

Supporting Information

Metal-free radical bicyclization/chloroalkylation of 1,6-enynes with chloroalkanes

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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 raw materials were purchased from Energy, Meryer, J&K Chemicals, or Aldrich and used without further purification.

Typical procedure for the reaction

Reaction conditions 1: A mixture of 1,6-enynes (1 equiv., 0.1 mmol), chloroform (7 mL), KI (0.1 equiv.), DTBP (3 equiv.) was added into a 15 mL sealed pipe, which was conducted at 130 °C in a heating mantle with an air atmosphere. After the bicyclization reaction was finished, the mixture was condensed under vacuum and purified by column chromatography to afford the final products.

Reaction conditions 2: A mixture of trichlorinated polycycles (1 equiv., 0.1 mmol), Pd (PPh_3)₄ (0.05 equiv.) or not, Cs_2CO_3 (2.5 or 5 equiv.), THF (anhydrous, 1 mL) was added into a 15 mL sealed pipe, which was conducted at 120 °C in an oil bath with an N_2 atmosphere. After the transformation was completed, a similar workup was operated.

Crystallographic details

(1) First, product **1**, **32**, or **36** was solved with the mixture of 1.5 mL dichloromethane and 3 mL petroleum ether in a sample bottle, respectively, which was sealed/placed on the desk of the laboratory. Next, the crystal of the fused cycles **1**, **32**, or **36** was separately precipitated via volatilizing after several days.

(2a) A single crystal of product **1** was obtained as follows: A proper crystal was selected and detected on a “Bruker APEX2” diffractometer. The crystal stayed at 273.0 K during data collection. With the assistance of Shelxtl, the structure was solved with the XShell structure solution program using Charge Flipping, and it was refined with the SHELXL [1] refinement package using Least Squares minimisation. Finally, crystal data and structure refinement parameters of product **1** are described as

shown in **Table S1**. CCDC No. 2330699.

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

Table S1. Crystal data and structure refinement for product **1**.

CCDC	2330699	
Displacement ellipsoids are drawn at the 30% probability level		
Empirical formula	C ₂₀ H ₁₅ Cl ₃ O ₂	
Formula weight	393.67	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 10.8147(18) Å	a = 90°
	b = 9.8903(15) Å	b = 104.319(6)°
	c = 16.969(3) Å	g = 90°
Volume	1758.6(5) Å ³	
Z	4	
Density (calculated)	1.487 Mg/m ³	
Absorption coefficient	0.532 mm ⁻¹	
F(000)	808	
Crystal size	0.390 x 0.240 x 0.190 mm ³	
Theta range for data collection	1.943 to 30.082/°	
Index ranges	-15<=h<=15, -13<=k<=13, -23<=l<=23	
Reflections collected	47379	
Independent reflections	5146 [R(int) = 0.0578]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5146 / 0 / 226	
Goodness-of-fit on F ²	1.151	
Final R indices [I>2sigma(I)]	R1 = 0.0528, wR2 = 0.1236	
R indices (all data)	R1 = 0.0630, wR2 = 0.1314	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.550 and -0.233 e.Å ⁻³	

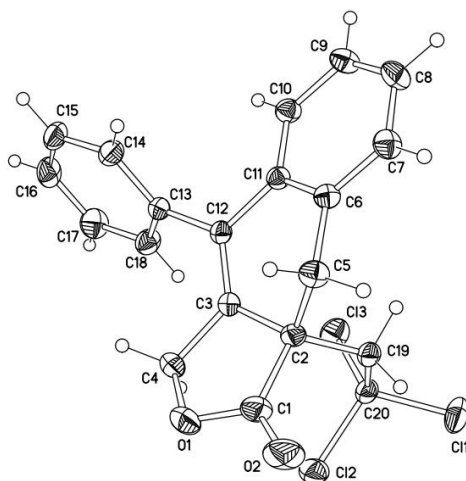


Fig. S1 Structure of product **1**.

(2b) A single crystal of product **32** was obtained via a similar operation, which was described as shown in **Table S2**. CCDC No. 2330700.

Table S2. Crystal data and structure refinement for product **32**.

CCDC	2330700	
Displacement ellipsoids are drawn at the 50% probability level		
Empirical formula	C ₂₄ H ₁₆ O ₂	
Formula weight	336.37	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 12.2366(11) Å	a = 90°.
	b = 17.3994(15) Å	b = 102.186(4)°.
	c = 8.2782(8) Å	g = 90°.
Volume	1722.8(3) Å ³	
Z	4	
Density (calculated)	1.297 Mg/m ³	
Absorption coefficient	0.081 mm ⁻¹	
F(000)	704	
Crystal size	0.320 x 0.210 x 0.110 mm ³	
Theta range for data collection	2.776 to 23.286°.	
Index ranges	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -9 ≤ l ≤ 9	
Reflections collected	15822	

Independent reflections	2481 [R(int) = 0.0835]
Completeness to theta = 23.286°	99.5 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2481 / 0 / 235
Goodness-of-fit on F ²	1.110
Final R indices [I>2sigma(I)]	R1 = 0.0686, wR2 = 0.1453
R indices (all data)	R1 = 0.1004, wR2 = 0.1630
Extinction coefficient	n/a
Largest diff. peak and hole	0.208 and -0.187 e.Å ⁻³

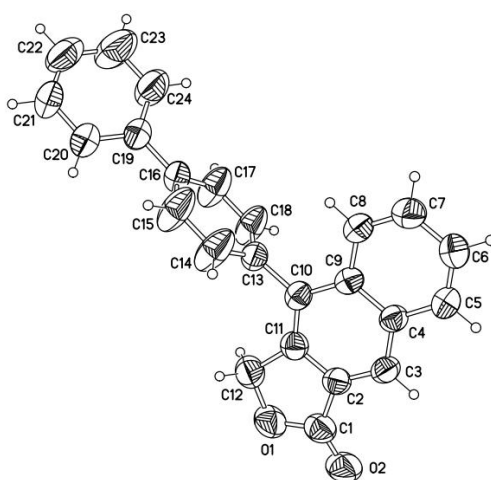


Fig. S2 Structure of product **32**.

(2c) A single crystal of product **36** was obtained via a similar operation, which was described as shown in **Table S3**. CCDC No. 2330702.

Table S3. Crystal data and structure refinement for product **36**.

CCDC	2330702
Displacement ellipsoids are drawn at the 50% probability level	
Empirical formula	C ₃₈ H ₃₀ Cl ₂ O ₂
Formula weight	589.52
Temperature [K]	296.15
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
<i>a</i> [Å]	9.6677(8)
<i>b</i> [Å]	12.9019(11)
<i>c</i> [Å]	13.3368(11)
α [°]	73.280(5)

β [°]	88.509(5)
γ [°]	71.049(5)
Volume [Å ³]	1502.7(2)
<i>Z</i>	2
ρ_{calc} [gcm ⁻³]	1.303
μ [mm ⁻¹]	0.250
<i>F</i> (000)	616
Crystal colour	colourless
Crystal shape	block
Radiation	MoK α (λ =0.71073 Å)
2 θ range [°]	3.20 to 53.00 (0.80 Å)
Index ranges	-12 ≤ <i>h</i> ≤ 12 -16 ≤ <i>k</i> ≤ 16 -16 ≤ <i>l</i> ≤ 15
Reflections collected	32520
Independent reflections	6150 <i>R</i> _{int} = 0.0550 <i>R</i> _{sigma} = 0.0811
Completeness to $\theta = 25.242^\circ$	99.8 %
Data / Restraints / Parameters	6150/0/382
Absorption correction	0.9158/1.0000
<i>T</i> _{min} / <i>T</i> _{max} (method)	(numerical)
Goodness-of-fit on <i>F</i> ²	1.008
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0552 <i>wR</i> ₂ = 0.1260
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1631 <i>wR</i> ₂ = 0.1600
Largest peak/hole [eÅ ⁻³]	0.38/-0.36
Extinction coefficient	0.0051(15)

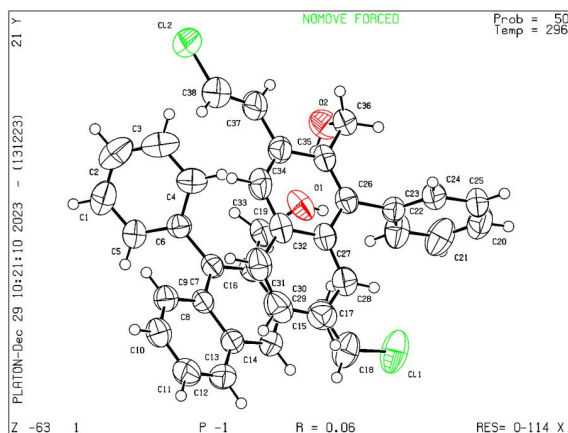
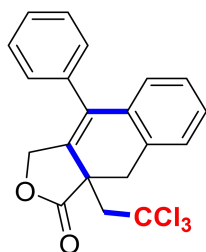


Fig. S3 Structure of product **36**.

Physical data for the following products:

1. 4-phenyl-9a-(2,2,2-trichloroethyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



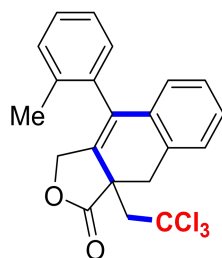
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 32.3 mg, 82% yield. Mp: 189-190 °C

¹H NMR (400 MHz, CDCl₃): δ 7.46 – 7.40 (m, 3H), 7.30 – 7.28 (m, 2H), 7.25 – 7.22 (m, 1H), 7.20 – 7.17 (m, 2H), 7.04 (d, *J* = 6.8 Hz, 1H), 5.36 (d, *J* = 13.2 Hz, 1H), 4.79 (d, *J* = 13.2 Hz, 1H), 3.27 (s, 2H), 3.20 (d, *J* = 15.6 Hz, 1H), 2.86 (d, *J* = 15.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 178.6, 135.9, 135.6, 134.1, 132.2, 130.3, 129.2, 128.9, 128.8, 128.7, 128.5, 127.9, 127.2, 96.2, 71.2, 55.0, 45.6, 38.4.

HRMS (ESI, *m/z*): calcd for C₂₀H₁₆Cl₃O₂ [M + H]⁺, 393.0210; Measured, 393.0221.

2. 4-(*o*-tolyl)-9a-(2,2,2-trichloroethyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



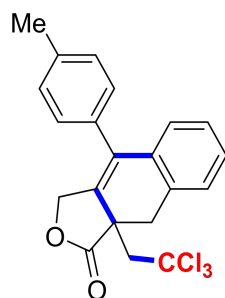
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 30.2 mg, 74% yield. Mp: 208-209 °C

¹H NMR (400 MHz, CDCl₃): δ 7.35 – 7.30 (m, 1H), 7.29 – 7.23 (m, 4H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.13 (d, *J* = 13.2 Hz, 1H), 4.59 (d, *J* = 13.6 Hz, 1H), 3.33 (d, *J* = 15.2 Hz, 1H), 3.28 (d, *J* = 15.2 Hz, 1H), 3.19 (d, *J* = 15.6 Hz, 1H), 2.91 (d, *J* = 15.6 Hz, 1H), 1.87 (s, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 178.6, 135.9, 135.7, 135.1, 134.1, 131.2, 131.2, 130.8, 129.4, 129.0, 128.8, 128.5, 128.2, 126.2, 126.0, 96.3, 70.8, 55.3, 45.2, 38.6, 19.7.

HRMS (ESI, m/z): calcd for C₂₁H₁₈Cl₃O₂ [M + H]⁺, 407.0367; Measured, 407.0362.

3. 4-(p-tolyl)-9a-(2,2,2-trichloroethyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



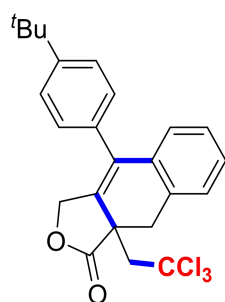
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 29.8 mg, 73% yield. Mp: 206-207 °C

¹H NMR (400 MHz, CDCl₃): δ 7.28 – 7.26 (m, 2H), 7.25 – 7.21 (m, 3H), 7.07 – 7.04 (m, 3H), 5.34 (d, *J* = 13.6 Hz, 1H), 4.79 (d, *J* = 13.2 Hz, 1H), 3.26 (s, 2H), 3.18 (d, *J* = 15.2 Hz, 1H), 2.85 (d, *J* = 15.2 Hz, 1H), 2.41 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 178.7, 138.6, 135.6, 134.3, 133.0, 132.3, 130.6, 129.8, 129.3, 128.9, 128.5, 127.9, 127.2, 96.3, 71.4, 55.1, 45.6, 38.5, 21.3.

HRMS (ESI, m/z): calcd for C₂₁H₂₁Cl₃NO₂ [M + NH₄]⁺, 424.0632; Measured, 424.0643.

4. 4-(4-(tert-butyl)phenyl)-9a-(2,2,2-trichloroethyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 30.2 mg, 67% yield. Mp: 210-211 °C

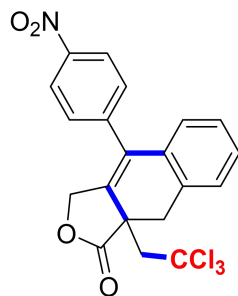
¹H NMR (400 MHz, CDCl₃): δ 7.45 – 7.41 (m, 2H), 7.29 – 7.27 (m, 2H), 7.25 – 7.22 (m, 1H), 7.13 – 7.08 (m, 3H), 5.37 (d, *J* = 13.2 Hz, 1H), 4.83 (d, *J* = 13.6 Hz, 1H),

3.26 (s, 2H), 3.18 (d, $J = 15.2$ Hz, 1H), 2.85 (d, $J = 15.2$ Hz, 1H), 1.36 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3): δ 178.8, 151.8, 135.5, 134.2, 132.9, 132.3, 130.6, 129.8, 128.9, 128.5, 127.8, 127.3, 125.5, 96.3, 71.5, 55.0, 45.7, 38.5, 34.7, 31.2.

HRMS (ESI, m/z): calcd for $\text{C}_{24}\text{H}_{23}\text{Cl}_3\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$, 471.0656; Measured, 471.0664.

5. 4-(4-nitrophenyl)-9a-(2,2,2-trichloroethyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



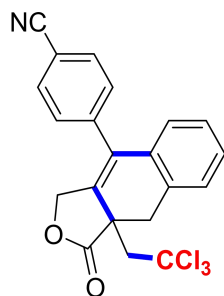
A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 27.2 mg, 62% yield. Mp: 234-235 °C

^1H NMR (400 MHz, CDCl_3): δ 8.35 – 8.27 (m, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 4.8$ Hz, 2H), 7.30 – 7.27 (m, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 5.37 (d, $J = 13.6$ Hz, 1H), 4.75 (d, $J = 13.6$ Hz, 1H), 3.31 (d, $J = 15.2$ Hz, 1H), 3.27 (d, $J = 15.2$ Hz, 1H), 3.21 (d, $J = 15.6$ Hz, 1H), 2.90 (d, $J = 15.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 177.9, 147.9, 142.9, 134.1, 133.4, 133.3, 132.2, 130.0, 129.4, 129.4, 128.4, 126.9, 124.2, 96.1, 70.7, 55.1, 45.8, 38.3.

HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{14}\text{Cl}_3\text{NO}_4\text{Na}$ $[\text{M} + \text{Na}]^+$, 459.9881; Measured, 459.9888.

6. 4-(1-oxo-9a-(2,2,2-trichloroethyl)-1,3,9,9a-tetrahydronaphtho[2,3-c]furan-4-yl)benzotrile



A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 31.4 mg, 75% yield. Mp: 211-212 °C

¹H NMR (400 MHz, CDCl₃): δ 7.78 – 7.71 (m, 2H), 7.34 – 7.31 (m, 4H), 7.29 – 7.27 (m, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 5.36 (d, *J* = 13.6 Hz, 1H), 4.75 (d, *J* = 13.6 Hz, 1H), 3.30 (d, *J* = 15.2 Hz, 1H), 3.26 (d, *J* = 14.8 Hz, 1H), 3.20 (d, *J* = 15.6 Hz, 1H), 2.89 (d, *J* = 15.2 Hz, 1H).

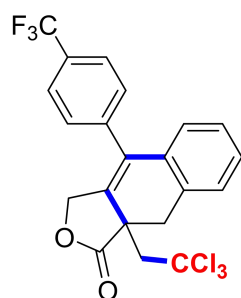
¹³C NMR (100 MHz, CDCl₃): δ 177.9, 140.9, 134.3, 133.2, 132.9, 132.1, 129.7, 129.2, 129.2, 128.2, 126.8, 118.3, 112.5, 96.1, 70.7, 55.0, 45.7, 38.2.

HRMS (ESI, m/z): calcd for C₂₁H₁₈Cl₃N₂O₂ [M + NH₄]⁺, 435.0428; Measured, 435.0434.

7.

9a-(2,2,2-trichloroethyl)-4-(4-(trifluoromethyl)phenyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one

e



A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 30.9 mg, 67% yield. Mp: 235-236 °C

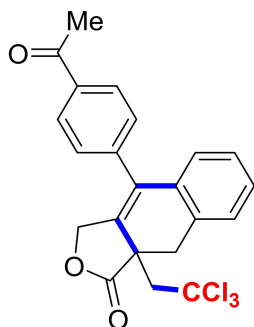
¹H NMR (400 MHz, CDCl₃): δ 7.74 – 7.68 (m, 2H), 7.33 – 7.31 (m, 4H), 7.28 – 7.24 (m, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 5.36 (d, *J* = 13.6 Hz, 1H), 4.76 (d, *J* = 13.2 Hz, 1H), 3.29 (s, 2H), 3.21 (d, *J* = 15.6 Hz, 1H), 2.89 (d, *J* = 15.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 178.1, 139.8, 134.5, 133.6, 132.2, 132.1, 130.7(q, *J* = 32.5 Hz), 129.4(d, *J* = 20.0 Hz), 129.1, 129.0, 128.1, 126.9, 125.7(d, *J* = 16.8 Hz), 123.8(q, *J* = 270.7 Hz), 96.1, 70.8, 55.0, 45.7, 38.3.

¹⁹F NMR (565 MHz, CDCl₃): δ -62.69 (s, 3F).

HRMS (ESI, m/z): calcd for C₂₁H₁₈Cl₃F₃NO₂ [M + NH₄]⁺, 478.0350; Measured, 478.0357.

8. 4-(4-acetylphenyl)-9a-(2,2,2-trichloroethyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



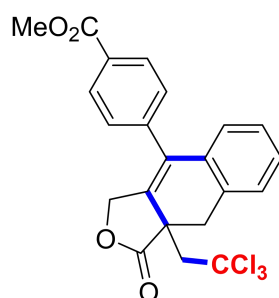
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 34.8 mg, 80% yield. Mp: 203-204 °C

¹H NMR (600 MHz, CDCl₃): δ 8.09 – 7.98 (m, 2H), 7.32 – 7.29 (m, 4H), 7.27 – 7.24 (m, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 5.36 (d, *J* = 13.8 Hz, 1H), 4.76 (d, *J* = 13.2 Hz, 1H), 3.29 (d, *J* = 15.0 Hz, 1H), 3.27 (d, *J* = 15.0 Hz, 1H), 3.20 (d, *J* = 15.0 Hz, 1H), 2.89 (d, *J* = 15.6 Hz, 1H), 2.66 (s, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 197.3, 178.1, 140.9, 137.1, 134.9, 133.6, 132.2, 132.0, 129.4, 129.1, 128.9, 128.8, 128.1, 127.0, 96.1, 70.9, 55.1, 45.7, 38.3, 26.6.

HRMS (ESI, *m/z*): calcd for C₂₂H₂₁Cl₃NO₃ [M + NH₄]⁺, 452.0582; Measured, 452.0588.

9. methyl-4-(1-oxo-9a-(2,2,2-trichloroethyl)-1,3,9a-tetrahydronaphtho[2,3-c]furan-4-yl)benzoate



A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 32.6 mg, 72% yield. Mp: 177-178 °C

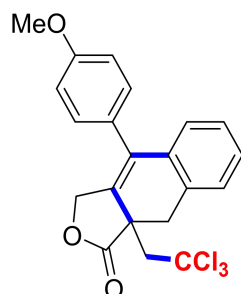
¹H NMR (600 MHz, CDCl₃): δ 8.16 – 8.05 (m, 2H), 7.31 – 7.30 (m, 2H), 7.27 – 7.24 (m, 3H), 6.98 (d, *J* = 7.8 Hz, 1H), 5.36 (d, *J* = 13.2 Hz, 1H), 4.75 (d, *J* = 13.8 Hz, 1H), 3.96 (s, 3H), 3.29 (d, *J* = 15.0 Hz, 1H), 3.26 (d, *J* = 15.0 Hz, 1H), 3.20 (d, *J* = 15.6 Hz, 1H), 2.88 (d, *J* = 15.6 Hz, 1H).

¹³C NMR (150 MHz, CDCl₃): δ 178.2, 166.4, 140.7, 134.9, 133.7, 132.2, 131.9,

130.3, 130.1, 129.7, 129.1, 128.9, 128.1, 127.0, 96.2, 70.9, 55.1, 52.3, 45.7, 38.3.

HRMS (ESI, m/z): calcd for C₂₂H₂₁Cl₃NO₄ [M + NH₄]⁺, 468.0531; Measured, 468.0536.

10. 4-(4-methoxyphenyl)-9a-(2,2,2-trichloroethyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



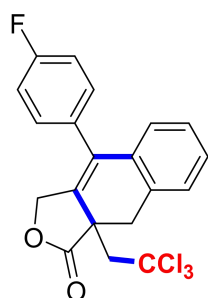
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 27.2 mg, 64% yield. Mp: 199-200 °C

¹H NMR (600 MHz, CDCl₃): δ 7.27 (d, *J* = 4.2 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 5.34 (d, *J* = 13.2 Hz, 1H), 4.79 (d, *J* = 13.2 Hz, 1H), 3.86 (s, 3H), 3.27 (d, *J* = 15.0 Hz, 1H), 3.24 (d, *J* = 15.0 Hz, 1H), 3.18 (d, *J* = 15.0 Hz, 1H), 2.84 (d, *J* = 15.0 Hz, 1H).

¹³C NMR (150 MHz, CDCl₃): δ 178.7, 159.8, 135.3, 134.3, 132.3, 130.6, 129.3, 128.9, 128.5, 128.2, 127.9, 127.2, 114.2, 96.3, 71.4, 55.3, 55.1, 45.6, 38.5.

HRMS (ESI, m/z): calcd for C₂₁H₁₈Cl₃O₃ [M + H]⁺, 423.0316; Measured, 423.0312.

11. 4-(4-fluorophenyl)-9a-(2,2,2-trichloroethyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 27.1 mg, 70% yield. Mp: 209-210 °C

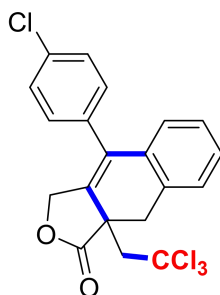
¹H NMR (400 MHz, CDCl₃): δ 5.67 – 5.65 (m, 2H), 5.64 – 5.60 (m, 1H), 5.56 – 5.49 (m, 4H), 5.37 (d, *J* = 7.2 Hz, 1H), 3.70 (d, *J* = 13.6 Hz, 1H), 3.14 (d, *J* = 13.2 Hz, 1H), 1.63 (s, 2H), 1.55 (d, *J* = 15.2 Hz, 1H), 1.23 (d, *J* = 15.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 178.5, 162.7(d, *J* = 247.8 Hz), 134.7, 134.0, 132.2, 132.0, 131.9(d, *J* = 4.1 Hz), 130.9, 129.0, 128.7, 128.0, 127.0, 116.0(d, *J* = 23.7 Hz), 96.2, 71.1, 55.0, 45.6, 38.4.

¹⁹F NMR (565 MHz, CDCl₃): δ -112.10 (s, 1F).

HRMS (ESI, m/z): calcd for C₂₀H₁₈Cl₃FNO₂ [M + NH₄]⁺, 428.0382; Measured, 428.0388.

12. 4-(4-chlorophenyl)-9a-(2,2,2-trichloroethyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



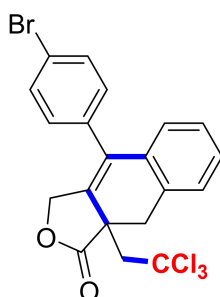
A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 25.7 mg, 60% yield. Mp: 208-209 °C

¹H NMR (400 MHz, CDCl₃): δ 7.45 – 7.37 (m, 2H), 7.30 (d, *J* = 4.0 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 1H), 5.33 (d, *J* = 13.2 Hz, 1H), 4.77 (d, *J* = 13.2 Hz, 1H), 3.28 (d, *J* = 15.2 Hz, 1H), 3.24 (d, *J* = 14.8 Hz, 1H), 3.18 (d, *J* = 15.2 Hz, 1H), 2.86 (d, *J* = 15.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 178.3, 134.7, 134.6, 134.4, 133.8, 132.2, 131.0, 130.4, 129.1, 129.0, 128.8, 128.0, 127.0, 96.2, 71.0, 55.0, 45.6, 38.3.

HRMS (ESI, m/z): calcd for C₂₀H₁₈Cl₄NO₂ [M + NH₄]⁺, 446.0059; Measured, 446.0063.

13. 4-(4-bromophenyl)-9a-(2,2,2-trichloroethyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



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

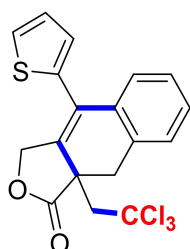
40/1). 41.0 mg, 87% yield. Mp: 211-212 °C

¹H NMR (600 MHz, CDCl₃): δ 7.62 – 7.51 (m, 2H), 7.29 (d, *J* = 4.2 Hz, 2H), 7.25 – 7.23 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 1H), 5.32 (d, *J* = 13.2 Hz, 1H), 4.76 (d, *J* = 13.8 Hz, 1H), 3.27 (d, *J* = 15.0 Hz, 1H), 3.24 (d, *J* = 15.0 Hz, 1H), 3.18 (d, *J* = 15.6 Hz, 1H), 2.86 (d, *J* = 15.6 Hz, 1H).

¹³C NMR (150 MHz, CDCl₃): δ 178.2, 134.9, 134.6, 133.7, 132.2, 131.9, 131.0, 130.7, 129.0, 128.8, 128.0, 126.9, 122.9, 96.2, 70.9, 55.0, 45.6, 38.3.

HRMS (ESI, m/z): calcd for C₂₀H₁₈BrCl₃NO₂ [M + NH₄]⁺, 489.9557; Measured, 489.9563.

14. 4-(thiophen-2-yl)-9a-(2,2,2-trichloroethyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



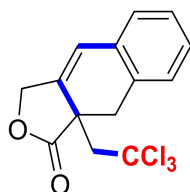
A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 19.2 mg, 48% yield. Mp: 213-214 °C

¹H NMR (600 MHz, CDCl₃): δ 7.45 (d, *J* = 4.8 Hz, 1H), 7.36 – 7.35 (m, 1H), 7.32 – 7.27 (m, 3H), 7.15 – 7.14 (m, 1H), 6.99 (d, *J* = 3.6 Hz, 1H), 5.37 (d, *J* = 13.8 Hz, 1H), 5.02 (d, *J* = 13.8 Hz, 1H), 3.26 (d, *J* = 15.0 Hz, 1H), 3.21 (d, *J* = 15.0 Hz, 1H), 3.17 (d, *J* = 15.6 Hz, 1H), 2.85 (d, *J* = 15.6 Hz, 1H).

¹³C NMR (150 MHz, CDCl₃): δ 178.3, 137.0, 133.7, 132.1, 131.2, 129.1, 129.0, 128.9, 128.5, 128.0, 127.5, 127.1, 127.0, 96.1, 71.4, 55.0, 45.7, 38.1.

HRMS (ESI, m/z): calcd for C₁₈H₁₇Cl₃NO₂S [M + NH₄]⁺, 418.0012; Measured, 418.0203.

15. 9a-(2,2,2-trichloroethyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



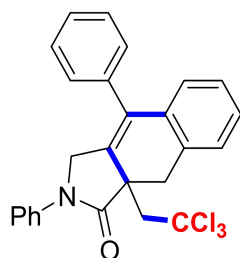
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 17.1 mg, 54% yield. Mp: 93-94 °C

¹H NMR (600 MHz, CDCl₃): δ 7.29 – 7.26 (m, 1H), 7.25 – 7.21 (m, 2H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.60 (s, 1H), 5.25 (dd, *J* = 13.2, 2.4 Hz, 1H), 5.04 (d, *J* = 12.6 Hz, 1H), 3.26 (d, *J* = 15.0 Hz, 1H), 3.18 (d, *J* = 15.0 Hz, 1H), 3.07 (d, *J* = 15.0 Hz, 1H), 2.86 (d, *J* = 15.6 Hz, 1H).

¹³C NMR (150 MHz, CDCl₃): δ 178.1, 135.0, 132.2, 131.0, 129.0, 128.5, 128.1, 127.0, 123.5, 95.9, 71.1, 55.2, 44.7, 38.1.

HRMS (ESI, m/z): calcd for C₁₄H₁₂Cl₃O₂ [M + H]⁺, 316.9897; Measured, 316.9890.

16. 2,4-diphenyl-9a-(2,2,2-trichloroethyl)-2,3,9a-tetrahydro-1H-benzo[f]isoindol-1-one



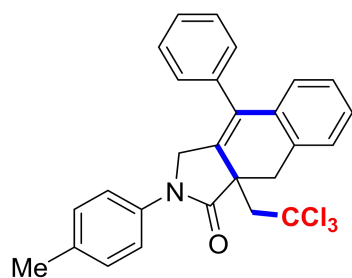
A yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 35.2 mg, 75% yield.

¹H NMR (600 MHz, CDCl₃): δ 7.65 (d, *J* = 7.8 Hz, 2H), 7.50 – 7.47 (m, 1H), 7.41 – 7.39 (m, 2H), 7.37 – 7.33 (m, 3H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.17 – 7.13 (m, 2H), 6.98 (d, *J* = 7.2 Hz, 1H), 4.93 (d, *J* = 13.8 Hz, 1H), 4.28 (d, *J* = 13.8 Hz, 1H), 3.36 (d, *J* = 15.0 Hz, 1H), 3.25 (d, *J* = 15.0 Hz, 1H), 3.23 (d, *J* = 16.2 Hz, 1H), 2.92 (d, *J* = 15.6 Hz, 1H).

¹³C NMR (150 MHz, CDCl₃): δ 174.1, 138.8, 136.9, 135.4, 135.1, 133.1, 129.3, 128.9, 128.9, 128.7, 128.5, 128.3, 128.1, 127.6, 126.9, 125.0, 120.1, 96.9, 54.8, 52.9, 48.9, 38.9.

HRMS (ESI, m/z): calcd for C₂₆H₂₁Cl₃NO [M + H]⁺, 468.0683; Measured, 468.0680.

17. 4-phenyl-2-(p-tolyl)-9a-(2,2,2-trichloroethyl)-2,3,9a-tetrahydro-1H-benzo[f]isoindol-1-one



A yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 23.2 mg, 48% yield.

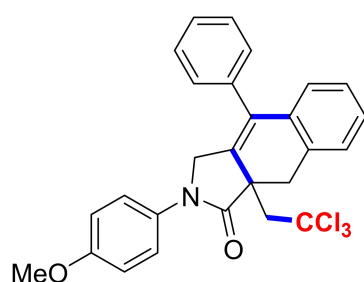
¹H NMR (600 MHz, CDCl₃): δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.47 (m, 1H), 7.41 – 7.39 (m, 2H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 3H), 6.98 (d, *J* = 7.8 Hz, 1H), 4.90 (d, *J* = 13.8 Hz, 1H), 4.25 (d, *J* = 13.8 Hz, 1H), 3.35 (d, *J* = 15.0 Hz, 1H), 3.24 (d, *J* = 14.4 Hz, 1H), 3.22 (d, *J* = 15.0 Hz, 1H), 2.91 (d, *J* = 15.6 Hz, 1H), 2.31 (s, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 173.9, 137.0, 136.3, 135.3, 135.1, 134.8, 133.2, 129.4, 129.1, 128.9, 128.6, 128.5, 128.2, 128.1, 127.6, 126.9, 120.1, 97.0, 54.8, 53.0, 48.9, 38.9, 20.9.

HRMS (ESI, *m/z*): calcd for C₂₇H₂₃Cl₃NO [M + H]⁺, 482.0840; Measured, 482.0835.

18.

2-(4-methoxyphenyl)-4-phenyl-9a-(2,2,2-trichloroethyl)-2,3,9a-tetrahydro-1H-benzo[f]isoindol-1-one



A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 30.9 mg, 62% yield. Mp: 168-169 °C

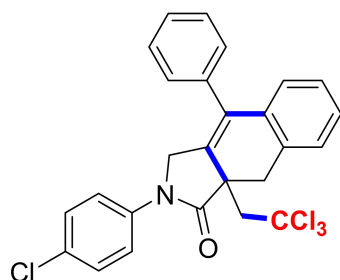
¹H NMR (600 MHz, CDCl₃): δ 7.55 – 7.53 (m, 2H), 7.47 – 7.45 (m, 1H), 7.40 – 7.37 (m, 2H), 7.36 – 7.32 (m, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.24 – 7.15 (m, 3H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.88 – 6.86 (m, 2H), 4.89 (d, *J* = 13.8 Hz, 1H), 4.23 (d, *J* = 13.8 Hz,

1H), 3.77 (s, 3H), 3.34 (d, $J = 15.0$ Hz, 1H), 3.23 (d, $J = 15.0$ Hz, 1H), 3.21 (d, $J = 15.6$ Hz, 1H), 2.91 (d, $J = 15.6$ Hz, 1H).

^{13}C NMR (150 MHz, CDCl_3): δ 173.7, 156.9, 137.0, 135.2, 135.1, 133.2, 132.1, 129.2, 128.9, 128.2, 128.1, 127.6, 126.9, 121.8, 114.1, 97.0, 55.4, 54.8, 53.3, 48.7, 38.9.

HRMS (ESI, m/z): calcd for $\text{C}_{27}\text{H}_{23}\text{Cl}_3\text{NO}_2$ [$\text{M} + \text{H}$] $^+$, 500.0764; Measured, 500.0757.

19. 9a-(2,2-dichloroethyl)-4-phenyl-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



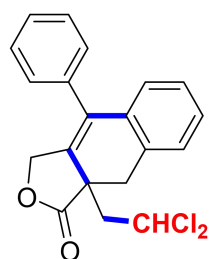
A yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 30.2 mg, 60% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.62 (d, $J = 8.8$ Hz, 2H), 7.50 – 7.47 (m, 1H), 7.43 – 7.39 (m, 2H), 7.36 – 7.34 (m, 1H), 7.31 – 7.28 (m, 3H), 7.25 – 7.23 (m, 1H), 7.21 – 7.14 (m, 2H), 6.98 (d, $J = 7.6$ Hz, 1H), 4.89 (d, $J = 14.0$ Hz, 1H), 4.25 (d, $J = 14.0$ Hz, 1H), 3.33 (d, $J = 15.2$ Hz, 1H), 3.25 (d, $J = 12.0$ Hz, 1H), 3.22 (d, $J = 12.0$ Hz, 1H), 2.91 (d, $J = 15.2$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 174.2, 137.4, 136.7, 135.6, 134.9, 132.9, 130.1, 129.3, 128.9, 128.7, 128.6, 128.3, 128.3, 128.2, 127.7, 127.0, 121.1, 96.9, 54.8, 52.7, 48.9, 38.8.

HRMS (ESI, m/z): calcd for $\text{C}_{26}\text{H}_{20}\text{Cl}_2\text{NO}$ [$\text{M} + \text{H}$] $^+$, 504.0267; Measured, 504.0261.

20. 9a-(2,2-dichloroethyl)-4-phenyl-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



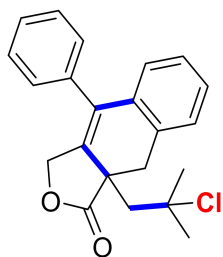
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 10.8 mg, 30% yield. Mp: 85-86 °C

¹H NMR (600 MHz, CDCl₃): δ 7.46 – 7.41 (m, 3H), 7.29 – 7.27 (m, 2H), 7.23 – 7.19 (m, 3H), 7.02 (d, *J* = 7.2 Hz, 1H), 5.86 (dd, *J* = 7.2, 4.8 Hz, 1H), 5.26 (d, *J* = 13.8 Hz, 1H), 4.73 (d, *J* = 13.8 Hz, 1H), 3.17 (d, *J* = 15.6 Hz, 1H), 3.05 (d, *J* = 15.6 Hz, 1H), 2.76 – 2.69 (m, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 178.1, 135.8, 135.7, 133.8, 132.3, 131.4, 129.1, 128.7, 128.7, 127.7, 127.1, 70.5, 69.3, 46.2, 44.9, 36.5.

HRMS (ESI, m/z): calcd for C₂₀H₂₀Cl₂NO₂ [M + NH₄]⁺, 376.0866; Measured, 376.0873.

21. 9a-(2-chloro-2-methylpropyl)-4-phenyl-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



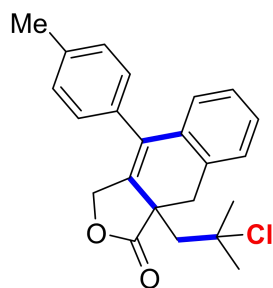
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 22.2 mg, 63% yield. Mp: 144-145 °C

¹H NMR (400 MHz, CDCl₃): δ 7.44 – 7.37 (m, 3H), 7.26 – 7.24 (m, 2H), 7.22 – 7.17 (m, 3H), 7.01 (d, *J* = 7.2 Hz, 1H), 5.43 (d, *J* = 13.6 Hz, 1H), 4.76 (d, *J* = 13.6 Hz, 1H), 3.14 (d, *J* = 15.2 Hz, 1H), 2.84 (d, *J* = 15.2 Hz, 1H), 2.37 (d, *J* = 14.8 Hz, 1H), 2.22 (d, *J* = 14.8 Hz, 1H), 1.62 (s, 3H), 1.57 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 180.2, 136.4, 134.3, 134.2, 133.2, 129.2, 128.9, 128.7, 128.4, 128.2, 127.4, 126.9, 71.1, 68.1, 47.4, 44.9, 39.1, 34.4, 33.3.

HRMS (ESI, m/z): calcd for C₂₂H₂₅ClNO₂ [M + NH₄]⁺, 370.1568; Measured, 370.1574.

22. 9a-(2-chloro-2-methylpropyl)-4-(p-tolyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



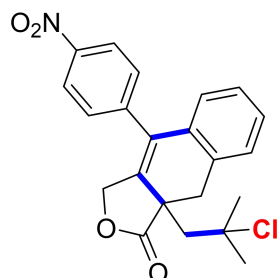
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 25.7 mg, 70% yield. Mp: 161-162 °C

¹H NMR (400 MHz, CDCl₃): δ 7.25 – 7.23 (m, 3H), 7.22 – 7.20 (m, 1H), 7.20 – 7.17 (m, 1H), 7.12 – 7.05 (m, 2H), 7.02 (d, *J* = 7.6 Hz, 1H), 5.42 (d, *J* = 13.2 Hz, 1H), 4.76 (d, *J* = 13.2 Hz, 1H), 3.13 (d, *J* = 15.2 Hz, 1H), 2.83 (d, *J* = 15.2 Hz, 1H), 2.41 (s, 3H), 2.36 (d, *J* = 14.8 Hz, 1H), 2.22 (d, *J* = 14.8 Hz, 1H), 1.62 (s, 3H), 1.57 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 180.3, 138.3, 134.4, 134.1, 133.4, 133.3, 132.7, 129.2, 128.8, 128.1, 127.4, 126.9, 71.2, 68.2, 47.4, 44.8, 39.1, 34.3, 33.4, 21.3.

HRMS (ESI, m/z): calcd for C₂₃H₂₇ClNO₂ [M + NH₄]⁺, 384.1725; Measured, 384.1731.

23. 9a-(2-chloro-2-methylpropyl)-4-(4-nitrophenyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 12.0 mg, 30% yield. Mp: 188-189 °C

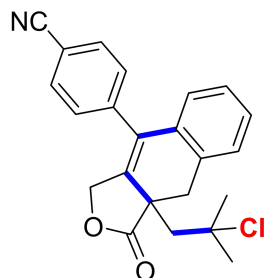
¹H NMR (400 MHz, CDCl₃): δ 8.30 (s, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 4.8 Hz, 2H), 7.24 – 7.21 (m, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 5.47 (d, *J* = 13.6 Hz, 1H), 4.72 (d, *J* = 14.0 Hz, 1H), 3.15 (d, *J* = 15.6 Hz, 1H), 2.87 (d, *J* = 15.6 Hz, 1H), 2.41 (d, *J* = 14.8 Hz, 1H), 2.19 (d, *J* = 14.8 Hz, 1H), 1.64 (s, 3H), 1.56 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 179.4, 147.6, 143.4, 136.3, 133.3, 133.1, 132.4, 130.0, 129.2, 128.9, 127.8, 126.5, 124.0, 70.7, 68.1, 47.6, 45.0, 38.9, 35.1, 32.6.

HRMS (ESI, m/z): calcd for C₂₂H₂₄ClN₂O₄ [M + NH₄]⁺, 415.1419; Measured, 415.1426.

24.

4-(9a-(2-chloro-2-methylpropyl)-1-oxo-1,3,9,9a-tetrahydronaphtho[2,3-c]furan-4-yl)benzonitrile



A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 25.7 mg, 68% yield. Mp: 168-169 °C

¹H NMR (400 MHz, CDCl₃): δ 7.76 – 7.70 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 (d, *J* = 4.0 Hz, 2H), 7.24 – 7.20 (m, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 5.44 (d, *J* = 13.6 Hz, 1H), 4.70 (d, *J* = 13.6 Hz, 1H), 3.13 (d, *J* = 15.2 Hz, 1H), 2.85 (d, *J* = 15.2 Hz, 1H), 2.39 (d, *J* = 14.8 Hz, 1H), 2.18 (d, *J* = 14.8 Hz, 1H), 1.62 (s, 3H), 1.55 (s, 3H).

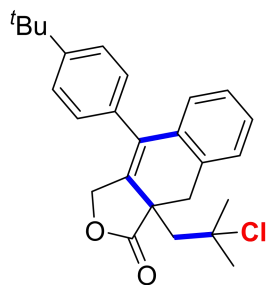
¹³C NMR (100 MHz, CDCl₃): δ 179.5, 141.4, 135.8, 133.3, 133.1, 132.6, 132.2, 129.8, 129.1, 128.7, 127.7, 126.5, 118.4, 112.1, 70.7, 68.1, 47.5, 44.9, 38.9, 35.0, 32.7.

HRMS (ESI, m/z): calcd for C₂₃H₂₄ClN₂O₂ [M + NH₄]⁺, 395.1521; Measured, 395.1526.

25.

4-(4-(tert-butyl)phenyl)-9a-(2-chloro-2-methylpropyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one

e



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

40/1). 25.0 mg, 61% yield. Mp: 139-140 °C

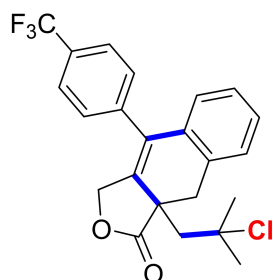
¹H NMR (400 MHz, CDCl₃): δ 7.47 – 7.40 (m, 2H), 7.25 – 7.23 (m, 2H), 7.22 – 7.18 (m, 1H), 7.13 – 7.11 (m, 2H), 7.06 (d, *J* = 6.8 Hz, 1H), 5.44 (d, *J* = 13.2 Hz, 1H), 4.81 (d, *J* = 13.6 Hz, 1H), 3.13 (d, *J* = 15.2 Hz, 1H), 2.83 (d, *J* = 15.2 Hz, 1H), 2.35 (d, *J* = 14.8 Hz, 1H), 2.23 (d, *J* = 15.2 Hz, 1H), 1.62 (s, 3H), 1.57 (s, 3H), 1.36 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ 180.4, 151.4, 134.3, 134.1, 133.4, 133.3, 132.7, 128.8, 128.5, 128.1, 127.4, 127.0, 125.4, 71.3, 68.2, 47.3, 44.9, 39.1, 34.7, 34.3, 33.4, 31.3.

HRMS (ESI, m/z): calcd for C₂₆H₃₃ClNO₂ [M + NH₄]⁺, 426.2194; Measured, 426.2200.

26.

9a-(2-chloro-2-methylpropyl)-4-(4-(trifluoromethyl)phenyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 22.7 mg, 54% yield. Mp: 175-176 °C

¹H NMR (400 MHz, CDCl₃): δ 7.73 – 7.66 (m, 2H), 7.36 – 7.32 (m, 2H), 7.28 – 7.26 (m, 2H), 7.25 – 7.20 (m, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 5.45 (d, *J* = 13.6 Hz, 1H), 4.73 (d, *J* = 13.6 Hz, 1H), 3.16 (d, *J* = 15.2 Hz, 1H), 2.86 (d, *J* = 15.2 Hz, 1H), 2.40 (d, *J* = 14.8 Hz, 1H), 2.21 (d, *J* = 14.8 Hz, 1H), 1.64 (s, 3H), 1.57 (s, 3H).

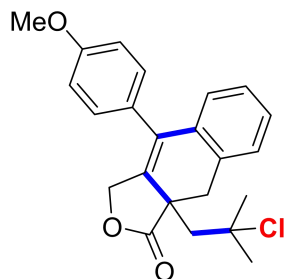
¹³C NMR (100 MHz, CDCl₃): δ 179.7, 140.3, 135.0, 133.7, 133.1, 132.9, 130.4(q, *J* = 32.3 Hz), 129.4(d, *J* = 28.7 Hz), 129.0, 128.6, 127.6, 126.6, 125.5(d, *J* = 15.7 Hz), 123.9(q, *J* = 270.9 Hz), 70.8, 68.1, 47.5, 44.9, 39.0, 34.9, 32.8.

¹⁹F NMR (565 MHz, CDCl₃): δ -62.66 (s, 3F).

HRMS (ESI, m/z): calcd for C₂₃H₂₄ClF₃NO₂ [M + NH₄]⁺, 438.1442; Measured, 438.1449.

27.

9a-(2-chloro-2-methylpropyl)-4-(4-methoxyphenyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



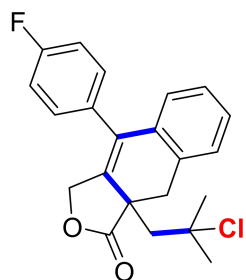
A white oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 20.3 mg, 53% yield.

¹H NMR (600 MHz, CDCl₃): δ 7.25 – 7.23 (m, 2H), 7.21 – 7.18 (m, 1H), 7.15 – 7.09 (m, 2H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 5.41 (d, *J* = 13.8 Hz, 1H), 4.77 (d, *J* = 13.2 Hz, 1H), 3.86 (s, 3H), 3.12 (d, *J* = 15.0 Hz, 1H), 2.82 (d, *J* = 15.0 Hz, 1H), 2.35 (d, *J* = 15.0 Hz, 1H), 2.21 (d, *J* = 15.0 Hz, 1H), 1.61 (s, 3H), 1.56 (s, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 180.3, 159.6, 134.4, 133.8, 133.4, 132.2, 128.8, 128.6, 128.1, 127.4, 126.8, 71.2, 68.2, 55.3, 47.4, 44.8, 39.1, 34.4, 33.3.

HRMS (ESI, *m/z*): calcd for C₂₃H₂₄ClO₃ [M + H]⁺, 383.1408; Measured, 383.1404.

28. 9a-(2-chloro-2-methylpropyl)-4-(4-fluorophenyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 27.1 mg, 73% yield. Mp: 157-158 °C

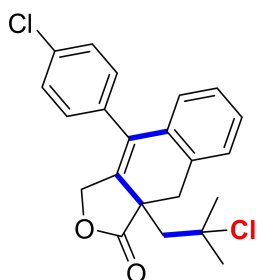
¹H NMR (400 MHz, CDCl₃): δ 7.27 – 7.25 (m, 2H), 7.23 – 7.19 (m, 2H), 7.16 – 7.11 (m, 3H), 6.97 (d, *J* = 7.6 Hz, 1H), 5.41 (d, *J* = 13.6 Hz, 1H), 4.74 (d, *J* = 13.6 Hz, 1H), 3.14 (d, *J* = 14.8 Hz, 1H), 2.84 (d, *J* = 15.2 Hz, 1H), 2.37 (d, *J* = 14.8 Hz, 1H), 2.20 (d, *J* = 14.8 Hz, 1H), 1.62 (s, 3H), 1.56 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 180.0, 162.6(d, *J* = 247.0 Hz), 134.1, 133.5, 133.2, 133.1, 132.3(d, *J* = 3.5 Hz), 130.8(d, *J* = 27.0 Hz), 128.9, 128.3, 127.5, 126.7, 115.8(d, *J* = 22.3 Hz), 71.0, 68.1, 47.4, 44.8, 39.0, 34.7, 33.0.

¹⁹F NMR (565 MHz, CDCl₃): δ -112.70 (s, 1F).

HRMS (ESI, m/z): calcd for C₂₂H₂₄ClFNO₂ [M + NH₄]⁺, 388.1474; Measured, 388.1479.

29. 9a-(2-chloro-2-methylpropyl)-4-(4-chlorophenyl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



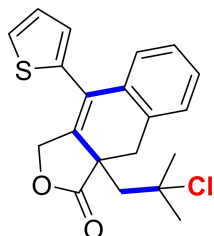
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 23.4 mg, 60% yield. Mp: 141-142 °C

¹H NMR (400 MHz, CDCl₃): δ 7.44 – 7.37 (m, 2H), 7.26 – 7.25 (m, 2H), 7.23 – 7.20 (m, 1H), 7.16 – 7.12 (m, 2H), 6.96 (d, *J* = 7.2 Hz, 1H), 5.42 (d, *J* = 13.2 Hz, 1H), 4.74 (d, *J* = 13.6 Hz, 1H), 3.13 (d, *J* = 15.2 Hz, 1H), 2.84 (d, *J* = 15.2 Hz, 1H), 2.37 (d, *J* = 14.8 Hz, 1H), 2.20 (d, *J* = 14.8 Hz, 1H), 1.62 (s, 3H), 1.56 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 179.9, 134.8, 134.3, 133.9, 133.2, 130.5, 130.1, 129.0, 128.9, 128.4, 127.5, 126.6, 70.9, 68.1, 47.4, 44.8, 39.0, 34.7, 33.0.

HRMS (ESI, m/z): calcd for C₂₂H₂₄Cl₂NO₂ [M + NH₄]⁺, 404.1179; Measured, 404.1187.

30. 9a-(2-chloro-2-methylpropyl)-4-(thiophen-2-yl)-9,9a-dihydronaphtho[2,3-c]furan-1(3H)-one



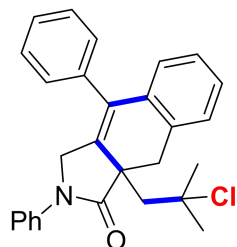
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 18.7 mg, 52% yield. Mp: 137-138 °C

¹H NMR (600 MHz, CDCl₃): δ 7.43 – 7.42 (m, 1H), 7.34 – 7.32 (m, 1H), 7.27 – 7.23 (m, 3H), 7.13 (dd, *J* = 5.4, 3.6 Hz, 1H), 7.00 – 6.99 (m, 1H), 5.45 (d, *J* = 13.8 Hz, 1H), 4.99 (d, *J* = 13.8 Hz, 1H), 3.11 (d, *J* = 15.6 Hz, 1H), 2.82 (d, *J* = 15.0 Hz, 1H), 2.31 (d, *J* = 15.0 Hz, 1H), 2.23 (d, *J* = 15.0 Hz, 1H), 1.59 (s, 3H), 1.53 (s, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 179.9, 137.4, 134.3, 133.9, 133.1, 128.9, 128.6, 128.2, 127.7, 127.6, 127.4, 126.7, 71.2, 68.0, 47.4, 45.0, 38.8, 34.1, 33.5.

HRMS (ESI, m/z): calcd for C₂₀H₂₃ClNO₂S [M + NH₄]⁺, 376.1133; Measured, 376.1137.

31. 9a-(2-chloro-2-methylpropyl)-2,4-diphenyl-2,3,9,9a-tetrahydro-1H-benzo[*f*]isoindol-1-one



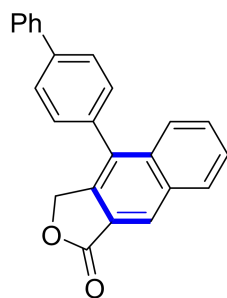
A yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 19.3 mg, 45% yield.

¹H NMR (600 MHz, CDCl₃): δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.47 (m, 1H), 7.42 – 7.39 (m, 3H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.23 – 7.21 (m, 1H), 7.19 – 7.13 (m, 3H), 6.95 (d, *J* = 7.2 Hz, 1H), 5.00 (d, *J* = 13.8 Hz, 1H), 4.26 (d, *J* = 13.8 Hz, 1H), 3.18 (d, *J* = 15.0 Hz, 1H), 2.90 (d, *J* = 15.0 Hz, 1H), 2.37 (d, *J* = 14.4 Hz, 1H), 2.29 (d, *J* = 14.4 Hz, 1H), 1.57 (s, 3H), 1.55 (s, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 175.9, 139.0, 137.4, 135.2, 134.2, 134.0, 131.8, 128.9, 128.8, 128.0, 127.7, 127.1, 126.6, 124.8, 120.1, 68.7, 52.9, 48.3, 47.2, 39.6, 34.8, 33.4.

HRMS (ESI, m/z): calcd for C₂₈H₂₇ClNO [M + H]⁺, 428.1776; Measured, 428.1772.

32. 4-([1,1'-biphenyl]-4-yl)naphtho[2,3-*c*]furan-1(3H)-one



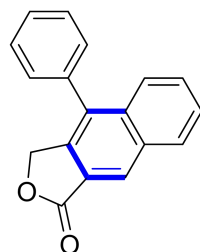
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 20.6 mg, 61% yield. Mp: 202-203 °C

¹H NMR (600 MHz, CDCl₃): δ 8.54 (s, 1H), 8.13 – 8.11 (m, 1H), 7.92 – 7.90 (m, 1H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.63 – 7.61 (m, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.41 (m, 1H), 5.33 (s, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 171.2, 141.3, 140.3, 138.5, 134.9, 134.7, 133.8, 133.7, 130.2, 129.8, 129.1, 129.0, 127.8, 127.7, 127.1, 126.8, 126.5, 125.9, 123.0, 69.6.

HRMS (ESI, m/z): calcd for C₂₄H₁₆O₂Na [M + Na]⁺, 359.1043; Measured, 359.1047.

33. 4-phenylnaphtho[2,3-c]furan-1(3H)-one



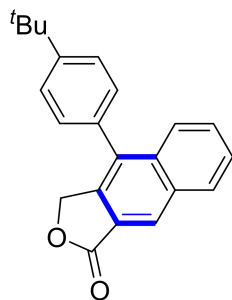
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 16.7 mg, 64% yield. Mp: 159-160 °C

¹H NMR (600 MHz, CDCl₃): δ 8.51 (s, 1H), 8.10 – 8.08 (m, 1H), 7.82 – 7.81 (m, 1H), 7.62 – 7.55 (m, 4H), 7.53 – 7.50 (m, 1H), 7.40 – 7.38 (m, 2H), 5.26 (s, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 171.2, 138.4, 135.8, 134.8, 134.1, 133.7, 130.1, 129.3, 129.0, 129.0, 128.4, 126.7, 126.4, 125.9, 122.9, 69.5.

HRMS (ESI, m/z): calcd for C₁₈H₁₃O₂ [M + H]⁺, 261.0910; Measured, 261.0909.

34. 4-(4-(tert-butyl)phenyl)naphtho[2,3-c]furan-1(3H)-one



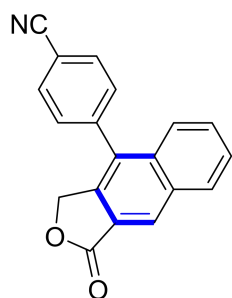
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 19.6 mg, 62% yield. Mp: 276-277 °C

¹H NMR (600 MHz, CDCl₃): δ 8.51 (s, 1H), 8.10 – 8.08 (m, 1H), 7.88 – 7.86 (m, 1H), 7.60 – 7.56 (m, 4H), 7.33 – 7.32 (m, 2H), 5.30 (s, 2H), 1.42 (s, 9H).

¹³C NMR (150 MHz, CDCl₃): δ 171.3, 151.4, 138.5, 135.0, 134.3, 133.7, 132.7, 130.1, 129.0, 128.9, 126.7, 126.2, 126.1, 125.9, 123.0, 69.8, 34.8, 31.3.

HRMS (ESI, m/z): calcd for C₂₂H₁₉O₂ [M – H]⁺, 315.1380; Measured, 315.1395.

35. 4-(1-oxo-1,3-dihydro-2H-naphtho[2,3-c]furan-4-yl)benzotrifluoride



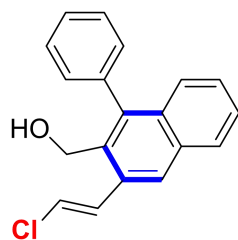
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1). 21.1 mg, 74% yield. Mp: 216-217 °C

¹H NMR (600 MHz, CDCl₃): δ 8.57 (s, 1H), 8.14 – 8.12 (m, 1H), 7.90 – 7.88 (m, 2H), 7.69 – 7.68 (m, 1H), 7.66 – 7.63 (m, 2H), 7.56 – 7.55 (m, 2H), 5.25 (s, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 170.6, 140.8, 138.4, 134.2, 133.7, 132.9, 131.9, 130.4, 130.3, 129.7, 127.6, 127.2, 125.1, 123.0, 118.3, 112.7, 69.1.

HRMS (ESI, m/z): calcd for C₁₉H₁₂NO₂ [M + H]⁺, 286.0863; Measured, 286.0862.

36. (3-(2-chlorovinyl)-1-phenylnaphthalen-2-yl)methanol



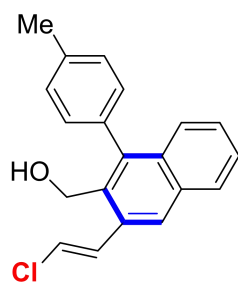
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 19.8 mg, 67% yield. Mp: 103-104 °C

¹H NMR (600 MHz, CDCl₃): δ 7.89 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.46 (m, 5H), 7.35 (d, *J* = 4.2 Hz, 2H), 7.32 – 7.30 (m, 2H), 6.75 (d, *J* = 13.2 Hz, 1H), 4.57 (s, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 140.4, 138.3, 133.2, 132.9, 132.8, 132.6, 131.9, 130.1, 128.4, 127.8, 127.6, 127.1, 126.5, 126.3, 125.9, 120.9, 60.4.

HRMS (ESI, m/z): calcd for C₁₉H₁₄ClO [M – H]⁺, 293.0728; Measured, 293.0744.

37. (3-(2-chlorovinyl)-1-(p-tolyl)naphthalen-2-yl)methanol



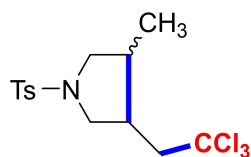
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). 17.9 mg, 58% yield. Mp: 103-104 °C

¹H NMR (400 MHz, CDCl₃): δ 7.87 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.38 – 7.31 (m, 4H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.74 (d, *J* = 13.2 Hz, 1H), 4.58 (s, 2H), 2.48 (s, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 140.5, 137.3, 135.2, 133.2, 132.9, 132.9, 132.7, 131.9, 130.0, 129.1, 127.8, 127.2, 126.4, 126.2, 125.7, 120.8, 60.4, 21.3.

HRMS (ESI, m/z): calcd for C₂₀H₁₆ClO [M – H]⁺, 307.0884; Measured, 307.0904.

38-a. 3-methyl-1-tosyl-4-(2,2,2-trichloroethyl)pyrrolidine



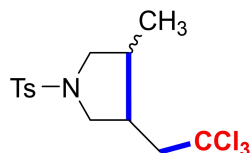
A transparent oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 22.6 mg, 61% yield.

^1H NMR (600 MHz, CDCl_3): δ 7.72 – 7.70 (m, 2H), 7.32 (d, $J = 7.8$ Hz, 2H), 3.67 – 3.64 (m, 1H), 3.37 – 3.34 (m, 1H), 3.18 – 3.15 (m, 1H), 3.06 (dd, $J = 10.2, 3.0$ Hz, 1H), 2.78 – 2.74 (m, 1H), 2.49 – 2.45 (m, 2H), 2.42 (s, 3H), 2.36 – 2.32 (m, 1H), 0.78 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 143.5, 133.9, 129.7, 127.3, 98.7, 54.3, 53.5, 51.0, 39.7, 35.9, 21.5, 13.5.

HRMS (ESI, m/z): calcd for $\text{C}_{14}\text{H}_{19}\text{Cl}_3\text{NO}_2\text{S}$ $[\text{M} + \text{H}]^+$, 370.0197; Measured, 370.0191.

38-b. 3-methyl-1-tosyl-4-(2,2,2-trichloroethyl)pyrrolidine



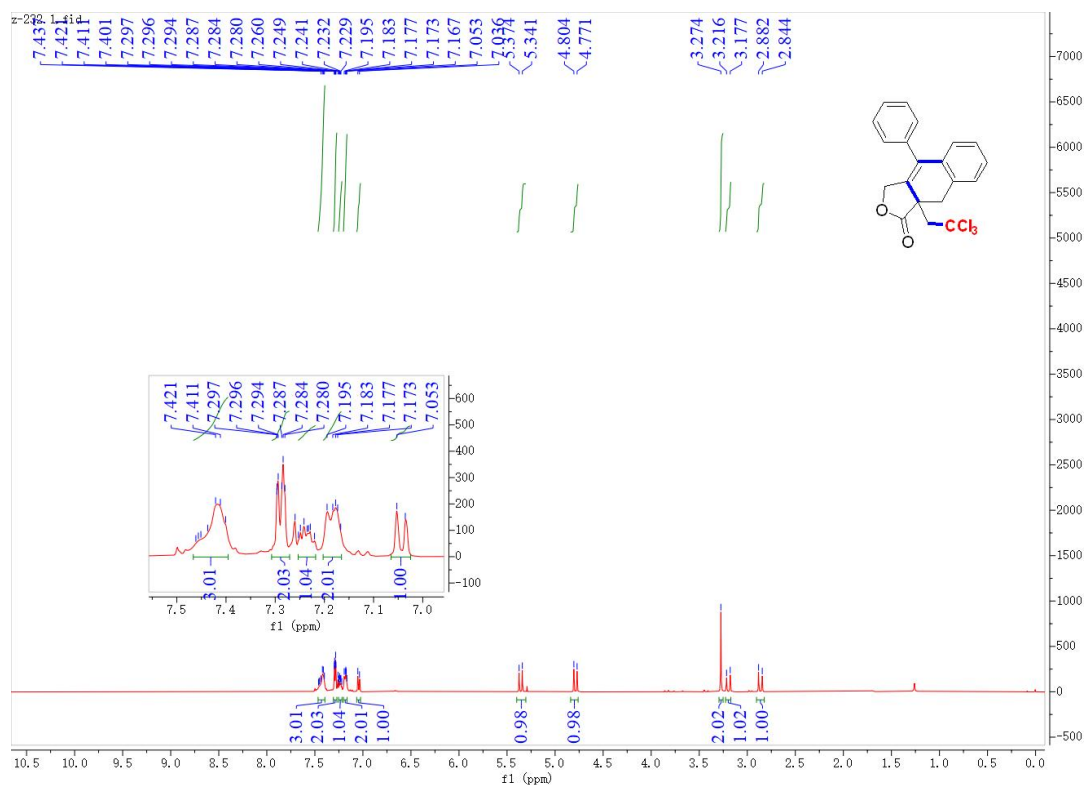
A transparent oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 9.3 mg, 25% yield.

^1H NMR (600 MHz, CDCl_3): δ 7.72 – 7.70 (m, 2H), 7.32 (d, $J = 7.8$ Hz, 2H), 3.84 (dd, $J = 10.2, 7.2$ Hz, 1H), 3.53 – 3.50 (m, 1H), 3.12 – 3.09 (m, 1H), 2.81 (dd, $J = 15.0, 1.8$ Hz, 1H), 2.78 – 2.74 (m, 1H), 2.58 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.43 (s, 3H), 2.00 – 1.94 (m, 1H), 1.83 – 1.77 (m, 1H), 0.99 (d, $J = 6.6$ Hz, 3H).

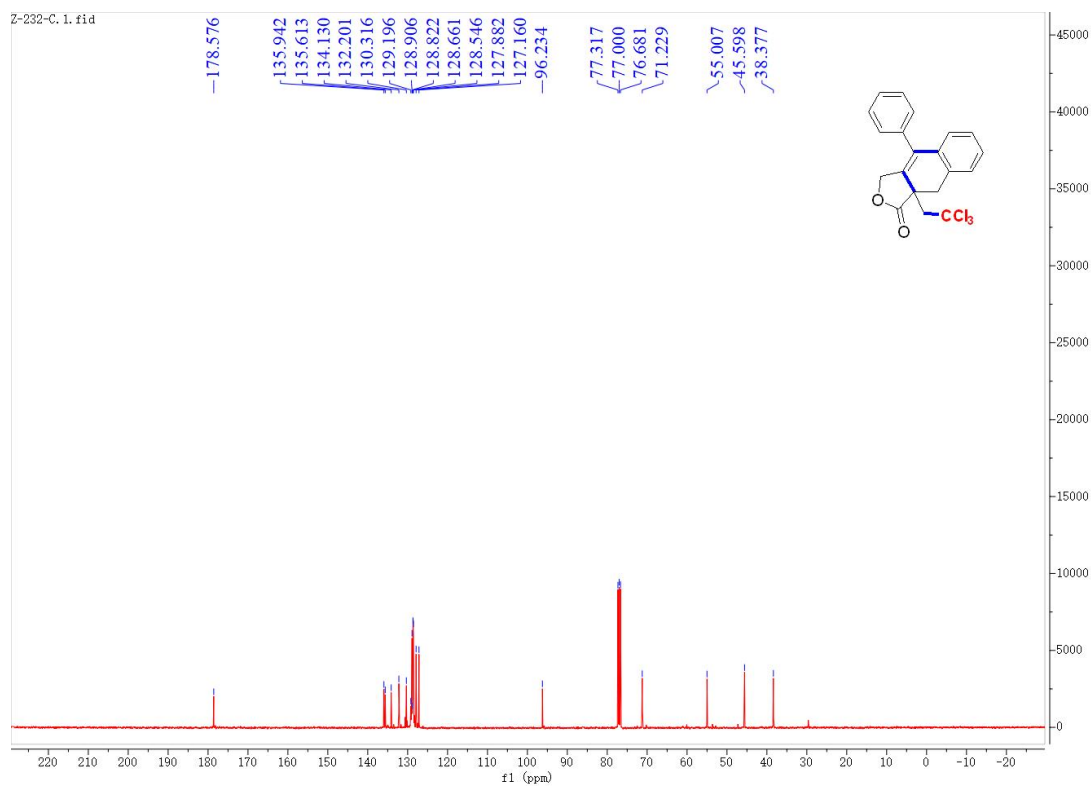
^{13}C NMR (150 MHz, CDCl_3): δ 143.5, 133.6, 129.7, 127.4, 98.4, 76.8, 57.3, 53.8, 53.5, 43.5, 38.8, 15.5.

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

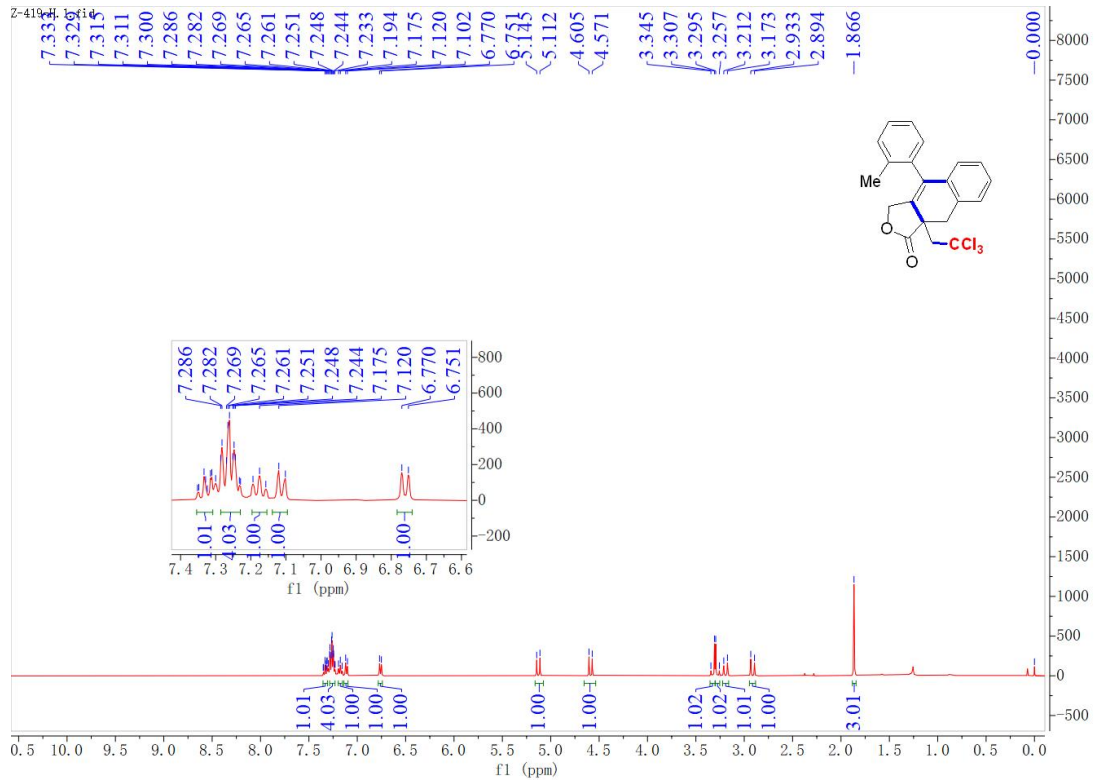
^1H NMR (400 MHz, CDCl_3)



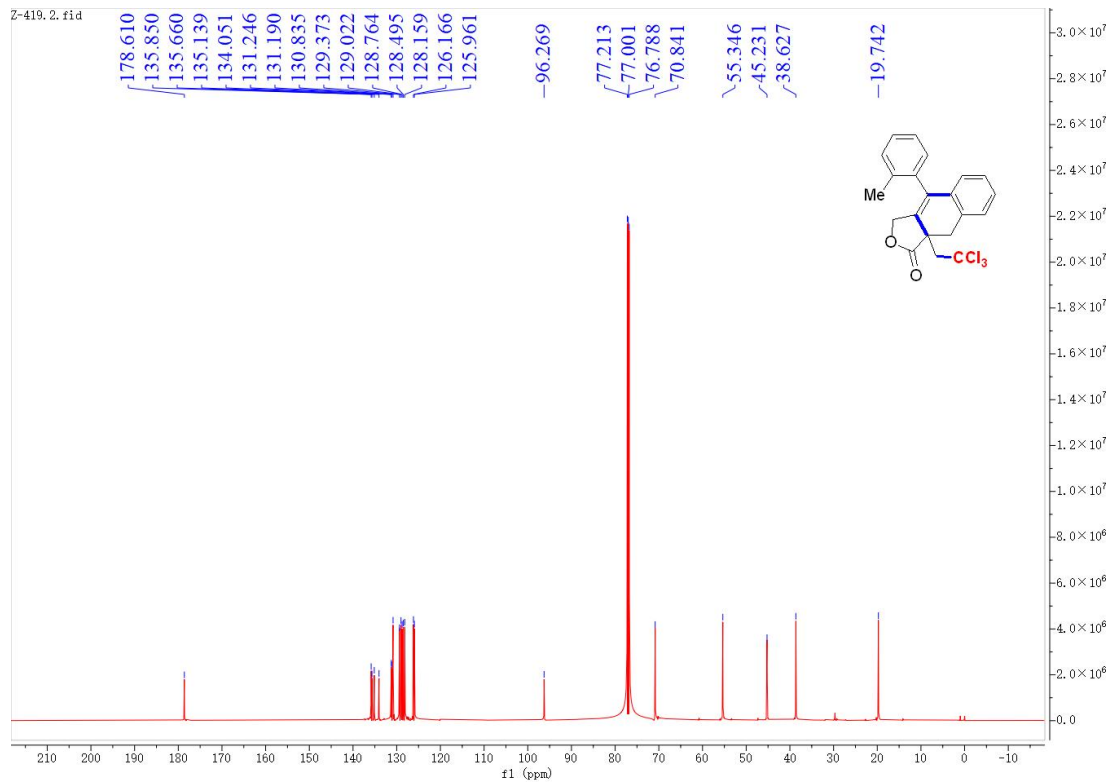
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



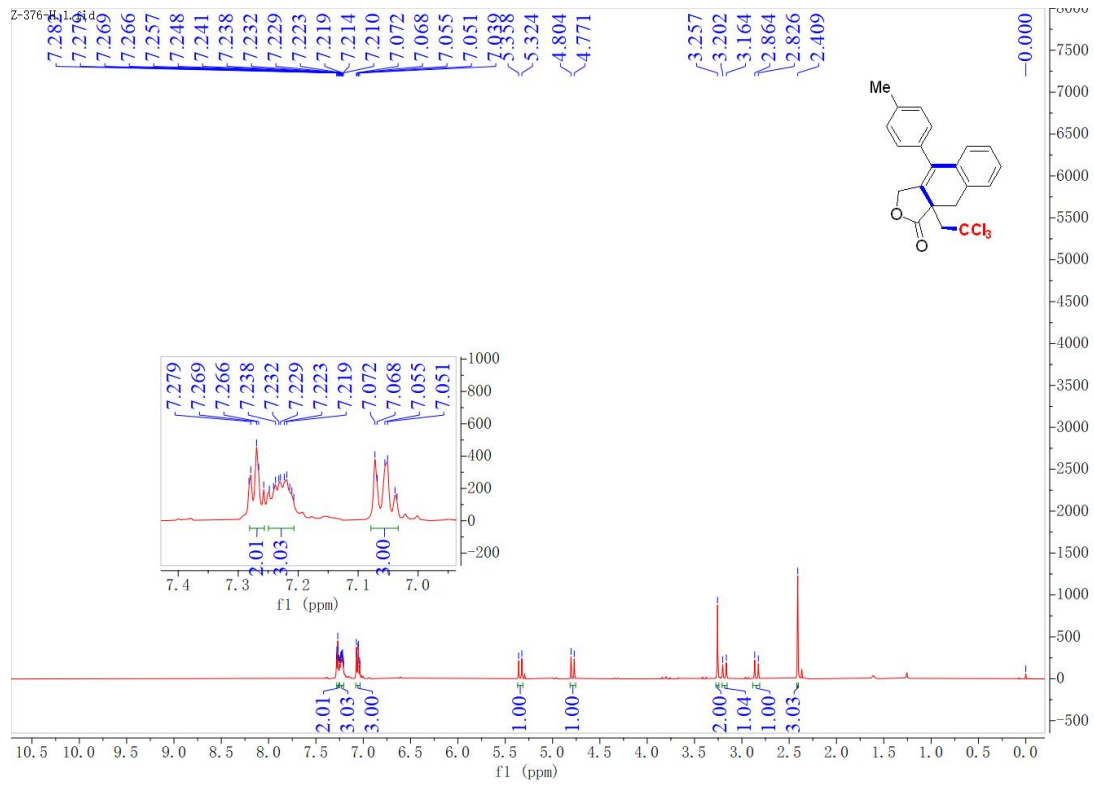
$^2\text{-}^1\text{H}$ NMR (400 MHz, CDCl_3)



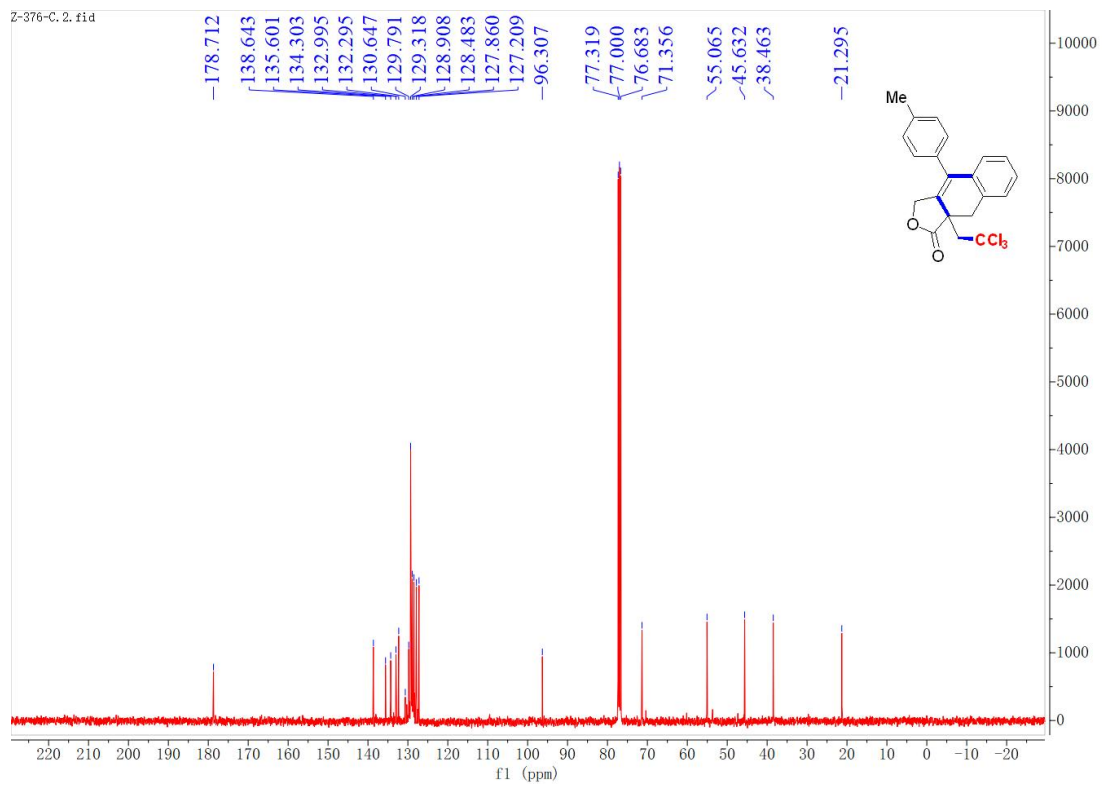
$^2\text{-}^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



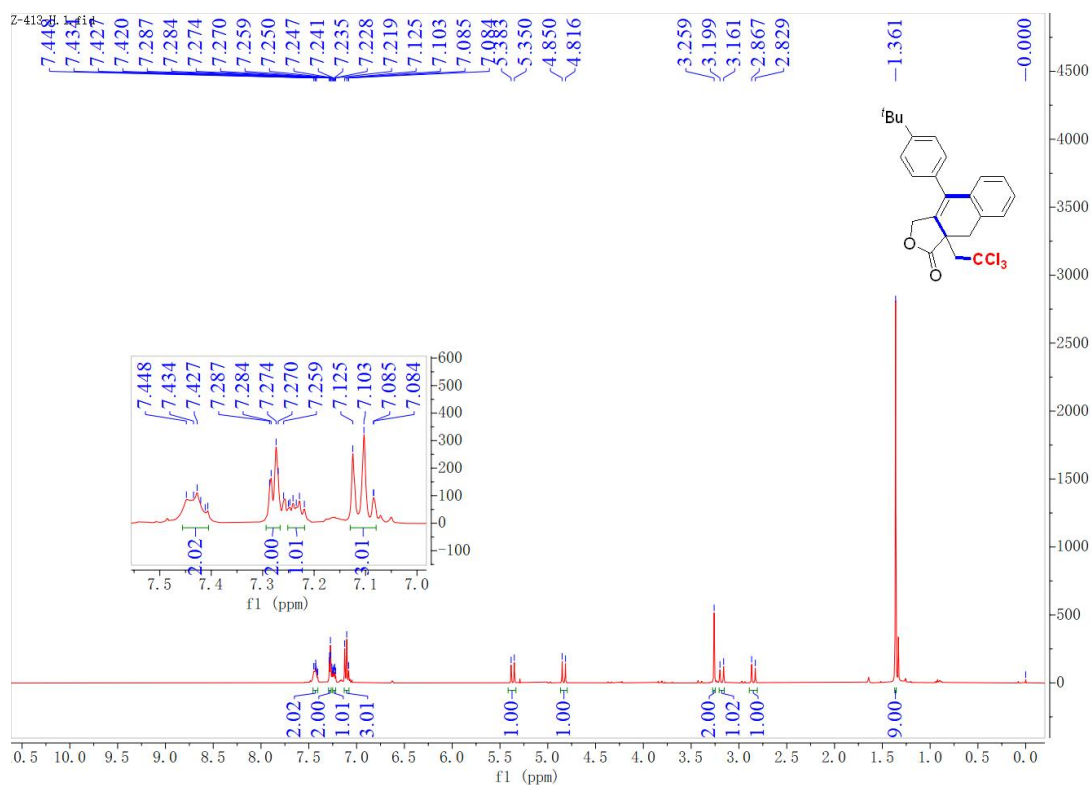
$^3\text{-}^1\text{H}$ NMR (400 MHz, CDCl_3)



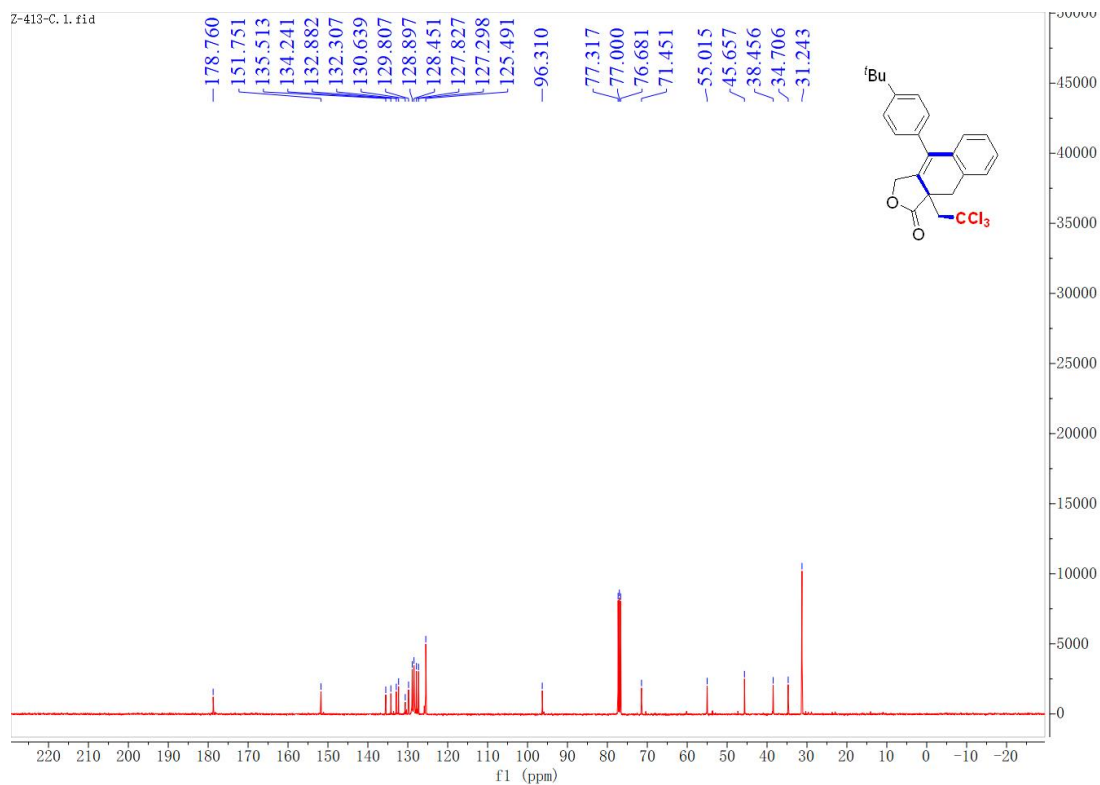
$^3\text{-}^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



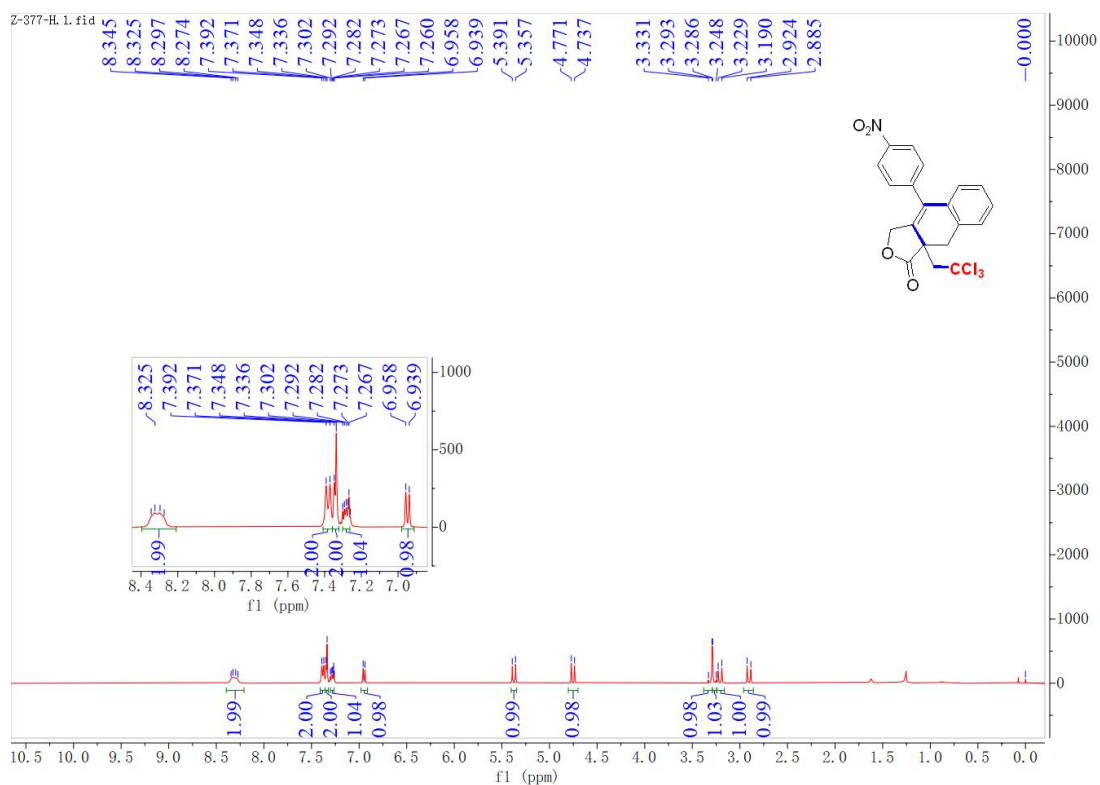
4-¹H NMR (400 MHz, CDCl₃)



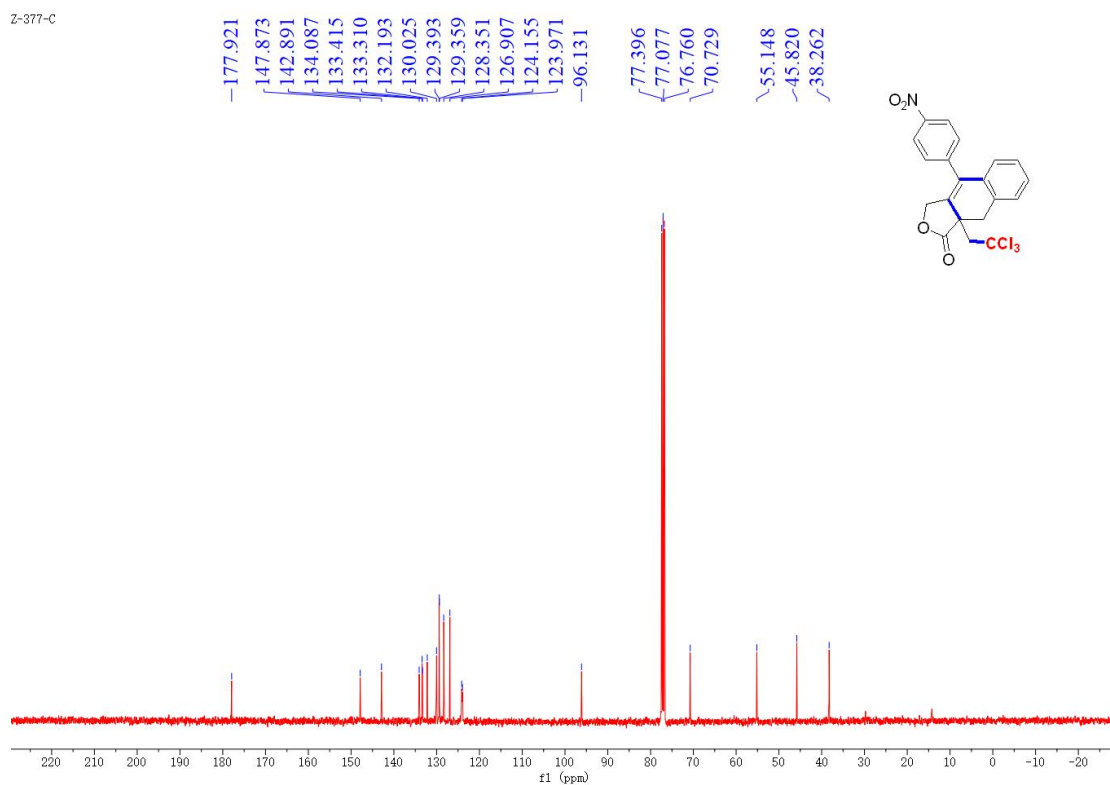
4-¹³C{¹H} NMR (100 MHz, CDCl₃)



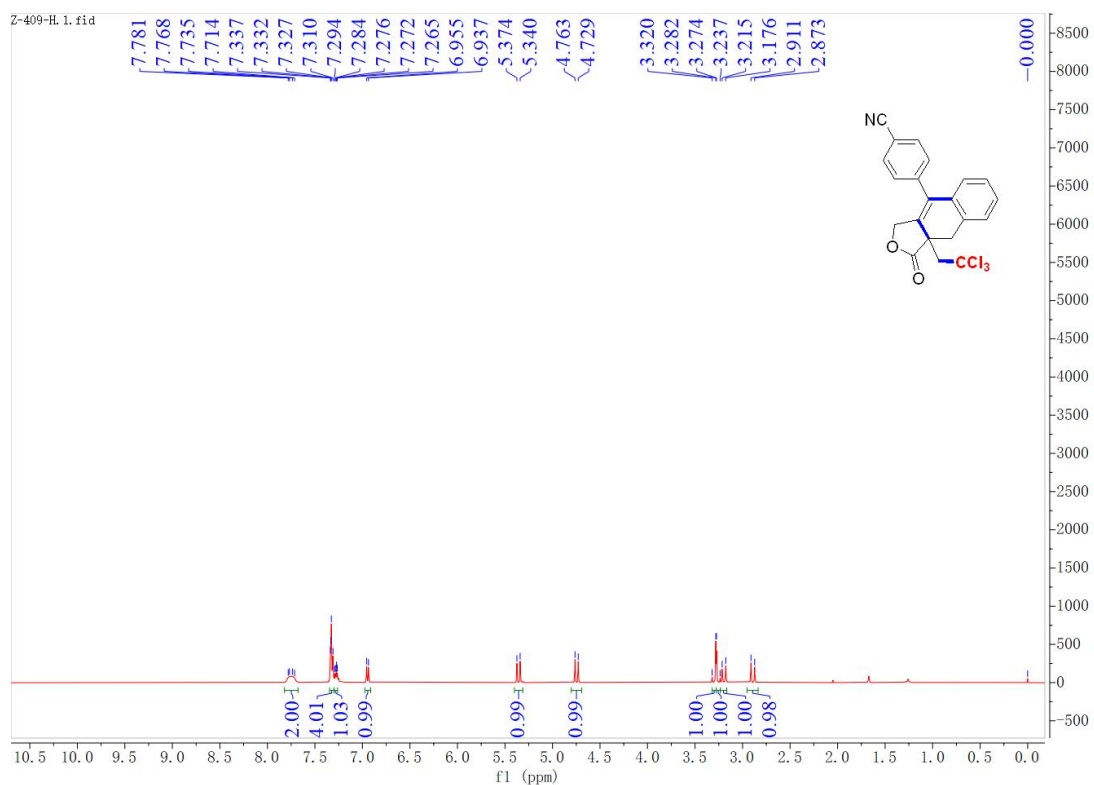
5-¹H NMR (400 MHz, CDCl₃)



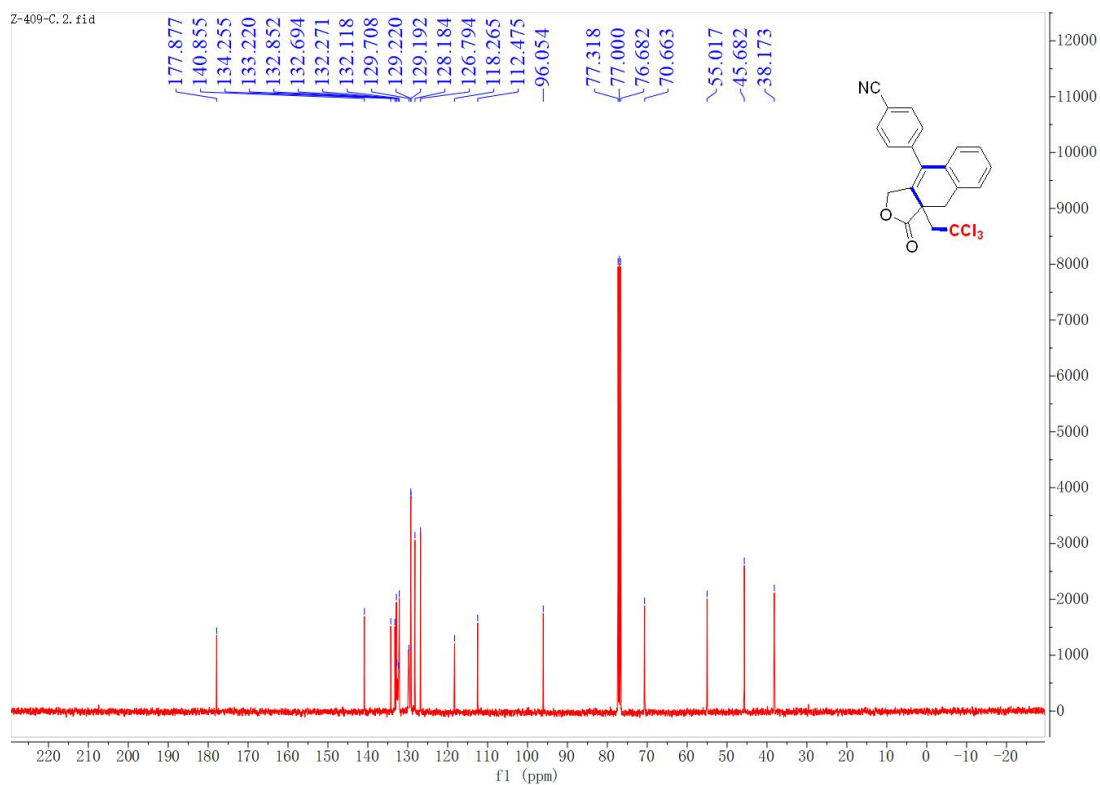
5-¹³C{¹H} NMR (100 MHz, CDCl₃)



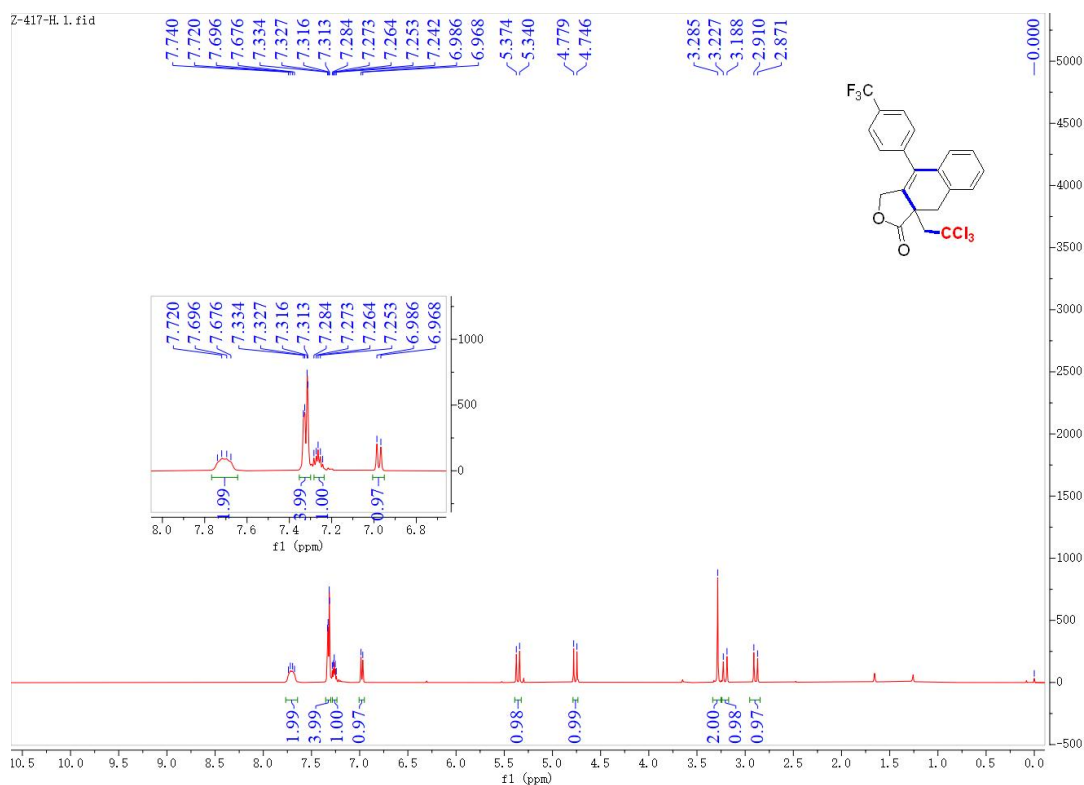
6-¹H NMR (400 MHz, CDCl₃)



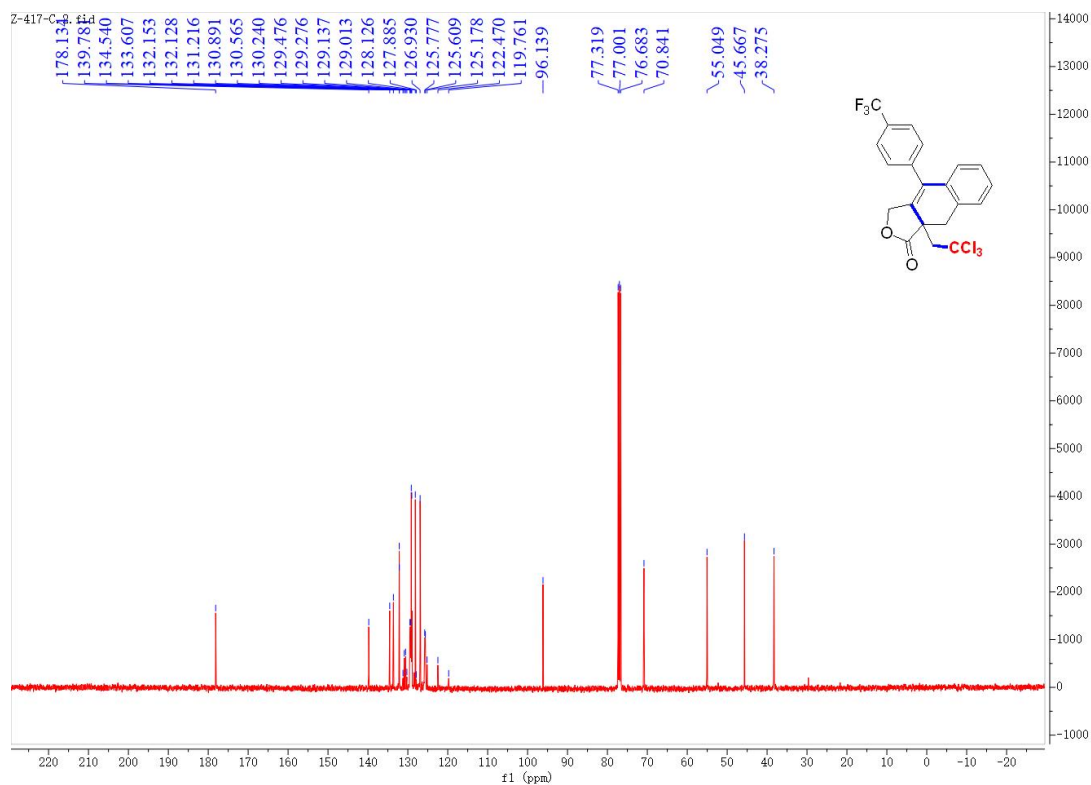
6-¹³C{¹H} NMR (100 MHz, CDCl₃)



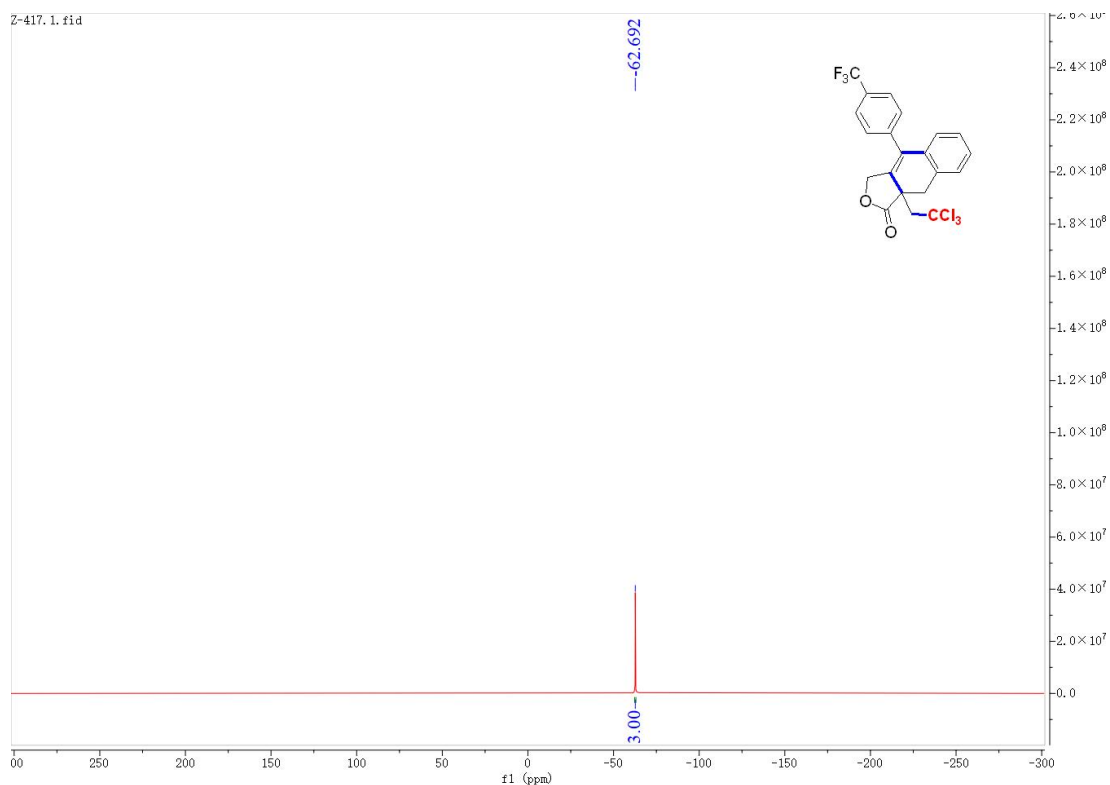
7-¹H NMR (400 MHz, CDCl₃)



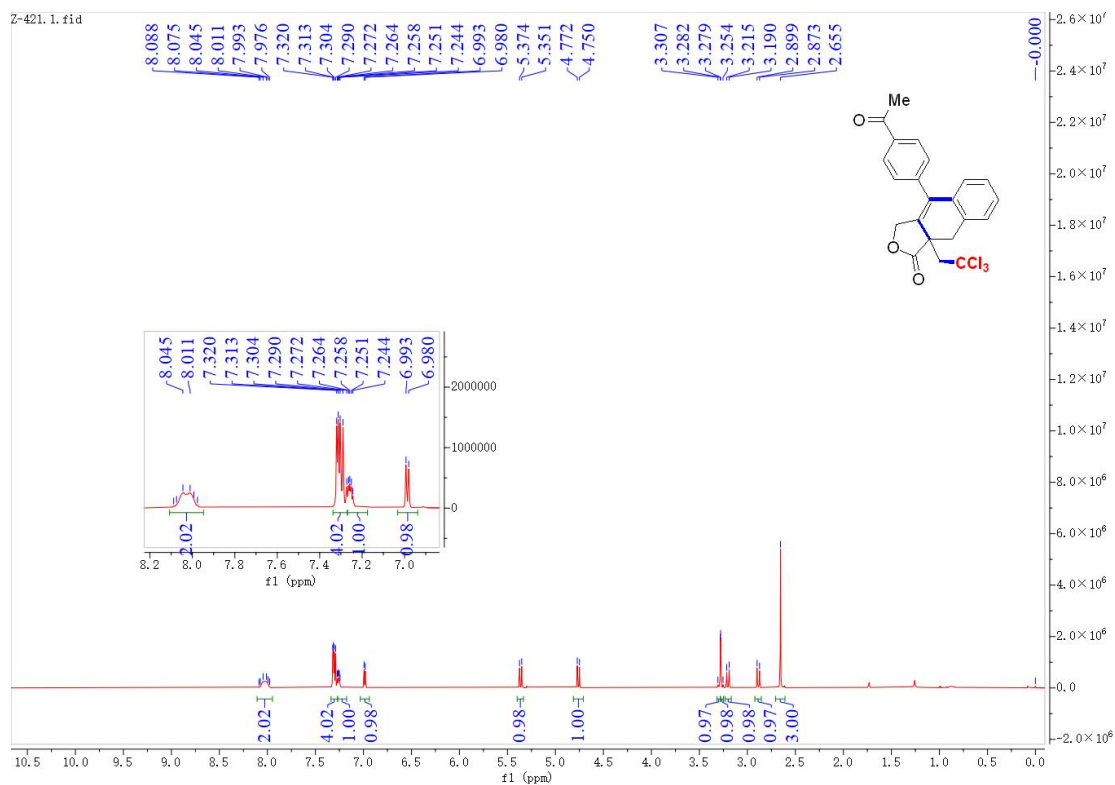
7-¹³C{¹H} NMR (100 MHz, CDCl₃)



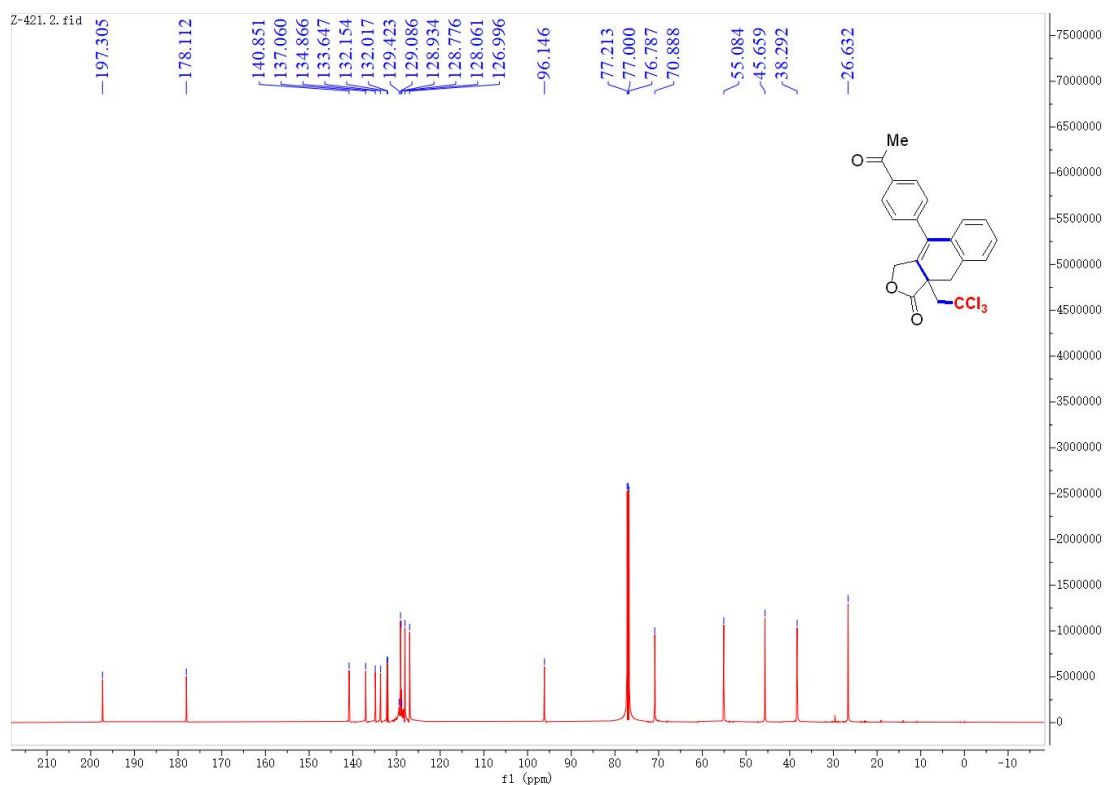
7-¹⁹F NMR (565 MHz, CDCl₃)



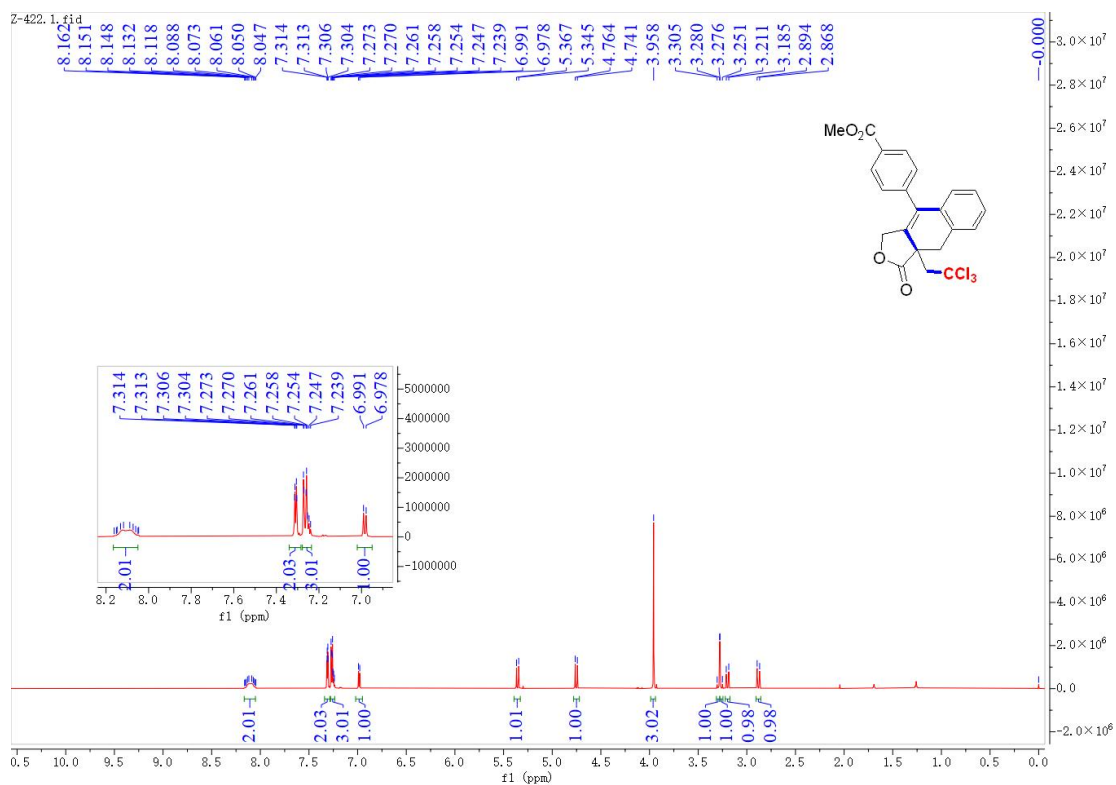
8-¹H NMR (600 MHz, CDCl₃)



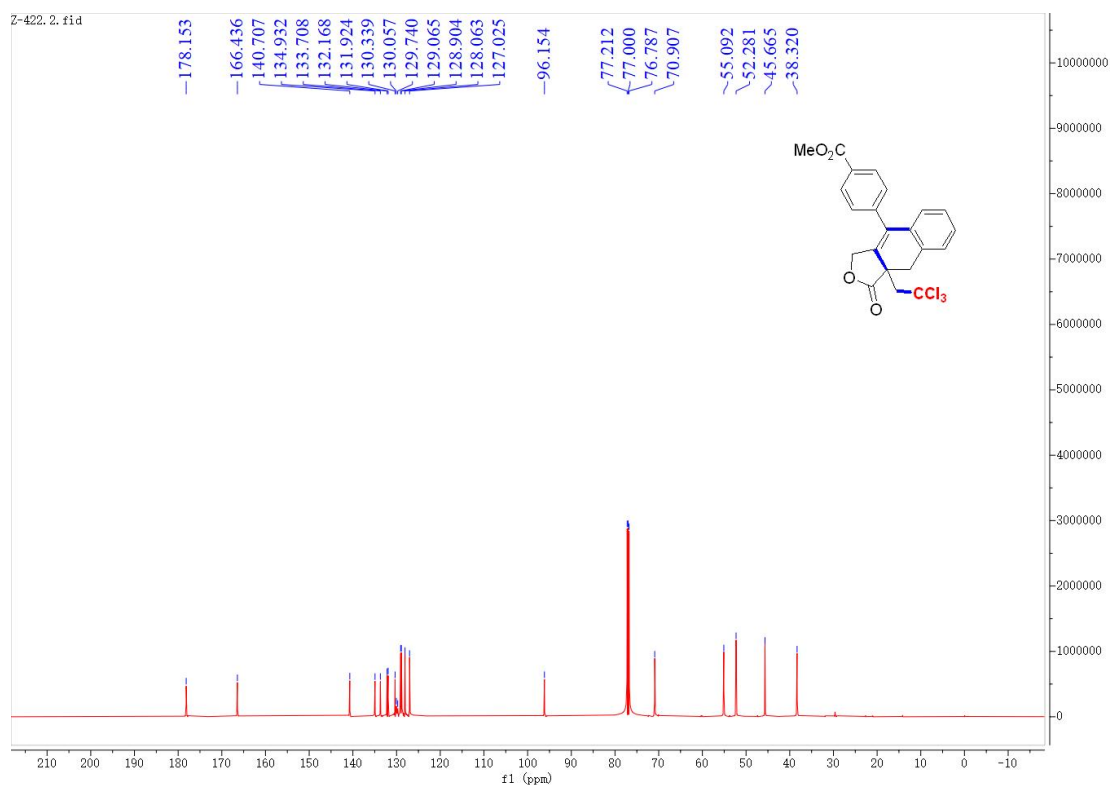
8-¹³C{¹H} NMR (150 MHz, CDCl₃)



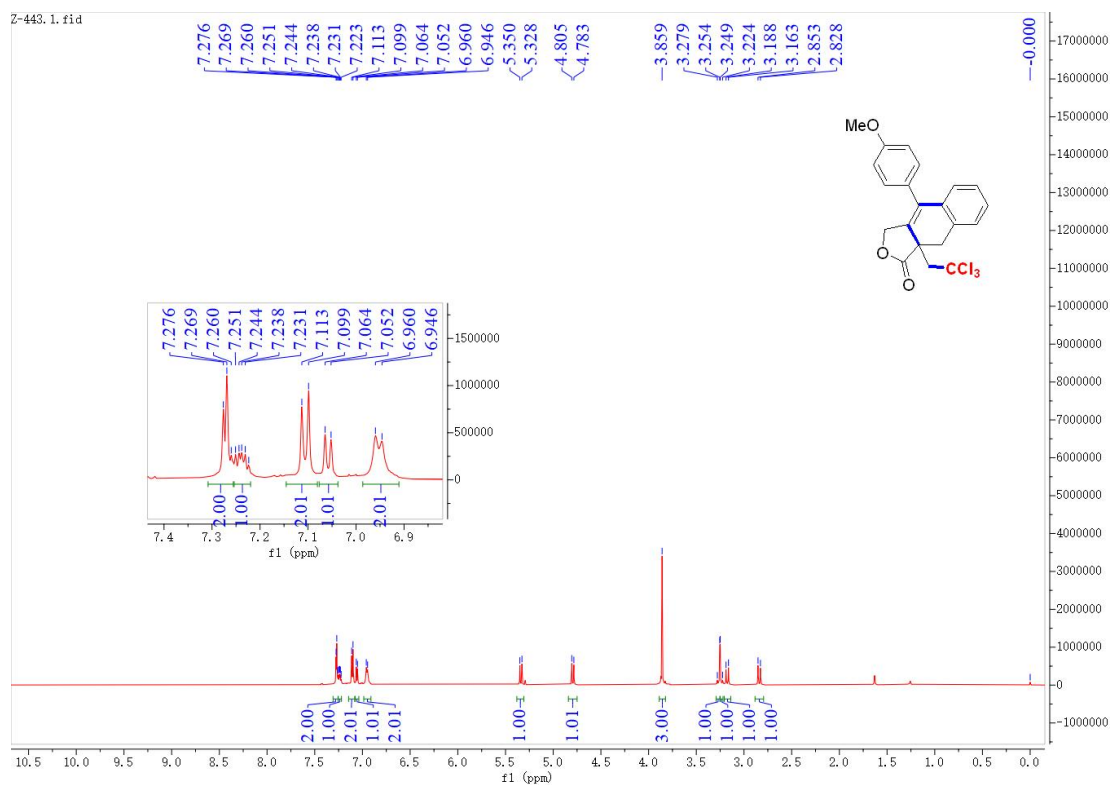
9-¹H NMR (600 MHz, CDCl₃)



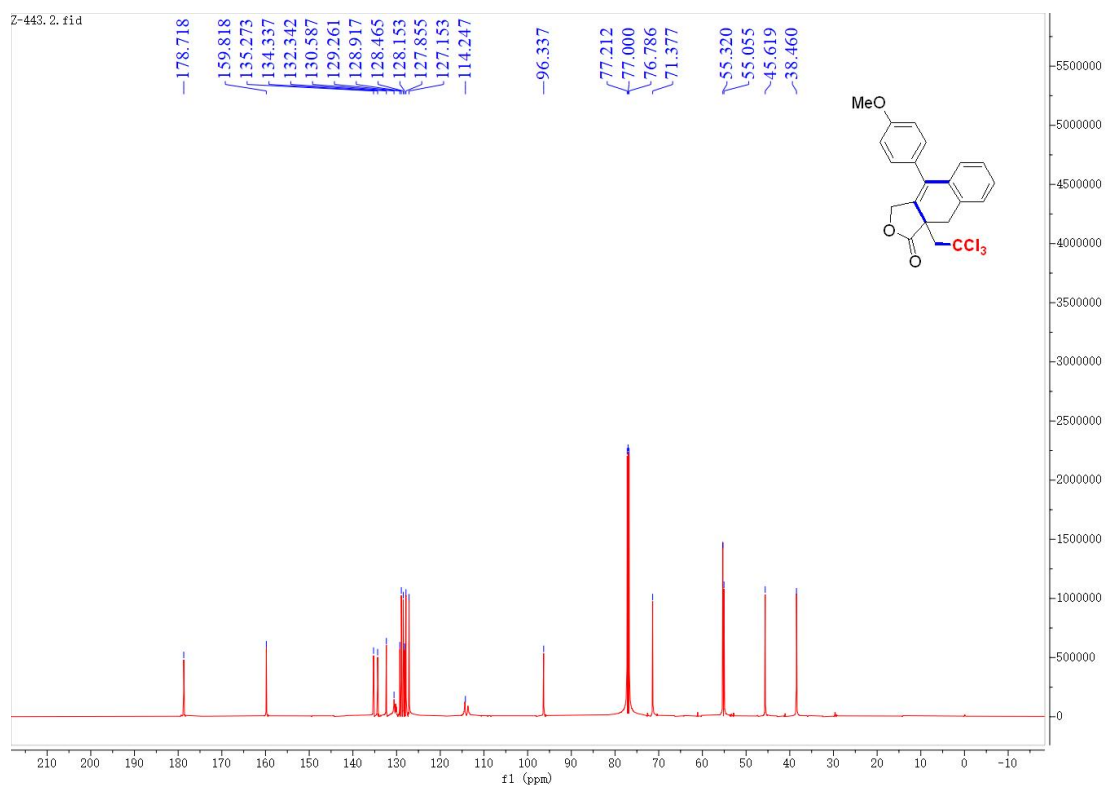
9-¹³C{¹H} NMR (150 MHz, CDCl₃)



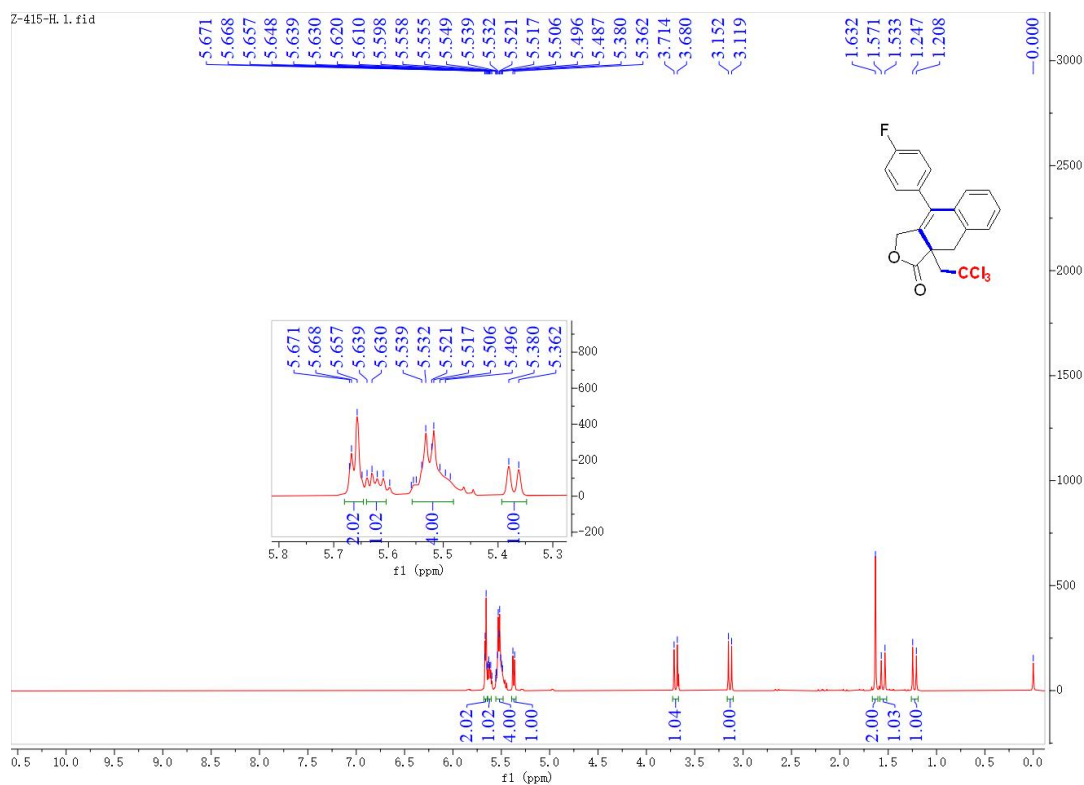
10-¹H NMR (600 MHz, CDCl₃)



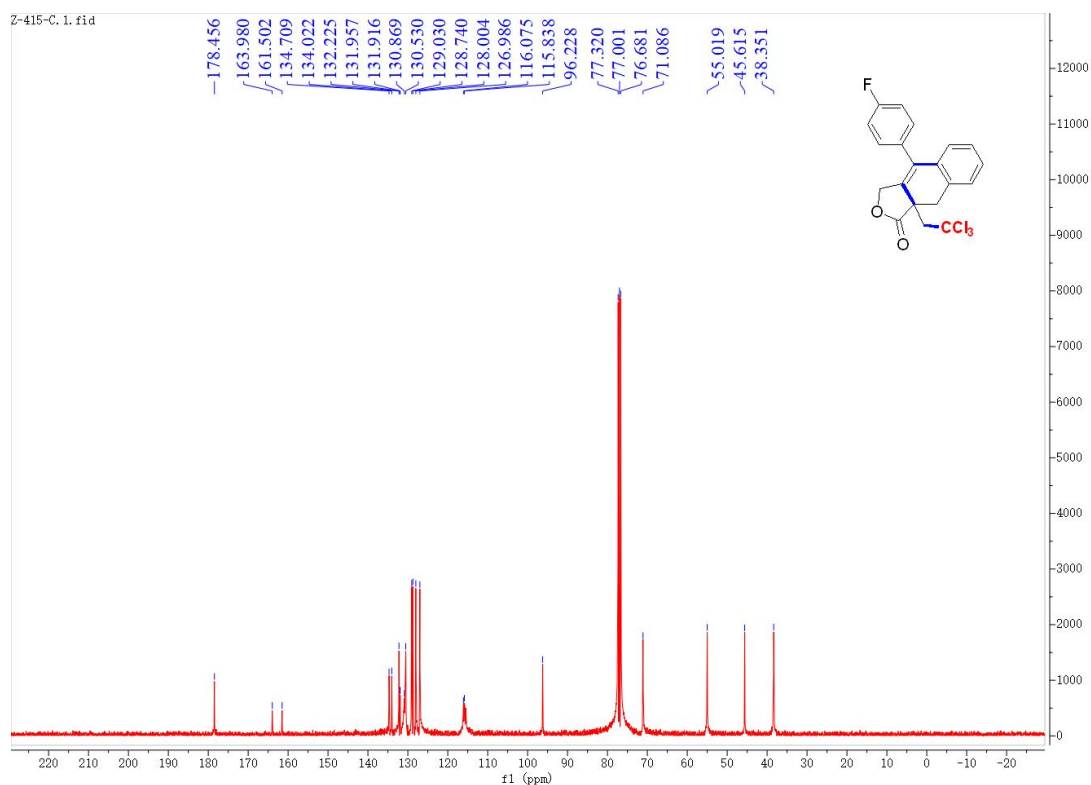
10-¹³C{¹H} NMR (150 MHz, CDCl₃)



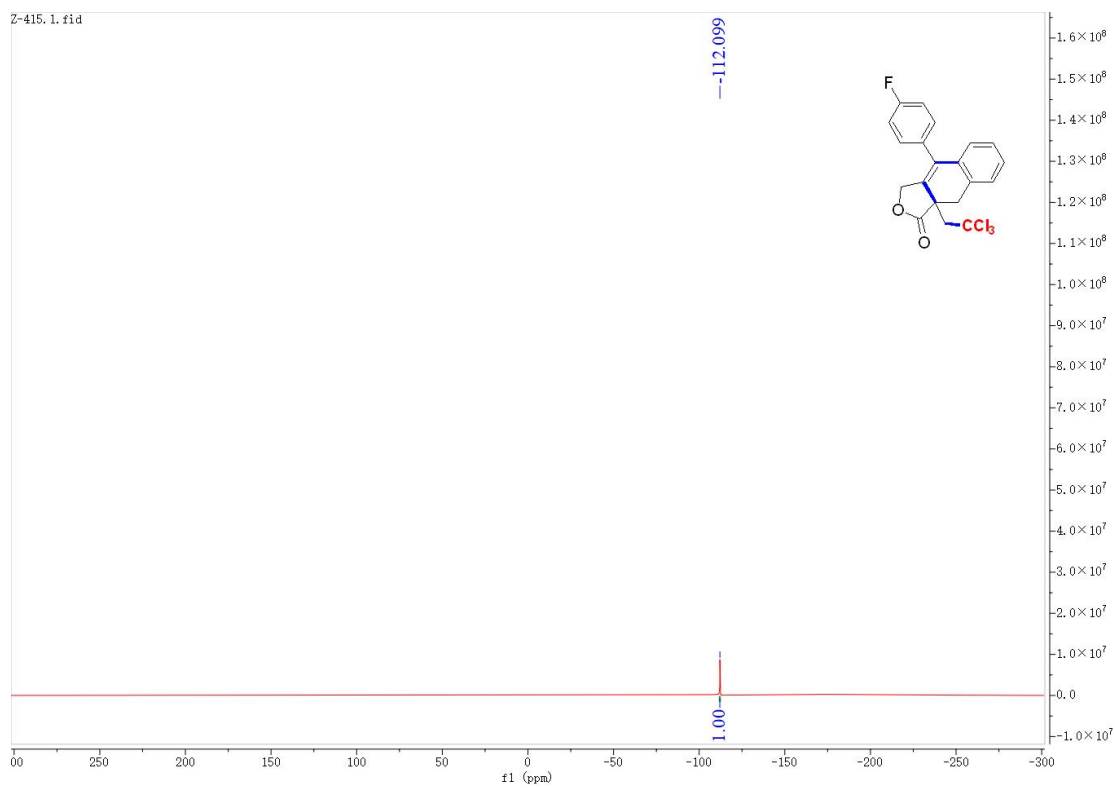
11-¹H NMR (400 MHz, CDCl₃)



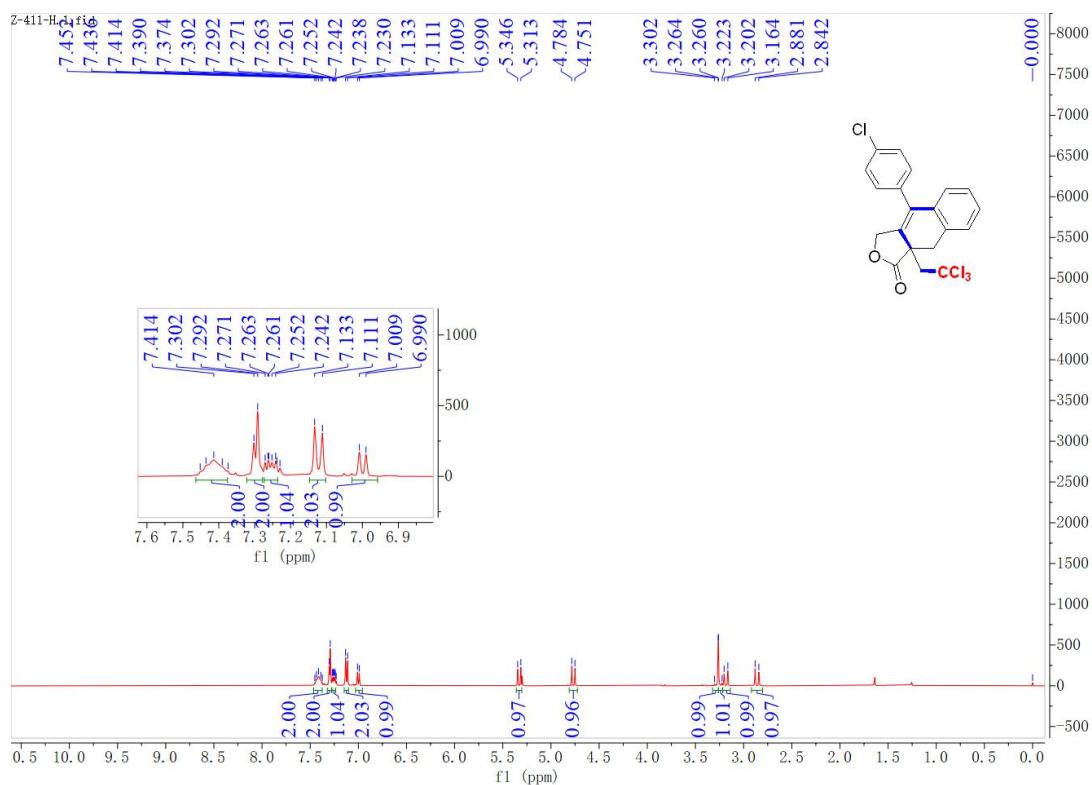
11-¹³C{¹H} NMR (100 MHz, CDCl₃)



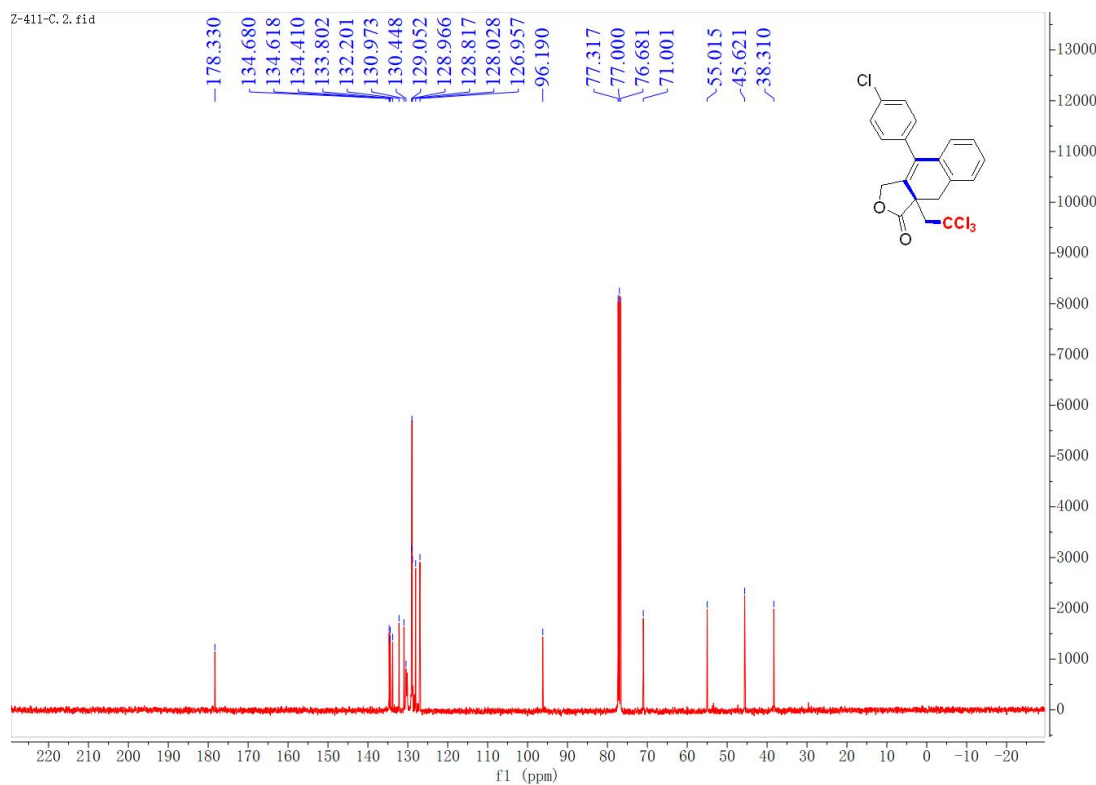
11-¹⁹F NMR (565 MHz, CDCl₃)



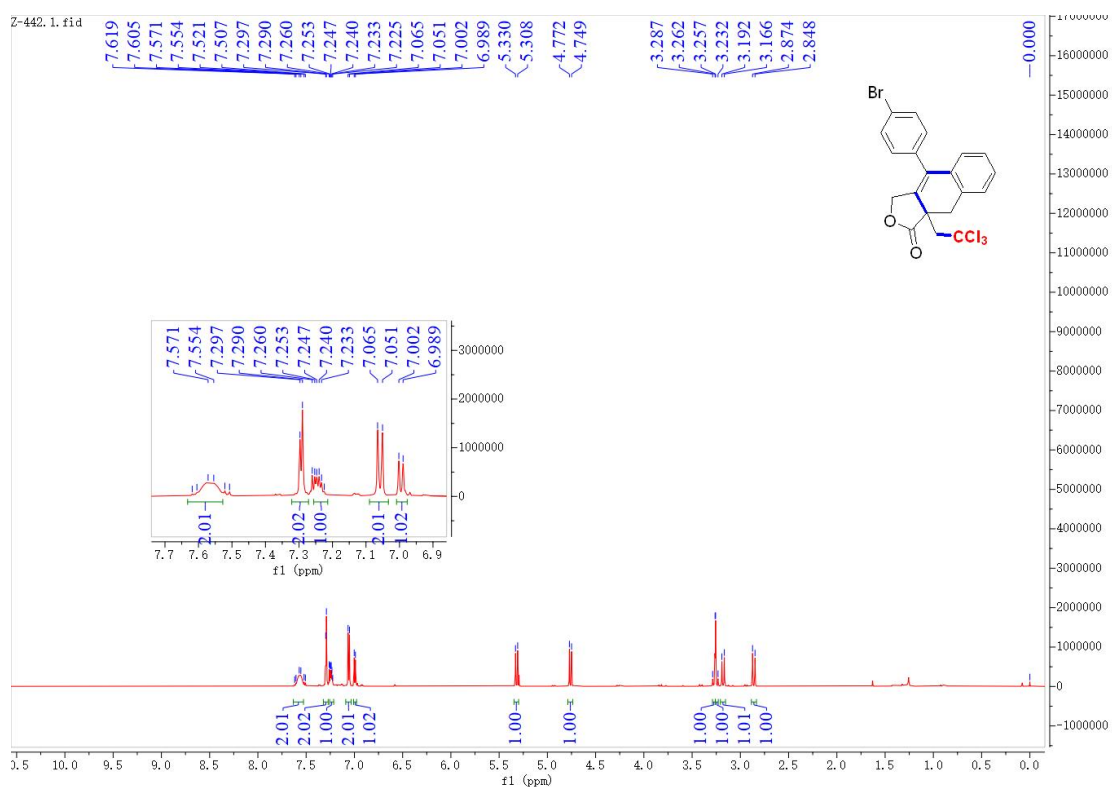
12-¹H NMR (400 MHz, CDCl₃)



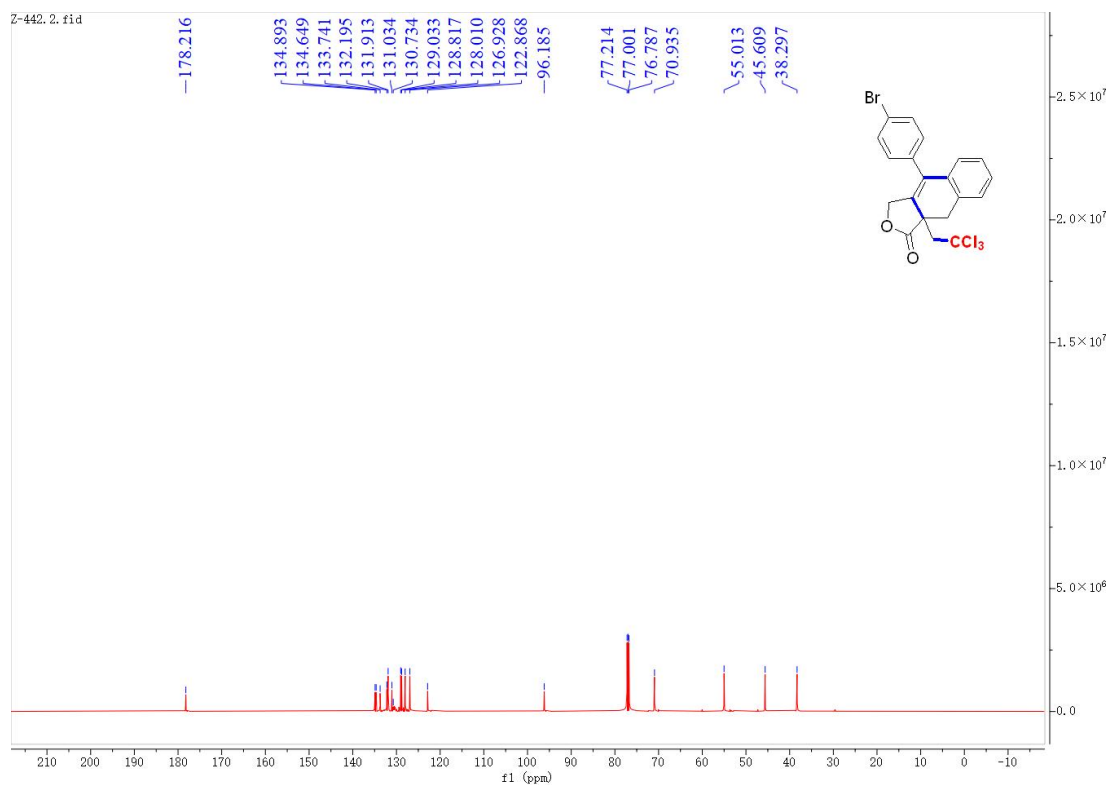
12-¹³C{¹H} NMR (100 MHz, CDCl₃)



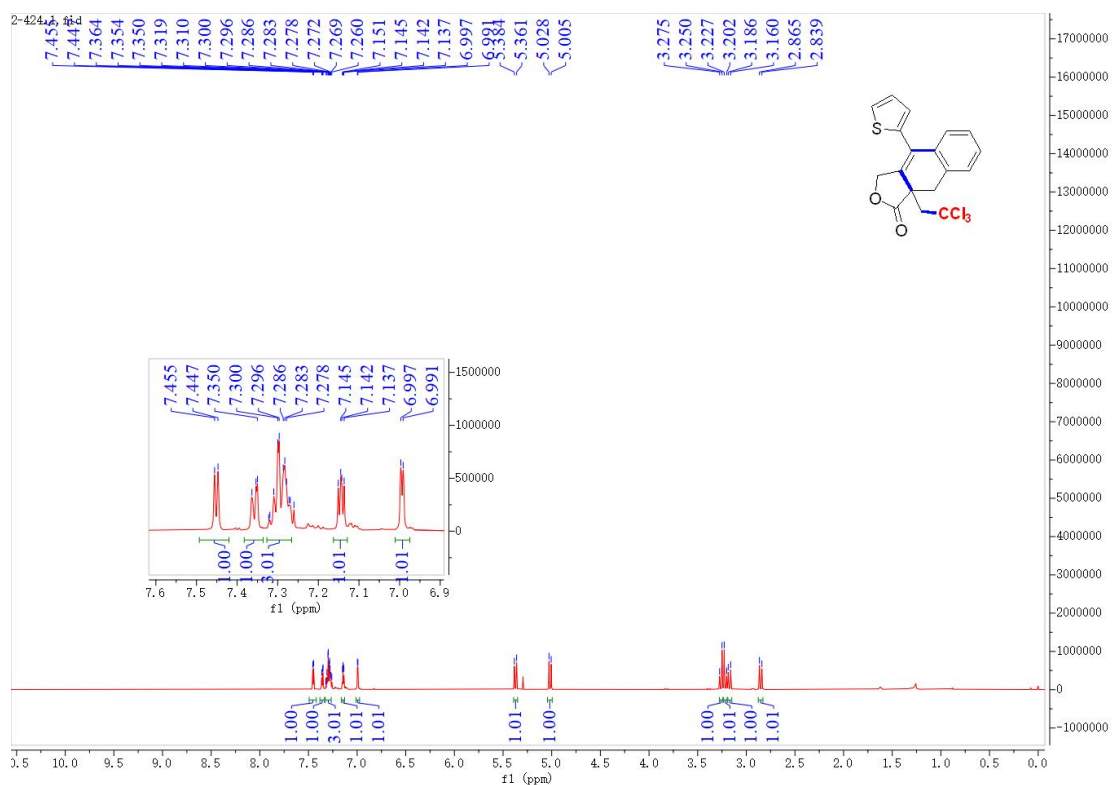
13-¹H NMR (600 MHz, CDCl₃)



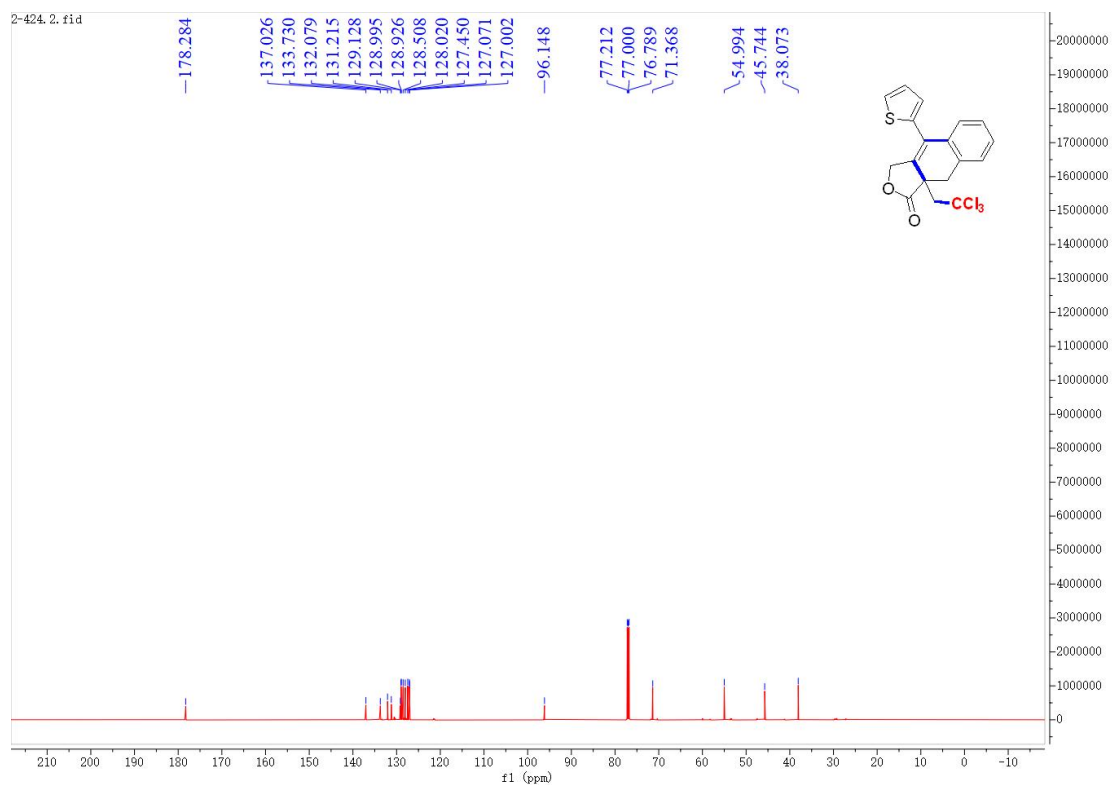
13-¹³C {¹H} NMR (150 MHz, CDCl₃)



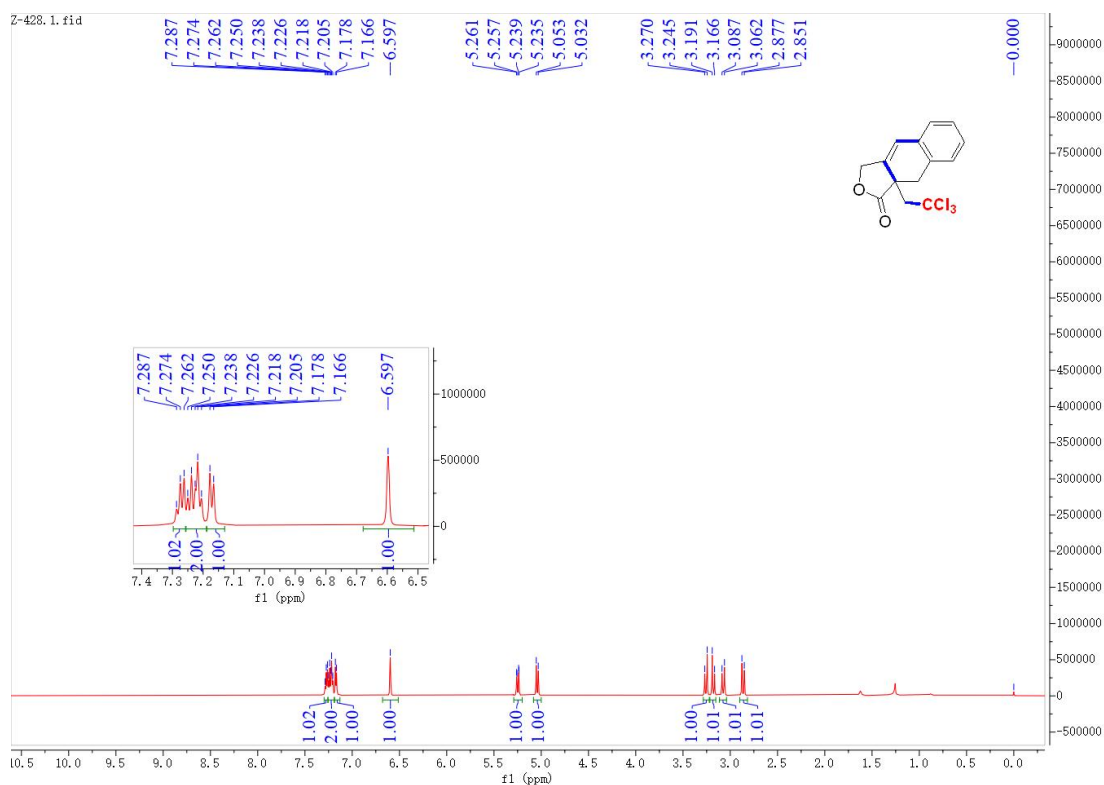
14-¹H NMR (600 MHz, CDCl₃)



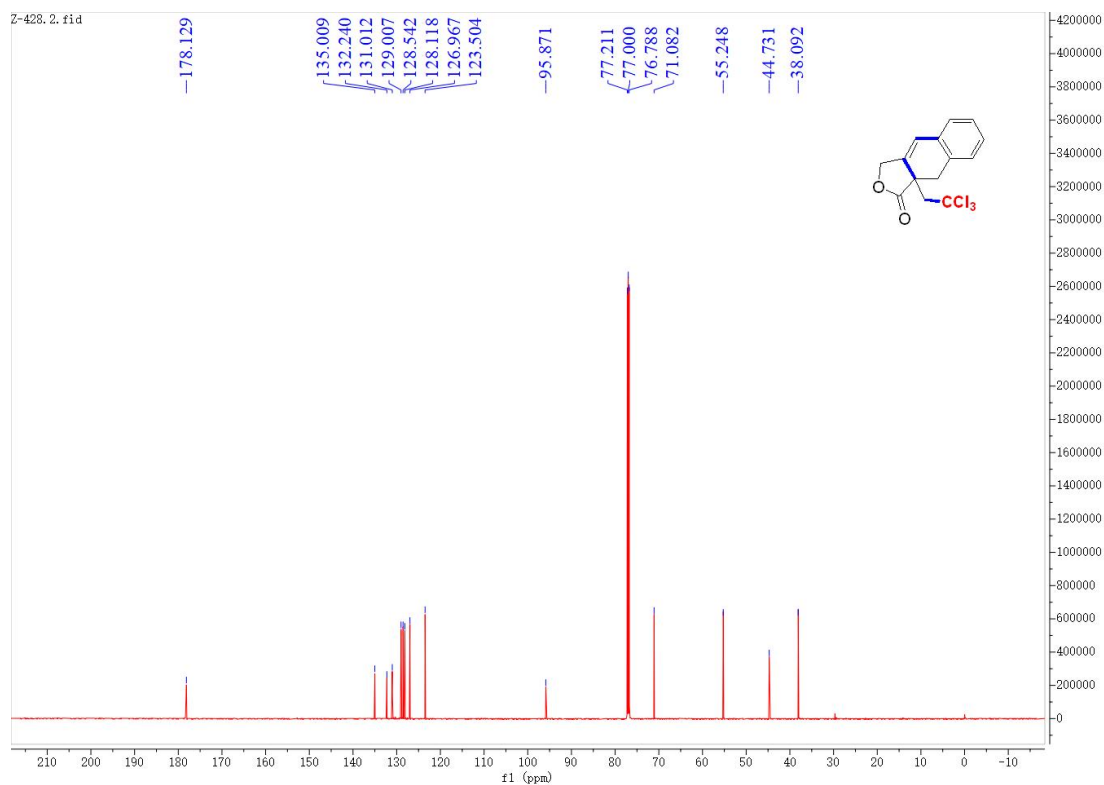
14-¹³C {¹H} NMR (150 MHz, CDCl₃)



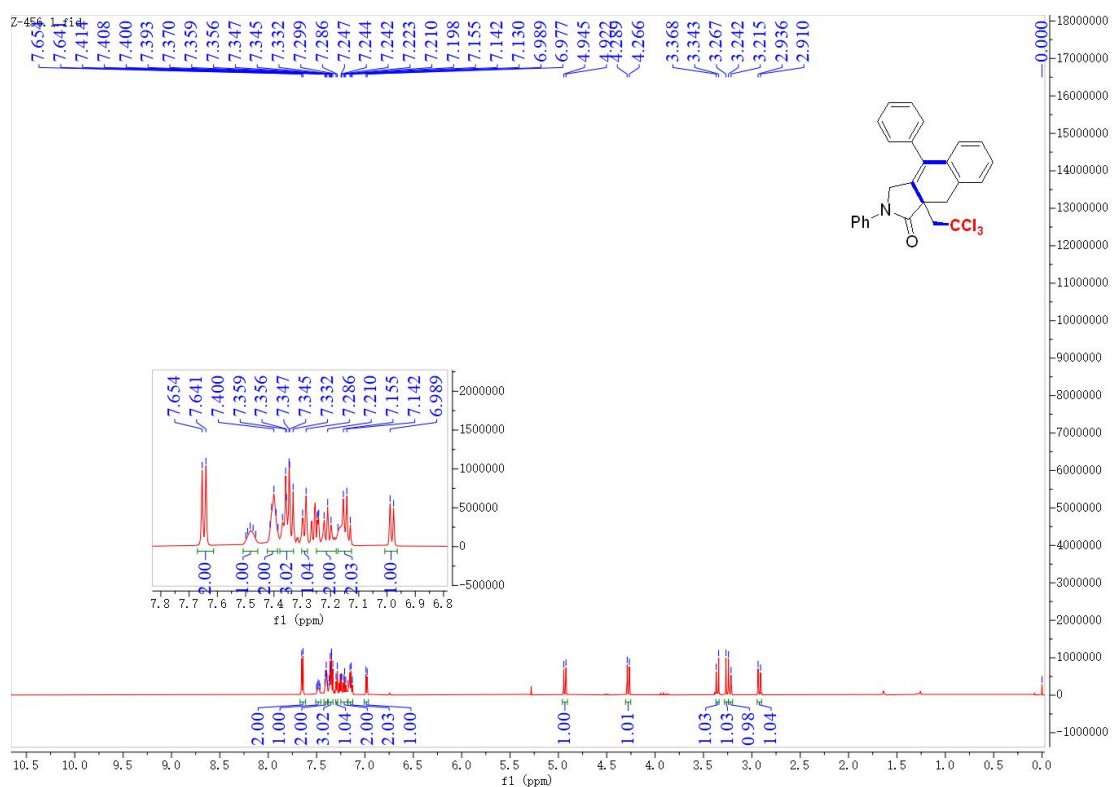
15-¹H NMR (600 MHz, CDCl₃)



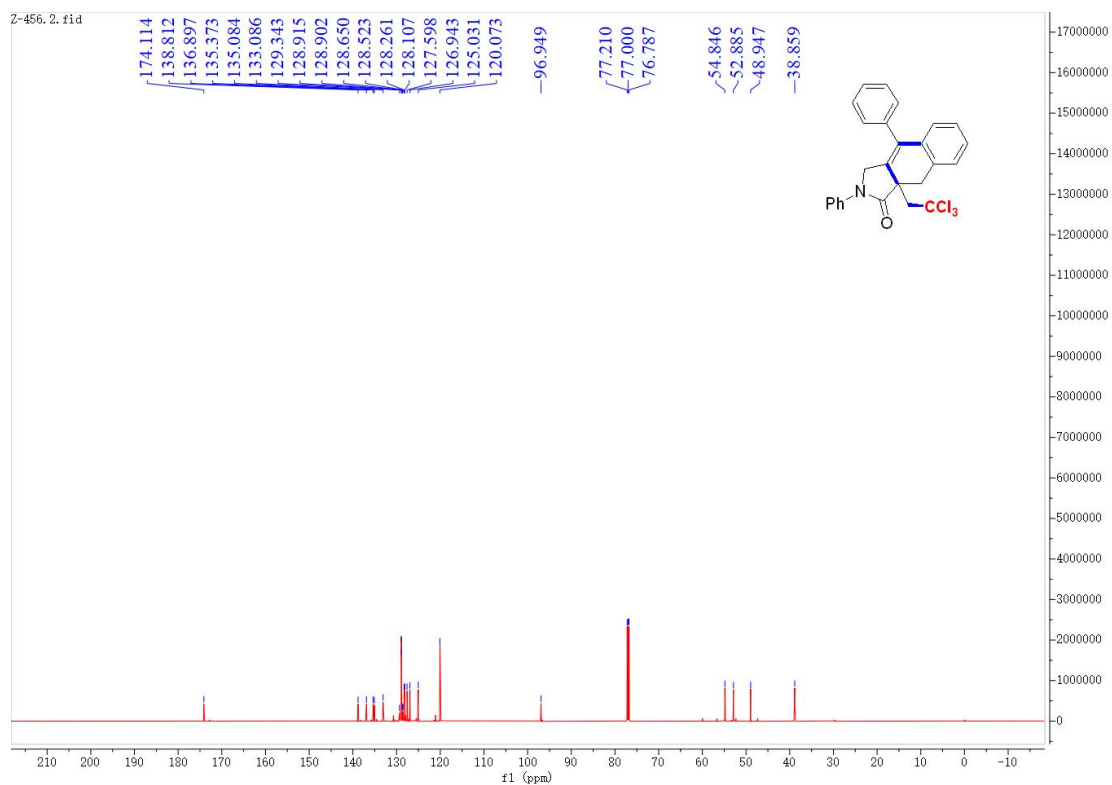
15-¹³C{¹H} NMR (150 MHz, CDCl₃)



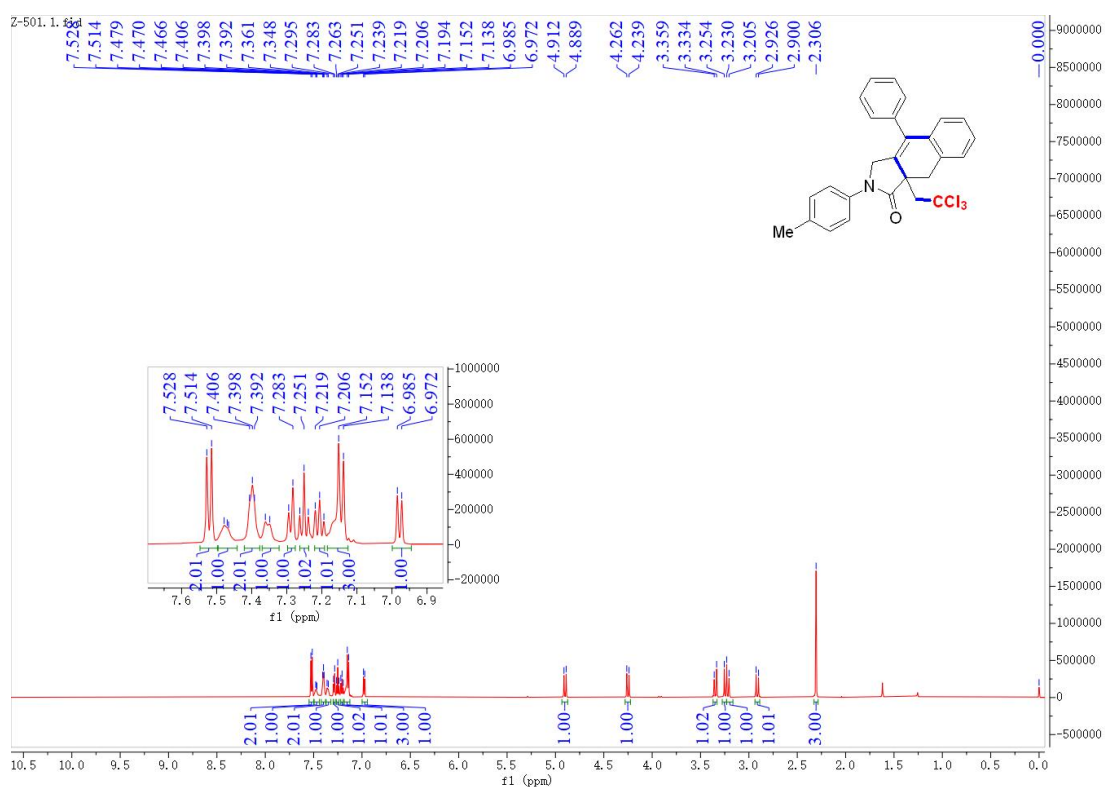
16-¹H NMR (600 MHz, CDCl₃)



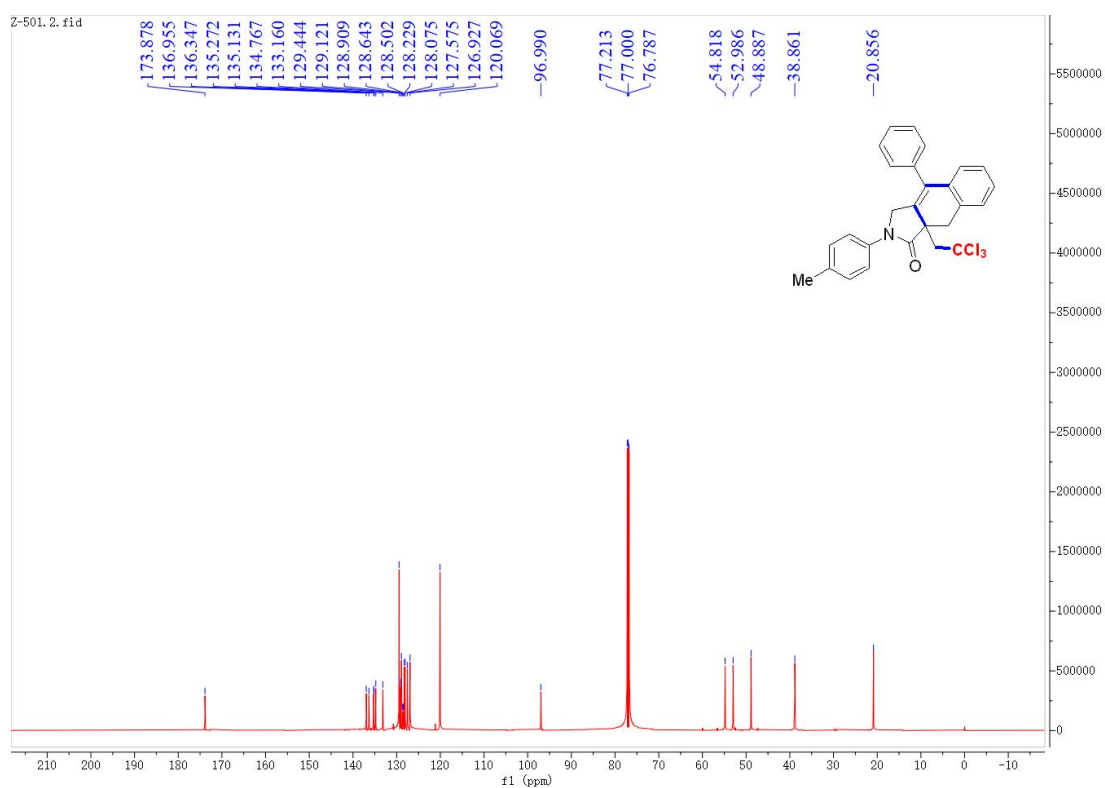
16-¹³C {¹H} NMR (150 MHz, CDCl₃)



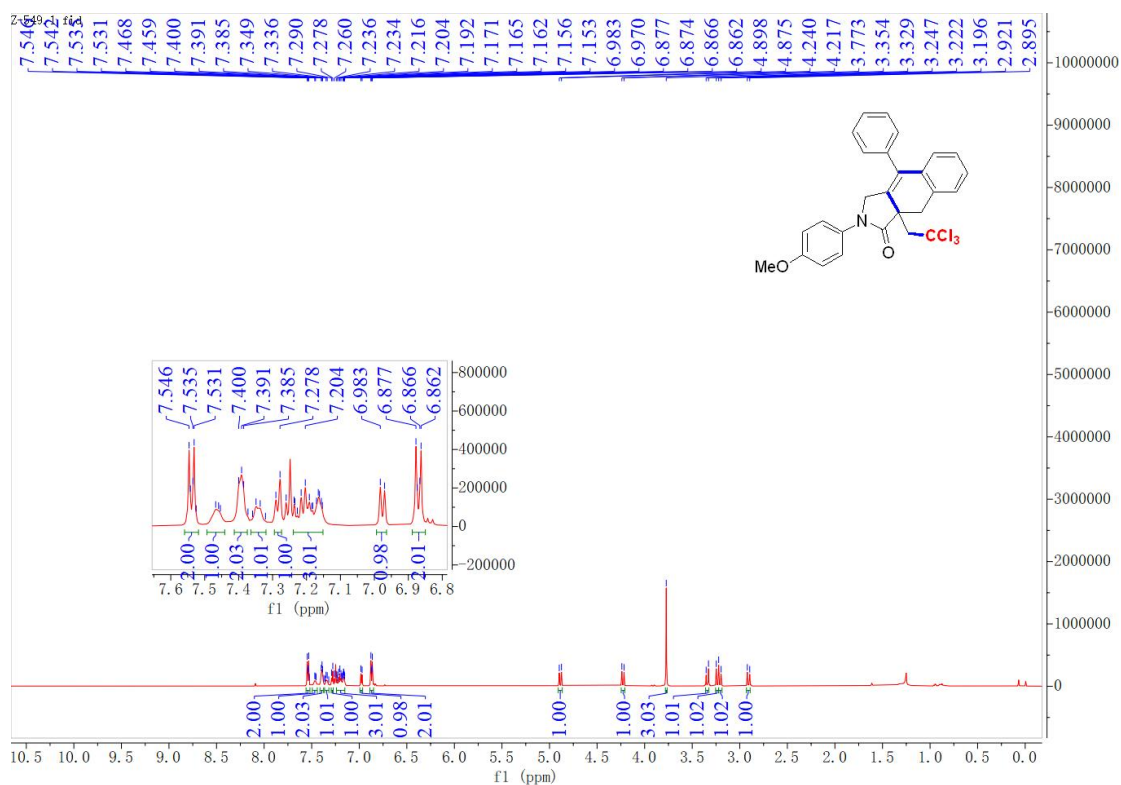
17-¹H NMR (600 MHz, CDCl₃)



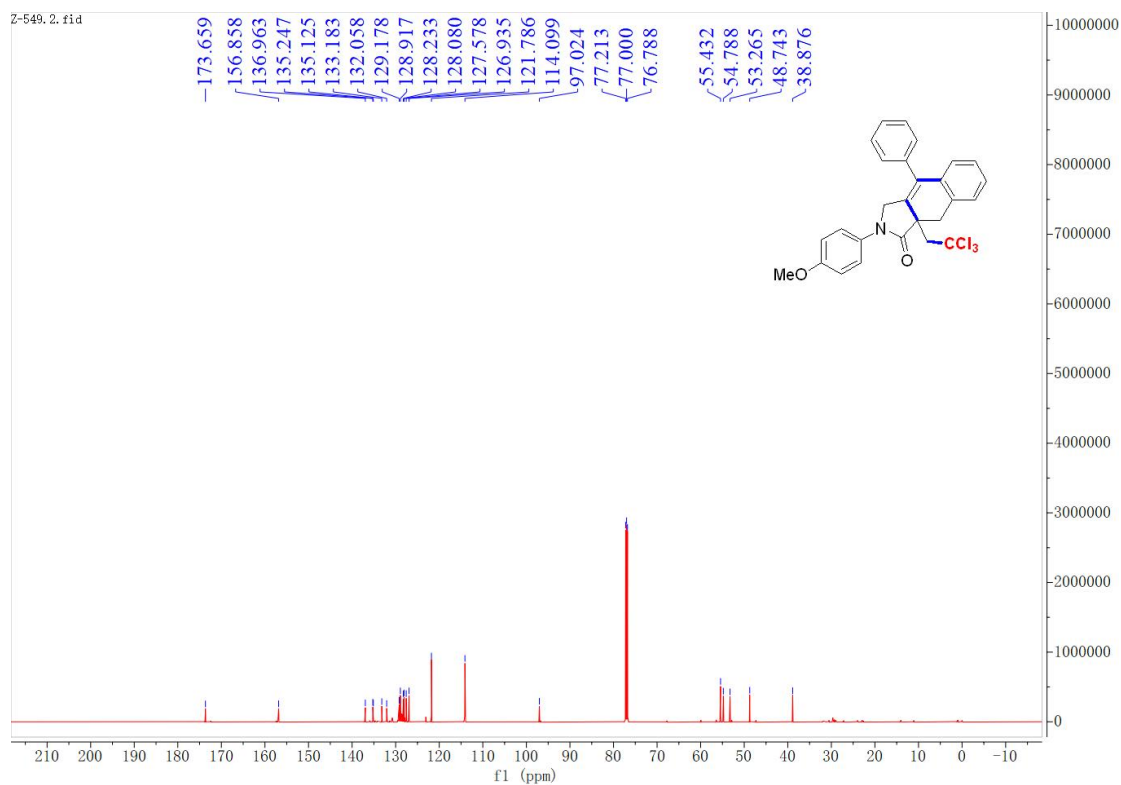
17-¹³C {¹H} NMR (150 MHz, CDCl₃)



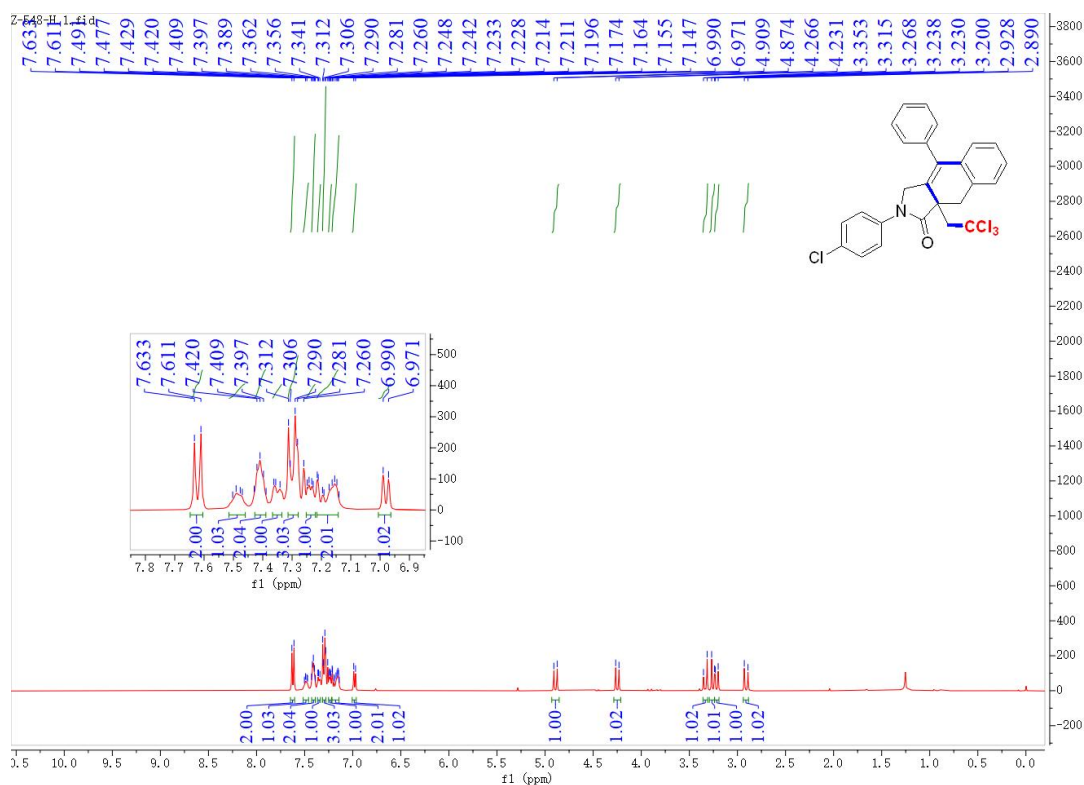
18-¹H NMR (600 MHz, CDCl₃)



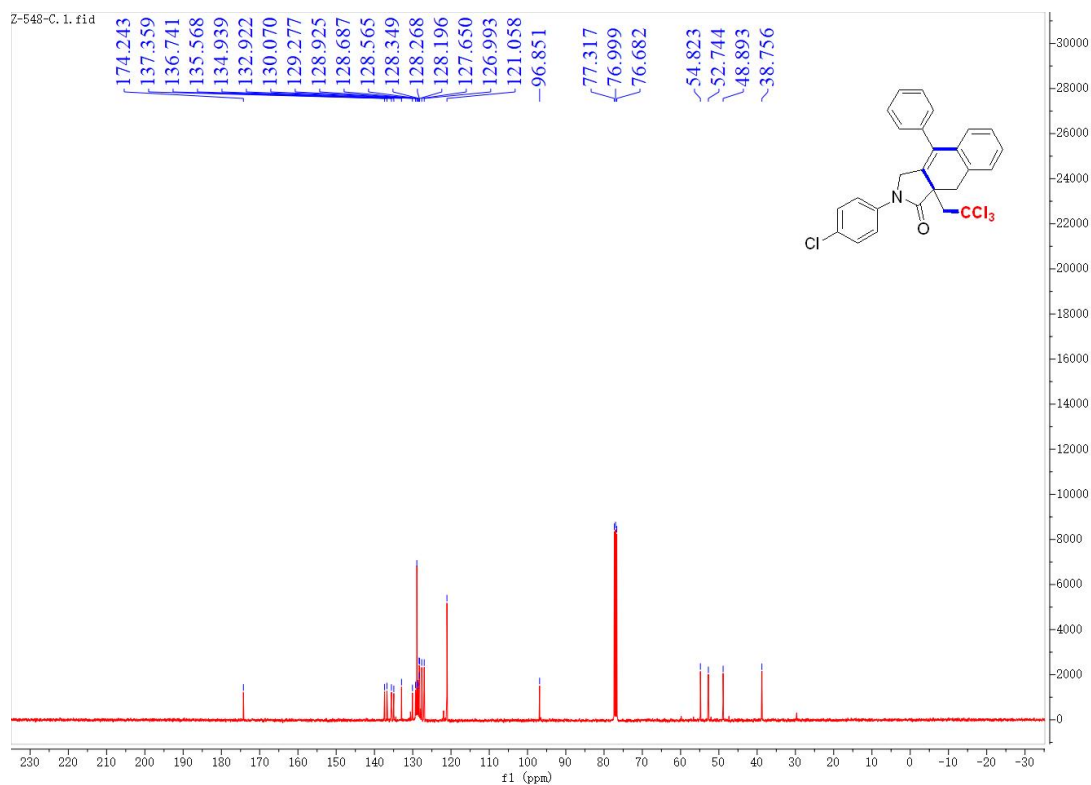
18-¹³C {¹H} NMR (150 MHz, CDCl₃)



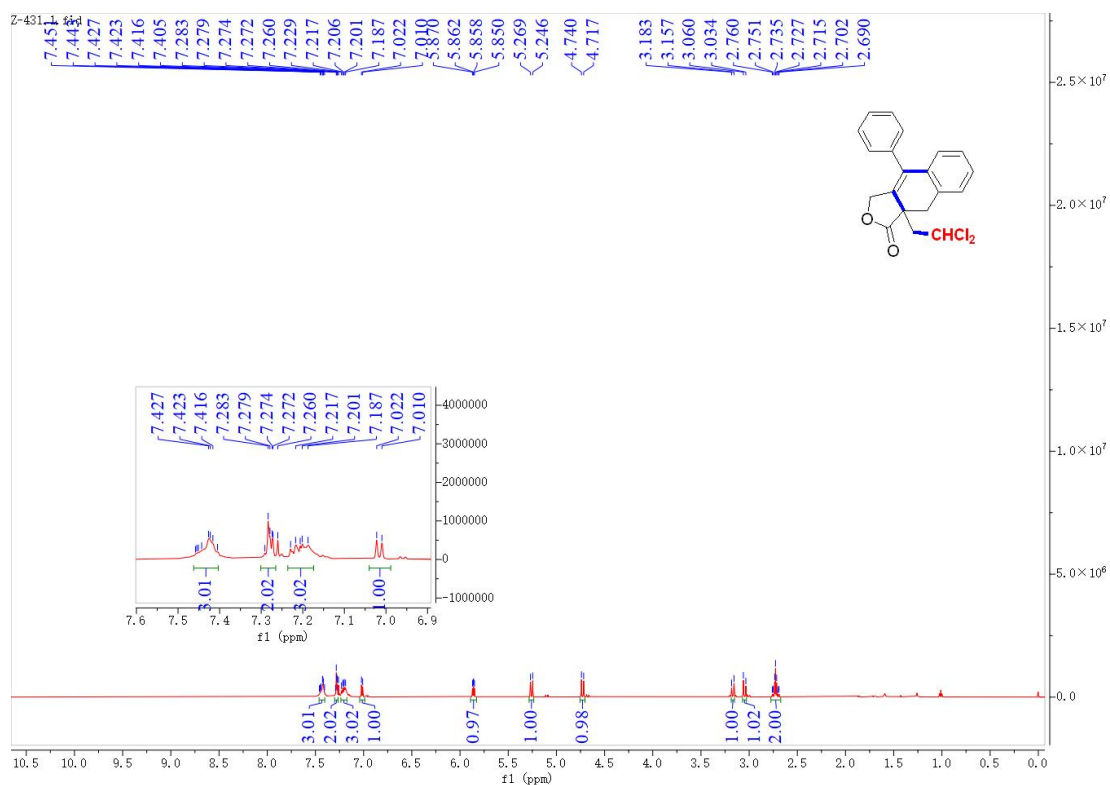
19-¹H NMR (400 MHz, CDCl₃)



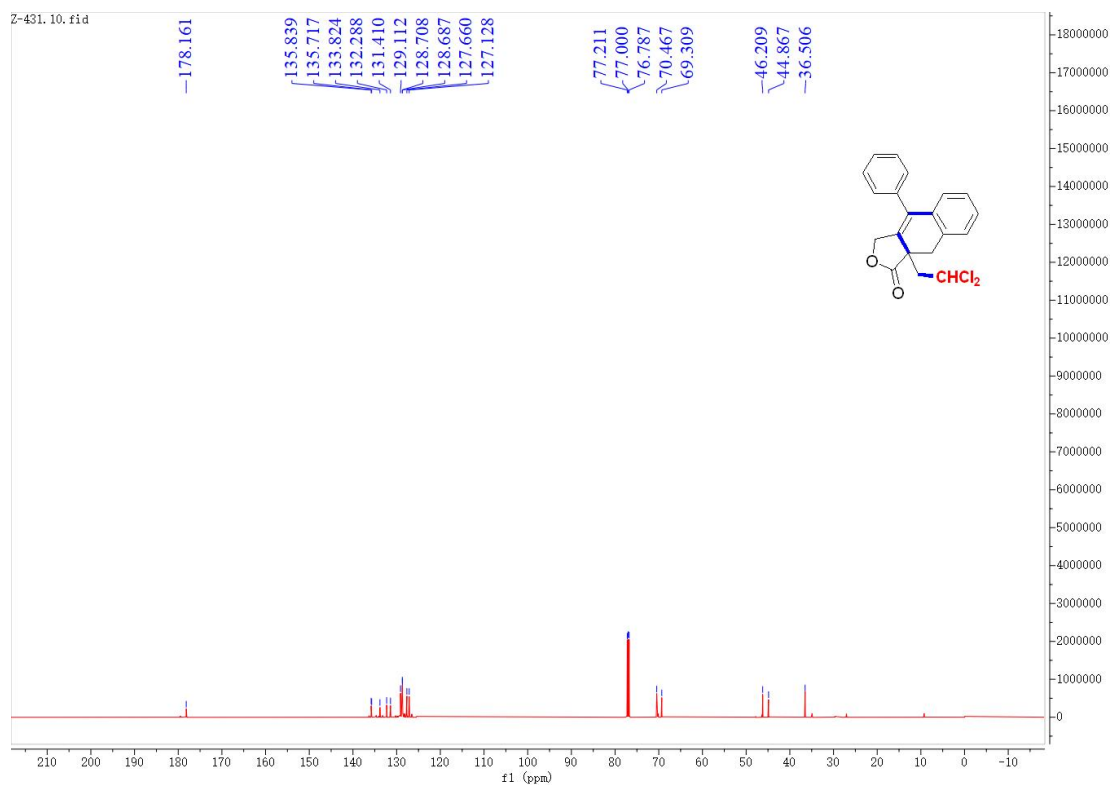
19-¹³C {¹H} NMR (100 MHz, CDCl₃)



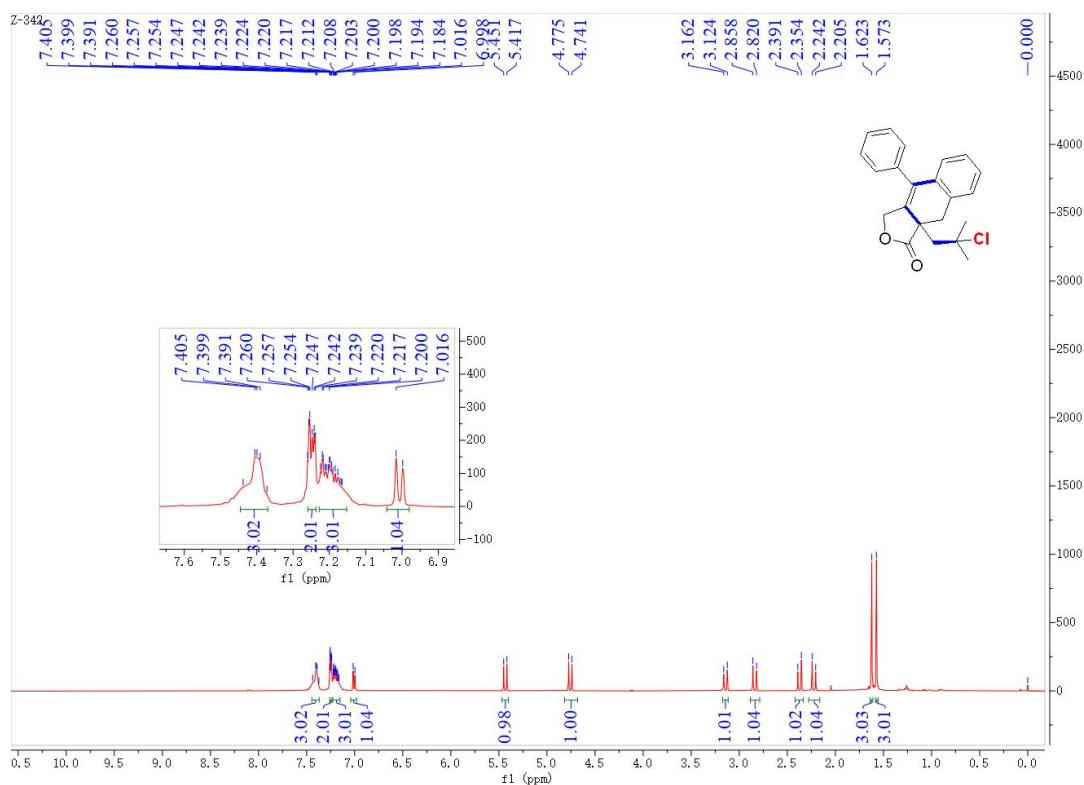
20-¹H NMR (600 MHz, CDCl₃)



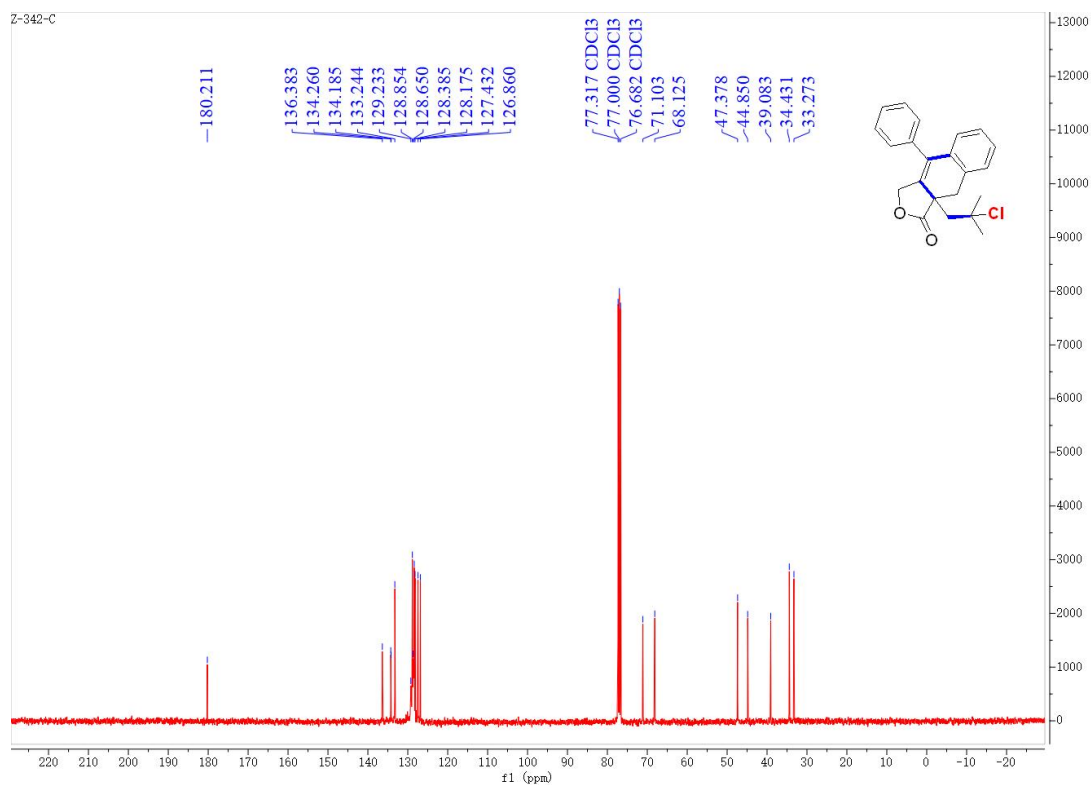
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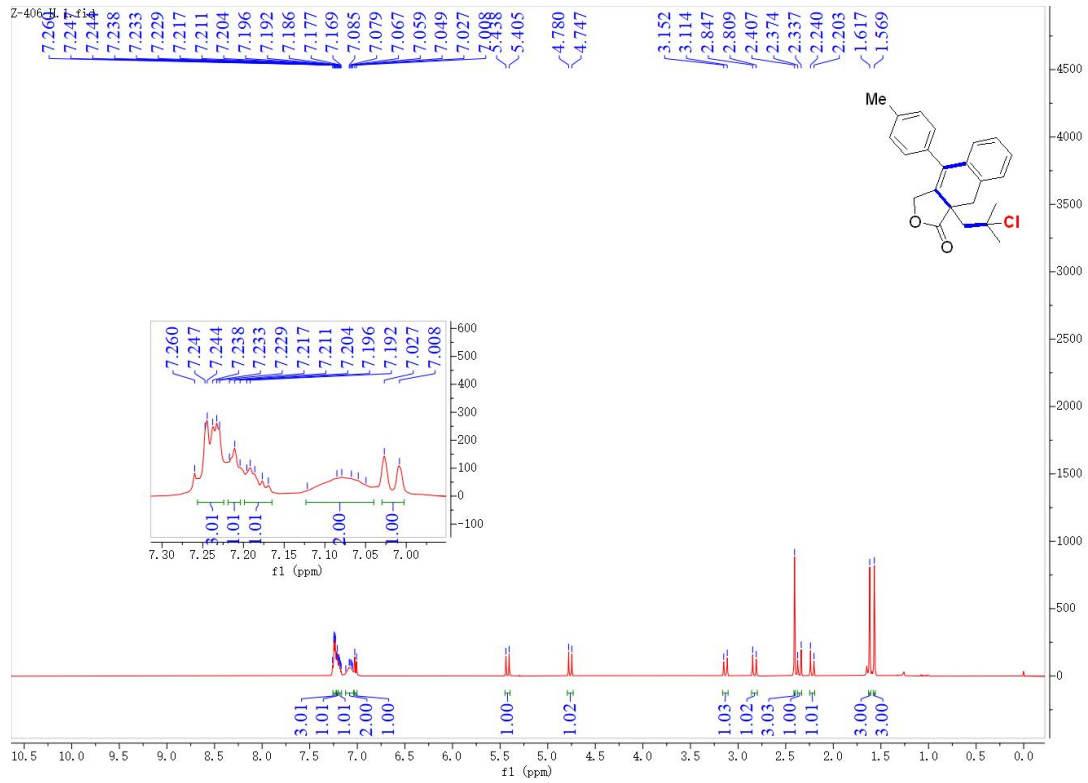
21-¹H NMR (400 MHz, CDCl₃)



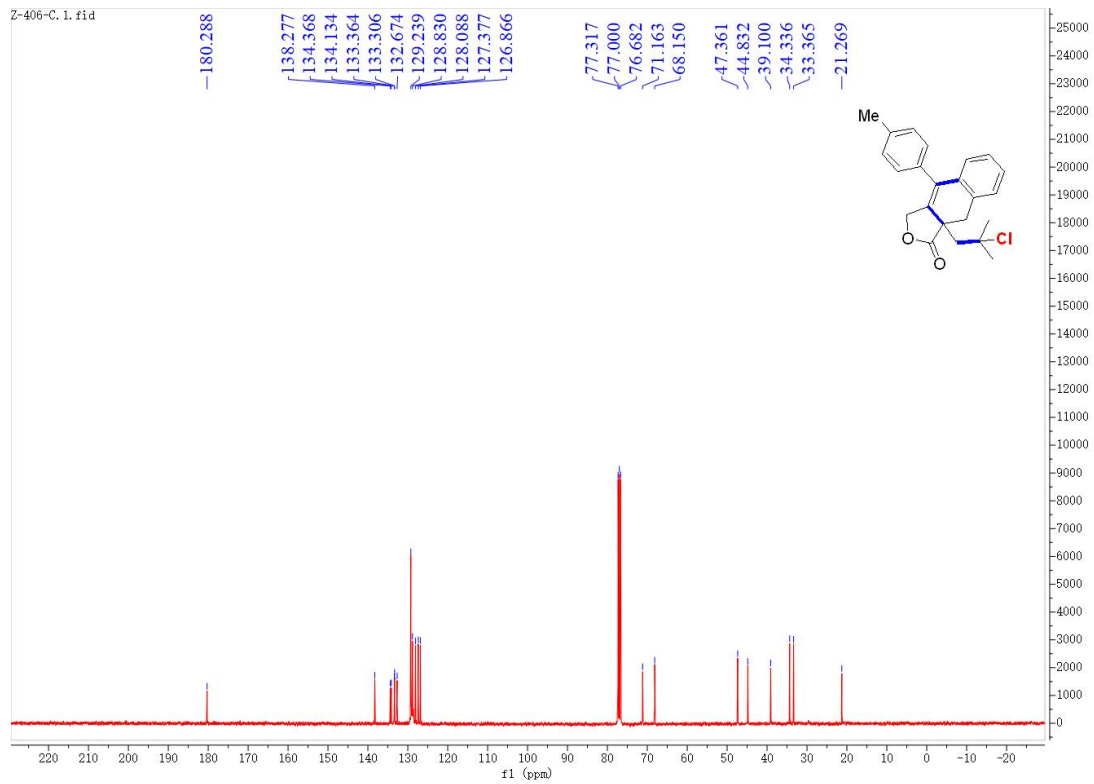
21-¹³C {¹H} NMR (100 MHz, CDCl₃)



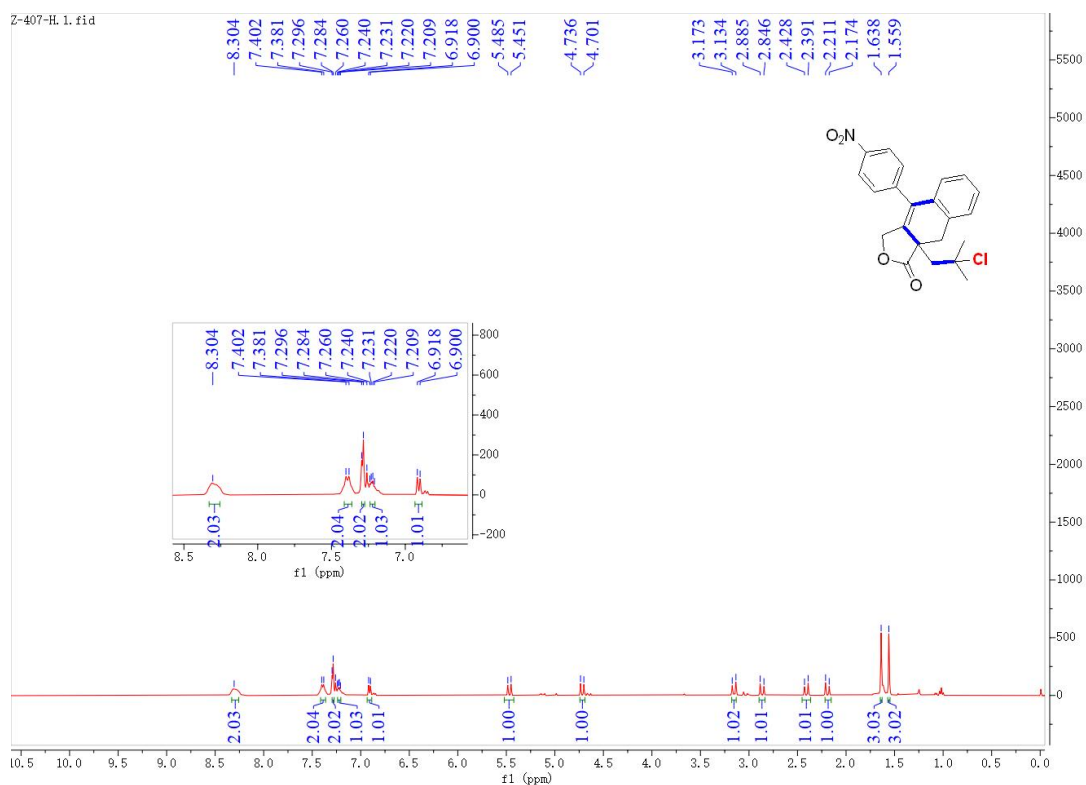
22-¹H NMR (400 MHz, CDCl₃)



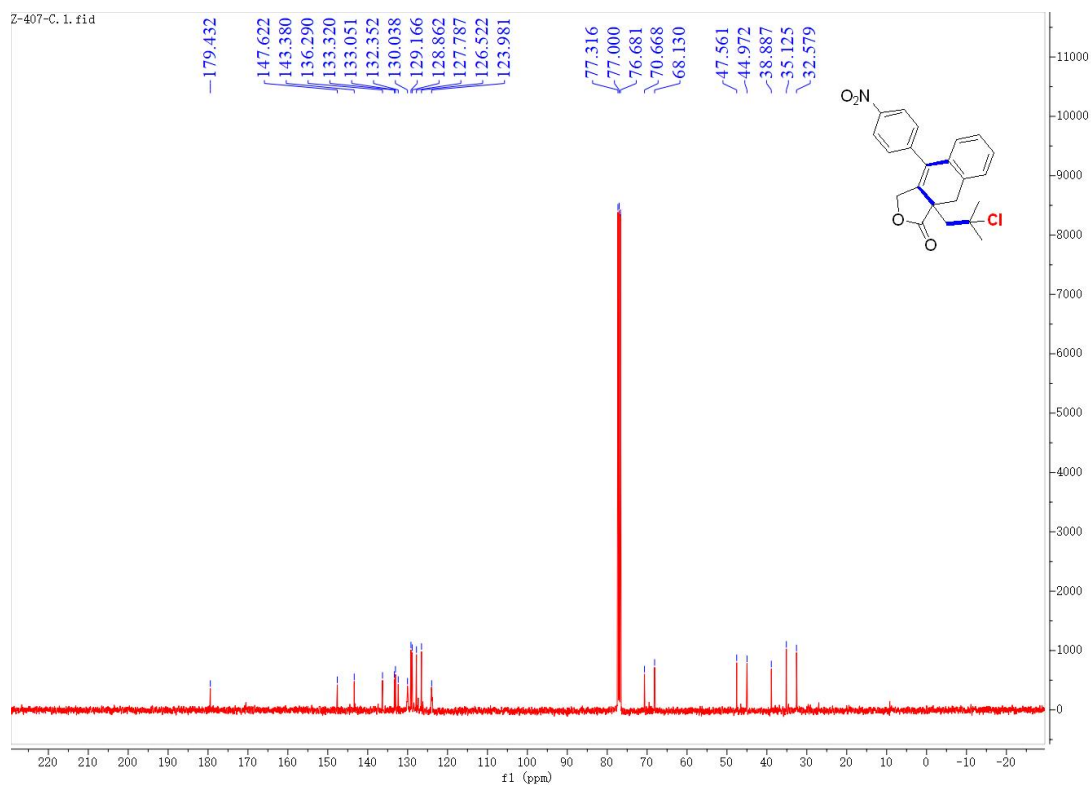
22-¹³C {¹H} NMR (100 MHz, CDCl₃)



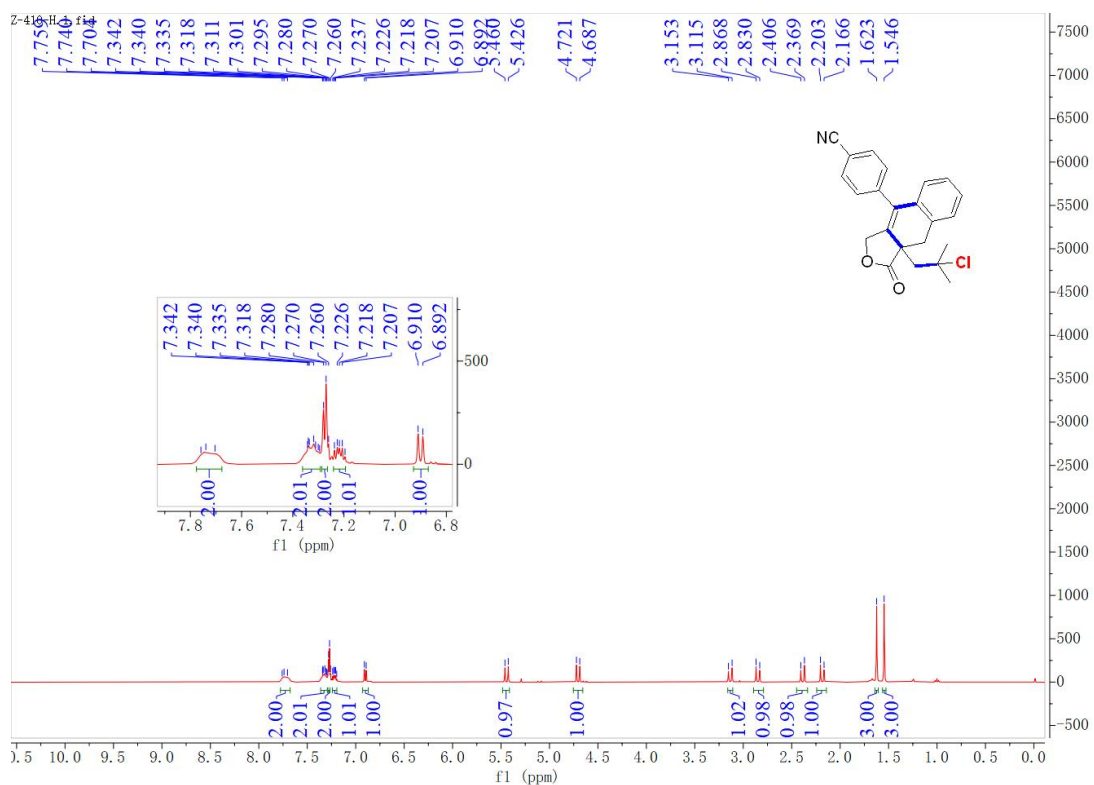
23-¹H NMR (400 MHz, CDCl₃)



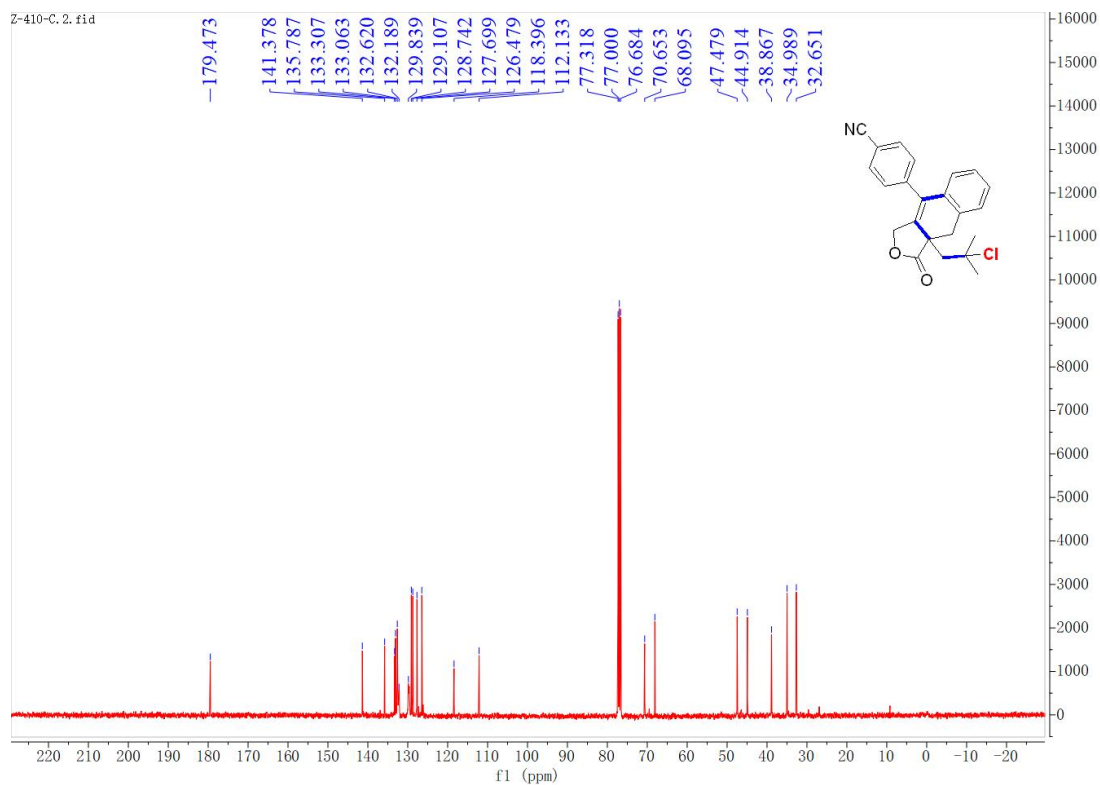
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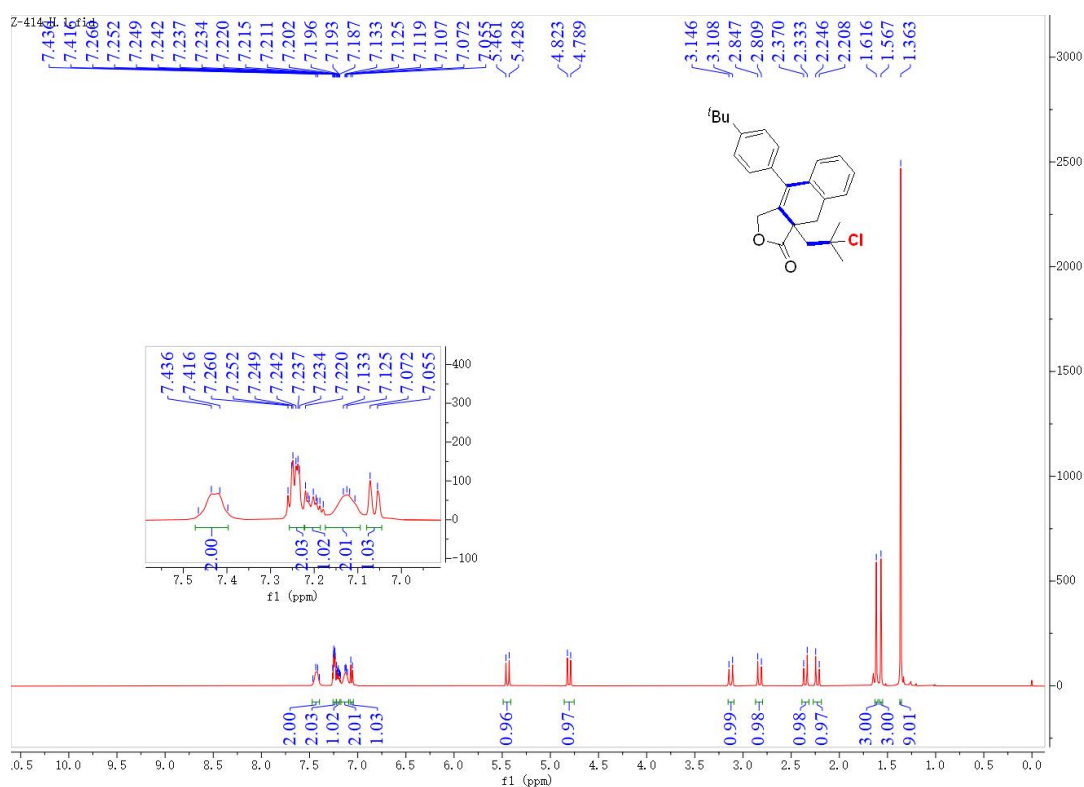
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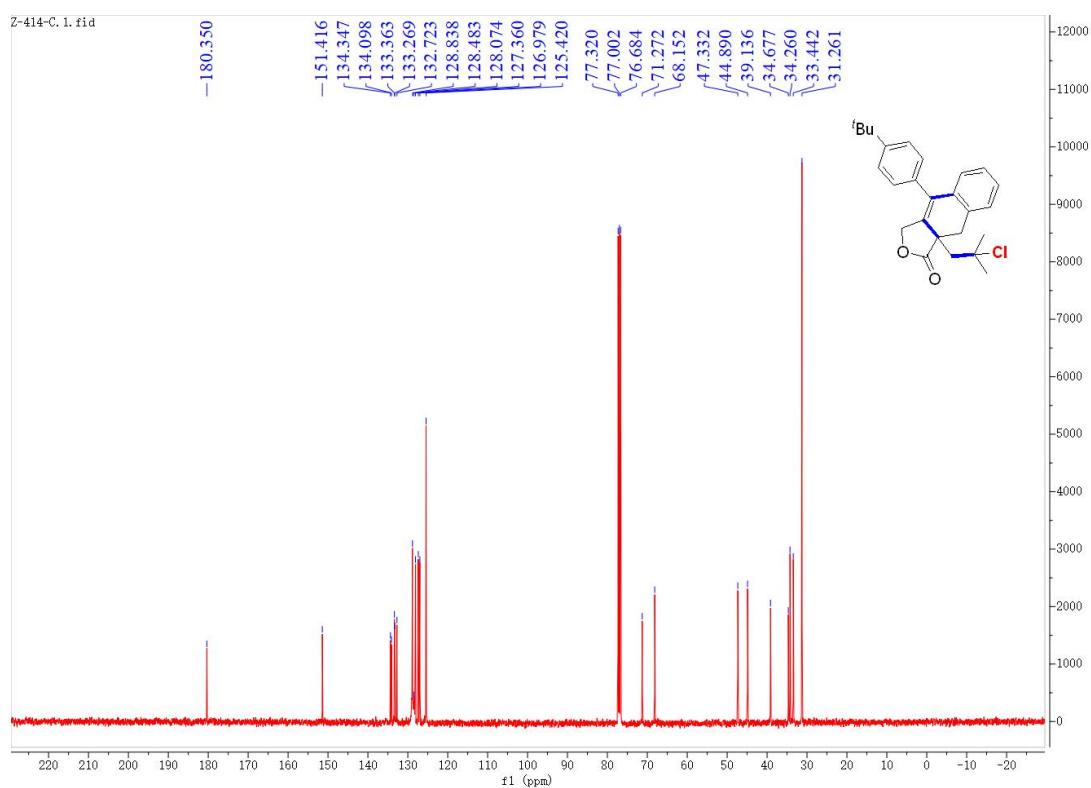
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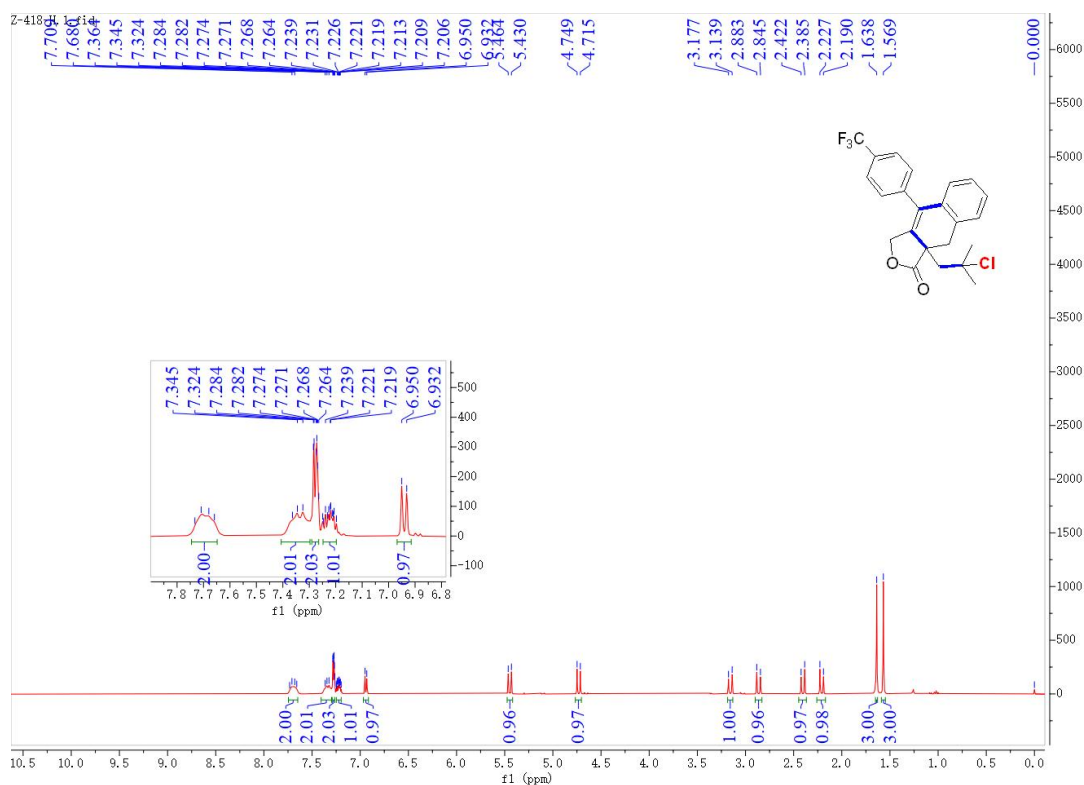
25-¹H NMR (400 MHz, CDCl₃)



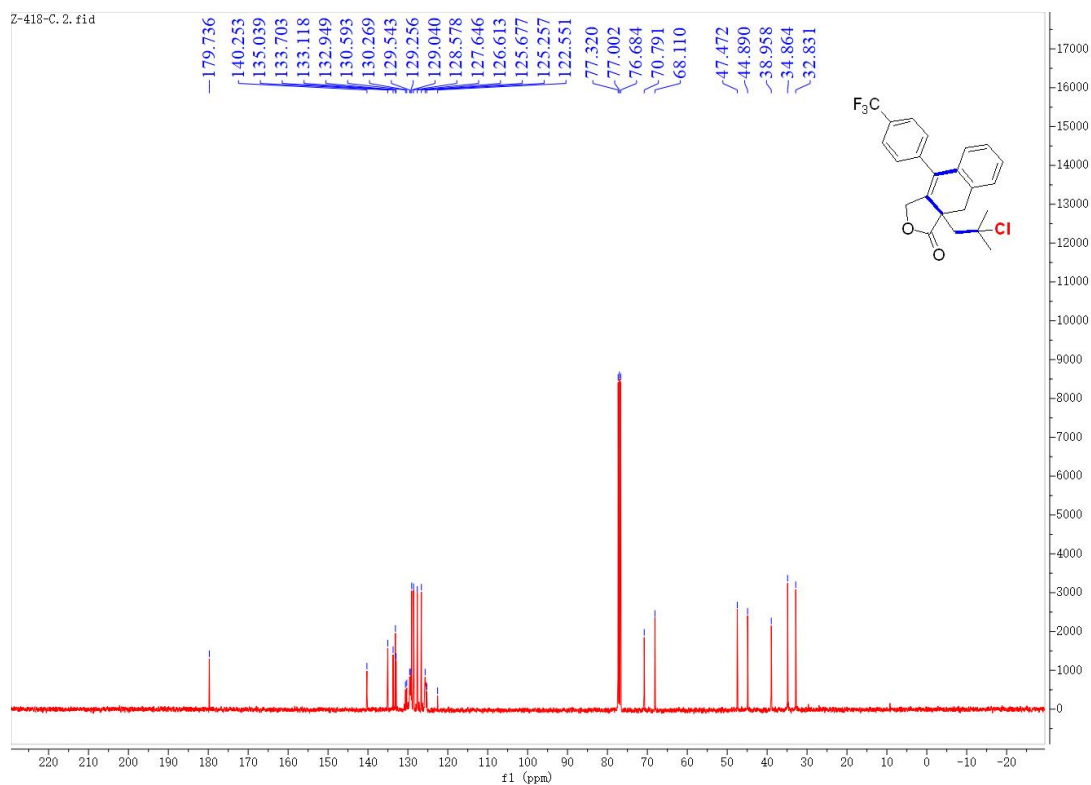
25-¹³C {¹H} NMR (100 MHz, CDCl₃)



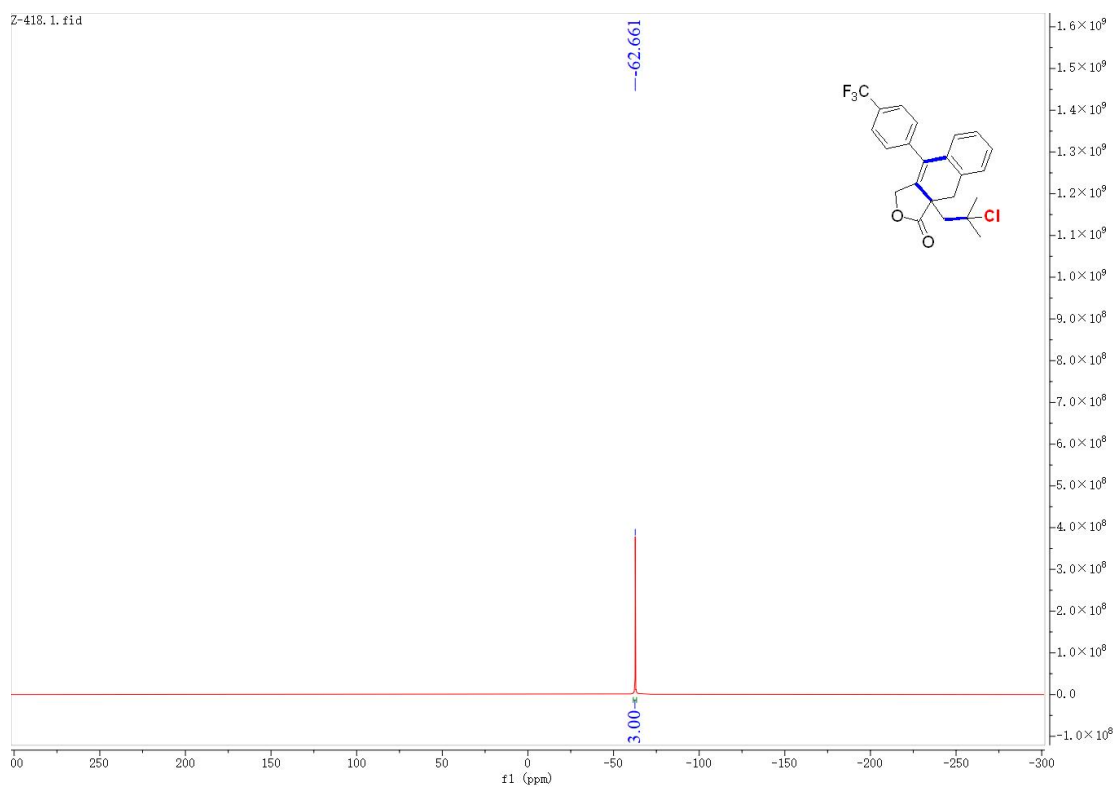
26-¹H NMR (400 MHz, CDCl₃)



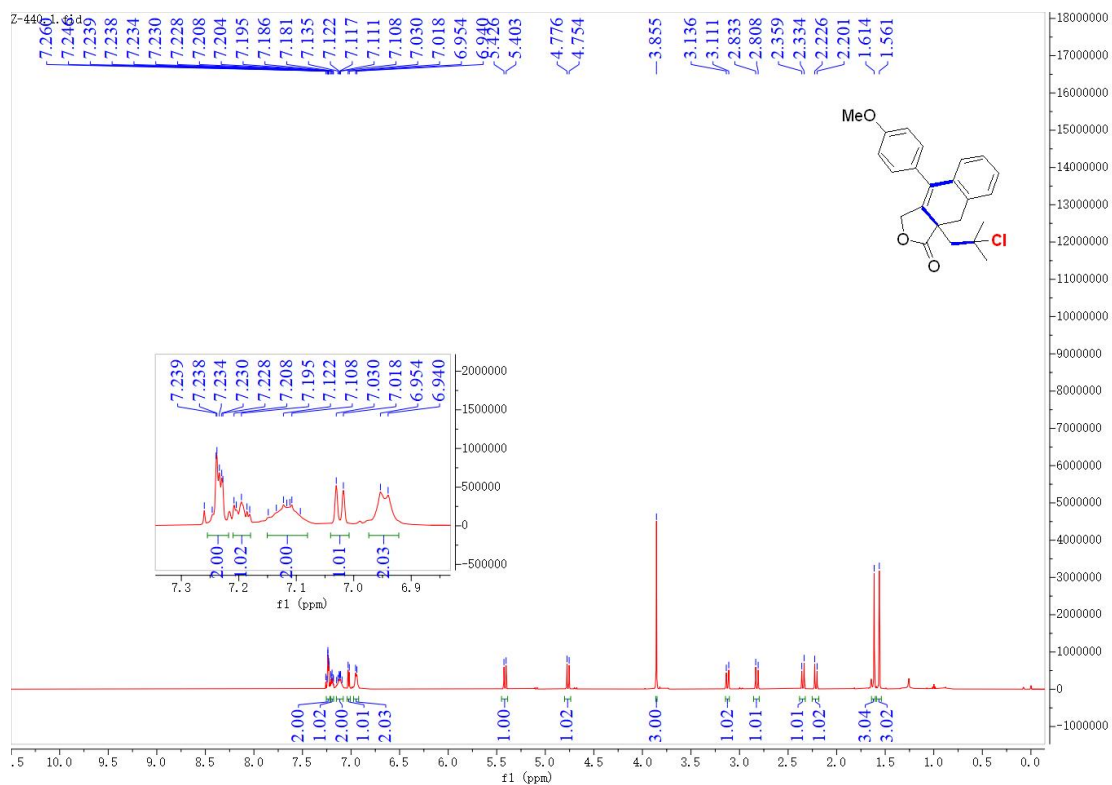
26-¹³C {¹H} NMR (100 MHz, CDCl₃)



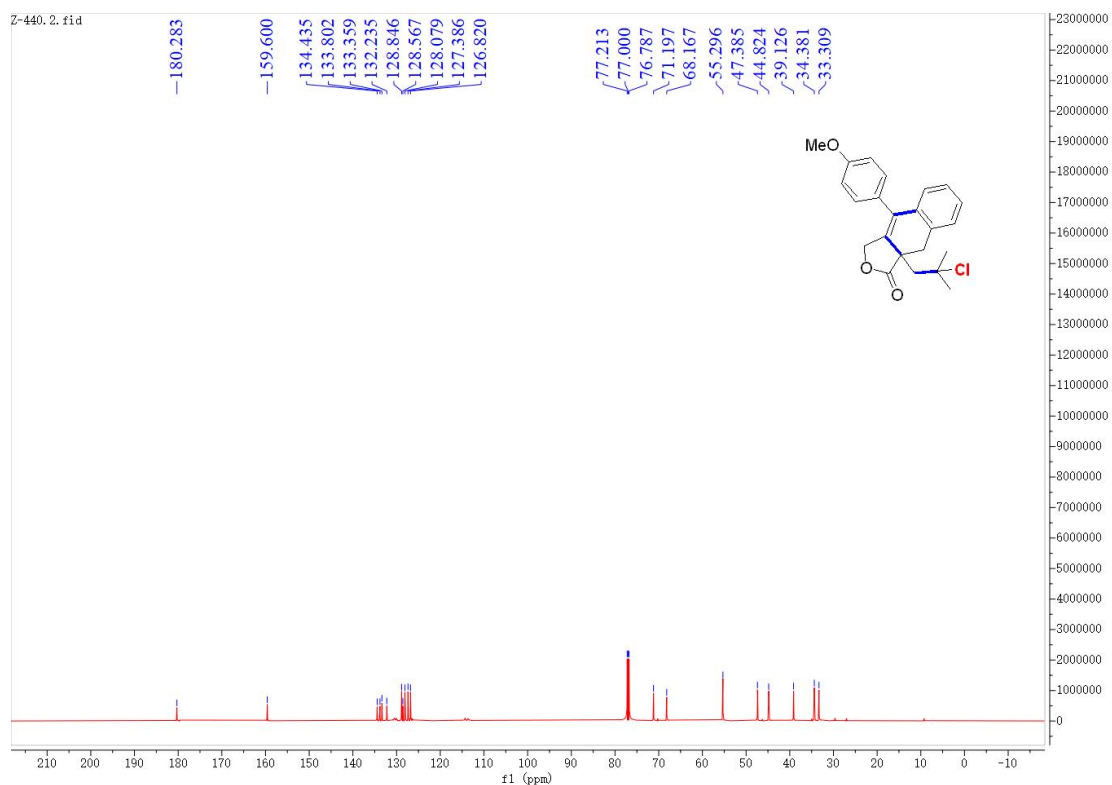
26-¹⁹F NMR (565 MHz, CDCl₃)



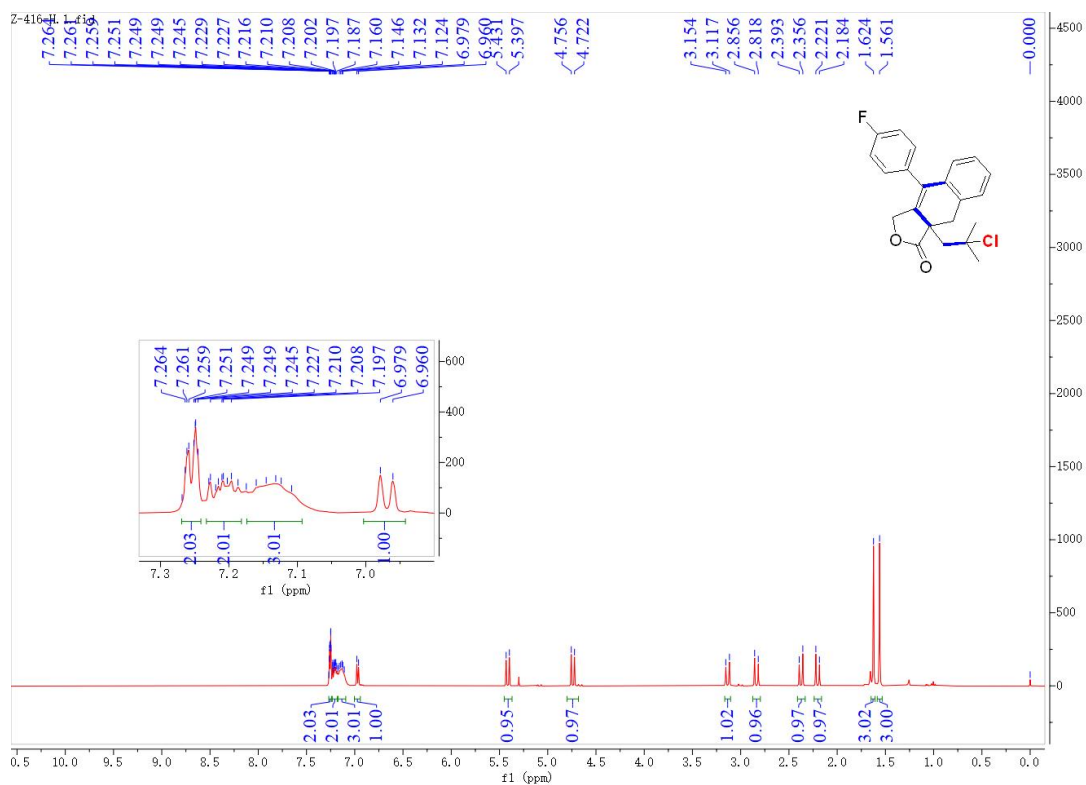
27-¹H NMR (600 MHz, CDCl₃)



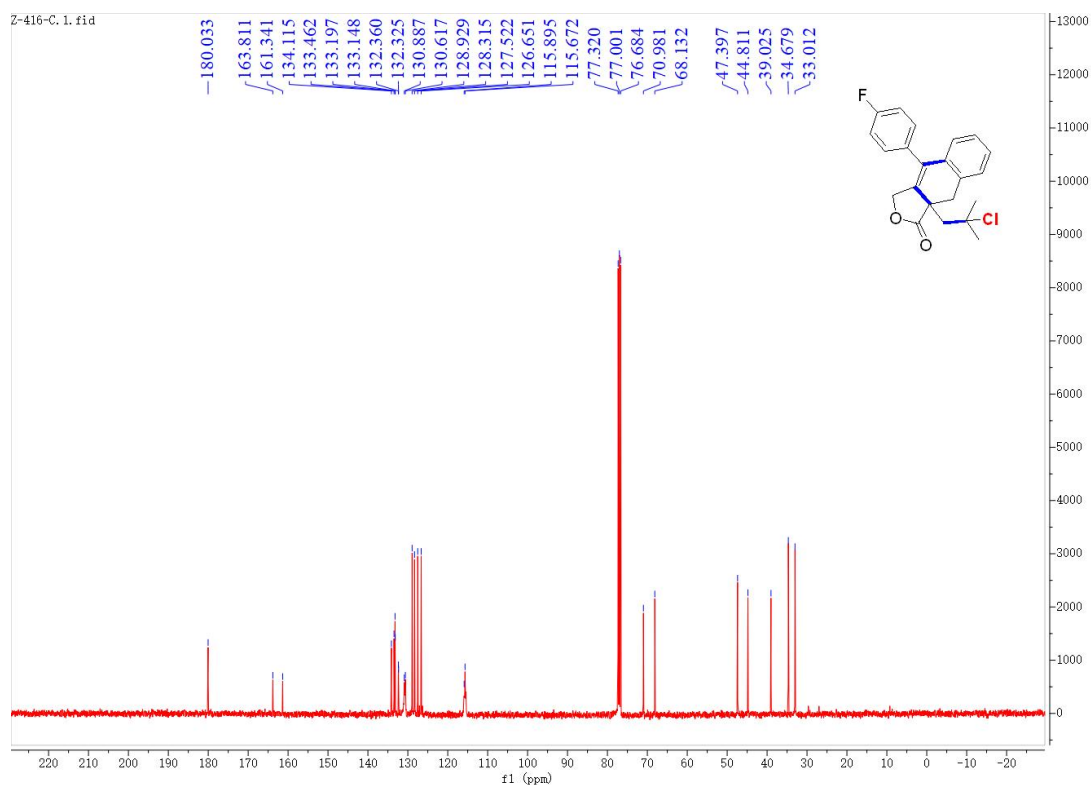
27-¹³C{¹H} NMR (150 MHz, CDCl₃)



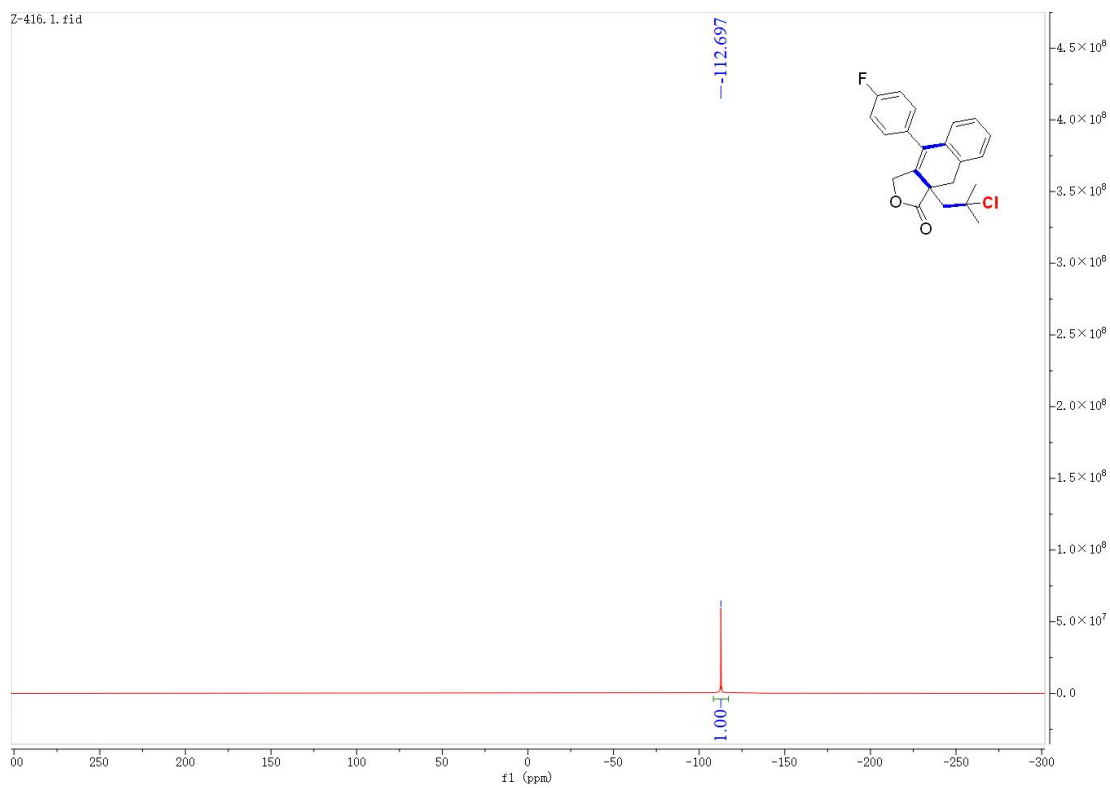
28-¹H NMR (400 MHz, CDCl₃)



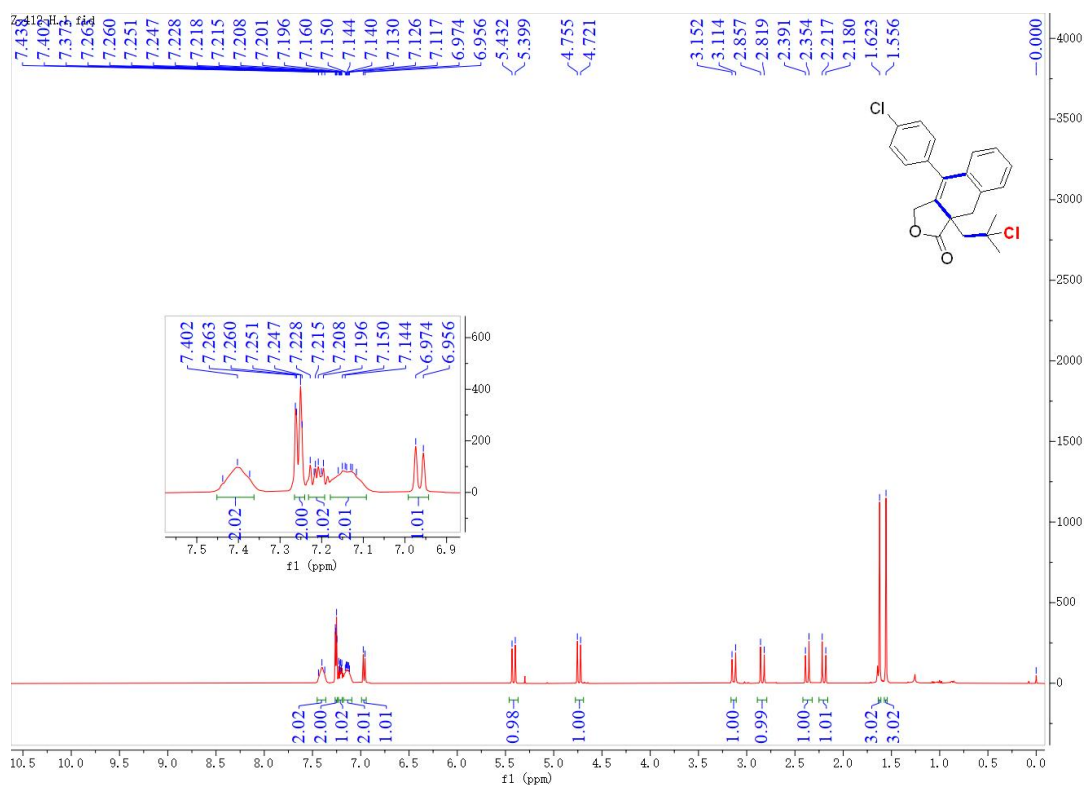
28-¹³C{¹H} NMR (100 MHz, CDCl₃)



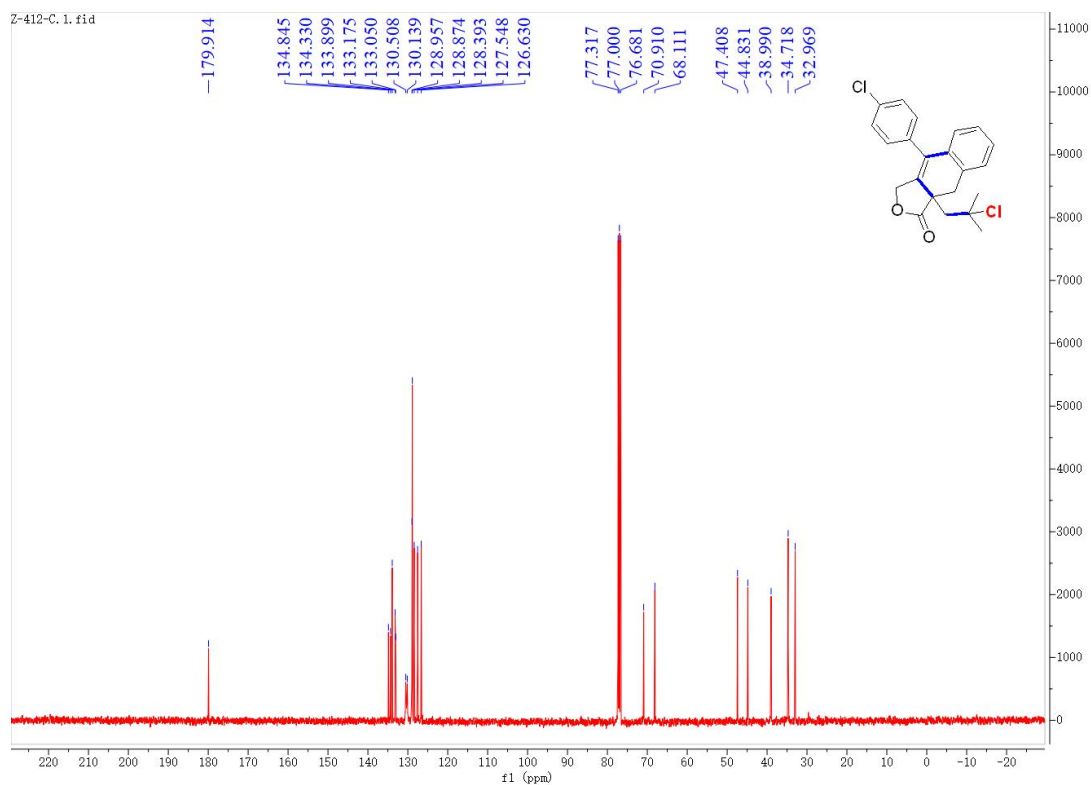
28-¹⁹F NMR (565 MHz, CDCl₃)



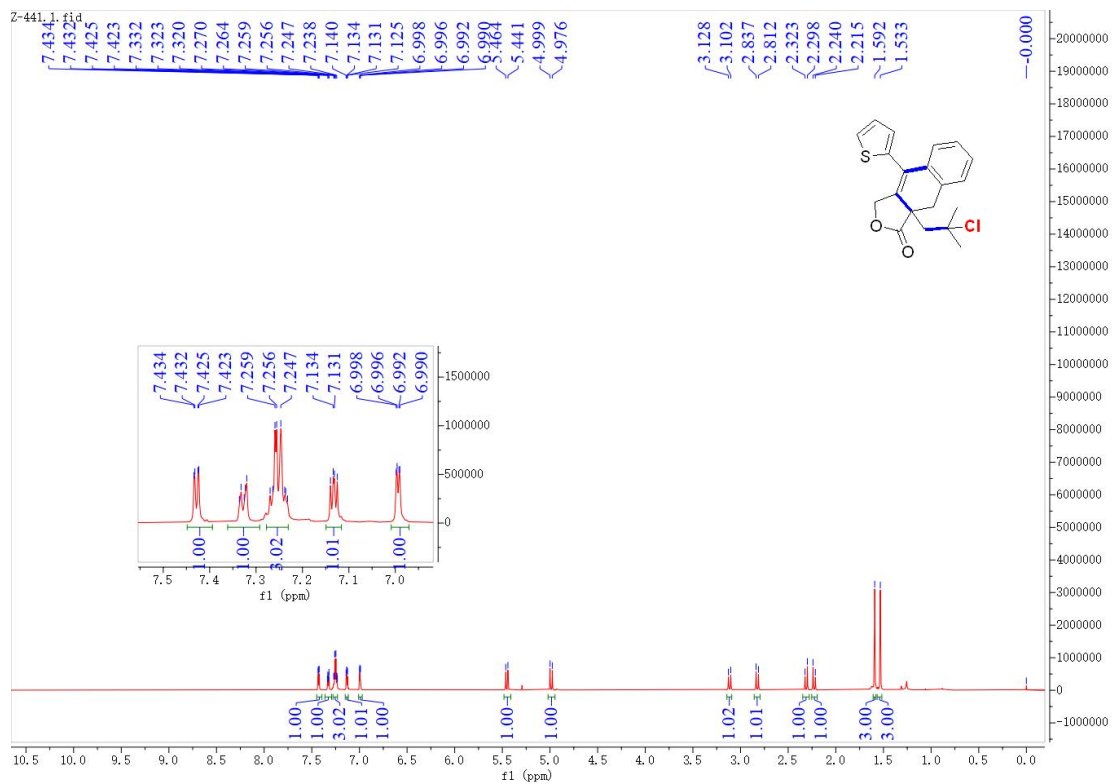
29-¹H NMR (400 MHz, CDCl₃)



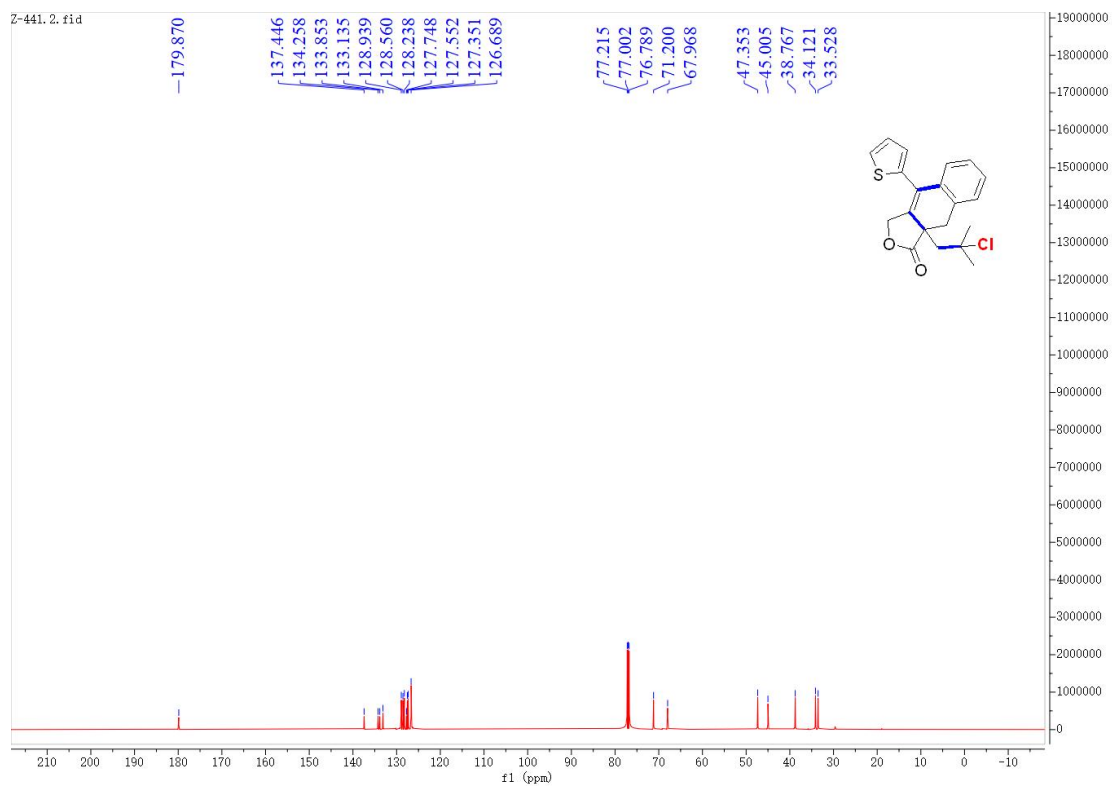
29-¹³C {¹H} NMR (100 MHz, CDCl₃)



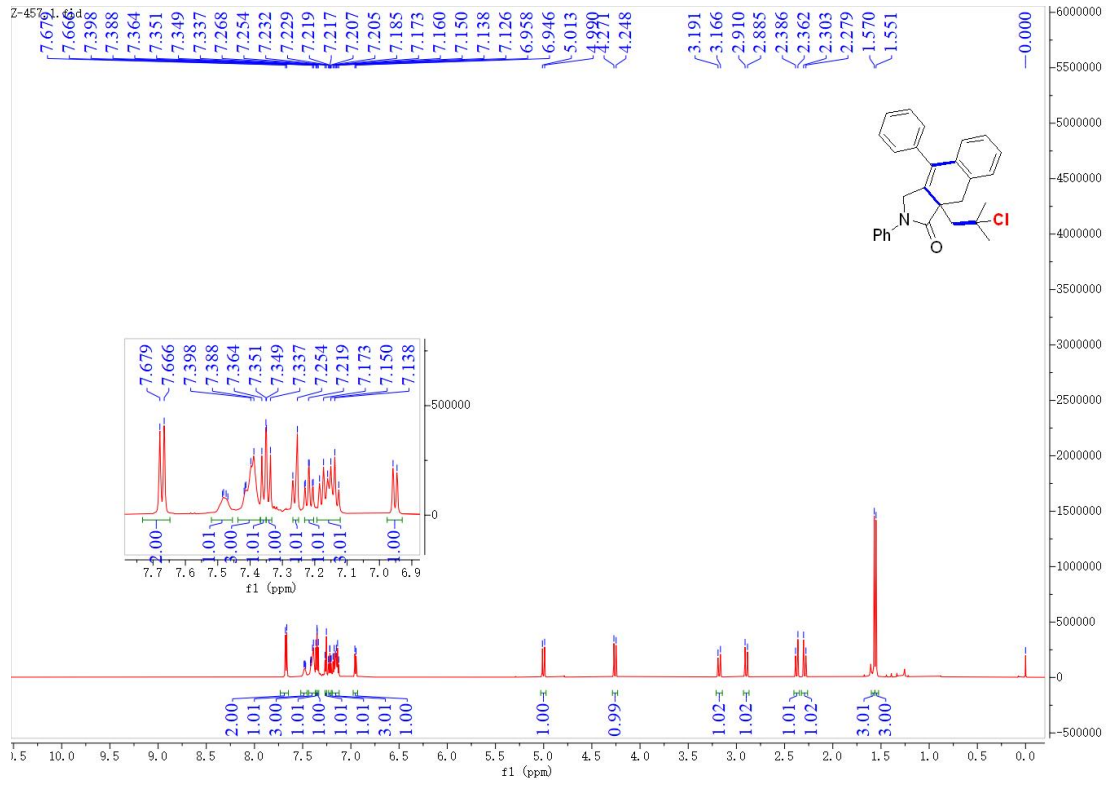
30-¹H NMR (600 MHz, CDCl₃)



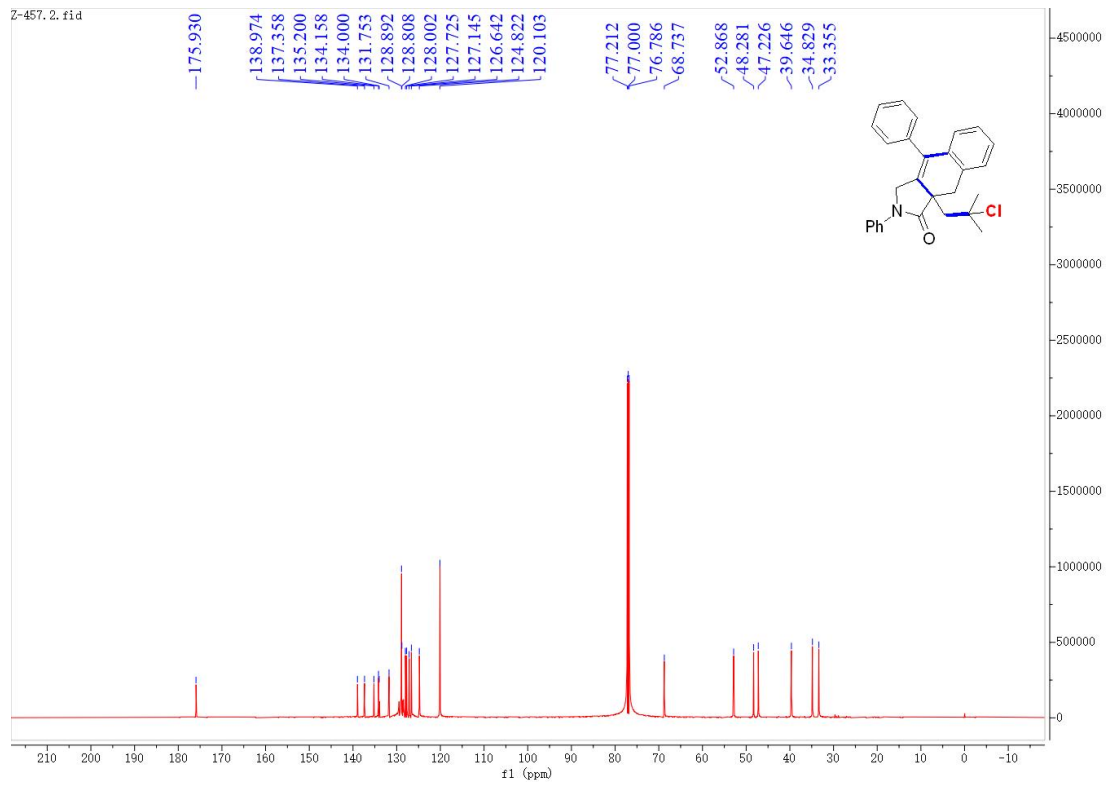
30-¹³C {¹H} NMR (150 MHz, CDCl₃)



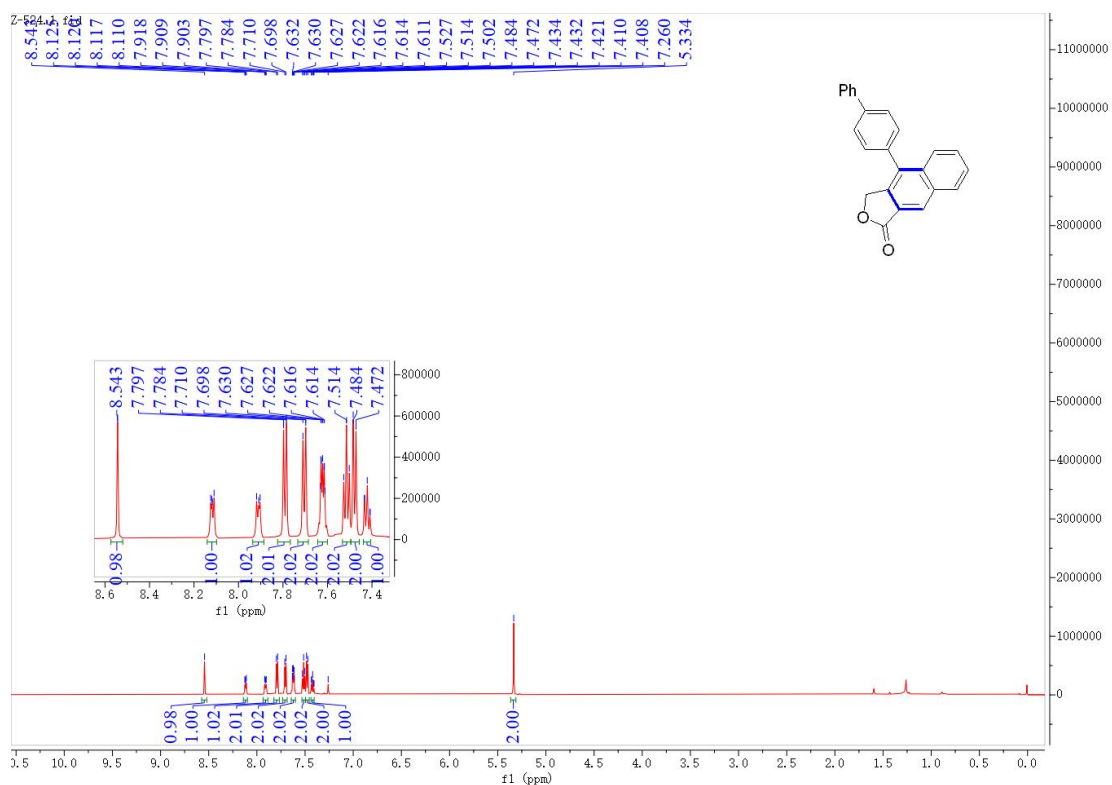
31-¹H NMR (600 MHz, CDCl₃)



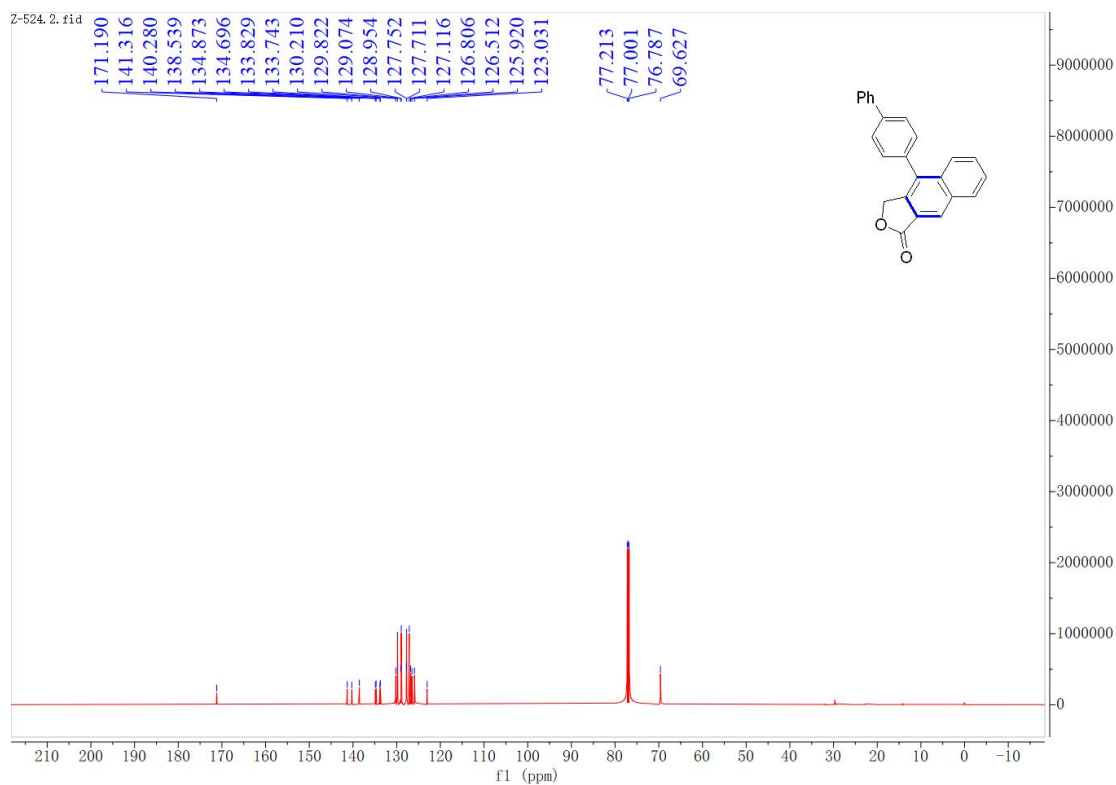
31-¹³C {¹H} NMR (150 MHz, CDCl₃)



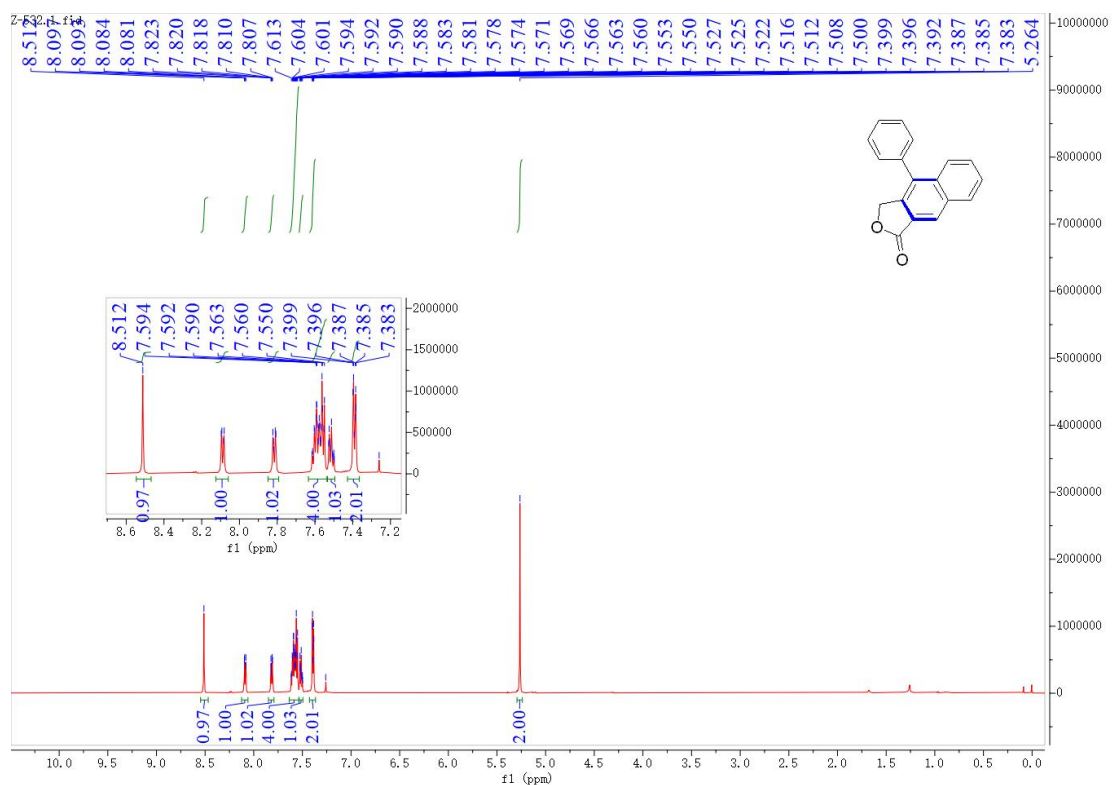
32-¹H NMR (600 MHz, CDCl₃)



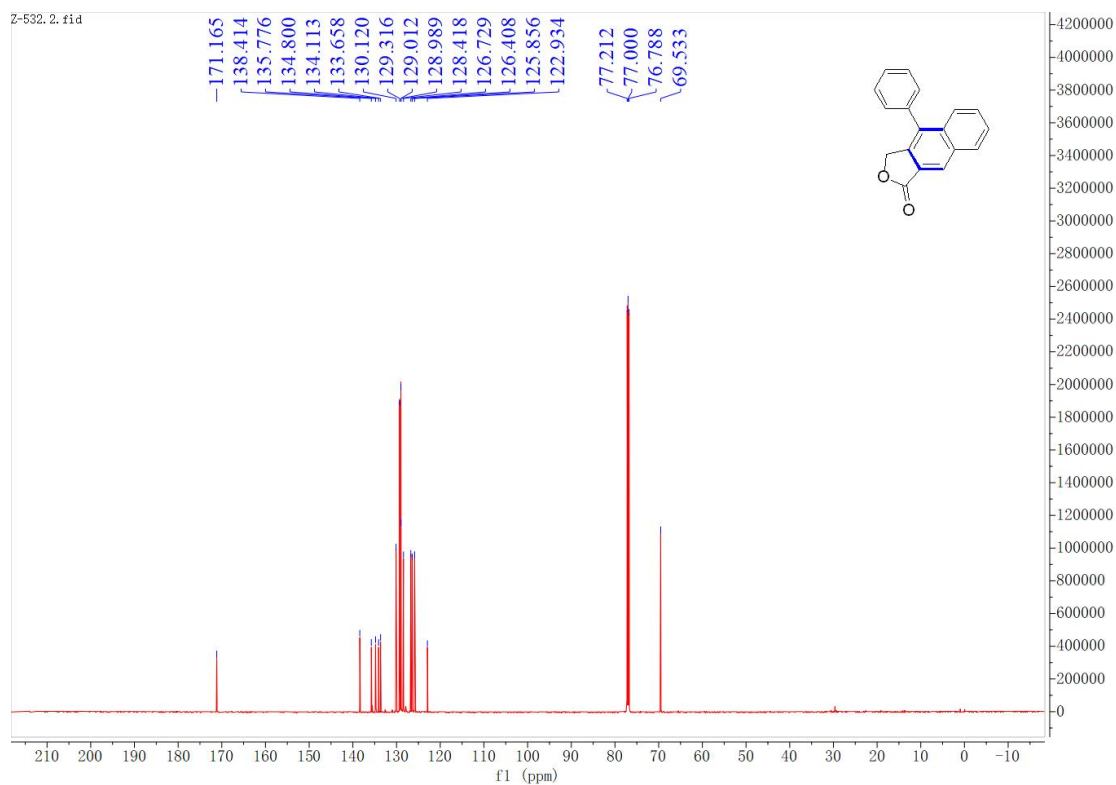
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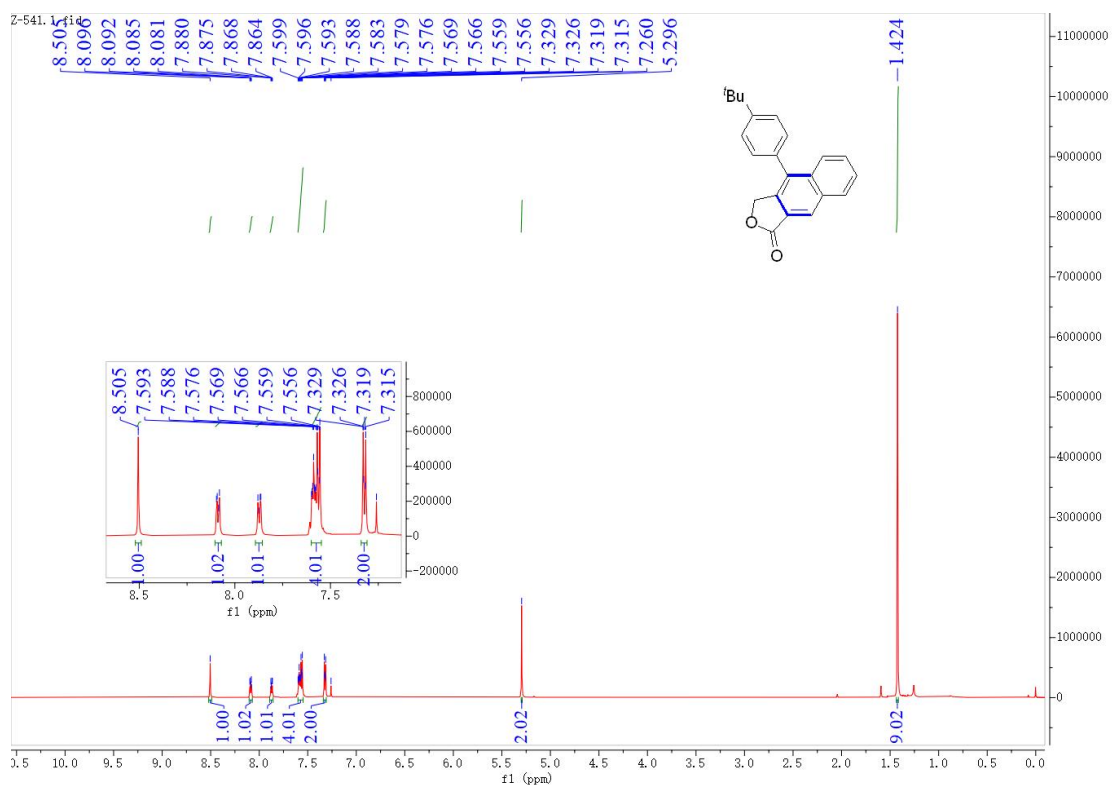
33-¹H NMR (600 MHz, CDCl₃)



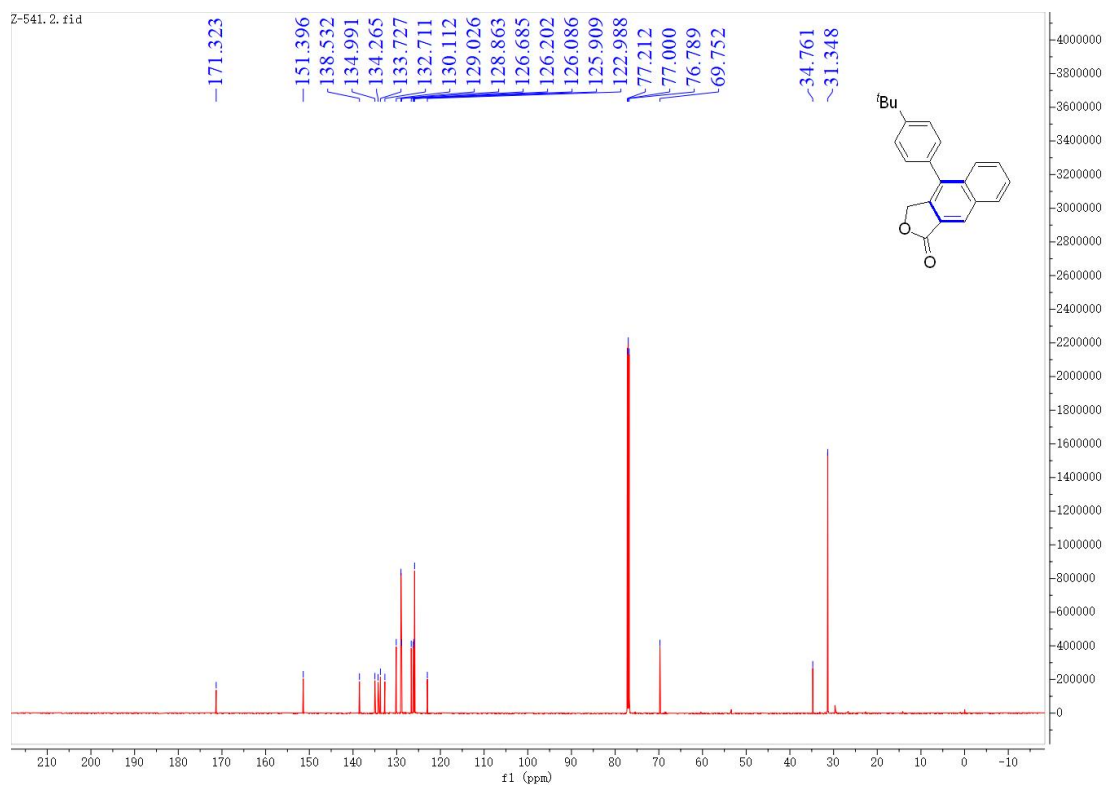
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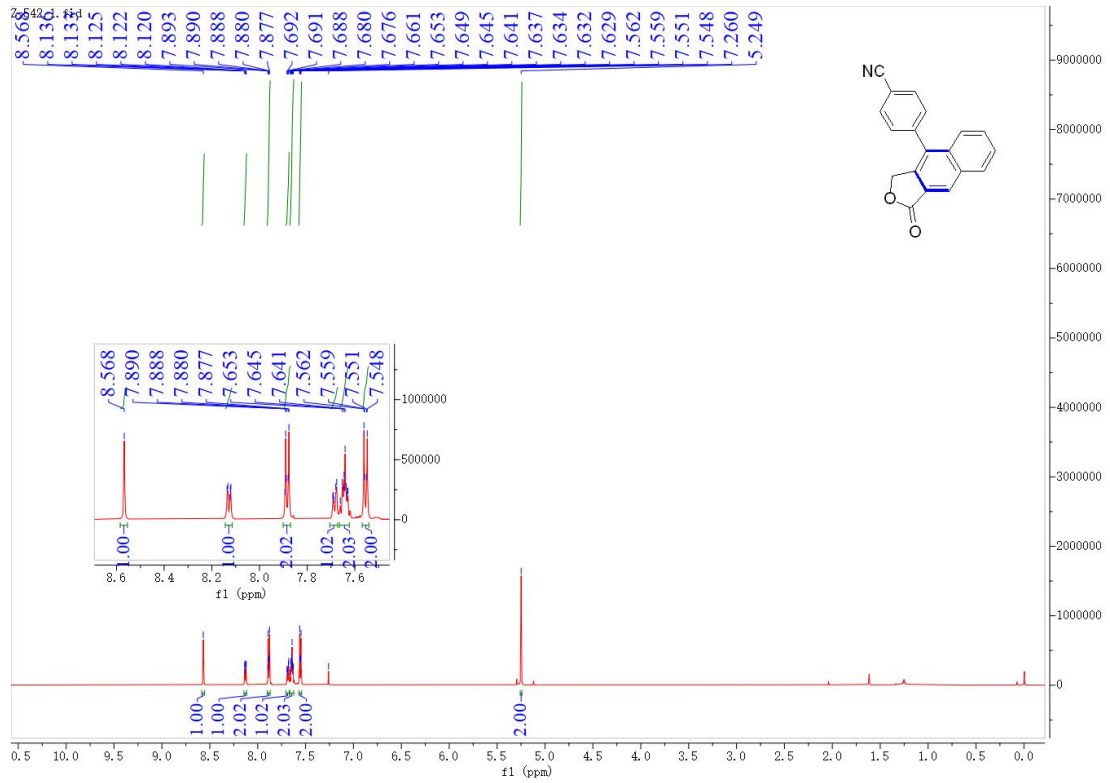
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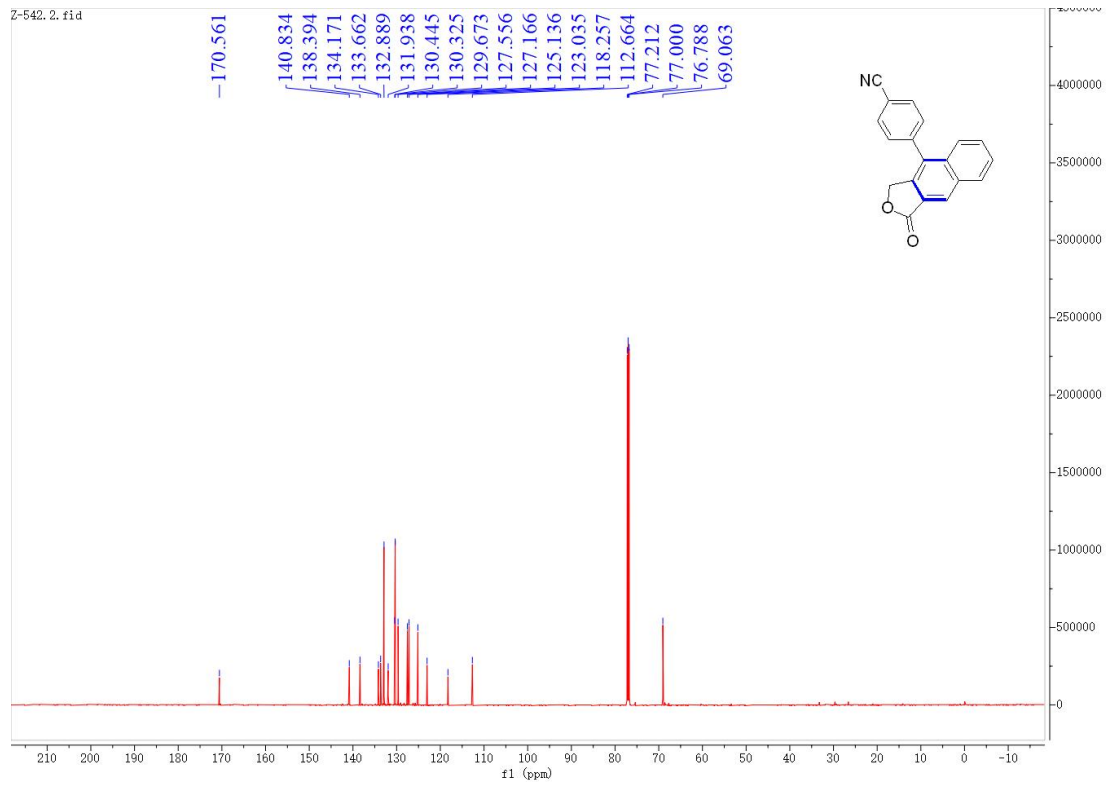
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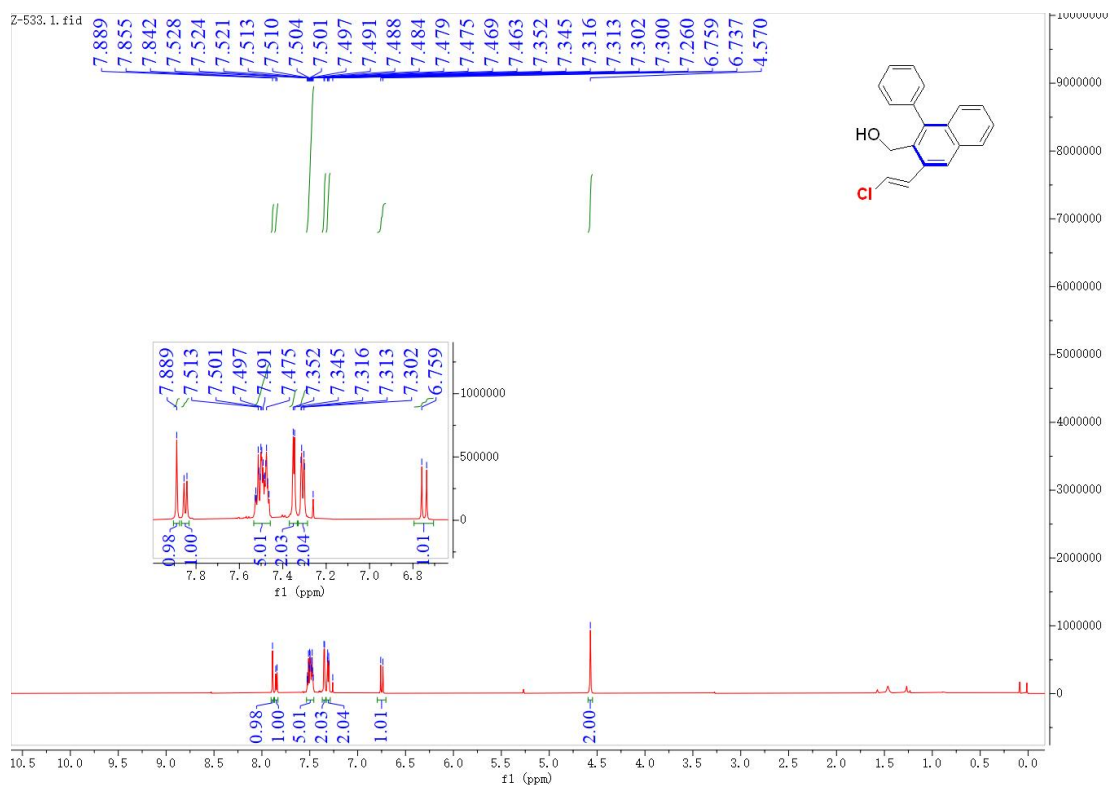
35-¹H NMR (600 MHz, CDCl₃)



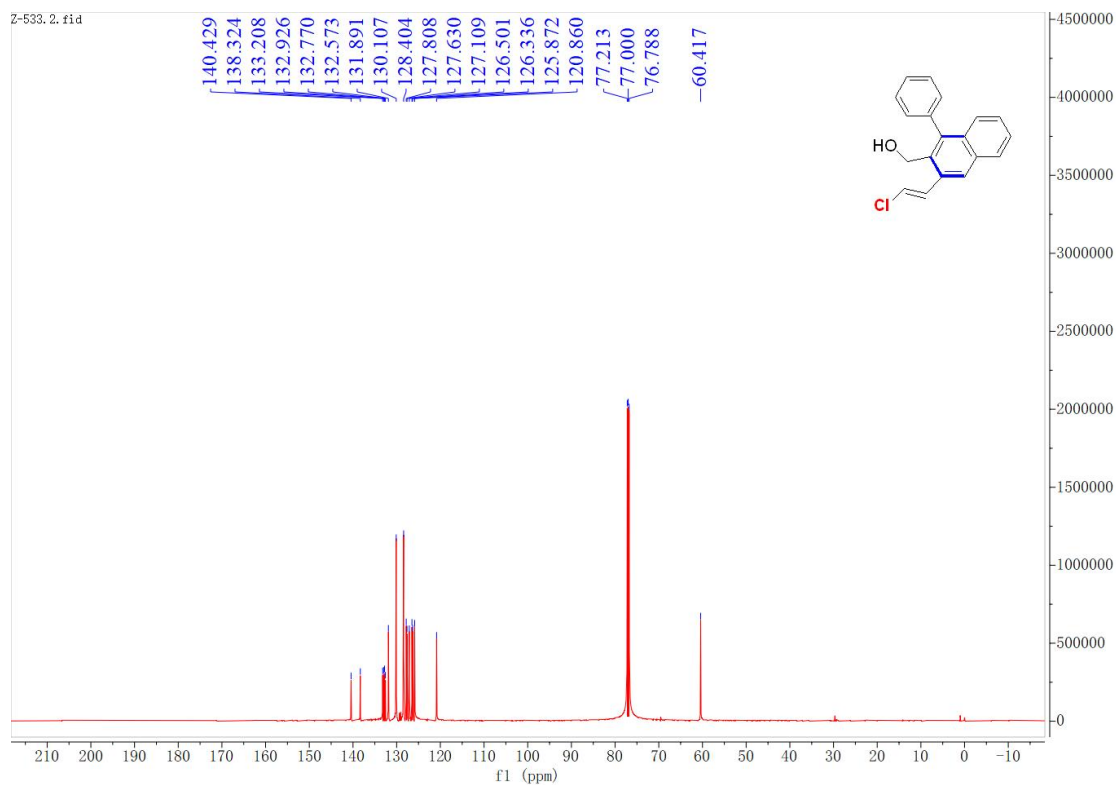
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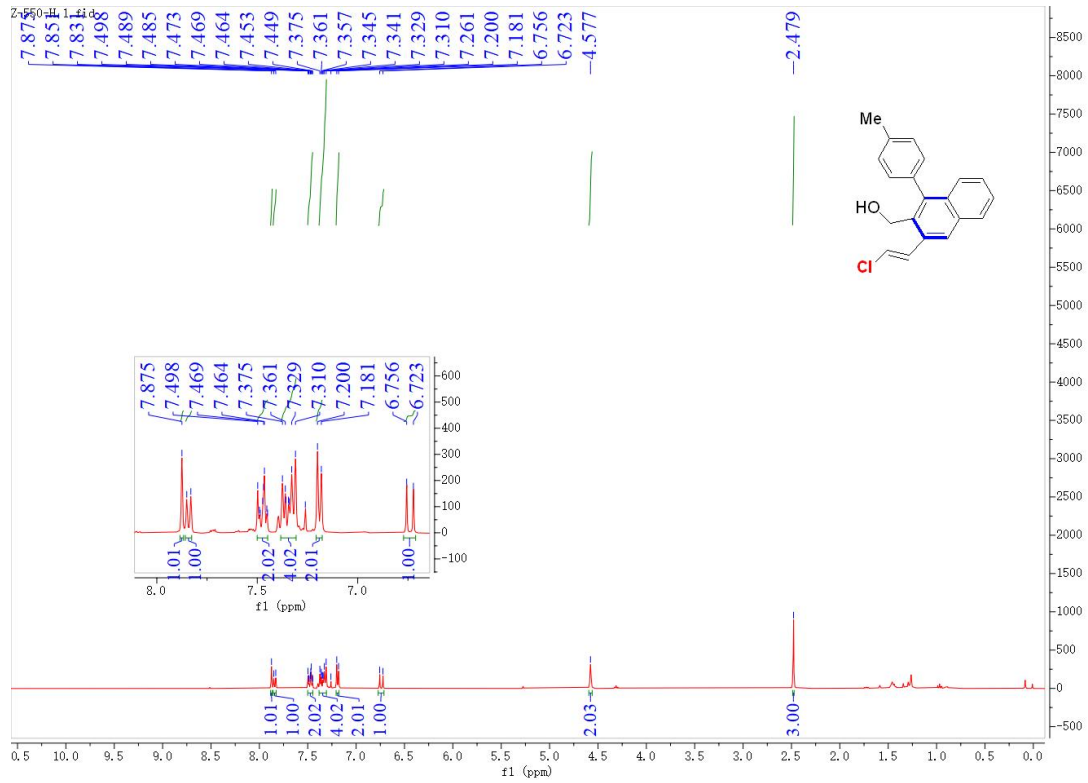
36-¹H NMR (600 MHz, CDCl₃)



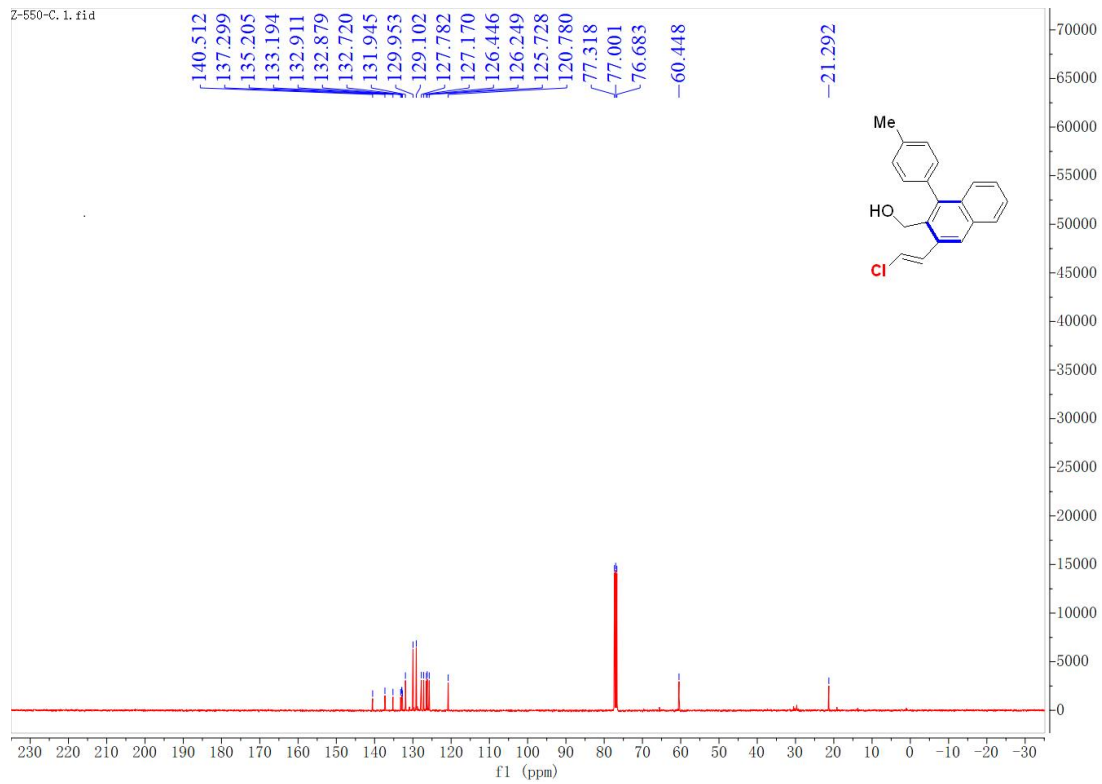
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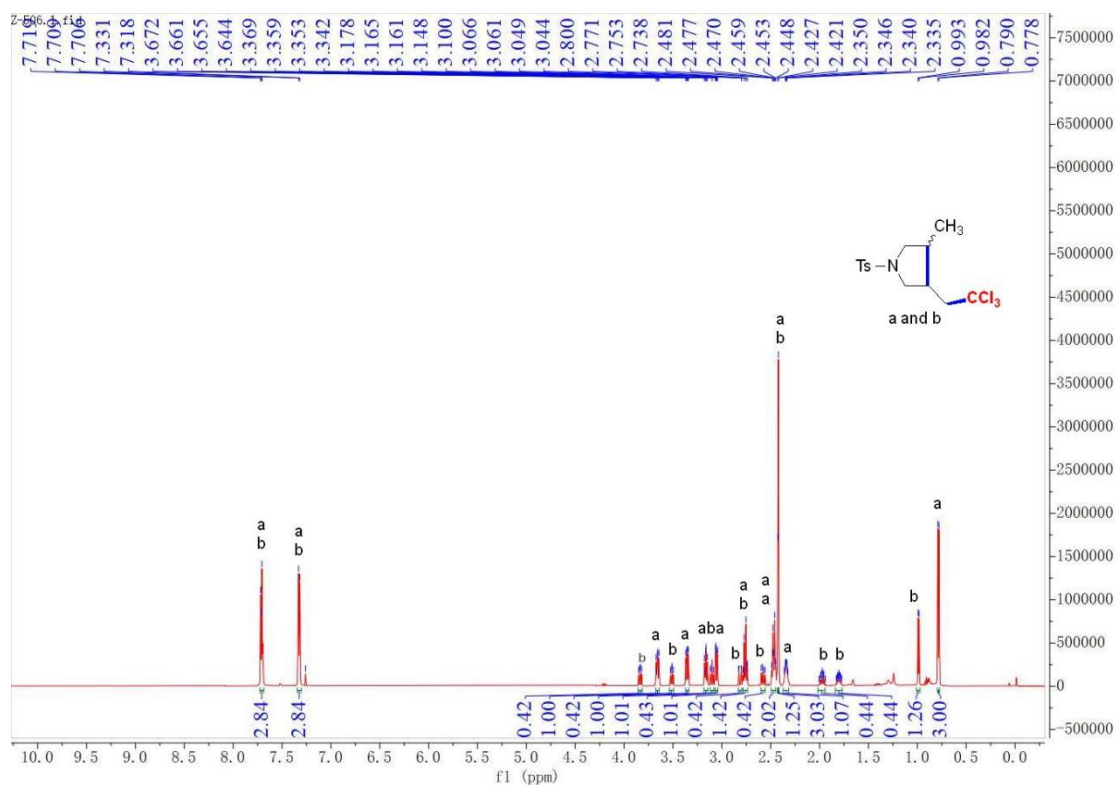
37-¹H NMR (400 MHz, CDCl₃)



37-¹³C {¹H} NMR (150 MHz, CDCl₃)



38-¹H NMR (600 MHz, CDCl₃)



38-¹³C {¹H} NMR (150 MHz, CDCl₃)

