

---

**Supplementary information****Axially chiral phenanthroline ligand-enabled Cu-catalyzed asymmetric acyloxylation of cyclic biaryliodonium salts**

Shouyi Cen, Yuzhen Ma, Yanfei Liu, Mingkun Lin, Yi Yu, Zhipeng Zhang

## Table of Contents

1. General information .....	S1
2. Optimization of the reaction conditions for the acyloxylation of cyclic diaryliodonium salts .....	S2
3. General procedures for asymmetric acyloxylation of cyclic diaryliodoniums .....	S6
4. Scaled-up reaction .....	S7
5. Unsuccessful substrates for the asymmetric acyloxylation of cyclic diaryliodoniums .....	S7
6. Synthetic transformations of the product <b>3a</b> .....	S8
7. Characterization of the products .....	S10
8. NMR and HPLC spectra .....	S26
9. References .....	S109

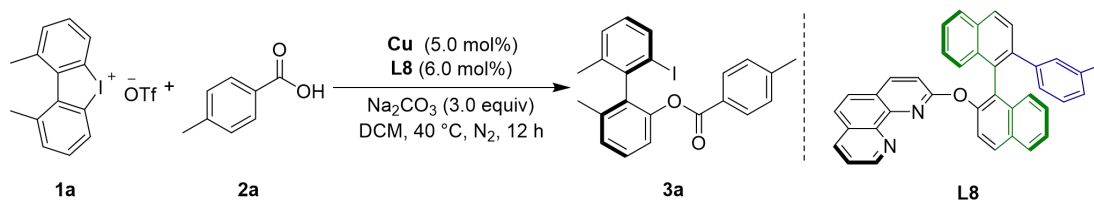
## 1. General information

Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel plates (SGF254). Flash column chromatography was performed on silica gel (300-400 mesh). Visualization of TLC was accomplished by irradiation with UV light at 254 nm. All new compounds were characterized by means of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and HR-MS.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE III 400. High-resolution mass spectra (HR-MS) were recorded on a JEOL AccuTOF LC-plus 4G or AB SCIEXX500R (ESI). Specific rotations were recorded on digital automatic polarimeter (WZZ-2S). Melting points were obtained for all crystalline solids on an INESA SGW X-4 Melting-Point Apparatus with microscope. Chemical shifts of  $^1\text{H}$  NMR spectra were reported in ppm ( $\delta$ ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ( $\text{CDCl}_3$ ,  $\delta$  7.26 ppm;  $\text{DMSO-}d_6$ ,  $\delta$  2.50 ppm). Chemical shifts of  $^{13}\text{C}$  NMR spectra are reported in ppm relative to  $\text{CDCl}_3$  (77.16 ppm) or  $\text{DMSO-}d_6$  (39.52 ppm), and were obtained with  $^1\text{H}$  decoupling.  $^{19}\text{F}$  NMR was recorded on a Bruker AVANCE III 400 NMR spectrometer ( $\text{CFCl}_3$  as an external standard) and were obtained with  $^1\text{H}$  decoupling. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, tt = triplet triplet, m = multiplet. The enantiomeric ratios (er) were determined via chiral HPLC (Shimadzu, Prominence LC-20A) using Daicel Chiralpak AD-H, IC, IG column or Daicel Chiralcel OD-H, OJ-H column. All cyclic diaryliodoniums<sup>[1]</sup> and ligands<sup>[2]</sup> were synthesized according to the reported procedures.

Abbreviations: DCM = dichloromethane, DMSO = dimethyl sulfoxide, EtOAc = ethyl acetate, THF = tetrahydrofuran, DCE = 1,2-dichloroethane, TBME = methyl tert-butyl ether, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, N.D. = Not Detected.

## 2. Optimization of the reaction conditions for the acyloxylation of cyclic diaryliodonium salts

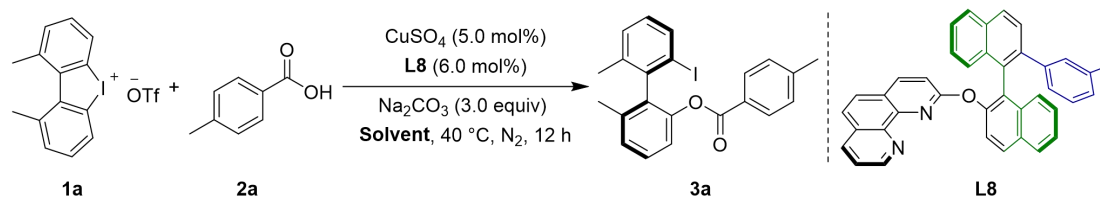
**Table S1. Screening of the copper salts<sup>a</sup>**



Entry	[Cu] (5 mol%)	Yield <sup>b</sup> (%)	er <sup>c</sup>
1	Cu(OTf) <sub>2</sub>	80	93.5:6.5
2	CuCl <sub>2</sub>	5	88:12
3	CuBr <sub>2</sub>	10	88:12
4	CuBr	70	71.5:28.5
5	CuCN	83	79.5:20.5
6	CuI	98	80:20
7	CuSCN	95	77:23
8	CuCl	94	60:40
9	Cu(CH <sub>3</sub> CN) <sub>4</sub> PF <sub>6</sub>	30	67.5:32.5
10	CuTc	40	50:50
11	CuSO <sub>4</sub>	80	94.5:5.5
12	Cu(acac) <sub>2</sub>	99	87.5:12.5
13	Cu(OAc) <sub>2</sub>	80	91:9

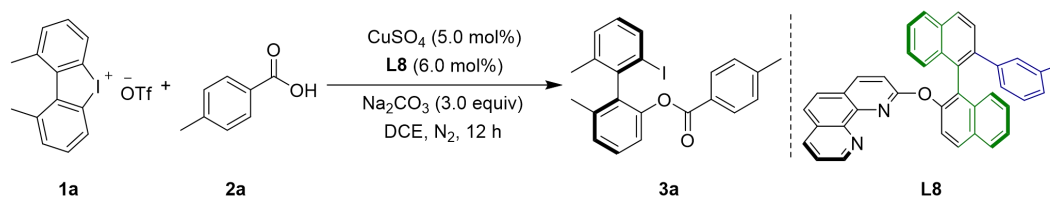
<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), [Cu] (5 mol%), **L8** (6 mol%), Na<sub>2</sub>CO<sub>3</sub> (3.0 equiv) in anhydrous DCM (4.0 mL) under N<sub>2</sub> atmosphere at 40 °C for 12 h. <sup>b</sup>Yield of the isolated products. <sup>c</sup>The er values were determined by HPLC analysis on a chiral stationary phase and reported as ratios of (*R*:*S*).

**Table S2. Screening of the solvents<sup>a</sup>**



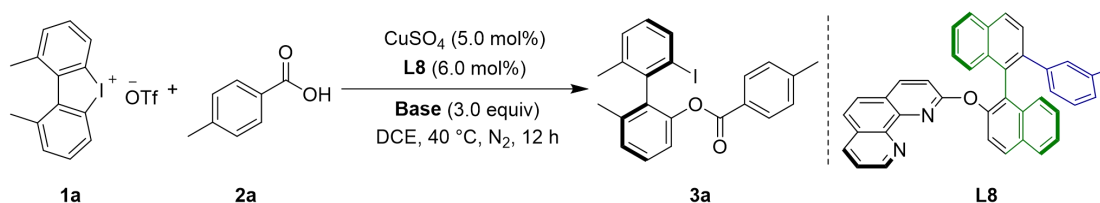
Entry	Solvent	Yield <sup>b</sup> (%)	er <sup>c</sup>
1	DCM	80	94.5:5.5 (92:8) <sup>d</sup>
2	DMSO	73	72:28
3	toluene	65	90.5:9.5
4	PhCl	94	93:7
5	1,4-dioxane	86	90:10
6	EtOAc	94	92:8
7	TBME	99	94:6
8	MeCN	98	90:10
9	THF	99	91:9
10	DCE	82	94.5:5.5
11	MeOH	N.D.	-

<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol),  $\text{CuSO}_4$  (5 mol%), **L8** (6 mol%),  $\text{Na}_2\text{CO}_3$  (3.0 equiv) in anhydrous solvent (4.0 mL) under  $\text{N}_2$  atmosphere at 40 °C for 12 h. <sup>b</sup>Yield of the isolated products. <sup>c</sup>The er values were determined by HPLC analysis on a chiral stationary phase and reported as ratios of (*R*:*S*). <sup>d</sup>Undried DCM was used as solvent.

**Table S3. Optimization of the reaction temperature<sup>a</sup>**

Entry	Temperature (°C)	Yield <sup>b</sup> (%)	er <sup>c</sup>
1	30	46	94.5:5.5
2	40	82	94.5:5.5
3	50	81	94:6

<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol),  $\text{CuSO}_4$  (5 mol%), **L8** (6 mol%),  $\text{Na}_2\text{CO}_3$  (3.0 equiv) in anhydrous DCE (4.0 mL) under  $\text{N}_2$  atmosphere for 12 h. <sup>b</sup>Yield of the isolated products. <sup>c</sup>The er values were determined by HPLC analysis on a chiral stationary phase and reported as ratios of (*R*:*S*).

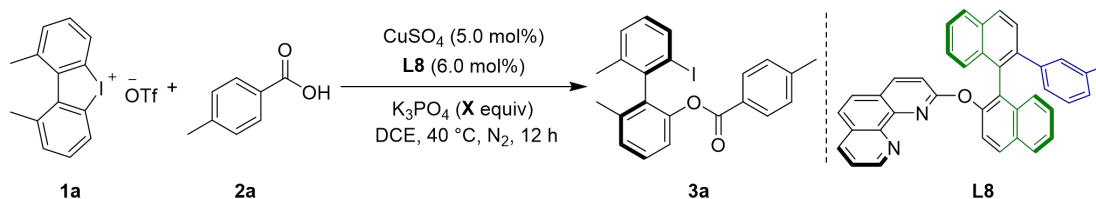
**Table S4. Screening of the bases<sup>a</sup>**

Entry	Base	Yield <sup>b</sup> (%)	er <sup>c</sup>
1	$\text{Na}_2\text{CO}_3$	82	94.5:5.5
2	$\text{K}_2\text{CO}_3$	97	94.5:5.5
3	$\text{Li}_2\text{CO}_3$	94	92:8
4	$\text{Cs}_2\text{CO}_3$	77	94.5:5.5
5	$\text{KHCO}_3$	92	94:6
6	$\text{NaHCO}_3$	56	93.5:6.5
7	KOH	90	94:6
8	NaOH	58	93.5:6.5

9	<sup>t</sup> BuONa	41	94:6
10	<sup>t</sup> BuOK	69	94:6
11	K <sub>3</sub> PO <sub>4</sub>	77	95.5:4.5
12	K <sub>2</sub> HPO <sub>4</sub>	90	94:6
13	KH <sub>2</sub> PO <sub>4</sub>	trace	-
14	NaOAc	92	93.5:6.5
15	KOAc	64	94:6
16	CsOAc	76	94.5:5.5
17	NEt <sub>3</sub>	91	94:6
18	DBU	28	64.5:35.5

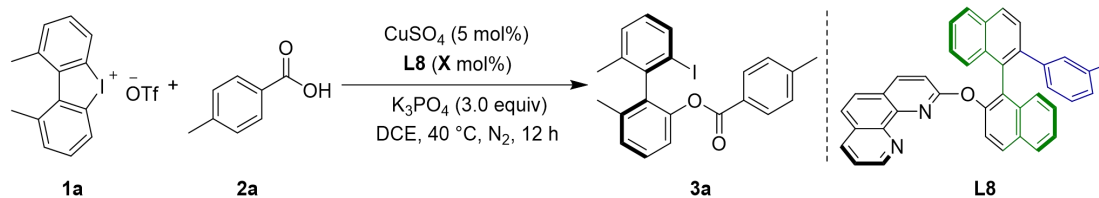
<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), CuSO<sub>4</sub> (5 mol%), **L8** (6 mol%), base (3.0 equiv) in anhydrous DCE (4.0 mL) under N<sub>2</sub> atmosphere at 40 °C for 12 h. <sup>b</sup>Yield of the isolated products. <sup>c</sup>The er values were determined by HPLC analysis on a chiral stationary phase and reported as ratios of (*R*:*S*).

**Table S5. Optimization of the loading of K<sub>3</sub>PO<sub>4</sub><sup>a</sup>**



Entry	K <sub>3</sub> PO <sub>4</sub> (X equiv)	Yield <sup>b</sup> (%)	er <sup>c</sup>
1	1.0	77	94.5:5.5
2	1.5	78	94:6
3	2.0	78	94:6
4	2.5	76	94:6
5	3.0	77	95.5:4.5
6	3.5	73	94:6

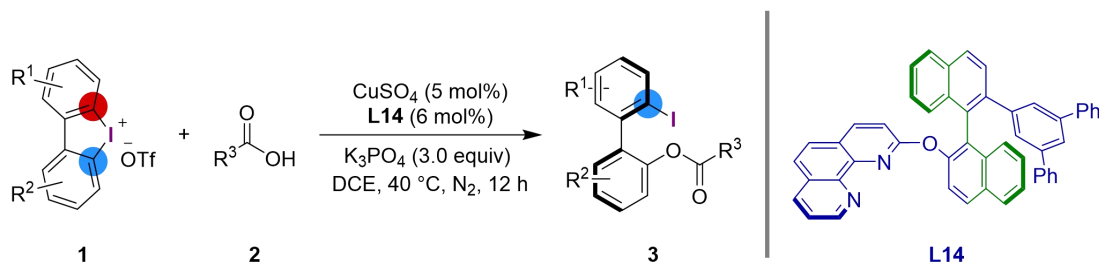
<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), CuSO<sub>4</sub> (5 mol%), **L8** (6 mol%), K<sub>3</sub>PO<sub>4</sub> (X equiv) in anhydrous DCE (4.0 mL) under N<sub>2</sub> atmosphere at 40 °C for 12 h. <sup>b</sup>Yield of the isolated products. <sup>c</sup>The er values were determined by HPLC analysis on a chiral stationary phase and reported as ratios of (*R*:*S*).

**Table S6. Optimization of the ratio of CuSO<sub>4</sub> and ligand L8<sup>a</sup>**

Entry	L8 (X mol%)	Yield <sup>b</sup> (%)	er <sup>c</sup>
1	5	73	94.5:5.5
2	6	77	95.5:4.5
3	7.5	78	94.5:5.5
4	10	78	94:6

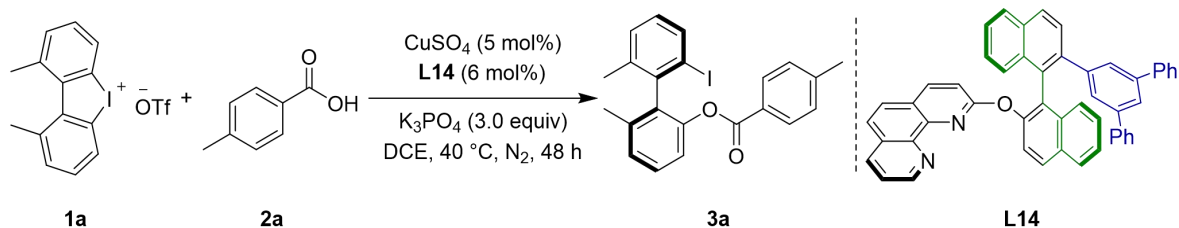
<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), CuSO<sub>4</sub> (5 mol%), L8 (X mol%), K<sub>3</sub>PO<sub>4</sub> (3.0 equiv) in anhydrous DCE (4.0 mL) under N<sub>2</sub> atmosphere at 40 °C for 12 h. <sup>b</sup>Yield of the isolated products. <sup>c</sup>The er values were determined by HPLC analysis on a chiral stationary phase and reported as ratios of (*R*:*S*).

### 3. General procedures for asymmetric acyloxylation of cyclic diaryliodoniums



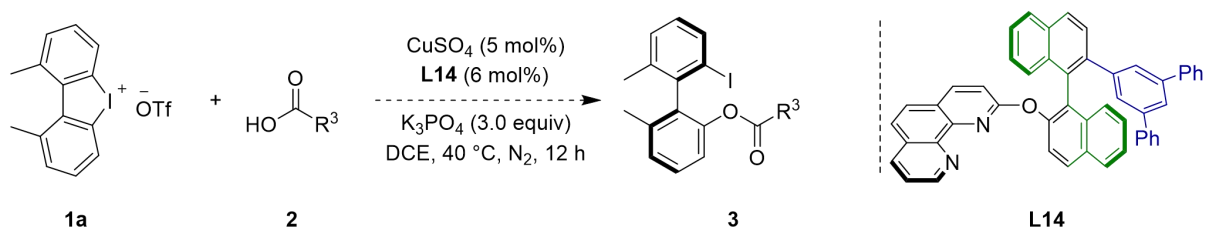
A flame-dried Schlenk tube (25 mL) equipped with a magnetic stir bar was charged with CuSO<sub>4</sub> (0.8 mg, 0.005 mmol, 5 mol%), L14 (4.0 mg, 0.006 mmol, 6 mol%), K<sub>3</sub>PO<sub>4</sub> (63.7 mg, 0.30 mmol, 3.0 equiv), cyclic diaryliodonium salt **1** (0.10 mmol, 1.0 equiv) and carboxylic acid **2** (0.12 mmol, 1.2 equiv), anhydrous DCE (4.0 mL) was added via a syringe under N<sub>2</sub> atmosphere and the resulting mixture was stirred at 40 °C (oil bath) for 12 hours. Upon completion, the solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford the corresponding product **3**.

#### 4. Scaled-up reaction

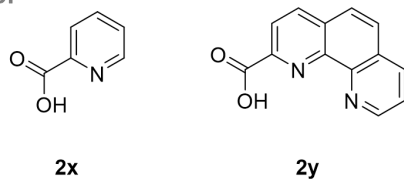


A flame-dried Schlenk tube (100 mL) equipped with a magnetic stir bar was charged with  $\text{CuSO}_4$  (7.9 mg, 0.05 mmol, 5 mol%), **L14** (40.5 mg, 0.06 mmol, 6 mol%),  $\text{K}_3\text{PO}_4$  (637 mg, 3.00 mmol, 3.0 equiv), cyclic diaryliodonium salt **1a** (456 mg, 1.00 mmol, 1.0 equiv) and benzoic acid **2a** (163 mg, 1.20 mmol, 1.2 equiv), anhydrous DCE (40.0 mL) was added via a syringe under  $\text{N}_2$  atmosphere and the resulting mixture was stirred at 40 °C (oil bath) for 48 hours. Upon completion, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20/1) as the eluent to afford the product **3a** as a yellow solid (438 mg, 99%, 97:3 er).

#### 5. Unsuccessful substrates for the asymmetric acyloxylation of cyclic diaryliodoniums

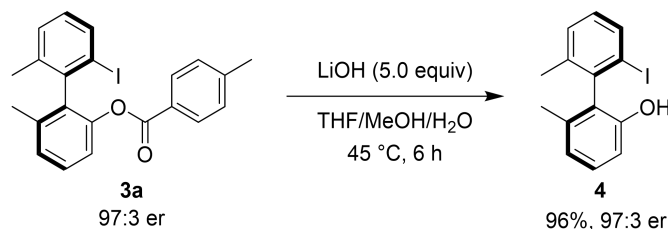


unsuccessful substrates:

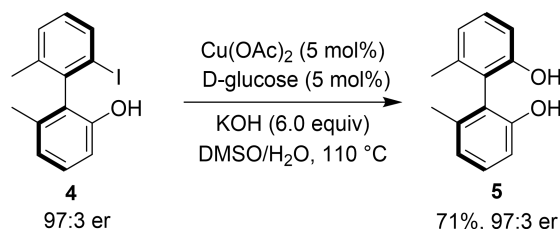


No desired products were obtained using **2x** or **2y** as nucleophile, in the absence or presence of  $\text{NiCl}_2(\text{dppe})$ .

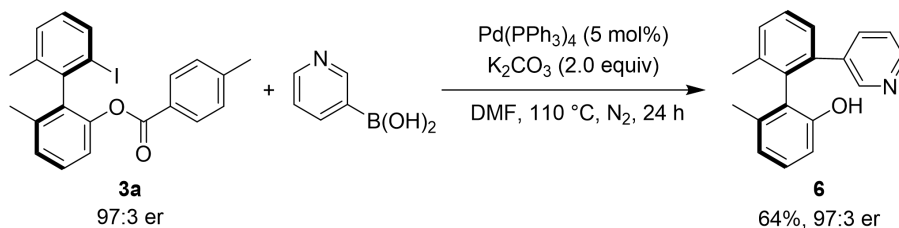
## 6. Synthetic transformations of the product 3a



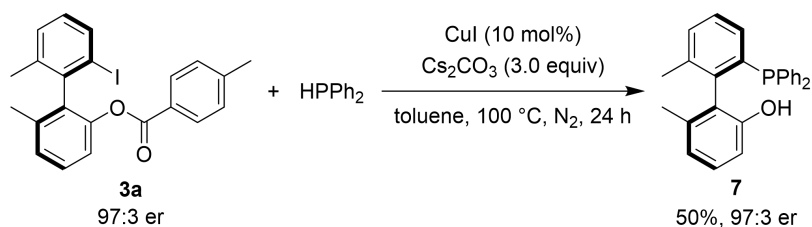
To a solution of **3a** (100.0 mg, 0.23 mmol) in THF/MeOH/H<sub>2</sub>O (2.0 mL, 1:3:1) was added LiOH (27.0 mg, 5.0 equiv), then the reaction mixture was stirred at 45 °C (oil bath) for 6 h. Upon completion, the resulting mixture was quenched with water and extracted with DCM. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10/1) as the eluent to afford the product **4** as a colorless oil (70.1 mg, 96%, 97:3 er).



A Schlenk tube (25 mL) with a magnetic stir bar was charged with **4** (70.0 mg, 0.22 mmol), Cu(OAc)<sub>2</sub> (2.0 mg, 5.0 mol%), D-glucose (1.6 mg, 5.0 mol%), KOH (70.5 mg, 6.0 equiv), DMSO (1.0 mL) and H<sub>2</sub>O (1.0 mL). Then the reaction mixture was stirred at 110 °C (oil bath) for 12 h. Upon completion, the resulting mixture was cooled to room temperature and quenched with water, and extracted with ethyl acetate. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (8/1) as the eluent to afford the product **5** as a white solid (32.8 mg, 71% for one step, 97:3 er).



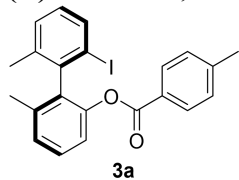
A Schlenk tube (25 mL) with a magnetic stir bar was charged with **3a** (96.0 mg, 0.22 mmol), 3-pyridylboronic acid (40.5 mg, 0.33 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (12.7 mg, 5.0 mol%), K<sub>2</sub>CO<sub>3</sub> (60.8 mg, 2.0 equiv), DMF (2.0 mL) under N<sub>2</sub> atmosphere. Then the reaction mixture was stirred at 110 °C (oil bath) for 24 h. Upon completion, the resulting mixture was cooled to room temperature and quenched with water, and extracted with ethyl acetate. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (3/1) as the eluent to afford the product **6** as a white solid (38.0 mg, 64%, 97:3 er).



A flame-dried sealed tube (25 mL) was charged with **3a** (100.0 mg, 0.23 mmol), CuI (4.38 mg, 10 mol%), Cs<sub>2</sub>CO<sub>3</sub> (224.8 mg, 3.0 equiv), anhydrous toluene (2.0 mL) and HPPH<sub>2</sub> (85.6 mg, 0.46 mmol) under N<sub>2</sub> atmosphere. Then the reaction mixture was stirred at 100 °C (oil bath) for 24 h. Upon completion, the resulting mixture was cooling to room temperature and quenched with water, and extracted with ethyl acetate. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20/1) as the eluent to afford the product **7** as a colorless oil (43.2 mg, 50%, 97:3 er).

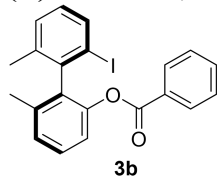
## 7. Characterization of the products

### (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-methylbenzoate (**3a**)



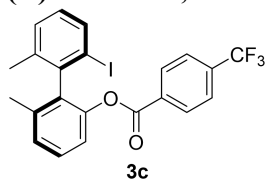
Yellow solid, 44.2 mg, Yield: 99%;  $[\alpha]_{\text{D}}^{15} = -87.2$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 8.0$  Hz, 1H), 7.65 (d,  $J = 8.0$  Hz, 2H), 7.40 (t,  $J = 7.6$  Hz, 1H), 7.28 (d,  $J = 8.0$  Hz, 1H), 7.74 (d,  $J = 7.6$  Hz, 1H), 7.16 (d,  $J = 8.4$  Hz, 1H), 7.14 (d,  $J = 8.4$  Hz, 2H), 6.88 (t,  $J = 7.6$  Hz, 1H), 2.37 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 148.1, 144.1, 141.1, 138.6, 137.7, 136.5 (2C), 130.0, 129.9, 129.3, 129.2, 128.7, 127.5, 126.8, 120.4, 101.1, 21.8, 21.4, 19.6. Known compound (ref. 3).

### (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl benzoate (**3b**)



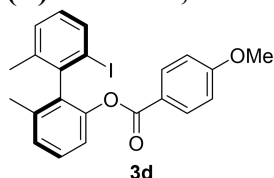
Yellow solid, 42.6 mg, Yield: 99%;  $[\alpha]_{\text{D}}^{15} = -57.4$  ( $c = 0.53$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 – 7.74 (m, 3H), 7.51 (t,  $J = 7.2$  Hz, 1H), 7.41 (t,  $J = 8.0$  Hz, 1H), 7.35 (t,  $J = 8.0$  Hz, 1H), 7.28 (d,  $J = 7.6$  Hz, 1H), 7.25 (d,  $J = 7.6$  Hz, 1H), 7.17 (d,  $J = 7.6$  Hz, 1H), 6.88 (t,  $J = 7.6$  Hz, 1H), 2.07 (s, 3H), 2.06 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 148.0, 141.0, 138.6, 137.8, 136.6, 136.5, 133.4, 130.0, 129.9, 129.6, 129.3, 128.8, 128.5, 127.6, 120.3, 101.0, 21.3, 19.6. Known compound (ref. 3). The absolute configuration of **3b** was established to be (*R*) by comparison of the specific rotation of it with the literature-reported value for a sample of (*S*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl benzoate. Specific rotation of **3b**:  $[\alpha]_{\text{D}}^{15} = -57.4$  ( $c = 0.53$ ,  $\text{CHCl}_3$ ); Ref. 4:  $[\alpha]_{\text{D}}^{20} = +60.2$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ) for a sample with 0.5:99.5 e.r. (*S*). All other compounds **3** (except **3i** and **3v**) were assigned to be (*R*) by analogy.

### (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-(trifluoromethyl)benzoate (**3c**)



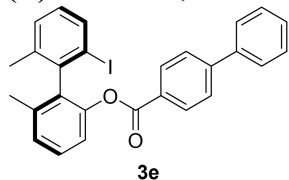
Yellow solid, 49.1 mg, Yield: 99%;  $[\alpha]_{\text{D}}^{15} = -60.0$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.0$  Hz, 2H), 7.75 (d,  $J = 8.0$  Hz, 1H), 7.61 (d,  $J = 8.4$  Hz, 2H), 7.43 (t,  $J = 8.0$  Hz, 1H), 7.30 (d,  $J = 8.0$  Hz, 1H), 7.27 (d,  $J = 7.6$  Hz, 1H), 7.18 (d,  $J = 7.6$  Hz, 1H), 6.90 (t,  $J = 7.6$  Hz, 1H), 2.06 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 147.8, 140.9, 138.6, 138.0, 136.7, 136.4, 134.8 (q,  $J_{\text{C-F}} = 33.3$  Hz), 132.8, 130.3, 130.0, 129.5, 128.9, 128.0, 125.5 (q,  $J_{\text{C-F}} = 4.0$  Hz), 123.7 (q,  $J_{\text{C-F}} = 273.7$  Hz), 120.1, 100.9, 21.3, 19.5.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.2; HRMS (ESI-TOF)  $m/z$  Calcd. for  $\text{C}_{22}\text{H}_{16}\text{O}_2\text{F}_3\text{NaI}^+$   $[\text{M}+\text{Na}]^+$ : 519.0039; Found: 519.0042.

**(*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-methoxybenzoate (3d)**



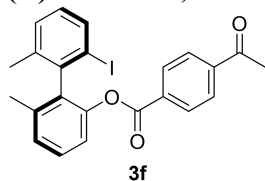
White solid, 45.3 mg, Yield: 99%;  $[\alpha]_{\text{D}}^{15} = -66.8$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 6.8$  Hz, 1H), 7.71 (d,  $J = 9.2$  Hz, 2H), 7.39 (t,  $J = 7.6$  Hz, 1H), 7.27 (d,  $J = 8.0$  Hz, 1H), 7.22 (d,  $J = 7.6$  Hz, 1H), 7.15 (d,  $J = 7.6$  Hz, 1H), 6.87 (t,  $J = 7.6$  Hz, 1H), 6.81 (d,  $J = 8.8$  Hz, 2H), 3.81 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.2, 163.7, 148.1, 141.2, 138.6, 137.6, 136.5, 132.1, 129.9, 129.2, 128.7, 127.4, 121.9, 120.4, 113.7, 101.1, 55.5, 21.3, 19.5. Known compound (ref. 3).

**(*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl [1,1'-biphenyl]-4-carboxylate (3e)**



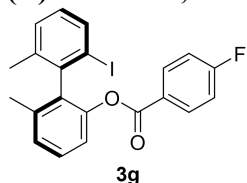
Colorless oil, 50.1 mg, Yield: 99%;  $[\alpha]_{\text{D}}^{15} = -49.6$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 8.4$  Hz, 2H), 7.77 (d,  $J = 8.0$  Hz, 1H), 7.61 – 7.56 (m, 4H), 7.48 – 7.37 (m, 4H), 7.32 (d,  $J = 7.6$  Hz, 1H), 7.26 (d,  $J = 7.6$  Hz, 1H), 7.19 (d,  $J = 7.6$  Hz, 1H), 6.90 (t,  $J = 8.0$  Hz, 1H), 2.09 (s, 3H), 2.07 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 148.1, 146.1, 141.1, 140.0, 138.7, 137.8, 136.6, 136.5, 130.5, 130.0, 129.3, 129.1, 128.8, 128.3 (2C), 127.6, 127.4, 127.1, 120.3, 101.1, 21.4, 19.6. HRMS (ESI-TOF)  $m/z$  Calcd. for  $\text{C}_{27}\text{H}_{21}\text{O}_2\text{NaI}^+$   $[\text{M}+\text{Na}]^+$ : 527.0478; Found: 527.0473.

**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-acetylbenzoate (3f)**



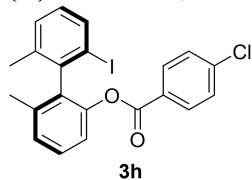
Colorless oil, 44.6 mg, Yield: 98%;  $[\alpha]_{\text{D}}^{15} = -51.2$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.4$  Hz, 2H), 7.81 (d,  $J = 8.4$  Hz, 2H), 7.74 (d,  $J = 8.0$  Hz, 1H), 7.42 (t,  $J = 8.0$  Hz, 1H), 7.29 (d,  $J = 8.4$  Hz, 1H), 7.26 (d,  $J = 7.6$  Hz, 1H), 7.17 (d,  $J = 7.6$  Hz, 1H), 6.88 (t,  $J = 7.6$  Hz, 1H), 2.61 (s, 3H), 2.06 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.6, 163.7, 147.8, 140.9, 140.5, 138.6, 137.9, 136.6, 136.4, 133.3, 130.2, 130.0, 129.4, 128.8, 128.3, 127.9, 120.1, 100.9, 27.0, 21.3, 19.5. Known compound (ref. 3).

**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-fluorobenzoate (3g)**



White solid, 43.6 mg, Yield: 98%;  $[\alpha]_{\text{D}}^{15} = -46.8$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 – 7.73 (m, 3H), 7.41 (t,  $J = 8.0$  Hz, 1H), 7.26 (t,  $J = 9.2$  Hz, 2H), 7.17 (d,  $J = 7.6$  Hz, 1H), 7.01 (t,  $J = 8.4$  Hz, 2H), 6.88 (t,  $J = 7.6$  Hz, 1H), 2.05 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1 (d,  $J_{\text{C-F}} = 255.5$  Hz), 163.6, 147.9, 141.0, 138.6, 137.8, 136.6, 136.4, 132.6 (d,  $J_{\text{C-F}} = 10.1$  Hz), 130.0, 129.4, 128.8, 127.7, 125.8 (d,  $J_{\text{C-F}} = 3.0$  Hz), 120.3, 115.7 (d,  $J_{\text{C-F}} = 22.2$  Hz), 101.0, 21.3, 19.5.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.9. Known compound (ref. 3).

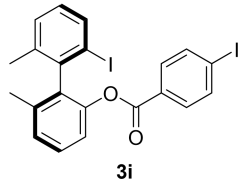
**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-chlorobenzoate (3h)**



White solid, 44.5 mg, Yield: 96%;  $[\alpha]_{\text{D}}^{15} = -56.4$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 7.6$  Hz, 1H), 7.67 (d,  $J = 8.4$  Hz, 2H), 7.41 (t,  $J = 8.0$  Hz, 1H), 7.32 (d,  $J = 8.4$  Hz, 2H), 7.28 (d,  $J = 6.8$  Hz, 1H), 7.25 (d,  $J = 8.0$  Hz, 1H), 7.17 (d,  $J = 7.6$  Hz, 1H), 6.89 (t,  $J = 7.6$  Hz, 1H), 2.05 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.7, 147.7, 141.0, 139.9, 138.6, 137.8,

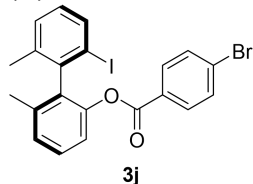
136.6, 136.4, 131.3, 130.0, 129.4, 128.9, 128.8, 128.0, 127.8, 120.2, 101.0, 21.3, 19.5. Known compound (ref. 3).

**(*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-iodobenzoate (3i)**



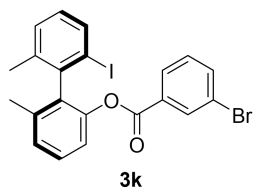
White solid, 54.3 mg, Yield: 98%;  $[\alpha]_{\text{D}}^{15} = -43.2$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 8.0$  Hz, 1H), 7.71 (d,  $J = 8.4$  Hz, 2H), 7.44 (d,  $J = 8.4$  Hz, 2H), 7.40 (d,  $J = 8.0$  Hz, 1H), 7.28 (d,  $J = 8.0$  Hz, 1H), 7.25 (d,  $J = 8.0$  Hz, 1H), 7.17 (d,  $J = 7.6$  Hz, 1H), 6.89 (t,  $J = 8.0$  Hz, 1H), 2.05 (s, 3H), 2.05 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.0, 147.8, 140.9, 138.6, 137.9, 137.8, 136.6, 136.4, 131.3, 130.0, 129.4, 129.0, 128.8, 127.8, 120.2, 101.4, 101.0, 21.3, 19.5. Known compound (ref. 3). The absolute configuration of **3i** was established to be (*R*) by comparison of the specific rotation of it with the literature-reported value for a sample of (*S*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-iodobenzoate. Specific rotation of **3i**:  $[\alpha]_{\text{D}}^{15} = -43.2$  ( $c = 0.50$ ,  $\text{CHCl}_3$ ); Ref. 4:  $[\alpha]_{\text{D}}^{20} = +46.0$  ( $c = 1.1$ ,  $\text{CHCl}_3$ ) for a sample with 99:1 e.r. (*S*). All other compounds **3** (except **3b** and **3v**) were assigned to be (*R*) by analogy.

**(*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-bromobenzoate (3j)**



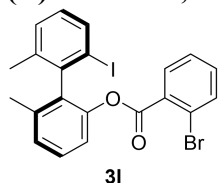
White solid, 50.7 mg, Yield: 99%;  $[\alpha]_{\text{D}}^{15} = -56.4$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 8.4$  Hz, 1H), 7.60 (d,  $J = 8.8$  Hz, 2H), 7.48 (d,  $J = 8.8$  Hz, 2H), 7.41 (t,  $J = 8.0$  Hz, 1H), 7.28 (d,  $J = 8.8$  Hz, 1H), 7.25 (d,  $J = 8.0$  Hz, 1H), 7.17 (d,  $J = 7.6$  Hz, 1H), 6.89 (t,  $J = 7.6$  Hz, 1H), 2.05 (s, 3H), 2.05 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.8, 147.8, 140.9, 138.6, 137.8, 136.6, 136.4, 131.9, 131.4, 130.0, 129.4, 128.8, 128.6, 128.5, 127.8, 120.2, 101.0, 21.3, 19.5. Known compound (ref. 3).

**(*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 3-bromobenzoate (3k)**



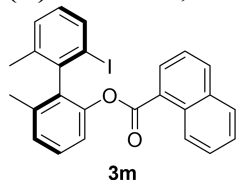
Yellow solid, 50.2 mg, Yield: 99%;  $[\alpha]_{\text{D}}^{15} = -40.8$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (t,  $J = 2.0$  Hz, 1H), 7.77 (d,  $J = 8.0$  Hz, 1H), 7.68 (dt,  $J = 8.0, 1.2$  Hz, 1H), 7.63 (ddd,  $J = 8.0, 2.0, 1.2$  Hz, 1H), 7.42 (t,  $J = 8.0$  Hz, 1H), 7.30 (d,  $J = 8.0$  Hz, 1H), 7.26 (d,  $J = 7.6$  Hz, 1H), 7.22 (t,  $J = 8.0$  Hz, 1H), 7.20 (d,  $J = 7.6$  Hz, 1H), 6.91 (t,  $J = 7.6$  Hz, 1H), 2.07 (s, 3H), 2.06 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 147.8, 140.9, 138.6, 137.9, 136.7, 136.4, 136.3, 133.0, 131.5, 130.0 (2C), 129.5, 128.8, 128.4, 127.8, 122.5, 120.1, 101.0, 21.3, 19.5; HRMS (ESI-TOF)  $m/z$  Calcd. for  $\text{C}_{21}\text{H}_{16}\text{O}_2\text{NaBrI}^+$   $[\text{M}+\text{Na}]^+$ : 528.9271; Found: 528.9266.

**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 2-bromobenzoate (3l)**



Yellow solid, 50.3 mg, Yield: 99%;  $[\alpha]_{\text{D}}^{15} = -44.4$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 8.0$  Hz, 1H), 7.59 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.42 (t,  $J = 8.0$  Hz, 1H), 7.28 – 7.24 (m, 3H), 7.22 (d,  $J = 7.6$  Hz, 1H), 7.18 (td,  $J = 7.6, 1.2$  Hz, 1H), 7.09 (dd,  $J = 7.6, 2.0$  Hz, 1H), 6.95 (t,  $J = 7.6$  Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 147.8, 141.0, 139.0, 137.9, 136.7, 136.5, 134.4, 132.9, 131.4, 130.1, 129.5, 128.9, 128.0, 127.2, 122.2, 120.5, 101.2, 21.4, 19.6; HRMS (ESI-TOF)  $m/z$  Calcd. for  $\text{C}_{21}\text{H}_{16}\text{O}_2\text{NaBrI}^+$   $[\text{M}+\text{Na}]^+$ : 528.9271; Found: 528.9265.

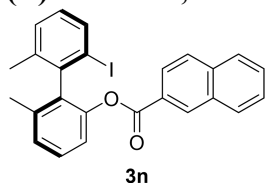
**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 1-naphthoate (3m)**



Yellow solid, 47.7 mg, Yield: 99%;  $[\alpha]_{\text{D}}^{15} = -66.4$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.69 (d,  $J = 8.4$  Hz, 1H), 7.97 (d,  $J = 8.0$ , 1H), 7.85 (d,  $J = 5.6$  Hz, 1H), 7.83 (d,  $J = 4.8$  Hz, 1H), 7.67 (dd,  $J = 7.6, 1.6$  Hz, 1H), 7.58 – 7.49 (m, 2H), 7.46 (d,  $J = 8.0$  Hz, 1H), 7.36 (t,  $J = 8.0$  Hz, 1H), 7.33 (d,  $J = 5.2$  Hz, 1H), 7.30 (d,  $J = 7.6$  Hz, 1H), 7.21 (d,  $J = 7.6$  Hz, 1H), 6.94 (t,  $J$

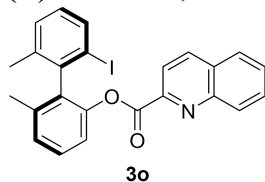
= 7.6 Hz, 1H), 2.13 (s, 3H), 2.10 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 148.2, 141.2, 138.9, 137.9, 136.7 (2C), 133.8 (2C), 131.5, 130.8, 130.1, 129.5, 128.8, 128.6, 128.0, 127.7, 126.3, 126.2, 125.8, 124.6, 120.8, 101.3, 21.4, 19.6. Known compound. 3m was synthesized according to the reported procedures (ref. 3).

**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 2-naphthoate (3n)**



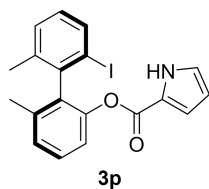
Colorless oil, 45.8 mg, Yield: 96%;  $[\alpha]_{\text{D}}^{15} = -41.2$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (s, 1H), 7.84 (d,  $J = 8.8$  Hz, 2H), 7.81 – 7.78 (m, 3H), 7.58 (t,  $J = 7.2$  Hz, 1H), 7.53 (t,  $J = 7.6$  Hz, 1H), 7.46 (t,  $J = 8.0$  Hz, 1H), 7.40 (d,  $J = 8.30$  Hz, 1H), 7.28 (d,  $J = 7.2$  Hz, 1H), 7.19 (d,  $J = 7.6$  Hz, 1H), 6.90 (t,  $J = 7.6$  Hz, 1H), 2.11 (s, 3H), 2.10 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 148.1, 141.2, 138.7, 137.7, 136.6, 136.5, 135.7, 132.5, 131.8, 130.0, 129.6, 129.4, 128.8, 128.5, 128.2, 127.8, 127.6, 126.8, 126.7, 125.3, 120.3, 101.1, 21.4, 19.6. Known compound (ref. 3).

**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl quinoline-2-carboxylate (3o)**



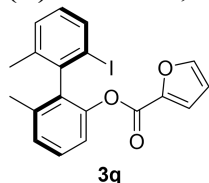
Yellow oil, 15.6 mg, Yield: 33%;  $[\alpha]_{\text{D}}^{21} = -103.1$  ( $c = 0.08$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (d,  $J = 8.8$  Hz, 1H), 8.16 (d,  $J = 8.4$  Hz, 1H), 7.83 (d,  $J = 8.0$  Hz, 1H), 7.77 (dd,  $J = 8.4$ , 1.6 Hz, 1H), 7.75 (d,  $J = 8.4$  Hz, 1H), 7.63 (dd,  $J = 8.4$ , 1.2 Hz, 1H), 7.61 (d,  $J = 8.4$  Hz, 1H), 7.44 (t,  $J = 8.0$  Hz, 1H), 7.37 (d,  $J = 8.0$  Hz, 1H), 7.28 (d,  $J = 7.6$  Hz, 1H), 7.15 (d,  $J = 7.6$  Hz, 1H), 6.86 (t,  $J = 8.0$  Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.6, 148.0, 147.9, 147.4, 140.9, 138.9, 137.9, 137.4, 136.6, 136.4, 131.1, 130.4, 130.1, 129.4, 129.0, 128.8, 128.0, 127.5, 121.0, 120.2, 101.0, 21.4, 19.6; HRMS (ESI-TOF)  $m/z$  Calcd. for  $\text{C}_{24}\text{H}_{19}\text{NO}_2\text{I}^+$   $[\text{M}+\text{H}]^+$ : 480.0455; Found: 480.0461.

**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 1H-pyrrole-2-carboxylate (3p)**



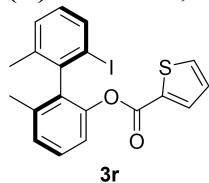
Yellow oil, 25.8 mg, Yield: 62%;  $[\alpha]_{\text{D}}^{21} = -278.2$  ( $c = 0.07$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.94 (s, 1H), 7.75 (d,  $J = 8.0$  Hz, 1H), 7.39 (t,  $J = 7.6$  Hz, 1H), 7.23 (d,  $J = 8.4$  Hz, 2H), 7.22 (d,  $J = 7.2$  Hz, 1H), 7.19 (d,  $J = 7.2$  Hz, 1H), 6.91 (d,  $J = 8.0$  Hz, 1H), 6.89 – 6.87 (m, 1H), 6.71 – 6.69 (m, 1H), 6.19 – 6.17 (m, 1H), 2.06 (s, 3H), 2.04 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.5, 147.6, 141.1, 138.6, 137.7, 136.6, 136.4, 129.9, 129.3, 128.7, 127.4, 123.7, 121.9, 120.2, 116.7, 110.8, 101.0, 21.4, 19.6; HRMS (ESI-TOF)  $m/z$  Calcd. for  $\text{C}_{19}\text{H}_{16}\text{NO}_2\text{NaI}^+$   $[\text{M}+\text{Na}]^+$ : 440.0118; Found: 440.0112.

**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl furan-2-carboxylate (3q)**



White solid, 39.4 mg, Yield: 94%;  $[\alpha]_{\text{D}}^{15} = -77.2$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 7.6$  Hz, 1H), 7.53 (dd,  $J = 1.6, 0.8$  Hz, 1H), 7.39 (t,  $J = 7.6$  Hz, 1H), 7.27 (d,  $J = 8.4$  Hz, 1H), 7.24 (d,  $J = 7.6$  Hz, 1H), 7.18 (d,  $J = 7.6$  Hz, 1H), 6.89 (t,  $J = 7.6$  Hz, 1H), 6.82 (dd,  $J = 3.6, 0.8$  Hz, 1H), 6.41 (dd,  $J = 3.6, 2.0$  Hz, 1H), 2.05 (s, 3H), 2.04 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.3, 147.4, 147.2, 143.8, 140.8, 138.7, 137.9, 136.5, 136.4, 129.9, 129.3, 128.8, 127.8, 120.1, 118.9, 112.0, 100.9, 21.3, 19.5. Known compound (ref. 3).

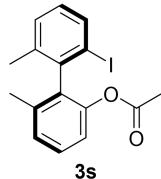
**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl thiophene-2-carboxylate (3r)**



Yellow solid, 43.6 mg, Yield: 99%;  $[\alpha]_{\text{D}}^{15} = -49.2$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 8.0$  Hz, 1H), 7.60 (dd,  $J = 3.6, 1.2$  Hz, 1H), 7.50 (dd,  $J = 5.2, 1.6$  Hz, 1H), 7.40 (t,  $J = 8.0$  Hz, 1H), 7.30 (d,  $J = 8.0$  Hz, 1H), 7.24 (d,  $J = 8.0$  Hz, 1H), 7.18 (d,  $J = 7.6$  Hz, 1H), 7.02 (dd,  $J = 5.2, 3.6$  Hz, 1H), 6.89 (t,  $J = 7.6$  Hz, 1H), 2.06 (s, 3H), 2.05 (s, 3H).  $^{13}\text{C NMR}$

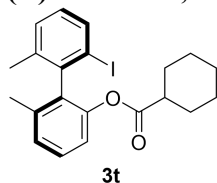
(101 MHz, CDCl<sub>3</sub>)  $\delta$  159.8, 147.7, 140.9, 138.6, 137.8, 136.6, 136.4, 134.3, 133.4, 132.8, 129.9, 129.3, 128.7, 127.9, 127.7, 120.1, 101.0, 21.4, 19.6. Known compound (ref. 3).

**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl acetate (3s)**



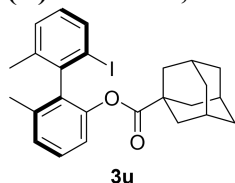
White solid, 36.4 mg, Yield: 99%;  $[\alpha]_D^{15} = -54.6$  ( $c = 0.33$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (d,  $J = 8.0$  Hz, 1H), 7.35 (t,  $J = 8.0$  Hz, 1H), 7.23 (d,  $J = 7.6$  Hz, 1H), 7.20 (d,  $J = 7.2$  Hz, 1H), 7.06 (d,  $J = 8.0$  Hz, 1H), 6.96 (t,  $J = 8.0$  Hz, 1H), 2.03 (s, 3H), 2.01 (s, 3H), 1.90 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.1, 148.0, 140.9, 138.7, 137.8, 136.6, 136.5, 129.9, 129.3, 128.7, 127.8, 120.3, 101.0, 21.2, 20.7, 19.6. Known compound (ref. 3).

**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl cyclohexanecarboxylate (3t)**



Colorless oil, 43.4 mg, Yield: 99%;  $[\alpha]_D^{15} = -61.73$  ( $c = 1.50$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.75 (d,  $J = 8.0$  Hz, 1H), 7.34 (t,  $J = 8.0$  Hz, 1H), 7.21 (d,  $J = 7.6$  Hz, 1H), 7.18 (d,  $J = 7.2$  Hz, 1H), 7.04 (d,  $J = 8.4$  Hz, 1H), 6.93 (t,  $J = 7.6$  Hz, 1H), 2.26 – 2.19 (m, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 1.60 – 1.49 (m, 5H), 1.21 – 1.01 (m, 5H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  174.0, 148.0, 141.0, 138.9, 137.7, 136.6 (2C), 129.9, 129.2, 128.7, 127.5, 120.4, 101.3, 43.0, 28.6, 28.4, 25.8, 25.3, 25.2, 21.3, 19.5. Known compound (ref. 3).

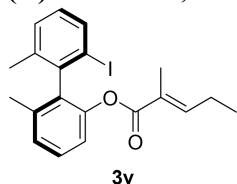
**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl adamantane-1-carboxylate (3u)**



Yellow solid, 48.6 mg, Yield: 99%;  $[\alpha]_D^{15} = -43.6$  ( $c = 0.55$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.76 (d,  $J = 7.6$  Hz, 1H), 7.34 (t,  $J = 8.0$  Hz, 1H), 7.22 (d,  $J = 7.6$  Hz, 1H), 7.18 (d,  $J = 7.6$  Hz, 1H), 7.05 (d,  $J = 8.0$  Hz, 1H), 6.93 (t,  $J = 7.6$  Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 1.90 –

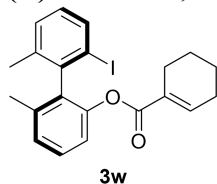
1.87 (m, 3H), 1.67 – 1.66 (m, 1H), 1.64 – 1.62 (m, 2H), 1.59 – 1.58 (m, 8H), 1.56 – 1.53 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.0, 148.0, 141.0, 138.9, 137.7, 136.6 (2C), 129.9, 129.2, 128.7, 127.5, 120.5, 101.3, 28.6, 28.4, 25.8, 25.4, 25.2, 21.3, 19.5. Known compound (ref. 3).

**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (E)-2-methylpent-2-enoate (3v)**



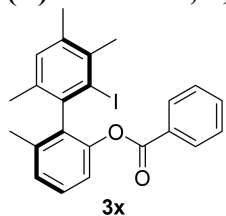
White solid, 41.5 mg, Yield: 99%;  $[\alpha]_D^{15} = -70.4$  ( $c = 5.00$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (d,  $J = 8.0$  Hz, 1H), 7.36 (t,  $J = 8.0$  Hz, 1H), 7.19 (t,  $J = 5.2$  Hz, 2H), 7.19 (d,  $J = 8.0$  Hz, 1H), 6.92 (t,  $J = 7.6$  Hz, 1H), 6.43 (td,  $J = 7.6, 1.6$  Hz, 1H), 2.07 (qd,  $J = 7.6, 1.2$  Hz, 2H), 2.02 (s, 3H), 2.02 (s, 3H), 1.62 – 1.61 (m, 3H), 0.93 (t,  $J = 7.2$  Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.1, 148.2, 145.7, 141.3, 138.7, 137.5, 136.5, 136.4, 129.8, 129.2, 128.6, 127.2, 126.4, 120.4, 101.2, 22.1, 21.3, 19.5, 13.0, 12.0. Known compound (ref. 3). The absolute configuration of **3v** was established to be (*R*) by comparison of the specific rotation of it with the literature-reported value for a sample of (*S*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (E)-2-methylpent-2-enoate. Specific rotation of **3v**:  $[\alpha]_D^{15} = -70.4$  ( $c = 0.50$ , CHCl<sub>3</sub>); Ref. 4:  $[\alpha]_D^{20} = +50.9$  ( $c = 0.9$ , CHCl<sub>3</sub>) for a sample with 0.2:99.8 e.r. (*S*). All other compounds **3** (except **3b** and **3i**) were assigned to be (*R*) by analogy.

**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl cyclohex-1-ene-1-carboxylate (3w)**



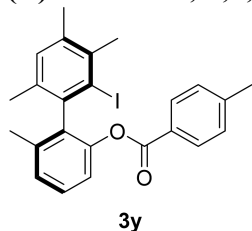
White solid, 42.2 mg, Yield: 98%;  $[\alpha]_D^{15} = -57.2$  ( $c = 0.50$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (d,  $J = 8.0$  Hz, 1H), 7.35 (t,  $J = 7.6$  Hz, 1H), 7.20 (d,  $J = 7.6$  Hz, 1H), 7.17 (t,  $J = 8.0$  Hz, 2H), 6.92 (t,  $J = 8.0$  Hz, 1H), 6.72 – 6.69 (m, 1H), 2.09 – 2.05 (m, 3H), 2.02 (s, 6H), 1.98 – 1.91 (m, 1H), 1.57 – 1.48 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.5, 148.2, 141.5, 141.3, 138.7, 137.5, 136.5 (2C), 129.8, 129.7, 129.1, 128.6, 127.2, 120.4, 101.2, 26.0, 23.9, 22.0, 21.4, 21.3, 19.5. Known compound (ref. 3).

**(R)-2'-iodo-3',4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl benzoate (3x)**



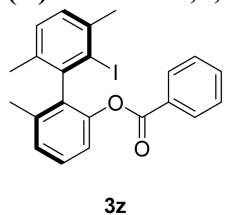
White solid, 31 mg, Yield: 70%;  $[\alpha]_{\text{D}}^{15} = -70.4$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 – 7.72 (m, 2H), 7.50 (tt,  $J = 7.6, 1.2$  Hz, 1H), 7.39 (t,  $J = 8.0$  Hz, 1H), 7.33 (t,  $J = 8.0$  Hz, 2H), 7.26 (d,  $J = 8.0$  Hz, 1H), 7.23 (d,  $J = 7.6$  Hz, 1H), 6.93 (s, 1H), 2.44 (s, 3H), 2.29 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 148.2, 139.4, 138.0, 137.9, 137.6, 136.2, 135.1, 133.2, 131.8, 130.1, 129.8, 128.4, 128.3, 127.5, 120.2, 109.3, 26.3, 21.9, 20.9, 19.6.; HRMS (ESI-TOF)  $m/z$  Calcd. for  $\text{C}_{23}\text{H}_{21}\text{O}_2\text{NaI}^+$   $[\text{M}+\text{Na}]^+$ : 479.0478; Found: 479.0474.

**(R)-2'-iodo-3',4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl 4-methylbenzoate (3y)**



white solid, 46.9 mg, Yield: 99%;  $[\alpha]_{\text{D}}^{15} = -63.2$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 8.4$  Hz, 2H), 7.39 (t,  $J = 7.6$  Hz, 1H), 7.28 (d,  $J = 8.0$  Hz, 1H), 7.23 (d,  $J = 8.0$  Hz, 1H), 7.13 (d,  $J = 8.0$  Hz, 2H), 6.94 (s, 1H), 2.45 (s, 3H), 2.37 (s, 3H), 2.30 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 148.2, 143.9, 139.4, 138.0, 137.8, 137.5, 136.1, 135.1, 131.7, 130.1, 129.1, 128.4, 127.4, 127.0, 120.3, 109.3, 26.3, 21.9, 21.8, 20.9, 19.6. Known compound (ref. 3).

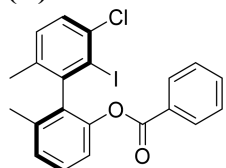
**(R)-2'-iodo-3',6,6'-trimethyl-[1,1'-biphenyl]-2-yl benzoate (3z)**



Yellow solid, 33.8 mg, Yield: 77%;  $[\alpha]_{\text{D}}^{15} = -49.6$  ( $c = 0.33$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 – 7.71 (m, 2H), 7.50 (tt,  $J = 7.2, 1$  Hz, 1H), 7.41 (t,  $J = 8.0$  Hz, 1H), 7.33 (t,  $J =$

8.0 Hz, 2H), 7.28 (d,  $J = 8.4$  Hz, 1H), 7.25 (d,  $J = 7.2$  Hz, 1H), 7.06 (s, 2H), 2.46 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.5, 148.0, 141.6, 139.7, 137.7, 137.5, 135.3, 133.3, 130.0, 129.7 (2C), 128.7, 128.6, 128.4, 127.6, 120.3, 107.8, 29.5, 21.0, 19.5. Known compound (ref. 3).

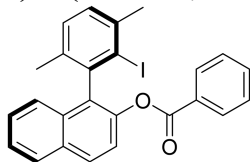
**(*R*)-3'-chloro-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl benzoate (3aa)**



**3aa**

White solid, 33.3 mg, Yield: 72%;  $[\alpha]_{\text{D}}^{15} = -88.0$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 6.8$  Hz, 2H), 7.53 (t,  $J = 7.6$  Hz, 1H), 7.42 (t,  $J = 8.0$  Hz, 1H), 7.36 (t,  $J = 8.0$  Hz, 1H), 7.29 (d,  $J = 4.8$  Hz, 1H), 7.26 (t,  $J = 6.4$  Hz, 2H), 7.11 (d,  $J = 8.0$  Hz, 1H), 2.04 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.5, 147.8, 143.9, 137.4, 137.0, 136.6, 136.4, 133.5, 131.0, 130.0, 129.4, 129.0, 128.5, 128.2, 127.7, 120.5, 105.1, 20.9, 19.5. Known compound (ref. 3).

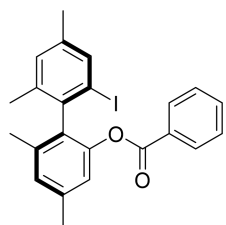
**(*R*)-1-(2-iodo-3,6-dimethylphenyl)naphthalen-2-yl benzoate (3ab)**



**3ab**

Yellow solid, 35.7 mg, Yield: 75%;  $[\alpha]_{\text{D}}^{15} = -26.8$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 9.2$  Hz, 1H), 7.96 (d,  $J = 8.0$  Hz, 1H), 7.87 – 7.84 (m, 2H), 7.58 (d,  $J = 8.8$  Hz, 1H), 7.56 – 7.49 (m, 2H), 7.43 (t,  $J = 8.0$  Hz, 1H), 7.37 (t,  $J = 7.6$  Hz, 2H), 7.32 (d,  $J = 8.4$  Hz, 1H), 7.14 (dd,  $J = 10.8, 8.0$  Hz, 2H), 2.50 (s, 3H), 1.96 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7, 145.5, 140.3, 139.8, 136.5, 133.5 (2C), 132.1, 131.9, 130.1, 129.8, 129.6, 129.3, 129.1, 128.5 (2C), 127.1, 125.9, 125.2, 122.0, 108.4, 29.6, 21.1. Known compound (ref. 3).

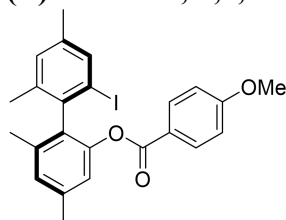
**(*R*)-2'-iodo-4,4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl benzoate (3ac)**



**3ac**

White solid, 45 mg, Yield: 99%;  $[\alpha]_{\text{D}}^{15} = -60.0$  ( $c = 0.50$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 – 7.79 (m, 2H), 7.58 (s, 1H), 7.51 (tt,  $J = 7.2, 1.6$  Hz, 1H), 7.38 – 7.34 (m, 2H), 7.07 (s, 1H), 7.06 (s, 1H), 6.97 (s, 1H), 2.43 (s, 3H), 2.22 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7, 148.1, 139.0, 138.7, 138.3, 138.0, 137.5, 136.9, 133.5, 133.2, 130.9, 130.0, 129.7, 128.5, 128.4, 120.8, 101.4, 21.5, 21.3, 20.6, 19.6. Known compound (ref. 3).

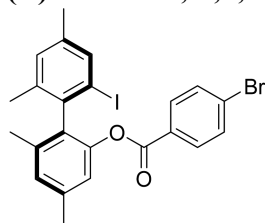
**(R)-2'-iodo-4,4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl 4-methoxybenzoate (3ad)**



**3ad**

Colorless oil, 32.0 mg, Yield: 66%;  $[\alpha]_{\text{D}}^{15} = -49.8$  ( $c = 1.00$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.8$  Hz, 2H), 7.57 (s, 1H), 7.06 (s, 1H), 7.04 (s, 1H), 6.96 (s, 1H), 6.83 (d,  $J = 8.8$  Hz, 2H), 3.83 (s, 3H), 2.42 (s, 3H), 2.22 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 163.6, 148.1, 138.9, 138.7, 138.3, 138.2, 137.4, 136.9, 133.5, 132.1, 130.9, 128.3, 122.1, 120.9, 113.7, 101.4, 55.5, 21.5, 21.3, 20.6, 19.6; HRMS (ESI-TOF)  $m/z$  Calcd. for  $\text{C}_{24}\text{H}_{23}\text{O}_3\text{NaI}^+$   $[\text{M}+\text{Na}]^+$ : 509.0584; Found: 509.0589.

**(R)-2'-iodo-4,4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl 4-bromobenzoate (3ae)**

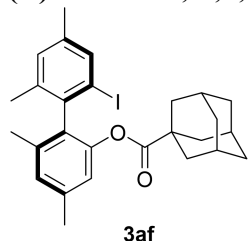


**3ae**

White solid, 41.2 mg, Yield: 77%;  $[\alpha]_{\text{D}}^{15} = -37.2$  ( $c = 1.00$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (d,  $J = 8.8$  Hz, 2H), 7.56 (s, 1H), 7.49 (d,  $J = 8.8$  Hz, 2H), 7.06 (s, 2H), 6.96 (s, 1H), 2.42 (s, 3H), 2.23 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.0, 147.9,

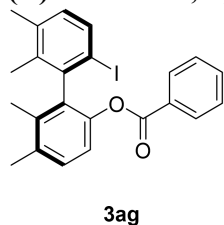
139.1, 138.8, 138.3, 137.9, 137.6, 137.0, 133.4, 131.8, 131.5, 130.9, 128.7, 128.6, 128.5, 120.7, 101.3, 21.5, 21.3, 20.6, 19.5; HRMS (ESI-TOF)  $m/z$  Calcd. for  $C_{23}H_{20}O_2NaBrI^+$   $[M+Na]^+$ : 556.9584; Found: 556.9588.

**(R)-2'-iodo-4,4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl adamantane-1-carboxylate (3af)**



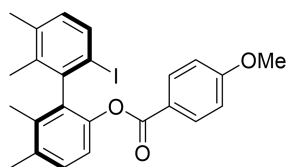
White solid, 32.5 mg, Yield: 63%;  $[\alpha]_D^{15} = -39.6$  ( $c = 0.55$ ,  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.60 (s, 1H), 7.02 (s, 1H), 6.99 (s, 1H), 6.86 (s, 1H), 2.38 (s, 3H), 2.28 (s, 3H), 1.98 (s, 6H), 1.90 – 1.87 (m, 3H), 1.67 – 1.66 (m, 1H), 1.64 – 1.63 (m, 2H), 1.58 – 1.57 (m, 8H), 1.55 – 1.54 (m, 1H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  175.6, 148.1, 139.0, 138.7, 138.6, 138.2, 137.3, 136.8, 133.6, 130.7, 128.2, 120.9, 101.9, 40.8, 38.4, 36.5, 28.0, 21.4, 21.2, 20.6, 19.5. HRMS (ESI-TOF)  $m/z$  Calcd. for  $C_{25}H_{29}N_3ONaI^+$   $[M+Na]^+$ : 537.1248; Found: 537.1253.

**(R)-6'-iodo-2',3',5,6-tetramethyl-[1,1'-biphenyl]-2-yl benzoate (3ag)**



Yellow oil, 45.5 mg, Yield: 99%;  $[\alpha]_D^{15} = -25.2$  ( $c = 0.50$ ,  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.75 – 7.73 (m, 2H), 7.65 (d,  $J = 8.0$  Hz, 1H), 7.50 (tt,  $J = 7.6, 2.0$  Hz, 1H), 7.34 (t,  $J = 8.0$  Hz, 2H), 7.30 (d,  $J = 8.4$  Hz, 1H), 7.18 (d,  $J = 8.4$  Hz, 1H), 6.78 (d,  $J = 8.0$  Hz, 1H), 2.37 (s, 3H), 2.17 (s, 3H), 1.97 (s, 3H), 1.94 (s, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  164.7, 146.2, 141.2, 137.4, 137.1, 137.0, 136.0, 135.9, 134.5, 133.2, 130.7, 129.9, 129.8, 128.4, 119.7, 97.9, 20.3 (2C), 18.0, 16.3. Known compound (ref. 3).

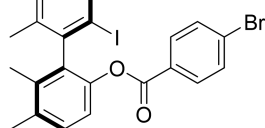
**(R)-6'-iodo-2',3',5,6-tetramethyl-[1,1'-biphenyl]-2-yl 4-methoxybenzoate (3ah)**



**3ah**

Colorless oil, 43.3 mg, Yield: 89%;  $[\alpha]_{D^{15}} = -13.8$  ( $c = 1.00$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 8.0$  Hz, 2H), 7.63 (d,  $J = 8.0$  Hz, 1H), 7.28 (d,  $J = 8.4$  Hz, 1H), 7.17 (d,  $J = 8.4$  Hz, 1H), 6.81 (d,  $J = 8.8$  Hz, 2H), 6.77 (d,  $J = 8.0$  Hz, 1H), 3.82 (s, 3H), 2.36 (s, 3H), 2.17 (s, 3H), 1.95 (s, 3H), 1.93 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 163.6, 146.3, 141.3, 137.4, 137.1, 137.0, 135.9, 135.8, 134.3, 132.0, 130.7, 129.9, 122.1, 119.8, 113.6, 97.9, 55.5, 20.3, 18.0, 16.3; HRMS (ESI-TOF)  $m/z$  Calcd. for  $\text{C}_{24}\text{H}_{23}\text{O}_3\text{Na}^+$   $[\text{M}+\text{Na}]^+$ : 509.0584; Found: 509.0588.

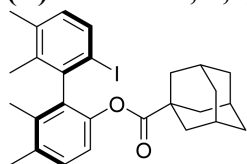
**(R)-6'-iodo-2',3',5,6-tetramethyl-[1,1'-biphenyl]-2-yl 4-bromobenzoate (3ai)**



**3ai**

White solid, 50.5 mg, Yield: 94%;  $[\alpha]_{D^{15}} = -9.7$  ( $c = 1.17$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (d,  $J = 8.0$  Hz, 1H), 7.57 (d,  $J = 8.4$  Hz, 2H), 7.47 (d,  $J = 8.4$  Hz, 2H), 7.29 (d,  $J = 8.0$  Hz, 1H), 7.17 (d,  $J = 8.4$  Hz, 1H), 6.78 (d,  $J = 8.0$  Hz, 1H), 2.36 (s, 3H), 2.17 (s, 3H), 1.94 (s, 3H), 1.93 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.0, 146.0, 141.1, 137.4, 137.1, 137.0, 136.1, 135.9, 134.8, 131.8, 131.4, 130.8, 130.0, 128.7, 128.4, 119.6, 97.8, 20.4, 18.0, 16.3; HRMS (ESI-TOF)  $m/z$  Calcd. for  $\text{C}_{23}\text{H}_{20}\text{O}_2\text{NaBr}^+$   $[\text{M}+\text{Na}]^+$ : 556.9584; Found: 556.9584.

**(R)-6'-iodo-2',3',5,6-tetramethyl-[1,1'-biphenyl]-2-yl adamantane-1-carboxylate (3aj)**

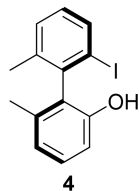


**3aj**

White solid, 49.5 mg, Yield: 97%;  $[\alpha]_{D^{15}} = -12.0$  ( $c = 1.33$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (d,  $J = 8.0$  Hz, 1H), 7.21 (d,  $J = 8.4$  Hz, 1H), 6.94 (d,  $J = 8.4$  Hz, 1H), 6.84 (d,  $J = 8.0$  Hz, 1H), 2.32 (s, 3H), 2.24 (s, 3H), 1.91 (s, 3H), 1.90 (s, 3H), 1.88 – 1.86 (m, 3H), 1.66 – 1.65 (m, 1H), 1.63 – 1.62 (m, 2H), 1.58 – 1.56 (m, 3H), 1.55 – 1.54 (m, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )

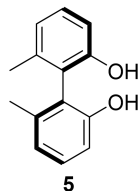
$\delta$  175.6, 146.2, 141.3, 137.7, 137.2, 137.0, 135.9, 135.8, 134.2, 130.5, 129.8, 119.8, 98.4, 40.8, 38.4, 36.5, 27.9, 20.3 (2C), 18.0, 16.3. HRMS (ESI-TOF)  $m/z$  Calcd. for  $C_{27}H_{31}O_2NaI^+$   $[M+Na]^+$ : 537.1261; Found: 537.1265.

**(R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-ol (4)**



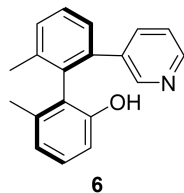
Colorless oil, 70.1 mg, Yield: 96%;  $[\alpha]_D^{20} = +3.5$  ( $c = 2.0$ ,  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.84 (d,  $J = 8.0$  Hz, 1H), 7.32 (d,  $J = 7.6$  Hz, 1H), 7.22 (d,  $J = 7.6$  Hz, 1H), 7.02 (t,  $J = 7.8$  Hz, 1H), 6.89 (d,  $J = 7.2$  Hz, 1H), 6.85 (d,  $J = 8.0$  Hz, 1H), 4.37 (s, 1H), 2.07 (s, 3H), 1.94 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  152.0, 139.8, 139.7, 137.5, 136.9, 130.6, 130.3(2C), 129.3, 122.4, 113.1, 102.6, 21.4, 19.7. Known compound (ref. 3).

**(R)-6,6'-dimethyl-[1,1'-biphenyl]-2,2'-diol (5)**



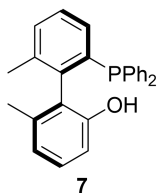
White solid, 32.8 mg, Yield: 71%;  $[\alpha]_D^{20} = +68.6$  ( $c = 0.93$ ,  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.25 (t,  $J = 8.0$  Hz, 2H), 6.92 (d,  $J = 7.6$  Hz, 2H), 6.90 (d,  $J = 8.4$  Hz, 2H), 4.72 (s, 2H), 2.01 (s, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  154.0, 139.1, 130.3, 122.7, 119.7, 113.3, 19.6. Known compound (ref. 3).

**(R)-2',6-dimethyl-6'-(pyridin-3-yl)-[1,1'-biphenyl]-2-ol (6)**



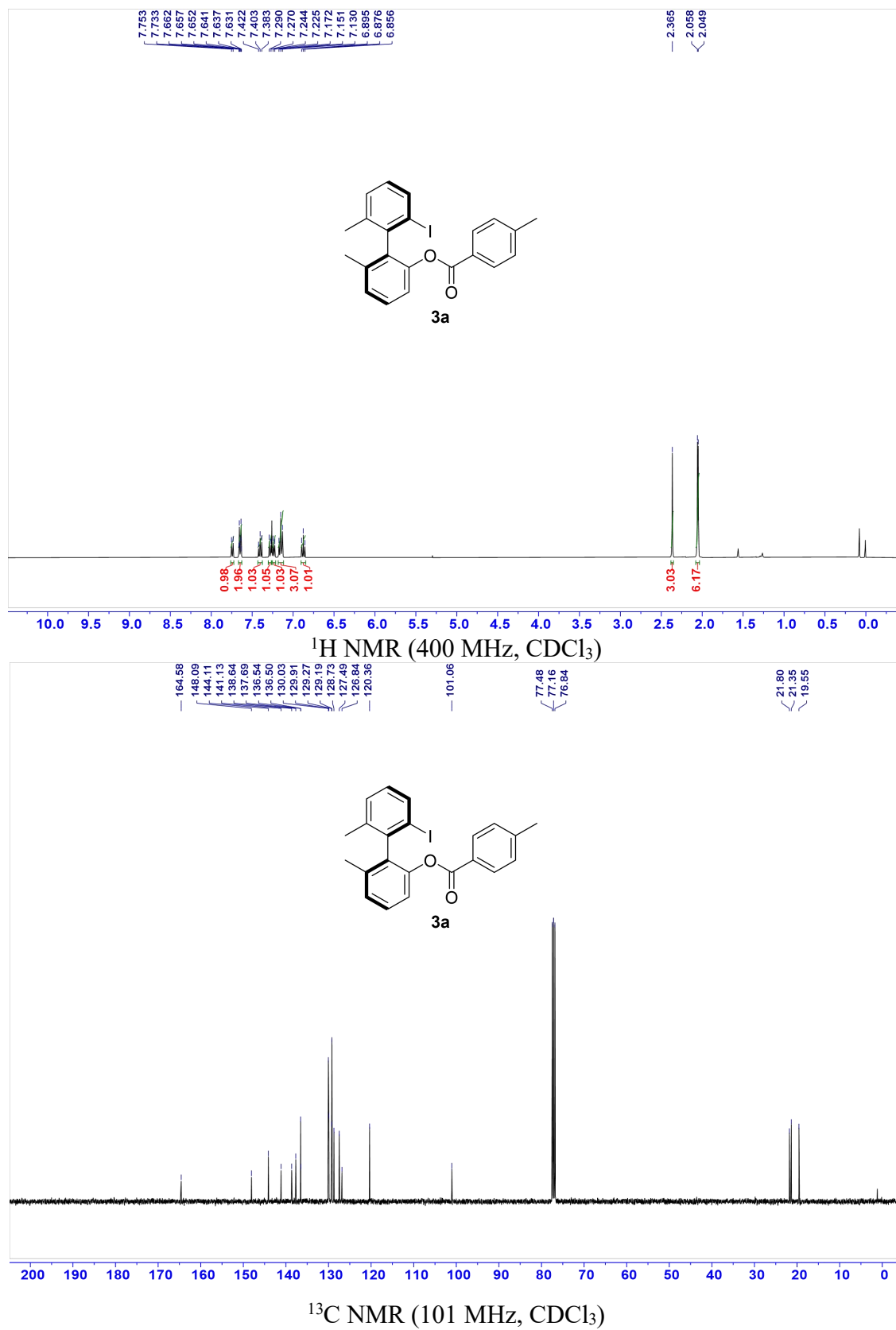
White solid, 38.0 mg, Yield: 64%;  $[\alpha]_{\text{D}}^{20} = -217.4$  ( $c = 0.93$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.33 (s, 1H), 8.38 (s, 1H), 8.32 (d,  $J = 3.6$  Hz, 1H), 7.54 (d,  $J = 7.6$  Hz, 1H), 7.35 (d,  $J = 4.8$  Hz, 2H), 7.24 – 7.22 (m, 1H), 7.17 (dd,  $J = 7.6, 4.8$  Hz, 1H), 6.94 (t,  $J = 7.8$  Hz, 1H), 6.71 (d,  $J = 8.0$  Hz, 1H), 6.51 (d,  $J = 7.6$  Hz, 1H), 1.97 (s, 3H), 1.60 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  154.8, 148.7, 147.4, 137.8, 137.2, 136.9, 136.3, 136.01, 135.5, 129.4, 128.0, 127.3, 127.2, 126.2, 122.6, 120.4, 112.4, 19.8, 19.5. Known compound (ref. 3).

**(*R*)-2'-(diphenylphosphanyl)-6,6'-dimethyl-[1,1'-biphenyl]-2-ol (7)**



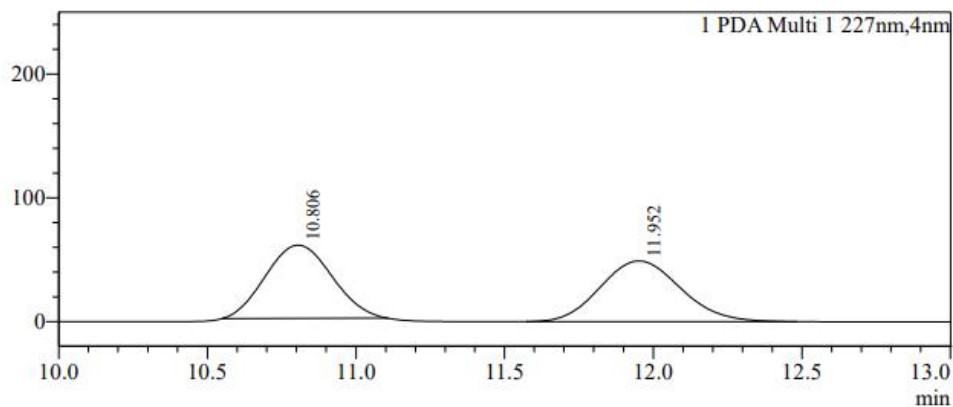
Colorless oil, 43.2 mg, Yield: 50%;  $[\alpha]_{\text{D}}^{20} = -15.2$  ( $c = 1.5$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.25 (m, 8H), 7.23 – 7.13 (m, 5H), 7.07 (dd,  $J = 7.2, 2.8$  Hz, 1H), 6.78 (d,  $J = 7.6$  Hz, 1H), 6.69 (d,  $J = 8.4$  Hz, 1H), 4.13 (s, 1H), 1.98 (s, 3H), 1.72 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.6 (d,  $J_{\text{C-P}} = 2.0$  Hz), 140.4, 140.1, 139.8 (d,  $J_{\text{C-P}} = 11.1$  Hz), 138.6 (d,  $J_{\text{C-P}} = 5.1$  Hz), 137.6 (d,  $J_{\text{C-P}} = 2.0$  Hz), 137.1 (d,  $J_{\text{C-P}} = 12.1$  Hz), 136.8 (d,  $J_{\text{C-P}} = 12.1$  Hz), 134.1 (d,  $J_{\text{C-P}} = 4.0$  Hz), 133.9 (d,  $J_{\text{C-P}} = 5.1$  Hz), 131.9, 131.4, 129.1, 128.8, 128.7, 128.6 (d,  $J_{\text{C-P}} = 7.1$  Hz), 128.4 (d,  $J_{\text{C-P}} = 6.1$  Hz), 126.5 (d,  $J_{\text{C-P}} = 8.1$  Hz), 122.2, 112.8, 19.9 (d,  $J_{\text{C-P}} = 2.0$  Hz), 19.8 (d,  $J_{\text{C-P}} = 3.0$  Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -13.64 (s). Known compound (ref. 3).

## 8. NMR and HPLC spectra



**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-methylbenzoate(3a).**  
 Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  
 $t_R(\text{major}) = 11.0$  min,  $t_R(\text{minor}) = 12.2$  min, e.r. = 97:3

mAU

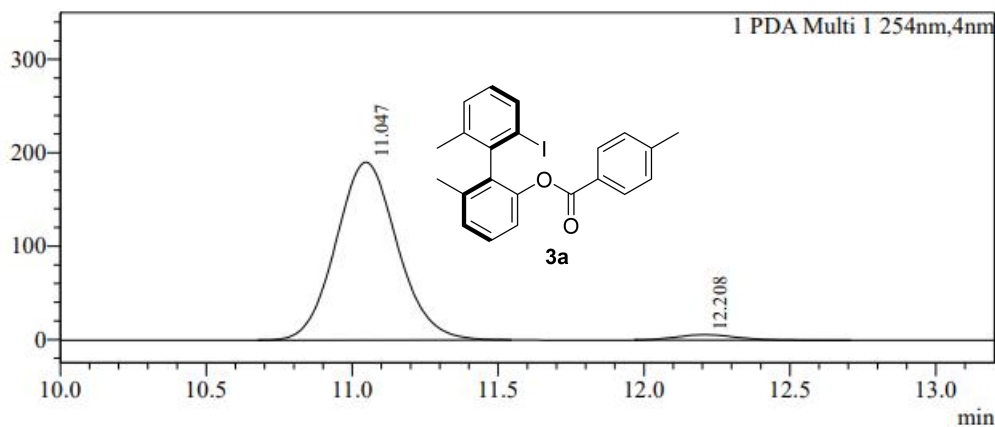


Peak Table

PDA Ch1 227nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	10.806	11.104	59282	921240	49.927
2	11.952	12.480	48991	923920	50.073
Total			108273	1845160	100.000

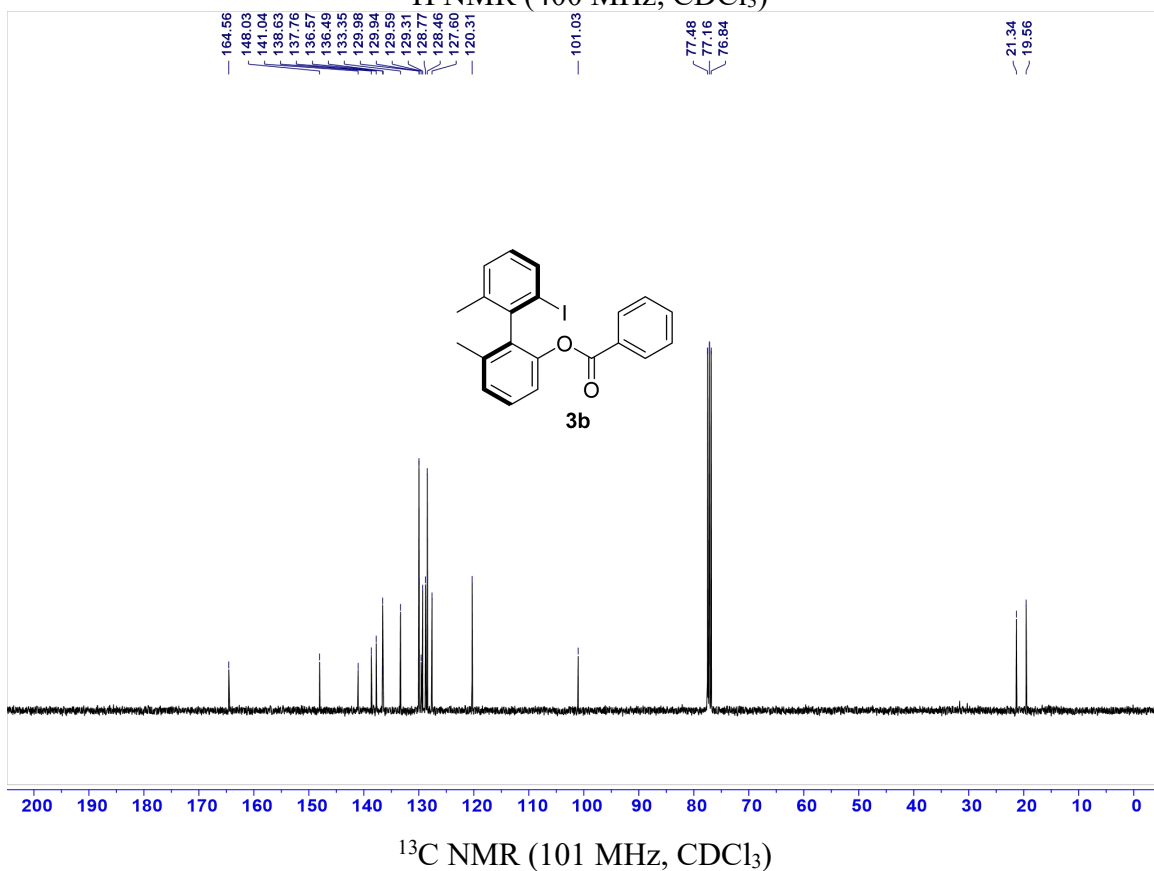
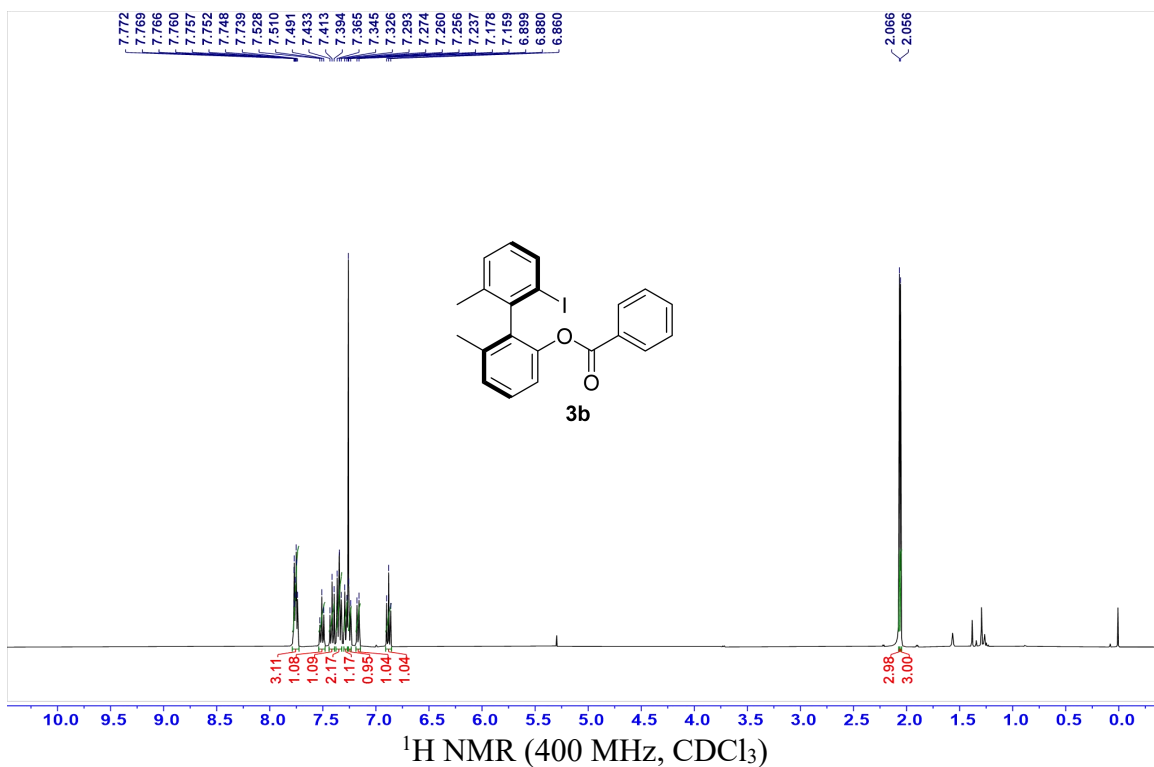
mAU



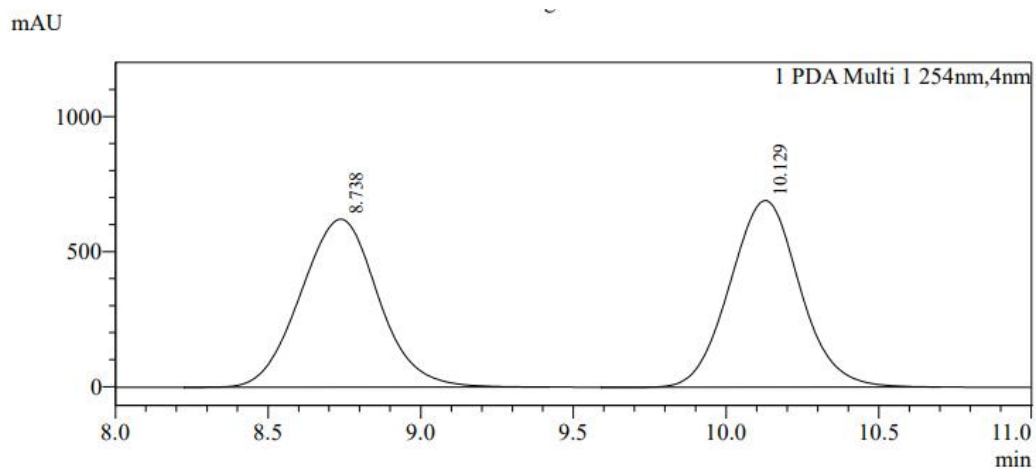
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	11.047	11.541	190481	2789319	97.122
2	12.208	12.704	5740	82657	2.878
Total			196222	2871976	100.000



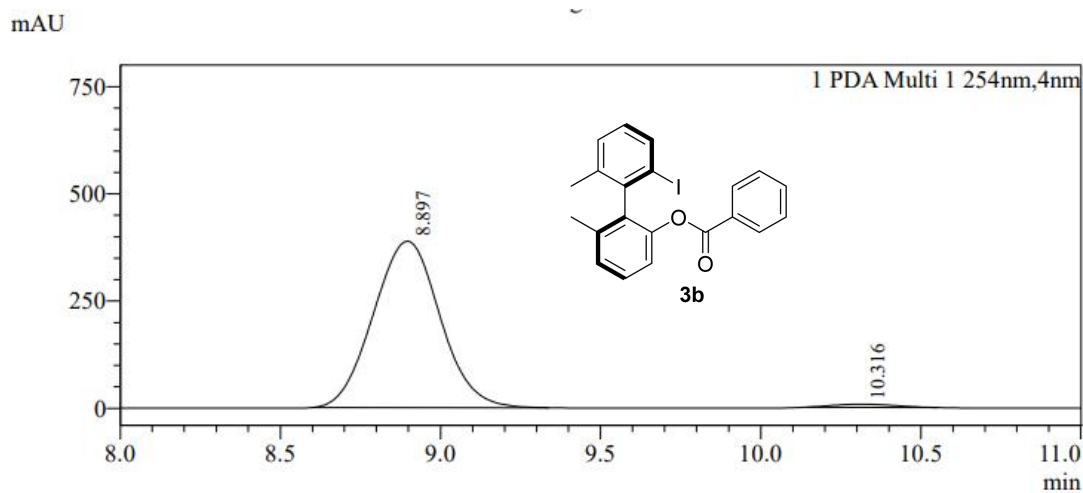
**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl benzoate(**3b**).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C, λ = 254 nm, t<sub>R</sub>(major) = 8.9 min, t<sub>R</sub>(minor) = 10.3 min, e.r. = 98.5:1.5



Peak Table

PDA Ch1 254nm

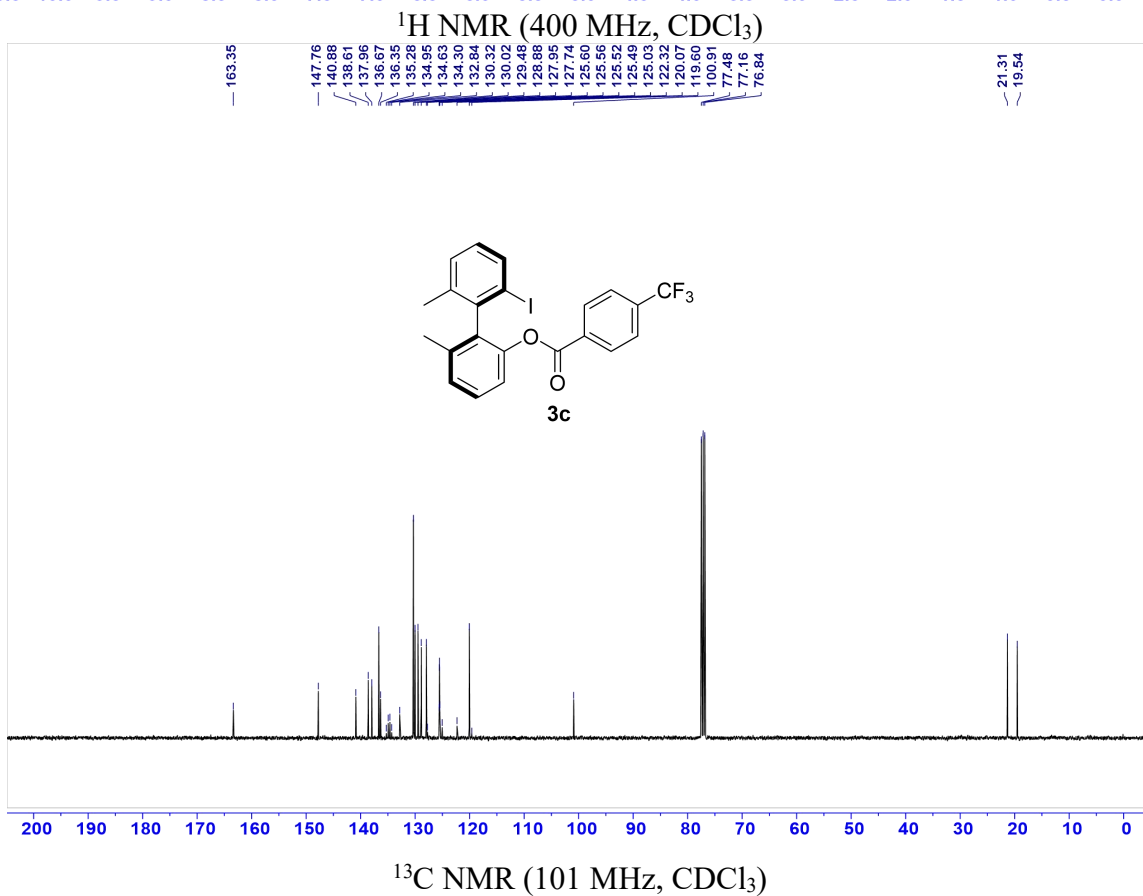
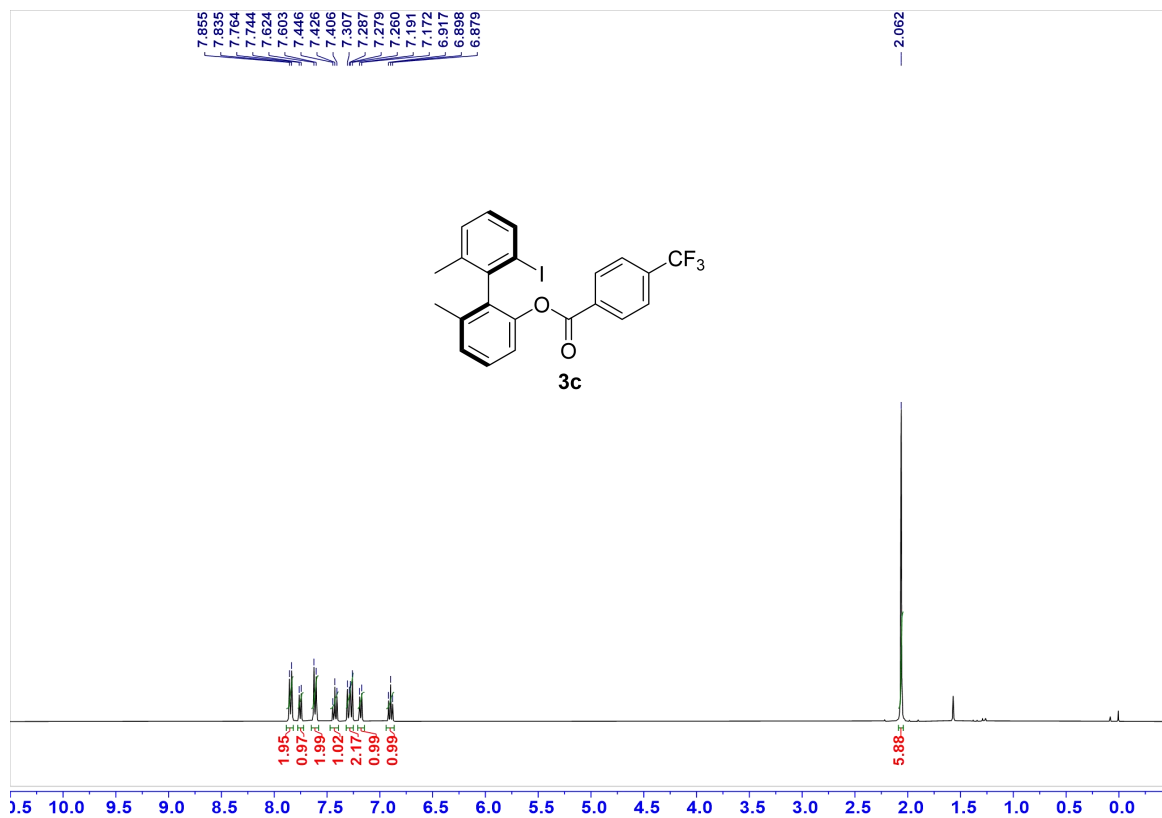
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	8.738	9.419	621995	11043403	50.001
2	10.129	10.699	690370	11042786	49.999
Total			1312365	22086189	100.000

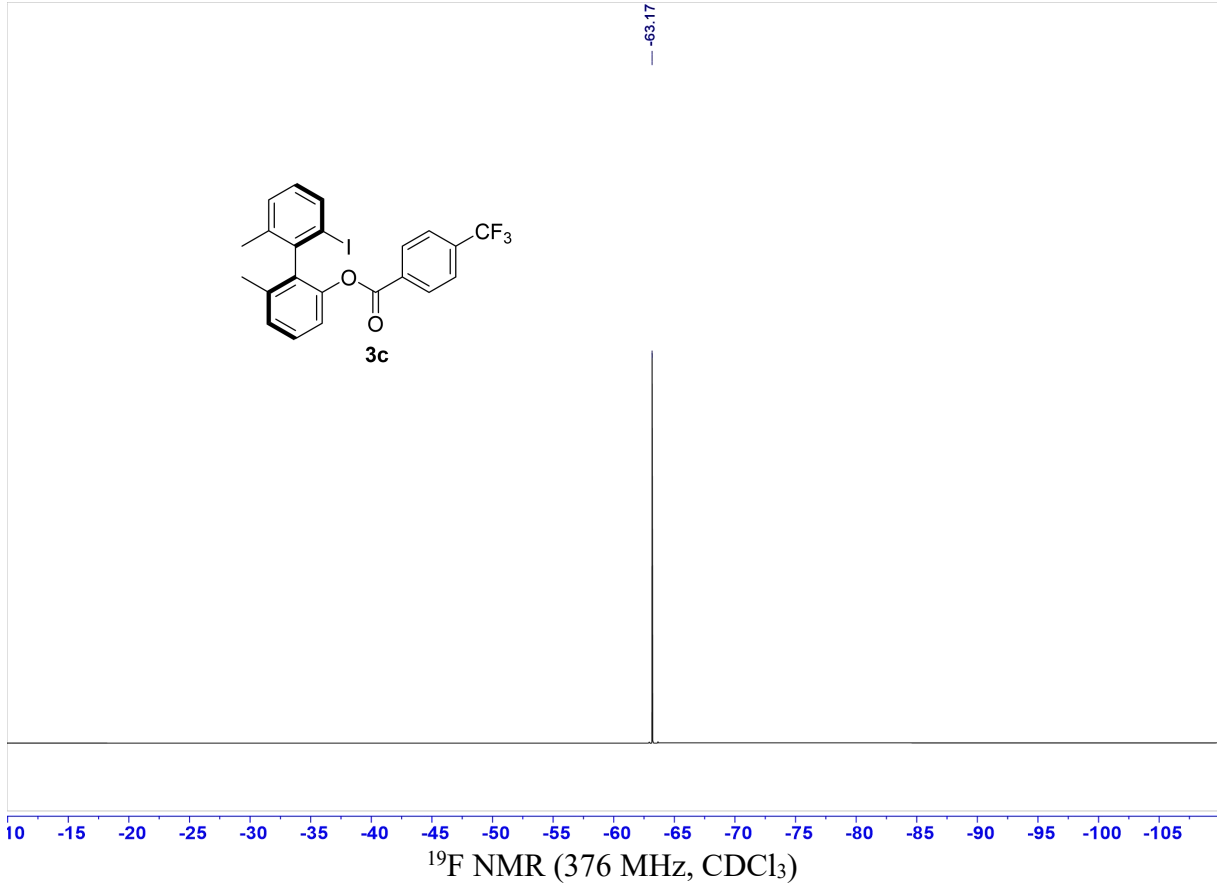


Peak Table

PDA Ch1 254nm

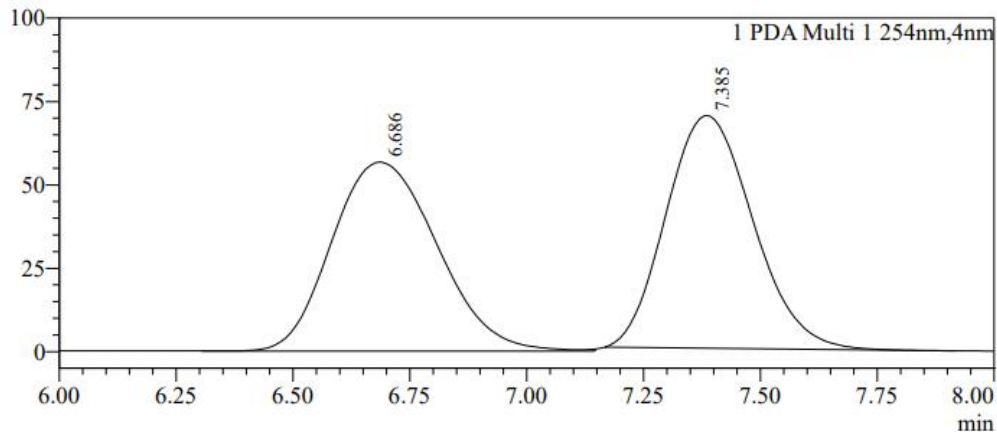
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	8.897	9.333	388543	5640324	98.274
2	10.316	10.549	7457	99051	1.726
Total			396001	5739375	100.000





**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-(trifluoromethyl)benzoate (**3c**).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 7.4 min,  $t_R$ (minor) = 6.6 min, e.r. = 97:3

mAU

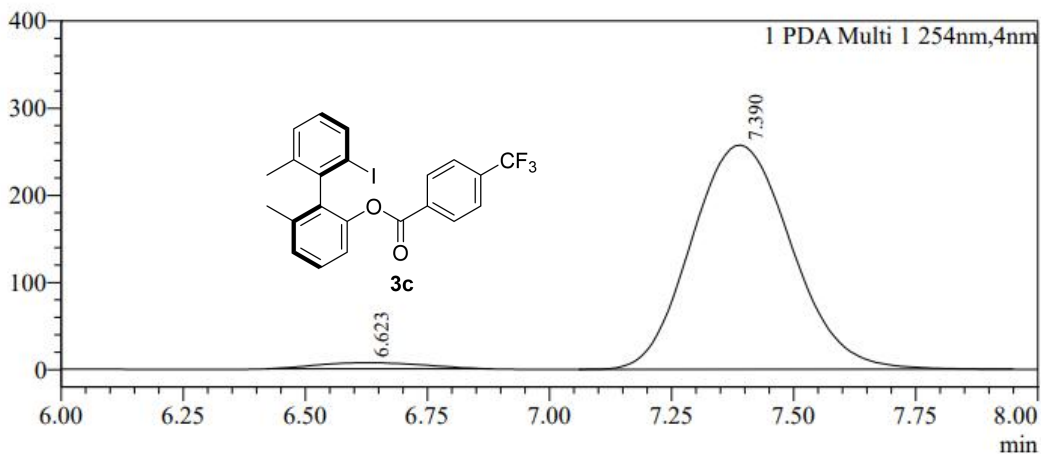


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	6.686	7.147	56674	889365	49.600
2	7.385	7.915	69733	903697	50.400
Total			126406	1793062	100.000

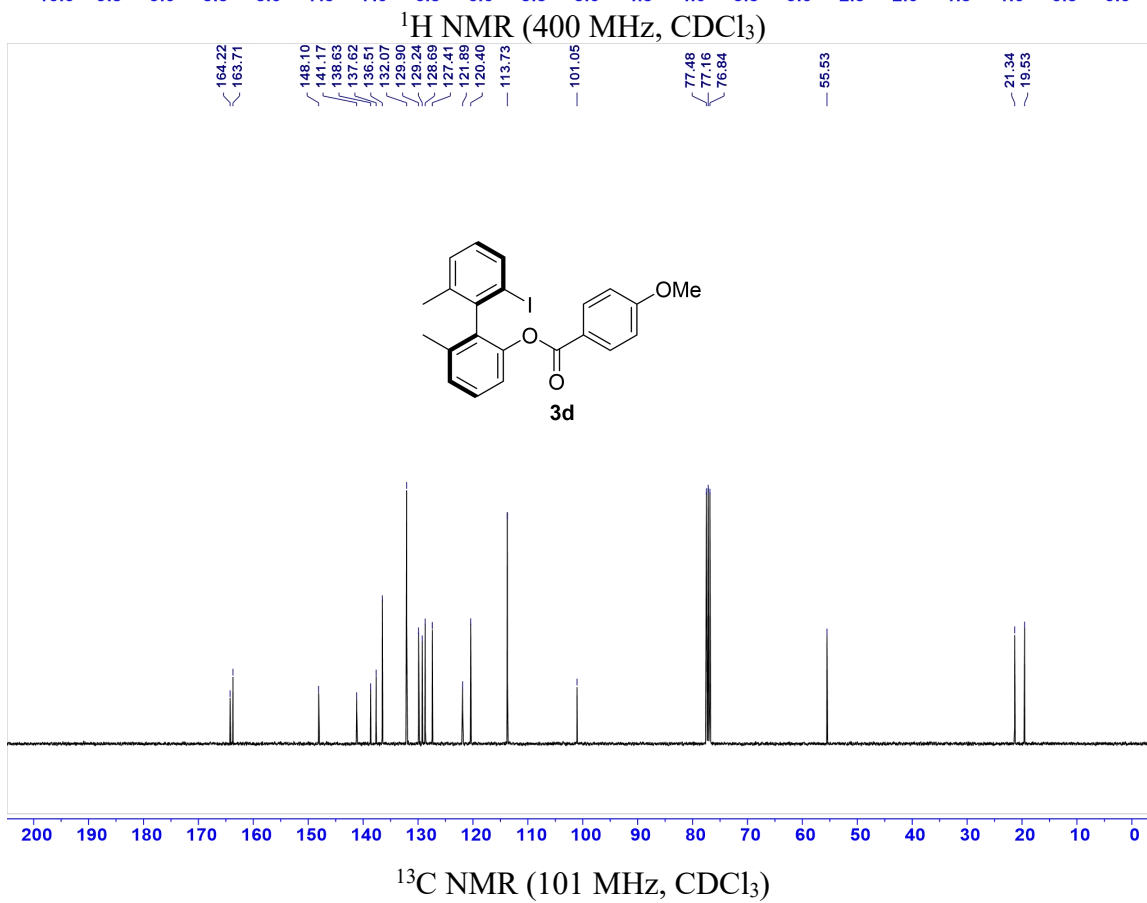
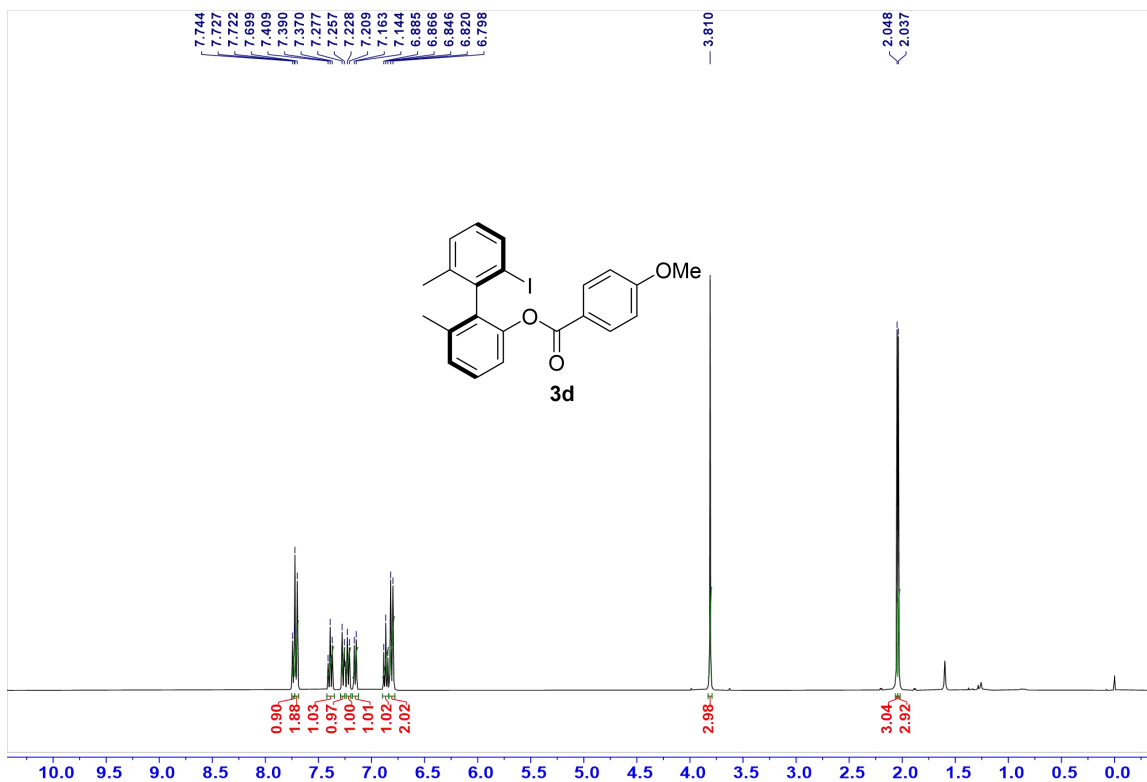
mAU



Peak Table

PDA Ch1 254nm

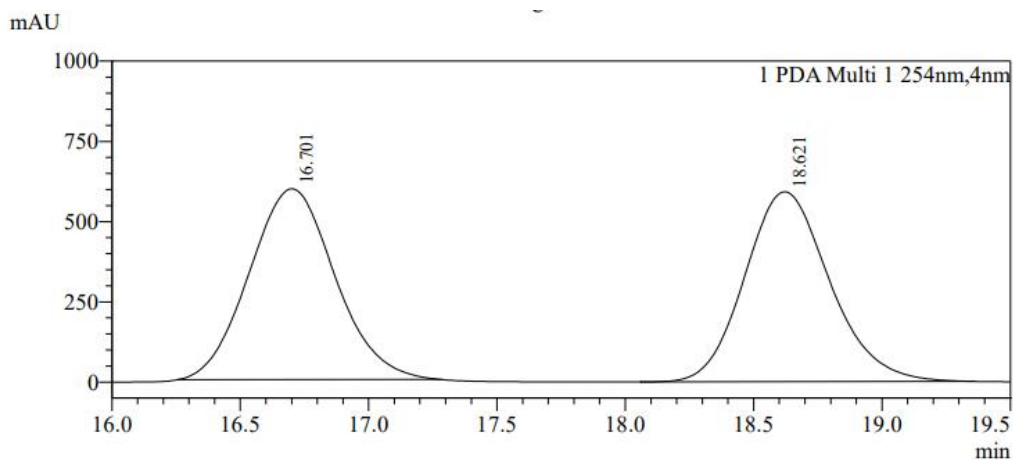
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	6.623	6.880	6989	107577	2.849
2	7.390	7.947	257242	3669038	97.151
Total			264231	3776615	100.000



**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-methoxybenzoate(3d).**

Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,

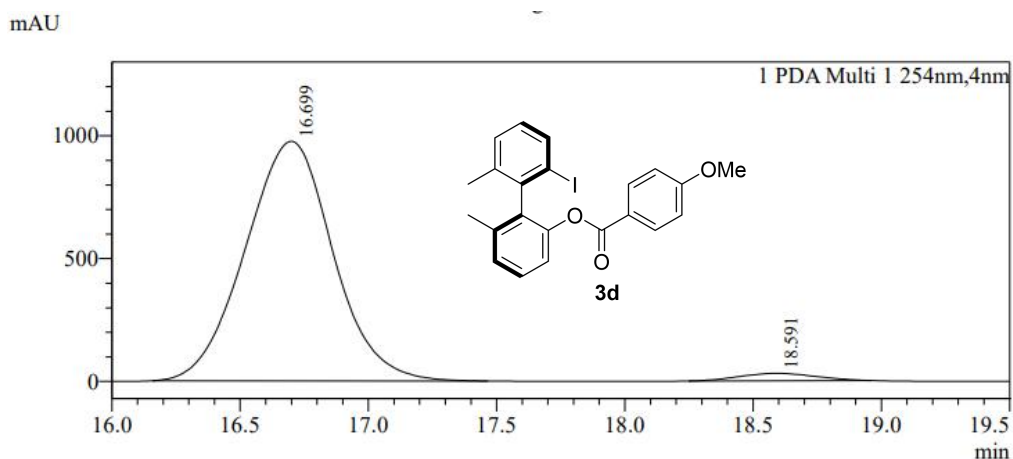
$t_R(\text{major}) = 16.7 \text{ min}$ ,  $t_R(\text{minor}) = 18.6 \text{ min}$ , e.r. = 97.5:2.5



Peak Table

PDA Ch1 254nm

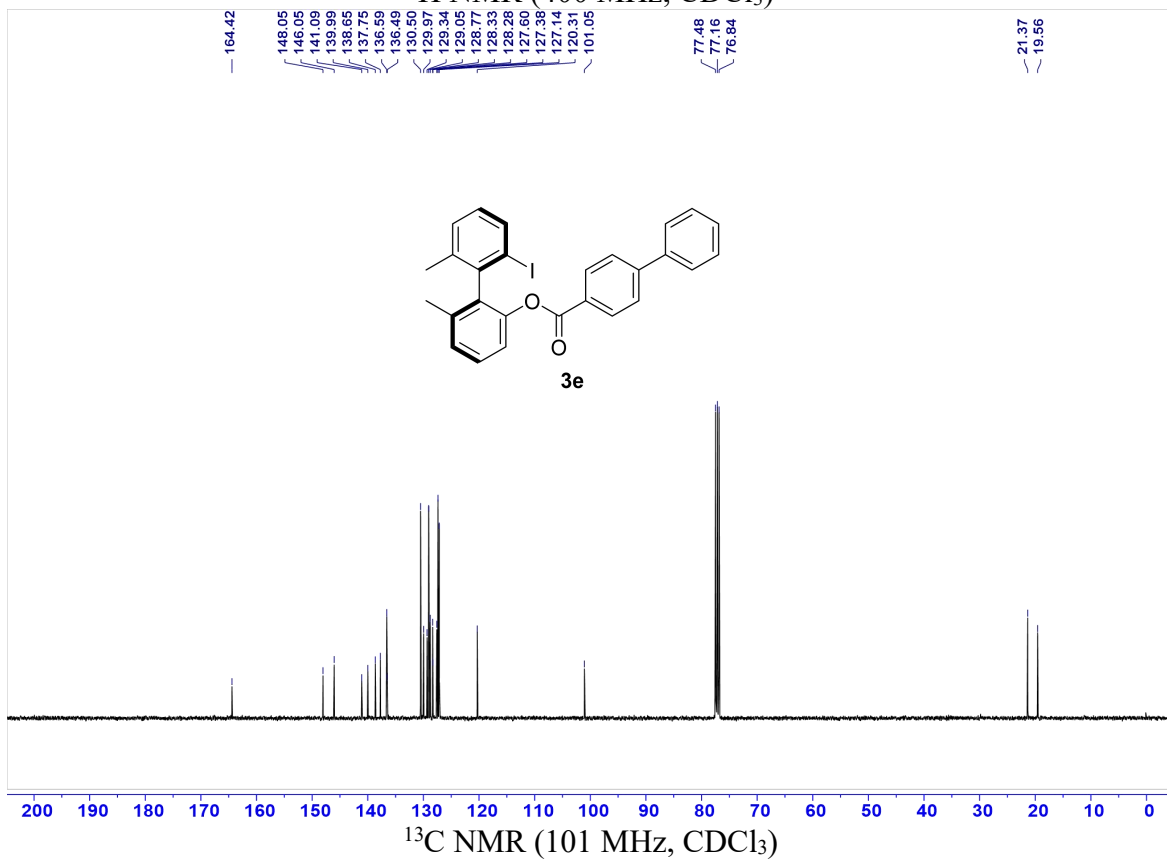
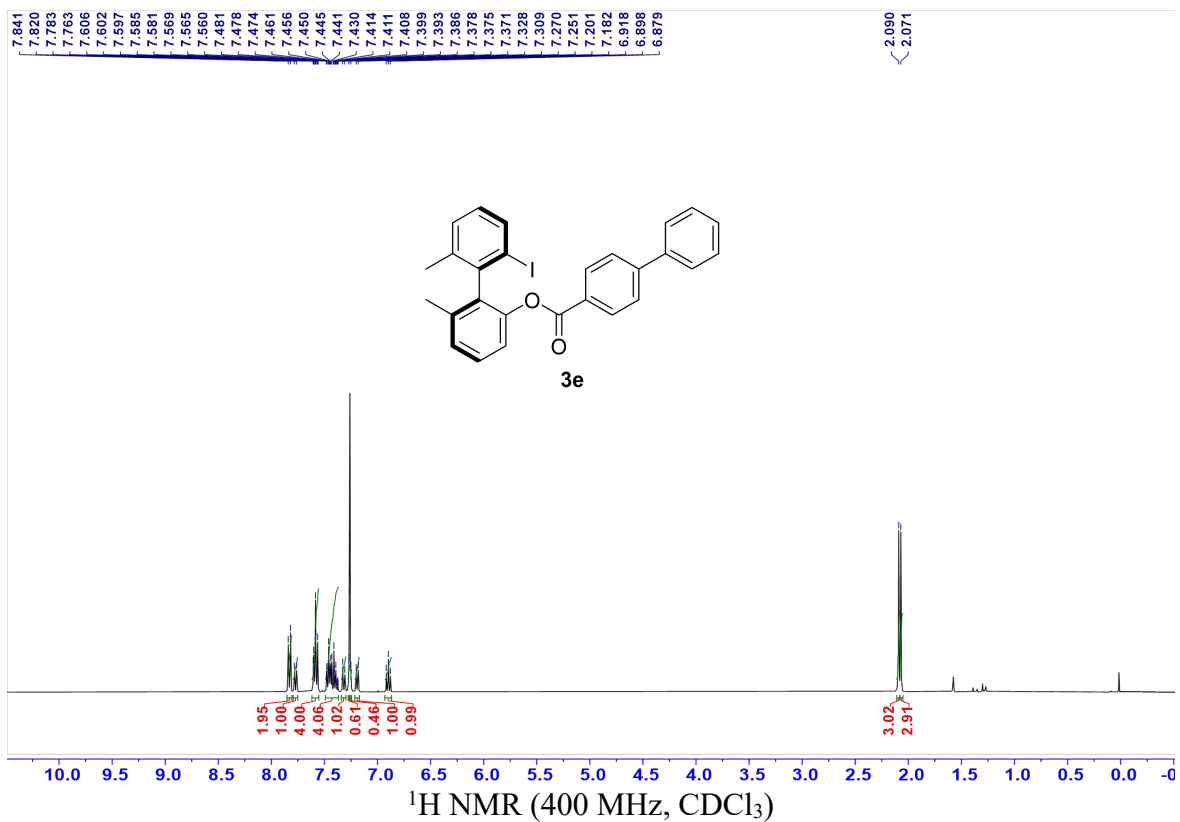
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	16.701	17.280	594679	13844586	50.400
2	18.621	19.360	592147	13624633	49.600
Total			1186827	27469219	100.000



Peak Table

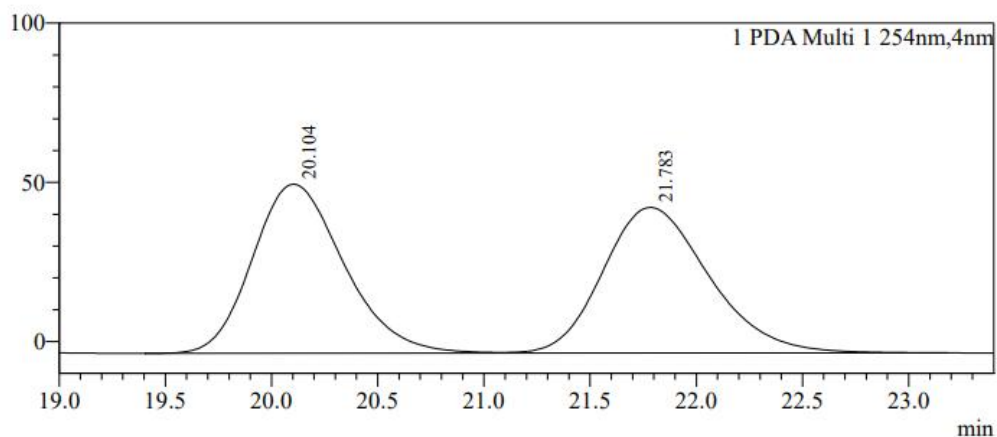
PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	16.699	17.461	974842	23248419	97.404
2	18.591	18.955	30103	619637	2.596
Total			1004944	23868056	100.000



**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl [1,1'-biphenyl]-4-carboxylate(3e).** Diacel Chiralpak IC, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 21.8 min,  $t_R$ (minor) = 20.1 min, e.r. = 83:17

mAU

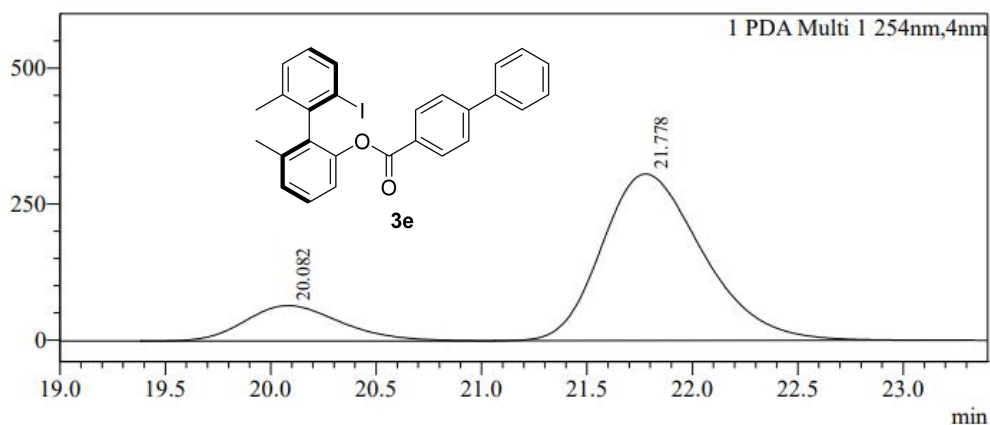


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	20.104	21.099	53137	1592417	50.018
2	21.783	23.179	45739	1591257	49.982
Total			98876	3183673	100.000

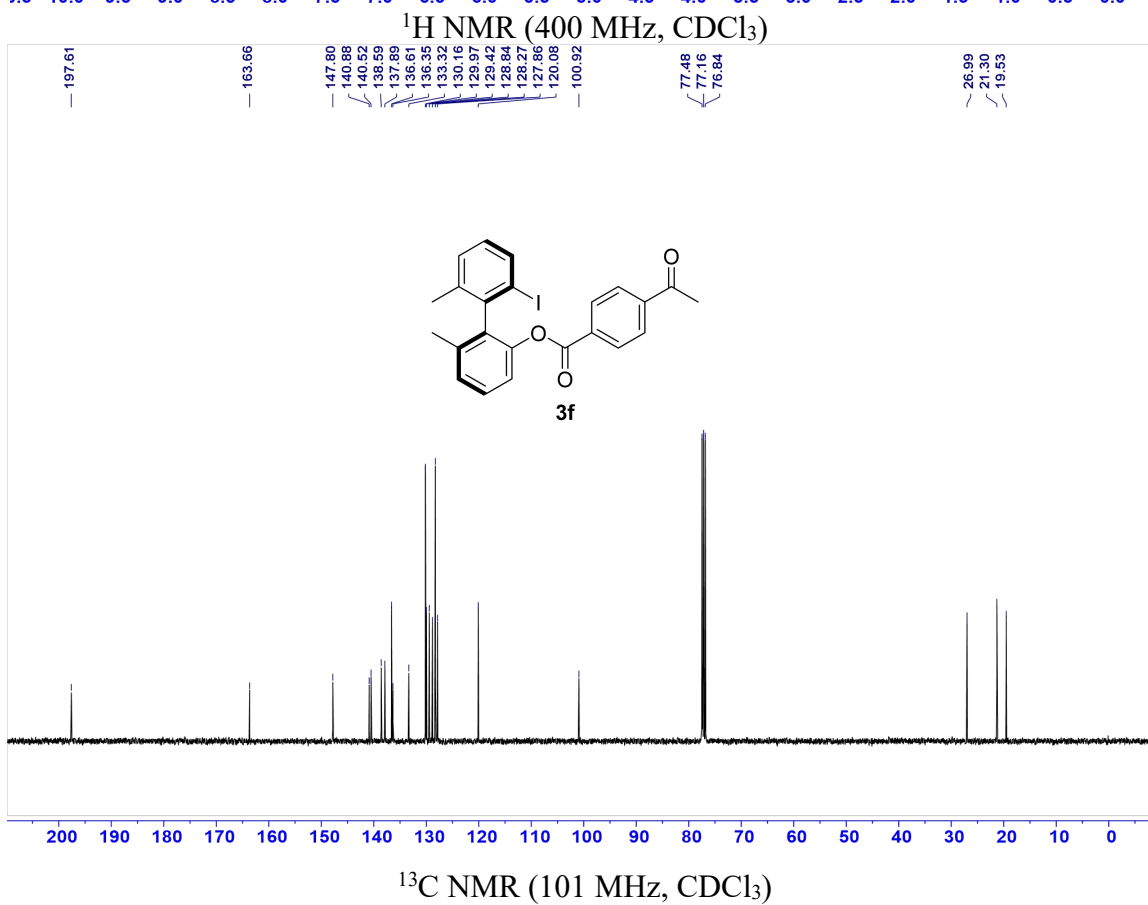
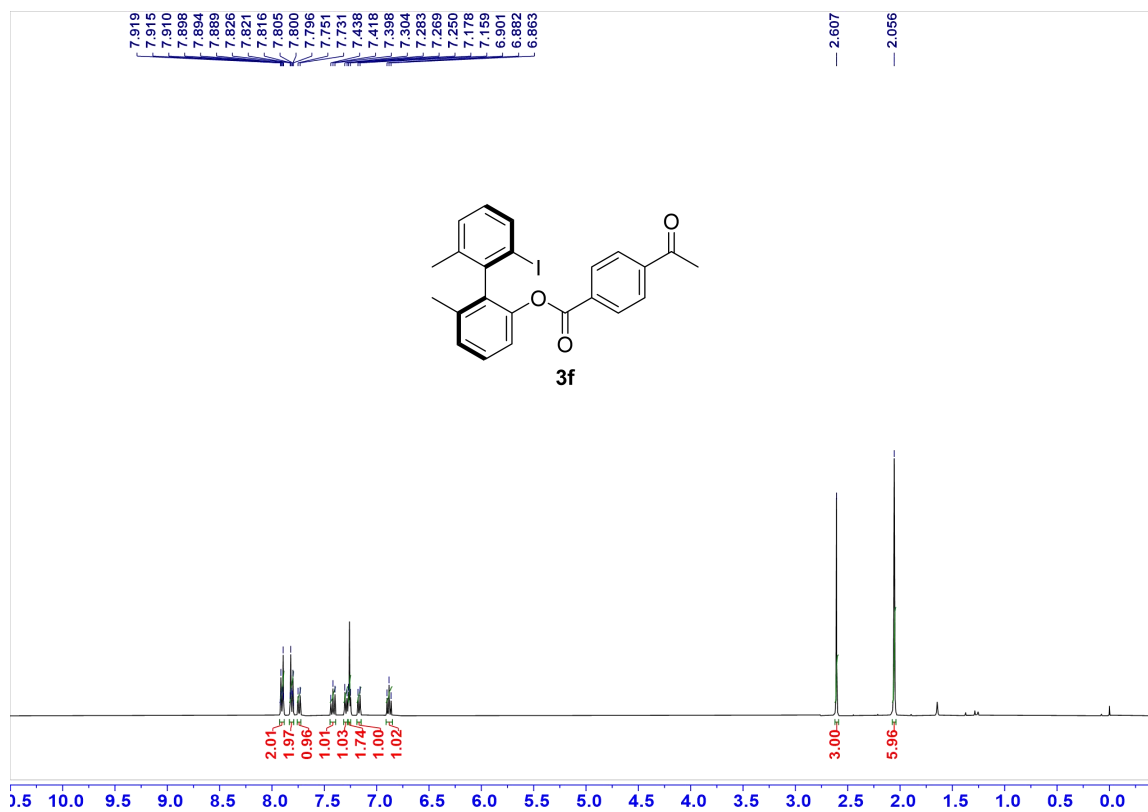
mAU



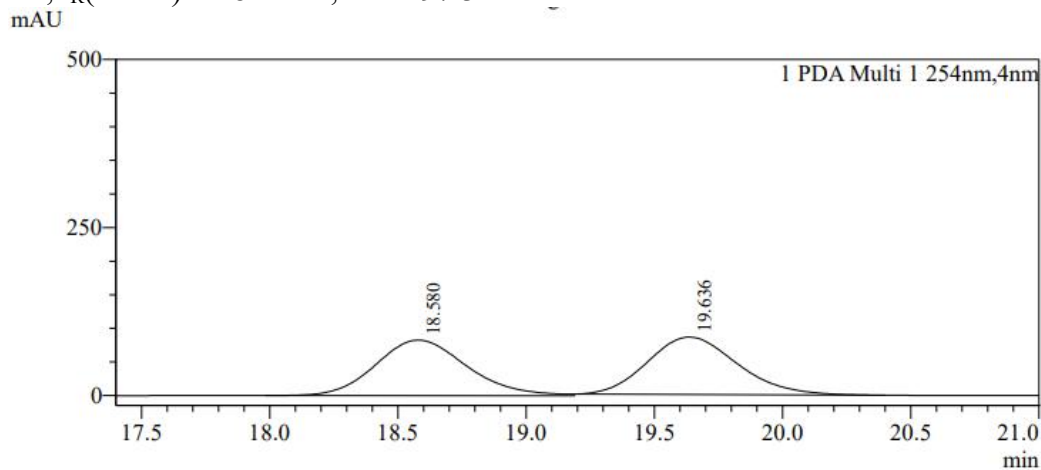
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	20.082	21.056	64954	2063849	16.791
2	21.778	23.328	306373	10227273	83.209
Total			371327	12291122	100.000

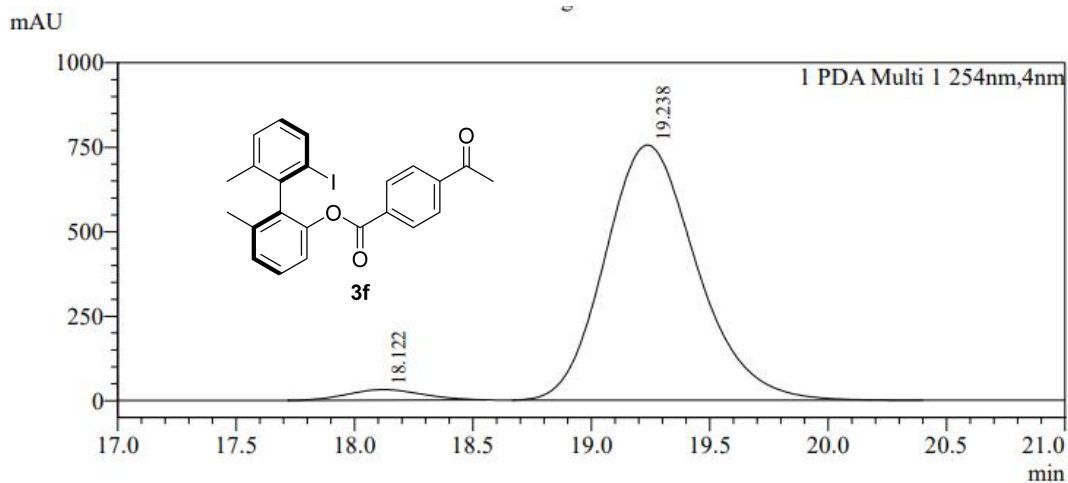


**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-acetylbenzoate(3f).**  
 Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 19.2 min,  $t_R$ (minor) = 18.1 min, e.r. = 97:3



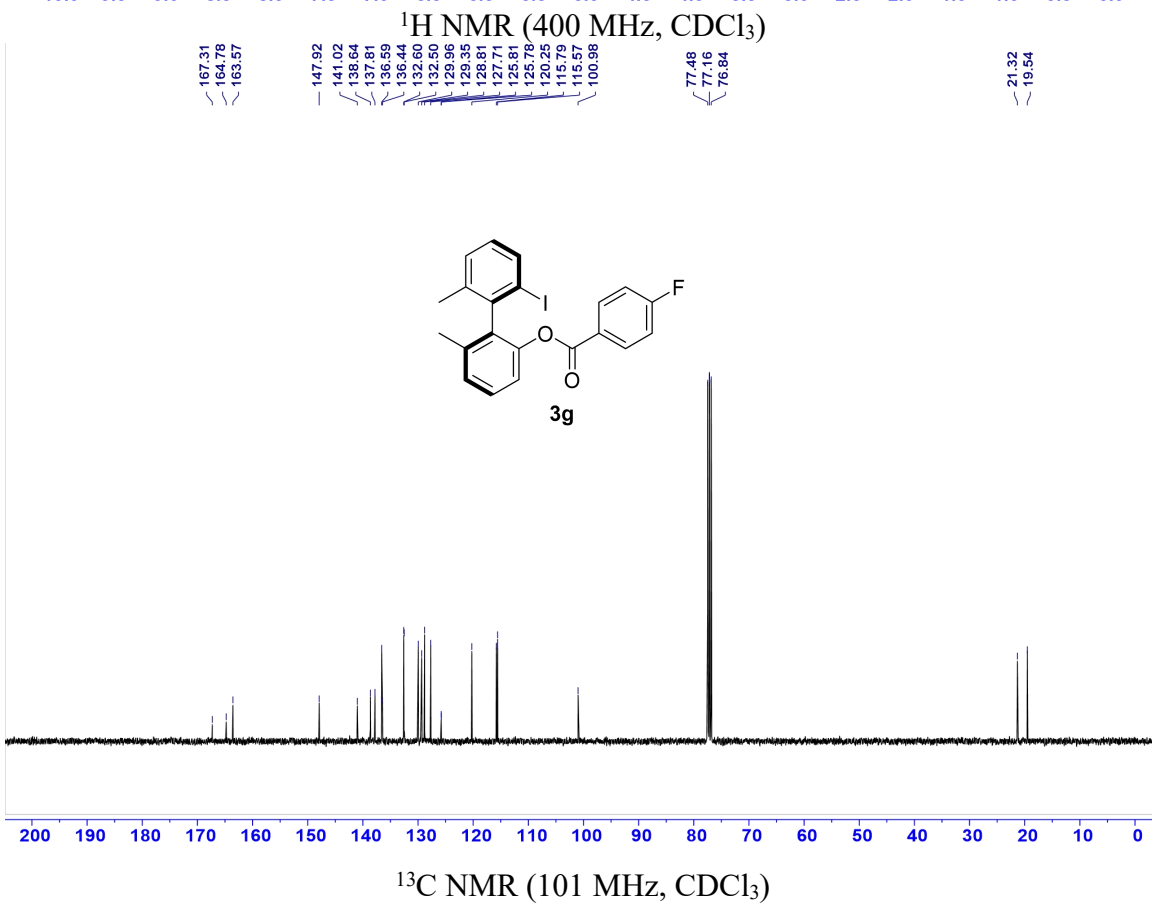
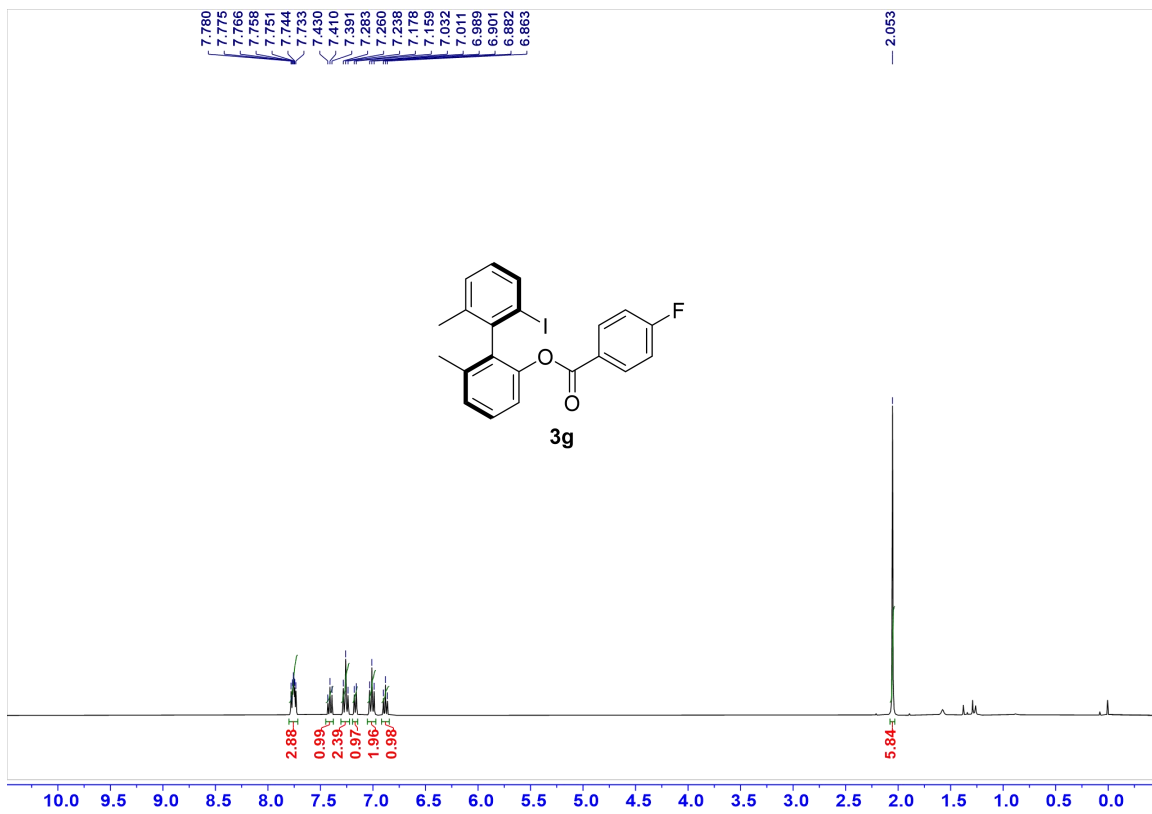
Peak Table

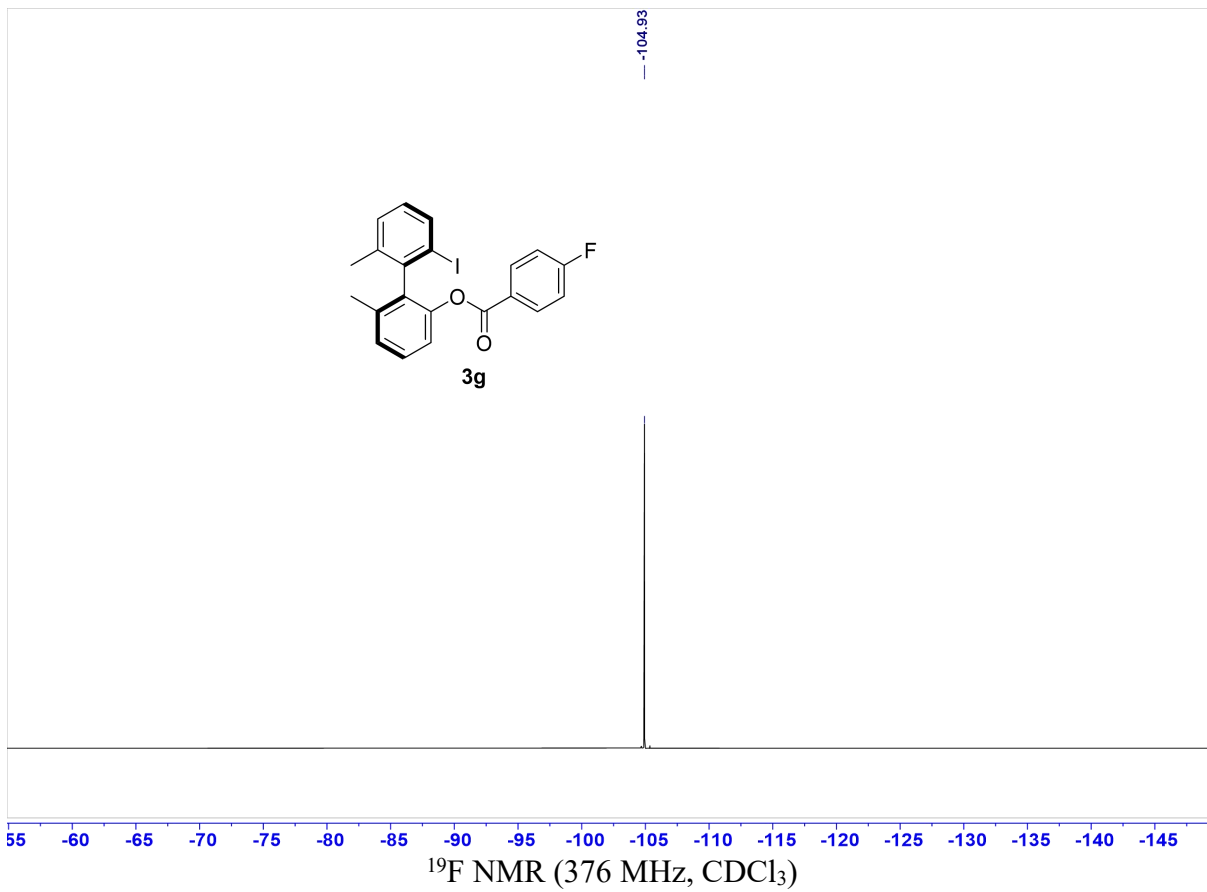
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	18.580	19.189	82871	2068359	49.859
2	19.636	20.395	85375	2080044	50.141
Total			168245	4148403	100.000



Peak Table

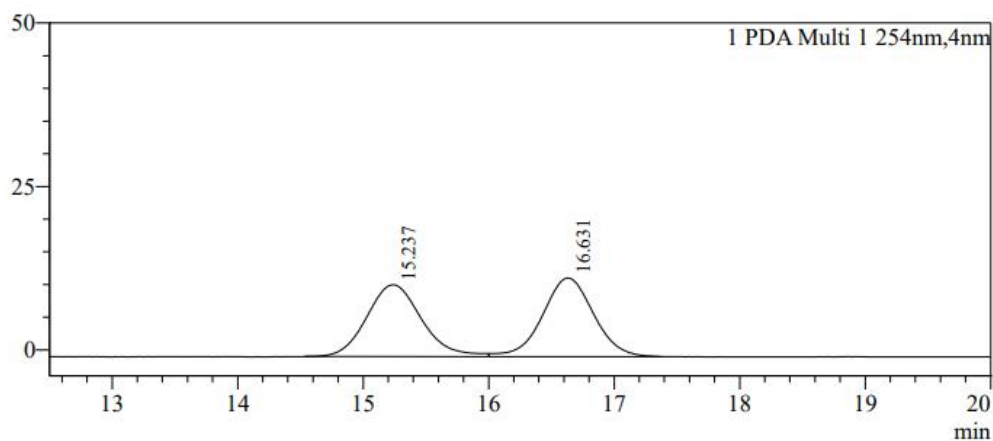
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	18.122	18.549	31010	677636	3.213
2	19.238	20.395	754582	20415008	96.787
Total			785591	21092643	100.000





**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-fluorobenzoate(3g).** Diacel Chiralcel OD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 16.7 min,  $t_R$ (minor) = 15.4 min, e.r. = 97:3

mAU

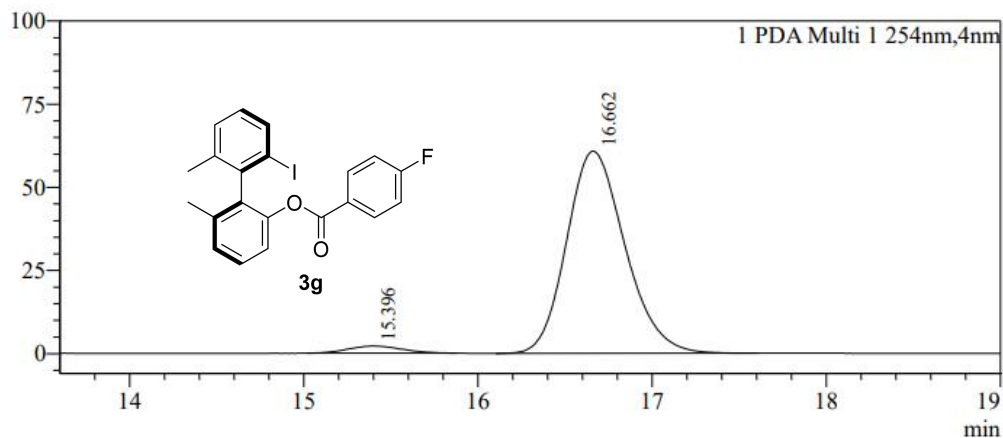


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	15.237	16.000	10980	333336	49.547
2	16.631	17.376	12022	339435	50.453
Total			23002	672771	100.000

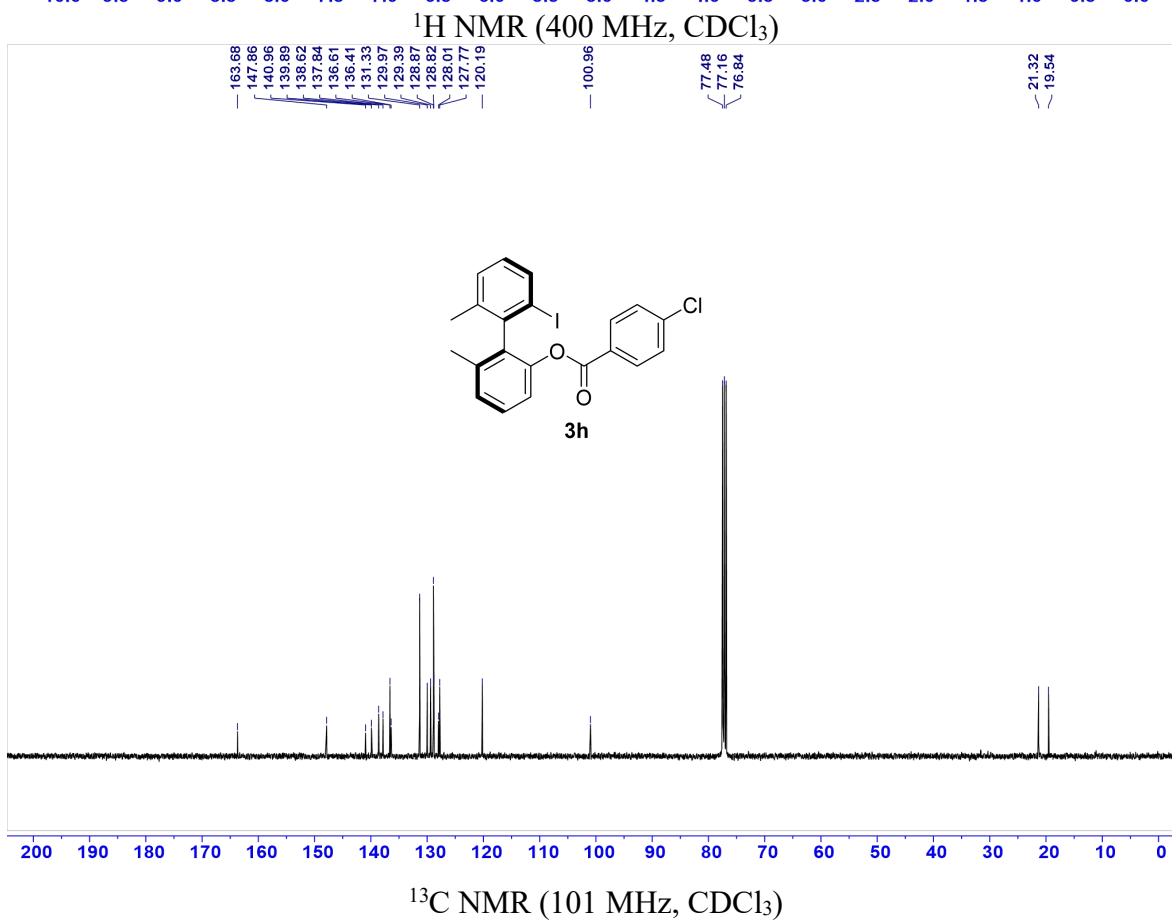
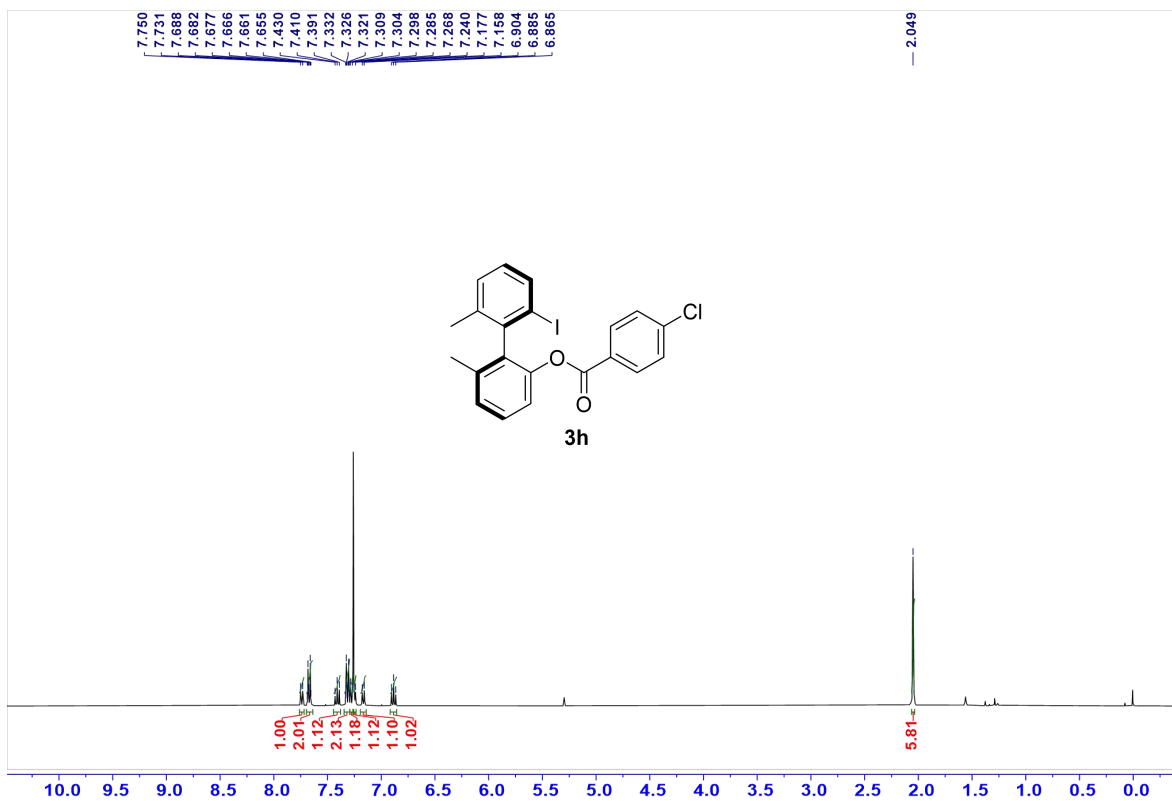
mAU



Peak Table

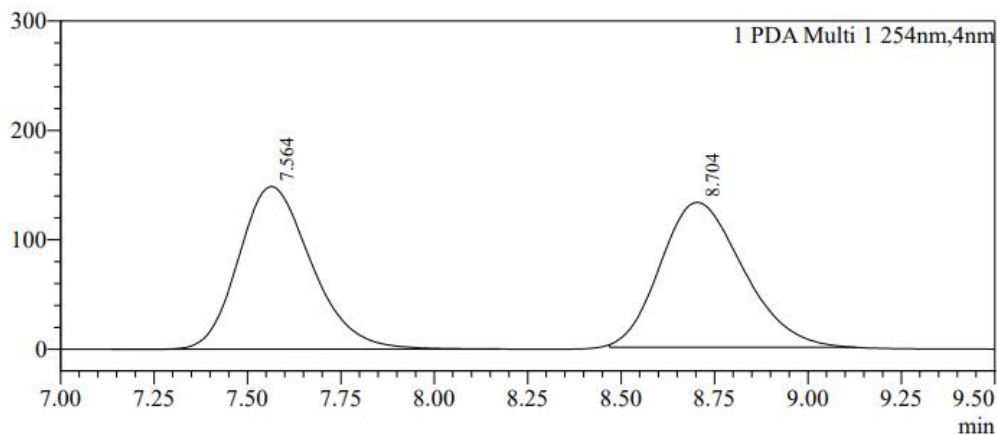
PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	15.396	15.872	2143	45924	3.140
2	16.662	17.600	60784	1416559	96.860
Total			62928	1462484	100.000



**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-chlorobenzoate(3h).** Diacel Chiralcel OD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 9.2 min,  $t_R$ (minor) = 7.9 min, e.r. = 97:3

mAU

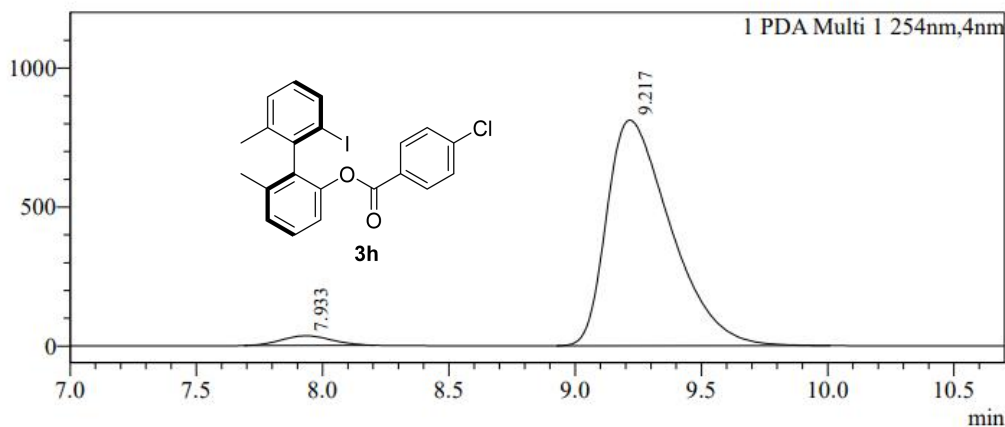


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	7.564	8.171	148744	2019228	49.658
2	8.704	9.131	132627	2047065	50.342
Total			281371	4066294	100.000

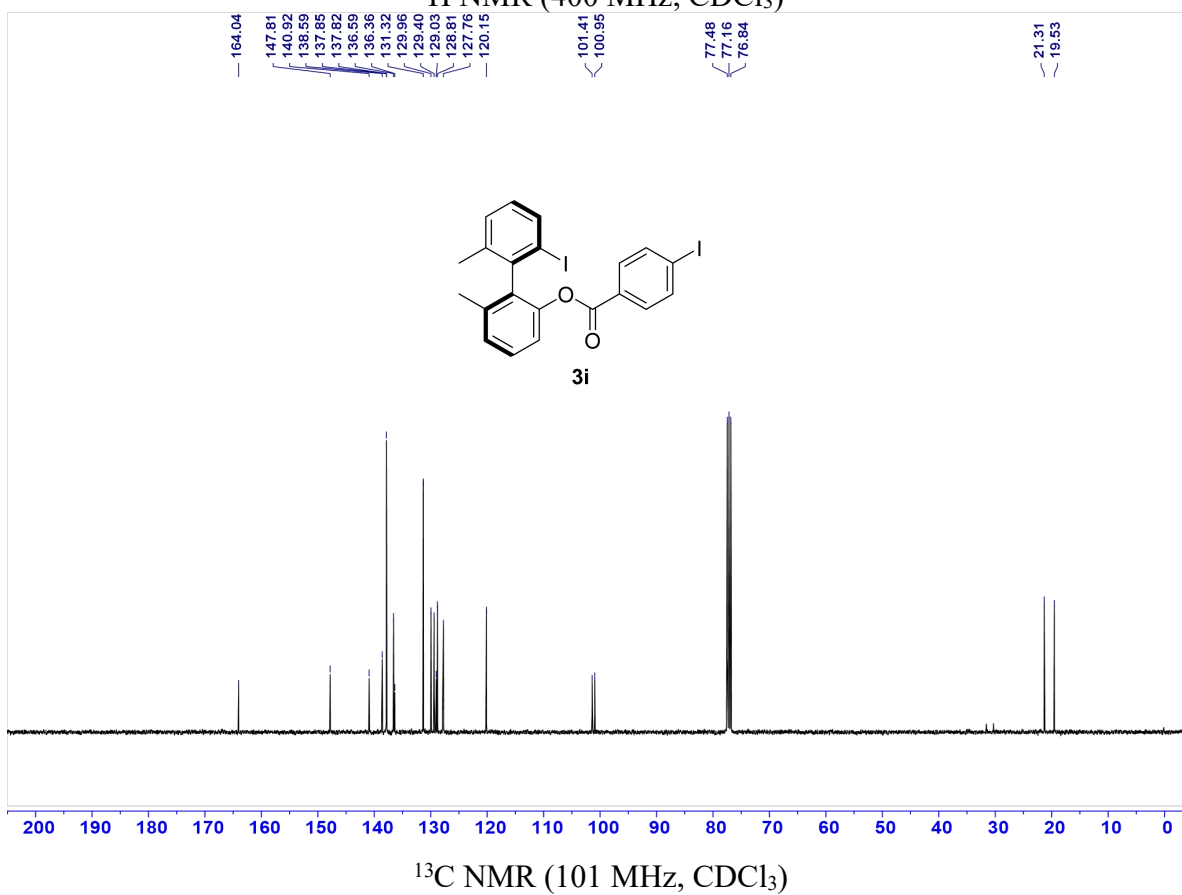
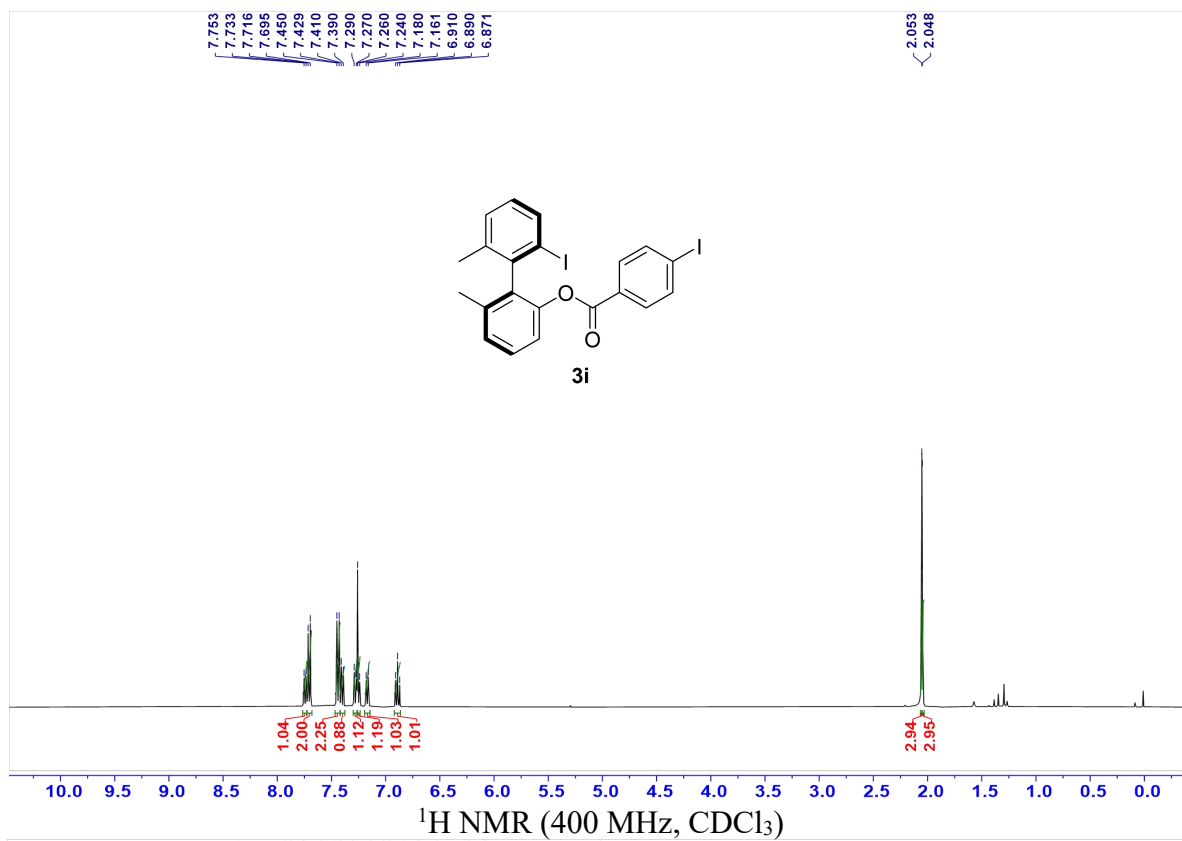
mAU



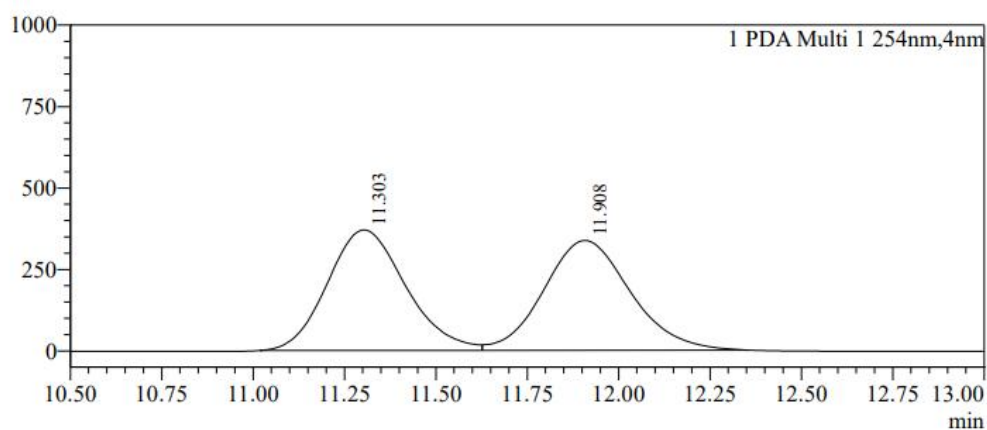
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	7.933	8.203	34741	479916	3.240
2	9.217	10.005	812255	14333106	96.760
Total			846995	14813022	100.000

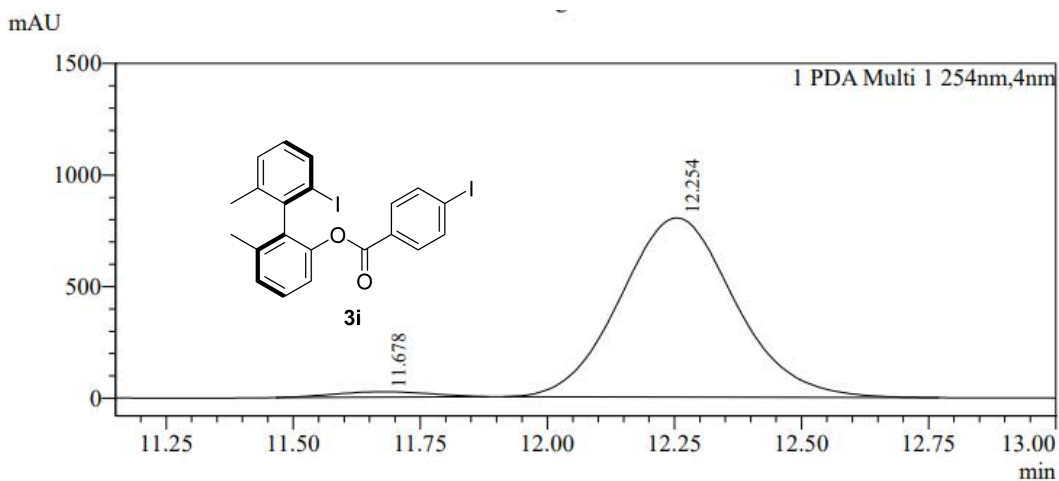


**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-iodobenzoate(3i).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 12.3 min,  $t_R$ (minor) = 11.7 min, e.r. = 97.5:2.5



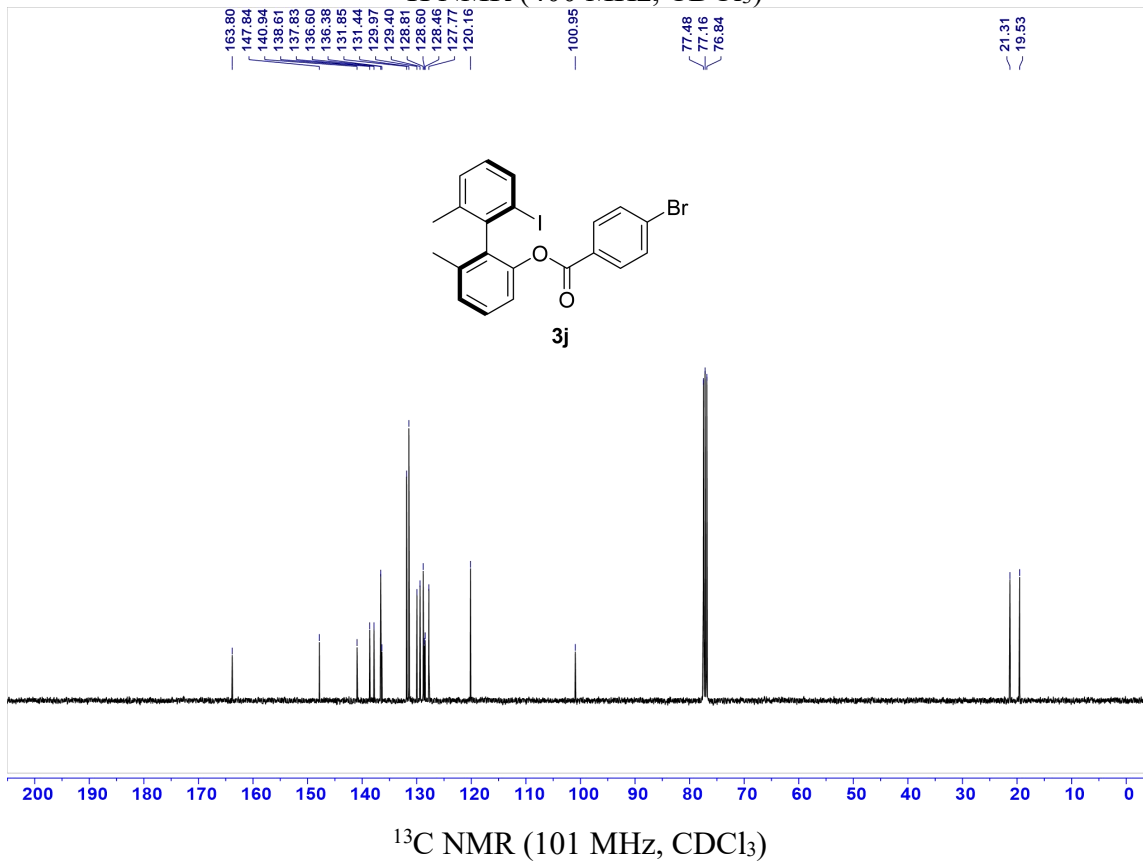
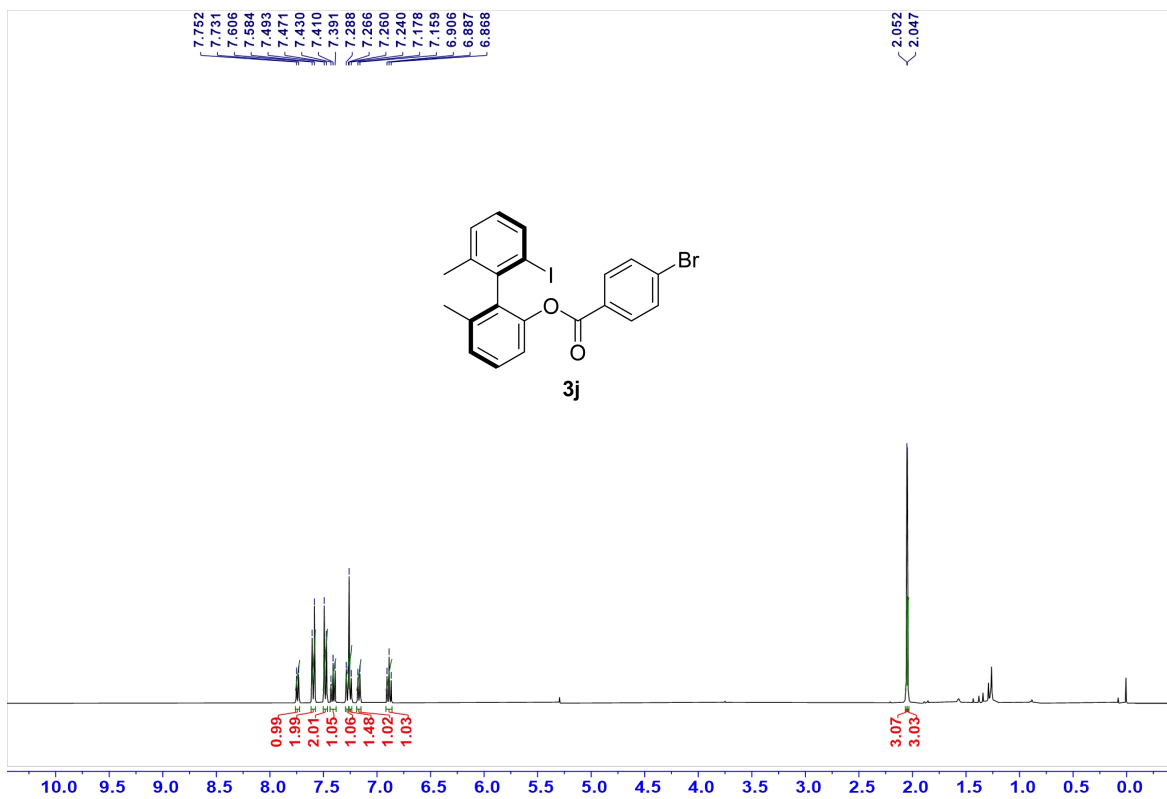
Peak Table

PDA Ch1 254nm					
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	11.303	11.627	370023	5521104	49.892
2	11.908	12.352	336740	5544985	50.108
Total			706764	11066088	100.000

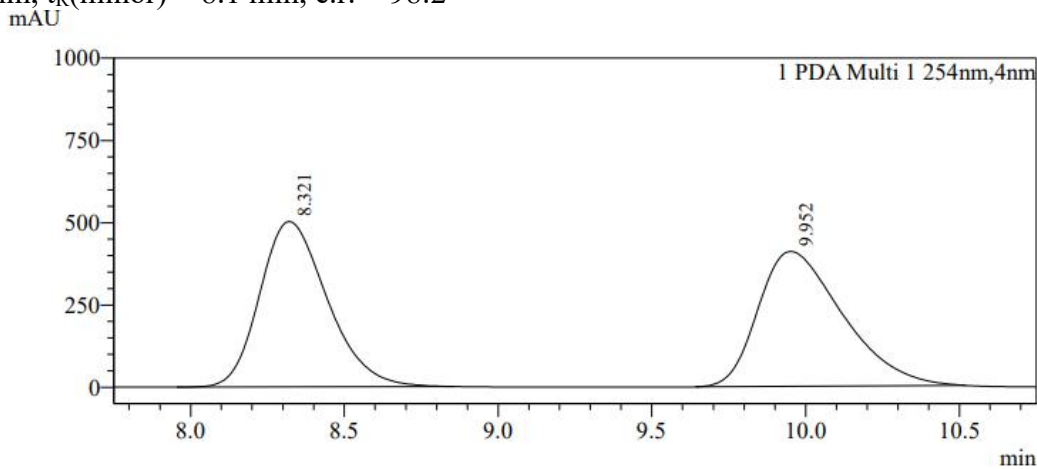


Peak Table

PDA Ch1 254nm					
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	11.678	11.883	23894	310712	2.399
2	12.254	12.768	803638	12640012	97.601
Total			827532	12950724	100.000



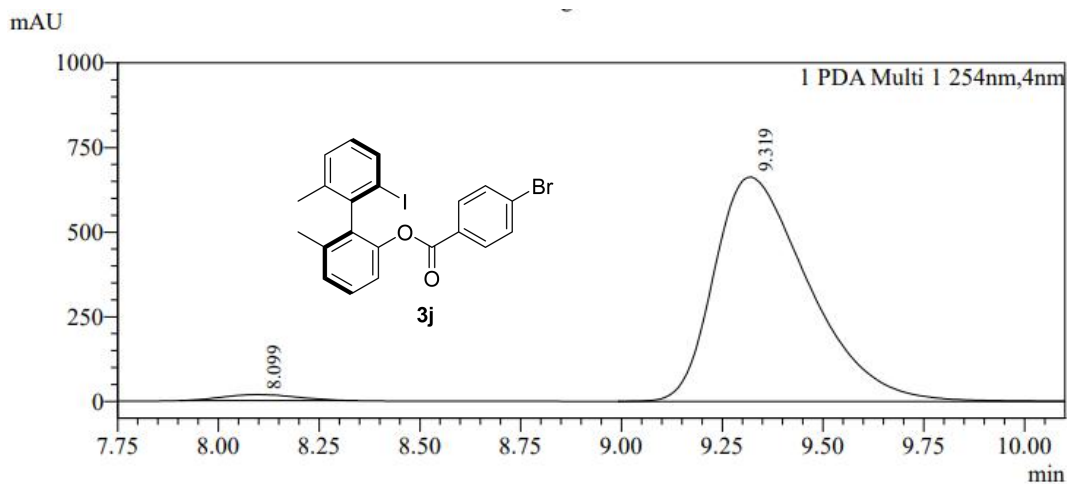
**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-bromobenzoate(3j).** Diacel Chiralcel OD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 9.3 min,  $t_R$ (minor) = 8.1 min, e.r. = 98:2



Peak Table

PDA Ch1 254nm

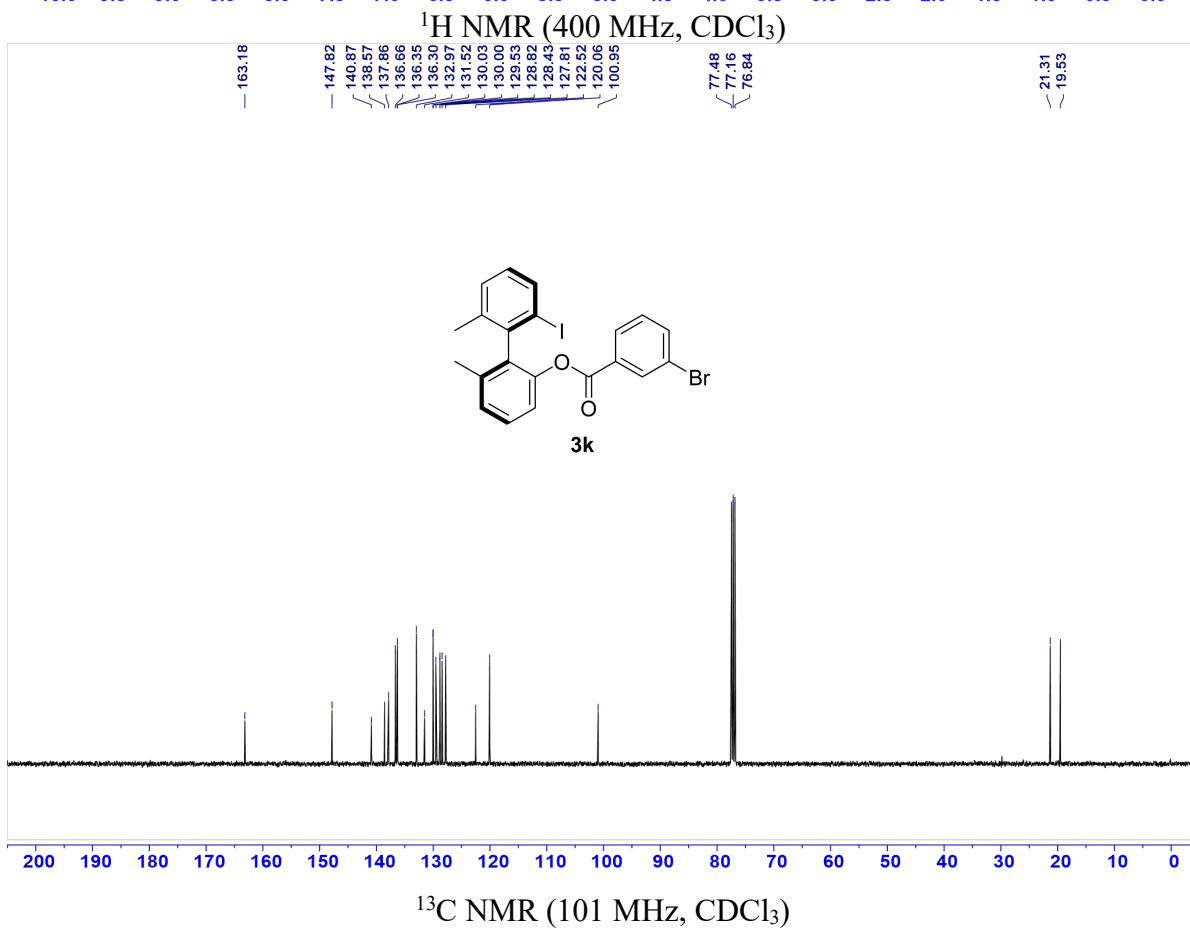
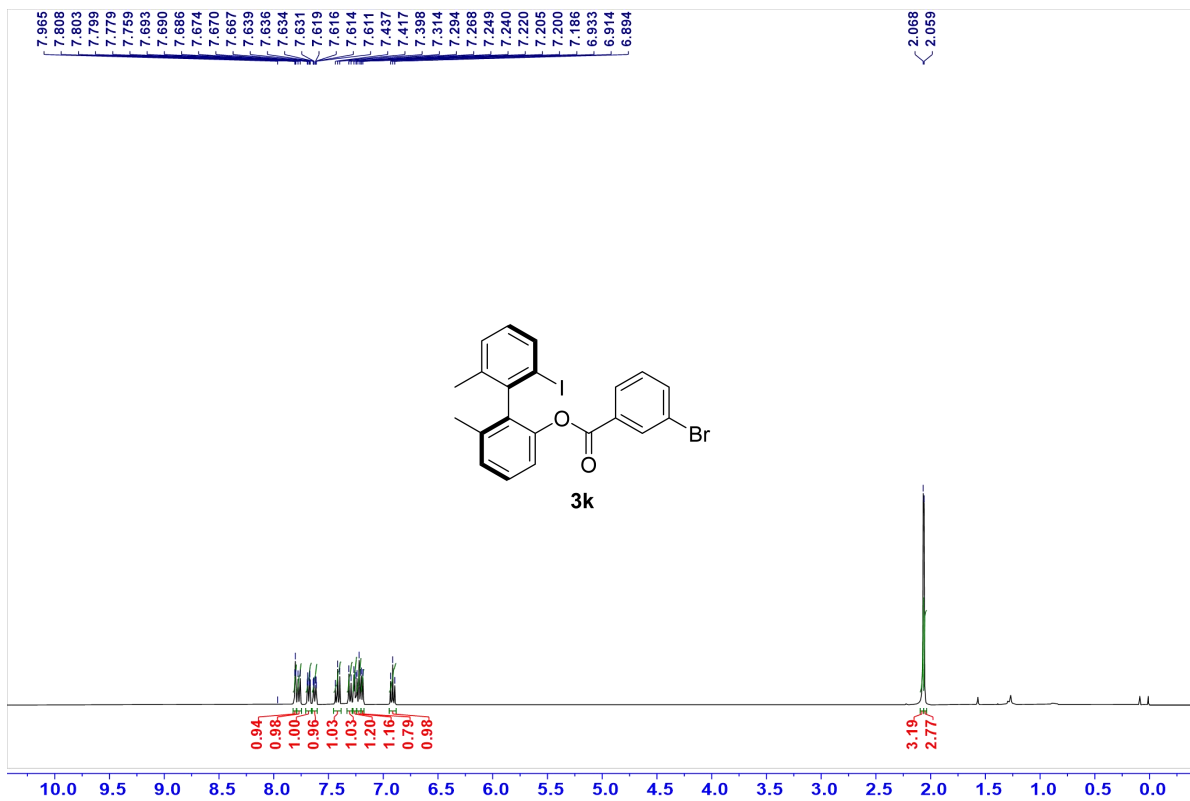
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	8.321	8.853	502971	7687898	49.523
2	9.952	10.517	410383	7835966	50.477
Total			913354	15523863	100.000



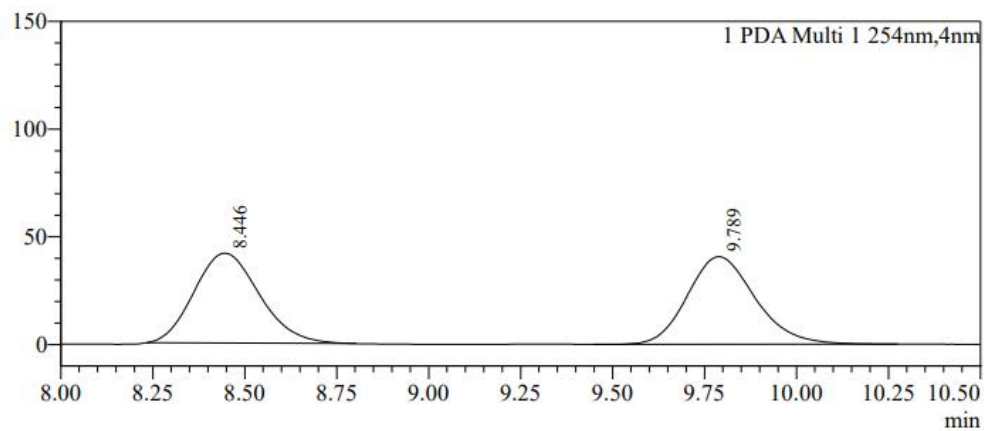
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	8.099	8.341	17981	230616	2.087
2	9.319	10.283	662797	10817218	97.913
Total			680778	11047834	100.000



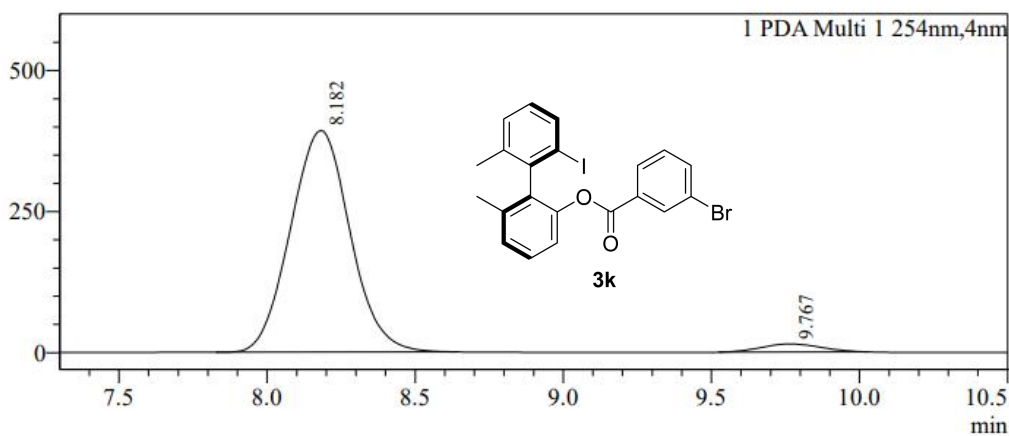
**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 3-bromobenzoate(3k).**  
 Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  
 $t_R(\text{major}) = 8.2$  min,  $t_R(\text{minor}) = 9.8$  min, e.r. = 96.5:3.5



Peak Table

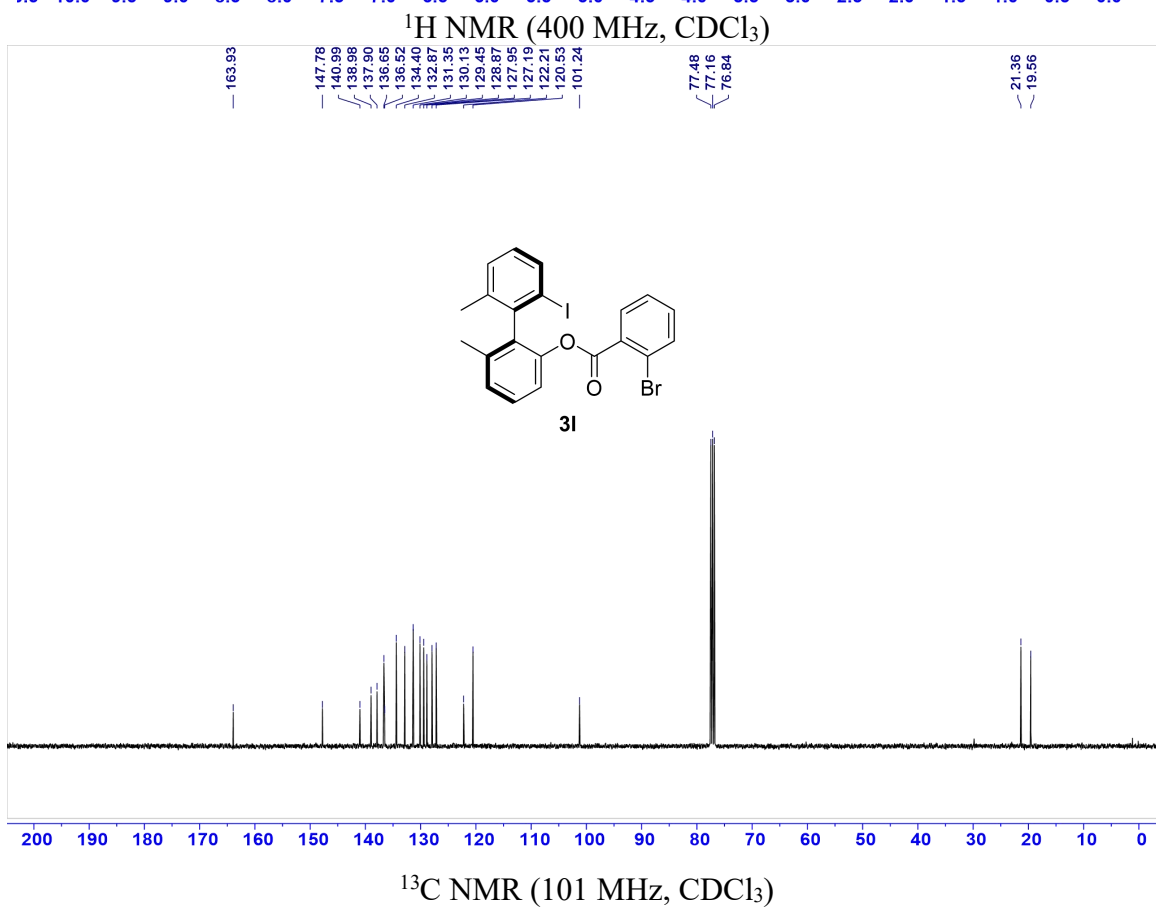
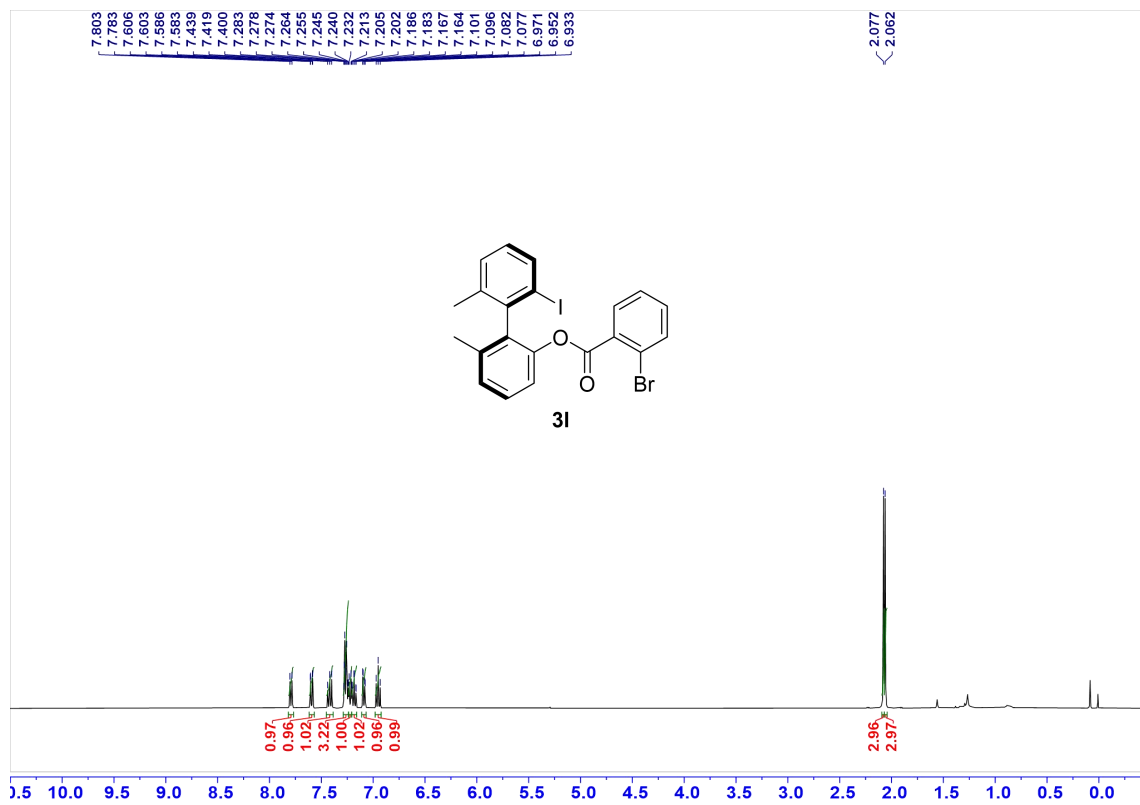
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	8.446	8.800	41745	516295	49.773
2	9.789	10.272	40642	521012	50.227
Total			82388	1037307	100.000

mAU

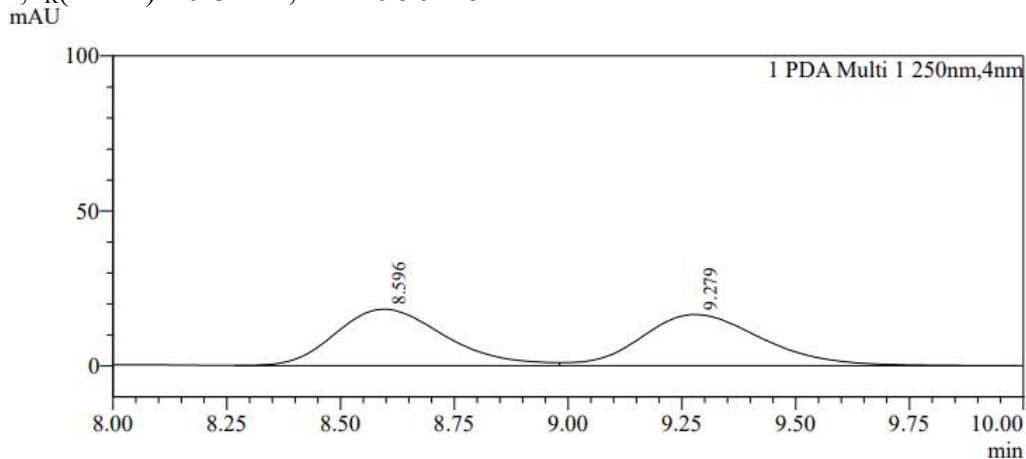


Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	8.182	8.640	392872	5495062	96.431
2	9.767	10.027	14524	203395	3.569
Total			407396	5698457	100.000



**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 2-bromobenzoate(3I).** Diacel Chiralcel OD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 8.4 min,  $t_R$ (minor) = 9.3 min, e.r. = 98.5:1.5

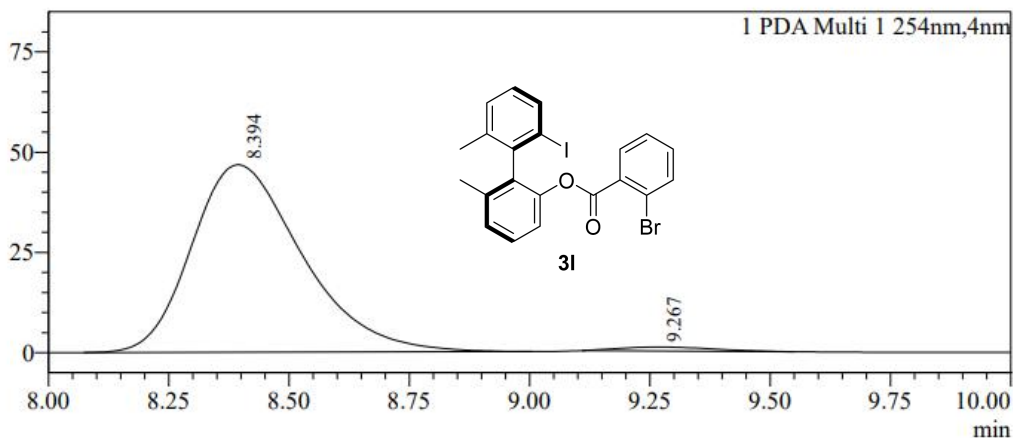


Peak Table

PDA Ch1 250nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	8.596	8.981	18224	305829	50.087
2	9.279	9.984	16521	304762	49.913
Total			34745	610592	100.000

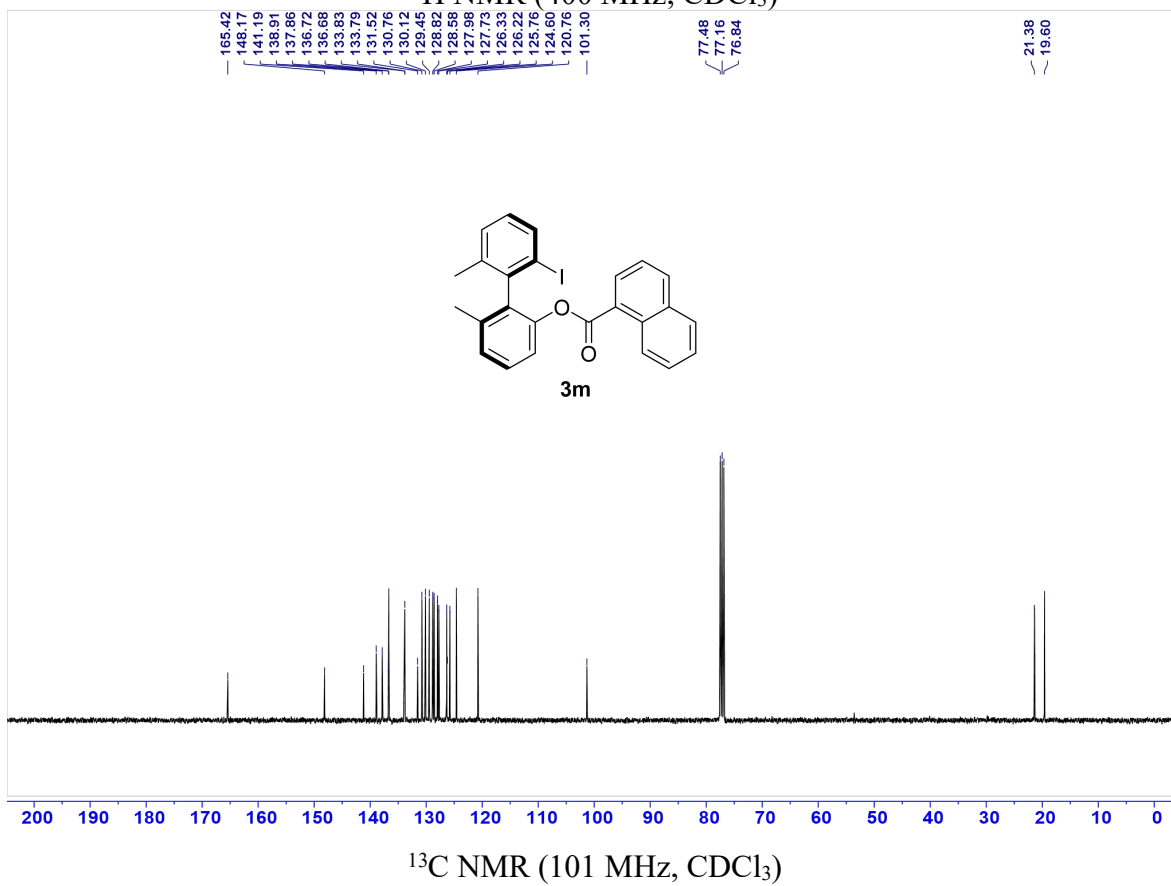
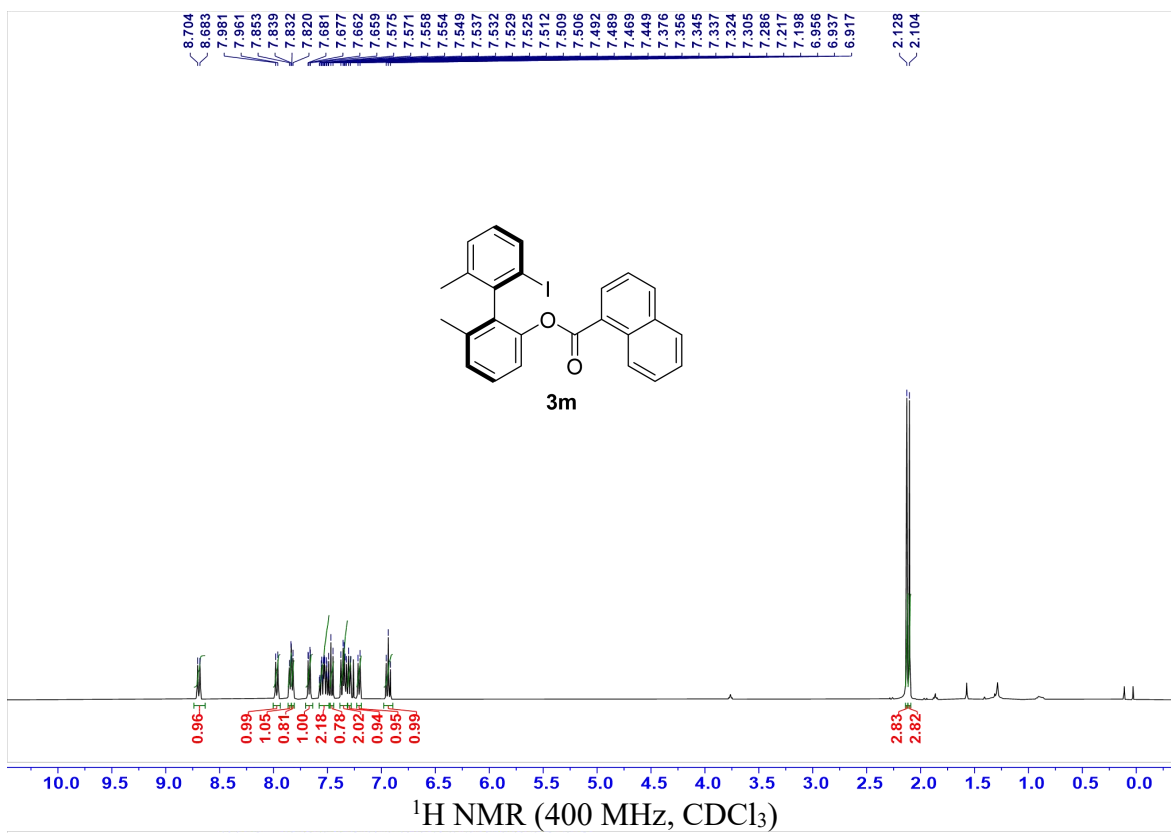
mAU



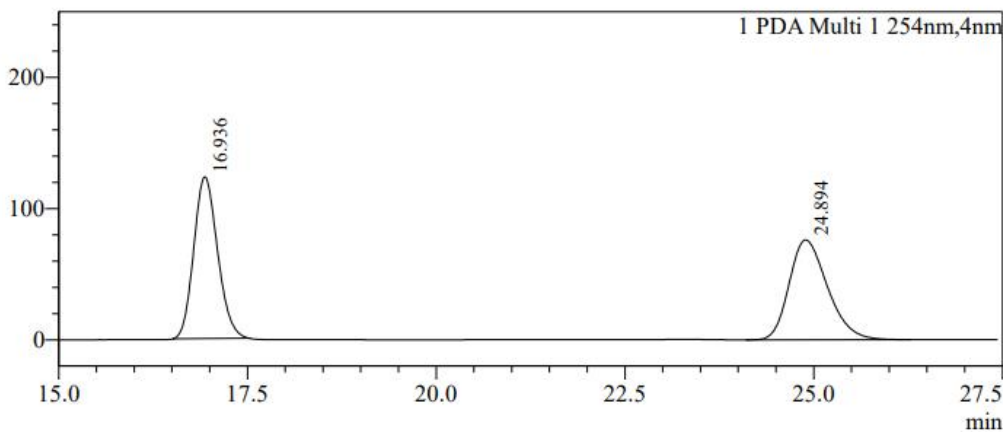
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	8.394	9.003	46812	748874	98.263
2	9.267	9.547	993	13240	1.737
Total			47804	762113	100.000

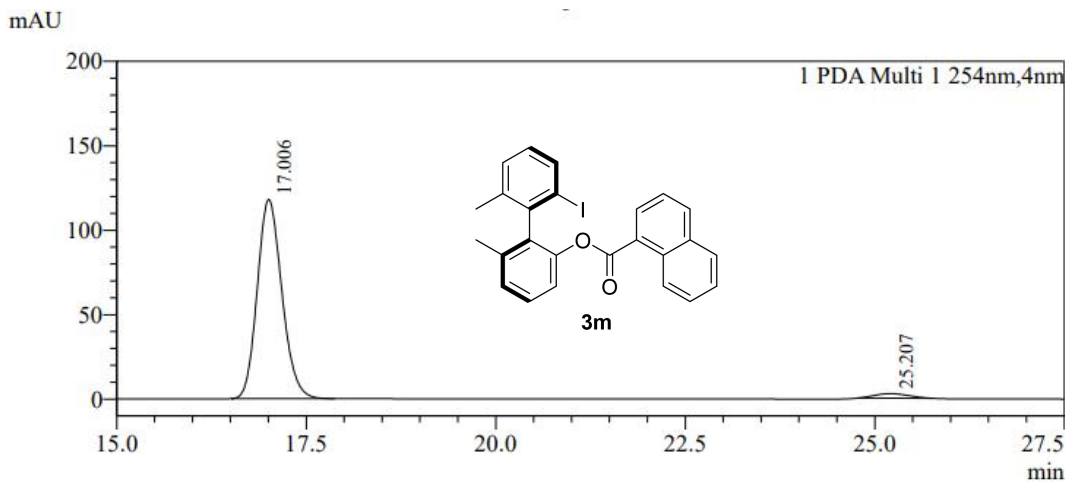


**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 1-naphthoate(3m).** Diacel Chiralcel AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 17.0 min,  $t_R$ (minor) = 25.2 min, e.r. = 97:3



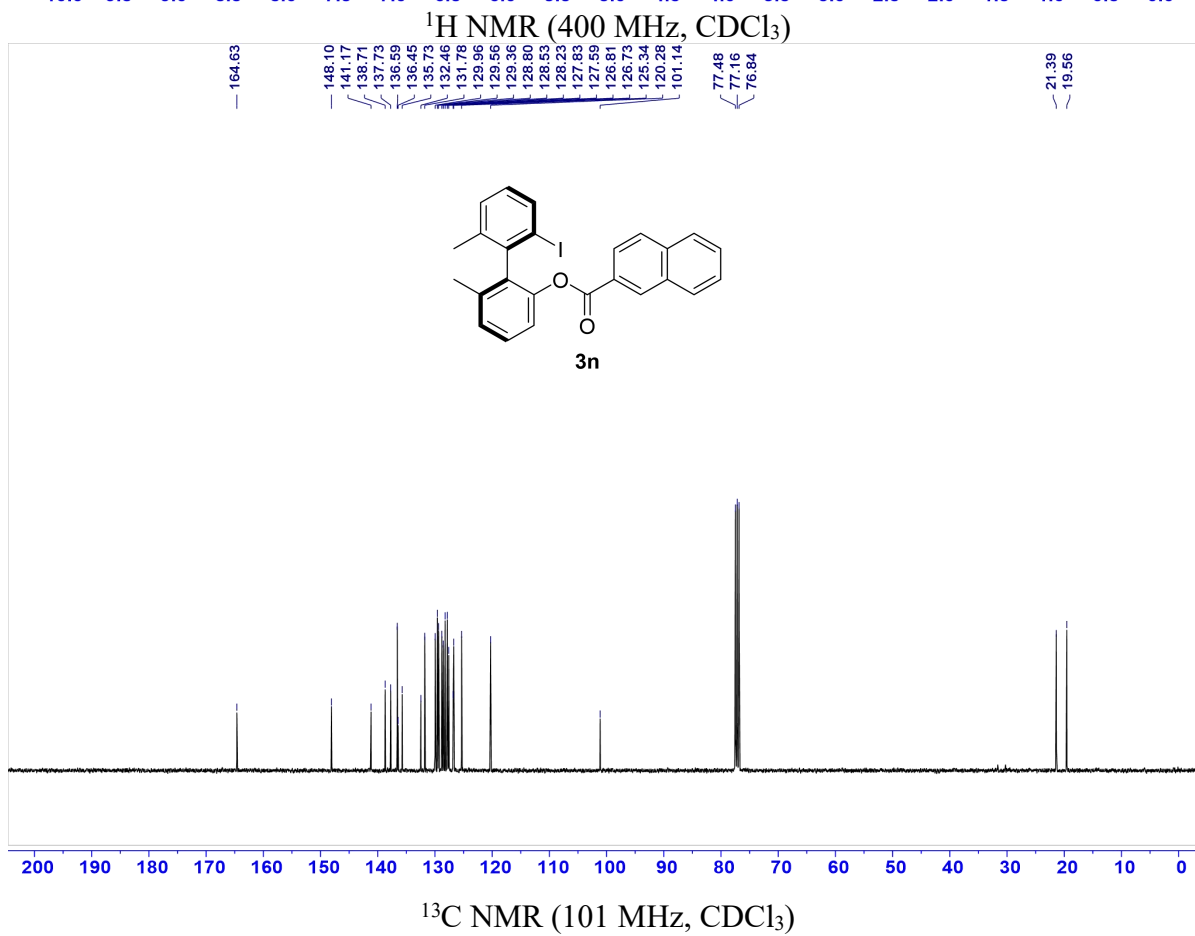
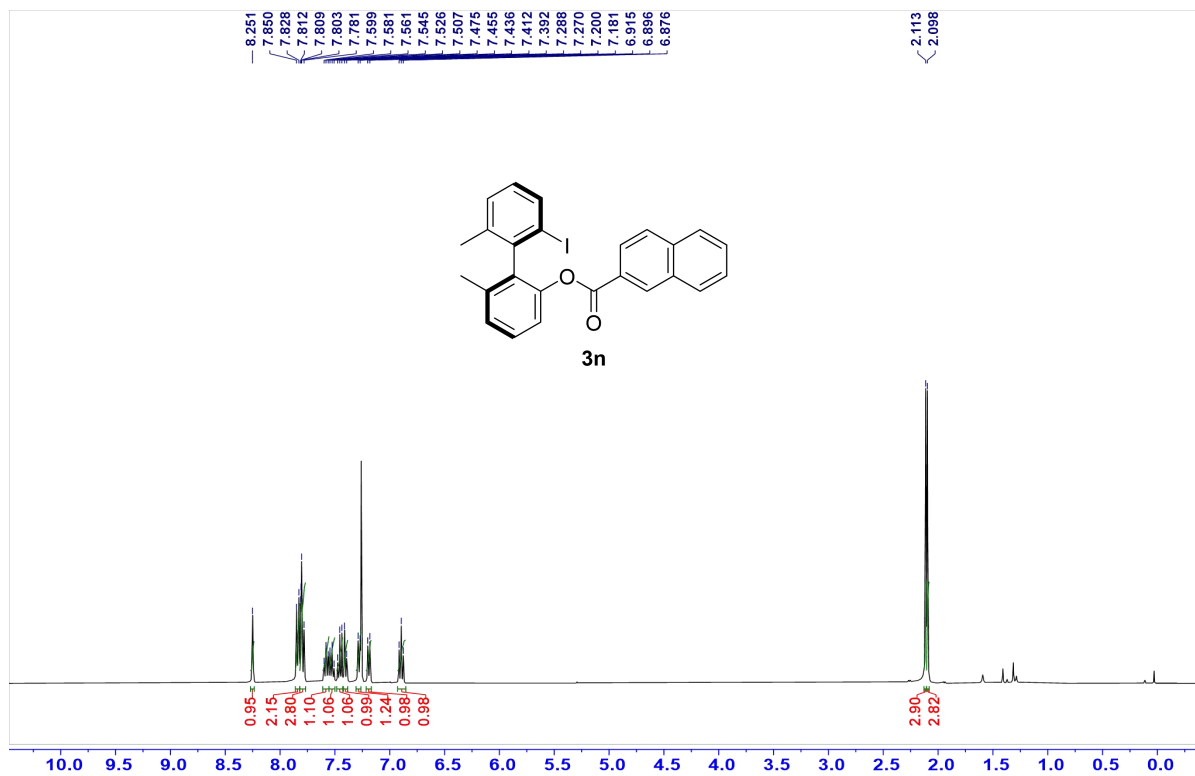
Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	16.936	17.525	123297	2707738	50.150
2	24.894	26.272	76126	2691590	49.850
Total			199423	5399328	100.000

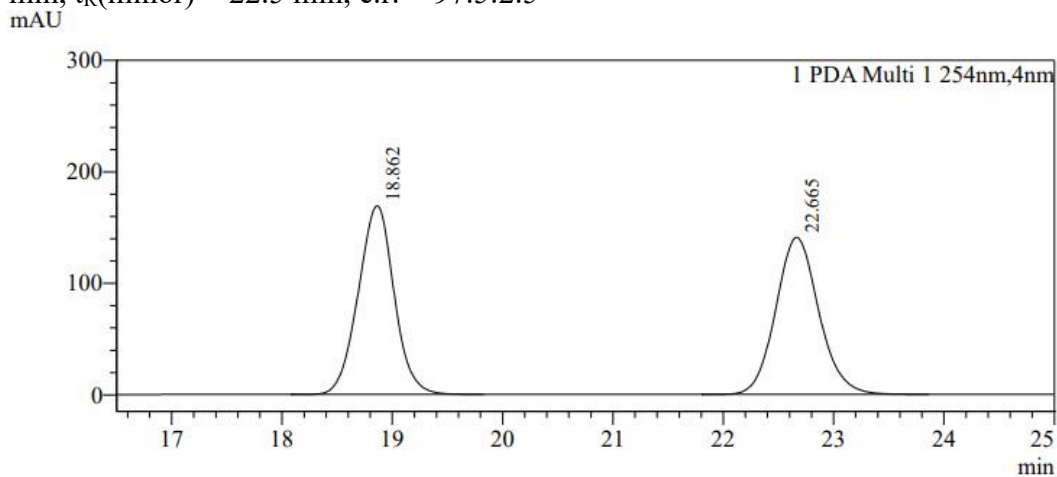


Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	17.006	17.856	117970	2667629	96.967
2	25.207	25.749	2665	83452	3.033
Total			120635	2751081	100.000

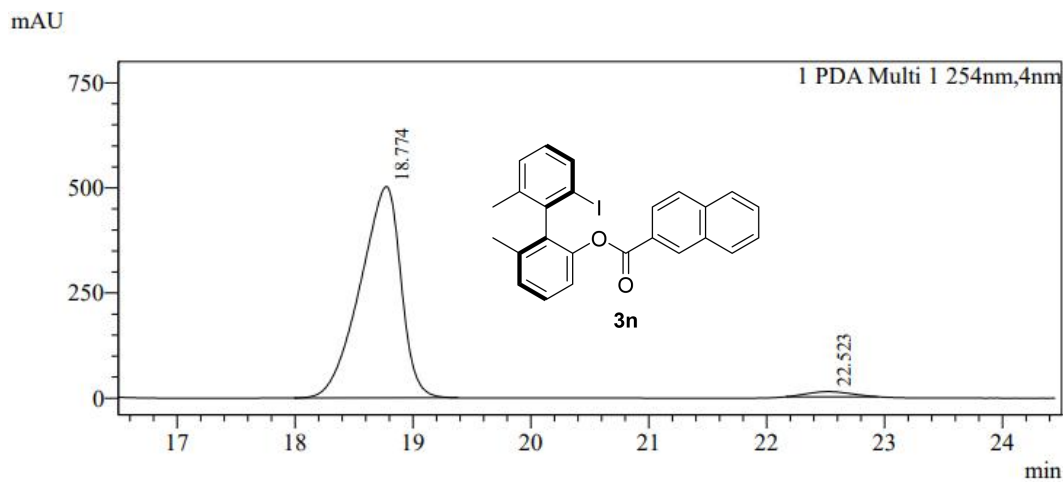


**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 2-naphthoate(3n).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 18.8 min,  $t_R$ (minor) = 22.5 min, e.r. = 97.5:2.5



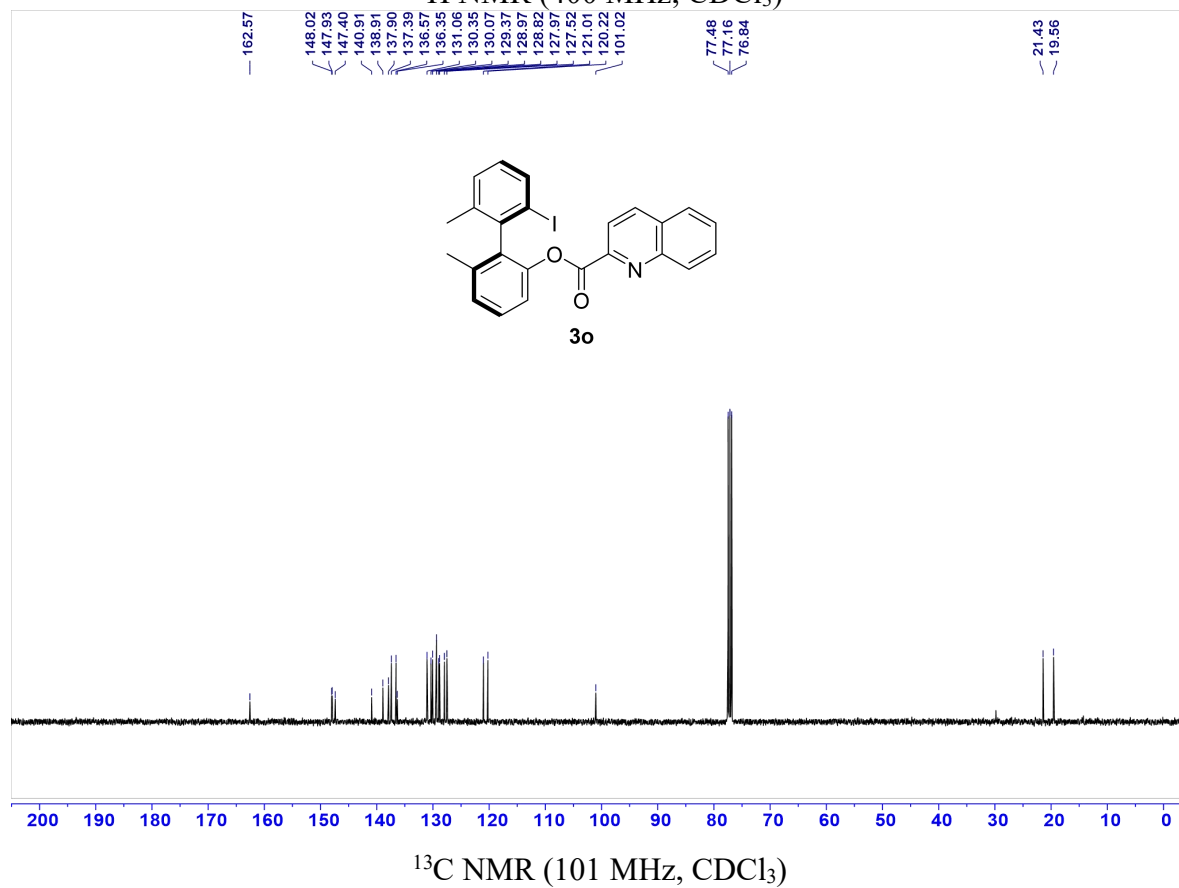
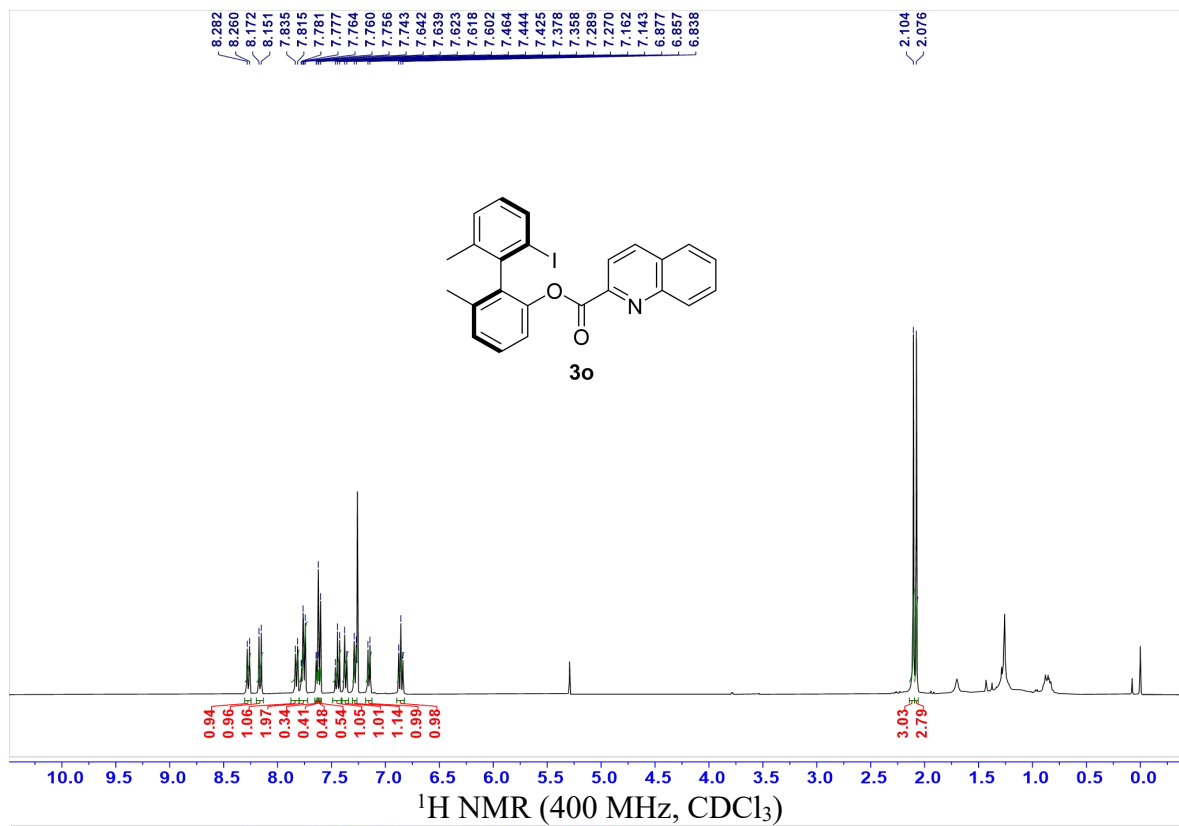
Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	18.862	19.819	169123	3830183	50.015
2	22.665	23.851	140858	3827961	49.985
Total			309981	7658145	100.000



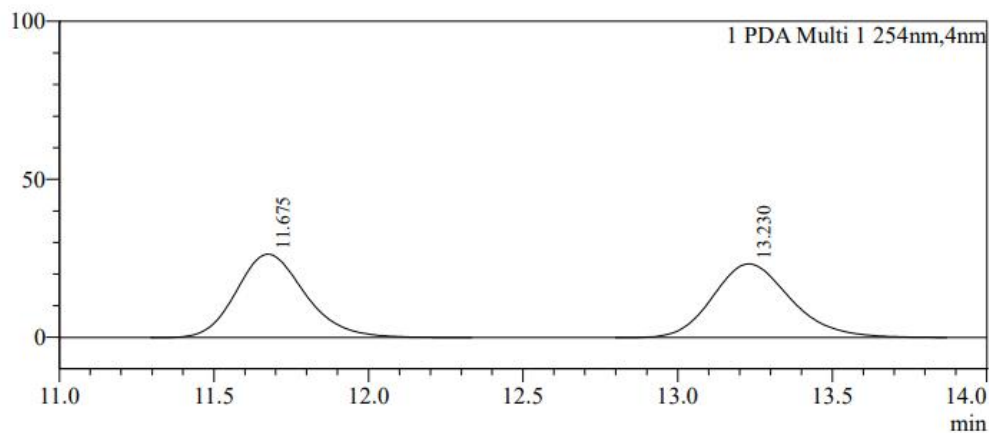
Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	18.774	19.371	502563	12131034	97.513
2	22.523	22.933	12062	309354	2.487
Total			514624	12440387	100.000



**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl quinoline-2-carboxylate(**3o**).**  
 Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 90:10, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  
 $t_R(\text{major}) = 12.2$  min,  $t_R(\text{minor}) = 13.8$  min, e.r. = 91:9

mAU

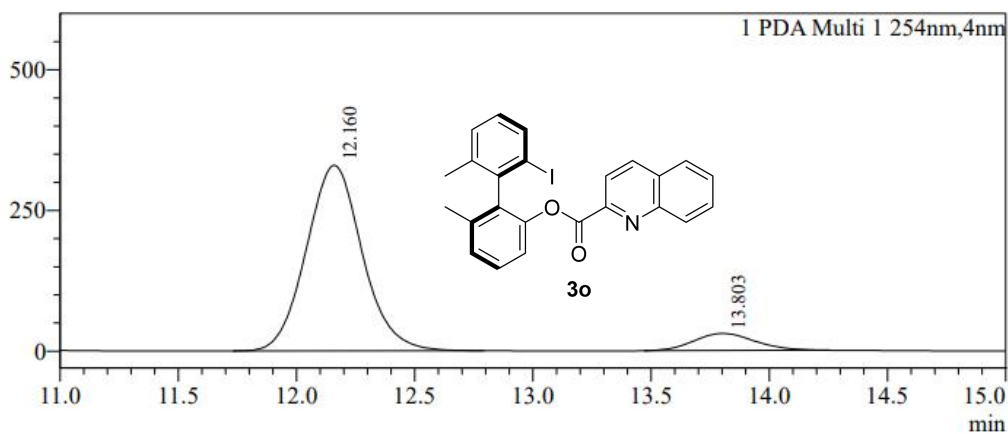


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	11.675	12.331	26368	410509	50.035
2	13.230	13.867	23297	409941	49.965
Total			49665	820450	100.000

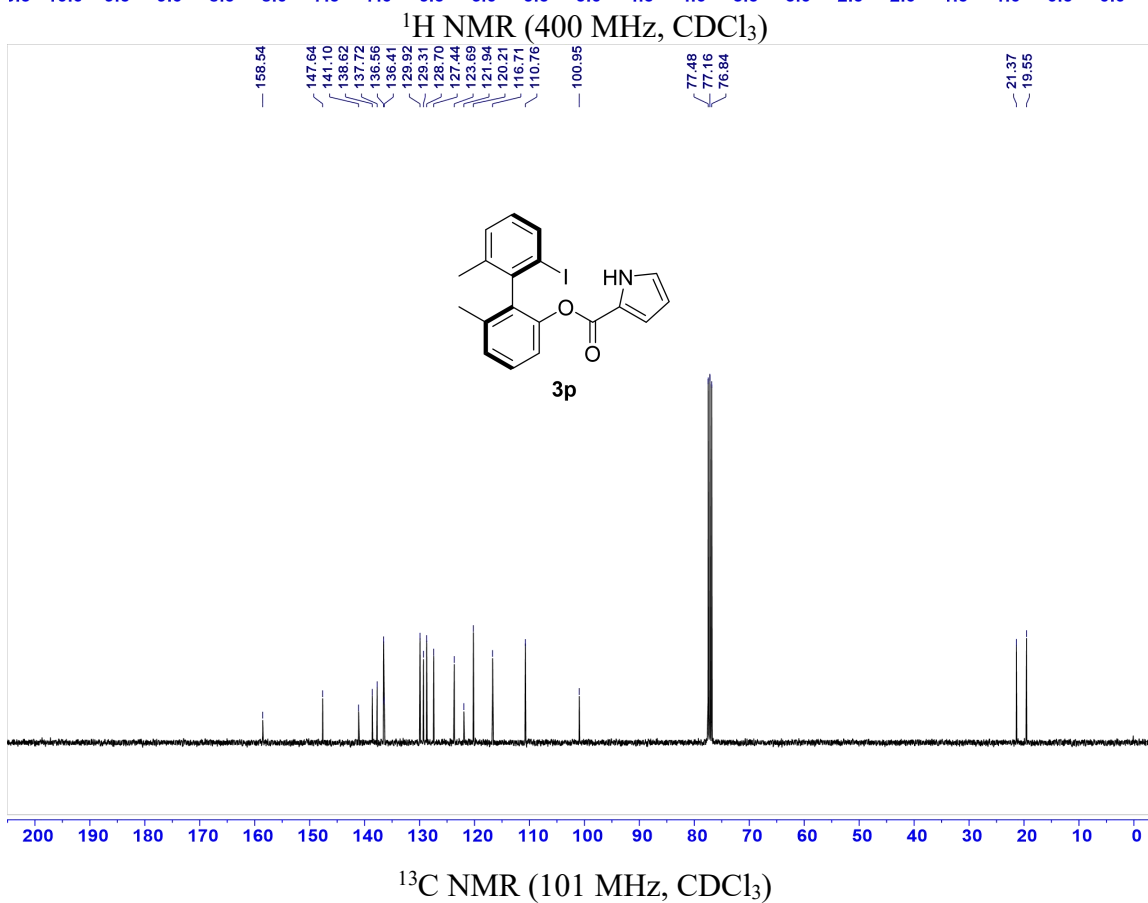
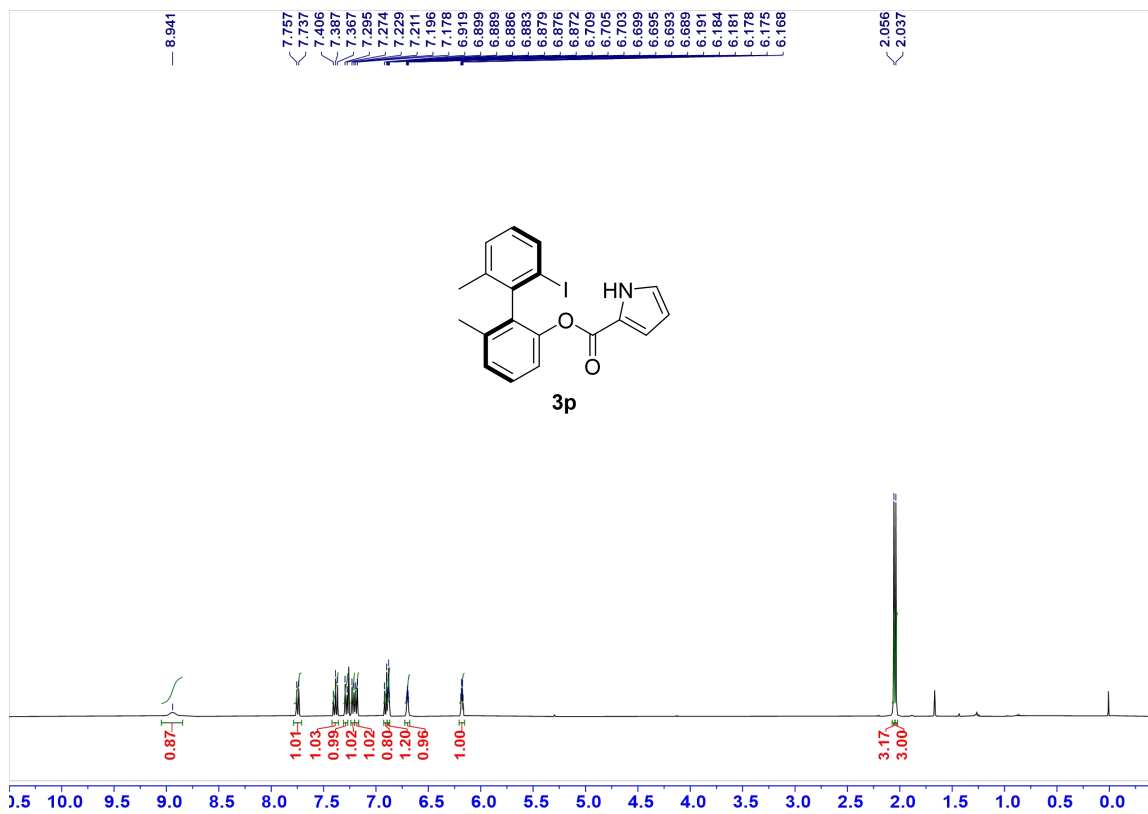
mAU



Peak Table

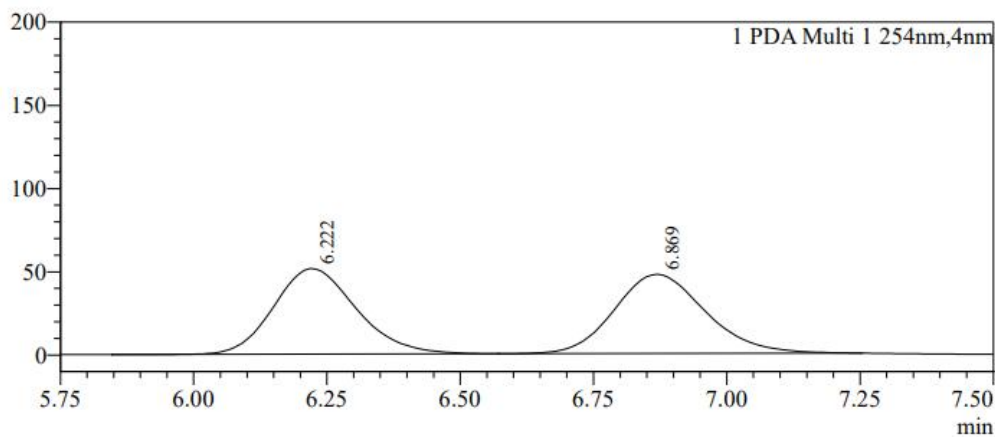
PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	12.160	12.789	329908	5439587	90.826
2	13.803	14.251	30462	549415	9.174
Total			360370	5989001	100.000



**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 1H-pyrrole-2-carboxylate(3p).** Diacel Chiralcel OD-H, *n*-Hexane:*i*-PrOH = 92:8, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 7.6 min,  $t_R$ (minor) = 6.7 min, e.r. = 96.5:3.5

mAU

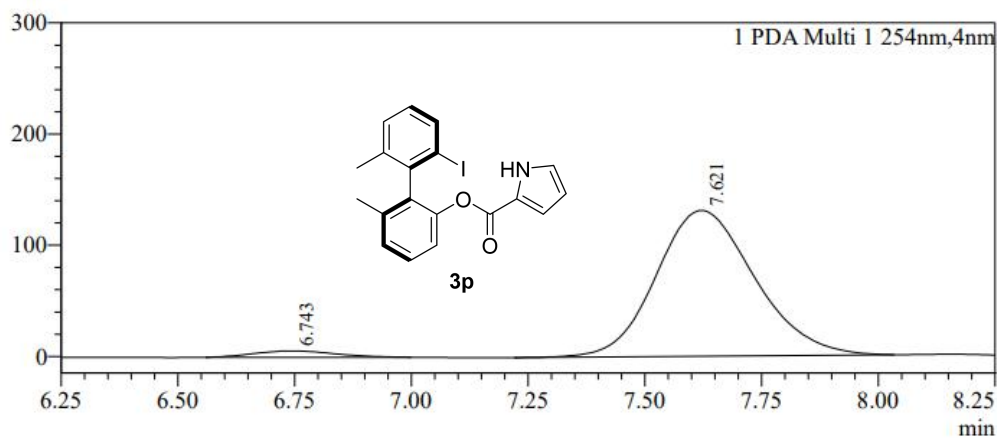


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	6.222	6.571	51464	557305	49.546
2	6.869	7.253	47628	567514	50.454
Total			99092	1124820	100.000

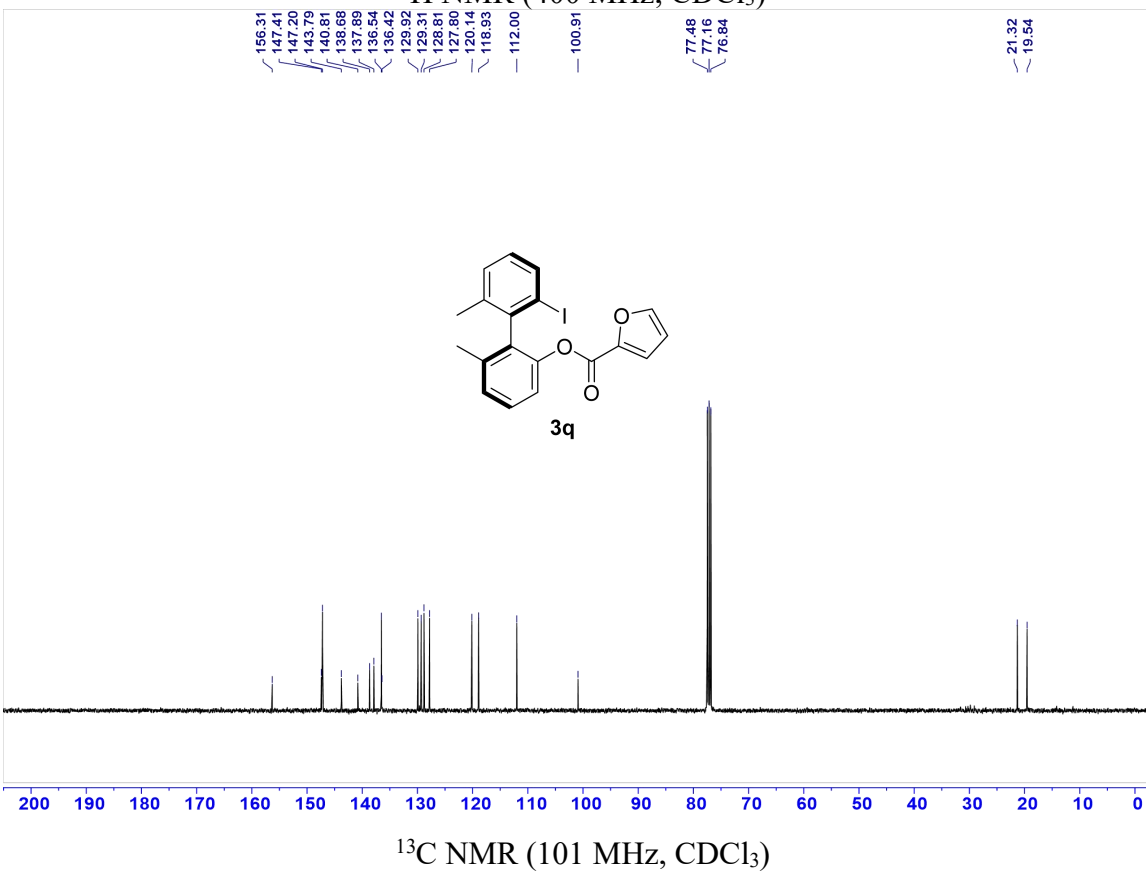
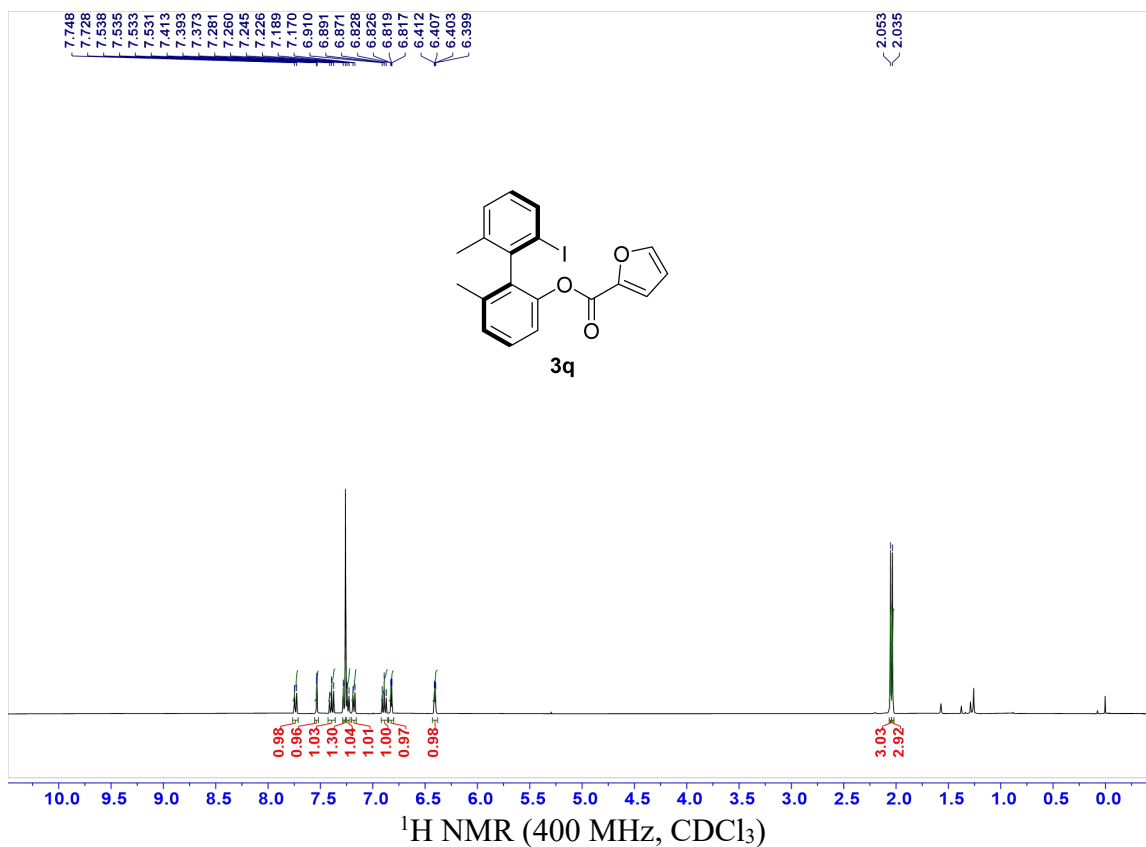
mAU



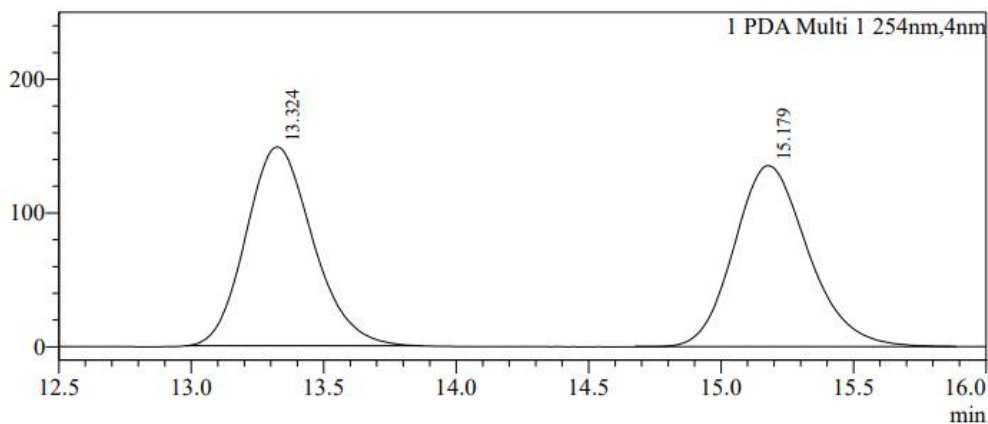
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	6.743	6.997	5716	67796	3.399
2	7.621	8.032	130915	1926551	96.601
Total			136632	1994347	100.000



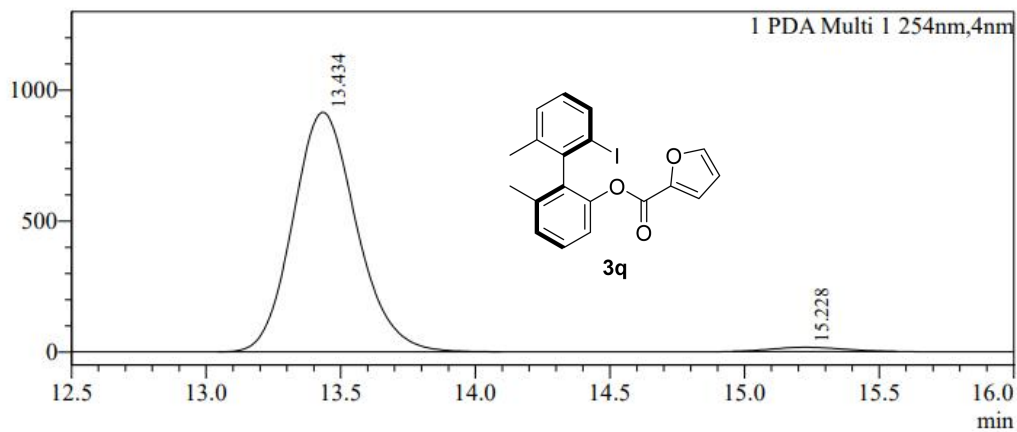
**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl furan-2-carboxylate(3q).**  
 Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  
 $t_R(\text{major})$  = 13.4 min,  $t_R(\text{minor})$  = 15.2 min, e.r. = 98:2  
 mAU



Peak Table

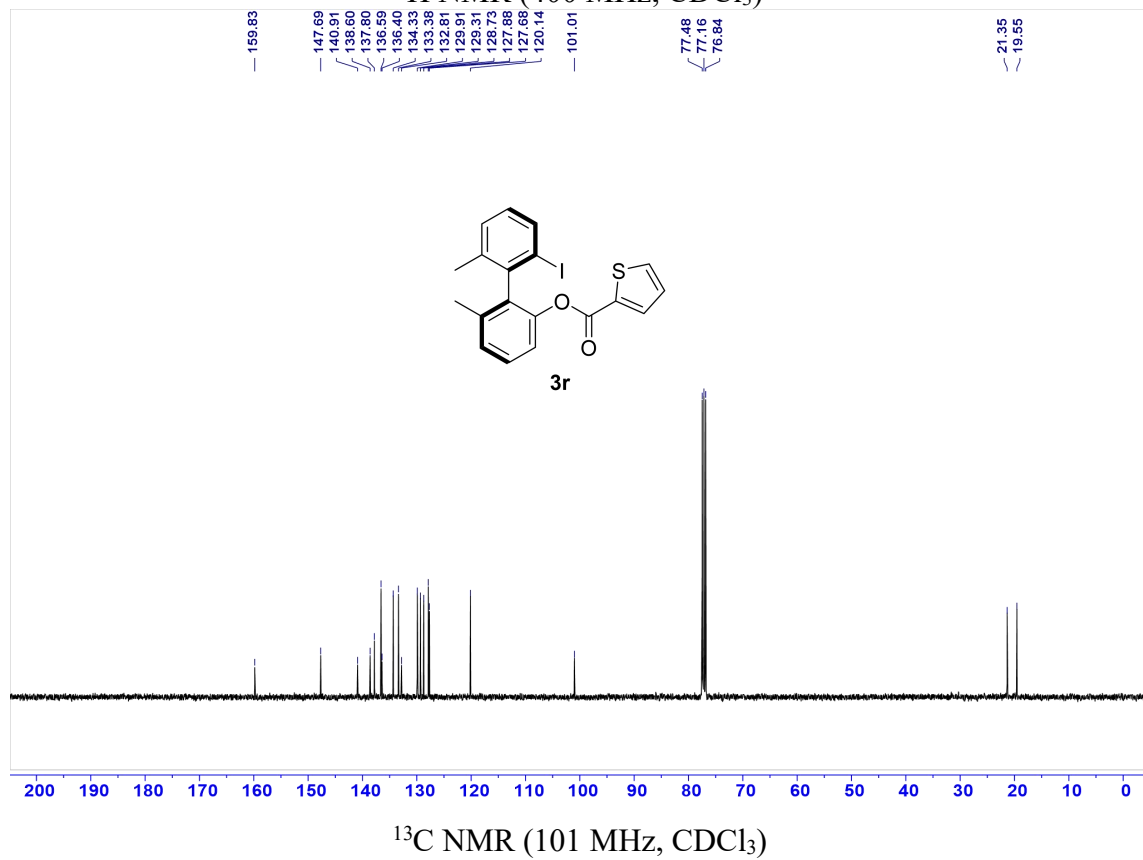
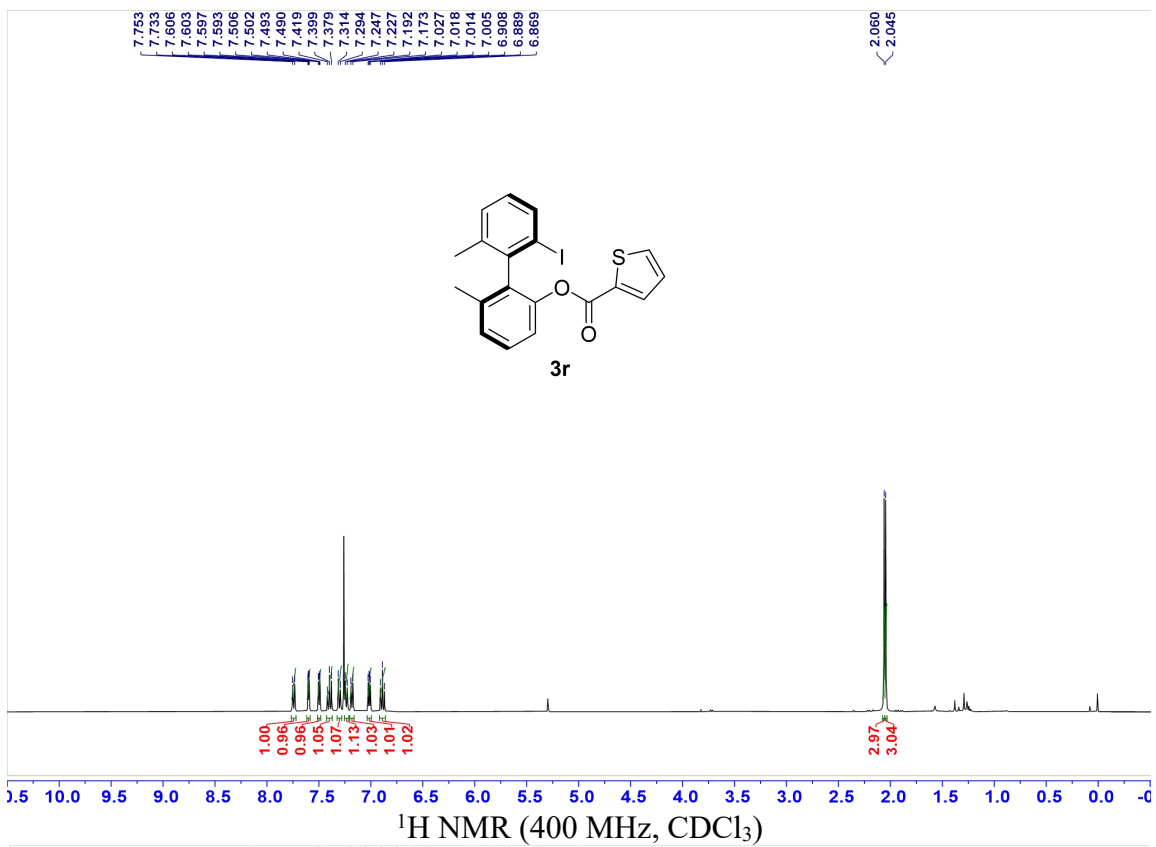
PDA Ch1 254nm					
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	13.324	13.867	148760	2615918	49.822
2	15.179	15.883	135347	2634631	50.178
Total			284107	5250549	100.000

mAU

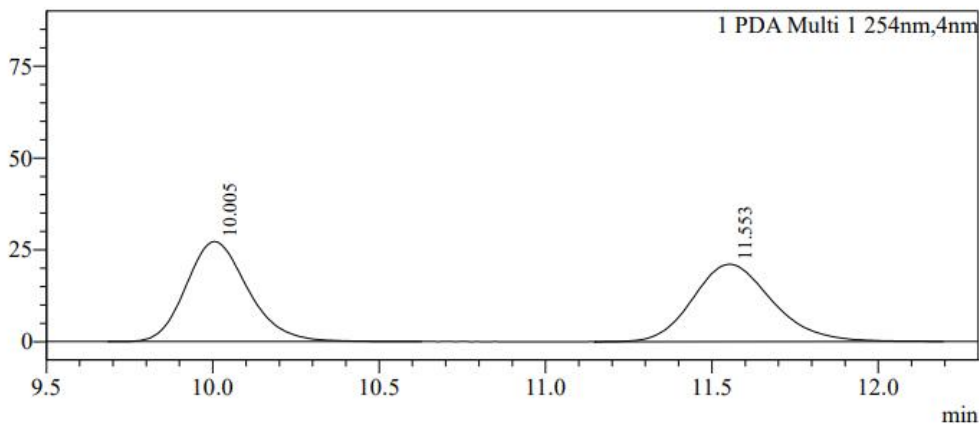


Peak Table

PDA Ch1 254nm					
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	13.434	14.091	914796	15053508	98.101
2	15.228	15.563	16089	291377	1.899
Total			930885	15344884	100.000

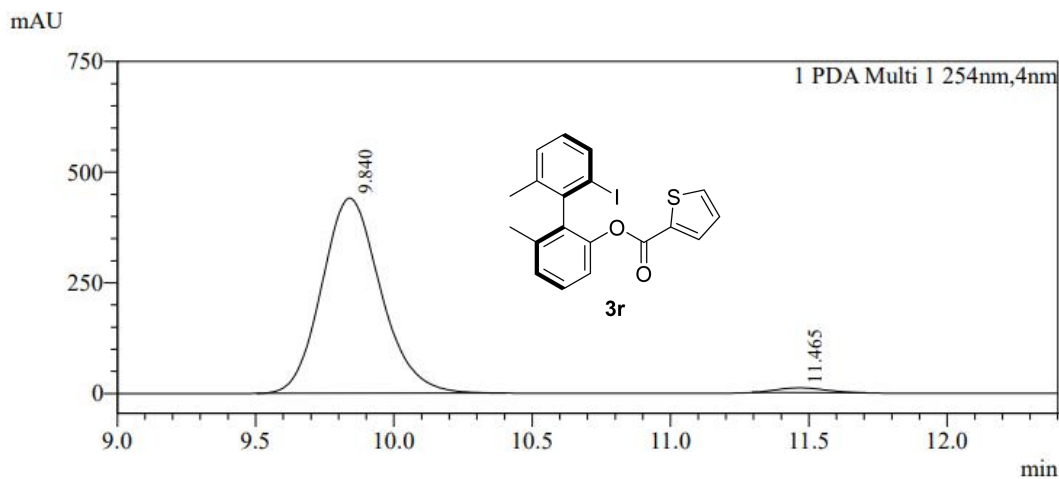


**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl thiophene-2-carboxylate(**3r**).**  
 Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda = 254$  nm,  
 $t_R(\text{major}) = 9.8$  min,  $t_R(\text{minor}) = 11.5$  min, e.r. = 98:2  
 mAU



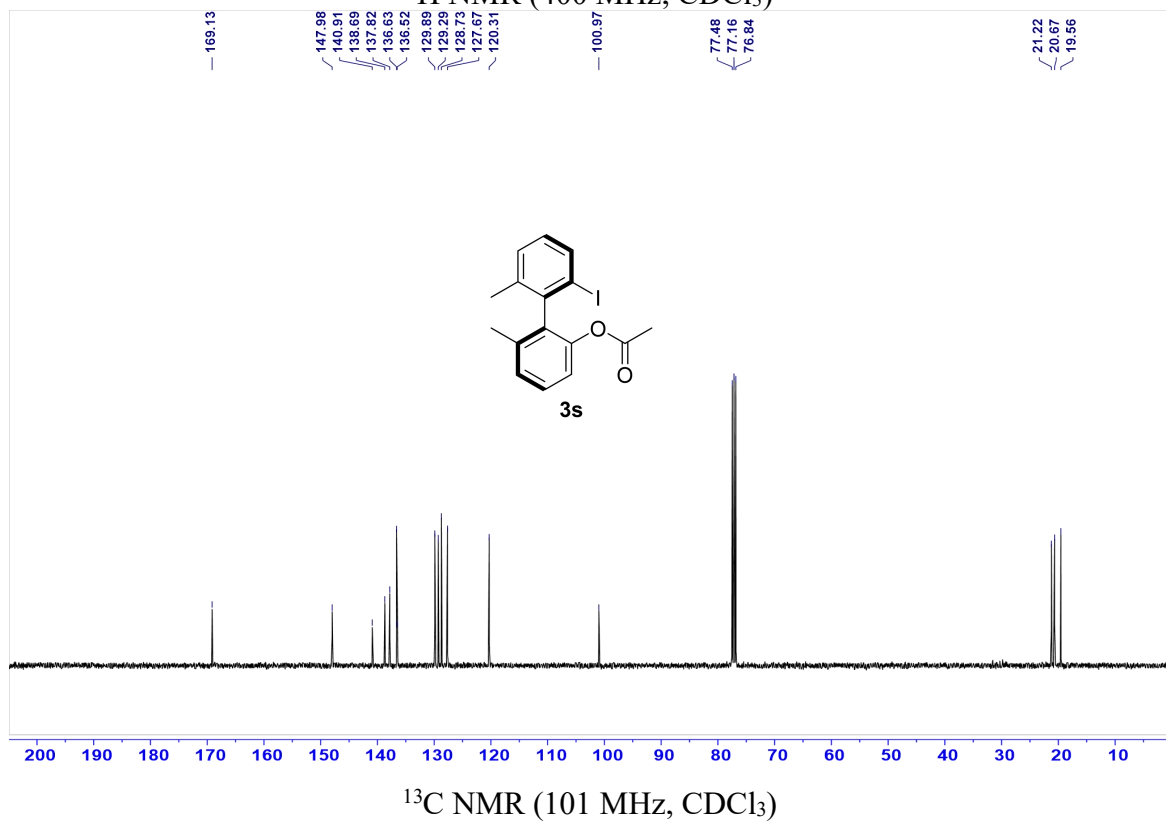
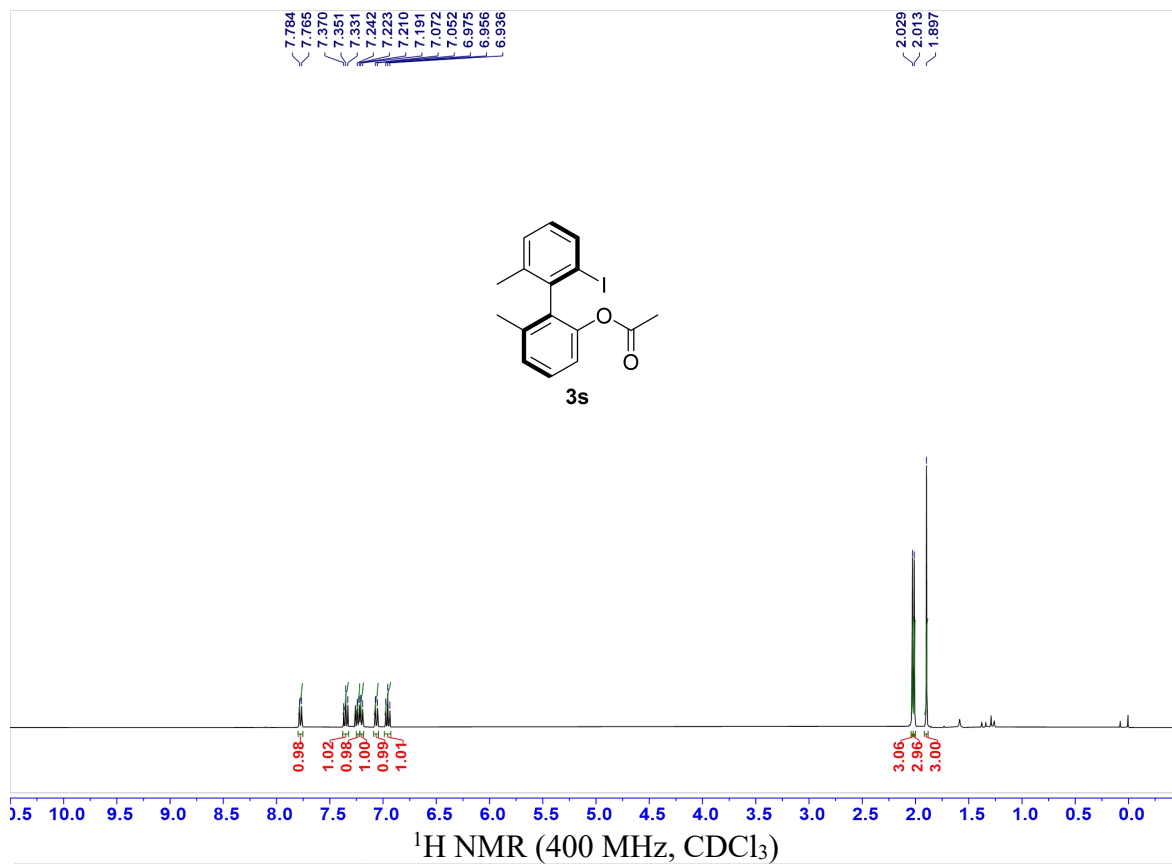
Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	10.005	10.624	27249	353174	50.219
2	11.553	12.192	21061	350088	49.781
Total			48310	703263	100.000

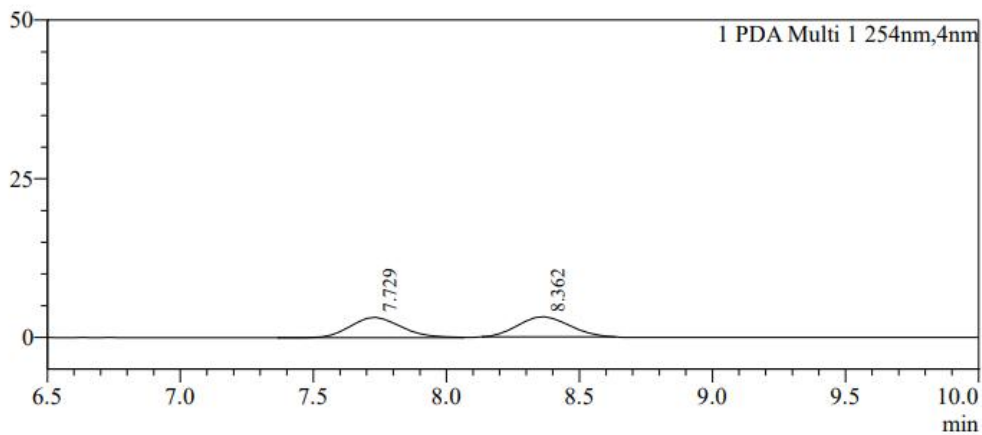


Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	9.840	10.400	440482	6548606	98.024
2	11.465	11.701	10809	132020	1.976
Total			451291	6680626	100.000

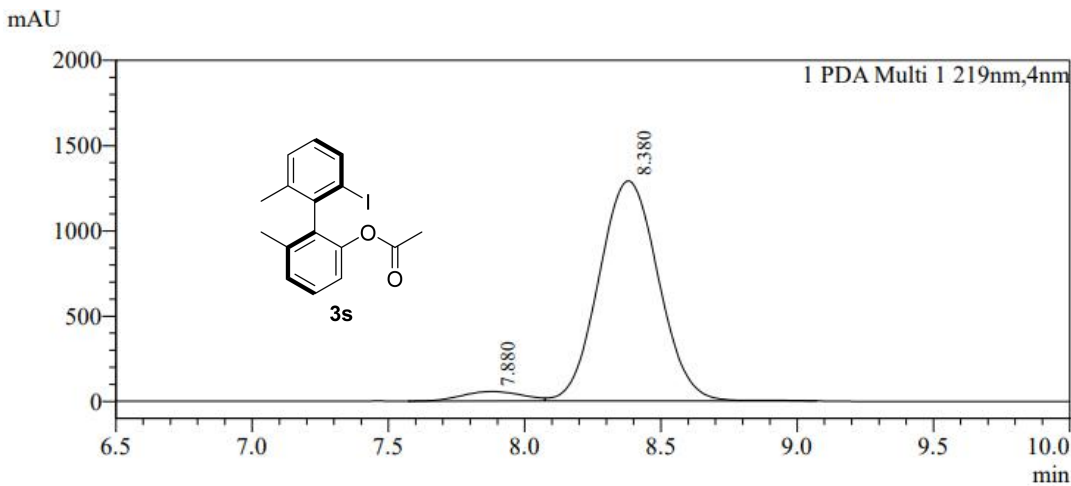


**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl acetate(3s).** Diacel Chiralpak IG, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 219 nm,  $t_R$ (major) = 8.4 min,  $t_R$ (minor) = 7.9 min, e.r. = 95.5:4.5



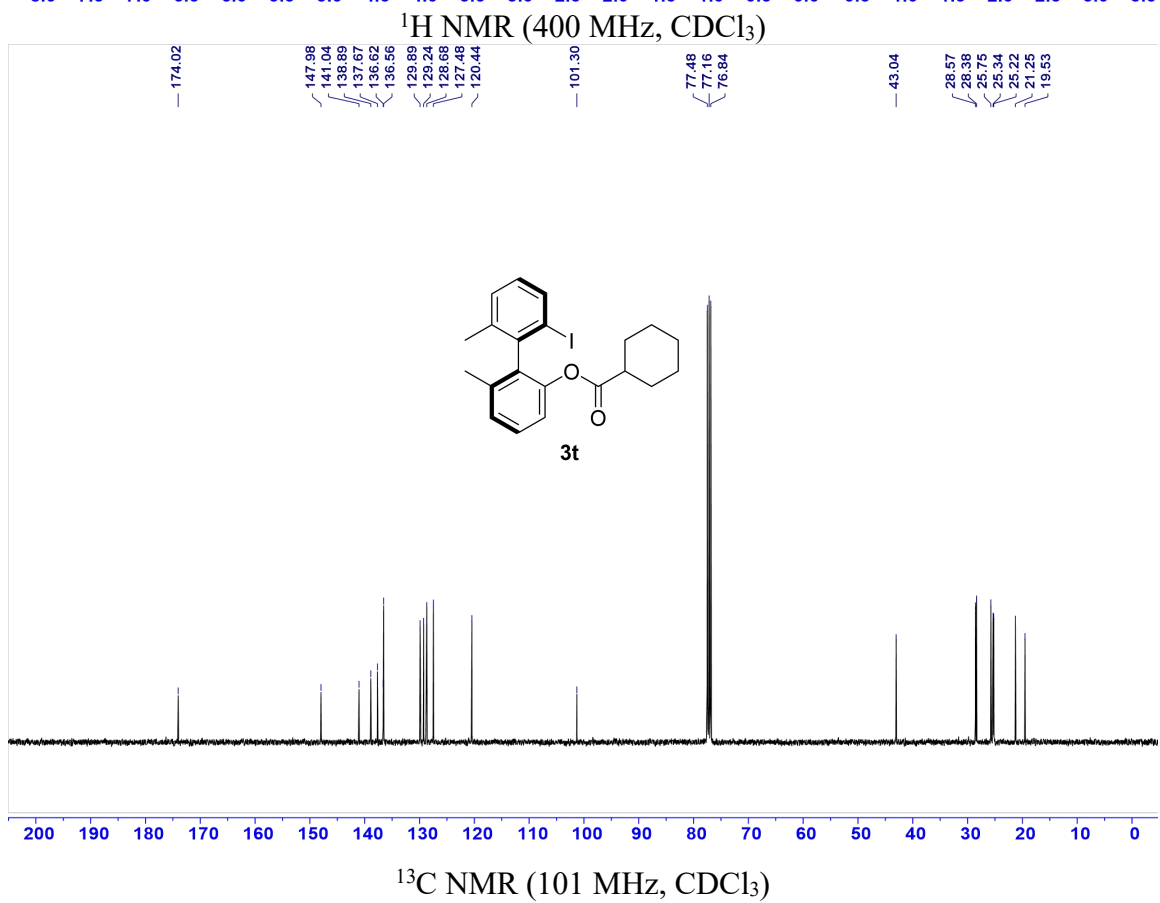
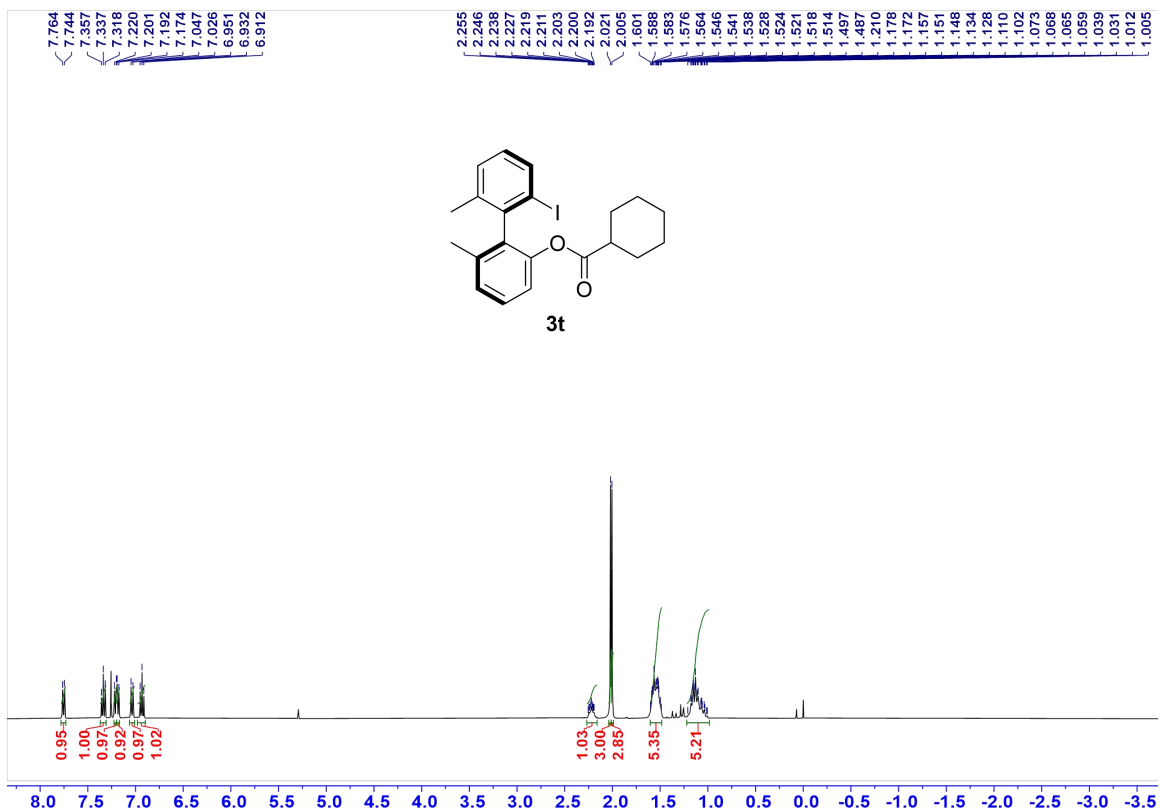
Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	7.729	8.067	3204	42850	50.031
2	8.362	8.633	3174	42797	49.969
Total			6378	85647	100.000

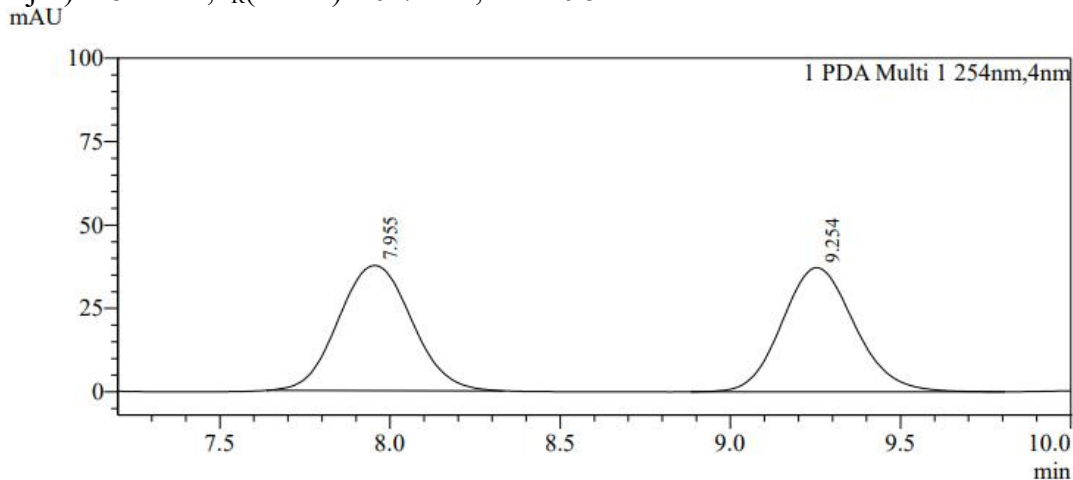


Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	7.880	8.075	56091	872611	4.253
2	8.380	9.067	1291634	19643450	95.747
Total			1347725	20516061	100.000



**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl cyclohexanecarboxylate(3t).**  
 Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  
 $t_R(\text{major}) = 8.1$  min,  $t_R(\text{minor}) = 9.7$  min, e.r. = 98:2

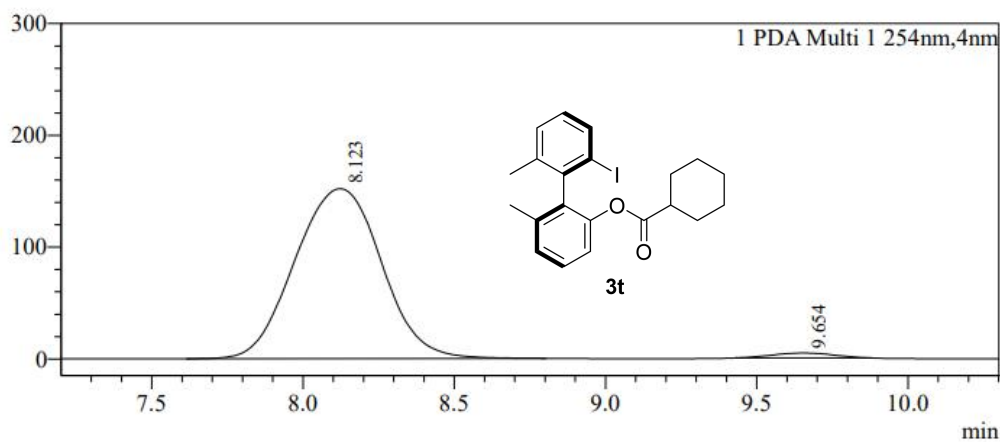


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	7.955	8.331	37550	563537	50.376
2	9.254	9.803	37188	555124	49.624
Total			74738	1118661	100.000

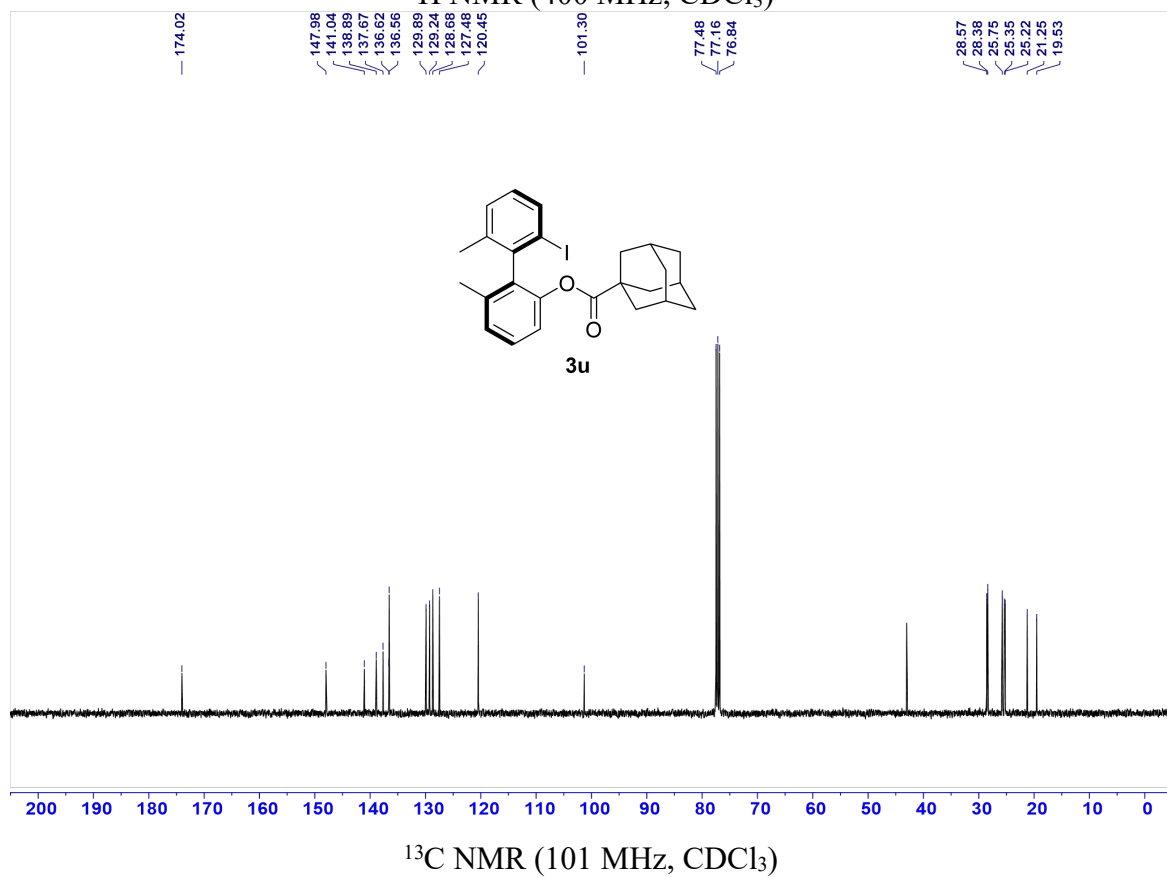
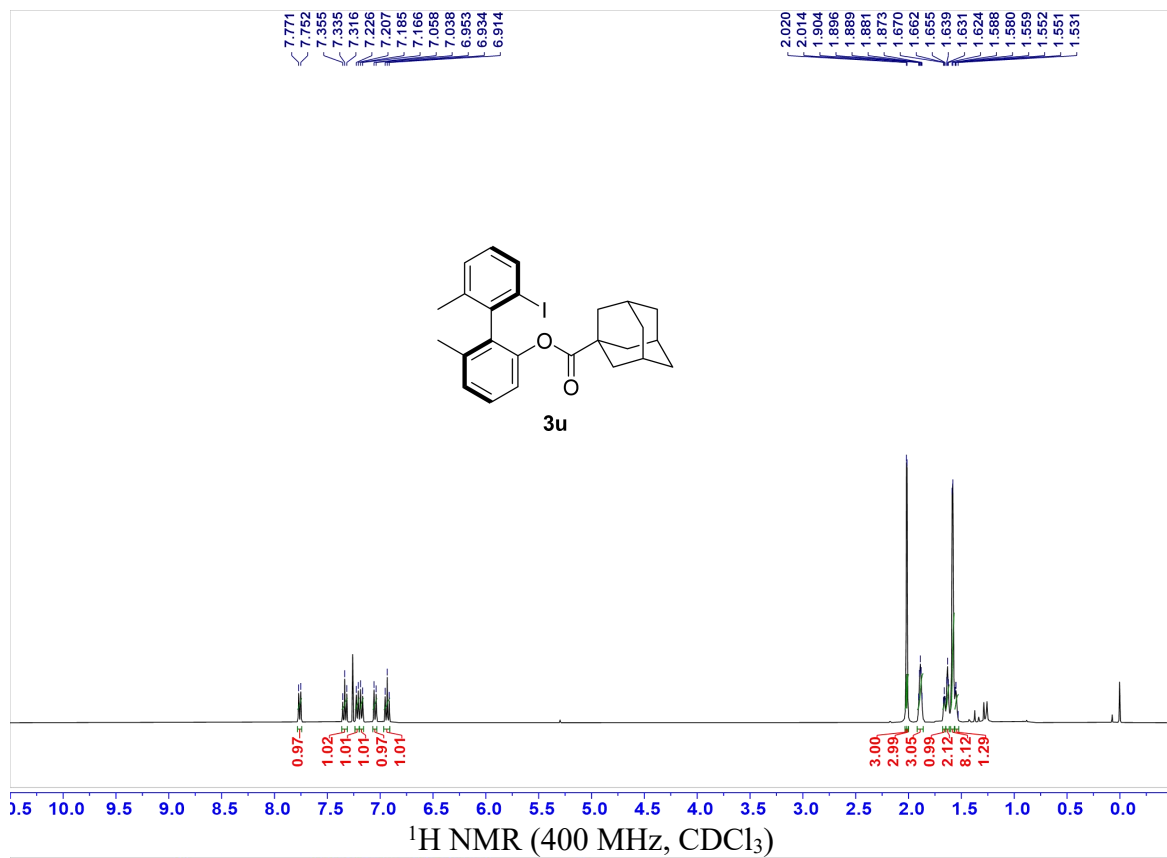
mAU



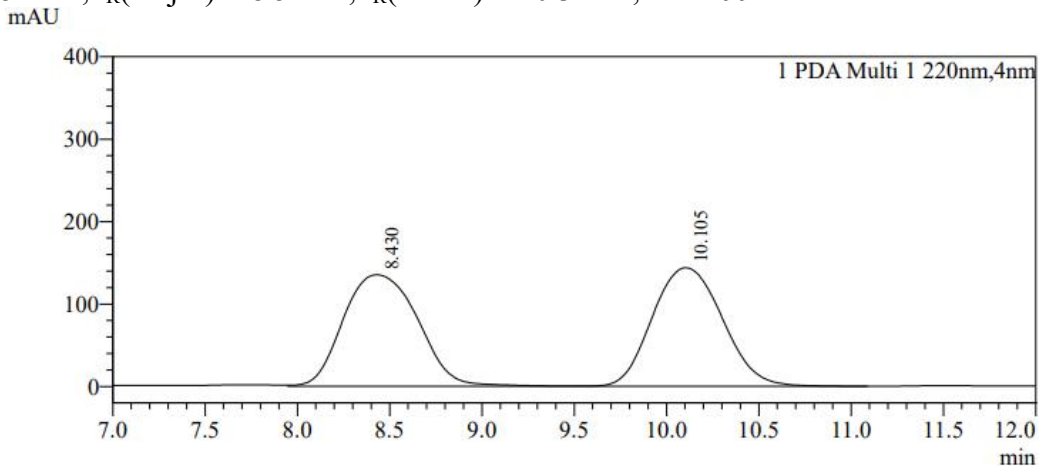
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	8.123	8.800	151814	3030450	97.983
2	9.654	9.877	4469	62375	2.017
Total			156283	3092825	100.000



**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl adamantane-1-carboxylate(3u).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda = 254$  nm,  $t_R(\text{major}) = 8.5$  min,  $t_R(\text{minor}) = 10.3$  min, e.r. = 99:1

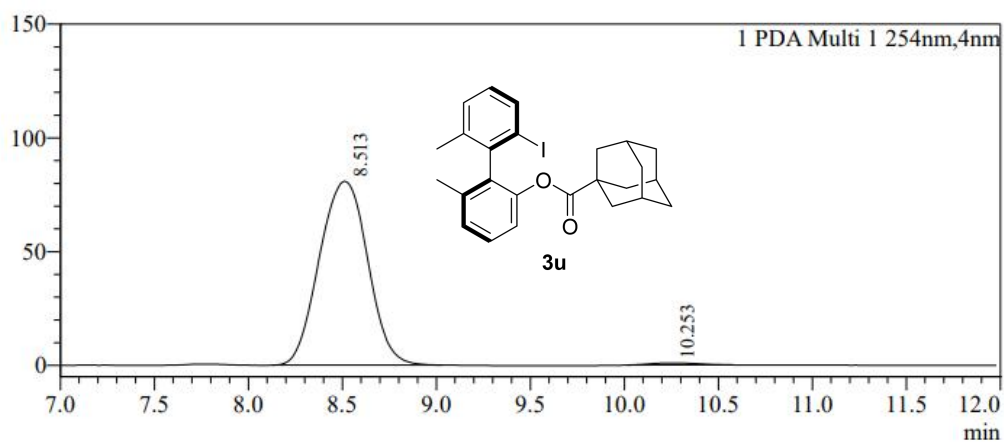


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	8.430	9.547	135329	3814116	50.079
2	10.105	11.083	143743	3802124	49.921
Total			279072	7616240	100.000

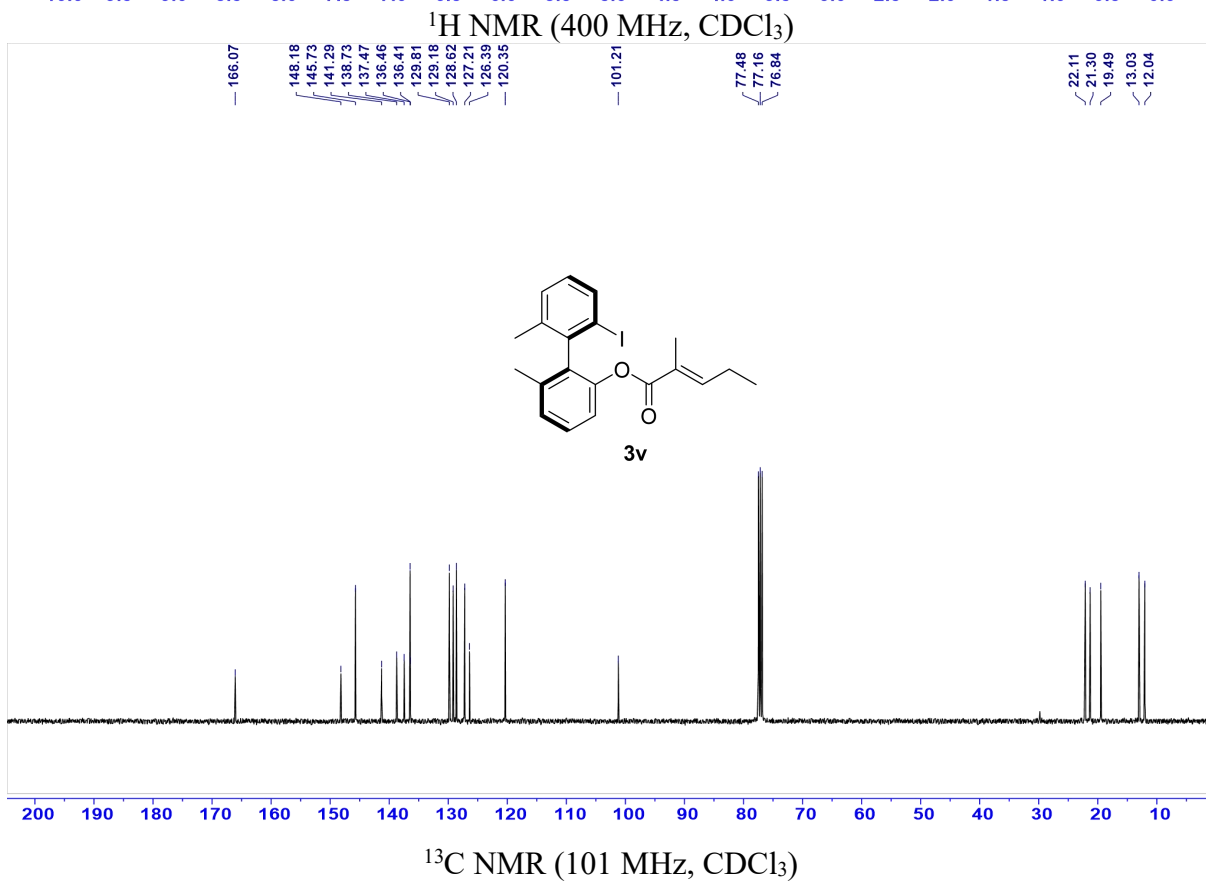
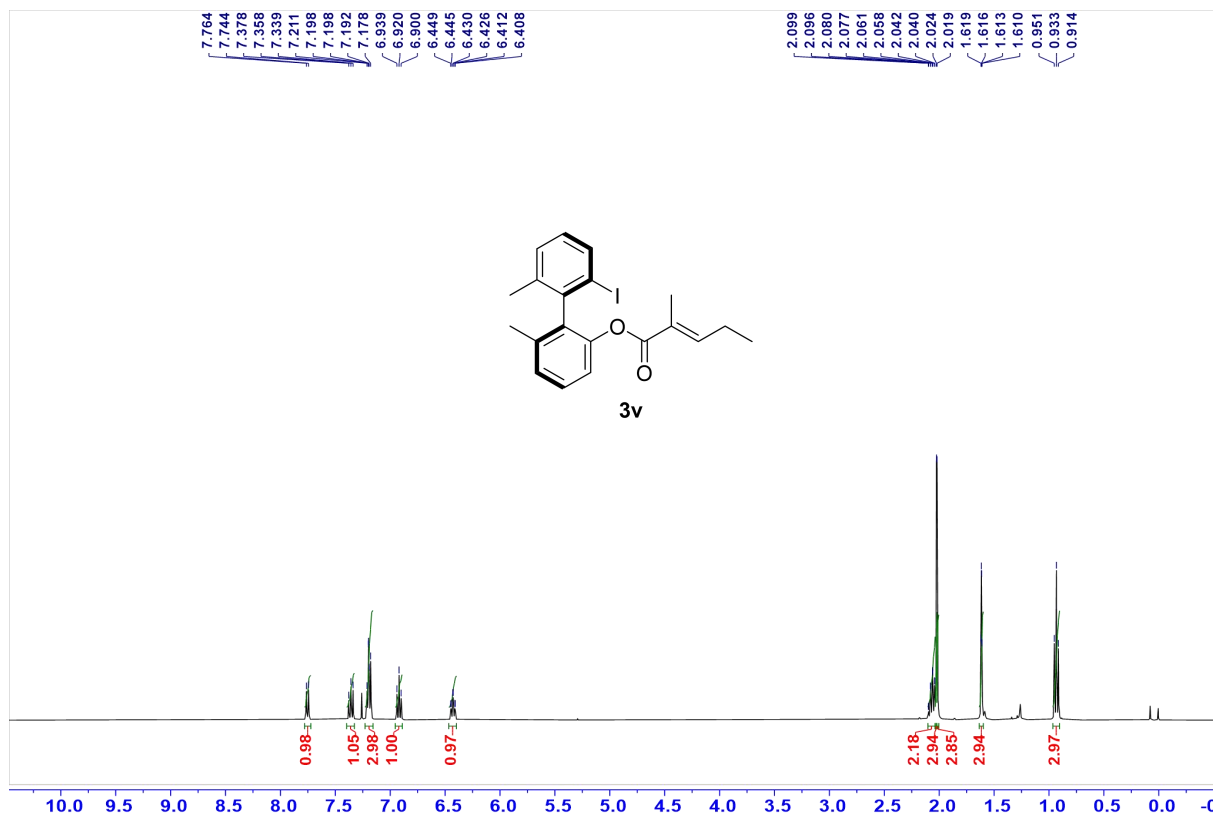
mAU



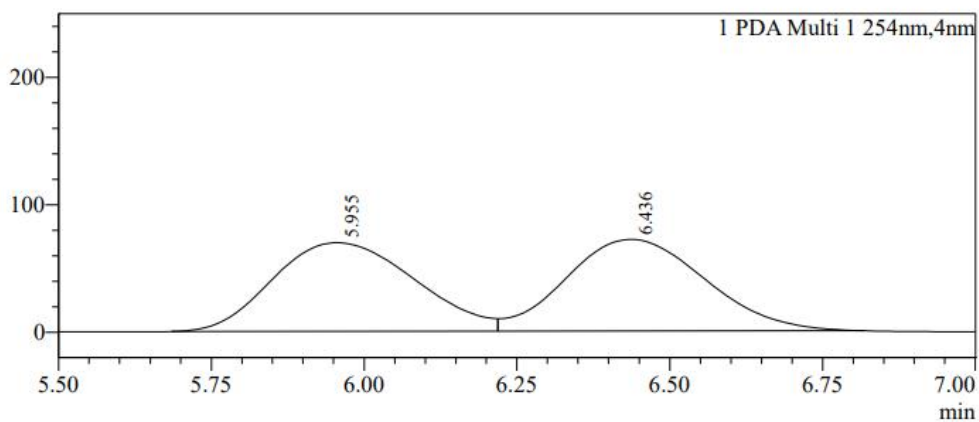
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	8.513	9.024	80794	1448784	98.887
2	10.253	10.571	924	16305	1.113
Total			81718	1465089	100.000



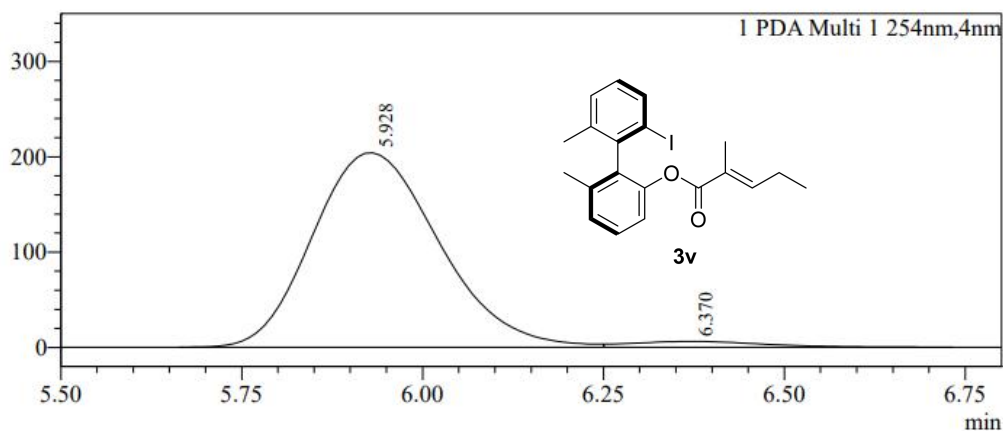
**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (*E*)-2-methylpent-2-enoate(**3v**).** Diacel Chiralpak IC, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 5.9 min,  $t_R$ (minor) = 6.4 min, e.r. = 97:3



Peak Table

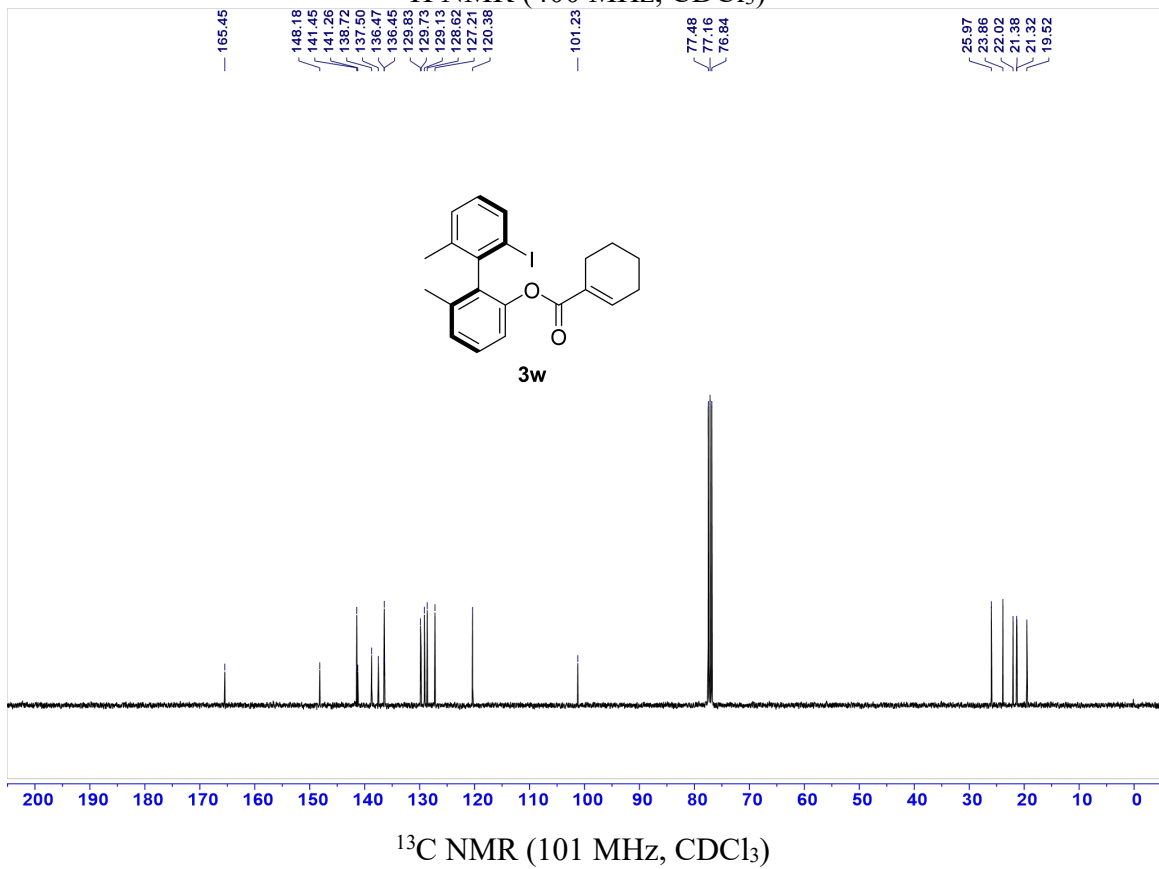
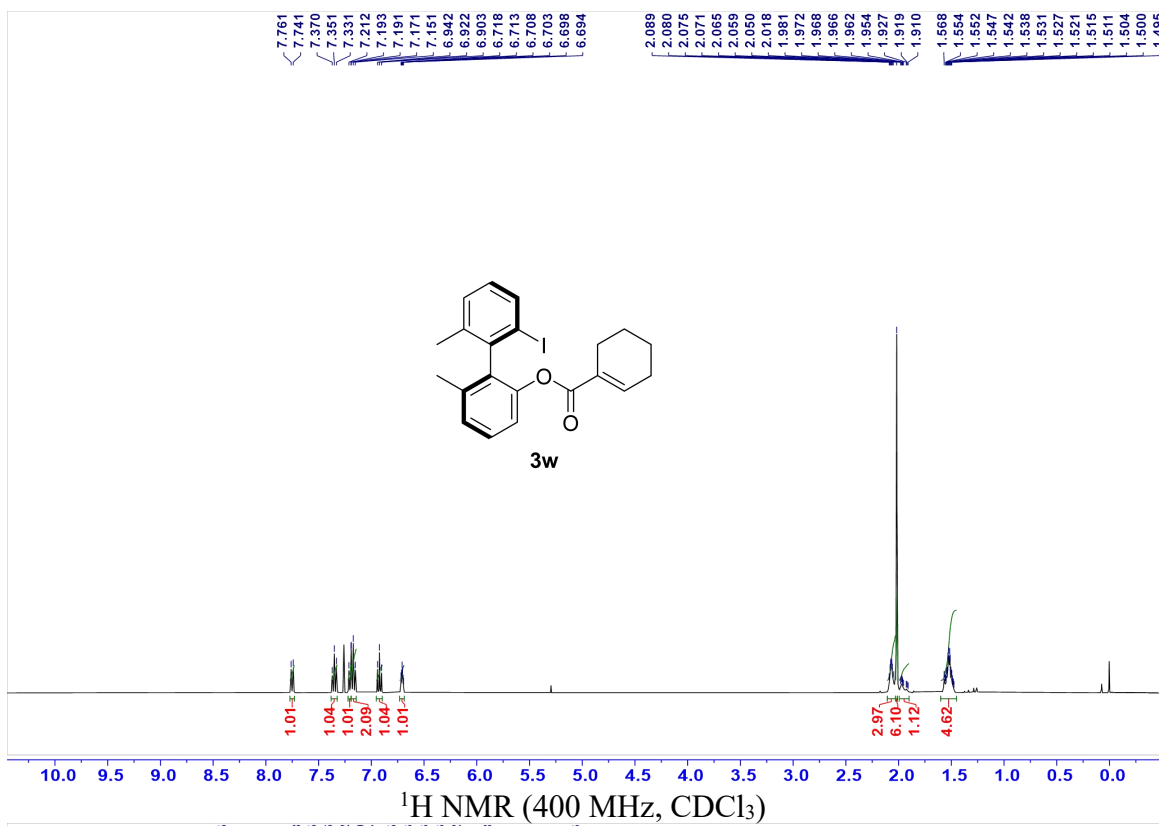
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	5.955	6.219	69603	1128831	49.735
2	6.436	6.816	71918	1140871	50.265
Total			141521	2269702	100.000

mAU

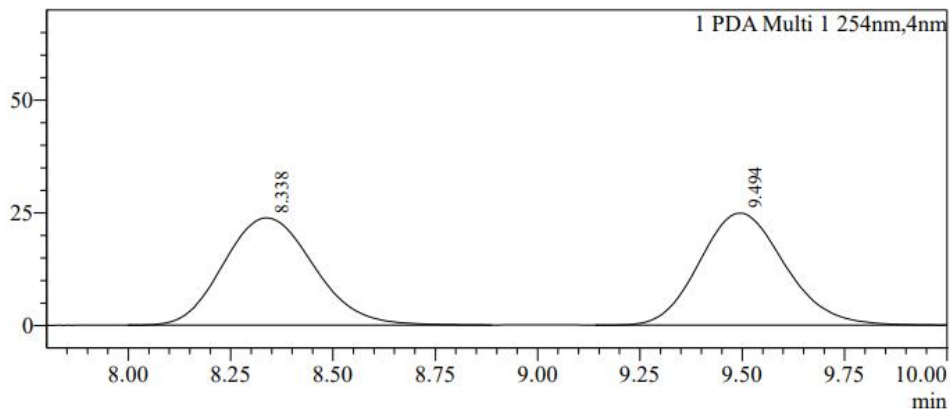


Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	5.928	6.251	203964	2480938	97.038
2	6.370	6.731	6065	75724	2.962
Total			210030	2556662	100.000



HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl cyclohex-1-ene-1-carboxylate(**3w**). Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda = 254$  nm,  $t_R(\text{major}) = 8.0$  min,  $t_R(\text{minor}) = 9.6$  min, e.r. = 98:2

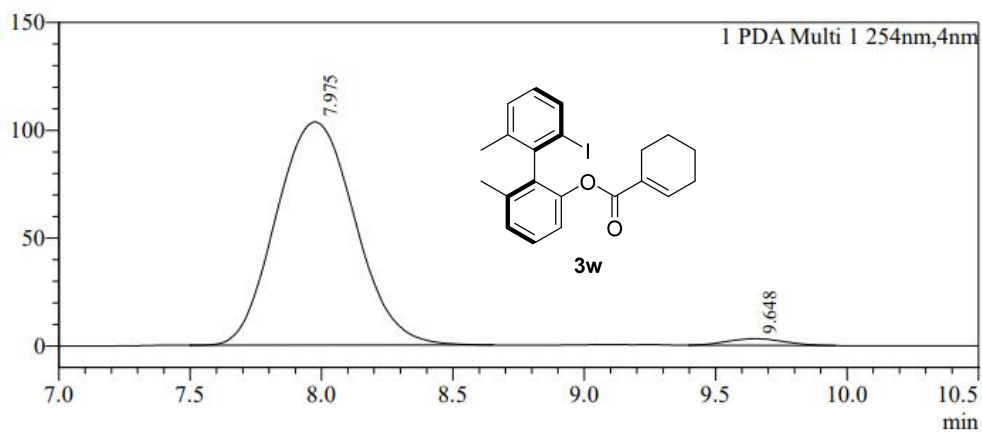


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	8.338	8.885	23800	366001	50.264
2	9.494	10.048	24873	362161	49.736
Total			48672	728162	100.000

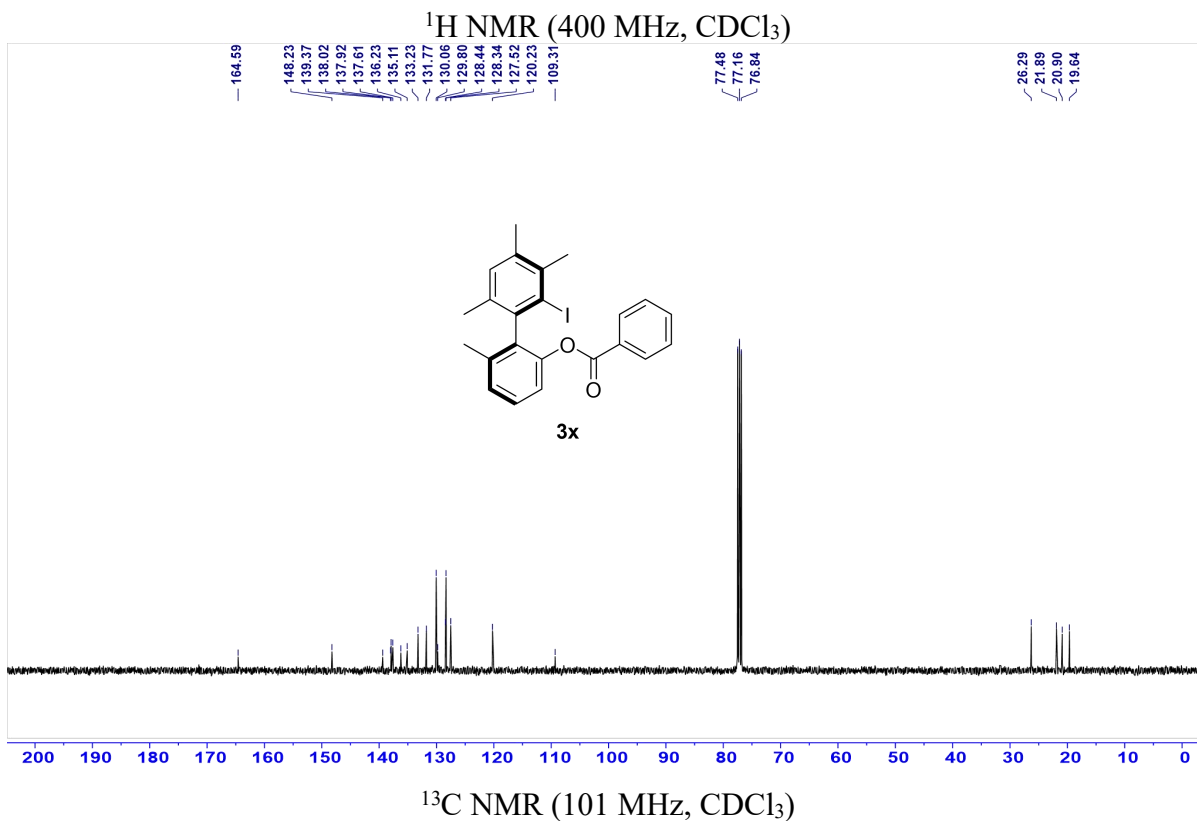
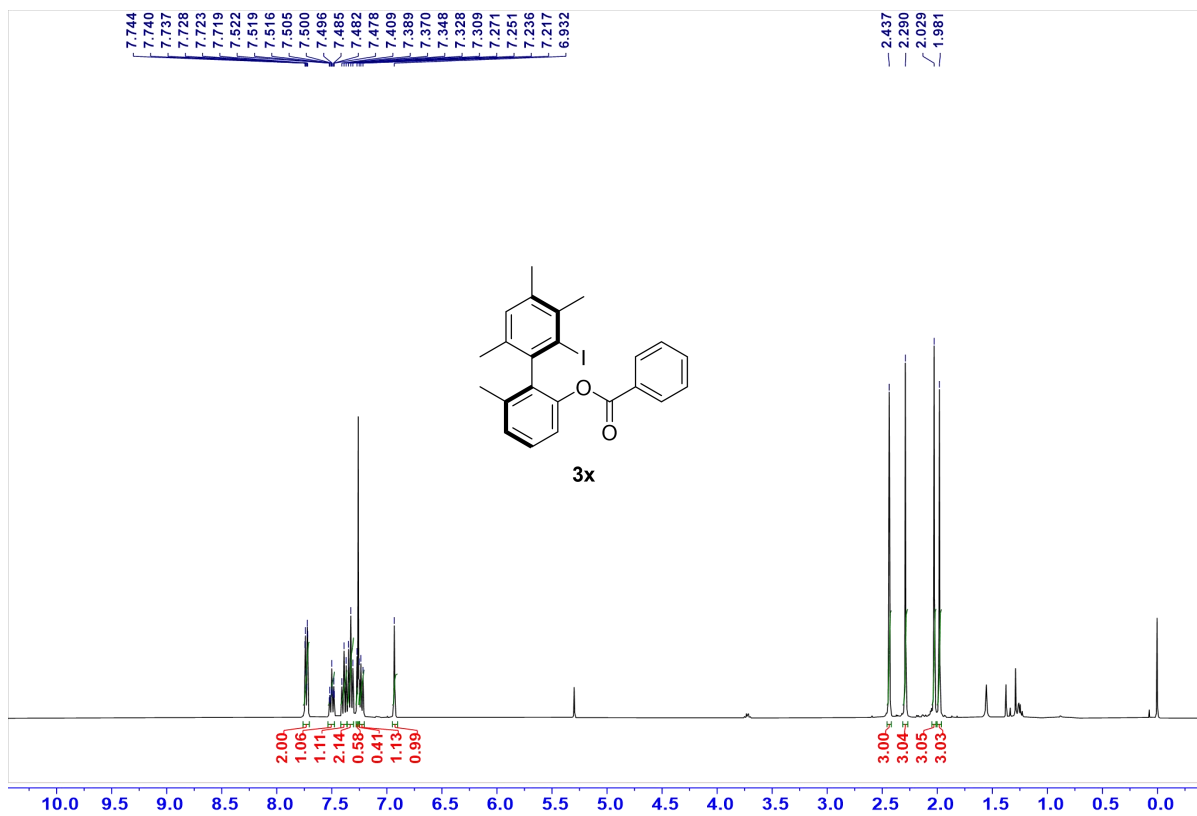
mAU



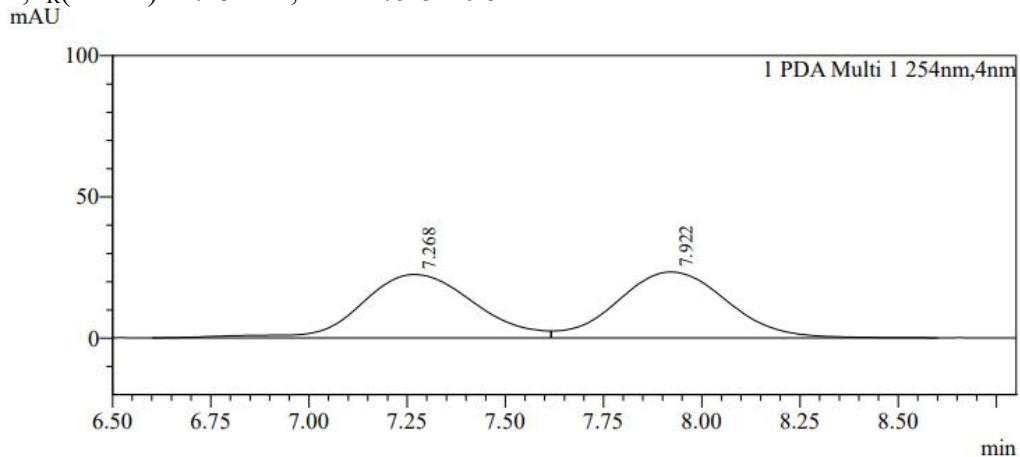
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	7.975	8.651	103507	2165606	97.905
2	9.648	9.952	3076	46351	2.095
Total			106583	2211956	100.000

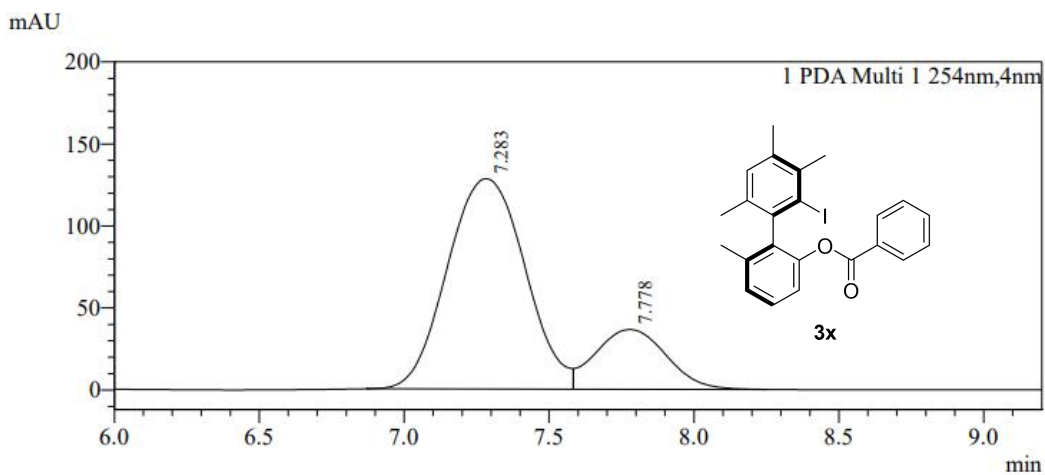


**HPLC spectra of (*R*)-2'-iodo-3',4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl benzoate(**3x**).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 7.3 min,  $t_R$ (minor) = 7.8 min, e.r. = 79.5:20.5



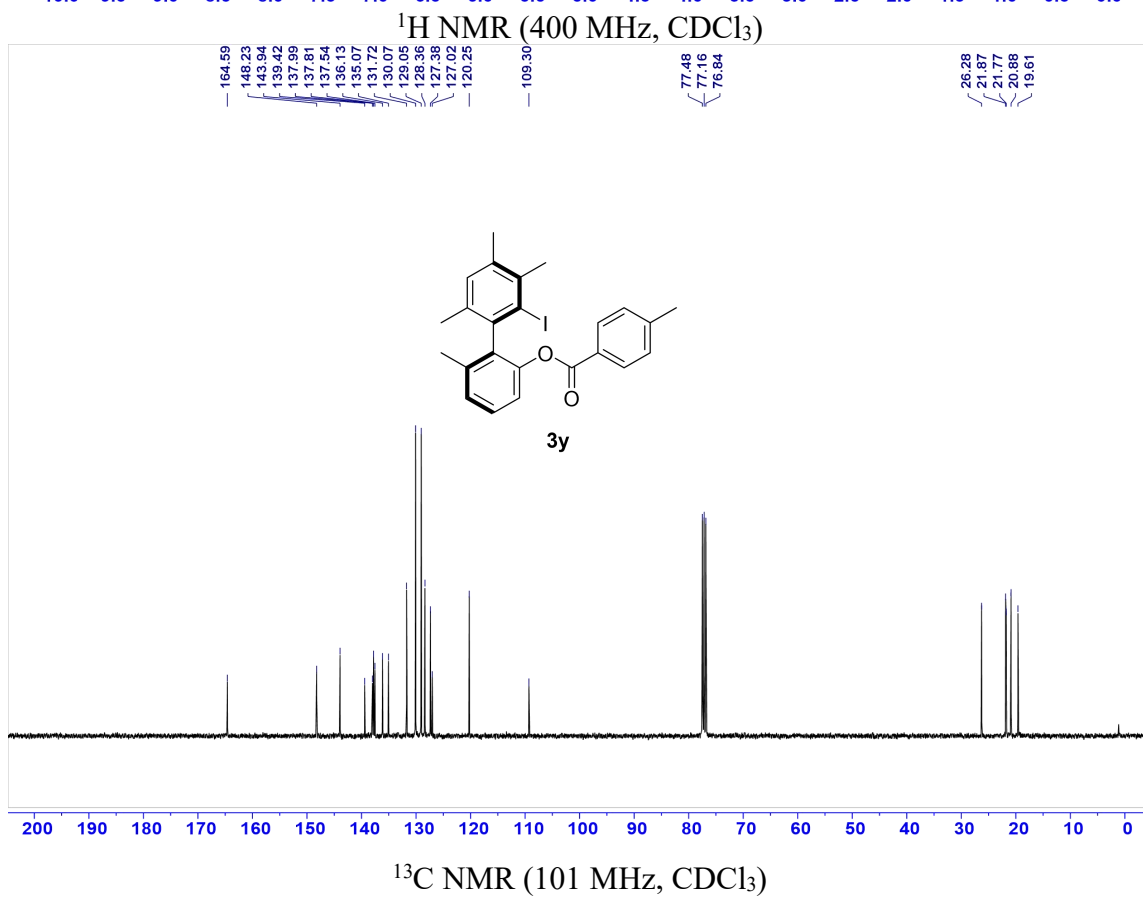
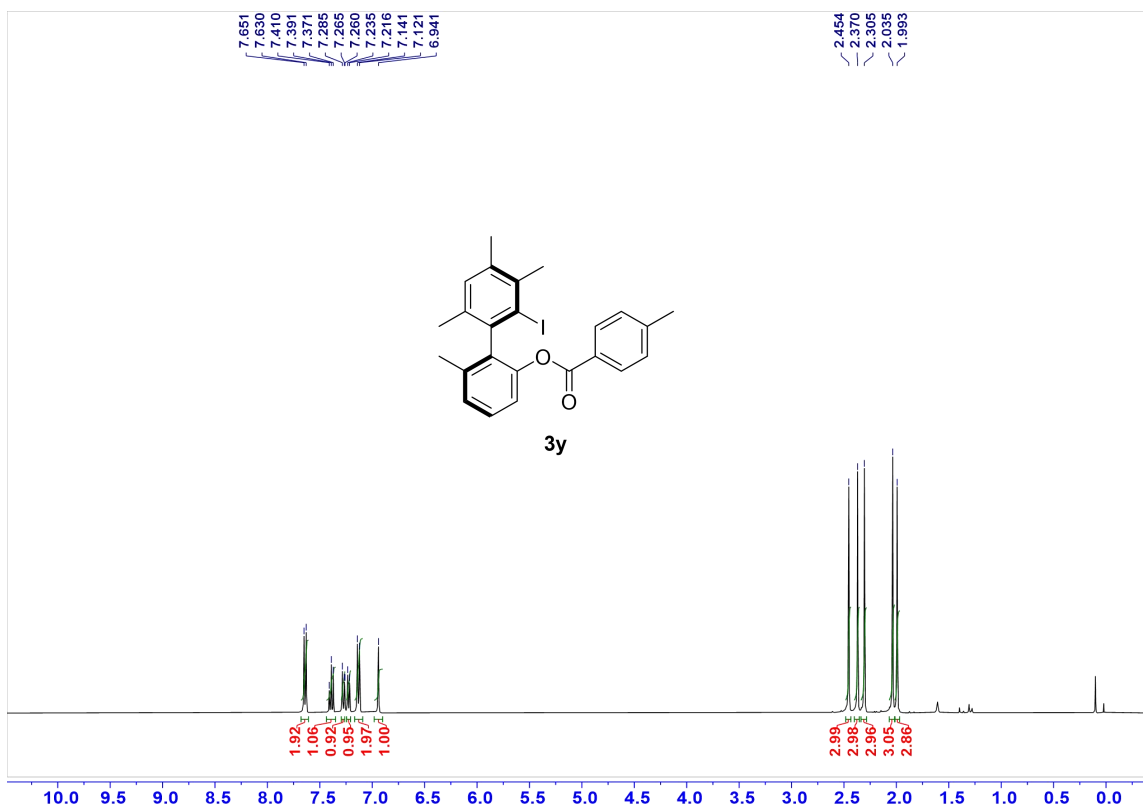
Peak Table

PDA Ch1 254nm					
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	7.268	7.616	22395	448503	49.786
2	7.922	8.597	23304	452353	50.214
Total			45699	900856	100.000

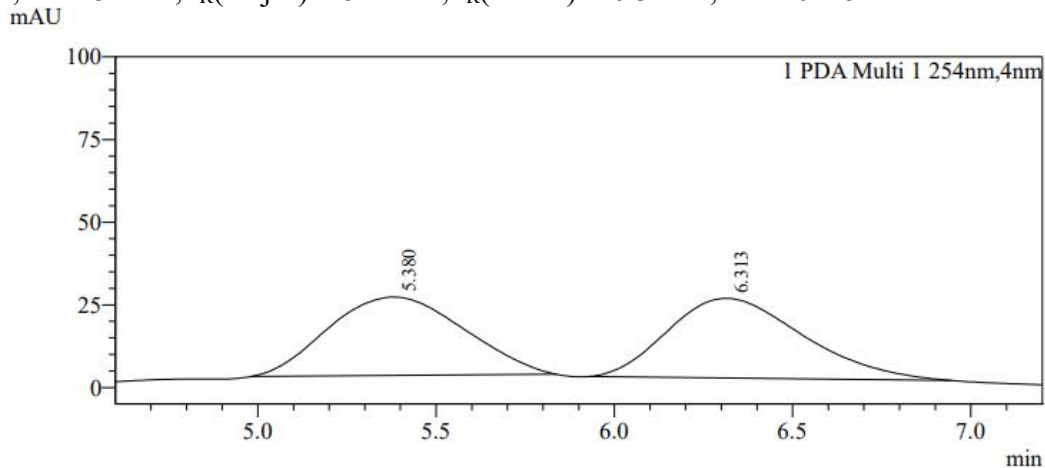


Peak Table

PDA Ch1 254nm					
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	7.283	7.584	128187	2391293	79.569
2	7.778	8.245	36405	614022	20.431
Total			164592	3005315	100.000

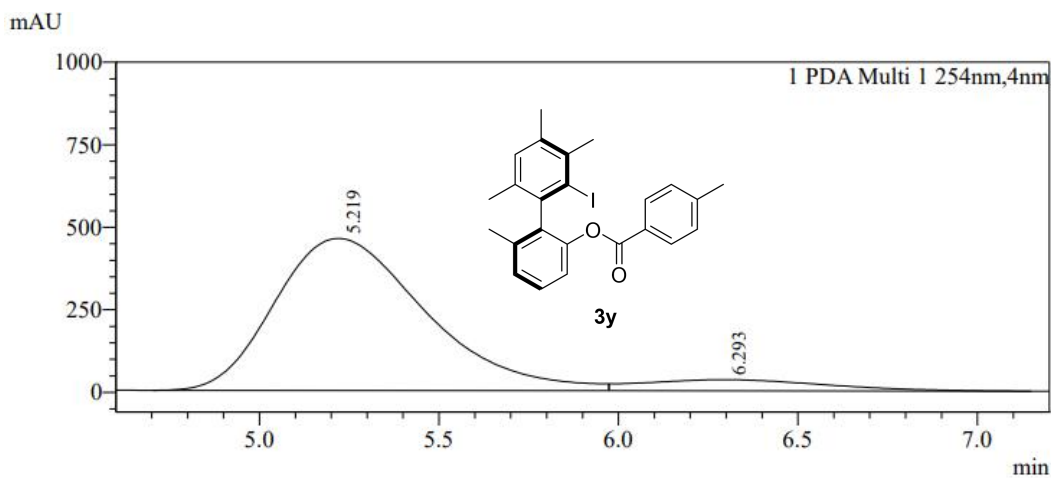


HPLC spectra of (*R*)-2'-iodo-3',4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl 4-methylbenzoate(**3y**). Diacel Chiralcel OJ-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 5.2 min,  $t_R$ (minor) = 6.3 min, e.r. = 92:8



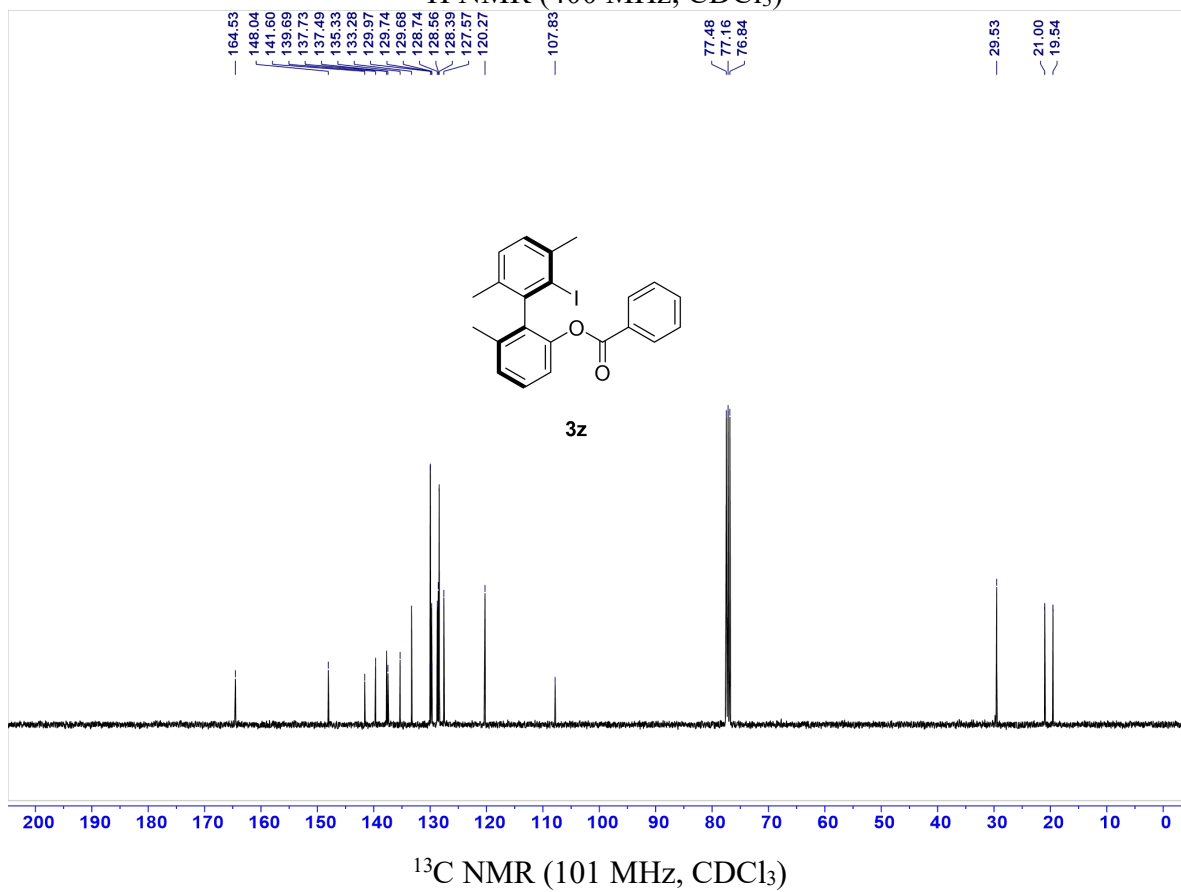
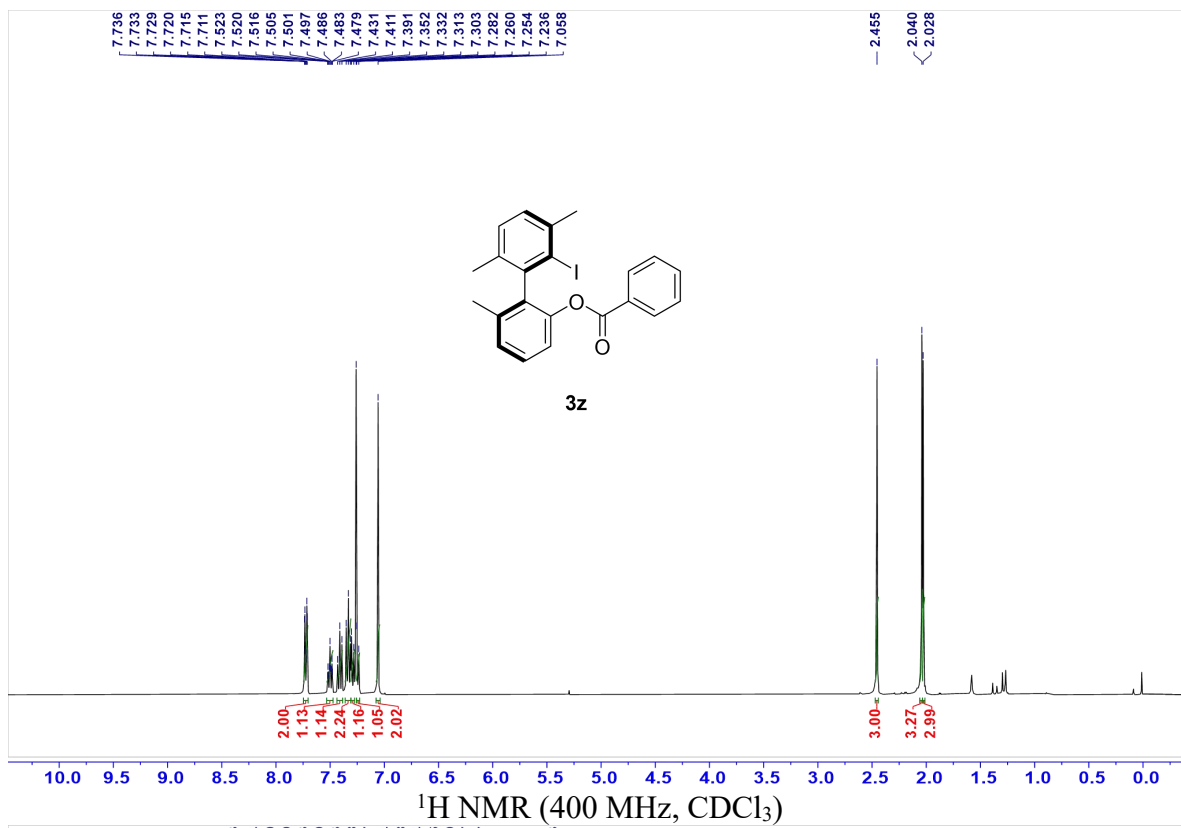
Peak Table

PDA Ch1 254nm					
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	5.380	5.835	23678	625898	49.586
2	6.313	6.944	24113	636337	50.414
Total			47791	1262235	100.000

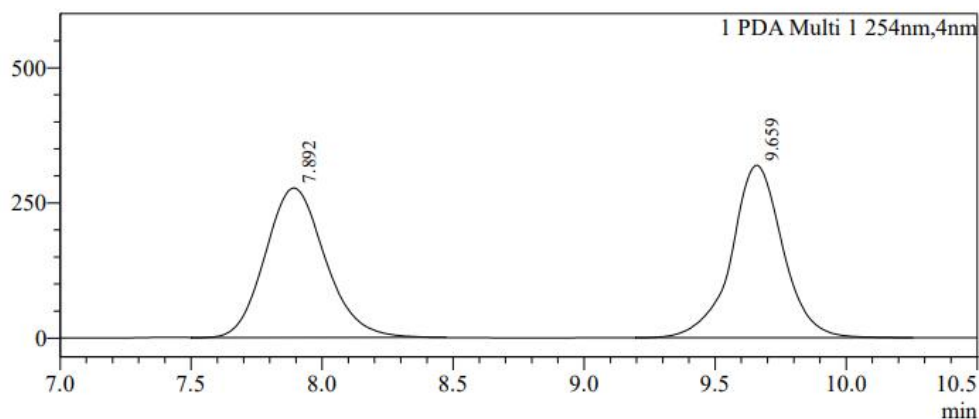


Peak Table

PDA Ch1 254nm					
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	5.219	5.973	460707	13494961	91.793
2	6.293	7.147	33953	1206595	8.207
Total			494659	14701556	100.000



**HPLC spectra of (*R*)-2'-iodo-3',6,6'-trimethyl-[1,1'-biphenyl]-2-yl benzoate(3z).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 7.9 min,  $t_R$ (minor) = 8.9 min, e.r. = 91:9

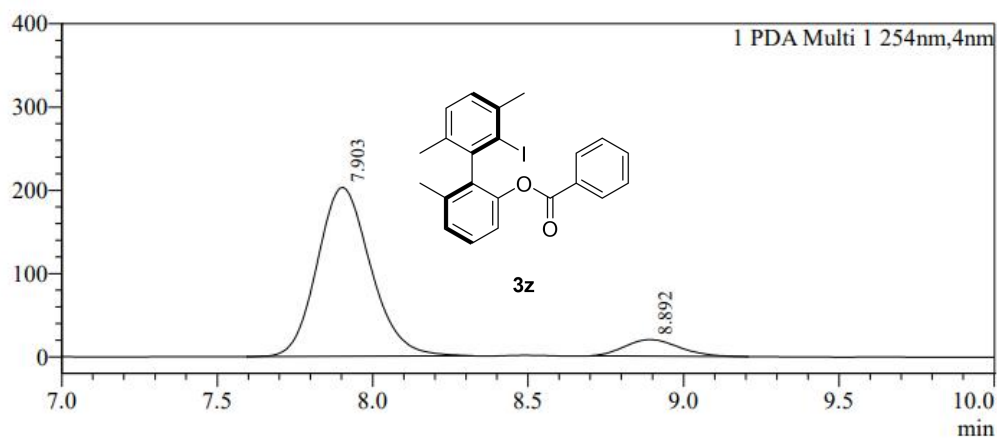


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	7.892	8.469	276774	4409727	50.279
2	9.659	10.251	318617	4360827	49.721
Total			595391	8770554	100.000

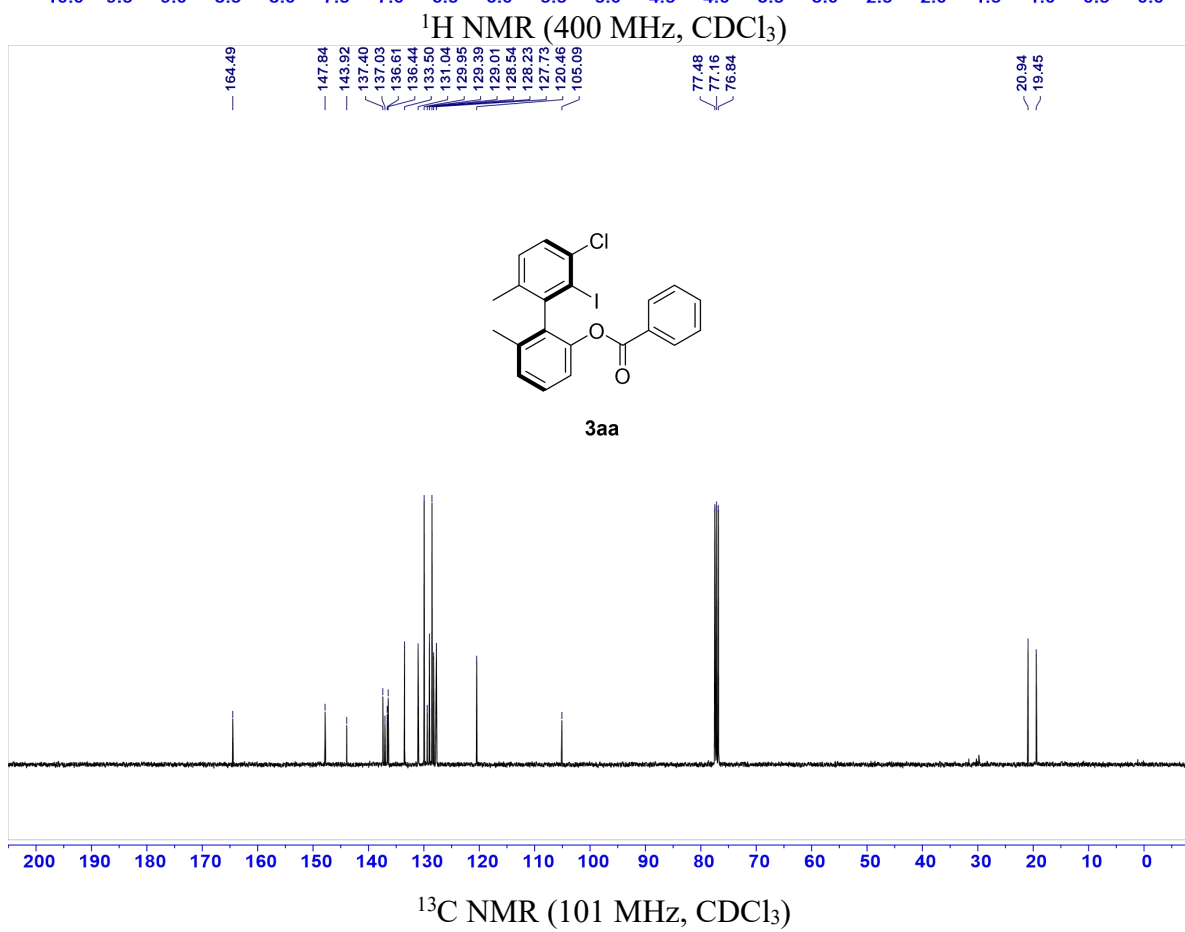
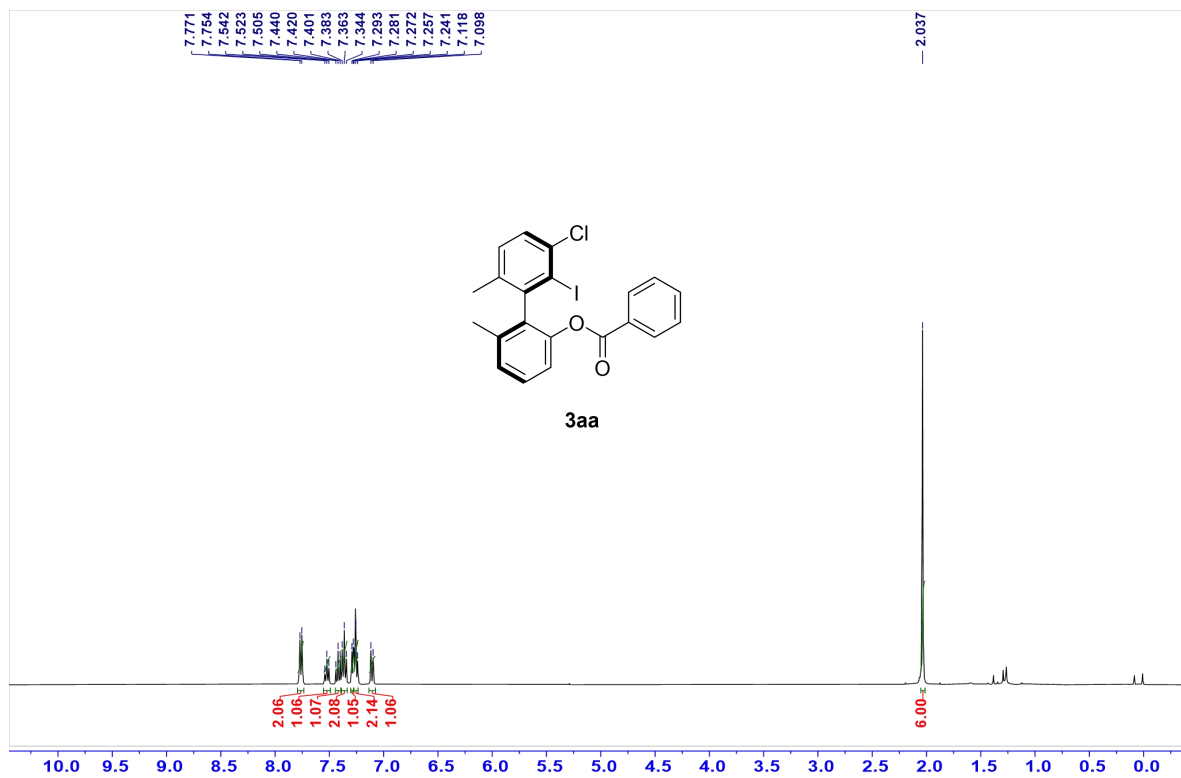
mAU



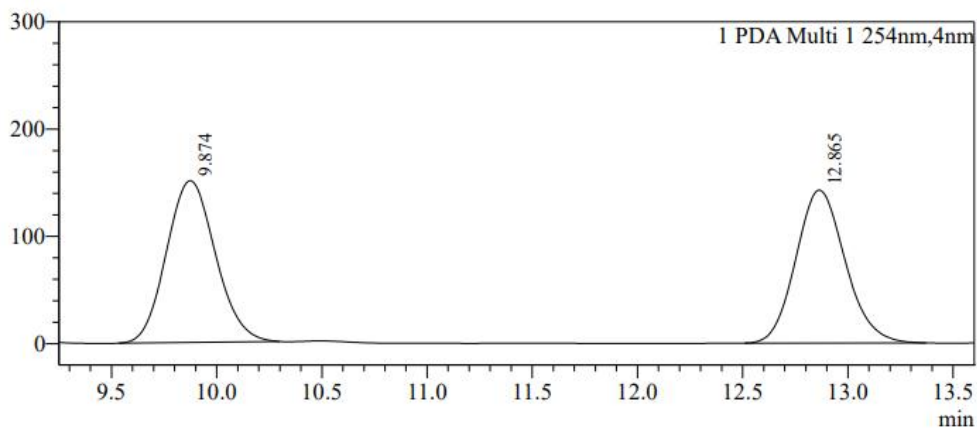
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	7.903	8.320	202998	2427428	91.016
2	8.892	9.205	19837	239619	8.984
Total			222835	2667047	100.000



**HPLC spectra of (*R*)-3'-chloro-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl benzoate(3aa).**  
 Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  
 $t_{R}(\text{major}) = 9.7$  min,  $t_{R}(\text{minor}) = 12.5$  min, e.r. = 91.5:8.5

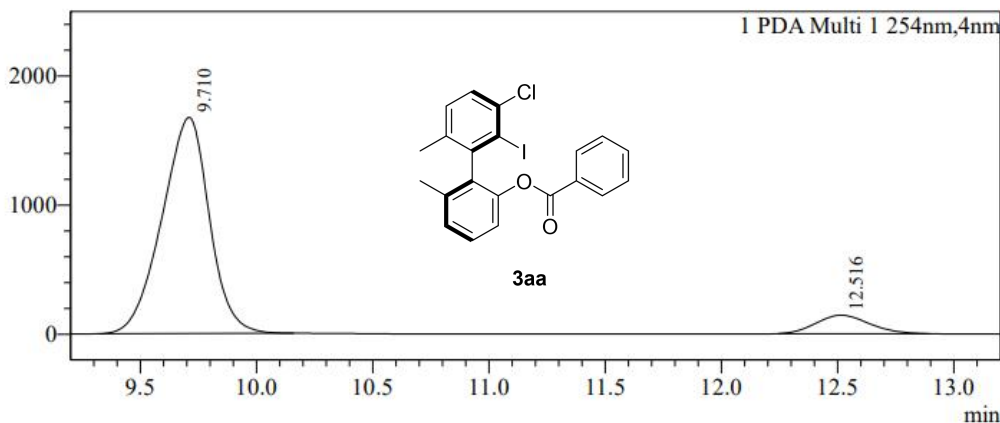


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	9.874	10.293	150795	2441165	51.224
2	12.865	13.365	142623	2324463	48.776
Total			293419	4765628	100.000

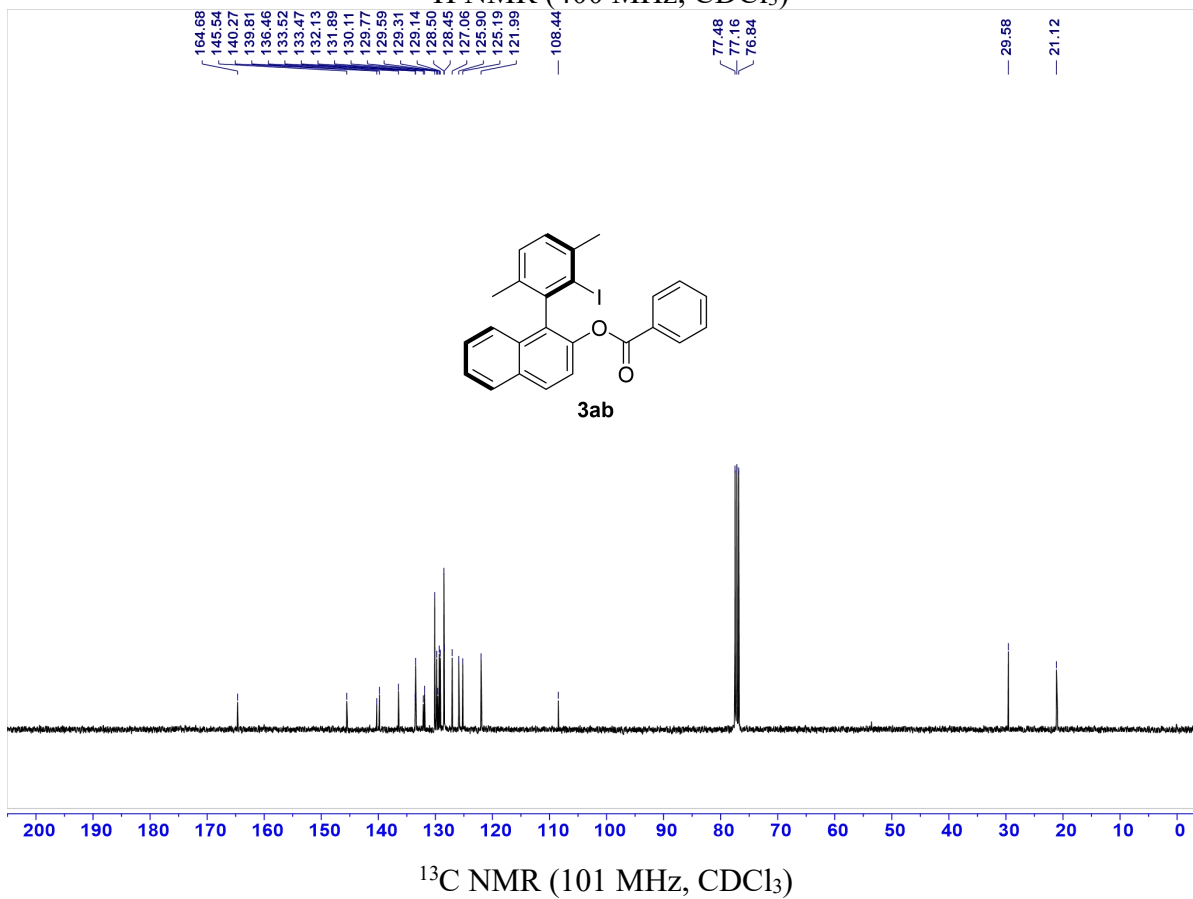
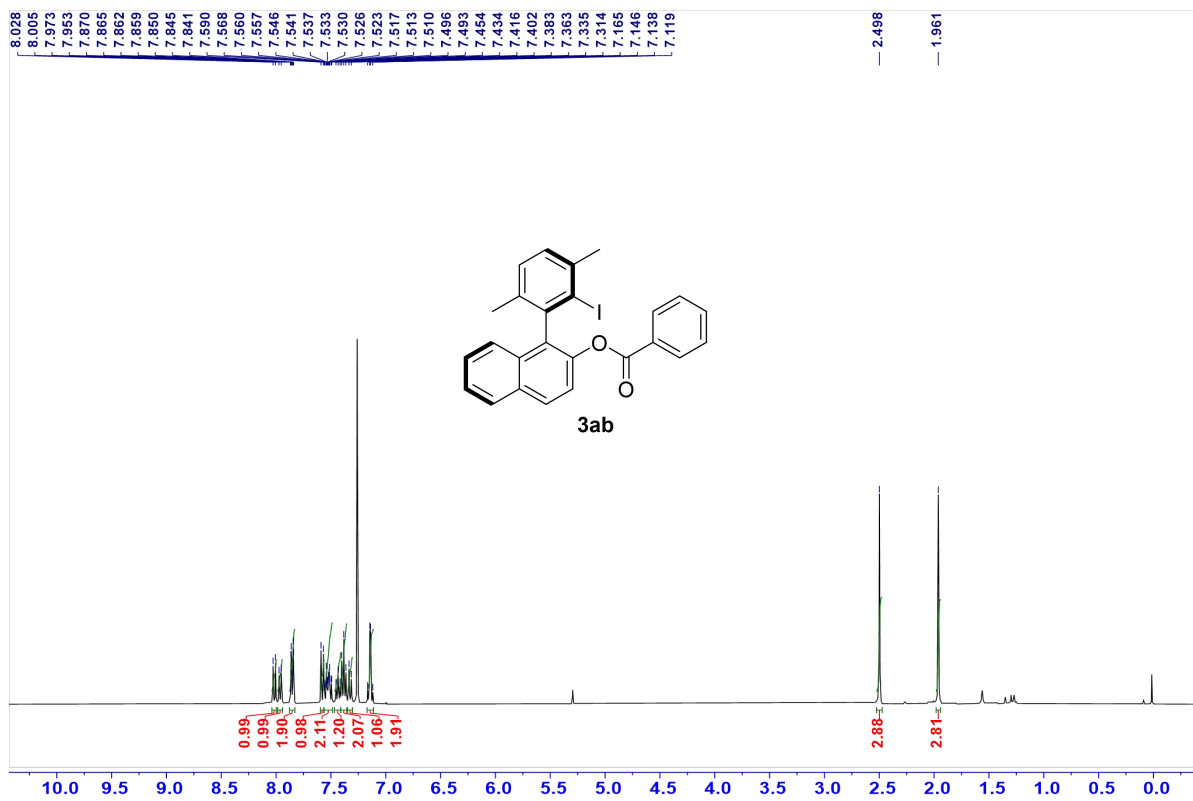
mAU



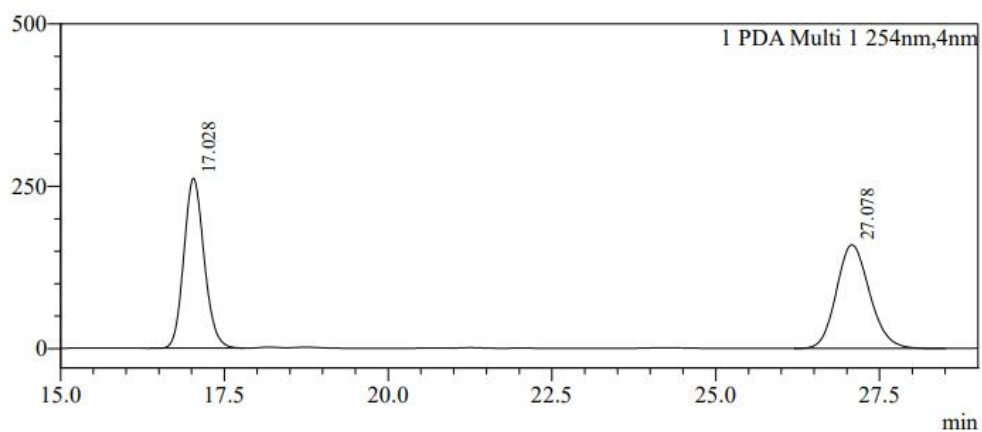
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	9.710	10.155	1675144	23804207	91.263
2	12.516	12.896	142775	2278825	8.737
Total			1817919	26083031	100.000



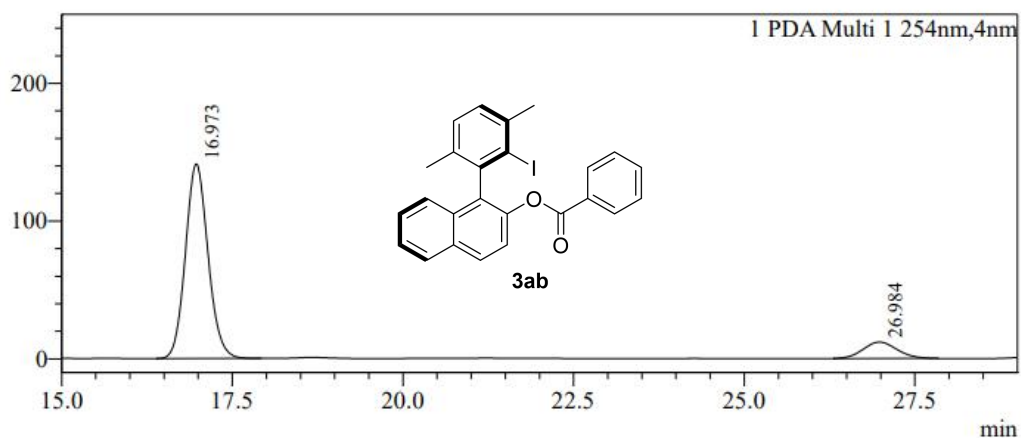
**HPLC spectra of (*R*)-1-(2-iodo-3,6-dimethylphenyl)naphthalen-2-yl benzoate(3ab).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 17.0 min,  $t_R$ (minor) = 27.0 min, e.r. = 88.5:11.5



Peak Table

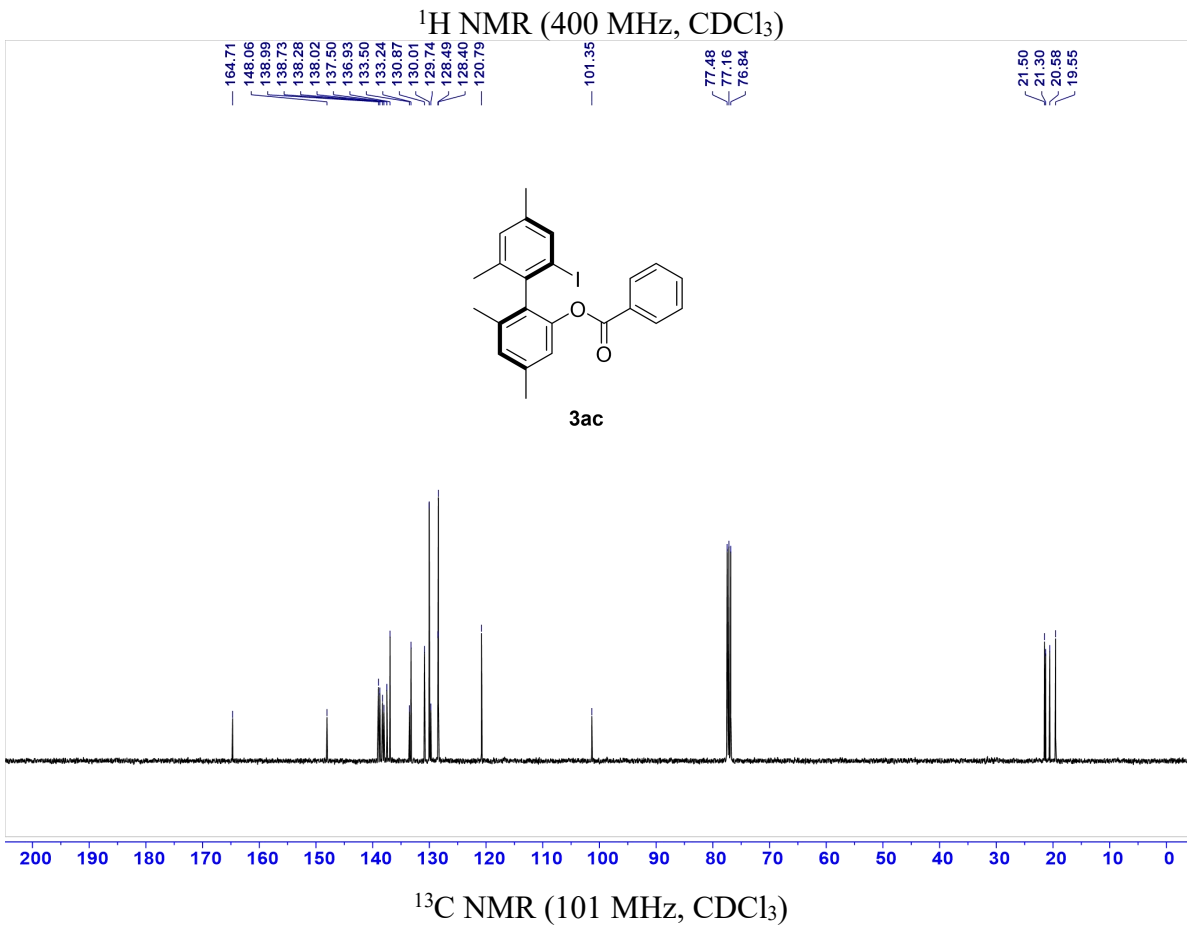
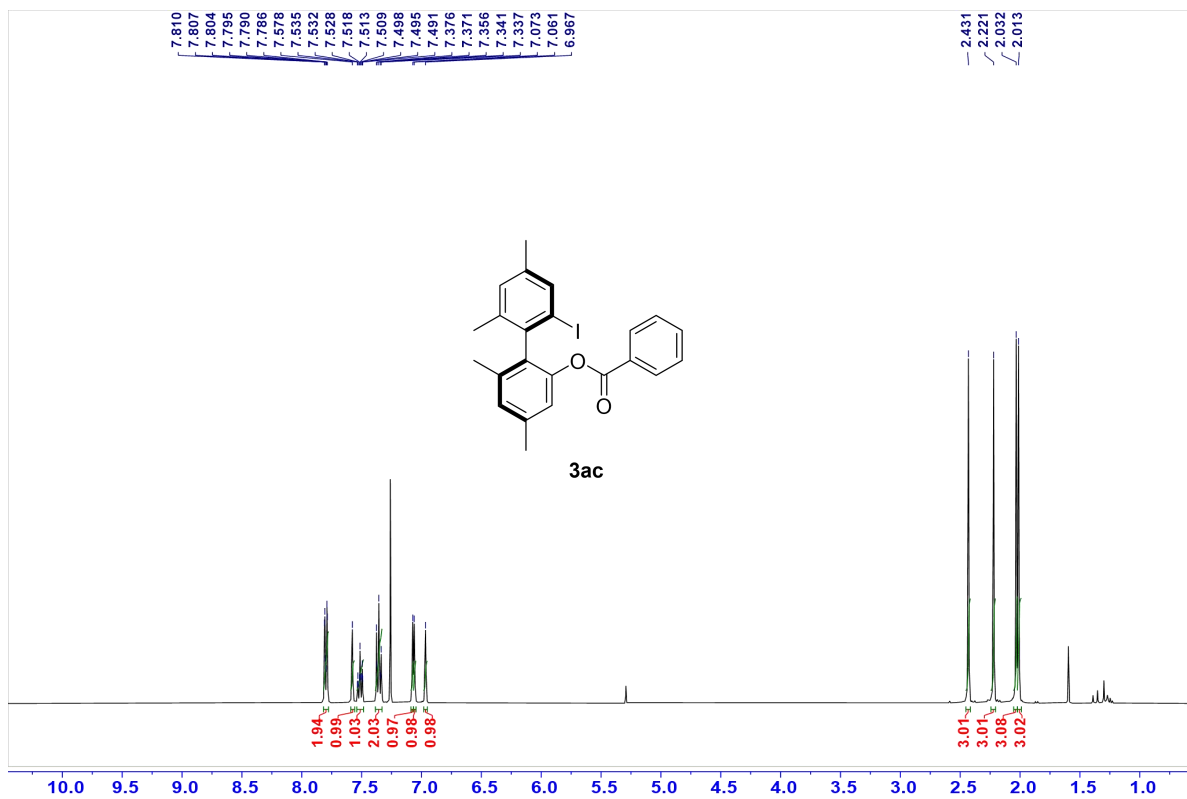
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	17.028	17.792	261770	5642050	50.037
2	27.078	28.491	159423	5633688	49.963
Total			421193	11275738	100.000

mAU



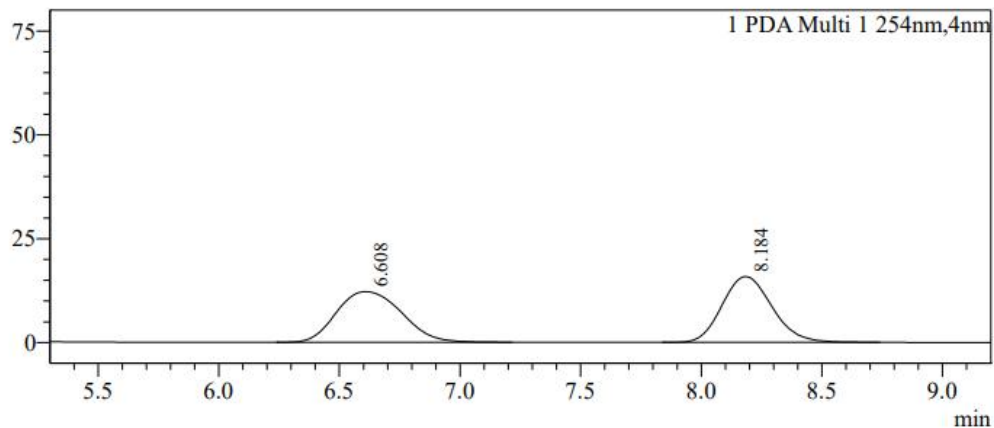
Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	16.973	17.909	141320	3256452	88.751
2	26.984	27.829	11905	412732	11.249
Total			153225	3669184	100.000



**HPLC spectra of (*R*)-2'-iodo-4,4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl benzoate(3ac).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 6.6 min,  $t_R$ (minor) = 8.6 min, e.r. = 98:2

mAU

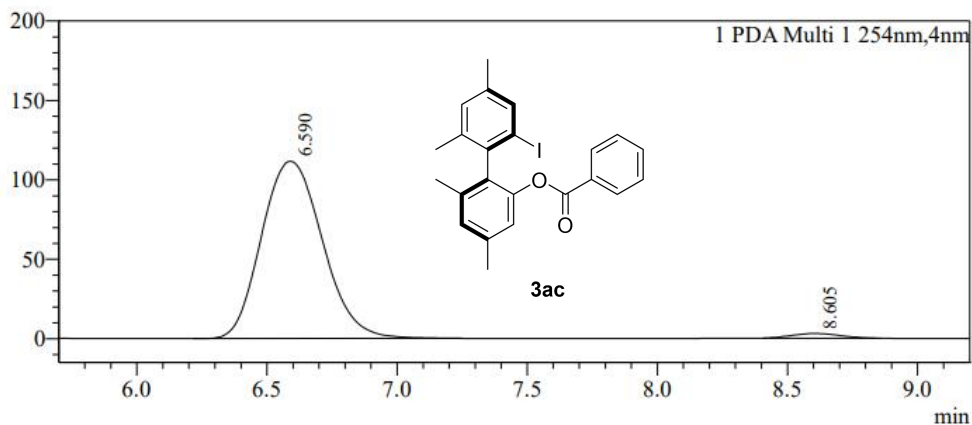


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	6.608	7.211	12206	229235	50.088
2	8.184	8.736	15850	228432	49.912
Total			28055	457667	100.000

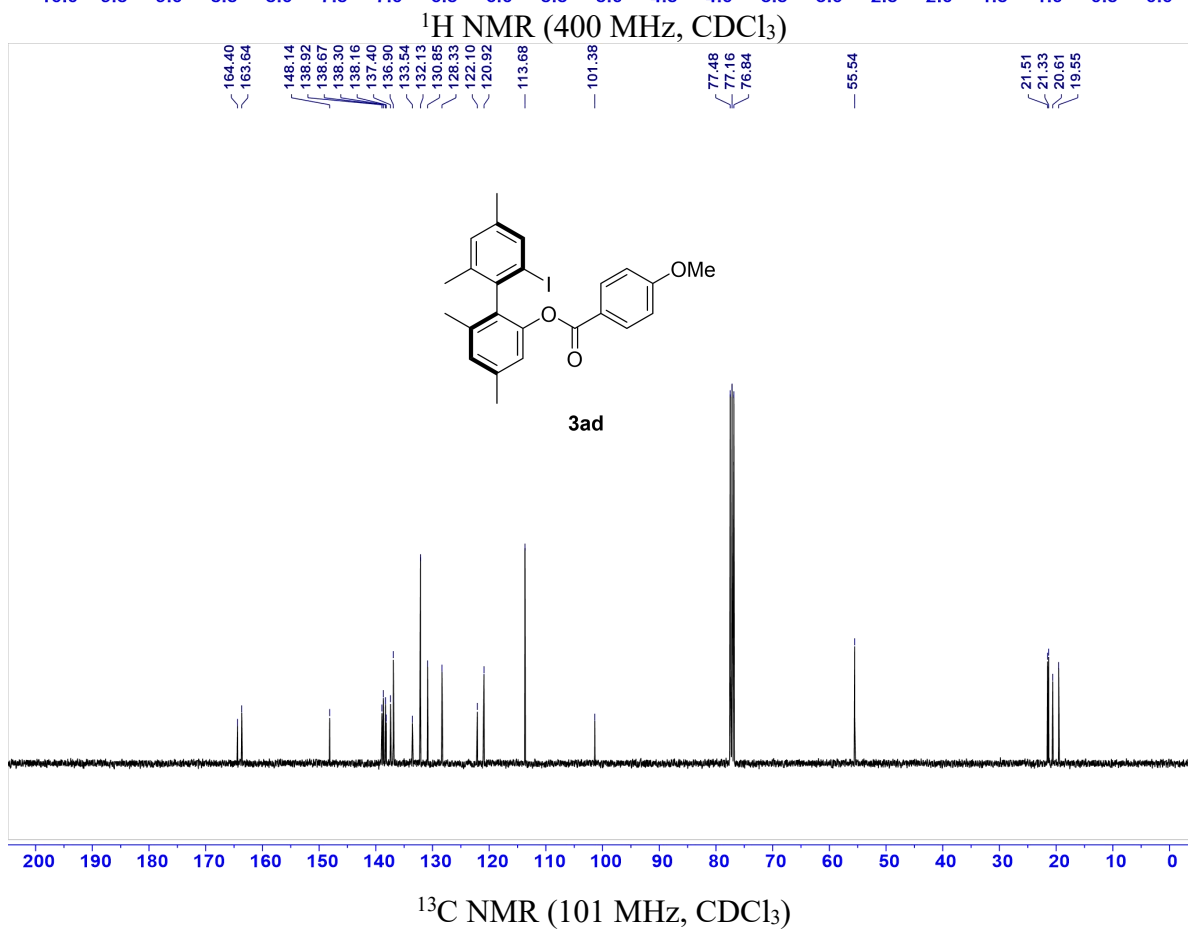
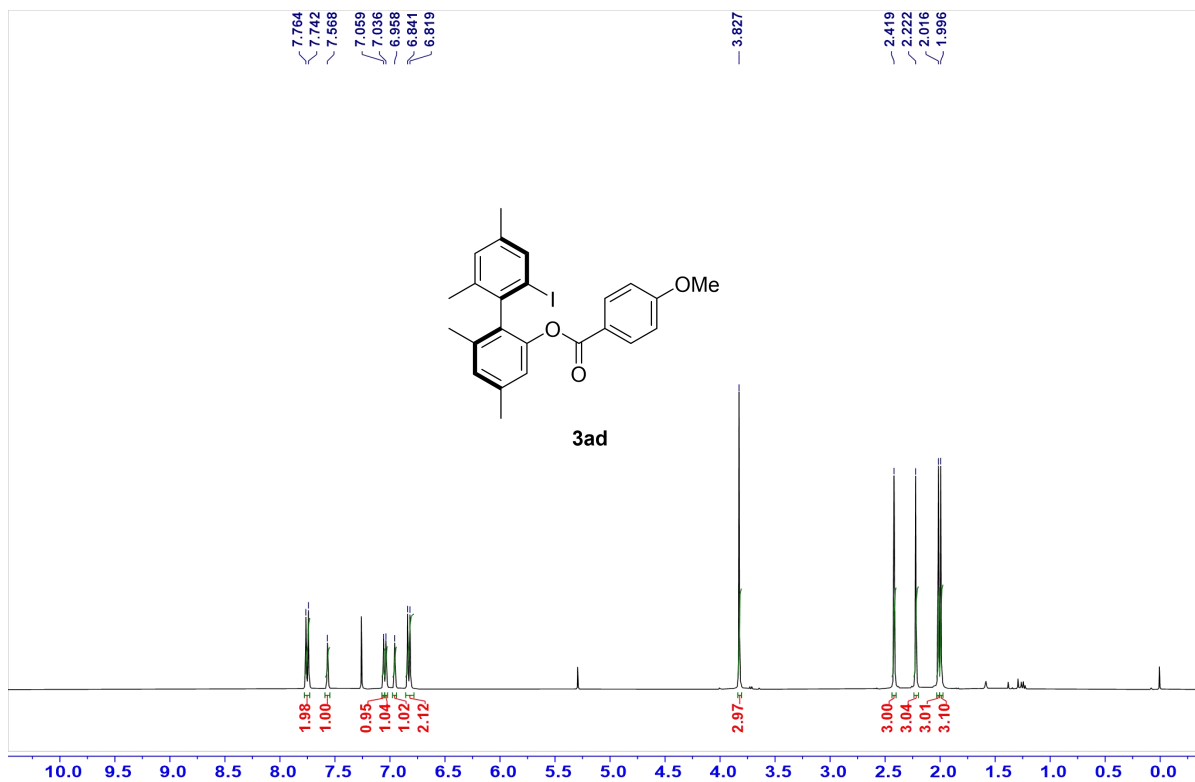
mAU



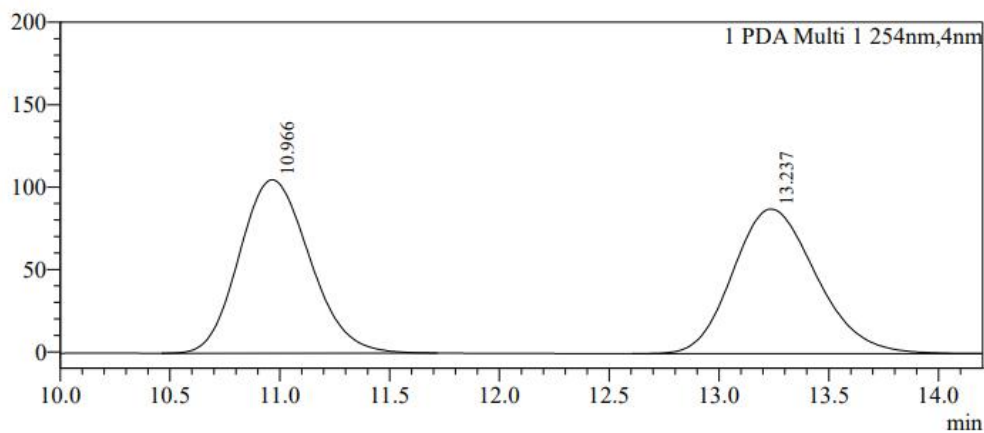
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	6.590	7.243	111626	1820508	97.971
2	8.605	8.853	2965	37699	2.029
Total			114591	1858208	100.000

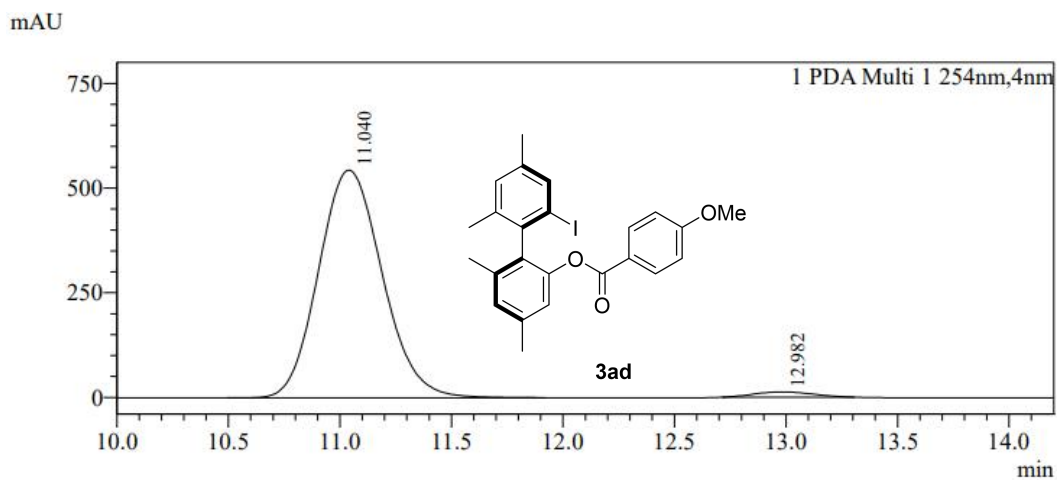


HPLC spectra of (*R*)-2'-iodo-4,4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl 4-methoxybenzoate (**3ad**). Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda = 254$  nm,  $t_R(\text{major}) = 11.0$  min,  $t_R(\text{minor}) = 13.0$  min, e.r. = 98:2



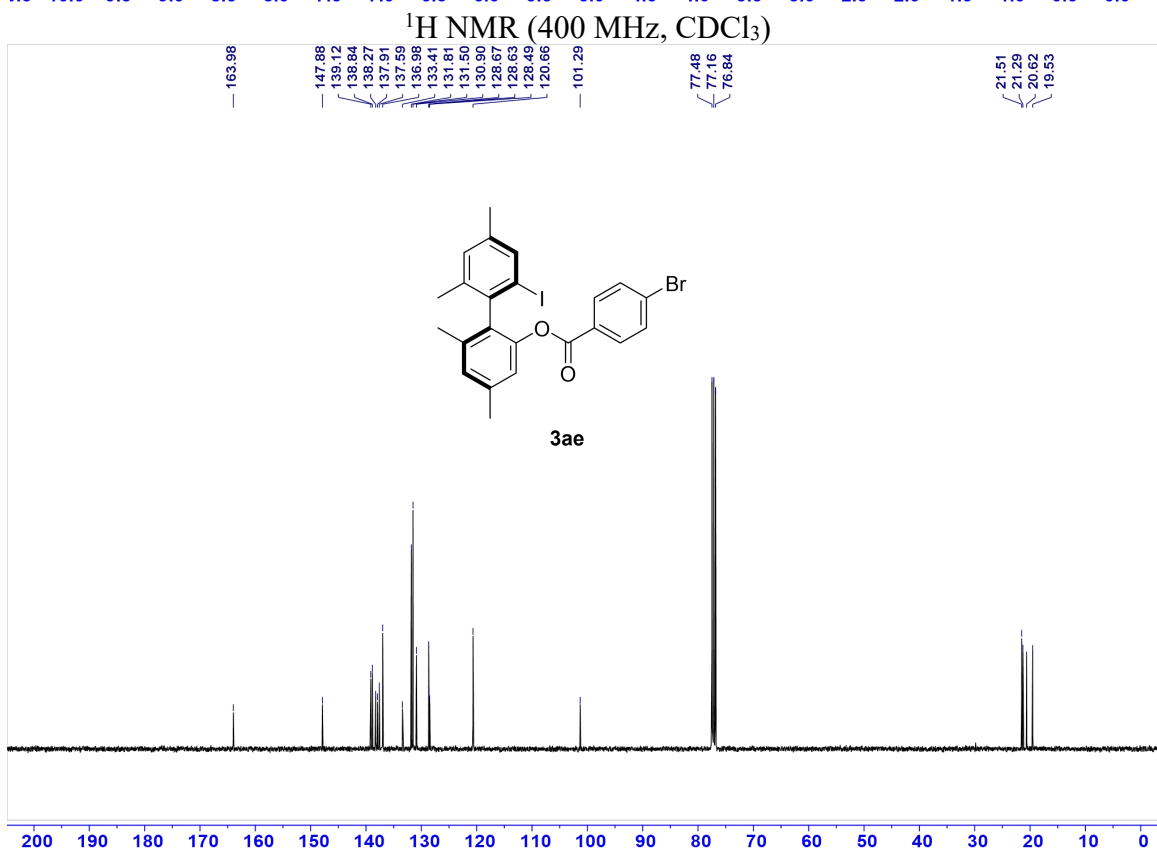
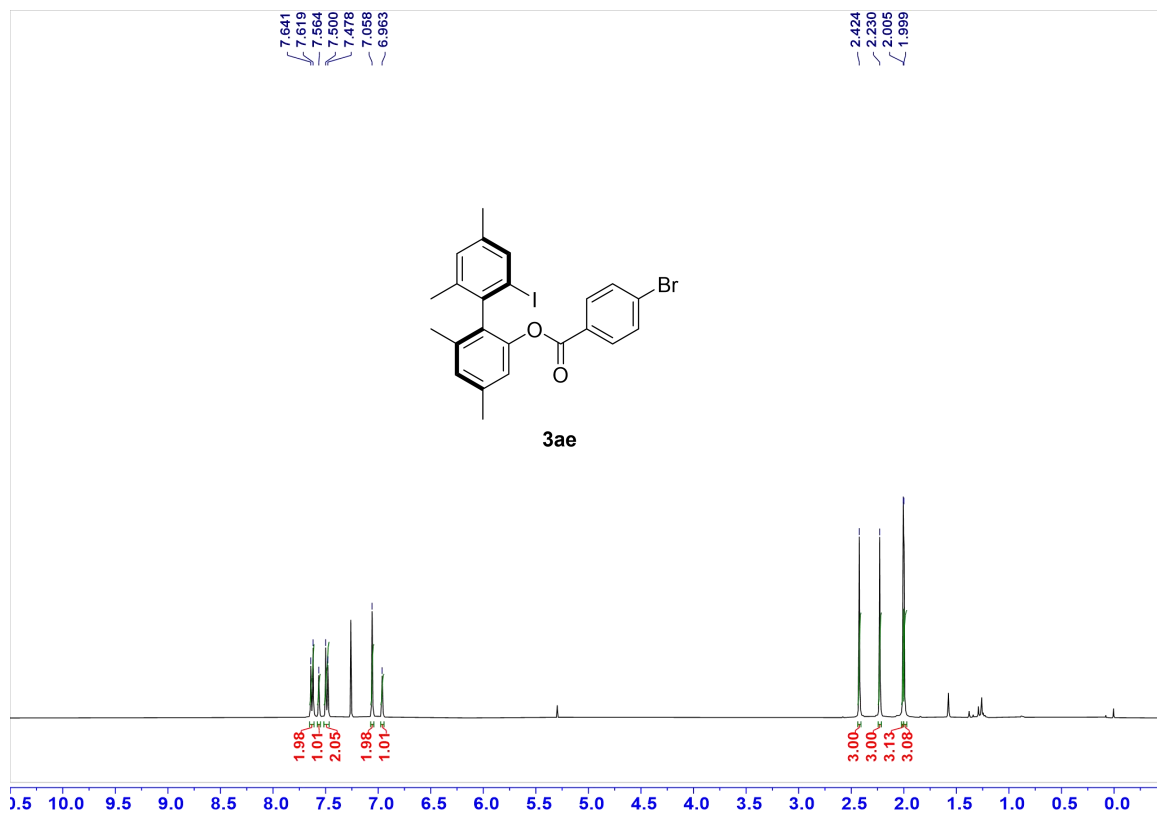
Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	10.966	11.712	105249	2351464	50.292
2	13.237	14.272	87756	2324169	49.708
Total			193005	4675634	100.000

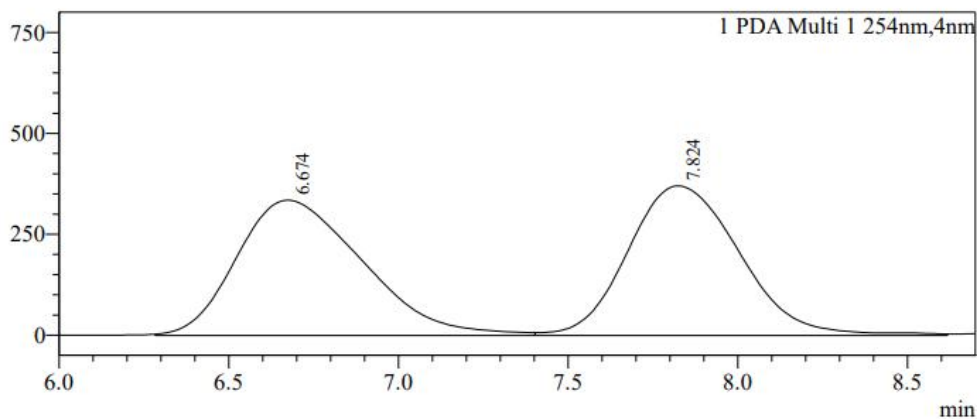


Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	11.040	11.915	544066	10802958	97.935
2	12.982	13.301	12664	227802	2.065
Total			556731	11030761	100.000



**HPLC spectra of (*R*)-2'-iodo-4,4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl 4-bromobenzoate(3ae).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 6.8 min,  $t_R$ (minor) = 7.7 min, e.r. = 97:3

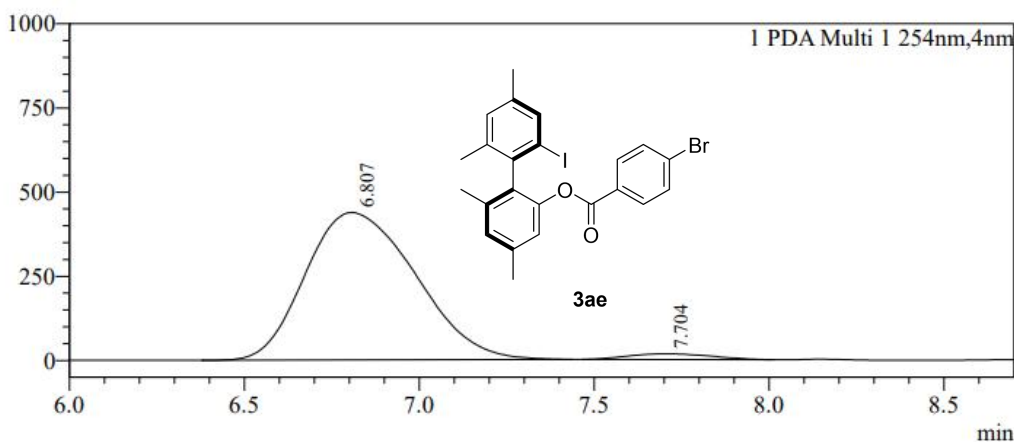


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	6.674	7.403	334961	8643110	50.387
2	7.824	8.619	370360	8510396	49.613
Total			705321	17153506	100.000

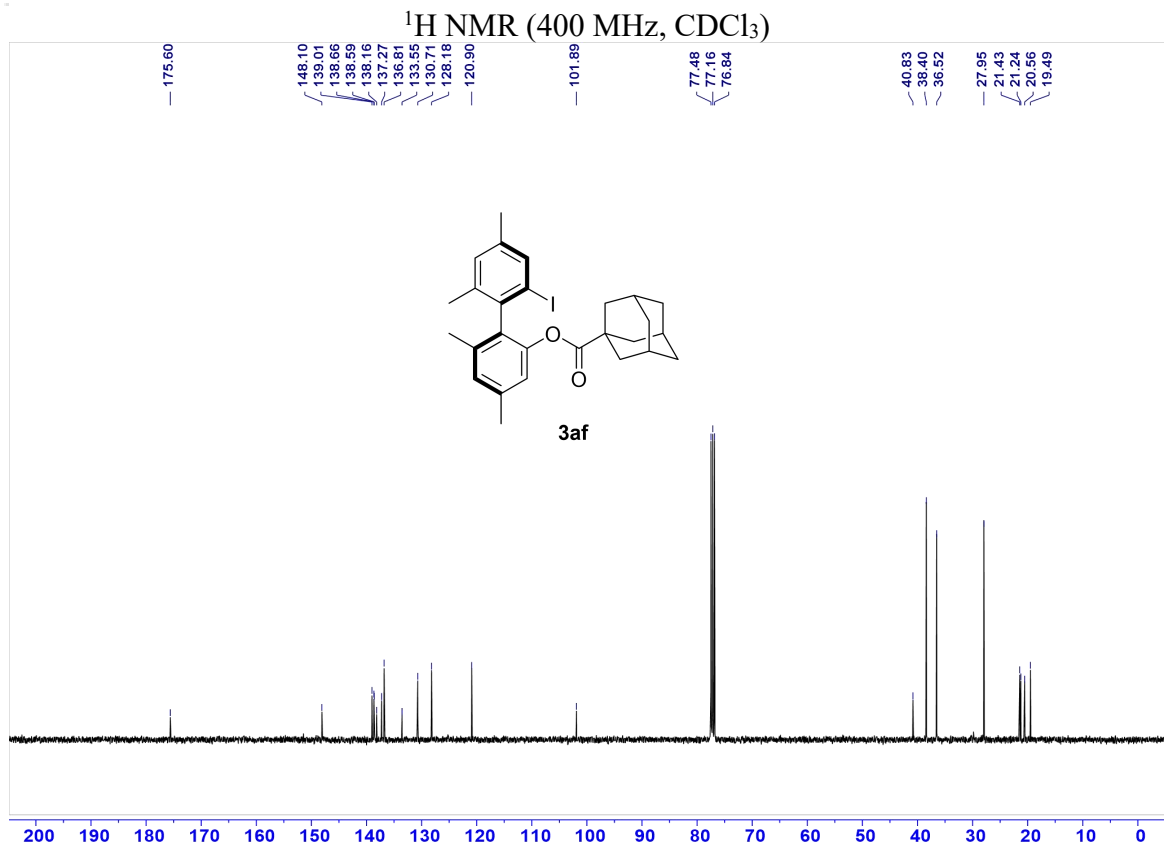
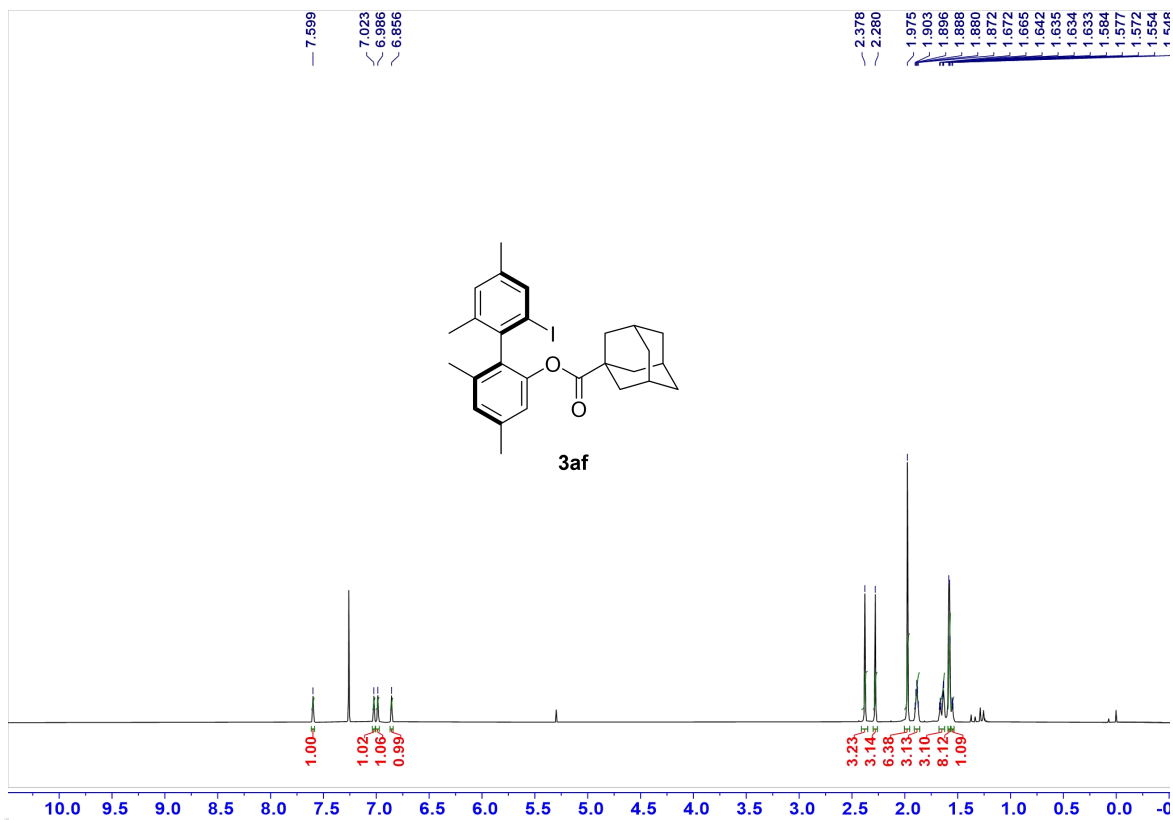
mAU



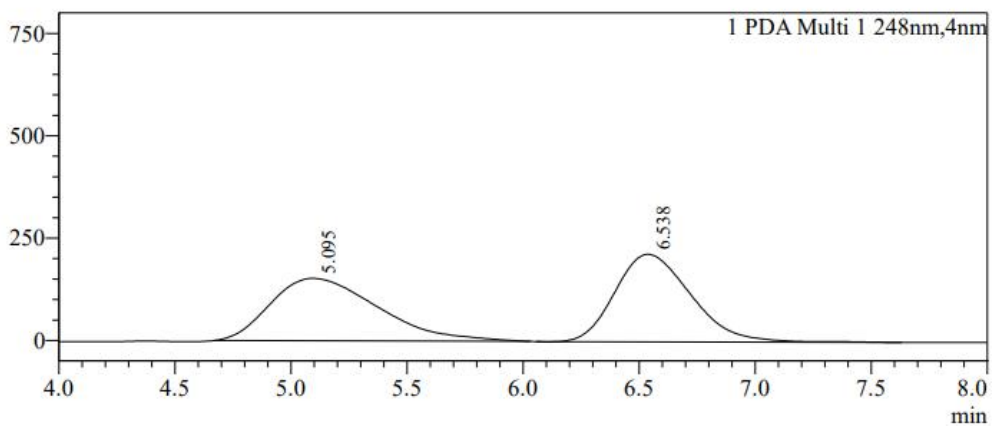
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	6.807	7.435	437843	9598261	97.173
2	7.704	8.011	16823	279191	2.827
Total			454667	9877452	100.000

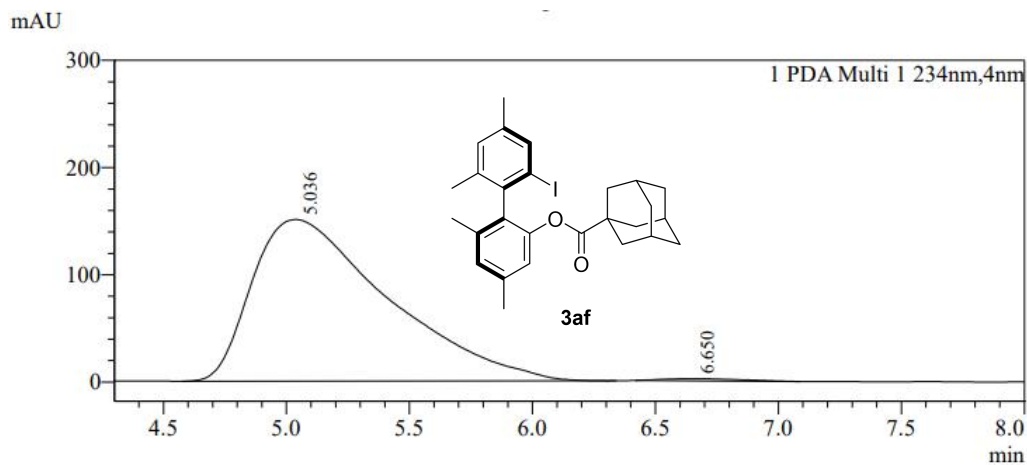


**HPLC spectra of (*R*)-2'-iodo-4,4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl adamantane-1-carboxylate(3af).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda = 234$  nm,  $t_R(\text{major}) = 5.0$  min,  $t_R(\text{minor}) = 6.7$  min, e.r. = 99.5:0.5



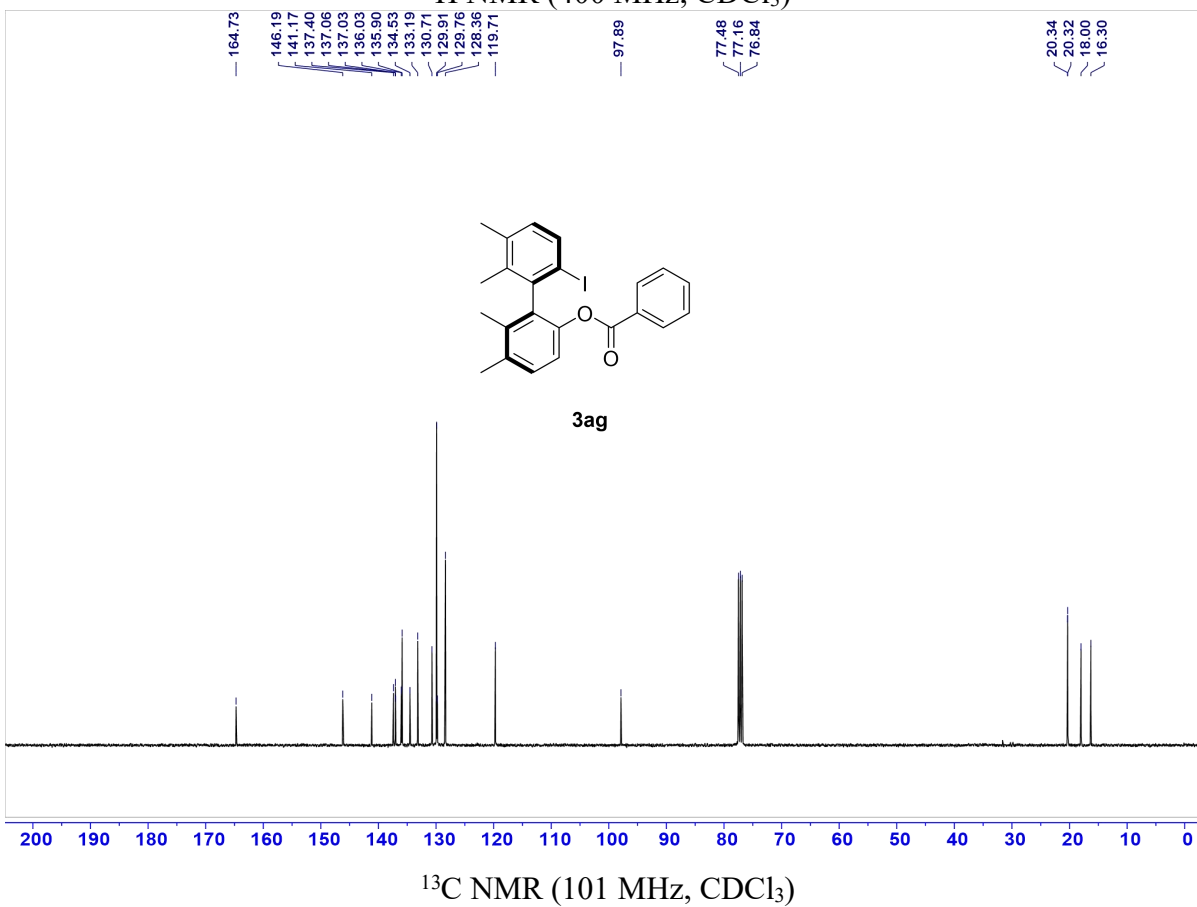
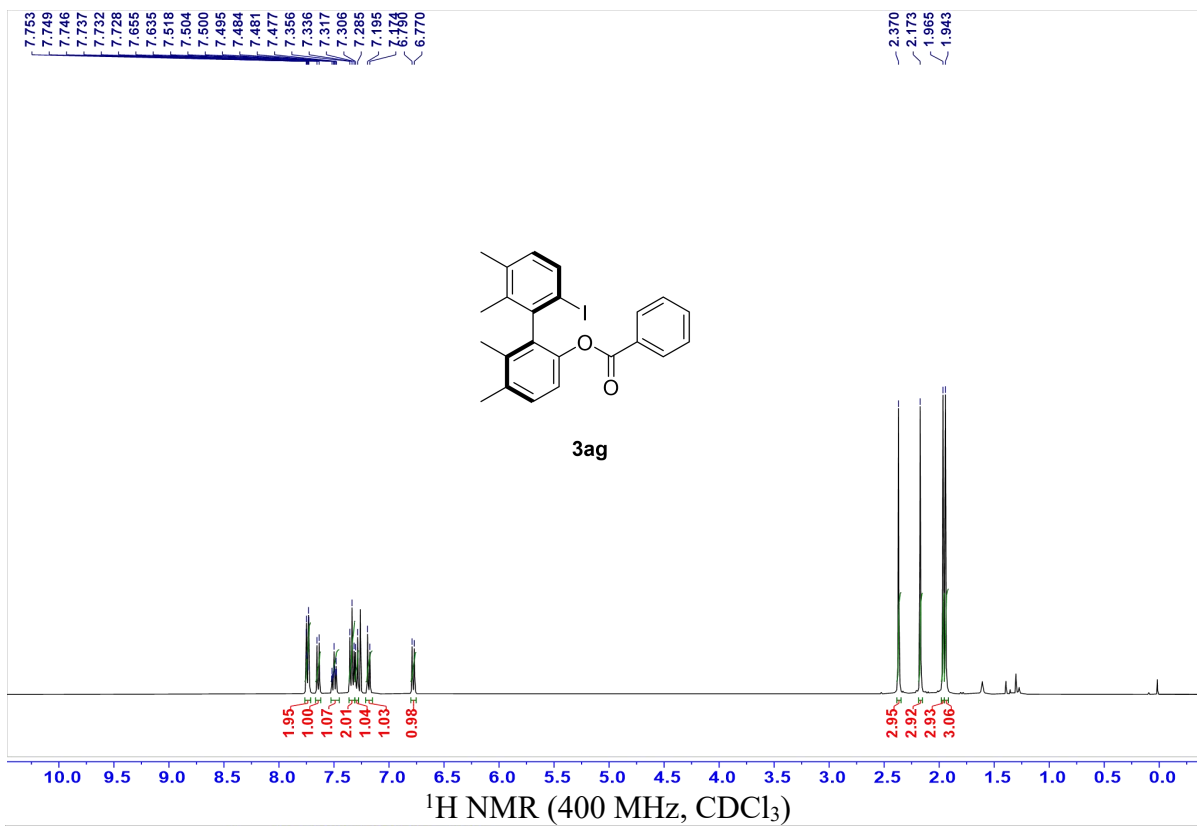
Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	5.095	6.027	152332	4905751	50.129
2	6.538	7.627	214005	4880584	49.871
Total			366337	9786335	100.000

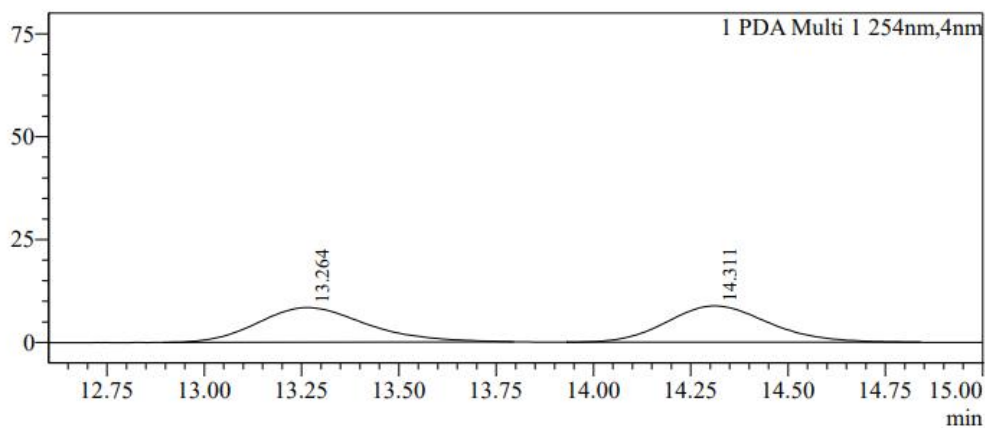


Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	5.036	6.336	150758	5780991	99.256
2	6.650	7.083	1948	43314	0.744
Total			152706	5824305	100.000



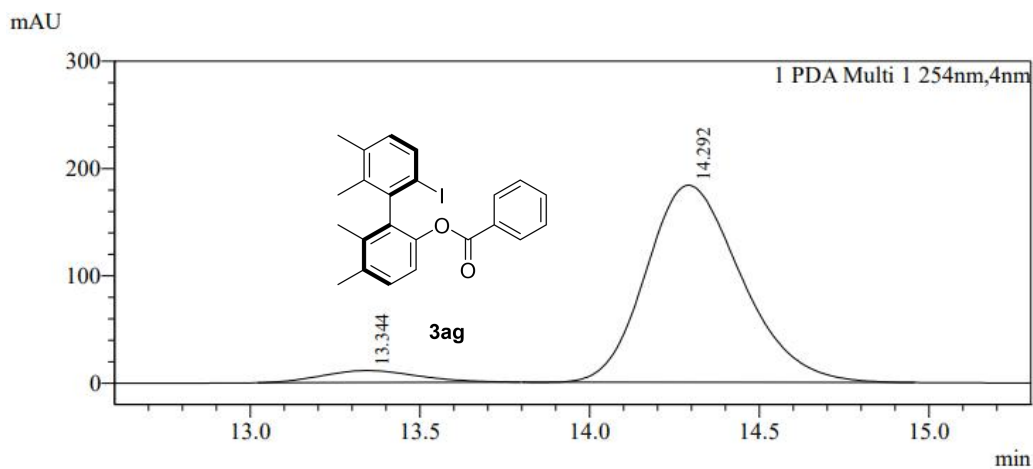
**HPLC spectra of (*R*)-6'-iodo-2',3',5,6-tetramethyl-[1,1'-biphenyl]-2-yl benzoate(3ag).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 14.3 min,  $t_R$ (minor) = 13.3 min, e.r. = 94.5:5.5



PDA Ch1 254nm

Peak Table

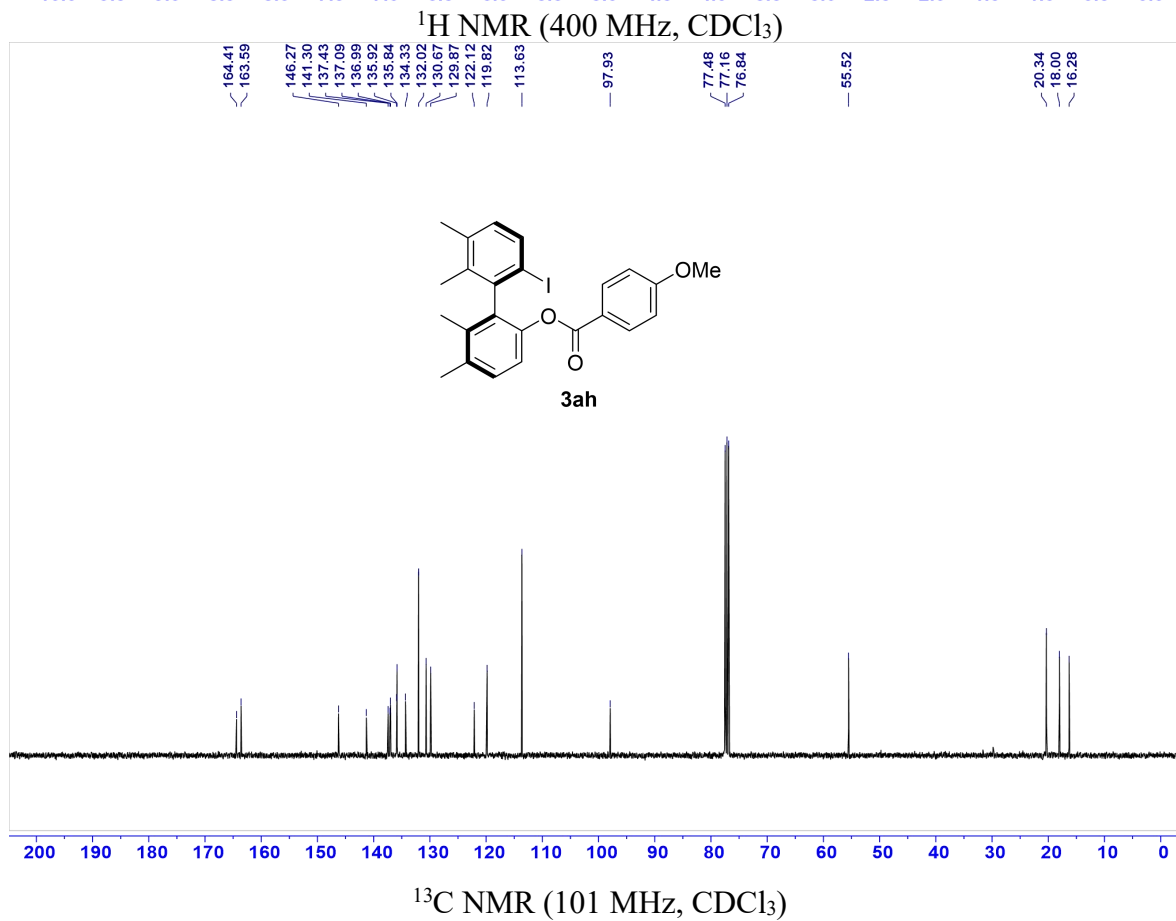
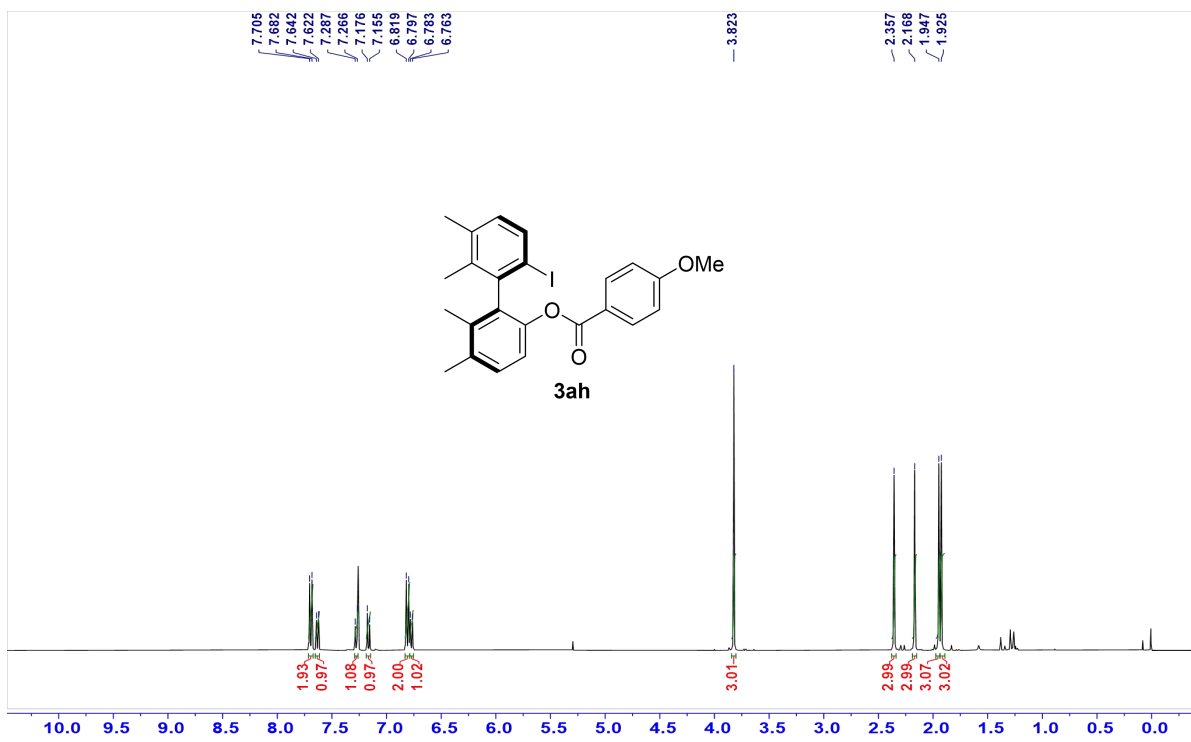
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	13.264	13.792	8379	163429	50.289
2	14.311	14.837	8820	161548	49.711
Total			17199	324976	100.000



PDA Ch1 254nm

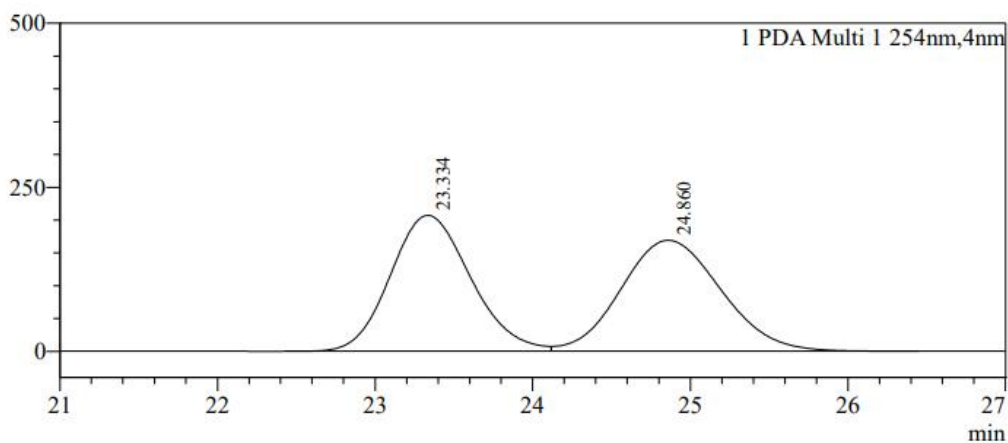
Peak Table

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	13.344	13.792	11094	218788	5.721
2	14.292	14.955	183839	3605391	94.279
Total			194933	3824179	100.000



**HPLC spectra of (*R*)-6'-iodo-2',3',5,6-tetramethyl-[1,1'-biphenyl]-2-yl 4-methoxybenzoate(3ah).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 24.3 min,  $t_R$ (minor) = 22.9 min, e.r. = 94:6

mAU

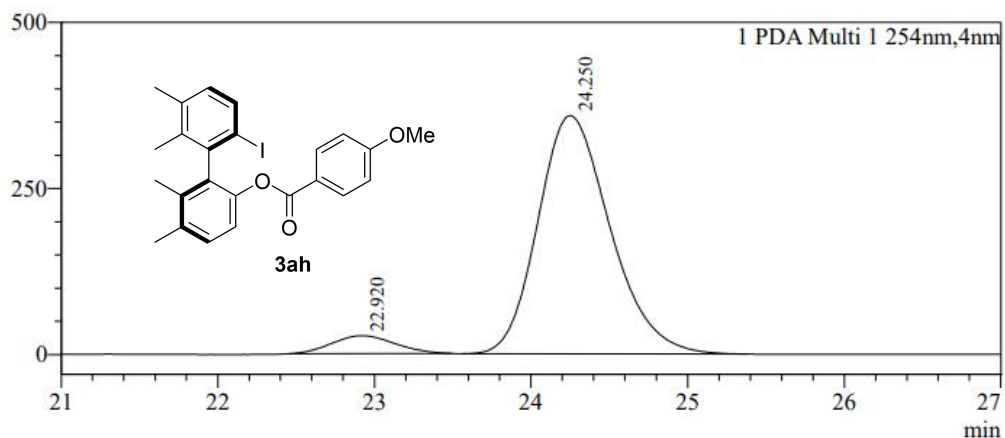


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	23.334	24.117	207219	7344800	49.583
2	24.860	26.443	169079	7468482	50.417
Total			376298	14813282	100.000

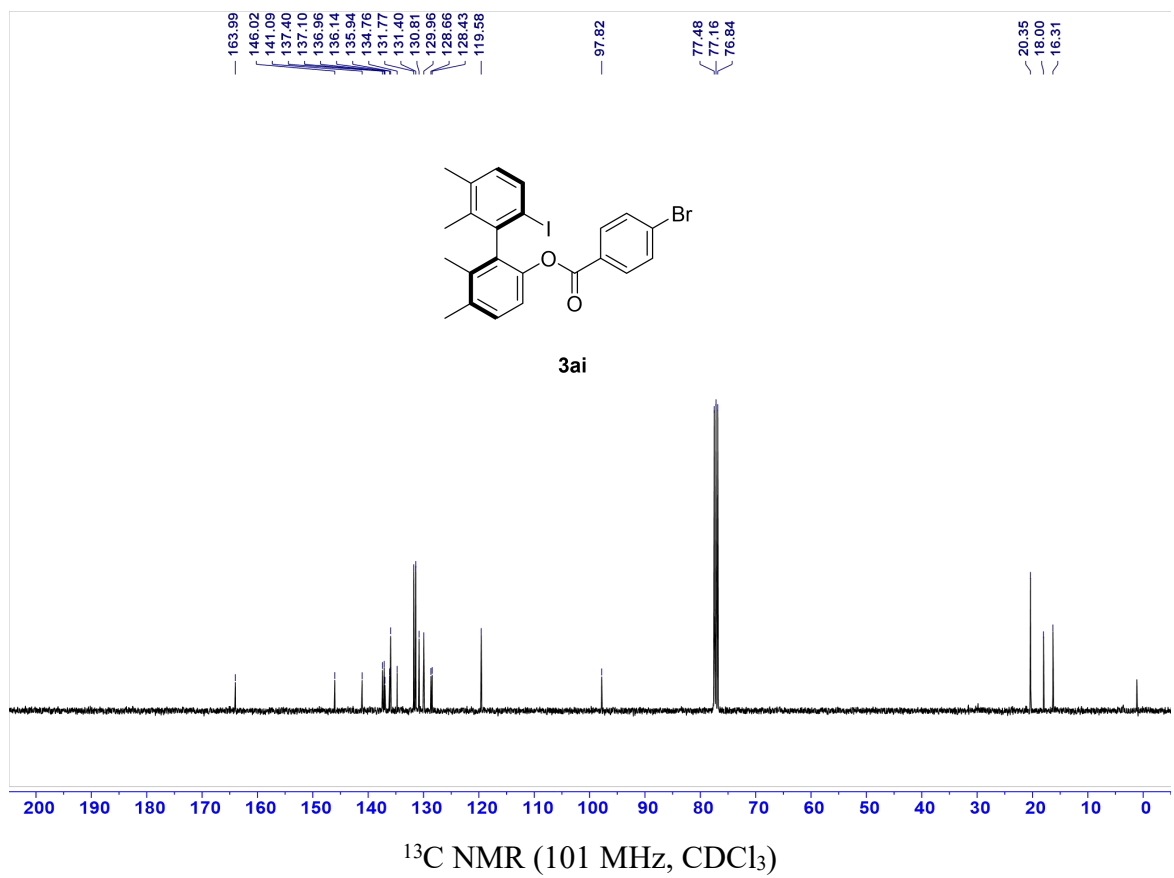
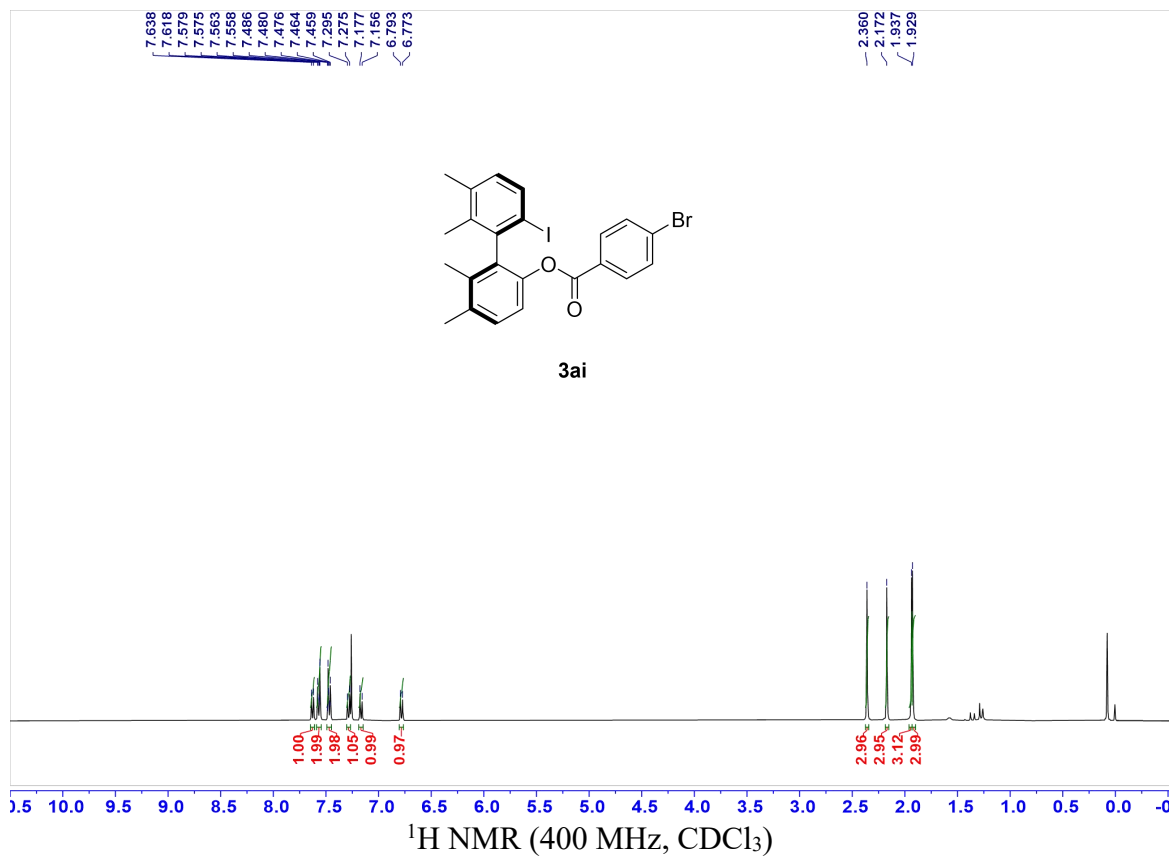
mAU



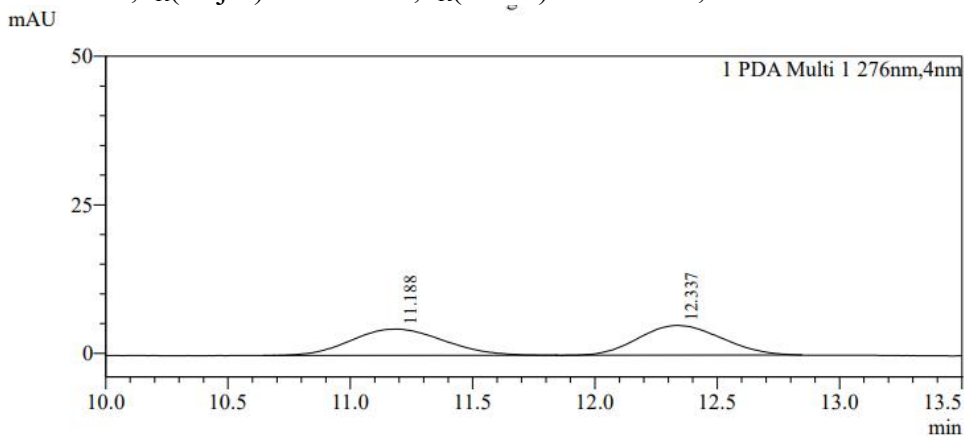
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	22.920	23.488	26980	754925	6.155
2	24.250	25.376	358624	11509469	93.845
Total			385603	12264394	100.000



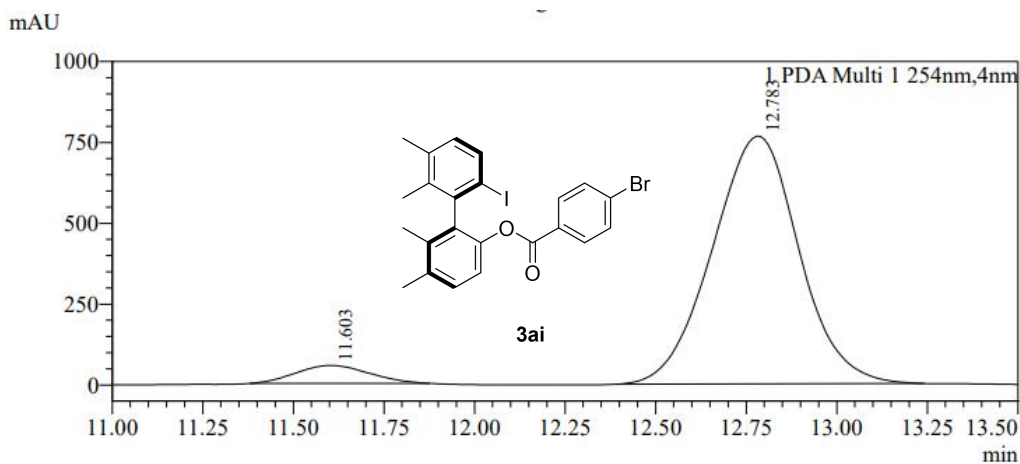
**HPLC spectra of (R)-6'-iodo-2',3',5,6-tetramethyl-[1,1'-biphenyl]-2-yl 4-bromobenzoate(3ai).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 12.8 min,  $t_R$ (minor) = 11.6 min, e.r. = 94:6



Peak Table

PDA Ch1 276nm

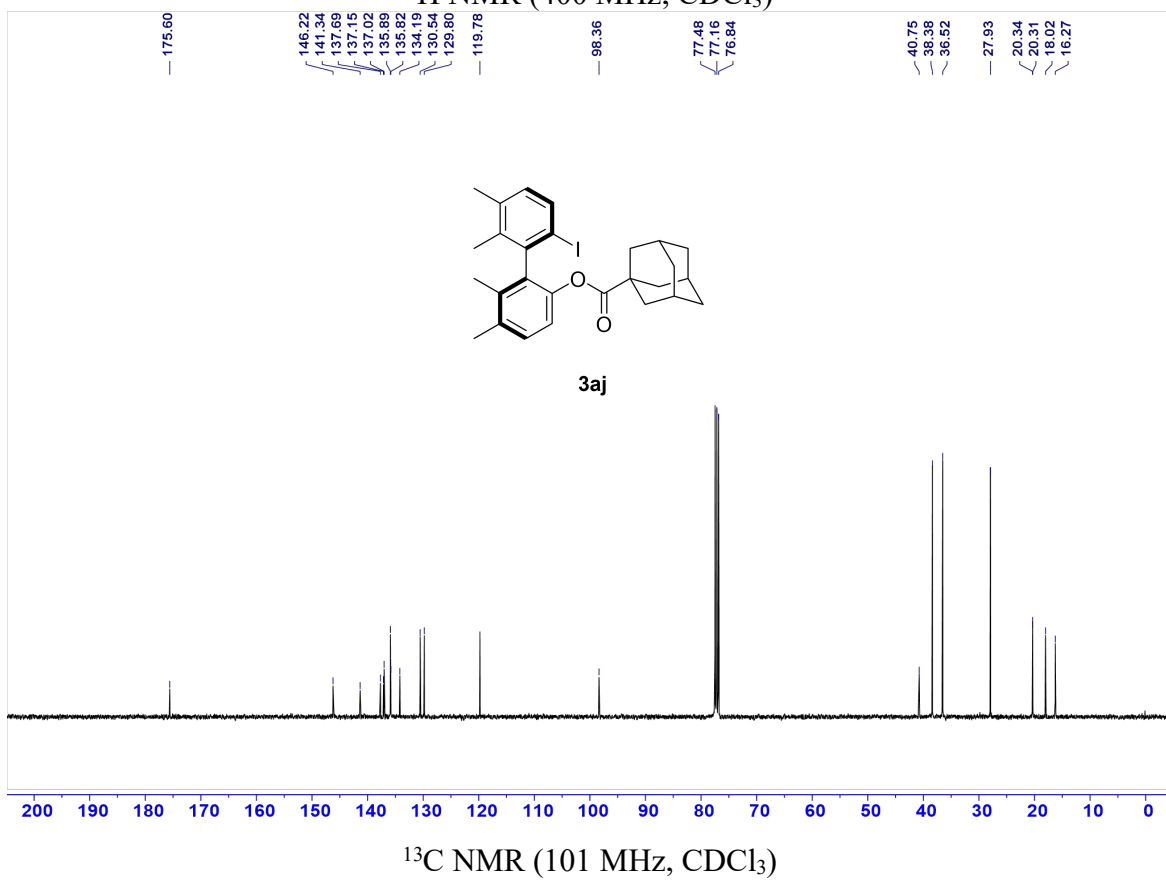
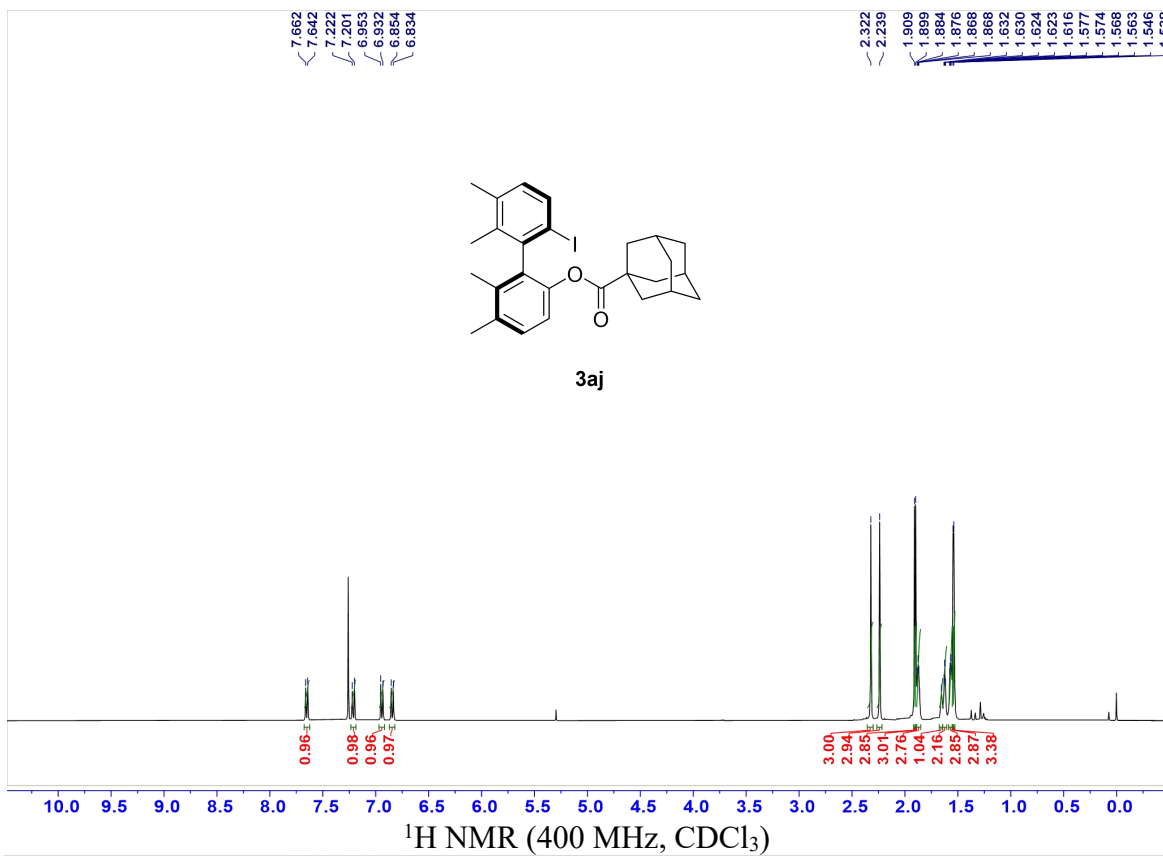
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	11.188	11.840	4431	117070	49.639
2	12.337	12.843	5012	118773	50.361
Total			9443	235843	100.000



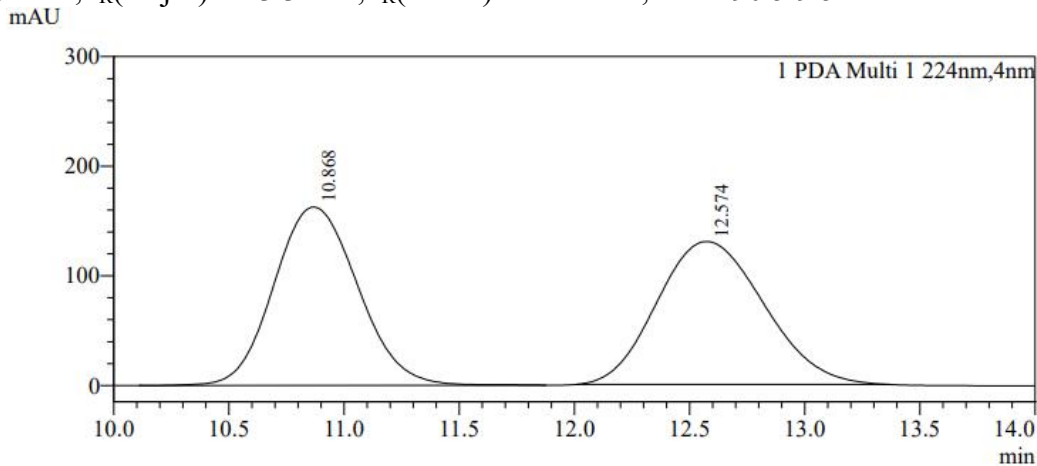
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	11.603	11.872	55325	778041	5.758
2	12.783	13.237	765976	12734150	94.242
Total			821301	13512192	100.000



**HPLC spectra of (*R*)-6'-iodo-2',3',5,6-tetramethyl-[1,1'-biphenyl]-2-yl adamantane-1-carboxylate(3aj).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 99:1, flow = 1.0 mL/min, 25 °C,  $\lambda = 254$  nm,  $t_R(\text{major}) = 13.3$  min,  $t_R(\text{minor}) = 11.4$  min, e.r. = 90.5:9.5

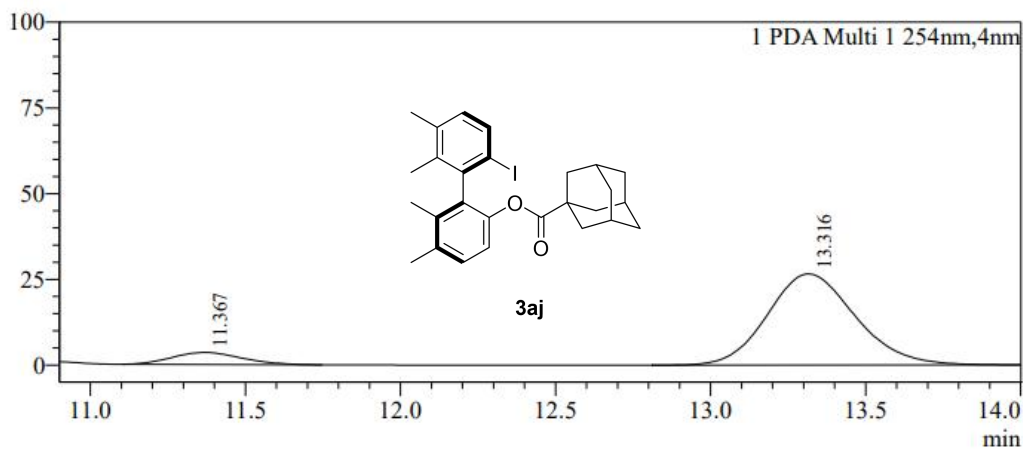


Peak Table

PDA Ch1 224nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	10.868	11.872	162772	4137871	49.579
2	12.574	13.365	130386	4208158	50.421
Total			293158	8346029	100.000

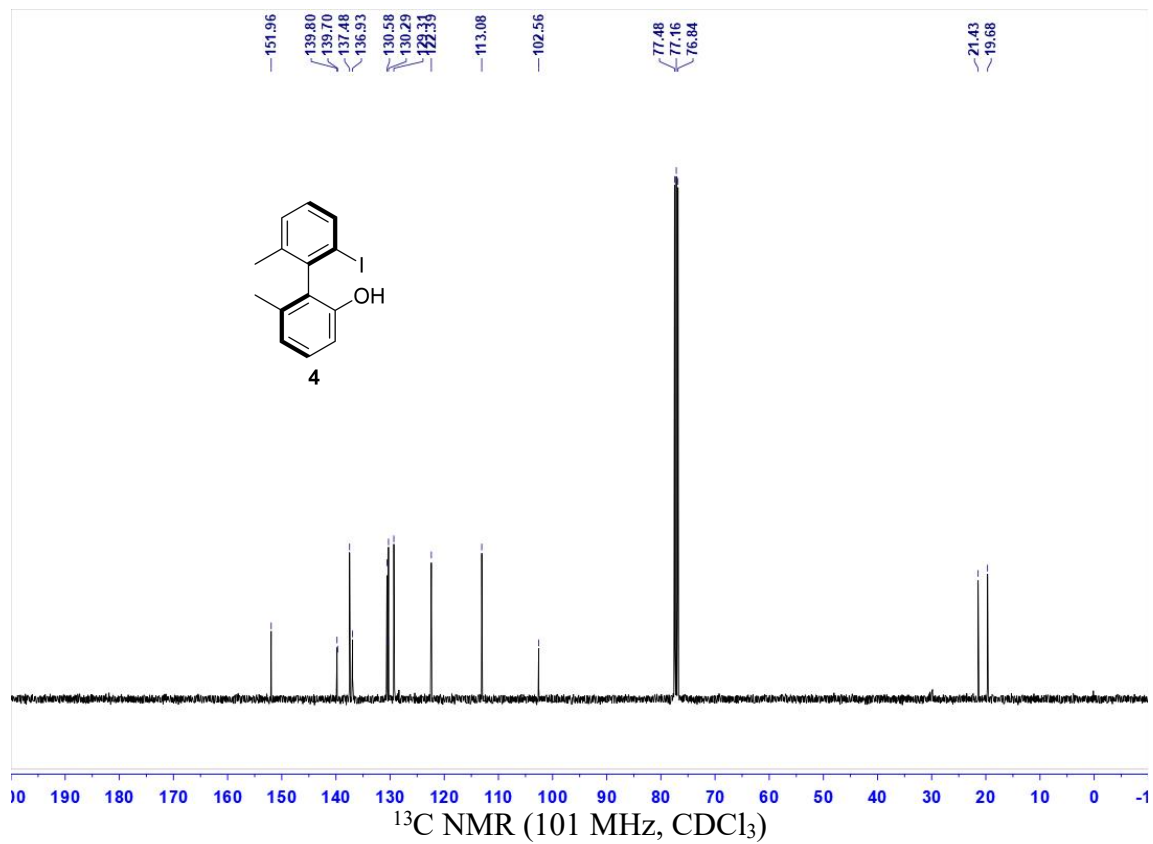
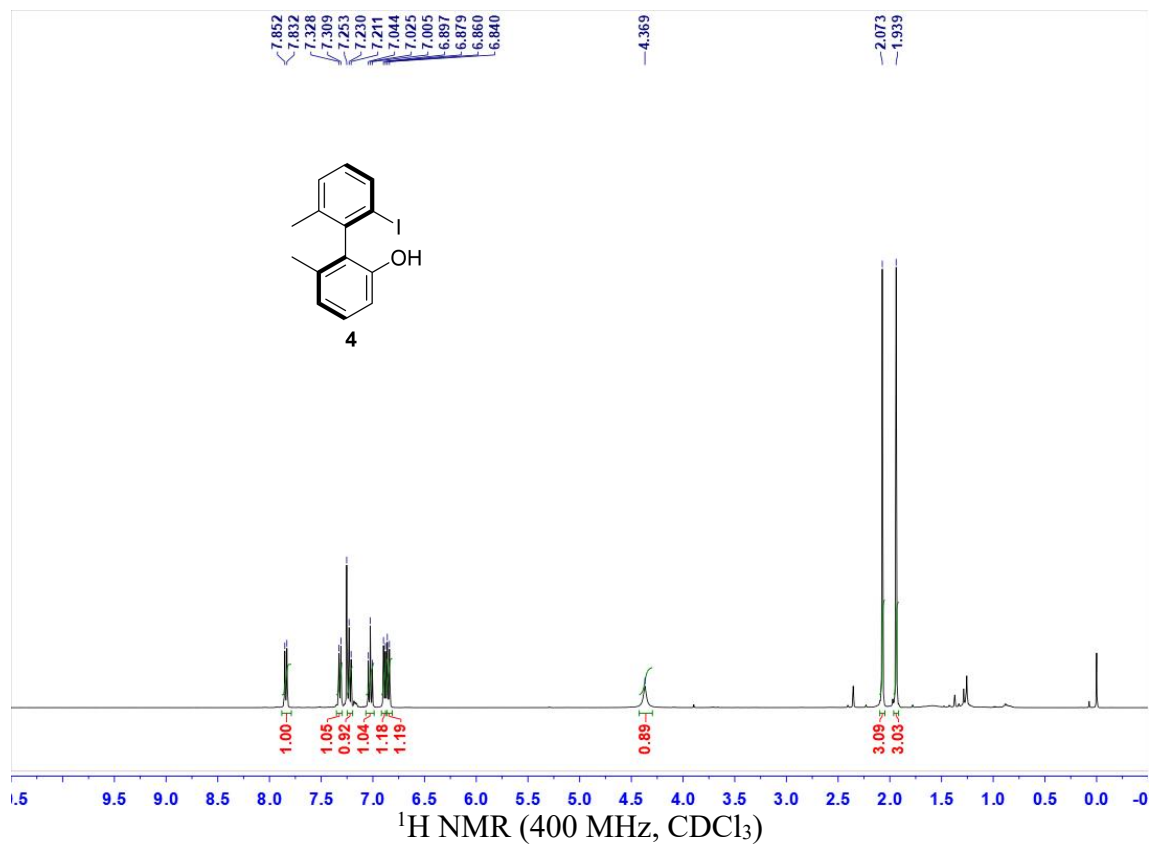
mAU



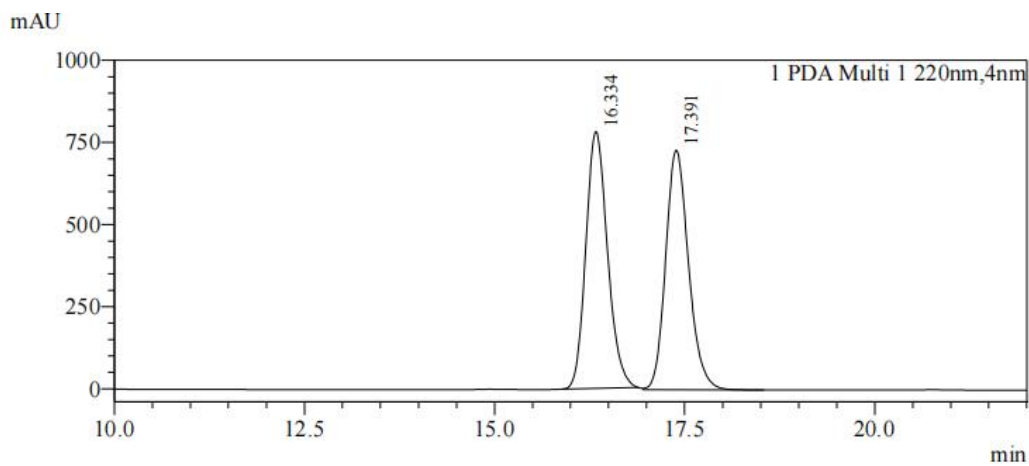
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	11.367	11.744	3517	55035	9.455
2	13.316	14.059	26590	527027	90.545
Total			30107	582061	100.000

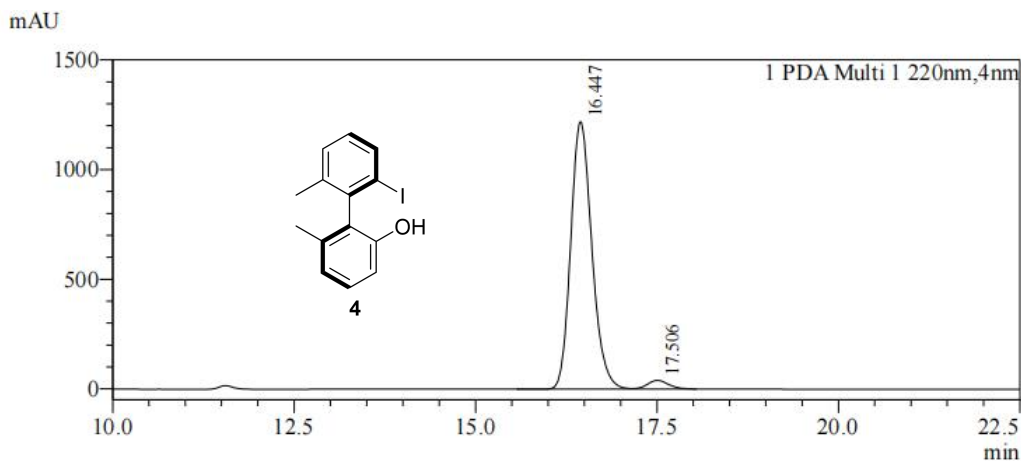


**HPLC spectra of (*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-ol (**4**).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 98:2, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 220 nm,  $t_R$ (major) = 16.4 min,  $t_R$ (minor) = 17.5 min, e.r. = 97:3



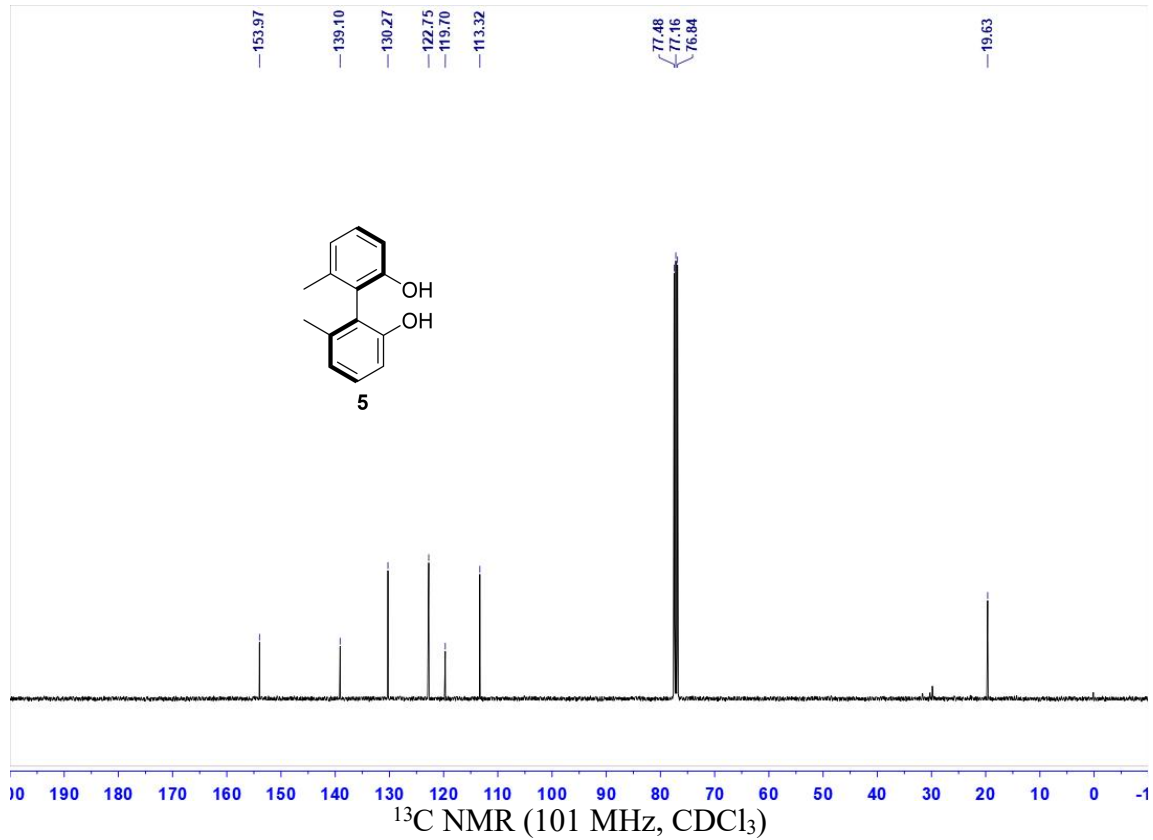
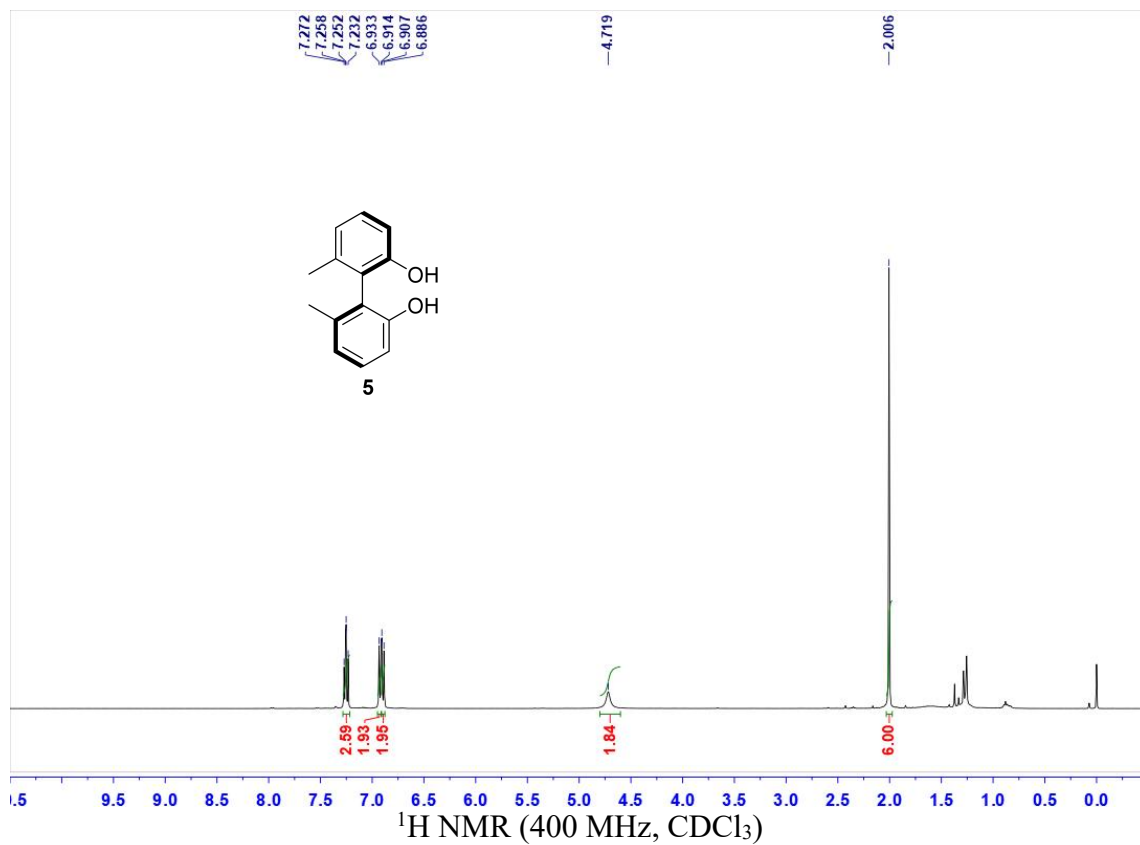
Peak Table

PDA Ch1 220nm					
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	16.334	16.885	781787	15484912	50.340
2	17.391	18.528	729501	15275729	49.660
Total			1511289	30760641	100.000



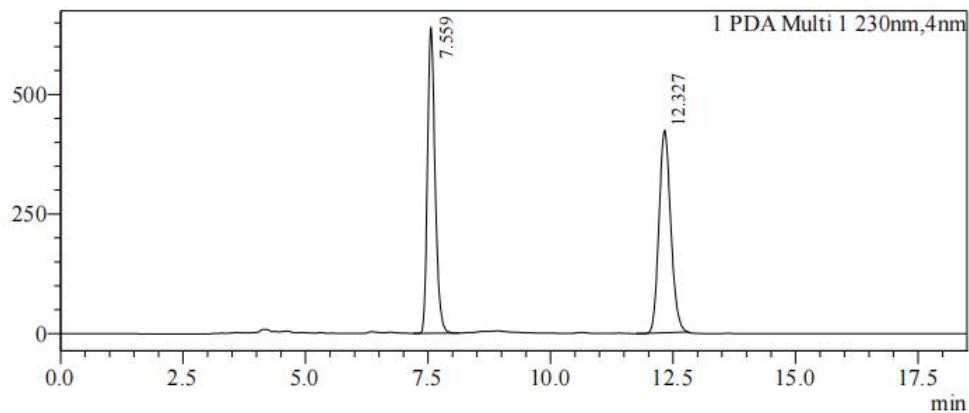
Peak Table

PDA Ch1 220nm					
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	16.447	17.163	1219488	24694561	96.865
2	17.506	18.027	39385	799158	3.135
Total			1258872	25493719	100.000



**HPLC spectra of (*R*)-6,6'-dimethyl-[1,1'-biphenyl]-2,2'-diol (**5**).** Diacel Chiralpak AD-H, *n*-Hexane:*i*-PrOH = 80:20, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 230 nm,  $t_R$ (major) = 12.2 min,  $t_R$ (minor) = 7.5 min, e.r. = 97:3

mAU

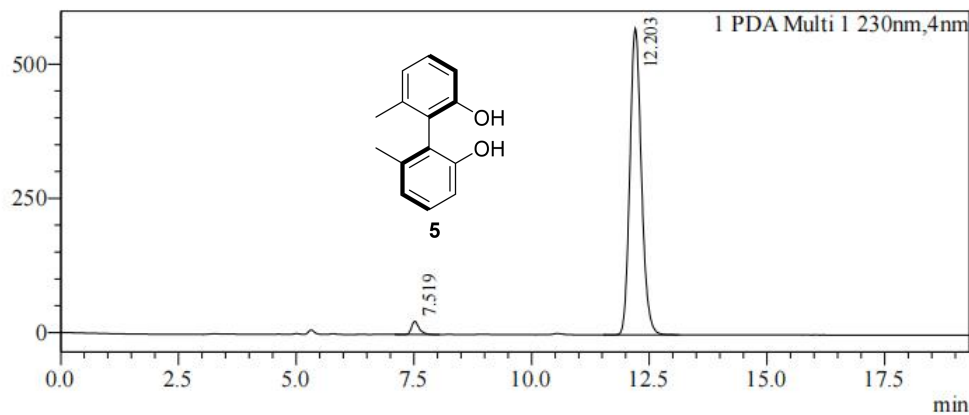


Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	7.559	8.117	638407	6915312	49.429
2	12.327	12.800	422914	7075175	50.571
Total			1061320	13990487	100.000

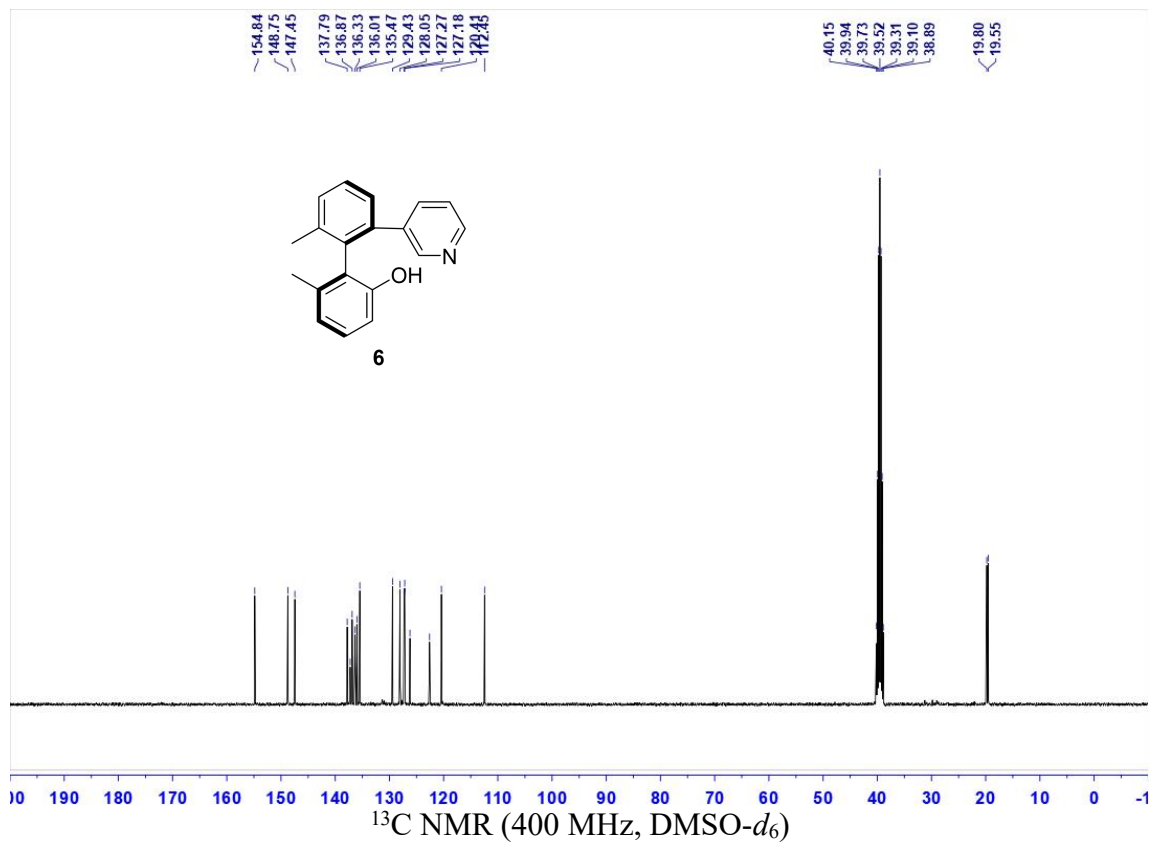
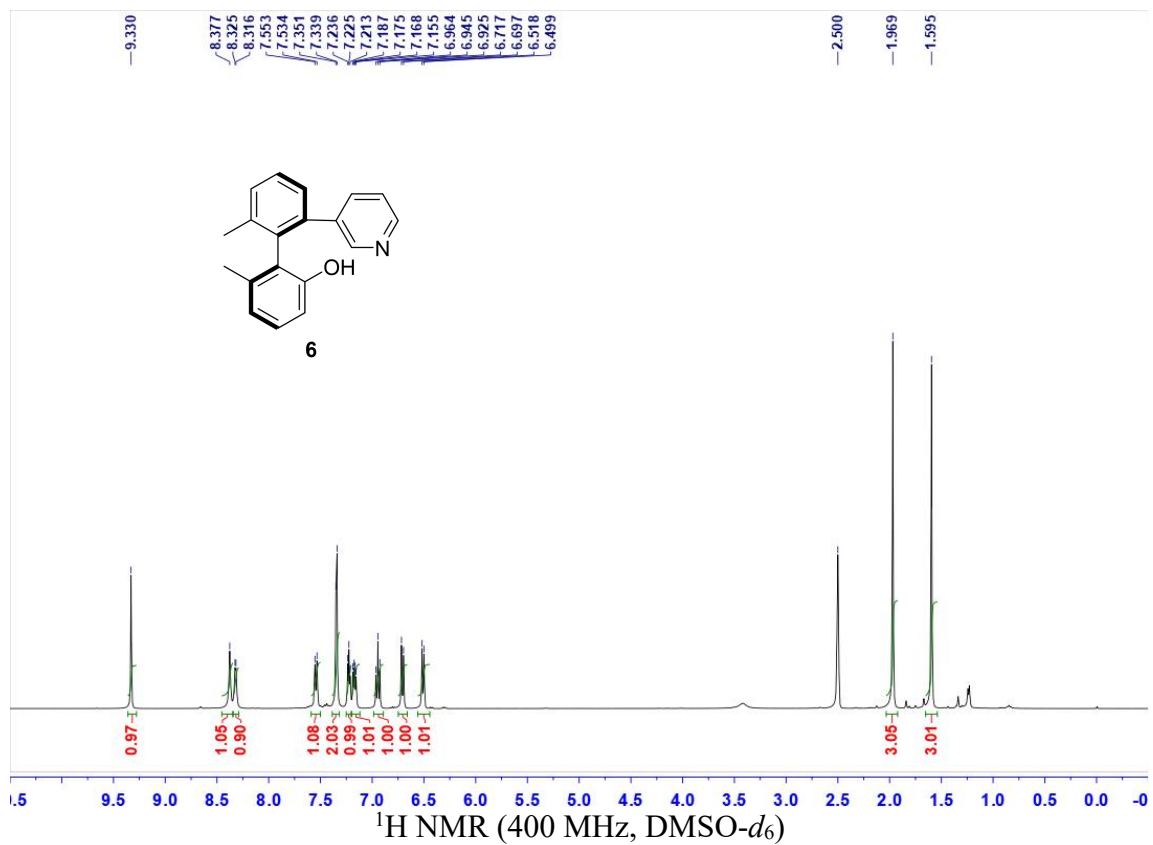
mAU



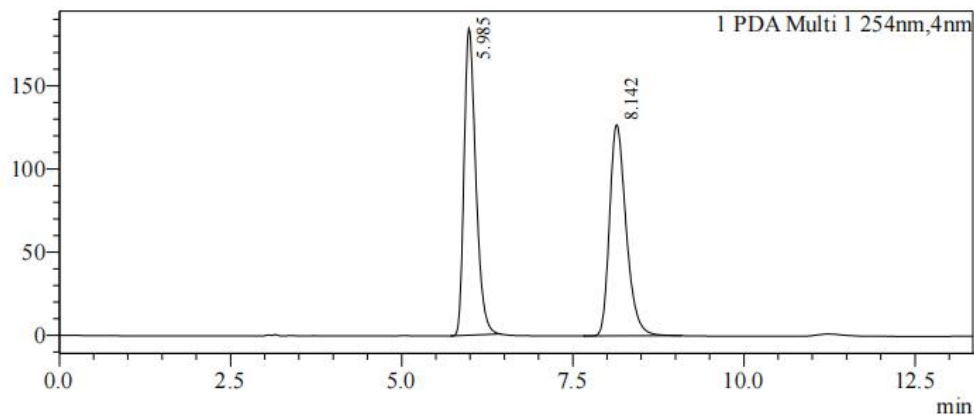
Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	7.519	8.021	24599	272673	2.729
2	12.203	13.109	570714	9720674	97.271
Total			595314	9993347	100.000



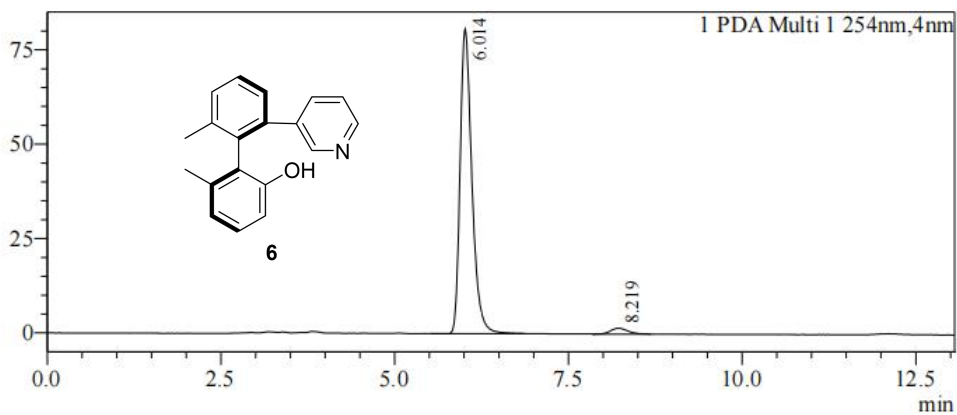
**HPLC spectra of (*R*)-2',6-dimethyl-6'-(pyridin-3-yl)-[1,1'-biphenyl]-2-ol (**6**).** Diacel Chiralcel OD-H, *n*-Hexane:*i*-PrOH = 92:8, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 6.0 min,  $t_R$ (minor) = 8.2 min, e.r. = 97:3



Peak Table

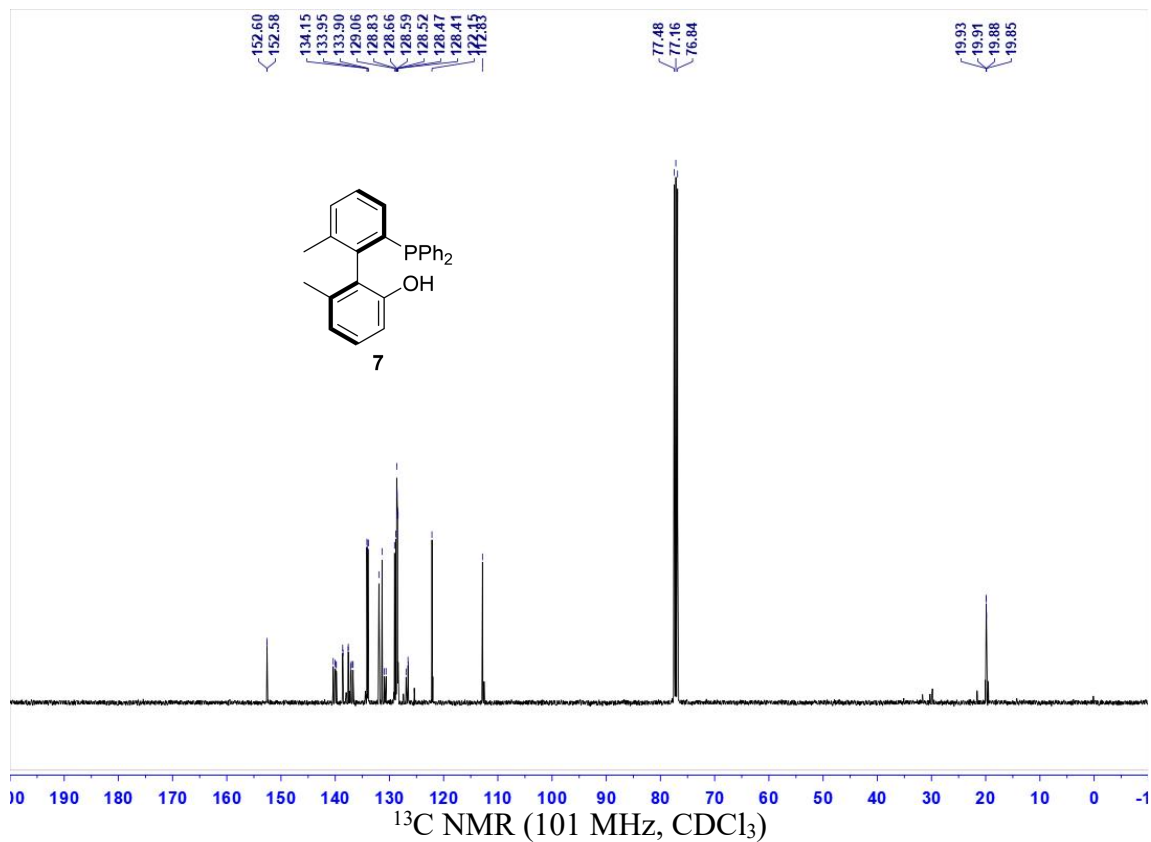
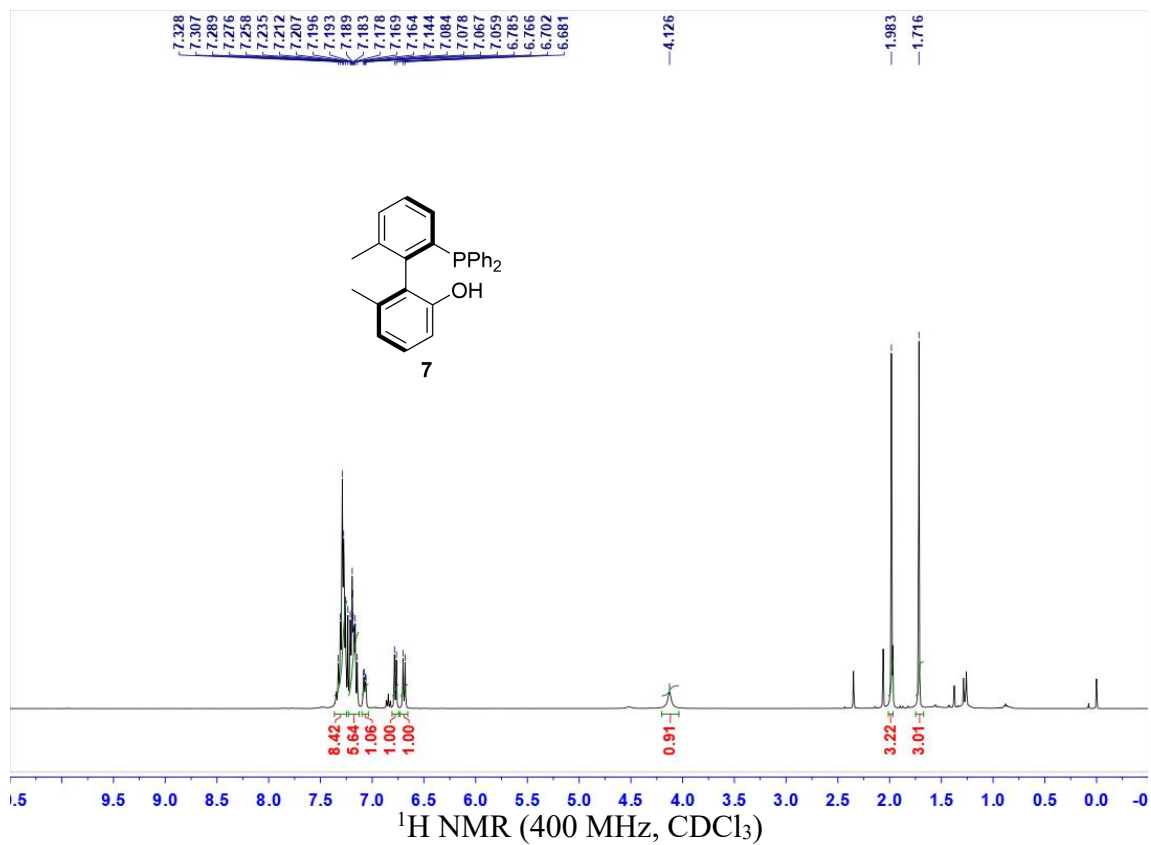
PDA Ch1 254nm					
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	5.985	6.443	184361	2205147	50.714
2	8.142	9.077	126832	2143031	49.286
Total			311193	4348179	100.000

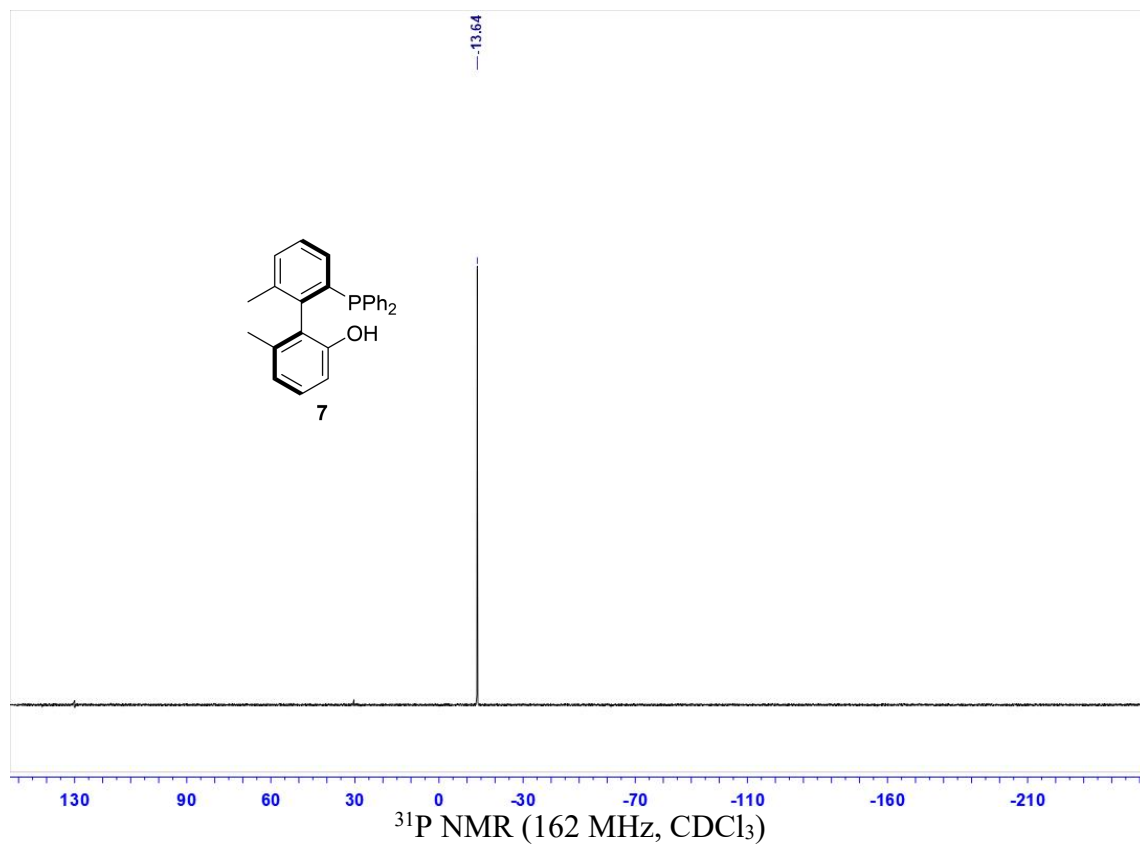
mAU



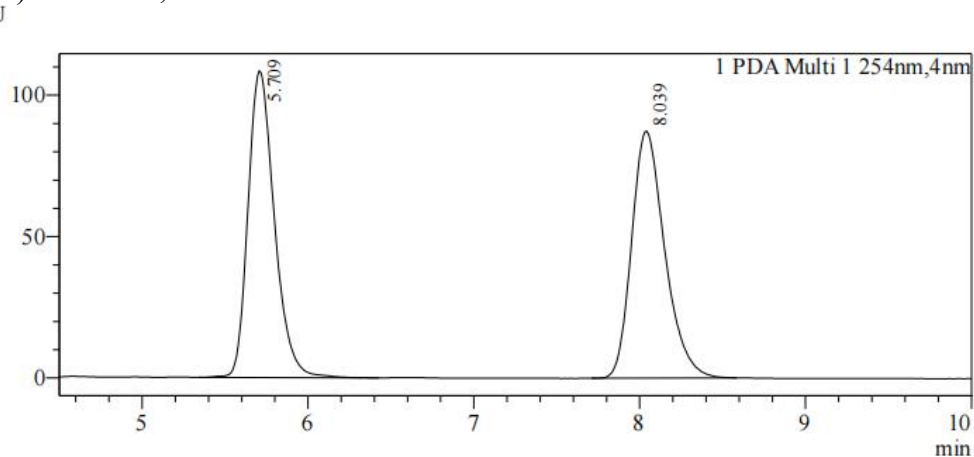
Peak Table

PDA Ch1 254nm					
Peak#	Ret. Time	Peak End	Height	Area	Area%
1	6.014	6.859	80653	951035	97.237
2	8.219	8.672	1566	27026	2.763
Total			82219	978062	100.000





**HPLC spectra of (*R*)-2'-(diphenylphosphanyl)-6,6'-dimethyl-[1,1'-biphenyl]-2-ol (7).** Diacel Chiralpak IC, *n*-Hexane:*i*-PrOH = 98:2, flow = 1.0 mL/min, 25 °C,  $\lambda$  = 254 nm,  $t_R$ (major) = 5.7 min,  $t_R$ (minor) = 8.0 min, e.r. = 97:3

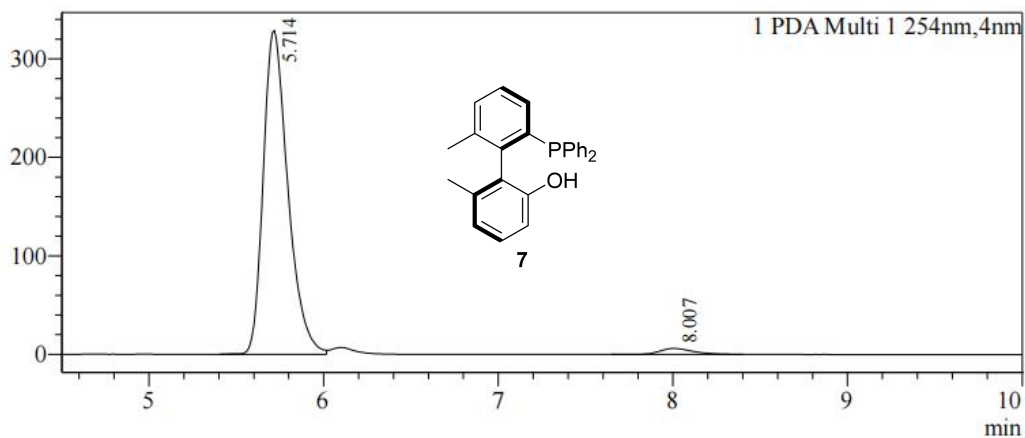


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	5.709	6.421	108412	1198610	49.728
2	8.039	8.576	87313	1211737	50.272
Total			195724	2410347	100.000

mAU



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Peak End	Height	Area	Area%
1	5.714	6.016	328557	3222892	97.589
2	8.007	8.395	6092	79618	2.411
Total			334649	3302511	100.000

## 9. References

1. Zhao K, Duan L, Xu S, Jiang J, Fu Y, Gu Z. Enhanced reactivity by torsional strain of cyclic diaryliodonium in Cu-catalyzed enantioselective ring-opening reaction. *Chem*. 2018;4(3):599-612. [DOI:10.1016/j.chempr.2018.01.017]
2. Liu Y, Ma Y, Liu PZ, Shen C, Cen S, Zhu YY, et al. Switchable phenanthroline-Cu catalysts for enantioselective alkynylation and amination of cyclic diaryliodonium salts. *Angew Chem Int Ed*. 2026;65(2):e14745. [DOI:10.1002/anie.202514745]
3. Zhu K, Xu K, Fang Q, Wang Y, Tang B, Zhang F. Enantioselective synthesis of axially chiral biaryls via Cu-catalyzed acyloxylation of cyclic diaryliodonium salts. *ACS Catal*. 2019;9(6):4951-4957. [DOI:10.1021/acscatal.9b00695]
4. Xue X, Gu Z. Synthesis of bridged biaryl atropisomers via sequential Cu- and Pd-catalyzed asymmetric ring opening and cyclization. *Org Lett*. 2019;21(11):3942-3945. [DOI:10.1021/acs.orglett.9b01062]