

Supporting Information

Photo-induced spirocyclization of biaryl ynones with ammonium thiocyanate: access to thiocyanate-featured spiro[5,5]trienones

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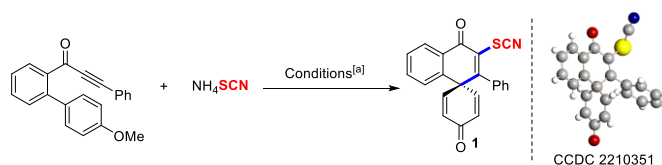
General Information

^1H 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 ^1H and ^{13}C NMR, HRMS. The starting materials were purchased from Energy, Meryer, J&K Chemicals, or Aldrich and used without further purification.

Typical procedure for the reaction

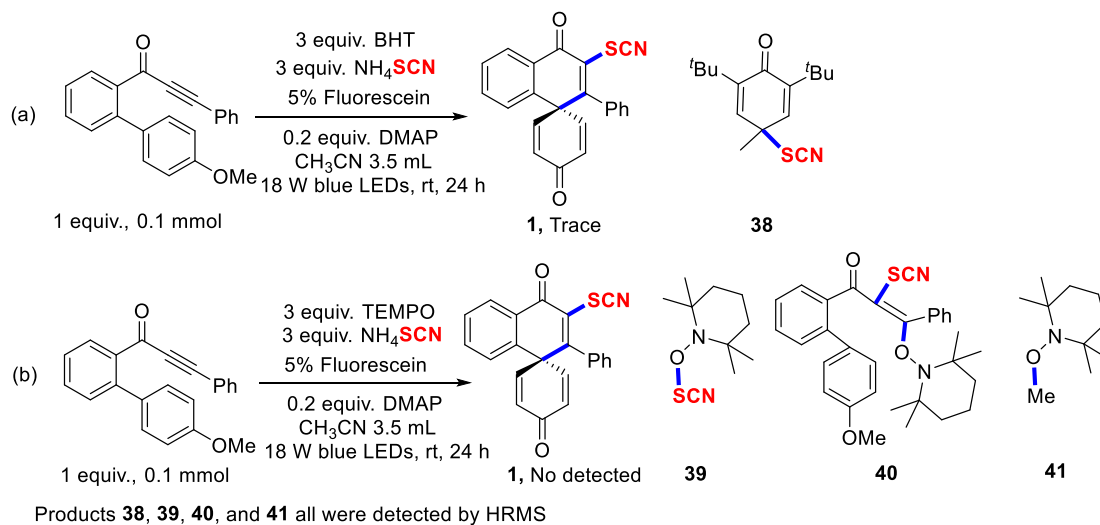
Reaction conditions: A mixture of biaryl ynones (1 equiv., 0.1 mmol), NH_4SCN (3 equiv., 0.3 mmol), fluorescein or rhodamine 6G (0.05 equiv., 0.005 mmol), DMAP (0.2 equiv., 0.02 mmol), CH_3CN (3.5 mL), was added into a 10 mL quartz tube, which was lighted by 18 W blue LEDs, rt. When the reaction system was finished via detected by TLC, the mixture was condensed under vacuum and purified by column chromatography to afford the desired products.

Table S1. Optimization of molar concentrations of product 1



Entry	Photocatalyst (mol %)	Thiocyanate (equiv.)	Base (equiv.)	Solvent (mL)	Yield ^b (%)
1	Fluorescein (5)	NH_4SCN (3)	DMAP (0.2)	CH_3CN (3.5)	74
2	Fluorescein (5)	NH_4SCN (3)	DMAP (0.2)	CH_3CN (2.5)	38
3	Fluorescein (5)	NH_4SCN (3)	DMAP (0.2)	CH_3CN (1.5)	36
4	Fluorescein (5)	NaSCN (3)	DMAP (0.2)	CH_3CN (3.5)	70
5	Fluorescein (5)	NaSCN (3)	DMAP (0.2)	CH_3CN (2.5)	50
6	Fluorescein (5)	NaSCN (3)	DMAP (0.2)	CH_3CN (1.5)	36
7	Fluorescein (5)	NH_4SCN (3)	DMAP (0.2)	DCE (3.5)	72
8	Fluorescein (5)	NH_4SCN (3)	DMAP (0.2)	DCE (2.5)	48
9	Fluorescein (5)	NH_4SCN (3)	DMAP (0.2)	DCE (1.5)	40

Mechanistic study

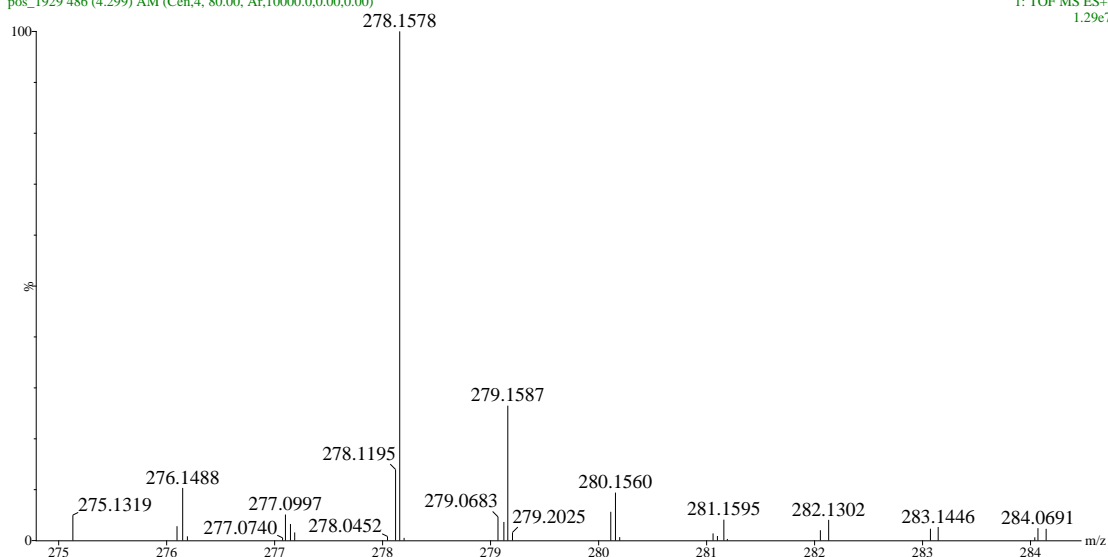


Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
38	C ₁₆ H ₂₃ NOS	C ₁₆ H ₂₄ NOS	278.1578	278.1579	-0.35

1929

pos_1929_486 (4.299) AM (Cen.4, 80.00, Ar.10000.0,0.00,0.00)

I: TOF MS ES+
1.29e7

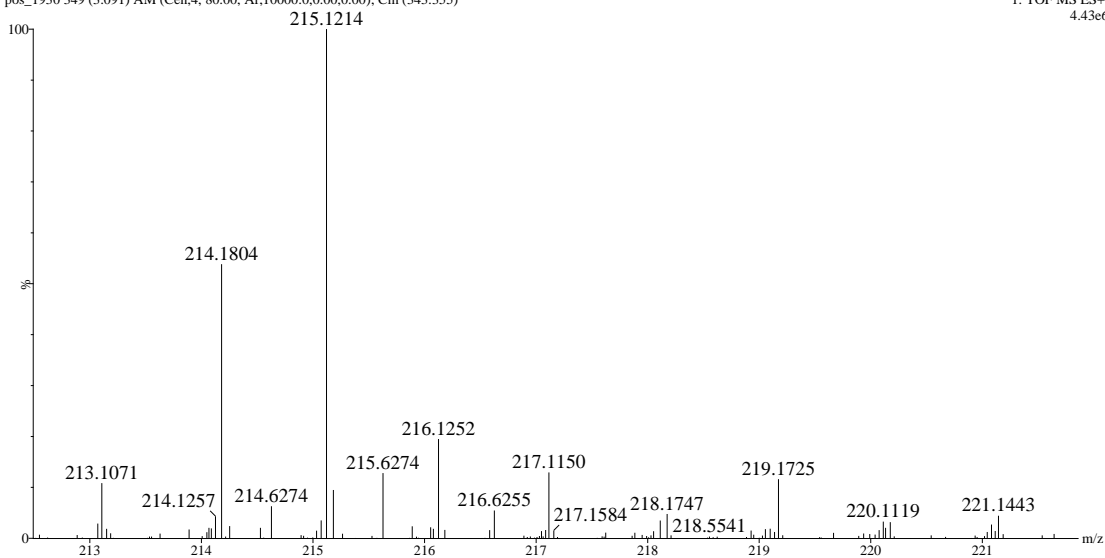


Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
39	C ₁₀ H ₁₈ N ₂ O ₃ S	C ₁₀ H ₁₉ N ₂ O ₃ S	215.1214	215.1218	-1.85

1930

pos_1930 349 (3.091) AM (Cen,4, 80.00, Ar,10000.0,0.00,0.00); Cm (343:355)

I: TOF MS ES+
4.43e6

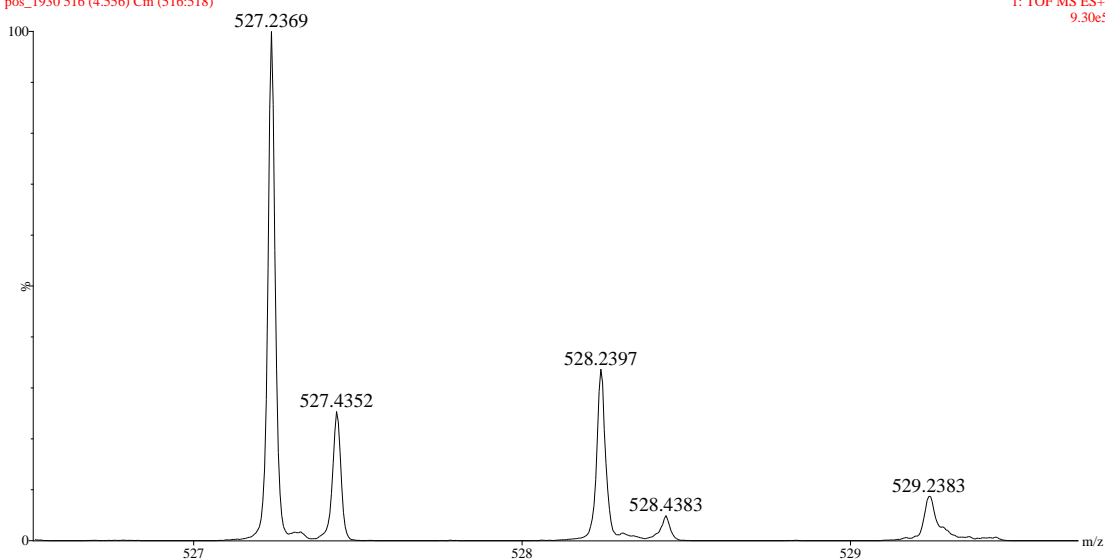


Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
40	C ₃₂ H ₃₄ N ₂ O ₃ S	C ₃₂ H ₃₅ N ₂ O ₃ S	527.2369	527.2368	0.18

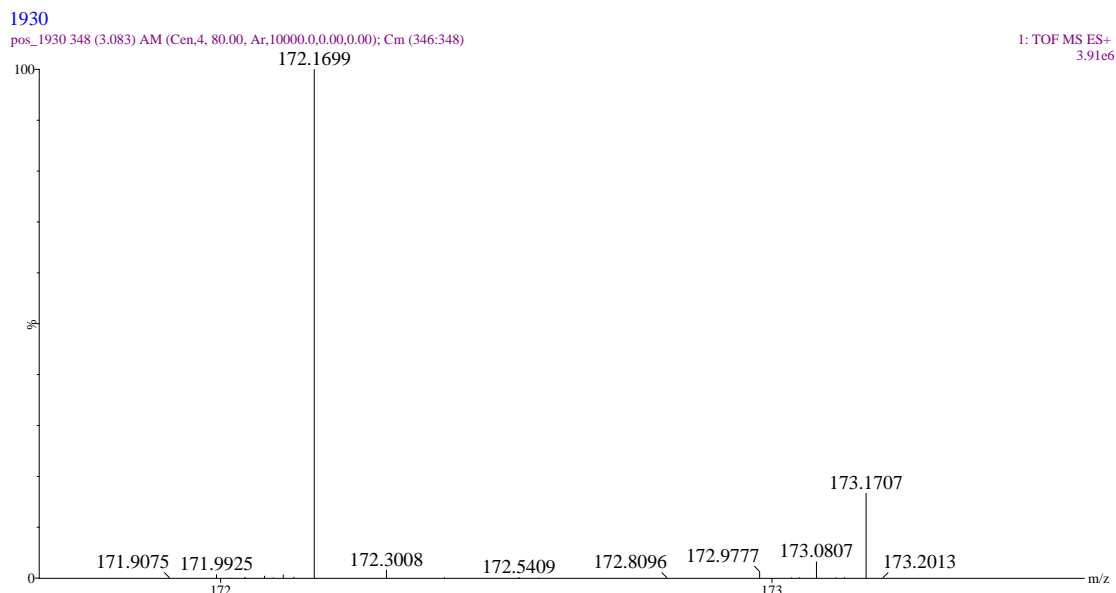
1930

pos_1930 516 (4.556) Cm (516:518)

I: TOF MS ES+
9.30e5



Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
41	C ₁₀ H ₂₁ NO	C ₁₀ H ₂₂ NO	172.1699	172.1701	-1.16



Crystallographic details

(1) Product **1** was added to a 5 mL sample bottle, which was solved with 1 mL of dichloromethane (DCM). Then the above mixture was added with 2 mL of petroleum ether (PE). Next, we sealed the sample bottle and placed it in a dark cabinet. Finally, the crystal was precipitated via volatilizing.

(2) Single crystal of Product **1** [C₂₂H₁₃NO₂S] was offered as follows: A proper crystal was used and detected on a “Bruker D8 VENTURE” diffractometer. The crystal stayed at 273.0 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 are described as shown in **Table S2**.
CCDC No. 2210351.

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

Table S2. Crystal data and structure refinement for product **1**.

CCDC	2210351
Displacement ellipsoids are drawn at the 30% probability level	
Empirical formula	C ₂₂ H ₁₃ N O ₂ S
Formula weight	355.39
Temperature	273 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pna2 ₁
Unit cell dimensions	a = 11.7823(9) Å α = 90 Å b = 17.2564(12) Å β = 90 Å c = 8.5563(5) Å γ = 90 Å
Volume	1739.7(2) Å ³
Z	4
Density (calculated)	1.357 Mg/m ³
Absorption coefficient	0.202 mm ⁻¹
F(000)	736
Crystal size	0.450 x 0.250 x 0.220 mm ³
Theta range for data collection	2.093 to 26.782/°
Index ranges	-14<=h<=14, -21<=k<=21, -10<=l<=9
Reflections collected	19380
Independent reflections	3566 [R(int) = 0.0393]
Completeness to theta = 25.242°	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3566 / 1 / 235
Goodness-of-fit on F ²	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0339, wR2 = 0.0732
R indices (all data)	R1 = 0.0415, wR2 = 0.0788
Absolute structure parameter	0.10(3)
Largest diff. peak and hole	0.175 and -0.189 e.Å ⁻³

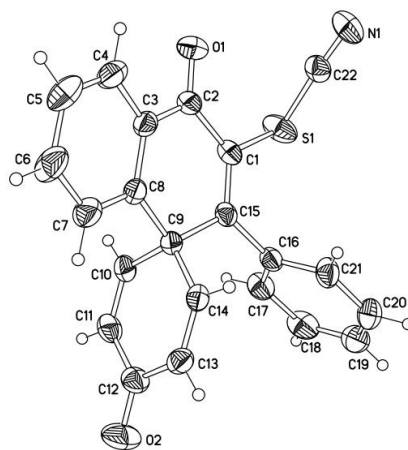


Fig. S1 Structure of product **1**.

Physical data and references for the following products

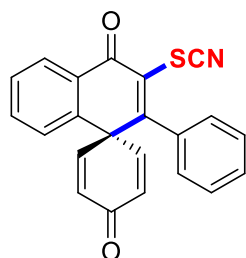
References:

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. P. Yuan, Q. Zhang, X. Jin, W. Lei, L.-Z. Wu and Q. Liu, *Green Chem.*, 2018, **20**, 5464.
3. C. Xu, Z. He, X. Kang, Q.-L. Zeng, *Green Chem.*, 2021, **23**, 7544.
4. P. Natarajan, Priya and D. Chuskit, *Green Chem.*, 2021, **23**, 4873.

Physical data for the following products:

1. 2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 26.30 mg, 74% yield. Mp: 166-167 °C.



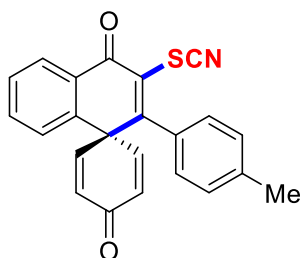
¹H NMR (400 MHz, CDCl₃): δ 8.33 (d, *J* = 7.6 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 6.4 Hz, 2H), 6.74 (d, *J* = 10.0 Hz, 2H), 6.37 (d, *J* = 10.0 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 184.0, 177.3, 160.4, 146.6, 137.6, 135.0, 134.3, 130.9, 130.0, 129.8, 129.6, 129.3, 128.7, 128.5, 128.3, 127.1, 108.6, 52.5.

HRMS (ESI, m/z): Calculated for C₂₂H₁₄NO₂S (M+H)⁺ 356.0740, Measured 356.0747.

2. 3'-thiocyanato-2'-(p-tolyl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 22.16 mg, 60% yield. Mp: 205-206 °C.



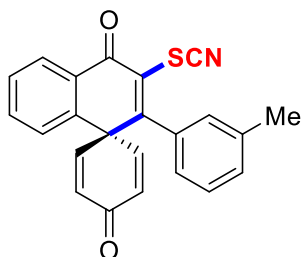
¹H NMR (400 MHz, CDCl₃): δ 8.34 (d, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 10.0 Hz, 2H), 6.37 (d, *J* = 10.0 Hz, 2H), 2.37 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 184.2, 177.3, 160.7, 146.7, 140.2, 137.6, 134.2, 132.2, 130.8, 129.7, 129.5, 129.4, 129.2, 128.6, 128.3, 127.0, 108.8, 52.6, 21.3.

HRMS (ESI, m/z): Calculated for C₂₃H₁₆NO₂S (M+H)⁺ 370.0896, Measured 370.0903.

3. 3'-thiocyanato-2'-(m-tolyl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 24.01 mg, 65% yield. Mp: 185-186 °C.



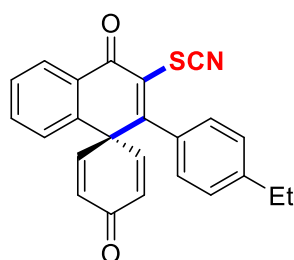
¹H NMR (400 MHz, CDCl₃): δ 8.35 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.31 – 7.29 (m, 1H), 7.28 (d, *J* = 3.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 2H), 6.73 (d, *J* = 10.0 Hz, 2H), 6.38 (d, *J* = 8.4 Hz, 2H), 2.36 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 184.2, 177.3, 160.6, 146.7, 138.4, 137.6, 135.0, 134.3, 130.8, 129.6, 129.5, 129.4, 128.6, 128.4, 128.2, 127.5, 124.1, 108.7, 52.5, 21.4.

HRMS (ESI, m/z): Calculated for C₂₃H₁₆NO₂S (M+H)⁺ 370.0896, Measured 370.0901.

4. 2'-(4-ethylphenyl)-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 33.75 mg, 88% yield. Mp: 139-140 °C.



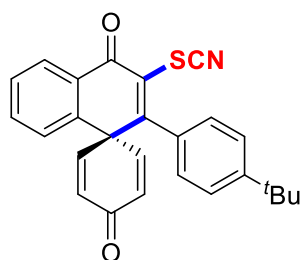
¹H NMR (400 MHz, CDCl₃): δ 8.34 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 10.0 Hz, 2H), 6.37 (d, *J* = 10.0 Hz, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 184.2, 177.4, 160.8, 146.8, 146.3, 137.6, 134.3, 132.4, 130.8, 129.7, 129.5, 129.4, 128.7, 128.2, 128.0, 127.0, 108.8, 52.6, 28.5, 14.9.

HRMS (ESI, m/z): Calculated for C₂₄H₁₈NO₂S (M+H)⁺ 384.1053, Measured 384.1061.

5. 2'-(4-(tert-butyl)phenyl)-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 26.75 mg, 65% yield. Mp: 218-219 °C.



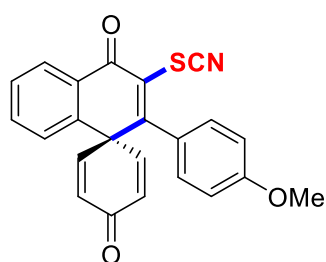
¹H NMR (400 MHz, CDCl₃): δ 8.33 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 10.4 Hz, 2H), 6.38 (d, *J* = 10.0 Hz, 2H), 1.31 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ 184.2, 177.3, 160.8, 153.3, 146.8, 137.6, 134.2, 132.3, 130.8, 129.7, 129.5, 129.4, 128.6, 128.2, 126.8, 125.4, 108.8, 52.6, 34.8, 31.1.

HRMS (ESI, m/z): Calculated for C₂₆H₂₂NO₂S (M+H)⁺ 412.1366, Measured 412.1370.

6. 2'-(4-methoxyphenyl)-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 28.90 mg, 75% yield. Mp: 149-150 °C.



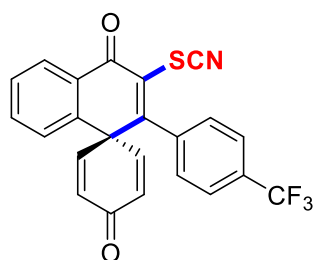
¹H NMR (400 MHz, CDCl₃): δ 8.31 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 10.0 Hz, 2H), 6.38 (d, *J* = 10.0 Hz, 2H), 3.82 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 184.2, 177.4, 160.6, 160.3, 146.9, 137.6, 134.2, 130.7, 129.9, 129.4, 129.3, 128.6, 128.5, 128.2, 127.4, 113.9, 108.8, 55.2, 52.8.

HRMS (ESI, m/z): Calculated for C₂₃H₁₆NO₃S (M+H)⁺ 386.0845, Measured 386.0853.

7. 3'-thiocyanato-2'-(4-(trifluoromethyl)phenyl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 22.44 mg, 53% yield. Mp: 178-179 °C.



¹H NMR (400 MHz, CDCl₃): δ 8.31 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 3H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 10.0 Hz, 2H), 6.41 (d, *J* = 10.0 Hz, 2H).

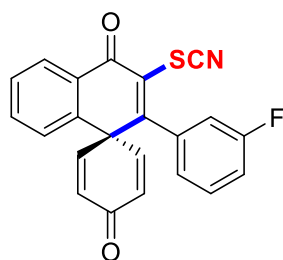
¹³C NMR (100 MHz, CDCl₃): δ 183.6, 177.0, 159.0, 146.1, 138.2, 137.3, 134.6, 131.9 (q, *J* = 33.0 Hz), 131.1, 130.2, 129.7, 129.1, 128.7, 128.3, 127.9, 125.6 (q, *J* = 3.8 Hz), 123.4 (q, *J* = 271.2 Hz), 113.8, 108.2, 52.2.

¹⁹F NMR (565 MHz, CDCl₃): δ -62.90 (s, 3F).

HRMS (ESI, *m/z*): Calculated for C₂₃H₁₃F₃NO₂S (M+H)⁺ 424.0614, Measured 424.0632.

8. 2'-(3-fluorophenyl)-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 25.02 mg, 67% yield. Mp: 194-195 °C.



¹H NMR (400 MHz, CDCl₃): δ 8.36 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 8.8 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.71 (dd, *J* = 10.0, 5.2 Hz, 2H), 6.41 (dd, *J* = 15.6, 9.6 Hz, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 183.8, 177.2, 162.2 (d, *J* = 248.4 Hz), 158.6 (d, *J* = 2.0 Hz), 146.32, 146.21, 137.50, 136.5 (d, *J* = 7.8 Hz), 134.5, 131.1 (d, *J* = 23.6 Hz), 130.6 (d, *J* = 8.2 Hz), 129.7, 129.2, 128.8, 128.3, 123.2 (d, *J* = 3.3 Hz), 117.2 (d, *J* = 20.8 Hz), 114.8 (d, *J* = 23.0 Hz), 108.2, 52.3.

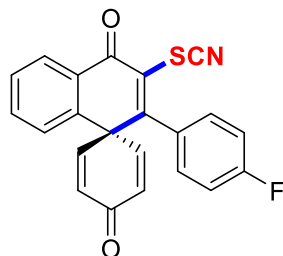
¹⁹F NMR (565 MHz, CDCl₃): δ -110.24 (s, 1F).

HRMS (ESI, *m/z*): Calculated for C₂₂H₁₃FNO₂S (M+H)⁺ 374.0645, Measured 374.0648.

9. 2'-(4-fluorophenyl)-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-

dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 25.76 mg, 69% yield. Mp: 218-219 °C.



¹H NMR (400 MHz, CDCl₃): δ 8.32 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 6.4 Hz, 4H), 6.72 (d, *J* = 10.0 Hz, 2H), 6.39 (d, *J* = 10.0 Hz, 2H).

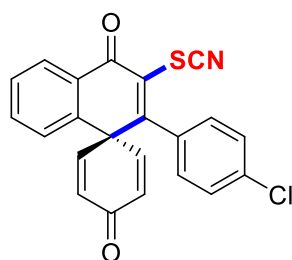
¹³C NMR (100 MHz, CDCl₃): δ 183.8, 177.2, 163.2 (d, *J* = 250.3 Hz), 159.3, 146.4, 137.5, 134.4, 131.0, 129.6, 129.4 (d, *J* = 8.5 Hz), 129.2, 128.6, 128.3, 116.0, 115.8, 108.4, 52.5.

¹⁹F NMR (565 MHz, CDCl₃): δ -109.42 (s, 1F).

HRMS (ESI, m/z): Calculated for C₂₂H₁₃FNO₂S (M+H)⁺ 374.0645, Measured 374.0651.

10. 2'-(4-chlorophenyl)-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 22.61 mg, 58% yield. Mp: 184-185 °C.



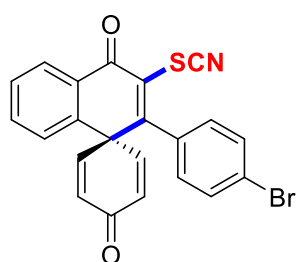
¹H NMR (400 MHz, CDCl₃): δ 8.33 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.66 (t, *J* = 6.8 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 10.0 Hz, 2H), 6.40 (d, *J* = 10.0 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 183.8, 177.2, 159.2, 146.3, 137.5, 136.3, 134.5, 133.2, 131.1, 130.3, 129.7, 129.2, 129.0, 128.7, 128.6, 128.3, 108.3, 52.4.

HRMS (ESI, m/z): Calculated for C₂₂H₁₃ClNO₂S (M+H)⁺ 390.0350, Measured 390.0352.

11. 2'-(4-bromophenyl)-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 31.27 mg, 72% yield.



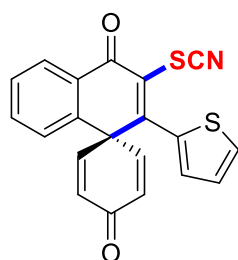
¹H NMR (400 MHz, CDCl₃): δ 8.32 (t, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.54 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 10.0 Hz, 2H), 6.40 (d, *J* = 8.0 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 183.8, 177.1, 159.2, 146.3, 137.4, 134.5, 133.7, 131.9, 131.1, 130.1, 129.7, 129.2, 128.8, 128.7, 128.3, 124.5, 108.3, 52.31.

HRMS (ESI, m/z): Calculated for C₂₂H₁₃BrNO₂S (M+H)⁺ 435.9826, Measured 435.9847.

12. 3'-thiocyanato-2'-(thiophen-2-yl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 23.85 mg, 66% yield. Mp: 197-198 °C.



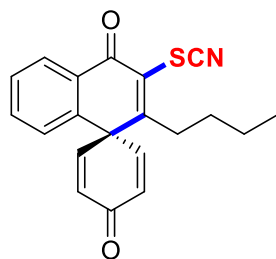
¹H NMR (400 MHz, CDCl₃): δ 8.33 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.50 (dd, *J* = 5.2, 1.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 3.6 Hz, 1H), 7.03 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.68 (d, *J* = 10.0 Hz, 2H), 6.47 (d, *J* = 10.0 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 184.2, 177.3, 152.6, 146.5, 137.4, 134.7, 134.4, 131.4, 131.3, 130.0, 129.6, 129.4, 129.1, 128.7, 128.4, 127.4, 108.4, 52.5.

HRMS (ESI, *m/z*): Calculated for C₂₀H₁₂NO₂S₂ (M+H)⁺ 362.0304, Measured 362.0314.

13. 2'-butyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 21.80 mg, 65% yield. Mp: 124-125 °C.



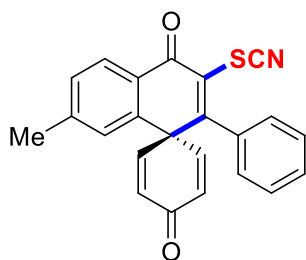
¹H NMR (400 MHz, CDCl₃): δ 8.31 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 2.0 Hz, 4H), 2.52 – 2.47 (m, 2H), 1.55 – 1.48 (m, 2H), 1.42 (q, *J* = 7.2 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 184.4, 176.8, 164.2, 147.1, 137.0, 134.0, 131.1, 129.5, 129.3, 128.6, 128.2, 128.0, 108.8, 52.8, 34.1, 32.5, 23.1, 13.4.

HRMS (ESI, *m/z*): Calculated for C₂₀H₁₈NO₂S (M+H)⁺ 336.1053, Measured 336.1061.

14. 7'-methyl-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 25.86 mg, 70% yield. Mp: 200-201 °C.



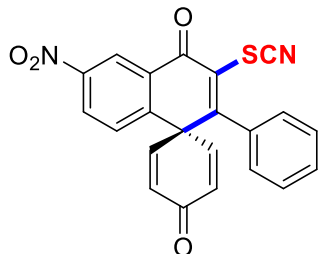
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.22 (d, $J = 8.0$ Hz, 1H), 7.42 – 7.36 (m, 4H), 7.07 – 7.04 (m, 3H), 6.71 (d, $J = 9.2$ Hz, 2H), 6.36 (d, $J = 10.0$ Hz, 2H), 2.41 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 184.2, 177.1, 159.9, 146.8, 145.7, 137.6, 135.1, 130.8, 130.6, 129.9, 129.8, 128.7, 128.5, 128.4, 127.2, 127.0, 108.7, 52.4, 21.9.

HRMS (ESI, m/z): Calculated for $\text{C}_{23}\text{H}_{16}\text{NO}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 370.0896, Measured 370.0902.

15. 6'-nitro-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 20.82 mg, 52% yield. Mp: 237-238 °C.



$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.12 (s, 1H), 8.44 (dd, $J = 8.8, 2.8$ Hz, 1H), 7.52 (d, $J = 8.4$ Hz, 1H), 7.47 – 7.41 (m, 3H), 7.08 (d, $J = 7.6$ Hz, 2H), 6.74 (d, $J = 8.8$ Hz, 2H), 6.45 (d, $J = 10.0$ Hz, 2H).

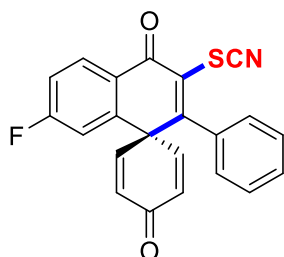
$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 183.2, 175.8, 161.0, 148.4, 144.9, 143.7, 134.4, 131.8, 130.5, 130.4, 129.7, 128.7, 128.0, 127.0, 123.8, 108.0, 52.4.

HRMS (ESI, m/z): Calculated for $\text{C}_{22}\text{H}_{13}\text{N}_2\text{O}_4\text{S}$ ($\text{M}+\text{H}$) $^+$ 401.0591, Measured 401.0604.

16. 7'-fluoro-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate =

3/1). 28.38 mg, 76% yield. Mp: 217-218 °C.



¹H NMR (400 MHz, CDCl₃): δ 8.37 (dd, *J* = 8.8, 5.6 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.30 – 7.26 (m, 1H), 7.06 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.96 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.72 (d, *J* = 10.0 Hz, 2H), 6.39 (d, *J* = 10.0 Hz, 2H).

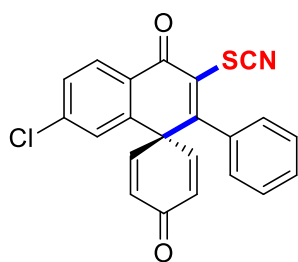
¹³C NMR (100 MHz, CDCl₃): δ 183.6, 176.2, 166.0 (d, *J* = 257.4 Hz), 160.2, 145.9, 140.8 (d, *J* = 8.5 Hz), 134.8, 131.9 (d, *J* = 9.6 Hz), 131.2, 130.1, 129.7, 128.6, 127.1, 126.0 (d, *J* = 2.7 Hz), 117.7 (d, *J* = 22.1 Hz), 115.0 (d, *J* = 23.3 Hz), 108.4, 52.3.

¹⁹F NMR (565 MHz, CDCl₃): δ -100.85 (s, 1F).

HRMS (ESI, *m/z*): Calculated for C₂₂H₁₃FNO₂S (M+H)⁺ 374.0645, Measured 374.0650.

17. 7'-chloro-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 30.02 mg, 77% yield. Mp: 172-173 °C.



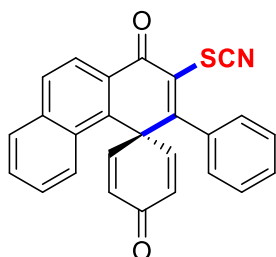
¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.55 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.06 (d, *J* = 6.8 Hz, 2H), 6.71 (d, *J* = 10.0 Hz, 2H), 6.40 (d, *J* = 10.0 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 183.6, 176.5, 160.2, 145.8, 141.2, 139.4, 134.7, 131.3, 130.2, 130.1, 129.7, 128.6, 128.3, 127.7, 127.1, 108.4, 52.2.

HRMS (ESI, m/z): Calculated for C₂₂H₁₃ClNO₂S (M+H)⁺ 390.0350, Measured 390.0366.

18. 3'-phenyl-2'-thiocyanato-1'H-spiro[cyclohexane-1,4'-phenanthrene]-2,5-diene-1',4-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 23.92 mg, 59% yield. Mp: 238-239 °C.



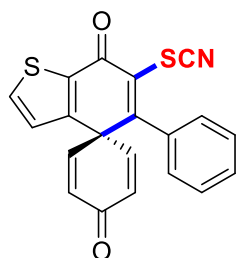
¹H NMR (400 MHz, CDCl₃): δ 8.46 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.8 Hz, 1H), 7.43 – 7.36 (m, 3H), 7.00 (d, *J* = 6.8 Hz, 2H), 6.86 (d, *J* = 10.0 Hz, 2H), 6.54 (d, *J* = 9.6 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 183.3, 177.5, 158.8, 147.3, 136.4, 136.3, 133.4, 133.2, 131.5, 131.1, 130.3, 129.8, 129.7, 129.5, 129.0, 128.1, 127.7, 127.4, 125.8, 123.2, 108.6, 53.5.

HRMS (ESI, m/z): Calculated for C₂₆H₁₆NO₂S (M+H)⁺ 406.0902, Measured 406.0900.

19. 5-phenyl-6-thiocyanato-7H-spiro[benzo[b]thiophene-4,1'-cyclohexane]-2',5'-diene-4',7-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 20.60 mg, 57% yield. Mp: 197-198 °C.



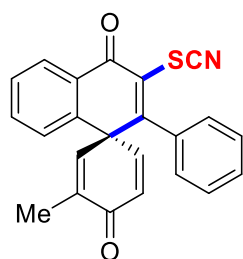
¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, *J* = 4.8 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.07 (d, *J* = 6.4 Hz, 2H), 6.90 (d, *J* = 4.8 Hz, 1H), 6.67 (d, *J* = 10.0 Hz, 2H), 6.38 (d, *J* = 10.0 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 183.7, 172.2, 160.6, 145.3, 144.7, 135.9, 135.4, 134.8, 131.3, 130.0, 129.6, 128.6, 127.4, 127.2, 108.4, 52.2.

HRMS (ESI, m/z): Calculated for C₂₀H₁₂NO₂S₂ (M+H)⁺ 362.0304, Measured 362.0315.

20. 3-methyl-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 31.03 mg, 84% yield. Mp: 208-209 °C.



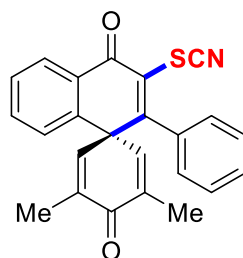
¹H NMR (400 MHz, CDCl₃): δ 8.33 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.06 – 7.02 (m, 2H), 6.70 (dd, *J* = 9.6, 2.8 Hz, 1H), 6.50 (s, 1H), 6.34 (d, *J* = 9.6 Hz, 1H), 1.86 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 184.7, 177.4, 161.4, 146.1, 141.7, 138.4, 138.1, 135.1, 134.2, 130.7, 129.8, 129.3, 129.2, 128.5, 128.4, 128.2, 127.3, 126.9, 108.8, 52.7, 15.8.

HRMS (ESI, m/z): Calculated for C₂₃H₁₆NO₂S (M+H)⁺ 370.0896, Measured 370.0912.

21. 3,5-dimethyl-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 27.23 mg, 71% yield. Mp: 207-208 °C.



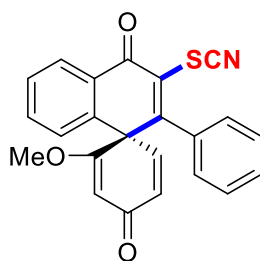
¹H NMR (400 MHz, CDCl₃): δ 8.32 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 7.6, 1.2 Hz, 2H), 6.46 (s, 2H), 1.83 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 185.3, 177.6, 162.4, 141.2, 139.3, 137.8, 135.2, 134.1, 129.6, 129.2, 129.1, 128.8, 128.4, 128.2, 128.1, 127.1, 108.9, 52.4, 16.0.

HRMS (ESI, *m/z*): Calculated for C₂₄H₁₈NO₂S (M+H)⁺ 384.1053, Measured 384.1060.

22. 2-methoxy-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 24.28 mg, 63% yield. Mp: 215-216 °C.



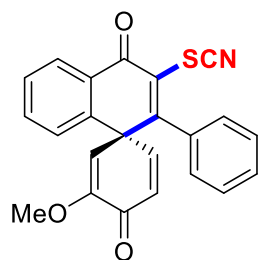
¹H NMR (400 MHz, CDCl₃): δ 8.34 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 6.8 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.97 (s, 1H), 6.44 (d, *J* = 9.6 Hz, 1H), 6.32 (dd, *J* = 9.6, 1.2 Hz, 1H), 5.60 (d, *J* = 1.2 Hz, 1H), 3.59 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 186.6, 177.6, 172.0, 160.2, 142.2, 138.3, 134.6, 134.3, 130.2, 130.0, 129.8, 129.5, 129.4, 128.8, 128.4, 127.0, 126.7, 108.8, 105.2, 56.2, 54.8.

HRMS (ESI, *m/z*): Calculated for C₂₃H₁₆NO₃S (M+H)⁺ 386.0845, Measured 386.0851.

23. 3-methoxy-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 20.04 mg, 52% yield. Mp: 219-220 °C.



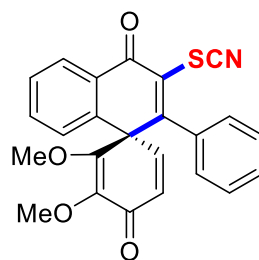
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.30 (d, $J = 8.0$ Hz, 1H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.43 – 7.36 (m, 3H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.05 (dd, $J = 16.4$, 7.2 Hz, 2H), 6.72 (dd, $J = 10.0$, 2.8 Hz, 1H), 6.38 (d, $J = 9.6$ Hz, 1H), 5.69 (s, 1H), 3.63 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 179.3, 177.4, 161.8, 152.6, 146.6, 139.1, 135.0, 134.3, 130.7, 129.9, 129.3, 129.1, 129.0, 128.5, 128.4, 128.3, 128.2, 127.2, 127.1, 114.6, 108.8, 55.3, 52.7.

HRMS (ESI, m/z): Calculated for $\text{C}_{23}\text{H}_{16}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 386.0845, Measured 386.0851.

24. 2,3-dimethoxy-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 22.44 mg, 54% yield. Mp: 155-156 °C.



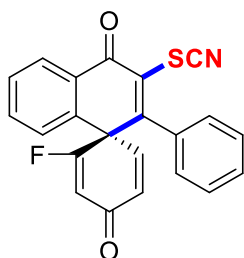
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.34 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.64 (t, $J = 7.2$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.47 – 7.38 (m, 3H), 7.28 (d, $J = 8.4$ Hz, 1H), 7.14 – 7.08 (m, 2H), 6.36 (d, $J = 9.6$ Hz, 1H), 6.31 (d, $J = 10.0$ Hz, 1H), 3.84 (s, 3H), 3.45 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 183.6, 177.6, 160.6, 158.9, 141.4, 140.0, 138.5, 134.7, 134.2, 130.0, 129.9, 129.8, 129.3, 128.6, 128.5, 128.4, 127.2, 126.9, 126.7, 108.8, 61.3, 60.7, 56.8.

HRMS (ESI, m/z): Calculated for C₂₄H₁₈NO₄S (M+H)⁺ 416.0951, Measured 416.0960.

25. 2-fluoro-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 19.42 mg, 52% yield. Mp: 214-215 °C.



¹H NMR (400 MHz, CDCl₃): δ 8.38 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.32 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.10 (dd, *J* = 21.2, 8.4 Hz, 2H), 6.57 (t, *J* = 9.6 Hz, 1H), 6.35 (d, *J* = 9.6 Hz, 1H), 6.05 (dd, *J* = 13.2, 1.2 Hz, 1H).

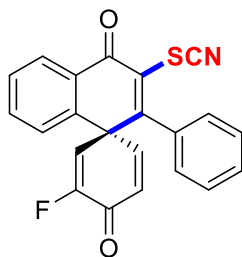
¹³C NMR (150 MHz, CDCl₃): δ 186.2 (d, *J* = 15.2 Hz), 177.0, 172.4 (d, *J* = 285.4 Hz), 157.0, 142.6 (d, *J* = 3.8 Hz), 135.3, 134.6, 133.8, 131.8, 130.4, 130.1, 130.0, 129.6, 129.1, 128.9, 128.6, 127.2, 127.0 (d, *J* = 24.8 Hz), 112.7 (d, *J* = 9.6 Hz), 108.2, 54.0 (d, *J* = 23.1 Hz).

¹⁹F NMR (565 MHz, CDCl₃): δ -85.79 (s, 1F).

HRMS (ESI, m/z): Calculated for C₂₂H₁₃FNO₂S (M+H)⁺ 374.0645, Measured 374.0650.

26. 3-fluoro-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 28.00 mg, 75% yield. Mp: 214-215 °C.



^1H NMR (400 MHz, CDCl_3): δ 8.34 (dd, $J = 1.6, 8.0$ Hz, 1H), 7.68 (t, $J = 7.2$ Hz, 1H), 7.61 (t, $J = 7.6$ Hz, 1H), 7.46 – 7.40 (m, 3H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.07 (dd, $J = 13.6, 6.4$ Hz, 2H), 6.74 (dd, $J = 10.0, 2.8$ Hz, 1H), 6.41 – 6.34 (m, 2H).

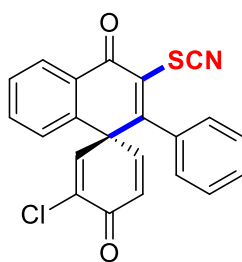
^{13}C NMR (100 MHz, CDCl_3): δ 177.0, 176.9, 176.6, 159.4, 155.1 (d, $J = 269.2$ Hz), 147.4, 136.9, 134.5 (d, $J = 4.1$ Hz), 130.6 (d, $J = 4.7$ Hz), 130.2, 130.1, 129.8, 129.1, 128.8, 128.7, 128.6, 128.0, 127.1 (d, $J = 7.4$ Hz), 123.5, 123.3, 108.4, 53.0 (d, $J = 6.5$ Hz)

^{19}F NMR (565 MHz, CDCl_3): δ -124.82 (s, 1F).

HRMS (ESI, m/z): Calculated for $\text{C}_{22}\text{H}_{13}\text{FNO}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 374.0645, Measured 374.0655.

27. 3-chloro-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 28.46 mg, 73% yield. Mp: 228-229 °C.



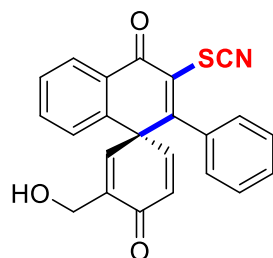
^1H NMR (400 MHz, CDCl_3): δ 8.35 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.69 (t, $J = 7.6$ Hz, 1H), 7.62 (t, $J = 7.6$ Hz, 1H), 7.46 – 7.41 (m, 3H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.05 (dd, $J = 7.6, 1.6$ Hz, 2H), 6.92 (d, $J = 2.8$ Hz, 1H), 6.75 (dd, $J = 10.0, 2.8$ Hz, 1H), 6.43 (d, $J = 9.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 177.1, 177.0, 159.0, 146.8, 142.2, 136.6, 135.3, 134.6, 134.4, 130.2, 129.9, 129.2, 128.9, 128.7, 128.2, 127.3, 126.9, 108.4, 54.1.

HRMS (ESI, m/z): Calculated for C₂₂H₁₃ClNO₂S (M+H)⁺ 390.0350, Measured 390.0367.

28. 3-(hydroxymethyl)-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 24.66 mg, 64% yield. Mp: 139-140 °C.



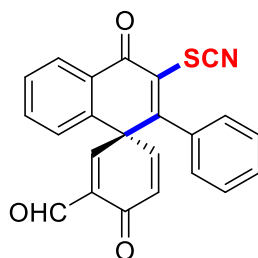
¹H NMR (400 MHz, CDCl₃): δ 8.36 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.64 (t, *J* = 6.8 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.76 (dd, *J* = 10.0, 3.2 Hz, 1H), 6.73 (s, 1H), 6.36 (d, *J* = 9.6 Hz, 1H), 4.37 (d, *J* = 14.4 Hz, 1H), 4.30 (d, *J* = 14.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 184.6, 177.4, 160.6, 146.9, 141.6, 139.9, 137.7, 134.9, 134.3, 130.7, 129.9, 129.7, 129.5, 129.3, 128.7, 128.4, 128.2, 127.3, 127.0, 108.7, 60.4, 52.5.

HRMS (ESI, m/z): Calculated for C₂₃H₁₆NO₃S (M+H)⁺ 386.0845, Measured 386.0848.

29. 4,4'-dioxo-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-3-carbaldehyde

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 14.95 mg, 39% yield. Mp: 87-88 °C.



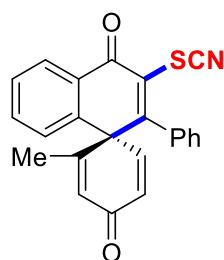
¹H NMR (400 MHz, CDCl₃): δ 10.10 (s, 1H), 8.42 – 8.39 (m, 1H), 7.68 – 7.62 (m, 2H), 7.44 – 7.37 (m, 4H), 7.17 (dd, *J* = 6.0, 2.4 Hz, 1H), 7.07 (d, *J* = 6.8 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.81 (dd, *J* = 10.0, 3.2 Hz, 1H), 6.47 (d, *J* = 10.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 187.8, 182.8, 176.9, 158.2, 150.7, 146.6, 136.0, 134.6, 134.4, 133.5, 131.0, 130.7, 130.3, 130.2, 129.3, 129.2, 128.8, 128.4, 127.2, 126.7, 108.2, 52.4.

HRMS (ESI, *m/z*): Calculated for C₂₃H₁₄NO₃S (M+H)⁺ 384.0694, Measured 384.0691.

30. 2-methyl-2'-phenyl-3'-thiocyanato-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 24.01 mg, 65% yield. Mp: 197-198 °C.



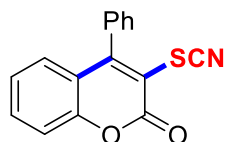
¹H NMR (400 MHz, CDCl₃): δ 8.36 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.17 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.07 – 7.02 (m, 2H), 6.68 (d, *J* = 9.6 Hz, 1H), 6.35 (dd, *J* = 10.0, 1.6 Hz, 1H), 6.28 (s, 1H), 1.73 (d, *J* = 1.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 184.9, 177.5, 160.6, 155.3, 146.6, 138.7, 134.6, 131.1, 130.7, 130.2, 129.9, 129.7, 129.5, 128.7, 128.6, 128.5, 127.6, 127.5, 108.7, 55.8, 20.3.

HRMS (ESI, *m/z*): Calculated for C₂₃H₁₆NO₂S (M+H)⁺ 370.0896, Measured 370.0899.

31. 4-phenyl-3-thiocyanato-2H-chromen-2-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 14.24 mg, 51% yield. Mp: 134-135 °C.



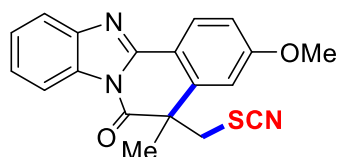
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.68 – 7.61 (m, 4H), 7.46 (d, $J = 8.4$ Hz, 1H), 7.32 (dd, $J = 7.2, 3.6$ Hz, 2H), 7.26 (t, $J = 6.8$ Hz, 1H), 7.16 (d, $J = 8.0$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 160.8, 157.3, 153.5, 134.0, 133.1, 130.3, 129.2, 128.6, 128.0, 125.0, 119.7, 117.2, 112.7, 108.1.

HRMS (ESI, m/z): Calculated for $\text{C}_{16}\text{H}_{10}\text{NO}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 280.0427, Measured 280.0436.

32. 3-methoxy-5-methyl-5-(thiocyanatomethyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 19.92 mg, 57% yield. Mp: 148-149 °C.



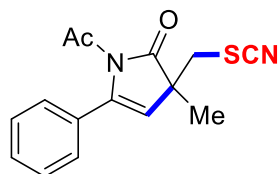
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.48 (d, $J = 8.8$ Hz, 1H), 8.30 (d, $J = 7.2$ Hz, 1H), 7.79 (d, $J = 7.2$ Hz, 1H), 7.47 – 7.39 (m, 2H), 7.13 (dd, $J = 8.8, 2.4$ Hz, 1H), 6.93 (d, $J = 2.4$ Hz, 1H), 3.96 (d, $J = 13.2$ Hz, 1H), 3.94 (s, 3H), 3.65 (d, $J = 13.2$ Hz, 1H), 1.83 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 170.4, 162.9, 149.2, 144.1, 139.2, 131.0, 128.6, 126.3, 125.5, 119.6, 116.1, 115.5, 114.7, 112.1, 110.5, 55.7, 50.5, 43.3, 29.2.

HRMS (ESI, m/z): Calculated for $\text{C}_{19}\text{H}_{16}\text{N}_3\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 350.0958, Measured 350.0972.

33. 1-acetyl-3-methyl-5-phenyl-3-(thiocyanatomethyl)-1,3-dihydro-2H-pyrrol-2-one

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1). 14.03 mg, 49% yield.



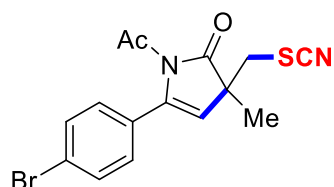
¹H NMR (400 MHz, CDCl₃): δ 7.39 – 7.37 (m, 3H), 7.31 (dd, *J* = 7.2, 3.6 Hz, 2H), 5.51 (s, 1H), 3.30 (d, *J* = 13.6 Hz, 1H), 3.26 (d, *J* = 13.2 Hz, 1H), 2.59 (s, 3H), 1.48 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 179.5, 169.0, 144.8, 132.2, 129.2, 128.8, 128.0, 126.9, 123.5, 114.5, 111.7, 51.8, 40.4, 26.2, 22.4.

HRMS (ESI, *m/z*): Calculated for C₁₅H₁₄N₂O₂SNa (M+Na)⁺ 309.0668, Measured 309.0674.

34. 1-acetyl-5-(4-bromophenyl)-3-methyl-3-(thiocyanatomethyl)-1,3-dihydro-2H-pyrrol-2-one

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1). 15.34 mg, 42% yield.



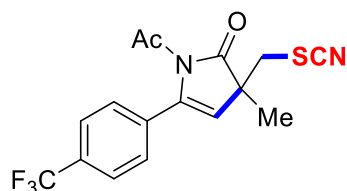
¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.53 (s, 1H), 3.29 (d, *J* = 13.6 Hz, 1H), 3.25 (d, *J* = 13.2 Hz, 1H), 2.59 (s, 3H), 1.47 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 179.2, 169.0, 143.8, 131.2, 128.5, 122.9, 115.1, 111.6, 51.9, 40.3, 26.2, 22.4.

HRMS (ESI, *m/z*): Calculated for C₁₅H₁₃BrN₂O₂SNa (M+Na)⁺ 386.9773, Measured 386.9776.

35. 1-acetyl-3-methyl-3-(thiocyanatomethyl)-5-(4-(trifluoromethyl)phenyl)-1,3-dihydro-2H-pyrrol-2-one

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 15.23 mg, 43% yield.



¹H NMR (400 MHz, CDCl₃): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 5.60 (s, 1H), 3.30 (d, *J* = 13.6 Hz, 1H), 3.26 (d, *J* = 13.6 Hz, 1H), 2.60 (s, 3H), 1.50 (s, 3H).

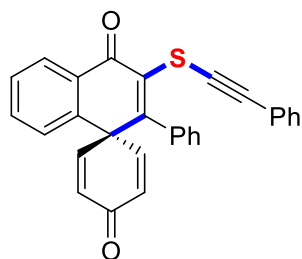
¹³C NMR (100 MHz, CDCl₃): δ 179.1, 168.9, 143.6, 135.9, 130.7 (q, *J* = 32.6 Hz), 127.3, 125.0 (d, *J* = 3.7 Hz), 124.1, 123.9 (q, *J* = 270.9 Hz), 116.1, 111.6, 52.1, 40.2, 26.1, 22.4.

¹⁹F NMR (565 MHz, CDCl₃): δ -62.75 (s, 3F).

HRMS (ESI, m/z): Calculated for C₁₆H₁₃F₃N₂O₂SNa (M+Na)⁺ 377.0542, Measured 377.0551.

36. 2'-phenyl-3'-((phenylethynyl)thio)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 32.28 mg, 75% yield.



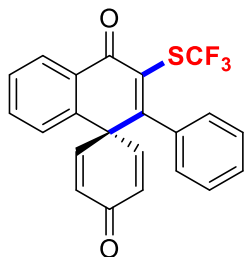
¹H NMR (400 MHz, CDCl₃): δ 8.34 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.34 – 7.29 (m, 6H), 7.26 – 7.24 (m, 3H), 7.15 (dd, *J* = 6.0, 2.4 Hz, 2H), 6.75 (d, *J* = 10.0 Hz, 2H), 6.34 (d, *J* = 10.0 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 184.6, 179.0, 155.9, 148.0, 137.6, 135.7, 134.9, 133.6, 131.8, 130.3, 130.0, 129.2, 129.1, 128.4, 128.2, 128.1, 128.0, 127.6, 122.9, 93.9, 75.7, 52.2.

HRMS (ESI, m/z): Calculated for C₂₉H₁₉O₂S (M+H)⁺ 431.1106, Measured 431.1108.

37. 2'-phenyl-3'-((trifluoromethyl)thio)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1). 27.49 mg, 69% yield. Mp: 169-170 °C.



¹H NMR (400 MHz, CDCl₃): δ 8.35 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 6.4 Hz, 2H), 6.75 (d, *J* = 10.0 Hz, 2H), 6.35 (d, *J* = 10.0 Hz, 2H).

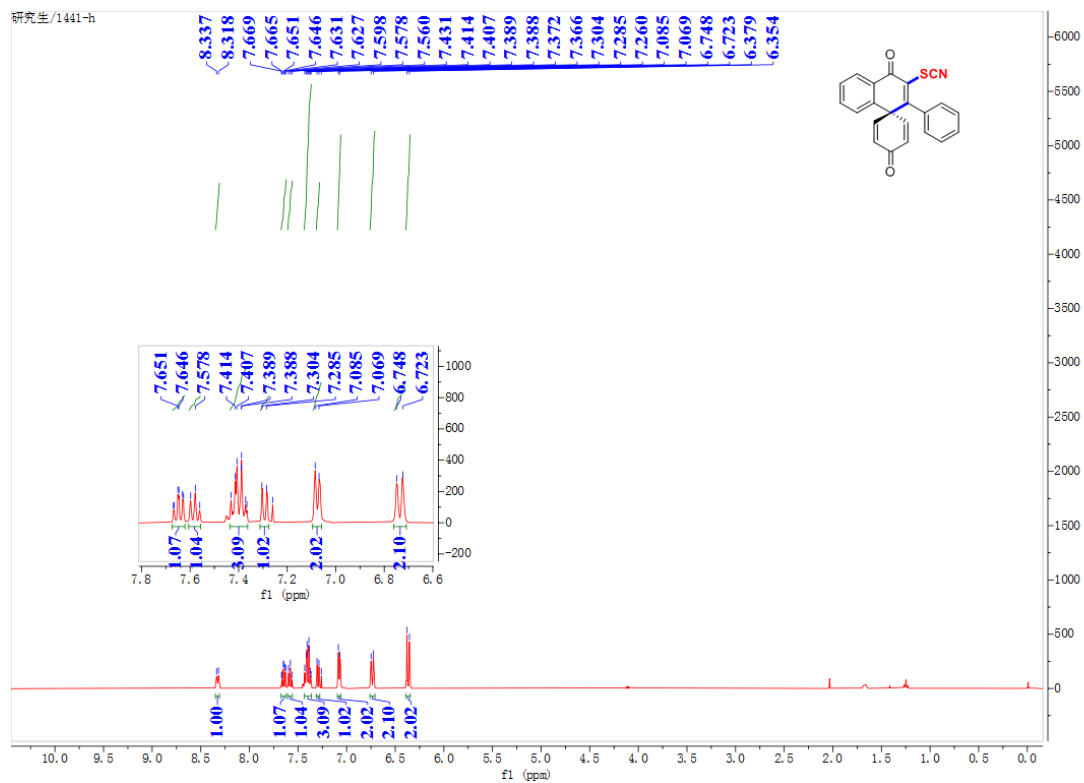
¹³C NMR (100 MHz, CDCl₃): δ 184.2, 179.3, 166.7, 147.1, 137.5, 135.9, 134.0, 130.6, 129.8, 129.4, 129.2, 128.7, 128.5 (q, *J* = 308.9 Hz), 128.1, 127.8, 127.2, 52.6.

¹⁹F NMR (565 MHz, CDCl₃): δ -39.45 (s, 3F).

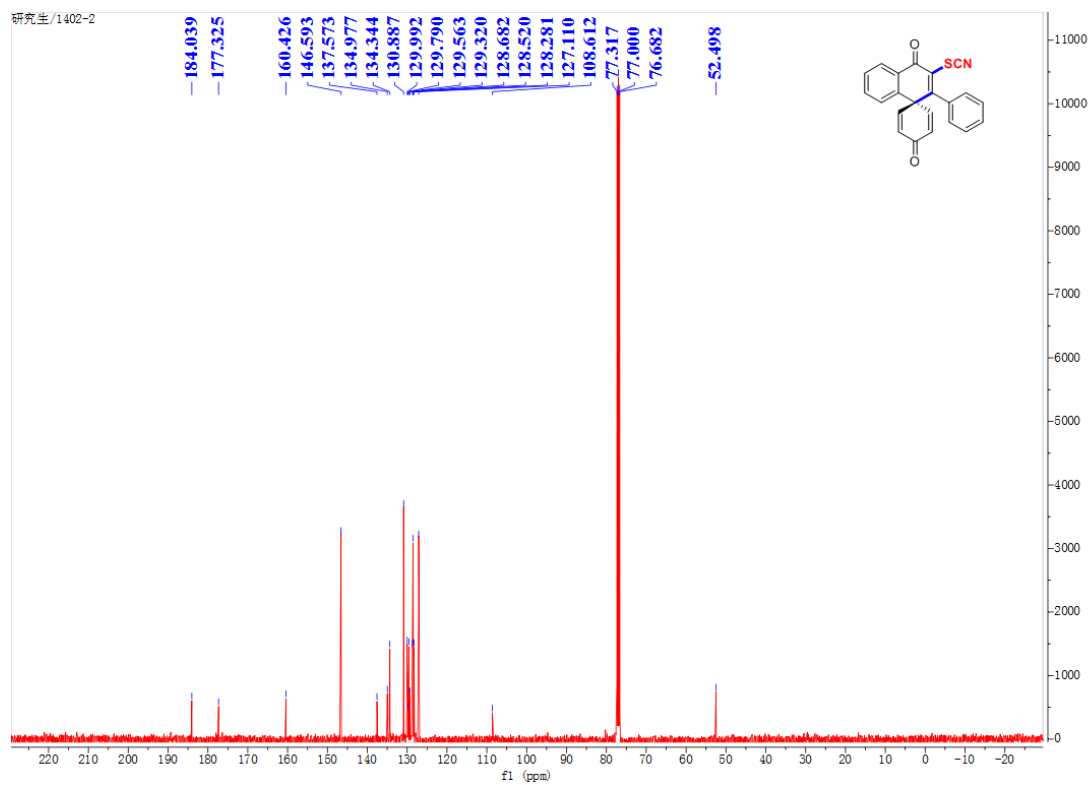
HRMS (ESI, *m/z*): Calculated for C₂₂H₁₄F₃O₂S (M+H)⁺ 399.0667, Measured 399.0667.

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

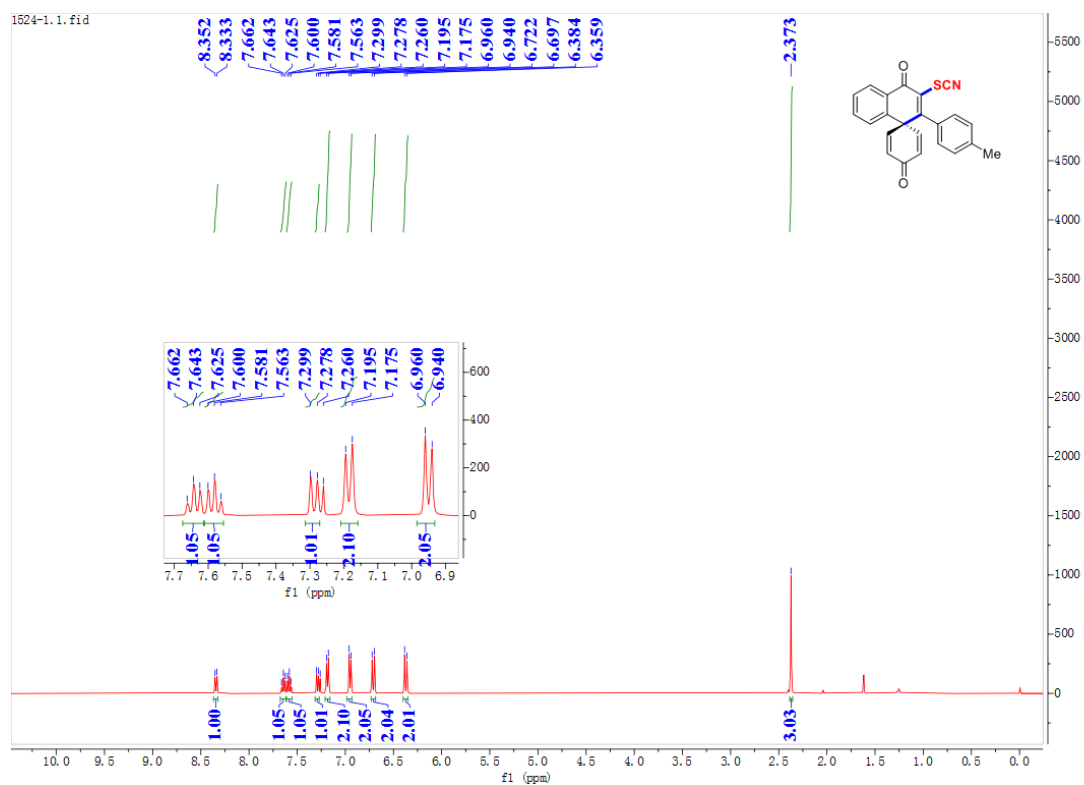
1- ^1H NMR



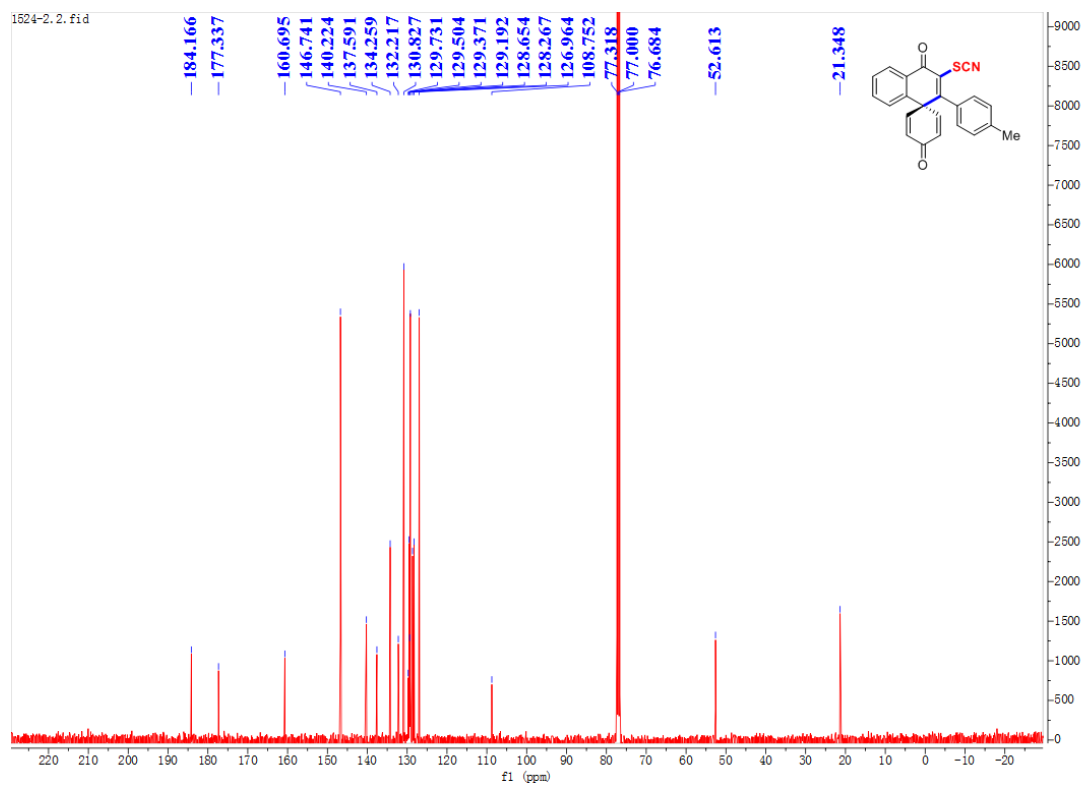
1- ^{13}C NMR



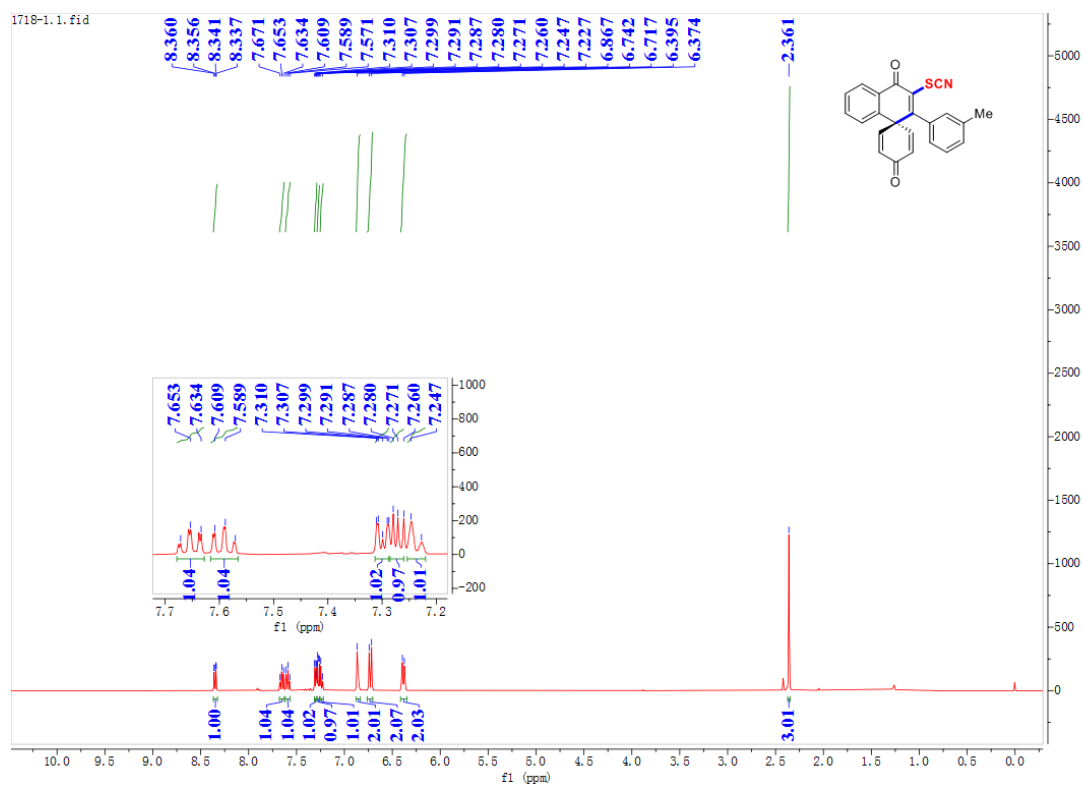
$^2\text{-}^1\text{H}$ NMR



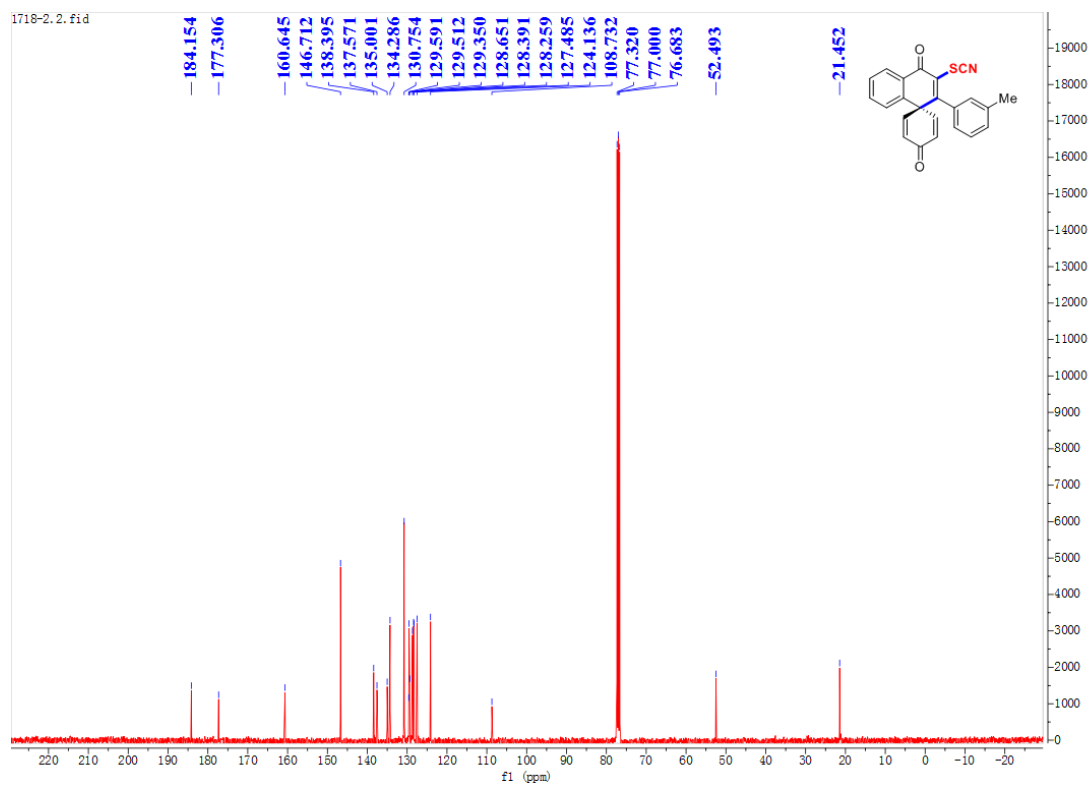
$^2\text{-}^{13}\text{C}$ NMR



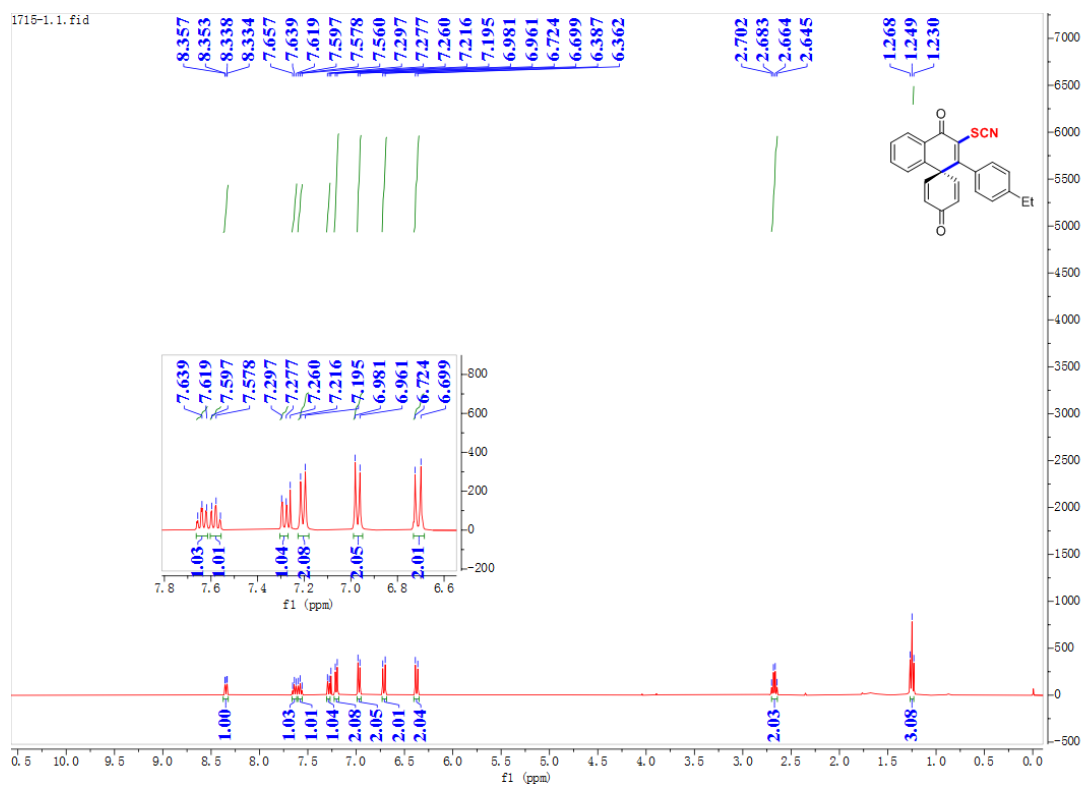
3-¹H NMR



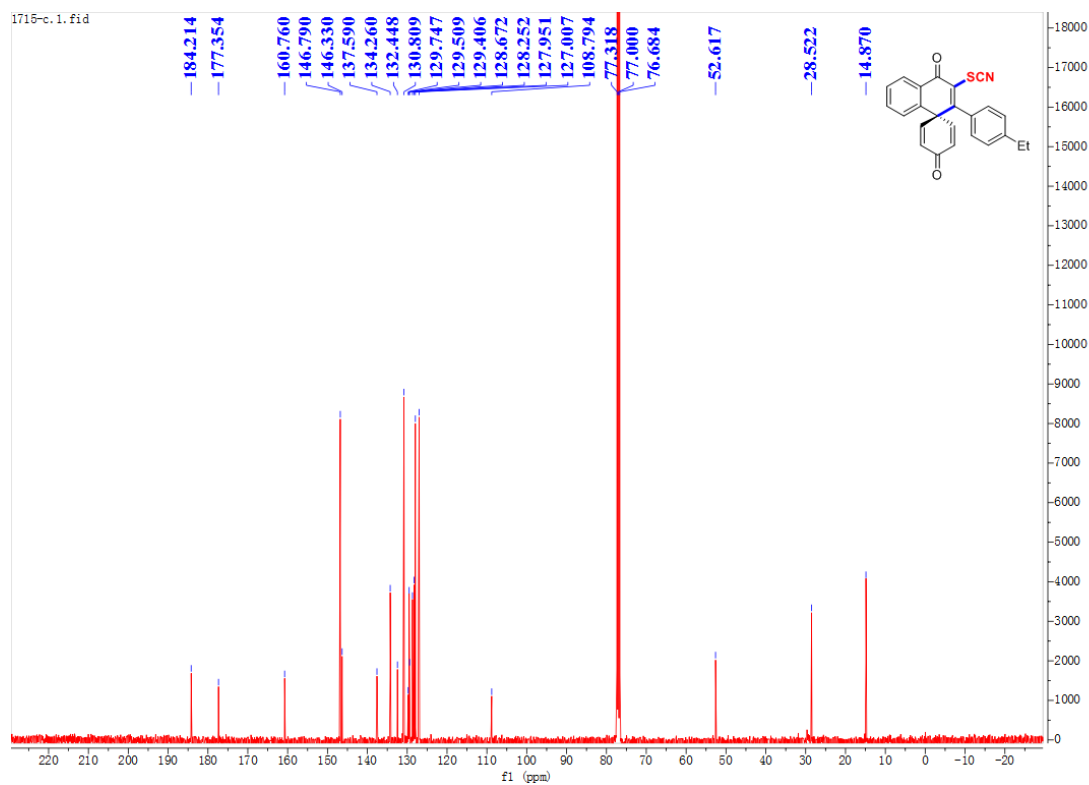
3-¹³C NMR



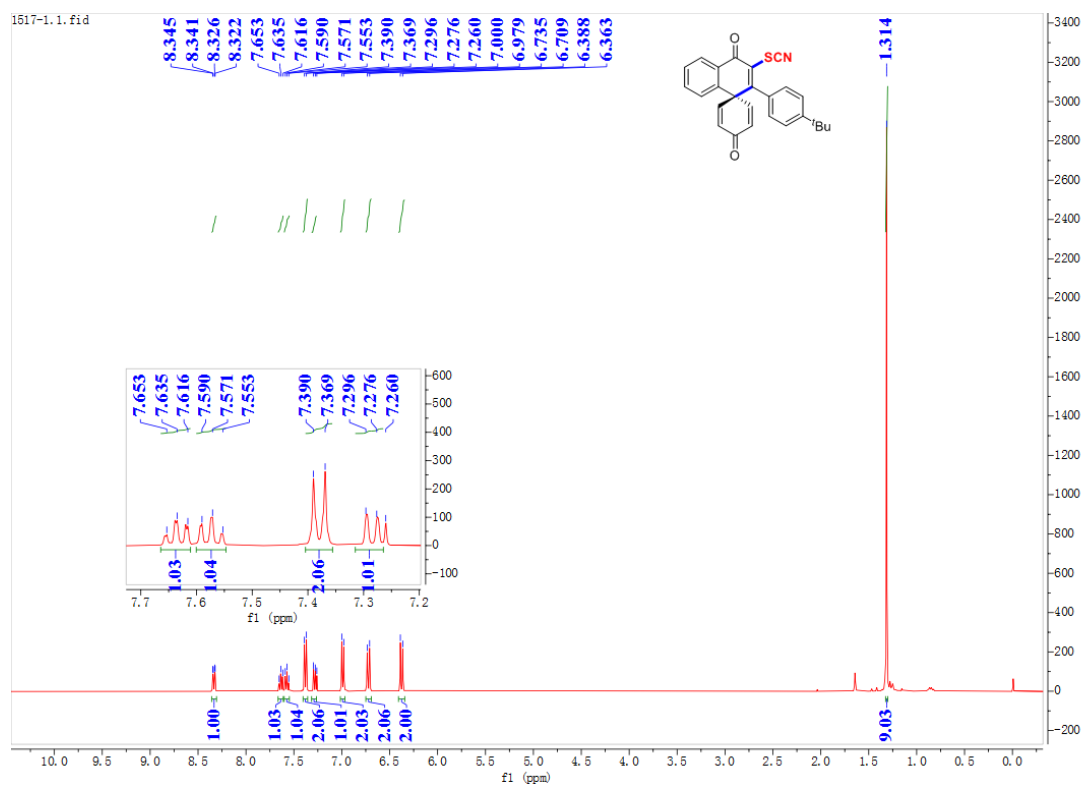
4-¹H NMR



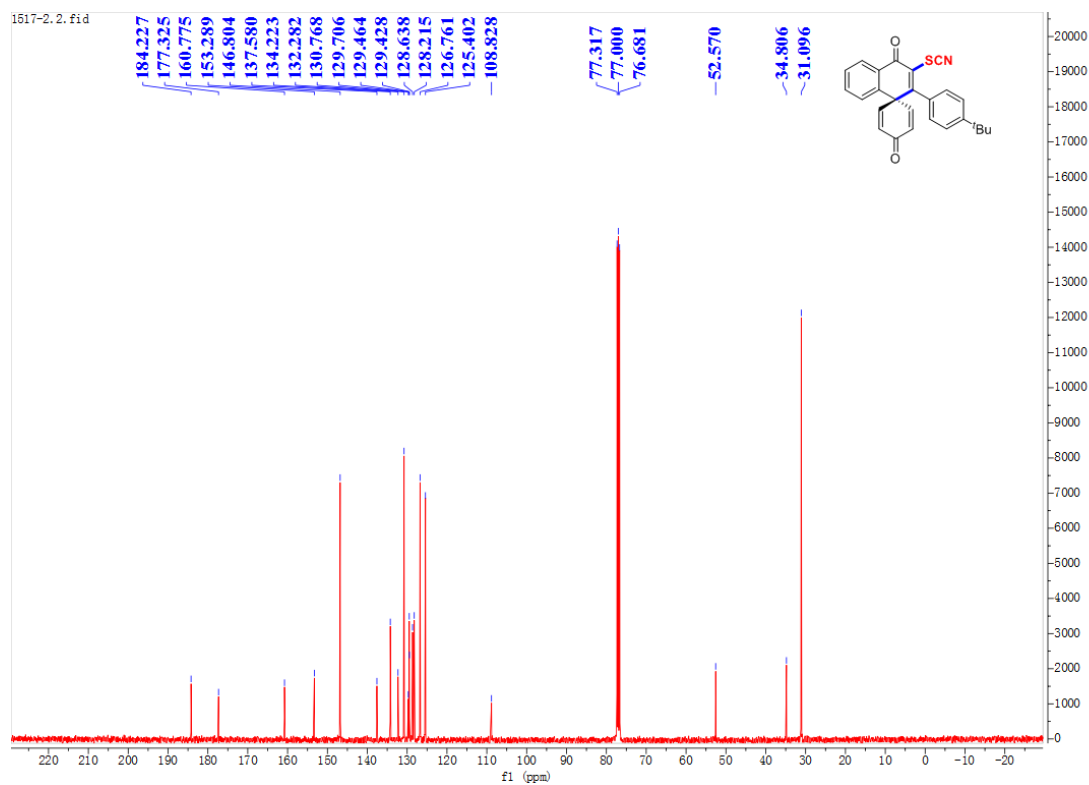
4-¹³C NMR



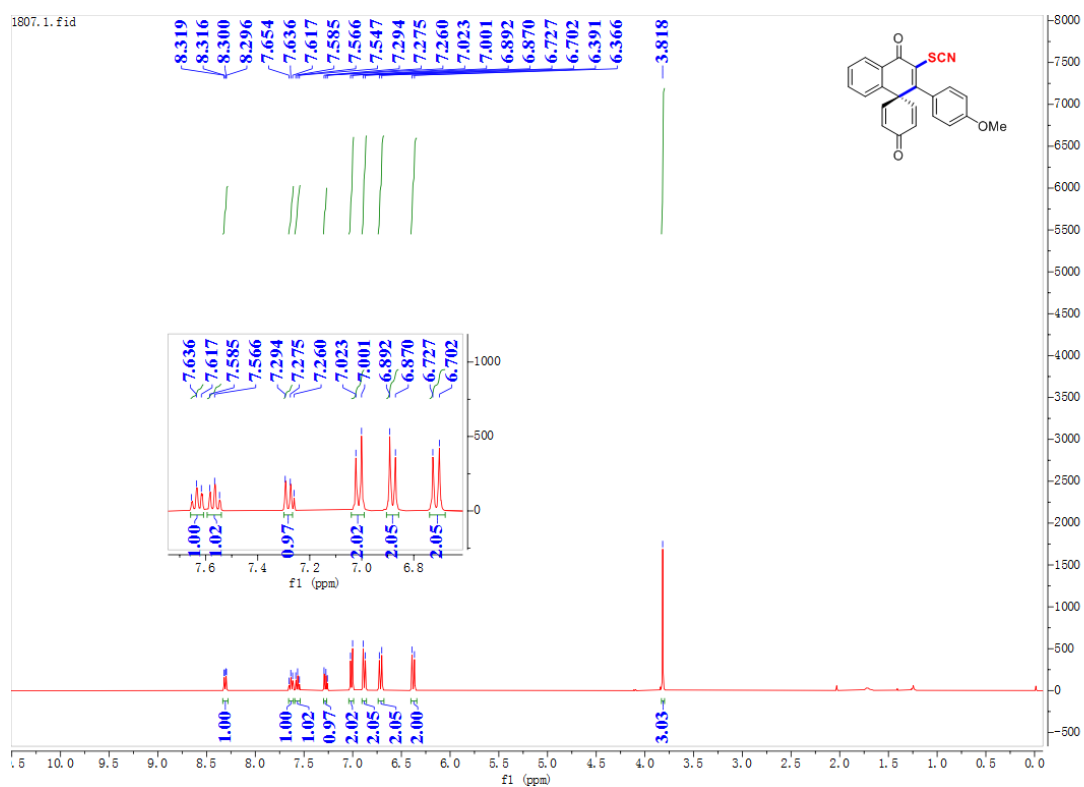
5-¹H NMR



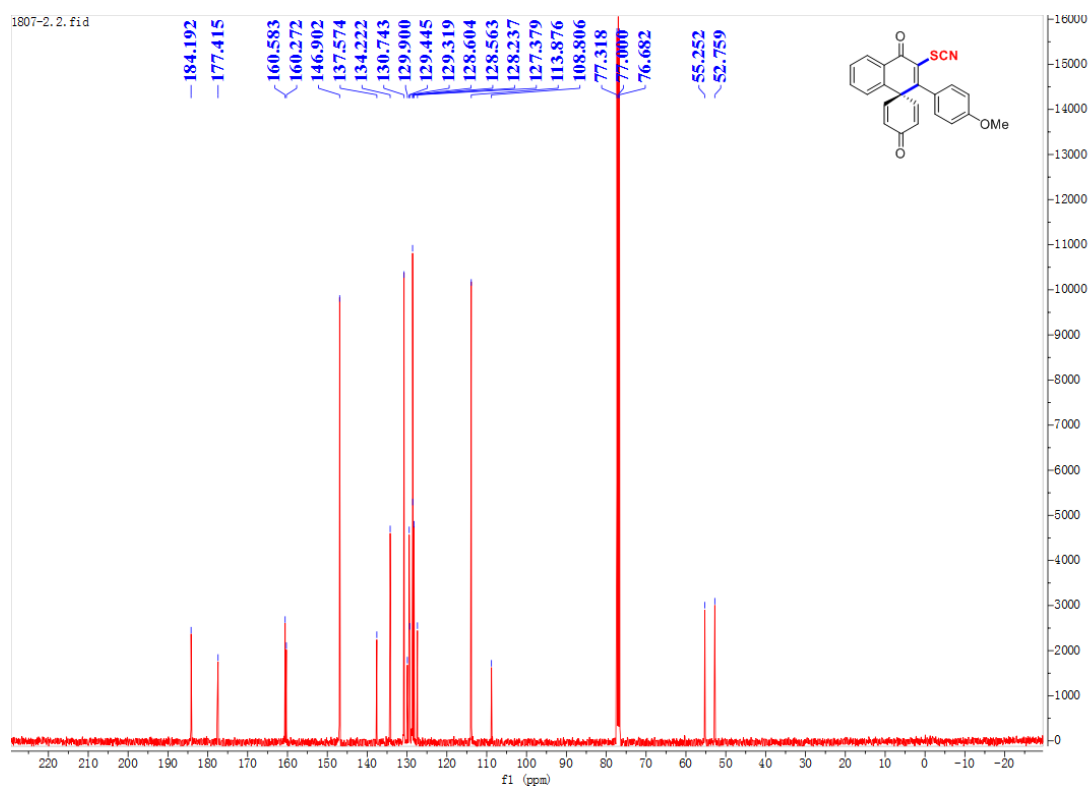
5-¹³C NMR



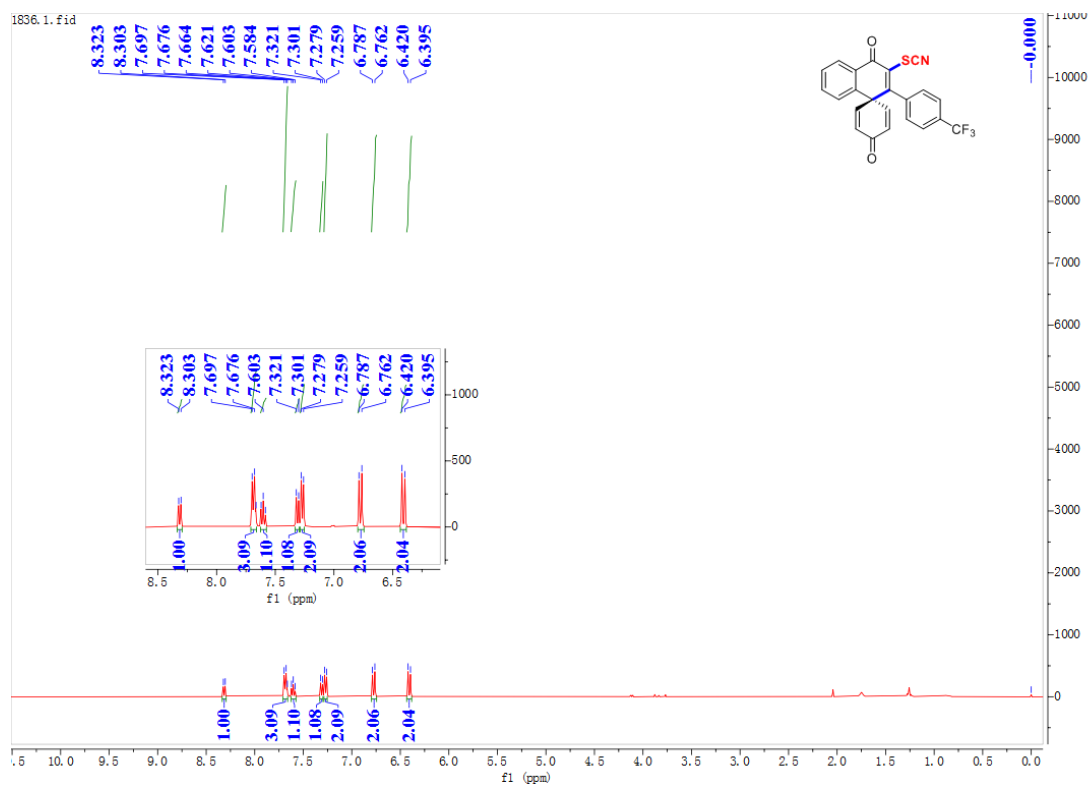
6-¹H NMR



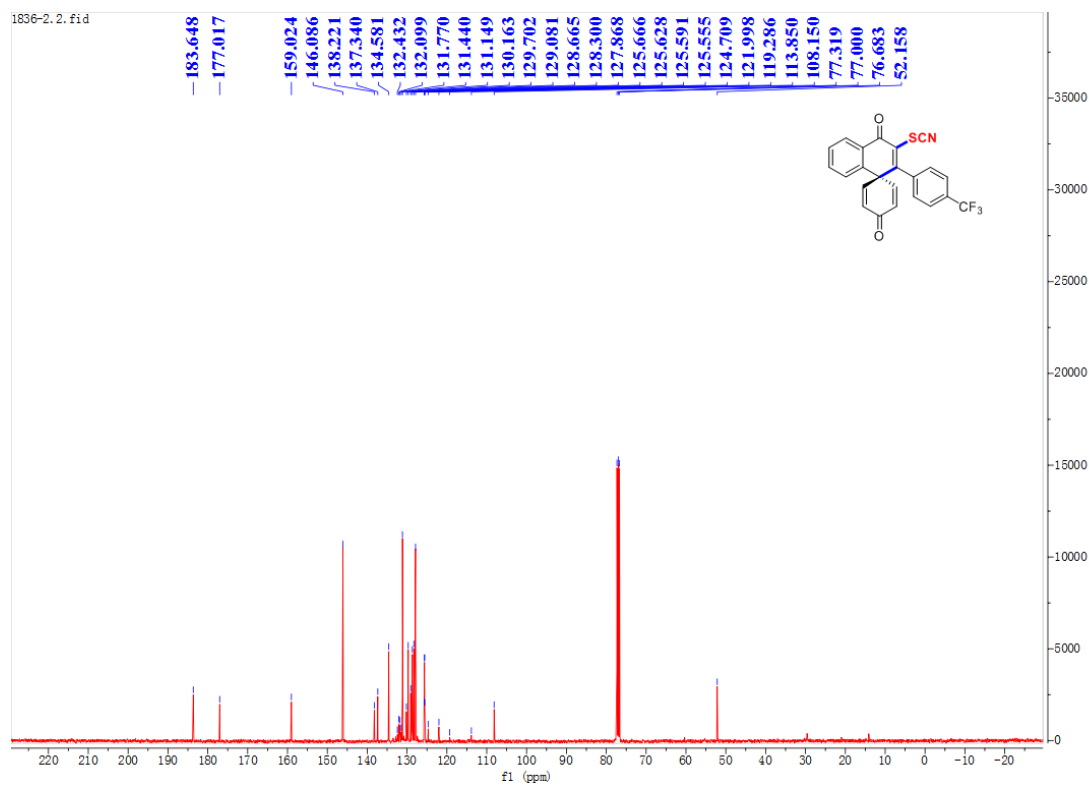
6-¹³C NMR



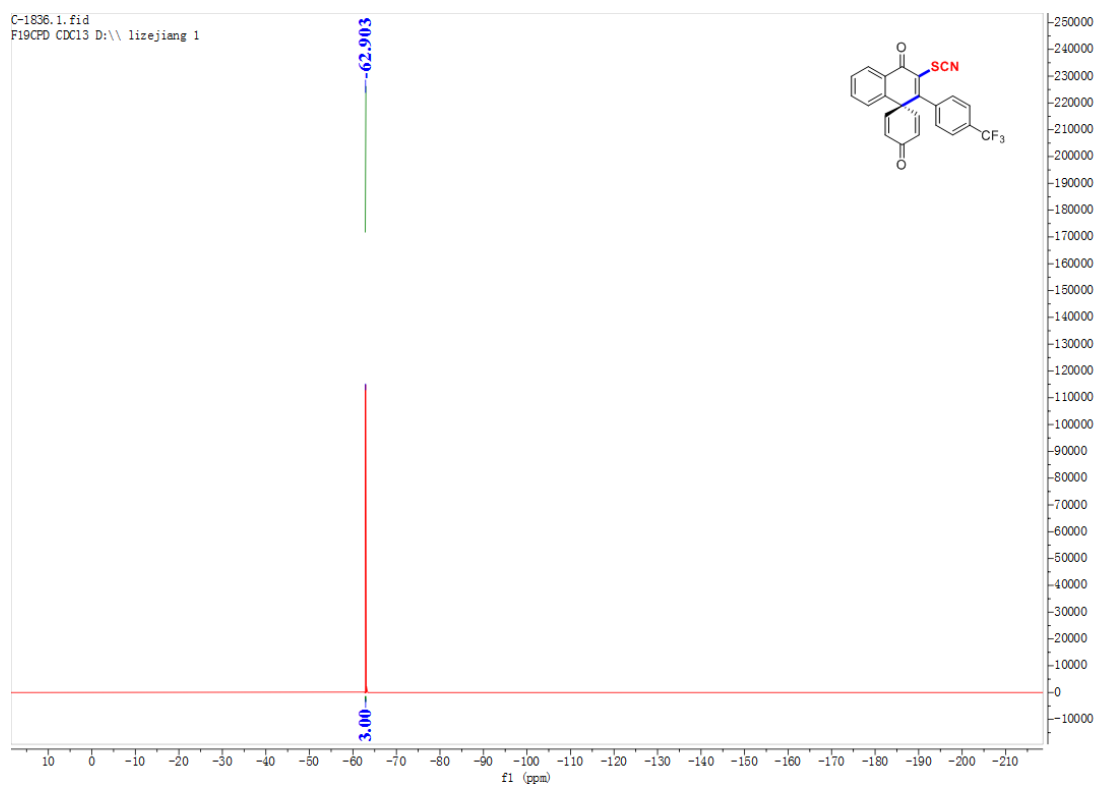
7-¹H NMR



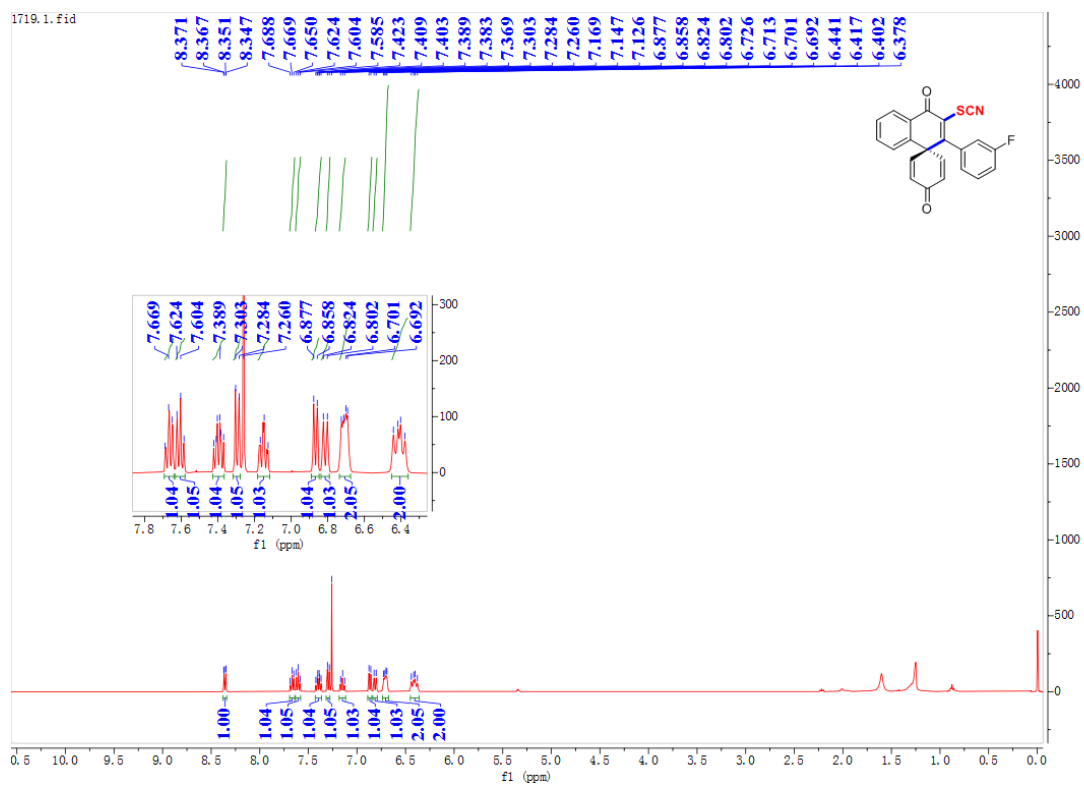
7-¹³C NMR



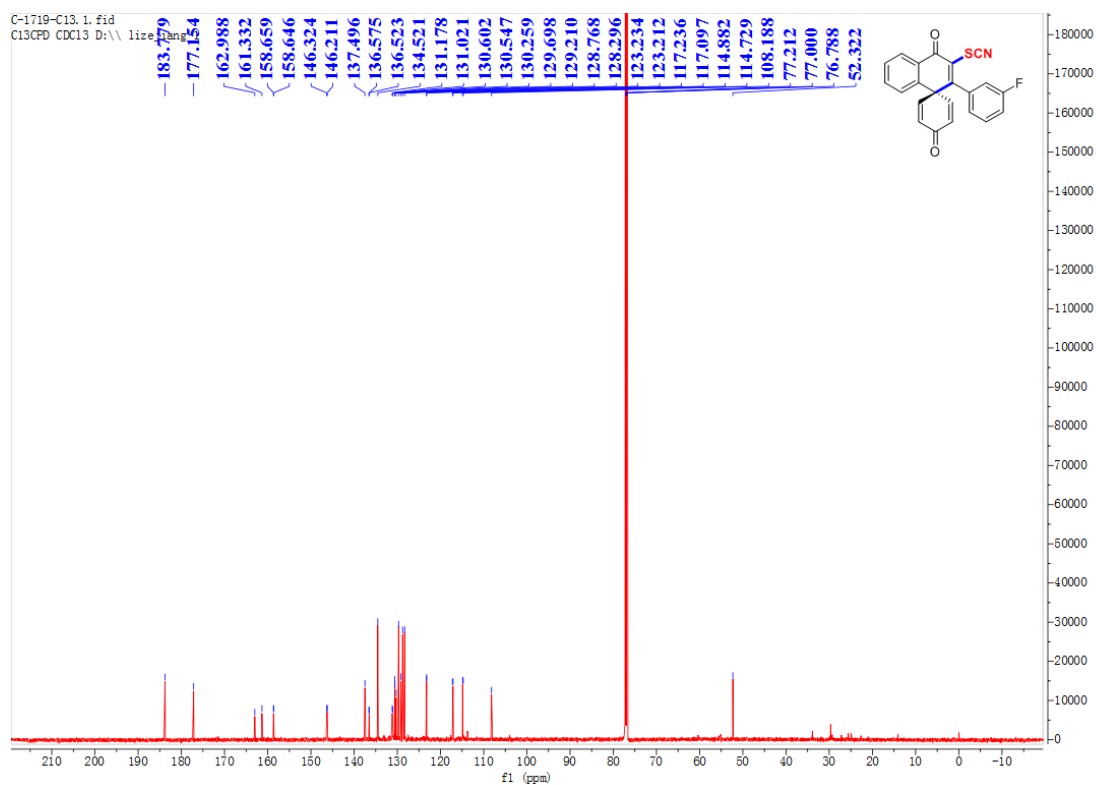
7-¹⁹F NMR



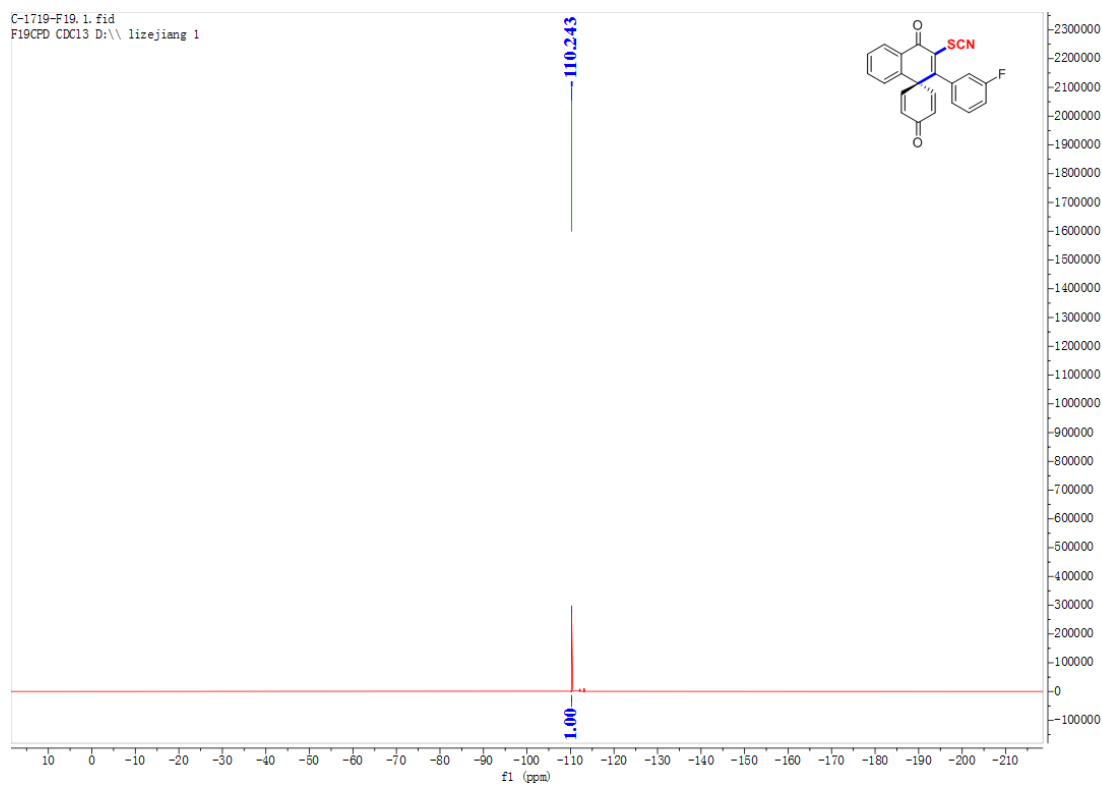
8-¹H NMR



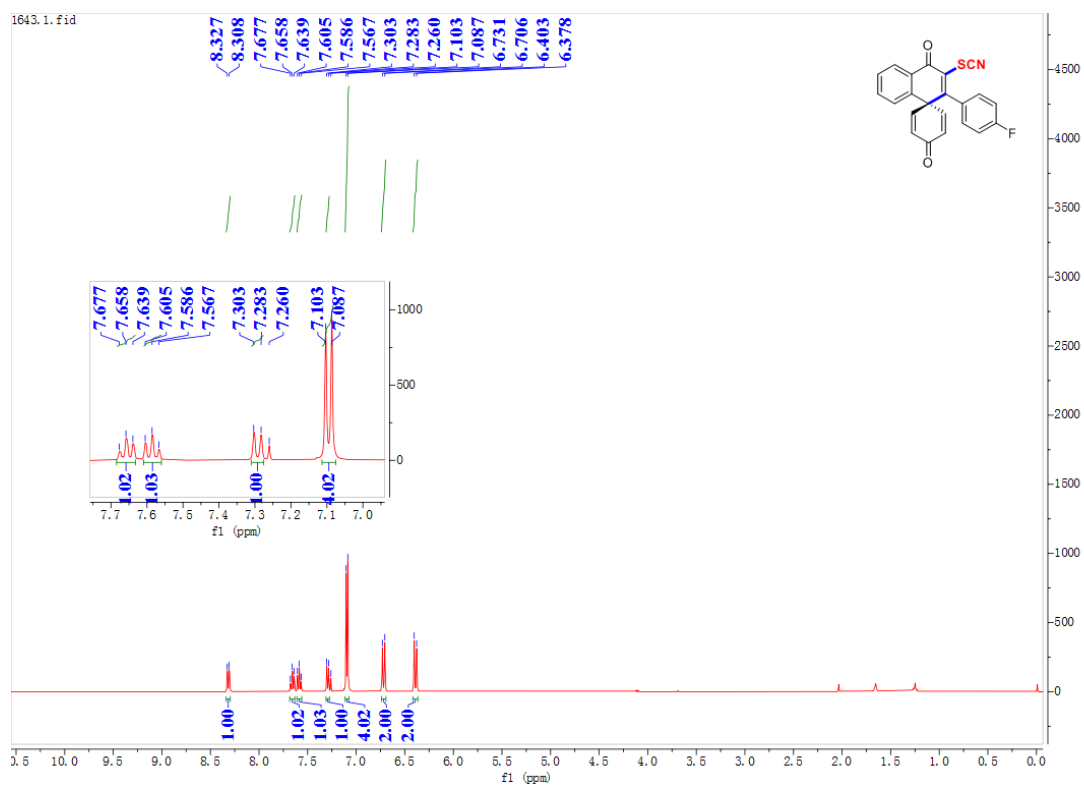
8-¹³C NMR



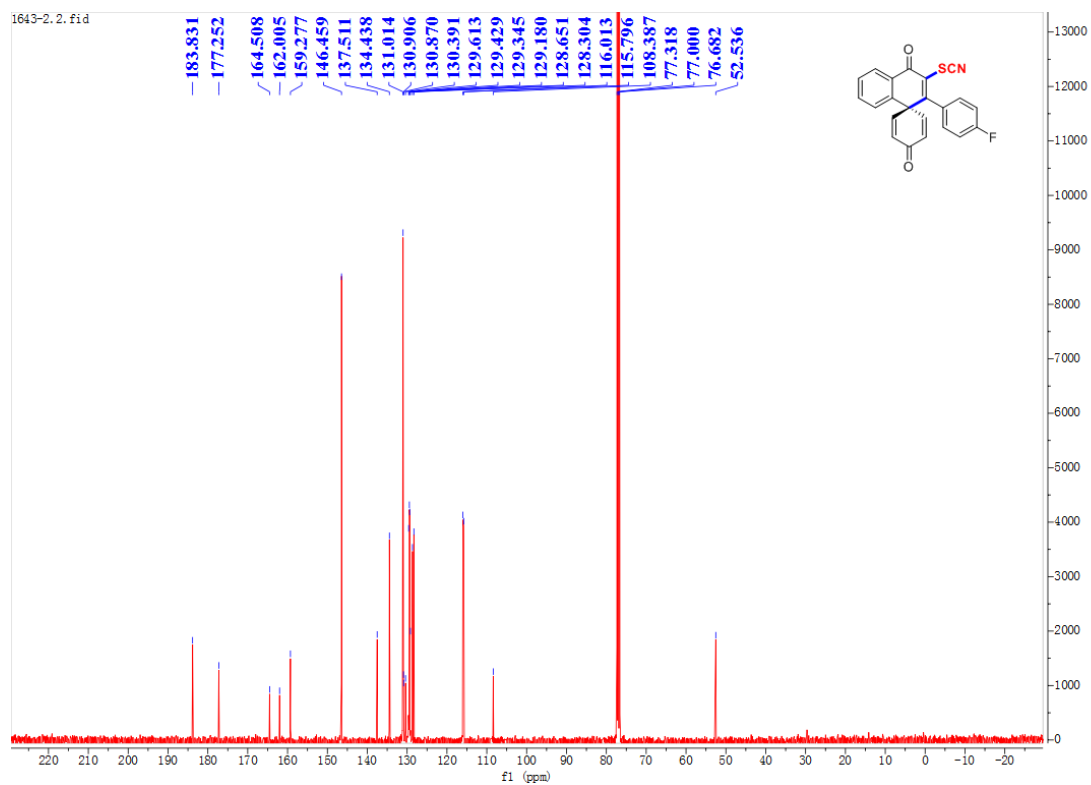
8-¹⁹F NMR



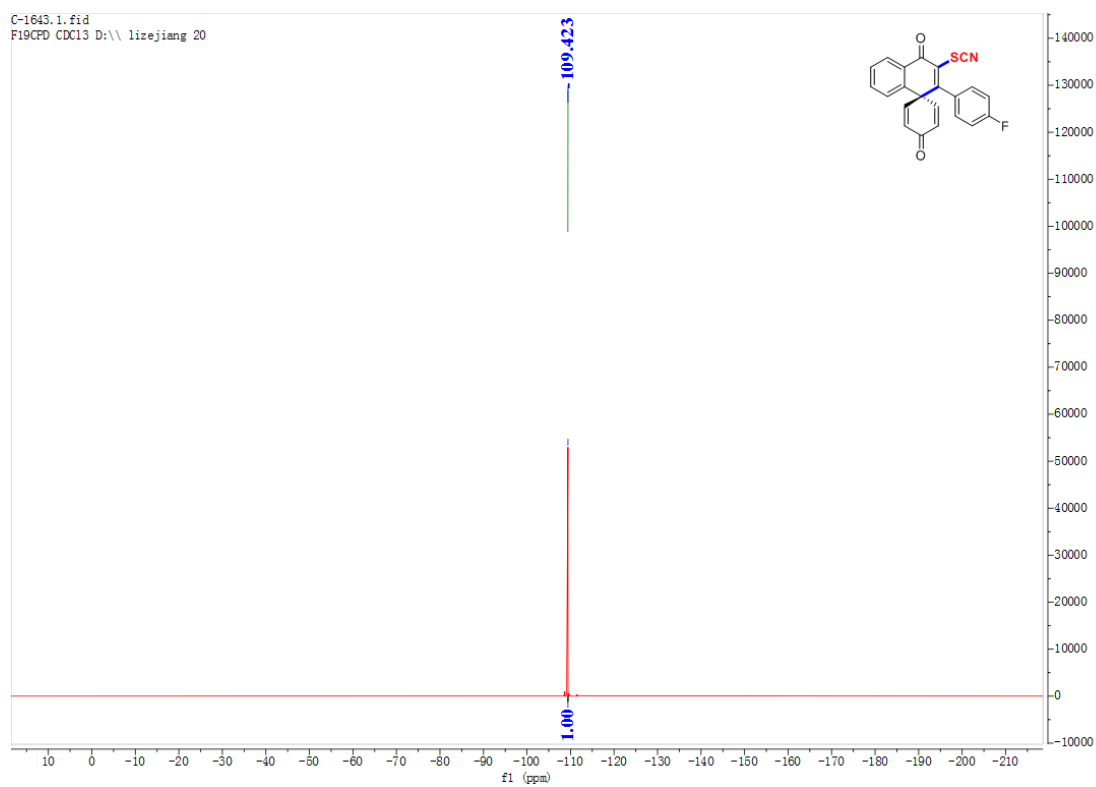
9-¹H NMR



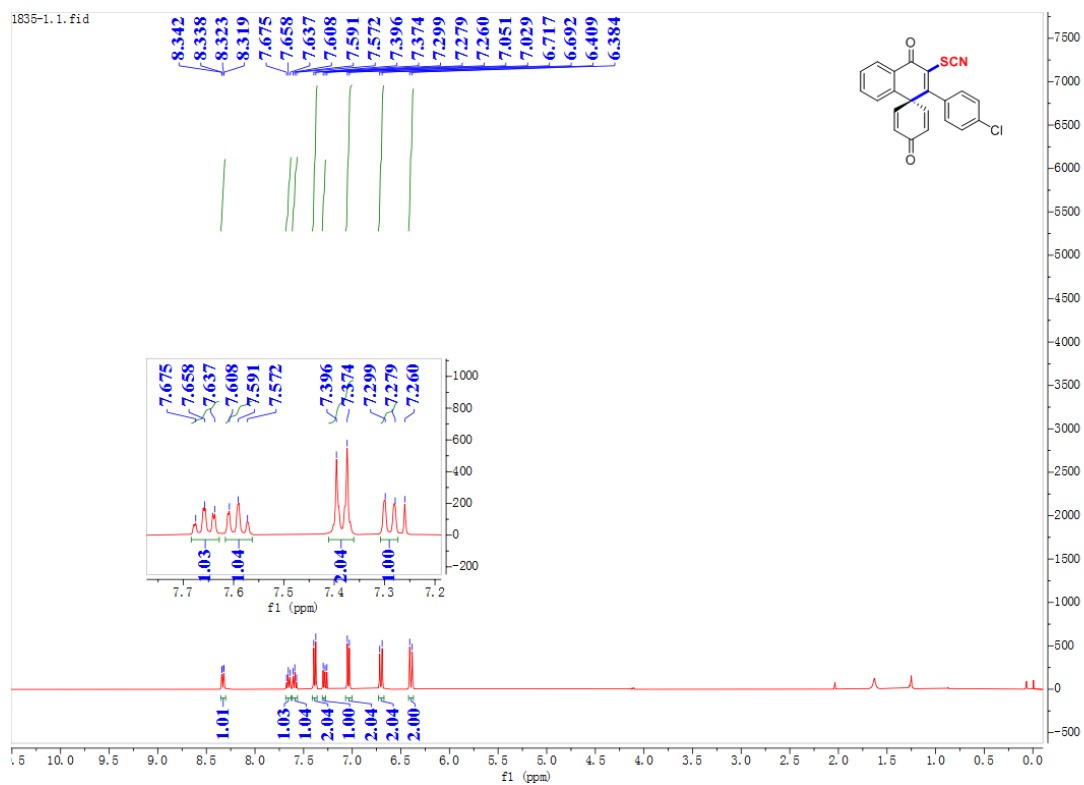
9-¹³C NMR



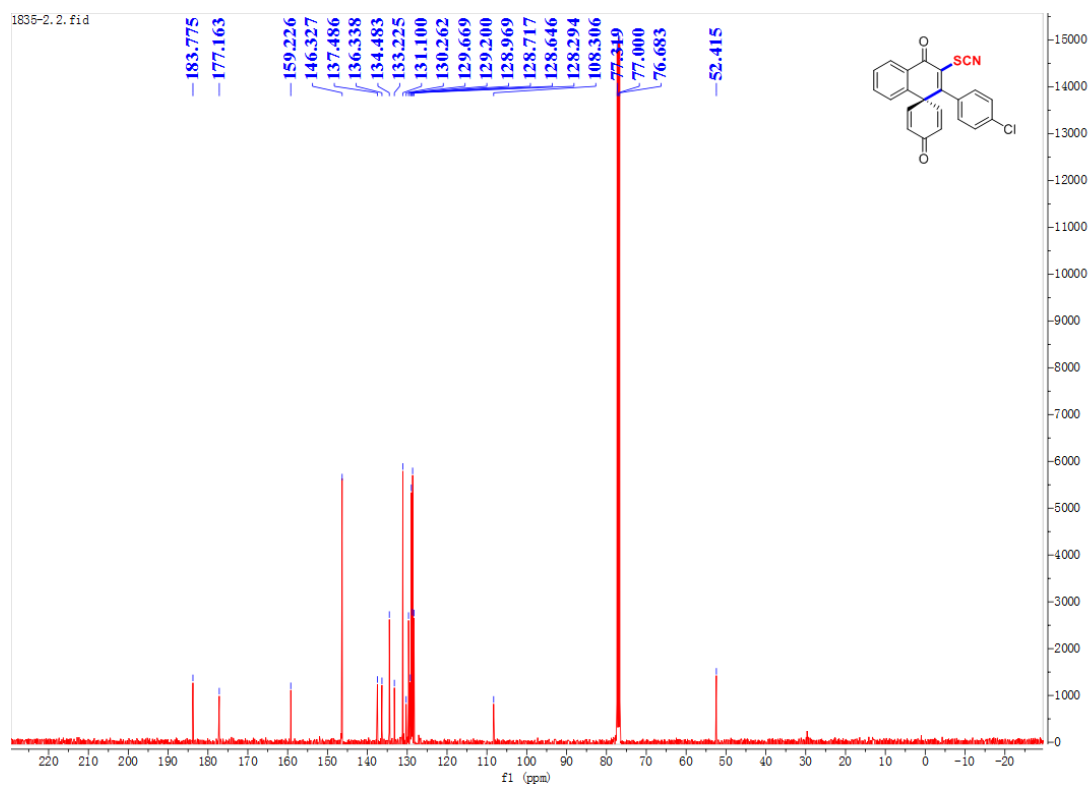
9-¹⁹F NMR



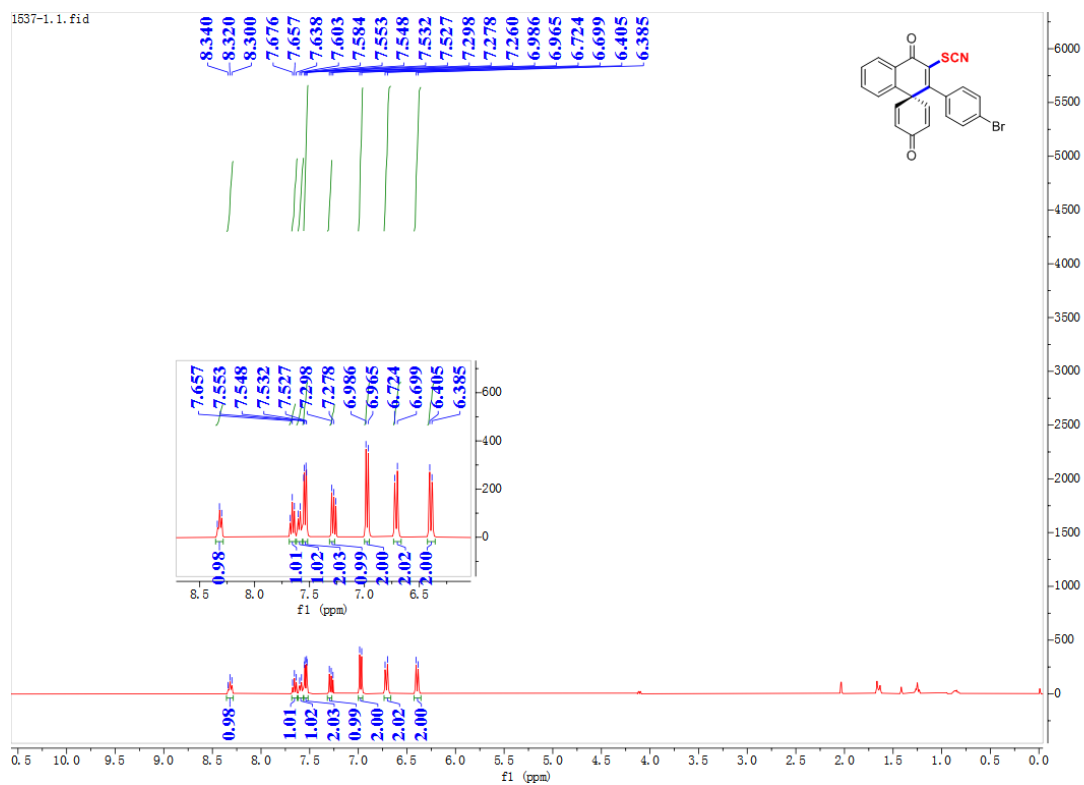
10-¹H NMR



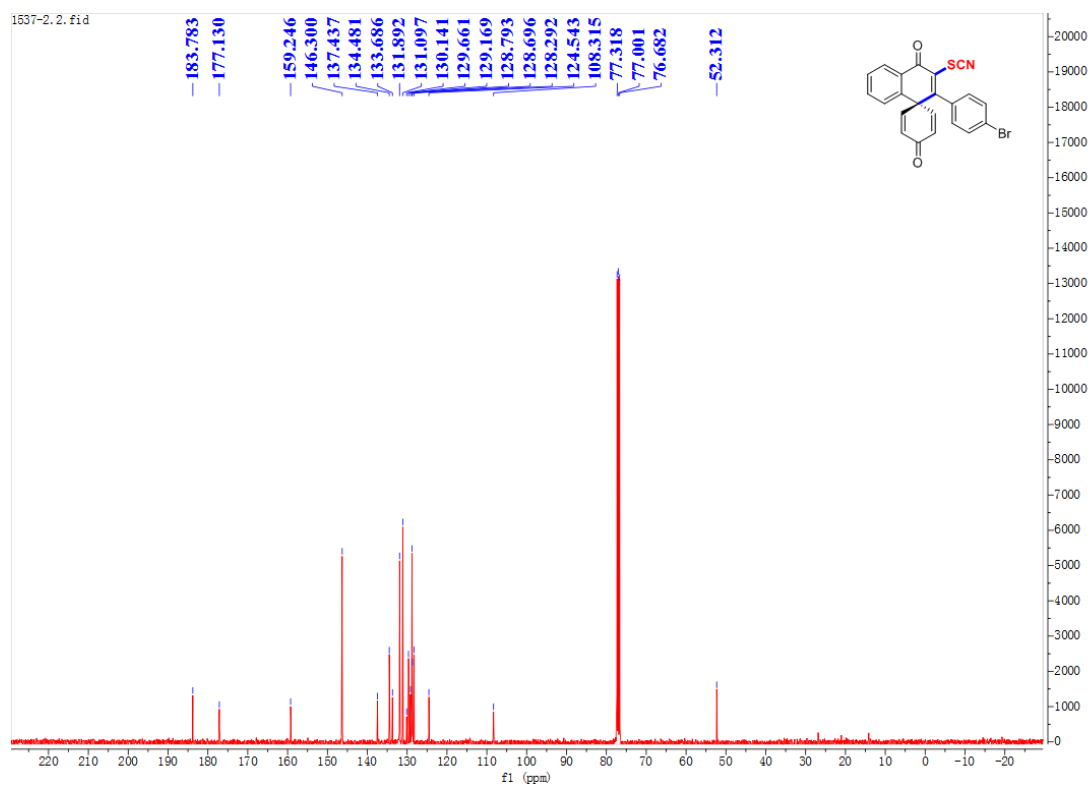
10-¹³C NMR



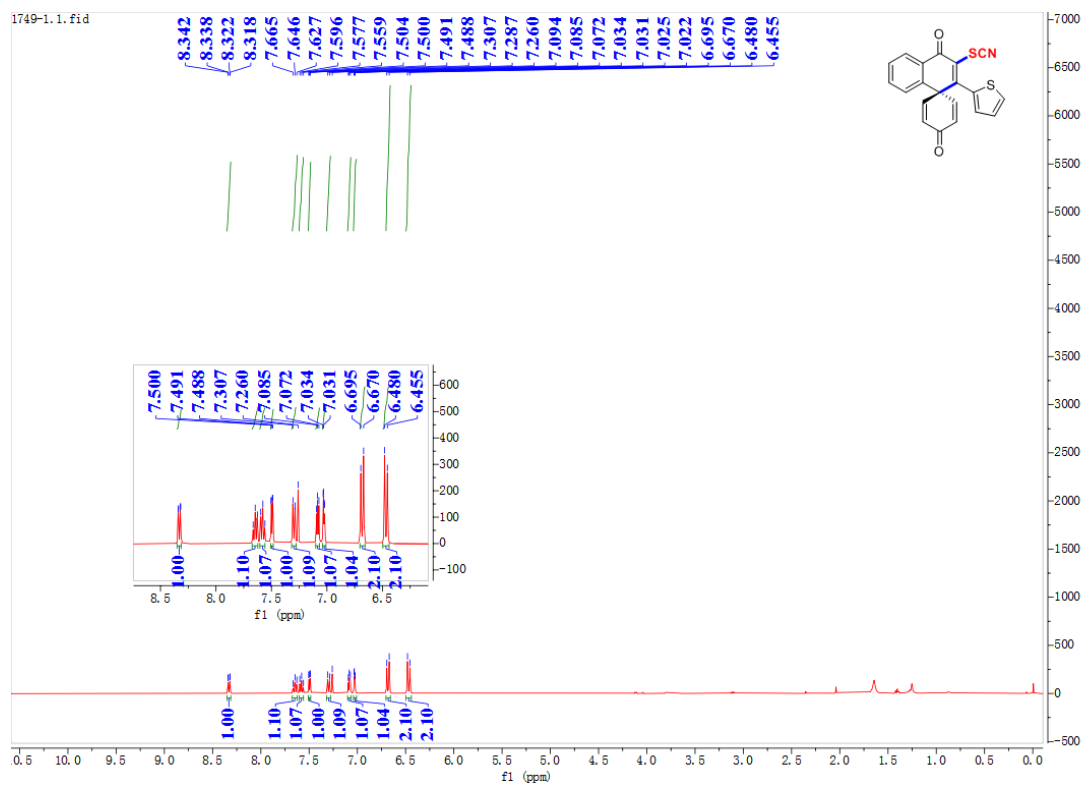
11-¹H NMR



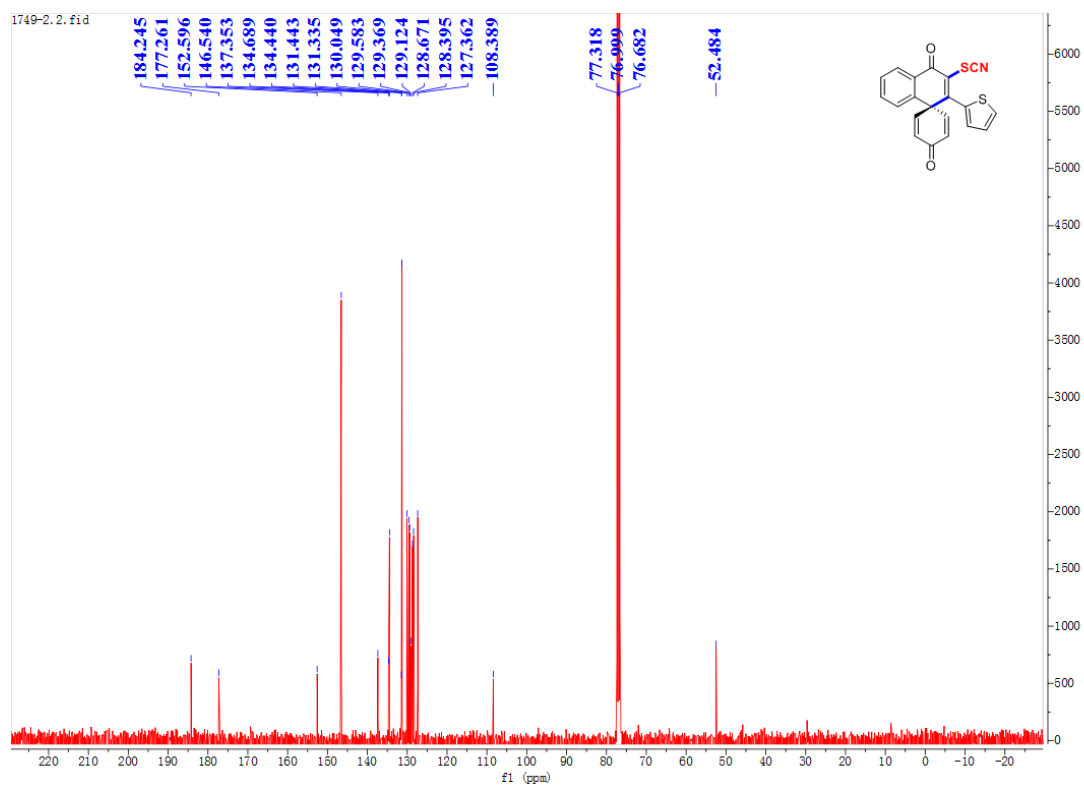
11-¹³C NMR



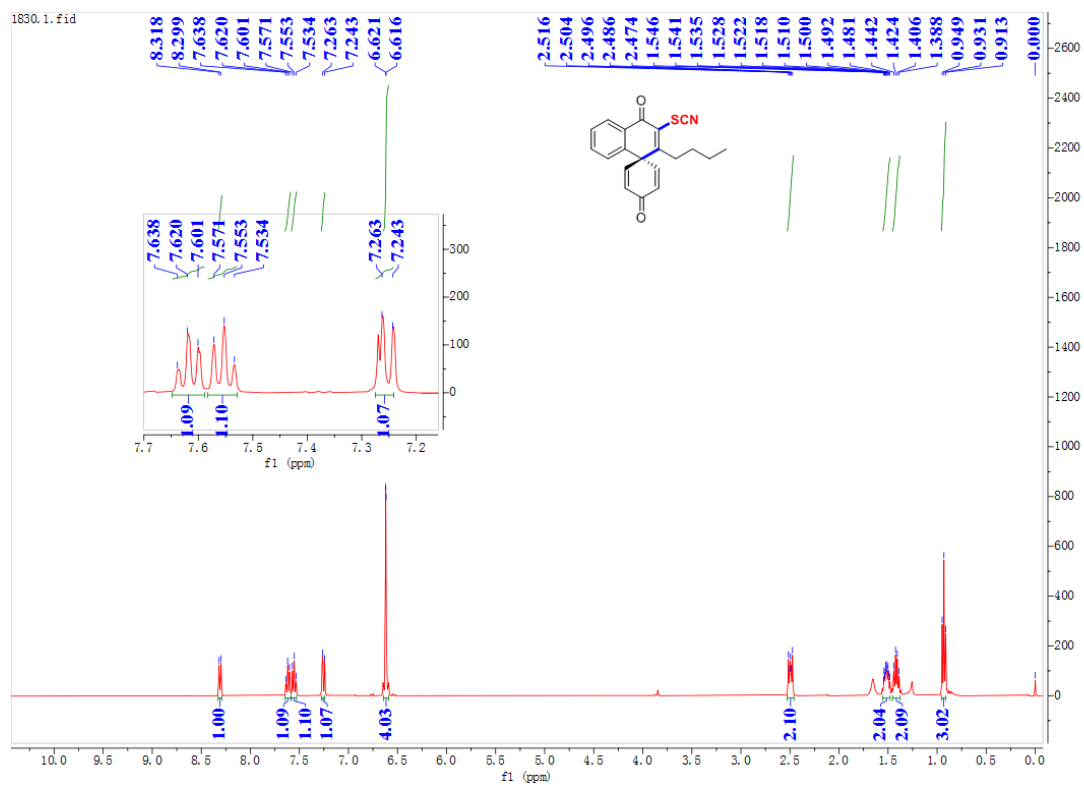
12-¹H NMR



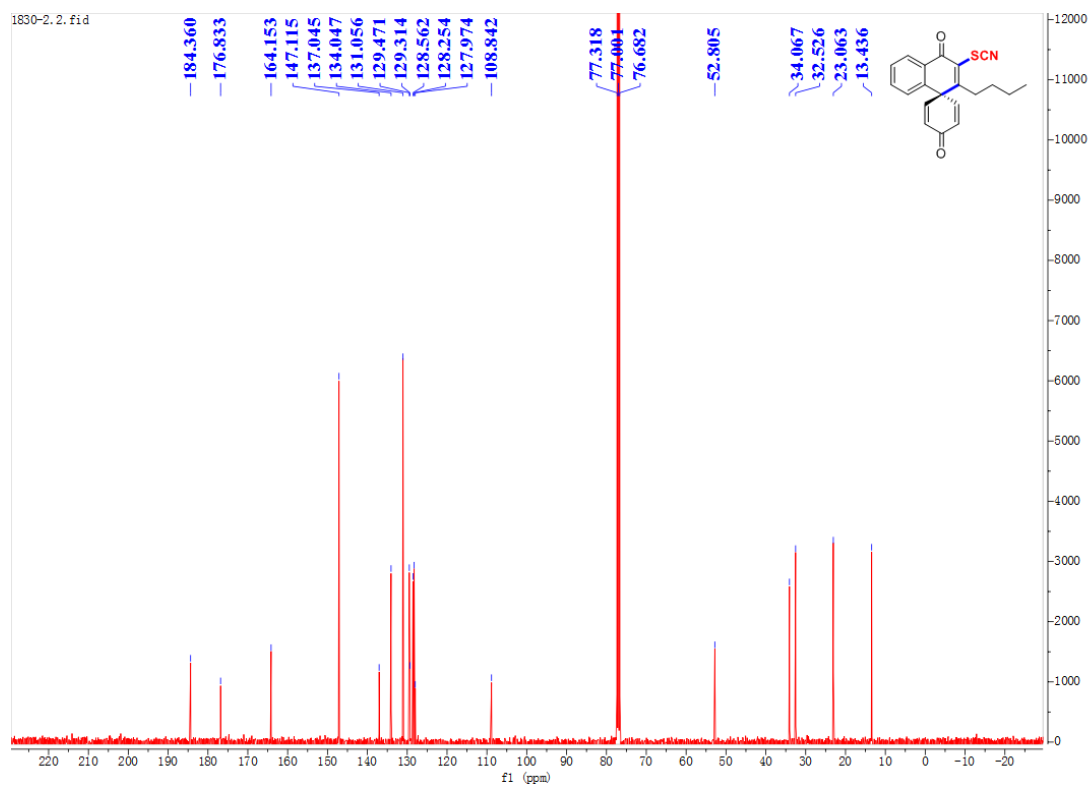
12-¹³C NMR



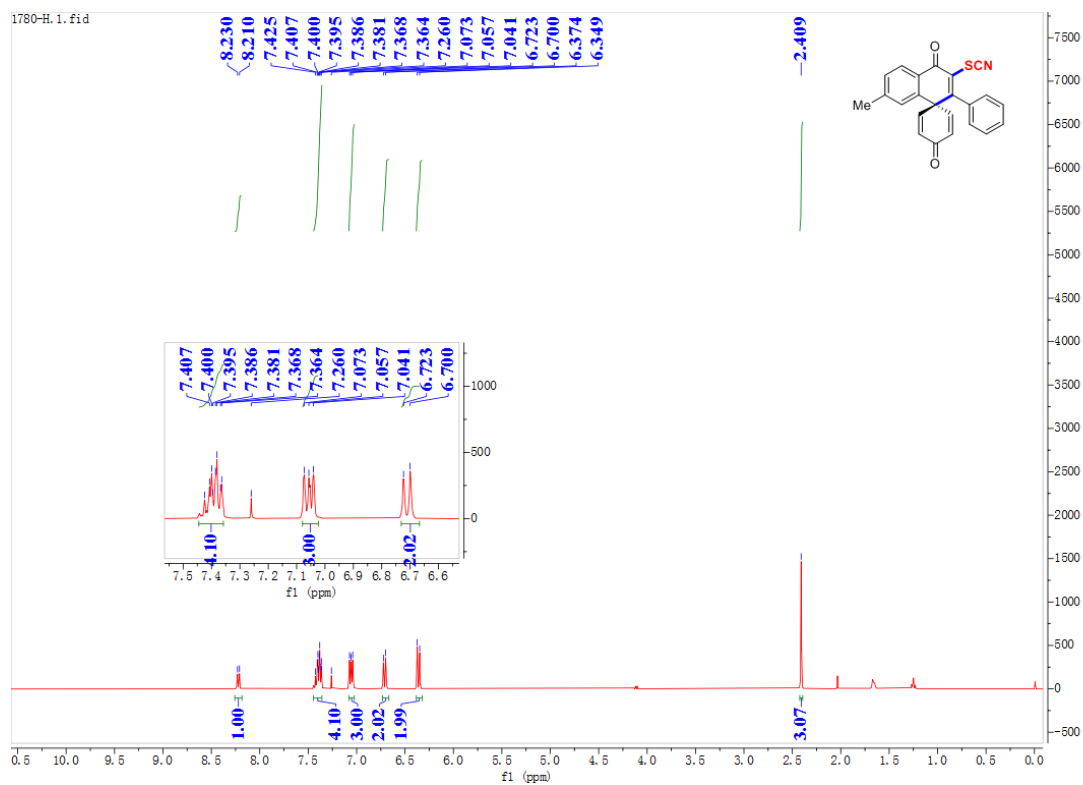
13-¹H NMR



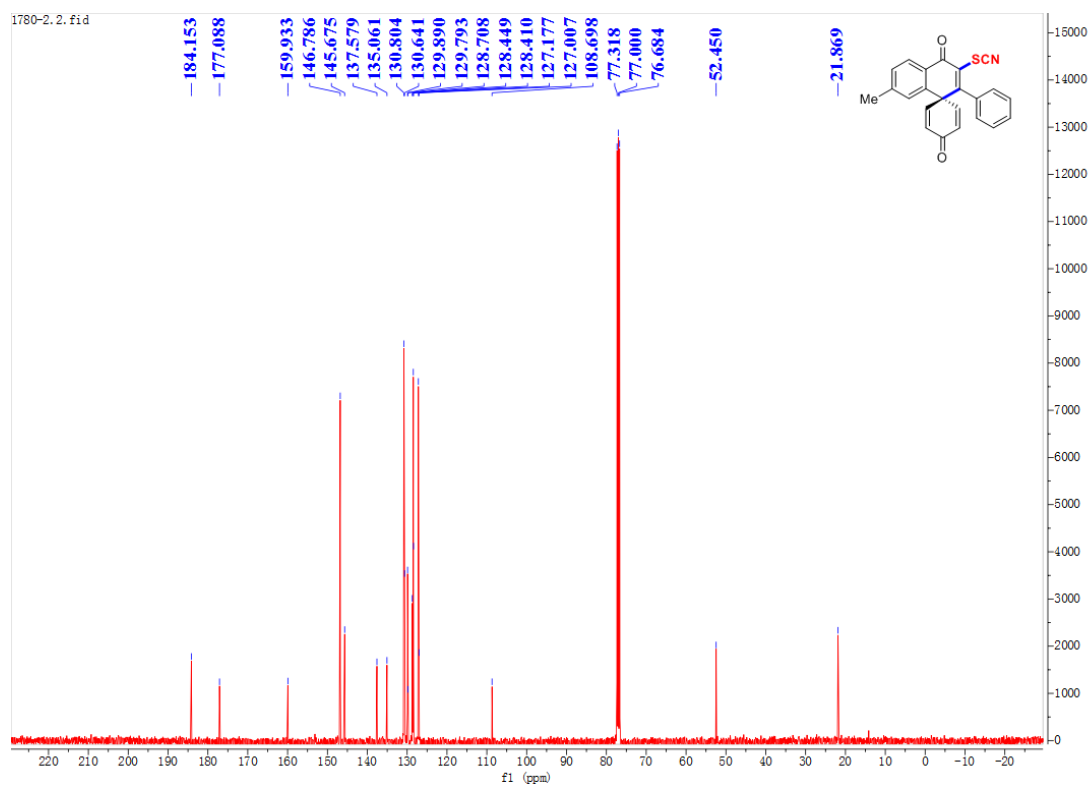
13-¹³C NMR



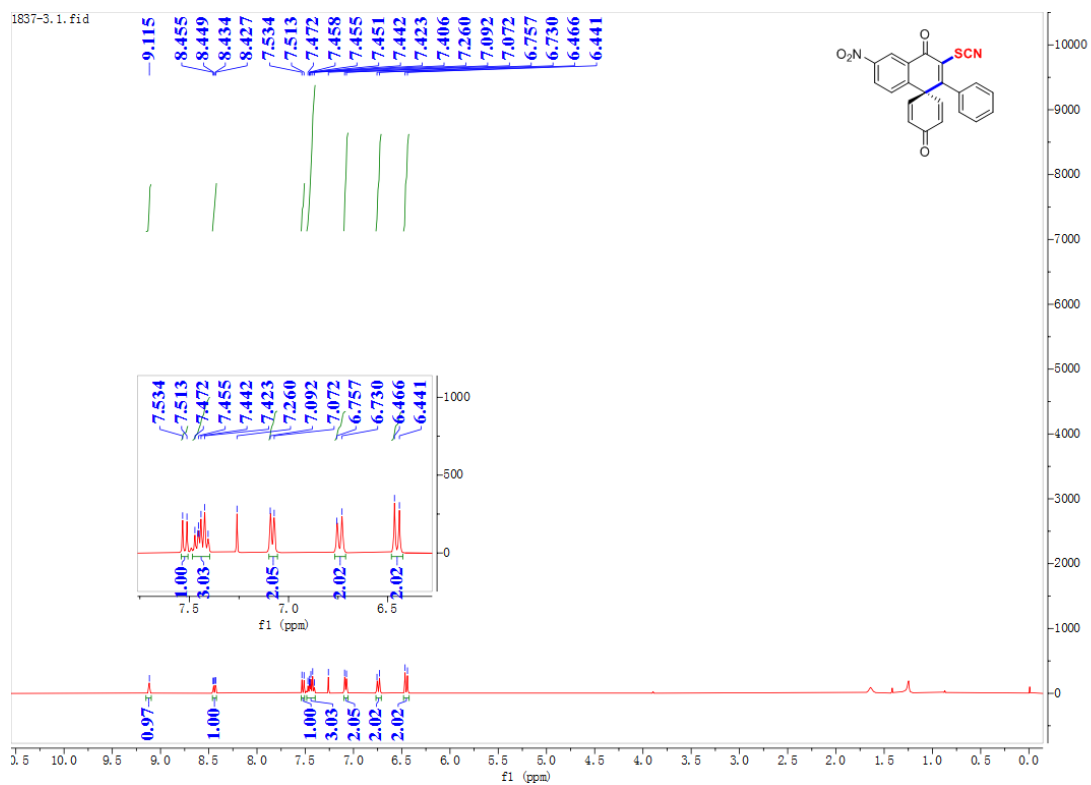
14-¹H NMR



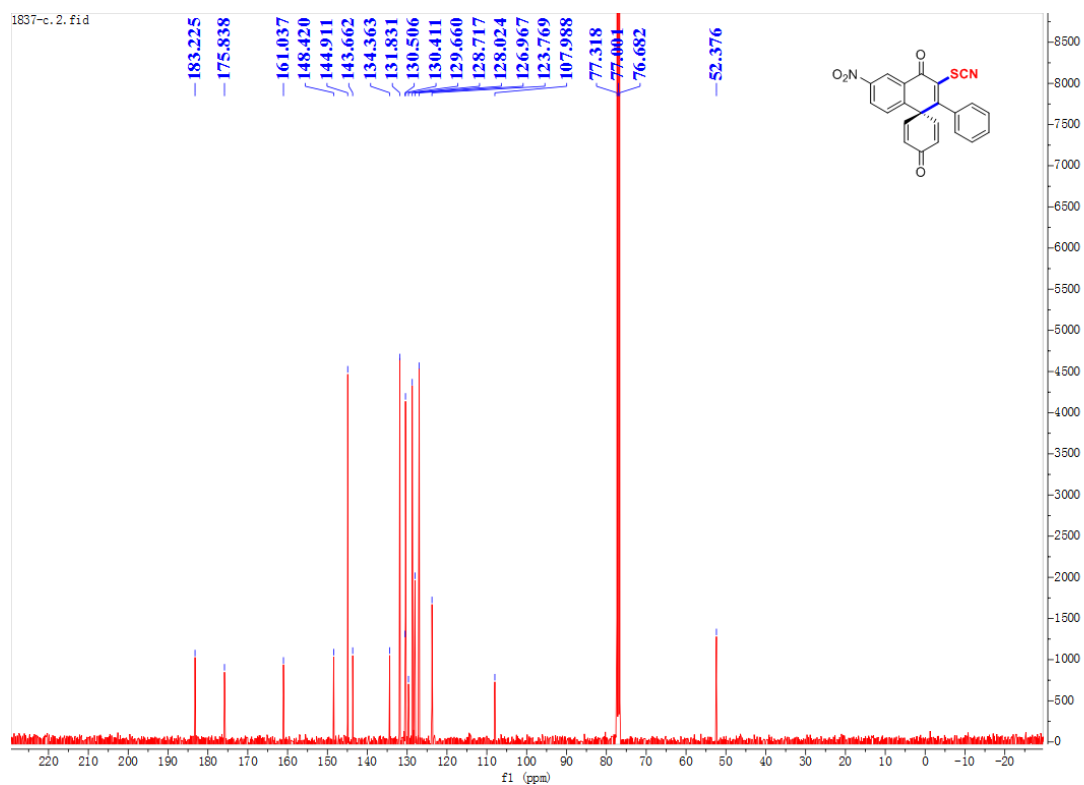
14-¹³C NMR



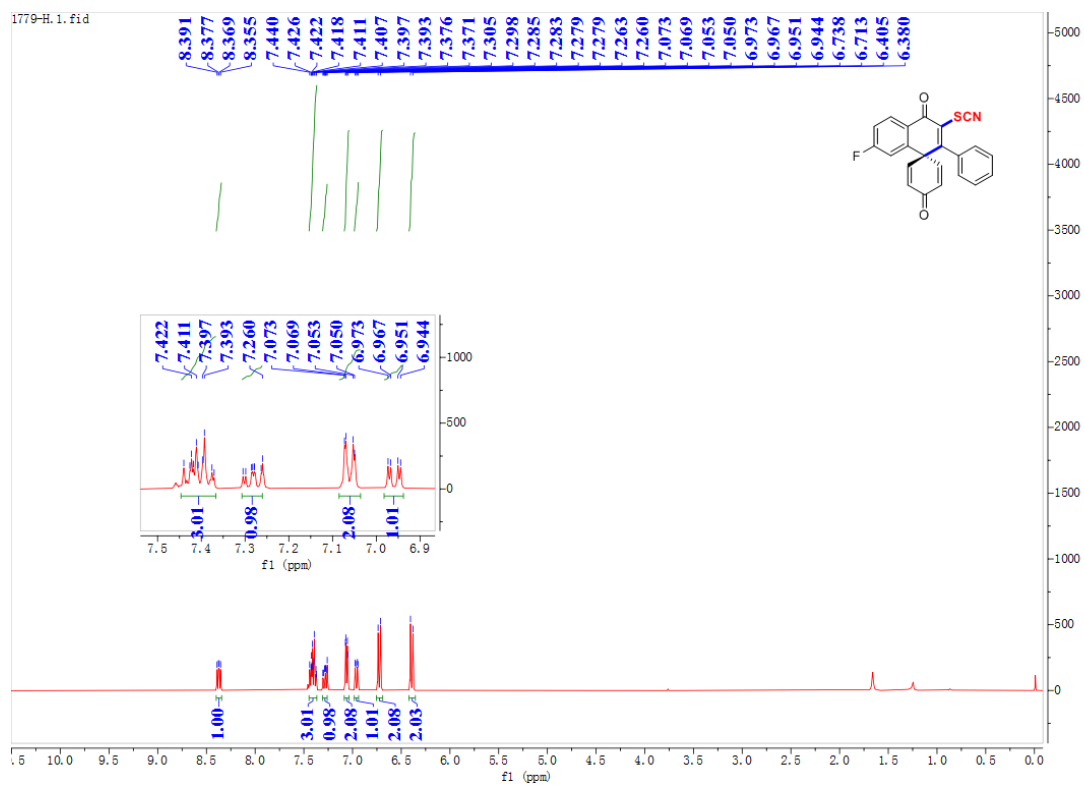
15-¹H NMR



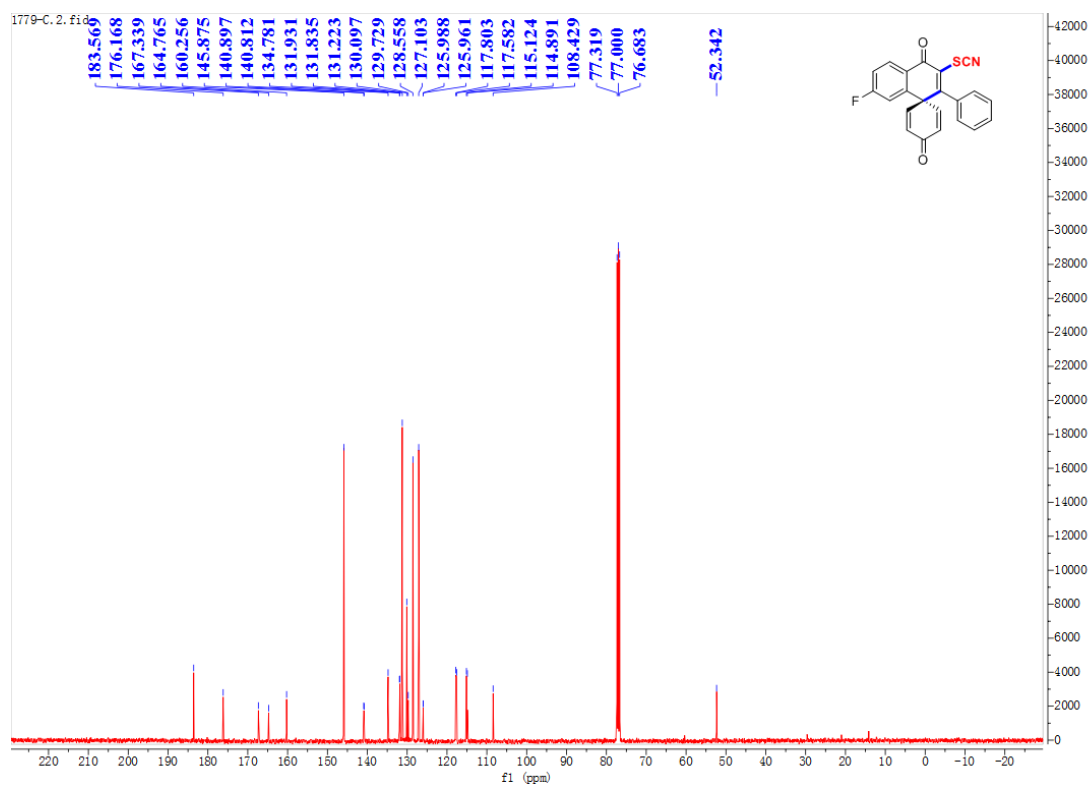
15-¹³C NMR



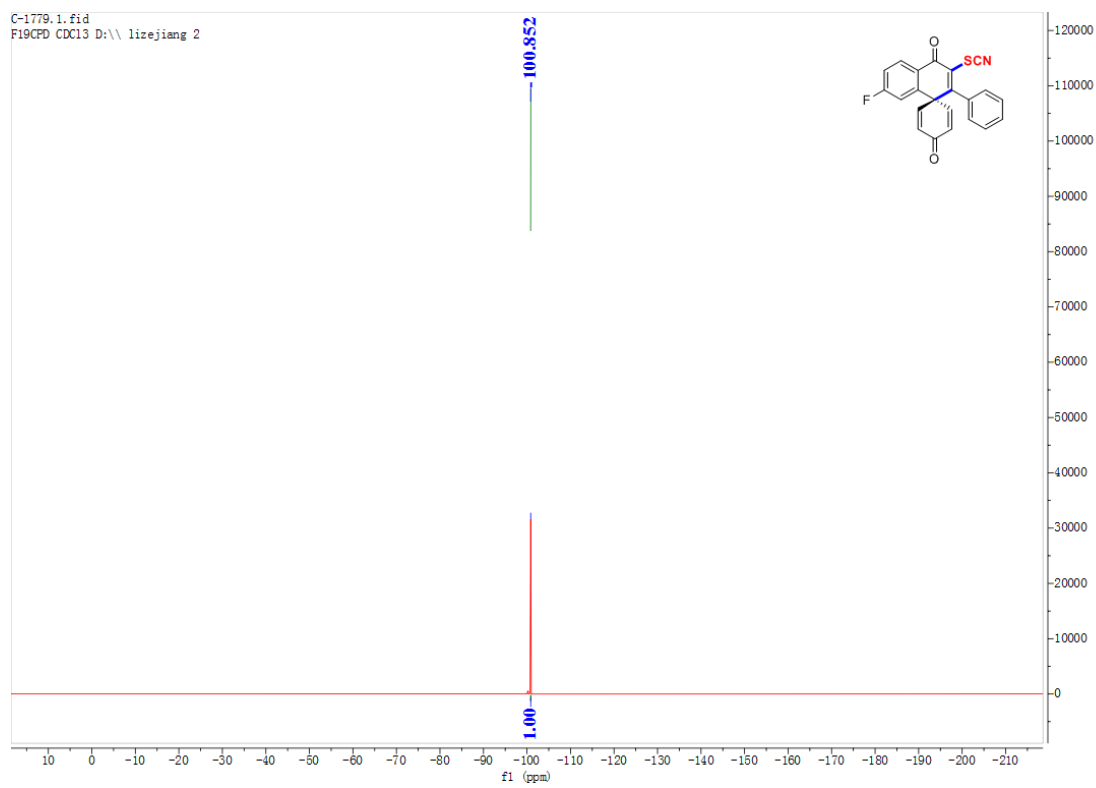
16-¹H NMR



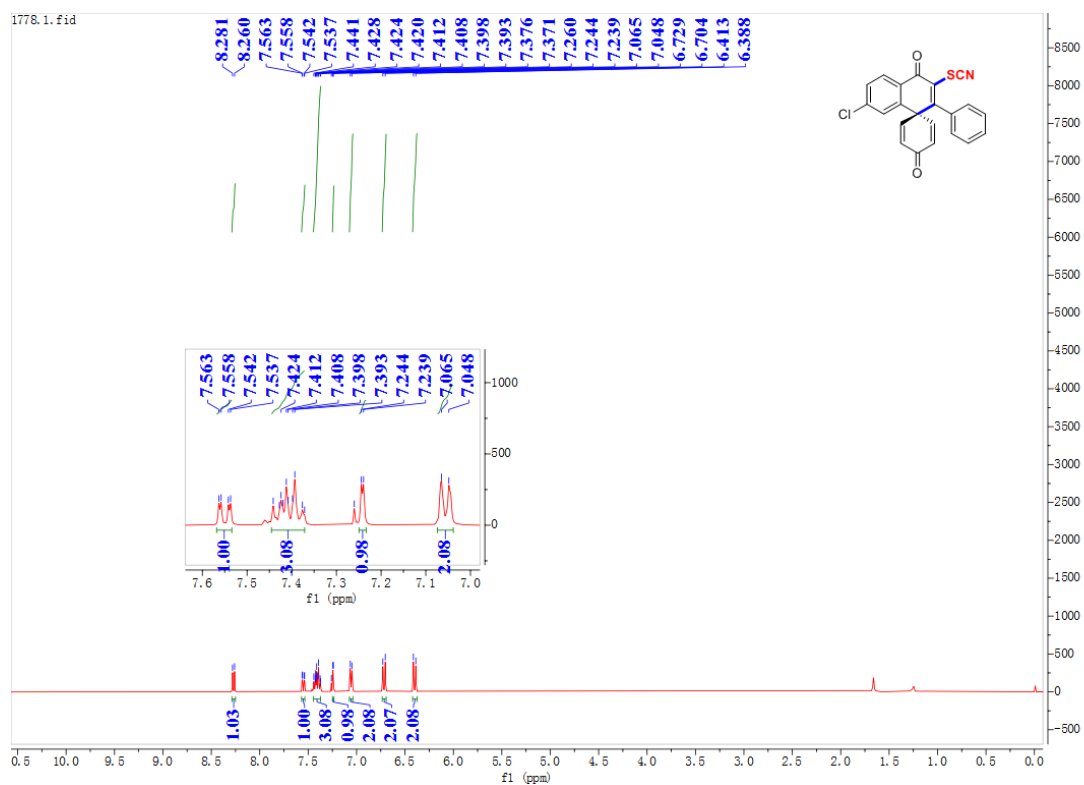
16-¹³C NMR



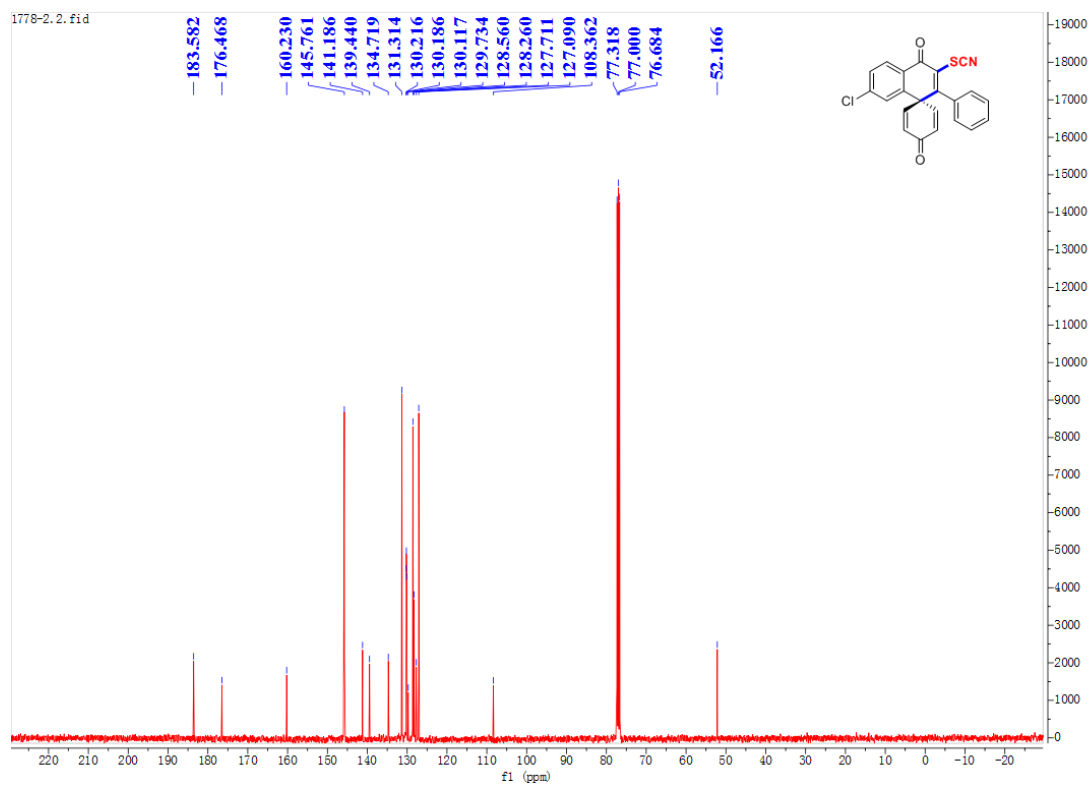
16-¹⁹F NMR



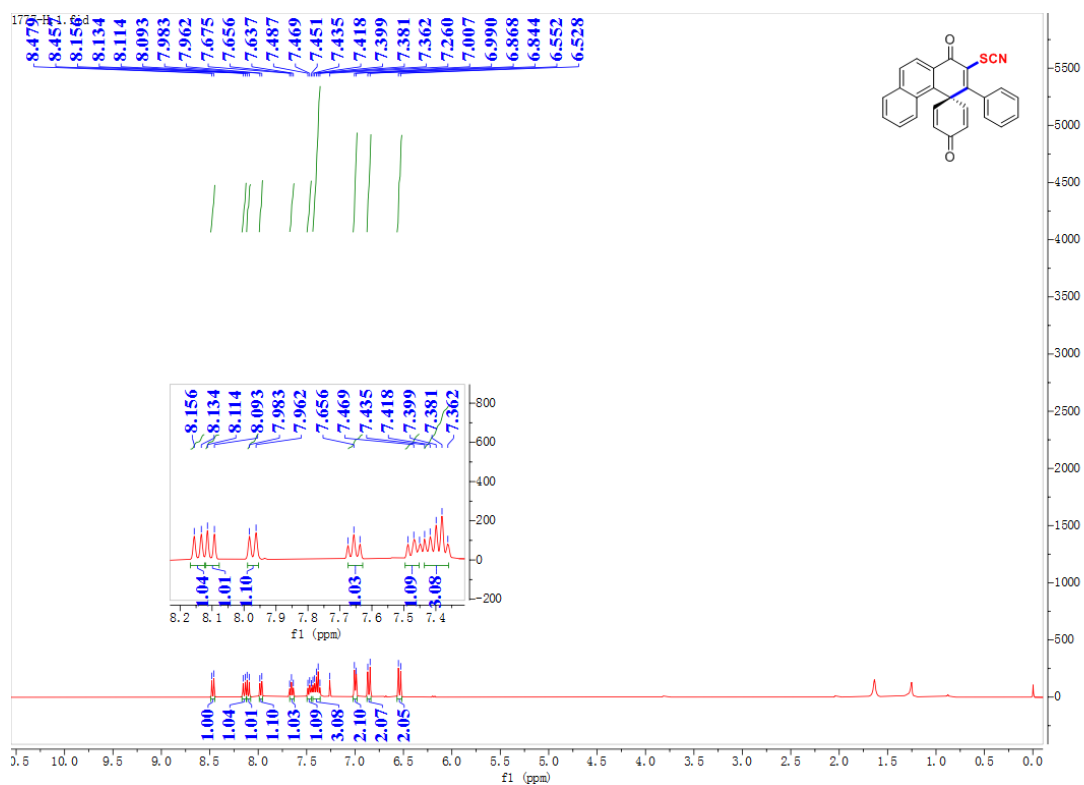
17-¹H NMR



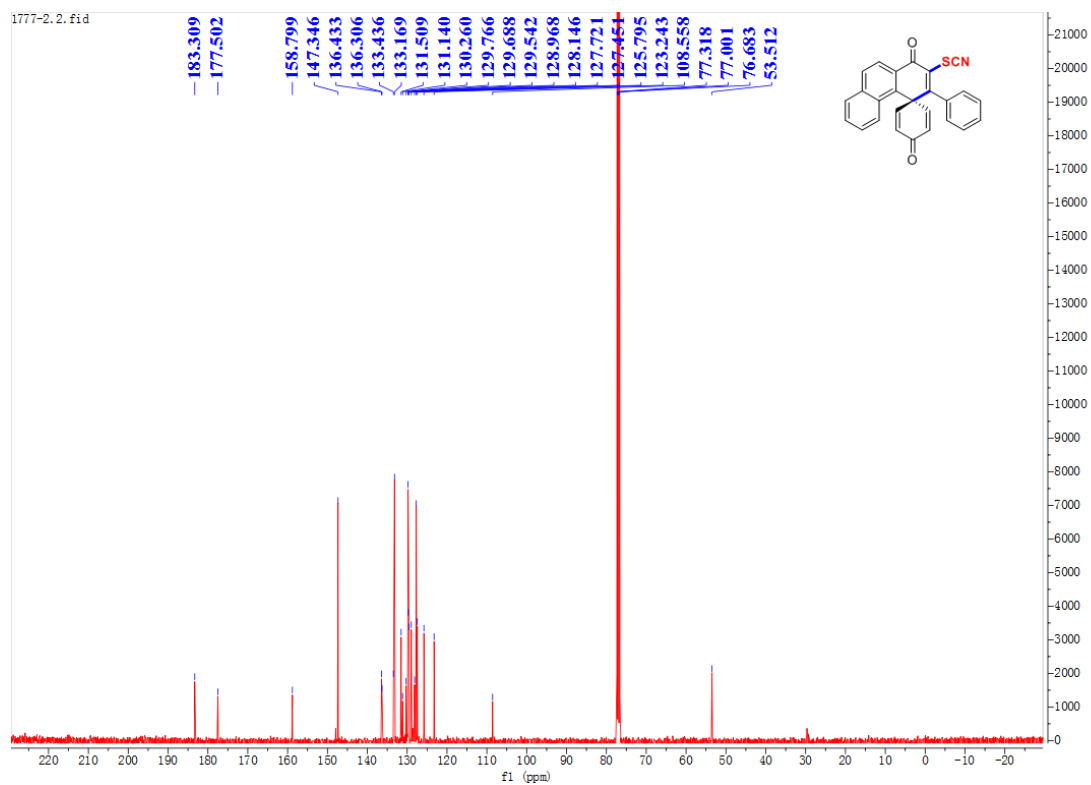
17-¹³C NMR



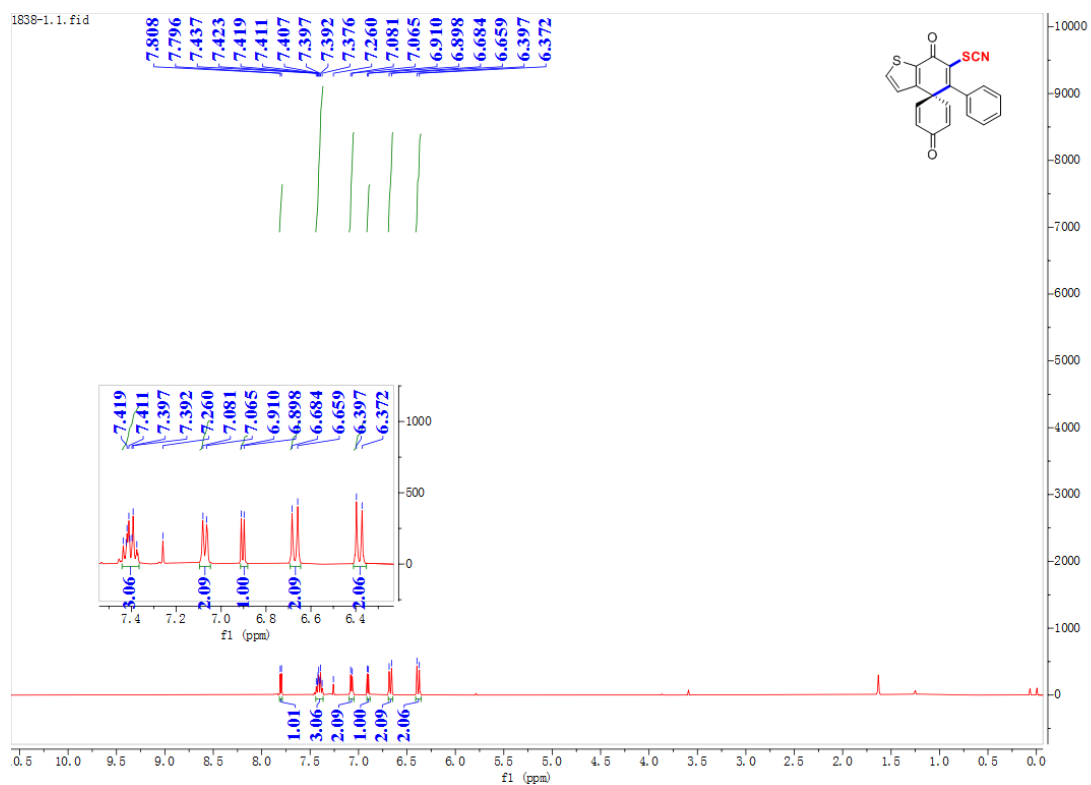
18-¹H NMR



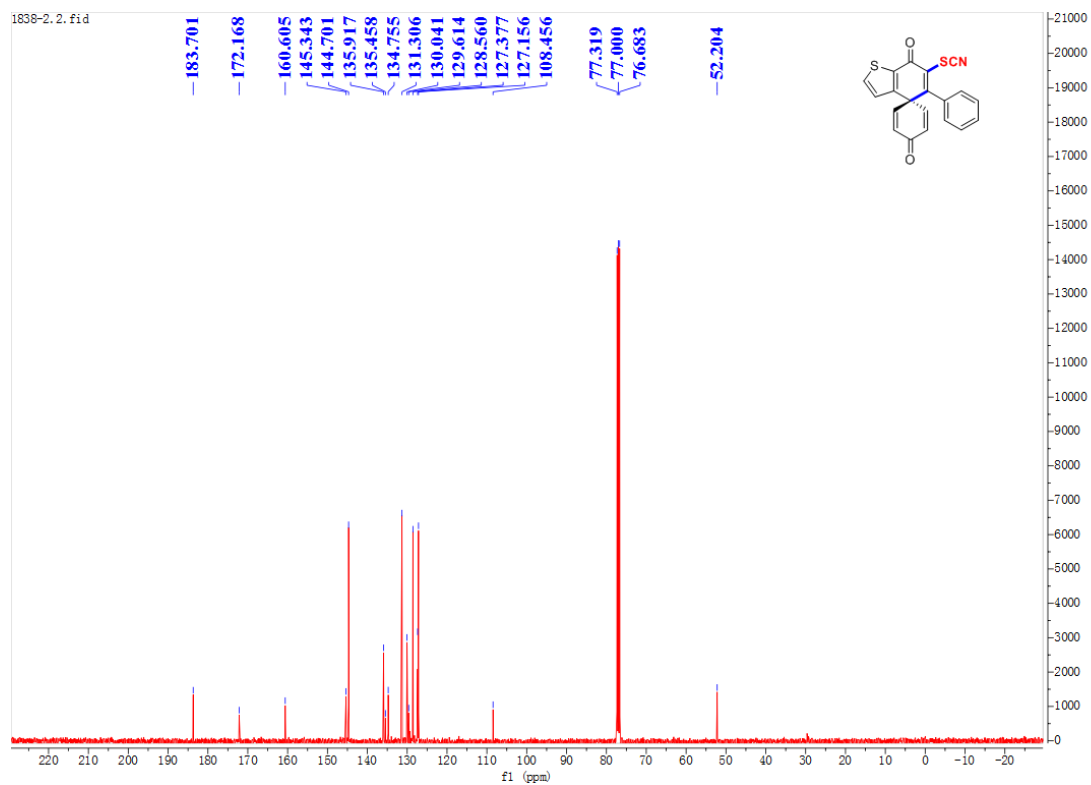
18-¹³C NMR



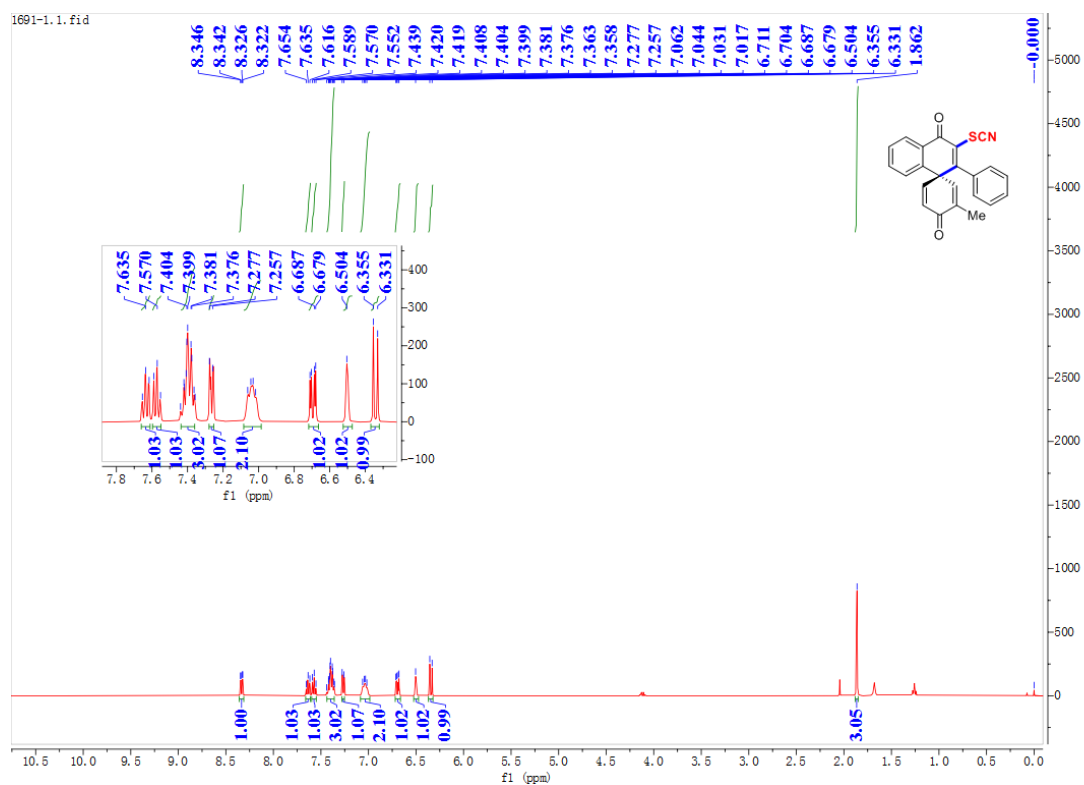
19-¹H NMR



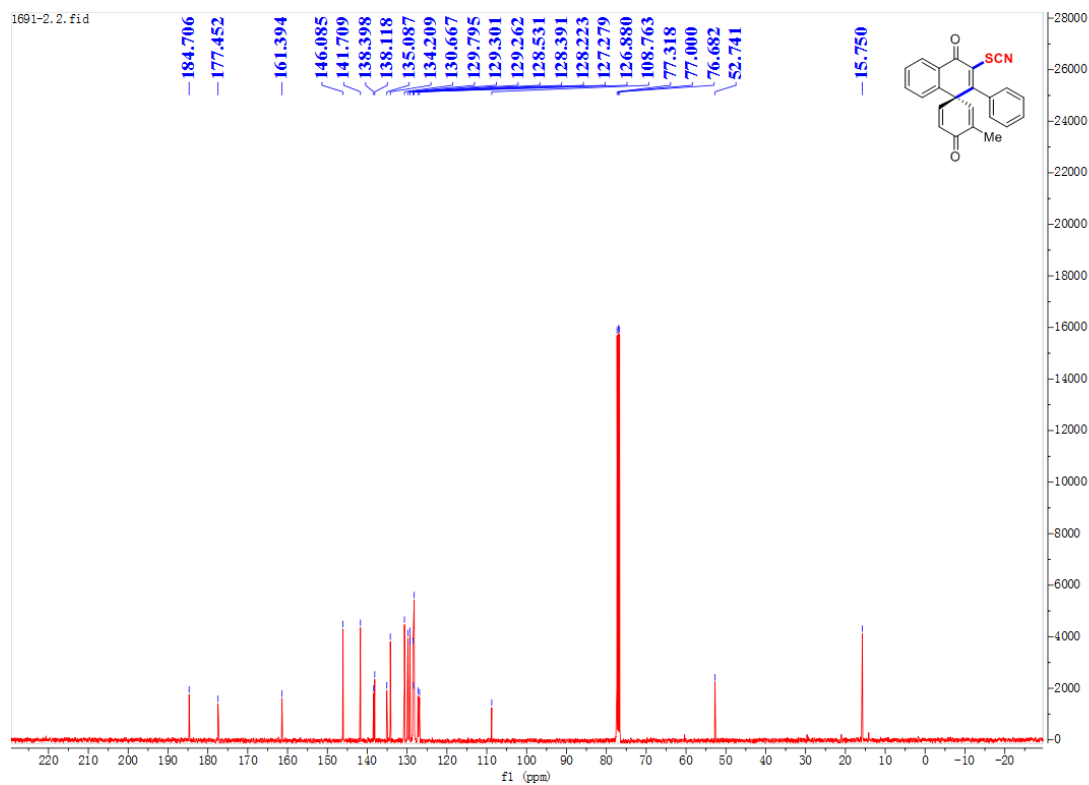
19-¹³C NMR



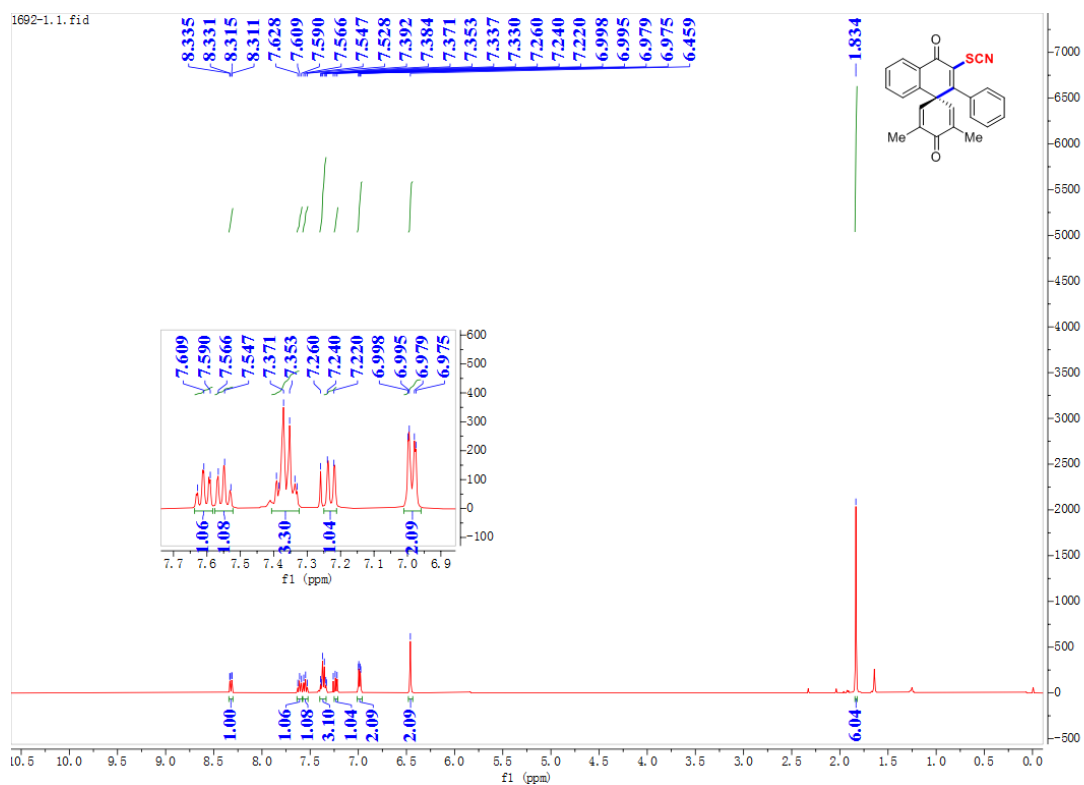
20-¹H NMR



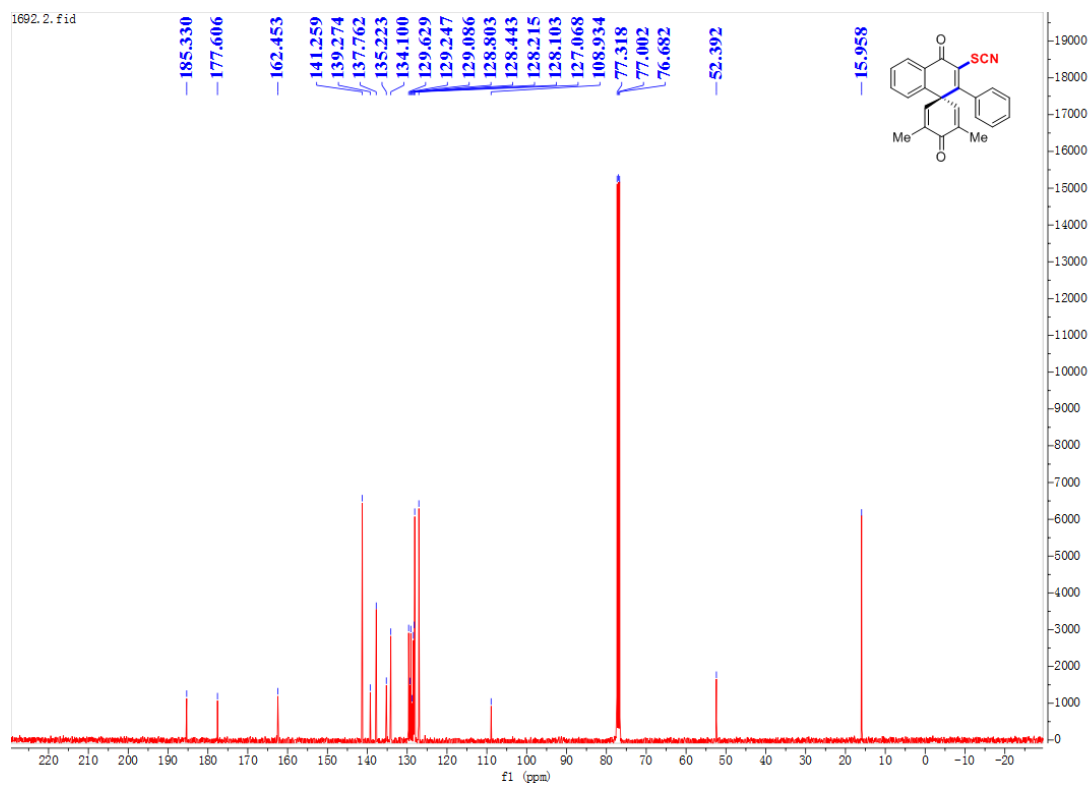
20-¹³C NMR



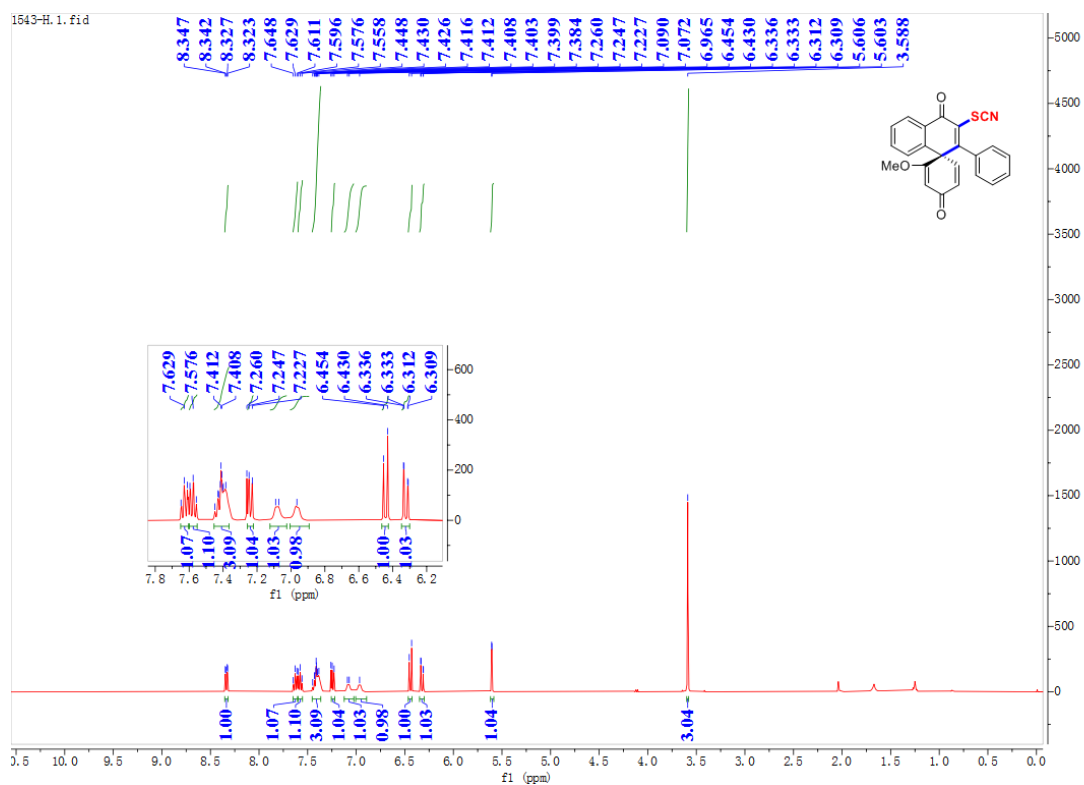
21-¹H NMR



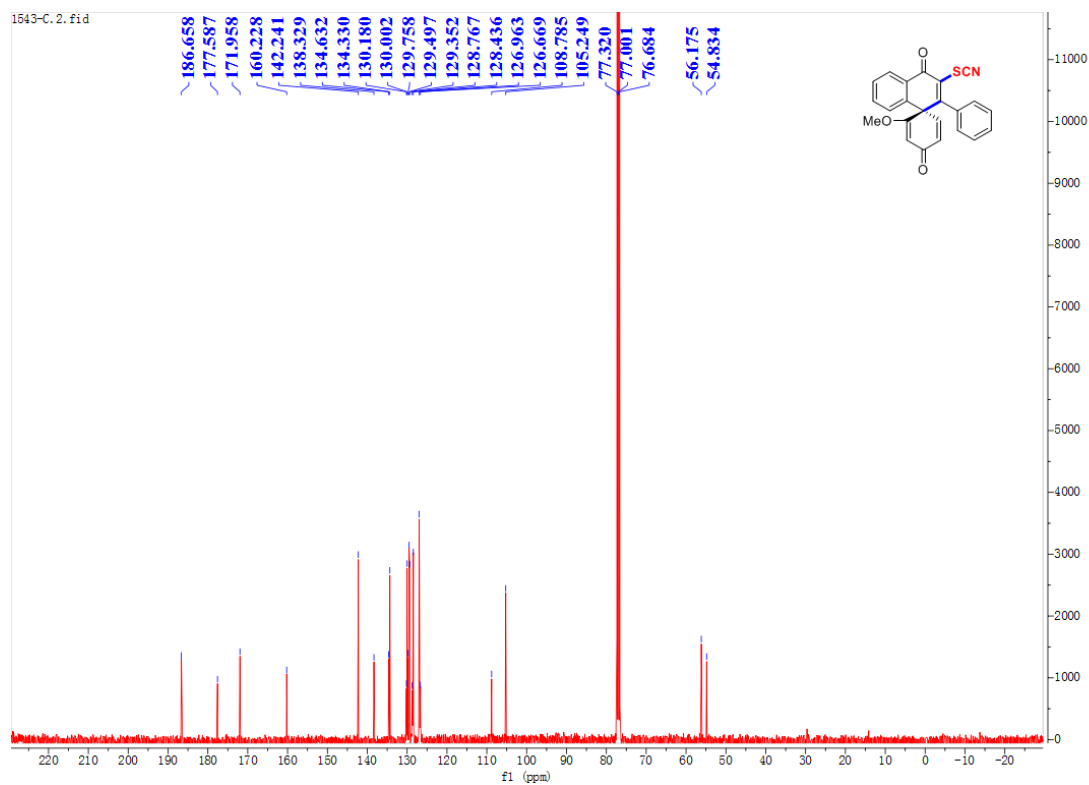
21-¹³C NMR



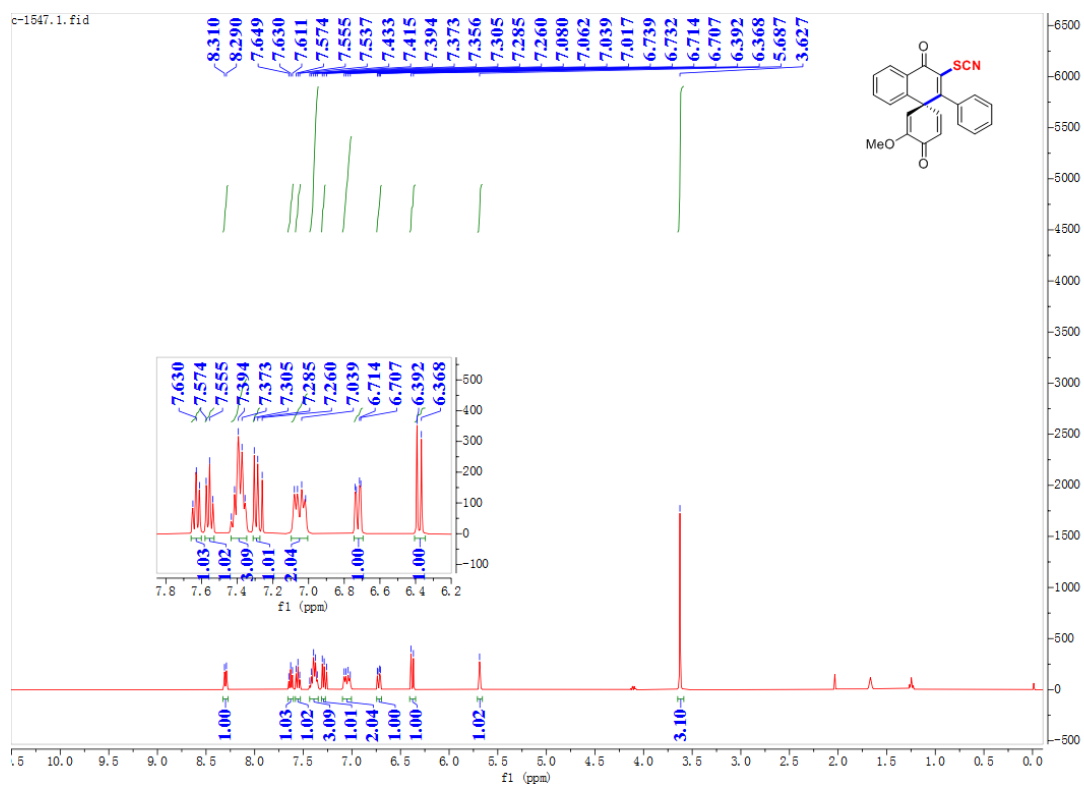
22-¹H NMR



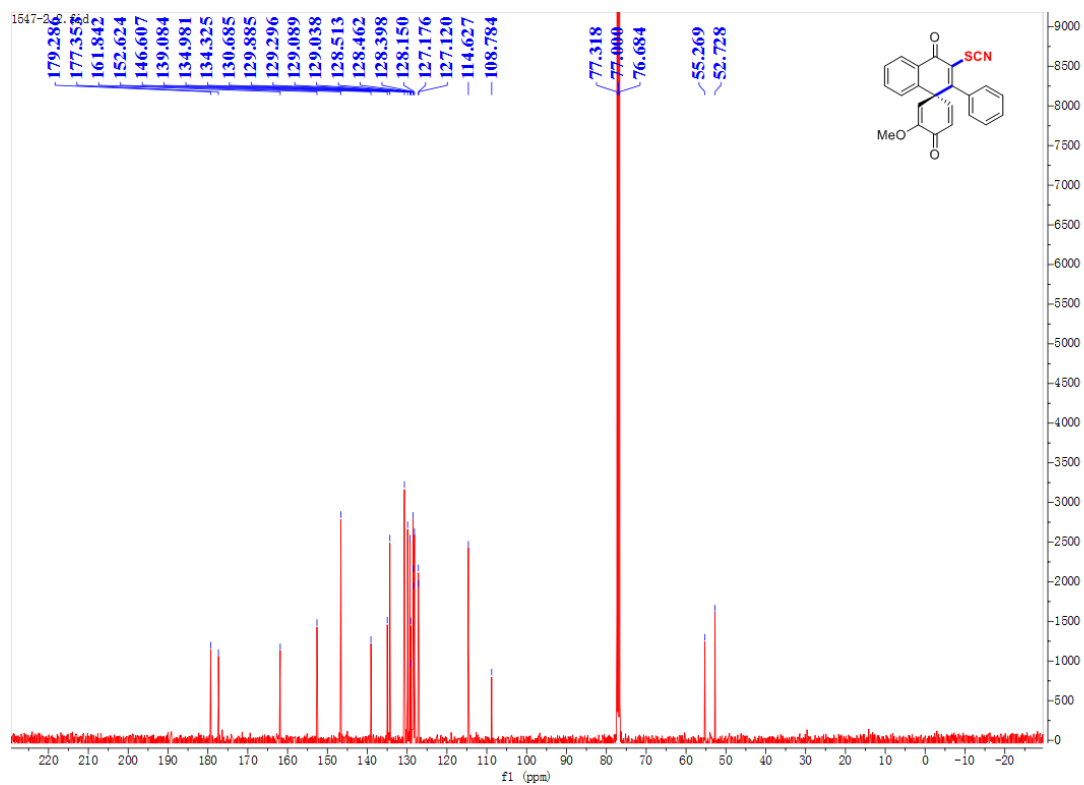
22-¹³C NMR



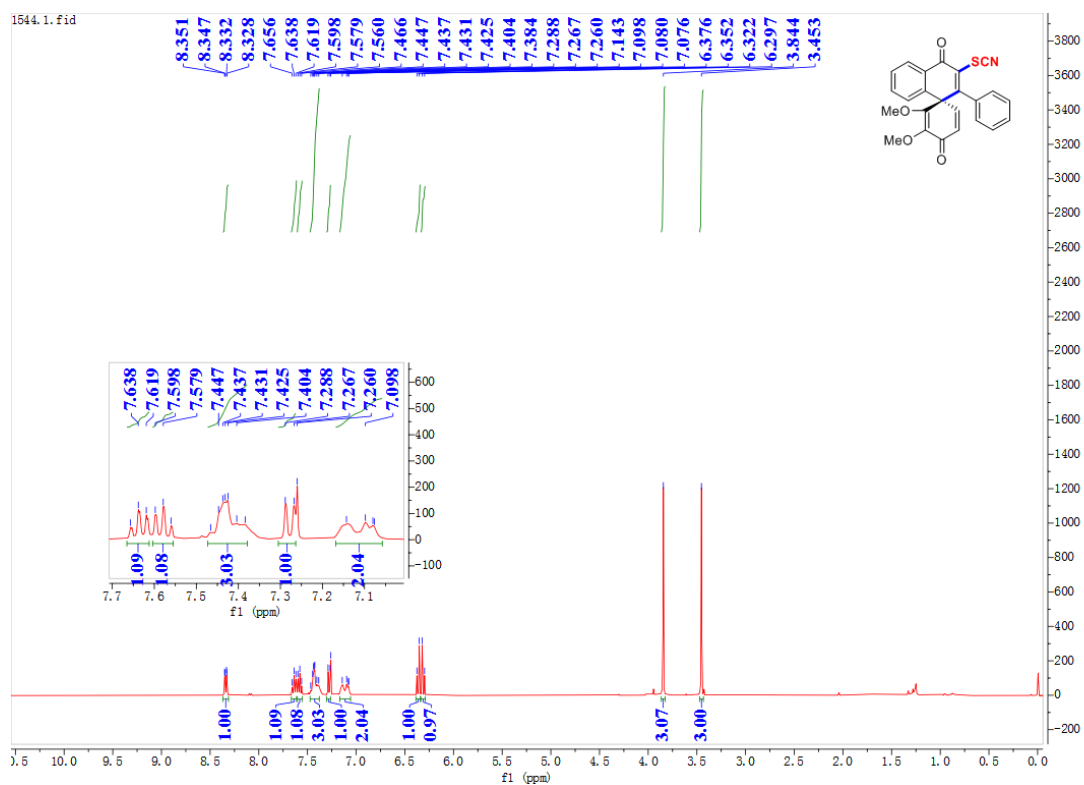
23-¹H NMR



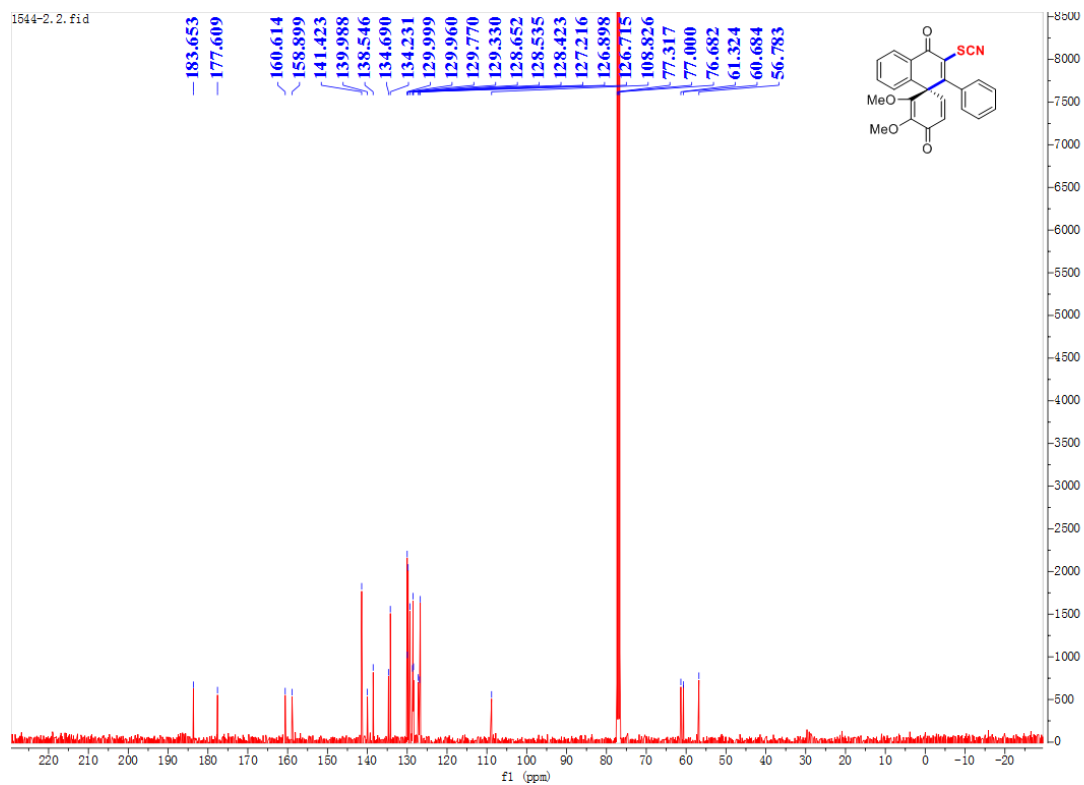
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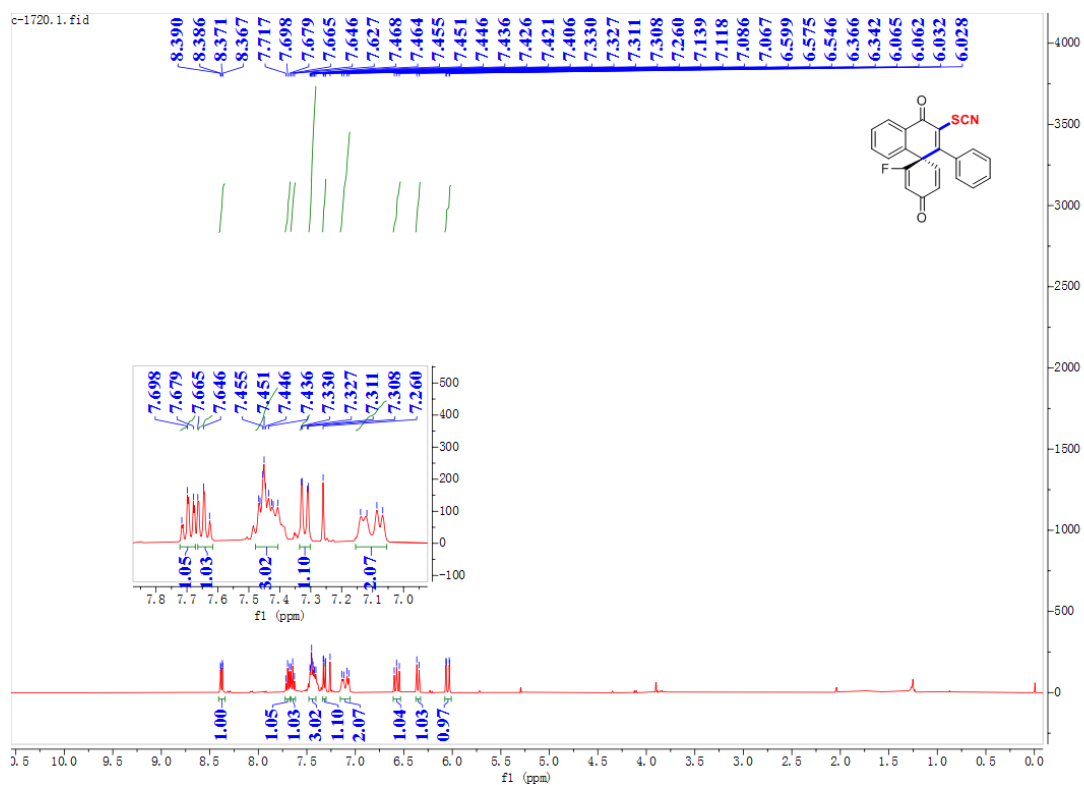
24-¹H NMR



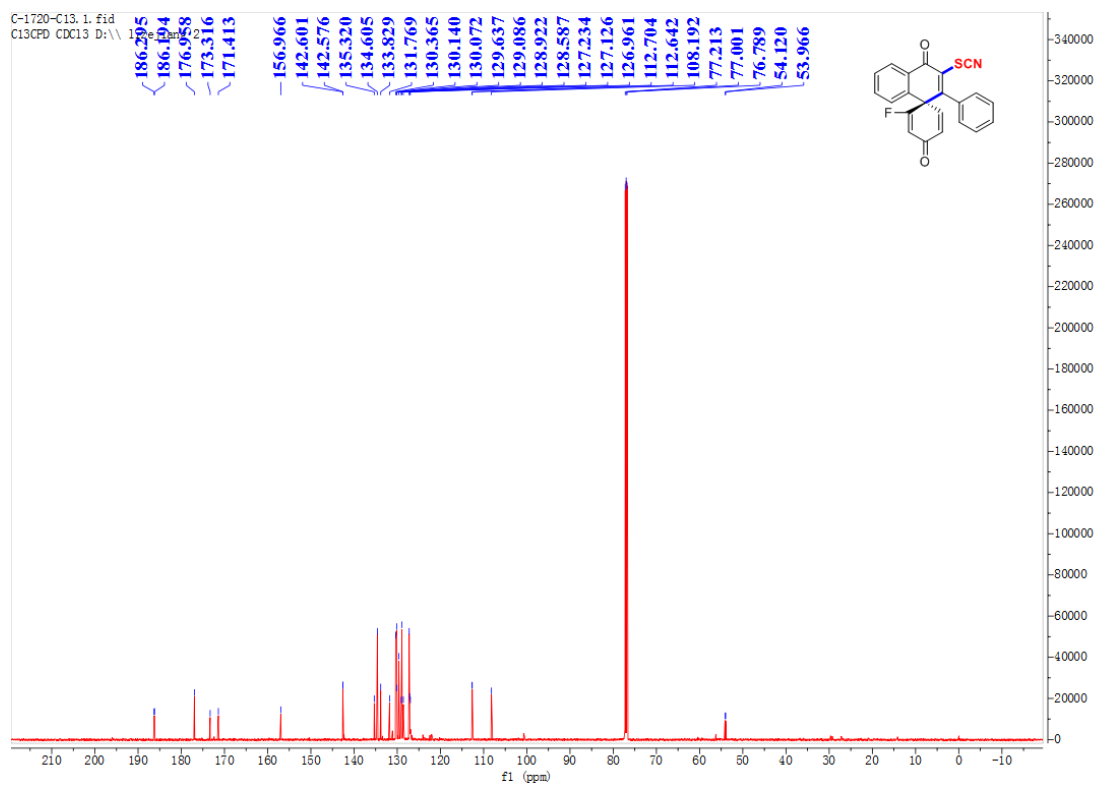
24-¹³C NMR



25-¹H NMR

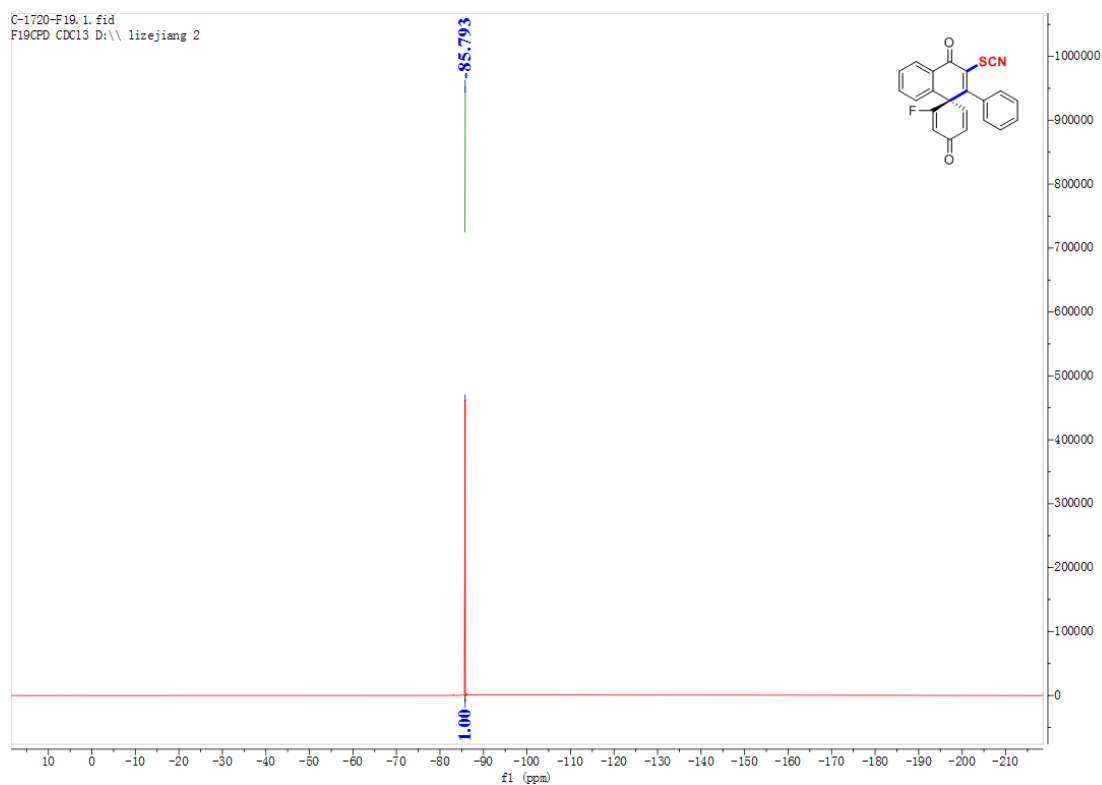


25-¹³C NMR



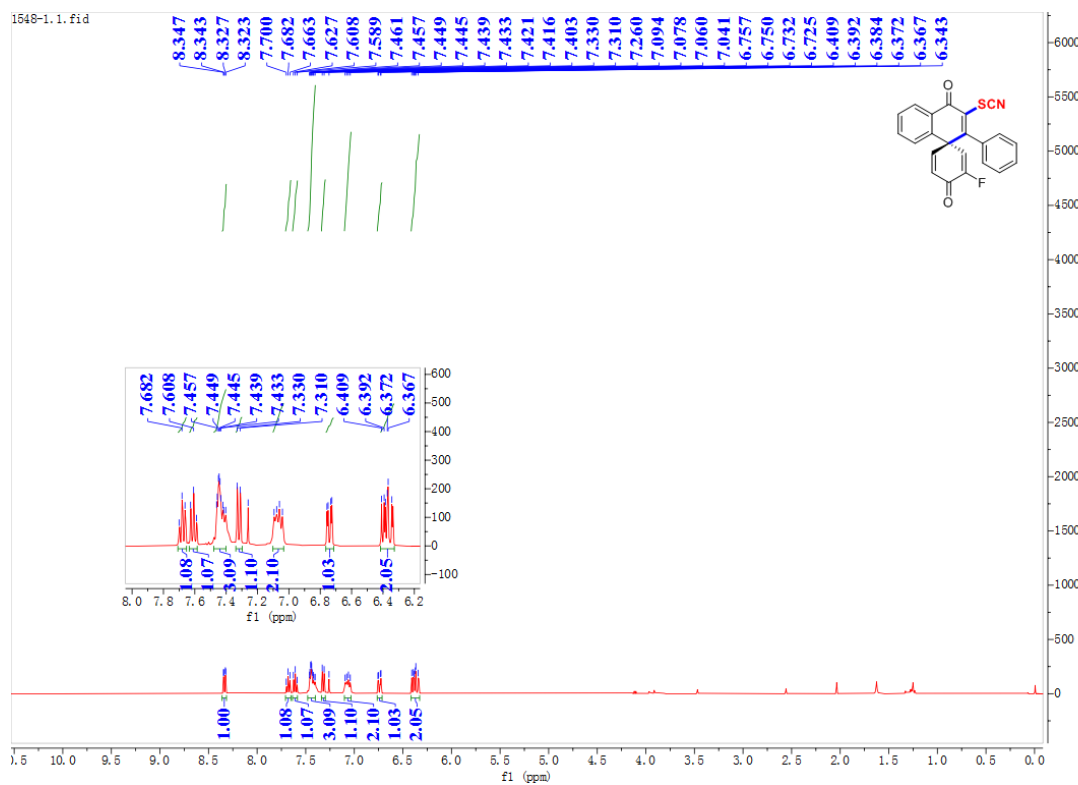
25-¹⁹F NMR

C-1720-F19.1.fid
F19CPD CDCl₃ D:\\ lizejiang 2

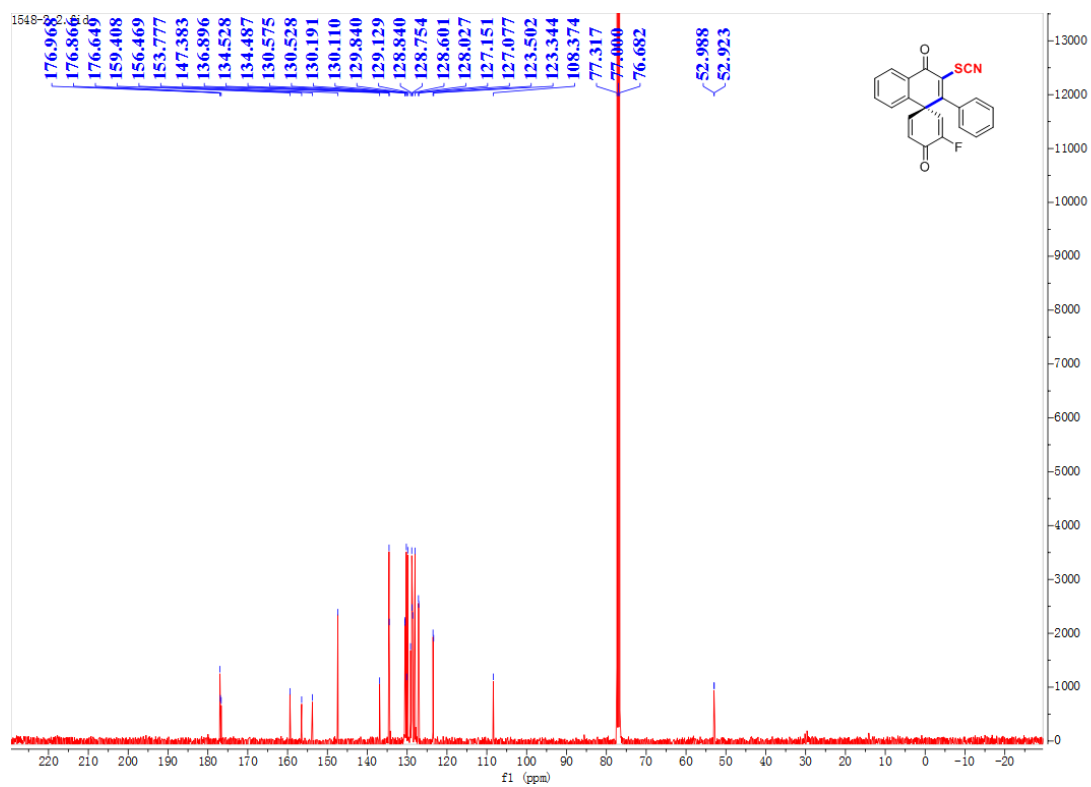


26-¹H NMR

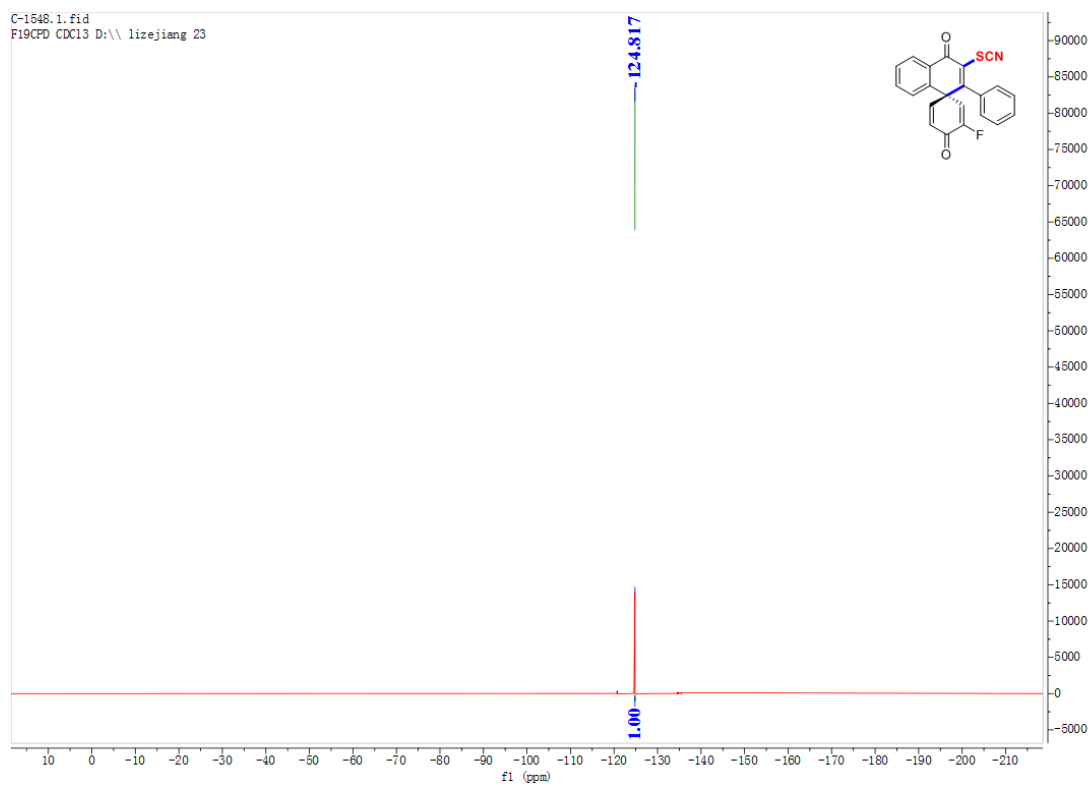
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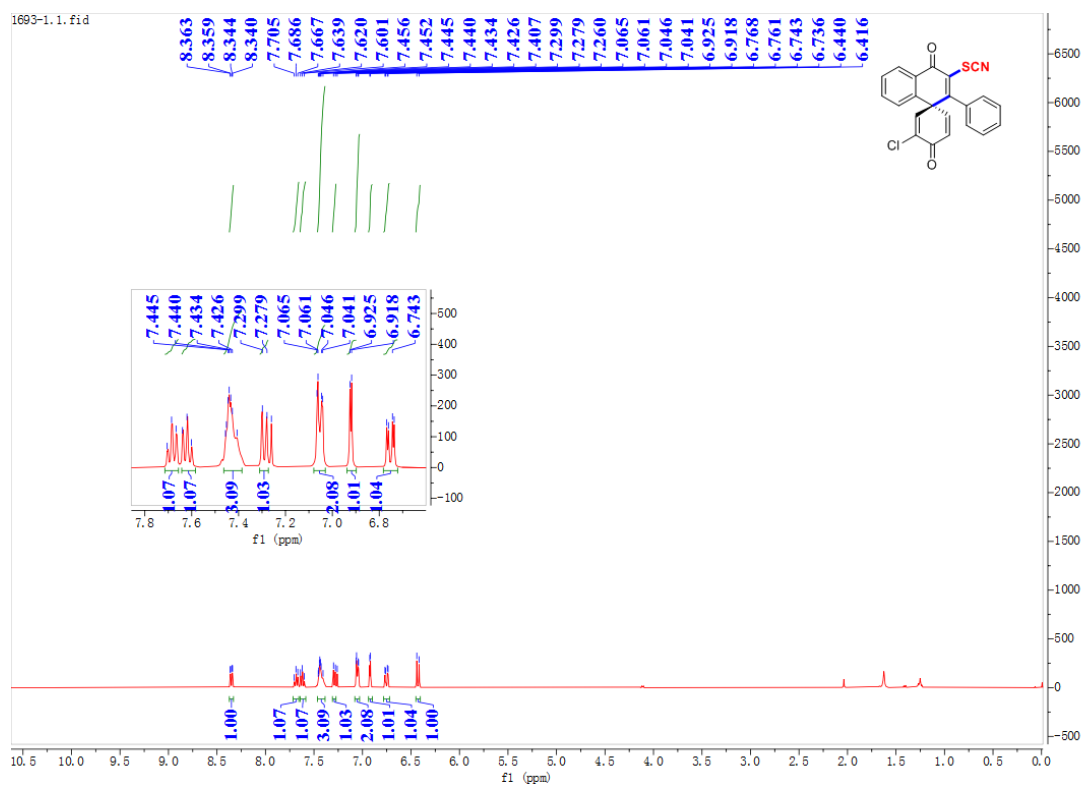
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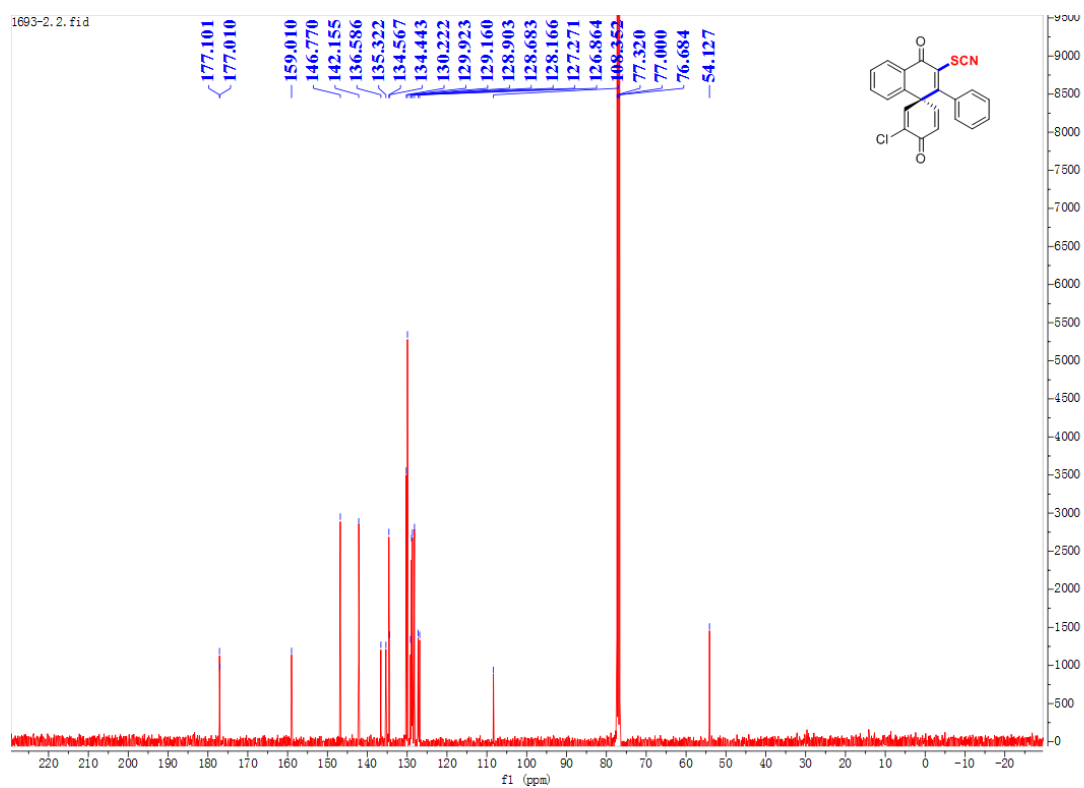
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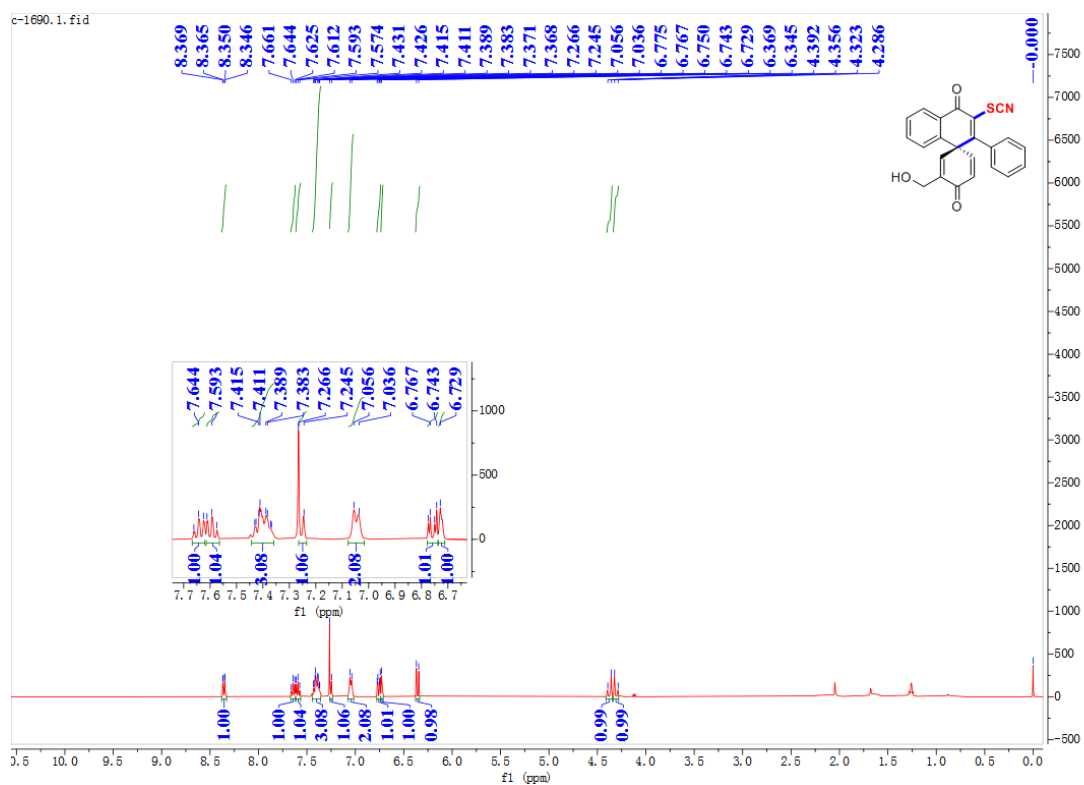
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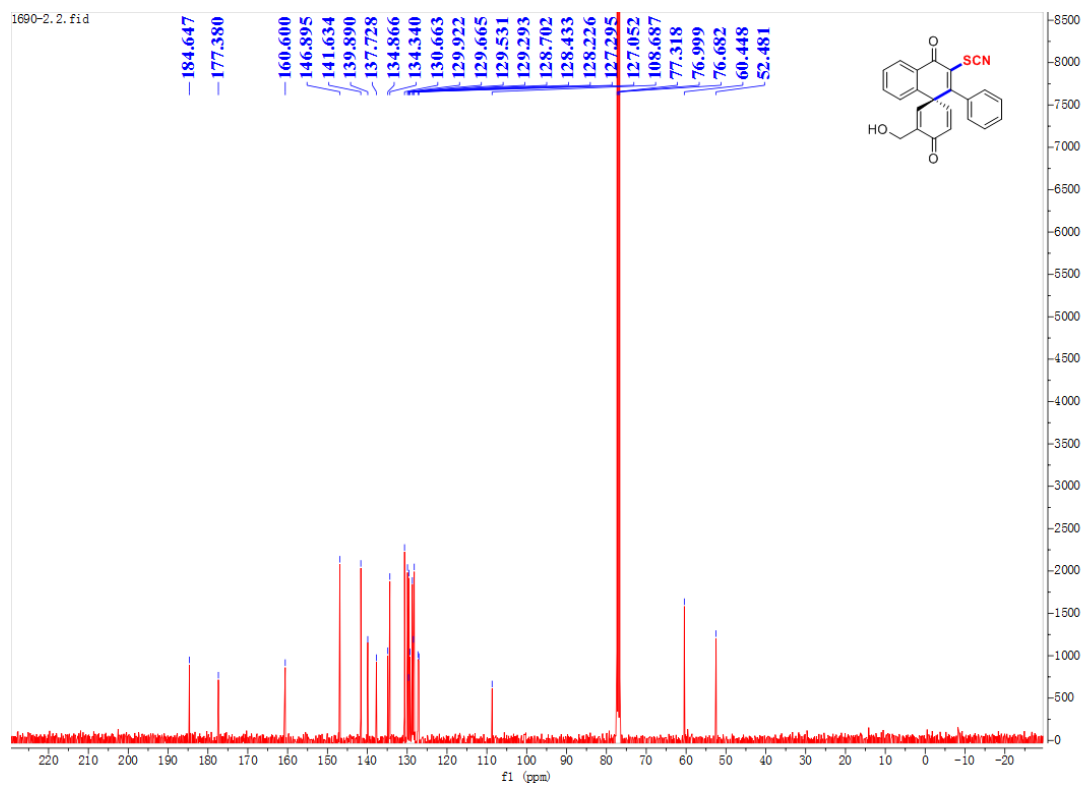
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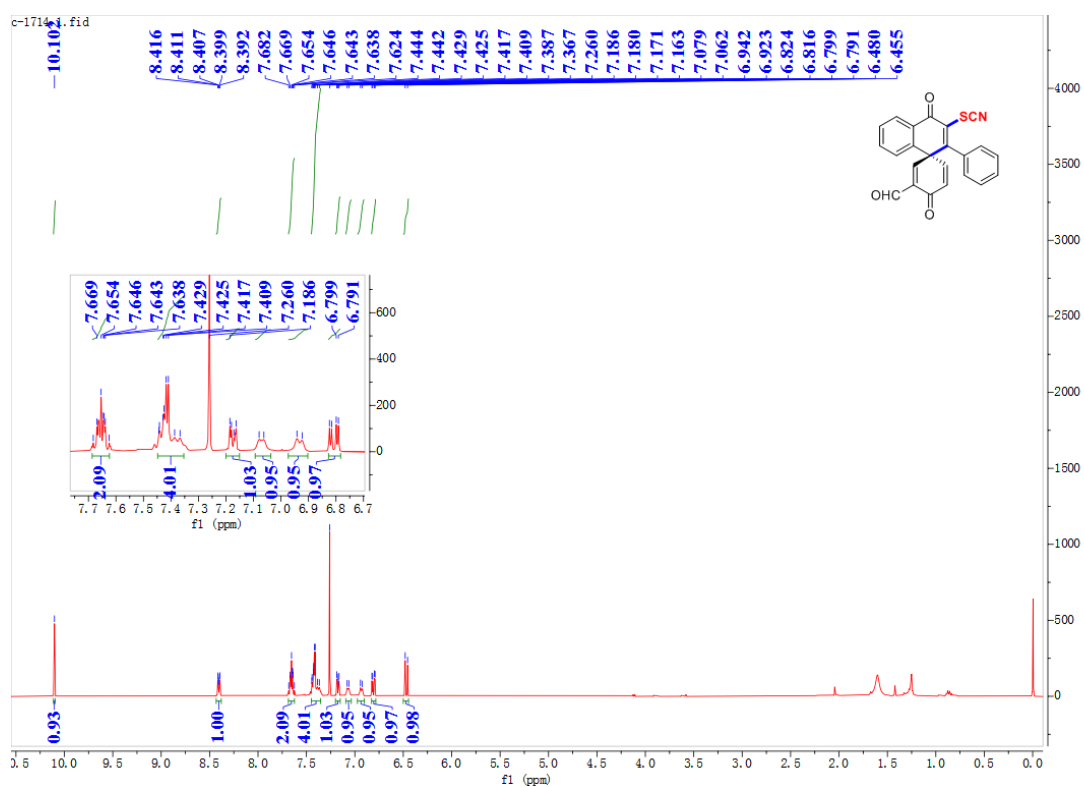
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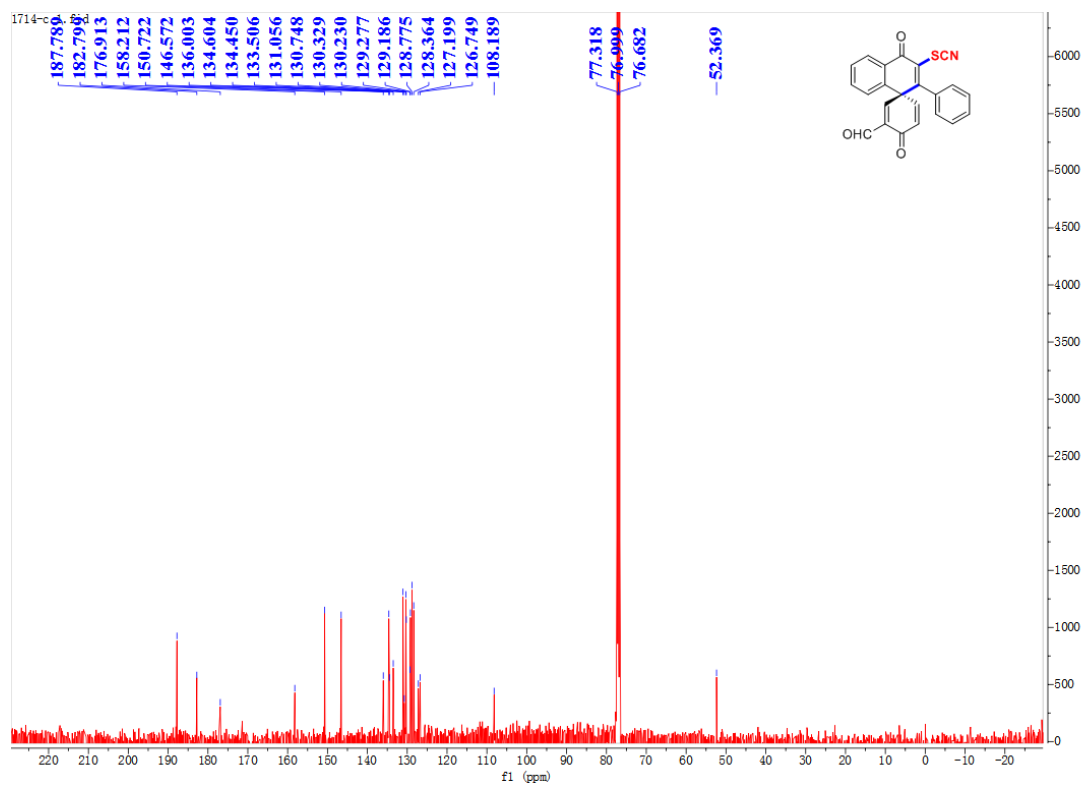
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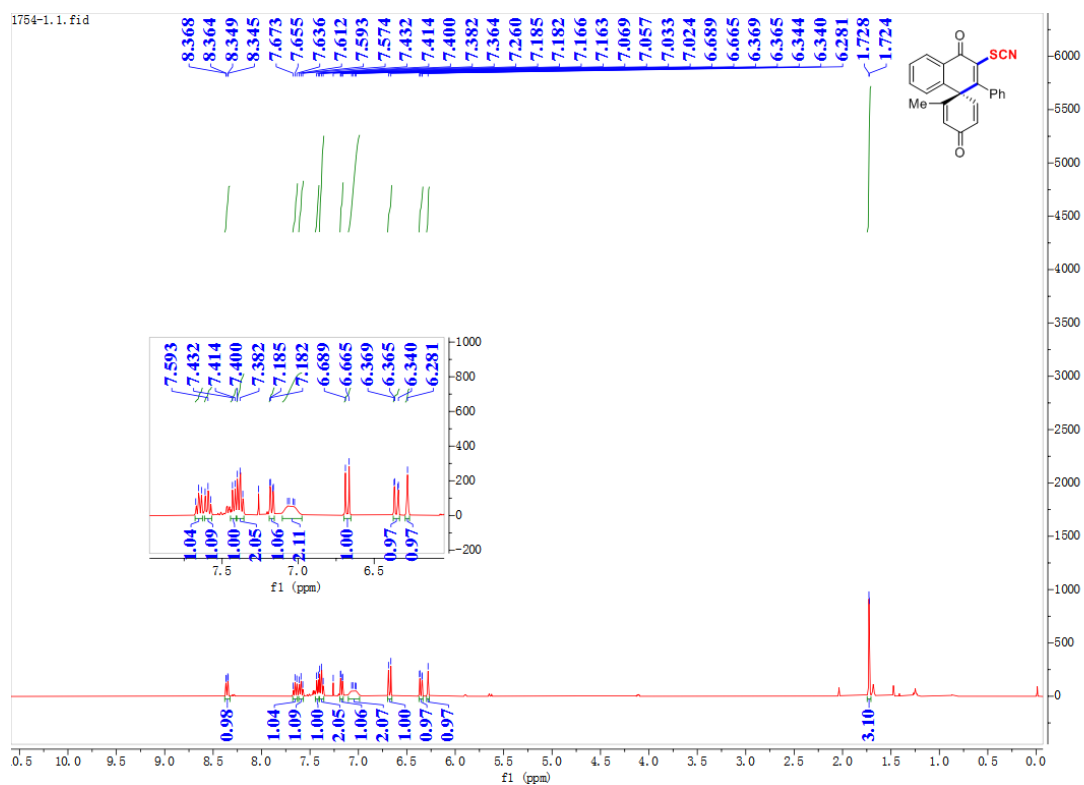
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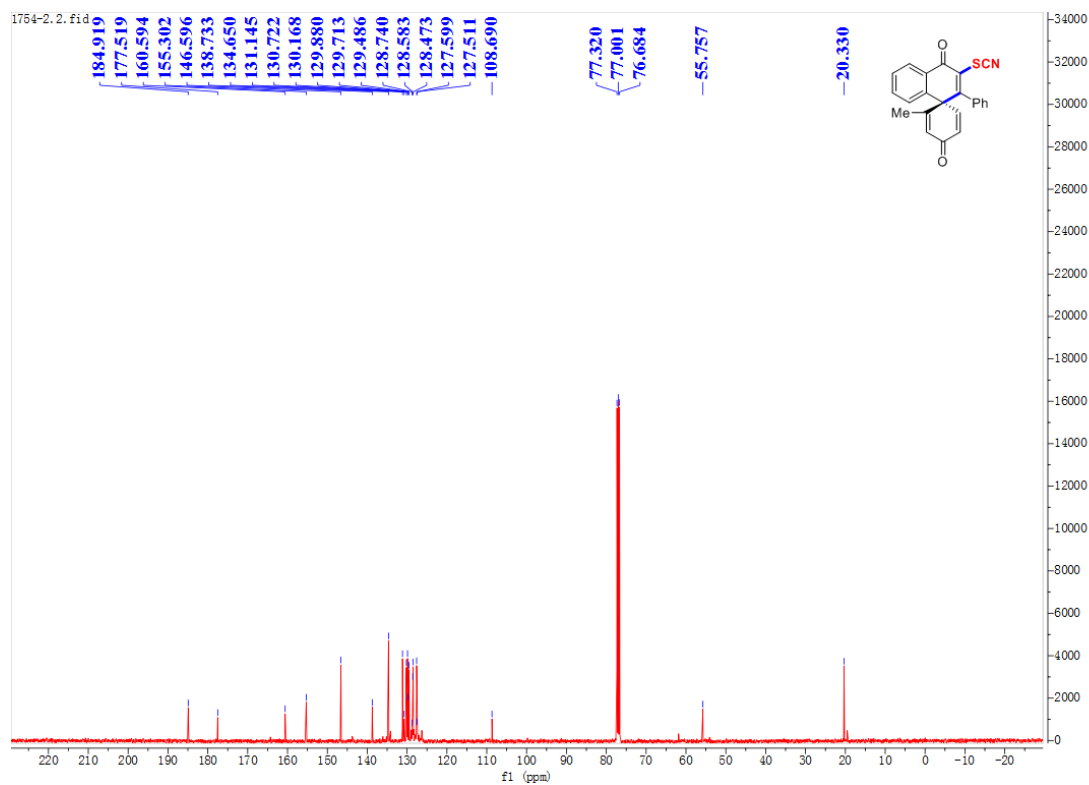
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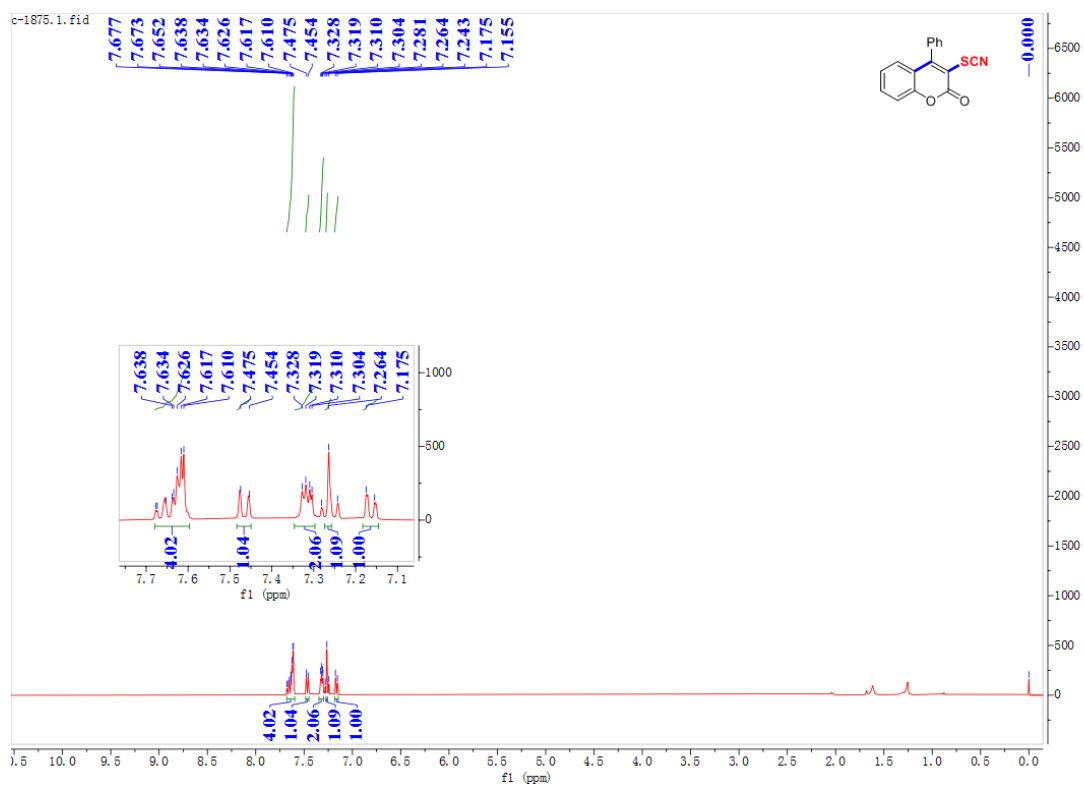
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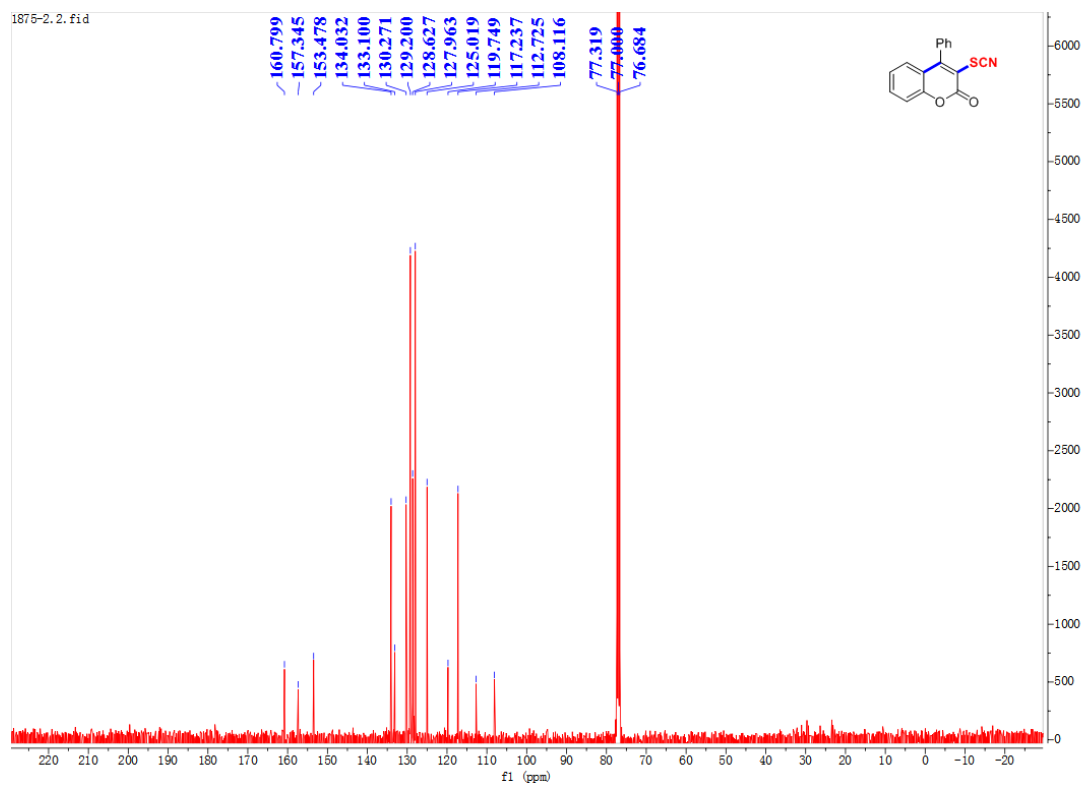
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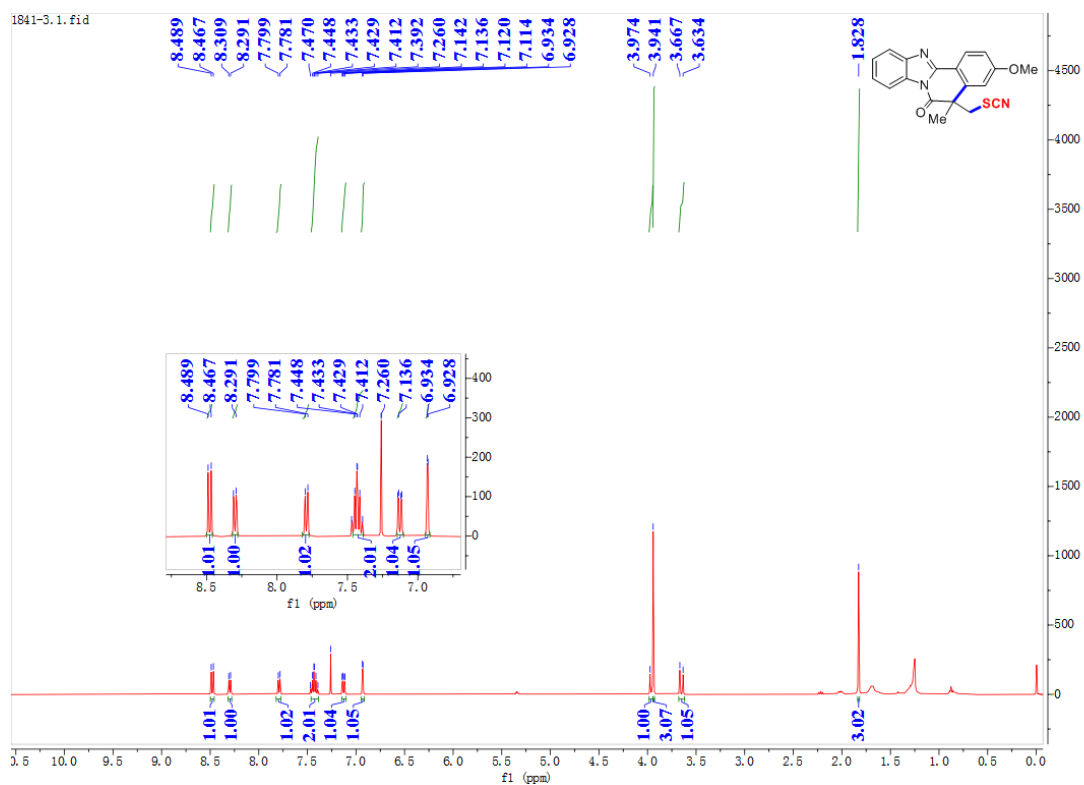
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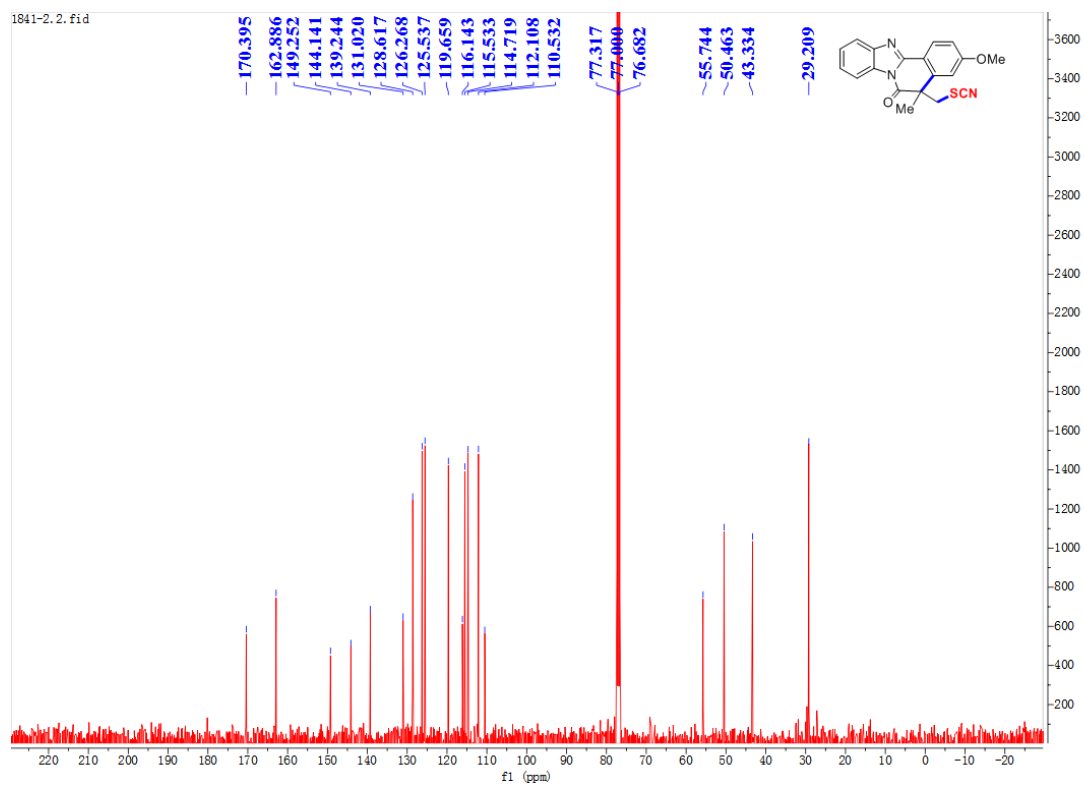
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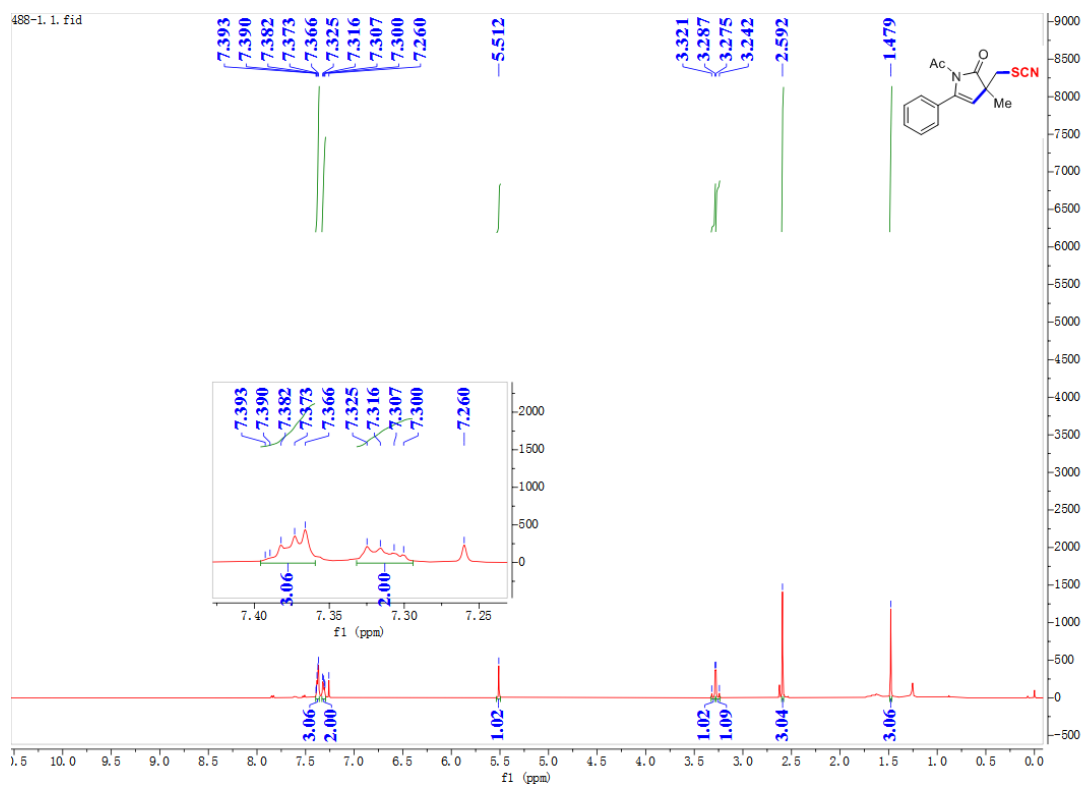
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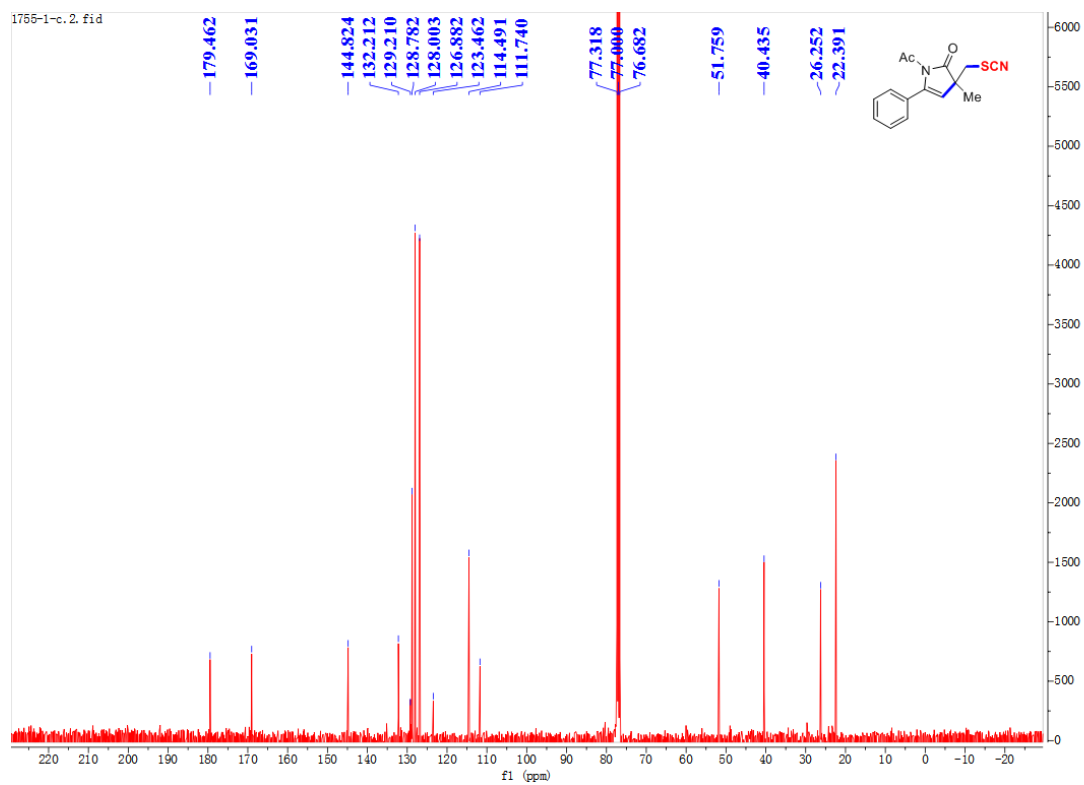
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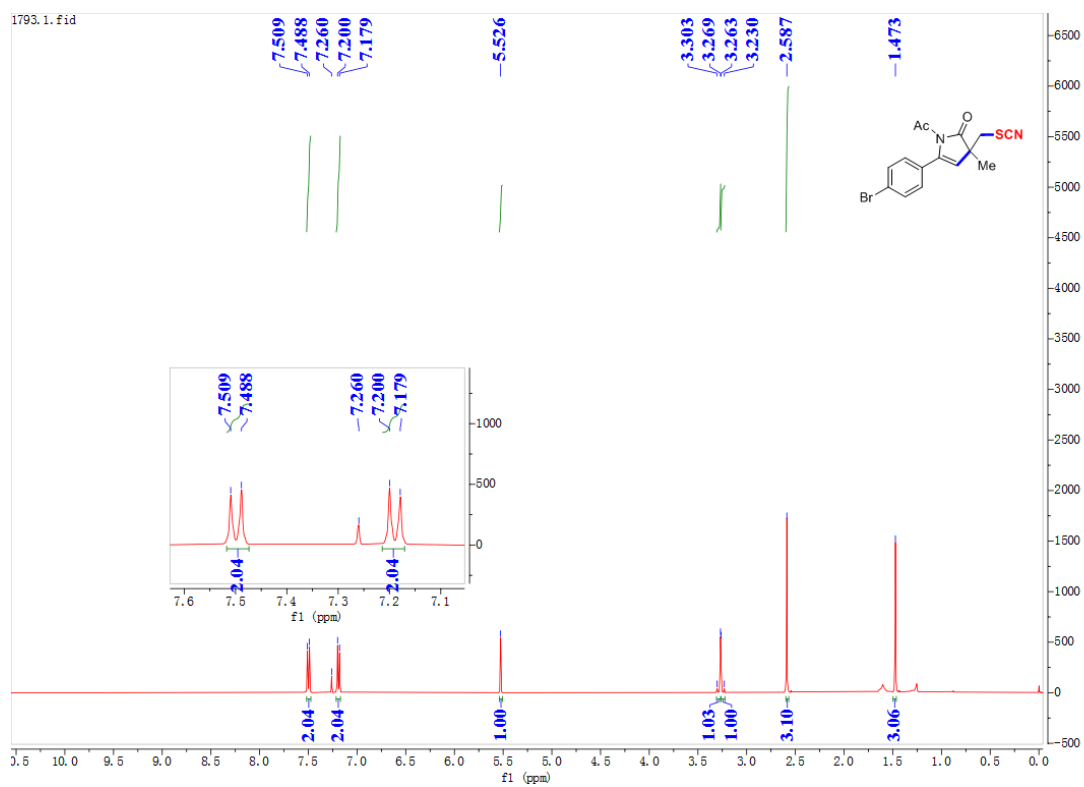
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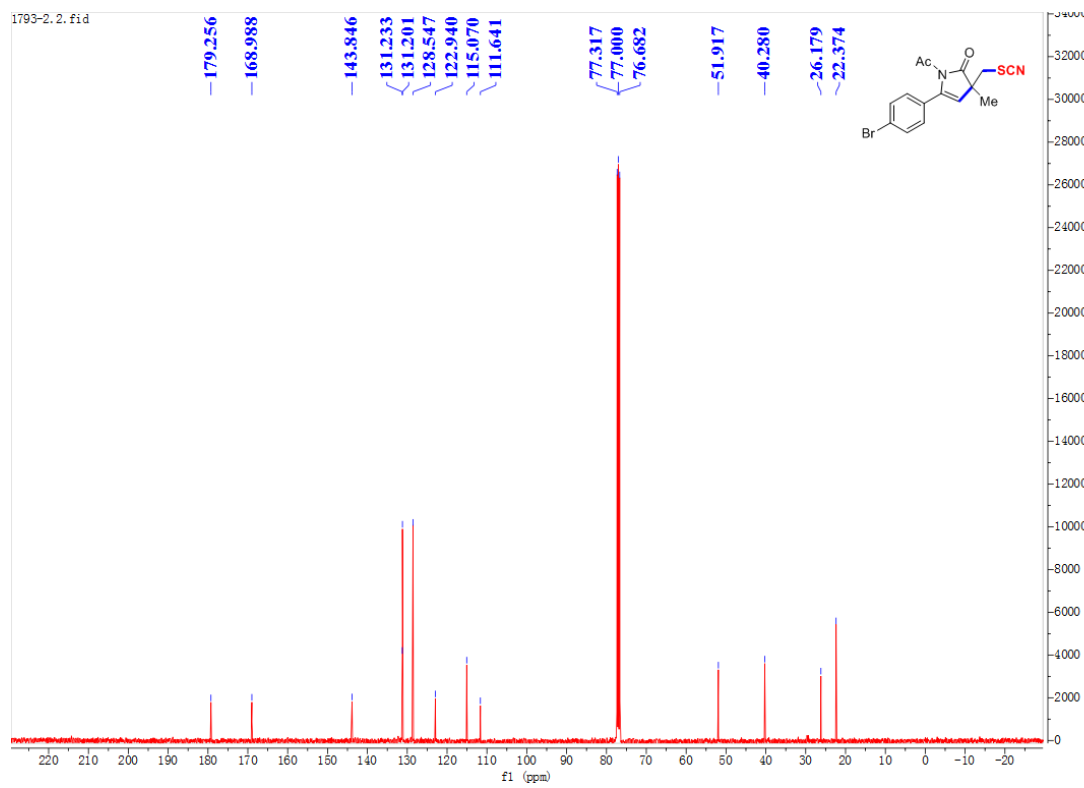
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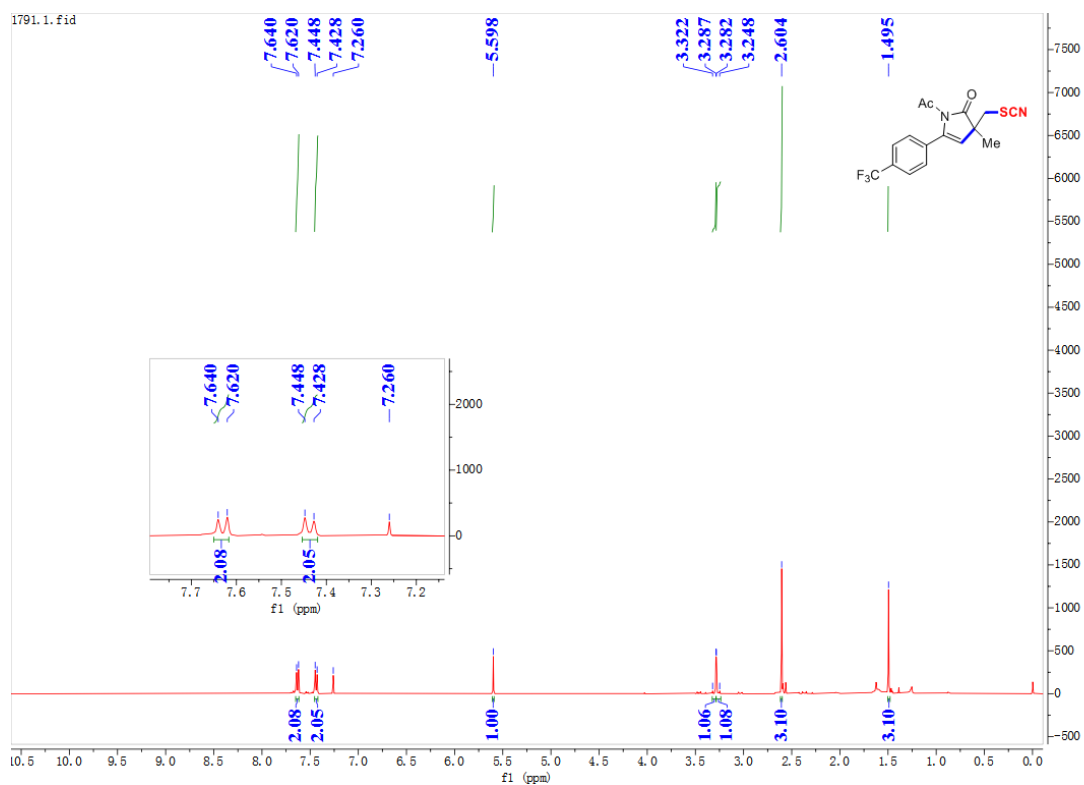
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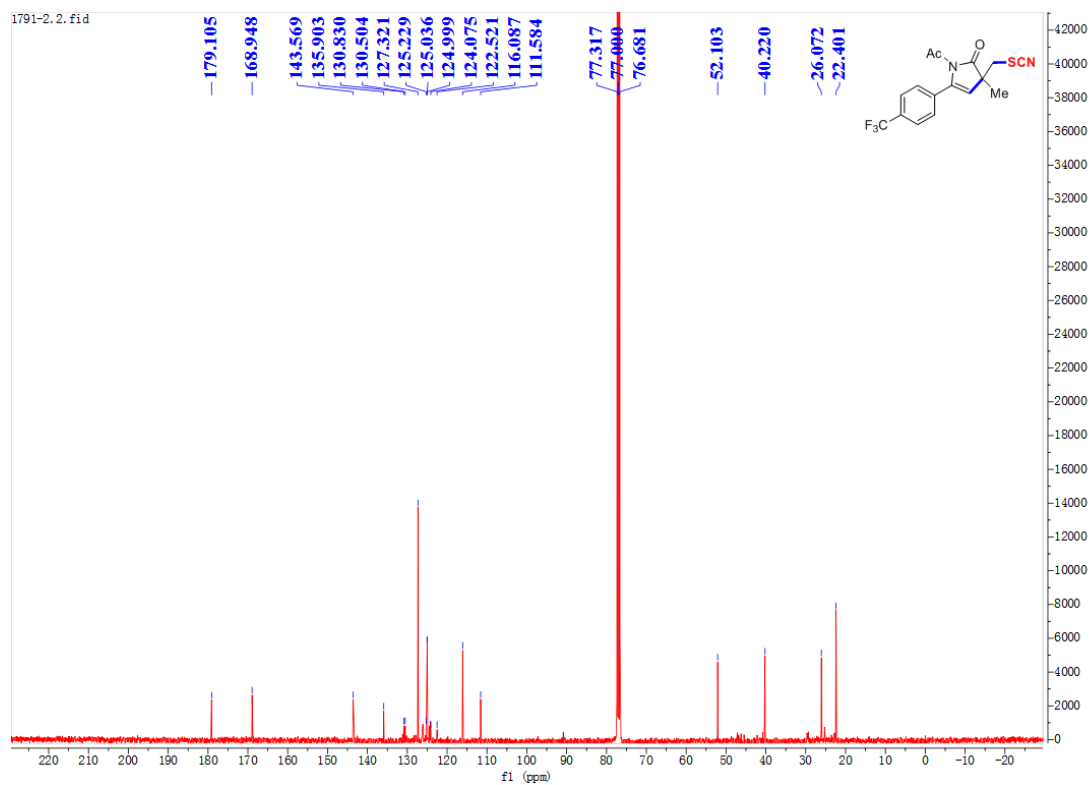
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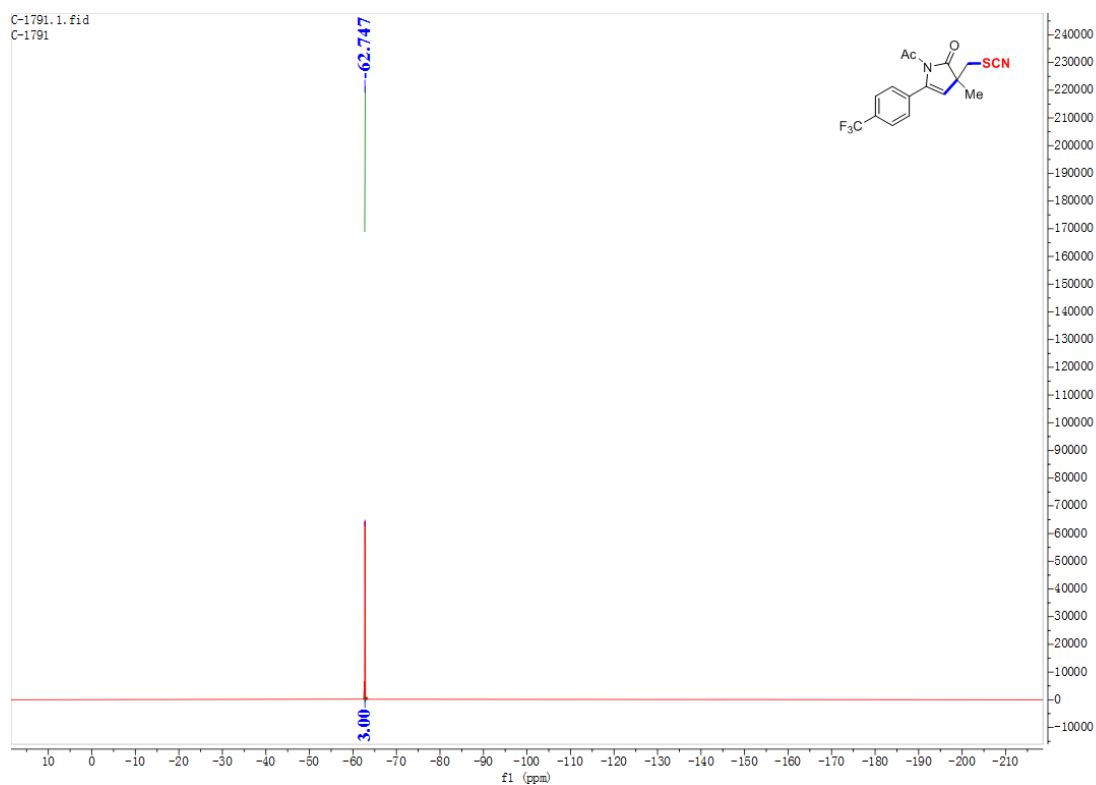
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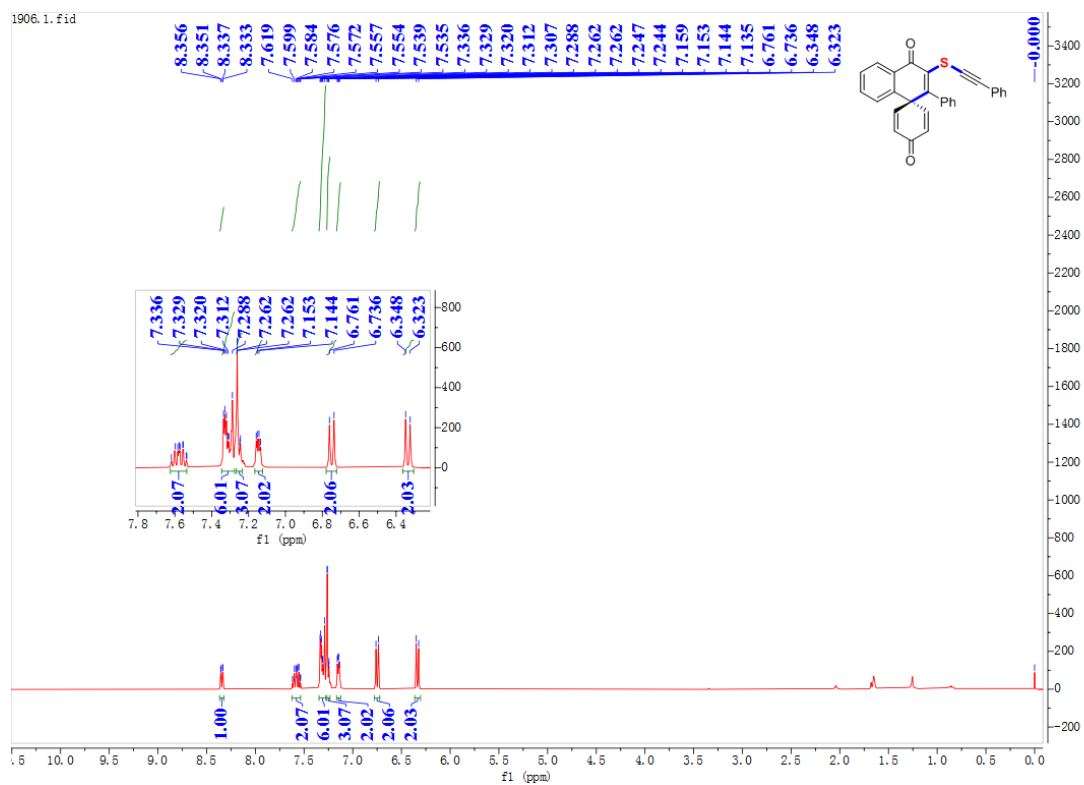
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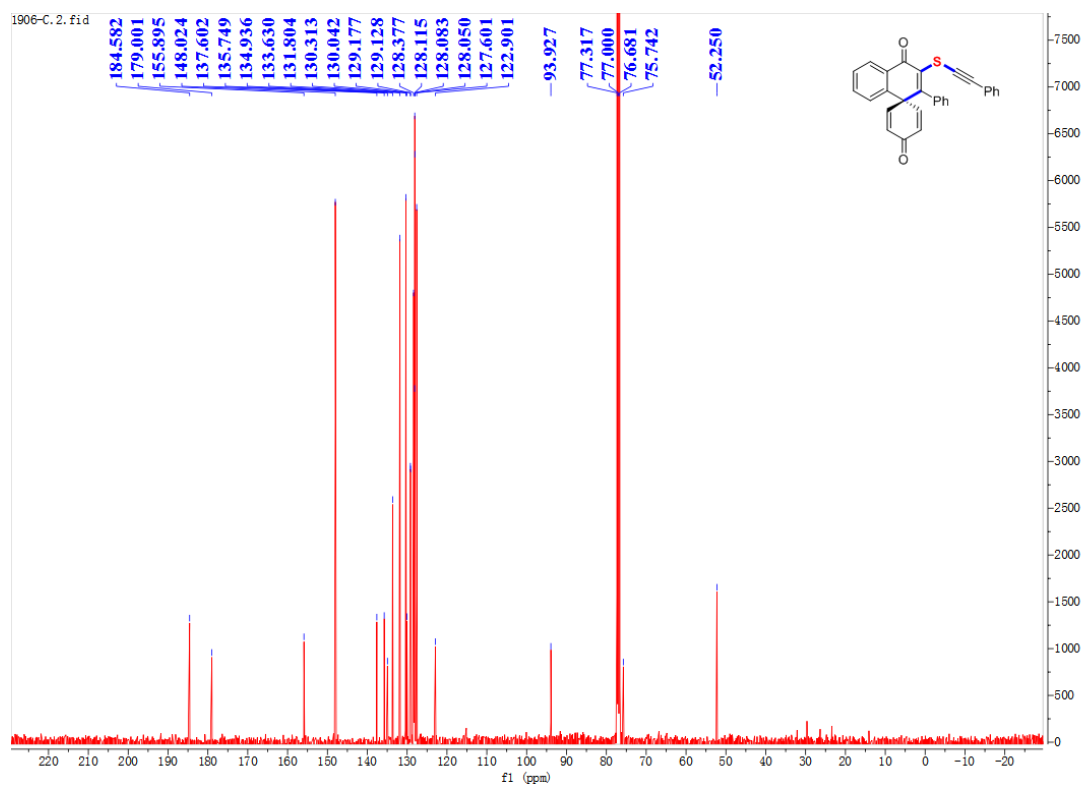
35-¹⁹F NMR



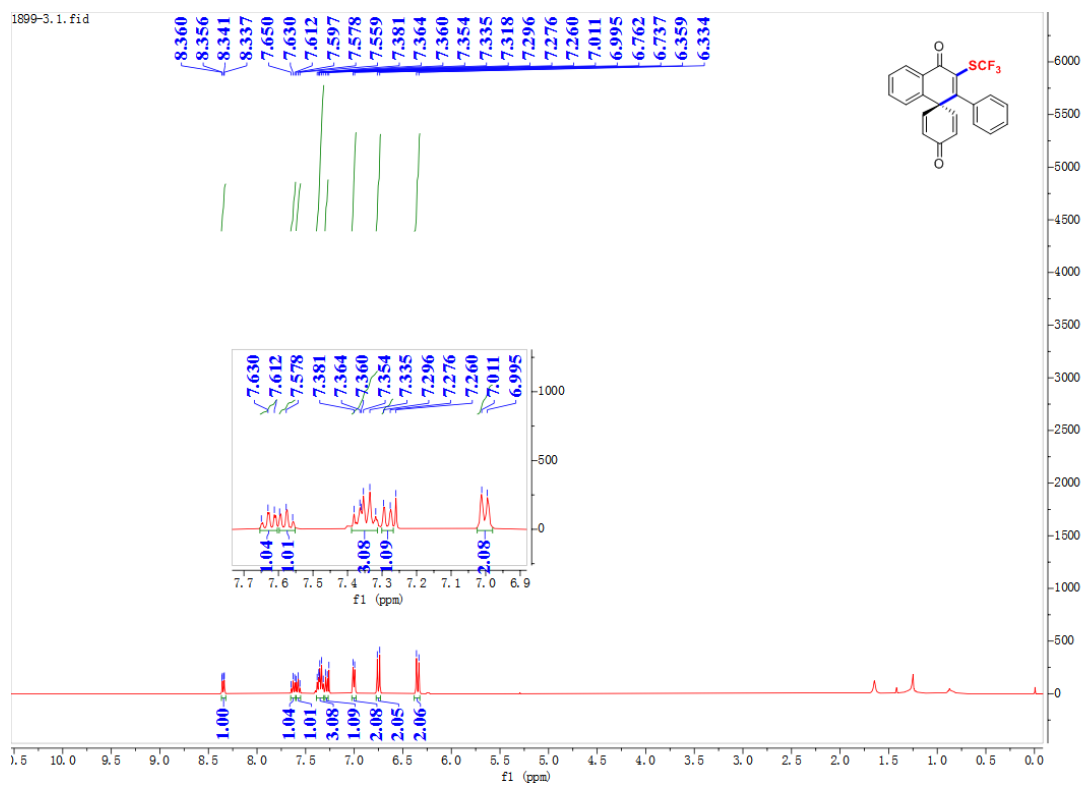
36-¹H NMR



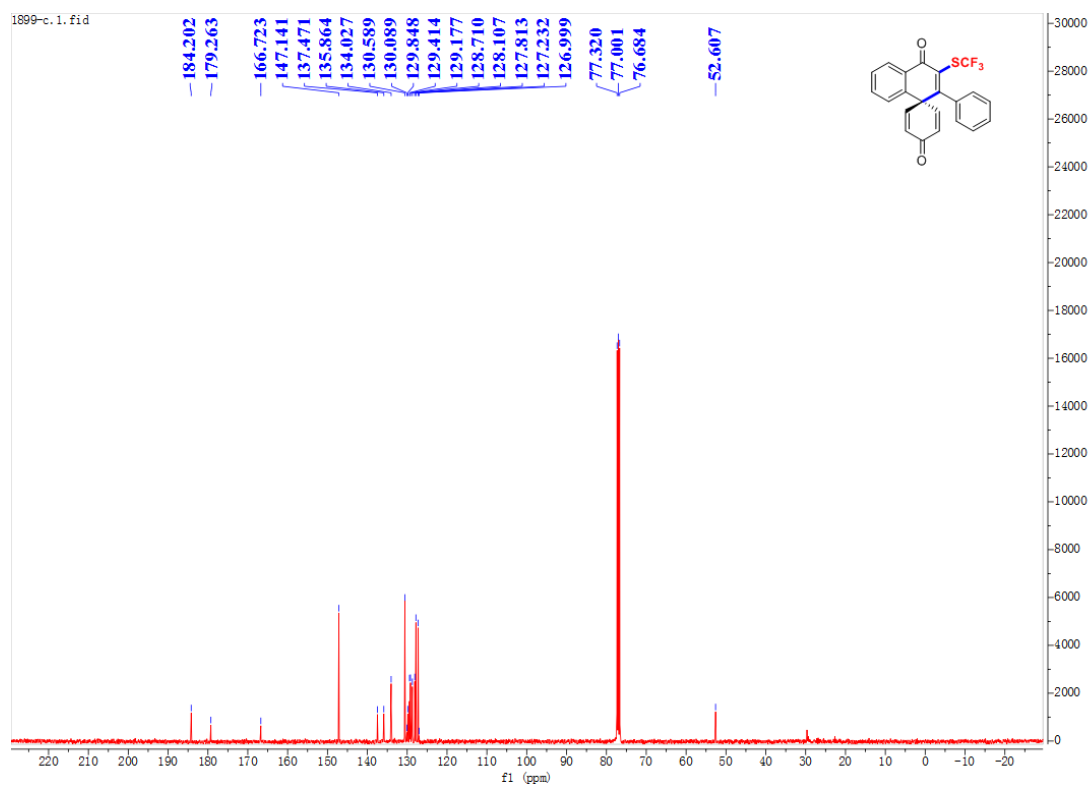
36-¹³C NMR



37-¹H NMR



37-¹³C NMR



37-¹⁹F NMR

