

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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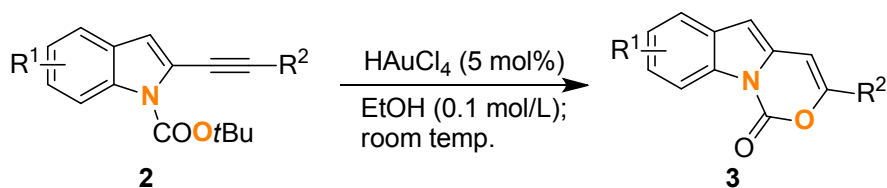
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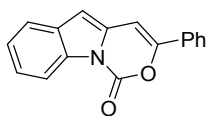
Experimental section.

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:



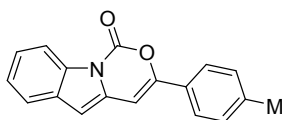
HAuCl_4 (8.5 mg, 40% aqueous solution) was added to a solution of compound **2** (0.2 mmol) in 2.0 mL of EtOH under N_2 . The reaction was stirred at room temperature for about 2 h. After completion of the reaction as indicated by TLC, solvent was evaporated under reduced pressure, and the residue was 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-1H-[1,3]oxazino[3,4-a]indol-1-one 3a.

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

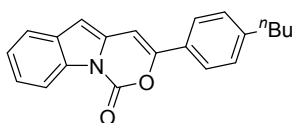
^1H NMR (400 MHz, CDCl_3): δ 6.62 (s, 1H), 6.94 (s, 1H), 7.26-7.46 (m, 5H), 7.62 (d, J = 4.0 Hz, 1H), 7.81 (t, J = 8.0 Hz, 2H), 8.46 (d, J = 8.0 Hz, 1H); **^{13}C NMR (100 MHz, CDCl_3):** δ 96.3, 102.0, 115.5, 120.4, 124.1, 124.4, 124.8, 124.9, 129.8, 130.0, 130.8, 132.8, 133.3, 144.6, 150.1; **HRMS** calcd. for $\text{C}_{17}\text{H}_{12}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 262.0852, found: 262.0863.



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

Yield 77%; white solid; 172-174 °C ;

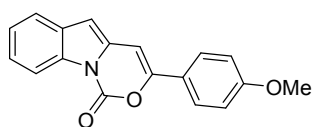
^1H NMR (400 MHz, CDCl_3): δ 2.43 (s, 3H), 6.63 (s, 1H), 6.92 (s, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 2H), 8.47 (d, J = 8.0 Hz, 1H); **^{13}C NMR (100 MHz, CDCl_3):** δ 21.3, 94.5, 101.5, 115.6, 120.3, 124.4, 124.8, 128.0, 129.6, 130.8, 133.0, 133.3, 140.3, 144.9, 150.3; **HRMS** calcd. for $\text{C}_{18}\text{H}_{14}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 276.1013, found: 276.1019.



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

Yield 86%; white solid; 151-153 °C;

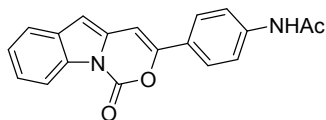
¹H NMR (400 MHz, CDCl₃): δ 0.96 (t, J = 12.0 Hz, 3H), 1.35-1.41 (m, 2H), 1.62 (t, J = 12.0 Hz, 2H), 2.64 (t, J = 16.0 Hz, 2H), 6.58 (s, 1H), 6.86 (s, 1H), 7.20-7.38 (m, 4H), 7.59 (d, J = 8.0 Hz, 1H), 7.69-7.71 (m, 2H), 8.48 (d, J = 8.0 Hz, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 19.9, 22.3, 32.6, 36.4, 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 C₂₁H₂₀NO₂ [M+H]⁺: 318.1498, found: 318.1489.



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

Yield 81%; yellow solid; 150-152 °C ;

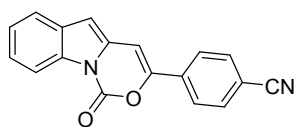
¹H NMR (400 MHz, CDCl₃): δ 3.79 (s, 3H), 6.51 (s, 1H), 6.76 (s, 1H), 6.89 (d, J = 12.0 Hz, 2H), 7.24-7.32 (m, 2H), 7.33 (d, J = 4.0 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 8.47 (d, J = 8.0 Hz, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 55.3, 93.4, 101.2, 114.4, 115.6, 120.5, 123.2, 124.4, 124.7, 124.9, 126.2, 130.9, 133.5, 144.6, 150.0, 161.3; **HRMS** calcd. for C₁₈H₁₄NO₃ [M+H]⁺: 292.0962, found: 292.0968.



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

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

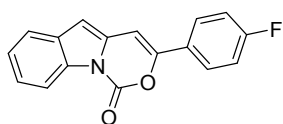
¹H NMR (400 MHz, DMSO-*d*₆): δ 2.09 (s, 3H), 6.87 (s, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 4.0 Hz, 1H), 7.50-7.55 (m, 2H), 7.59 (d, J = 12.0 Hz, 1H), 7.70-7.74 (m, 2H), 8.10 (s, 1H), 8.30 (d, J = 8.0 Hz, 1H), 10.18 (br, 1H); **¹³C NMR (100 MHz, DMSO-*d*₆):** δ 24.7, 96.3, 102.8, 115.1, 119.7, 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 C₁₉H₁₅N₂O₃ [M+H]⁺: 319.1083, found: 319.1077.



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

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

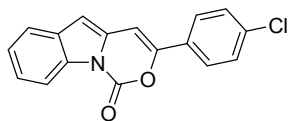
¹H NMR (400 MHz, DMSO-*d*₆): δ 6.94 (s, 1H), 7.40-7.45 (m, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.86 (s, 1H), 7.97 (d, J = 8.0 Hz, 2H), 8.05 (d, J = 8.0 Hz, 2H), 8.29 (d, J = 12.0 Hz, 1H); **¹³C NMR (100 MHz, DMSO-*d*₆):** δ 99.2, 104.4, 112.2, 115.3, 121.5, 126.1, 126.2, 126.6, 129.2, 131.0, 131.9, 132.0, 133.2, 133.4, 135.2, 147.3;



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

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

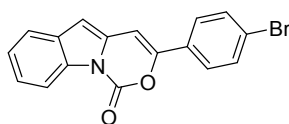
¹H NMR (400 MHz, CDCl₃): δ 6.64 (s, 1H), 6.89 (s, 1H), 7.16 (s, 2H), 7.40 (d, J = 4.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.79-7.83 (m, 2H), 8.44 (d, J = 8.0 Hz, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 96.0, 102.2, 115.8 (d, 2J = 21.0 Hz), 116.2, 120.4, 124.6, 124.9, 126.9, 127.0, 130.8, 132.7, 133.3, 144.4, 149.1, 161.3 (d, 1J = 248.0 Hz); **HRMS** calcd. for C₁₇H₁₁NO₂F [M+H]⁺: 280.0774, found: 280.0768.



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

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

¹H NMR (400 MHz, CDCl₃): δ 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); **¹³C NMR (100 MHz, DMSO-*d*₆):** δ 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 C₁₇H₁₁NO₂Cl [M+H]⁺: 296.0478, found: 296.0473.

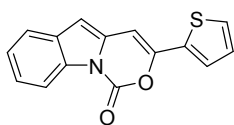


3-(4-Bromophenyl)-1H-[1,3]oxazino[3,4-*a*]indol-1-one 3i.

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

¹H NMR (400 MHz, CDCl₃): δ 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); **¹³C NMR (100 MHz, CDCl₃):** δ 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**

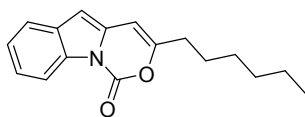
calcd. for C₁₇H₁₁BrNO₂ [M+H]⁺: 339.9979, found: 339.9968.



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

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

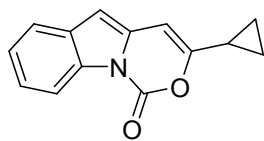
¹H NMR (400 MHz, CDCl₃): δ 6.62 (s, 1H), 6.80 (s, 1H), 7.13 (d, J = 8.0 Hz, 1H), 7.38-7.42 (m, 3H), 7.57 (d, J = 4.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 8.44 (d, J = 8.0 Hz, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 94.2, 102.0, 115.6, 120.4, 124.5, 124.9, 126.2, 127.5, 128.2, 130.9, 132.4, 133.7, 134.4, 144.1, 146.9; **HRMS** calcd. for C₁₅H₁₀NO₂S [M+H]⁺: 268.0432, found: 268.0427.



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

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

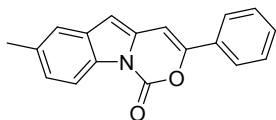
¹H NMR (400 MHz, CDCl₃): δ 0.82 (t, J = 12.0 Hz, 3H), 1.22-1.25 (m, 6H), 1.53-1.58 (m, 2H), 2.35 (t, J = 16.0 Hz, 2H), 6.10 (s, 1H), 6.30 (s, 1H), 7.22-7.25 (m, 2H), 7.45 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 14.0, 22.4, 25.8, 28.5, 31.5, 32.2, 95.6, 99.5, 99.7, 115.6, 120.2, 124.9, 130.4, 132.7, 133.2, 145.0, 154.7; **HRMS** calcd. for C₁₇H₂₀NO₂ [M+H]⁺: 270.1494, found: 270.1500.



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

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

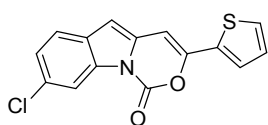
¹H NMR (400 MHz, CDCl₃): δ 0.83-0.88 (m, 2H), 0.94-0.97 (m, 2H), 1.62-1.71 (m, 1H), 6.17 (s, 1H), 6.29 (s, 1H), 7.20-7.28 (m, 2H), 7.46 (t, J = 8.0 Hz, 1H), 8.29 (d, J = 4.0 Hz, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 6.6, 12.9, 94.9, 99.3, 115.5, 120.1, 123.8, 124.6, 130.7, 133.0, 133.1, 144.9, 154.8; **HRMS** calcd. for C₁₄H₁₂NO₂ [M+H]⁺: 226.0868, found: 226.0896



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

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

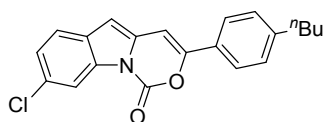
¹H NMR (400 MHz, CDCl₃): δ 2.43 (s, 3H), 6.63 (s, 1H), 6.82 (s, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.34-7.42 (m, 2H), 7.38-7.44 (m, 2H), 7.63-7.73 (m, 2H), 8.36 (d, J = 8.0 Hz, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 21.5, 96.1, 101.6, 115.3, 120.2, 124.7, 126.9, 128.8, 129.8, 130.8, 131.1, 132.9, 134.4, 144.7, 149.0, 149.7; **HRMS** calcd. for C₁₈H₁₄NO₂ [M+H]⁺: 276.1025, found: 276.1019.



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

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

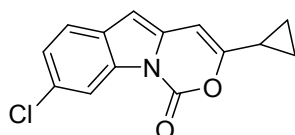
¹H NMR (400 MHz, DMSO-*d*6): δ 6.82 (s, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.40-7.44 (m, 2H), 7.70-7.73 (m, 2H), 7.79 (d, J = 4.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H); **¹³C NMR (100 MHz, DMSO-*d*6):** δ 94.2, 101.3, 114.5, 122.0, 124.8, 126.4, 128.2, 128.7, 128.8, 129.6, 133.2, 133.7, 140.0, 143.5, 146.7; **HRMS** calcd. for C₁₅H₉ClNO₂S [M+H]⁺: 302.0043, found: 302.004351.



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

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

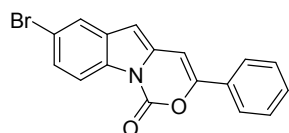
¹H NMR (400 MHz, CDCl₃): δ 0.94 (t, J = 12.0 Hz, 3H), 1.33-1.39 (m, 2H), 1.56-1.62 (m, 2H), 2.60 (t, J = 8.0 Hz, 2H), 6.47 (s, 1H), 6.76 (d, J = 8.0 Hz, 1H), 7.19-7.38 (m, 3H), 8.41 (d, J = 8.0 Hz, 1H), 7.61-7.65 (m, 2H), 8.36 (d, J = 8.0 Hz, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 13.8, 22.4, 33.2, 35.4, 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 C₂₁H₁₉NO₂Cl [M+H]⁺: 352.1104, found: 352.1098.



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

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

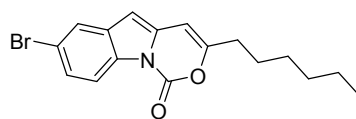
¹H NMR (400 MHz, CDCl₃): δ 0.92-0.98 (m, 2H), 1.00-1.04 (m, 2H), 1.71-1.78 (m, 1H), 6.21 (s, 1H), 6.28 (s, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 8.39 (d, J = 4.0 Hz, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 6.3, 13.1, 94.9, 98.8, 116.4, 120.8, 125.0, 129.1, 129.5, 133.2, 133.7, 144.4, 155.3; **HRMS** calcd. for C₁₄H₁₁NO₂Cl [M+H]⁺: 260.0478, found: 260.0487.



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

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

¹H NMR (400 MHz, DMSO-*d*₆): 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); **¹³C NMR (100 MHz, DMSO-*d*₆):** 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 C₁₇H₁₁NO₂Br [M+H]⁺: 339.9973, found: 339.9968.

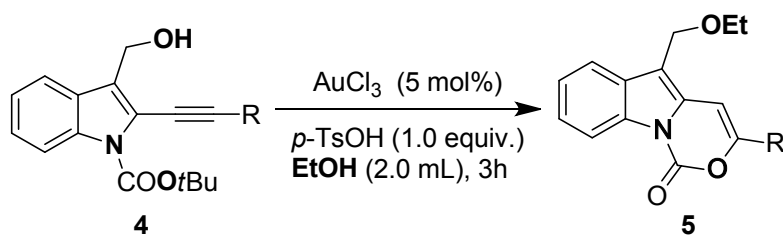


7-bromo-3-hexyl-1H-[1,3]oxazino[3,4-a]indol-1-one 3r.

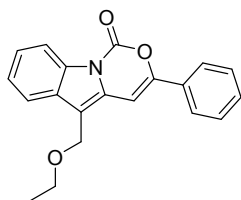
Yield 90%; white solid; mp: 73-75 °C ;

¹H NMR (400 MHz, CDCl₃): δ 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); **¹³C NMR (100 MHz, CDCl₃):** δ 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 C₁₇H₁₉NO₂Br [M+H]⁺: 348.0599, found: 348.0594.

General procedure for the preparation of compound 5:



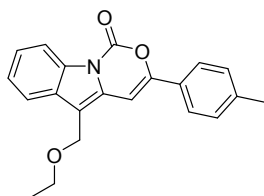
Substrate **4** was added to a stirred suspension of *p*-TsOH (17.2 mg, 0.2 mmol) and AuCl₃ (3.1 mg, 0.05 mmol) in 2.0 mL of EtOH at room temperature under N₂ atmosphere. The reaction was monitored by TLC. Upon completion, EtOH was evaporated in reduced pressure, and the resulting residue was purified 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-4a-aza-fluoren-4-one 5a.

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

¹H NMR (400 MHz, CDCl₃): 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); **¹³C NMR (100 MHz, CDCl₃):** 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 C₂₀H₁₈NO₃ [M+H]⁺: 320.1287, found: 320.1281.

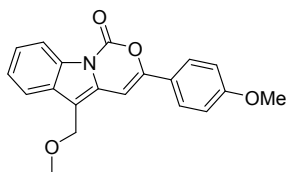


5-(Ethoxymethyl)-3-(*p*-tolyl)-1H-[1,3]oxazino[3,4-*a*]indol-1-one 5b.

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

¹H NMR (400 MHz, CDCl₃): 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); **¹³C NMR (100 MHz, CDCl₃):** 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**

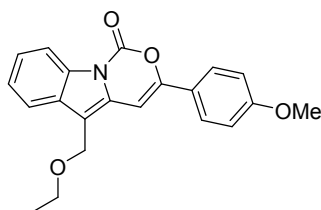
calcd. for $C_{21}H_{20}NO_3[M+H]^+$: 334.1443, found: 334.1438.



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

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

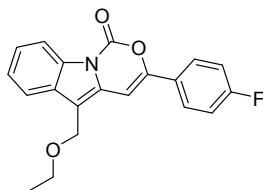
1H NMR (400 MHz, $CDCl_3$): δ 3.36 (s, 3H), 3.78 (s, 3H), 4.70 (s, 2H), 6.85 (s, 1H), 6.88 (d, J = 8.0 Hz, 2H), 7.31-7.34 (m, 2H), 7.59-7.71 (m, 3H), 8.35 (d, J = 8.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 54.9, 57.5, 64.4, 91.4, 109.7, 113.8, 115.1, 118.2, 122.8, 124.1, 124.5, 125.9, 130.3, 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)-1H-[1,3]oxazino[3,4-a]indol-1-one 5d.

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

1H 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.

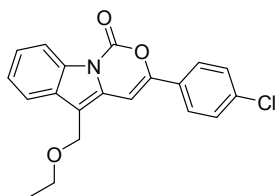


5-(Ethoxymethyl)-3-(4-fluorophenyl)-1H-[1,3]oxazino[3,4-a]indol-1-one 5e.

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

1H 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,

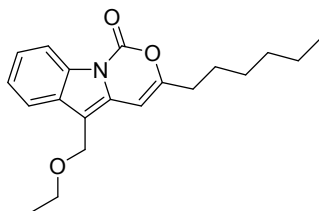
1H), 7.09-7.29 (m, 2H), 7.35-7.48 (m, 2H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.76-7.80 (m, 2H), 8.40 (d, $J = 8.0$ Hz, 1H); **^{13}C NMR (100 MHz, CDCl_3)**: δ 15.3, 62.9, 66.0, 93.6, 111.8, 115.6 (d, $^2J = 21.0$ Hz), 116.0, 116.2, 118.8, 124.8, 126.9, 130.6, 130.7, 132.9, 143.9, 149.2, 164.3 (d, $^1J = 248.1$ Hz); **HRMS** calcd. for $\text{C}_{20}\text{H}_{17}\text{FNO}_3$ $[\text{M}+\text{H}]^+$: 338.1192, found: 338.1187.



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

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

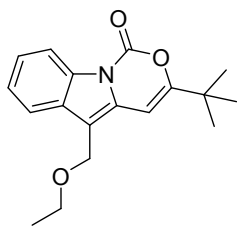
^1H NMR (400 MHz, CDCl_3): δ 1.29 (t, $J = 12.0$ Hz, 3H), 3.61-3.66 (m, 2H), 4.82 (s, 2H), 7.10 (s, 1H), 7.44 (d, $J = 8.0$ Hz, 4H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.76-7.80 (m, 2H), 8.44 (d, $J = 8.0$ Hz, 1H); **^{13}C NMR (100 MHz, CDCl_3)**: δ 19.0, 62.9, 66.4, 94.2, 112.1, 115.5, 118.9, 124.9, 125.0, 126.1, 129.2, 130.9, 132.3, 133.1, 136.0, 144.2, 148.8, 167.5; **HRMS** calcd. for $\text{C}_{20}\text{H}_{17}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$: 354.0897, found: 355.0925.



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

Yield 57%; yellow oil;

^1H 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 $\text{C}_{20}\text{H}_{26}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 328.1913, found: 328.1907.



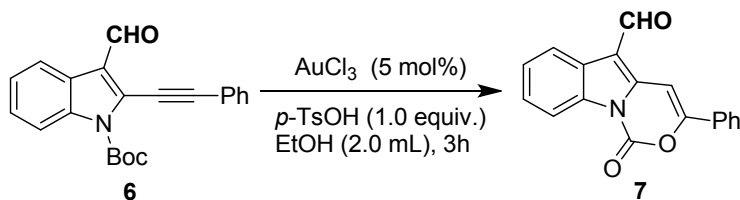
3-(*tert*-Butyl)-5-(ethoxymethyl)-1*H*-[1,3]oxazino[3,4-*a*]indol-1-one 5h.

Yield 30%; yellow oil;

¹H NMR (400 MHz, CDCl₃): 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);

¹³C NMR (100 MHz, CDCl₃): 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 C₁₇H₁₈NO₃ [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 AuCl₃ (3.1 mg, 0.05 mmol) in 2.0 mL of EtOH under N₂ 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.

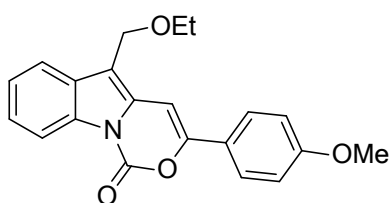
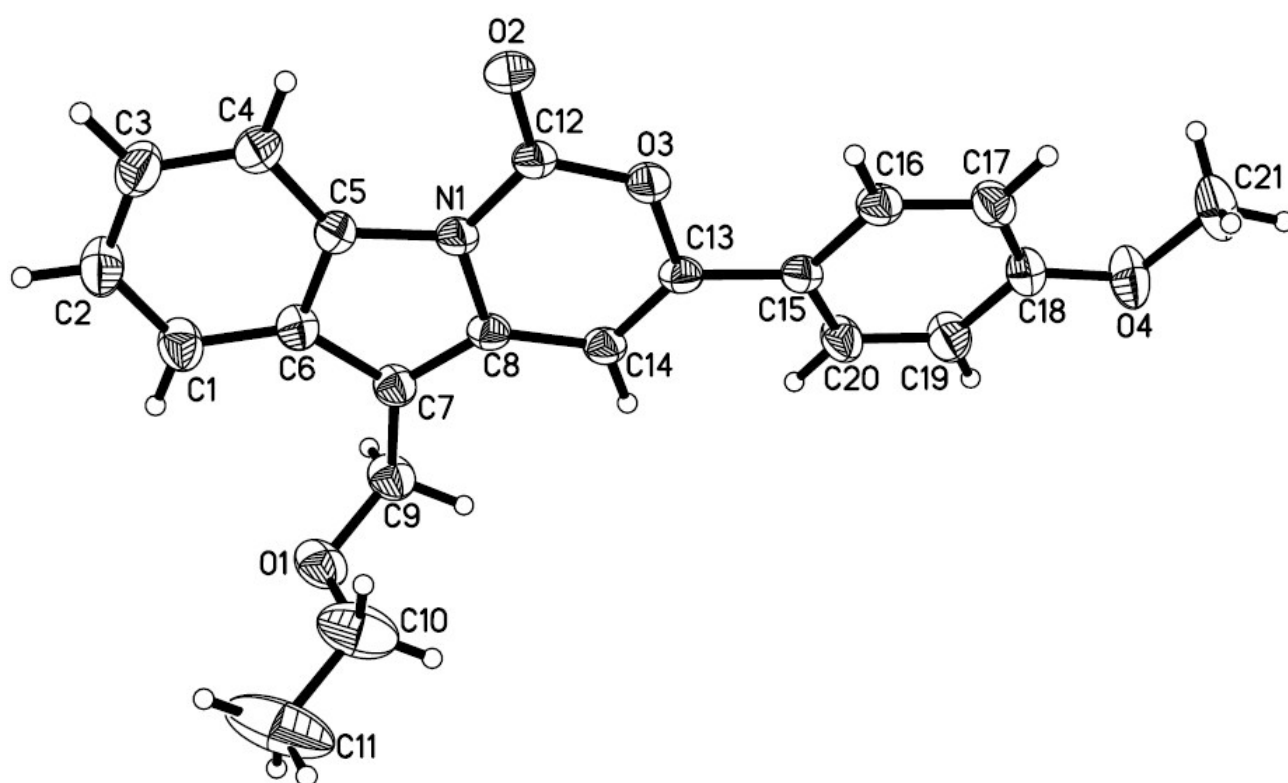
1-Oxo-3-phenyl-1*H*-[1,3]oxazino[3,4-*a*]indole-5-carbaldehyde 7.

Yield 80%; yellow solid; mp: 119-121 °C ;

¹H NMR (400 MHz, CDCl₃): 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); **¹³C NMR (100 MHz, CDCl₃):** 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;

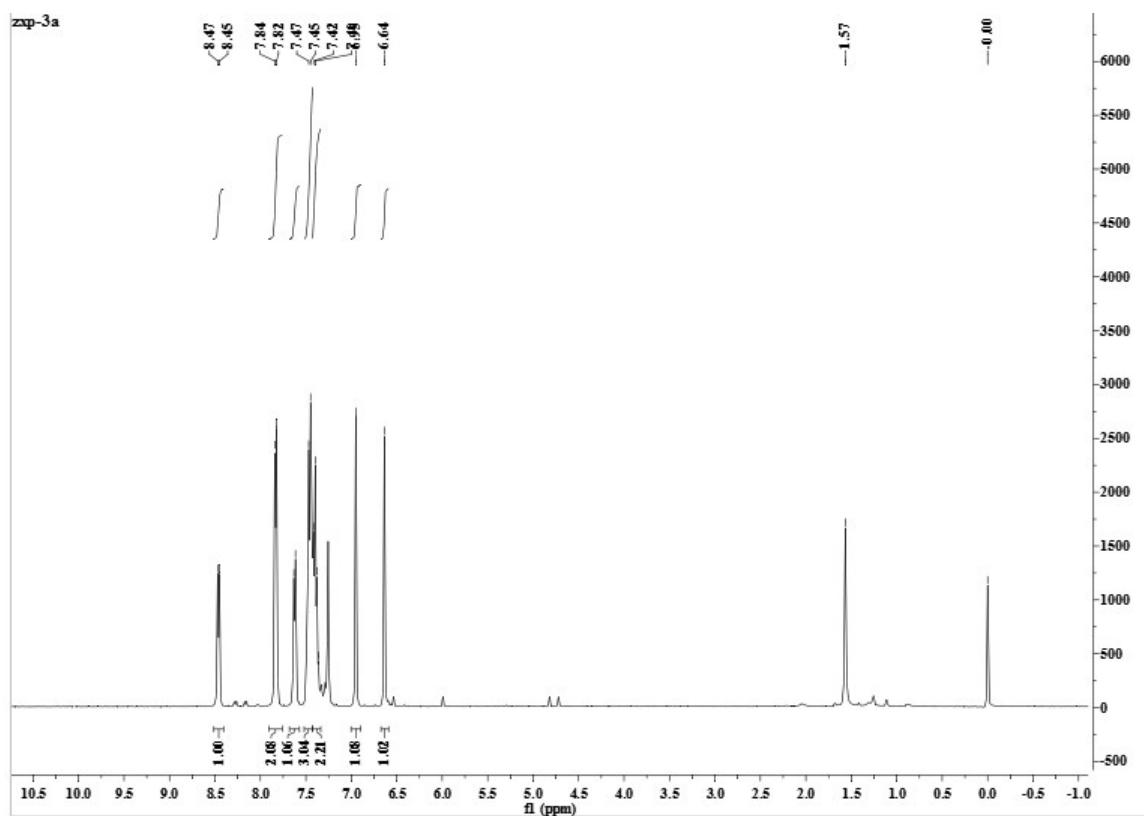
HRMS calcd. for C₁₈H₁₂NO₃ [M+H]⁺: 290.0817, found: 290.0809.

X-Ray ORTEP illustration of compound 5d.

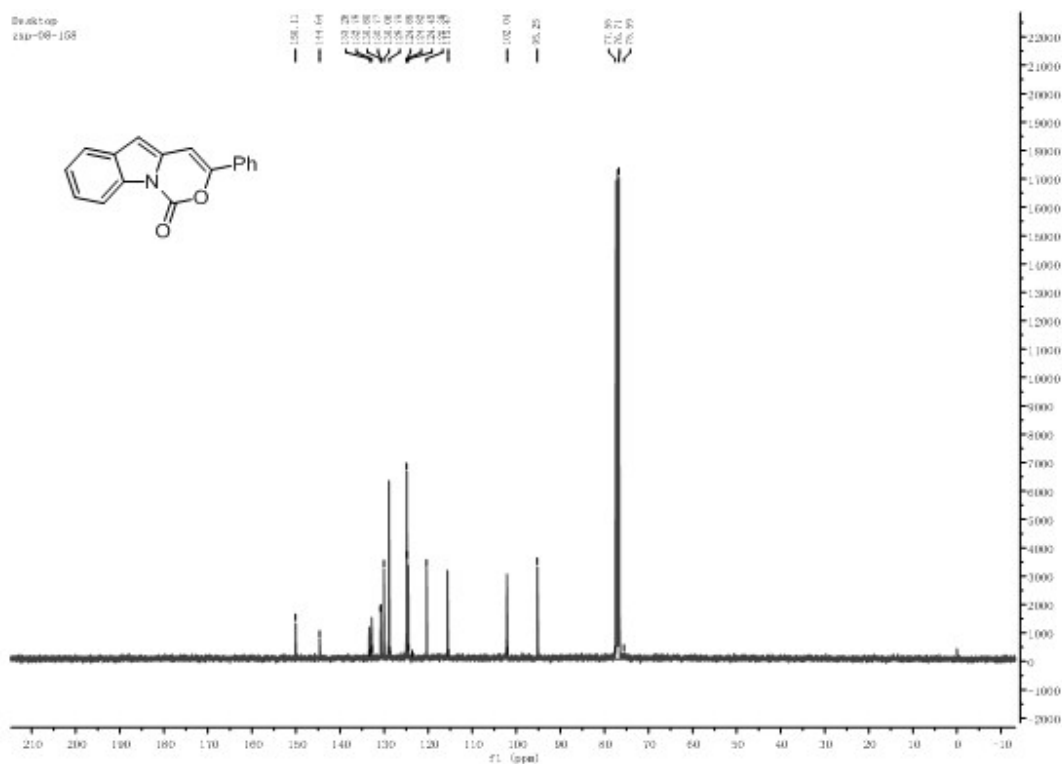


5d

3a



230p-08-108

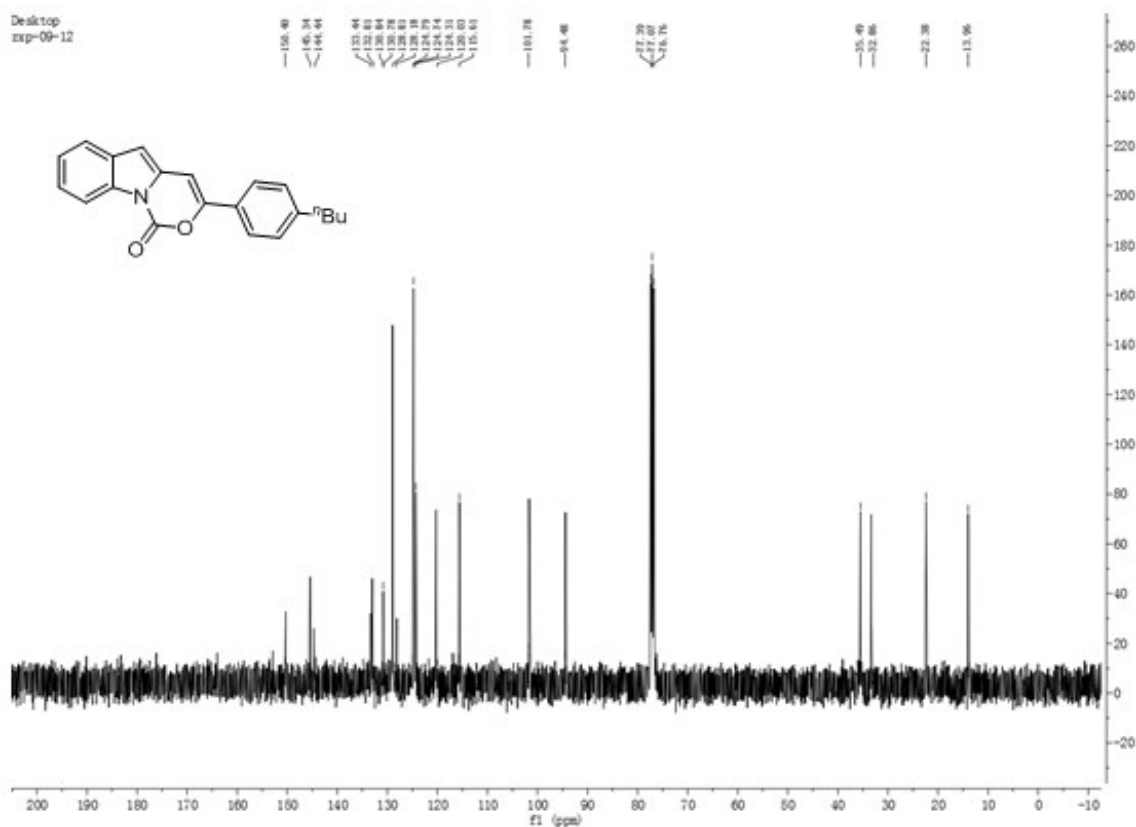
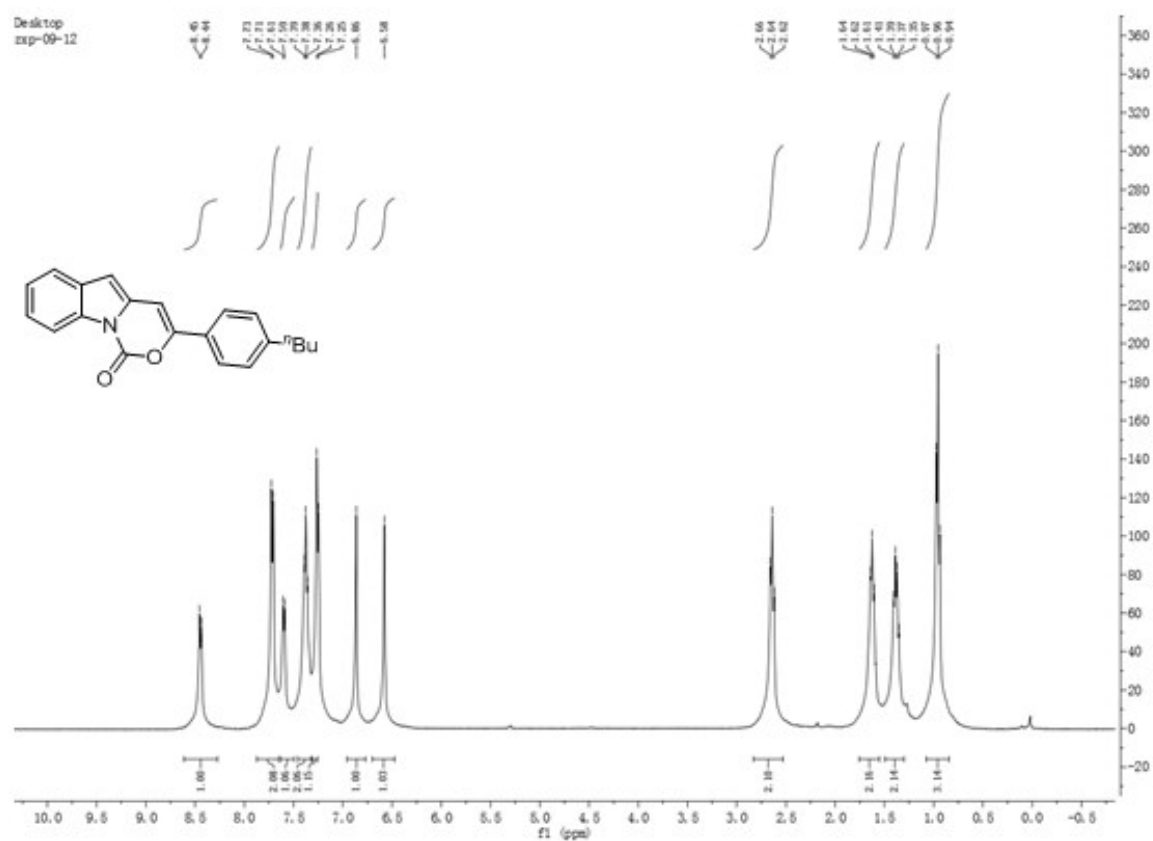


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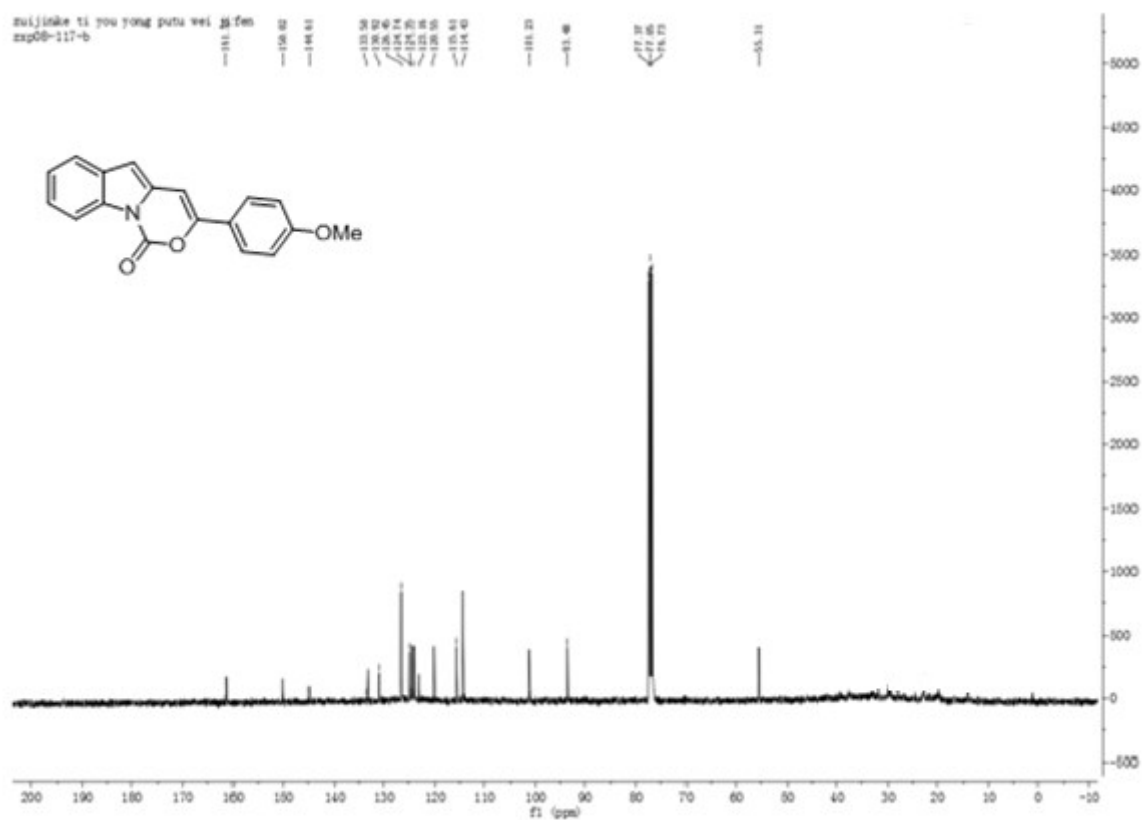
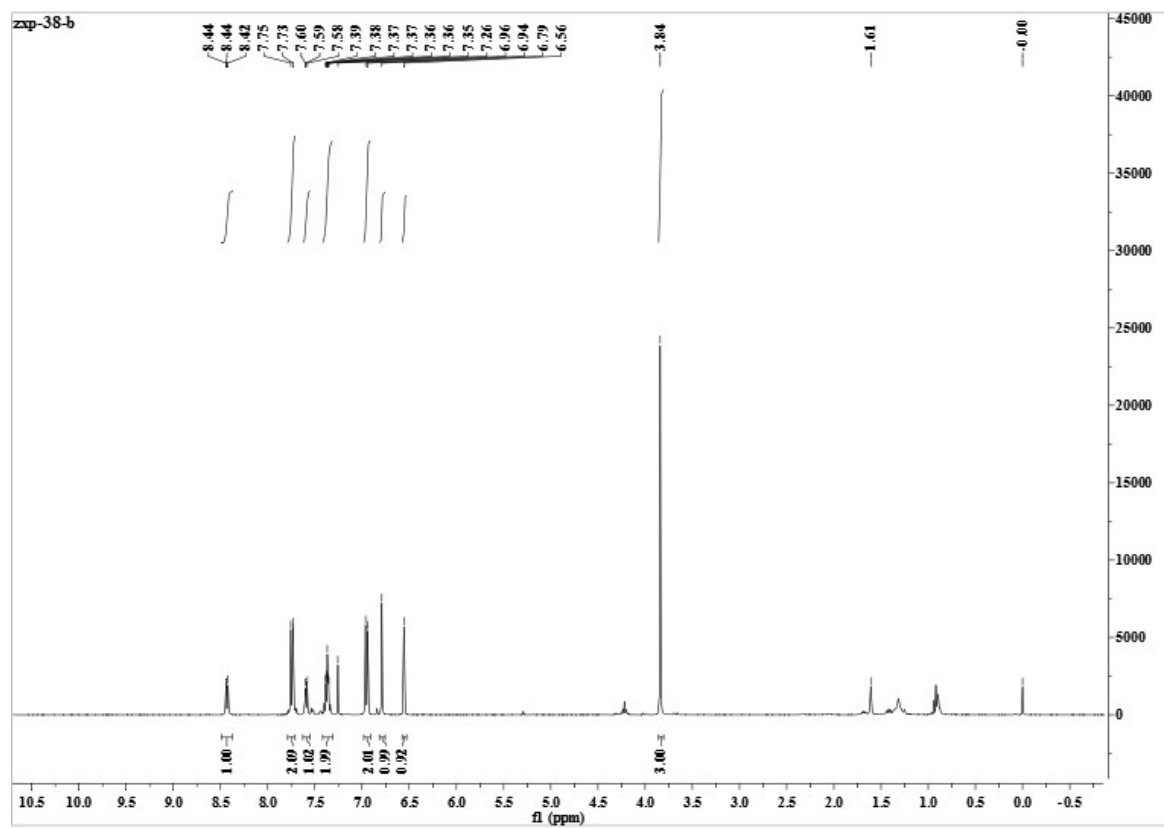
8.44
7.72 7.70 7.68 7.66 7.64 7.62 7.60 7.58 7.56 7.54 7.52 7.50 7.48 7.46 7.44 7.42 7.40 7.38 7.36 7.34 7.32 7.30 7.28 7.26 7.24 7.22 7.20 7.18 7.16 7.14 7.12 7.10 7.08 7.06 7.04 7.02 7.00 6.98 6.96 6.94 6.92 6.90 6.88 6.86 6.84 6.82 6.80 6.78 6.76 6.74 6.72 6.70 6.68 6.66 6.64 6.62 6.60 6.58 6.56 6.54 6.52 6.50 6.48 6.46 6.44 6.42 6.40 6.38 6.36 6.34 6.32 6.30 6.28 6.26 6.24 6.22 6.20 6.18 6.16 6.14 6.12 6.10 6.08 6.06 6.04 6.02 6.00 5.98 5.96 5.94 5.92 5.90 5.88 5.86 5.84 5.82 5.80 5.78 5.76 5.74 5.72 5.70 5.68 5.66 5.64 5.62 5.60 5.58 5.56 5.54 5.52 5.50 5.48 5.46 5.44 5.42 5.40 5.38 5.36 5.34 5.32 5.30 5.28 5.26 5.24 5.22 5.20 5.18 5.16 5.14 5.12 5.10 5.08 5.06 5.04 5.02 5.00 4.98 4.96 4.94 4.92 4.90 4.88 4.86 4.84 4.82 4.80 4.78 4.76 4.74 4.72 4.70 4.68 4.66 4.64 4.62 4.60 4.58 4.56 4.54 4.52 4.50 4.48 4.46 4.44 4.42 4.40 4.38 4.36 4.34 4.32 4.30 4.28 4.26 4.24 4.22 4.20 4.18 4.16 4.14 4.12 4.10 4.08 4.06 4.04 4.02 4.00 3.98 3.96 3.94 3.92 3.90 3.88 3.86 3.84 3.82 3.80 3.78 3.76 3.74 3.72 3.70 3.68 3.66 3.64 3.62 3.60 3.58 3.56 3.54 3.52 3.50 3.48 3.46 3.44 3.42 3.40 3.38 3.36 3.34 3.32 3.30 3.28 3.26 3.24 3.22 3.20 3.18 3.16 3.14 3.12 3.10 3.08 3.06 3.04 3.02 3.00 2.98 2.96 2.94 2.92 2.90 2.88 2.86 2.84 2.82 2.80 2.78 2.76 2.74 2.72 2.70 2.68 2.66 2.64 2.62 2.60 2.58 2.56 2.54 2.52 2.50 2.48 2.46 2.44 2.42 2.40 2.38 2.36 2.34 2.32 2.30 2.28 2.26 2.24 2.22 2.20 2.18 2.16 2.14 2.12 2.10 2.08 2.06 2.04 2.02 2.00 1.98 1.96 1.94 1.92 1.90 1.88 1.86 1.84 1.82 1.80 1.78 1.76 1.74 1.72 1.70 1.68 1.66 1.64 1.62 1.60 1.58 1.56 1.54 1.52 1.50 1.48 1.46 1.44 1.42 1.40 1.38 1.36 1.34 1.32 1.30 1.28 1.26 1.24 1.22 1.20 1.18 1.16 1.14 1.12 1.10 1.08 1.06 1.04 1.02 1.00 0.98 0.96 0.94 0.92 0.90 0.88 0.86 0.84 0.82 0.80 0.78 0.76 0.74 0.72 0.70 0.68 0.66 0.64 0.62 0.60 0.58 0.56 0.54 0.52 0.50 0.48 0.46 0.44 0.42 0.40 0.38 0.36 0.34 0.32 0.30 0.28 0.26 0.24 0.22 0.20 0.18 0.16 0.14 0.12 0.10 0.08 0.06 0.04 0.02 0.00 -0.02 -0.04 -0.06 -0.08 -0.10 -0.12 -0.14 -0.16 -0.18 -0.20 -0.22 -0.24 -0.26 -0.28 -0.30 -0.32 -0.34 -0.36 -0.38 -0.40 -0.42 -0.44 -0.46 -0.48 -0.50 -0.52 -0.54 -0.56 -0.58 -0.60 -0.62 -0.64 -0.66 -0.68 -0.70 -0.72 -0.74 -0.76 -0.78 -0.80 -0.82 -0.84 -0.86 -0.88 -0.90 -0.92 -0.94 -0.96 -0.98 -1.00 -1.02 -1.04 -1.06 -1.08 -1.10 -1.12 -1.14 -1.16 -1.18 -1.20 -1.22 -1.24 -1.26 -1.28 -1.30 -1.32 -1.34 -1.36 -1.38 -1.40 -1.42 -1.44 -1.46 -1.48 -1.50 -1.52 -1.54 -1.56 -1.58 -1.60 -1.62 -1.64 -1.66 -1.68 -1.70 -1.72 -1.74 -1.76 -1.78 -1.80 -1.82 -1.84 -1.86 -1.88 -1.90 -1.92 -1.94 -1.96 -1.98 -2.00 -2.02 -2.04 -2.06 -2.08 -2.10 -2.12 -2.14 -2.16 -2.18 -2.20 -2.22 -2.24 -2.26 -2.28 -2.30 -2.32 -2.34 -2.36 -2.38 -2.40 -2.42 -2.44 -2.46 -2.48 -2.50 -2.52 -2.54 -2.56 -2.58 -2.60 -2.62 -2.64 -2.66 -2.68 -2.70 -2.72 -2.74 -2.76 -2.78 -2.80 -2.82 -2.84 -2.86 -2.88 -2.90 -2.92 -2.94 -2.96 -2.98 -3.00 -3.02 -3.04 -3.06 -3.08 -3.10 -3.12 -3.14 -3.16 -3.18 -3.20 -3.22 -3.24 -3.26 -3.28 -3.30 -3.32 -3.34 -3.36 -3.38 -3.40 -3.42 -3.44 -3.46 -3.48 -3.50 -3.52 -3.54 -3.56 -3.58 -3.60 -3.62 -3.64 -3.66 -3.68 -3.70 -3.72 -3.74 -3.76 -3.78 -3.80 -3.82 -3.84 -3.86 -3.88 -3.90 -3.92 -3.94 -3.96 -3.98 -4.00 -4.02 -4.04 -4.06 -4.08 -4.10 -4.12 -4.14 -4.16 -4.18 -4.20 -4.22 -4.24 -4.26 -4.28 -4.30 -4.32 -4.34 -4.36 -4.38 -4.40 -4.42 -4.44 -4.46 -4.48 -4.50 -4.52 -4.54 -4.56 -4.58 -4.60 -4.62 -4.64 -4.66 -4.68 -4.70 -4.72 -4.74 -4.76 -4.78 -4.80 -4.82 -4.84 -4.86 -4.88 -4.90 -4.92 -4.94 -4.96 -4.98 -5.00 -5.02 -5.04 -5.06 -5.08 -5.10 -5.12 -5.14 -5.16 -5.18 -5.20 -5.22 -5.24 -5.26 -5.28 -5.30 -5.32 -5.34 -5.36 -5.38 -5.40 -5.42 -5.44 -5.46 -5.48 -5.50 -5.52 -5.54 -5.56 -5.58 -5.60 -5.62 -5.64 -5.66 -5.68 -5.70 -5.72 -5.74 -5.76 -5.78 -5.80 -5.82 -5.84 -5.86 -5.88 -5.90 -5.92 -5.94 -5.96 -5.98 -6.00 -6.02 -6.04 -6.06 -6.08 -6.10 -6.12 -6.14 -6.16 -6.18 -6.20 -6.22 -6.24 -6.26 -6.28 -6.30 -6.32 -6.34 -6.36 -6.38 -6.40 -6.42 -6.44 -6.46 -6.48 -6.50 -6.52 -6.54 -6.56 -6.58 -6.60 -6.62 -6.64 -6.66 -6.68 -6.70 -6.72 -6.74 -6.76 -6.78 -6.80 -6.82 -6.84 -6.86 -6.88 -6.90 -6.92 -6.94 -6.96 -6.98 -7.00 -7.02 -7.04 -7.06 -7.08 -7.10 -7.12 -7.14 -7.16 -7.18 -7.20 -7.22 -7.24 -7.26 -7.28 -7.30 -7.32 -7.34 -7.36 -7.38 -7.40 -7.42 -7.44 -7.46 -7.48 -7.50 -7.52 -7.54 -7.56 -7.58 -7.60 -7.62 -7.64 -7.66 -7.68 -7.70 -7.72 -7.74 -7.76 -7.78 -7.80 -7.82 -7.84 -7.86 -7.88 -7.90 -7.92 -7.94 -7.96 -7.98 -8.00 -8.02 -8.04 -8.06 -8.08 -8.10 -8.12 -8.14 -8.16 -8.18 -8.20 -8.22 -8.24 -8.26 -8.28 -8.30 -8.32 -8.34 -8.36 -8.38 -8.40 -8.42 -8.44 -8.46 -8.48 -8.50 -8.52 -8.54 -8.



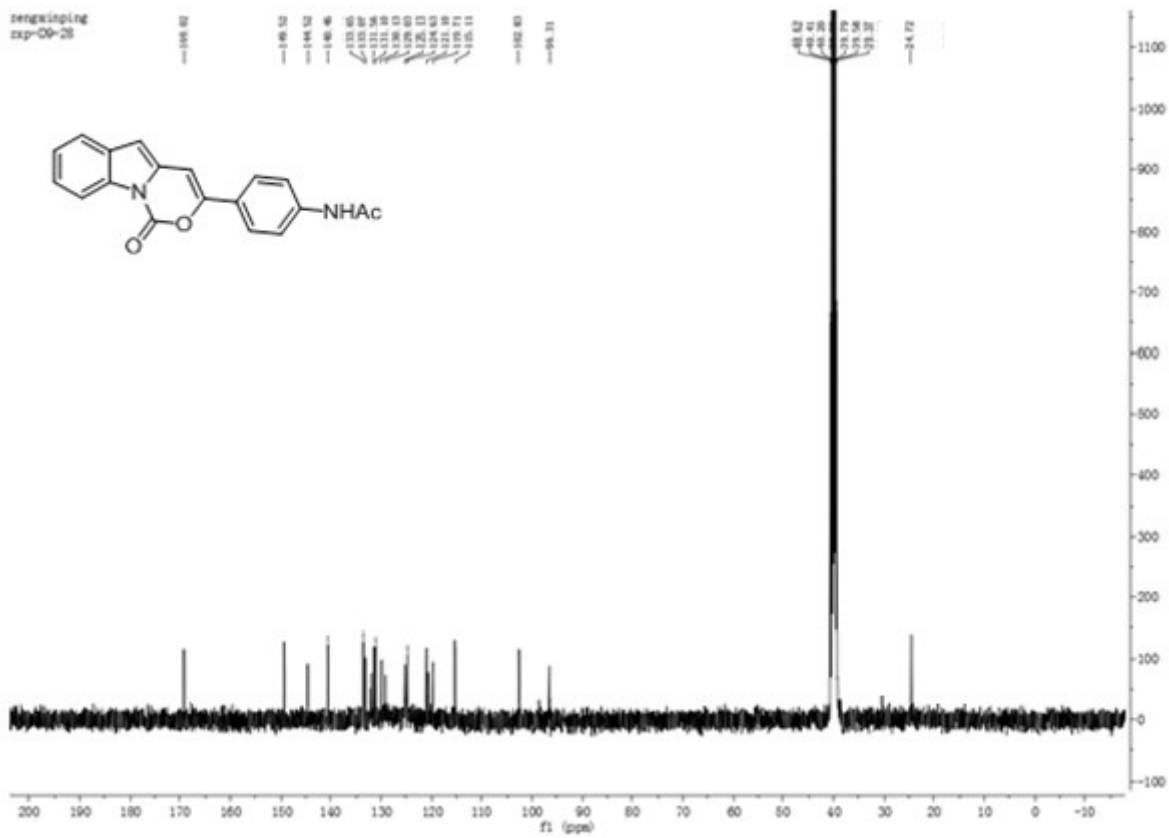
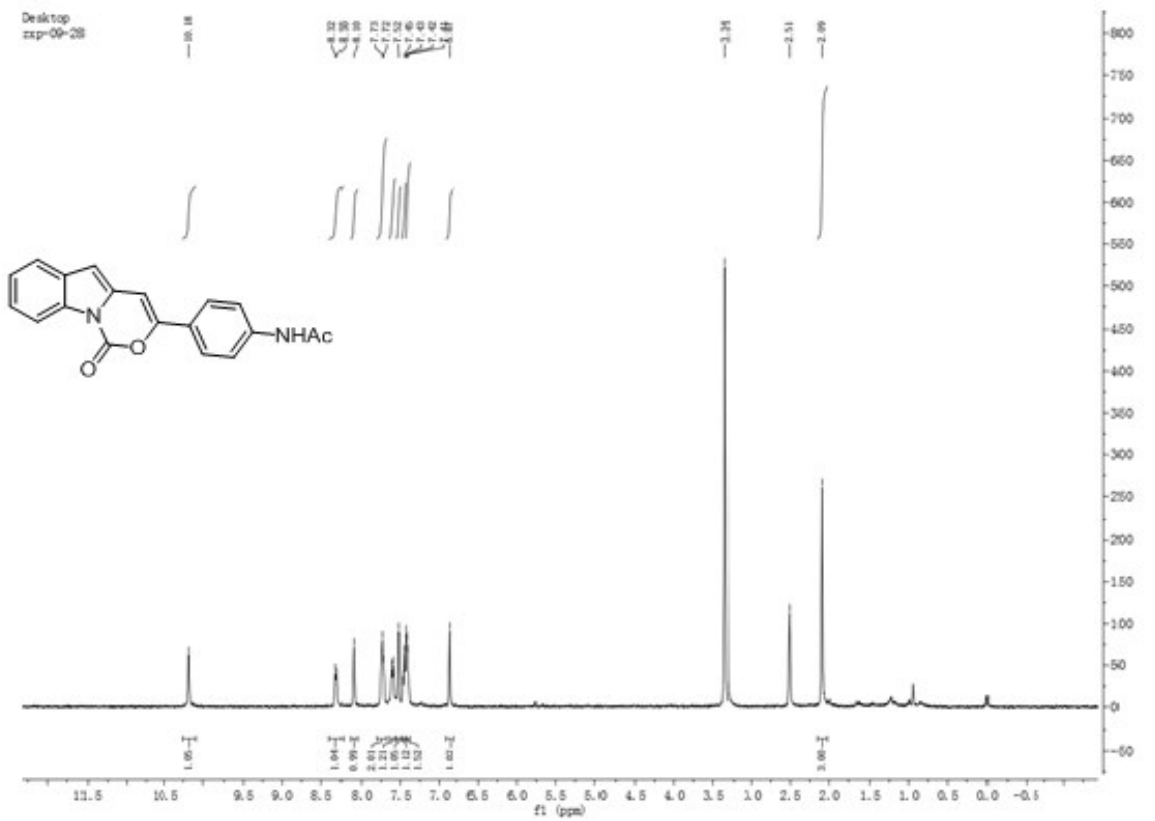
3c



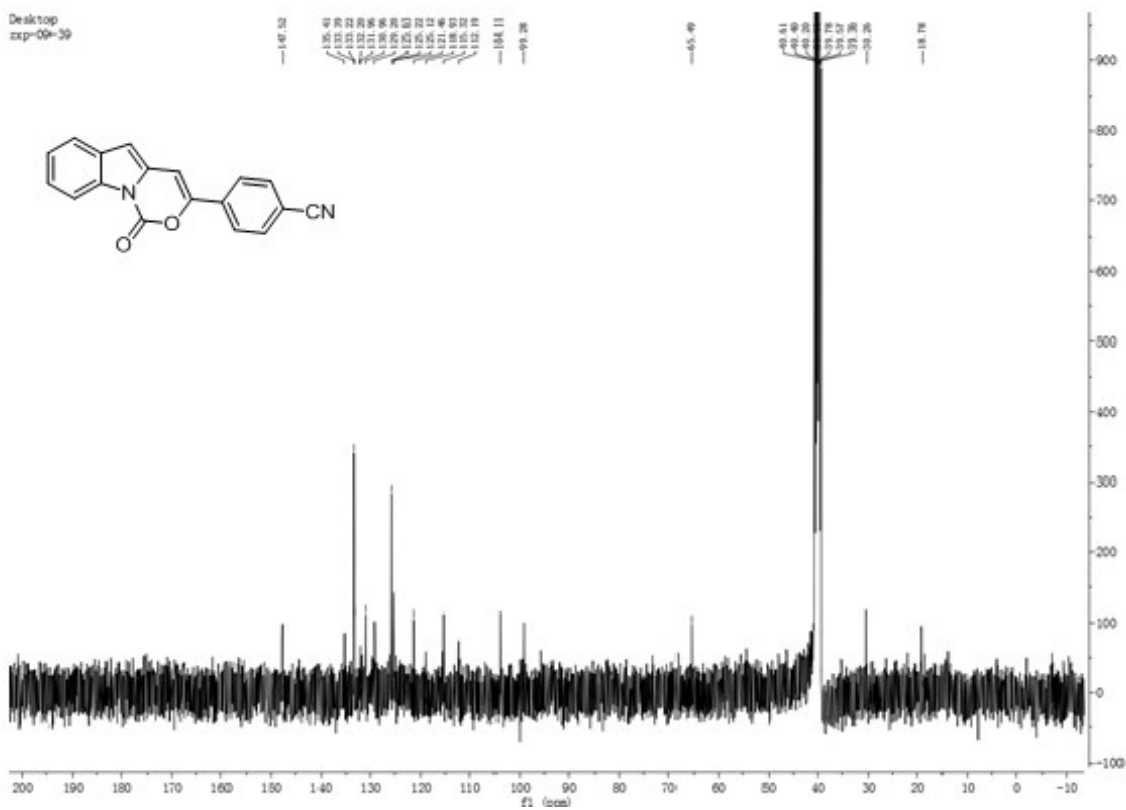
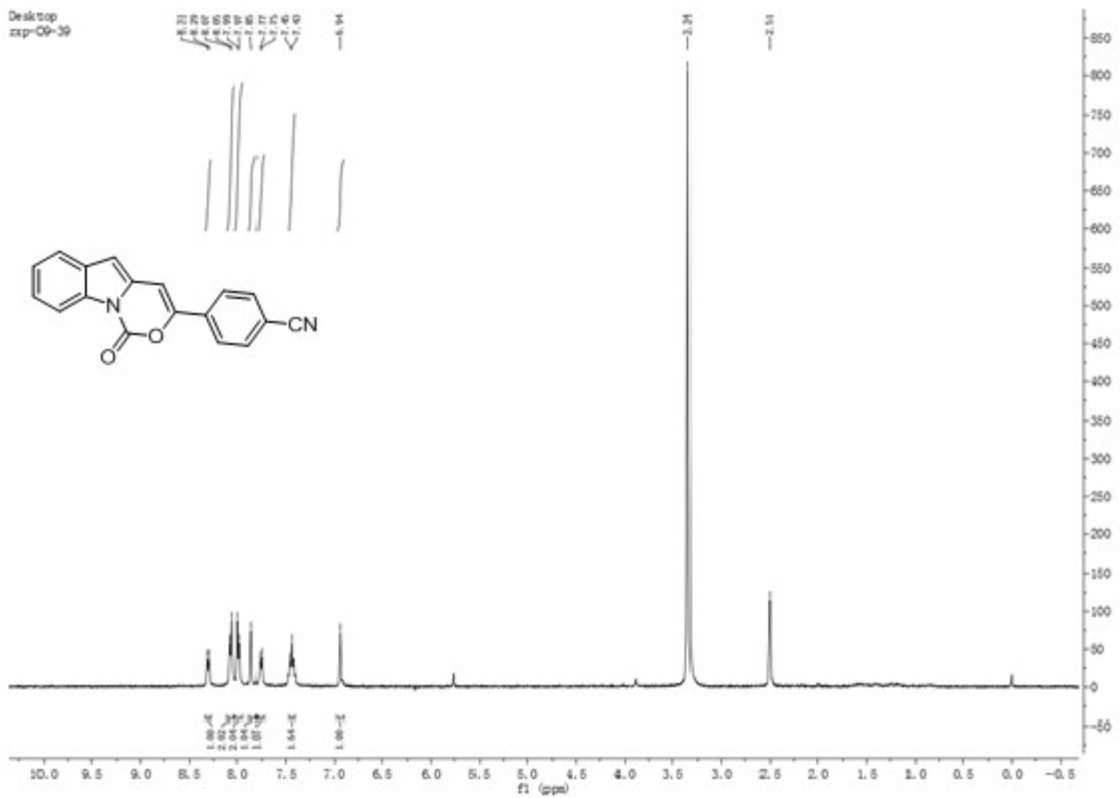
3d



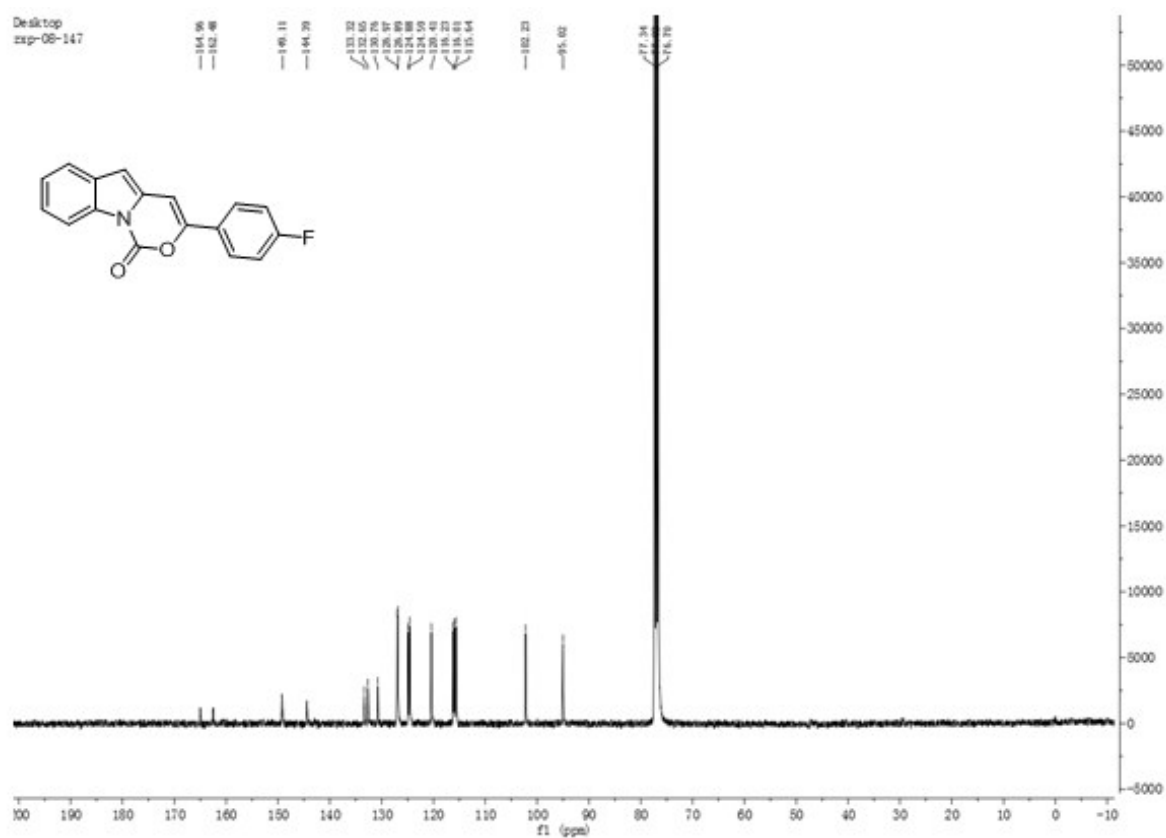
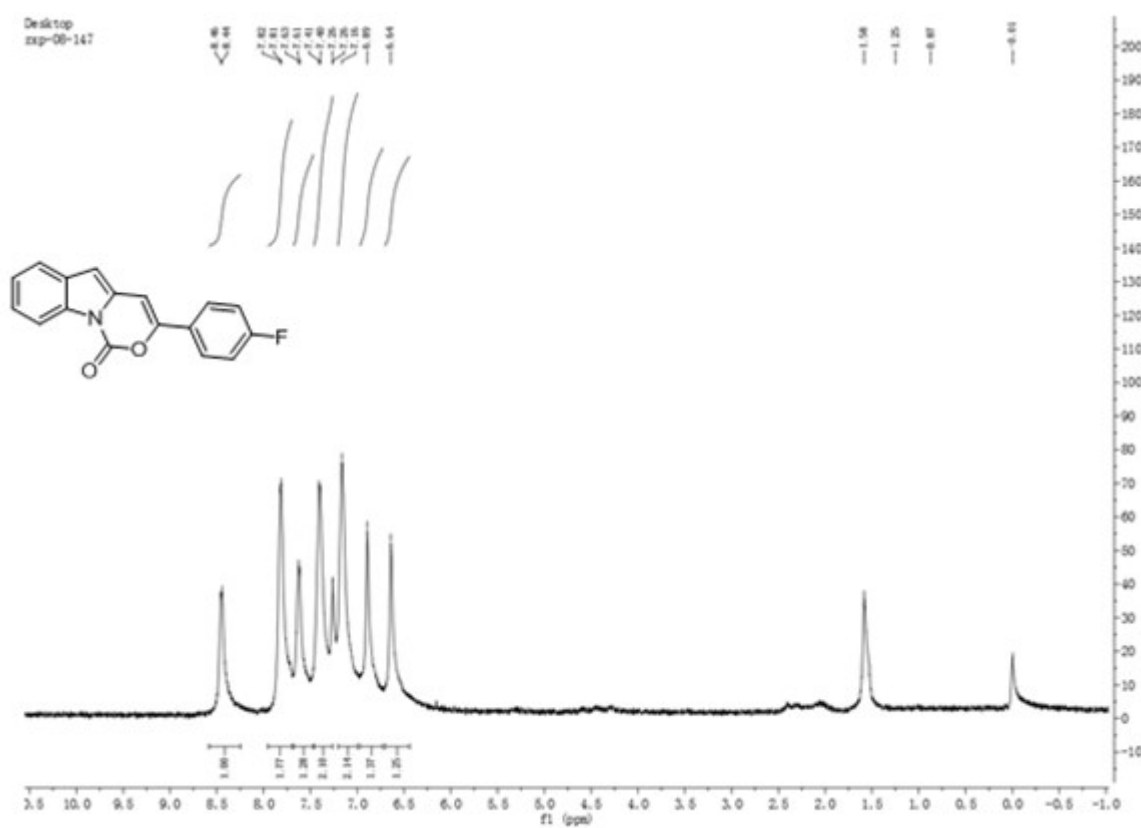
3e



3f

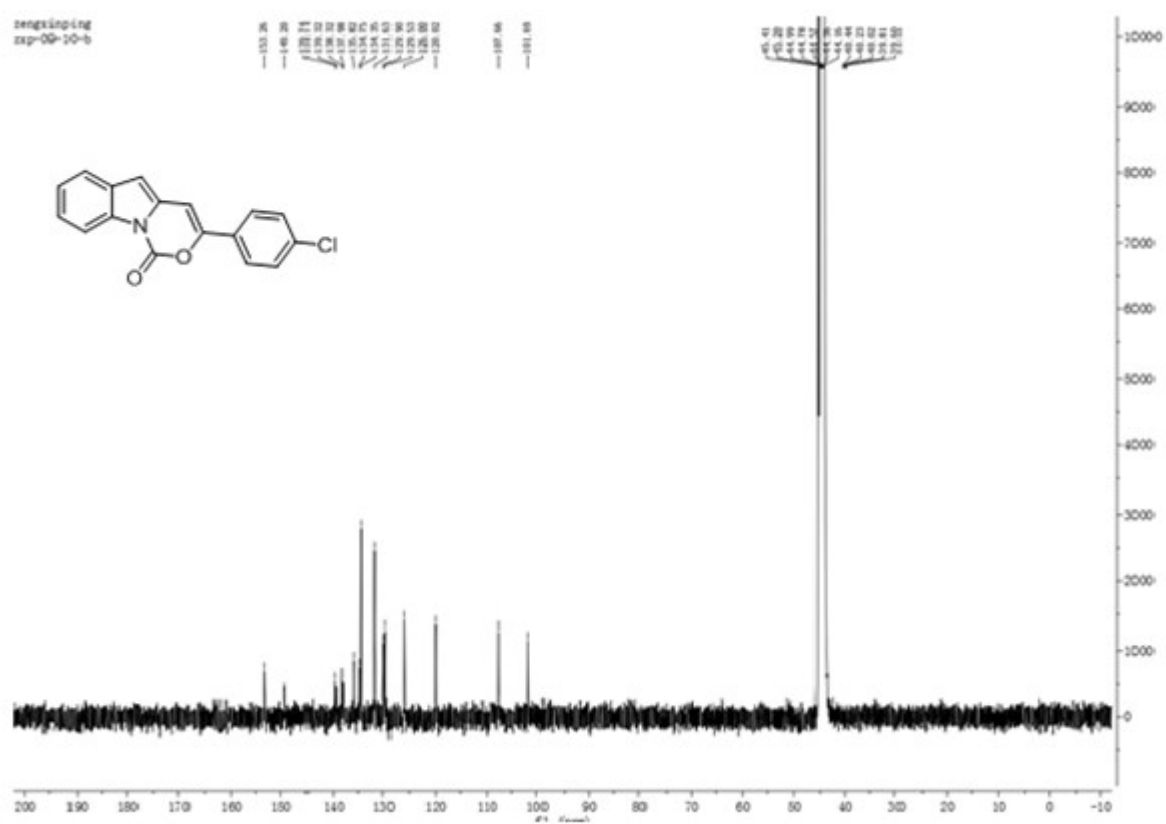


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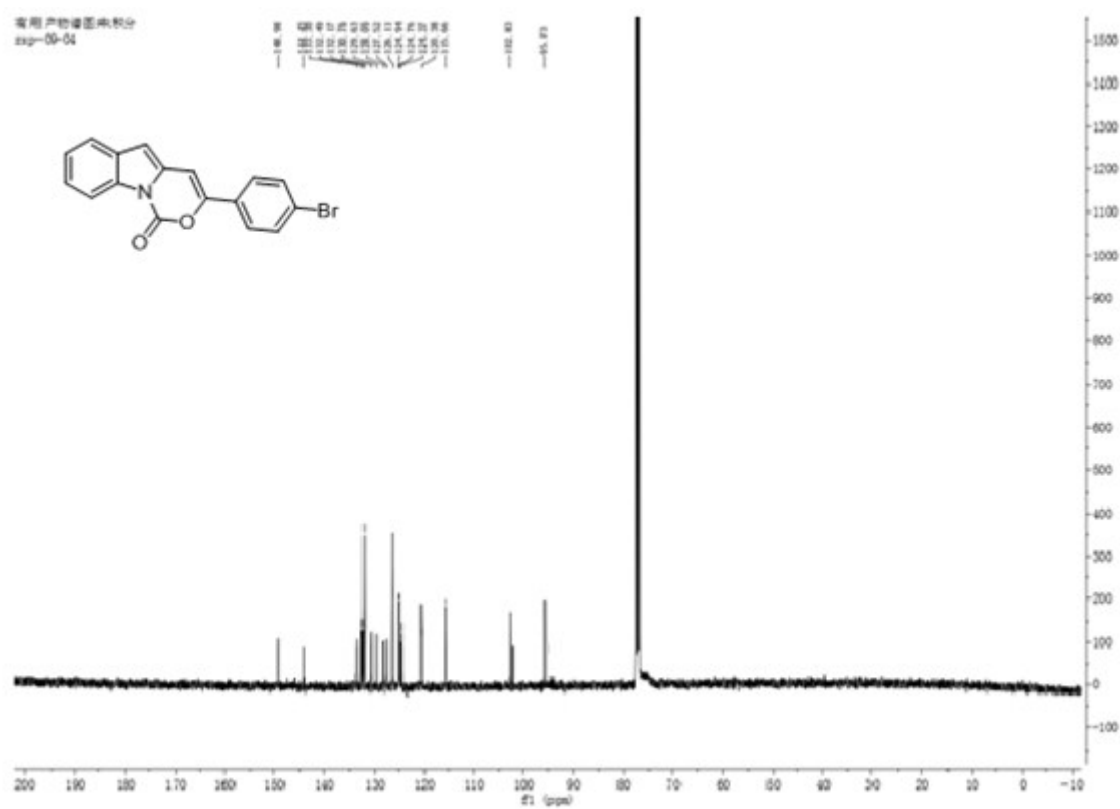
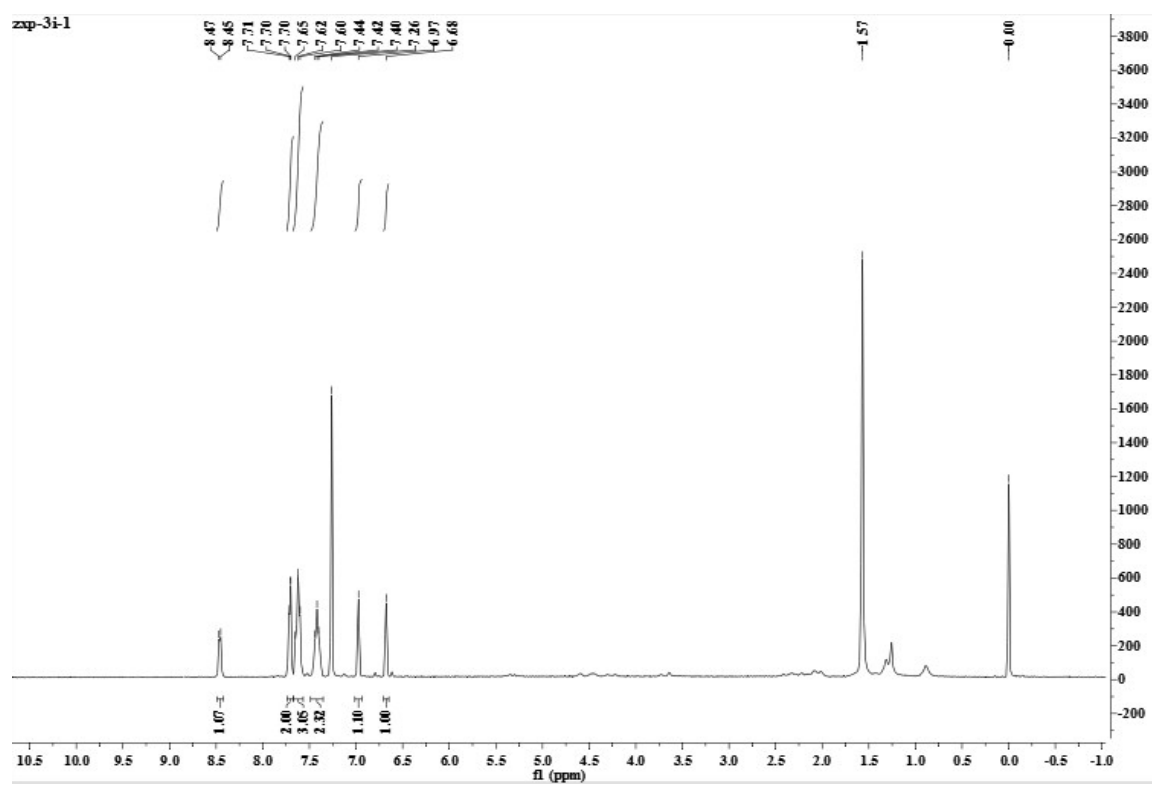


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exp-00-160-a

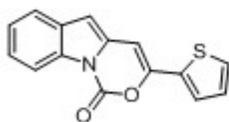
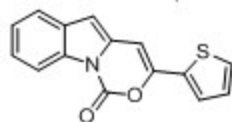
Chemical structure of 4-(4-chlorophenyl)-2,3-dihydro-1H-indole-1,3-dione is shown. The spectrum displays peaks corresponding to the structure, with integration values provided below the baseline.



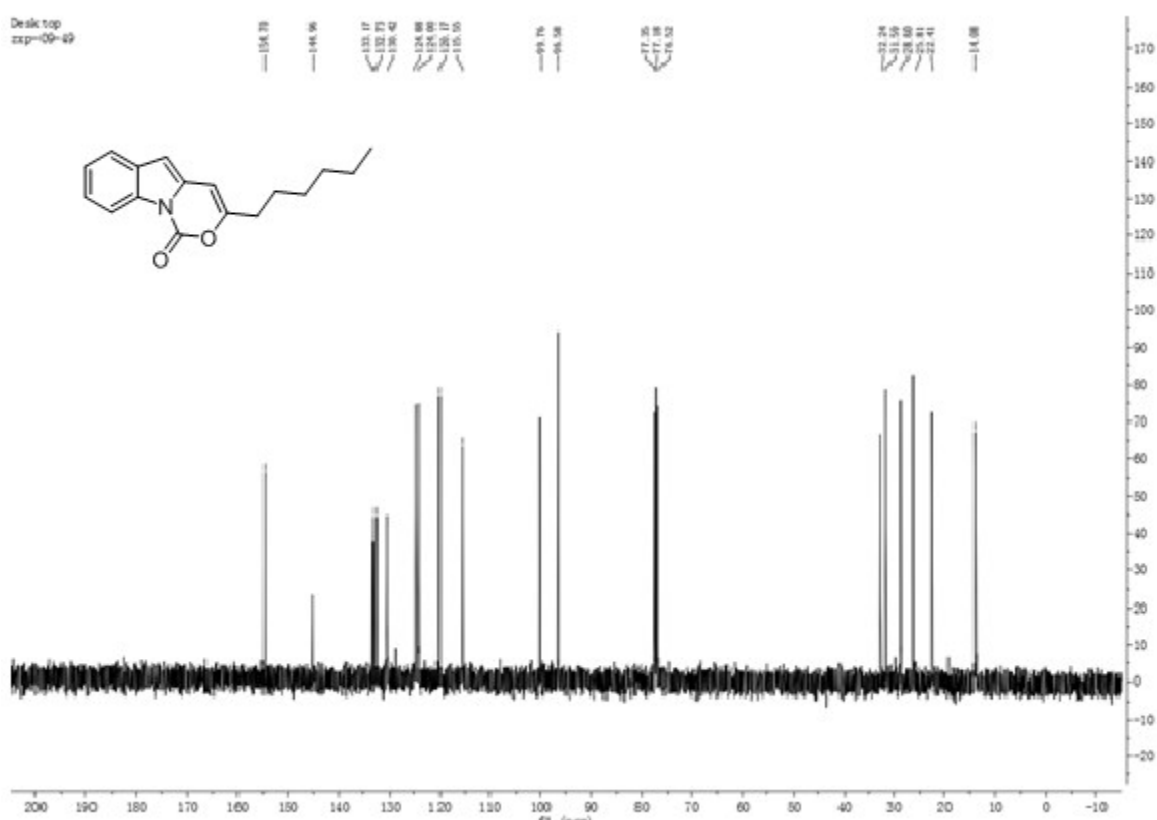
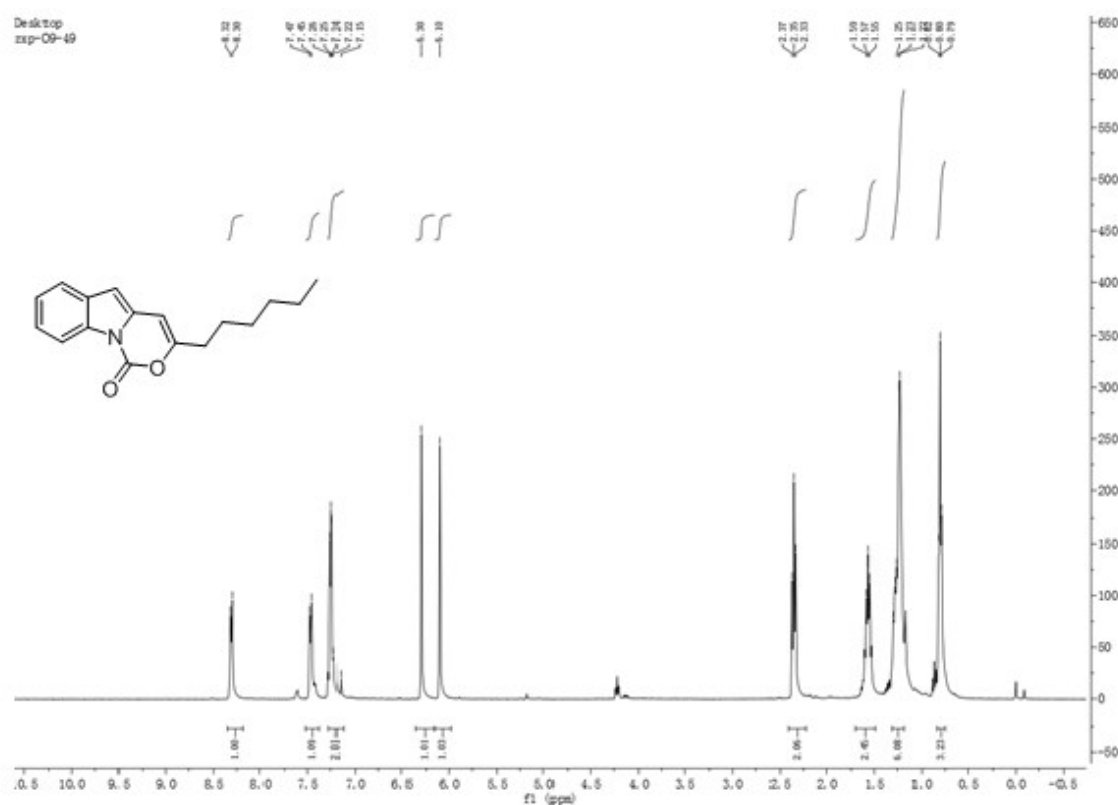
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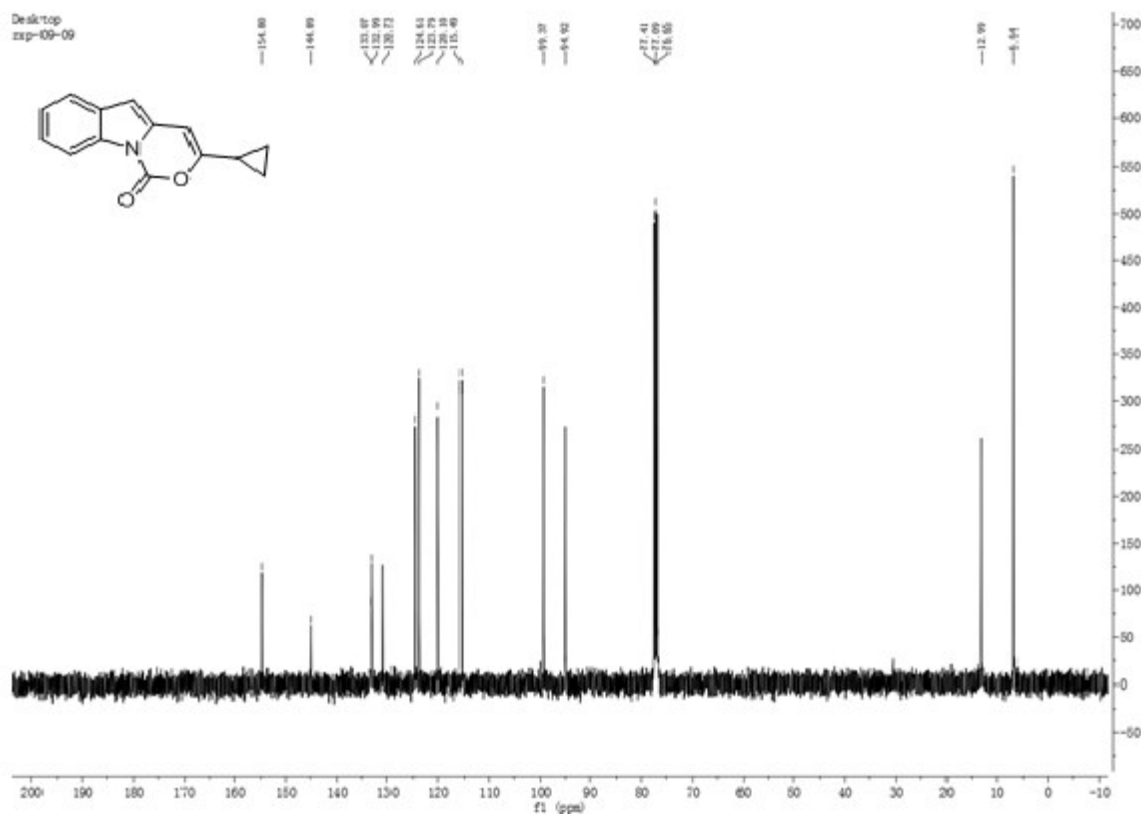
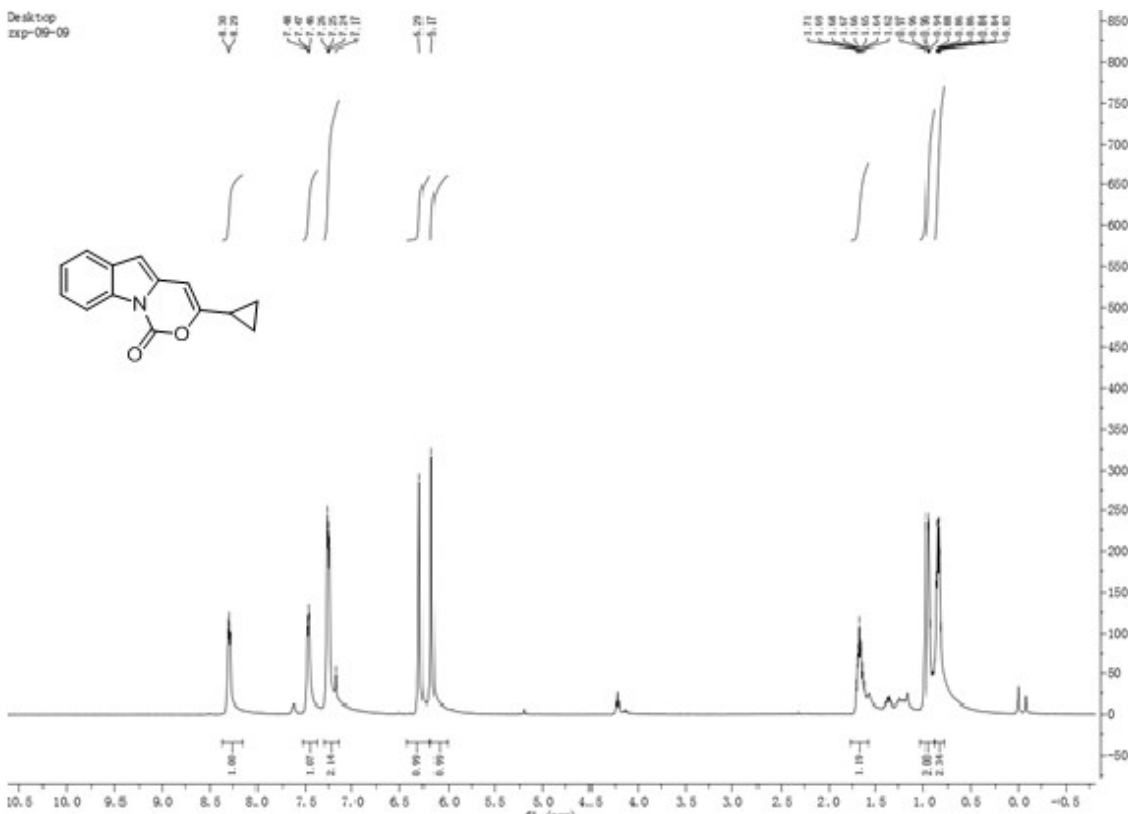
Desk:top
exp-09-07



3k

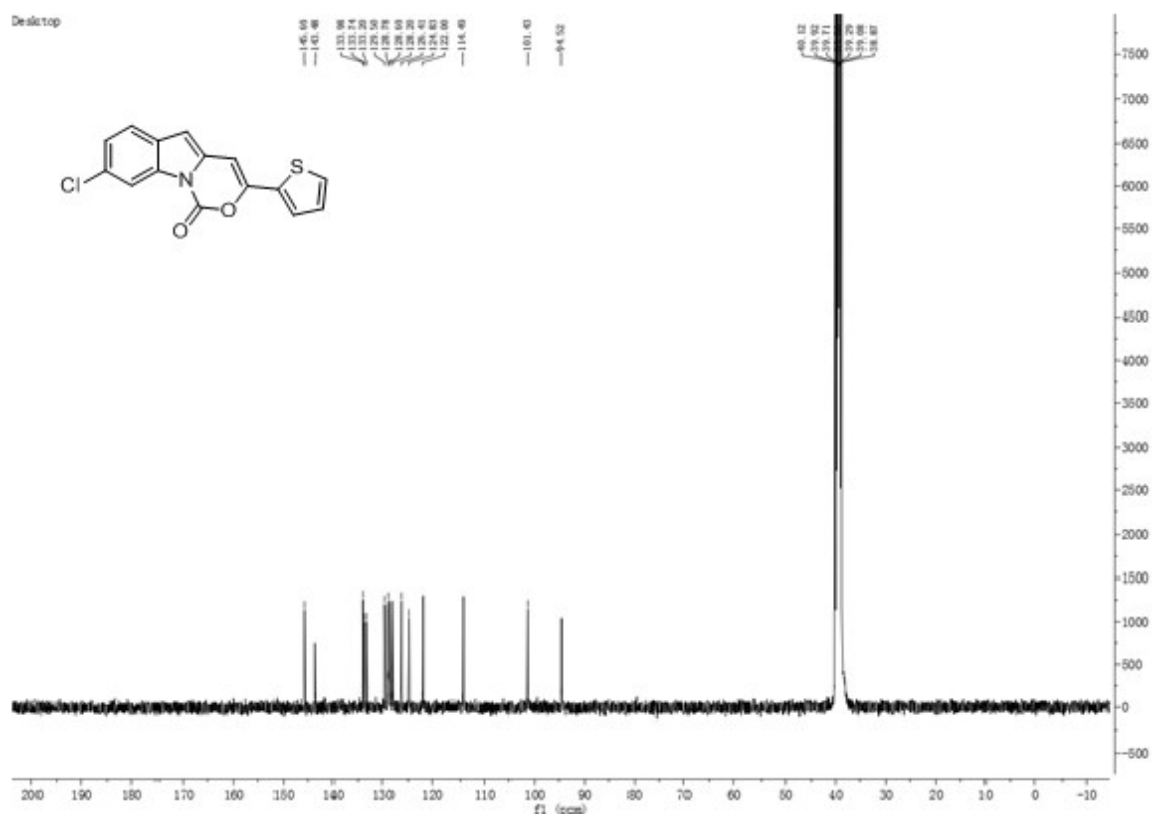
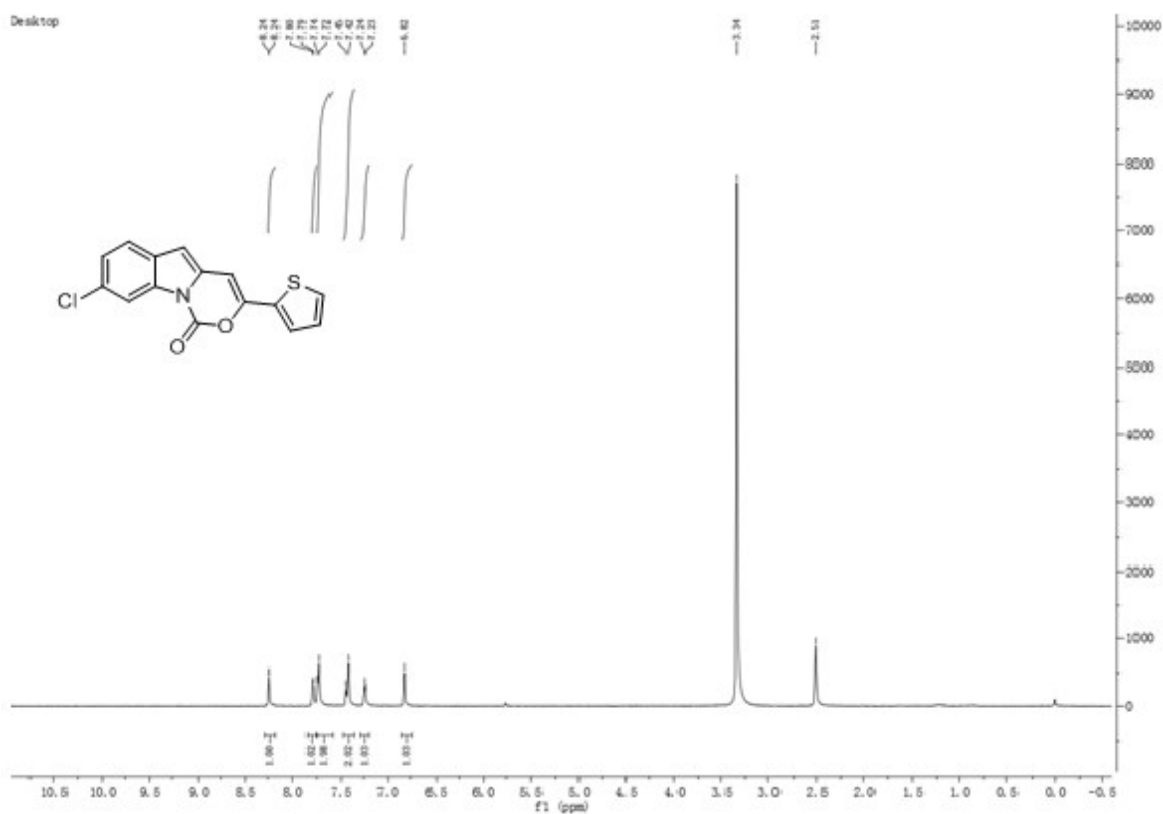


31

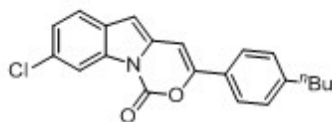
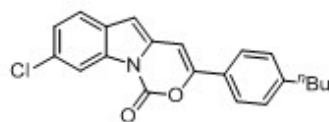


[illegible]

3n

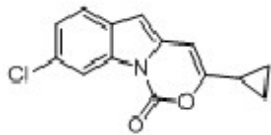


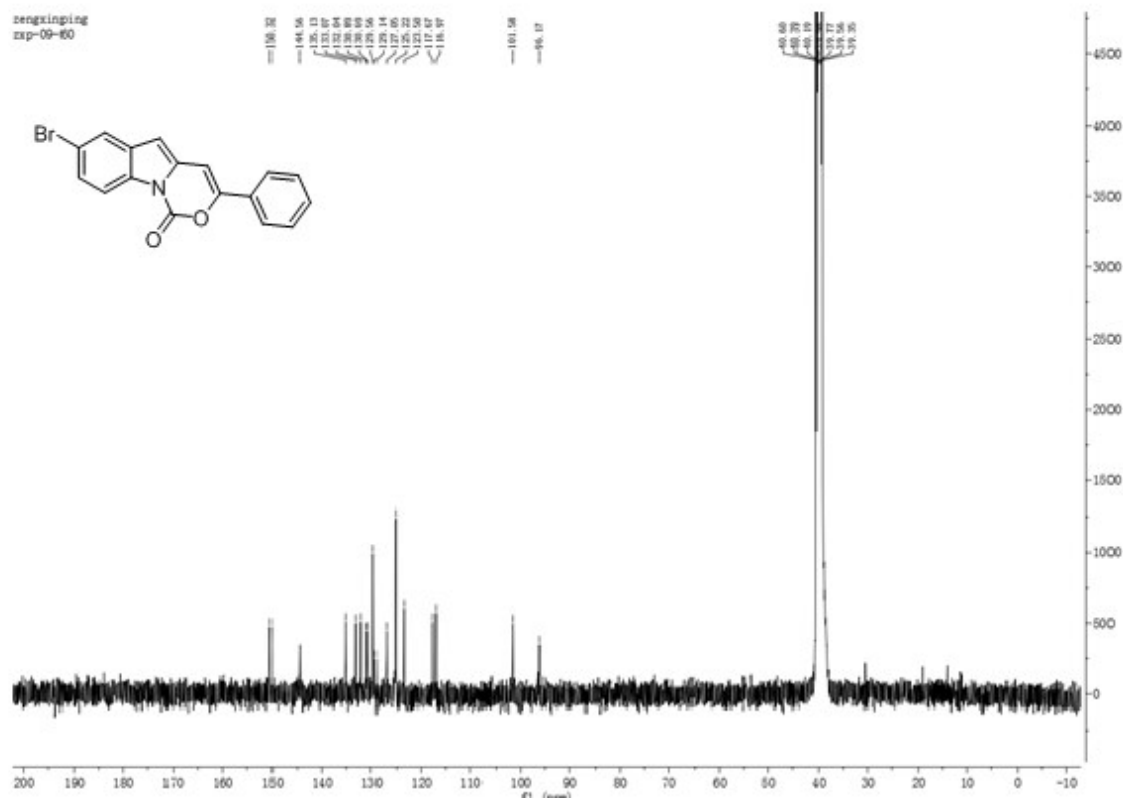
Desktop
exp-09-53



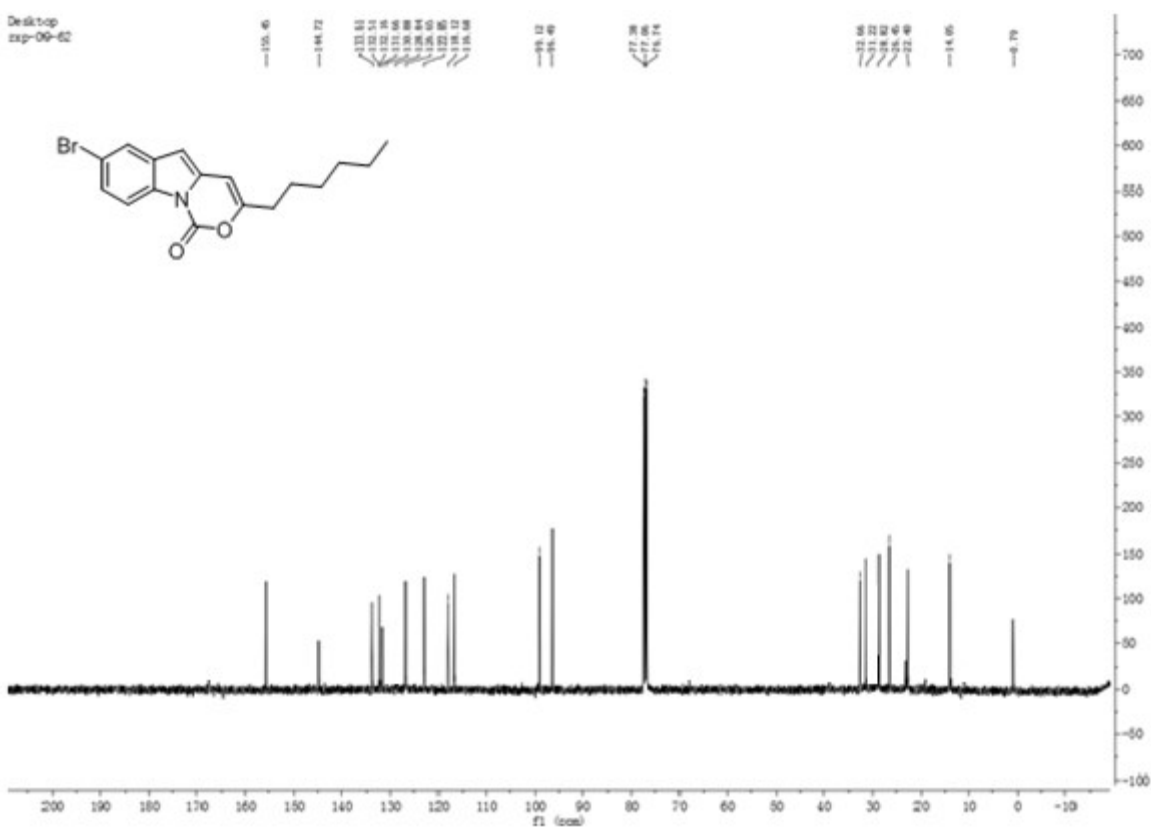
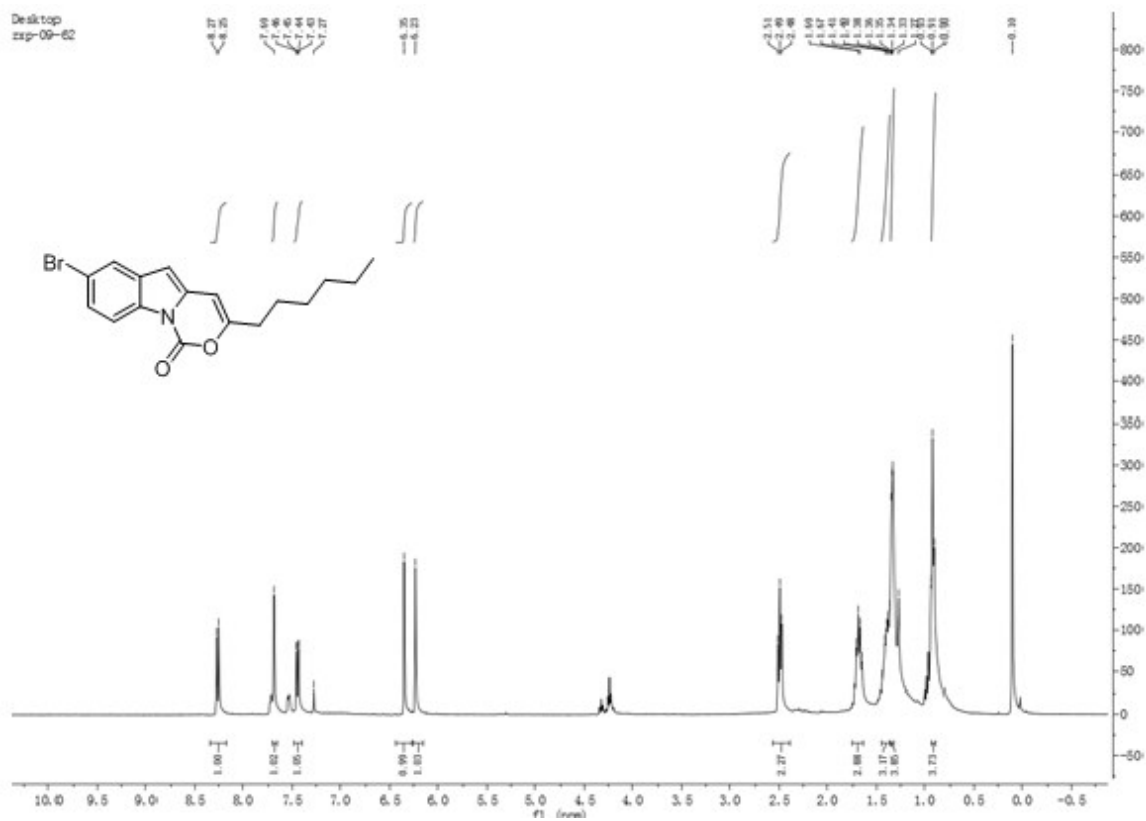
¹H NMR spectrum (CDCl₃) of compound 10a. The x-axis represents the chemical shift (δ) in ppm, ranging from 10.5 to -1.0. The y-axis represents the intensity. The spectrum shows several peaks with corresponding integrations and chemical shift values indicated above the peaks.

Chemical Shift (ppm)	Integration
~8.40	0.96
7.26 - 7.47	1.02, 1.00
6.28 - 6.36	0.99, 0.99
~1.80	1.00
0.96 - 1.06	2.01, 2.04
0.00	-

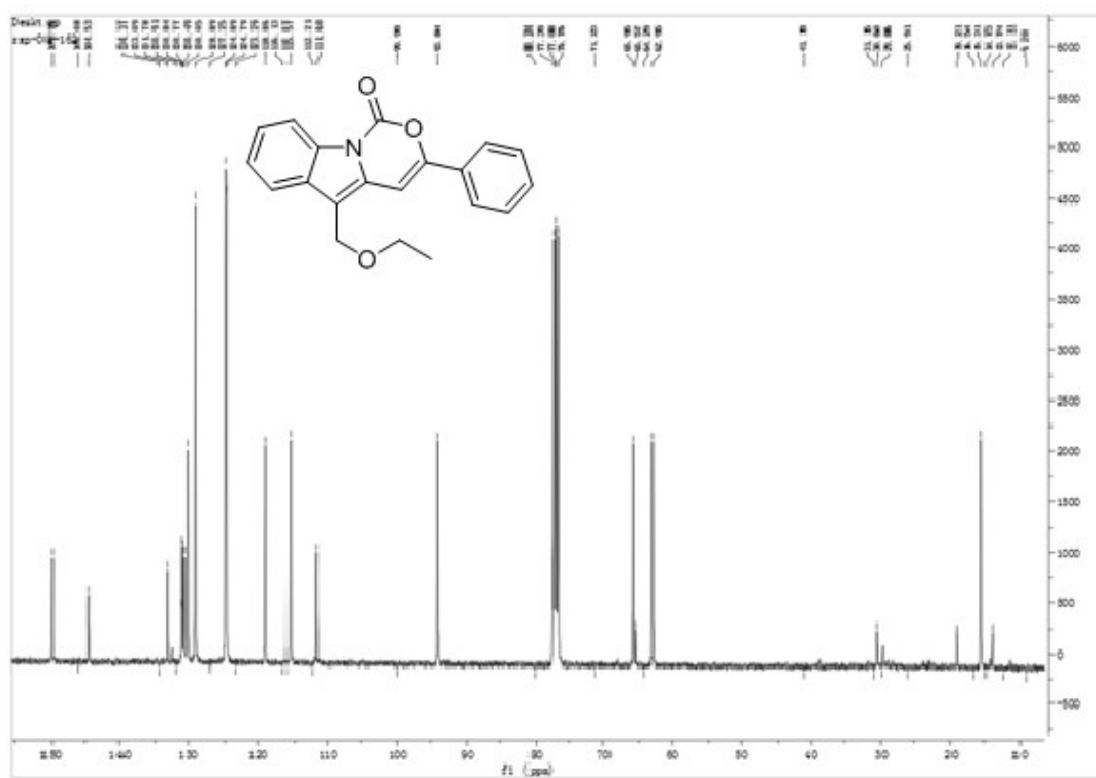
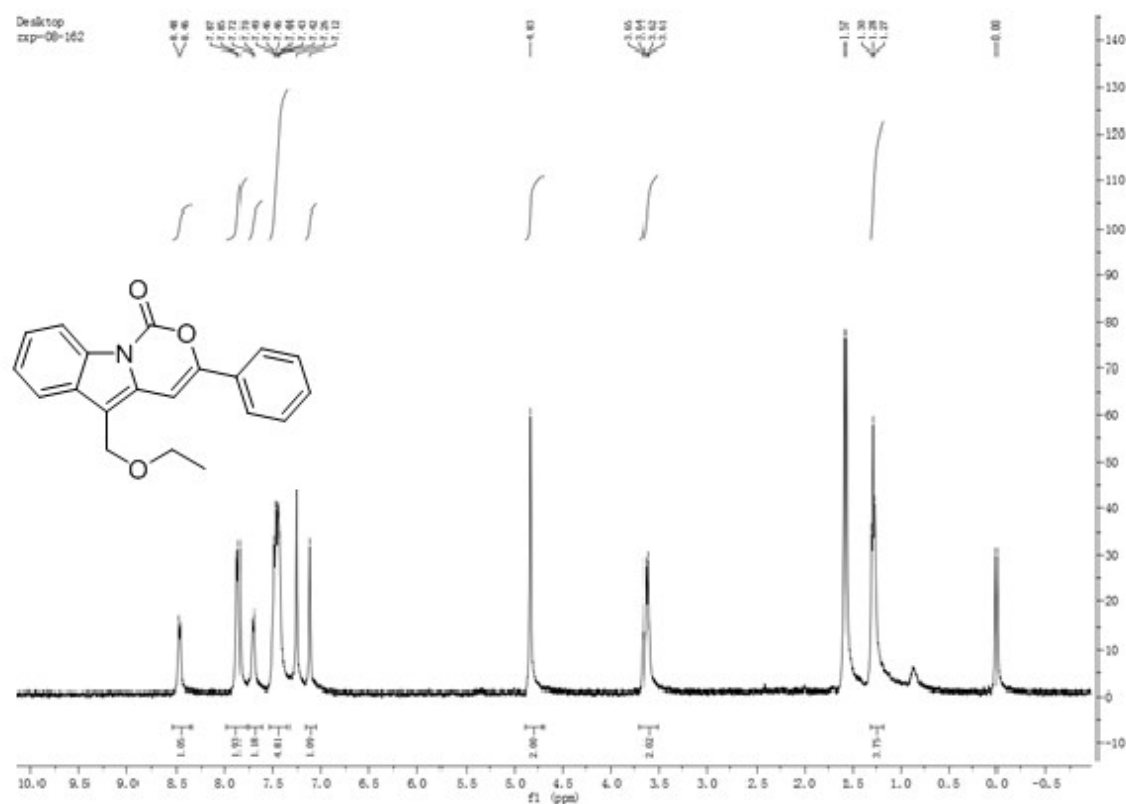


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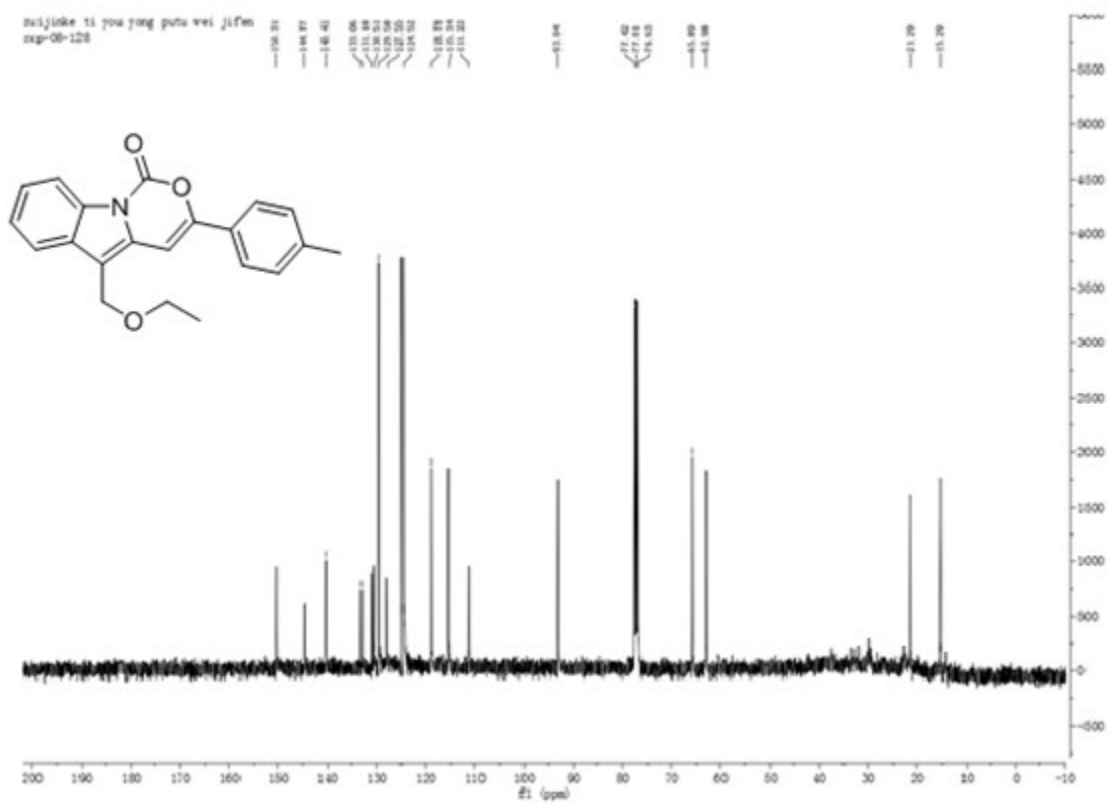
3r



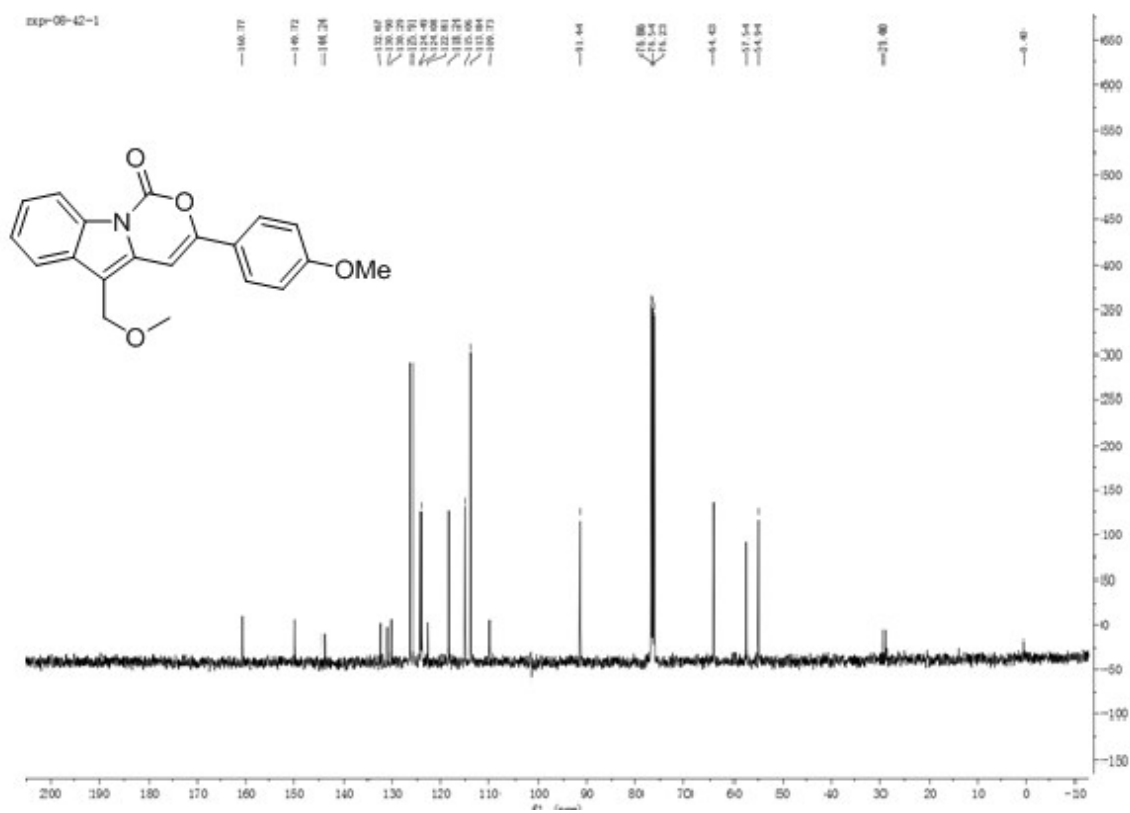
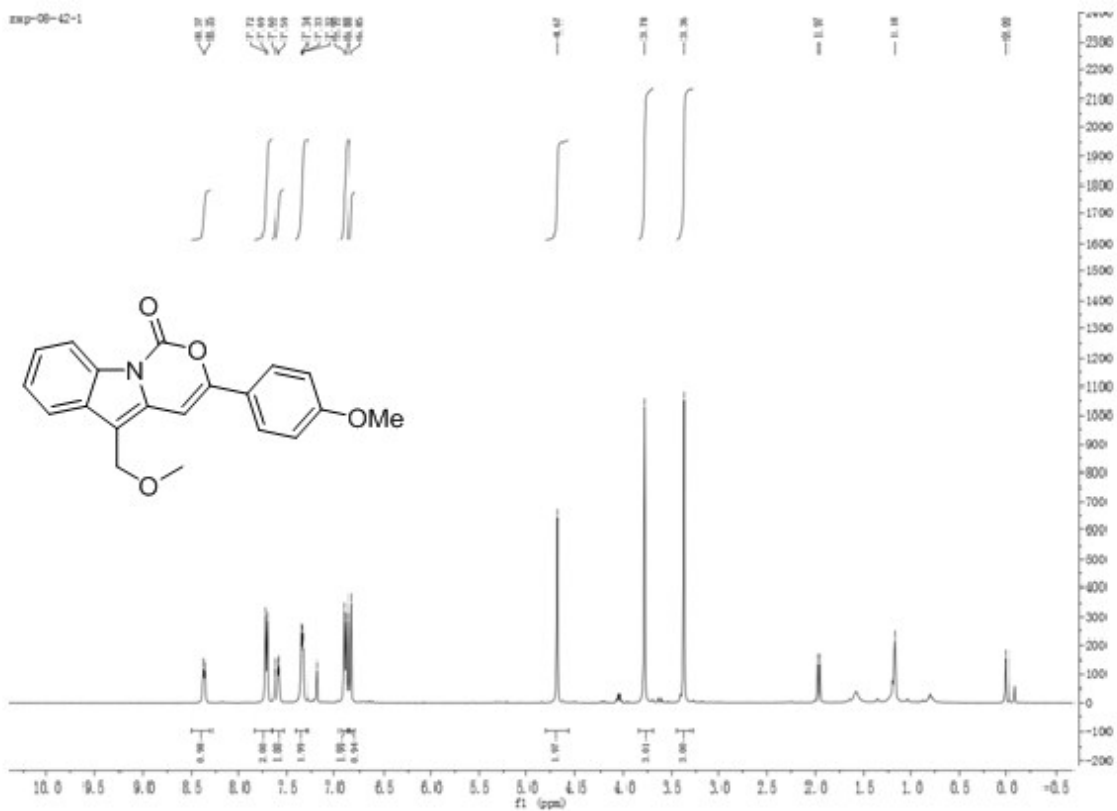
5a



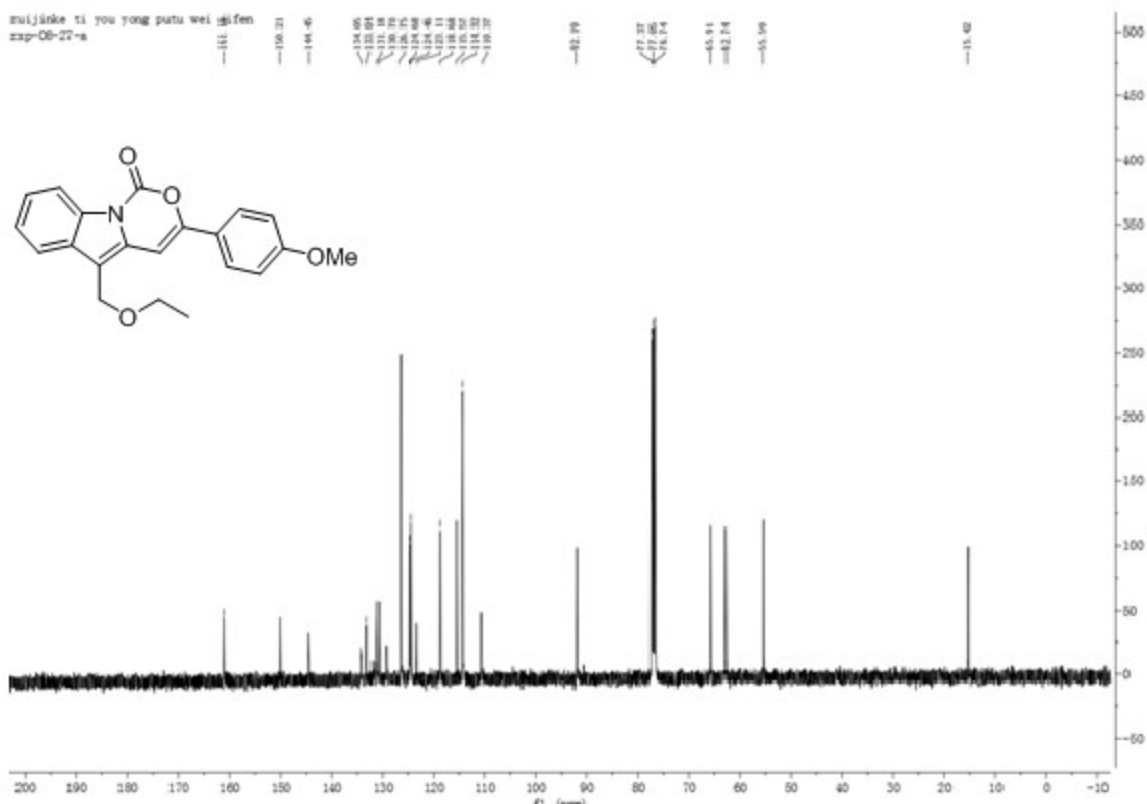
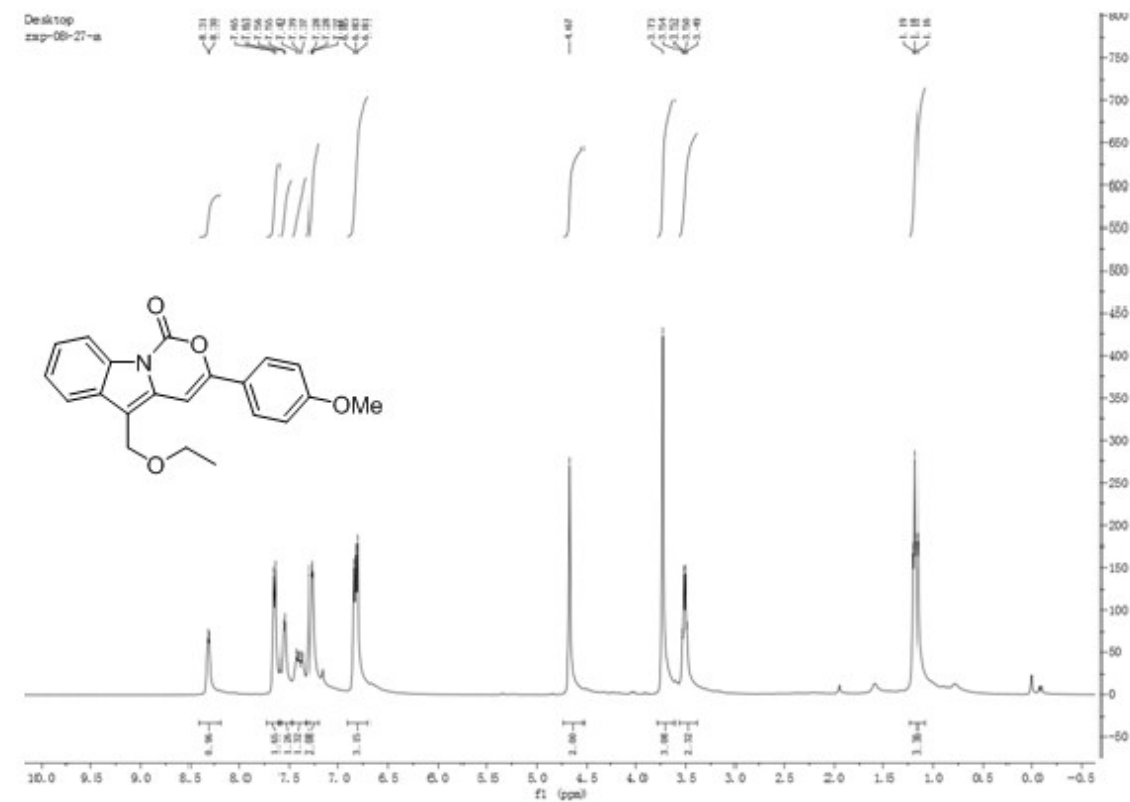
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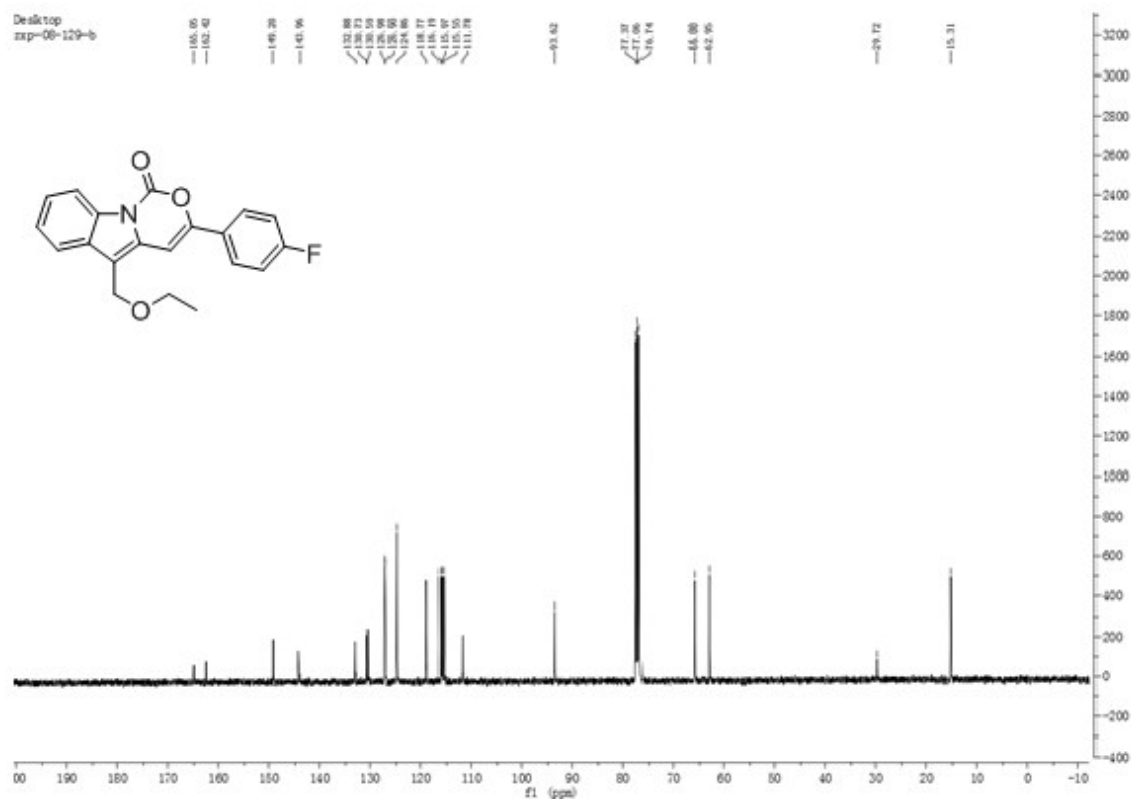
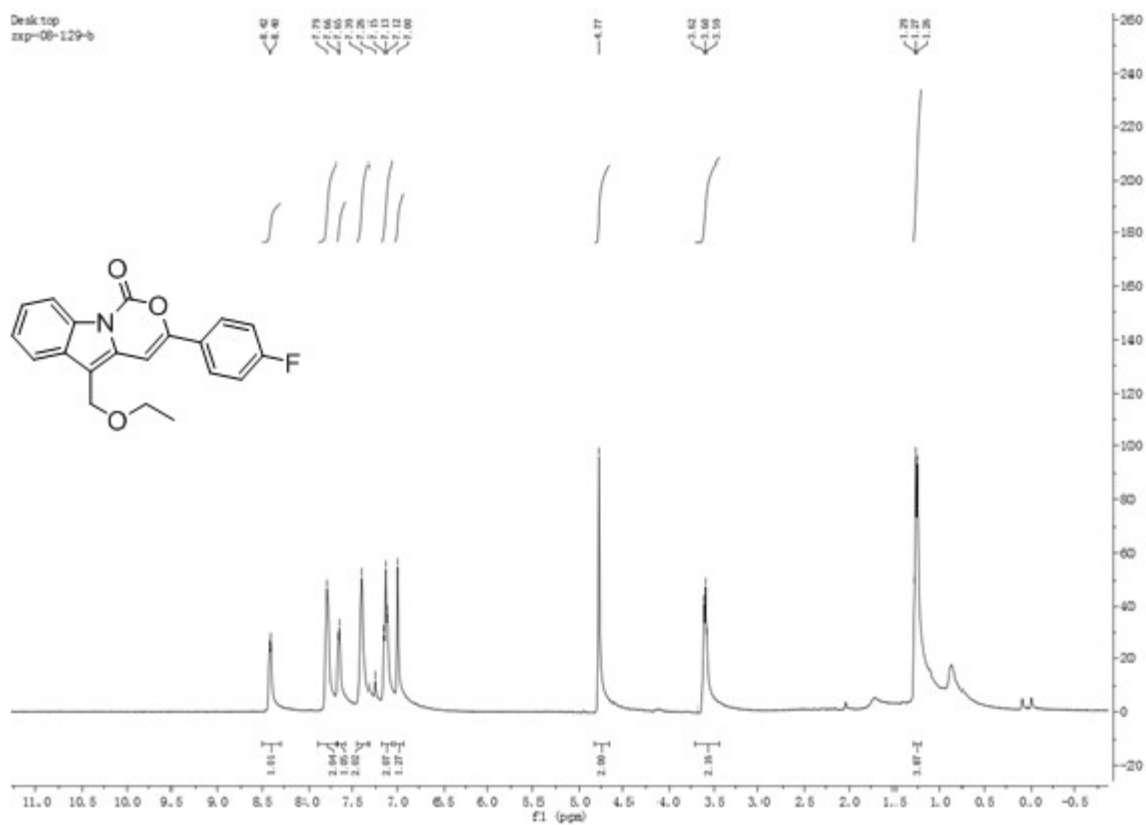
5c



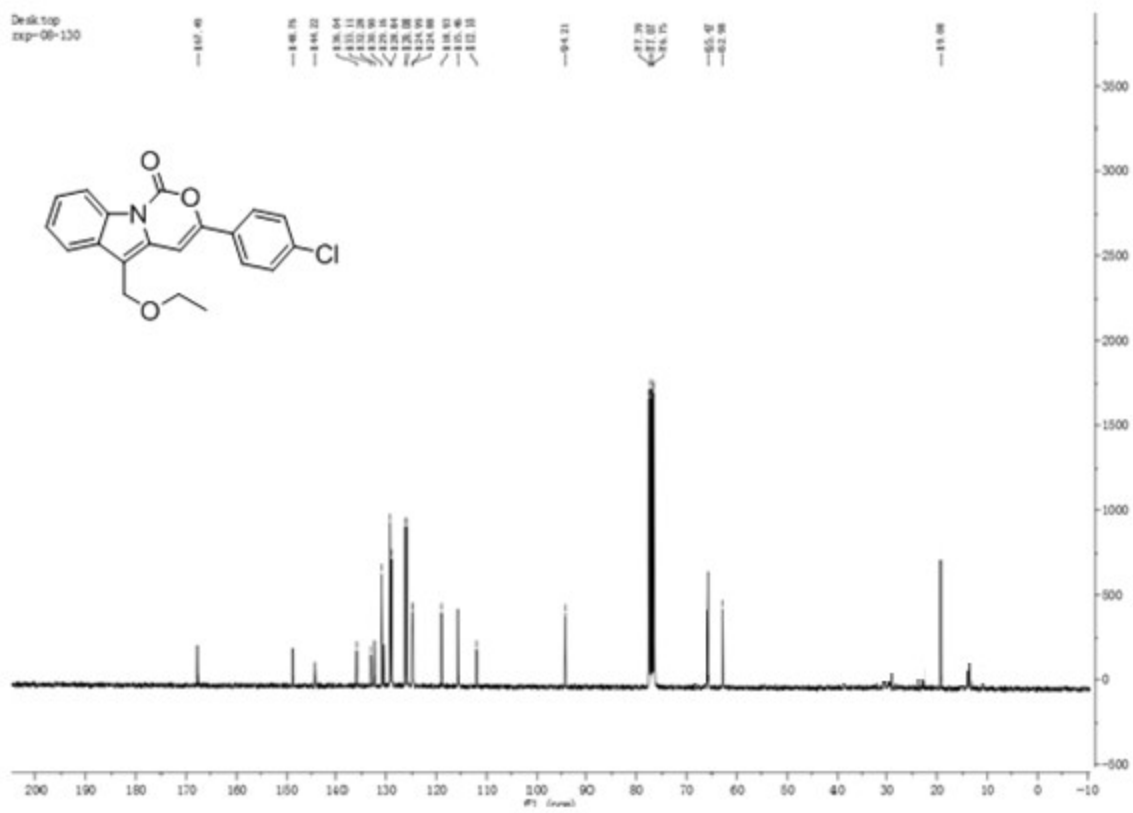
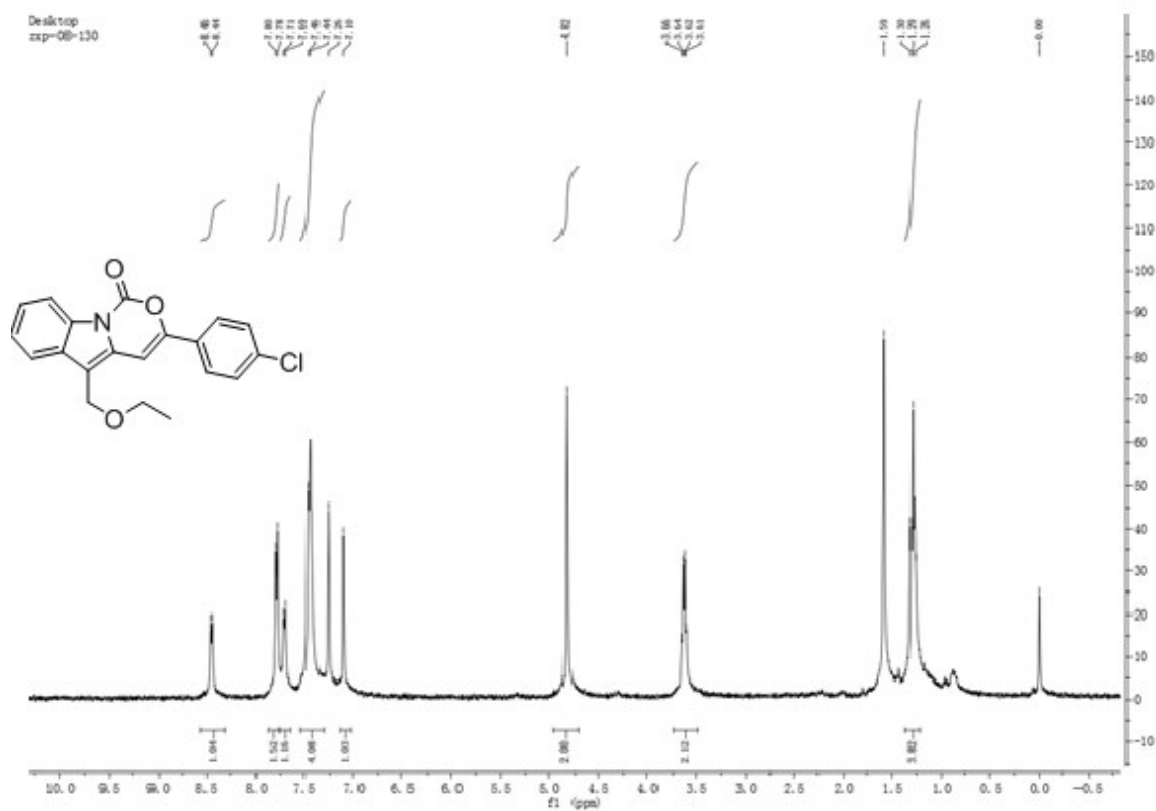
5d



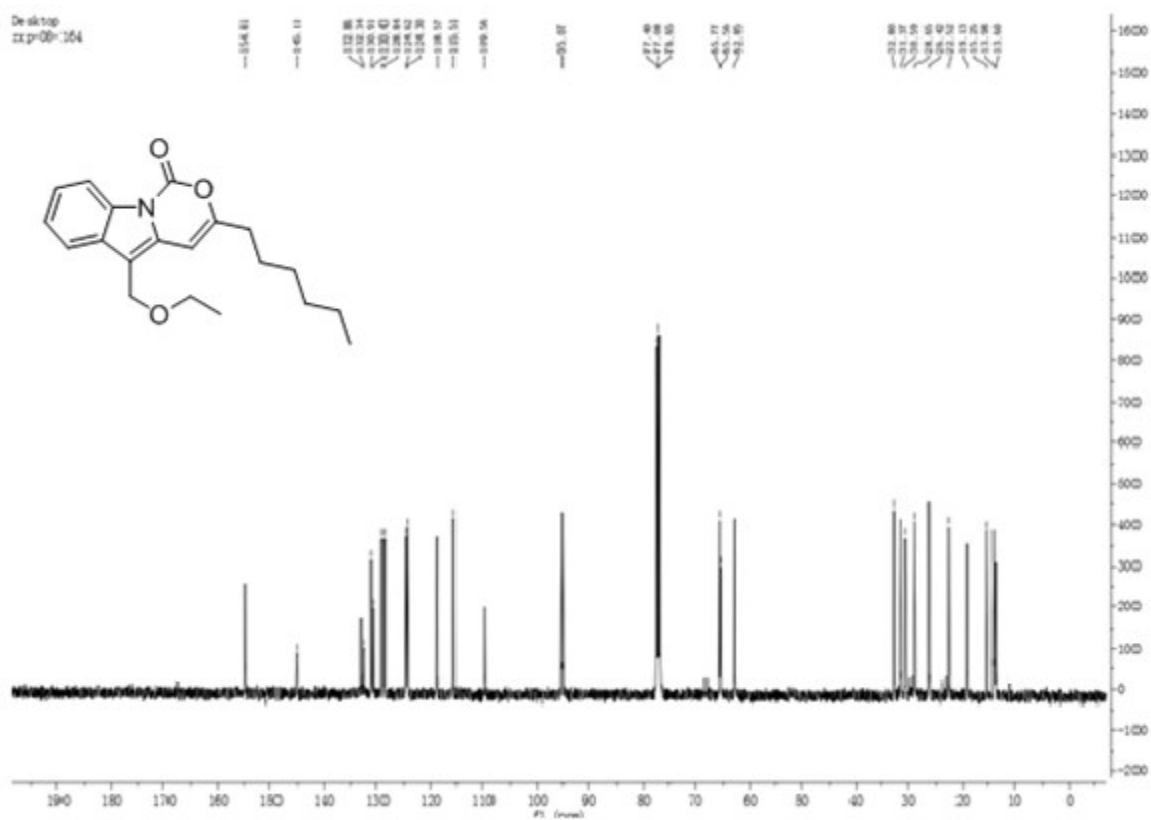
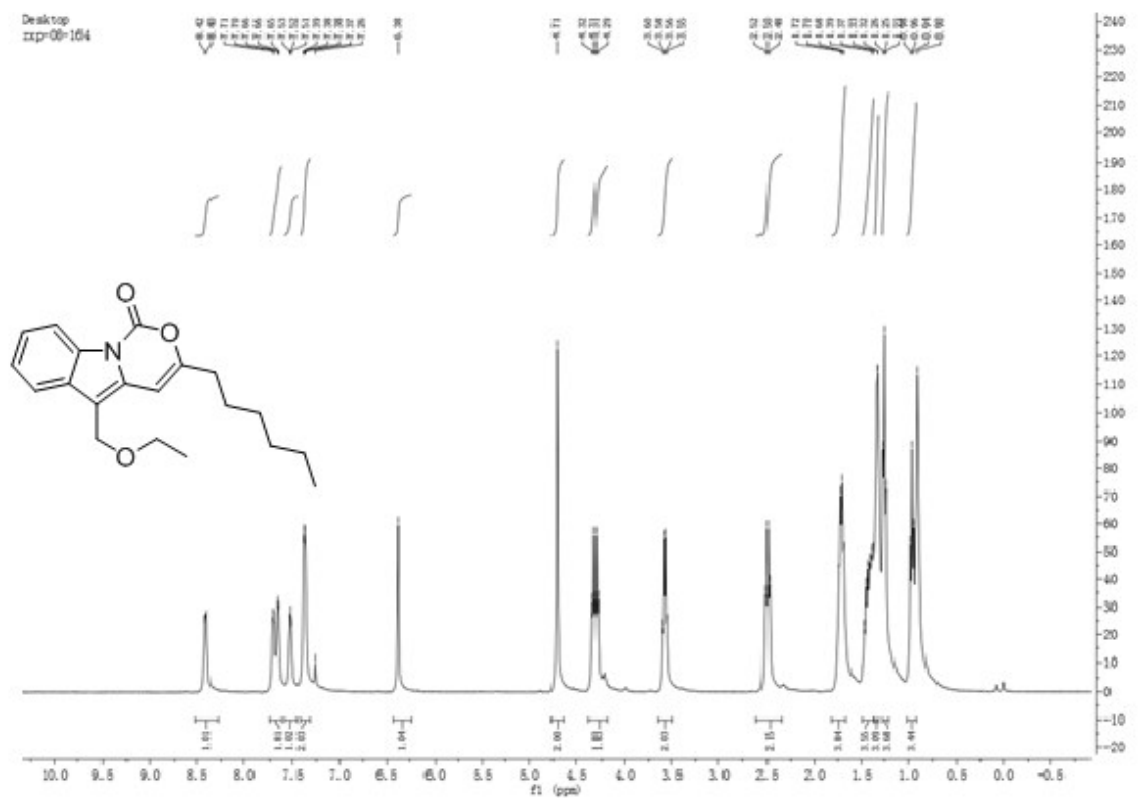
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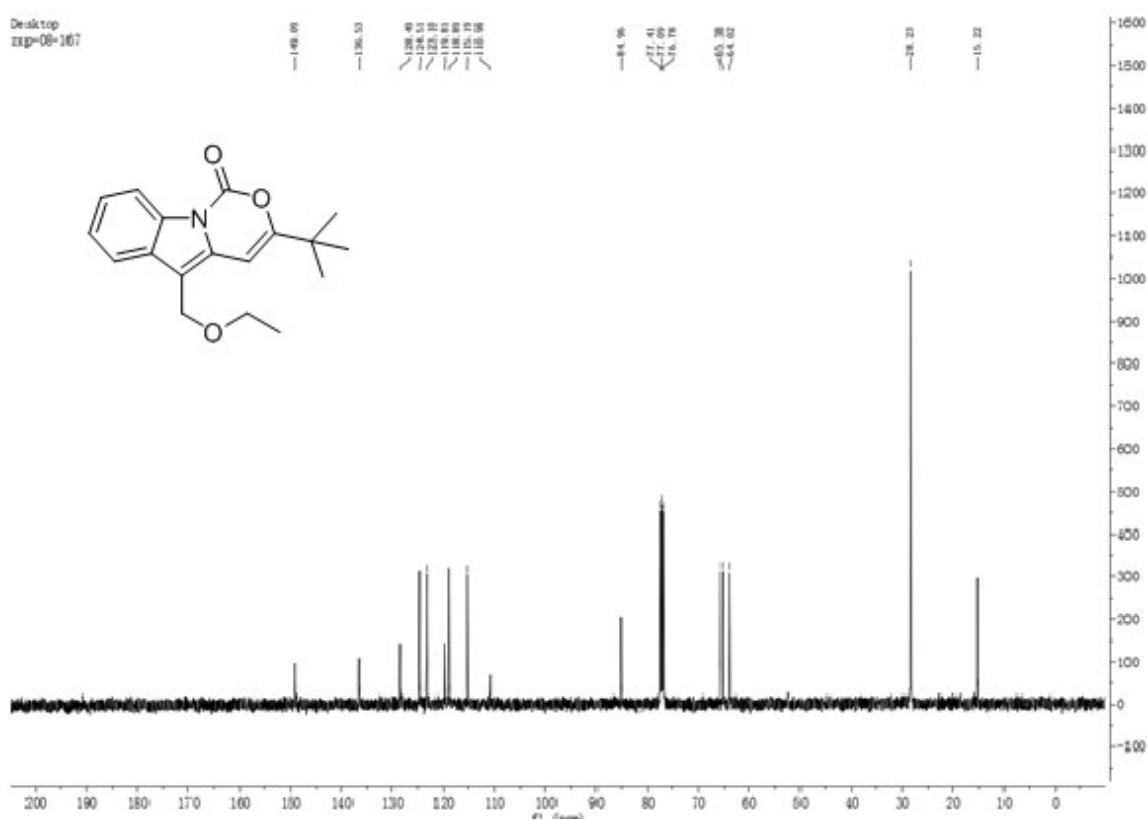
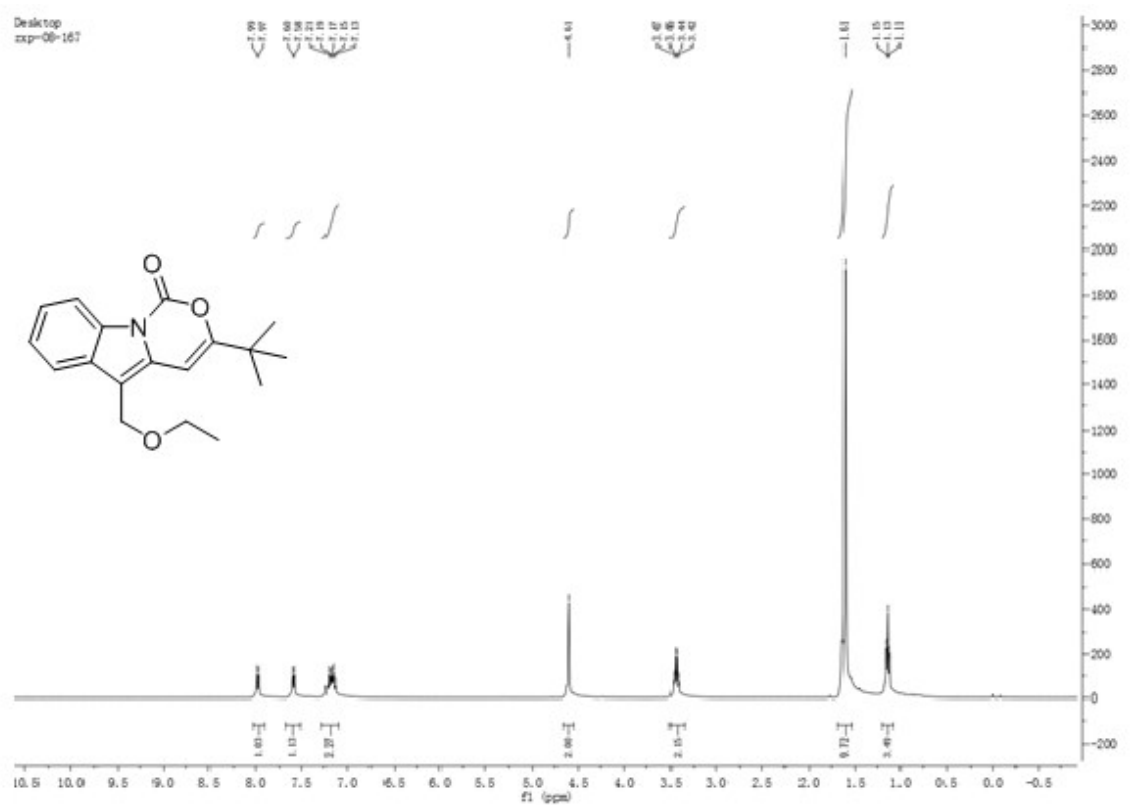
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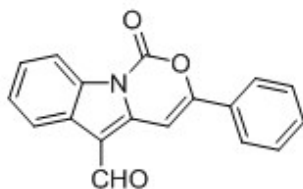
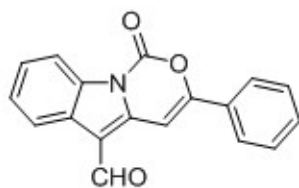
5g



5h



Desktop
img-09-7.2



8.

