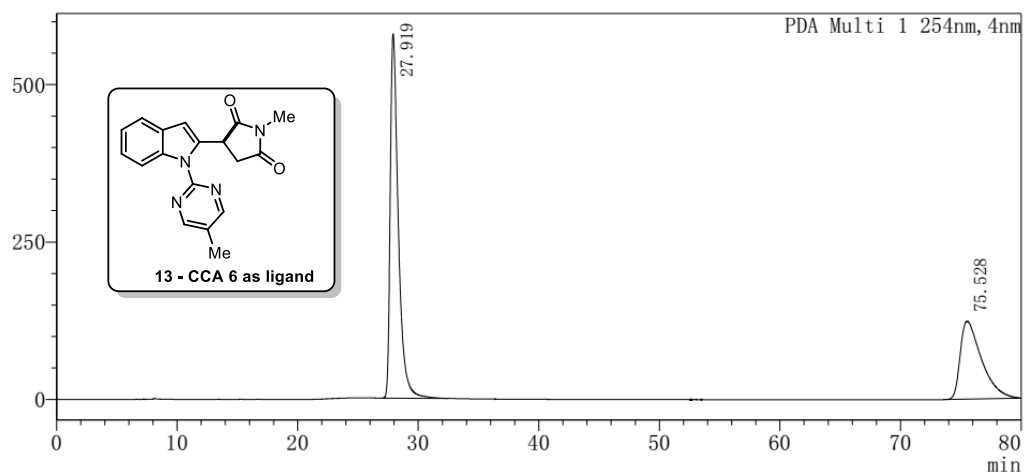
<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	27.906	3749206	82709	77.357
2	75.477	1097420	9389	22.643
总计		4846625	92097	100.000

<色谱图>

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	27.919	27080288	578476	64.012
2	75.528	15224723	123744	35.988
总计		42305011	702220	100.000