Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Photo-promoted cascade cyclization of aryl alkynes: access to thiocyanate/trifluoromethylthio-featured quinolino[2,1-b]quinazolinones

Jie Fan,[a] Qinqin Yan,[a] Huaqing Liu,[a] Lijun Li,[*,a] Zhong-Quan Liu[*, b] and Zejiang Li[*,a]

[a]Key Laboratory of Medicinal Chemistry and Molecular Diagnosis of the Ministry of Education, State Key Laboratory of New Pharmaceutical Preparations and Excipients, College of Chemistry and Materials Science, Key Laboratory of Chemical Biology of Hebei Province, Hebei University, Baoding, Hebei, 071002, P. R. China. E-mail: lizejiang898@126.com, llj@hbu.edu.cn.

[b]Jiangsu Collaborative Innovation Center of Chinese Medicinal Resources Industrialization, College of Pharmacy, Nanjing University of Chinese Medicine, Nanjing, Jiangsu 210023, P. R. China; Email: liuzq@njucm.edu.cn.

General Information

^{1}H and ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker advance III 400 or 600 spectrometer in $CDCl_3$ with TMS as the internal standard. High-resolution mass spectral analysis (HRMS) data were measured on a Waters Xevo G2-XS qTOF. All products were identified by ^{1}H and ^{13}C NMR, HRMS. The raw materials were purchased from Energy, Meryer, J&K Chemicals, or Aldrich and used without further purification.

Typical procedure for the reaction

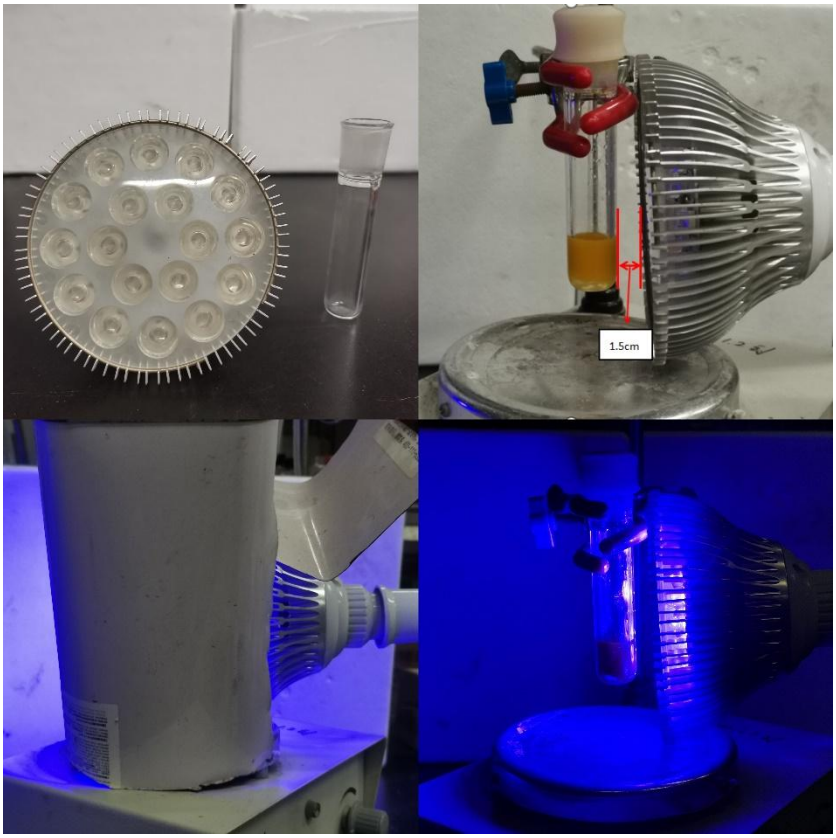


Fig. S1 Photochemical setup of the cyclization reaction

Reaction conditions: A mixture of alkynes (1 equiv., 0.1 mmol), NH_4SCN or $AgSCF_3$ (3 equiv., 0.3 mmol), $(NH_4)_2S_2O_8$ (4 equiv., 0.4 mmol), CH_3CN (2 mL), H_2O (0.5 mL), was added into a 10 mL quartz tube, which was initiated by 18 W blue LEDs, rt, N_2 (Fig. S1). After the cyclization reaction was finished, the mixture was condensed under vacuum and purified by column chromatography to afford the final products.

Supplementary notes: The 18 W blue LEDs were purchased from Shenzhen Jinrui photoelectric Company, CN. The light flux was 140 μw/cm^2. In addition, the emission spectrum of the blue light was described as shown in Figure 2.

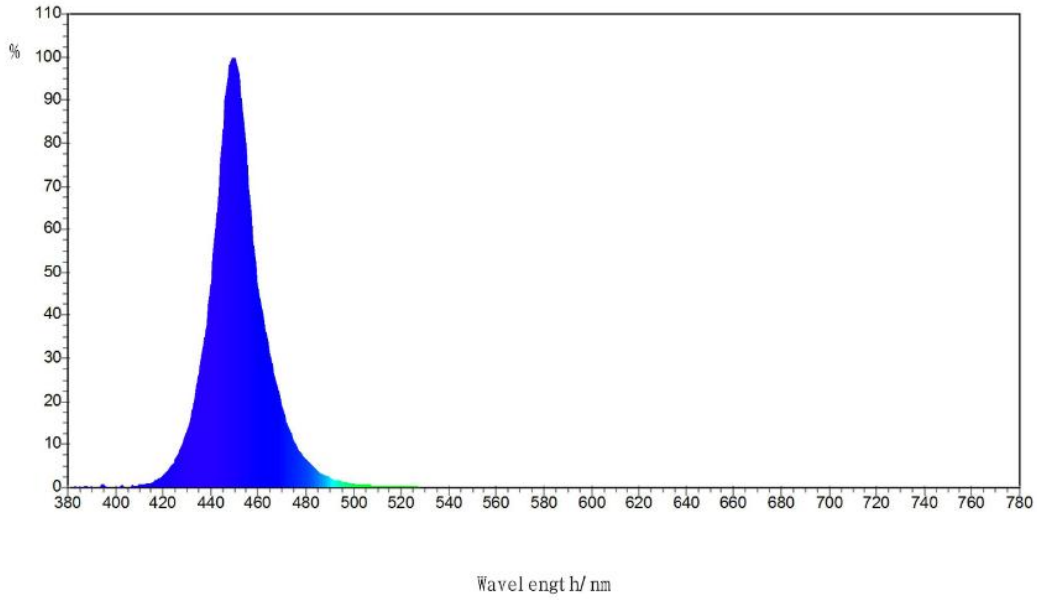


Fig. S2 The emission spectrum of the blue light

On/Off light experiments

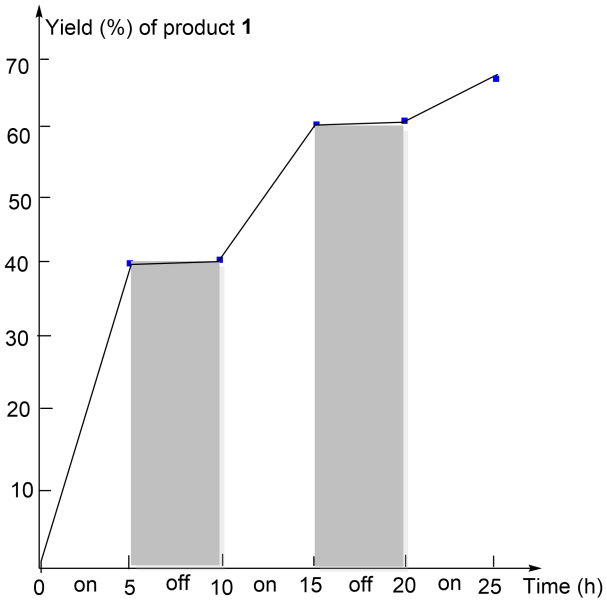
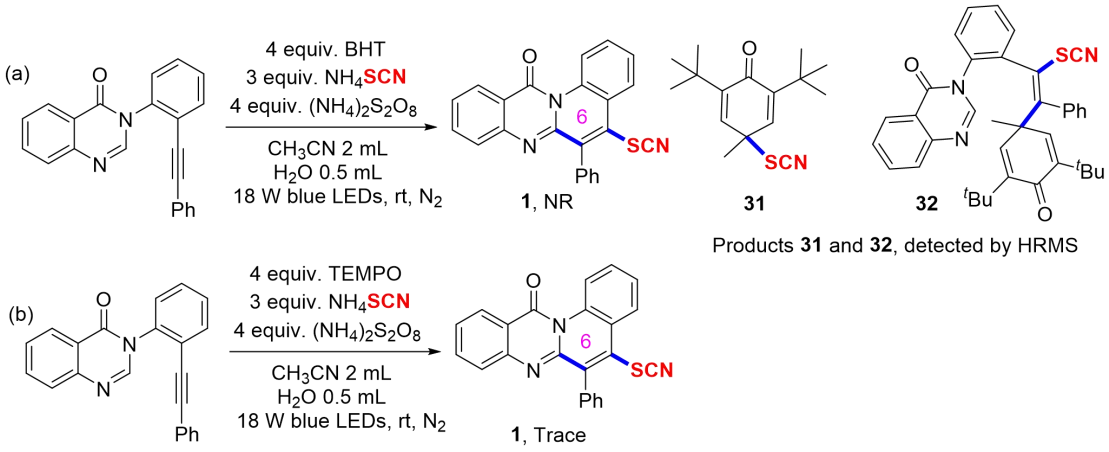


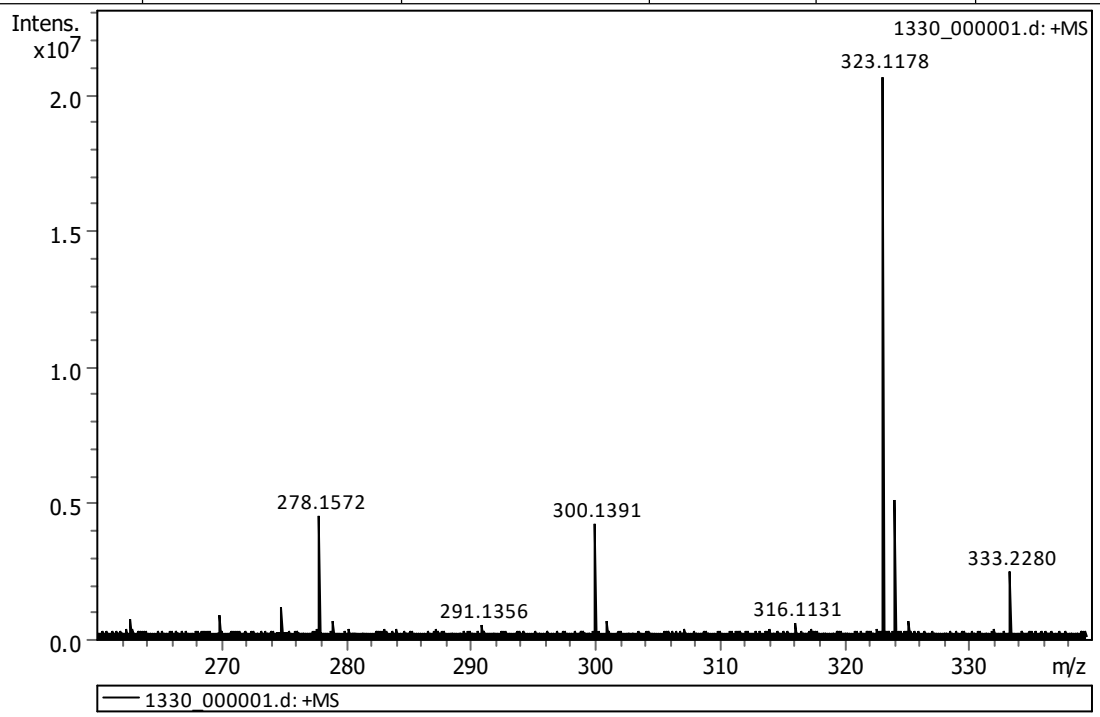
Fig. S3 On/Off light experiments of product **1**

Under the typical conditions, we controlled the time of light/dark and gave five different yields of product **1**, respectively (Figure S3).

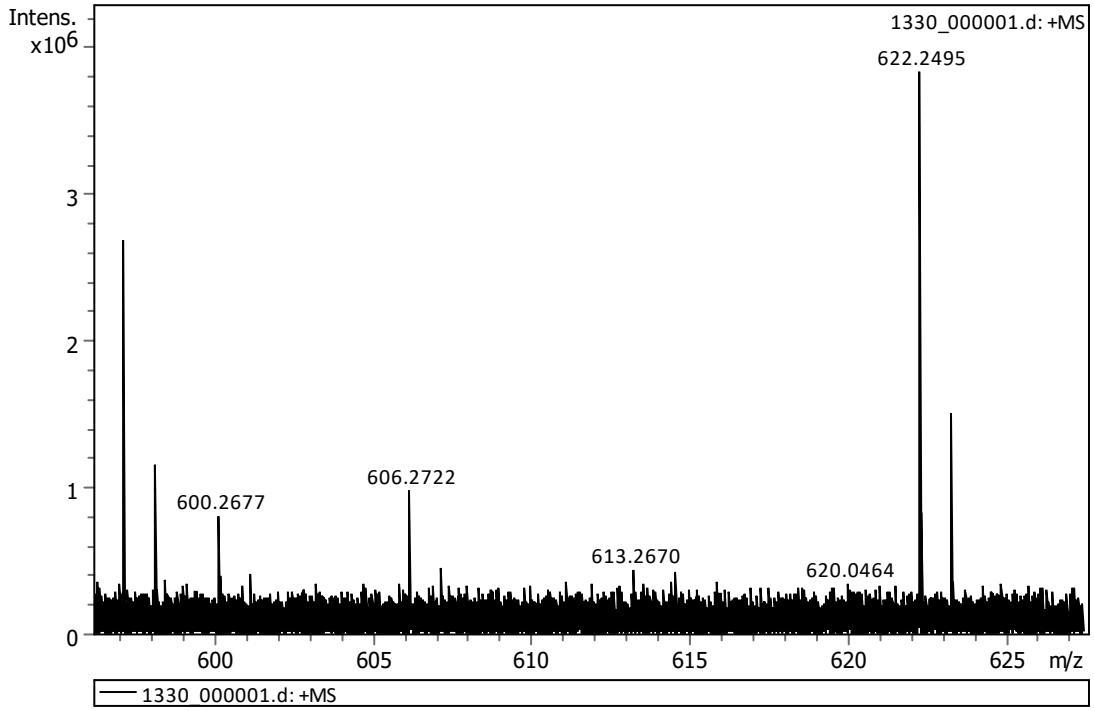
Mechanistic study



Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
31	$C_{16}H_{23}NOS$	$C_{16}H_{24}NOS$	278.1572	278.1573	-0.04



Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
32	$C_{38}H_{37}N_3O_2S$	$C_{38}H_{37}N_3O_2SNa$	622.2495	622.2499	-0.06



Crystallographic details

(1) First, product **9** was solved with the mixture of 1.5 mL dichloromethane and 3 mL petroleum ether in a sample bottle, which was sealed/placed on the desk of the laboratory. Next, the crystal of the fused cycle **9** was precipitated via volatilizing after several days.

(2) Single crystal of product **9 [**$C_{23}H_{12}ClN_3OS$**]** was obtained as follows: A proper crystal was selected and detected on a "Bruker APEX2" diffractometer. The crystal stayed at 273.0 K during data collection. With the assistance of Shelxtl, the structure was solved with the XShell structure solution program using Charge Flipping, and it was refined with the SHELXL [1] refinement package using Least Squares minimisation. Finally, crystal data and structure refinement parameters of product **9** are described as shown in **Table S1**. CCDC No. 2292600.

[1]. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Table 1. Crystal data and structure refinement for product **9**.

CCDC	2292600

Displacement ellipsoids are drawn at the 50% probability level

Empirical formula	$C_{23}H_{12}ClN_3OS$
Formula weight	413.87
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.2573(3) Å a= 95.3900(10) Å b = 11.1099(4) Å b= 107.9320(10) Å c = 11.4634(4) Å g = 109.8590(10) Å
Volume	917.59(6) $Å^3$
Z	2
Density (calculated)	1.498 Mg/m^3
Absorption coefficient	0.343 mm^{-1}
F(000)	424
Crystal size	0.460 x 0.220 x 0.150 mm^3
Theta range for data collection	1.999 to 29.620/°
Index ranges	-11<=h<=11, -15<=k<=15, -15<=l<=15
Reflections collected	57866
Independent reflections	5165 [R(int) = 0.0627]
Completeness to theta = 25.242°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5165 / 0 / 262
Goodness-of-fit on F^2	1.098
Final R indices [I>2sigma(I)]	R1 = 0.0531, wR2 = 0.1343
R indices (all data)	R1 = 0.0626, wR2 = 0.1451
Largest diff. peak and hole	0.610 and -0.266 e.$Å^3$

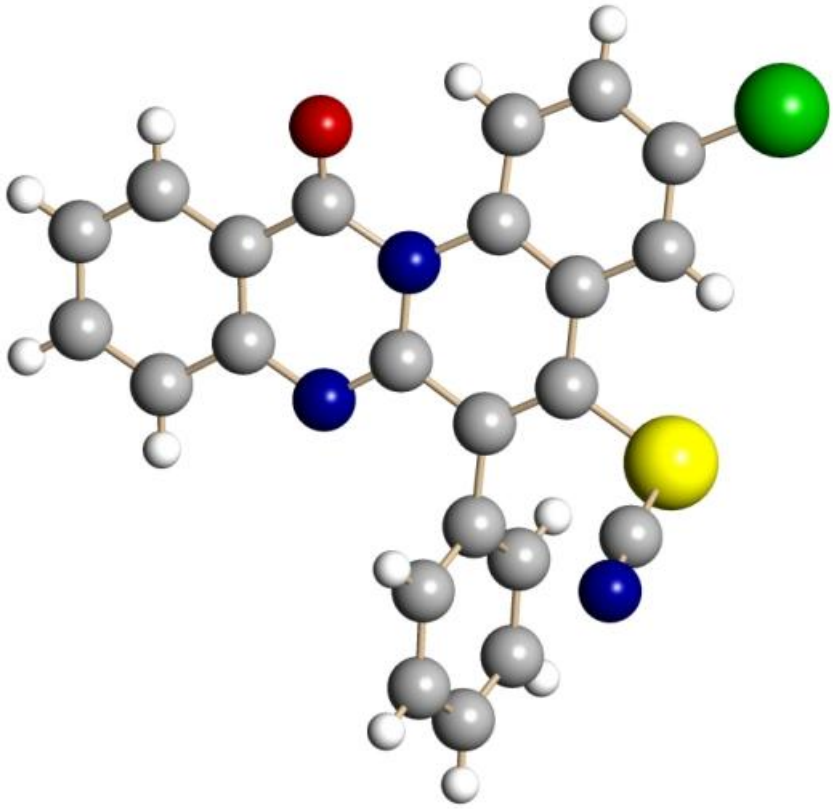


Fig. S4 Structure of product **9**.

Physical data and references for the following products

References:

1. S. Chen, Q. Yan, J. Fan, Y. Gao, X. Yang, L.-J. Li, Z.-Q. Liu and Z.-J. Li, *Green Chem.*, 2022, **24**, 4742.

2. S. Chen, Q. Yan, J. Fan, C. Guo, L.-J. Li, Z.-Q. Liu and Z.-J. Li, *Green Chem.*, 2023, **25**, 153-160.

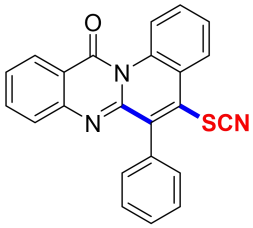
3. F. Zeng, Z. Zhang, P. Yin, F. Cheng, X.-L. Chen, L.-B. Qu, Z.-Y. Cao and B. Yu, *Org. Lett.*, 2022, **24**, 7912−7917.

4. A. Huang, H. Zhu, F. Zeng, X.-L. Chen, X. Huang, L. Qu and B. Yu, *Org. Lett.*, 2022, **24**, 3014−3018.

Physical data for the following products:

1. 6-phenyl-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/1). 26.8 mg, 71% yield. Mp: 216-217 ℃.



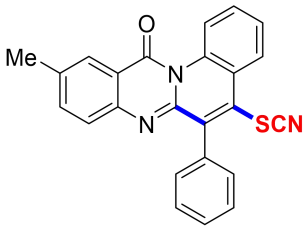
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.36 (dd, *J* = 8.8, 1.2 Hz, 1H), 8.44 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.30 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.72 – 7.69 (m, 1H), 7.66 – 7.62 (m, 1H), 7.60 – 7.53 (m, 5H), 7.37 – 7.35 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 146.1, 145.6, 144.1, 136.2, 135.0, 134.7, 130.2, 129.9, 129.3, 128.9, 128.4, 127.9, 127.5, 127.3, 127.0, 126.7, 122.3, 121.6, 120.1, 108.9.

HRMS (ESI, m/z): Calculated for $C_{23}H_{14}N_3OS$ $(M+H)^+$ 380.0852, Measured 380.0852.

2. 10-methyl-6-phenyl-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/2). 31.3 mg, 80% yield. Mp: 229-230 ℃.



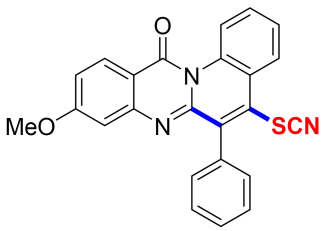
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (d, *J* = 8.4 Hz, 1H), 8.28 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.21 (s, 1H), 7.71 – 7.67 (m, 1H), 7.64 – 7.60 (m, 1H), 7.58 – 7.53 (m, 4H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.37 – 7.34 (m, 2H), 2.53 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 145.5, 144.3, 143.7, 138.0, 136.3, 135.1, 130.1, 129.9, 128.9, 128.7, 128.3, 127.7, 126.9, 126.7, 126.5, 122.3, 121.6, 119.8, 109.0, 21.6.

HRMS (ESI, m/z): Calculated for $C_{24}H_{16}N_3OS$ $(M+H)^+$ 394.1009, Measured 394.1007.

3. 9-methoxy-6-phenyl-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/3). 28.5 mg, 70% yield. Mp: 203-204 ℃.



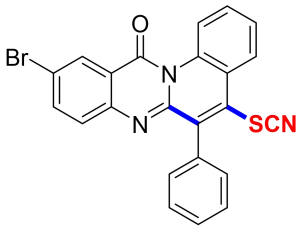
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.38 (d, *J* = 8.8, 1H), 8.32 – 8.27 (m, 2H), 7.71 – 7.67 (m, 1H), 7.64 – 7.59 (m, 1H), 7.57 – 7.55 (m, 3H), 7.38 – 7.35 (m, 2H), 7.10 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 3.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 162.0, 147.9, 146.8, 143.9, 136.3, 135.2, 130.5, 130.2, 129.9, 129.6, 128.9, 128.4, 126.8, 126.7, 122.2, 121.7, 118.3, 113.7, 109.0, 107.7, 55.8.

HRMS (ESI, m/z): Calculated for $C_{24}H_{16}N_3O_2S$ $(M+H)^+$ 410.0958, Measured 410.0956.

4. 10-bromo-6-phenyl-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/2). 36.2 mg, 79% yield. Mp: 233-234 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.34 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 8.30 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.79 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.56 – 7.55 (m, 3H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.36 – 7.33 (m, 2H).

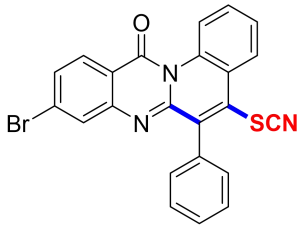
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 146.3, 144.4, 143.9, 137.9, 135.9, 134.9, 130.4, 129.9, 129.8, 129.7, 129.6, 129.0, 128.4, 127.3, 126.8, 122.3, 121.9, 121.2, 121.0, 108.7.

HRMS (ESI, m/z): Calculated for $C_{23}H_{13}BrN_3OS$ $(M+H)^+$ 459.9939, Measured 459.9936.

5. 9-bromo-6-phenyl-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum

ether/dichloromethane = 1/1). 39.4 mg, 86% yield. Mp: 231-232 ℃.



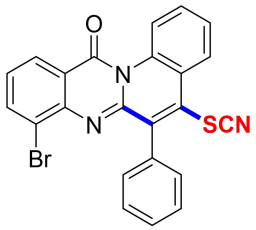
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.34 (d, *J* = 8.8 Hz, 1H), 8.31 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.74 (dd, *J* = 4.4, 1.6 Hz, 1H), 7.71 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.61 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.57 – 7.55 (m, 3H), 7.35 – 7.33 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0, 147.0, 146.4, 143.8, 135.9, 134.9, 130.7, 130.4, 130.3, 130.2, 129.8, 129.6, 129.1, 128.7, 128.4, 127.2, 126.8, 122.2, 121.6, 118.8, 108.7.

HRMS (ESI, m/z): Calculated for $C_{23}H_{13}BrN_3OS$ $(M+H)^+$ 459.9939, Measured 459.9935.

6. 8-bromo-6-phenyl-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 3/1). 28.3 mg, 62% yield. Mp: 212-213 ℃.



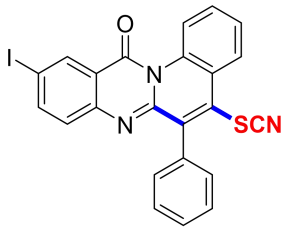
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39 (d, *J* = 8.8 Hz, 1H), 8.37 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.33 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.01 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.68 – 7.64 (m, 1H), 7.59 – 7.52 (m, 3H), 7.43 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1, 146.4, 144.2, 143.4, 138.2, 135.5, 134.8, 130.4, 130.2, 129.8, 129.0, 128.2, 127.7, 127.3, 126.9, 126.8, 123.2, 122.4, 121.5, 121.3, 108.8.

HRMS (ESI, m/z): Calculated for $C_{23}H_{13}BrN_3OS$ $(M+H)^+$ 459.9939, Measured 459.9936.

7. 10-iodo-6-phenyl-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/1). 43.3 mg, 86% yield. Mp: 213-214 ℃.



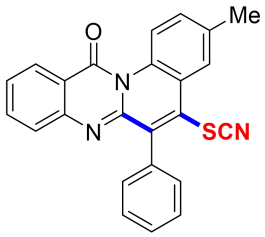
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.31 (d, *J* = 8.4 Hz, 1H), 8.74 (d, *J* = 2.0 Hz, 1H), 8.30 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.98 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.56 – 7.55 (m, 3H), 7.35 – 7.33 (m, 2H), 7.29 (d, *J* = 8.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 146.5, 144.8, 143.9, 143.4, 136.0, 135.9, 134.9, 130.4, 129.9, 129.8, 129.5, 129.0, 128.4, 127.3, 126.8, 122.3, 121.6, 121.5, 108.7, 91.9.

HRMS (ESI, m/z): Calculated for $C_{23}H_{13}IN_3OS$ $(M+H)^+$ 505.9819, Measured 505.9817.

8. 3-methyl-6-phenyl-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/1). 28.8 mg, 73% yield. Mp: 222-223 ℃.



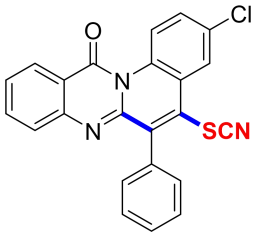
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.27 (d, *J* = 8.8 Hz, 1H), 8.42 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.06 (d, *J* = 1.2 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.58 – 7.55 (m, 4H), 7.53 – 7.49 (m, 2H), 7.37 – 7.35 (m, 2H), 2.57 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 146.1, 145.6, 144.1, 137.1, 136.3, 134.5, 132.9, 131.2, 129.9, 129.3, 128.9, 128.3, 127.8, 127.3, 127.2, 126.6, 122.2, 121.5, 120.0, 109.0, 21.3.

HRMS (ESI, m/z): Calculated for $C_{24}H_{16}N_3OS$ $(M+H)^+$ 394.1009, Measured 394.1007.

9. 3-chloro-6-phenyl-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 2/1). 28.9 mg, 70% yield. Mp: 220-221 ℃.



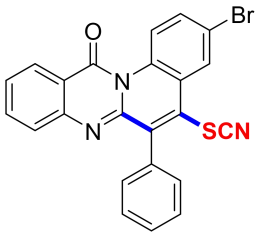
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (d, *J* = 9.6 Hz, 1H), 8.39 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.23 (d, *J* = 2.4 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.62 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.58 – 7.53 (m, 5H), 7.37 – 7.34 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 145.8, 145.7, 145.4, 135.9, 134.9, 133.5, 132.7, 130.4, 130.1, 129.7, 129.1, 128.4, 128.0, 127.8, 127.3, 126.1, 124.0, 123.1, 119.9, 108.5.

HRMS (ESI, m/z): Calculated for $C_{23}H_{13}ClN_3OS$ $(M+H)^+$ 414.0462, Measured 414.0461.

10. 3-bromo-6-phenyl-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/1). 27.7 mg, 60% yield. Mp: 216-217 ℃.



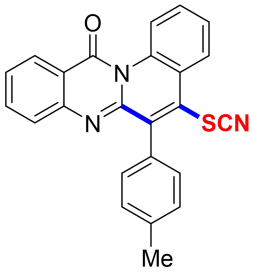
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.29 (d, *J* = 9.2 Hz, 1H), 8.43 – 8.39 (m, 2H), 7.79 – 7.75 (m, 2H), 7.59 – 7.54 (m, 5H), 7.36 – 7.34 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 145.8, 145.6, 145.4, 135.9, 134.9, 134.0, 133.0, 129.7, 129.1, 129.0, 128.4, 128.0, 127.9, 127.8, 127.3, 124.2, 123.2, 120.4, 119.9, 108.4.

HRMS (ESI, m/z): Calculated for $C_{23}H_{13}BrN_3OS$ $(M+H)^+$ 459.9939, Measured 459.9936.

11. 5-thiocyanato-6-(p-tolyl)-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/1). 31.7 mg, 81% yield. Mp: 178-179 ℃.



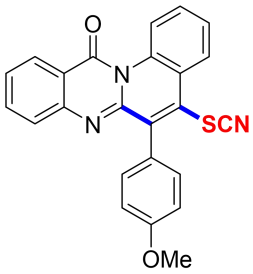
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (d, *J* = 8.8 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.28 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.71 – 7.66 (m, 1H), 7.64 – 7.59 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.51 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 146.2, 145.7, 144.1, 139.0, 135.0, 134.6, 133.2, 130.0, 129.9, 129.2, 129.1, 127.9, 127.4, 127.3, 127.0, 126.7, 122.3, 121.6, 120.1, 109.1, 21.5.

HRMS (ESI, m/z): Calculated for $C_{24}H_{16}N_3OS$ $(M+H)^+$ 394.1009, Measured 394.1007.

12. 6-(4-methoxyphenyl)-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/1). 31.9 mg, 78% yield. Mp: 192-193 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.31 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.28 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.71 – 7.67 (m, 1H), 7.63 (t, *J* =

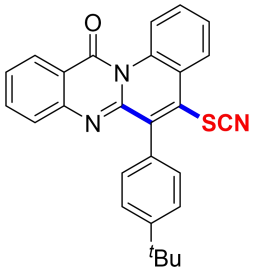
8.0 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 3.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 160.1, 146.3, 145.7, 143.6, 134.9, 134.7, 131.6, 130.0, 129.3, 128.2, 127.9, 127.4, 127.3, 127.0, 126.8, 122.4, 121.6, 120.1, 113.7, 109.1, 55.4.

HRMS (ESI, m/z): Calculated for $C_{24}H_{16}N_3O_2S$ $(M+H)^+$ 410.0958, Measured 410.0956.

13. 6-(4-(tert-butyl)phenyl)-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/1). 36.9 mg, 85% yield. Mp: 180-181 ℃.



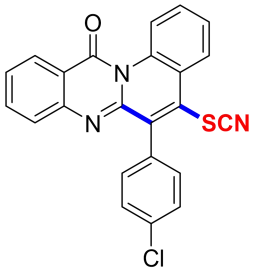
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (d, *J* = 8.8 Hz, 1H), 8.43 (d, *J* = 7.6 Hz, 1H), 8.29 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.71 – 7.67 (m, 1H), 7.64 – 7.61 (m, 2H), 7.54 (dd, *J* = 10.8, 8.0 Hz, 3H), 7.29 (d, *J* = 8.4 Hz, 2H), 1.44 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 152.1, 146.2, 145.7, 144.0, 134.9, 134.6, 133.0, 130.0, 129.7, 129.3, 127.9, 127.4, 127.3, 127.0, 126.8, 125.3, 122.4, 121.6, 120.1, 109.2, 34.9, 31.3.

HRMS (ESI, m/z): Calculated for $C_{27}H_{22}N_3OS$ $(M+H)^+$ 436.1478, Measured 436.1477.

14. 6-(4-chlorophenyl)-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/1). 35.7 mg, 86% yield. Mp: 214-215 ℃.



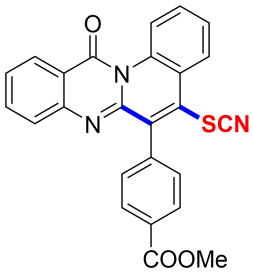
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (d, *J* = 8.8 Hz, 1H), 8.42 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.28 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.70 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.56 (dd, *J* = 16.0, 8.4 Hz, 4H), 7.32 – 7.30 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4, 145.8, 145.5, 143.1, 135.1, 135.0, 134.8, 134.5, 131.3, 130.4, 129.5, 128.7, 127.8, 127.6, 127.3, 127.1, 126.7, 122.1, 121.6, 120.1, 108.6.

HRMS (ESI, m/z): Calculated for $C_{23}H_{13}ClN_3OS$ $(M+H)^+$ 414.0462, Measured 414.0461.

15. methyl 4-(12-oxo-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-6-yl)benzoate

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/3). 33.9 mg, 77% yield. Mp: 215-216 ℃.



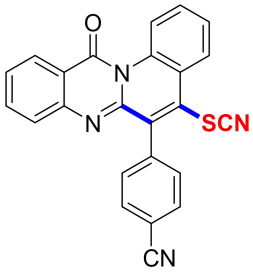
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 7.6 Hz, 1H), 8.29 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.70 (m, 2H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 4.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 162.4, 145.7, 145.4, 143.5, 140.7, 135.2, 134.8, 130.6, 130.5, 130.0, 129.6, 129.3, 127.7, 127.6, 127.3, 127.1, 126.7, 122.1, 121.7, 120.1, 108.5, 52.3.

HRMS (ESI, m/z): Calculated for $C_{25}H_{16}N_3O_3S$ $(M+H)^+$ 438.0907, Measured 438.0905.

16. 4-(12-oxo-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-6-yl)benzonitrile

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/4). 31.2 mg, 77% yield. Mp: 213-214 ℃.



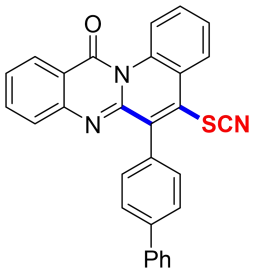
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41 (d, *J* = 8.4 Hz, 1H), 8.43 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.31 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.80 – 7.72 (m, 2H), 7.67 – 7.63 (m, 1H), 7.59 – 7.50 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 145.5, 145.3, 142.7, 140.8, 135.3, 134.9, 132.2, 130.9, 130.8, 129.5, 127.8, 127.7, 127.4, 127.2, 126.8, 122.0, 121.8, 120.1, 118.5, 112.8, 108.2.

HRMS (ESI, m/z): Calculated for $C_{24}H_{13}N_4OS$ $(M+H)^+$ 405.0805, Measured 405.0804.

17. 6-([1,1'-biphenyl]-4-yl)-5-thiocyanato-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/2). 40.4 mg, 89% yield. Mp: 230-231 ℃.



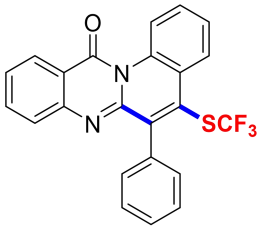
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.36 (dd, *J* = 8.8, 0.8 Hz, 1H), 8.44 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.31 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.76 – 7.69 (m, 4H), 7.66 – 7.61 (m, 2H), 7.57 – 7.49 (m, 3H), 7.43 (dd, *J* = 15.2, 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 146.1, 145.6, 143.8, 141.7, 140.3, 135.0, 134.9, 134.7, 130.5, 130.2, 129.4, 128.9, 127.9, 127.7, 127.5, 127.3, 127.2, 127.0, 126.9, 126.8, 122.3, 121.6, 120.1, 109.0.

HRMS (ESI, m/z): Calculated for $C_{29}H_{18}N_3OS$ $(M+H)^+$ 456.1165, Measured 456.1164.

18. 6-phenyl-5-((trifluoromethyl)thio)-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 38.5 mg, 91% yield. Mp: 160-161 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.29 (d, *J* = 8.8 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.56 – 7.47 (m, 6H), 7.34 (d, *J* = 4.0 Hz, 2H).

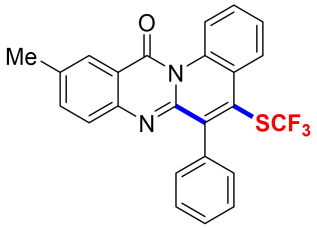
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 147.6, 146.7, 145.7, 136.9, 134.6, 134.5, 130.1, 129.9, 129.5, 128.4 (q, *J* = 308.5 Hz), 128.1, 127.9, 127.7, 127.3, 127.1, 126.5, 124.7, 121.2, 120.0.

^{19}F NMR (565 MHz, $CDCl_3$): δ -39.21 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{23}H_{14}F_3N_2OS$ $(M+H)^+$ 423.0773, Measured 423.0756.

19. 10-methyl-6-phenyl-5-((trifluoromethyl)thio)-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 35.1 mg, 80% yield. Mp: 167-168 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.28 (d, *J* = 8.8 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.22 (s, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.56 – 7.46 (m, 6H), 7.31 – 7.26 (m, 2H), 2.53 (s, 3H).

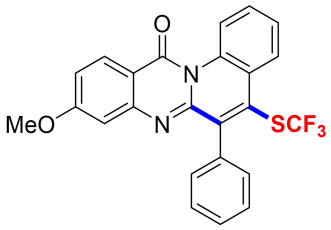
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 147.7, 146.0, 143.8, 137.7, 136.9, 136.1, 134.7, 130.1, 129.4, 129.3, 128.5 (q, J = 309.9 Hz), 128.0, 127.8, 127.7, 127.6, 126.4 (d, J = 2.5 Hz), 124.8, 121.2, 119.8, 21.5.

^{19}F NMR (565 MHz, $CDCl_3$): δ -39.29 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{24}H_{16}F_3N_2OS$ $(M+H)^+$ 437.0930, Measured 437.0928.

20. 9-methoxy-6-phenyl-5-((trifluoromethyl)thio)-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 38.5 mg, 85% yield. Mp: 207-208 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (d, J = 8.4 Hz, 1H), 8.45 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.8 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.57 – 7.51 (m, 4H), 7.31 – 7.29 (m, 2H), 7.09 (dd, J = 8.8, 2.4 Hz, 1H), 6.88 (d, J = 2.4 Hz, 1H), 3.85 (s, 3H).

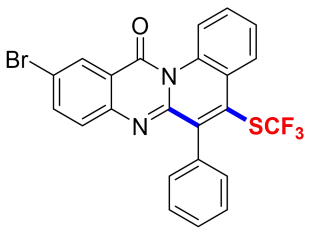
^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 162.1, 148.0, 147.3, 137.0, 134.8, 130.2, 129.5, 128.7, 128.4 (q, J = 309.9 Hz), 128.0, 127.8, 127.7, 126.3, 124.7, 121.3, 118.2, 113.7, 107.6, 55.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ -39.21 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{24}H_{16}F_3N_2O_2S$ $(M+H)^+$ 453.0879, Measured 453.0877.

21. 10-bromo-6-phenyl-5-((trifluoromethyl)thio)-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 44.5 mg, 89% yield. Mp: 182-183 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (d, *J* = 8.4 Hz, 1H), 8.52 (d, *J* = 2.0 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 7.77 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.51 – 7.50 (m, 3H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.29 – 7.28 (m, 2H).

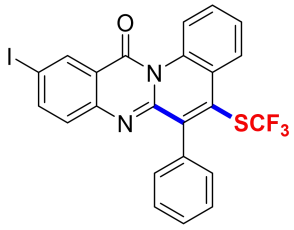
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 147.4, 146.9, 144.4, 137.7, 136.6, 134.5, 130.4, 130.1, 129.7, 129.6, 128.3 (q, *J* = 313.5 Hz), 128.1, 127.8, 124.8, 121.2, 120.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -39.13 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{23}H_{13}BrF_3N_2OS$ $(M+H)^+$ 500.9879, Measured 500.9876.

22. 10-iodo-6-phenyl-5-((trifluoromethyl)thio)-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 48.0 mg, 88% yield. Mp: 192-193 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.23 (d, *J* = 8.8 Hz, 1H), 8.72 (d, *J* = 2.0 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 7.93 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.49 – 7.48 (m, 3H), 7.27 – 7.25 (m, 3H).

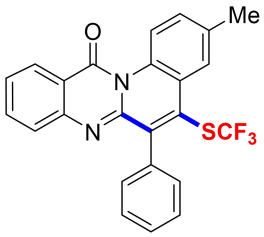
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 147.4, 147.1, 144.9, 143.2, 136.6, 135.9, 134.5, 130.5, 130.1, 129.8, 129.6, 128.3 (q, *J* = 312.1 Hz), 128.2, 127.8, 127.7, 124.8, 121.4, 121.1, 91.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -39.10 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{23}H_{13}F_3IN_2OS$ $(M+H)^+$ 548.9740, Measured 548.9737.

23. 3-methyl-6-phenyl-5-((trifluoromethyl)thio)-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 41.0 mg, 94% yield. Mp: 225-226 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.21 (d, *J* = 8.8 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.23 (s, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.57 – 7.45 (m, 6H), 7.30 – 7.29 (m, 2H), 2.53 (s, 3H).

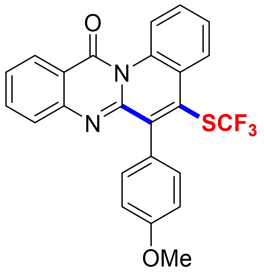
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 147.5, 146.7, 145.8, 137.0, 136.5, 134.4, 132.5, 130.6, 130.2, 129.9, 128.5 (q, *J* = 309.9 Hz), 128.0, 127.9, 127.7, 127.6, 127.1 (d, *J* = 3.1 Hz), 124.7, 121.1, 120.0, 21.2.

^{19}F NMR (565 MHz, $CDCl_3$): δ -39.23 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{24}H_{16}F_3N_2OS$ $(M+H)^+$ 437.0930, Measured 437.0929.

24. 6-(4-methoxyphenyl)-5-((trifluoromethyl)thio)-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 27.0 mg, 60% yield. Mp: 152-153 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (d, *J* = 8.0 Hz, 1H), 8.46 – 8.42 (m, 2H), 7.76 – 7.72 (m, 1H), 7.66 – 7.60 (m, 2H), 7.57 – 7.51 (m, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 3.93 (s, 3H).

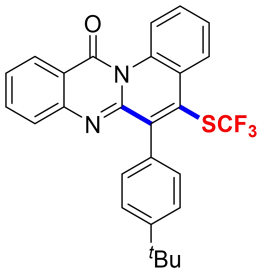
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 159.4, 147.3, 146.9, 145.8, 134.5, 131.7, 129.9, 129.4, 129.0, 128.5 (q, *J* = 309.9 Hz), 127.9, 127.7, 127.2 (d, *J* = 7.5 Hz), 126.5, 124.9, 121.2, 120.0, 113.1, 55.2.

^{19}F NMR (565 MHz, $CDCl_3$): δ -39.38 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{24}H_{16}F_3N_2O_2S$ $(M+H)^+$ 453.0879, Measured 453.0877.

25. 6-(4-(tert-butyl)phenyl)-5-((trifluoromethyl)thio)-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 42.2 mg, 88% yield. Mp: 147-148 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (d, *J* = 8.8 Hz, 1H), 8.44 (t, *J* = 8.4 Hz, 2H), 7.73 (t, *J* = 7.2 Hz, 1H), 7.63 (dd, *J* = 15.6, 8.4 Hz, 2H), 7.57 – 7.50 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 2H), 1.44 (s, 9H).

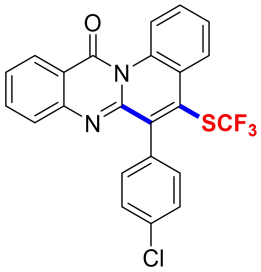
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 151.0, 147.7, 146.8, 145.8, 134.5, 134.4, 133.7, 129.9, 129.8, 129.4, 128.5 (q, *J* = 309.9 Hz), 128.0, 127.7, 127.2 (d, *J* = 7.7 Hz), 126.4, 124.9, 124.6, 121.2, 120.0, 34.7, 31.4.

^{19}F NMR (565 MHz, $CDCl_3$): δ -39.30 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{27}H_{22}F_3N_2OS$ $(M+H)^+$ 479.1399, Measured 479.1397.

26. 6-(4-chlorophenyl)-5-((trifluoromethyl)thio)-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 40.2 mg, 88% yield. Mp: 183-184 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.29 (d, *J* = 8.8 Hz, 1H), 8.45 – 8.41 (m, 2H), 7.77 – 7.73 (m, 1H), 7.68 – 7.64 (m, 1H), 7.58 – 7.51 (m, 3H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H).

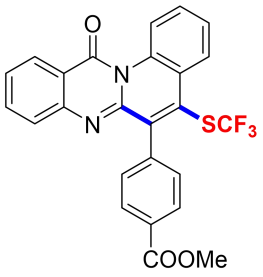
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 146.5, 146.4, 145.6, 135.2, 134.7, 134.6, 134.1, 131.6, 130.1, 129.8, 128.4 (q, *J* = 310.0 Hz), 128.1, 127.8, 127.4, 127.2, 126.6, 124.6, 121.2, 120.1.

^{19}F NMR (565 MHz, $CDCl_3$): δ -39.19 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{23}H_{13}ClF_3N_2OS$ $(M+H)^+$ 457.0384, Measured 457.0381.

27. methyl 4-(12-oxo-5-((trifluoromethyl)thio)-12H-quinolino[2,1-b]quinazolin-6-yl)benzoate

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 43.2 mg, 90% yield. Mp: 200-201 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (d, *J* = 8.4 Hz, 1H), 8.43 (t, *J* = 8.4 Hz, 2H), 8.18 (d, *J* = 8.0 Hz, 2H), 7.75 – 7.71 (m, 1H), 7.69 – 7.65 (m, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 3.99 (s, 3H).

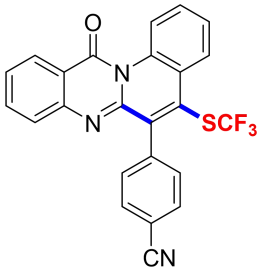
^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 162.5, 146.7, 146.3, 145.6, 141.6, 134.8, 134.6, 130.3, 129.9, 129.8, 129.1, 128.3 (q, *J* = 310.2 Hz), 127.8, 127.4, 127.2, 126.6, 124.5, 121.3, 120.1, 52.2.

^{19}F NMR (565 MHz, $CDCl_3$): δ -39.13 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{25}H_{16}F_3N_2O_3S$ $(M+H)^+$ 481.0828, Measured 481.0826.

28. 4-(12-oxo-5-((trifluoromethyl)thio)-12H-quinolino[2,1-b]quinazolin-6-yl)benzonitrile

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 38.5 mg, 86% yield. Mp: 169-170 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.34 (d, *J* = 8.8 Hz, 1H), 8.44 (t, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.69 (t, *J* = 8.4 Hz, 1H), 7.60 – 7.51 (m, 3H), 7.42 (d, *J* = 7.6 Hz, 2H).

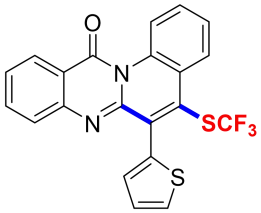
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4, 146.0, 145.8, 145.4, 141.6, 134.9, 134.8, 131.7, 131.1, 130.3, 130.2, 128.2 (q, *J* = 307.7 Hz), 127.8, 127.6 (d, *J* = 5.8 Hz), 127.3, 124.2, 121.3, 120.1, 118.8, 112.0.

^{19}F NMR (565 MHz, $CDCl_3$): δ -39.06 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{24}H_{13}F_3N_3OS$ $(M+H)^+$ 448.0726, Measured 448.0724.

29. 6-(thiophen-2-yl)-5-((trifluoromethyl)thio)-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 35.3 mg, 82% yield. Mp: 180-181 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22 (d, *J* = 8.8 Hz, 1H), 8.43 (t, *J* = 6.8 Hz, 2H), 7.79 – 7.75 (m, 1H), 7.69 – 7.62 (m, 3H), 7.57 – 7.52 (m, 2H), 7.21 – 7.16 (m, 2H).

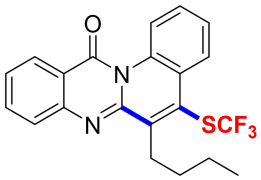
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 146.4, 145.6, 140.5, 136.2, 134.6, 134.5, 131.8, 130.7, 129.8, 128.4 (q, *J* = 310.2 Hz), 128.2, 127.8, 127.4, 127.2, 126.5, 126.1, 124.7, 121.2, 120.1.

^{19}F NMR (565 MHz, $CDCl_3$): δ -39.27 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{21}H_{12}F_3N_2OS_2$ $(M+H)^+$ 429.0338, Measured 429.0336.

30. 6-butyl-5-((trifluoromethyl)thio)-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 20.2 mg, 50% yield. Mp: 115-116 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.23 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 7.6 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 7.86 – 7.81 (m, 2H), 7.59 – 7.54 (m, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 3.51 – 3.48 (m, 2H), 1.71 – 1.64 (m, 2H), 1.54 (dd, *J* = 14.4, 7.2 Hz, 2H), 1.03 (t, *J* = 7.2 Hz, 3H).

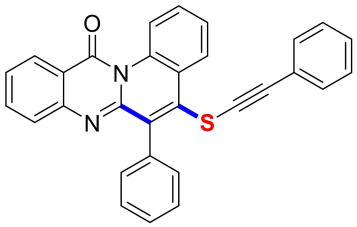
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 148.3, 145.8, 145.6, 134.6, 134.0, 129.5, 128.9 (q, *J* = 311.8 Hz), 128.7, 127.6, 127.2, 127.1, 126.3, 124.9, 121.0, 120.4, 31.7, 23.0, 13.9, 1.0.

^{19}F NMR (565 MHz, $CDCl_3$): δ -39.57 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{21}H_{18}F_3N_2OS$ $(M+H)^+$ 403.1086, Measured 403.1086.

31. 6-phenyl-5-((phenylethynyl)thio)-12H-quinolino[2,1-b]quinazolin-12-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 12.7 mg, 28% yield.



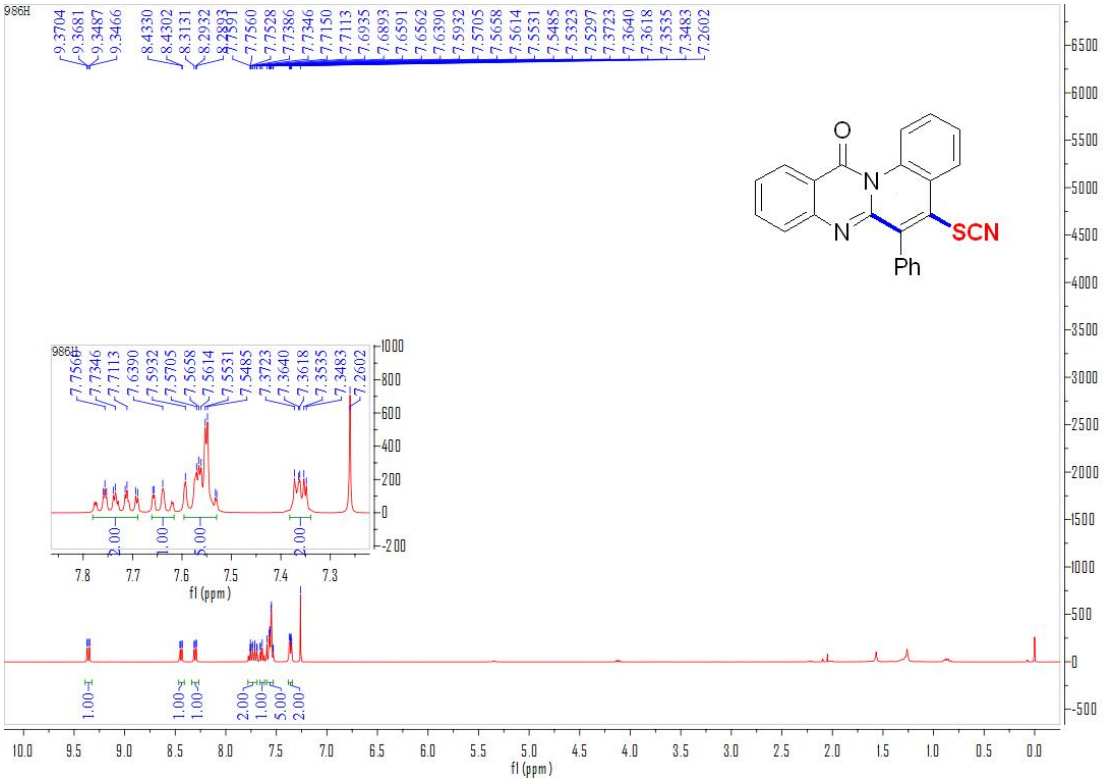
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (dd, *J* = 8.5, 0.8 Hz, 1H), 8.57 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.42 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.66 – 7.62 (m, 1H), 7.60 – 7.56 (m, 2H), 7.54 – 7.48 (m, 4H), 7.41 (dd, *J* = 7.8, 2.0 Hz, 2H), 7.29 – 7.24 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 146.6, 146.1, 139.9, 136.9, 136.6, 134.8, 134.4, 131.4, 130.4, 129.2, 128.6, 128.4, 128.2, 128.0, 127.8, 127.7, 127.2, 126.7, 126.3, 123.1, 122.5, 121.3, 120.8, 119.9, 94.6, 76.3.

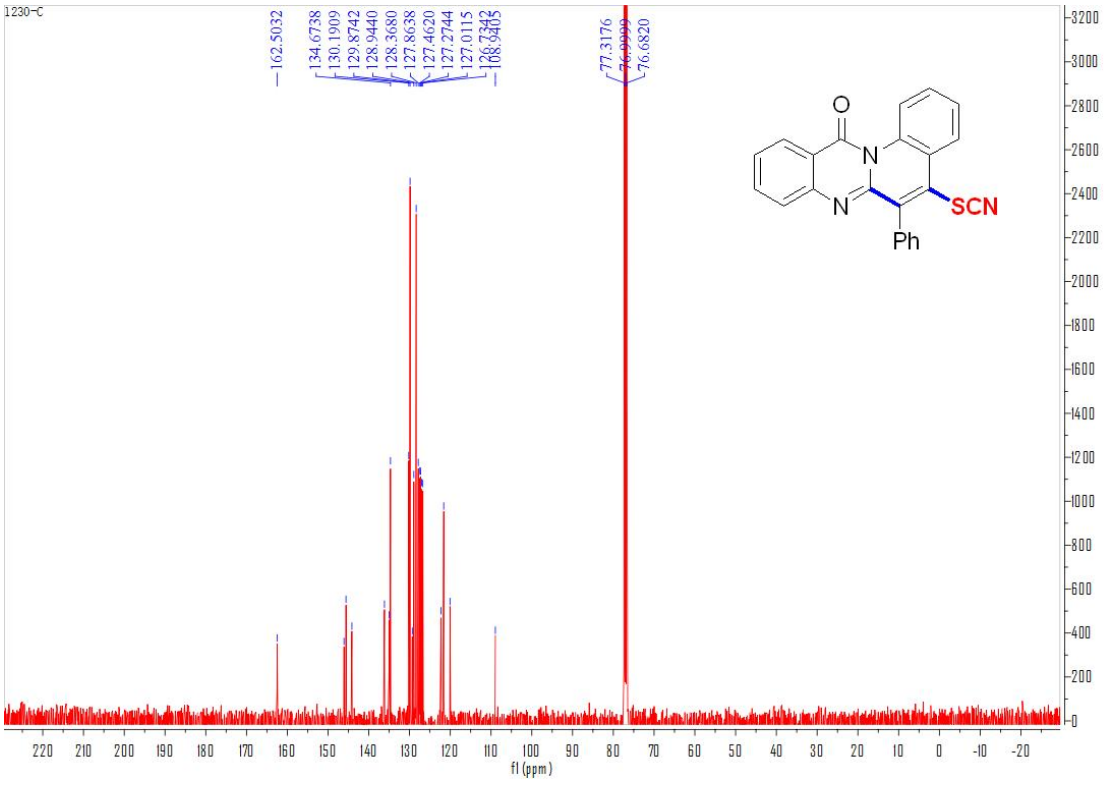
HRMS (ESI, m/z): Calculated for $C_{30}H_{19}N_2OS$ $(M+H)^+$ 455.1213, Measured 455.1221.

Copies of the ^{1}H NMR, ^{13}C NMR, ^{19}F NMR

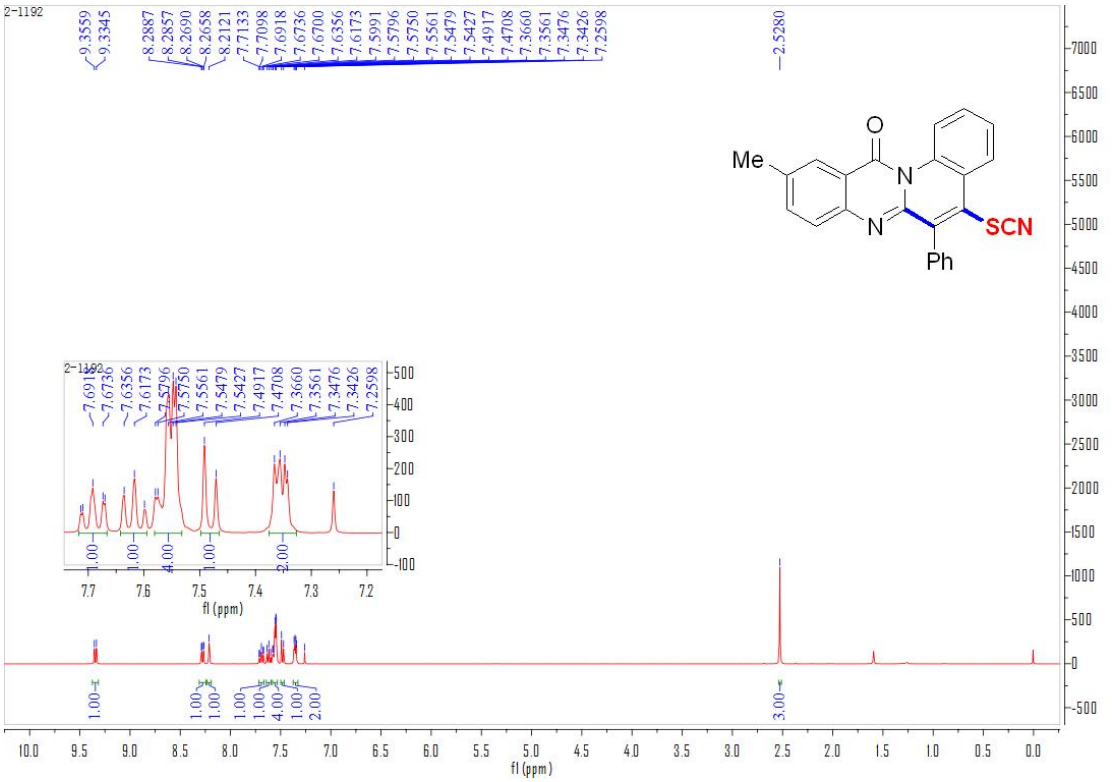
1-^{1}H NMR (400 MHz, $CDCl_3$)



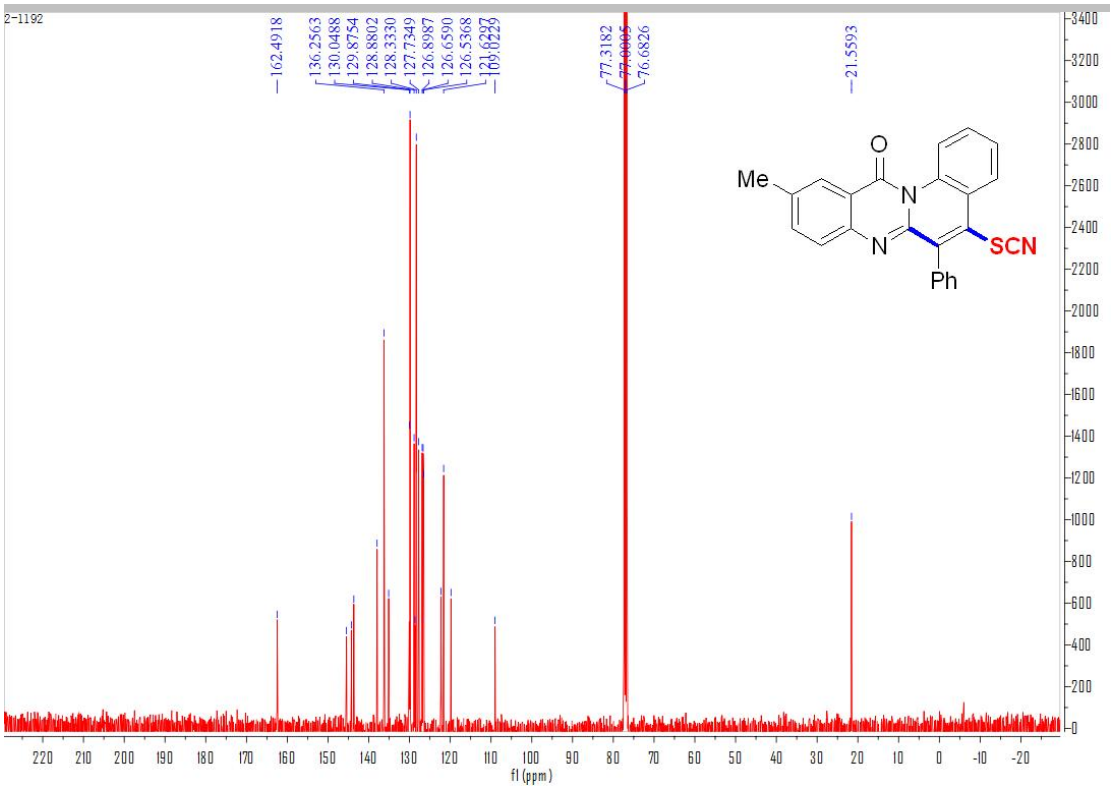
1-^{13}C NMR (100 MHz, $CDCl_3$)



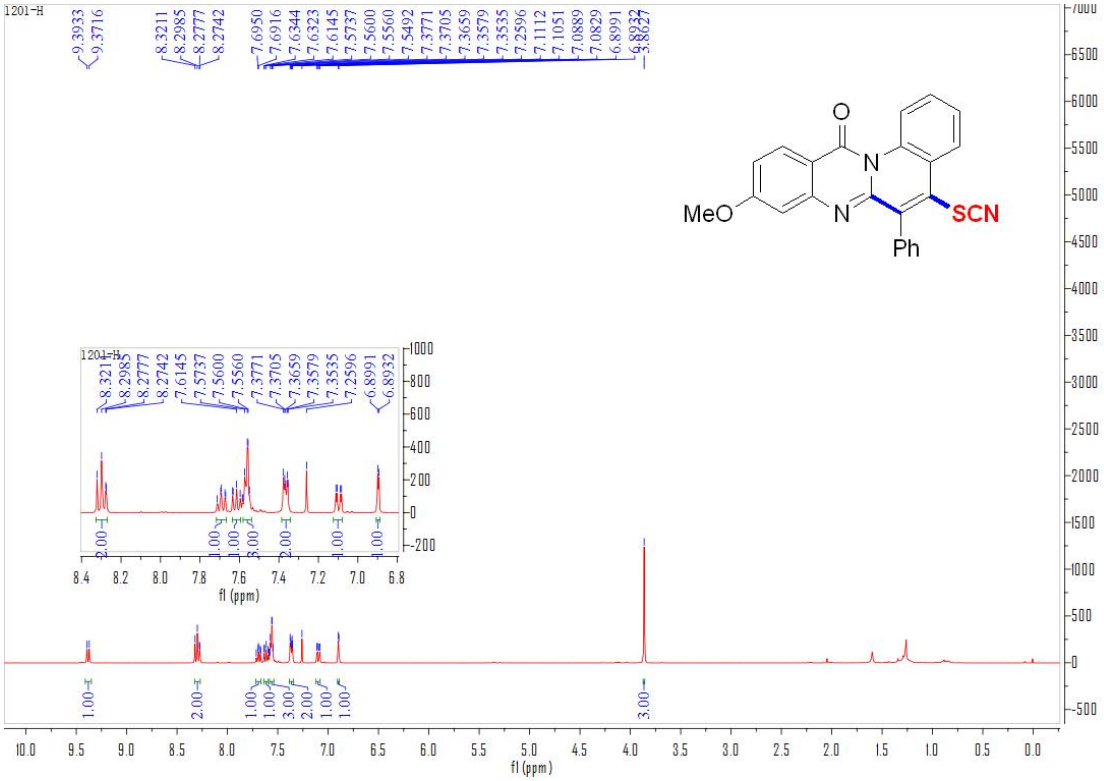
2-^{1}H NMR (400 MHz, $CDCl_3$)



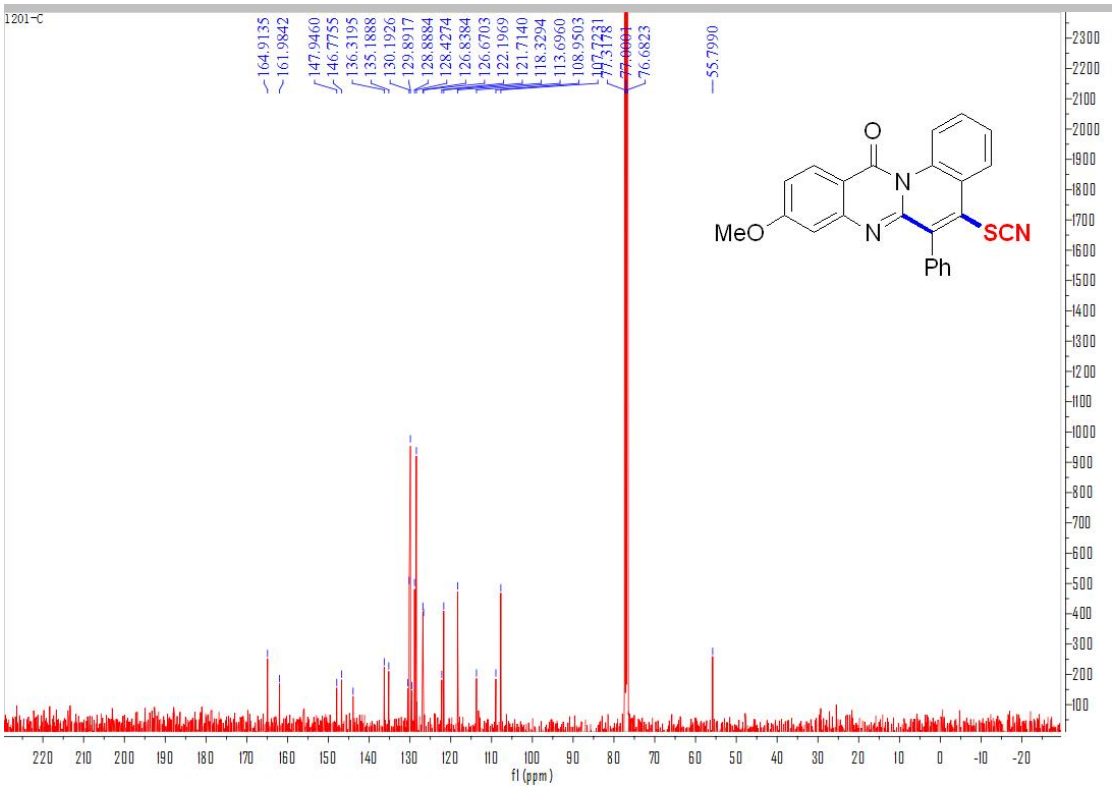
2-^{13}C NMR (100 MHz, $CDCl_3$)



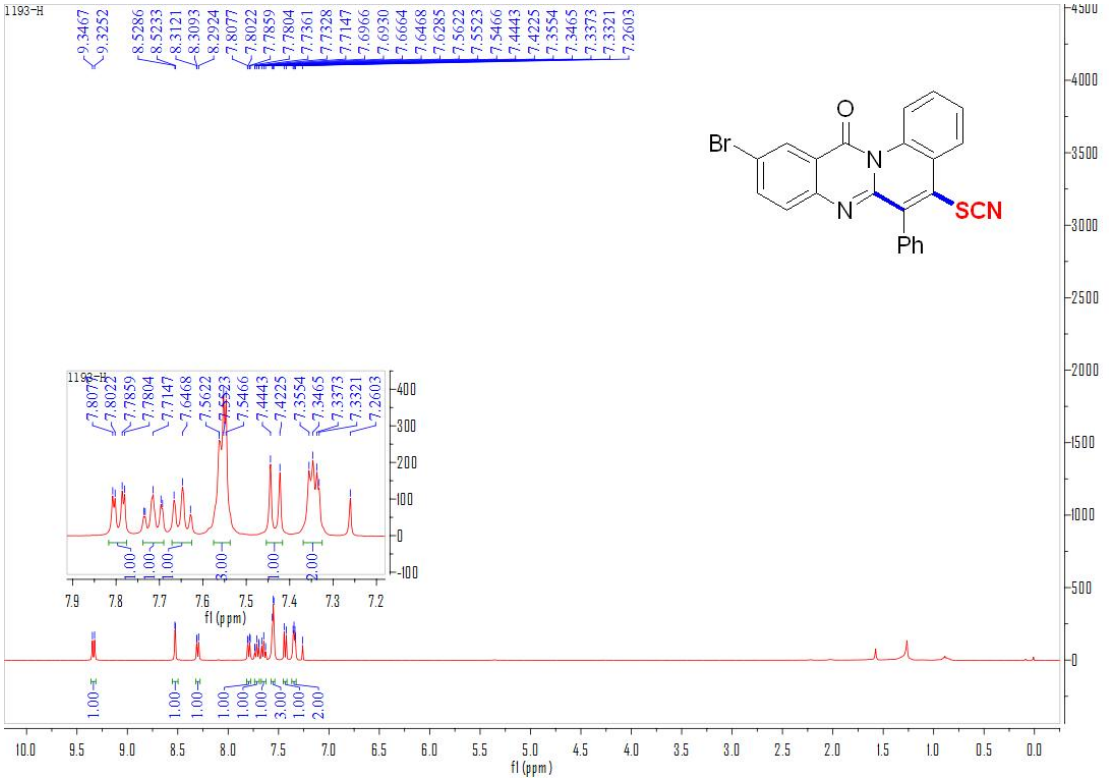
3-^{1}H NMR (400 MHz, $CDCl_3$)



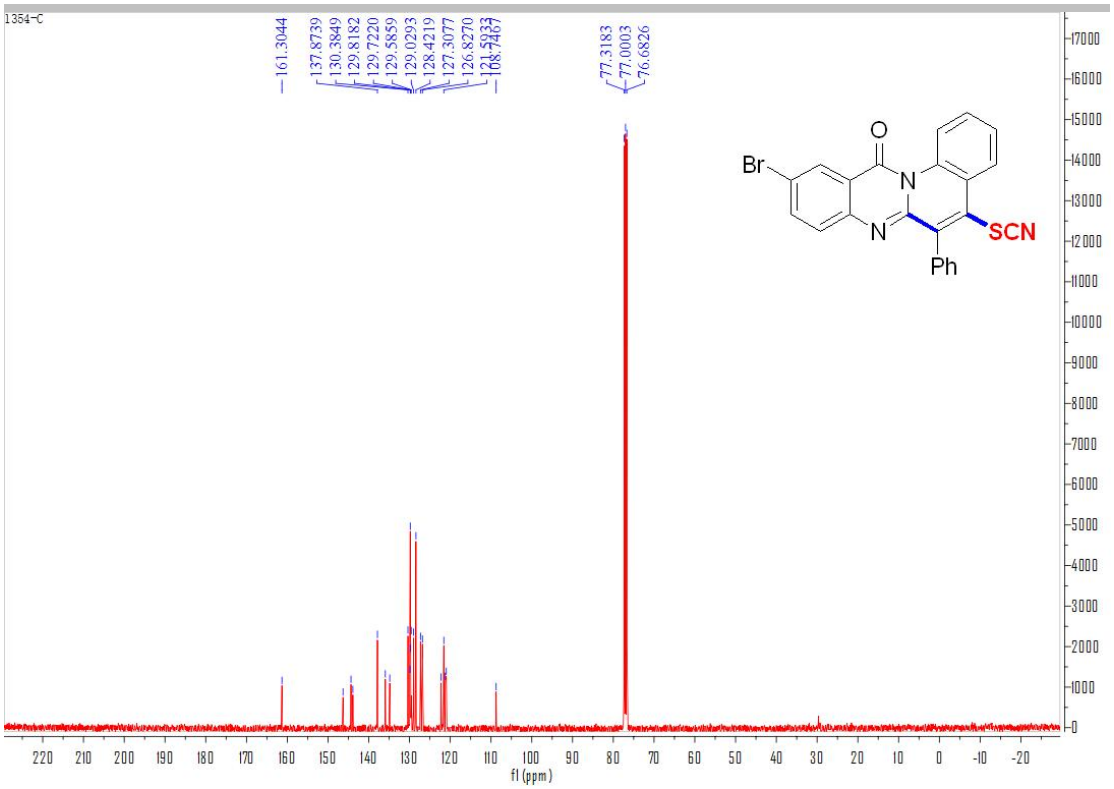
3-^{13}C NMR (100 MHz, $CDCl_3$)



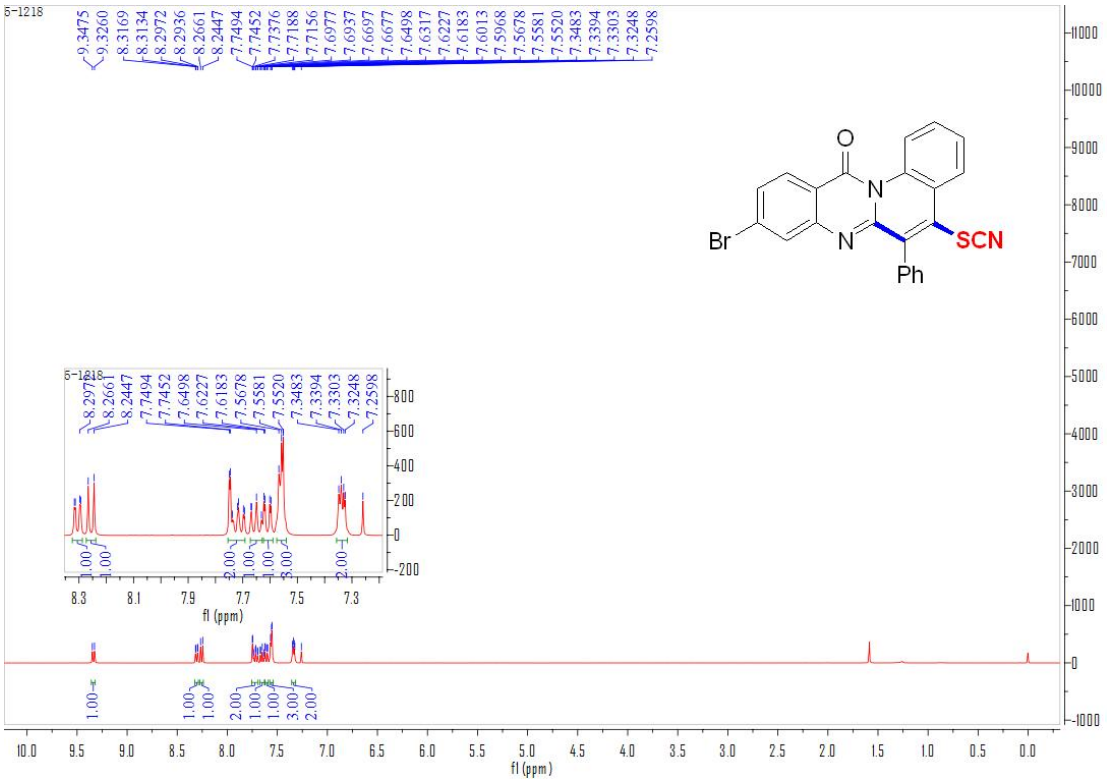
4-^{1}H NMR (400 MHz, $CDCl_3$)



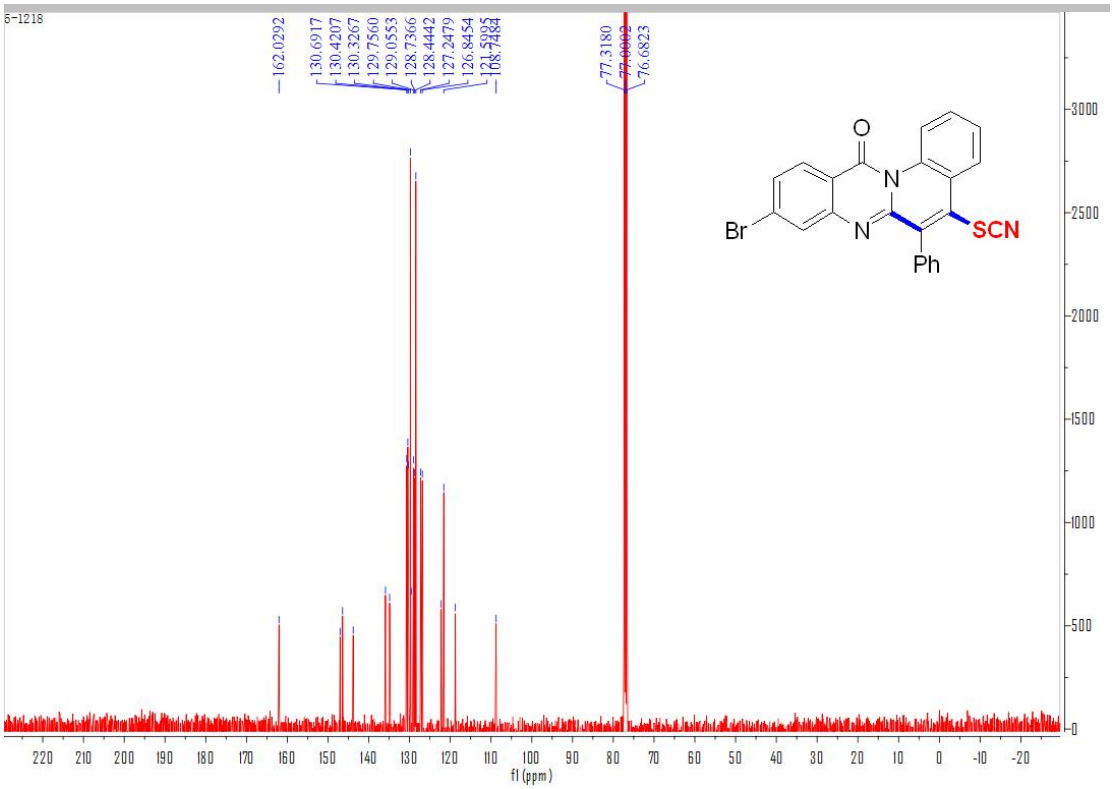
4-^{13}C NMR (100 MHz, $CDCl_3$)



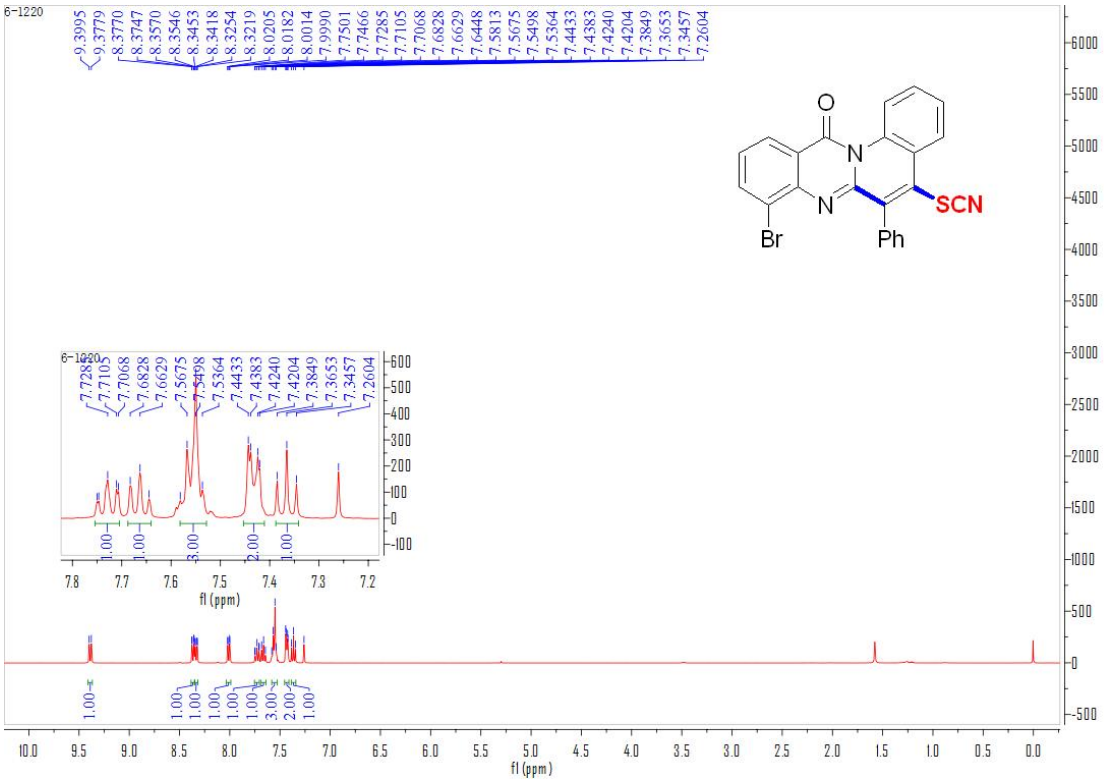
5-^{1}H NMR (400 MHz, $CDCl_3$)



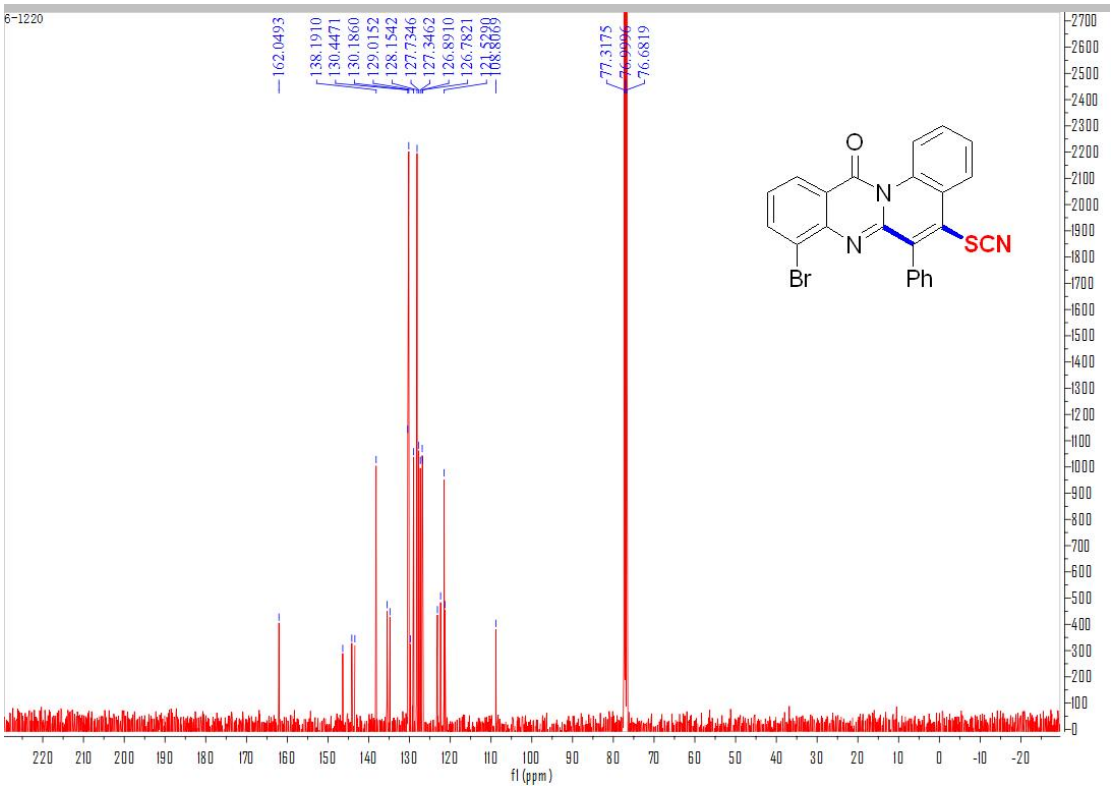
5-^{13}C NMR (100 MHz, $CDCl_3$)



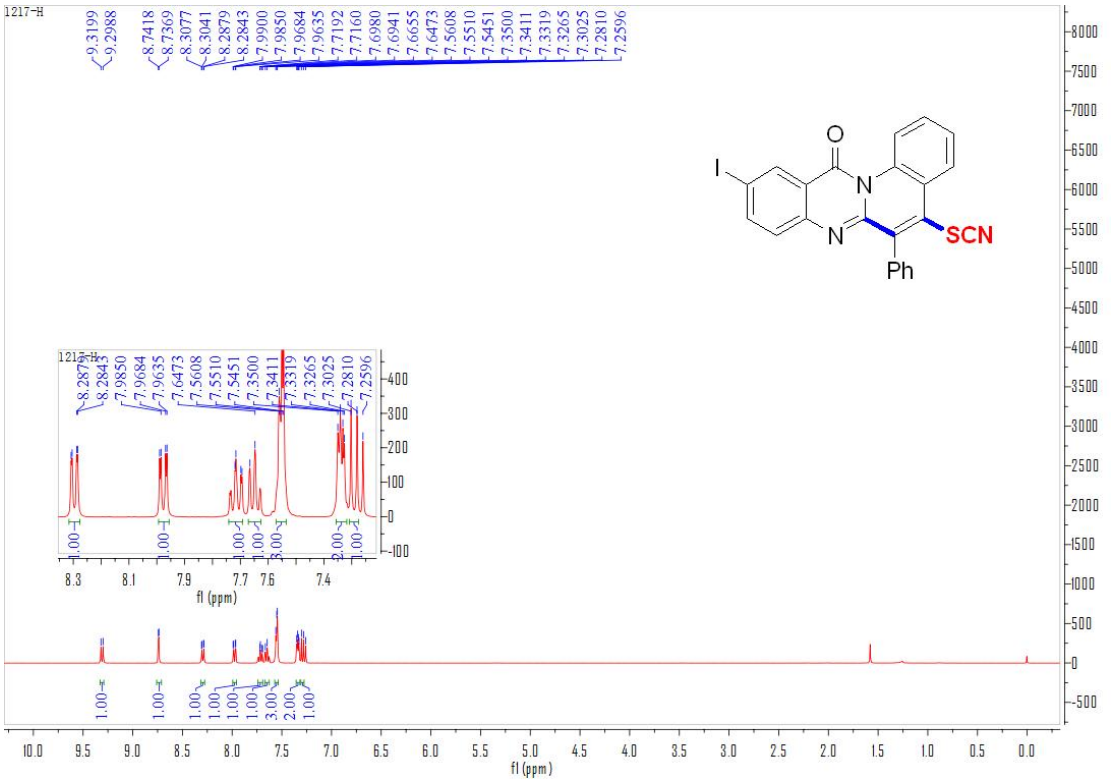
6-^{1}H NMR (400 MHz, $CDCl_3$)



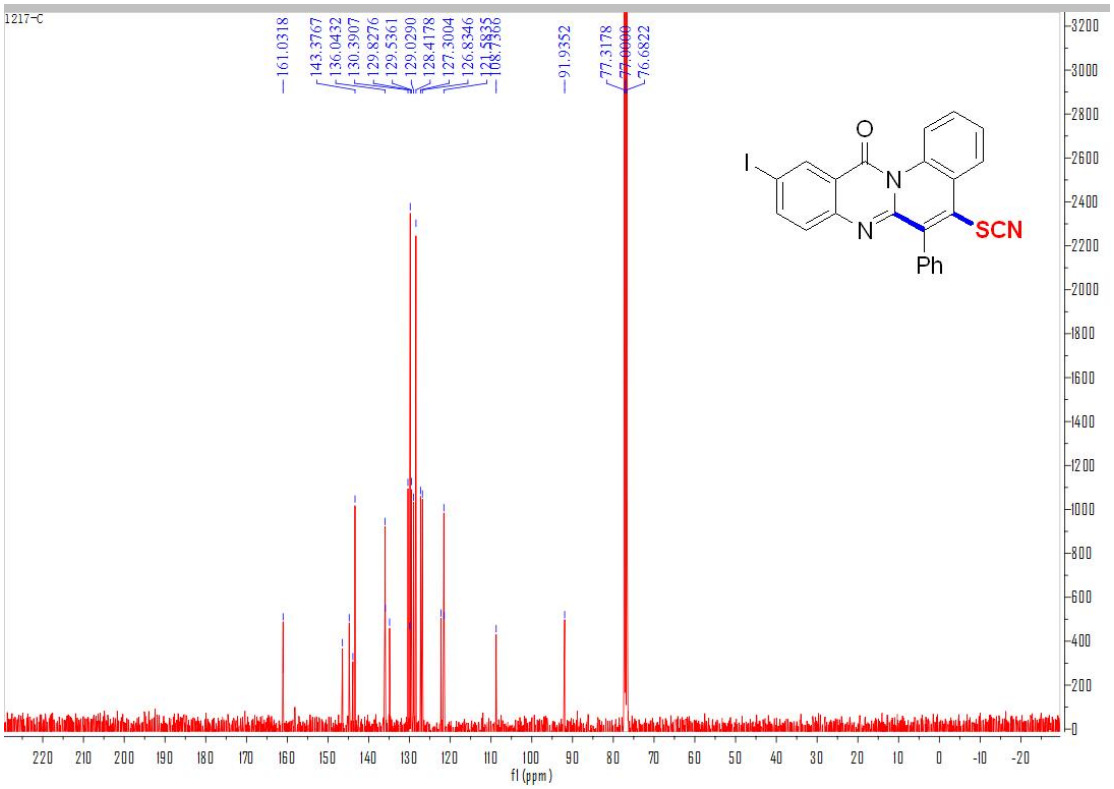
6-^{13}C NMR (100 MHz, $CDCl_3$)



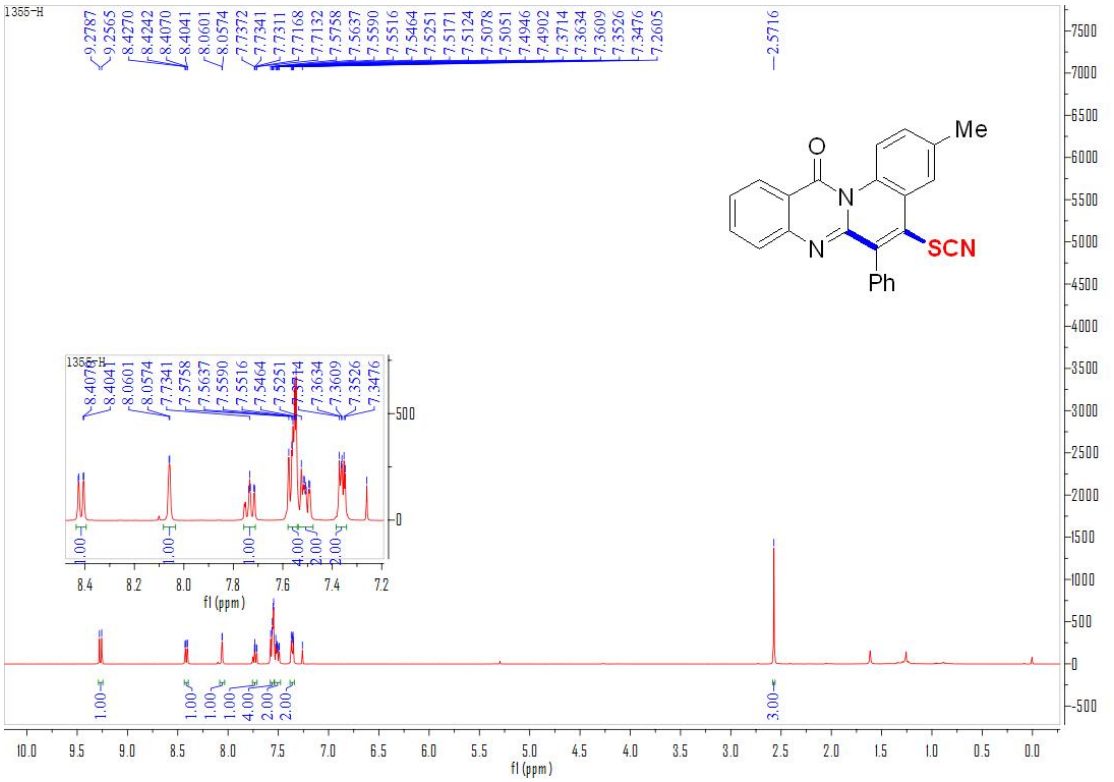
7-^{1}H NMR (400 MHz, $CDCl_3$)



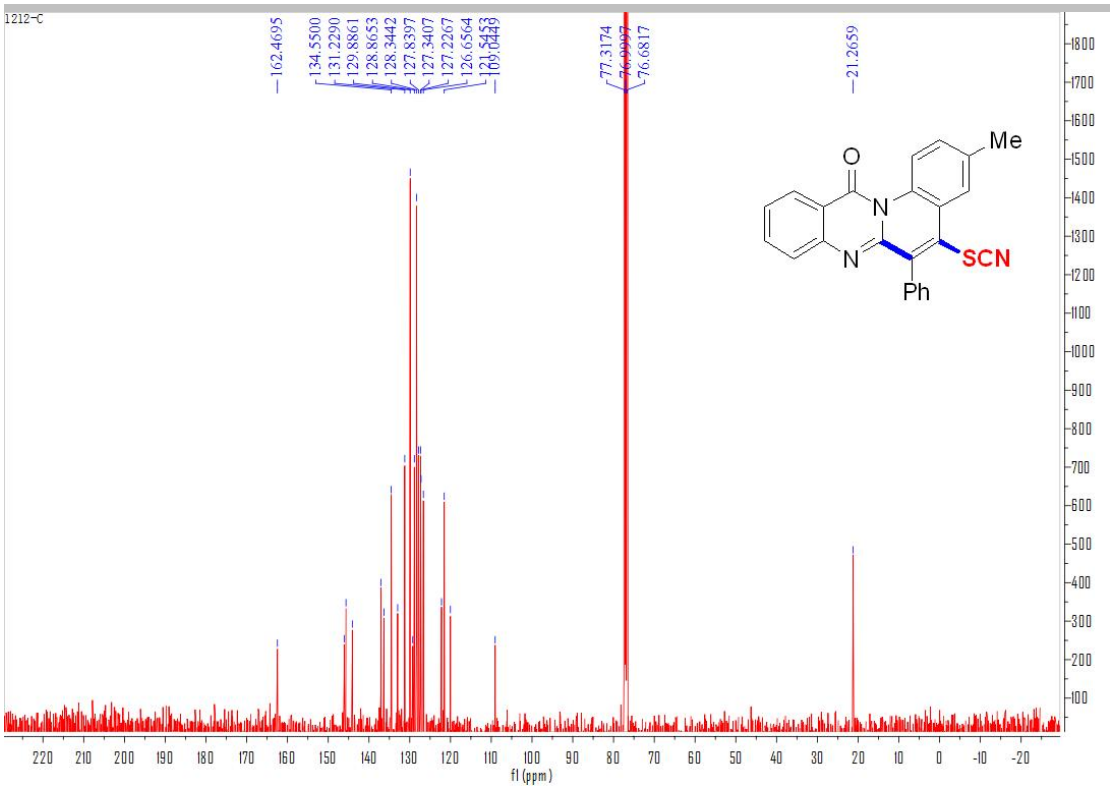
7-^{13}C NMR (100 MHz, $CDCl_3$)



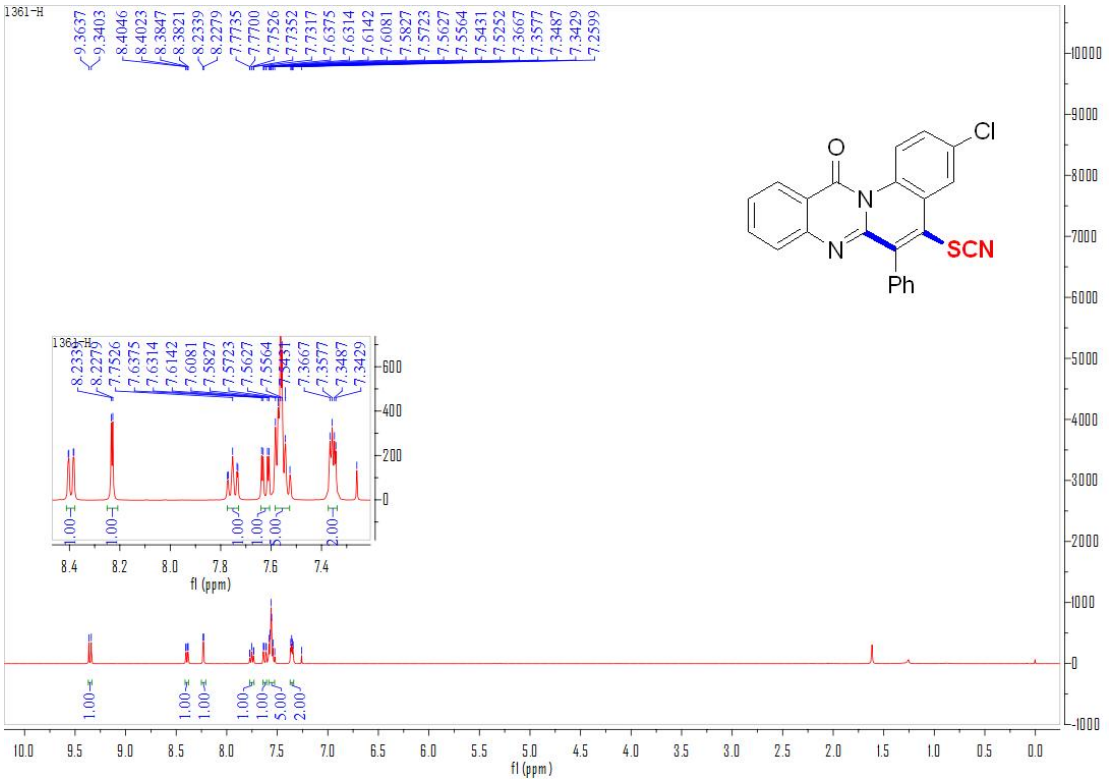
8-^{1}H NMR (400 MHz, $CDCl_3$)



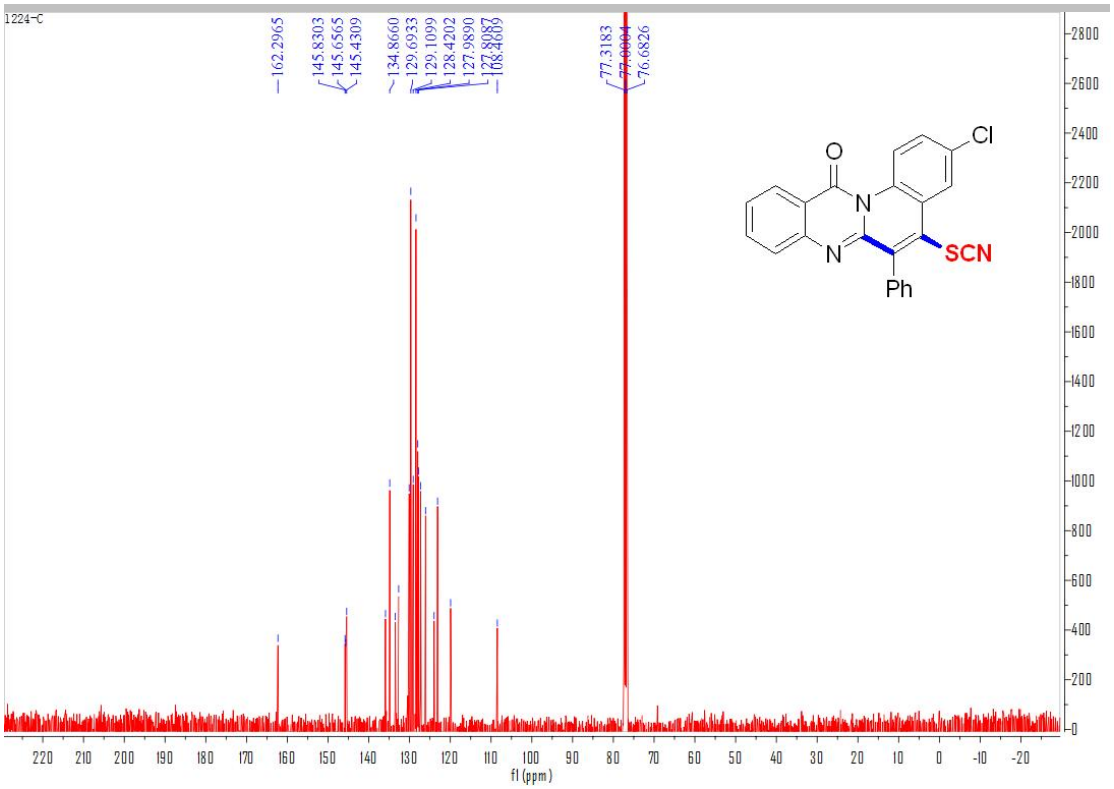
8-^{13}C NMR (100 MHz, $CDCl_3$)



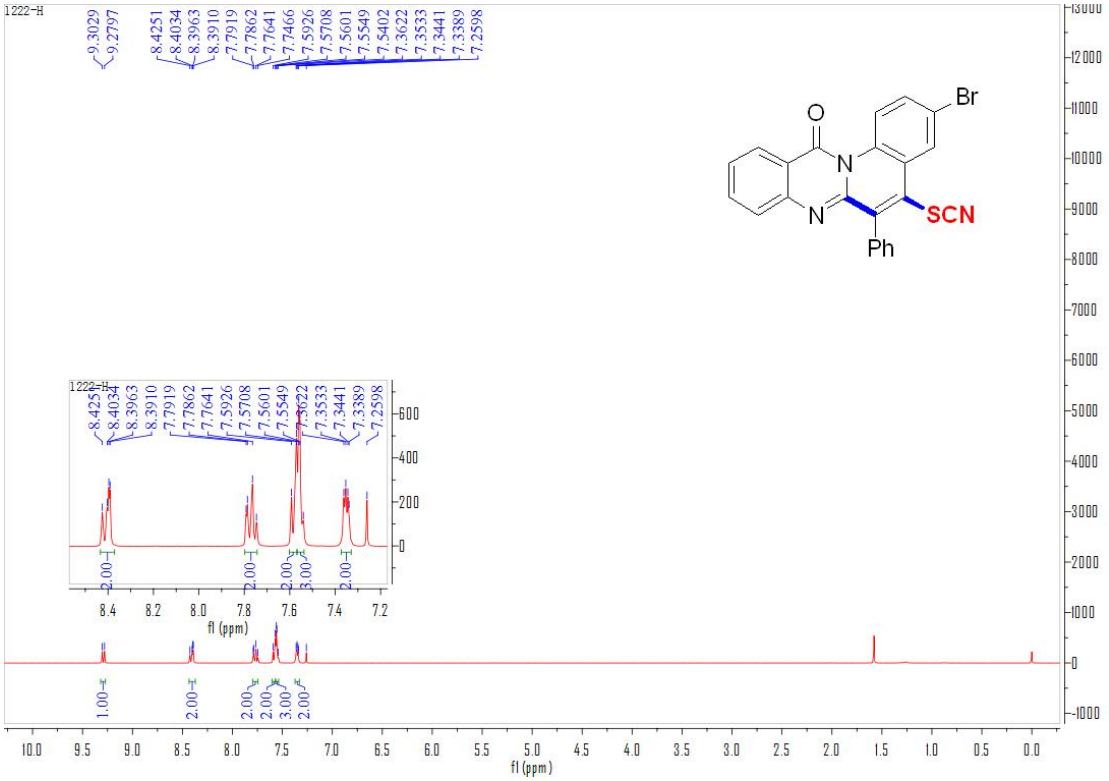
9-^{1}H NMR (400 MHz, $CDCl_3$)



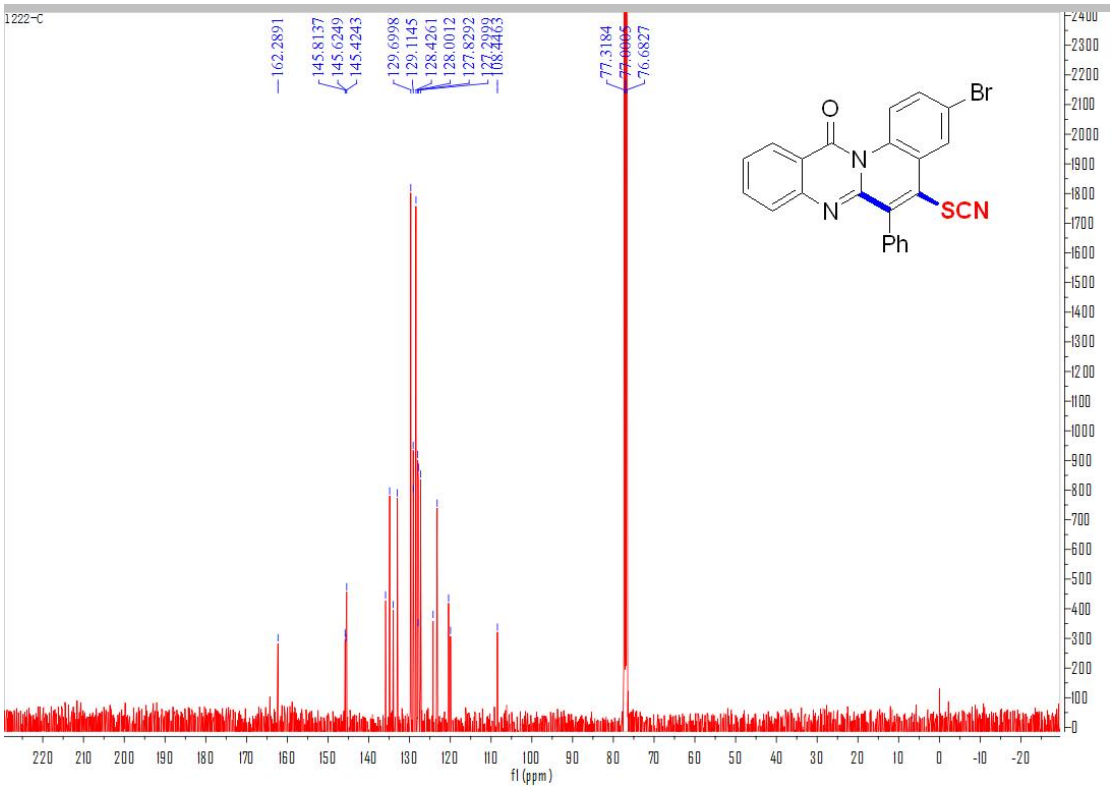
9-^{13}C NMR (100 MHz, $CDCl_3$)



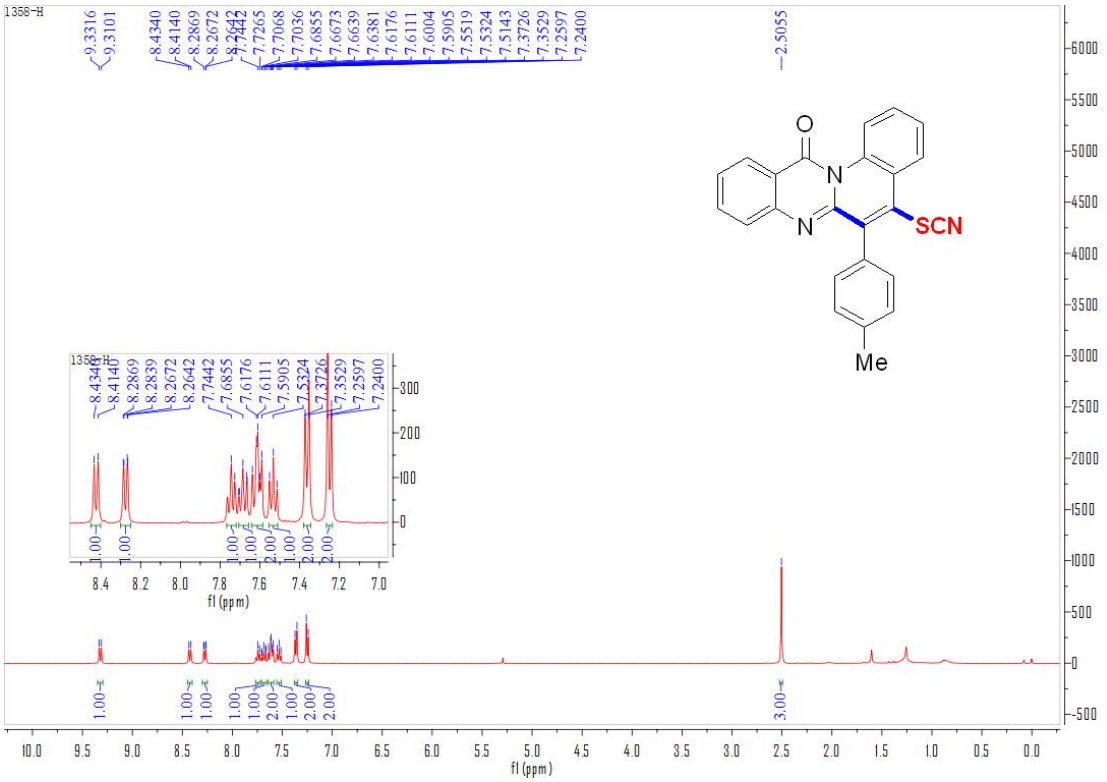
10-^{1}H NMR (400 MHz, $CDCl_3$)



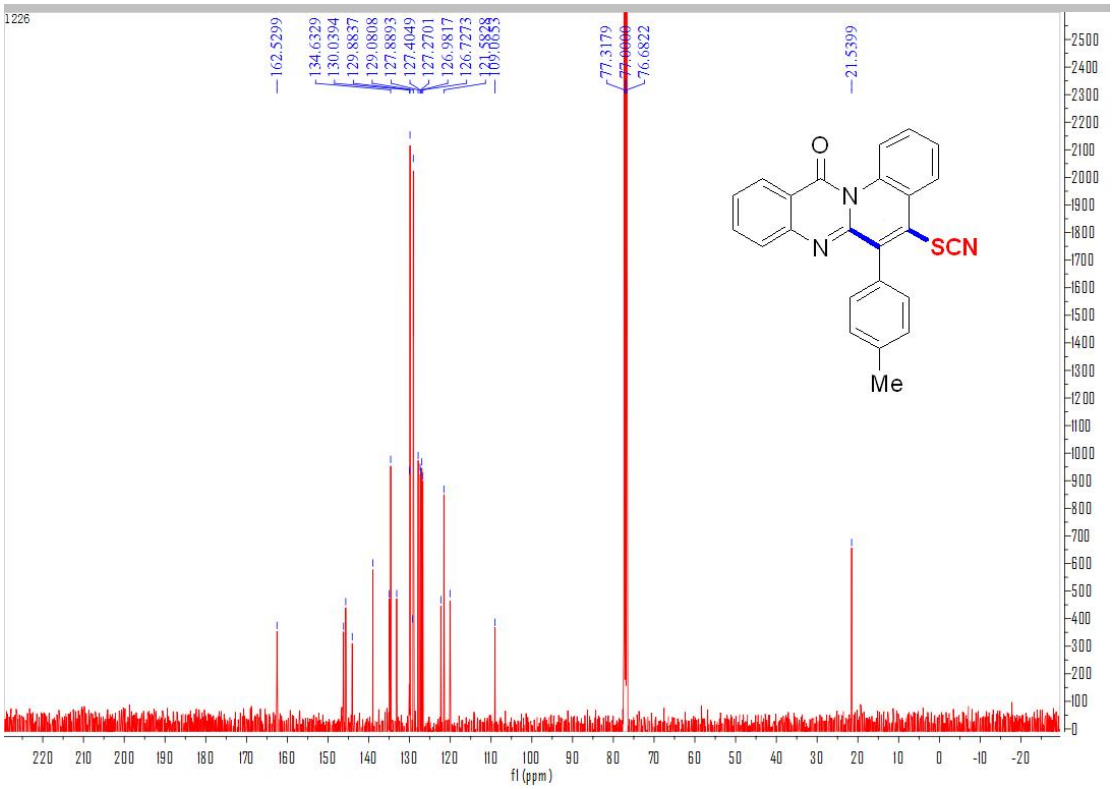
10-^{13}C NMR (100 MHz, $CDCl_3$)



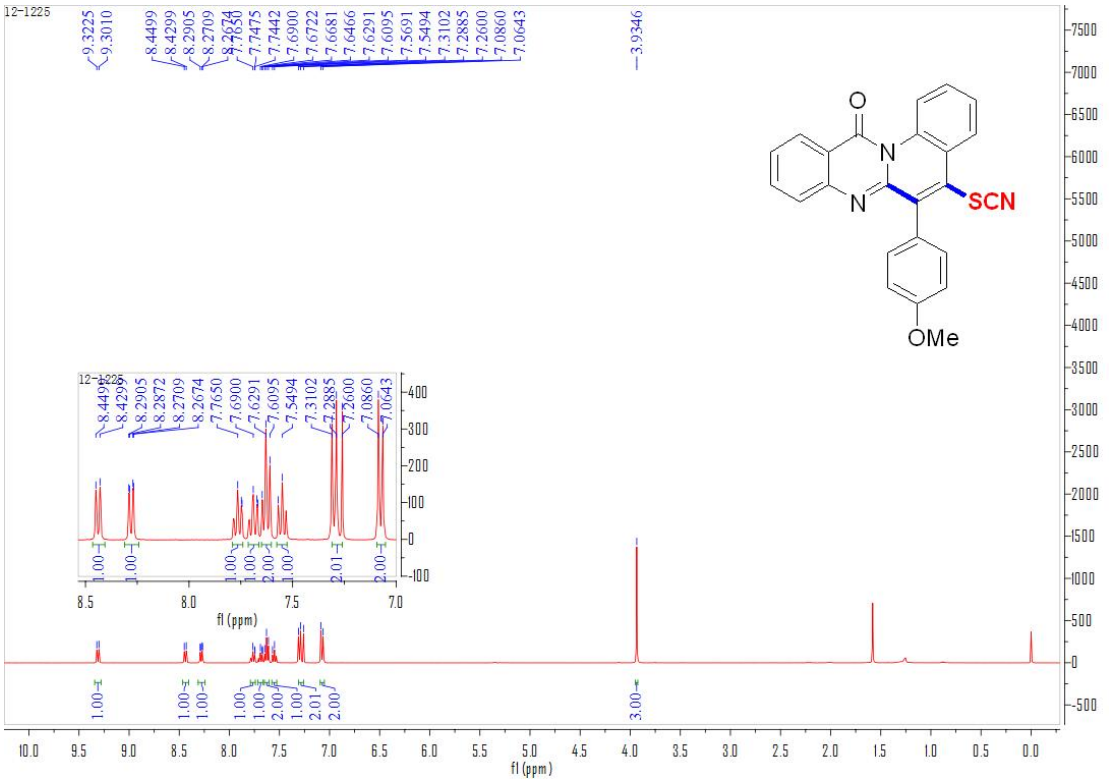
11-^{1}H NMR (400 MHz, $CDCl_3$)



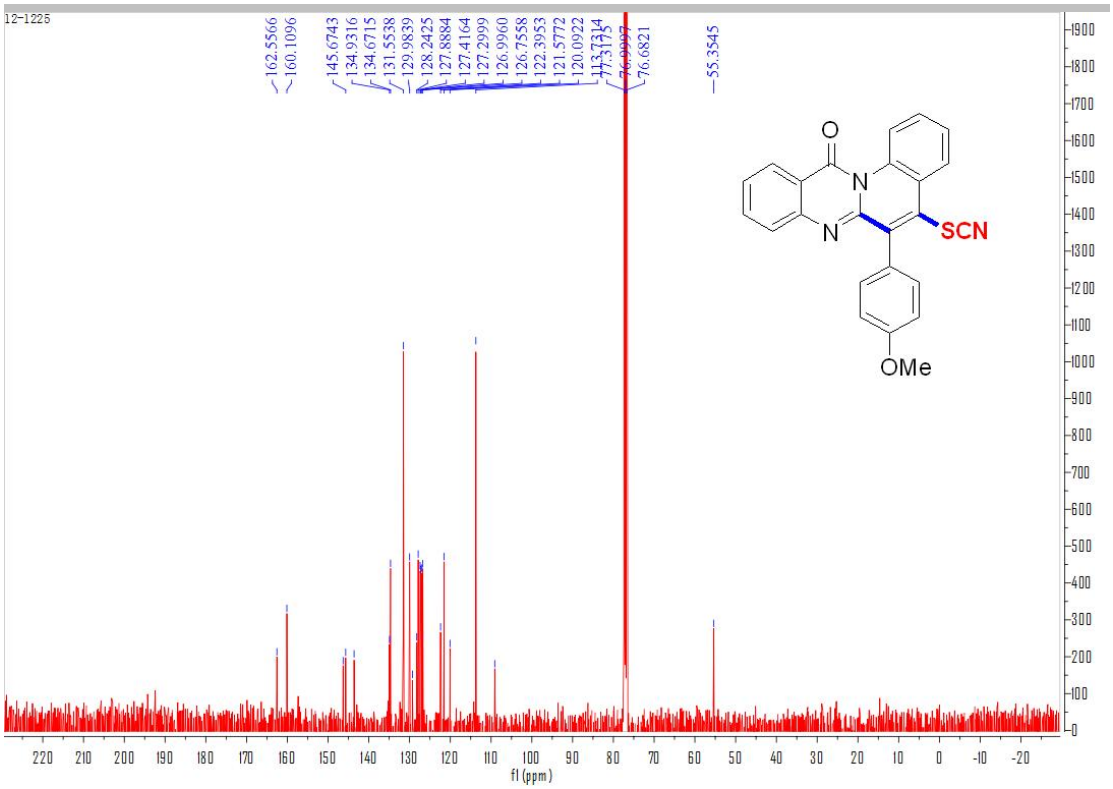
11-^{13}C NMR (100 MHz, $CDCl_3$)



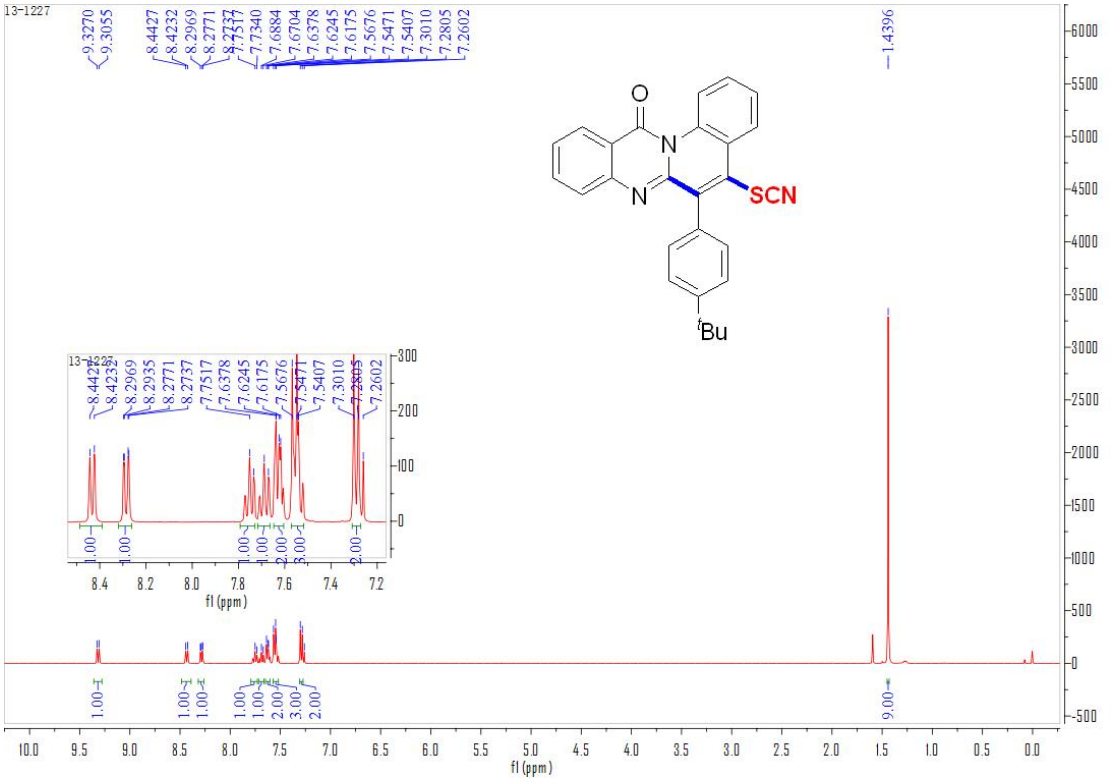
12-^{1}H NMR (400 MHz, $CDCl_3$)



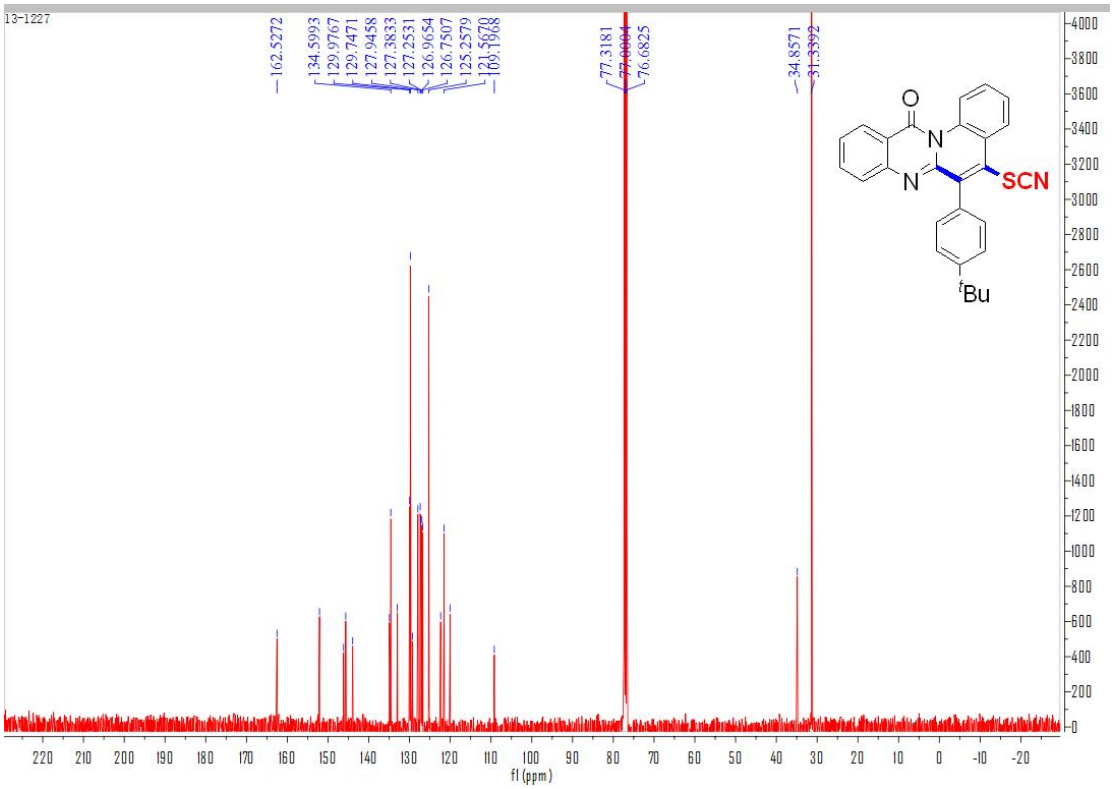
12-^{13}C NMR (100 MHz, $CDCl_3$)



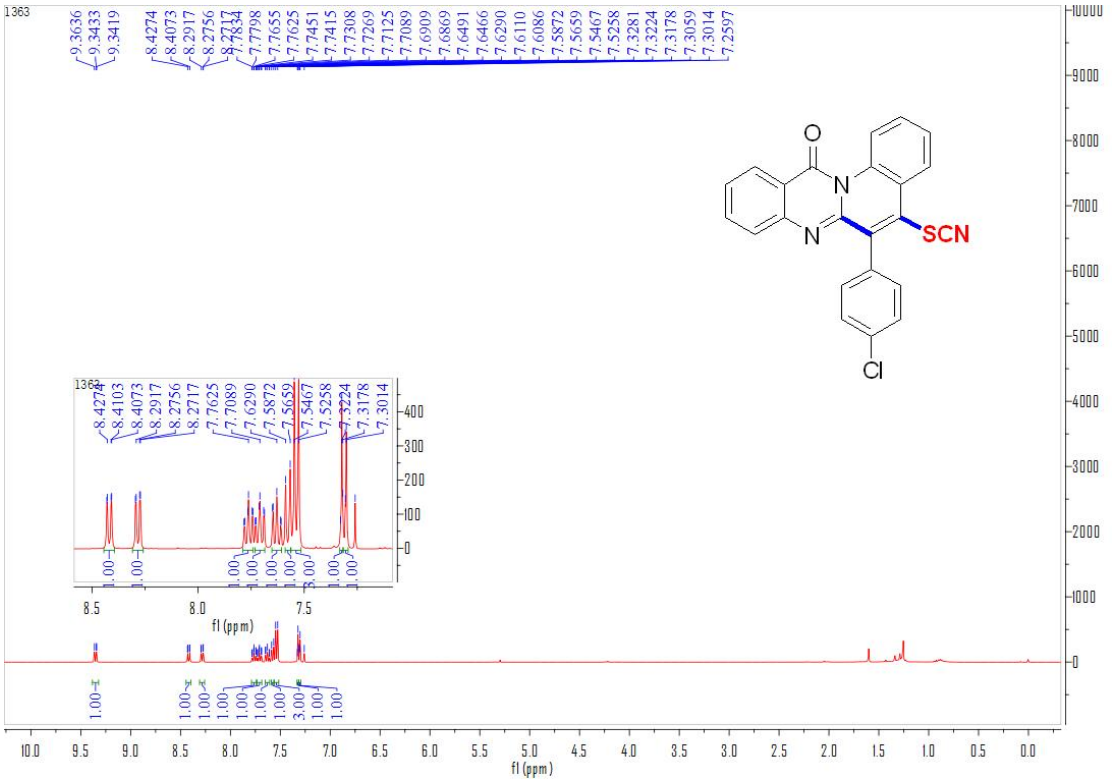
13-^{1}H NMR (400 MHz, $CDCl_3$)



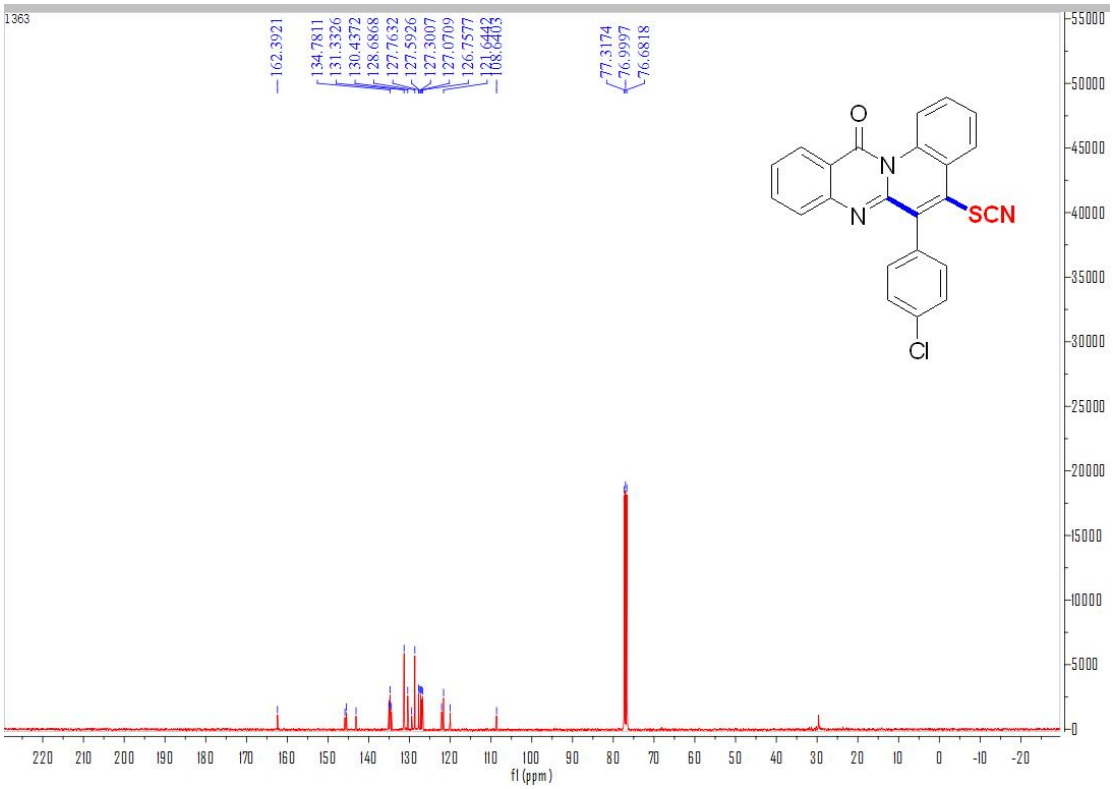
13-^{13}C NMR (100 MHz, $CDCl_3$)



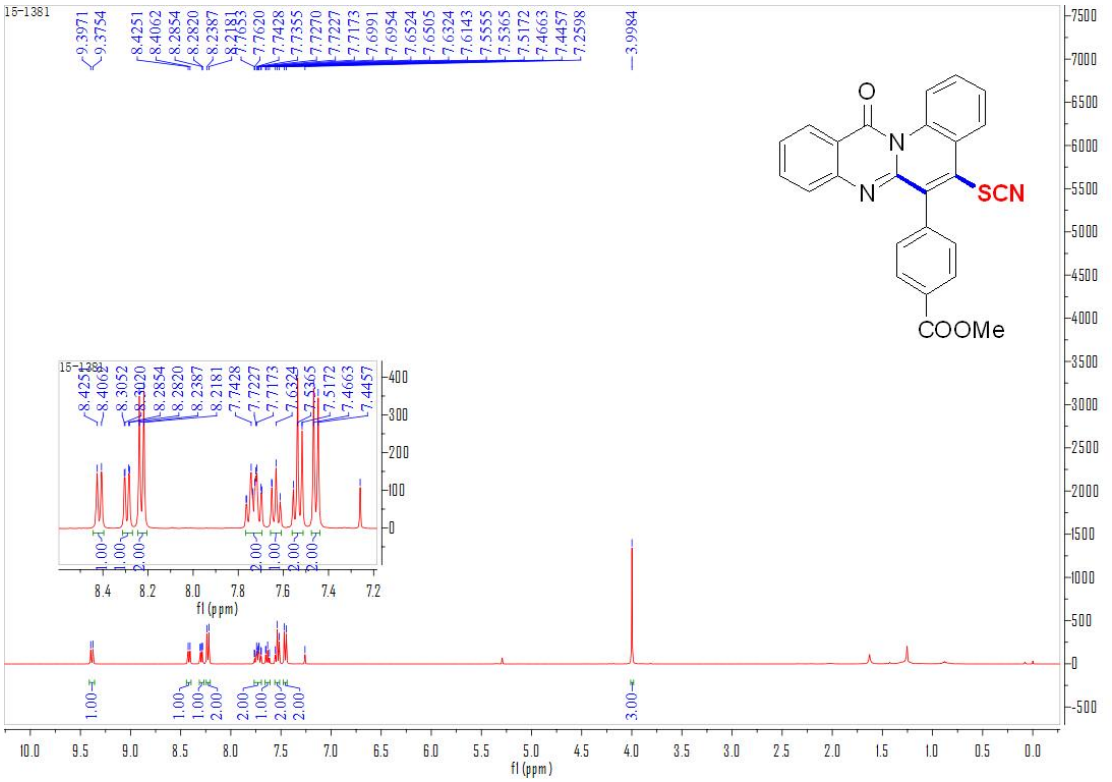
14-^{1}H NMR (400 MHz, $CDCl_3$)



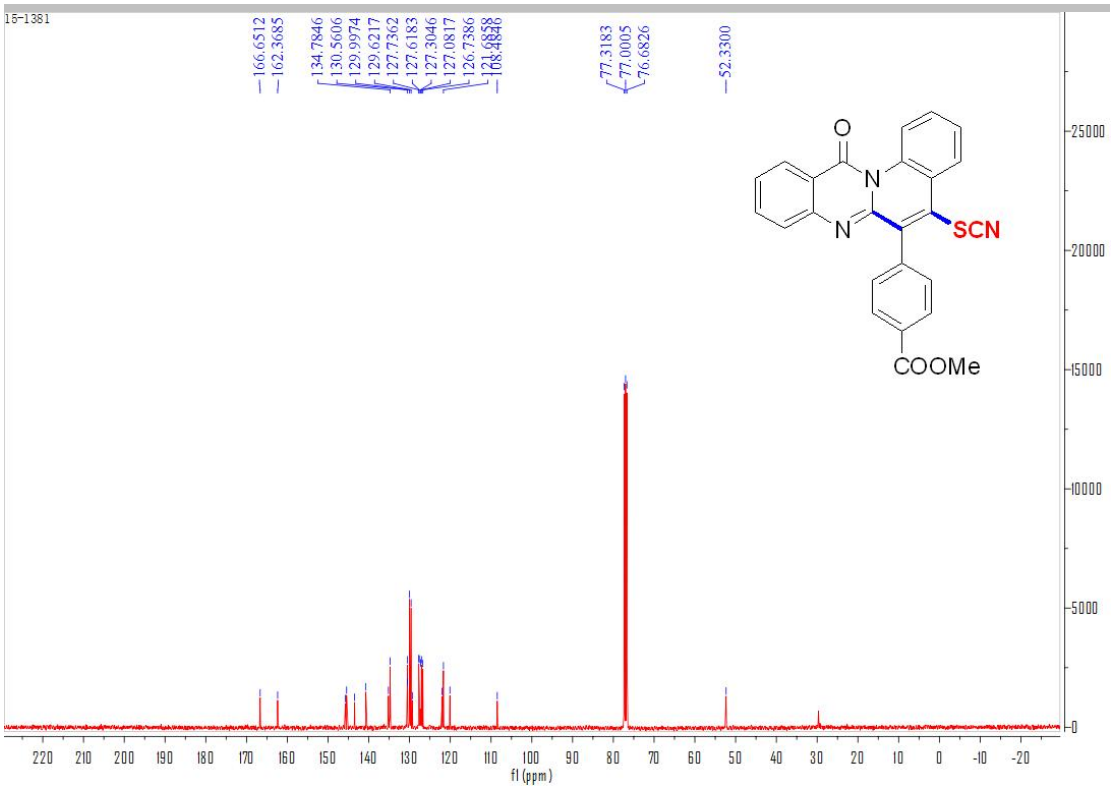
14-^{13}C NMR (100 MHz, $CDCl_3$)



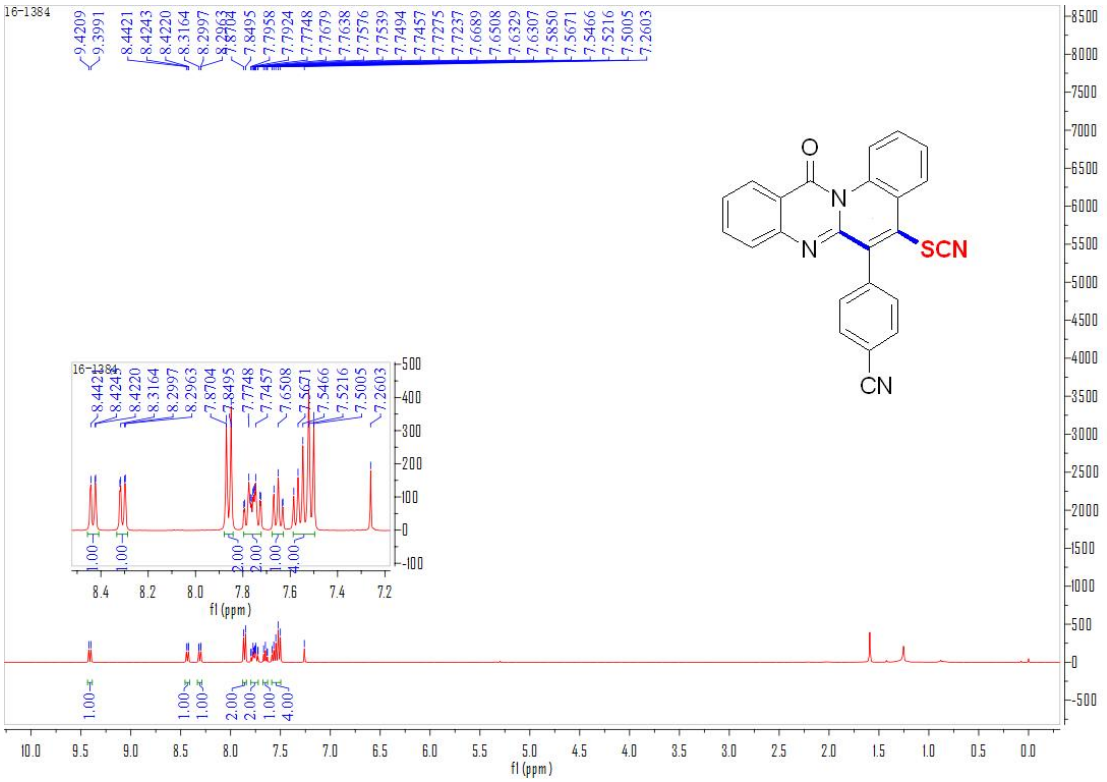
15-^{1}H NMR (400 MHz, $CDCl_3$)



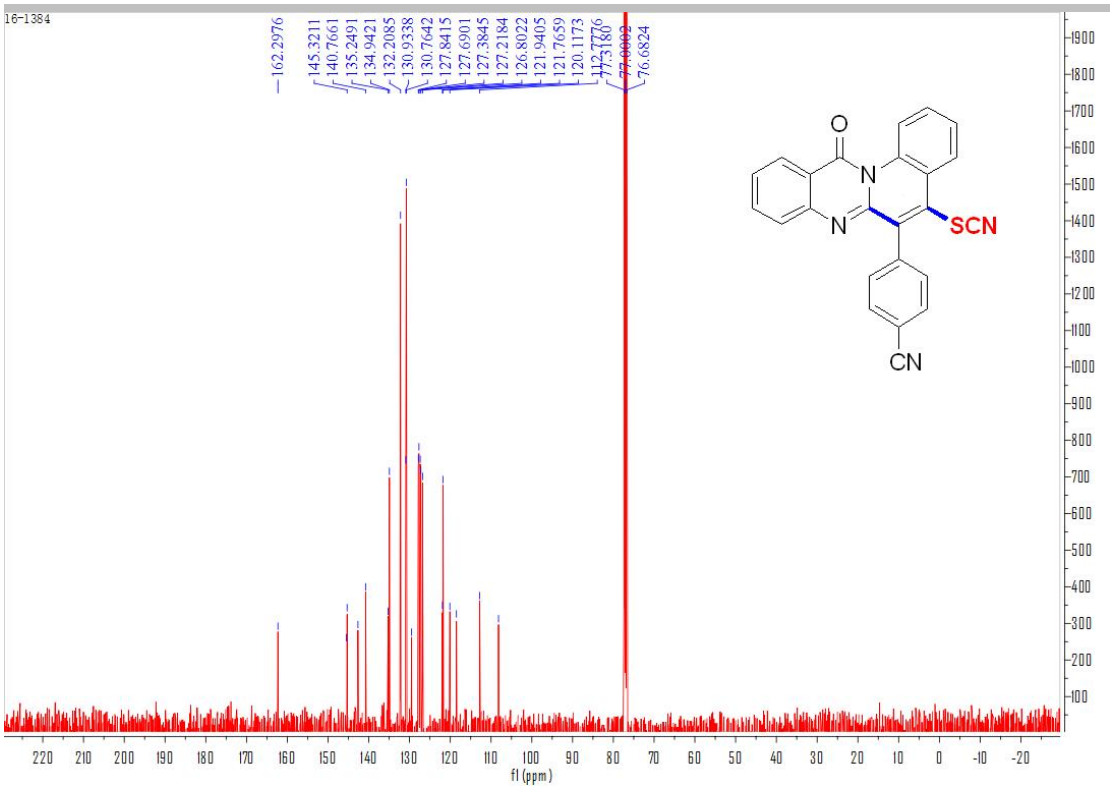
15-^{13}C NMR (100 MHz, $CDCl_3$)



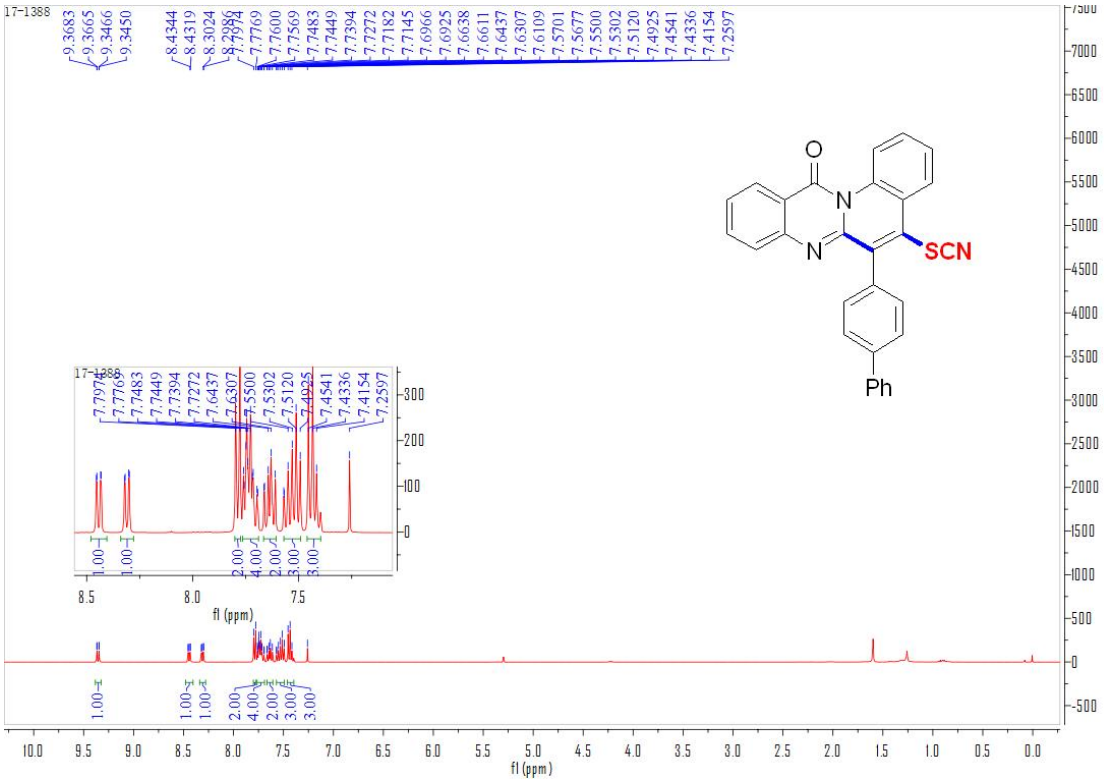
16-^{1}H NMR (400 MHz, $CDCl_3$)



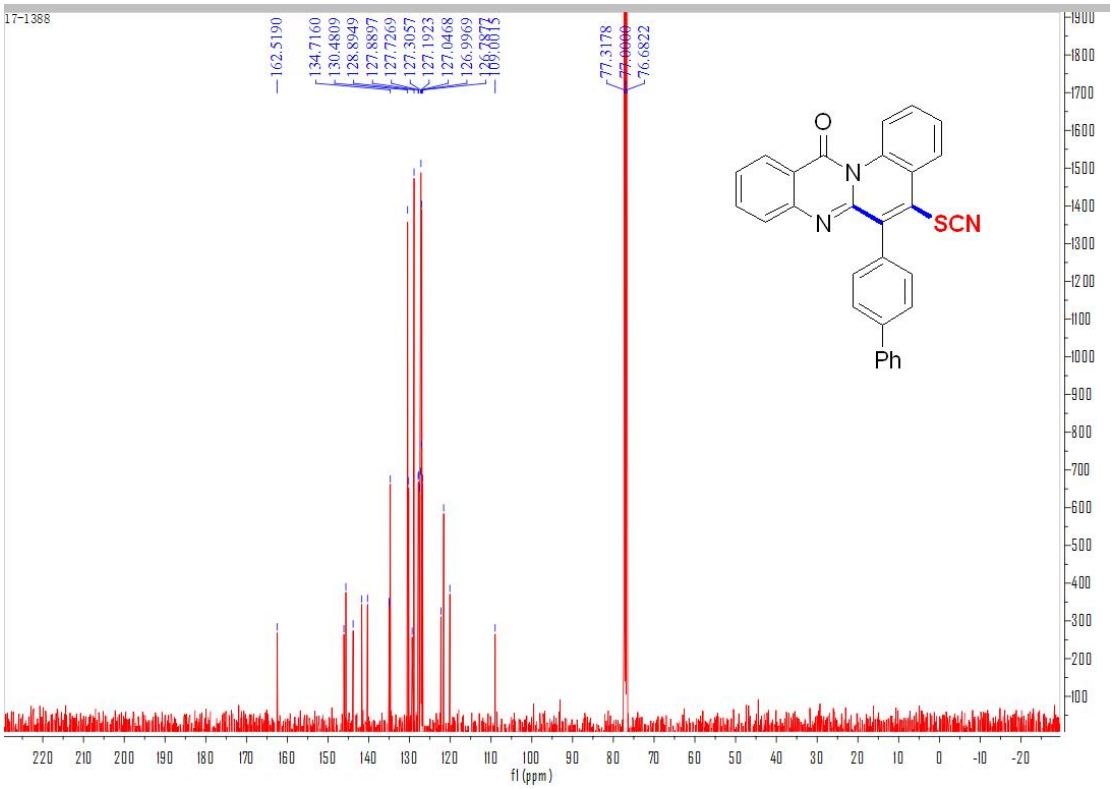
16-^{13}C NMR (100 MHz, $CDCl_3$)



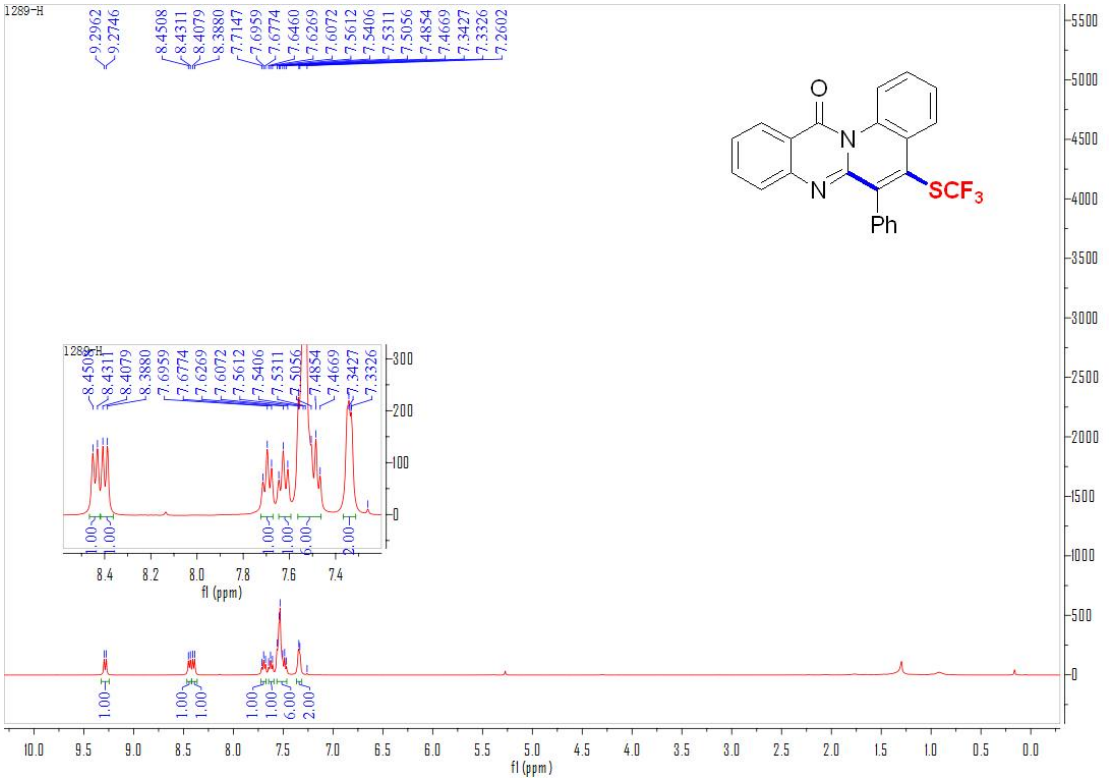
17-^{1}H NMR (400 MHz, $CDCl_3$)



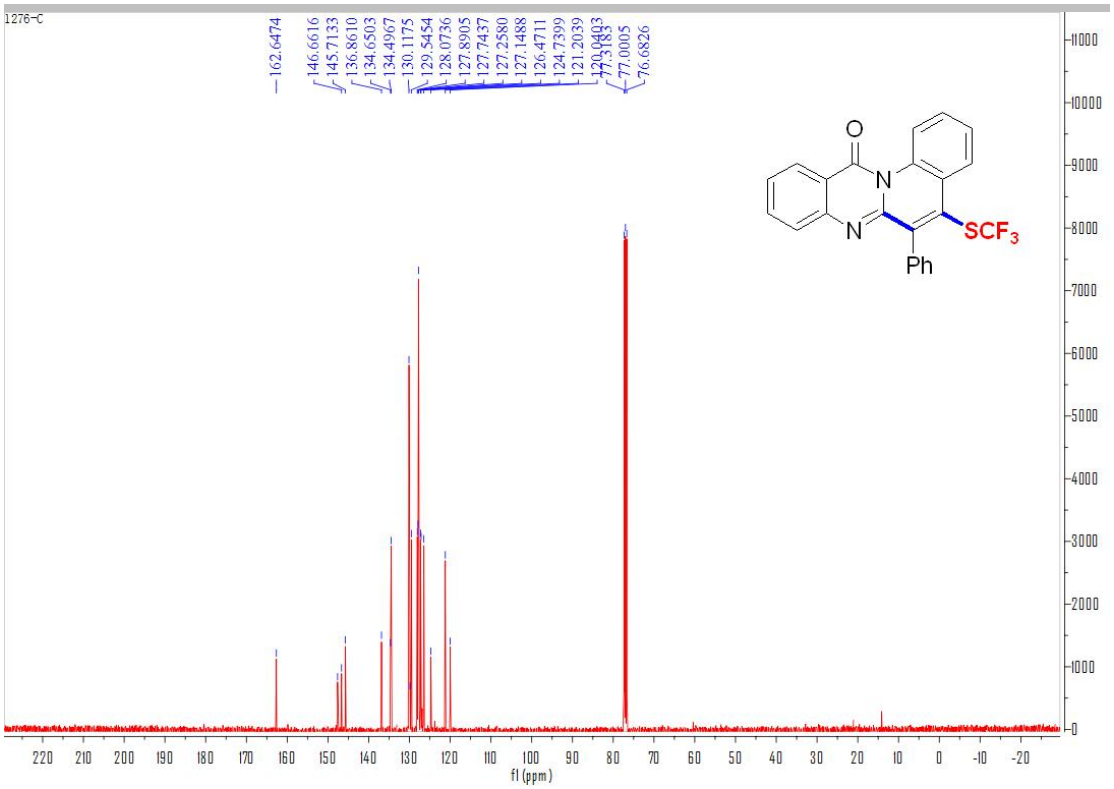
17-^{13}C NMR (100 MHz, $CDCl_3$)



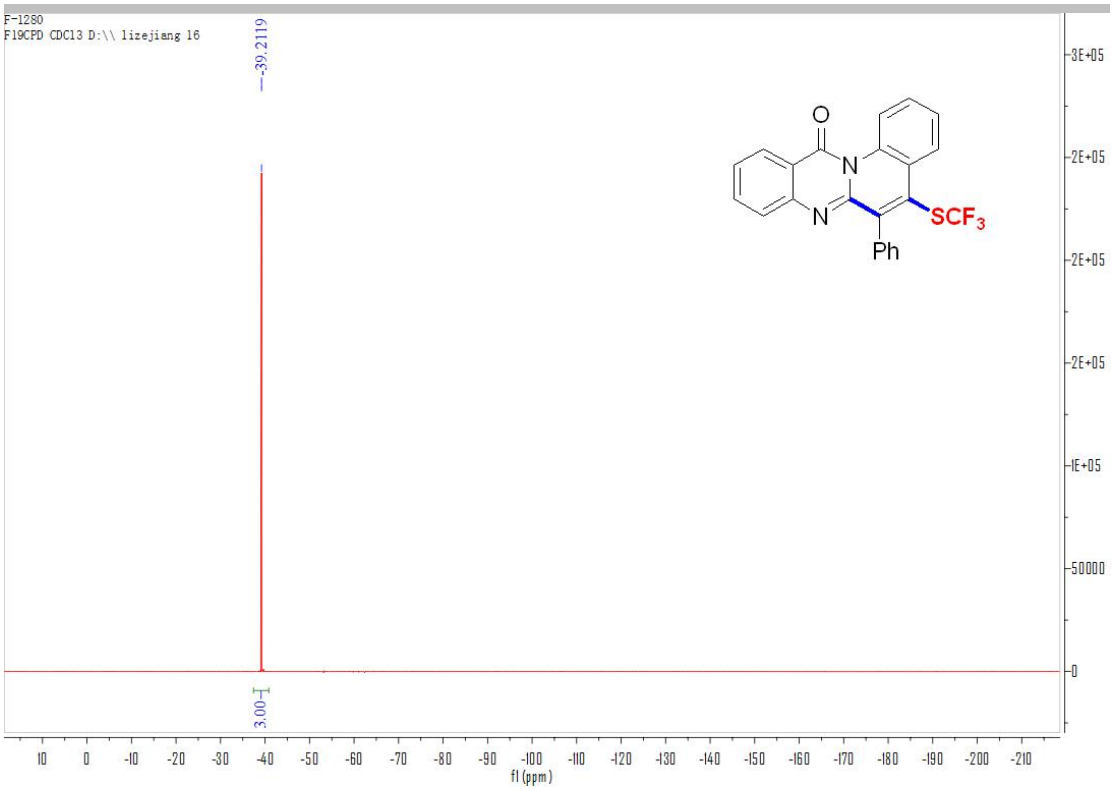
18-^{1}H NMR (400 MHz, $CDCl_3$)



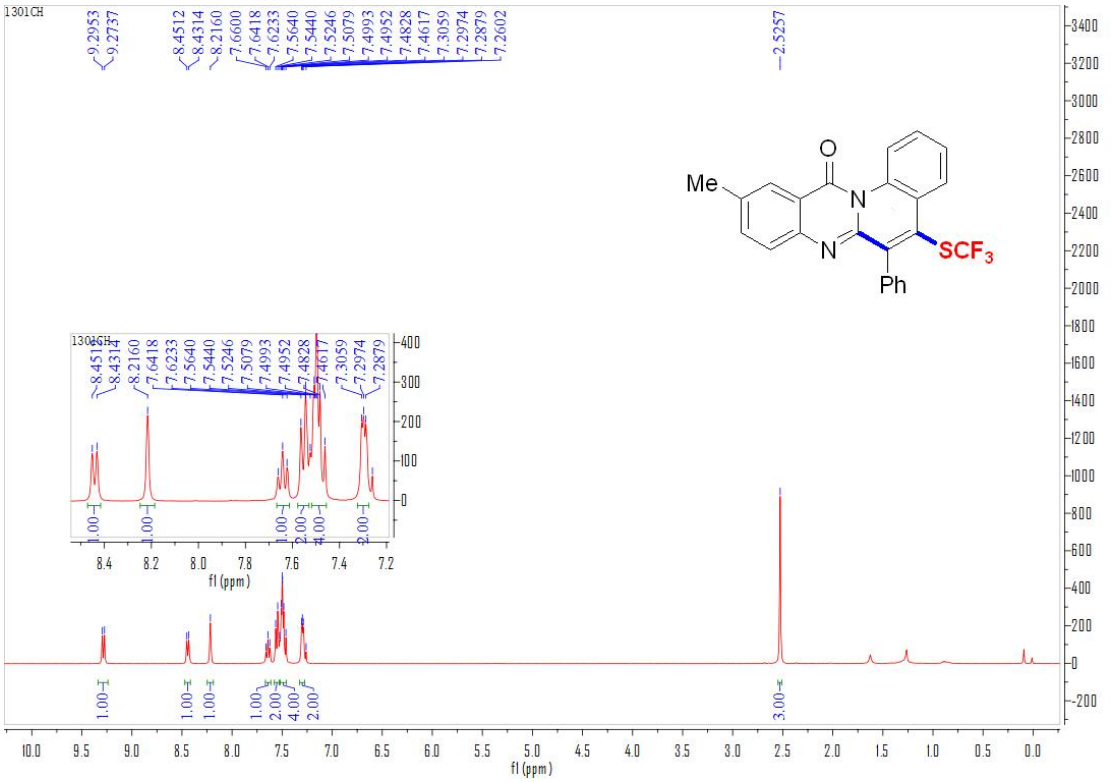
18-^{13}C NMR (100 MHz, $CDCl_3$)



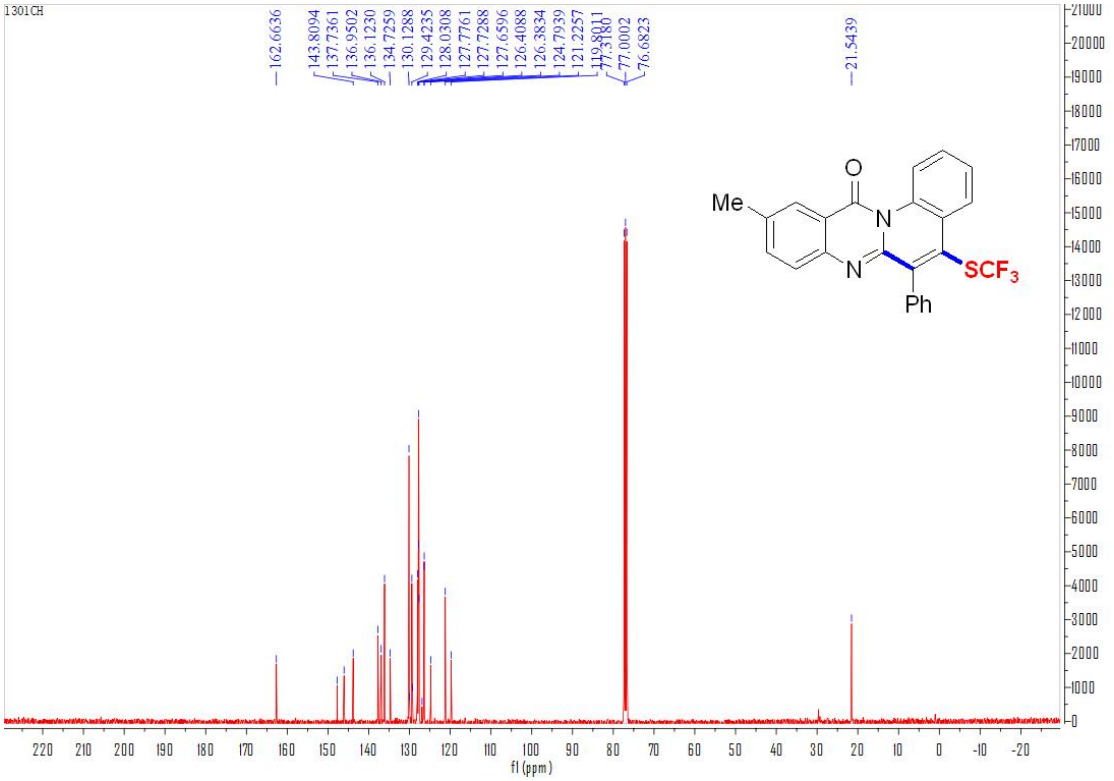
18-^{19}F NMR (565 MHz, $CDCl_3$)



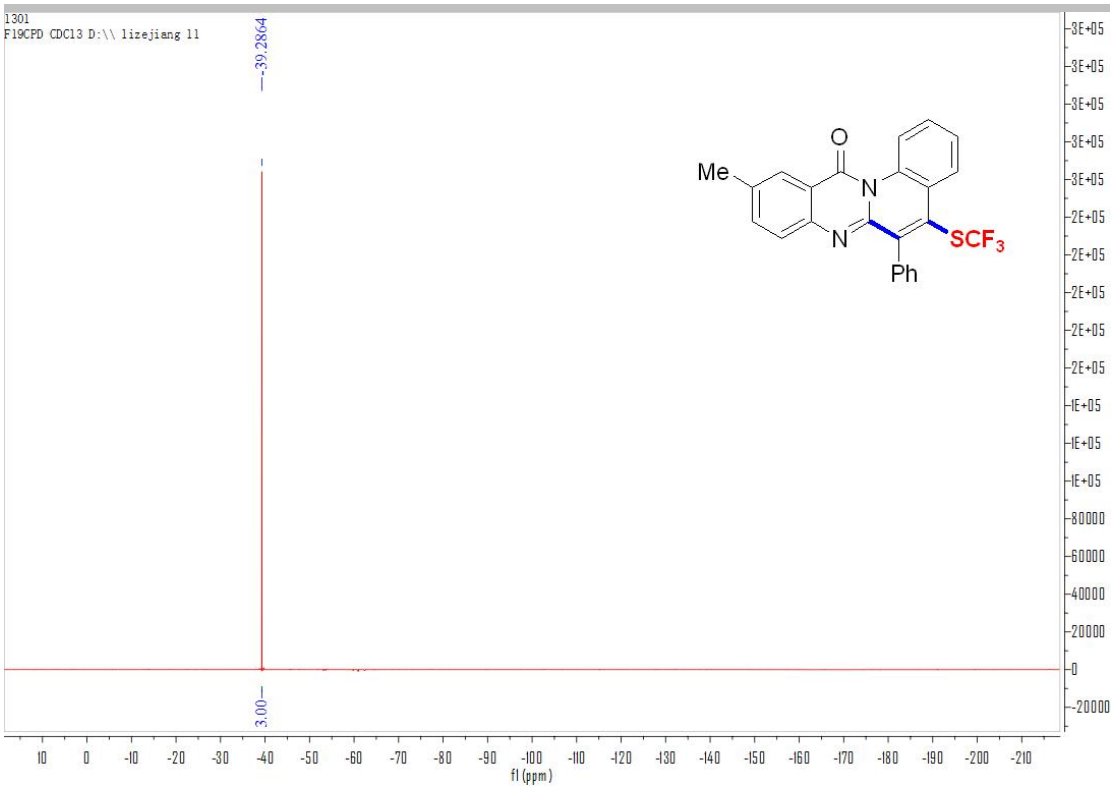
19-^{1}H NMR (400 MHz, $CDCl_3$)



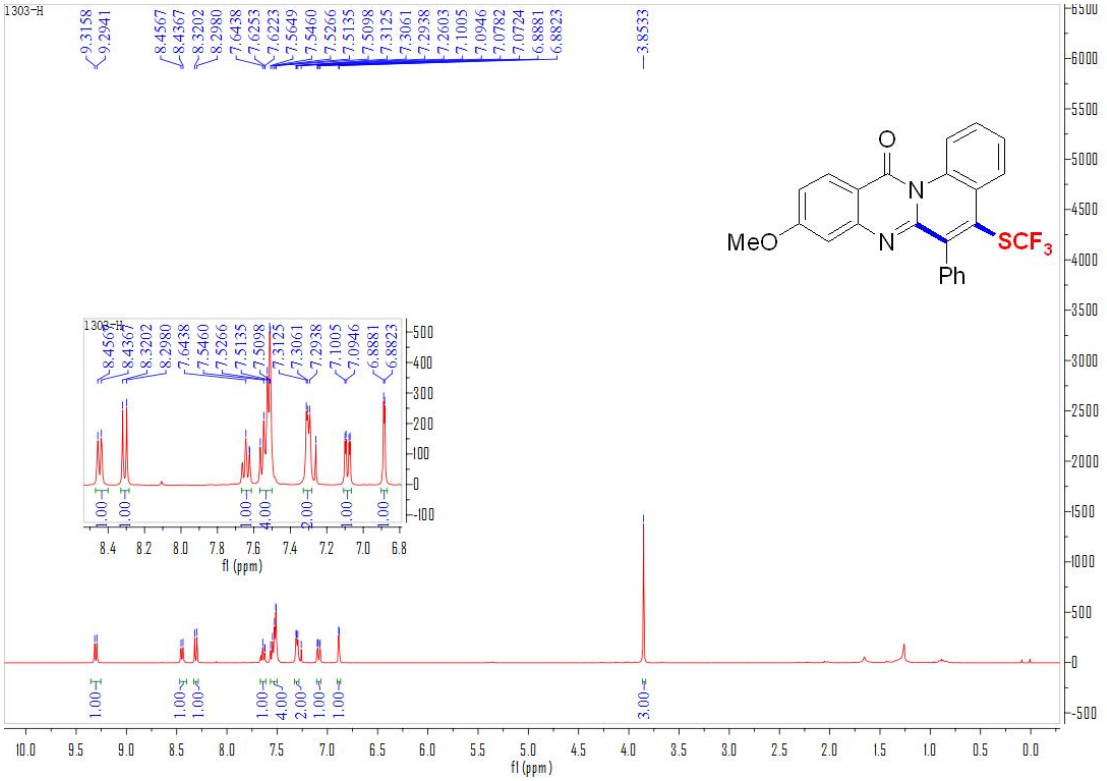
19-^{13}C NMR (100 MHz, $CDCl_3$)



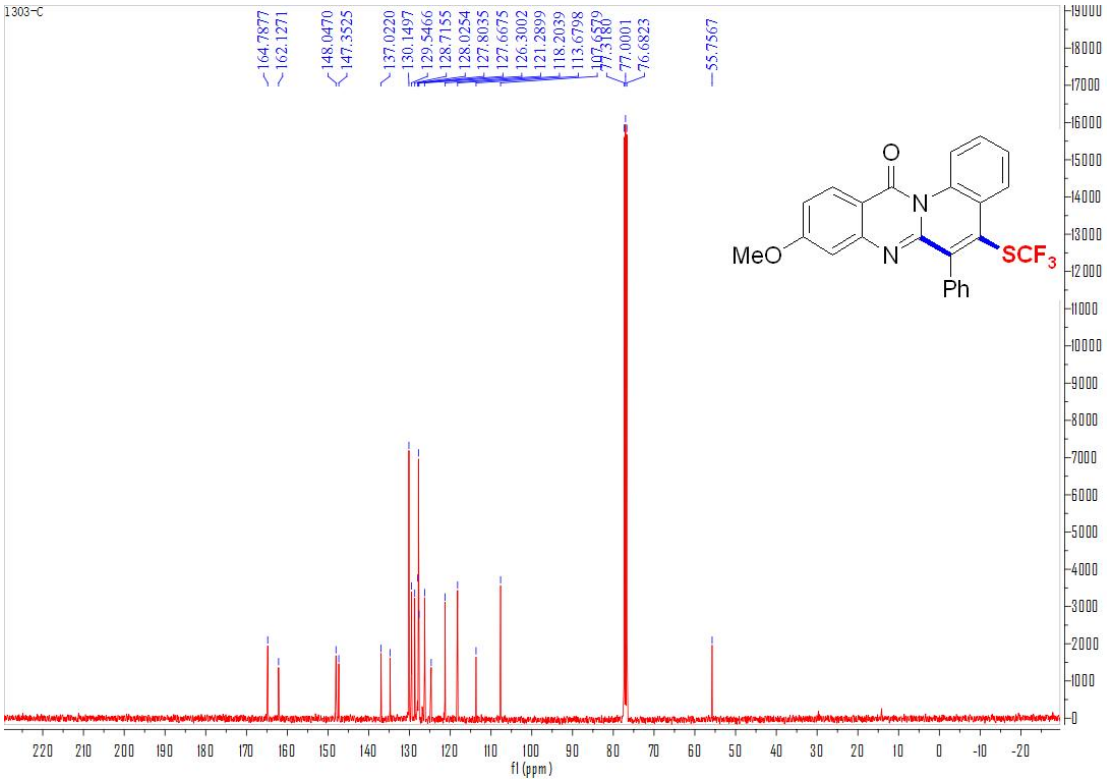
19-^{19}F NMR (565 MHz, $CDCl_3$)



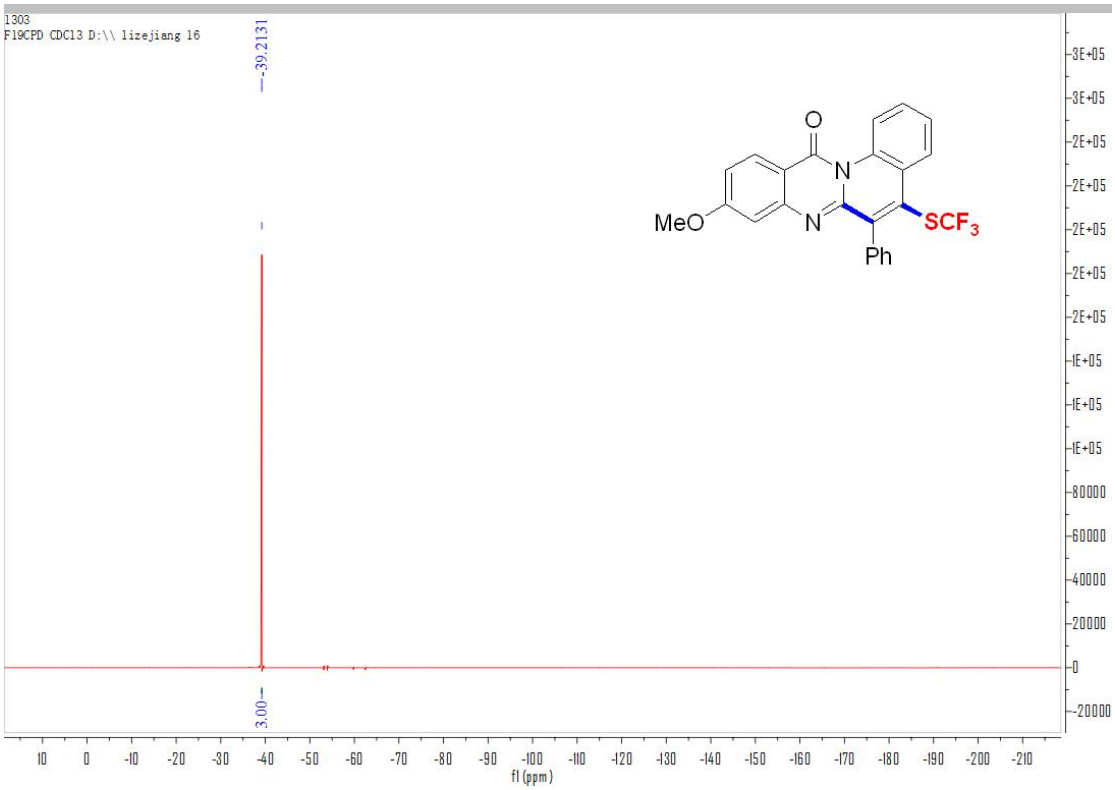
20-^{1}H NMR (400 MHz, $CDCl_3$)



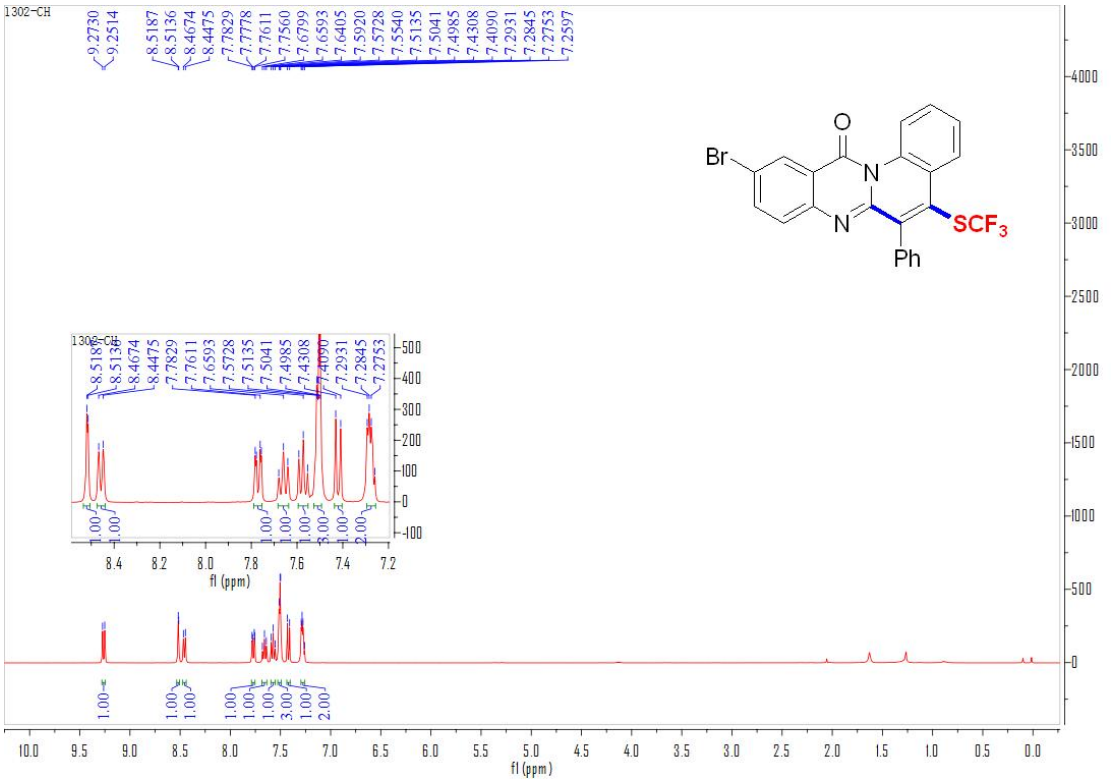
20-^{13}C NMR (100 MHz, $CDCl_3$)



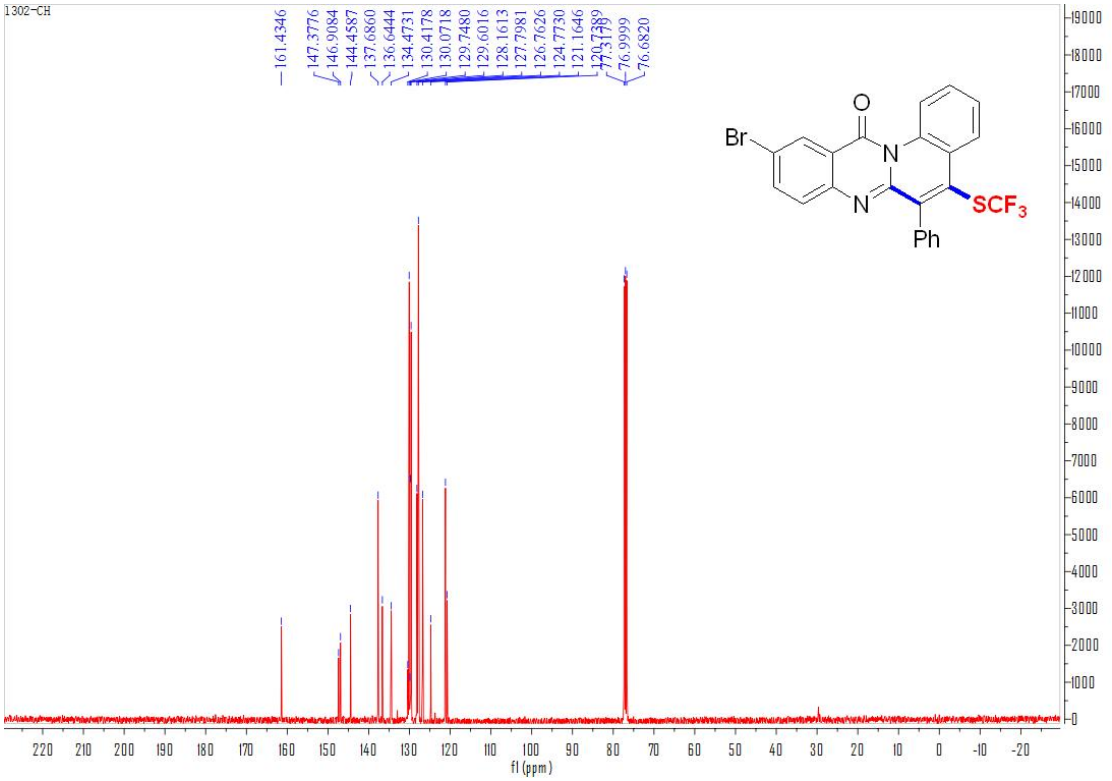
20-^{19}F NMR (565 MHz, $CDCl_3$)



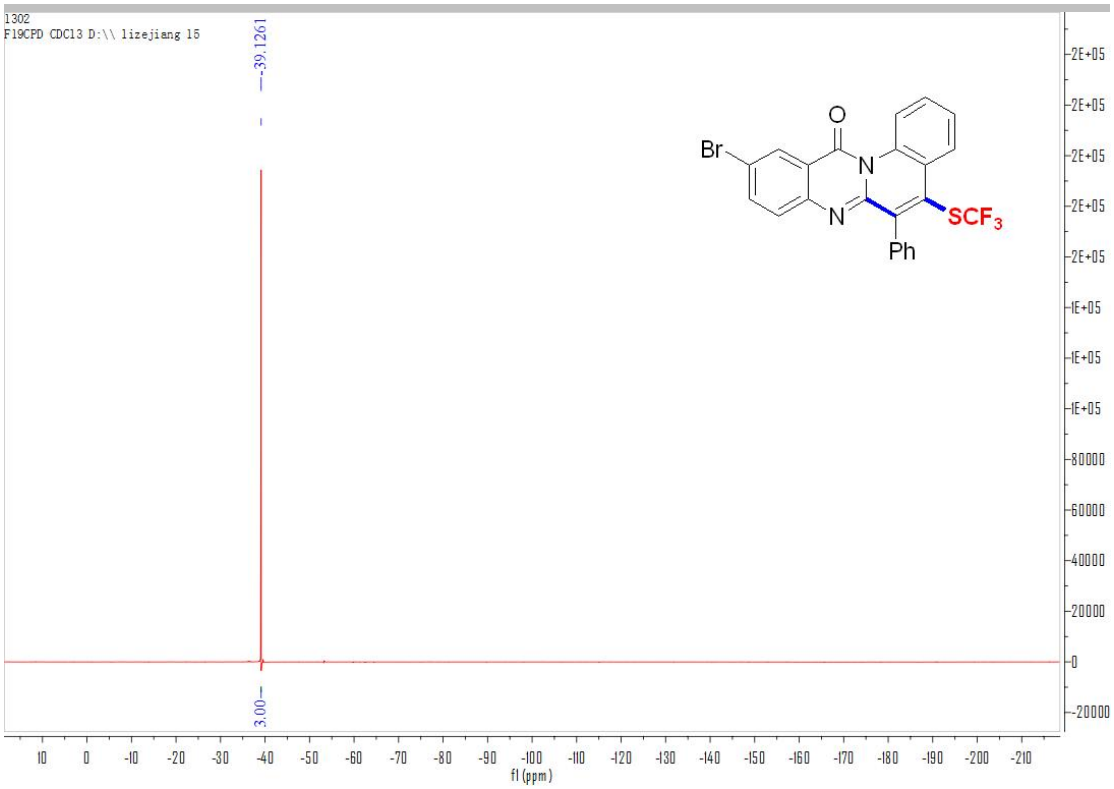
21-^{1}H NMR (400 MHz, $CDCl_3$)



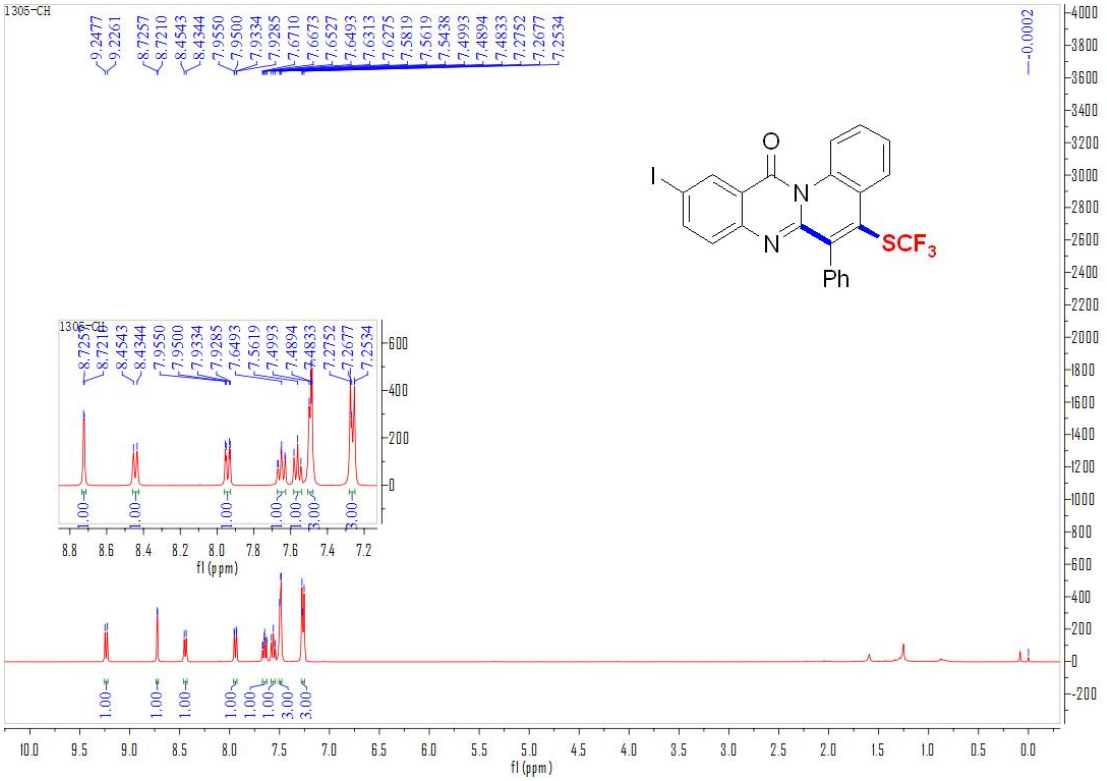
21-^{13}C NMR (100 MHz, $CDCl_3$)



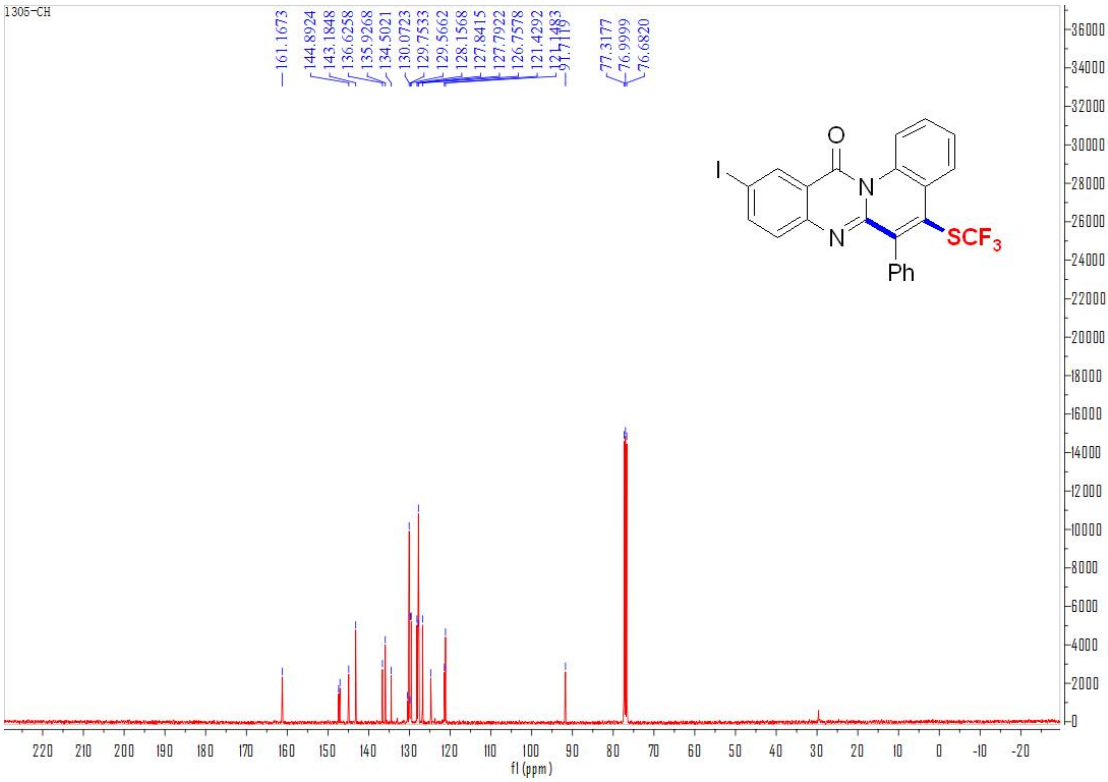
21-^{19}F NMR (565 MHz, $CDCl_3$)



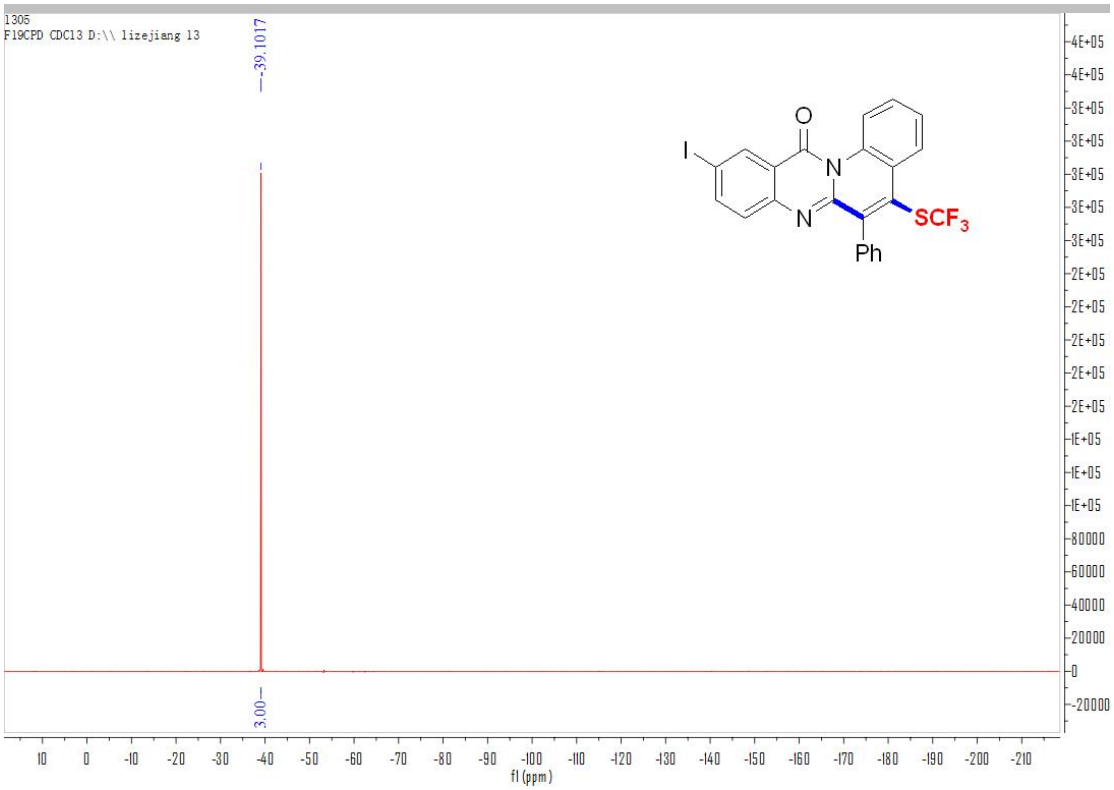
22-^{1}H NMR (400 MHz, $CDCl_3$)



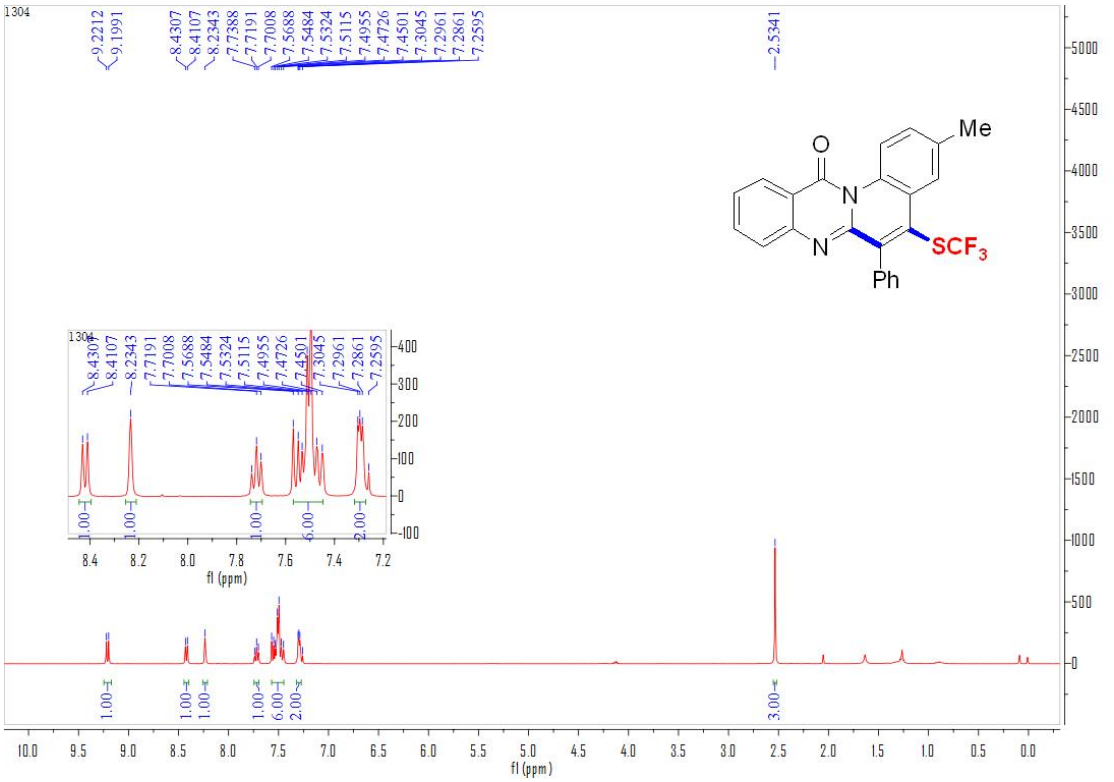
22-^{13}C NMR (100 MHz, $CDCl_3$)



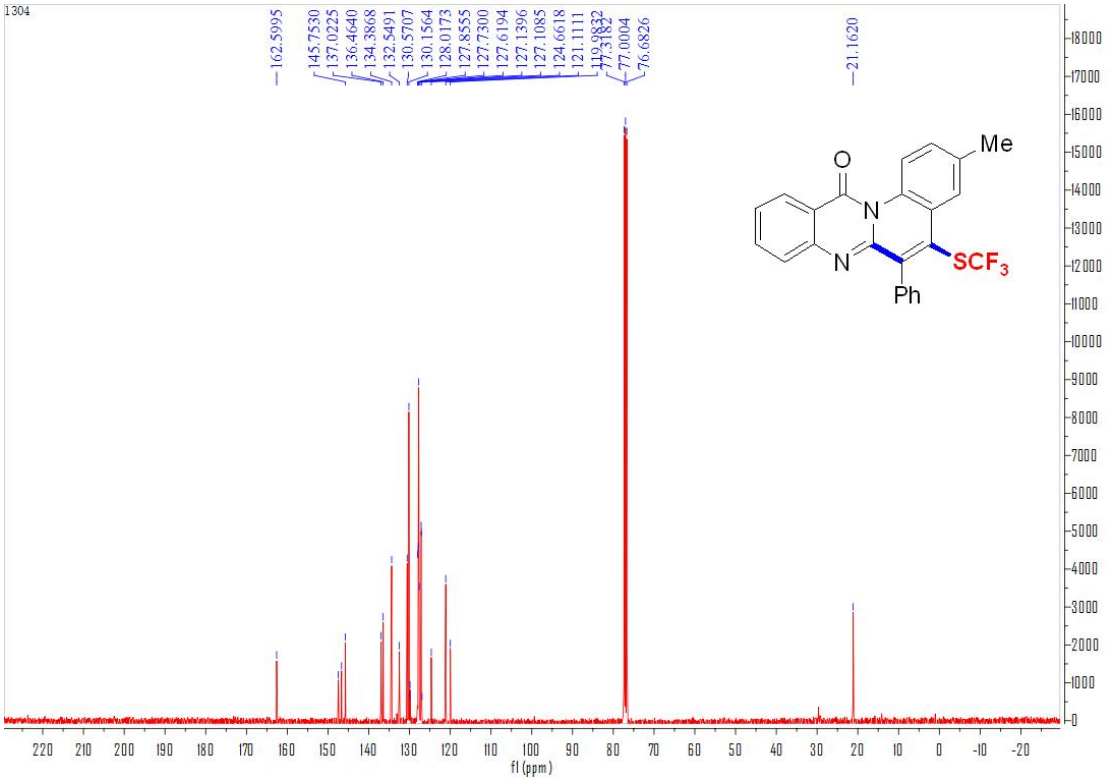
22-^{19}F NMR (565 MHz, $CDCl_3$)



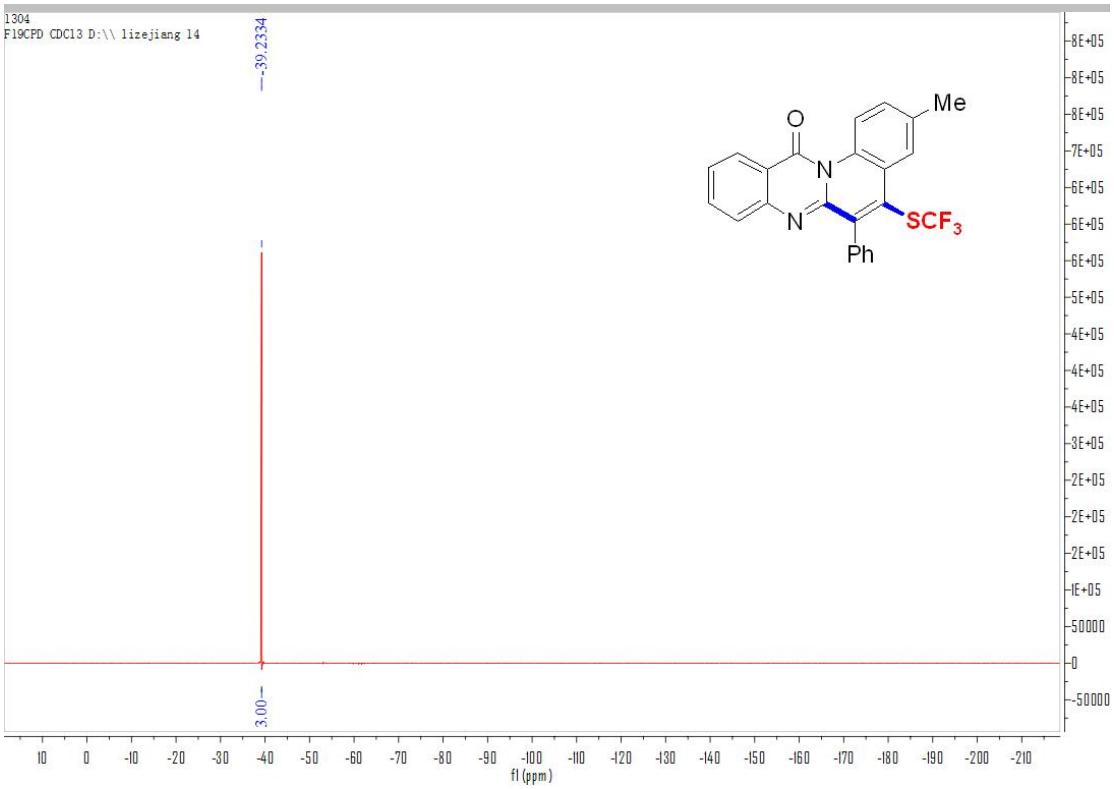
23-^{1}H NMR (400 MHz, $CDCl_3$)



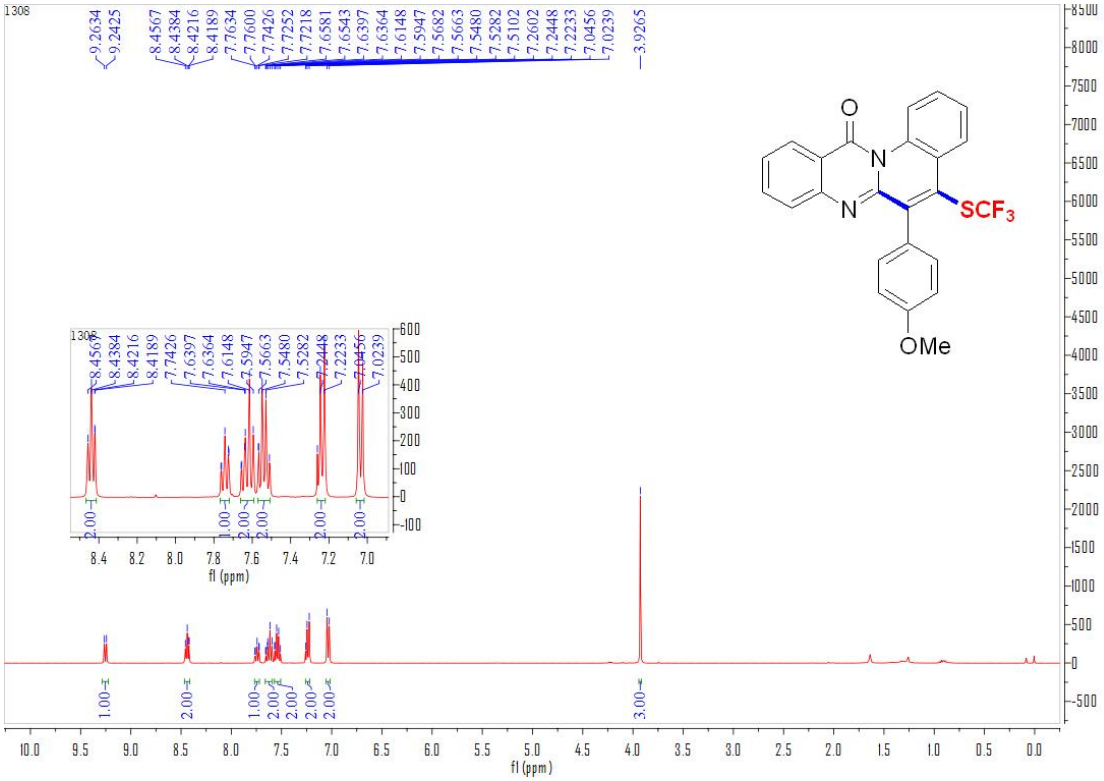
23-^{13}C NMR (100 MHz, $CDCl_3$)



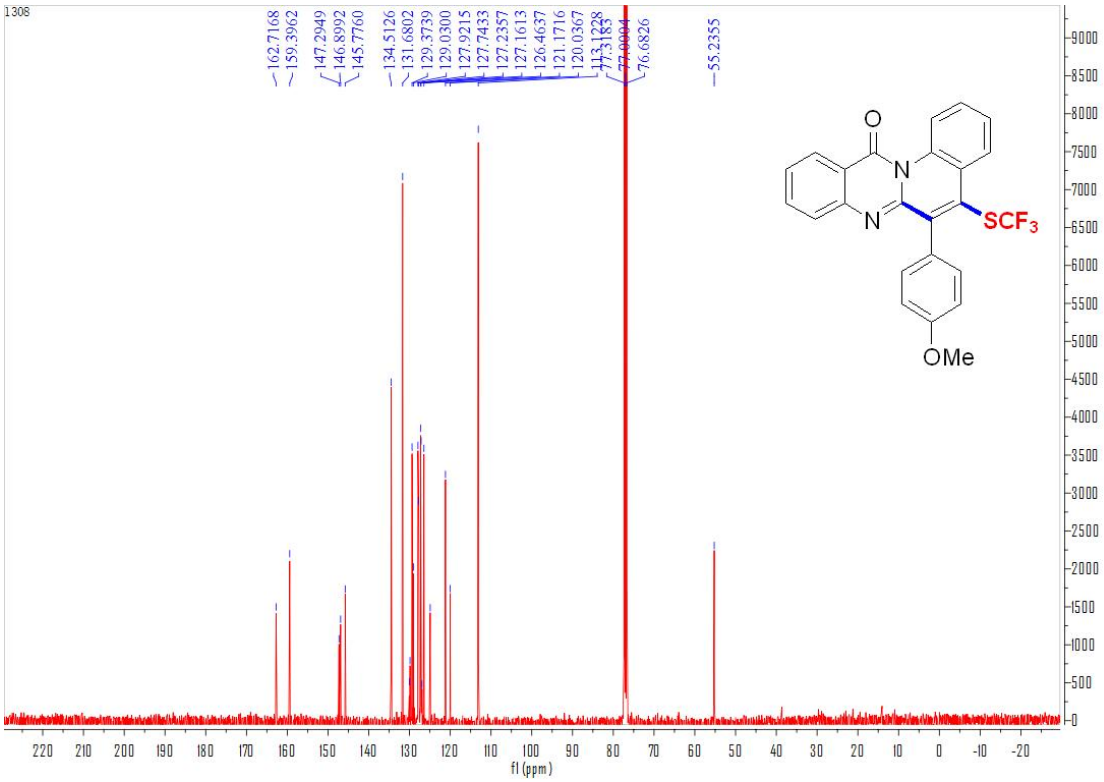
23-^{19}F NMR (565 MHz, $CDCl_3$)



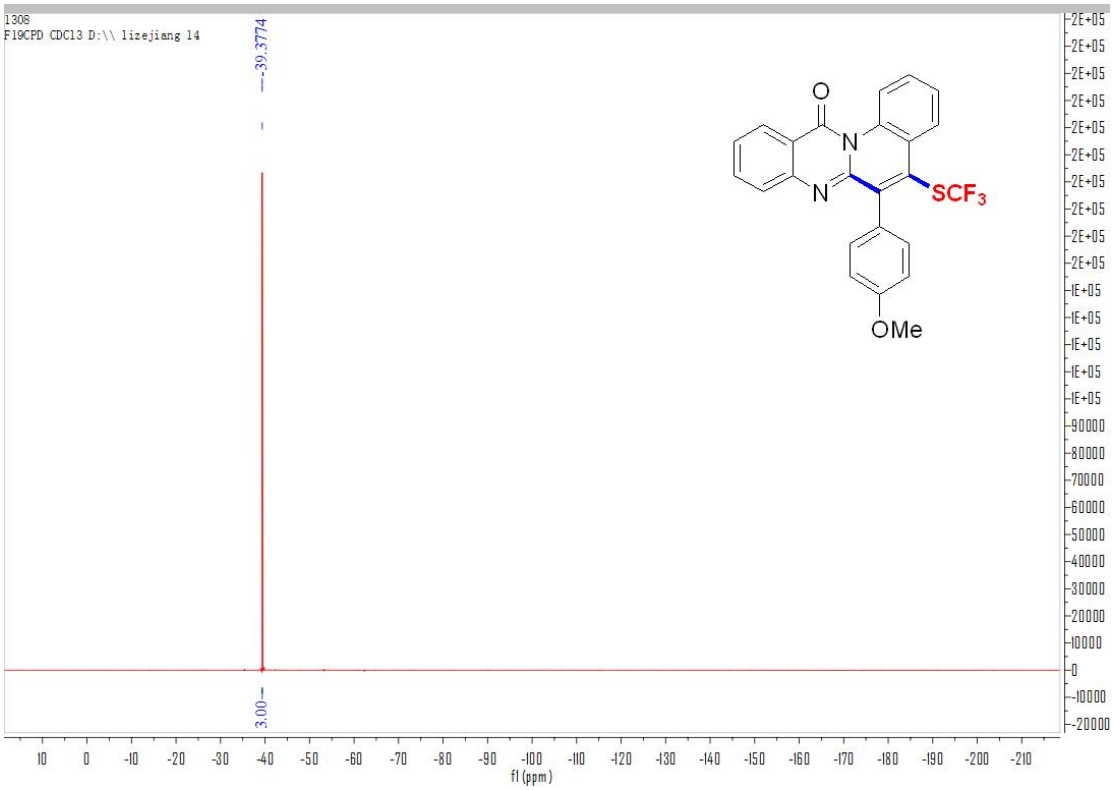
24-^{1}H NMR (400 MHz, $CDCl_3$)



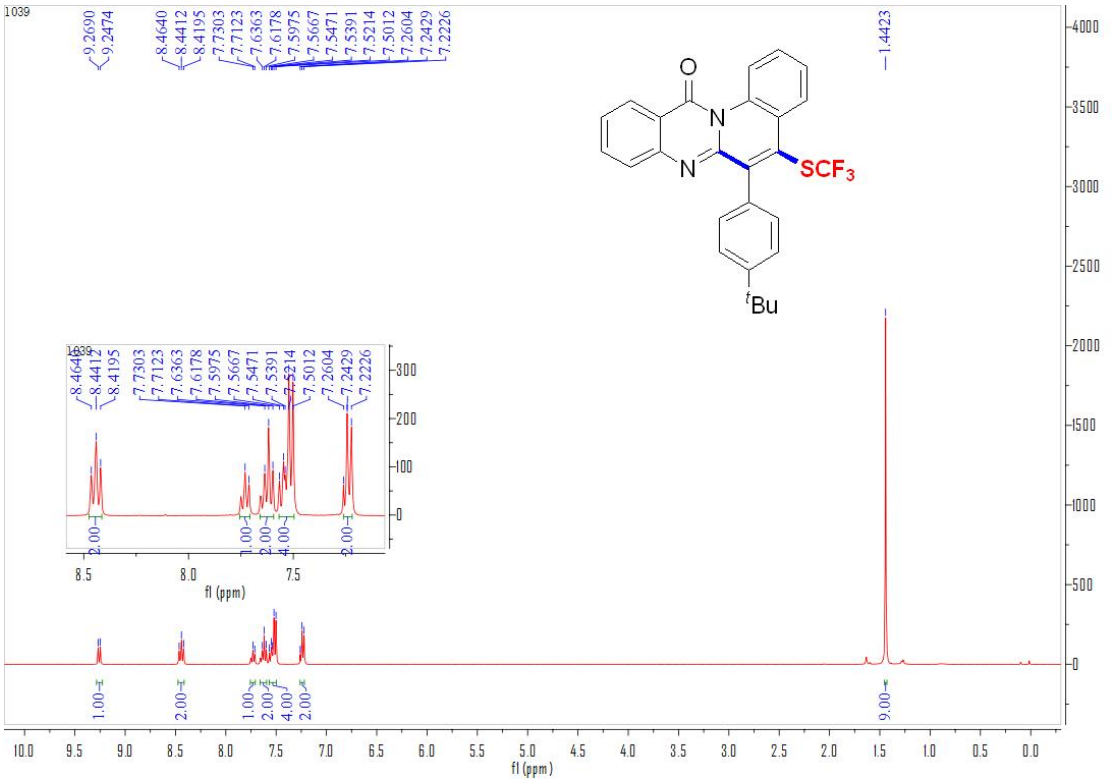
24-^{13}C NMR (100 MHz, $CDCl_3$)



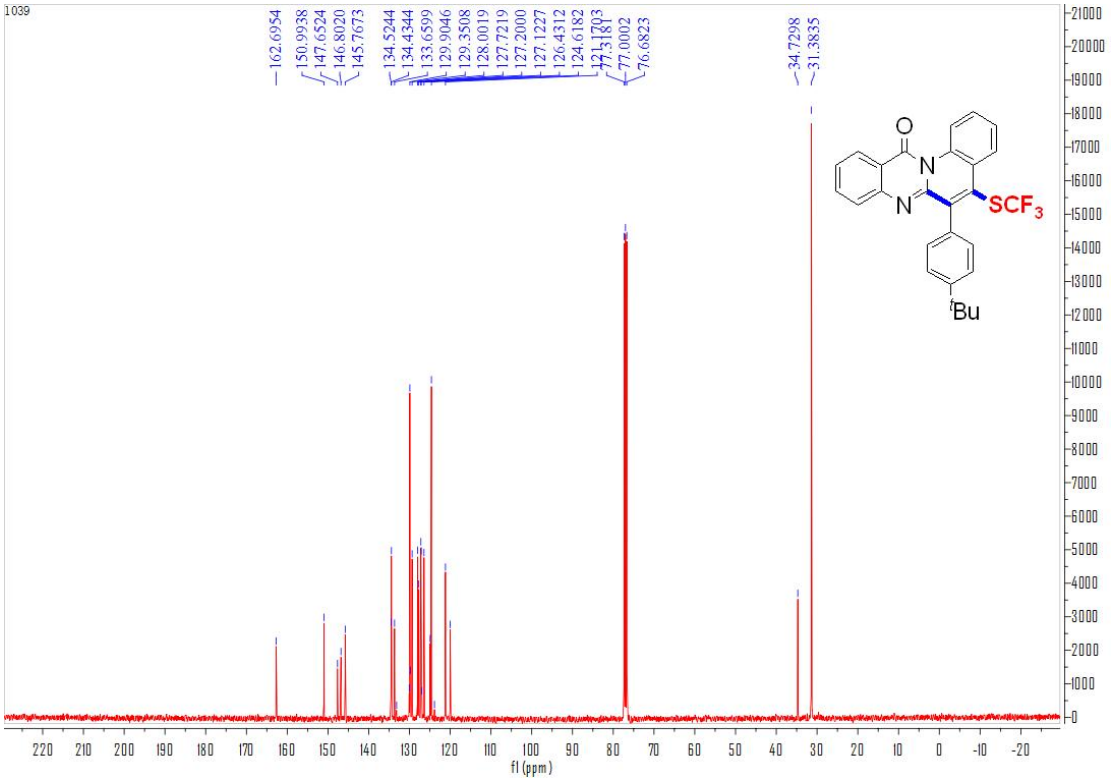
24-^{19}F NMR (565 MHz, $CDCl_3$)



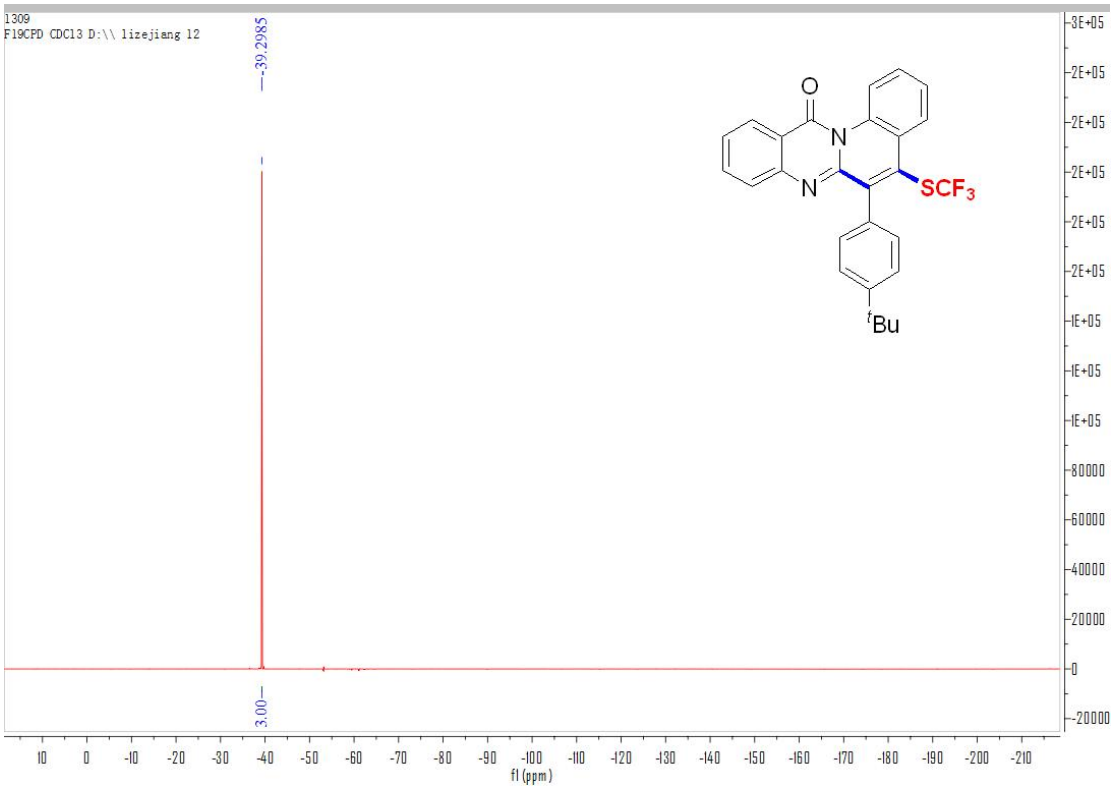
25-^{1}H NMR (400 MHz, $CDCl_3$)



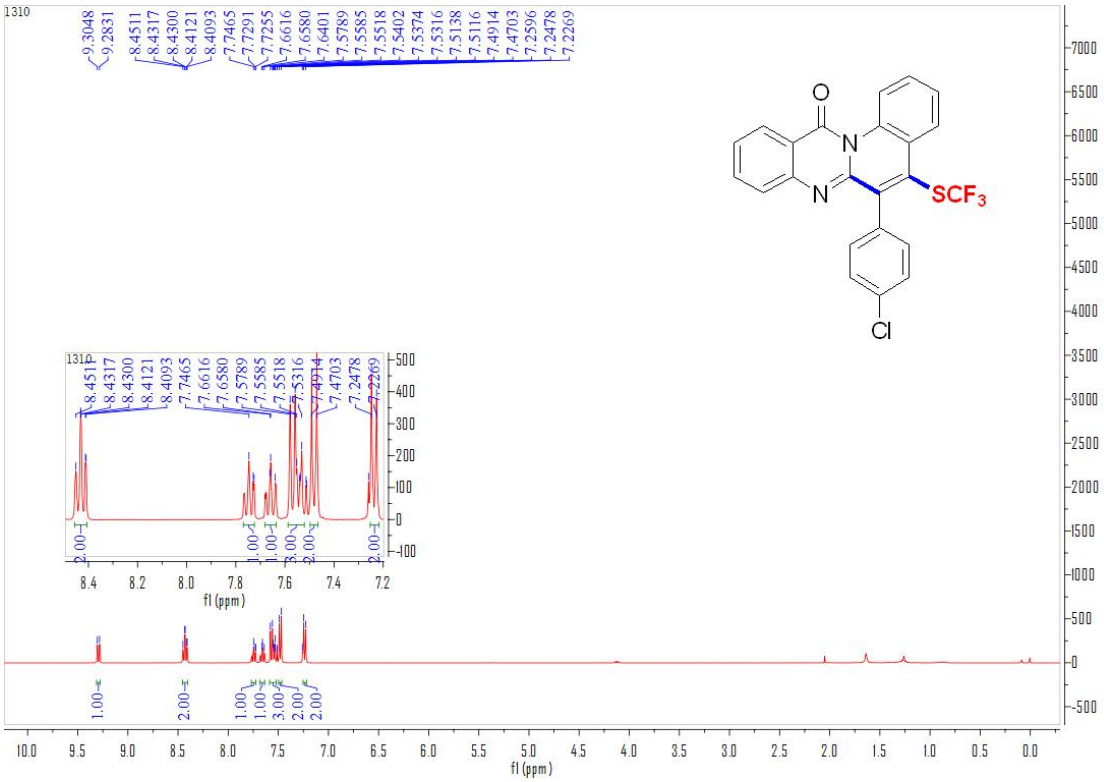
25-^{13}C NMR (100 MHz, $CDCl_3$)



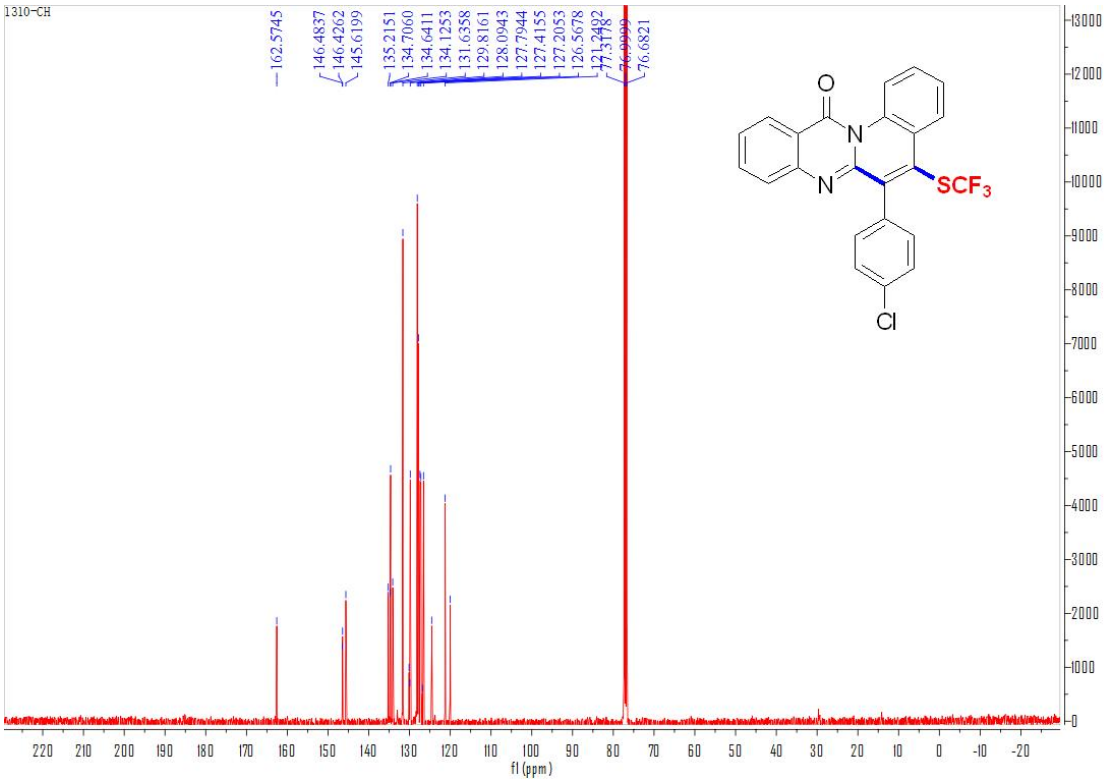
25-^{19}F NMR (565 MHz, $CDCl_3$)



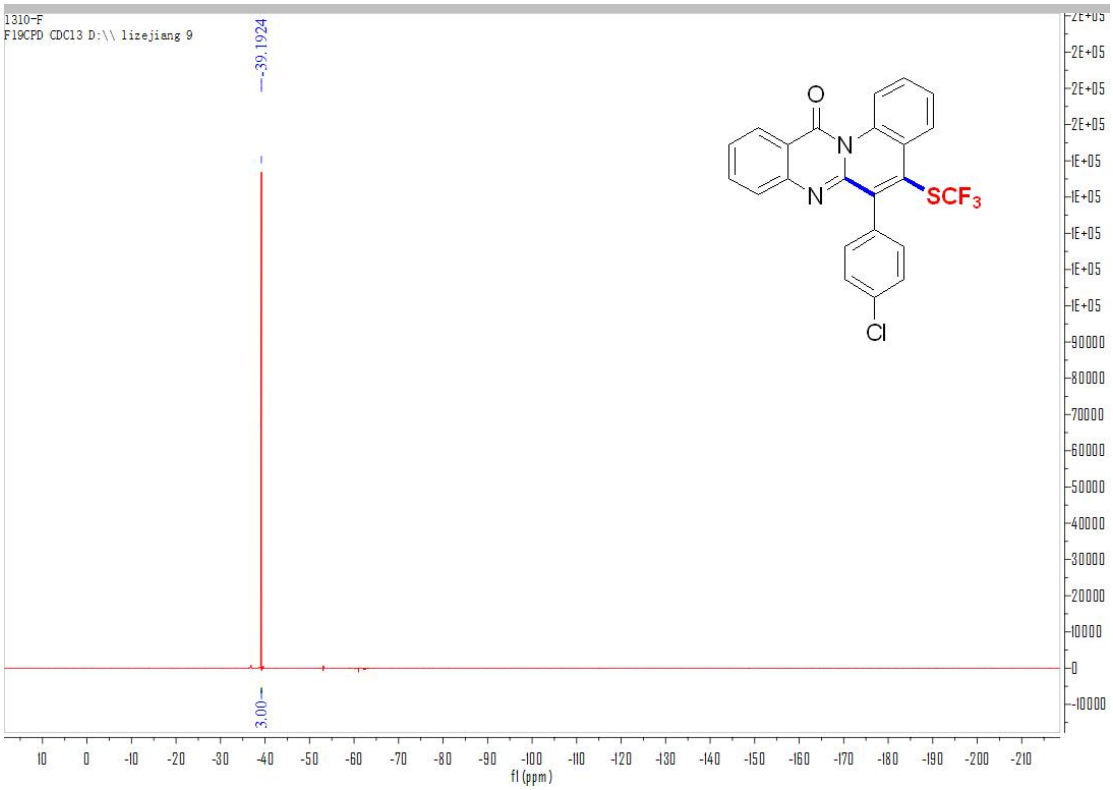
26-^{1}H NMR (400 MHz, $CDCl_3$)



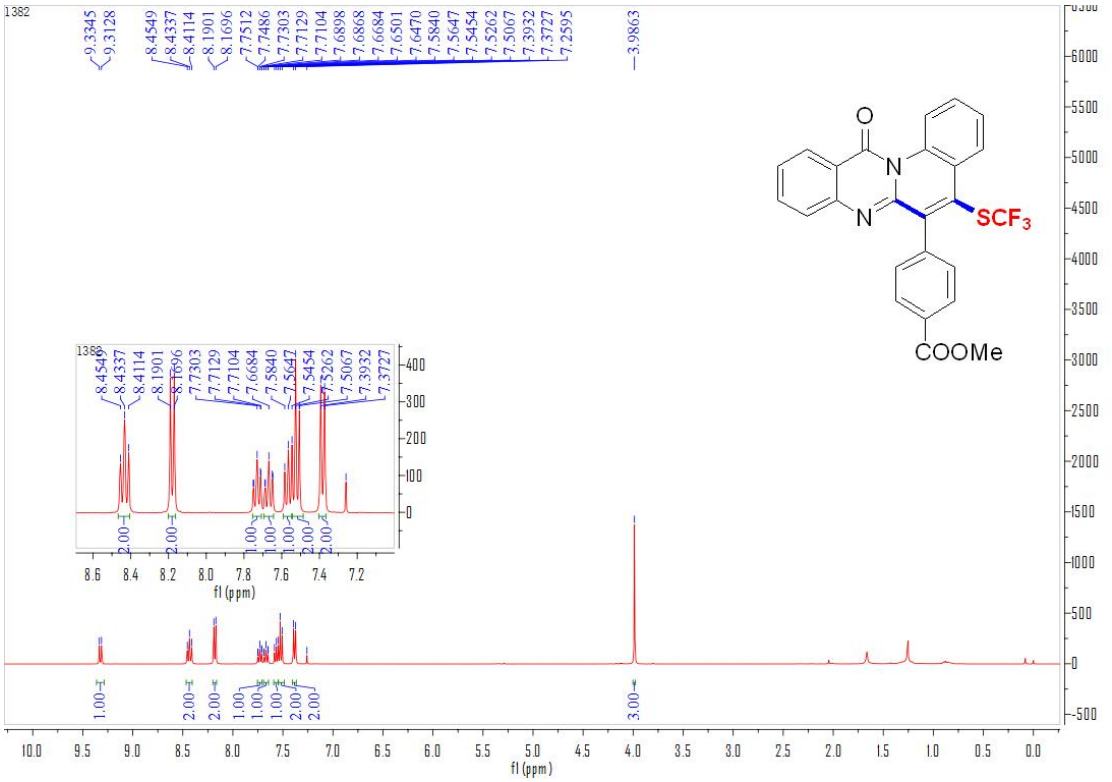
26-^{13}C NMR (100 MHz, $CDCl_3$)



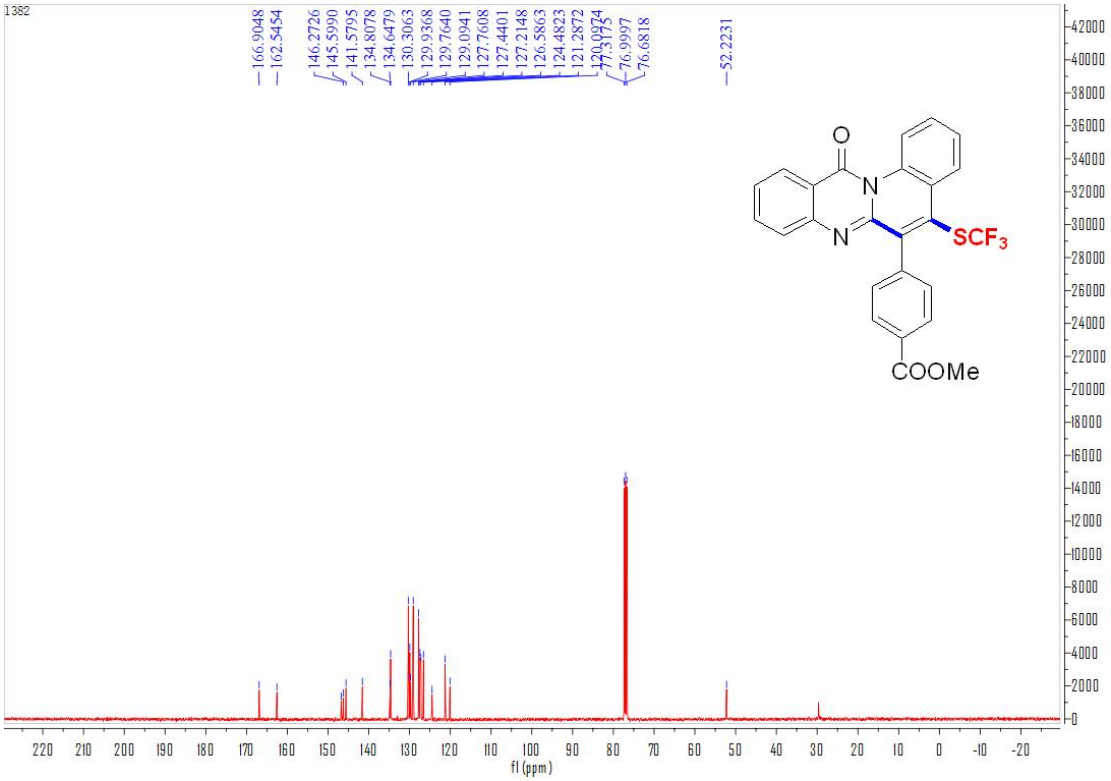
26-^{19}F NMR (565 MHz, $CDCl_3$)



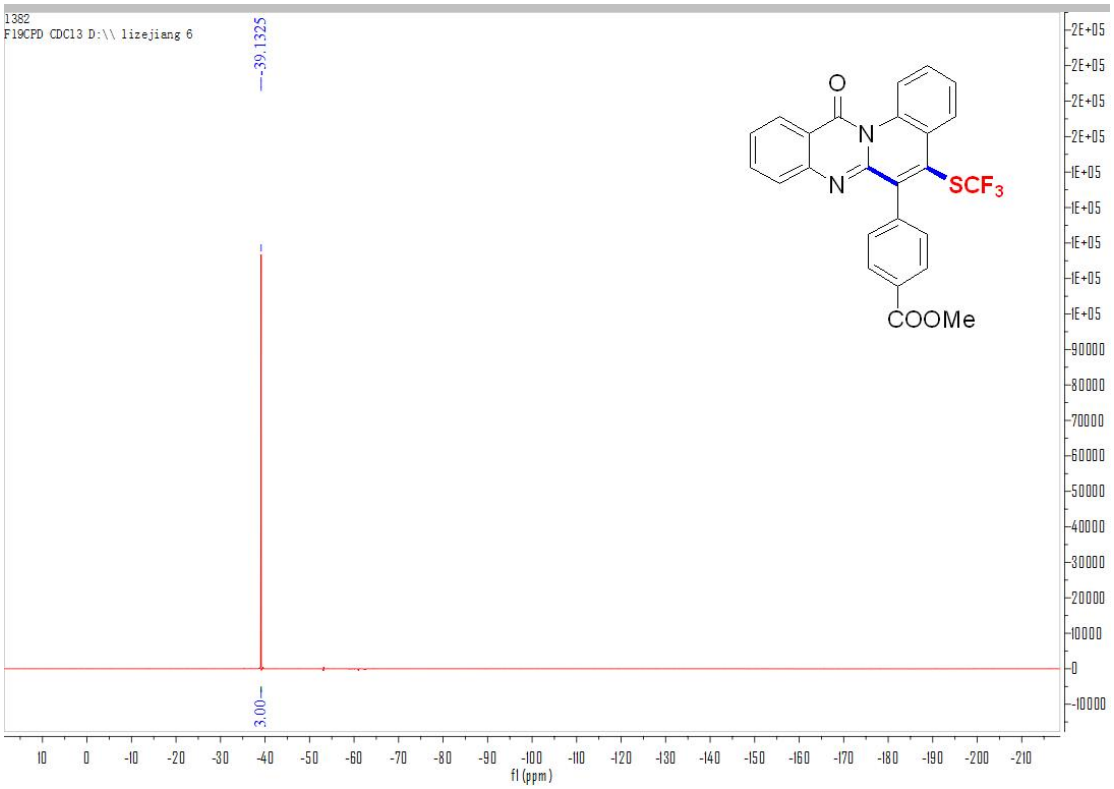
27-^{1}H NMR (400 MHz, $CDCl_3$)



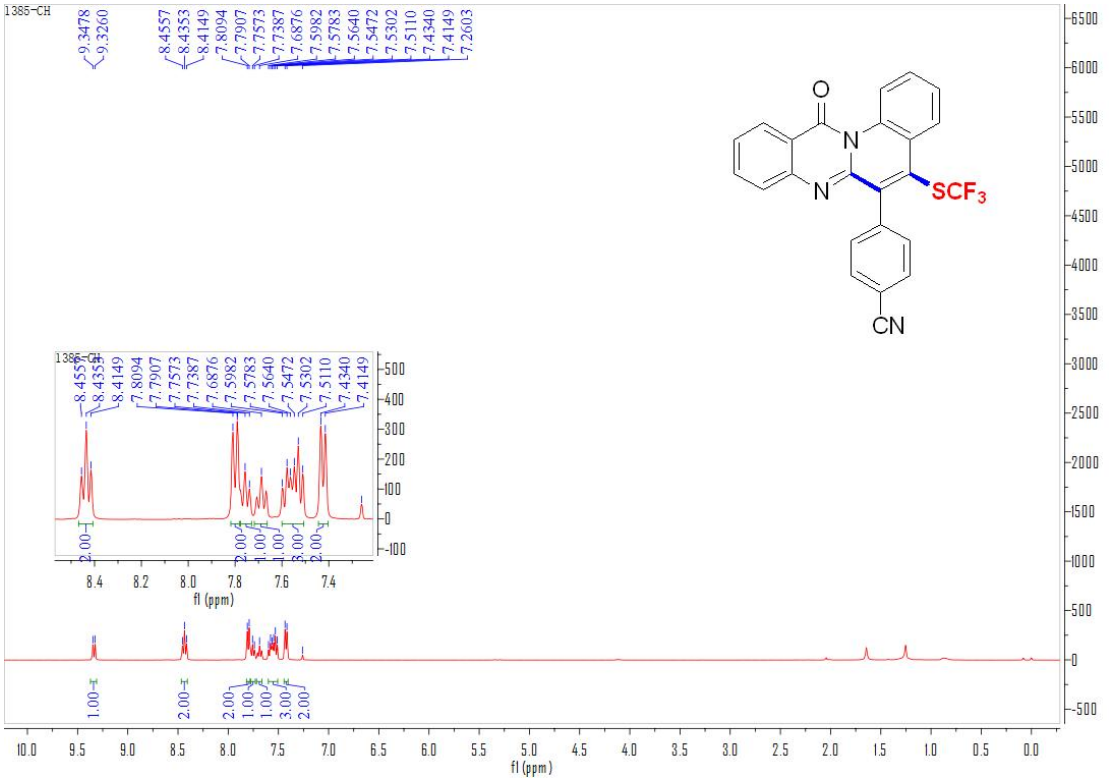
27-^{13}C NMR (100 MHz, $CDCl_3$)



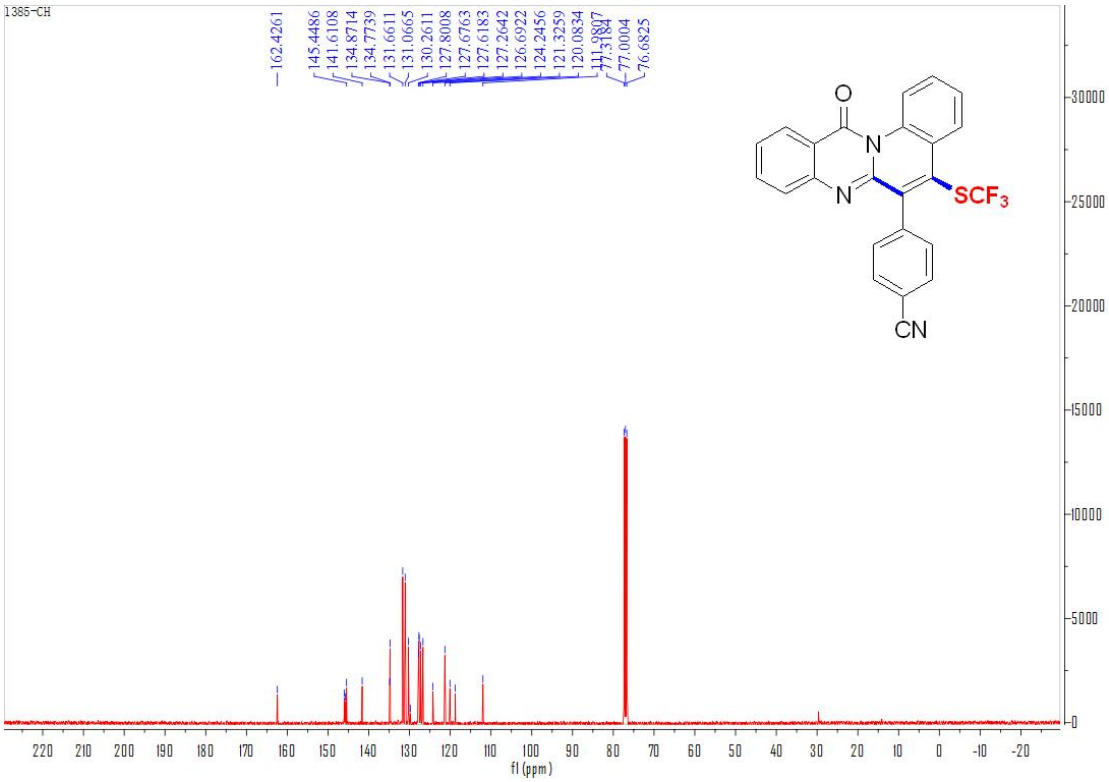
27-^{19}F NMR (565 MHz, $CDCl_3$)



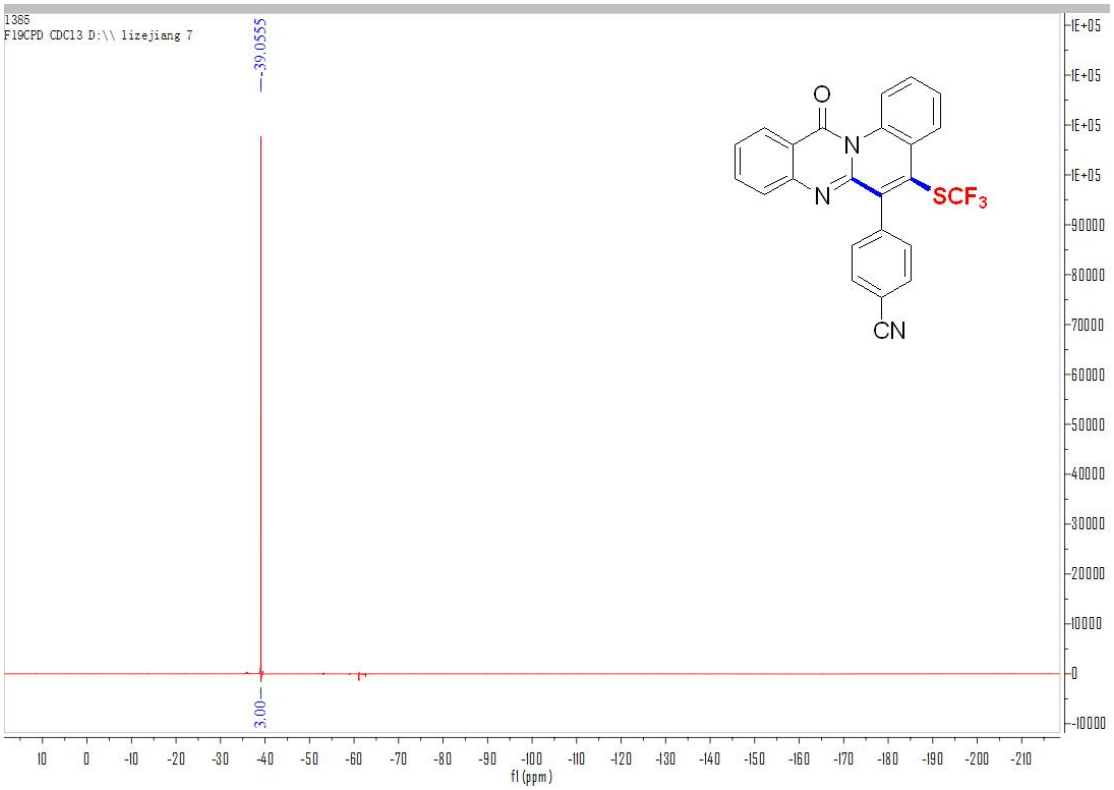
28-^{1}H NMR (400 MHz, $CDCl_3$)



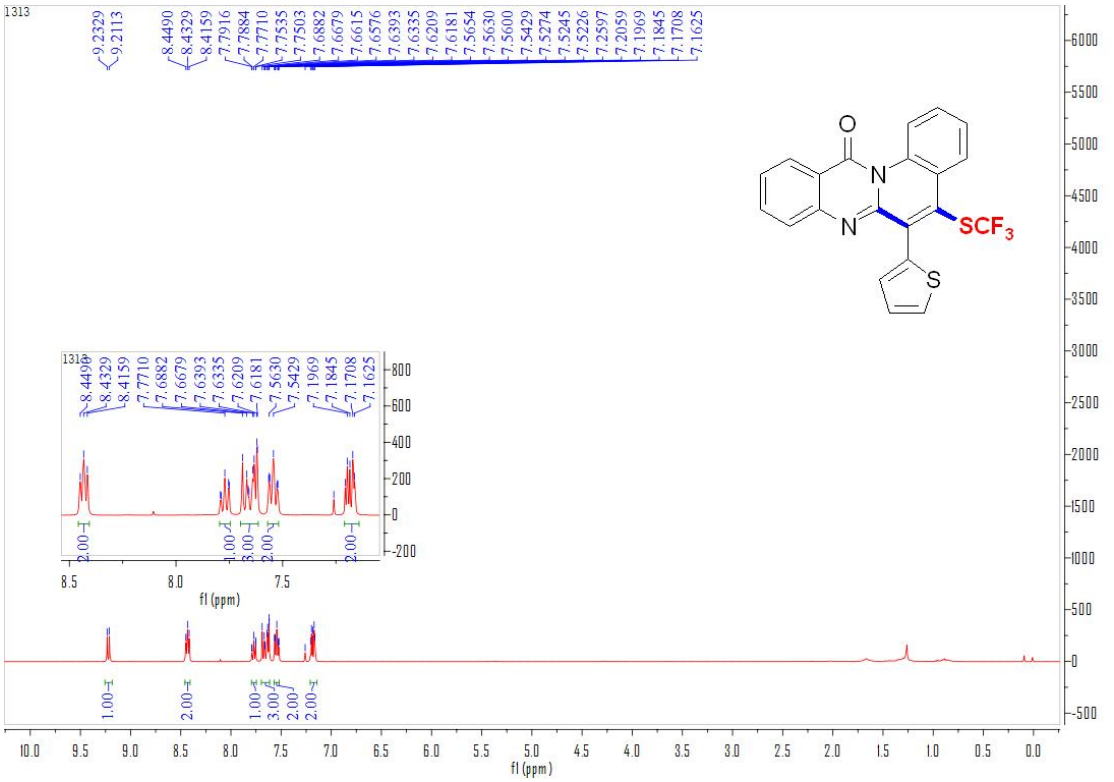
28-^{13}C NMR (100 MHz, $CDCl_3$)



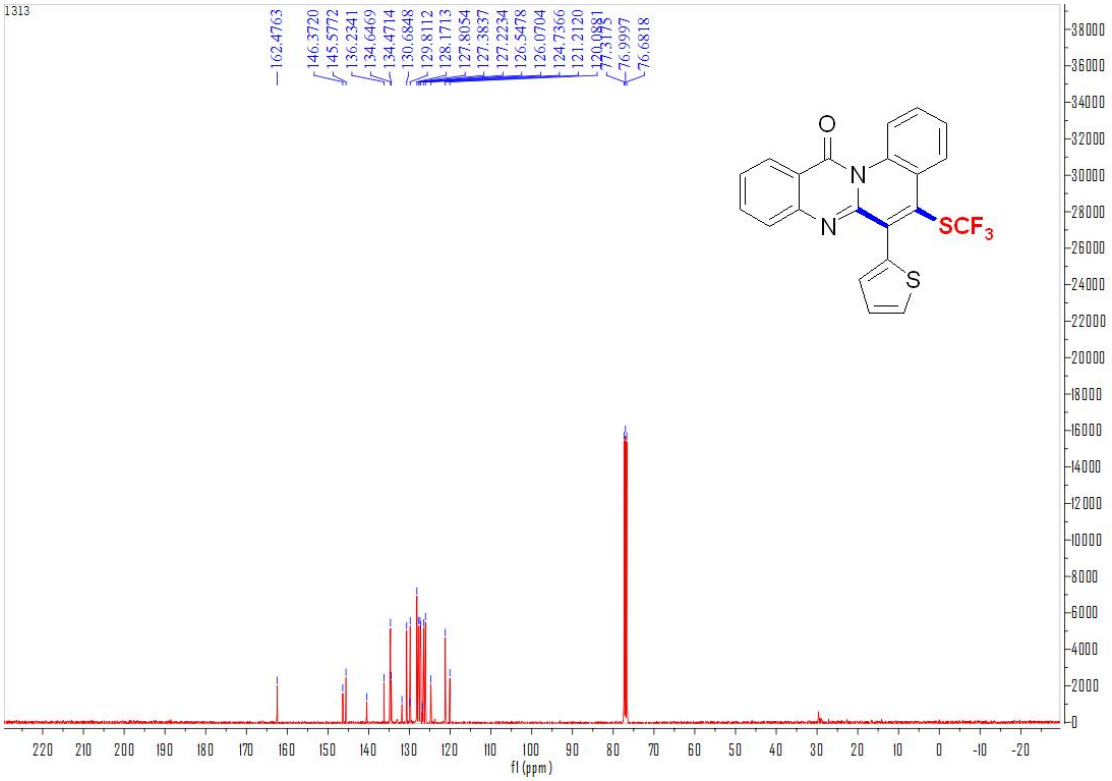
28-^{19}F NMR (565 MHz, $CDCl_3$)



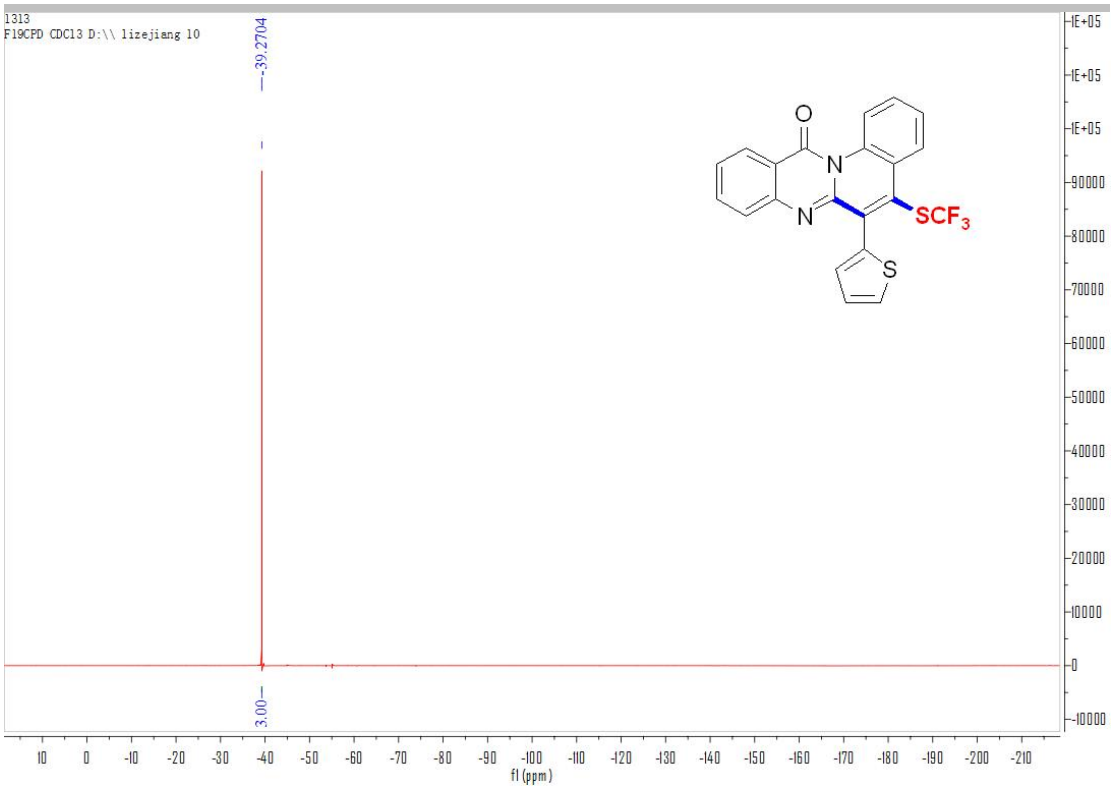
29-^{1}H NMR (400 MHz, $CDCl_3$)



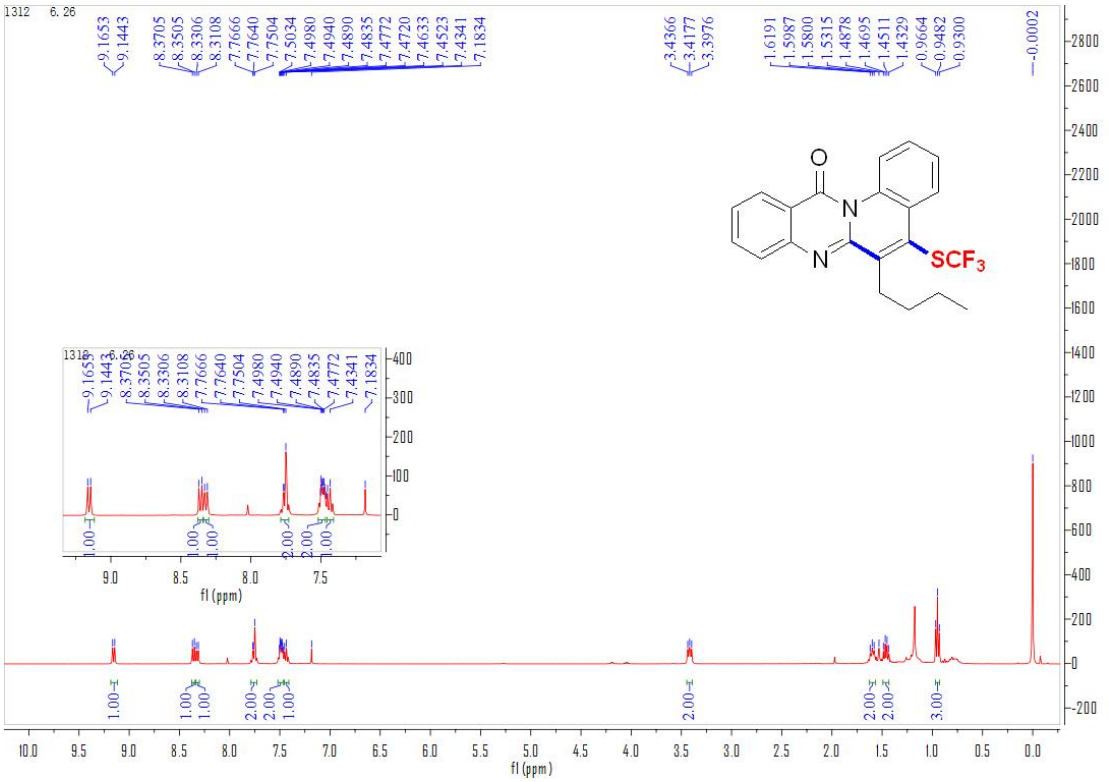
29-^{13}C NMR (100 MHz, $CDCl_3$)



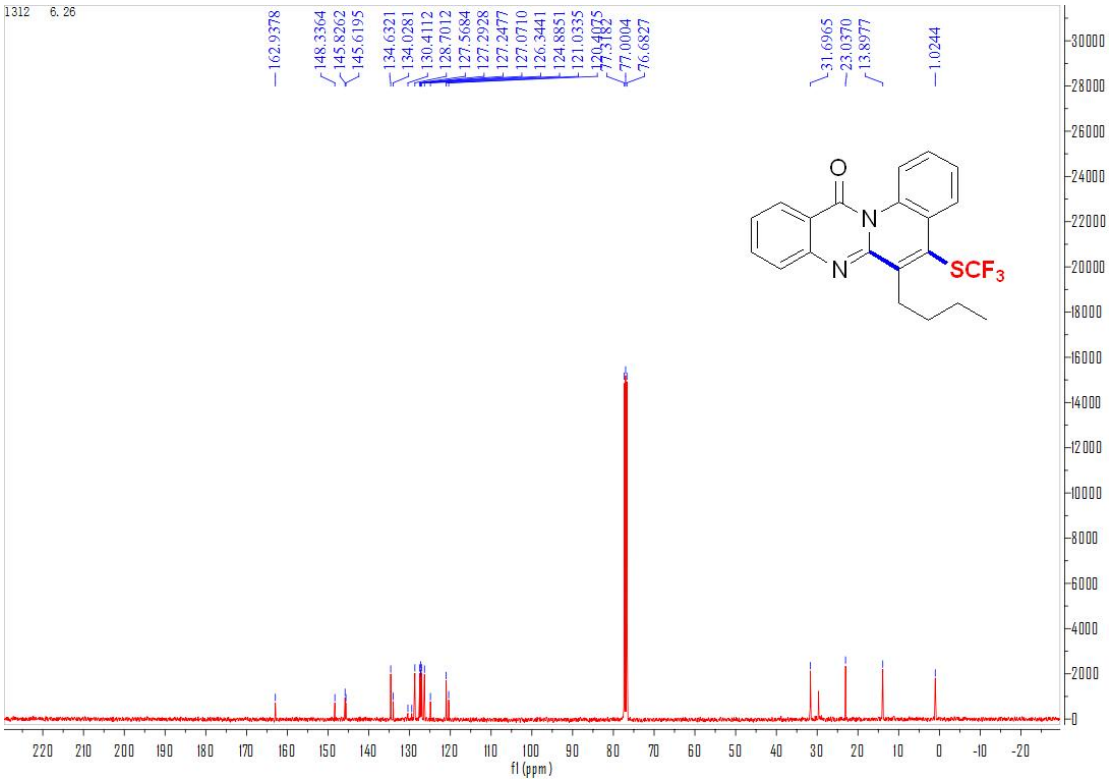
29-^{19}F NMR (565 MHz, $CDCl_3$)



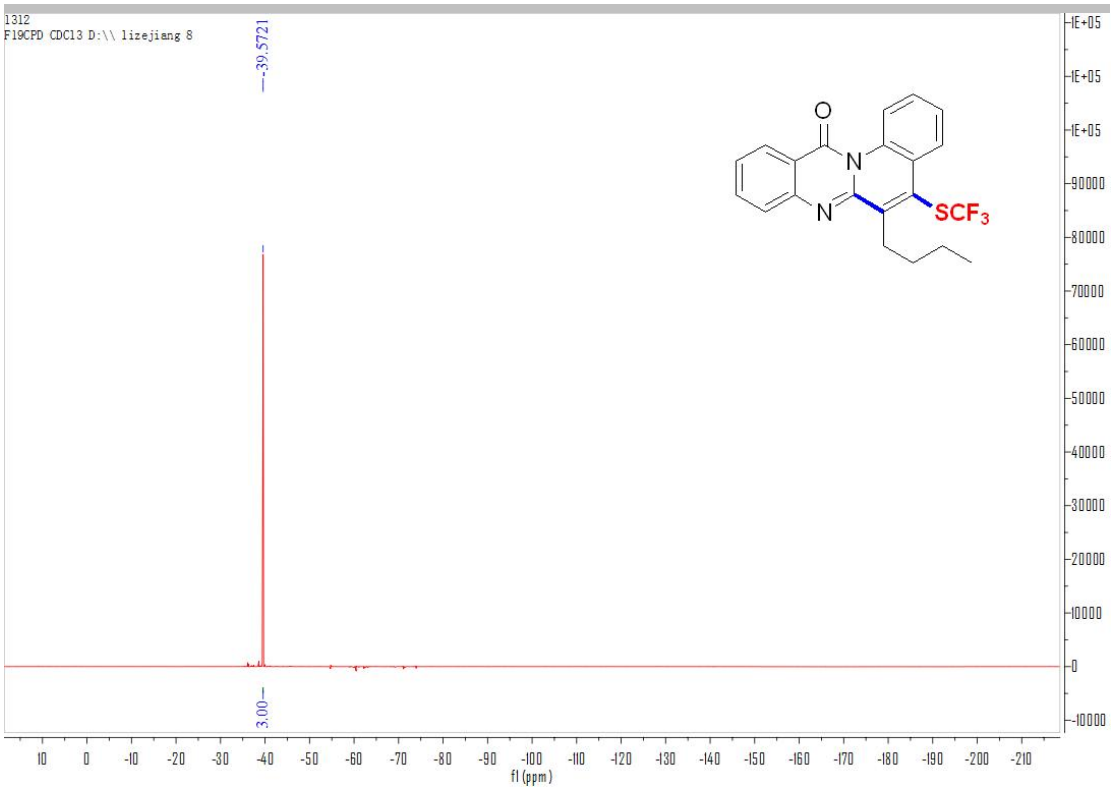
30-^{1}H NMR (400 MHz, $CDCl_3$)



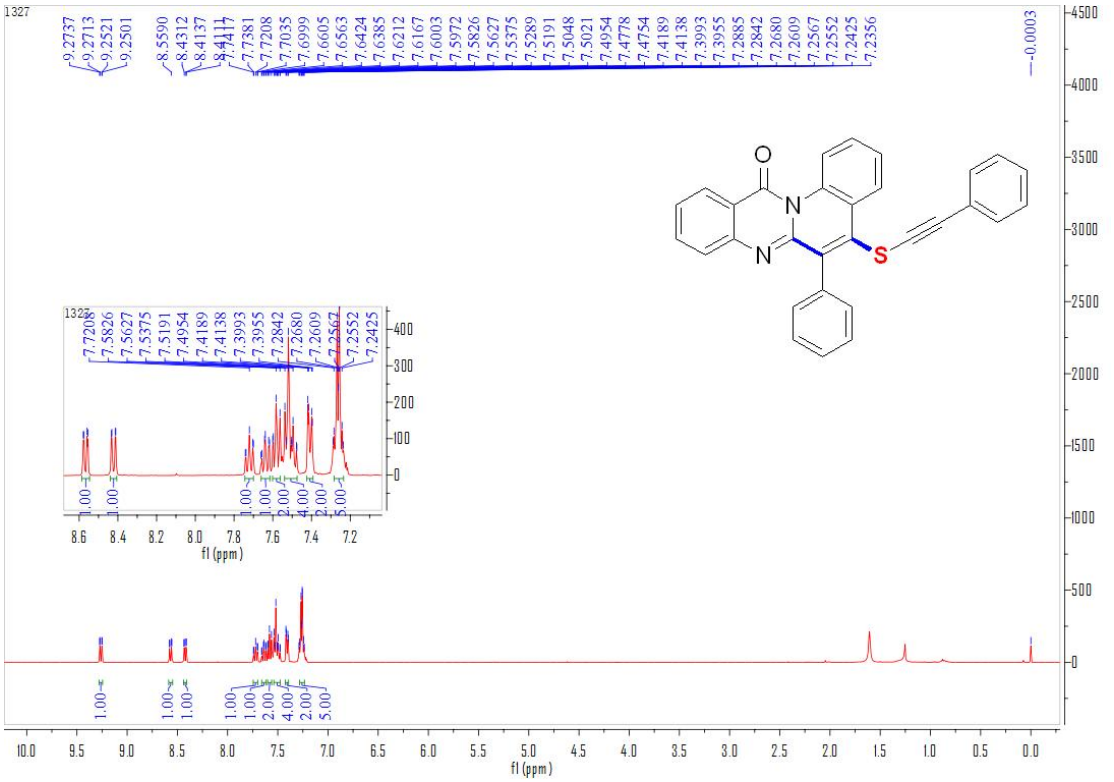
30-^{13}C NMR (100 MHz, $CDCl_3$)



30-^{19}F NMR (565 MHz, $CDCl_3$)



31-^{1}H NMR (400 MHz, $CDCl_3$)



31-^{13}C NMR (100 MHz, $CDCl_3$)