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Supporting Information

# Au-Catalyzed Intramolecular Annulations Toward Fused Tricyclic [1,3]Oxazino[3,4-a]indol-1-ones under Extremely Mild Conditions

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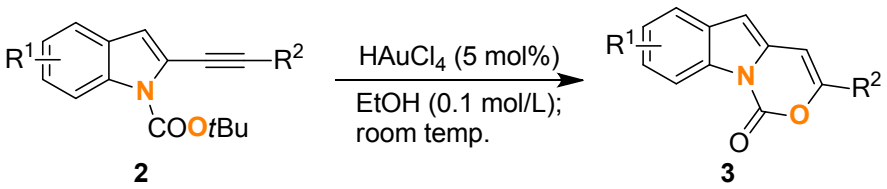
# Contents



# Experimental section.

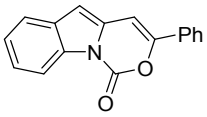
**General experimental methods**: Unless otherwise noted, commercial solvents and reagents were purchased from commercial suppliers, and were used as received. Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard grade). Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25-35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million (ppm) from internal standard tetramethylsilane (TMS) on the δ scale. High resolution mass spectrometry (HRMS) spectra analysis was performed by electrospray ionization (ESI-micrOTOF).

***General procedure for the preparation of compound 3:***




**2** **3**

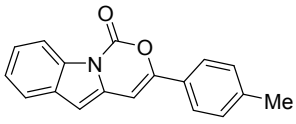
$HAuCl_4$ (8.5 mg, 40% aqueous solution) was added to a solution of compound **2** (0.2 mmol) in 2.0 mL of EtOH under $N_2$. The reaction was stirred at room temperature for about 2 h. After completion of the reaction as indicated by TLC, solvent was evaporated under reduced pressure, and the residue was purified via silica-gel column chromatography (petroleum ether/DCM = 20:1) to give the desired product **3**, as a white solid (48 mg, yield 92%).




**3-Phenyl-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3a**.

Yield 92%; white solid; mp: 176-178 °C;

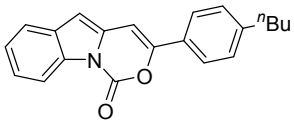
**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 6.62 (s, 1H), 6.94 (s, 1H), 7.26-7.46 (m, 5H), 7.62 (d, *J* = 4.0 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 2H), 8.46 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 96.3, 102.0, 115.5, 120.4, 124.1, 124.4, 124.8, 124.9, 129.8, 130.0, 130.8, 132.8, 133.3, 144.6, 150.1; **HRMS** calcd. for $C_{17}H_{12}NO_2$ $[M+H]^+$: 262.0852, found: 262.0863.




**3-(*p*-Tolyl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3b**.

Yield 77%; white solid; 172-174 °C ;

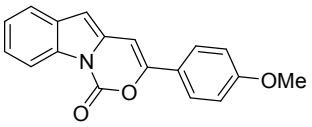
**$^1$H NMR (400 MHz, $CDCl_3$)**: *δ* 2.43 (s, 3H), 6.63 (s, 1H), 6.92 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 8.47 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: *δ* 21.3, 94.5, 101.5, 115.6, 120.3, 124.4, 124.8, 128.0, 129.6, 130.8, 133.0, 133.3, 140.3, 144.9, 150.3; **HRMS** calcd. for $C_{18}H_{14}NO_2$ $[M+H]^+$: 276.1013, found: 276.1019.




**3-(4-Butylphenyl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3c.**

Yield 86%; white solid; 151-153 °C;

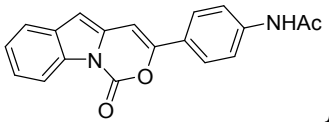
**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ 0.96 (t, $J$ = 12.0 Hz, 3H), 1.35-1.41 (m, 2H), 1.62 (t, $J$ = 12.0 Hz, 2H), 2.64 (t, $J$ = 16.0 Hz, 2H), 6.58 (s, 1H), 6.86 (s, 1H), 7.20-7.38 (m, 4H), 7.59 (d, $J$ = 8.0 Hz, 1H), 7.69-7.71 (m, 2H), 8.48 (d, $J$ = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: $\delta$ 19.9, 22.3, 32.6, 36.4, 94.4, 101.8, 115.6, 120.1, 124.3, 124.7, 128.2, 128.8, 130.8, 130.9, 132.8, 133.4, 144.4, 146.3, 150.4; **HRMS** calcd. for $C_{21}H_{20}NO_2$ $[M+H^+]$: 318.1498, found: 318.1489.




**3-(4-Methoxyphenyl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3d.**

Yield 81%; yellow solid; 150-152 °C ;

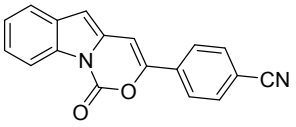
**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ 3.79 (s, 3H), 6.51 (s, 1H), 6.76 (s, 1H), 6.89 (d, $J$ = 12.0 Hz, 2H), 7.24-7.32 (m, 2H), 7.33 (d, $J$ = 4.0 Hz, 1H), 7.53 (d, $J$ = 8.0 Hz, 1H), 7.69 (d, $J$ = 8.0 Hz, 1H), 8.47 (d, $J$ = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: $\delta$ 55.3, 93.4, 101.2, 114.4, 115.6, 120.5, 123.2, 124.4, 124.7, 124.9, 126.2, 130.9, 133.5, 144.6, 150.0, 161.3; **HRMS** calcd. for $C_{18}H_{14}NO_3$ $[M+H]^+$: 292.0962, found: 292.0968.




***N*-(4-(1-Oxo-1*H*-[1,3]oxazino[3,4-*a*]indol-3-yl)phenyl)acetamide 3e**.

Yield 75%; yellow solid; mp: 121-123 °C;

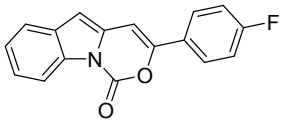
**$^1$H NMR (400 MHz, DMSO-*d6*)**: $\delta$ 2.09 (s, 3H), 6.87 (s, 1H), 7.42 (t, $J$ = 8.0 Hz, 1H), 7.46 (t, $J$ = 4.0 Hz, 1H), 7.50-7.55 (m, 2H), 7.59 (d, $J$ = 12.0 Hz, 1H), 7.70-7.74 (m, 2H), 8.10 (s, 1H), 8.30 (d, $J$ = 8.0 Hz, 1H), 10.18 (br, 1H); **$^{13}$C NMR (100 MHz, DMSO-*d6*)**: $\delta$ 24.7, 96.3, 102.8, 115.1, 119.7, 121.1, 124.6, 126.1, 129.0, 131.0, 131.6, 133.0, 133.7, 140.5, 144.6, 149.5, 169.2; **HRMS** calcd. for $C_{19}H_{15}N_2O_3$ $[M+H]^+$: 319.1083, found: 319.1077.




**4-(1-Oxo-1*H*-[1,3]oxazino[3,4-*a*]indol-3-yl)benzonitrile 3f**.

Yield 71%; yellow solid; mp: 102-104 °C;

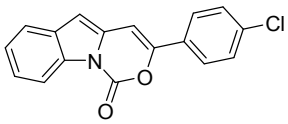
**$^1$H NMR (400 MHz, DMSO-*d6*)**: $\delta$ 6.94 (s, 1H), 7.40-7.45 (m, 2H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.86 (s, 1H), 7.97 (d, $J$ = 8.0 Hz, 2H), 8.05 (d, $J$ = 8.0 Hz, 2H), 8.29 (d, $J$ = 12.0 Hz, 1H); **$^{13}$C NMR (100 MHz, DMSO-*d6*)**: δ 99.2, 104.4, 112.2, 115.3, 121.5, 126.1, 126.2, 126.6, 129.2, 131.0, 131.9, 132.0, 133.2, 133.4, 135.2, 147.3;



**3-(4-Fluorophenyl)-1*H*-[1, 3]oxazino[3, 4-*a*]indol-1-one 3g**.

Yield 45%; white solid; mp: 149-151 °C;

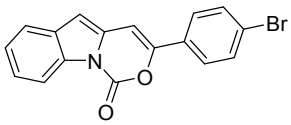
**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ 6.64 (s, 1H), 6.89 (s, 1H), 7.16 (s, 2H), 7.40 (d, $J$ = 4.0 Hz, 2H), 7.61 (d, $J$ = 8.0 Hz, 1H), 7.79-7.83 (m, 2H), 8.44 (d, $J$ = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: $\delta$ 96.0, 102.2, 115.8 (d, $^2J$ = 21.0 Hz), 116.2, 120.4, 124.6, 124.9, 126.9, 127.0, 130.8, 132.7, 133.3, 144.4, 149.1, 161.3 (d, $^1J$ = 248.0 Hz); **HRMS** calcd. for $C_{17}H_{11}NO_2F$ $[M+H]^+$: 280.0774, found: 280.0768.



**3-(4-Chlorophenyl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3h**.

Yield 78%; white solid; mp: 117-119 °C ;

**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ 6.66 (s, 1H), 6.96 (s, 1H), 7.35-7.39 (m, 2H), 7.43 (t, $J$ = 12.0 Hz, 2H), 7.63 (d, $J$ = 4.0 Hz, 1H), 7.74-7.78 (m, 2H), 8.44 (d, $J$ = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, DMSO-*d6*)**: $\delta$ 101.7, 107.7, 119.9, 126.5, 129.6, 129.9, 134.3, 134.8, 135.8, 137.9, 138.3, 139.3, 139.7, 149.2, 153.3; **HRMS** calcd. for $C_{17}H_{11}NO_2Cl$ $[M+H]^+$: 296.0478, found: 296.0473.

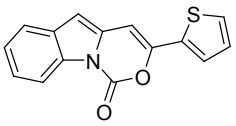


**3-(4-Bromophenyl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3i**.

Yield 52%; yellow solid; mp: 176-178 °C ;

**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ 6.60 (s, 1H), 6.96 (s, 1H), 7.12 (d, $J$ = 8.0 Hz, 1H), 7.39-7.59 (m, 4H), 7.66-7.72 (m, 2H), 8.44 (d, $J$ = 8 .0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: $\delta$ 96.4, 102.7, 115.0, 120.5, 124.4, 124.8, 124.9, 126.3, 127.5, 128.0, 129.7, 130.7, 132.5, 144.6, 149.1; **HRMS**

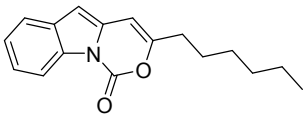
calcd. for $C_{17}H_{11}BrNO_2$ $[M+H]^+$: 339.9979, found: 339.9968.



**3-(Thiophen-2-yl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3j.**

Yield 77%; yellow solid; mp: 186-188 °C;

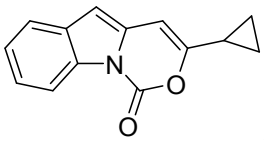
**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ 6.62 (s, 1H), 6.80 (s, 1H), 7.13 (d, $J$ = 8.0 Hz, 1H), 7.38-7.42 (m, 3H), 7.57 (d, $J$ = 4.0 Hz, 1H), 7.61 (d, $J$ = 8.0 Hz, 1H), 8.44 (d, $J$ = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: $\delta$ 94.2, 102.0, 115.6, 120.4, 124.5, 124.9, 126.2, 127.5, 128.2, 130.9, 132.4, 133.7, 134.4, 144.1, 146.9; **HRMS** calcd. for $C_{15}H_{10}NO_2S$ $[M+H]^+$: 268.0432, found: 268.0427.



**3-Hexyl-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3k.**

Yield 86%; white solid; mp: 75-78 °C ;

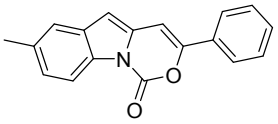
**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ 0.82 (t, $J$ = 12.0 Hz, 3H), 1.22-1.25 (m, 6H), 1.53-1.58 (m, 2H), 2.35 (t, $J$ =16.0 Hz, 2H), 6.10 (s, 1H), 6.30 (s, 1H), 7.22-7.25 (m, 2H), 7.45 (d, $J$ = 8.0 Hz, 1H), 8.30 (d, $J$ = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: $\delta$ 14.0, 22.4, 25.8, 28.5, 31.5, 32.2, 95.6, 99.5, 99.7, 115.6, 120.2, 124.9, 130.4, 132.7, 133.2, 145.0, 154.7; **HRMS** calcd. for $C_{17}H_{20}NO_2$ $[M+H]^+$: 270.1494, found: 270.1500.



**3-Cyclopropyl-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3l**.

Yield 86%; white solid; mp: 100-102 °C ;

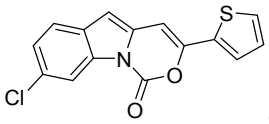
**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ 0.83-0.88 (m, 2H), 0.94-0.97 (m, 2H), 1.62-1.71 (m, 1H), 6.17 (s, 1H), 6.29 (s, 1H), 7.20-7.28 (m, 2H), 7.46 (t, $J$ = 8.0 Hz, 1H), 8.29 (d, $J$ = 4.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: $\delta$ 6.6, 12.9, 94.9, 99.3, 115.5, 120.1, 123.8, 124.6, 130.7, 133.0, 133.1, 144.9, 154.8; **HRMS** calcd. for $C_{14}H_{12}NO_2$ $[M+H]^+$: 226.0868, found:226.0896



**7-Methyl-3-phenyl-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3m.**

Yield 88%; white solid; mp: 153-155 °C ;

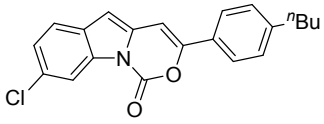
**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ 2.43 (s, 3H), 6.63 (s, 1H), 6.82 (s, 1H), 7.16 (d, $J$ = 8.0 Hz, 1H), 7.34-7.42 (m, 2H), 7.38-7.44 (m, 2H), 7.63-7.73 (m, 2H), 8.36 (d, $J$ = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: $\delta$ 21.5, 96.1, 101.6, 115.3, 120.2, 124.7, 126.9, 128.8, 129.8, 130.8, 131.1, 132.9, 134.4, 144.7, 149.0, 149.7; **HRMS** calcd. for $C_{18}H_{14}NO_2$ $[M+H]^+$: 276.1025, found: 276.1019.



**8-Chloro-3-(thiophen-2-yl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3n.**

Yield 80%; yellow solid; mp: 91-93 °C ;

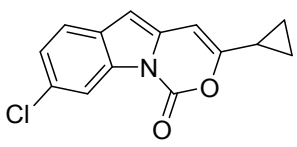
**$^1$H NMR (400 MHz, DMSO-*d6*)**: $\delta$ 6.82 (s, 1H), 7.23 (d, $J$ = 8.0 Hz, 1H), 7.40-7.44 (m, 2H), 7.70-7.73 (m, 2H), 7.79 (d, $J$ = 4.0 Hz, 1H), 8.24 (d, $J$ = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, DMSO-*d6*)**: $\delta$ 94.2, 101.3, 114.5, 122.0, 124.8, 126.4, 128.2, 128.7, 128.8, 129.6, 133.2, 133.7, 140.0, 143.5, 146.7; **HRMS** calcd. for $C_{15}H_{19}ClNO_2S$ $[M+H]^+$: 302.0043, found: 302.004351.



**3-(4-Butylphenyl)-8-chloro-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3o.**

Yield 76%; white solid; mp: 151-153 °C ;

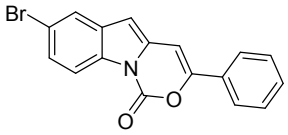
**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ 0.94 (t, $J$ = 12.0 Hz, 3H), 1.33-1.39 (m, 2H), 1.56-1.62 (m, 2H), 2.60 (t, $J$ = 8.0 Hz, 2H), 6.47 (s, 1H), 6.76 (d, $J$ = 8.0 Hz, 1H), 7.19-7.38 (m, 3H), 8.41 (d, $J$ = 8.0 Hz, 1H), 7.61-7.65 (m, 2H), 8.36 (d, $J$ = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: $\delta$ 13.8, 22.4, 33.2, 35.4, 94.1, 101.2, 115.7, 120.9, 124.8, 125.4, 127.7, 129.0, 129.3, 130.1, 133.4, 133.6, 144.2, 145.6, 150.7; **HRMS** calcd. for $C_{21}H_{19}NO_2Cl[M+H]^+$: 352.1104, found: 352.1098.



**8-Chloro-3-cyclopropyl-1*H*-[1, 3]oxazino[3, 4-*a*]indol-1-one 3p.**

Yield 67%; white solid; mp: 105-107 °C ;

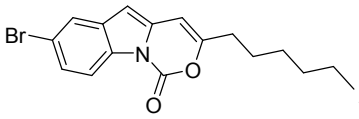
**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ 0.92-0.98 (m, 2H), 1.00-1.04 (m, 2H), 1.71-1.78 (m, 1H), 6.21 (s, 1H), 6.28 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 8.39 (d, *J* = 4 .0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: $\delta$ 6.3, 13.1, 94.9, 98.8, 116.4, 120.8, 125.0, 129.1, 129.5, 133.2, 133.7, 144.4, 155.3; **HRMS** calcd. for $C_{14}H_{11}NO_2Cl$ $[M+H]^+$: 260.0478, found: 260.0487.




**7-Bromo-3-phenyl-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3q.**

Yield 71%; white solid; mp: 103-105 °C ;

**$^1$H NMR (400 MHz, DMSO-*d6*)**: δ 6.81 (s, 1H), 7.48-7.52 (m, 2H), 7.62-7.66 (m, 3H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.96 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, DMSO-*d6*)**: δ 96.2, 101.6, 117.0, 117.7, 123.5, 125.2, 127.1, 129.5, 129.7, 130.7, 132.0, 133.1, 135.1, 144.5, 150.3; **HRMS** calcd. for $C_{17}H_{11}NO_2Br$ $[M+H]^+$: 339.9973, found: 339.9968.

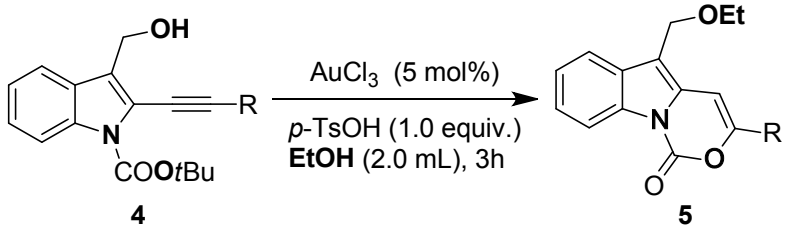



**7-bromo-3-hexyl-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 3r.**

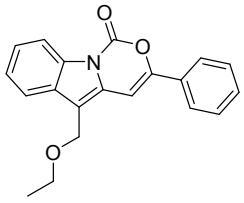
Yield 90%; white solid; mp: 73-75 °C;

**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ 0.91 (t, *J* = 12.0 Hz, 3H), 1.33-1.38 (m, 6H), 1.39-1.44 (m, 2H), 1.66-1.71 (m, 2H), 6.23 (s, 1H), 6.36 (s, 1H), 7.43-7.46 (m, 1H), 7.69 (s, 1H), 8.26 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: $\delta$ 14.0, 22.4, 26.4, 28.8, 31.2, 32.6, 96.4, 99.1, 116.7, 118.1, 122.9, 126.7, 131.7, 132.6, 133.6, 144.7, 155.5; **HRMS** calcd. for $C_{17}H_{19}NO_2Br$ $[M+H]^+$: 348.0599, found: 348.0594.

***General procedure for the preparation of compound 5:***



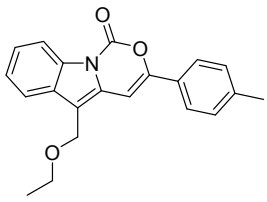

Substrate **4** was added to a stirred suspension of *p*-TsOH (17.2 mg, 0.2 mmol) and $AuCl_3$ (3.1 mg, 0.05 mmol) in 2.0 mL of EtOH at room temperature under $N_2$ atmosphere. The reaction was monitored by TLC. Upon completion, EtOH was evaporated in reduced pressure, and the resulting residue was purified by silica-gel column chromatography (petroleum ether/EA = 10:1) to afford the desired product **5** as light yellow solids.



**9-Ethoxymethyl-2-phenyl-3-oxa-4*a*-aza-fluoren-4-one 5a**.

Yield 75%; yellow solid; mp: 98-100 °C;

**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 1.28 (t, *J* = 8.0 Hz, 3H), 3.63 (q, *J* = 4.0 Hz, 12.0 Hz, 2H), 4.83 (s, 2H), 7.12 (s, 1H), 7.42-7.53 (m, 5H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.83-7.87 (m, 2H), 8.46 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 13.7, 62.9, 65.9, 93.8, 112.2, 115.6, 118.9, 123.3, 127.3, 128.9, 129.9, 130.5, 130.8, 131.8, 133.1, 134.4, 146.1, 151.9; **HRMS** calcd. for $C_{20}H_{18}NO_3$ $[M+H]^+$: 320.1287, found: 320.1281.

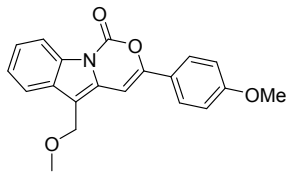


**5-(Ethoxymethyl)-3-(*p*-tolyl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 5b.**

Yield 90%; yellow solid; mp: 123-125 °C;

**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 1.19 (t, *J* = 16.0 Hz, 3H), 2.29 (s, 3H), 3.52 (q, *J* = 12.0 Hz, 2H), 4.70 (s, 2H), 6.92 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.28-7.32 (m, 2H), 7.45 (s, 1H), 7.59-7.63 (m, 2H), 8.33 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 15.2, 21.2, 62.9, 65.8, 93.0, 112.2, 115.3, 116.8, 124.5, 124.7, 127.6, 129.6, 130.4, 130.5, 131.2, 133.1, 140.2, 144.8, 150.3; **HRMS**

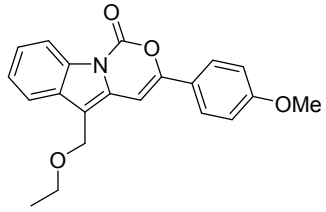
calcd. for $C_{21}H_{20}NO_3[M+H]^+$: 334.1443, found: 334.1438.



**5-(Methoxymethyl)-3-(4-methoxyphenyl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 5c.**

Yield 62%; yellow solid; mp: 129-131 °C;

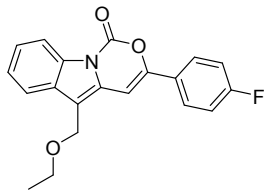
**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 3.36 (s, 3H), 3.78 (s, 3H), 4.70 (s, 2H), 6.85 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 7.31-7.34 (m, 2H), 7.59-7.71 (m, 3H), 8.35 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 54.9, 57.5, 64.4, 91.4, 109.7, 113.8, 115.1, 118.2, 122.8, 124.1, 124.5, 125.9, 130.3, 131.0, 132.7, 144.2, 149.7, 160.8; **HRMS** calcd. for $C_{20}H_{18}NO_4$ $[M+H]^+$: 336.1236, found: 336.1230.



**5-(Ethoxymethyl)-3-(4-methoxyphenyl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 5d.**

Yield 80%; yellow solid; mp: 112-114 °C

**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 1.18 (t, *J* = 16.0 Hz, 3H), 3.49-3.54 (m, 2H), 3.78 (s, 3H), 4.67 (s, 2H), 6.73-6.82 (m, 3H), 7.27-7.39 (m, 3H), 7.55 (d, *J* = 4.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 15.4, 55.5, 62.7, 65.9, 92.1, 110.4, 114.3, 115.6, 118.7, 123.1, 124.5, 126.8, 130.7, 131.2, 133.0, 134.1, 144.5, 150.2, 161.2; **HRMS** calcd. for $C_{21}H_{20}NO_4$ $[M+H]^+$: 350.1392, found: 350.1387.

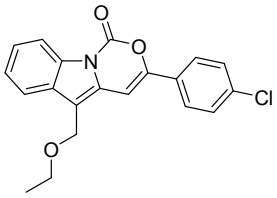


**5-(Ethoxymethyl)-3-(4-fluorophenyl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 5e.**

Yield 60%; yellow solid; mp: 118-120 °C;

**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 1.15 (t, *J* = 12.0 Hz, 3H), 3.46-3.51 (m, 2H), 4.77 (s, 2H), 7.00 (s,

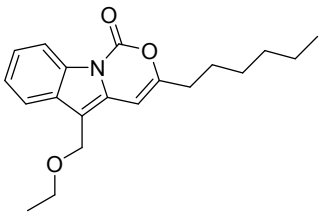
1H), 7.09-7.29 (m, 2H), 7.35-7.48 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.76-7.80 (m, 2H), 8.40 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 15.3, 62.9, 66.0, 93.6, 111.8, 115.6 (d, $^{2}J$ = 21.0 Hz), 116.0, 116.2, 118.8, 124.8, 126.9, 130.6, 130.7, 132.9, 143.9, 149.2, 164.3 (d, $^{1}J$ = 248.1 Hz); **HRMS** calcd. for $C_{20}H_{17}FNO_3$ $[M+H]^+$: 338.1192, found: 338.1187.



**3-(4-Chlorophenyl)-5-(ethoxymethyl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 5f.**

Yield 86%; yellow solid; mp: 119-121 °C;

**$^{1}$H NMR (400 MHz, $CDCl_3$)**: δ 1.29 (t, *J* = 12.0 Hz, 3H), 3.61-3.66 (m, 2H), 4.82 (s, 2H), 7.10 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 4H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.76-7.80 (m, 2H), 8.44 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 19.0, 62.9, 66.4, 94.2, 112.1, 115.5, 118.9, 124.9, 125.0, 126.1, 129.2, 130.9, 132.3, 133.1, 136.0, 144.2, 148.8, 167.5; **HRMS** calcd. for $C_{20}H_{17}ClNO_3[M+H]^+$: 354.0897, found: 355.0925.

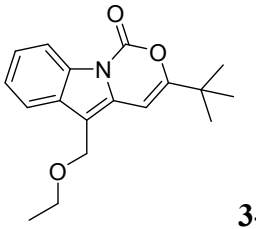


**5-(Ethoxymethyl)-3-hexyl-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 5g.**

Yield 57%; yellow oil;

**$^{1}$H NMR (400 MHz, $CDCl_3$)**: δ 0.96 (t, *J* = 12.0 Hz, 3H), 1.06-1.48 (m, 7H), 1.68-1.72 (m, 2H), 2.41-2.53 (m, 2H), 3.54-3.62 (m, 2H), 4.31 (t, *J* = 12.0 Hz, 2H), 4.71 (s, 2H), 6.38 (s, 1H), 7.37-7.39 (m, 2H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 15.2, 19.1, 22.6, 26.5, 28.6, 31.4, 32.8, 64.0, 66.4, 95.2, 109.5, 115.5, 118.7, 124.3, 128.8, 128.9, 130.4, 132.9, 146.0, 154.7;

**HRMS** calcd. for $C_{20}H_{26}NO_3$ $[M+H]^+$: 328.1913, found: 328.1907.



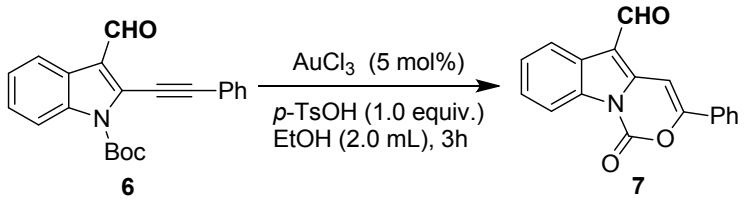
**3-(*tert*-Butyl)-5-(ethoxymethyl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 5h.**

Yield 30%; yellow oil;

**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 1.13 (t, *J* = 12.0 Hz, 3H), 1.61 (s, 9H), 3.42-3.47 (m, 2H), 4.61 (s, 2H), 7.13-7.21 (m, 3H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H);

**$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 15.2, 28.2, 64.0, 65.9, 66.3, 84.9, 111.0, 115.2, 118.9, 119.4, 123.1, 124.6, 124.9, 128.5, 136.5, 149.1; **HRMS** calcd. for $C_{17}H_{18}NO_3$ $[M+H]^+$: 300.1600, found: 300.1611.

***General procedure for the preparation of compound 7:***




Compound **6** (0.2 mmol) was added to a stirred suspension of *p*-TsOH (17.2 mg, 0.2 mmol) and $AuCl_3$ (3.1 mg, 0.05 mmol) in 2.0 mL of EtOH under $N_2$ atmosphere. The reaction was stirred at room temperature for 3h. Upon completion, EtOH was evaporated under reduced pressure, and the resulting residue was purified by silica-gel column chromatography (petroleum ether/EA = 10:1) to afford the desired product **7** as a light yellow solid.

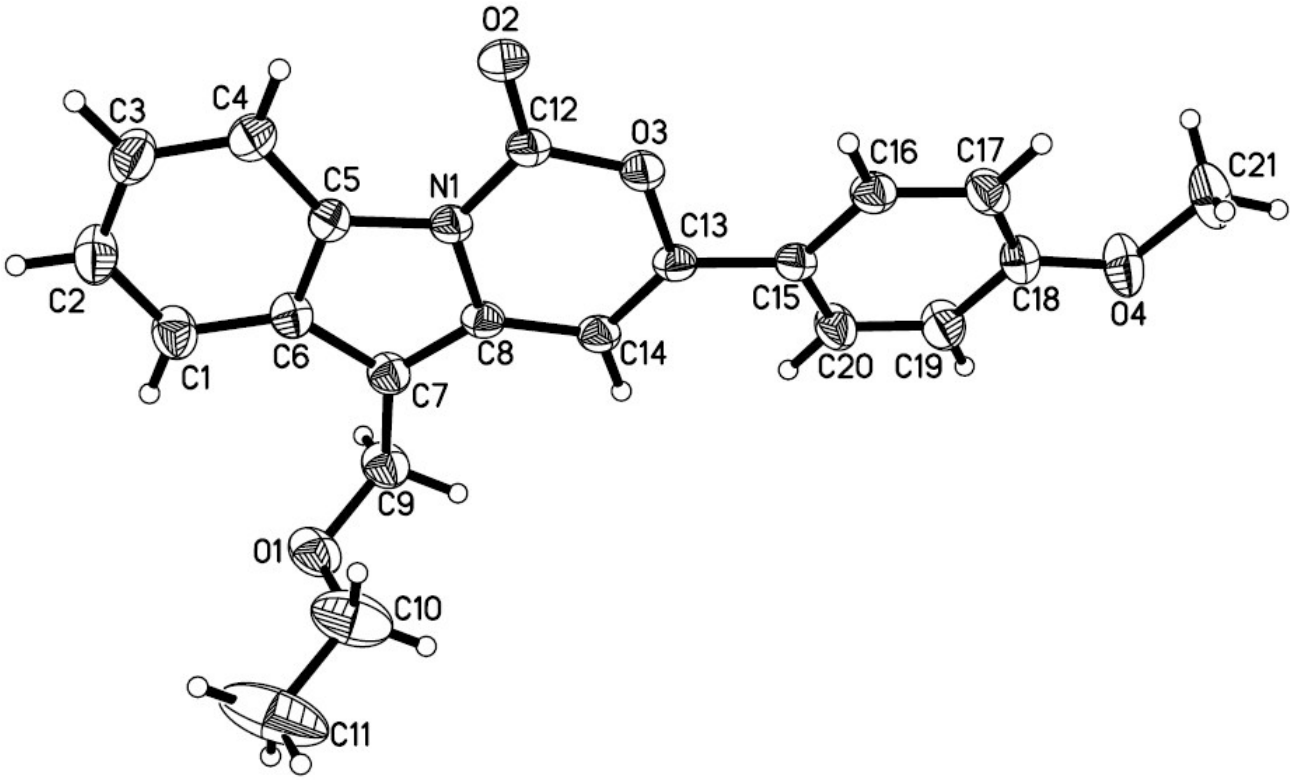
**1-Oxo-3-phenyl-1*H*-[1,3]oxazino[3,4-*a*]indole-5-carbaldehyde 7.**

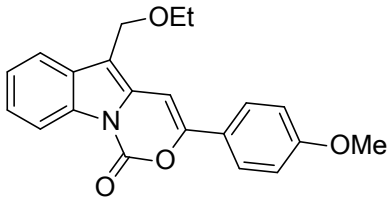
Yield 80%; yellow solid; mp: 119-121℃ ;

**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.52-7.53 (m, 5H), 7.59 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 8.22 (t, *J* = 12.0 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 10.43 (s, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 93.4, 112.9, 115.6, 120.2, 125.7, 126.1, 126.4, 127.7, 129.2, 129.6, 131.7, 133.1, 140.0, 143.4, 155.3, 184.0;

**HRMS** calcd. for $C1_8H_{12}NO_3$ $[M+H]^+$: 290.0817, found: 290.0809.

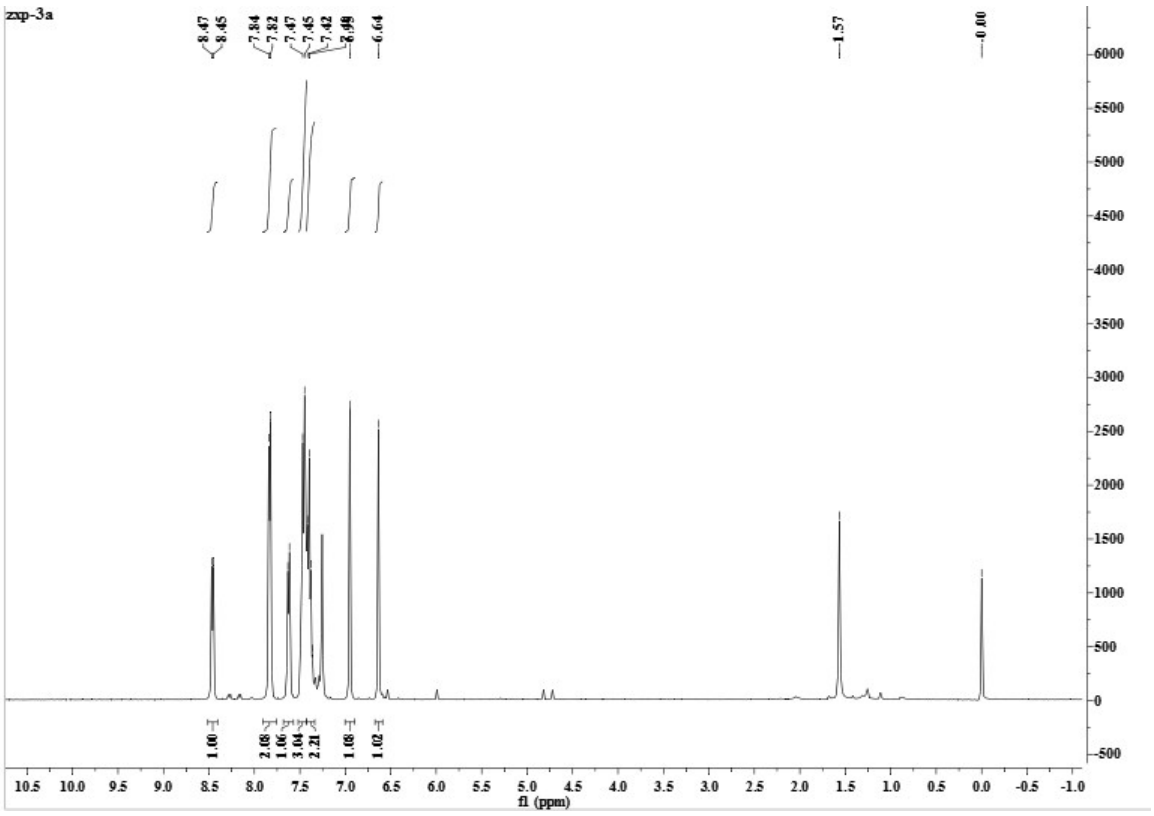
***X-Ray ORTEP illustration of compound 5d.***




**5d**

**3a**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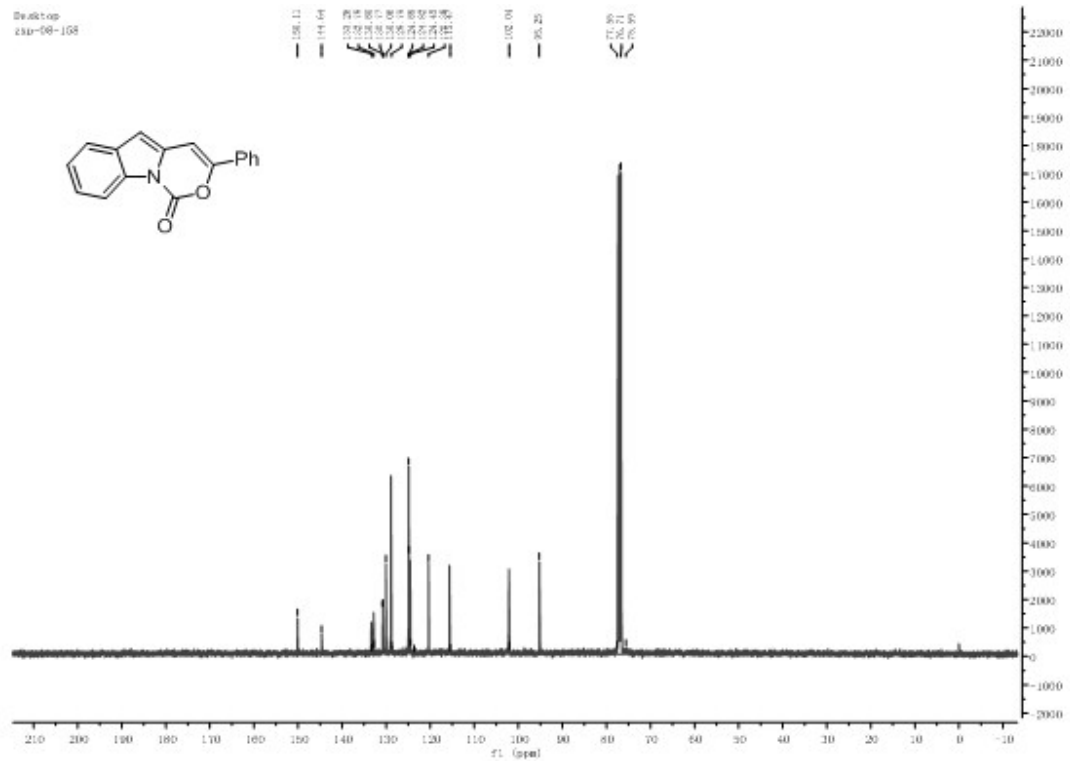
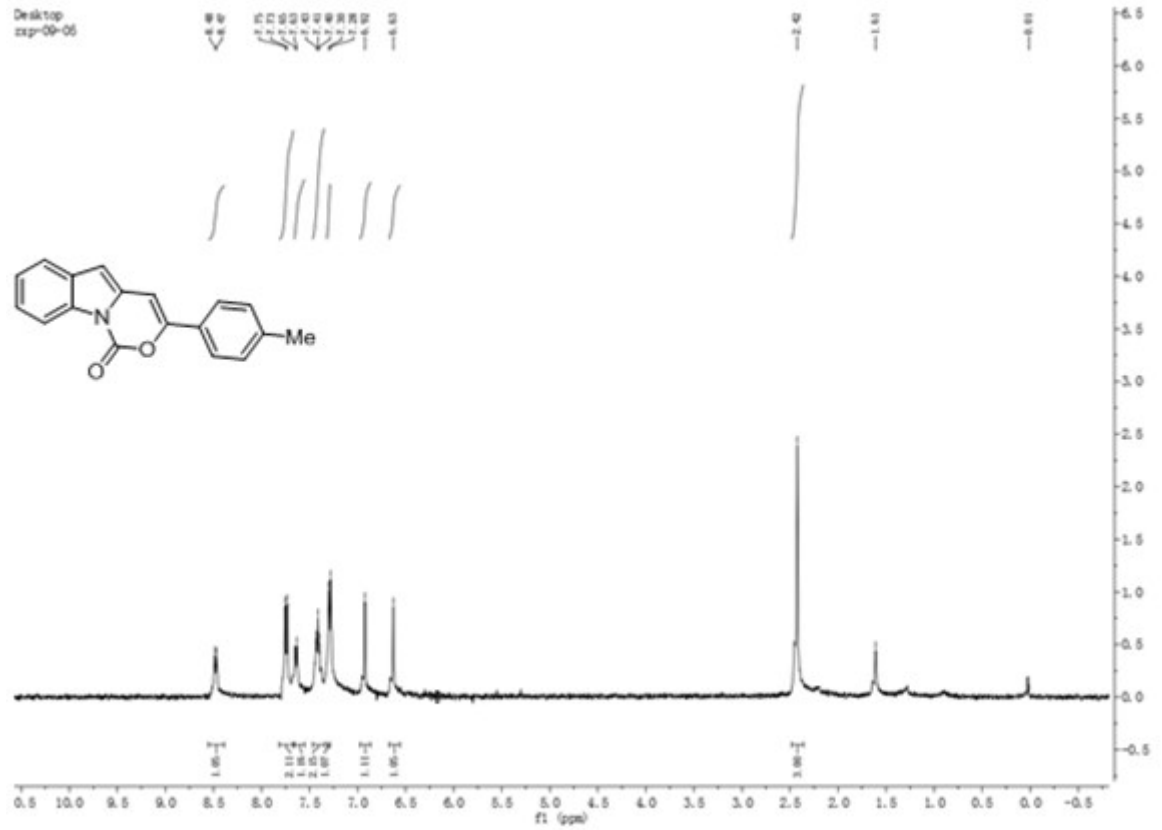
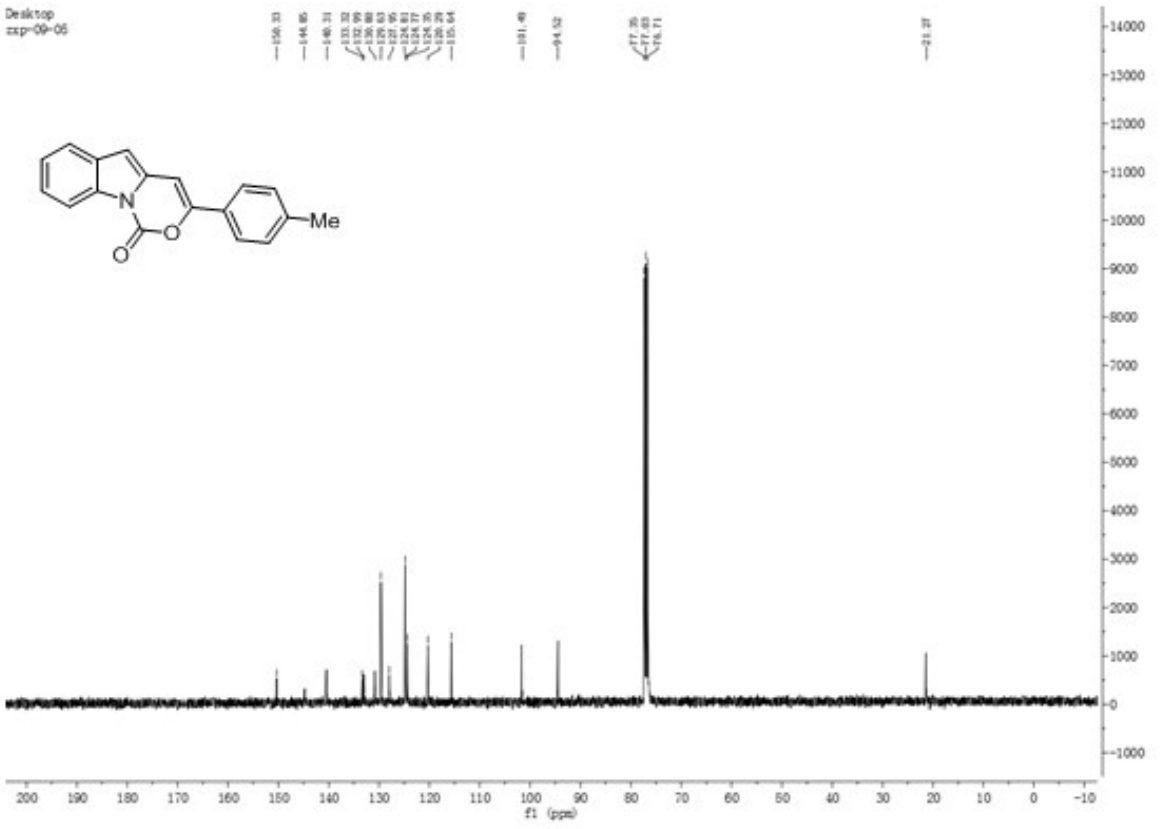
8.45
7.84
7.82
7.47
7.45
7.42
6.99
6.64
1.57
0.00
1.00
2.08
1.06
3.04
2.21
1.08
1.02
f1 (ppm)

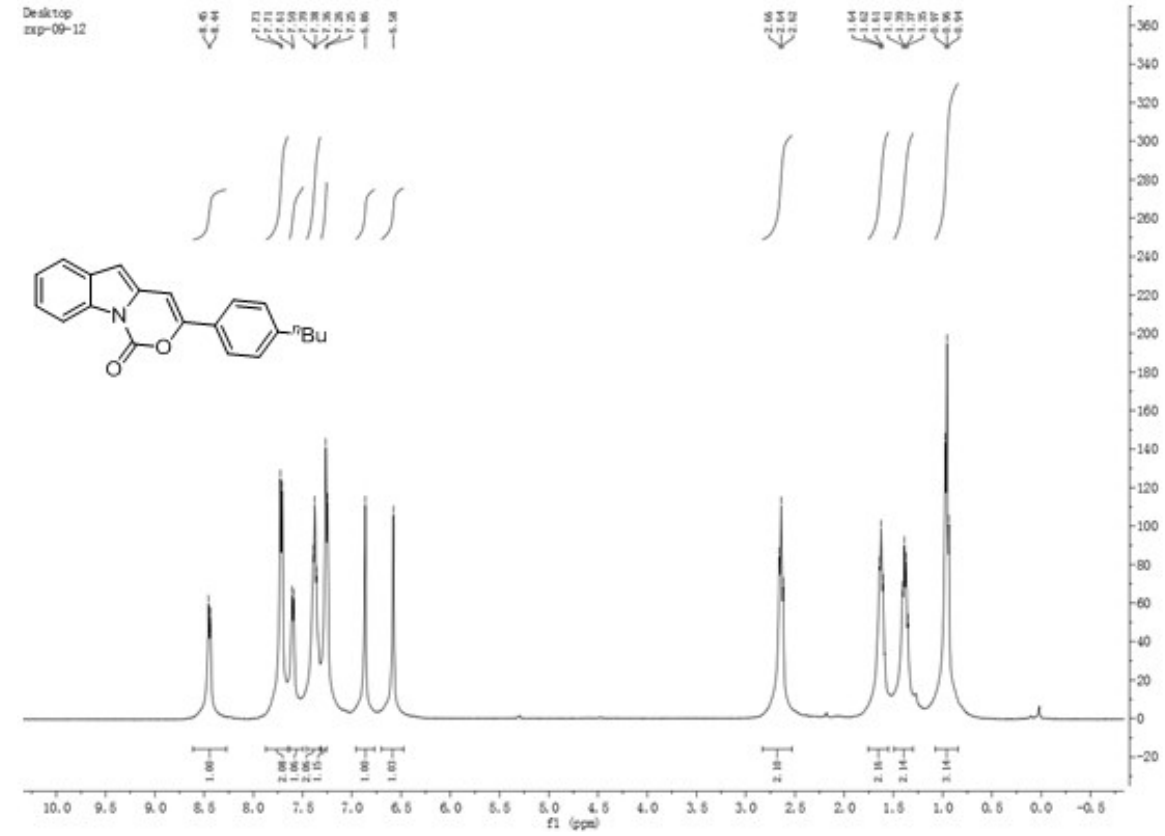

Ph
N
O
O
f1 (ppm)

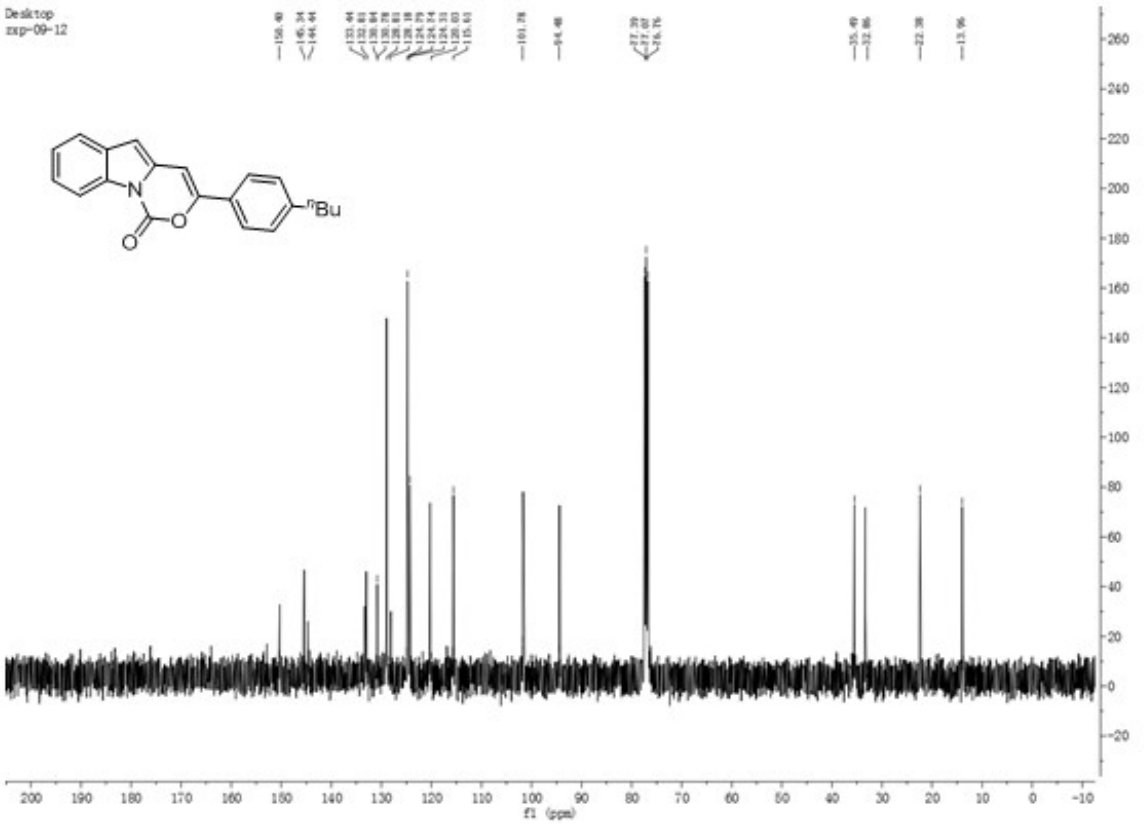
**3b**



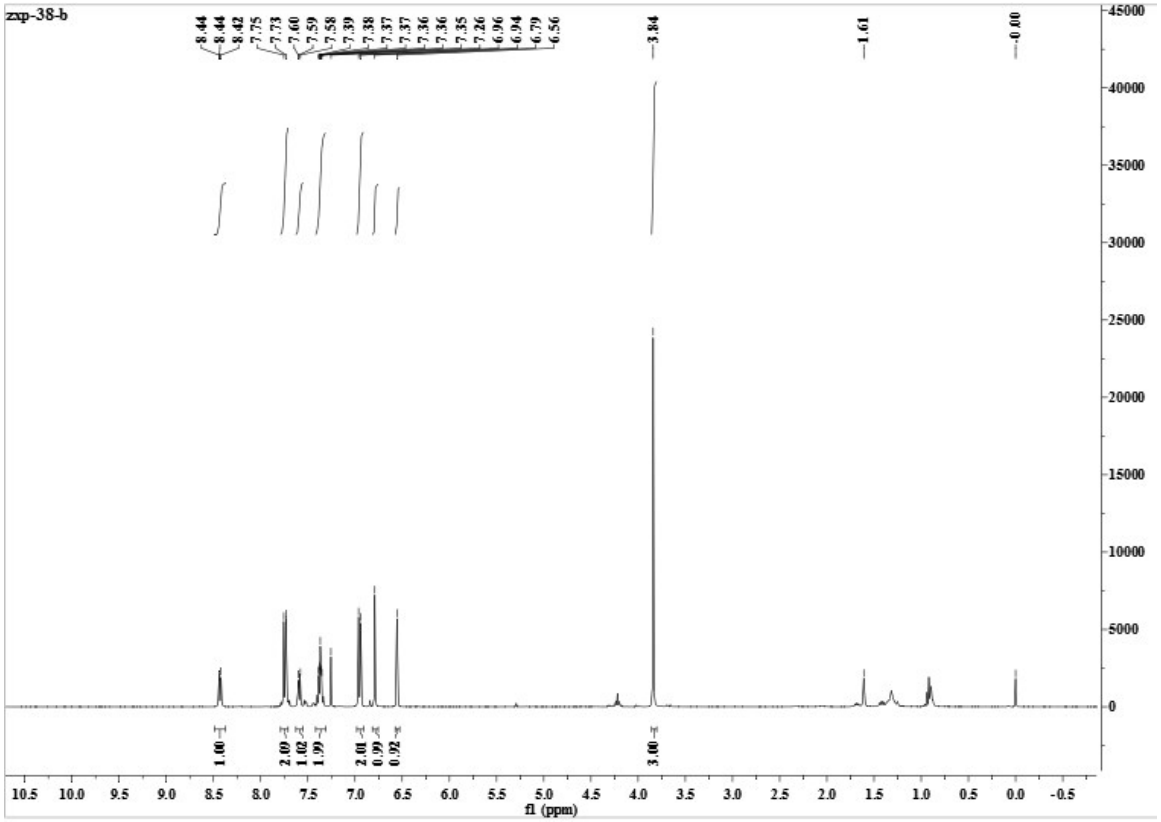



**3c**



**3d**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8.42
7.75
7.73
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7.59
7.58
7.39
7.38
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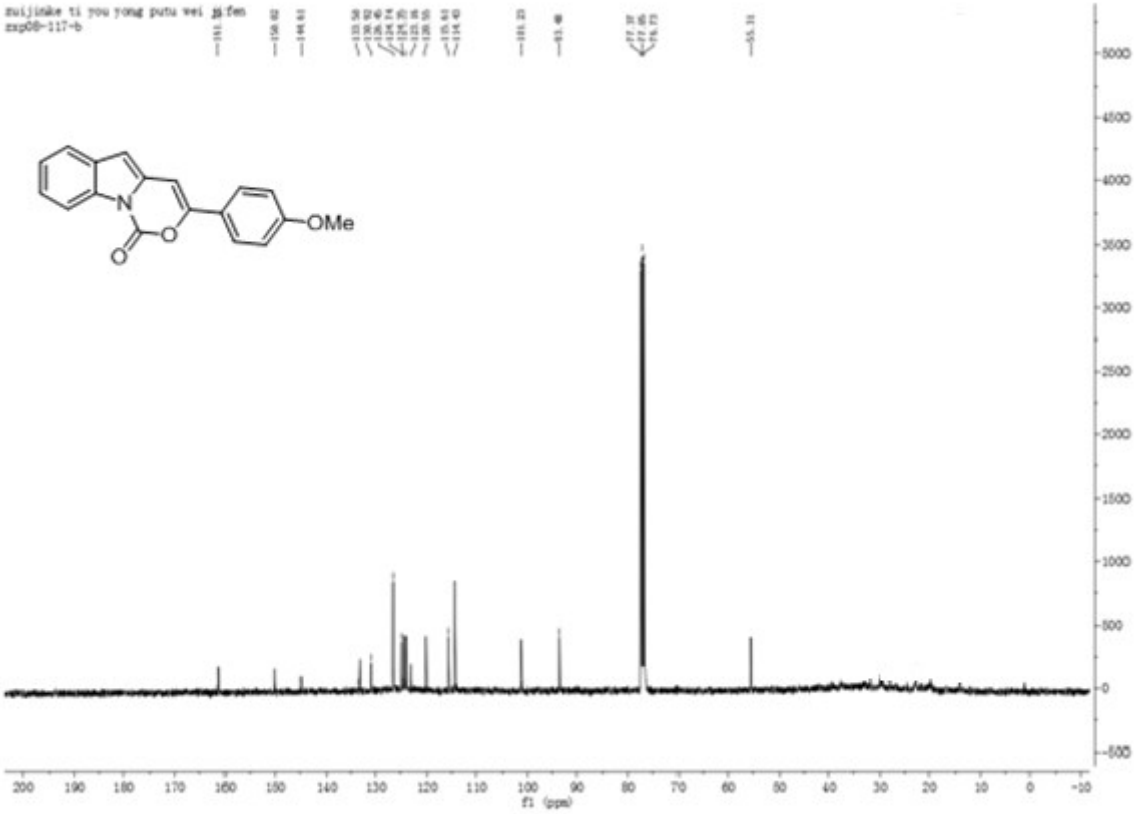
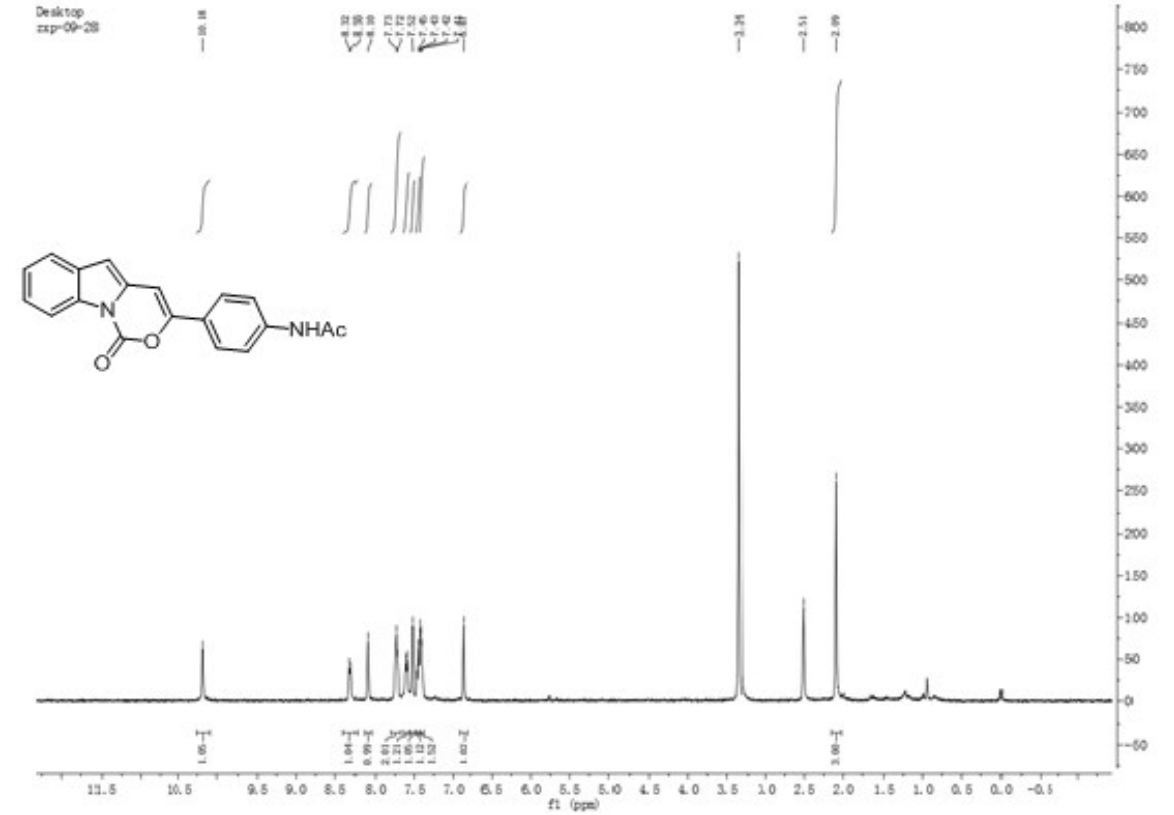
7.36
7.36
7.35
7.26
6.96
6.94
6.79
6.56
3.84
1.61
0.00
1.00
2.09
1.02
1.99
2.01
0.99
0.92
3.00
f1 (ppm)


zuijinke ti you yong putu wei ji fen
zxp08-117-b
OMe
f1 (ppm)

**3e**


Desktop
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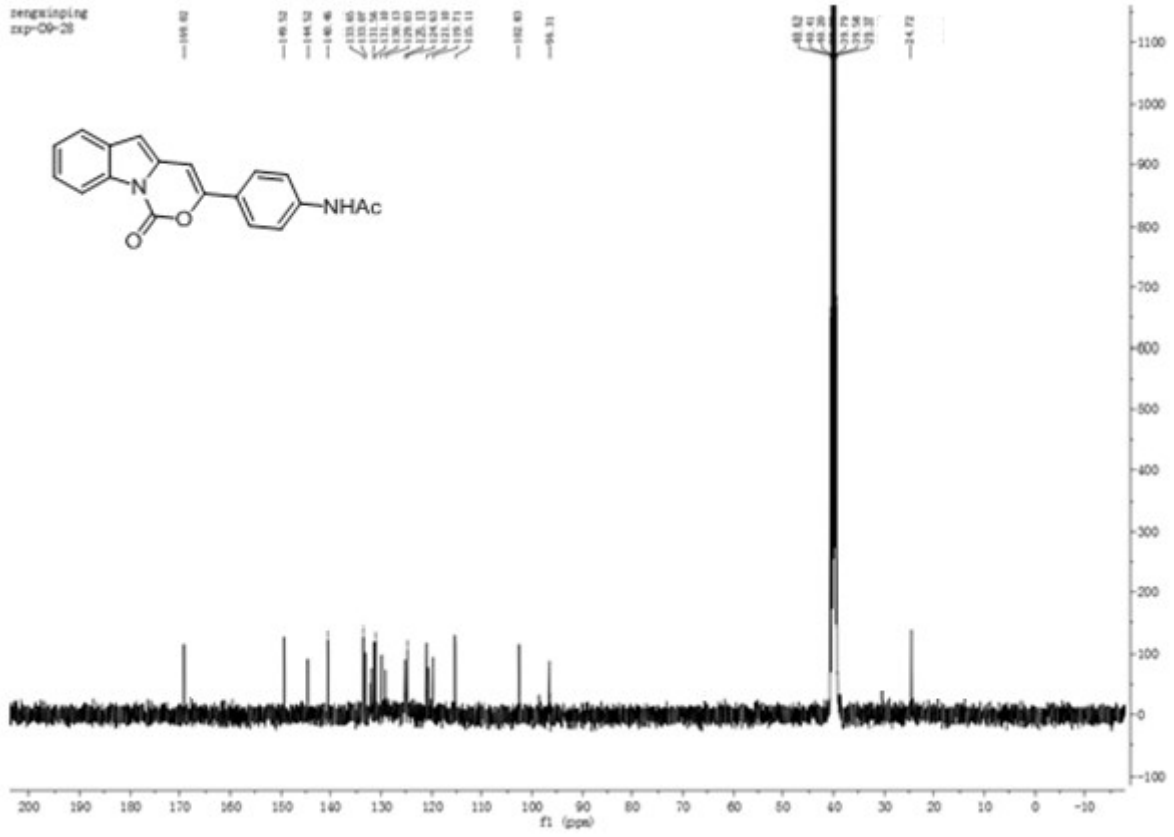
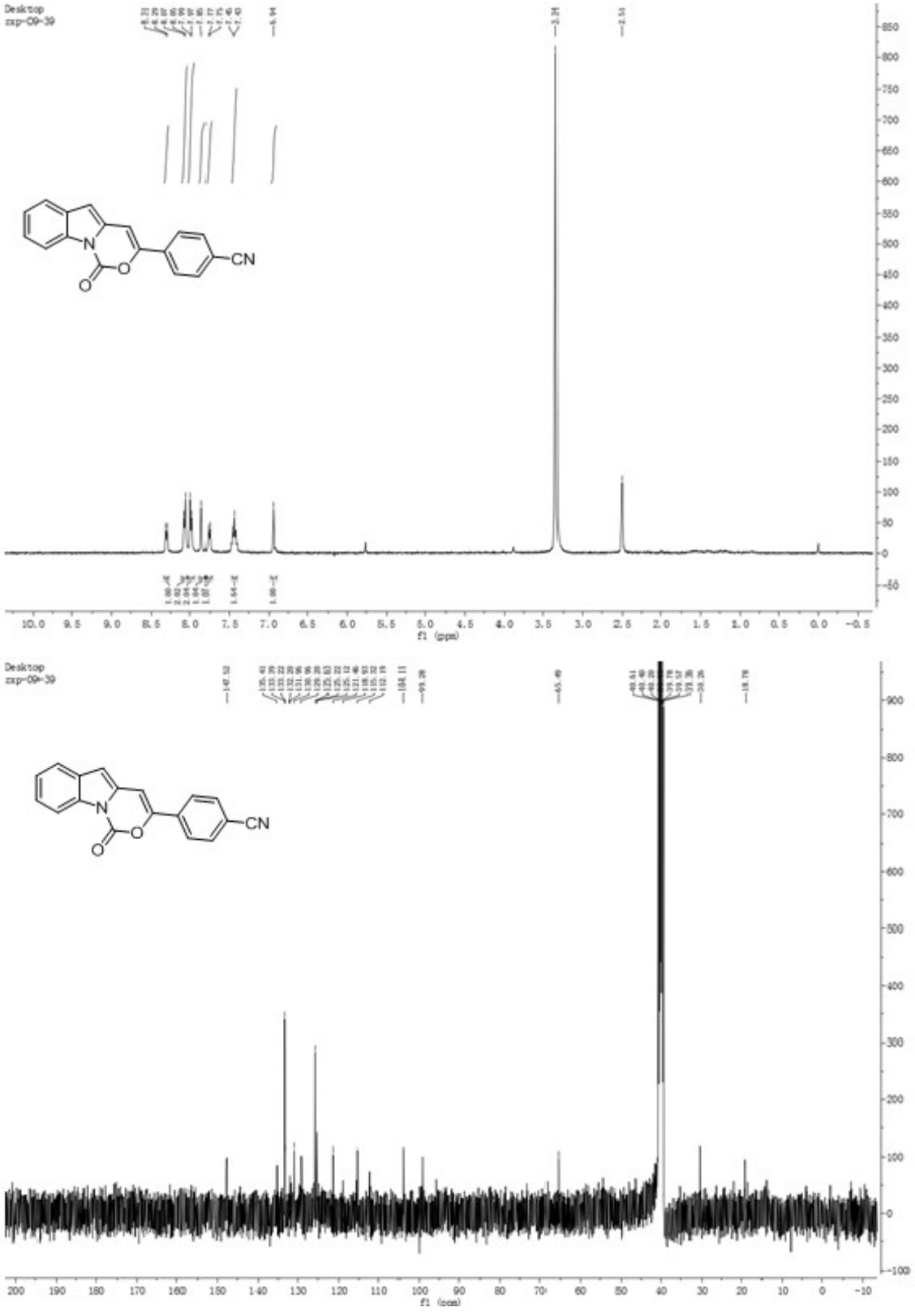
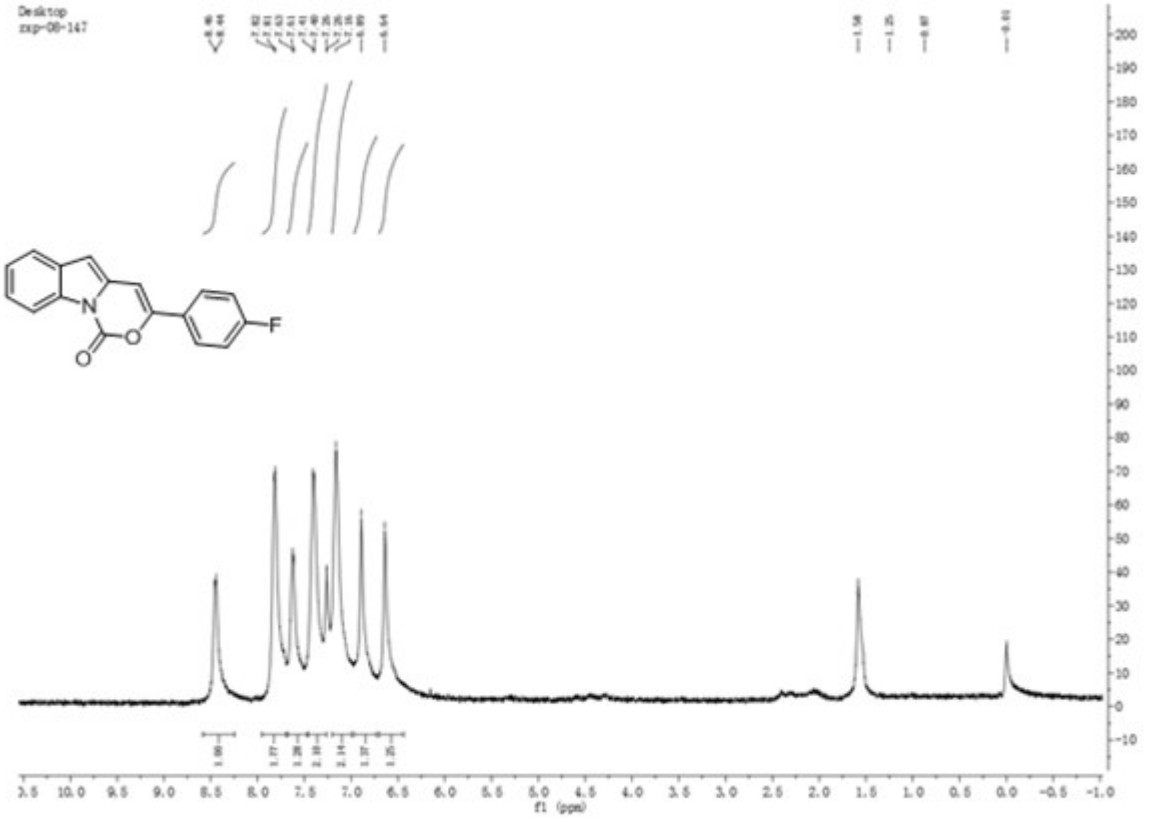
NHAc
f1 (ppm)

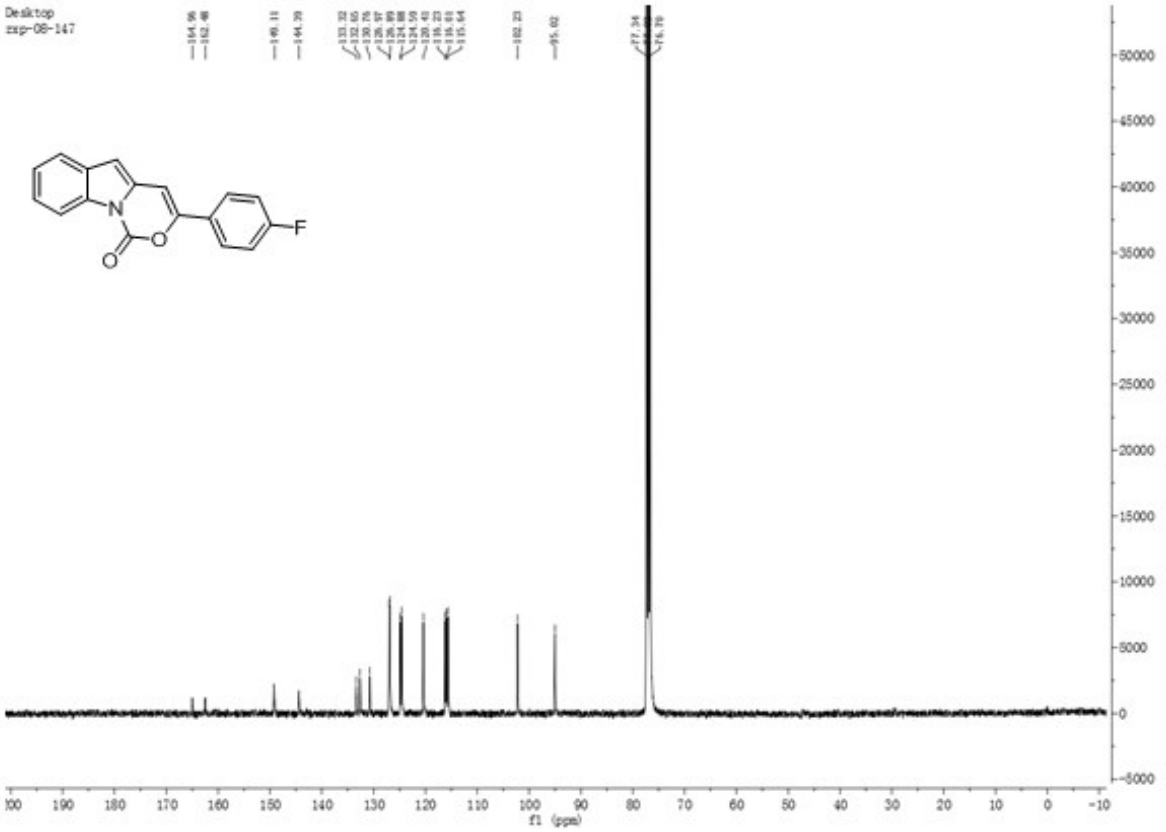

zengxinping
zxp-09-28
NHAc
f1 (ppm)

**3f**

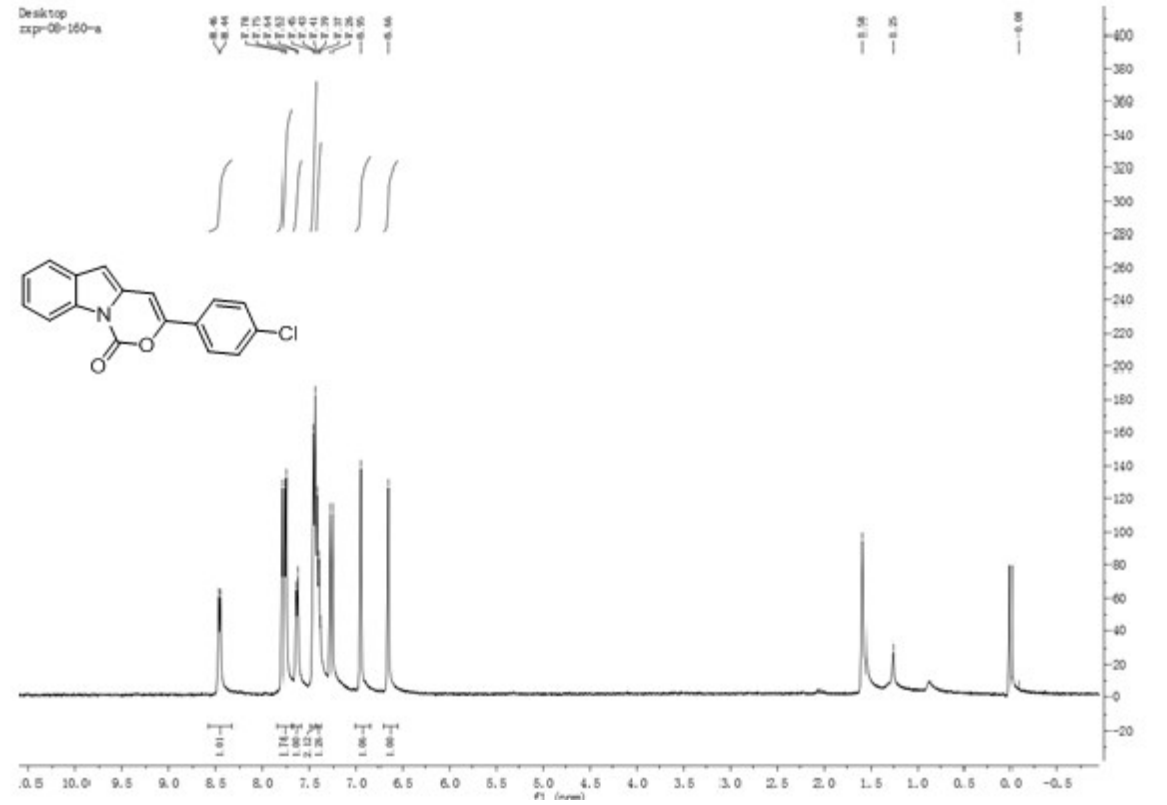


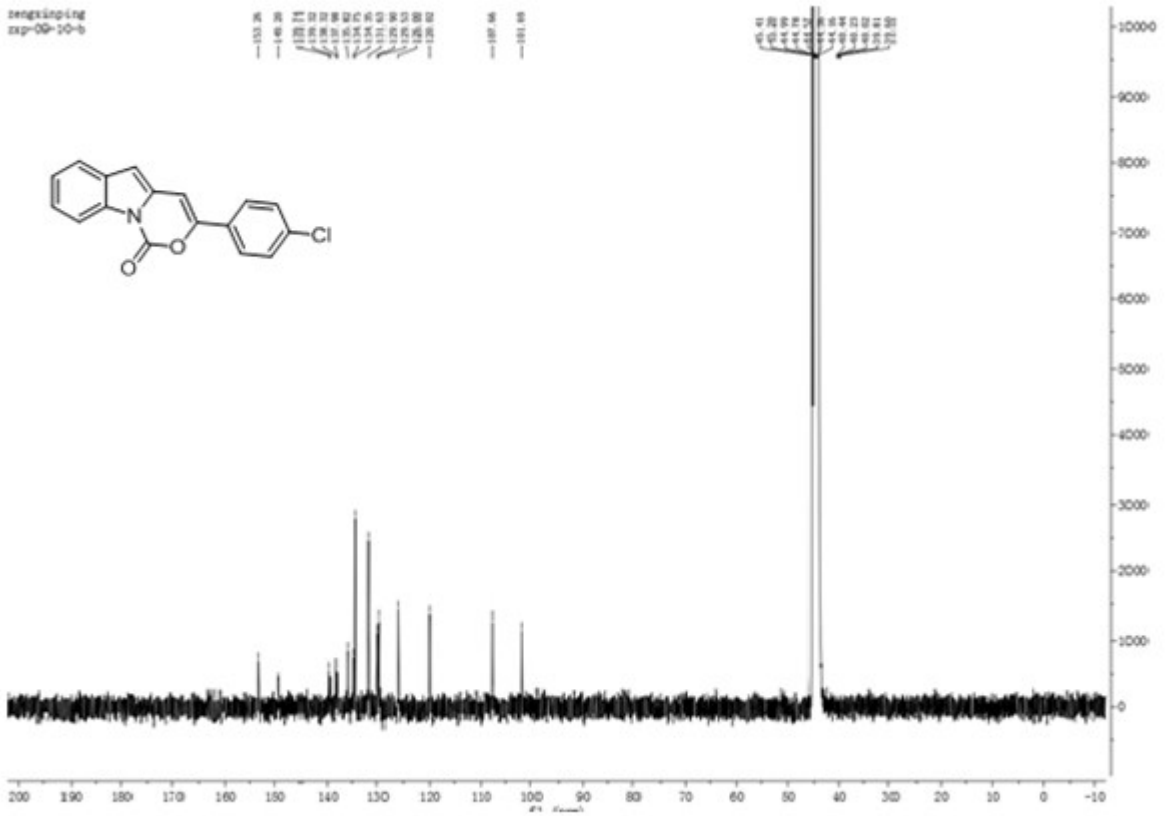
**3g**



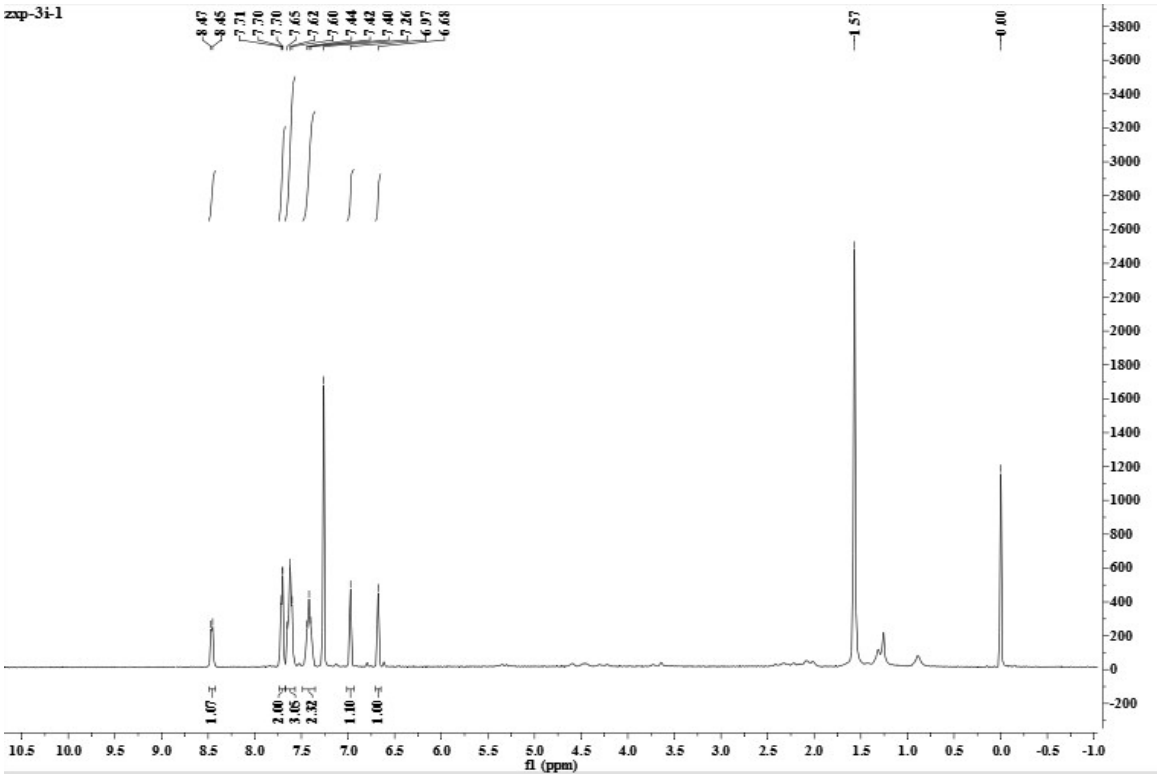



**3h**



**3i**


zxp-3i-1
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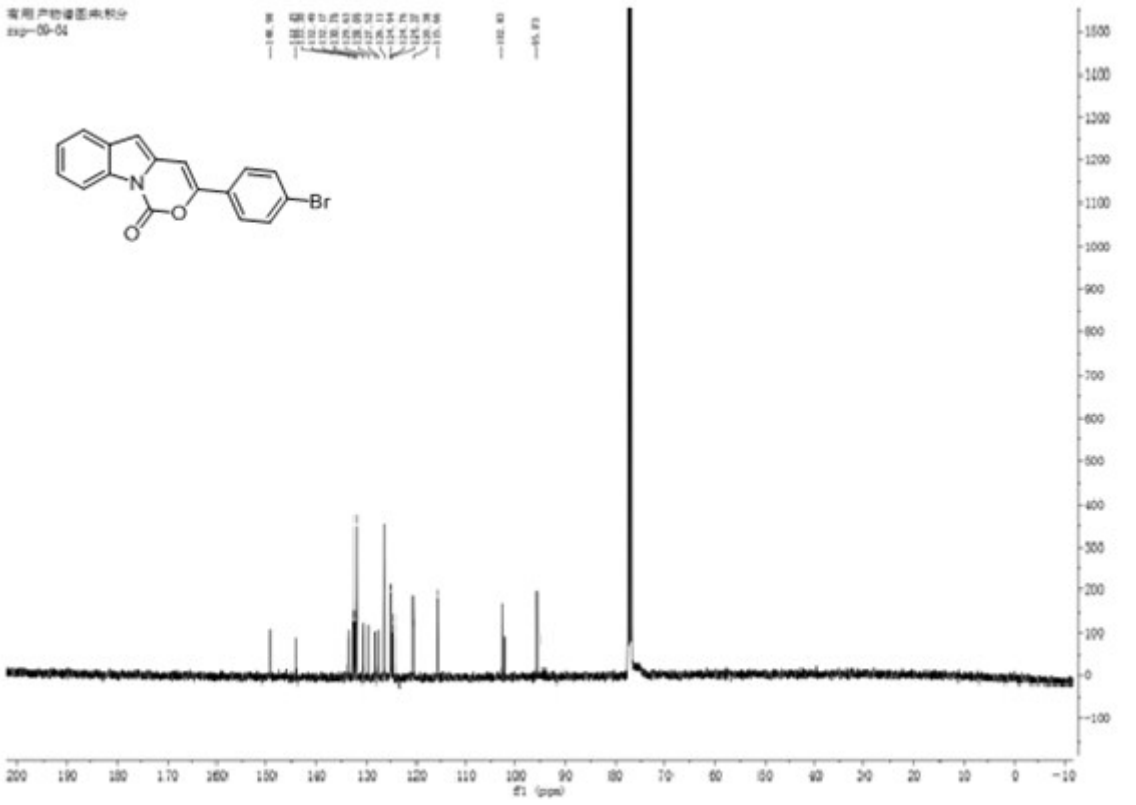
8.45
7.71
7.70
7.70
7.65
7.62
7.60
7.44
7.42
7.40
7.26
6.97
6.68
1.57
0.00
1.07
2.00
3.65
2.32
1.10
1.00
f1 (ppm)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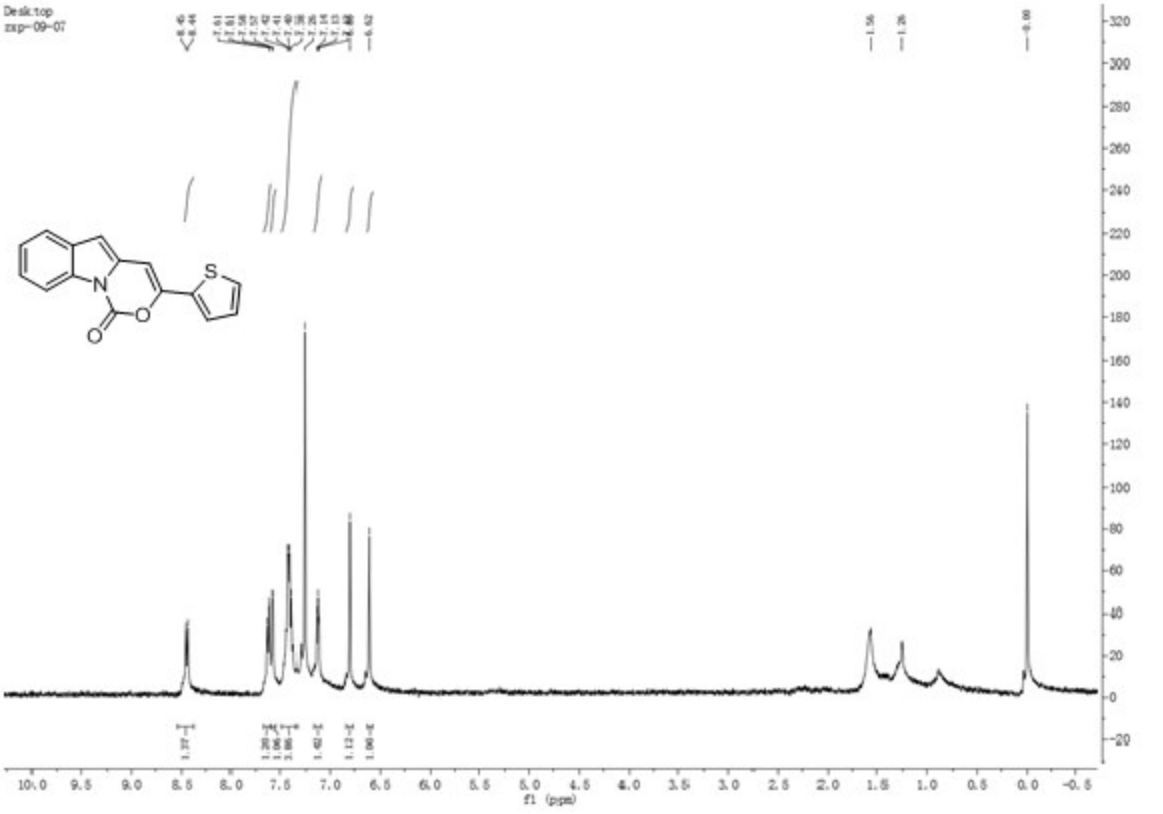
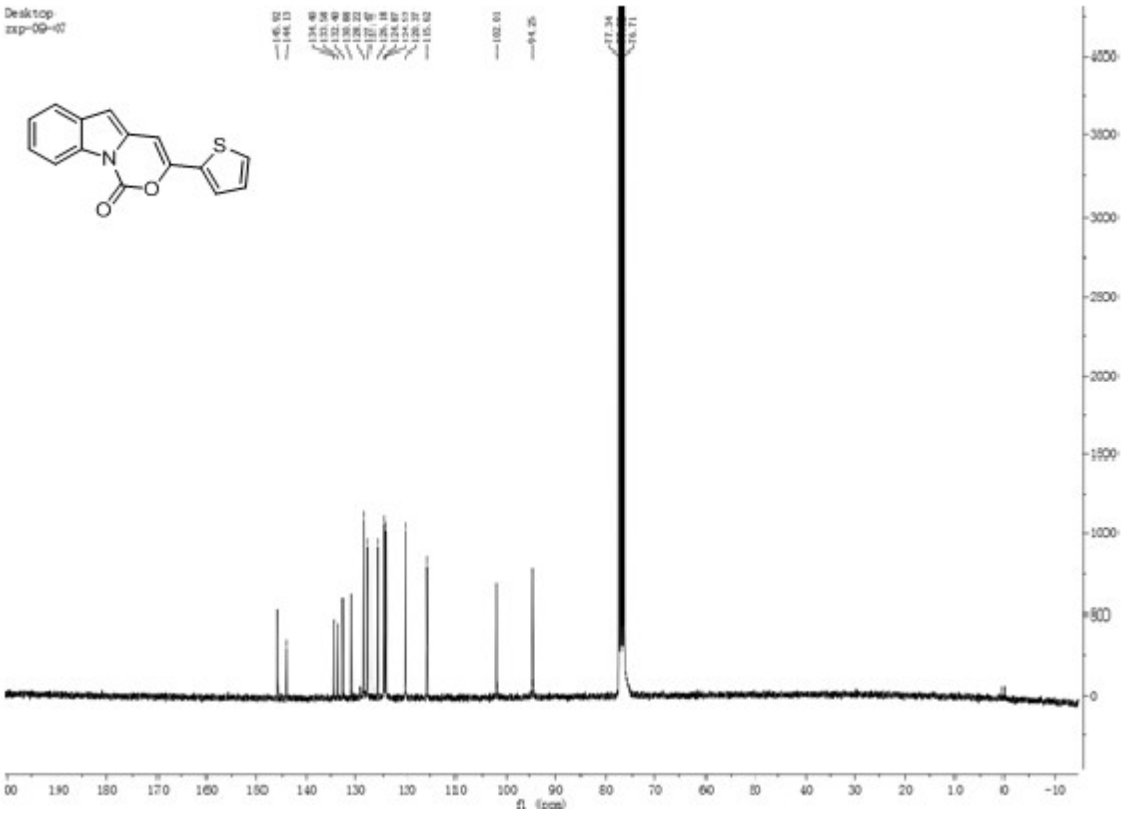
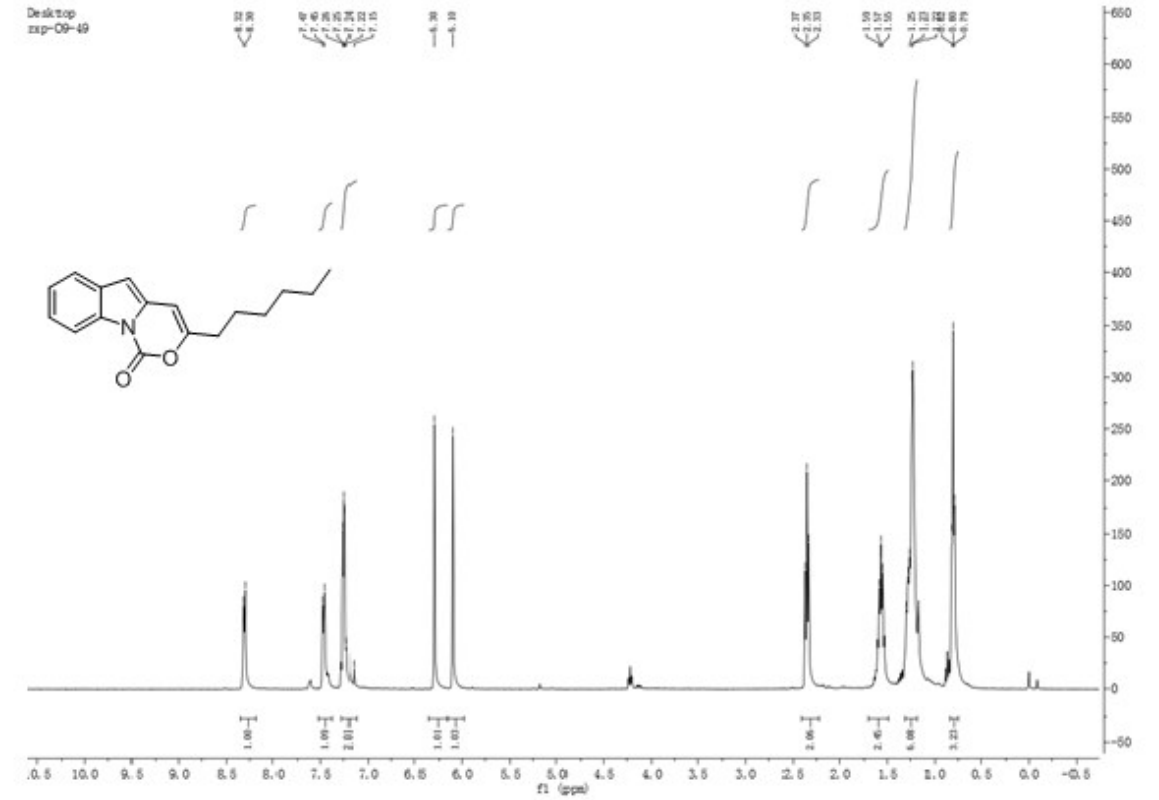
Br
f1 (ppm)

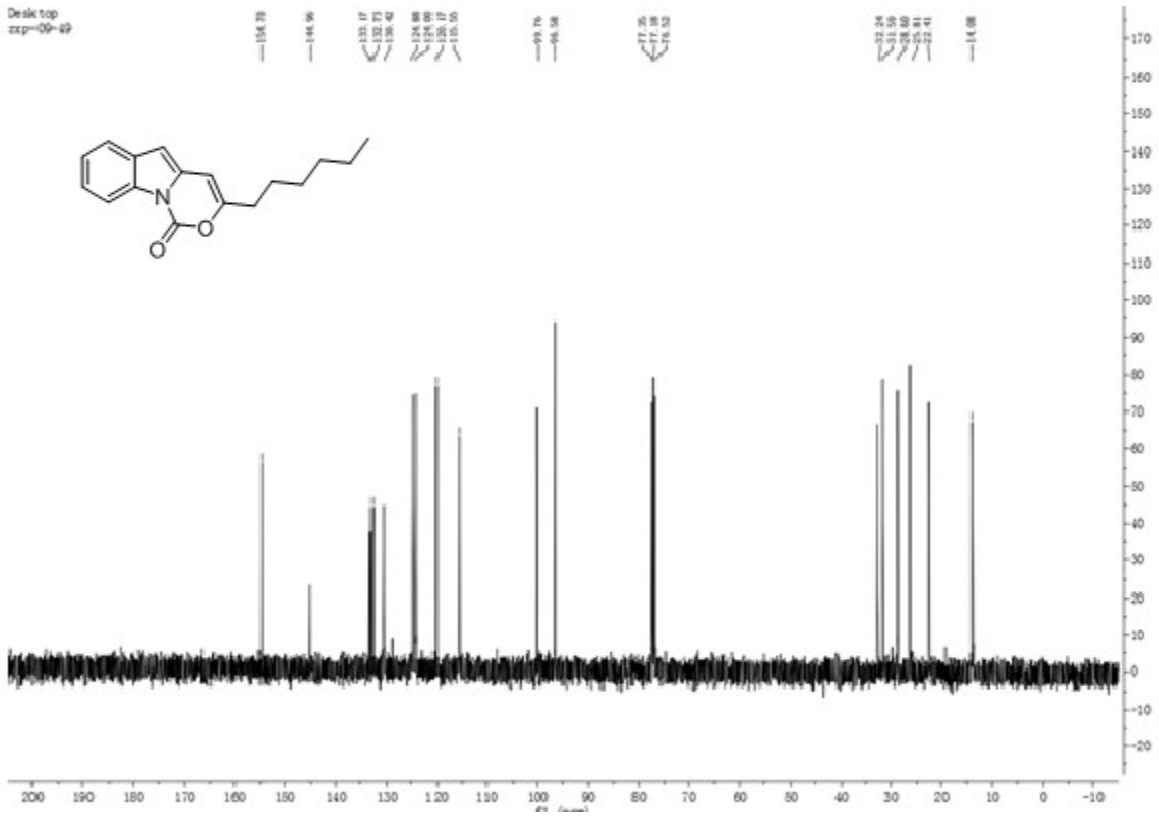
**3j**



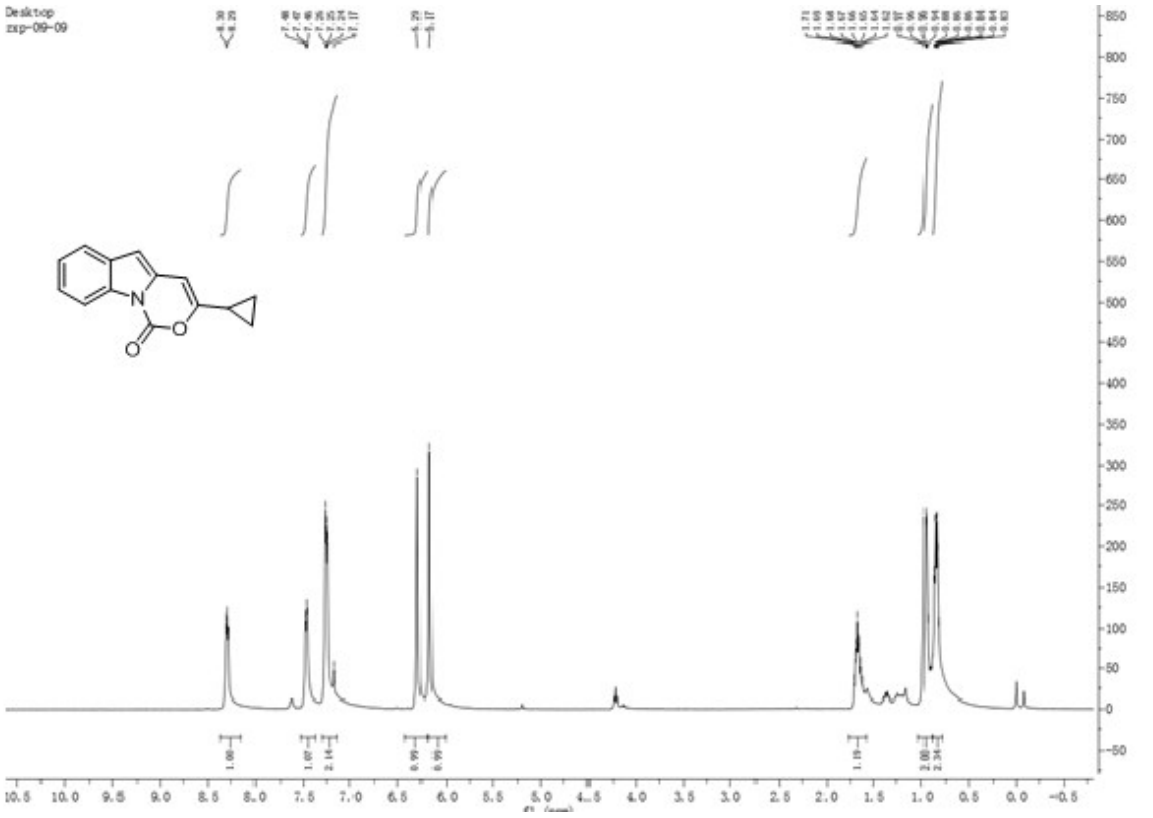



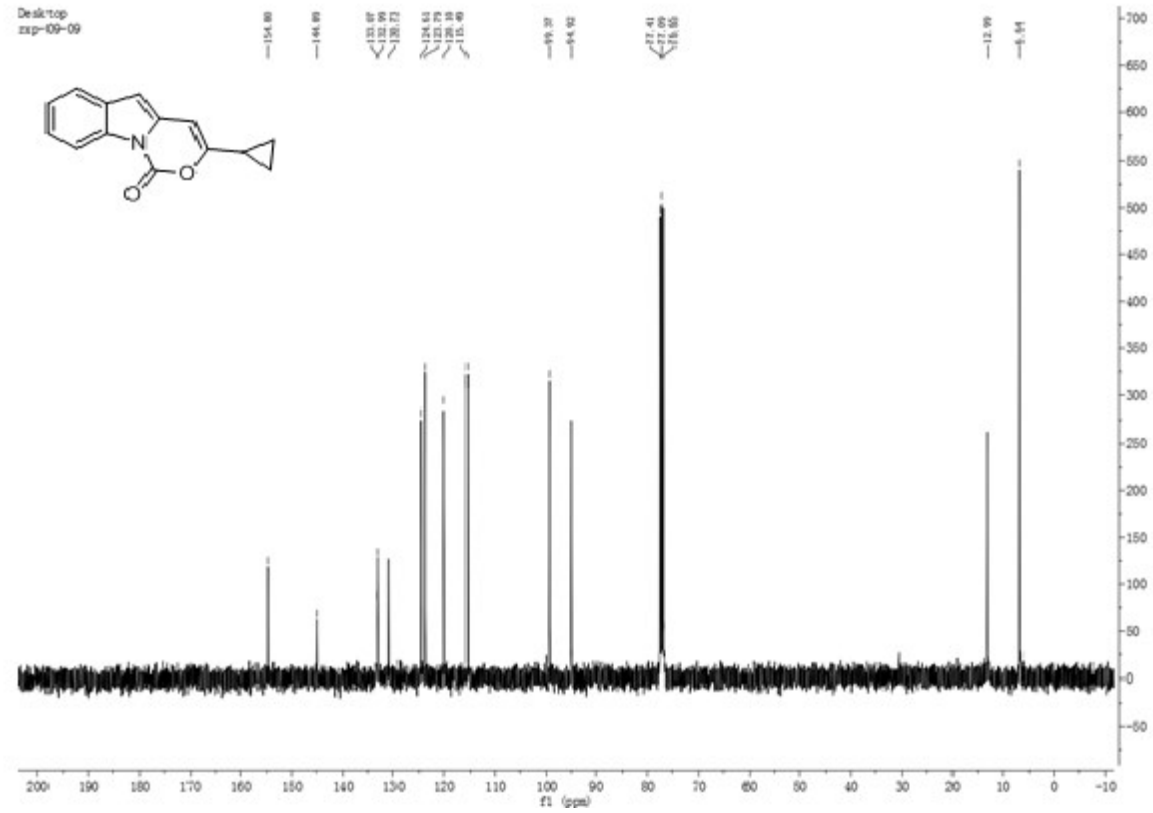
**3k**



**3l**



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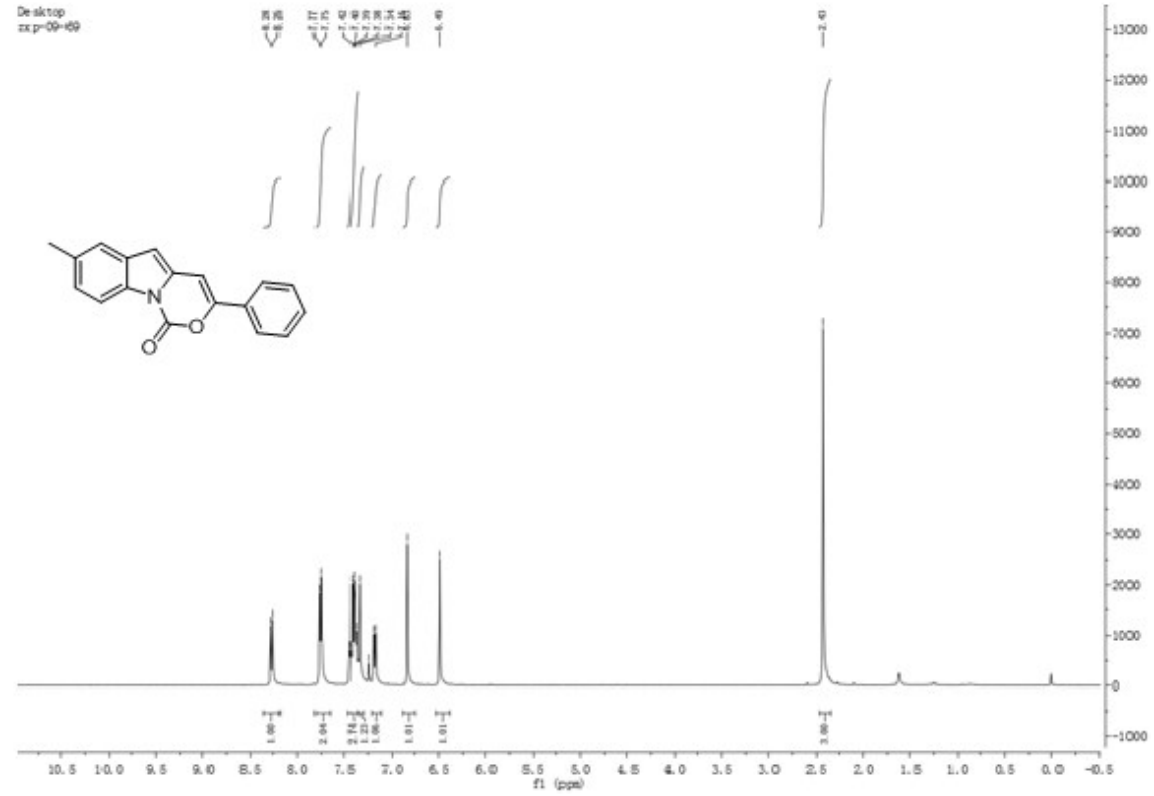
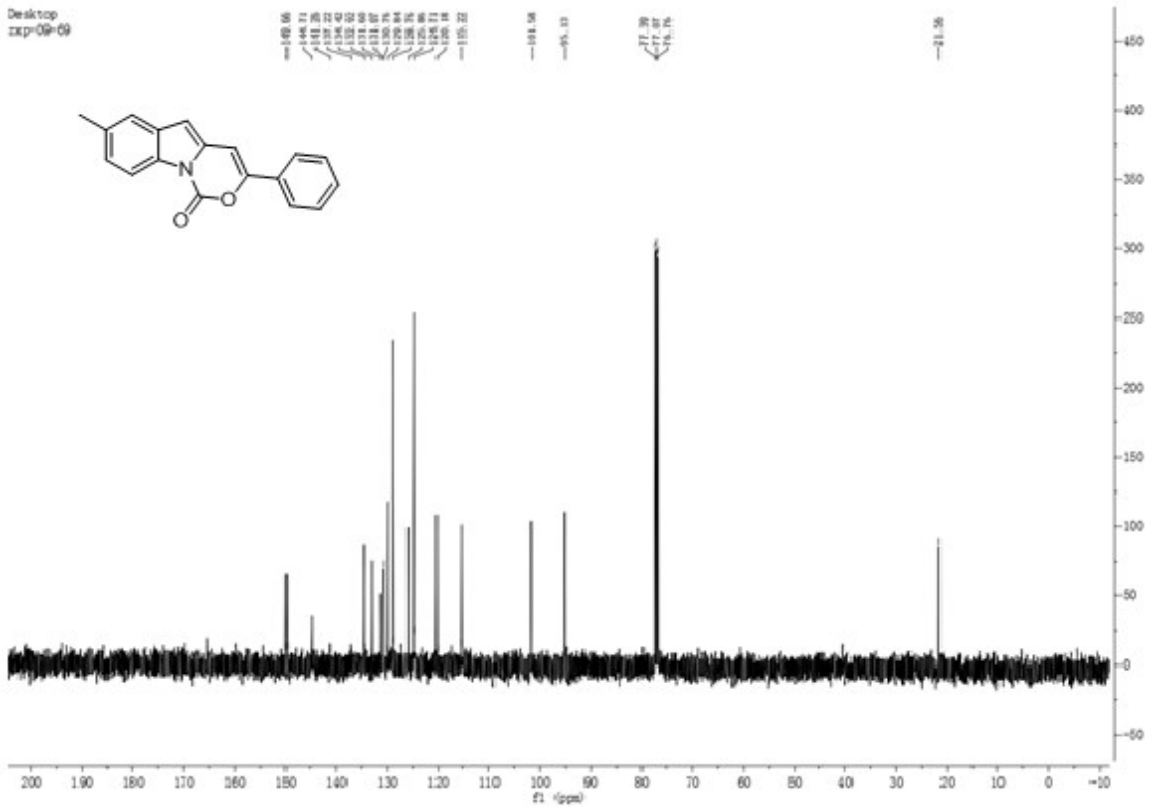
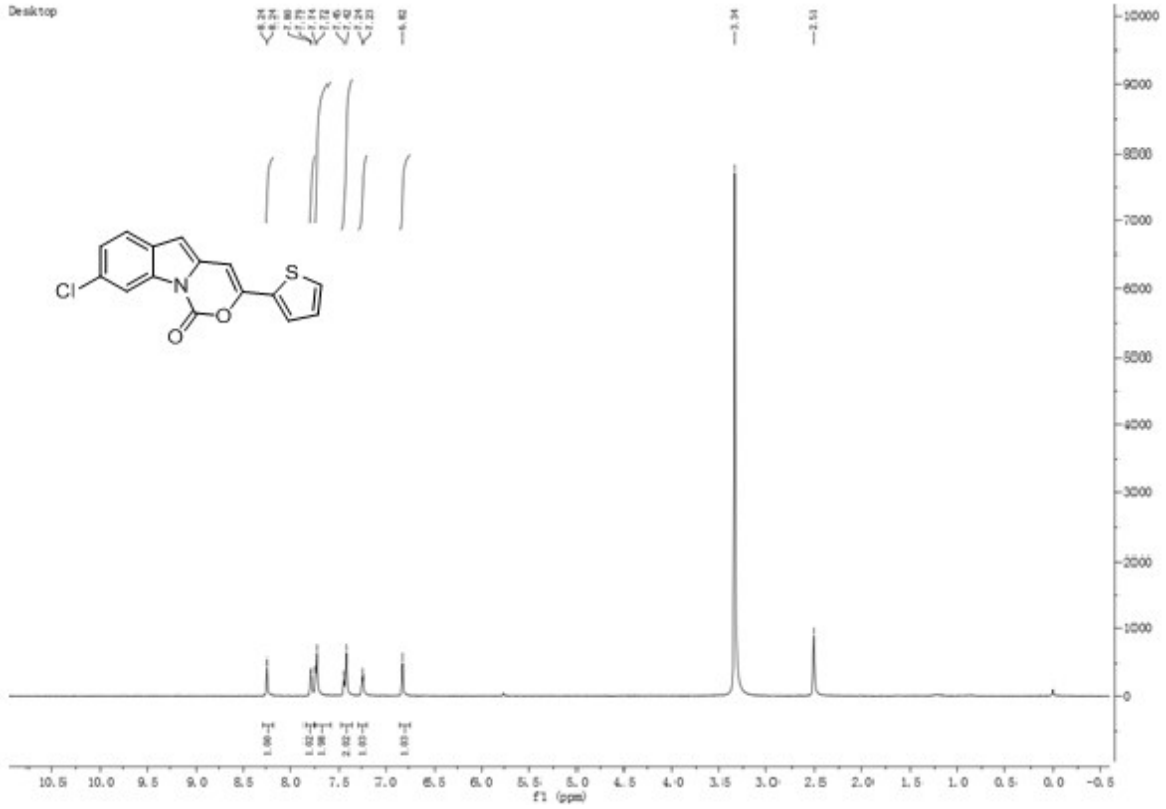
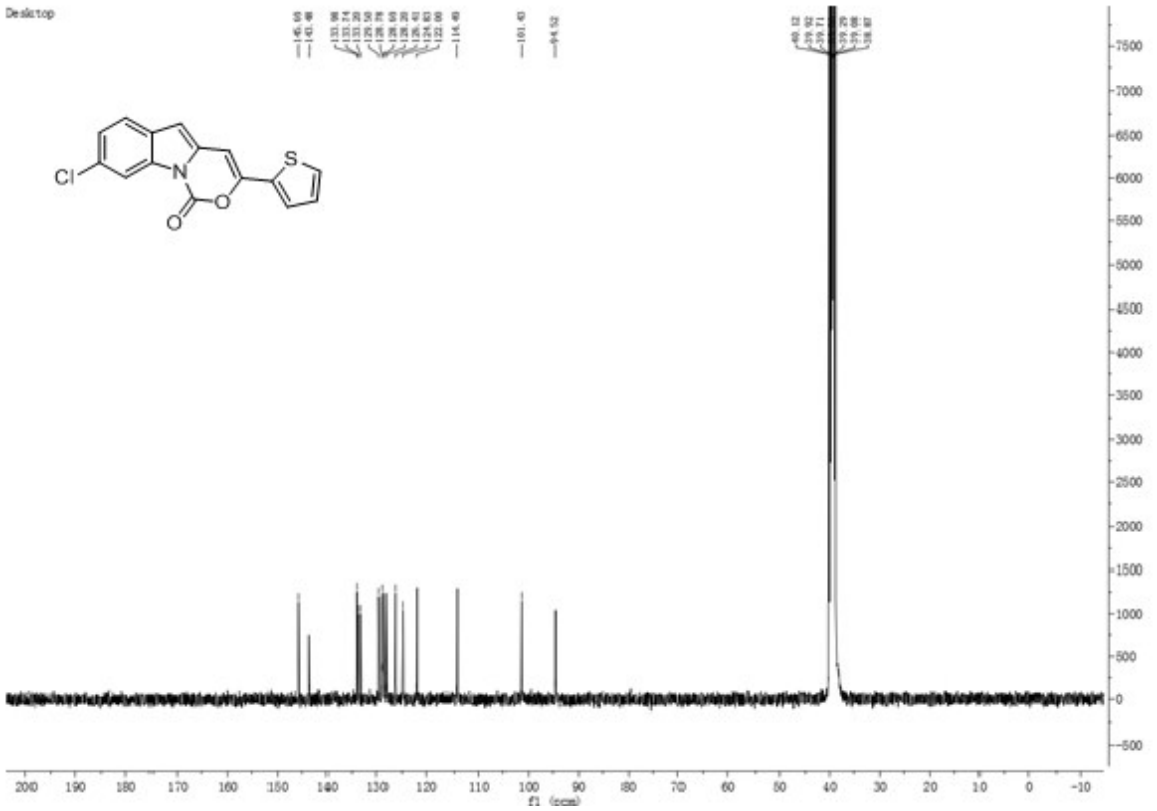


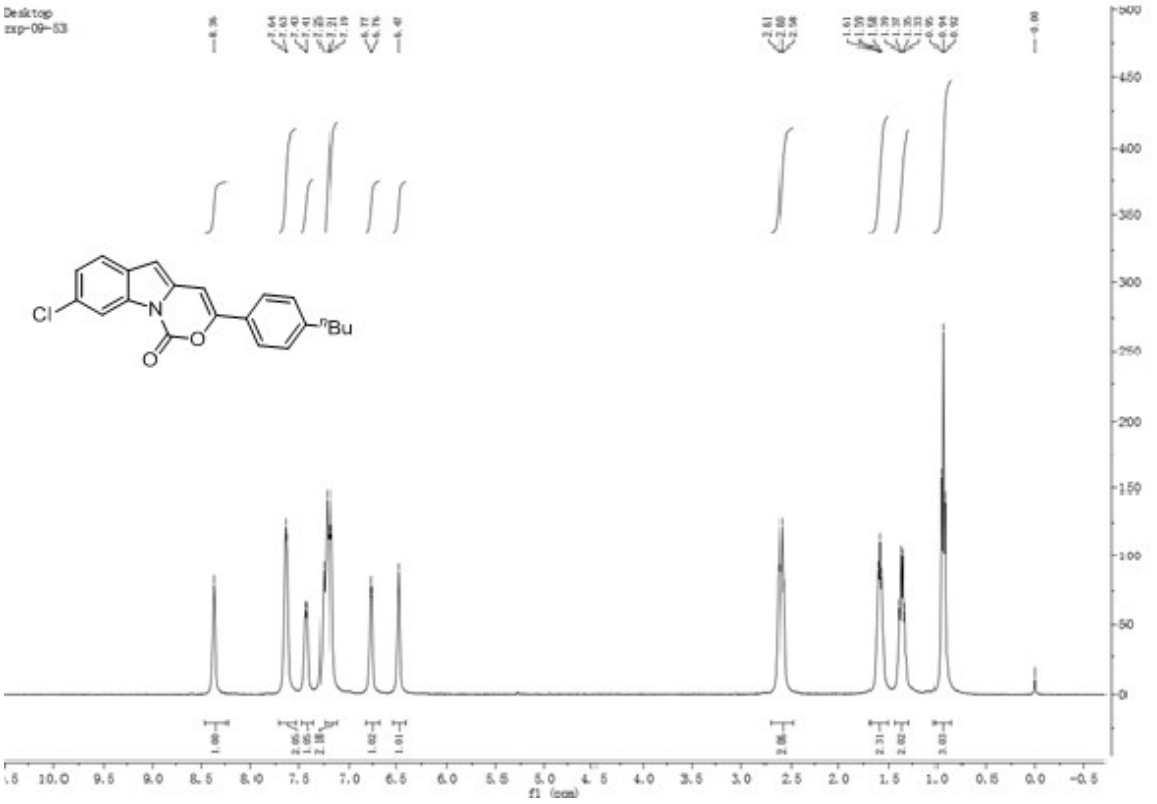


**3n**



**3o**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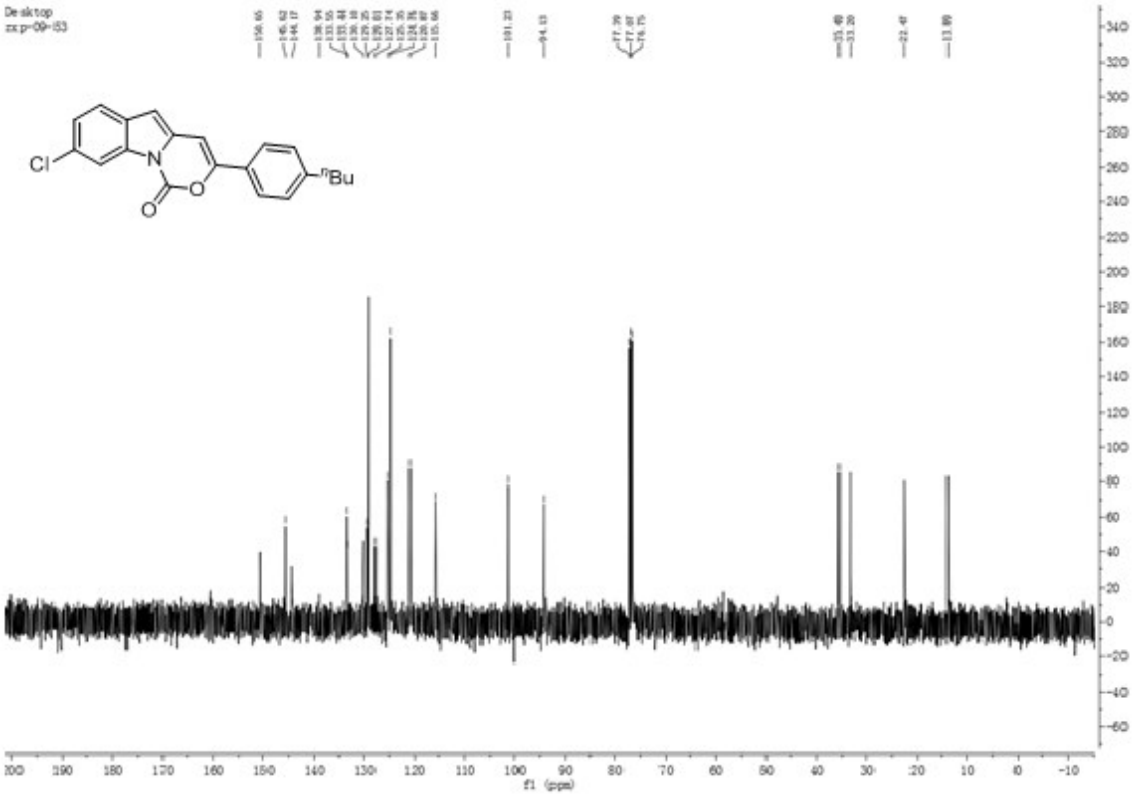
Cl
N
O
O
nBu
f1 (ppm)


Desktop
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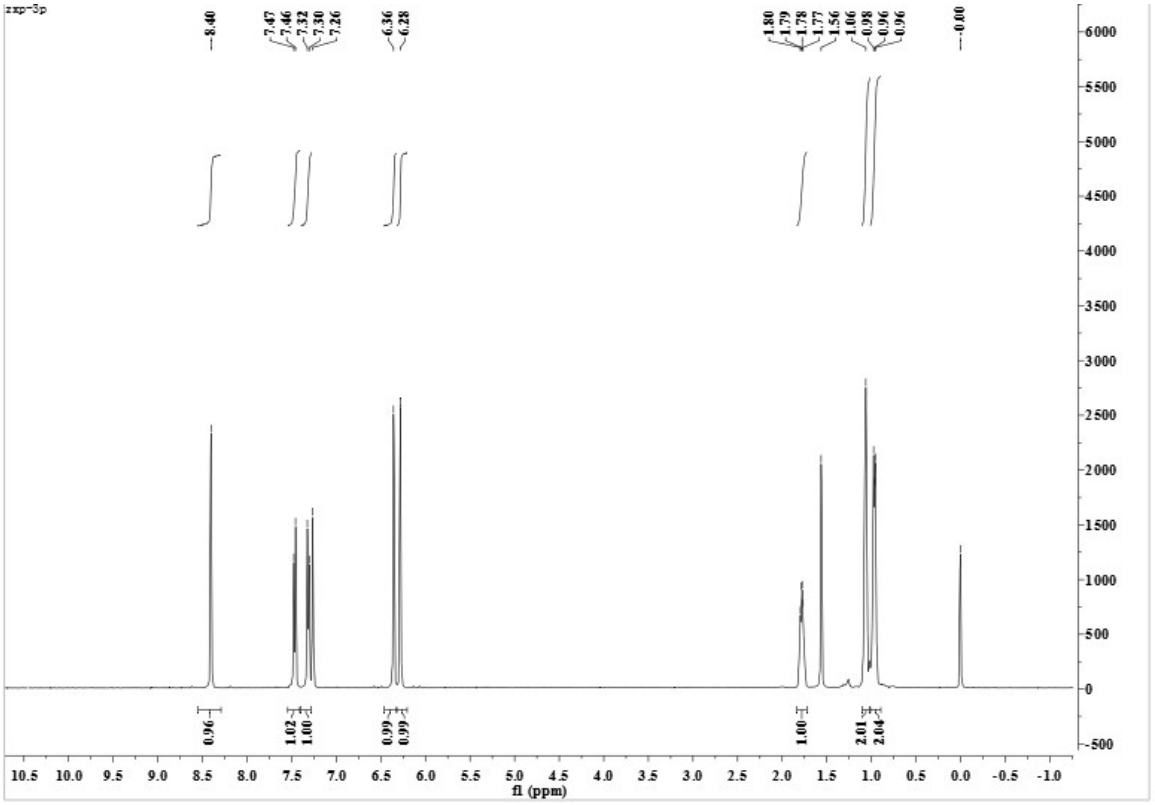
Cl
N
O
O
nBu
f1 (ppm)

**3p**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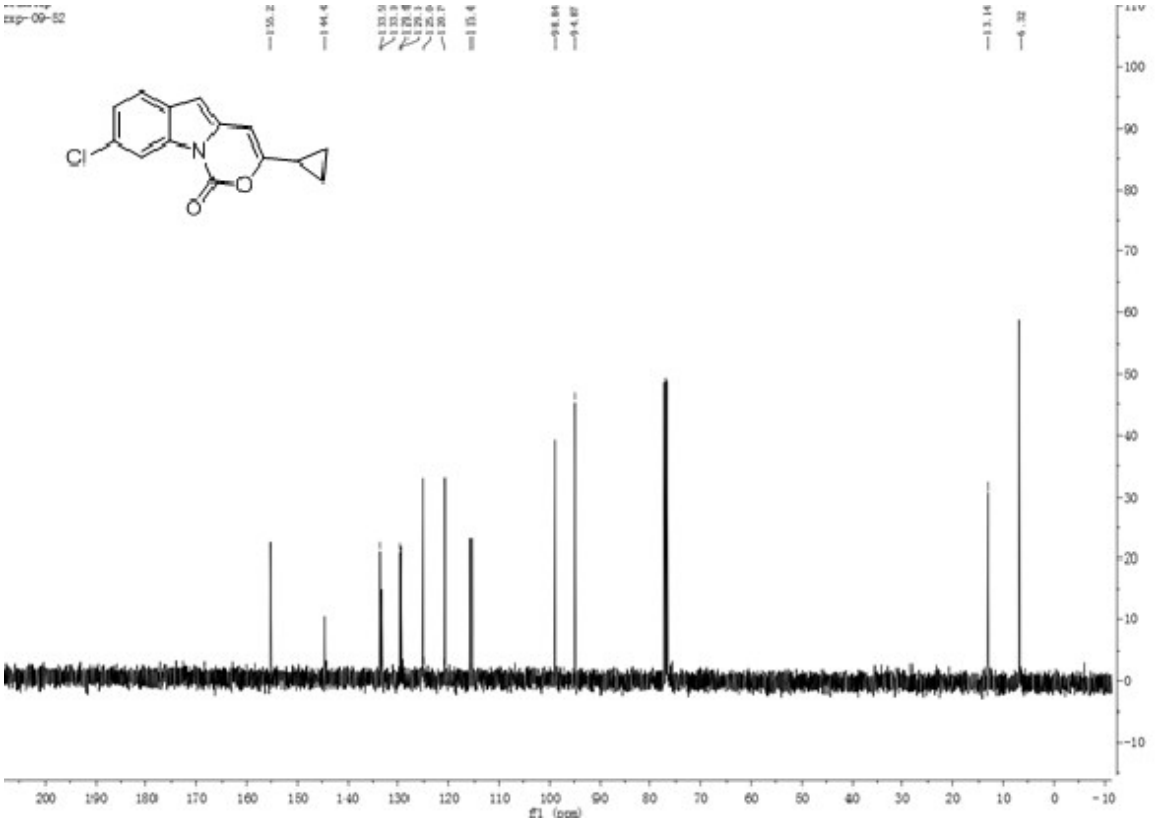
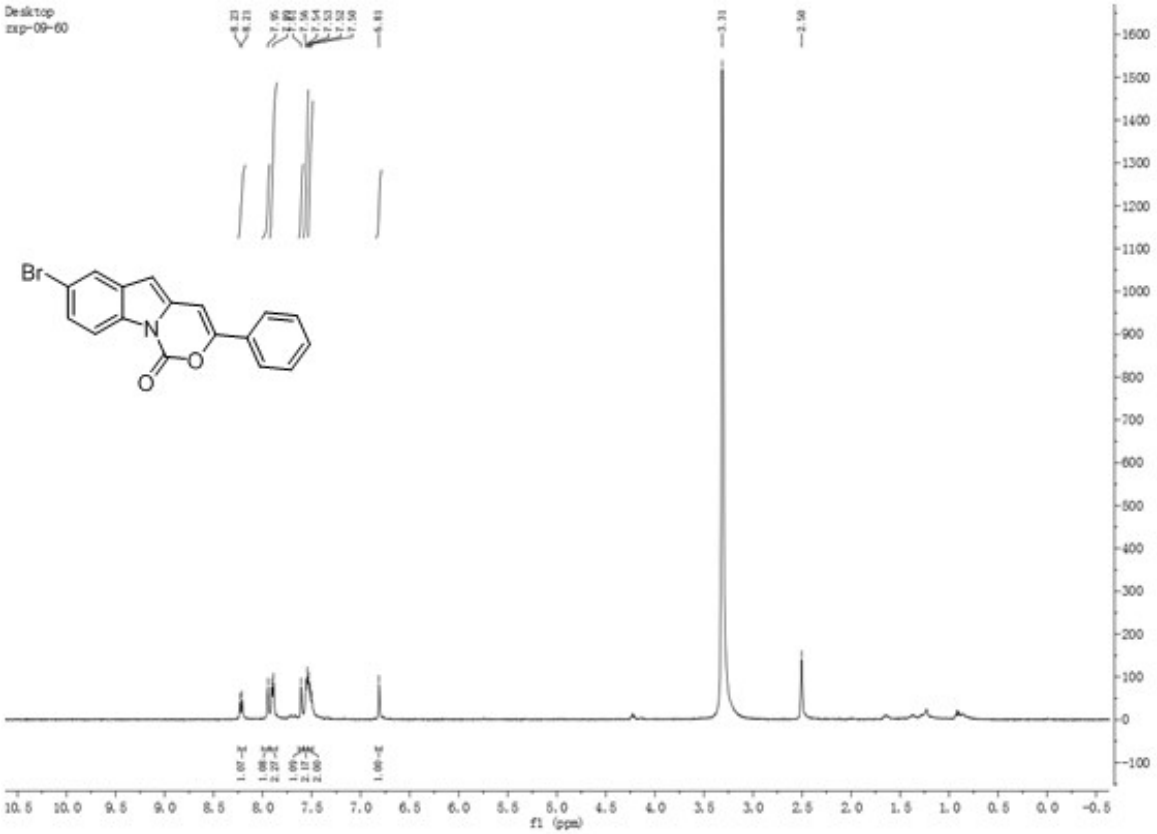
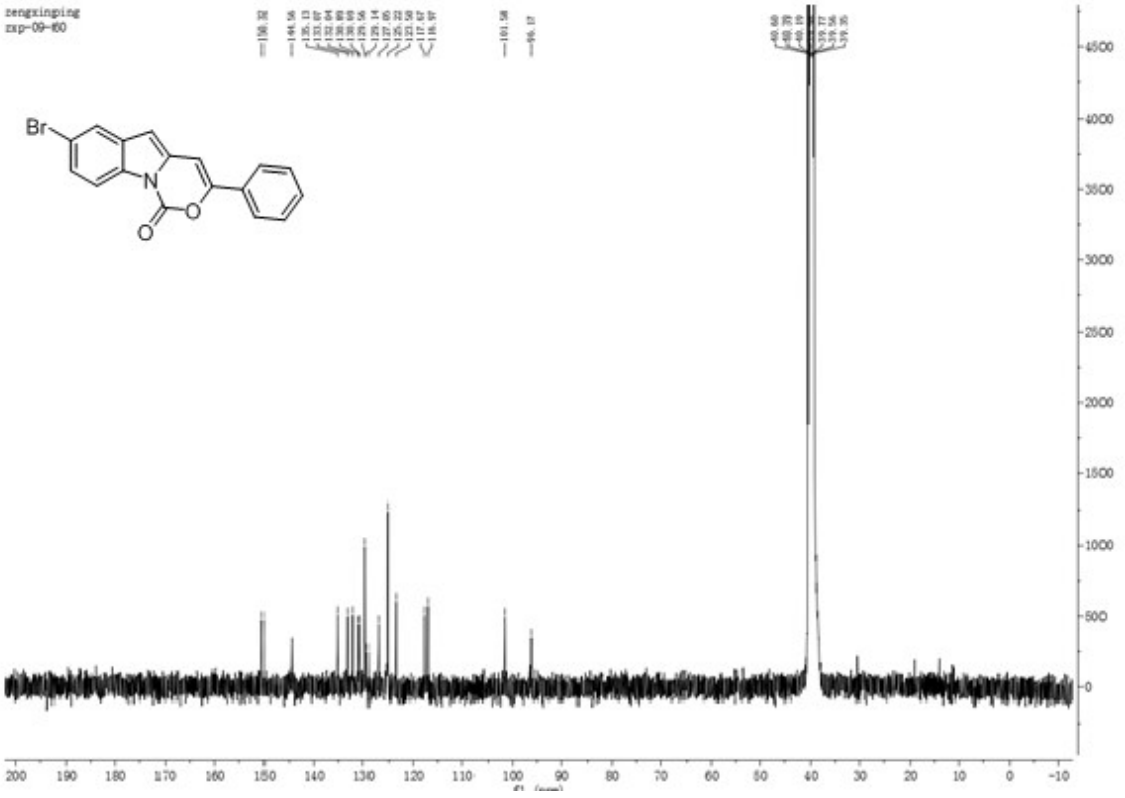
7.32
7.30
7.26
6.36
6.28
1.80
1.79
1.78
1.77
1.56
1.06
0.98
0.96
0.96
0.00
0.96
1.02
1.00
0.99
0.99
1.00
2.01
2.04
f1 (ppm)

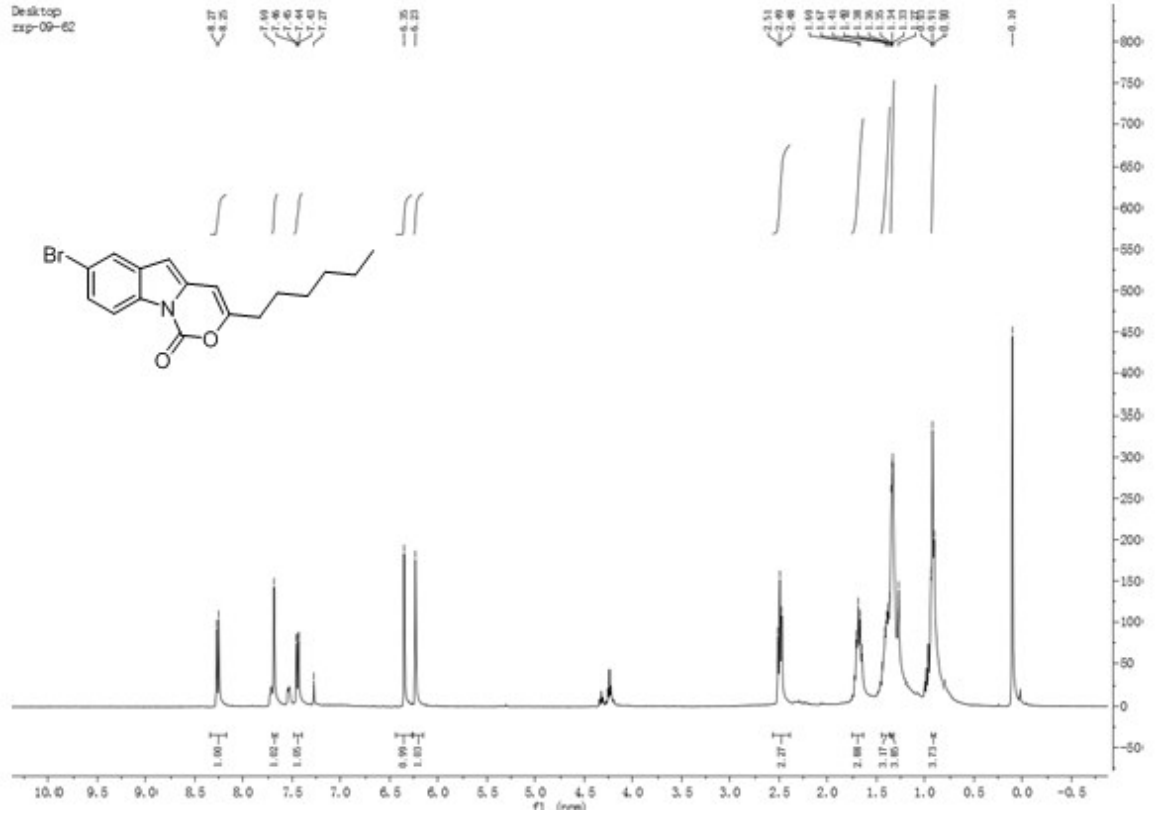

exp-09-52
Cl
N
O
O
f1 (ppm)

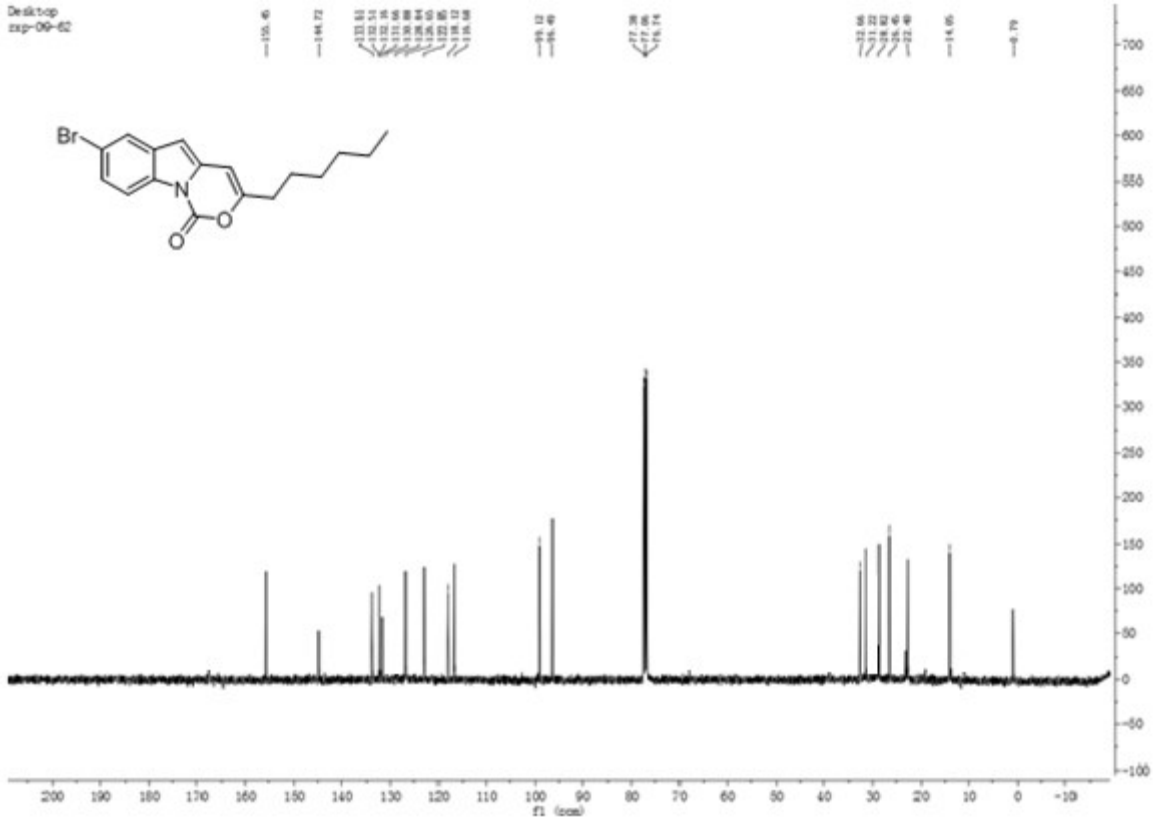
**3q**


Desktop
zxp-09-60
Br
N
O
O
f1 (ppm)

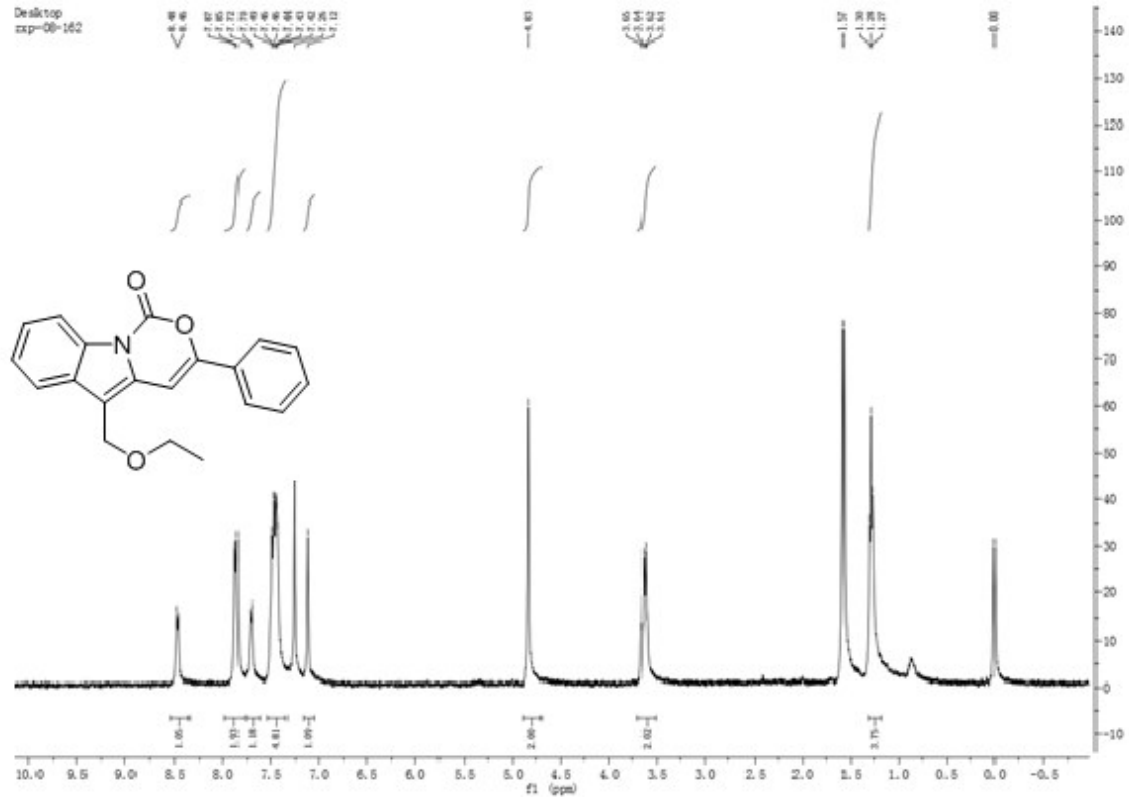

zengxinping
zxp-09-60
Br
N
O
O
f1 (ppm)

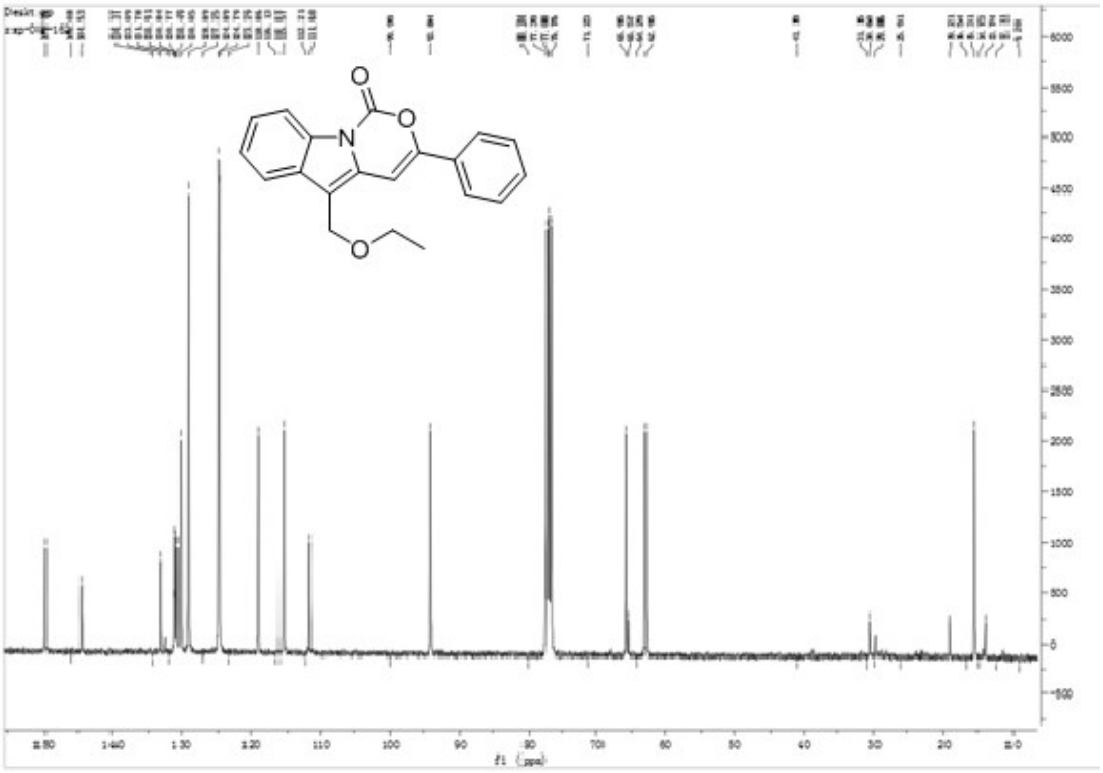
**3r**



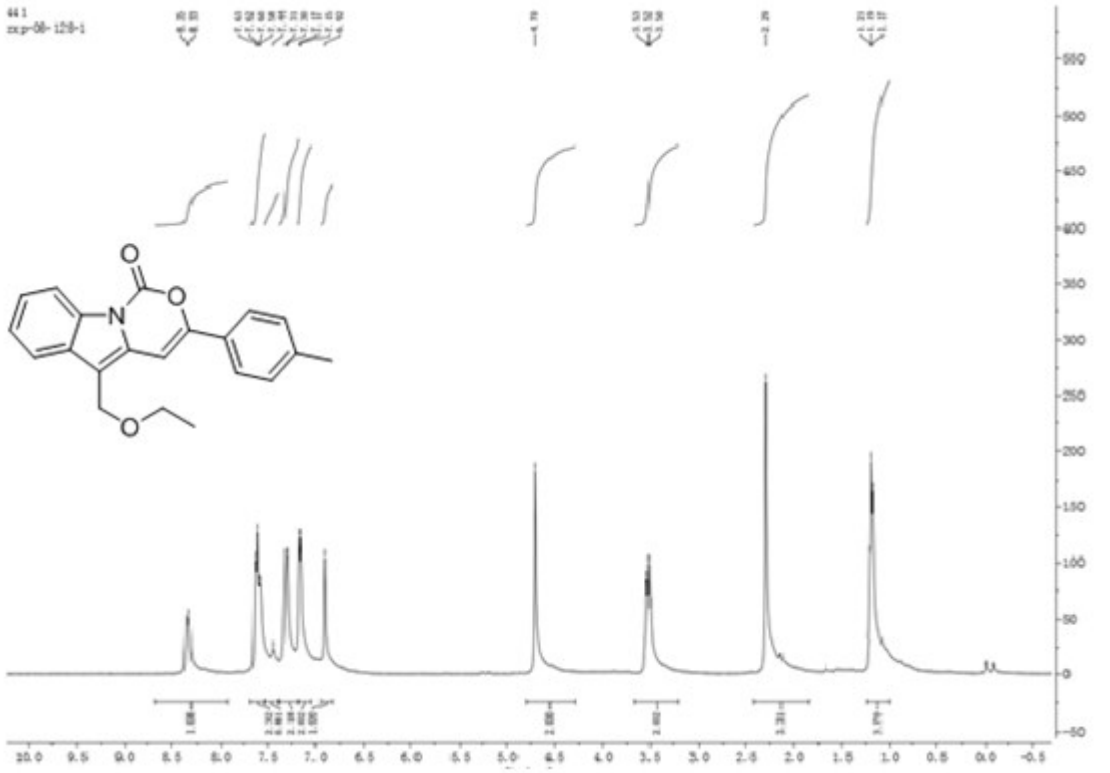



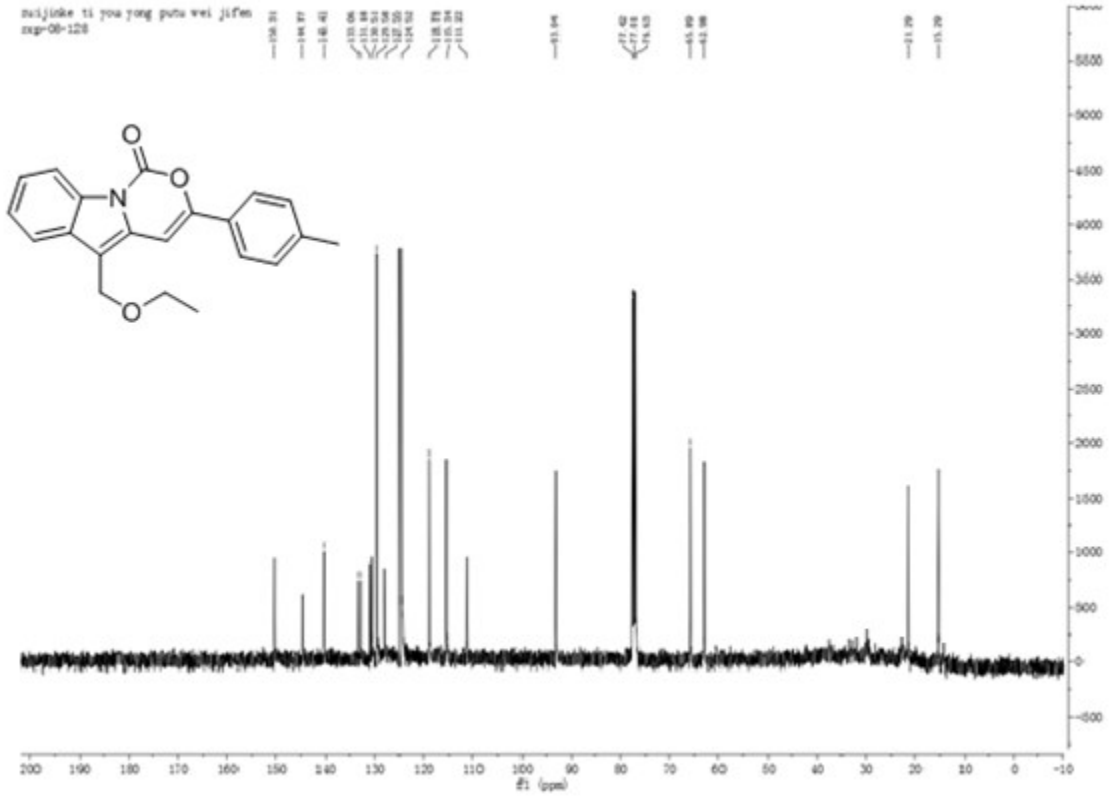
**5a**



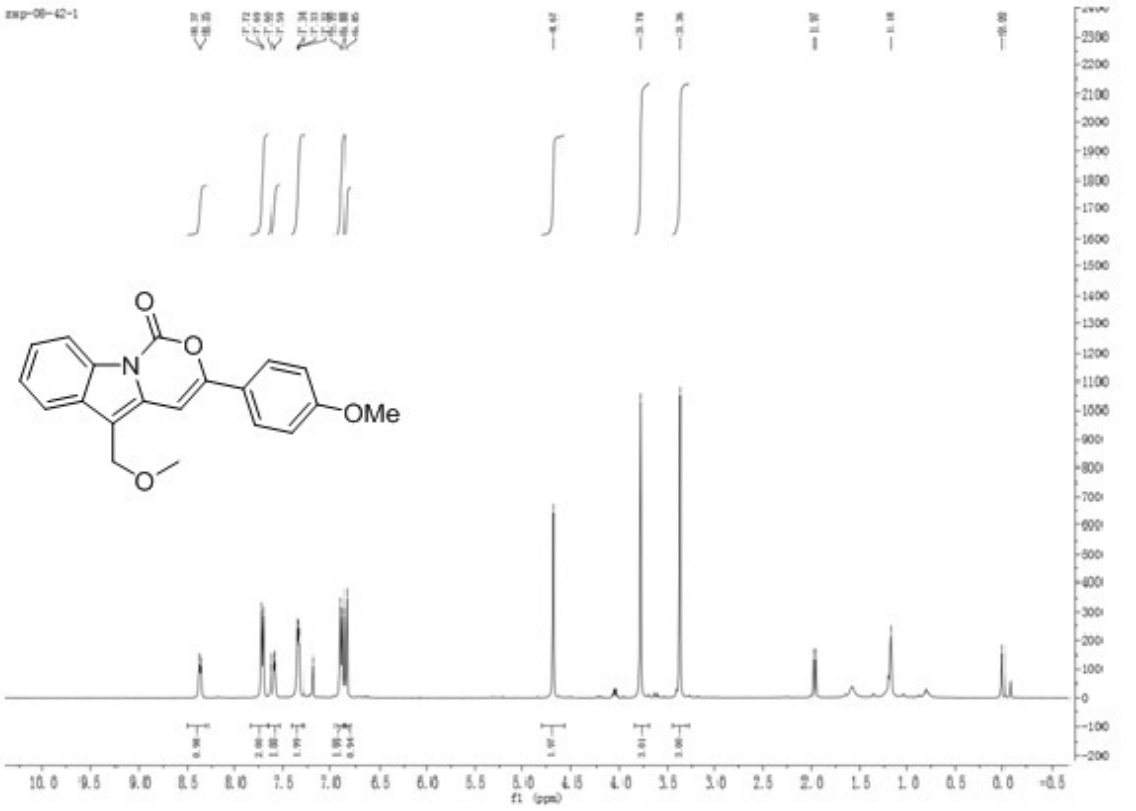



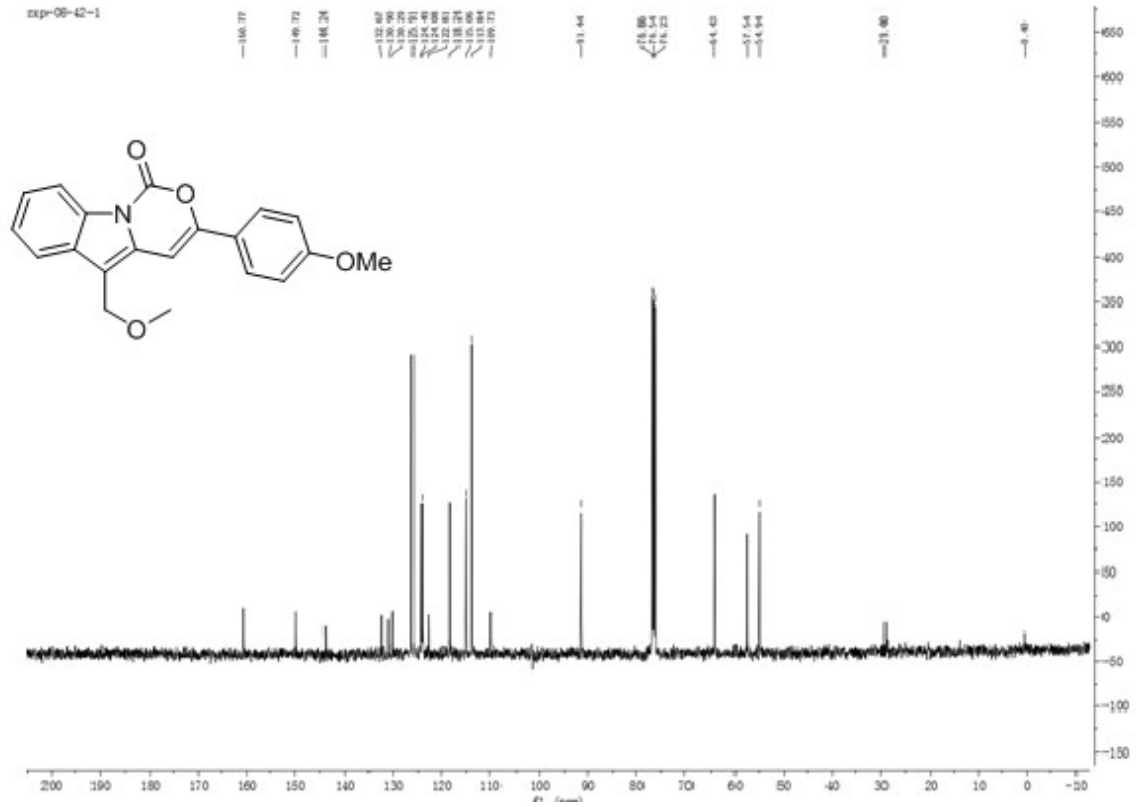
**5b**



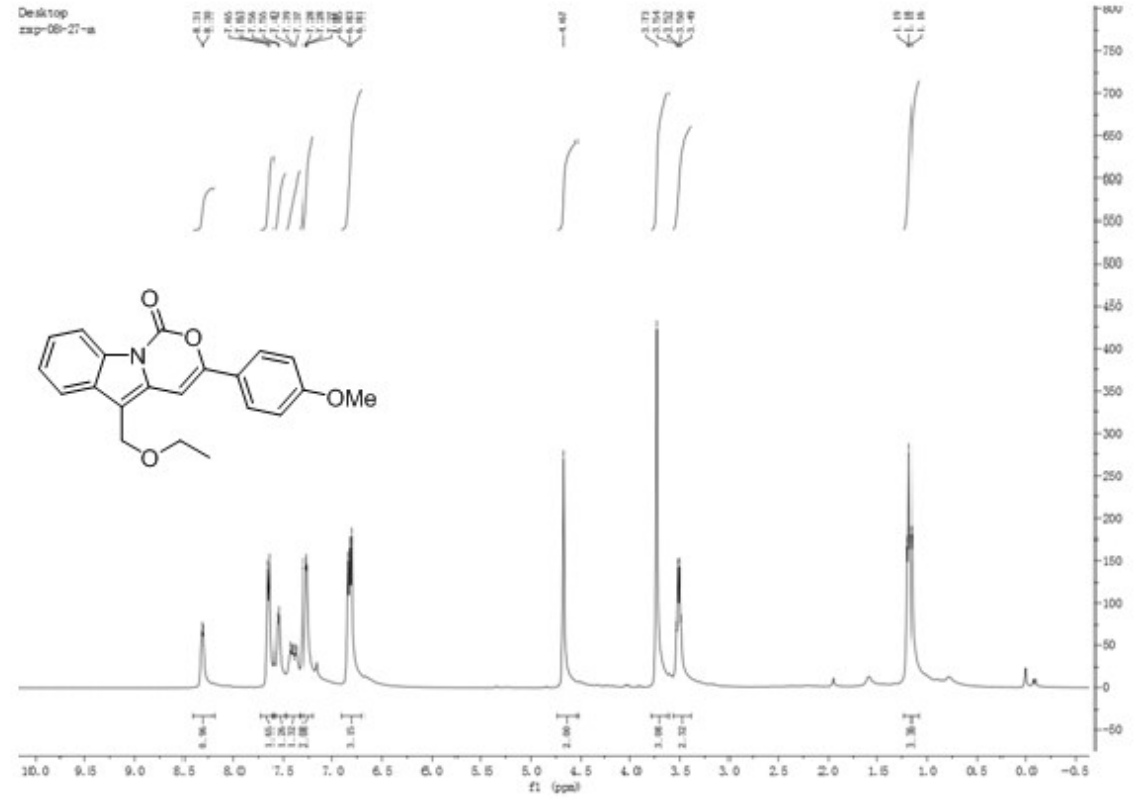


**5c**



**5d**


Desktop
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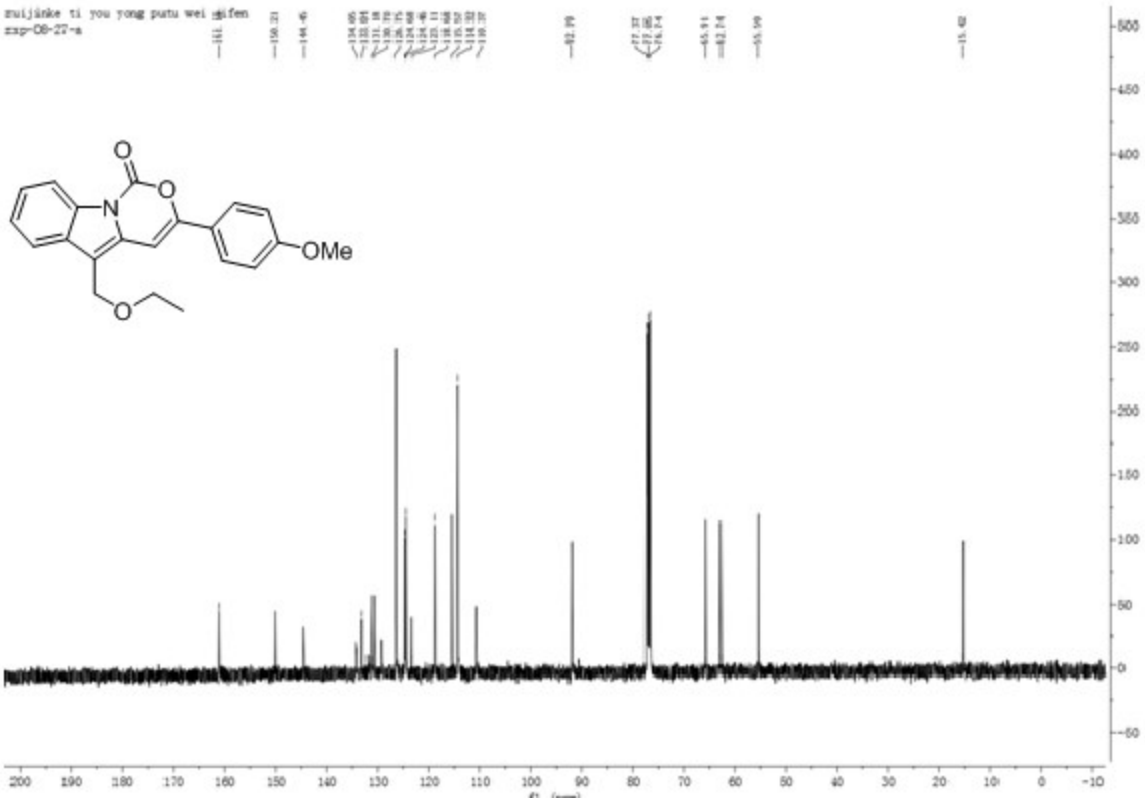
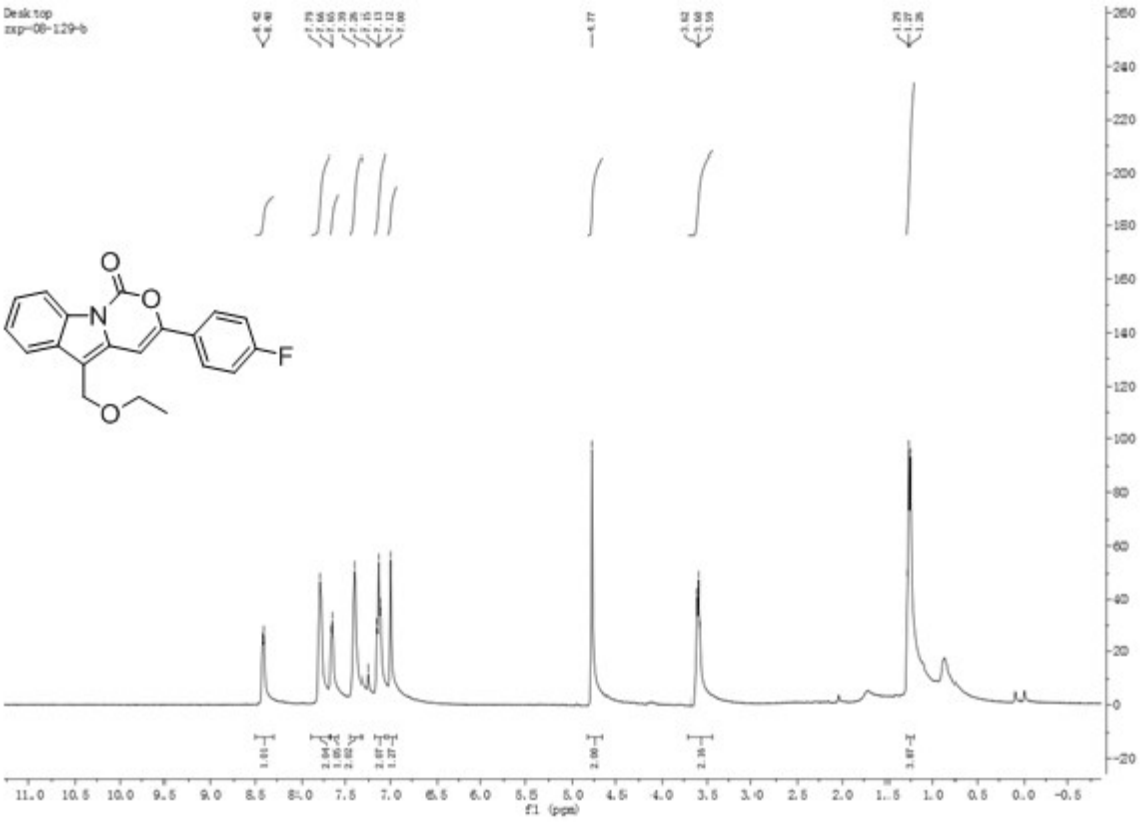
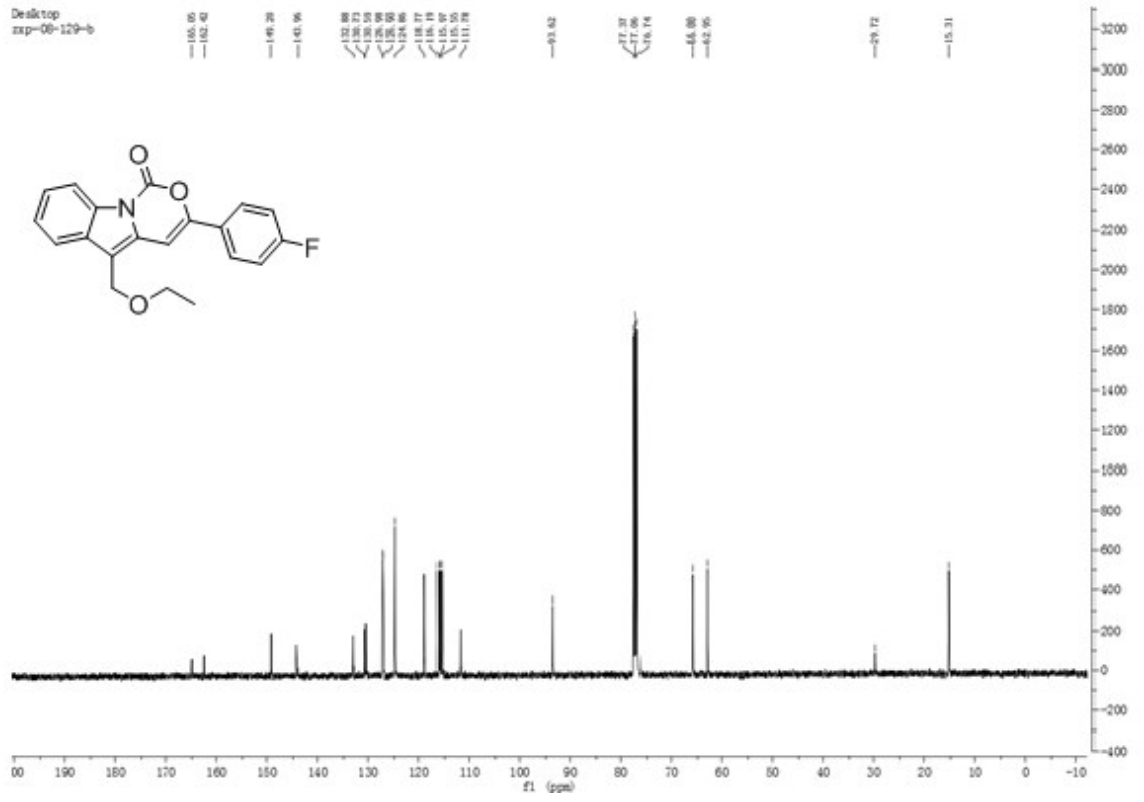
OMe
f1 (ppm)


zuijinke ti you yong putu wei qifen
zxp-08-27-a
OMe

**5e**



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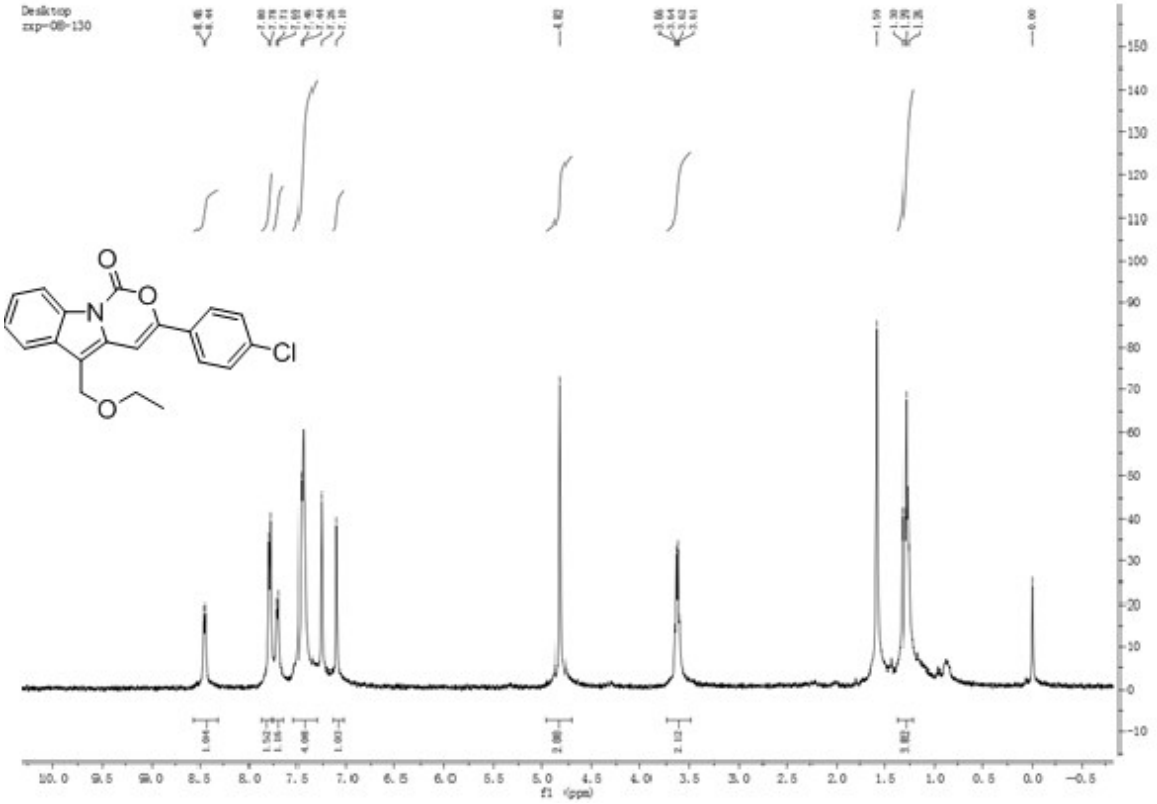
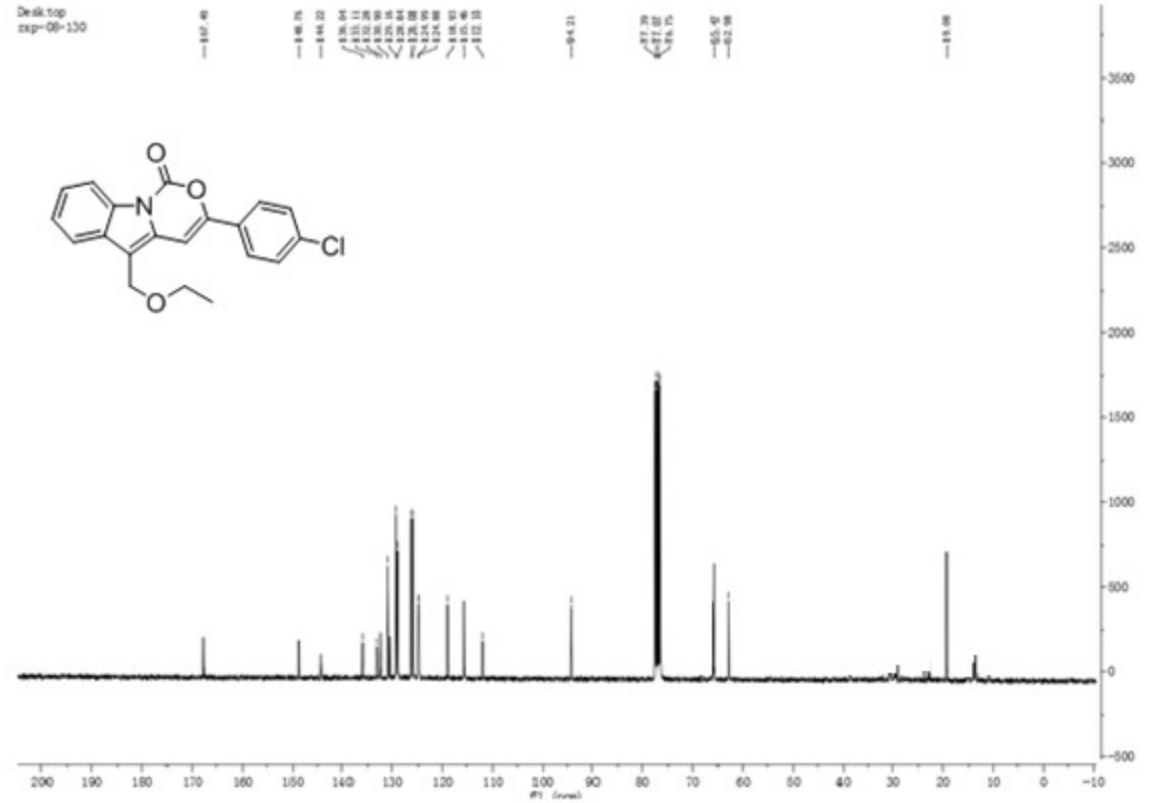
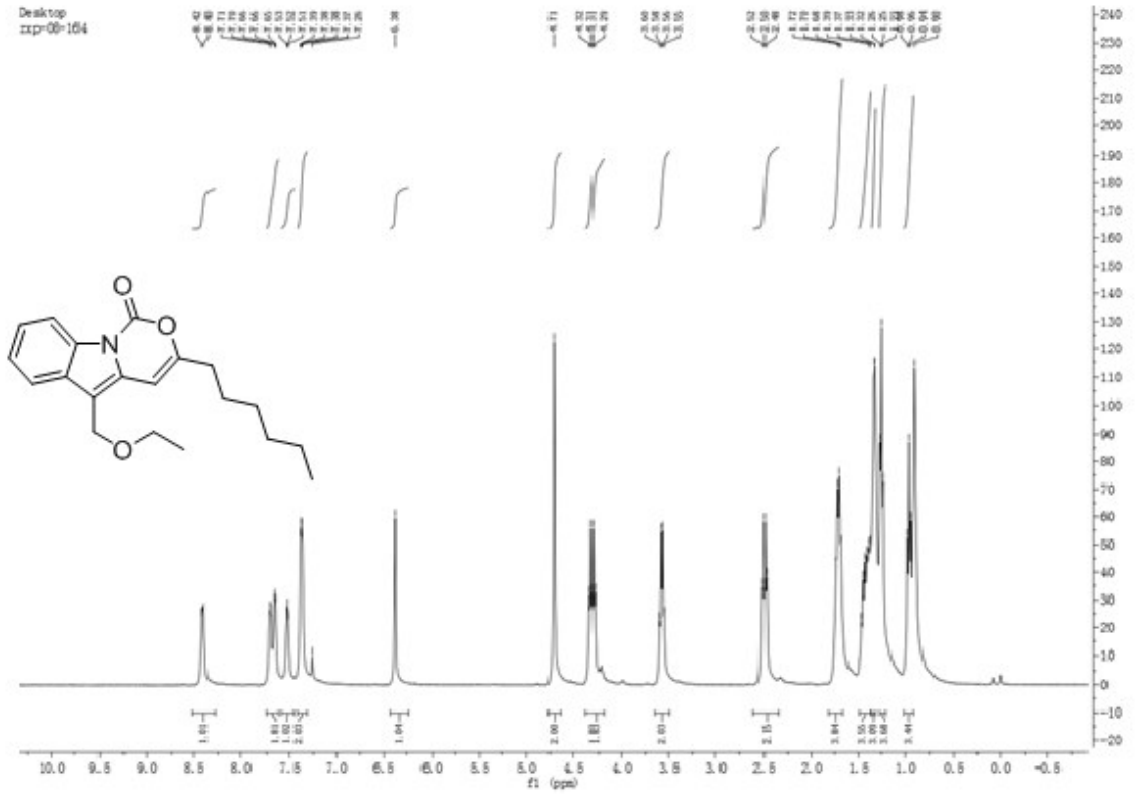
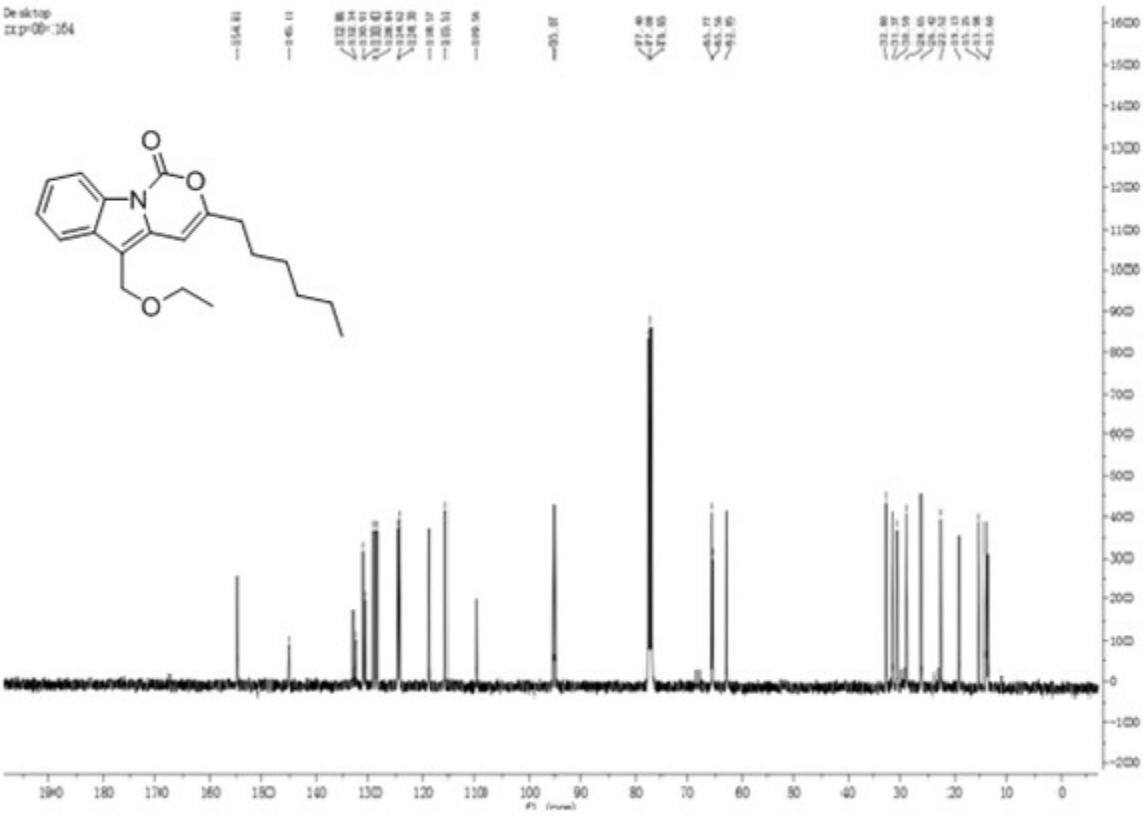


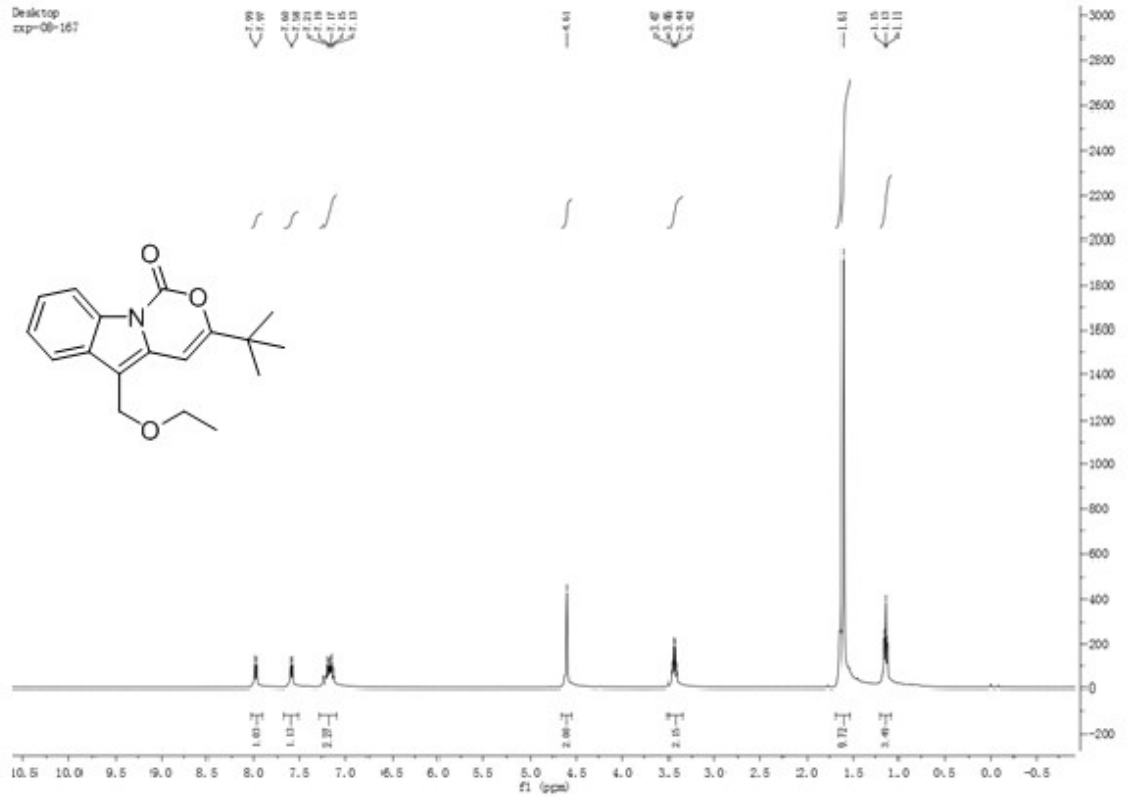



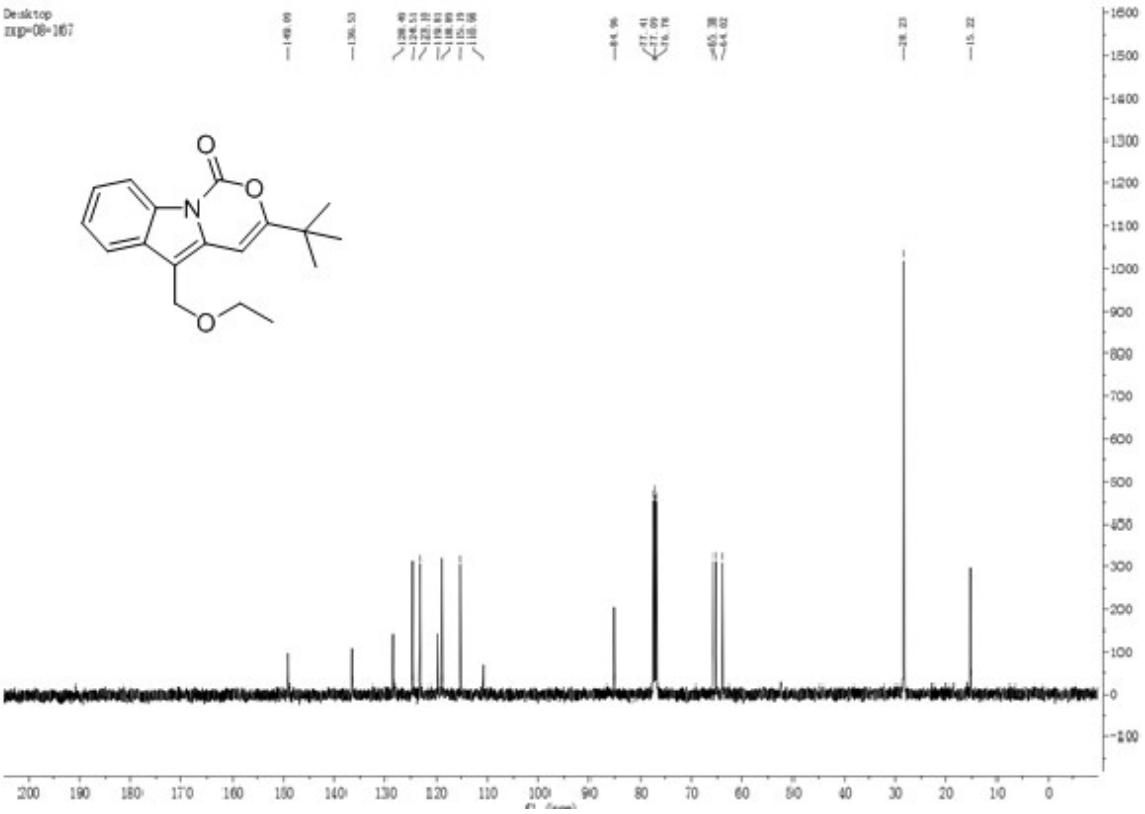
**5g**



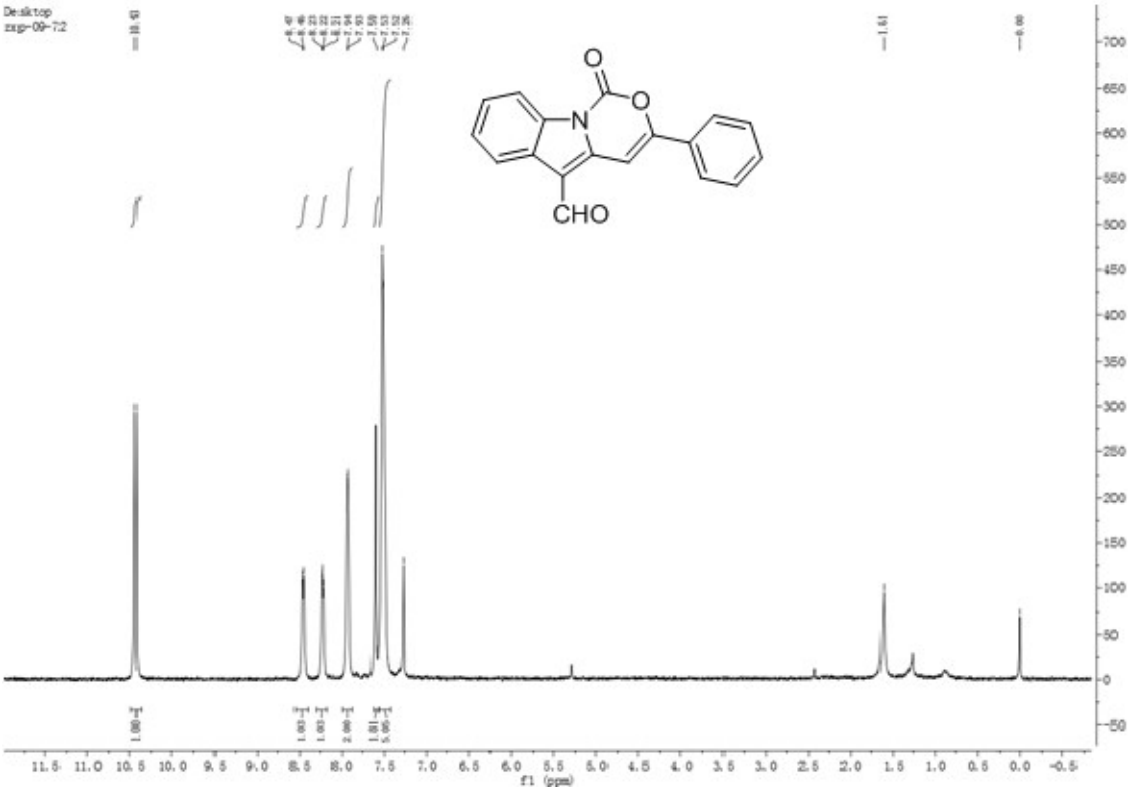


**5h**



**6**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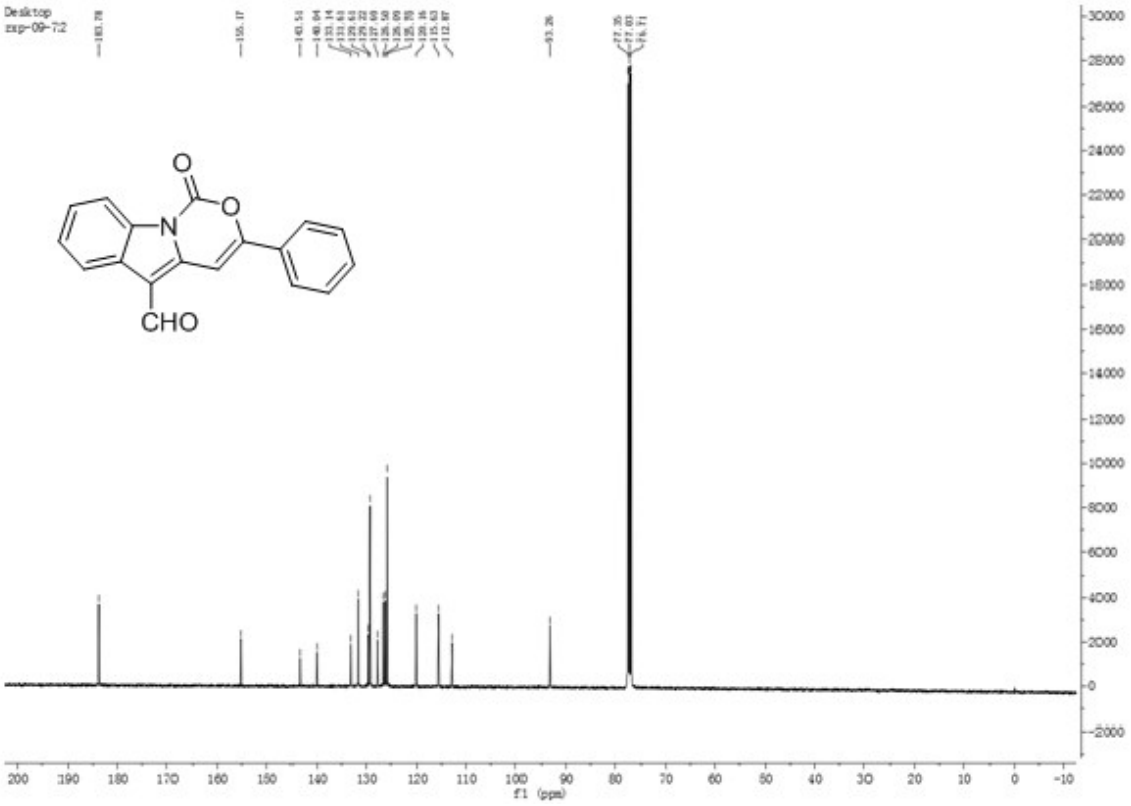
O
CHO
f1 (ppm)


Desktop
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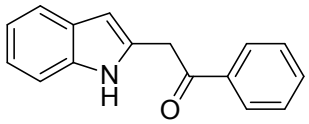
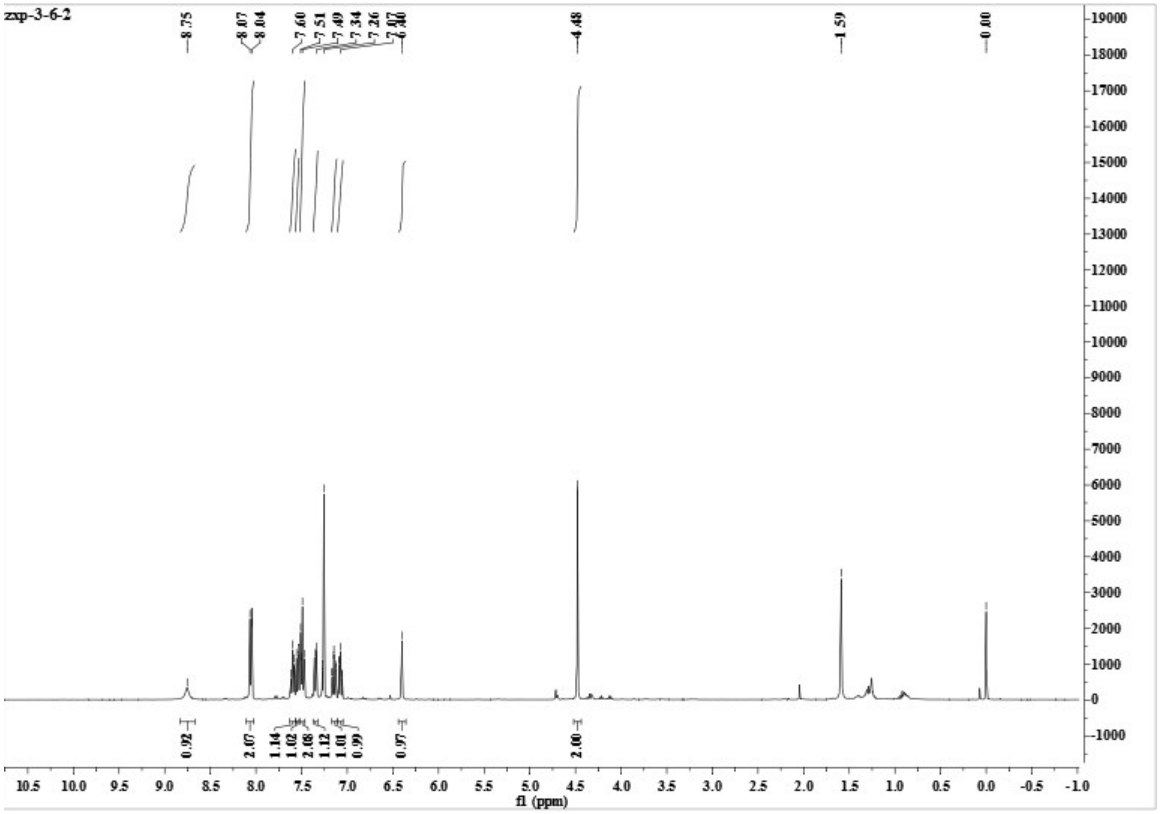
O
N
O
CHO
f1 (ppm)

8.


N
H
O


zxp-3-6-2
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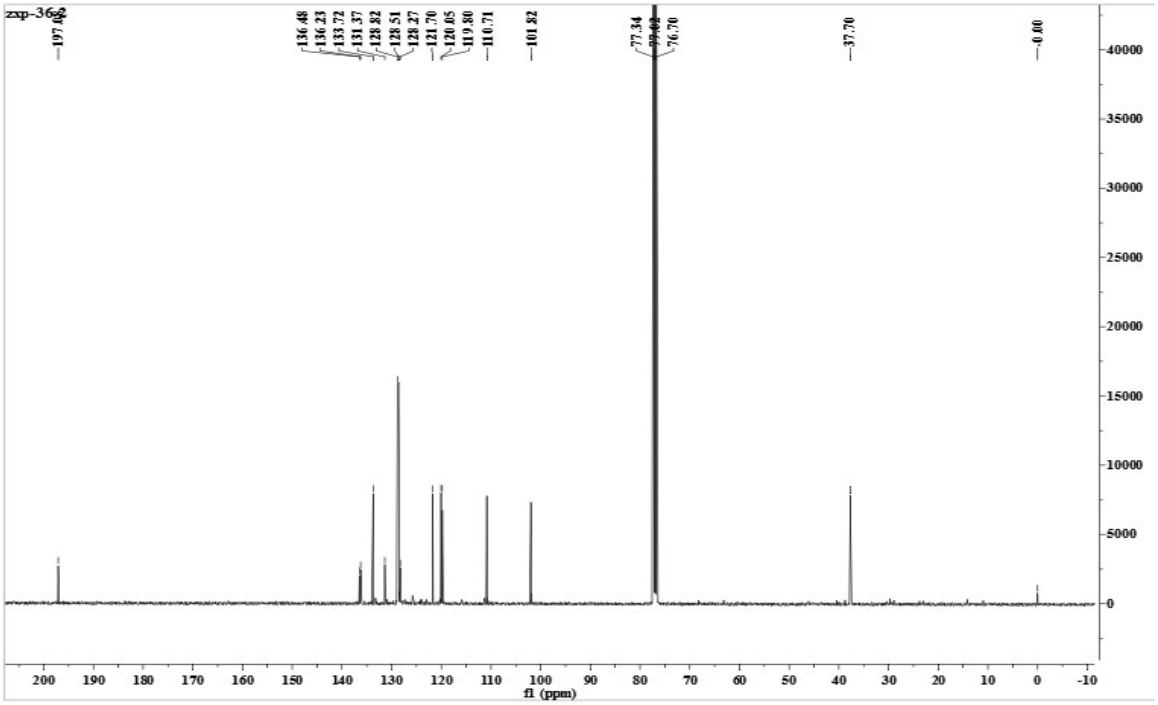
8.04
7.60
7.51
7.49
7.34
7.26
4.48
1.59
0.00
0.92
2.07
1.14
1.02
2.08
1.12
1.00
0.99
0.97
2.00
fl (ppm)


zxp-36-2
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136.23
133.72
131.37
128.82
128.51
128.27
121.70
120.65
119.80
110.71
101.82
77.34
76.70
37.70
0.00
fl (ppm)