Supporting Information

Photo-induced thio/selenocyanation-annulation-rearrangement of indole-tethered 1,6-enynes

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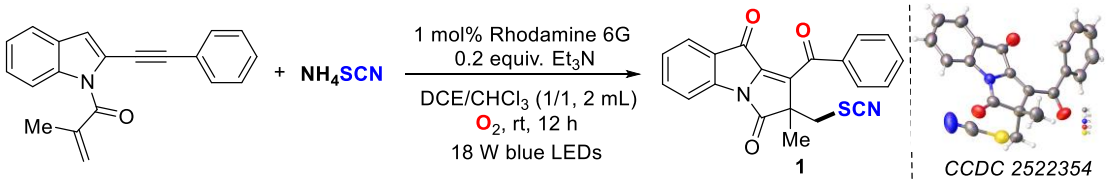
General Information

^{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 (ESI-TOF)) 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.

Condition optimization

Table S1 Optimization of thiocyanation reaction conditions.[a]



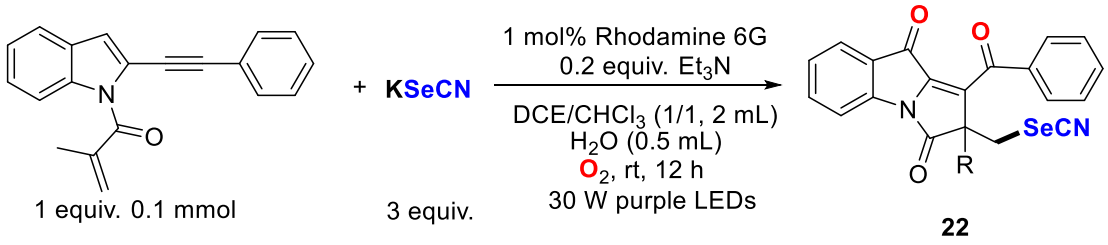
Entry	Photocatalyst (mol%)	Thiocyanate (equiv.)	Base (equiv.)	Solvent (mL)	Time (h)	Yield[b] (%)
1	Rhodamine 6G (1)	NH_4SCN (3)	DMAP (0.2)	$CHCl_3$ (2)	12 h	48
2	4CzIPN (1)	NH_4SCN (3)	DMAP (0.2)	$CHCl_3$ (2)	12 h	31
3	$Ir(ppy)_3$ (1)	NH_4SCN (3)	DMAP (0.2)	$CHCl_3$ (2)	12 h	26
4	Fluorescent (1)	NH_4SCN (3)	DMAP (0.2)	$CHCl_3$ (2)	12 h	15
5	Methylene Blue (1)	NH_4SCN (3)	DMAP (0.2)	$CHCl_3$ (2)	12 h	26
6	Acid red 94 (1)	NH_4SCN (3)	DMAP (0.2)	$CHCl_3$ (2)	12 h	trace
7	Sodium rhodizonate (1)	NH_4SCN (3)	DMAP (0.2)	$CHCl_3$ (2)	12 h	27
8	Solvent red 43 (1)	NH_4SCN (3)	DMAP (0.2)	$CHCl_3$ (2)	12 h	45
9	Rhodamine 6G (2)	NH_4SCN (3)	DMAP (0.2)	$CHCl_3$ (2)	12 h	44
10	Rhodamine 6G (3)	NH_4SCN (3)	DMAP (0.2)	$CHCl_3$ (2)	12 h	43
11	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (2)	12 h	54
12	Rhodamine 6G (1)	NH_4SCN (3)	K_2CO_3 (0.2)	$CHCl_3$ (2)	12 h	35
13	Rhodamine 6G (1)	NH_4SCN (3)	Cs_2CO_3 (0.2)	$CHCl_3$ (2)	12 h	35
14	Rhodamine 6G (1)	NH_4SCN (3)	$K_2HPO_4 \cdot 3H_2O$ (0.2)	$CHCl_3$ (2)	12 h	30
15	Rhodamine 6G (1)	NH_4SCN (3)	Ag_2CO_3 (0.2)	$CHCl_3$ (2)	12 h	38
16	Rhodamine 6G (1)	NH_4SCN (3)	$^{i}Pr_2NH$ (0.2)	$CHCl_3$ (2)	12 h	51
17	Rhodamine 6G (1)	NH_4SCN (3)	DABCO (0.2)	$CHCl_3$ (2)	12 h	42
18	Rhodamine 6G (1)	NH_4SCN (3)	Pyridine (0.2)	$CHCl_3$ (2)	12 h	31
19	Rhodamine 6G (1)	NH_4SCN (3)	CH_3CO_2Na (0.2)	$CHCl_3$ (2)	12 h	32
20	Rhodamine 6G (1)	NH_4SCN (3)	HOSA (0.2)	$CHCl_3$ (2)	12 h	30

21	Rhodamine 6G (1)	NH_4SCN (3)	4-cyanopyridine	$CHCl_3$ (2)	12 h	42
22	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.25)	$CHCl_3$ (2)	12 h	45
23	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.15)	$CHCl_3$ (2)	12 h	46
24	Rhodamine 6G (1)	NaSCN (3)	Et_3N (0.2)	$CHCl_3$ (2)	12 h	38
25	Rhodamine 6G (1)	KSCN (3)	Et_3N (0.2)	$CHCl_3$ (2)	12 h	37
26	Rhodamine 6G (1)	LiSCN (3)	Et_3N (0.2)	$CHCl_3$(2)	12 h	trace
27	Rhodamine 6G (1)	CuSCN (3)	Et_3N (0.2)	$CHCl_3$(2)	12 h	NR
28	Rhodamine 6G (1)	CoSCN (3)	Et_3N (0.2)	$CHCl_3$(2)	12 h	NR
29	Rhodamine 6G (1)	NH_4SCN (2.5)	Et_3N (0.2)	$CHCl_3$(2)	12 h	40
30	Rhodamine 6G (1)	NH_4SCN (3.5)	Et_3N (0.2)	$CHCl_3$(2)	12 h	44
31	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	CH_3CN (2)	12 h	23
32	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	THF (2)	12 h	NR
33	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	DCE (2)	12 h	50
34	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	DMF (2)	12 h	trace
35	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	DMSO (2)	12 h	trace
36	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	Acetone (2)	12 h	trace
37	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	EA (2)	12 h	trace
38	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	DCM (2)	12 h	38
39	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	MeOH (2)	12 h	NR
40	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	EtOH (2)	12 h	NR
41	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	2-chloropropane (2)	12 h	45
42	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (3)	12 h	43
43	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (4)	12 h	37
44	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (2.5)	12 h	48
45	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (1.5)	12 h	27
46	**Rhodamine 6G (1)**	**NH_4SCN (3)**	**Et_3N (0.2)**	**$CHCl_3$ (1) DCE (1)**	**12 h**	**61**
47	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (1.5) DCE (1)	12 h	58
48	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1.5)	12 h	50
49	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (1.5) DCE (1.5)	12 h	56
50	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (0.5) DCE (0.5)	12 h	45
51	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1)	3 h	18

52	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1)	6 h	31
53	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1)	9 h	50
54	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1)	15 h	52
55[c]	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1)	12 h	15
56[d]	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1)	12 h	39
57[e]	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1)	12 h	trace
58[f]	Rhodamine 6G (1)	NH_4SCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1)	12 h	53

[a]Reaction conditions: indole-tethered 1,6-enyne (1 equiv., 0.1 mmol), NH_4SCN (3 equiv.), Rhodamine 6G (1 mol%), Et_3N (0.2 equiv.), $CHCl_3$ (1 mL), DCE (1 mL), O_2, 18 W blue LEDs, rt, 12 h. [b]Isolated yields. [c]9 W blue LEDs. [d]12 W blue LEDs. [e]12 W purple LEDs. [f]25 W blue LEDs.

Table S2 Optimization of selenocyanation reaction conditions.[a]



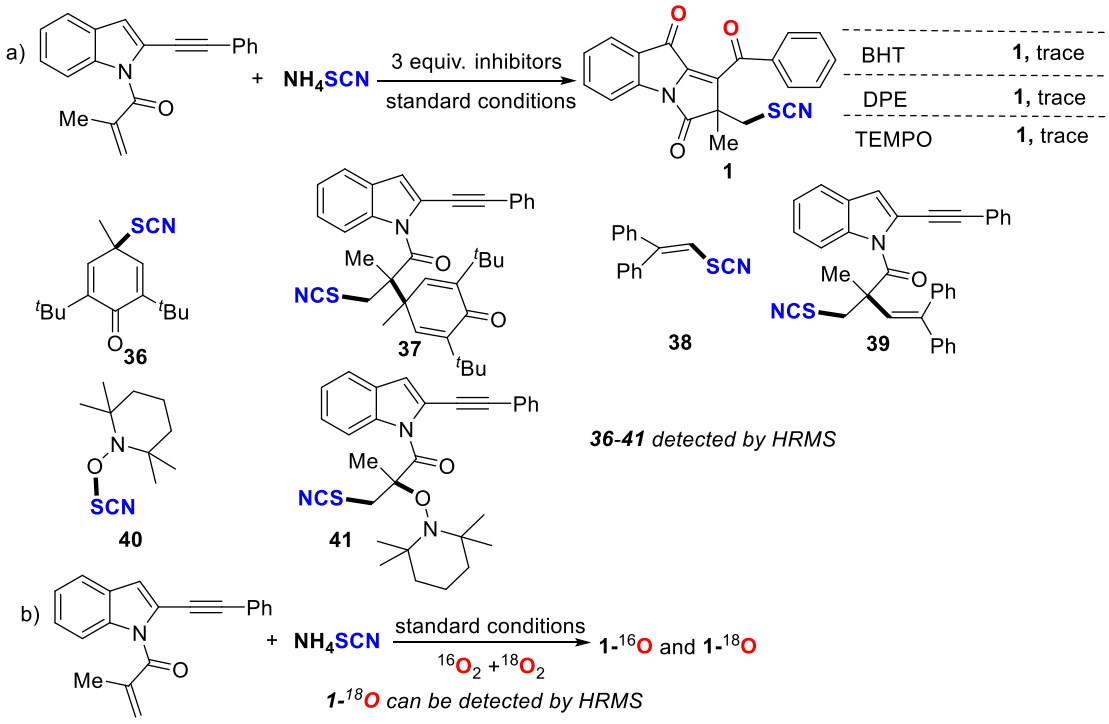
22

Entry (equiv.)	Photocatalyst (mol%)	Thiocyanate (equiv.)	Base (equiv.)	Solvent (mL)	Time (h)	Yield[b] (%)
1	**Rhodamine 6G (1)**	**KSeCN (3)**	**Et_3N (0.2)**	**$CHCl_3$ (1) DCE (1) H_2O (0.5)**	**12 h**	**43**
2	Rhodamine 6G (1)	KSeCN (3)	Et_3N (0.2)	$CHCl_3$ (2) H_2O (0.5)	12 h	36
3	Rhodamine 6G (1)	KSeCN (3)	Et_3N (0.2)	DCE (2) H_2O (0.5)	12 h	31
4	Rhodamine 6G (1)	KSeCN (3)	Et_3N (0.2)	EA (2) H_2O (0.5)	12 h	trace
5	Rhodamine 6G (1)	KSeCN (3)	Et_3N (0.2)	DCM (2) H_2O (0.5)	12 h	26
6	Rhodamine 6G (1)	KSeCN (3)	Et_3N (0.2)	1,4-dioxane (2) H_2O (0.5)	12 h	NR
7	Rhodamine 6G (1)	KSeCN (3)	Et_3N (0.2)	CH_3CN (2) H_2O (0.5)	12 h	trace

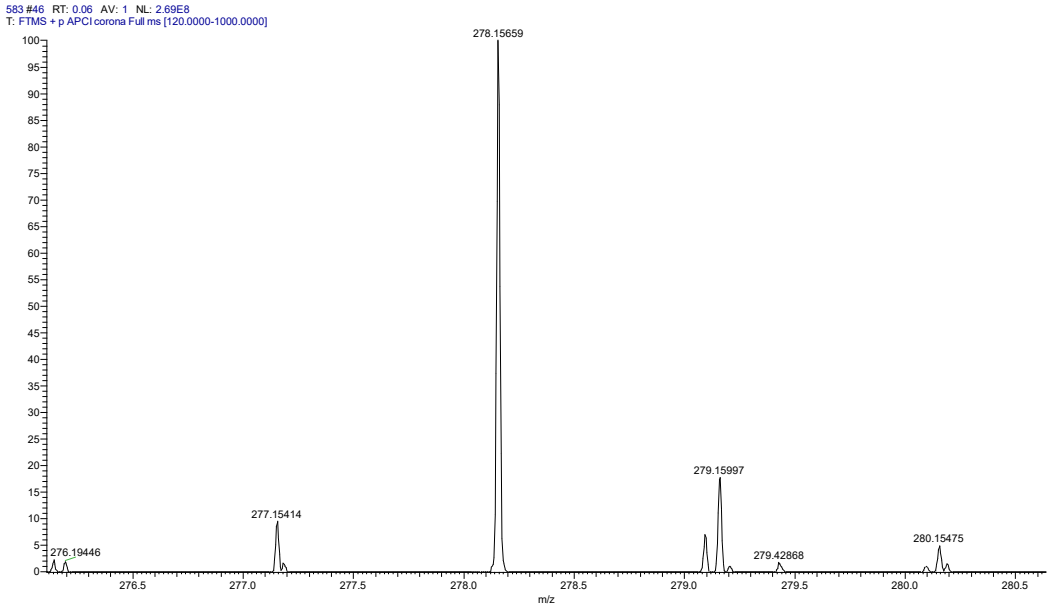
8	Rhodamine 6G (1)	KSeCN (3)	Et_3N (0.2)	THF (2) H_2O (0.5)	12 h	NR
9	Rhodamine 6G (1)	KSeCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1) H_2O (0.8)	12 h	33
10	Rhodamine 6G (1)	KSeCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1)	12 h	NR
11	Rhodamine 6G (1)	KSeCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1) H_2O (0.5)	6 h	29
12	Rhodamine 6G (1)	KSeCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1) H_2O (0.5)	18 h	36
13[c]	Rhodamine 6G (1)	KSeCN (3)	Et_3N (0.2)	$CHCl_3$ (1) DCE (1) H_2O (0.5)	12 h	15

[a]Reaction conditions: indole-tethered 1,6-enynes (1 equiv., 0.1 mmol), KSeCN (3 equiv.), Rhodamine 6G (1 mol%), Et_3N (0.2 equiv.), $CHCl_3$ (1 mL), DCE (1 mL), H_2O (0.5 mL), O_2, 30 W purple LEDs, rt, 12 h. [b]Isolated yields. [c]18 W blue LEDs.

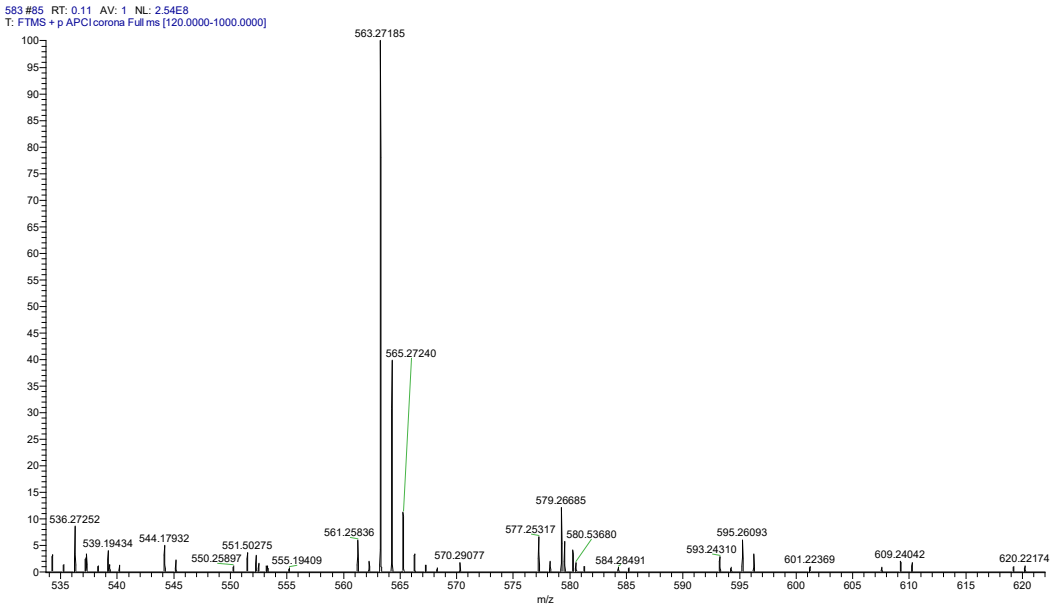
Mechanistic studies



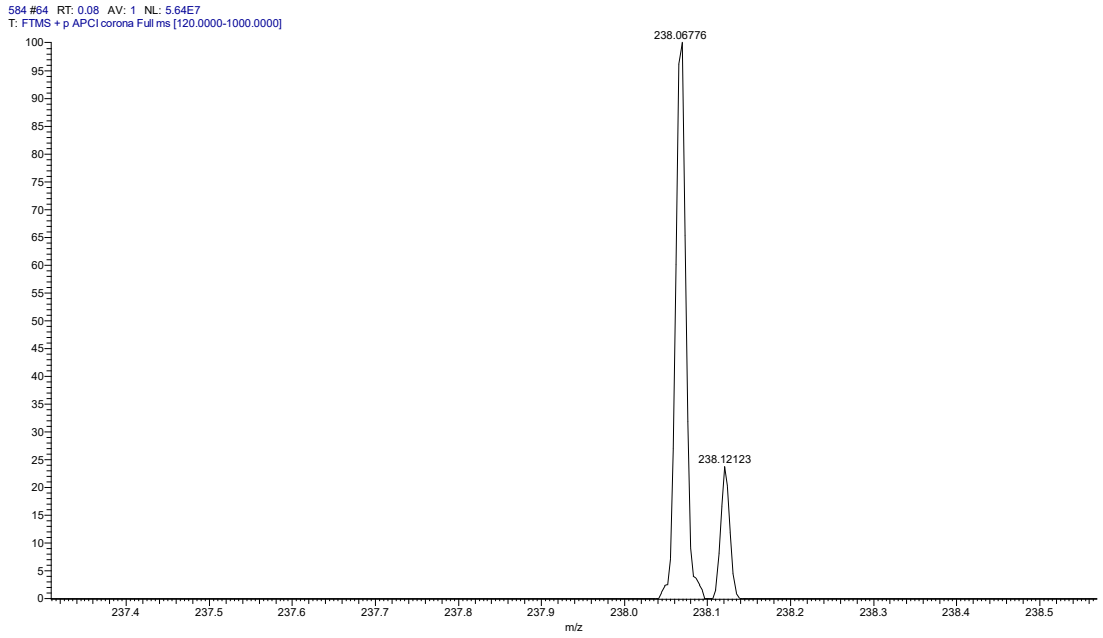
Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
36	$C_{16}H_{23}NOS$	$C_{16}H_{24}NOS$	278.1566	278.1573	-2.52



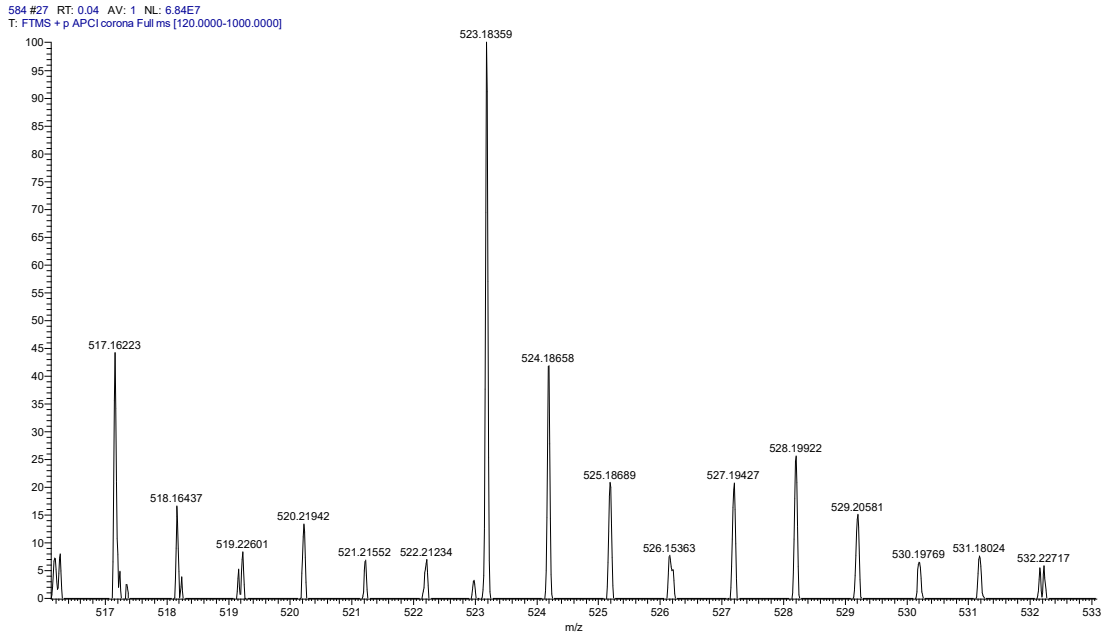
Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
37	$C_{36}H_{38}N_2O_2S$	$C_{36}H_{39}N_2O_2S$	563.2719	563.2727	-1.42



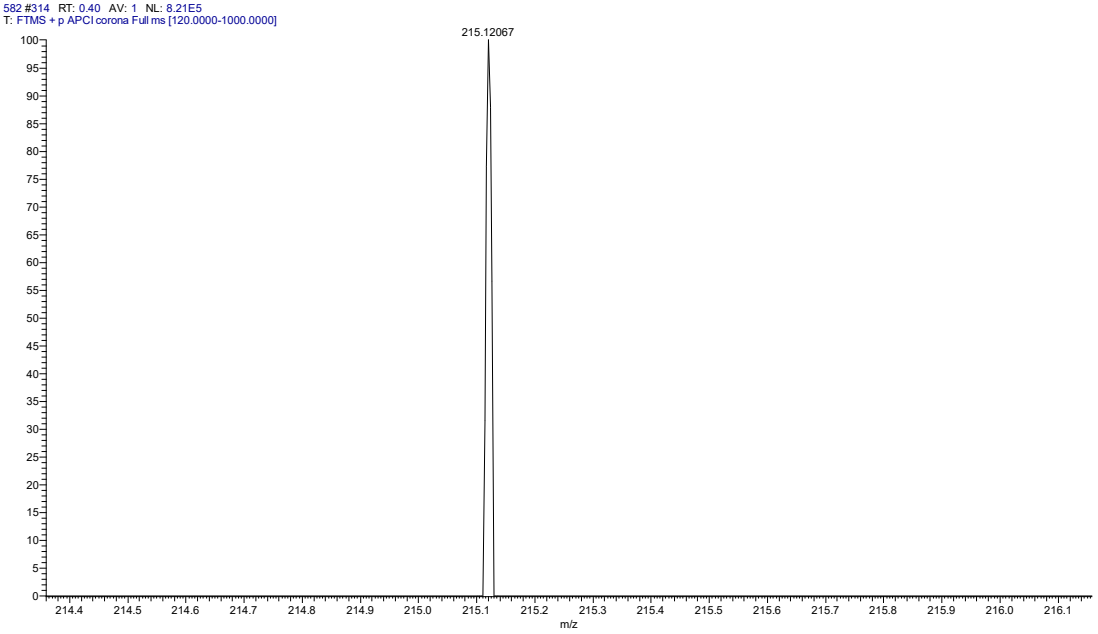
Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
38	$C_{15}H_{11}NS$	$C_{15}H_{12}NS$	238.0678	238.0685	-2.94



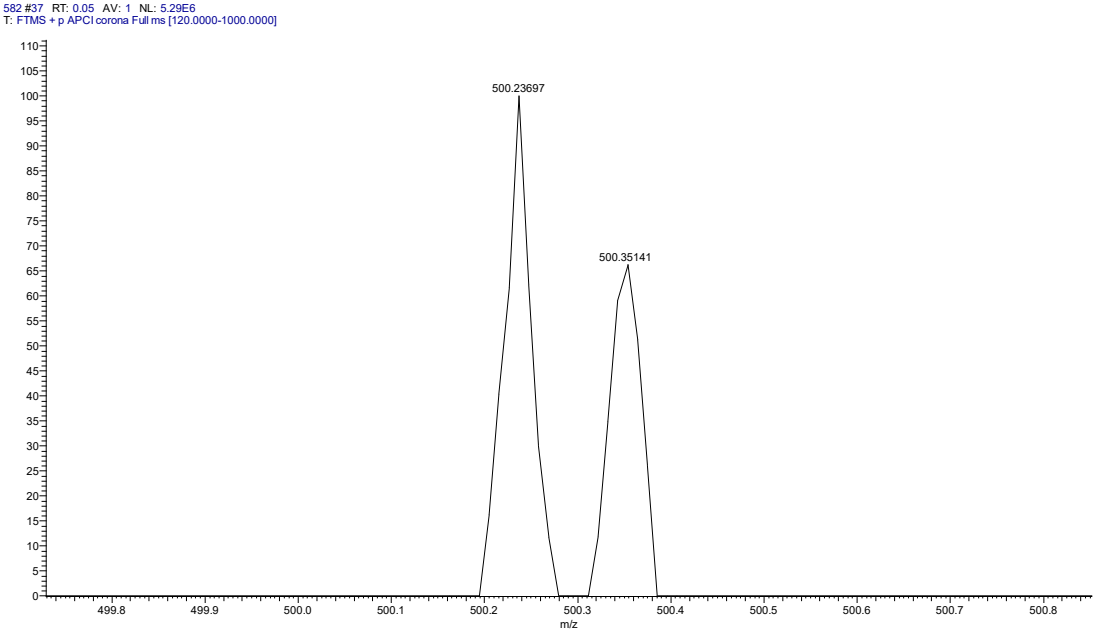
Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
39	$C_{35}H_{26}N_2OS$	$C_{35}H_{27}N_2OS$	523.1836	523.1839	-0.57



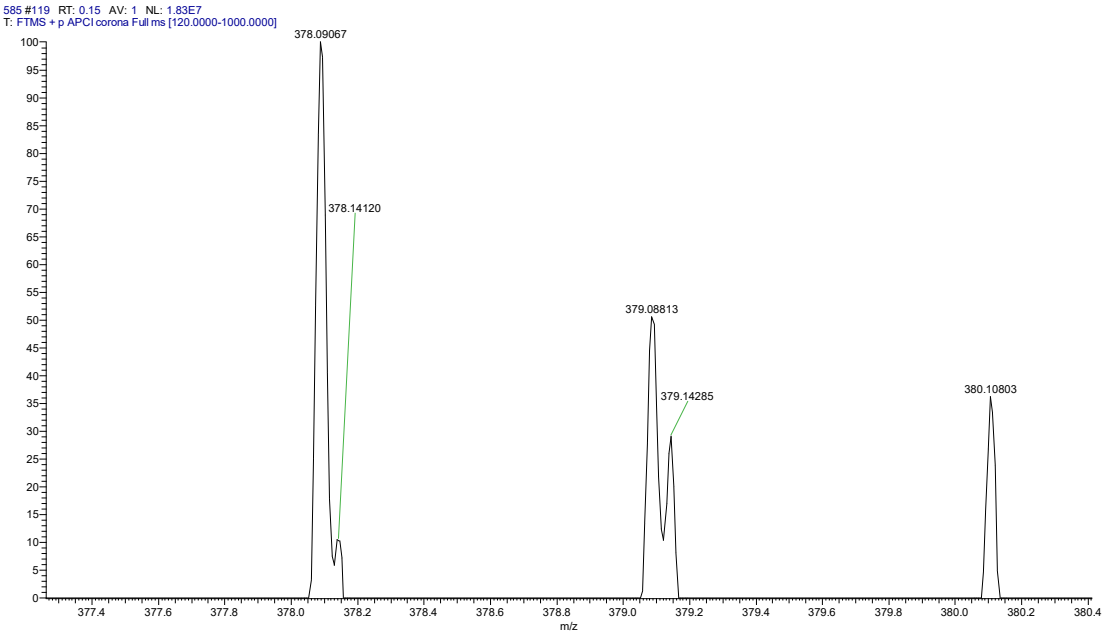
Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
40	$C_{10}H_{18}N_2OS$	$C_{10}H_{19}N_2OS$	215.1207	215.1213	-2.79



Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
41	$C_{30}H_{33}N_3O_2S$	$C_{30}H_{34}N_3O_2S$	500.2370	500.2366	0.8



Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
1-^{18}O	$C_{21}H_{14}N_2O^{18}O_2S$	$C_{21}H_{15}N_2O^{18}O_2S$	379.0881	379.0883	-0.53



Crystallographic details

(1) First, the thiocyanated fused cycle **1** was dissolved with the mixture of 1.0 mL dichloromethane (DCM) and 3.0 mL petroleum ether (PE) in a sample bottle, which was sealed/placed on the desk of the laboratory. After some days, the crystal of the final product **1** was precipitated via a volatilizing process.

(2) Single crystal of product **1** [$C_{21}H_{14}N_2O_3S$] was obtained as follows: A proper crystal was selected and detected on a "Bruker APEX2" diffractometer. The crystal stayed at 293.0 K during data collection. With the help 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 **1** are performed as depicted in Table S3.

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

Table S3. Crystal data and structure refinement for product **1**.

CCDC	2522354

Displacement ellipsoids are drawn at the 50% probability level

Empirical formula	$C_{21}H_{14}N_2O_3S$
Formula weight	374.40
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	15.719(4)
b/Å	10.479(3)
c/Å	21.491(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3540.3(18)
Z	8
ρ_{calc}g/cm^3	1.405
μ/mm^{-1}	0.208
F(000)	1552.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.79 to 55.176
Index ranges	$-18 \leq h \leq 20$, $-13 \leq k \leq 13$, $-27 \leq l \leq 27$
Reflections collected	50126
Independent reflections	4064 [R_{int} = 0.0813, R_{sigma} = 0.0323]
Data/restraints/parameters	4064/0/245
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0479, wR_2 = 0.1043
Final R indexes [all data]	R_1 = 0.0831, wR_2 = 0.1216
Largest diff. peak/hole /eÅ^{-3}	0.17/-0.28

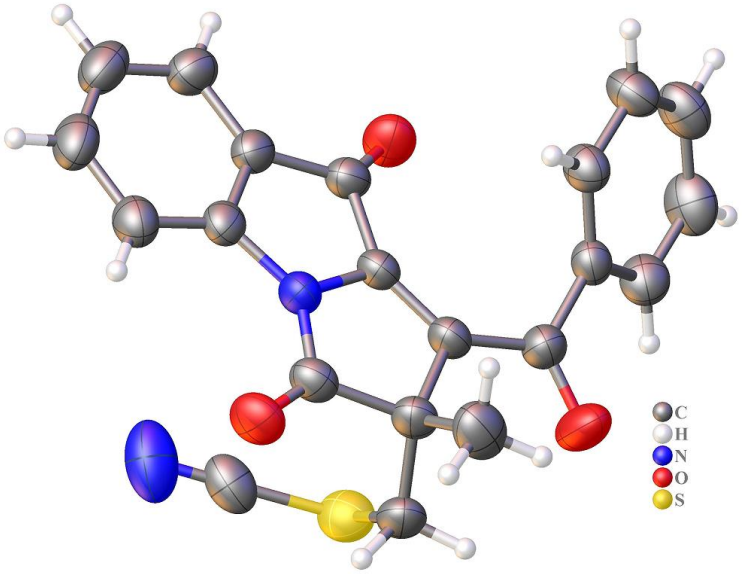


Fig. S1 Structure of thiocyanated product **1**.

Luminescence quenching experiments

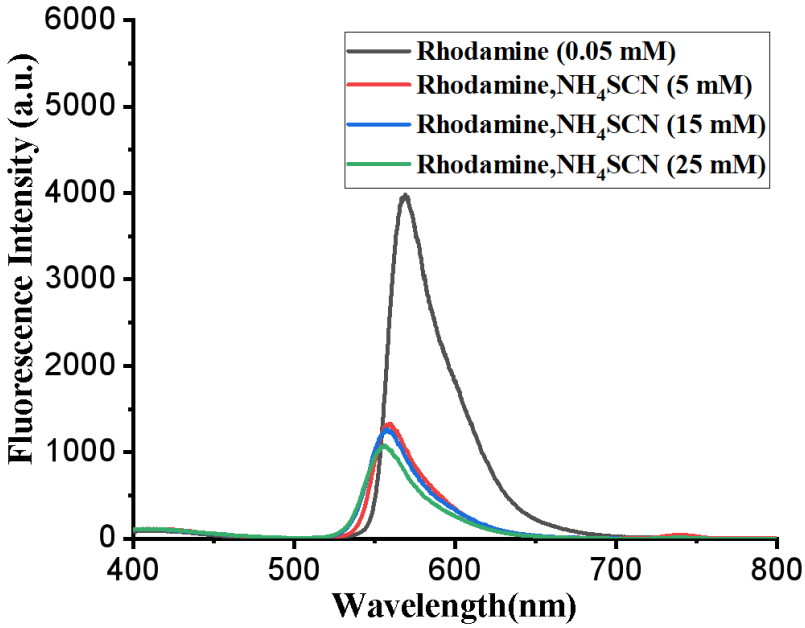


Figure S2. Fluorescence quenching of Rhodamine 6G with NH_4SCN.

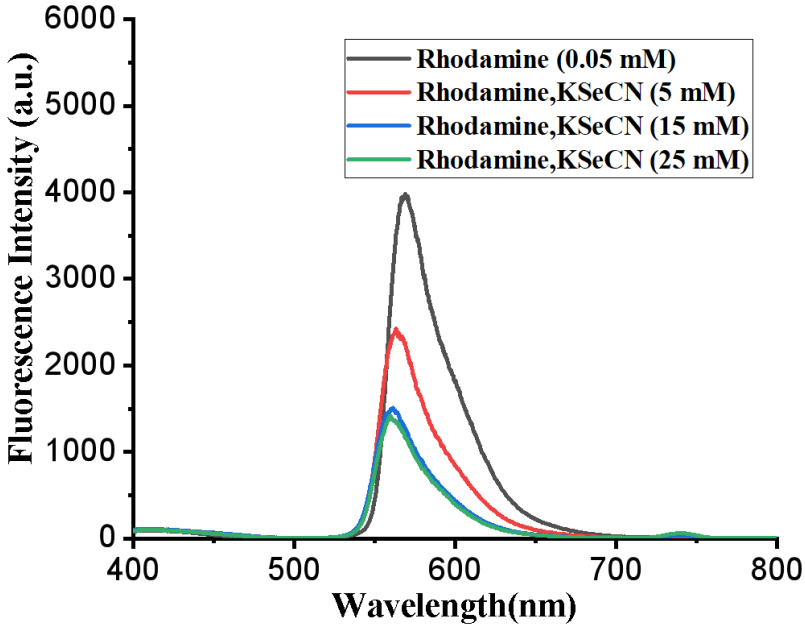


Figure S3. Fluorescence quenching of Rhodamine 6G with KSeCN.

Emission intensities were recorded using a HITACHI F7000 photoluminescence spectrometer from 400 nm to 800 nm. After irradiation of 5×10^{-5} M of Rhodamine 6G and different concentrations of quencher in solvent (DCE and $CHCl_3$) at 370 nm, its

fluorescence was measured. As shown in Figures S2-S3, the emission intensity of the excited state of photocatalyst Rhodamine 6G is decreased in the presence of NH_4SCN or KSeCN.

Physical data and references for the following products

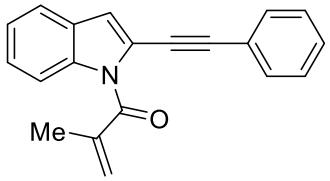
References:

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**, 4742-4747.
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. H.-D. Zuo, X. Chen, Y. Yuan, Y. Zhang, J.-W. Liu, S.-H. Yan, W.-J. Hao and B. Jiang, *Org. Lett.,* 2024, **26**, 3810-3815.
4. H.-D. Zuo, X. Chen, Y. Zhang, J.-W. Liu, S.-H. Yan, G.-G. Li and J.-Y. Wang, *Org. Lett.,* 2024, **26**, 3828-3833.

Physical data for the following products:

2-methyl-1-(2-(phenylethynyl)-1H-indol-1-yl)prop-2-en-1-one (1-s)

Brown solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). 0.43g, the overall yield after four steps 30%. (with the initial system scale up to 5 mmol).

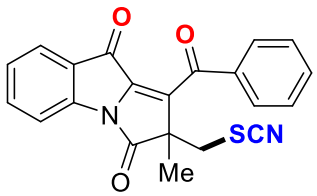


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.49 (m, 2H), 7.41 – 7.37 (m, 4H), 7.30 (t, J= 7.6 Hz, 1H), 7.00 (s, 1H), 5.76 (s, 1H), 5.60 (s, 1H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 140.5, 136.8, 131.0, 128.8, 128.7, 128.5, 125.7, 124.6, 123.7, 122.4, 120.7, 120.6, 116.0, 115.1, 97.6, 81.5, 19.2.

1-benzoyl-2-methyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (1)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 22.8 mg, 61% yield. Mp: 147-148℃



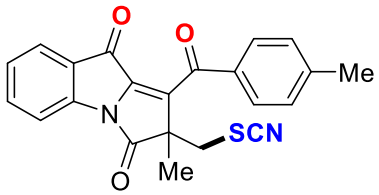
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.75 – 7.66 (m, 3H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 3.80 (d, *J* = 13.6 Hz, 1H), 3.66 (d, *J* = 13.6 Hz, 1H), 1.73 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 177.2, 170.1, 143.2, 141.6, 137.8, 137.6, 133.9, 128.9, 128.6, 128.1, 125.8, 125.8, 124.9, 115.0, 110.7, 61.2, 38.9, 22.5.

HRMS (ESI, m/z): calcd for $C_{21}H_{14}NaN_2O_3S$ $[M + Na]^+$, 397.0617; Measured, 397.0609.

2-methyl-1-(4-methylbenzoyl)-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (2)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 18.8 mg, 51% yield. Mp: 127-128℃



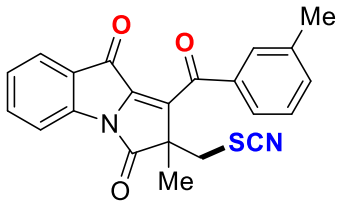
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.79 – 7.73 (m, 4H), 7.31 (t, *J* = 8.2 Hz, 3H), 3.78 (d, *J* = 13.6 Hz, 1H), 3.68 (d, *J* = 13.6 Hz, 1H), 2.47 (s, 3H), 1.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 177.5, 170.1, 145.4, 143.3, 141.1, 137.6, 135.1, 129.5, 129.3, 128.2, 125.9, 125.3, 115.2, 110.9, 61.4, 39.2, 22.5, 21.9.

HRMS (ESI, m/z): calcd for $C_{22}H_{16}NaN_2O_3S$ $[M + Na]^+$, 411.0774; Measured, 411.0778.

2-methyl-1-(3-methylbenzoyl)-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (3)

A yellow solid after purification by flash column chromatography (petroleum ether/ dichloromethane = 10/1). 15.9 mg, 41% yield. Mp: 158-159℃



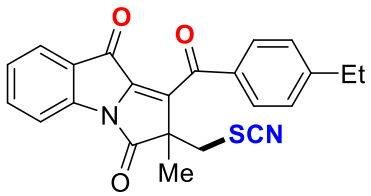
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 12.8 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 3.81 (d, *J* = 13.6 Hz, 1H), 3.68 (d, *J* = 13.6 Hz, 1H), 2.43 (s, 3H), 1.73 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 177.3, 170.2, 143.3, 141.5, 138.7, 137.9, 137.6, 134.9, 129.2, 128.5, 128.2, 126.5, 125.9, 125.2, 115.2, 110.8, 61.3, 39.1, 22.5, 21.4.

HRMS (ESI, m/z): calcd for $C_{22}H_{16}NaN_2O_3S$ $[M + Na]^+$, 411.0774; Measured, 411.0776.

1-(4-ethylbenzoyl)-2-methyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (4)

A yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1). 27 mg, 67% yield.



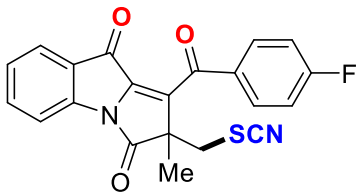
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.75 – 7.73 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 3H), 3.78 (d, *J* = 13.6 Hz, 1H), 3.68 (d, *J* = 11.6 Hz, 1H), 2.76 (q, *J* = 8.2 Hz, 2H), 1.70 (s, 3H), 1.31 – 1.25 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 177.5, 170.0, 151.5, 143.3, 141.0, 137.6, 135.2, 129.4, 128.3, 125.9, 125.8, 125.6, 125.3, 115.2, 110.9, 61.4, 39.2, 29.1, 22.5, 15.0.

HRMS (ESI, m/z): calcd for $C_{23}H_{18}NaN_2O_3S$ $[M + Na]^+$, 425.0930; Measured, 425.0927.

1-(4-fluorobenzoyl)-2-methyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (5)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 23.2 mg, 60% yield. Mp: 117-118℃



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.6 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.77 – 7.73 (m, 2H), 7.32 (t, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 8.6 Hz, 2H), 3.80 (d, *J* = 13.6 Hz, 1H), 3.66 (d, *J* = 13.6 Hz, 1H), 1.74 (s, 3H).

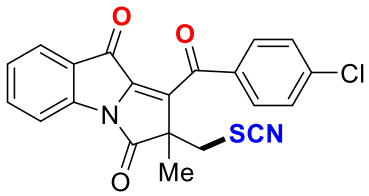
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.3, 177.5, 170.2, 166.5 (d, *J* =255.3 Hz), 143.4, 141.8, 138.4, 134.3, 132.8, 131.9 (d, *J* = 9.5 Hz), 128.2, 126.0 (d, *J* =6.3 Hz), 124.9, 116.2, 115.3, 110.7, 61.5, 39.0, 22.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ -103.08 (s, 1F)

HRMS (ESI, m/z): calcd for $C_{21}H_{13}FNaN_2O_3S$ $[M + Na]^+$, 415.0523; Measured, 415.0529.

1-(4-chlorobenzoyl)-2-methyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (6)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 20.7 mg, 51% yield. Mp: 146-147℃



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.77 (dd, *J* = 17.2, 8.4 Hz, 4H), 7.47 (d, *J* = 6.8 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 3.80 (d, *J* = 14.8 Hz, 1H), 3.66 (d, *J* = 13.2 Hz, 1H), 1.74 (s, 3H).

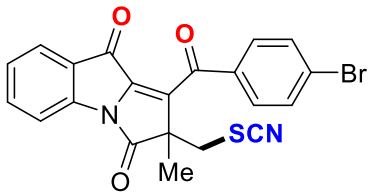
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.5, 177.4, 170.1, 143.3, 141.9, 140.6, 137.8, 136.2, 130.9, 129.1, 128.0, 126.1, 126.0, 124.5, 115.2, 110.6, 61.4, 38.9, 22.8.

HRMS (ESI, m/z): calcd for $C_{21}H_{13}ClNaN_2O_3S$ $[M + Na]^+$, 431.0228; Measured, 431.0227.

1-(4-bromobenzoyl)-2-methyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (7)

A yellow oil after purification by flash column chromatography (petroleum ether/ethyl

acetate = 10/1). 28.1 mg, 62% yield.



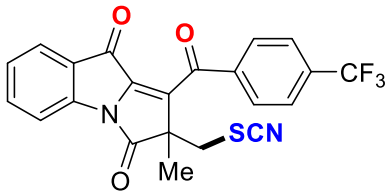
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.78 – 7.70 (m, 4H),7.64 (d, *J* = 6.8 Hz, 2H), 7.33 (t, *J* = 8.2 Hz, 1H), 3.80 (d, *J* = 13.6 Hz, 1H), 3.66 (d, *J* = 13.6 Hz, 1H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 188.7, 177.4, 170.1, 143.3, 142.0, 137.8, 136.6, 132.0, 130.4, 129.5, 129.4, 128.0, 126.1, 124.5, 115.2, 110.6, 61.4, 38.8, 22.8.

HRMS (ESI, m/z): calcd for $C_{21}H_{14}BrN_2O_3S$ $[M+H]^+$, 452.9903; Measured, 452.9894

2-methyl-2-(thiocyanatomethyl)-1-(4-(trifluoromethyl)benzoyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (8)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 28 mg, 63% yield. Mp: 143-144℃



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.72 (m, 4H), 7.33 (t, *J* = 7.6 Hz, 1H), 3.85 (d, *J* = 14.0 Hz, 1H), 3.64 (d, *J* = 13.6 Hz, 1H), 1.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.0, 177.2, 170.2, 143.0 (q, *J* = 56.9 Hz), 141.0, 137.9, 136.2, 129.1, 126.2, 126.1, 126.0 (q, *J* = 278.6 Hz), 125.7, 125.6, 115.2, 110.5, 61.4, 38.7, 22.9.

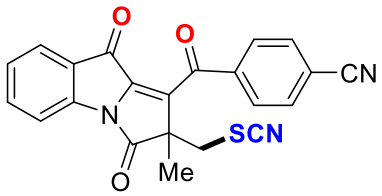
^{19}F NMR (565 MHz, $CDCl_3$): δ -62.99 (s, 3F)

HRMS (ESI, m/z): calcd for $C_{22}H_{13}F_3NaN_2O_3S$ $[M + Na]^+$, 465.0491; Measured, 465.0494.

4-(2-methyl-3,9-dioxo-2-(thiocyanatomethyl)-2,9-dihydro-3H-pyrrolo[1,2-a]indole-1-carbonyl)benzonitrile (9)

A yellow solid after purification by flash column chromatography (petroleum

ether/ethyl acetate = 10/1). 20 mg, 50% yield. Mp: 165-166℃



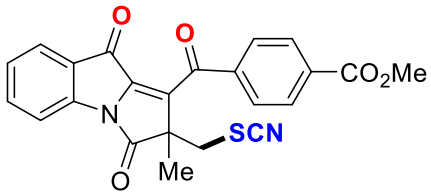
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.80 – 7.76 (m, 3H), 7.74 – 7.71 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.86 (d, *J* = 14.0 Hz, 1H), 3.61 (d, *J* = 14.0 Hz, 1H), 1.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 188.7, 177.2, 170.3, 143.3, 141.7, 138.0, 132.4, 130.9, 129.0, 127.8, 126.3, 126.1, 123.9, 118.0, 116.5, 115.2, 110.5, 61.4, 38.5, 23.1.

HRMS (ESI, m/z): calcd for $C_{22}H_{14}O_3N_3S$ $[M + H]^+$, 400.0750; Measured, 400.0742.

methyl 4-(2-methyl-3,9-dioxo-2-(thiocyanatomethyl)-2,9-dihydro-3H-pyrrolo[1,2-a]indole-1-carbonyl)benzoate (10)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 8/1). 25.6 mg, 60% yield. Mp: 116-117℃



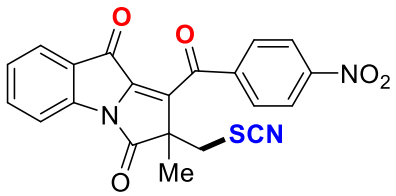
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.70 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 3.96 (s, 3H), 3.85 (d, *J* = 13.6 Hz, 1H), 3.66 (d, *J* = 13.6 Hz, 1H), 1.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.5, 177.2, 170.2, 166.1, 143.3, 142.6, 141.6, 137.8, 134.2, 129.9, 128.6, 128.0, 126.1, 126.0, 124.4, 115.2, 110.6, 61.3, 52.5, 38.7, 22.8.

HRMS (ESI, m/z): calcd for $C_{23}H_{16}NaN_2O_5S$ $[M + Na]^+$, 455.0672; Measured, 455.0677.

2-methyl-1-(4-nitrobenzoyl)-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (11)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1). 20 mg, 48% yield. Mp: 104-105℃



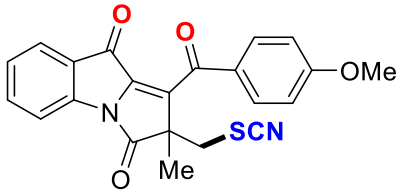
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 9.2 Hz, 2H), 7.96 – 7.91 (m, 3H), 7.76 (t, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 6.8 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.89 (d, *J* = 13.6 Hz, 1H), 3.61 (d, *J* = 14.0 Hz, 1H), 1.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 188.5, 177.2, 170.3, 150.3, 143.5, 143.4, 143.3, 138.0, 129.5, 128.8, 127.7, 126.4, 126.2, 123.9, 115.2, 110.5, 61.4, 38.4, 23.1.

HRMS (ESI, m/z): calcd for $C_{21}H_{14}N_3O_5S$ $[M + H]^+$, 420.0649; Measured, 420.0642.

1-(4-methoxybenzoyl)-2-methyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (12)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1). 18.5 mg, 46% yield. Mp: 124-125℃



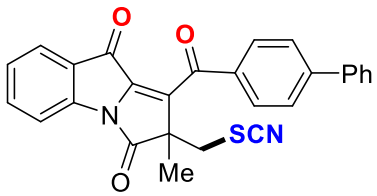
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 6.8 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H), 3.76 (d, *J* = 13.2 Hz, 1H), 3.68 (d, *J* = 13.6 Hz, 1H), 1.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 187.8, 177.6, 170.0, 164.7, 143.3, 140.4, 137.6, 131.8, 130.3, 128.3, 125.8, 125.6, 115.2, 114.0, 111.1, 61.5, 55.6, 39.3, 22.4.

HRMS (ESI, m/z): calcd for $C_{22}H_{16}NaN_2O_4S$ $[M + Na]^+$, 427.0723; Measured, 427.0728.

1-([1,1'-biphenyl]-4-carbonyl)-2-methyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (13)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 8/1). 27.4 mg, 61% yield. Mp: 159-160℃



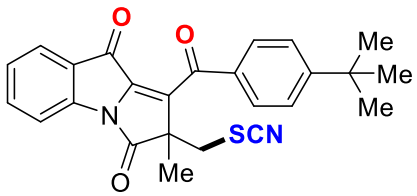
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.95 (m, 3H), 7.78 – 7.72 (m, 4H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 3.81 (d, *J* = 13.6 Hz, 1H), 3.70 (d, *J* = 13.6 Hz, 1H), 1.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.2, 177.4, 170.1, 146.8, 143.4, 141.3, 139.6, 137.7, 136.3, 129.8, 128.9, 128.4, 128.2, 127.4, 127.3, 125.9, 125.1, 115.2, 110.8, 61.5, 39.1, 22.6.

HRMS (ESI, m/z): calcd for $C_{27}H_{18}NaN_2O_3S$ $[M + H]^+$, 473.0930; Measured, 473.0931.

1-(4-(tert-butyl)benzoyl)-2-methyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (14)

A yellow solid after purification by flash column chromatography (petroleum ether/ dichloromethane = 10/1). 22 mg, 51% yield. Mp: 120-121℃



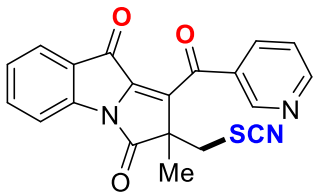
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.73 (m, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 3.77 (d, *J* = 13.6 Hz, 1H), 3.68 (d, *J* = 13.6 Hz, 1H), 1.70 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.2, 177.4, 170.0, 158.3, 143.3, 140.7, 137.6, 134.7, 129.3, 128.3, 125.8, 125.8, 125.7, 125.3, 115.2, 110.9, 61.5, 39.2, 35.3, 31.0, 22.4.

HRMS (ESI, m/z): calcd for $C_{25}H_{22}NaN_2O_3S$ $[M + Na]^+$, 453.1243; Measured, 453.1257.

2-methyl-1-nicotinoyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (15)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1). 15 mg, 40% yield. Mp: 120-121℃



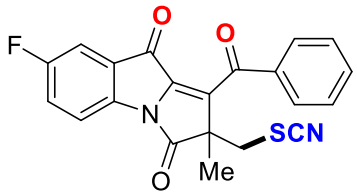
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, *J* = 4.8 Hz, 1H), 7.96 – 7.89 (m, 3H), 7.78 – 7.69 (m, 2H), 7.58 – 7.58 (m, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 3.98 (d, *J* = 13.6 Hz, 1H), 3.61 (d, *J* = 13.2 Hz, 1H), 1.76 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.6, 177.3, 170.4, 155.0, 149.1, 143.5, 143.2, 137.4, 137.1, 128.2, 127.3, 125.9, 125.8, 123.3, 122.7, 115.1, 110.9, 60.9, 39.3, 21.8.

HRMS (ESI, m/z): calcd for $C_{20}H_{13}NaN_3O_3S$ $[M + Na]^+$, 398.0570; Measured, 398.0567.

1-benzoyl-7-fluoro-2-methyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (16)

A yellow solid after purification by flash column chromatography (petroleum ether/dichloromethane = 1/1). 24.5 mg, 63% yield. Mp: 153-154℃



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.8, 4.0 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.72 – 7.68 (m, 1H), 7.53 – 7.44 (m, 3H), 7.39 (dd, *J* = 7.0, 3.0 Hz, 1H), 3.79 (d, *J* = 13.6 Hz, 1H), 3.68 (d, *J* = 13.2 Hz, 1H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 176.4, 169.8, 160.2 (d, *J* =247.8 Hz), 141.6, 139.7, 137.8, 134.1, 130.9, 128.9 (d, *J* = 15.4 Hz), 125.9, 124.9 (d, *J* = 24.9 Hz), 116.6 (d, *J* = 7.9 Hz), 112.1 (d, *J* = 24.1 Hz), 110.6, 61.4, 39.0, 22.6.

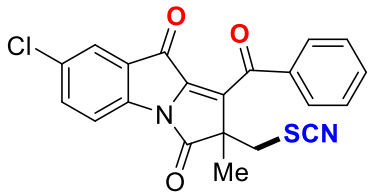
^{19}F NMR (565 MHz, $CDCl_3$): δ -113.62 (s, 1F)

HRMS (ESI, m/z): calcd for $C_{21}H_{13}FNaN_2O_3S$ $[M + Na]^+$, 415.0523; Measured, 415.0521.

1-benzoyl-7-chloro-2-methyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (17)

A yellow solid after purification by flash column chromatography (petroleum

ether/dichloromethane = 1/1). 27.8 mg, 71% yield. Mp: 191-192℃



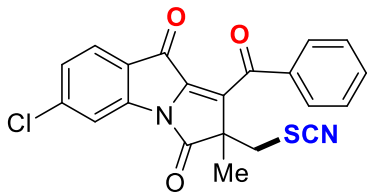
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.71 – 7.68 (m, 3H), 7.51 (t, *J* = 7.8 Hz, 2H), 3.78 (d, *J* = 13.6 Hz, 1H), 3.69 (d, *J* = 13.6 Hz, 1H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 176.1, 169.9, 141.6, 141.3, 137.7, 137.4, 134.1, 131.9, 129.2, 128.9, 128.8, 125.8, 125.7, 116.3, 110.6, 61.4, 39.0, 22.6.

HRMS (ESI, m/z): calcd for $C_{21}H_{13}ClNaN_2O_3S$ $[M + Na]^+$, 431.0228; Measured, 431.0229.

1-benzoyl-6-chloro-2-methyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (18)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 28.5 mg, 70% yield. Mp: 185-186℃



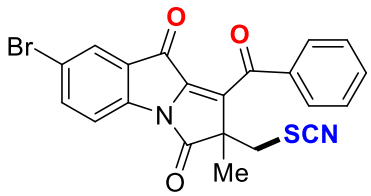
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 1.6 Hz, 1H), 7.84 (d, *J* = 6.8 Hz, 2H), 7.70 – 7.64 (m, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.26 (m, 1H), 3.79 (d, *J* = 13.6 Hz, 1H), 3.68 (d, *J* = 13.6 Hz, 1H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 176.0, 170.1, 144.3, 143.7, 141.5, 137.8, 134.1, 129.5, 128.9, 128.7, 126.8, 126.5, 125.5, 115.6, 110.6, 61.4, 38.9, 22.7.

HRMS (ESI, m/z): calcd for $C_{21}H_{13}ClNaN_2O_3S$ $[M + Na]^+$, 431.0228; Measured, 431.0232.

1-benzoyl-7-bromo-2-methyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (19)

A yellow solid after purification by flash column chromatography (petroleum ether/ dichloromethane = 1/1). 29 mg, 64% yield. Mp: 191-192℃



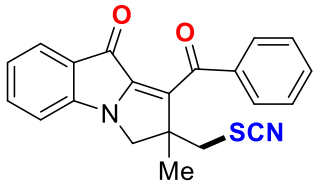
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.2 Hz, 5H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 3.78 (d, *J* = 13.6 Hz, 1H), 3.69 (d, *J* = 13.2 Hz, 1H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 176.0, 169.9, 141.9, 141.1, 140.2, 137.6, 134.2, 129.5, 128.9, 128.8, 128.7, 125.6, 119.2, 116.6, 110.6, 61.4, 38.9, 22.6.

HRMS (ESI, m/z): calcd for $C_{21}H_{13}BrNaN_2O_3S$ $[M + Na]^+$, 476.9704; Measured, 476.9701.

1-benzoyl-2-methyl-2-(thiocyanatomethyl)-2,3-dihydro-9H-pyrrolo[1,2-a]indol-9-one (20)

A purple oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 8/1). 11 mg, 30% yield.



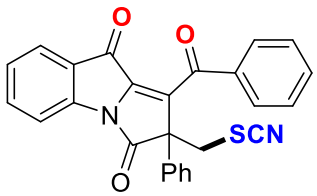
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.43 (m, 4H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.16 (d, *J* = 10.4 Hz, 1H), 3.82 (d, *J* = 13.2 Hz, 1H), 3.74 (d, *J* = 10.4 Hz, 1H), 3.55 (d, *J* = 13.6 Hz, 1H), 1.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 179.8, 150.2, 147.3, 139.6, 137.3, 132.9, 128.6, 128.4, 125.9, 125.2, 121.2, 120.5, 113.2, 109.9, 57.0, 54.4, 42.9, 24.8.

HRMS (ESI, m/z): calcd for $C_{21}H_{16}NaN_2O_2S$ $[M + Na]^+$, 383.0825; Measured, 383.0823.

1-benzoyl-2-phenyl-2-(thiocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (21)

A yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 18 mg, 41% yield.



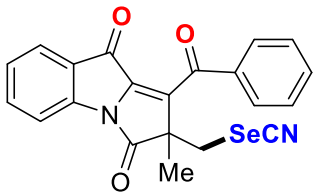
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.78 – 7.73 (m, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.44 (m, 2H), 7.39 – 7.34 (m, 3H), 7.32 (d, *J* = 7.6 Hz, 1H), 4.37 (d, *J* = 13.6 Hz, 1H), 4.09 (d, *J* = 13.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 177.3, 168.5, 143.4, 142.1, 137.7, 137.5, 135.5, 134.2, 129.6, 129.3, 129.2, 128.8, 128.3, 126.3, 126.1, 125.9, 124.4, 115.3, 111.1, 68.5, 40.0.

HRMS (ESI, m/z): calcd for $C_{26}H_{16}NaN_2O_3S$ $[M + Na]^+$, 459.0774; Measured, 459.0771.

1-benzoyl-2-methyl-2-(selenocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (22)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 8/1). 18 mg, 43% yield. Mp: 98-99℃



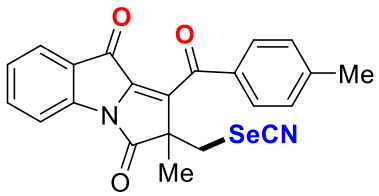
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.77 – 7.68 (m, 3H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 3.76 (s, 2H), 1.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.3, 177.5, 170.4, 143.4, 140.9, 137.7, 137.5, 134.3, 129.2, 128.8, 128.2, 126.1, 125.9, 115.2, 101.0, 61.1, 33.9, 22.9.

HRMS (ESI, m/z): calcd for $C_{21}H_{15}N_2O_3Se$ $[M + H]^+$, 423.0242; Measured, 423.0233.

2-methyl-1-(4-methylbenzoyl)-2-(selenocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (23)

A yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 8/1). 16 mg, 37% yield.



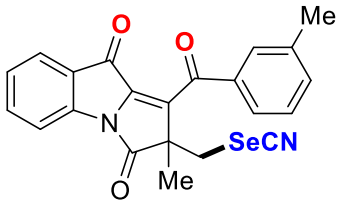
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.77 – 7.73 (m, 2H), 7.33 – 7.30 (m, 3H), 3.76 (d, *J* = 12.4 Hz, 1H), 3.72 (d, *J* = 12.4 Hz, 1H), 2.47 (s, 3H), 1.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 177.6, 170.3, 145.8, 143.4, 140.2, 137.6, 134.7, 129.6, 129.5, 128.3, 126.5, 125.8, 115.2, 101.3, 61.1, 34.0, 22.8, 22.0.

HRMS (ESI, m/z): calcd for $C_{22}H_{17}N_2O_3Se$ $[M + H]^+$, 437.0399; Measured, 437.0392.

2-methyl-1-(3-methylbenzoyl)-2-(selenocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (24)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 8/1). 19 mg, 44% yield. Mp: 103-104℃



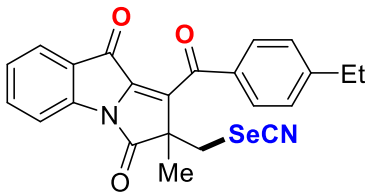
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.68 – 7.65 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 2H), 2.43 (s, 3H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 177.4, 170.3, 143.4, 140.6, 138.8, 137.6, 137.5, 135.2, 129.3, 128.6, 128.3, 126.7, 126.3, 125.8, 115.2, 101.1, 61.0, 34.0, 22.9, 21.4.

HRMS (ESI, m/z): calcd for $C_{22}H_{17}N_2O_3Se$ $[M + H]^+$, 437.0399; Measured, 437.0391.

1-(4-ethylbenzoyl)-2-methyl-2-(selenocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (25)

A yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 8/1). 20 mg, 45% yield.



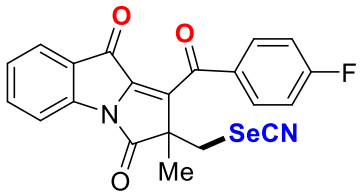
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.75 (t, *J* = 8.0 Hz, 2H), 7.34 – 7.29 (m, 3H), 3.76 (d, *J* = 12.4 Hz, 1H), 3.71 (d, *J* = 12.4 Hz, 1H), 2.77 (q, *J* = 7.8 Hz, 2H), 1.71 (s, 3H), 1.31 – 1.25 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 177.6, 170.3, 151.9, 143.4, 140.0, 137.6, 134.8, 129.6, 128.4, 128.3, 126.5, 125.8, 125.7, 115.2, 101.3, 61.1, 34.0, 29.1, 22.8, 14.9.

HRMS (ESI, m/z): calcd for $C_{23}H_{18}NaN_2O_3Se$ $[M + Na]^+$, 473.0376; Measured, 473.0375.

1-(4-fluorobenzoyl)-2-methyl-2-(selenocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (26)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 8/1). 24.3 mg, 55% yield. Mp: 135-136℃



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.93 – 7.90 (m, 2H), 7.75 (t, *J* = 8.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 8.6 Hz, 2H), 3.75 (s, 2H), 1.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 188.5, 177.5, 170.3, 166.6 (d, *J* =256.1 Hz), 143.4, 140.9, 137.8, 133.9, 132.0 (d, *J* = 9.7 Hz), 129.5, 128.1, 125.9 (d, *J* = 6.5 Hz), 116.0 (d, *J* = 22.1 Hz), 115.2, 100.8, 61.1, 33.8, 23.0.

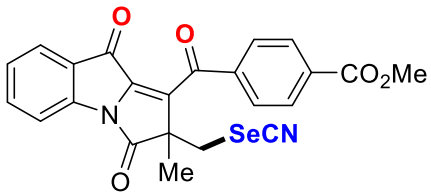
^{19}F NMR (565 MHz, $CDCl_3$): δ-102.40 (s, 1F)

HRMS (ESI, m/z): calcd for $C_{21}H_{13}FNaN_2O_3Se$ $[M + Na]^+$, 462.9969; Measured, 462.9966.

methyl-4-(2-methyl-3,9-dioxo-2-(selenocyanatomethyl)-2,9-dihydro-3H-pyrrolo[1,2-a]indole-1-carbonyl)benzoate (27)

A yellow oil after purification by flash column chromatography (petroleum ether/ethyl

acetate = 8/1). 25 mg, 52% yield.



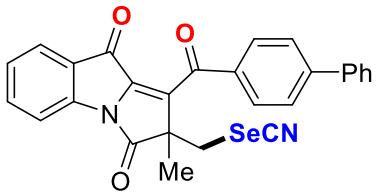
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.70 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 3.96 (s, 3H), 3.82 (d, *J* = 12.8 Hz, 1H), 3.74 (d, *J* = 12.8 Hz, 1H), 1.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 177.3, 170.4, 166.1, 143.3, 141.8, 141.2, 137.8, 134.4, 129.9, 128.8, 128.0, 126.1, 126.0, 125.4, 115.2, 100.6, 61.0, 52.5, 33.6, 23.1.

HRMS (ESI, m/z): calcd for $C_{23}H_{17}N_2O_5Se$ $[M + H]^+$, 481.0297; Measured, 481.0289.

1-([1,1'-biphenyl]-4-carbonyl)-2-methyl-2-(selenocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (28)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 8/1). 22.6 mg, 45% yield. Mp: 104-105℃



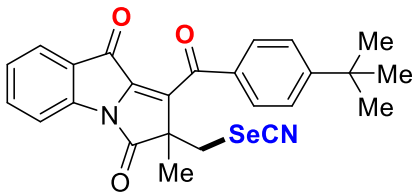
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.0 – 7.97 (m, 3H), 7.76 – 7.72 (m, 4H), 7.69 – 7.66 (m, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 3.78 (d, *J* = 12.4 Hz, 1H), 3.75 (d, *J* = 12.4 Hz, 1H), 1.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.6, 177.6, 170.3, 147.2, 143.4, 140.4, 139.5, 137.7, 135.9, 130.0, 129.0, 128.5, 128.3, 127.4, 127.4, 127.1, 126.2, 125.8, 115.3, 101.2, 61.2, 34.0, 22.9.

HRMS (ESI, m/z): calcd for $C_{27}H_{19}N_2O_3Se$ $[M + H]^+$, 499.0555; Measured, 499.0549.

1-(4-(tert-butyl)benzoyl)-2-methyl-2-(selenocyanatomethyl)-3H-pyrrolo[1,2-a]indole-3,9(2H)-dione (29)

A yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 8/1). 21.5 mg, 45% yield.



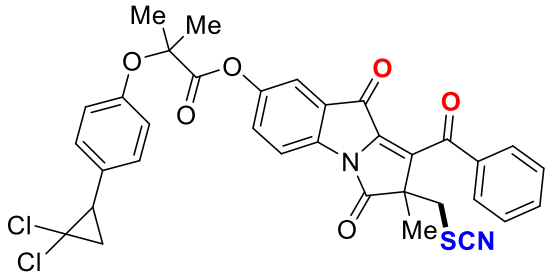
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.74 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 3.76 (d, *J* = 12.8 Hz, 1H), 3.69 (d, *J* = 12.4 Hz, 1H), 1.70 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.6, 177.6, 170.2, 158.8, 143.40, 139.7, 137.6, 134.2, 129.5, 128.3, 126.4, 125.9, 125.8, 125.7, 115.2, 101.5, 61.20, 35.4, 34.0, 31.0, 22.8.

HRMS (ESI, m/z): calcd for $C_{25}H_{22}NaN_2O_3Se$ $[M + Na]^+$, 501.0689; Measured, 501.0687.

1-benzoyl-2-methyl-3,9-dioxo-2-(thiocyanatomethyl)-2,9-dihydro-3H-pyrrolo[1,2-a]indol-7-yl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (30)

A yellow oil after purification by flash column chromatography (petroleum ether/ dichloromethane = 1/1). 37 mg, 56% yield.



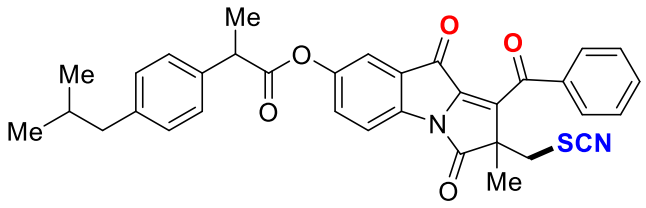
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.84 – 7.82 (m, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 2.4 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.80 (d, *J* = 13.6 Hz, 1H), 3.67 (d, *J* = 13.6 Hz, 1H), 2.88 – 2.83 (m, 1H), 1.98 – 1.94 (m, 1H), 1.82 – 1.78 (m, 1H), 1.75 (s, 6H), 1.73 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 176.4, 172.8, 169.8, 154.7, 148.0, 141.6, 141.0, 137.7, 134.1, 130.8, 130.0, 129.0, 128.9, 128.8, 128.7, 125.7, 118.8, 118.2, 116.0, 110.7, 79.1, 61.4, 60.8, 38.9, 34.7, 25.8, 25.4, 22.6.

HRMS (ESI, m/z): calcd for $C_{34}H_{27}Cl_2N_2O_6S$ $[M + H]^+$, 661.0961; Measured, 661.0955.

1-benzoyl-2-methyl-3,9-dioxo-2-(thiocyanatomethyl)-2,9-dihydro-3H-pyrrolo[1,2-a]indol-7-yl 2-(4-isobutylphenyl)propanoate (31)

A yellow oil after purification by flash column chromatography (petroleum ether/ dichloromethane = 1/1). 25 mg, 43% yield.



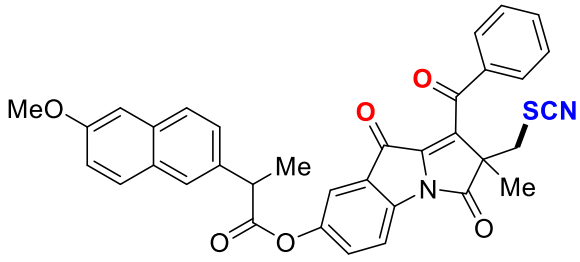
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.83 (d, *J* = 6.8 Hz, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.37 – 7.32 (m, 2H), 7.26 – 7.25 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.93 (q, *J* = 7.2 Hz, 1H), 3.80 (d, *J* = 13.2 Hz, 1H), 3.66 (d, *J* = 13.6 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.89 – 1.83 (m, 1H), 1.73 (s, 3H), 1.59 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 176.5, 173.0, 169.8, 148.4, 141.7, 141.1, 140.7, 137.7, 136.6, 134.0, 131.1, 129.7, 129.0, 128.9, 128.7, 127.1, 125.5, 118.9, 115.8, 110.7, 61.3, 45.1, 45.0, 39.0, 30.2, 22.6, 22.4, 18.4.

HRMS (ESI, m/z): calcd for $C_{34}H_{31}N_2O_5S$ $[M + H]^+$, 579.1948; Measured, 579.1941.

1-benzoyl-2-methyl-3,9-dioxo-2-(thiocyanatomethyl)-2,9-dihydro-3H-pyrrolo[1,2-a]indol-7-yl 2-(6-methoxynaphthalen-2-yl)propanoate (32)

A yellow oil after purification by flash column chromatography (petroleum ether/ dichloromethane = 1/1). 31mg, 51% yield.



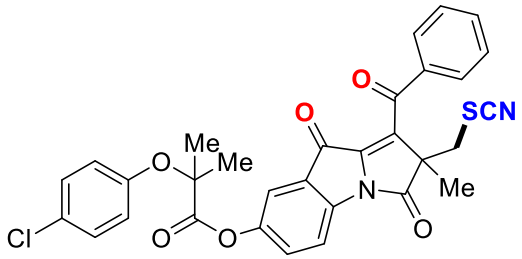
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 8.6, 3.4 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.77 – 7.72 (m, 3H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.35 – 7.31 (m, 2H), 7.18 – 7.14 (m, 2H), 4.10 (q, *J* = 7.2 Hz, 1H), 3.93 (s, 3H), 3.79 (d, *J* = 13.6 Hz, 1H), 3.65 (d, *J* = 13.6 Hz, 1H), 1.72 (s, 3H), 1.68 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 176.4, 172.9, 169.8, 157.8, 148.4, 141.7, 140.7, 137.7, 134.4, 134.0, 133.9, 131.0, 129.3, 128.9, 128.9, 128.7, 127.6, 126.2, 125.7, 125.5, 119.3, 118.9, 115.8, 110.7, 105.5, 61.3, 55.3, 45.4, 38.9, 22.6, 18.3.

HRMS (ESI, m/z): calcd for $C_{35}H_{27}N_2O_6S$ $[M + H]^+$, 603.1584; Measured, 603.1575.

1-benzoyl-2-methyl-3,9-dioxo-2-(thiocyanatomethyl)-2,9-dihydro-3H-pyrrolo[1,2-a]indol-7-yl 2-(4-chlorophenoxy)-2-methylpropanoate (33)

A yellow oil after purification by flash column chromatography (petroleum ether/ dichloromethane = 1/1). 20.5 mg, 35% yield.



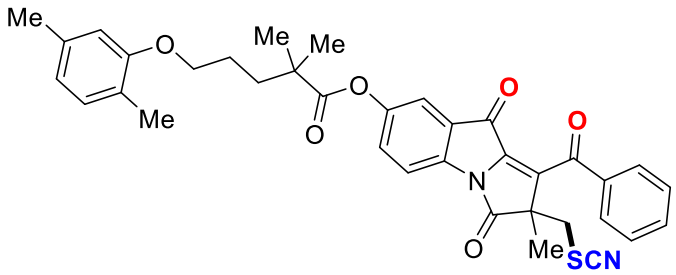
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.35 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.23 (s, 2H), 6.86 (d, *J* = 9.2 Hz, 2H), 3.80 (d, *J* = 13.6 Hz, 1H), 3.68 (d, *J* = 13.6 Hz, 1H), 1.79 (s, 3H), 1.73 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 176.4, 172.5, 169.8, 153.7, 148.0, 141.6, 141.0, 137.7, 134.1, 130.9, 129.4, 129.0, 128.8, 127.8, 125.8, 120.5, 120.3, 118.7, 116.1, 110.7, 79.4, 61.4, 38.9, 25.2, 22.6.

HRMS (ESI, m/z): calcd for $C_{31}H_{24}ClN_2O_6S$ $[M + H]^+$, 587.1038; Measured, 587.1029.

1-benzoyl-2-methyl-3,9-dioxo-2-(thiocyanatomethyl)-2,9-dihydro-3H-pyrrolo[1,2-a]indol-7-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (34)

A yellow solid after purification by flash column chromatography (petroleum ether/ dichloromethane = 1/1). 40 mg, 64% yield. Mp: 122-123℃



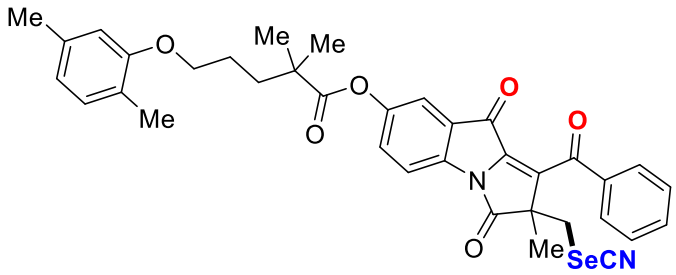
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.00 (d, J = 7.6 Hz, 1H), 6.67 (d, *J* = 7.2 Hz, 1H), 6.62 (s, 1H), 3.98 (t, *J* = 5.8 Hz, 2H), 3.81 (d, *J* = 13.6 Hz, 1H), 3.68 (d, *J* = 13.6 Hz, 1H), 2.30 (s, 3H), 2.16 (s, 3H), 1.93 – 1.85 (m, 4H), 1.74 (s, 3H), 1.37 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 176.5, 176.1, 169.8, 156.7, 148.6, 141.7, 140.7, 137.7, 136.5, 134.1, 131.1, 130.3, 129.2, 129.0, 128.7, 125.5, 123.5, 120.8, 118.9, 115.9, 111.8, 110.7, 67.4, 61.3, 42.5, 39.0, 37.0, 25.2, 25.0, 22.6, 21.4, 15.8.

HRMS (ESI, m/z): calcd for $C_{36}H_{35}N_2O_6S$ $[M + H]^+$, 623.2210; Measured, 623.2203.

1-benzoyl-2-methyl-3,9-dioxo-2-(selenocyanatomethyl)-2,9-dihydro-3H-pyrrolo[1,2-a]indol-7-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (35)

A yellow oil after purification by flash column chromatography (petroleum ether/ dichloromethane = 1/1). 20 mg, 30% yield.



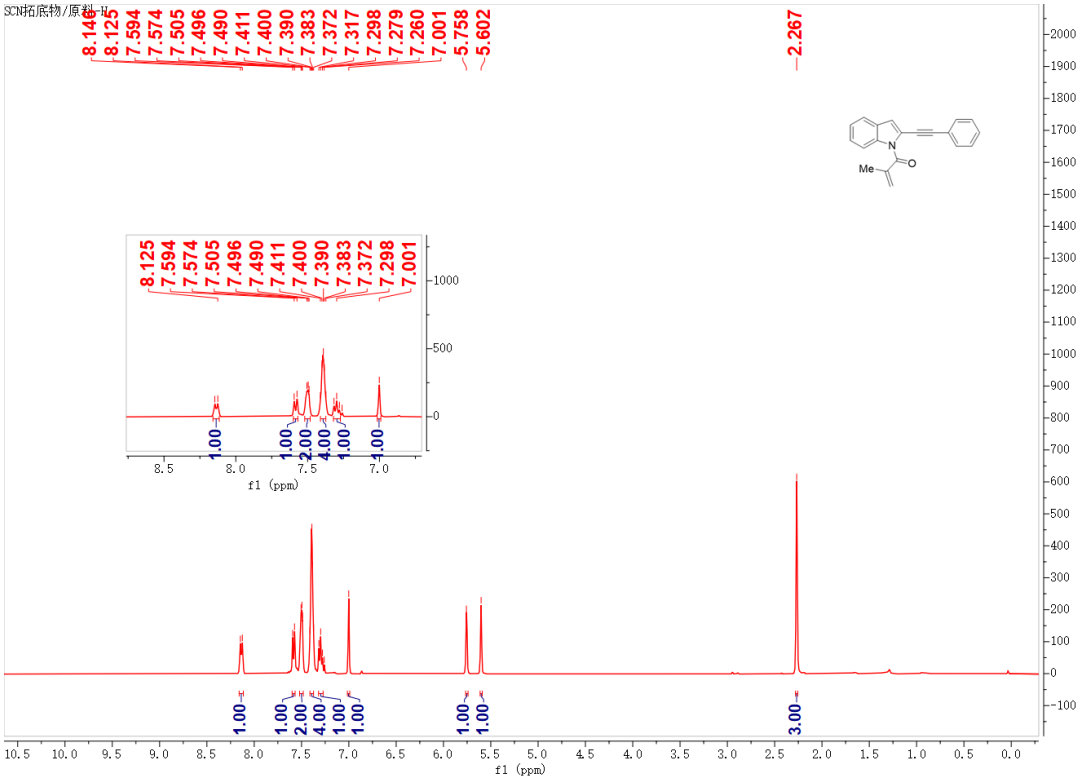
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.40 – 7.36 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.61 (s, 1H), 3.97 (s, 2H), 3.76 (s, 2H), 2.30 (s, 3H), 2.16 (s, 3H), 1.90 – 1.85 (m, 4H), 1.75 (s, 3H), 1.37 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 176.6, 176.1, 170.0, 164.8, 156.7, 151.4, 148.6, 140.8, 137.3, 136.5, 134.4, 131.1, 130.3, 129.2, 128.8, 123.5, 120.8, 118.9, 115.9, 111.8, 109.9, 101.0, 67.5, 61.1, 42.5, 37.0, 33.8, 25.2, 25.0, 22.9, 21.4, 15.8.

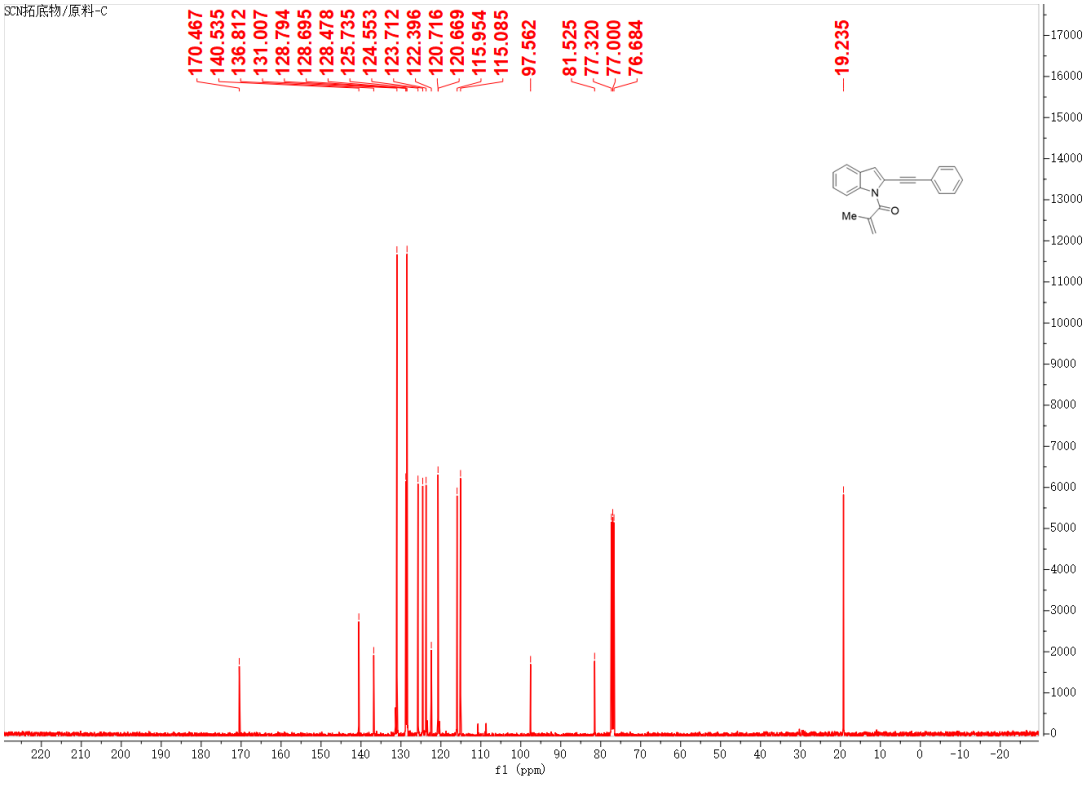
HRMS (ESI, m/z): calcd for $C_{36}H_{35}N_2O_6Se$ $[M + H]^+$, 671.1658; Measured, 671.1660.

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

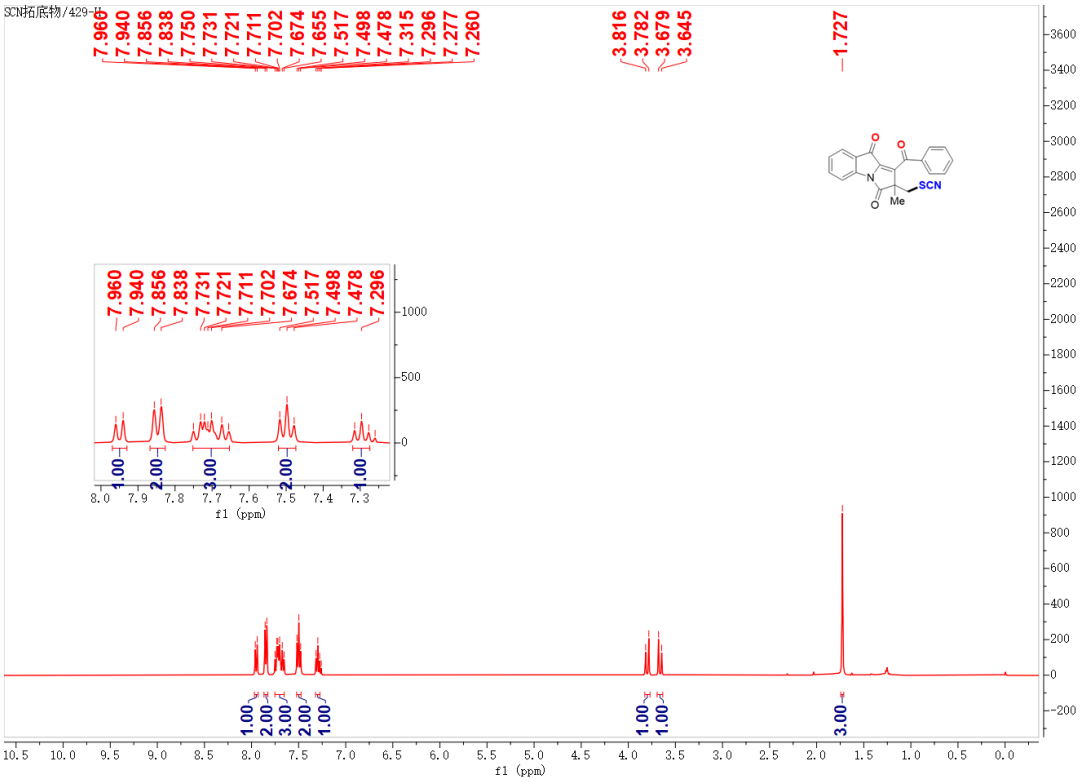
1-s^{1}H NMR (400 MHz, $CDCl_3$)



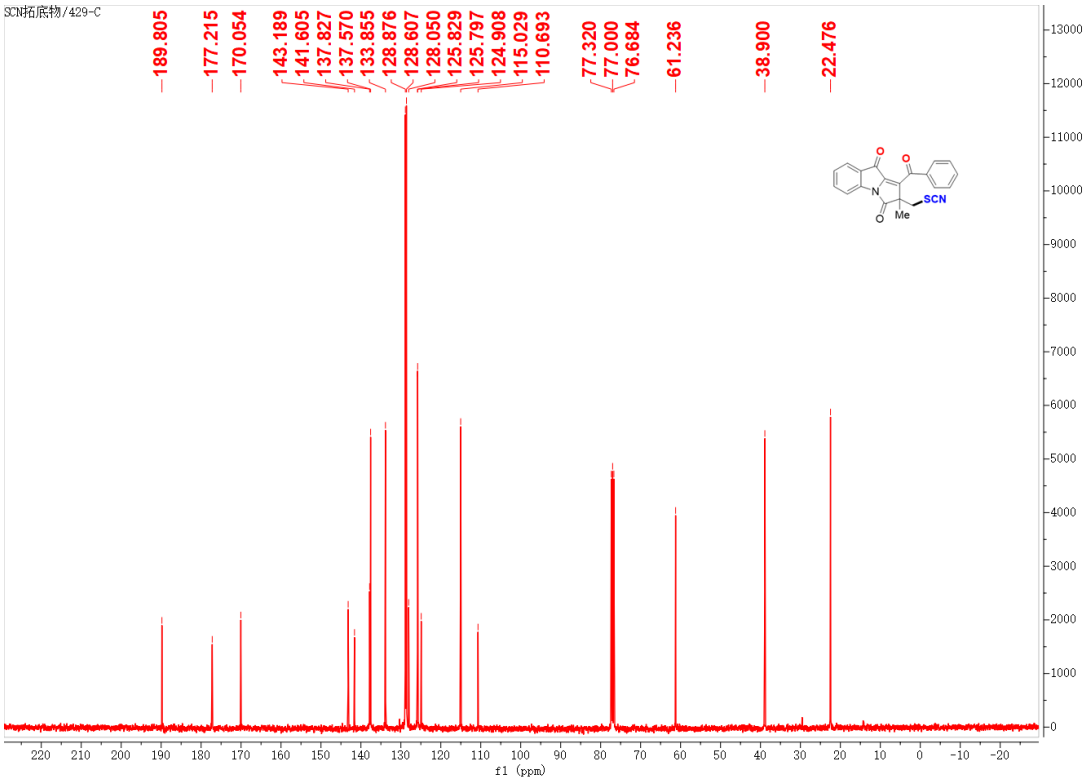
1-s^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



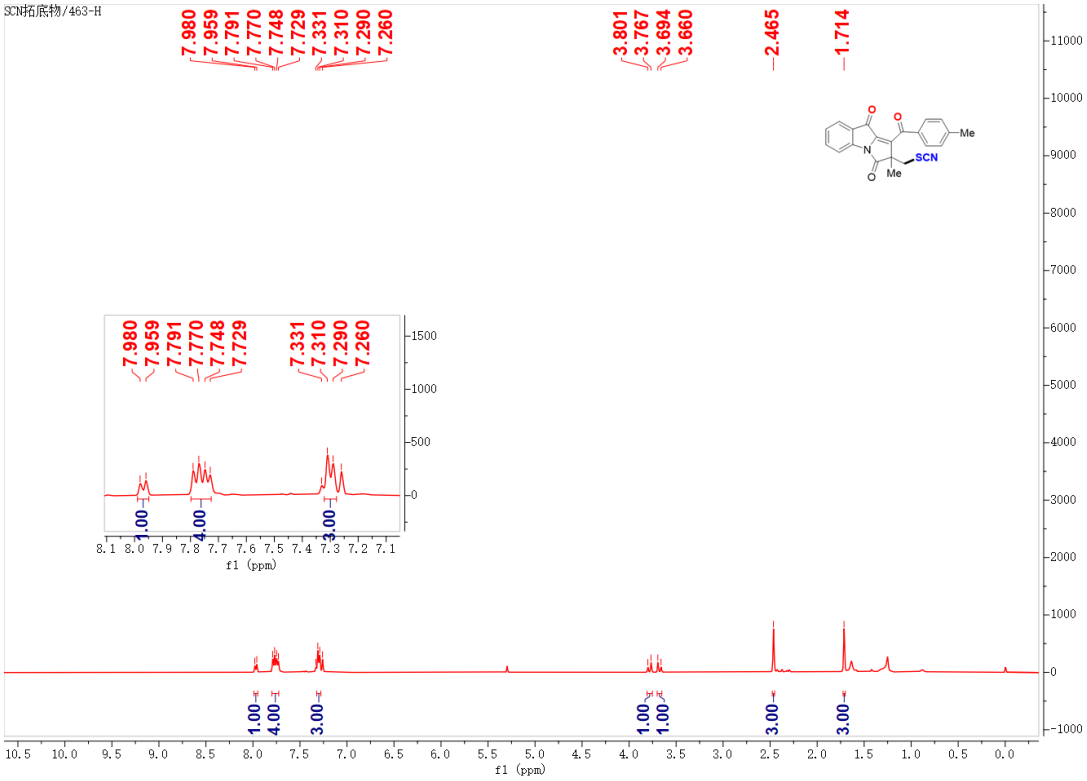
1-^{1}H NMR (400 MHz, $CDCl_3$)



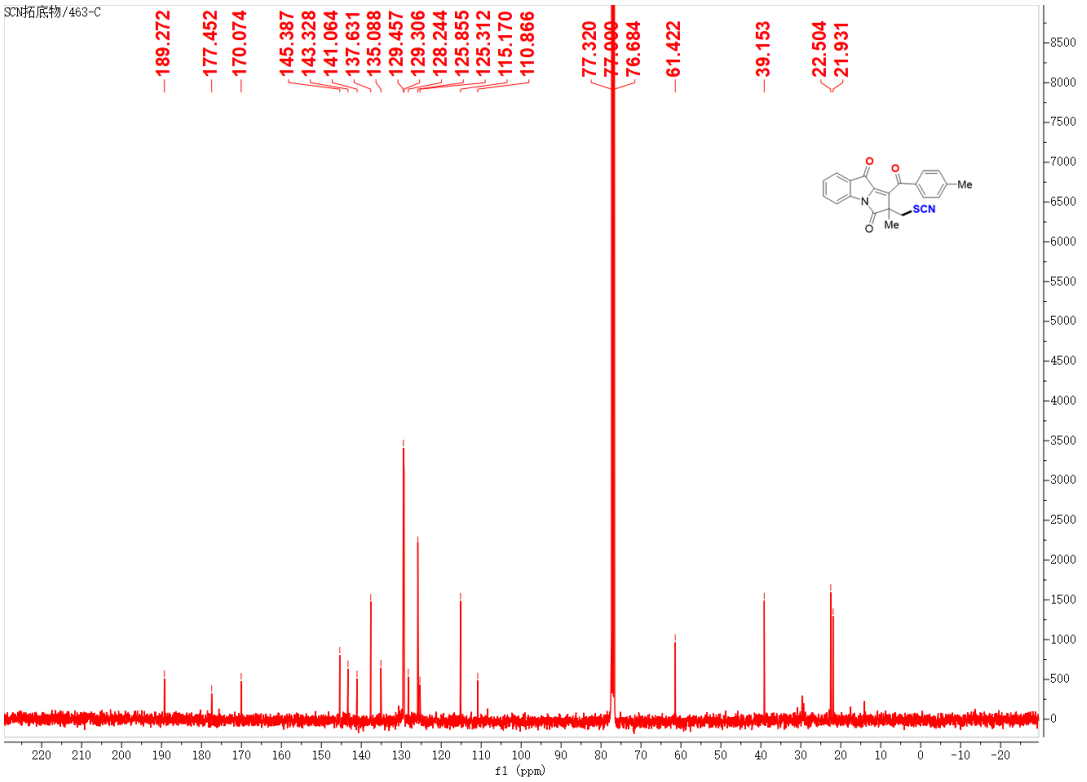
1-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



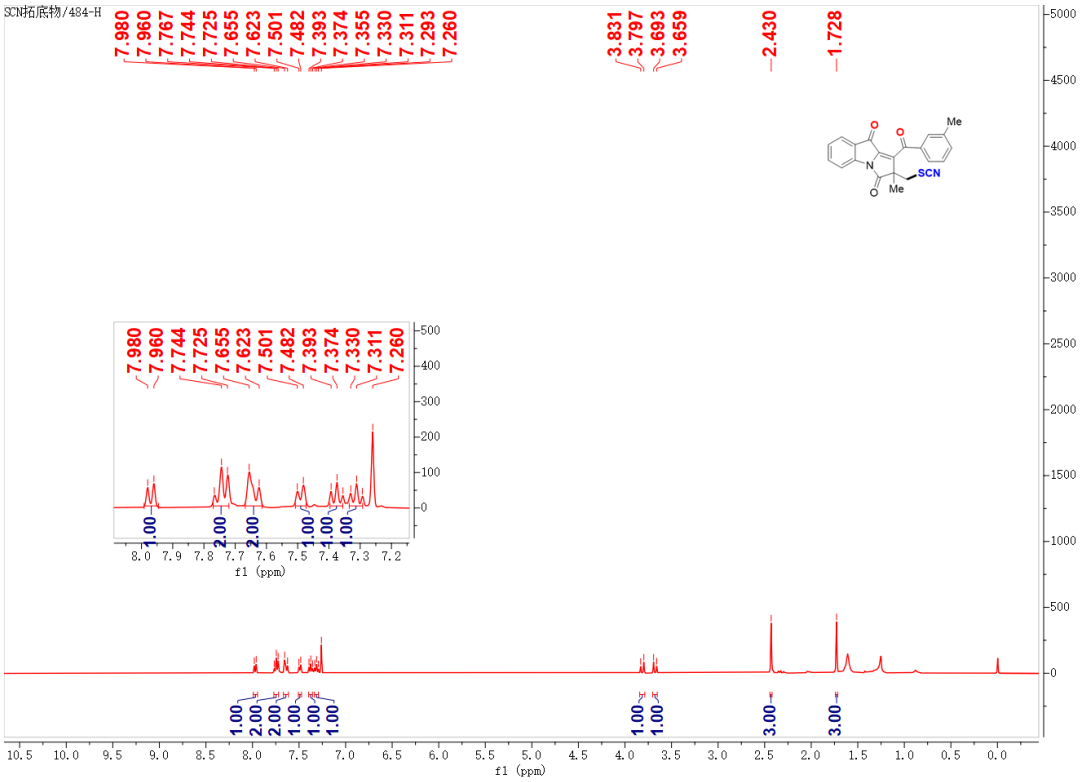
2-^{1}H NMR (400 MHz, $CDCl_3$)



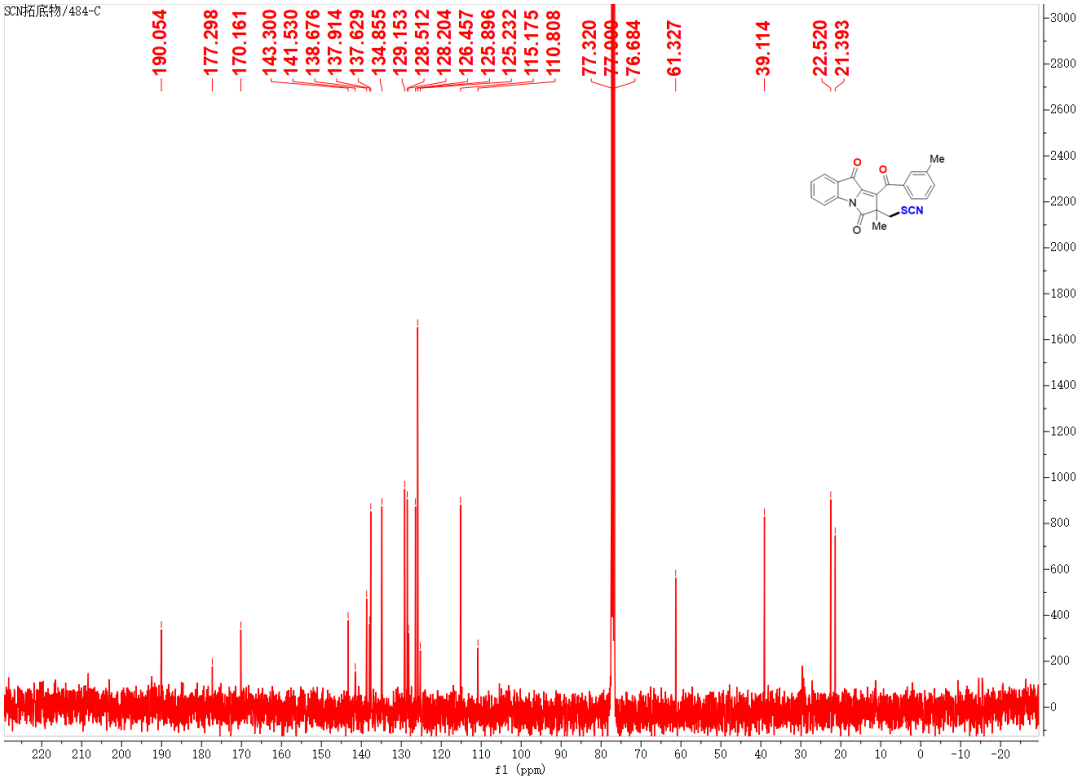
2-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



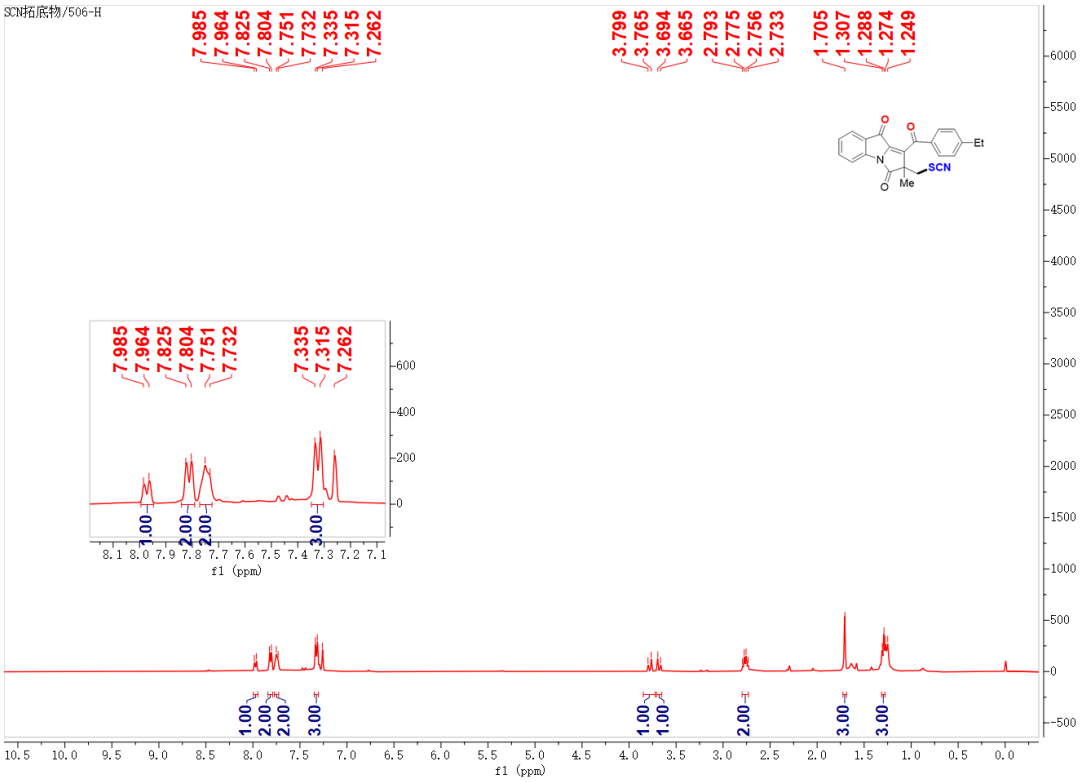
3-^{1}H NMR (400 MHz, $CDCl_3$)



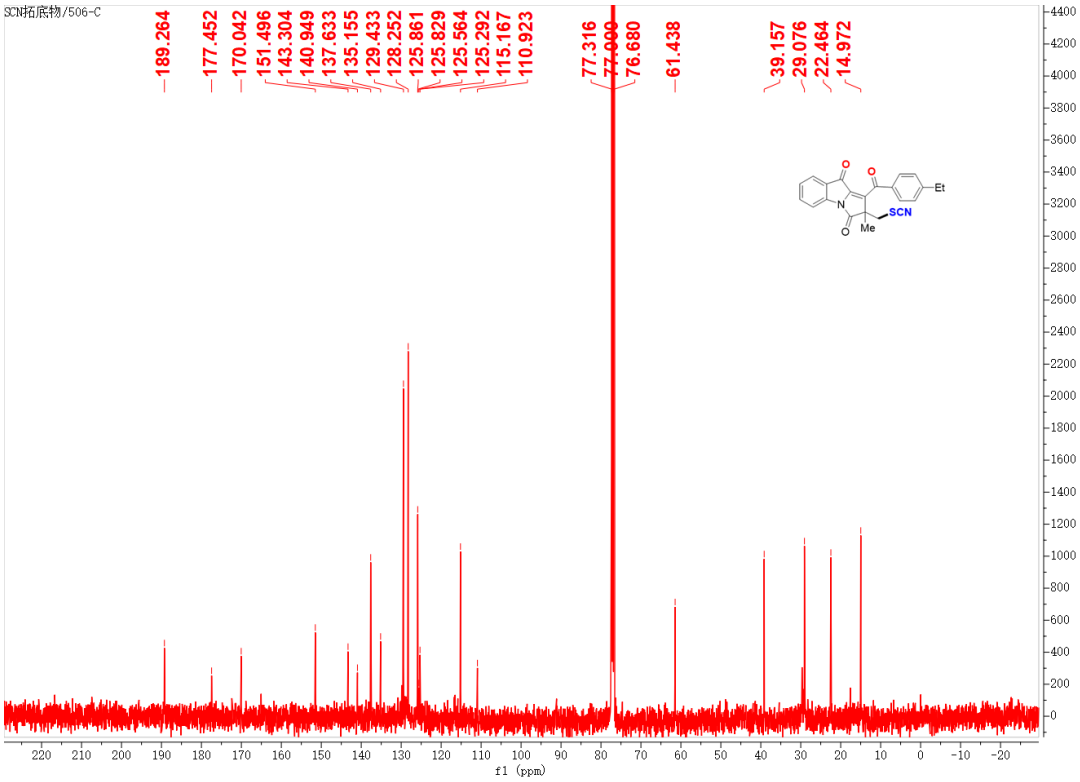
3-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



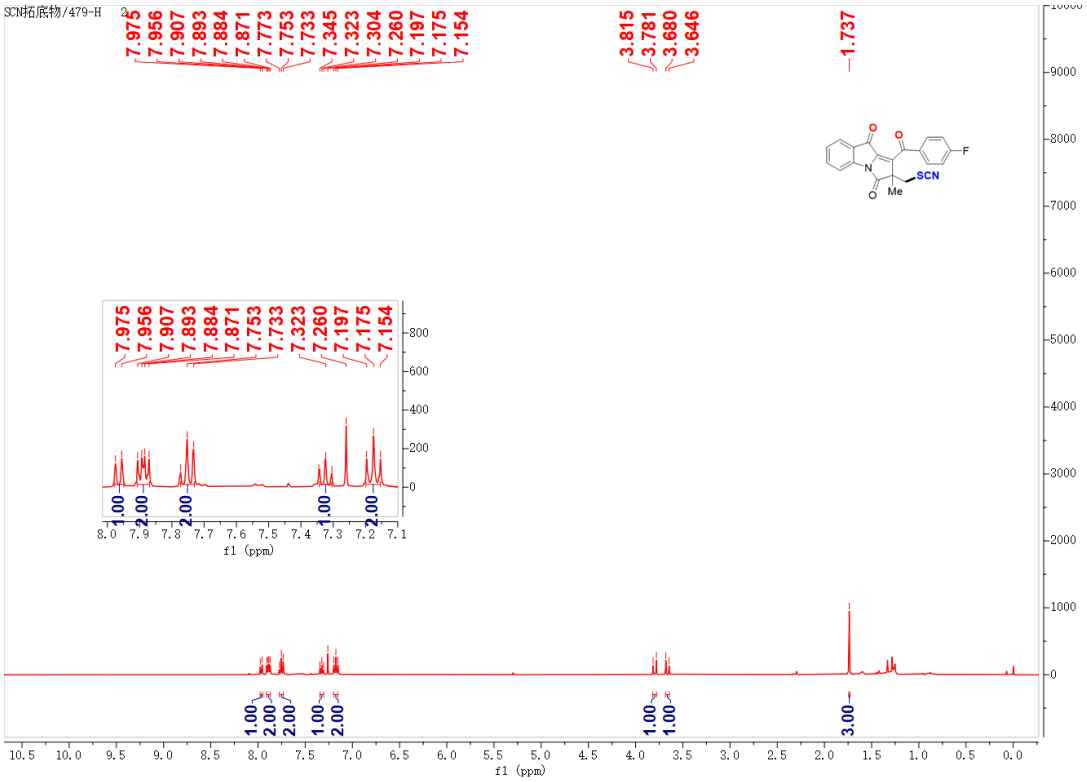
4-^{1}H NMR (400 MHz, $CDCl_3$)



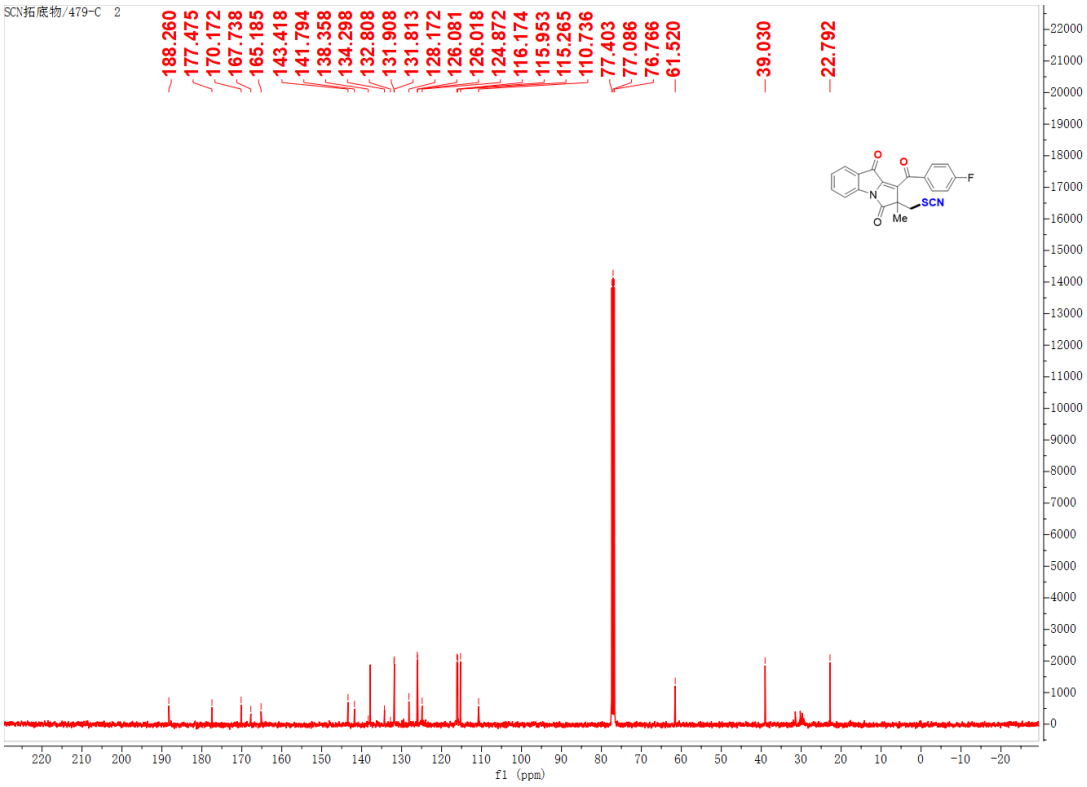
4-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



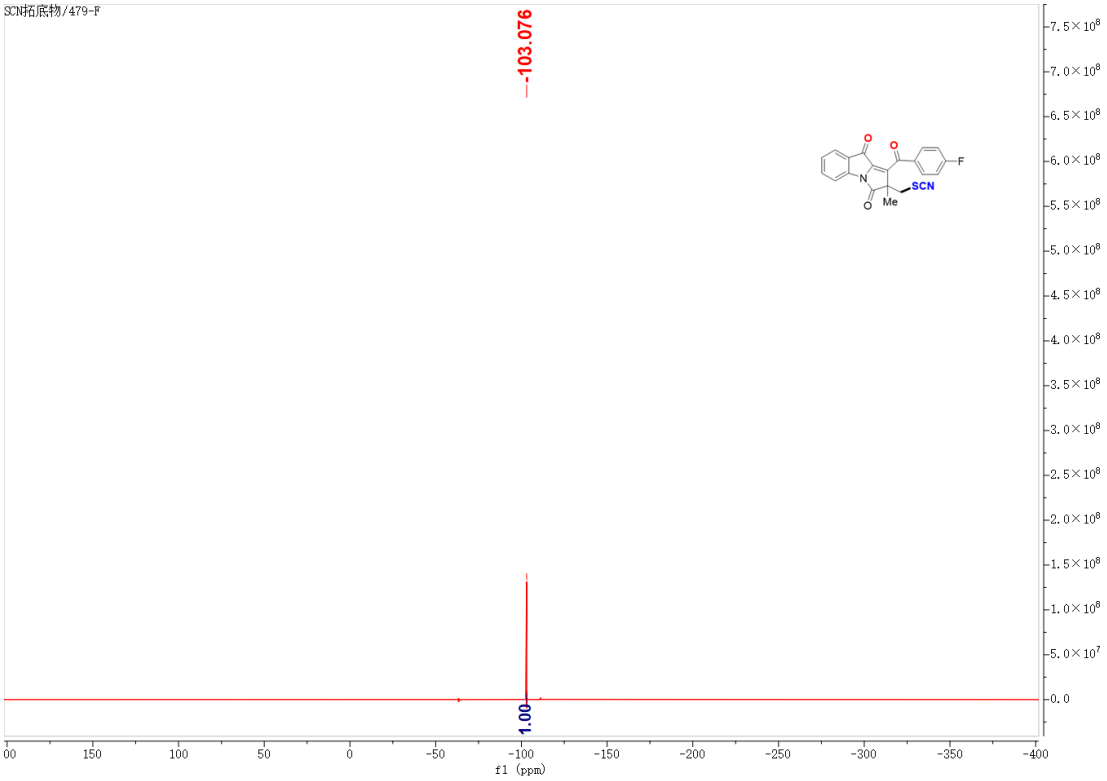
5-^{1}H NMR (400 MHz, $CDCl_3$)



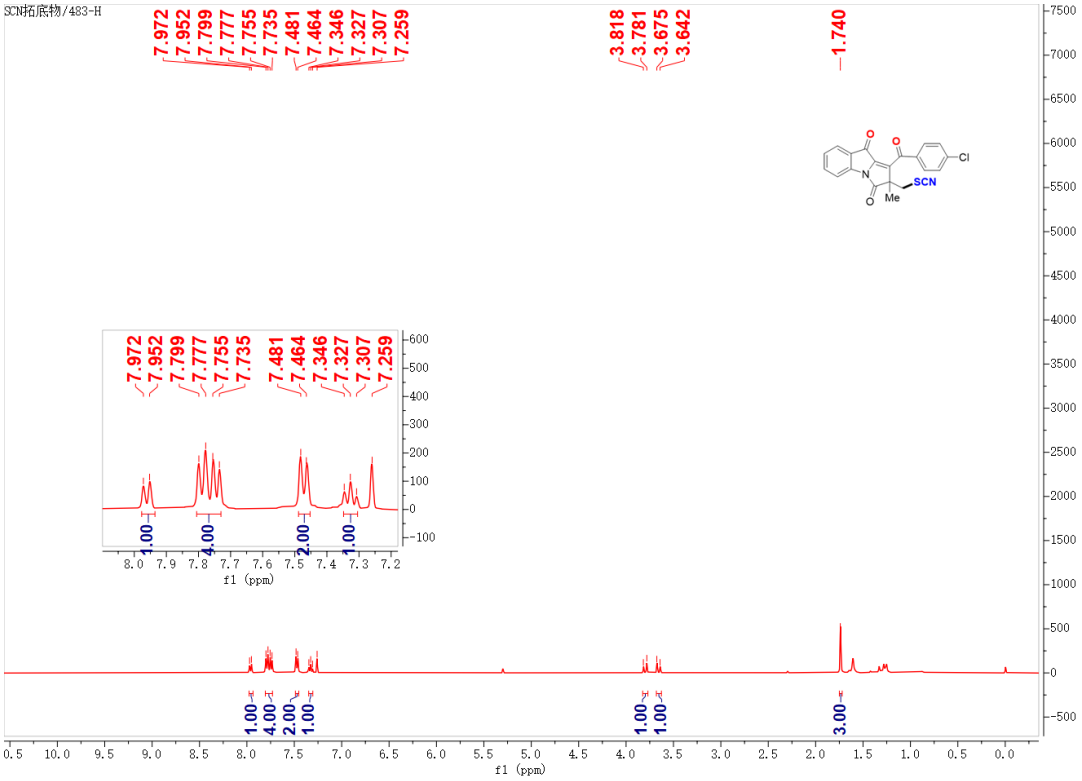
5-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



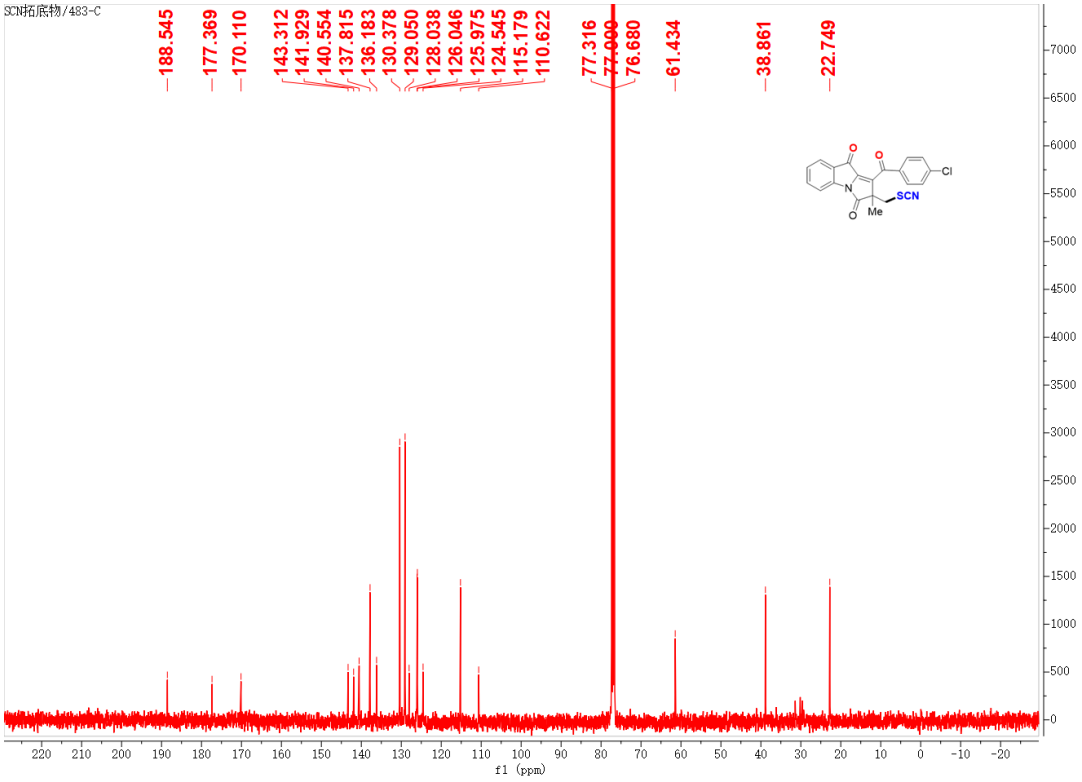
5-^{19}F NMR (565 MHz, $CDCl_3$)



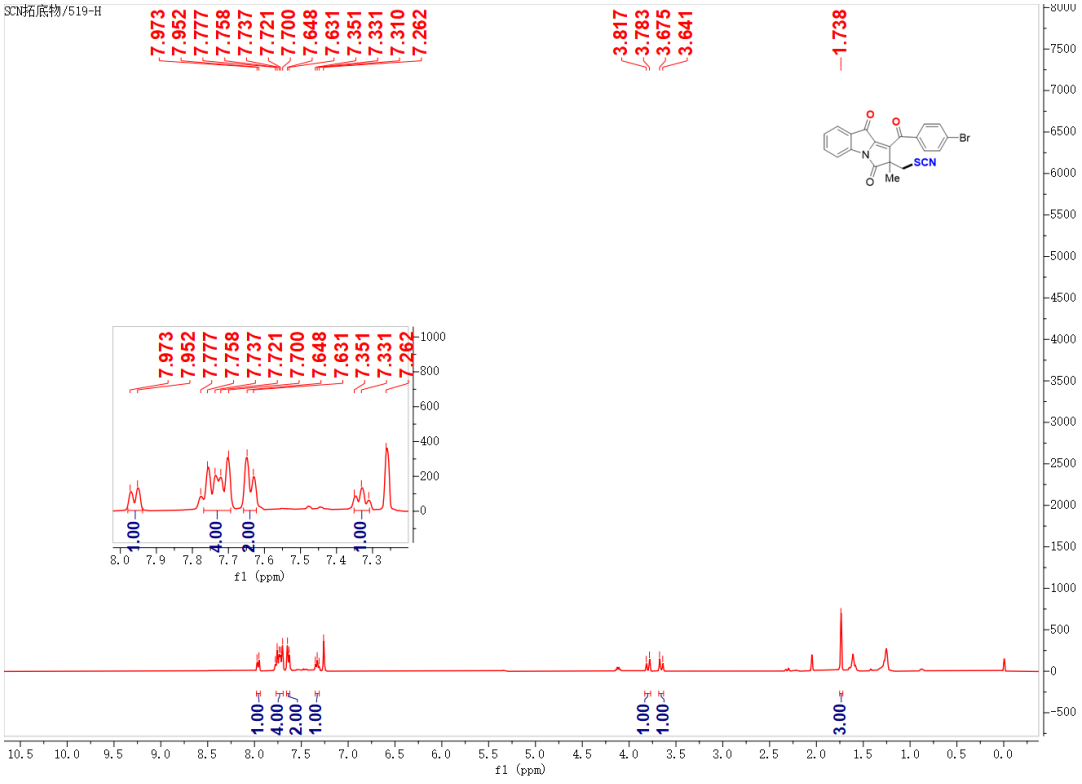
6-^{1}H NMR (400 MHz, $CDCl_3$)



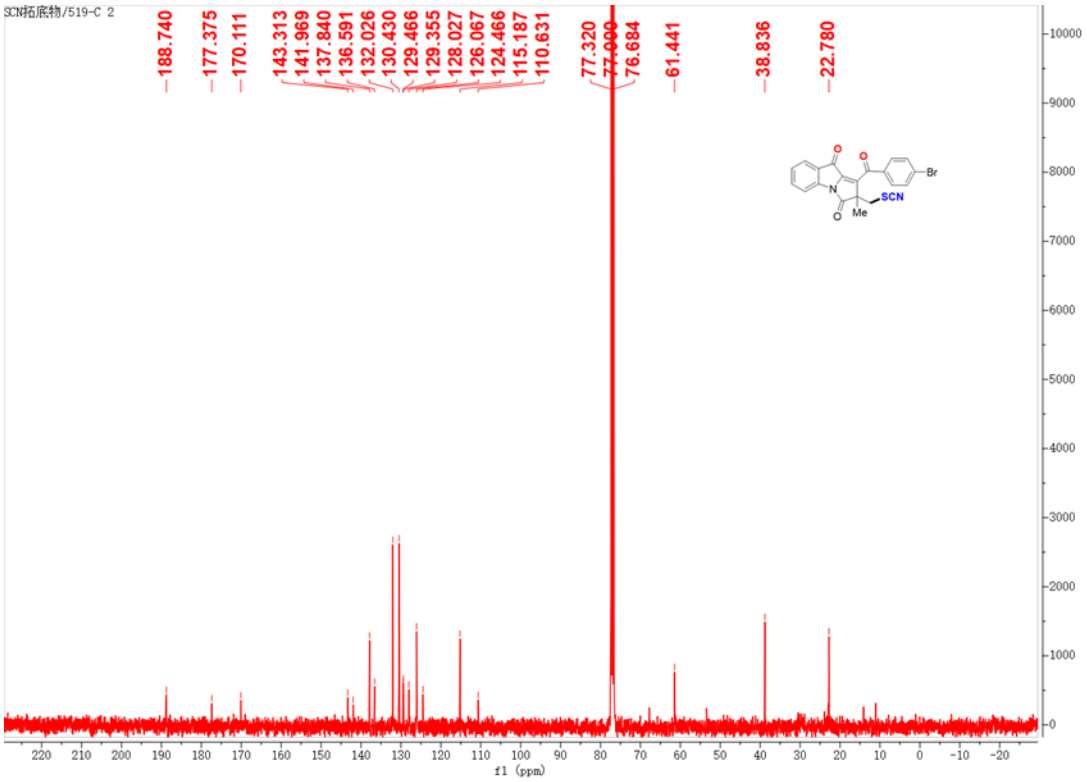
6-$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



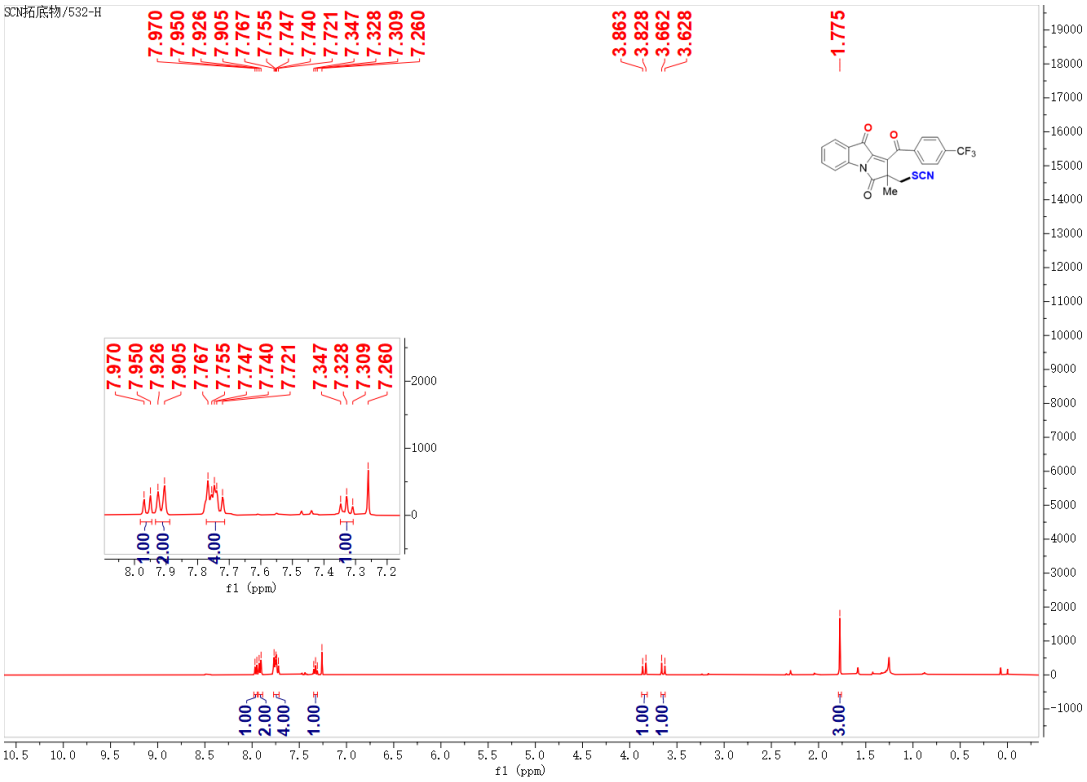
7-^{1}H NMR (400 MHz, $CDCl_3$)



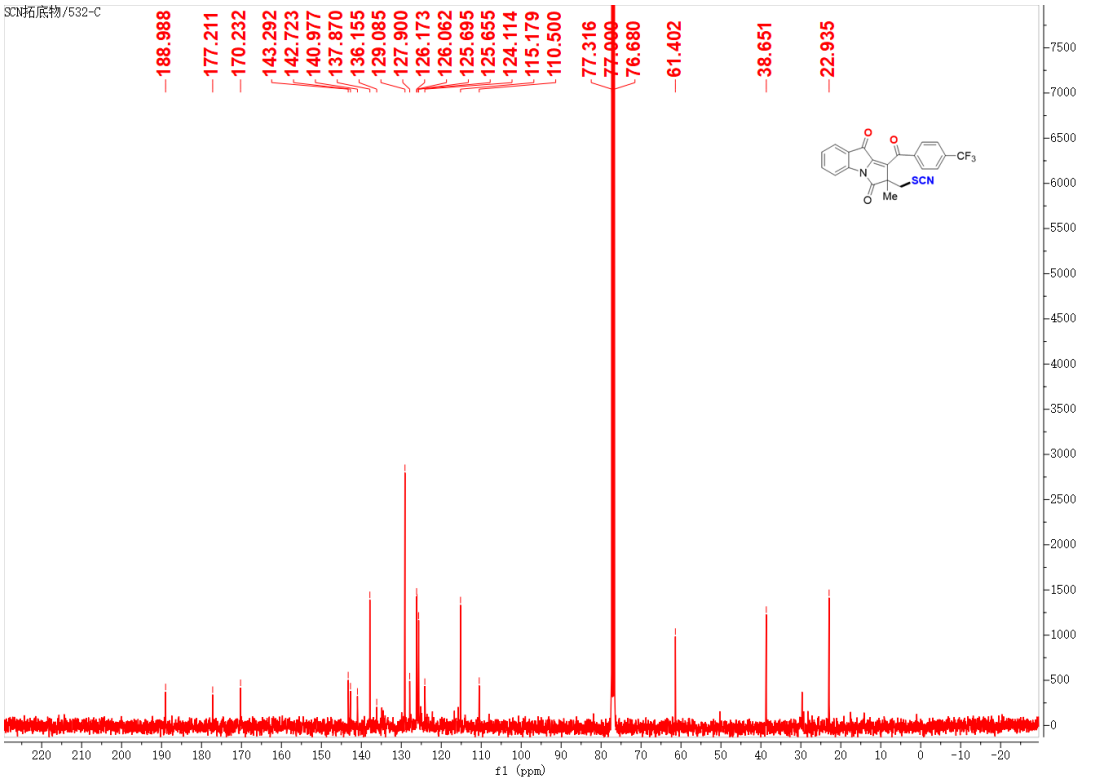
7-$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



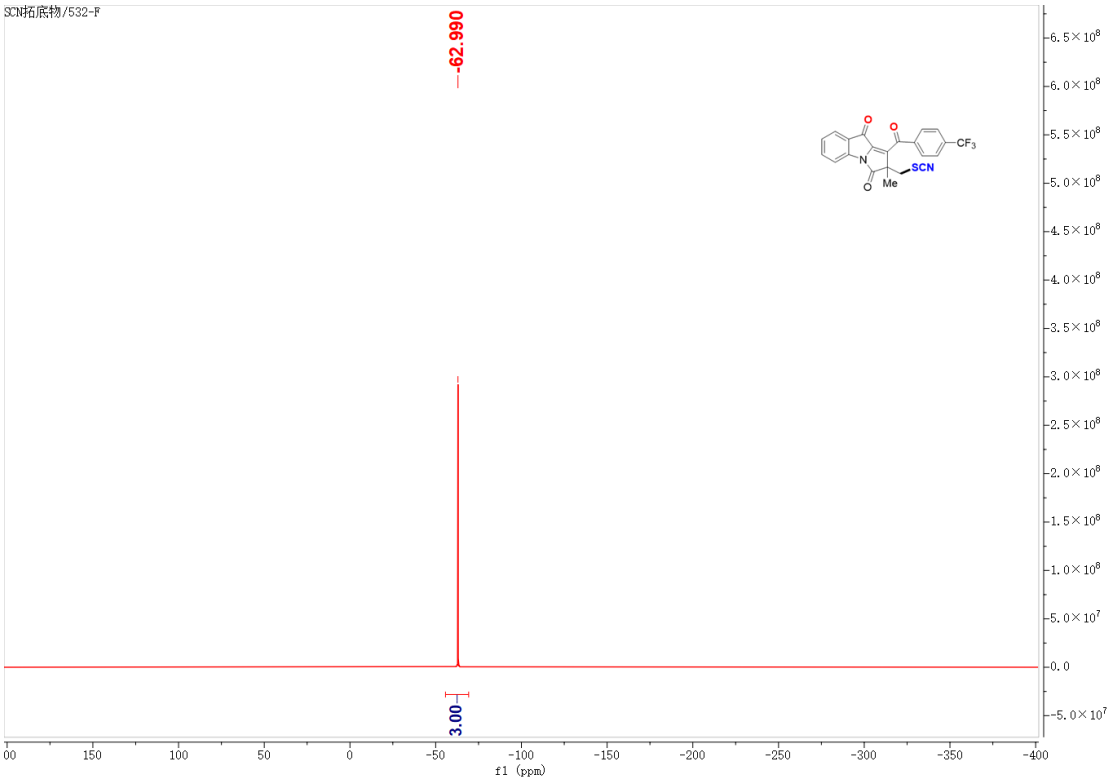
8-^{1}H NMR (400 MHz, $CDCl_3$)



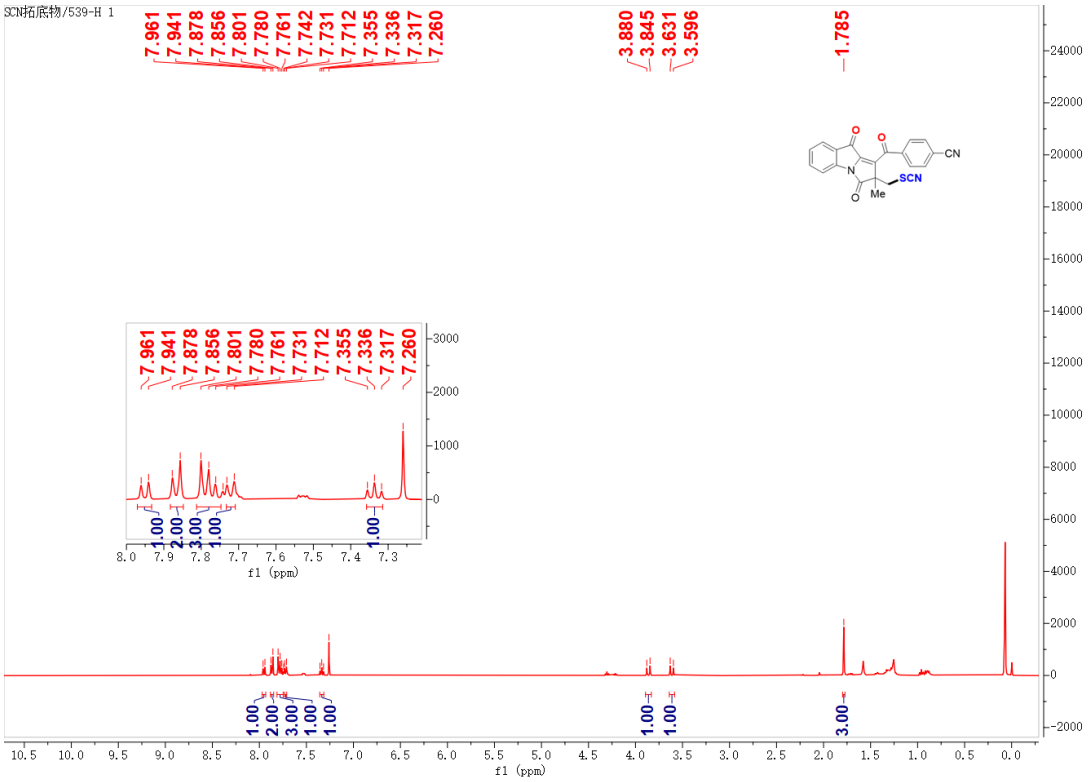
8-$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



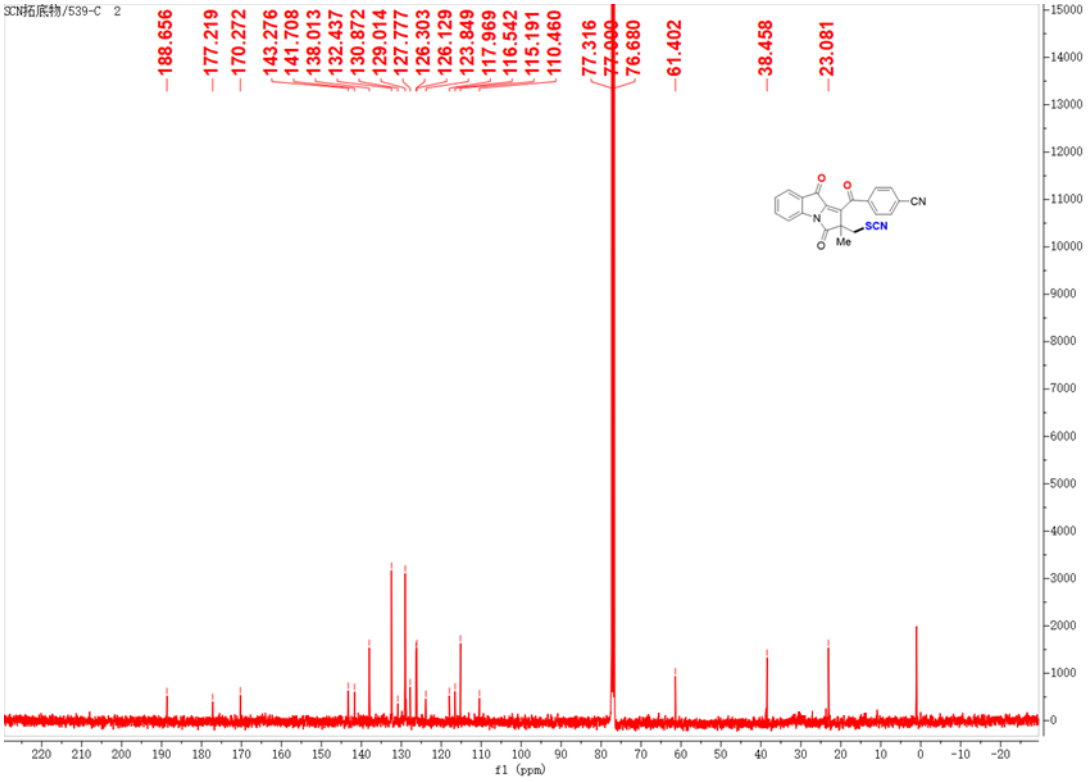
8-^{19}F NMR (565 MHz, $CDCl_3$)



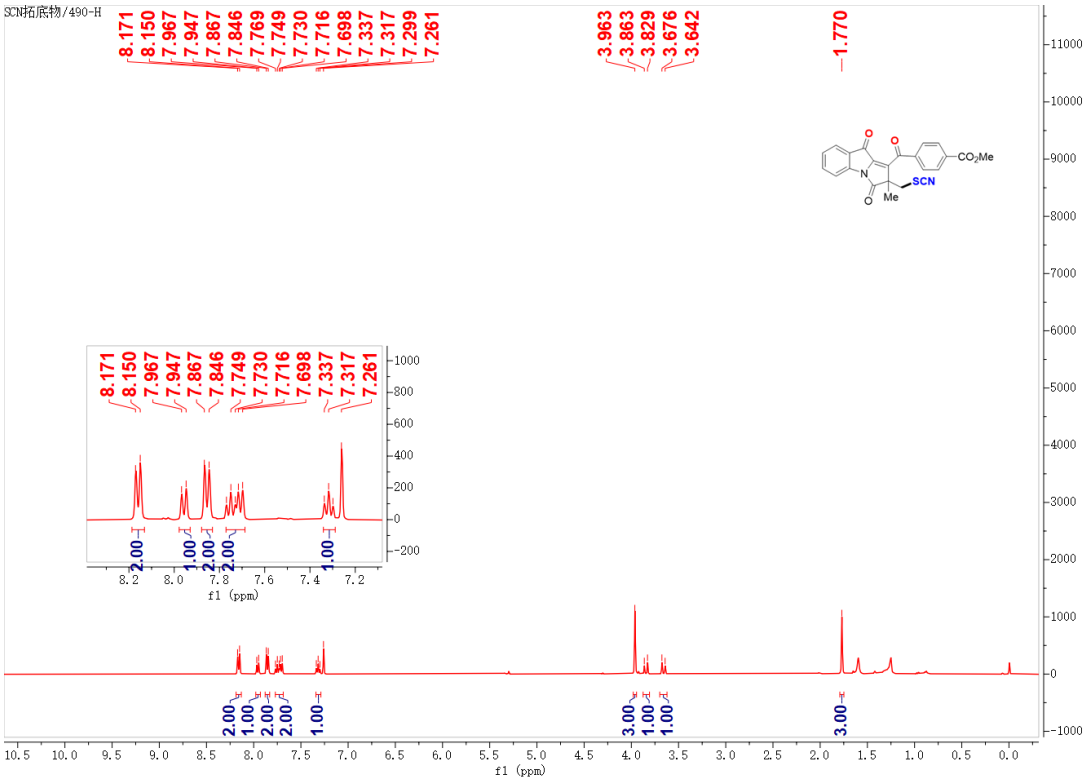
9-^{1}H NMR (400 MHz, $CDCl_3$)



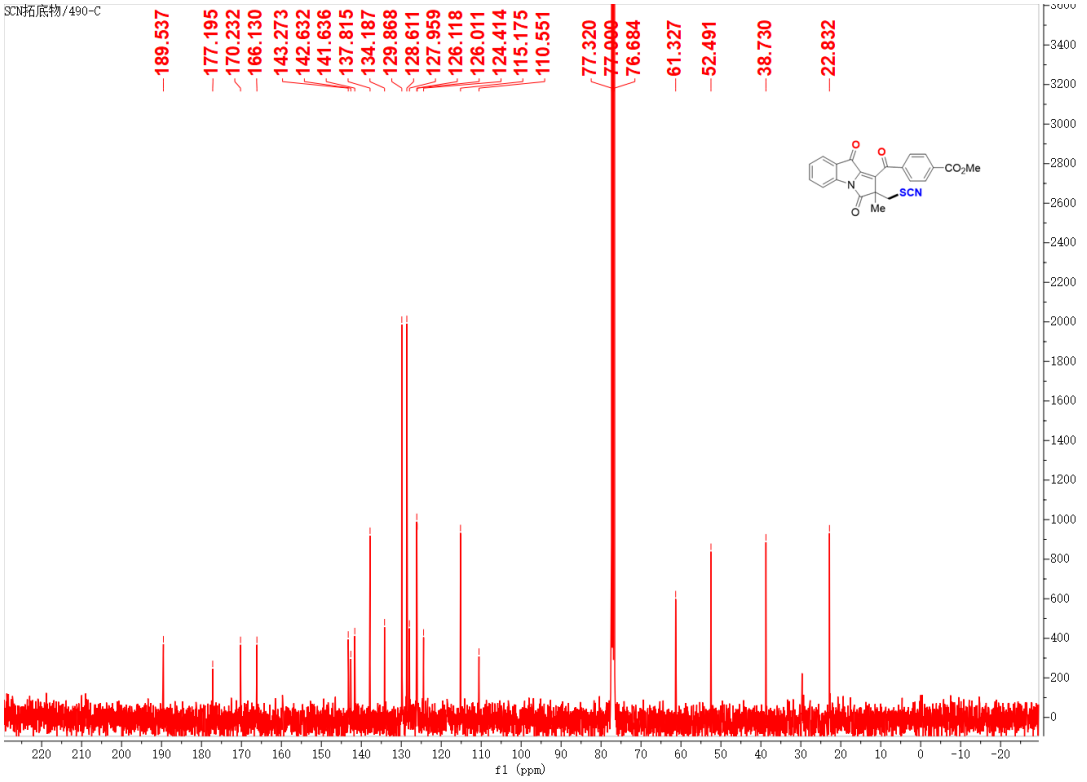
9-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



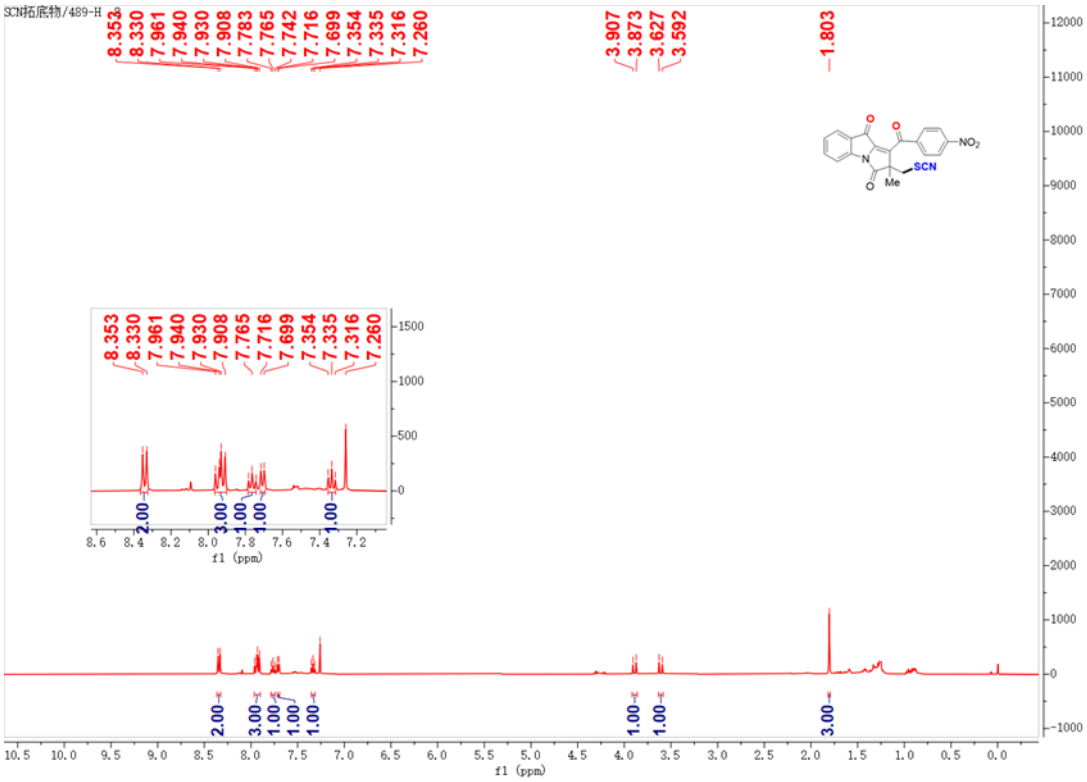
10-^{1}H NMR (400 MHz, $CDCl_3$)



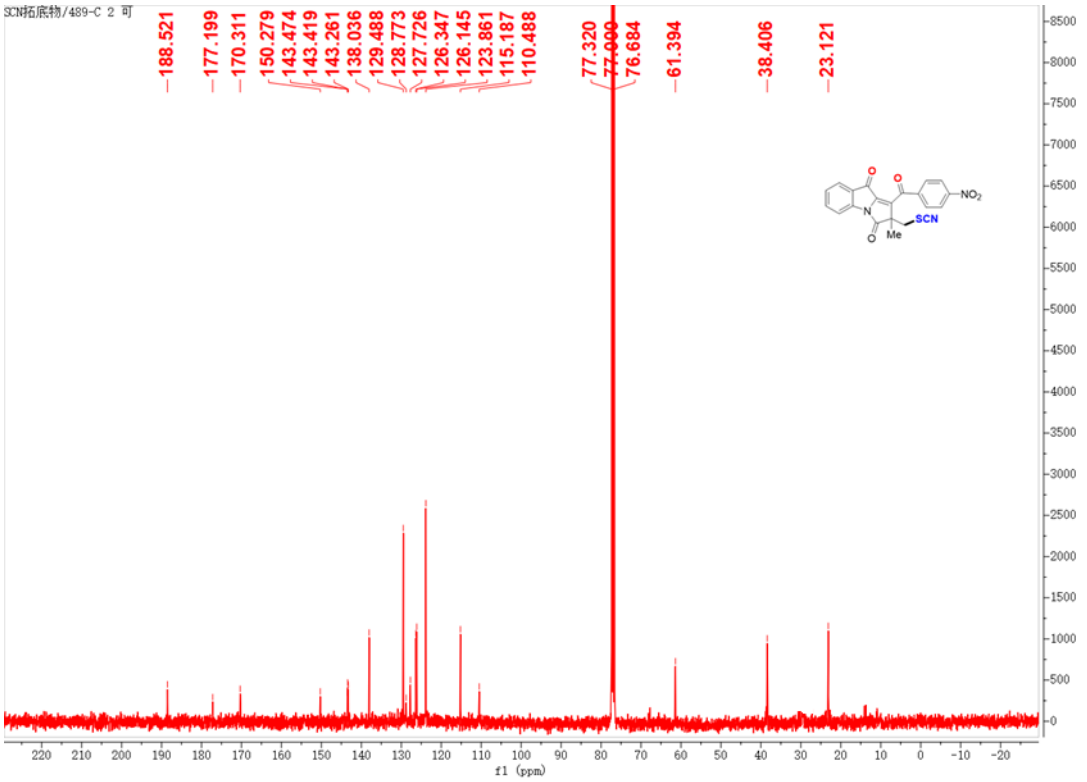
10-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



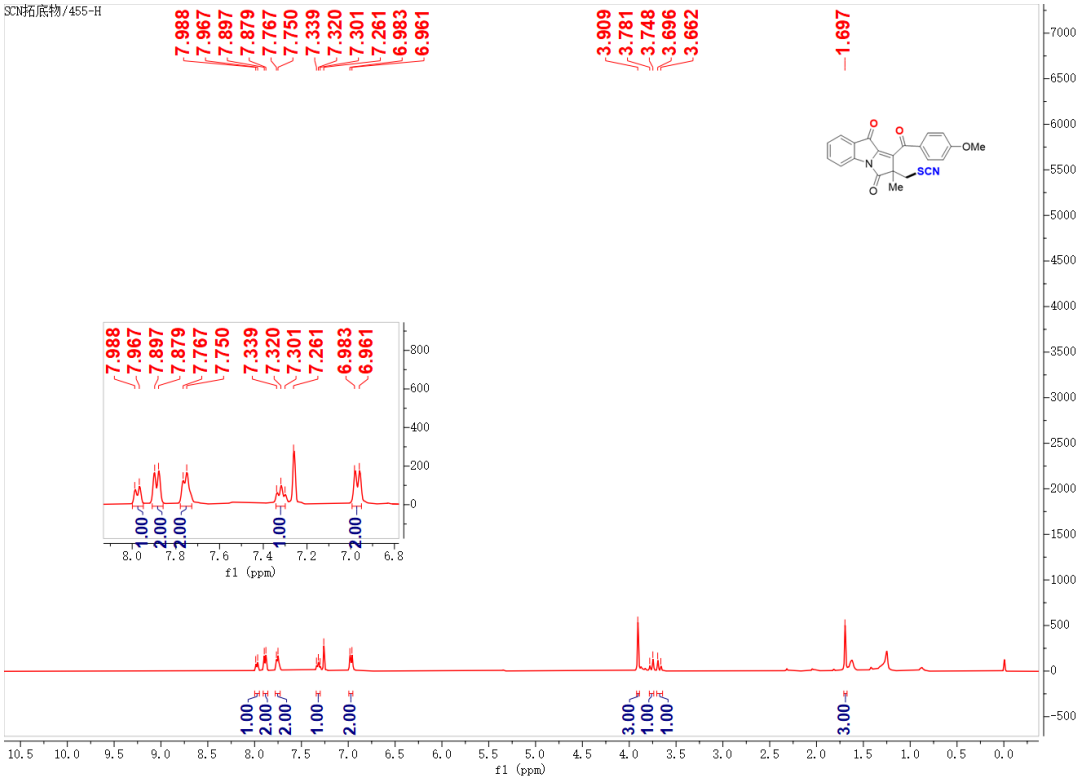
11-^{1}H NMR (400 MHz, $CDCl_3$)



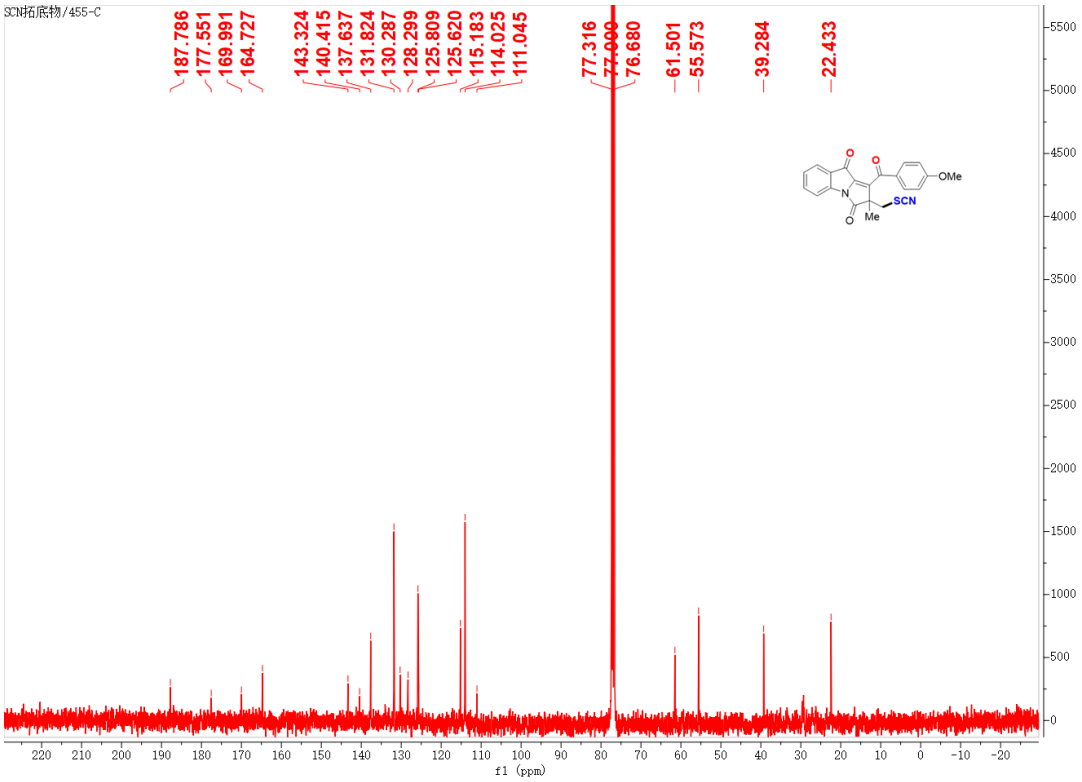
11-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



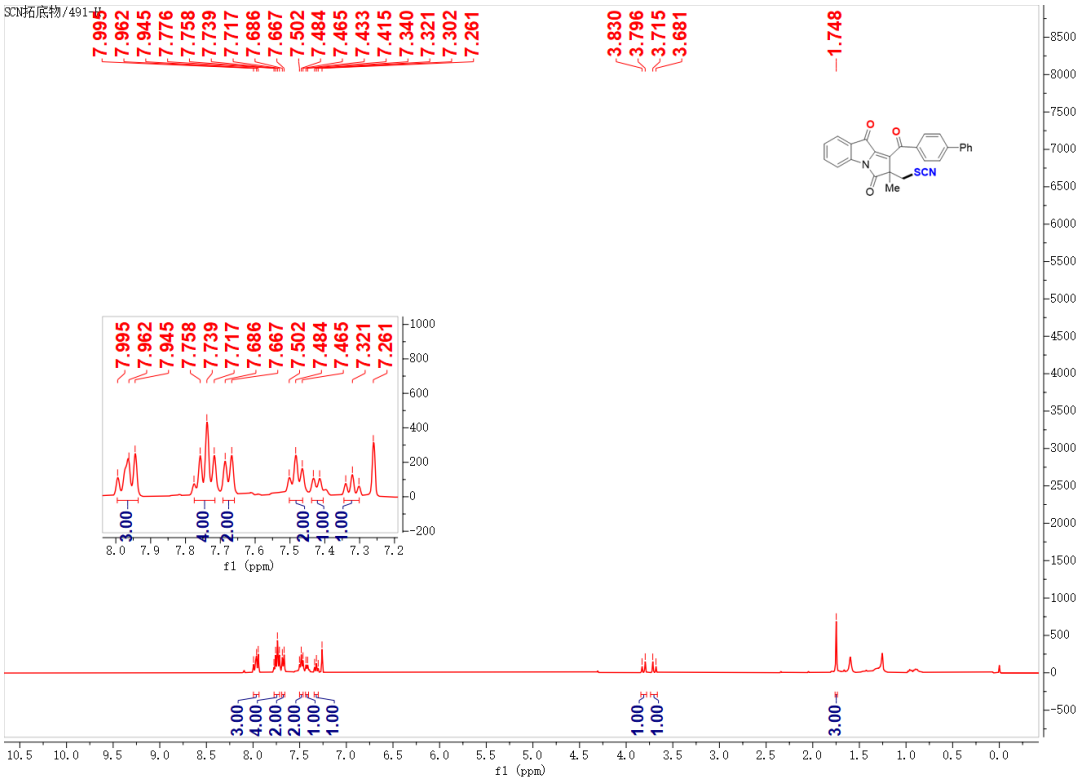
12-^{1}H NMR (400 MHz, $CDCl_3$)



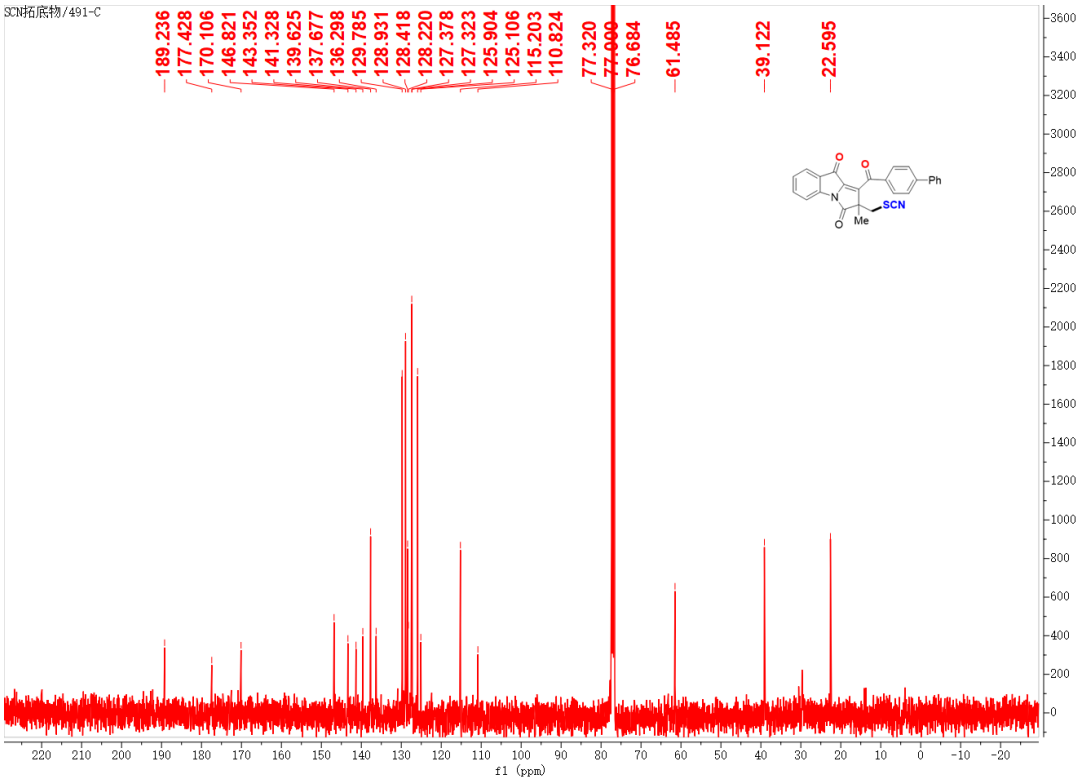
12-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



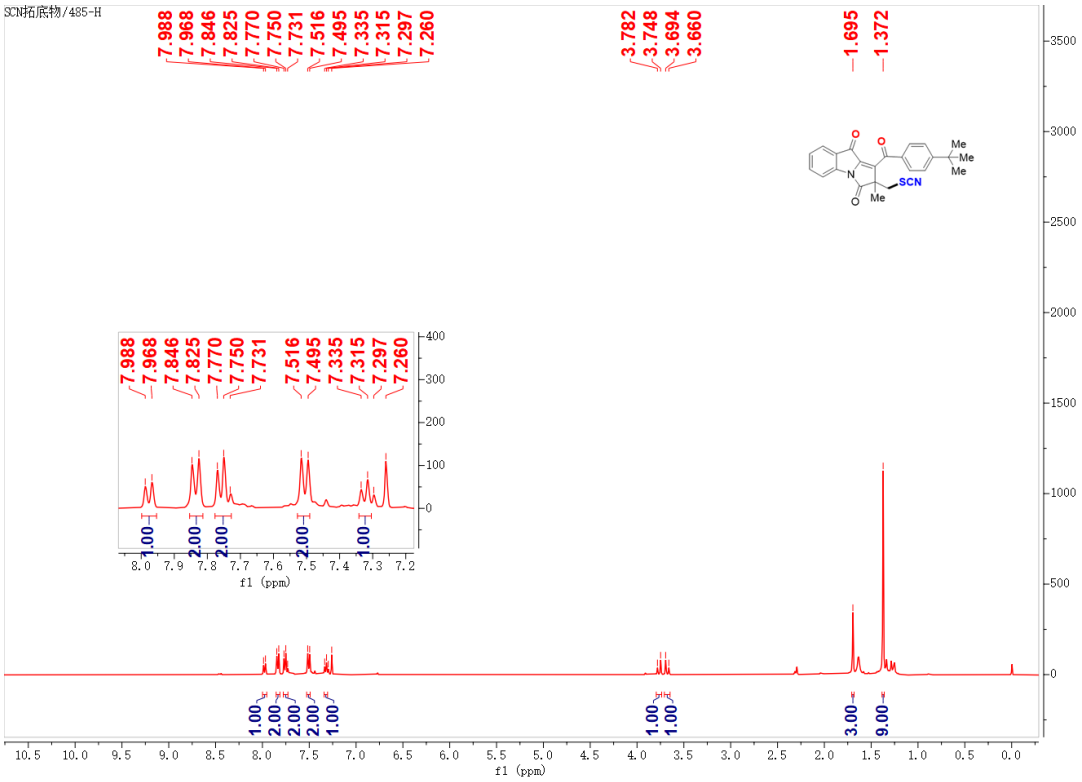
13-^{1}H NMR (400 MHz, $CDCl_3$)



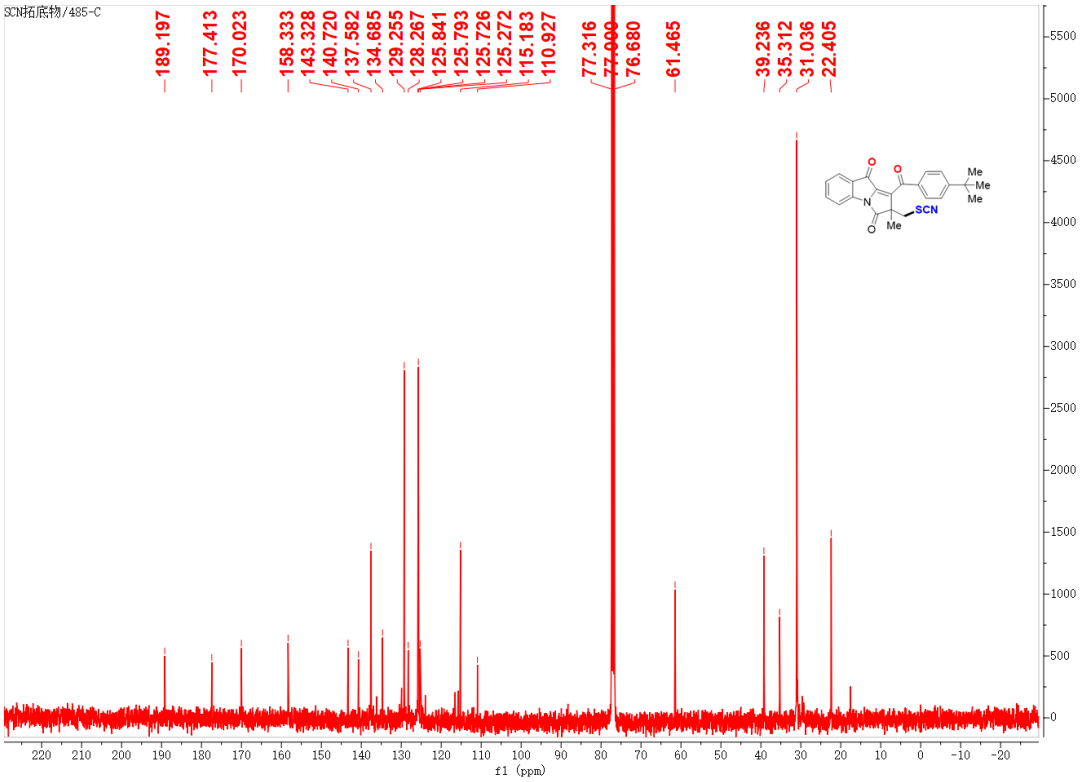
13-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



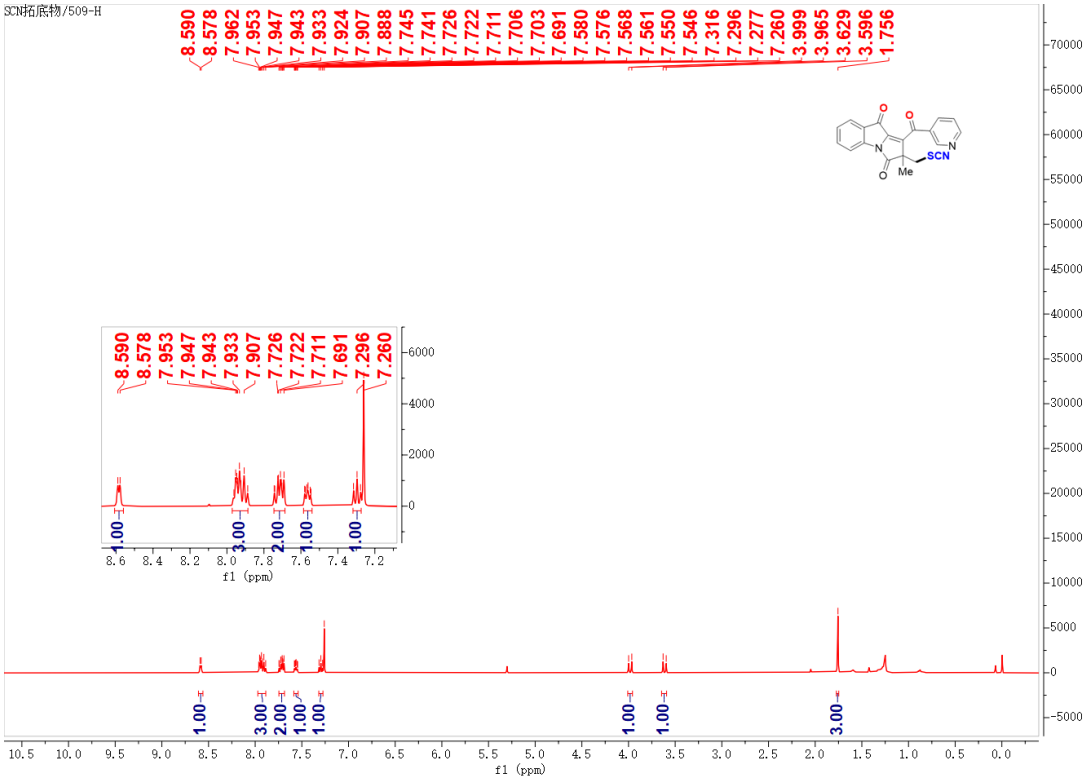
14-^{1}H NMR (400 MHz, $CDCl_3$)



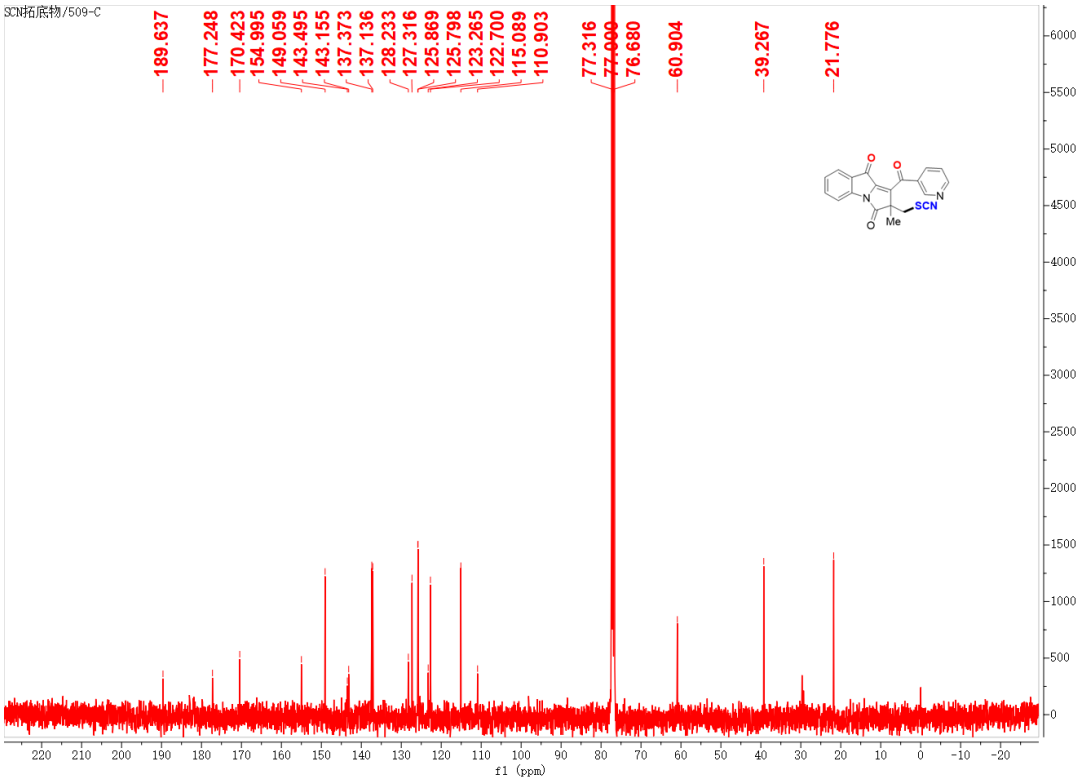
14-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



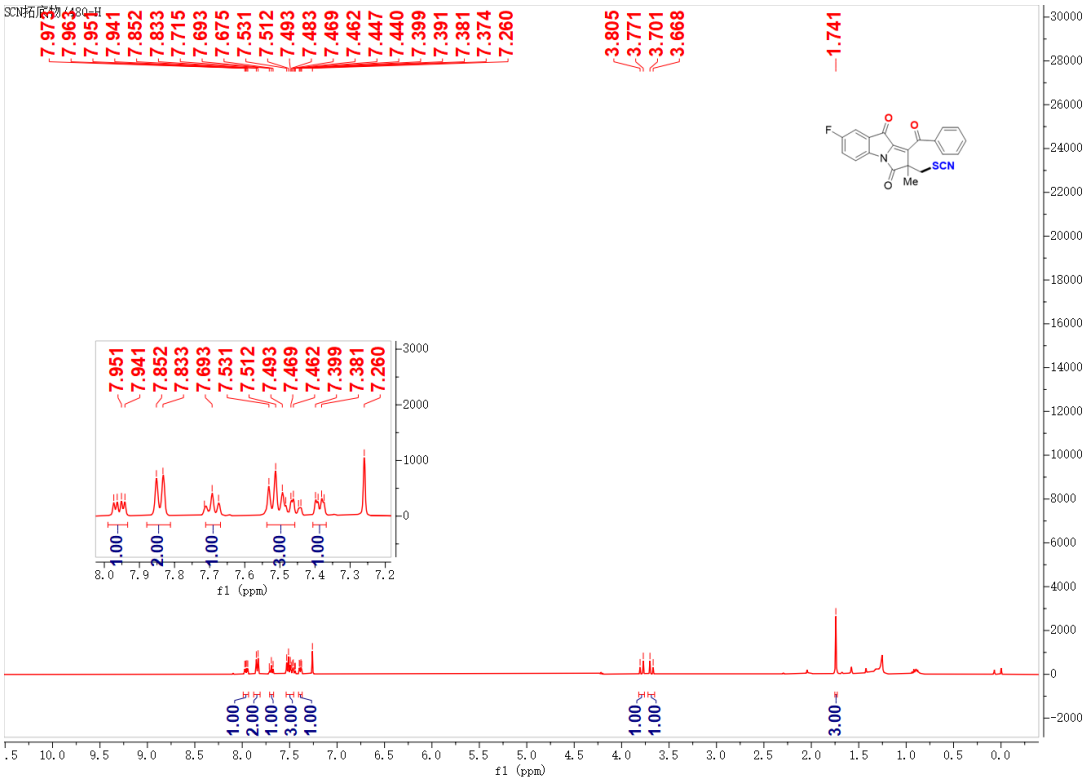
15-^{1}H NMR (400 MHz, $CDCl_3$)



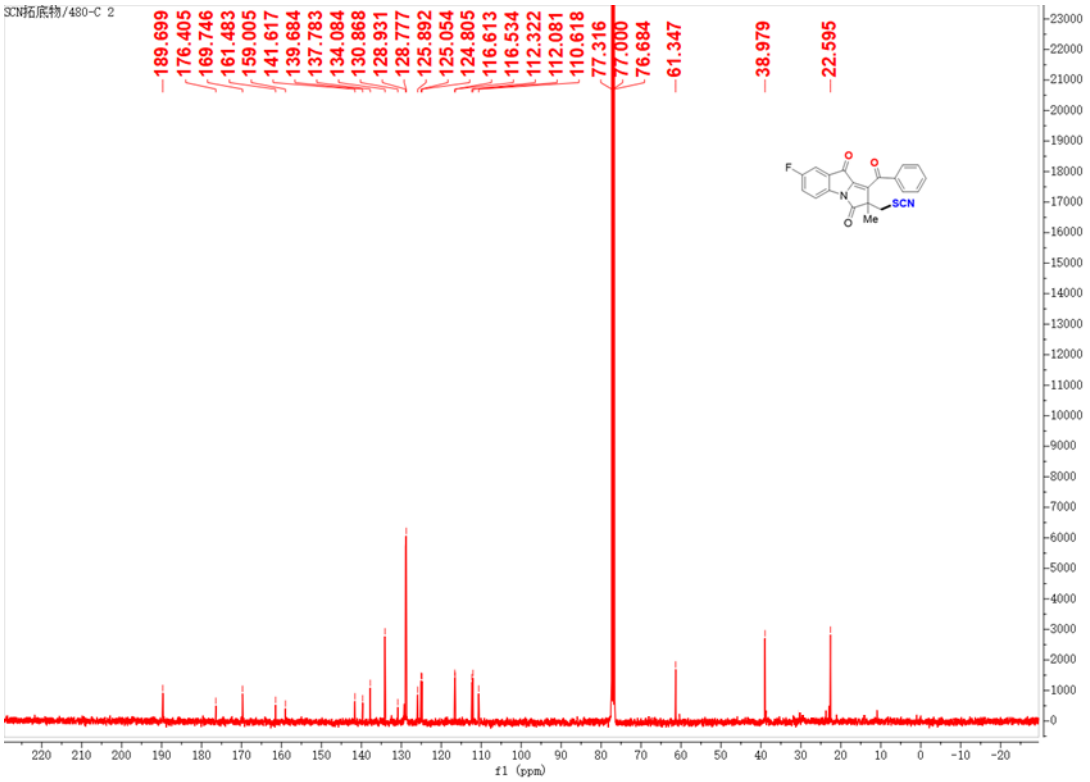
15-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



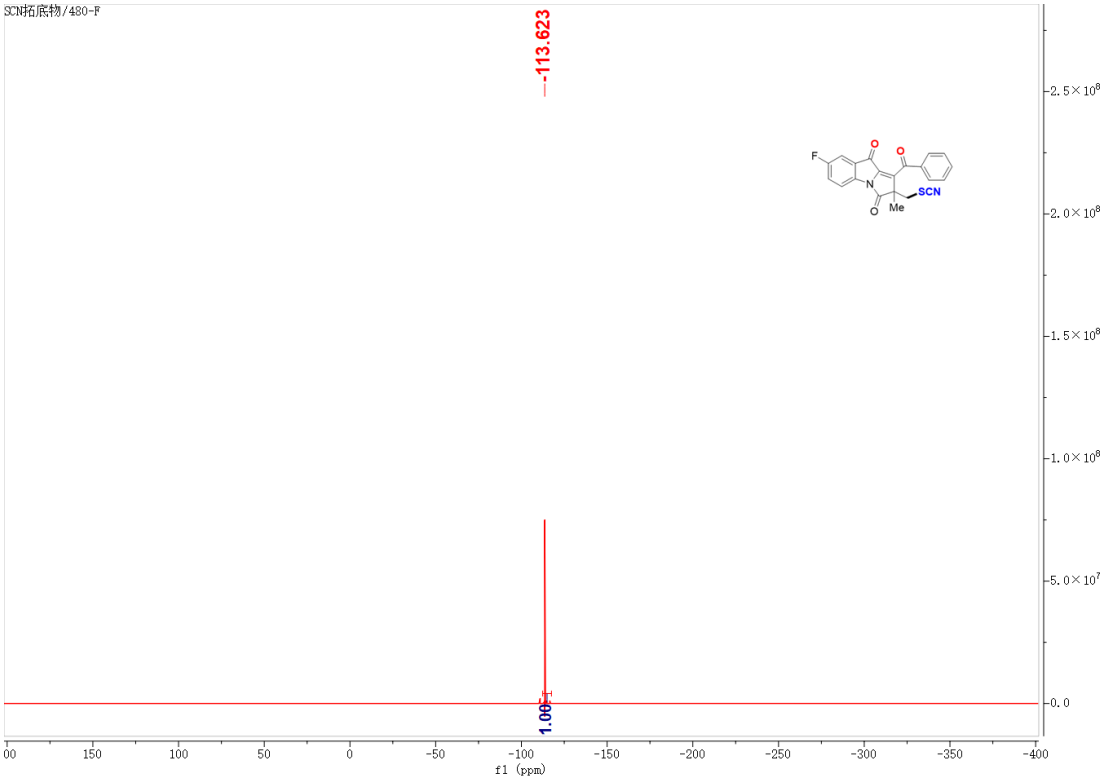
16-^{1}H NMR (400 MHz, $CDCl_3$)



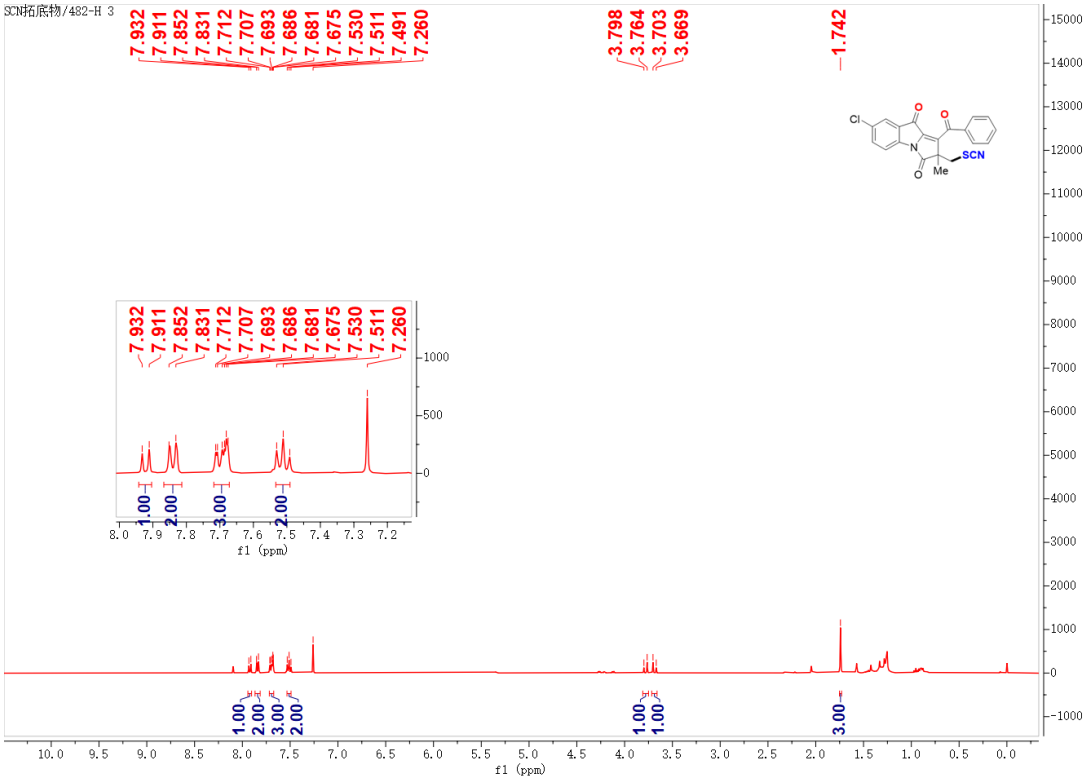
16-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



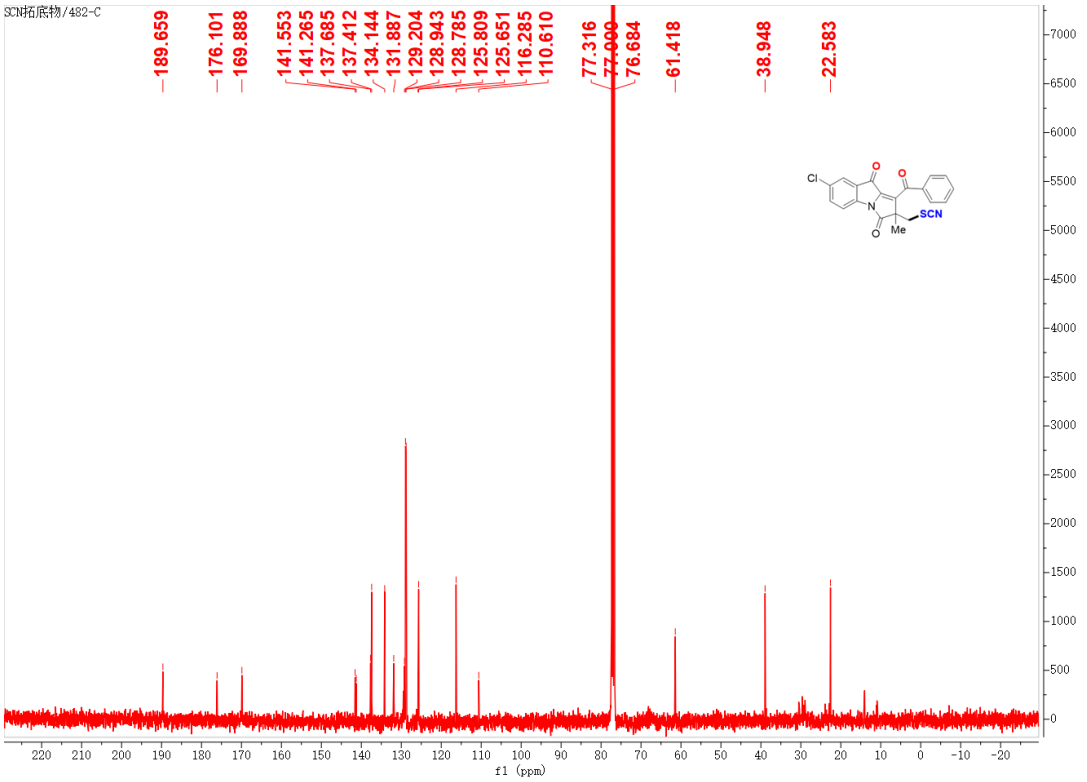
16-^{19}FNMR(565MHz,CDCl3)



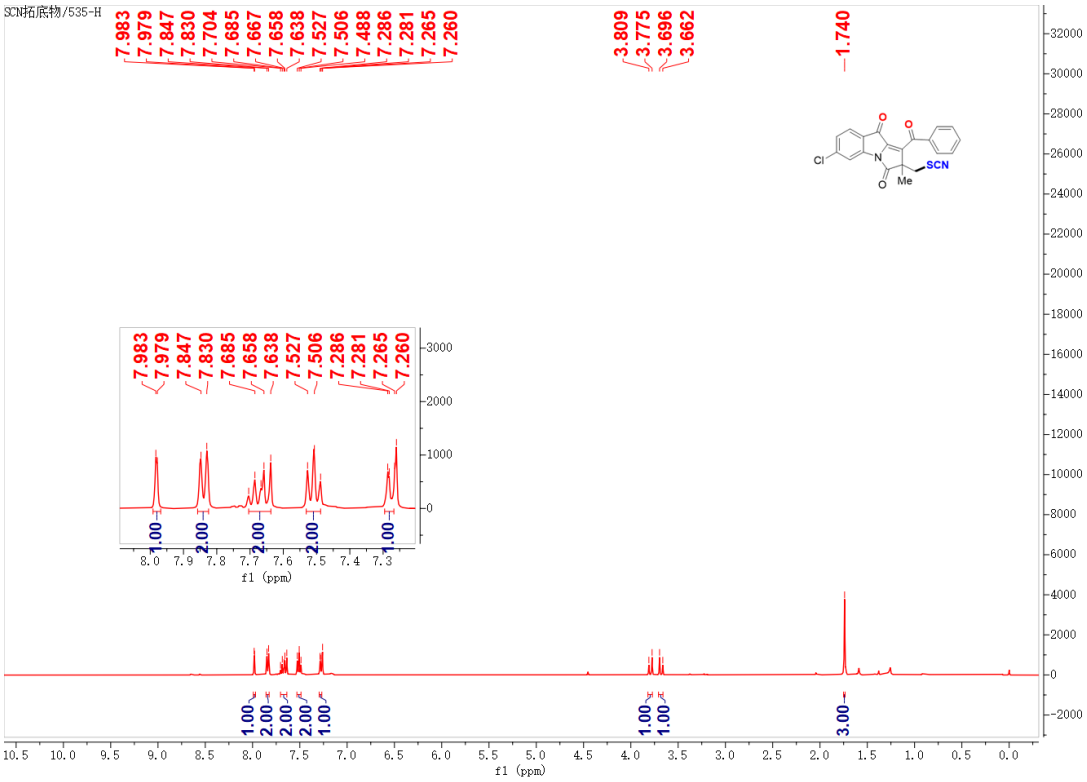
17-^{1}H NMR (400 MHz, $CDCl_3$)



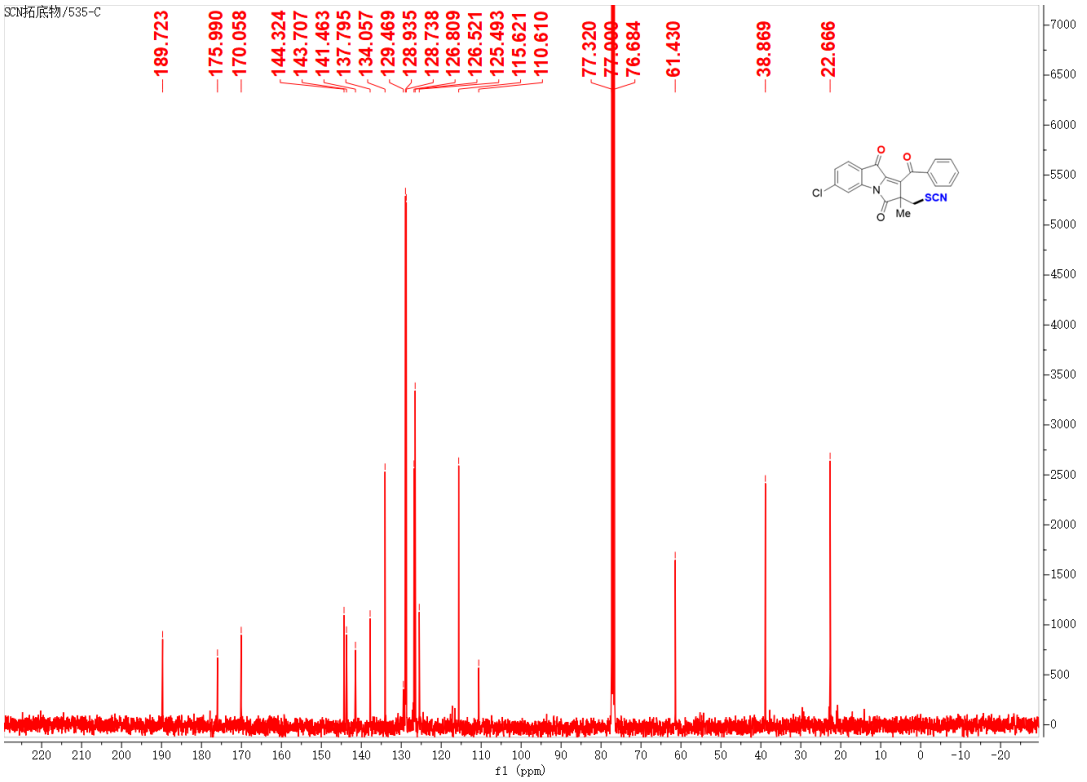
17-$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



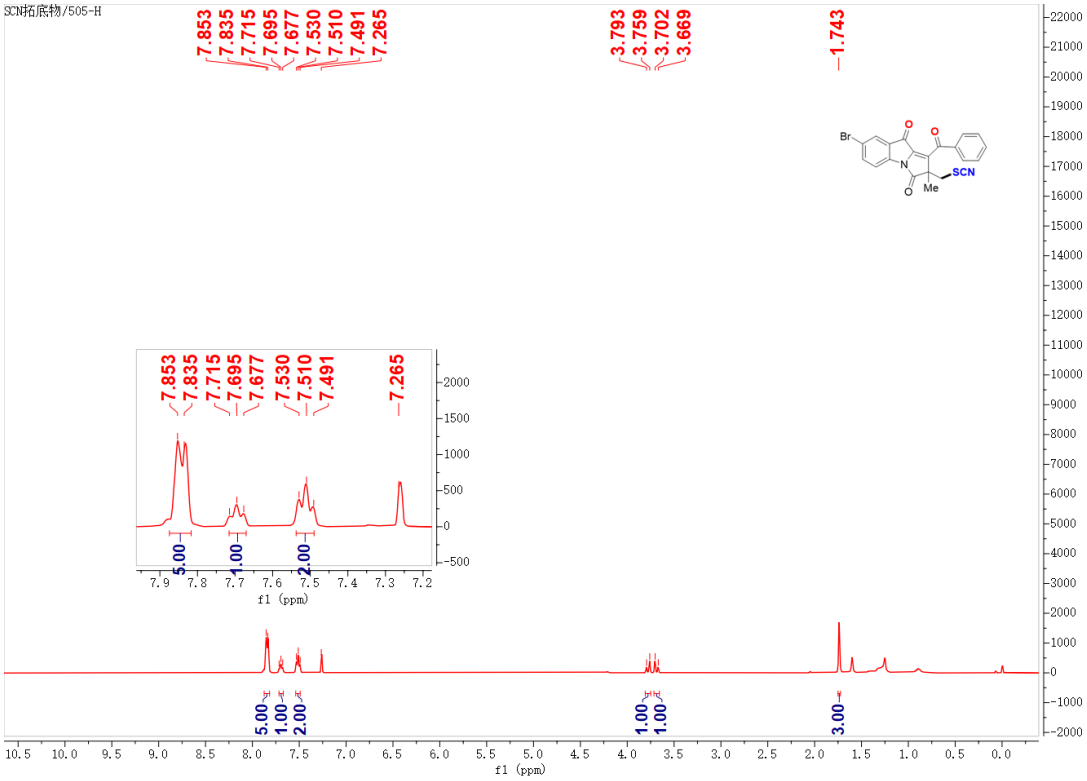
18-^{1}H NMR (400 MHz, $CDCl_3$)



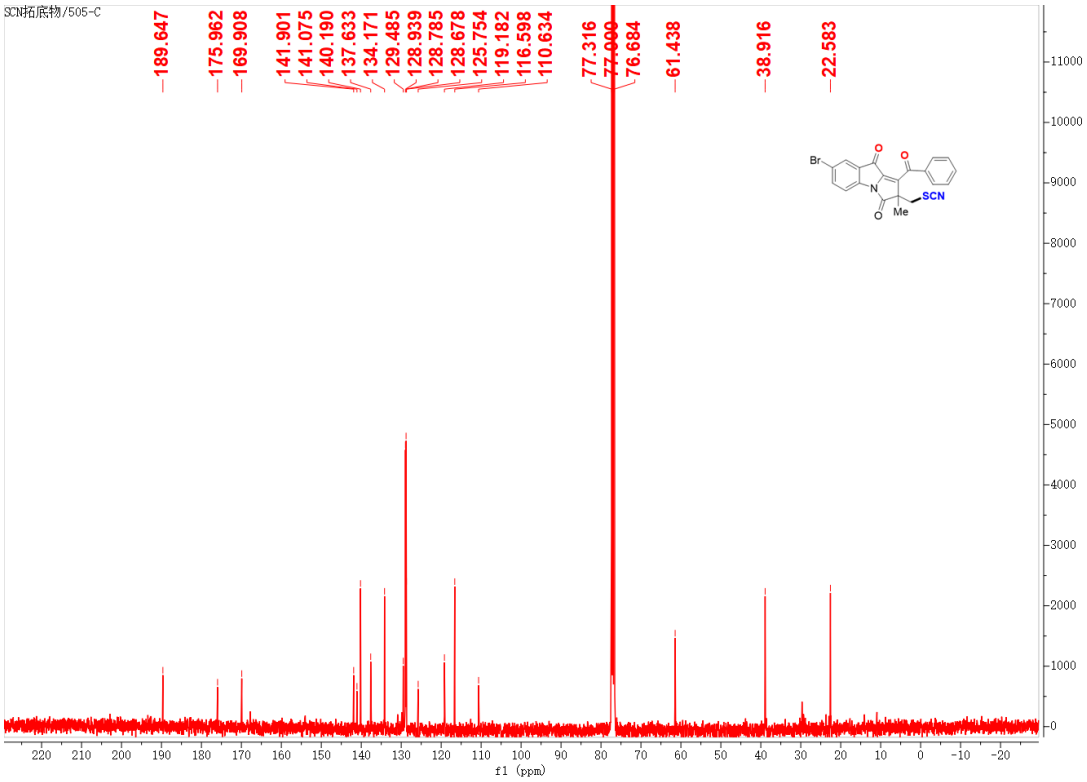
18-$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



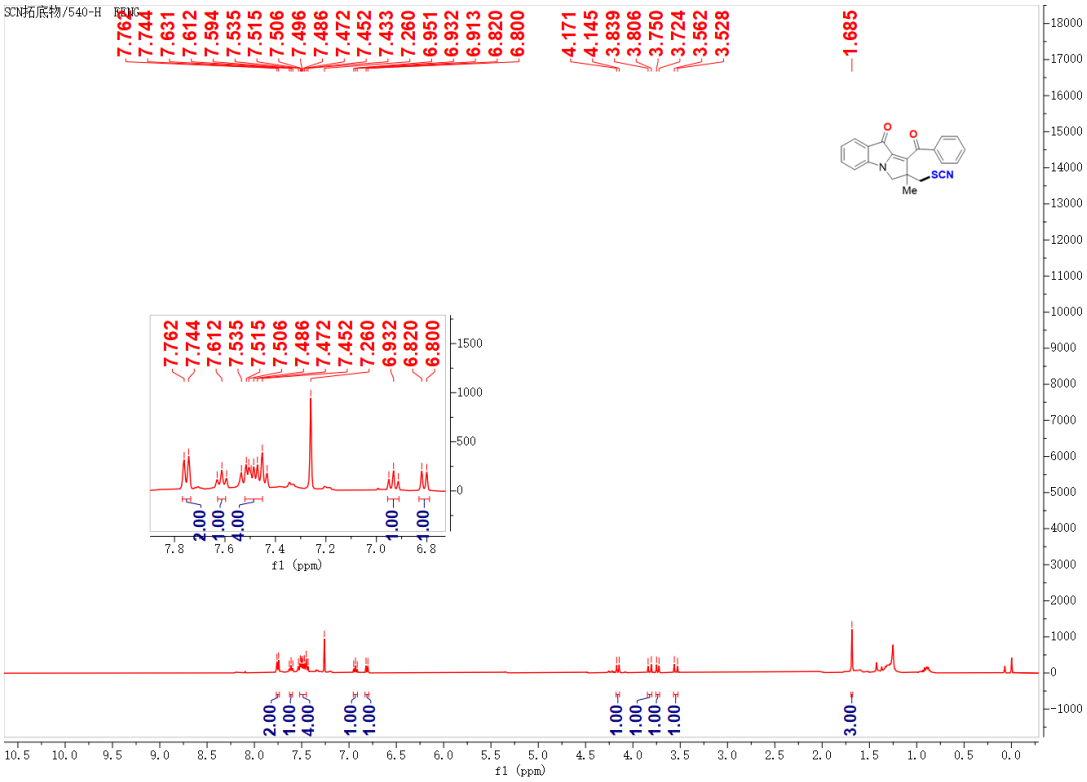
19-^{1}H NMR (400 MHz, $CDCl_3$)



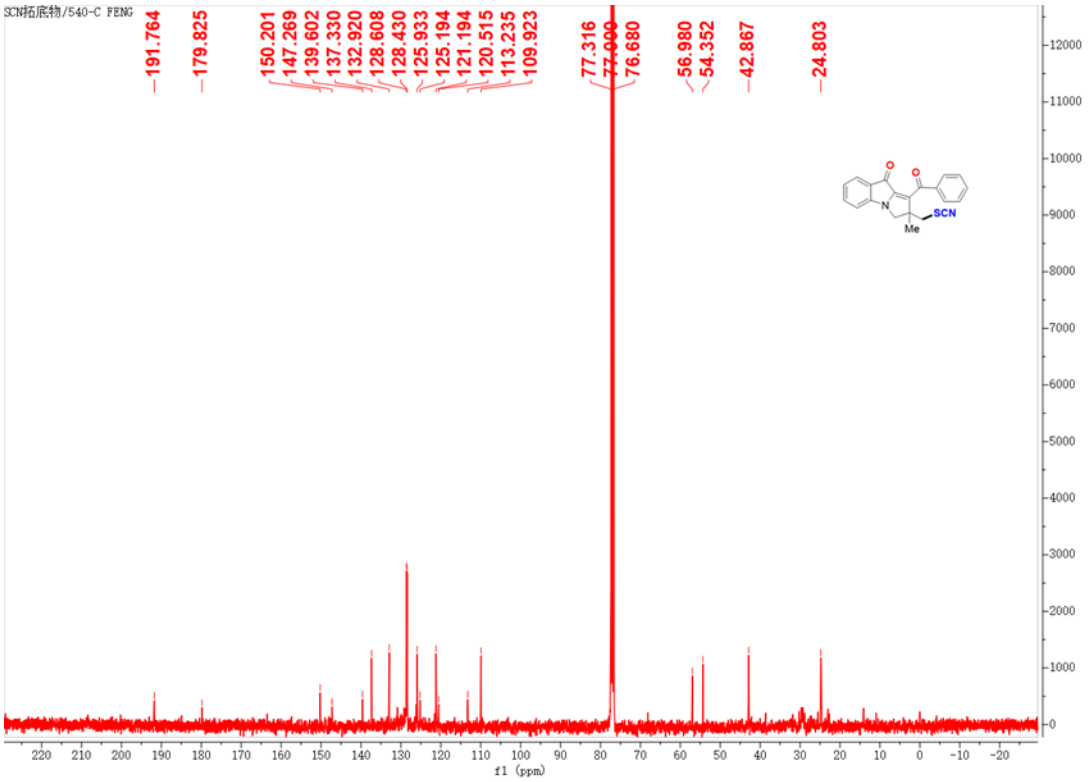
19-$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



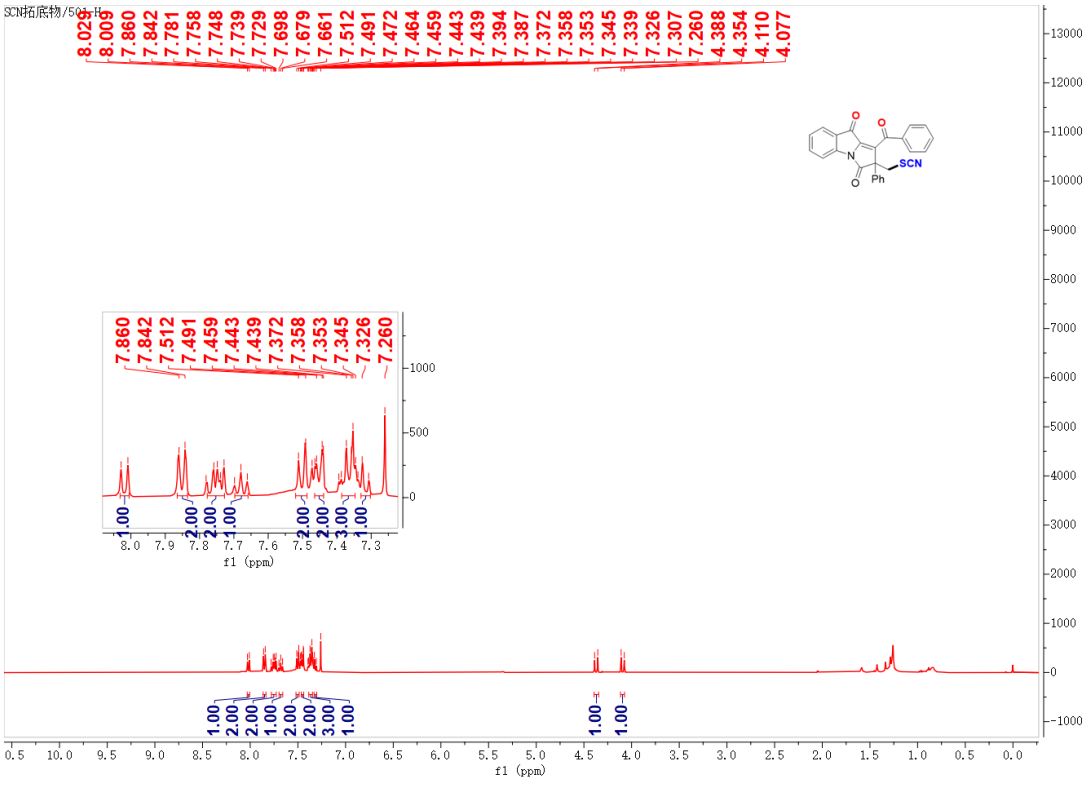
20-^{1}H NMR (400 MHz, $CDCl_3$)



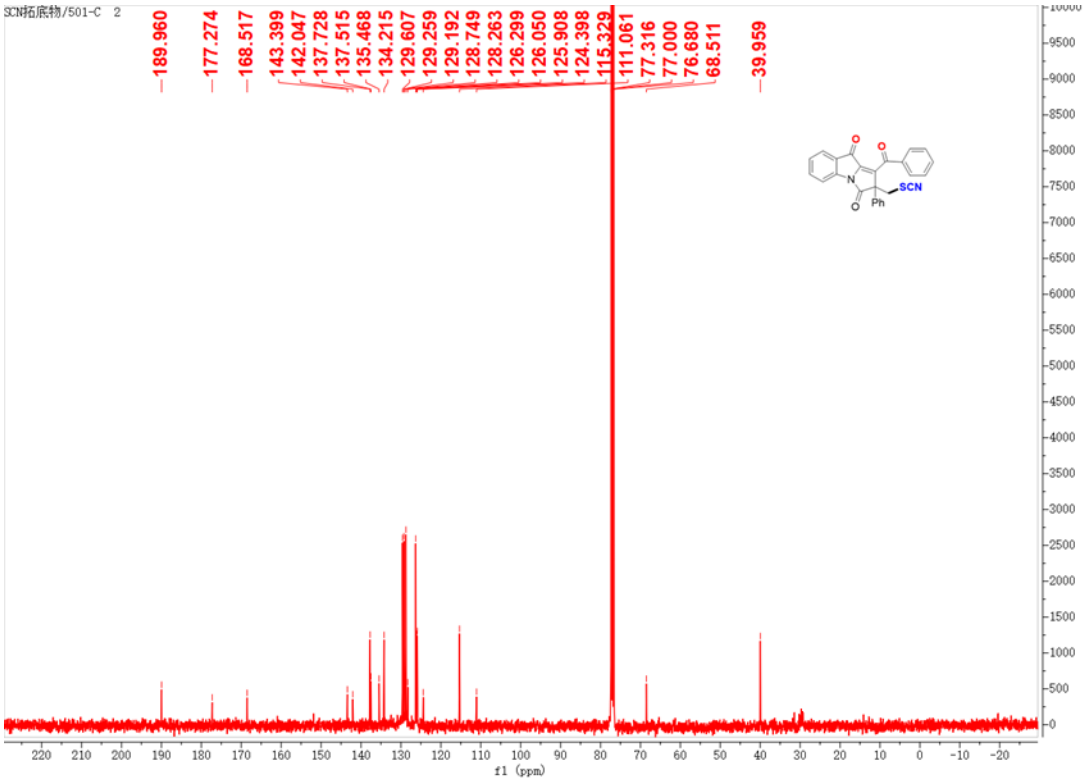
20-$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



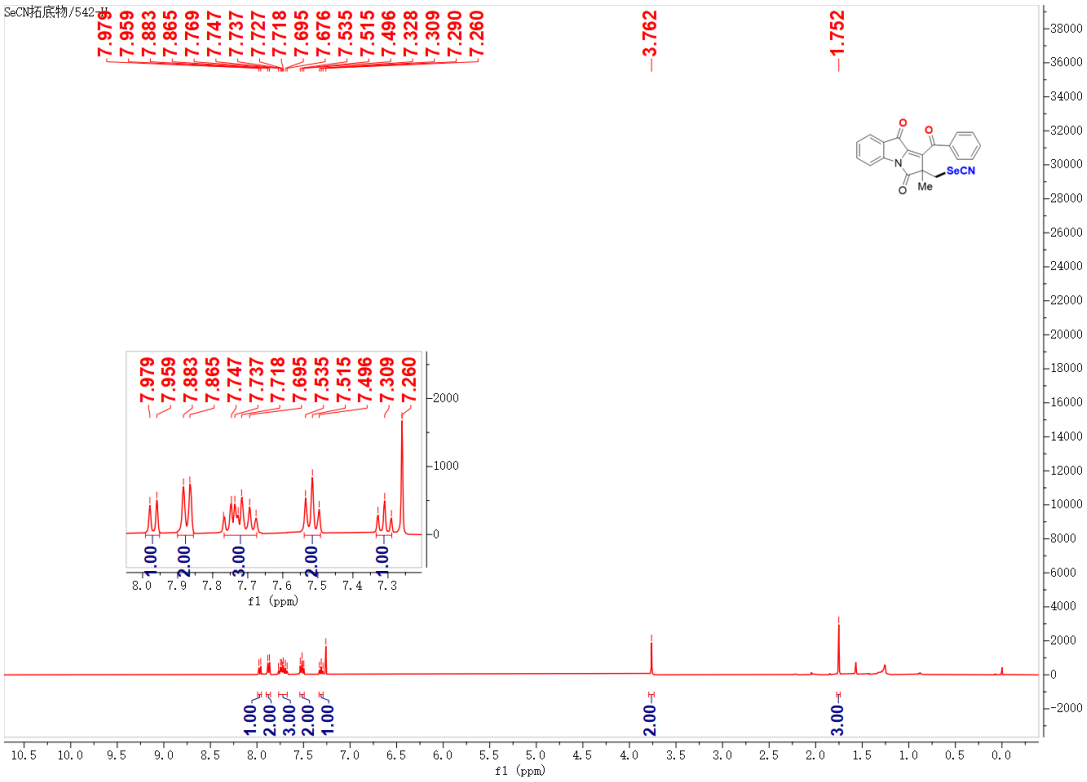
21-^{1}H NMR (400 MHz, $CDCl_3$)



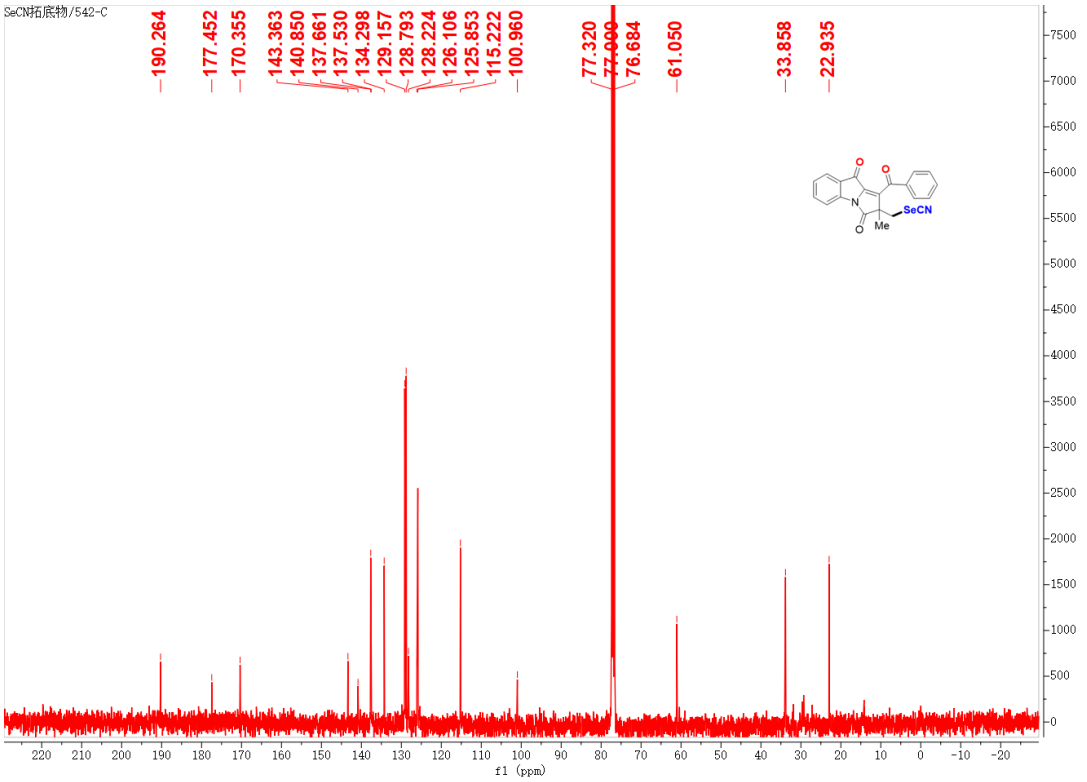
21-$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



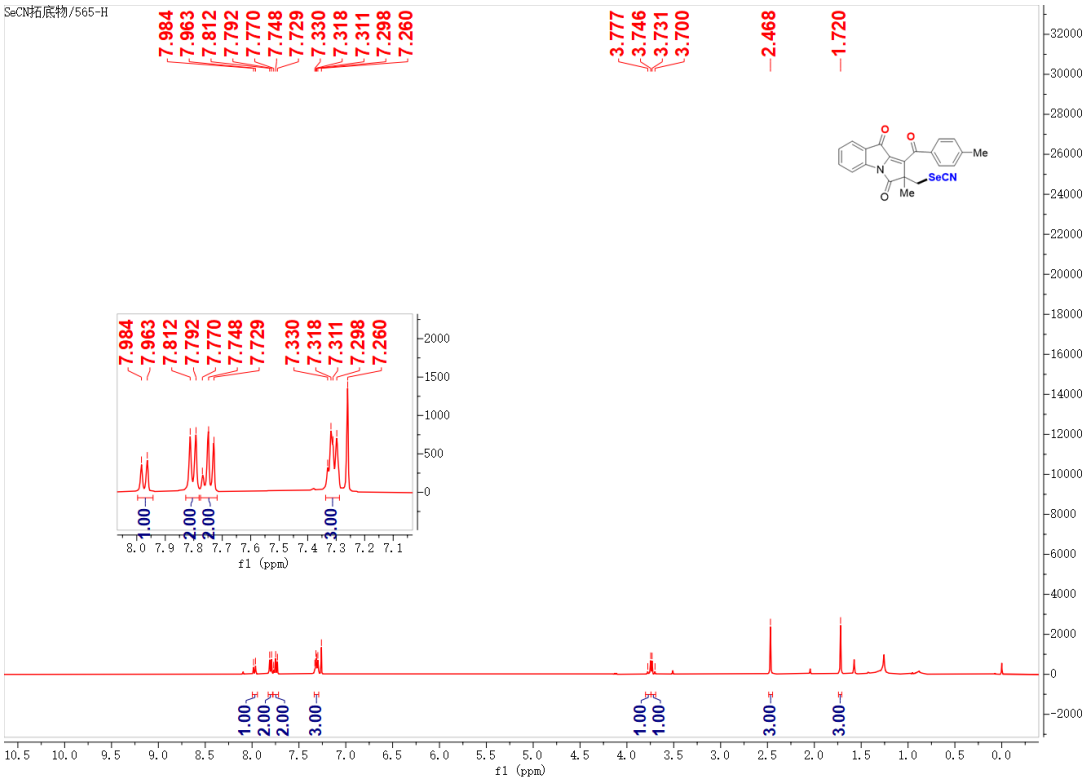
22-^{1}H NMR (400 MHz, $CDCl_3$)



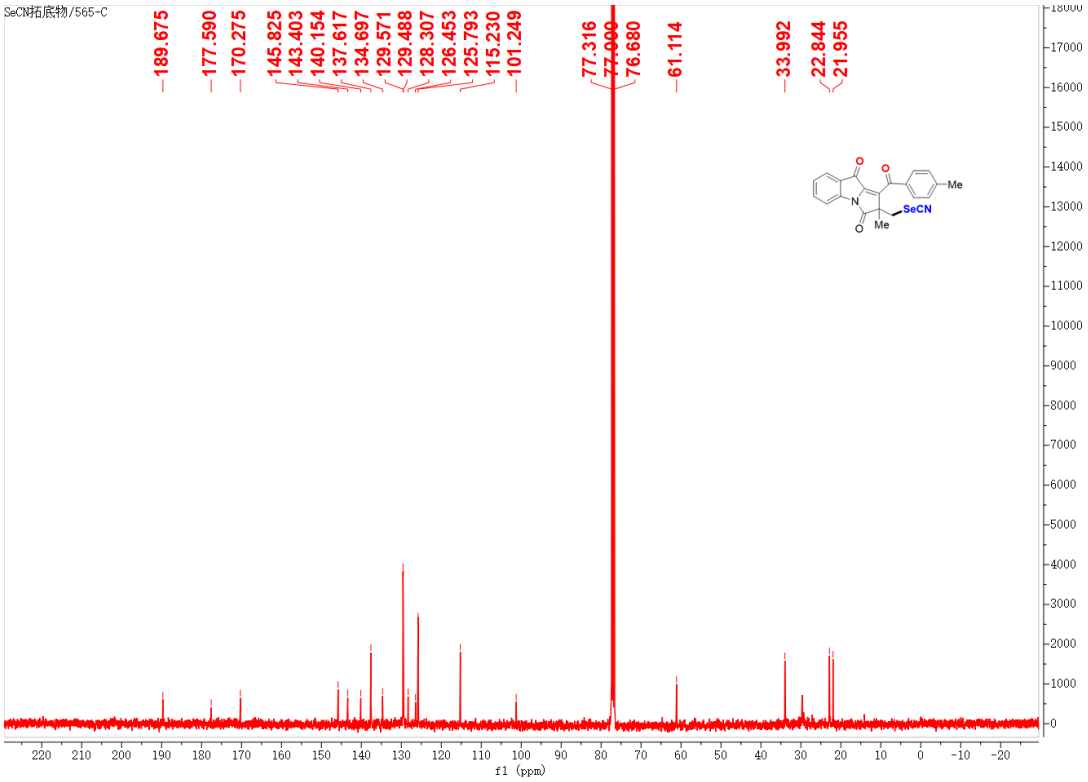
22-$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



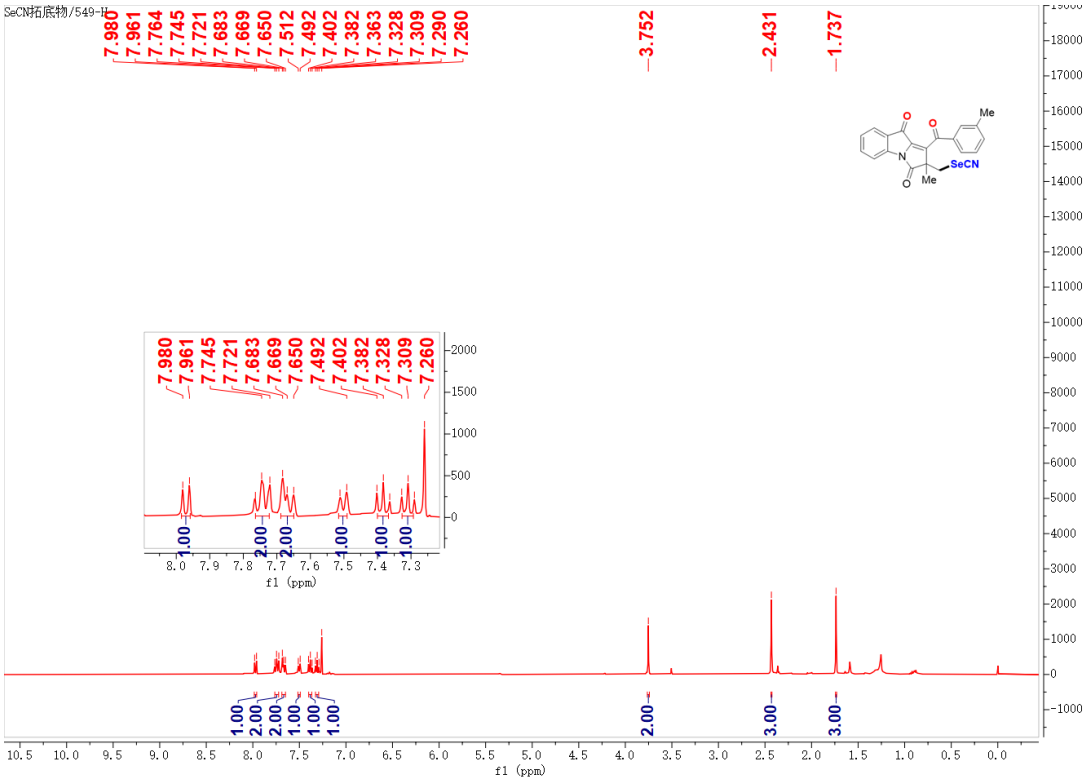
23-^{1}H NMR (400 MHz, $CDCl_3$)



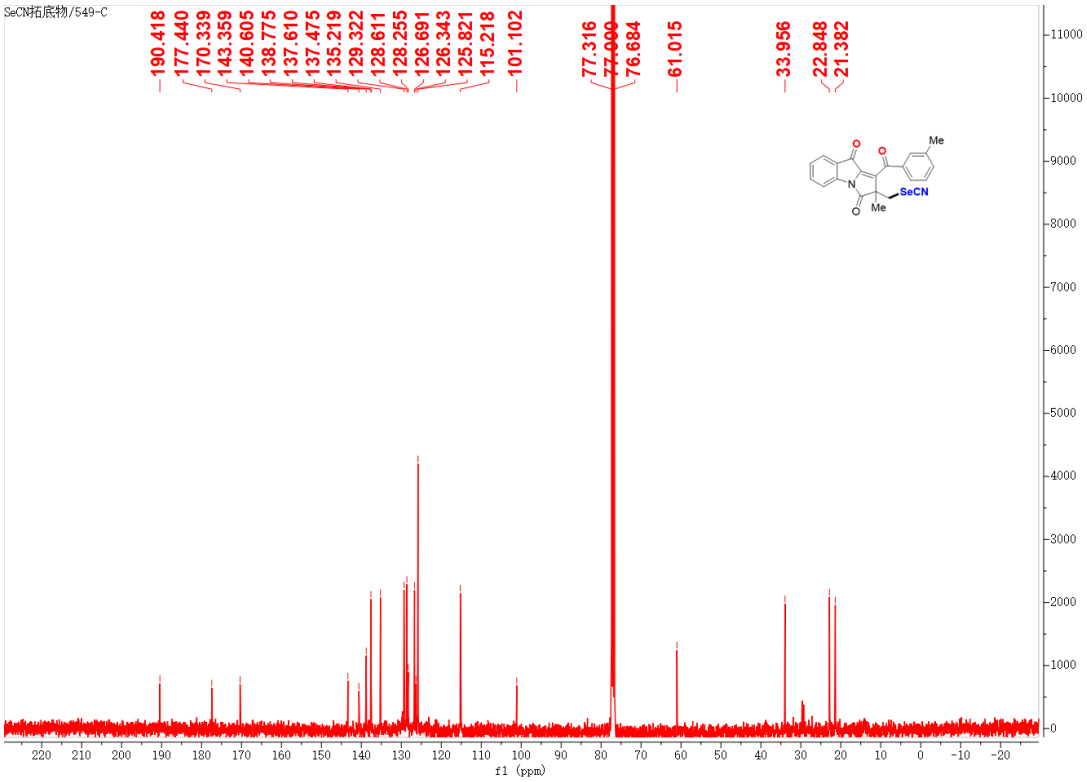
23-$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



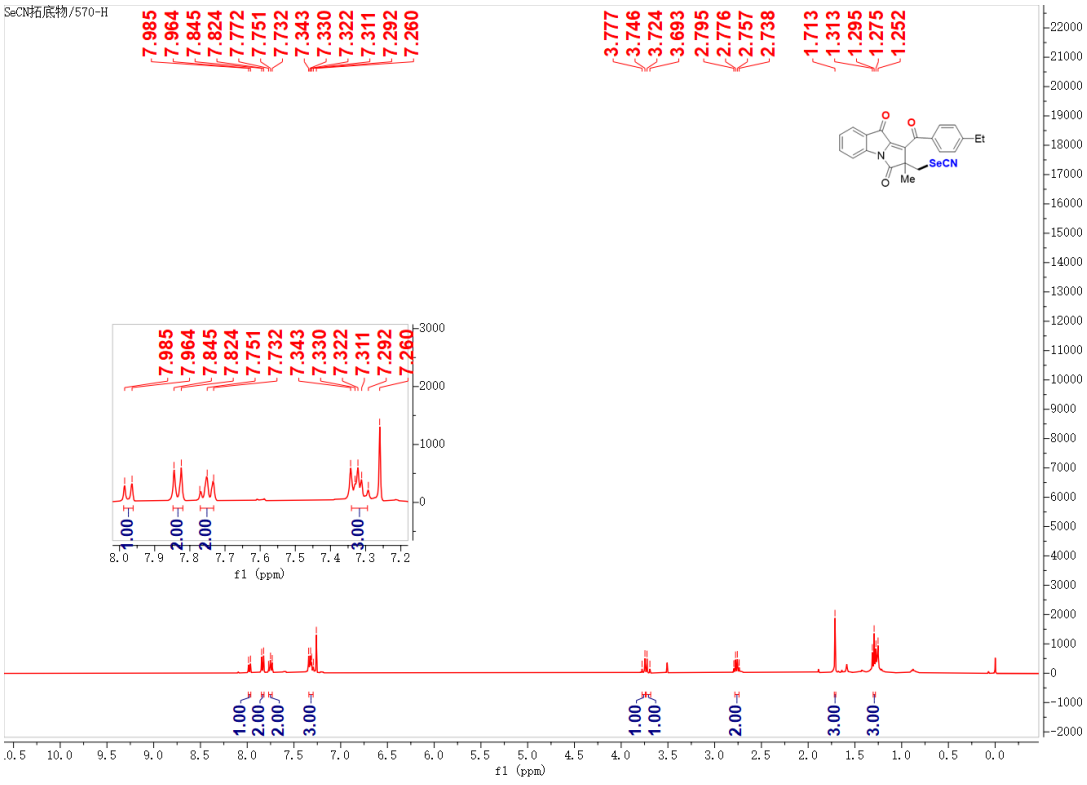
24-^{1}H NMR (400 MHz, $CDCl_3$)



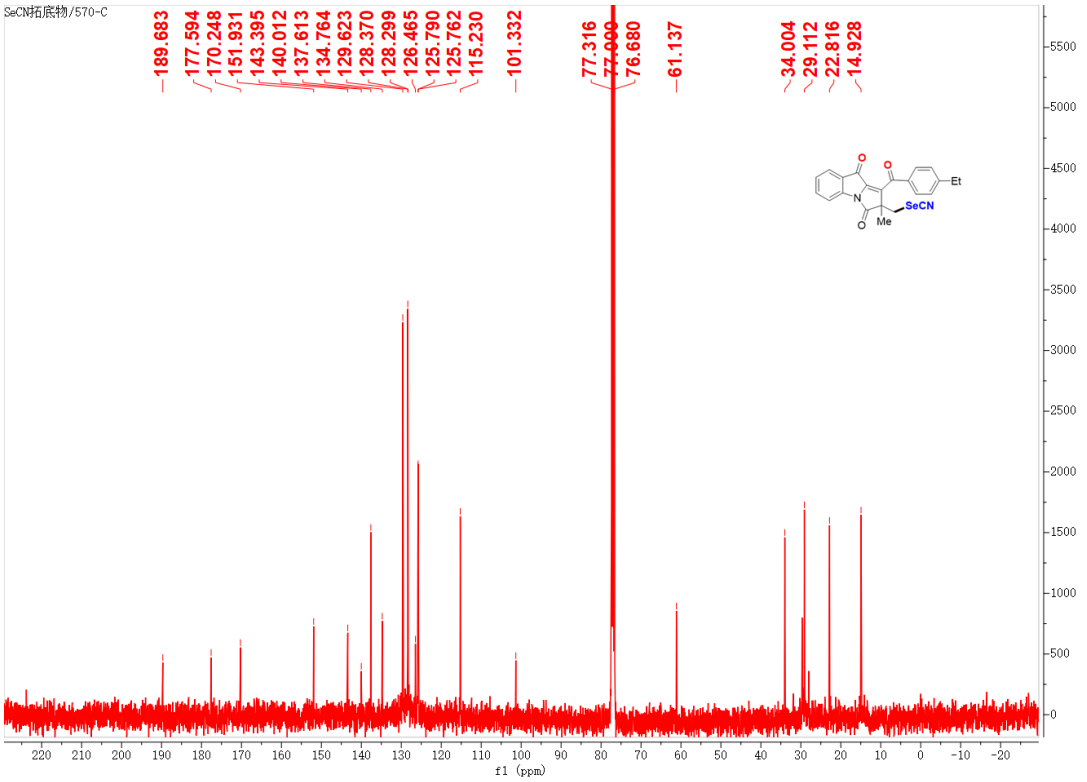
24-$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



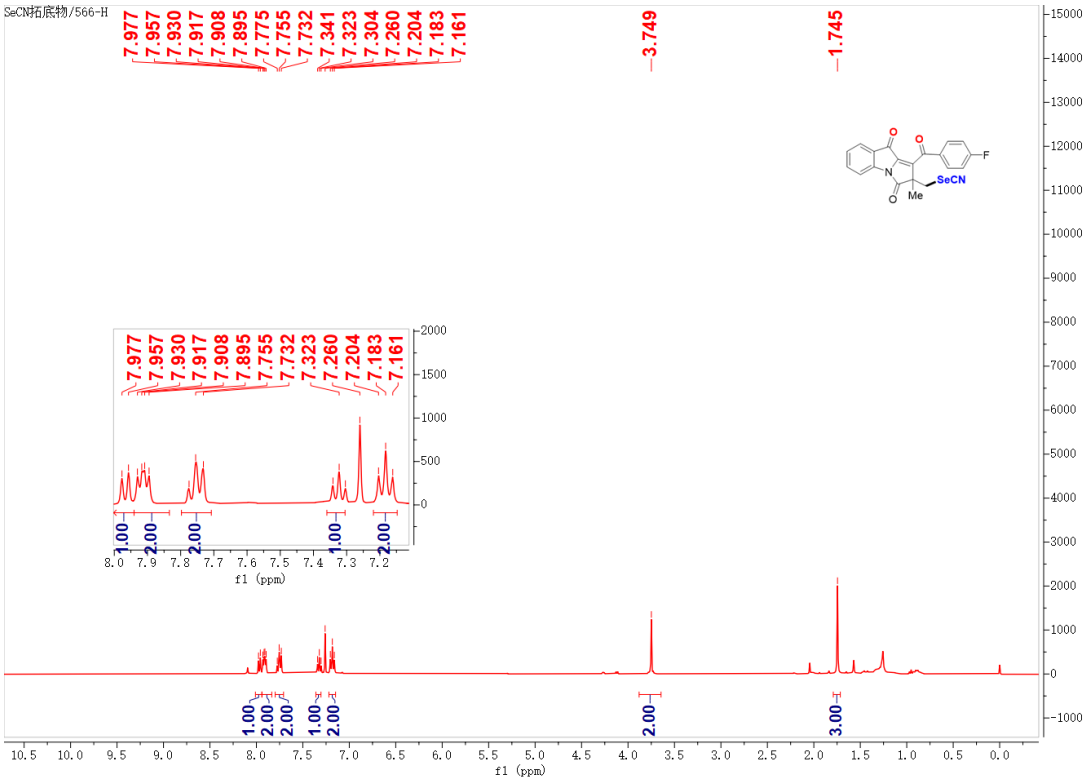
25-^{1}H NMR (400 MHz, $CDCl_3$)



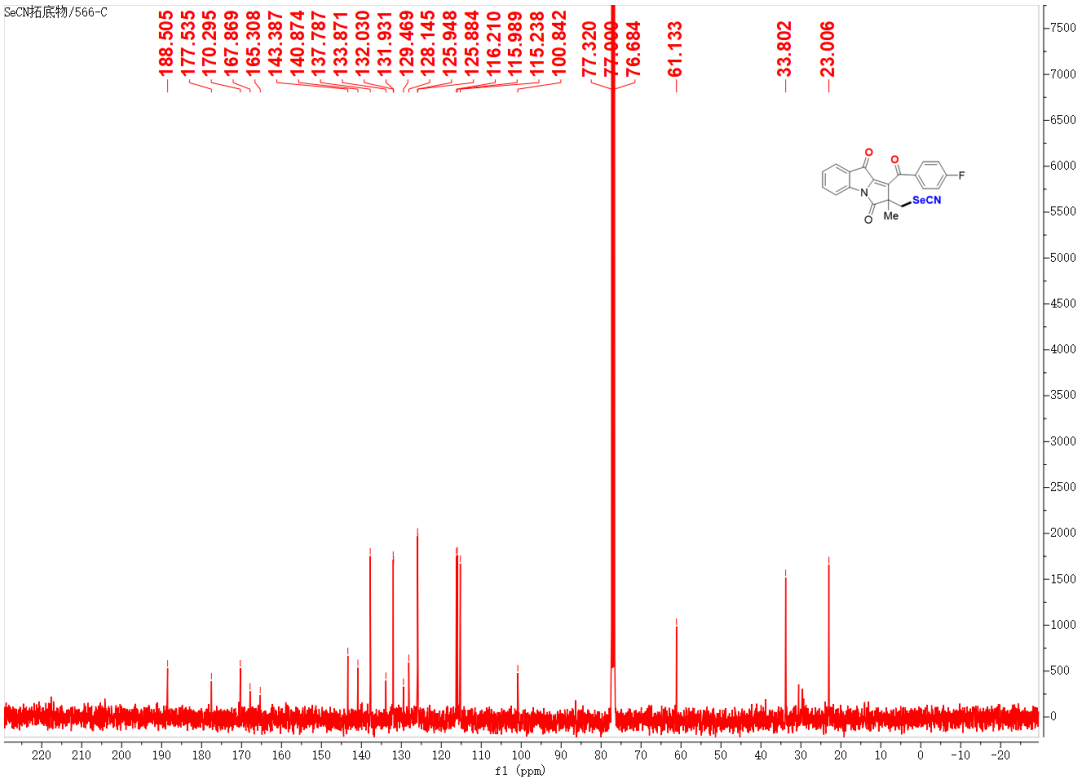
25-$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



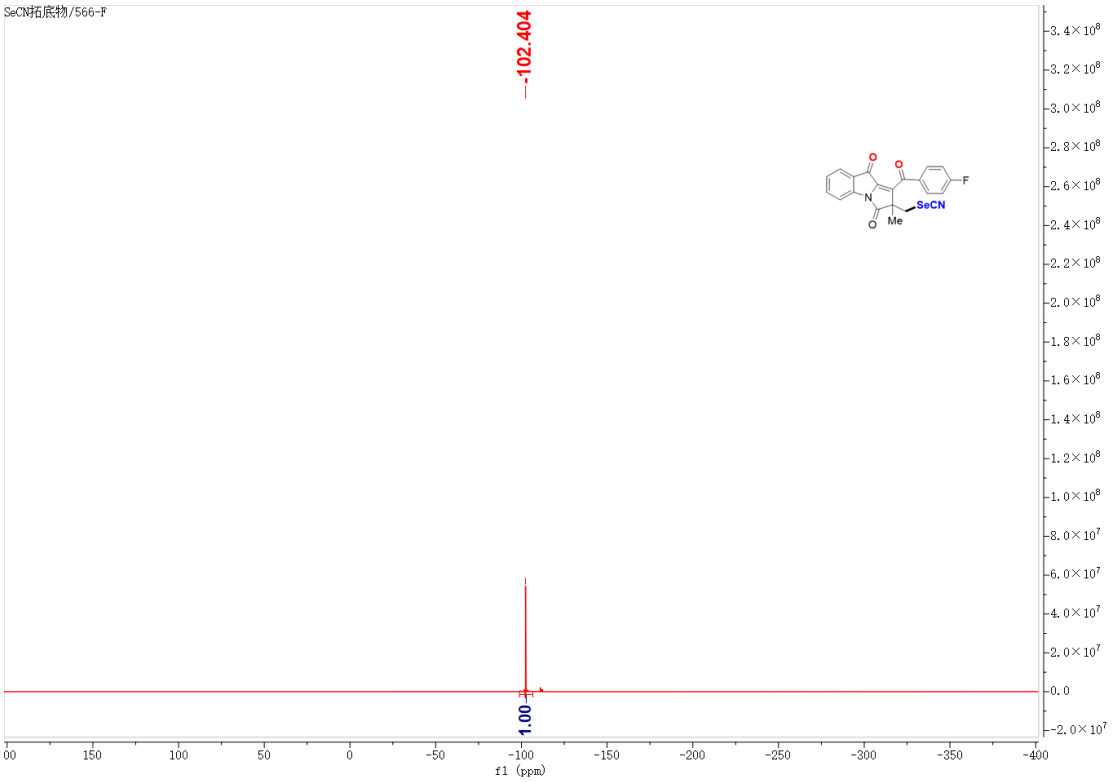
26-^{1}H NMR (400 MHz, $CDCl_3$)



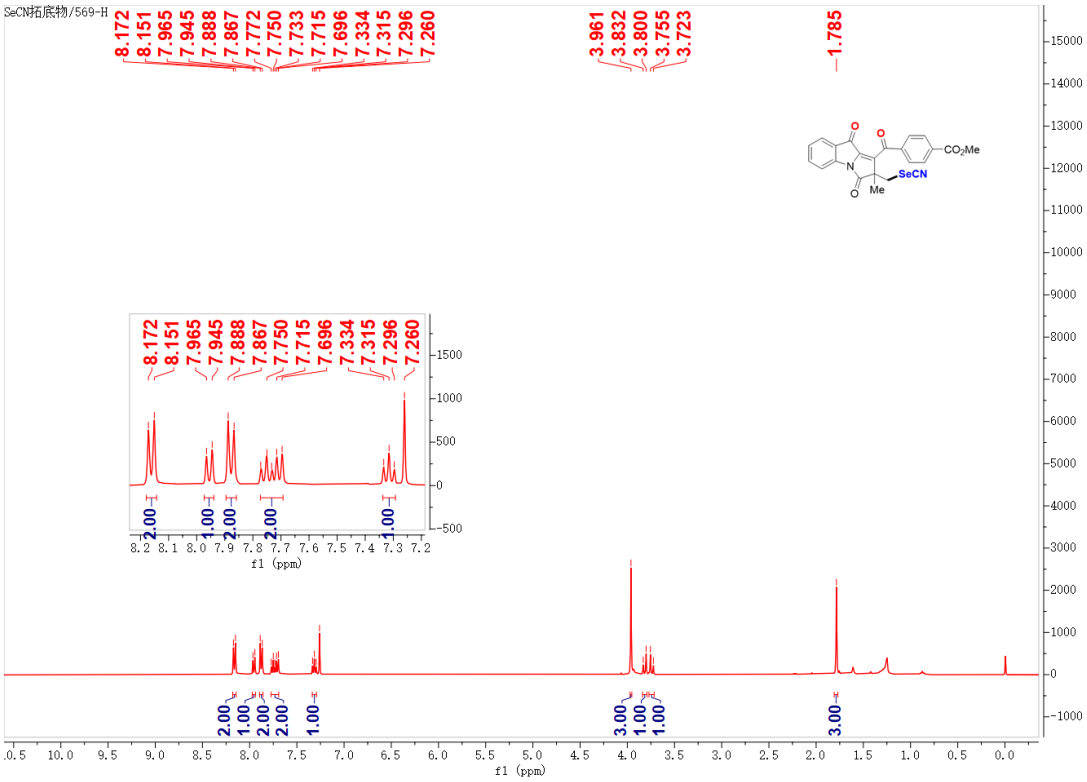
26-$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



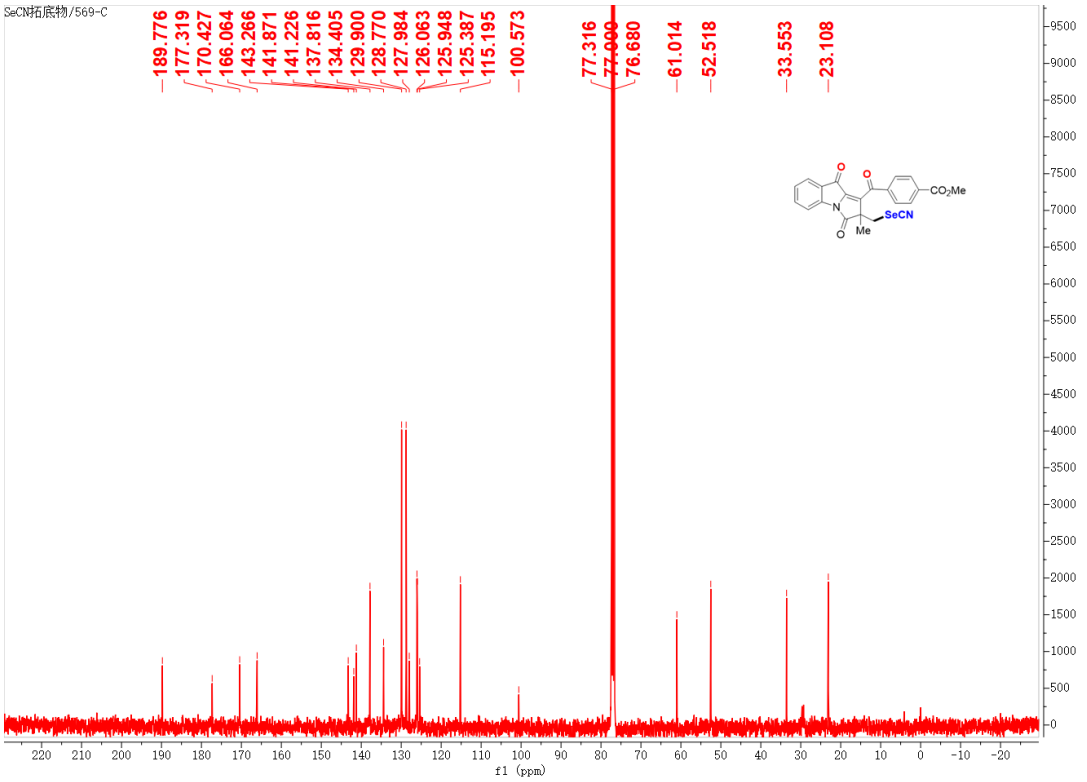
26-^{19}F NMR (565 MHz, $CDCl_3$)



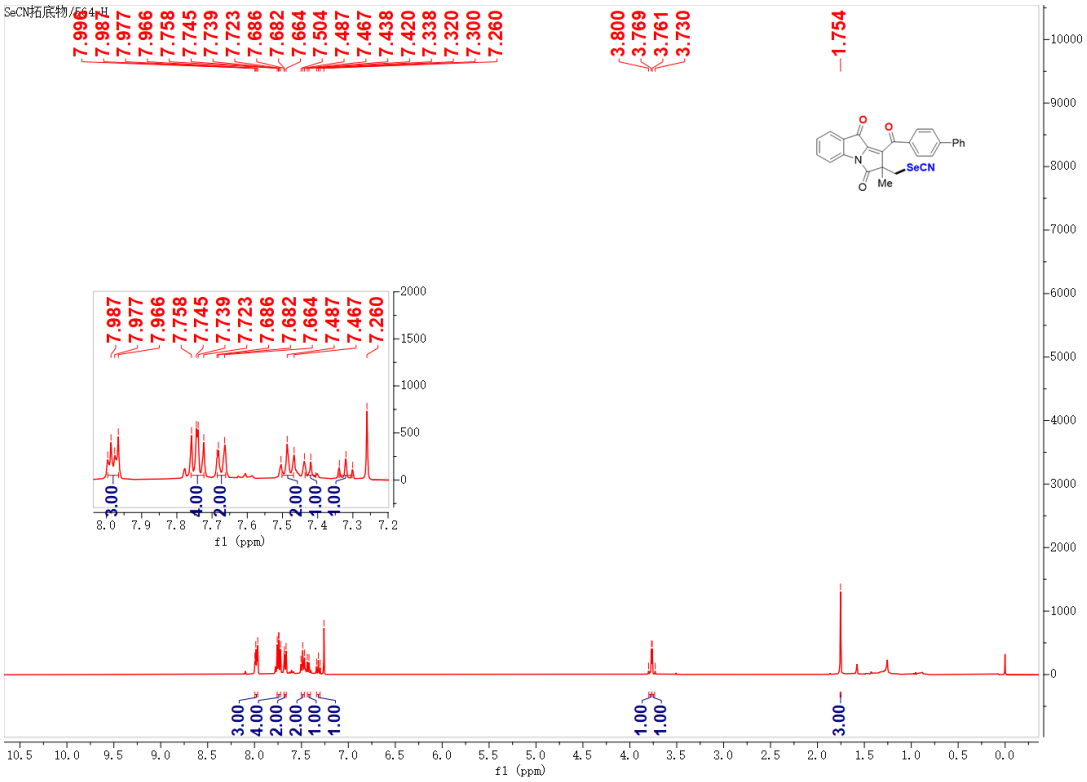
27-^{1}H NMR (400 MHz, $CDCl_3$)



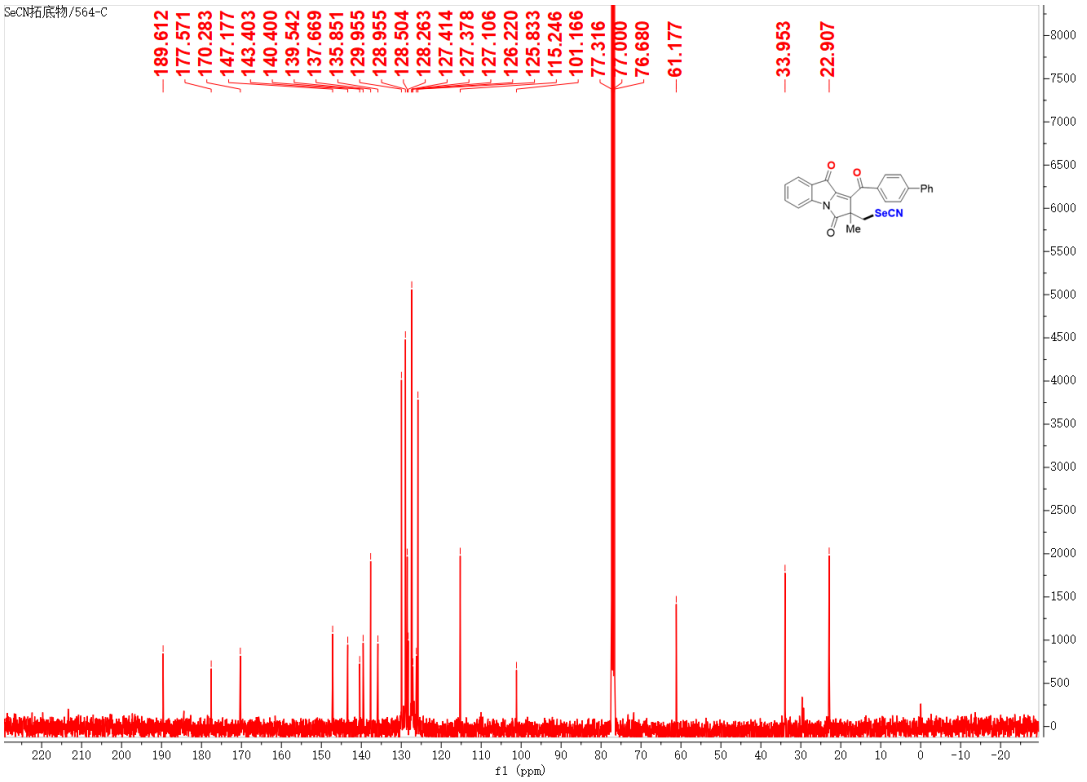
27-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



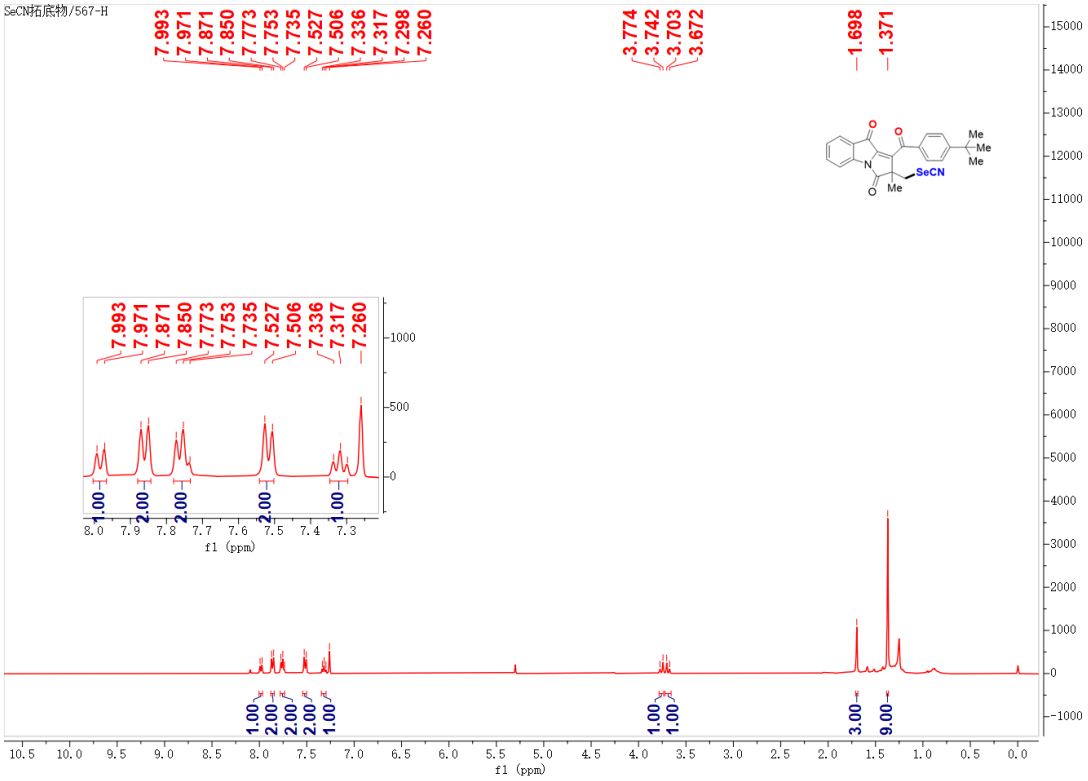
28-^{1}H NMR (400 MHz, $CDCl_3$)



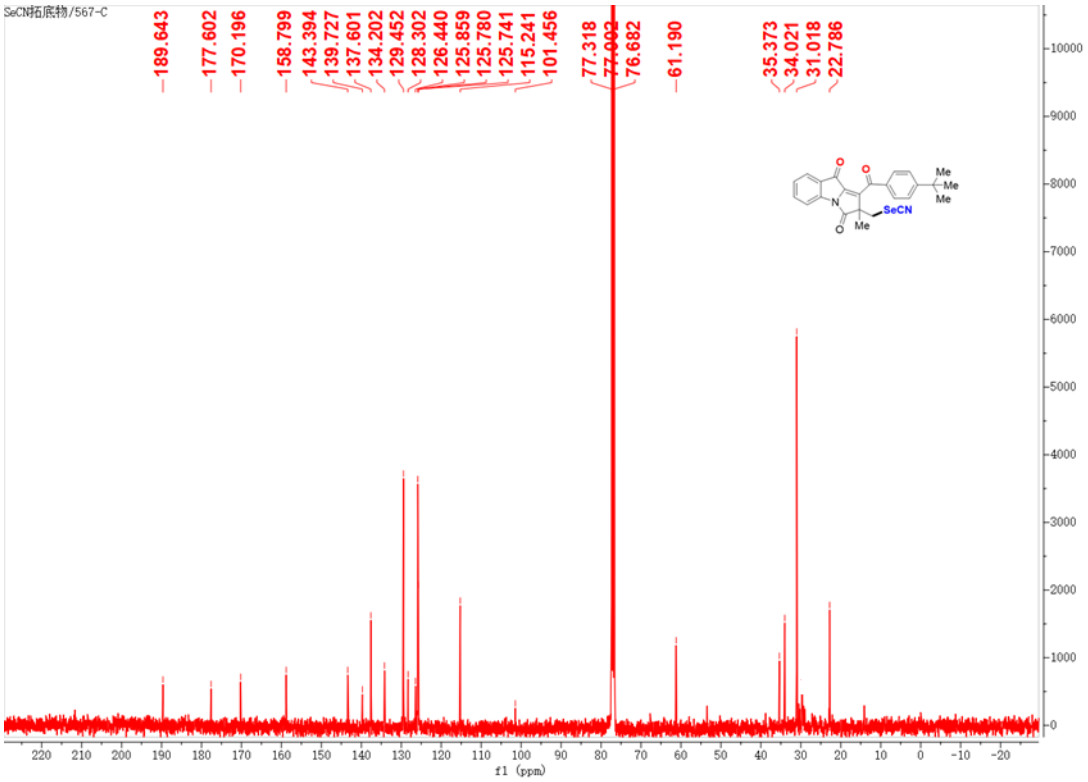
28-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



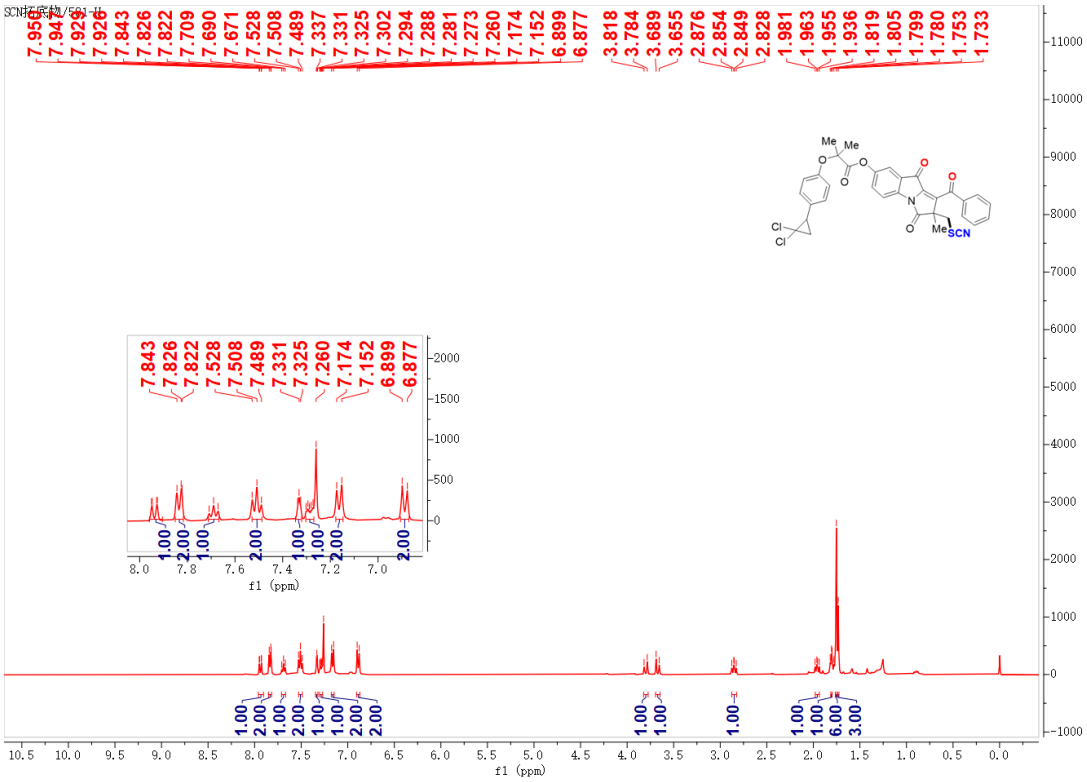
29-^{1}H NMR (400 MHz, $CDCl_3$)



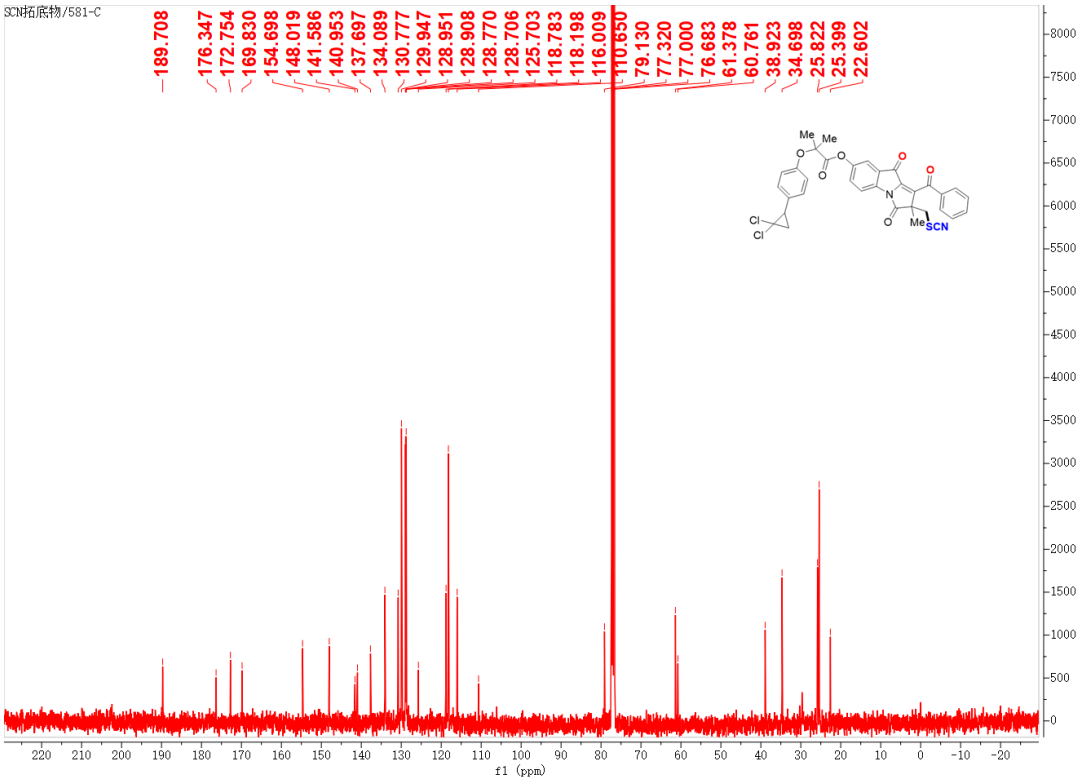
29-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



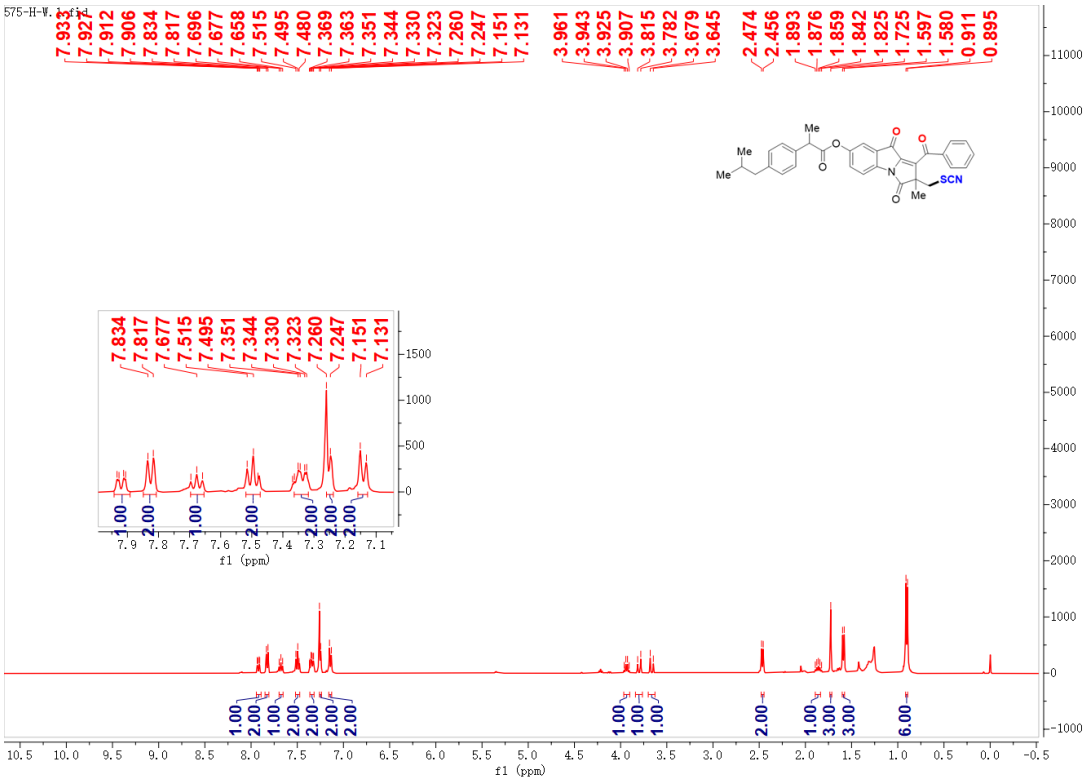
30-^{1}H NMR (400 MHz, $CDCl_3$)\



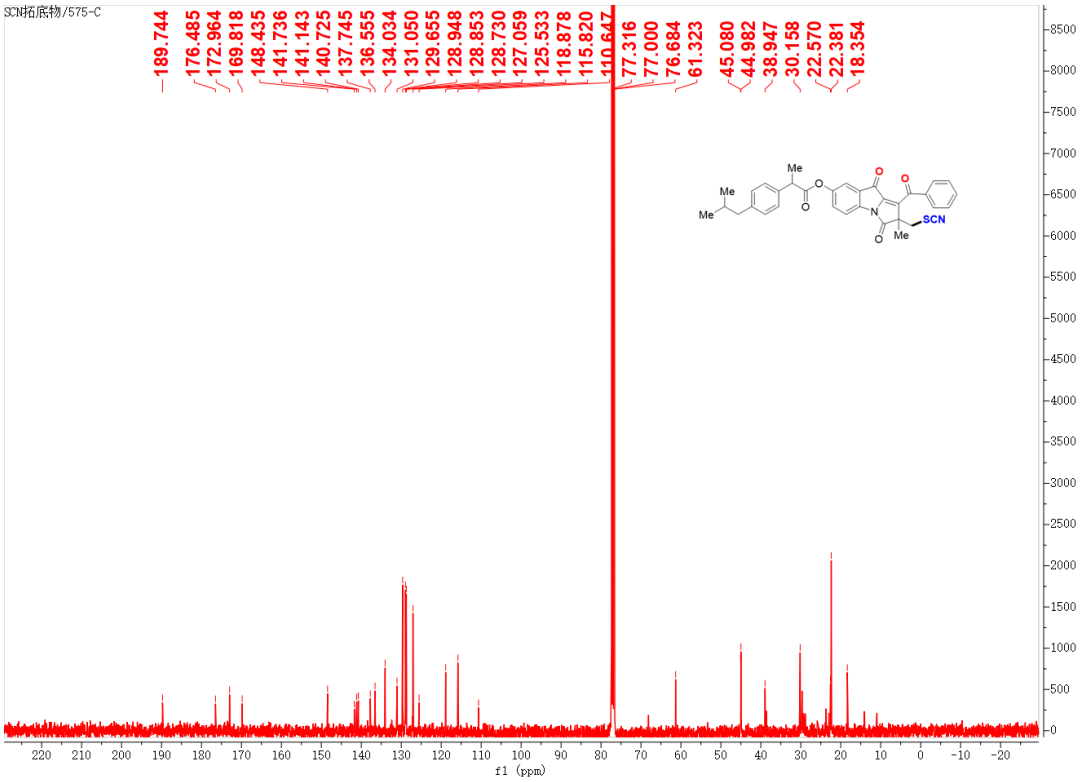
30-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



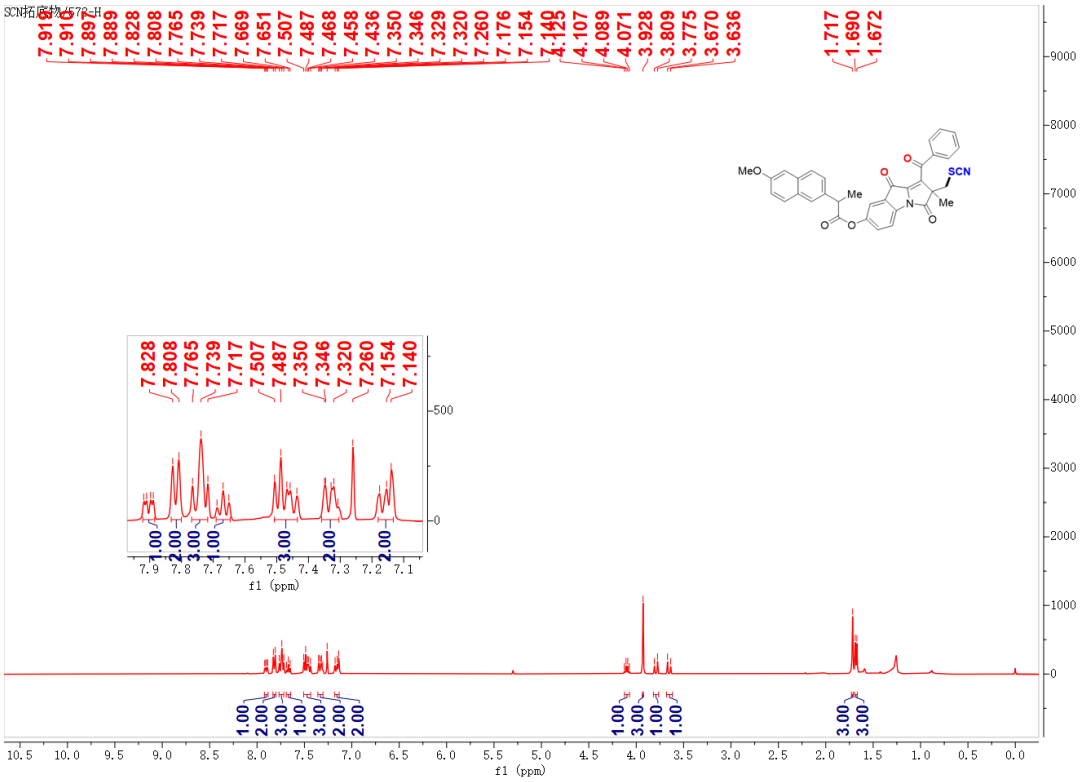
31-^{1}H NMR (400 MHz, $CDCl_3$)



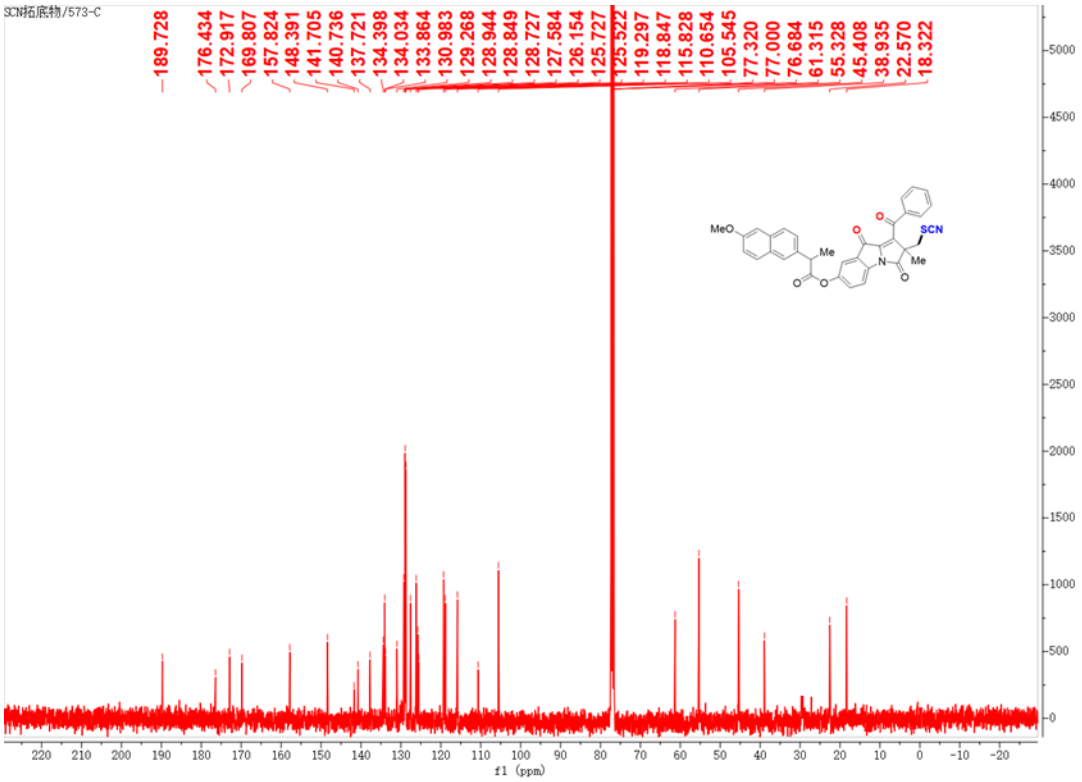
31-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



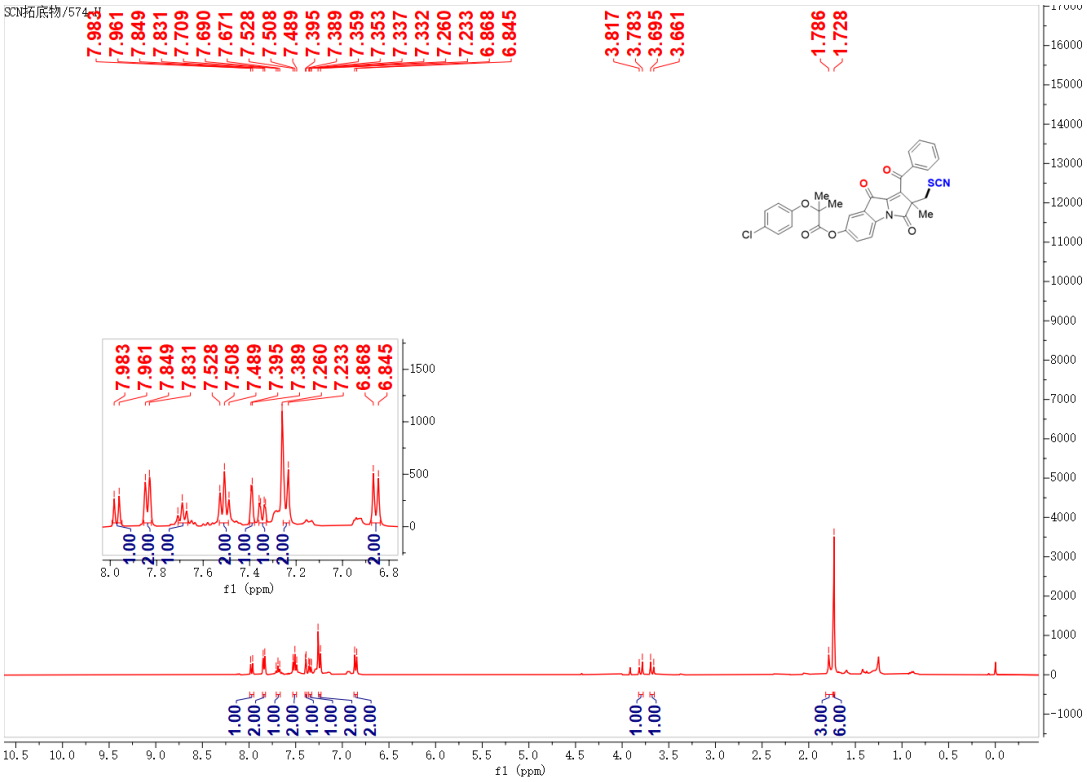
32-^{1}H NMR (400 MHz, $CDCl_3$)



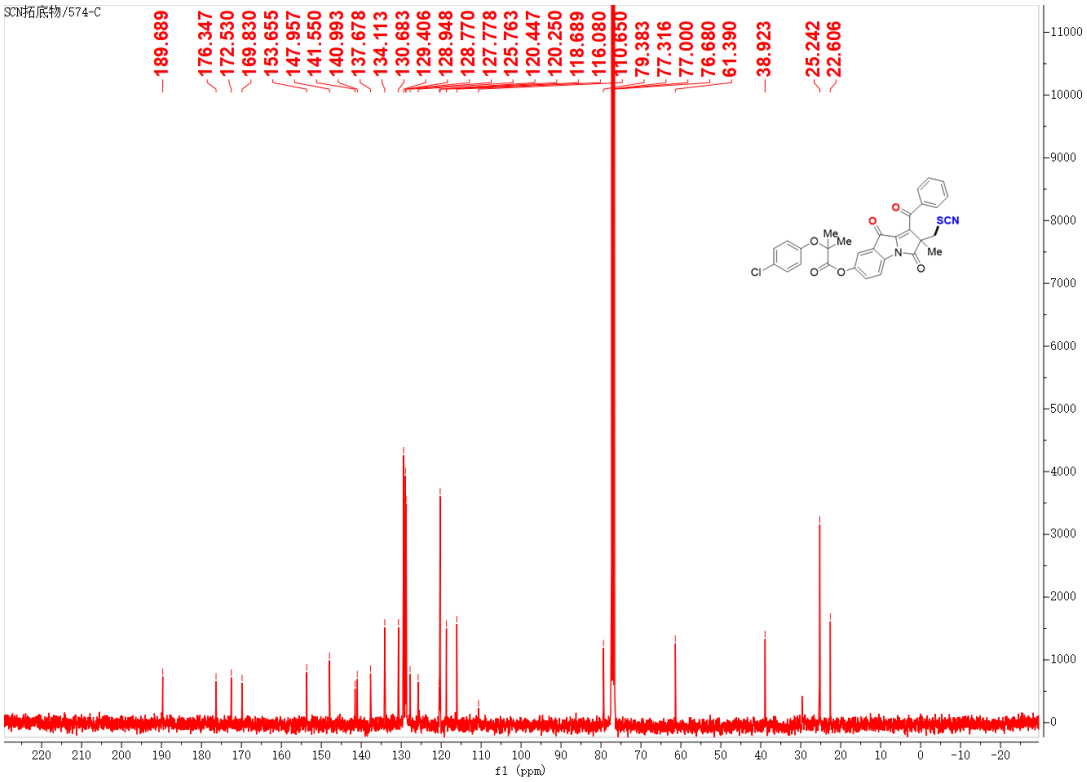
32-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



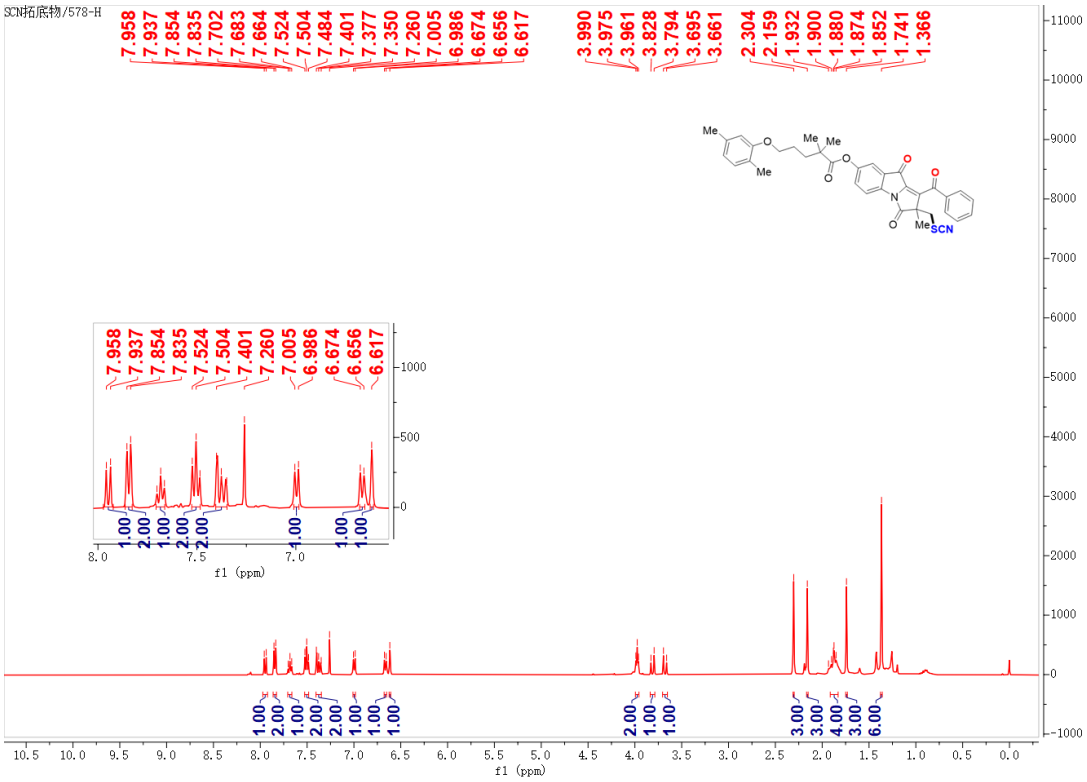
33-^{1}H NMR (400 MHz, $CDCl_3$)



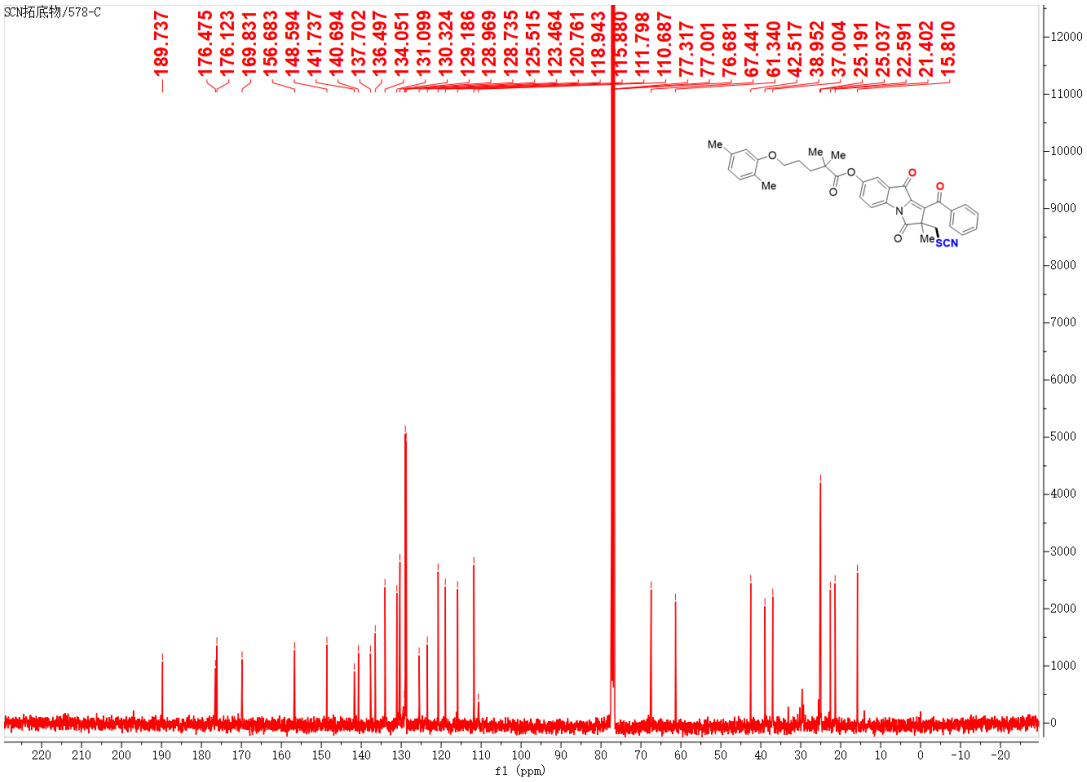
33-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



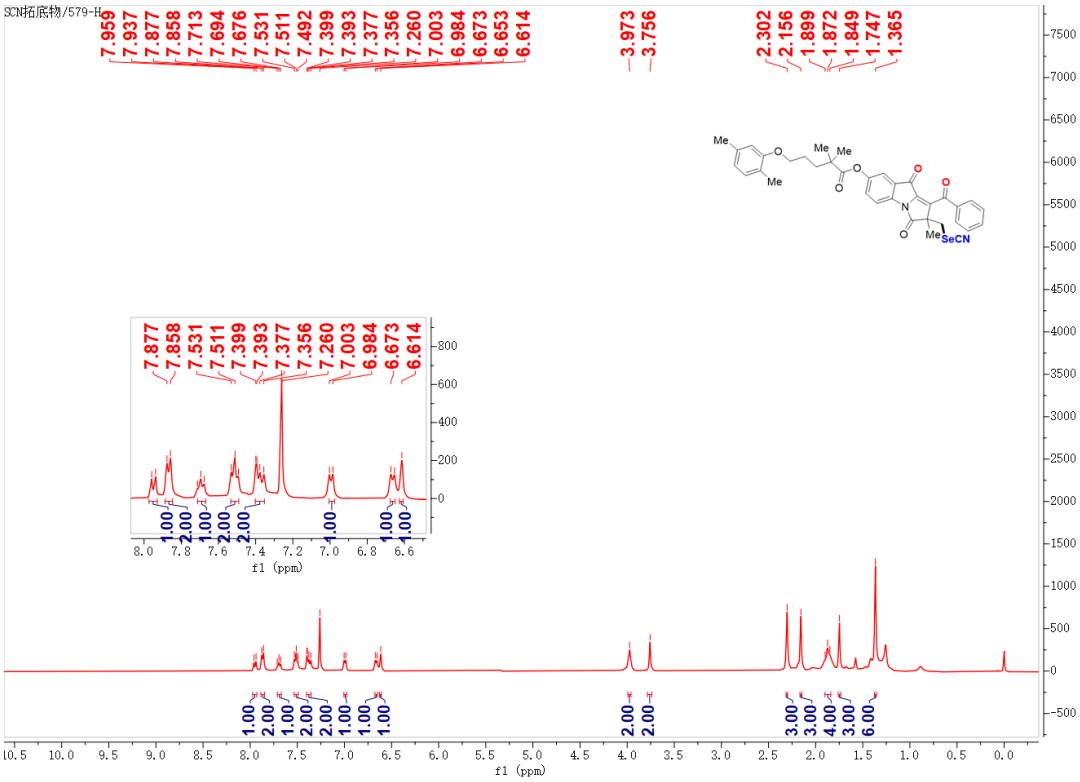
34-^{1}H NMR (400 MHz, $CDCl_3$)



34-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



35-^{1}H NMR (400 MHz, $CDCl_3$)



35-^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)