

## *Supporting Information*

### **Nickel- and Copper-Cocatalyzed Atroposelective C–Si Cross-Coupling to Axially Chiral Heterobiaryl Silanes**

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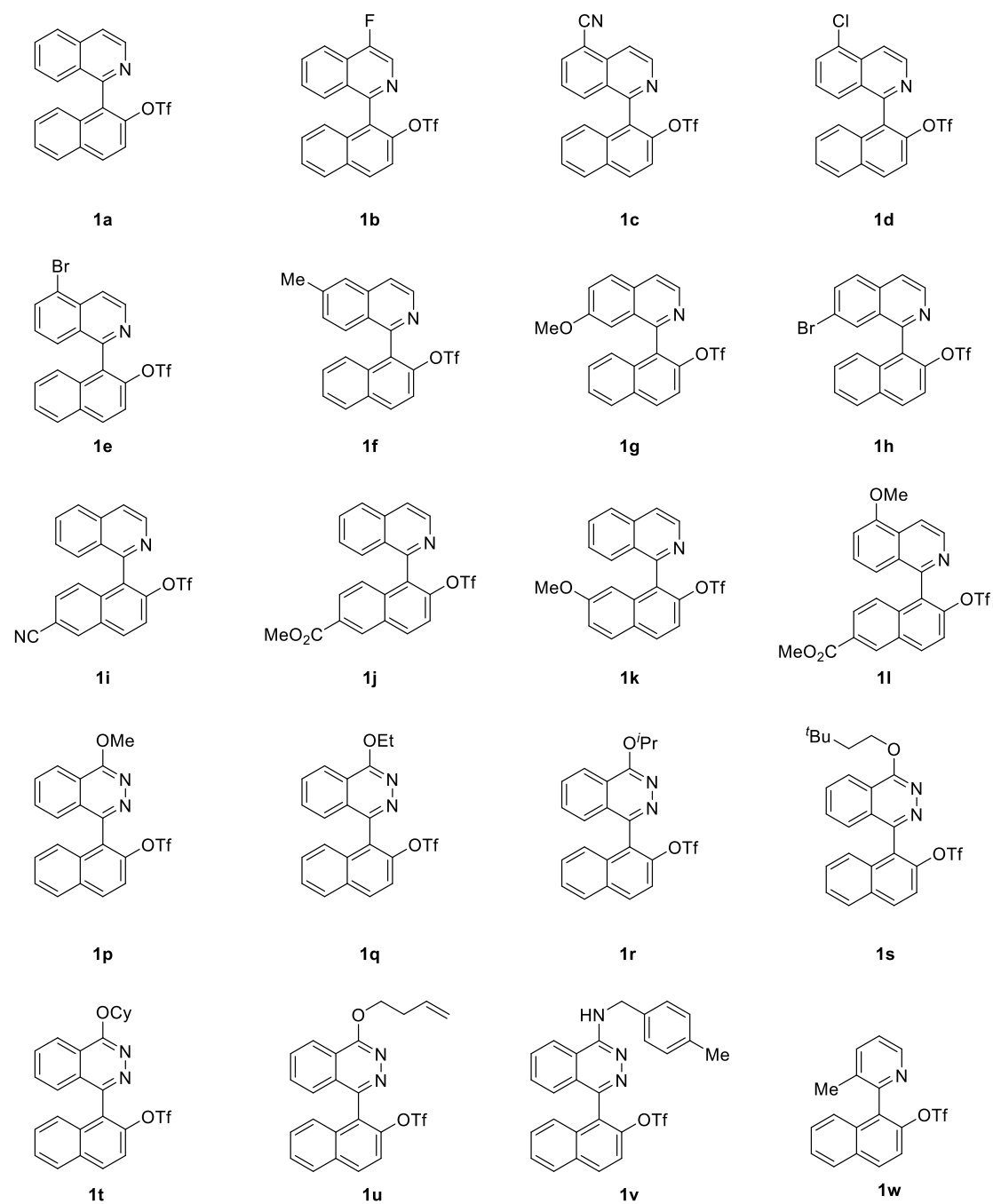
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## General Information

Unless otherwise noted, all reactions and manipulations were performed using standard Schlenk techniques or in a glovebox. All the chemicals were commercially purchased from Adamas-beta, Energy Chemical, Aladdin, Bide, Daicel Chiral Technologies (China) Co., and directly used without further purification. Anhydrous  $\text{CH}_2\text{Cl}_2$ , DCE, DME, DMF, THF, 1,4-Dioxane, and acetic ether were purchased from Adamas-beta.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were recorded on Bruker Avance 500 MHz spectrometer at STP unless otherwise indicated.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shifts were reported in  $\delta$  units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were set at 7.26 ppm and 77.16 ppm, respectively. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; *br*, broad. High-resolution mass spectra (HRMS) were obtained using a Bruker APEXIII 7.0 and IonSpec 4.7 TESLA FTMS. Optical rotations were determined using a Perkin Elmer 341 MC polarimeter. HPLC analyses were performed on a Agilent 7890 liquid chromatograph.

# 1. Syntheses of substrates

## 1.1 Syntheses of Heterobiaryl triflates



Compounds **1a-1l** and **1p-1w** are known compounds, and they were synthesized according to the literature procedure<sup>[1-2]</sup>.

## 2. Nickel and Copper co-catalyzed atroposelective C–Si cross-coupling

### 2.1 Optimization of reaction conditions

**Table S1.** Ligand screening on nickel catalyzed atroposelective silylation of heterobiaryls <sup>a</sup>

(*rac*)-**1a** (0.05 mmol) + PhMe<sub>2</sub>SiBpin (1.2 equiv) → (*R*)-**2a**

Conditions: 10 mol% Ni(COD)<sub>2</sub>, 20 mol% Ligand, CuF<sub>2</sub> (0.3 equiv), CsF (1.5 equiv), Toluene (0.05 M), 50 °C, 24 h

**L1**

**L2:** R = Ph  
**L3:** R = <sup>i</sup>Pr  
**L4:** R = <sup>t</sup>Bu

**L5:** R = <sup>i</sup>Bu  
**L6:** R = Me

**L7**

**L8**

**L9**

**L10**

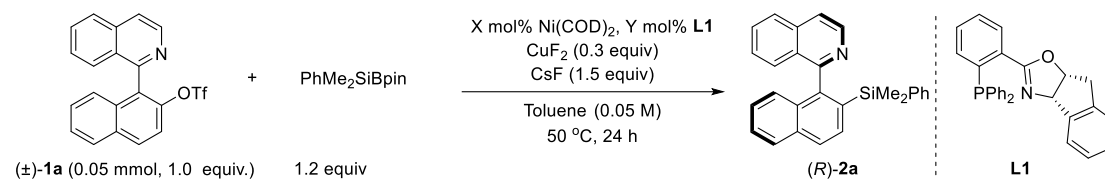
**L11**

**L12**

Entry	Ligand	Yield of <b>2a</b> (%)	<i>ee</i> of <b>2a</b> (%)
1	<b>PCy<sub>3</sub></b>	69	-
2	<b>L1</b>	69(70 <sup>b</sup> )	96
3	<b>L2</b>	20	54
4	<b>L3</b>	72	91
5	<b>L4</b>	26	97
6	<b>L5</b>	40	-85
7	<b>L6</b>	24	-82
8	<b>L7</b>	30	-54
9	<b>L8</b>	28	1
10	<b>L9</b>	17	3
11	<b>L10</b>	24	-2
12	<b>L11</b>	16	0
13	<b>L12</b>	50	-18

<sup>a</sup> The yields were determined by GC analysis using dodecane as the internal standard. The *ee* value was determined by HPLC using a chiral column. <sup>b</sup> Isolated yield.

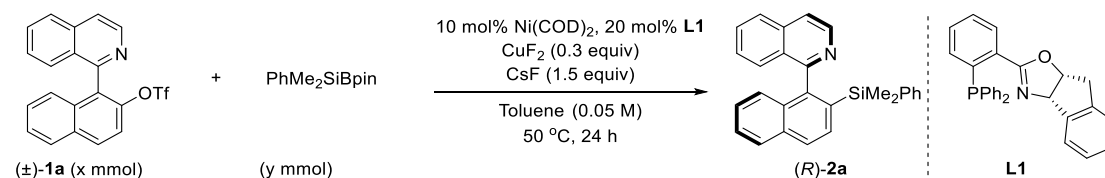
**Table S2.** Effect of catalyst loading and Ni/L ratio on nickel catalyzed atroposelective silylation of heterobiaryls <sup>a</sup>



Entry	X/Y	Yield of <b>2a</b> (%)	<i>ee</i> of <b>2a</b> (%)
1	10/20	69(70 <sup>b</sup> )	96
2	5/10	50	86
3	10/10	9	75
4	10/12	9	27
5	15/30	63	93

<sup>a</sup> The yields were determined by GC analysis using dodecane as the internal standard, The *ee* value was determined by HPLC using a chiral column. <sup>b</sup> Isolated yield.

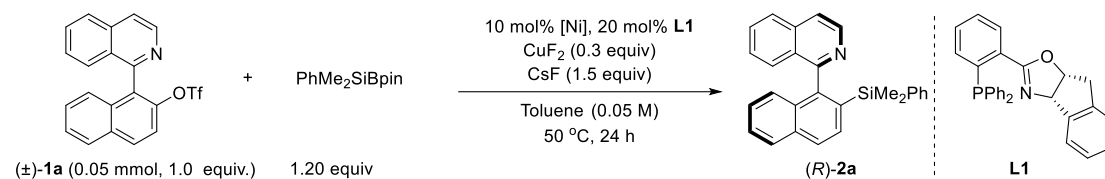
**Table S3.** Effect of ratio of substrate on nickel catalyzed atroposelective silylation of heterobiaryls <sup>a</sup>



Entry	X:Y	Yield of <b>2a</b> (%)	<i>ee</i> of <b>2a</b> (%)
1	0.05 : 0.06	69(70 <sup>b</sup> )	96
2	0.05 : 0.10	43	94
3	0.05 : 0.075	59	96
4	0.05 : 0.05	48	95
5	0.10 : 0.05	55	90

<sup>a</sup> The yields were determined by GC analysis using dodecane as the internal standard. The *ee* value was determined by HPLC using a chiral column. <sup>b</sup> Isolated yield.

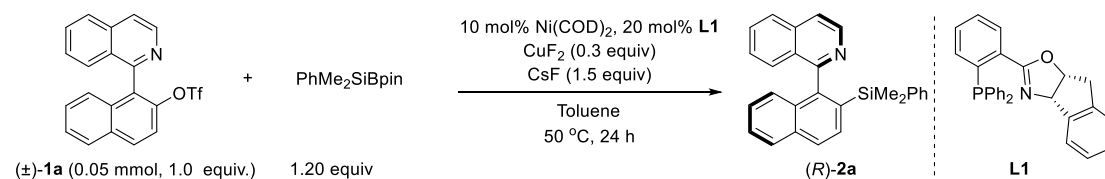
**Table S4.** Effect of nickel source on nickel catalyzed atroposelective silylation of heterobiaryls <sup>a</sup>



Entry	Nickel	Yield of 2a (%)	ee of 2a (%)
1	Ni(COD) <sub>2</sub>	69(70 <sup>b</sup> )	96
2	w/o Nickel	trace	-
3	NiBr <sub>2</sub> ·dme	20	90
4 <sup>c</sup>	NiBr <sub>2</sub> ·dme	trace	-

<sup>a</sup> The yields were determined by GC analysis using dodecane as the internal standard. The *ee* value was determined by HPLC using a chiral column. <sup>b</sup> Isolated yield. <sup>c</sup> with extra 0.3 equiv Mn powder.

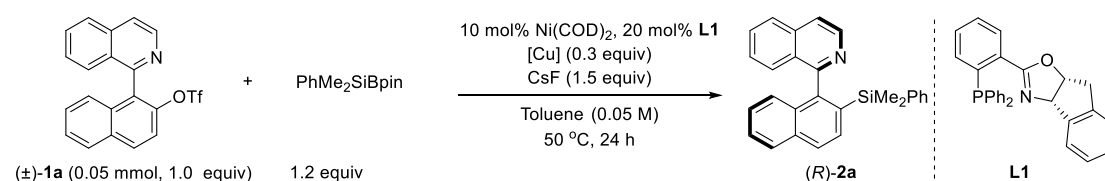
**Table S5.** Effect of concentration on nickel catalyzed atroposelective silylation of heterobiaryls <sup>a</sup>



Entry	Concentration (M)	Yield of 2a (%)	ee of 2a (%)
1	0.05	69(70 <sup>b</sup> )	96
2	0.2	48	92
3	0.1	51	95
4	0.067	57	94
5	0.033	36	94
6	0.025	25	90

<sup>a</sup> The yields were determined by GC analysis using dodecane as the internal standard. The *ee* value was determined by HPLC using a chiral column. <sup>b</sup> Isolated yield.

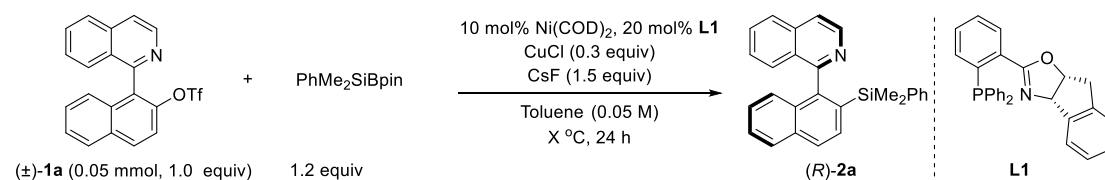
**Table S6.** Effect of copper salt on nickel catalyzed atroposelective silylation of heterobiaryls <sup>a</sup>



Entry	Copper Salt	Yield of <b>2a</b> (%)	<i>ee</i> of <b>2a</b> (%)
1	CuCl	70(70 <sup>b</sup> )	99
2	none	20	90
3	CuBr	70	99
4	CuI	35	80
5	CuF <sub>2</sub>	69	96
6	TcCu	60	97
7	Cu(CH <sub>3</sub> CN) <sub>4</sub> BF <sub>4</sub>	17	95
8	CuCl <sub>2</sub>	35	98
9	Cu(OTf) <sub>2</sub>	trace	-
10	Cu(acac) <sub>2</sub>	28	60
11	CuC <sub>2</sub> O <sub>4</sub>	49	94
12 <sup>c</sup>	CuCl	26	99
13 <sup>d</sup>	CuCl	60	99

<sup>a</sup> The yields were determined by GC analysis using dodecane as the internal standard. The *ee* value was determined by HPLC using a chiral column. <sup>b</sup> Isolated yield. <sup>c</sup> 0.1 equiv CuCl. <sup>d</sup> 0.5 equiv CuCl.

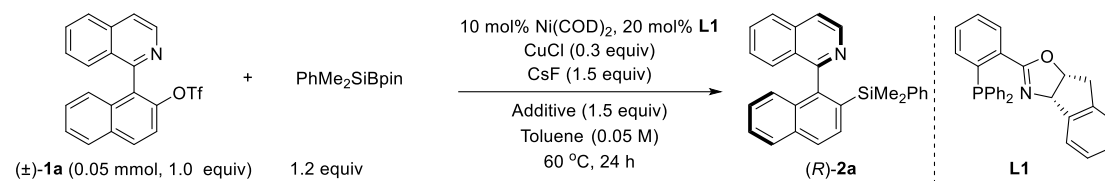
**Table S7.** Effect of reaction temperature on nickel catalyzed atroposelective silylation of heterobiaryls <sup>a</sup>



Entry	Temperature (°C)	Yield of <b>2a</b> (%)	<i>ee</i> of <b>2a</b> (%)
1	60	75(72 <sup>b</sup> )	98
2	25	trace	-
3	50	70	99
4	70	75	97

<sup>a</sup> The yields were determined by GC analysis using dodecane as the internal standard. The *ee* value was determined by HPLC using a chiral column. <sup>b</sup> Isolated yield.

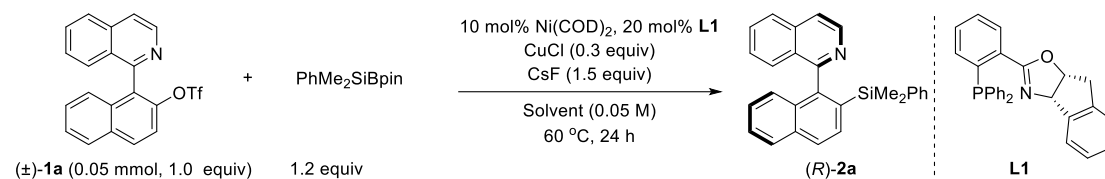
**Table S8.** Effect of the additive on nickel catalyzed atroposelective silylation of heterobiaryls <sup>a</sup>



Entry	Additive	Yield of <b>2a</b> (%)	<i>ee</i> of <b>2a</b> (%)
1	CsF	75(72 <sup>b</sup> )	98
2	none	N.R.	-
3	LiOMe	80	94
4	K <sub>3</sub> PO <sub>4</sub>	66	98
5	LiF	trace	-
6	KF	8	-
7	LiO <sup>t</sup> Bu	81	96
8 <sup>c</sup>	CsF	20	98
9 <sup>d</sup>	CsF	70	98

<sup>a</sup> The yields were determined by GC analysis using dodecane as the internal standard. The *ee* value was determined by HPLC using a chiral column. <sup>b</sup> Isolated yield. <sup>c</sup> 0.5 equiv CsF. <sup>d</sup> 1.0 equiv CsF. <sup>f</sup>

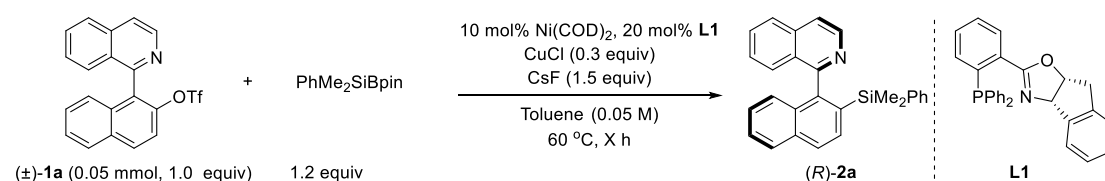
**Table S9.** Effect of solvent on nickel catalyzed atroposelective silylation of heterobiaryls <sup>a</sup>



Entry	Solvent	Yield of <b>2a</b> (%)	<i>ee</i> of <b>2a</b> (%)
1	toluene	75(72 <sup>c</sup> )	98
2	xylene	64	97
3	PhCl	61	98
4	DMF	75	89
5	DMAc	75	94
6	THF	58	92
7	1,4-dioxane	81	96
8	cyclohexane	35	85
9	CPME	67	97
10	DME	75	84
11	EtOAc	61	90
12	MeCN	58	89
13	MeOH	17	77

<sup>a</sup> The yields were determined by GC analysis using dodecane as the internal standard. The *ee* value was determined by HPLC using a chiral column. <sup>b</sup> Isolated yield.

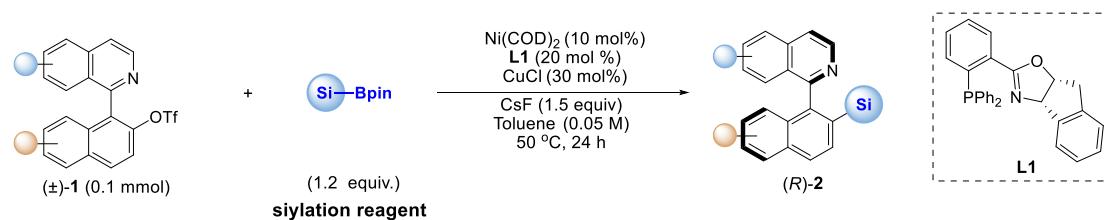
**Table S10.** Effect of the reaction time on nickel catalyzed atroposelective silylation of heterobiaryls <sup>[a]</sup>



Entry	Time	Yield of <b>2a</b> (%)	<i>ee</i> of <b>2a</b> (%)
1	24 h	75(72 <sup>b</sup> )	98
2	3 h	20	98
3	6 h	41	98
4	12 h	67	98

<sup>a</sup> The yields were determined by GC analysis using dodecane as the internal standard. The *ee* value was determined by HPLC using a chiral column. <sup>b</sup> Isolated yield.

## 2.2 General procedures for the Nickel and Copper co-catalyzed atroposelective C–Si cross-coupling



**General procedure :** In a glovebox, to a 4 mL screw-cap vial equipped with an oven-dried stirring bar were added the  $\text{Ni}(\text{COD})_2$  (2.75 mg, 0.01 mmol, 10 mol%), CuCl (3.0 mg, 0.03 mmol, 30 mol%), L1 (8.4 mg, 0.02 mmol, 20 mol%), CsF (22.8 mg, 0.15 mmol, 150 mol%), heterobiaryl triflates **1** (0.1 mmol, 1.0 equiv.), and Toluene (2.0 mL), and silylation reagent (0.12 mmol, 1.2 equiv.). After sealed with a teflon-lined screw cap, the vial was removed from the glove box and stirred at 60 °C for 24 h (the mixture was stirred at 500 rpm). After the reaction was complete, the reaction mixture was quenched by the addition of water (1 ml), the organic phase was separated and filtered through a short pad of silica gel (EtOAc) to give the crude product. Dodecane (10  $\mu\text{L}$ ) was added as an internal standard for GC analysis. The product was purified by chromatography on silica gel for each substrate.

Racemic silylation product was synthesized according to the general procedure using  $\text{PCy}_3$  as ligand in 0.025 mmol scale and was purified by PTLC for HPLC analysis.

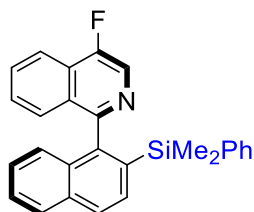
## 2.3 Characterization data of products.

### (R)-1-(2-(Dimethyl(phenyl)silyl)naphthalen-1-yl)isoquinoline (2a).

White solid, 72% (28.0 mg) isolated yield (eluent: PE:EA=10:1),  $[\alpha]_{\text{D}}^{20} = -61.02$  ( $c = 1.0$  in  $\text{CHCl}_3$ ); 98% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 96:4 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 7.85 min,  $t_{\text{R}}$  (minor) = 20.76 min.;  **$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)**  $\delta$  8.61 (d,  $J = 5.8$  Hz, 1H), 7.92 (d,  $J = 8.3$  Hz, 1H), 7.87 (d,  $J = 8.2$  Hz, 1H), 7.79 (d,  $J = 8.2$  Hz, 1H), 7.73 (d,  $J = 8.4$  Hz, 1H), 7.66 (d,  $J = 5.7$  Hz, 1H), 7.59-7.52 (m, 1H), 7.45-7.38 (m, 1H), 7.25-7.15 (m, 5H), 7.17-7.09 (m, 1H), 7.10-7.03 (m, 2H), 6.97 (d,  $J = 8.5$  Hz, 1H), 0.16 (s, 3H), -0.03 (s, 3H) ppm.  **$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  161.44, 144.03, 142.15, 138.27, 135.91,

135.72, 133.83, 133.76, 132.58, 131.53, 130.11, 129.31, 128.57, 127.98, 127.94, 127.51, 127.40, 127.08, 126.72, 126.43, 126.40, 126.24, 120.72, -1.09, -1.77 ppm. **HRMS** (ESI) calcd. for  $C_{27}H_{24}NSi^+$   $[M+H]^+$   $m/z$  390.1673, found 390.1673.

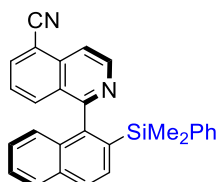
**(R)-1-(2-(Dimethyl(phenyl)silyl)naphthalen-1-yl)-4-fluoroisoquinoline (2b).**



White solid, 67% (27.3 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_D^{20} = -68.61$  ( $c = 1.0$  in  $CHCl_3$ ); 95% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 4.60 min;  $t_R$  (minor) = 5.08 min;

**$^1H$  NMR (500 MHz, Chloroform-*d*)**  $\delta$  8.41 (d,  $J = 2.0$  Hz, 1H), 8.02 (d,  $J = 8.4$  Hz, 1H), 7.96 (d,  $J = 8.3$  Hz, 1H), 7.89 (d,  $J = 8.2$  Hz, 1H), 7.79 (d,  $J = 8.3$  Hz, 1H), 7.66-7.59 (m, 1H), 7.47-7.40 (m, 1H), 7.30-7.23 (m, 1H), 7.24-7.17 (m, 2H), 7.11-7.04 (m, 3H), 7.02-6.95 (m, 2H), 6.93 (d,  $J = 8.5$  Hz, 1H), 0.25 (s, 3H), 0.13 (s, 3H) ppm.  **$^{13}C$  NMR (125 MHz, Chloroform-*d*)**  $\delta$  157.53 (d,  $J = 5.2$  Hz), 156.03, 153.96, 143.35, 137.49, 136.42, 133.81, 133.57, 132.66, 131.41, 130.44 (d,  $J = 2.9$  Hz), 130.23 (d,  $J = 1.2$  Hz), 128.51, 128.06, 127.84, 127.77, 127.76, 127.23, 127.06, 126.51, 126.36, 126.42 (d,  $J = 15.2$  Hz), 126.23, 119.65 (d,  $J = 4.1$  Hz), -1.01, -1.54 ppm.  **$^{19}F$  NMR (470 MHz,  $CDCl_3$ )**  $\delta$  -140.4 ppm. **HRMS** (ESI) calcd. for  $C_{27}H_{23}FNSi^+$   $[M+H]^+$   $m/z$  408.1578, found 408.1578.

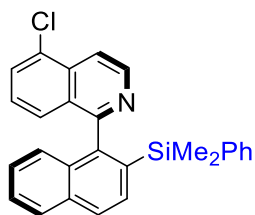
**(R)-1-(2-(Dimethyl(phenyl)silyl)naphthalen-1-yl)isoquinoline-5-carbonitrile (2c).**



White solid, 42% (17.5 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_D^{20} = -58.69$  ( $c = 1.0$  in  $CHCl_3$ ); 96% *ee*, determined by HPLC analysis (Chiralpak OD-3 column, *n*-hexane/*i*-PrOH = 70:30 (v/v), flow rate 0.7 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 7.04 min;  $t_R$  (minor) = 17.74 min;  **$^1H$  NMR (500**

**MHz, Chloroform-*d*)**  $\delta$  8.78 (d,  $J = 5.8$  Hz, 1H), 8.00 (d,  $J = 8.3$  Hz, 1H), 7.97-7.94 (m, 1H), 7.94-7.89 (m, 2H), 7.85 (d,  $J = 8.4$  Hz, 1H), 7.48-7.43 (m, 1H), 7.40-7.37 (m, 1H), 7.22-7.16 (m, 2H), 7.05-6.99 (m, 1H), 6.98-6.93 (m, 2H), 6.90 (t,  $J = 7.4$  Hz, 2H), 6.82 (d,  $J = 8.4$  Hz, 1H), 0.33 (s, 3H), 0.18 (s, 3H) ppm.  **$^{13}C$  NMR (125 MHz, Chloroform-*d*)**  $\delta$  162.44, 144.49, 142.69, 137.13, 136.35, 136.16, 135.22, 133.79, 133.40, 133.21, 132.43, 131.29, 128.51, 128.47, 128.19, 128.12, 127.22, 126.68, 126.62, 126.11, 125.95, 117.89, 116.90, 109.58, -0.92, -1.61 ppm. **HRMS** (ESI) calcd. for  $C_{28}H_{23}N_2Si^+$   $[M+H]^+$   $m/z$  415.1625, found 415.1625.

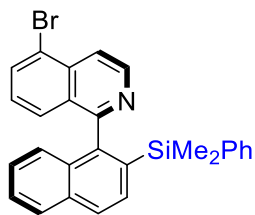
**(R)-5-Chloro-1-(2-(dimethyl(phenyl)silyl)naphthalen-1-yl)isoquinoline (2d).**



Colorless oil, 37% (15.6 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_D^{20}$  = -65.41 ( $c = 1.0$  in  $\text{CHCl}_3$ ); 98% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 4.99 min;  $t_R$  (minor) = 9.08 min;

**$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)**  $\delta$  8.70 (d,  $J = 6.0$  Hz, 1H), 8.01 (d,  $J = 6.0$  Hz, 1H), 7.96 (d,  $J = 8.4$  Hz, 1H), 7.89 (d,  $J = 8.2$  Hz, 1H), 7.78 (d,  $J = 8.3$  Hz, 1H), 7.64-7.59 (m, 1H), 7.47-7.40 (m, 1H), 7.23-7.16 (m, 1H), 7.16-7.04 (m, 5H), 7.02-6.96 (m, 2H), 6.89 (d,  $J = 8.5$  Hz, 1H), 0.25 (s, 3H), 0.10 (s, 3H) ppm.  **$^{13}\text{C}$  NMR (125 MHz, Chloroform-*d*)**  $\delta$  161.70, 143.58, 143.18, 137.57, 136.00, 133.77, 133.73, 133.58, 132.51, 131.39, 131.16, 130.15, 129.95, 128.55, 128.06, 127.77, 127.23, 127.07, 126.79, 126.54, 126.40, 126.25, 117.16, -1.02, -1.63 ppm. **HRMS** (ESI) calcd. for  $\text{C}_{27}\text{H}_{23}\text{ClNSi}^+$   $[\text{M}+\text{H}]^+$   $m/z$  424.1283, found 424.1285.

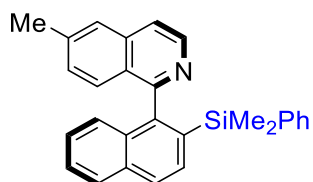
**(R)-5-Bromo-1-(2-(dimethyl(phenyl)silyl)naphthalen-1-yl)isoquinoline (2e).**



Colorless oil, 54% (25.1 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_D^{25}$  = -48.57 ( $c = 1.0$  in  $\text{CHCl}_3$ ); 95% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 5.21 min;  $t_R$  (minor) = 9.49 min;

**$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)**  $\delta$  8.69 (d,  $J = 6.0$  Hz, 1H), 7.96 (t,  $J = 6.5$  Hz, 2H), 7.89 (d,  $J = 8.2$  Hz, 1H), 7.83-7.75 (m, 2H), 7.44 (t,  $J = 7.5$  Hz, 1H), 7.22-7.15 (m, 2H), 7.09-6.95 (m, 6H), 6.88 (d,  $J = 8.6$  Hz, 1H), 0.26 (s, 3H), 0.11 (s, 3H) ppm.  **$^{13}\text{C}$  NMR (125 MHz, Chloroform-*d*)**  $\delta$  161.81, 143.50, 143.42, 137.49, 136.06, 134.96, 133.77, 133.70, 133.55, 132.52, 131.38, 130.30, 128.57, 128.06, 127.80, 127.78, 127.31, 127.21, 126.54, 126.41, 126.26, 121.78, 119.74, -1.01, -1.61 ppm. **HRMS** (ESI) calcd. for  $\text{C}_{27}\text{H}_{23}\text{BrNSi}^+$   $[\text{M}+\text{H}]^+$   $m/z$  468.0778, found 468.0772.

**(R)-1-(2-(Dimethyl(phenyl)silyl)naphthalen-1-yl)-6-methylisoquinoline (2f).**



Colorless oil, 68% (27.3 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_D^{20} = -65.26$  ( $c = 1.0$  in  $\text{CHCl}_3$ ); 98% *ee*, determined by HPLC analysis (Chiralpak IA-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 6.11 min;  $t_R$

(minor) = 14.52 min;  **$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)**  $\delta$  8.58 (d,  $J = 5.7$  Hz, 1H), 7.93-7.85

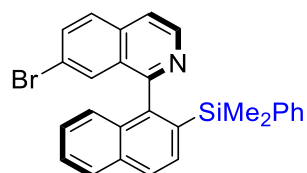
(m, 2H), 7.71 (d,  $J = 8.4$  Hz, 1H), 7.62-7.55 (m, 2H), 7.45-7.40 (m, 1H), 7.24-7.09 (m, 7H), 7.05-6.98 (m, 2H), 2.49 (s, 3H), 0.17 (s, 3H), -0.06 (s, 3H) ppm.  $^{13}\text{C}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  161.03, 144.25, 142.31, 140.46, 138.56, 136.28, 135.59, 133.93, 133.77, 132.60, 131.56, 129.35, 128.52, 127.95, 127.78, 127.76, 127.45, 127.40, 126.44, 126.41, 126.20, 125.64, 120.22, 22.05, -1.09, -1.84 ppm. HRMS (ESI) calcd. for  $\text{C}_{28}\text{H}_{26}\text{NSi}^+$   $[\text{M}+\text{H}]^+$   $m/z$  404.1829, found 404.1837.

**(R)-1-(2-(dimethyl(phenyl)silyl)naphthalen-1-yl)-7-methoxyisoquinoline (2g).**



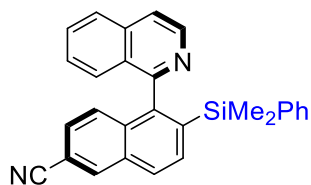
Colorless oil, 70% (29.6 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_{\text{D}}^{20} = -53.45$  ( $c = 1.0$  in  $\text{CHCl}_3$ ); 98% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 0.7 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 6.64 min;  $t_{\text{R}}$  (minor) = 12.77 min;  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.54 (d,  $J = 5.6$  Hz, 1H), 7.95-7.90 (m, 1H), 7.90-7.85 (m, 1H), 7.80-7.70 (m, 2H), 7.65-7.60 (m, 1H), 7.47-7.40 (m, 1H), 7.27-7.18 (m, 3H), 7.20-7.12 (m, 4H), 7.12 - 7.05 (m, 2H), 7.04-6.98 (m, 1H), 6.40 (d,  $J = 2.6$  Hz, 1H), 3.36 (s, 3H), 0.24 (s, 3H), -0.05 (s, 3H) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.78, 158.11, 144.20, 140.44, 138.49, 135.55, 133.89, 133.78, 132.43, 131.68, 131.50, 130.42, 128.64, 128.34, 127.96, 127.50, 127.40, 126.45, 126.37, 126.23, 123.20, 120.41, 105.44, 55.18, -0.94, -1.98 ppm. HRMS (ESI) calcd. for  $\text{C}_{28}\text{H}_{26}\text{NOSi}^+$   $[\text{M}+\text{H}]^+$   $m/z$  420.1778, found 420.1783.

**(R)-7-Bromo-1-(2-(dimethyl(phenyl)silyl)naphthalen-1-yl)isoquinoline (2h).**



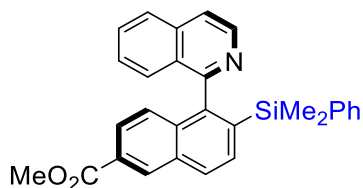
White solid, 52% (24.3 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_{\text{D}}^{20} = -37.51$  ( $c = 1.0$  in  $\text{CHCl}_3$ ); 96% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 5.20 min;  $t_{\text{R}}$  (major) = 8.82 min;  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.63 (d,  $J = 5.7$  Hz, 1H), 7.97 (d,  $J = 8.4$  Hz, 1H), 7.90 (d,  $J = 8.2$  Hz, 1H), 7.80 (d,  $J = 8.4$  Hz, 1H), 7.64-7.58 (m, 3H), 7.47-7.43 (m, 1H), 7.32-7.31 (m, 1H), 7.26-7.18 (m, 1H), 7.09-7.05 (m, 3H), 7.04-7.00 (m, 2H), 6.89 (d,  $J = 8.4$  Hz, 1H), 0.27 (s, 3H), 0.09 (s, 3H) ppm.  $^{13}\text{C}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  160.60, 143.18, 142.53, 137.65, 135.96, 134.33, 133.88, 133.67, 133.55, 132.49, 131.37, 130.20, 129.98, 128.67, 128.46, 128.12, 127.89, 127.36, 126.59, 126.49, 126.09, 121.04, 120.45, -1.01, -1.71 ppm. HRMS (ESI) calcd. for  $\text{C}_{27}\text{H}_{23}\text{BrNSi}^+$   $[\text{M}+\text{H}]^+$   $m/z$  468.0778, found 468.0781.

**(R)-6-(Dimethyl(phenyl)silyl)-5-(isoquinolin-1-yl)-2-naphthonitrile (2i).**



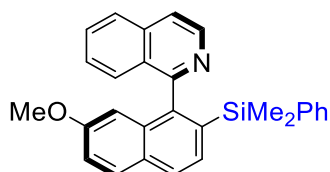
White solid, 78% (32.5 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_D^{20} = -91.92$  ( $c = 1.0$  in  $\text{CHCl}_3$ ); 91% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 80:20 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 14.41 min;  $t_R$  (minor) = 22.64 min;  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  8.62 (d,  $J = 5.7$  Hz, 1H), 8.28 (d,  $J = 1.7$  Hz, 1H), 7.97 (d,  $J = 8.4$  Hz, 1H), 7.89-7.81 (m, 2H), 7.71 (d,  $J = 5.7$  Hz, 1H), 7.64-7.57 (m, 1H), 7.35-7.29 (m, 1H), 7.29-7.22 (m, 1H), 7.18-7.11 (m, 4H), 7.10-7.03 (m, 3H), 0.20 (s, 3H), -0.00 (s, 3H) ppm.  $^{13}\text{C NMR}$  (125 MHz, Chloroform-*d*)  $\delta$  160.04, 144.27, 142.22, 140.52, 137.30, 135.99, 134.22, 133.75, 133.59, 133.43, 132.56, 130.40, 129.09, 128.86, 127.74, 127.70, 127.54, 127.46, 127.36, 126.98, 126.72, 121.21, 119.22, 109.90, -1.27, -1.97 ppm. HRMS (ESI) calcd. for  $\text{C}_{28}\text{H}_{23}\text{N}_2\text{Si}^+$   $[\text{M}+\text{H}]^+$   $m/z$  415.1625, found 415.1628.

**(R)-Methyl 6-(dimethyl(phenyl)silyl)-5-(isoquinolin-1-yl)-2-naphthoate (2j).**



Yellow oil, 84% (37.5 mg) isolated yield (eluent: PE:EA=1:1),  $[\alpha]_D^{25} = -107.18$  ( $c = 1.0$  in  $\text{CHCl}_3$ ); 97% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 14.59 min;  $t_R$  (minor) = 26.34 min;  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  8.67-8.60 (m, 2H), 8.03 (d,  $J = 8.4$  Hz, 1H), 7.85-7.74 (m, 3H), 7.69 (d,  $J = 5.7$  Hz, 1H), 7.62-7.55 (m, 1H), 7.26-7.11 (m, 5H), 7.10-7.04 (m, 2H), 7.02 (d,  $J = 8.9$  Hz, 1H), 3.94 (s, 3H), 0.20 (s, 3H), -0.01 (s, 3H) ppm.  $^{13}\text{C NMR}$  (125 MHz, Chloroform-*d*)  $\delta$  167.21, 160.76, 144.00, 142.17, 139.14, 137.73, 135.97, 134.45, 133.79, 132.86, 132.44, 131.10, 130.25, 129.19, 128.78, 128.72, 127.79, 127.66, 127.47, 127.27, 126.86, 126.70, 125.56, 121.00, 52.34, -1.19, -1.89 ppm. HRMS (ESI)  $m/z$  calculated for  $\text{C}_{29}\text{H}_{25}\text{NO}_2\text{Si}^+$   $[\text{M}+\text{H}]^+$ : 448.1727, found 448.1773.

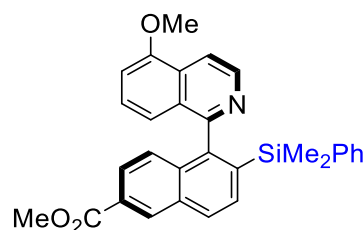
**(R)-1-(2-(Dimethyl(phenyl)silyl)-7-methoxynaphthalen-1-yl)isoquinoline (2k).**



Colorless oil, 79% (32.2 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_D^{20} = -128.64$  ( $c = 1.0$  in  $\text{CHCl}_3$ ); 98% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 5.85 min;  $t_R$  (minor) = 12.23 min;  $^1\text{H NMR}$

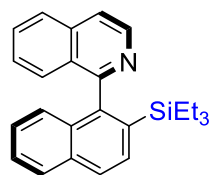
(400 MHz, CDCl<sub>3</sub>) δ 8.62 (d, *J* = 5.7 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.83-7.76 (m, 2H), 7.66 (d, *J* = 5.7 Hz, 1H), 7.64-7.54 (m, 2H), 7.32-7.25 (m, 1H), 7.25-7.02 (m, 7H), 6.24 (d, *J* = 2.5 Hz, 1H), 3.40 (s, 3H), 0.14 (s, 3H), -0.02 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.58, 157.70, 142.66, 142.22, 138.38, 136.25, 135.95, 133.82, 133.58, 130.13, 129.52, 129.51, 129.47, 129.12, 128.52, 127.97, 127.38, 127.21, 127.09, 126.72, 120.72, 118.86, 105.11, 55.04, -1.08, -1.73 ppm. HRMS (ESI) calcd. for C<sub>28</sub>H<sub>26</sub>NOSi<sup>+</sup> [M+H]<sup>+</sup> *m/z* 420.1778, found 420.1779.

**(*R*)-Methyl 6-(dimethyl(phenyl)silyl)-5-(5-methoxyisoquinolin-1-yl)-2-naphthoate (21).**



White solid, 52% (24.7 mg) isolated yield (eluent: PE:EA=20:1), [α]<sub>D</sub><sup>20</sup> = -91.26 (*c* = 1.0 in CHCl<sub>3</sub>); 95% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 85:15 (v/v), flow rate 1.0 mL/min, λ = 254 nm, 25 °C), *t<sub>R</sub>* (major) = 14.30 min; *t<sub>R</sub>* (major) = 18.92 min; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.62 (d, *J* = 5.8 Hz, 2H), 8.09-8.06 (m, 1H), 8.02-7.98 (m, 1H), 7.78-7.74 (m, 2H), 7.23-7.19 (m, 2H), 7.17-7.08 (m, 4H), 7.02 (d, *J* = 8.8 Hz, 1H), 6.92-6.89 (m, 1H), 6.79-6.75 (m, 1H), 4.04 (s, 3H), 3.94 (s, 3H), 0.17 (s, 3H), -0.02 (s, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 167.26, 160.02, 154.66, 144.36, 141.85, 139.04, 137.88, 134.44, 133.86, 132.84, 132.46, 131.08, 129.95, 128.72, 128.68, 128.67, 127.74, 127.46, 127.24, 126.77, 125.50, 119.50, 115.42, 107.44, 55.86, 52.34, -1.25, -1.85 ppm. HRMS (ESI) calcd. for C<sub>30</sub>H<sub>27</sub>NO<sub>3</sub>Si<sup>+</sup> [M+H]<sup>+</sup> *m/z* 478.1833, found 478.1836.

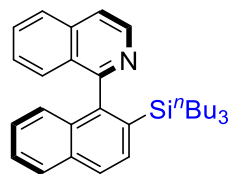
**(*R*)-1-(2-(Triethylsilyl)naphthalen-1-yl)isoquinoline (2m).**



White solid, 86% (31.7 mg) isolated yield (eluent: PE:EA=10:1), [α]<sub>D</sub><sup>20</sup> = -42.88 (*c* = 1.0 in CHCl<sub>3</sub>); 99% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 96:4 (v/v), flow rate 1.0 mL/min, λ = 254 nm, 25 °C), *t<sub>R</sub>* (major) = 5.30 min; *t<sub>R</sub>* (minor) = 6.01 min; <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 5.7 Hz, 1H), 7.99-7.87 (m, 3H), 7.82-7.76 (m, 2H), 7.69-7.62 (m, 1H), 7.46-7.39 (m, 1H), 7.42-7.36 (m, 1H), 7.37-7.30 (m, 1H), 7.23-7.16 (m, 1H), 6.97 (d, *J* = 8.6 Hz, 1H), 0.72 (t, *J* = 7.9 Hz, 9H), 0.39-0.11 (m, 6H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.91, 144.10, 142.28, 135.97, 135.05, 133.59, 132.73, 131.52, 130.32, 129.49, 128.15, 127.90, 127.20, 127.10, 126.88, 126.39,

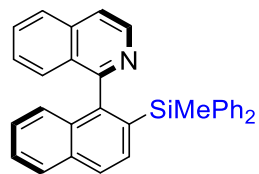
126.24, 126.11, 120.59, 7.51, 3.51 ppm. **HRMS** (ESI) calcd. for  $C_{25}H_{28}NSi^+$   $[M+H]^+$   $m/z$  370.1986, found 370.1992.

**(R)-1-(2-(Tributylsilyl)naphthalen-1-yl)isoquinoline (2n).**



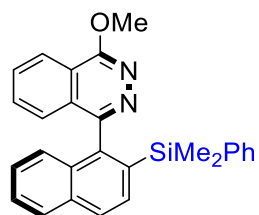
Colorless oil, 66% (29.9 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_D^{20} = -45.69$  ( $c = 1.0$  in  $CHCl_3$ ); 99% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 99:1 (v/v), flow rate 0.2 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 20.50 min;  $t_R$  (major) = 21.59 min;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )** 8.69 (d,  $J = 5.7$  Hz, 1H), 7.97-7.87 (m, 3H), 7.81-7.75 (m, 2H), 7.69-7.62 (m, 1H), 7.45-7.37 (m, 2H), 7.36-7.31 (m, 1H), 7.23-7.16 (m, 1H), 6.99 (d,  $J = 8.5$  Hz, 1H), 1.13-0.96 (m, 12H), 0.73 (t,  $J = 6.9$  Hz, 9H), 0.36-0.11 (m, 6H) ppm.  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  161.96, 143.95, 142.39, 136.09, 135.77, 133.55, 132.70, 131.55, 130.26, 129.50, 128.21, 127.90, 127.17, 127.09, 126.84, 126.45, 126.20, 126.09, 120.52, 26.73, 26.03, 13.74, 12.47 ppm. **HRMS** (ESI) calcd. for  $C_{31}H_{40}NSi^+$   $[M+H]^+$   $m/z$  454.2925, found 454.2927.

**(R)-1-(2-(methylphenylsilyl)naphthalen-1-yl)isoquinoline (2o).**



Colorless oil, 82% (36.9 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_D^{20} = -26.76$  ( $c = 1.0$  in  $CHCl_3$ ); 98% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 96:4 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 7.07 min;  $t_R$  (major) = 14.01 min;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  8.48 (d,  $J = 5.7$  Hz, 1H), 7.90 (t,  $J = 8.2$  Hz, 2H), 7.70 (dd,  $J = 8.4, 4.6$  Hz, 2H), 7.53-7.49 (m, 2H), 7.47-7.44 (m, 1H), 7.33-7.31 (m, 2H), 7.26-7.05 (m, 11H), 7.00-6.99 (m, 1H), 0.17 (s, 3H) ppm.  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  161.08, 144.95, 142.00, 136.76, 135.96, 135.79, 135.09, 134.93, 133.94, 133.84, 132.72, 132.62, 129.92, 129.12, 128.89, 128.80, 128.02, 127.90, 127.55, 127.38, 126.87, 126.66, 126.62, 126.54, 126.31, 120.77, -2.58 ppm. **HRMS** (ESI) calcd. for  $C_{32}H_{26}NSi^+$   $[M+H]^+$   $m/z$  452.1829, found 454.2927.

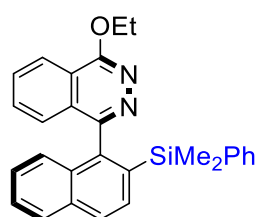
**(R)-1-(2-(Dimethyl(phenyl)silyl)naphthalen-1-yl)-4-methoxyphthalazine (2p).**



White solid, 73% (30.9 mg) isolated yield (eluent: PE:EA=10:1),  $[\alpha]_D^{20} = -83.39$  ( $c = 1.0$  in  $CHCl_3$ ); 97% *ee*, determined by HPLC analysis (Chiralpak IA-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 12.59 min;  $t_R$  (major) = 23.51

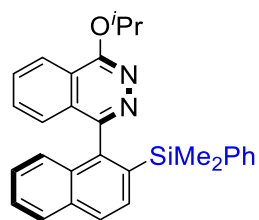
min; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.43 (dt, *J* = 15.3, 7.6 Hz, 2H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 3H), 7.00-6.95 (m, 2H), 6.86 (t, *J* = 7.4 Hz, 2H), 4.36 (s, 3H), 0.41 (s, 3H), 0.31 (s, 3H) ppm. **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 160.41, 157.75, 140.88, 137.43, 137.02, 133.73, 133.59, 132.86, 131.54, 131.36, 131.20, 129.98, 128.34, 128.06, 128.03, 126.97, 126.49, 126.39, 126.38, 126.30, 122.85, 119.29, 55.01, -0.76, -1.23 ppm. **HRMS (ESI)** calcd. for C<sub>27</sub>H<sub>24</sub>N<sub>2</sub>NaOSi<sup>+</sup> [M+Na]<sup>+</sup> *m/z* 443.1550, found 443.1549.

**(R)-1-(2-(Dimethyl(phenyl)silyl)naphthalen-1-yl)-4-ethoxyphthalazine (2q).**



White solid, 56% (24.4 mg) isolated yield (eluent: PE:EA=10:1), [α]<sub>D</sub><sup>20</sup> = -67.83 (*c* = 1.0 in CHCl<sub>3</sub>); 96% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min, λ = 254 nm, 25 °C), *t<sub>R</sub>* (major) = 9.97 min; *t<sub>R</sub>* (minor) = 18.25 min; **<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)** δ 8.08 (d, *J* = 8.3, 1.0 Hz, 1H), 7.98 (d, *J* = 8.3, 0.9 Hz, 1H), 7.93-7.87 (m, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.67-7.61 (m, 1H), 7.46-7.38 (m, 2H), 7.23-7.18 (m, 1H), 7.09-6.93 (m, 5H), 6.87 (t, *J* = 7.5 Hz, 2H), 4.82 (qd, *J* = 7.0, 1.8 Hz, 2H), 1.63 (t, *J* = 7.1 Hz, 3H), 0.40 (s, 3H), 0.30 (s, 3H) ppm. **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 160.18, 157.45, 140.99, 137.42, 137.14, 133.73, 133.60, 132.87, 131.47, 131.39, 131.10, 129.98, 128.34, 128.05, 127.99, 127.02, 126.48, 126.41, 126.35, 126.28, 122.93, 119.36, 63.41, 14.86, -0.75, -1.25 ppm. **HRMS (ESI)** calcd. for C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>OSi<sup>+</sup> [M+H]<sup>+</sup> *m/z* 435.1887, found 435.1888.

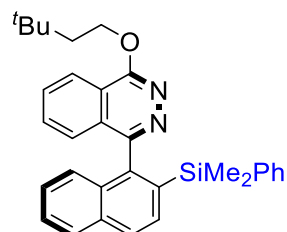
**(R)-1-(2-(Dimethyl(phenyl)silyl)naphthalen-1-yl)-4-isopropoxyphthalazine (2r).**



White solid, 90% (41.7 mg) isolated yield (eluent: PE:EA=20:1), [α]<sub>D</sub><sup>20</sup> = -81.86 (*c* = 1.0 in CHCl<sub>3</sub>); 96% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min, λ = 254 nm, 25 °C), *t<sub>R</sub>* (minor) = 36.14 min; *t<sub>R</sub>* (major) = 38.43 min; **<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)** δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.48-7.41 (m, 1H), 7.42-7.35 (m, 1H), 7.24-7.17 (m, 1H), 7.10-7.02 (m, 3H), 7.00-6.92 (m, 2H), 6.86 (t, *J* = 7.4 Hz, 2H), 5.87 (hept, *J* = 6.0 Hz, 1H), 1.64 (d, *J* = 6.1 Hz, 3H), 1.57 (d, *J* = 6.1 Hz, 3H), 0.41 (s, 3H), 0.33 (s, 3H) ppm. **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 159.70, 157.01, 141.16, 137.43, 137.14, 133.72, 133.54,

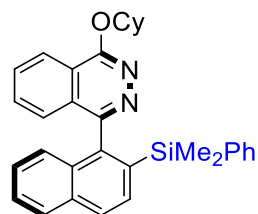
132.88, 131.39, 131.32, 130.94, 129.99, 128.30, 128.03, 127.93, 127.03, 126.47, 126.44, 126.33, 126.22, 122.99, 119.65, 69.89, 22.32, -0.72, -1.26 ppm. **HRMS** (ESI) calcd. for C<sub>29</sub>H<sub>29</sub>N<sub>2</sub>OSi<sup>+</sup> [M+H]<sup>+</sup> m/z 449.2044, found 449.2046.

**(R)-1-(2-(dimethyl(phenyl)silyl)naphthalen-1-yl)-4-(3,3-dimethylbutoxy)phthalazine (2s).**



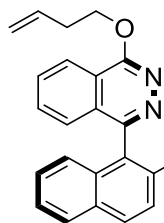
White solid, 80% (39.2 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_{\text{D}}^{20} = -54.38$  ( $c = 1.0$  in CHCl<sub>3</sub>); 97% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 6.93 min;  $t_{\text{R}}$  (minor) = 17.84 min; **<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)**  $\delta$  8.05 (d,  $J = 8.2$  Hz, 1H), 7.98 (d,  $J = 8.3$  Hz, 1H), 7.90 (d,  $J = 8.2$  Hz, 1H), 7.81 (d,  $J = 8.4$  Hz, 1H), 7.67-7.60 (m, 1H), 7.48-7.37 (m, 2H), 7.24-7.17 (m, 1H), 7.08-7.01 (m, 3H), 7.02-6.94 (m, 2H), 6.88 (t,  $J = 7.4$  Hz, 2H), 4.86-4.75 (m, 2H), 1.96 (t,  $J = 7.1$  Hz, 2H), 1.13 (s, 9H), 0.40 (s, 3H), 0.30 (s, 3H) ppm. **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  161.50, 158.64, 142.22, 138.60, 138.40, 134.95, 134.86, 134.11, 132.69, 132.61, 132.37, 131.22, 129.57, 129.28, 129.21, 128.25, 127.71, 127.66, 127.59, 127.50, 124.16, 120.62, 66.54, 43.80, 31.40, 31.30, 0.49, 0.00 ppm. **HRMS** (ESI) calcd. for C<sub>32</sub>H<sub>35</sub>N<sub>2</sub>OSi<sup>+</sup> [M+H]<sup>+</sup> m/z 491.2513, found 491.2517.

**(R)-1-(Cyclohexyloxy)-4-(2-(dimethyl(phenyl)silyl)naphthalen-1-yl)phthalazine (2t).**



White solid, 86% (42.2 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_{\text{D}}^{20} = -60.74$  ( $c = 1.0$  in CHCl<sub>3</sub>); 96% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 6.41 min;  $t_{\text{R}}$  (major) = 13.42 min; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.11-8.04 (m, 1H), 8.01-7.94 (m, 1H), 7.93-7.86 (m, 1H), 7.82 (d,  $J = 8.3$  Hz, 1H), 7.66-7.57 (m, 1H), 7.48-7.40 (m, 1H), 7.42-7.34 (m, 1H), 7.25-7.16 (m, 1H), 7.09-7.00 (m, 3H), 7.01-6.90 (m, 2H), 6.89-6.81 (m, 2H), 5.65 (tt,  $J = 8.5, 3.8$  Hz, 1H), 2.35-2.16 (m, 2H), 1.97-1.74 (m, 5H), 1.68-1.48 (m, 3H), 0.41 (s, 3H), 0.33 (s, 3H) ppm. **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  159.65, 156.98, 141.15, 137.40, 137.12, 133.71, 133.55, 132.89, 131.37, 131.32, 130.94, 130.05, 128.29, 128.03, 127.92, 127.04, 126.48, 126.44, 126.33, 126.22, 123.02, 119.73, 74.46, 31.92, 31.88, 25.95, 24.03, 23.97, -0.72, -1.23 ppm. **HRMS** (ESI) calcd. for C<sub>32</sub>H<sub>33</sub>N<sub>2</sub>OSi<sup>+</sup> [M+H]<sup>+</sup> m/z 489.2357, found 489.2357.

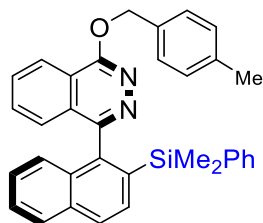
**(R)-1-(But-3-en-1-yloxy)-4-(2-(dimethyl(phenyl)silyl)naphthalen-1-yl)phthalazine (2u).**



Colorless oil, 78% (35.8 mg) isolated yield (eluent: PE:EA=20:1),  $[\alpha]_{\text{D}}^{20} = -67.47$  ( $c = 1.0$  in  $\text{CHCl}_3$ ); 97% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 9.64 min;  $t_{\text{R}}$  (minor) = 19.31

min;  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  8.09-8.04 (m, 1H), 8.00-7.96 (m, 1H), 7.92-7.88 (m, 1H), 7.82 (d,  $J = 8.3$  Hz, 1H), 7.66-7.62 (m, 1H), 7.47-7.39 (m, 2H), 7.23-7.19 (m, 1H), 7.07-7.02 (m, 3H), 7.00-6.95 (m, 2H), 6.87 (t,  $J = 7.5$  Hz, 2H), 6.08 (ddt,  $J = 17.0, 10.2, 6.7$  Hz, 1H), 5.32 (dq,  $J = 17.2, 1.7$  Hz, 1H), 5.21 (dq,  $J = 10.2, 1.3$  Hz, 1H), 4.82 (t,  $J = 6.6$  Hz, 2H), 2.81-2.76 (m, 2H), 0.41 (s, 3H), 0.31 (s, 3H) ppm.  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.13, 157.58, 140.89, 137.41, 137.06, 134.86, 133.72, 133.57, 132.84, 131.53, 131.36, 131.17, 130.00, 128.34, 128.05, 128.01, 127.01, 126.48, 126.37, 126.29, 122.87, 119.31, 117.22, 66.58, 33.64, -0.76, -1.24 ppm. HRMS (ESI) calcd. for  $\text{C}_{30}\text{H}_{29}\text{N}_2\text{OSi}^+$   $[\text{M}+\text{H}]^+$   $m/z$  461.2044, found 461.2045.

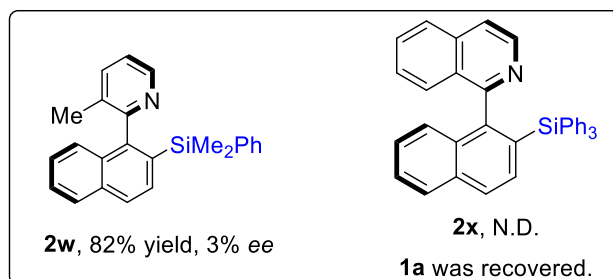
**(R)-1-(2-(Dimethyl(phenyl)silyl)naphthalen-1-yl)-4-((4-methylbenzyl)oxy)phthalazine (2v).**



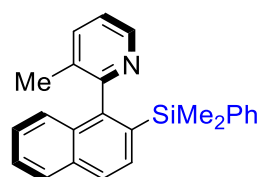
White solid, 78% (38.8 mg) isolated yield (eluent: PE:EA=12:1),  $[\alpha]_{\text{D}}^{20} = -67.84$  ( $c = 1.0$  in  $\text{CHCl}_3$ ); 97% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 11.28 min;  $t_{\text{R}}$  (major) = 19.31

min;  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  8.08 (d,  $J = 8.2$  Hz, 1H), 7.99 (d,  $J = 8.2$  Hz, 1H), 7.91 (d,  $J = 8.2$  Hz, 1H), 7.84 (d,  $J = 8.3$  Hz, 1H), 7.64-7.57 (m, 3H), 7.47-7.43 (m, 1H), 7.42-7.38 (m, 1H), 7.30 (d,  $J = 7.6$  Hz, 2H), 7.23-7.19 (m, 1H), 7.06 (d,  $J = 8.6$  Hz, 1H), 7.02-6.93 (m, 4H), 6.81 (t,  $J = 7.4$  Hz, 2H), 5.77 (q,  $J = 12.1$  Hz, 2H), 2.43 (s, 3H), 0.42 (s, 3H), 0.34 (s, 3H) ppm.  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.07, 157.82, 140.89, 138.13, 137.53, 136.97, 134.07, 133.74, 133.57, 132.85, 131.57, 131.37, 131.17, 130.04, 129.38, 128.82, 128.33, 128.07, 128.06, 126.99, 126.51, 126.40, 126.32, 122.99, 119.34, 69.14, 21.44, -0.73, -1.20 ppm. HRMS (ESI) calcd. for  $\text{C}_{34}\text{H}_{31}\text{N}_2\text{OSi}^+$   $[\text{M}+\text{H}]^+$   $m/z$  511.2200, found 511.2200.

## 2.4 Inefficient heterobiaryl triflates or silylation reagent.



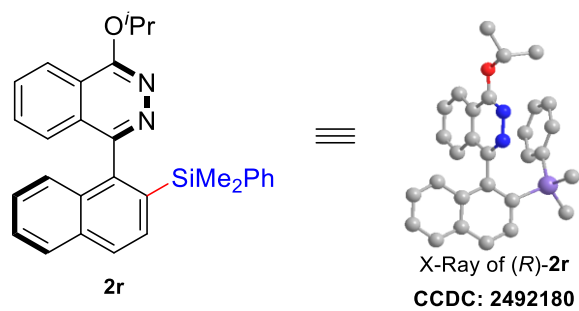
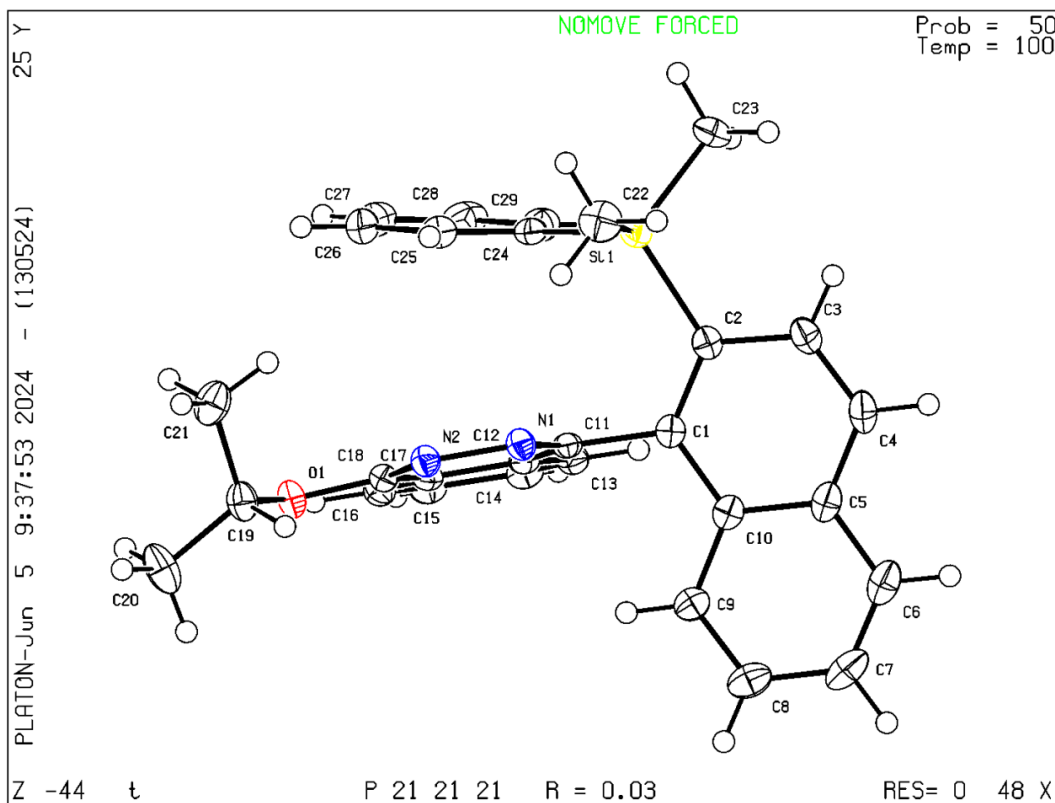
### (*R*)-2-(2-(Dimethyl(phenyl)silyl)naphthalen-1-yl)-3-methylpyridine (**2w**).



Colorless oil, 82% (28.9 mg) isolated yield (eluent: PE:EA=10:1),  $[\alpha]_{\text{D}}^{20} = -11.13$  ( $c = 1.0$  in  $\text{CHCl}_3$ ); 3% *ee*, determined by HPLC analysis (Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 90:10 (v/v), flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 5.19 min;  $t_{\text{R}}$  (major) = 8.58 min;  **$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)**  $\delta$  8.56 (d,  $J = 4.9$  Hz, 1H), 7.88-7.81 (m, 2H), 7.69 (d,  $J = 8.3$  Hz, 1H), 7.62-7.37 (m, 3H), 7.38-7.31 (m, 3H), 7.35-7.25 (m, 4H), 7.27-7.20 (m, 3H), 7.09 (d,  $J = 8.5$  Hz, 1H), 1.74 (s, 3H), 0.36 (s, 3H), 0.17 (s, 3H) ppm.  **$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  159.20, 146.71, 145.38, 138.87, 137.36, 134.06, 133.92, 133.71, 133.16, 131.64, 131.52, 128.81, 128.17, 127.63, 127.09, 126.42, 126.35, 125.47, 123.04, 19.01, -0.99, -1.80 ppm. **HRMS** (ESI) calcd. for  $\text{C}_{24}\text{H}_{24}\text{NSi}^+$   $[\text{M}+\text{H}]^+$   $m/z$  354.1673, found 354.1674.

## 2.5 Crystal data of compounds **2r**.

The crystals suitable for single-crystal structure analysis was obtained via evaporation method of compounds **2r** DCM/*n*-Hexane. The absolute configuration of the **2r** was determined to be *R* configuration via X-ray crystal structure analysis (CCDC number: 2492180).



**Figure S1.** X-ray crystal structure of (*R*)-**2r**

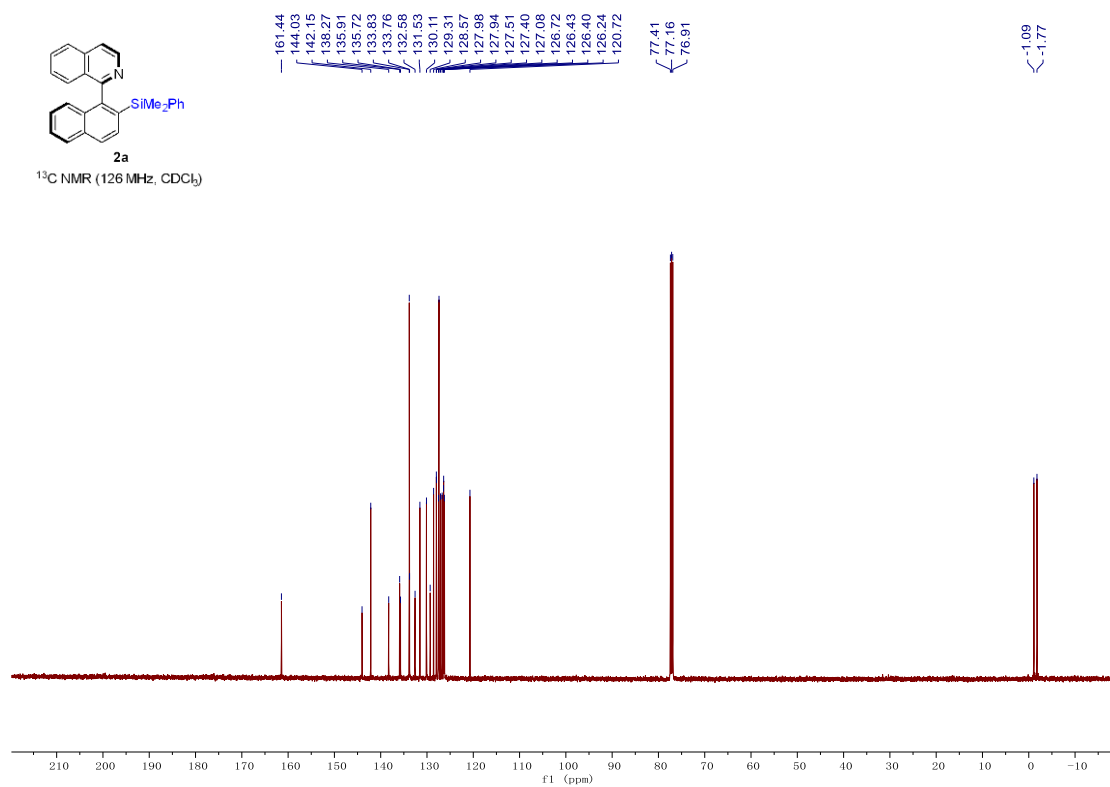
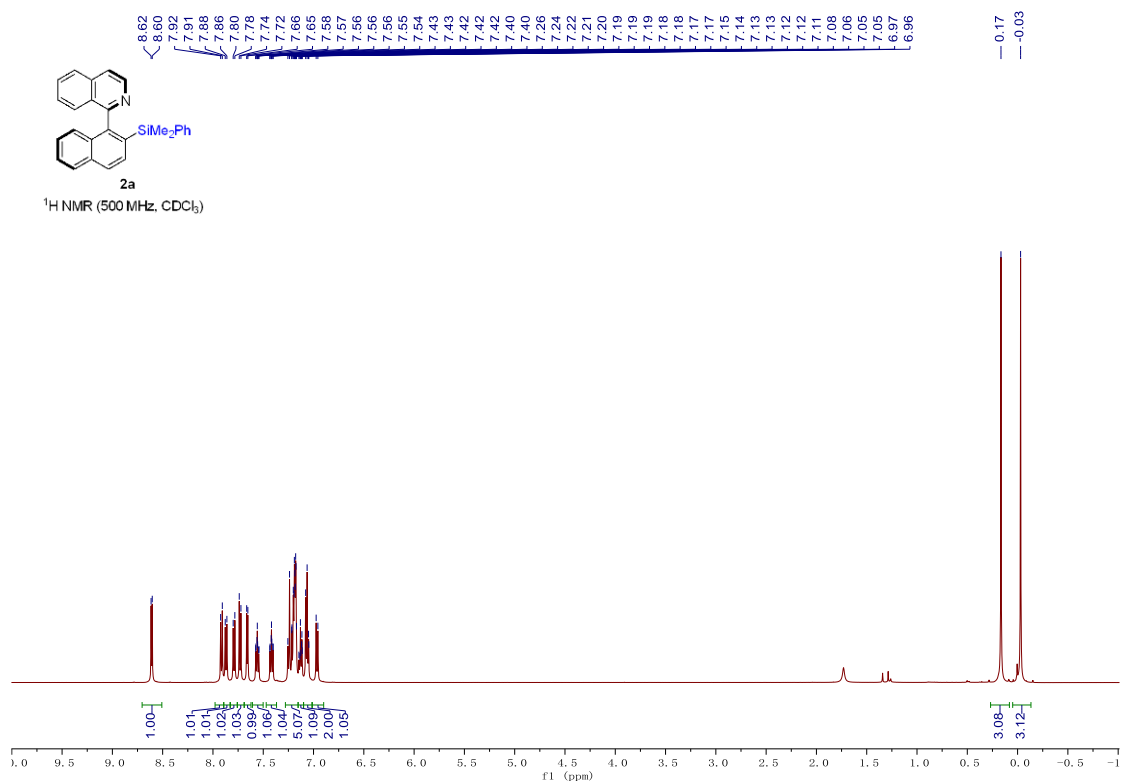
**Table S11. Crystal data and structure refinement for 2r**

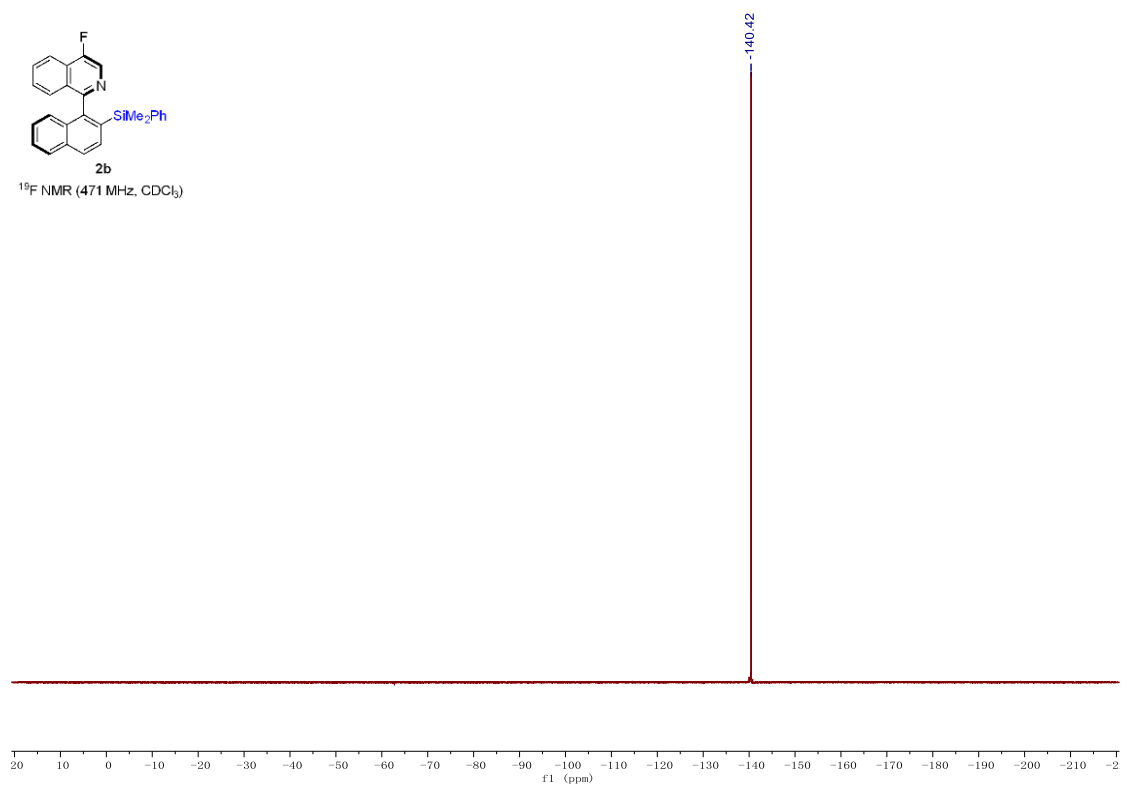
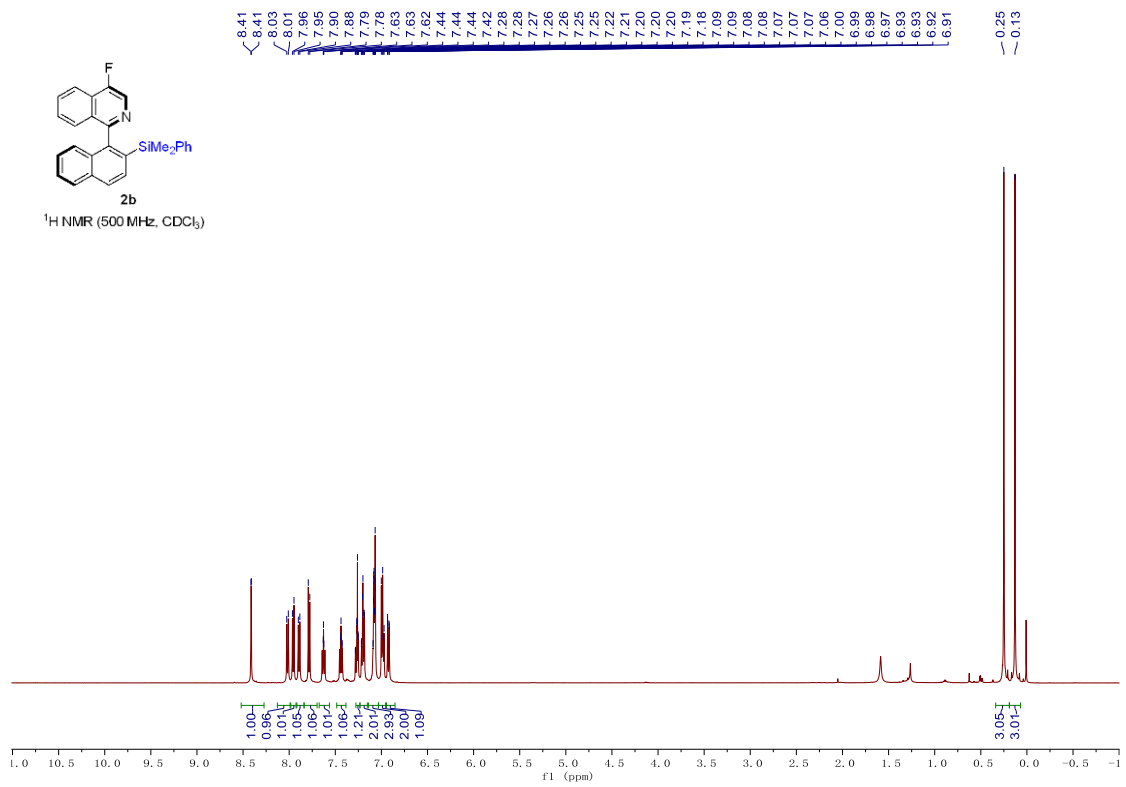
Identification code	<b>2r</b>	
Empirical formula	C <sub>29</sub> H <sub>28</sub> N <sub>2</sub> O <sub>Si</sub>	
Formula weight	448.62	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	
Unit cell dimensions	a = 11.12920(10) Å	α = 90°.
	b = 12.8003(2) Å	β = 90°.
	c = 16.8233(2) Å	γ = 90°.
Volume	2396.60(5) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.243 Mg/m <sup>3</sup>	
Absorption coefficient	1.042 mm <sup>-1</sup>	
F(000)	952	
Crystal size	0.180 x 0.160 x 0.140 mm <sup>3</sup>	
Theta range for data collection	4.340 to 76.348°.	
Index ranges	-8<=h<=13, -16<=k<=16, -21<=l<=20	
Reflections collected	29026	
Independent reflections	4951 [R(int) = 0.0269]	
Completeness to theta = 67.684°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.83897	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4951 / 0 / 303	
Goodness-of-fit on F <sup>2</sup>	1.036	
Final R indices [I>2σ(I)]	R1 = 0.0273, wR2 = 0.0687	
R indices (all data)	R1 = 0.0294, wR2 = 0.0696	
Absolute structure parameter	-0.003(7)	
Extinction coefficient	0.00080(18)	
Largest diff. peak and hole	0.168 and -0.203 e.Å <sup>-3</sup>	

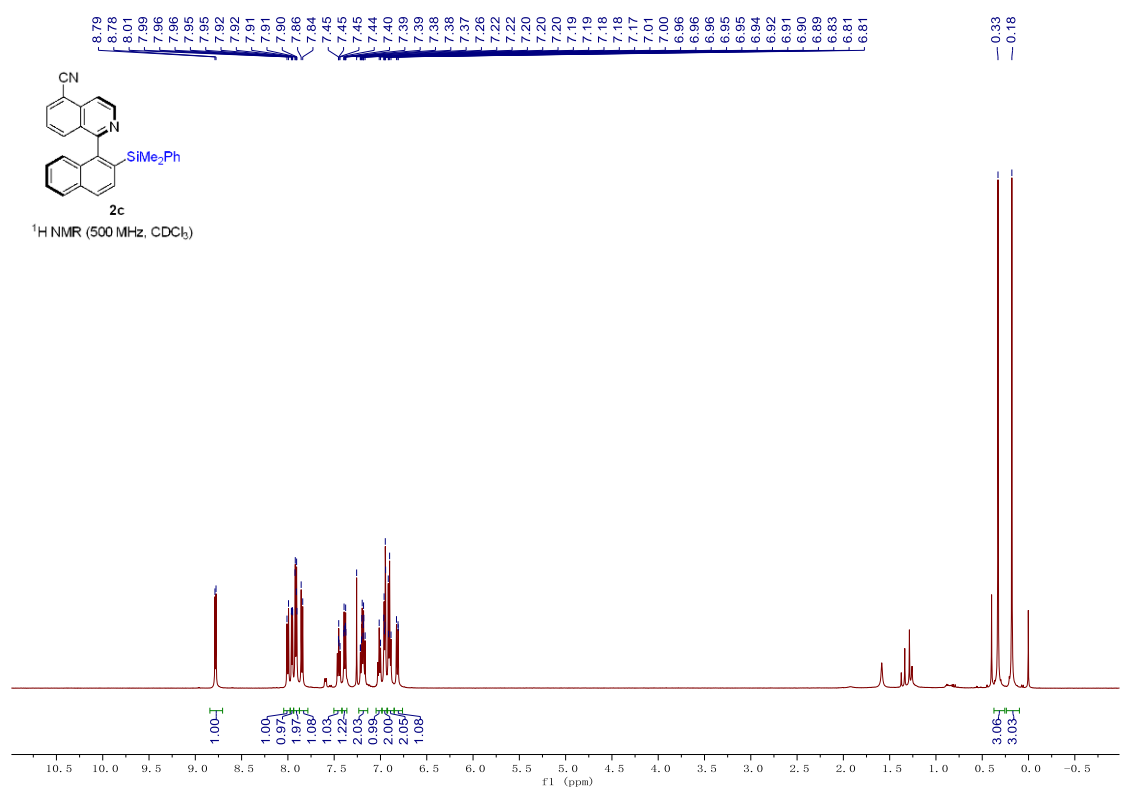
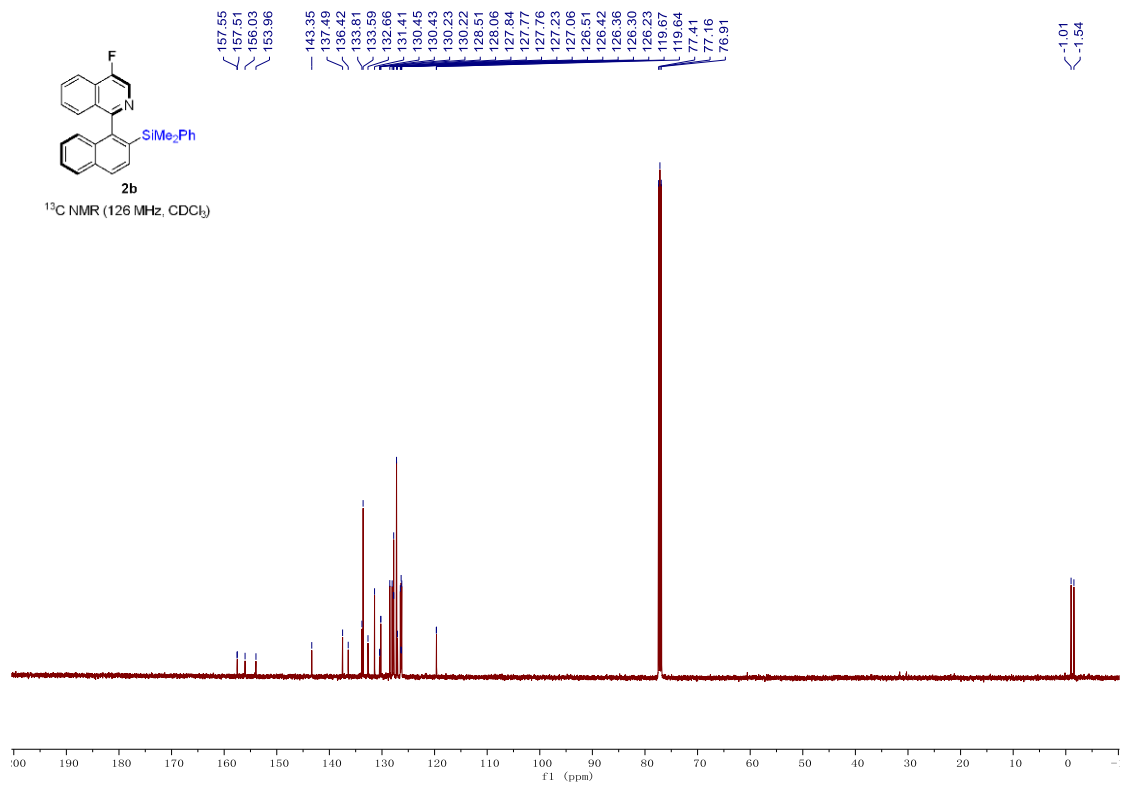
## References

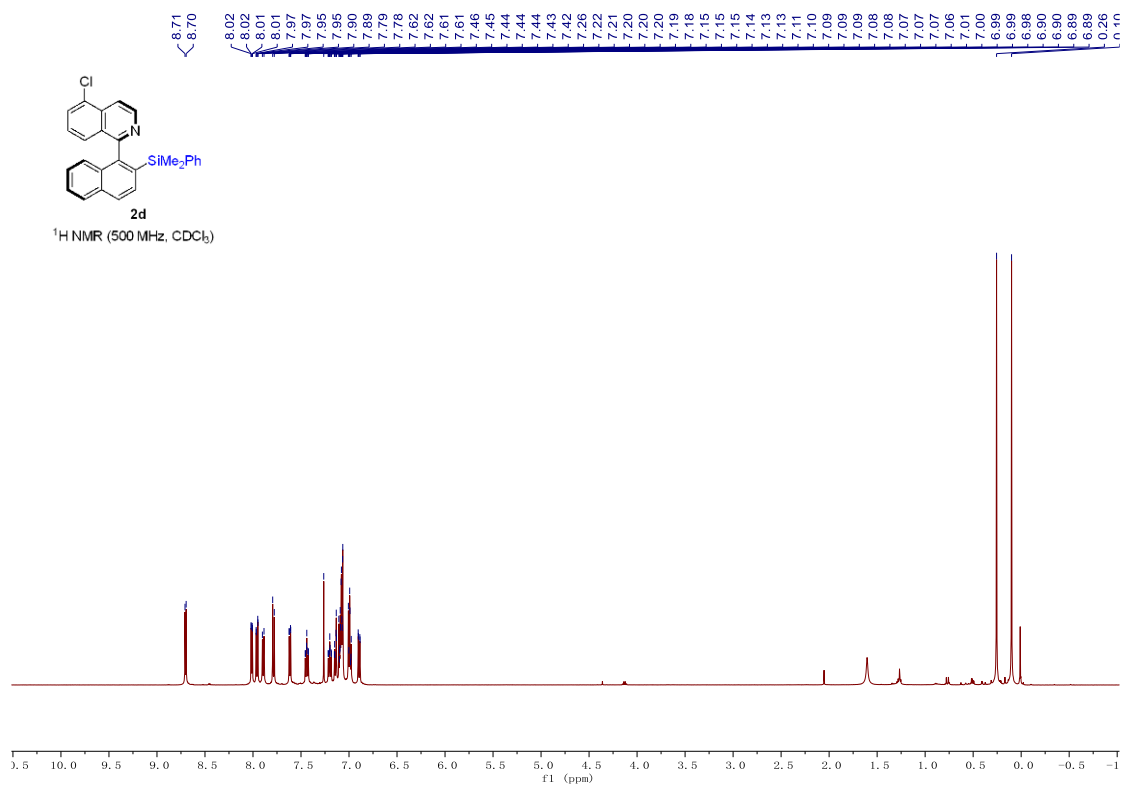
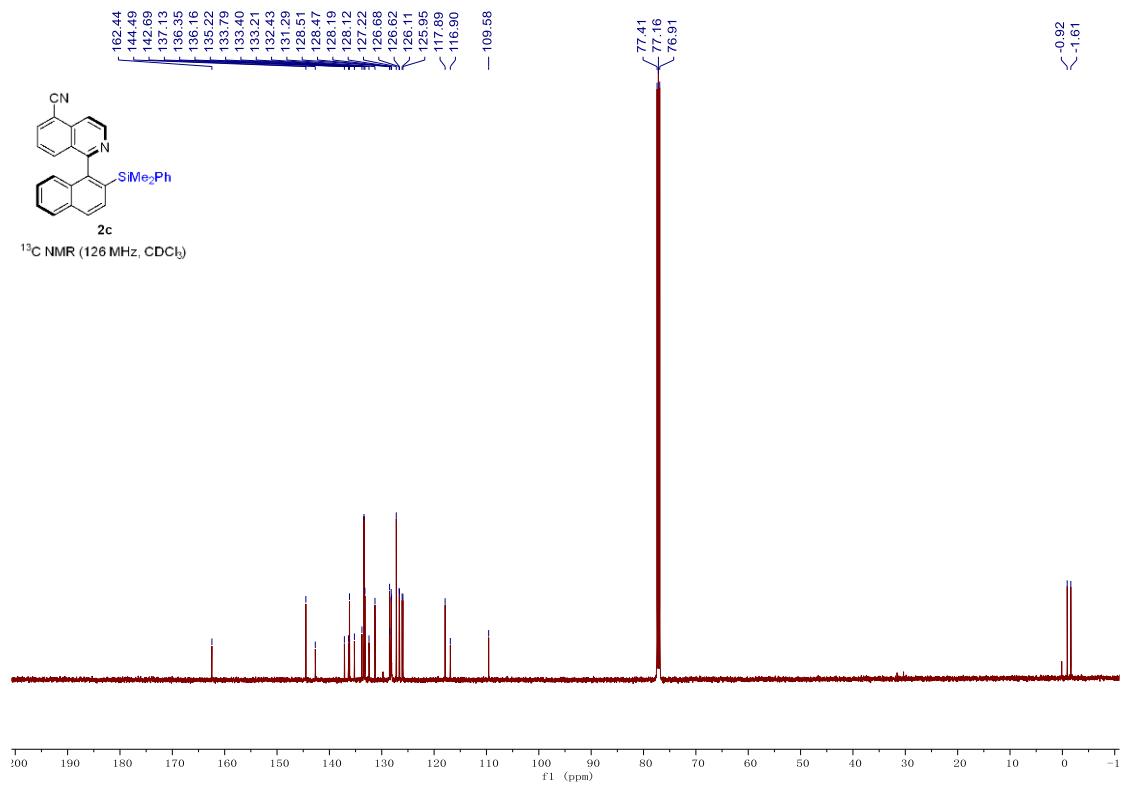
- [1] Jiang, X.; Xiong, W.; Deng, S.; Lu, F.-D.; Jia, Y.; Yang, Q.; Xue, L.-Y.; Qi, X.; Tunge, J. A.; Lu, L.-Q.; Xiao, W.-J. Construction of axial chirality *via* asymmetric radical trapping by cobalt under visible light. *Nat. Catal.* **2022**, *5*, 788.
- [2] (a) Su, L.; Gao, S.; Liu, J. Enantioconvergent synthesis of axially chiral amides enabled by Pd-catalyzed dynamic kinetic asymmetric aminocarbonylation *Nat. Commun.* **2024**, *15*, 7248. (b) Gao, S.; Su, L.; Liu, J. Diastereo- and Enantioselective Pd-Catalyzed C–P Coupling for Axially and P-Chiral Phosphine Oxides *via* Simultaneous Dynamic Kinetic Asymmetric Transformation and Kinetic Resolution *J. Am. Chem. Soc.* **2025**, *147*, 23946.

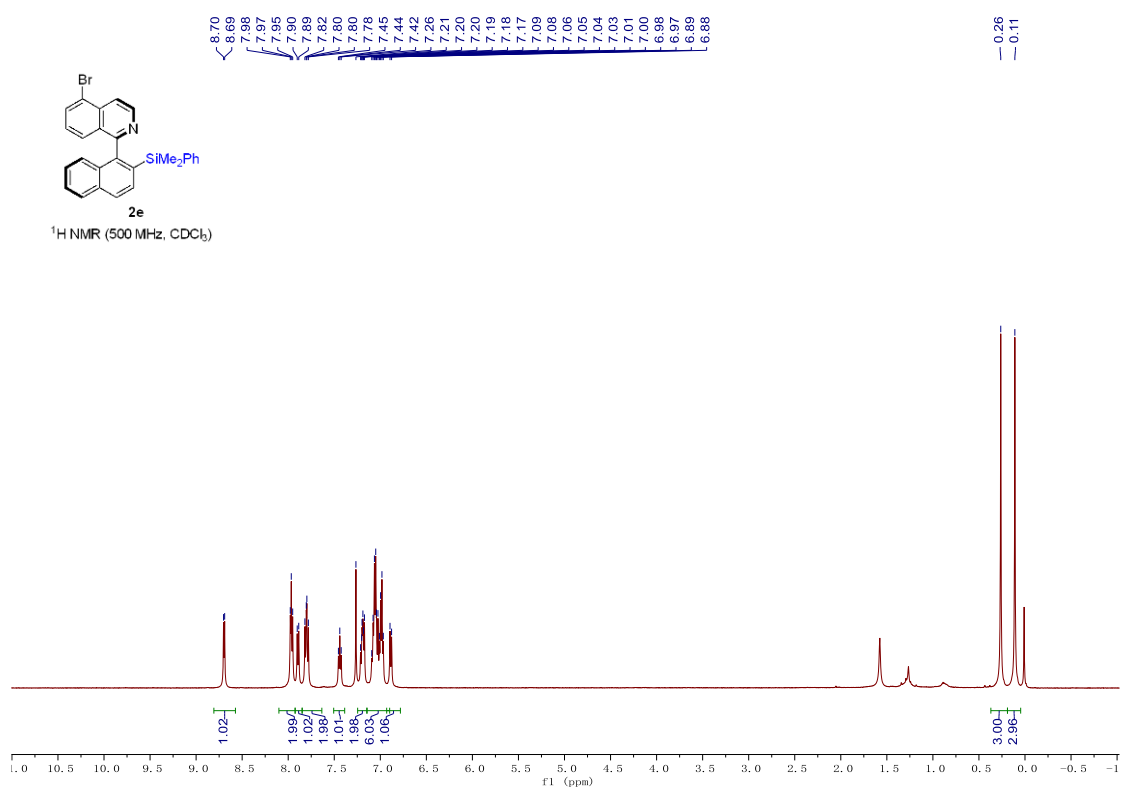
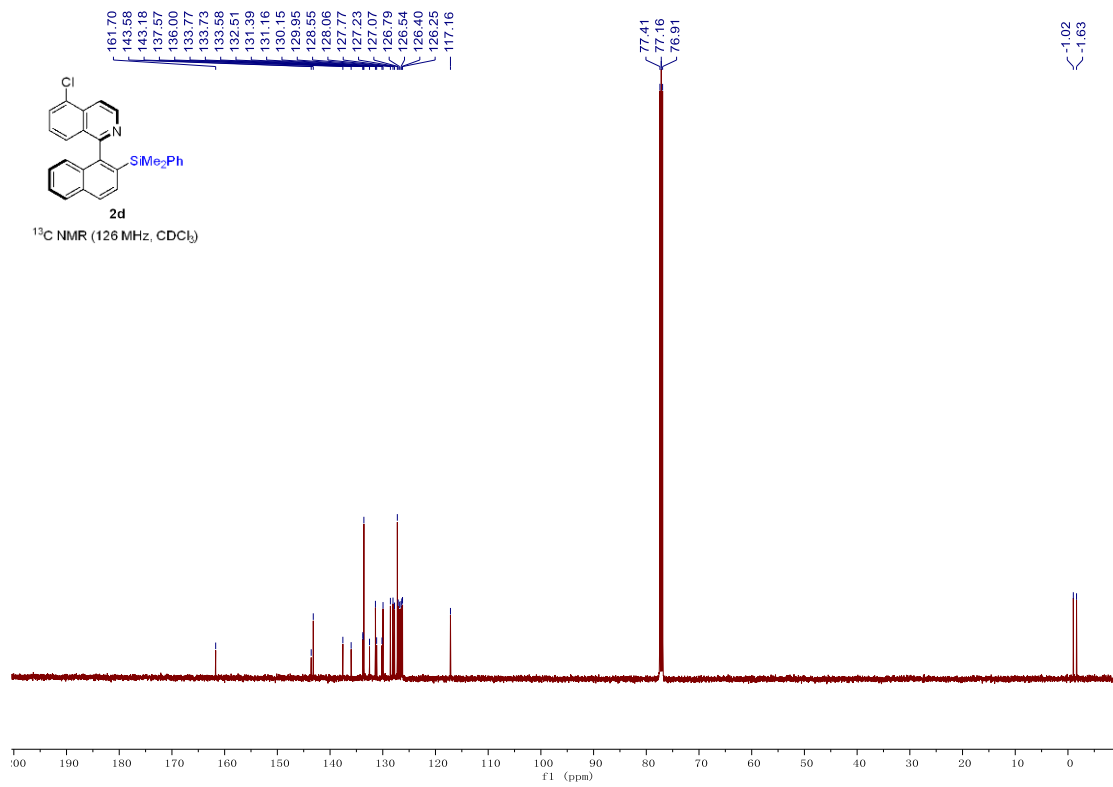
# NMR Spectra

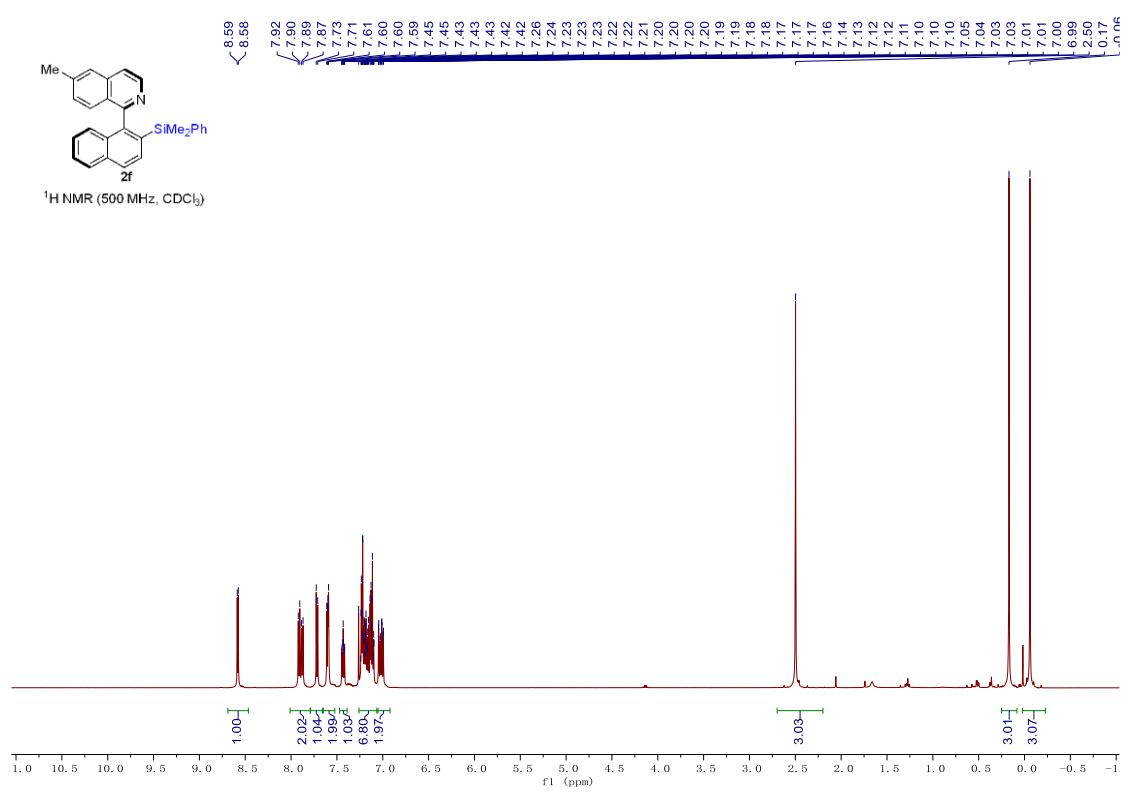
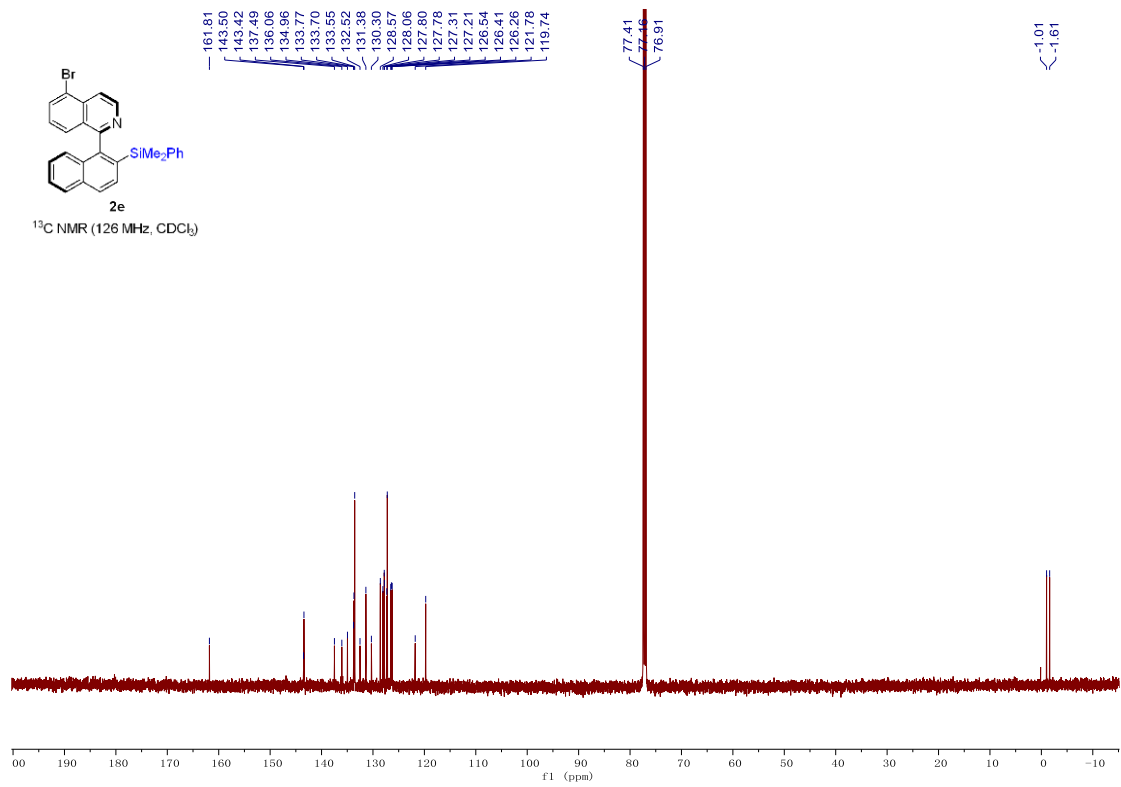


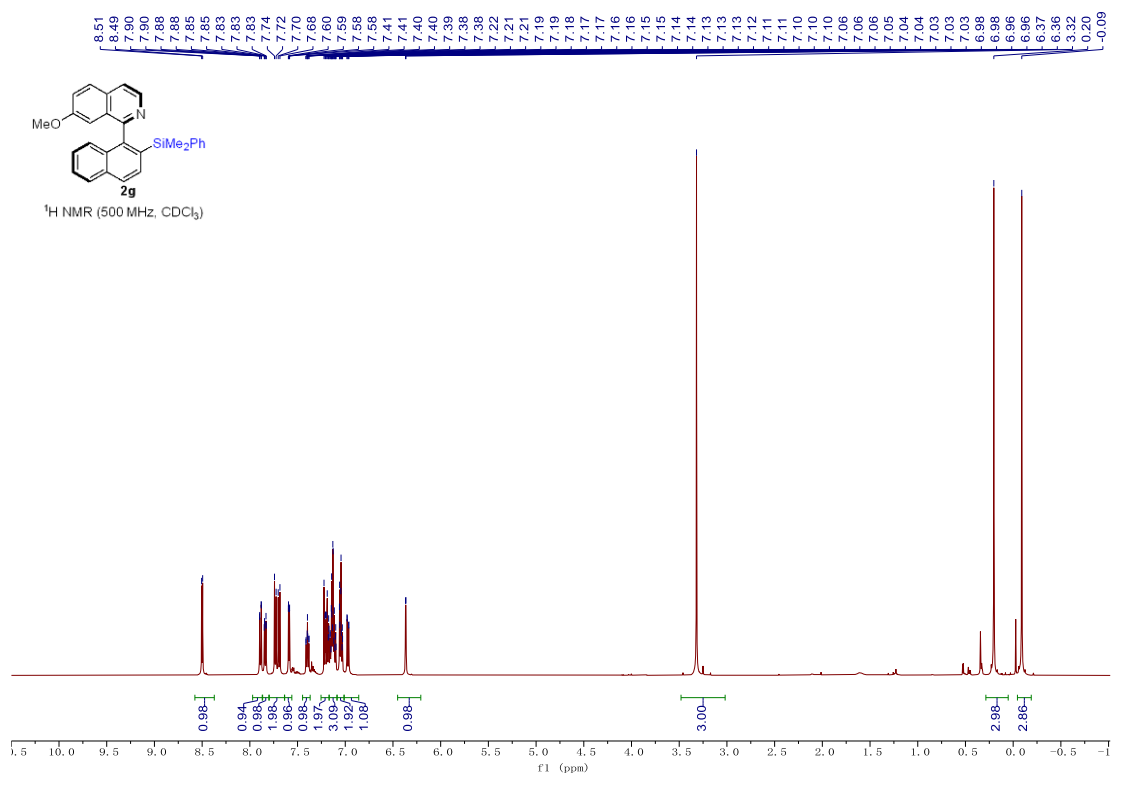
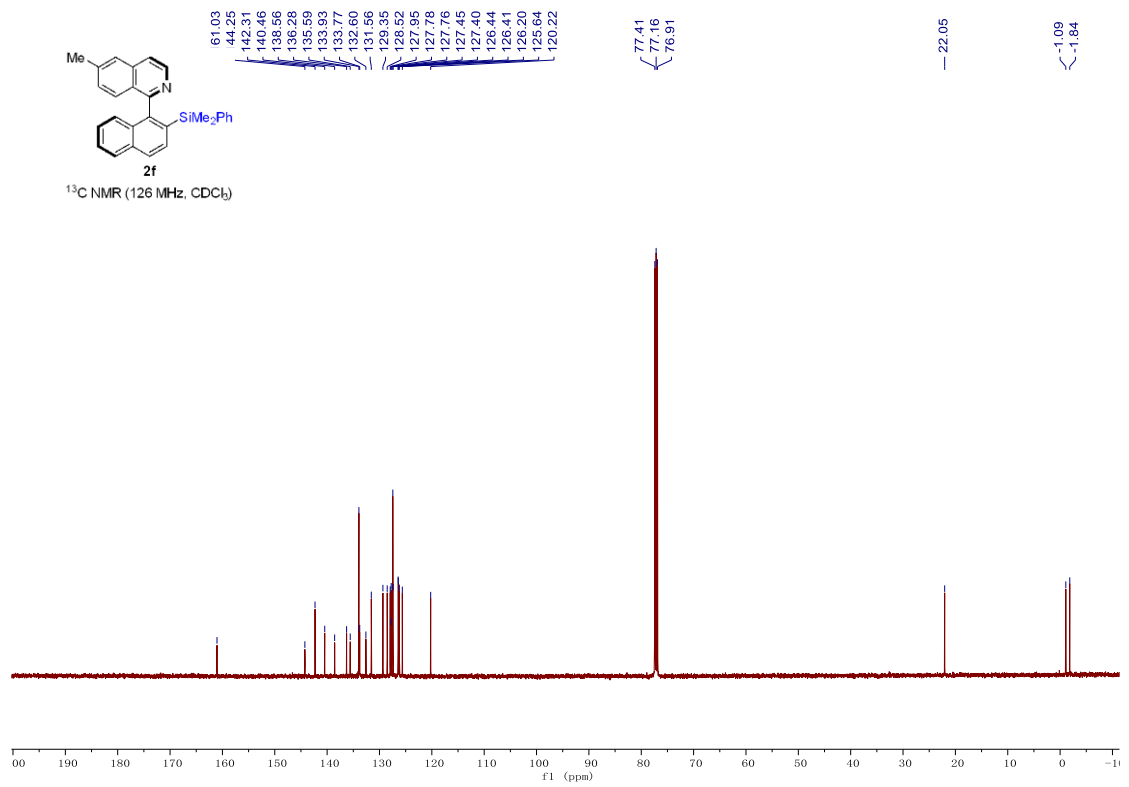


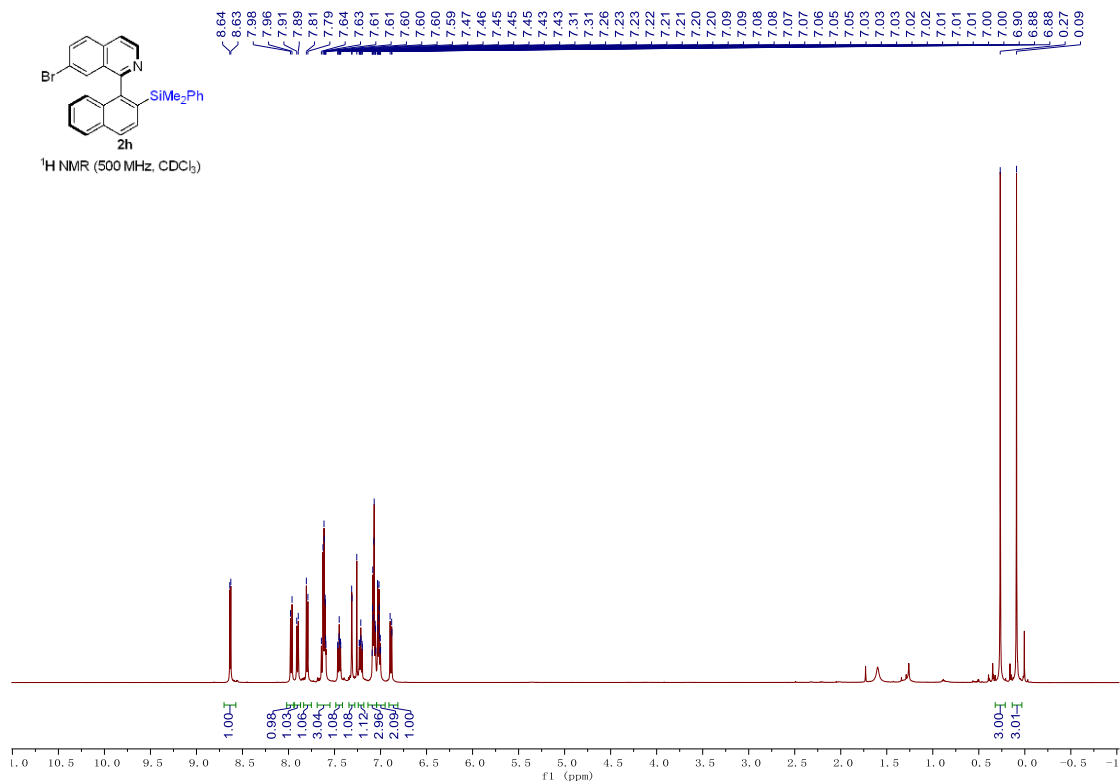
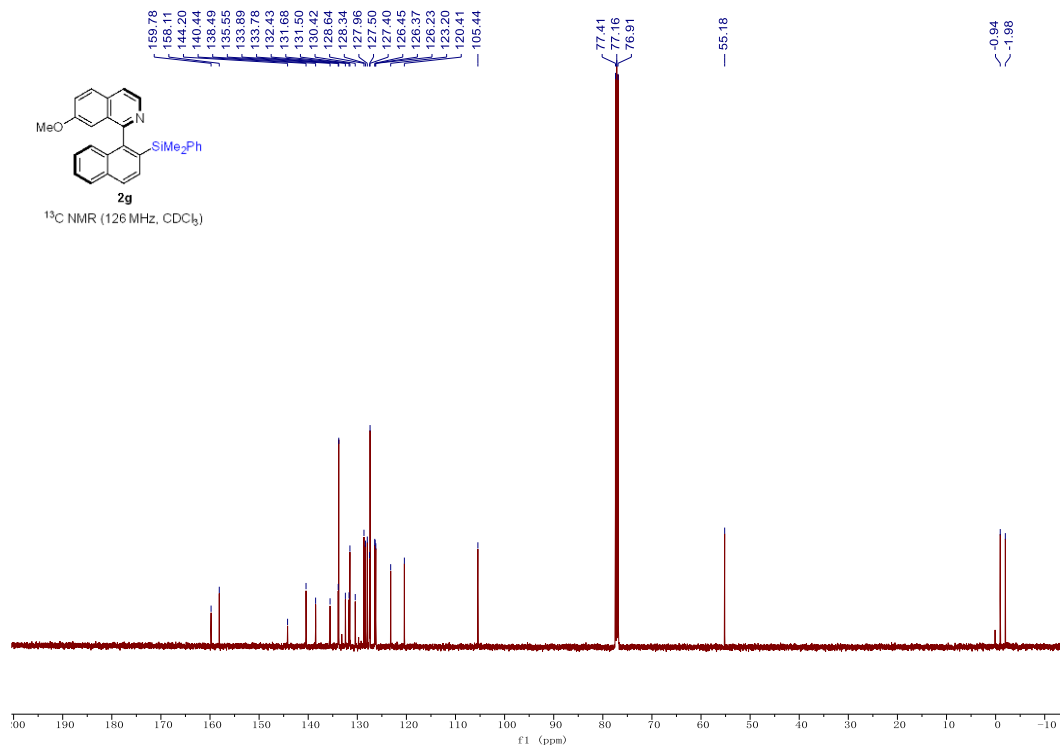


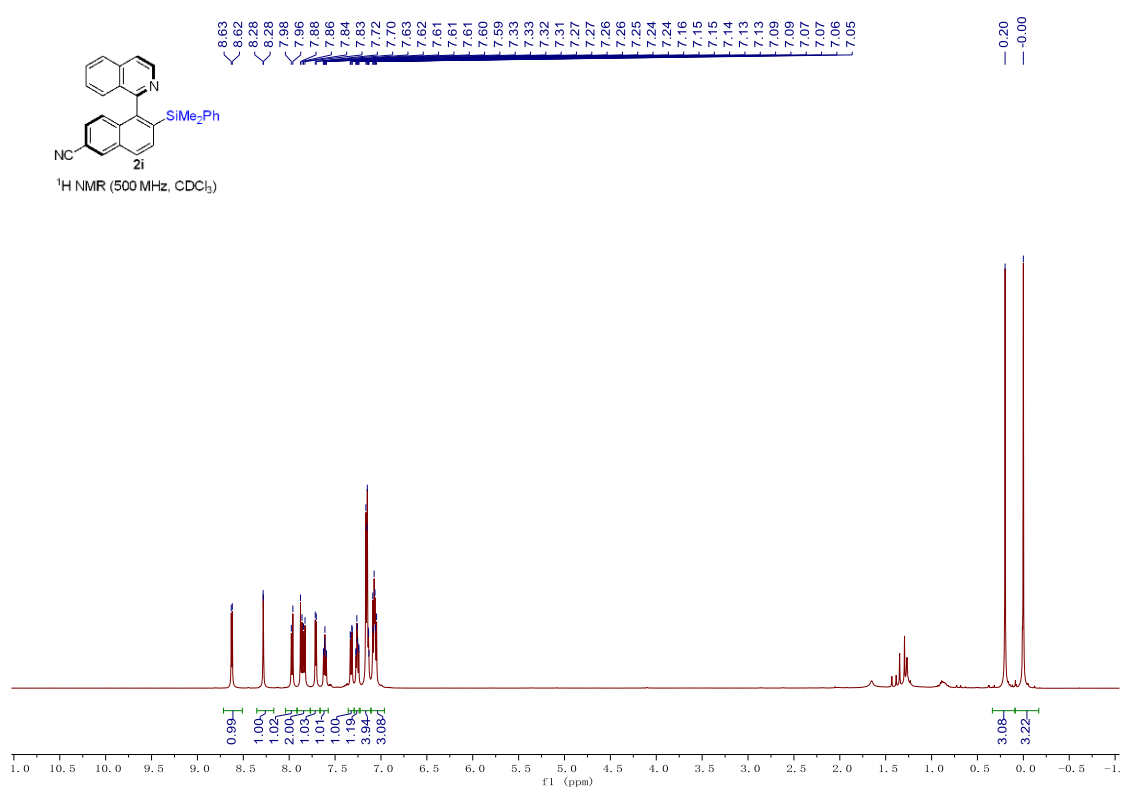
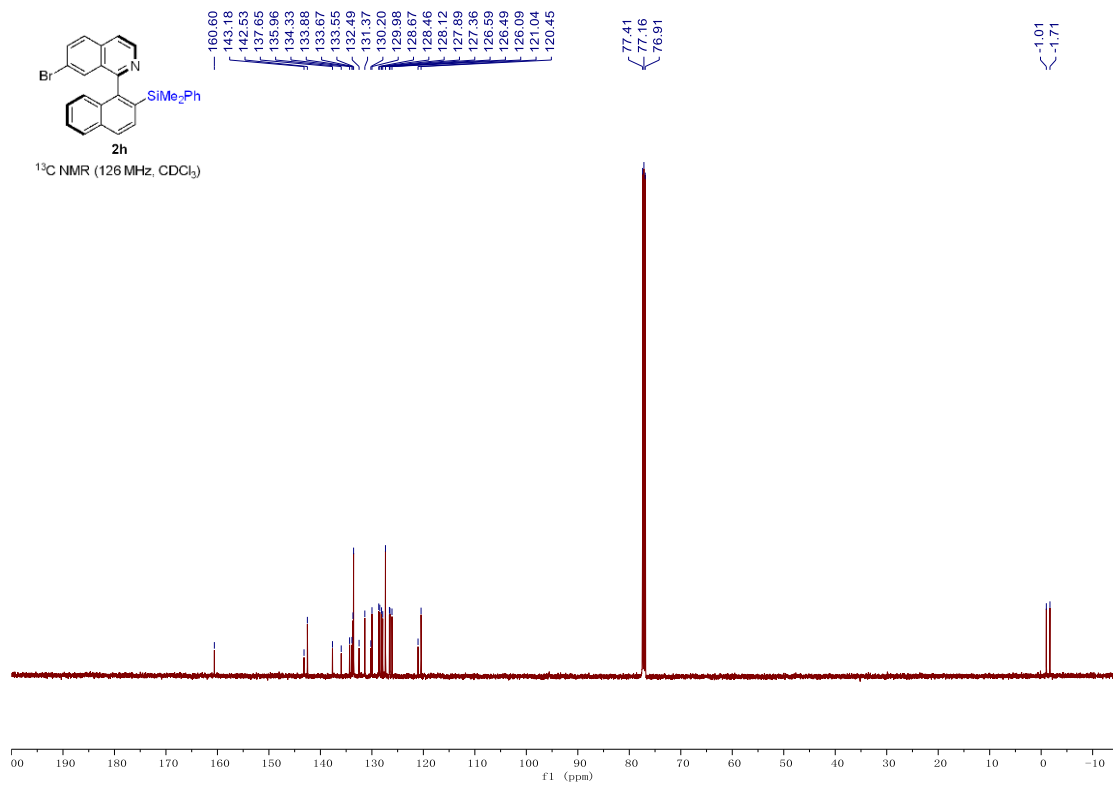


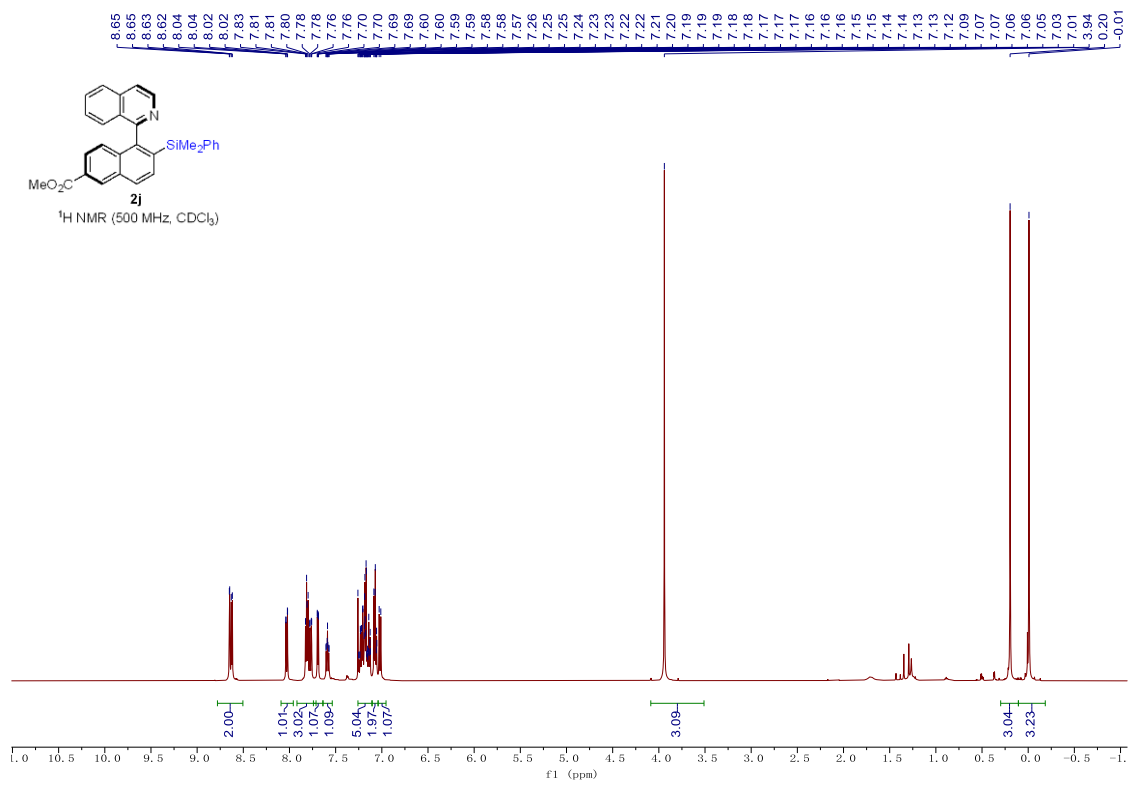
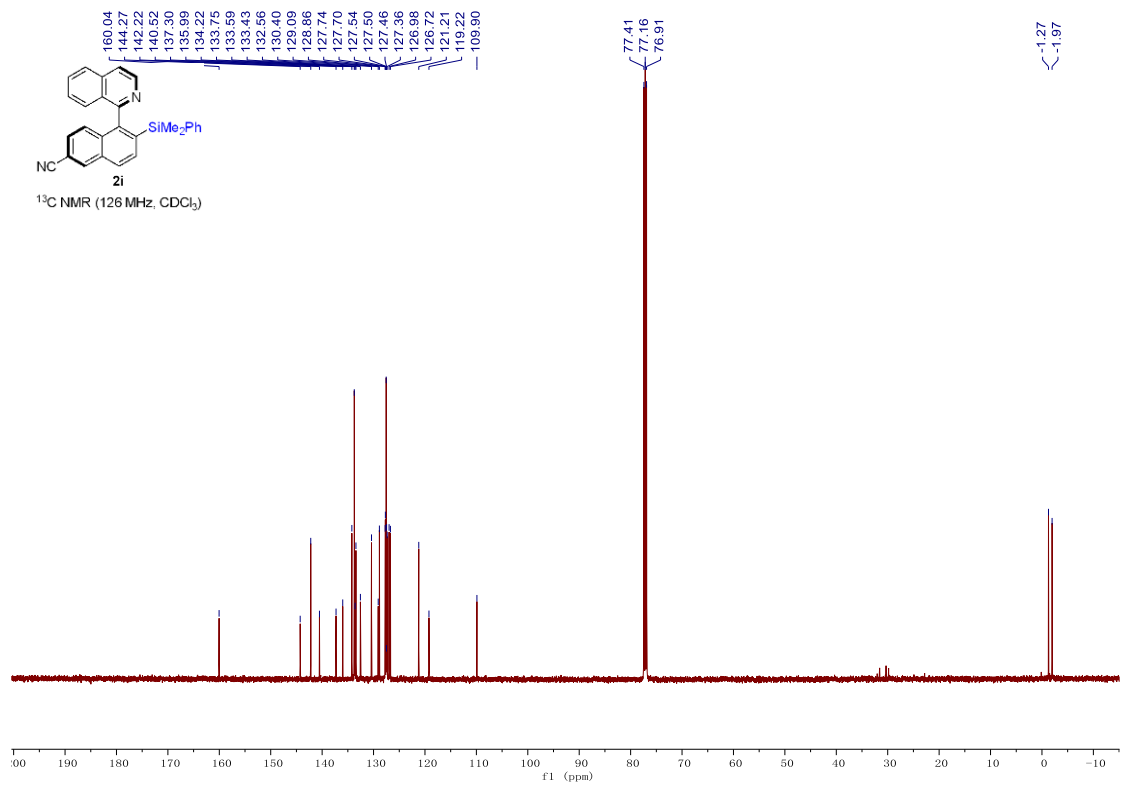


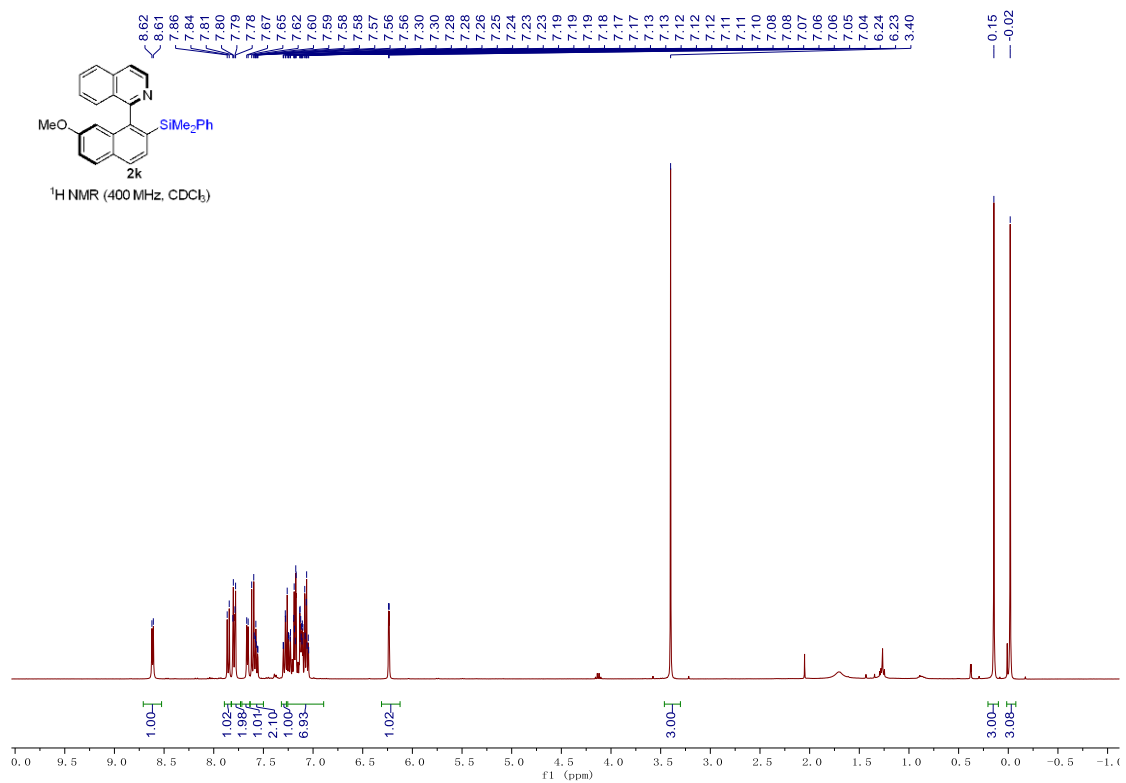
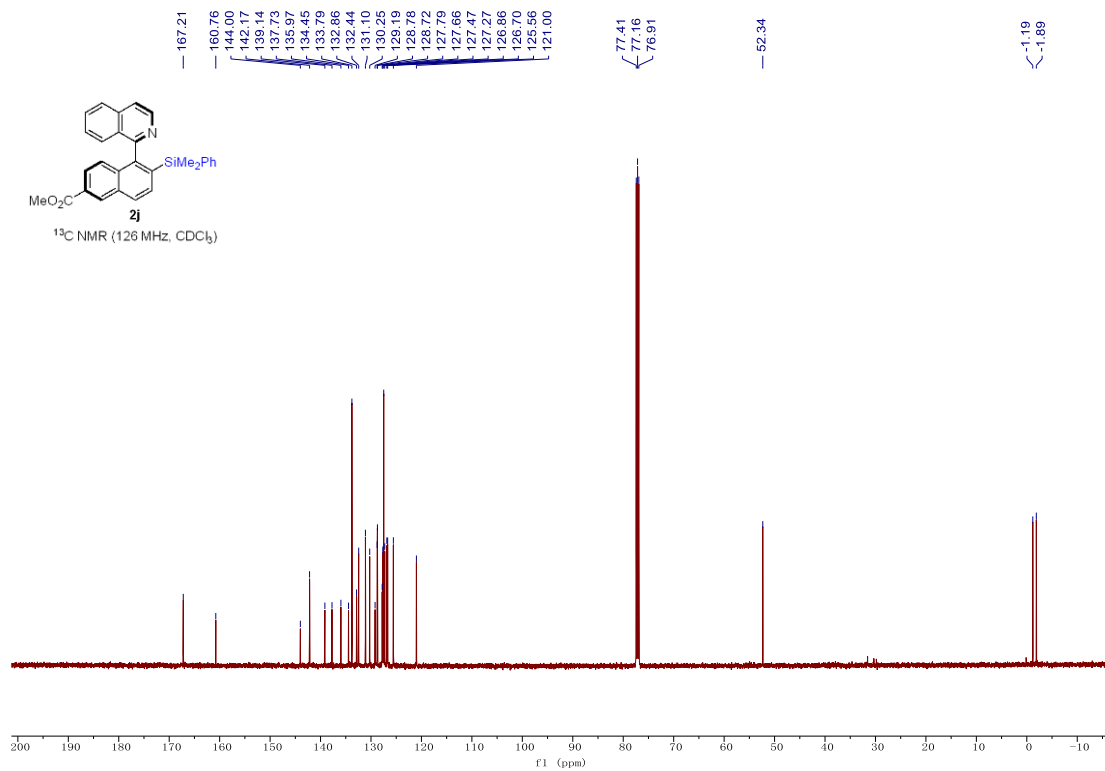


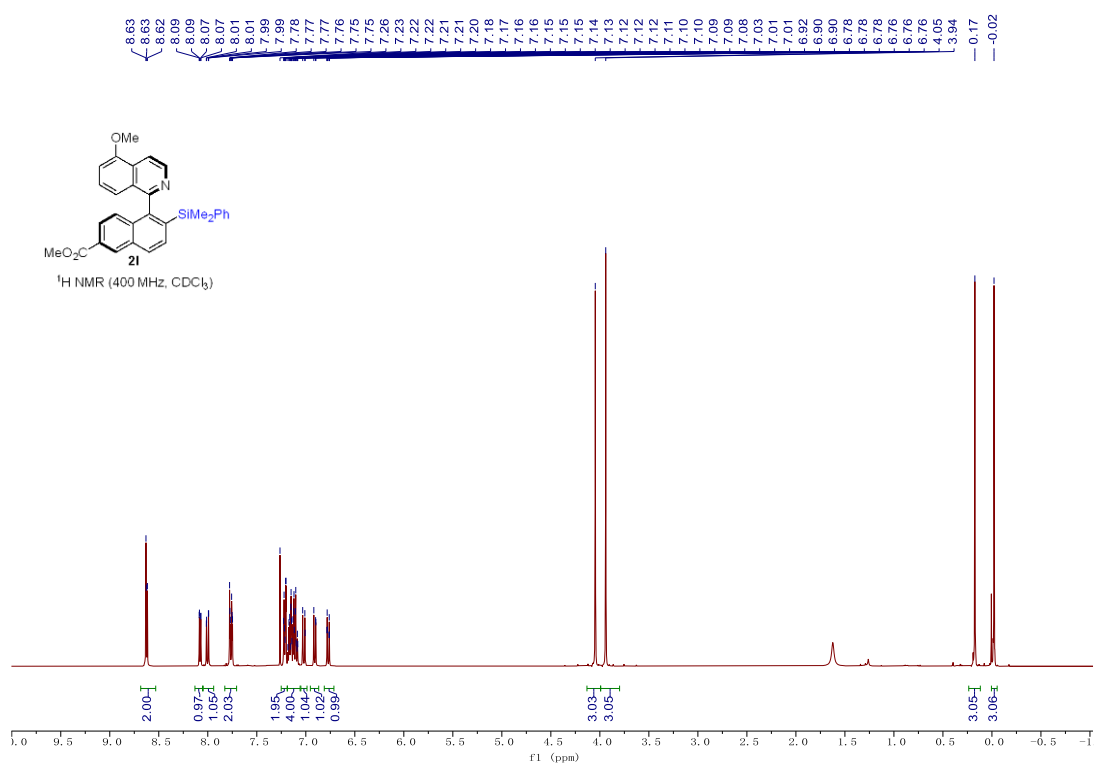
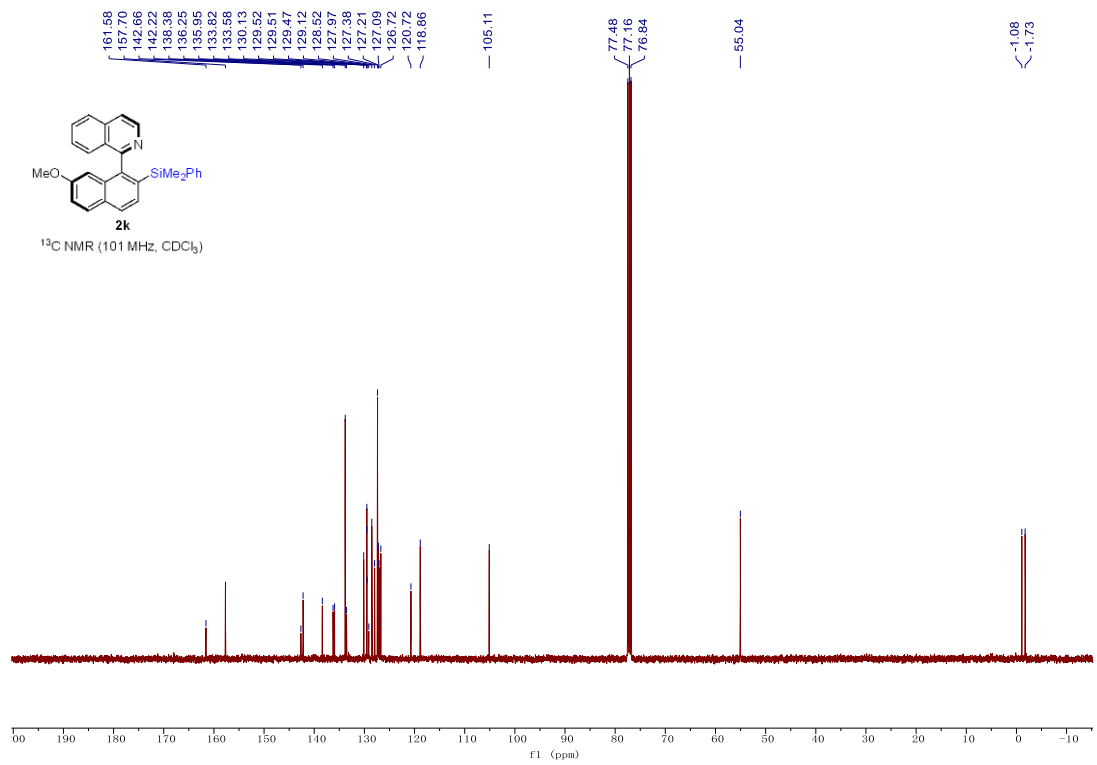


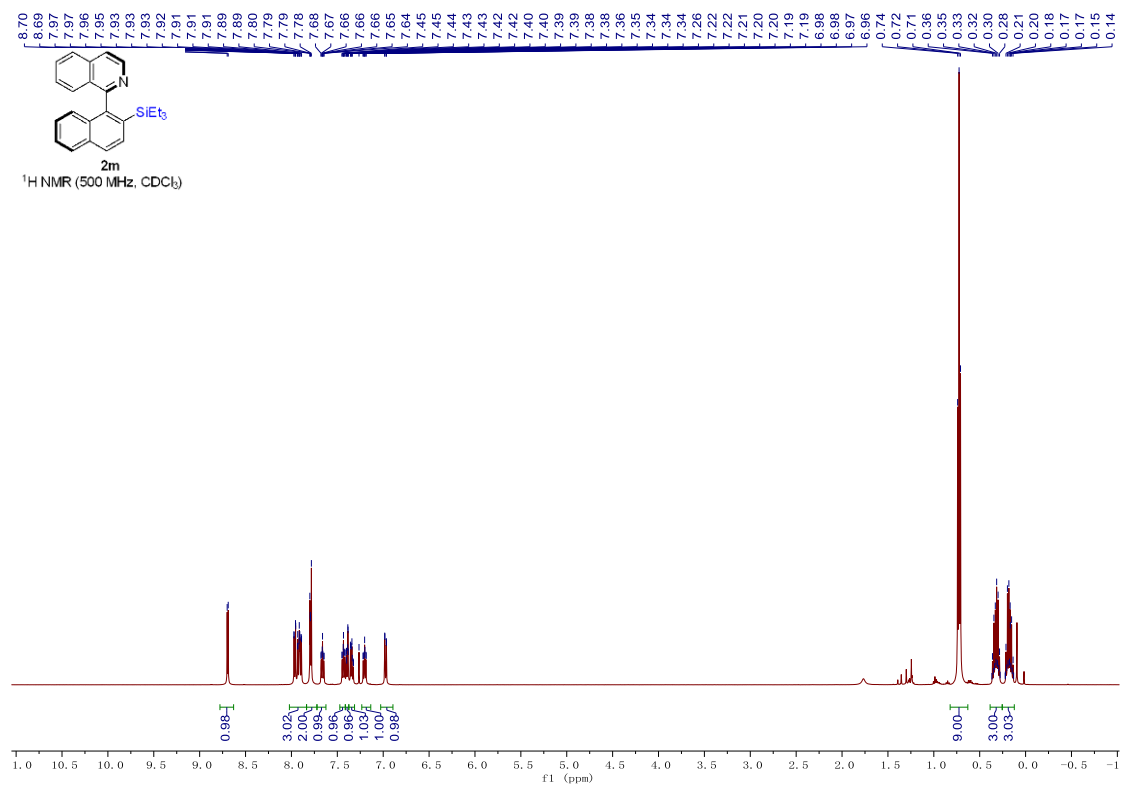
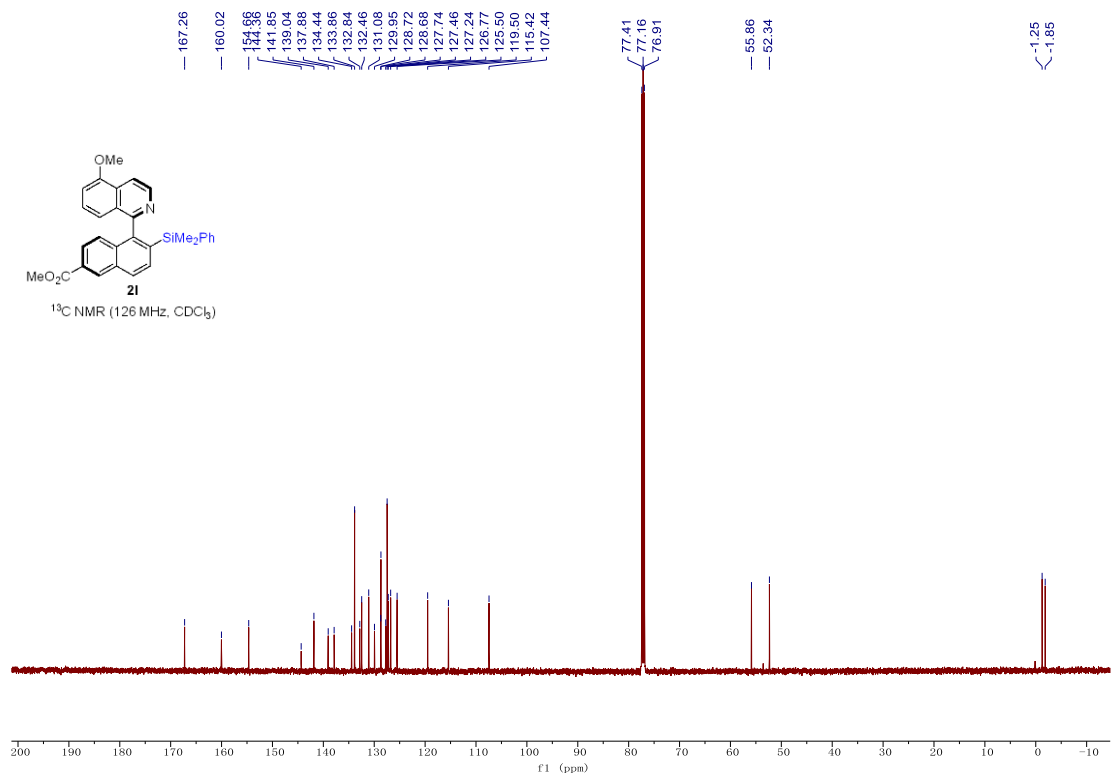


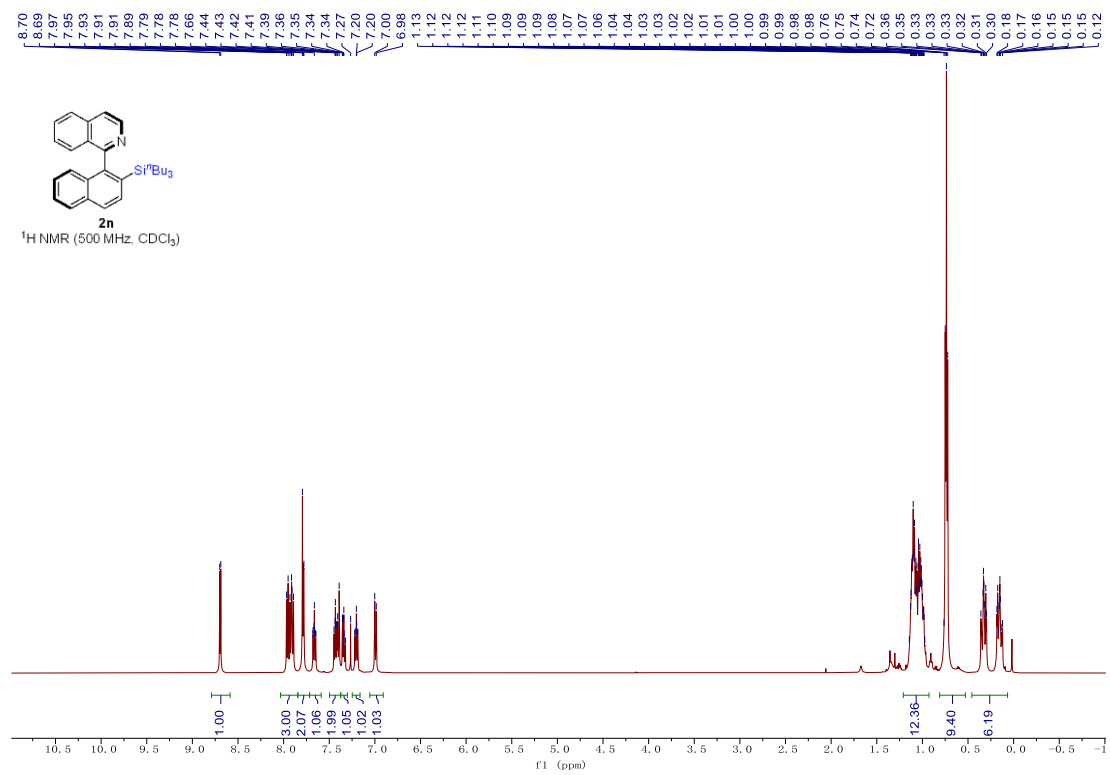
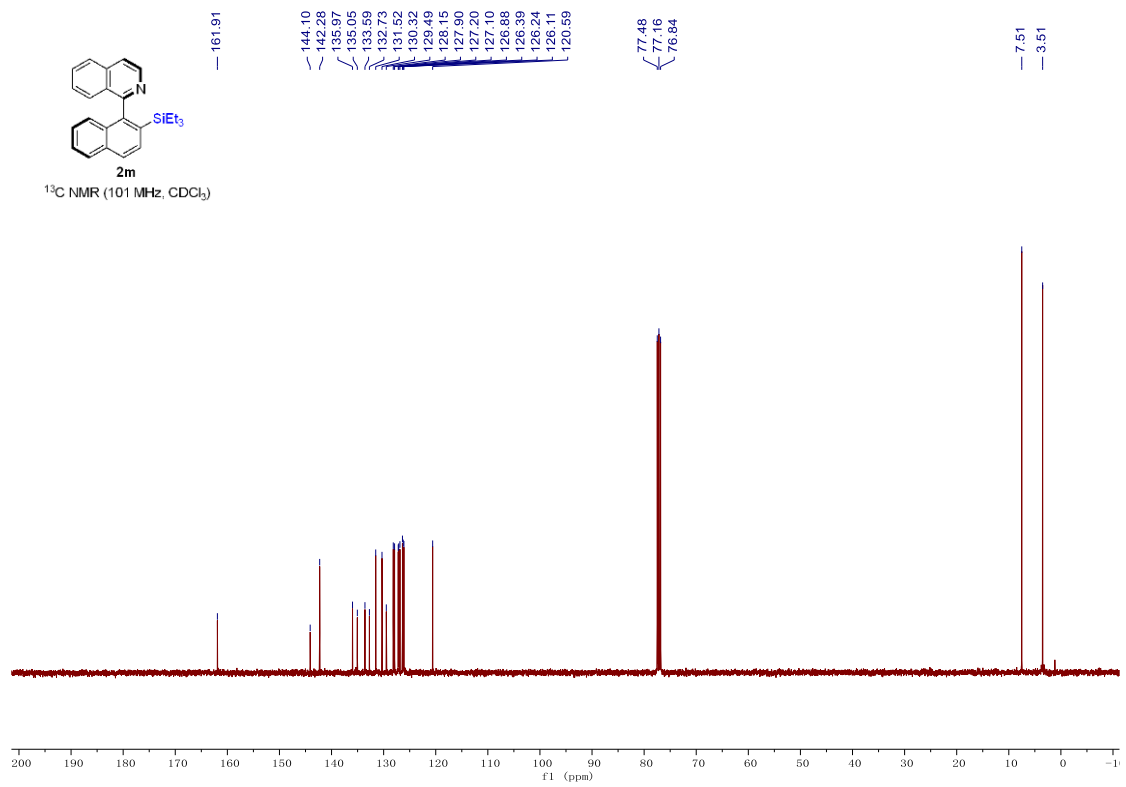


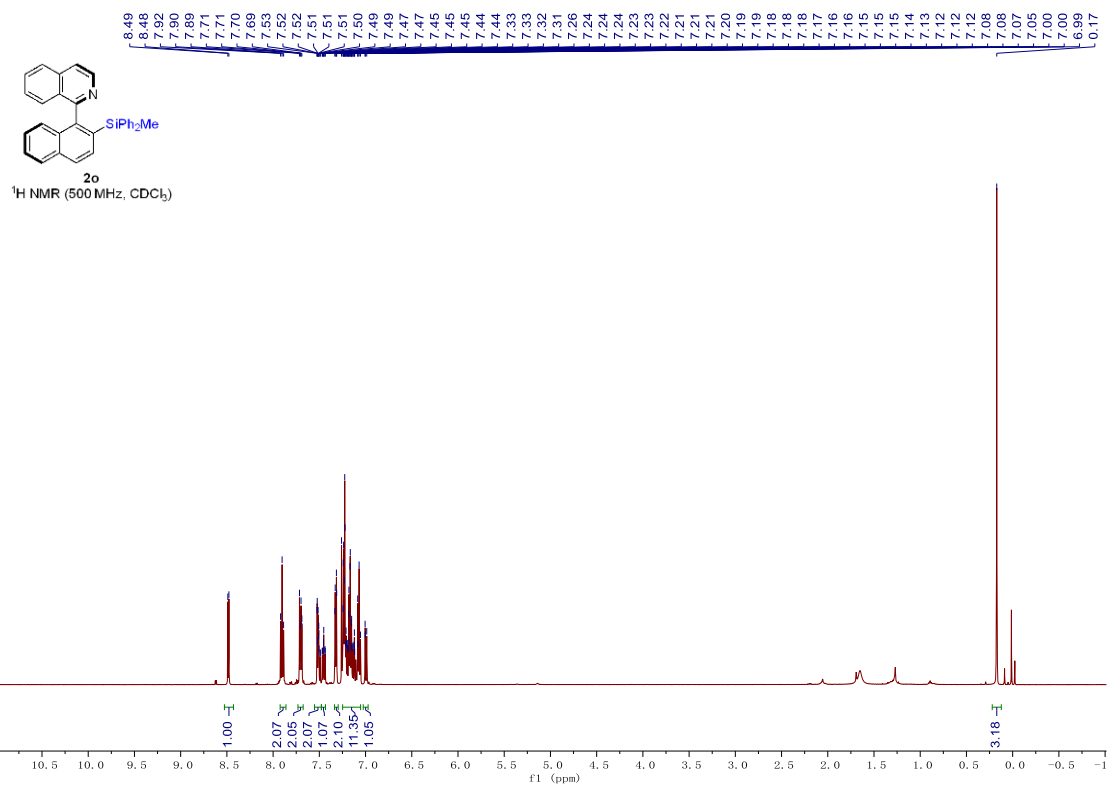
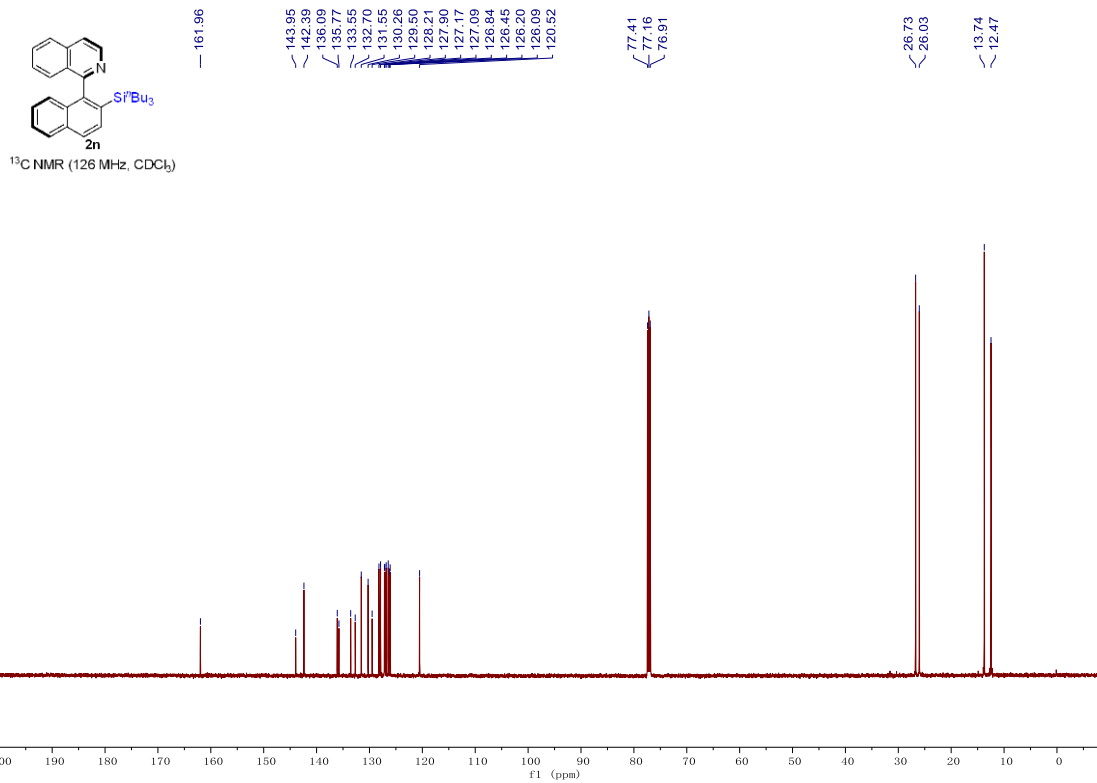




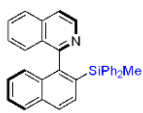




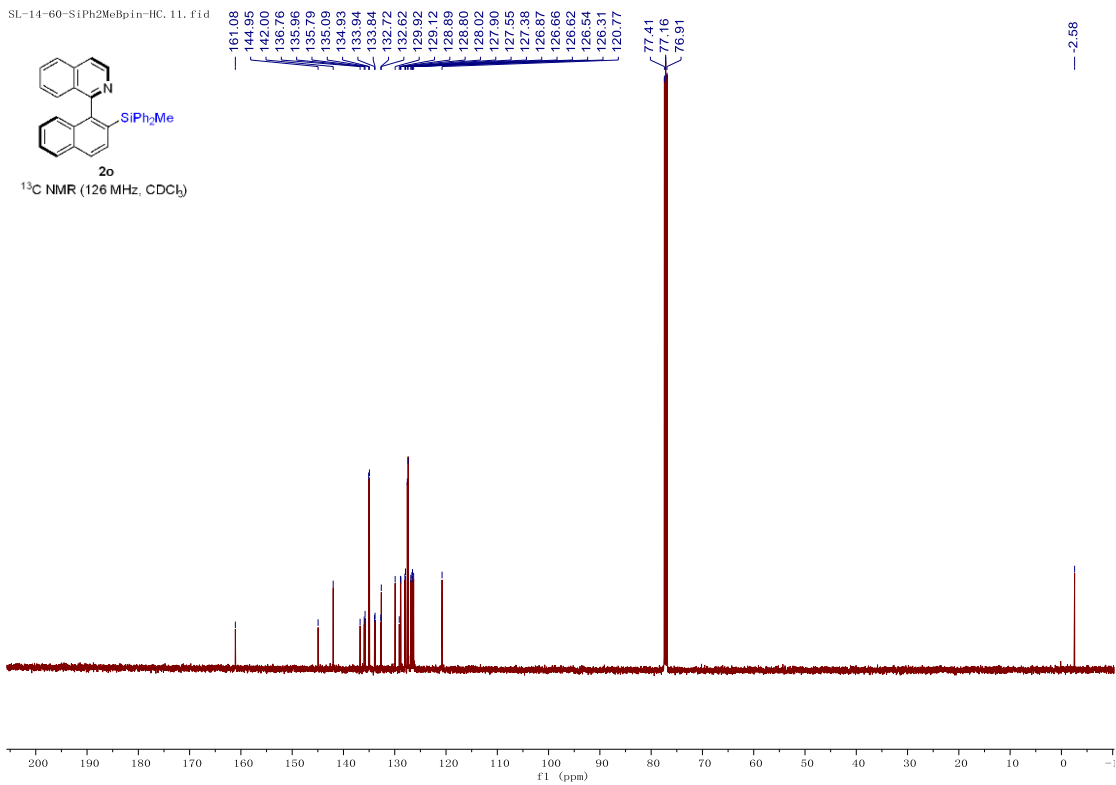




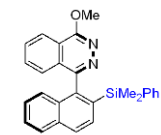
SL-14-60-SiPh2MeBpin-HC. 11. F1d



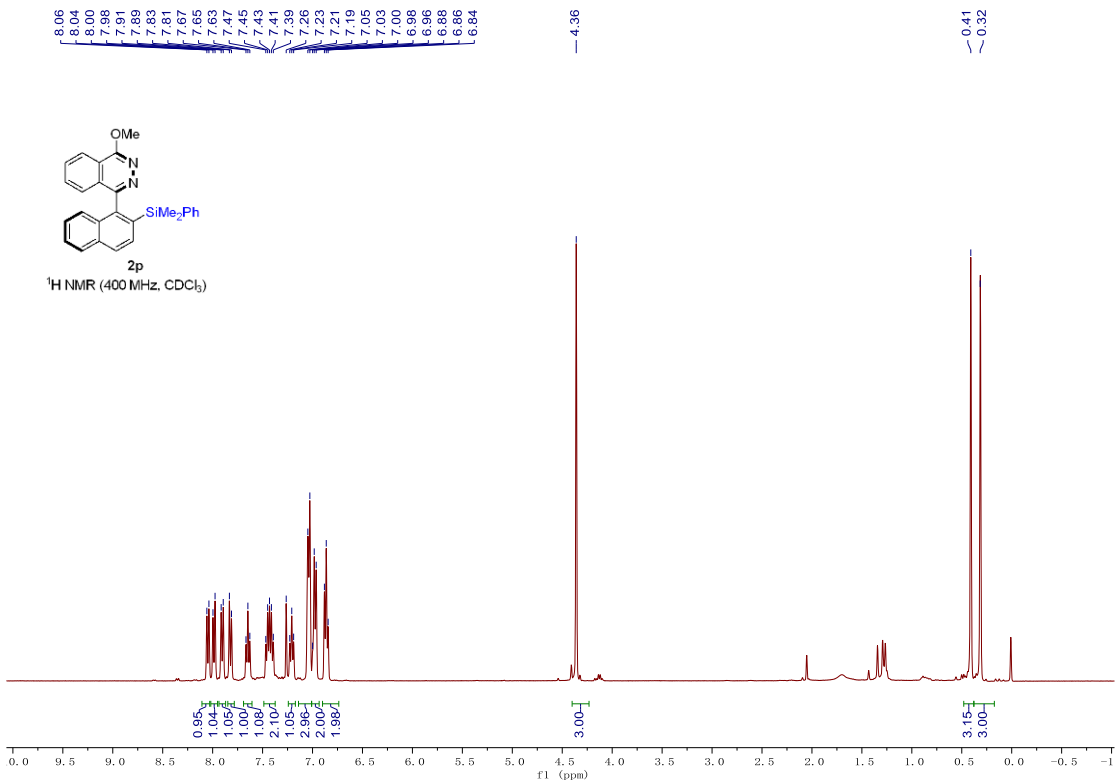
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

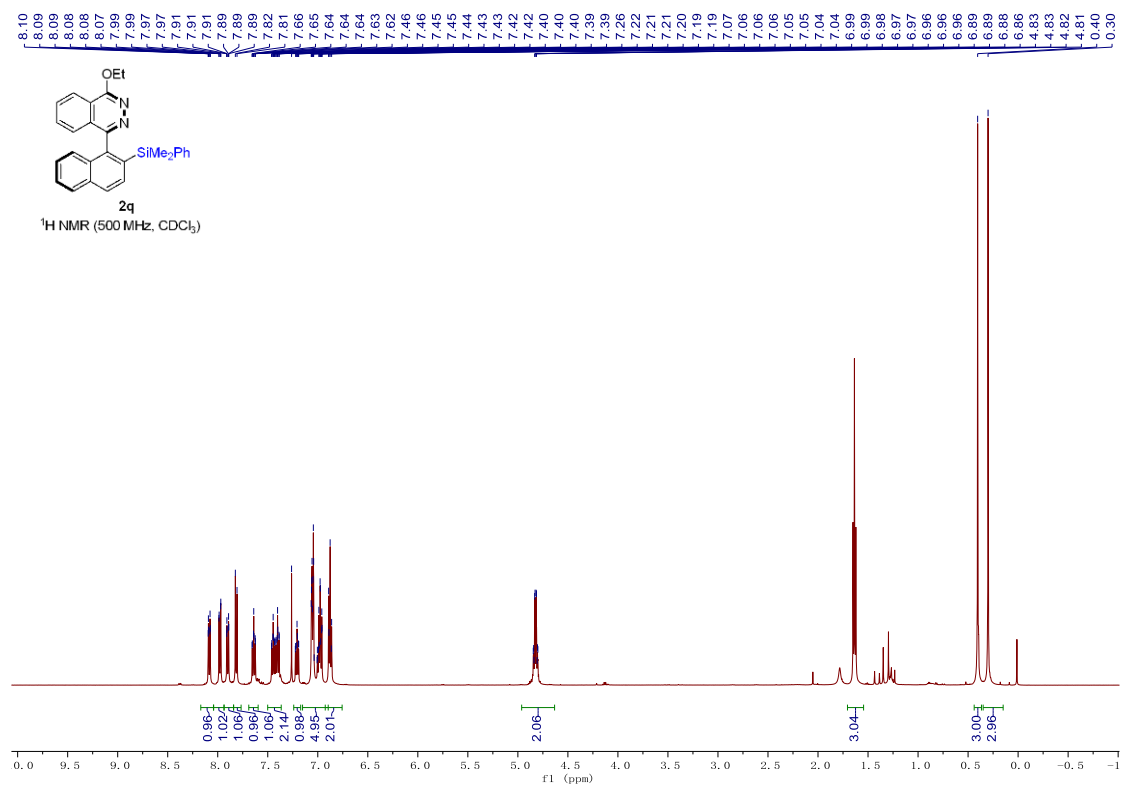
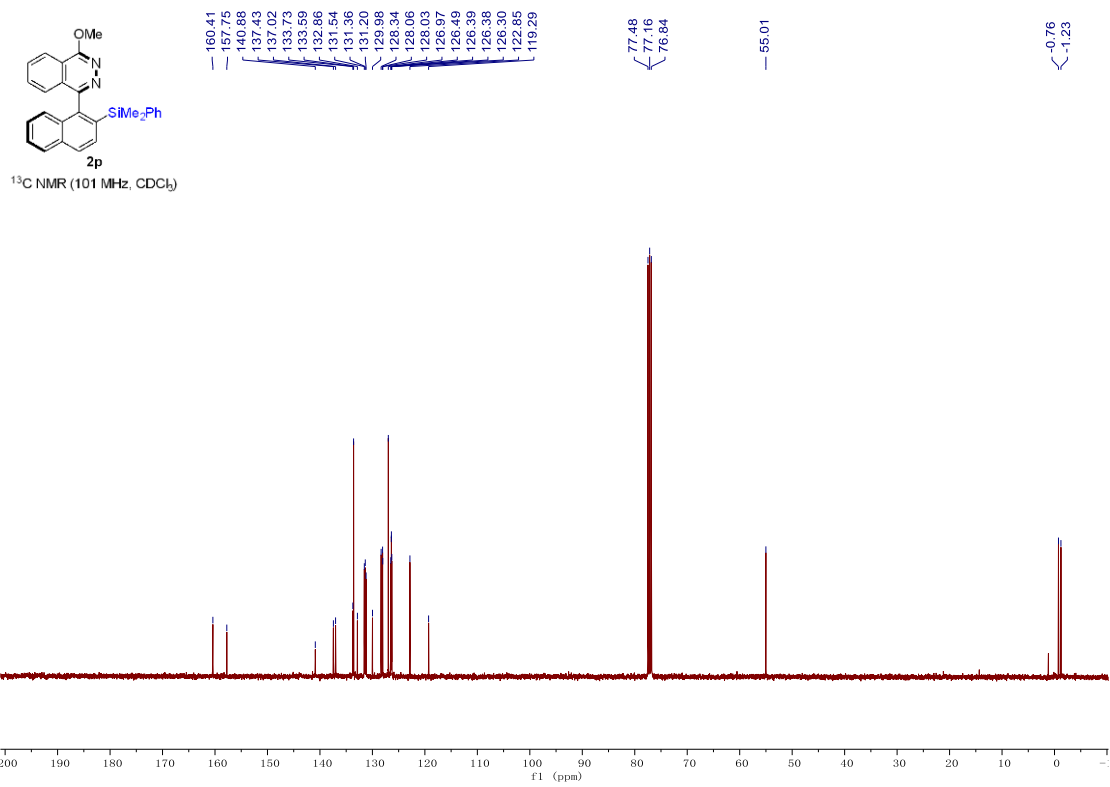


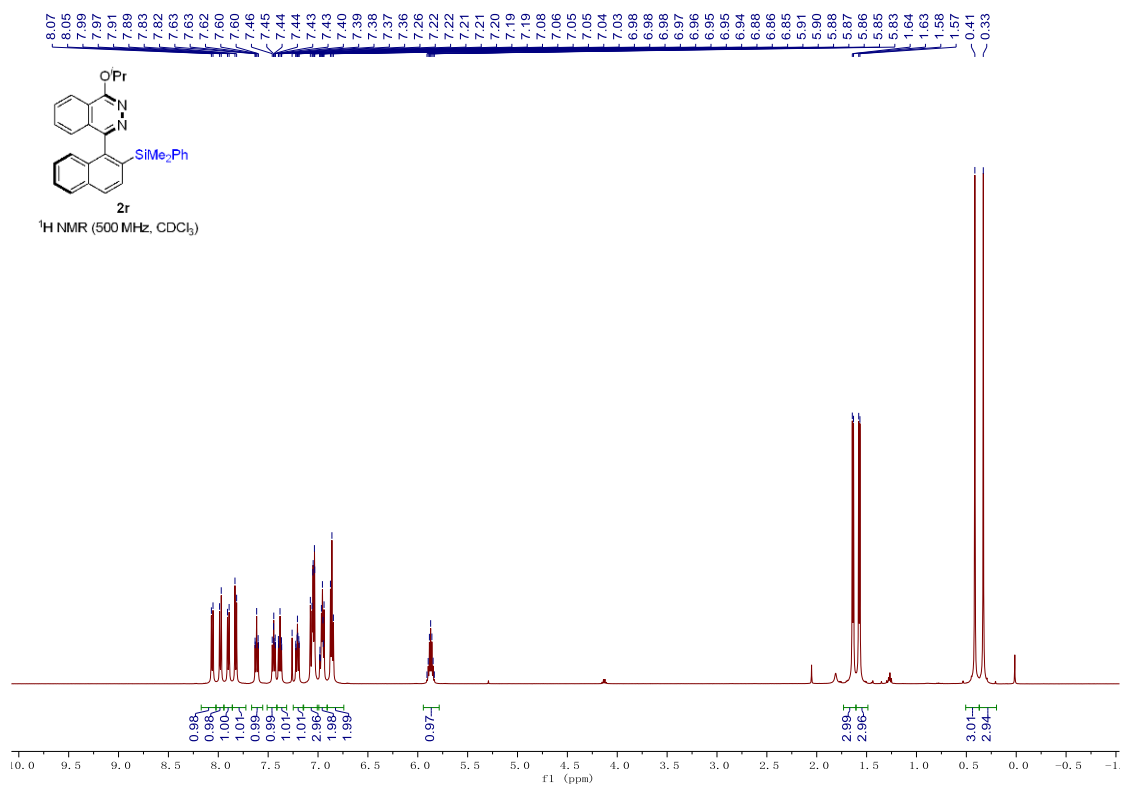
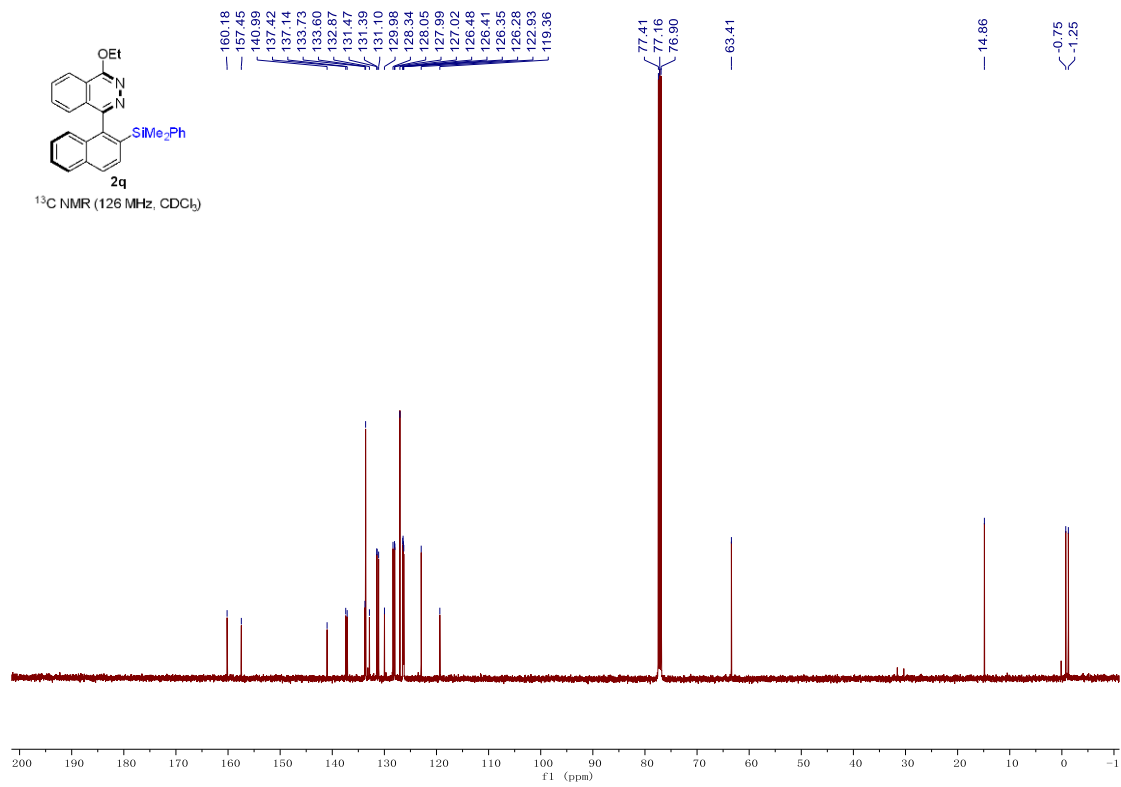
8.06  
8.04  
8.00  
7.98  
7.91  
7.89  
7.83  
7.81  
7.67  
7.65  
7.63  
7.47  
7.43  
7.41  
7.39  
7.26  
7.23  
7.21  
7.19  
7.05  
7.03  
7.00  
6.98  
6.96  
6.88  
6.86  
6.84

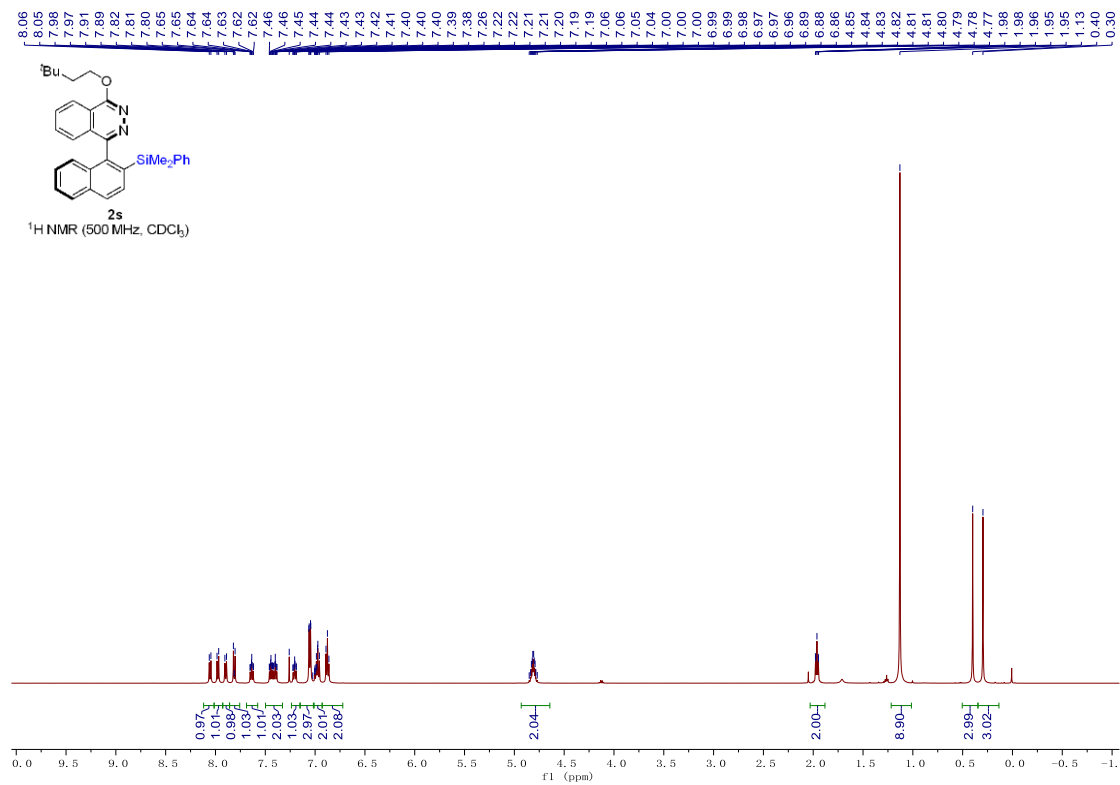
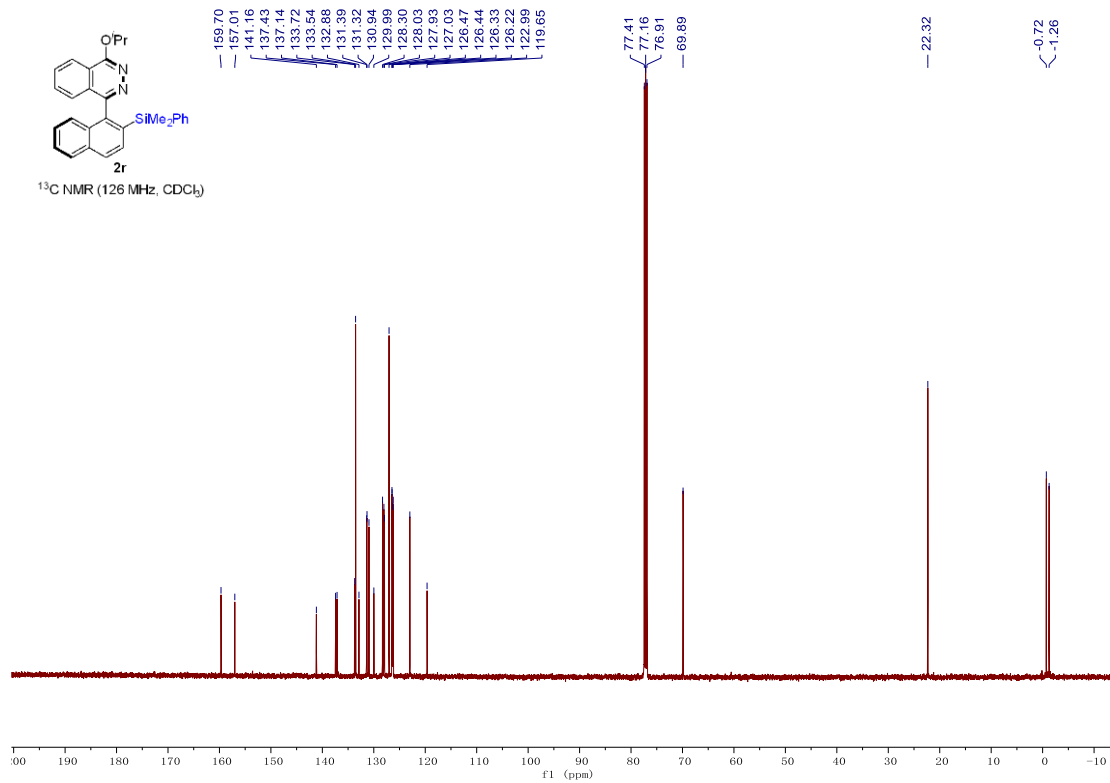


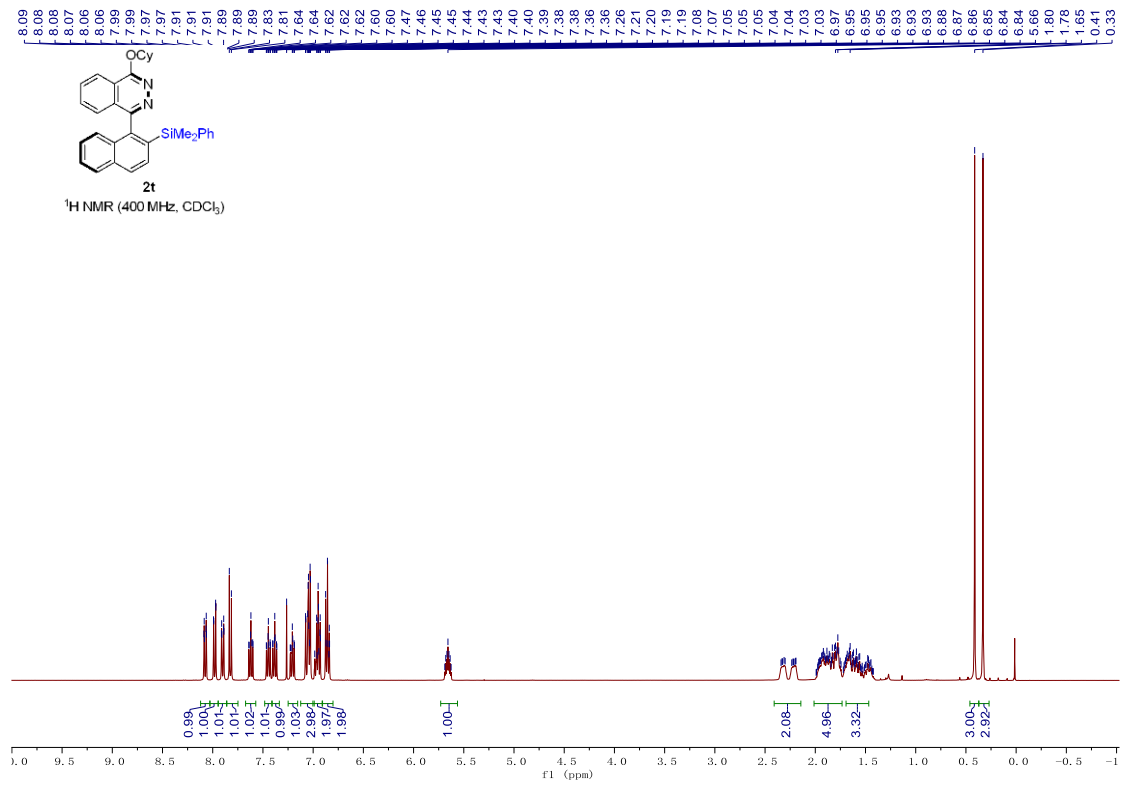
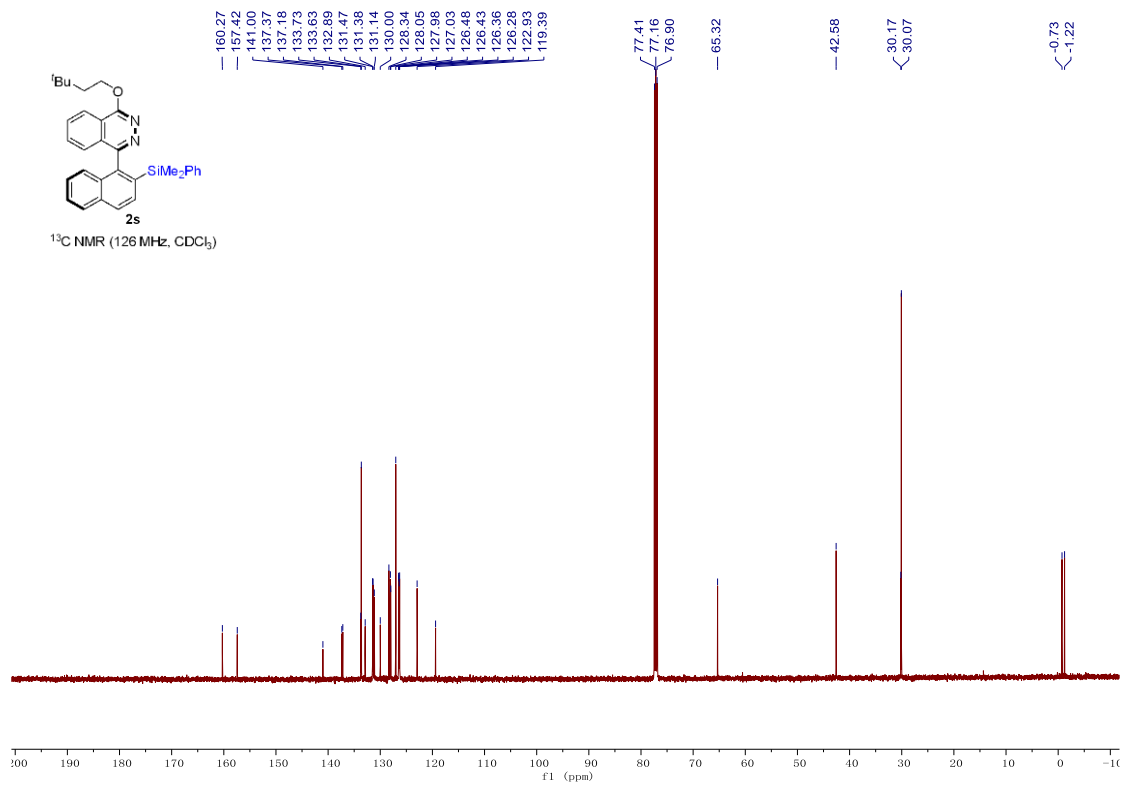
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

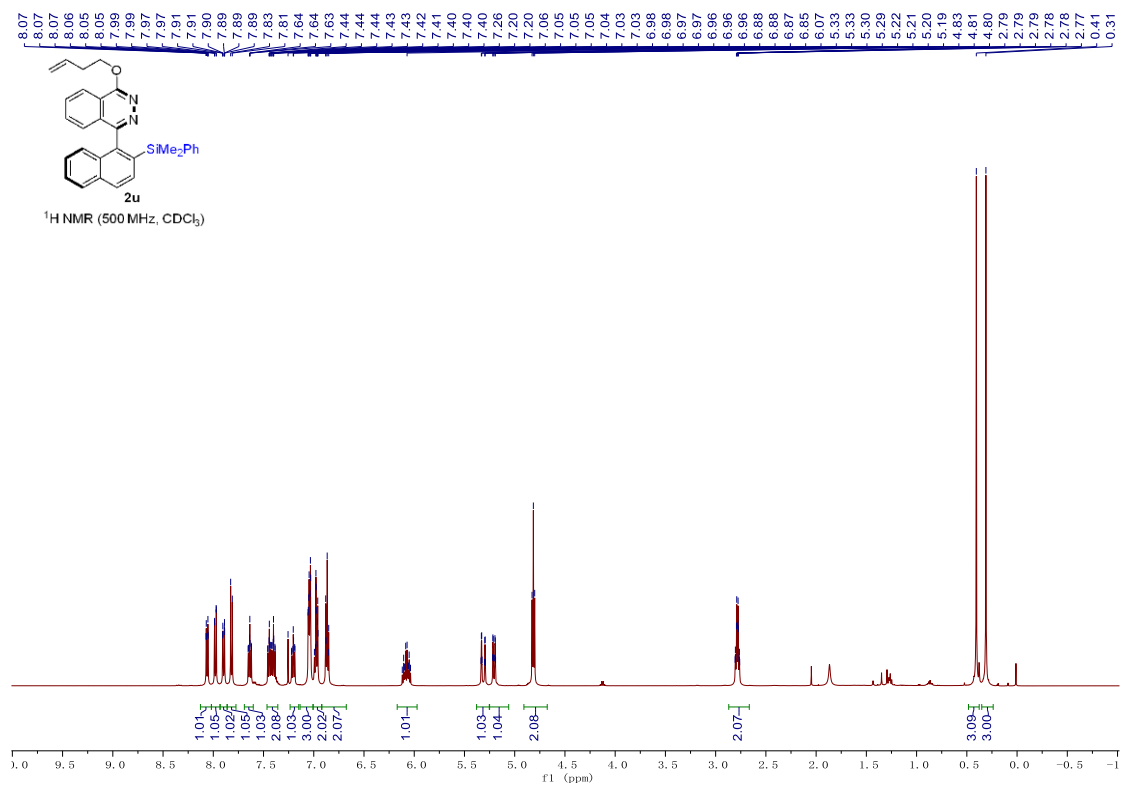
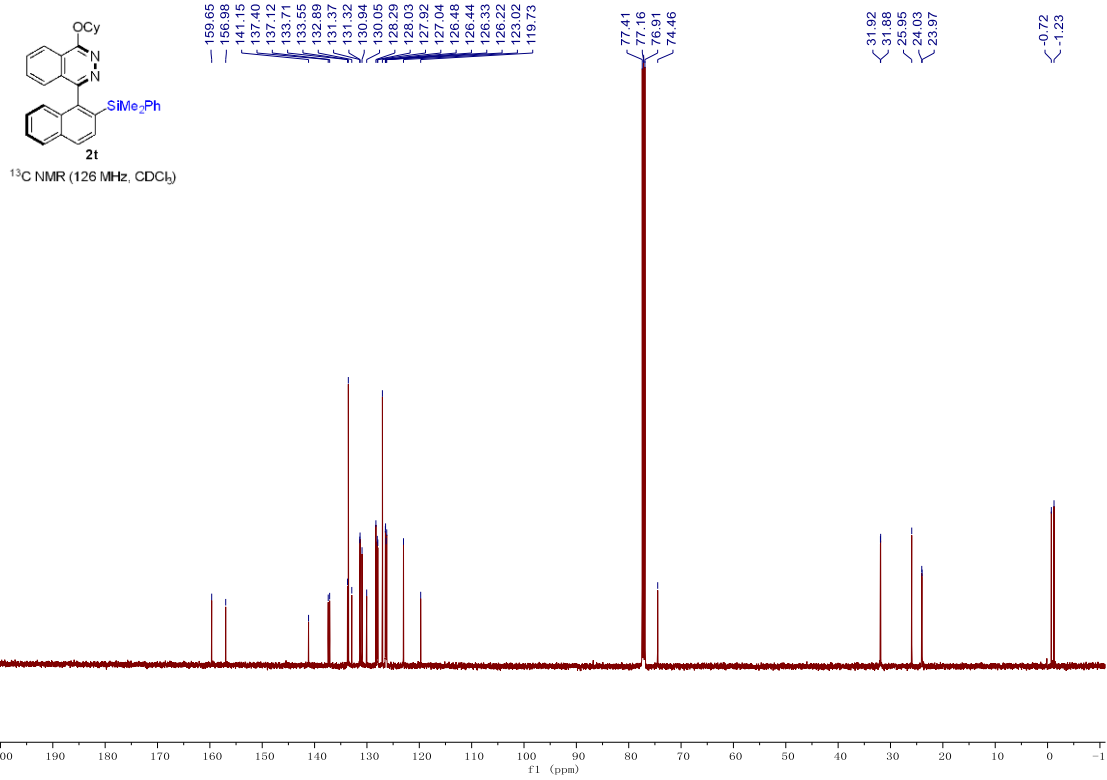


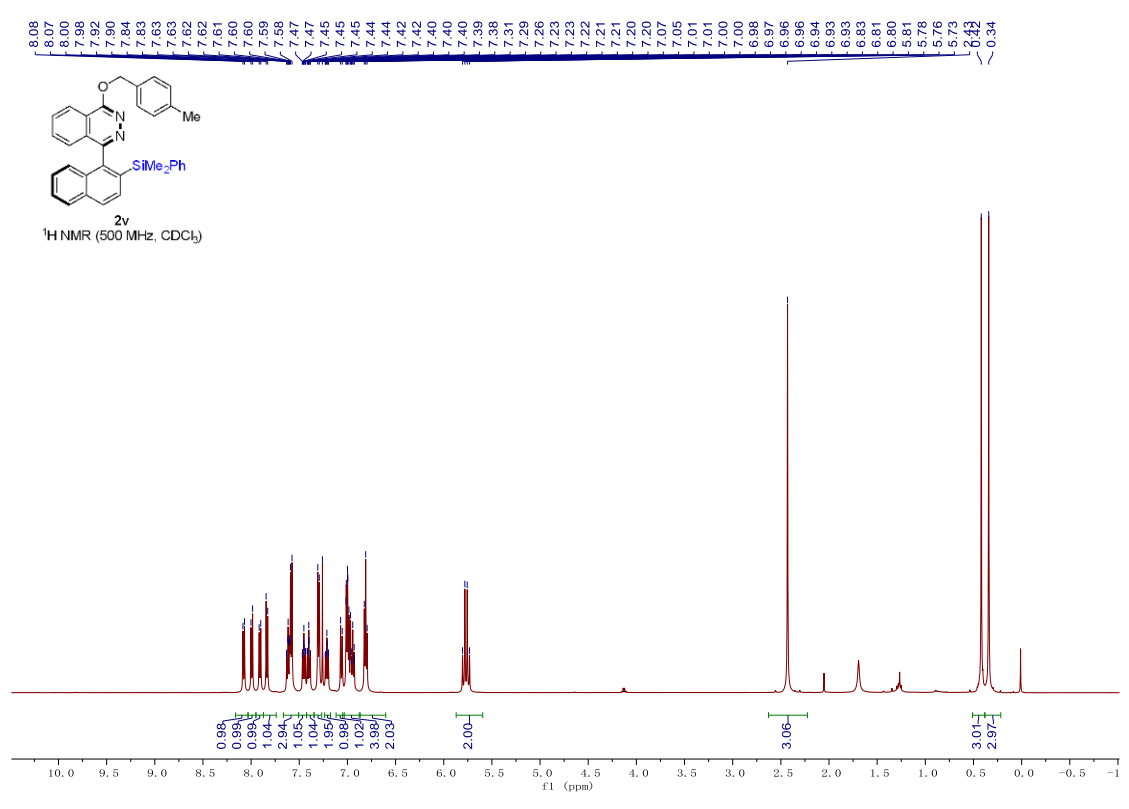
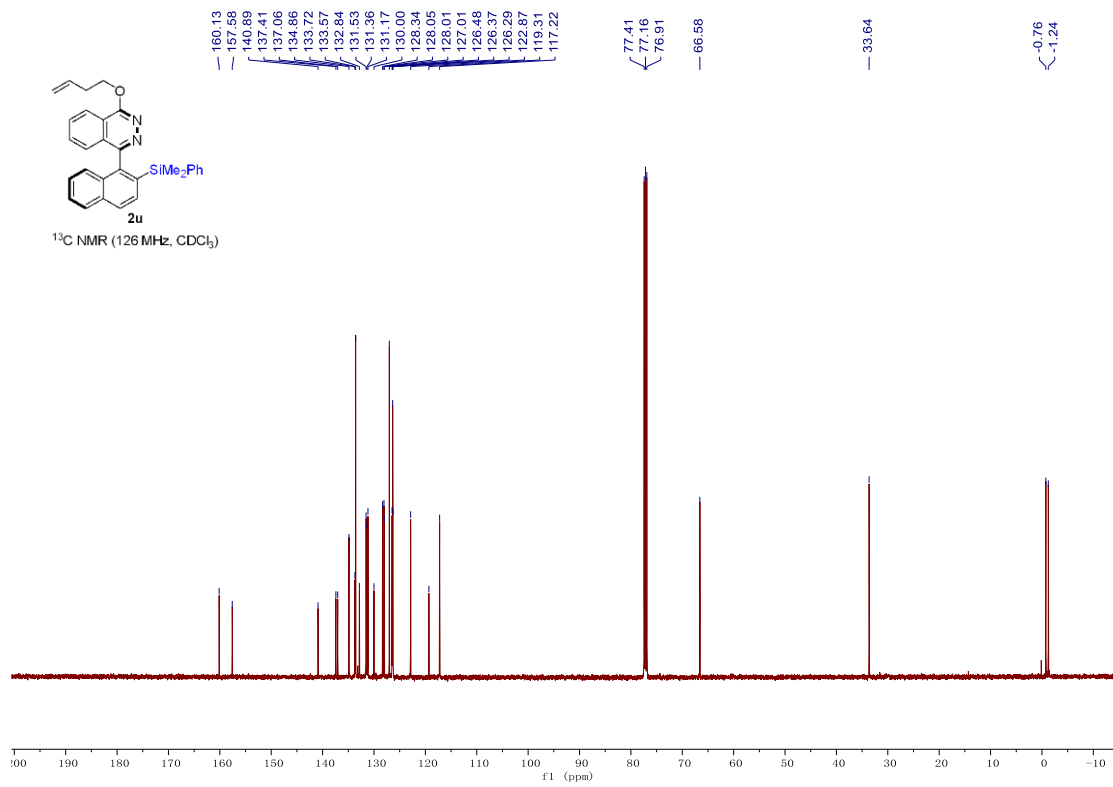


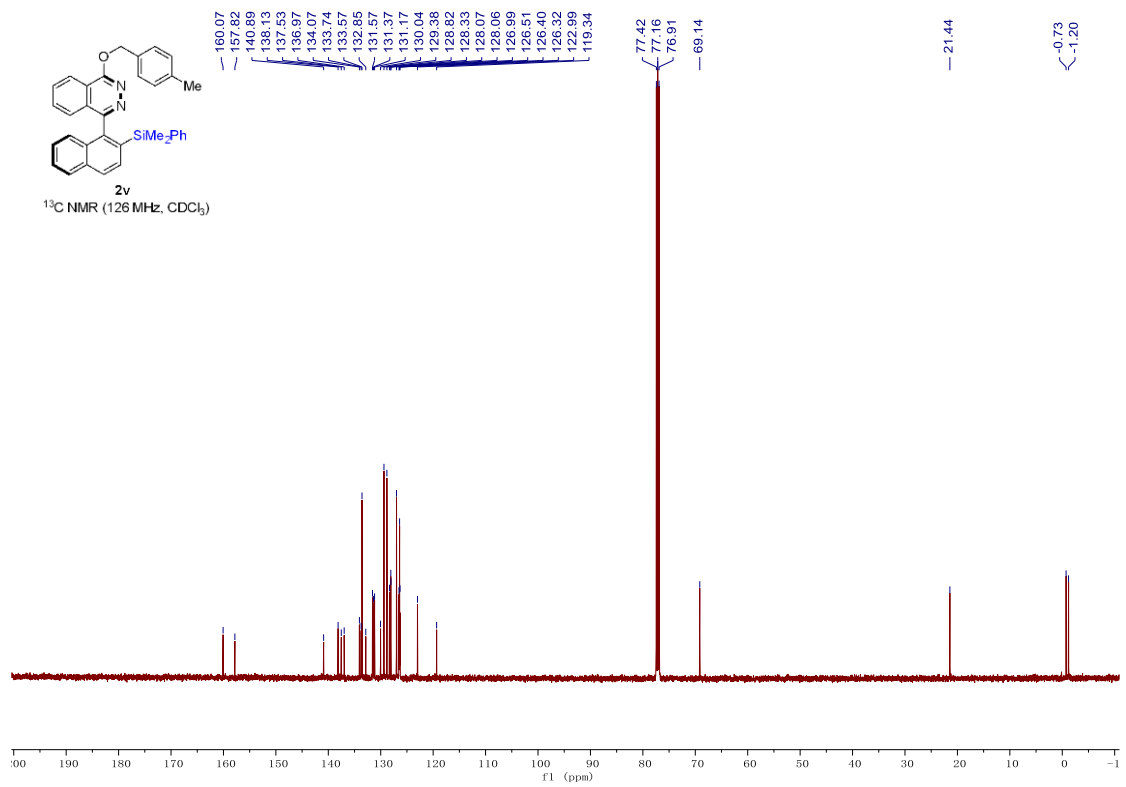
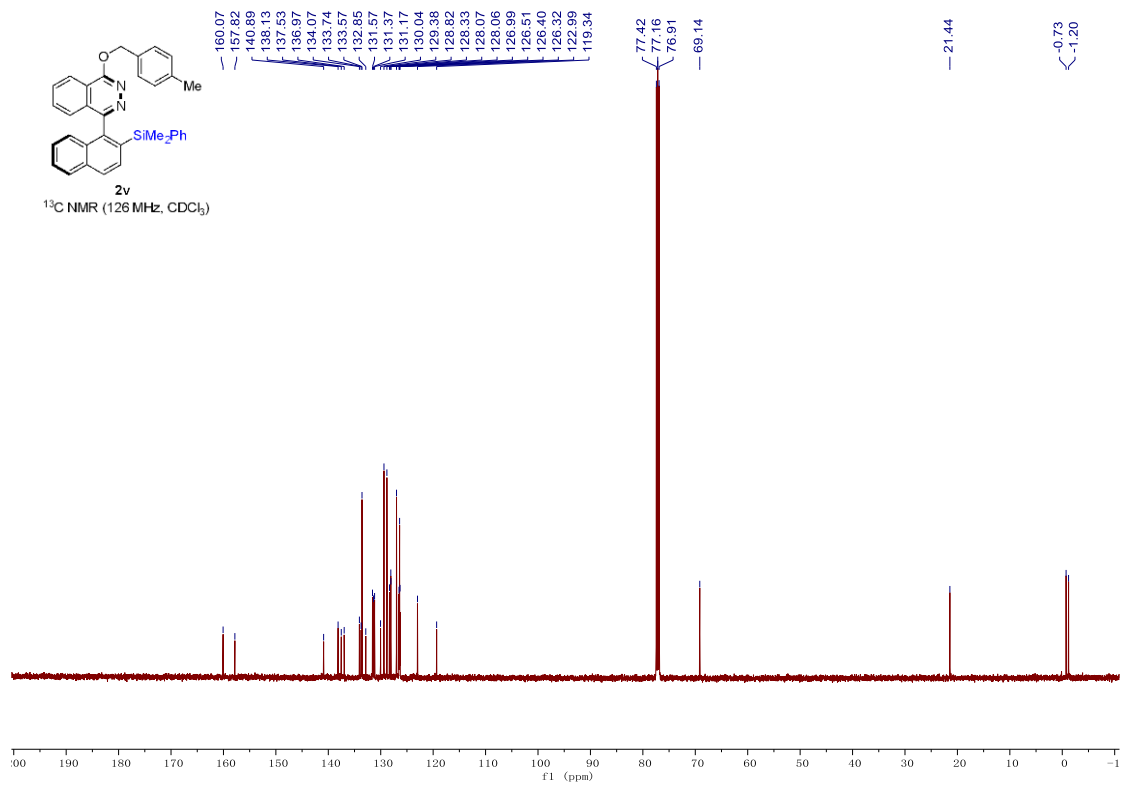


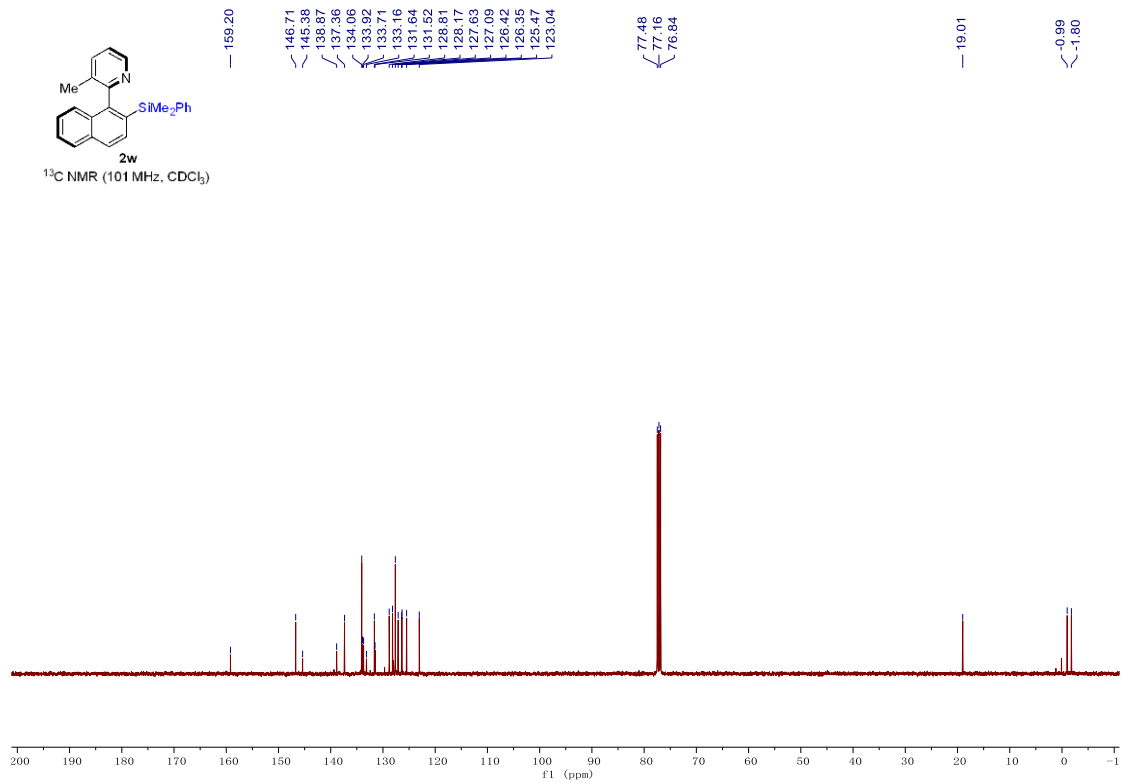
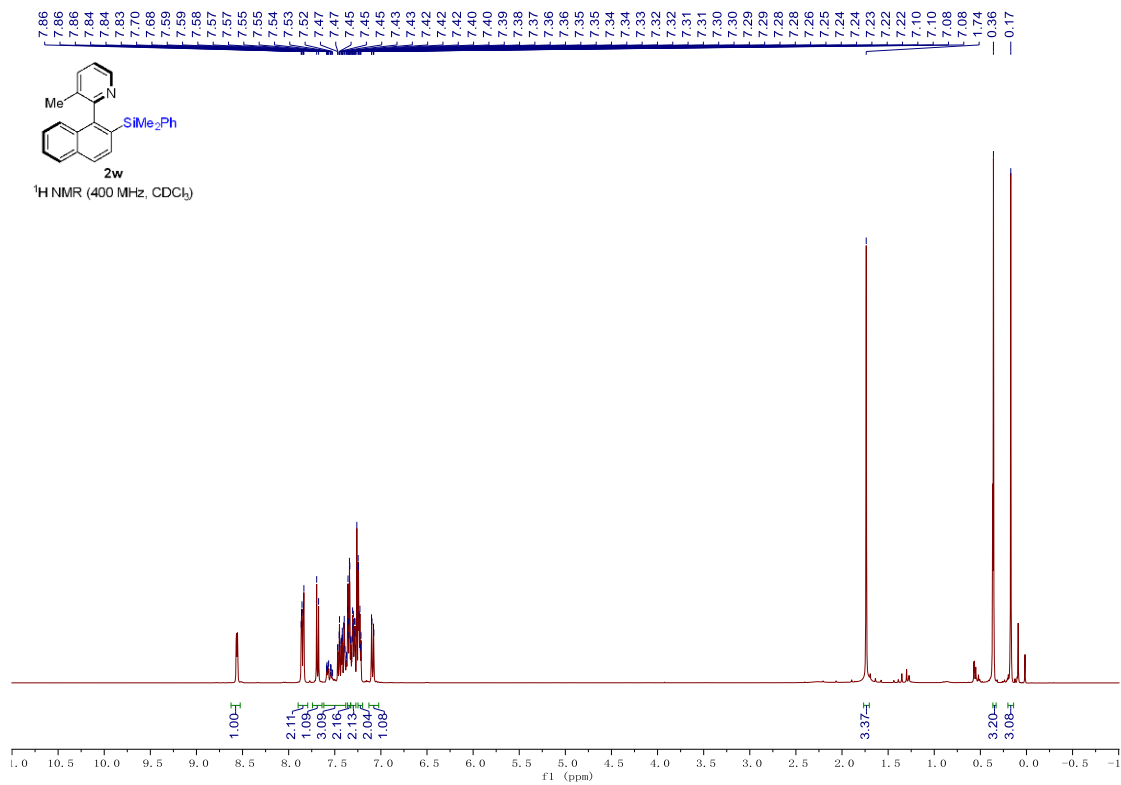




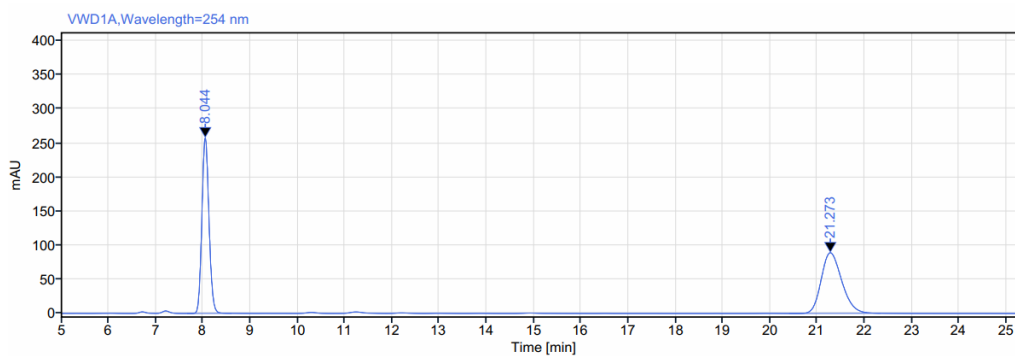
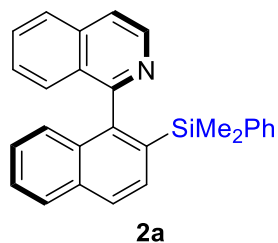






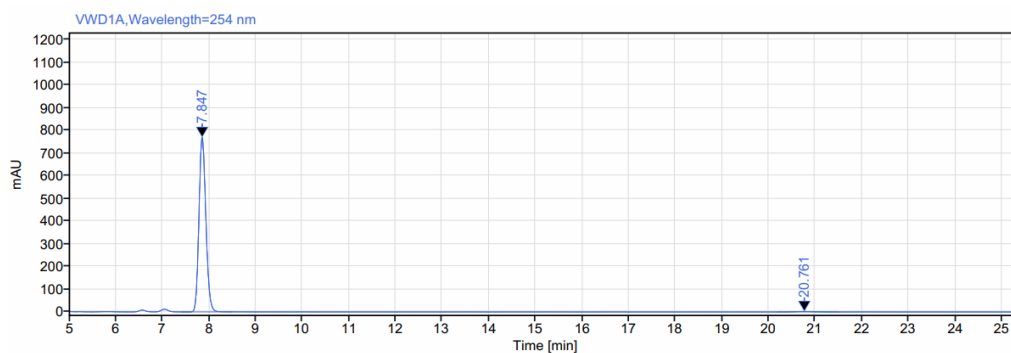


## HPLC Chromatograms



Signal: VWD1A, Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.044	MM m	0.94	2684.39	257.83	49.92	
21.273	MM m	1.93	2693.06	89.13	50.08	
<b>Sum</b>			<b>5377.45</b>			

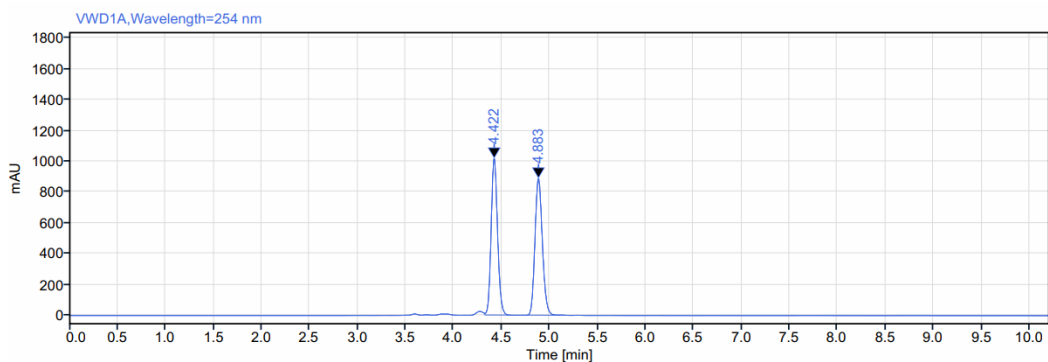
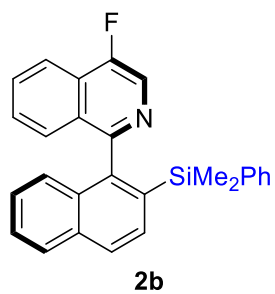


Signal: VWD1A, Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.847	MM m	1.10	7915.26	769.16	99.26	
20.761	MM m	1.34	58.72	2.01	0.74	
<b>Sum</b>			<b>7973.97</b>			

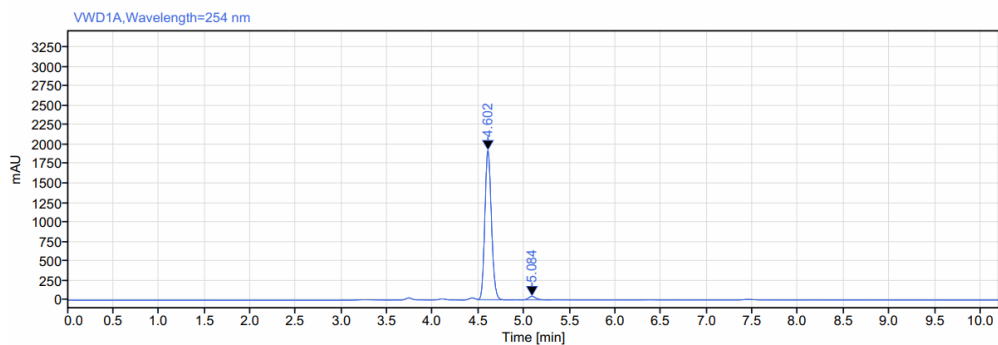
HPLC (Chiralpak IC-3):  $t_R = 7.85$  (major),  $20.76$  (minor)

Condition: 96:4, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
4.422	MM m	0.35	4721.91	1017.57	49.84	
4.883	MM m	0.49	4753.13	888.88	50.16	
<b>Sum</b>			<b>9475.03</b>			

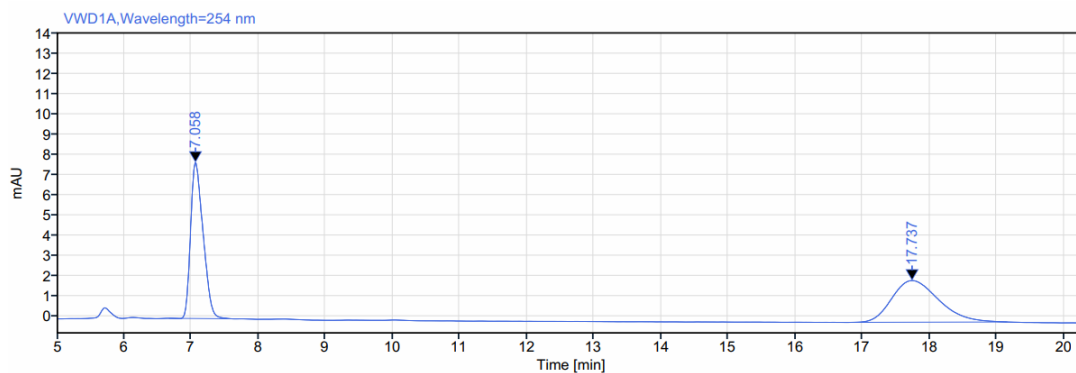
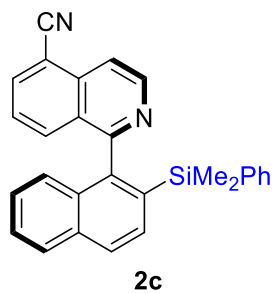


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
4.602	MM m	0.40	9610.73	1922.95	97.36	
5.084	MM m	0.32	260.53	45.20	2.64	
<b>Sum</b>			<b>9871.27</b>			

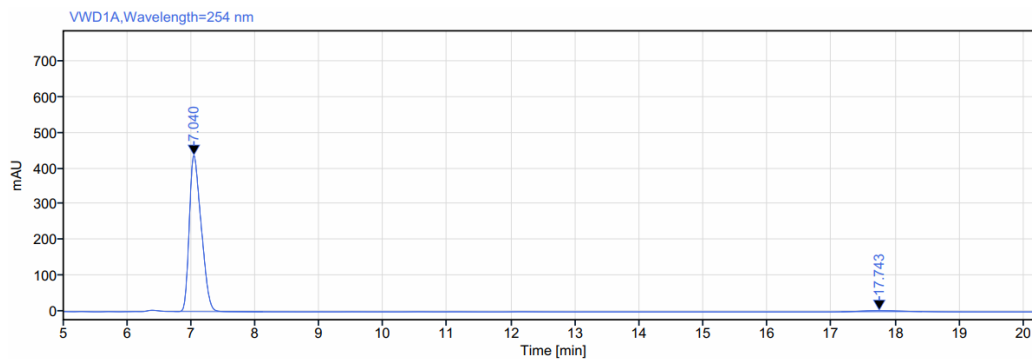
HPLC (Chiralpak IC-3):  $t_R = 4.60$  (major), 5.08 (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A, Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.058	MM m	1.03	99.64	7.71	49.88	
17.737	MM m	2.46	100.10	2.06	50.12	
<b>Sum</b>			<b>199.74</b>			

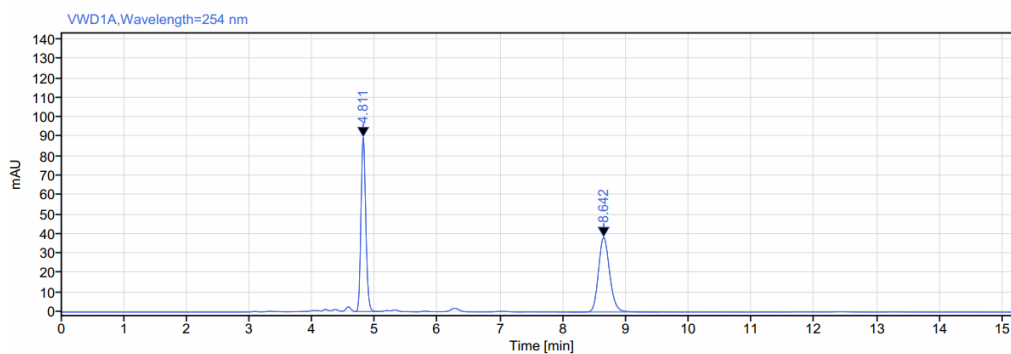
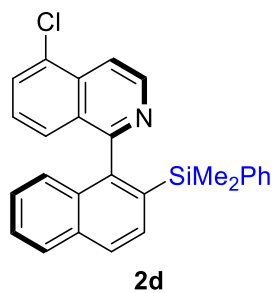


Signal: VWD1A, Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.040	MM m	1.38	5626.87	435.42	97.98	
17.743	MM m	1.26	116.04	2.85	2.02	
<b>Sum</b>			<b>5742.92</b>			

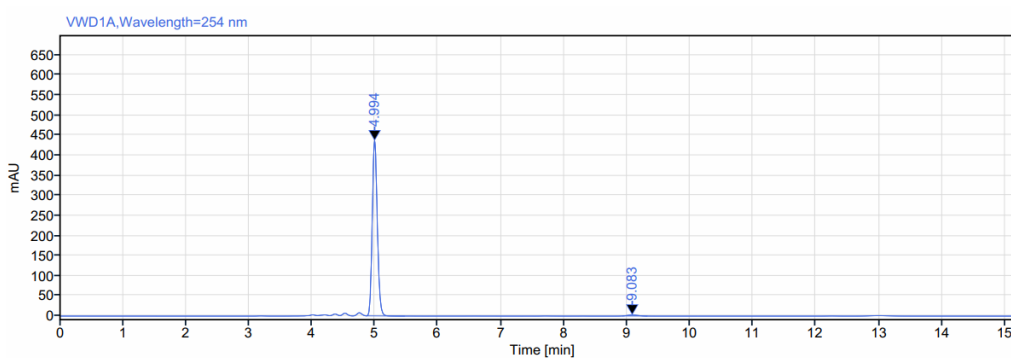
HPLC (Chiralpak OD-3):  $t_R = 7.04$  (major),  $17.74$  (minor)

Condition: 70:30, *n*-Hexane:*i*-PrOH, flow rate 0.7 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
4.811	MM m	0.37	474.54	89.39	50.04	
8.642	MM m	1.41	473.86	38.31	49.96	
<b>Sum</b>			<b>948.41</b>			

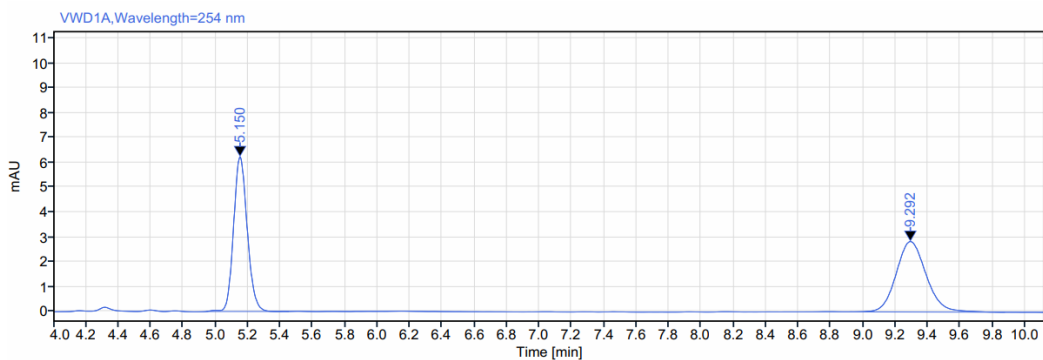
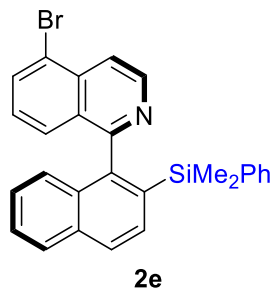


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
4.994	MM m	0.62	2442.96	436.18	98.90	
9.083	MM m	0.40	27.24	2.38	1.10	
<b>Sum</b>			<b>2470.21</b>			

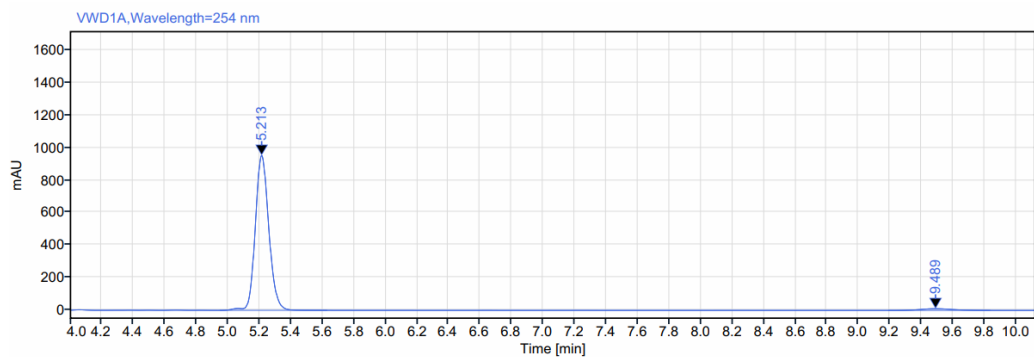
HPLC (Chiralpak IC-3):  $t_R = 4.99$  (major), 9.08 (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.150	MM m	0.51	36.50	6.22	50.01	
9.292	MM m	0.96	36.47	2.83	49.99	
<b>Sum</b>			<b>72.97</b>			

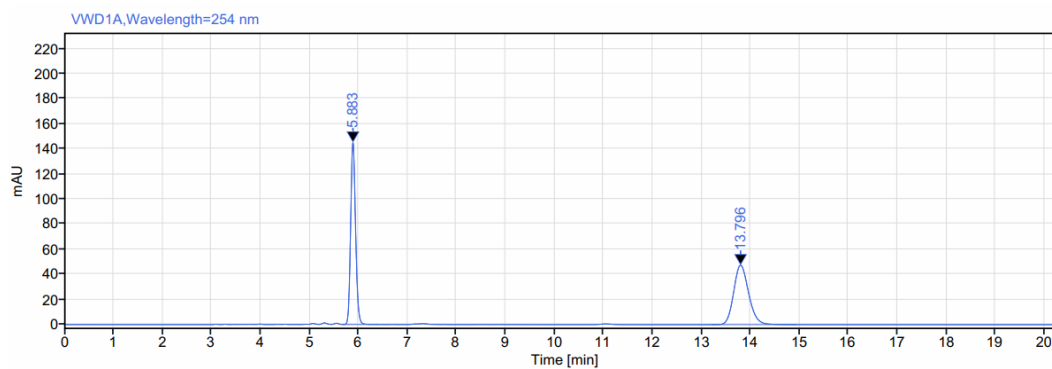
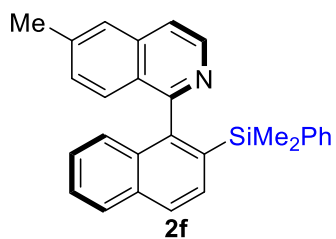


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.213	MM m	0.68	5689.62	951.95	97.58	
9.489	MM m	0.65	140.92	10.39	2.42	
<b>Sum</b>			<b>5830.54</b>			

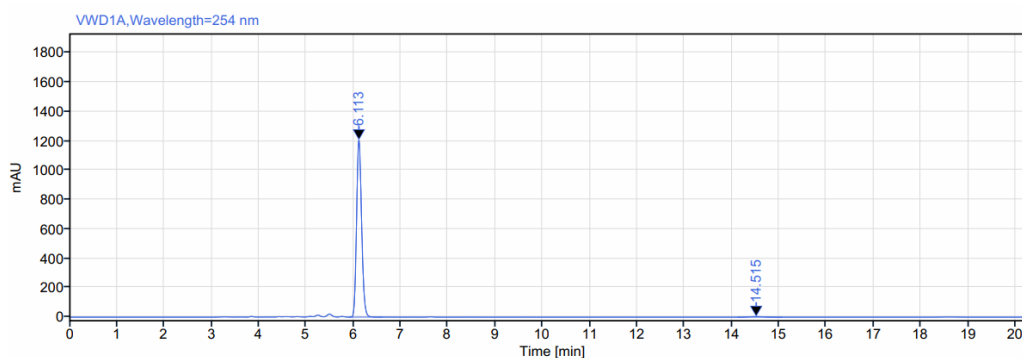
HPLC (Chiralpak IC-3):  $t_R = 5.21$  (major), 9.49 (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.883	MM m	0.72	1011.14	145.23	50.16	
13.796	MM m	1.74	1004.77	47.44	49.84	
<b>Sum</b>			<b>2015.91</b>			

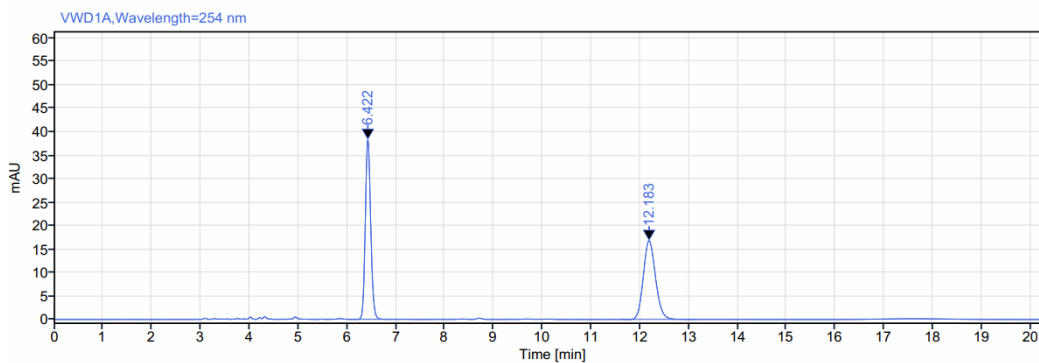
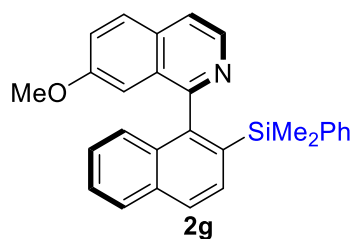


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.113	MM m	0.72	8934.30	1207.05	99.00	
14.515	MM m	0.96	90.22	3.96	1.00	
<b>Sum</b>			<b>9024.52</b>			

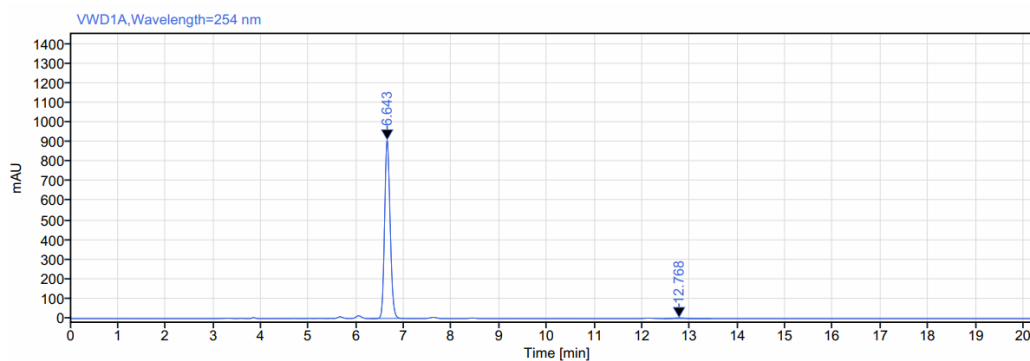
HPLC (Chiralpak IC-3):  $t_R = 6.11$  (major),  $14.52$  (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A, Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.422	MM m	0.87	294.56	38.36	50.23	
12.183	MM m	1.51	291.84	16.81	49.77	
<b>Sum</b>			<b>586.41</b>			

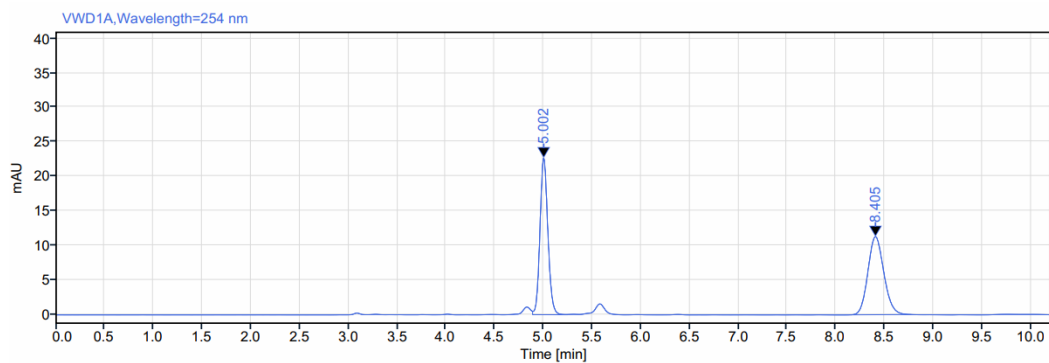
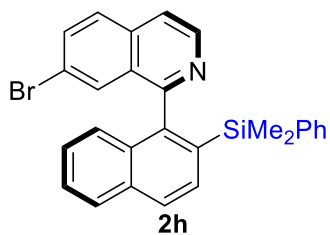


Signal: VWD1A, Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.643	MM m	0.67	7335.00	907.96	99.09	
12.768	MM m	0.99	67.07	3.67	0.91	
<b>Sum</b>			<b>7402.07</b>			

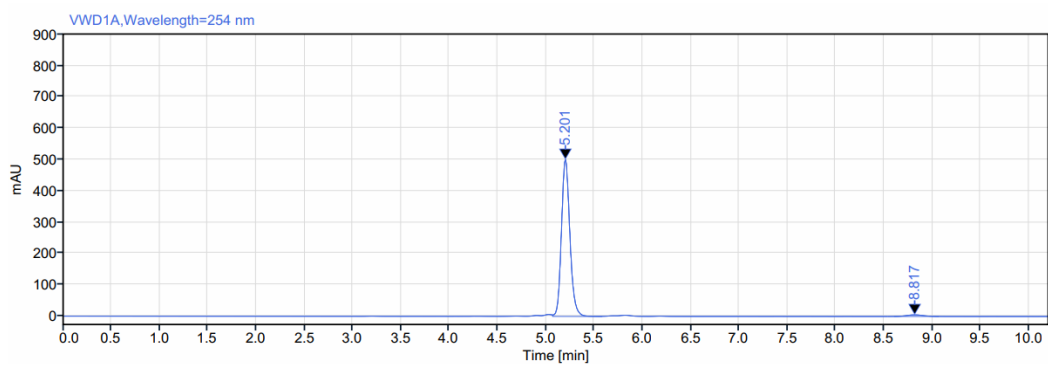
HPLC (Chiralpak IC-3):  $t_R = 6.64$  (major),  $12.77$  (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.002	MM m	0.36	127.74	22.68	49.88	
8.405	MM m	0.62	128.34	11.30	50.12	
<b>Sum</b>			<b>256.08</b>			

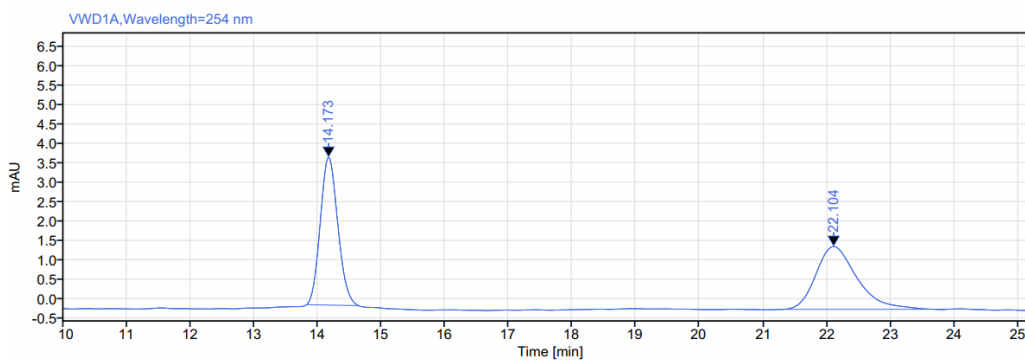
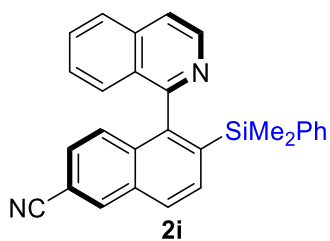


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.201	MM m	0.51	3050.86	501.11	98.09	
8.817	MM m	0.46	59.32	5.12	1.91	
<b>Sum</b>			<b>3110.19</b>			

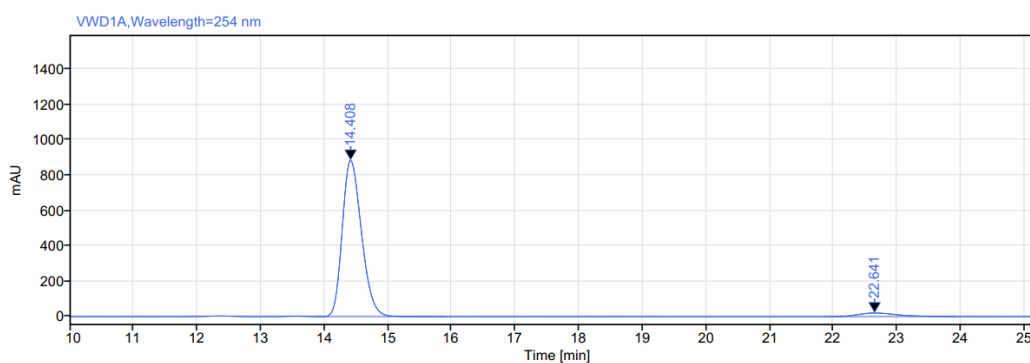
HPLC (Chiralpak IC-3):  $t_R = 5.20$  (major), 8.82 (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
14.173	MM m	0.82	73.00	3.81	50.19	
22.104	MM m	2.58	72.44	1.62	49.81	
<b>Sum</b>			<b>145.44</b>			

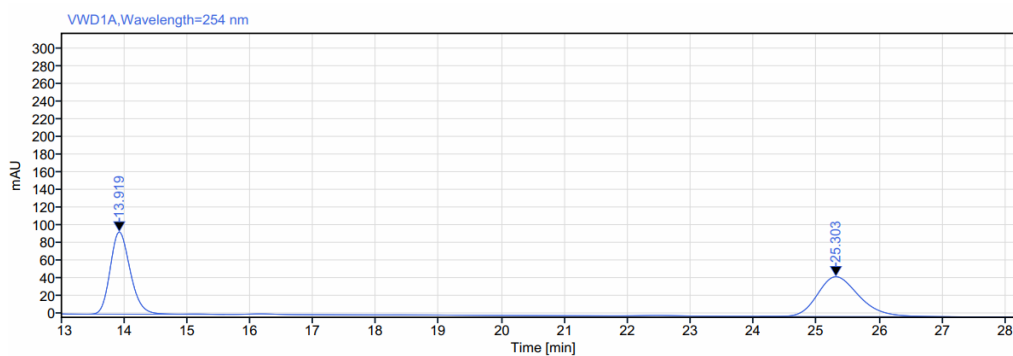
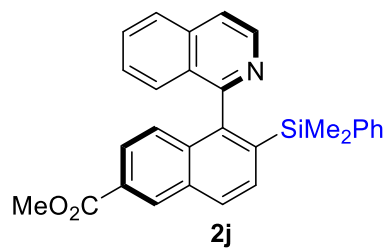


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
14.408	MM m	2.04	18596.17	885.36	95.42	
22.641	MM m	2.07	893.31	20.58	4.58	
<b>Sum</b>			<b>19489.48</b>			

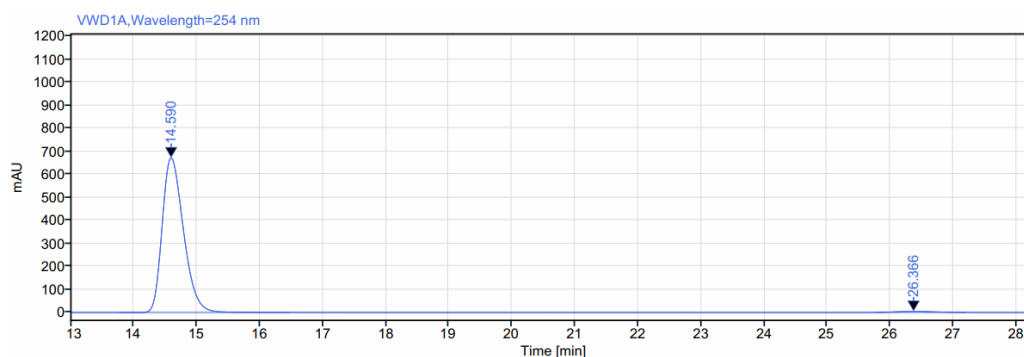
HPLC (Chiralpak IC-3):  $t_R = 14.41$  (major),  $22.64$  (minor)

Condition: 80:20, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.919	MM m	2.45	2060.51	92.94	50.05	
25.303	MM m	3.02	2056.52	44.96	49.95	
<b>Sum</b>			<b>4117.03</b>			

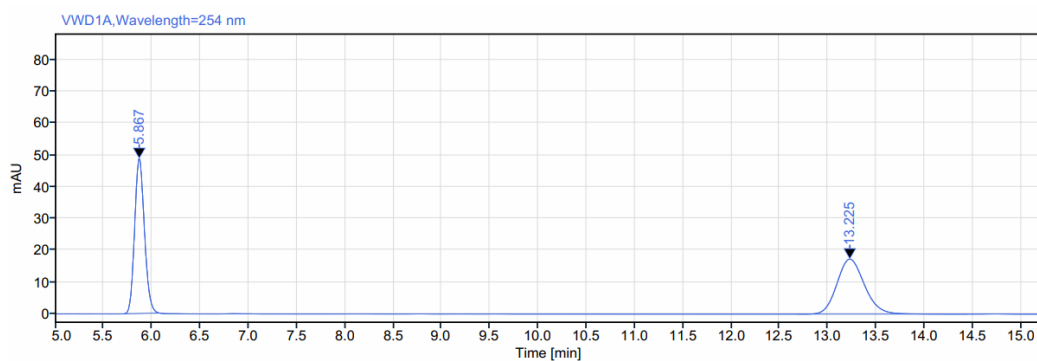
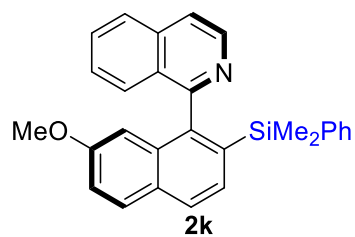


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
14.590	MM m	2.70	15795.13	673.52	98.66	
26.366	MM m	1.43	214.71	5.15	1.34	
<b>Sum</b>			<b>16009.84</b>			

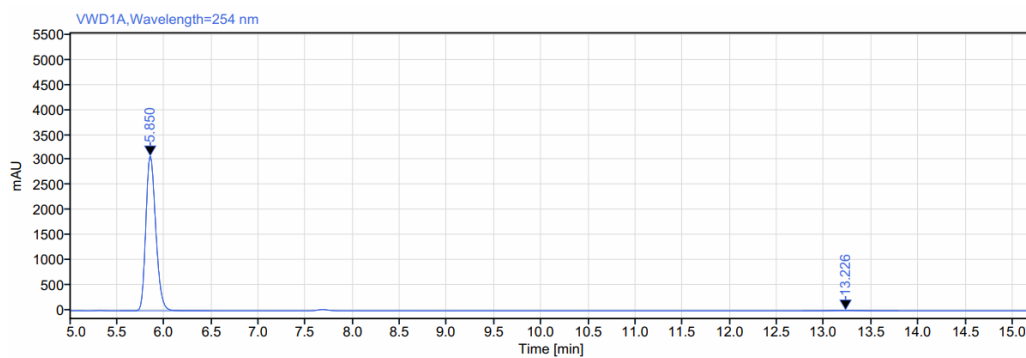
HPLC (Chiralpak IC-3):  $t_R = 14.59$  (major),  $26.34$  (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.867	MM m	0.39	344.24	48.77	50.08	
13.225	MM m	1.76	343.08	17.32	49.92	
<b>Sum</b>			<b>687.32</b>			

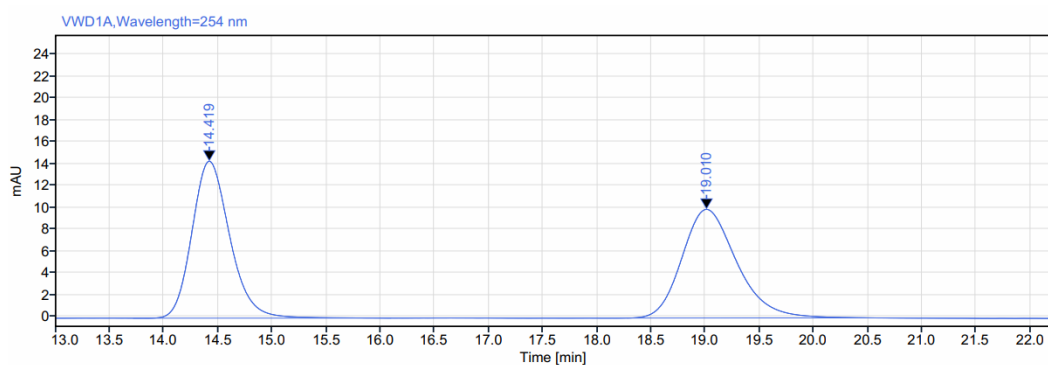
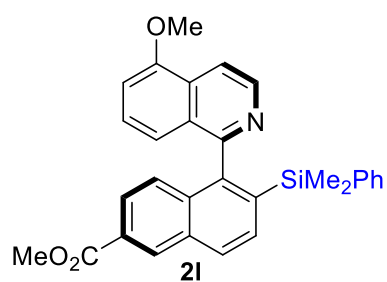


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.850	MM m	0.94	22485.31	3075.07	99.27	
13.226	MM m	1.03	165.27	8.42	0.73	
<b>Sum</b>			<b>22650.58</b>			

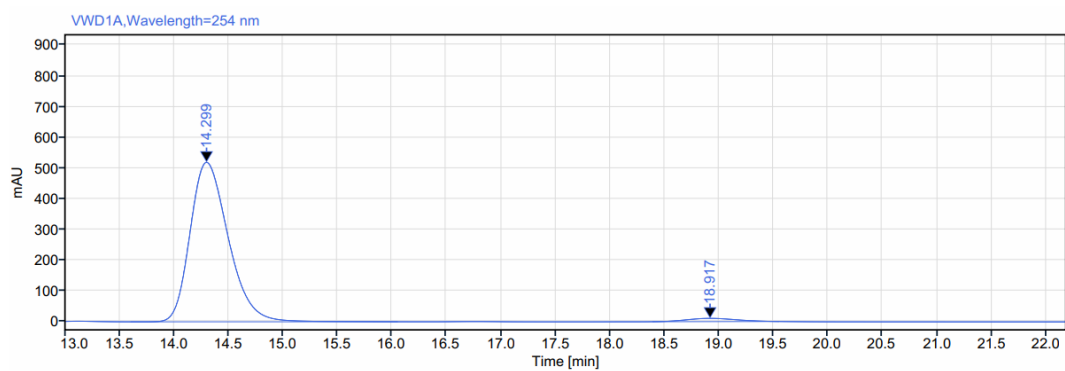
HPLC (Chiralpak IC-3):  $t_R = 5.85$  (major), 13.23 (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
14.419	MM m	2.38	347.83	14.33	49.94	
19.010	MM m	2.21	348.64	9.92	50.06	
<b>Sum</b>			<b>696.47</b>			

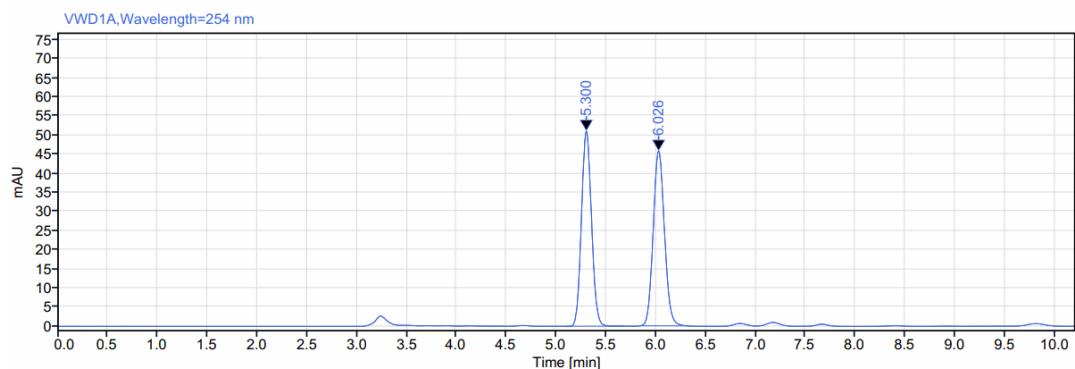
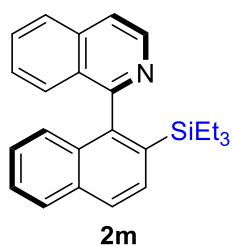


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
14.299	MM m	2.45	12639.93	519.08	97.42	
18.917	MM m	1.16	334.10	10.58	2.58	
<b>Sum</b>			<b>12974.03</b>			

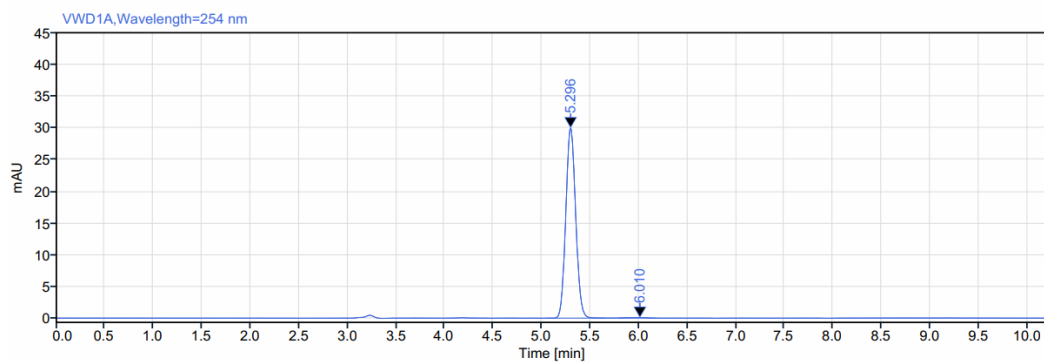
HPLC (Chiralpak IC-3):  $t_R$  = 14.30 (major), 18.92 (minor)

Condition: 85:15, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.300	MM m	0.59	358.74	51.13	49.92	
6.026	MM m	0.46	359.86	45.79	50.08	
<b>Sum</b>			<b>718.61</b>			

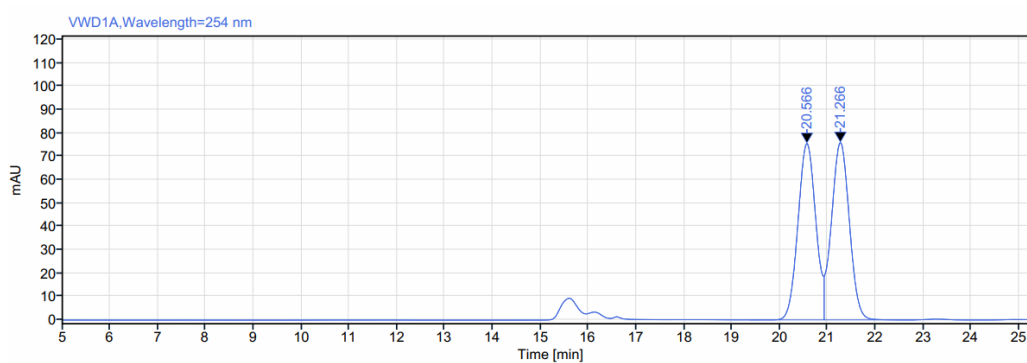
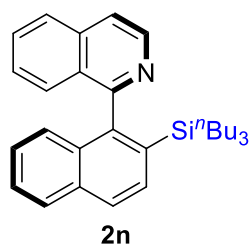


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.296	MM m	0.62	212.80	30.11	99.61	
6.010	MM m	0.38	0.82	0.08	0.39	
<b>Sum</b>			<b>213.63</b>			

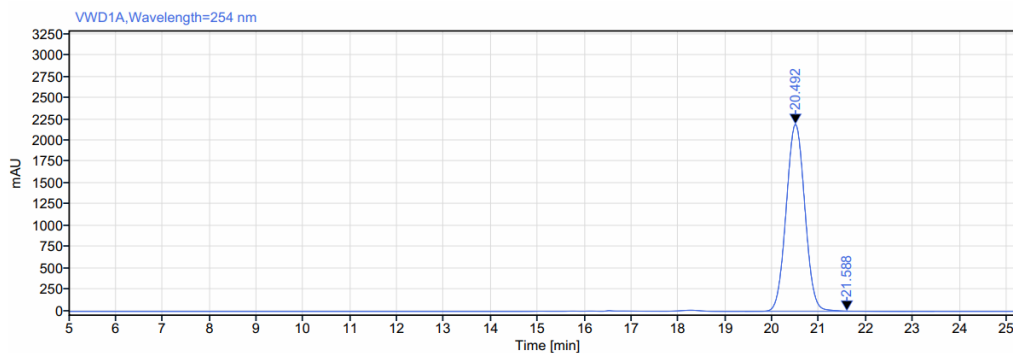
HPLC (Chiralpak IC-3):  $t_R = 5.30$  (major),  $6.01$  (minor)

Condition: 96:4, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
20.566	MM m	1.56	1956.71	75.50	49.81	
21.266	MM m	1.91	1971.56	75.92	50.19	
<b>Sum</b>			<b>3928.27</b>			

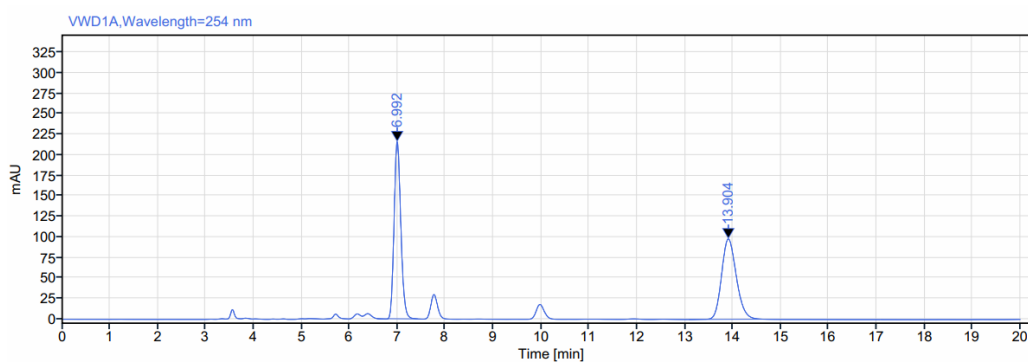
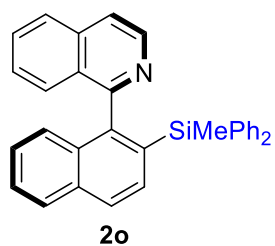


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
20.492	MM m	2.17	60586.26	2189.64	99.87	
21.588	MM m	1.86	76.40	2.57	0.13	
<b>Sum</b>			<b>60662.65</b>			

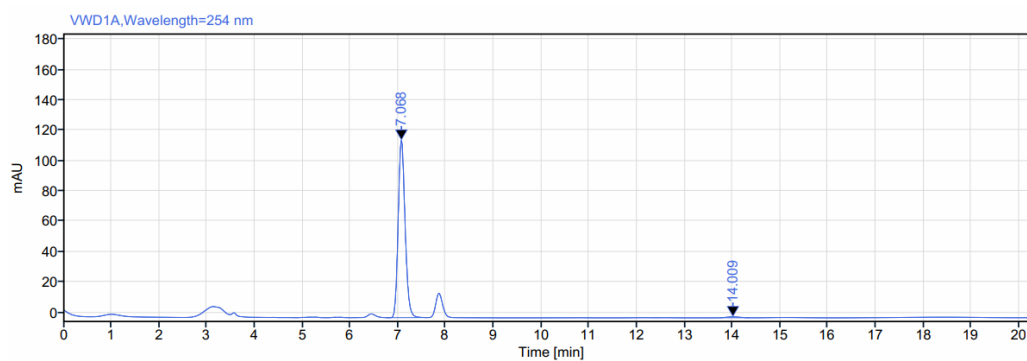
HPLC (Chiralpak IC-3):  $t_R = 20.50$  (major),  $21.59$  (minor)

Condition: 99:1, *n*-Hexane:*i*-PrOH, flow rate 0.2 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.992	MM m	0.85	2103.51	215.53	50.12	
13.904	MM m	1.58	2093.20	97.94	49.88	
<b>Sum</b>			<b>4196.71</b>			

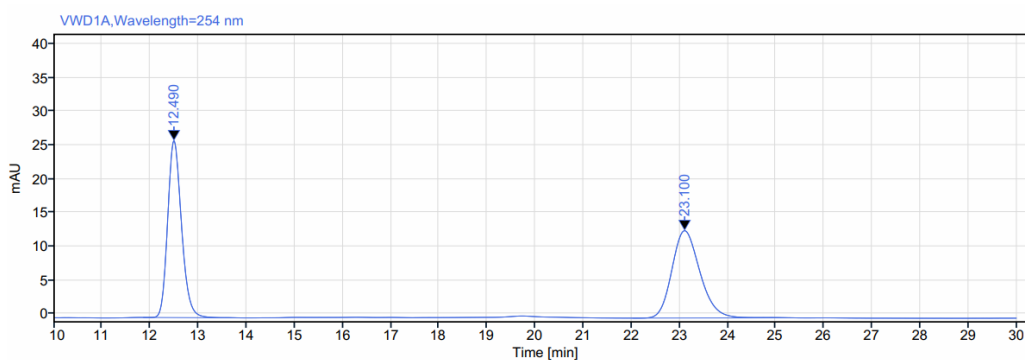
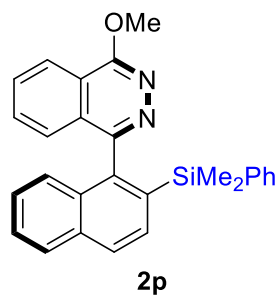


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.068	MM m	0.85	1170.49	116.81	99.07	
14.009	MM m	0.61	11.00	0.59	0.93	
<b>Sum</b>			<b>1181.49</b>			

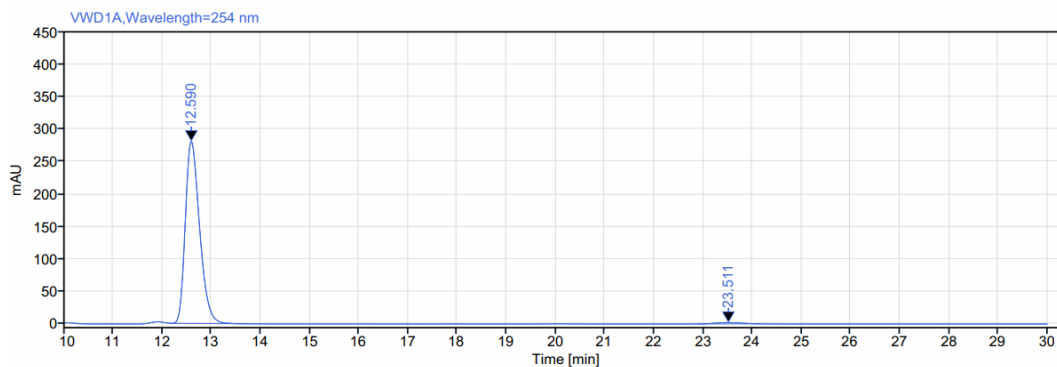
HPLC (Chiralpak IC-3):  $t_R = 7.07$  (major), 14.01 (minor)

Condition: 96:4, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.490	MM m	2.03	522.97	26.15	49.98	
23.100	MM m	3.35	523.44	12.92	50.02	
<b>Sum</b>			<b>1046.40</b>			

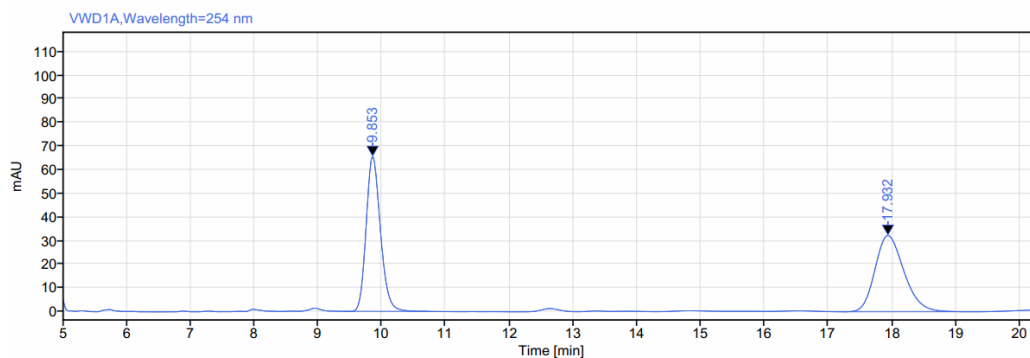
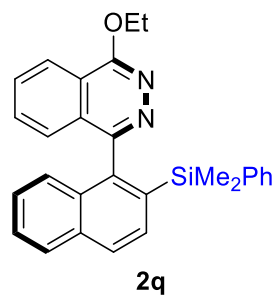


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.590	MM m	1.54	5673.94	281.12	98.67	
23.511	MM m	1.29	76.51	2.05	1.33	
<b>Sum</b>			<b>5750.45</b>			

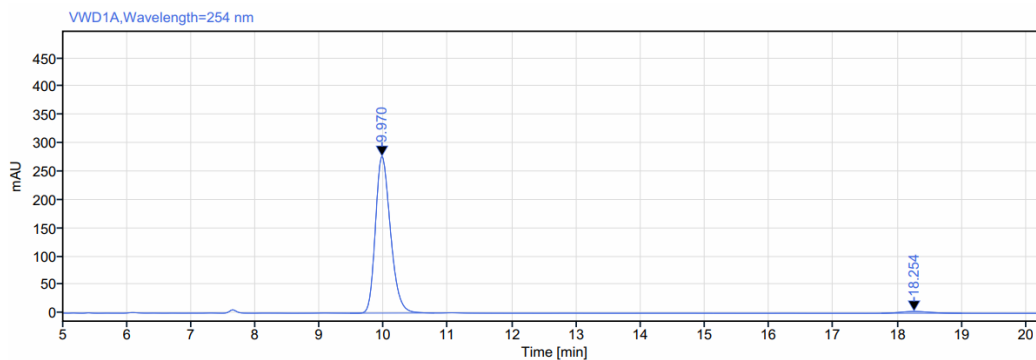
HPLC (Chiralpak IC-3):  $t_R = 12.59$  (major), 23.51 (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.853	MM m	1.34	1020.49	65.46	50.10	
17.932	MM m	1.91	1016.45	32.26	49.90	
<b>Sum</b>			<b>2036.94</b>			

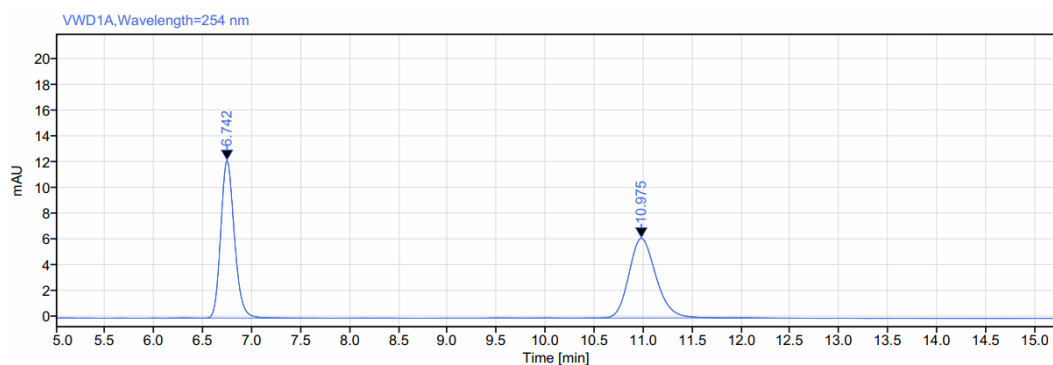
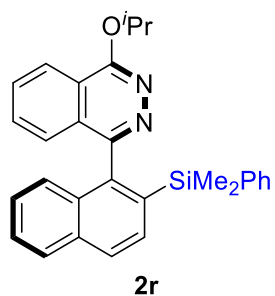


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.970	MM m	1.31	4494.18	276.57	97.85	
18.254	MM m	1.25	98.62	3.14	2.15	
<b>Sum</b>			<b>4592.80</b>			

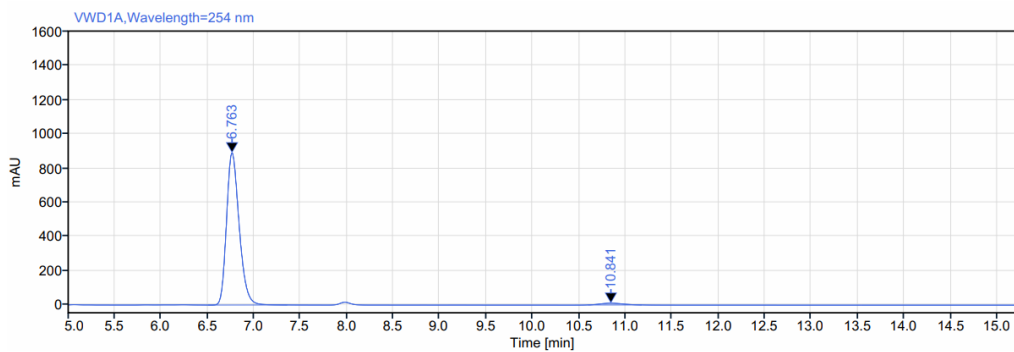
HPLC (Chiralpak IC-3):  $t_R = 9.97$  (major), 18.25 (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.742	MM m	1.26	117.70	12.16	49.97	
10.975	MM m	1.71	117.84	6.15	50.03	
<b>Sum</b>			<b>235.53</b>			

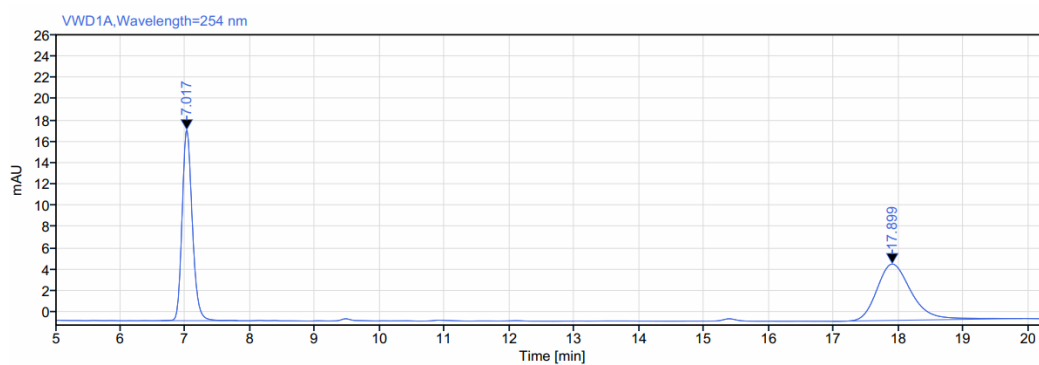
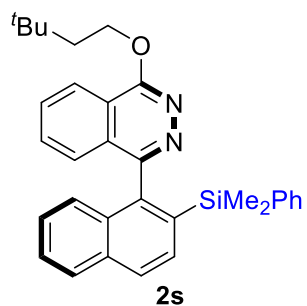


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.763	MM m	0.85	8424.83	891.48	98.01	
10.841	MM m	0.58	171.20	10.31	1.99	
<b>Sum</b>			<b>8596.04</b>			

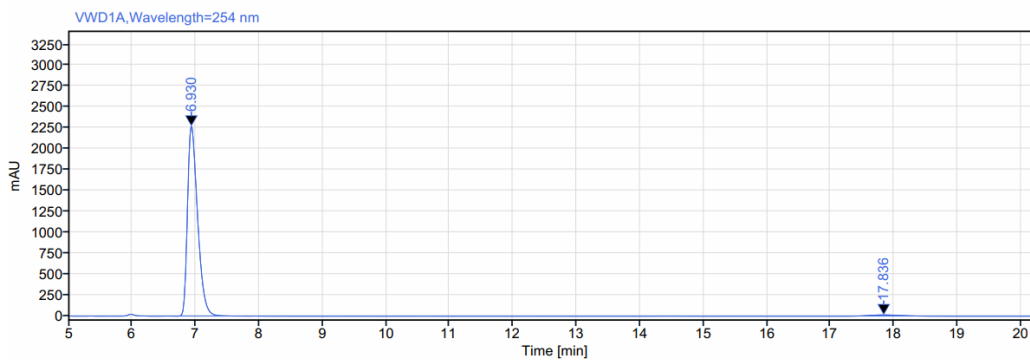
HPLC (Chiralpak IC-3):  $t_R = 6.76$  (major), 10.84 (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.017	MM m	1.18	195.50	17.90	50.03	
17.899	MM m	2.93	195.26	5.29	49.97	
<b>Sum</b>			<b>390.77</b>			

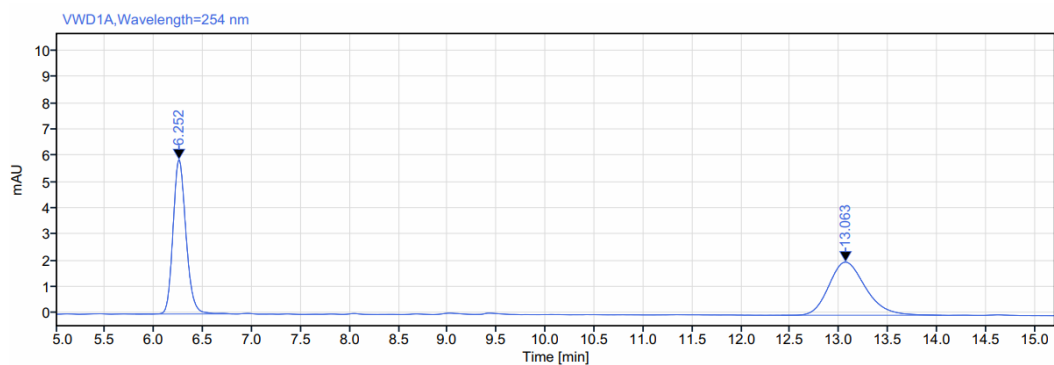
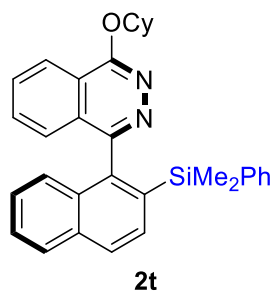


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.930	MM m	1.12	25097.46	2273.20	98.41	
17.836	MM m	0.97	404.32	13.40	1.59	
<b>Sum</b>			<b>25501.78</b>			

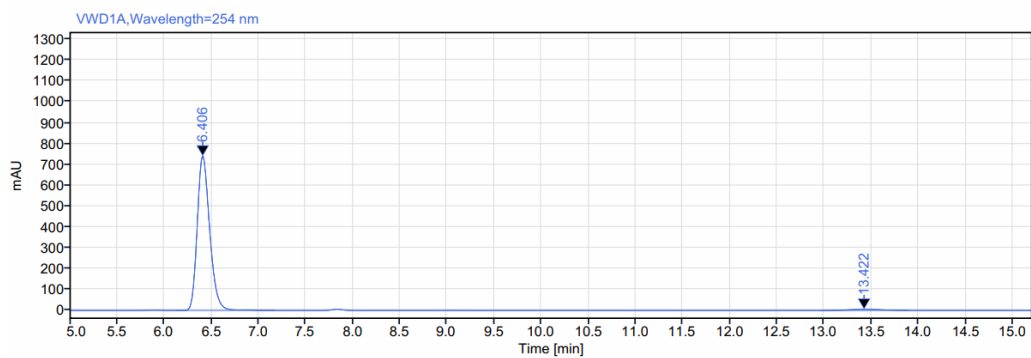
HPLC (Chiralpak IC-3):  $t_R = 6.93$  (major),  $17.84$  (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.252	MM m	0.99	53.96	5.87	50.61	
13.063	MM m	1.64	52.65	2.02	49.39	
<b>Sum</b>			<b>106.61</b>			

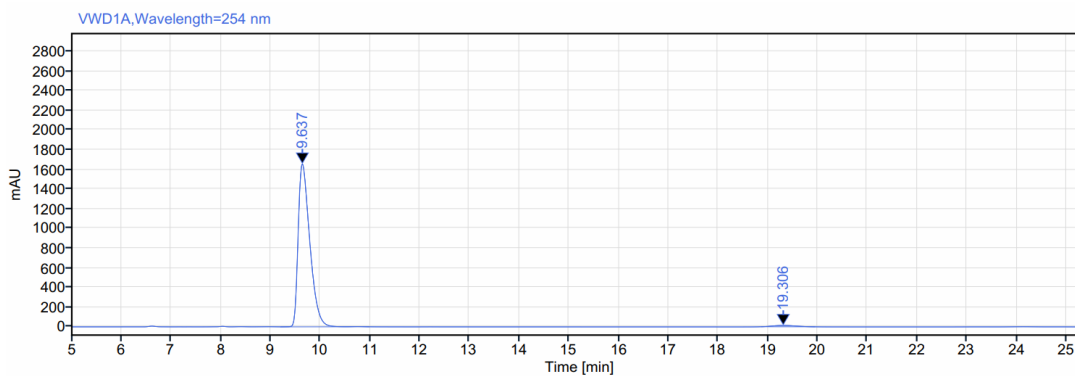
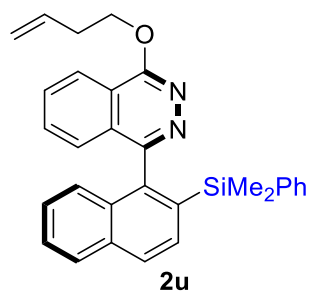


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.406	MM m	1.05	6813.21	740.72	98.07	
13.422	MM m	0.93	134.05	5.57	1.93	
<b>Sum</b>			<b>6947.26</b>			

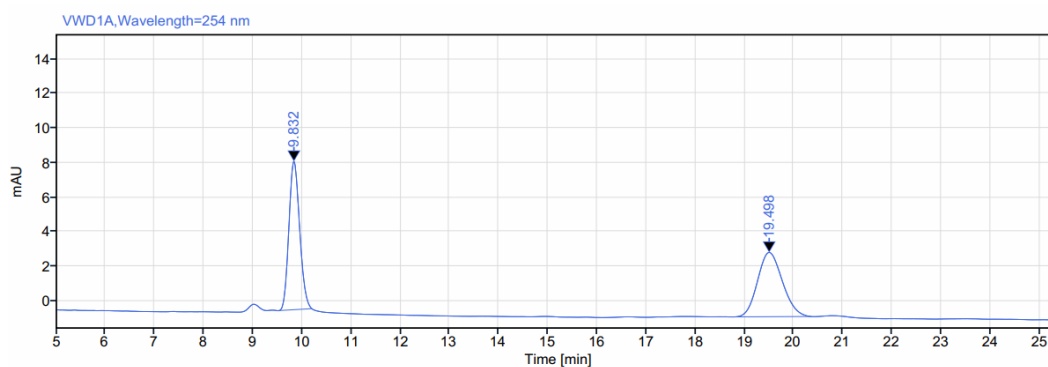
HPLC (Chiralpak IC-3):  $t_R = 6.41$  (major), 13.42 (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.637	VM m	1.79	26897.34	1656.98	98.38	
19.306	MM m	1.08	442.97	13.86	1.62	
<b>Sum</b>			<b>27340.32</b>			

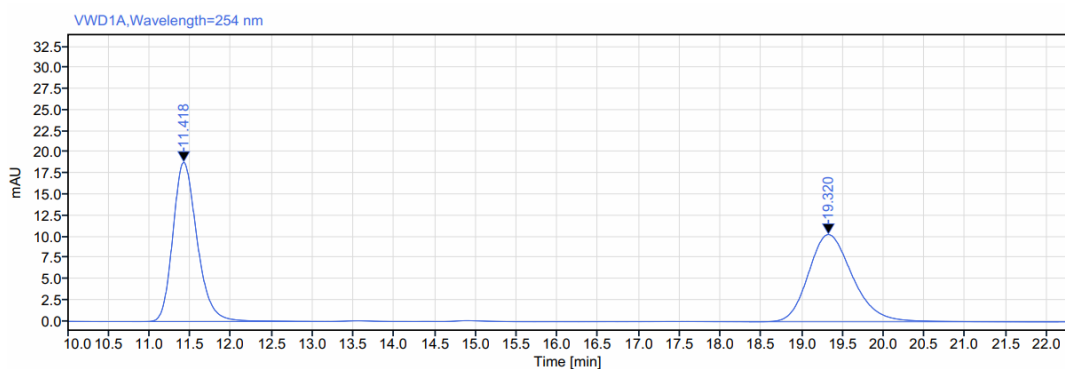
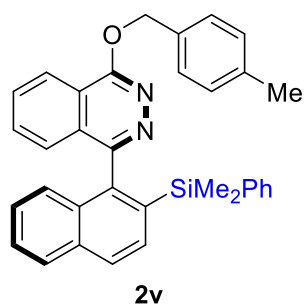


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.832	MM m	0.71	129.98	8.56	49.96	
19.498	MM m	1.61	130.19	3.71	50.04	
<b>Sum</b>			<b>260.17</b>			

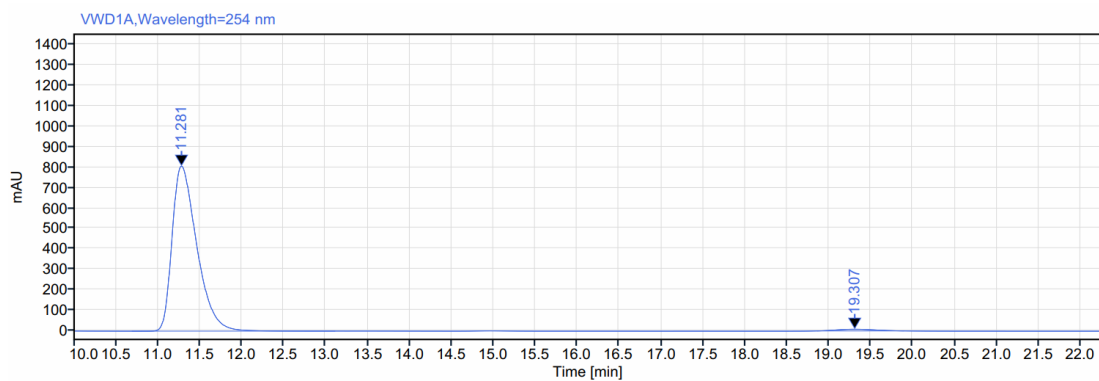
HPLC (Chiralpak IC-3):  $t_R = 9.83$  (major), 19.50 (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.418	MM m	2.18	389.61	18.85	50.08	
19.320	MM m	3.79	388.42	10.33	49.92	
<b>Sum</b>			<b>778.03</b>			

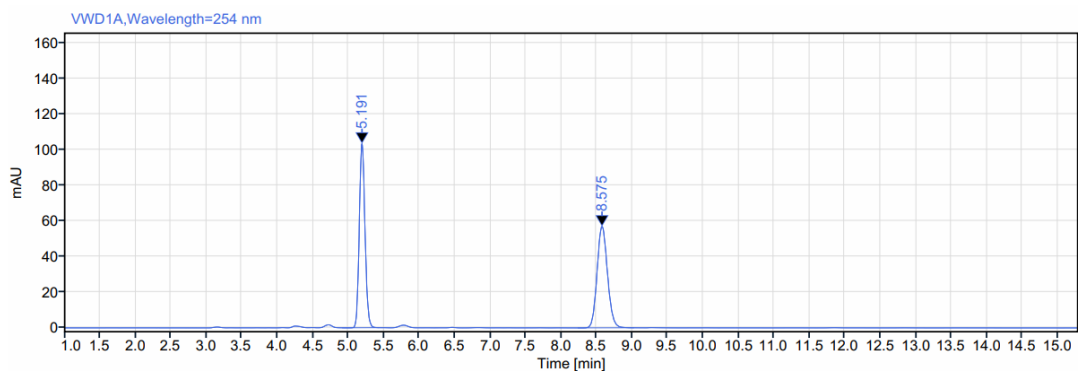
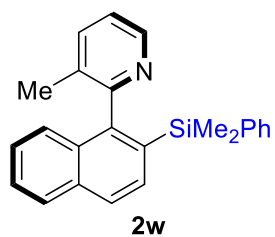


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.281	MM m	2.43	16482.03	804.92	98.39	
19.307	MM m	1.04	269.12	8.44	1.61	
<b>Sum</b>			<b>16751.15</b>			

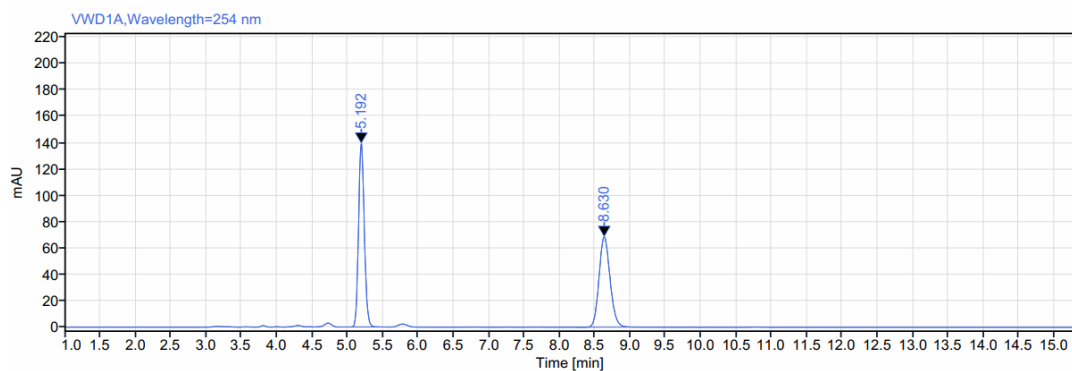
HPLC (Chiralpak IC-3):  $t_R = 11.28$  (major),  $19.30$  (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.191	MM m	0.52	581.65	103.74	49.95	
8.575	MM m	0.79	582.85	57.12	50.05	
<b>Sum</b>			<b>1164.49</b>			



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.192	MM m	0.50	790.66	139.33	51.54	
8.630	MM m	0.87	743.51	68.54	48.46	
<b>Sum</b>			<b>1534.16</b>			

HPLC (Chiralpak IC-3):  $t_R = 5.19$  (major),  $8.63$  (minor)

Condition: 90:10, *n*-Hexane:*i*-PrOH, flow rate 1.0 mL/min, 25 °C, 254 nm.