# Electronic Supplementary Information

# Cobalt Covalent Organic Framework: A Dual-Functional Atomic-Level Catalyst for Visible-Light-Driven C-H Annulation of Amides with Alkynes

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#### I. General remarks

Unless otherwise specified, all reactions were performed under air. <sup>1</sup>H NMR spectra were recorded on Bruker 400 or 500 MHz spectrometer with CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> as the solvent; <sup>13</sup>C NMR spectra were recorded on Bruker 101 or 126 MHz spectrometer with CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> as the solvent. Chemical shifts were reported in parts per million ( $\delta$ ) with TMS (0 ppm) as the internal standard. The peak patterns are indicated as follows: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), m (multiplet). The coupling constants (*J*) are reported in Hertz (Hz). The unknown products were additionally characterized by high resolution mass spectrometry (HRMS).

**Powder X-ray diffraction:** Powder X-ray diffraction (PXRD) patterns of the as-prepared samples were obtained on a powder Xray diffractometer (Cu K $\alpha$  radiation source, Ultima IV, Rigaku), from  $2\vartheta = 1.5^{\circ}$  up to 40° with 0.04° increment.

**UV-Vis diffuse reflectance spectroscopy:** UV-Vis diffuse reflectance spectra were recorded on a Hitachi UH4150 spectrophotometer in the wavelength range of 200  $\sim$  800 nm, v = 200 nm/min, and BaSO<sub>4</sub> was used as a reference.

**Fourier-transform infrared spectroscopy:** Fourier-transform infrared (FT-IR) spectra were collected in the range of 400  $\sim$  4000 cm<sup>-1</sup> on a Bruker IFS 66 v/s Fourier transform infrared spectrometer.

**Gas sorption isotherms:** The nitrogen adsorption and desorption isotherms were measured at 77 K using an ASAP 2460 instrument.

**Scanning electron microscopy:** Scanning electron microscopy (SEM) images were captured on a ZEISS Gemini 300, microscope operated at an accelerating voltage of 0.02-30 kV.

**Transmission electron microscopy:** Transmission electron microscopy (TEM) images were captured on a JEOL 2100FCs microscope at an accelerating voltage of 200 kV. The samples were prepared by drop-casting sonicated ethyl alcohol suspensions of the materials onto a copper grid.

<sup>13</sup>C CP/MAS NMR: The solid phases <sup>13</sup>C CP/MAS NMR spectra were collected on a Bruker Avance III 500 MHz WB solid-state NMR spectrometer.

**Thermogravimetric analysis:** Thermogravimetric analysis (TGA) was performed on an STA449 F5/QMS 403D instrument from room temperature to 500 °C or 800 °C at 10 °C/min rate under argon atmosphere.

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**X-ray photoelectron spectroscopy:** X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha system (excitation source is Al Kα ray, 1486.6 eV). All measurements were performed in the CAE mode with the reference of C 1s (284.8 eV).

Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM): Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (ACHAADF-STEM) images were captured on a JEOL 2100FCs microscope at an accelerating voltage of 200 kV. The samples were prepared by drop-casting sonicated ethyl alcohol suspensions of the materials onto a copper grid.

**X-ray absorption near-edge structure:** The X-ray absorption spectra (XAS) including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of the samples were collected at the Singapore Synchrotron Light Source (SSLS) center, where a pair of channel-cut Si (111) crystals was used in the monochromator. The storage ring was working at the energy of 2.5 GeV with average electron current of below 200 mA.

**Wavelet Transform:** For Wavelet Transform analysis, the  $\chi(k)$  exported from Athena was imported into the Hama Fortran code. The parameters were listed as follow: R range,  $1 \sim 4$  Å, k range,  $0 \sim 15.0$  Å<sup>-1</sup> for Co sample ( $0 \sim 15.0$  Å<sup>-1</sup> for Co foil, CoO and CoPc: cobalt phthalocyanine); k weight, 2; and Morlet function with  $\kappa = 5$ ,  $\sigma = 1$  was used as the mother wavelet to provide the overall distribution.

**Inductively coupled plasma mass spectrometry:** Inductively coupled plasma mass spectrometry (ICP-MS) was performed on an Agilent 5110 instrument. By ICP-MS, the amount of cobalt content in CoCOF-SYNU-1 was determined to be 11.01 wt %, and the amount of cobalt content in recycled CoCOF-SYNU-1 was determined to be 10.18 wt %.

$$C_{x}(mg/kg) = \frac{C_{0}(mg/L) \times f \times V_{0}(mL) \times 10^{-3}}{m(g) \times 10^{13}} = \frac{C_{1}(mg/L) \times V_{0}(mL) \times 10^{-3}}{m(g) \times 10^{-3}}$$
$$W\% = \frac{C_{x}(mg/kg)}{10^{6}} \times 100\%$$

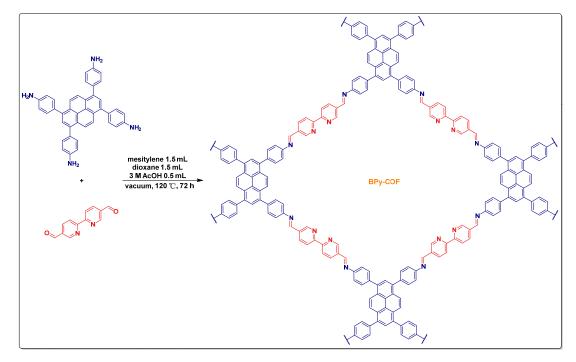
**Ultraviolet photoelectron spectroscopy:** Ultraviolet photoelectron spectroscopy (UPS) was performed on a PHI5000 VersaProbe III (Scanning ESCA Microprobe) SCA (Spherical Analyzer) with He I, 21.2 eV (80 mA, 530 V,  $5.0 \times 10^{-2}$  mbar) as UV light source. And the sample bias is -5 V.

**Electron spin resonance measurements:** Electron spin resonance (ESR) spectra were collected on a JES-FA200 (JEOL) electron paramagnetic resonance spectrometer under visible-light irradiation. Electrochemical measurements: Electrochemical measurements were carried out on a threeelectrode system with a CHI660E electrochemical workstation. Indium-tin oxide (ITO) glasses were cleaned by sonication in acetone for 15 min and dried under UV lamp. 5 mg of CoCOF-SYNU-1 powder was mixed with 0.2 mL of *N*,*N*-Dimethylformamide (DMF) and 0.2 mL 5 wt% Nafion to get slurry, which was spreading on the surface of ITO glass and the boundary were protected by Scotch tape. Then put it in the vacuum oven at 100 °C for 2 h. After to the room temperature and removed the Scotch tape. The measurements were carried out in a 0.1 M Sodium sulfate, Ag/AgCl electrode (saturated KCl) as reference electrode, a platinum wire as the counter electrode for photocurrent responses, electrochemical impedance spectra (It was performed in a frequency range of  $10^{5}$ -0.1 Hz with amplitude of 10 mV of alternating current) and Mott-Schottky (M-S) experiments. Visible-light-irradiation was provided by a 300 W xenon lamp with a  $\lambda$  > 400 nm cut-off filter. The applied potentials vs. Ag/AgCl were converted to NHE or RHE potentials using the following equations:

$$E_{NHE} = E_{Ag/AgCl} + E_{Ag/AgCl}^{\theta} \left( E_{Ag/AgCl}^{\theta} = 0.199 V \right)$$
$$E_{RHE} = E_{Ag/AgCl} + 0.0591pH + E_{Ag/AgCl}^{\theta} \left( E_{Ag/AgCl}^{\theta} = 0.199 V \right)$$

Vacuum level values were converted to electrochemical potentials according to: -4.44 eV vs. vacuum level is equal to -0.4 V vs. NHE at pH 6.8.<sup>[1]</sup>

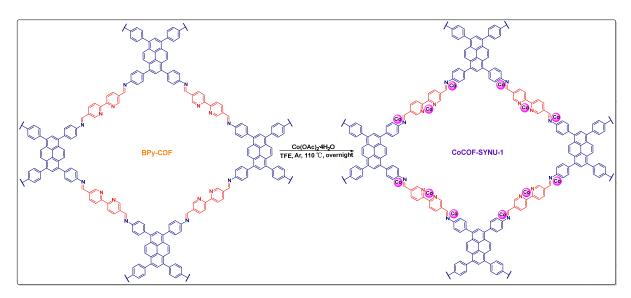
# II. General procedures for the synthesis of BPy-COF and CoCOF-SYNU-1



#### i. Preparation of BPy-COF<sup>[2-4]</sup>

A glass ampoule was charged with 4,4',4'',4'''-(1,9-dihydropyrene-1,3,6,8-tetrayl)tetraaniline (85 mg, 0.15 mmol) and [2,2'-bipyridine]-5,5'-dicarbaldehyde (64 mg, 0.3 mmol). To the mixture were added dioxane (1.5 mL) and mesitylene (1.5 mL). The tube was immersed in an ultrasonic bath for 10 min; following sonication, 0.5 mL of 3 M aqueous acetic acid were added and the Pyrex tube was degassed by three freeze-pump-thaw cycles. The tube was then sealed off and heated at 120 °C and left undisturbed for 72 h, yielding a yellow solid at the bottom of the tube. The precipitate was isolated by filtration and washed with tetrahydrofuran (3×10 mL) and acetone (3×10 mL), the resulting powder was dried at 80 °C under vacuum for 12 h to yield BPy-COF as an orange powder (135 mg, 97%).

## ii. Preparation of CoCOF-SYNU-1



A Schlenk bottle (25 mL) was charged with BPy-COF (160 mg, 0.17 mmol), Co(OAc)<sub>2</sub>•4H<sub>2</sub>O (127 mg, 0.51 mmol), and 2,2,2-trifluoroethanol (TFE, 10 mL) under argon atmosphere. The mixture was then refluxed under argon overnight. The precipitate was isolated by filtration and washed with TFE (50 mL), the resulting powder was dried at 80 °C under vacuum for 12 h to CoCOF-SYNU-1 as a dark red powder (263 mg, Co: 11.01 wt% by ICP-MS).

III. Structural characterizations and photoelectrochemical measurements of BPy-COF and CoCOF-SYNU-1

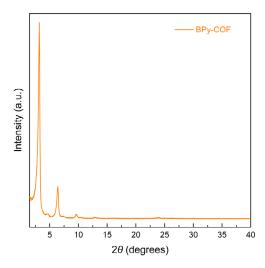


Figure S1. The PXRD pattern of BPy-COF.

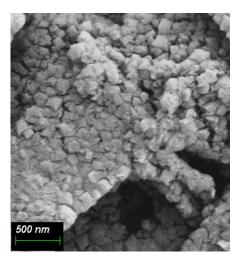


Figure S2. The SEM image of BPy-COF.

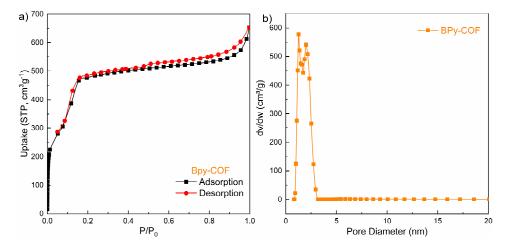


Figure S3. a) N<sub>2</sub> adsorption and desorption isotherms of BPy-COF measured at 77 K. b) Pore size distributions of BPy-COF.

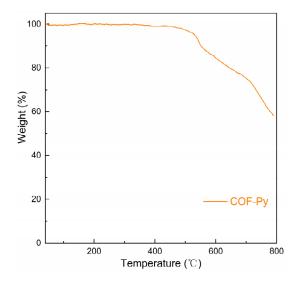


Figure S4. The TGA curve of BPy-COF.

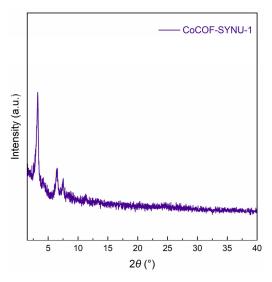


Figure S5. The PXRD pattern of CoCOF-SYNU-1.

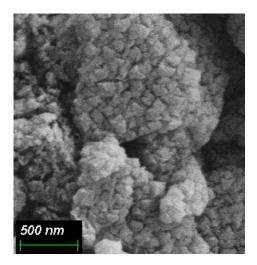


Figure S6. The SEM image of CoCOF-SYNU-1.

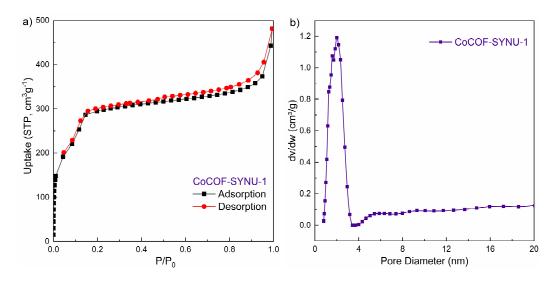


Figure S7. a) N<sub>2</sub> adsorption and desorption isotherms of CoCOF-SYNU-1 measured at 77 K. b)

Pore size distributions of CoCOF-SYNU-1.

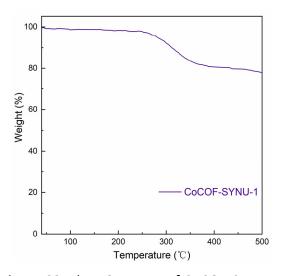


Figure S8. The TGA curve of CoCOF-SYNU-1.

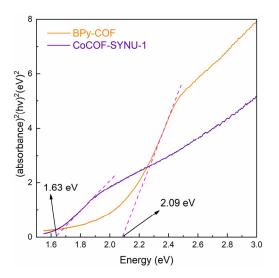


Figure S9. Optical band gaps of BPy-COF and CoCOF-SYNU-1 determined from the Kubelka-Munk-transformed reflectance.

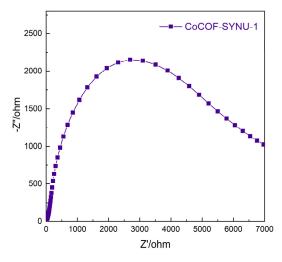


Figure S10. The electrochemical impedance spectrum of CoCOF-SYNU-1.

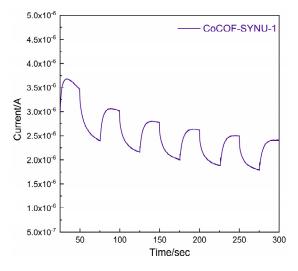
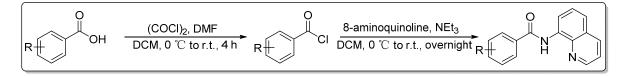


Figure S11. Photocurrent response of CoCOF-SYNU-1.

# IV. General procedures for the synthesis of starting materials

#### i. General procedure for preparation of *N*-(quinolin-8-yl)benzamide<sup>[5, 6]</sup>

# Method A:



A 100 mL round bottom flask was charged with carboxylic acid (11 mmol) to which oxalyl chloride (20 mmol) was added dropwise at 0 °C in dichloromethane as the solvent. The catalytic amount of DMF was added into the reaction mixture. The reaction mixture was stirred at room temperature for 4 h, then the excess (COCl)<sub>2</sub> was removed in vacuum to afford the crude acid chloride on one hand, whereas in another flask solution of 8-aminoquinoline (10 mmol) and NEt<sub>3</sub> (11 mmol) in dichloromethane (20 mL) was stirred for 10-15 minutes.

Deprotonated amine was then added into the solution of acid chloride at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. Upon completion, it was quenched with saturated NaHCO<sub>3</sub> solution and extracted with dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). The combined organic layer dried over anhydrous MgSO<sub>4</sub>, filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography (PE/EtOAc = 10/1) to give the compound as light-yellow solid.

Method B:

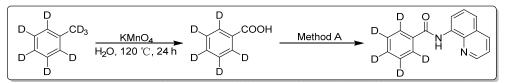


A 100 mL round bottom flask was charged with dichloromethane as the solvent, then benzoyl chloride (11 mmol) was added at 0 °C. In another flask, solution of 8-aminoquinoline (10 mmol) and NEt<sub>3</sub> (11 mmol) in dichloromethane (20 mL) was stirred for 10-15 minutes. Deprotonated amine was then added into the solution of acid chloride at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. Upon completion, it was quenched with saturated NaHCO<sub>3</sub> solution and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer dried over anhydrous MgSO<sub>4</sub>, filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography (PE/EtOAc = 10/1) to give the compound as light-yellow solid.

#### ii. General procedure for preparation of 2-phenylethyn-1-silane<sup>[7]</sup>

In a 25 mL Schlenk tube, Pd(OAc)<sub>2</sub> 2 mol%, PPh<sub>3</sub> 4 mol%, CuI 6 mol% and a stir bar was added under argon. Subsequently, iodobenzene derivative (5 mmol) dissolved in Et<sub>3</sub>N (10 mL) was added. The mixture was stirred for 30 min at room temperature. Then the ethynylsilane (1.2 equiv.) was added and the stirring was continued for another 6 h. The reaction mixture was filtered through a pad of celite, and the filtrate was quenched with 1 M aqueous HCl. The resulting mixture was extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether) to give the compound as colorless oil.

# iii. General procedure for preparation of N-(quinolin-8-yl)benzamide-2,3,4,5,6-d<sub>5</sub>



KMnO<sub>4</sub> (10 mmol), H<sub>2</sub>O (10 mL) and toluene- $d_8$  (5 mmol) were placed in a 50 mL sealed Schlenk tube with a magnetic stirrer. The mixture was stirred at 120 °C for 24 h. Then the reaction mixture was filtered, and the filter residue was washed with hot water. Subsequently, the concentrated hydrochloric acid was added into the filtrate. The suspension liquid was extracted with EtOAc (3×15 mL). The combined organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered and evaporated under reduced pressure to obtain the crude benzoic acid- $d_5$ . Then the *N*-(quinolin-8-yl)benzamide-2,3,4,5,6- $d_5$  was prepared according to the general procedure for the synthesis of *N*-(quinolin-8-yl)benzamide-2,3,4,5,6- $d_5$  (**Method A**).

## V. Optimization of the reaction conditions

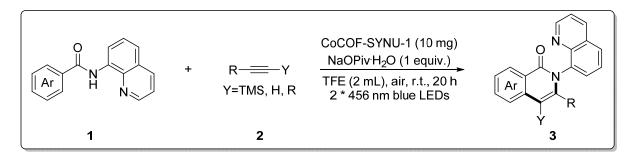
		solvent (2 mL), a	catalyst, additive (1 equiv.) solvent (2 mL), atmosphere, r.t., 20 h 2 * 456 nm blue LEDs		N N N TMS 3aa	
entry	catalyst		atmosphere	additive	solvent	yields (%) <sup>b</sup>
1	CoCOF-SYNU	J-1 (10 mg)	air	-	TFE	76
2	CoCOF-SYNU	J-1 (10 mg)	air	NaOPiv·H <sub>2</sub> O	TFE	90
3	CoCOF-SYNU	J-1 (10 mg)	air	Et₃N	TFE	trace
4	CoCOF-SYNU	J-1 (10 mg)	air	<i>t</i> -BuOK	TFE	14
5	CoCOF-SYNU	J-1 (10 mg)	air	Pyridine	TFE	trace
6	CoCOF-SYNU	J-1 (10 mg)	air	HCOONa	TFE	29
7	CoCOF-SYNU	J-1(10 mg)	air	NaOAc	TFE	62
8	CoCOF-SYNU	J-1 (10 mg)	Ar	$NaOPiv \cdot H_2O$	TFE	N.R.
9	CoCOF-SYNU	J-1 (10 mg)	O <sub>2</sub>	$NaOPiv \cdot H_2O$	TFE	76
10	CoCOF-SYNL	J-1 (10 mg)	air	NaOPiv·H <sub>2</sub> O	MeOH	19

Table S1. Screening of the reaction conditions.<sup>a</sup>

11	CoCOF-SYNU-1 (10 mg)	air	NaOPiv·H <sub>2</sub> O	EtOH	24
12	CoCOF-SYNU-1 (10 mg)	air	NaOPiv·H <sub>2</sub> O	IPA	10
13	CoCOF-SYNU-1 (10 mg)	air	NaOPiv·H <sub>2</sub> O	HFIP	71
14	CoCOF-SYNU-1 (10 mg)	air	NaOPiv·H <sub>2</sub> O	DCE	12
15	CoCOF-SYNU-1 (10 mg)	air	NaOPiv·H <sub>2</sub> O	toluene	19
16	CoCOF-SYNU-1 (5 mg)	air	NaOPiv·H <sub>2</sub> O	TFE	79
17	-	air	NaOPiv·H <sub>2</sub> O	TFE	N.R.
18	BPy-COF (10 mg)	air	NaOPiv·H <sub>2</sub> O	TFE	N.R.
19 <sup>c</sup>	CoCOF-SYNU-1 (10 mg)	air	NaOPiv·H <sub>2</sub> O	TFE	10
20	Na2Eosin Y (10 mol%) Co(OAc)2·4H2O (20 mol%)	air	NaOPiv·H <sub>2</sub> O	TFE	67
21	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> ·6H <sub>2</sub> O (10 mol%) Co(OAc) <sub>2</sub> ·4H <sub>2</sub> O (20 mol%)	air	NaOPiv·H <sub>2</sub> O	TFE	52
22 <sup>d</sup>	CoCOF-SYNU-1 (10 mg)	air	NaOPiv·H <sub>2</sub> O	TFE	14
23 <sup>e</sup>	CoCOF-SYNU-1 (10 mg)	air	NaOPiv·H <sub>2</sub> O	TFE	19

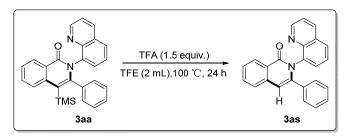
<sup>a)</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (1.5 equiv.), catalyst, additive (1 equiv.), solvent (2 mL), r.t., atmosphere, 20 h, 2 \* 456 nm blue LEDs. <sup>b)</sup> Isolated yield. <sup>c)</sup> Under dark. <sup>d)</sup> 50 °C, under dark. <sup>e)</sup> 80 °C, under dark. N.R.= no reaction.

#### VI. General procedure for the synthesis of compounds 3



A 10 mL glass tube was charged with the benzamide **1** (0.1 mmol), CoCOF-SYNU-1 (10 mg), NaOPiv•H<sub>2</sub>O (1 equiv.), the alkyne **2** (0.15 mmol), and TFE (2 mL). The mixture was stirred (1000 rpm) under air with the blue light irradiation (Two Kessil PR160L blue LEDs, 456 nm, 40 W; the distance between reactor and lamp is approximately 5 cm) for 20 h at room temperature. Upon completion, the CoCOF-SYNU-1 was filtered while the solvent was removed under the reduced pressure. The residue was then purified by silica gel flash chromatography (PE/EA=2/1) to afford the desired product **3**.

# VII. General procedure for the desilylation



3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one **3aa** (0.1 mmol), TFA (0.15 mmol) and TFE (2 mL) was placed in a sealed 10 mL glass tube. The mixture was stirred at 100 °C for 24 h. Then the mixture was cooled to room temperature. The solvent was removed under the reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EA=1/1) to afford the desired product **3as** in 95% yield. The position of TMS on **3aa** was validated by the 2D-HMQC analysis of **3as**.

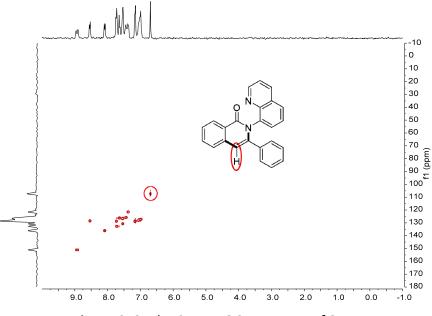
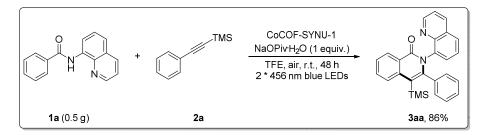


Figure S12. The 2D-HMQC spectrum of 3as.

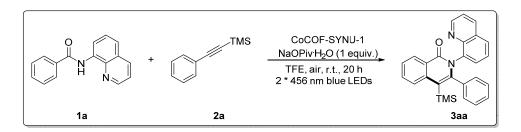
# VIII. Scale-up experiment



A 100 mL round bottom flask was charged with *N*-(quinolin-8-yl)benzamide **1a** (2 mmol), CoCOF-SYNU-1 (150 mg), NaOPiv•H<sub>2</sub>O (1 equiv.), trimethyl(phenylethynyl)silane **2a** (3 mmol),

and TFE (50 mL). The mixture was stirred (1500 rpm) under air with the blue light irradiation (Two Kessil PR160L blue LEDs, 456 nm, 40 W; the distance between reactor and lamp is approximately 5 cm) for 48 h at room temperature. Upon completion, the CoCOF-SYNU-1 was filtered while the solvent was removed under the reduced pressure. The residue was then purified by silica gel flash chromatography (PE/EA=2/1) to afford the desired product **3aa** (724 mg, 86%).

#### **IX. Recycling experiments**



A 50 mL round bottom flask was charged with *N*-(quinolin-8-yl)benzamide **1a** (0.1 mmol), CoCOF-SYNU-1 (120 mg), NaOPiv•H<sub>2</sub>O (1 equiv.), trimethyl(phenylethynyl)silane **2a** (0.15 mmol), and TFE (20 mL). The mixture was stirred (1500 rpm) under air with the blue light irradiation (Two Kessil PR160L blue LEDs, 456 nm, 40 W; the distance between reactor and lamp is approximately 5 cm) for 20 h at room temperature. Upon completion, the cetifigureation and washing with  $CH_2Cl_2$  was conducted for the recovery CoCOF-SYNU-1. Meanwhile, the remaining solvent was removed under the reduced pressure. The residue was purified by silica gel flash chromatography to afford the desired product **3aa**. After the recycling experiments, the resulting CoCOF-SYNU-1 was dried at 80 °C under vacuum for 12 h as a dark red solid. And the Co content was determined to be 10.18 wt% by ICP-MS.

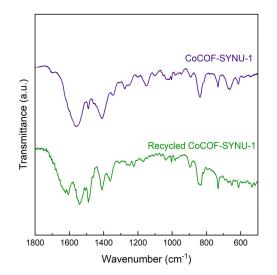


Figure S13. FT-TR spectra of CoCOF-SYNU-1 and Recycled CoCOF-SYNU-1.

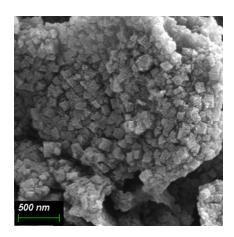


Figure S14. The SEM image of Recycled CoCOF-SYNU-1.

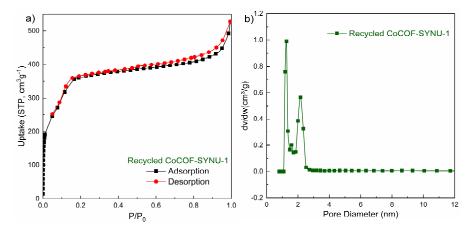
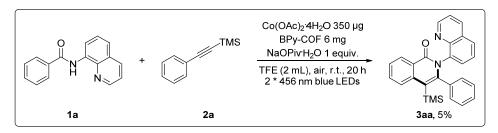


Figure S15. a) N<sub>2</sub> adsorption and desorption isotherms of Recycled CoCOF-SYNU-1 measured at 77 K. b) Pore size distribution of Recycled CoCOF-SYNU-1.

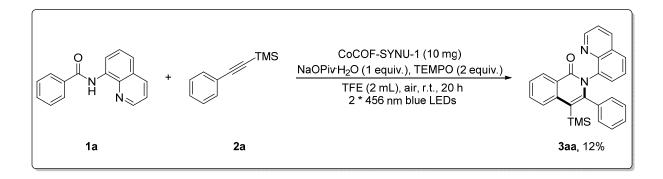
# X. The investigation of Co-leaching



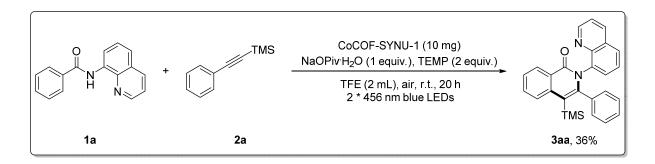
*N*-(quinolin-8-yl)benzamide **1a** (0.1 mmol),  $Co(OAc)_2 \cdot 4H_2O$  (350 µg, it was calculated by the difference of Co content before and after recycling), BPy-COF (6 mg), NaOPiv \cdot H\_2O (1 equiv.), trimethyl(phenylethynyl)silane **2a** (0.15 mmol), and TFE (2 mL) was placed in a sealed 10 mL glass tube. The mixture was stirred (1000 rpm) under air with the blue light irradiation (Two Kessil PR160L blue LEDs, 456 nm, 40 W; the distance between reactor and lamp is approximately 5 cm) for 20 h at room temperature. The residue was then purified by silica gel flash chromatography (PE/EA=2/1) to afford the desired product **3aa** (2 mg, 5%).

#### **XI.** Mechanistic studies

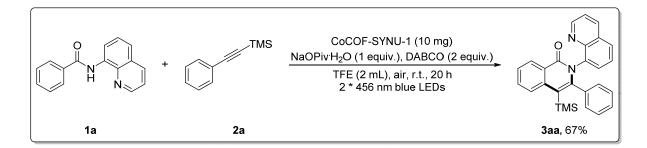
# i. Control experiments



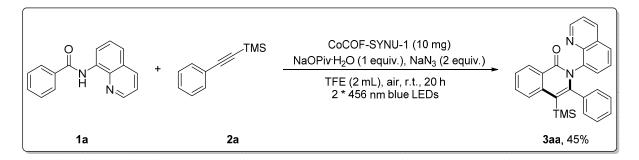
A 10 mL glass tube was charged with *N*-(quinolin-8-yl)benzamide **1a** (0.1 mmol), CoCOF-SYNU-1 (10 mg), NaOPiv•H<sub>2</sub>O (1 equiv.), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 2 equiv.), trimethyl(phenylethynyl)silane **2a** (0.15 mmol) and TFE (2 mL). The mixture was stirred (1000 rpm) under air with the blue light irradiation (Two Kessil PR160L blue LEDs, 456 nm, 40 W; the distance between reactor and lamp is approximately 5 cm) for 20 h at room temperature. Upon completion, the CoCOF-SYNU-1 was filtered while the solvent was removed under the reduced pressure. The residue was then purified by silica gel flash chromatography to afford the desired product **3aa** (5 mg, 12%).



A 10 mL glass tube was charged with *N*-(quinolin-8-yl)benzamide **1a** (0.1 mmol), CoCOF-SYNU-1 (10 mg), NaOPiv•H<sub>2</sub>O (1 equiv.) 2,2,6,6-tetramethylpiperidine (TEMP, 2 equiv.), trimethyl(phenylethynyl)silane **2a** (0.15 mmol) and TFE (2 mL). The mixture was stirred (1000 rpm) under air with the blue light irradiation (Two Kessil PR160L blue LEDs, 456 nm, 40 W; the distance between reactor and lamp is approximately 5 cm) for 20 h at room temperature. Upon completion, the CoCOF-SYNU-1 was filtered while the solvent was removed under the reduced pressure. The residue was then purified by silica gel flash chromatography to afford the desired product **3aa** (15 mg, 36%).



A 10 mL glass tube was charged with *N*-(quinolin-8-yl)benzamide **1a** (0.1 mmol), CoCOF-SYNU-1 (10 mg), NaOPiv•H<sub>2</sub>O (1 equiv.) 1,4-diazabicyclo[2.2.2]octane (DABCO, 2 equiv.), trimethyl(phenylethynyl)silane **2a** (0.15 mmol) and TFE (2 mL). The mixture was stirred (1000 rpm) under air with the blue light irradiation (Two Kessil PR160L blue LEDs, 456 nm, 40 W; the distance between reactor and lamp is approximately 5 cm) for 20 h at room temperature. Upon completion, the CoCOF-SYNU-1 was filtered while the solvent was removed under the reduced pressure. The residue was then purified by silica gel flash chromatography to afford the desired product **3aa** (28 mg, 67%).



A 10 mL glass tube was charged with *N*-(quinolin-8-yl)benzamide **1a** (0.1 mmol), CoCOF-SYNU-1 (10 mg), NaOPiv•H<sub>2</sub>O (1 equiv.) NaN<sub>3</sub> (2 equiv.), trimethyl(phenylethynyl)silane **2a** (0.15 mmol) and TFE (2 mL). The mixture was stirred (1000 rpm) under air with the blue light irradiation (Two Kessil PR160L blue LEDs, 456 nm, 40 W; the distance between reactor and lamp is approximately 5 cm) for 20 h at room temperature. Upon completion, the CoCOF-SYNU-1 was filtered while the solvent was removed under the reduced pressure. The residue was then purified by silica gel flash chromatography to afford the desired product **3aa** (19 mg, 45%).

#### ii. In-situ ESR measurements

A glass tube was charged with BPy-COF (0.1 mg/mL) and TFE in the dark room. The suspension was degassed by bubbling with N<sub>2</sub> for 5 minutes. Under nitrogen atmosphere, 50  $\mu$ L of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) was added. The formed mixture (50-100  $\mu$ L) was transferred into the ESR capillary and sealed quickly and subsequently. The ESR spectrum was

firstly recorded under dark. Then it was recorded with the light irradiation from a 300 W Xenon lamp ( $\lambda$  >400 nm) for 6 minutes and 11 minutes.

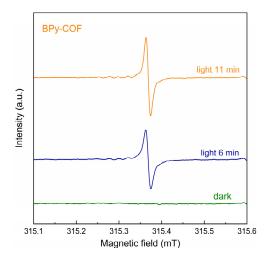
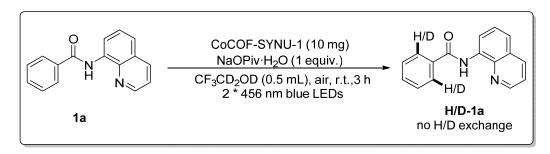


Figure S16. ESR spectra of Bpy-COF under the visible-light- irradiation.

A glass tube was charged with CoCOF-SYNU-1 (0.1 mg/mL) and TFE in the dark room. The suspension was bubbled with air for 5 minutes. Subsequently, 50  $\mu$ L of DMPO was added. The formed mixture (50-100  $\mu$ L) was transferred into the ESR capillary quickly. The ESR spectrum was firstly recorded under dark. Then it was recorded with the light irradiation from a 300 W Xenon lamp ( $\lambda$  >400 nm) for 4 minutes and 10 minutes.

A glass tube was charged with CoCOF-SYNU-1(0.1 mg/mL) and TFE in the dark room. The suspension was bubbled with air for 5 minutes. Subsequently, the TEMP (20 mM) was added. The formed mixture (50-100  $\mu$ L) was transferred into the ESR capillary quickly. The ESR spectrum was firstly recorded under dark. Then it was recorded with the light irradiation from a 100 W Xenon lamp ( $\lambda$  >420 nm) for 5 minutes and 10 minutes.

iii. The H/D exchange experiment



A 10 mL glass tube was charged with *N*-(quinolin-8-yl)benzamide **1a** (0.1 mmol), CoCOF-SYNU-1 (10 mg), NaOPiv•H<sub>2</sub>O (1 equiv.) and CF<sub>3</sub>CD<sub>2</sub>OD (0.5 mL). The mixture was stirred (1000 rpm) under air with the blue light irradiation (Two Kessil PR160L blue LEDs, 456 nm, 40 W; the distance between reactor and lamp is approximately 5 cm) for 3 h at room temperature. Upon completion, the CoCOFSYNU-1 was filtered while the solvent was removed under the reduced pressure. The residue was then purified by silica gel flash chromatography to afford the desired product **H/D-1a**. The deuterium incorporation was calculated from <sup>1</sup>H NMR.

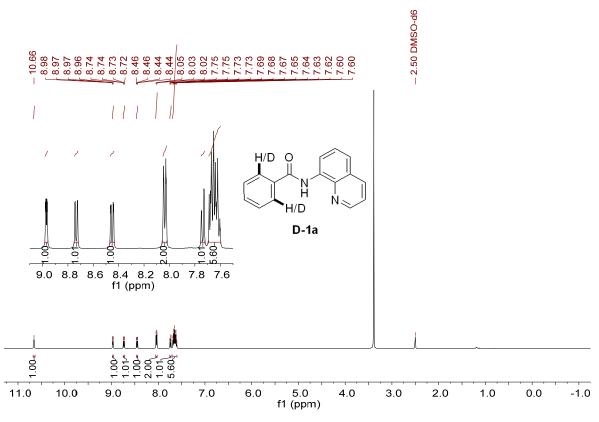
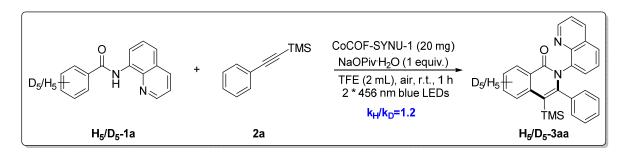


Figure S17. The <sup>1</sup>H NMR spectrum of **H/D-1a**.

# iv. Kinetic isotope effect (KIE) experiments



A 10 mL glass tube was charged with *N*-(quinolin-8-yl)benzamide **1a** (0.1 mmol) and *N*-(quinolin-8-yl)benzamide-2,3,4,5,6- $d_5$  **1a-D**<sub>5</sub> (0.1 mmol), CoCOF-SYNU-1 (20 mg), NaOPiv•H<sub>2</sub>O (1 equiv.), trimethyl(phenylethynyl)silane **2a** (0.3 mmol) and TFE (2 mL). The mixture was stirred (1000 rpm) under air with the blue light irradiation (Two Kessil PR160L blue LEDs, 456 nm, 40 W; the distance between reactor and lamp is approximately 5 cm) for 1 h at room temperature. Upon completion, the CoCOF-SYNU-1 was filtered while the solvent was

removed under the reduced pressure. The residue was then purified by silica gel flash chromatography to afford the desired product  $H_5/D_5$ -**3aa**. The deuterium incorporation was calculated from <sup>1</sup>H NMR. Based on the integrations related to different hydrogen resonances, the kinetic isotope effect value is calculated to be  $k_H/k_D = 1.2$ .

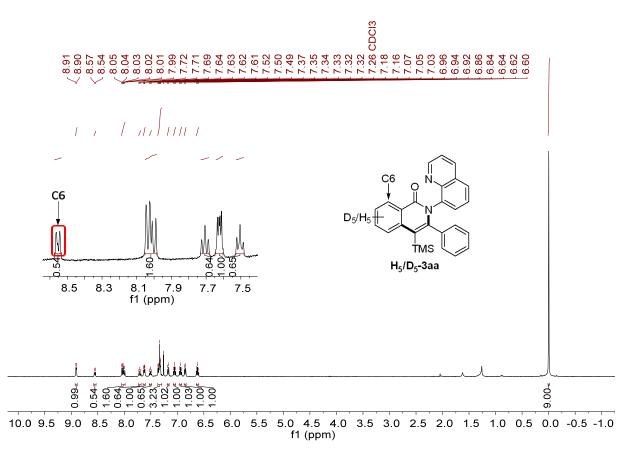
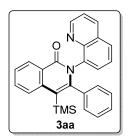


Figure S18. The <sup>1</sup>H NMR spectrum of  $H_5/D_5$ -3aa.

# XII. Characterization data of compounds

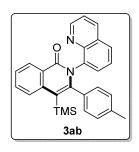
#### 3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3aa)<sup>[8]</sup>



According to the general procedure (PE/EtOAc = 2/1), **3aa** was obtained in 90% yield (38 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.91 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.58-8.56 (m, 1H), 8.04-8.00 (m, 2H), 7.73-7.69 (m, 1H), 7.62 (dd, *J* = 7.0, 2.6 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.36-7.30 (m, 3H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H),

6.86 (d, *J* = 7.7 Hz, 1H), 6.62 (t, *J* = 7.6 Hz, 1H), 0.01 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 163.0, 150.7, 149.5, 144.9, 140.6, 137.8, 137.4, 136.0, 131.7, 131.3, 131.1, 130.1, 128.9, 128.7, 128.4, 128.3, 127.6, 126.9, 126.6, 126.1, 126.1, 125.7, 121.5, 111.5, 2.2. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>27</sub>H<sub>25</sub>N<sub>2</sub>OSi 421.1720, found 421.1731.

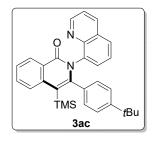
## 2-(quinolin-8-yl)-3-(p-tolyl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ab)



According to the general procedure (PE/EtOAc = 2/1), **3ab** was obtained in 90% yield (39 mg). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.90 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.55-8.53 (m, 1H), 8.04 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.71-7.68 (m, 1H), 7.63 (dd, *J* = 7.3, 2.3 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.36-7.30 (m, 3H), 7.05 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.70 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.42 (d, *J* = 7.8

Hz , 1H), 2.08 (s, 3H), 0.00 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  163.1, 150.8, 149.8, 145.1, 140.8, 138.0, 136.0, 134.7, 131.7, 131.3, 131.0, 130.0, 128.9, 128.7, 128.4, 127.6, 127.6, 127.4, 126.2, 126.0, 125.8, 121.5, 111.7, 21.2, 2.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>OSi 435.1874, found 435.1887.

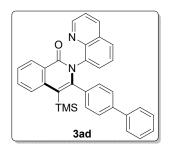
#### 3-(4-(tert-butyl)phenyl)-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ac)



According to the general procedure (PE/EtOAc = 2/1), **3ac** was obtained in 86% yield (41 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.91 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.55 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.05-7.98 (m, 2H), 7.72-7.68 (m, 1H), 7.60 (t, *J* = 4.8 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.37-7.33 (m, 1H), 7.30 (d, *J* = 4.8 Hz, 2H), 7.05 (s, 2H),

6.70 (d, *J* = 8.3 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 1.07 (s, 9H), 0.00 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 163.1, 151.5, 150.6, 149.8, 144.9, 140.7, 137.9, 136.1, 134.5, 131.7, 131.1, 131.0, 129.8, 128.9, 128.7, 128.2, 127.6, 126.2, 126.0, 125.8, 123.6, 123.4, 121.4, 111.6, 34.4, 31.1, 2.2. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>31</sub>H<sub>33</sub>N<sub>2</sub>OSi 477.2368, found 477.2357.

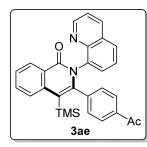
#### 3-([1,1'-biphenyl]-4-yl)-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ad)



According to the general procedure (PE/EtOAc = 2/1), **3ad** was obtained in 77% yield (38 mg). Light yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.87 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.53-8.51 (m, 1H), 7.99-7.95 (m, 2H), 7.68-7.65 (m, 1H), 7.57-7.55 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.34-7.30 (m, 4H), 7.30-7.26 (m, 4H), 7.22 (d, *J* = 7.1 Hz, 1H),

7.20-7.18 (m, 1H), 6.88-6.83 (m, 2H), -0.01 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 163.1, 150.8, 149.3, 145.0, 140.7, 140.7, 140.1, 137.9, 136.5, 136.1, 131.8, 131.7, 131.1, 130.6, 128.9, 128.8, 128.8, 128.6, 127.7, 127.6, 126.9, 126.2, 126.2, 125.8, 125.4, 125.2, 121.5, 111.8, 2.4. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>33</sub>H<sub>29</sub>N<sub>2</sub>OSi 497.2029, found 497.2029.

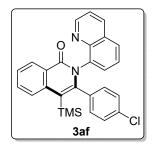
#### 3-(4-acetylphenyl)-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ae)



According to the general procedure (PE/EtOAc = 2/1), **3ae** was obtained in 87% yield (40 mg). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.91 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.04 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.72-7.71 (m, 1H), 7.67-7.62 (m, 2H), 7.54-7.51 (m, 1H), 7.38-7.30 (m, 4H), 7.24 (dd, *J* = 8.1,

1.7 Hz, 1H), 7.01 (dd, J = 8.1, 1.6 Hz, 1H), 2.42 (s, 3H), 0.00 (d, J = 3.0 Hz, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 197.5, 162.9, 150.9, 148.2, 144.9, 142.1, 140.4, 137.5, 136.5, 136.2, 131.9, 131.7, 131.2, 130.6, 129.0, 128.9, 128.8, 127.7, 127.0, 126.7, 126.5, 126.3, 125.9, 121.7, 111.8, 26.7, 2.4. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>29</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub>Si 463.1841, found 463.1836.

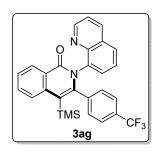
## 3-(4-chlorophenyl)-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3af)



According to the general procedure (PE/EtOAc = 2/1), **3af** was obtained in 86% yield (39 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.88 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.55 (d, *J* = 7.9 Hz, 1H), 8.06 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.73-7.66 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.35 (q, *J* = 4.1, 3.5 Hz, 3H), 7.12 (dd, *J* = 8.2, 2.0 Hz,

1H), 7.04 (dd, J = 8.2, 2.0 Hz, 1H), 6.84 (dd, J = 8.3, 2.0 Hz, 1H), 6.63 (dd, J = 8.3, 2.0 Hz, 1H), 0.03 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 163.0, 150.8, 148.1, 144.8, 140.4, 137.6, 136.2, 136.0, 134.3, 132.6, 131.8, 131.5, 131.1, 128.9, 128.8, 128.8, 127.7, 127.2, 126.9, 126.4, 126.3, 125.8, 121.6, 111.9, 2.4. HR-MS (ESI) [M+Na]<sup>+</sup> m/z calcd for C<sub>27</sub>H<sub>23</sub>ClN<sub>2</sub>OSiNa 477.1165, found 477.1165.

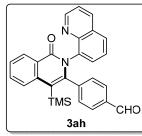
#### 2-(quinolin-8-yl)-3-(4-(trifluoromethyl)phenyl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ag)



According to the general procedure (PE/EtOAc = 2/1), **3ag** was obtained in 86% yield (42 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.89 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.58-8.55 (m, 1H), 8.06-8.00 (m, 2H), 7.75-7.71 (m, 1H), 7.65 (dd, *J* = 7.3, 2.3 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.38-7.32 (m, 5H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 0.00 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 162.9, 150.9,

147.8, 144.8, 140.9 (q, J = 1.2 Hz), 140.3, 137.4, 136.2, 131.9, 131.7, 131.1, 130.7, 130.4 (q, J = 32.7 Hz), 129.0, 128.9, 128.8, 127.7, 126.6, 126.3, 125.8, 123.9 (q, J = 3.7 Hz), 123.7 (q, J = 272.2 Hz), 123.5 (q, J = 3.7 Hz), 121.7, 111.9, 2.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -62.85. HR-MS (ESI) [M+Na]<sup>+</sup> m/z calcd for C<sub>28</sub>H<sub>23</sub>F<sub>3</sub>N<sub>2</sub>OSiNa 511.1129, found 511.1427.

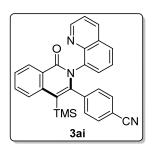
#### 4-(1-oxo-2-(quinolin-8-yl)-4-(trimethylsilyl)-1,2-dihydroisoquinolin-3-yl)benzaldehyde (3ah)



According to the general procedure (PE/EtOAc = 2/1), **3ah** was obtained in 94% yield (42 mg). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 9.76 (s, 1H), 8.91 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.57-8.55 (m, 1H), 8.05-7.99 (m, 2H), 7.75-7.71 (m, 1H), 7.63 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.58 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.39-7.31 (m,

4H), 7.17 (dd, J = 7.9, 1.3 Hz, 1H), 7.11-7.10 (m, 1H), 0.00 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 191.7, 162.9, 151.0, 147.9, 144.8, 143.3, 140.4, 137.4, 136.2, 135.7, 132.1, 132.0, 131.2, 131.1, 129.0, 128.9, 128.2, 128.0, 127.7, 126.6, 126.3, 125.8, 121.8, 111.8, 2.4. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>28</sub>H<sub>25</sub>N<sub>2</sub>O<sub>2</sub>Si 449.1701, found 449.1680.

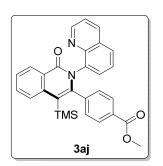
#### 4-(1-oxo-2-(quinolin-8-yl)-4-(trimethylsilyl)-1,2-dihydroisoquinolin-3-yl)benzonitrile (3ai)



According to the general procedure (PE/EtOAc = 2/1), **3ai** was obtained in 88% yield (39 mg). Yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.88 (d, *J* = 2.8 Hz, 1H), 8.55 (d, *J* = 7.7 Hz, 1H), 8.06 (d, *J* = 7.3 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.75-7.67 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.39-7.29 (m, 5H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H),

0.00 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 162.8, 151.0, 147.1, 144.6, 141.8, 140.2, 137.2, 136.3, 132.0, 131.2, 131.1, 130.7, 130.4, 129.2, 129.0, 128.9, 127.7, 126.8, 126.3, 125.9, 121.8, 118.3, 112.1, 112.0, 2.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>28</sub>H<sub>24</sub>N<sub>3</sub>OSi 446.1701, found 446.1683.

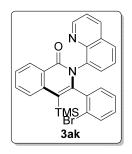
# methyl 4-(1-oxo-2-(quinolin-8-yl)-4-(trimethylsilyl)-1,2-dihydroisoquinolin-3-yl)benzoate (3aj)



According to the general procedure (PE/EtOAc = 2/1), **3aj** was obtained in 90% yield (43 mg). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.90 (dd, *J* = 4.1, 1.3 Hz, 1H), 8.56-8.55 (m, 1H), 8.04-7.99 (m, 2H), 7.76-7.70 (m, 2H), 7.63-7.62 (m, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.36-7.32 (m, 4H), 7.30-7.27 (m, 1H), 6.99 (dd, *J* = 8.0, 1.3 Hz, 1H), 3.79 (s, 3H), -0.01 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 166.5, 162.9,

150.9, 148.3, 144.8, 141.9, 140.4, 137.5, 136.2, 131.9, 131.5, 131.1, 130.3, 129.7, 128.9, 128.9, 128.8, 128.2, 127.9, 127.7, 126.4, 126.3, 125.8, 121.7, 111.7, 52.2, 2.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>29</sub>H<sub>27</sub>N<sub>2</sub>O<sub>3</sub>Si 479.1798, found 479.1785.

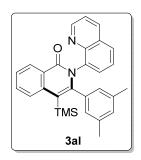
#### 3-(2-bromophenyl)-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ak)



According to the general procedure (PE/EtOAc = 2/1), **3ak** was obtained in 94% yield (47 mg). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.82 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.51 (d, *J* = 8.1 Hz, 1H), 7.99-7.94 (m, 2H), 7.86-7.84 (m, 1H), 7.67-7.64 (m, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.31-7.26 (m, 2H), 7.19 (d, *J* = 1.7 Hz, 1H), 6.96 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.72-6.70 (m, 1H), 6.49 (t, *J* = 7.5 Hz, 1H), -0.01 (s, 9H). <sup>13</sup>C NMR (126

MHz, CDCl<sub>3</sub>) δ (ppm) 163.3, 150.7, 147.0, 144.6, 140.2, 138.0, 137.4, 136.0, 132.0, 131.8, 131.7, 130.1, 129.2, 129.0, 128.9, 128.7, 127.7, 126.5, 126.4, 126.0, 125.9, 125.5, 121.5, 111.9, 1.9. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>27</sub>H<sub>24</sub>BrN<sub>2</sub>OSi 499.0857, found 499.0836.

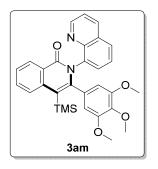
#### 3-(3,5-dimethylphenyl)-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3al)



According to the general procedure (PE/EtOAc = 2/1), **3al** was obtained in 89% yield (40 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.93 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.56 (d, *J* = 6.9 Hz, 1H), 8.05 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.72-7.67 (m, 1H), 7.62 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.36-7.30 (m, 3H), 6.75 (s, 1H), 6.54 (s, 1H), 6.42 (s, 1H), 2.14 (s, 3H), 1.66 (s, 3H), 0.01 (s, 9H). <sup>13</sup>C NMR (101

MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 163.1, 150.6, 150.0, 145.2, 140.7, 138.0, 137.1, 136.2, 136.1, 136.0, 131.7, 130.9, 129.5, 129.2, 128.9, 128.7, 128.4, 128.2, 127.6, 126.2, 126.0, 125.7, 121.3, 111.2, 21.1, 20.6, 2.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>29</sub>H<sub>29</sub>N<sub>2</sub>OSi 449.2051, found 449.2044.

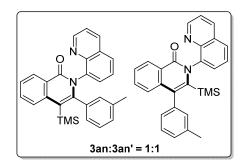
2-(quinolin-8-yl)-3-(3,4,5-trimethoxyphenyl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3am)



According to the general procedure (PE/EtOAc = 2/1), **3am** was obtained in 84% yield (43 mg). Light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.94 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.55-8.52 (m, 1H), 8.10 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.72-7.66 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.28-7.26 (m, 1H), 6.45 (d, *J* = 1.6 Hz, 1H), 6.08 (d, *J* = 1.5 Hz, 1H), 3.77

(s, 3H), 3.63 (s, 3H), 2.96 (s, 3H), 0.08 (s, 9H).  $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 163.0, 152.1, 151.7, 150.7, 149.2, 145.5, 140.6, 138.3, 138.0, 136.4, 132.8, 131.8, 130.5, 128.9, 128.8, 128.7, 127.6, 126.3, 126.2, 126.1, 121.4, 111.5, 109.2, 108.2, 61.0, 56.4, 55.4, 2.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>30</sub>H<sub>31</sub>N<sub>2</sub>OSi 511.2071, found 511.2048.

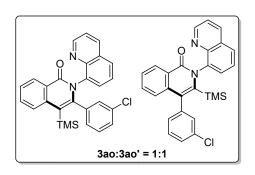
2-(quinolin-8-yl)-3-(m-tolyl)-4-(trimethylsilyl)isoquinolin-1(2H)-one:2-(quinolin-8-yl)-4-(m-tolyl)-3-(trimethylsilyl)isoquinolin-1(2H)-one (3an:3an' = 1:1)



According to the general procedure (PE/EtOAc = 2/1), **3an** and **3an'** was obtained in 94% yield (41 mg). Yellow solid. The ratio of two isomers was 1:1 as determined by <sup>1</sup>H NMR spectra. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.93 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.90 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.58-8.56 (m, 2H), 8.05-8.03 (m, 2H), 8.00 (d, *J* = 8.3 Hz, 2H),

7.72-7.69 (m, 2H), 7.63-7.61 (m, 2H), 7.52- 7.48 (m, 2H), 7.36-7.31 (m, 6H), 7.00 (s, 1H), 6.95-6.89 (m, 2H), 6.74 (dd, J = 13.8, 7.4 Hz, 2H), 6.67 (s, 1H), 6.62 (d, J = 7.7 Hz, 1H), 6.50 (t, J = 7.6 Hz, 1H), 2.20 (s, 3H), 1.71 (s, 3H), 0.01 (d, J = 3.1 Hz, 18H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 163.1, 163.1, 150.8, 150.6, 149.8, 149.7, 145.1, 140.7, 140.7, 138.0, 137.9, 137.3, 137.2, 136.4, 136.2, 136.0, 132.1, 131.7, 131.1, 131.0, 131.0, 128.9, 128.9, 128.9, 128.8, 128.7, 128.7, 128.4, 128.4, 127.6, 127.2, 126.8, 126.6, 126.2, 126.2, 126.1, 125.8, 125.6, 121.5, 121.4, 111.4, 111.3, 21.2, 20.7, 2.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>OSi 435.1864, found 435.1887.

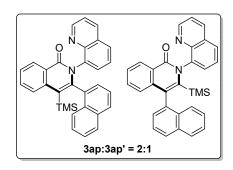
# 3-(3-chlorophenyl)-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one:4-(3chlorophenyl)-2-(quinolin-8-yl)-3-(trimethylsilyl)isoquinolin-1(2H)-one (3ao:3ao' = 1:1)<sup>[8]</sup>



According to the general procedure (PE/EtOAc = 2/1), **3ao** and **3ao'** was obtained in 86% yield (39 mg). White solid. The ratio of two isomers was 1:1 as determined by <sup>1</sup>H NMR spectra. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.93 (dd, J = 4.1, 1.5 Hz, 1H), 8.89 (dd, J = 4.1, 1.5 Hz, 1H), 8.57-8.55 (m, 2H), 8.08-8.04 (m, 2H), 8.00 (d, J = 8.3

Hz, 2H), 7.72 (t, J = 7.8 Hz, 2H), 7.67 (dd, J = 7.1, 2.2 Hz, 2H), 7.52 (t, J = 7.5 Hz, 2H), 7.42-7.33 (m, 6H), 7.20 (s, 1H), 7.03 (d, J = 7.5 Hz, 1H), 6.97-6.89 (m, 4H), 6.77 (d, J = 7.7 Hz, 1H), 6.57 (t, J = 7.9 Hz, 1H), 0.04 (s, 18H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 162.9, 162.9, 150.9, 150.9, 147.8, 147.8, 144.9, 144.8, 140.4, 139.0, 138.9, 137.6, 137.6, 136.1, 136.1, 132.9, 132.8, 131.9, 131.4, 131.2, 131.0, 130.7, 129.4, 129.0, 128.9, 128.9, 128.8, 128.8, 128.4, 128.4, 128.3, 128.1, 128.0, 127.7, 127.7, 126.5, 126.3, 126.3, 125.9, 125.8, 121.7, 121.6, 111.9, 111.8, 2.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>27</sub>H<sub>24</sub>ClN<sub>2</sub>OSi 455.1355, found 455.1341.

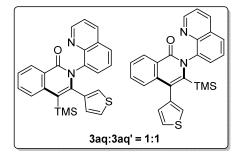
# 3-(naphthalen-1-yl)-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one:4-(naphthalen-1-yl)-2-(quinolin-8-yl)-3-(trimethylsilyl)isoquinolin-1(2H)-one (3ap:3ap' = 2:1)



According to the general procedure (PE/EtOAc = 2/1), **3ap** and **3ap'**was obtained in 85% yield (40 mg). Yellow solid. The ratio of two isomers was 2:1 as determined by <sup>1</sup>H NMR spectra and 2D HMQC analysis. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 9.14 (dd, *J* = 4.2, 1.6 Hz, 2H), 8.88 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.86 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.83 (dd, *J* = 8.0, 1.2

Hz, 2H), 8.27 (d, *J* = 8.3 Hz, 3H), 8.16 (dd, *J* = 8.3, 1.5 Hz, 2H), 8.13 (d, *J* = 8.4 Hz, 2H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.98-7.96 (m, 1H), 7.96-7.94 (m, 2H), 7.94-7.93 (m, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.79-7.73 (m, 4H), 7.73-7.69 (m, 3H), 7.64 (d, *J* = 7.8 Hz, 4H), 7.61-7.57 (m, 3H), 7.55-7.53 (m, 3H), 7.48-7.44 (m, 2H), 7.34-7.31 (m, 1H), 7.31-7.28 (m, 3H), 7.28-7.24 (m, 3H), 7.12-7.09 (m, 1H), 7.05 (t, *J* = 7.8 Hz, 2H), 6.93-6.90 (m, 2H), 0.01 (s, 9H), 0.00 (s, 18H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ (ppm) 163.4, 163.3, 150.7, 150.3, 147.6, 146.8, 144.6, 144.3, 140.5, 140.4, 137.3, 137.3, 136.0, 135.5, 135.2, 134.4, 133.4, 132.6, 132.5, 131.9, 131.9, 131.7, 130.3, 129.2, 129.2, 129.1, 128.9, 128.9, 128.5, 128.5, 128.4, 128.3, 128.2, 128.0, 127.6, 127.5, 127.0, 126.7, 126.5, 126.5, 126.4, 126.3, 125.9, 125.7, 125.7, 125.2, 125.0, 124.8, 123.9, 123.8, 121.4, 121.2, 113.3, 112.6, 2.0. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>31H27</sub>N<sub>2</sub>OSi 471.1912, found 471.1887.

2-(quinolin-8-yl)-3-(thiophen-3-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one:2-(quinolin-8-yl)-4-(thiophen-3-yl)-3-(trimethylsilyl)isoquinolin-1(2H)-one (3aq:3aq' = 1:1)

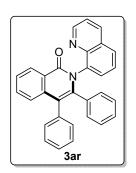


According to the general procedure (PE/EtOAc = 2/1), **3aq:3aq'** was obtained in 89% yield (38 mg). White solid. The ratio of two isomers was 1:1 as determined by <sup>1</sup>H NMR spectra. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.95 (dd, J = 4.1, 1.5 Hz, 1H), 8.85 (dd, J = 4.1, 1.5 Hz, 1H), 8.54 (dd, J = 7.9, 2.1 Hz, 2H), 8.12 (dd, J = 8.3, 1.5 Hz, 1H), 8.05 (dd,

 $J = 8.3, 1.5 \text{ Hz}, 1\text{H}, 8.00-7.96 \text{ (m, 2H)}, 7.72-7.68 \text{ (m, 4H)}, 7.50 \text{ (t, } J = 7.6 \text{ Hz}, 3\text{H}), 7.44-7.39 \text{ (m, 2H)}, 7.36-7.32 \text{ (m, 2H)}, 7.26-7.23 \text{ (m, 1H)}, 7.10-7.09 \text{ (m, 1H)}, 6.83 \text{ (dd, } J = 5.0, 3.0 \text{ Hz}, 1\text{H}), 6.77-6.74 \text{ (m, 2H)}, 6.58 \text{ (dd, } J = 5.0, 3.0 \text{ Hz}, 1\text{H}), 6.19 \text{ (dd, } J = 5.0, 1.3 \text{ Hz}, 1\text{H}), 0.08 \text{ (s, 18H)}. {}^{13}\text{C} \text{ NMR} \text{ (101 MHz, CDCl}_3) \delta \text{ (ppm) 163.2, 163.0, 151.0, 150.7, 145.3, 144.6, 144.6, 144.4, 140.5, 140.5, 138.4, 137.8, 137.7, 137.2, 136.3, 136.1, 131.8, 131.7, 130.6, 130.6, 130.5, 129.3, 128.9, 128.8, 128.8, 128.7, 128.5, 127.6, 127.4, 127.0, 126.3, 126.3, 126.2, 126.0, 125.8, 124.2, 123.6, 121.6, 128.8, 128.7, 128.5, 127.6, 127.4, 127.0, 126.3, 126.3, 126.2, 126.0, 125.8, 124.2, 123.6, 121.6, 128.8, 128.7, 128.5, 127.6, 127.4, 127.0, 126.3, 126.3, 126.2, 126.0, 125.8, 124.2, 123.6, 121.6, 128.8, 128.7, 128.5, 127.6, 127.4, 127.0, 126.3, 126.3, 126.2, 126.0, 125.8, 124.2, 123.6, 121.6, 128.8, 128.7, 128.5, 127.6, 127.4, 127.0, 126.3, 126.3, 126.2, 126.0, 125.8, 124.2, 123.6, 121.6, 128.8, 128.7, 128.5, 127.6, 127.4, 127.0, 126.3, 126.3, 126.2, 126.0, 125.8, 124.2, 123.6, 121.6, 128.8, 128.7, 128.5, 127.6, 127.4, 127.0, 126.3, 126.3, 126.2, 126.0, 125.8, 124.2, 123.6, 121.6, 128.8, 128.7, 128.5, 127.6, 127.4, 127.0, 126.3, 126.3, 126.2, 126.0, 125.8, 124.2, 123.6, 121.6, 128.8, 128.7, 128.8, 128.7, 128.5, 127.6, 127.4, 127.0, 126.3, 126.3, 126.2, 126.0, 125.8, 124.2, 123.6, 121.6, 128.8, 128.7, 128.8, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128.7, 128.8, 128$ 

121.5, 113.1, 112.8, 2.0, 2.0 HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>25</sub>H<sub>23</sub>N<sub>2</sub>OSSi 455.1355, found 455.1341.

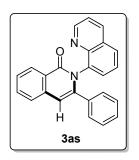
# 3,4-diphenyl-2-(quinolin-8-yl)isoquinolin-1(2H)-one (3ar)<sup>[5]</sup>



According to the general procedure (PE/EtOAc = 2/1), **3ar** was obtained in 87% yield (37 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.94-8.93 (m, 1H), 8.60 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.53 (dd, *J* = 13.3, 7.0 Hz, 2H), 7.40-7.35 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.26 (s, 2H), 7.19-7.16 (m, 3H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.78-6.71 (m, 2H), 6.50 (t, *J* =

7.5 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 162.8, 150.9, 144.8, 142.0, 138.3, 137.8, 136.7, 136.1, 135.0, 132.5, 132.0, 131.8, 131.0, 130.9, 129.9, 128.8, 128.7, 128.5, 128.1, 127.9, 127.3, 126.9, 126.8, 126.7, 126.5, 125.8, 125.7, 125.7, 121.6, 118.6. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>30</sub>H<sub>21</sub>N<sub>2</sub>O 425.1647, found 425.1648.

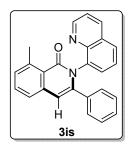
# 3-phenyl-2-(quinolin-8-yl)isoquinolin-1(2H)-one (3as)<sup>[8]</sup>



According to the general procedure (PE/EtOAc = 2/1), **3as** was obtained in 83% yield (29 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.91-8.90 (m, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 8.08-8.06 (m, 1H), 7.70 (t, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.35 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 2H), 6.66 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

δ (ppm) 163.3, 151.0, 144.8, 144.6, 137.4, 137.3, 136.4, 136.1, 132.8, 130.8, 128.8, 128.8, 128.5, 128.0, 127.4, 126.8, 126.2, 125.9, 125.5, 121.6, 107.5. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for  $C_{24}H_{17}N_2O$  349.1326, found 349.1335.

# 8-methyl-3-phenyl-2-(quinolin-8-yl)isoquinolin-1(2H)-one (3is)<sup>[8]</sup>

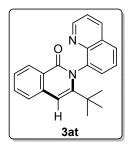


According to the general procedure (PE/EtOAc = 2/1), **3is** was obtained in 80% yield (29 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.92-8.91 (m, 1H), 8.08-8.05 (m, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.55-7.51 (m, 2H), 7.43 (m, 2H), 7.35 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.27-7.25 (m, 1H), 7.12 (d, *J* = 7.2 Hz, 2H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.94 (t, *J* = 7.3 Hz, 2H), 6.60 (s, 1H),

2.92 (s, 3H).  $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 164.1, 151.0, 144.9, 144.3, 142.5, 139.1, 137.8,

136.4, 136.2, 132.0, 131.0, 129.9, 128.9, 128.8, 128.6, 127.9, 127.3, 126.0, 124.7, 124.0, 121.6, 107.9, 24.0. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>25</sub>H<sub>19</sub>N<sub>2</sub>O 363.1487, found 363.1492.

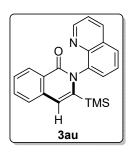
#### 3-(tert-butyl)-2-(quinolin-8-yl)isoquinolin-1(2H)-one (3at)<sup>[9]</sup>



According to the general procedure (PE/EtOAc = 2/1), **3at** was obtained in 40% yield (13 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.83 (d, *J* = 4.0 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.68-7.63 (m, 2H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.37 (dd, *J* = 8.1, 4.1 Hz, 1H), 6.81 (s, 1H),

1.05 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 165.2, 151.6, 151.1, 146.4, 139.2, 137.4, 136.2, 132.6, 131.9, 129.4, 129.1, 128.1, 126.5, 126.3, 125.7, 124.7, 121.7, 104.5, 36.7, 31.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O 329.1639, found 329.1648.

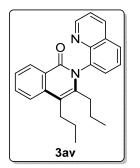
## 2-(quinolin-8-yl)-3-(trimethylsilyl)isoquinolin-1(2H)-one (3au)<sup>[8]</sup>



According to the general procedure (PE/EtOAc = 2/1), **3au** was obtained in 78% yield (27 mg). Light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.88 (d, J = 4.1 Hz, 1H), 8.44 (d, J = 8.0 Hz, 1H), 8.22 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.73-7.65 (m, 3H), 7.60 (d, J = 7.9 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.41 (dd, J = 7.6, 3.5 Hz, 1H), 6.91 (s, 1H), -0.26 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 163.7, 151.4, 146.8, 145.5, 139.4, 137.0,

136.2, 132.4, 130.5, 129.6, 129.3, 128.1, 127.4, 126.5, 126.3, 126.0, 121.9, 115.5, -0.1. HR-MS (ESI)  $[M+H]^+$  m/z calcd for C<sub>21</sub>H<sub>21</sub>N<sub>2</sub>OSi 345.1409, found 345.1418.

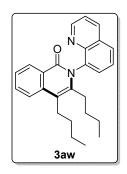
# 3,4-dipropyl-2-(quinolin-8-yl)isoquinolin-1(2H)-one (3av)<sup>[10]</sup>



According to the general procedure (PE/EtOAc = 2/1), **3av** was obtained in 98% yield (35 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.85 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.47 (d, *J* = 7.8 Hz, 1H), 8.23 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.95 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.76-7.65 (m, 4H), 7.46-7.40 (m, 2H), 2.82-2.73 (m, 2H), 2.53-2.45 (m, 1H), 1.98-1.91 (m, 1H), 1.79-1.69 (m, 2H), 1.43-1.26 (m, 2H), 1.12 (t, *J* = 7.3 Hz, 3H), 0.54 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C

NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 163.3, 151.4, 144.9, 141.1, 137.7, 137.6, 136.3, 132.4, 130.4, 129.3, 129.1, 128.8, 126.2, 125.7, 125.6, 123.0, 121.8, 113.6, 32.9, 30.0, 23.8, 23.1, 14.6, 14.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>O 357.1952, found 357.1961.

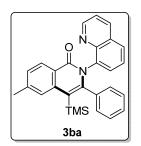
#### 3,4-dibutyl-2-(quinolin-8-yl)isoquinolin-1(2H)-one (3aw)<sup>[10]</sup>



According to the general procedure (PE/EtOAc = 2/1), **3aw** was obtained in 86% yield (33 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.86 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.47 (d, *J* = 7.4 Hz, 1H), 8.22 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.95 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.76-7.67 (m, 4H), 7.46-7.40 (m, 2H), 2.86-2.74 (m, 2H), 2.52-2.45 (m, 1H), 2.05-1.96 (m, 1H), 1.76-1.64 (m, 2H), 1.59-1.50 (m, 2H), 1.41-1.22 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.96-0.87 (m,

2H), 0.49 (t, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 163.2, 151.4, 145.0, 141.0, 137.7, 137.6, 136.3, 132.4, 130.4, 129.4, 129.1, 128.8, 126.2, 125.6, 125.6, 122.9, 121.8, 113.7, 32.7, 31.5, 30.3, 27.6, 23.3, 22.6, 14.1, 13.2. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>26</sub>H<sub>29</sub>N<sub>2</sub>O 385.2266, found 385.2274.

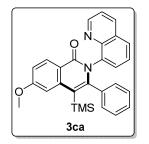
#### 6-methyl-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ba)



According to the general procedure (PE/EtOAc = 2/1), **3ba** was obtained in 92% yield (40 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.88 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.48 (d, *J* = 8.1 Hz, 1H), 7.99 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.81 (s, 1H), 7.59 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.35-7.28 (m, 4H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* =

7.7 Hz, 1H), 6.63 (t, J = 7.5 Hz, 1H), 2.56 (s, 3H), 0.03 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 162.9, 150.6, 149.6, 144.9, 141.9, 140.7, 137.8, 137.4, 135.9, 131.3, 131.0, 130.0, 128.7, 128.6, 128.3, 128.1, 127.6, 127.5, 126.8, 126.5, 125.6, 123.8, 121.3, 111.1, 22.3, 2.2. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>OSi 435.1873, found 435.1887.

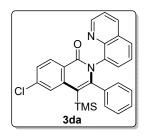
#### 6-methoxy-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ca)



According to the general procedure (PE/EtOAc = 2/1), **3ca** was obtained in 91% yield (41 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.91 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.48 (d, *J* = 8.9 Hz, 1H), 8.02 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.61 (dd, *J* = 7.0, 2.5 Hz, 1H), 7.39 (d, *J* = 2.3 Hz, 1H), 7.35-7.29 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.09 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.05

(t, J = 7.5 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 6.62 (t, J = 7.6 Hz, 1H), 3.96 (s, 3H), 0.01 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 162.7, 162.3, 150.8, 150.3, 145.0, 142.6, 137.9, 137.5, 136.0, 131.3, 131.2, 130.9, 130.1, 128.7, 128.4, 128.3, 127.0, 126.6, 125.7, 121.5, 120.0, 114.9, 110.9, 109.9, 55.5, 2.2. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub>Si 451.1827, found 451.1836.

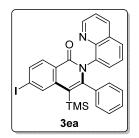
#### 6-chloro-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3da)



According to the general procedure (PE/EtOAc = 2/1), **3da** was obtained in 95% yield (43 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.90 (d, *J* = 2.9 Hz, 1H), 8.48 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.97 (s, 1H), 7.63 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.46-7.44 (m, 1H), 7.37-7.30 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.95 (t, *J* =

7.4 Hz, 1H), 6.83 (d, J = 7.7 Hz, 1H), 6.63 (t, J = 7.6 Hz, 1H), 0.00 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 162.5, 150.9, 150.8, 144.8, 142.0, 138.3, 137.5, 137.1, 136.1, 131.2, 131.0, 130.6, 129.9, 128.7, 128.6, 128.5, 127.1, 127.0, 126.7, 126.6, 125.7, 124.6, 121.6, 110.8, 2.1. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>27</sub>H<sub>24</sub>ClN<sub>2</sub>OSi 455.1325, found 455.1341.

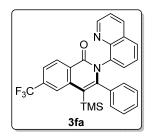
#### 6-iodo-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ea)



According to the general procedure (PE/EtOAc = 2/1), **3ea** was obtained in 84% yield (46 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.89 (d, *J* = 3.0 Hz, 1H), 8.38 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.62 (dd, *J* = 5.7, 3.9 Hz, 1H), 7.36-7.30 (m, 3H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.4 Hz,

1H), 6.83 (d, J = 7.7 Hz, 1H), 6.63 (t, J = 7.5 Hz, 1H), 0.00 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 162.8, 150.8, 150.7, 144.8, 142.3, 137.5, 137.1, 136.8, 136.1, 134.9, 131.2, 131.0, 130.4, 130.0, 128.7, 128.6, 128.5, 127.0, 126.7, 125.7, 125.4, 121.6, 110.6, 99.8, 2.1. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>27</sub>H<sub>24</sub>IN<sub>2</sub>OSi 547.0679, found 547.0697.

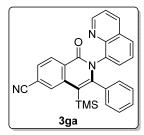
#### 3-phenyl-2-(quinolin-8-yl)-6-(trifluoromethyl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3fa)



According to the general procedure (PE/EtOAc = 2/1), **3fa** was obtained in 90% yield (44 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.89 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.66 (d, *J* = 8.3 Hz, 1H), 8.32 (s, 1H), 8.04 (d, *J* = 9.5 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.64 (dd, *J* = 6.7, 2.8 Hz, 1H), 7.37-7.31 (m, 3H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.5

Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 7.7 Hz, 1H), 6.65 (t, J = 7.5 Hz, 1H), 0.02 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 162.9, 150.9, 147.8, 144.8, 140.9 (q, J = 1.2 Hz), 140.3, 137.4, 136.2, 131.9, 131.7, 131.1, 130.7, 130.4 (q, J = 32.7 Hz), 129.0, 128.9, 128.8, 127.7, 126.6, 126.3, 125.8, 123.9 (q, J = 3.9 Hz), 123.7 (q, J = 273.7 Hz), 123.53 (q, J = 3.7 Hz), 121.7, 111.9, 2.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>28</sub>H<sub>24</sub> F<sub>3</sub>N<sub>2</sub>OSi 489.1614, found 489.1605.

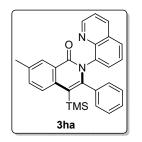
# 1-oxo-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)-1,2-dihydroisoquinoline-6-carbonitrile (3ga)



According to the general procedure (PE/EtOAc = 2/1), **3ga** was obtained in 70% yield (31 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.88 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.62 (d, *J* = 8.2 Hz, 1H), 8.30 (s, 1H), 8.04 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.69 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.64 (t, *J* = 4.8 Hz, 1H), 7.36 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.33 (d, *J* = 4.8 Hz, 2H),

7.16 (d, J = 7.6 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 7.8 Hz, 1H), 6.64 (t, J = 7.5 Hz, 1H), 0.01 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 161.6, 151.2, 150.5, 144.2, 140.5, 136.8, 136.3, 135.8, 131.9, 130.7, 130.5, 129.7, 129.5, 128.5, 128.4, 127.5, 126.8, 126.5, 125.4, 121.4, 118.5, 114.9, 110.6, 1.7. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>28</sub>H<sub>24</sub>N<sub>3</sub>OSi 446.1671, found 446.1683.

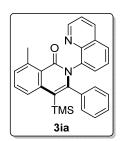
#### 7-methyl-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ha)



According to the general procedure (PE/EtOAc = 2/1), **3ha** was obtained in 74% yield (32 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.89 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.00 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.71 (s, 1H), 7.63 (s, 1H), 7.60-7.58 (m, 1H), 7.37-7.26 (m, 4H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.05-7.01 (m, 1H), 6.93 (d, *J* = 14.9 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.63-6.59

(m, 1H), 2.48 (s, 3H), -0.03 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 163.0, 150.7, 148.6, 145.0, 138.2, 138.0, 137.5, 136.0, 136.0, 133.2, 131.4, 131.1, 130.2, 128.7, 128.4, 128.4, 128.2, 127.6, 126.9, 126.6, 126.1, 125.7, 121.4, 111.3, 21.4, 2.2. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>OSi 435.1873, found 435.1887.

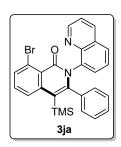
#### 8-methyl-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ia)



According to the general procedure (PE/EtOAc = 2/1), **3ia** was obtained in 90% yield (39 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.93 (d, *J* = 4.0 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.61 (dd, *J* = 6.9, 2.5 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.37-7.31 (m, 3H), 7.28-7.26 (m, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.3 Hz, 1H),

6.86 (d, J = 7.7 Hz, 1H), 6.61 (t, J = 7.5 Hz, 1H), 2.91 (s, 3H), -0.02 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 163.7, 150.7, 149.6, 145.1, 142.9, 142.5, 138.3, 137.5, 136.1, 131.3, 131.2, 130.8, 130.2, 129.5, 128.8, 128.3, 128.2, 126.9, 126.6, 126.1, 125.8, 124.8, 121.5, 111.4, 24.9, 2.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>OSi 435.1900, found 435.1887.

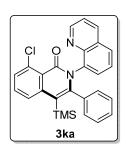
#### 8-bromo-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ja)



According to the general procedure (PE/EtOAc = 2/1), **3ja** was obtained in 90% yield (45 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.90 (dd, J = 4.2, 1.6 Hz, 1H), 8.01 (dd, J = 8.3, 1.6 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.79-7.76 (m, 1H), 7.60 (dd, J = 7.8, 1.7 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.37-7.30 (m, 3H), 7.14 (d, J = 7.6 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.93 (t, J = 7.5

Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 6.62 (t, J = 7.3 Hz, 1H), -0.03 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 161.1, 150.7, 150.5, 144.9, 143.9, 137.8, 137.1, 136.0, 133.5, 131.3, 131.2, 131.2, 130.1, 128.8, 128.5, 128.5, 127.6, 127.0, 126.7, 125.8, 123.9, 123.6, 121.5, 111.1, 2.3.HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>27</sub>H<sub>24</sub>BrN<sub>2</sub>OSi 499.0837, found 499.0836.

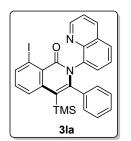
### 8-chloro-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ka)



According to the general procedure (PE/EtOAc = 2/1), **3ka** was obtained in 93% yield (42 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.90 (dd, J = 4.2, 1.7 Hz, 1H), 8.01 (dd, J = 8.3, 1.6 Hz, 1H), 7.89 (dd, J = 7.8, 1.6 Hz, 1H), 7.61 (dd, J = 7.6, 2.0 Hz, 1H), 7.56-7.52 (m, 1H), 7.50 (dd, J = 7.8, 1.6 Hz, 1H), 7.35-7.29 (m, 3H), 7.15 (d, J = 7.6 Hz, 1H), 7.06-7.02 (m, 1H), 6.94 (d, J = 8.6 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.64-6.60 (m, 1H), -0.03 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 161.1, 150.7, 150.6, 144.9, 144.0, 137.7, 137.1, 136.3, 136.0, 131.2, 131.1, 131.1, 130.0, 129.5, 128.7, 128.5, 128.4, 127.0, 126.9, 126.7, 125.7, 122.8, 121.5, 111.0, 2.2. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>27</sub>H<sub>24</sub>ClN<sub>2</sub>OSi 455.1331, found 455.1341.

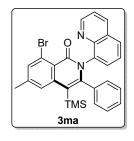
#### 8-iodo-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3la)



According to the general procedure (PE/EtOAc = 2/1), **3la** was obtained in 27% yield (15 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.89 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.21 (d, *J* = 7.5 Hz, 1H), 8.02-7.97 (m, 2H), 7.60 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.38-7.30 (m, 3H), 7.26-7.21 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.8

Hz, 1H), 6.61 (t, J = 7.5 Hz, 1H), -0.04 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 160.7, 150.7, 150.1, 144.8, 142.9, 141.3, 137.8, 137.1, 136.0, 131.6, 131.3, 131.2, 130.1, 128.8, 128.6, 128.5, 128.4, 127.0, 126.6, 125.8, 124.7, 121.5, 111.5, 94.6, 2.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>27</sub>H<sub>24</sub>IN<sub>2</sub>OSi 547.0680, found 547.0697.

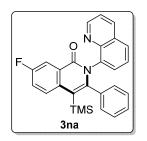
#### 8-bromo-6-methyl-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3ma)



According to the general procedure (PE/EtOAc = 2/1), **3ma** was obtained in 78% yield (40 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.89 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.00 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.71 (s, 1H), 7.63-7.62 (m, 1H), 7.59 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.37-7.29 (m, 3H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.05-7.01 (m, 1H), 6.93 (d, *J* = 14.9 Hz, 1H), 6.86 (d, *J* = 7.8 Hz,

1H), 6.64-6.59 (m, 1H), 2.48 (s, 3H), -0.03 (s, 9H).  $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 161.1, 150.7, 150.6, 144.9, 143.8, 141.8, 137.8, 137.2, 136.0, 134.7, 131.3, 131.2, 130.1, 128.8, 128.4, 128.4, 127.9, 127.0, 126.6, 125.7, 123.6, 121.5, 121.3, 110.8, 21.6, 2.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>28</sub>H<sub>26</sub>BrN<sub>2</sub>OSi 513.0978, found 513.0992.

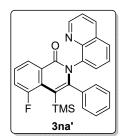
#### 7-fluoro-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3na)



According to the general procedure (PE/EtOAc = 2/1), **3na** was obtained in 32% yield (14 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.90 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.19 (dd, *J* = 9.3, 2.9 Hz, 1H), 8.04 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.00 (dd, *J* = 9.1, 5.0 Hz, 1H), 7.63 (dd, *J* = 5.6, 4.0 Hz, 1H), 7.47-7.43 (m, 1H), 7.37-7.32 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.08-

7.04 (m, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.62 (t, J = 7.6 Hz, 1H), -0.01 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 162.3, 161.0 (d, J = 252.5 Hz), 150.8, 148.8 (d, J = 2.4 Hz), 144.8, 137.6, 137.2, 137.2, 136.1, 131.4, 131.0, 130.2, 129.9 (d, J = 7.5 Hz), 128.8, 128.6, 128.4, 128.0, (d, J = 7.8 Hz), 127.0, 126.7, 125.8, 121.6, 120.3 (d, J = 23.1 Hz), 113.8 (d, J = 22.3 Hz), 111.2, 2.2. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -114.63. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>27</sub>H<sub>24</sub>FN<sub>2</sub>OSi 439.1625, found 439.1636.

#### 5-fluoro-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3na')

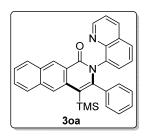


According to the general procedure (PE/EtOAc = 2/1), **3na'** was obtained in 43% yield (19 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.33 (dd, *J* = 7.4, 1.8 Hz, 1H), 8.05 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.65 (dd, *J* = 7.3, 2.3 Hz, 1H), 7.46-7.41 (m, 2H), 7.38-7.35 (m, 1H), 7.35-7.30 (m, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.98 (t, *J* 

= 7.5 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.65 (t, J = 8.0 Hz, 1H), -0.12 (d, J = 4.3 Hz, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 162.1, 161.1 (d, J = 207.1 Hz), 157.6, 151.1, 150.8, 145.0, 137.7 (d, J = 2.4 Hz), 136.1, 131.7, 130.9, 130.7, 130.6 (d, J = 15.5 Hz), 128.7, 128.6 (d, J = 10.3 Hz), 128.4 (d, J = 4.8 Hz), 127.1, 126.8, 126.8 (d, J = 9.1 Hz), 125.8, 124.6 (d, J = 3.2 Hz), 121.6, 118.6,

118.4, 108.1 (d, J = 1.8 Hz), 2.1 (d, J = 10.7 Hz). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) -103.06. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>27</sub>H<sub>24</sub>FN<sub>2</sub>OSi 439.1619, found 439.1636.

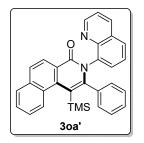
#### 3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)benzo[g]isoquinolin-1(2H)-one (3oa)



According to the general procedure (PE/EtOAc = 2/1), **3oa** was obtained in 53% yield (25 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 9.17 (s, 1H), 8.91 (dd, *J* = 4.0, 1.3 Hz, 1H), 8.45 (s, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 8.05-8.02 (m, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.64-7.59 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.39-7.31 (m, 3H), 7.26-7.23 (m, 1H), 7.08

(t, J = 7.5 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 7.7 Hz, 1H), 6.64 (t, J = 7.5 Hz, 1H), 0.08 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  163.6, 150.7, 148.7, 145.1, 137.9, 137.6, 136.3, 136.0, 135.1, 131.5, 131.3, 130.3, 129.8, 129.4, 128.7, 128.4, 128.3, 128.0, 128.0, 127.0, 126.6, 126.4, 125.9, 125.7, 124.8, 121.5, 111.3, 2.3. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>31</sub>H<sub>27</sub>N<sub>2</sub>OSi 471.1882, found 471.1887.

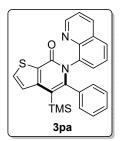
#### 2-phenyl-3-(quinolin-8-yl)-1-(trimethylsilyl)benzo[f]isoquinolin-4(3H)-one (3oa')



According to the general procedure (PE/EtOAc = 2/1), **30a'** was obtained in 28% yield (13 mg). Light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.97-8.96 (m, 1H), 8.70 (d, *J* = 8.3 Hz, 1H), 8.42 (d, *J* = 8.6 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.41-7.34 (m,

3H), 7.18 (d, J = 7.8 Hz, 1H), 7.14 (t, J = 7.7 Hz, 1H), 7.05 (t, J = 7.4 Hz, 1H), 6.73 (t, J = 7.5 Hz, 1H), -0.16 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 162.9, 154.7, 153.2, 150.8, 145.1, 142.8, 138.0, 137.9, 136.1, 135.7, 132.4, 131.5, 131.3, 130.7, 129.4, 129.1, 128.7, 128.5, 128.2, 128.0, 127.1, 126.8, 125.8, 124.4, 124.3, 124.2, 121.5, 111.8, 4.1.HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>31</sub>H<sub>27</sub>N<sub>2</sub>OSi 471.1881, found 471.1887.

#### 5-phenyl-6-(quinolin-8-yl)-4-(trimethylsilyl)thieno[2,3-c]pyridin-7(6H)-one (3pa)



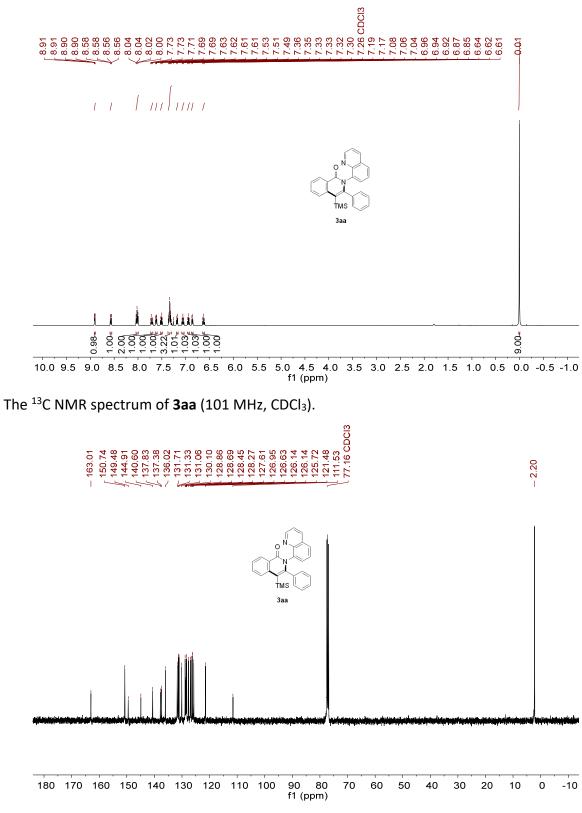
According to the general procedure (PE/EtOAc = 2/1), **3pa** was obtained in 68% yield (29 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.90-8.89 (m, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 5.3 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 5.3 Hz, 1H), 7.38-7.35 (m, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.85

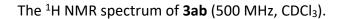
(d, *J* = 7.7 Hz, 1H), 6.63 (t, *J* = 7.5 Hz, 1H), -0.03 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 158.9, 150.8, 150.2, 148.8, 144.8, 137.2, 137.0, 136.0, 132.8, 131.2, 130.0, 129.9, 128.7, 128.2,

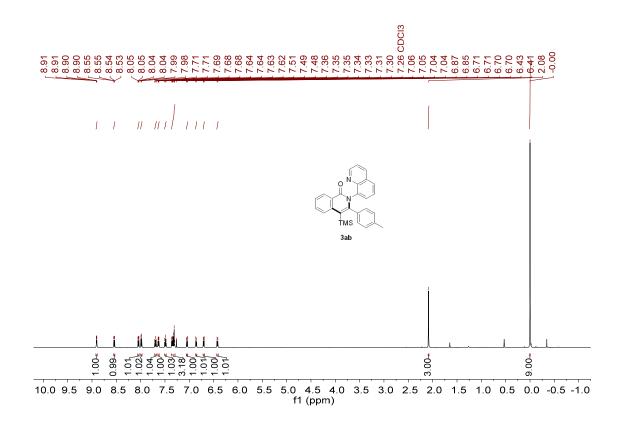
126.9, 126.6, 126.4, 125.6, 121.5, 110.4, 100.0, 1.4. HR-MS (ESI)  $[M+H]^+$  m/z calcd for  $C_{25}H_{23}N_2OSSi$  427.1290, found 427.1295.

# XIII. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds

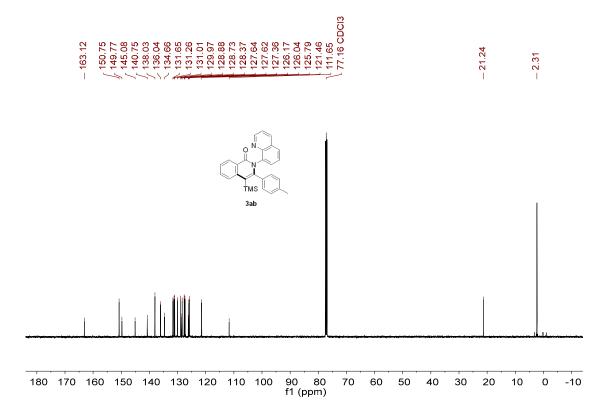
The <sup>1</sup>H NMR spectrum of **3aa** (400 MHz, CDCl<sub>3</sub>).



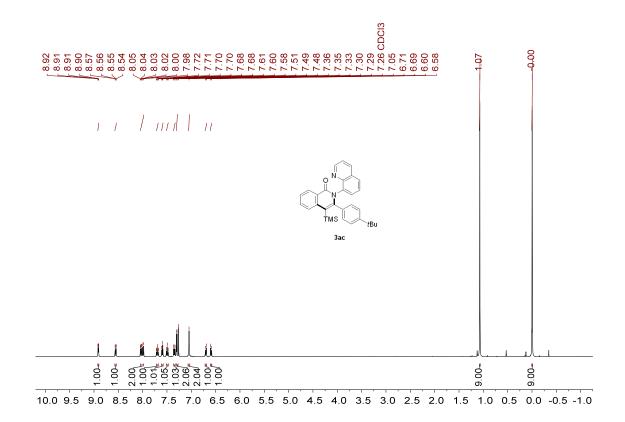




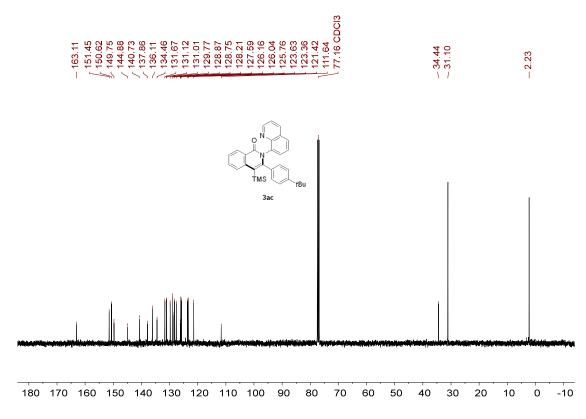
The <sup>13</sup>C NMR spectrum of **3ab** (126 MHz, CDCl<sub>3</sub>).



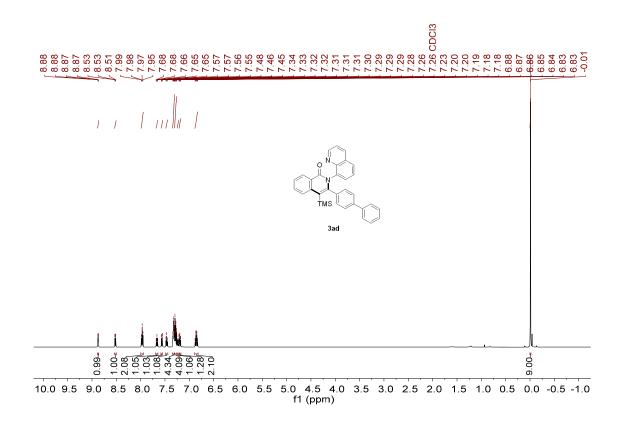
The <sup>1</sup>H NMR spectrum of **3ac** (400 MHz, CDCl<sub>3</sub>).



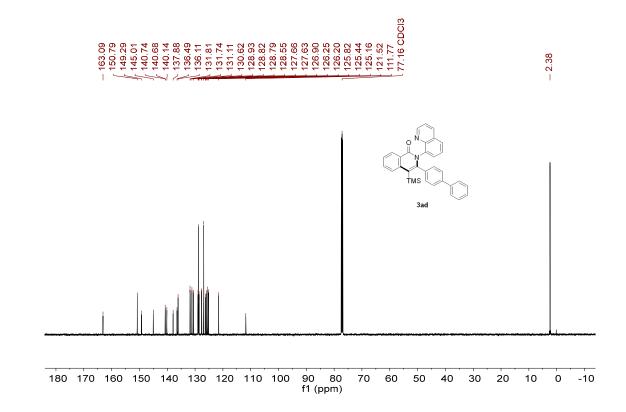
The <sup>13</sup>C NMR spectrum of **3ac** (101 MHz, CDCl<sub>3</sub>).

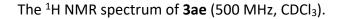


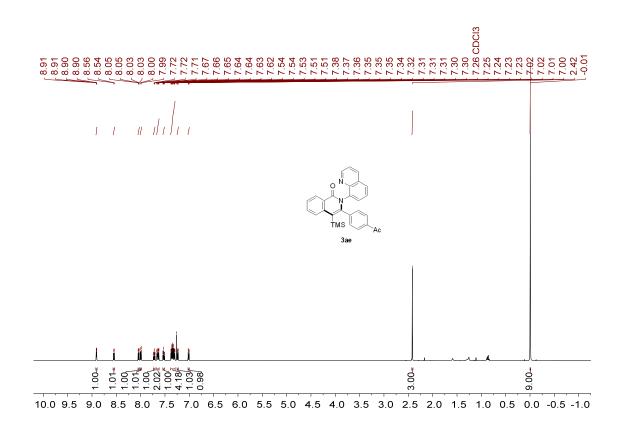
The <sup>1</sup>H NMR spectrum of **3ad** (500 MHz, CDCl<sub>3</sub>).



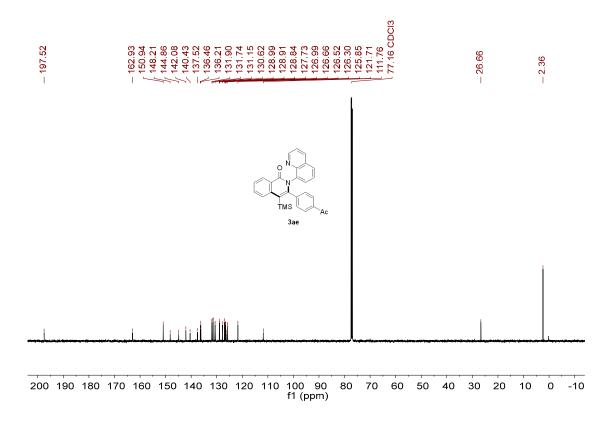
The <sup>13</sup>C NMR spectrum of **3ad** (126 MHz, CDCl<sub>3</sub>).



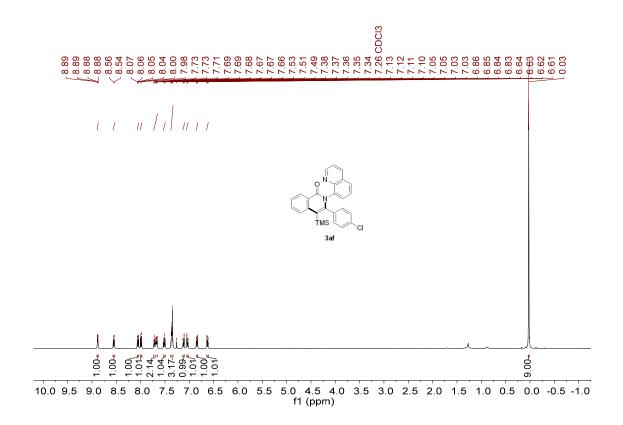




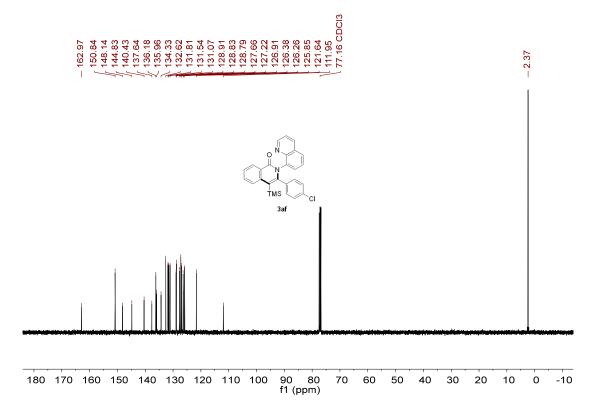
The <sup>13</sup>C NMR spectrum of **3ae** (126 MHz, CDCl<sub>3</sub>).



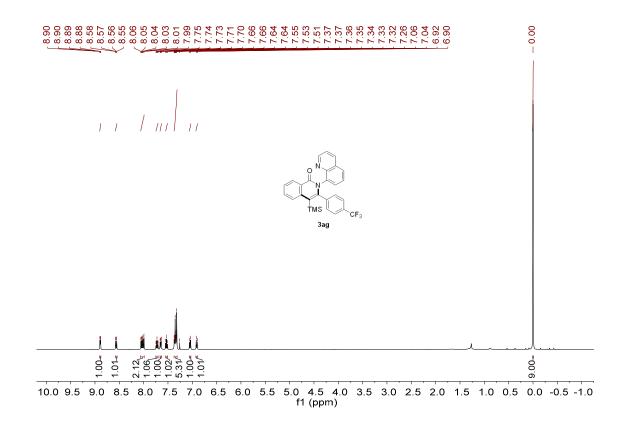
The <sup>1</sup>H NMR spectrum of **3af** (400 MHz, CDCl<sub>3</sub>).



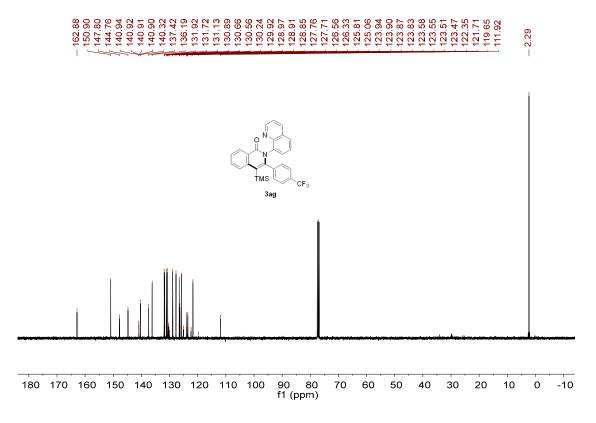
The <sup>13</sup>C NMR spectrum of **3af** (101 MHz, CDCl<sub>3</sub>).



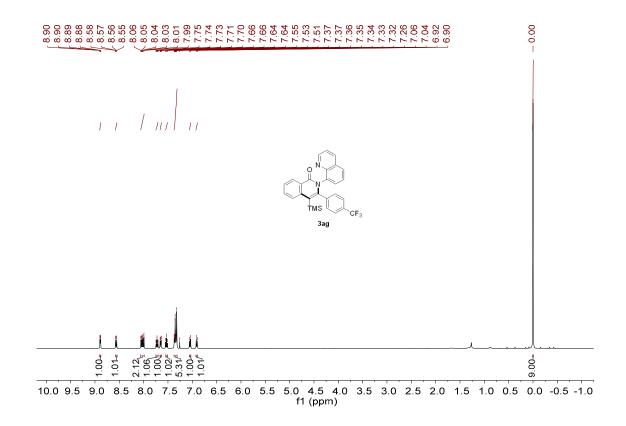
The <sup>1</sup>H NMR spectrum of **3ag** (400 MHz, CDCl<sub>3</sub>).



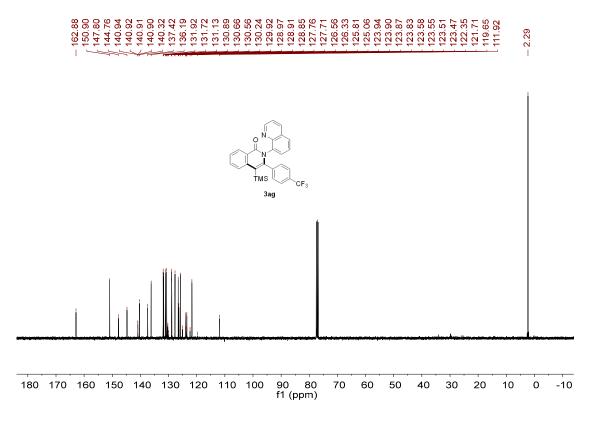
The <sup>13</sup>C NMR spectrum of **3ag** (101 MHz, CDCl<sub>3</sub>).



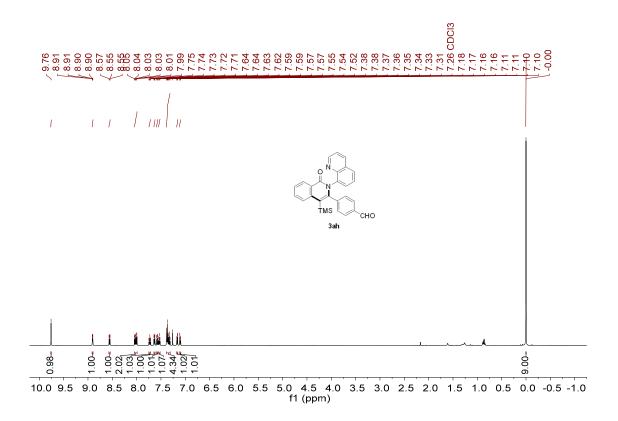
The <sup>1</sup>H NMR spectrum of **3ag** (400 MHz, CDCl<sub>3</sub>).



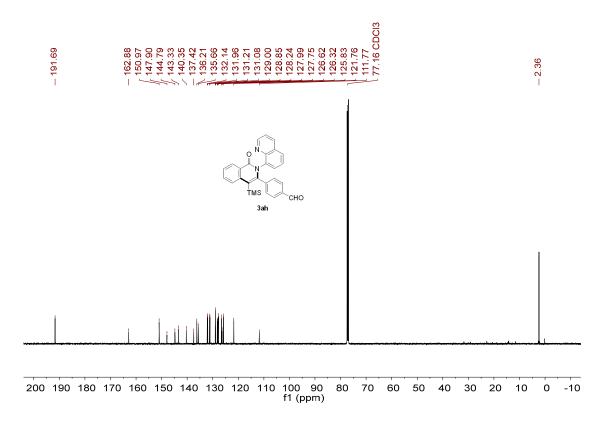
The <sup>13</sup>C NMR spectrum of **3ag** (101 MHz, CDCl<sub>3</sub>).



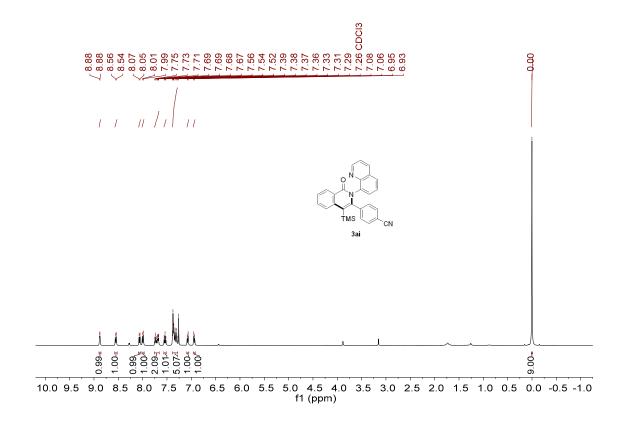
The <sup>1</sup>H NMR spectrum of **3ah** (500 MHz, CDCl<sub>3</sub>).



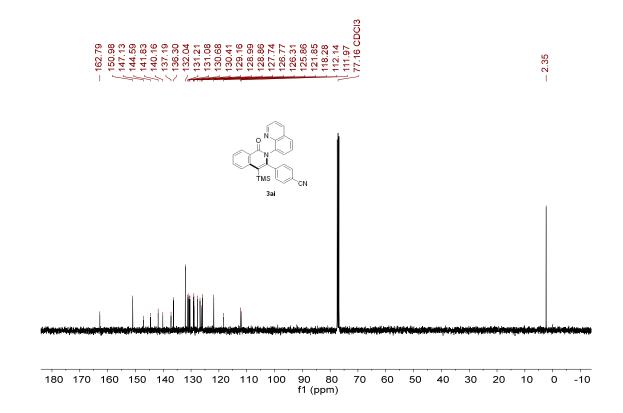
The  $^{13}$ C NMR spectrum of **3ah** (126 MHz, CDCl<sub>3</sub>).

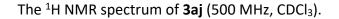


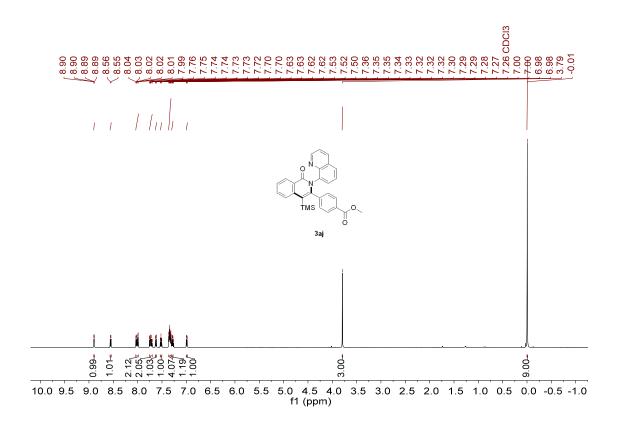
The <sup>1</sup>H NMR spectrum of **3ai** (400 MHz, CDCl<sub>3</sub>).



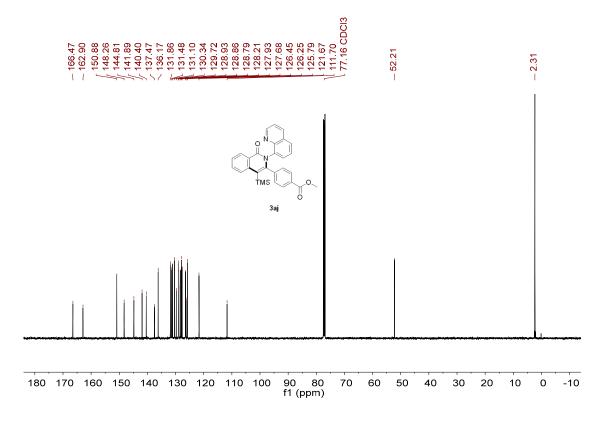
The <sup>13</sup>C NMR spectrum of **3ai** (101 MHz, CDCl<sub>3</sub>).



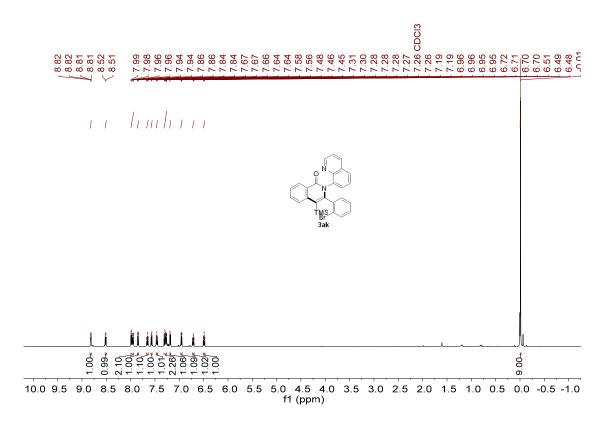




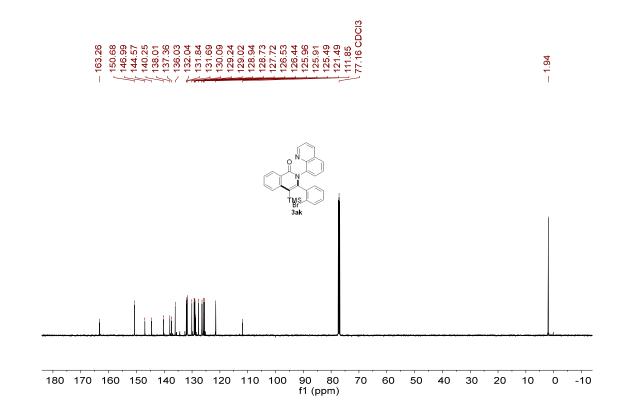
The <sup>13</sup>C NMR spectrum of **3ah** (126 MHz, CDCl<sub>3</sub>).



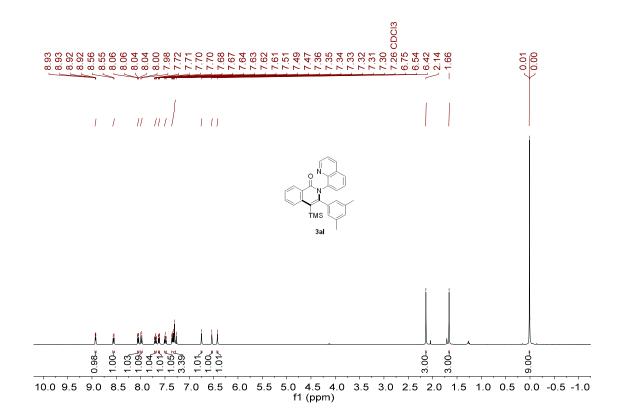
The <sup>1</sup>H NMR spectrum of **3ak** (500 MHz, CDCl<sub>3</sub>).



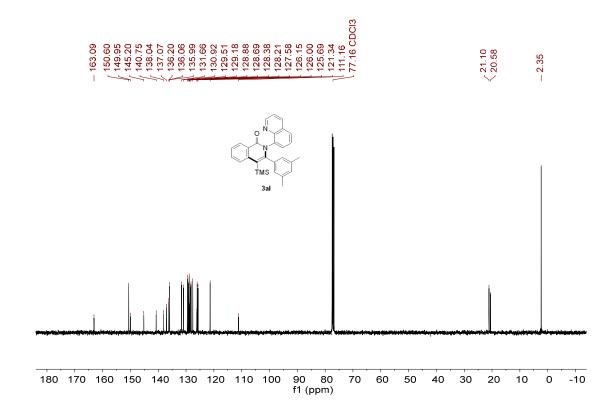
The <sup>13</sup>C NMR spectrum of **3ak** (126 MHz, CDCl<sub>3</sub>).

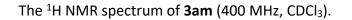


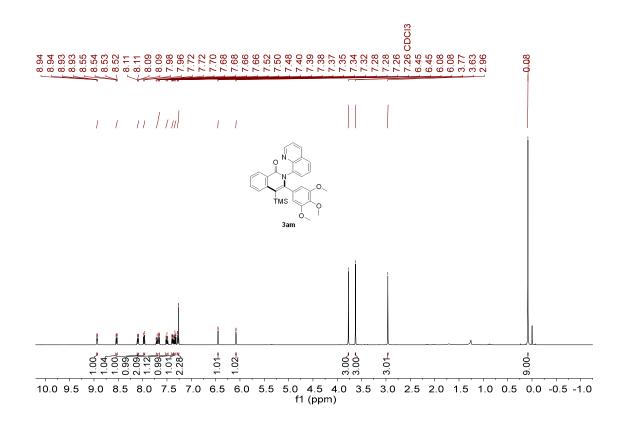
The <sup>1</sup>H NMR spectrum of **3al** (400 MHz, CDCl<sub>3</sub>).



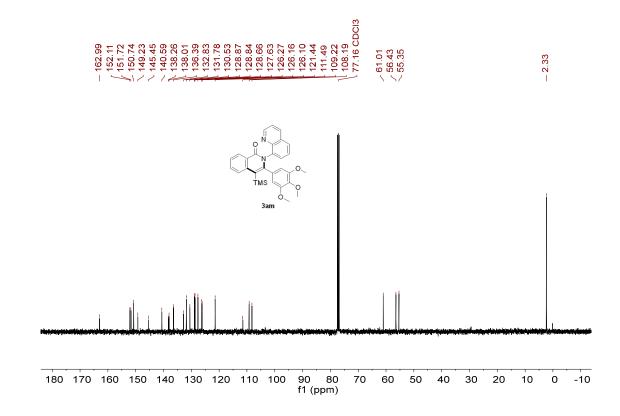
The <sup>13</sup>C NMR spectrum of **3al** (101 MHz, CDCl<sub>3</sub>).

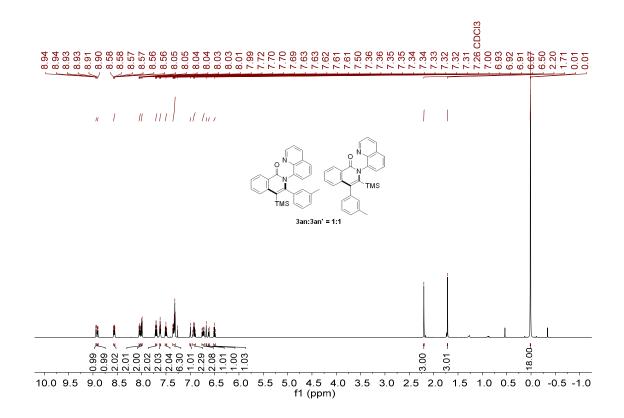






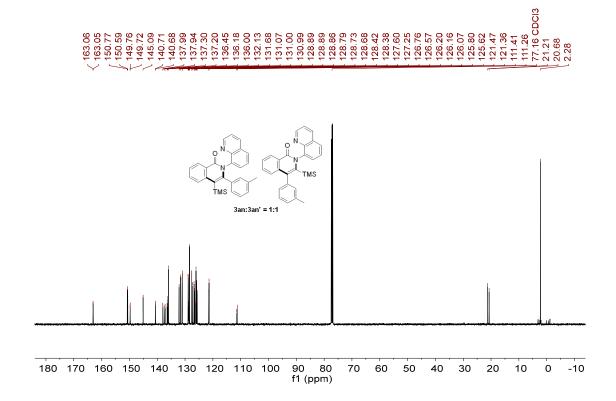
The <sup>13</sup>C NMR spectrum of **3am** (101 MHz, CDCl<sub>3</sub>).

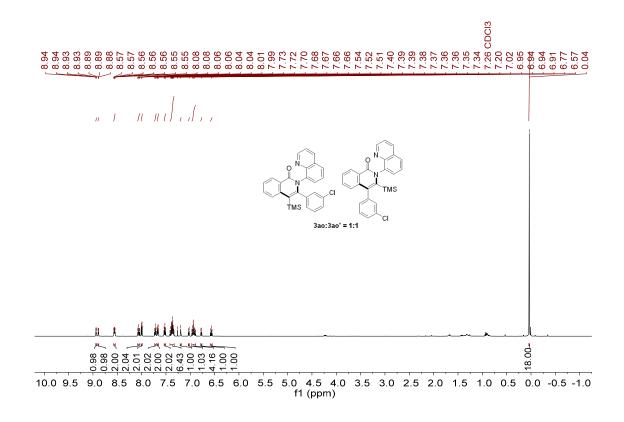




The <sup>1</sup>H NMR spectrum of **3an** and **3an'** (500 MHz, CDCl<sub>3</sub>).

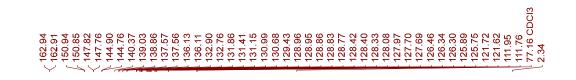
The <sup>13</sup>C NMR spectrum of **3an** and **3an'** (126 MHz, CDCl<sub>3</sub>).

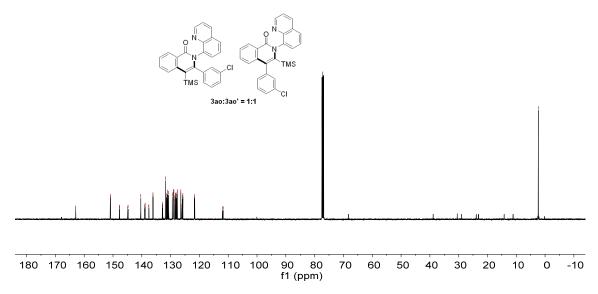


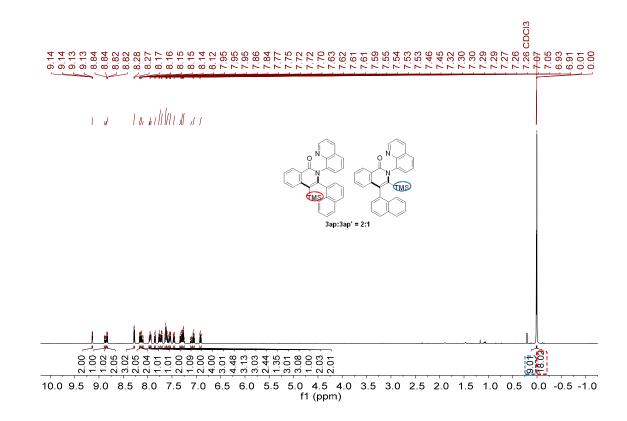


The <sup>1</sup>H NMR spectrum of **3ao** and **3ao'** (500 MHz, CDCl<sub>3</sub>).

The <sup>13</sup>C NMR spectrum of **3ao** and **3ao'** (126 MHz, CDCl<sub>3</sub>).



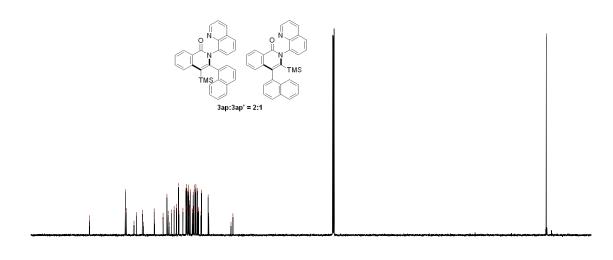




The <sup>1</sup>H NMR spectrum of **3ap** and **3ap'** (500 MHz, CDCl<sub>3</sub>).

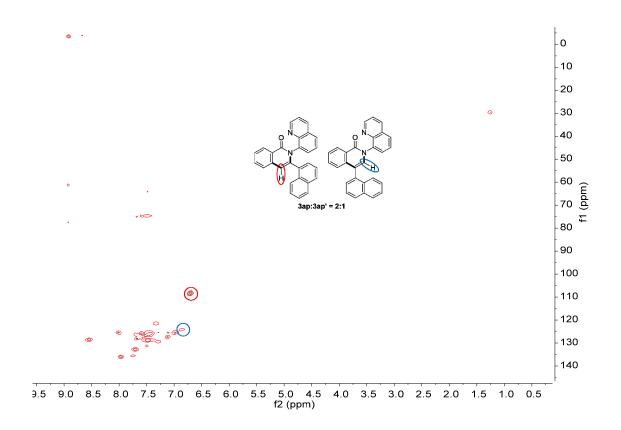
The <sup>13</sup>C NMR spectrum of **3ap** and **3ap'** (126 MHz, CDCl<sub>3</sub>).



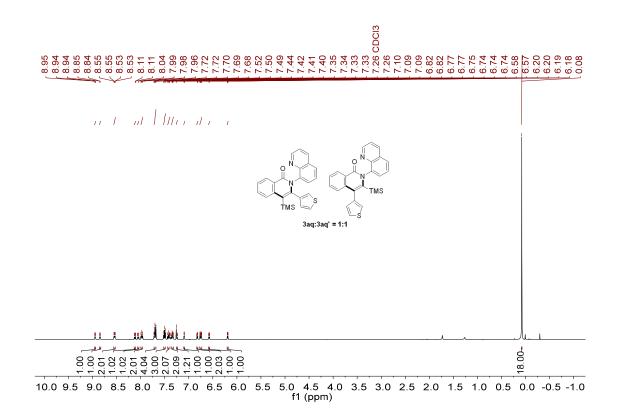


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

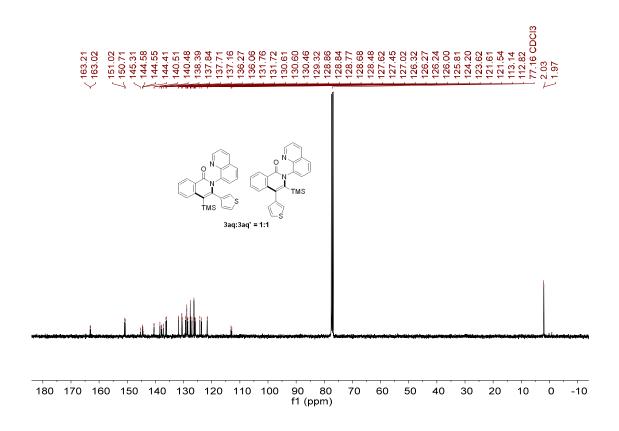
The 2D-HMQC analysis of **3ap** and **3ap'**.



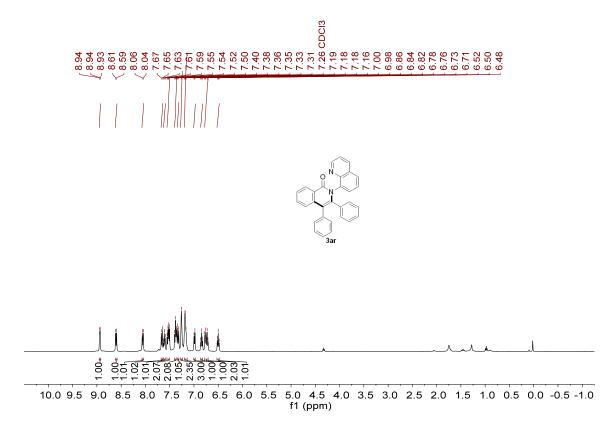
The <sup>1</sup>H NMR spectrum of **3aq** and **3aq'** (400 MHz, CDCl<sub>3</sub>).



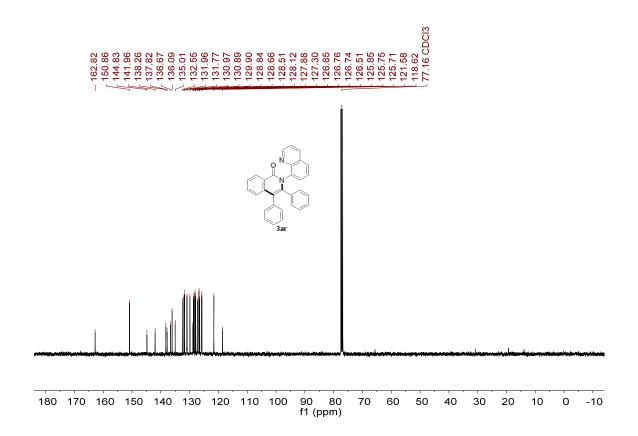
The <sup>13</sup>C NMR spectrum of **3aq** and **3aq'** (101 MHz, CDCl<sub>3</sub>).



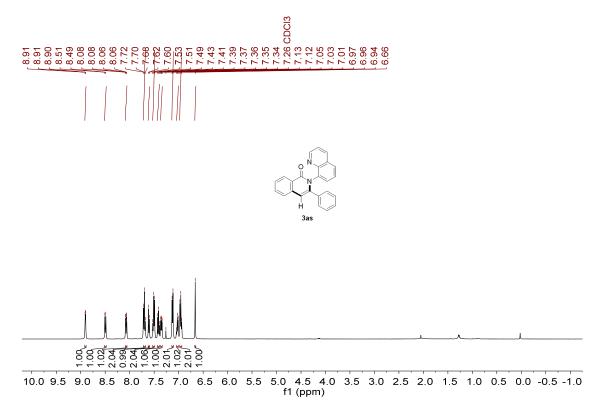
The <sup>1</sup>H NMR spectrum of **3ar** (400 MHz,  $CDCl_3$ ).



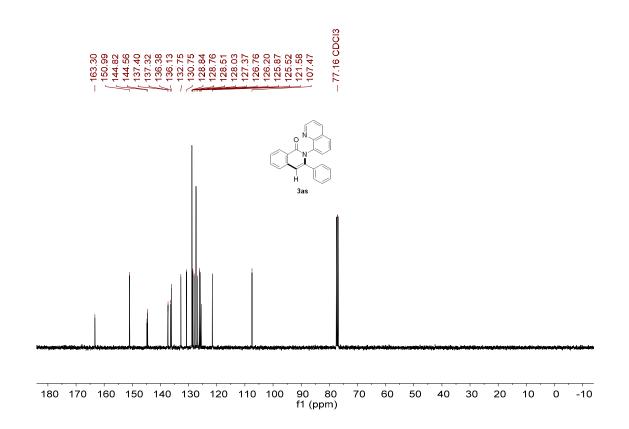
The <sup>13</sup>C NMR spectrum of **3ar** (101 MHz, CDCl<sub>3</sub>).



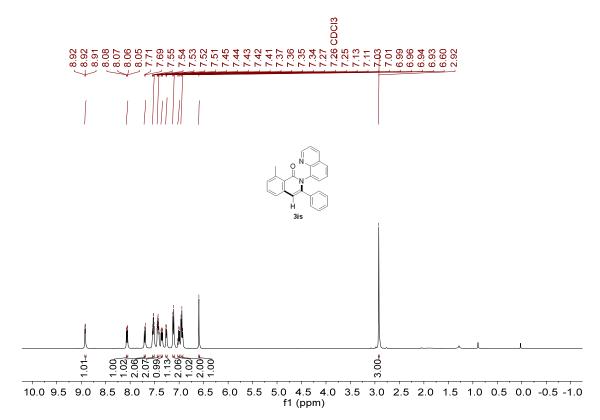
The <sup>1</sup>H NMR spectrum of **3as** (400 MHz, CDCl<sub>3</sub>).



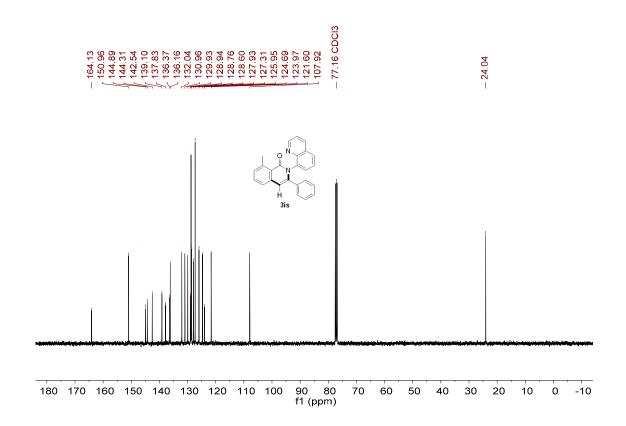
The <sup>13</sup>C NMR spectrum of **3as** (101 MHz, CDCl<sub>3</sub>).



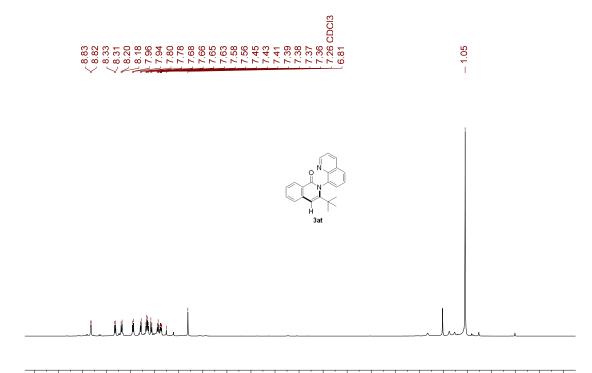
The <sup>1</sup>H NMR spectrum of **3is** (400 MHz, CDCl<sub>3</sub>).



The <sup>13</sup>C NMR spectrum of **3is** (101 MHz, CDCl<sub>3</sub>).

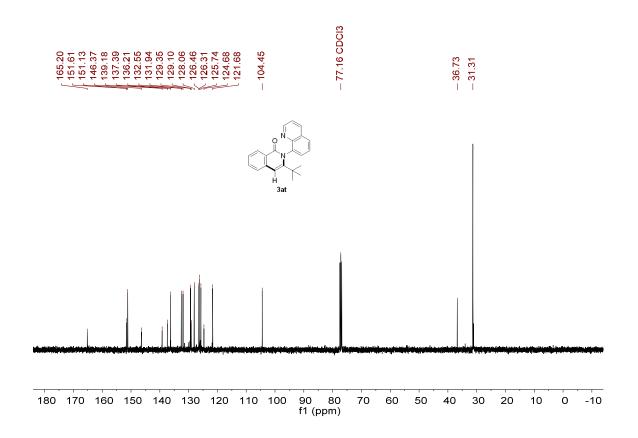


The <sup>1</sup>H NMR spectrum of **3at** (400 MHz, CDCl<sub>3</sub>).

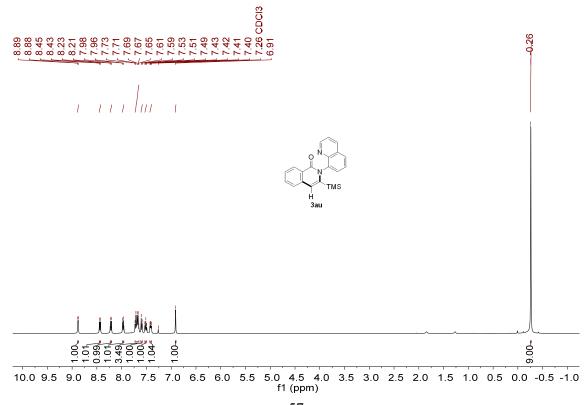


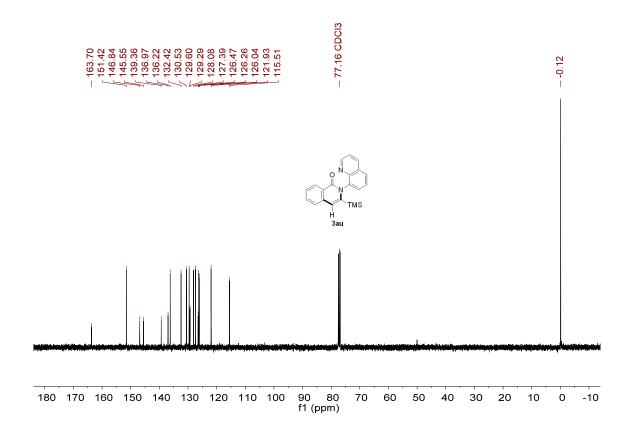
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 f1 (ppm)

The <sup>13</sup>C NMR spectrum of **3at** (101 MHz, CDCl<sub>3</sub>).

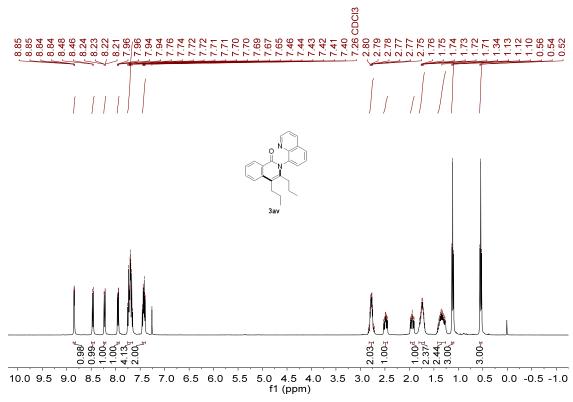


The <sup>1</sup>H NMR spectrum of **3au** (400 MHz, CDCl<sub>3</sub>).

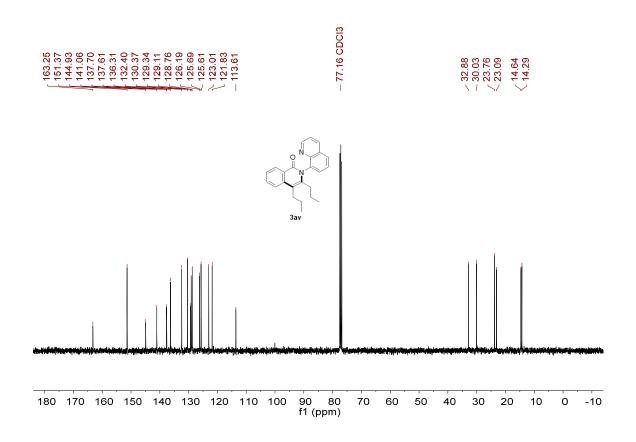




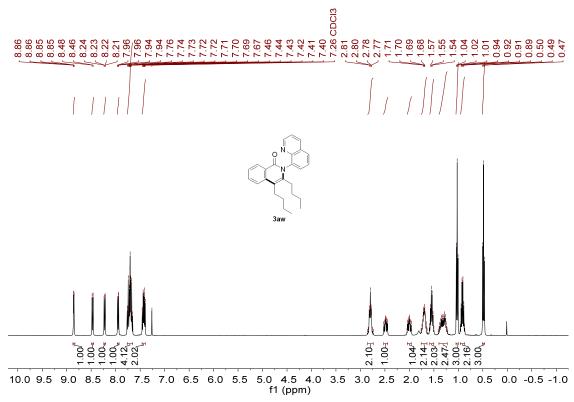
The <sup>1</sup>H NMR spectrum of **3av** (400 MHz, CDCl<sub>3</sub>).



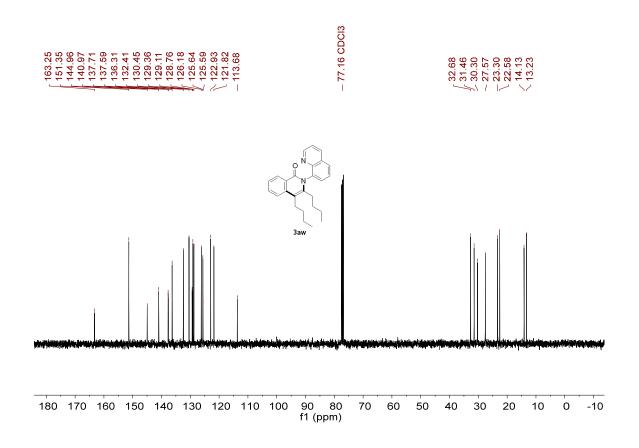
The <sup>13</sup>C NMR spectrum of **3av** (101 MHz, CDCl<sub>3</sub>).



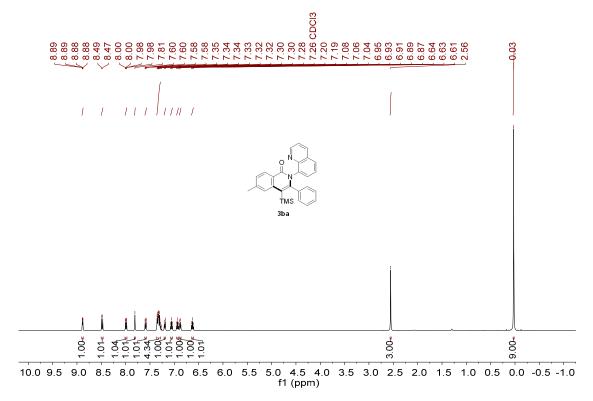
The <sup>1</sup>H NMR spectrum of **3aw** (400 MHz, CDCl<sub>3</sub>).

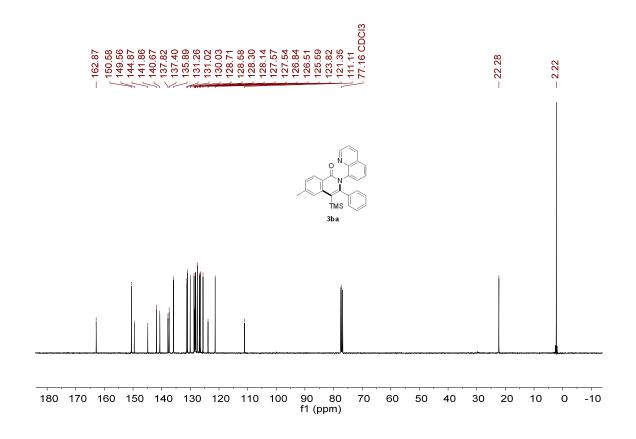


The <sup>13</sup>C NMR spectrum of **3aw** (101 MHz, CDCl<sub>3</sub>).

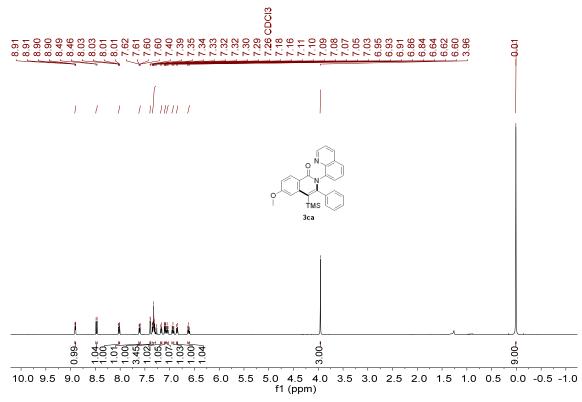


The <sup>1</sup>H NMR spectrum of **3ba** (400 MHz, CDCl<sub>3</sub>).

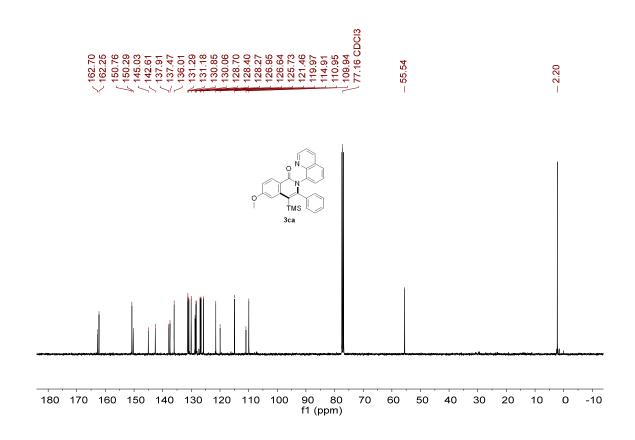




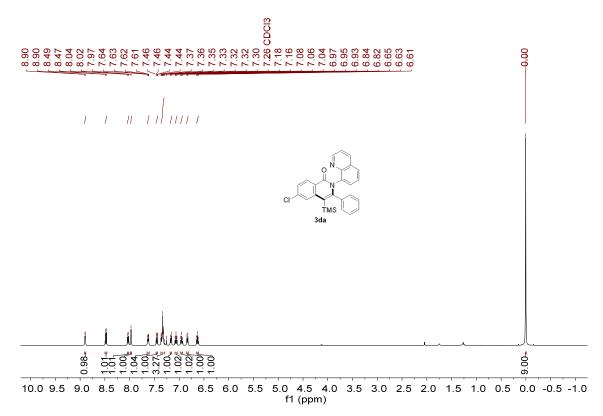
The <sup>1</sup>H NMR spectrum of **3ca** (400 MHz, CDCl<sub>3</sub>).



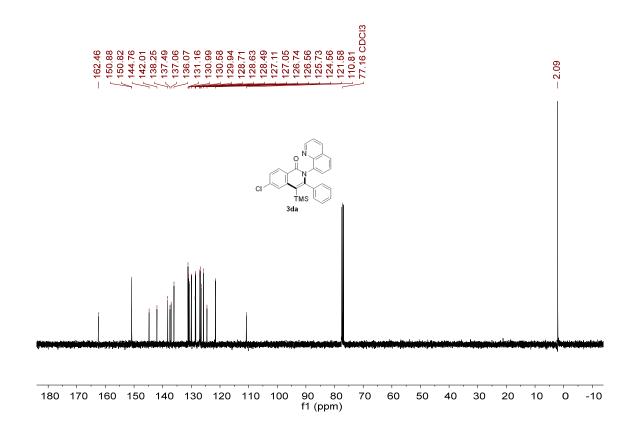
The <sup>13</sup>C NMR spectrum of **3ca** (101 MHz, CDCl<sub>3</sub>).



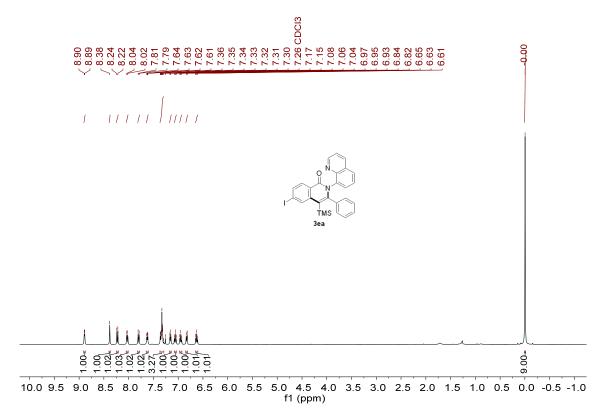
The <sup>1</sup>H NMR spectrum of **3da** (400 MHz, CDCl<sub>3</sub>).



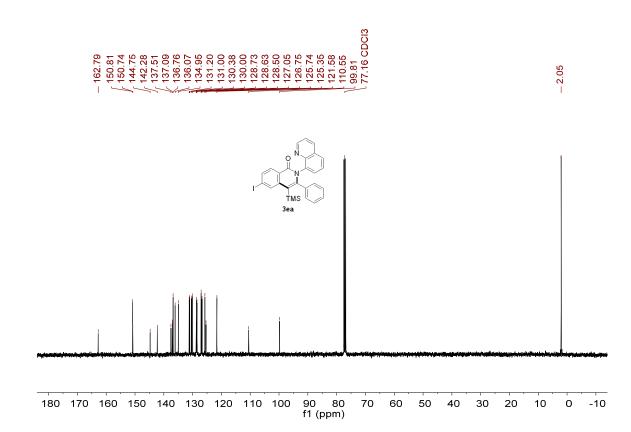
The <sup>13</sup>C NMR spectrum of **3da** (101 MHz, CDCl<sub>3</sub>).



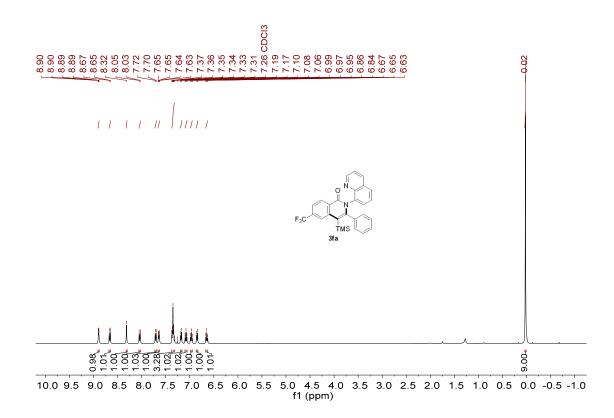
The <sup>1</sup>H NMR spectrum of **3ea** (400 MHz, CDCl<sub>3</sub>).



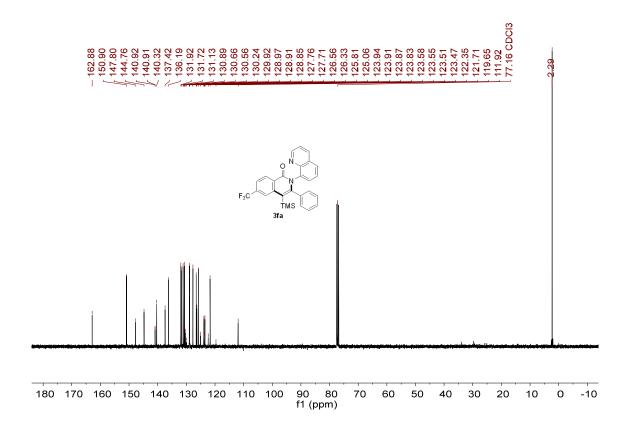
The <sup>13</sup>C NMR spectrum of **3ea** (101 MHz, CDCl<sub>3</sub>).



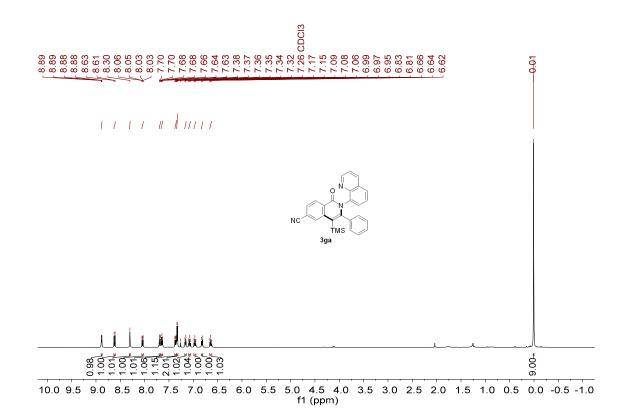
The <sup>1</sup>H NMR spectrum of **3fa** (400 MHz, CDCl<sub>3</sub>).



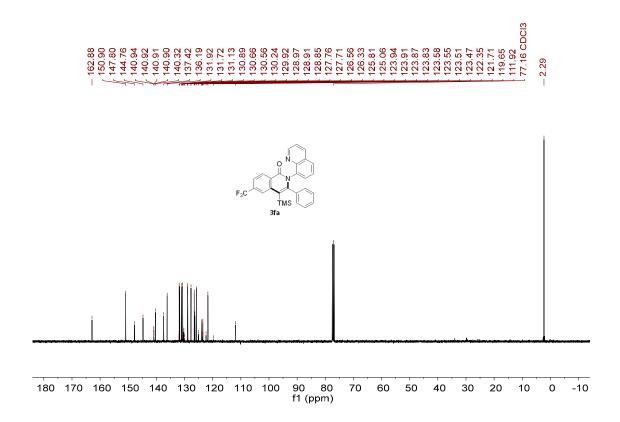
The <sup>13</sup>C NMR spectrum of **3fa** (101 MHz, CDCl<sub>3</sub>).



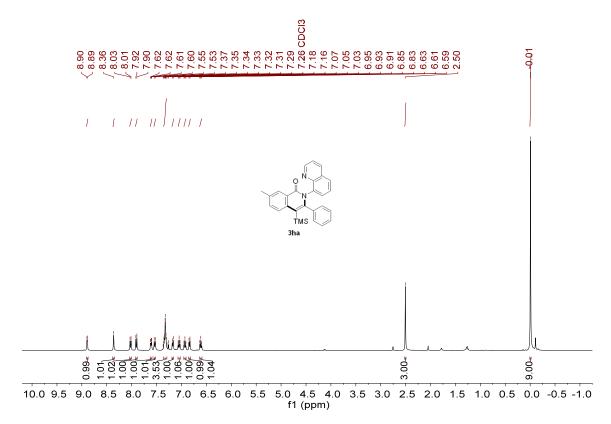
The <sup>1</sup>H NMR spectrum of **3ga** (400 MHz, CDCl<sub>3</sub>).



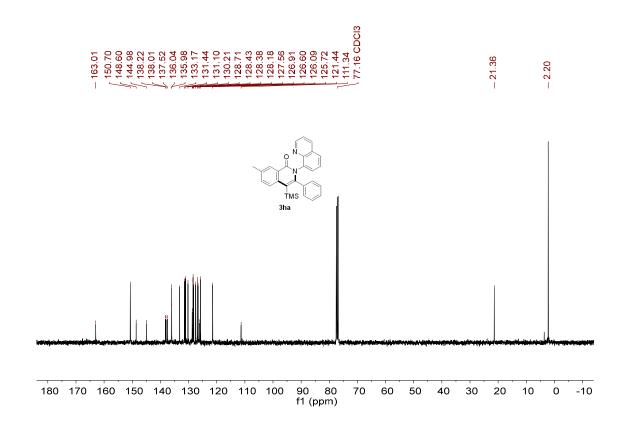
The <sup>13</sup>C NMR spectrum of **3ga** (101 MHz, CDCl<sub>3</sub>).



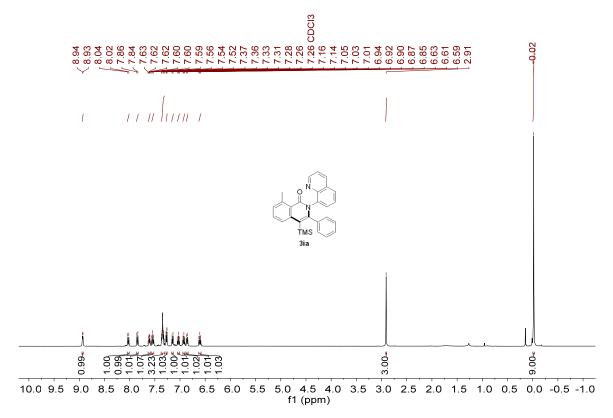
The <sup>1</sup>H NMR spectrum of **3ha** (400 MHz, CDCl<sub>3</sub>).



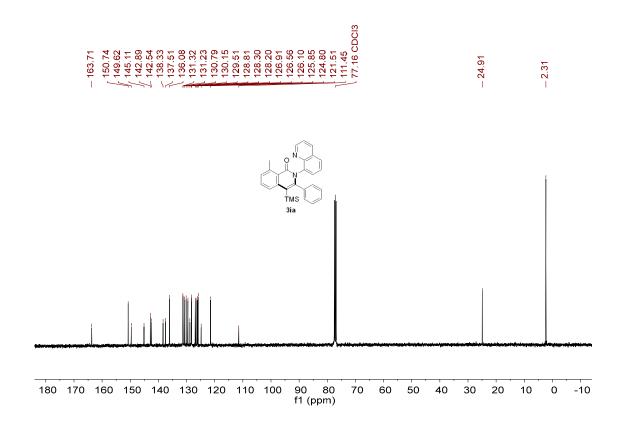
The <sup>13</sup>C NMR spectrum of **3ha** (101 MHz, CDCl<sub>3</sub>).



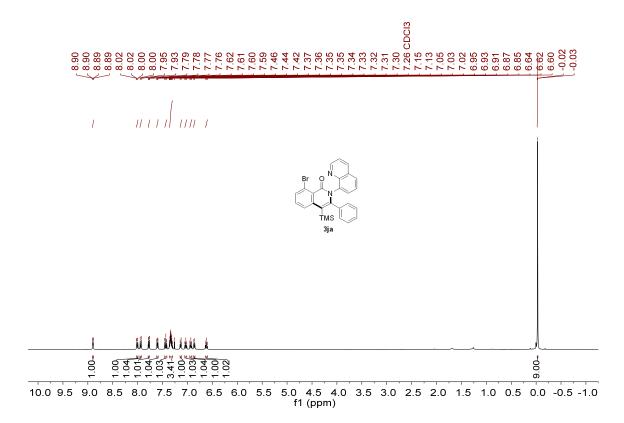
The  $^1\text{H}$  NMR spectrum of **3ia** (400 MHz, CDCl<sub>3</sub>).



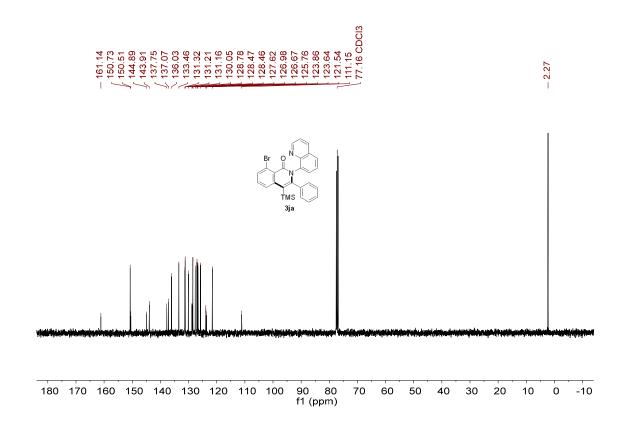
The <sup>13</sup>C NMR spectrum of **3ia** (101 MHz, CDCl<sub>3</sub>).



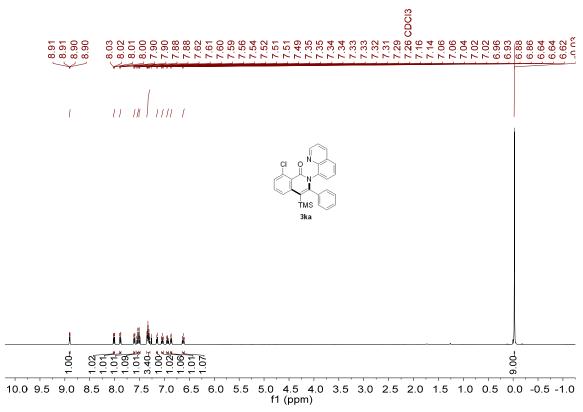
The <sup>1</sup>H NMR spectrum of **3ja** (400 MHz,  $CDCI_3$ ).



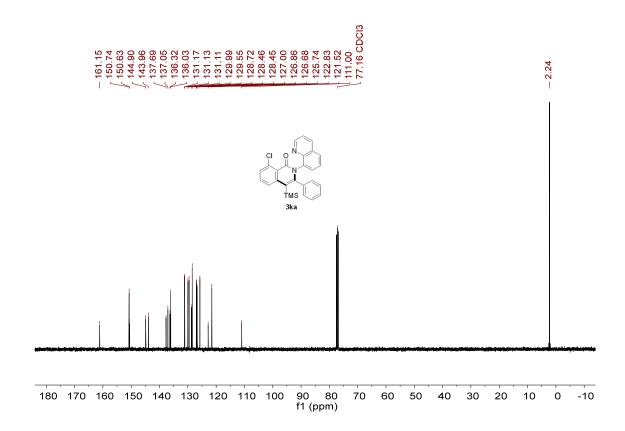
The <sup>13</sup>C NMR spectrum of **3ja** (101 MHz, CDCl<sub>3</sub>).



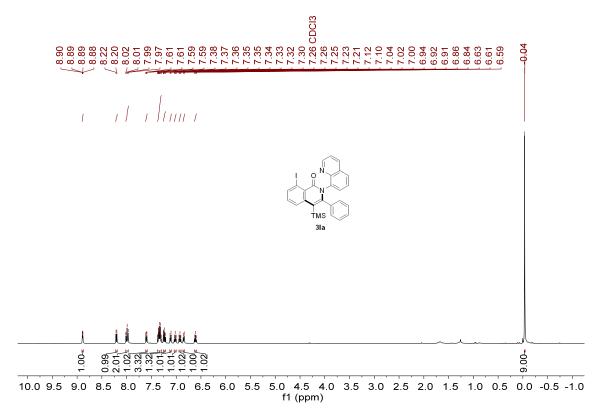
The <sup>1</sup>H NMR spectrum of **3ka** (400 MHz, CDCl<sub>3</sub>).



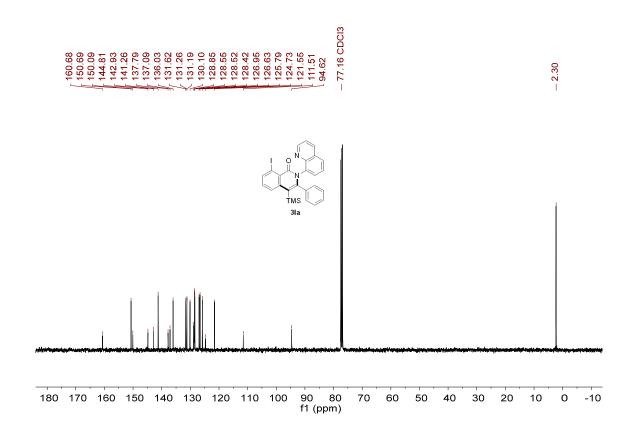
The <sup>13</sup>C NMR spectrum of **3ka** (101 MHz, CDCl<sub>3</sub>).



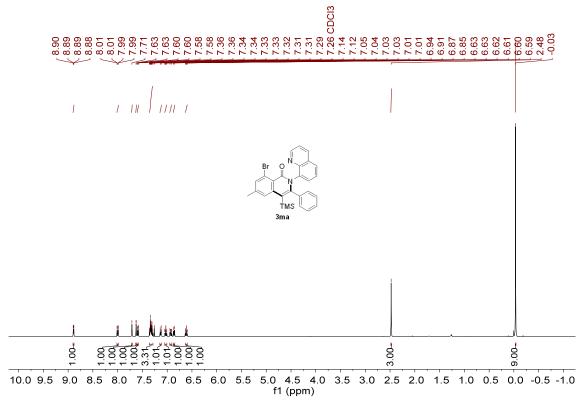
The <sup>1</sup>H NMR spectrum of **3la** (400 MHz, CDCl<sub>3</sub>).



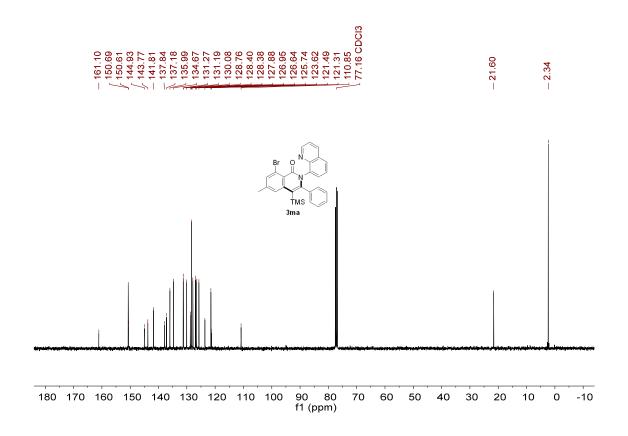
The <sup>13</sup>C NMR spectrum of **3la** (101 MHz, CDCl<sub>3</sub>).



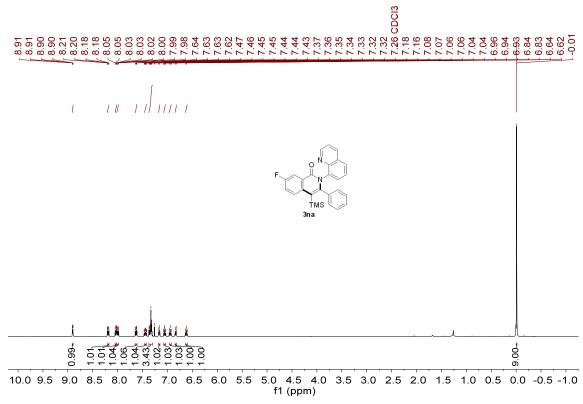
The <sup>1</sup>H NMR spectrum of **3ma** (400 MHz, CDCl<sub>3</sub>).

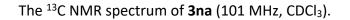


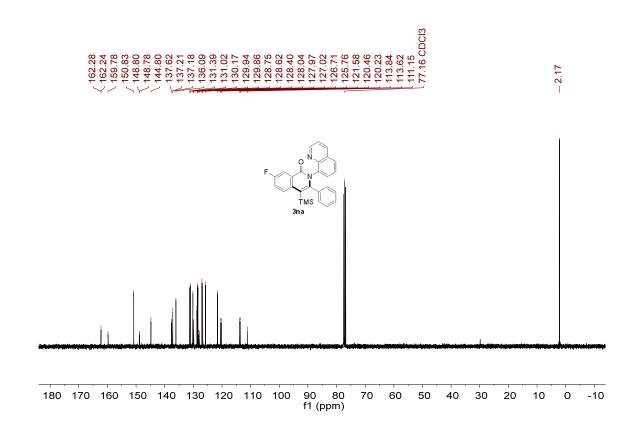
The  $^{\rm 13}C$  NMR spectrum of 3ma (101 MHz, CDCl\_3).



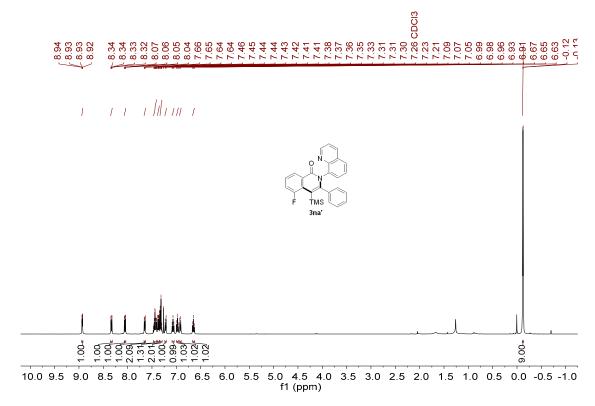
The <sup>1</sup>H NMR spectrum of **3na** (400 MHz, CDCl<sub>3</sub>).



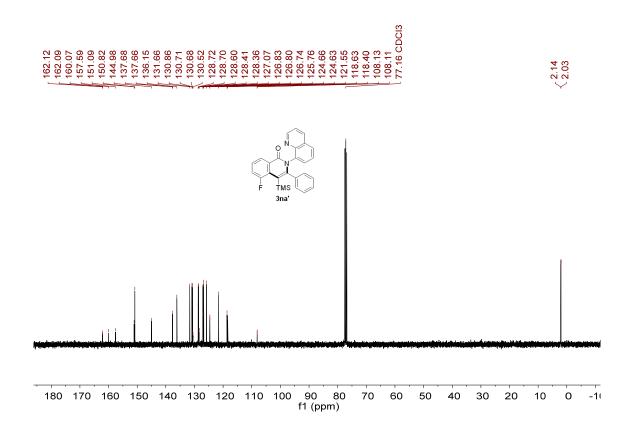




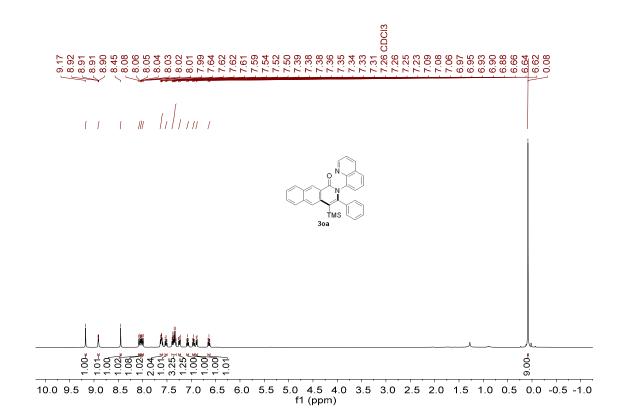
The <sup>1</sup>H NMR spectrum of **3na'** (400 MHz, CDCl<sub>3</sub>).



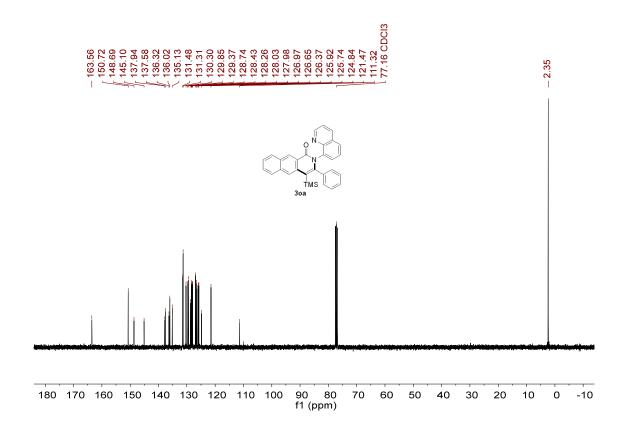
The <sup>13</sup>C NMR spectrum of **3na'** (101 MHz, CDCl<sub>3</sub>).



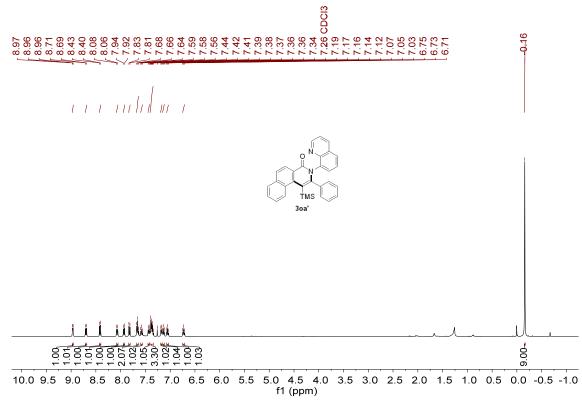
The <sup>1</sup>H NMR spectrum of **3oa** (400 MHz, CDCl<sub>3</sub>).



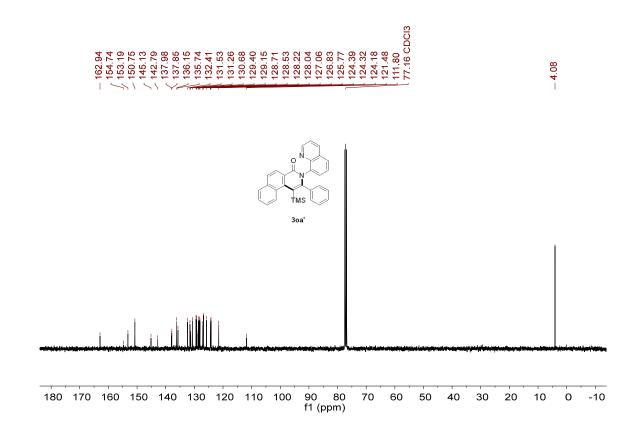
The <sup>13</sup>C NMR spectrum of **3oa** (101 MHz, CDCl<sub>3</sub>).



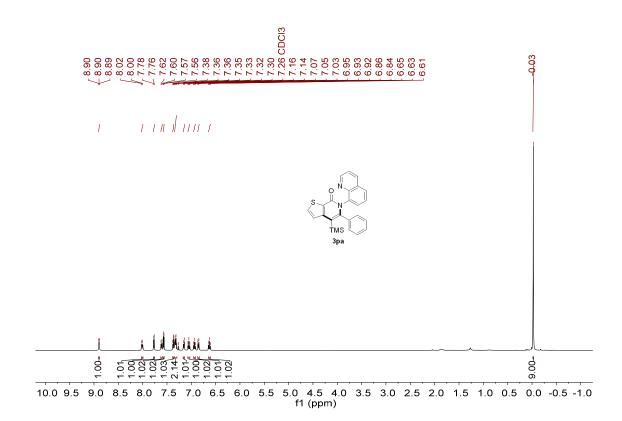
The <sup>1</sup>H NMR spectrum of **3oa'** (400 MHz, CDCl<sub>3</sub>).

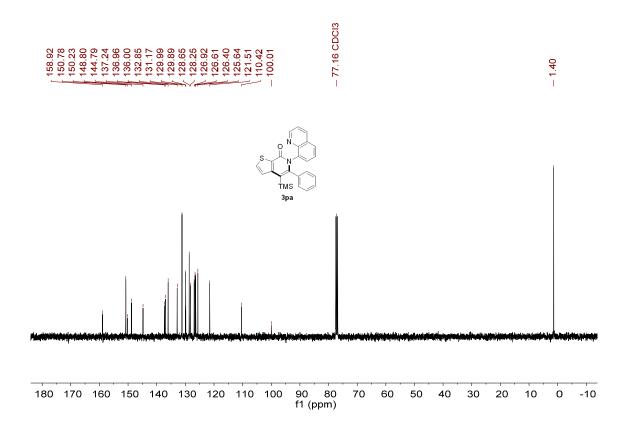


The <sup>13</sup>C NMR spectrum of **30a'** (101 MHz, CDCl<sub>3</sub>).



The <sup>1</sup>H NMR spectrum of **3pa** (400 MHz, CDCl<sub>3</sub>).





## **XIV. References**

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