Supporting Information

Rhodium-catalyzed C-H activation/annulation of amidines with 4-diazoisochroman-3-imines toward isochromeno[3,4-*c*]isoquinolines

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1. General considerations:

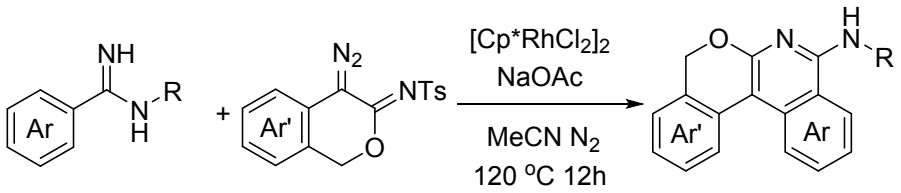
Unless otherwise noted, all the reactions were carried out under nitrogen atmosphere using standard Schlenk technique，and all chemicals were purchased from commercial suppliers and used without further purification. The ^{1}H NMR spectra were recorded on a 300 MHz or 400 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 75 MHz or 100 MHz. NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.26 ppm) as the internal standard. The coupling constants J are given in Hz. High-resolution mass spectra (HRMS) were obtained using an agilent 6230 TOF focus spectrometer (ESI). Absorption data were recorded on a SHIMADZU UV-3600 spectrophotometer. Fluorescence data were recorded on a PerkinElmer LS45 fluorescence spectrometer. Column chromatography was performed using EM Silica gel 60 (300-400 mesh), and the eluent was a mixture of petroleum ether (PE) and ethyl acetate (EA).

All compounds of **3** were unknown (based on SciFinder and Reaxys databases).

The substrates **1**[1]and **2**[2] were prepared according to the published procedures.

2. Synthetic Procedure

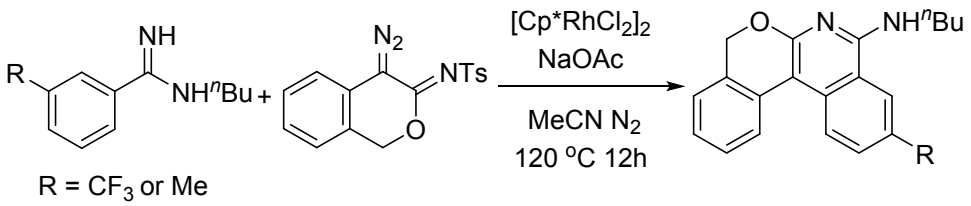
2.1 Synthetic Procedure for Compound 3



1 **2** **3**

To an oven-dried Schlenk tube equipped with a magnetic stirring bar was added sequentially **1** (0.2 mmol), **2** (0.24 mmol), $[Cp^*RhCl_2]_2$ (5 mol %, 0.01 mmol), and NaOAc (0.4 mmol). After vacuuming and backfilling with N_2 three times, MeCN (3 mL) was injected by syringe. The reaction mixture was stirred at 120 °C (oil bath) for 12 h. After cooling to room temperature, the resultant mixture was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether /ethyl acetate = 15:1 to 10:1, v/v) to give pure product.

2.2 Procedure for the Preparation of Crude Mixture of Compounds 3ka and 3la

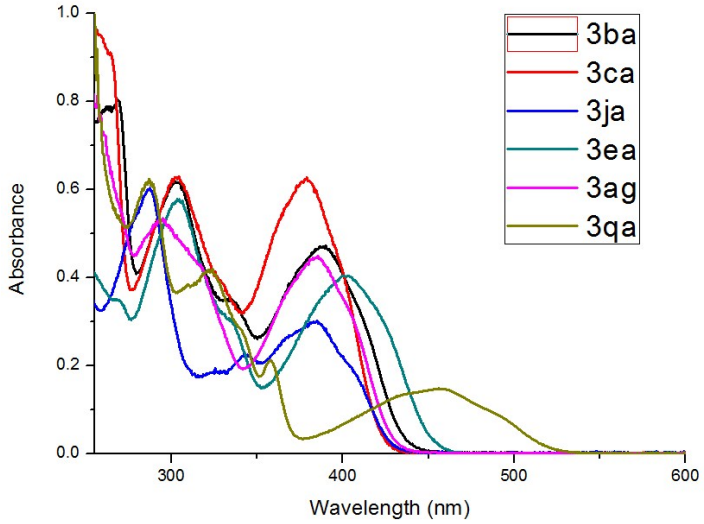


1k or **1l** **2a** **3ak** or **3al**

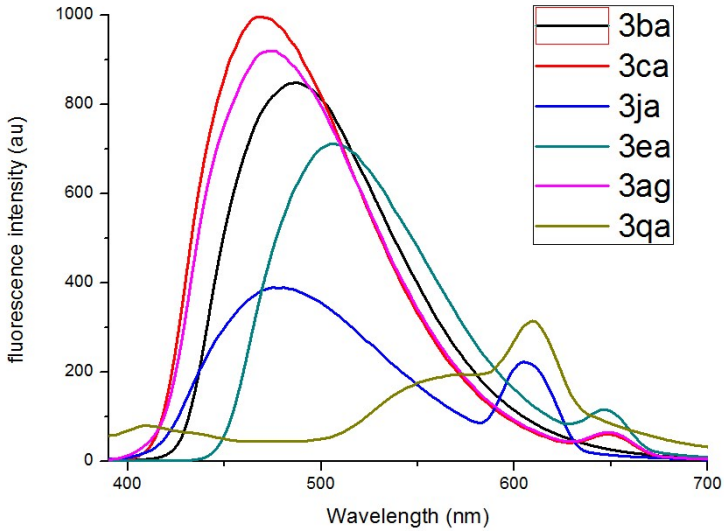
To an oven-dried Schlenk tube equipped with a magnetic stirring bar was added sequentially **1k** (or **1l**) (0.2 mmol), **2a** (0.24 mmol), $[Cp^*RhCl_2]_2$ (5 mol %, 0.01 mmol), and NaOAc (0.4 mmol). After vacuuming and backfilling with N_2 three times, MeCN (3 mL) was injected by syringe. The reaction mixture was stirred at 120 °C

(oil bath) for 12 h. After cooling to room temperature, the resultant mixture was filtered and concentrated under reduced pressure. The mixture was dissolved with 10 mL ethyl acetate and washed with 15 mL water and then 15 mL brine, and dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude product for **3ka** (or **3la**). The mixture of **3ka** and **3la** was tested (^{1}H NMR) without further purification.

3. UV-vis and Fluorescence Experimental Data



UV-vis spectra



Fluorescence spectra

Absorption and Emission Data[a,b]

Compounds	**3ba**	**3ca**	**3ja**	**3ea**	**3ag**	**3qa**
λ_{abs} (nm)	389	379	382	400	385	456
λ_{em} (nm)	487	468	475	506	476	573
Stokes shift (nm)	98	89	93	106	91	117

[a] In DCM (10-4 M). [b] * = blank signal for DCM

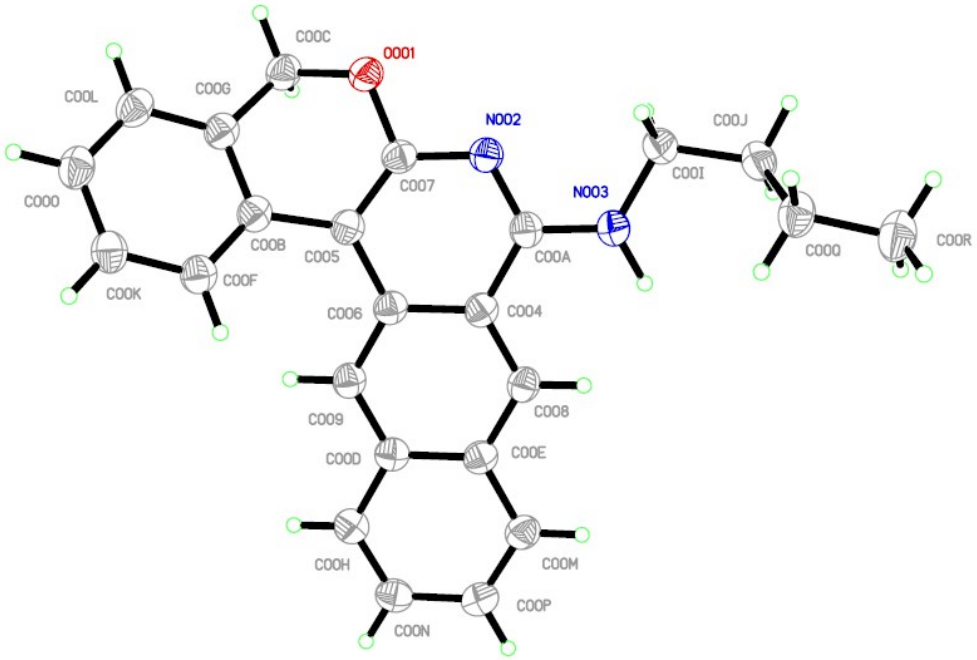
4. Single Crystal Datas for the 3qa

CCDC 1911441

Summary of Data CCDC 1911441

Formula: $C_{24}H_{22}N_2O_1$

Unit Cell Parameters: a 28.608(3) b 28.608(3) c 11.5472(12) R-3



Crystal structure of 3qa

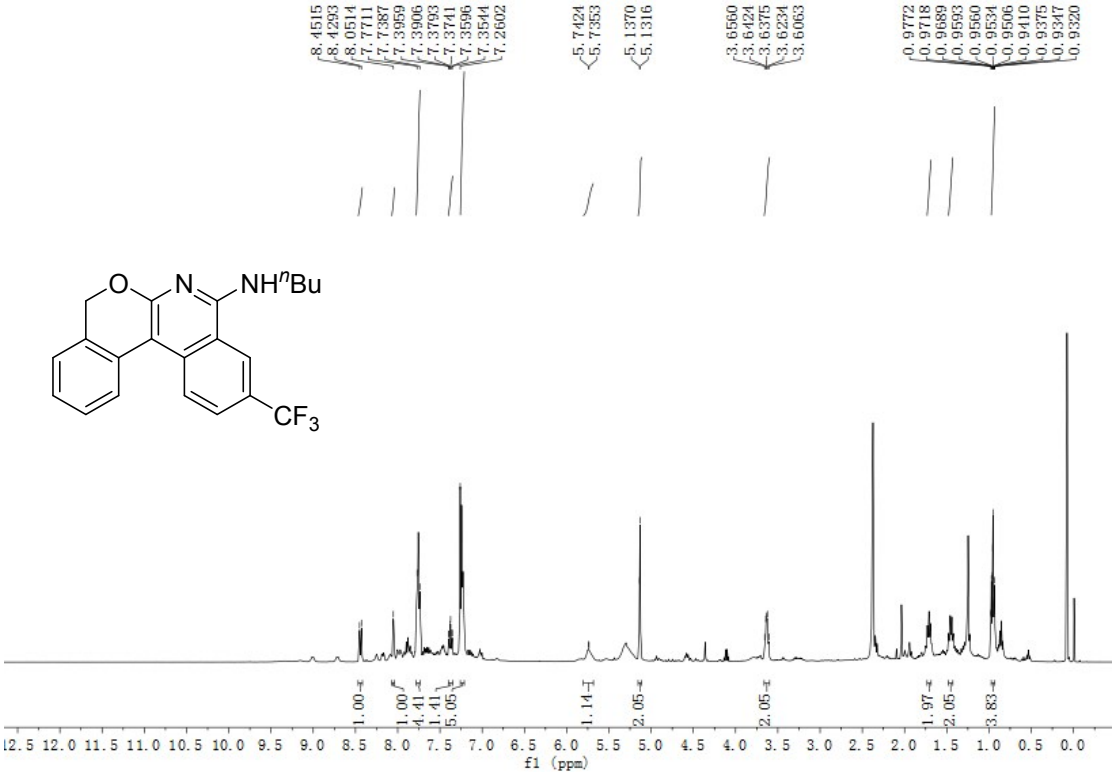
References:

(1) P. Debnath, M. Baeten, N. Lefèvre, S. Daele and B. Maes, *Adv. Synth. Catal*. 2015, **357**, 197.

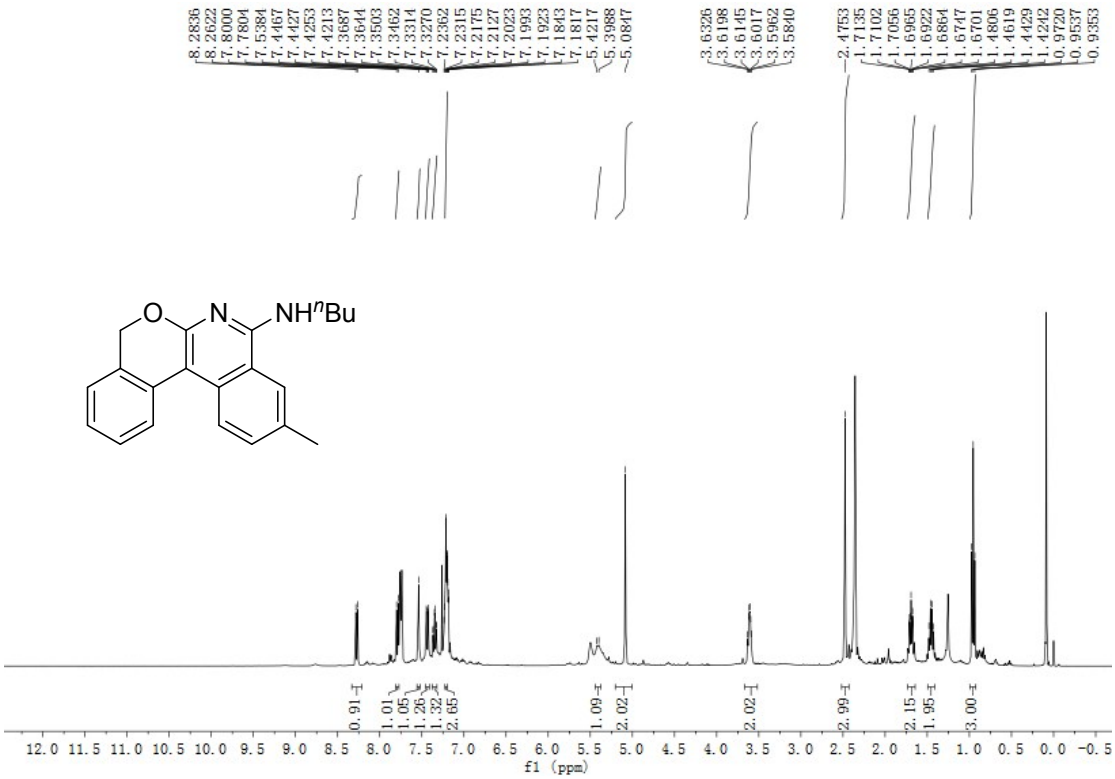
(2) A. Ren, P. Lv and Y. Wang, *Chem. Commun.* 2017, **53**, 3769.

5. Copies of the ^{1}H NMR, ^{13}C NMR Spectra

^{1}H NMR spectrum of the crude mixture of 3ka:



^{1}H NMR spectrum of the crude mixture of 3la:



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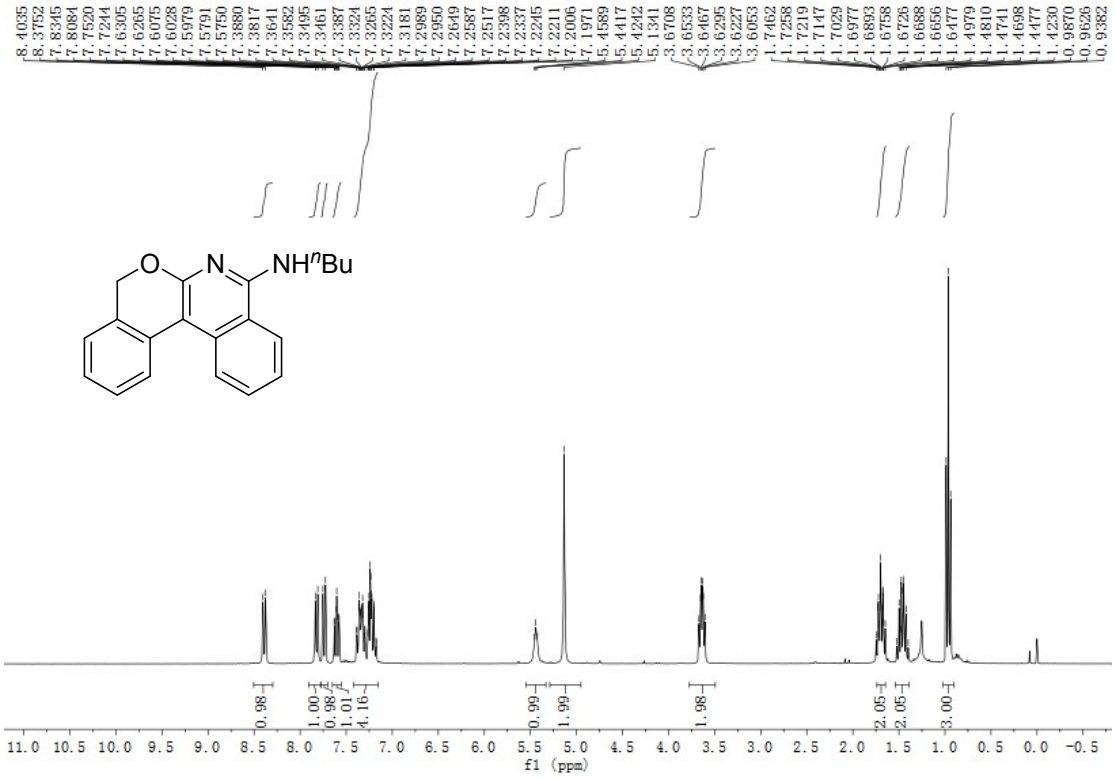
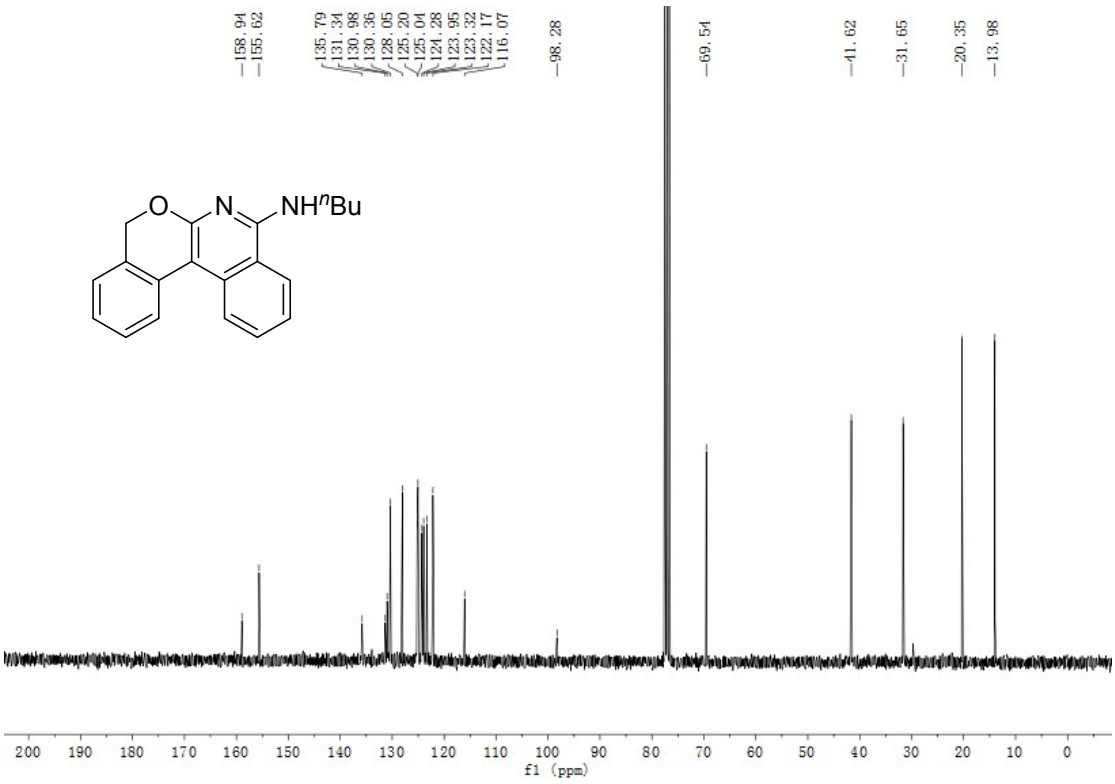
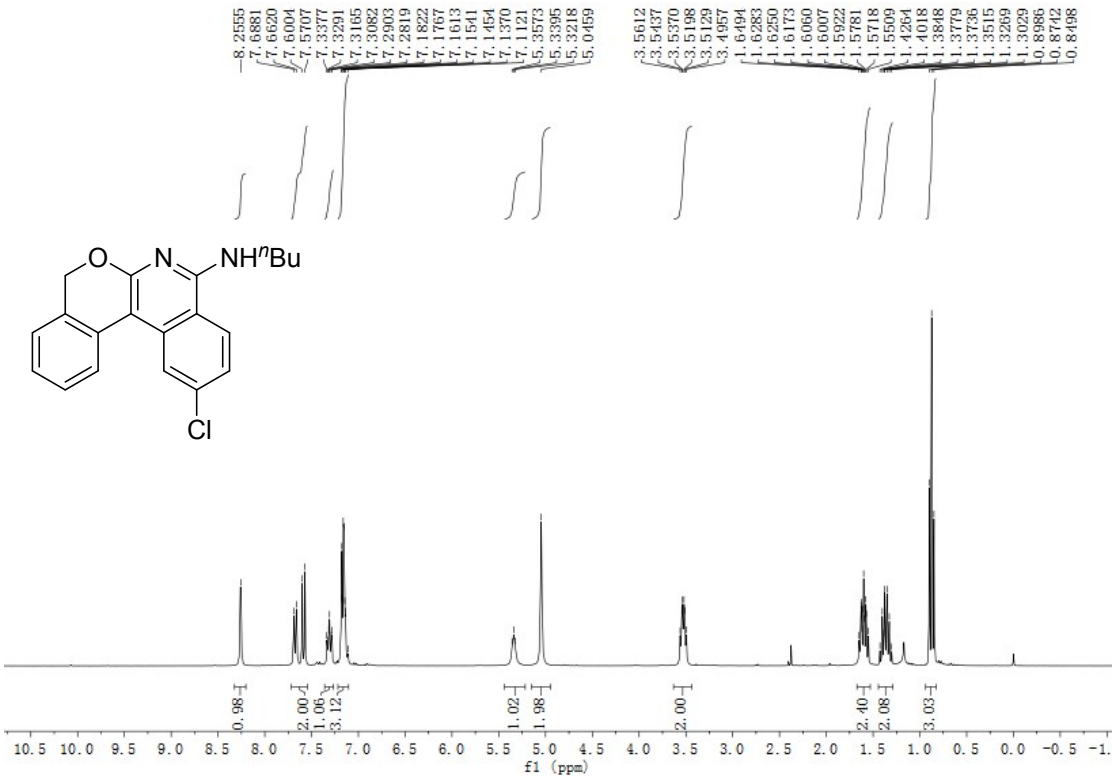
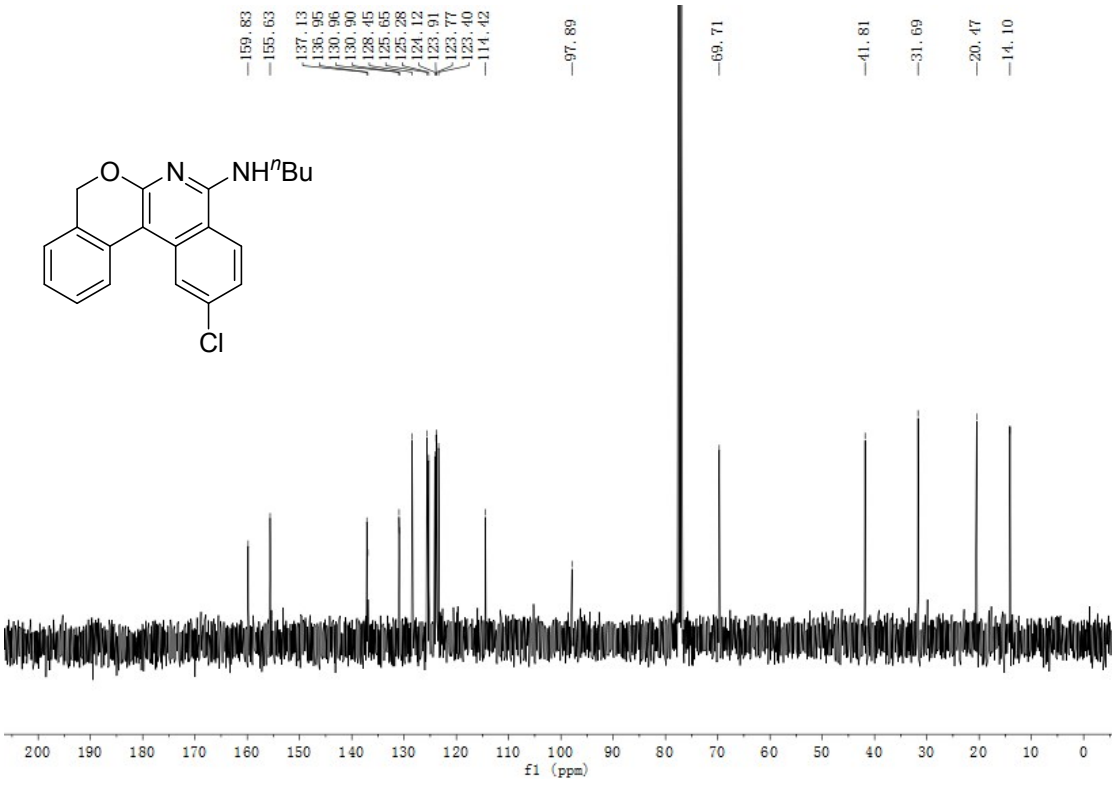




_N_-butyl-11-chloro-5_H_-isochromeno[3,4-_c_]isoquinolin-8-amine (3ba):





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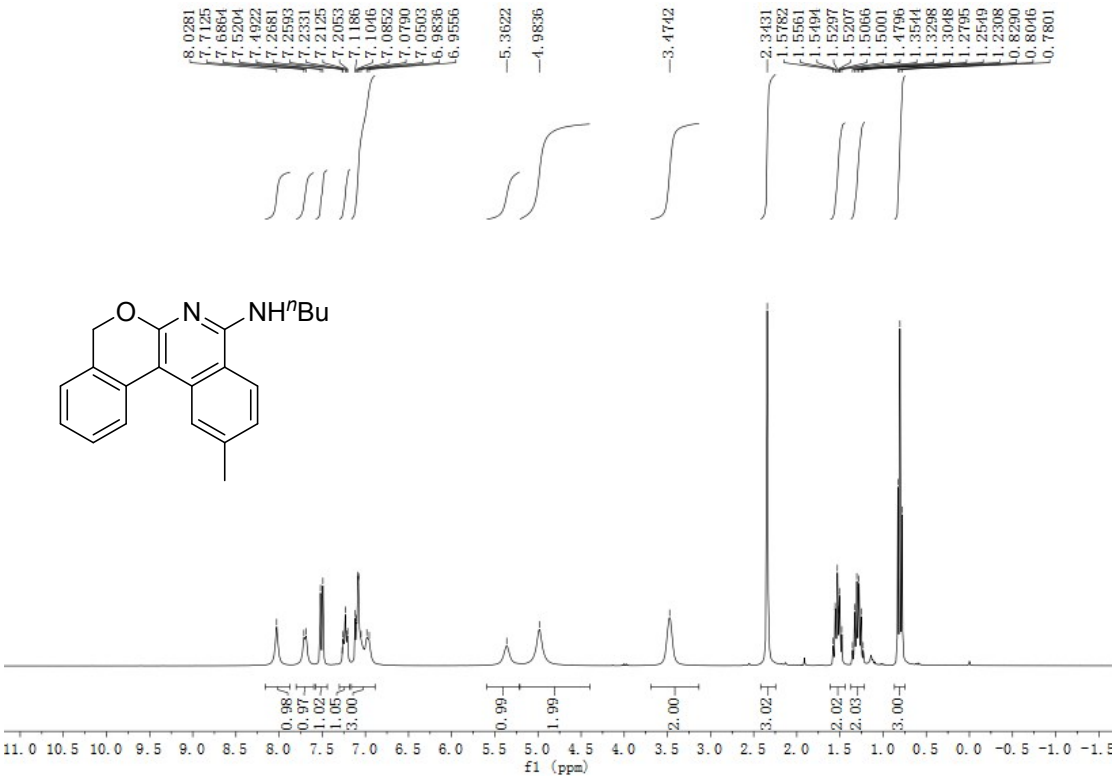
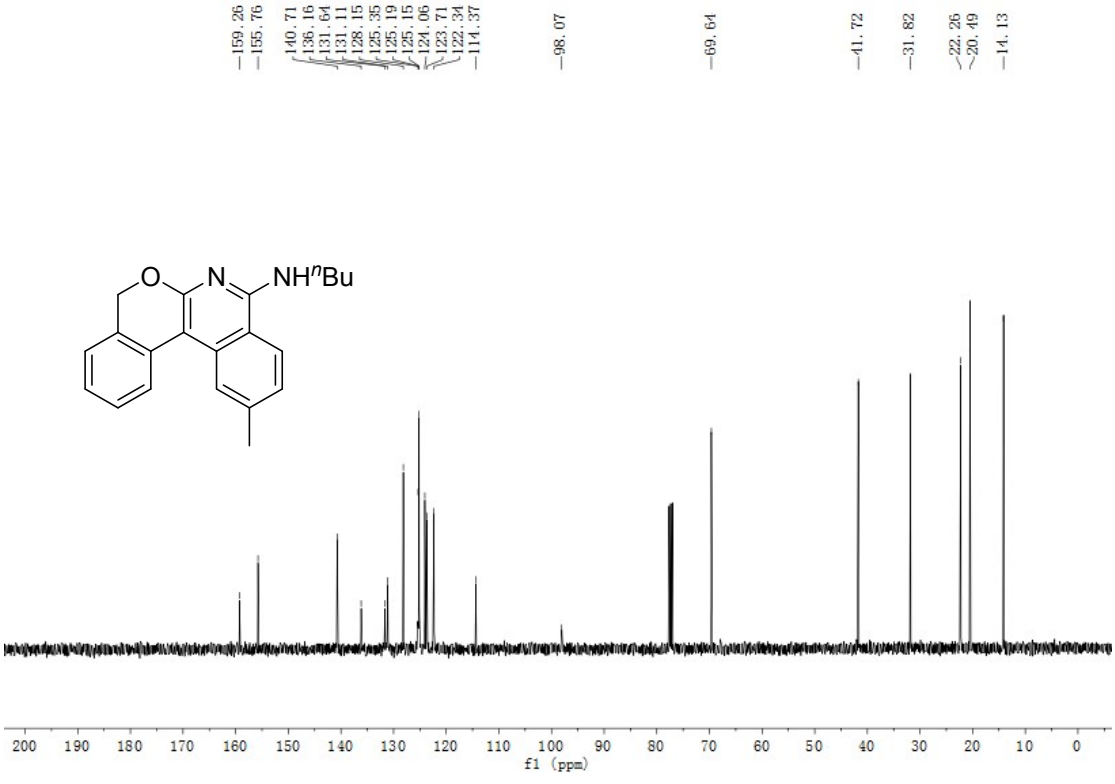
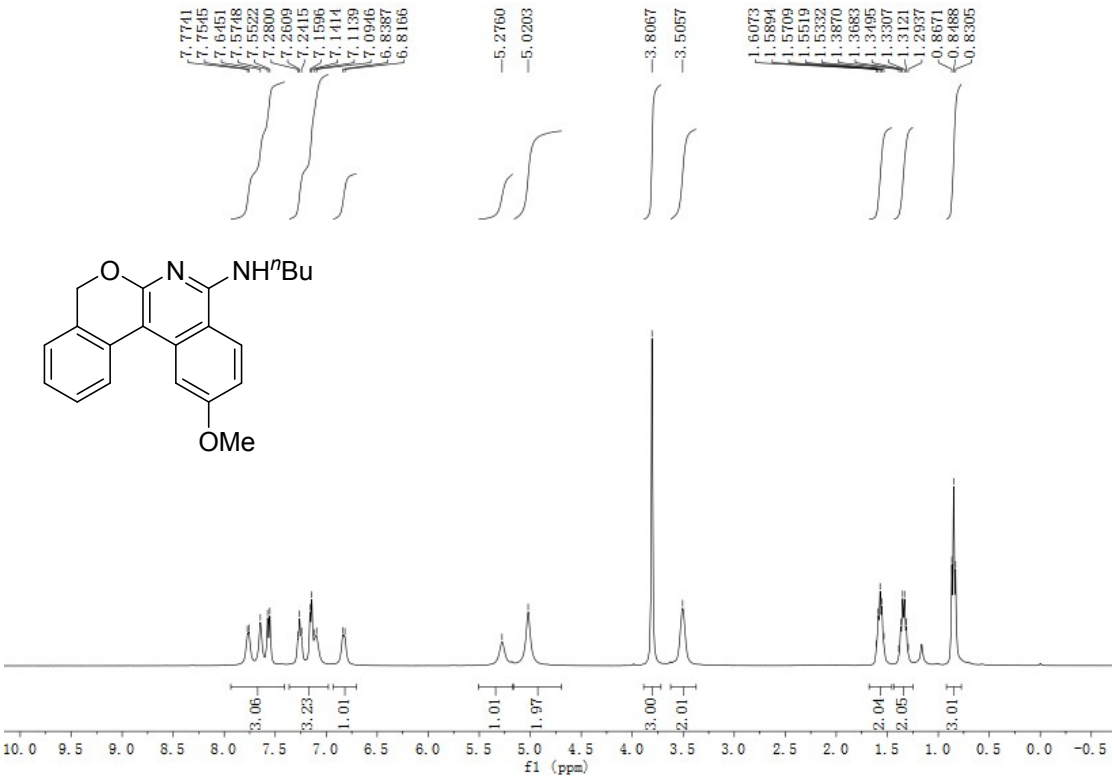
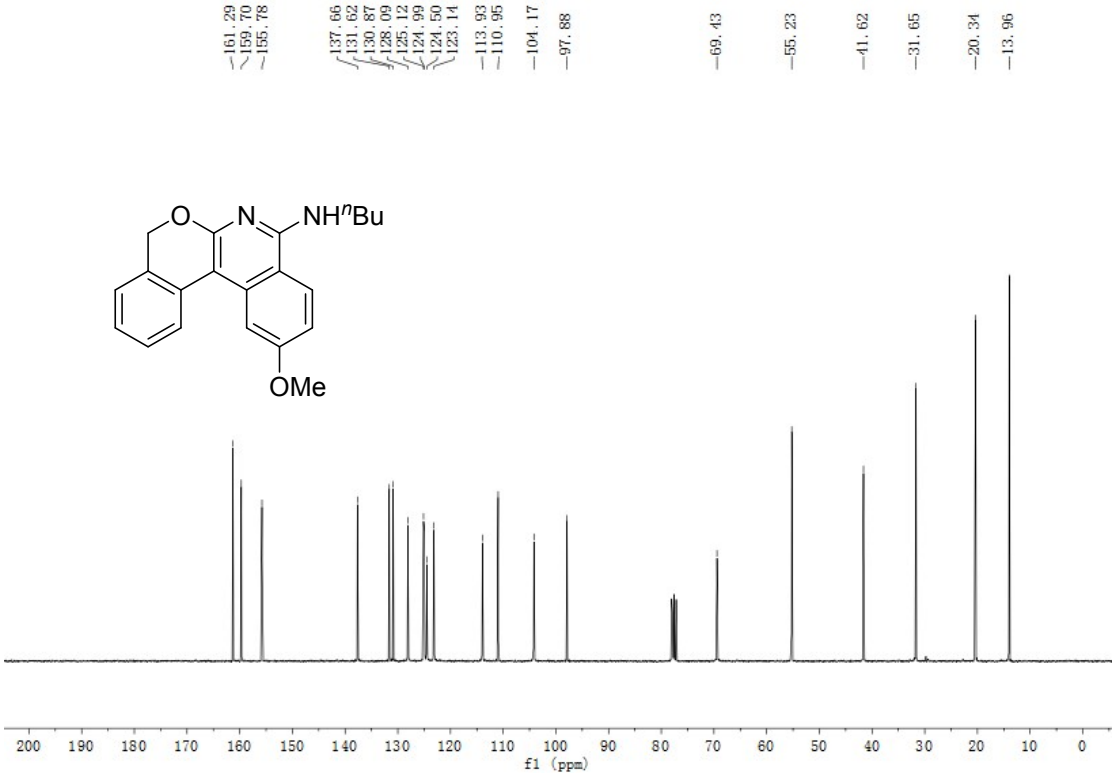




_N_-butyl-11-methoxy-5_H_-isochromeno[3,4-_c_]isoquinolin-8-amine (3da):





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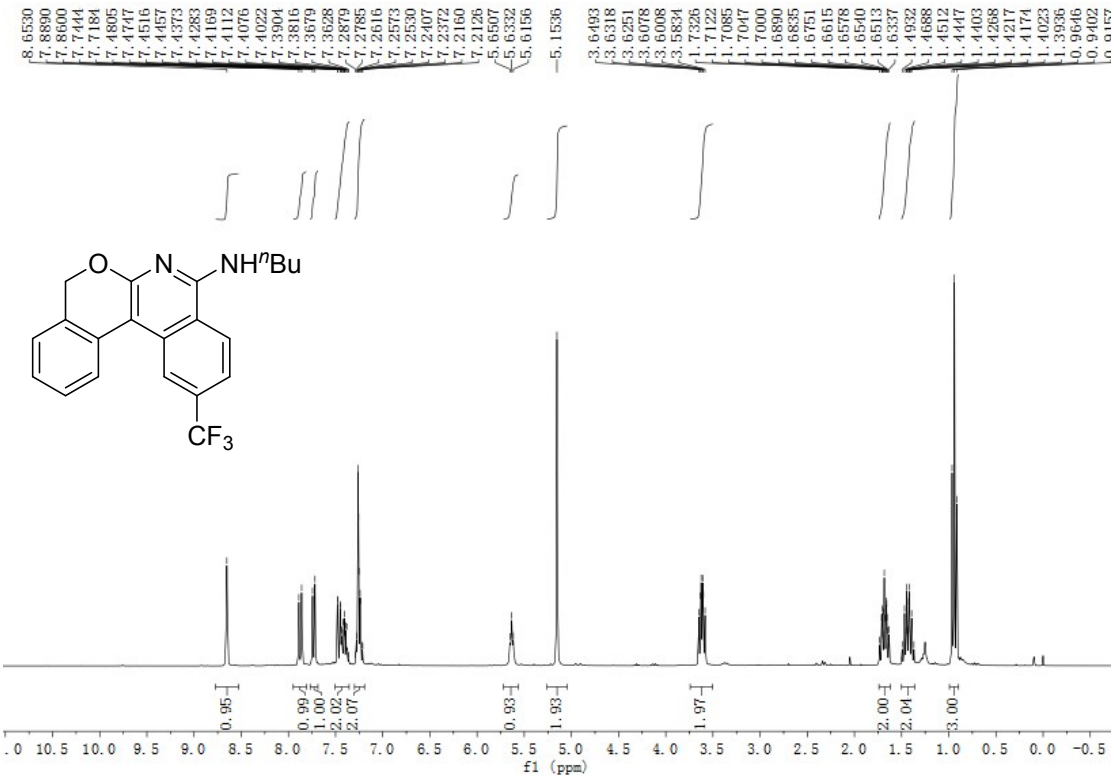

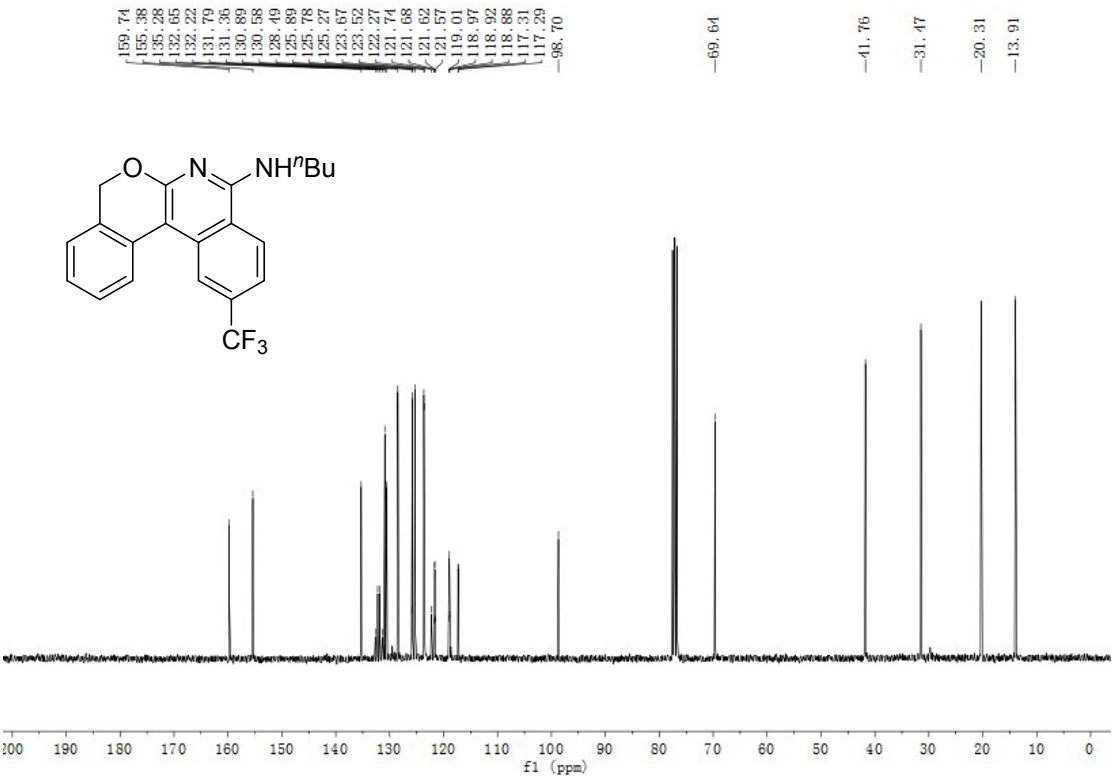

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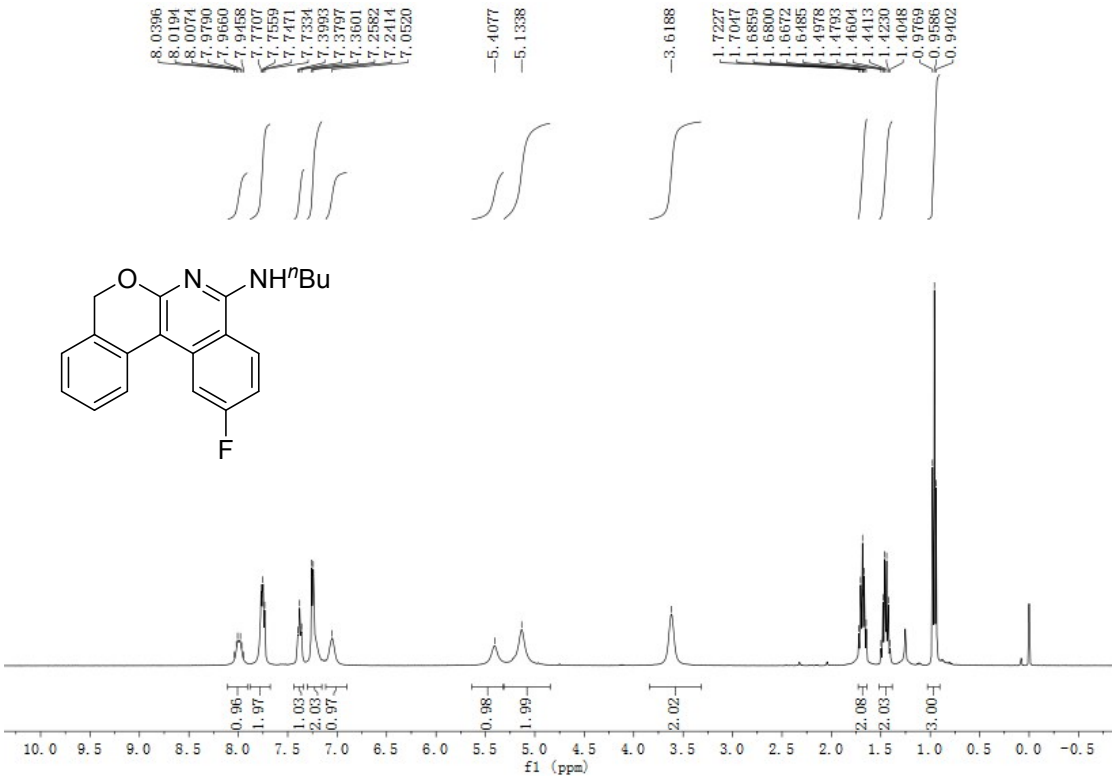
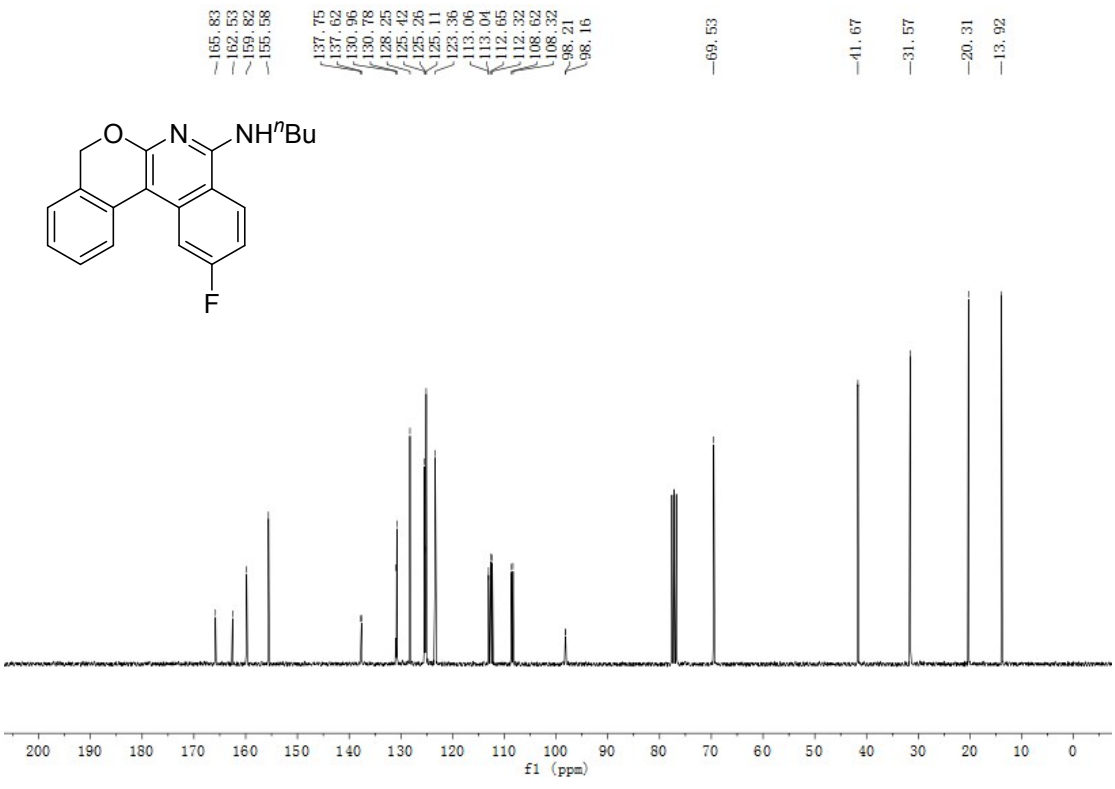
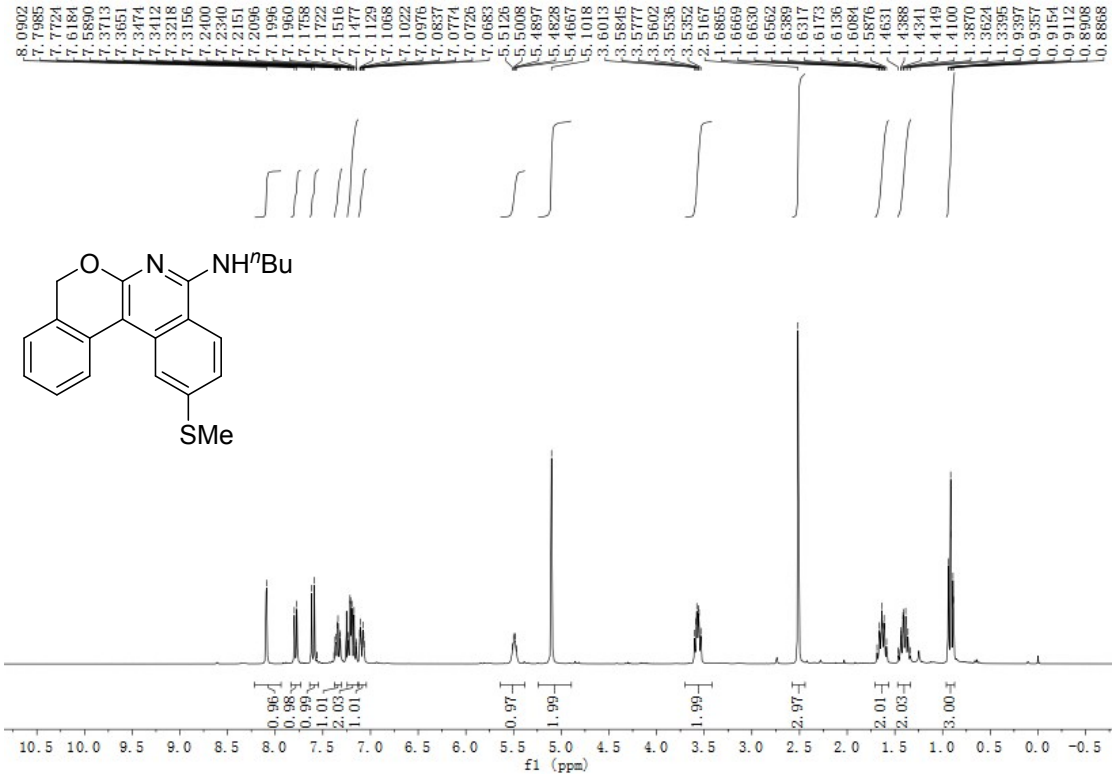
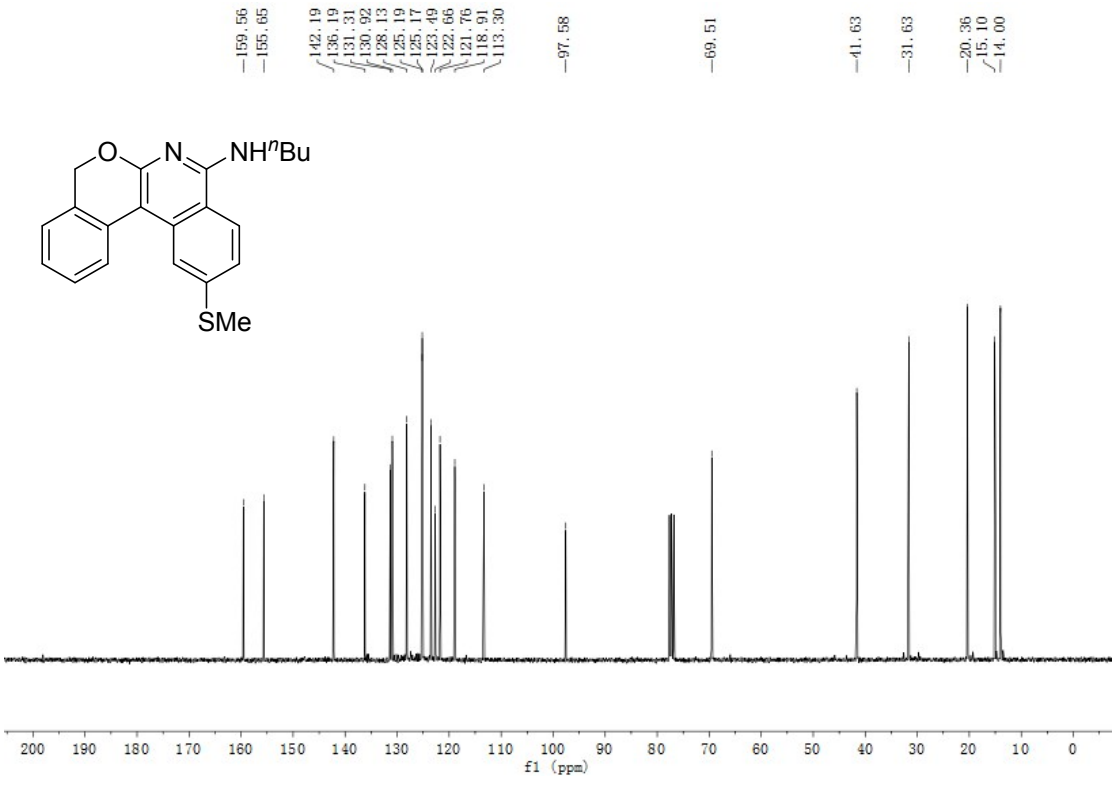


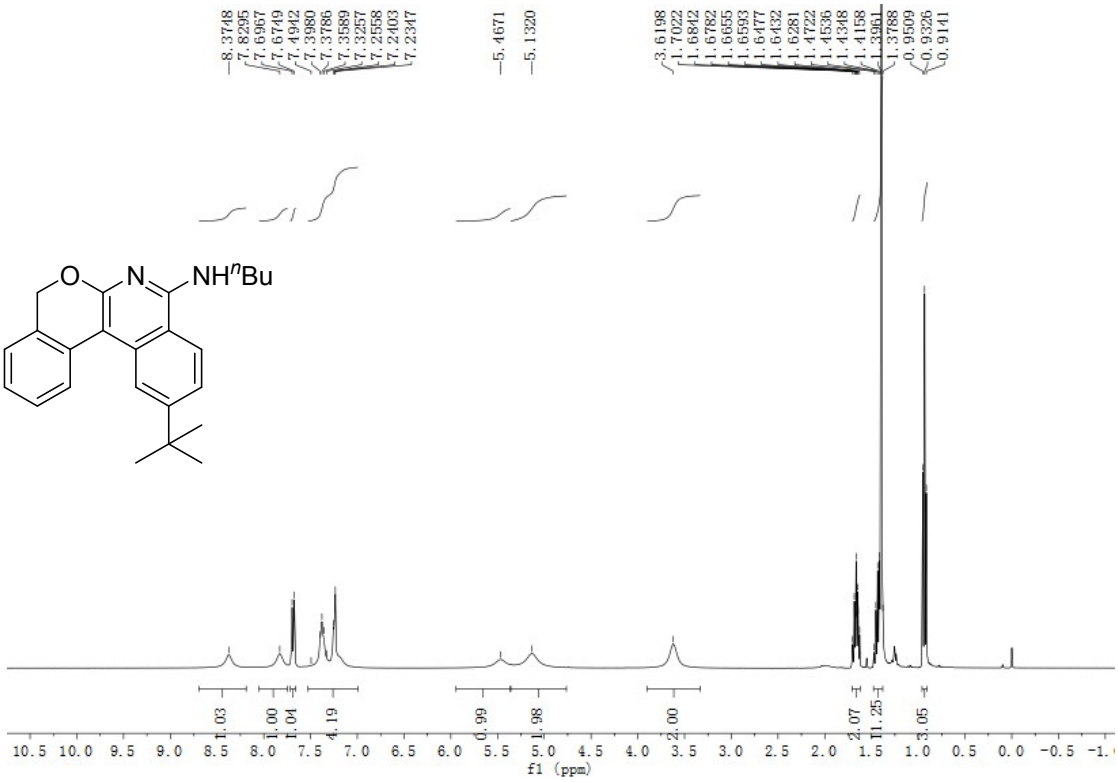


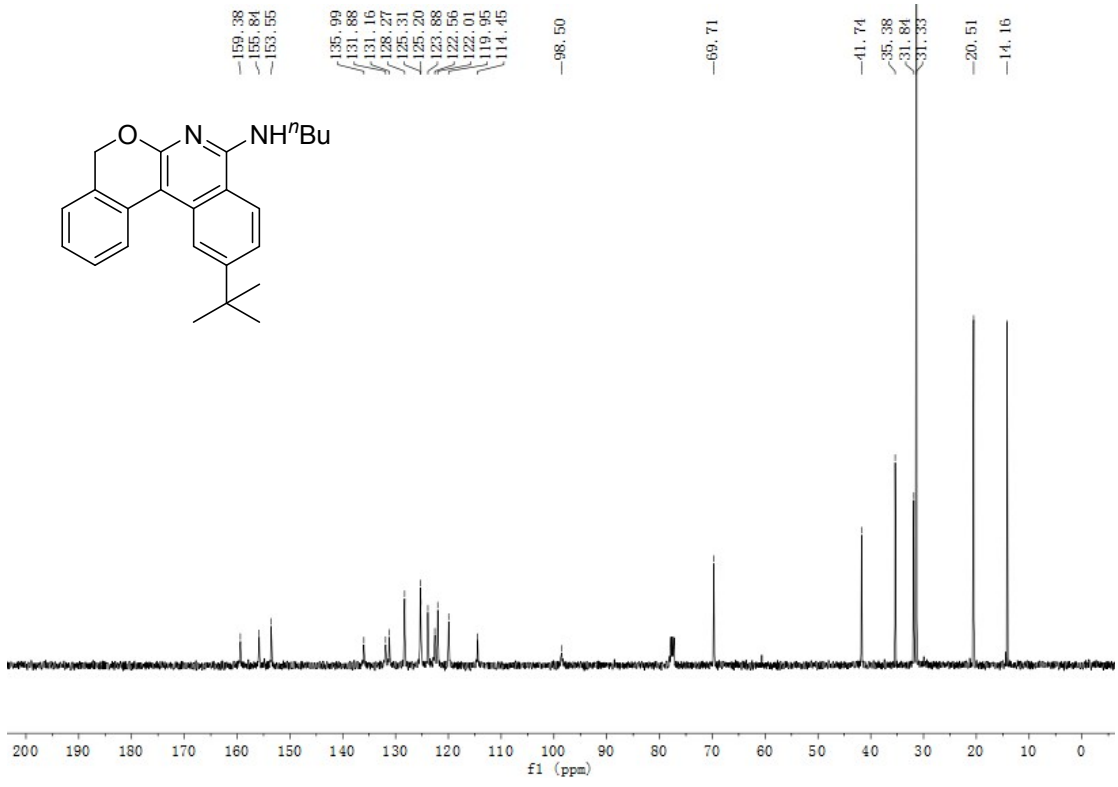
_N_-butyl-11-(methylthio)-5_H_-isochromeno[3,4-_c_]isoquinolin-8-amine (3ga):



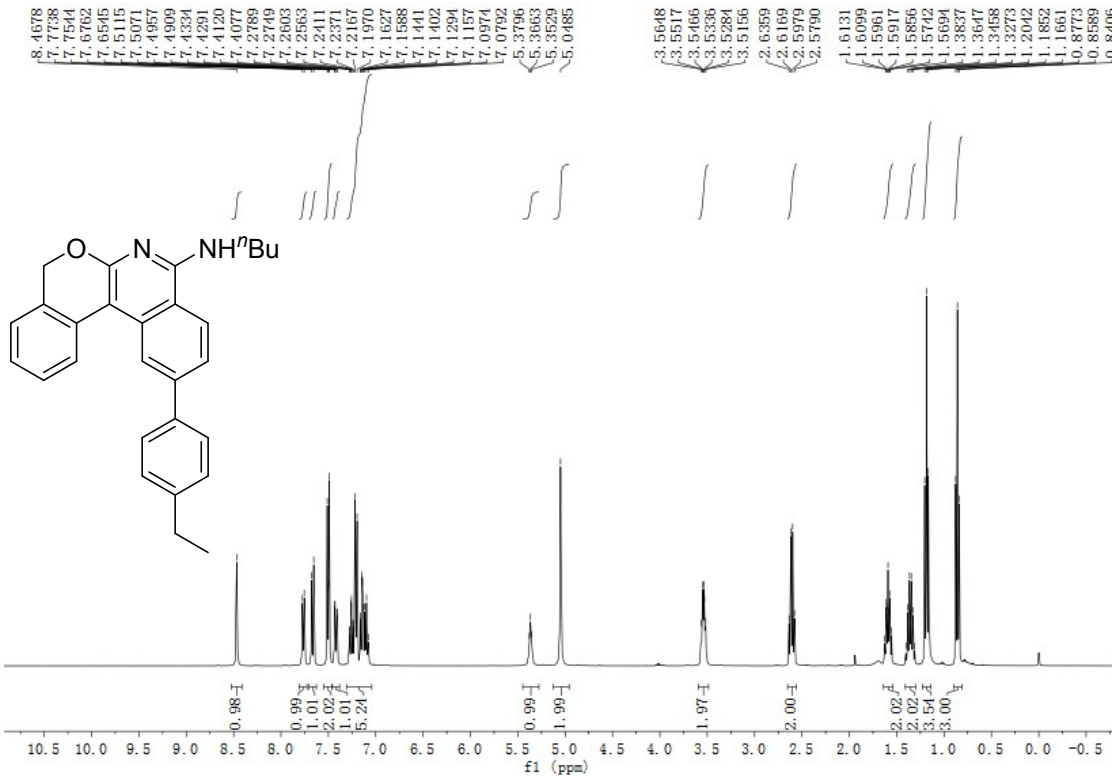


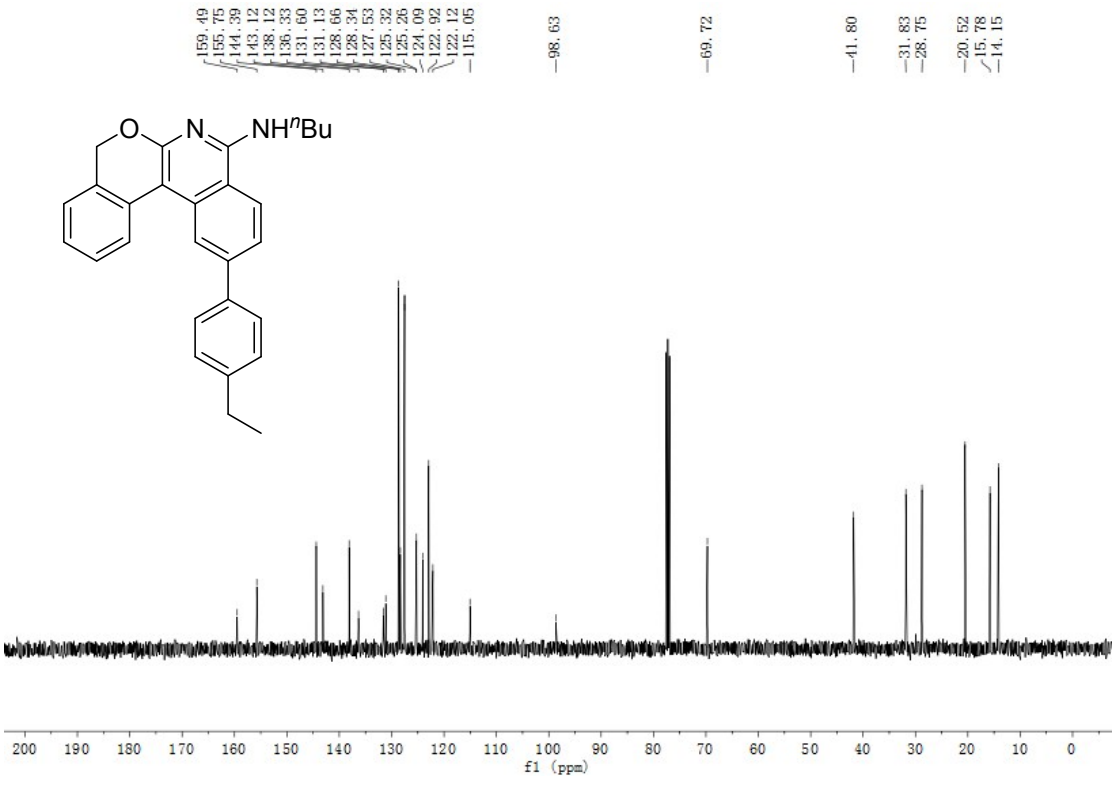
11-(*tert*-butyl)-*N*-butyl-5*H*-isochromeno[3,4-*c*]isoquinolin-8-amine (3ha):



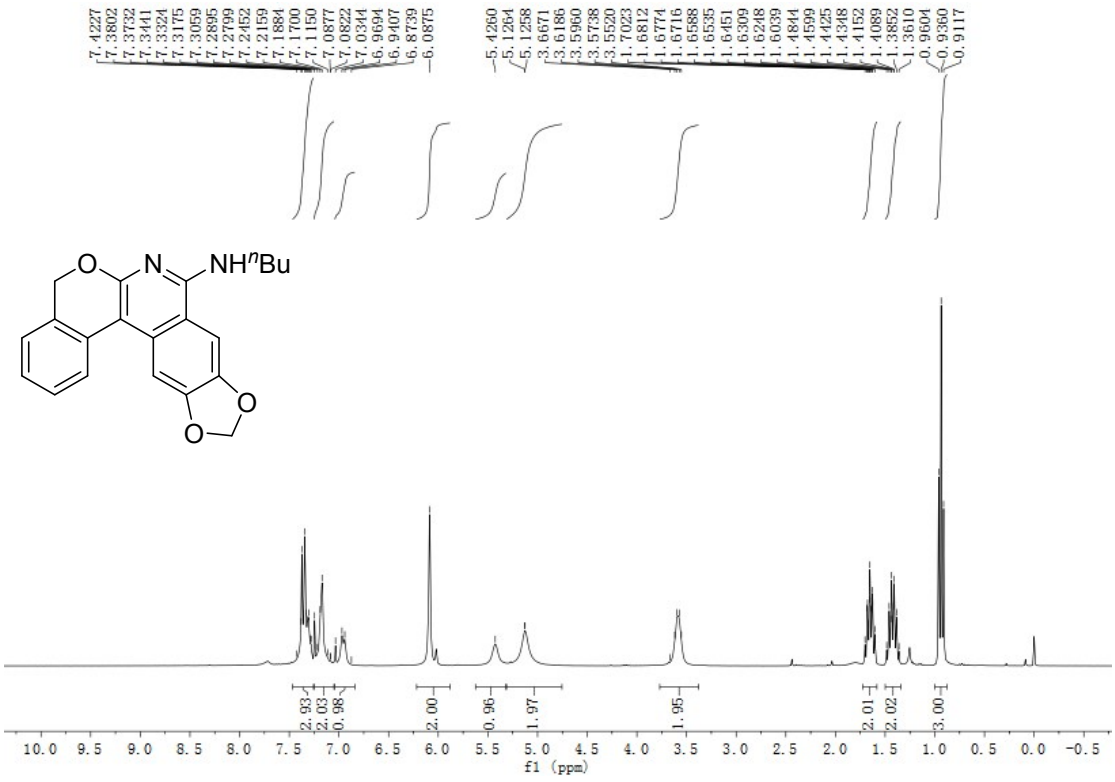


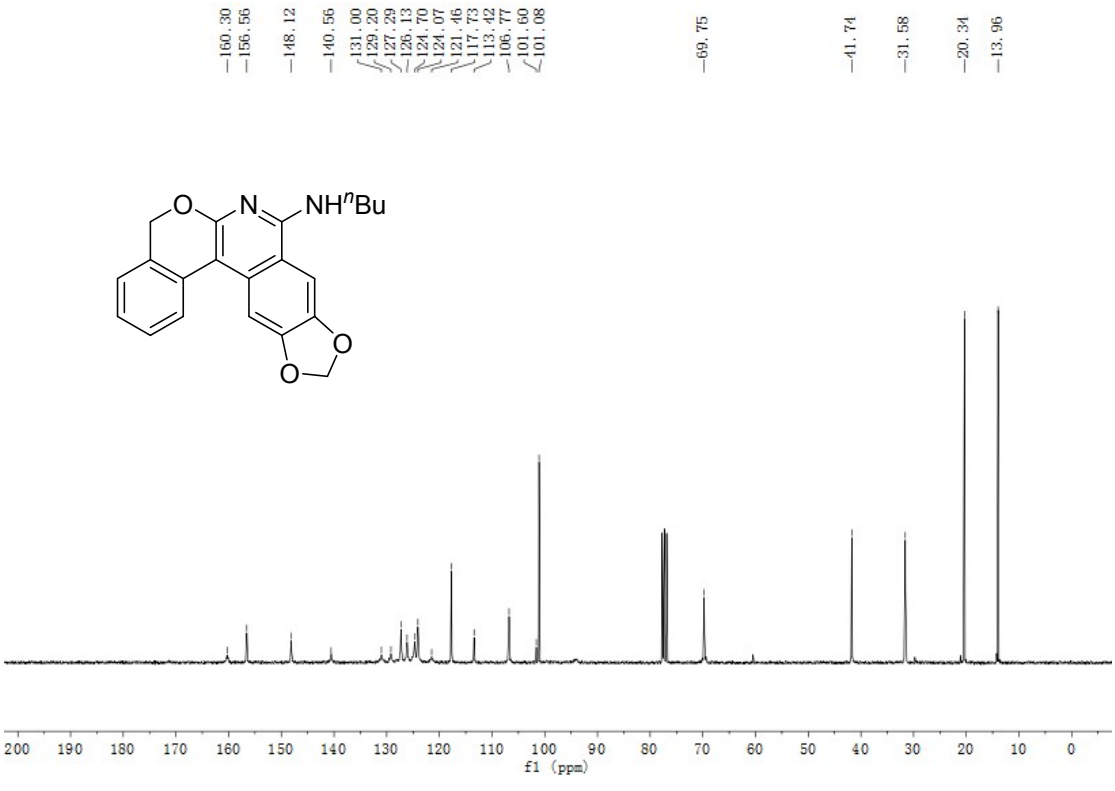
N-butyl-11-(4-ethylphenyl)-5H-isochromeno[3,4-c]isoquinolin-8-amine (3ia):



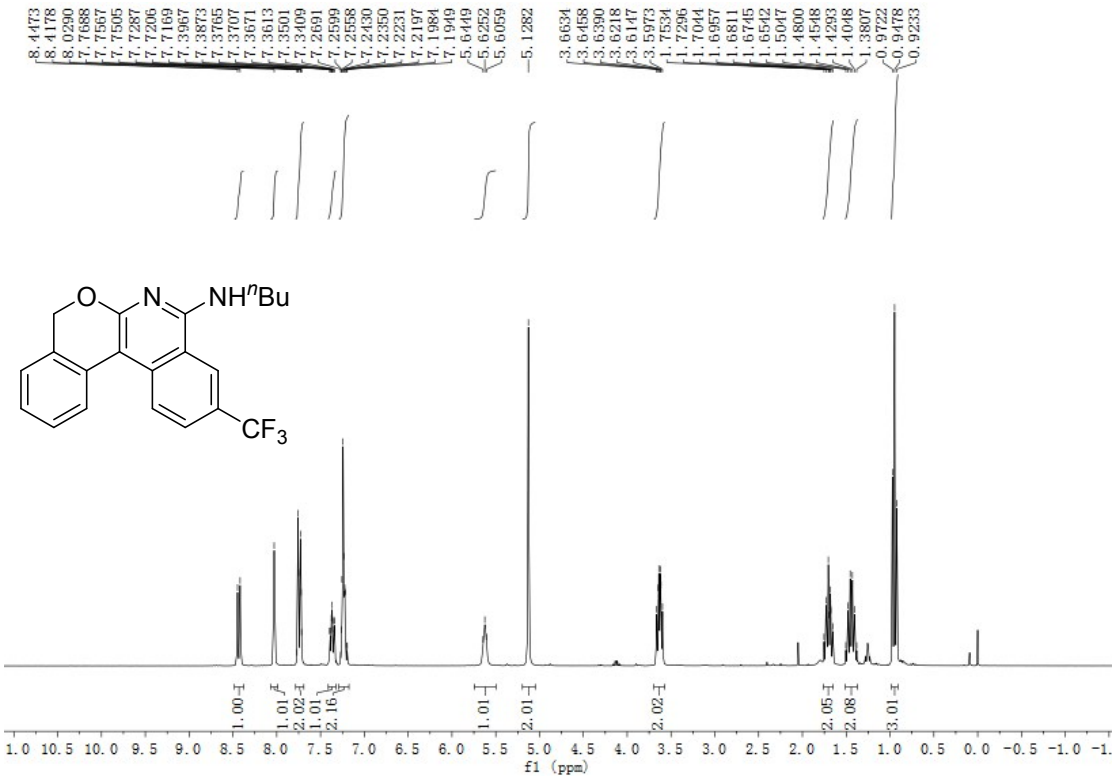


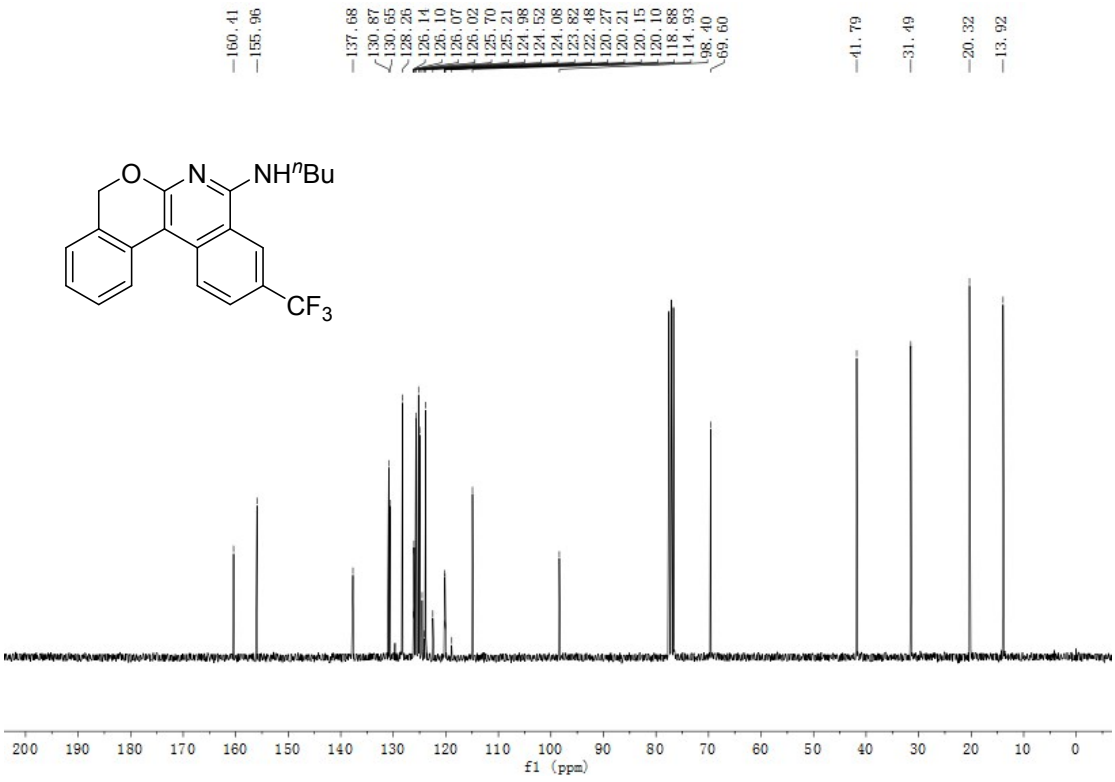
***N*-butyl-5*H*-[1,3]dioxolo[4,5-*g*]isochromeno[3,4-*c*]isoquinolin-8-amine (3ja):**



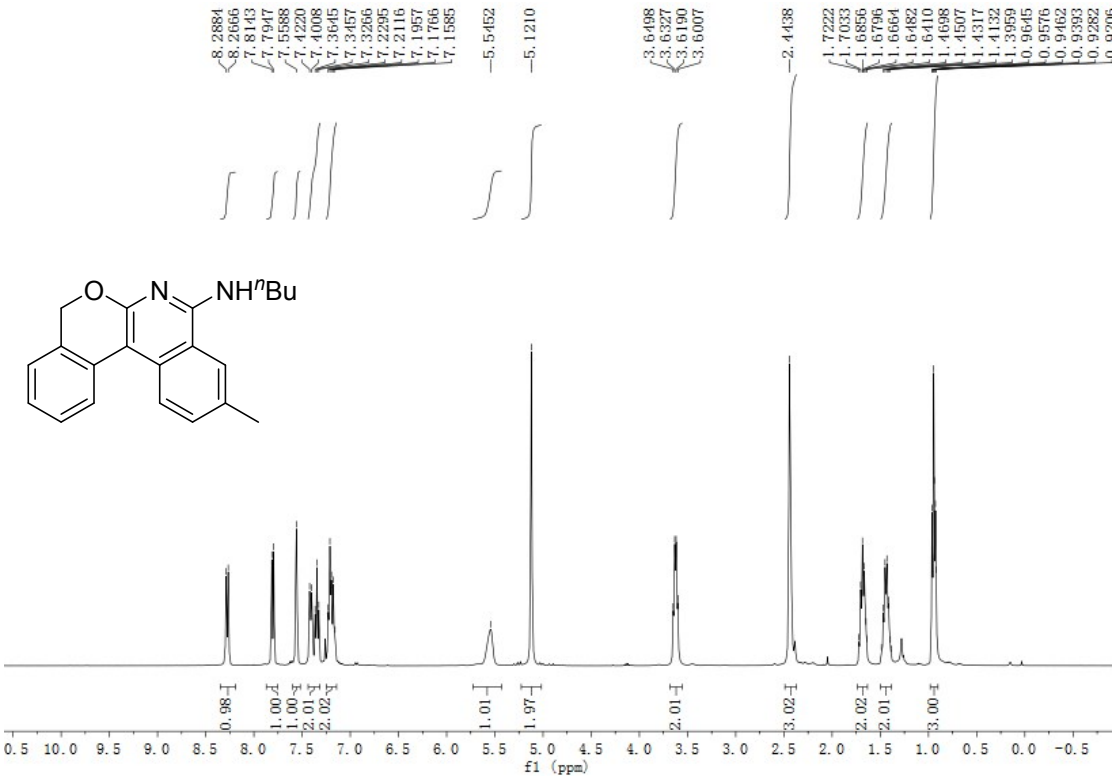


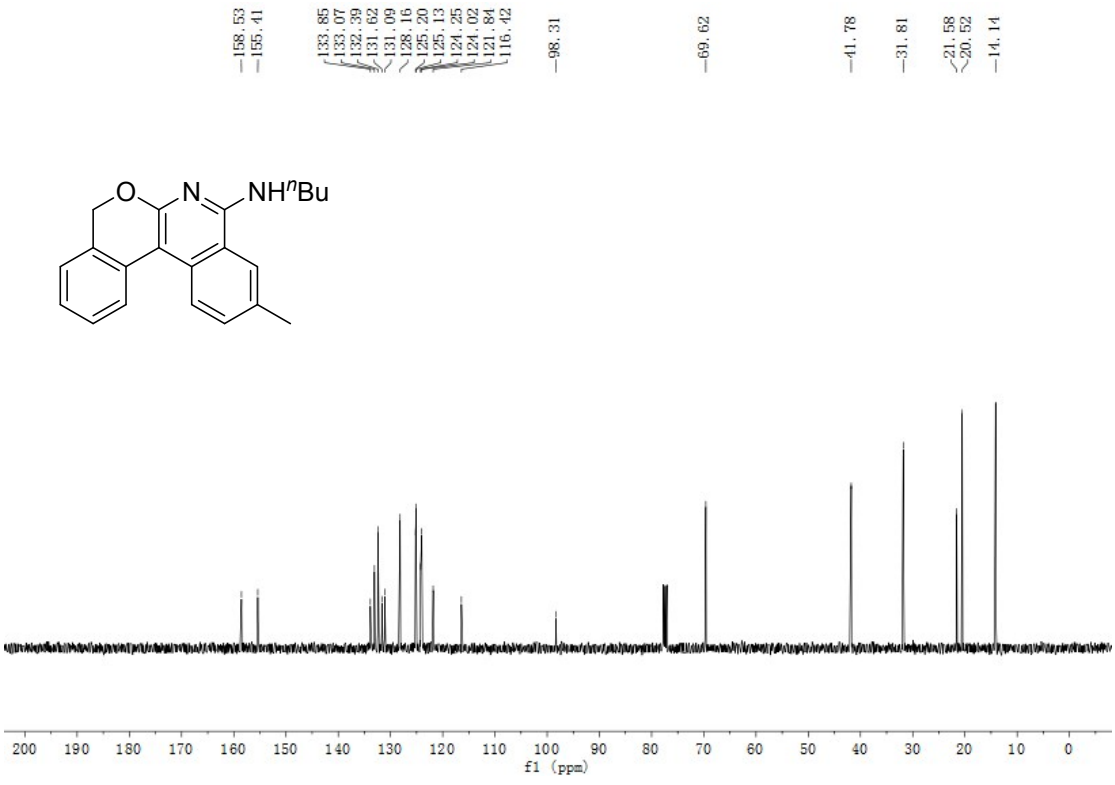
_N_-butyl-10-(trifluoromethyl)-5_H_-isochromeno[3,4-_c_]isoquinolin-8-amine (3ka):





_N_-butyl-10-methyl-5_H_-isochromeno[3,4-_c_]isoquinolin-8-amine (3la):





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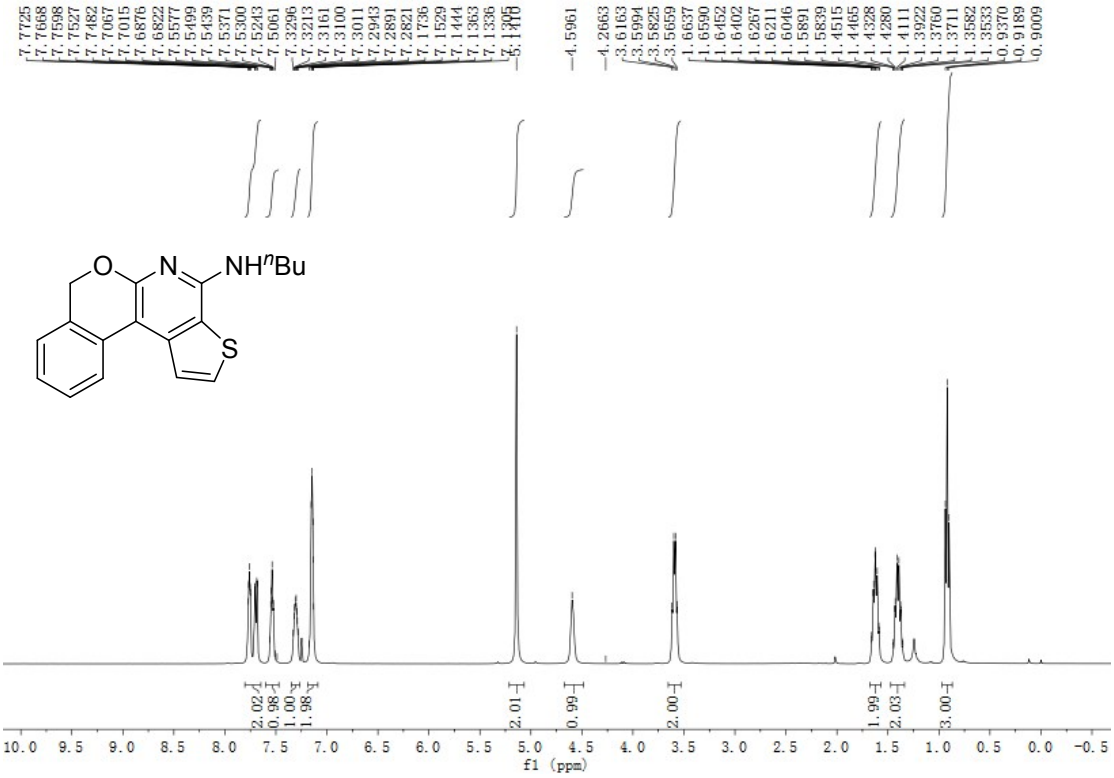
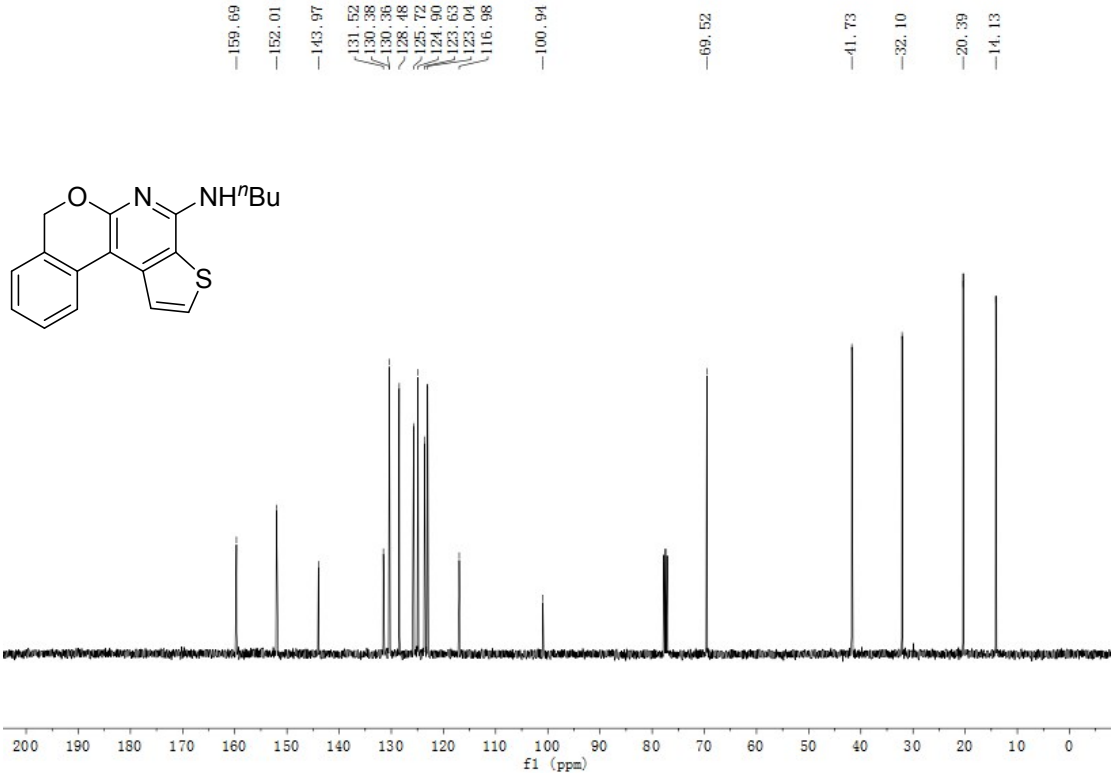
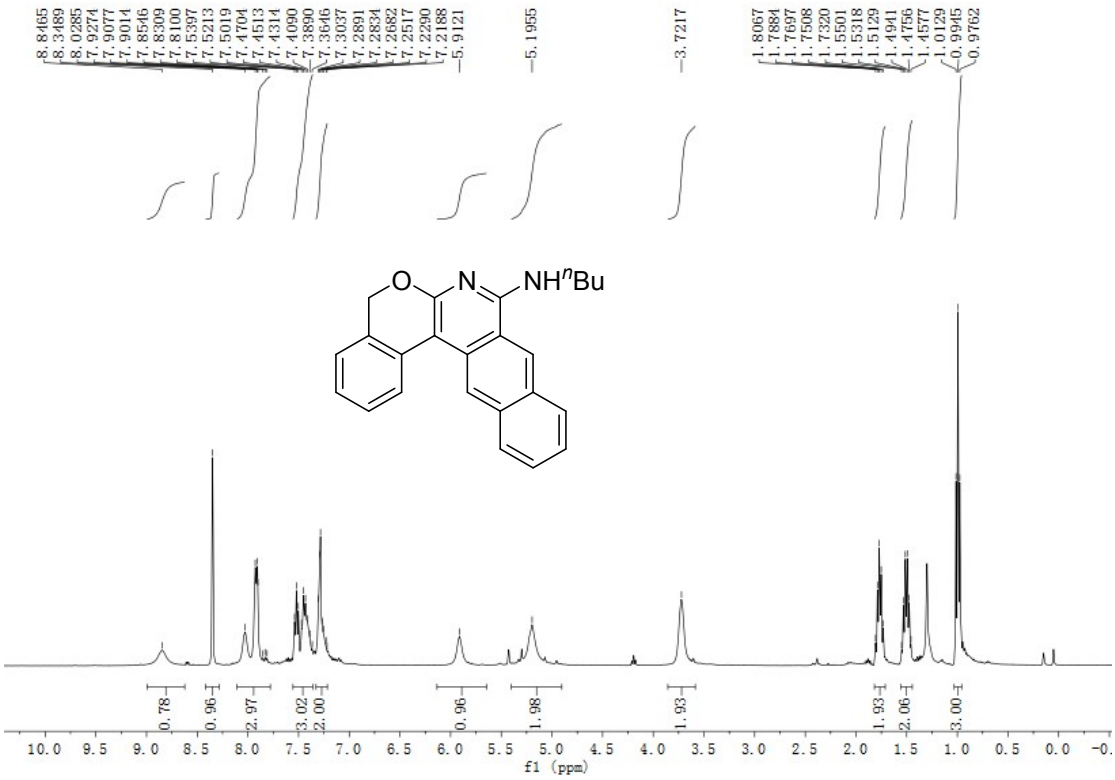
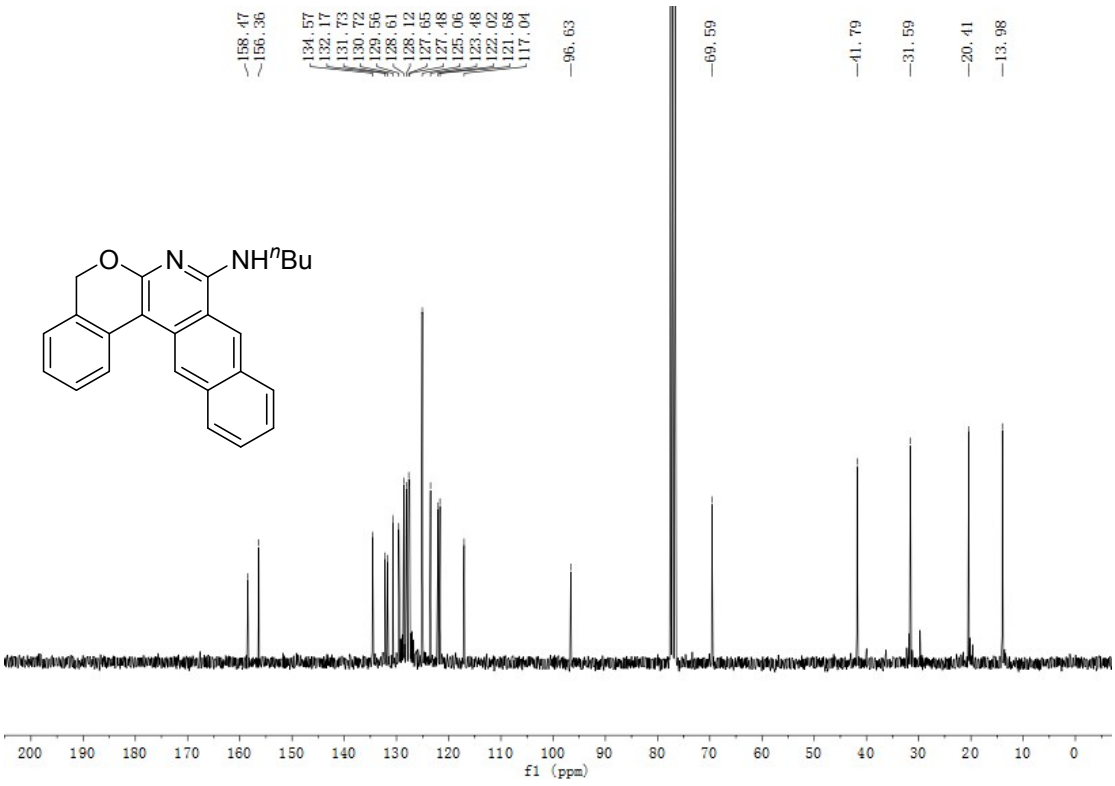




***N*-butyl-5*H*-benzo[*g*]isochromeno[3,4-*c*]isoquinolin-8-amine (3qa):**





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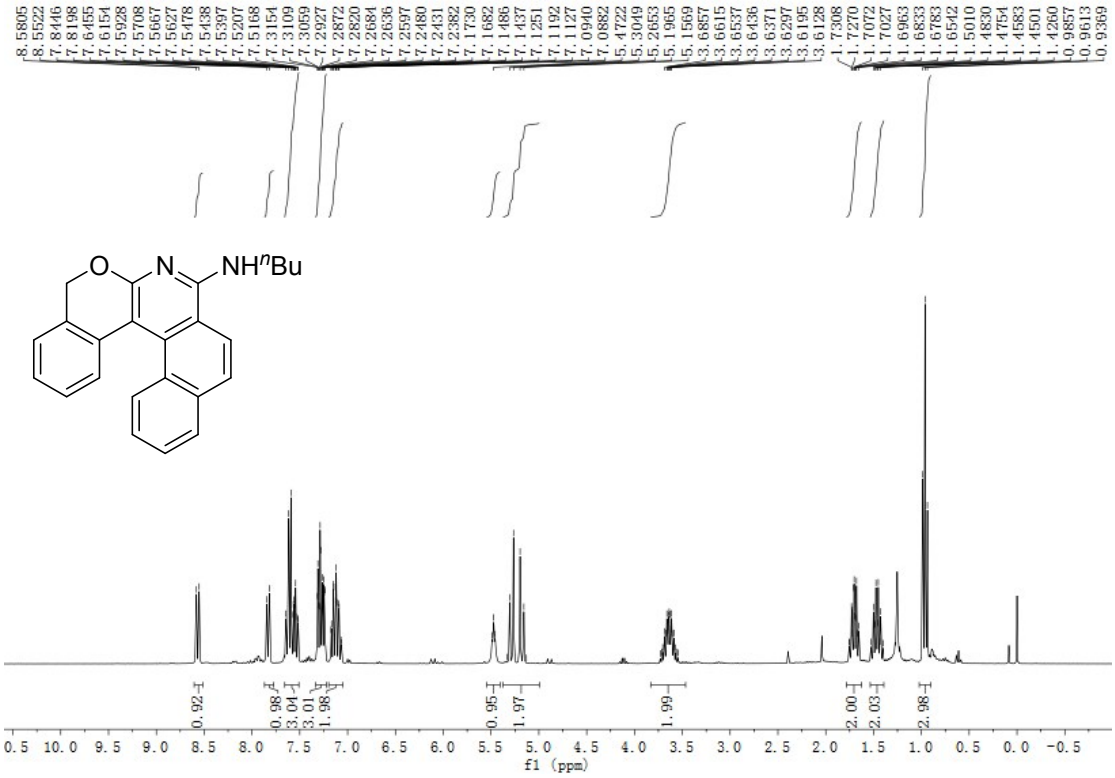

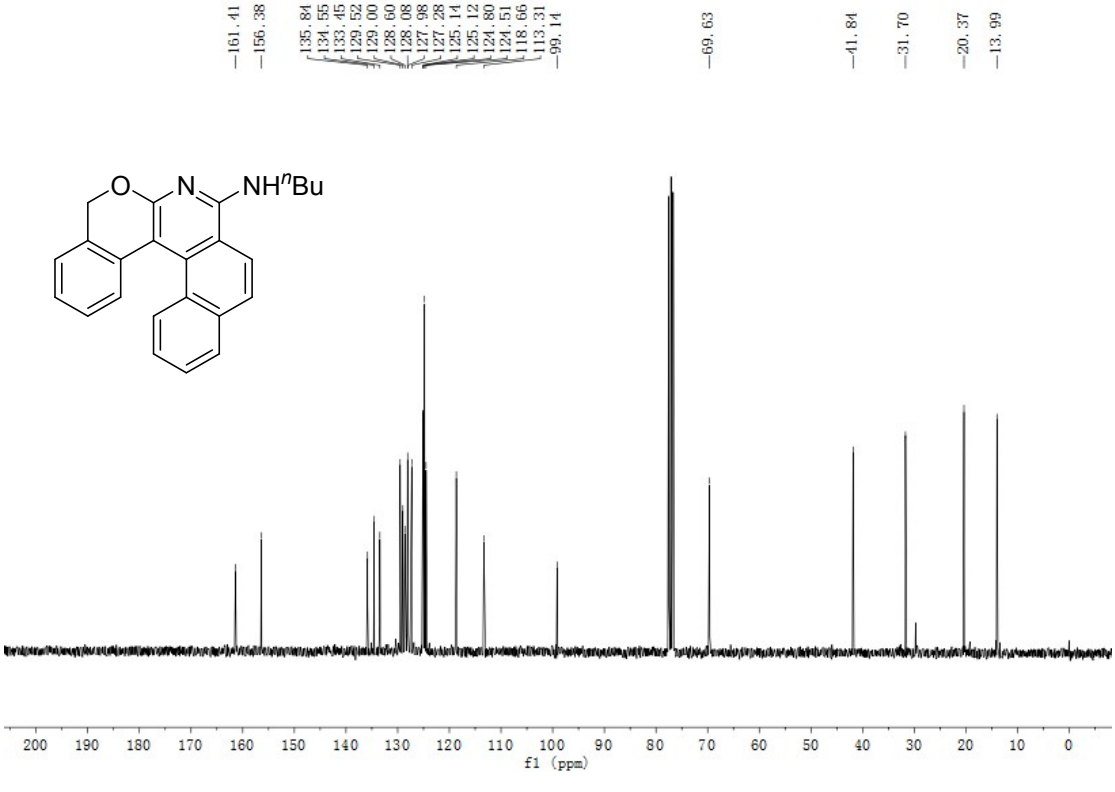

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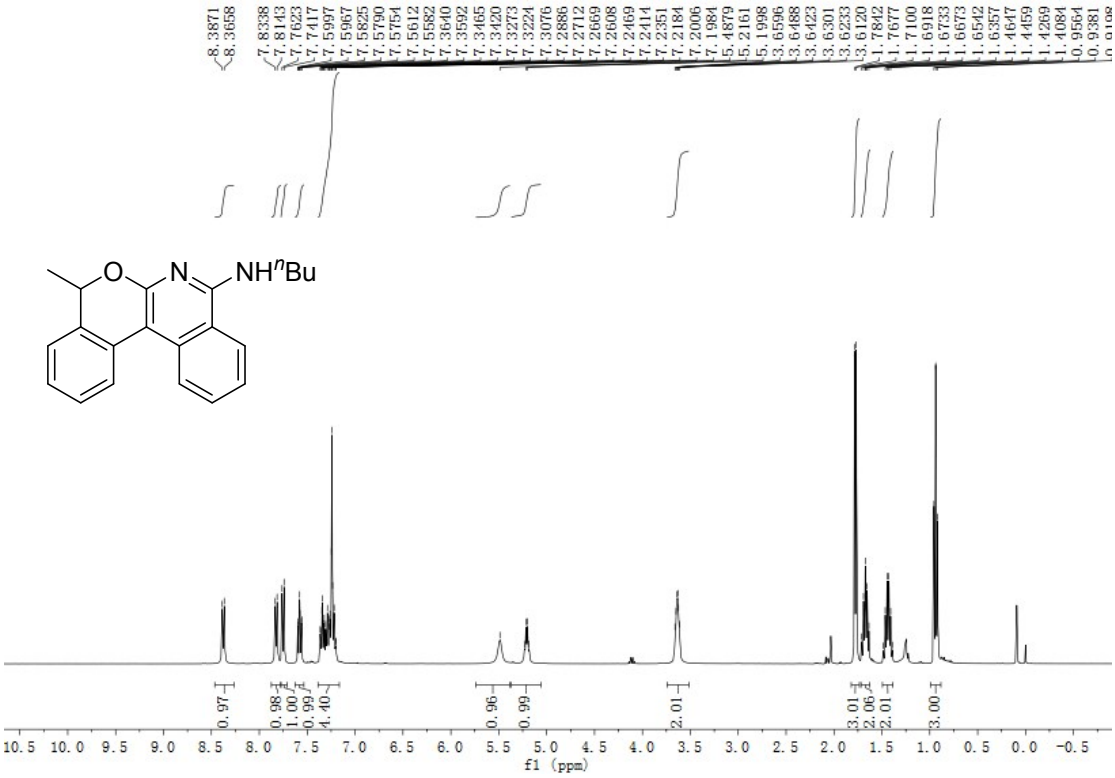

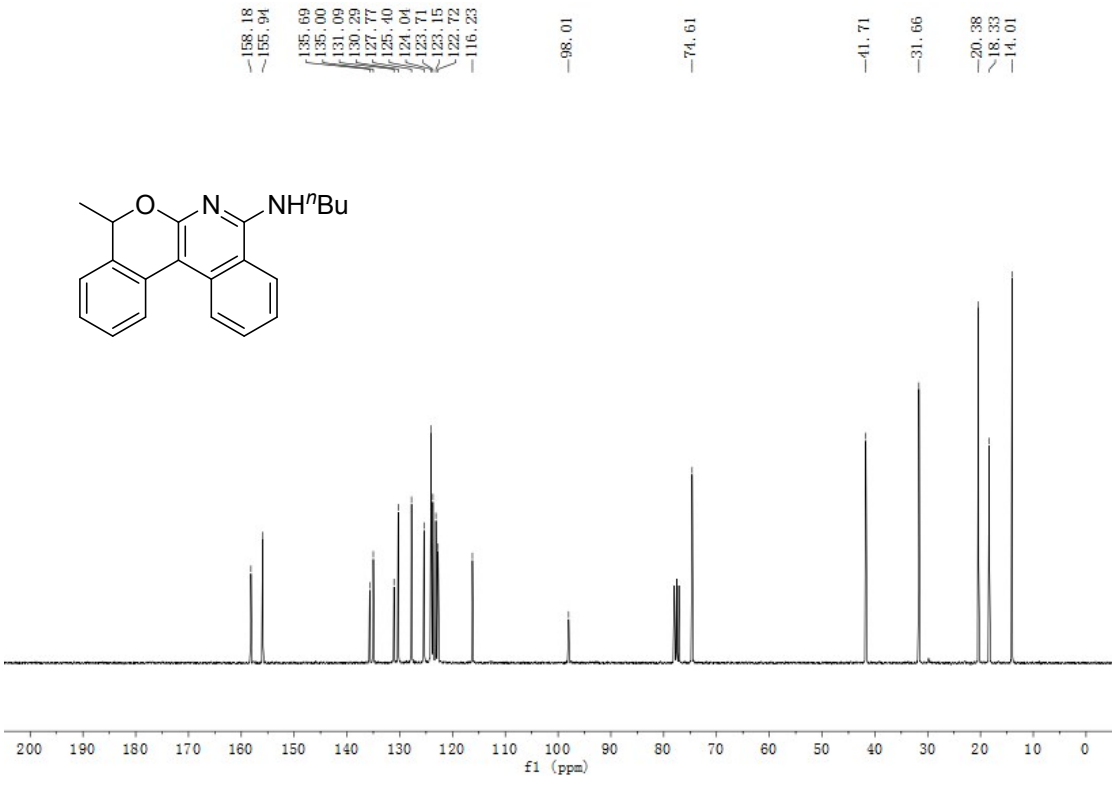

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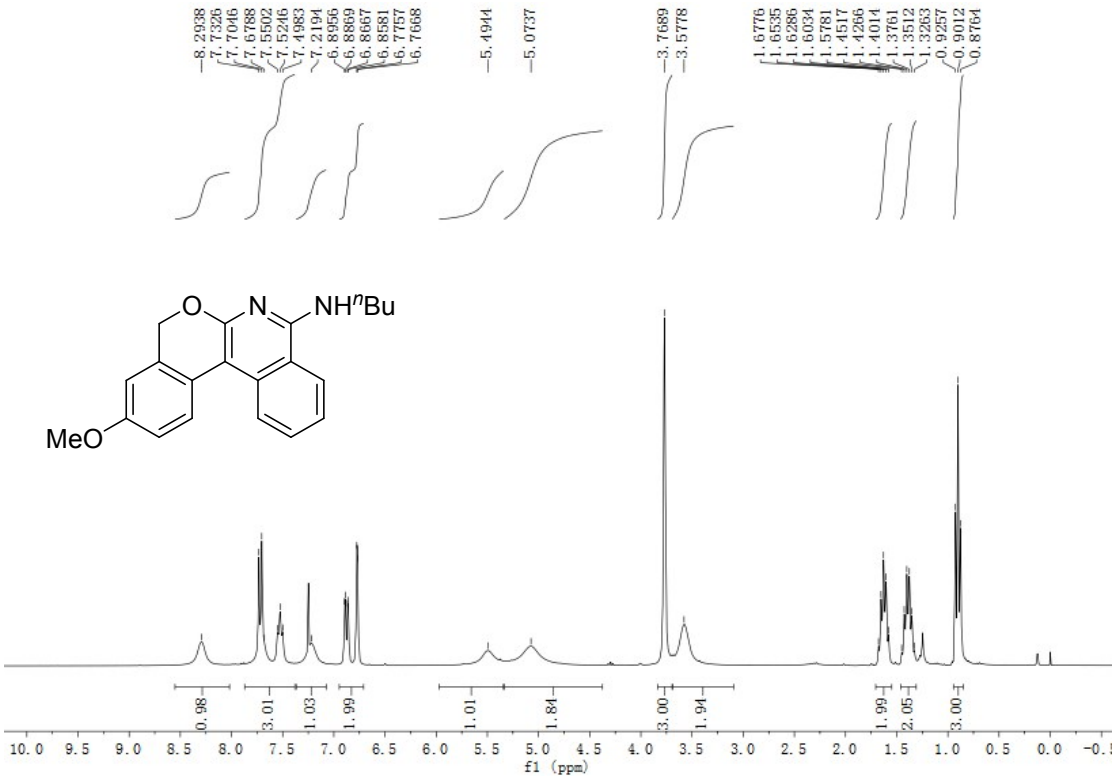

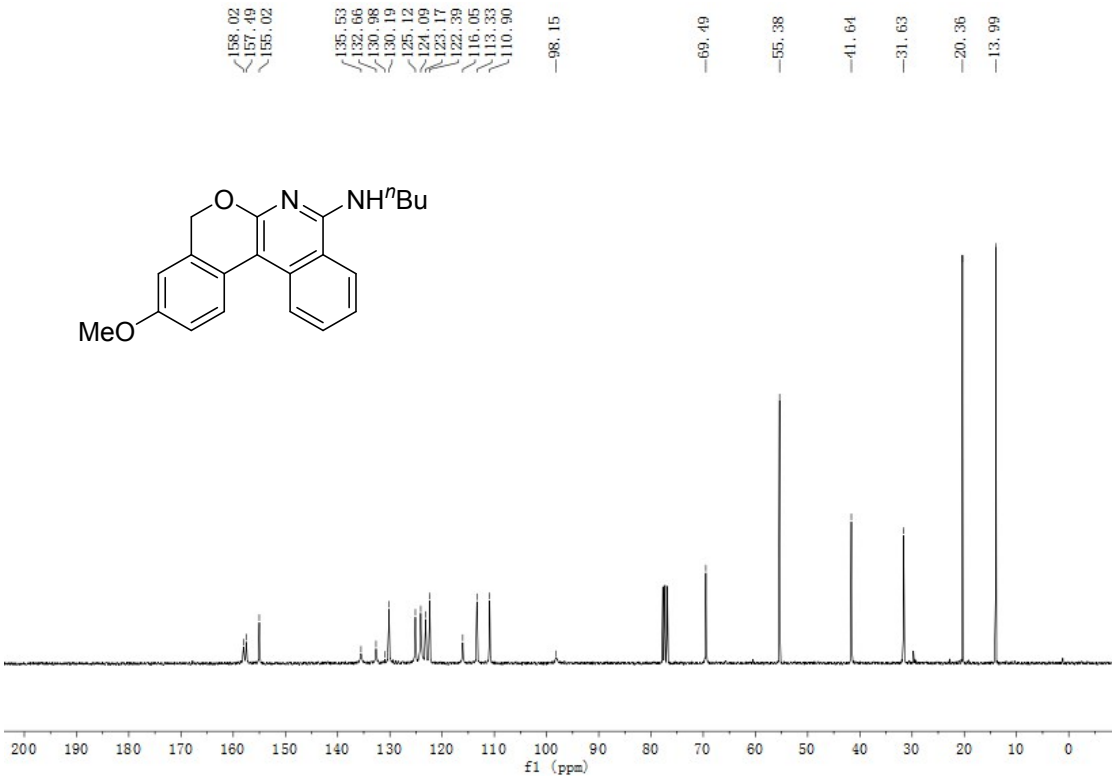

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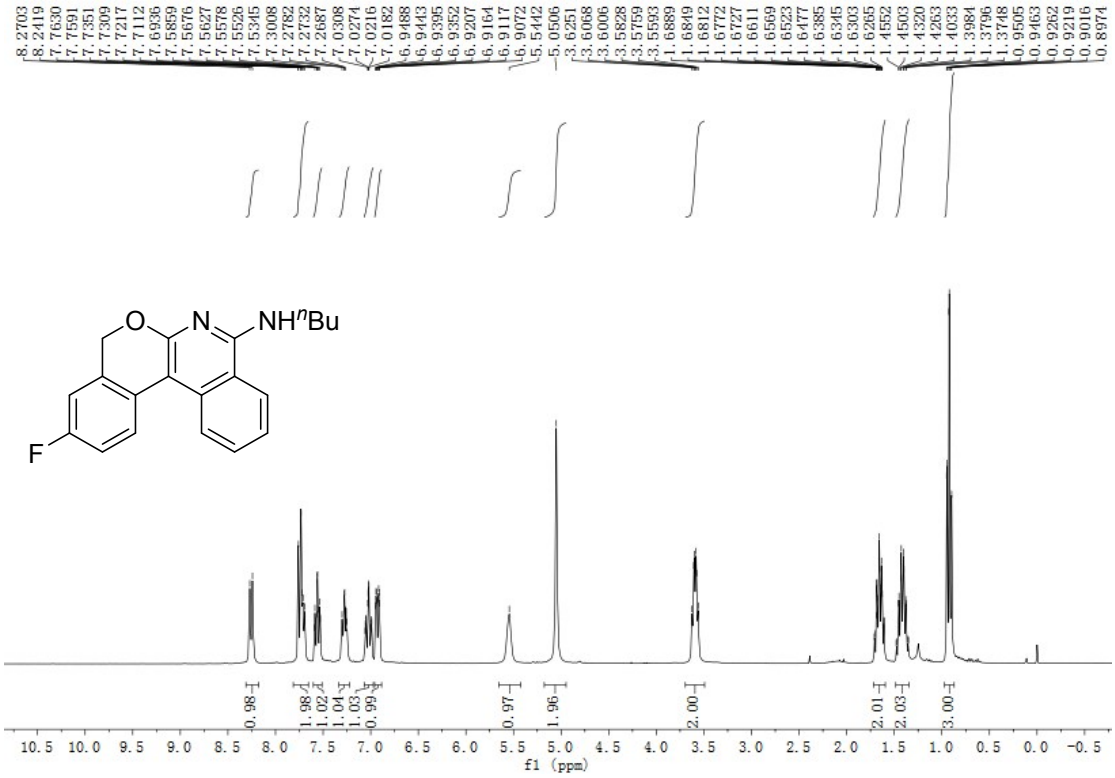

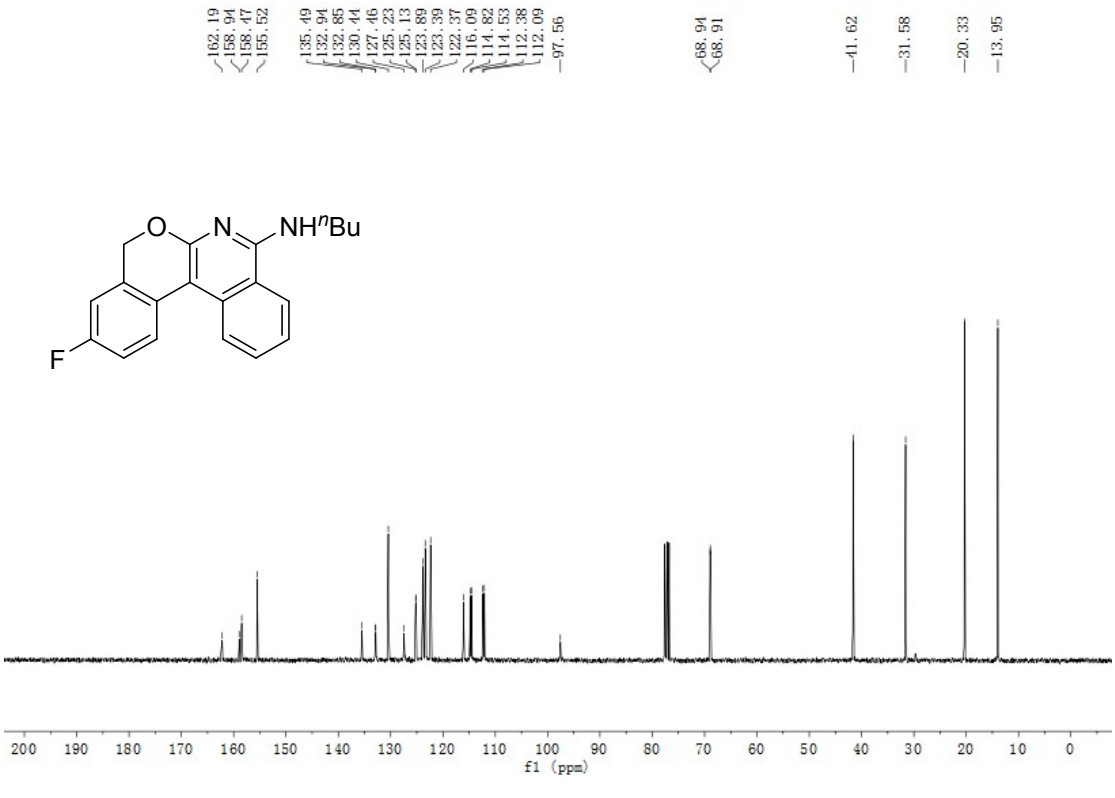

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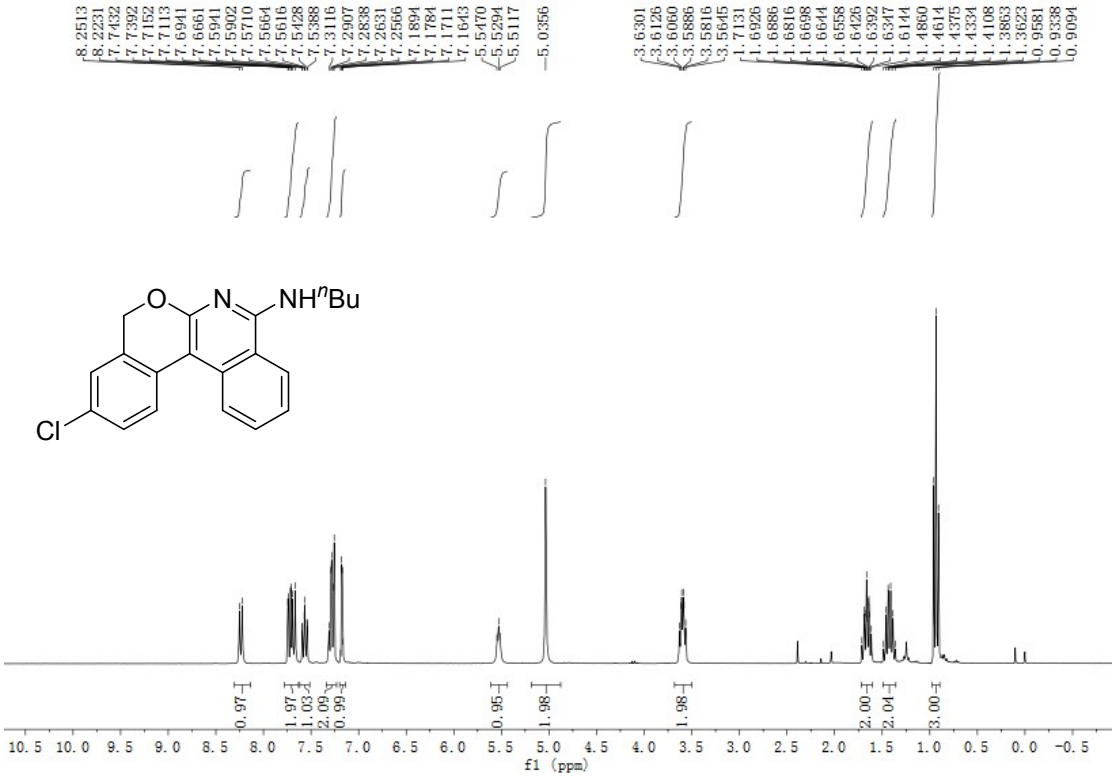
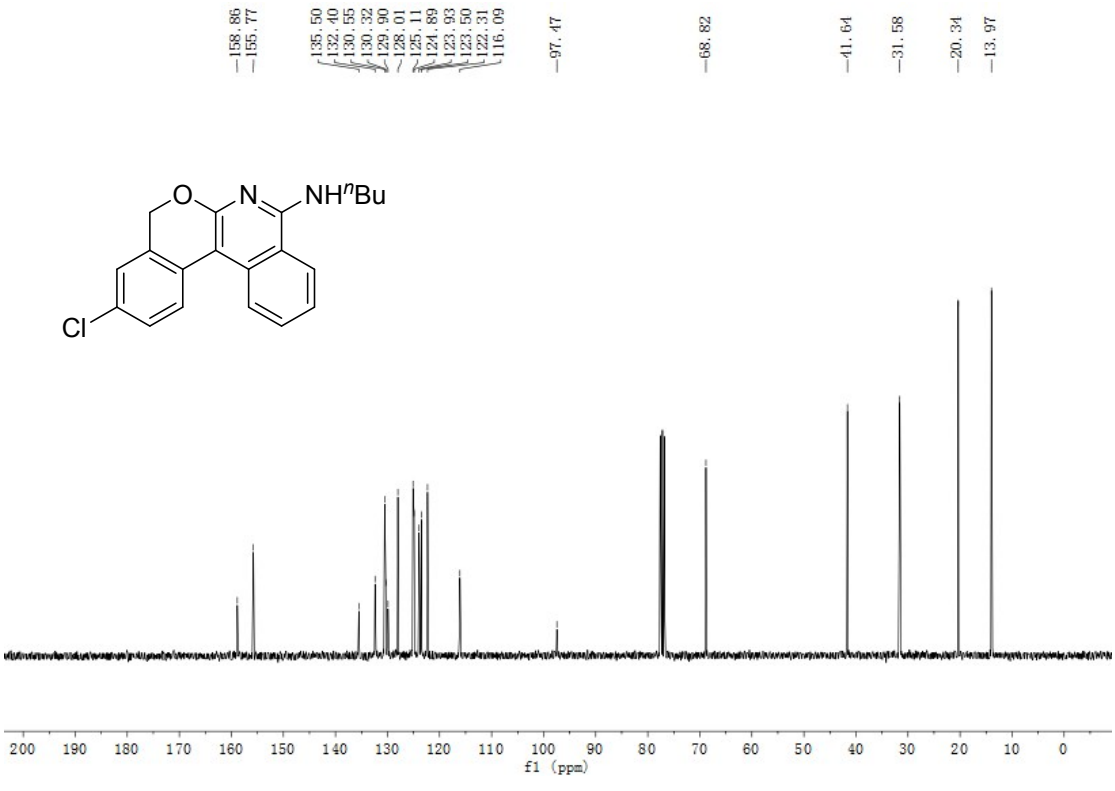
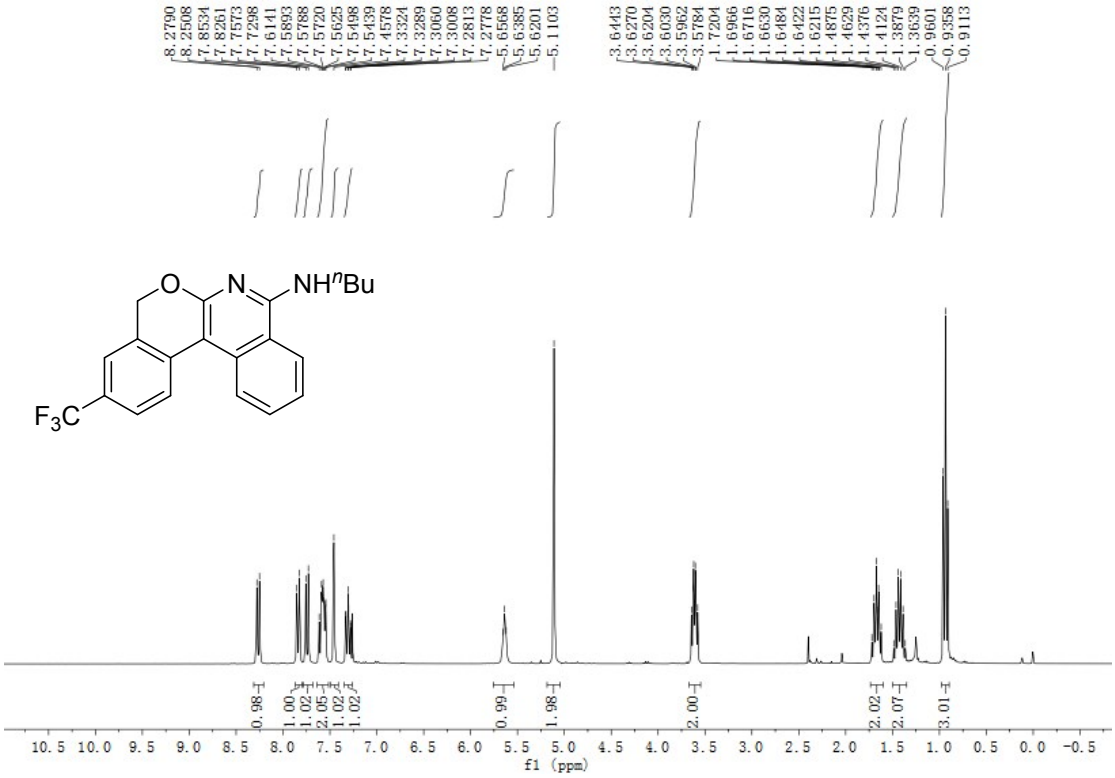
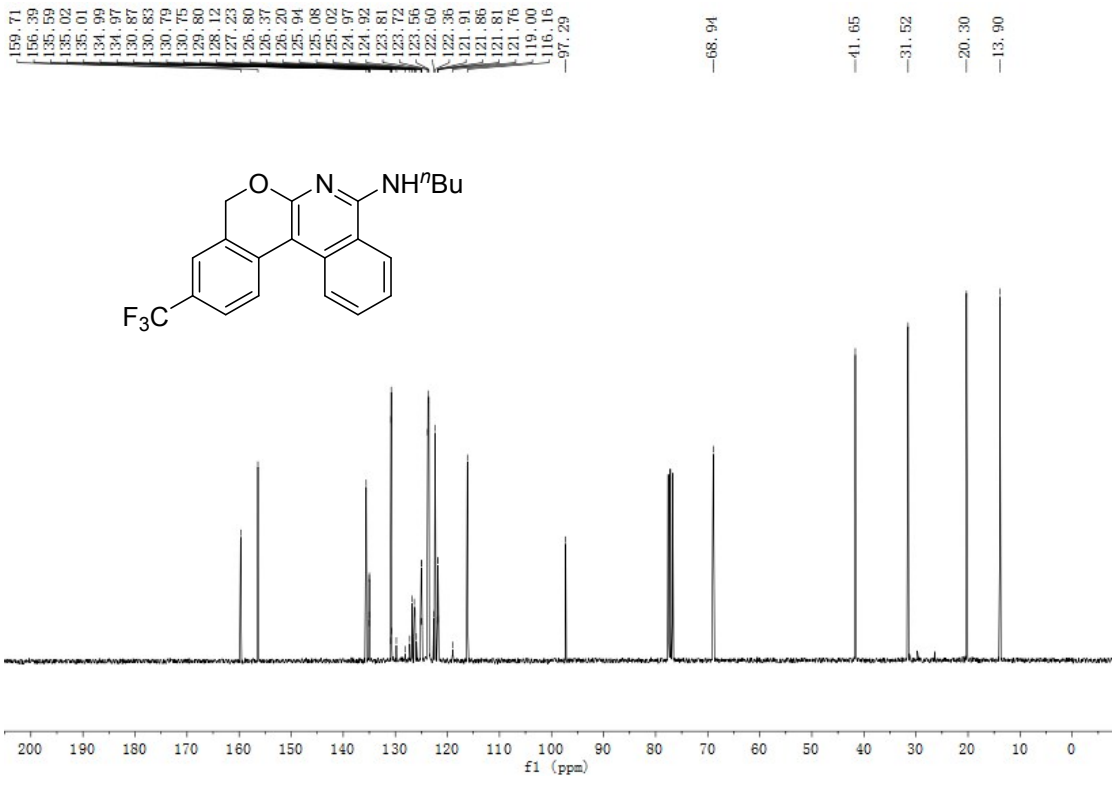


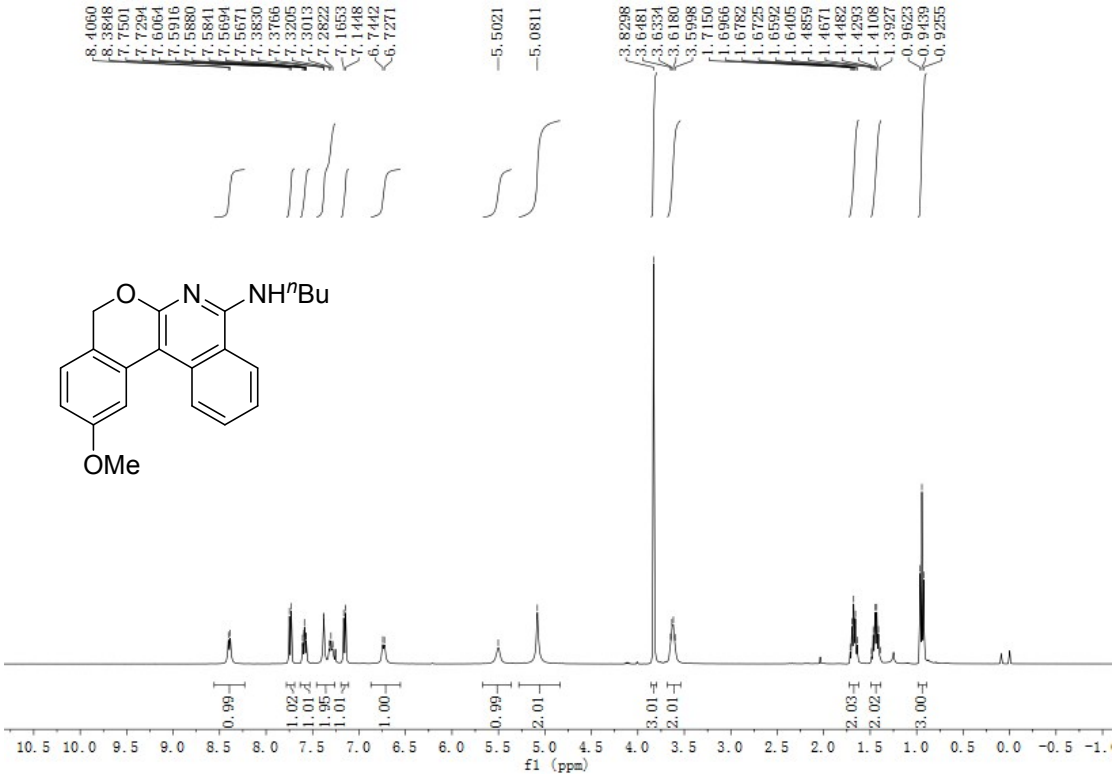


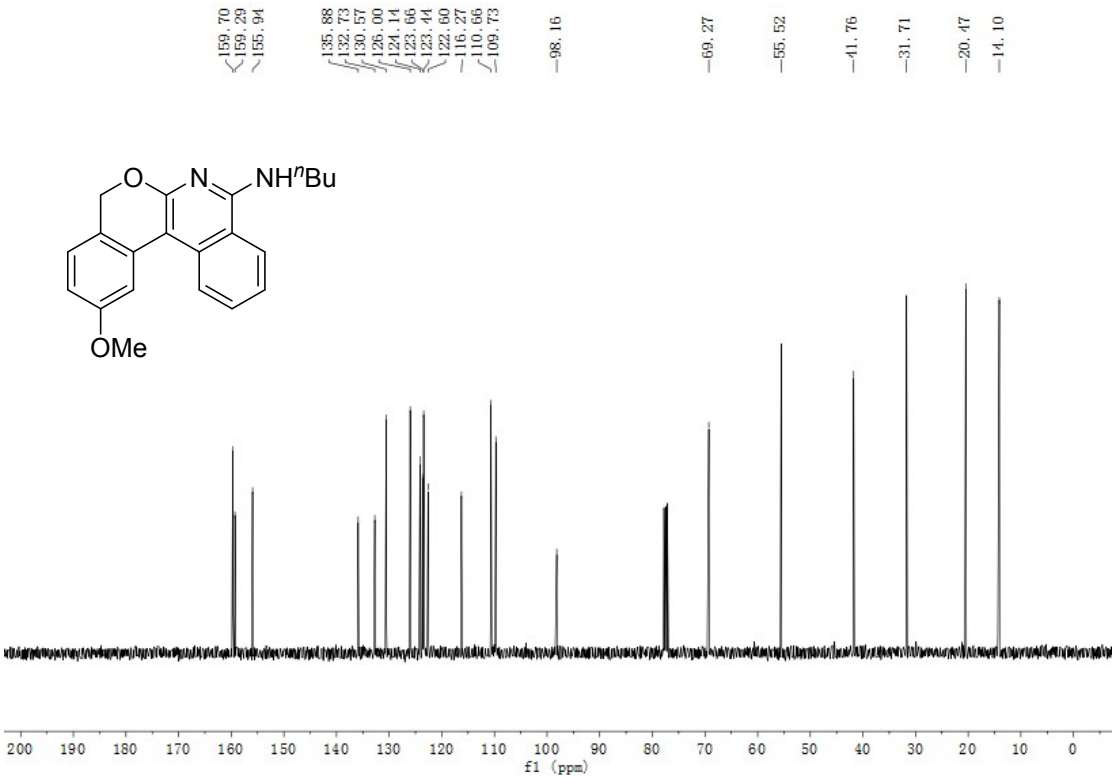
***N*-butyl-3-(trifluoromethyl)-5*H*-isochromeno[3,4-*c*]isoquinolin-8-amine (3af):**



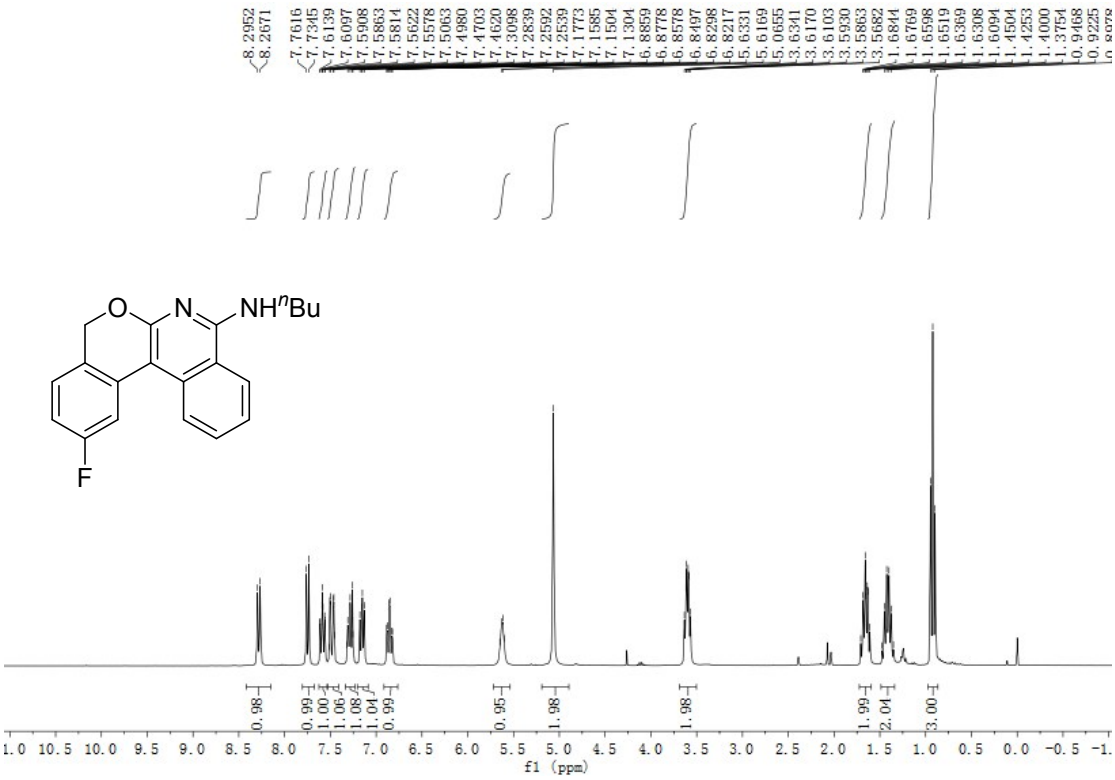


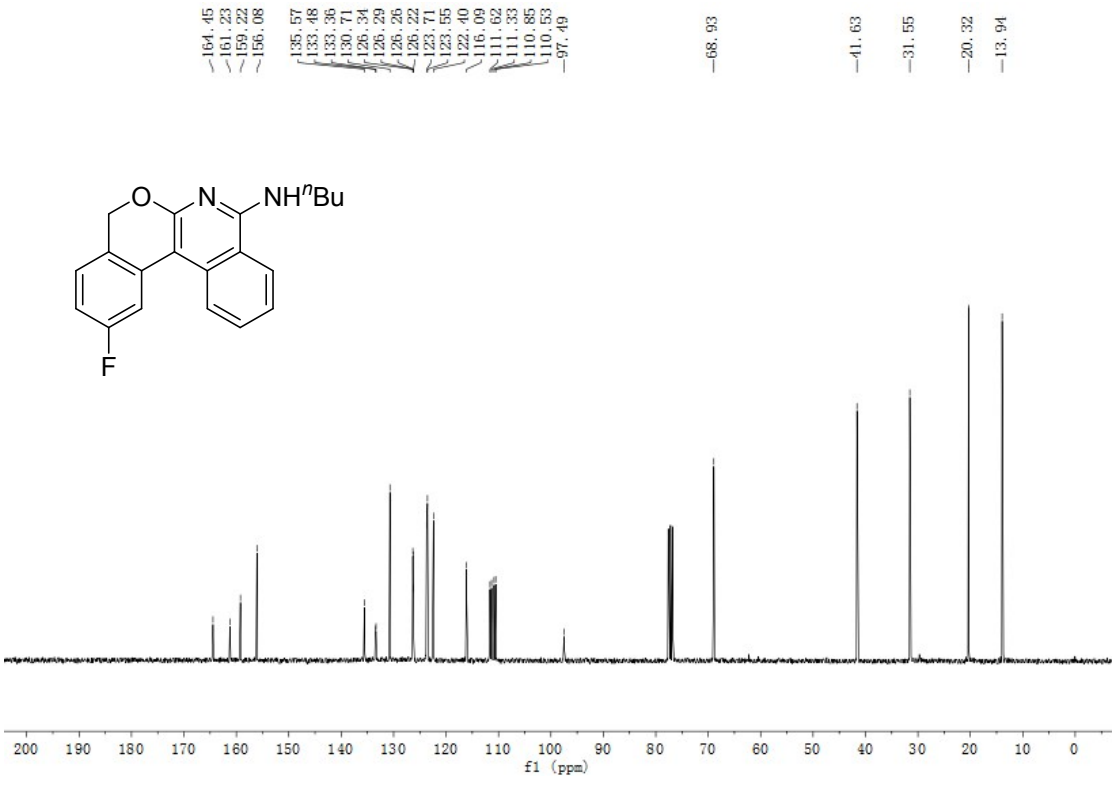
_N_-butyl-2-methoxy-5_H_-isochromeno[3,4-_c_]isoquinolin-8-amine (3ag):



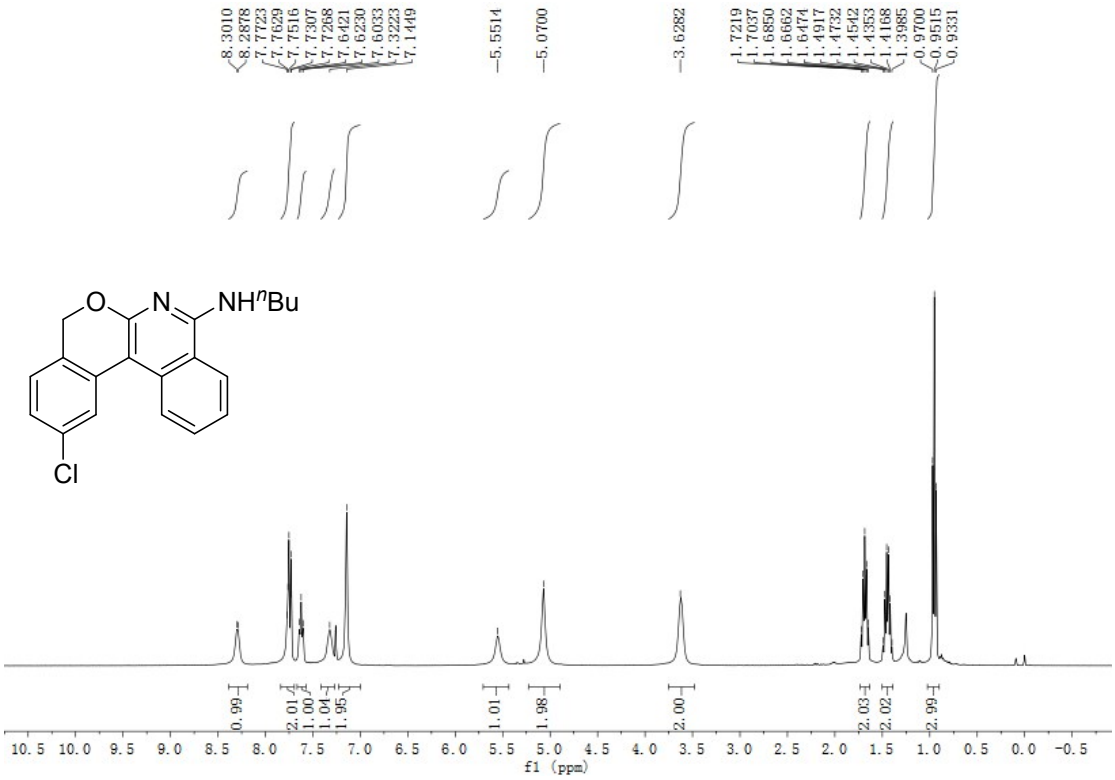


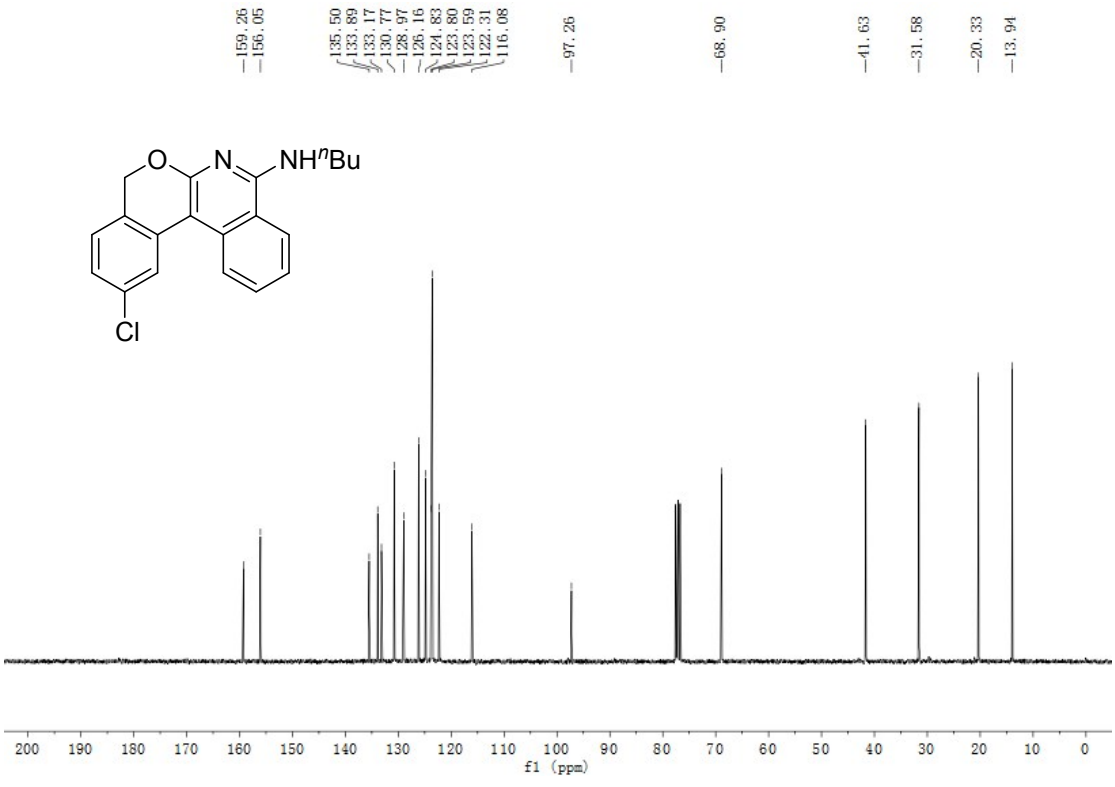
_N_-butyl-2-fluoro-5_H_-isochromeno[3,4-_c_]isoquinolin-8-amine (3ah):





***N*-butyl-2-chloro-5*H*-isochromeno[3,4-*c*]isoquinolin-8-amine (3ai):**





3-methoxy-*N*-phenyl-5*H*-isochromeno[3,4-*c*]isoquinolin-8-amine (3sd):