Electronic Supporting Information

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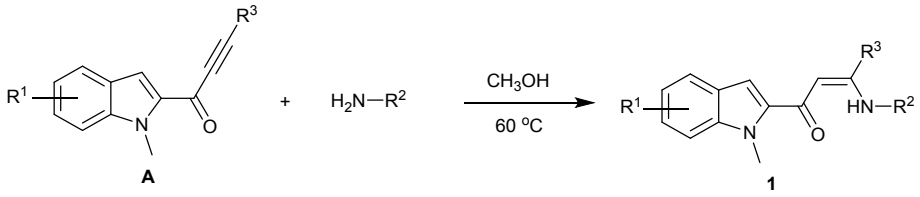
1. General Details.

All reactions under N_2 were performed in flame-dried glassware under an atmosphere of dry nitrogen, unless otherwise noted. Column chromatographic purification of products was carried out using silica gel (200~300 mesh). The reagents were used without further purification. ^{1}H NMR spectra was recorded at 400 MHz or 500 MHz, ^{13}C NMR spectra was recorded at 100 MHz or 125 MHz, and in $CDCl_3$ or d^6-DMSO (containing 0.03% TMS) solutions. ^{1}H NMR spectra were recorded with tetramethyl silane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.00 ppm) or d^6-DMSO (δ = 39.52 ppm) as internal reference. High-resolution mass spectra were performed on a mass spectrometer with a TOF (for EI or ESI) or FT-ICR (for MALDI) analyzer. Single crystal X-ray diffraction data was collected in Bruker SMARTAPEX diffractometers with molybdenum cathodes.

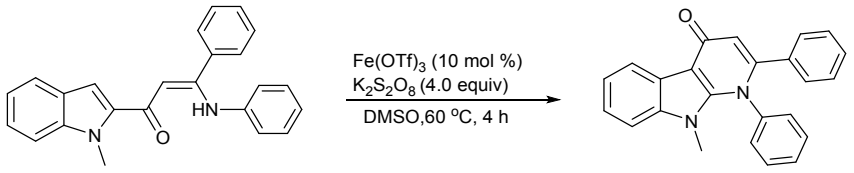
2. Methods for the synthesis of substrates 1a



Scheme S1: Synthetic route for the synthesis of **1**

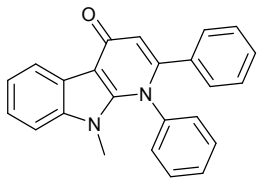
Substrate **1** were prepared according to the reported literature modified.[1] A typical procedure for the synthesis of **1a** as follows: To a solution of the Indolyl alkynyl ketones **A**(R^1= H, R^3= Ph) (519 mg, 2.0 mmol) in CH_3OH (10 mL) in Schlenk tube was added aniline (220 μL, 1.2 eq.) dropwise at 60 °C until the reaction was complete as monitored by thin-layer chromatography. The resulting mixture was quenched with water, and extracted with ethyl acetate (3x30 mL). The organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash chromatography on silica gel with (petroleum ether/ethyl acetate = 10:1) afforded desired substrate **1a** (670 mg, 96%) as a yellow solid.

3. Methods for the synthesis of product 2a



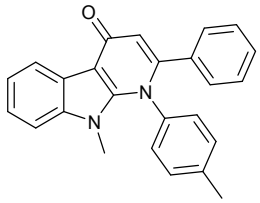
1a **2a**

A typical procedure for the synthesis of **2a** as follows: Indolyl enaminone **1a** (0.2 mmol, 70.5 mg), $Fe(OTf)_3$ (0.02 mmol, 10.1 mg), $K_2S_2O_8$ (0.8 mmol, 216.3 mg) and DMSO (2.0 mL) were placed in an schlenk tube under N_2. Then the reaction mixture was allowed to react at 60 °C for 4 h. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (dichloromethane/ethyl acetate = 1:1) afforded desired compound **2a**.



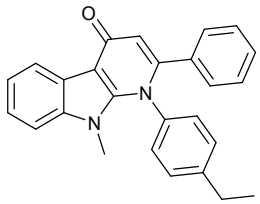
2a

9-Methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2a**), yellow solid, 51.8 mg, 74%. m.p. 298-300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (s, 3H), 6.41 (s, 1H), 7.12-7.21 (m, 6H), 7.25-7.28 (m, 2H), 7.31-7.36 (m, 5H), 8.59-8.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.6, 108.6, 116.2, 122.0, 122.3, 122.6, 124.0, 127.9, 128.6, 129.5, 129.8, 130.1, 130.6, 135.0, 137.3, 138.6, 144.7, 149.2, 175.9. HRMS (ESI) calcd for $C_{24}H_{19}N_2O$ $[M+H]^+$: 351.1492, found: 351.1498.



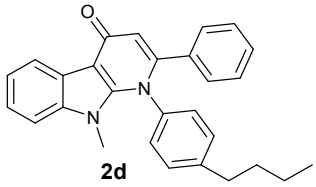
2b

9-Methyl-2-phenyl-1-(p-tolyl)-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2b**), white solid, 67.8 mg, 62%. m.p. 273-275 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.91 (s, 3H), 6.39 (s, 1H), 7.11-7.14 (m, 7H), 7.17-7.21 (m, 3H), 7.29-7.32 (m, 2H), 8.57-8.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 31.6, 108.6, 116.1, 122.0, 122.3, 122.6, 123.9, 127.9, 128.5, 130.0, 130.1, 130.2, 135.1, 135.8, 137.3, 140.1, 144.8, 149.4, 175.9. HRMS (ESI) calcd for $C_{25}H_{21}N_2O$ $[M+H]^+$: 365.1648, found: 365.1643.



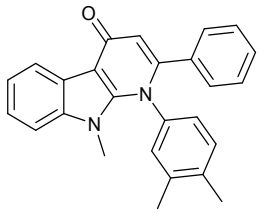
2c

1-(4-Ethylphenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2c)**, white solid, 71.6 mg, 63%. m.p. 225-226 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J = 7.6 Hz, 3H), 2.63 (q, J = 7.6 Hz, 2H), 2.86 (s, 3H), 6.38 (s, 1H), 7.07-7.18 (m, 10H), 7.27-7.29 (m, 2H), 8.57-8.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 28.1, 31.5, 108.4, 108.5, 116.0, 121.8, 122.2, 122.5, 123.8, 127.8, 128.4, 128.7, 130.0, 130.3, 135.0, 135.9, 137.2, 144.7, 146.4, 149.4, 175.8. HRMS (ESI) calcd for $C_{26}H_{23}N_2O$ $[M+H]^+$: 379.1805, found: 379.1794.



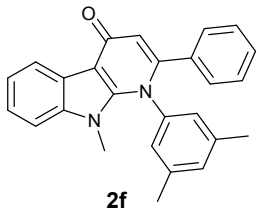
2d

1-(4-Butylphenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2d**), yellow solid, 83.0 mg, 68%. m.p. 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 7.6 Hz, 3H), 1.22-1.29 (m, 2H), 1.50-1.59 (m, 2H), 2.59 (t, J = 7.6 Hz, 2H), 2.95 (s, 3H), 6.41 (s, 1H), 7.12-7.20 (m, 10H), 7.30-7.33 (m, 2H) 8.58-8.61 (m, 1H); ^{3}C NMR (100 MHz, $CDCl_3$) δ 13.5, 21.7, 31.6, 32.9, 34.8, 108.6, 116.1, 122.0, 122.4, 122.6, 123.9, 127.8, 128.5, 129.4, 130.1, 130.2, 135.1, 136.0, 137.3, 144.8, 145.1, 149.4, 175.9. HRMS (ESI) calcd for $C_{28}H_{27}N_2O$ $[M+H]^+$: 407.2118, found: 407.2109.



2e

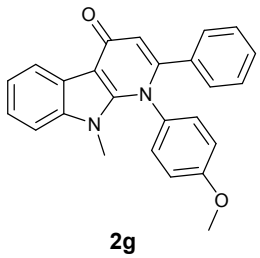
1-(3,4-Dimethylphenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2e**), white solid, 73.3 mg, 68%. m.p. 266-267 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 3H), 2.23 (s, 3H), 2.92 (s, 3H), 6.38 (s, 1H), 6.93-6.98 (m, 2H), 7.04-7.07 (m, 1H), 7.12-7.19 (m, 6H), 7.29-7.32 (m, 2H), 8.59-8.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 19.3, 31.6, 108.5, 116.1, 121.9, 122.3, 122.6, 123.8, 127.7, 127.8, 128.5, 130.1, 130.4, 131.1, 135.2, 136.0, 137.3, 138.2, 138.6, 144.9, 149.4, 175.9. HRMS (ESI) calcd for $C_{26}H_{23}N_2O$ $[M+H]^+$: 379.1805, found: 379.1800.



2f

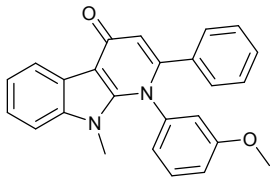
1-(3,5-Dimethylphenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2f**), white solid, 71.0 mg, 62%. m.p. 254-255 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24

(s, 6H), 2.96 (s, 3H), 6.39 (s, 1H), 6.84 (s, 2H), 6.96 (s, 1H), 7.12-7.21 (m, 6H), 7.31-7.34 (m, 2H), 8.59-8.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 31.6, 108.6, 116.1, 122.0, 122.4, 122.7, 123.9, 127.7, 128.0, 128.5, 130.1, 131.2, 135.1, 137.3, 138.2, 139.4, 144.8, 149.2, 175.9. HRMS (ESI) calcd for $C_{26}H_{23}N_2O$ $[M+H]^+$: 379.1805, found: 379.1796.



2g

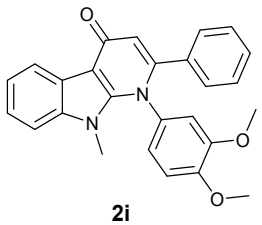
1-(4-Methoxyphenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2g**), white solid, 79.9 mg, 70%. m.p. 273-275 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (s, 3H), 3.80 (s, 3H), 6.39 (s, 1H), 6.80-6.83 (m, 2H), 7.15-7.21 (m, 8H), 7.30-7.33 (m, 2H), 8.58-8.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.6, 55.4, 108.6, 114.4, 116.1, 122.0, 122.3, 122.6, 123.9, 127.9, 128.5, 130.1, 131.0, 131.6, 135.2, 137.3, 145.0, 149.7, 160.3, 175.9. HRMS (ESI) calcd for $C_{25}H_{21}N_2O_2$ $[M+H]^+$: 381.1598, found: 381.1595.



2h

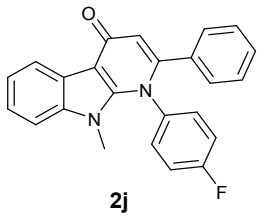
1-(3-Methoxyphenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2h**), white solid , 65.2 mg, 57%. m.p 253-255 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (s, 3H), 3.75 (s, 3H), 6.39 (s, 1H), 6.86-6.90 (m, 3H), 7.06-7.09 (m, 1H), 7.19-7.25 (m, 6H), 7.27-7.30 (m, 2H), 8.56-8.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.5, 55.5, 108.6, 115.7, 116.0, 116.2, 122.1, 122.3, 122.6, 122.7, 124.0, 127.9, 128.7, 130.0, 135.0, 137.3, 139.5, 144.6, 149.1, 160.5, 175.9. HRMS (ESI) calcd for $C_{25}H_{21}N_2O_2$ $[M+H]^+$: 381.1598,

found: 381.1597.



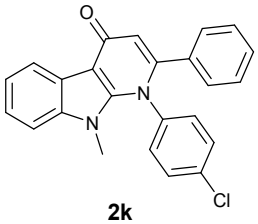
2i

1-(3,4-Dimethoxyphenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2i**), white solid, 74.0 mg, 60%. m.p. 263-265 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (s, 3H), 3.80 (s, 3H), 3.88 (s, 3H), 6.37 (s, 1H), 6.74-6.77 (m, 1H), 6.83-6.89 (m, 2H), 7.06-7.09 (m, 1H), 7.20-7.24 (m, 6H), 7.28-7.31 (m, 2H), 8.56-8.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.3, 55.8, 56.3, 108.2, 108.6, 110.3, 113.9, 115.9, 121,8, 122.0, 122.4, 122.9, 123.7, 127.9, 128.6, 130.1, 131.0, 135.2, 137.0, 144.6, 149.4, 149.6, 149.8, 175.7. HRMS (ESI) calcd for $C_{26}H_{23}N_2O_3$ $[M+H]^+$: 411.1703, found: 411.1692.



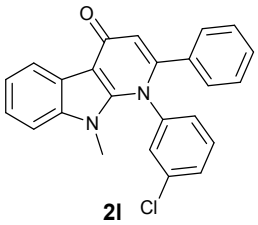
2j

1-(4-Fluorophenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2j**), white solid, 71.8 mg. 65%. m.p. 296-298 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (s, 3H), 6.38 (s, 1H), 7.01-7.09 (m, 3H), 7.15-7.23 (m, 5H), 7.29-7.34 (m, 4H), 8.55-8.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.6, 108.5, 108.6, 116.1, 116.2 ($J_{C\text{-}F}$ = 8.0 Hz), 116.4, 116.6, 122.1, 122.2, 122.5, 124.0, 128.1, 128.8, 130.1, 132.5 ($J_{C\text{-}F}$ = 9.0 Hz), 134.6 ($J_{C\text{-}F}$ = 3.0 Hz), 134.8, 137.1, 144.6, 149.3, 162.9 ($J_{C\text{-}F}$ = 252.0 Hz), 175.8; ^{19}F NMR (470.2 MHz, $CDCl_3$) δ -109.5 (s, 1F). HRMS (ESI) calcd for $C_{24}H_{18}FN_2O$ $[M+H]^+$: 369.1398, found: 369.1404.



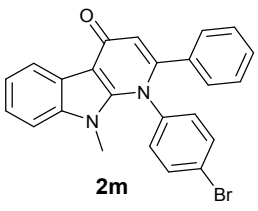
2k

1-(4-Chlorophenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2k**), yellow solid, 70.4 mg, 61%. m.p. 303-304 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.79 (s, 3H), 6.34 (s, 1H), 6.99-7.01 (m, 1H), 7.18-7.23 (m, 5H), 7.25-7.31 (m, 6H), 8.52-8.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.7, 108.5, 108.7, 116.3, 122.1, 122.4, 124.0, 128.1, 128.8, 129.7, 130.1, 131.9, 134.7, 135.9, 137.1, 137.2, 144.5, 149.1, 175.8. HRMS (ESI) calcd for $C_{24}H_{18}ClN_2O$ $[M+H]^+$: 385.1102, found: 385.1093.



2l

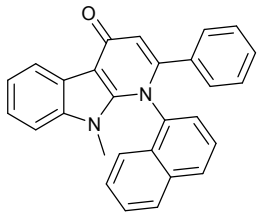
1-(3-Chlorophenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2l**), yellow solid, 61.2 mg, 53%. m.p. 310-312 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (s, 3H), 6.38 (s, 1H), 7.07-7.10 (m, 1H), 7.18-7.25 (m, 6H), 7.28-7.36 (m, 5H), 8.56-8.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.7, 108.5, 108.7, 116.3, 122.1, 122.3, 122.4, 124.0, 128.1, 128.9, 129.0, 130.1, 130.1, 130.3, 130.8, 134.6, 135.2, 137.1, 139.8, 144.4, 149.0, 175.8. HRMS (ESI) calcd for $C_{24}H_{18}ClN_2O$ $[M+H]^+$: 385.1102, found: 385.1100.



2m

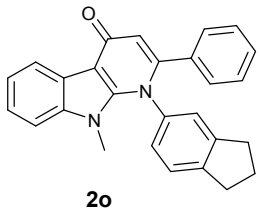
1-(4-Bromophenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one

(**2m**),white solid, 80.4 mg, 62%. m.p. 315-317 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (s, 3H), 6.35 (s, 1H), 7.01-7.04 (m, 1H), 7.15-7.24 (m, 7H), 7.26-7.30 (m, 2H), 7.46-7.49 (m, 2H), 8.53-8.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.7, 108.3, 108.7, 116.2, 121.9, 122.0, 122.3, 123.9, 123.9, 128.1, 128.8, 130.1, 132.3, 132.6, 134.7, 137.0, 137.7, 144.3, 149.1, 175.7. HRMS (ESI) calcd for $C_{24}H_{18}BrN_2O$ $[M+H]^+$: 429.0597, found: 429.0605.



2n

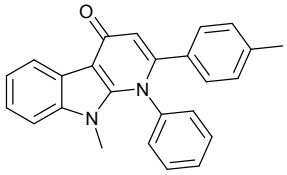
9-Methyl-1-(naphthalen-1-yl)-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2n**), white solid, 63.8 mg, 53%. m.p. 293-294 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (s, 3H), 6.52 (s, 1H), 6.96-7.12 (m, 6H), 7.31-7.43 (m, 4H), 7.46-7.56 (m, 3H), 7.86-7.90 (m, 2H), 8.66-8.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.9, 108.4, 108.6, 116.5, 122.2, 122.4, 122.6, 122.7, 124.0, 124.9, 127.5, 127.6, 128.7, 128.8, 128.8, 129.4, 130.7, 132.3, 133.8, 134.7, 134.8, 137.2, 144.9, 149.8, 176.1. HRMS (ESI) calcd for $C_{28}H_{21}N_2O$ $[M+H]^+$: 401.1648, found: 401.1637.



2o

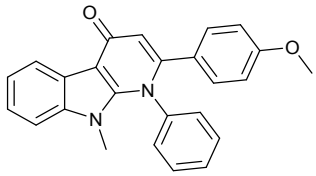
1-(2,3-Dihydro-1H-inden-5-yl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2o**), white solid, 69.3 mg, 59%. m.p. 268-270 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04-2.12 (m, 2H), 2.86-2.90 (m, 4H), 2.98 (s, 3H), 6.40 (s, 1H), 6.96-6.99 (m, 1H), 7.04 (s, 1H), 7.12-7.22 (m, 7H), 7.32-7.35 (m, 2H), 8.59-8.62 (m, 1H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 25.1, 31.7, 32.3, 32.4, 108.6, 116.1, 122.0, 122.4, 122.7, 123.9, 124.9, 126.2, 127.8, 128.2, 128.5, 130.1, 135.2, 136.4, 137.3, 145.0, 146.0, 146.3, 149.4, 175.9. HRMS (ESI) calcd for $C_{27}H_{23}N_2O$ $[M+H]^+$: 391.1805, found: 391.1799.



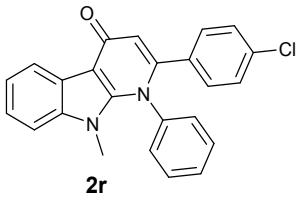
2p

9-Methyl-1-phenyl-2-(p-tolyl)-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2p**), white solid 58.0 mg, 53%. m.p. 238-240 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.96 (s, 3H), 6.41 (s, 1H), 6.96-7.02 (m, 4H), 7.16-7.20 (m, 1H), 7.24-7.27 (m, 2H), 7.32-7.38 (m, 5H), 8.59-8.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 31.7, 108.6, 108.7, 116.3, 122.1, 122.5, 122.7, 124.0, 128.6, 129.5, 129.8, 130.0, 130.6, 132.1, 137.4, 138.6, 138.8, 144.9, 149.4, 176.1. HRMS (ESI) calcd for $C_{25}H_{21}N_2O$ $[M+H]^+$: 365.1648, found: 365.1652.



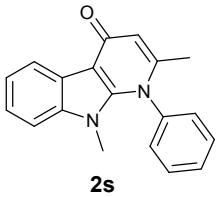
2q

2-(4-Methoxyphenyl)-9-methyl-1-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2q**), white solid, 52.5 mg, 46%. m.p. 311-313 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 2.95 (s, 3H), 3.76 (s, 3H), 6.42 (s, 1H), 6.70-6.72 (m, 2H), 7.05-7.08 (m, 2H), 7.17-7.19 (m, 1H), 7.26-7.28 (m, 2H), 7.33-7.39 (m, 5H), 8.61-8.63 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.9, 55.20, 108.5, 113.2, 116.3, 121.9, 122.2, 122.5, 123.8, 127.1, 129.3, 129.6, 130.4, 131.2, 137.1, 138.6, 144.6, 148.8, 159.4, 175.6. HRMS (ESI) calcd for $C_{25}H_{21}N_2O_2$ $[M+H]^+$: 381.1598, found: 381.1601.



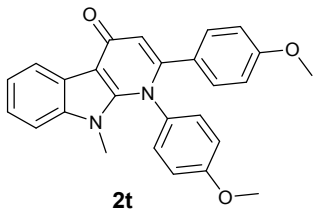
2r

2-(4-Chlorophenyl)-9-methyl-1-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2r**), white solid, 34.7 mg, 30%. m.p. 300-301 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.99 (s, 3H), 6.41 (s, 1H), 7.09-7.12 (m, 2H), 7.18-7.20 (m, 2H), 7.28-7.30 (m, 3H), 7.36-7.38 (m, 2H), 7.40-7.44 (m, 3H), 8.60-8.63 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.9, 108.5, 116.3, 122.1, 122.3, 122.4, 124.0, 128.1, 129.6, 129.9, 130.2, 131.2, 133.2, 134.7, 137.1, 138.2, 144.5, 147.6, 175.3. HRMS (ESI) calcd for $C_{24}H_{18}ClN_2O$ $[M+H]^+$: 385.1102, found: 385.1106.



2s

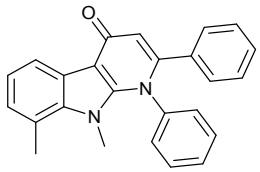
2,9-Dimethyl-1-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2s**), white solid, 19.1 mg, 22%. m.p. 256-257 °C. ^{1}H NMR (500 MHz, DMSO) δ 1.98 (s, 3H), 2.93 (s, 3H), 6.15 (s, 1H), 7.21-7.24 (m, 1H), 7.26-7.31 (m, 1H), 7.41-7.43 (m, 1H), 7.66-7.70 (m, 5H), 8.26-8.28 (m, 1H); ^{13}C NMR (125 MHz, DMSO) δ 20.8, 31.9, 107.2, 109.9, 113.8, 120.9, 121.7, 122.5, 123.5, 130.3, 130.5, 130.8, 137.1, 138.2, 144.7, 145.8, 175.0. HRMS (ESI) calcd for $C_{19}H_{17}N_2O$ $[M+H]^+$: 289.1335, found: 289.1335.



2t

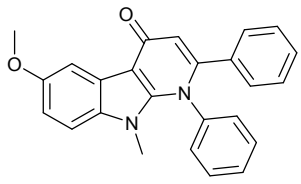
1,2-Bis(4-methoxyphenyl)-9-methyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2t**),

white solid, 60.4 mg, 49%. m.p. 313-315 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (s, 3H), 3.73 (s, 3H), 3.80 (s, 3H), 6.39 (s, 1H), 6.67-6.69 (m, 2H), 6.81-6.84 (m, 2H), 7.02-7.08 (m, 3H), 7.14-7.16 (m, 2H), 7.25-7.28 (m, 3H), 8.53-8.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.6, 55.0, 55.4, 108.3, 108.6, 113.3, 114.4, 115.8, 121.9, 122.2, 122.4, 123.9, 127.3, 130.9, 131.4, 131.6, 137.3, 145.0, 149.7, 159.7, 160.3, 175.5. HRMS (ESI) calcd for $C_{26}H_{23}N_2O_3$ $[M+H]^+$: 411.1703, found: 411.1716.



2u

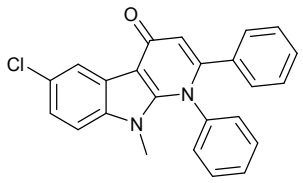
8,9-Dimethyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2u**), white solid, 56.9 mg, 52%. m.p**.** 296-297 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 3H), 3.16 (s, 3H), 6.40 (s, 1H), 7.04-7.07 (m, 1H), 7.09-7.12 (m, 2H), 7.16-7.22 (m, 6H), 7.31-7.33 (m, 3H), 8.45-8.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 35.1, 109.4, 116.7, 120.4, 120.6, 122.3, 123.9, 127.8, 127.9, 128.6, 129.2, 129.5, 129.8, 130.0, 135.2, 137.3, 139.4, 147.0, 149.4, 175.9. HRMS (ESI) calcd for $C_{25}H_{21}N_2O$ $[M+H]^+$: 365.1648, found: 365.1639.



2v

6-Methoxy-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2v**), white solid, 53.7 mg, 47%. m.p.314-316 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (s, 3H), 3.94 (s, 3H), 6.37 (s, 1H), 6.91-6.94 (m, 1H), 7.01-7.04 (m, 1H), 7.14-7.21 (m, 5H), 7.25-7.28 (m, 2H), 7.33-7.35 (m, 3H), 8.11-8.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.7,

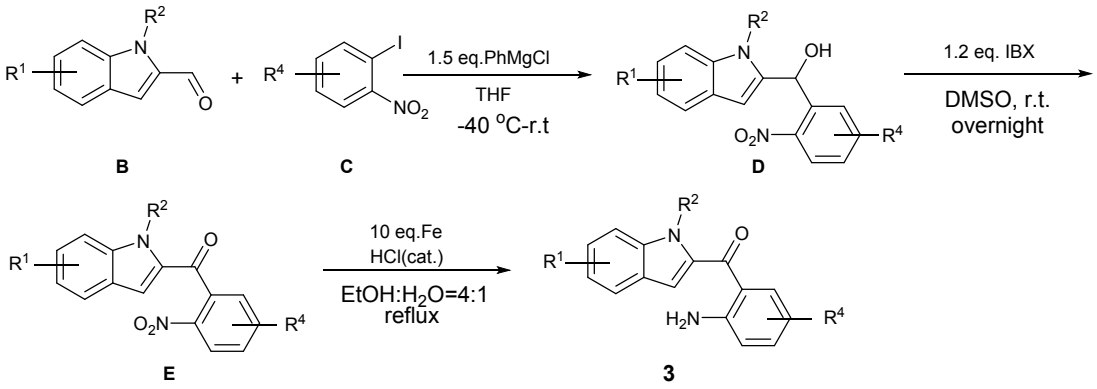
55.9, 104.1, 108.6, 109.5, 113.6, 115.8, 123.1, 127.9, 128.6, 129.4, 129.8, 130.1, 130.6, 131.9, 135.0, 138.5, 144.8, 149.1, 155.9, 175.9. HRMS (ESI) calcd for $C_{25}H_{21}N_2O_2$ $[M+H]^+$: 381.1598, found: 381.1610.



2w

6-chloro-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**2w**), white solid, 56.5 mg, 49%. m.p. 310-313 oC. 1H NMR (400 MHz, CDCl3) δ 2.90 (s, 3H), 6.35 (s, 1H), 6.94-6.97 (m, 1H), 7.16-7.19 (m, 6H), 7.36-7.39 (m, 5H), 8.48-8.50 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 31.8, 107.8, 109.6, 116.1, 121.4, 123.5, 123.9, 127.4, 127.9, 128.7, 129.5, 130.0, 130.1, 130.7, 134.8, 135.5, 138.3, 145.0, 149.6, 175.6. HRMS (ESI) calcd for $C_{24}H_{18}ClN_2O$ [M+H]+: 385.1102, found: 385.1097.

4. Methods for the synthesis of substrates 3a



Scheme S2: Synthetic route for the synthesis of **3**

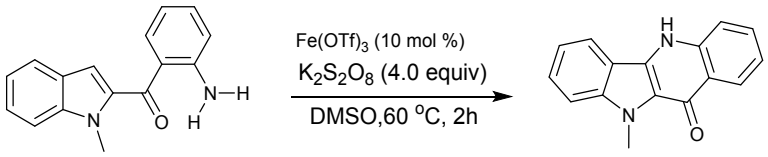
Substrate **3** were prepared according to the reported literature modified.[2] A typical procedure for the synthesis of **3a** as follows: To a solution of 1-iodo-2-nitrobenzene **C** (R^4= H) (218 mg, 1.5 mmol) in dry THF (3 mL) was added PhMgCl (0.80 mL, 2 M in THF, 1.6 mmol) at -40 °C, and the mixture was stirred at -40 °C for 15 min. To the dark mixture was then added a solution **B** (R^1= H, R^2= Me) (125 mg, 0.50 mmol) in THF (3 mL) at -40 °C, and the resulting mixture was stirred at room temperature for 30 min and then quenched with a saturated aqueous solution of NaCl.[2] The mixture was extracted with EtOAc, and the organic layer was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. Purification of the crude residue by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) gave **D**.

Then corresponding compound **D** (270 mg, 0.5 mmol) was dissolved in DMSO (5 mL) and IBX (420 mg, 1.50 mmol) was added under air and stirred overnight. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with EtOAc (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude residue by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) gave **E**.

Finally, to a solution of compound **E** (134 mg, 0.5 mmol) in mixed solvent (EtOH/H_2O=4:1) in a

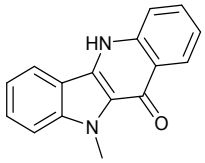
Schlenk tube was added Fe (280 mg, 5 mmol) , HCl (20 μL) , and the mixture was stirred under 100 °C for 1h. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with EtOAc (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude residue by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) gave **3a** (92.2 mg, 78 %) as a yellow solid.

5. Methods for the synthesis of product 4a



3a **4a**

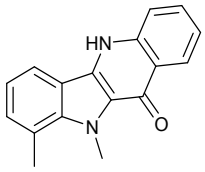
A typical procedure for the synthesis of **4a** as follows: The substrate **3a** (0.2 mmol, 50.1 mg), $Fe(OTf)_3$ (0.02 mmol, 10.1 mg), $K_2S_2O_8$ (0.8 mmol, 216.3 mg) and DMSO (2.0 mL) were placed in an schlenk tube under N_2. Then the reaction mixture was allowed to react at 60 °C for 2 h. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) afforded desired compound **4a**.



4a

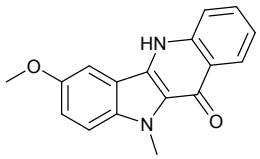
10-Methyl-5,10-dihydro-11H-indolo[3,2-b]quinolin-11-one (**4a**), yellow solid, 38.8 mg, 78% . m.p. 225-227 °C. ^{1}H NMR (400 MHz, DMSO) δ 4.27 (s, 3H), 7.21-7.29 (m, 2H), 7.50-7.59 (m, 2H), 7.66-7.72 (m, 2H), 8.22 (d, *J* = 6.8 Hz, 1H), 8.34 (d, *J* =7.2 Hz,

1H), 12.46 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 31.1, 110.7, 115.4, 118.0, 119.4, 121.0, 121.3, 122.1, 124.0, 125.6, 128.1, 129.7, 131.2, 139.2, 140.1, 169.1. HRMS (ESI) calcd for $C_{16}H_{12}N_2NaO$ $[M+Na]^+$: 271.0842, found: 271.0838.



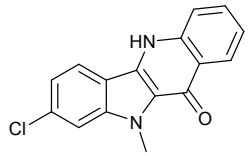
4b

9,10-Dimethyl-5,10-dihydro-11H-indolo[3,2-b]quinolin-11-one (**4b**), white solid, 40.4 mg, 77%. m.p. 256-257 °C. ^{1}H NMR (400 MHz, DMSO) δ 2.80 (s, 3H), 4.58 (s, 3H), 7.07-7.12 (m, 1H), 7.21-7.28 (m, 2H), 7.63-7.70 (m, 2H), 8.05 (d, J = 7.6 Hz), 8.33 (d, J = 8.0 Hz), 12.31 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 19.7, 33.7, 116.5, 117.8, 119.0, 119.7, 120.9, 122.2, 122.8, 124.1, 125.7, 130.0, 130.6, 131.2, 139.1, 139.5, 169.1. HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO$ $[M+Na]^+$: 285.0998, found: 285.0992.



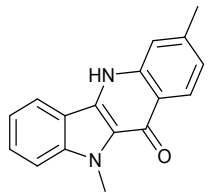
4c

7-Methoxy-10-methyl-5,10-dihydro-11H-indolo[3,2-b]quinolin-11-one (**4c**), white solid, 47.3 mg, 85%. m.p. 265-268 °C. ^{1}H NMR (400 MHz, DMSO) δ 3.85 (s, 3H), 4.24 (s, 3H), 7.17-7.26 (m, 2H), 7.52 (d, J = 9.2 Hz, 1H), 7.61-7.66 (m, 1H), 7.83 (d, J = 8.4 Hz, 1H), 8.03 (s, 1H), 8.31 (d, J = 8.4 Hz, 1H), 13.08 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 31.2, 55.6, 103.0, 111.7, 115.4, 118.0, 118.8, 120.6, 122.6, 123.7, 125.5, 129.6, 131.0, 135.8, 139.3, 153.5, 169.1. HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_2$ $[M+Na]^+$: 301.0947, found: 301.0944.



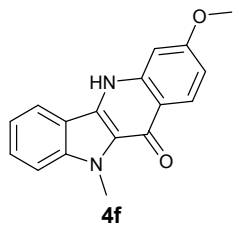
4d

8-Chloro-10-methyl-5,10-dihydro-11H-indolo[3,2-b]quinolin-11-one (**4d**), yellow solid, 37.9 mg, 67 %. m.p. 170-172 ^{o}C. ^{1}H NMR (400 MHz, DMSO) δ 4.25 (s, 3H), 7.25-7.29 (m, 1H), 7.50-7.53 (m, 1H), 7.61-7.67 (m, 3H), 8.24-8.32 (m, 2H), 12.37 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 31.3, 112.6, 116.2, 118.0, 120.5, 121.1, 122,8, 123.6, 124.0, 125.7, 127.9, 128.7, 131.6, 138.3, 139.2, 169.3. HRMS (ESI) calcd for $C_{16}H_{12}ClN_2O$ $[M+H]^+$: 283.0633, found: 283.0634.



4e

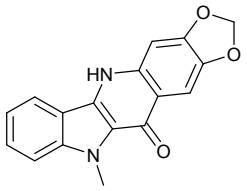
3,10-Dimethyl-5,10-dihydro-11H-indolo[3,2-b]quinolin-11-one (**4e**), brown solid, 38.3 mg, 73%. m.p. 177-179 ^{o}C. ^{1}H NMR (400 MHz, DMSO) δ 2.47 (s, 3H), 4.26 (s, 3H), 7.08 (d, J = 8.0 Hz, 1H), 7.21-7.25 (m, 1H), 7.45 (s, 1H), 7.50-7.60 (m, 2H), 8.21 (d, J = 8.4 Hz, 2H), 12.32 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 21.4, 31.1, 110.7, 115.5, 117.2, 119.4, 121.3, 122.0, 122.1, 122.9, 125.6, 128.0, 129.48, 139.5, 140.0, 141.4, 169.1. HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO$ $[M+Na]^+$: 285.0998, found: 285.0995.



4f

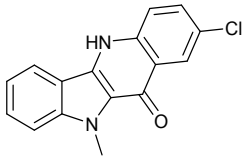
3-Methoxy-10-methyl-5,10-dihydro-11H-indolo[3,2-b]quinolin-11-one (**4f**), white

solid, 34.0 mg, 61%. m.p. 181-183 °C. ^{1}H NMR (500 MHz, DMSO) δ 3.89 (s, 3H), 4.23 (s, 3H), 6.85-6.88 (m, 1H), 7.01-7.03 (m, 1H), 7.20-7.23 (m, 1H), 7.47-7.51 (m, 1H), 7.53-7.55 (m, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 12.29 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 31.1, 55.5, 98.3, 110.7, 111.7, 115.4, 118.6, 119.4, 121.0, 121.8, 127.4, 127.8, 129.3, 139.8, 141.1, 162.0, 169.0. HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_2$ $[M+Na]^+$: 301.0947, found: 301.0946.



4g

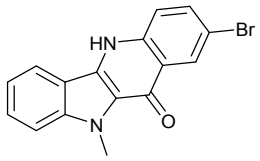
10-Methyl-5,10-dihydro-11H-[1,3]dioxolo[4,5-g]indolo[3,2-b]quinolin-11-one (**4g**), yellow solid, 28.7 mg, 49%. m.p. 213-214 °C. ^{1}H NMR (400 MHz, DMSO) δ 4.25 (s, 3H), 6.15 (s, 2H), 7.11 (s, 1H), 7.21-7.25 m, 1H), 7.50-7.55 (m, 1H), 7.58-7.61 (m, 2H), 8.15 (d, *J* = 8.0 Hz, 1H), 12.41 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 31.0, 96.2, 101.6, 102.1, 110.7, 115.4, 119.1, 119.4, 120.9, 121.8, 127.7, 128.9, 136.3, 139.9, 144.2, 151.4, 168.0. HRMS (ESI) calcd for $C_{17}H_{13}N_2O_3$ $[M+H]^+$: 293.0921, found: 293.0925.



4h

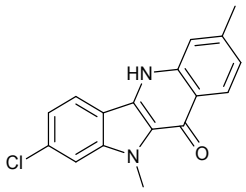
2-Chloro-10-methyl-5,10-dihydro-11H-indolo[3,2-b]quinolin-11-one (**4h**), yellow solid, 24.4 mg, 43%. m.p. 200-201 °C. ^{1}H NMR (400 MHz, DMSO) δ 4.25 (s, 3H), 7.24-7.29 (m, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.56-7.63 (m, 2H), 7.84 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 12.51 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 31.1, 110.9, 115.2, 119.7, 120.0, 121.1, 122.2, 122.89, 124.0, 124.6, 128.0, 128.4, 129.6, 139.9, 140.2,

168.6. HRMS (ESI) calcd for $C_{16}H_{12}ClN_2O$ $[M+H]^+$: 283.0633, found: 283.0634.



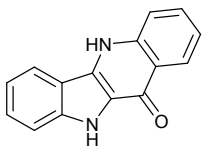
4i

2-Bromo-10-methyl-5,10-dihydro-11H-indolo[3,2-b]quinolin-11-one (**4i**), white solid, 34.1 mg, 52%. m.p. 225-227 °C. ^{1}H NMR (400 MHz, DMSO) δ 4.26 (s, 3H), 7.24-7.29 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.54-7.65 (m, 2H), 7.85 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 12.55 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 31.1, 110.9, 115.2, 119.8, 120.0, 121.2, 122.2, 122.9, 124.0, 124.6, 128.0, 128.4, 129.6, 140.0, 140.2, 168.7. HRMS (ESI) calcd for $C_{16}H_{11}BrN_2NaO$ $[M+Na]^+$: 348.9947, found: 348.9959.



4j

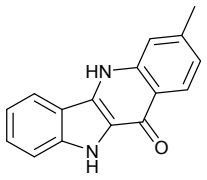
8-Chloro-3,10-dimethyl-5,10-dihydro-11H-indolo[3,2-b]quinolin-11-one (**4j**), brown solid, 38.0 mg, 64%. m.p. 205-207 °C. ^{1}H NMR (400 MHz, DMSO) δ 2.46 (s, 3H), 4.25 (s, 3H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.63-7.65 (m, 2H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.64 (s, 1H), 13.38 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 21.3, 31.3, 112.4, 116.5, 117.3, 121.6, 122.0, 122.6, 122.9, 123.4, 125.5, 127.7, 128.8, 138.3, 139.7, 141.3, 169.2. HRMS (ESI) calcd for $C_{17}H_{13}ClN_2NaO$ $[M+Na]^+$: 319.0609, found: 319.0615.



4k

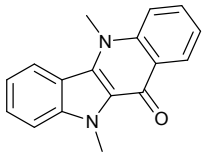
5,10-Dihydro-11H-indolo[3,2-b]quinolin-11-one (**4k**), yellow solid, 35.7 mg, 76%.

m.p. >330 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.20 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.44-7.53 (m, 2H), 7.66-7.75 (m, 2H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 11.71 (s, 1H), 12.49 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 21.4, 111.2, 112.9, 116.3, 117.3, 119.2, 121.1, 122.8, 123.4, 125.6, 127.6, 129.1, 138.9, 139.8, 141.2, 168.0. HRMS (ESI) calcd for $C_{15}H_{11}N_2O$ $[M+H]^+$: 235.0866, found: 235.0861.



4l

3-Methyl-5,10-dihydro-11H-indolo[3,2-b]quinolin-11-one (**4l**), white solid, 30.3 mg, 61%. m.p. 315-317 °C. ^{1}H NMR (400 MHz, DMSO) δ 2.54 (s, 3H), 7.15-7.26 (m, 2H), 7.45-7.55 (m, 3H), 8.21-8.30 (m, 2H), 11.70 (s, 1H), 12.36 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ 21.9, 113.0, 116.4, 117.4, 119.3, 121.2, 121.4, 122.8, 123.5, 125.6, 127.7, 129.1, 138.9, 139.8, 141.1, 167.8. HRMS (ESI) calcd for C16H12N2NaO [M+Na]+: 271.0842, found: 271.0845.

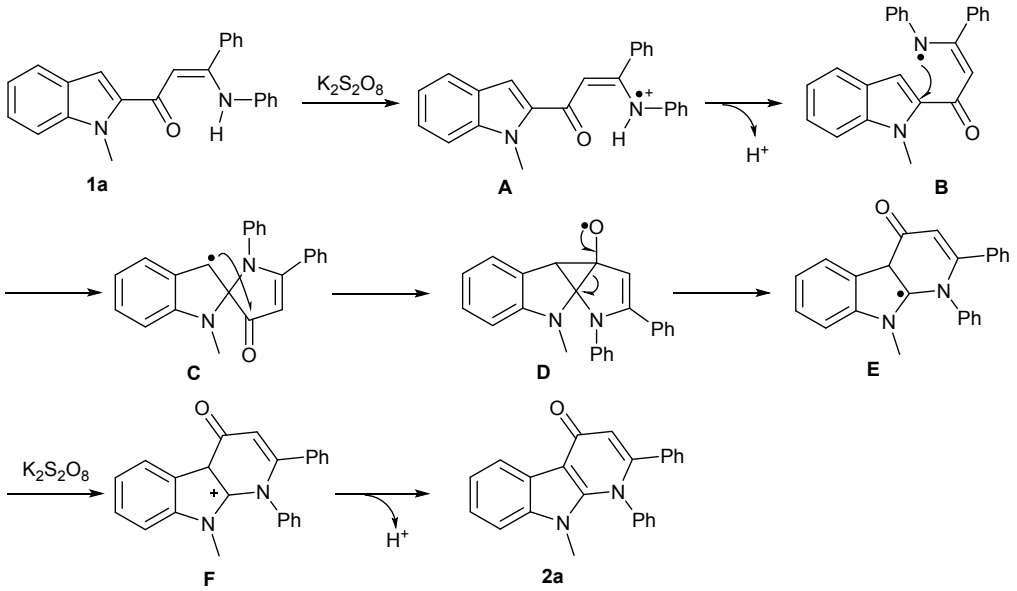


4m

5,10-Dimethyl-5,10-dihydro-11H-indolo[3,2-b]quinolin-11-one (**4m**),[3] yellow solid, 14.2 mg, 27%. m.p. 190-191 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24-4.26 (m, 6H), 7.19-7.24 (m, 1H), 7.29-7.33 (m, 1H), 7.51-7.60 (m, 2H), 7.70-7.75 (m, 1H), 7.85-7.88 (m, 1H), 8.33-8.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.1, 35.7, 110.3, 114.3, 115.8, 119.4, 121.0, 122.8, 123.0, 125.1, 126.8, 127.4, 131.4, 131.5, 140.4, 169.9. HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO$ $[M+Na]^+$: 285.0998, found: 285.0994.

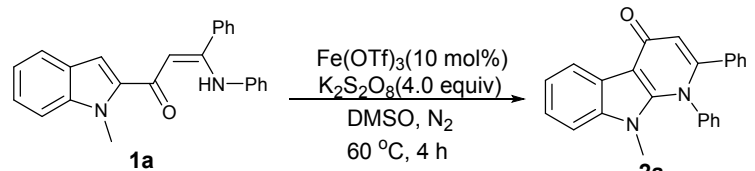
Substrate **3m** were prepared according to the reported literature modified.[4] A typical procedure for the synthesis of **3m** as follows: To a solution of **3a** (250 mg, 1.0 mmol) in DMF (3 mL) was added NaH (36 mg, 1.5 mmol) at 0 ^{o}C slowly. The mixture was stirred for 30 minutes, and CH_3I (1.3 mmol, 81 μL) was added dropwise to the above solution via syringe. The reaction was stirred for 3.0 h at room temperature. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (petroleum ether/ethyl acetate = 10 : 1) to afford the compound **3m** (127.6 mg, 51%)as a yellow liquid.

6. Tentative mechanism using $K_2S_2O_8$ only



Scheme **S3**. Tentative mechanism to **2a** using $K_2S_2O_8$ only

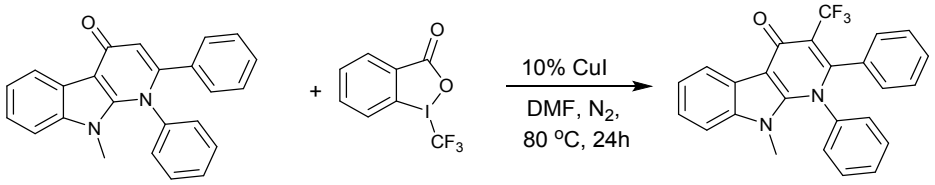
7. Gram Scale



Scales: 3 mmol

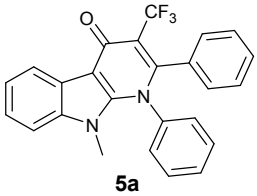
In a schlenk tube indolyl Amine ketene **1a** (3.0 mmol, 1.057 g), $Fe(OTf)_3$ (0.3 mmol, 0.151 g), $K_2S_2O_8$ (12 mmol, 3.244 g) and DMSO (30.0 mL) were stirred at 60 °C. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (dichloromethane/ethyl acetate = 1:1) afforded desired compound **2a** (yellow solid, 0.610 g, 58%)

8. Formation of 3 -Substituted Indole Quinolone



2a **5a,** 53%

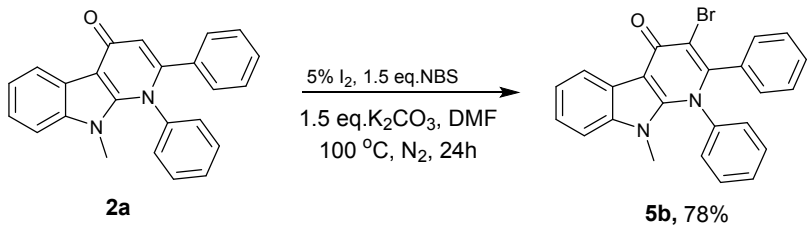
Substrate **5a** were prepared according to the reported literature modified.[5] A typical procedure for the synthesis of **5a** as follows: To a mixture of **2a** (0.20 mmol, 85.9 mg) , Togni reagent (0.30 mmol, 94.8 mg) ,CuI (0.02 mmol, 3.8 mg), N,N-dimethylformamide (DMF, 2.0 mL) was added under nitrogen at 80 °C for 30 h. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) afforded desired compound **5a** (yellow solid, 44.4 mg, 53%)



5a

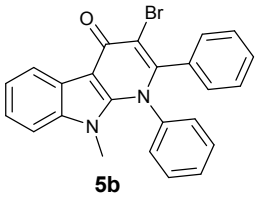
9-methyl-1,2-diphenyl-3-(trifluoromethyl)-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**5a**), yellow solid, 44.4 mg, 53%. m.p. 303-304 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (s, 3H), 7.05-7.09 (m, 2H), 7.14-7.19 (m, 6H), 7.30-7.36 (m, 5H), 8.60-8.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.6, 108.7, 108.9, 122.3, 122.44, 124.5, 127.5, 127.6, 128.8, 129.3, 129.4, 129.8 (q, J = 2.0 Hz), 130.5, 132.5 (q, J = 181 Hz), 137.2, 137.6, 143.4, 149.6, 171.7. ^{19}F NMR (470.2 MHz, $CDCl_3$) δ -54.8 (s, 3F). HRMS (ESI) calcd for $C_{25}H_{18}F_3N_2O$

$[M+H]^+$: 419.1366, found: 419.1374.



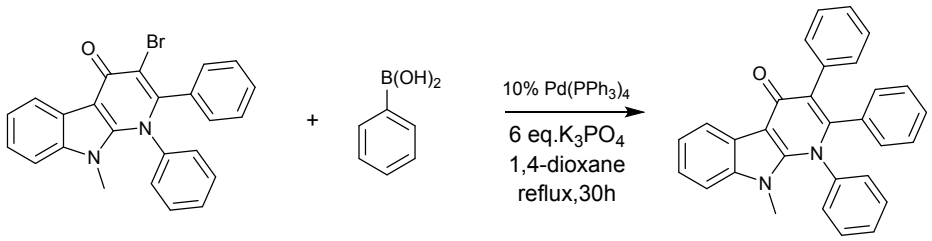
2a **5b,** 78%

Substrate **5b** were prepared according to the reported literature modified.[6] A typical procedure for the synthesis of **5b** as follows: To a mixture of **2a** (0.2 mmol, 70.1mg),iodine (0.01 mmol, 2.5 mg), N-bromosuccinimide (NBS, 0.30 mmol, 53.4 mg) and K_2CO_3 (0.3 mmol 41.5 mg), N,N-dimethylformamide (DMF, 2.0 mL) was added under nitrogen at 100 ^oC for 24 h. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by Ammonium chloride in aqueous solution, and the water layers were extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) afforded desired compound **5b** (yellow solid, 67.0 mg, 78%)



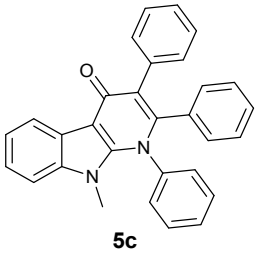
5b

3-bromo-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**5b**), yellow solid, 67.0 mg, 78%. m.p. 323-325 ^oC. ^1H NMR (400 MHz, DMSO) δ 2.87 (s, 3H), 7.22-7.26 (m, 4H), 7.30-7.38 (m, 5H), 7.45-7.48 (m, 1H), 7.53-7.56 (m, 2H), 8.36-8.39 (m, 1H); ^{13}C NMR (100 MHz, DMSO) δ 31.6, 106.0, 110.1, 112.4, 121.1, 122.1, 122.2, 124.4, 128.3, 129.0, 129.4, 130.3, 130.5, 131.3, 135.6, 137.7, 138.7, 143.8, 147.6, 169.0. HRMS (ESI) calcd for $C_{24}H_{18}BrN_2O$ $[M+H]^+$: 429.0597, found: 429.0602.



5b **5c,** 73%

Substrate **5c** were prepared according to the reported literature modified.[7] A typical procedure for the synthesis of **5c** as follows: To a mixture of **5b** (0.20 mmol, 85.9 mg) , boronic acid (0.6 mmol, 73.2 mg) ,$Pd(PPh_3)_4$ (0.02 mmol, 23.1 mg), K_3PO_4 (1.2 mmol, 254.7 mg), 1,4-dioxane (2 mL) was added under nitrogen and reflux for 30 h. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by Ammonium chloride in aqueous solution, and the water layers were extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) afforded desired compound **5c** (white solid, 62.3 mg, 73%)



5c

9-methyl-1,2,3-triphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (**5c**), white solid, 62.3 mg, 73%. m.p. 313-315 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 3.02 (s, 3H), 5.32 (s, 1H), 6.95-6.99 (m, 4H), 7.05-7.09 (m, 1H), 7.12-7.16 (m, 4H), 7.24-7.29 (m, 4H), 7.33-7.34 (m, 2H), 7.36-7.39 (m, 2H), 8.64-8.67 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.8, 108.4, 122.1, 122.3, 123.1, 123.8, 126.2, 127.2, 127.4, 127.7, 129.2, 129.4, 130.5, 131.2, 131.4, 134.0, 135.4, 137.3, 138.9, 144.1, 146.5, 174.3. HRMS (ESI) calcd for $C_{30}H_{23}N_2O$

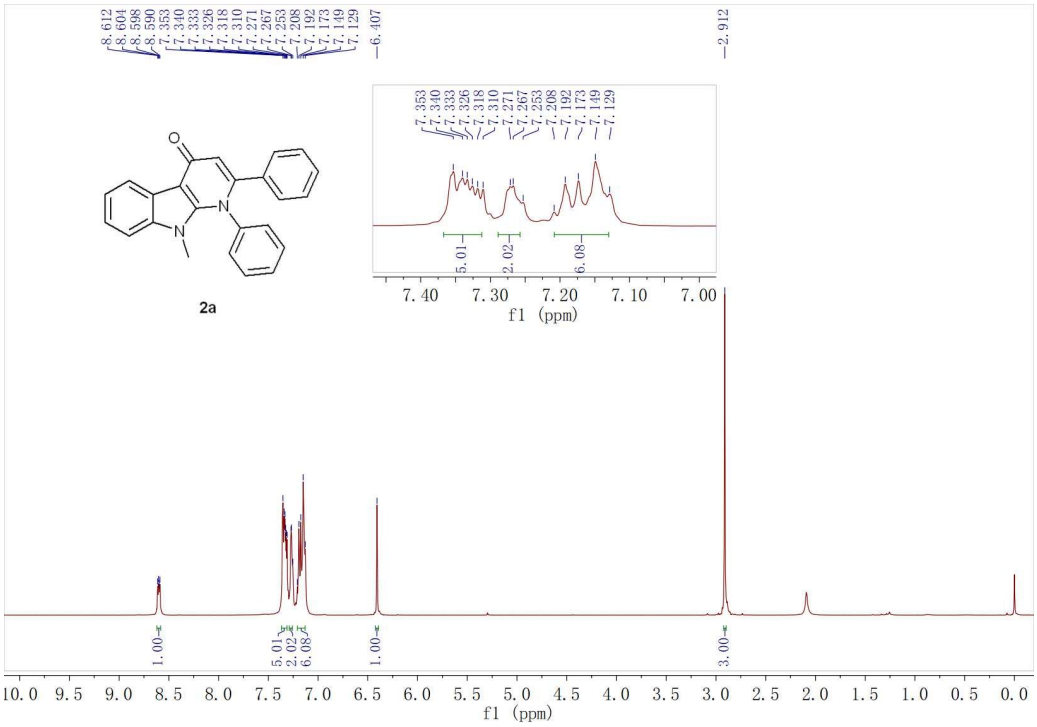
$[M+H]^+$: 427.1805, found: 427.1817.

Note and references:

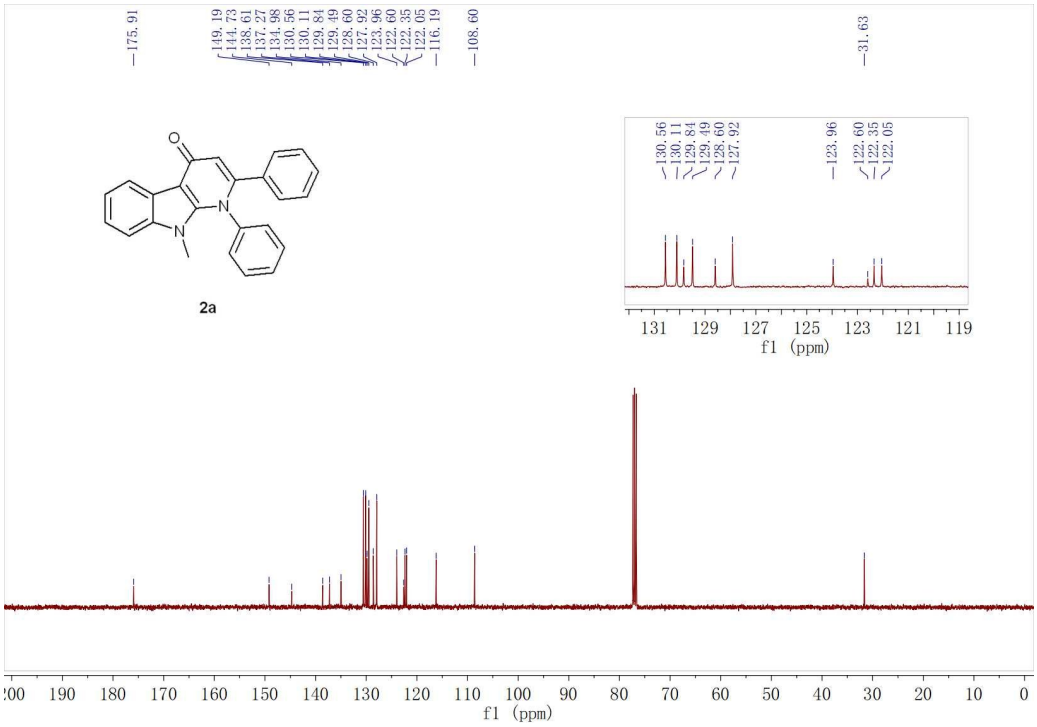
(1) J. Yang, C. Wang, X. Xie, H. Li, and Y. Li, *Eur. J. Org. Chem.* 2010, 4189.
(2) S. Suetsugu, C. Tsukano, and Y. Takemoto. *Eur. J. Org. Chem.* 2016, 108
(3) D. S. Jang, E. J. Park, Y-H. Kang, B-N. Su, M. E. Hawthorne, J. S. Vigo, J. G. Graham, F. Cabieses, H. H. S. Fong, R.G. Mehta, J. M. Pezzuto, and A. D. Kinghorn, *Arch Pharm Res.* 2003, **26**, 585.
(4) J. Huang, C. Wan, M.-F. Xu, and Q. Zhu, *Eur. J. Org. Chem*. 2013, 1876
(5) Z. Fang, Y. Ning, P. Mi, P. Liao, and X. Bi, *Org. Lett.* 2014, **16**, 1522.
(6) Z. He, W. Liu, and Z. Li, *Chem. Asian J.* 2011, **6**, 1340
(7) T. Zhao, and B. Xu, *Org. Lett.* 2010, **12**, 212.

9. Copies of Spectra of New Products

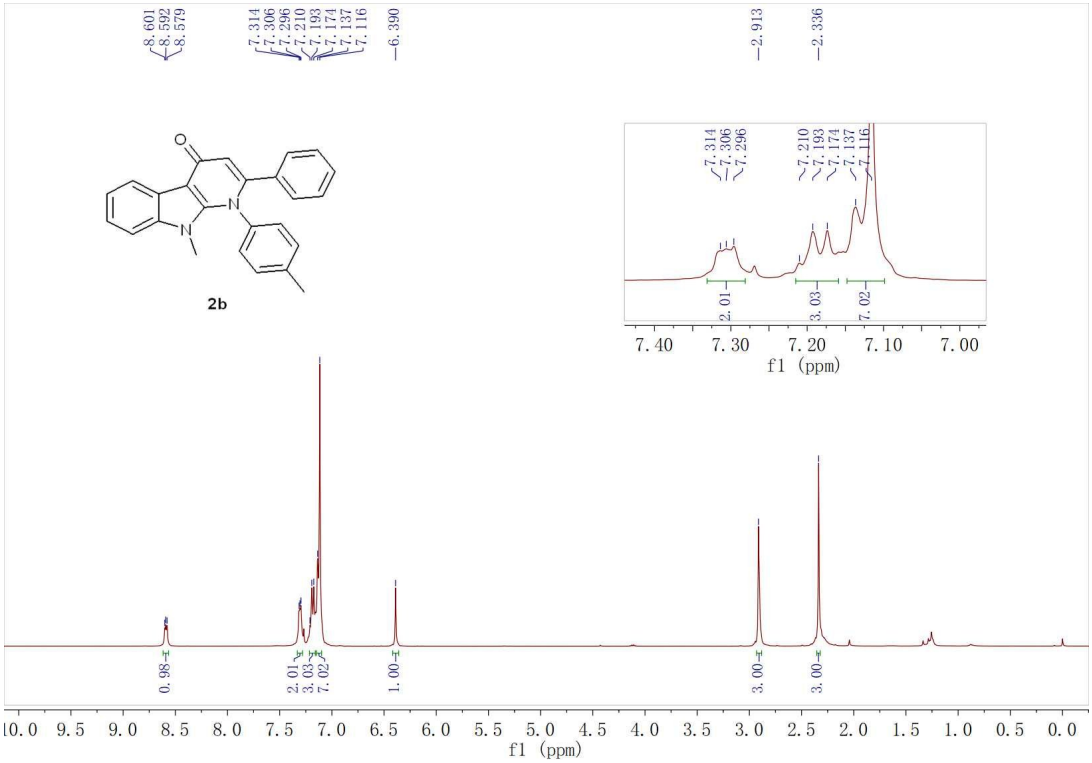
^{1}H NMR (400 MHz, $CDCl_3$)



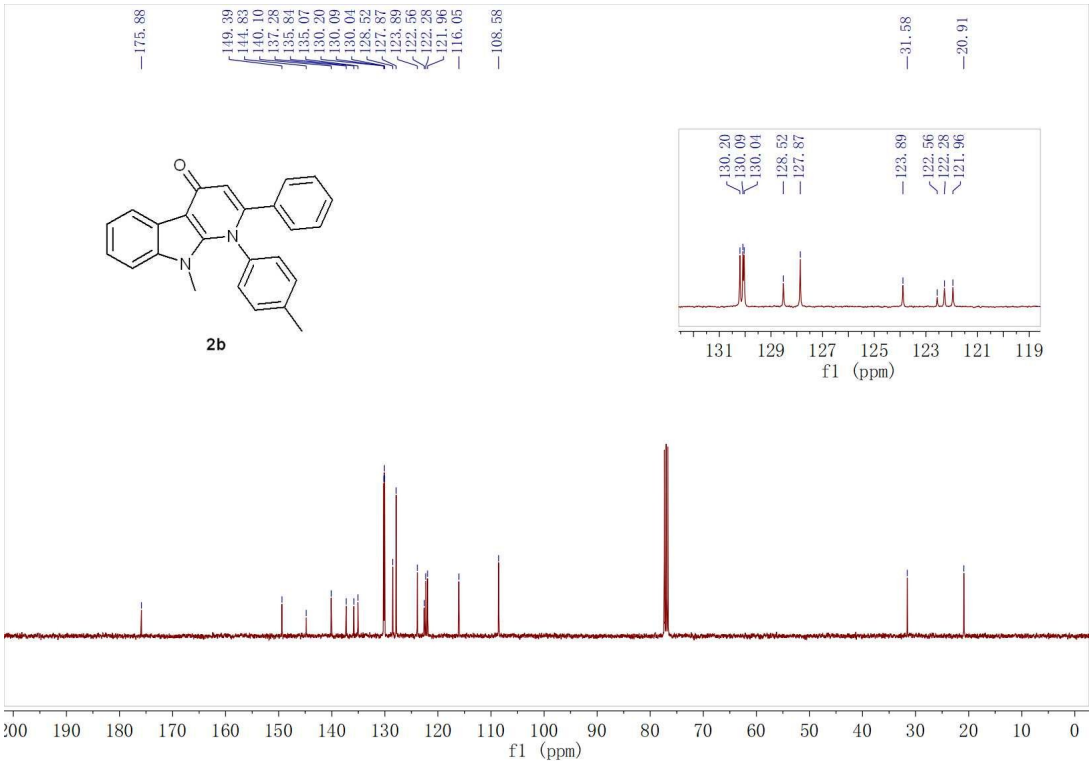
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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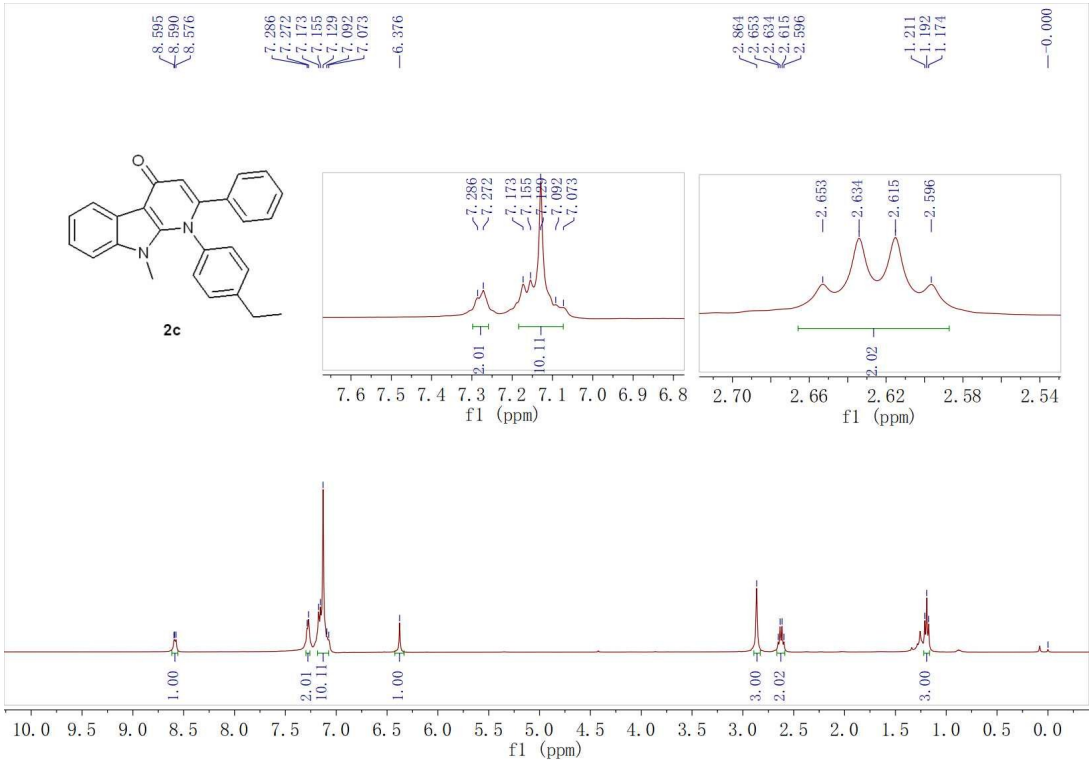

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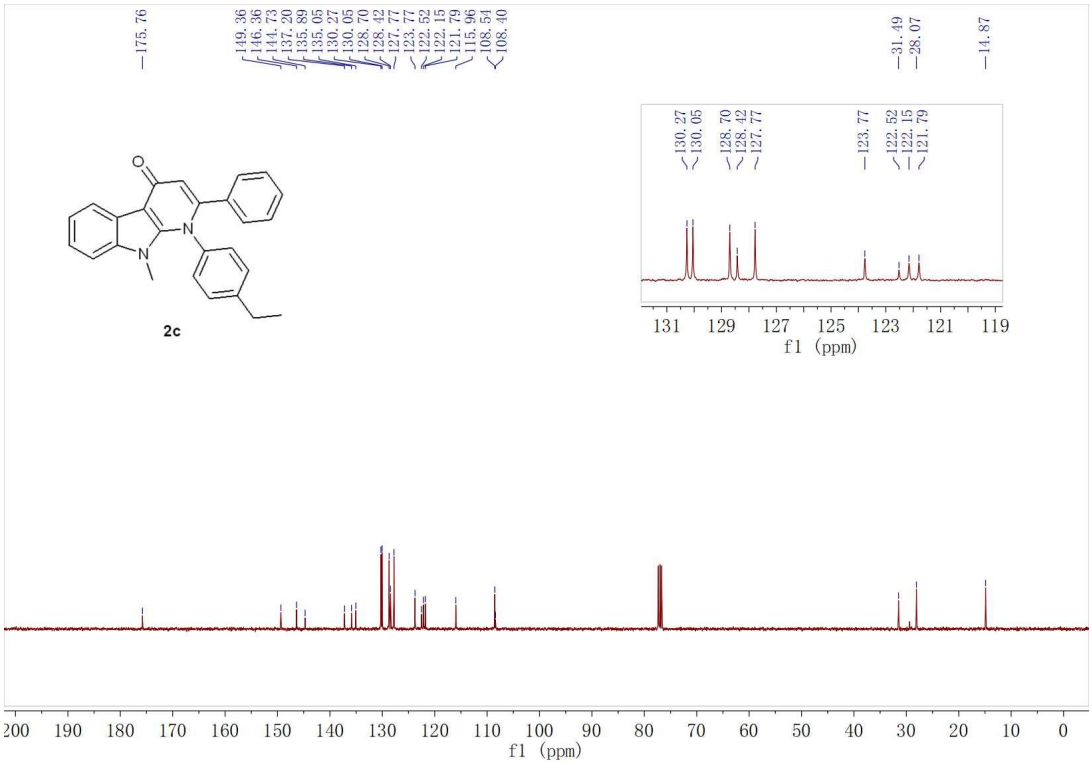

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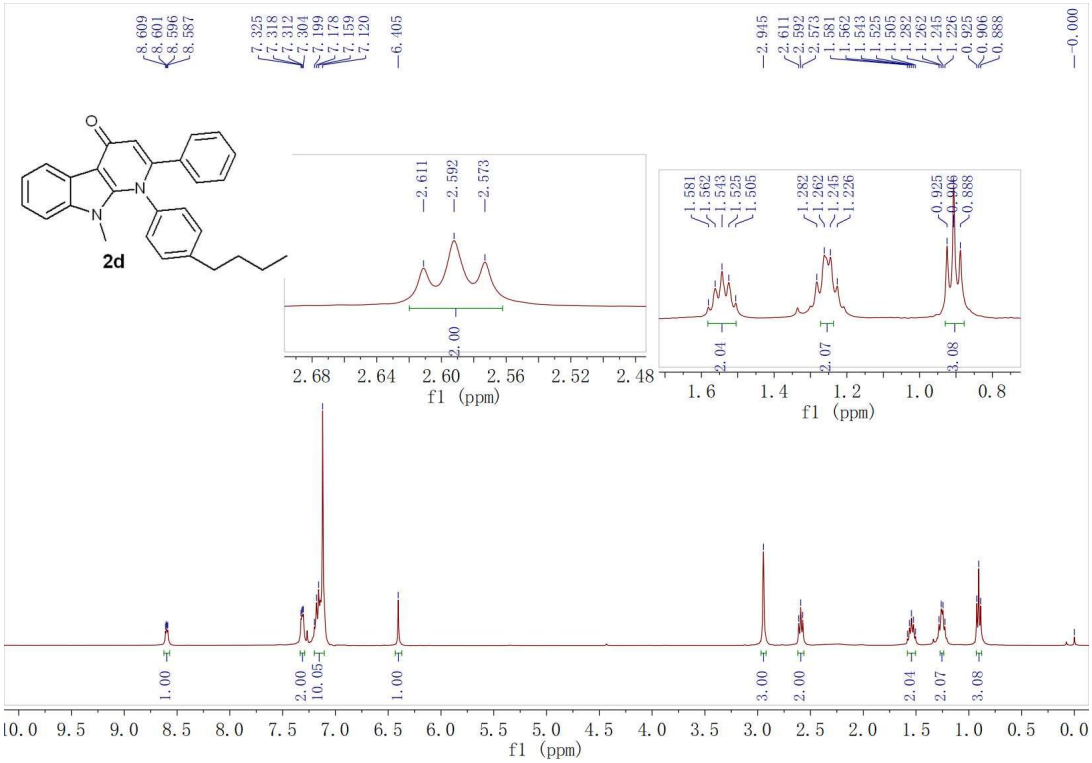
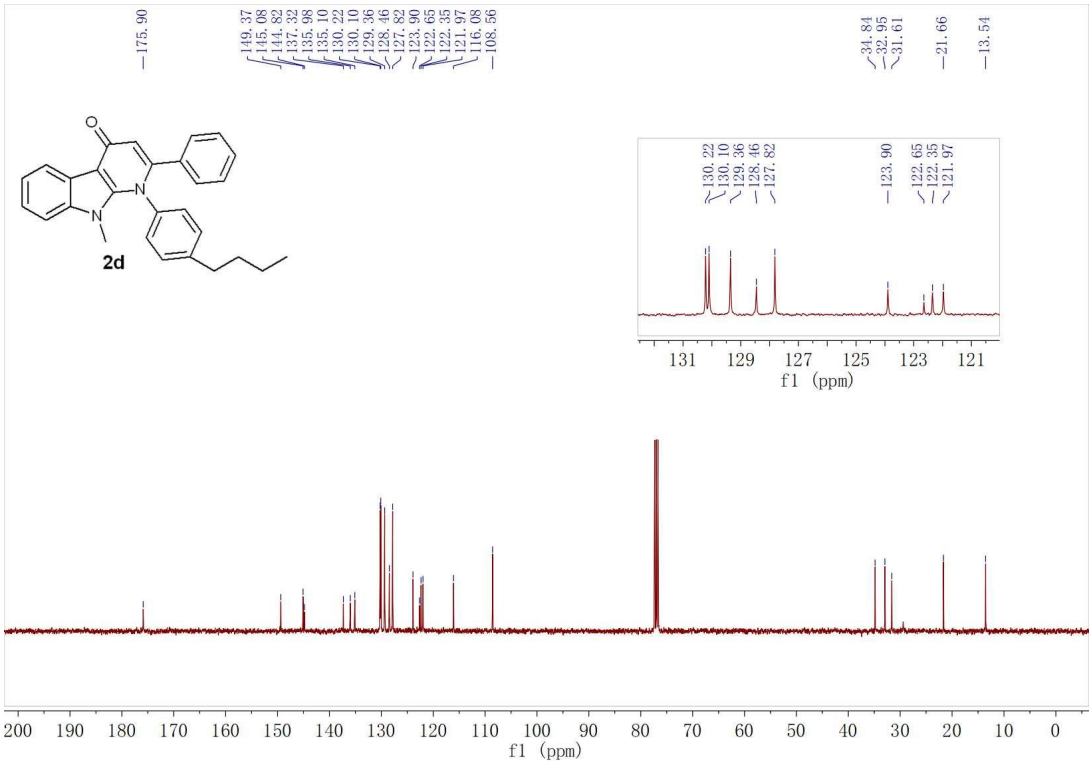
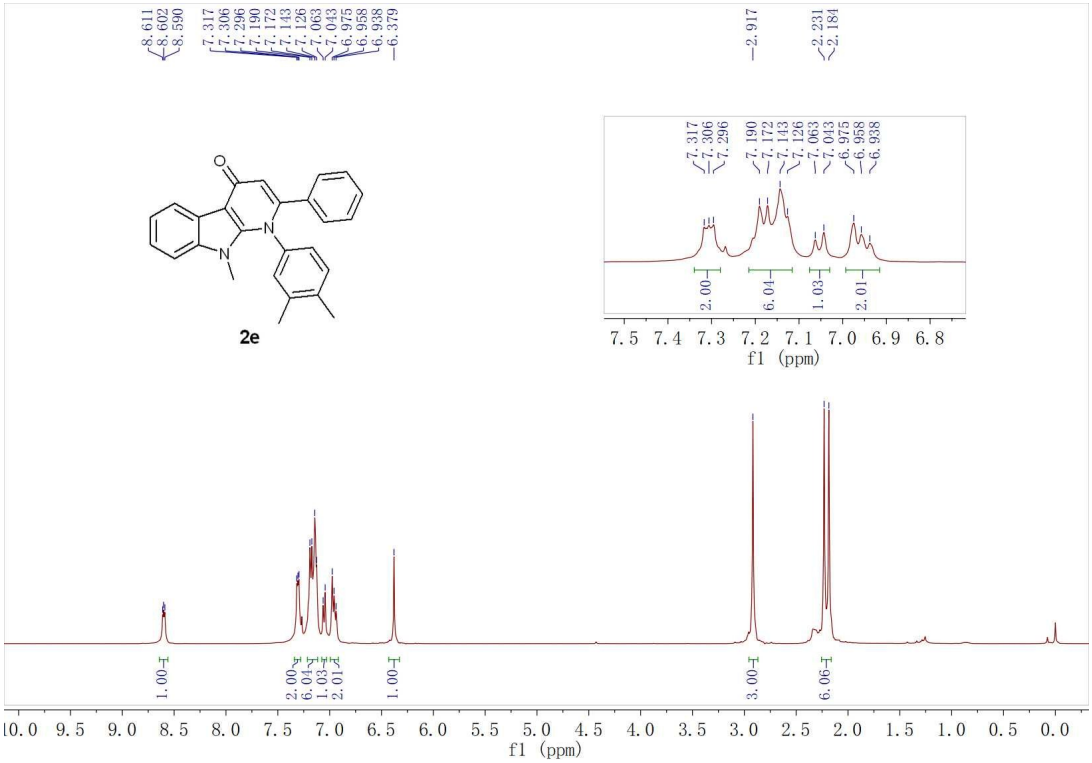


^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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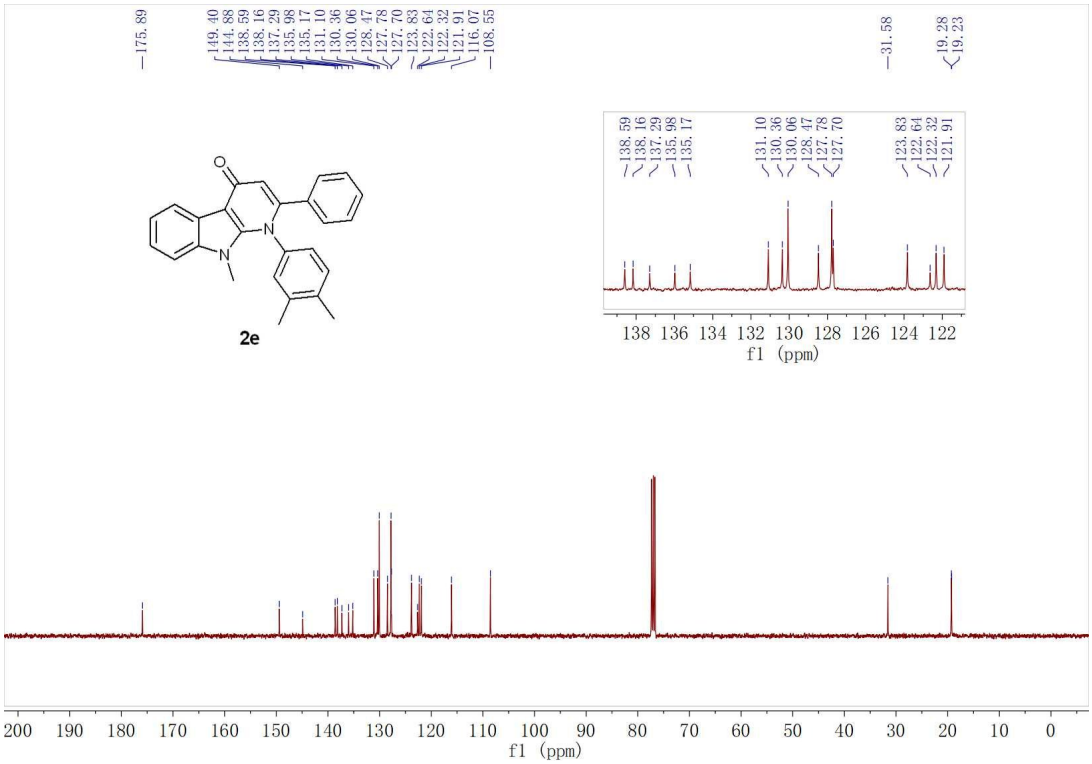

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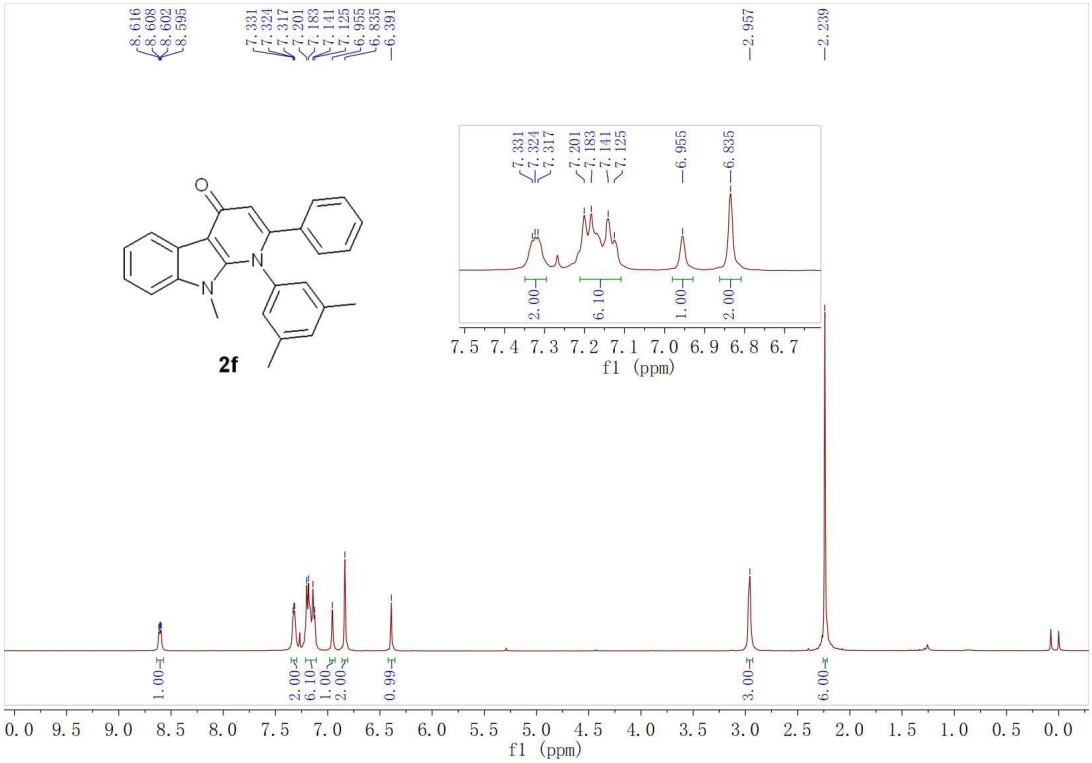
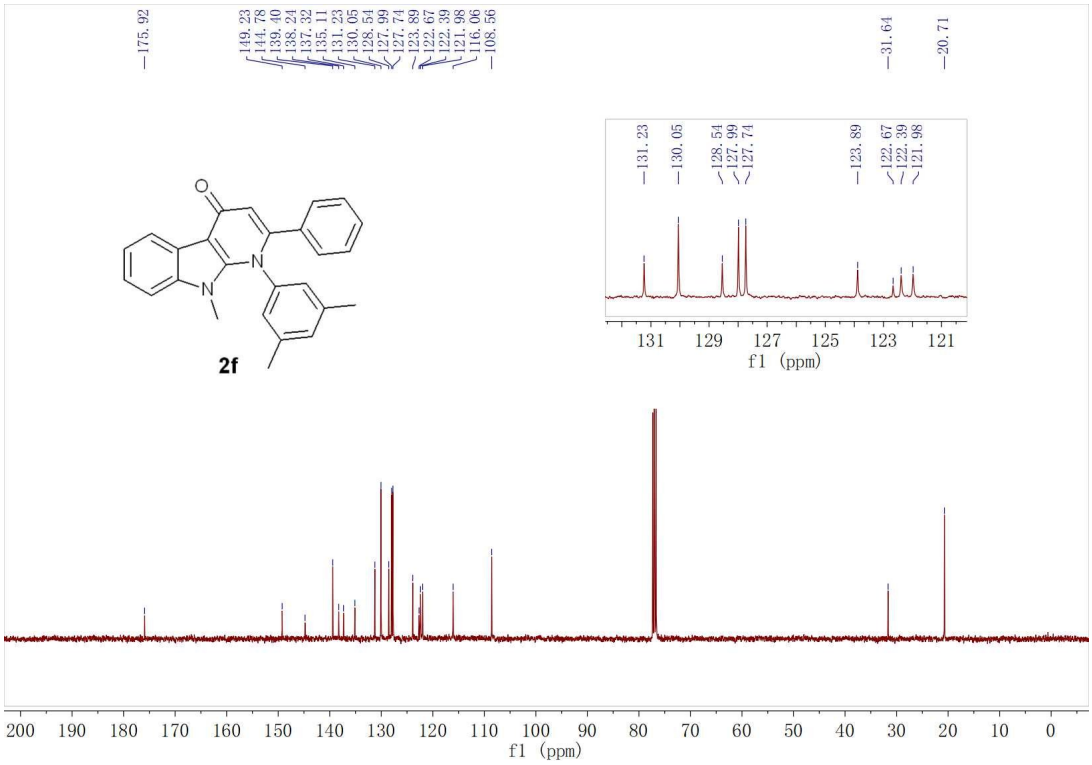


^{13}C NMR (100 MHz, $CDCl_3$)



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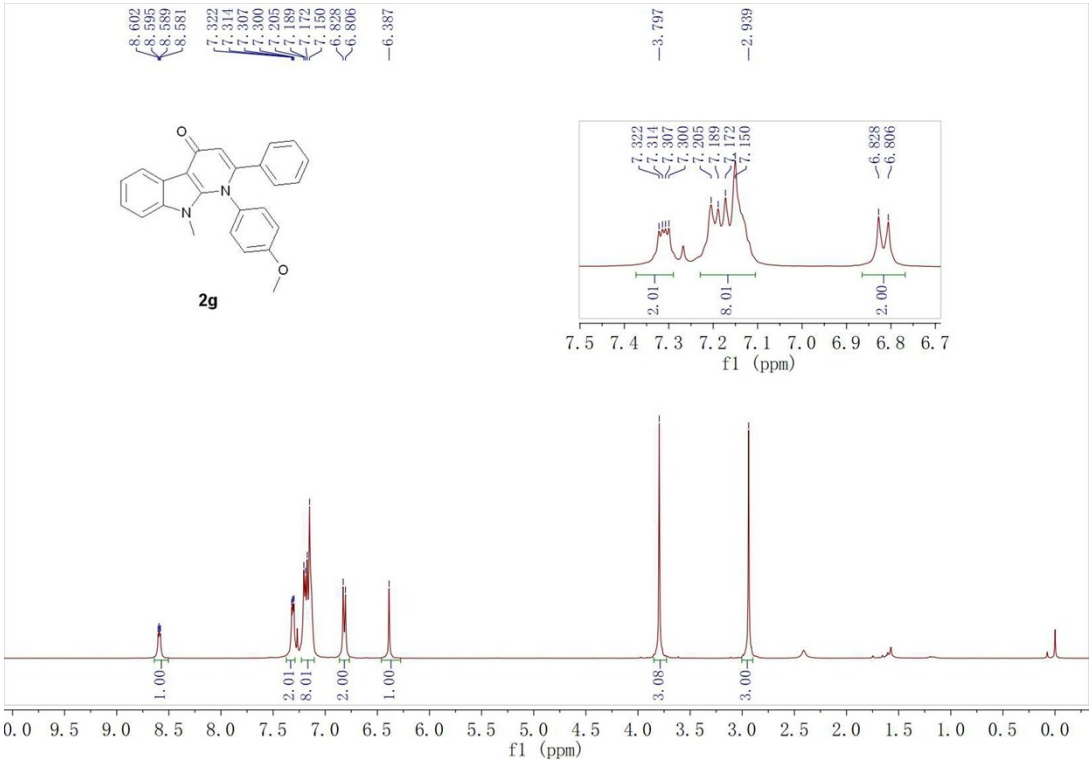
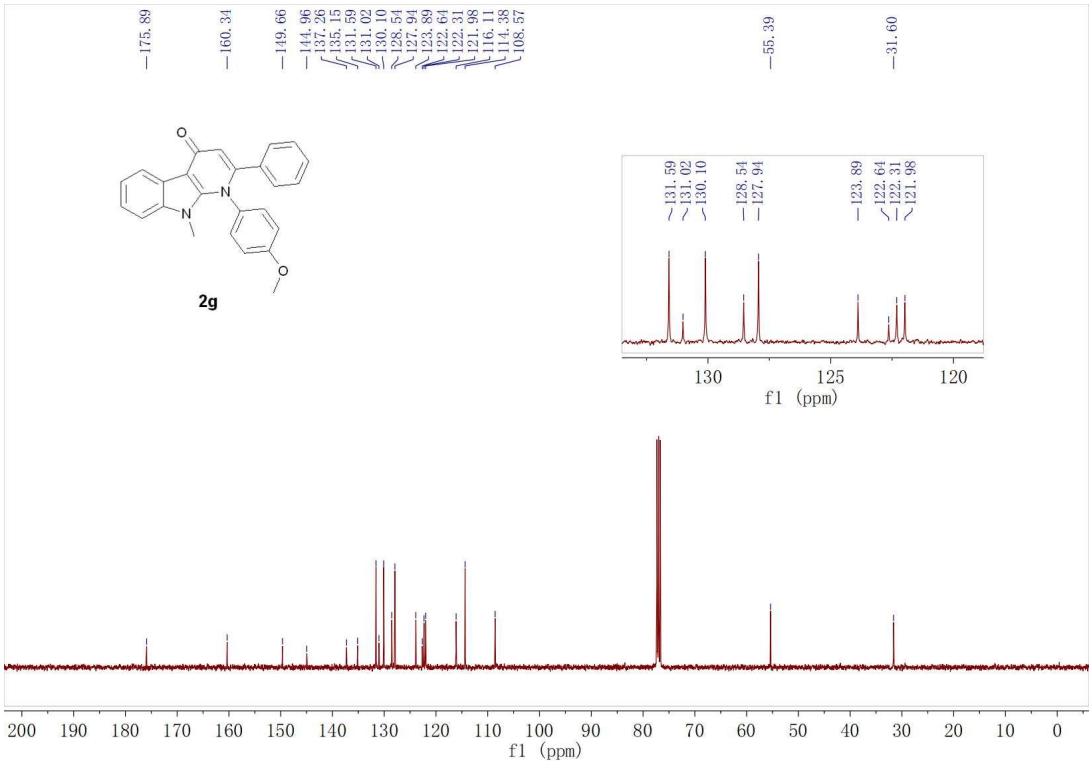
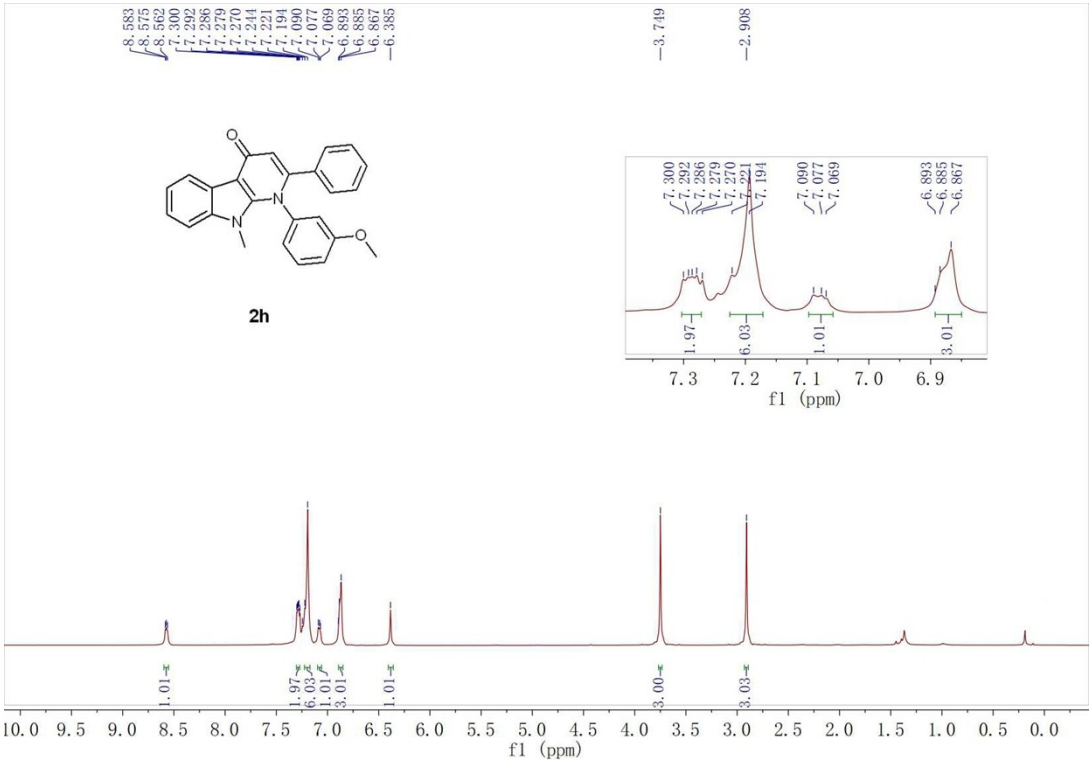


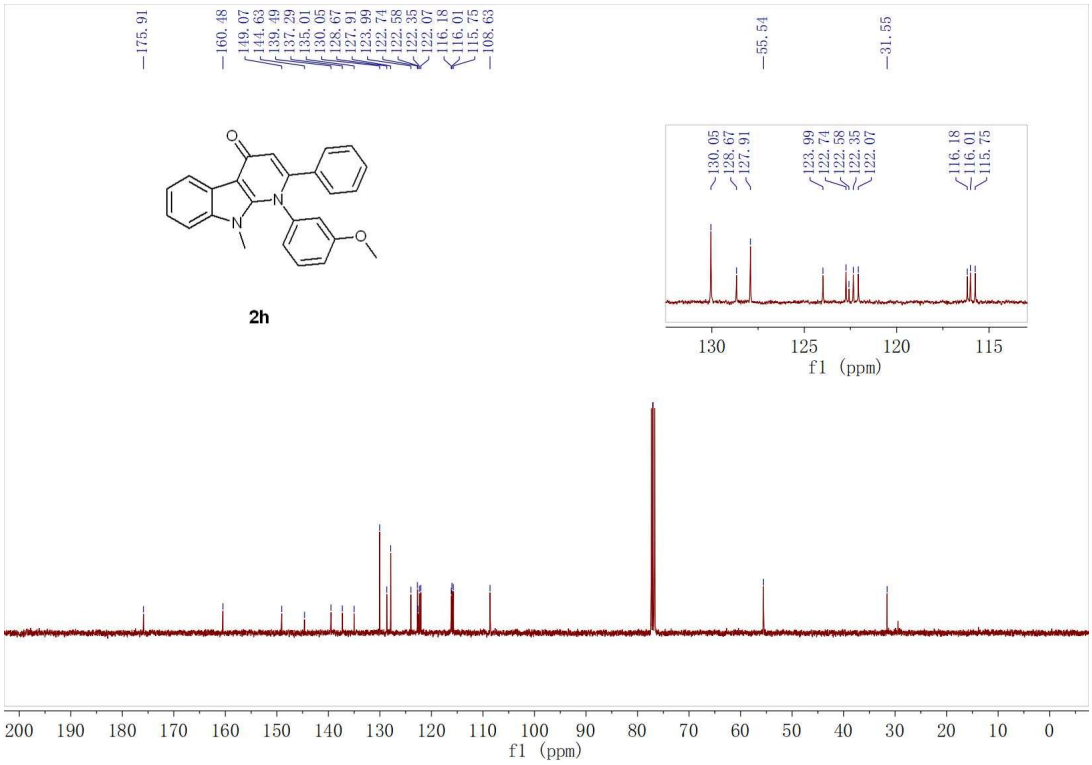
^{13}C NMR (100 MHz, $CDCl_3$)



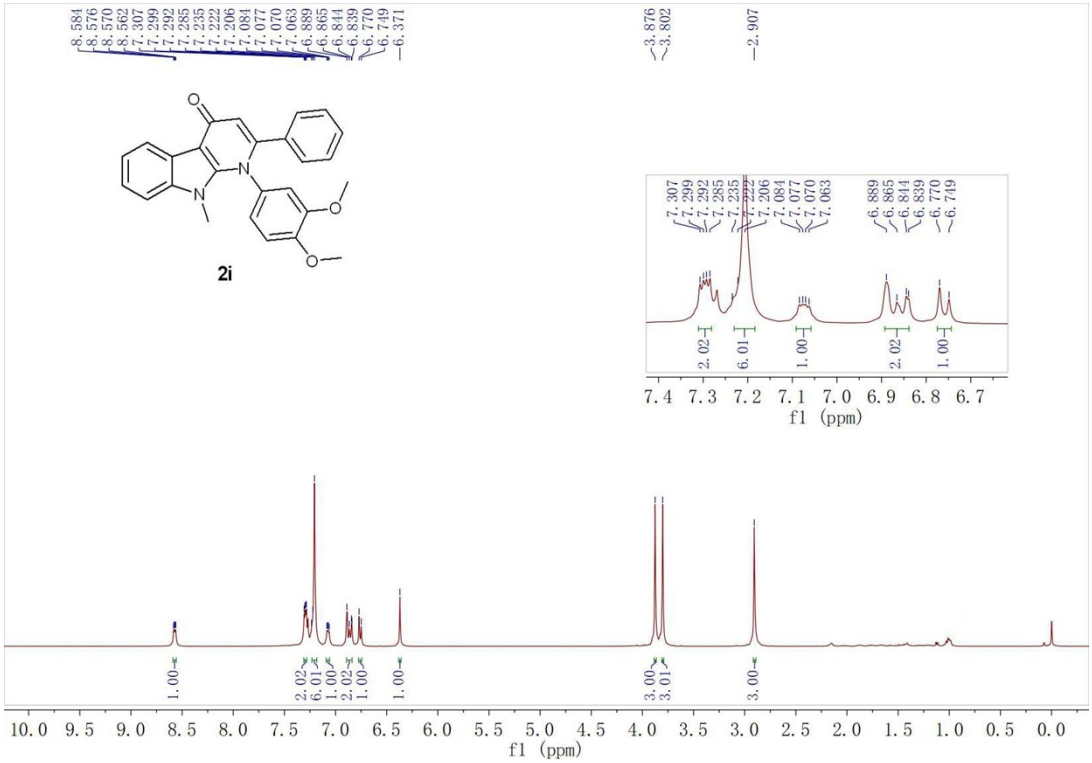
^{1}H NMR (400 MHz, $CDCl_3$)



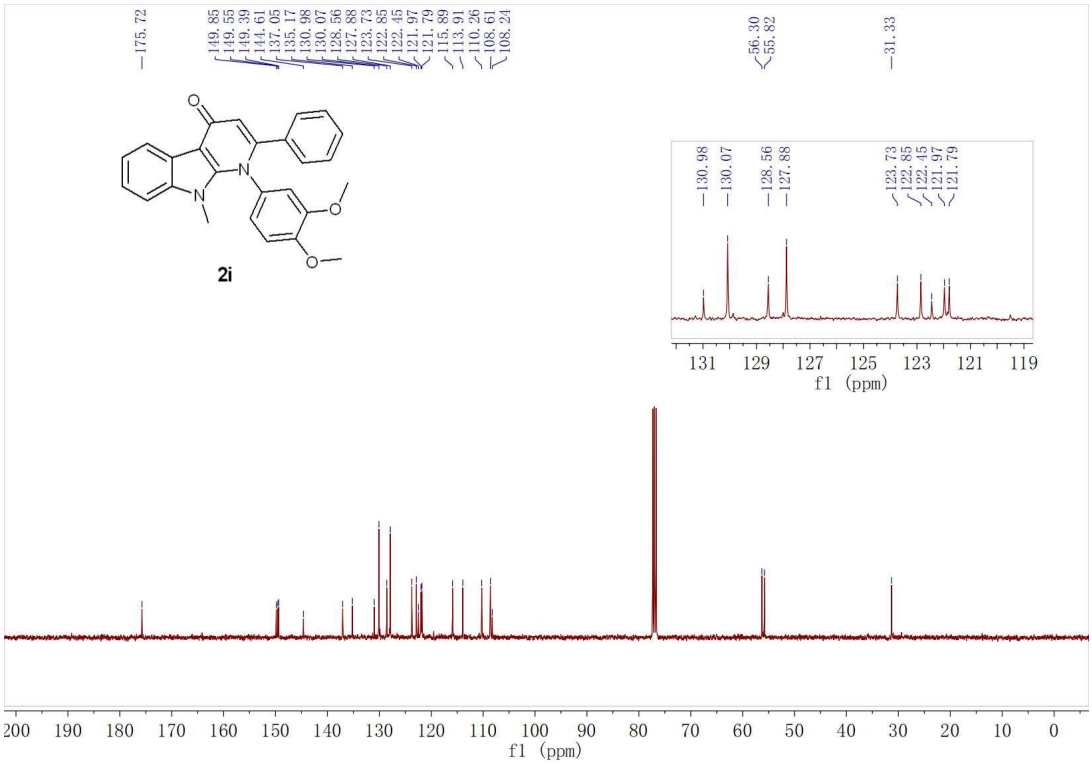
^{13}C NMR (100 MHz, $CDCl_3$)



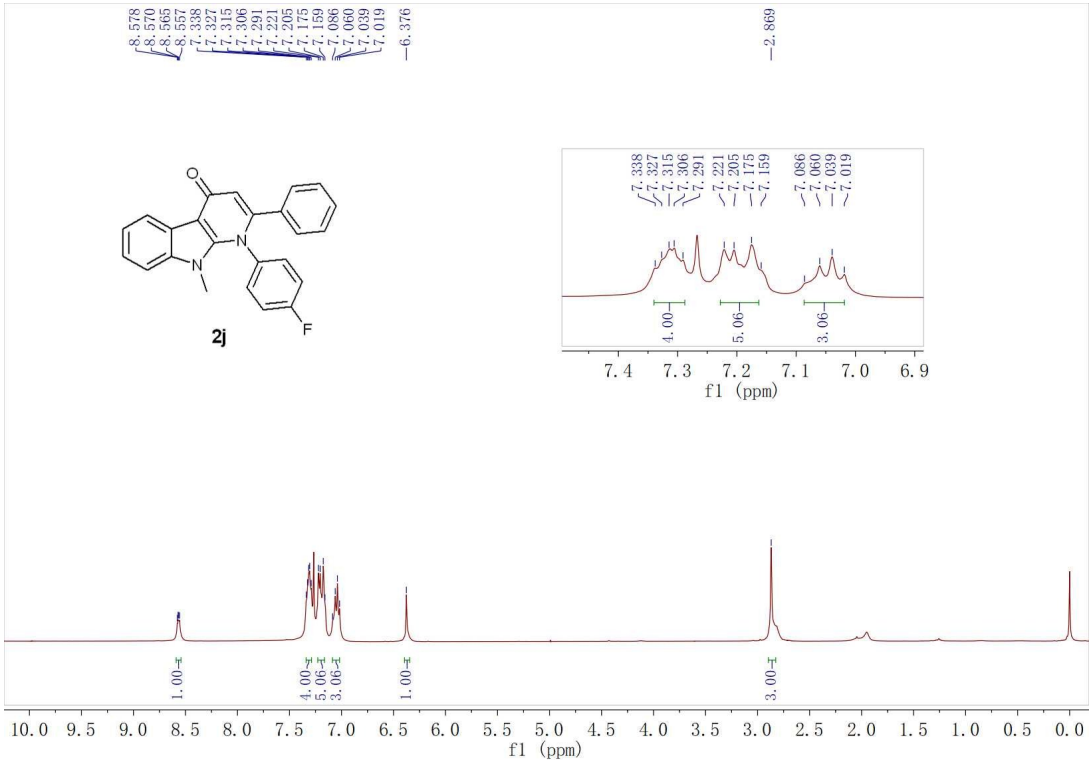
^{1}H NMR (400 MHz, $CDCl_3$)



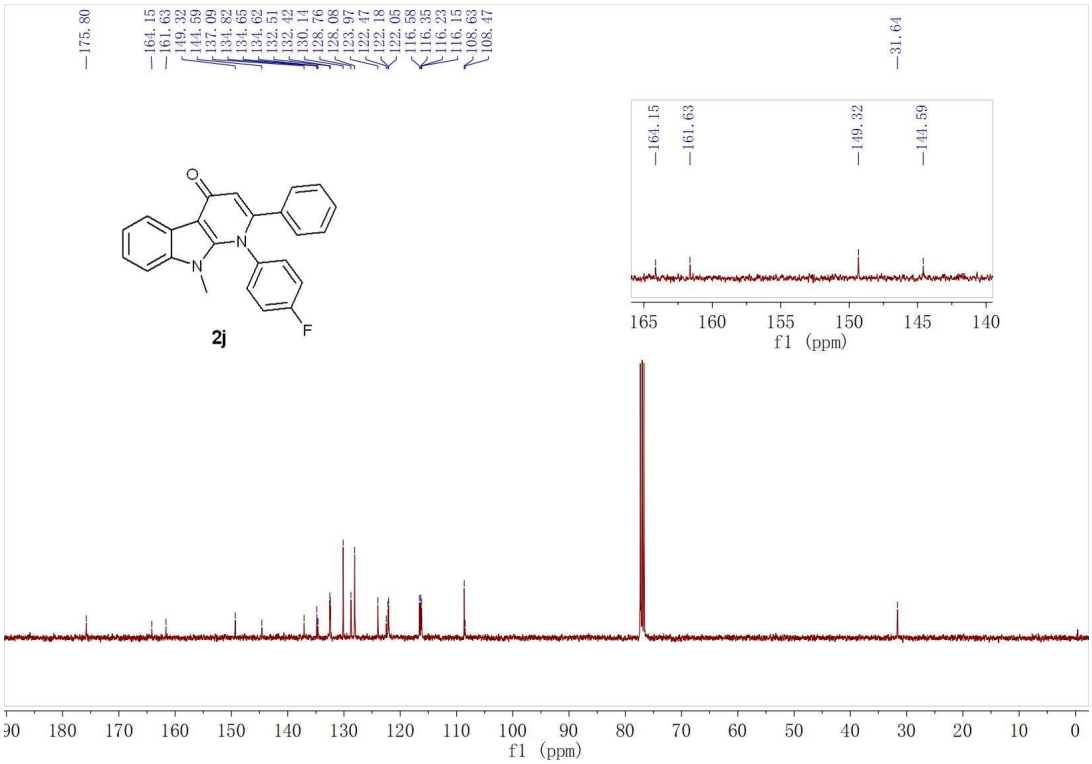
^{13}C NMR (100 MHz, $CDCl_3$)



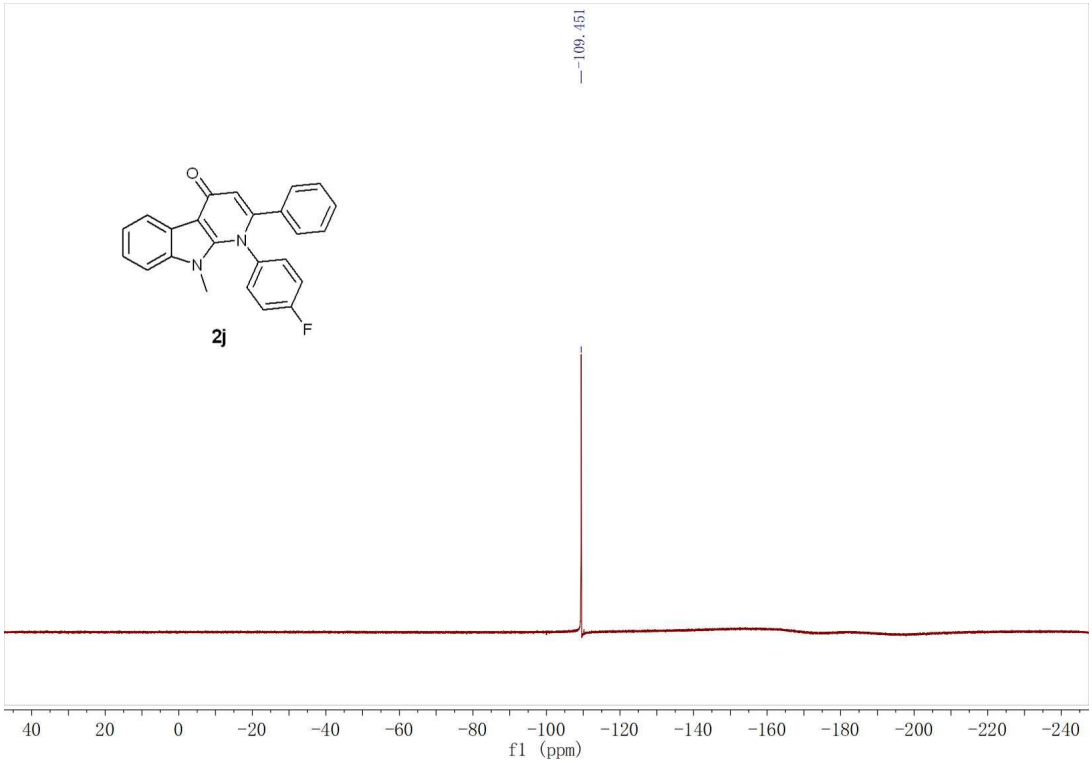
^{1}H NMR (400 MHz, $CDCl_3$)



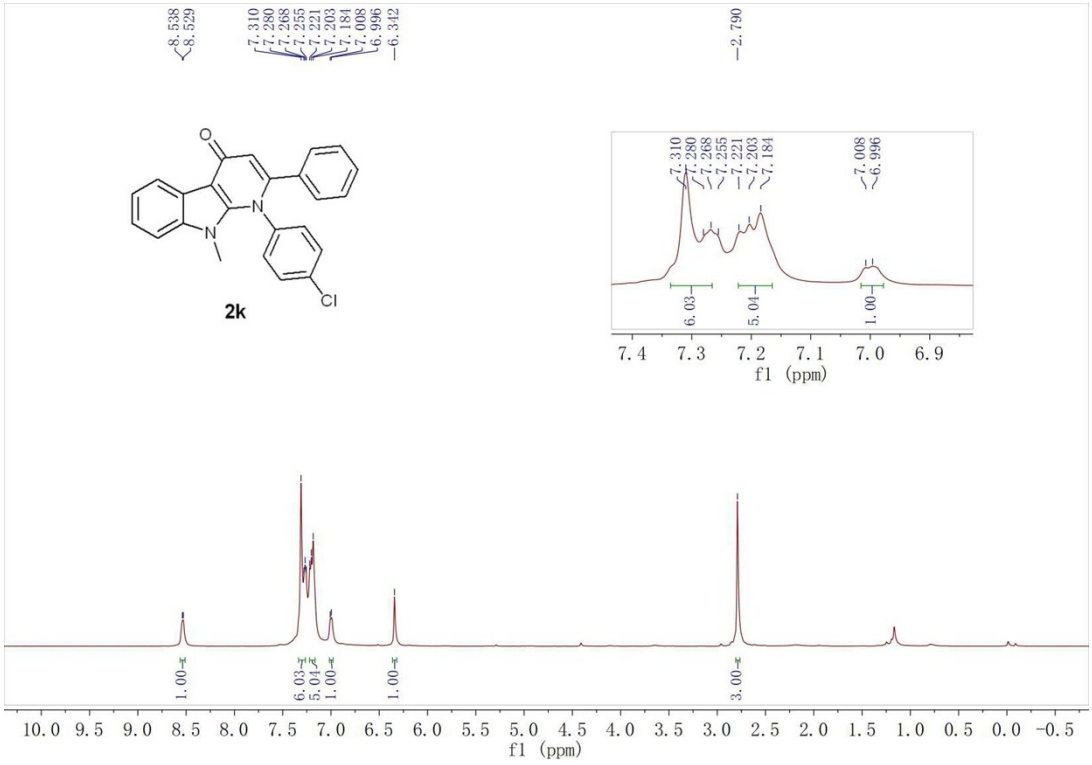
^{13}C NMR (100 MHz, $CDCl_3$)



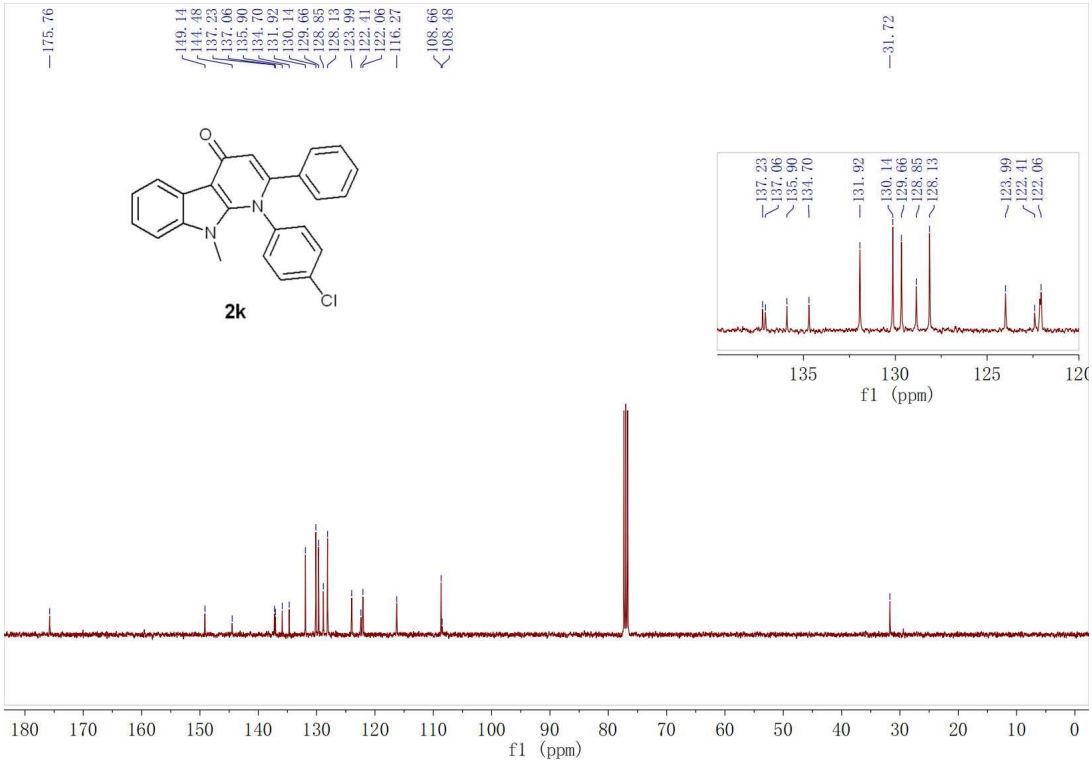
^{19}F NMR (470.2 MHz, $CDCl_3$)



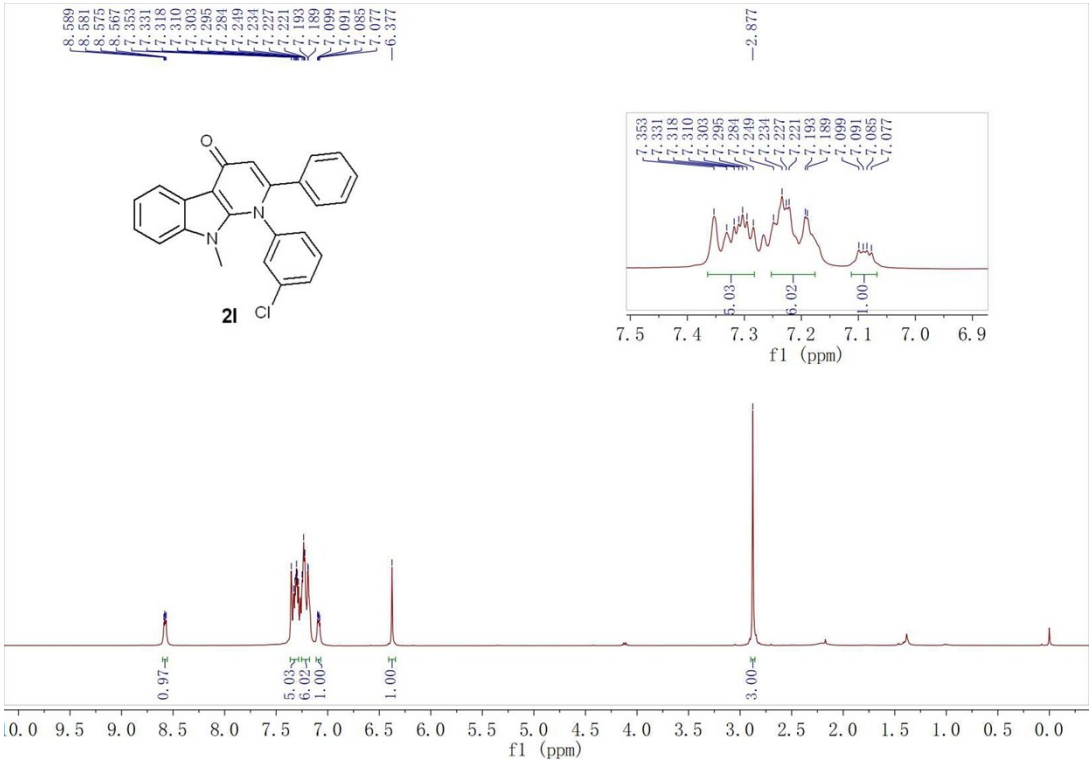
^{1}H NMR (400 MHz, $CDCl_3$)



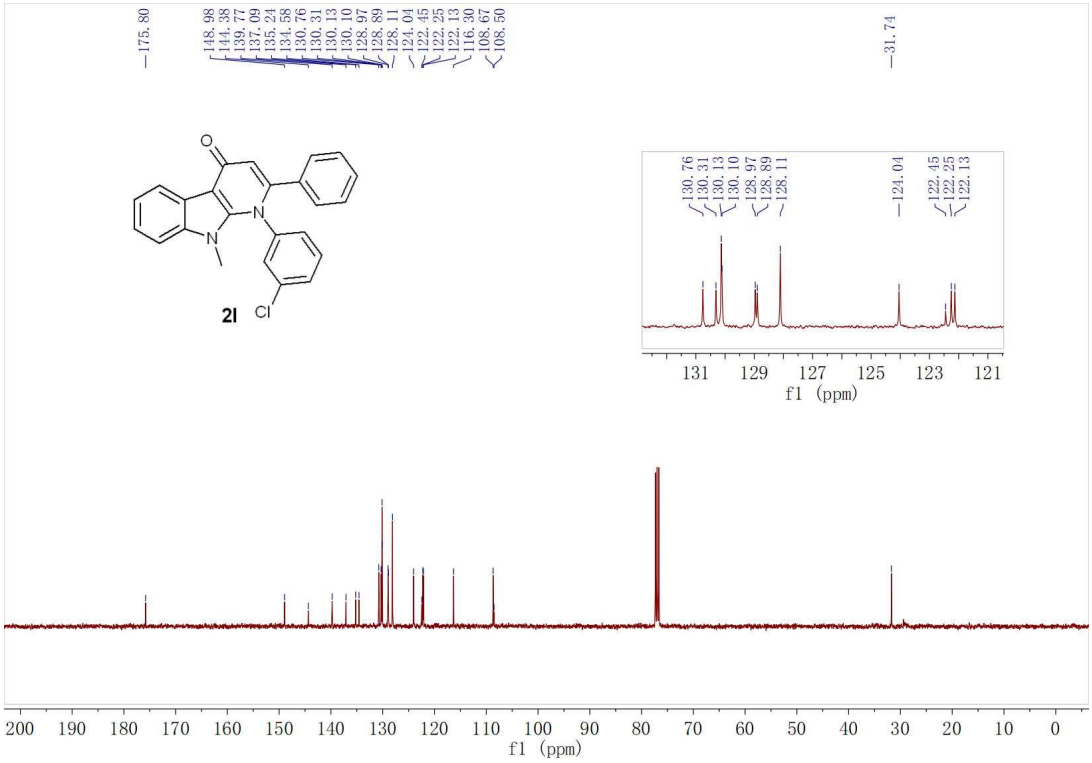
^{13}C NMR (100 MHz, $CDCl_3$)



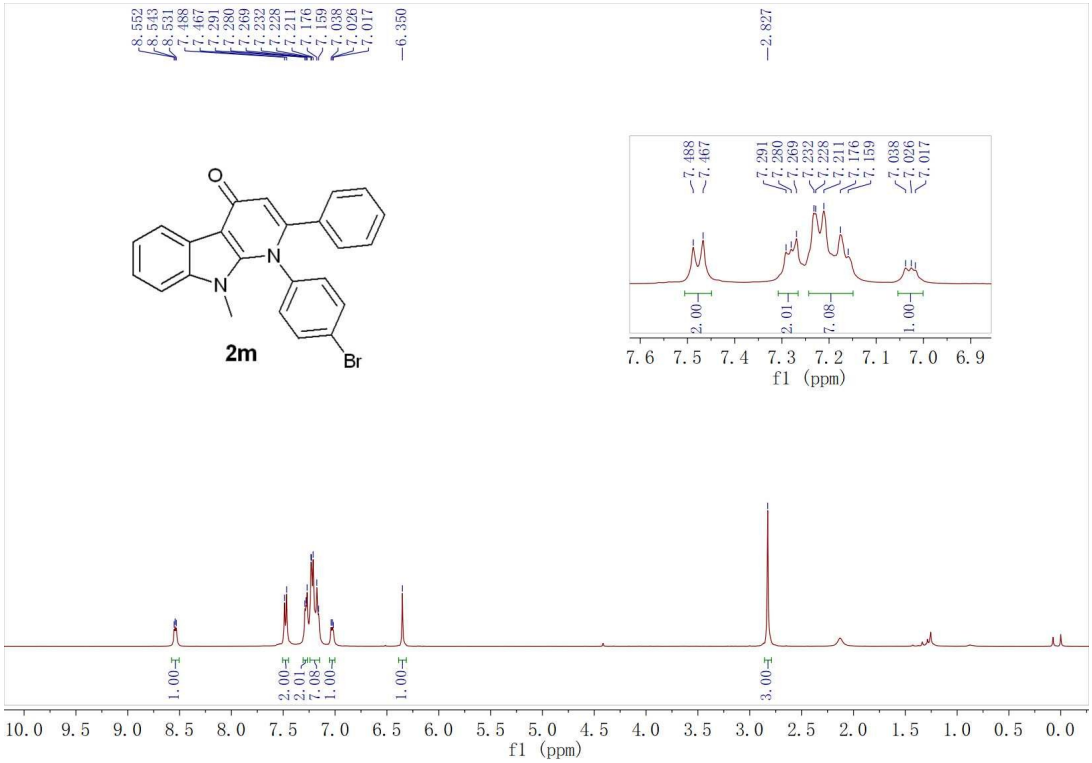
^{1}H NMR (400 MHz, $CDCl_3$)



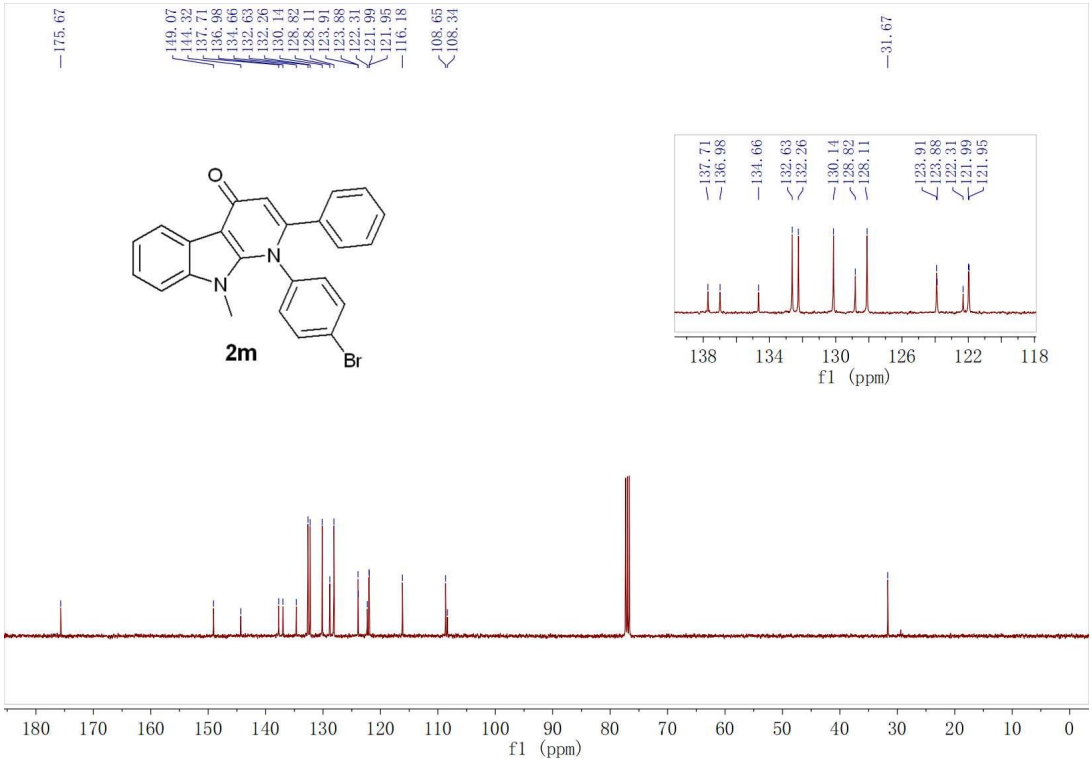
^{13}C NMR (100 MHz, $CDCl_3$)



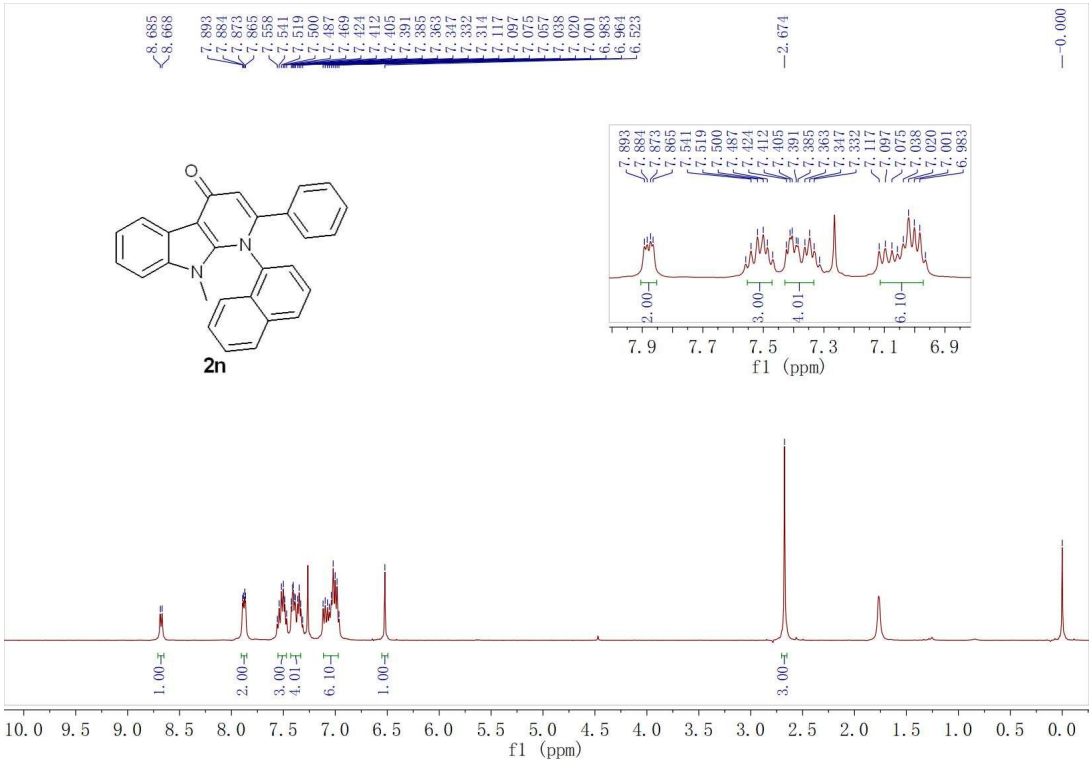
^{1}H NMR (400 MHz, $CDCl_3$)



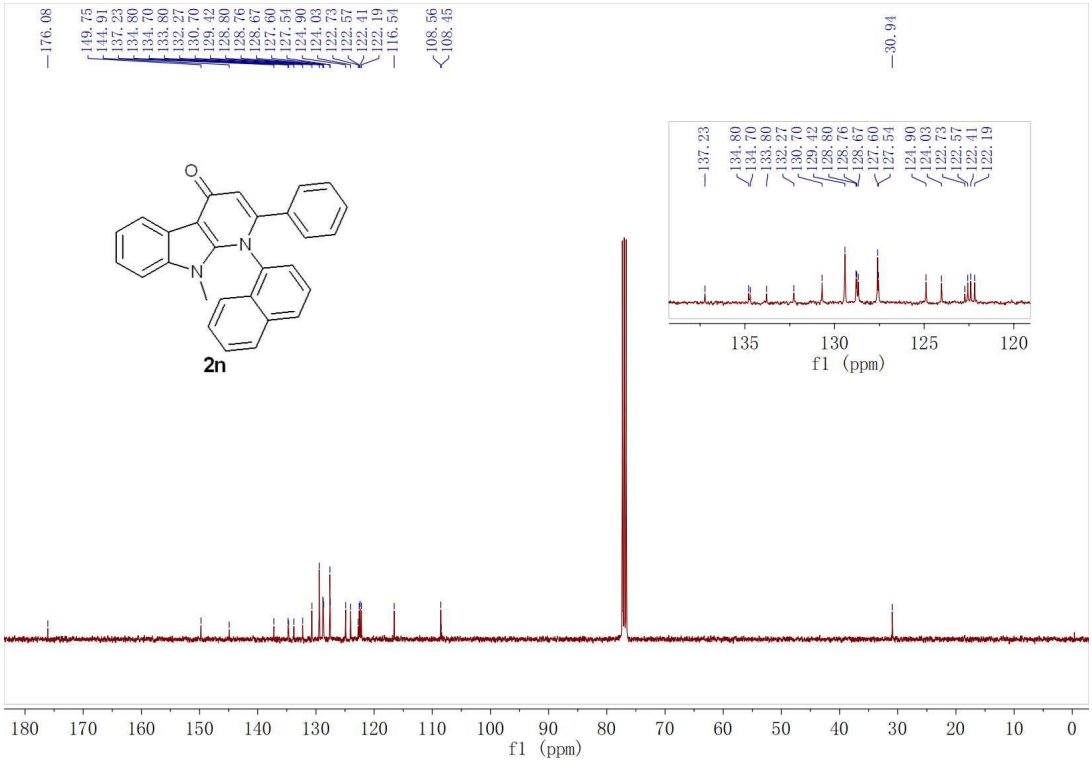
^{13}C NMR (100 MHz, $CDCl_3$)



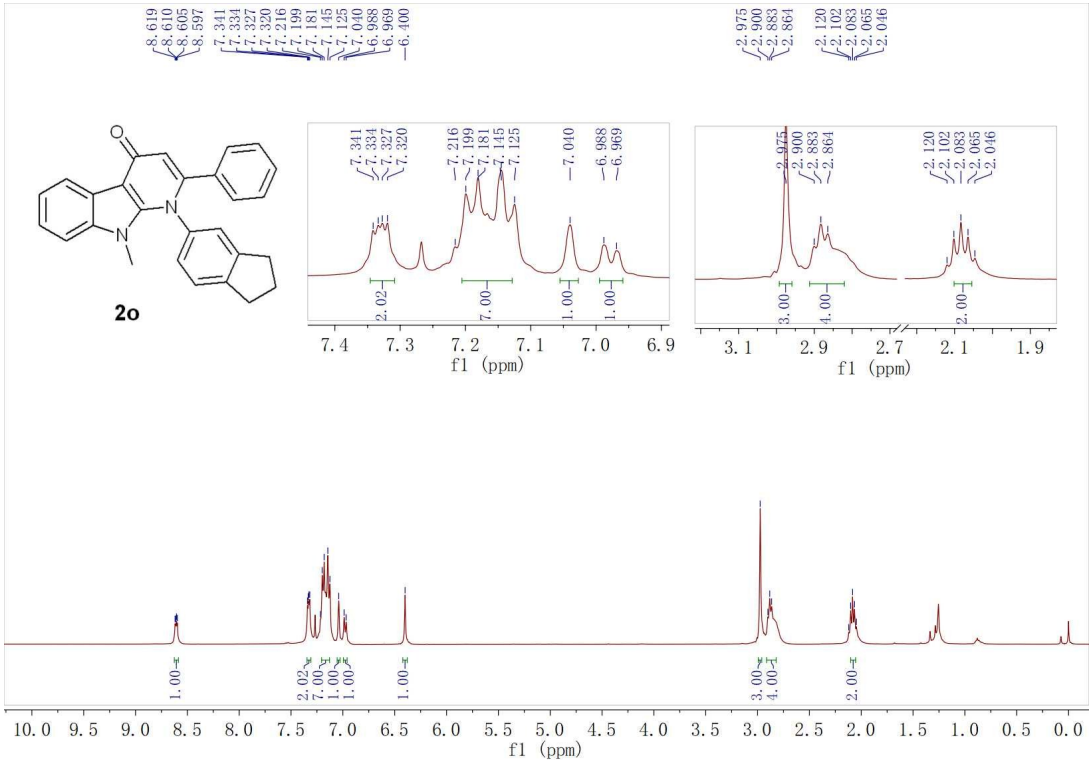
^{1}H NMR (400 MHz, $CDCl_3$)



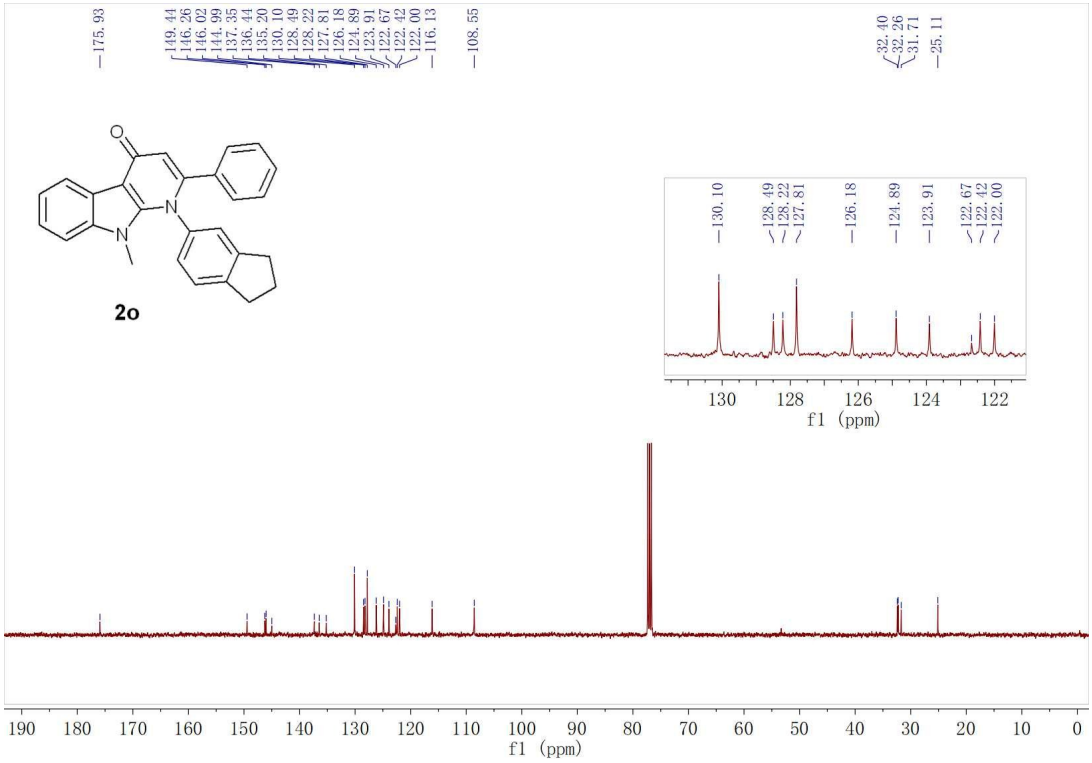
^{13}C NMR (100 MHz, $CDCl_3$)



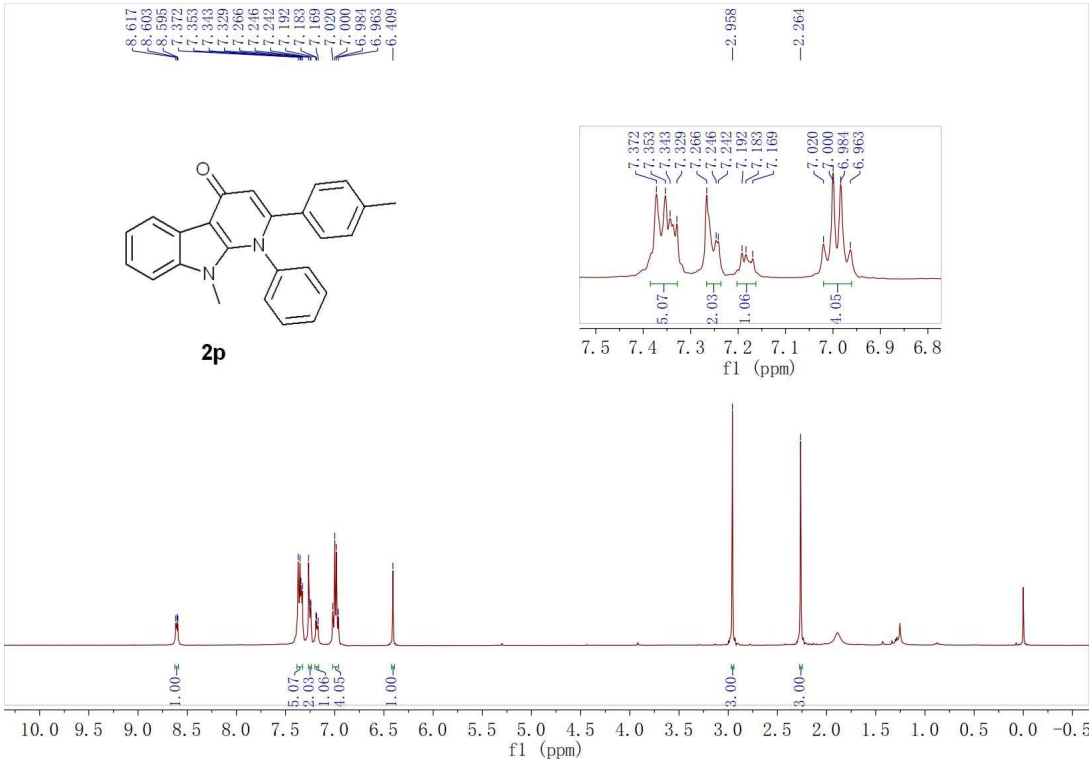
^{1}H NMR (400 MHz, $CDCl_3$)



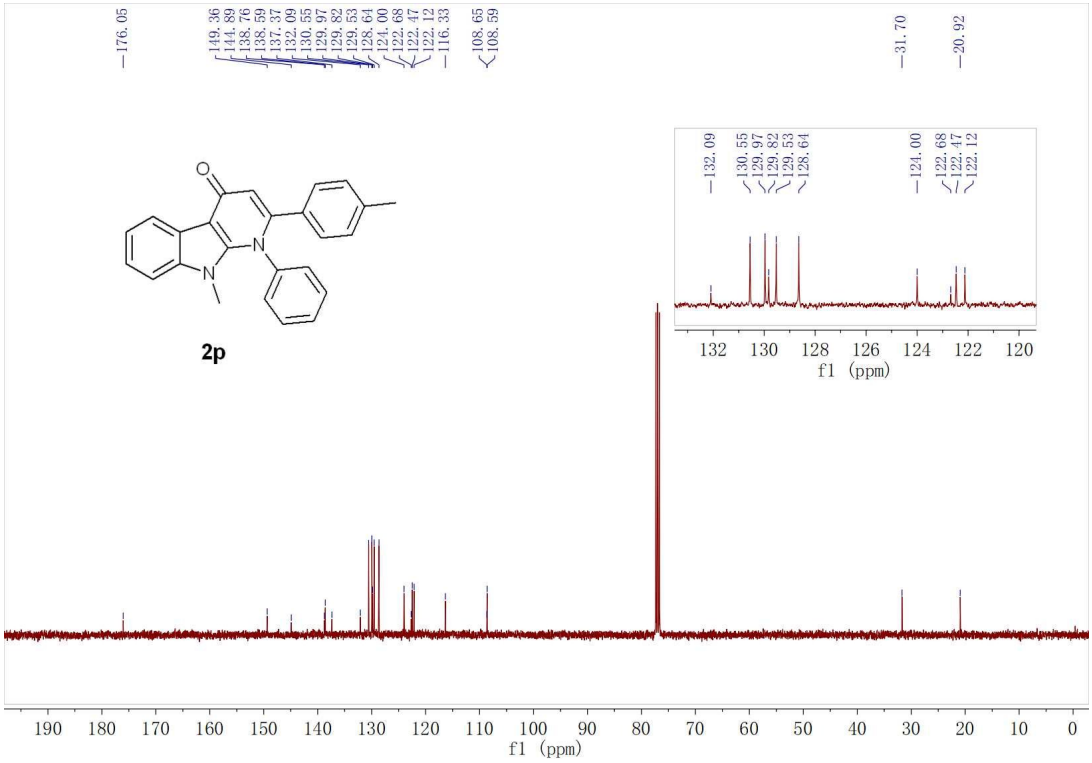
^{13}C NMR (100 MHz, $CDCl_3$)



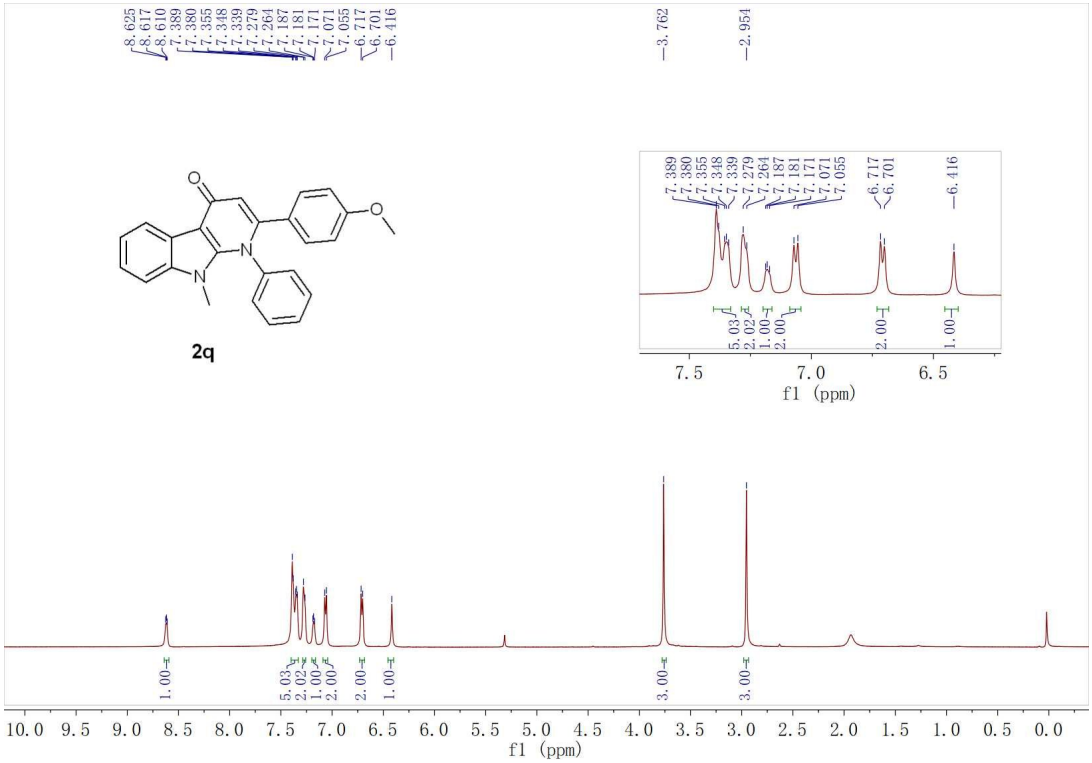
^{1}H NMR (400 MHz, $CDCl_3$)



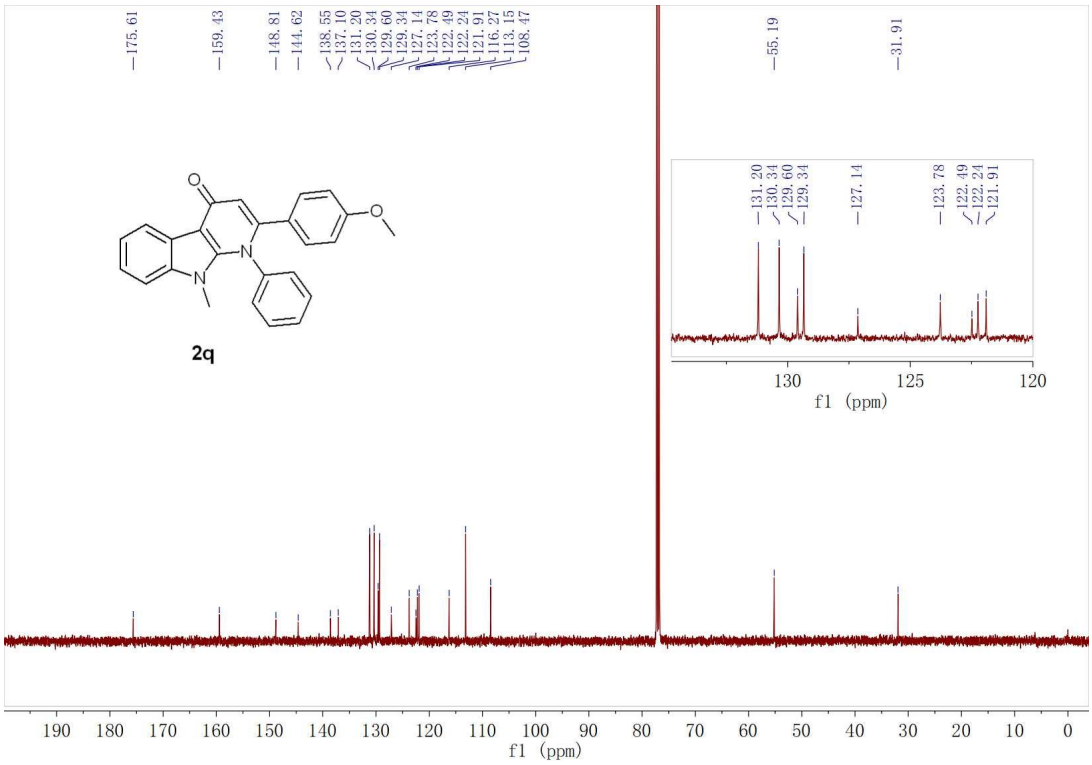
^{13}C NMR (100 MHz, $CDCl_3$)



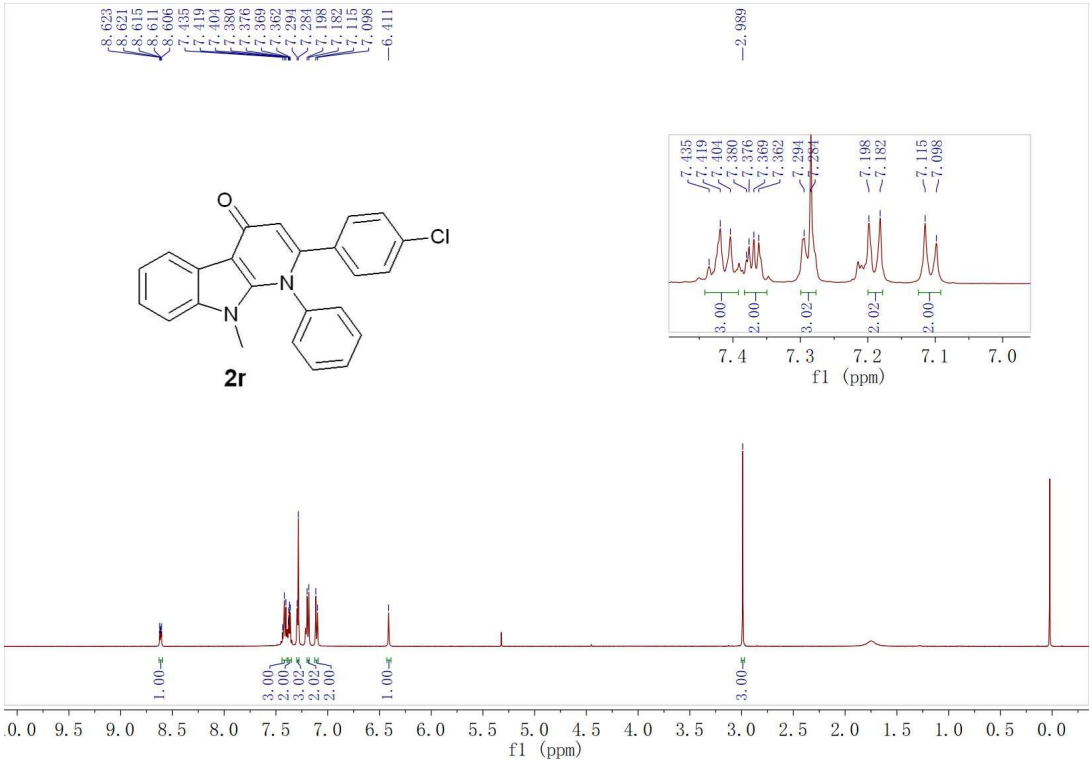
^{1}H NMR (500 MHz, $CDCl_3$)



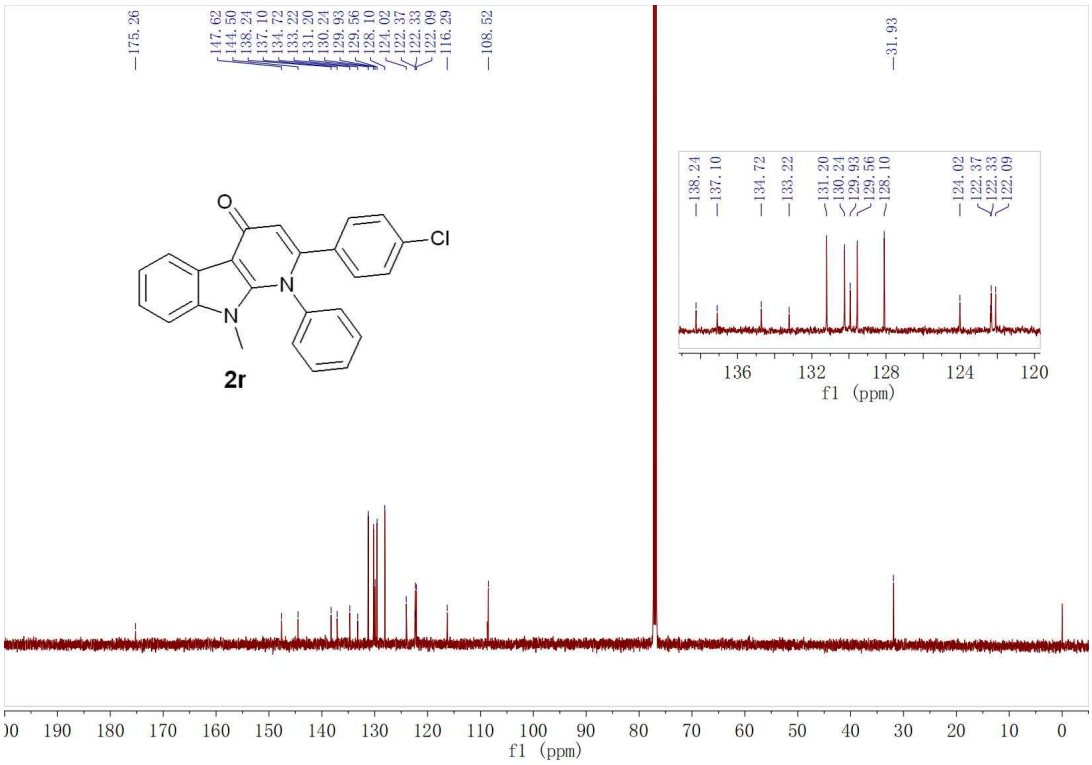
^{13}C NMR (125 MHz, $CDCl_3$)



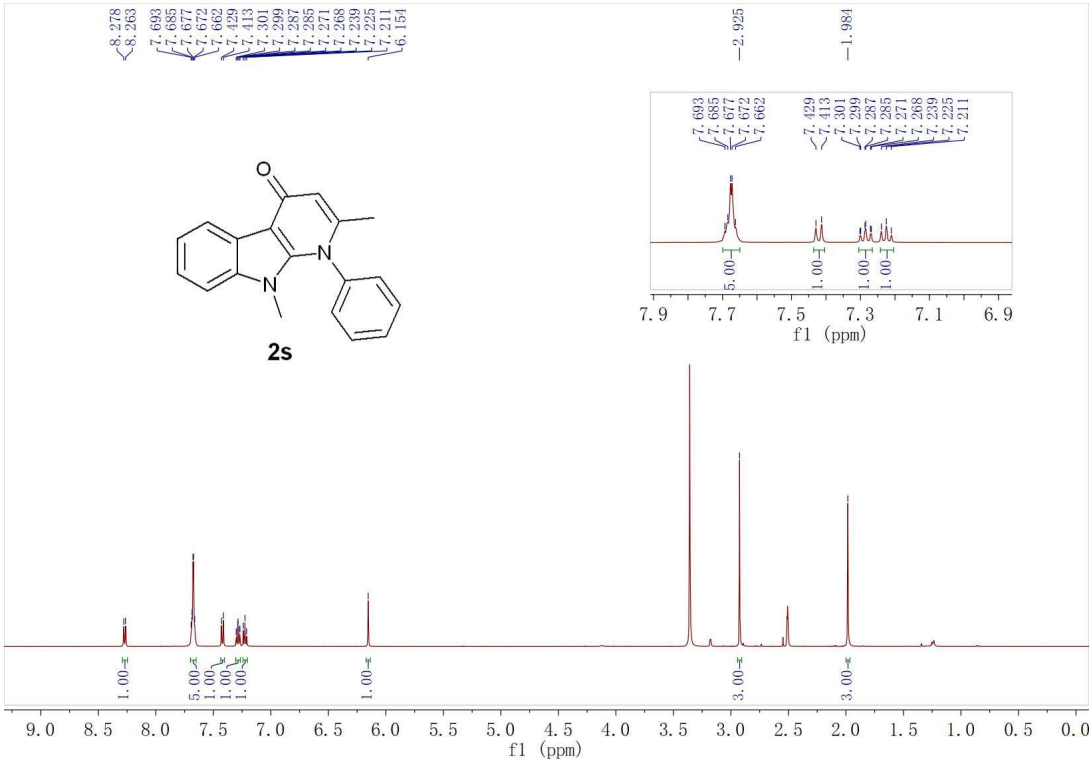
^{1}H NMR (500 MHz, $CDCl_3$)



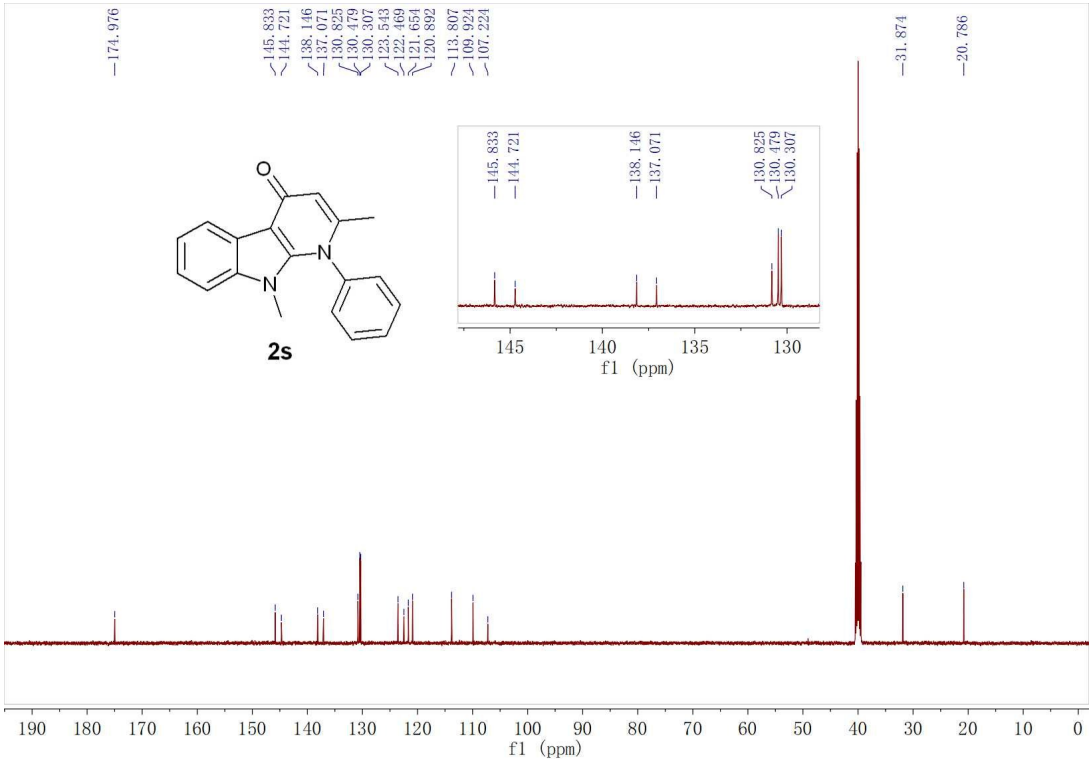
^{13}C NMR (125 MHz, $CDCl_3$)



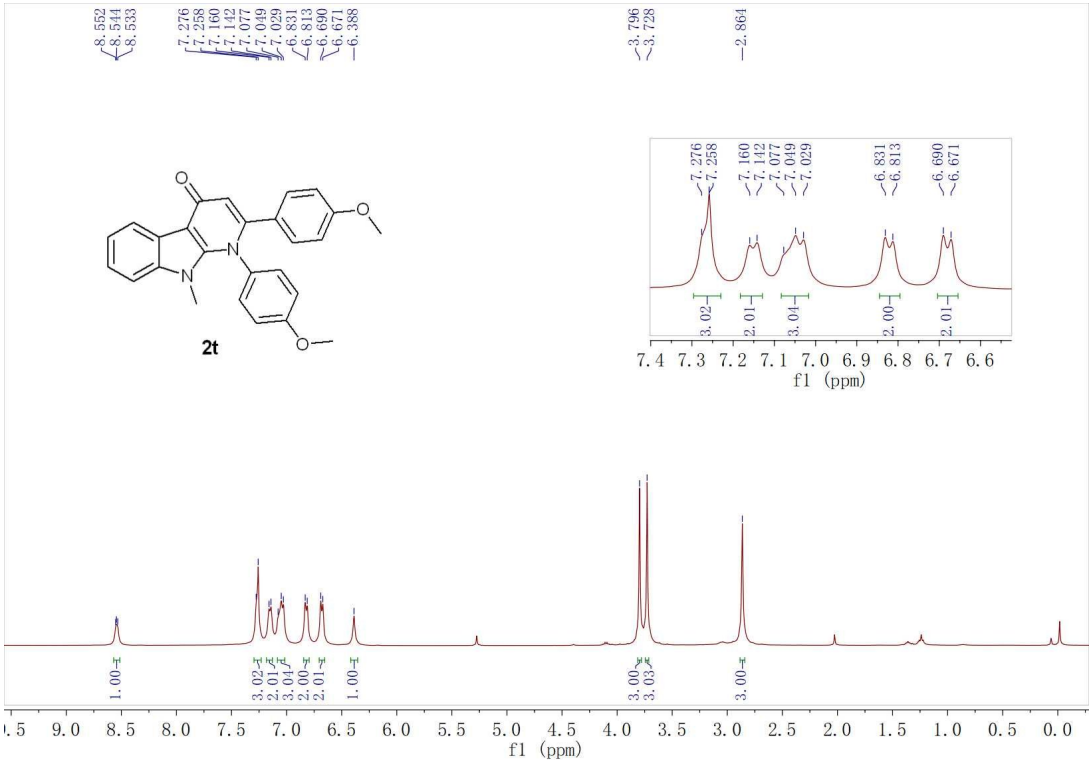
^{1}H NMR (500 MHz, DMSO)



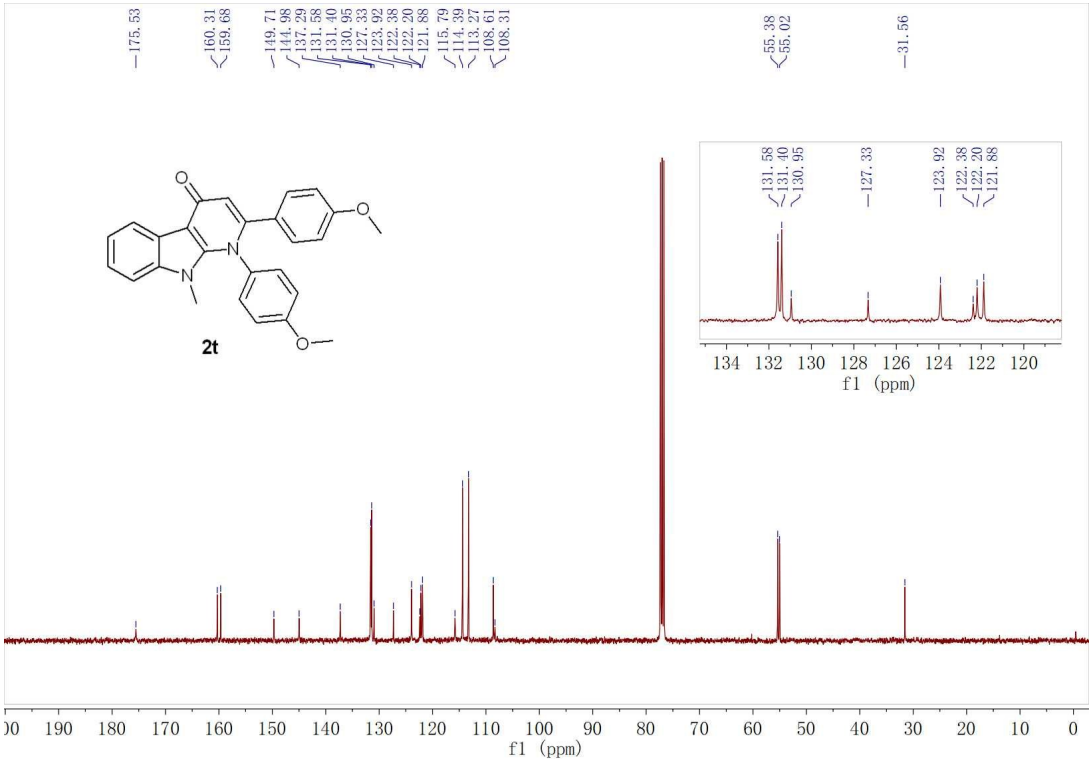
^{13}C NMR (125 MHz, DMSO)



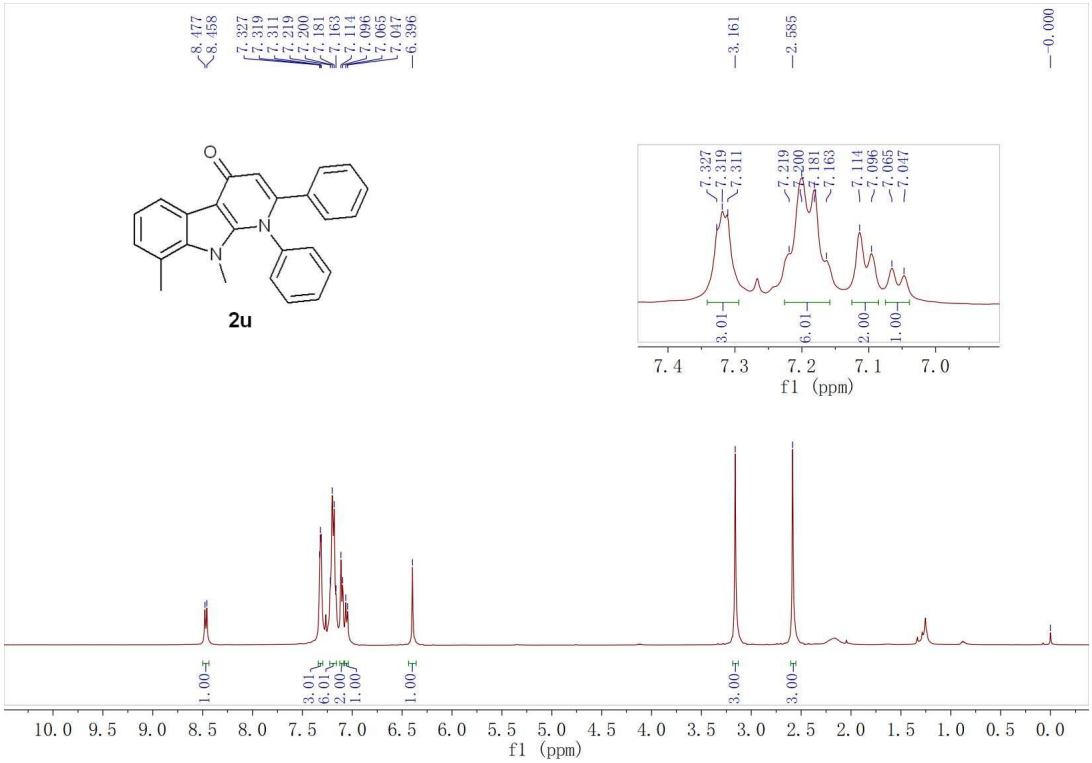
^{1}H NMR (400 MHz, $CDCl_3$)



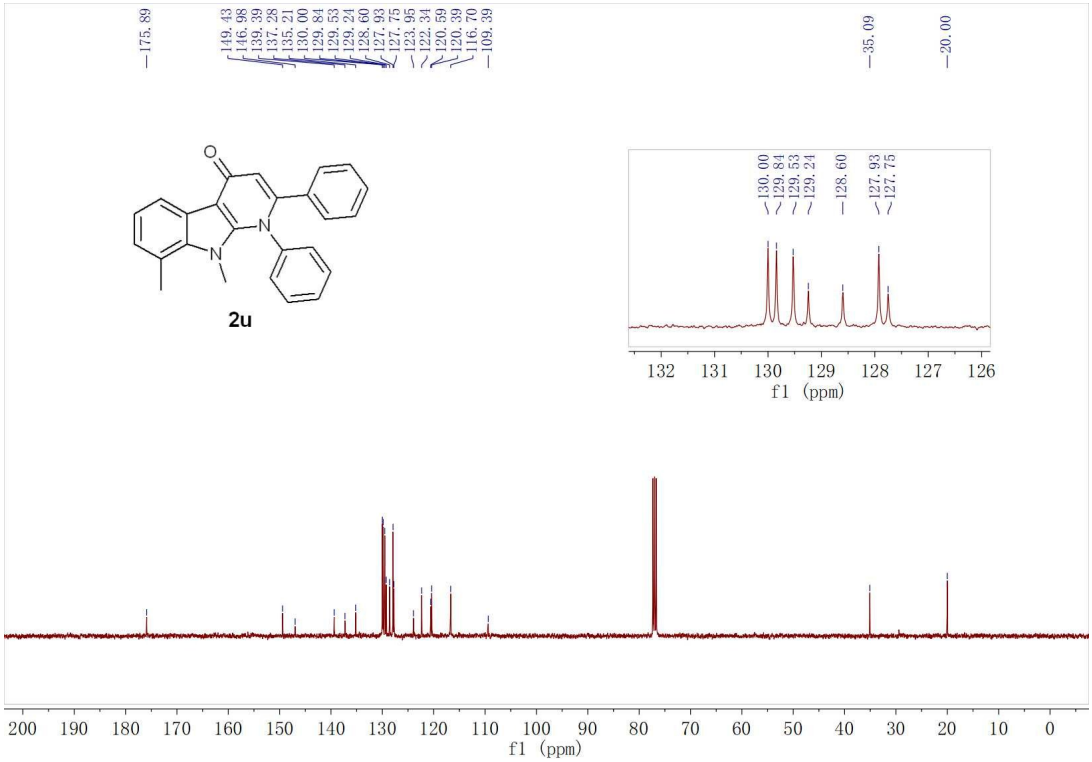
^{13}C NMR (100 MHz, $CDCl_3$)



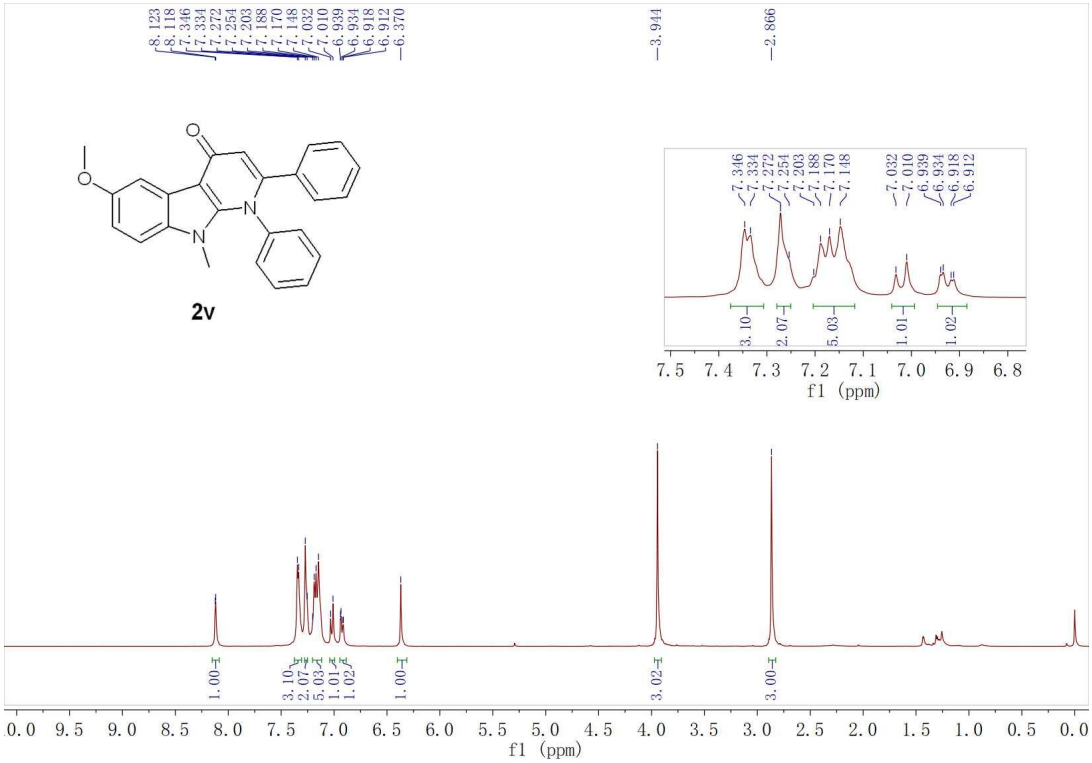
^{1}H NMR (400 MHz, $CDCl_3$)



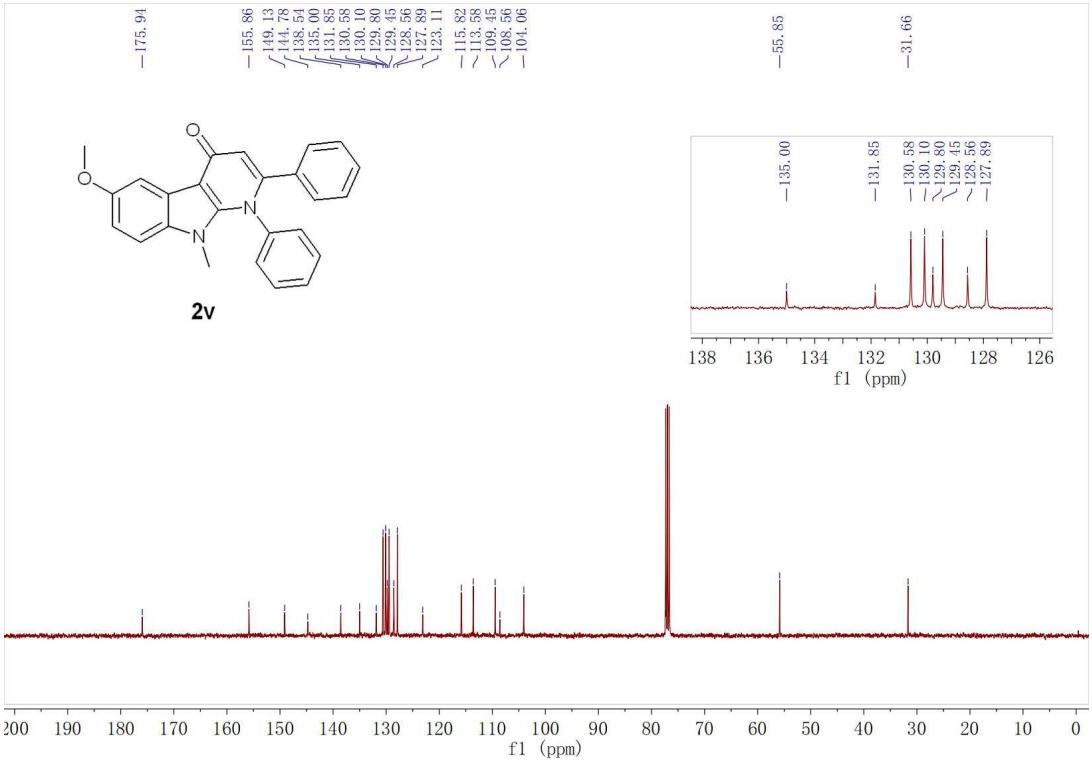
^{13}C NMR (100 MHz, $CDCl_3$)



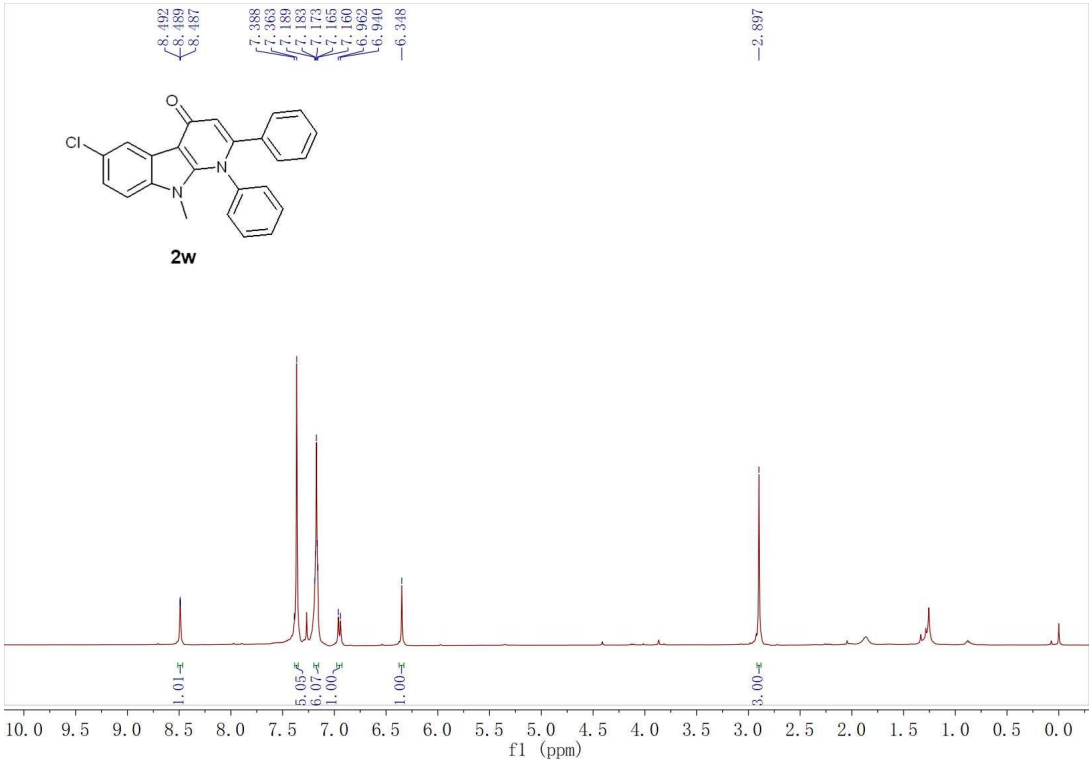
^{1}H NMR (400 MHz, $CDCl_3$)



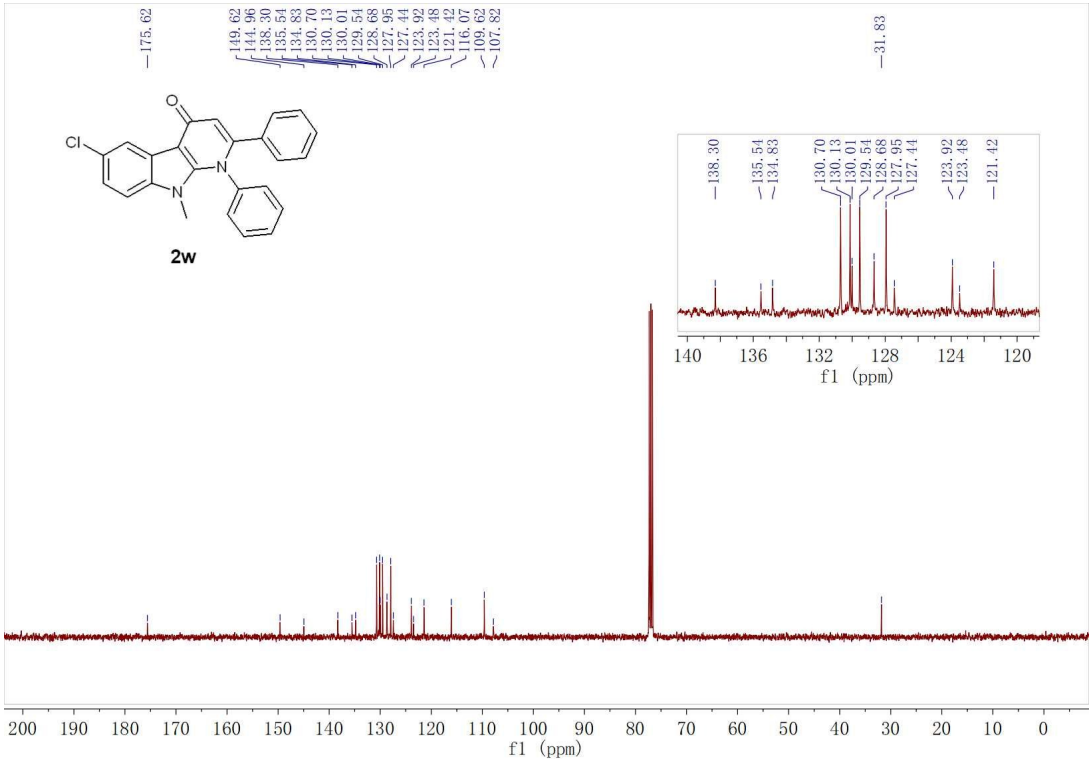
^{13}C NMR (100 MHz, $CDCl_3$)



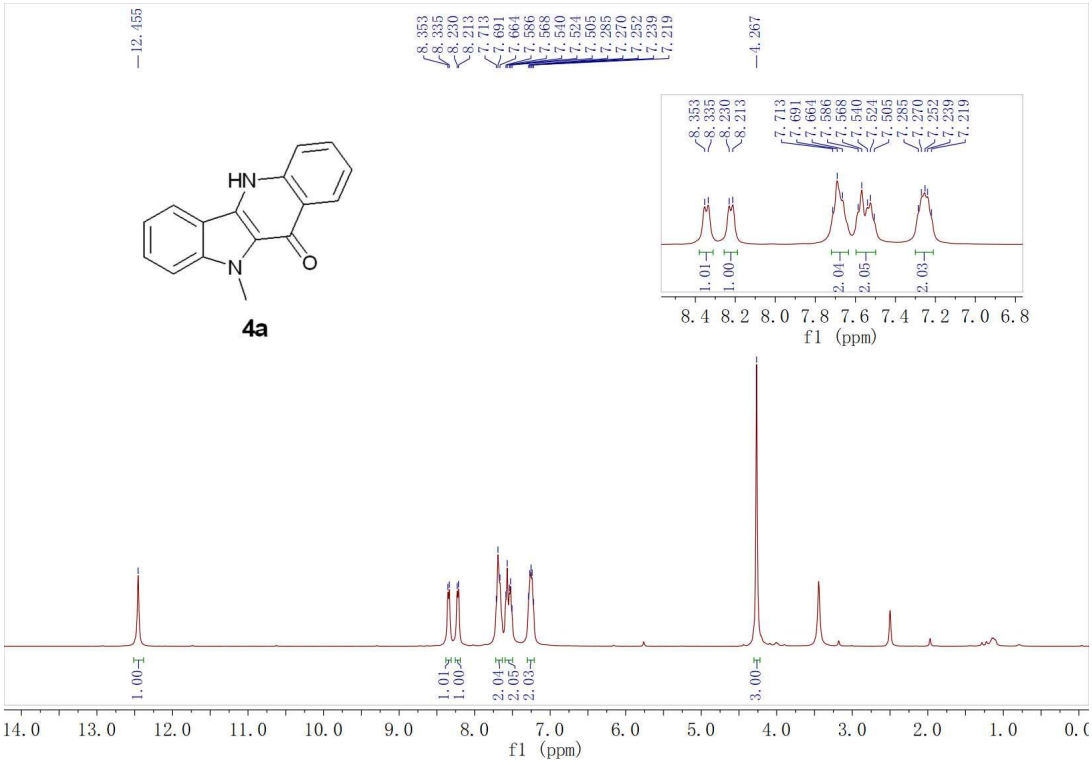
^{1}H NMR (400 MHz, $CDCl_3$)



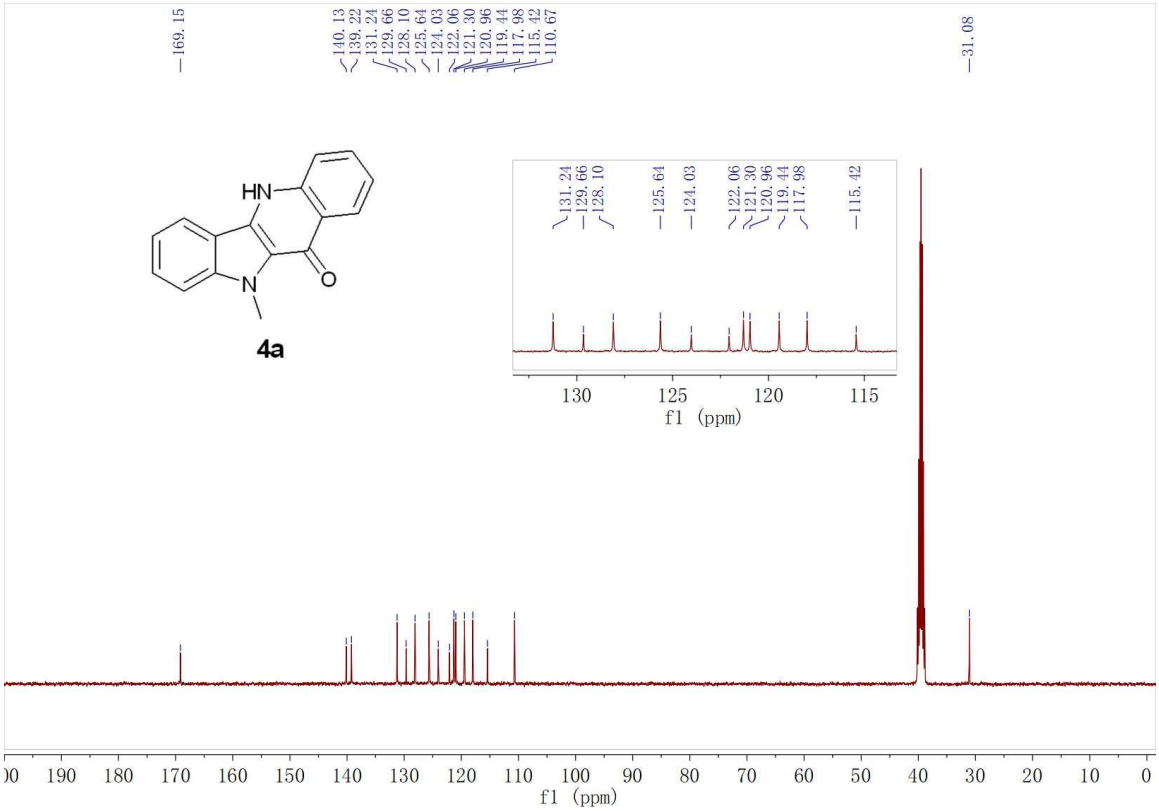
^{13}C NMR (100 MHz, $CDCl_3$)



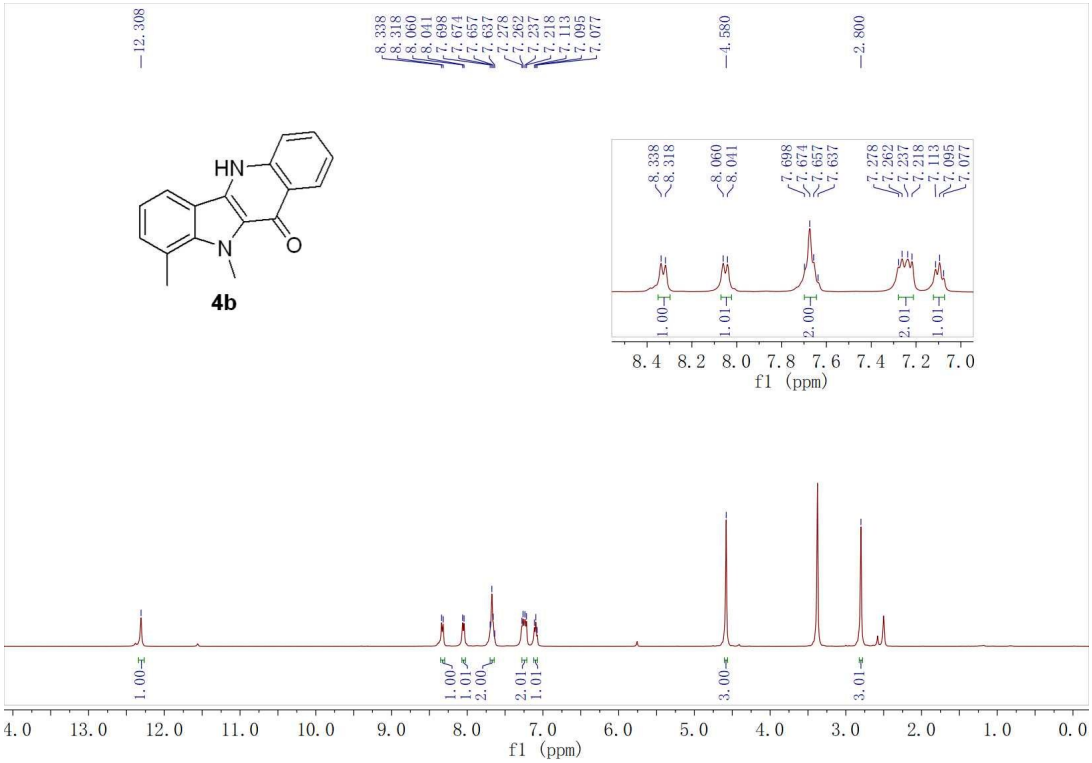
^{1}H NMR (400 MHz, DMSO)



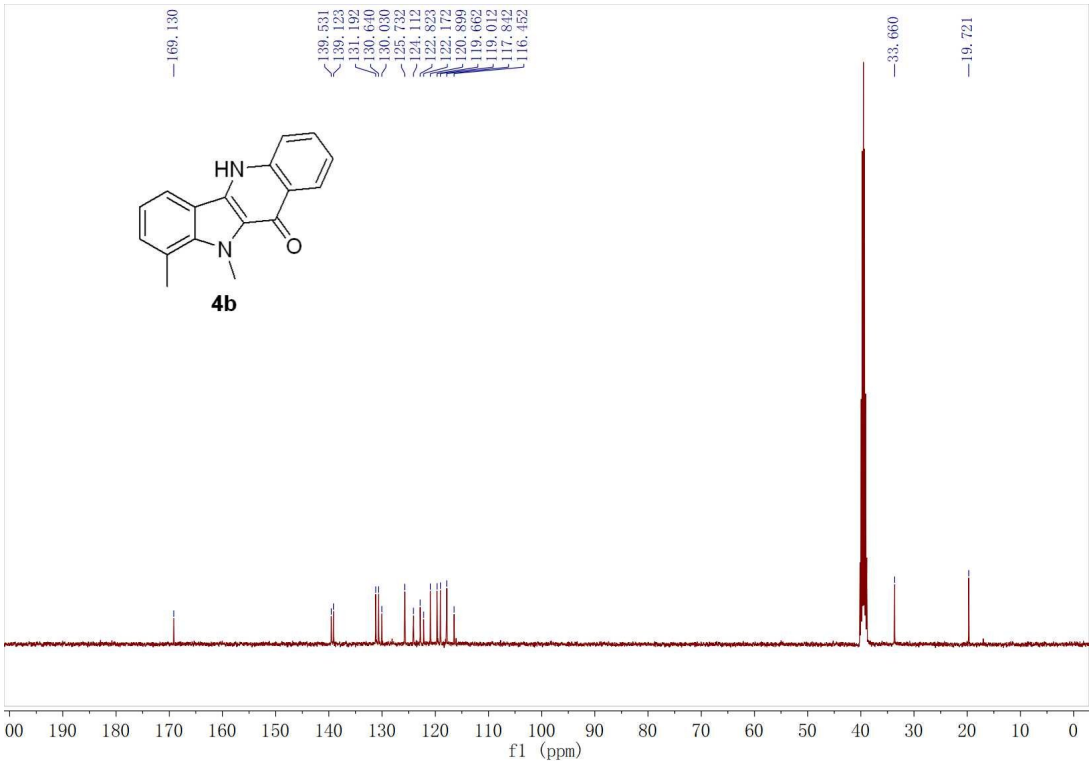
^{13}C NMR (100 MHz, DMSO)



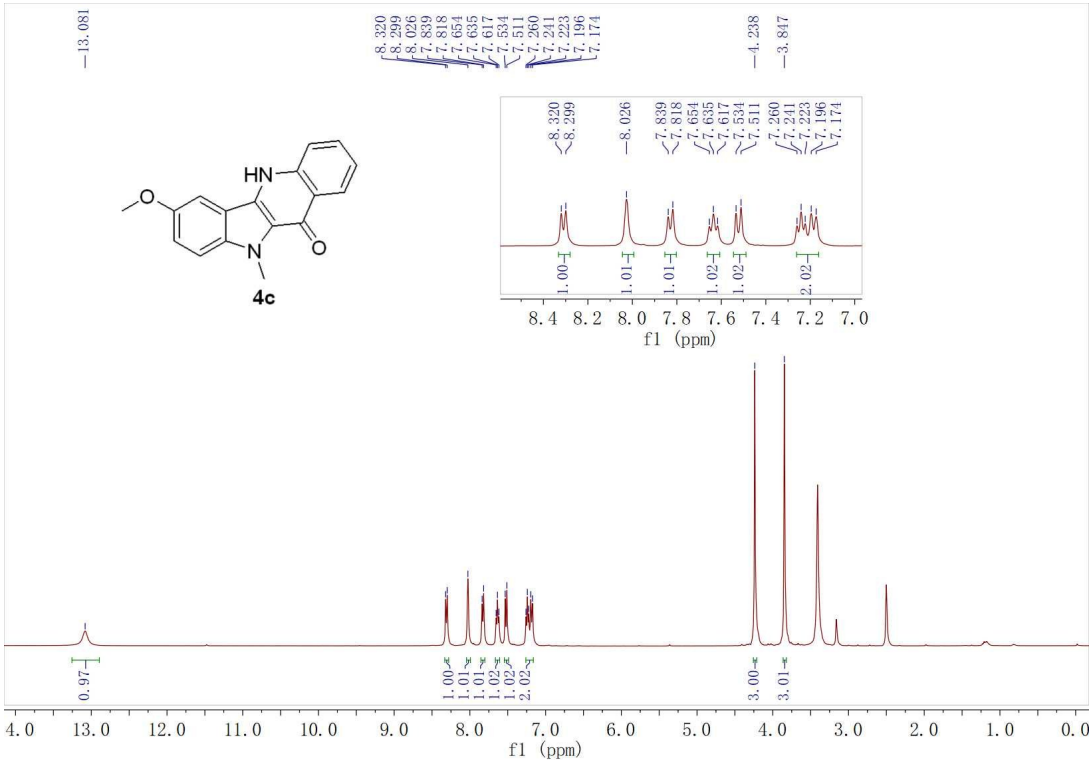
^{1}H NMR (400 MHz, DMSO)



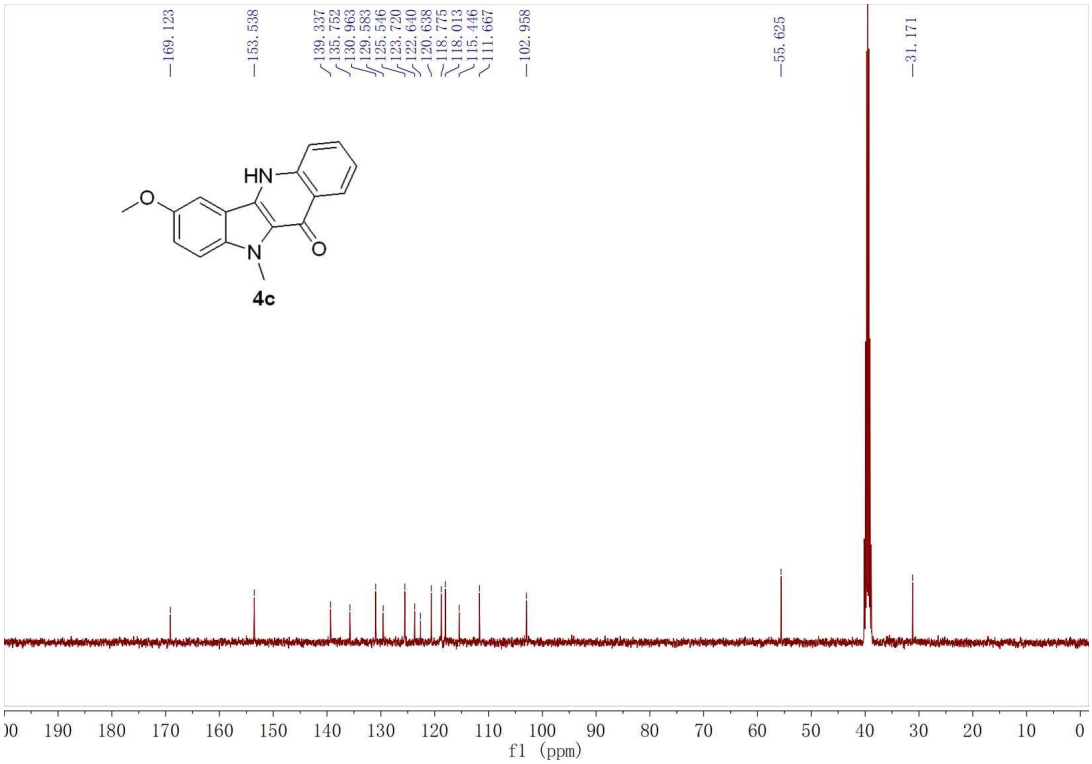
^{13}C NMR (100 MHz, DMSO)



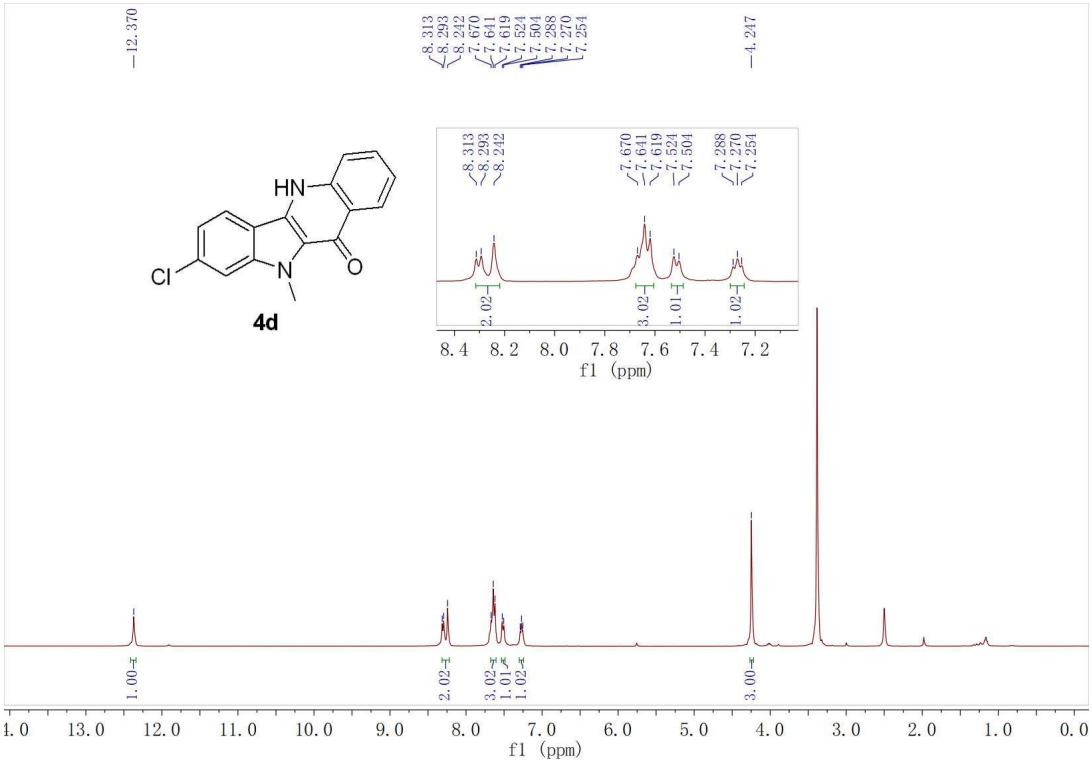
^{1}H NMR (400 MHz, DMSO)



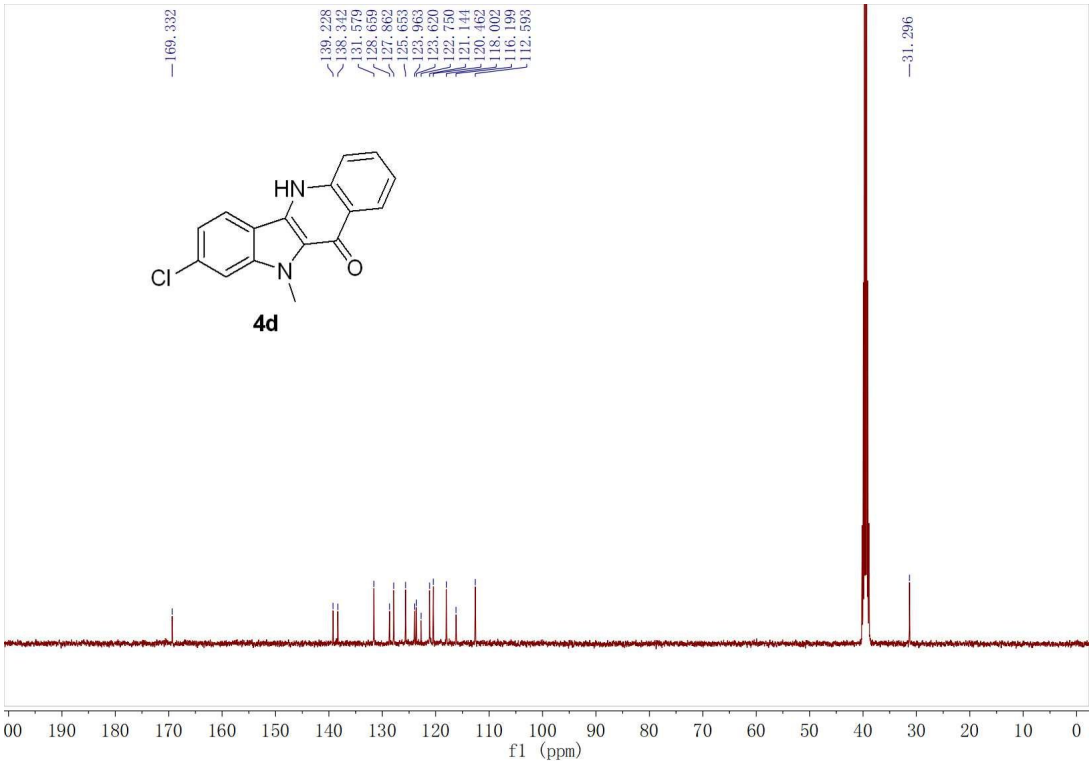
^{13}C NMR (100 MHz, DMSO)



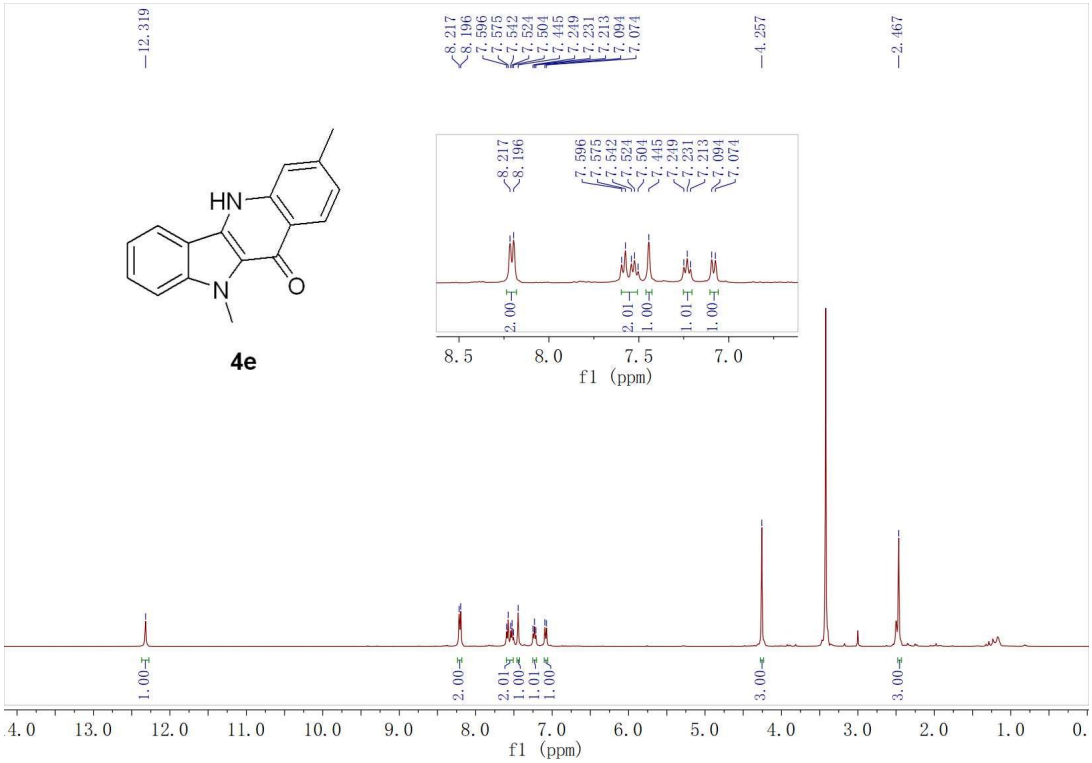
^{1}H NMR (400 MHz, DMSO)



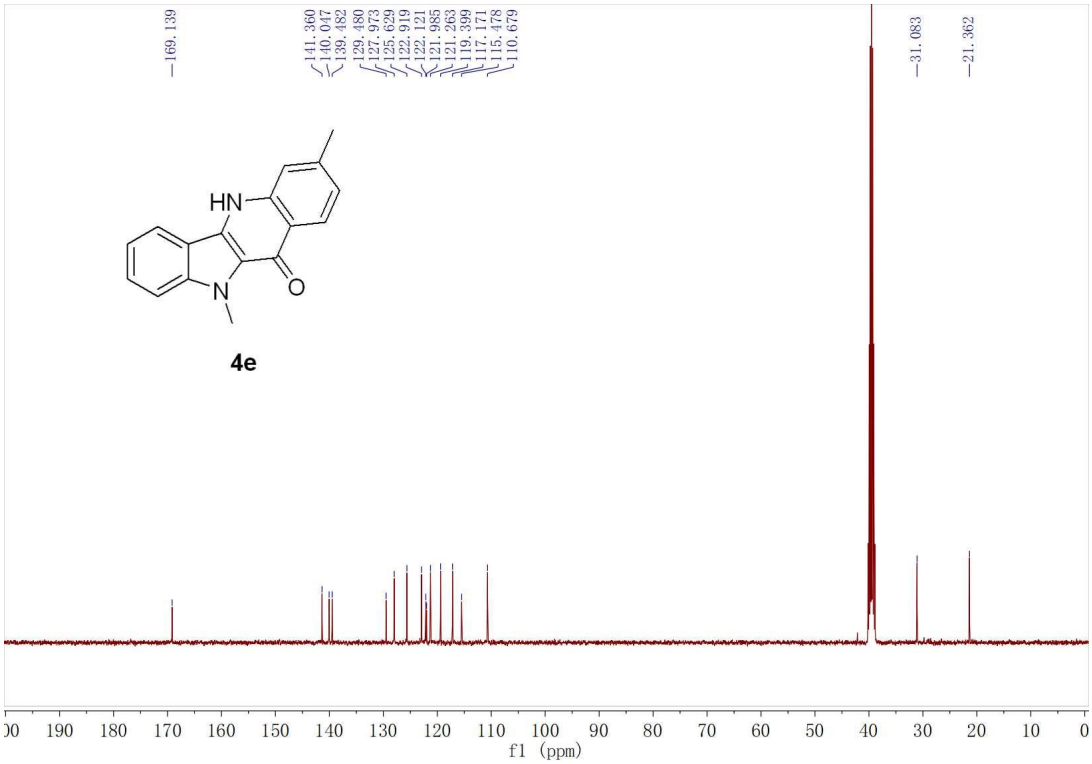
^{13}C NMR (100 MHz, DMSO)



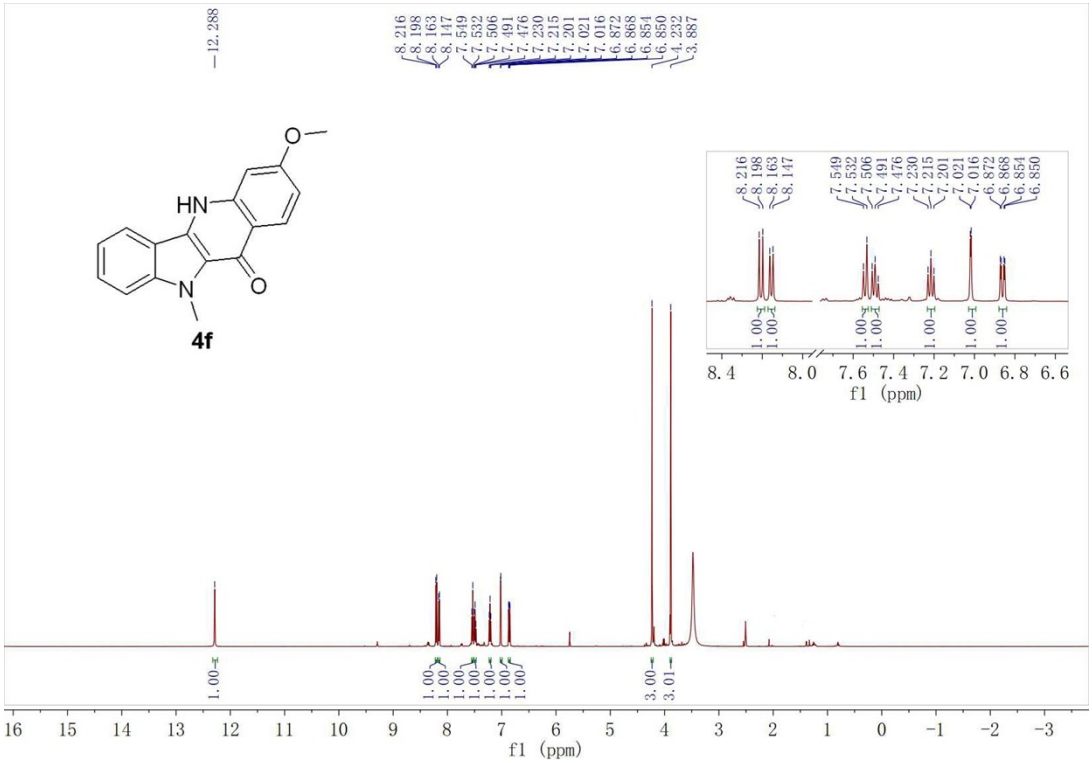
^{1}H NMR (400 MHz, DMSO)



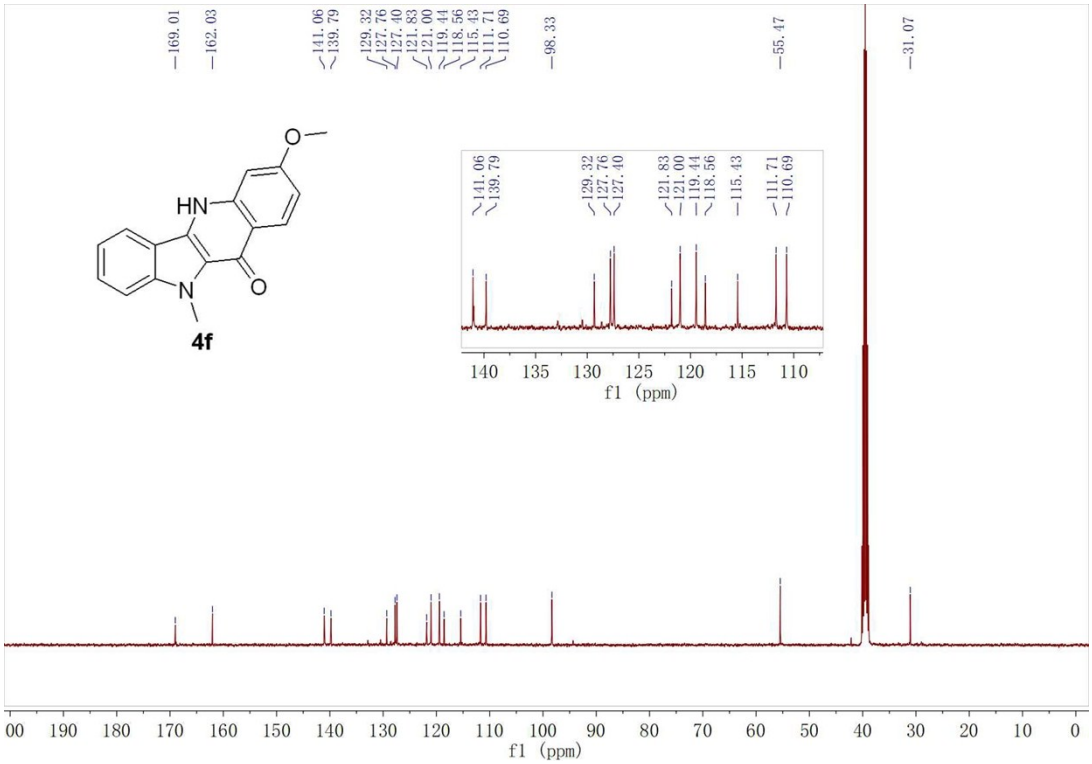
^{13}C NMR (100 MHz, DMSO)



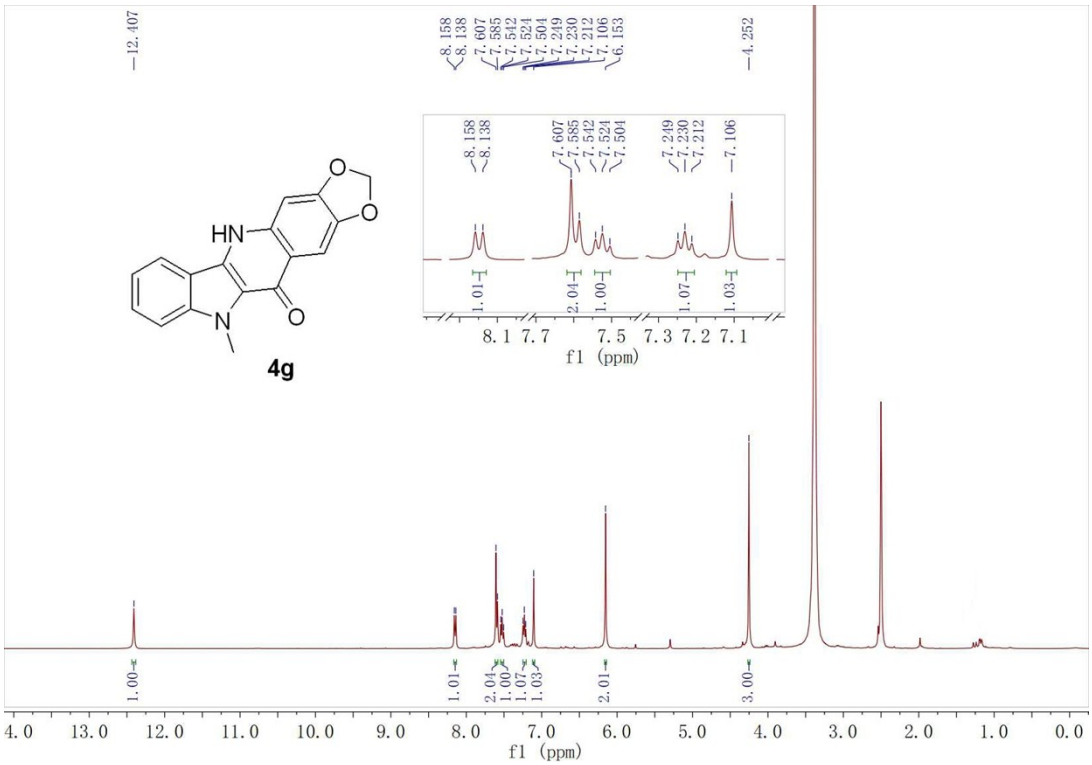
^{1}H NMR (500 MHz, DMSO)



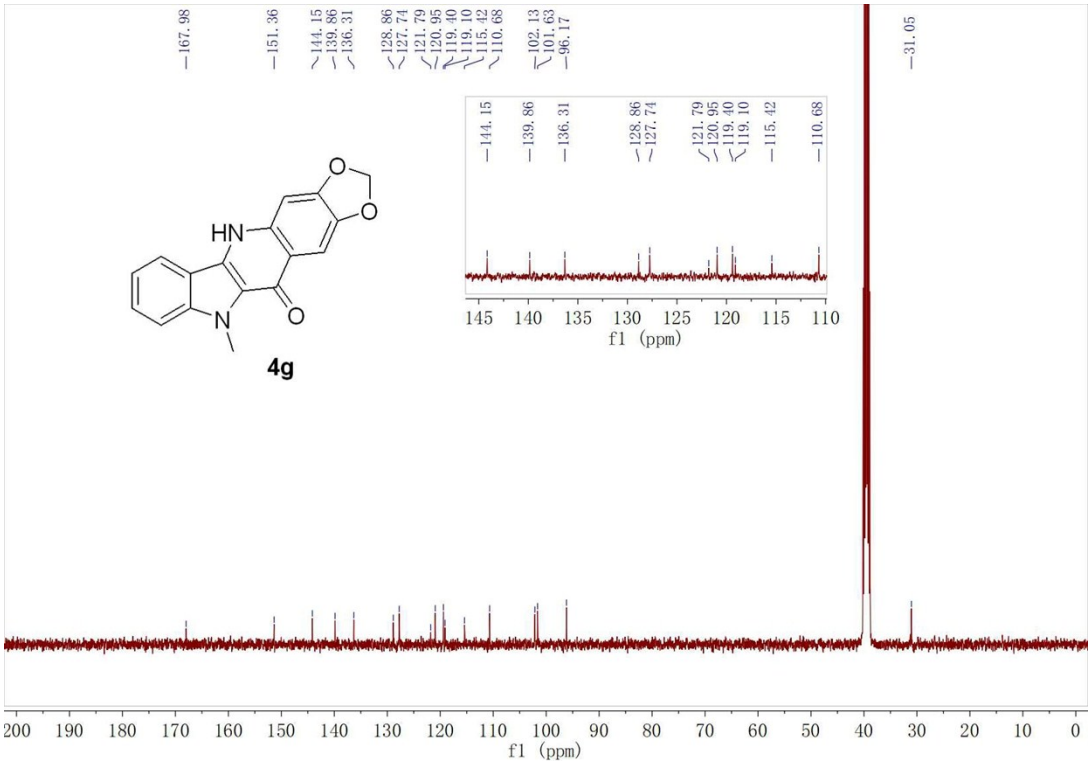
^{13}C NMR (100 MHz, DMSO)



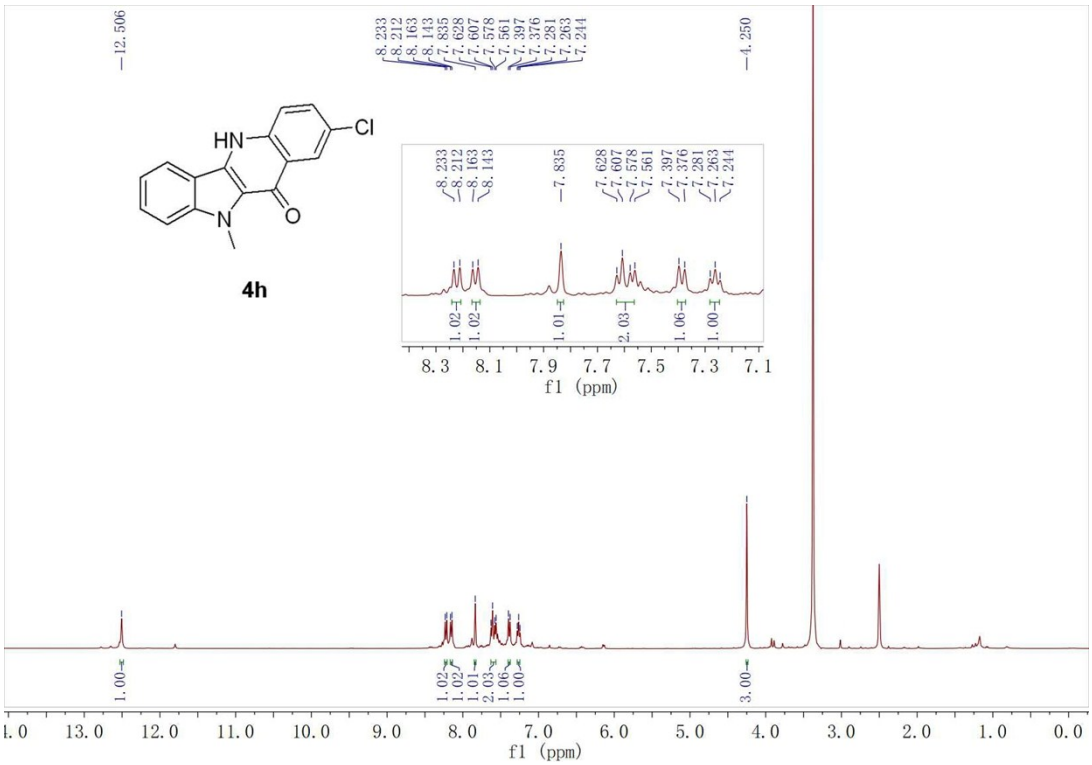
^{1}H NMR (400 MHz, DMSO)



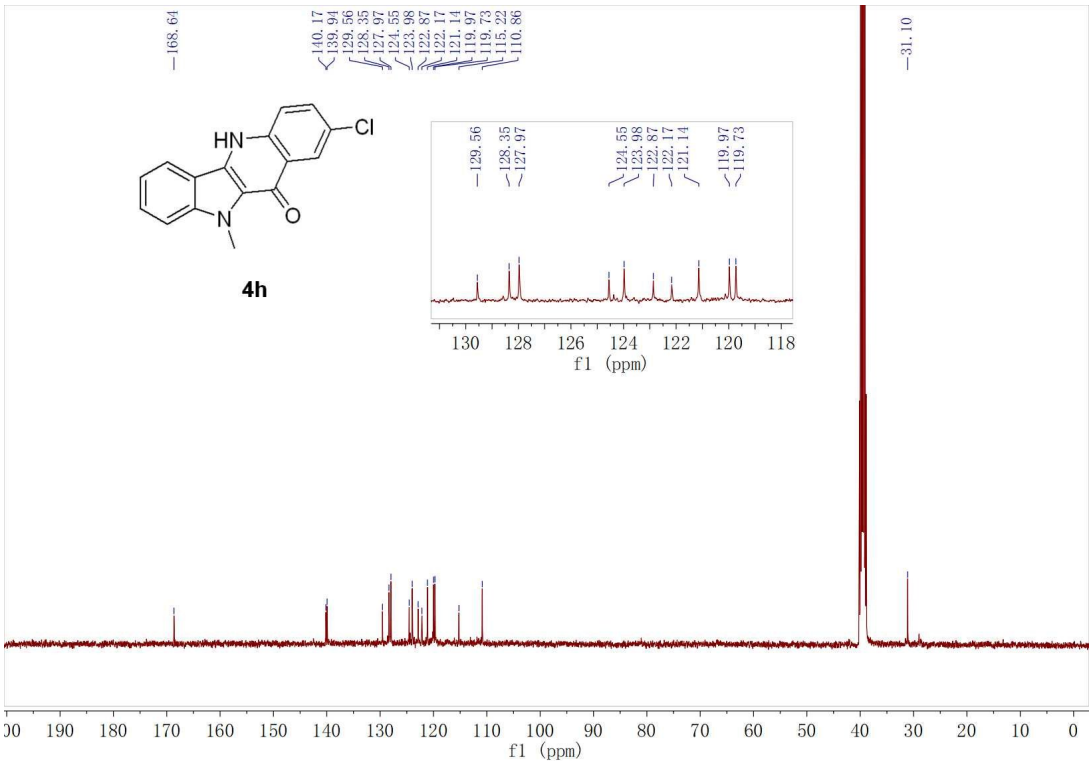
^{13}C NMR (100 MHz, DMSO)



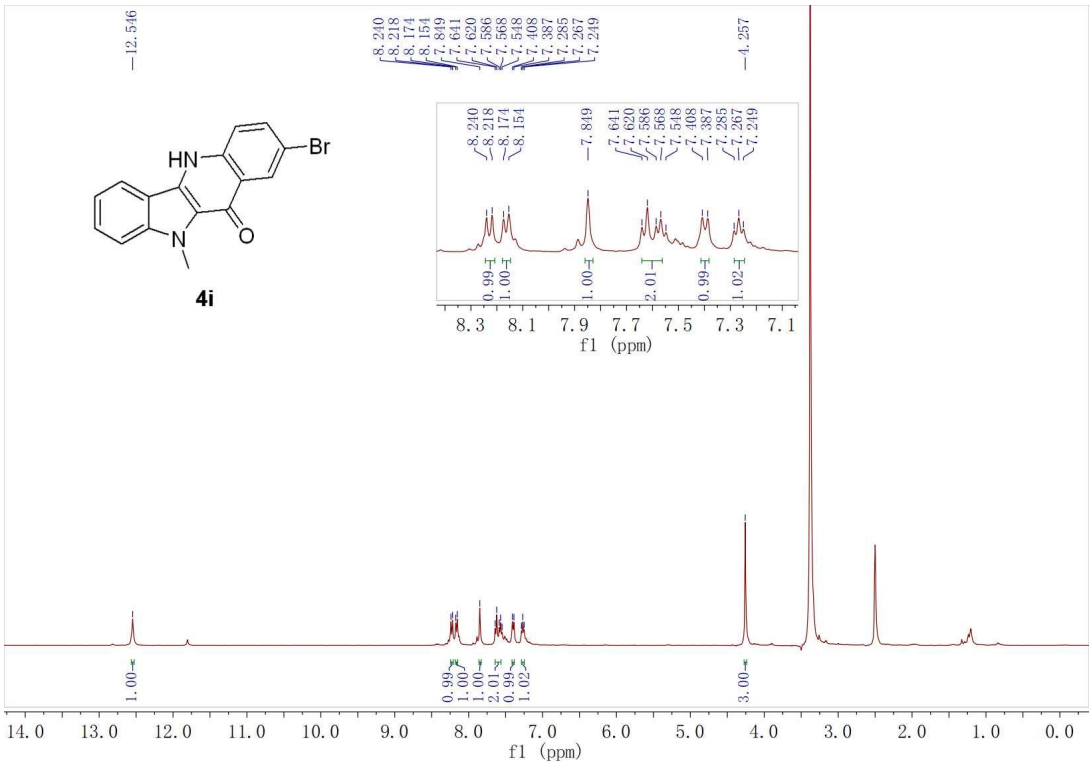
^{1}H NMR (400 MHz, DMSO)



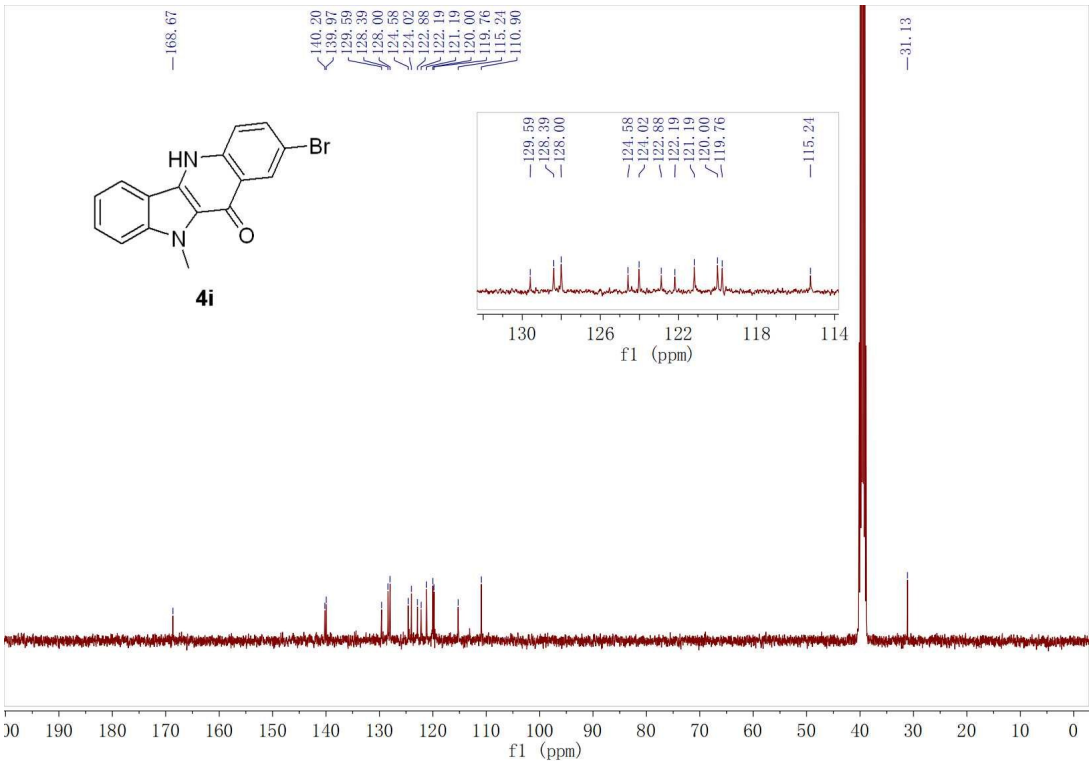
^{13}C NMR (100 MHz, DMSO)



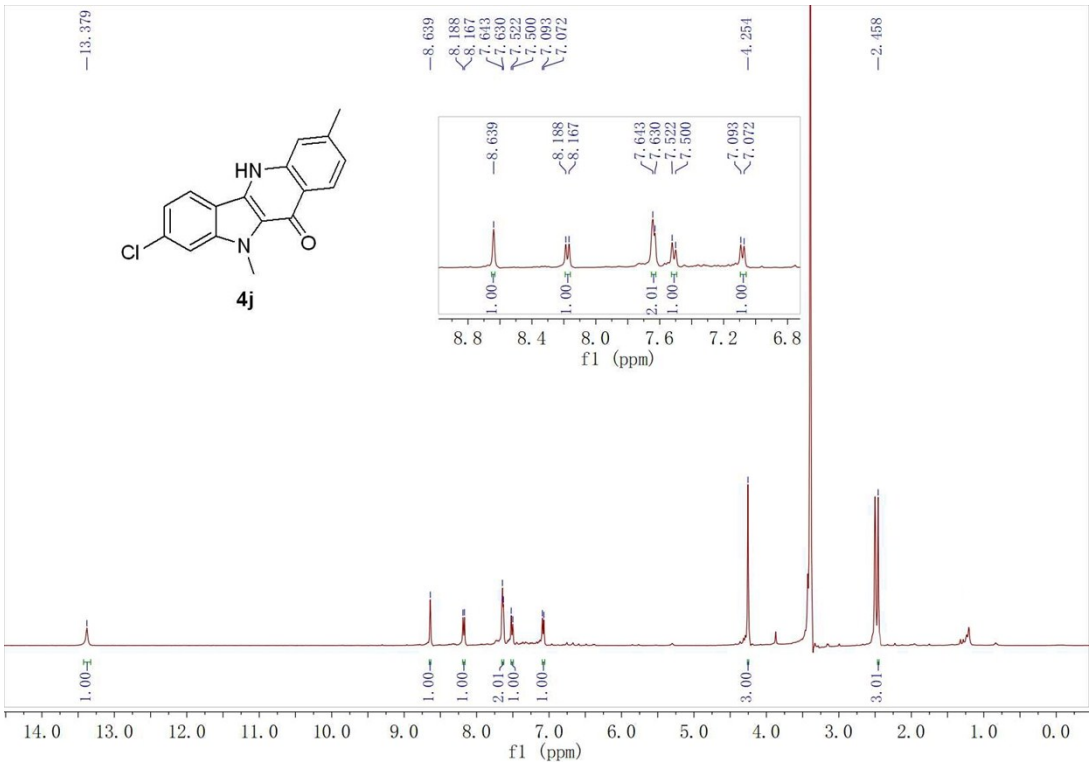
^{1}H NMR (400 MHz, DMSO)



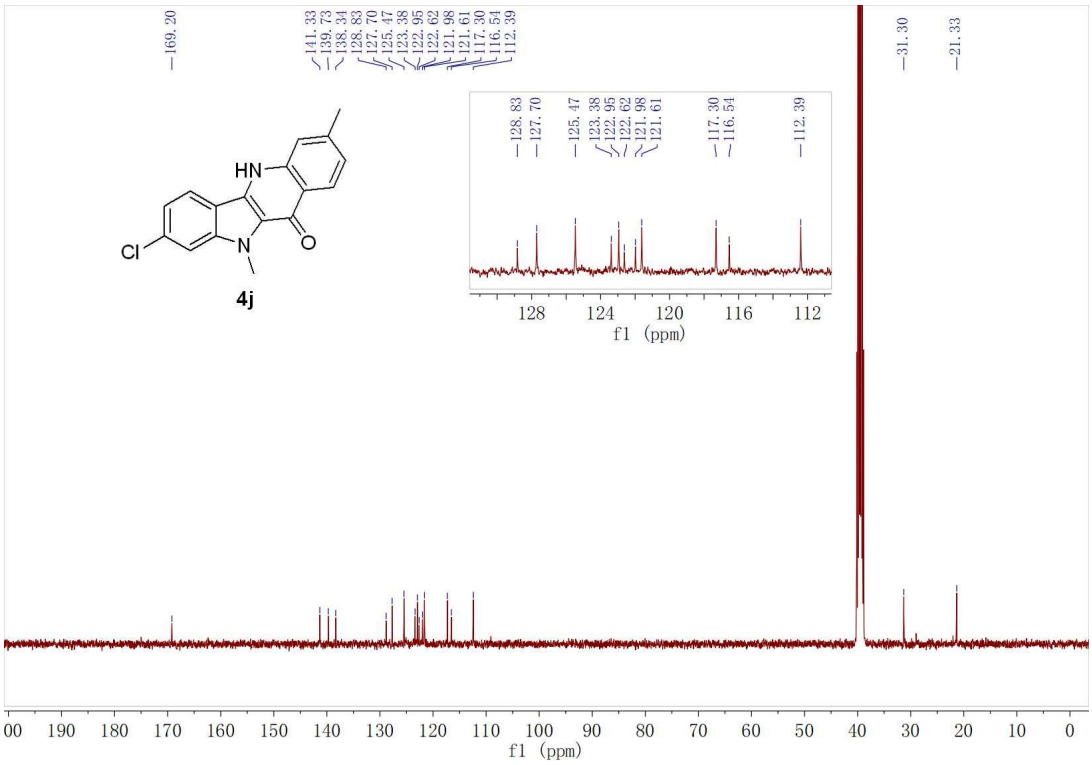
^{13}C NMR (100 MHz, DMSO)



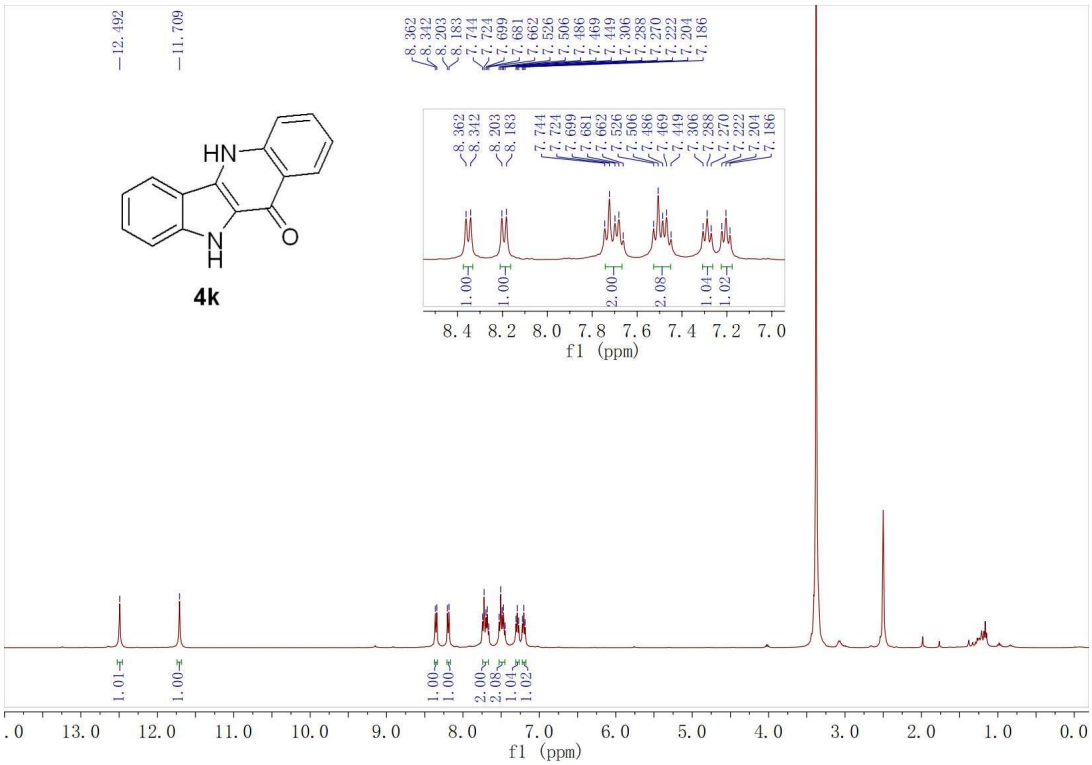
^{1}H NMR (400 MHz, DMSO)



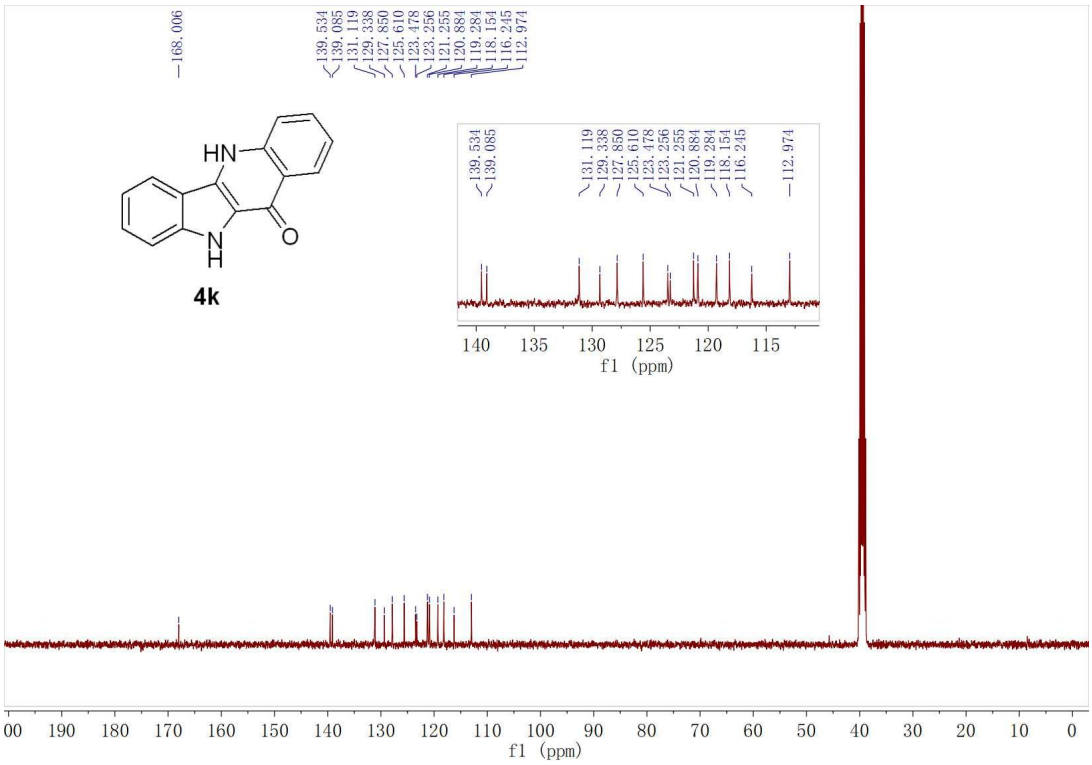
^{13}C NMR (100 MHz, DMSO)



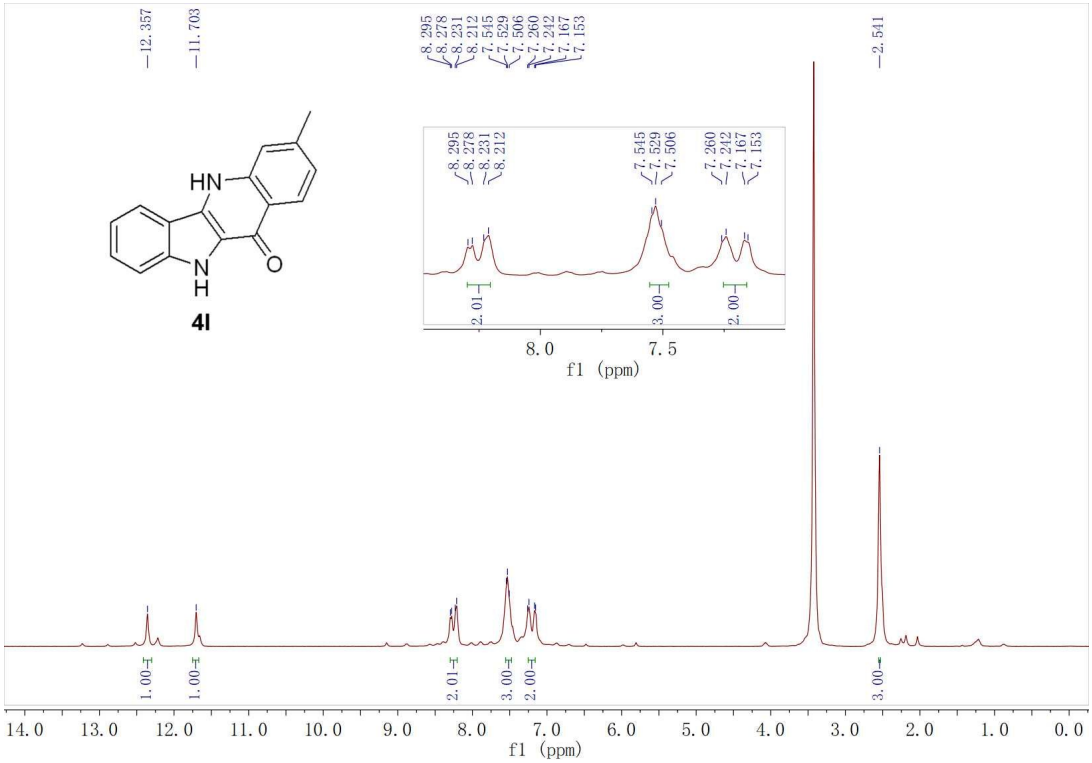
^{1}H NMR (400 MHz, DMSO)



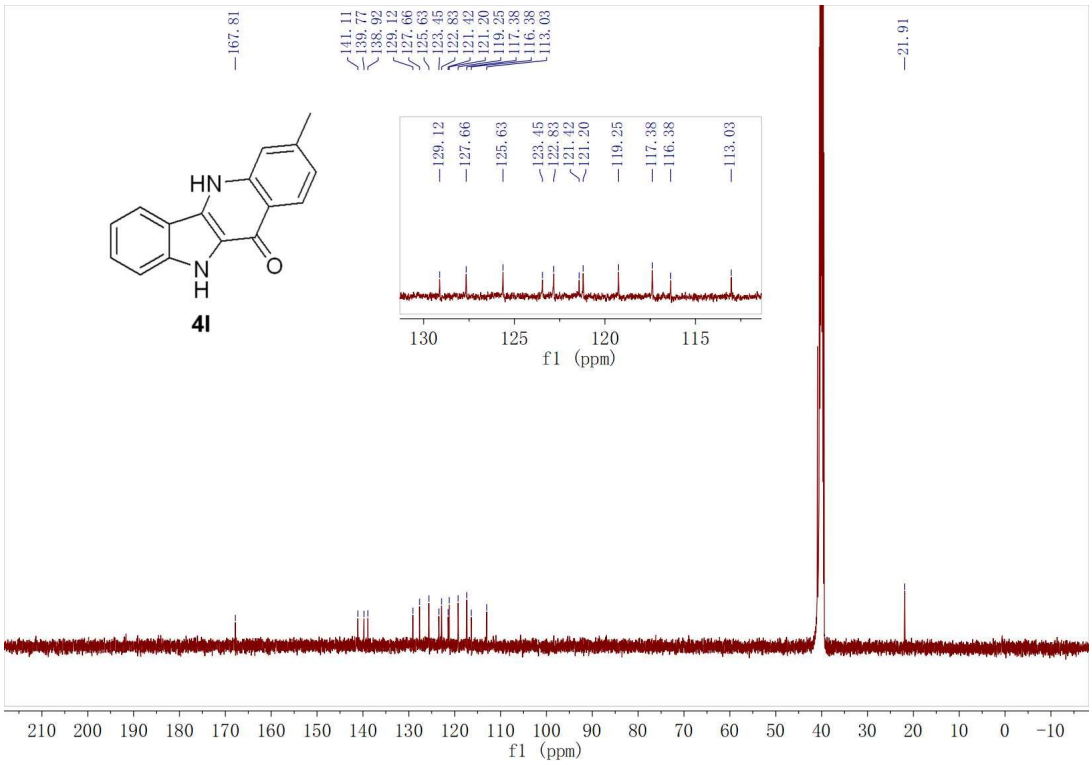
^{13}C NMR (100 MHz, DMSO)



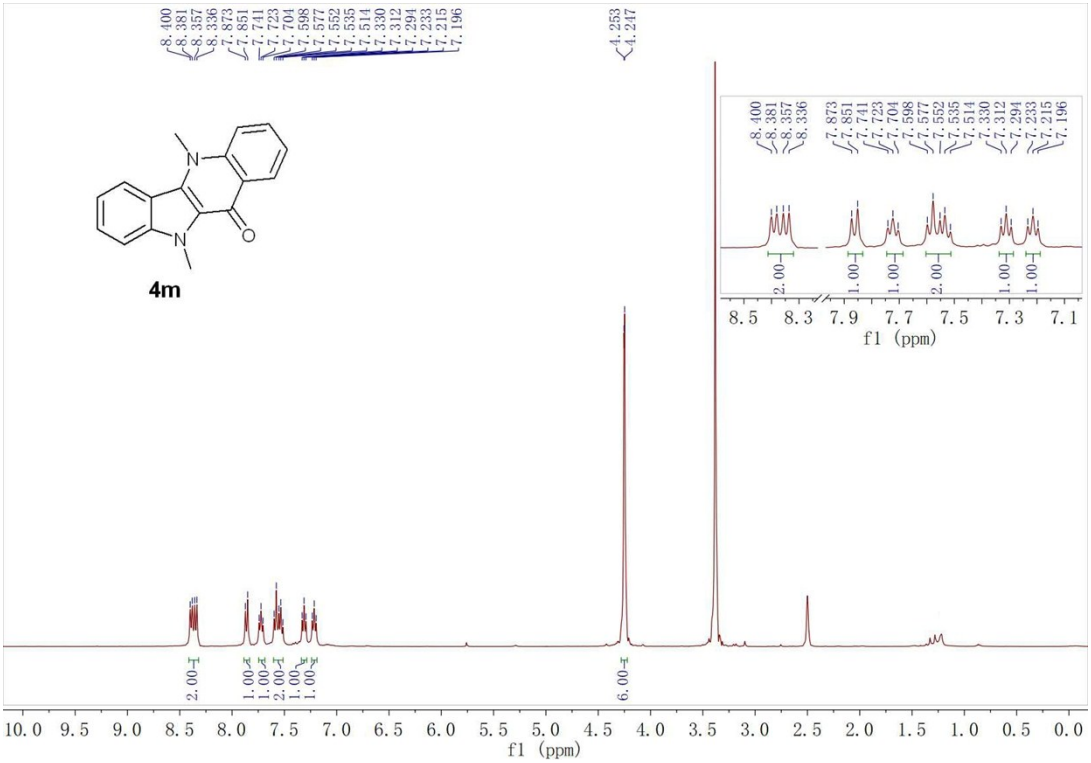
^{1}H NMR (400 MHz, DMSO)



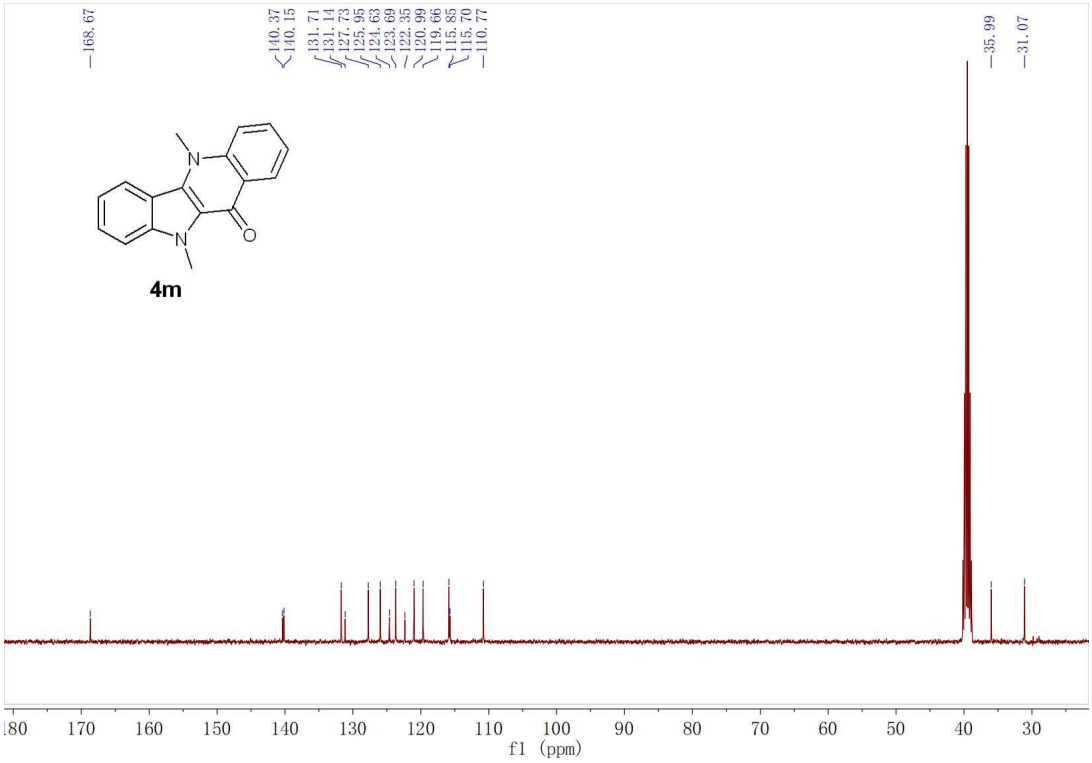
^{13}C NMR (125 MHz, DMSO)



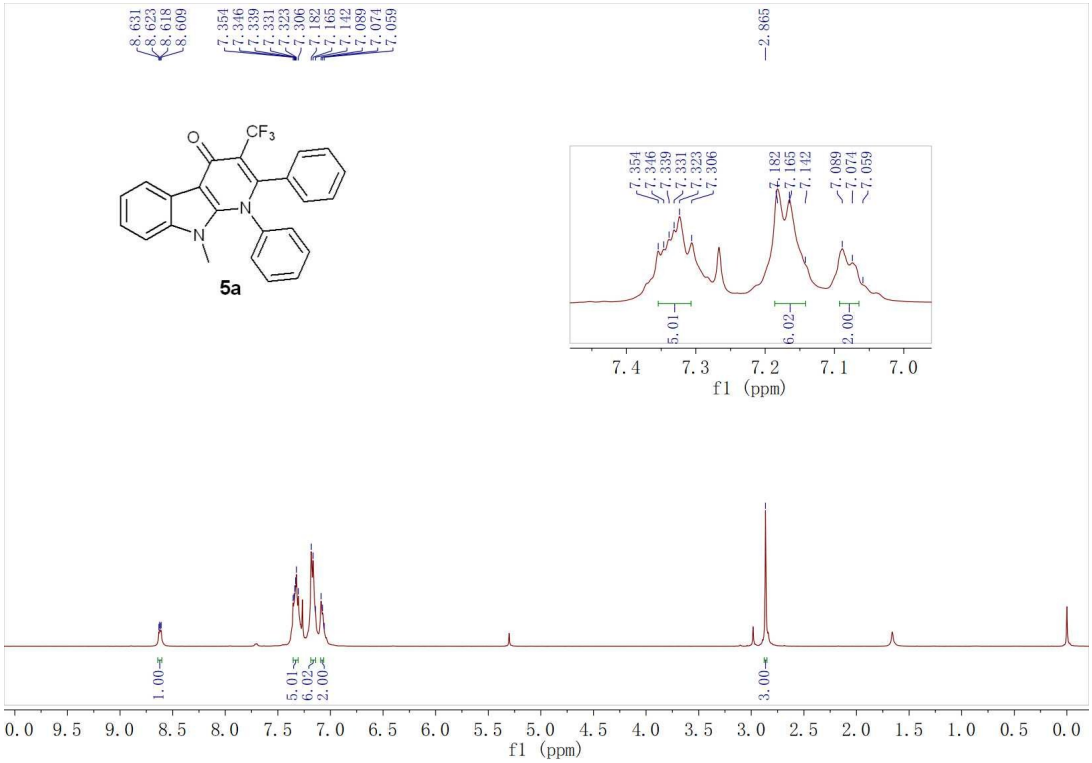
^{1}H NMR (400 MHz, $CDCl_3$)



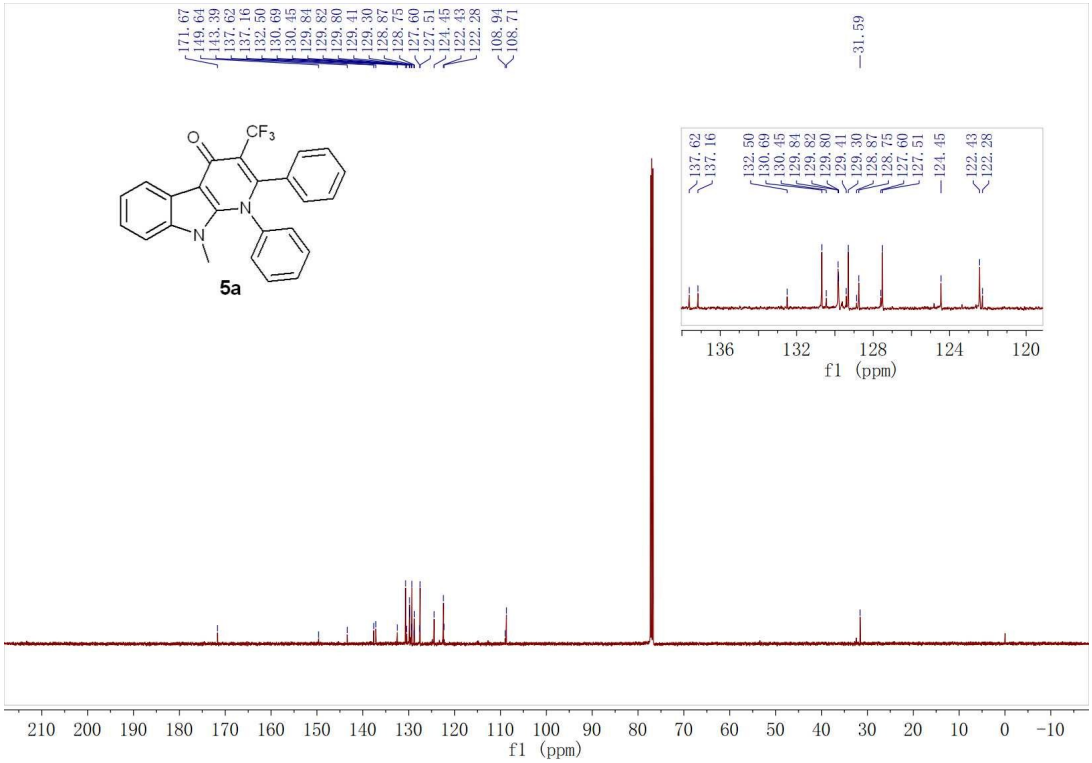
^{13}C NMR (100 MHz, $CDCl_3$)



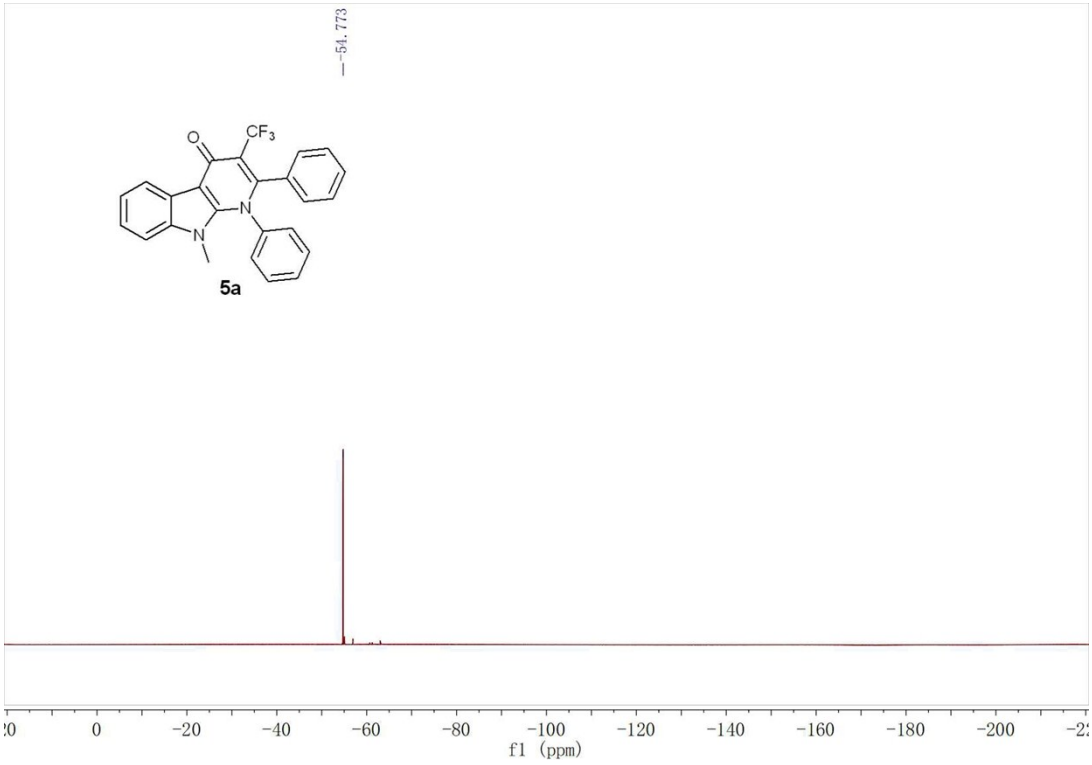
^{1}H NMR (400 MHz, $CDCl_3$)



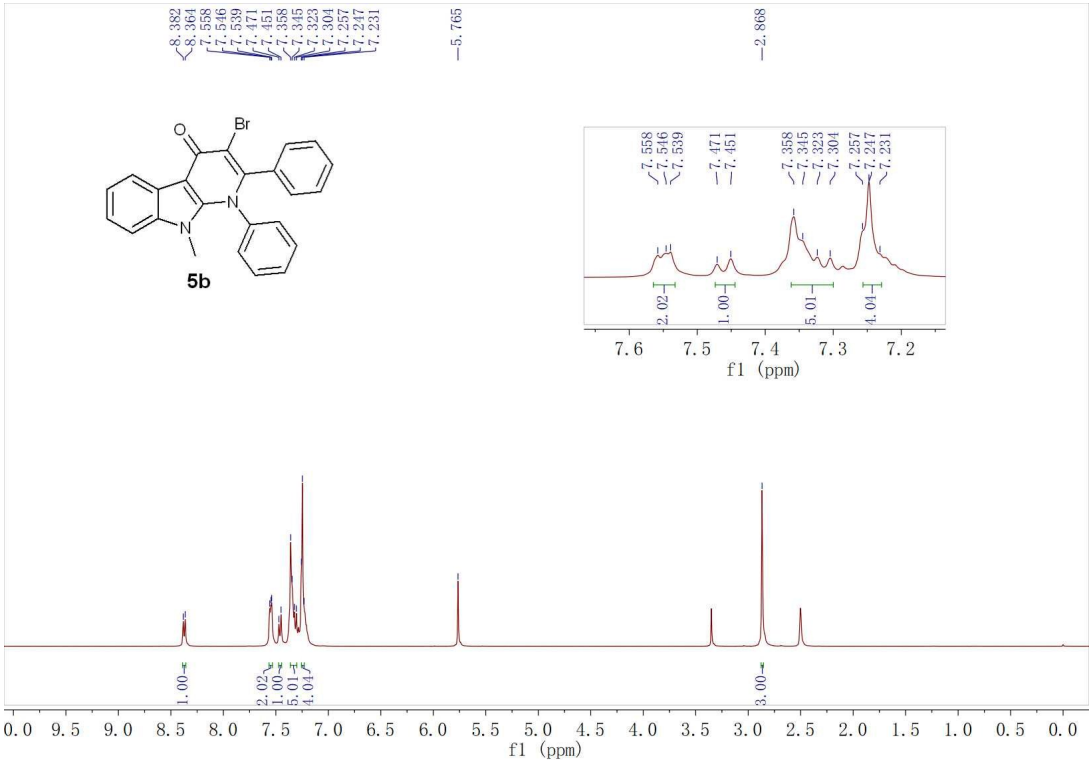
^{13}C NMR (100 MHz, $CDCl_3$)



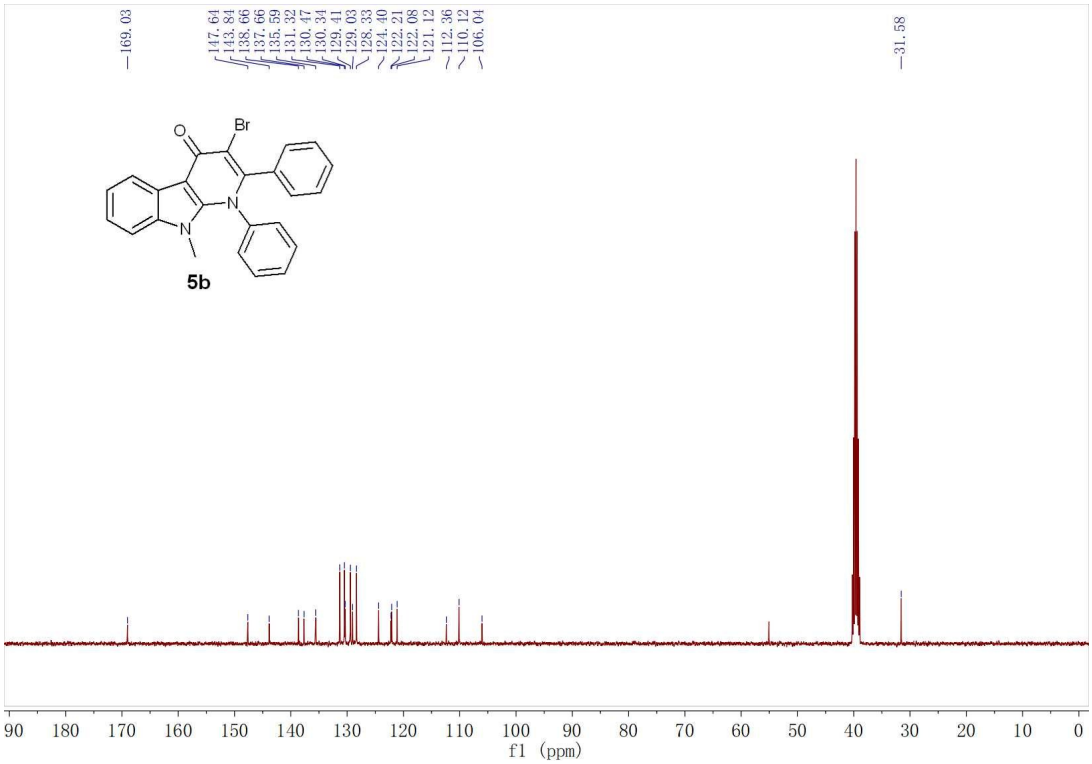
^{19}F NMR (476.2 MHz, $CDCl_3$)



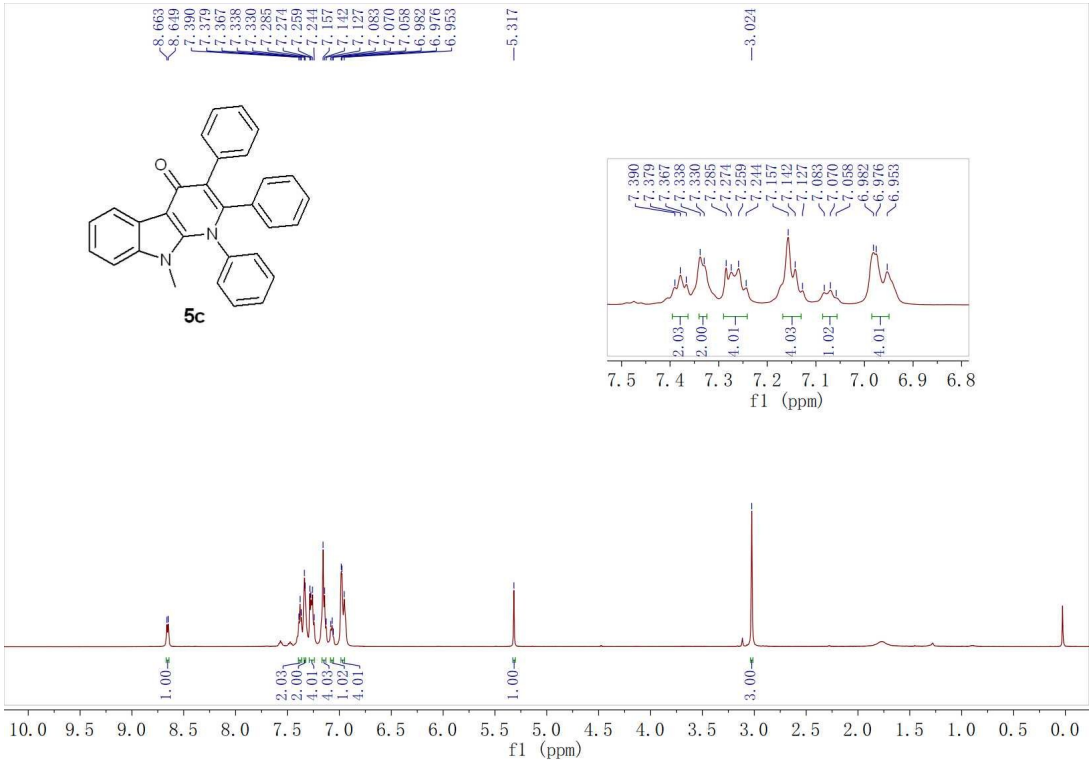
^{1}H NMR (400 MHz, DMSO)



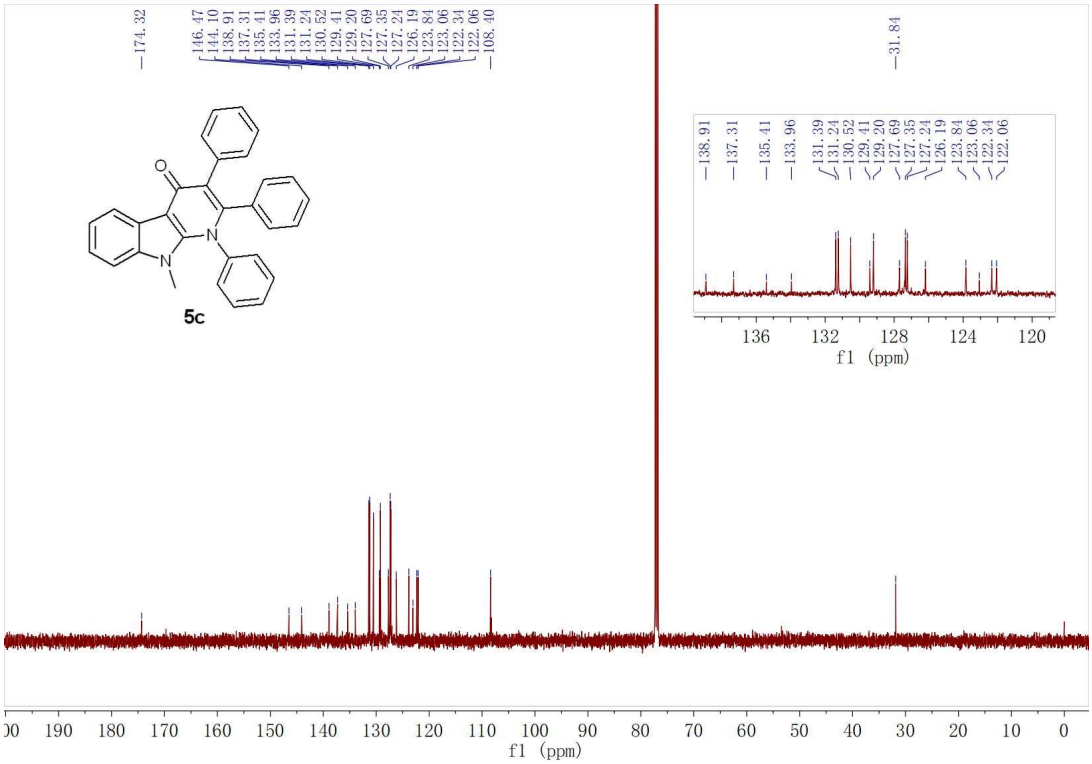
^{13}C NMR (100 MHz, DMSO)



^{1}H NMR (500 MHz, $CDCl_3$)

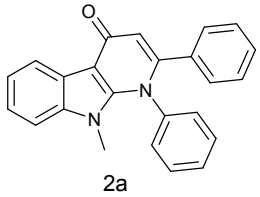


^{13}C NMR (125 MHz, $CDCl_3$)



10. X-ray crystallography of compounds 2a

9-Mthyl-1,2-diphenyl-1,9-dihydro-4*H*-pyrido[2,3-*b*]indol-4-one(2a, CCDC: 1943909)
(Ortep ellipsoids are depicted at the 50% level)

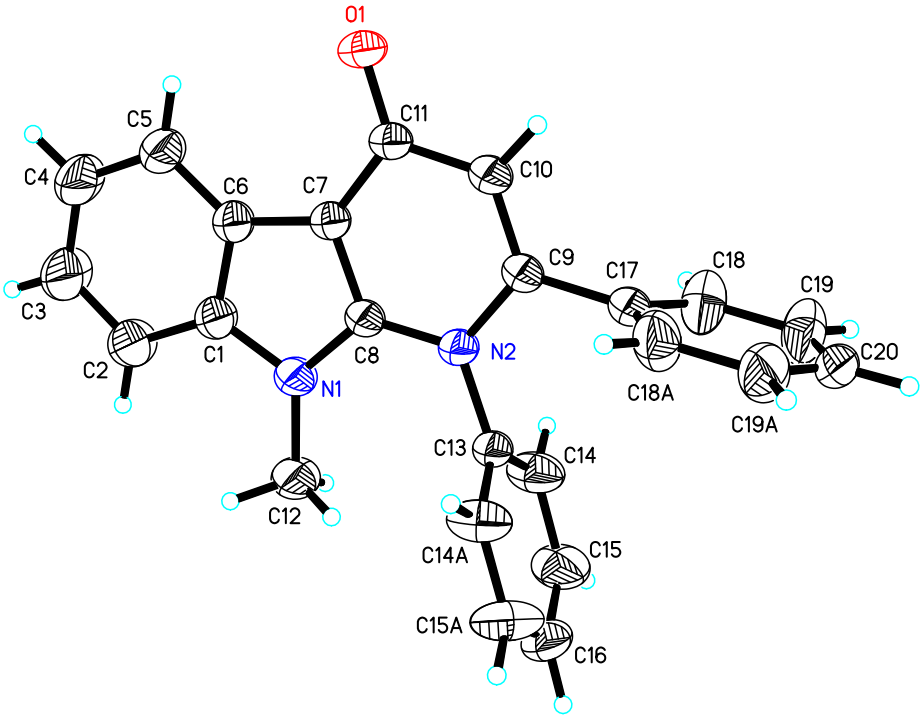


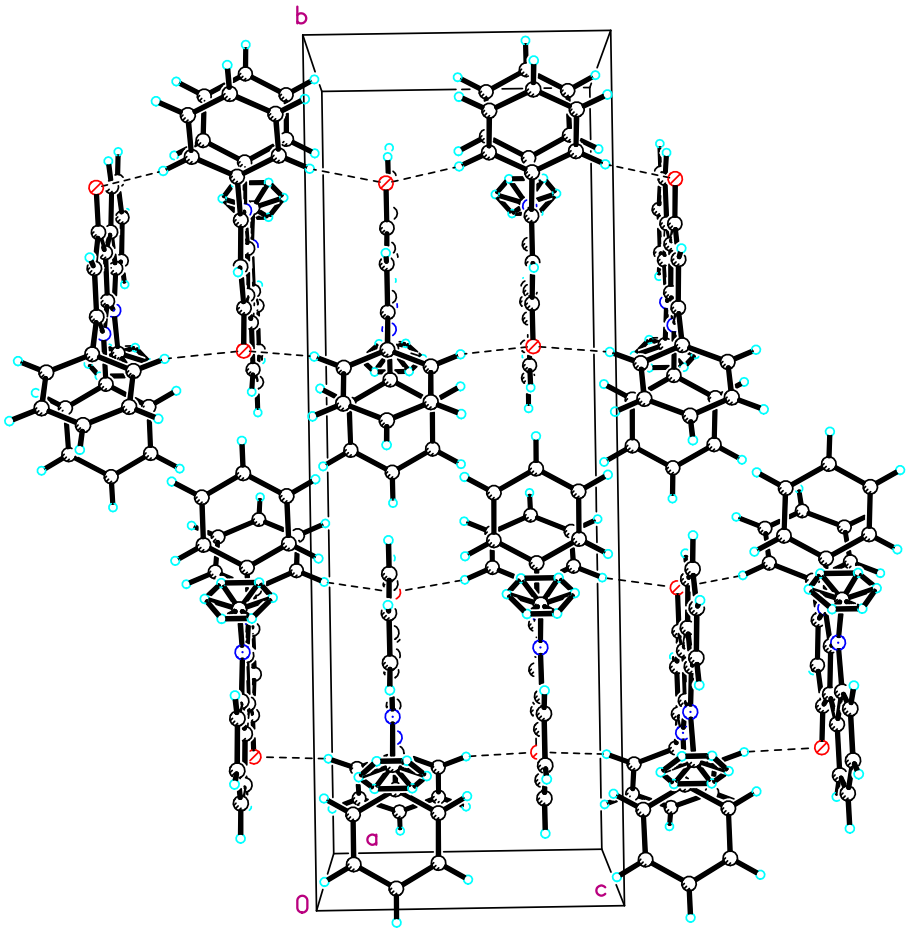
2a

Table S1. Crystal data and structure refinement for **2a**.

Identification code	**2a**
Empirical formula	$C_{24}H_{18}N_2O$
Formula weight	350.40
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system Space group	Orthorhombic P b c m
Unit cell dimensions	a = 9.9294(3) Å α= 90°. b = 22.8248(8) Å β=90°. c = 8.0346(3) Å γ = 90°.
Volume	1820.93(11) $Å^3$
Z	4
Density (calculated)	1.278 Mg/m^3
Absorption coefficient	0.079 mm^{-1}
F(000)	736
Crystal size	0.200 x 0.150 x 0.100 mm^3
Theta range for data collection	2.237 to 25.000°.
Index ranges	-11<=h<=11, -27<=k<=27, -9<=l<=9
Reflections collected	44964
Independent reflections	1722 [R(int) = 0.0633]
Completeness to theta = 25.242°	96.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5617
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1722 / 0 / 153
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1542
R indices (all data)	R1 = 0.0574, wR2 = 0.1661
Extinction coefficient	0.126(17)

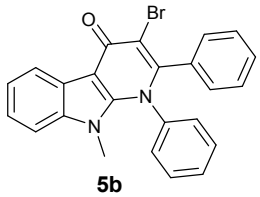
Largest diff. peak and hole	0.190 and -0.128 e.Å^{-3}





11. X-ray crystallography of compounds 5b

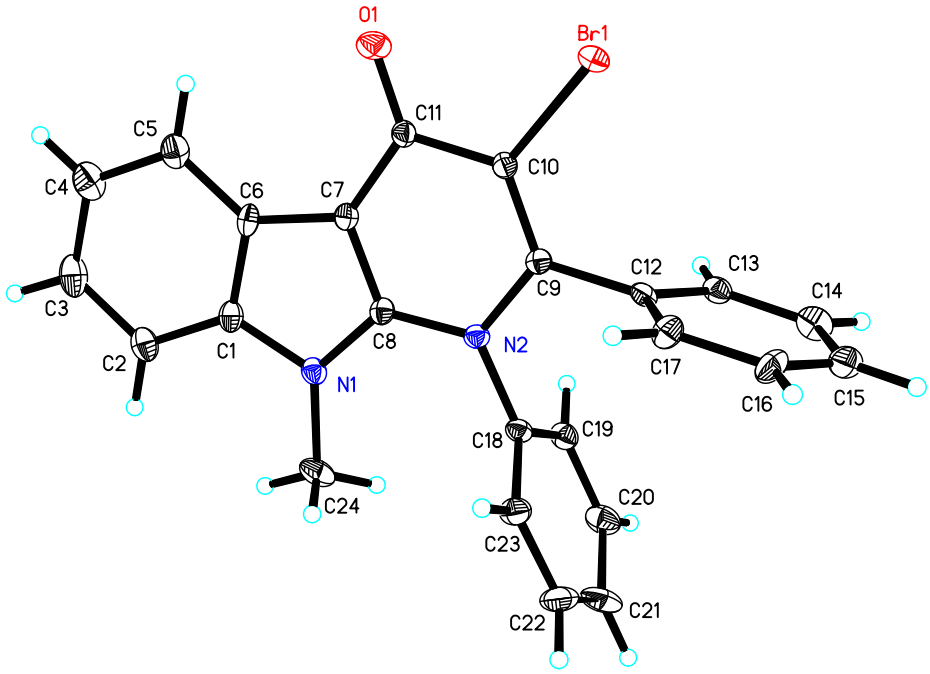
3-Bomo-9-methyl-1,2-diphenyl-1,9-dihydro-4*H*-pyrido[2,3-*b*]indol-4-one (5b, CCDC: 1943920)
(Ortep ellipsoids are depicted at the 50% level)

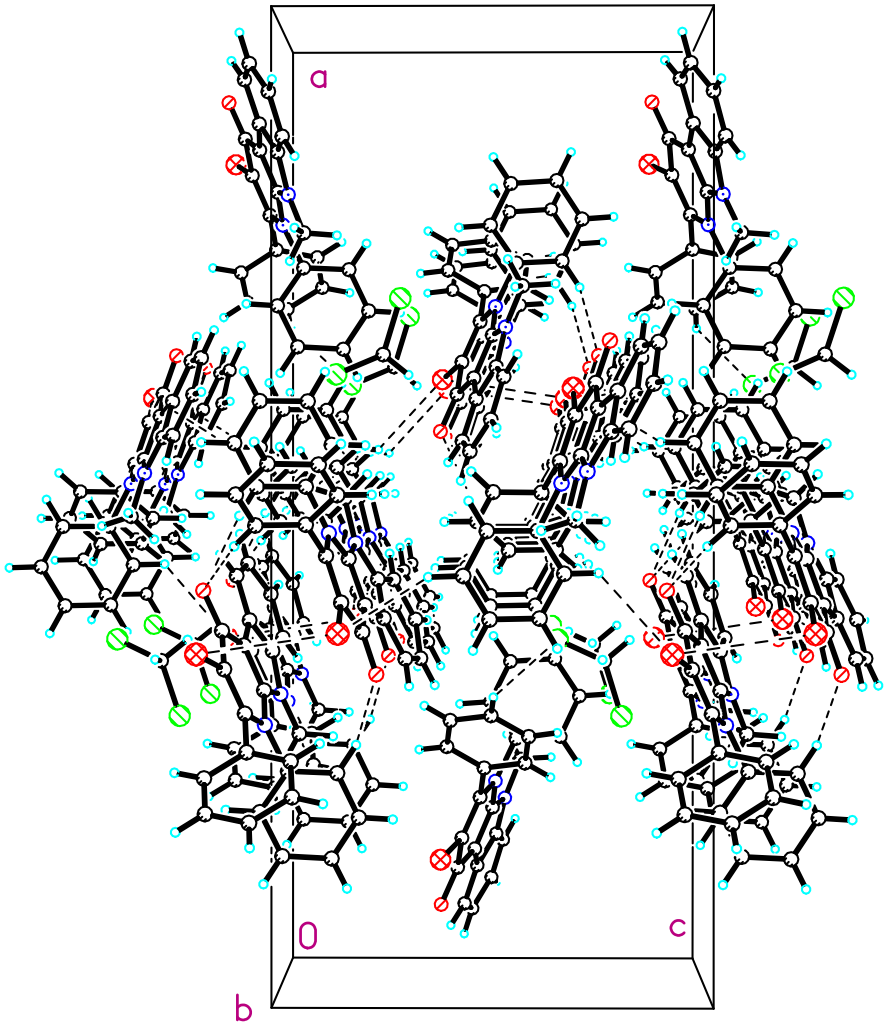


5b

Table S2. Crystal data and structure refinement for **5b**.

Identification code	**5b**
Empirical formula	$C_{24}H_{18}BrN_2O$
Formula weight	471.77
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system Space group	Orthorhombic P c a 21
Unit cell dimensions	a = 29.0281(10) Å α= 90°. b = 11.0265(3) Å β=90°. c = 12.8199(4) Å γ = 90°.
Volume	4103.4(2) $Å^3$
Z	8
Density (calculated)	1.527 Mg/m^3
Absorption coefficient	2.153 mm^{-1}
F(000)	1912
Crystal size	0.180 x 0.150 x 0.120 mm^3
Theta range for data collection	2.535 to 25.999°.
Index ranges	-35<=h<=35, -12<=k<=13, -15<=l<=15
Reflections collected	37638
Independent reflections	8004 [R(int) = 0.0511]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5705
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8004 / 13 / 535
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0744
R indices (all data)	R1 = 0.0431, wR2 = 0.0783
Extinction coefficient	0.018(4)
Largest diff. peak and hole	1.375 and -1.337 $e.Å^{-3}$


O1
Br1
C11
C10
C5
C4
C6
C7
C12
C13
C14
C9
C3
C8
N2
C17
C2
C1
N1
C16
C15
C18
C19
C24
C20
C23
C21
C22


a
0
c
b