

Supplementary Information

Diversity-Oriented and Diastereoselective Synthesis of Diverse Polycyclic Thieno(2,3-*b*)-quinolines Derivatives Using a Synergistic Strategy

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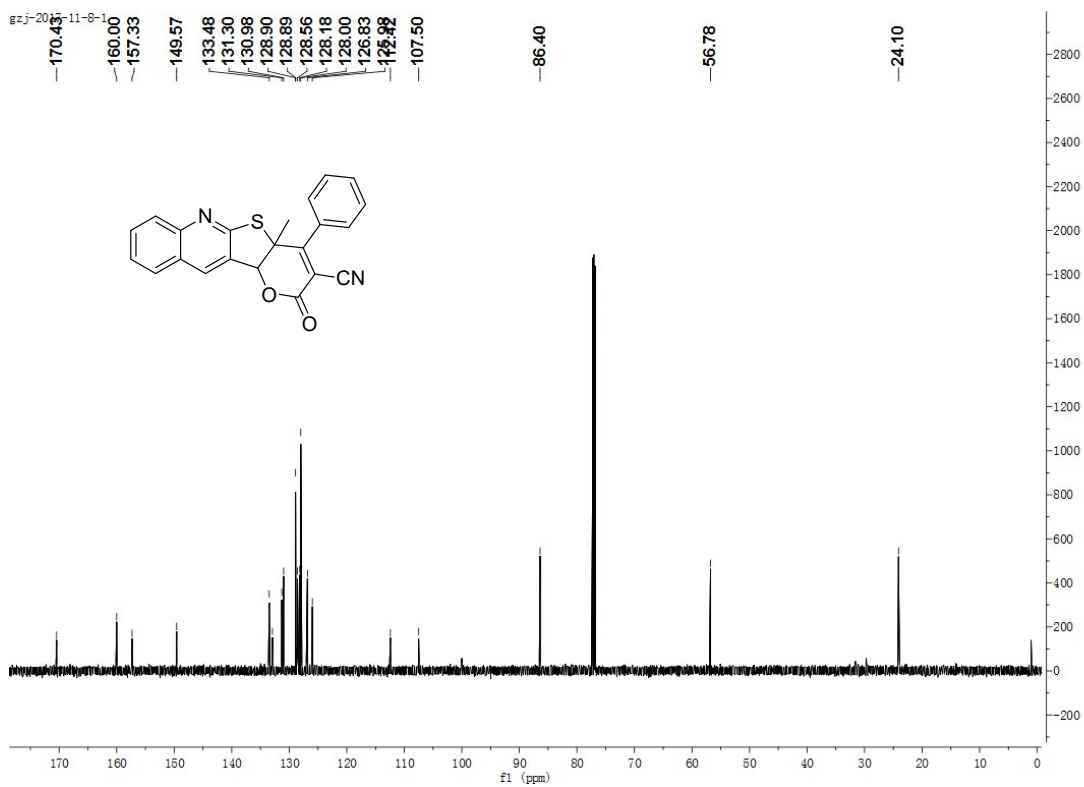
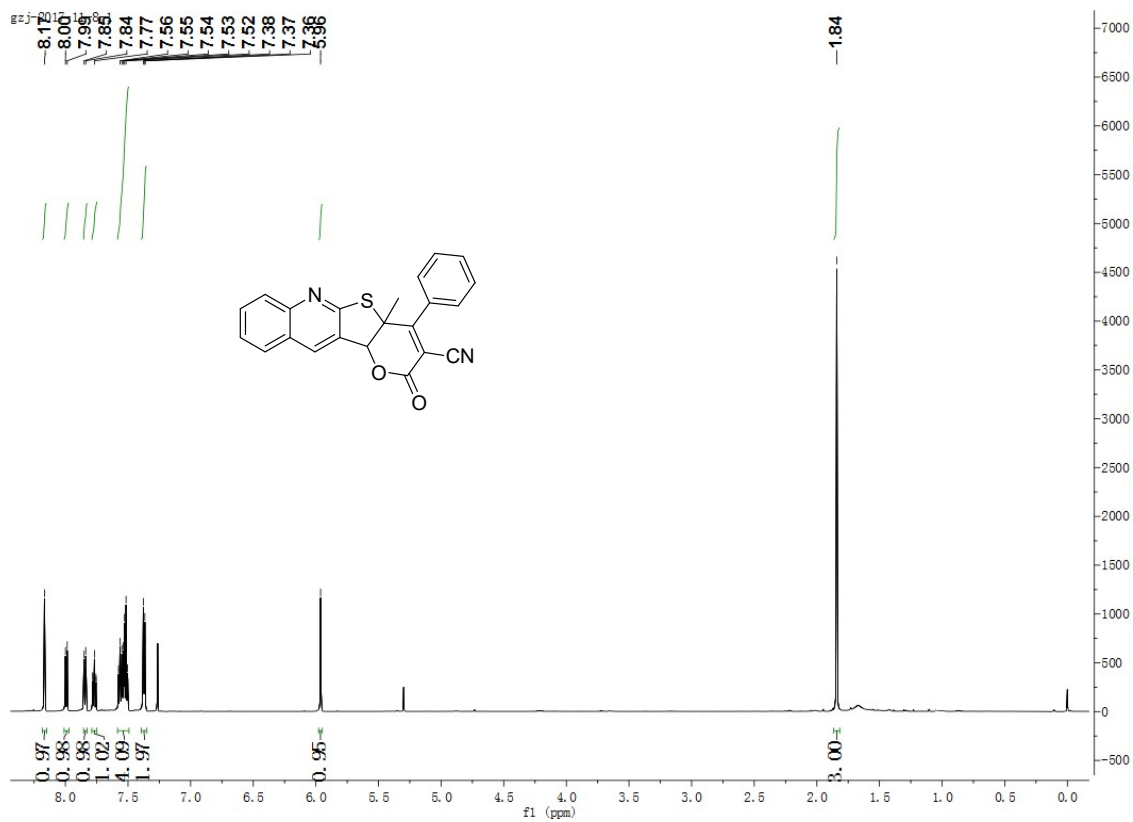
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R. China, *E-mail: xiejw@sust.edu.cn; xiejw@zjnu.cn

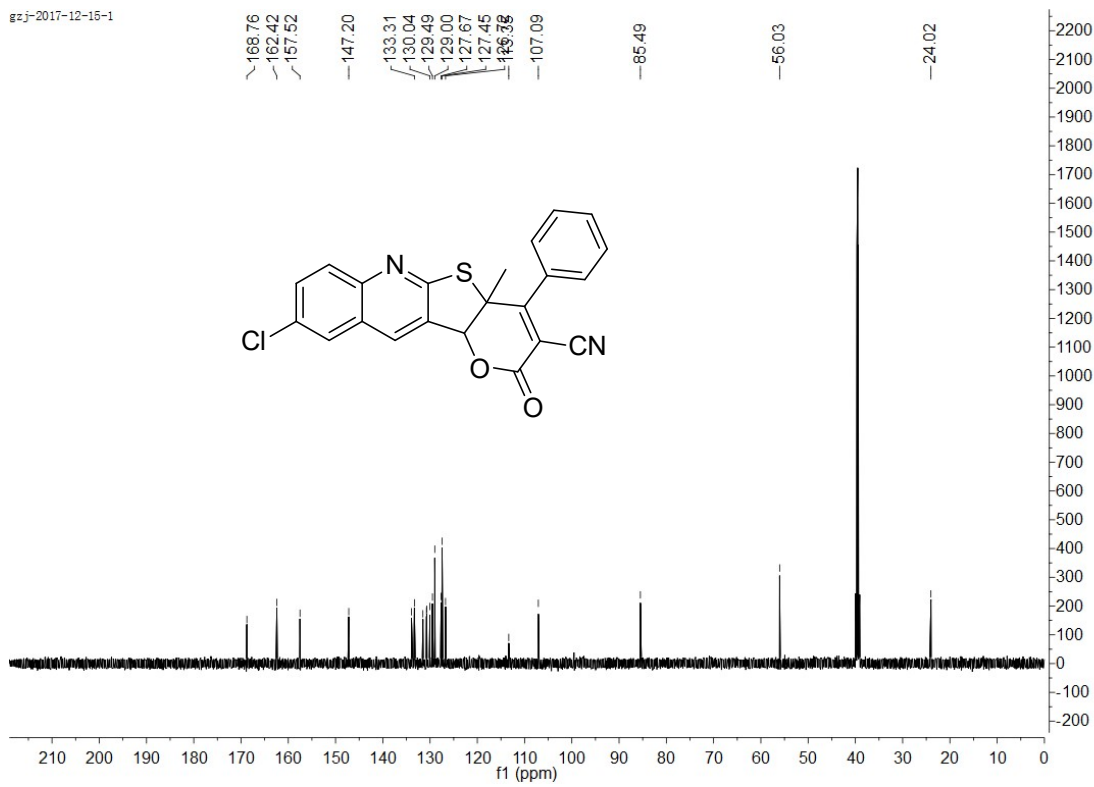
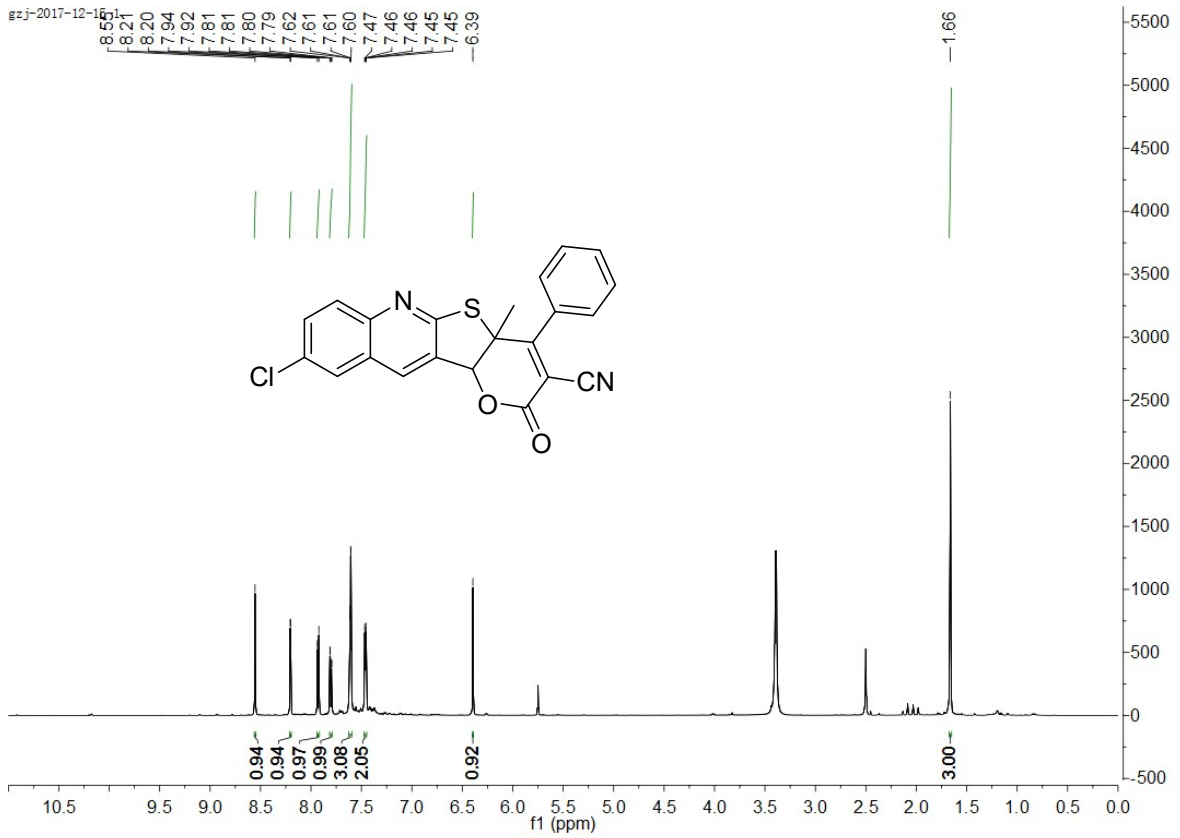
1. ¹H NMR and ¹³C NMR spectra	S2
2. X-ray data of compounds 3fa, 3ia, 3ka, 5ca, 5'ce.....	S56

1. ^1H , ^{13}C NMR

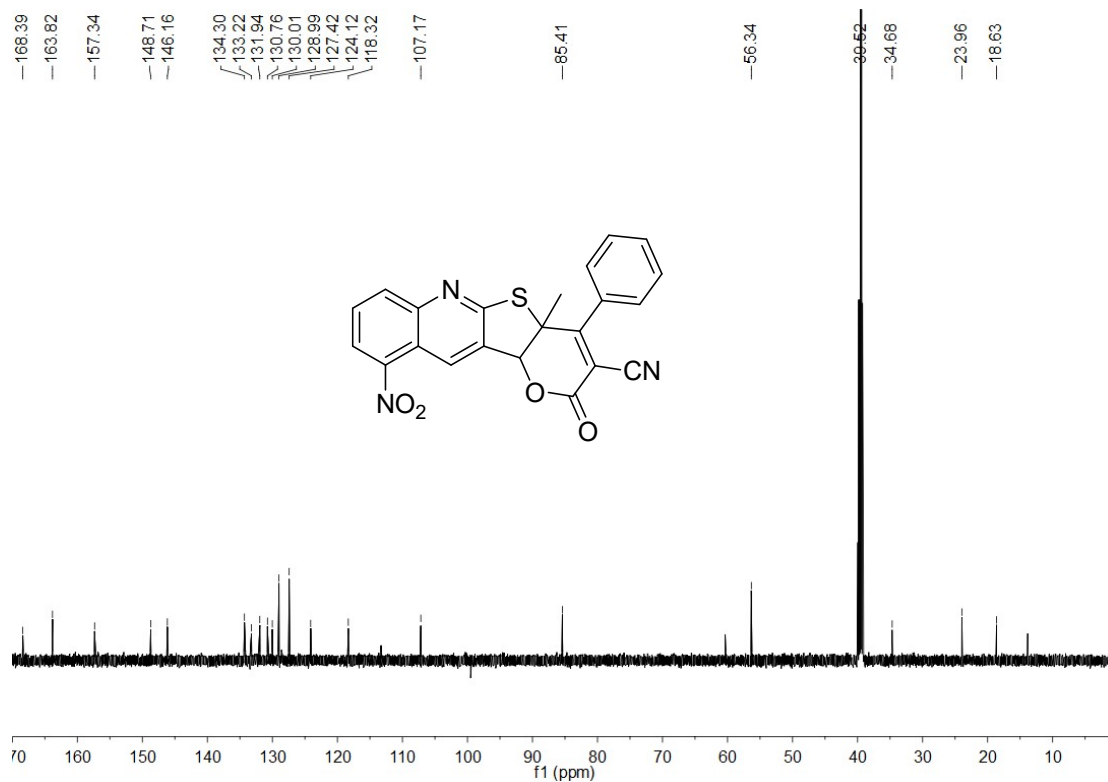
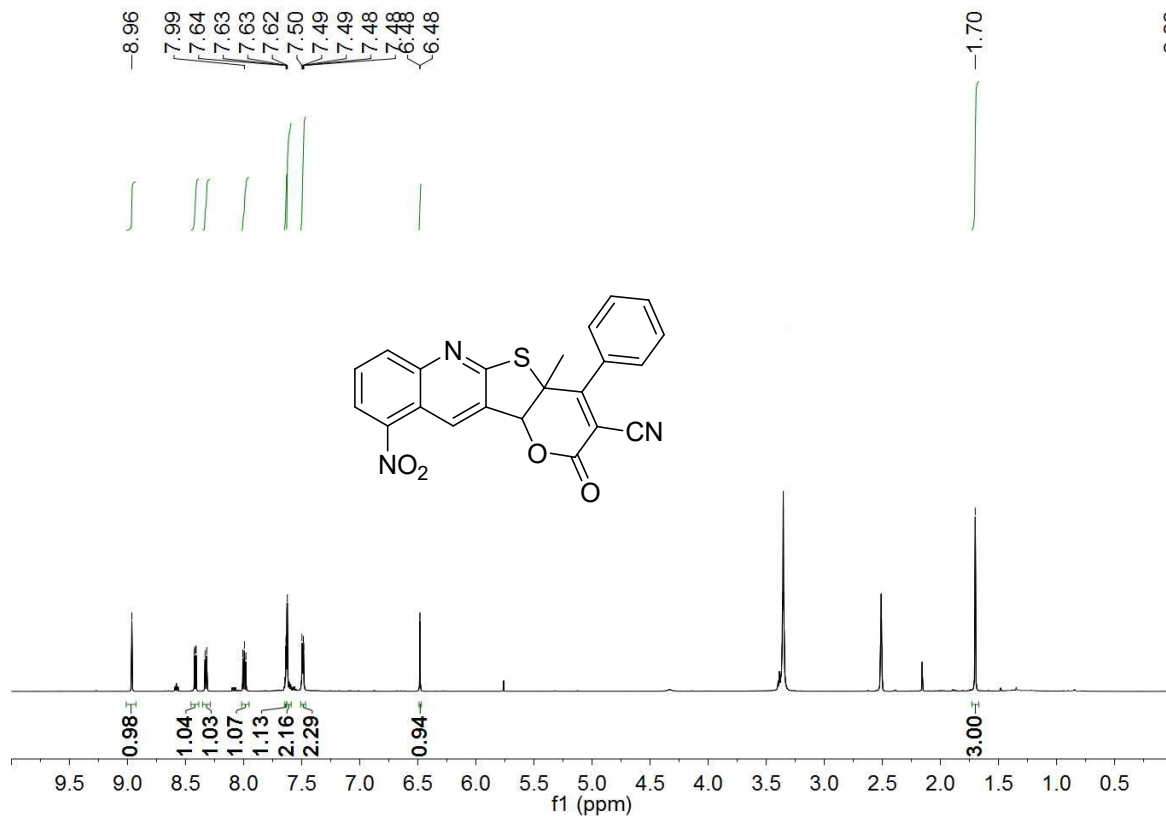
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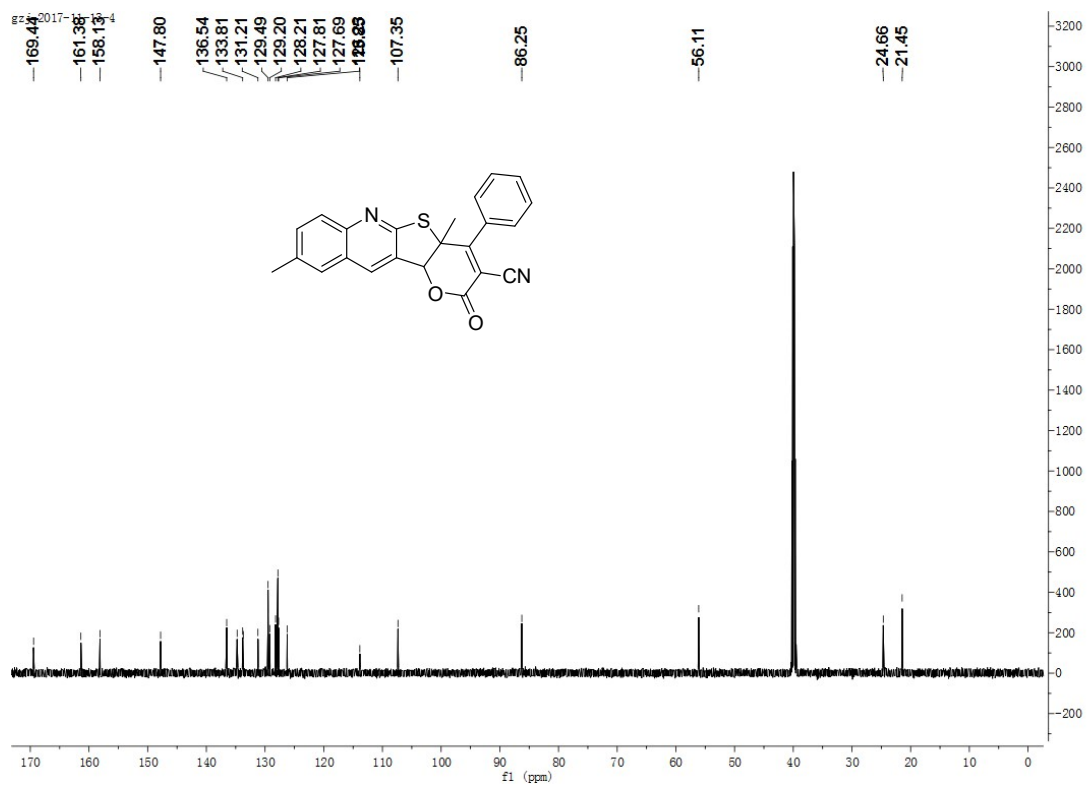
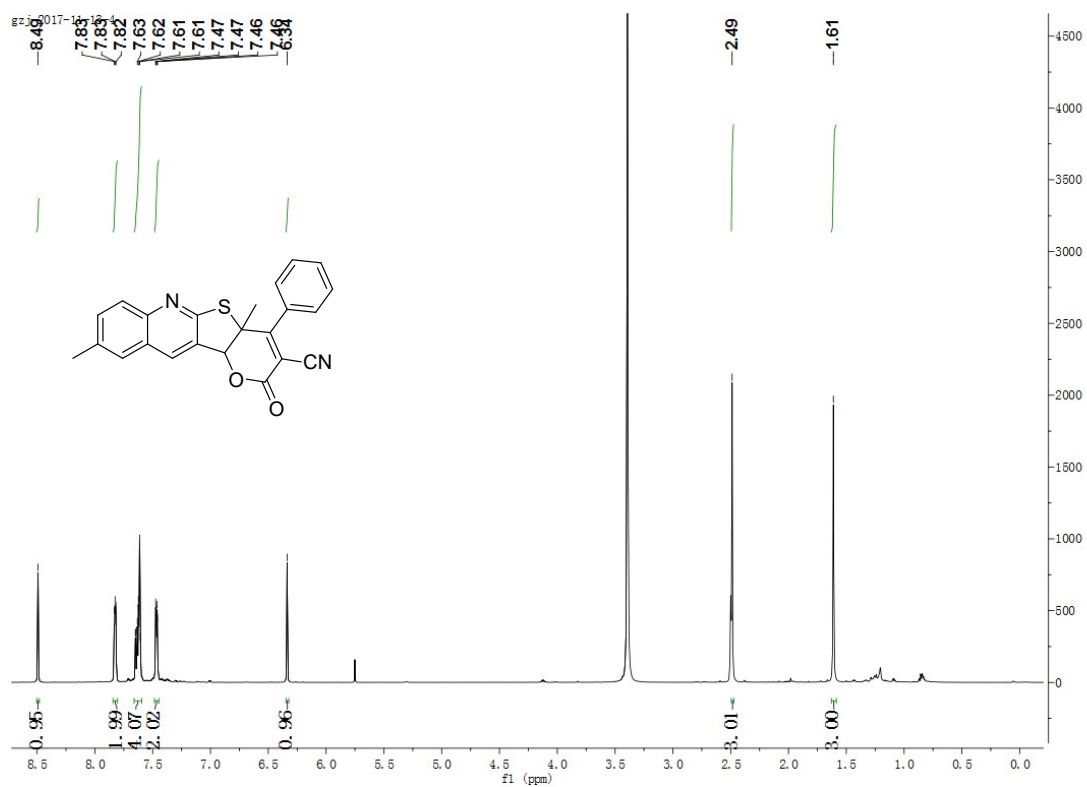
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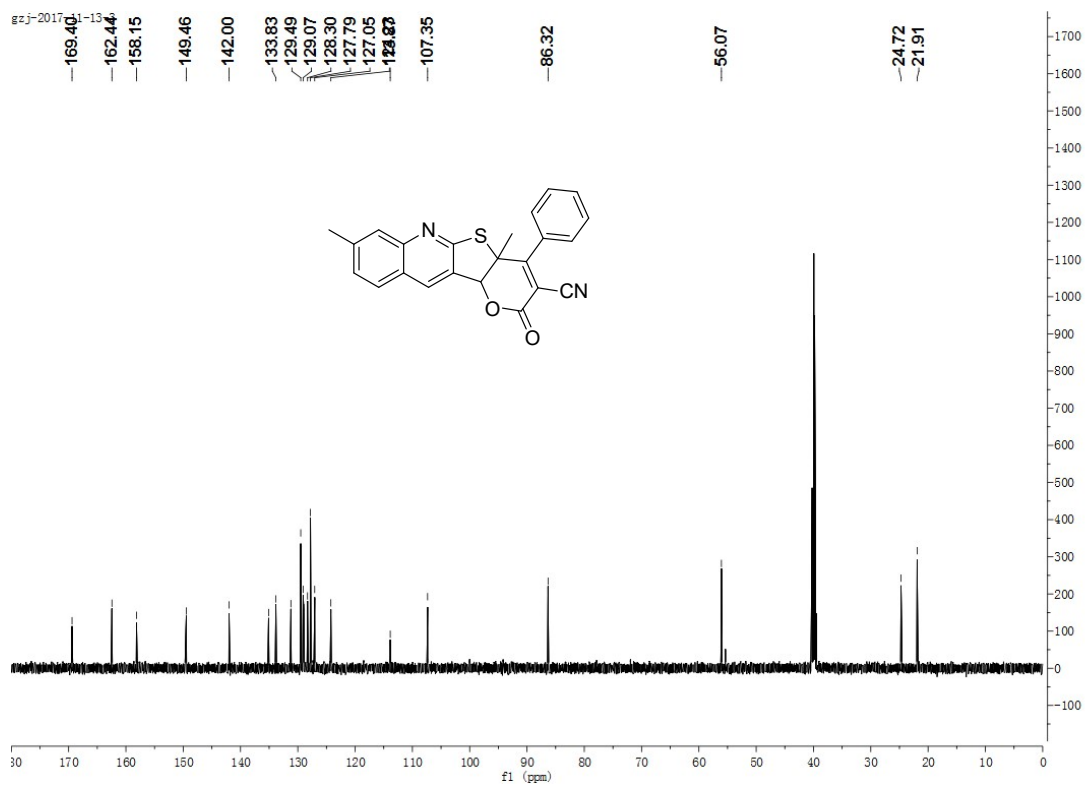
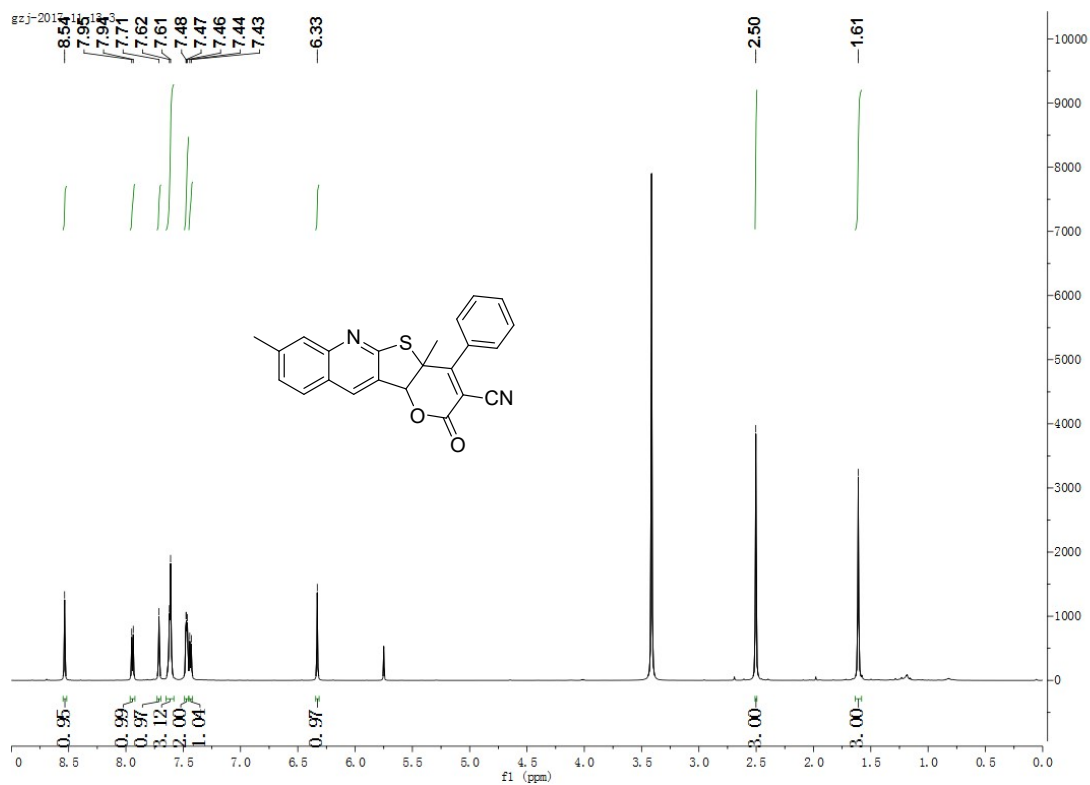
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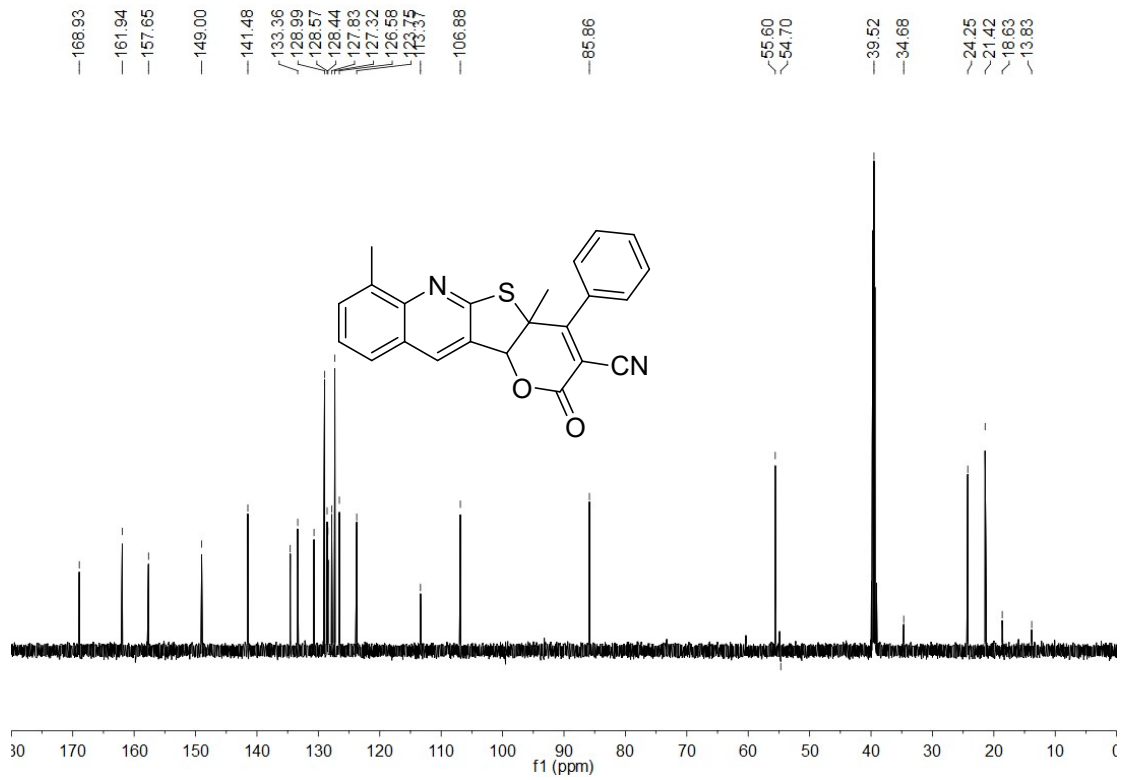
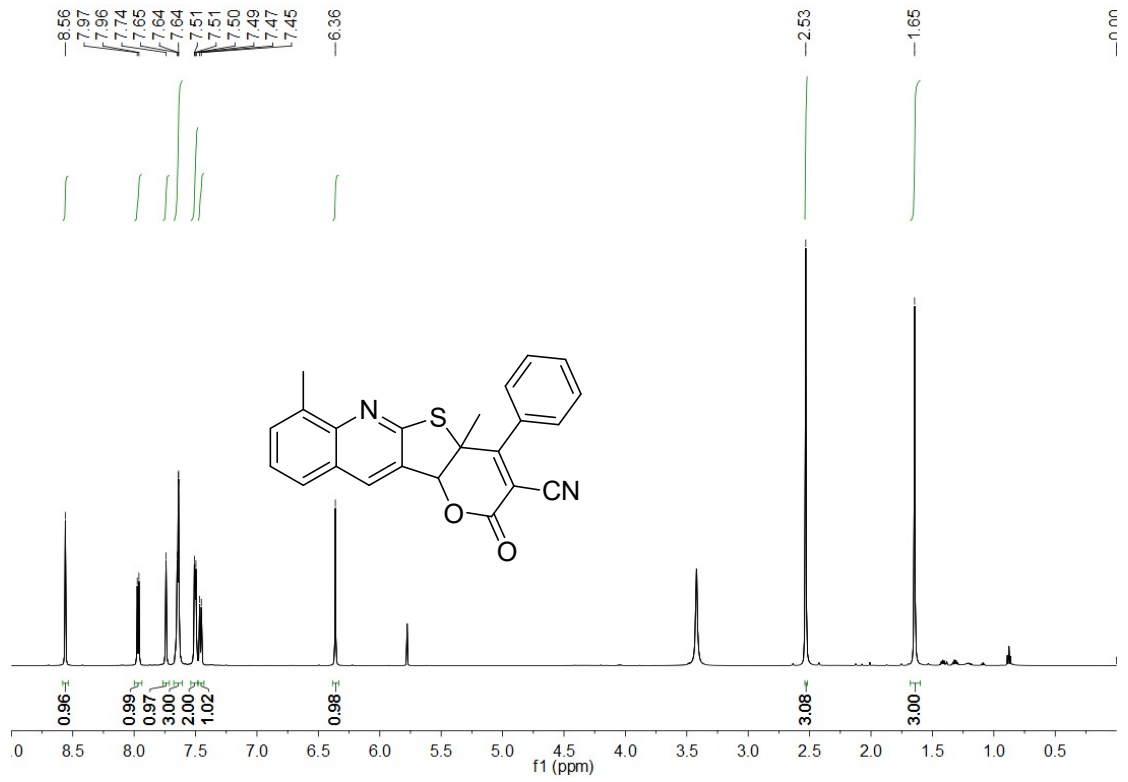
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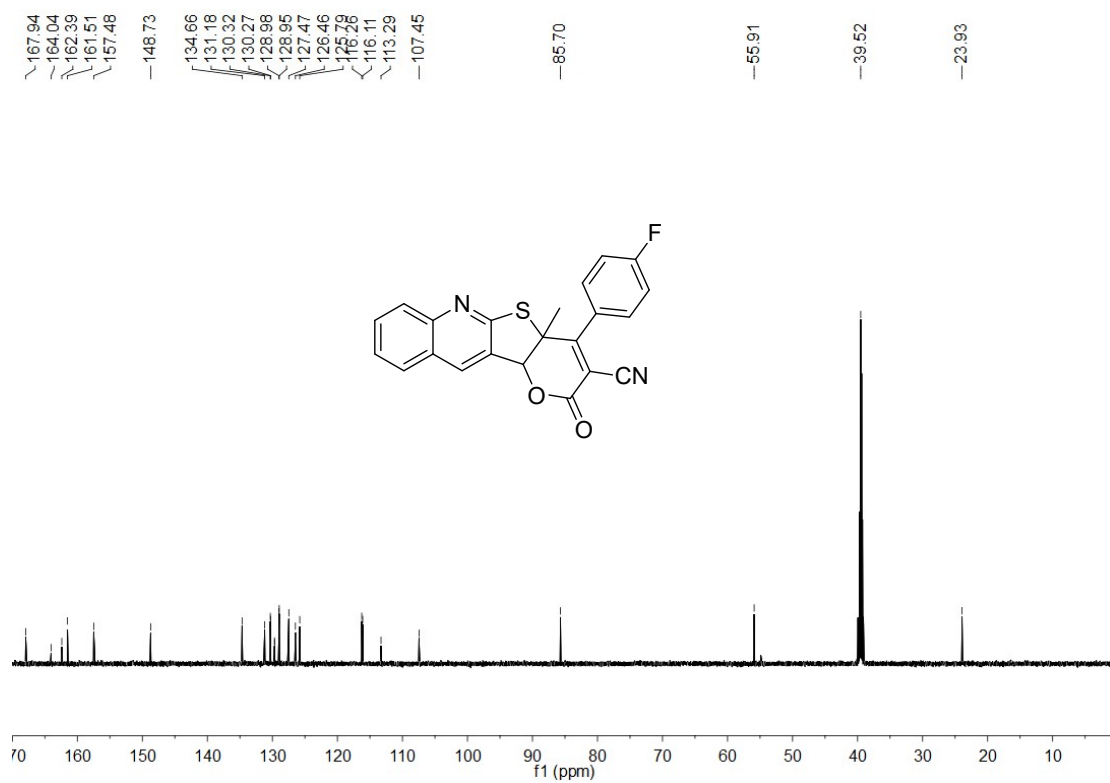
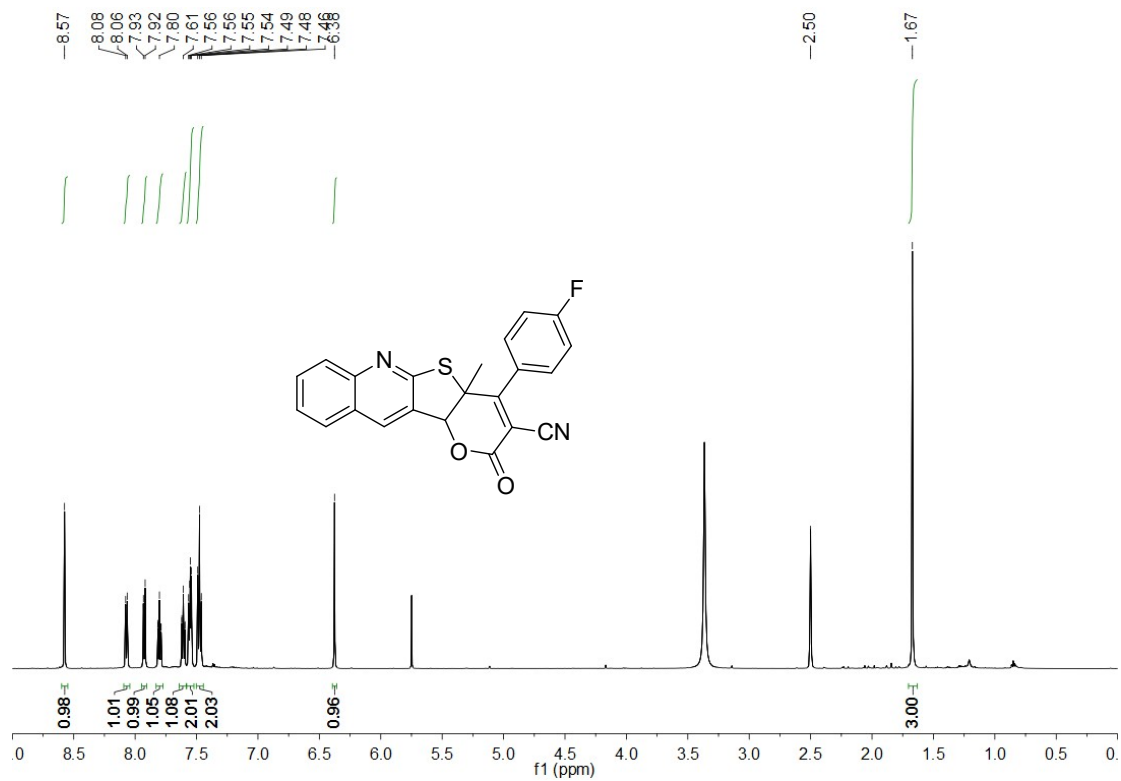
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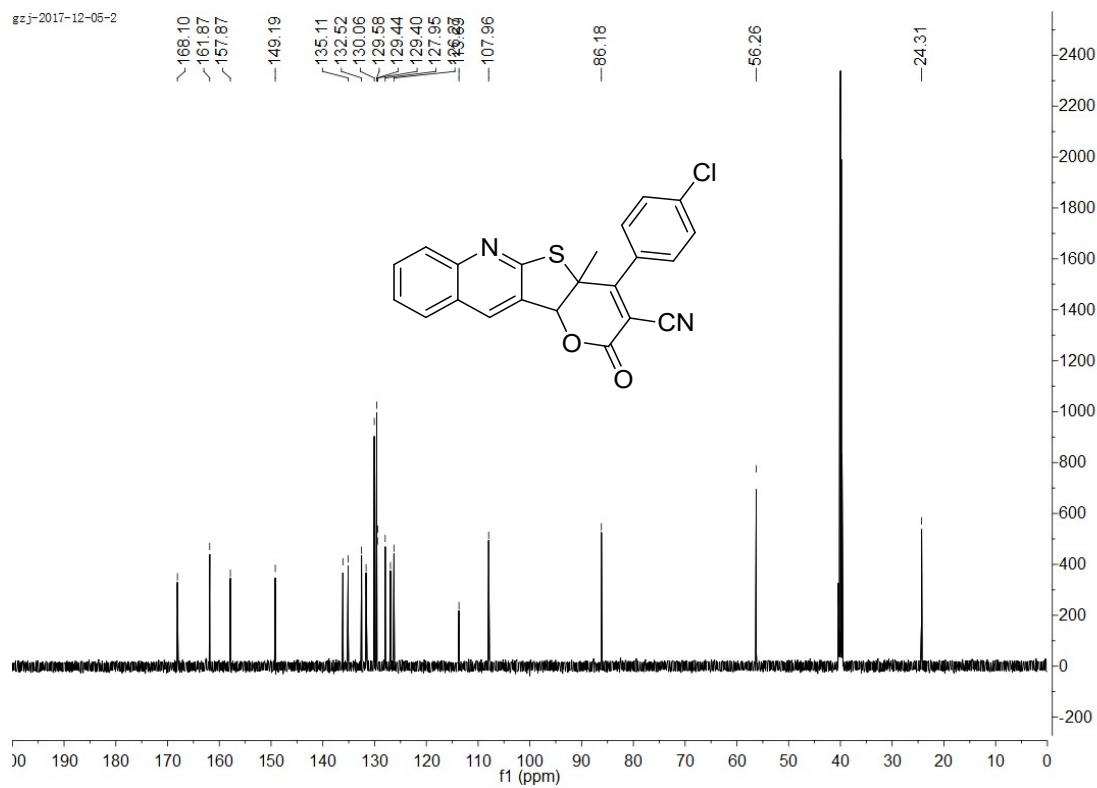
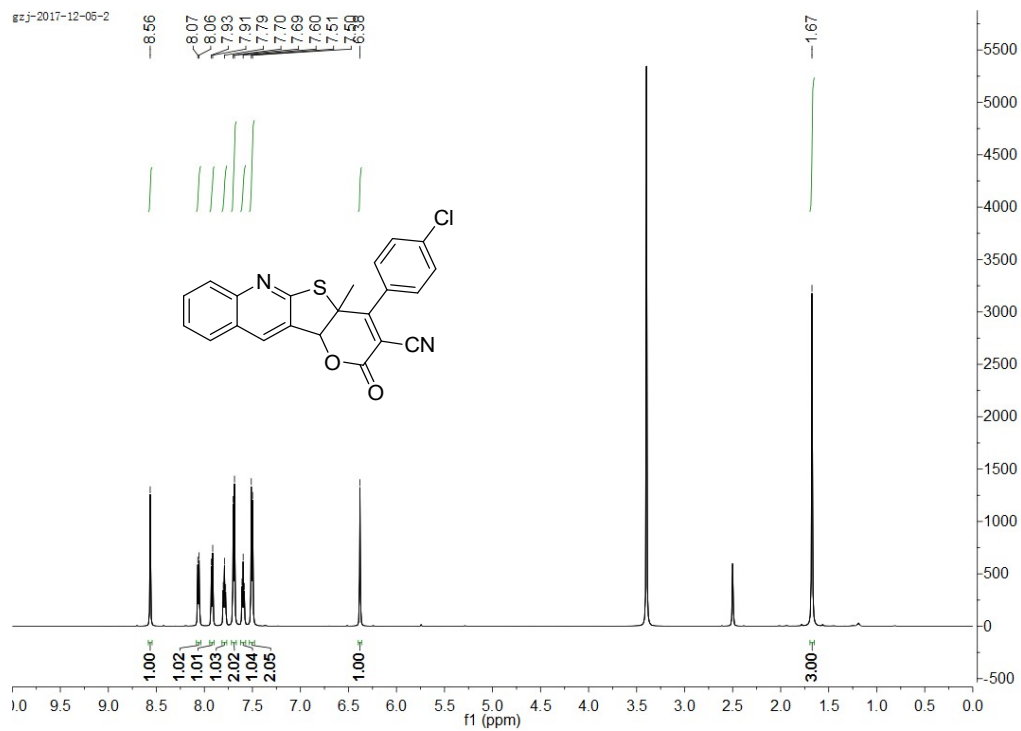
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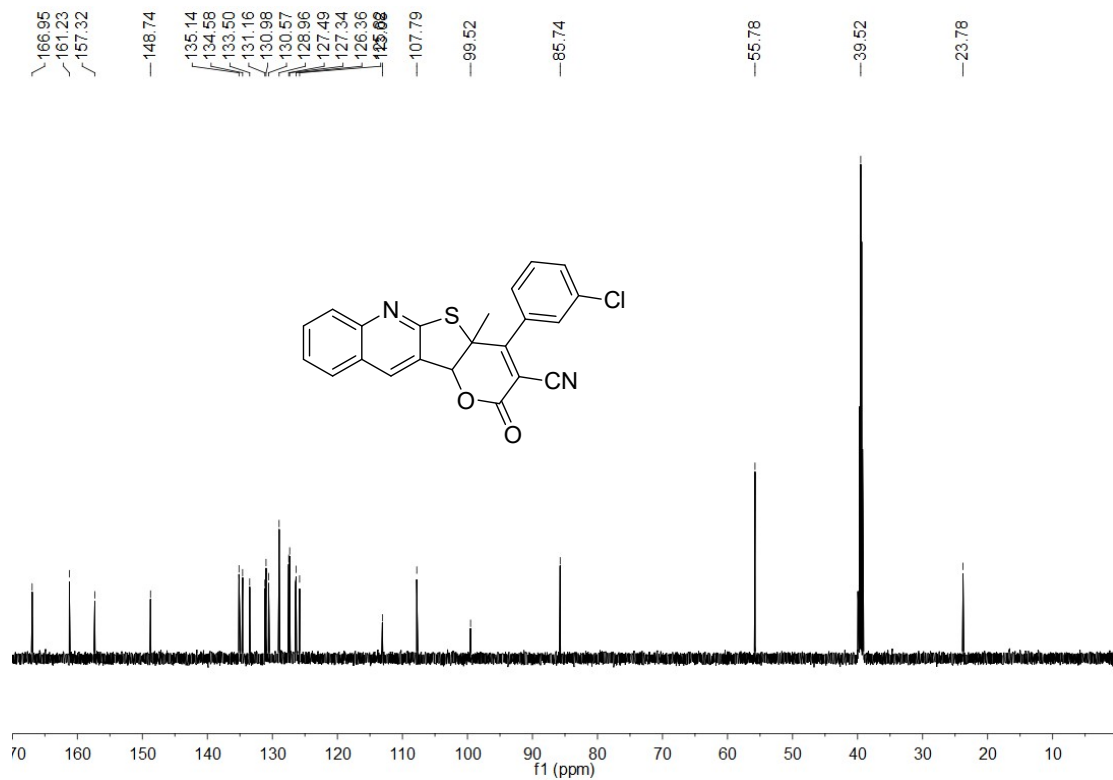
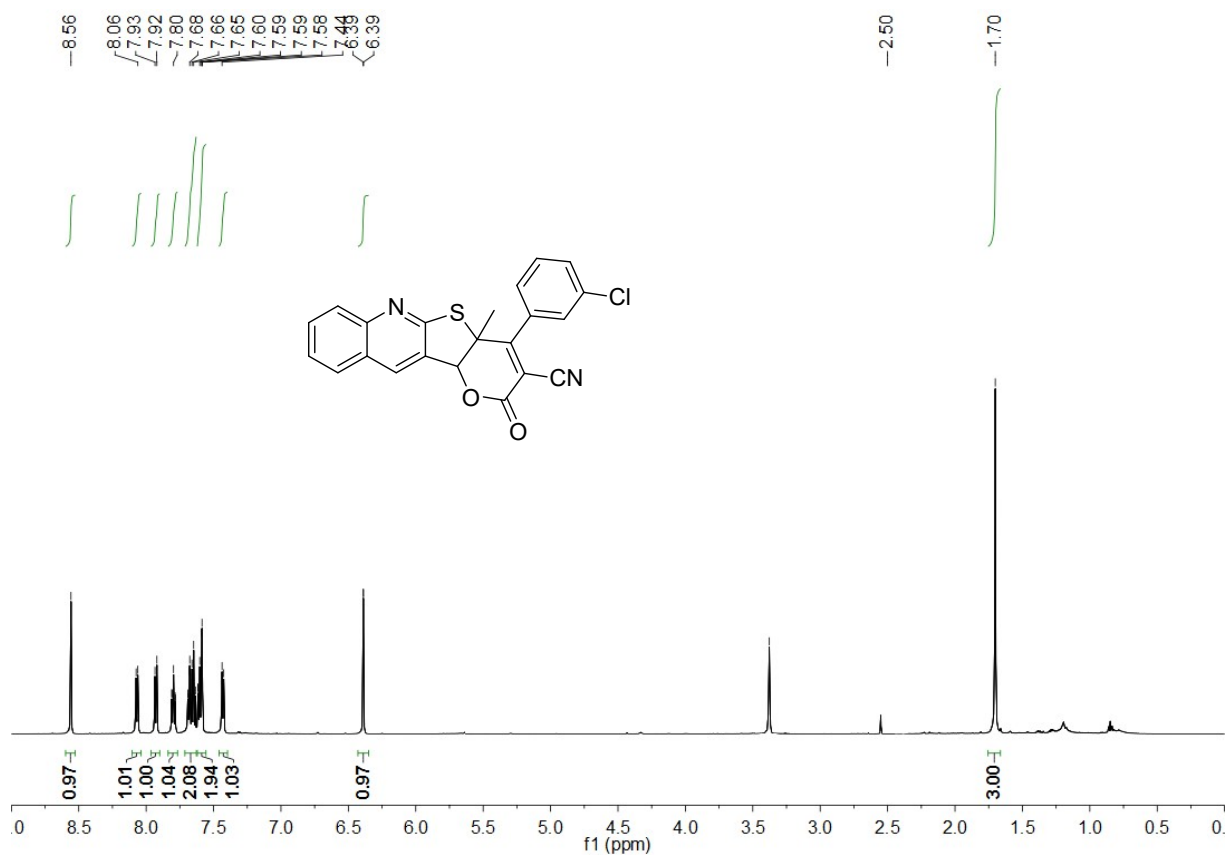
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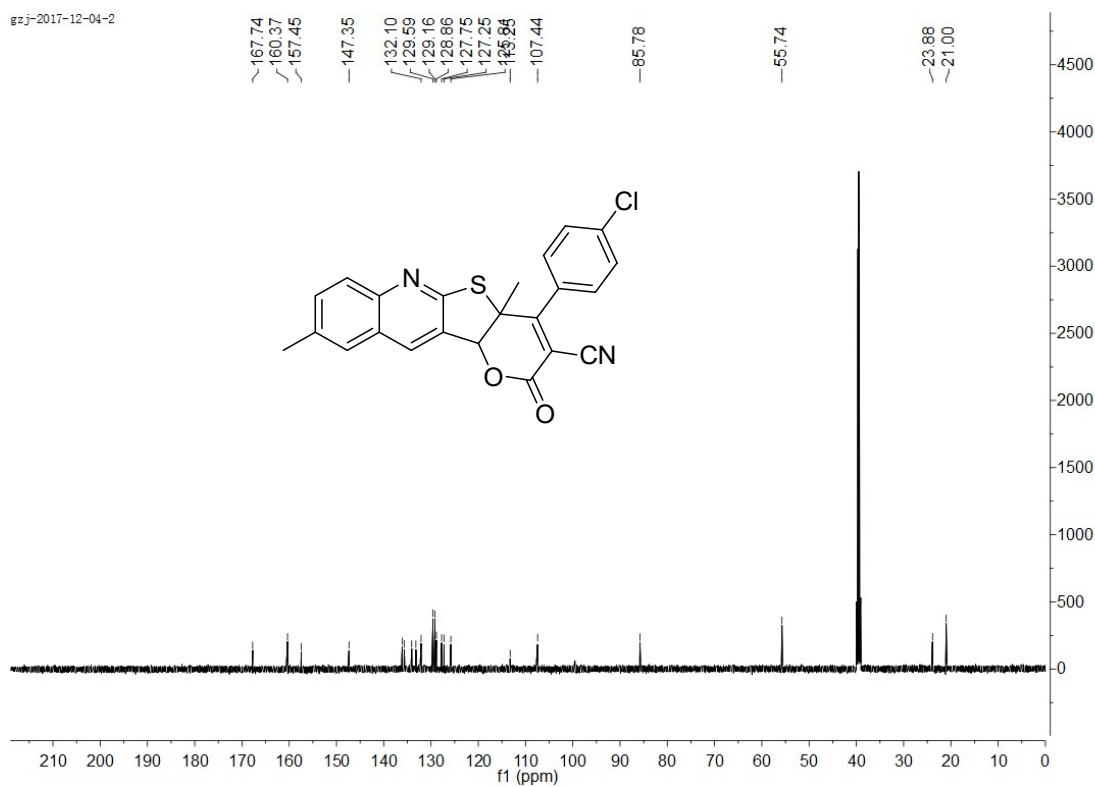
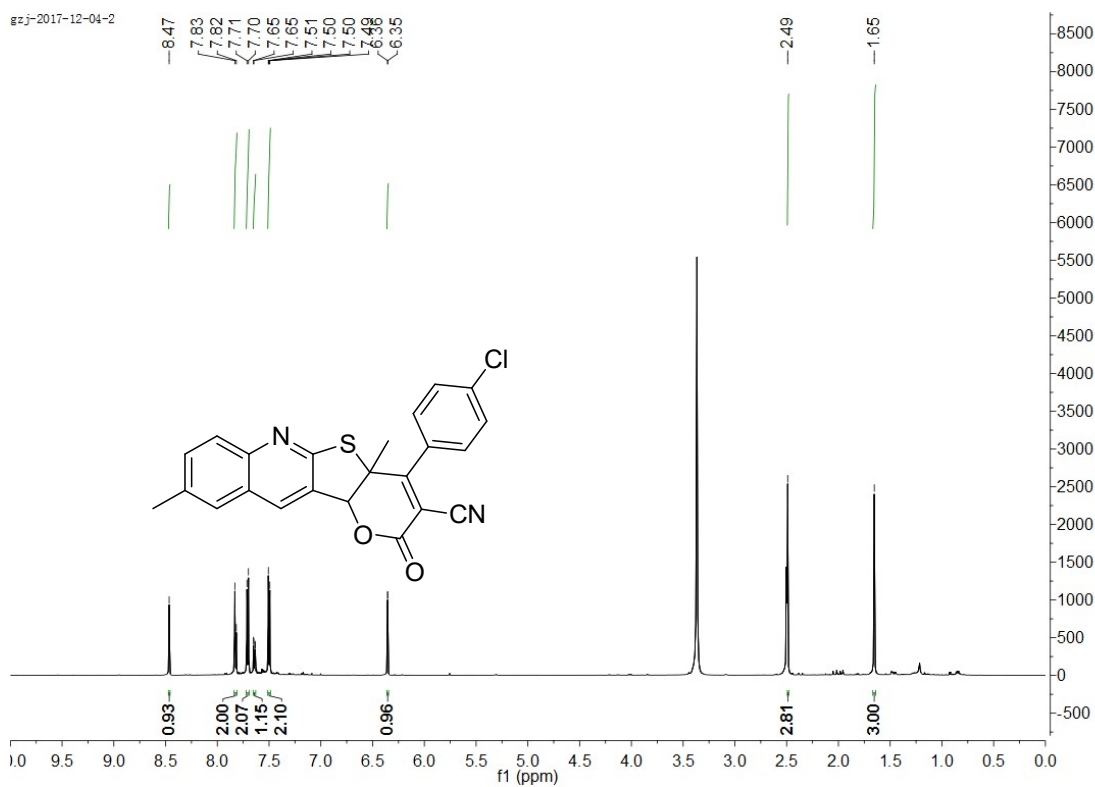
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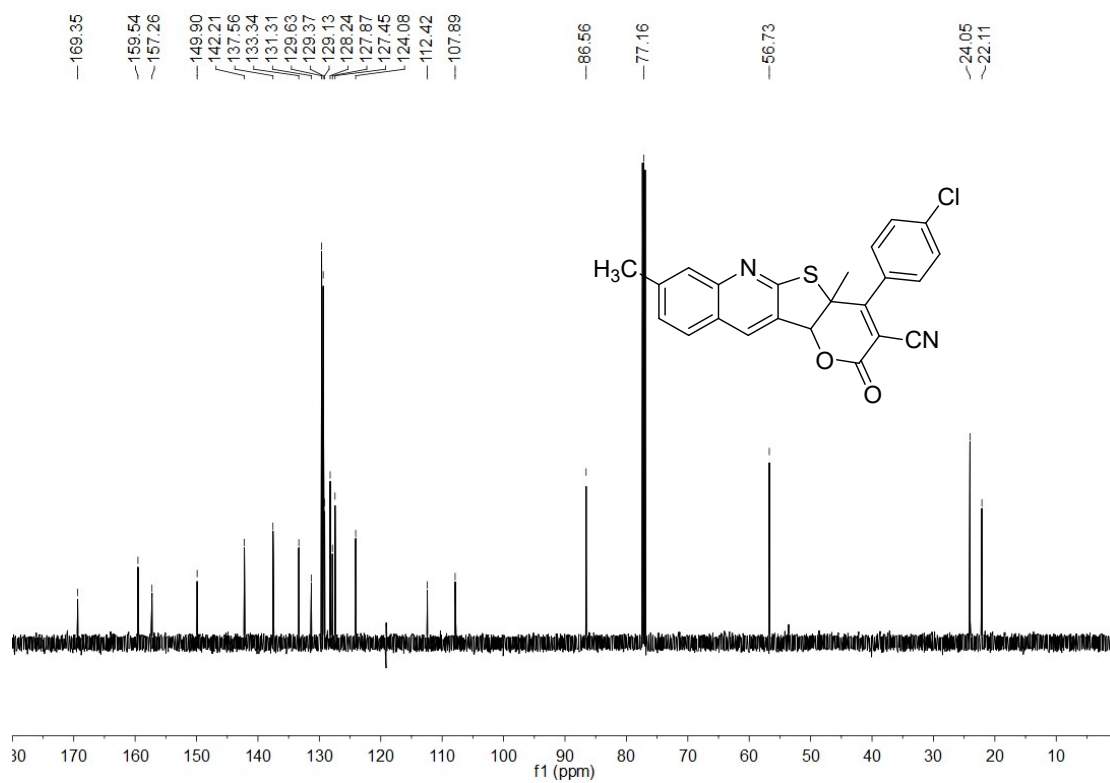
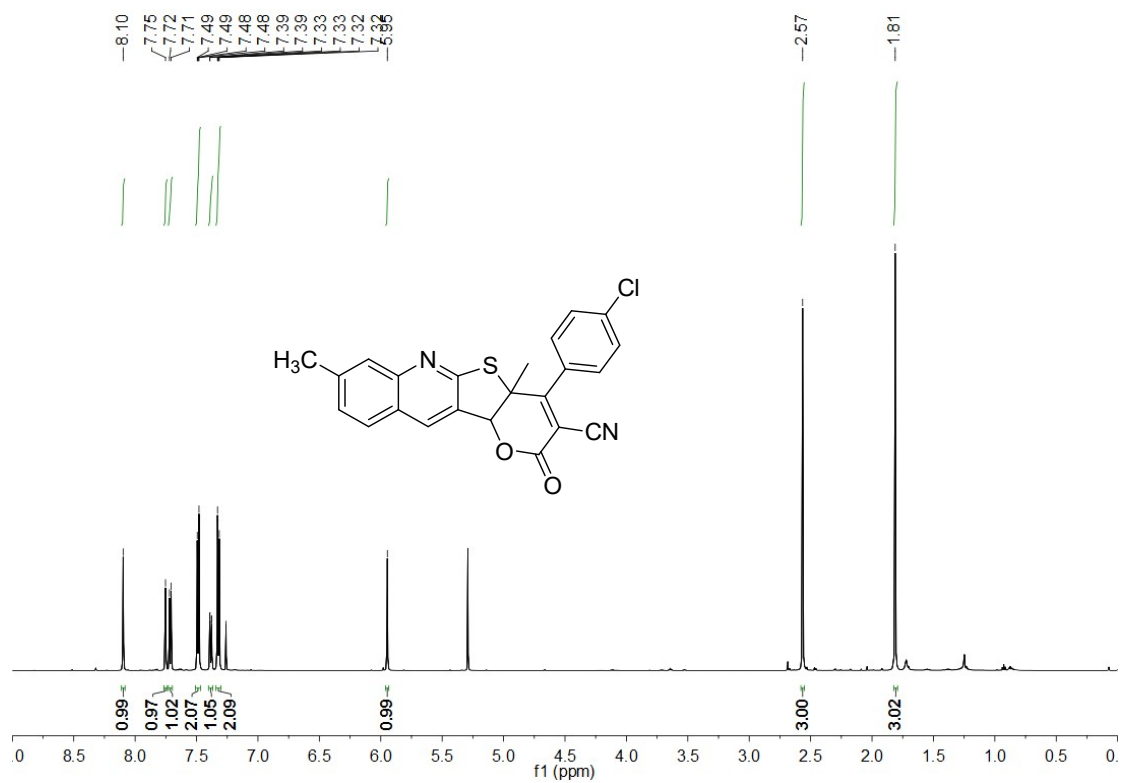
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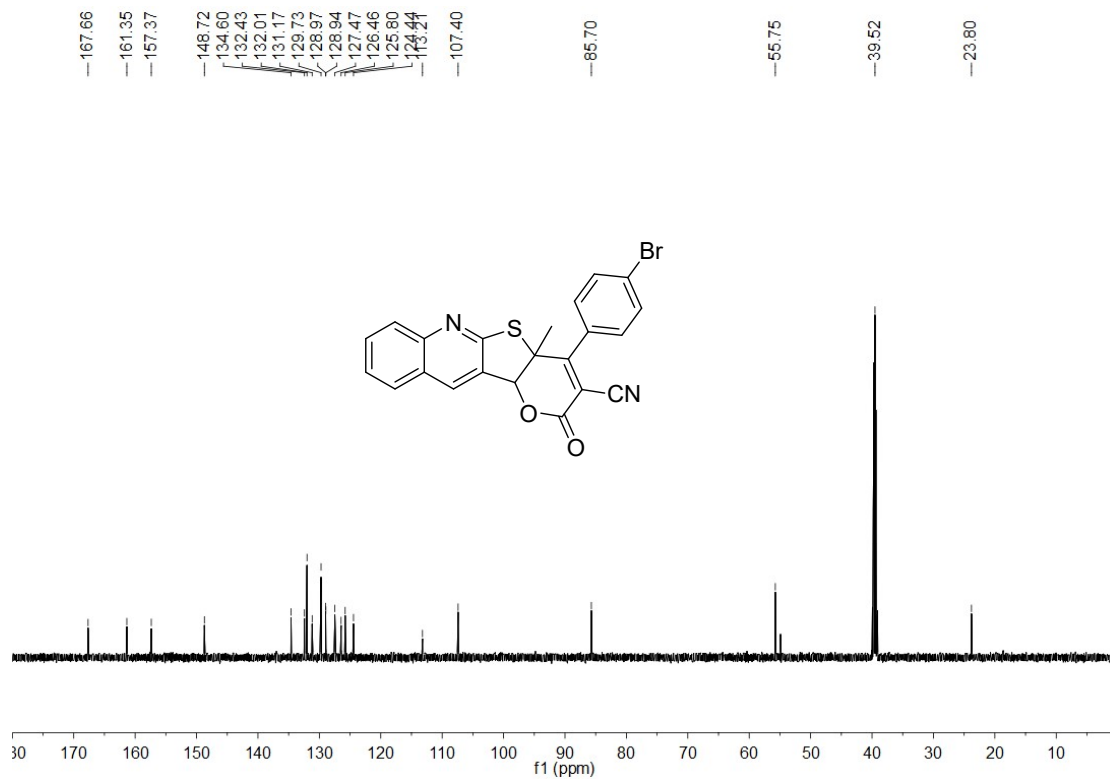
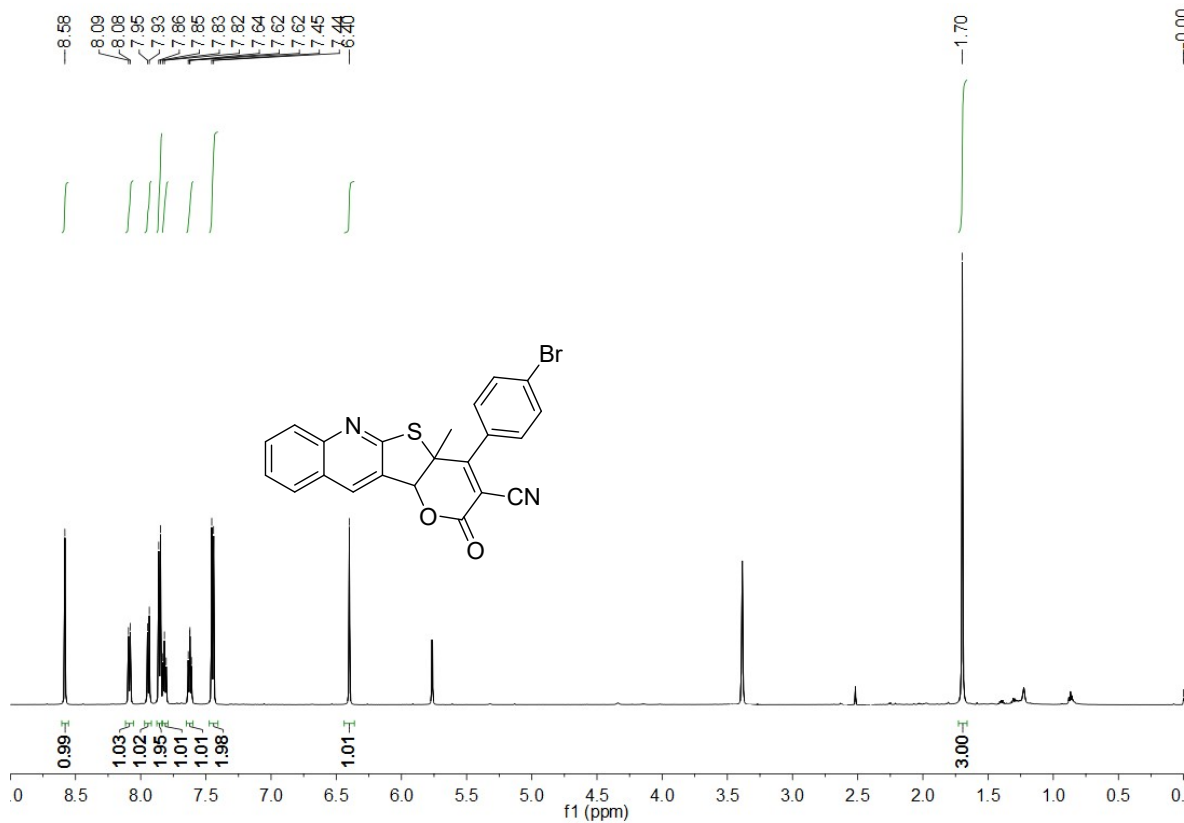
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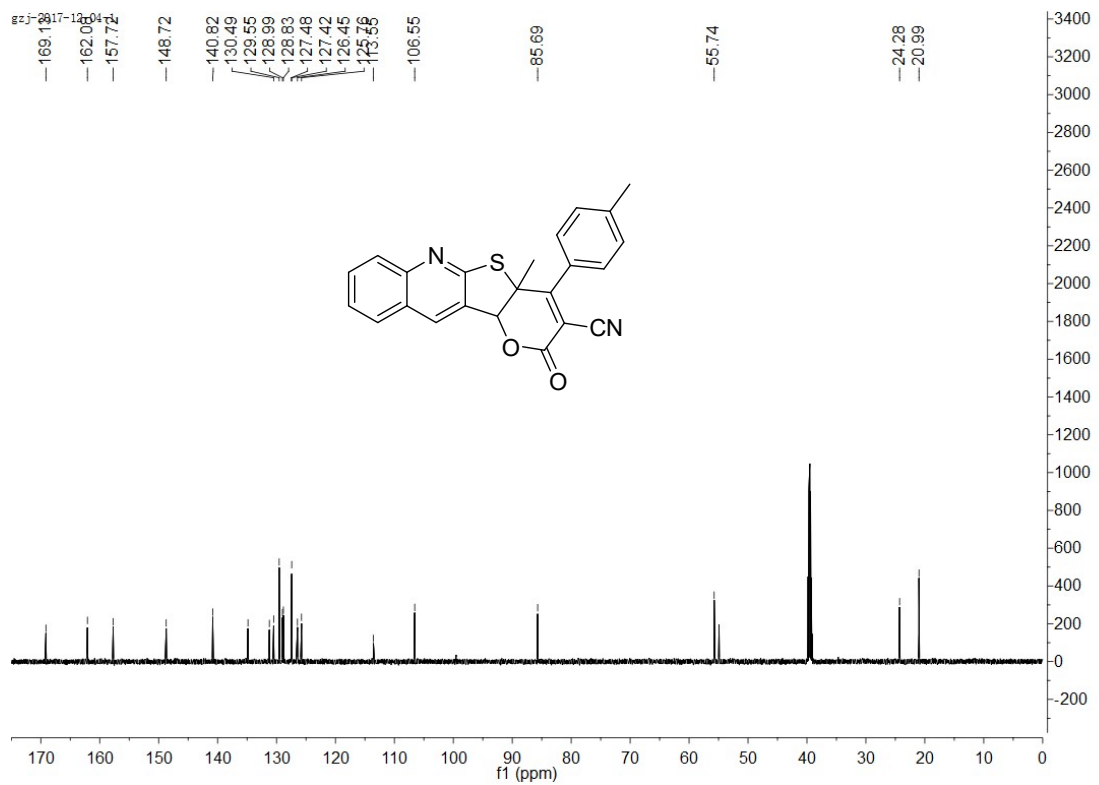
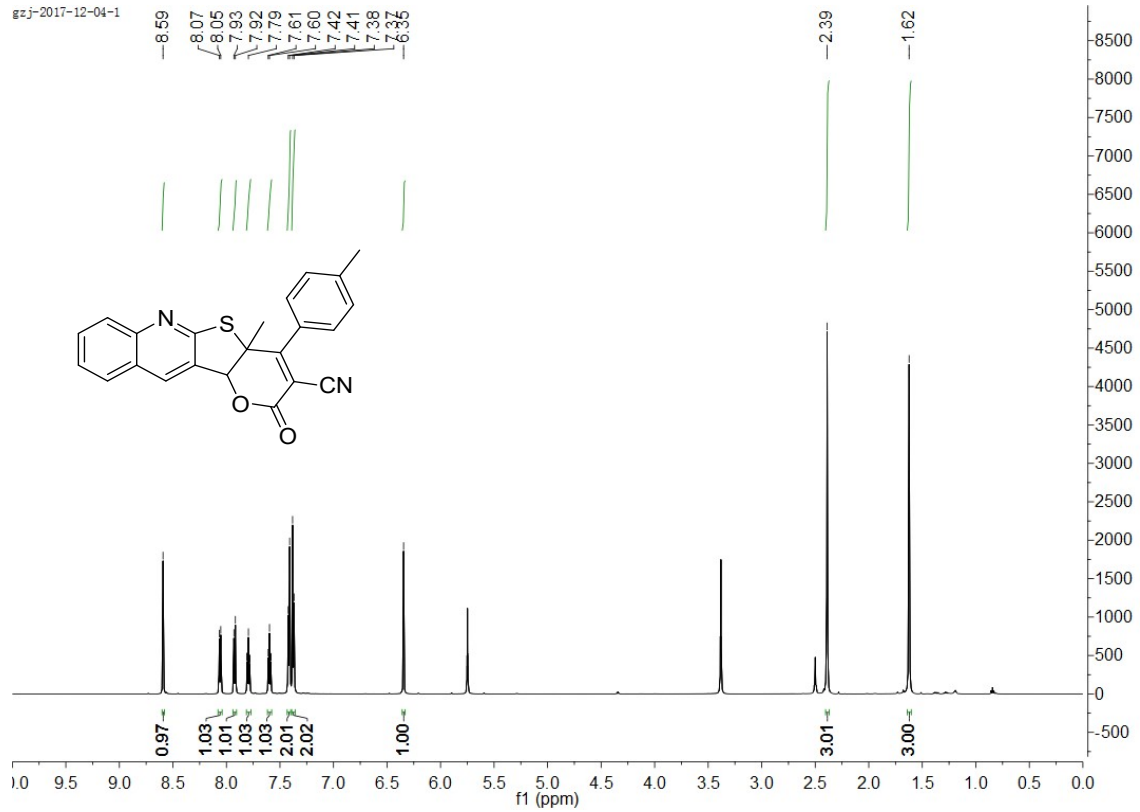
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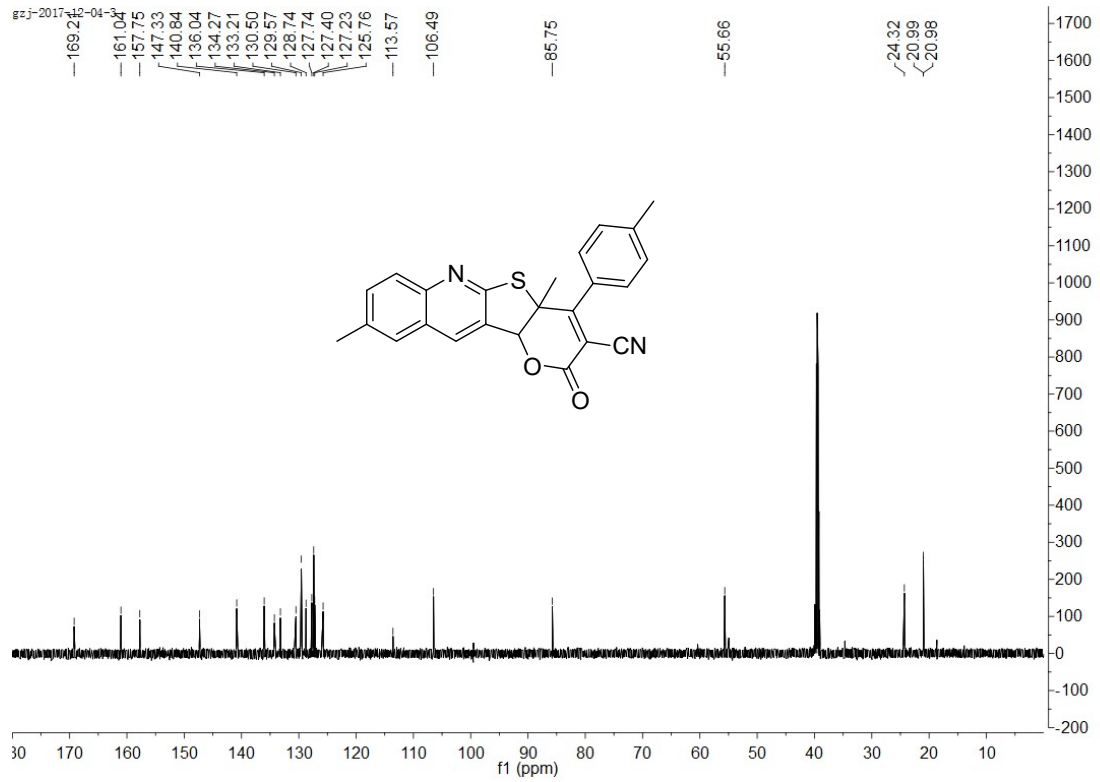
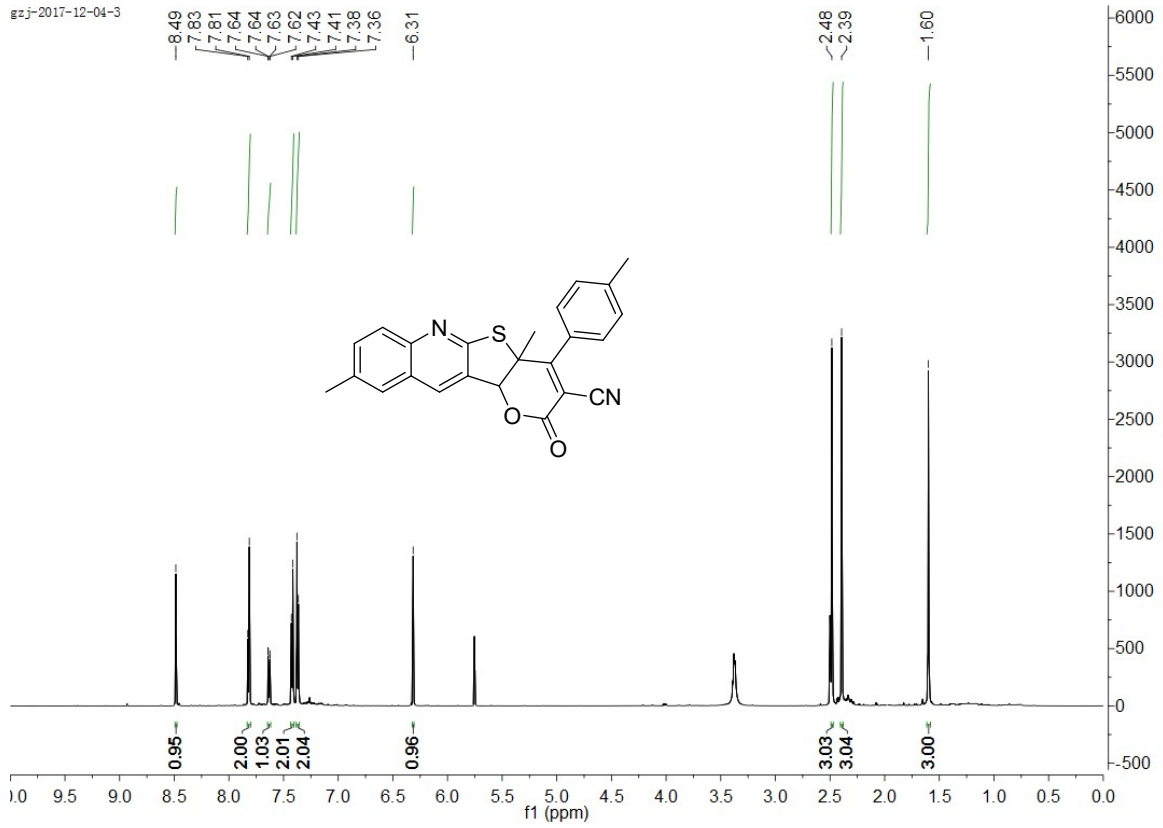
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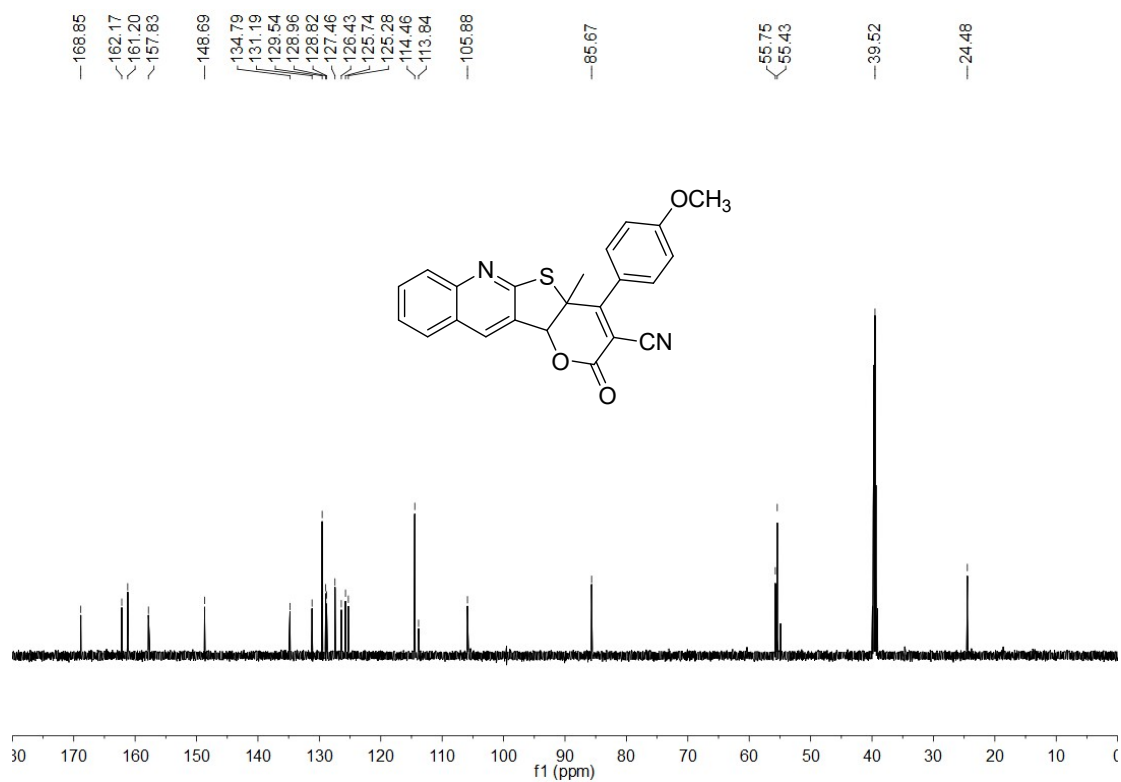
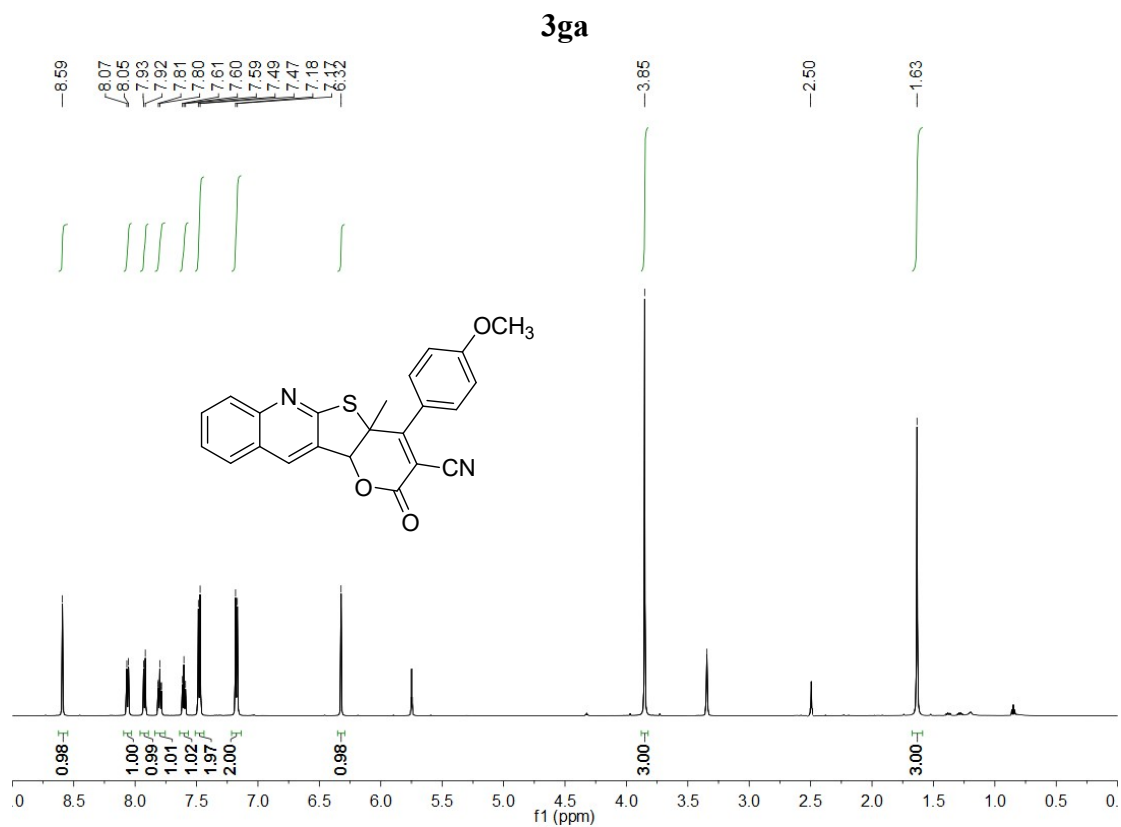


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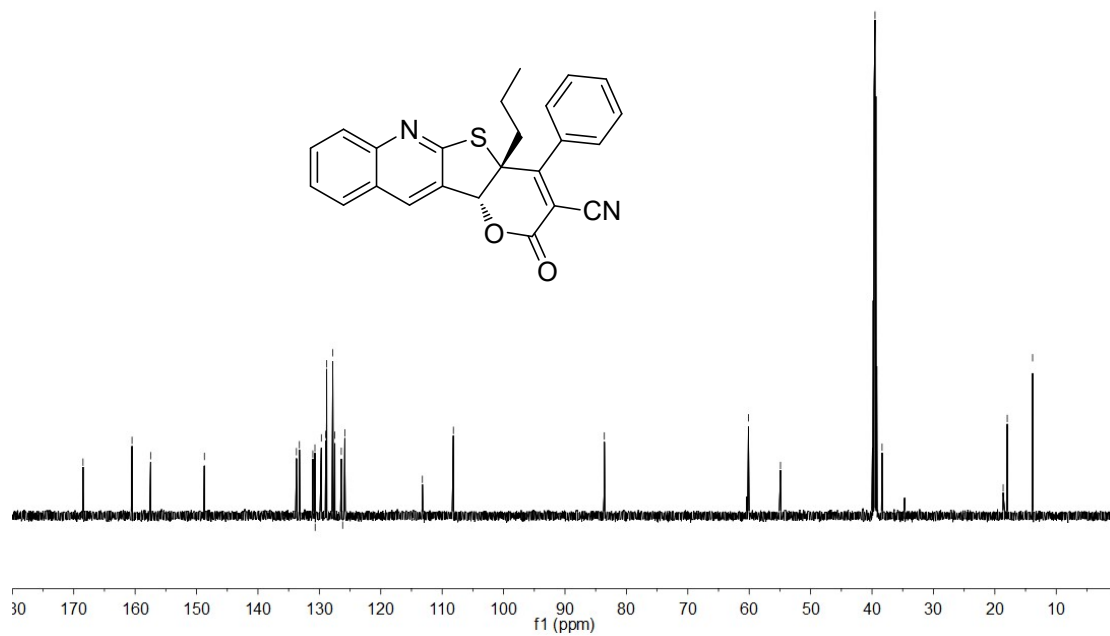
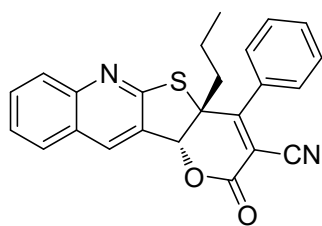
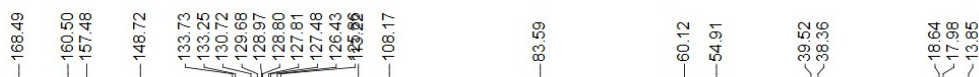
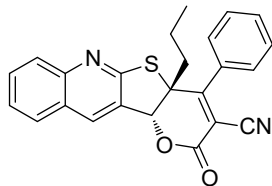
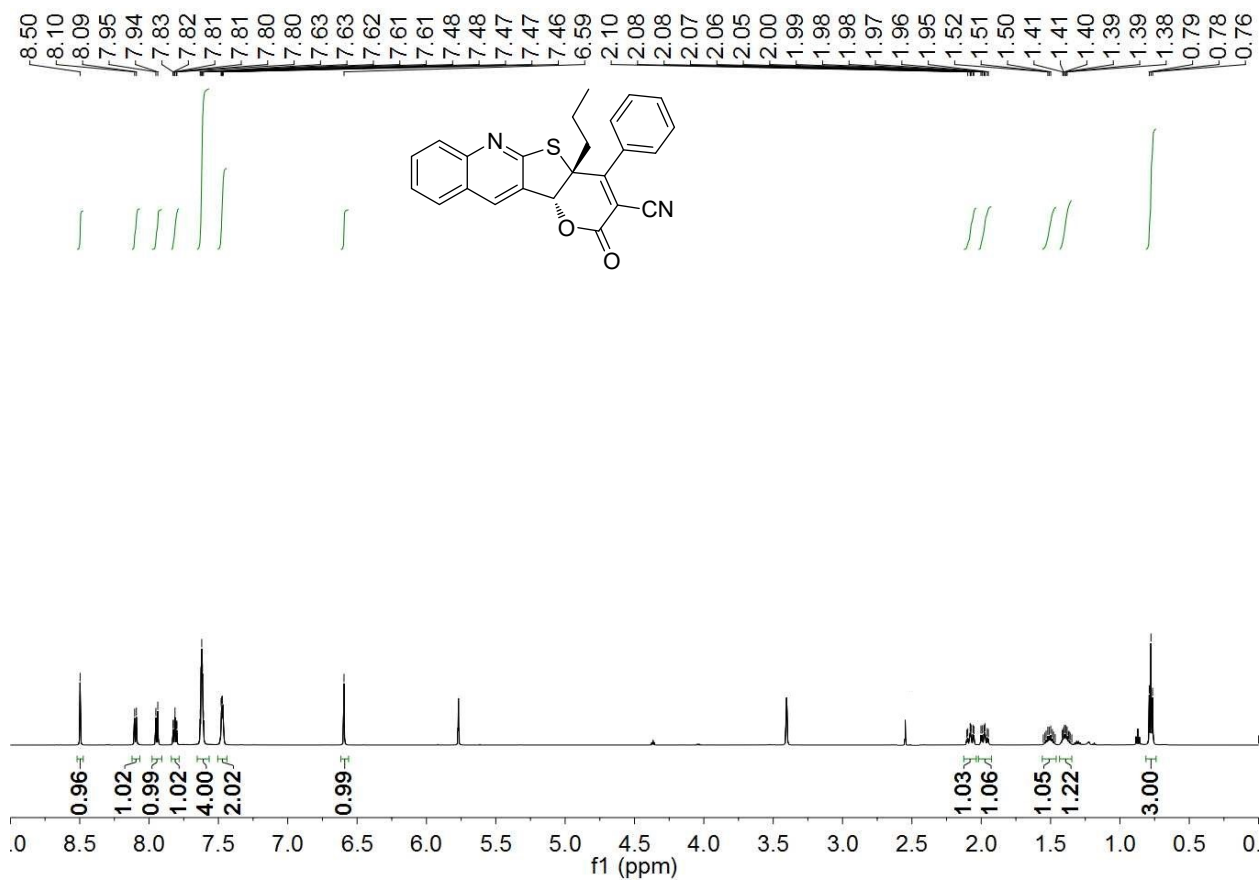


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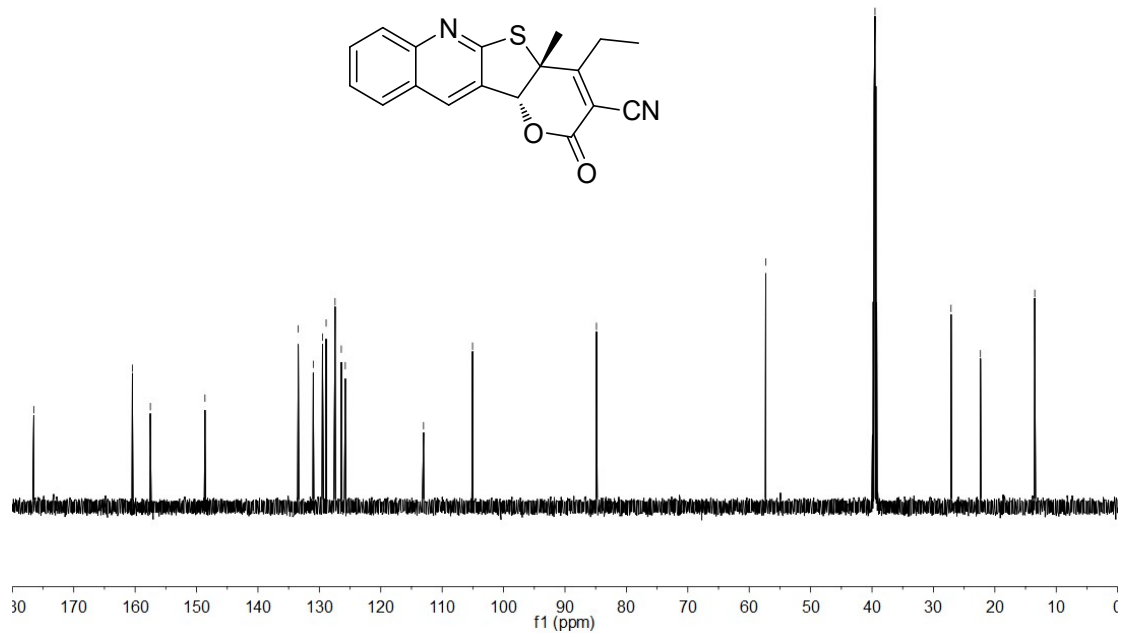
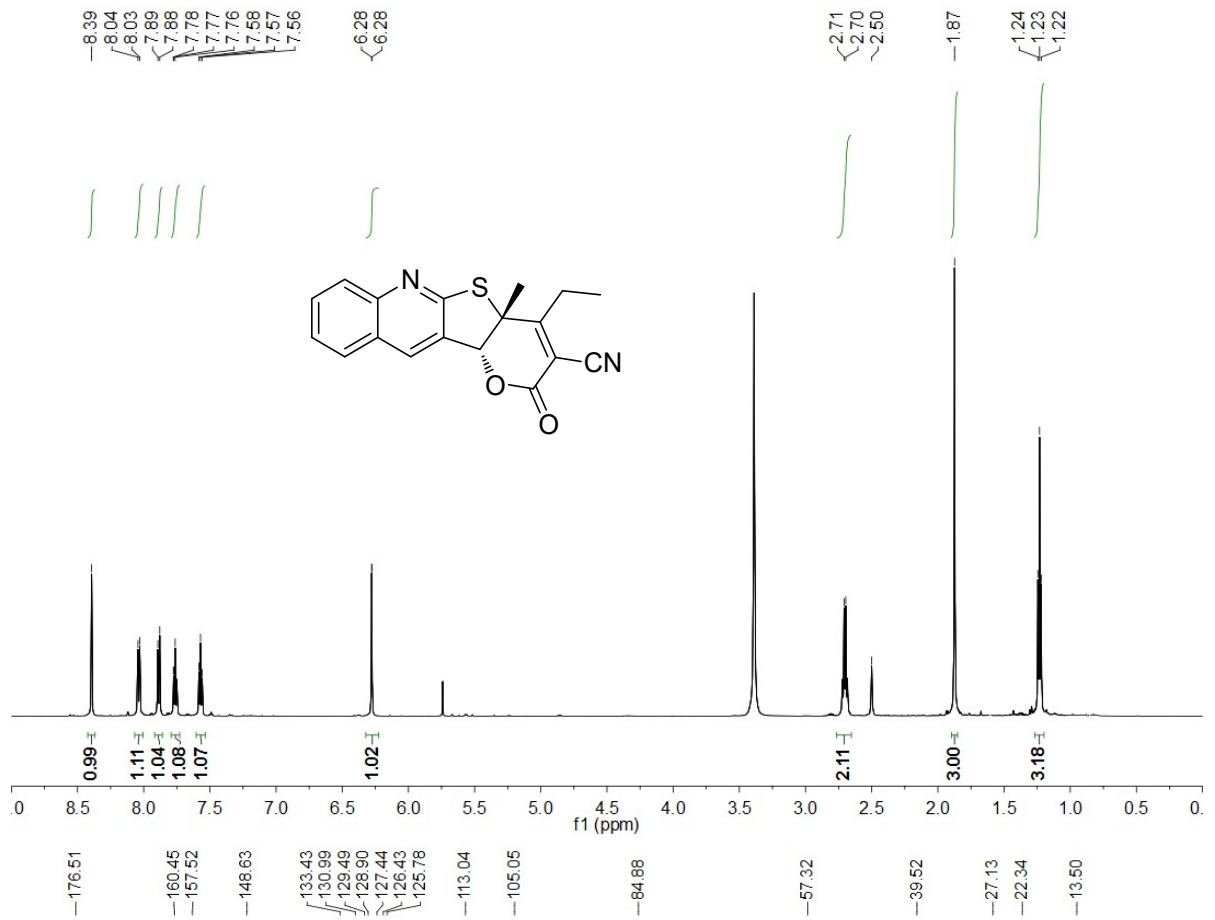




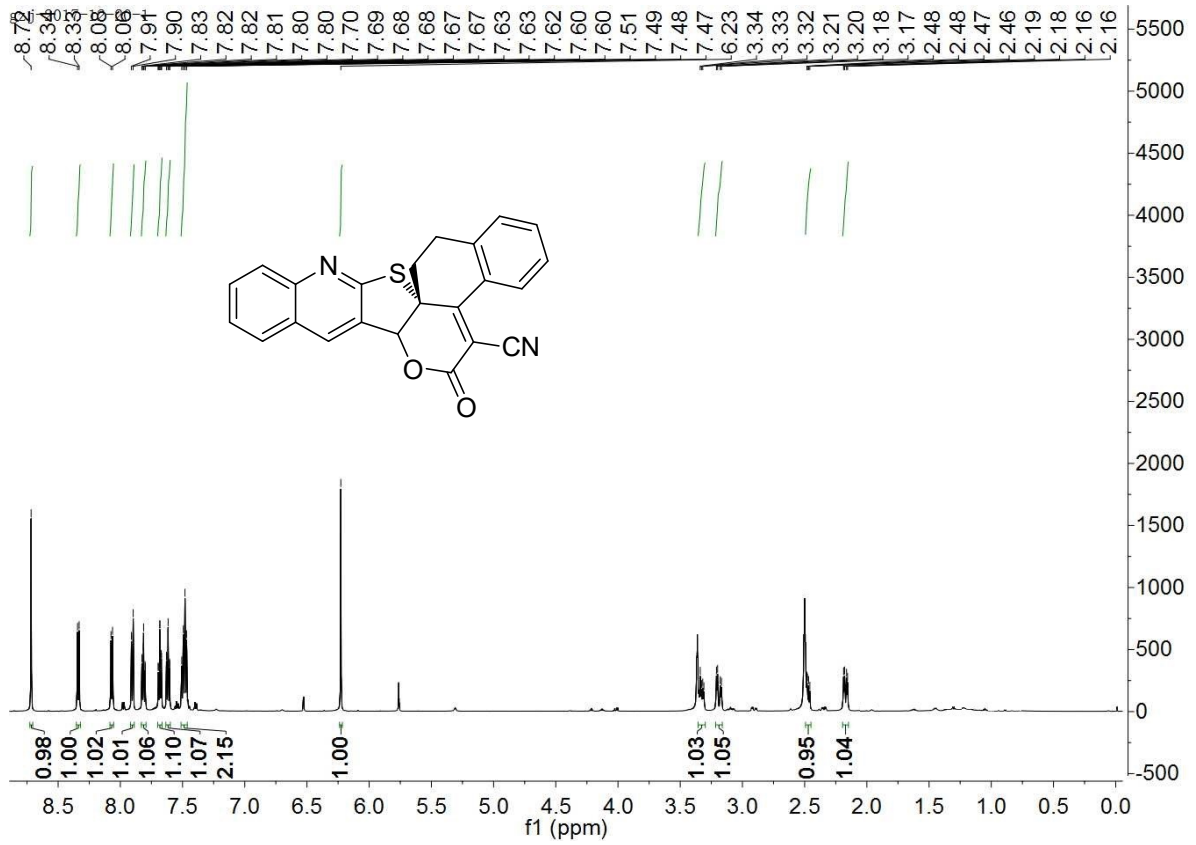
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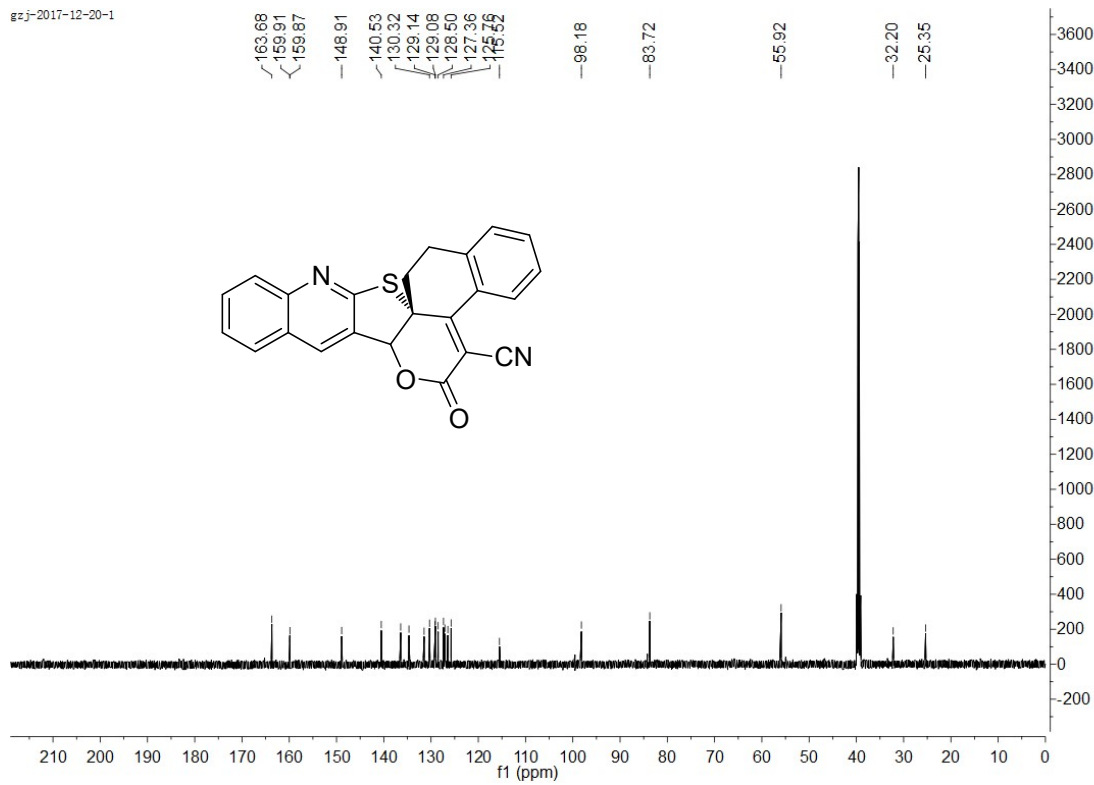
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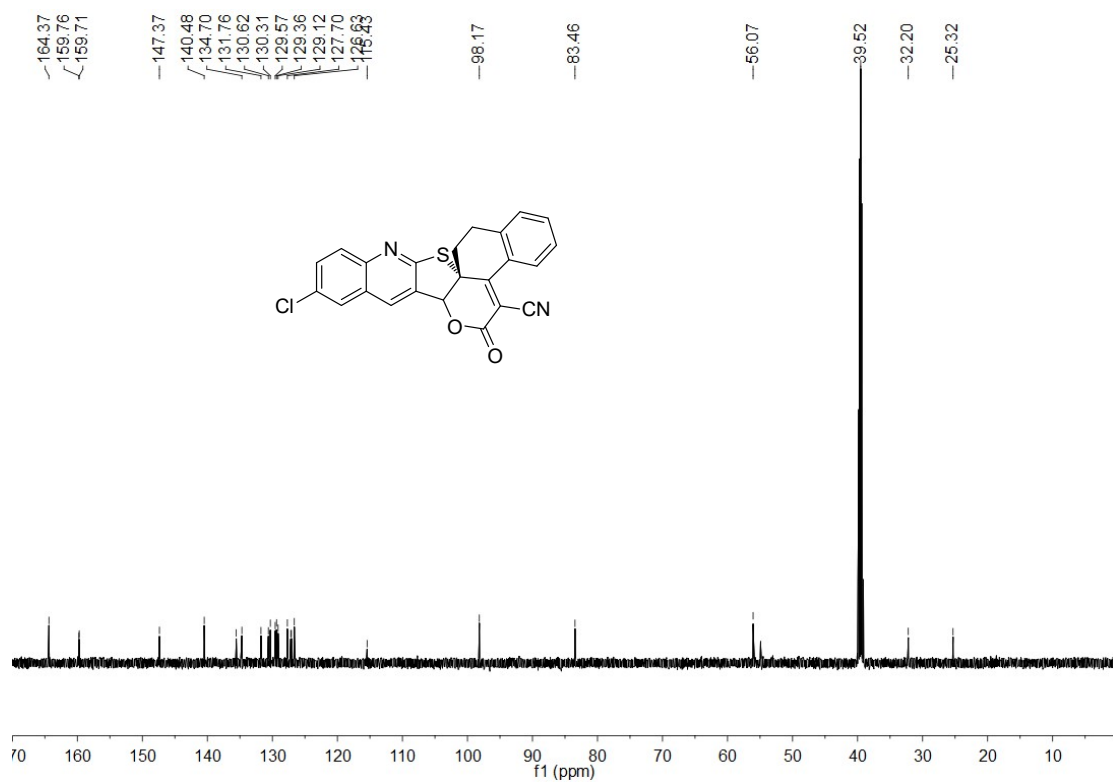
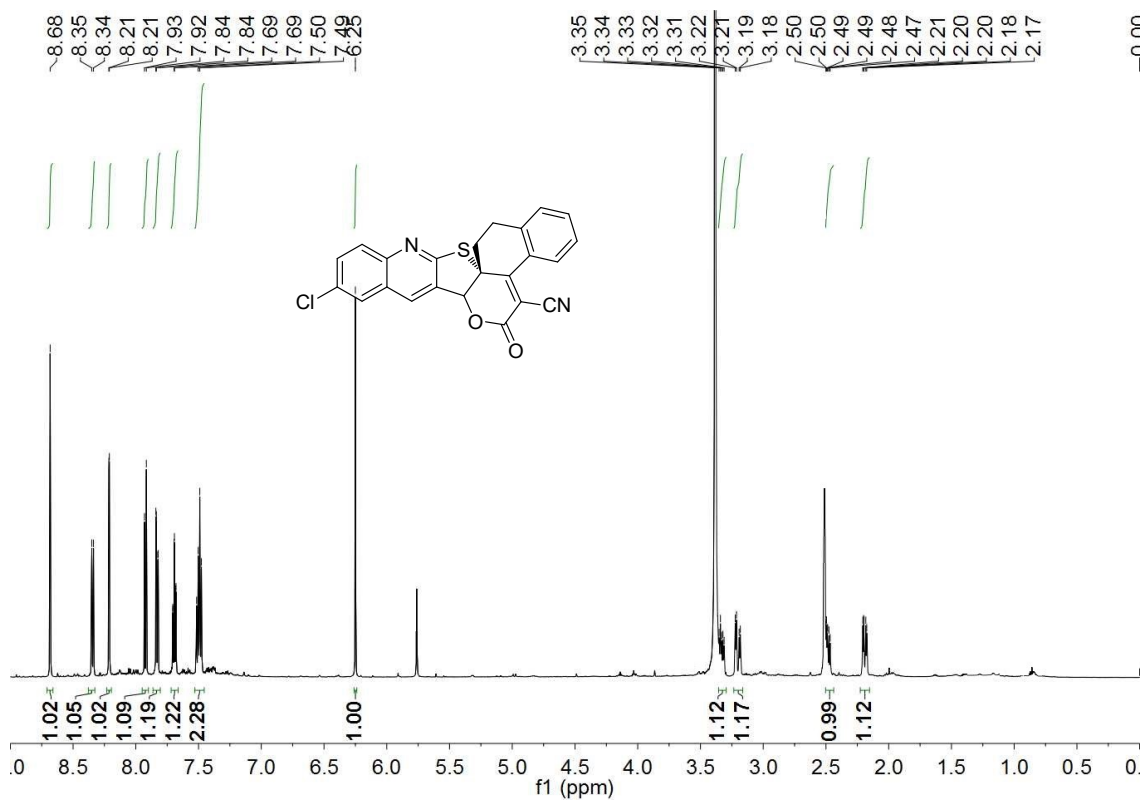
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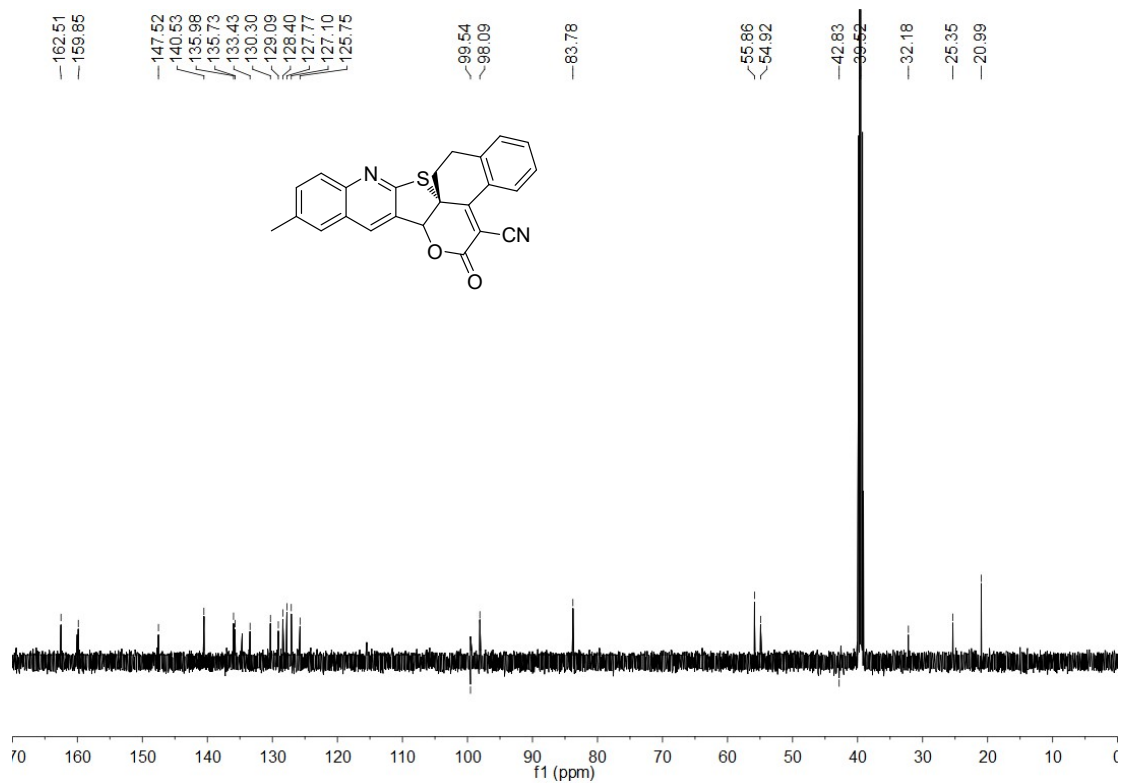
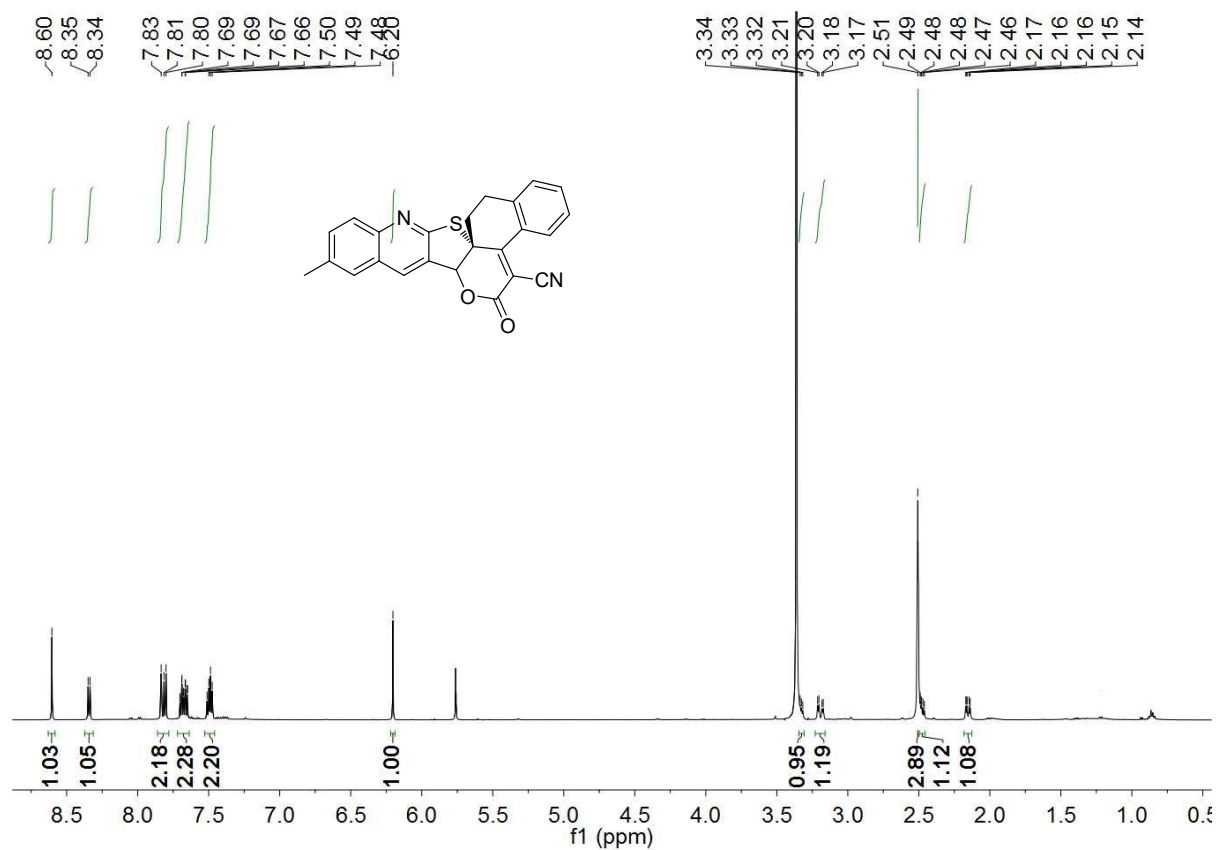
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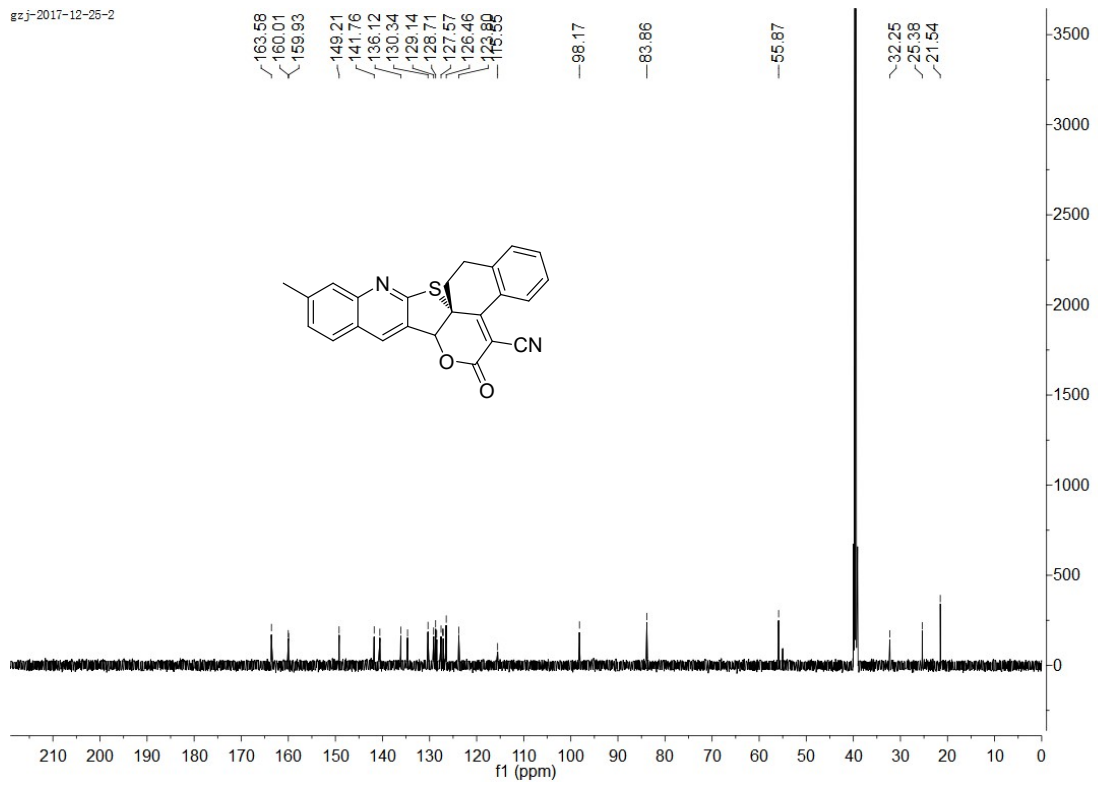
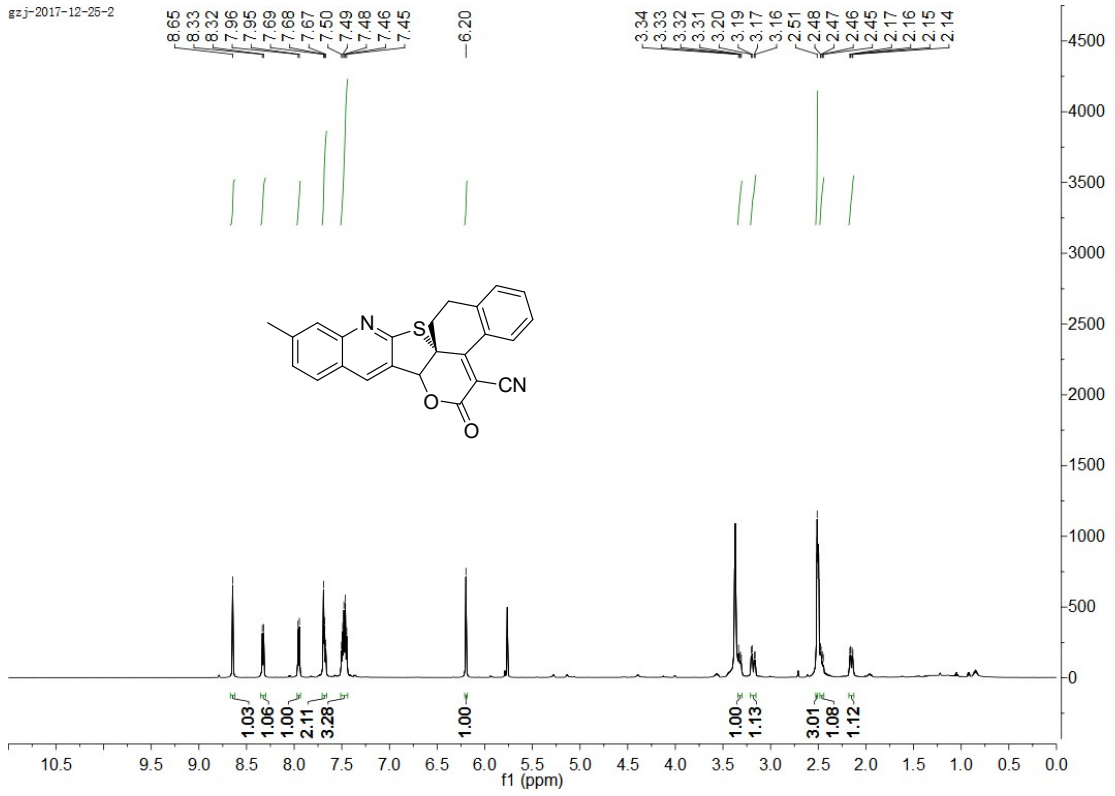
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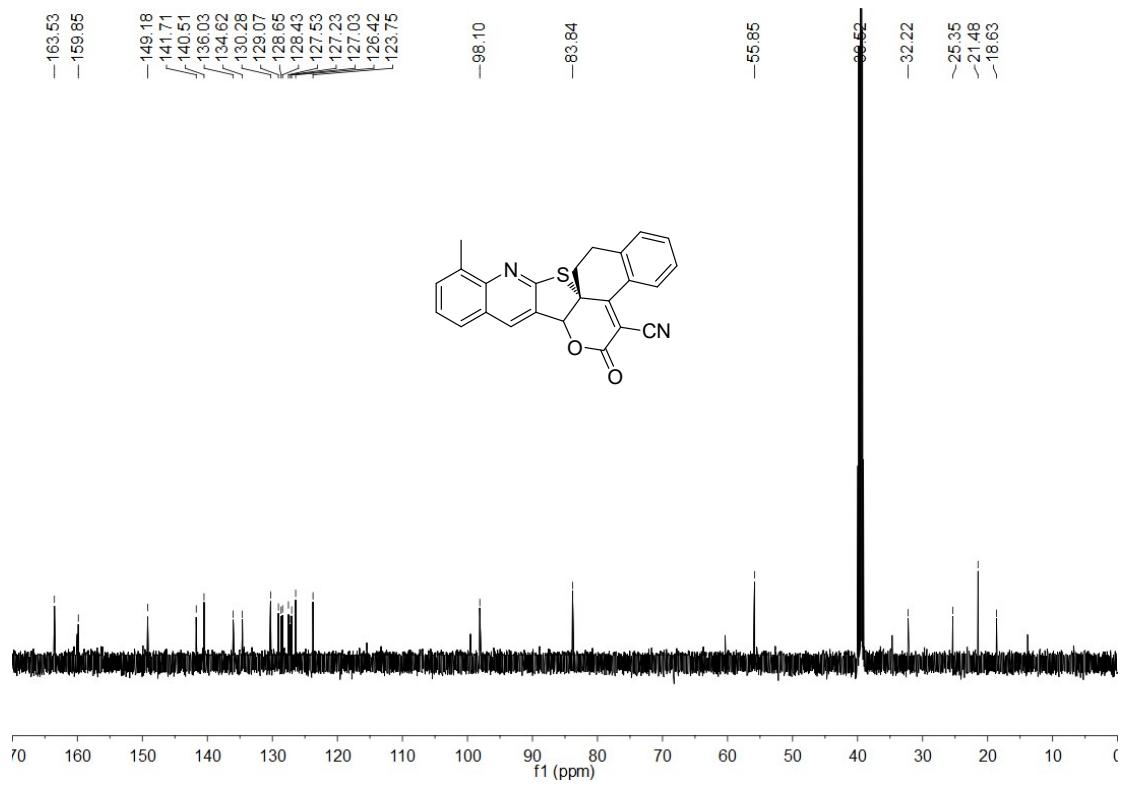
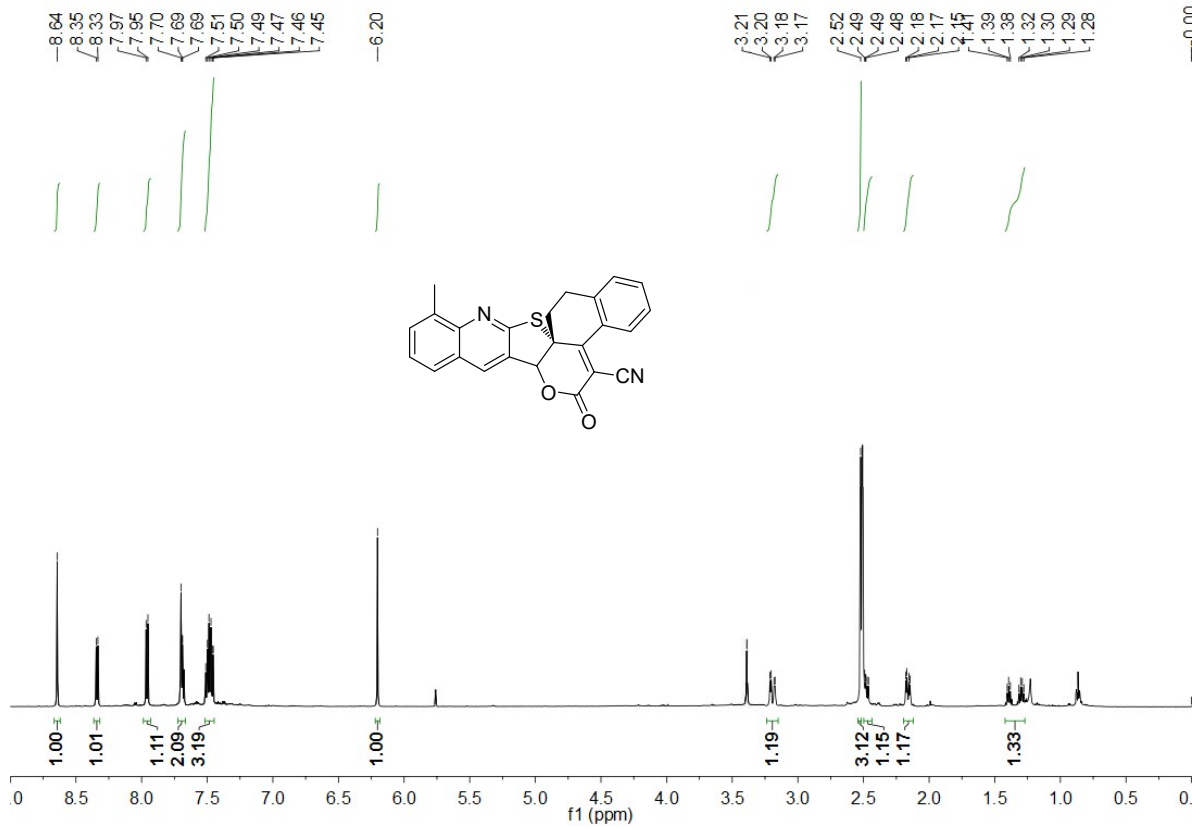
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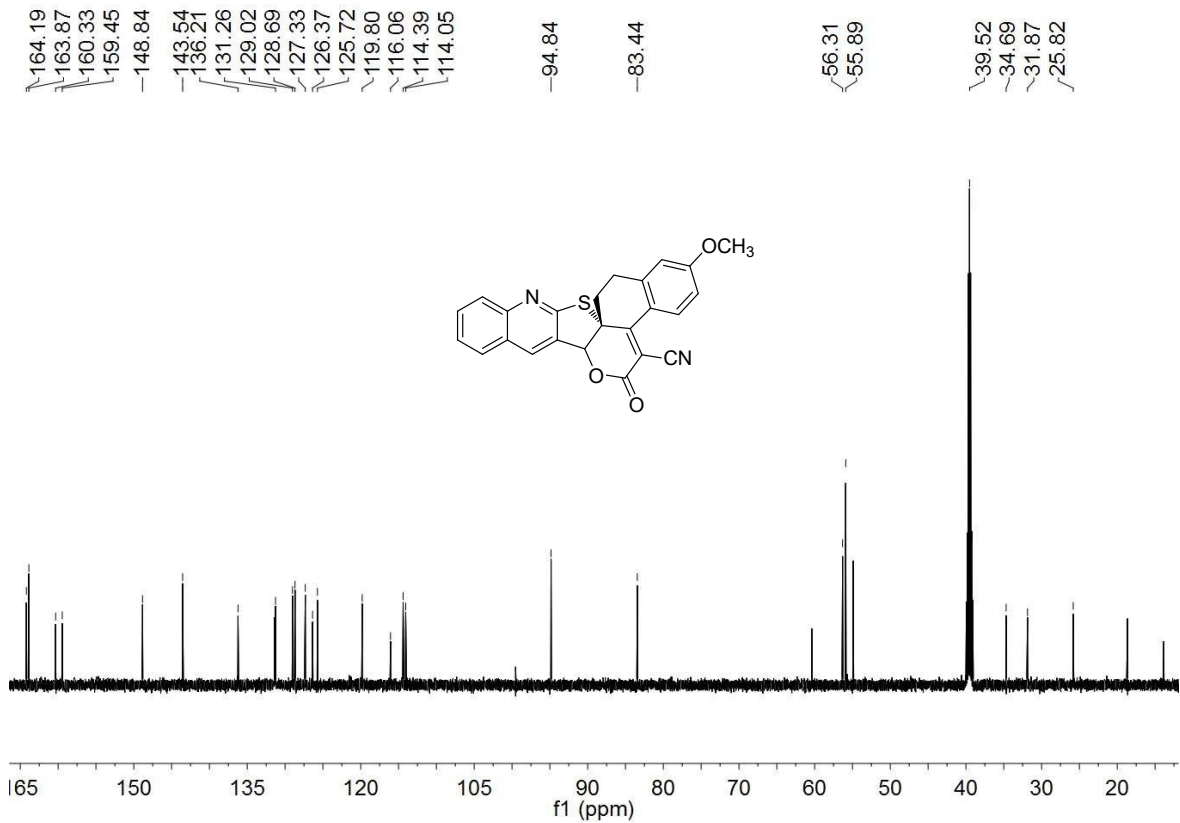
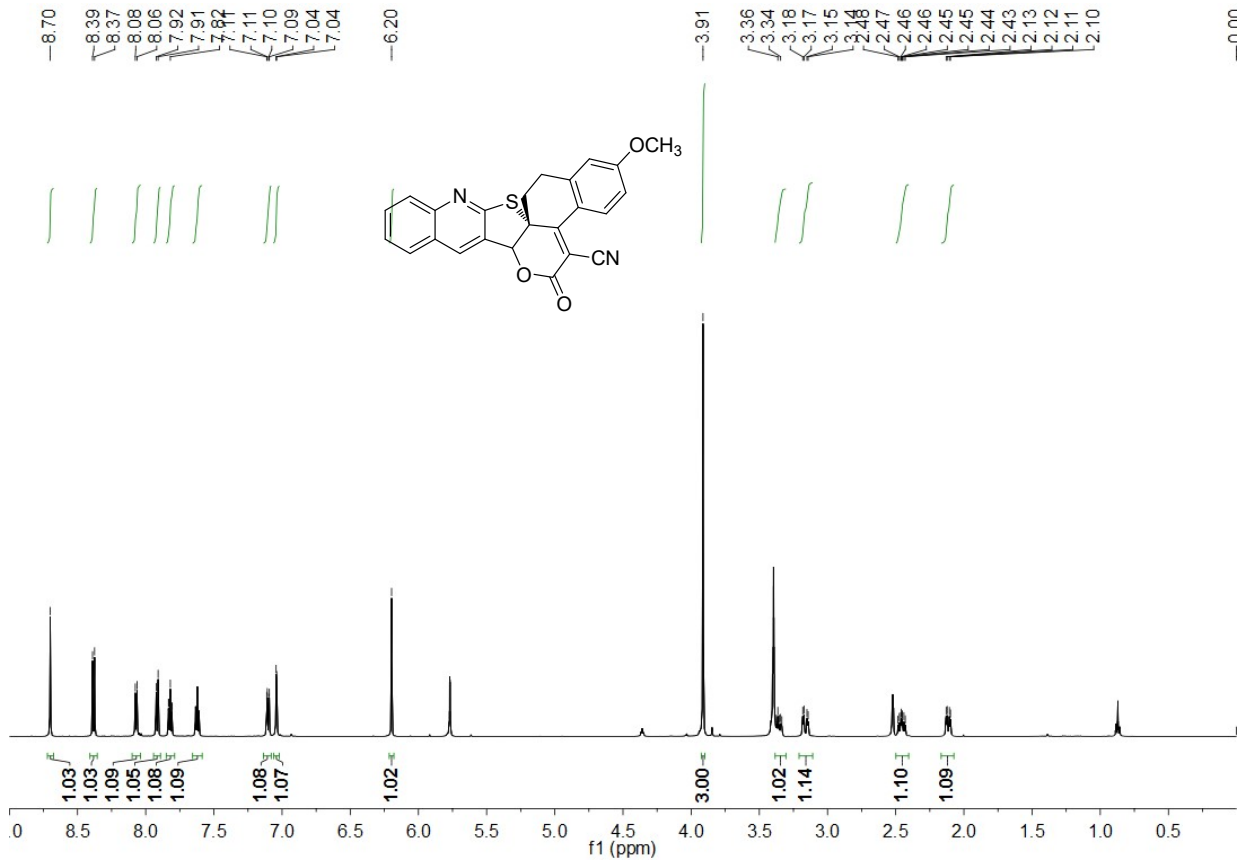
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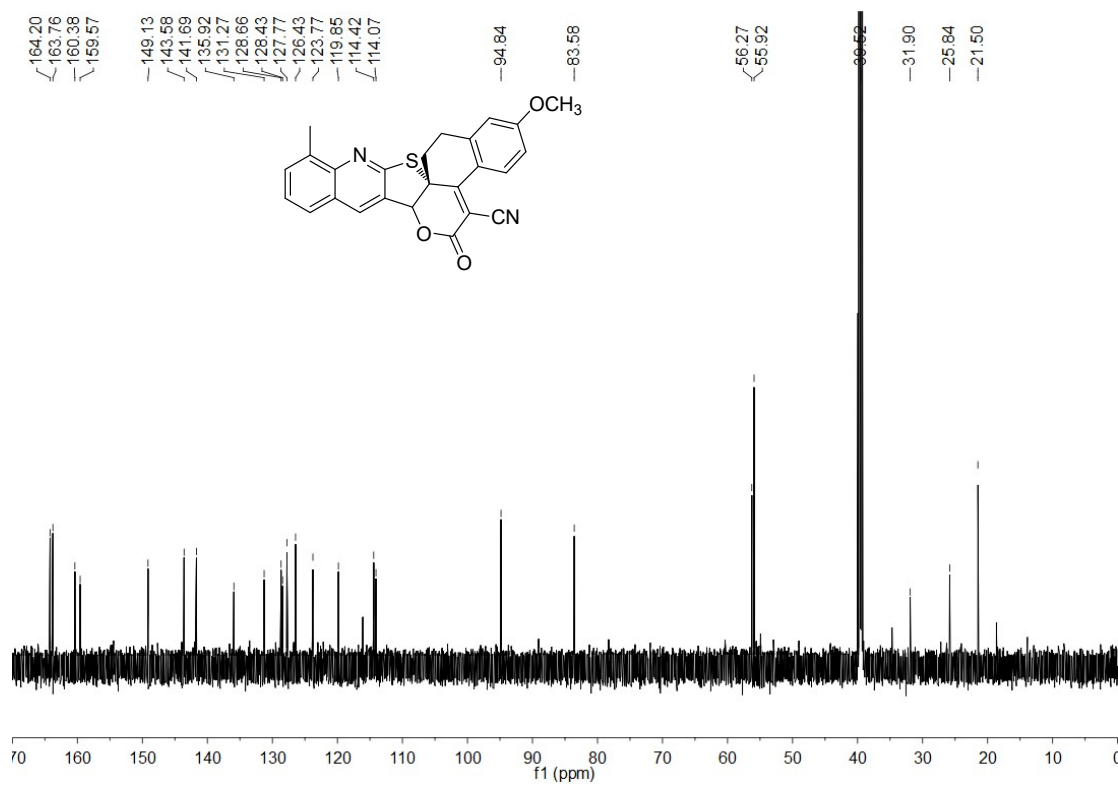
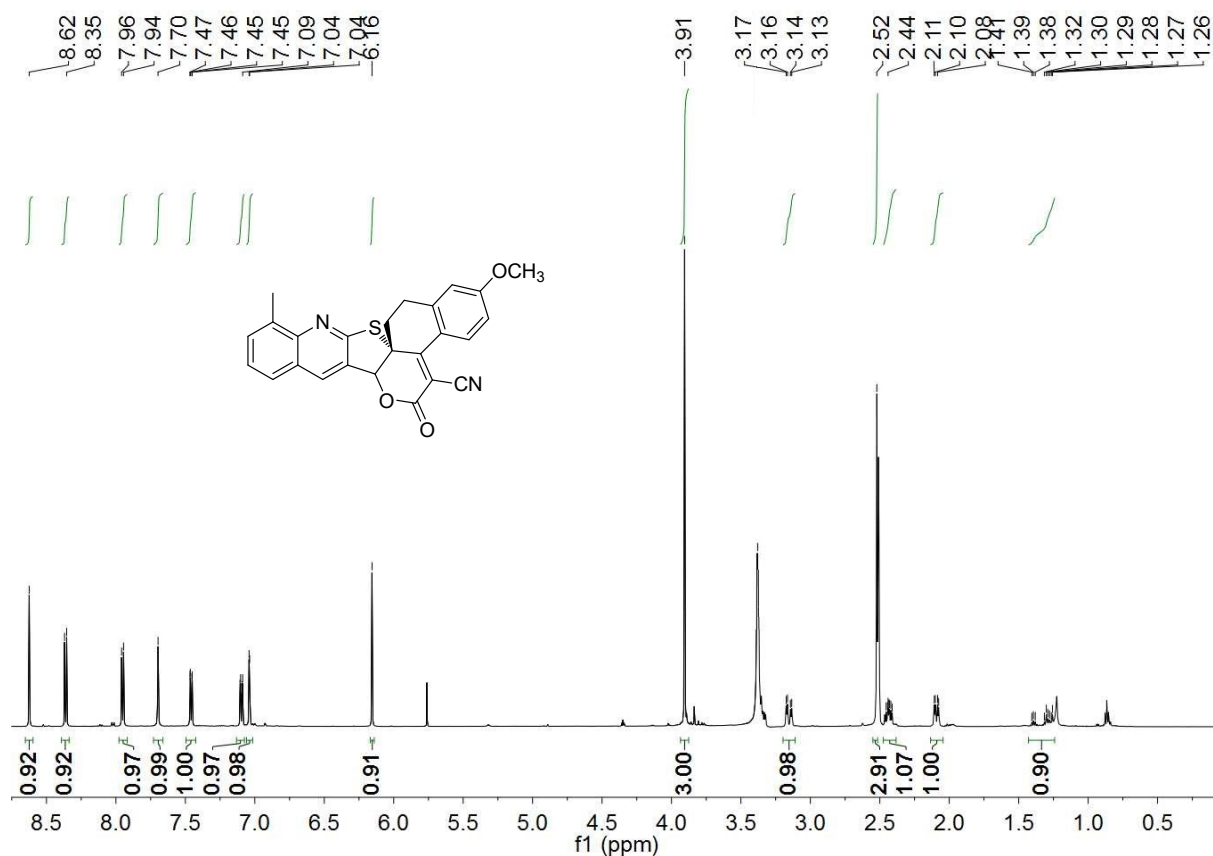
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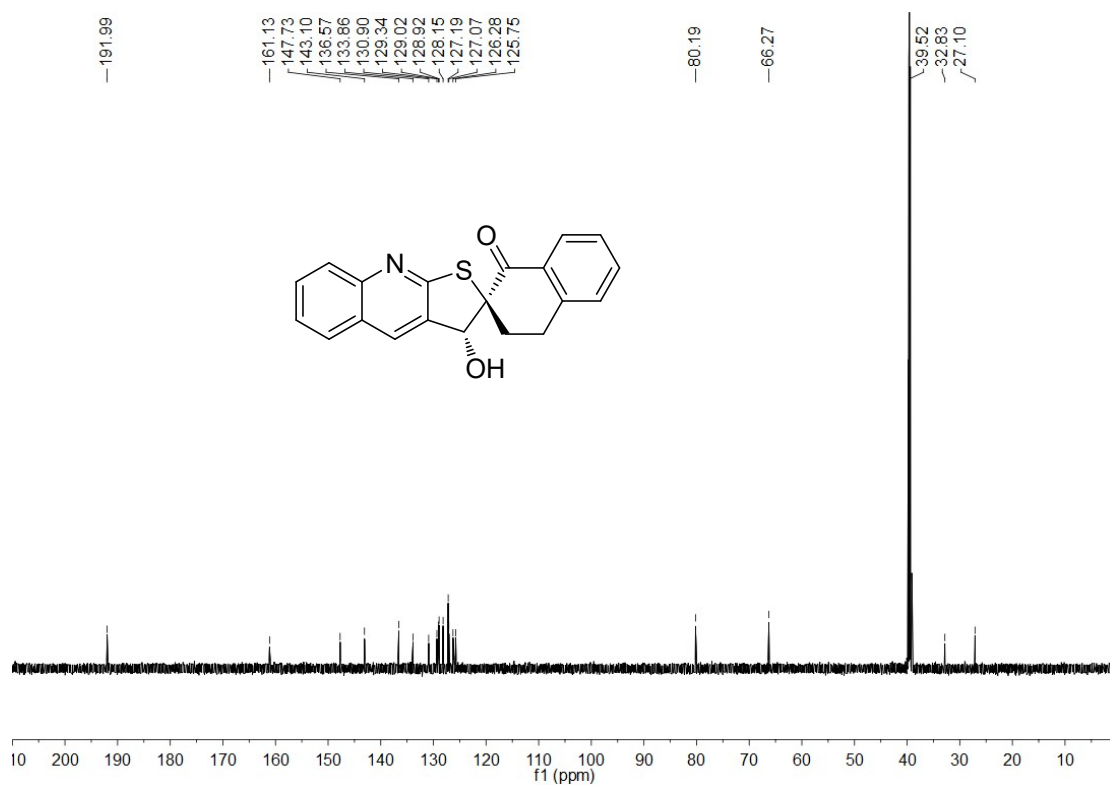
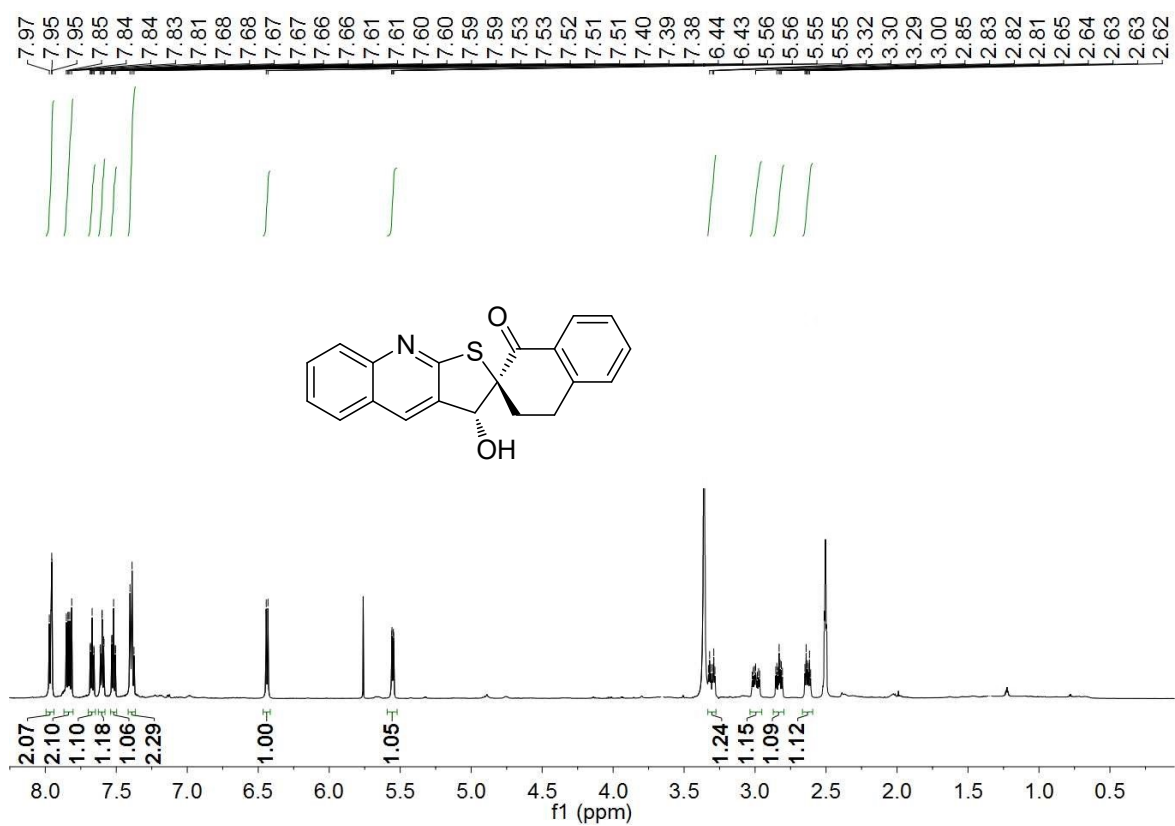
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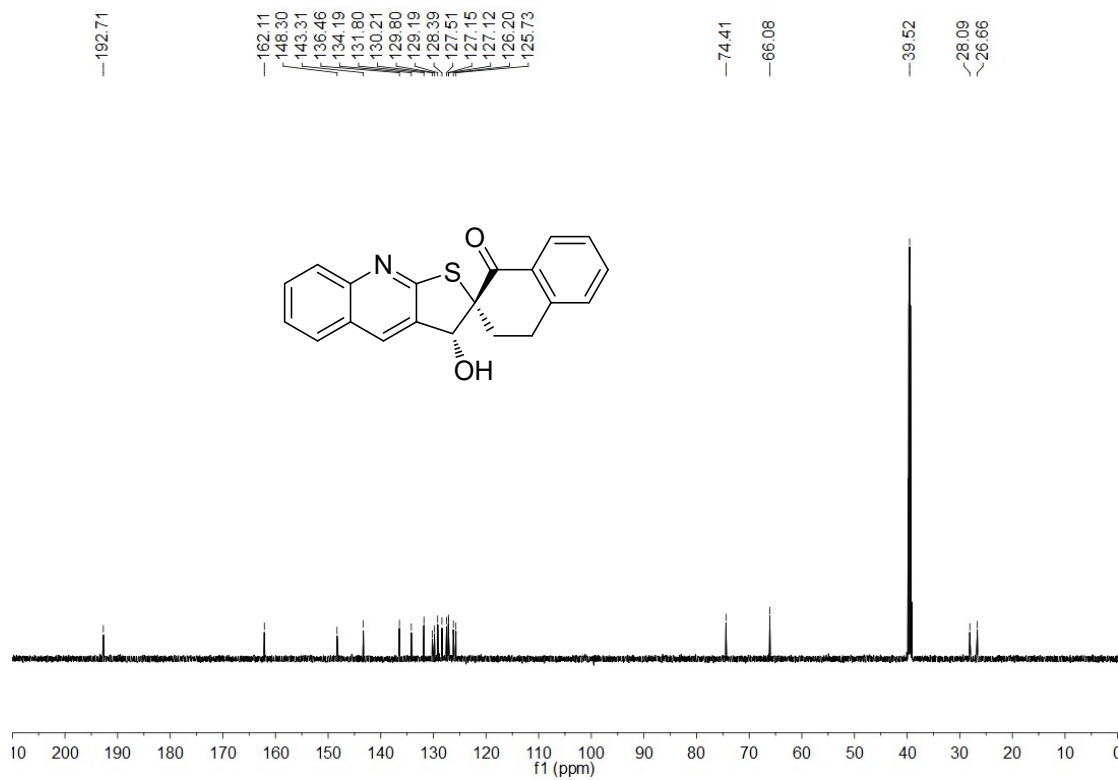
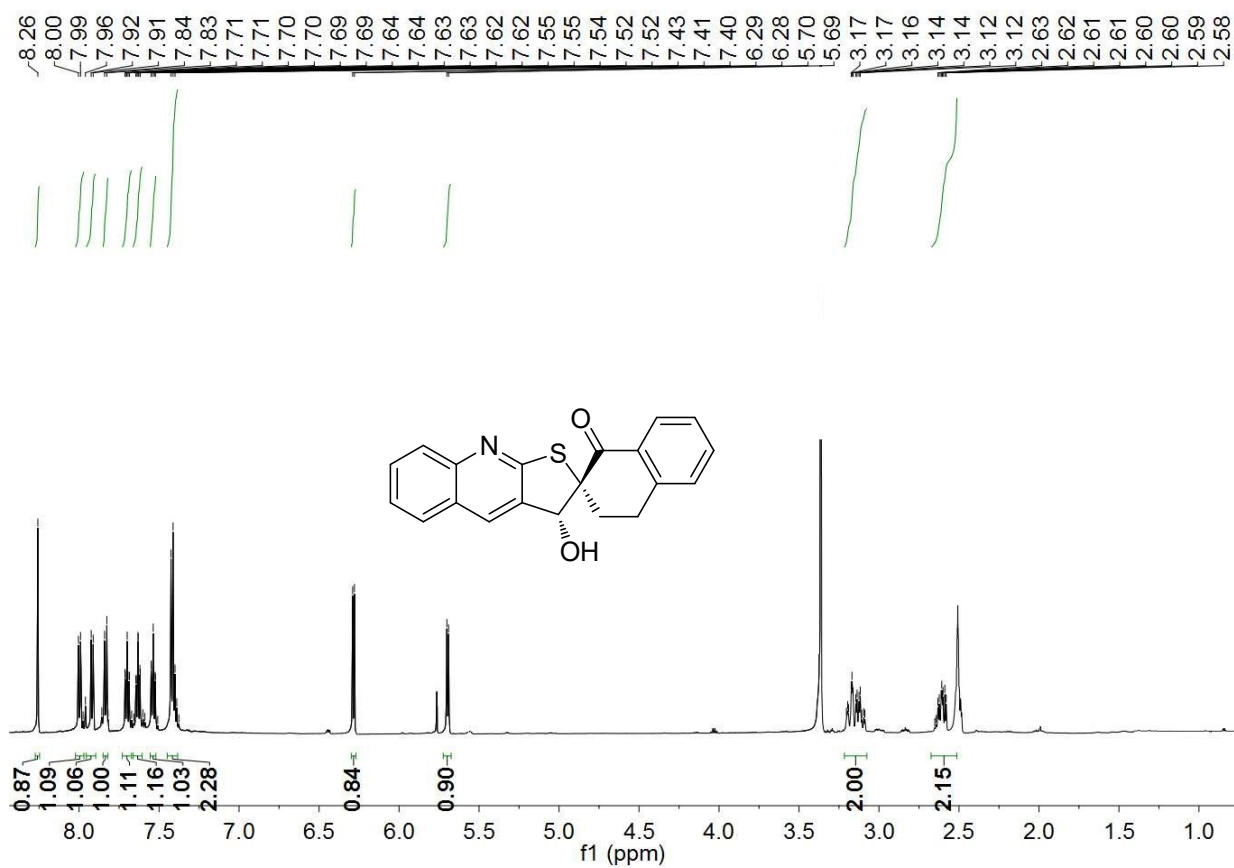
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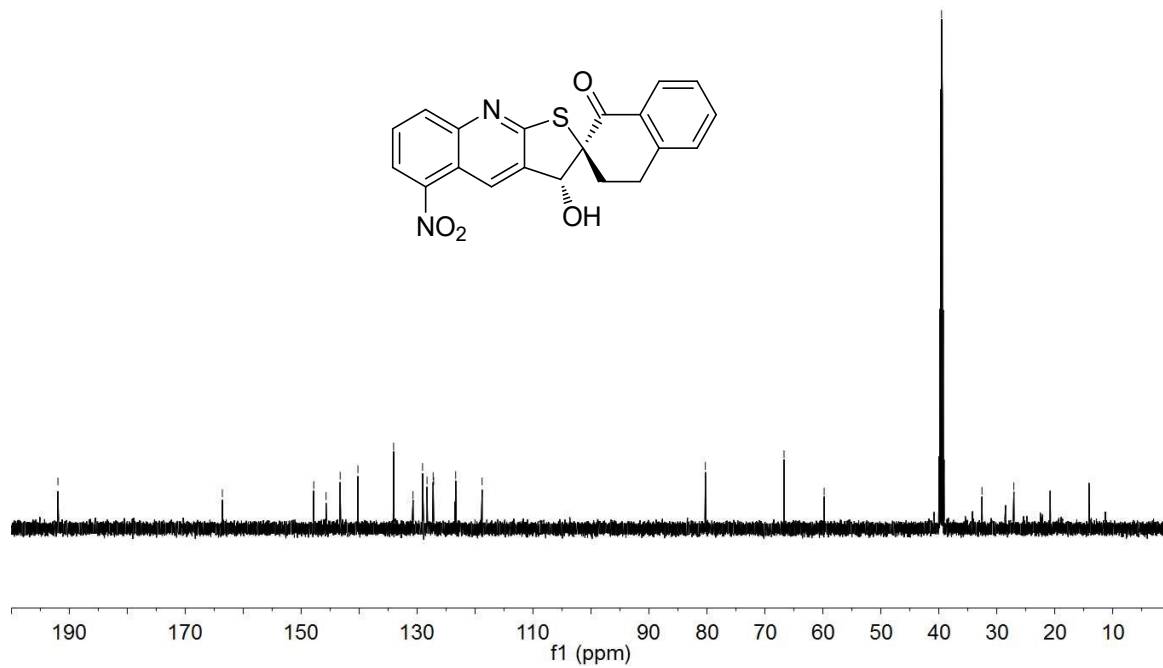
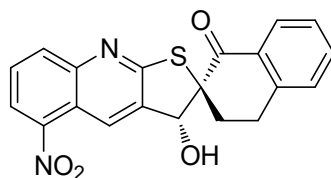
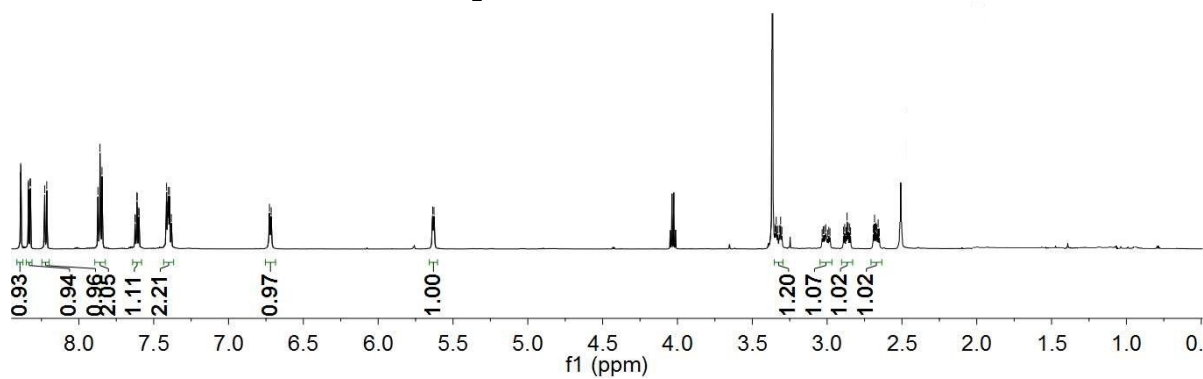
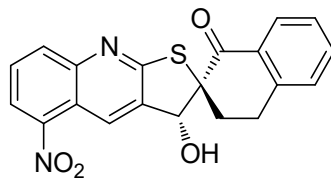
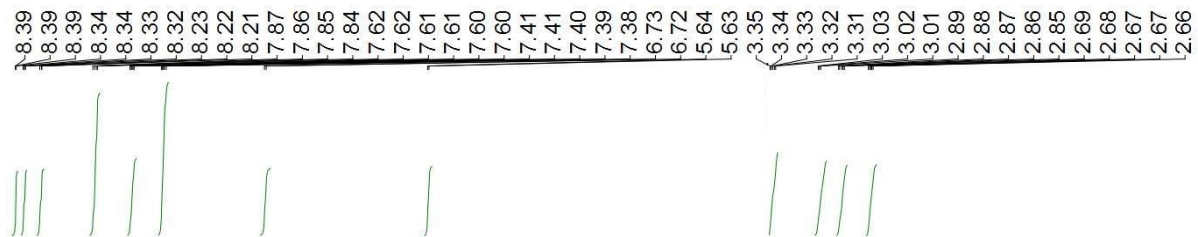
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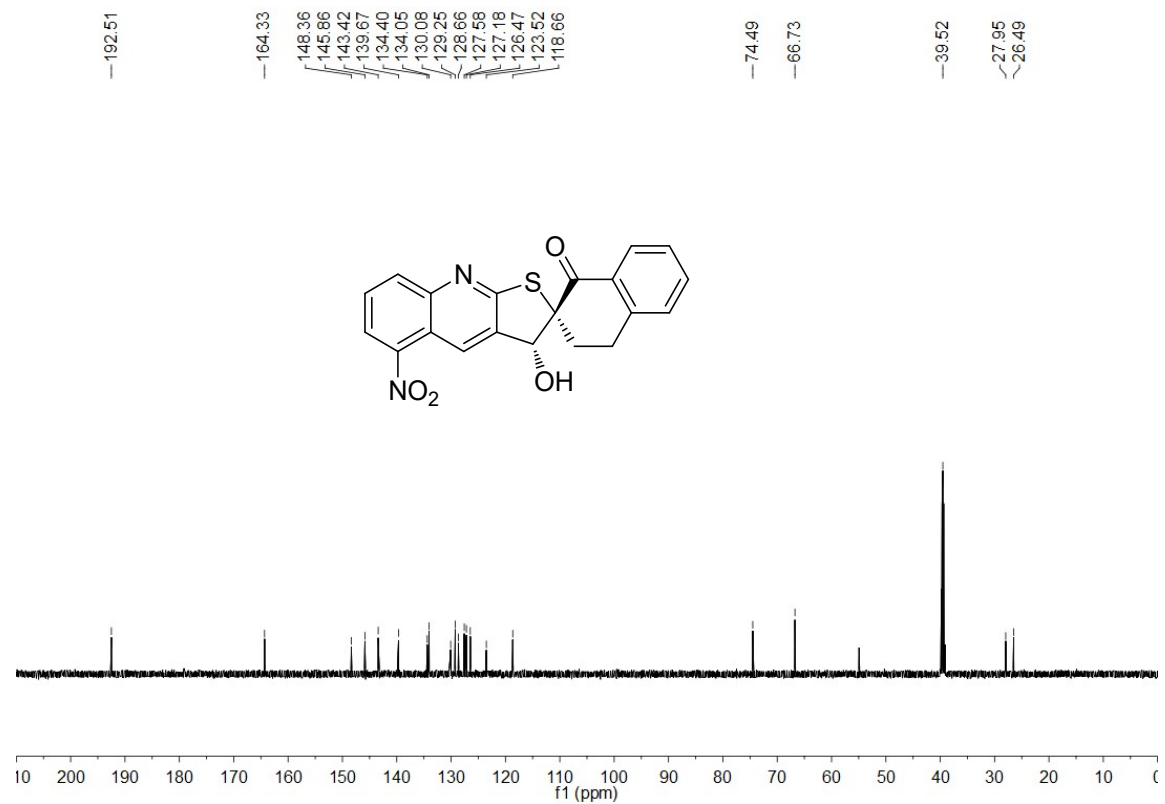
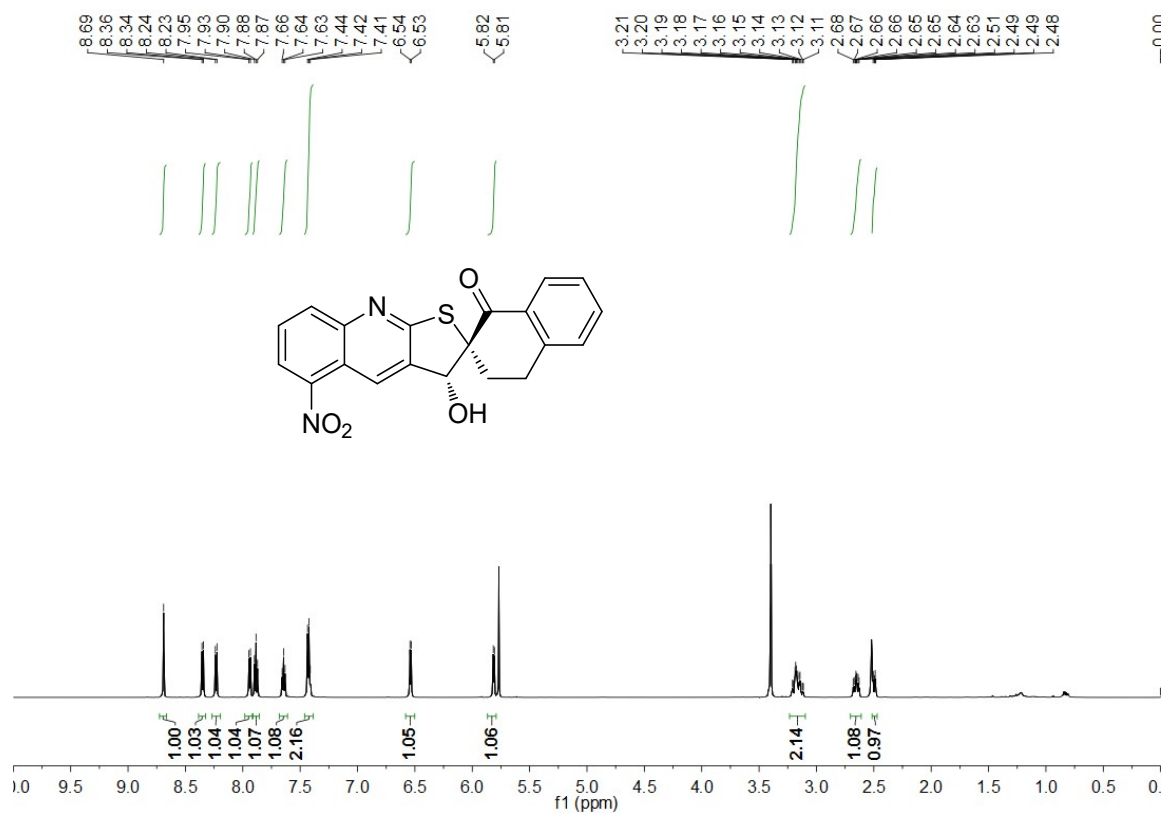
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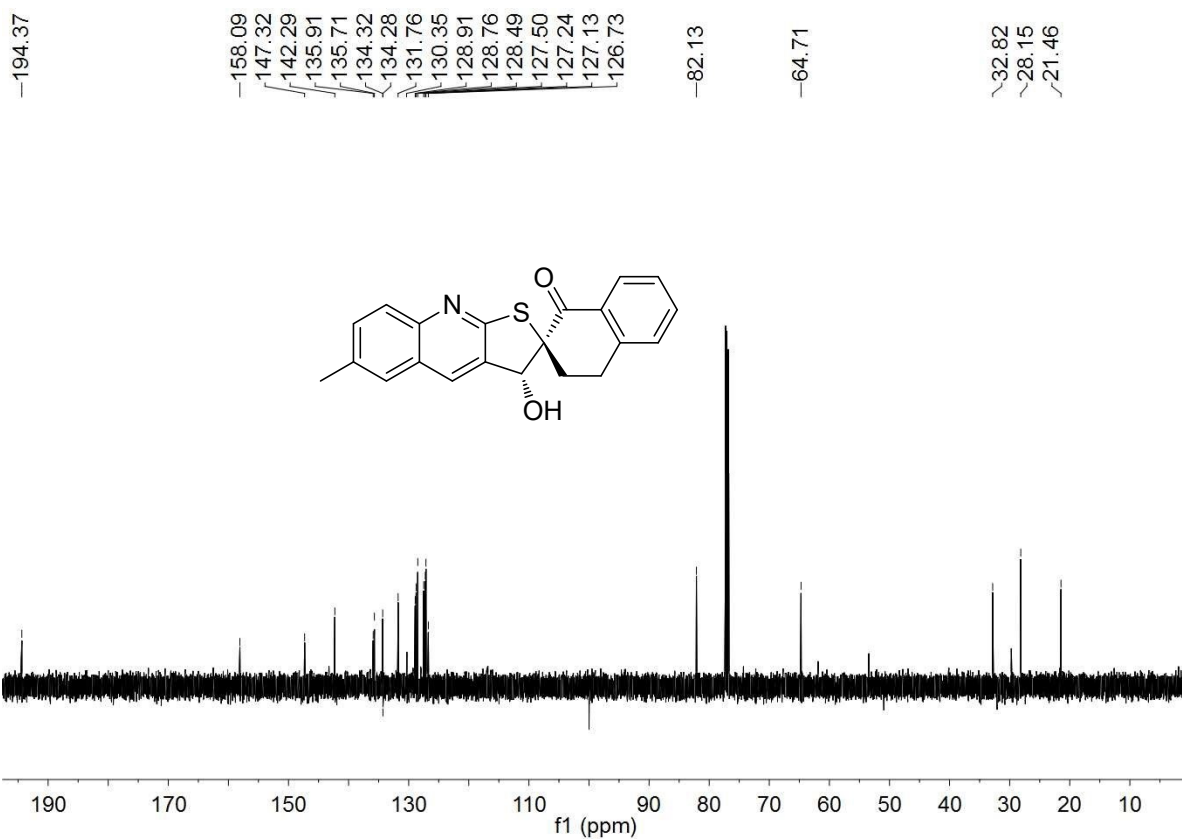
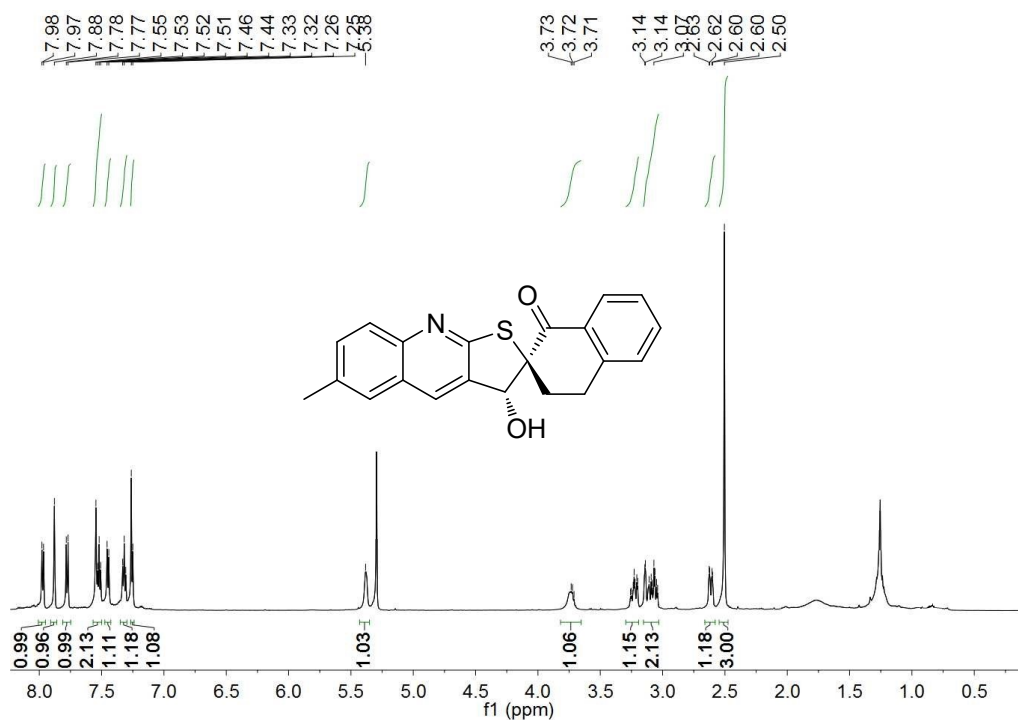
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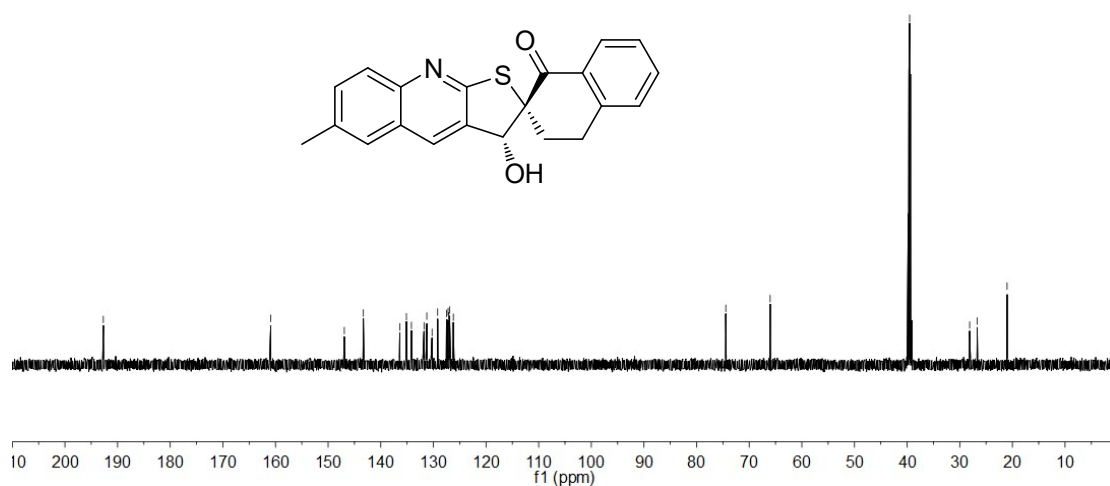
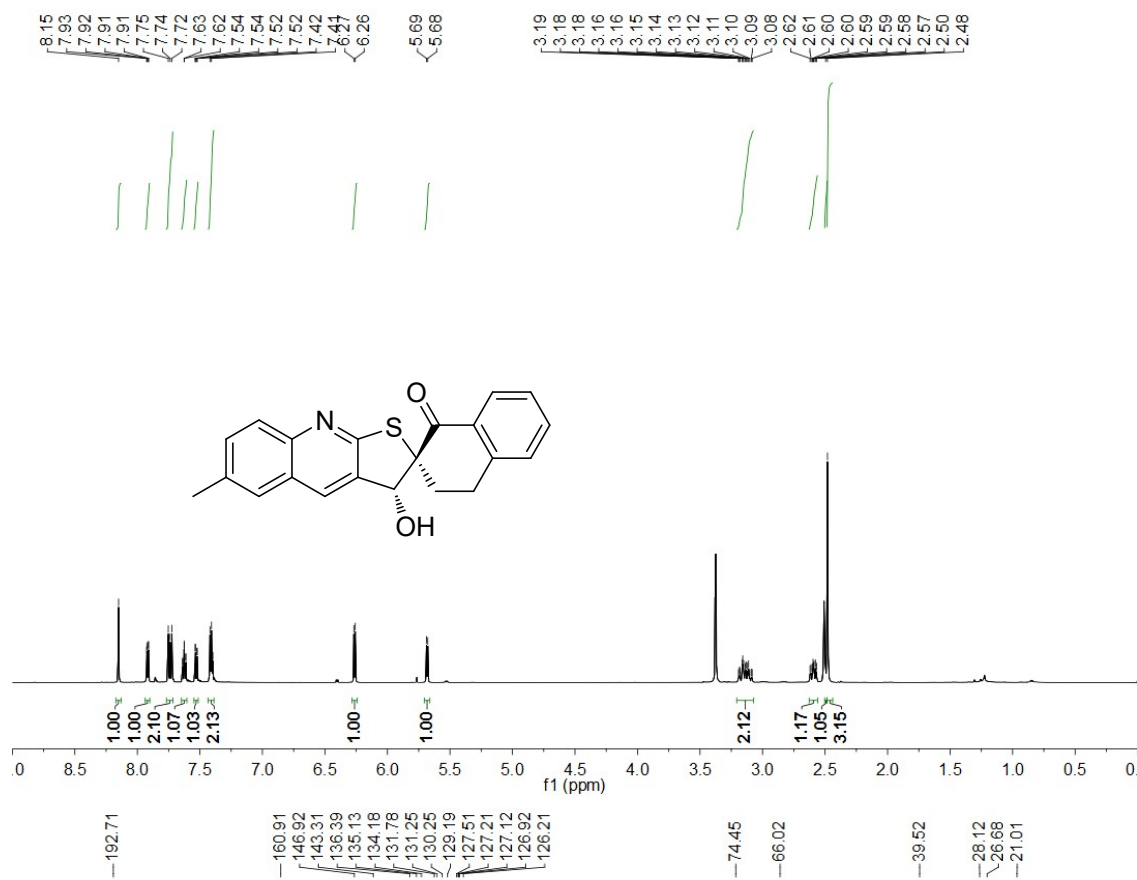
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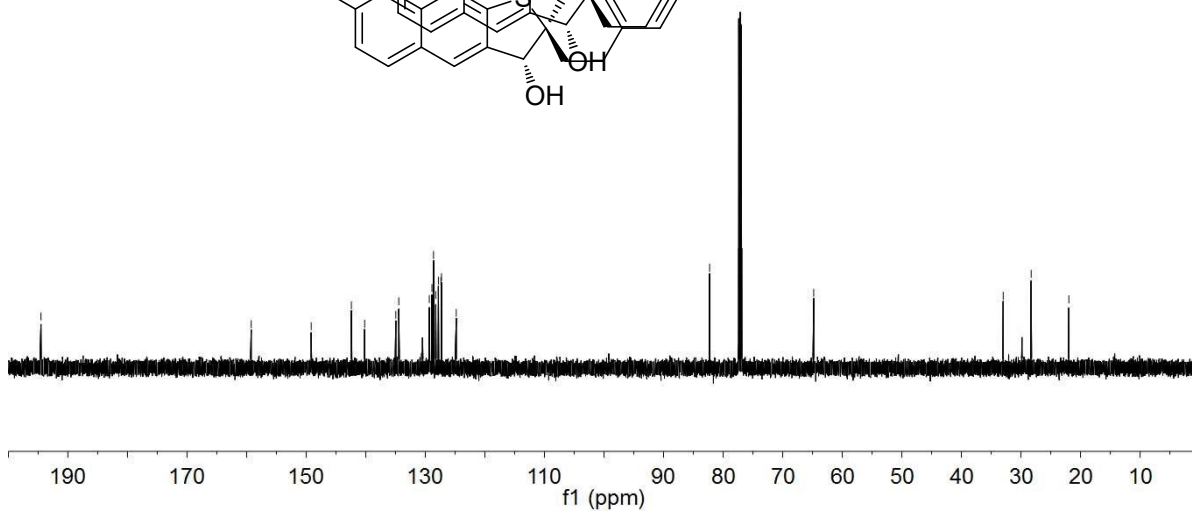
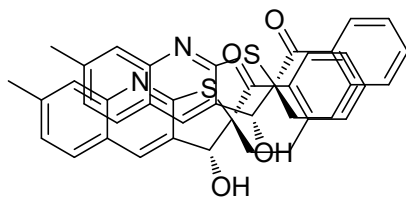
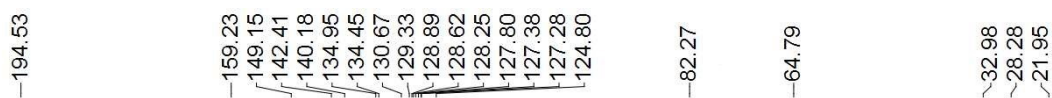
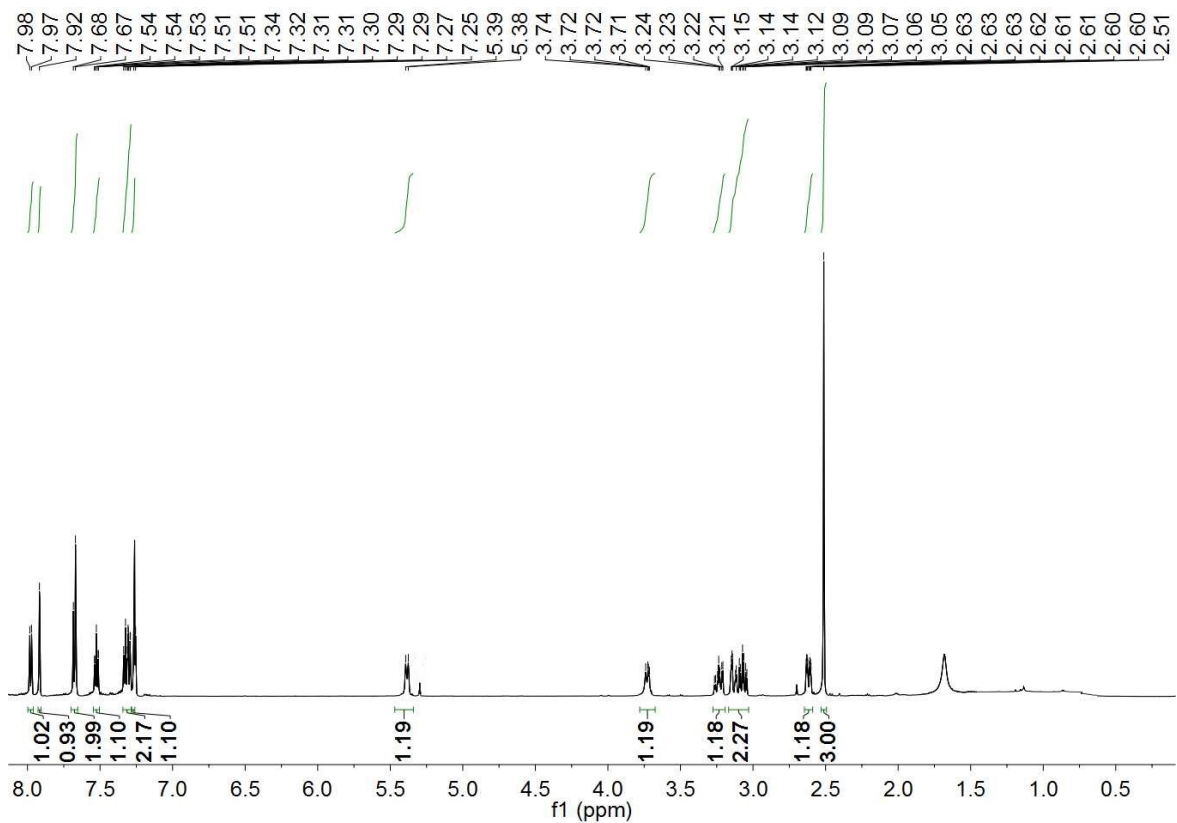
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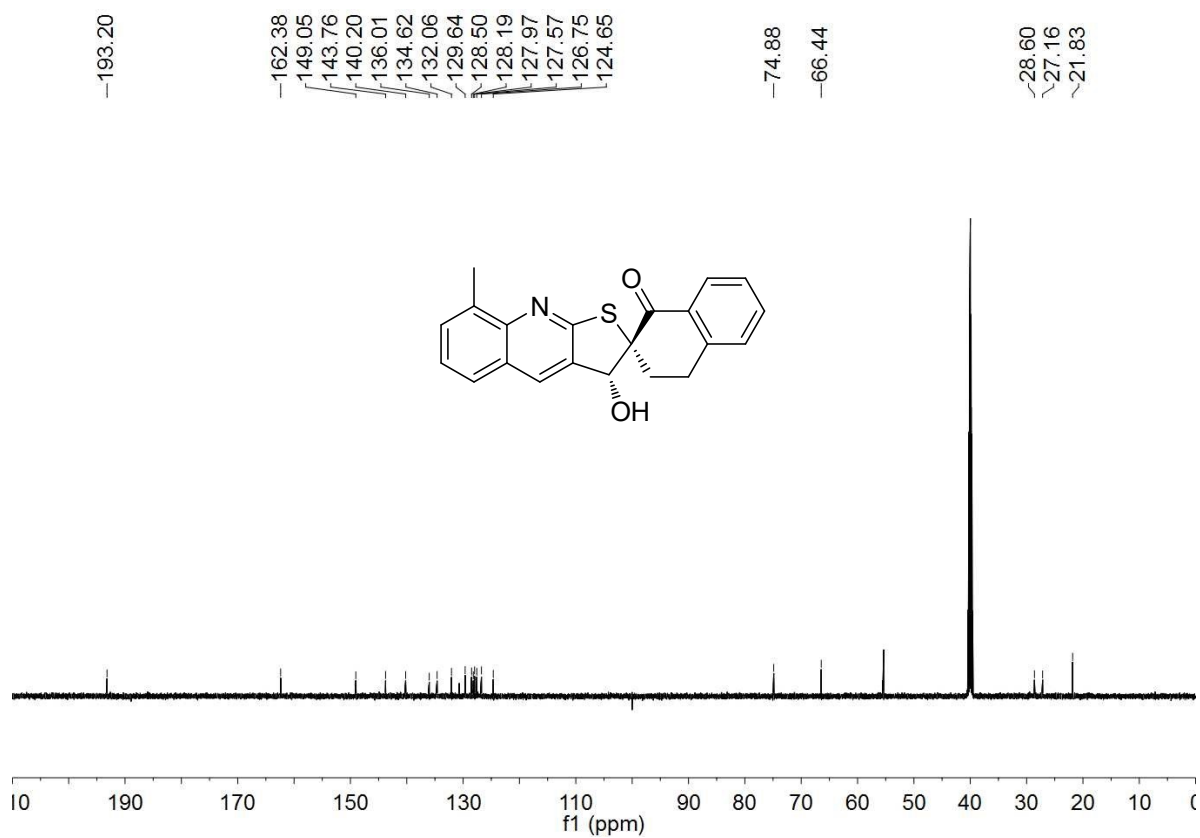
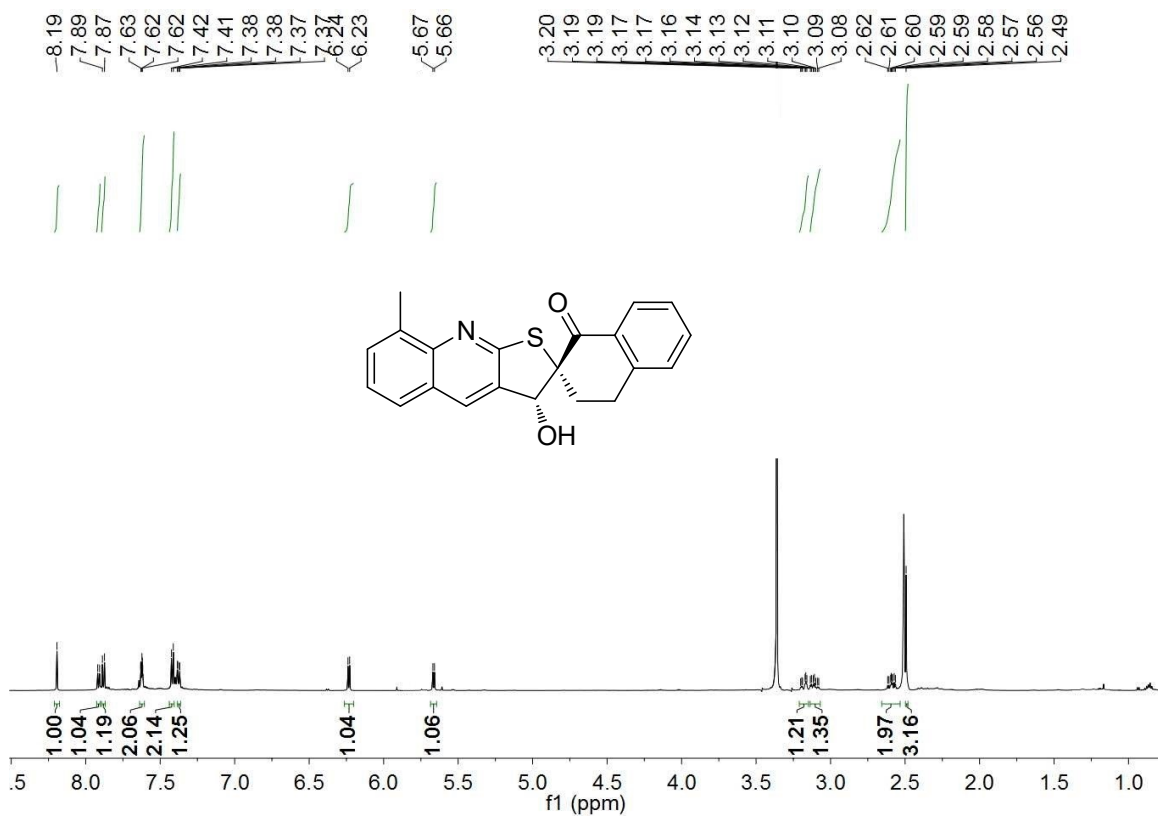
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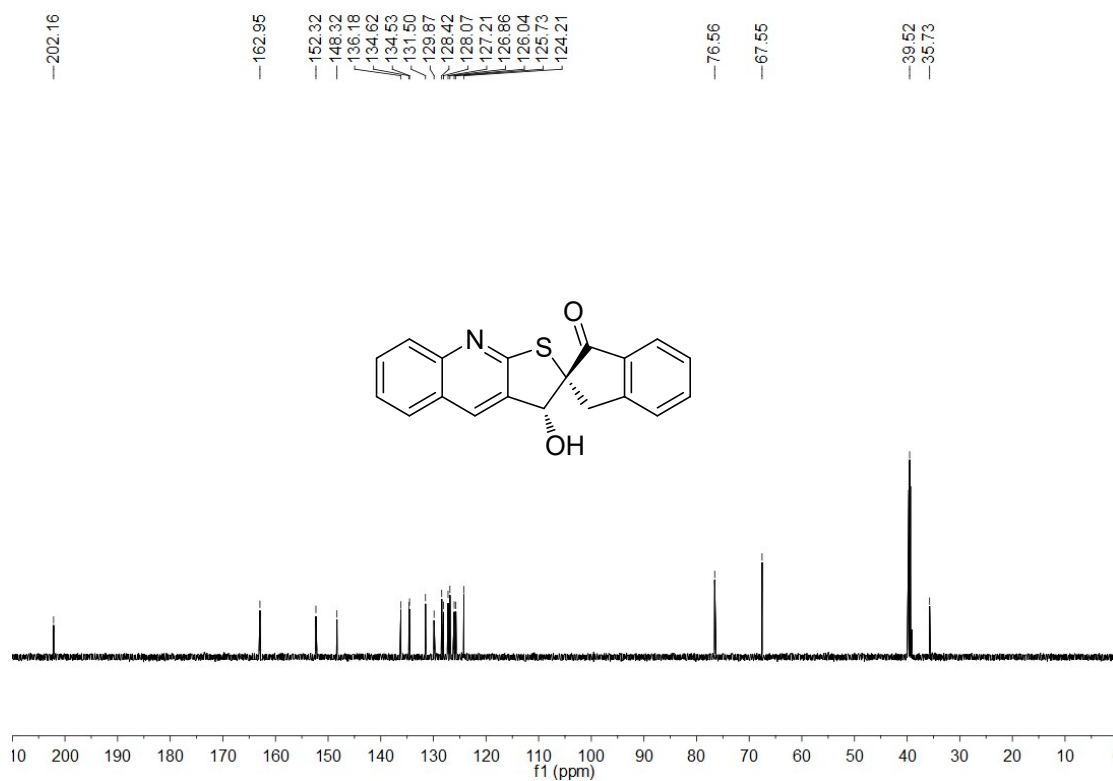
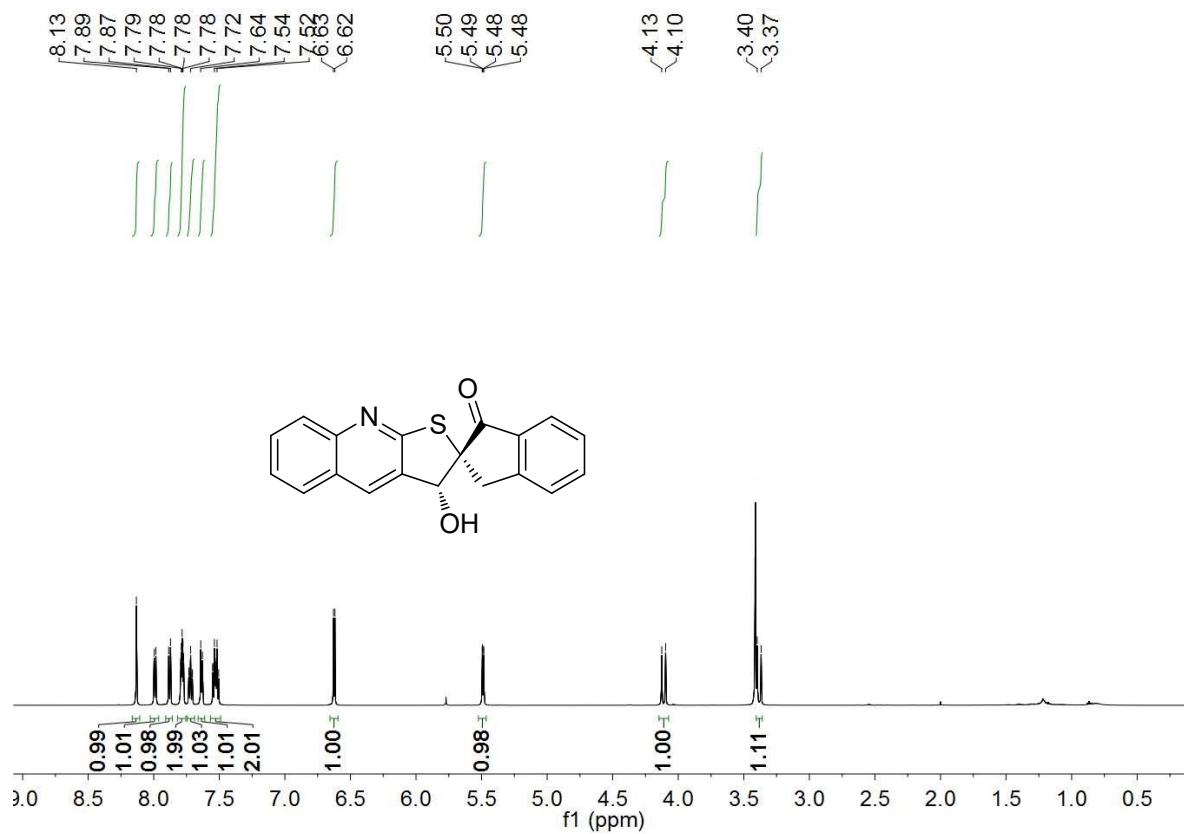
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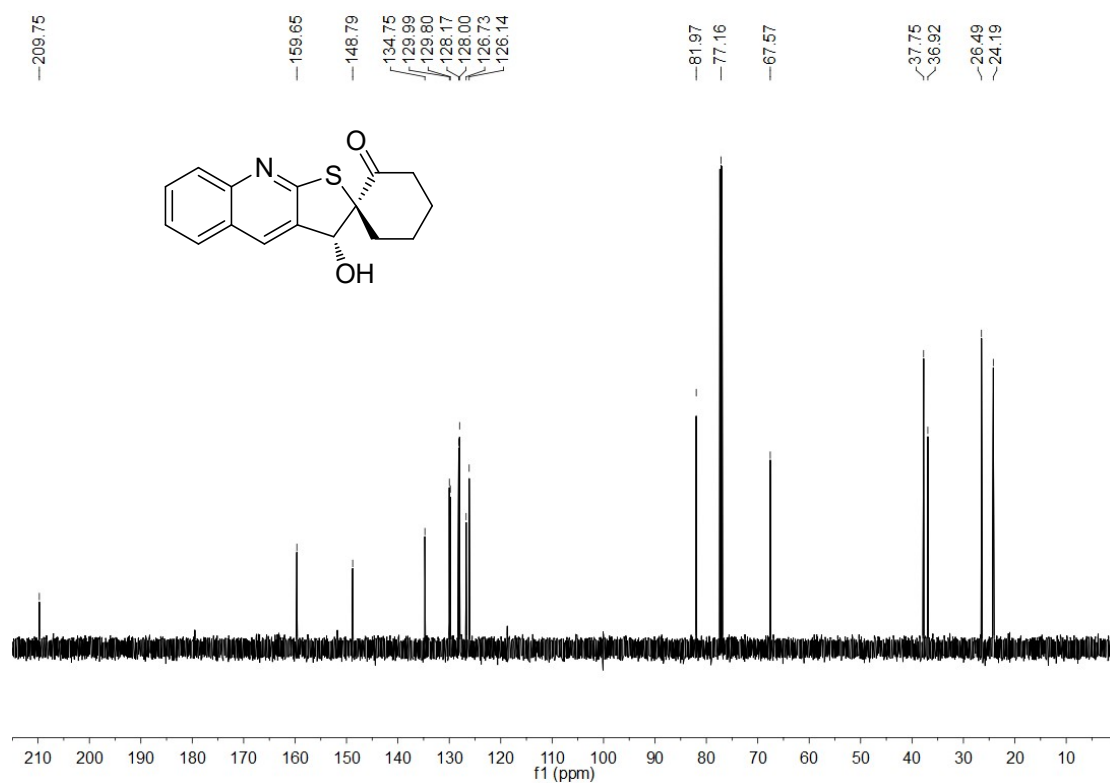
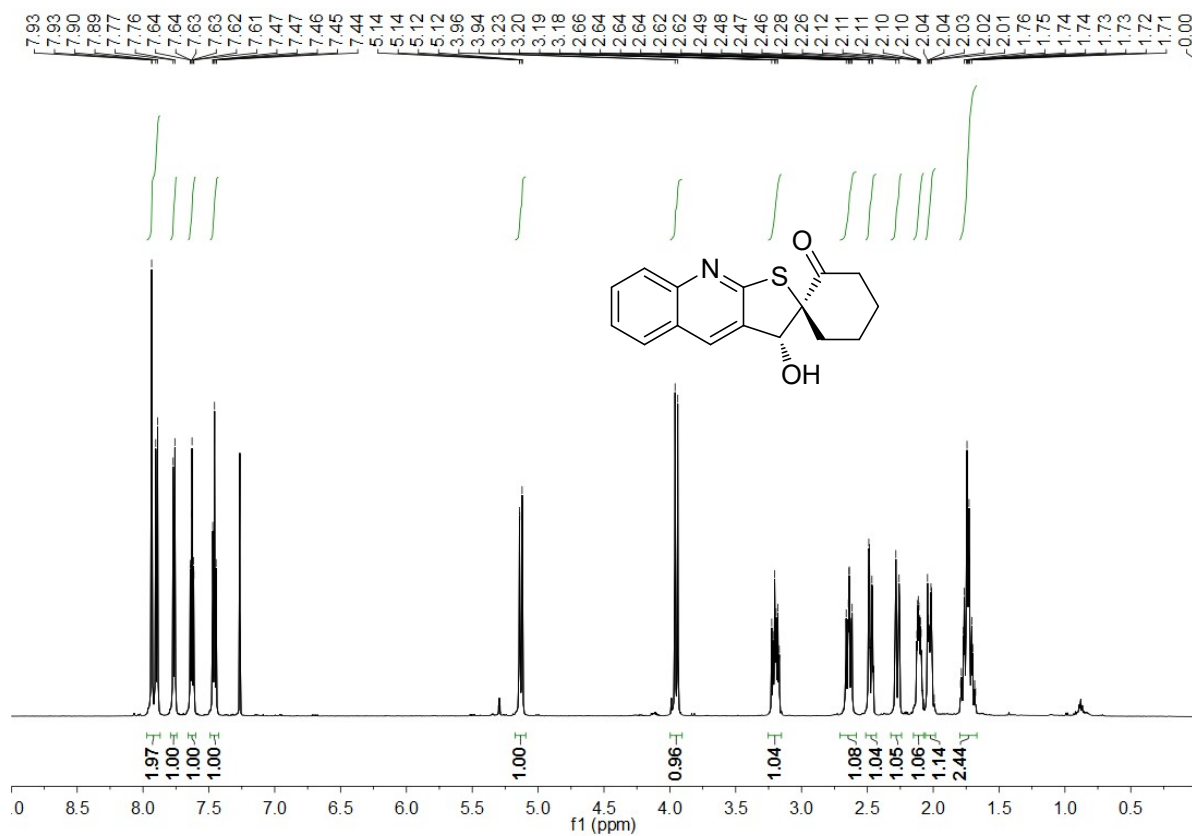
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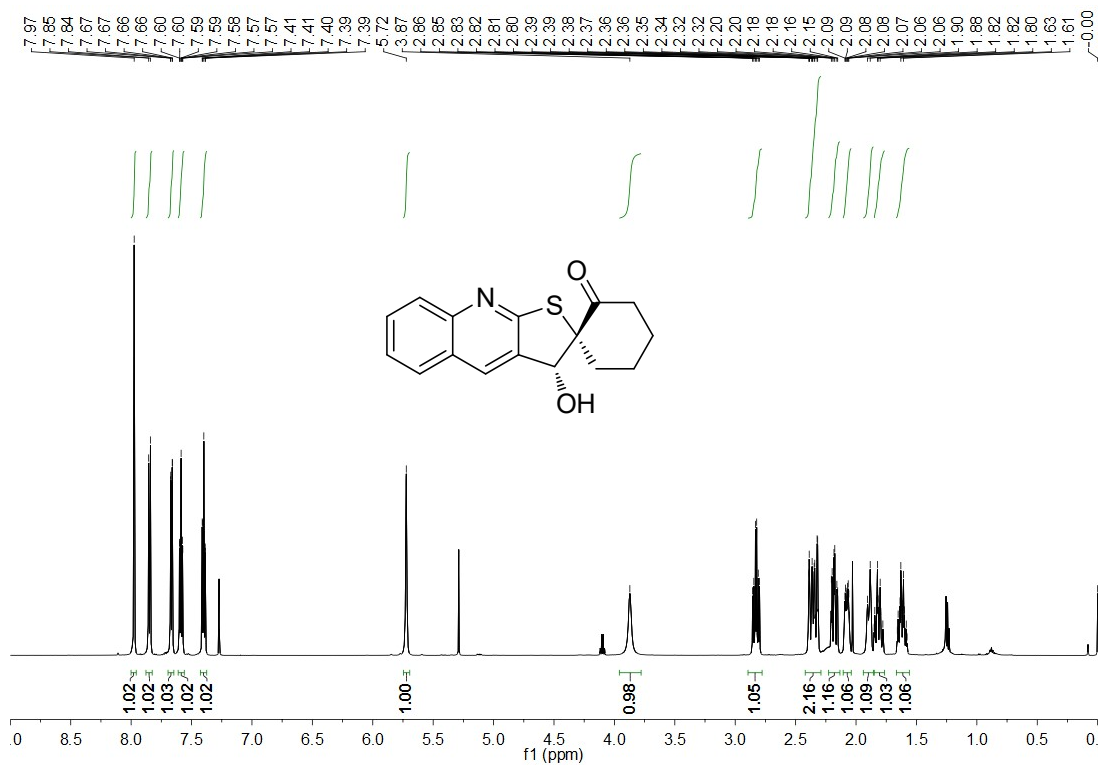
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5ca



5'ca



-206.95

-162.09

-148.84

134.72

132.51

130.01

128.22

127.56

126.44

125.90

-75.17

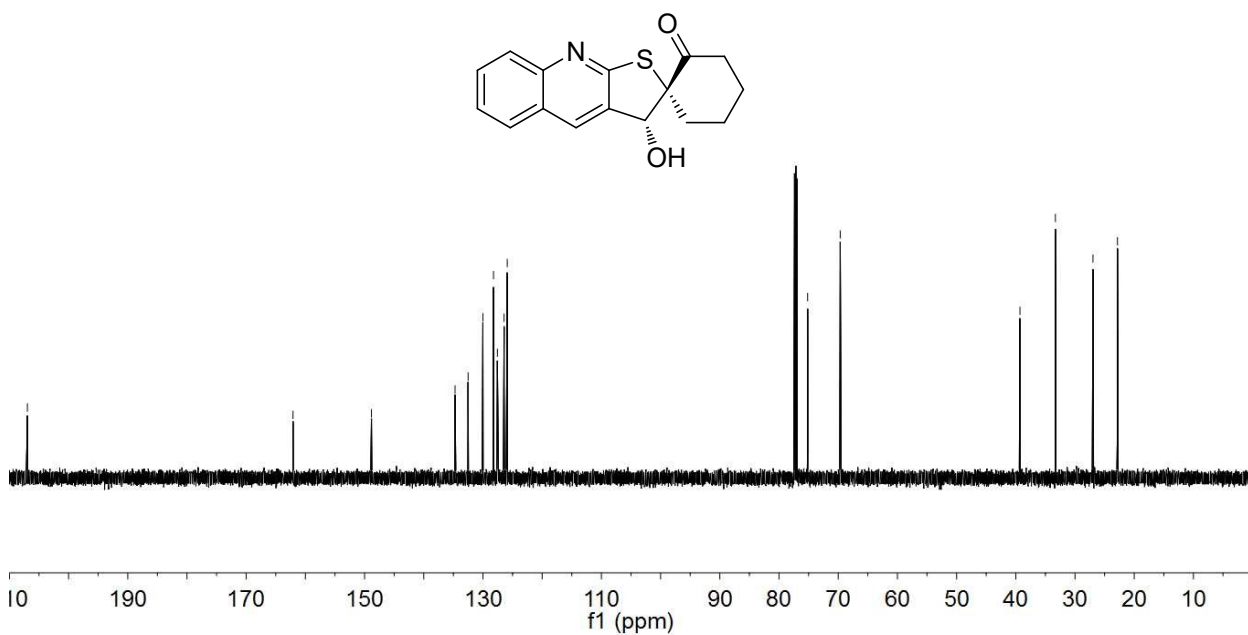
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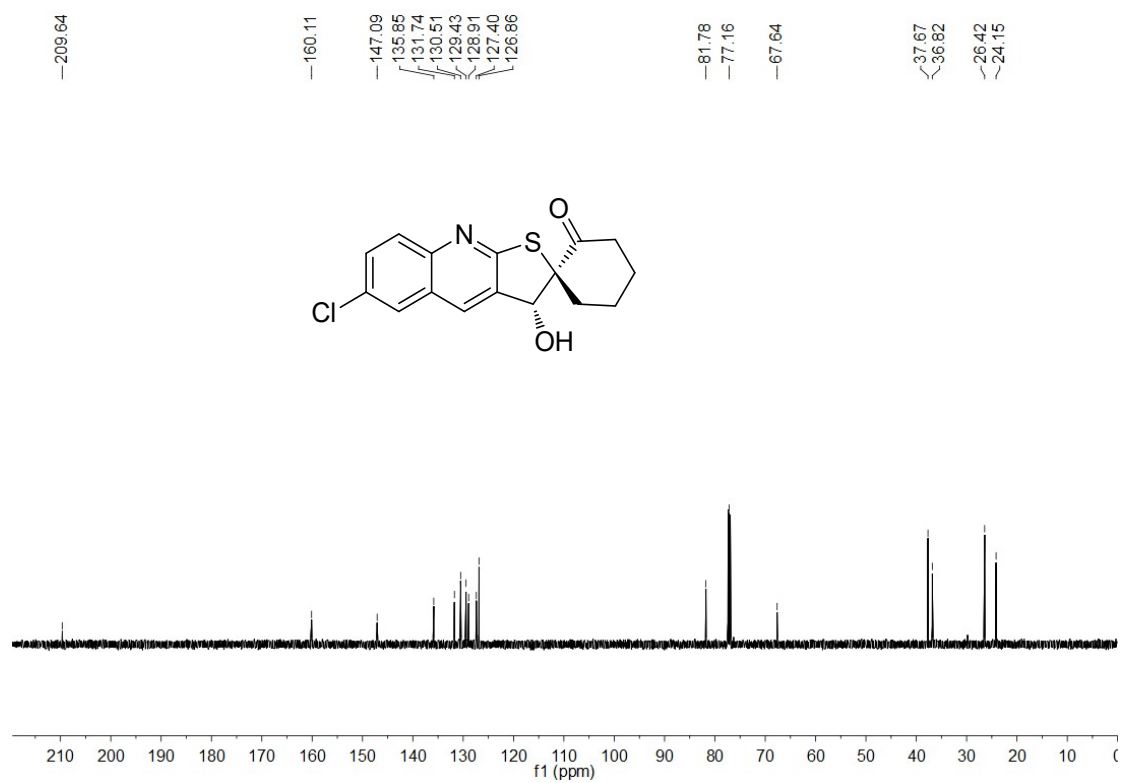
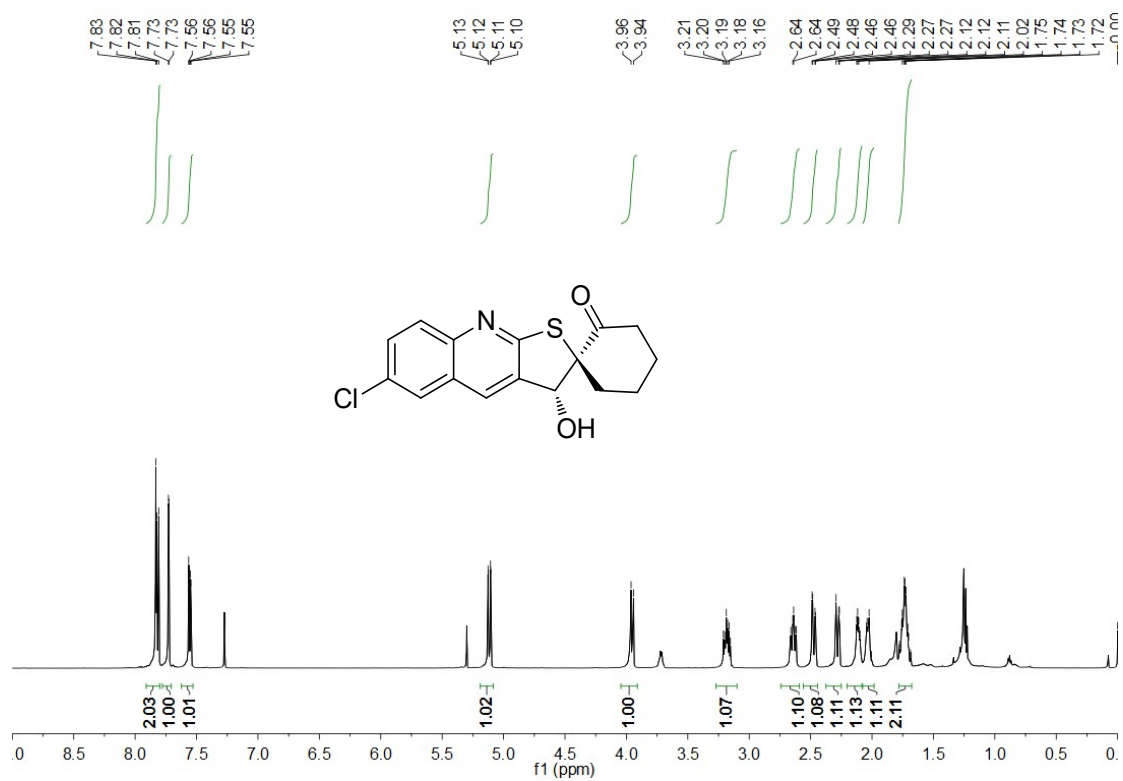
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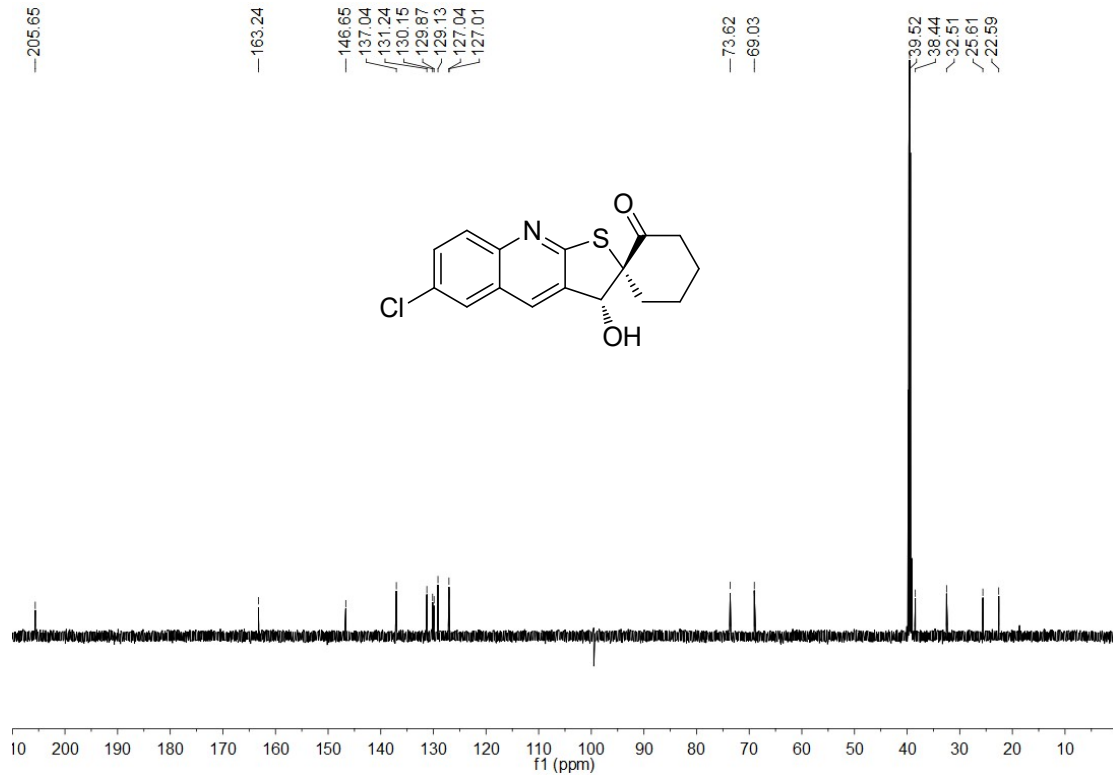
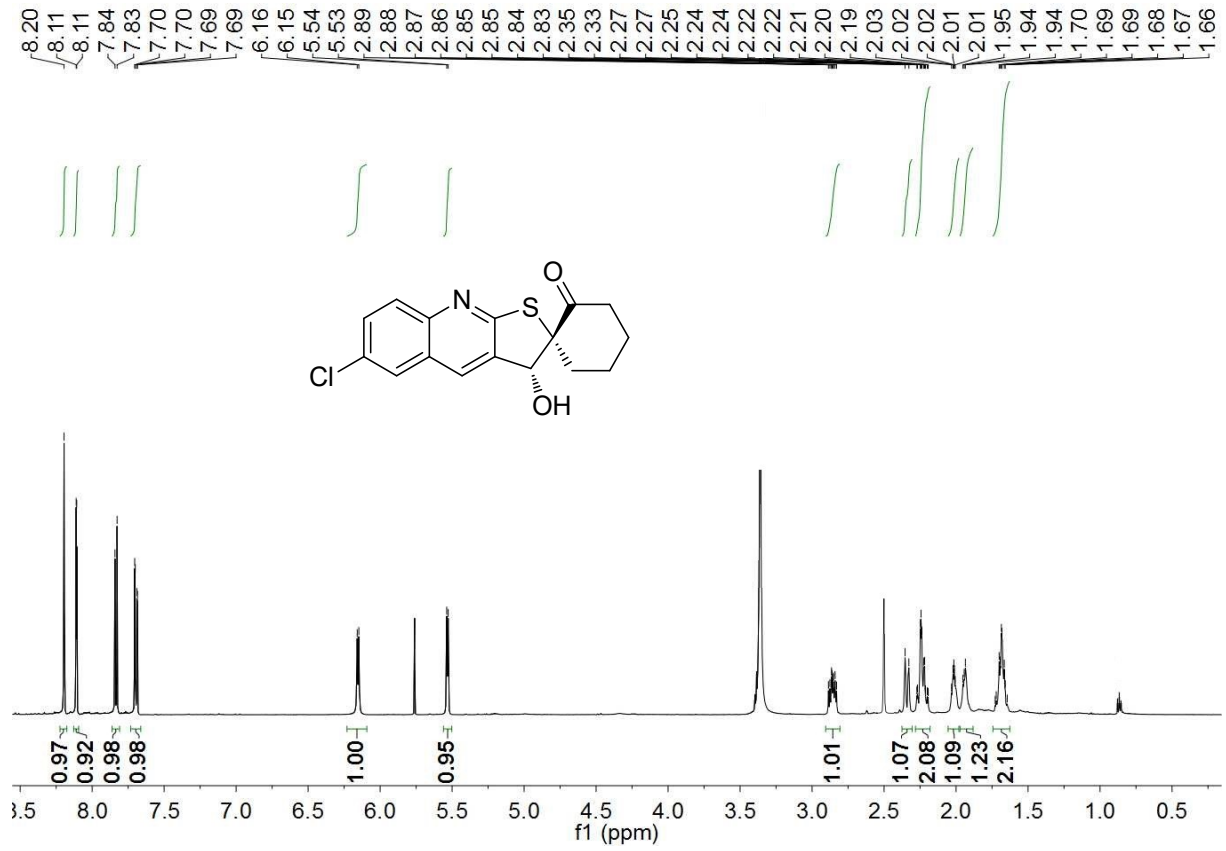
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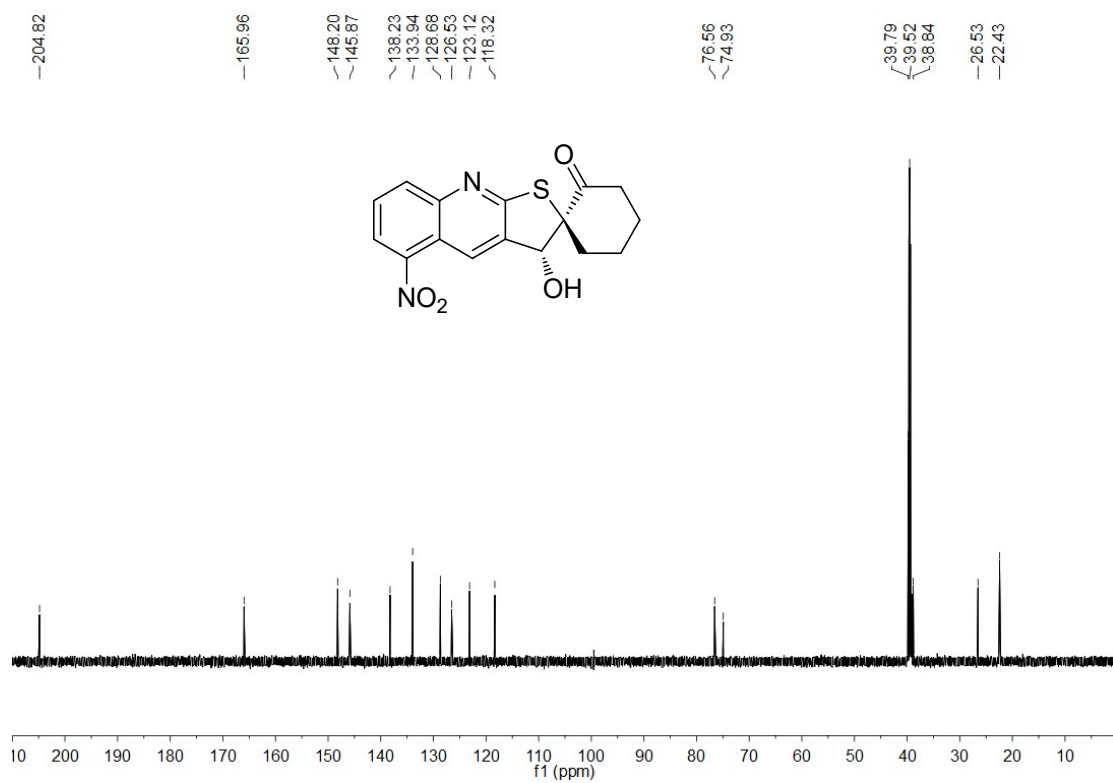
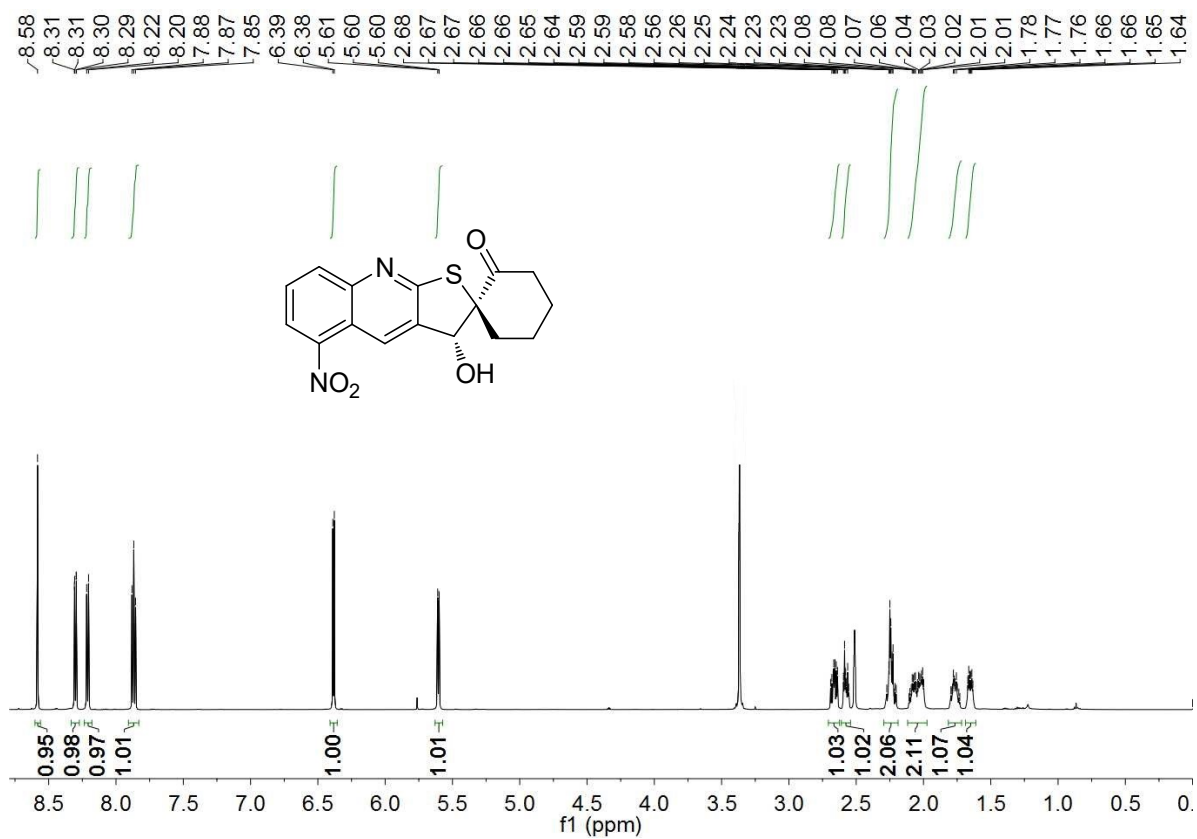
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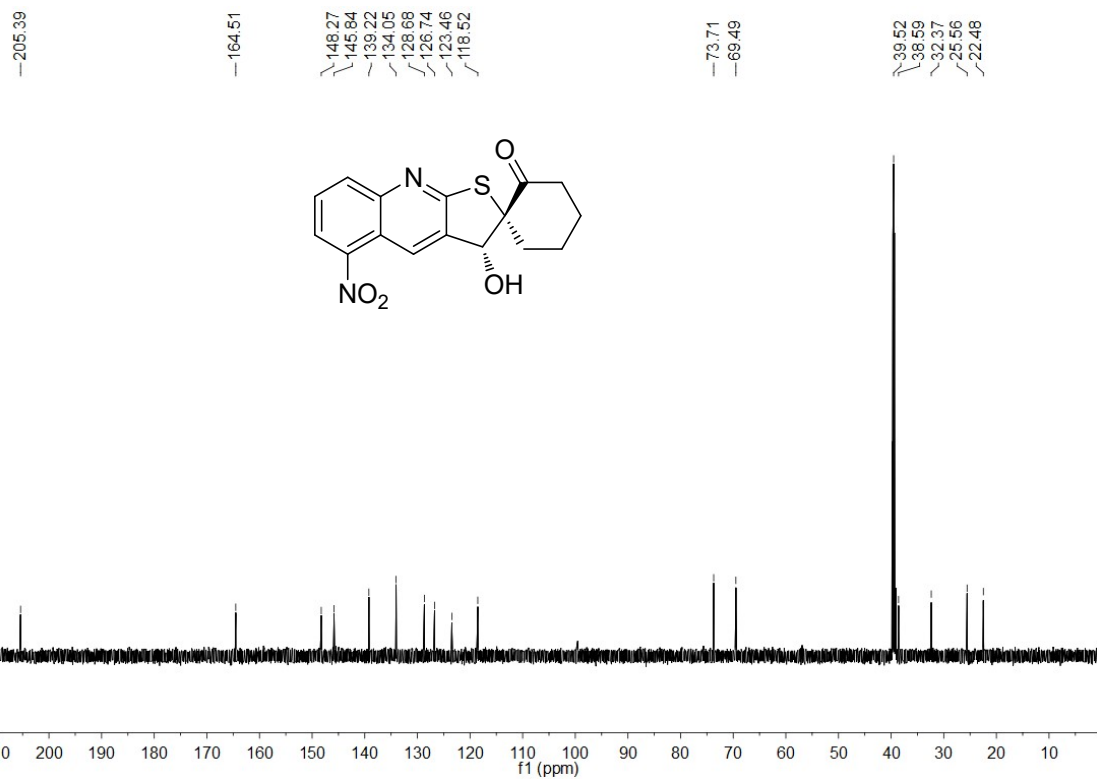
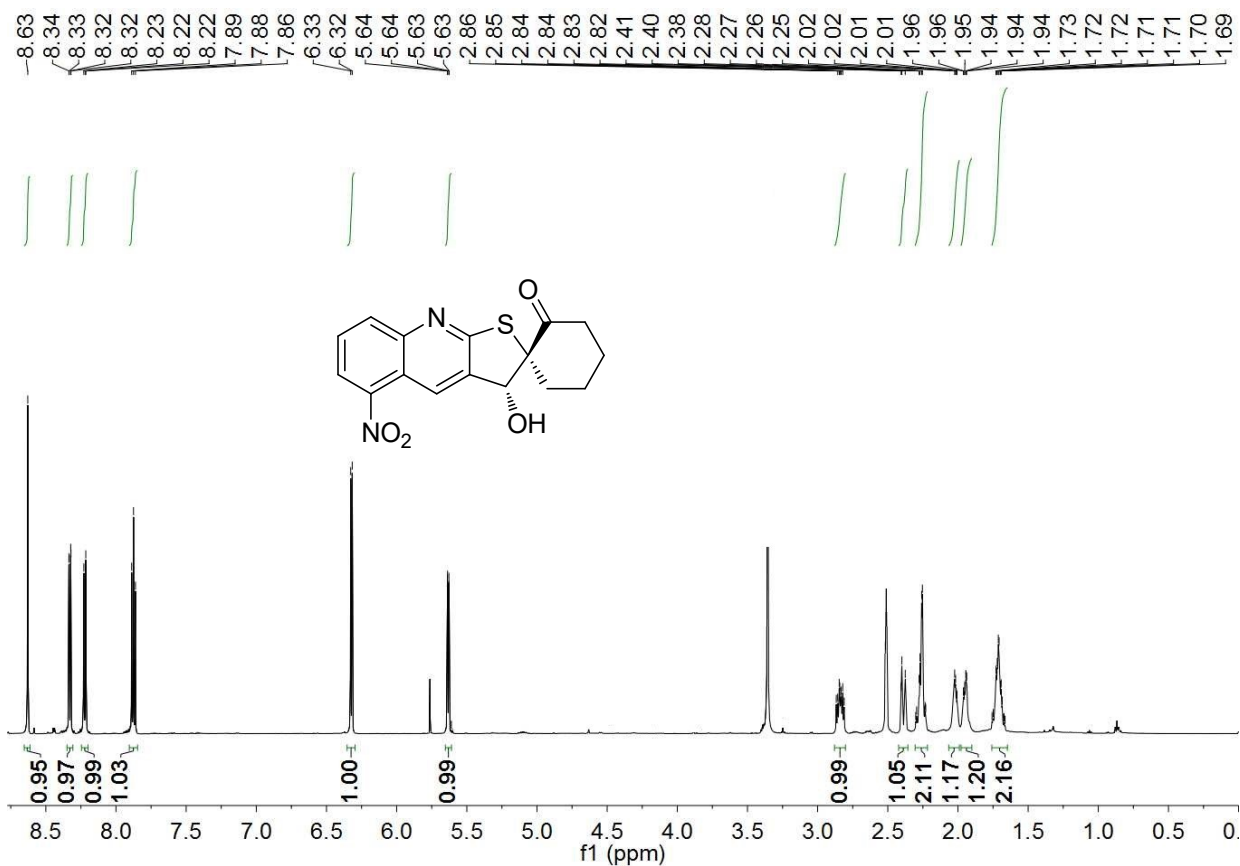
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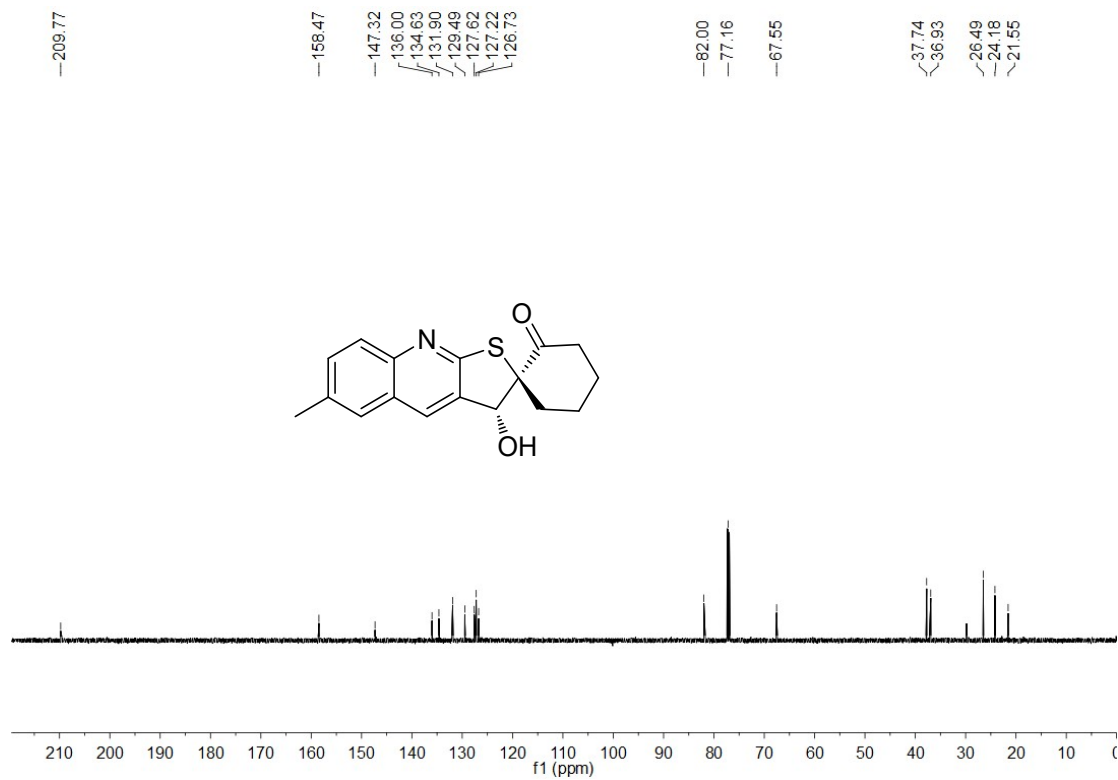
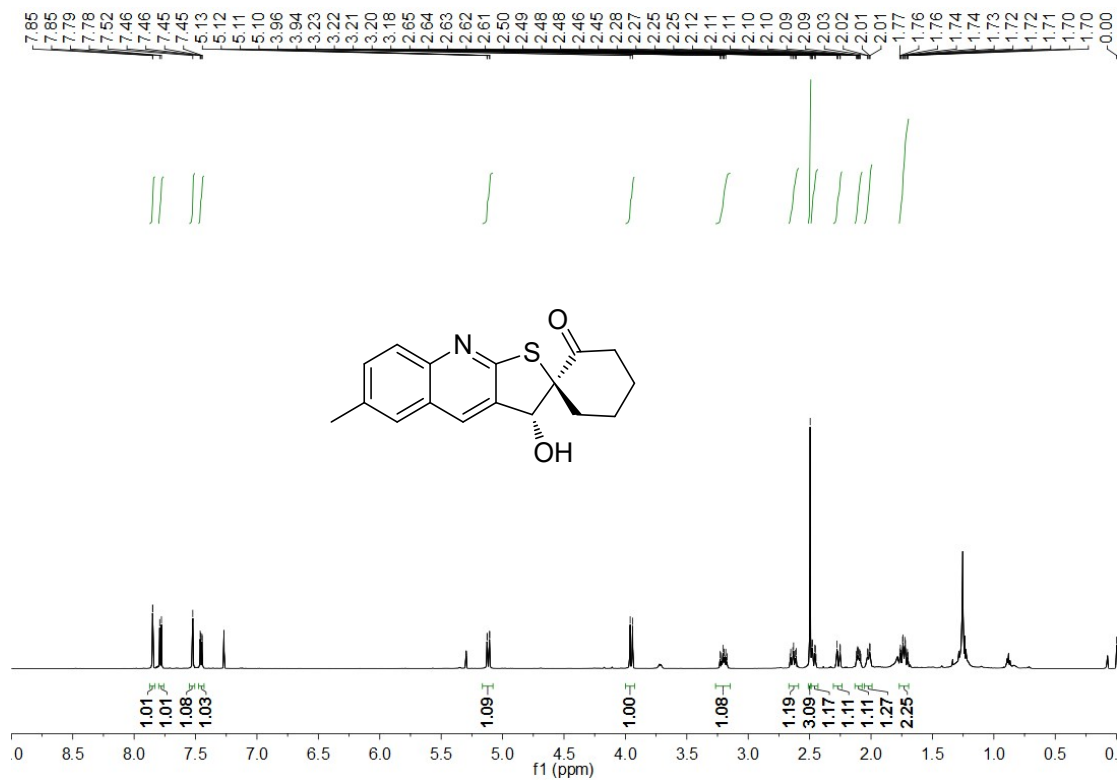
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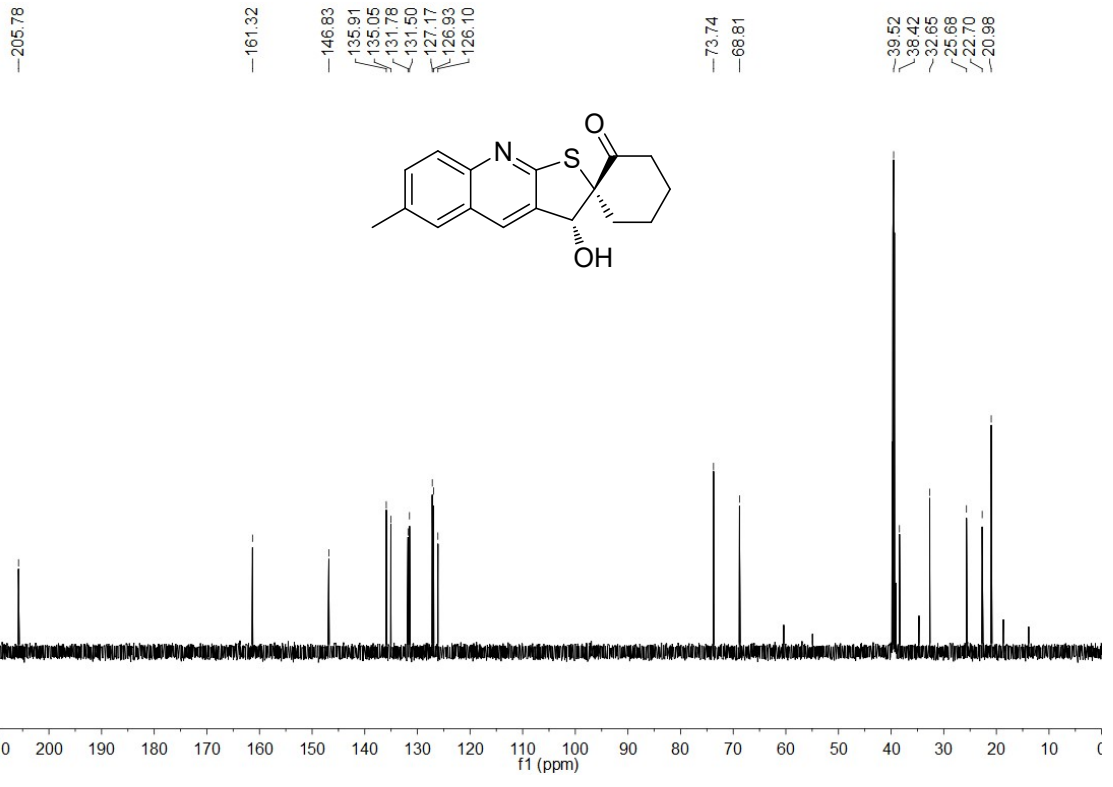
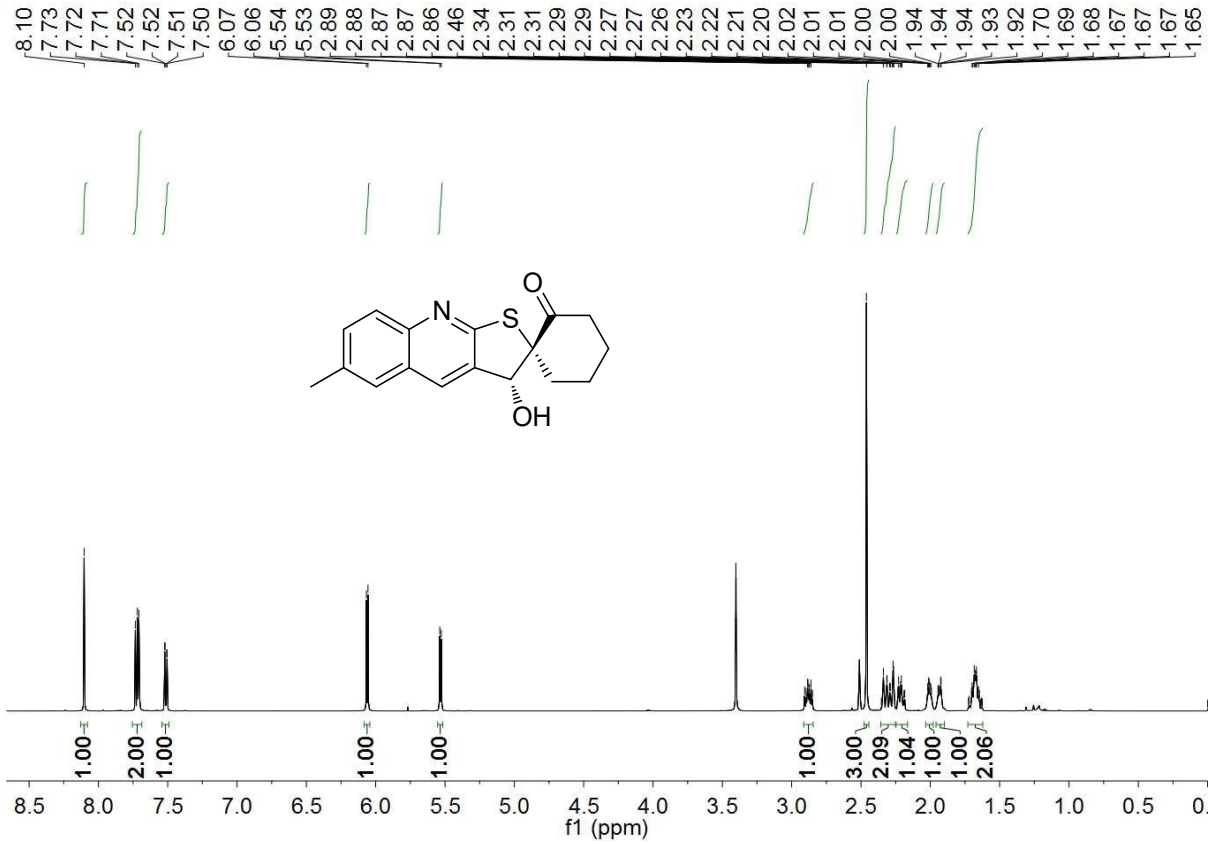
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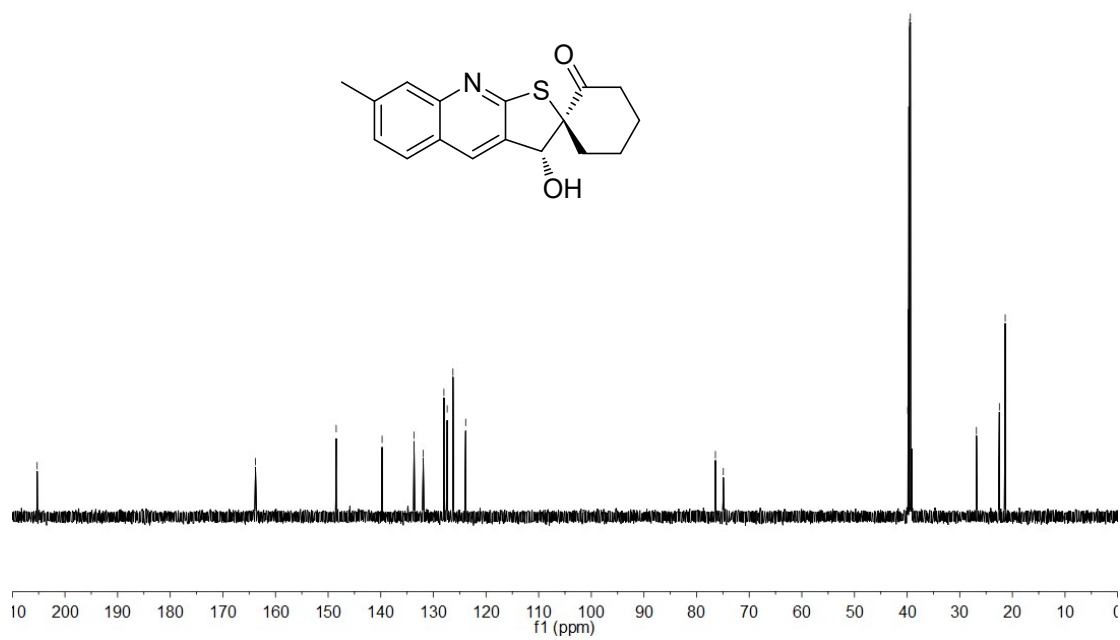
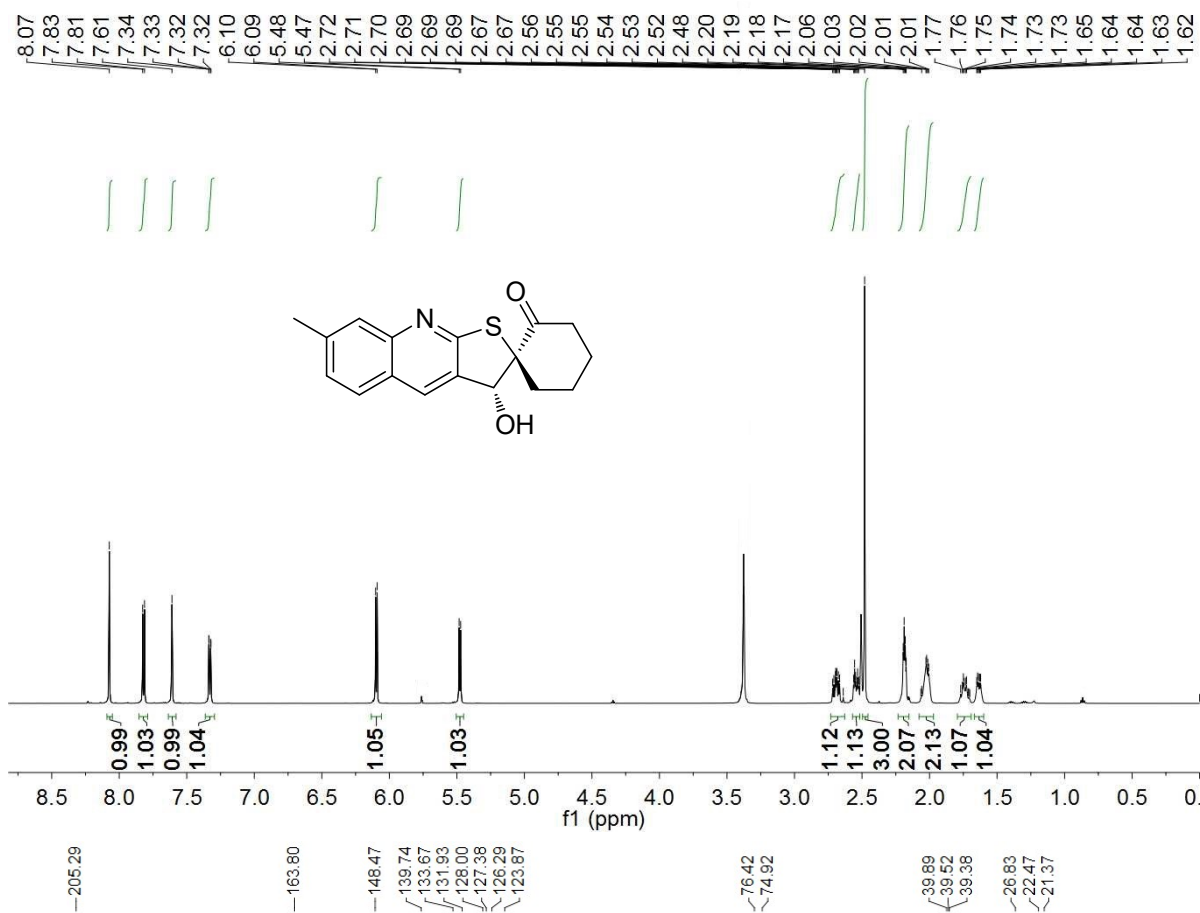
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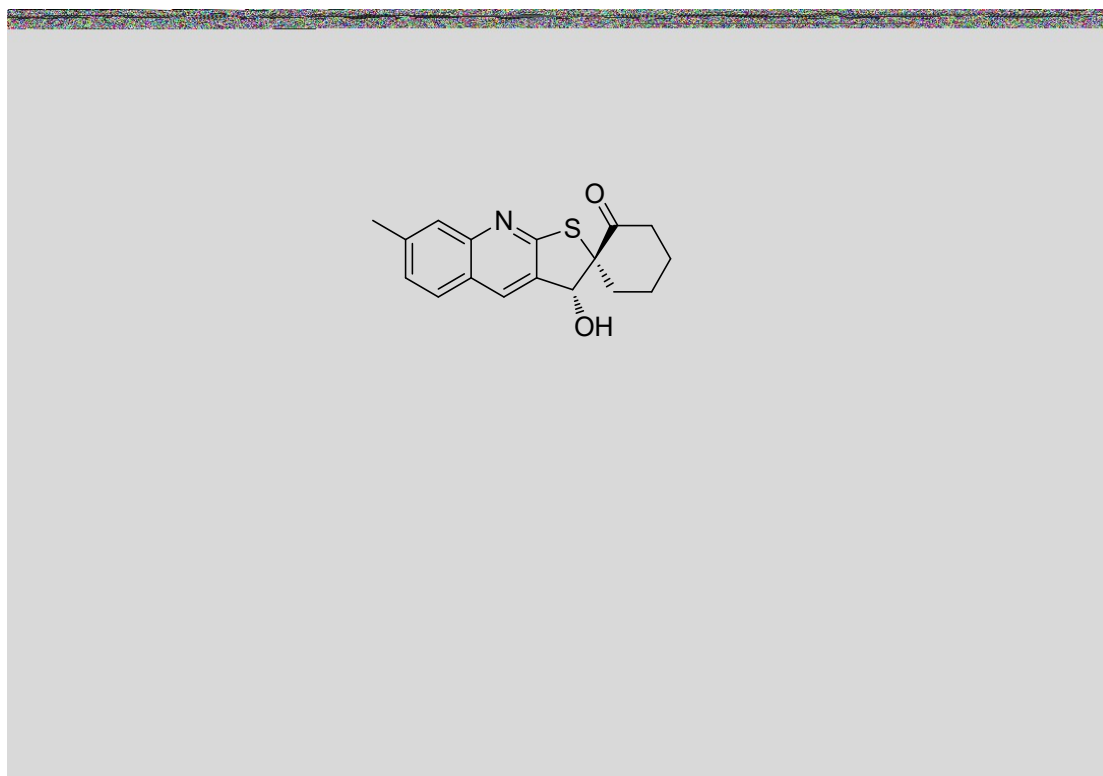
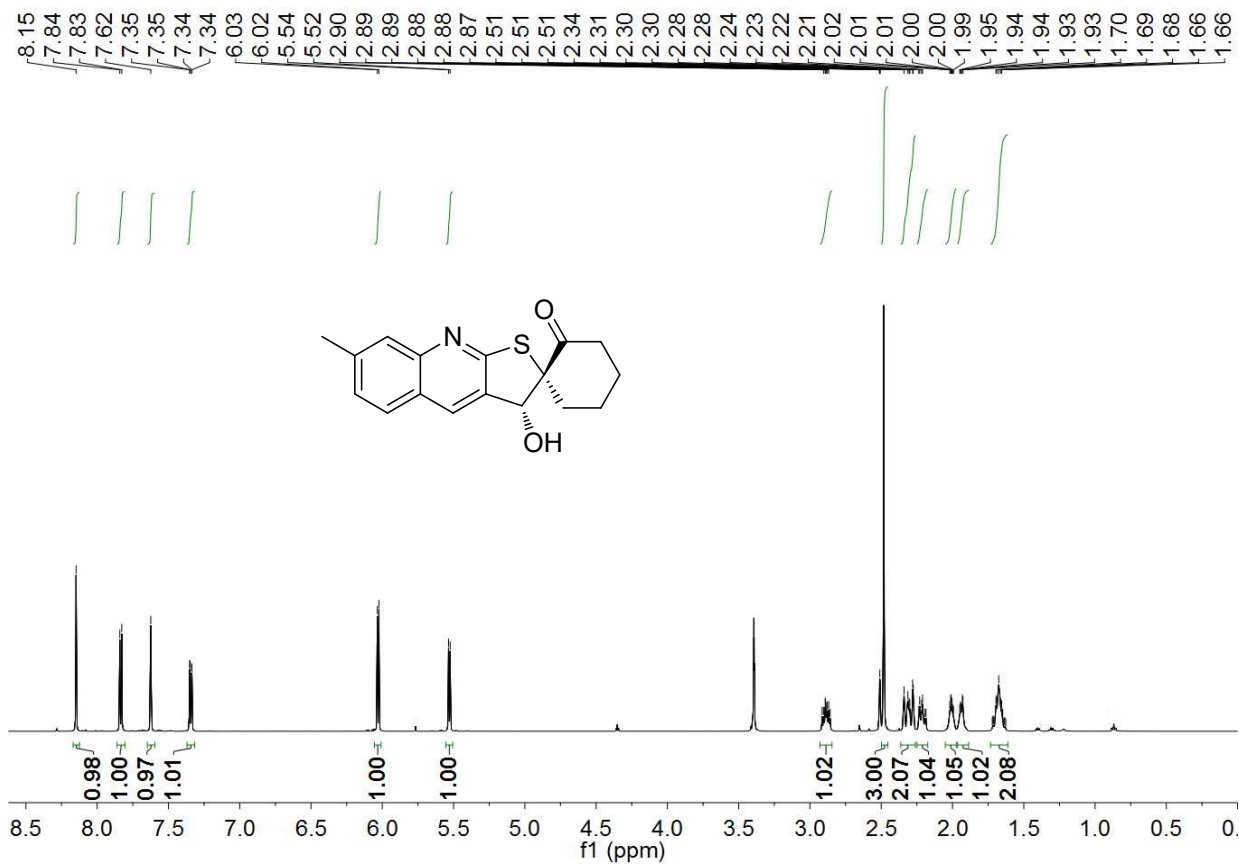
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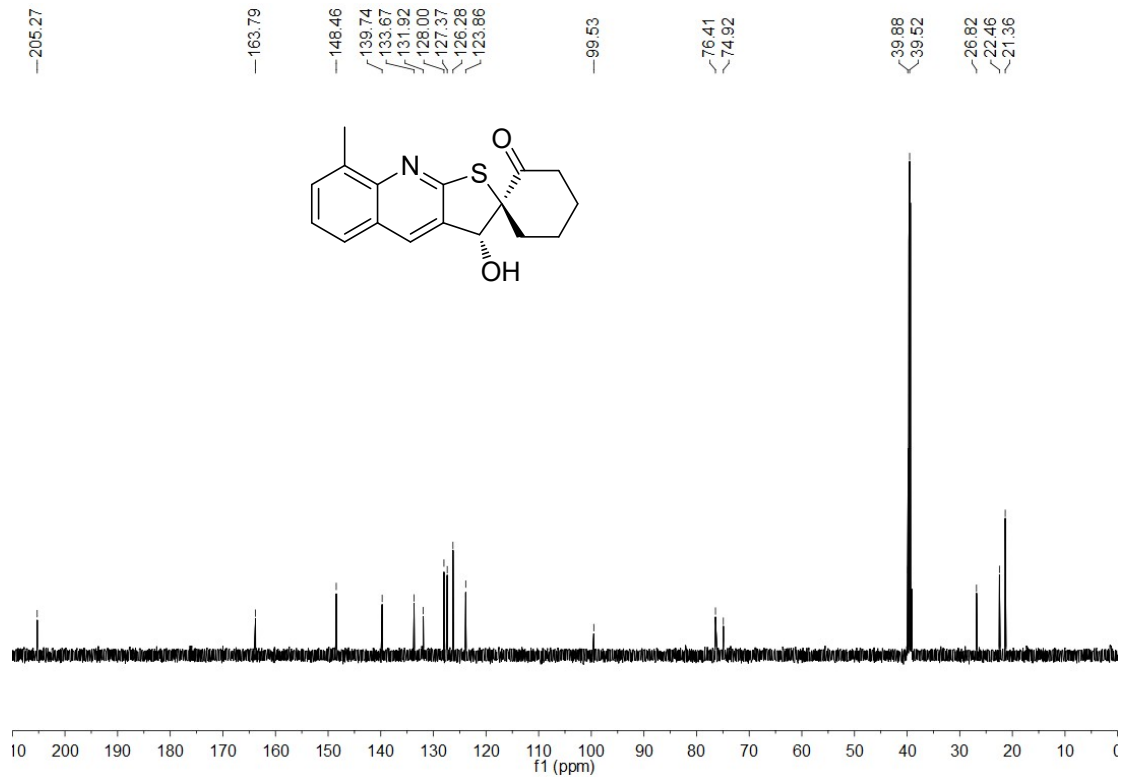
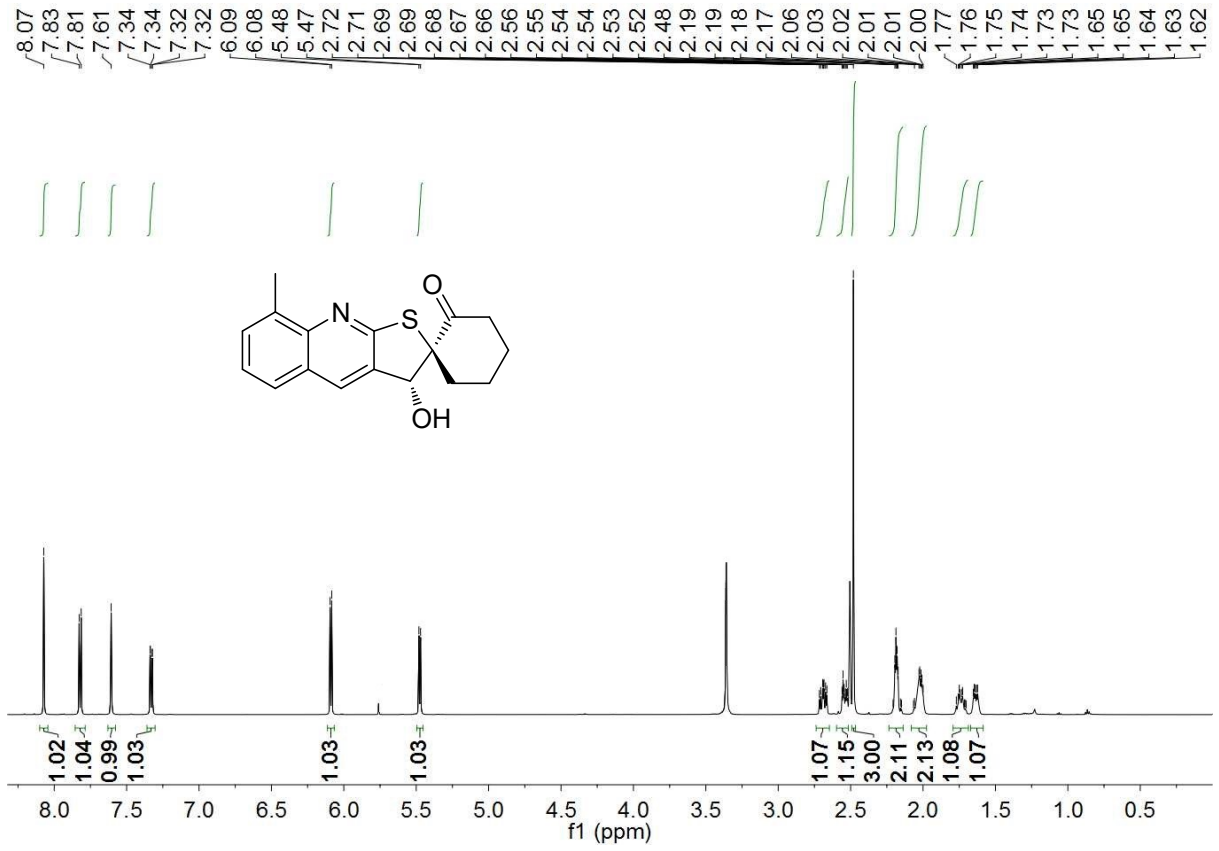
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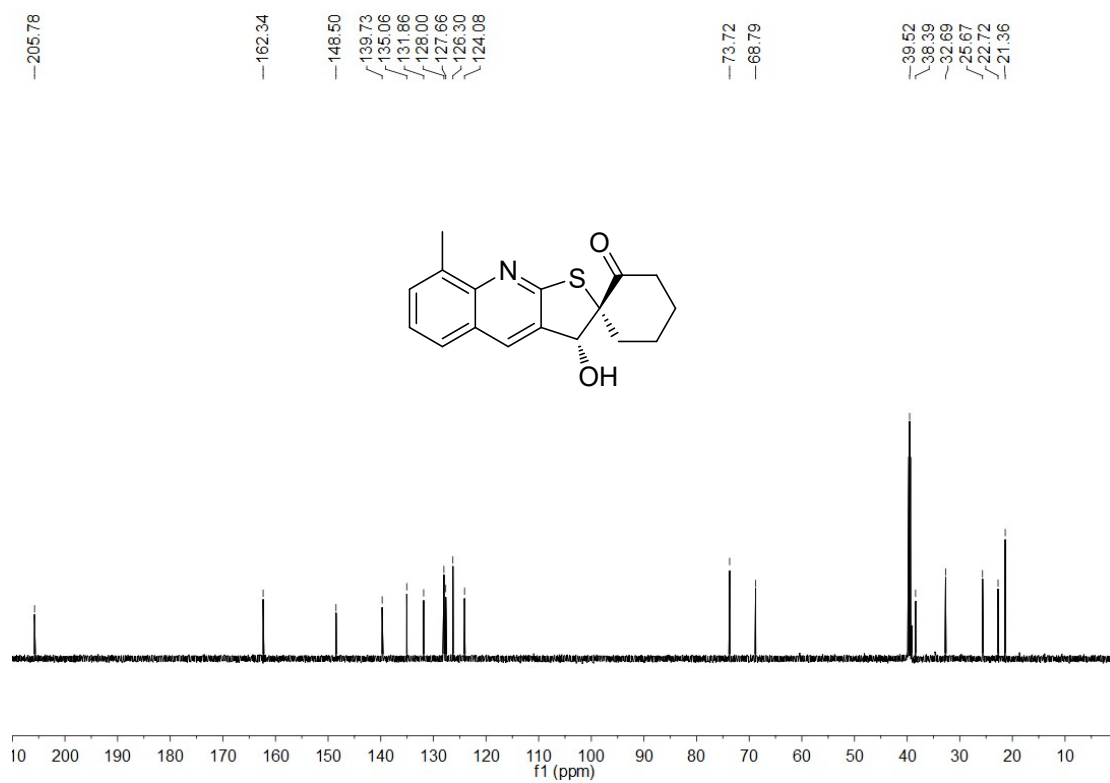
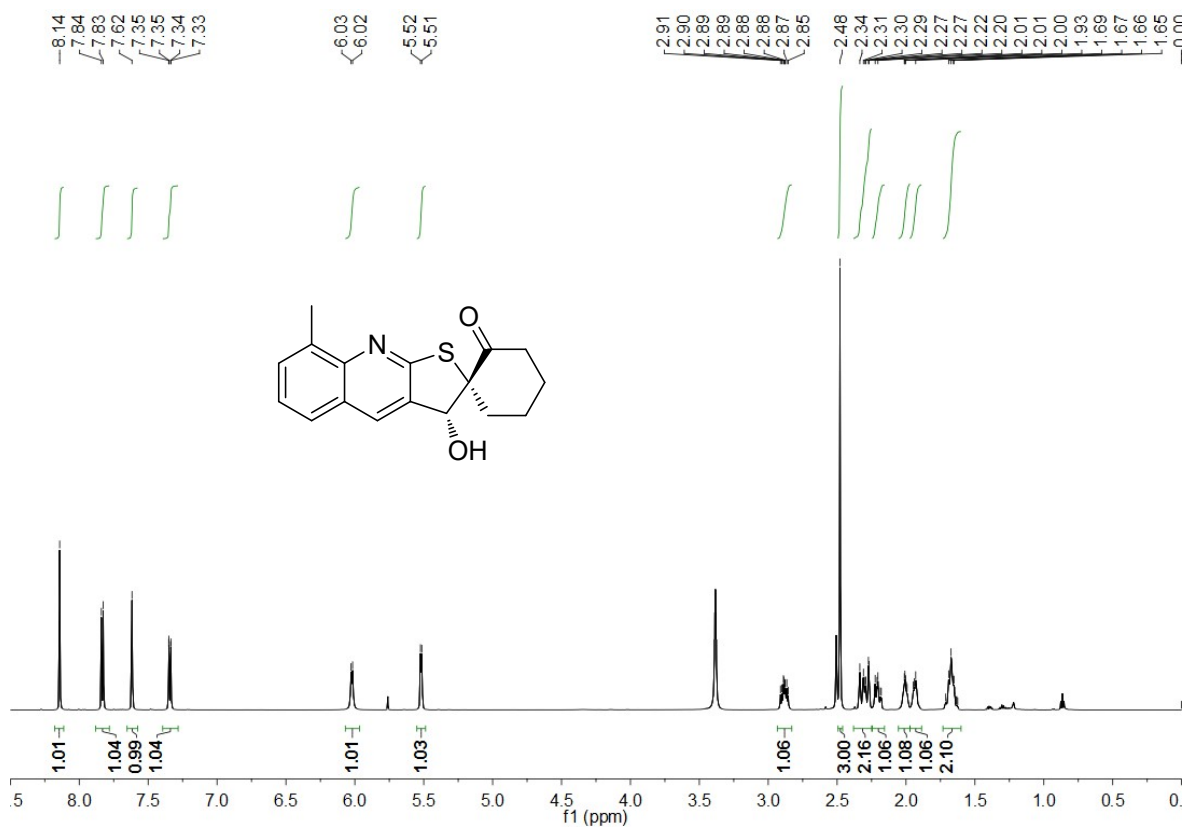
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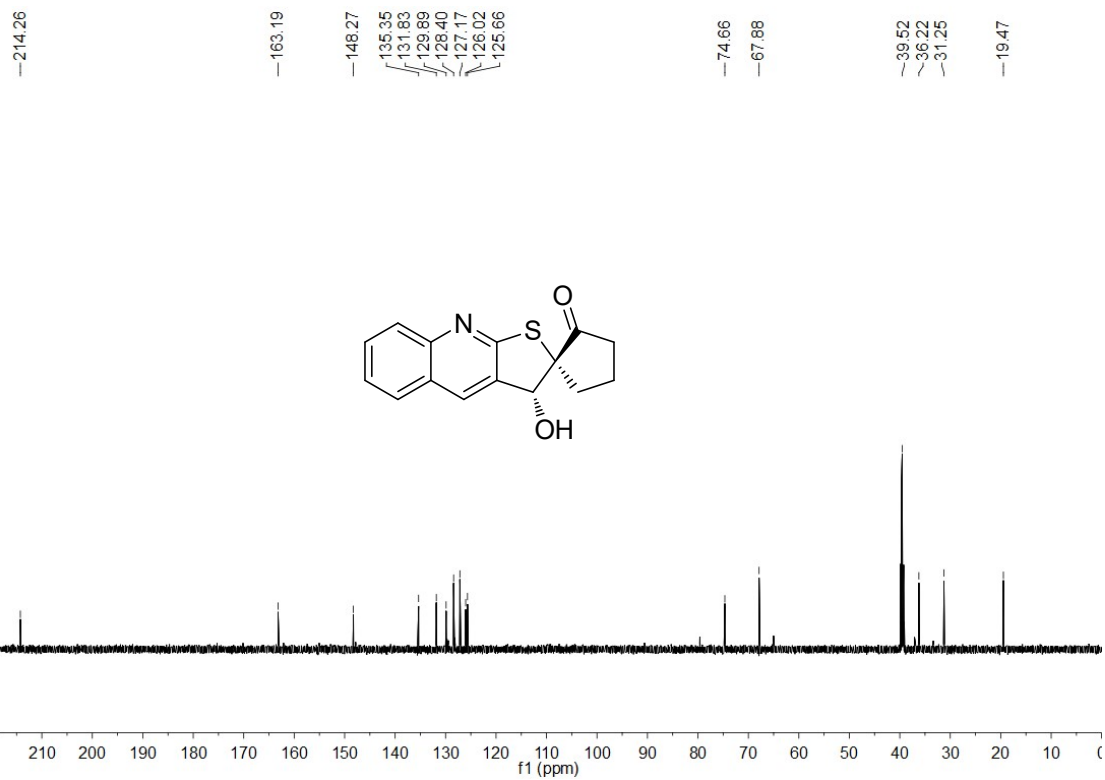
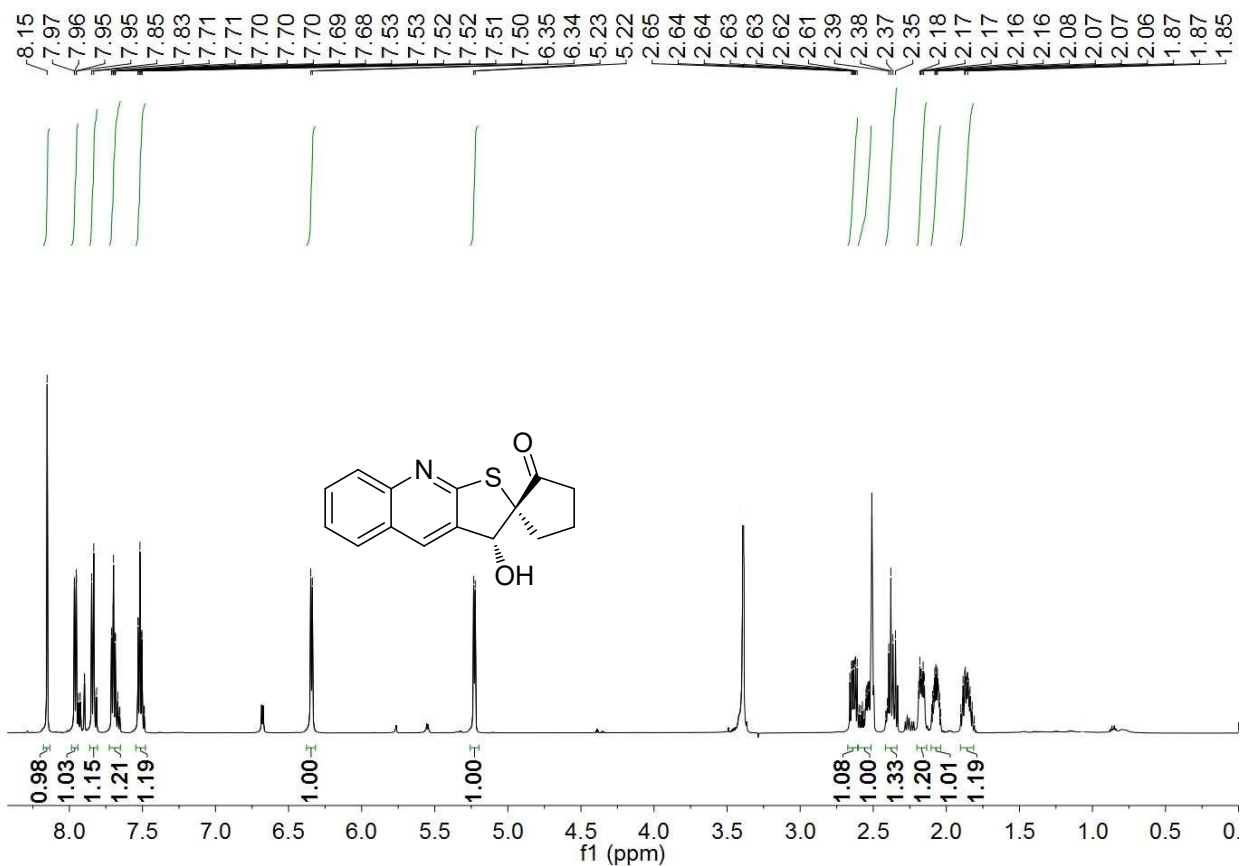
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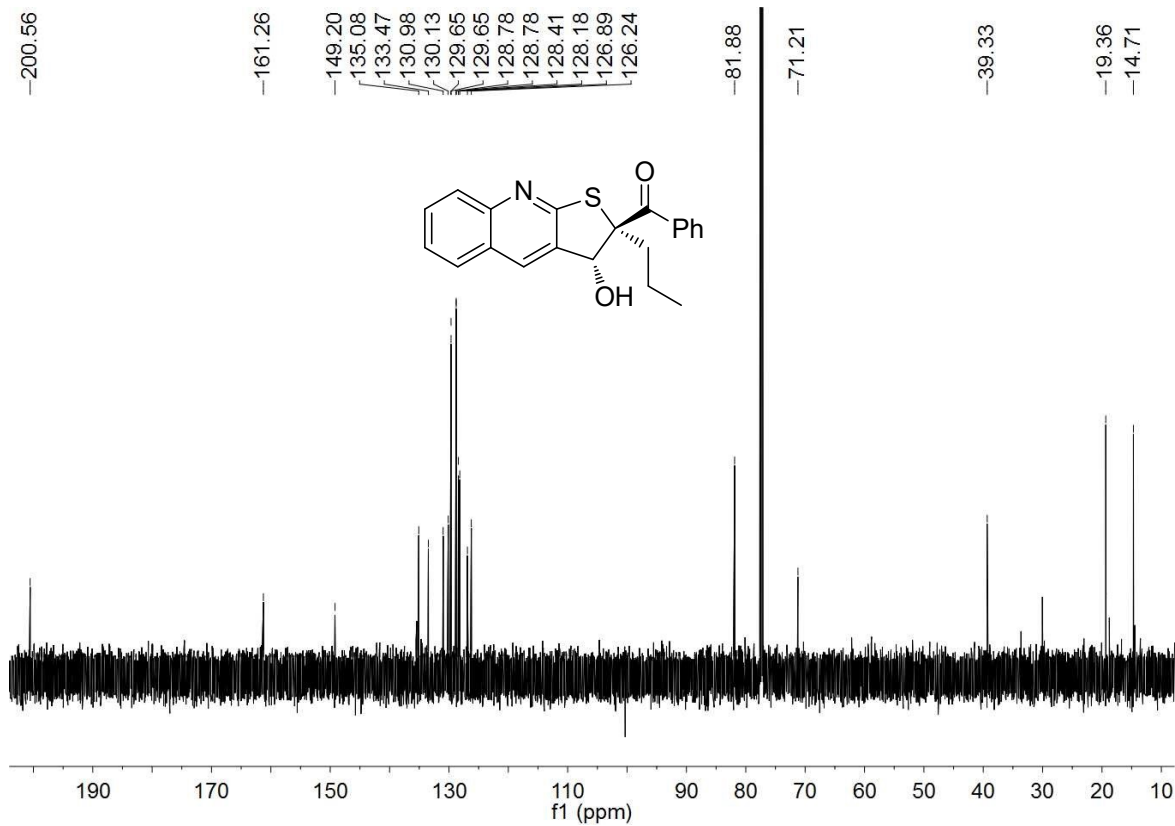
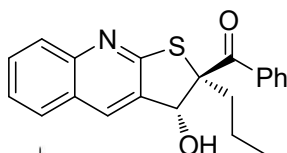
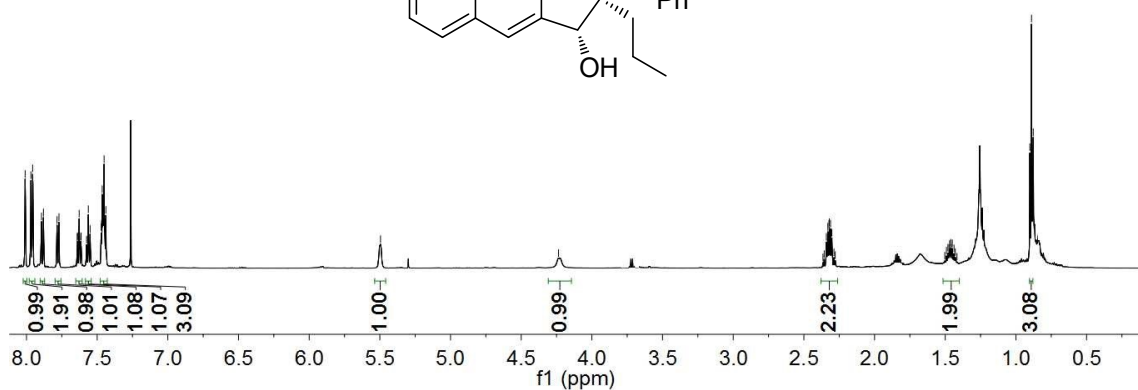
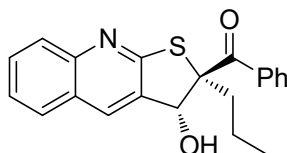
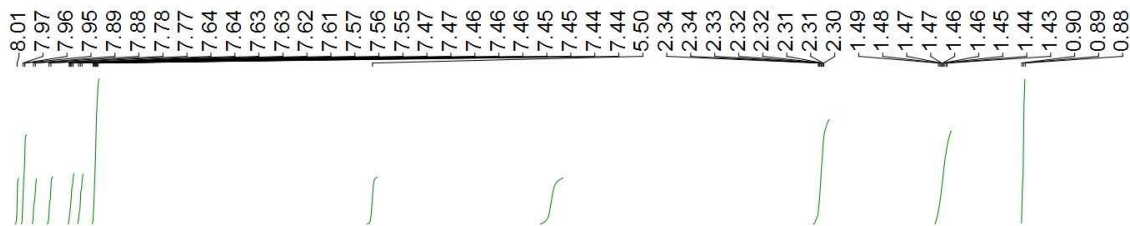
5'cf



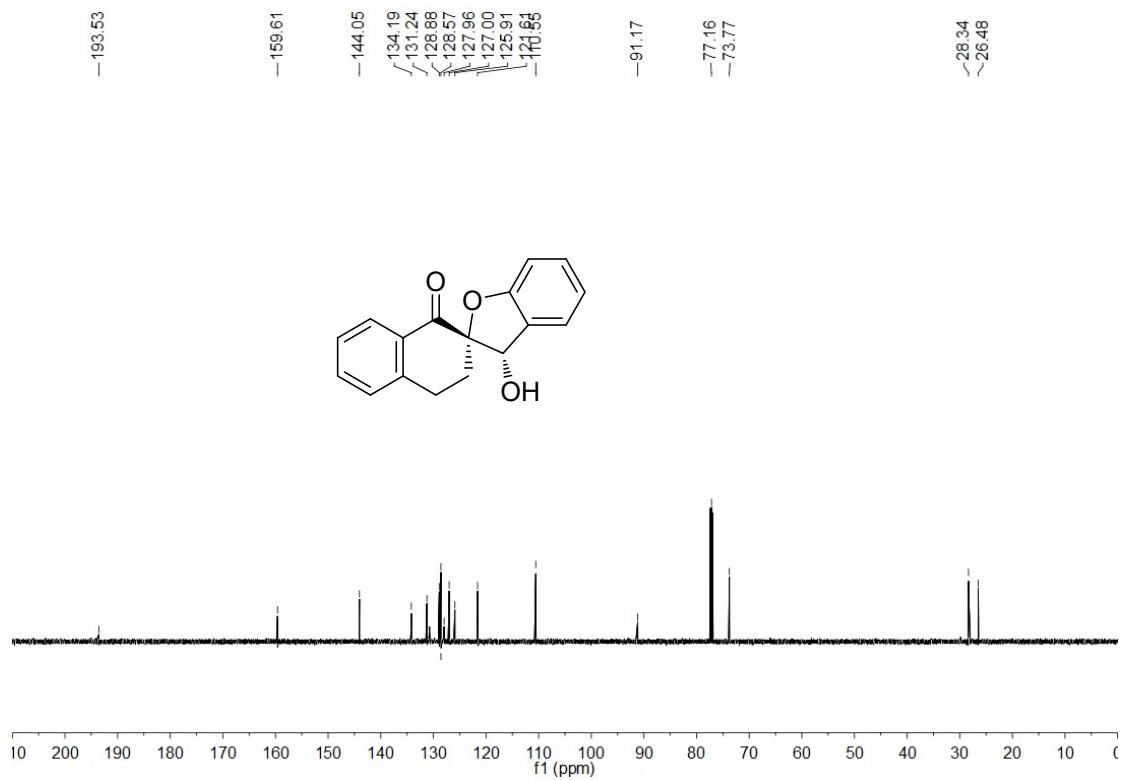
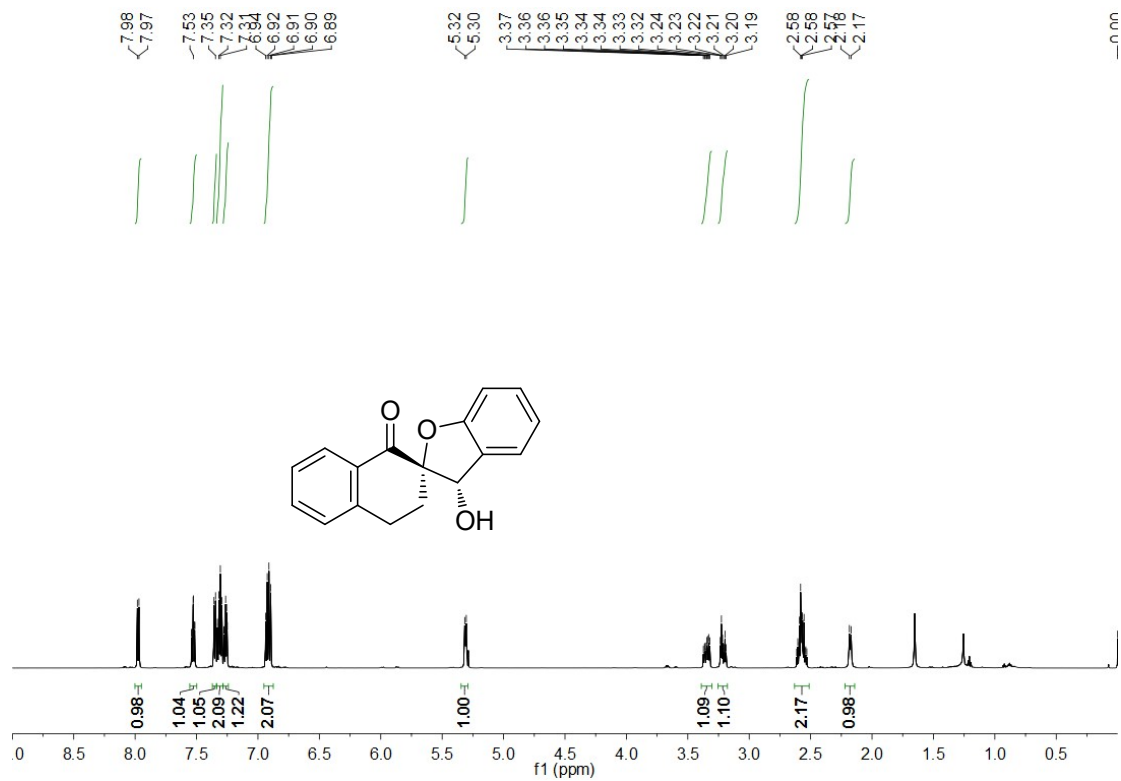
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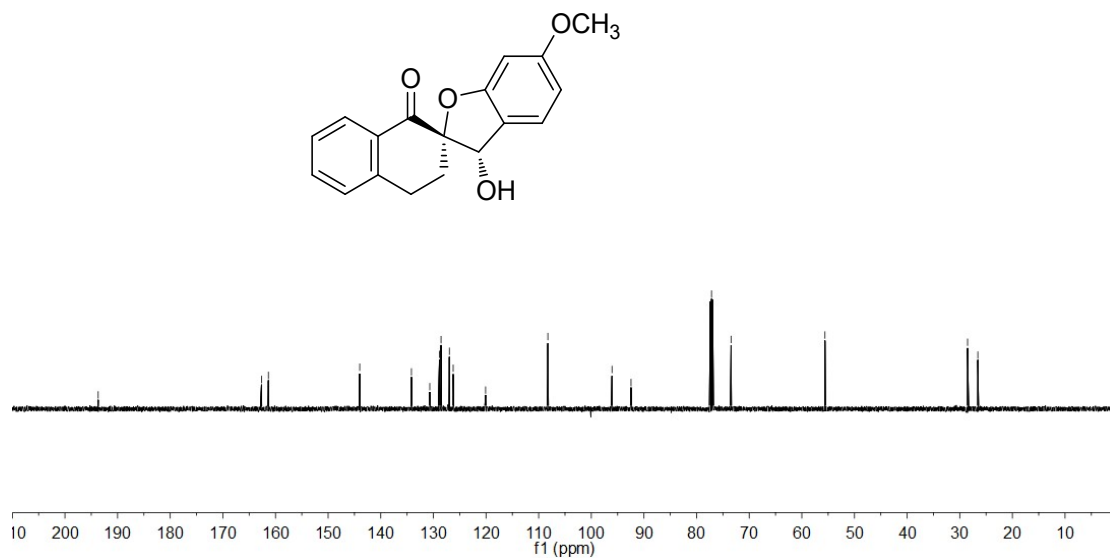
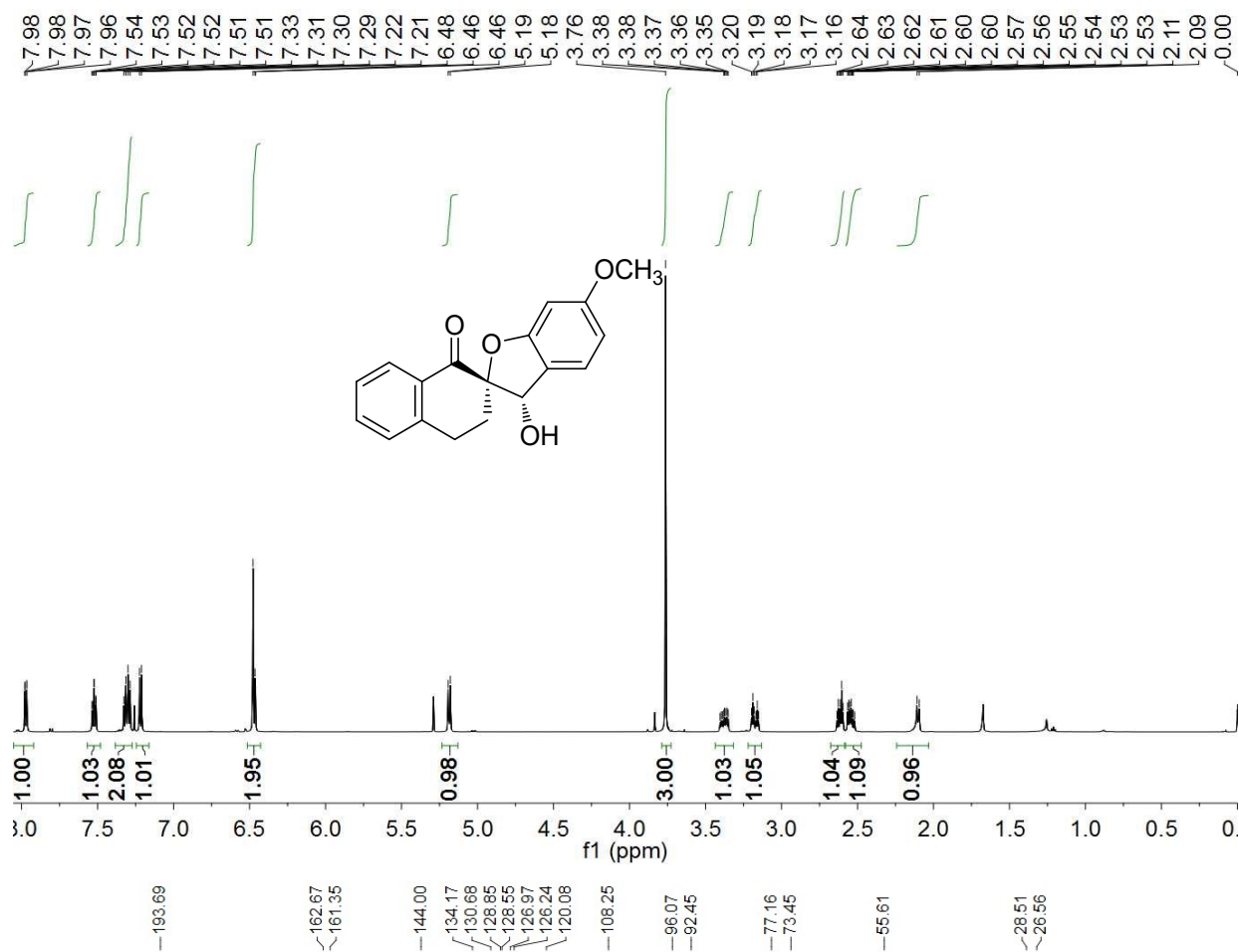
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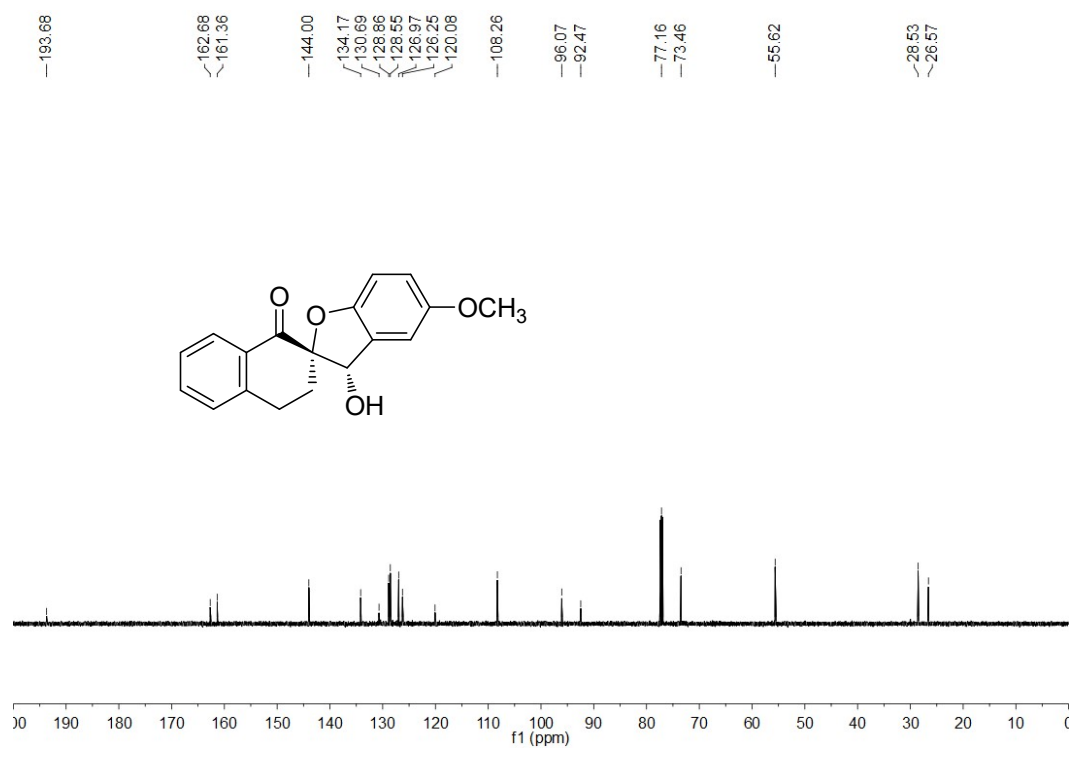
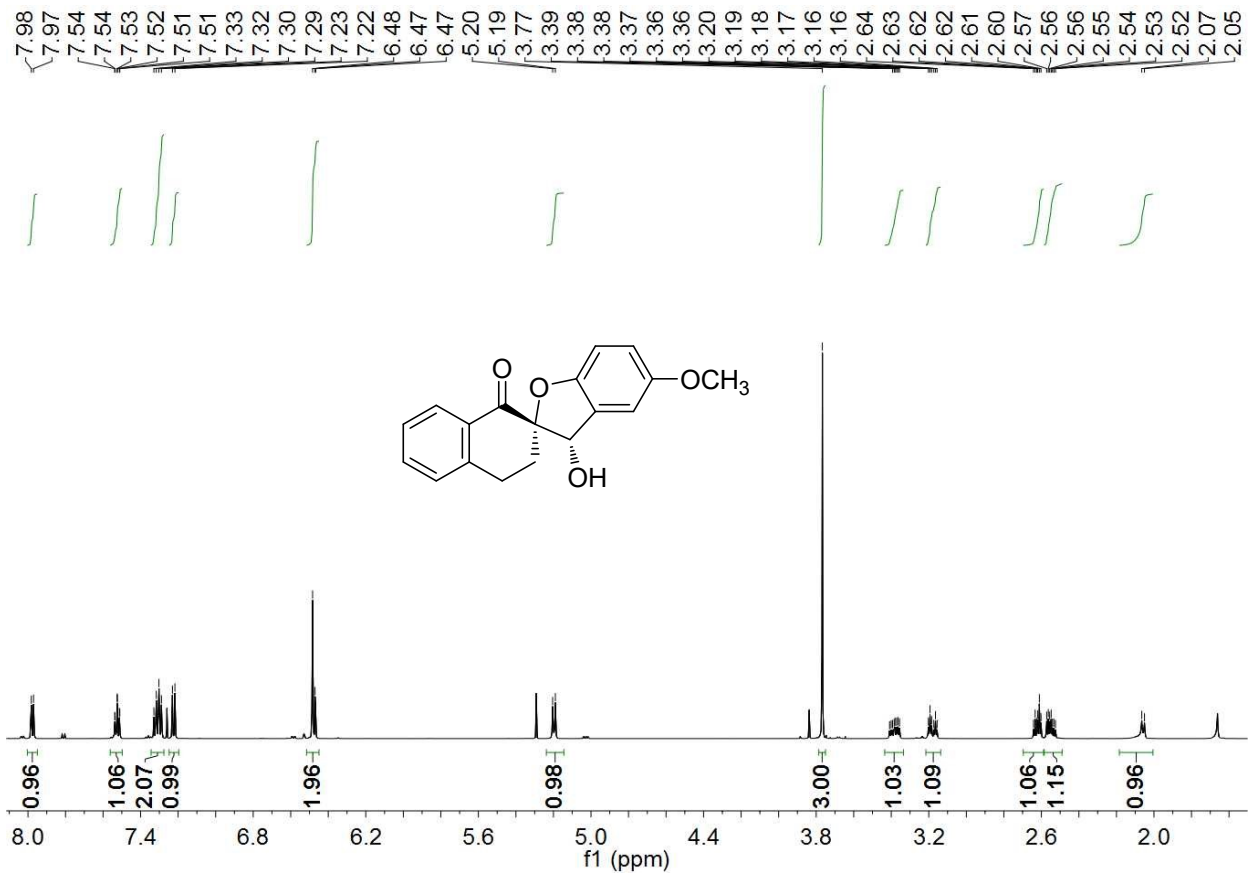
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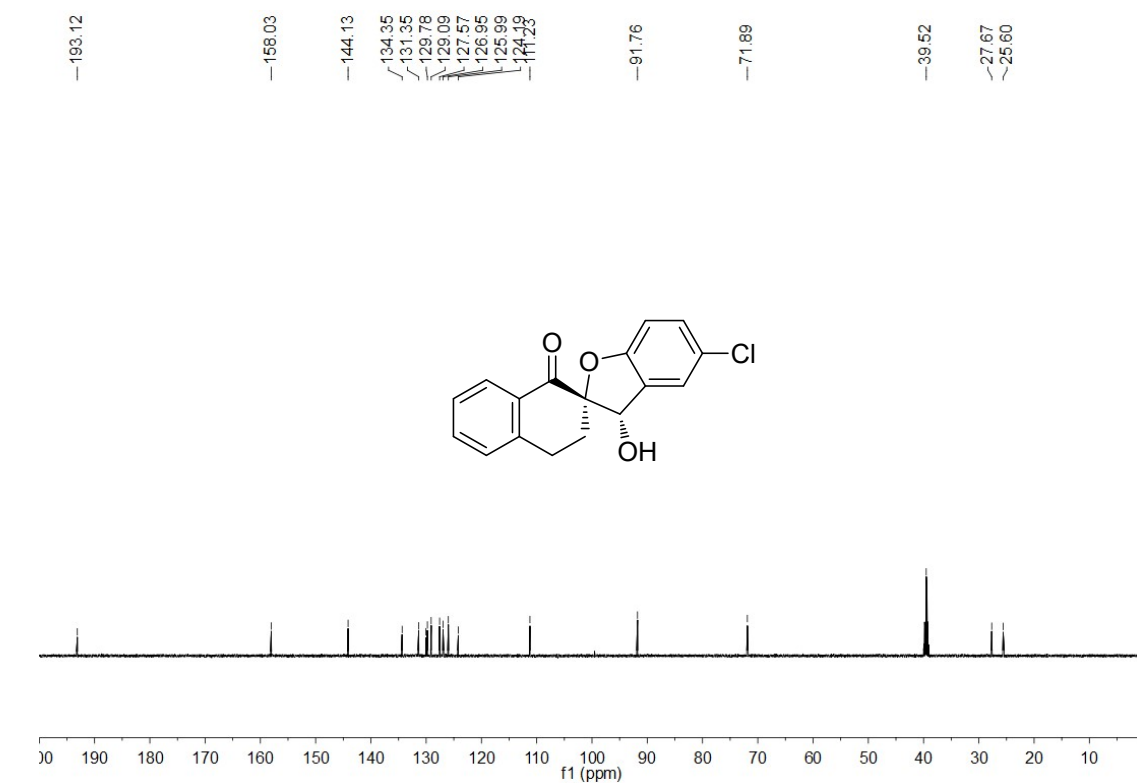
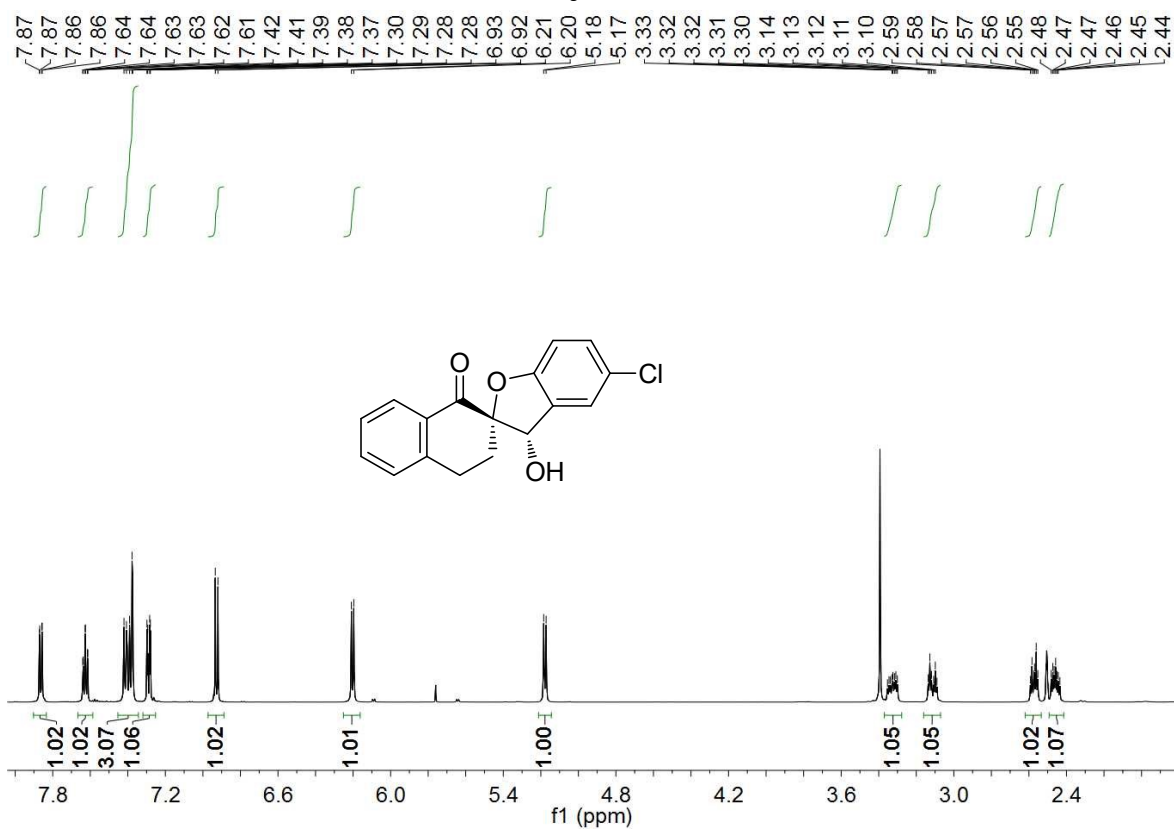
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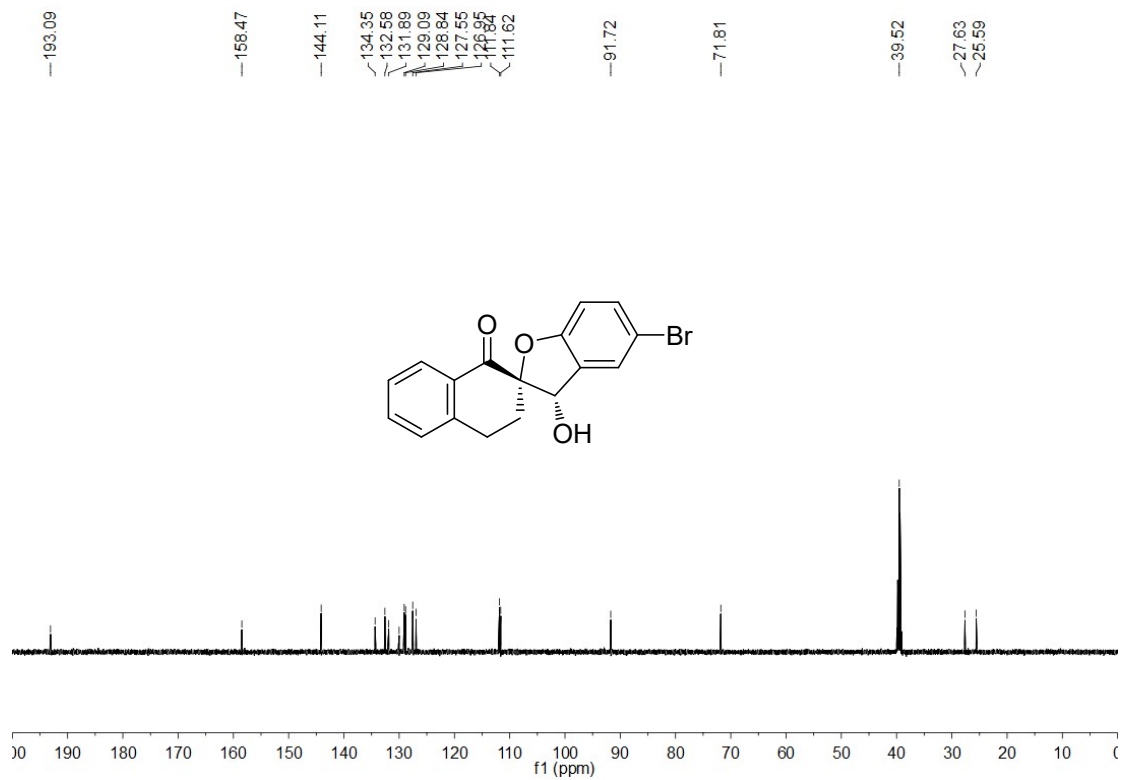
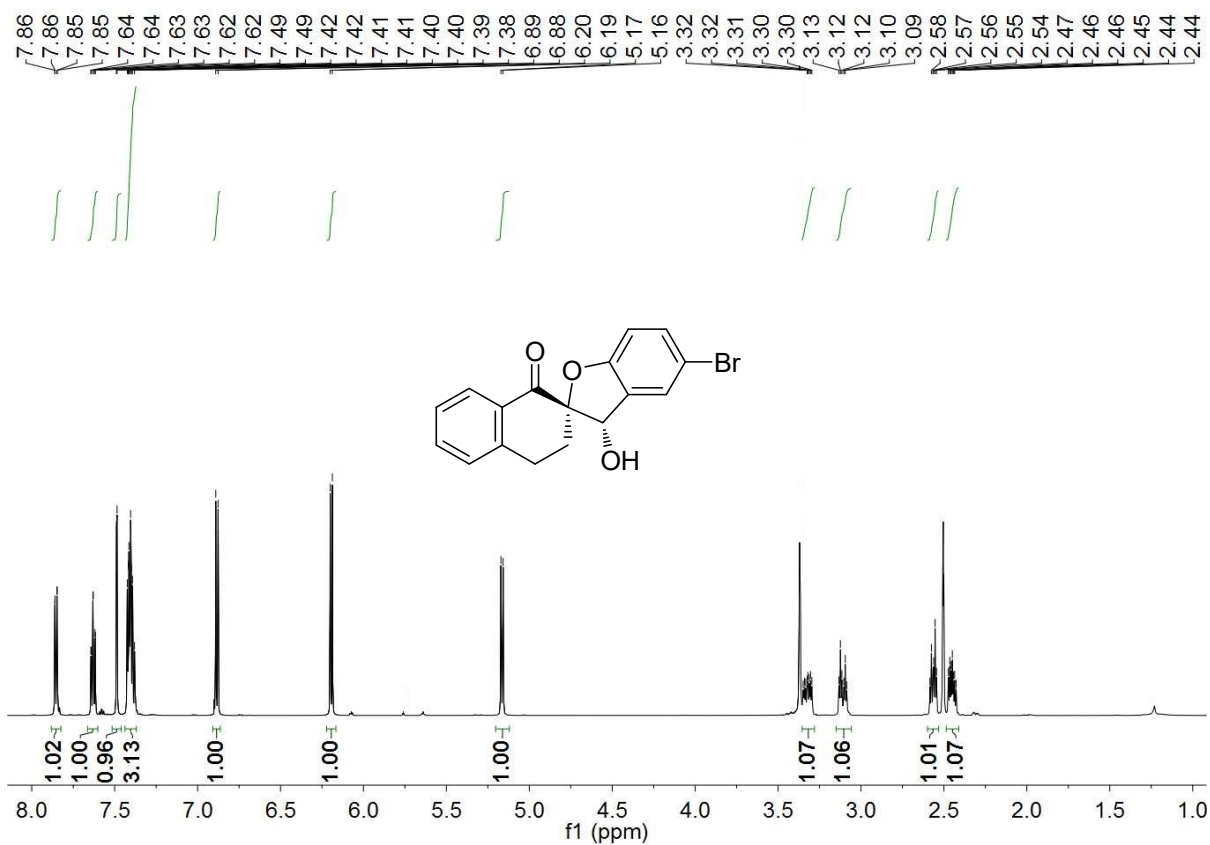
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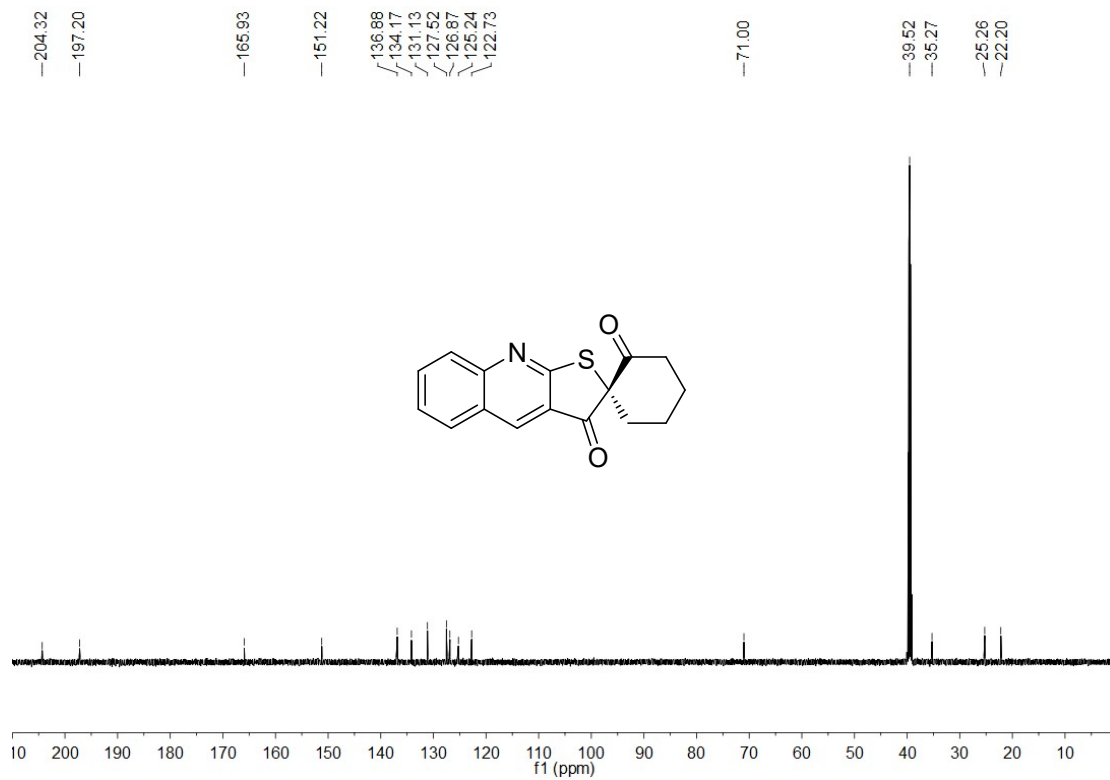
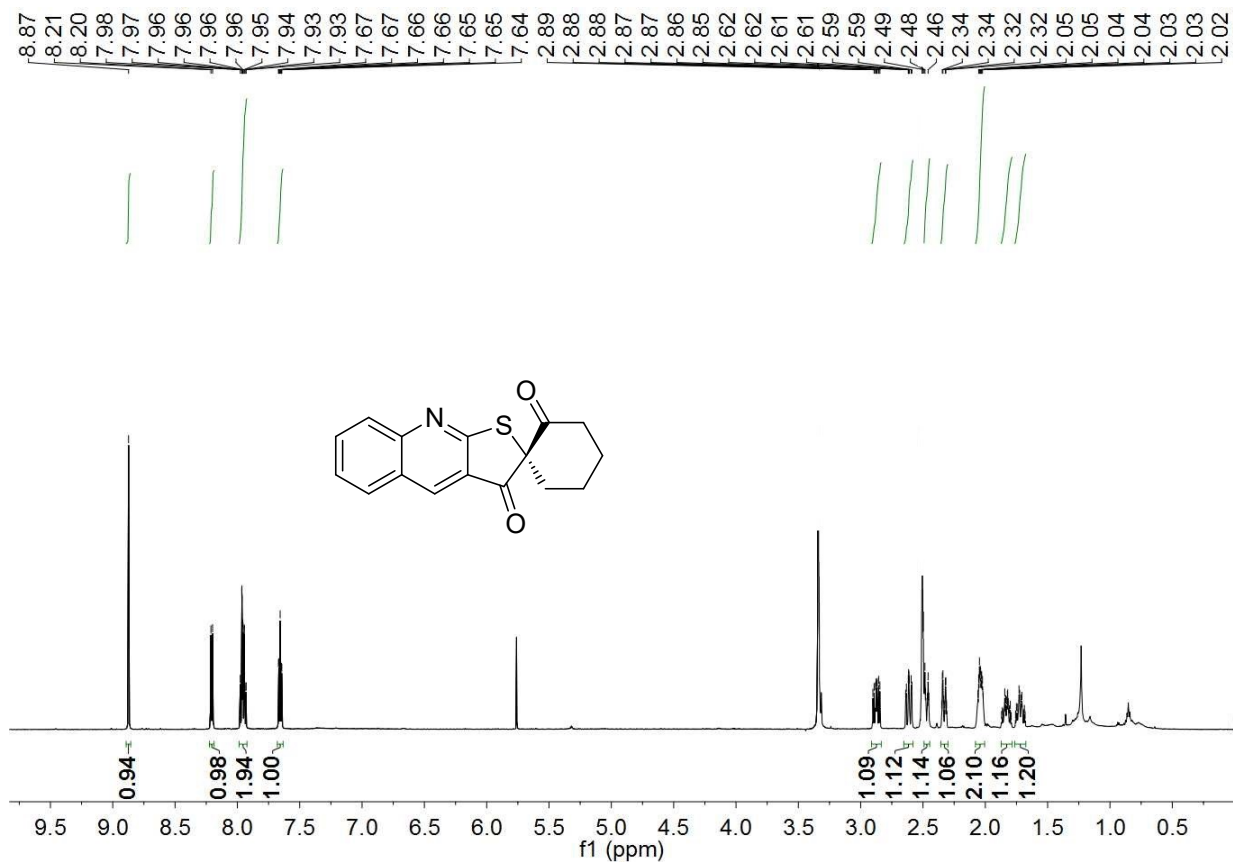
5aj



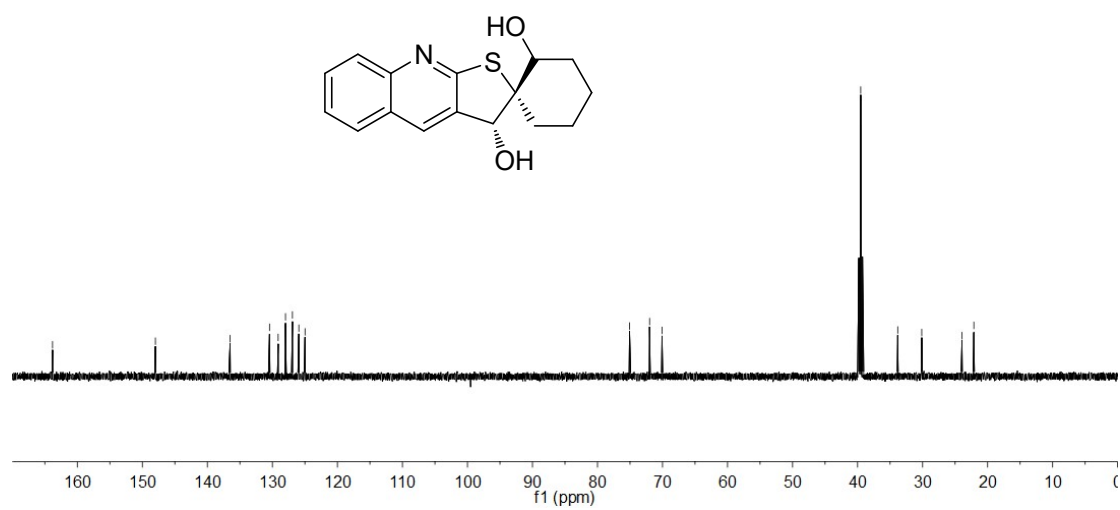
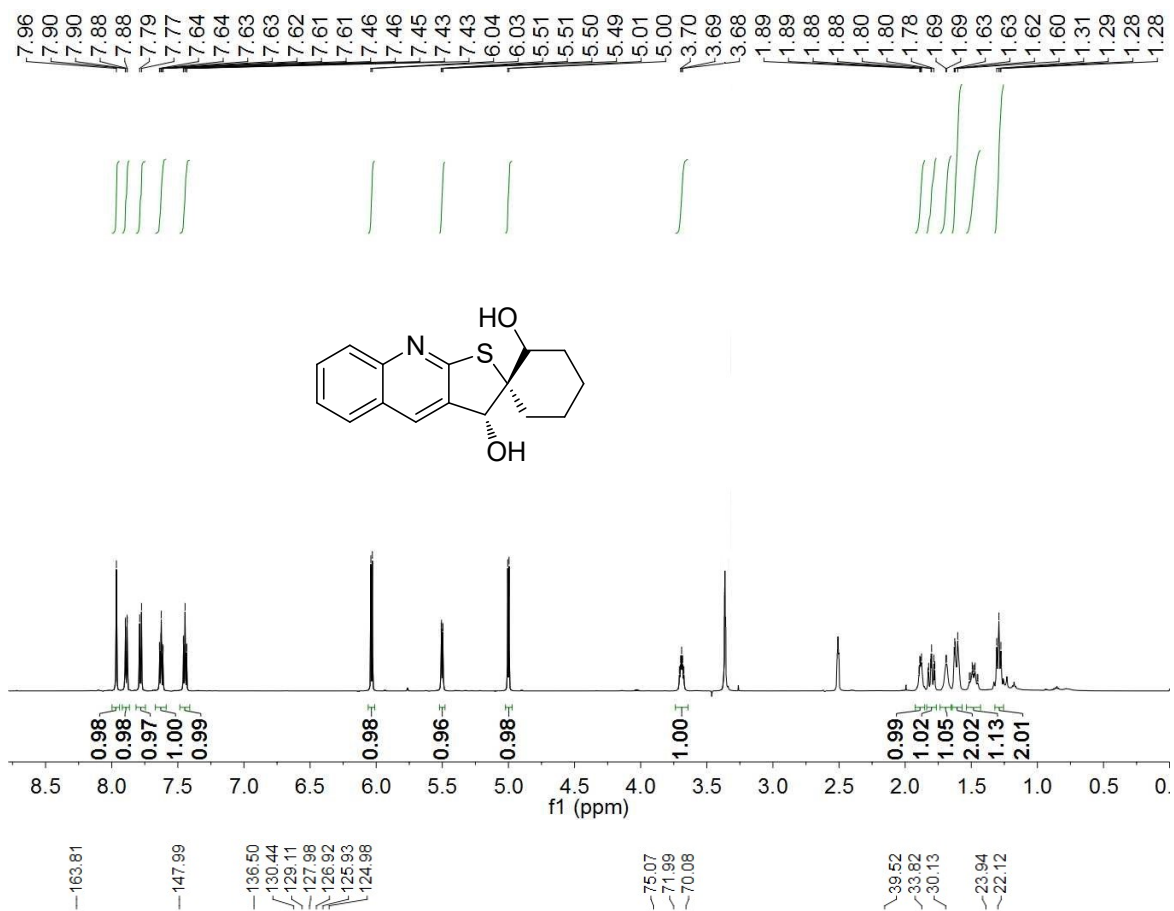
5ak



6'ca



7'ca



2. X-ray data of enantiopure of 3fa, 3ia, 3ka and 5ca

Single crystals (**3fa**, **3ia**, **3ka** and **5ca**) were crystallized by the slow solvent (ethyl acetate/petroleum ether) evaporation method. The crystals were characterized using single crystal X-ray diffraction.

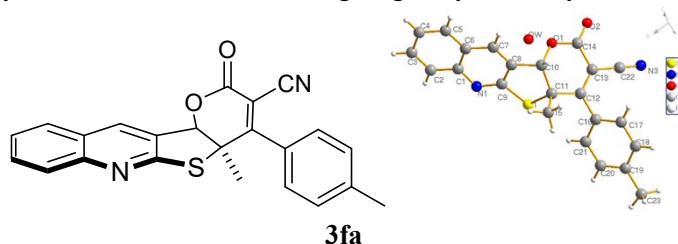


Figure S1. Displacement Ellipsoids Are Drawn at the 30% Probability Level.

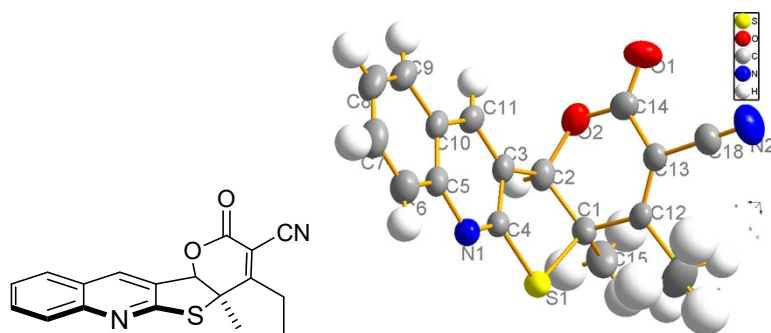
Crystal data for **3fa** (CCDC 2013515) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax.: (internat.) (+44)-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]

XRD Data for Compound **3fa**

Crystal data and structure refinement for 3fa .	
Identification code	3fa
Empirical formula	C _{4.60} H _{3.20} Cl ₁₀ N _{0.40} O _{0.50} S _{0.20}
Formula weight	78.49
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 16.2300(9) Å alpha = 90 °. b = 6.6999(4) Å beta = 98.587(3) °. c = 19.3383(11) Å gamma = 90 °.
Volume	2079.3(2) Å ³
Z, Calculated density	20, 1.254 Mg/m ³
Absorption coefficient	0.178 mm ⁻¹
F(000)	816
Crystal size	.36 x .27 x .18 mm
Theta range for data collection	1.53 to 27.56 °.
Limiting indices	-21<=h<=21, -8<=k<=8, -25<=l<=25
Reflections collected / unique	67116 / 4800 [R(int) = 0.0524]
Completeness to theta = 27.56	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4800 / 0 / 263
Goodness-of-fit on F ²	1.169
Final R indices [I>2sigma(I)]	R1 = 0.0779, wR2 = 0.2424
R indices (all data)	R1 = 0.0936, wR2 = 0.2634
Extinction coefficient	0.010(3)

Largest diff. peak and hole

1.407 and -0.282 e.Å⁻³



3ia

Figure S2. Displacement Ellipsoids Are Drawn at the 30% Probability Level.

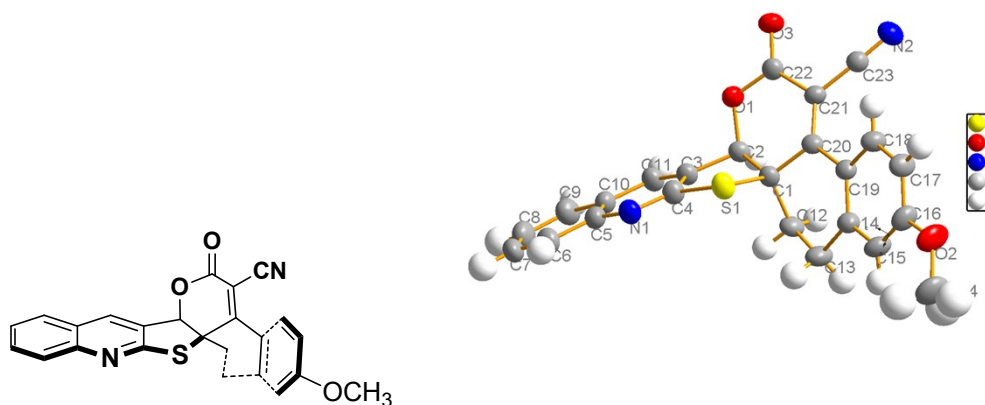
Crystal data for **3ia** (CCDC 2013516) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax.: (internat.) (+44)-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]

XRD Data for Compound **3ia**

Crystal data and structure refinement for **3ia**.

Identification code	3ia
Empirical formula	C ₁₈ H ₁₄ N ₂ O ₂ S
Formula weight	322.08
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pccn
Unit cell dimensions	a = 26.8368(6) Å alpha = 90 °. b = 8.8018(2) Å beta = 90 °. c = 12.9450(3) Å gamma = 90 °.
Volume	3057.77(12) Å ³
Z, Calculated density	40, 1.401 Mg/m ³
Absorption coefficient	0.223 mm ⁻¹
F(000)	1344
Crystal size	.36 x .23 x .11 mm
Theta range for data collection	1.52 to 27.43 °.
Limiting indices	-34<=h<=34, -11<=k<=11, -16<=l<=16
Reflections collected / unique	94617 / 3494 [R(int) = 0.1036]
Completeness to theta = 27.43	99.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3494 / 0 / 209
Goodness-of-fit on F ²	1.104
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.0959
R indices (all data)	R1 = 0.0535, wR2 = 0.1079
Extinction coefficient	0.0060(5)

Largest diff. peak and hole 0.243 and -0.209 e. Å⁻³



3ka

Figure S3. Displacement Ellipsoids Are Drawn at the 30% Probability Level.

Crystal data for **3ka** (CCDC 2013517) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax.: (internat.) (+44)-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]

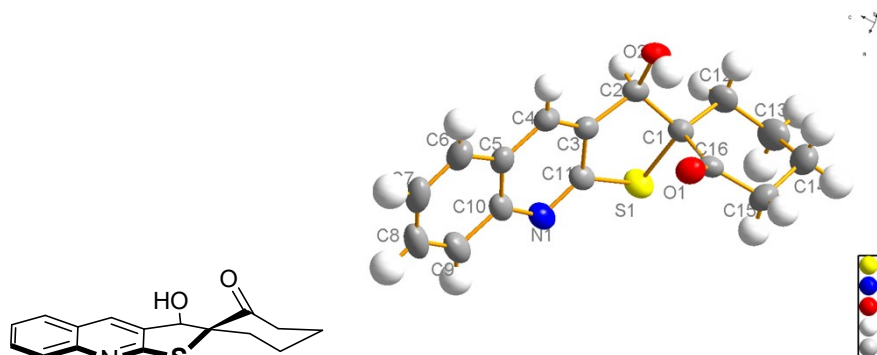
XRD Data for Compound **3ka**

Crystal data and structure refinement for **3ka**.

Empirical formula	C ₂₄ H ₁₆ N ₂ O ₃ S
Formula weight	412.09
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 8.2185(6) Å alpha = 90 ° b = 15.6692(11) Å beta = 92.798(4) ° c = 16.9546(13) Å gamma = 90 °
Volume	2180.8(3) Å ³
Z, Calculated density	28, 1.354 Mg/m ³
Absorption coefficient	0.187 mm ⁻¹
F(000)	920
Crystal size	.38 x .26 x .18 mm
Theta range for data collection	1.77 to 27.45 °
Limiting indices	-10<=h<=10, -20<=k<=20, -21<=l<=21
Reflections collected / unique	71857 / 4967 [R(int) = 0.0468]
Completeness to theta = 27.45	99.9 %
Absorption correction	None

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4967 / 0 / 290
Goodness-of-fit on F ²	1.129
Final R indices [I>2sigma(I)]	R1 = 0.0899, wR2 = 0.2813

R indices (all data)	R1 = 0.1065, wR2 = 0.3095
Extinction coefficient	0.018(4)
Largest diff. peak and hole	1.950 and -0.625 e.Å ⁻³



5ca

Figure S4. Displacement Ellipsoids Are Drawn at the 30% Probability Level.

Crystal data for **5ca** (CCDC 2013518) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax.: (internat.) (+44)-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]

XRD Data for Compound **5ca**

Crystal data and structure refinement for **5ca**.

Empirical formula	C ₁₆ H ₁₅ NO ₂ S
Formula weight	285.08
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 6.5115(13) Å alpha = 90 °. b = 10.484(2) Å beta = 94.411(11) °. c = 20.277(4) Å gamma = 90 °.
Volume	1380.1(5) Å ³
Z, Calculated density	18, 1.373 Mg/m ³
Absorption coefficient	0.235 mm ⁻¹
F(000)	600
Crystal size	.32 x 21 x 16 mm
Theta range for data collection	2.01 to 27.28 °.
Limiting indices	-8<=h<=8, -13<=k<=13, -26<=l<=26
Reflections collected / unique	44448 / 3095 [R(int) = 0.0573]
Completeness to theta = 27.28	99.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3095 / 0 / 182
Goodness-of-fit on F ²	1.121

Final R indices [$I > 2\sigma(I)$]	R1 = 0.0479, wR2 = 0.1027
R indices (all data)	R1 = 0.0619, wR2 = 0.1113
Extinction coefficient	0.0206(17)
Largest diff. peak and hole	0.211 and -0.216 e. Å ⁻³

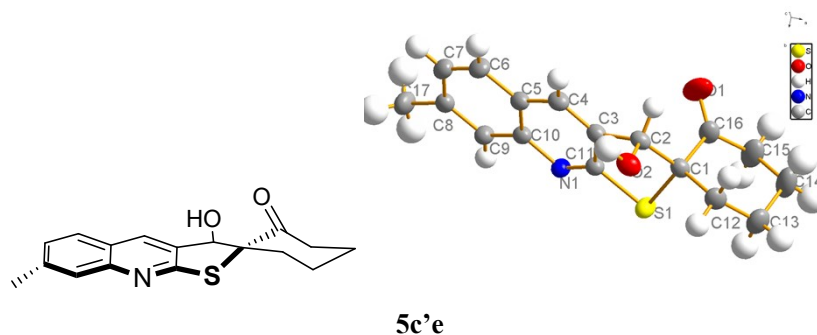


Figure S5. Displacement Ellipsoids Are Drawn at the 30% Probability Level.

Crystal data for **5c'e** (CCDC 2013519) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax.: (internat.) (+44)-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]

XRD Data for Compound **5c'e**

Crystal data and structure refinement for **5c'e**.

Empirical formula	C ₁₇ H ₁₇ NO ₂ S
Formula weight	299.10
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 12.5624(3) Å alpha = 90 °. b = 11.3761(2) Å beta = 99.5230(10) °. c = 10.3690(2) Å gamma = 90 °.
Volume	1461.42(5) Å ³
Z, Calculated density	19, 1.361 Mg/m ³
Absorption coefficient	0.225 mm ⁻¹
F(000)	632
Crystal size	.42 x 32 x 22 mm
Theta range for data collection	1.64 to 27.51 °.
Limiting indices	-16 ≤ h ≤ 16, -14 ≤ k ≤ 14, -13 ≤ l ≤ 13
Reflections collected / unique	51602 / 3356 [R(int) = 0.0488]
Completeness to theta = 27.28	99.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3356 / 0 / 191
Goodness-of-fit on F ²	1.067
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0457, wR2 = 0.1209

R indices (all data)	R1 = 0.0569, wR2 = 0.1356
Extinction coefficient	0.010(2)
Largest diff. peak and hole	0.651 and -0.496 e. Å ⁻³