Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Base-promoted fused *β*-carboline formation from 2-(1*H*-indol-3-yl)cyclohexan-1-ones, aldehydes and ammonium salts

Jinjin Chen,‡[a,b] Yu Zhang,‡[a] Xinping Liu,*[,a] Kang Liu,[a] Junting Wu,[a] Xinlei Peng[a] and Guo-Jun Deng*[,b]

[a] *School of Pharmaceutical Science, Hengyang Medical School, University of South China, Hengyang 421001, China. E-mail: xinpingliu@usc.edu.cn.*

[b] *Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China. E-mail: gjdeng@xtu.edu.cn.*

‡ *These authors contributed equally.*

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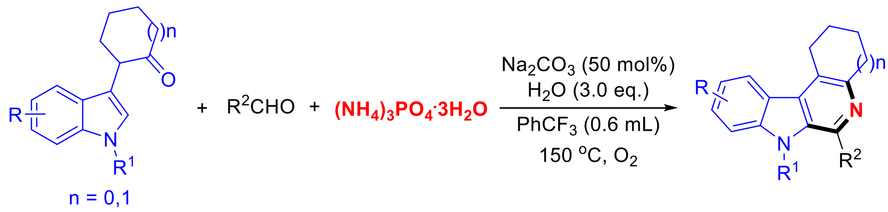
1. General information

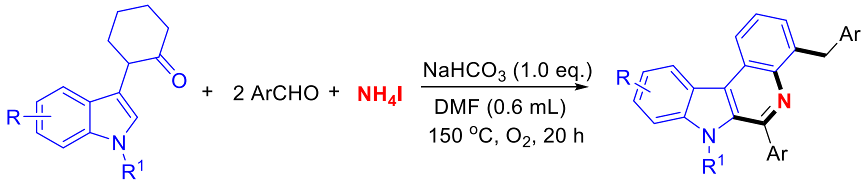
All reactions were carried out under an atmosphere of air unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform. High-resolution mass spectra (HRMS) was performed on FTMS ICR MS BRUKER 7T or Agilent 6230 TOF LC/MS. Melting points were measured on BÜCHI B-545 melting point instrument and were uncorrected. The structure of known compounds was further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature.

2. General procedure for the synthesis of *β*-carbolines.



A 10 mL oven-dried reaction vessel was charged with 2-(1*H*-indol-3-yl)cyclohexan-1-ones (0.2 mmol), aldehydes (0.4 mmol), $(NH_4)_3PO_4\cdot3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 °C for 12 h under oxygen atmosphere. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel to give the products.

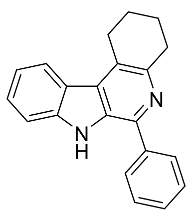
3. General procedure for the synthesis of Benzo-*β*-carbolines.



A 10 mL oven-dried reaction vessel was charged with 2-(1*H*-indol-3-yl)cyclohexan-1-ones (0.2 mmol), aldehydes (0.6 mmol), NH_4I (0.4 mmol, 58.0 mg), $NaHCO_3$ (0.2 mmol, 16.8 mg), and DMF (0.6 mL). The reaction vessel stirred at 150 °C for 20 h under oxygen atmosphere. After cooling to room temperature, the reaction was diluted with ethyl acetate (6 mL) and washed with saturated salt water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over sodium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel to give the products.

4. Characterization of products

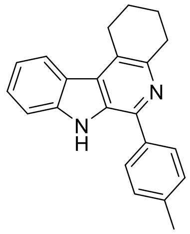
6-phenyl-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3a)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), benzaldehyde (**2a,** 0.4 mmol, 40.8 μL), $(NH_4)_3PO_4{\cdot}3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 °C for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3a** as white solid, yield: 53.6 mg (90%), mp 196-199 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.42 (s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 7.1 Hz, 2H), 7.58 – 7.43 (m, 5H), 7.29 (d, J = 7.8 Hz, 1H), 3.41 (t, J = 5.6 Hz, 2H), 3.16 (t, J = 5.6 Hz, 2H), 2.06 – 2.03 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.8, 140.5, 139.9, 138.8, 131.7, 129.2, 128.4, 128.4, 128.2, 127.5, 125.4, 124.0, 122.6, 119.9, 111.2, 32.7, 27.1, 23.4, 22.8. HRMS (ESI) m/z calcd for $C_{21}H_{19}N_2^+$ $[M+H]^+$ 299.1543, found 299.1543.

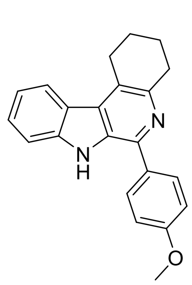
6-(*p*-Tolyl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3b)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 4-methylbenzaldehyde (**2b,** 0.4 mmol, 47.3 μL), $(NH_4)_3PO_4{\cdot}3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 °C for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3b** as white solid, yield: 54.1 mg (87%), mp 253-256 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.49 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.9 Hz, 2H), 7.52 – 7.44 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 3.39 (t, *J* = 5.8 Hz, 2H), 3.15 (t, *J* = 5.6 Hz, 2H), 2.41 (s, 3H), 2.04 – 2.01 (m, 4H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.6, 140.4, 140.1, 138.2, 135.9, 131.7, 129.7, 128.3, 128.0, 127.3, 125.1, 123.9, 122.6, 119.7, 111.2, 32.7, 27.1, 23.4, 22.8, 21.3. HRMS (ESI) m/z calcd for $C_{22}H_{21}N_2^+$ $[M+H]^+$ 313.1699, found 313.1699.

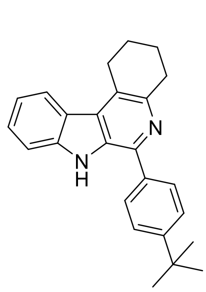
6-(4-Methoxyphenyl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3c)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 4-methoxybenzaldehyde (**2c,** 0.4 mmol, 48.6 μL), $(NH_4)_3PO_4{\cdot}3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3c** as white solid, yield: 54.8 mg (84%), mp 233-236 °C.

^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.57 (s, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.51 – 7.43 (m, 2H), 7.28 – 7.23 (m, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 3.38 (t, *J* = 5.5 Hz, 2H), 3.14 (t, *J* = 5.4 Hz, 2H), 2.03 – 2.00 (m, 4H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$, ppm): δ 159.7, 146.5, 140.5, 139.8, 131.6, 131.3, 129.4, 128.2, 127.3, 124.8, 123.9, 122.6, 119.7, 114.4, 111.2, 55.3, 32.6, 27.1, 23.4, 22.8. HRMS (ESI) m/z calcd for $C_{22}H_{21}N_2O^+$ $[M+H]^+$ 329.1648, found 329.1655.

6-(4-(*tert*-Butyl)phenyl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3d)

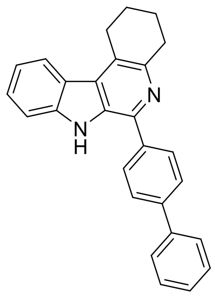


The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 4-*tert*-butylbenzaldehyde (**2d,** 0.4 mmol, 66.5 μL), $(NH_4)_3PO_4{\cdot}3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3d** as yellow solid, yield: 58.7 mg (83%), mp 111-114 °C.

^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.53 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.42 (m, 2H), 7.27 (d, *J* = 7.1 Hz, 1H), 3.39 (t, *J* = 5.8 Hz, 2H), 3.16

(t, J = 5.6 Hz, 2H), 2.04 – 2.01 (m, 4H), 1.35 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 151.4, 146.6, 140.5, 140.0, 135.8, 131.7, 128.3, 127.8, 127.3, 126.0, 125.1, 123.9, 122.6, 119.7, 111.2, 34.7, 32.6, 31.3, 27.1, 23.4, 22.8. HRMS (ESI) m/z calcd for $C_{25}H_{27}N_2^+$ $[M+H]^+$ 355.2169, found 355.2178.

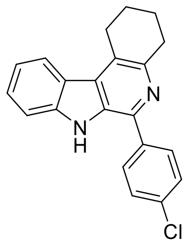
6-([1,1'-Biphenyl]-4-yl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3e)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 4-biphenylcarboxaldehyde (**2e,** 0.4 mmol, 72.9 mg), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3e** as yellow solid, yield: 56.0 mg (75%), mp 214-217 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.59 (s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 7.3 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 3.41 (t, J = 5.8 Hz, 2H), 3.18 (t, J = 5.8 Hz, 2H), 2.05 – 2.02 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6, ppm): δ 145.1, 141.3, 139.8, 138.5, 137.6, 131.5, 129.1, 128.9, 127.8, 127.7, 127.3, 126.9, 126.7, 124.7, 123.5, 121.4, 119.4, 119.4, 112.3, 32.3, 26.5, 23.1, 22.5. HRMS (ESI) m/z calcd for $C_{27}H_{23}N_2^+$ $[M+H]^+$ 375.1856, found 375.1866.

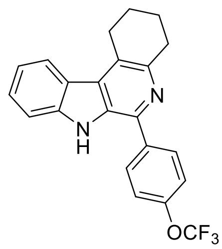
6-(4-Chlorophenyl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3f)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 4-chlorobenzaldehyde (**2f,** 0.4 mmol, 56.2 mg), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to yield the desired product **3f** as white solid, yield: 54.4 mg (82%), mp 197-199 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.61 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.51 (t, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 7.2 Hz, 1H), 3.39 (t, J = 5.0 Hz, 2H), 3.13 (t, J = 5.7 Hz, 2H), 2.05 – 1.98 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.8, 140.6, 138.5, 137.1, 134.2, 131.7, 129.4, 129.1, 128.7, 127.6, 125.8, 124.0, 122.5, 119.9, 111.3, 32.5, 27.1, 23.3, 22.7. HRMS (ESI) m/z calcd for $C_{21}H_{18}ClN_2^+$ $[M+H]^+$ 333.1153, found 333.1160.

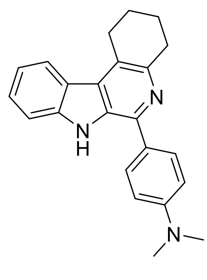
6-(4-(Trifluoromethoxy)phenyl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3g)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 4-trifluoromethoxybenzaldehyde (**2g,** 0.4 mmol, 57.1 μL), $(NH_4)_3PO_4 \cdot 3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3g** as white solid, yield: 61.3 mg (80%), mp 139-142 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.55 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.6 Hz, 2H), 7.50 (t, J = 7.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.33 – 7.25 (m, 3H), 3.39 (t, J = 5.6 Hz, 2H), 3.14 (t, J = 5.3 Hz, 2H), 2.06 – 1.99 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 149.1, 146.9, 140.6, 138.3, 137.5, 131.7, 129.6, 128.7, 127.6, 125.9, 124.0, 122.5, 121.5, 120.4 (q, J = 255.8 Hz), 120.0, 111.3, 32.6, 27.1, 23.3, 22.7. ^{19}F NMR (471 MHz, $CDCl_3$, ppm) δ -62.5. HRMS (ESI) m/z calcd for $C_{22}H_{18}F_3N_2O^+$ $[M+H]^+$ 383.1366, found 383.1375.

***N*,*N*-Dimethyl-4-(2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolin-6-yl)aniline (3h)**

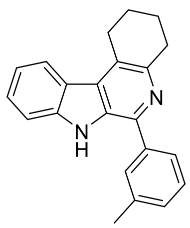


The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), *p*-dimethylaminobenzaldehyde (**2h,** 0.4 mmol, 59.7 mg), $(NH_4)_3PO_4 \cdot 3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) to yield the desired product **3h** as white solid, yield: 29.0 mg (43%), mp 216-219 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.62 (s, 1H), 8.19 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.7 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.27 – 7.22 (m, 1H), 6.81 (d, J = 8.7 Hz, 2H), 3.37 (t, J = 5.4 Hz, 2H), 3.15 (t,

J = 5.4 Hz, 2H), 2.97 (s, 6H), 2.03 – 1.99 (m, 4H). $^{13}C\ \{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 150.5, 146.2, 140.5, 140.4, 131.6, 129.0, 128.1, 127.1, 126.5, 124.1, 123.9, 122.6, 119.6, 112.7, 111.2, 40.4, 32.5, 27.0, 23.4, 22.8. HRMS (ESI) m/z calcd for $C_{23}H_{24}N_3^+$ $[M+H]^+$ 342.1965, found 342.1970.

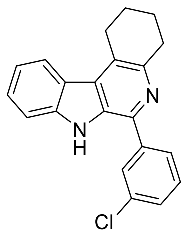
6-(*m*-Tolyl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3i)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 3-methylbenzaldehyde (**2i,** 0.4 mmol, 47.2 μL), $(NH_4)_3PO_4 \cdot 3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to yield the desired product **3i** as white solid, yield: 50.6 mg (81%), mp 170-173 °C.

^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.50 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.69 (s, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.28 – 7.21 (m, 2H), 3.39 (t, J = 5.2 Hz, 2H), 3.16 (t, J = 5.1 Hz, 2H), 2.43 (s, 3H), 2.03 (s, 4H). $^{13}C\ \{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 146.6, 140.4, 140.1, 138.9, 138.6, 131.7, 129.1, 129.0, 128.8, 128.3, 127.4, 125.3, 125.0, 124.0, 122.6, 119.7, 111.2, 32.6, 27.1, 23.4, 22.8, 21.5. HRMS (ESI) m/z calcd for $C_{22}H_{21}N_2^+$ $[M+H]^+$ 313.1699, found 313.1699.

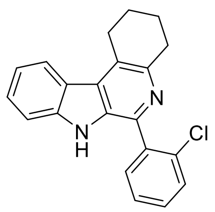
6-(3-Chlorophenyl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3j)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 3-chlorobenzaldehyde (**2j,** 0.4 mmol, 45.3 μL), $(NH_4)_3PO_4 \cdot 3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to yield the desired product **3j** as white solid, yield: 57.0 mg (86%), mp 149-152 °C.

^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.55 (s, 1H), 8.20 (d, J = 7.9 Hz, 1H), 7.86 (s, 1H), 7.74 (d, J = 7.3 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.42 – 7.34 (m, 2H), 7.30 – 7.24 (m, 1H), 3.39 (t, J = 5.8 Hz, 2H), 3.15 (t, J = 5.6 Hz, 2H), 2.03 (s, 4H). $^{13}C\ \{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 146.9, 140.5, 138.2, 135.0, 131.7, 130.2, 128.7, 128.3, 128.3, 127.6, 126.2, 126.0, 124.0, 122.5, 120.0, 111.3, 32.6, 27.1, 23.3, 22.7. HRMS (ESI) m/z calcd for $C_{21}H_{18}ClN_2^+$ $[M+H]^+$ 333.1153, found 333.1160.

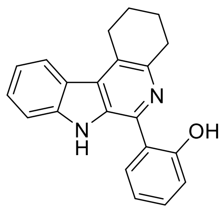
6-(2-Chlorophenyl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3k)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 2-chlorobenzaldehyde (**2k,** 0.4 mmol, 45.1 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 °C for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3k** as white solid, yield: 52.3 mg (79%), mp 219-222 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.21 (d, J = 8.0 Hz, 1H), 8.06 (s, 1H), 7.59 – 7.56 (m, 1H), 7.55 – 7.52 (m, 1H), 7.49 (d, J = 7.4 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.29 – 7.24 (m, 1H), 3.43 (t, J = 5.8 Hz, 2H), 3.14 (t, J = 5.6 Hz, 2H), 2.08 – 2.01 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.5, 140.5, 138.1, 137.2, 132.9, 132.2, 132.2, 129.9, 129.8, 128.0, 127.5, 127.4, 126.0, 124.0, 122.4, 119.8, 111.2, 32.5, 27.1, 23.3, 22.7. HRMS (ESI) m/z calcd for $C_{21}H_{18}ClN_2^+$ $[M+H]^+$ 333.1153, found 333.1160.

2-(2,3,4,7-Tetrahydro-1*H*-indolo[2,3-*c*]quinolin-6-yl)phenol (3l)

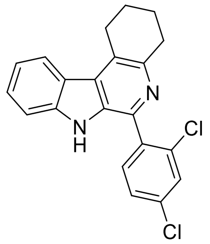


The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 2-hydroxybenzaldehyde (**2l,** 0.4 mmol, 42.6 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 °C for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3l** as yellow solid, yield: 40.0 mg (64%), mp 226-229 °C.

^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 14.15 (s, 1H), 11.63 (s, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.63 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 3.40 (d, J = 5.8 Hz, 2H), 3.07 (t, J = 5.4 Hz, 2H), 2.06 – 1.99 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 158.9, 143.4, 140.8, 138.6, 130.4, 130.1, 129.7, 127.8, 126.4, 125.5, 123.9, 122.0, 120.2, 119.9, 118.9, 118.4, 111.6, 31.5, 26.8, 22.8, 22.5. HRMS (ESI) m/z calcd for $C_{21}H_{19}N_2O^+$ $[M+H]^+$ 315.1492, found

315.1502.

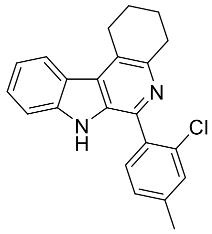
6-(2,4-Dichlorophenyl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3m)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 2,4-dichlorobenzaldehyde (**2m,** 0.4 mmol, 70.0 mg), $(NH_4)_3PO_4\cdot 3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 °C for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to yield the desired product **3m** as white solid, yield: 66.4 mg (91%), mp 260-263 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.22 (d, J = 8.0 Hz, 1H), 8.04 (s, 1H), 7.57 – 7.49 (m, 3H), 7.45 (d, J = 8.1 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 3.43 (t, J = 5.6 Hz, 2H), 3.14 (t, J = 5.5 Hz, 2H), 2.08 – 2.04 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.6, 146.0, 136.9, 135.7, 135.1, 133.6, 132.9, 132.2, 129.6, 128.2, 127.7, 127.6, 126.4, 124.0, 122.3, 119.9, 111.3, 32.4, 27.1, 23.2, 22.6. HRMS (ESI) m/z calcd for $C_{21}H_{17}Cl_2N_2^+$ $[M+H]^+$ 367.0763, found 367.0775.

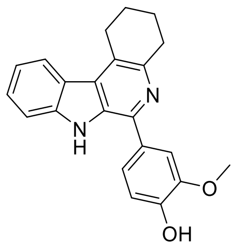
6-(2-Chloro-4-methylphenyl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3n)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 2-chloro-4-methylbenzaldehyde (**2n,** 0.4 mmol, 61.8 mg), $(NH_4)_3PO_4\cdot 3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 °C for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3n** as yellow solid, yield: 66.3 mg (96%), mp 293-295 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.21 (d, J = 8.0 Hz, 1H), 8.03 (s, 1H), 7.52 – 7.42 (m, 3H), 7.37 (s, 1H), 7.29 – 7.25 (m, 1H), 7.22 (d, J = 7.6 Hz, 1H), 3.43 (t, J = 5.6 Hz, 2H), 3.16 (t, J = 5.2 Hz, 2H), 2.42 (s, 3H), 2.06 – 2.01 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.4, 140.5, 140.2, 138.3, 134.2, 132.5, 132.3, 131.8, 130.3, 128.2, 127.9, 127.4, 125.8, 123.9, 122.4, 119.7, 111.2, 32.5, 27.1, 23.3, 22.7, 21.0. HRMS (ESI) m/z calcd for $C_{22}H_{20}ClN_2^+$ $[M+H]^+$ 347.1310, found 347.1323.

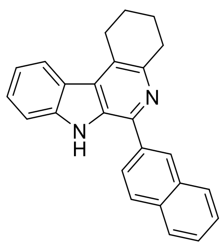
2-Methoxy-4-(2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolin-6-yl)phenol (3o)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 4-hydroxy-3-methoxybenzaldehyde (**2o,** 0.4 mmol, 60.9 mg), $(NH_4)_3PO_4 \cdot 3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 °C for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) to yield the desired product **3o** as white solid, yield: 29.9 mg (43%).

^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 11.29 (s, 1H), 9.33 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.38 (d, J = 8.1 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 3.88 (s, 3H), 3.31 (t, J = 5.8 Hz, 2H), 3.00 (t, J = 5.8 Hz, 2H), 1.96 – 1.90 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6, ppm): δ 147.7, 147.1, 144.7, 144.3, 139.6, 131.2, 129.7, 127.6, 127.2, 123.9, 123.5, 121.5, 121.2, 119.3, 115.6, 112.4, 112.3, 55.6, 32.2, 26.5, 23.1, 22.6. HRMS (ESI) m/z calcd for $C_{22}H_{21}N_2O_2^+$ [M+H]$^+$ 345.1598, found 345.1608.

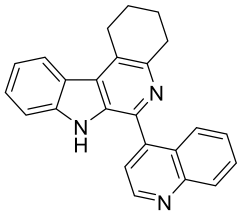
6-(Naphthalen-2-yl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3p)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 2-naphthaldehyde (**2p,** 0.4 mmol, 62.5 mg), $(NH_4)_3PO_4 \cdot 3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 °C for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3p** as yellow solid, yield: 56.0 mg (80%), mp 179-181 °C.

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.62 (s, 1H), 8.30 (s, 1H), 8.21 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.53 – 7.47 (m, 4H), 7.28 (t, J = 7.4 Hz, 1H), 3.40 (t, J = 5.5 Hz, 2H), 3.19 (t, J = 5.5 Hz, 2H), 2.06 – 2.03 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.8, 140.6, 139.8, 136.1, 133.4, 133.1, 132.0, 128.8, 128.5, 128.2, 127.7, 127.4, 127.1, 126.3, 126.1, 125.4, 124.0, 122.6, 119.8, 111.3, 32.7, 27.1, 23.4, 22.8. HRMS (ESI) m/z calcd for $C_{25}H_{21}N_2^+$ [M+H]$^+$ 349.1699, found 349.1716.

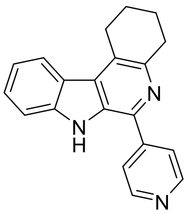
6-(Quinolin-4-yl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3q)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), quinoline-4-carbaldehyde (**2q,** 0.4 mmol, 62.9 mg), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) to yield the desired product **3q** as white solid, yield: 33.5 mg (48%), mp 294-296 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 10.89 (s, 1H), 8.45 (d, *J* = 4.3 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.35 (q, *J* = 7.7 Hz, 2H), 3.54 (t, *J* = 5.1 Hz, 2H), 3.20 (t, *J* = 5.5 Hz, 2H), 2.16 – 2.07 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): *δ* 148.6, 147.3, 146.2, 145.0, 141.7, 136.7, 133.5, 129.3, 128.5, 128.4, 127.7, 127.1, 126.6, 126.5, 125.9, 124.0, 122.1, 122.0, 119.7, 111.9, 32.6, 27.3, 23.4, 22.8. HRMS (ESI) m/z calcd for $C_{24}H_{20}N_3^+$ $[M+H]^+$ 350.1652, found 350.1663.

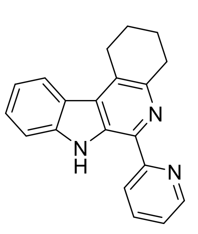
6-(Pyridin-4-yl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3r)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 4-pyridinecarboxaldehyde (**2r,** 0.4 mmol, 37.7 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) to yield the desired product **3r** as white solid, yield: 25.8 mg (43%), mp 278-280 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 9.76 (s, 1H), 8.61 (d, *J* = 5.6 Hz, 2H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 5.8 Hz, 2H), 7.54 (d, *J* = 3.8 Hz, 2H), 7.32 – 7.27 (m, 1H), 3.43 (t, *J* = 5.8 Hz, 2H), 3.17 (t, *J* = 5.6 Hz, 2H), 2.06 – 2.02 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): *δ* 149.9, 147.0, 146.7, 141.1, 136.4, 132.2, 129.2, 127.9, 127.1, 124.0, 123.1, 122.2, 120.1, 111.6, 32.6, 27.2, 23.3, 22.7. HRMS (ESI) m/z calcd for $C_{20}H_{18}N_3^+$ $[M+H]^+$ 300.1495, found 300.1508.

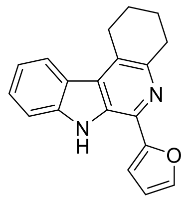
6-(Pyridin-2-yl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3s)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 2-pyridinecarboxaldehyde (**2s,** 0.4 mmol, 38.0 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3s** as white solid, yield: 19.5 mg (33%), mp 225-227 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 11.22 (s, 1H), 8.74 (t, *J* = 7.5 Hz, 2H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.85 (t, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.22 (m, 2H), 3.42 (t, *J* = 5.2 Hz, 2H), 3.17 (t, *J* = 5.6 Hz, 2H), 2.04 (p, *J* = 3.2 Hz, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): *δ* 158.3, 148.2, 145.6, 140.7, 136.7, 134.8, 133.2, 128.9, 127.6, 127.3, 123.8, 122.4, 121.8, 121.0, 119.3, 111.6, 32.9, 27.3, 23.5, 22.9. HRMS (ESI) m/z calcd for $C_{20}H_{18}N_3^+$ $[M+H]^+$ 300.1495, found 300.1508.

6-(Furan-2-yl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3t)

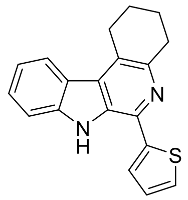


The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 2-furaldehyde (**2t,** 0.4 mmol, 33.1 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3t** as yellow solid, yield: 35.9 mg (62%), mp 125-128 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 9.30 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.64 (s, 1H), 7.54 – 7.51 (m, 2H), 7.27 – 7.22 (m, 2H), 6.61 – 6.59 (m,1H), 3.33 (t, *J* = 5.8 Hz, 1H), 3.10 (t, *J* = 5.6 Hz, 1H), 2.02 – 1.95 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): *δ* 154.6, 146.3, 142.3, 140.5, 130.3, 129.8, 128.7, 127.5, 125.6, 123.9, 121.9, 119.7, 112.1, 111.3, 107.8, 32.6, 27.2, 23.3, 22.7. HRMS (ESI) m/z calcd for $C_{19}H_{17}N_2O^+$ $[M+H]^+$ 289.1335, found 289.1345.

6-(Thiophen-2-yl)-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3u)

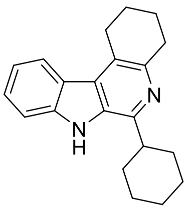
The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 2-



thenaldehyde (**2u,** 0.4 mmol, 36.9 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 °C for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3u** as yellow solid, yield: 38.2 mg (63%), mp 238-241 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.55 (s, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 3.5 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.40 (d, J = 5.0 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.15 (dd, J = 5.0, 3.7 Hz, 1H), 3.31 (t, J = 5.3 Hz, 2H), 3.09 (t, J = 5.1 Hz, 2H), 1.98 (p, J = 4.3 Hz, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.7, 142.9, 140.6, 133.8, 130.7, 128.8, 127.8, 127.5, 126.4, 125.6, 124.6, 123.9, 122.5, 120.0, 111.4, 32.5, 27.1, 23.2, 22.7. HRMS (ESI) m/z calcd for $C_{19}H_{17}N_2S^+$ [M+H]$^+$ 305.1107, found 305.1115.

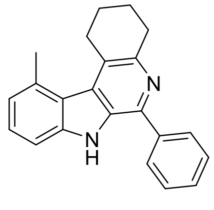
6-Cyclohexyl-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3v)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), cyclohexanecarboxaldehyde (**2v,** 0.4 mmol, 48.4 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 °C for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to yield the desired product **3v** as white solid, yield: 28.0 mg (46%), mp 217-219 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.77 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.26 – 7.21 (m, 1H), 3.34 (t, J = 5.7 Hz, 2H), 3.11 – 3.05 (m, 3H), 2.00 – 1.85 (m, 10H), 1.71 (d, J = 7.8 Hz, 1H), 1.42 – 1.25 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.5, 145.7, 140.1, 131.5, 127.6, 127.1, 123.8, 123.8, 122.7, 119.5, 111.2, 43.0, 32.5, 31.7, 27.0, 26.7, 26.0, 23.4, 22.8. HRMS (ESI) m/z calcd for $C_{21}H_{25}N_2^+$ [M+H]$^+$ 305.2012, found 305.2023.

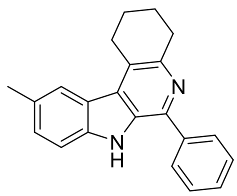
11-Methyl-6-phenyl-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3w)



The reaction was conducted with 2-(4-methyl-1*H*-indol-3-yl)cyclohexan-1-one (**1b**, 0.2 mmol, 45.4 mg), benzaldehyde (**2a,** 0.4 mmol, 40.8 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3w** as white solid, yield: 29.4 mg (47%), mp 210-213 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.55 (s, 1H), 7.81 (d, J = 7.1 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.24 (d, J = 5.9 Hz, 1H), 7.02 (d, J = 7.1 Hz, 1H), 3.54 (t, J = 6.2 Hz, 2H), 3.19 (t, J = 6.4 Hz, 2H), 3.00 (s, 3H), 2.01 – 1.89 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.7, 141.3, 140.7, 138.6, 133.6, 131.7, 129.6, 129.1, 128.4, 128.3, 127.6, 124.5, 123.3, 121.8, 109.4, 33.4, 31.4, 26.4, 23.5, 23.1. HRMS (ESI) m/z calcd for $C_{22}H_{21}N_2^+$ $[M+H]^+$ 313.1699, found 313.1711.

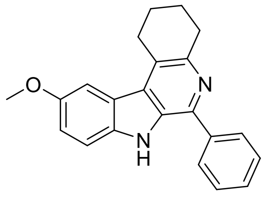
10-Methyl-6-phenyl-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3x)



The reaction was conducted with 2-(5-methyl-1*H*-indol-3-yl)cyclohexan-1-one (**1c**, 0.2 mmol, 45.4 mg), benzaldehyde (**2a,** 0.4 mmol, 40.8 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3x** as white solid, yield: 54.2 mg (87%), mp 237-238 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.44 (s, 1H), 7.97 (s, 1H), 7.86 (d, J = 7.4 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 9.0 Hz, 2H), 3.37 (t, J = 5.4 Hz, 2H), 3.14 (t, J = 5.4 Hz, 2H), 2.53 (s, 3H), 2.05 – 2.00 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.4, 139.8, 138.8, 138.7, 132.0, 129.0, 128.8, 128.2, 128.2, 128.2, 125.3, 123.7, 122.7, 110.9, 32.6, 27.2, 23.4, 22.8, 21.5. HRMS (ESI) m/z calcd for $C_{22}H_{21}N_2^+$ $[M+H]^+$ 313.1699, found 313.1711.

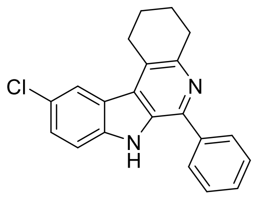
10-Methoxy-6-phenyl-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3y)



The reaction was conducted with 2-(5-methoxy-1*H*-indol-3-yl)cyclohexan-1-one (**1d**, 0.2 mmol, 48.6 mg), benzaldehyde (**2a,** 0.4 mmol, 40.8 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3y** as white solid, yield: 49.2 mg (75%), mp 119-122 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.46 (s, 1H), 7.85 (d, J = 7.1 Hz, 2H), 7.64 (s, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.32 (d, J = 8.8 Hz, 1H), 7.14 (d, J = 8.8 Hz, 1H), 3.91 (s, 3H), 3.35 (t, J = 5.3 Hz, 2H), 3.13 (t, J = 5.3 Hz, 2H), 2.03 – 1.99 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 153.8, 146.1, 140.0, 138.7, 135.5, 132.5, 129.0, 128.3, 128.2, 128.1, 125.2, 122.8, 116.7, 111.9, 106.6, 56.1, 32.5, 27.0, 23.3, 22.8. HRMS (ESI) m/z calcd for $C_{22}H_{21}N_2O^+$ $[M+H]^+$ 329.1648, found 329.1658.

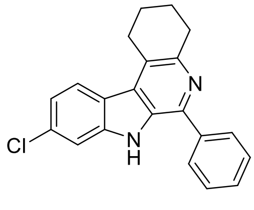
10-Chloro-6-phenyl-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3z)



The reaction was conducted with 2-(5-chloro-1*H*-indol-3-yl)cyclohexan-1-one (**1e**, 0.2 mmol, 49.4 mg), benzaldehyde (**2a,** 0.4 mmol, 40.8 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3z** as white solid, yield: 50.8 mg (77%), mp 222-224 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.44 (s, 1H), 8.17 (s, 1H), 7.88 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.5 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.40 (d, J = 8.7 Hz, 1H), 3.36 (t, J = 5.6 Hz, 2H), 3.16 (t, J = 5.4 Hz, 2H), 2.07 – 2.02 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 147.0, 140.2, 138.7, 138.4, 132.2, 129.1, 128.5, 128.1, 127.5, 125.4, 125.1, 123.5, 123.4, 112.2, 32.6, 27.0, 23.3, 22.6. HRMS (ESI) m/z calcd for $C_{21}H_{18}ClN_2^+$ $[M+H]^+$ 333.1153, found 333.1168.

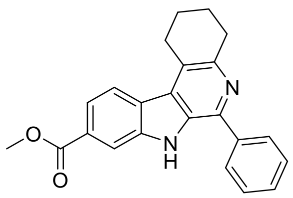
9-Chloro-6-phenyl-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3aa)



The reaction was conducted with 2-(6-chloro-1*H*-indol-3-yl)cyclohexan-1-one (**1f**, 0.2 mmol, 49.4 mg), benzaldehyde (**2a,** 0.4 mmol, 40.8 μL), $(NH_4)_3PO_4\cdot 3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3aa** as white solid, yield: 56.6 mg (85%), mp 206-208 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.47 (s, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 7.1 Hz, 2H), 7.54 (t, J = 7.5 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.23 (d, J = 8.5 Hz, 1H), 3.35 (t, J = 5.4 Hz, 2H), 3.15 (t, J = 5.2 Hz, 2H), 2.05 – 2.01 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 147.3, 140.9, 140.1, 138.4, 133.3, 132.0, 129.1, 128.5, 128.1, 127.9, 125.2, 124.7, 121.1, 120.5, 111.2, 32.6, 27.0, 23.3, 22.7. HRMS (ESI) m/z calcd for $C_{21}H_{18}ClN_2^+$ $[M+H]^+$ 333.1153, found 333.1168.

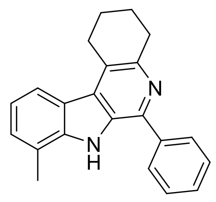
Methyl 6-phenyl-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinoline-9-carboxylate (3ab)



The reaction was conducted with methyl 3-(2-oxocyclohexyl)-1*H*-indole-6-carboxylate (**1g**, 0.2 mmol, 54.2 mg), benzaldehyde (**2a,** 0.4 mmol, 40.8 μL), $(NH_4)_3PO_4\cdot 3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ab** as white solid, yield: 57.6 mg (81%), mp 224-227 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.75 (s, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.18 (s, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H), 3.94 (s, 3H), 3.38 (t, J = 5.4 Hz, 2H), 3.15 (t, J = 5.2 Hz, 2H), 2.04 – 1.99 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 167.4, 147.1, 140.4, 139.8, 138.4, 132.9, 129.2, 128.6, 128.6, 128.1, 127.6, 126.0, 125.8, 123.6, 120.6, 113.2, 52.3, 32.6, 27.1, 23.3, 22.7. HRMS (ESI) m/z calcd for $C_{23}H_{21}N_2O_2^+$ $[M+H]^+$ 357.1598, found 357.1605.

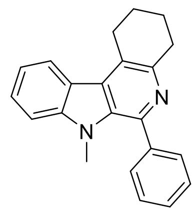
8-Methyl-6-phenyl-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3ac)



The reaction was conducted with 2-(7-methyl-1*H*-indol-3-yl)cyclohexan-1-one (**1h**, 0.2 mmol, 45.4 mg), benzaldehyde (**2a,** 0.4 mmol, 40.8 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3ac** as white solid, yield: 49.1 mg (79%), mp 237-239 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.15 (s, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 7.1 Hz, 2H), 7.57 (t, J = 7.6 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 3.38 (t, J = 5.8 Hz, 2H), 3.17 (t, J = 6.0 Hz, 2H), 2.53 (s, 3H), 2.06 – 2.00 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.8, 139.9, 139.8, 139.0, 131.6, 129.2, 128.9, 128.3, 128.1, 127.9, 125.4, 122.1, 121.5, 120.3, 120.0, 32.7, 27.0, 23.4, 22.8, 16.9. HRMS (ESI) m/z calcd for $C_{22}H_{21}N_2^+$ $[M+H]^+$ 313.1699, found 313.1711.

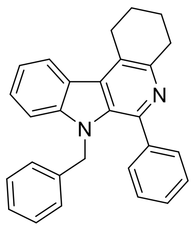
7-Methyl-6-phenyl-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3ad)



The reaction was conducted with 2-(1-methyl-1*H*-indol-3-yl)cyclohexan-1-one (**1i**, 0.2 mmol, 45.4 mg), benzaldehyde (**2a,** 0.4 mmol, 40.8 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15:1) to yield the desired product **3ad** as yellow solid, yield: 46.4 mg (74%), mp 175-178 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.25 (d, J = 8.0 Hz, 1H), 7.62 – 7.54 (m, 3H), 7.52 – 7.43 (m, 3H), 7.40 (d, J = 8.3 Hz, 1H), 7.28 (t, J = 7.8 Hz, 1H), 3.42 (t, J = 5.9 Hz, 2H), 3.39 (s, 3H), 3.14 (t, J = 5.7 Hz, 2H), 2.08 – 2.00 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 145.6, 143.0, 141.1, 140.2, 133.4, 129.7, 128.5, 128.1, 128.0, 127.3, 125.1, 124.0, 121.8, 119.4, 109.4, 32.7, 32.6, 27.2, 23.3, 22.8. HRMS (ESI) m/z calcd for $C_{22}H_{21}N_2^+$ $[M+H]^+$ 313.1699, found 313.1709.

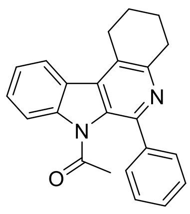
7-Benzyl-6-phenyl-2,3,4,7-tetrahydro-1*H*-indolo[2,3-*c*]quinolone (3ae)



The reaction was conducted with 2-(1-benzyl-1*H*-indol-3-yl)cyclohexan-1-one (**1j**, 0.2 mmol, 60.6 mg), benzaldehyde (**2a,** 0.4 mmol, 40.8 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3ae** as yellow solid, yield: 37.8 mg (49%), mp 157-160 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.28 (d, J = 8.1 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.33 – 7.23 (m, 7H), 7.09 (q, J = 7.5 Hz, 3H), 6.54 (d, J = 7.1 Hz, 2H), 5.13 (s, 2H), 3.45 (t, J = 6.0 Hz, 2H), 3.13 (t, J = 5.8 Hz, 2H), 2.09 – 1.99 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 145.8, 142.6, 141.4, 139.8, 137.2, 132.7, 129.3, 128.8, 128.2, 128.0, 127.5, 126.8, 125.6, 125.3, 124.1, 122.0, 119.7, 110.2, 47.8, 32.6, 27.2, 23.3, 22.8. HRMS (ESI) m/z calcd for $C_{28}H_{25}N_2^+$ $[M+H]^+$ 389.2012, found 389.2027.

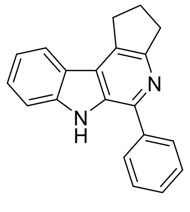
1-(6-Phenyl-1,2,3,4-tetrahydro-7*H*-indolo[2,3-*c*]quinolin-7-yl)ethan-1-one (3af)



The reaction was conducted with 2-(1-acetyl-1*H*-indol-3-yl)cyclohexan-1-one (**1k**, 0.2 mmol, 51.0 mg), benzaldehyde (**2a,** 0.4 mmol, 40.8 μL), $(NH_4)_3PO_4·3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15:1) to yield the desired product **3af** as yellow solid, yield: 20.9 mg (30%), mp 151-152 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.34 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 7.9 Hz, 1H), 7.83 (d, J = 7.0 Hz, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.46 – 7.39 (m, 2H), 3.36 (t, J = 5.4 Hz, 2H), 3.15 (t, J = 5.3 Hz, 2H), 2.08 – 2.00 (m, 4H), 1.79 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 172.0, 151.8, 143.7, 140.9, 140.6, 133.3, 131.4, 129.4, 129.2, 128.6, 128.0, 124.9, 124.4, 123.6, 123.6, 115.2, 32.9, 26.9, 26.6, 22.9, 22.7. HRMS (ESI) m/z calcd for $C_{23}H_{21}N_2O^+$ $[M+H]^+$ 341.1648, found 341.1661.

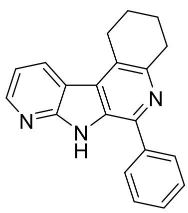
5-Phenyl-1,2,3,6-tetrahydrocyclopenta[5,6]pyrido[3,4-*b*]indole (3ag)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclopentan-1-one (**1l**, 0.2 mmol, 39.8 mg), benzaldehyde (**2a,** 0.4 mmol, 40.8 μL), $(NH_4)_3PO_4 \cdot 3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3ag** as yellow solid, yield: 39.7 mg (70%), mp 193-196 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.50 (s, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 7.2 Hz, 2H), 7.57 – 7.50 (m, 3H), 7.48 – 7.41 (m, 2H), 7.28 (t, J = 7.4 Hz, 1H), 3.46 (t, J = 7.4 Hz, 2H), 3.24 (t, J = 7.6 Hz, 2H), 2.36 (p, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 155.1, 140.7, 140.6, 139.0, 132.4, 129.1, 128.3, 128.3, 128.1, 127.9, 127.0, 123.0, 121.9, 119.9, 111.2, 33.5, 29.9, 23.5. HRMS (ESI) m/z calcd for $C_{20}H_{17}N_2^+$ $[M+H]^+$ 285.1386, found 285.1387.

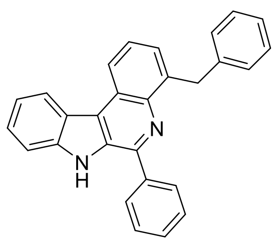
6-Phenyl-2,3,4,7-tetrahydro-1*H*-pyrido[3',2':4,5]pyrrolo[2,3-*c*]quinolone (3ah)



The reaction was conducted with 2-(1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)cyclohexan-1-one (**1m**, 0.2 mmol, 42.8 mg), benzaldehyde (**2a,** 0.4 mmol, 40.8 μL), $(NH_4)_3PO_4 \cdot 3H_2O$ (0.2 mmol, 40.6 mg), Na_2CO_3 (0.1 mmol, 10.6 mg), H_2O (0.6 mmol, 10.8 μL), and $PhCF_3$ (0.6 mL). The reaction vessel stirred at 150 ºC for 12 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ah** as yellow solid, yield: 22.1 mg (37%), mp 243-245 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 11.32 (s, 1H), 8.41 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 7.9 Hz, 2H), 7.72 (d, J = 4.4 Hz, 1H), 7.55 (t, J = 7.5 Hz, 2H), 7.49 (d, J = 7.2 Hz, 1H), 7.07 (dd, J = 7.7, 4.9 Hz, 1H), 3.33 (t, J = 5.2 Hz, 2H), 3.17 (t, J = 5.6 Hz, 2H), 2.04 (p, J = 3.1 Hz, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 152.7, 147.6, 147.5, 140.8, 138.8, 132.2, 130.8, 129.2, 128.5, 128.5, 128.5, 126.5, 125.6, 115.5, 115.4, 32.6, 27.0, 23.4, 22.6. HRMS (ESI) m/z calcd for $C_{20}H_{18}N_3^+$ $[M+H]^+$ 300.1495, found 300.1507.

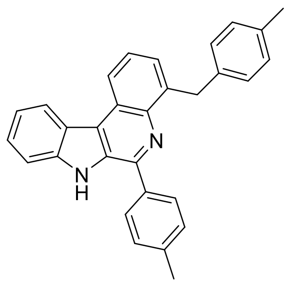
4-Benzyl-6-phenyl-7*H*-indolo[2,3-*c*]quinolone (4a)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), benzaldehyde (**2a,** 0.6 mmol, 61.2 μL), NH_4I (0.4 mmol, 58.0 mg), $NaHCO_3$ (0.2 mmol, 16.8 mg), and DMF (0.6 mL). The reaction vessel stirred at 150 ºC for 20 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to yield the desired product **4a** as white solid, yield: 42.4 mg (55%), mp 86-89 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.75 (s, 1H), 8.58 (dd, J = 14.5, 8.1 Hz, 2H), 8.05 (d, J = 7.2 Hz, 2H), 7.61 (t, J = 7.7 Hz, 3H), 7.57 – 7.50 (m, 3H), 7.46 (d, J = 7.1 Hz, 1H), 7.39 (t, J = 7.2 Hz, 3H), 7.27 (t, J = 7.5 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H), 4.83 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 145.0, 142.3, 141.4, 141.2, 139.0, 138.9, 130.6, 129.4, 129.2, 129.2, 128.6, 128.1, 126.8, 126.7, 126.4, 125.6, 124.4, 123.2, 122.9, 122.6, 121.5, 120.8, 112.0, 38.1. HRMS (ESI) m/z calcd for $C_{28}H_{21}N_2^+$ $[M+H]^+$ 385.1699, found 385.1700.

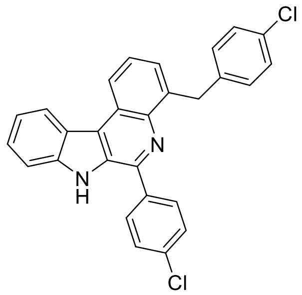
4-(4-Methylbenzyl)-6-(*p*-tolyl)-7*H*-indolo[2,3-*c*]quinolone (4b)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 4-methylbenzaldehyde (**2b,** 0.6 mmol, 71.0 μL), NH_4I (0.4 mmol, 58.0 mg), $NaHCO_3$ (0.2 mmol, 16.8 mg), and DMF (0.6 mL). The reaction vessel stirred at 150 ºC for 20 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to yield the desired product **4b** as white solid, yield: 41.7 mg (51%), mp 183-185 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.73 (s, 1H), 8.57 (t, J = 7.9 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.61 – 7.50 (m, 3H), 7.45 – 7.37 (m, 4H), 7.30 (d, J = 7.9 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 4.79 (s, 2H), 2.47 (s, 3H), 2.30 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 145.0, 141.4, 141.4, 139.3, 139.2, 139.0, 136.0, 135.0, 130.7, 129.8, 129.3, 128.8, 128.5, 126.7, 126.5, 126.2, 124.3, 123.2, 123.0, 122.5, 121.3, 120.8, 111.9, 37.6, 21.4, 21.0. HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2^+$ $[M+H]^+$ 413.2012, found 413.2020.

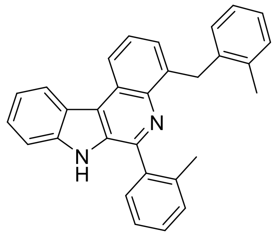
4-(4-Chlorobenzyl)-6-(4-chlorophenyl)-7*H*-indolo[2,3-*c*]quinolone (4c)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 4-chlorobenzaldehyde (**2f,** 0.6 mmol, 84.3 mg), NH_4I (0.4 mmol, 58.0 mg), $NaHCO_3$ (0.2 mmol, 16.8 mg), and DMF (0.6 mL). The reaction vessel stirred at 150 ºC for 20 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **4c** as white solid, yield: 31.1 mg (34%), mp 196-198 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.68 (s, 1H), 8.60 (d, J = 8.2 Hz, 1H), 8.55 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.62 (t, J = 7.7 Hz, 1H), 7.59 – 7.53 (m, 4H), 7.45 (d, J = 7.0 Hz, 1H), 7.40 (t, J = 6.8 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.22 (t, J = 8.0 Hz, 3H), 4.72 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 143.8, 141.3, 140.7, 140.5, 139.1, 137.1, 135.3, 131.3, 130.6, 130.4, 129.8, 129.4, 128.2, 127.0, 126.9, 126.5, 124.5, 123.2, 122.9, 122.8, 121.8, 121.0, 112.0, 37.6. HRMS (ESI) m/z calcd for $C_{28}H_{19}Cl_2N_2^+$ $[M+H]^+$ 453.0920, found 453.0924.

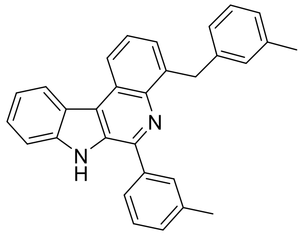
4-(2-Methylbenzyl)-6-(*o*-tolyl)-7*H*-indolo[2,3-*c*]quinolone (4d)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 2-methylbenzaldehyde (**2w,** 0.6 mmol, 69.5 μL), NH_4I (0.4 mmol, 58.0 mg), $NaHCO_3$ (0.2 mmol, 16.8 mg), and DMF (0.6 mL). The reaction vessel stirred at 150 ºC for 20 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **4d** as white solid, yield: 39.6 mg (48%), mp 184-187 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.62 (dd, J = 12.8, 8.1 Hz, 2H), 8.41 (s, 1H), 7.63 – 7.57 (m, 2H), 7.53 – 7.51 (m, 2H), 7.44 – 7.36 (m, 4H), 7.20 – 7.09 (m, 5H), 4.80 (s, 2H), 2.30 (s, 3H), 2.25 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.2, 141.2, 140.5, 139.9, 138.9, 137.5, 137.2, 137.0, 131.5, 131.4, 130.4, 130.0, 129.1, 129.0, 126.8, 126.7, 126.1, 126.0, 125.8, 125.6, 124.1, 123.3, 123.0, 122.1, 121.3, 120.8, 111.9, 35.4, 20.0, 19.7. HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2^+$ $[M+H]^+$ 413.2012, found 413.2020.

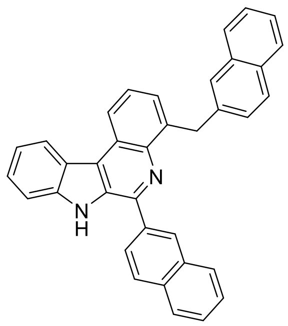
4-(3-Methylbenzyl)-6-(*m*-tolyl)-7*H*-indolo[2,3-*c*]quinolone (4e)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 3-methylbenzaldehyde (**2i,** 0.6 mmol, 70.8 μL), NH_4I (0.4 mmol, 58.0 mg), $NaHCO_3$ (0.2 mmol, 16.8 mg), and DMF (0.6 mL). The reaction vessel stirred at 150 ºC for 20 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **4e** as white solid, yield: 44.4 mg (54%), mp 182-184 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.74 (s, 1H), 8.57 (dd, *J* = 13.5, 8.2 Hz, 2H), 7.82 (d, *J* = 6.2 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.52 – 7.46 (m, 3H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.26 (s, 1H), 7.20 – 7.15 (m, 2H), 6.99 (d, *J* = 7.1 Hz, 1H), 4.78 (s, 2H), 2.49 (s, 3H), 2.30 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): *δ* 145.2, 142.2, 141.4, 141.3, 139.0, 139.0, 138.8, 137.6, 130.7, 130.2, 130.0, 129.4, 129.0, 128.0, 126.7, 126.6, 126.5, 126.4, 126.3, 125.5, 124.4, 123.2, 123.0, 122.5, 121.4, 120.8, 111.9, 38.1, 21.7, 21.4. (PE/EA = 10:1), white solid, yield: 44.4 mg (54%), mp 182-184 °C, HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2^+$ $[M+H]^+$ 413.2012, found 413.2020.

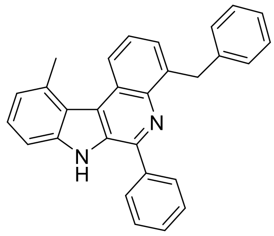
6-(Naphthalen-2-yl)-4-(naphthalen-2-ylmethyl)-7*H*-indolo[2,3-*c*]quinolone (4f)



The reaction was conducted with 2-(1*H*-indol-3-yl)cyclohexan-1-one (**1a**, 0.2 mmol, 42.6 mg), 2-naphthaldehyde (**2p,** 0.6 mmol, 93.4 mg), NH_4I (0.4 mmol, 58.0 mg), $NaHCO_3$ (0.2 mmol, 16.8 mg), and DMF (0.6 mL). The reaction vessel stirred at 150 ºC for 20 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **4f** as white solid, yield: 35.4 mg (37%), mp 162-164 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.80 (s, 1H), 8.61 (d, *J* = 7.5 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.38 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.92 – 7.86 (m, 3H), 7.76 (q, *J* = 8.3 Hz, 3H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.49 (m, 6H), 7.43 – 7.36 (m, 3H), 4.98 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): *δ* 145.0, 141.6, 141.0, 139.9, 139.1, 136.2, 133.6, 133.6, 133.3, 131.9, 130.9, 129.0, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5, 126.8, 126.8, 126.7, 126.6, 126.6, 126.4, 125.7, 125.0, 124.4, 123.2, 123.0, 122.7, 121.7, 120.9, 112.0, 38.6. HRMS (ESI) m/z calcd for $C_{36}H_{25}N_2^+$ [M+H]$^+$ 485.2012, found 485.2023.

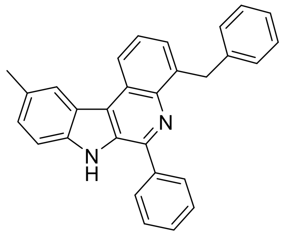
4-Benzyl-11-methyl-6-phenyl-7*H*-indolo[2,3-*c*]quinolone (4g)



The reaction was conducted with 2-(4-methyl-1*H*-indol-3-yl)cyclohexan-1-one (**1b**, 0.2 mmol, 45.4 mg), benzaldehyde (**2a,** 0.6 mmol, 61.2 μL), NH_4I (0.4 mmol, 58.0 mg), $NaHCO_3$ (0.2 mmol, 16.8 mg), and DMF (0.6 mL). The reaction vessel stirred at 150 °C for 20 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **4g** as white solid, yield: 35.8 mg (45%), mp 112-114 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.94 (d, *J* = 8.4 Hz, 1H), 8.79 (s, 1H), 7.99 (d, *J* = 7.1 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.9 Hz, 2H), 7.45 – 7.36 (m, 5H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 4.82 (s, 2H), 3.22 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 145.1, 142.4, 142.0, 141.2, 139.9, 138.8, 133.3, 130.7, 129.4, 129.2, 129.2, 128.7, 128.1, 126.9, 126.1, 125.5, 124.1, 124.0, 124.0, 123.7, 122.9, 109.7, 38.5, 26.8. HRMS (ESI) m/z calcd for $C_{29}H_{23}N_2^+$ [M+H]$^+$ 399.1856, found 399.1865.

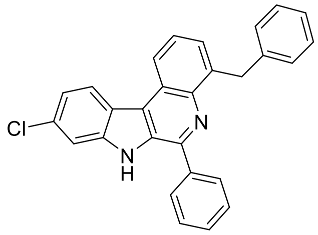
4-Benzyl-10-methyl-6-phenyl-7*H*-indolo[2,3-*c*]quinolone (4h)



The reaction was conducted with 2-(5-methyl-1*H*-indol-3-yl)cyclohexan-1-one (**1c**, 0.2 mmol, 45.4 mg), benzaldehyde (**2a,** 0.6 mmol, 61.2 μL), NH_4I (0.4 mmol, 58.0 mg), $NaHCO_3$ (0.2 mmol, 16.8 mg), and DMF (0.6 mL). The reaction vessel stirred at 150 °C for 20 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **4h** as white solid, yield: 39.0 mg (49%), mp 143-146 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.64 – 8.54 (m, 2H), 8.32 (s, 1H), 8.03 (d, *J* = 7.7 Hz, 2H), 7.61 – 7.55 (m, 3H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.41 (dd, *J* = 15.2, 6.8 Hz, 4H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 4.81 (s, 2H), 2.58 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 144.9, 142.3, 141.3, 141.1, 138.9, 137.3, 130.8, 130.1, 129.4, 129.1, 129.1, 128.6, 128.3, 128.1, 126.5, 126.2, 125.6, 124.5, 123.1, 122.8, 122.3, 121.5, 111.6, 38.1, 21.7. HRMS (ESI) m/z calcd for $C_{29}H_{23}N_2^+$ [M+H]$^+$ 399.1856, found 399.1865.

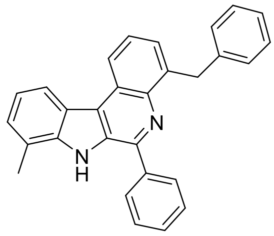
4-Benzyl-9-chloro-6-phenyl-7*H*-indolo[2,3-*c*]quinolone (4i)



The reaction was conducted with 2-(6-chloro-1*H*-indol-3-yl)cyclohexan-1-one (**1f**, 0.2 mmol, 49.4 mg), benzaldehyde (**2a,** 0.6 mmol, 61.2 μL), NH_4I (0.4 mmol, 58.0 mg), $NaHCO_3$ (0.2 mmol, 16.8 mg), and DMF (0.6 mL). The reaction vessel stirred at 150 ºC for 20 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **4i** as white solid, yield: 54.2 mg (65%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.69 (s, 1H), 8.47 (d, J = 8.2 Hz, 1H), 8.40 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 7.1 Hz, 2H), 7.60 (q, J = 8.3, 7.8 Hz, 3H), 7.56 (d, J = 7.3 Hz, 1H), 7.52 (s, 1H), 7.47 (d, J = 7.0 Hz, 1H), 7.39 (d, J = 7.2 Hz, 2H), 7.33 (d, J = 8.6 Hz, 1H), 7.27 (t, J = 7.5 Hz, 2H), 7.18 (t, J = 7.3 Hz, 1H), 4.80 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 144.9, 142.2, 141.6, 141.3, 139.5, 138.6, 132.6, 130.9, 129.4, 129.2, 128.5, 128.2, 126.9, 126.8, 125.7, 124.0, 122.3, 121.6, 121.5, 121.2, 111.9, 38.1. HRMS (ESI) m/z calcd for $C_{28}H_{20}ClN_2^+$ $[M+H]^+$ 419.1310, found 419.1319.

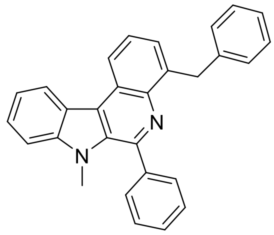
4-Benzyl-8-methyl-6-phenyl-7*H*-indolo[2,3-*c*]quinolone (4j)



The reaction was conducted with 2-(7-methyl-1*H*-indol-3-yl)cyclohexan-1-one (**1h**, 0.2 mmol, 45.4 mg), benzaldehyde (**2a,** 0.6 mmol, 61.2 μL), NH_4I (0.4 mmol, 58.0 mg), $NaHCO_3$ (0.2 mmol, 16.8 mg), and DMF (0.6 mL). The reaction vessel stirred at 150 ºC for 20 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **4j** as white solid, yield: 40.9 mg (51%), mp 182-185 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.57 (d, J = 8.1 Hz, 1H), 8.52 (s, 1H), 8.38 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 7.4 Hz, 2H), 7.64 – 7.55 (m, 4H), 7.44 (d, J = 6.9 Hz, 1H), 7.40 (d, J = 7.6 Hz, 2H), 7.28 (dd, J = 15.2, 7.6 Hz, 4H), 7.17 (t, J = 7.3 Hz, 1H), 4.82 (s, 2H), 2.56 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 144.9, 142.3, 141.5, 141.2, 139.0, 138.5, 130.4, 129.4, 129.2, 129.2, 129.2, 128.5, 128.1, 127.2, 126.6, 126.4, 125.6, 124.4, 123.2, 122.5, 121.5, 121.0, 120.8, 38.1, 16.9. HRMS (ESI) m/z calcd for $C_{29}H_{23}N_2^+$ $[M+H]^+$ 399.1856, found 399.1865.

4-Benzyl-7-methyl-6-phenyl-7*H*-indolo[2,3-*c*]quinolone (4k)



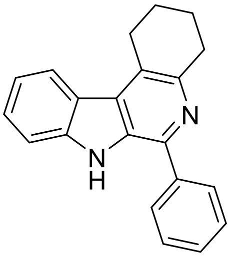
The reaction was conducted with 2-(1-methyl-1*H*-indol-3-yl)cyclohexan-1-one (**1i**, 0.2 mmol, 45.4 mg), benzaldehyde (**2a,** 0.6 mmol, 61.2 μL), NH_4I (0.4 mmol, 58.0 mg), $NaHCO_3$ (0.2 mmol, 16.8 mg), and DMF (0.6 mL). The reaction vessel stirred at 150 ºC for 20 h under oxygen atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1) to yield the desired product **4k** as white solid, yield: 30.0 mg (38%), mp 126-128 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.64 (t, J = 9.0 Hz, 2H), 7.74 (d, J = 7.5 Hz, 2H), 7.64 – 7.52 (m, 6H), 7.44 (t, J = 7.0 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.27 – 7.23 (m, 2H), 7.15 (t, J = 7.2 Hz, 1H), 4.77 (s, 2H), 3.55 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 146.3, 142.3, 141.9, 141.1, 140.7, 140.6, 132.5, 129.7, 129.5, 128.6, 128.2, 128.1, 126.7, 126.7, 126.1, 125.5, 124.2, 123.2, 122.9, 122.2, 121.3, 120.5, 110.4, 38.0, 33.6. HRMS (ESI) m/z calcd for $C_{29}H_{23}N_2^+$ [M+H]$^+$ 399.1856, found 399.1860.

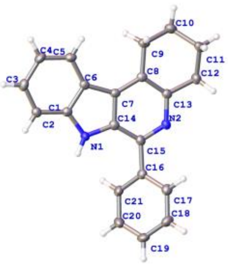
5. Crystal data and structure refinement for 3a and 4b

The single crystal of compound **3a** and **4b** were obtained by slowly evaporating a mixture of dichloromethane and petroleum ether solution at ambient temperature.

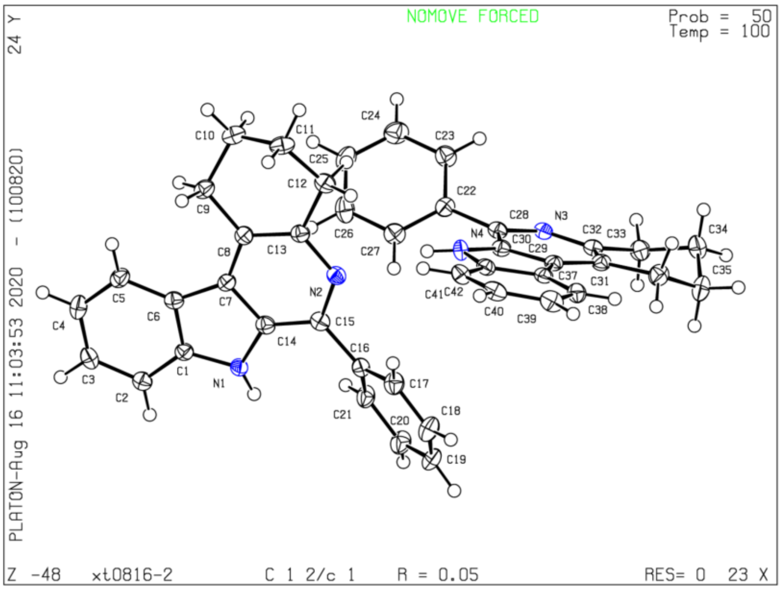
The single crystal X-ray diffraction data were collected at 150 K by a diffractometer Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation (1.54178 Å) by using a w scan mode. The data were collected and processed using CrysAlisPro. The structures were solved by direct methods using Olex2 software with the SHELXT structure solution program via intrinsic phasing algorithm, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018 using a full-matrix least squares procedure based on F^2. The weighted R factor, wR and goodness-of-fit S values were obtained based on F^2. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center.



3a



CCDC: 2032228



The ellipsoids are shown at 50% probability levels.

Table 1 Crystal data and structure refinement for 3a.

Identification code	**3a**
Empirical formula	$C_{42}H_{36}N_4$
Formula weight	596.75
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	25.8205(14)
b/Å	9.6194(4)
c/Å	25.2718(13)
α/°	90
β/°	97.967(6)
γ/°	90
Volume/Å^3	6216.4(5)
Z	8
ρ_{calc}g/cm^3	1.275

μ/mm^{-1}	0.075
F(000)	2528.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.228 to 49.994
Index ranges	$-30 \leq h \leq 27$, $-11 \leq k \leq 11$, $-30 \leq l \leq 29$
Reflections collected	13722
Independent reflections	5481 [R_{int} = 0.0248, R_{sigma} = 0.0349]
Data/restraints/parameters	5481/0/423
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0491, wR_2 = 0.1150
Final R indexes [all data]	R_1 = 0.0589, wR_2 = 0.1215
Largest diff. peak/hole / e $Å^{-3}$	0.39/-0.23

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 3a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
N1	4358.5(6)	4535.7(17)	3964.0(6)	19.1(4)
N2	5794.4(6)	4120.8(16)	4064.9(6)	19.9(4)
C1	4148.1(7)	5677.8(19)	4185.6(7)	18.7(4)
C2	3619.8(7)	5996.6(19)	4182.4(7)	21.0(4)
C3	3502.3(8)	7185(2)	4449.5(8)	23.9(4)
C4	3890.6(8)	8051(2)	4698.7(8)	26.9(5)
C5	4416.3(8)	7740(2)	4703.0(7)	23.1(4)
C6	4551.2(7)	6531.9(19)	4439.8(7)	19.2(4)
C7	5039.2(7)	5888.1(18)	4354.3(7)	18.3(4)
C8	5566.4(7)	6231.8(19)	4495.8(7)	19.1(4)
C9	5735.8(8)	7517.8(19)	4814.7(8)	22.9(4)
C10	6293.0(8)	7948(2)	4768.3(8)	27.5(5)
C11	6661.1(8)	6714(2)	4839.3(8)	26.3(5)
C12	6508.8(8)	5628(2)	4416.0(8)	25.8(5)
C13	5931.9(7)	5316.9(19)	4328.0(7)	19.6(4)
C14	4900.2(7)	4662.0(19)	4058.1(7)	20.3(4)
C15	5289.9(7)	3765.8(19)	3933.1(7)	20.5(4)
C16	5170.0(7)	2387.1(19)	3680.7(7)	21.0(4)
C17	5454.1(8)	1216(2)	3875.4(8)	25.8(4)
C18	5316.8(9)	-85(2)	3669.2(8)	30.1(5)
C19	4902.5(8)	-243(2)	3268.1(8)	29.4(5)

C20	4631.0(8)	915(2)	3055.5(9)	30.3(5)
C21	4767.8(8)	2224(2)	3259.3(8)	25.3(4)
N3	6452.8(6)	3100.9(16)	1918.6(6)	18.6(3)
N4	6553.7(6)	2810.7(17)	3388.9(6)	19.1(4)
C22	6162.6(7)	4882.1(19)	2496.3(7)	20.9(4)
C23	6344.4(8)	6054(2)	2248.9(8)	26.1(5)
C24	6160.0(9)	7359(2)	2357.2(9)	31.5(5)
C25	5800.9(8)	7519(2)	2706.9(8)	29.3(5)
C26	5605.9(8)	6369(2)	2940.7(8)	30.0(5)
C27	5784.7(8)	5052(2)	2829.9(8)	25.2(5)
C28	6390.7(7)	3493.4(19)	2416.4(7)	20.1(4)
C29	6565.4(7)	2625.4(19)	2844.9(7)	19.7(4)
C30	6843.6(7)	1389.9(19)	2763.3(7)	18.8(4)
C31	6915.9(7)	1014.8(19)	2242.4(7)	19.5(4)
C32	6695.8(7)	1893.3(19)	1831.5(7)	20.0(4)
C33	6707.5(8)	1532(2)	1254.2(8)	24.3(4)
C34	7144.2(8)	523(2)	1176.7(8)	28.7(5)
C35	7135.7(9)	-709(2)	1550.0(8)	29.2(5)
C36	7231.0(8)	-251(2)	2130.3(8)	25.3(4)
C37	6998.7(7)	796.6(19)	3287.0(7)	19.2(4)
C38	7272.1(7)	-401(2)	3482.0(8)	23.6(4)
C39	7347.2(8)	-644(2)	4027.3(8)	26.0(5)
C40	7169.2(8)	292(2)	4381.5(8)	24.7(4)
C41	6895.2(7)	1471(2)	4206.8(8)	22.9(4)
C42	6809.0(7)	1709.4(19)	3653.7(7)	19.4(4)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 3a. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	15.7(8)	21.0(8)	20.6(8)	-3.1(7)	2.3(7)	-1.1(7)
N2	17.5(8)	23.1(8)	18.9(8)	0.1(7)	1.4(6)	-0.8(7)
C1	22.3(10)	17.7(9)	16.4(9)	2.2(7)	3.8(8)	-1.3(8)
C2	21.0(10)	22.9(10)	18.9(9)	1.5(8)	2.4(8)	-0.9(8)
C3	22.6(10)	27.8(10)	22.6(10)	3.7(8)	8.2(8)	5.0(9)
C4	31.5(12)	23.6(10)	26.3(10)	-2.8(8)	6.6(9)	7.7(9)
C5	30.0(11)	20.1(10)	19.2(10)	-2.4(8)	3.5(8)	-2.1(9)
C6	21.8(10)	19.6(9)	16.2(9)	3.3(8)	2.5(8)	-1.6(8)
C7	24.4(10)	16.5(9)	14.4(9)	0.8(7)	3.6(8)	-1.8(8)
C8	24.4(10)	19.7(9)	13.8(9)	1.9(7)	4.3(8)	-0.7(8)

C9	28.6(11)	20.0(10)	19.8(10)	-1.3(8)	1.9(8)	-2.8(8)
C10	30.2(11)	21.8(10)	29.9(11)	-1.3(9)	1.9(9)	-6.1(9)
C11	24.4(11)	24.1(10)	28.2(11)	2.4(9)	-4.5(9)	-5.7(9)
C12	20.0(10)	27.6(11)	29.7(11)	-1.0(9)	3.2(9)	-1.5(9)
C13	21.5(10)	20.4(9)	16.9(9)	0.8(8)	2.6(8)	-2.3(8)
C14	22.7(10)	21.6(9)	17.1(9)	2.6(8)	4.2(8)	-1.6(8)
C15	20.2(10)	23.2(10)	18.0(9)	2.3(8)	1.7(8)	-0.4(8)
C16	20.4(10)	22.2(10)	21.0(10)	-1.1(8)	4.9(8)	0.5(8)
C17	25.9(11)	28.7(11)	22.1(10)	-2.0(8)	1.5(8)	2.4(9)
C18	37.2(12)	22.7(10)	29.7(11)	-2.1(9)	1.9(10)	6.9(9)
C19	34.0(12)	20.7(10)	33.8(11)	-9.6(9)	5.8(10)	-0.5(9)
C20	24.1(11)	33.0(12)	31.9(11)	-11.7(9)	-2.3(9)	1.1(9)
C21	22.7(10)	24.3(10)	28.4(11)	-4.0(9)	2.1(9)	5.8(9)
N3	16.6(8)	20.8(8)	18.6(8)	0.7(6)	2.9(6)	-2.2(7)
N4	19.9(8)	21.4(8)	16.7(8)	-1.5(7)	5.1(7)	4.4(7)
C22	19.0(10)	21.2(10)	21.3(10)	-0.6(8)	-1.7(8)	1.3(8)
C23	26.0(11)	26.6(11)	26.0(10)	4.1(9)	5.4(9)	2.0(9)
C24	34.6(12)	23.8(11)	35.5(12)	7.6(9)	3.5(10)	1.3(9)
C25	34.2(12)	20.3(10)	32.8(12)	-0.1(9)	2.6(10)	8.7(9)
C26	30.5(12)	33.1(11)	27.1(11)	2.5(9)	6.2(9)	11.8(10)
C27	26.6(11)	24.8(10)	23.9(10)	4.0(8)	3.1(9)	1.3(9)
C28	16.7(9)	22.3(10)	21.2(10)	0.3(8)	2.3(8)	-2.7(8)
C29	16.7(9)	20.5(9)	21.5(10)	-1.0(8)	1.3(8)	-2.6(8)
C30	12.8(9)	17.5(9)	25.5(10)	0.0(8)	1.1(8)	-1.3(8)
C31	14.9(9)	19.6(9)	23.1(10)	-0.4(8)	-0.3(8)	-1.6(8)
C32	16.1(9)	21.3(10)	22.5(10)	-0.2(8)	2.2(8)	-3.2(8)
C33	26.2(11)	25.6(10)	21.3(10)	0.0(8)	4.2(8)	-0.5(9)
C34	29.0(12)	32.5(11)	26.6(11)	-2.9(9)	10.6(9)	3.3(9)
C35	31.7(12)	26.9(11)	28.7(11)	-6.6(9)	3.1(9)	8.4(9)
C36	21.5(10)	24.5(10)	28.9(11)	-1.7(9)	-0.5(9)	3.6(9)
C37	14.3(9)	19.5(9)	24.1(10)	-0.1(8)	3.4(8)	-2.7(8)
C38	19.7(10)	21.2(10)	30.4(11)	0.4(8)	5.5(9)	2.6(8)
C39	22.1(10)	26.7(10)	28.5(11)	10.1(9)	0.7(9)	4.1(9)
C40	20.4(10)	31.0(11)	22.2(10)	7.3(9)	1.2(8)	-2.2(9)
C41	21.2(10)	26.6(10)	21.9(10)	2.2(8)	6.4(8)	0.4(9)
C42	15.6(9)	19.5(9)	23.5(10)	1.9(8)	3.9(8)	-0.8(8)

Table 4 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å

N1	C1	1.378(2)	N3	C28	1.344(2)
N1	C14	1.391(2)	N3	C32	1.353(2)
N2	C13	1.351(2)	N4	C29	1.391(2)
N2	C15	1.343(2)	N4	C42	1.372(2)
C1	C2	1.397(3)	C22	C23	1.401(3)
C1	C6	1.409(3)	C22	C27	1.385(3)
C2	C3	1.383(3)	C22	C28	1.485(3)
C3	C4	1.386(3)	C23	C24	1.384(3)
C4	C5	1.388(3)	C24	C25	1.376(3)
C5	C6	1.407(3)	C25	C26	1.382(3)
C6	C7	1.447(3)	C26	C27	1.390(3)
C7	C8	1.398(3)	C28	C29	1.392(3)
C7	C14	1.416(3)	C29	C30	1.419(3)
C8	C9	1.508(3)	C30	C31	1.402(3)
C8	C13	1.399(3)	C30	C37	1.446(3)
C9	C10	1.517(3)	C31	C32	1.397(3)
C10	C11	1.516(3)	C31	C36	1.513(3)
C11	C12	1.508(3)	C32	C33	1.504(3)
C12	C13	1.505(3)	C33	C34	1.521(3)
C14	C15	1.394(3)	C34	C35	1.517(3)
C15	C16	1.485(3)	C35	C36	1.518(3)
C16	C17	1.396(3)	C37	C38	1.404(3)
C16	C21	1.390(3)	C37	C42	1.413(3)
C17	C18	1.383(3)	C38	C39	1.385(3)
C18	C19	1.376(3)	C39	C40	1.392(3)
C19	C20	1.385(3)	C40	C41	1.377(3)
C20	C21	1.387(3)	C41	C42	1.403(3)

Table 5 Bond Angles for 3a.

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
C1	N1	C14	107.73(16)	C28	N3	C32	120.78(16)
C15	N2	C13	121.22(16)	C42	N4	C29	107.96(16)
N1	C1	C2	127.73(17)	C23	C22	C28	119.95(17)
N1	C1	C6	110.01(16)	C27	C22	C23	119.01(18)
C2	C1	C6	122.25(17)	C27	C22	C28	120.99(17)
C3	C2	C1	117.31(18)	C24	C23	C22	119.73(18)
C2	C3	C4	121.67(18)	C25	C24	C23	120.66(19)
C3	C4	C5	121.25(18)	C24	C25	C26	120.20(19)
C4	C5	C6	118.70(18)	C25	C26	C27	119.54(19)

C1	C6	C7	106.60(16)	C22	C27	C26	120.77(19)
C5	C6	C1	118.80(17)	N3	C28	C22	118.75(16)
C5	C6	C7	134.60(18)	N3	C28	C29	119.45(17)
C8	C7	C6	134.24(17)	C29	C28	C22	121.72(17)
C8	C7	C14	119.91(17)	N4	C29	C28	130.01(17)
C14	C7	C6	105.86(16)	N4	C29	C30	109.38(16)
C7	C8	C9	122.06(17)	C28	C29	C30	120.37(17)
C7	C8	C13	116.59(17)	C29	C30	C37	106.22(16)
C13	C8	C9	121.36(17)	C31	C30	C29	119.21(17)
C8	C9	C10	112.98(16)	C31	C30	C37	134.56(17)
C11	C10	C9	111.28(16)	C30	C31	C36	121.87(17)
C12	C11	C10	111.17(17)	C32	C31	C30	116.67(17)
C13	C12	C11	113.44(16)	C32	C31	C36	121.44(17)
N2	C13	C8	122.85(17)	N3	C32	C31	123.27(17)
N2	C13	C12	115.41(16)	N3	C32	C33	115.36(16)
C8	C13	C12	121.71(17)	C31	C32	C33	121.36(17)
N1	C14	C7	109.77(16)	C32	C33	C34	112.78(17)
N1	C14	C15	130.35(17)	C35	C34	C33	110.10(16)
C15	C14	C7	119.78(18)	C34	C35	C36	111.08(17)
N2	C15	C14	119.48(17)	C31	C36	C35	113.26(16)
N2	C15	C16	118.09(16)	C38	C37	C30	134.99(18)
C14	C15	C16	122.36(17)	C38	C37	C42	118.88(17)
C17	C16	C15	120.05(17)	C42	C37	C30	106.13(16)
C21	C16	C15	121.29(17)	C39	C38	C37	118.82(18)
C21	C16	C17	118.64(18)	C38	C39	C40	121.16(18)
C18	C17	C16	120.17(19)	C41	C40	C39	121.85(18)
C19	C18	C17	120.68(19)	C40	C41	C42	117.21(18)
C18	C19	C20	119.78(19)	N4	C42	C37	110.29(16)
C19	C20	C21	119.79(19)	N4	C42	C41	127.65(17)
C20	C21	C16	120.82(19)	C41	C42	C37	122.04(17)

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C1	C2	C3	177.72(17)	N3	C28	C29	N4	178.75(18)
N1	C1	C6	C5	-178.50(16)	N3	C28	C29	C30	5.0(3)
N1	C1	C6	C7	1.7(2)	N3	C32	C33	C34	157.90(16)
N1	C14	C15	N2	179.77(17)	N4	C29	C30	C31	-178.37(16)
N1	C14	C15	C16	-3.3(3)	N4	C29	C30	C37	0.9(2)
N2	C15	C16	C17	42.6(2)	C22	C23	C24	C25	0.2(3)

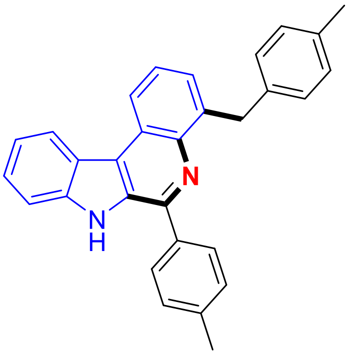
N2	C15	C16	C21	-139.17(19)	C22	C28	C29	N4	2.2(3)
C1	N1	C14	C7	1.3(2)	C22	C28	C29	C30	-171.61(17)
C1	N1	C14	C15	177.49(19)	C23	C22	C27	C26	-3.2(3)
C1	C2	C3	C4	1.7(3)	C23	C22	C28	N3	-46.5(3)
C1	C6	C7	C8	178.82(19)	C23	C22	C28	C29	130.1(2)
C1	C6	C7	C14	-0.90(19)	C23	C24	C25	C26	-2.3(3)
C2	C1	C6	C5	0.5(3)	C24	C25	C26	C27	1.5(3)
C2	C1	C6	C7	-179.25(16)	C25	C26	C27	C22	1.2(3)
C2	C3	C4	C5	-1.8(3)	C27	C22	C23	C24	2.5(3)
C3	C4	C5	C6	1.1(3)	C27	C22	C28	N3	136.02(19)
C4	C5	C6	C1	-0.5(3)	C27	C22	C28	C29	-47.4(3)
C4	C5	C6	C7	179.23(19)	C28	N3	C32	C31	-2.9(3)
C5	C6	C7	C8	-0.9(4)	C28	N3	C32	C33	176.08(16)
C5	C6	C7	C14	179.4(2)	C28	C22	C23	C24	-175.00(19)
C6	C1	C2	C3	-1.1(3)	C28	C22	C27	C26	174.24(18)
C6	C7	C8	C9	0.8(3)	C28	C29	C30	C31	-3.4(3)
C6	C7	C8	C13	-179.38(18)	C28	C29	C30	C37	175.87(17)
C6	C7	C14	N1	-0.2(2)	C29	N4	C42	C37	0.9(2)
C6	C7	C14	C15	-176.90(16)	C29	N4	C42	C41	179.47(18)
C7	C8	C9	C10	-160.93(17)	C29	C30	C31	C32	-1.1(3)
C7	C8	C13	N2	-3.2(3)	C29	C30	C31	C36	176.99(17)
C7	C8	C13	C12	174.97(17)	C29	C30	C37	C38	179.1(2)
C7	C14	C15	N2	-4.3(3)	C29	C30	C37	C42	-0.4(2)
C7	C14	C15	C16	172.61(16)	C30	C31	C32	N3	4.3(3)
C8	C7	C14	N1	-179.97(16)	C30	C31	C32	C33	-174.61(17)
C8	C7	C14	C15	3.3(3)	C30	C31	C36	C35	163.50(18)
C8	C9	C10	C11	-46.5(2)	C30	C37	C38	C39	-179.6(2)
C9	C8	C13	N2	176.62(17)	C30	C37	C42	N4	-0.3(2)
C9	C8	C13	C12	-5.2(3)	C30	C37	C42	C41	-178.98(17)
C9	C10	C11	C12	61.0(2)	C31	C30	C37	C38	-1.7(4)
C10	C11	C12	C13	-45.8(2)	C31	C30	C37	C42	178.8(2)
C11	C12	C13	N2	-163.13(16)	C31	C32	C33	C34	-23.1(3)
C11	C12	C13	C8	18.6(3)	C32	N3	C28	C22	174.83(16)
C13	N2	C15	C14	1.6(3)	C32	N3	C28	C29	-1.9(3)
C13	N2	C15	C16	-175.49(16)	C32	C31	C36	C35	-18.5(3)
C13	C8	C9	C10	19.3(2)	C32	C33	C34	C35	49.7(2)
C14	N1	C1	C2	179.18(18)	C33	C34	C35	C36	-62.2(2)
C14	N1	C1	C6	-1.8(2)	C34	C35	C36	C31	45.6(2)
C14	C7	C8	C9	-179.47(16)	C36	C31	C32	N3	-173.75(17)
C14	C7	C8	C13	0.3(2)	C36	C31	C32	C33	7.3(3)

C14	C15	C16	C17	-134.4(2)	C37	C30	C31	C32	179.86(19)
C14	C15	C16	C21	43.9(3)	C37	C30	C31	C36	-2.1(3)
C15	N2	C13	C8	2.3(3)	C37	C38	C39	C40	-1.7(3)
C15	N2	C13	C12	-175.96(16)	C38	C37	C42	N4	-179.91(16)
C15	C16	C17	C18	174.92(18)	C38	C37	C42	C41	1.4(3)
C15	C16	C21	C20	-174.65(18)	C38	C39	C40	C41	2.4(3)
C16	C17	C18	C19	0.5(3)	C39	C40	C41	C42	-1.1(3)
C17	C16	C21	C20	3.6(3)	C40	C41	C42	N4	-179.22(18)
C17	C18	C19	C20	2.2(3)	C40	C41	C42	C37	-0.8(3)
C18	C19	C20	C21	-2.0(3)	C42	N4	C29	C28	-175.43(19)
C19	C20	C21	C16	-1.0(3)	C42	N4	C29	C30	-1.1(2)
C21	C16	C17	C18	-3.4(3)	C42	C37	C38	C39	-0.1(3)

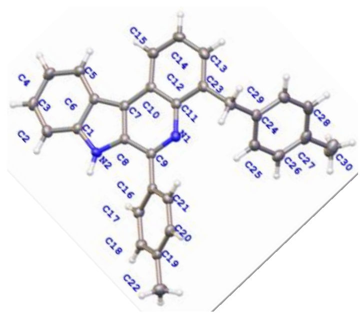
Table 7 Hydrogen Atom Coordinates (Å×10[4]) and Isotropic Displacement Parameters (Å[2]×10[3]) for 3a.

Atom	***x***	***y***	***z***	**U(eq)**
H1	4180(8)	3980(20)	3753(9)	24(6)
H2	3357.72	5432.04	4007.68	25
H3	3153.83	7409.3	4462.21	29
H4A	3797.34	8856.28	4866.2	32
H5	4674.17	8319.37	4876.45	28
H9A	5705.72	7348.77	5187.64	28
H9B	5501.91	8276.46	4692.52	28
H10A	6304.84	8363.05	4420.34	33
H10B	6406.92	8641.91	5037.92	33
H11A	7015.18	7025.07	4819.47	32
H11B	6653.68	6307.79	5189.49	32
H12A	6613.75	5943.4	4082.14	31
H12B	6698.21	4776.93	4518.23	31
H17	5736.45	1311.73	4144.54	31
H18	5506.41	-860.45	3802.92	36
H19	4805.23	-1125.3	3140.41	35
H20	4357.7	816.37	2776.86	36
H21	4588.21	3000.97	3112.06	30
H4	6357(8)	3320(20)	3525(8)	20(6)
H23	6588.02	5954.33	2012.8	31
H24	6279.99	8135.74	2191.8	38
H25	5688.95	8404.45	2786.3	35
H26	5356.93	6475.32	3170.6	36

H27	5648.84	4275.35	2981.58	30
H33A	6751.82	2377.73	1056.28	29
H33B	6374.68	1123.36	1108.44	29
H34A	7100.27	201.72	809.44	34
H34B	7479.04	992.68	1248.98	34
H35A	7403.25	-1369.29	1483.83	35
H35B	6799.2	-1170.36	1479.01	35
H36A	7144	-1012.07	2353.91	30
H36B	7599.84	-46.63	2227.01	30
H38	7400.37	-1019.92	3249	28
H39	7519.46	-1447.53	4159.23	31
H40	7237.44	116.61	4746.41	30
H41	6772.25	2084.43	4445.34	28



4b



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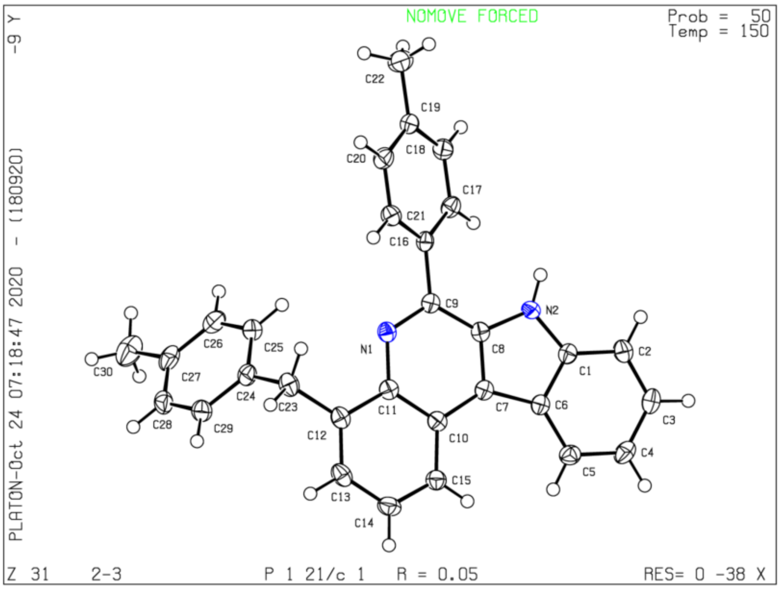


The ellipsoids are shown at 50% probability levels.

Table 1 Crystal data and structure refinement for 4b.

Identification code	**4b**
Empirical formula	$C_{30}H_{24}N_2$
Formula weight	412.51
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.7202(8)
b/Å	11.7394(7)
c/Å	11.6984(6)
α/°	90
β/°	96.880(5)
γ/°	90
Volume/Å^3	2143.3(2)
Z	4
ρ_{calc}g/cm^3	1.278
μ/mm^{-1}	0.074
F(000)	872.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.342 to 49.988
Index ranges	-18 ≤ h ≤ 18, -11 ≤ k ≤ 13, -13 ≤ l ≤ 13
Reflections collected	10160
Independent reflections	3764 [R_{int} = 0.0330, R_{sigma} = 0.0416]
Data/restraints/parameters	3764/0/295
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0456, wR_2 = 0.1045
Final R indexes [all data]	R_1 = 0.0576, wR_2 = 0.1122
Largest diff. peak/hole / e Å^{-3}	0.25/-0.26

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 4b. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
N1	3062.5(8)	4521.7(12)	3586.4(11)	21.6(3)
N2	4706.1(9)	5610.2(13)	1870.9(12)	23.2(3)
C1	5559.7(10)	5311.1(14)	2092.0(14)	21.8(4)
C2	6241.5(11)	5678.5(16)	1532.5(15)	26.7(4)

C3	7037.7(11)	5239.5(16)	1903.8(15)	28.4(4)
C4	7153.6(11)	4454.9(16)	2804.4(16)	28.6(4)
C5	6478.2(10)	4099.2(15)	3367.1(15)	25.2(4)
C6	5657.9(10)	4532.9(14)	3014.4(14)	20.3(4)
C7	4814.2(10)	4375.1(14)	3364.6(14)	19.6(4)
C8	4255.0(10)	5045.8(14)	2639.8(13)	20.2(4)
C9	3368.6(10)	5105.8(14)	2762.0(14)	19.8(4)
C10	4486.9(10)	3743.8(14)	4250.0(13)	20.5(4)
C11	3591.2(10)	3852.3(14)	4325.9(14)	20.9(4)
C12	3218.4(11)	3268.0(15)	5209.2(14)	22.8(4)
C13	3734.3(11)	2614.2(15)	5977.4(15)	26.9(4)
C14	4616.3(11)	2507.9(16)	5908.5(15)	28.1(4)
C15	4985.7(11)	3060.9(15)	5064.9(15)	24.6(4)
C16	2752.7(10)	5825.1(14)	2028.0(14)	20.6(4)
C17	2810.0(10)	6034.9(15)	866.2(14)	24.0(4)
C18	2203.0(10)	6702.1(15)	221.4(15)	25.3(4)
C19	1519.5(10)	7177.8(15)	699.5(15)	24.0(4)
C20	1462.1(11)	6958.0(15)	1852.2(15)	26.2(4)
C21	2062.8(11)	6301.9(15)	2504.1(15)	25.2(4)
C22	854.4(11)	7896.7(18)	2.3(16)	36.0(5)
C23	2269.2(11)	3386.7(16)	5316.2(15)	26.9(4)
C24	1713.7(10)	2519.6(15)	4626.0(15)	24.2(4)
C25	1419.3(10)	2691.5(16)	3470.2(15)	27.4(4)
C26	922.6(11)	1884.5(17)	2844.6(16)	30.9(4)
C27	694.5(11)	870.5(16)	3338.0(17)	31.0(4)
C28	974.6(11)	709.1(16)	4498.2(17)	29.9(4)
C29	1477.2(11)	1509.5(15)	5125.4(15)	27.7(4)
C30	185.2(13)	-32.2(19)	2646(2)	46.5(6)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 4b. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	22.7(7)	22.4(8)	20.2(7)	-0.4(6)	4.0(6)	-2.1(6)
N2	21.3(7)	26.7(8)	22.1(8)	7.8(7)	3.8(6)	1.6(7)
C1	20.1(8)	22.1(9)	23.4(9)	-2.2(7)	3.0(7)	-1.0(7)
C2	27.7(9)	28.3(10)	25.1(9)	1.3(8)	7.4(8)	-2.8(8)
C3	22.0(9)	33.2(11)	31.2(10)	-4.1(9)	8.5(8)	-4.4(8)
C4	19.4(8)	30.0(10)	36.2(11)	-4.9(9)	2.9(8)	2.9(8)
C5	24.9(9)	22.2(9)	27.8(10)	-1.0(8)	0.7(7)	1.6(8)

C6	21.1(8)	19.4(9)	20.3(9)	-4.1(7)	1.8(7)	-2.1(7)
C7	20.9(8)	19.0(9)	18.7(8)	-4.6(7)	1.6(7)	-1.7(7)
C8	22.3(8)	21.0(9)	17.6(8)	-1.7(7)	3.3(7)	-2.0(7)
C9	20.5(8)	19.6(9)	19.3(8)	-2.9(7)	2.5(7)	-1.0(7)
C10	24.4(8)	18.7(9)	17.8(8)	-3.5(7)	0.2(7)	-3.0(7)
C11	23.2(8)	20.6(9)	18.6(8)	-3.2(7)	1.8(7)	-2.0(7)
C12	27.7(9)	20.8(9)	20.1(9)	-3.0(7)	3.4(7)	-4.6(8)
C13	35.6(10)	25.4(10)	20.2(9)	0.6(8)	5.6(8)	-5.4(8)
C14	33.0(10)	25.3(10)	24.4(9)	4.0(8)	-3.3(8)	0.1(8)
C15	25.0(9)	23.1(9)	25.2(9)	0.8(8)	0.6(7)	-1.1(8)
C16	19.1(8)	20.9(9)	21.5(9)	-2.1(7)	1.8(7)	-3.6(7)
C17	20.2(8)	29.2(10)	23.0(9)	-2.6(8)	3.8(7)	-0.3(8)
C18	25.5(9)	30.3(10)	19.9(9)	1.0(8)	2.0(7)	-2.6(8)
C19	21.3(8)	23.9(9)	26.1(9)	1.3(8)	0.3(7)	-3.0(7)
C20	21.6(8)	28.5(10)	29.5(10)	-0.4(8)	6.9(8)	2.5(8)
C21	25.8(9)	28.9(10)	21.5(9)	2.8(8)	5.6(7)	0.3(8)
C22	29.5(10)	45.1(12)	33.2(11)	6.9(10)	2.9(8)	6.7(9)
C23	30.5(9)	28.3(10)	23.5(9)	-0.6(8)	10.2(8)	-2.0(8)
C24	20.1(8)	28.1(10)	25.9(10)	-0.4(8)	9.5(7)	1.8(8)
C25	23.8(9)	29.3(10)	29.7(10)	4.9(8)	5.5(8)	-0.2(8)
C26	21.7(9)	40.9(12)	29.6(10)	-0.6(9)	1.1(8)	2.3(9)
C27	18.3(8)	31.4(11)	44.2(12)	-8.1(9)	7.0(8)	1.5(8)
C28	23.6(9)	22.5(10)	45.4(12)	2.5(9)	12.3(8)	0.6(8)
C29	25.7(9)	31.2(10)	27.5(10)	4.0(8)	9.0(8)	2.3(8)
C30	32.3(11)	41.8(13)	64.9(15)	-15.6(12)	3.8(10)	-1.5(10)

Table 4 Bond Lengths for 4b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C9	1.320(2)	C12	C23	1.519(2)
N1	C11	1.373(2)	C13	C14	1.404(2)
N2	C1	1.381(2)	C14	C15	1.367(2)
N2	C8	1.380(2)	C16	C17	1.395(2)
C1	C2	1.390(2)	C16	C21	1.394(2)
C1	C6	1.408(2)	C17	C18	1.386(2)
C2	C3	1.375(2)	C18	C19	1.387(2)
C3	C4	1.395(3)	C19	C20	1.386(2)
C4	C5	1.379(2)	C19	C22	1.505(2)
C5	C6	1.402(2)	C20	C21	1.376(2)
C6	C7	1.446(2)	C23	C24	1.511(2)

C7	C8	1.390(2)	C24	C25	1.390(2)
C7	C10	1.419(2)	C24	C29	1.392(2)
C8	C9	1.419(2)	C25	C26	1.380(3)
C9	C16	1.479(2)	C26	C27	1.389(3)
C10	C11	1.427(2)	C27	C28	1.389(3)
C10	C15	1.410(2)	C27	C30	1.505(3)
C11	C12	1.424(2)	C28	C29	1.381(3)
C12	C13	1.371(2)			

Table 5 Bond Angles for 4b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	N1	C11	120.77(14)	C11	C12	C23	120.64(15)
C8	N2	C1	108.63(14)	C13	C12	C11	118.87(15)
N2	C1	C2	128.30(16)	C13	C12	C23	120.48(15)
N2	C1	C6	108.86(14)	C12	C13	C14	121.52(16)
C2	C1	C6	122.84(15)	C15	C14	C13	120.46(17)
C3	C2	C1	117.33(16)	C14	C15	C10	120.54(16)
C2	C3	C4	121.18(16)	C17	C16	C9	123.52(15)
C5	C4	C3	121.46(16)	C21	C16	C9	118.91(15)
C4	C5	C6	118.89(16)	C21	C16	C17	117.55(15)
C1	C6	C7	106.27(14)	C18	C17	C16	120.63(16)
C5	C6	C1	118.28(15)	C17	C18	C19	121.62(16)
C5	C6	C7	135.45(16)	C18	C19	C22	121.91(16)
C8	C7	C6	106.80(14)	C20	C19	C18	117.47(16)
C8	C7	C10	118.86(15)	C20	C19	C22	120.62(16)
C10	C7	C6	134.32(15)	C21	C20	C19	121.52(16)
N2	C8	C7	109.43(14)	C20	C21	C16	121.21(16)
N2	C8	C9	128.99(15)	C24	C23	C12	113.89(14)
C7	C8	C9	121.56(15)	C25	C24	C23	121.72(16)
N1	C9	C8	119.73(15)	C25	C24	C29	117.21(16)
N1	C9	C16	116.75(14)	C29	C24	C23	121.07(16)
C8	C9	C16	123.50(15)	C26	C25	C24	121.15(17)
C7	C10	C11	116.46(15)	C25	C26	C27	121.71(17)
C15	C10	C7	124.72(15)	C26	C27	C28	117.12(17)
C15	C10	C11	118.79(15)	C26	C27	C30	121.81(18)
N1	C11	C10	122.63(15)	C28	C27	C30	121.05(18)
N1	C11	C12	117.54(14)	C29	C28	C27	121.38(17)
C12	C11	C10	119.82(15)	C28	C29	C24	121.42(17)

Table 6 Torsion Angles for 4b.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C9	C16	C17	-147.34(16)	C9	N1	C11	C12	178.62(15)
N1	C9	C16	C21	31.0(2)	C9	C16	C17	C18	178.91(16)
N1	C11	C12	C13	-178.49(15)	C9	C16	C21	C20	-178.65(16)
N1	C11	C12	C23	0.2(2)	C10	C7	C8	N2	178.12(14)
N2	C1	C2	C3	-178.98(17)	C10	C7	C8	C9	-0.4(2)
N2	C1	C6	C5	178.76(14)	C10	C11	C12	C13	0.4(2)
N2	C1	C6	C7	-0.67(18)	C10	C11	C12	C23	179.05(15)
N2	C8	C9	N1	-177.63(16)	C11	N1	C9	C8	-0.2(2)
N2	C8	C9	C16	0.5(3)	C11	N1	C9	C16	-178.48(14)
C1	N2	C8	C7	-0.07(19)	C11	C10	C15	C14	0.4(3)
C1	N2	C8	C9	178.30(17)	C11	C12	C13	C14	-0.2(3)
C1	C2	C3	C4	0.1(3)	C11	C12	C23	C24	89.4(2)
C1	C6	C7	C8	0.62(18)	C12	C13	C14	C15	0.1(3)
C1	C6	C7	C10	-177.50(18)	C12	C23	C24	C25	-85.3(2)
C2	C1	C6	C5	-1.1(3)	C12	C23	C24	C29	94.54(19)
C2	C1	C6	C7	179.51(16)	C13	C12	C23	C24	-91.92(19)
C2	C3	C4	C5	-0.8(3)	C13	C14	C15	C10	-0.2(3)
C3	C4	C5	C6	0.5(3)	C15	C10	C11	N1	178.34(15)
C4	C5	C6	C1	0.4(2)	C15	C10	C11	C12	-0.5(2)
C4	C5	C6	C7	179.59(18)	C16	C17	C18	C19	-0.3(3)
C5	C6	C7	C8	-178.66(18)	C17	C16	C21	C20	-0.2(3)
C5	C6	C7	C10	3.2(3)	C17	C18	C19	C20	-0.2(3)
C6	C1	C2	C3	0.8(3)	C17	C18	C19	C22	-179.57(17)
C6	C7	C8	N2	-0.35(18)	C18	C19	C20	C21	0.6(3)
C6	C7	C8	C9	-178.86(15)	C19	C20	C21	C16	-0.4(3)
C6	C7	C10	C11	177.89(17)	C21	C16	C17	C18	0.5(2)
C6	C7	C10	C15	0.1(3)	C22	C19	C20	C21	179.92(17)
C7	C8	C9	N1	0.6(2)	C23	C12	C13	C14	-178.84(16)
C7	C8	C9	C16	178.68(15)	C23	C24	C25	C26	179.02(15)
C7	C10	C11	N1	0.4(2)	C23	C24	C29	C28	-179.53(15)
C7	C10	C11	C12	-178.44(15)	C24	C25	C26	C27	0.1(3)
C7	C10	C15	C14	178.15(16)	C25	C24	C29	C28	0.3(2)
C8	N2	C1	C2	-179.72(17)	C25	C26	C27	C28	1.2(3)
C8	N2	C1	C6	0.47(19)	C25	C26	C27	C30	-177.32(17)
C8	C7	C10	C11	-0.1(2)	C26	C27	C28	C29	-1.7(3)
C8	C7	C10	C15	-177.89(15)	C27	C28	C29	C24	1.0(3)
C8	C9	C16	C17	34.5(3)	C29	C24	C25	C26	-0.8(2)

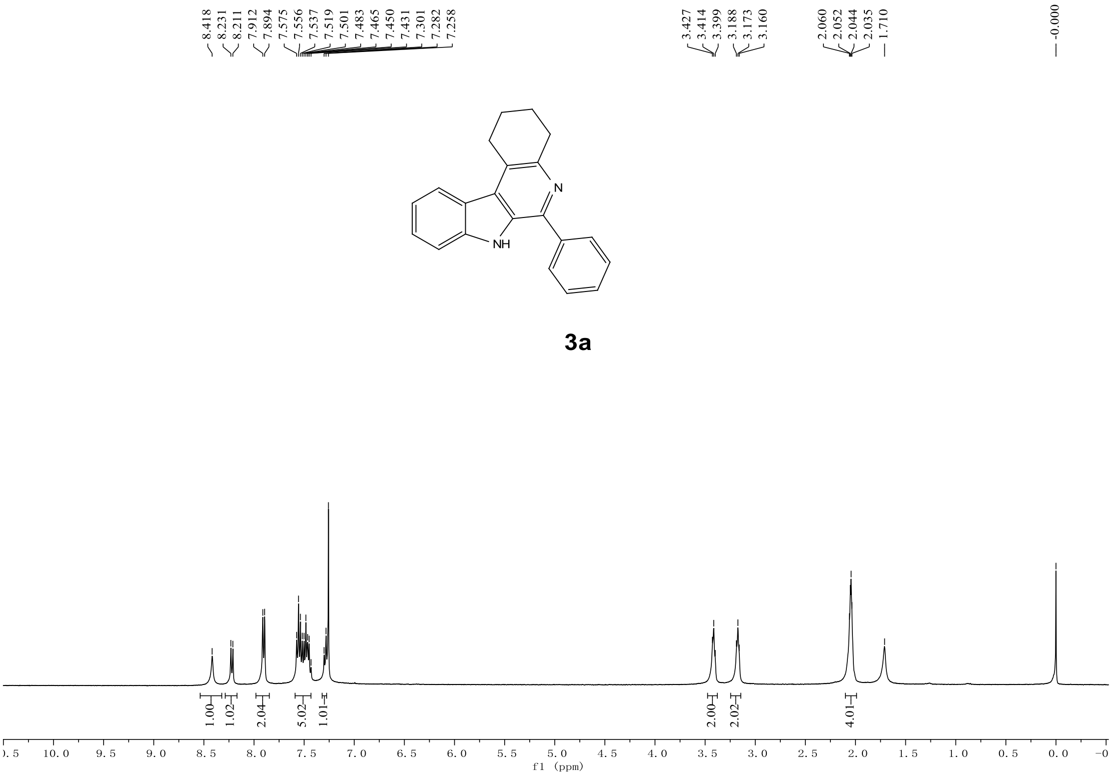
C8	C9	C16	C21	-147.14(17)	C30	C27	C28	C29	176.82(16)
C9	N1	C11	C10	-0.2(2)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4b.

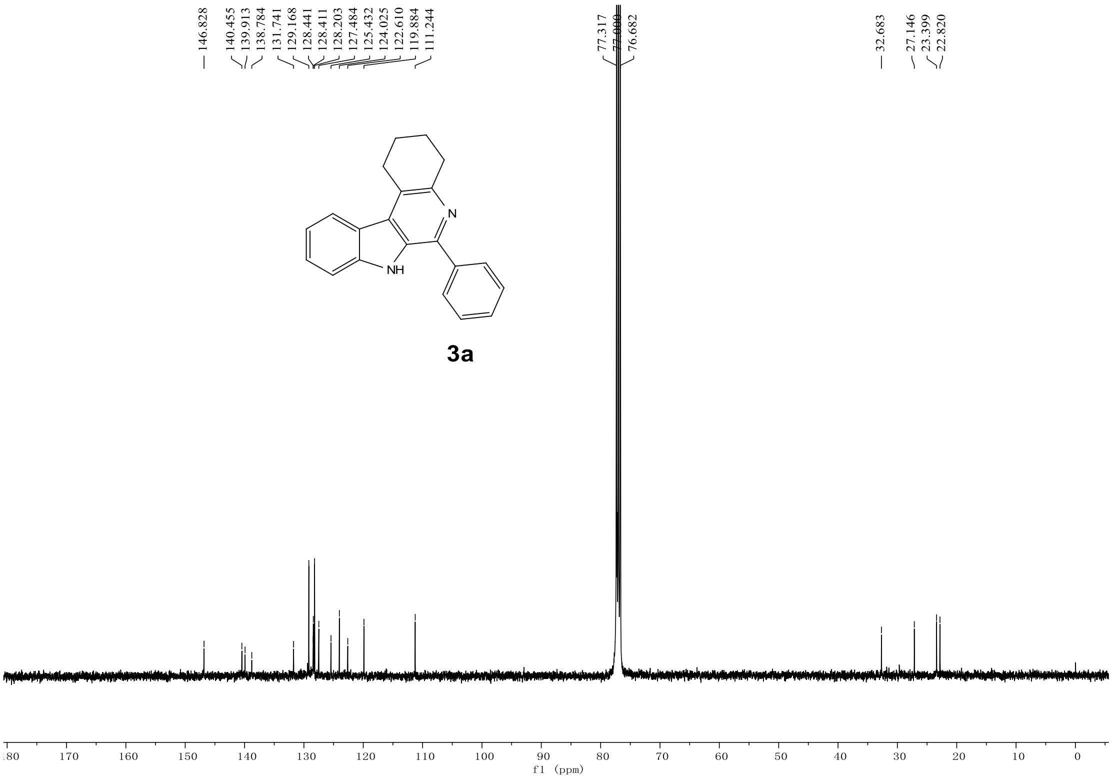
Atom	*x*	*y*	*z*	U(eq)
H2	4514(12)	6136(17)	1384(16)	30(5)
H2A	6162.45	6200.36	931.1	32
H3	7507.29	5469.77	1548.06	34
H4	7698.4	4165.13	3030.52	34
H5	6565.52	3580.34	3970.43	30
H13	3494.53	2232.22	6557.41	32
H14	4951.63	2058.35	6440.29	34
H15	5570.77	2985.94	5028.56	30
H17	3259.9	5723.97	520.93	29
H18	2255.34	6834.15	-550.95	30
H20	1007.17	7260.96	2192.71	31
H21	2007.6	6174.11	3276.32	30
H22A	1029.89	8680.39	43.48	54
H22B	315.83	7819.02	304.18	54
H22C	793.49	7649.15	-785.39	54
H23A	2184.84	3314.08	6120.85	32
H23B	2083.68	4143.86	5065.01	32
H25	1559.37	3361.67	3112.33	33
H26	735.85	2023.64	2072.65	37
H28	820.43	48.08	4860.3	36
H29	1661.6	1370.8	5898.13	33
H30A	565.55	-612.82	2430.34	70
H30B	-114.34	304.03	1965.14	70
H30C	-220.39	-363.63	3099.97	70

6. ^{1}H and ^{13}C NMR spectra of all products

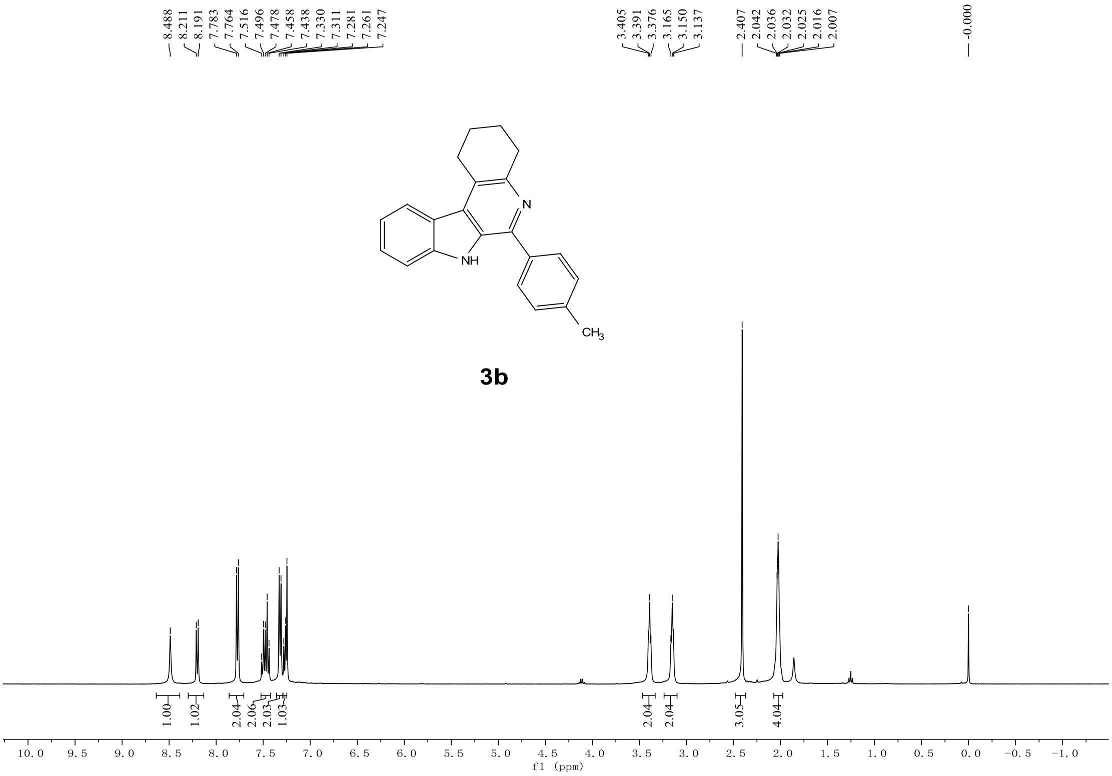
^{1}H NMR of **3a** (400 MHz, $CDCl_3$):



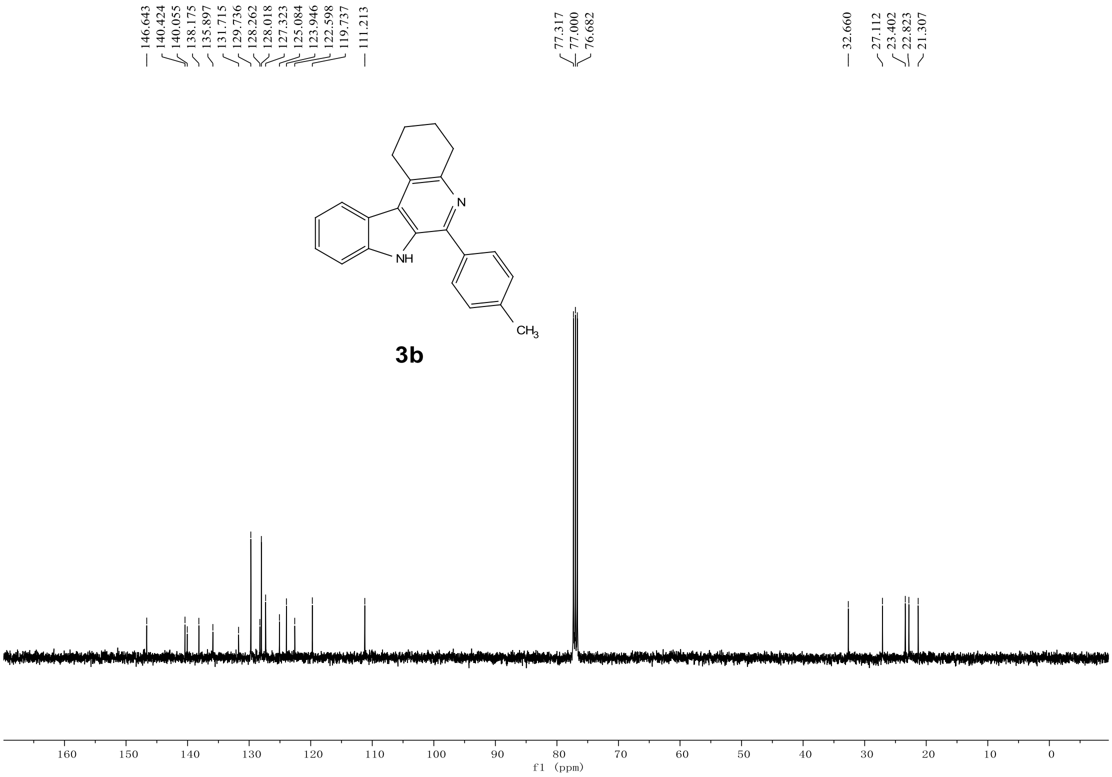
^{13}C NMR of **3a** (400 MHz, $CDCl_3$):



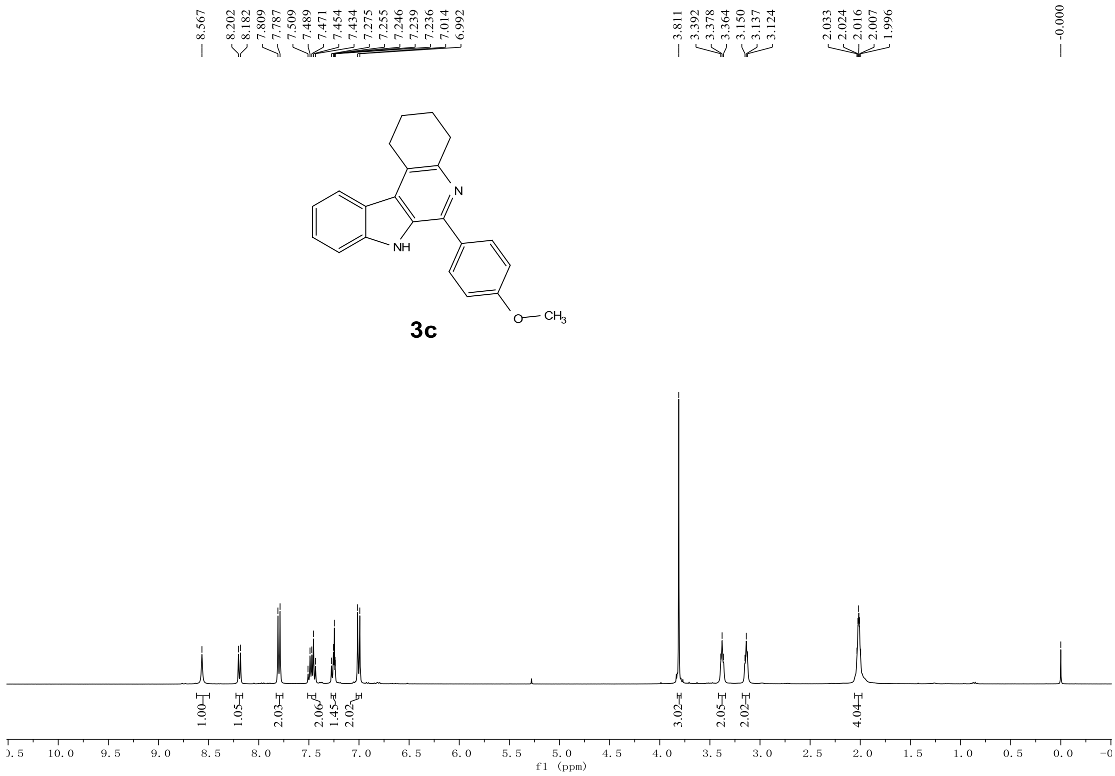
^{1}H NMR of **3b** (400 MHz, $CDCl_3$):



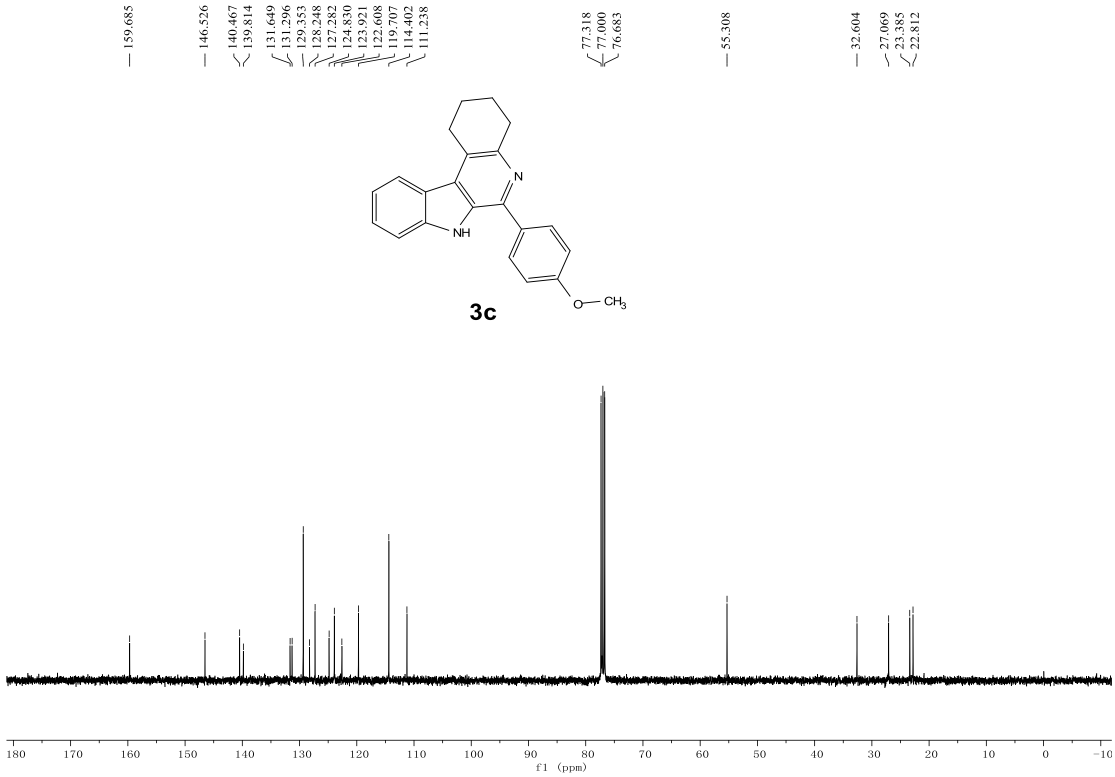
^{13}C NMR of **3b** (400 MHz, $CDCl_3$):



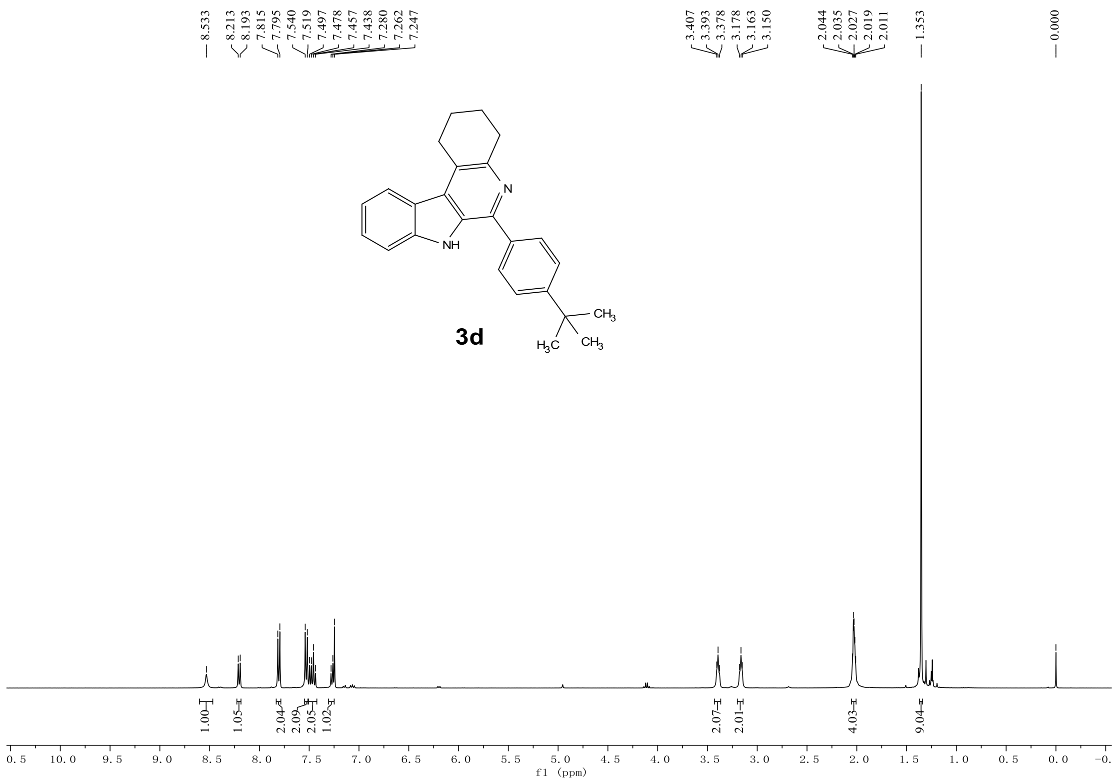
^{1}H NMR of **3c** (400 MHz, $CDCl_3$):



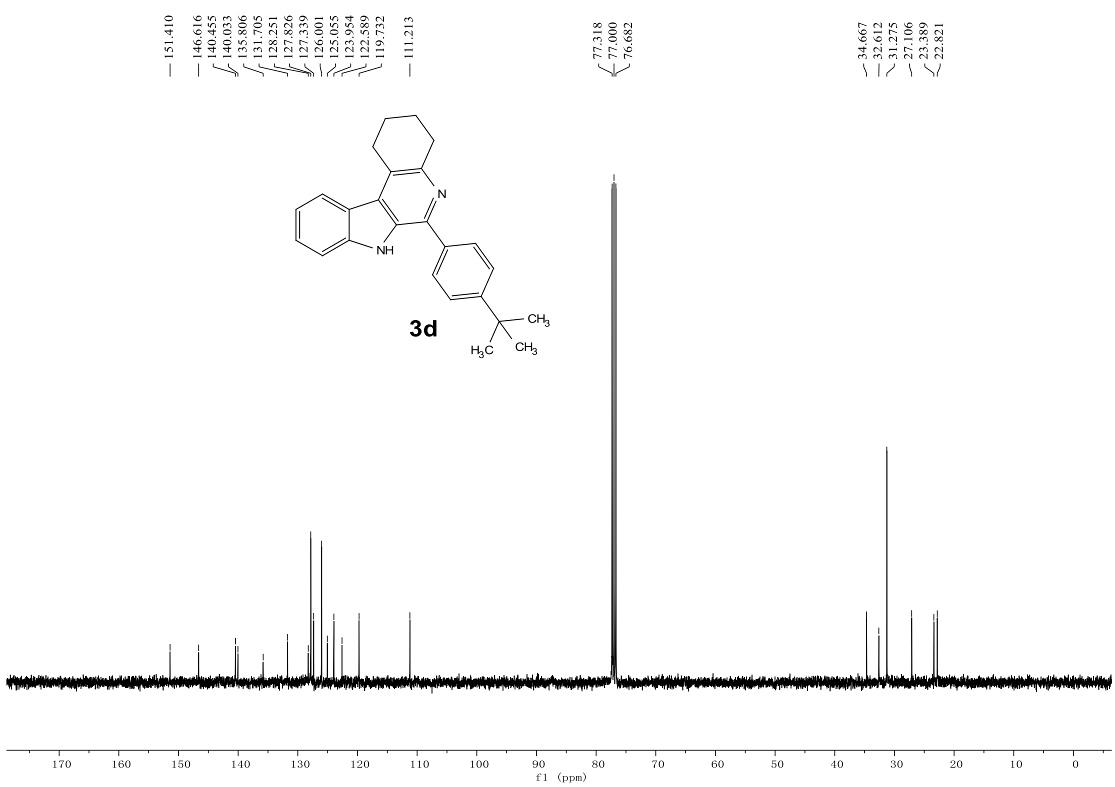
^{13}C NMR of **3c** (400 MHz, $CDCl_3$):



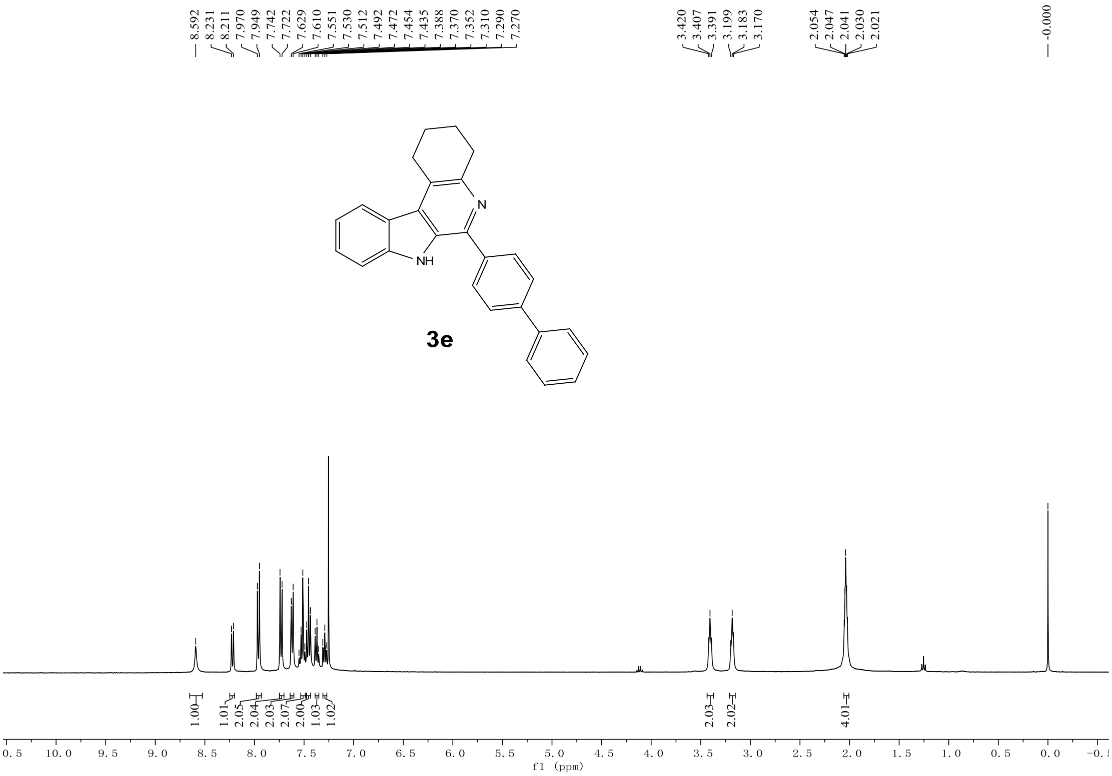
^{1}H NMR of **3d** (400 MHz, $CDCl_3$):



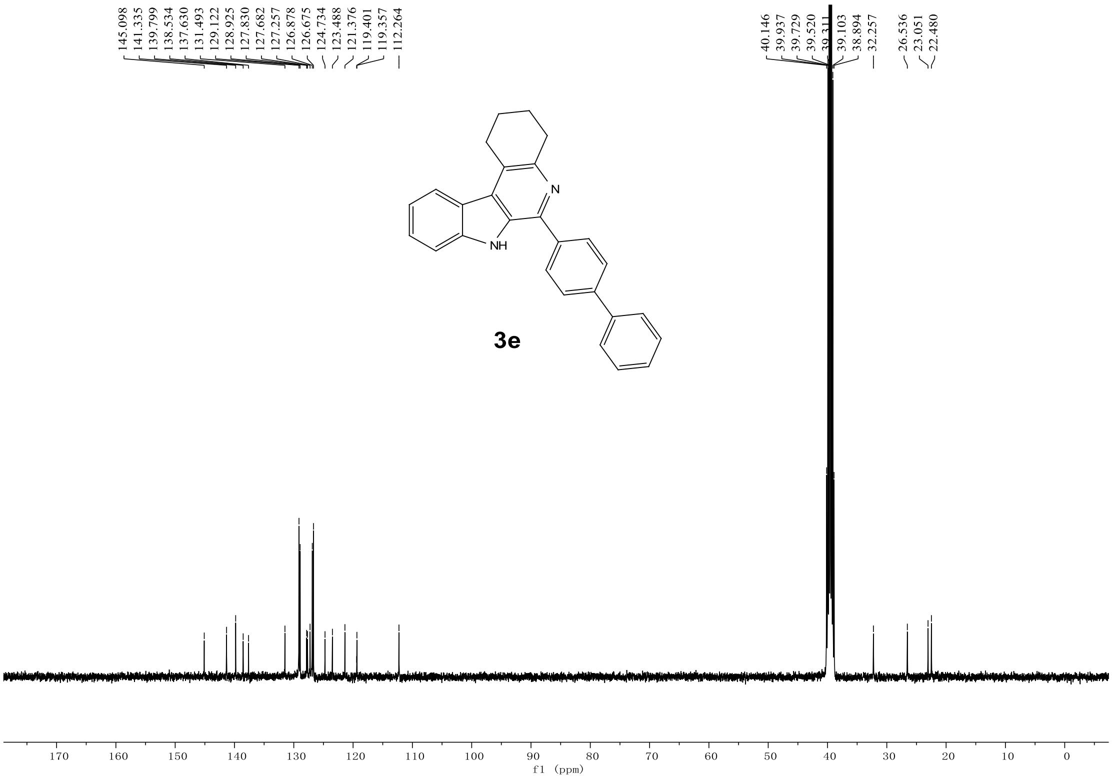
^{13}C NMR of **3d** (400 MHz, $CDCl_3$):



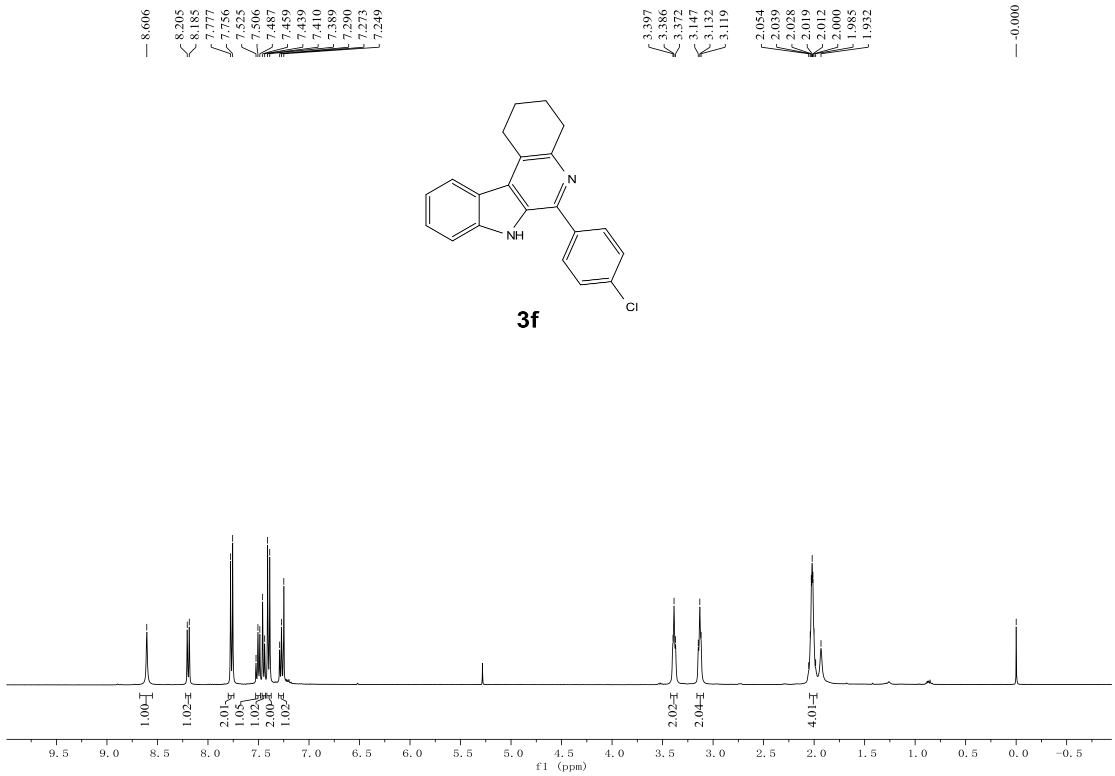
^{1}H NMR of **3e** (400 MHz, $CDCl_3$):



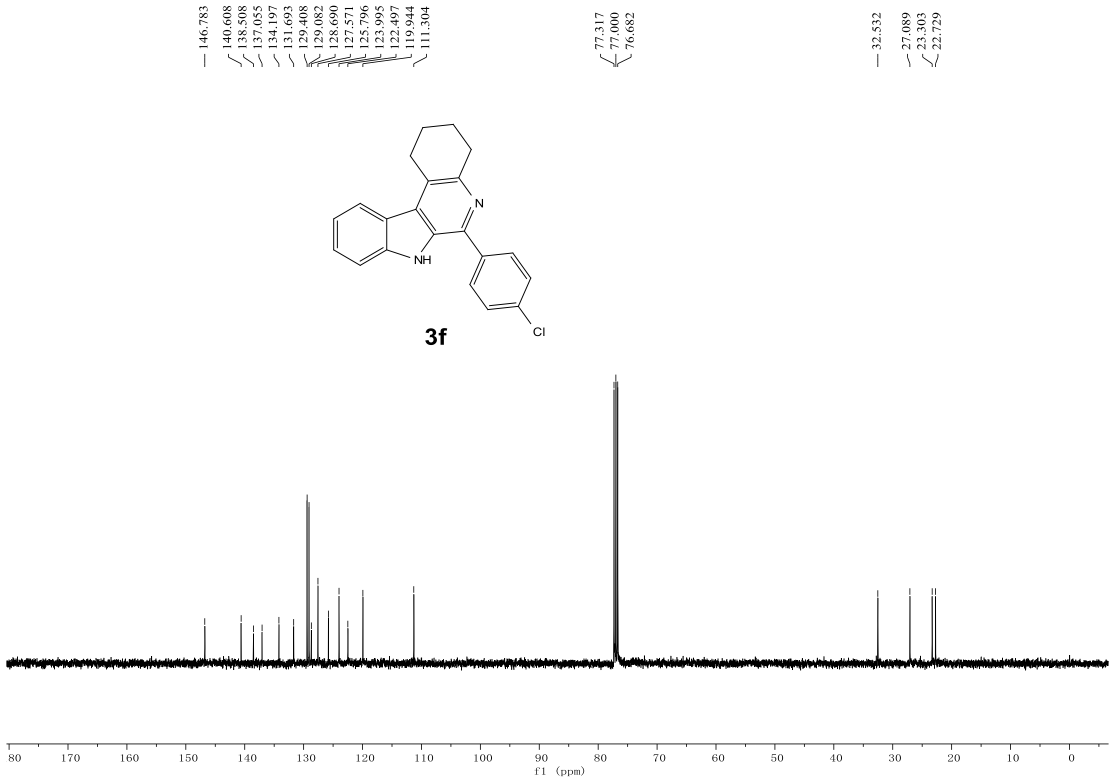
^{13}C NMR of **3e** (400 MHz, DMSO-*d*6):



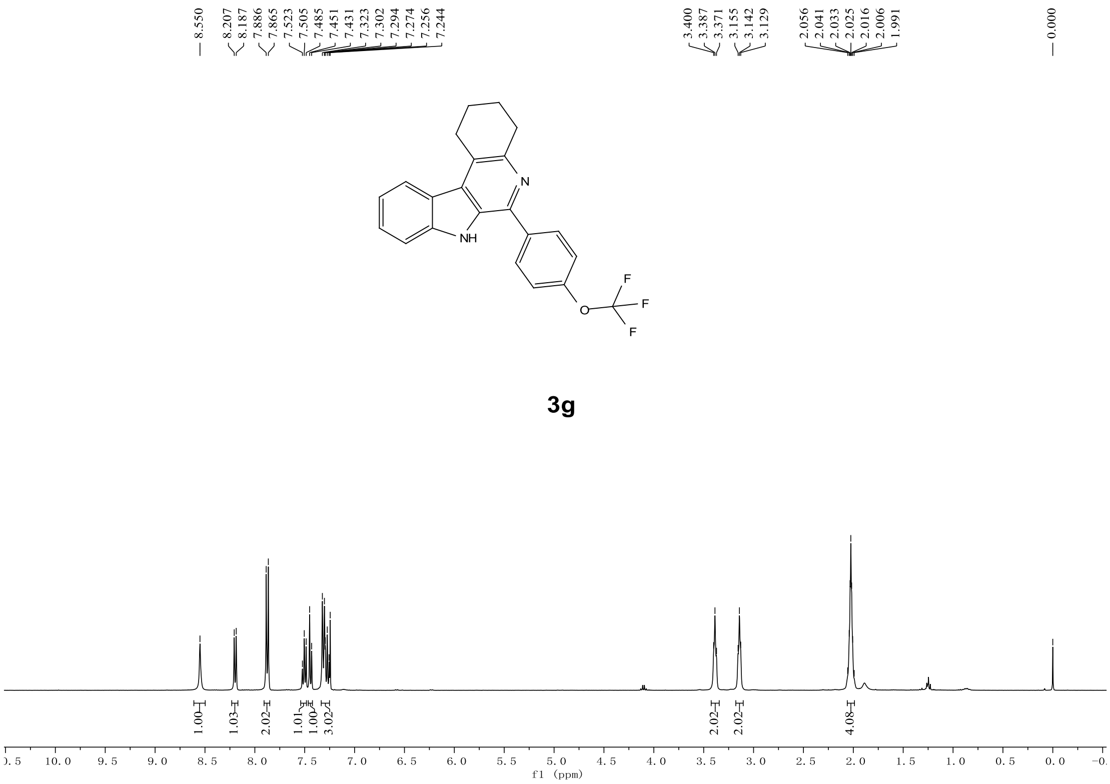
^{1}H NMR of **3f** (400 MHz, $CDCl_3$):



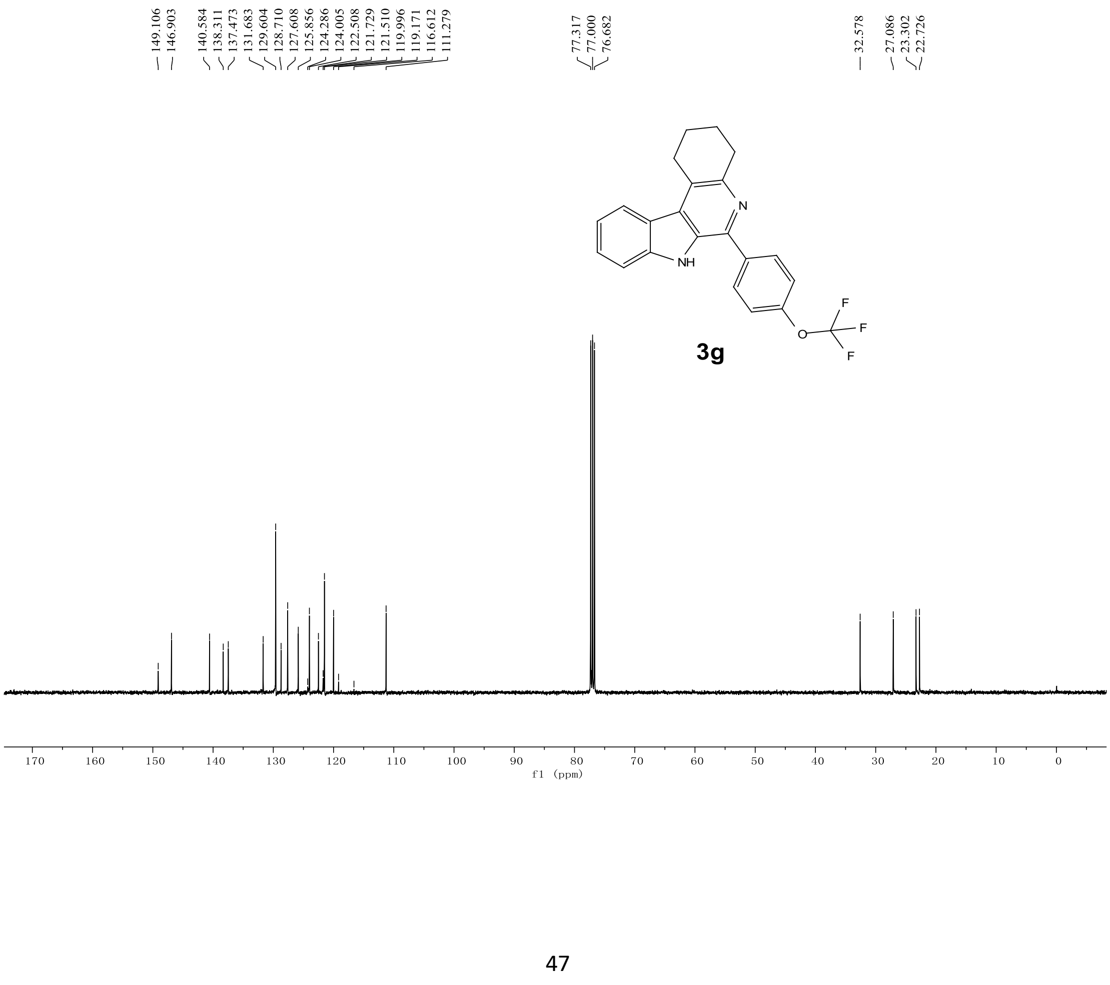
^{13}C NMR of **3f** (400 MHz, $CDCl_3$):



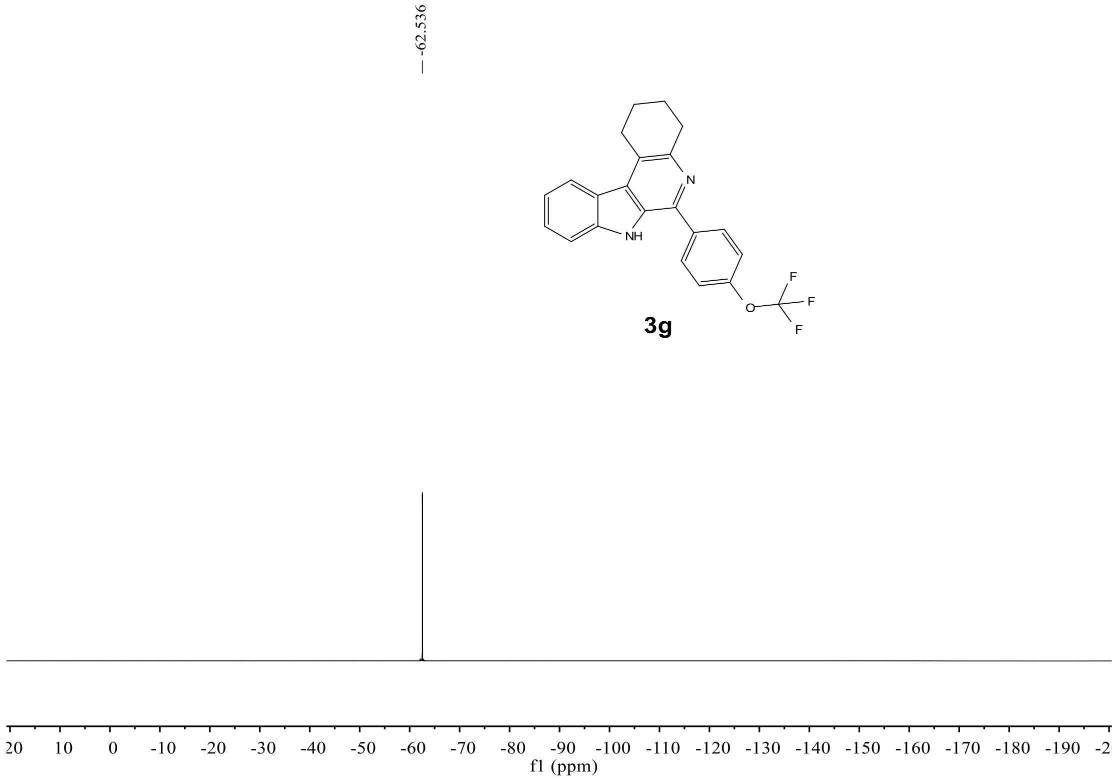
^{1}H NMR of **3g** (400 MHz, $CDCl_3$):



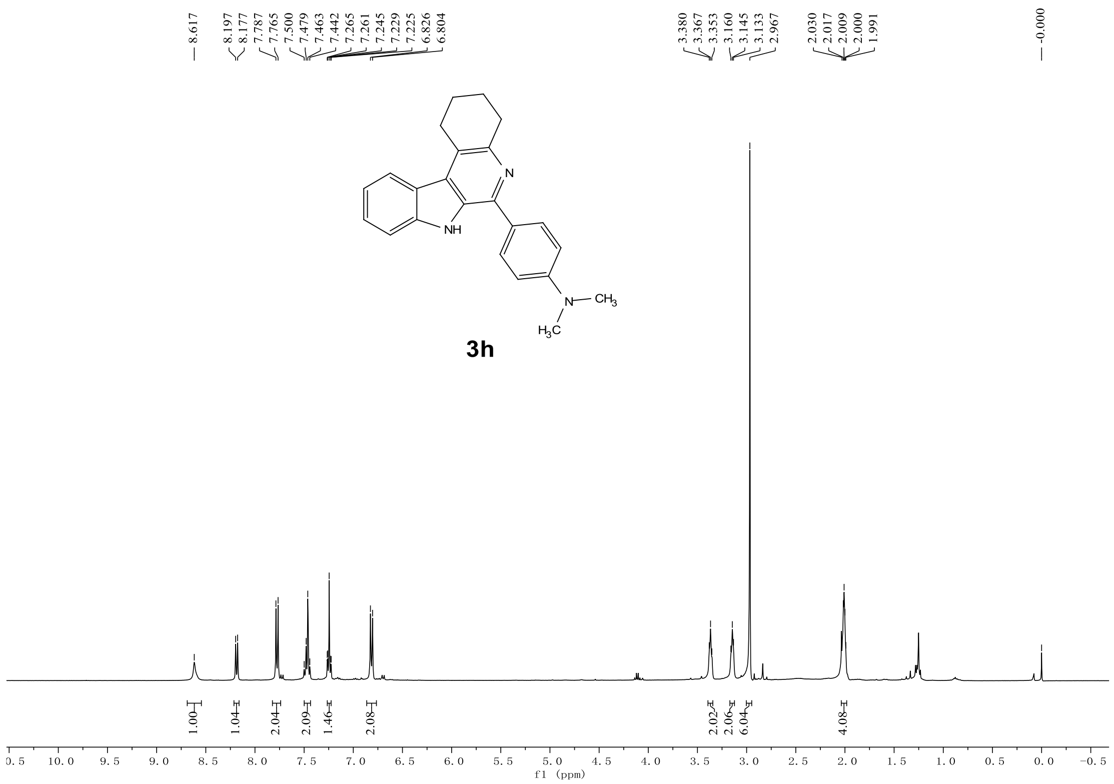
^{13}C NMR of **3g** (400 MHz, $CDCl_3$):



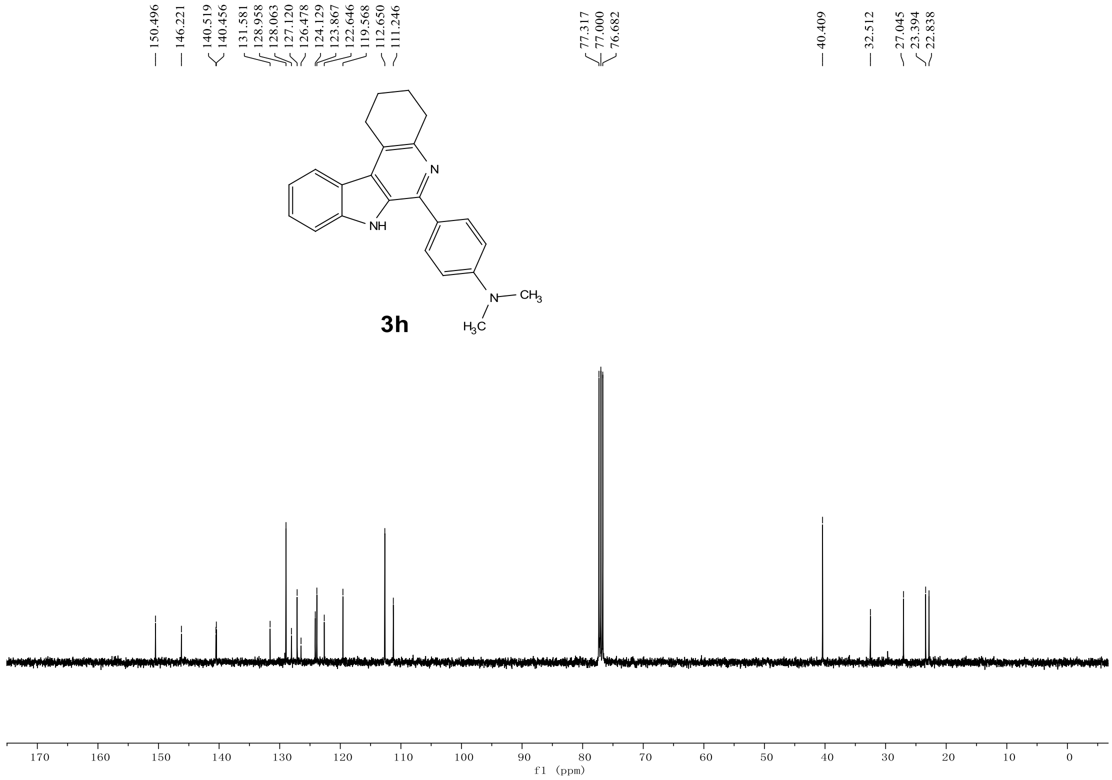
^{19}F NMR of **3g** (471 MHz, $CDCl_3$):



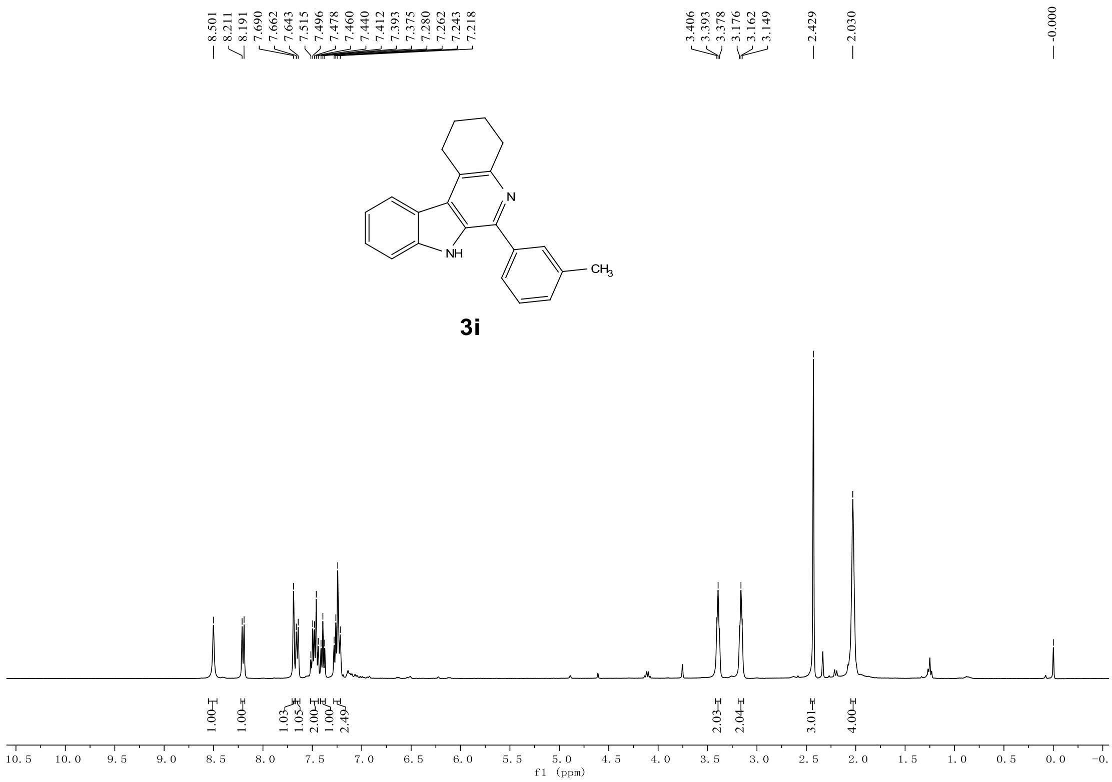
^{1}H NMR of **3h** (400 MHz, $CDCl_3$):



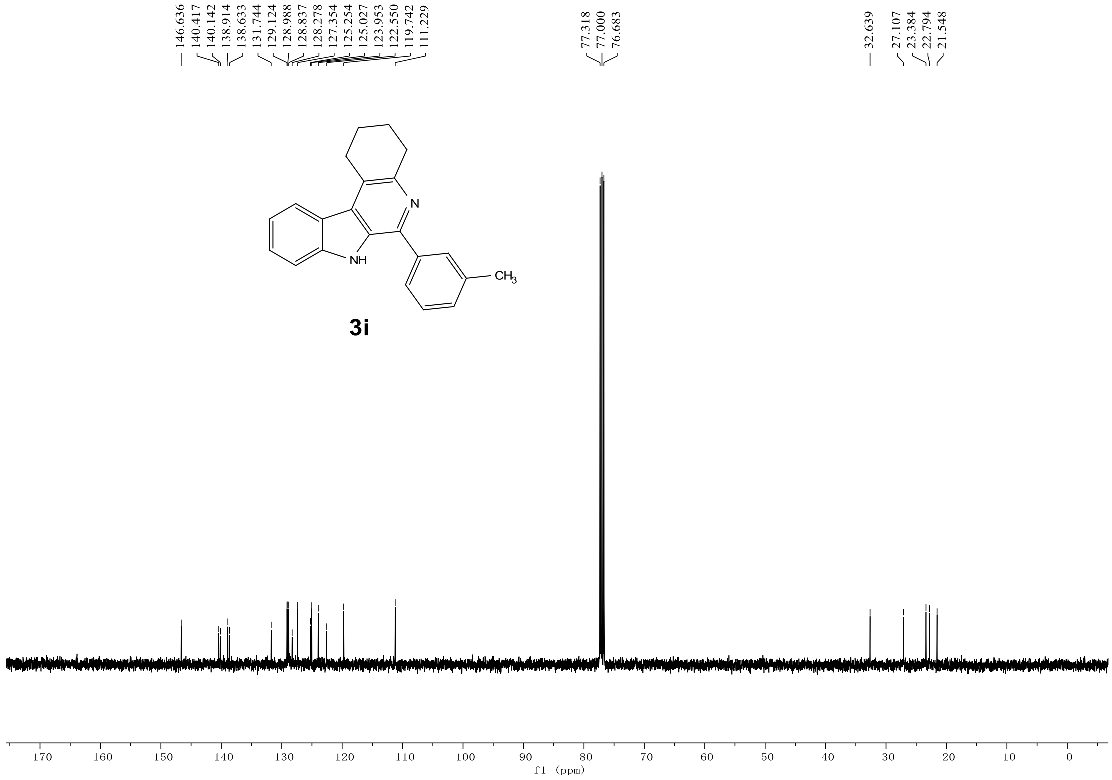
^{13}C NMR of **3h** (400 MHz, $CDCl_3$):



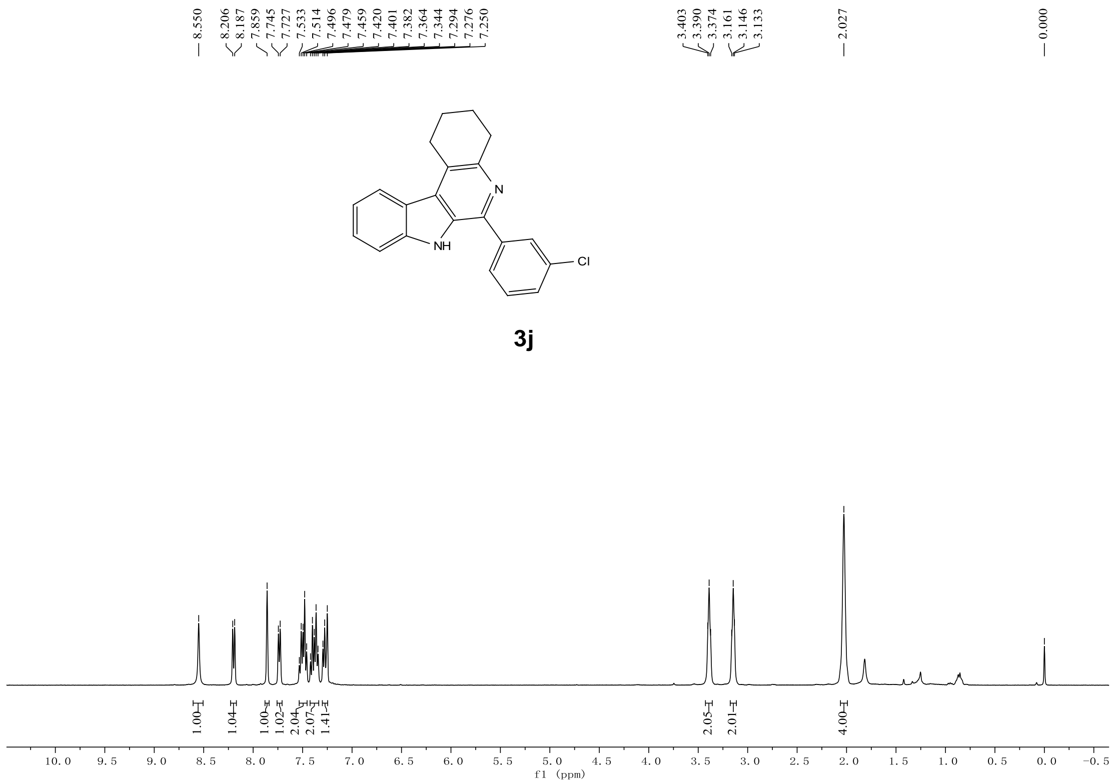
^{1}H NMR of **3i** (400 MHz, $CDCl_3$):



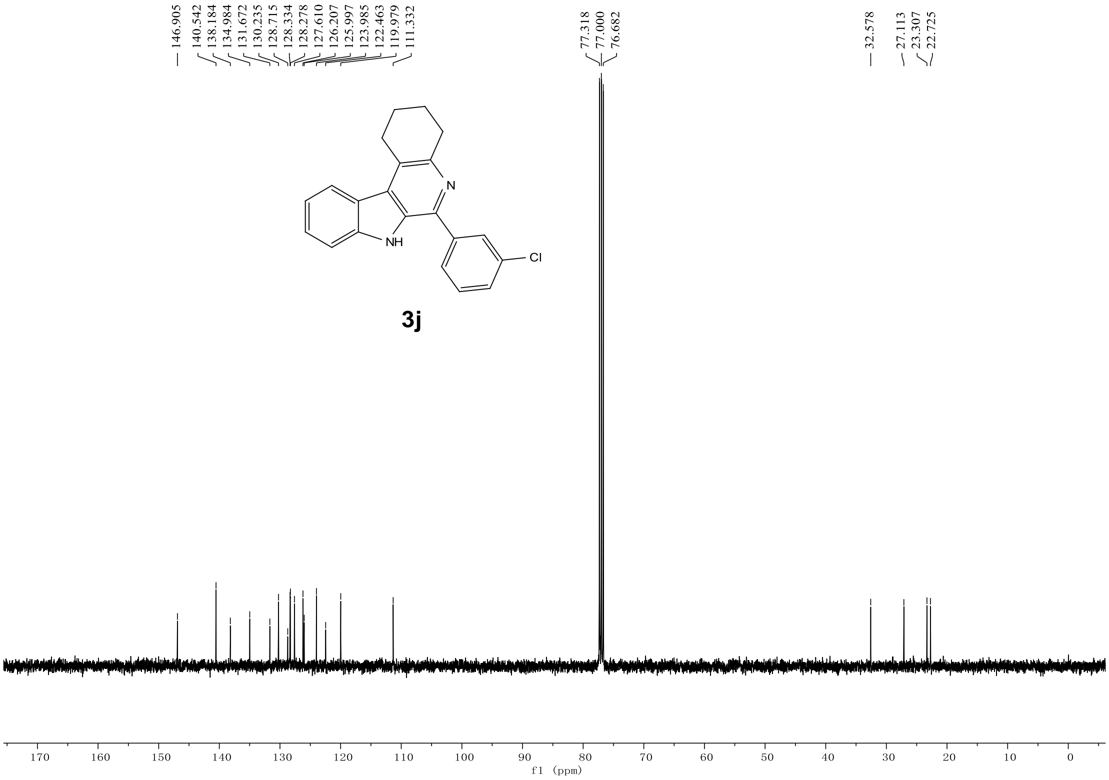
^{13}C NMR of **3i** (400 MHz, $CDCl_3$):



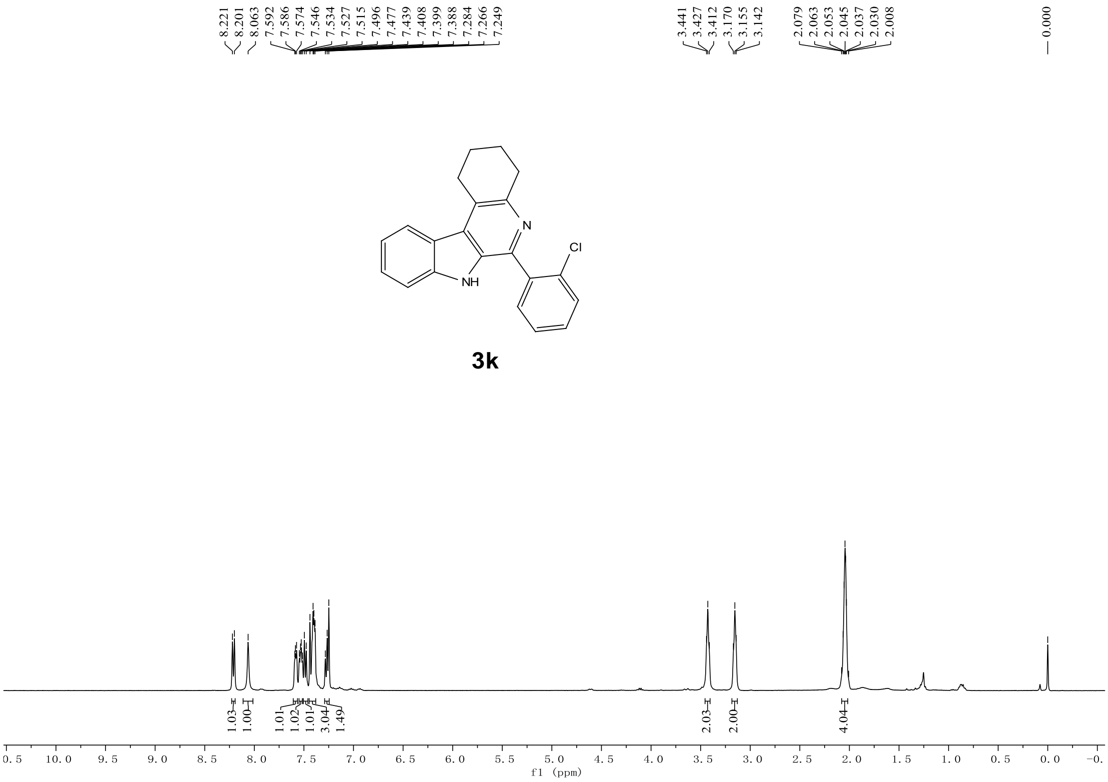
^{1}H NMR of **3j** (400 MHz, $CDCl_3$):



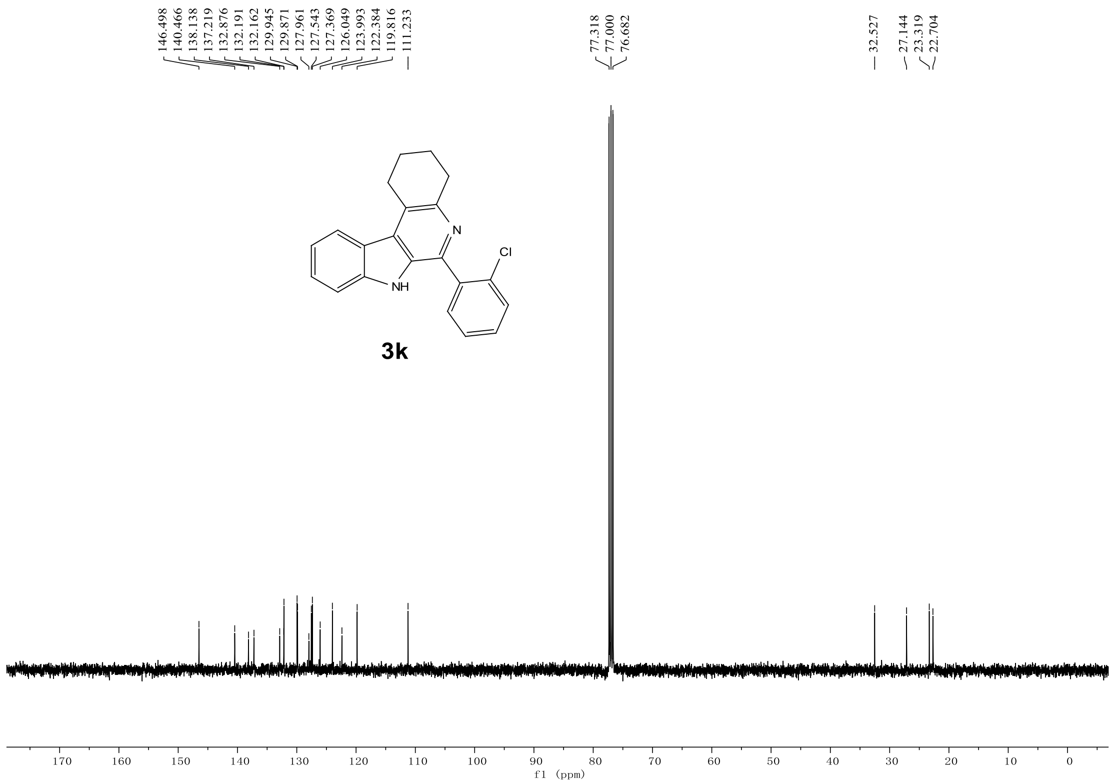
^{13}C NMR of **3j** (400 MHz, $CDCl_3$):



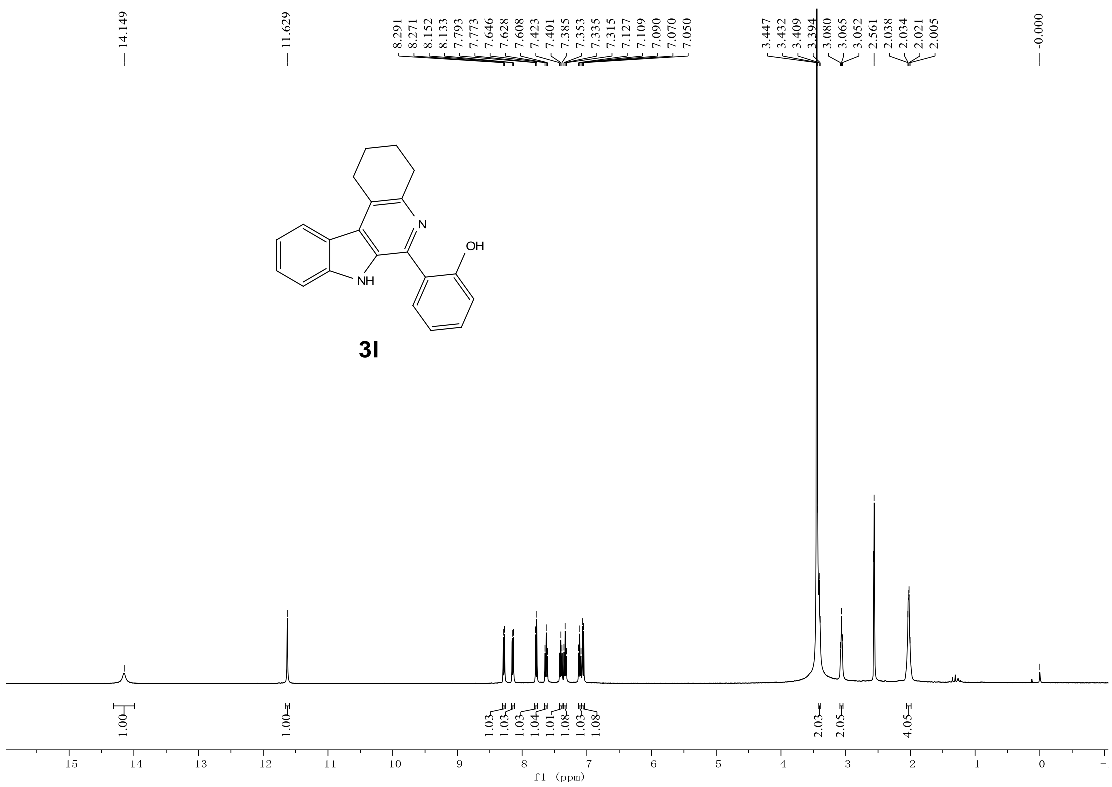
^{1}H NMR of **3k** (400 MHz, $CDCl_3$):



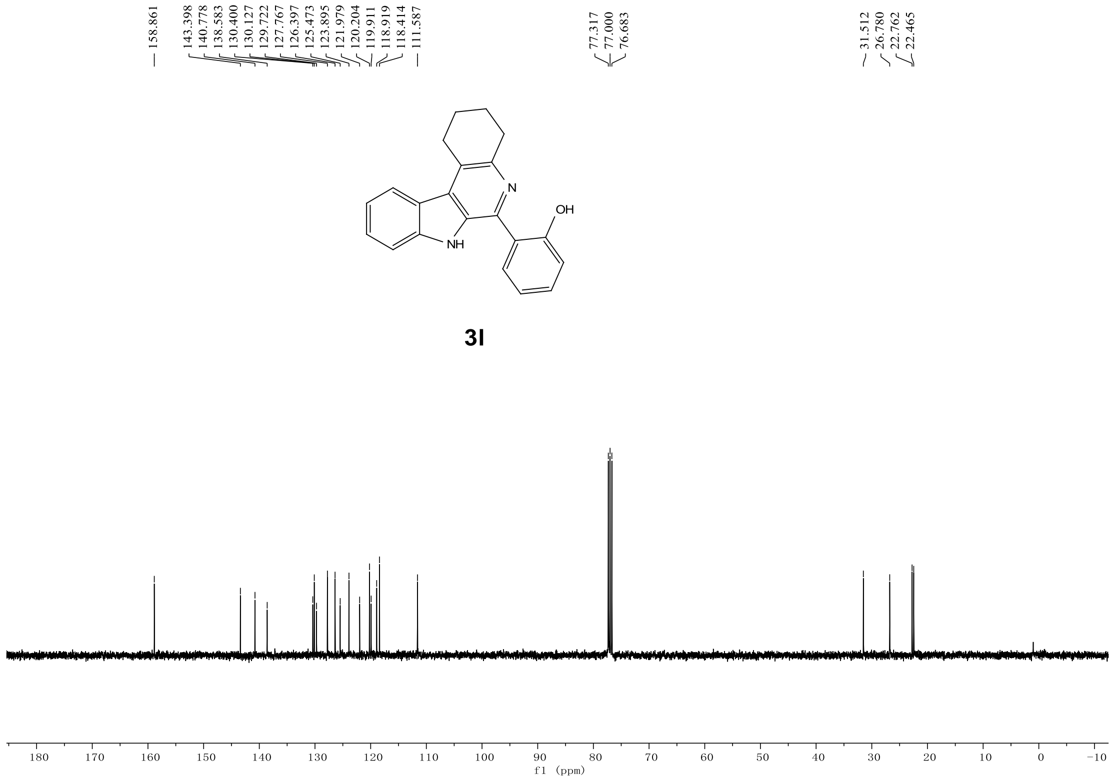
^{13}C NMR of **3k** (400 MHz, $CDCl_3$):



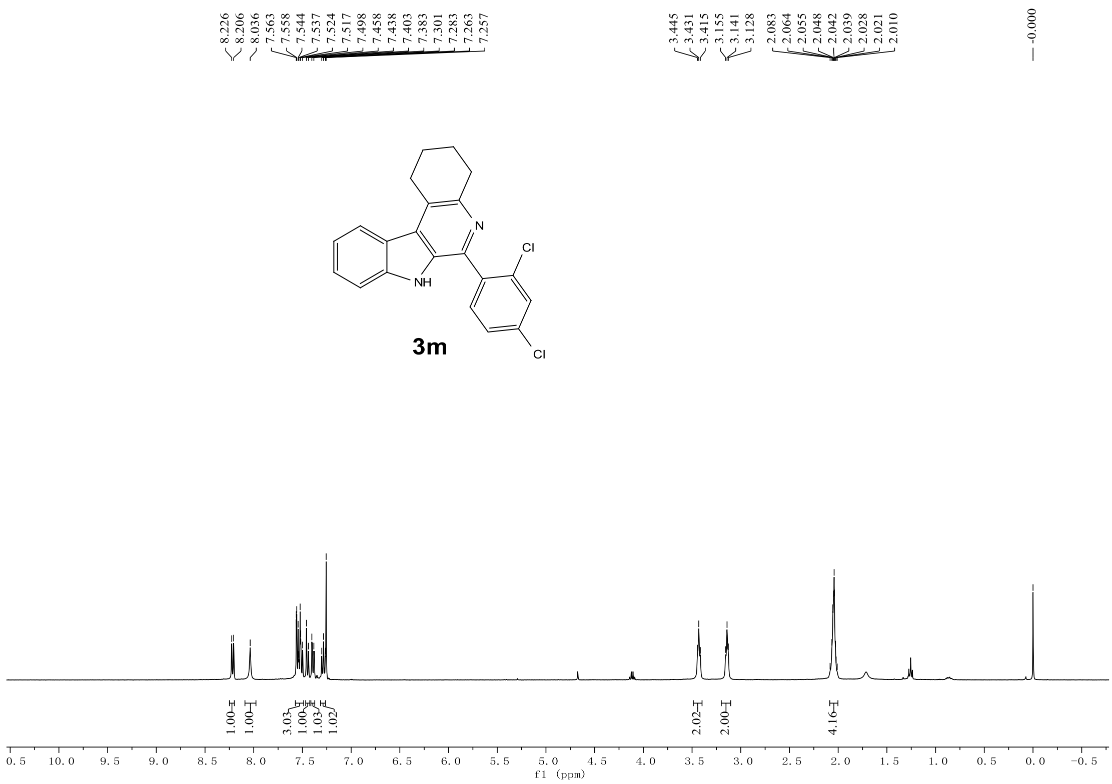
^{1}H NMR of **3l** (400 MHz, DMSO-d_6):



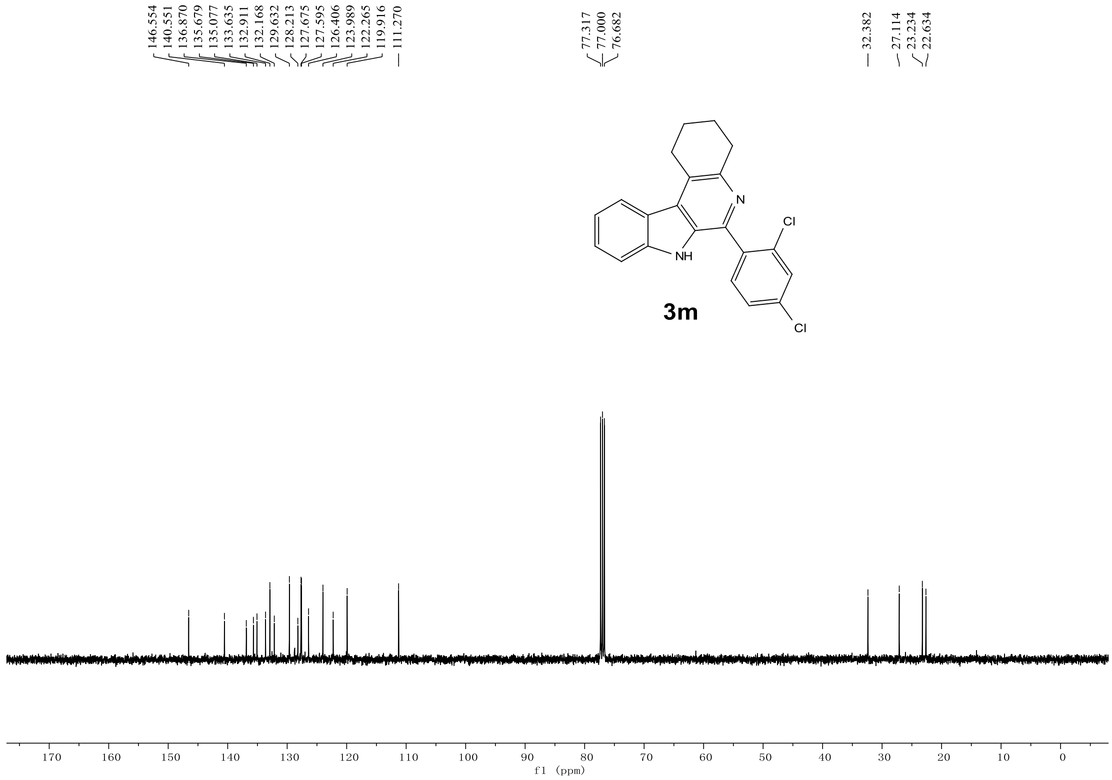
[13]C NMR of **3l** (400 MHz, $CDCl_3$):



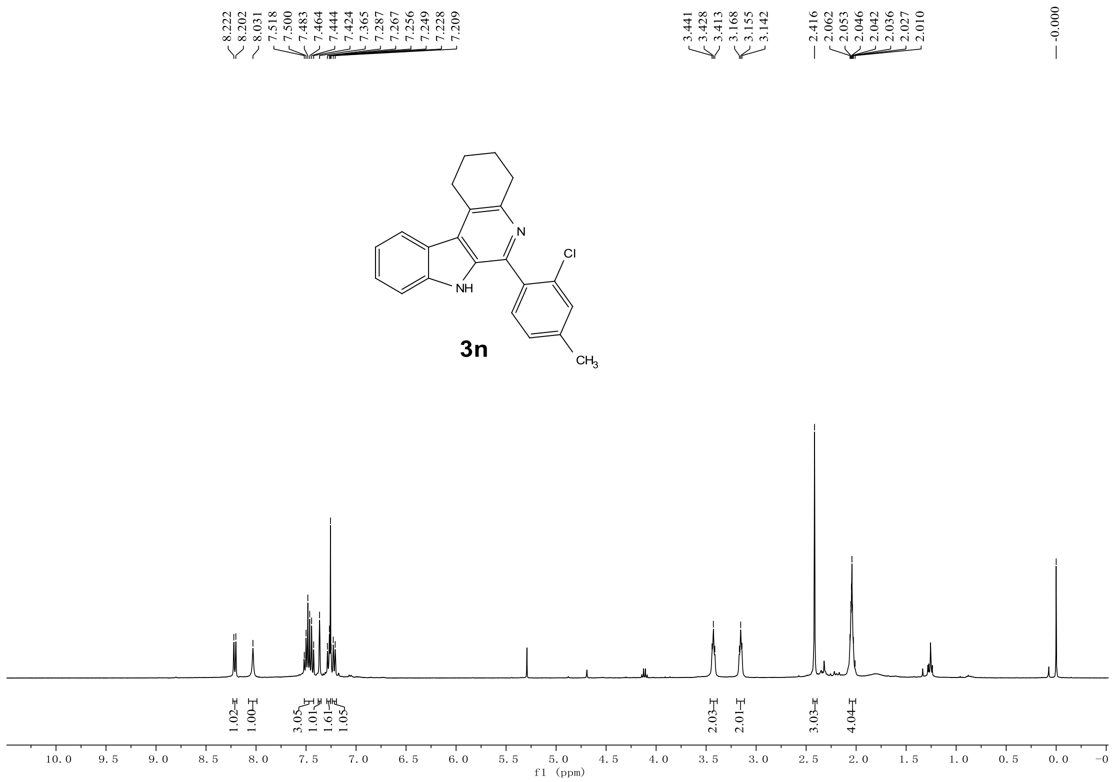
[1]H NMR of **3m** (400 MHz, $CDCl_3$):



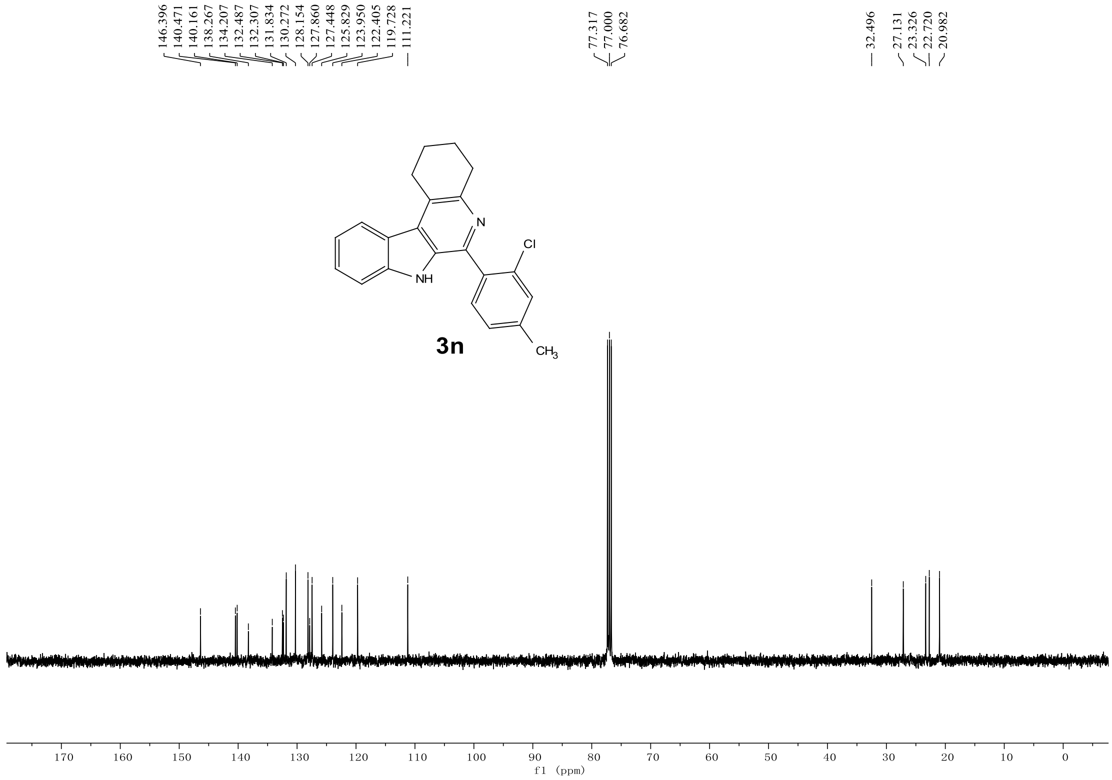
[13]C NMR of **3m** (400 MHz, $CDCl_3$):



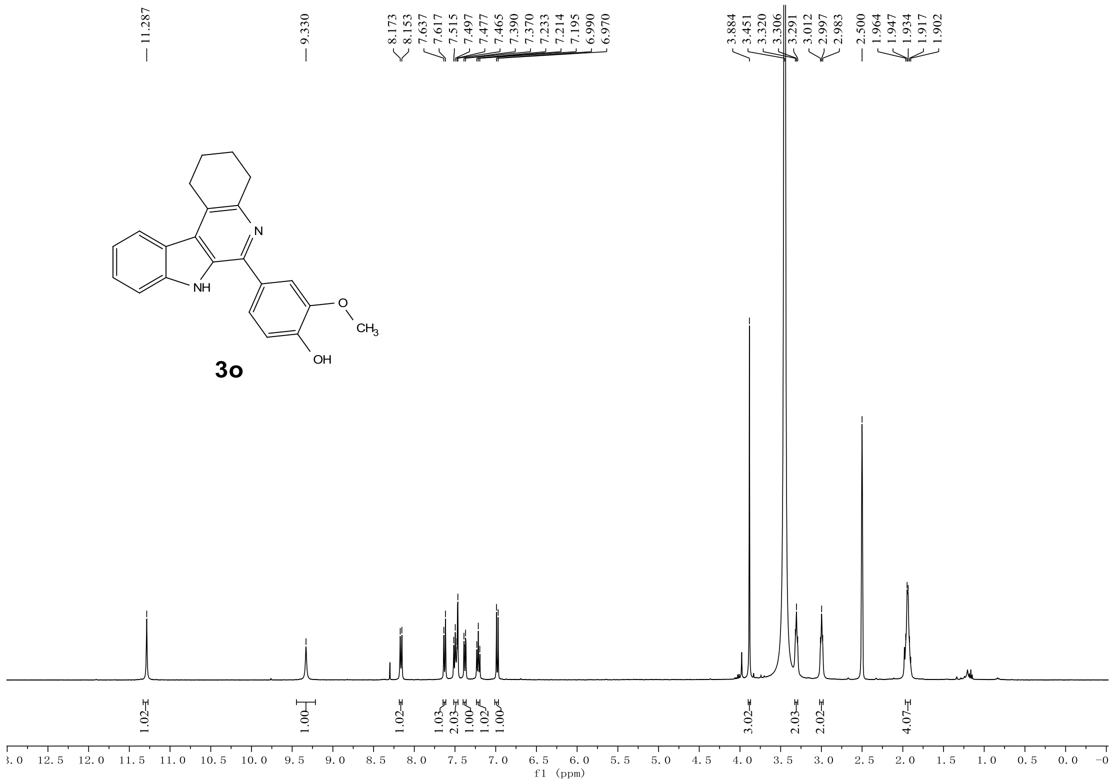
[1]H NMR of **3n** (400 MHz, $CDCl_3$):



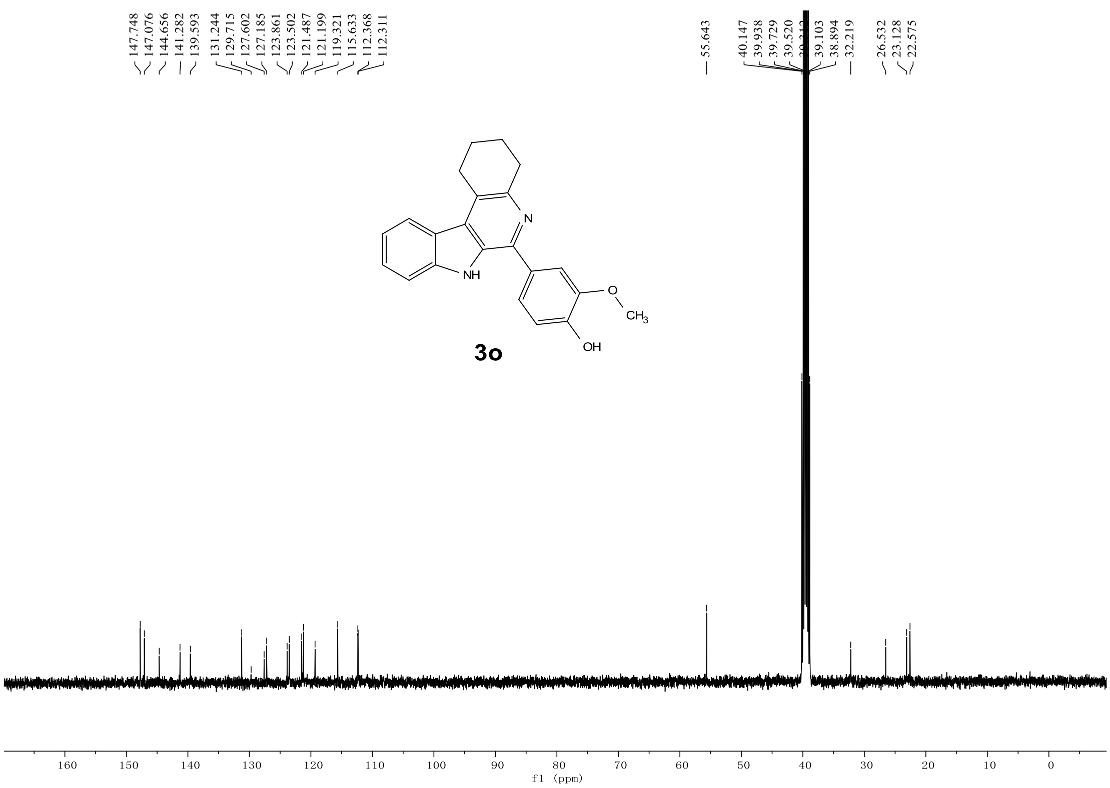
[13]C NMR of **3n** (400 MHz, $CDCl_3$):



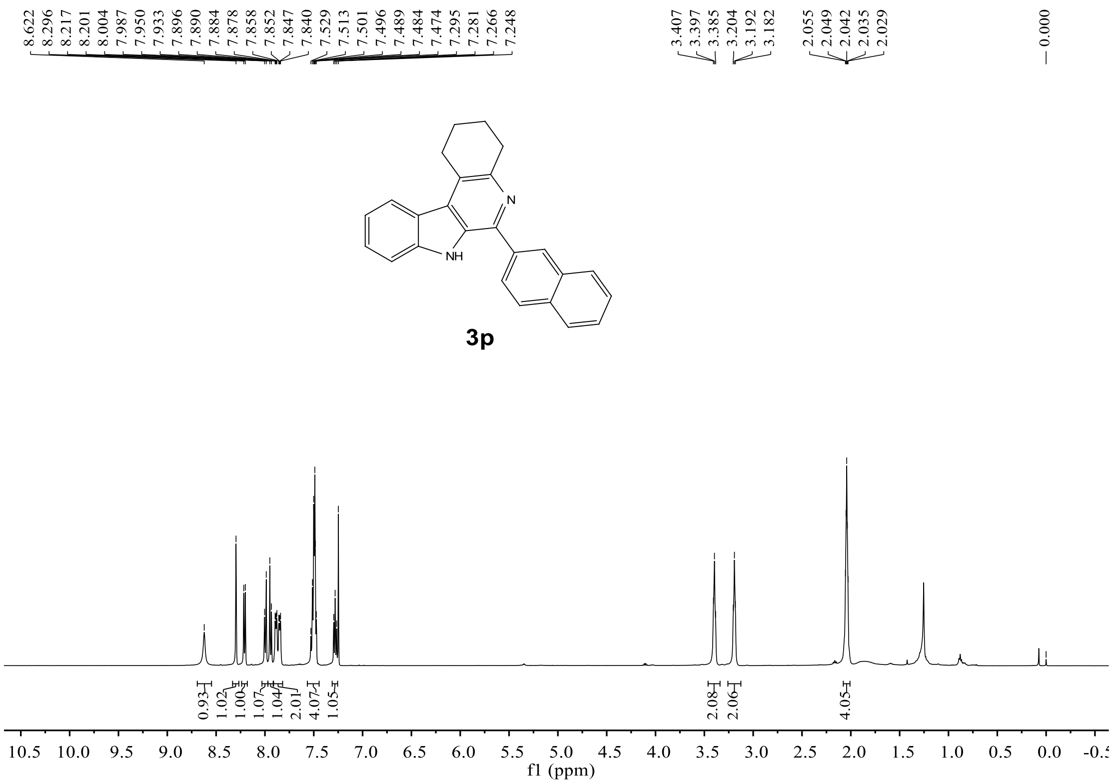
[1]H NMR of **3o** (400 MHz, DMSO-d_6):



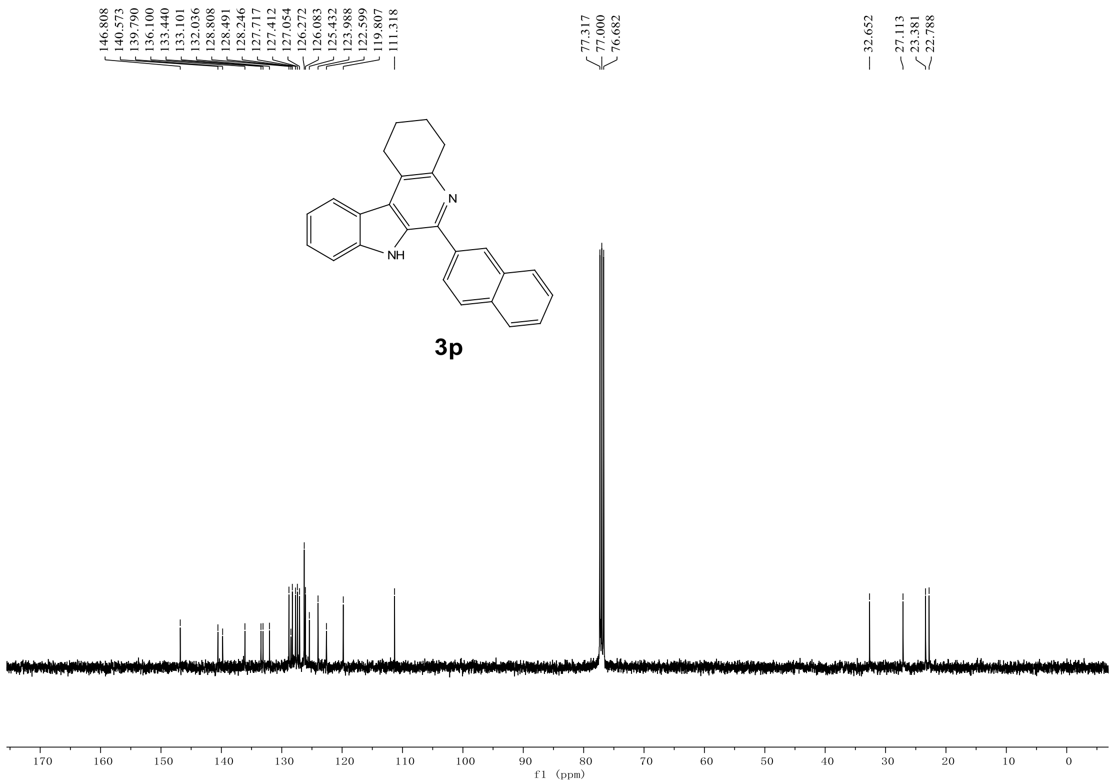
^{13}C NMR of **3o** (400 MHz, DMSO-d_6):



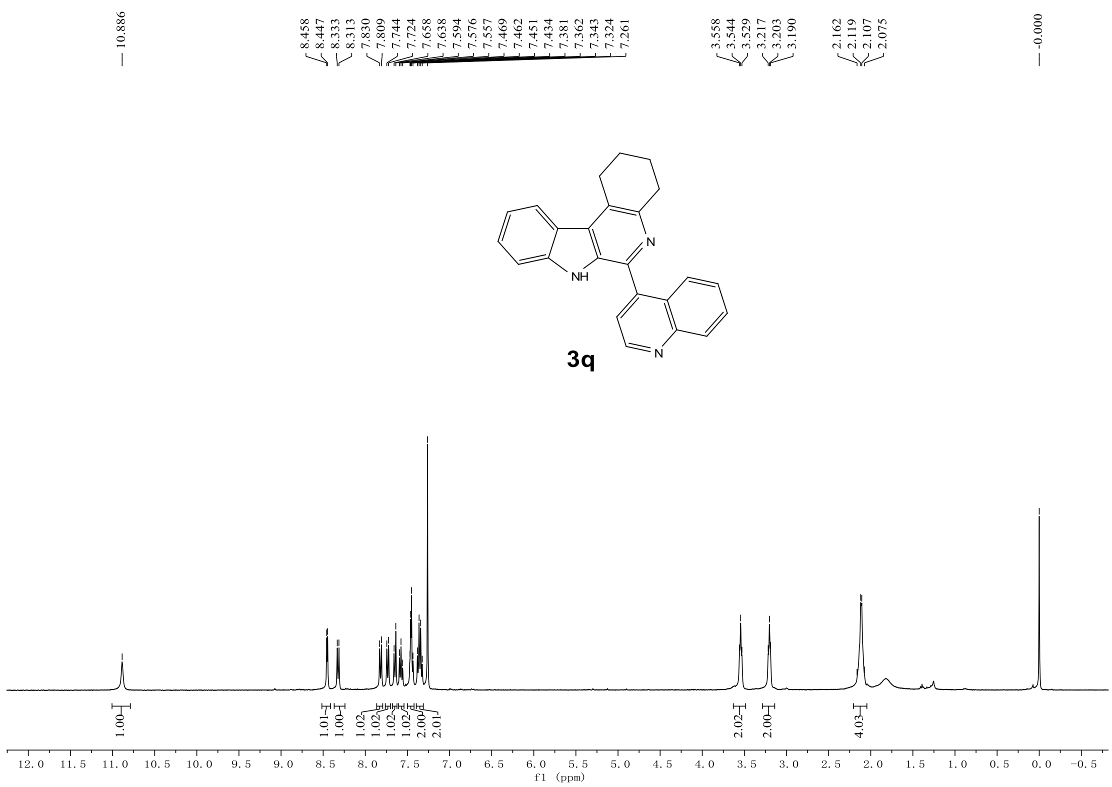
^{1}H NMR of **3p** (500 MHz, $CDCl_3$):



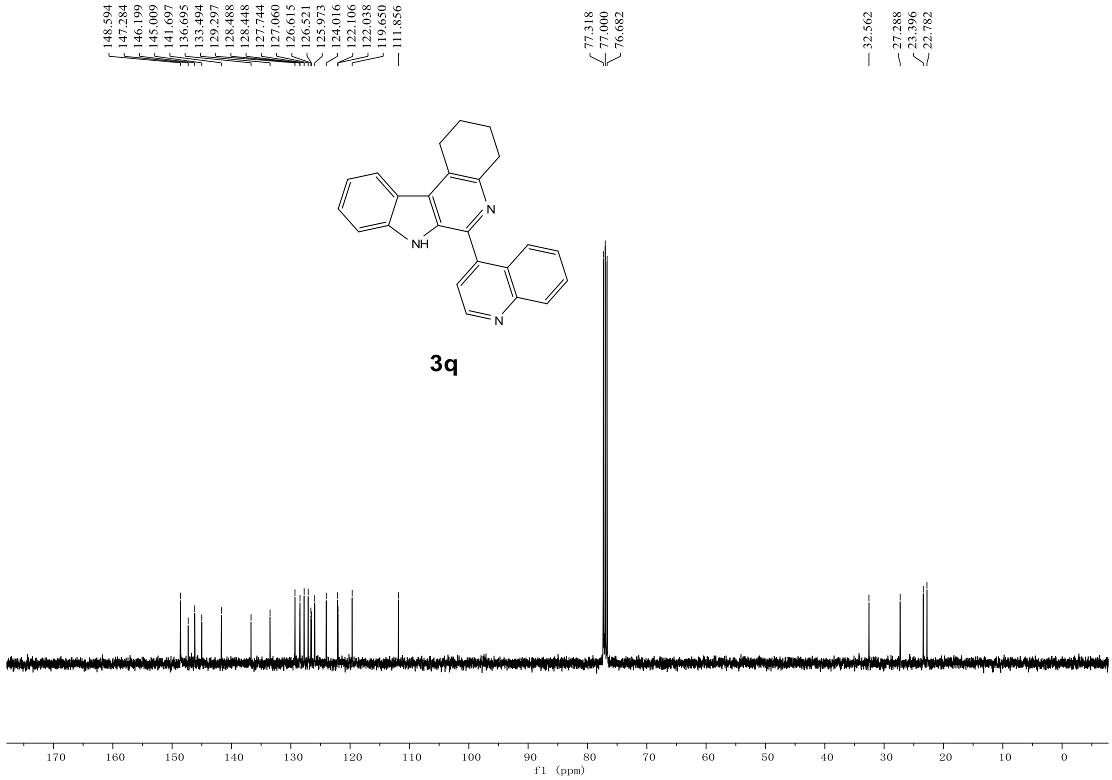
^{13}C NMR of **3p** (400 MHz, $CDCl_3$):



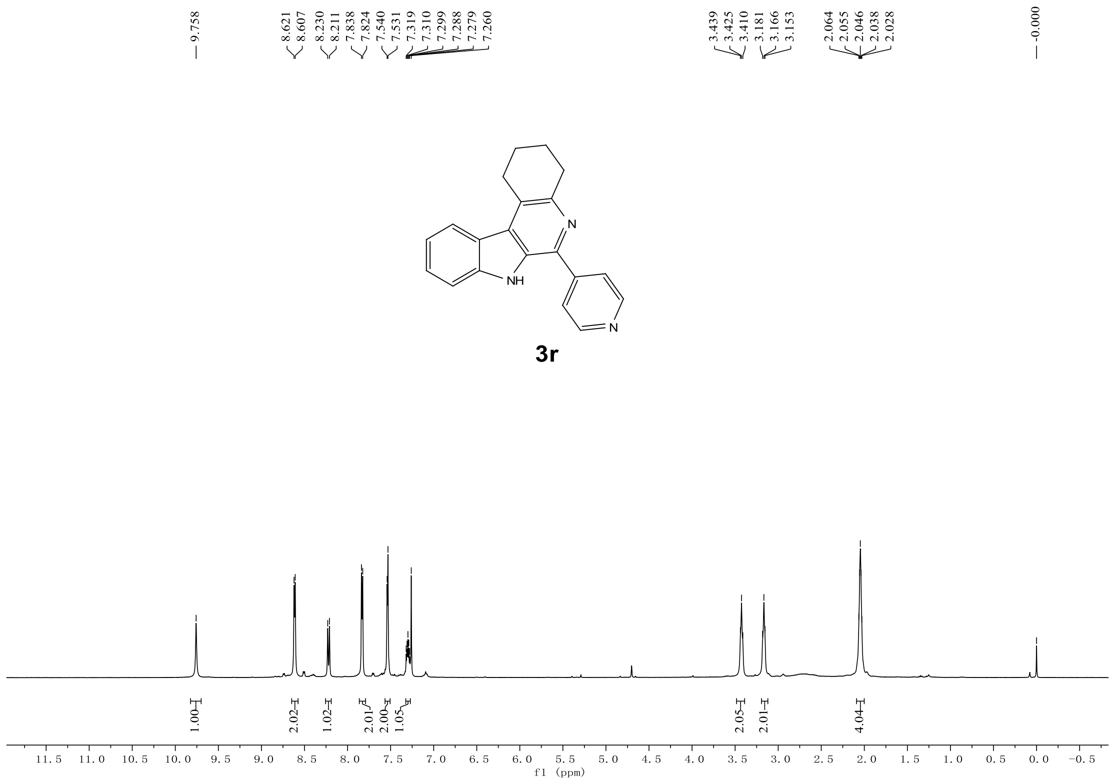
^{1}H NMR of **3q** (400 MHz, $CDCl_3$):



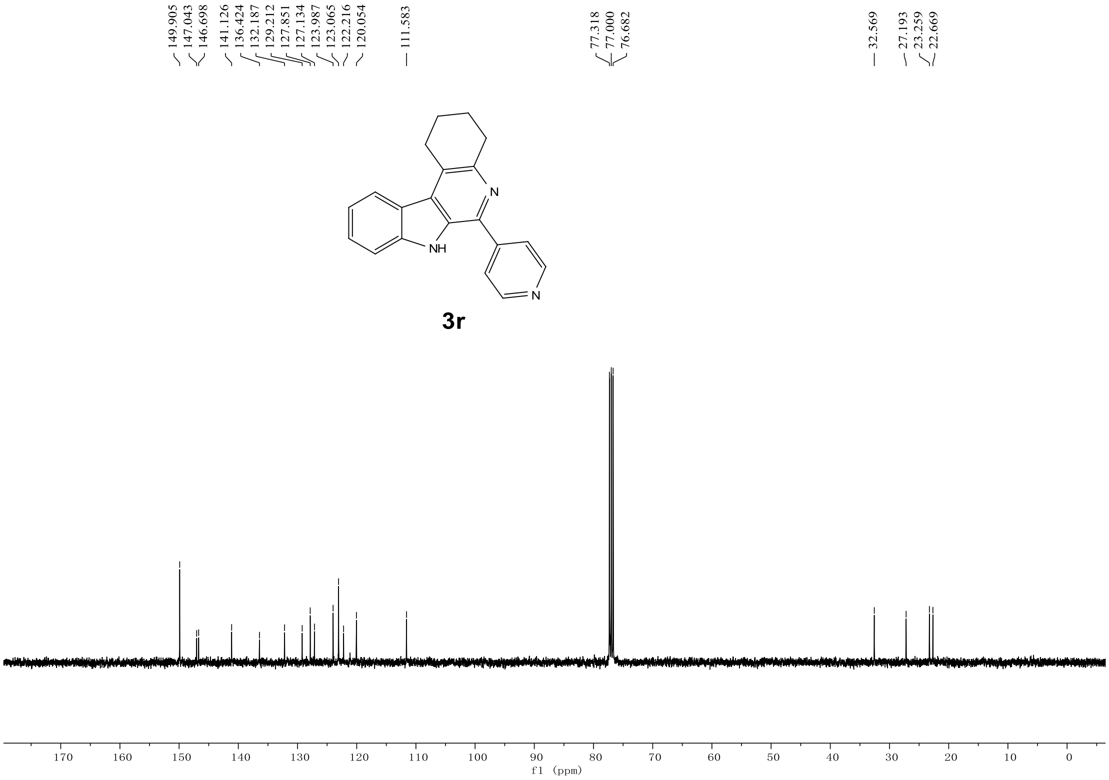
^{13}C NMR of **3q** (400 MHz, $CDCl_3$):



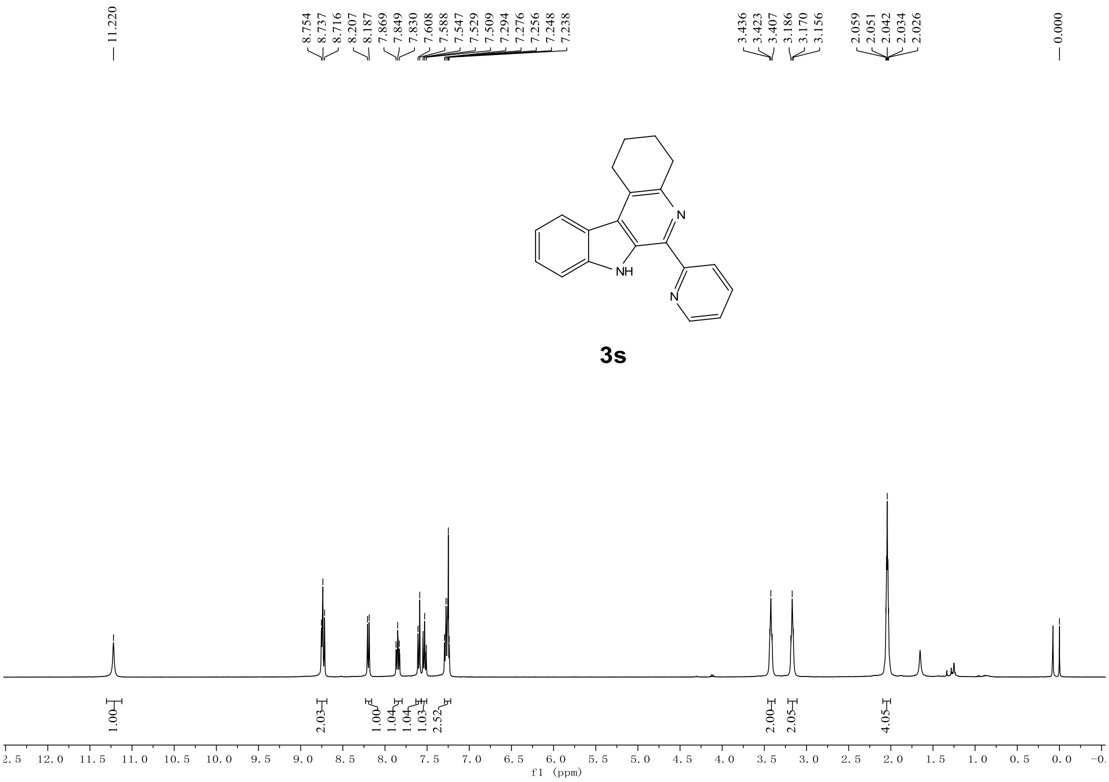
^{1}H NMR of **3r** (400 MHz, $CDCl_3$):



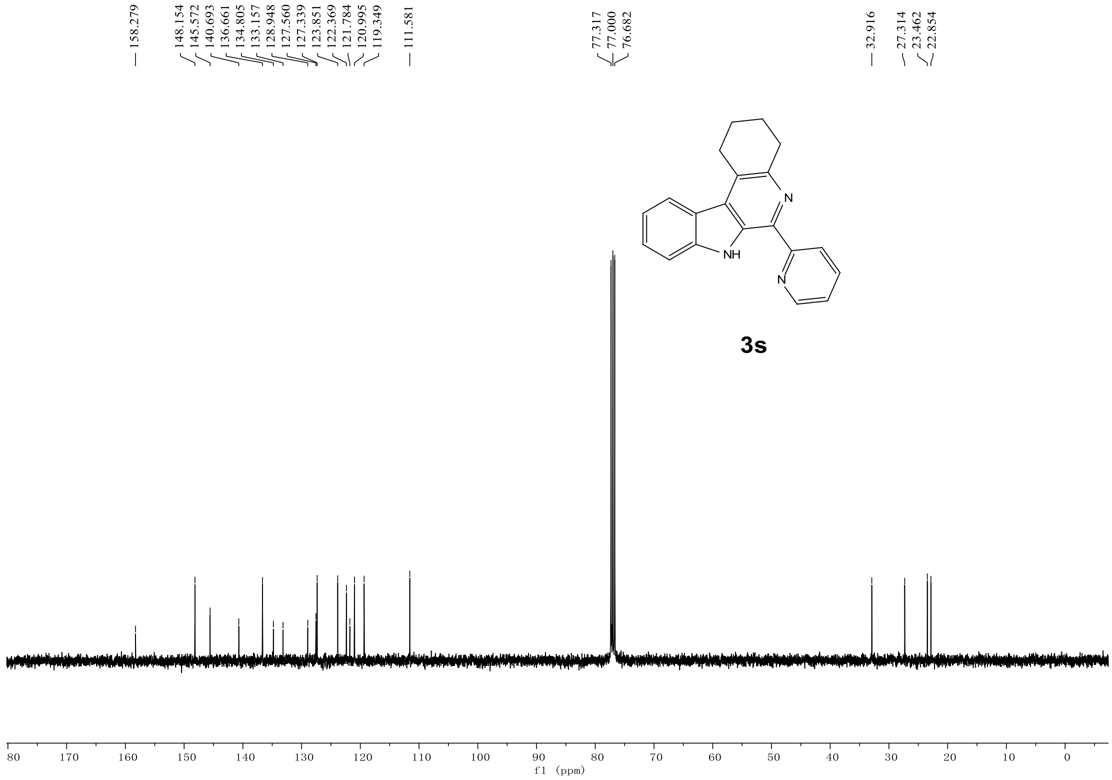
^{13}C NMR of **3r** (400 MHz, $CDCl_3$):



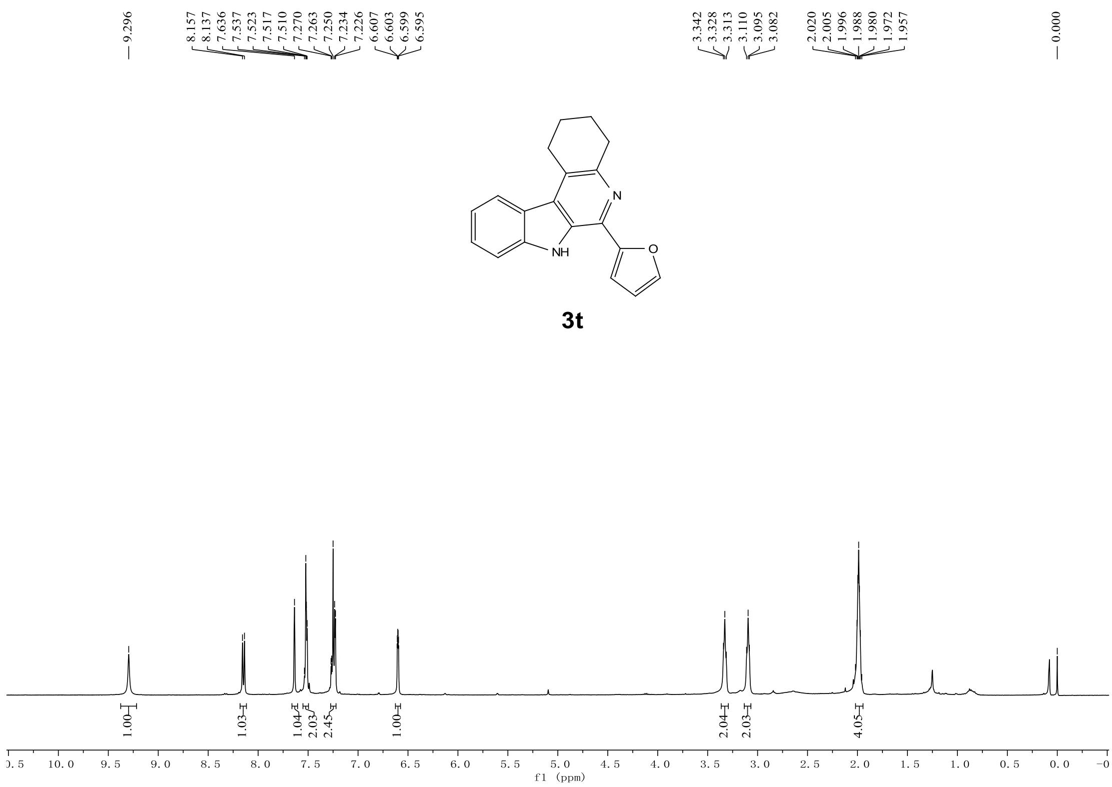
^{1}H NMR of **3s** (400 MHz, $CDCl_3$):



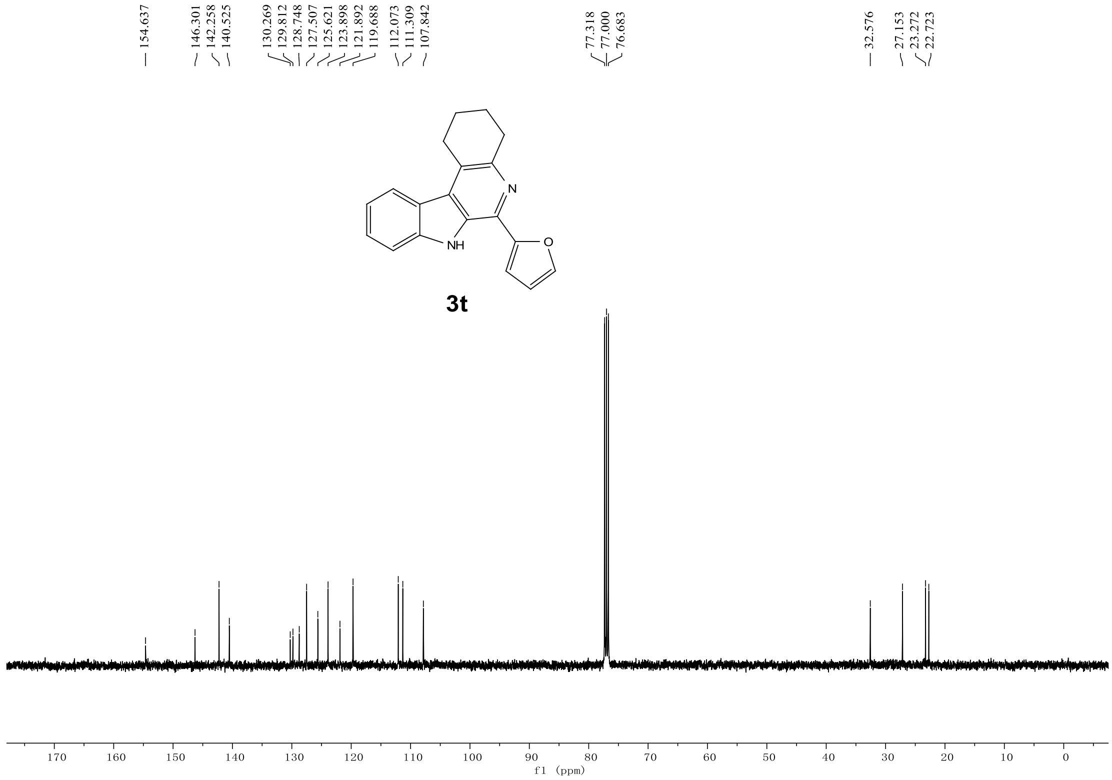
^{13}C NMR of **3s** (400 MHz, $CDCl_3$):



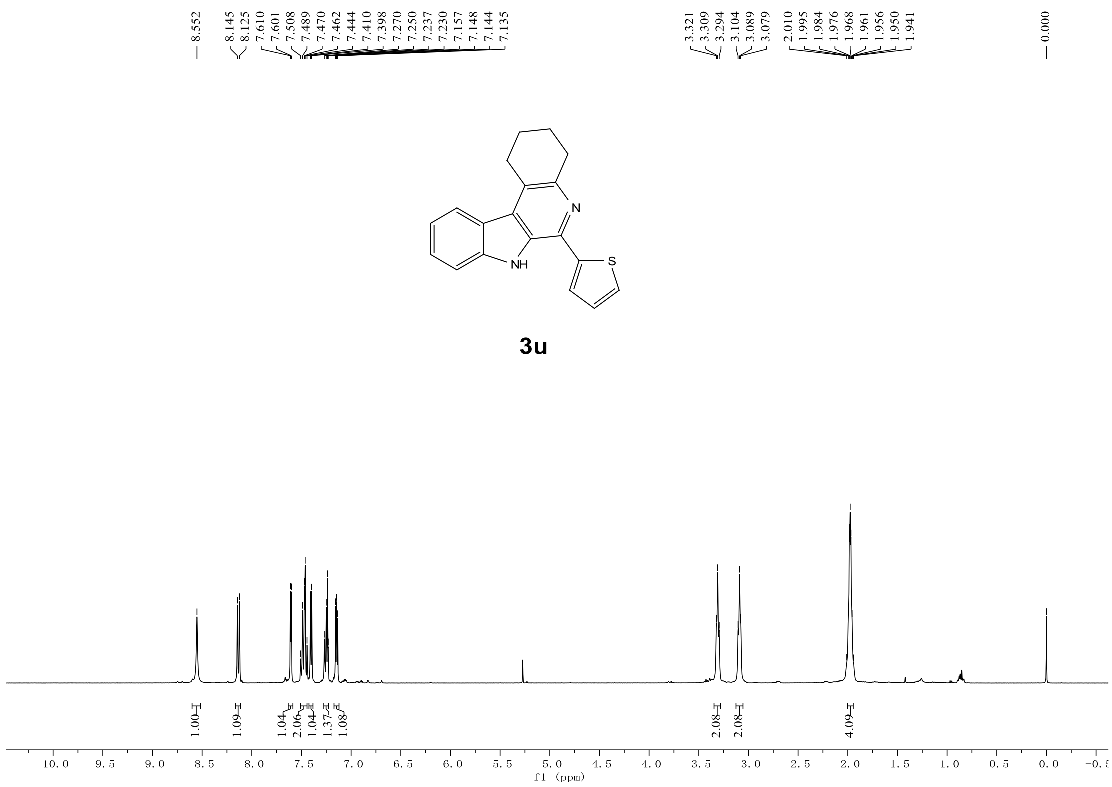
^{1}H NMR of **3t** (400 MHz, $CDCl_3$):



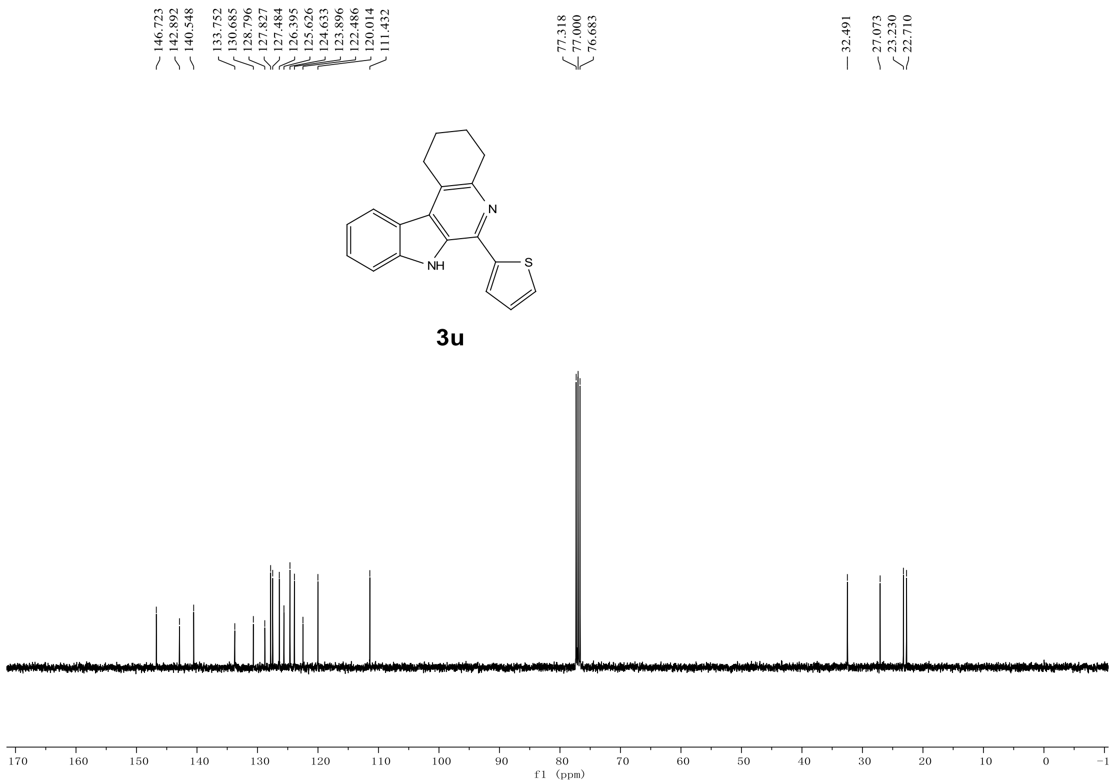
^{13}C NMR of **3t** (400 MHz, $CDCl_3$):



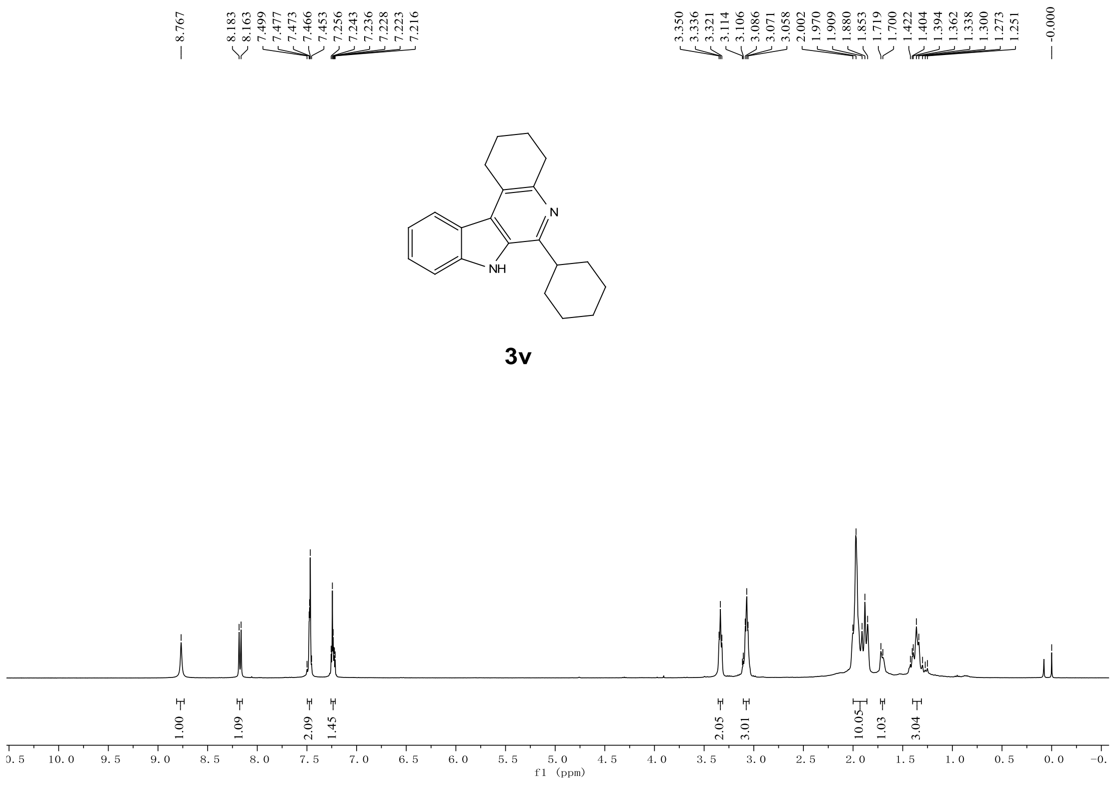
^{1}H NMR of **3u** (400 MHz, $CDCl_3$):



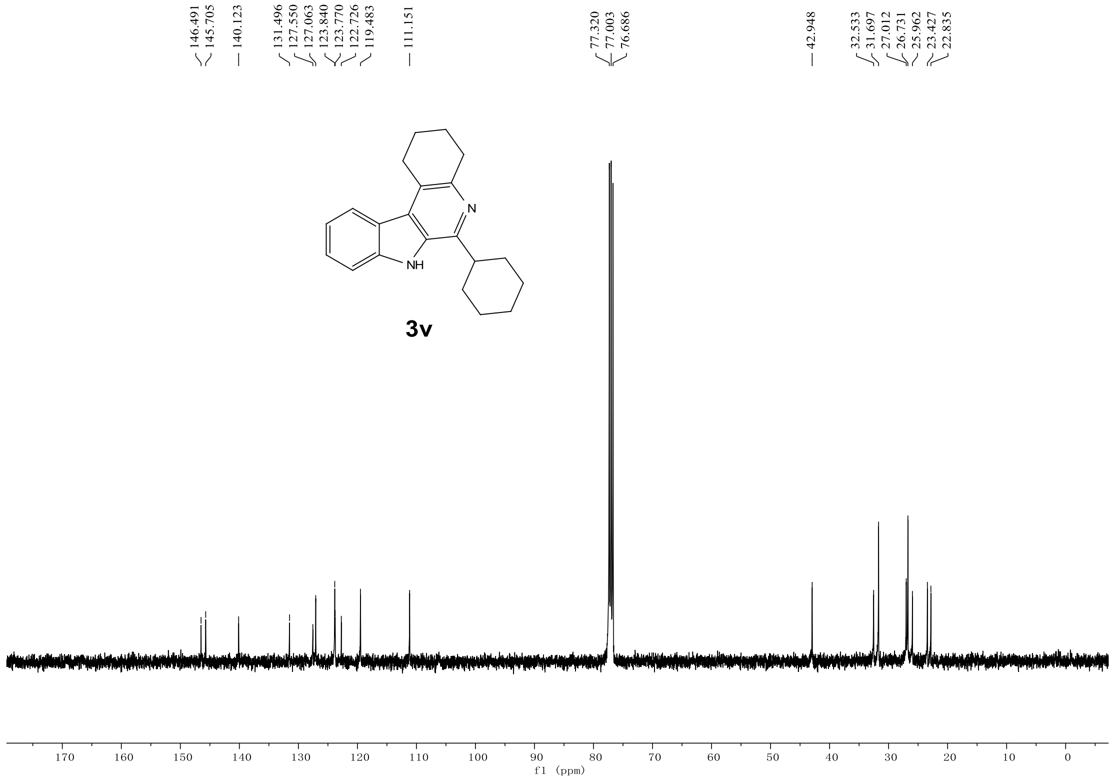
^{13}C NMR of **3u** (400 MHz, $CDCl_3$):



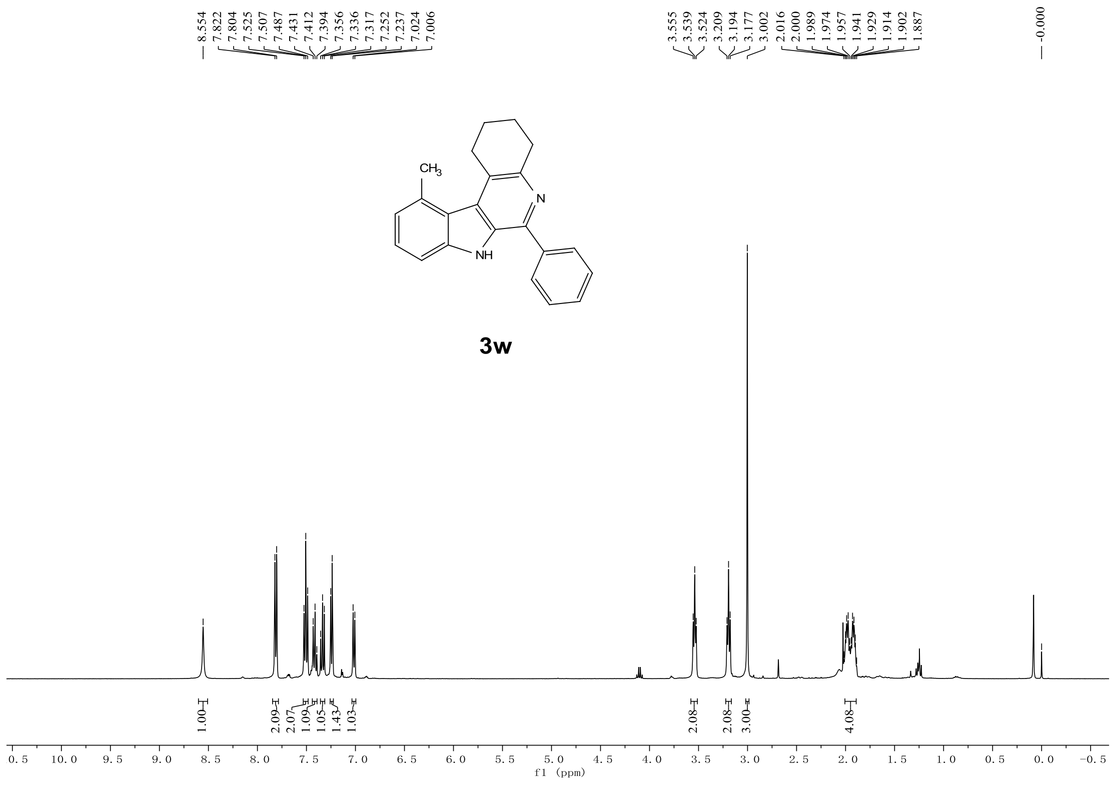
^{1}H NMR of **3v** (400 MHz, $CDCl_3$):



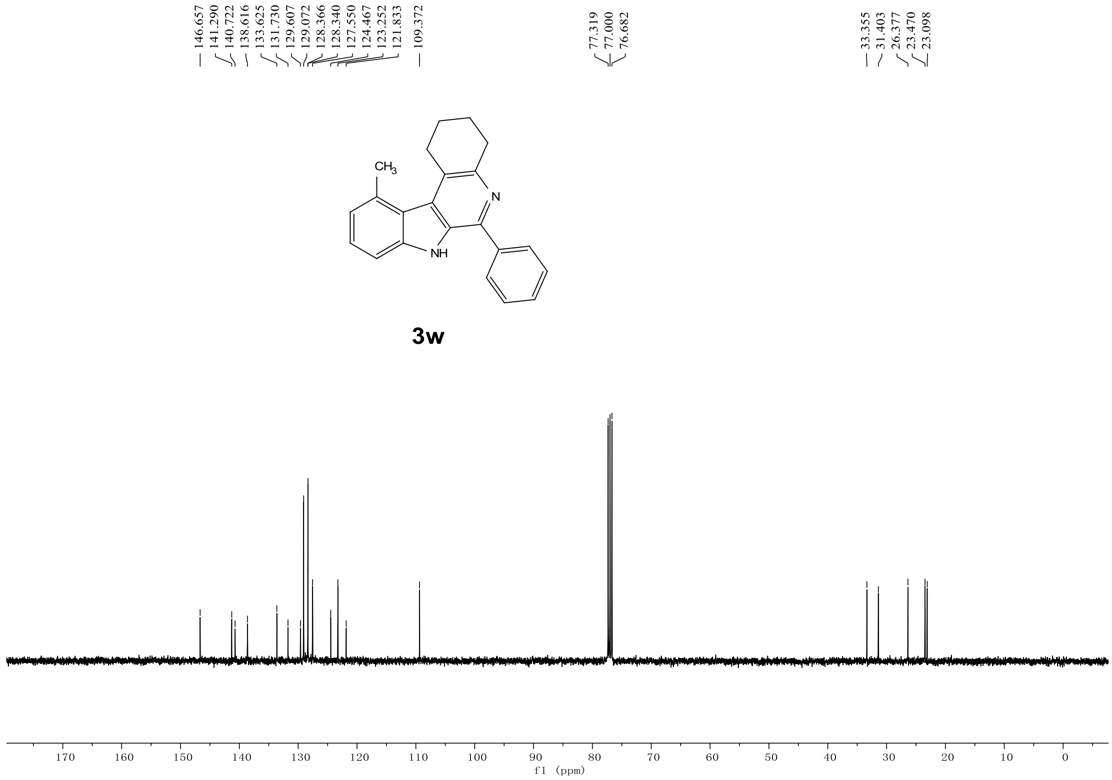
^{13}C NMR of **3v** (400 MHz, $CDCl_3$):



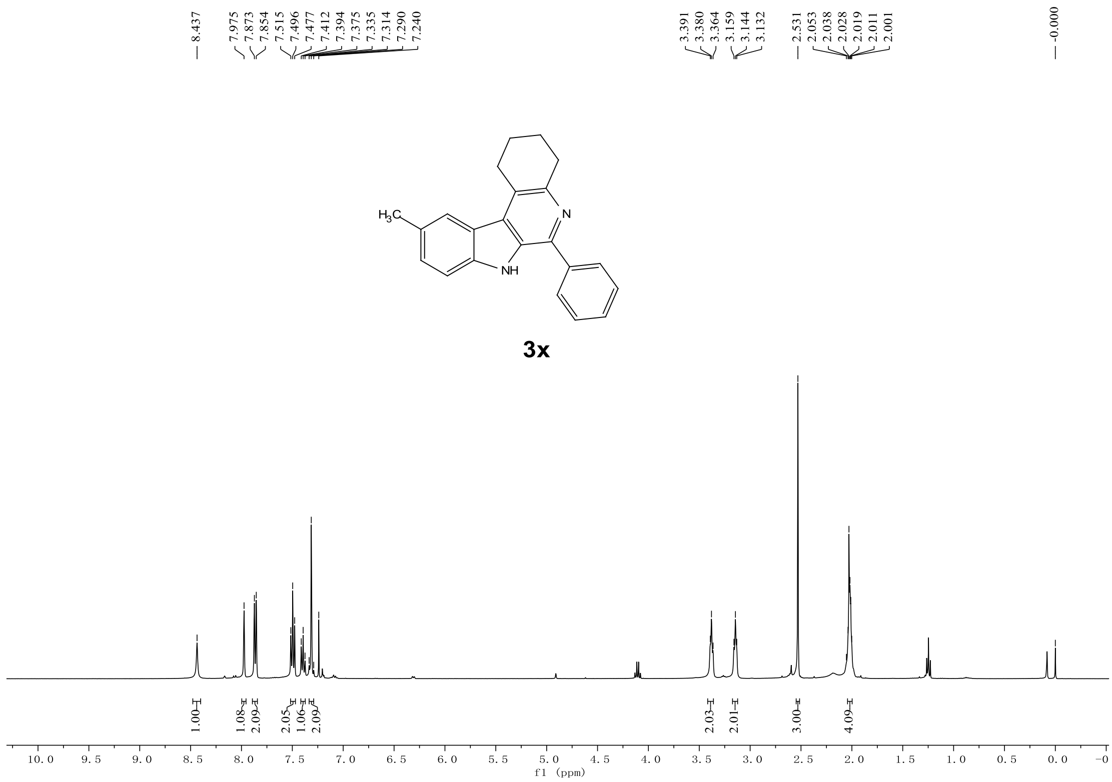
^{1}H NMR of **3w** (400 MHz, $CDCl_3$):



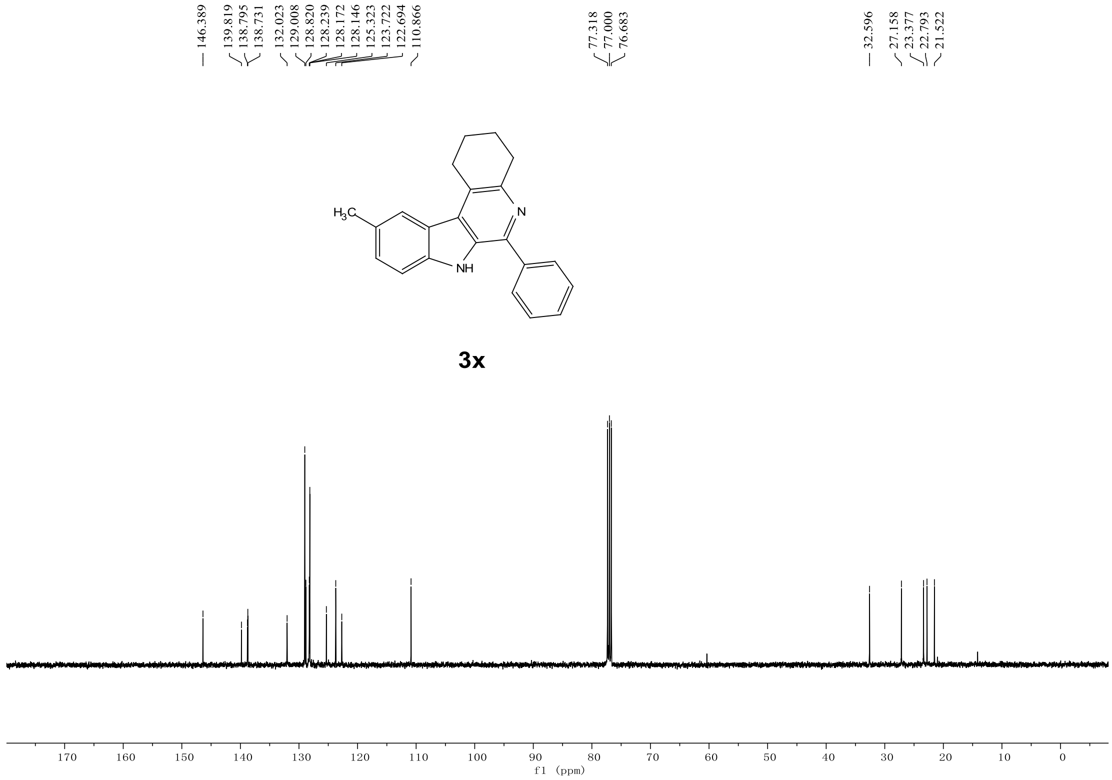
^{13}C NMR of **3w** (400 MHz, $CDCl_3$):



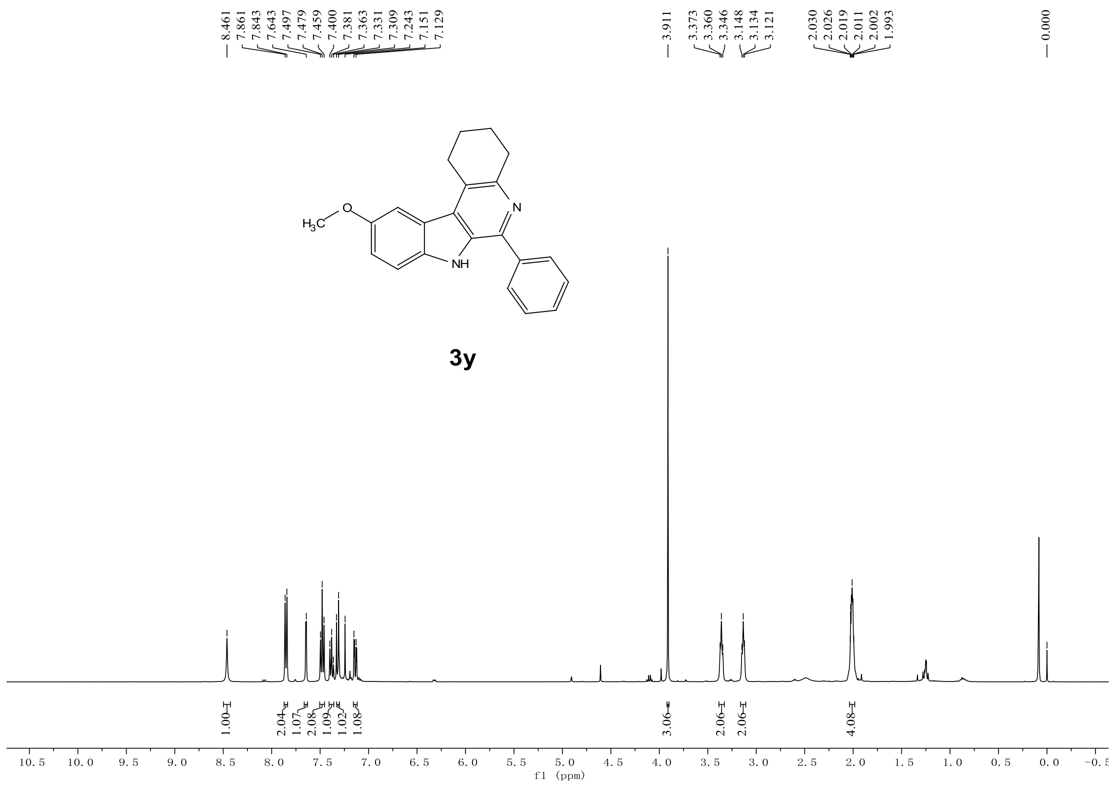
^{1}H NMR of **3x** (400 MHz, $CDCl_3$):



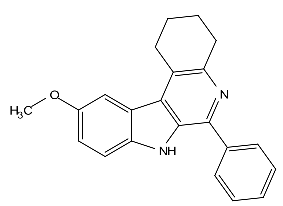
^{13}C NMR of **3x** (400 MHz, $CDCl_3$):



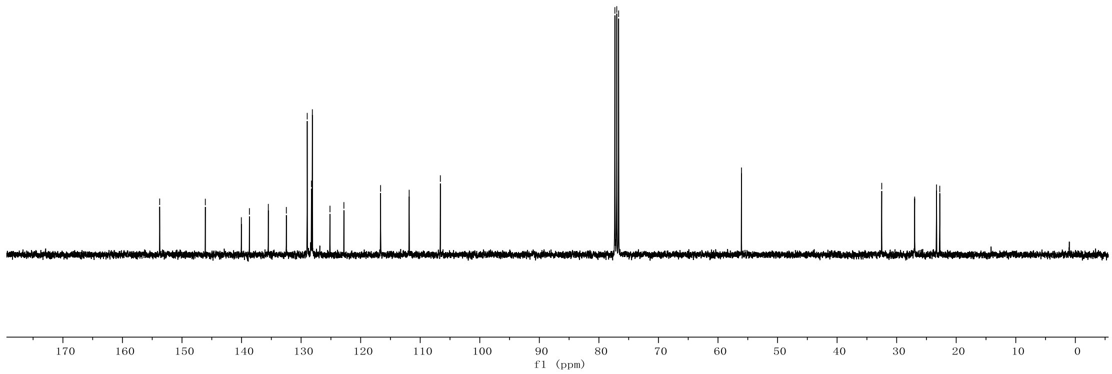
^{1}H NMR of **3y** (400 MHz, $CDCl_3$):



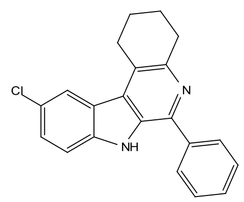
^{13}C NMR of **3y** (400 MHz, $CDCl_3$):



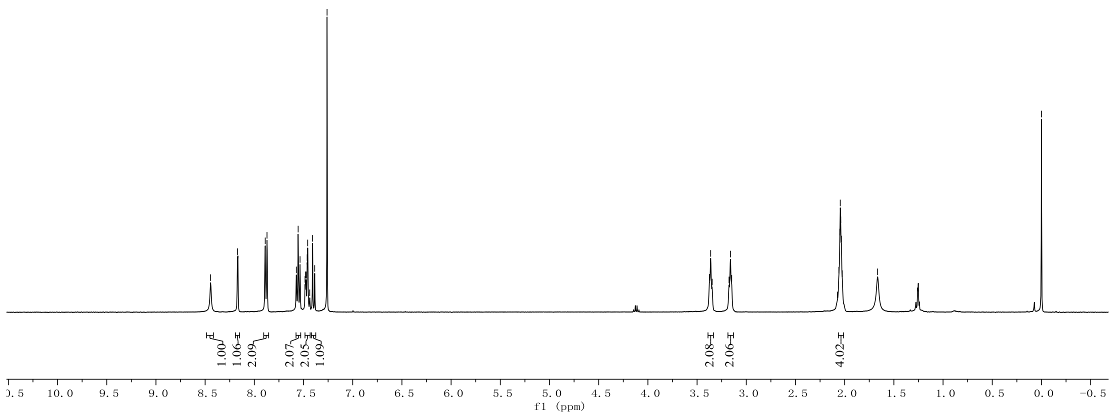
3y



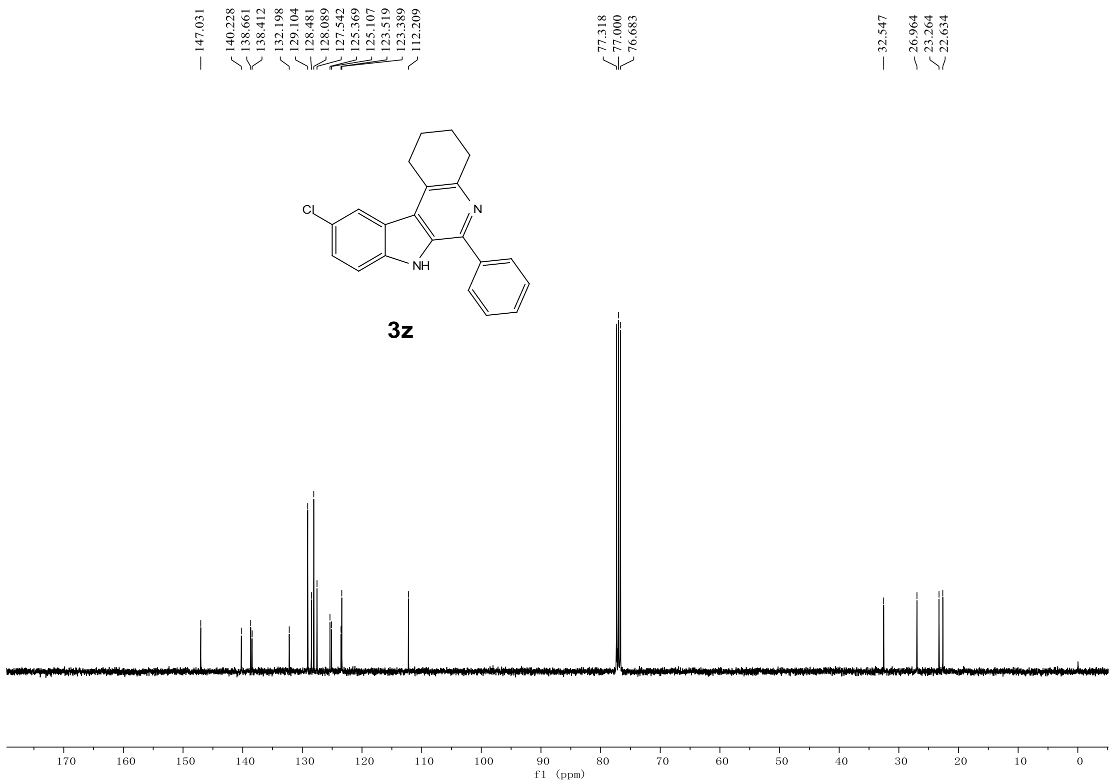
^{1}H NMR of **3z** (400 MHz, $CDCl_3$):



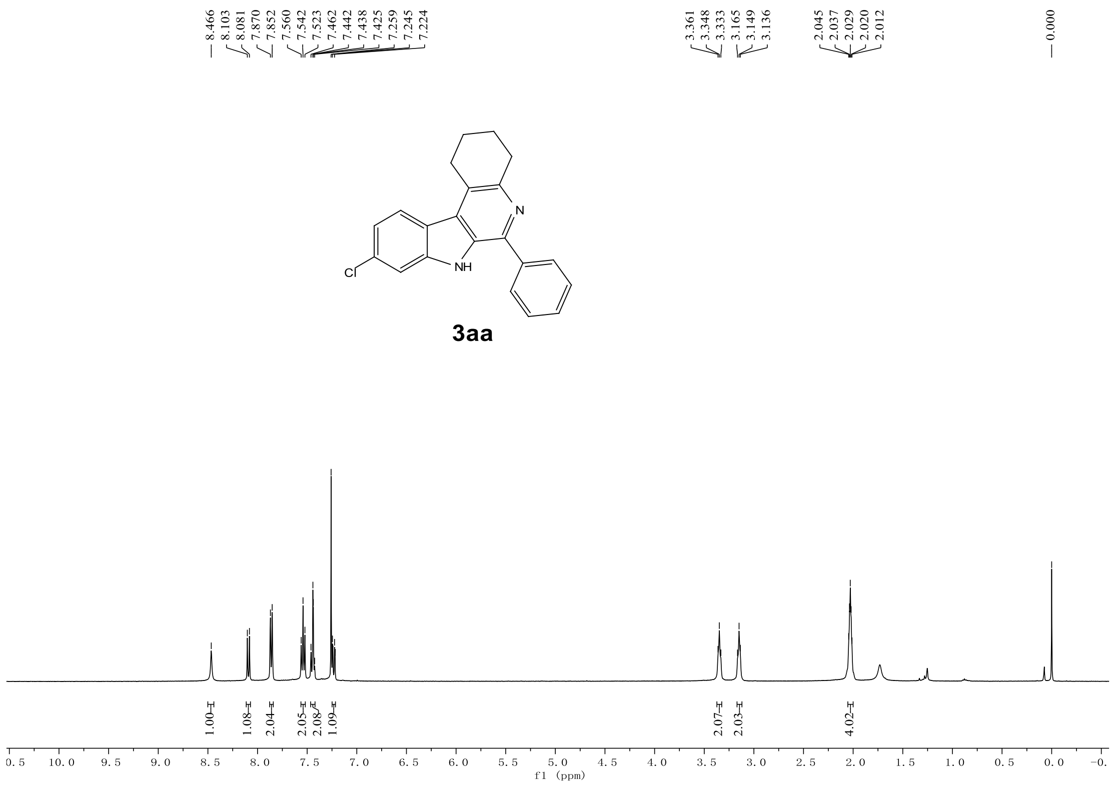
3z



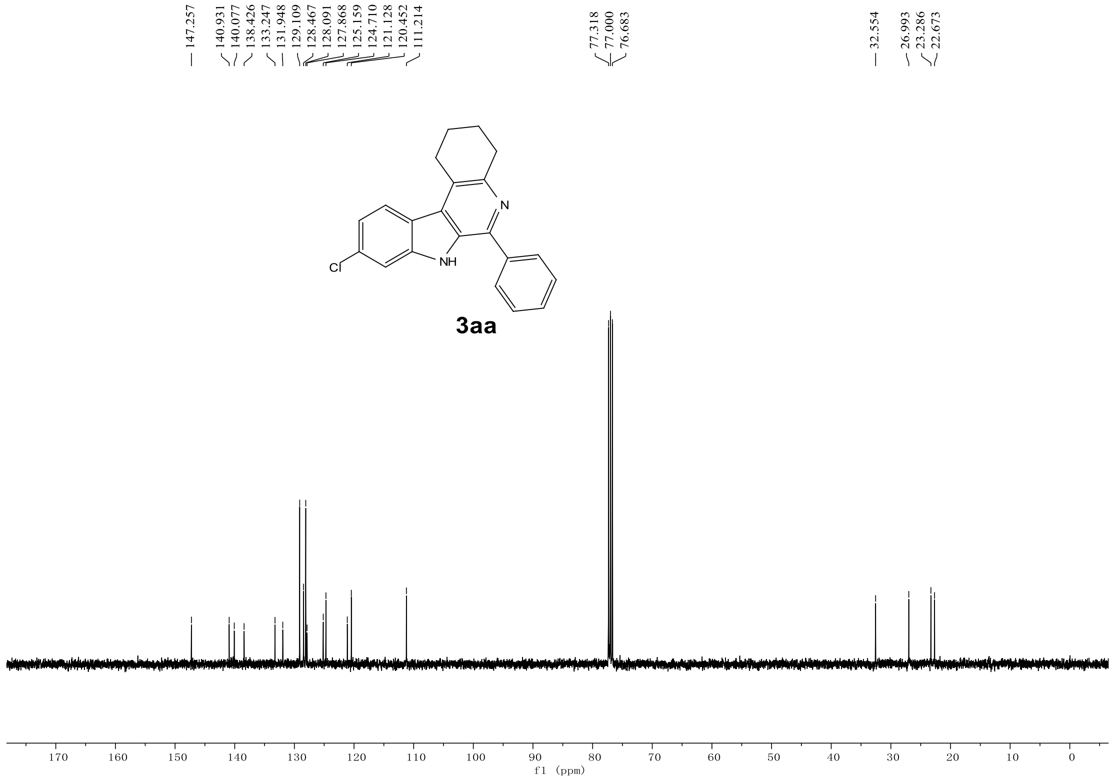
^{13}C NMR of **3z** (400 MHz, $CDCl_3$):



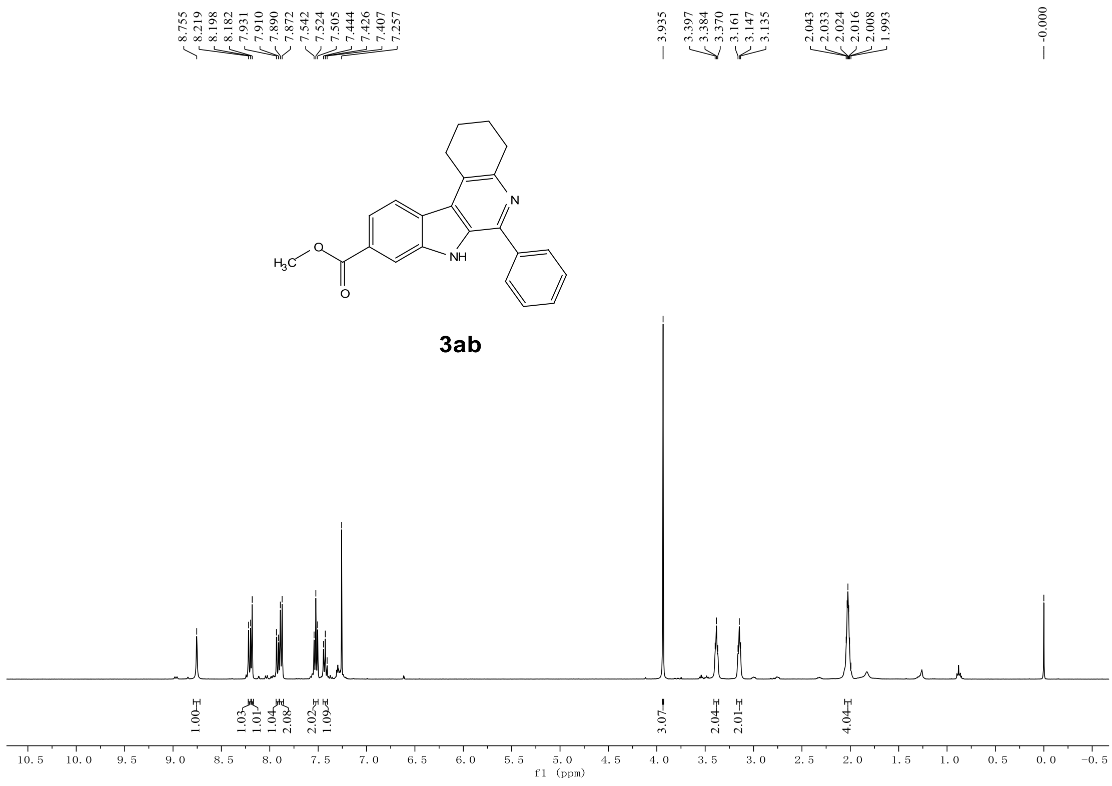
^{1}H NMR of **3aa** (400 MHz, $CDCl_3$):



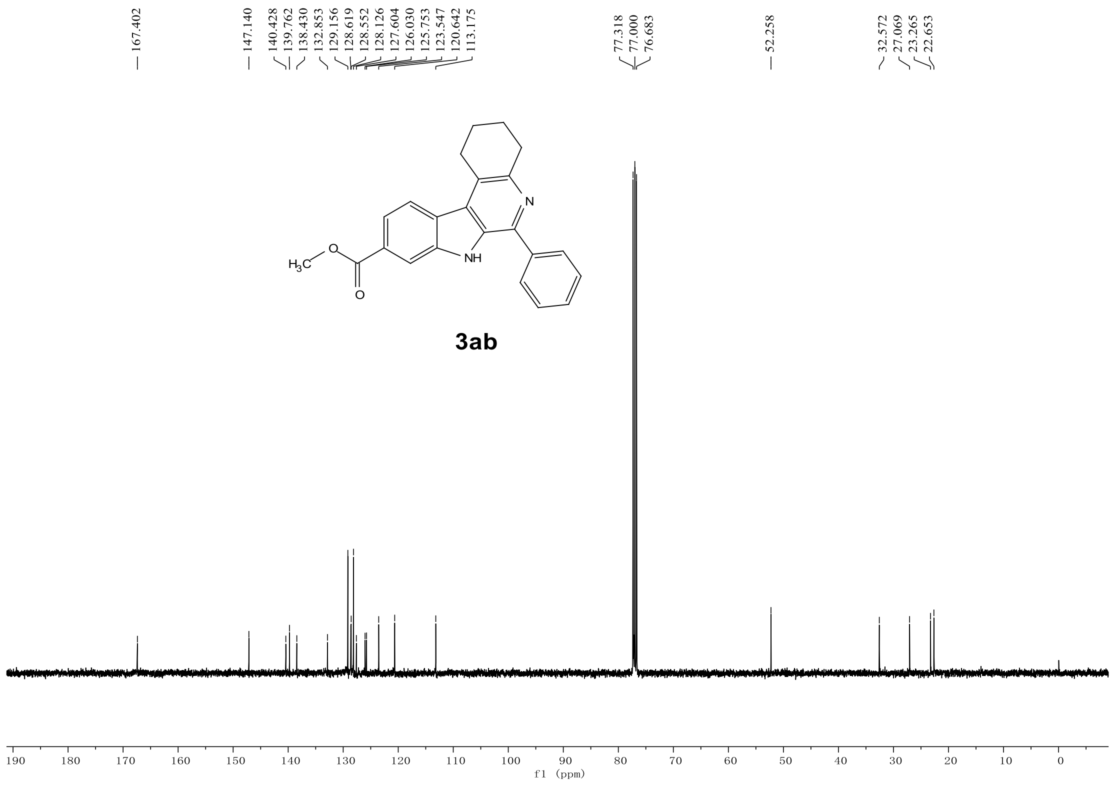
^{13}C NMR of **3aa** (400 MHz, $CDCl_3$):



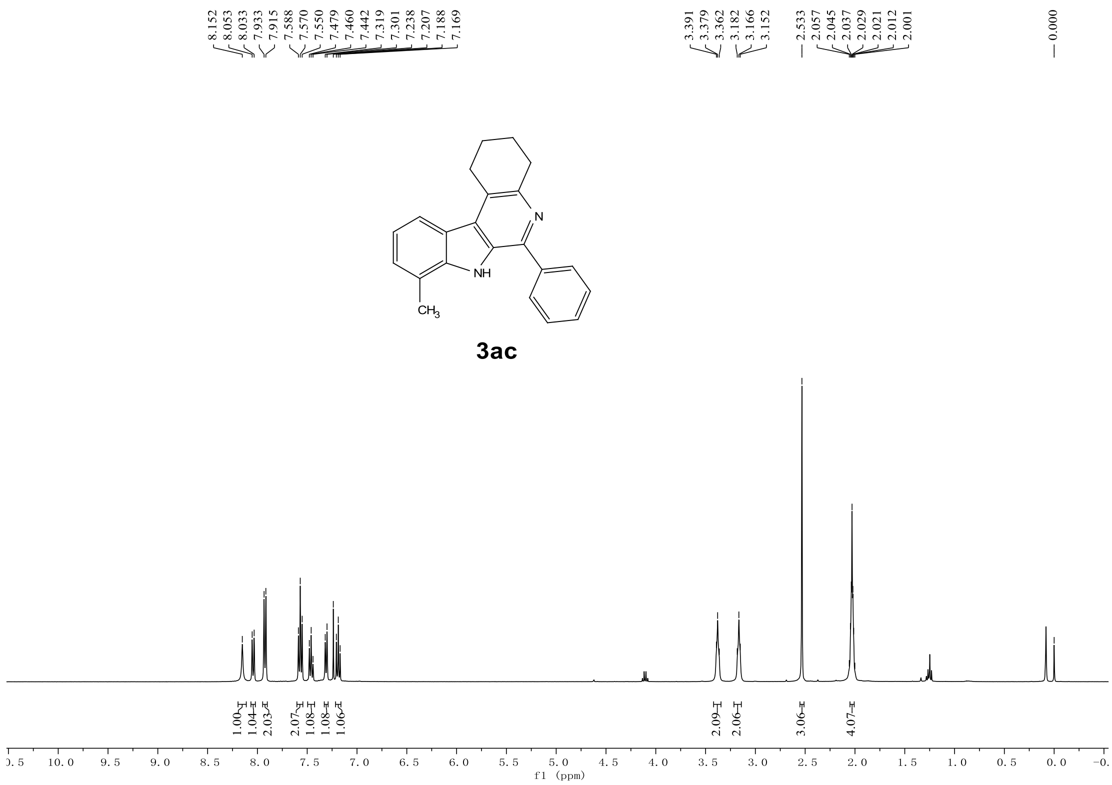
^{1}H NMR of **3ab** (400 MHz, $CDCl_3$):



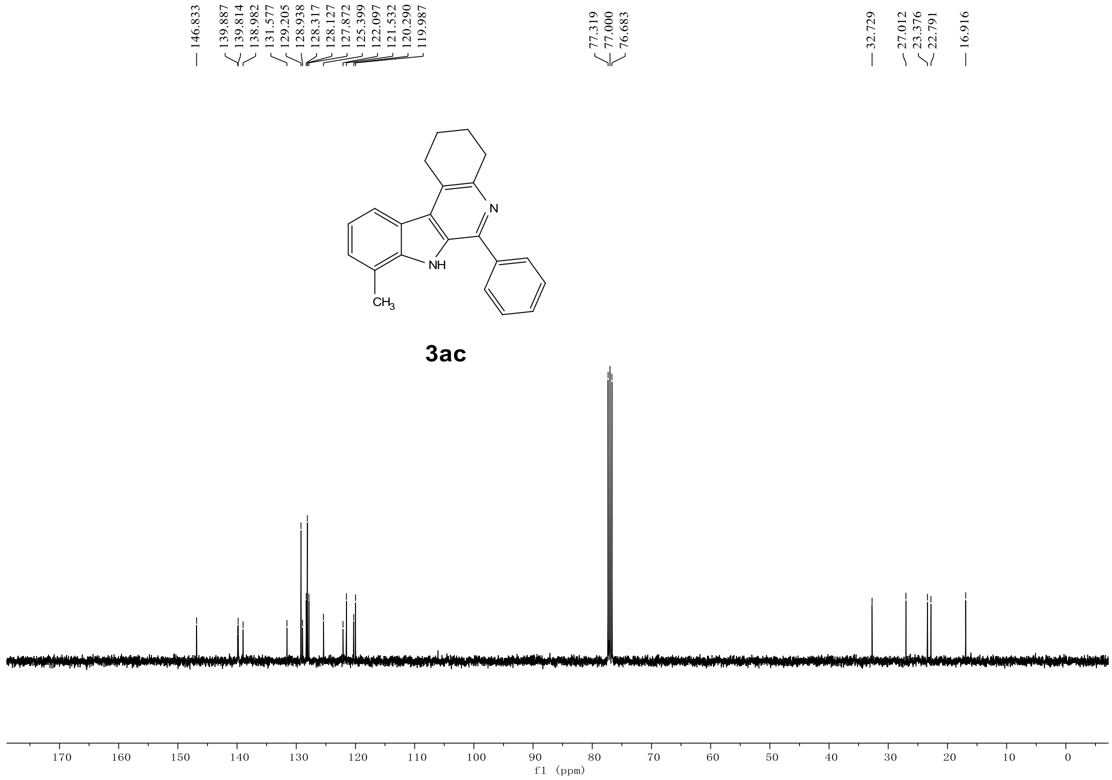
[13] C NMR of **3ab** (400 MHz, $CDCl_3$):



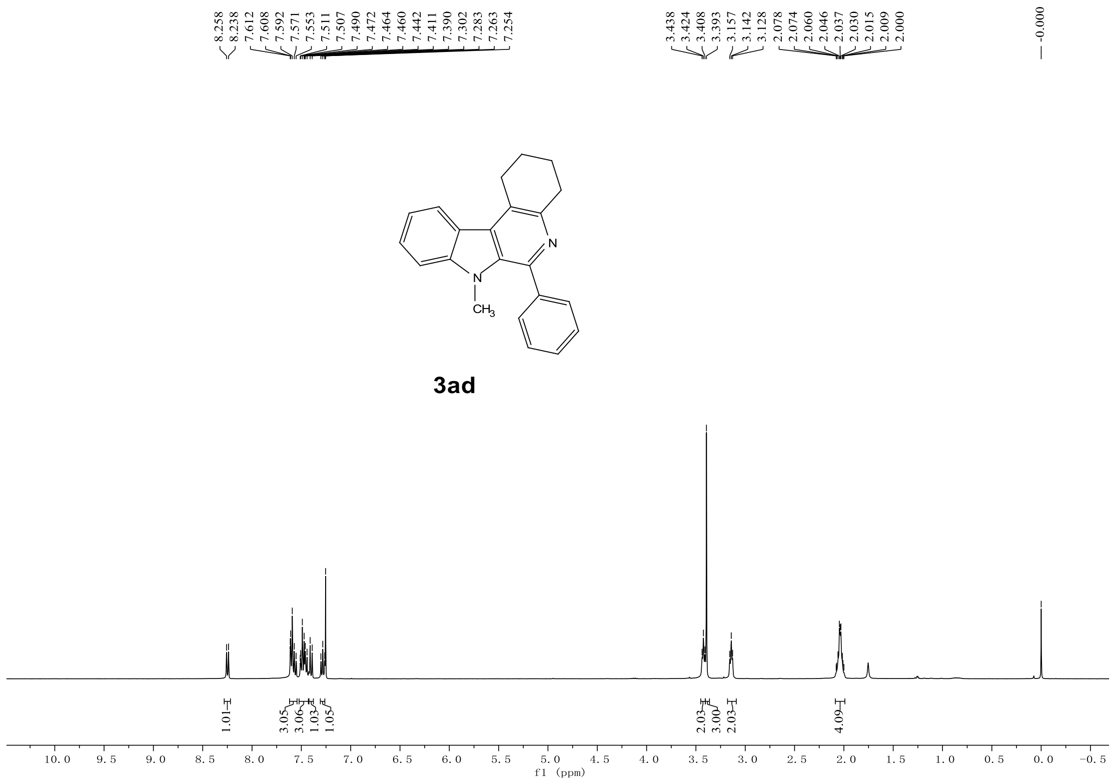
[1] H NMR of **3ac** (400 MHz, $CDCl_3$):



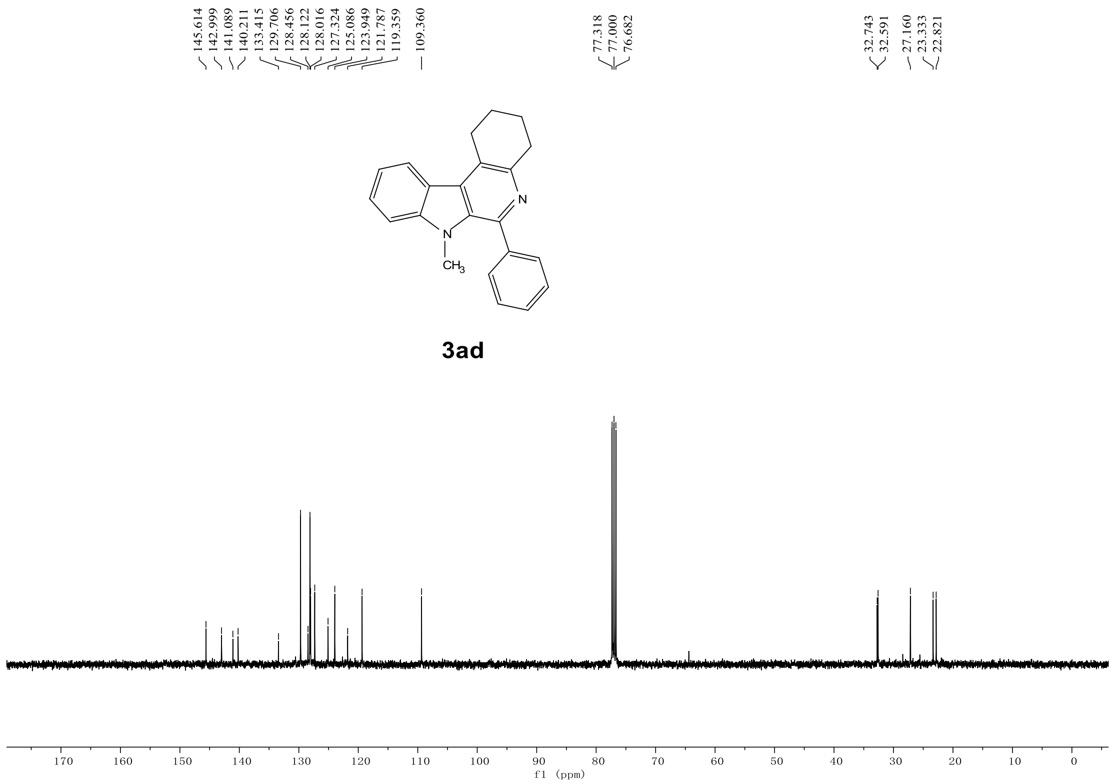
[13]C NMR of **3ac** (400 MHz, $CDCl_3$):



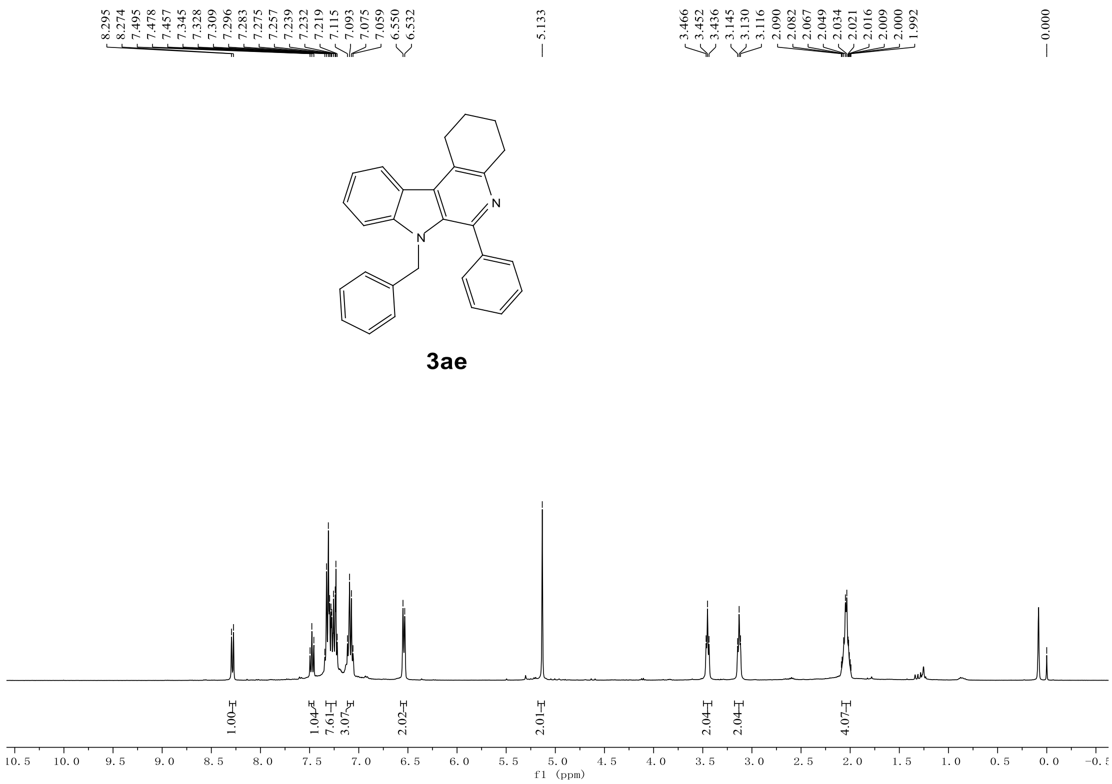
[1]H NMR of **3ad** (400 MHz, $CDCl_3$):



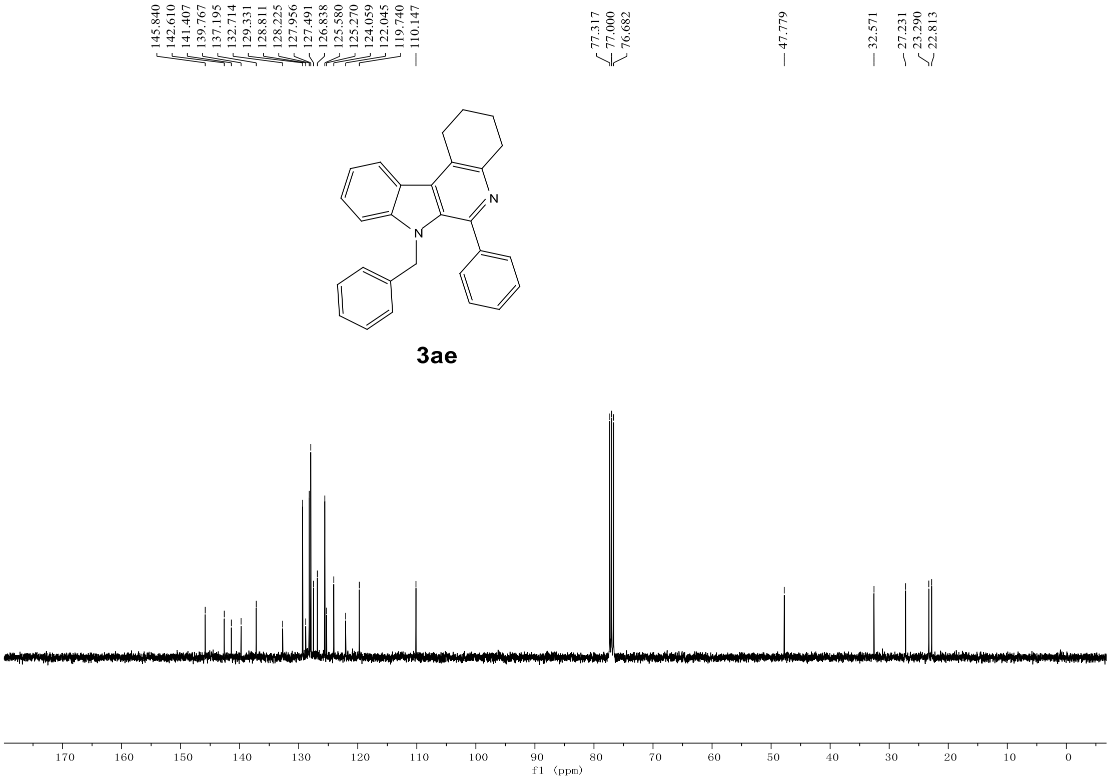
^{13}C NMR of **3ad** (400 MHz, $CDCl_3$):



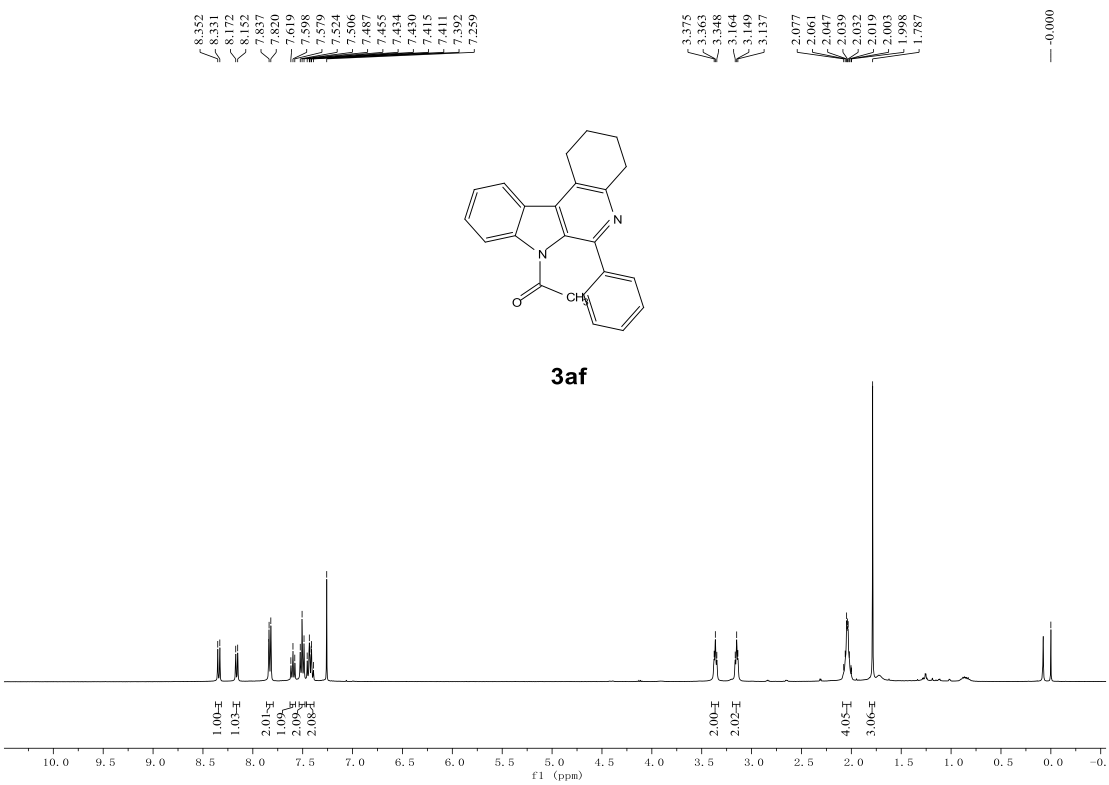
^{1}H NMR of **3ae** (400 MHz, $CDCl_3$):



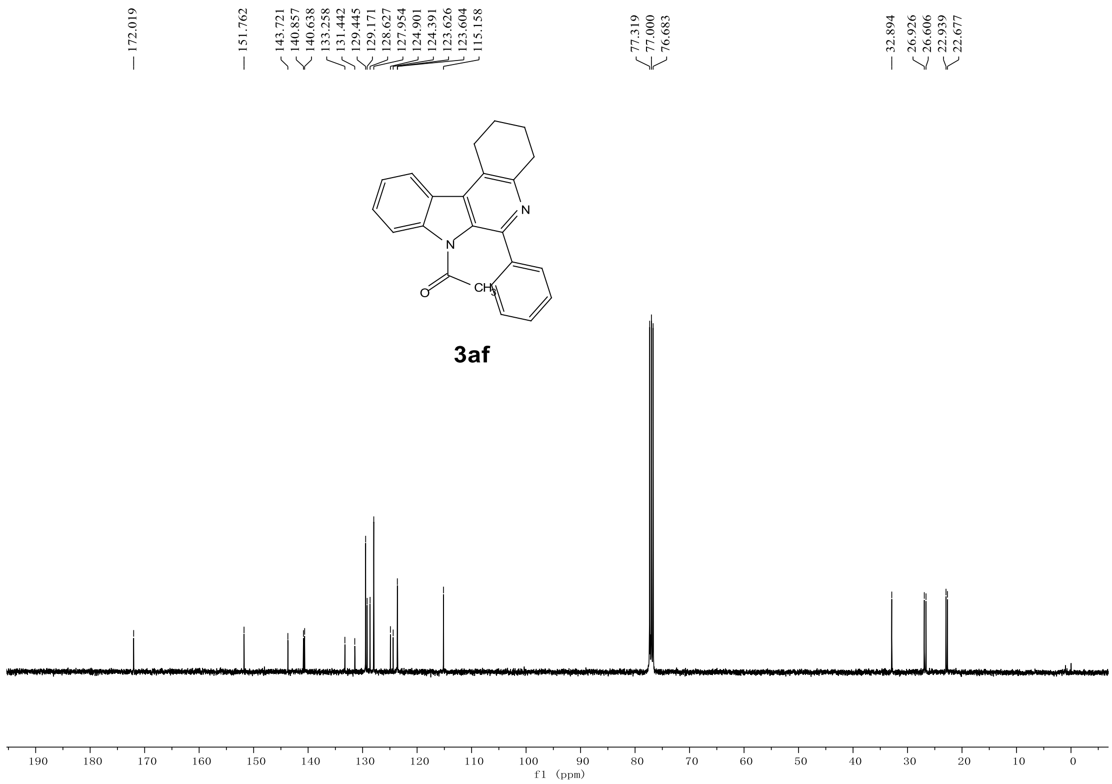
[13]C NMR of **3ae** (400 MHz, $CDCl_3$):



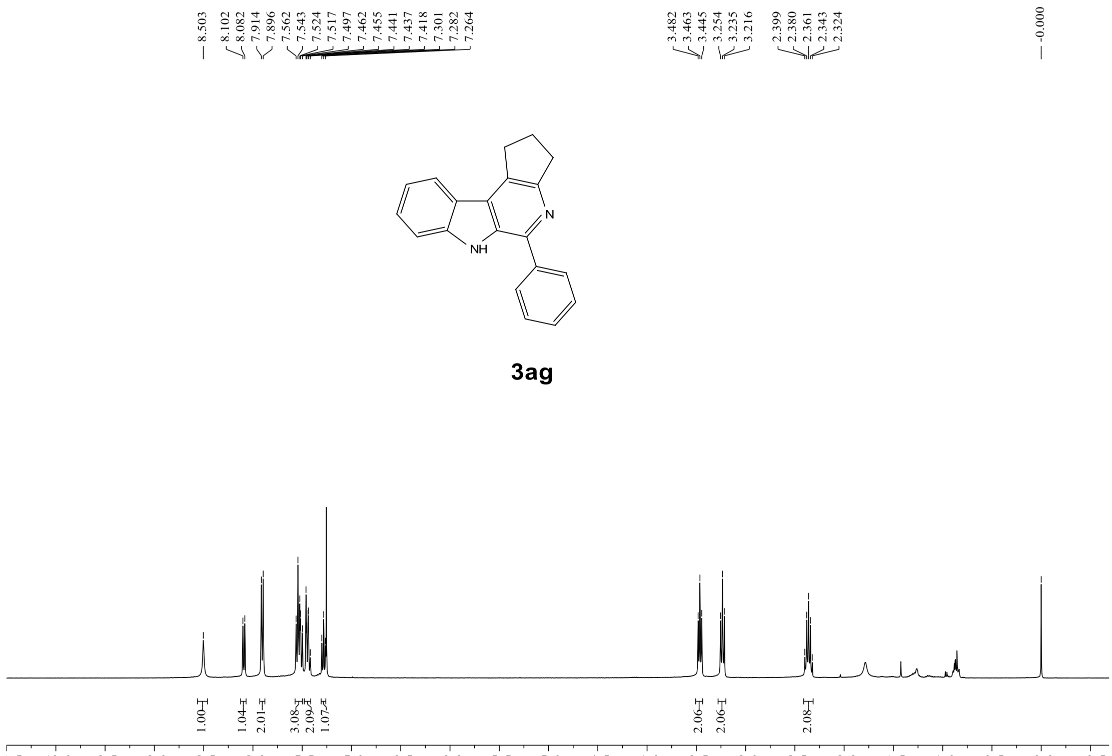
[1]H NMR of **3af** (400 MHz, $CDCl_3$):



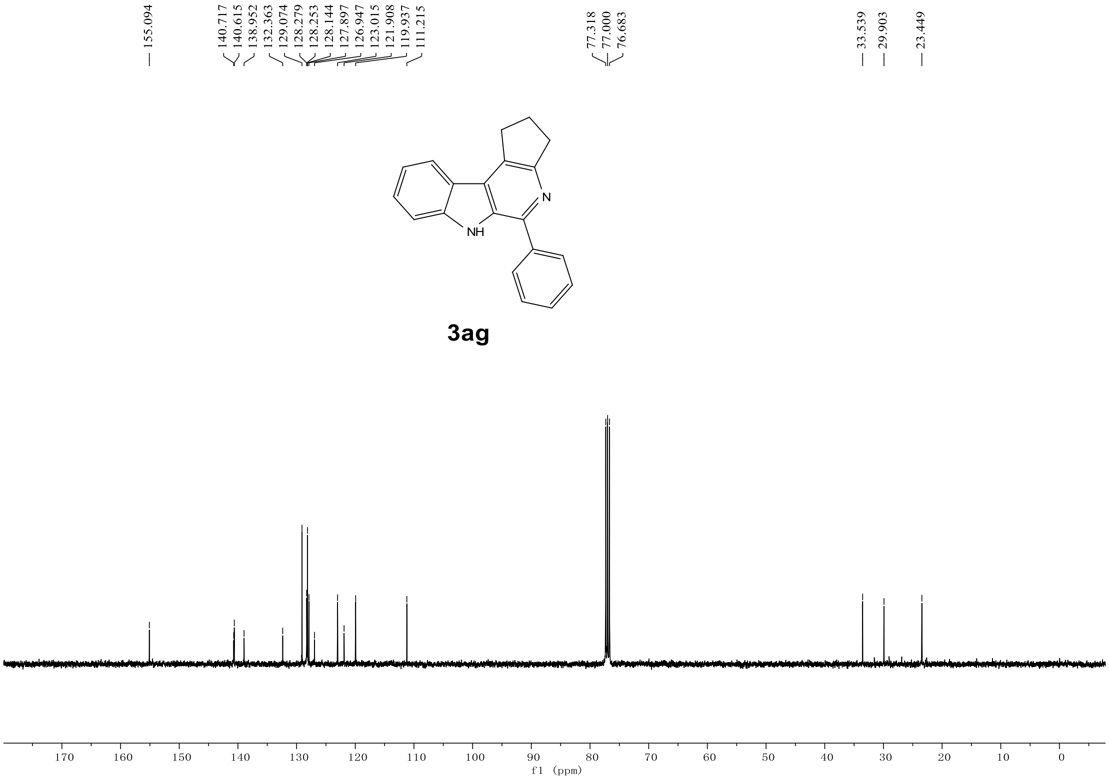
^{13}C NMR of **3af** (400 MHz, $CDCl_3$):



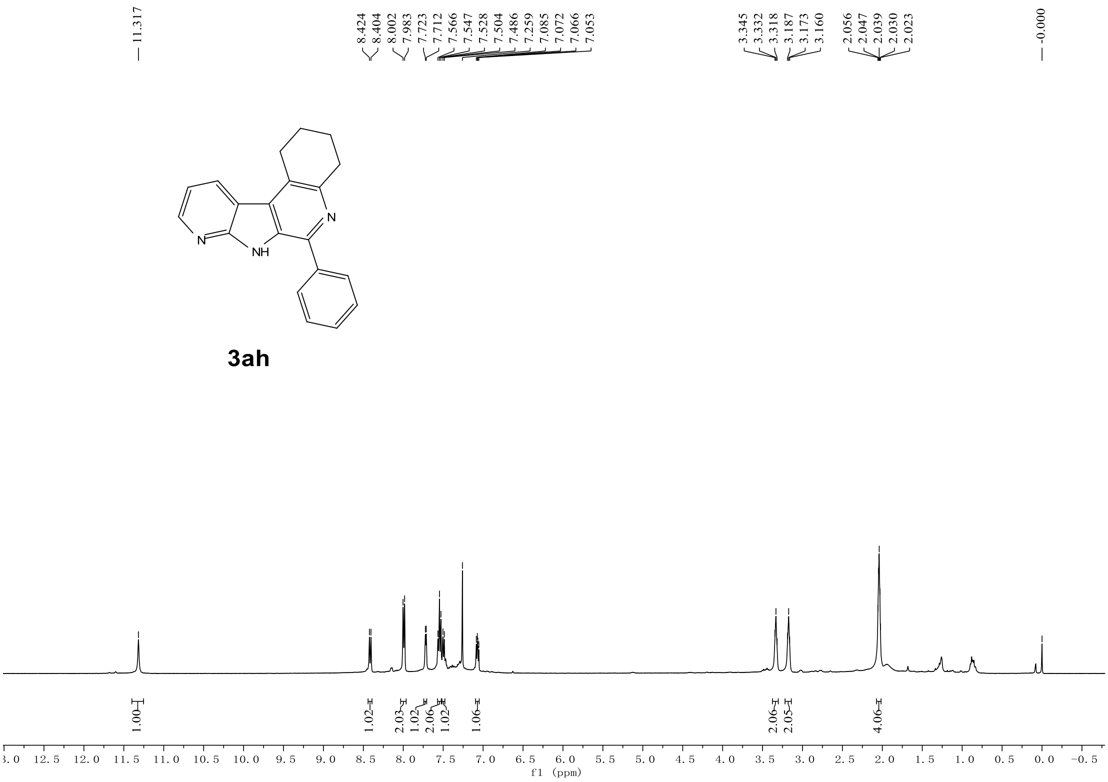
^{1}H NMR of **3ag** (400 MHz, $CDCl_3$):



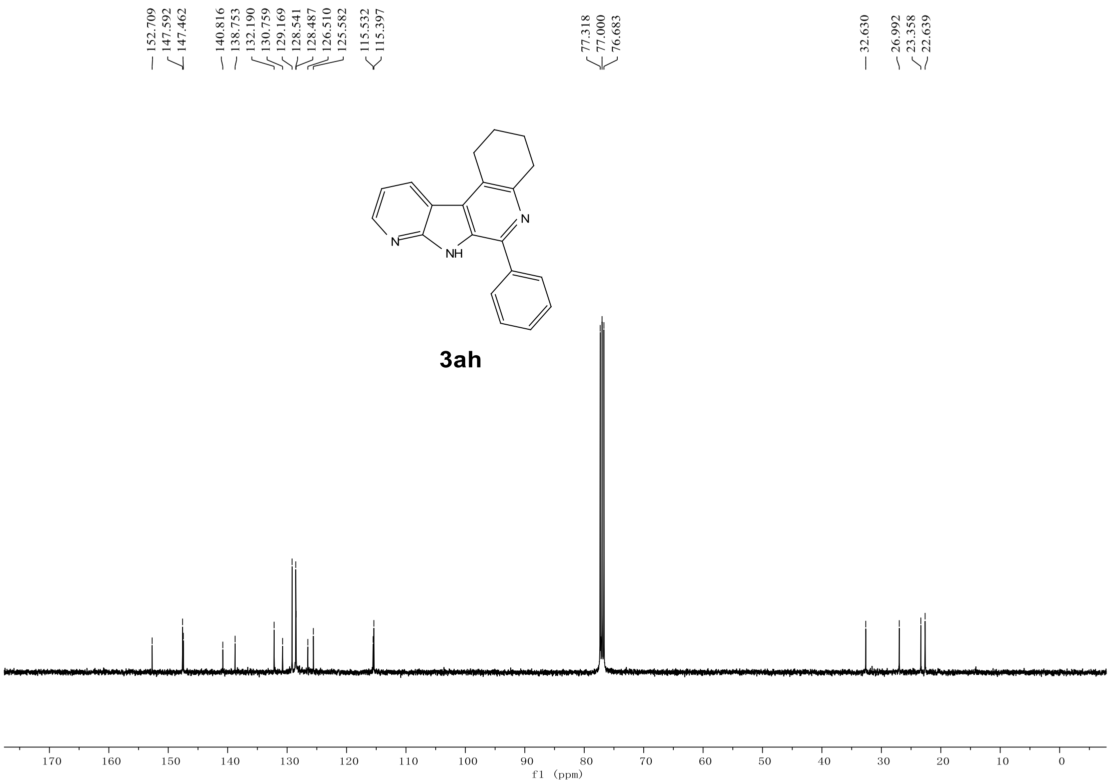
^{13}C NMR of **3ag** (400 MHz, $CDCl_3$):



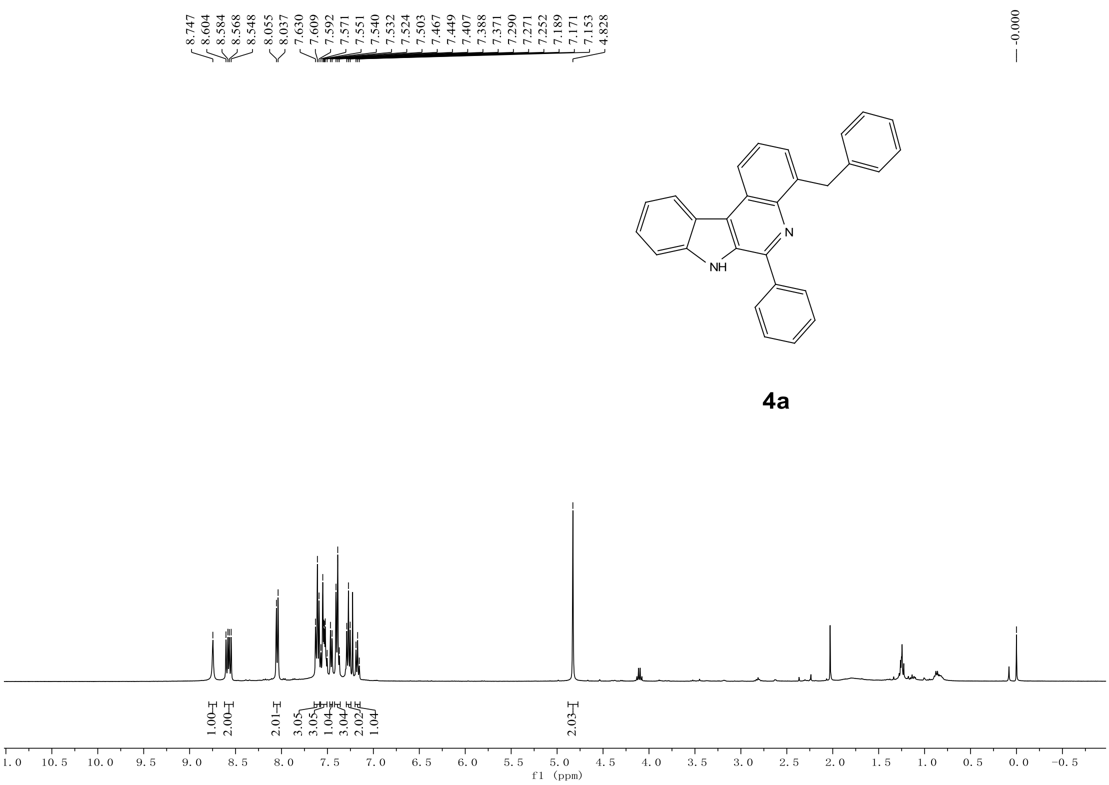
^{1}H NMR of **3ah** (400 MHz, $CDCl_3$):



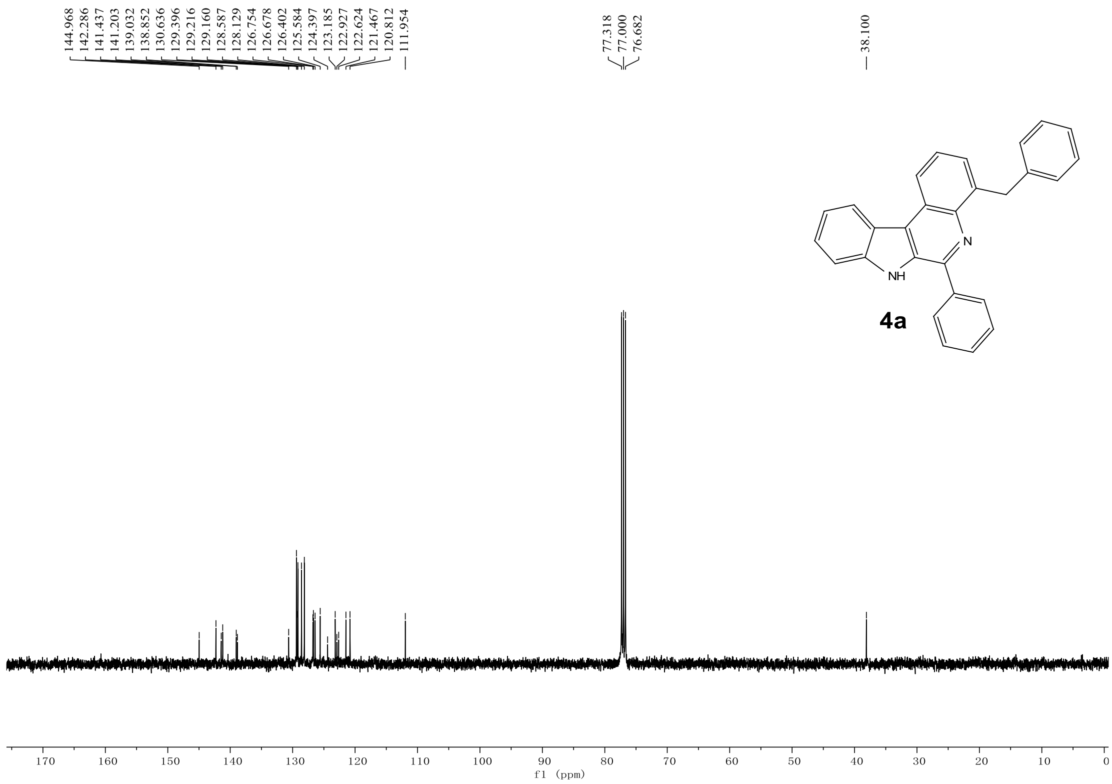
[13]C NMR of **3ah** (400 MHz, $CDCl_3$):



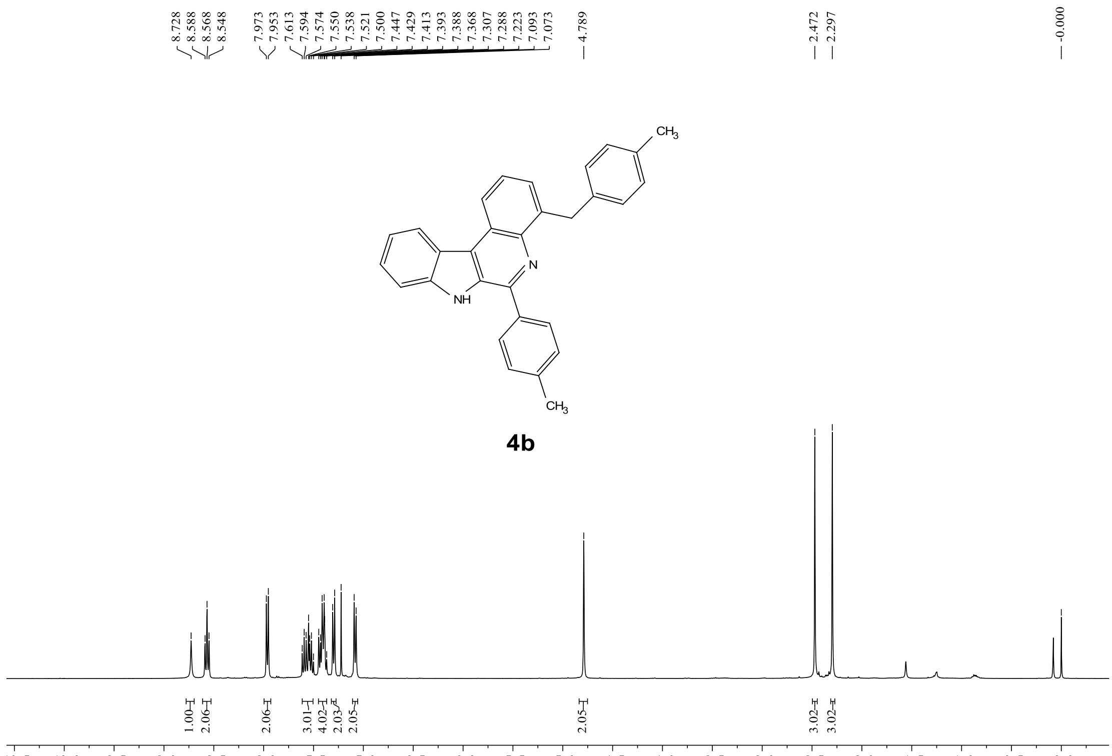
[1]H NMR of **4a** (400 MHz, $CDCl_3$):



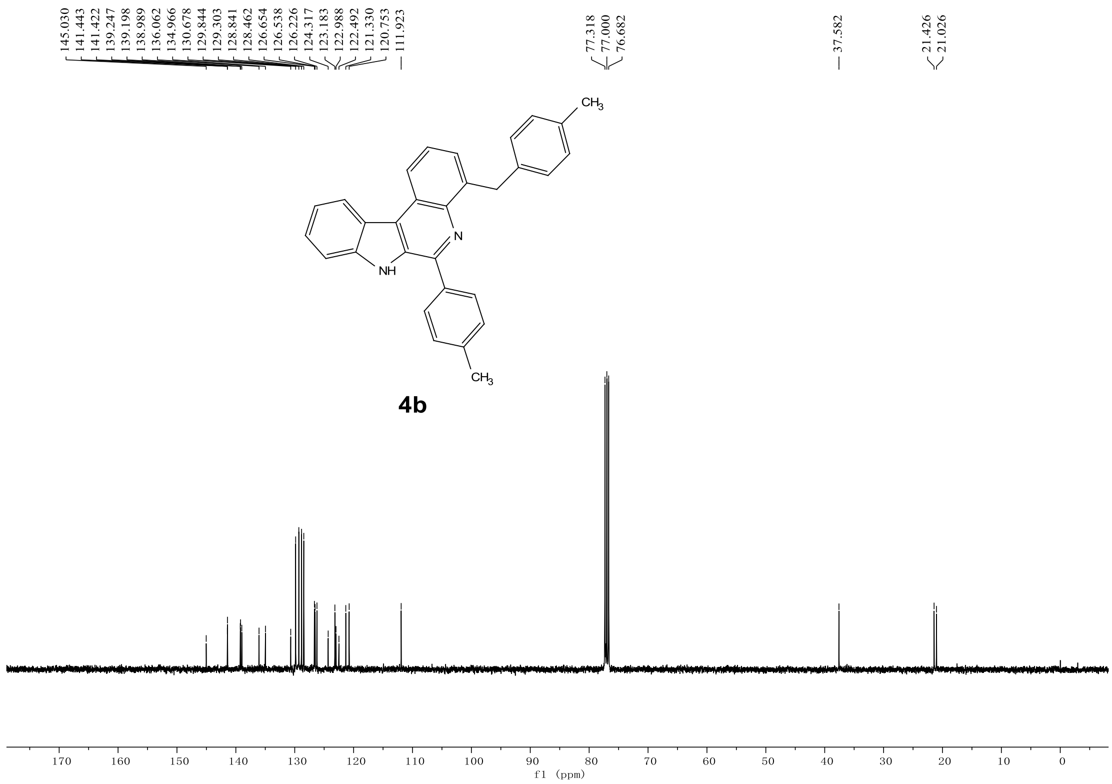
^{13}C NMR of **4a** (400 MHz, $CDCl_3$):



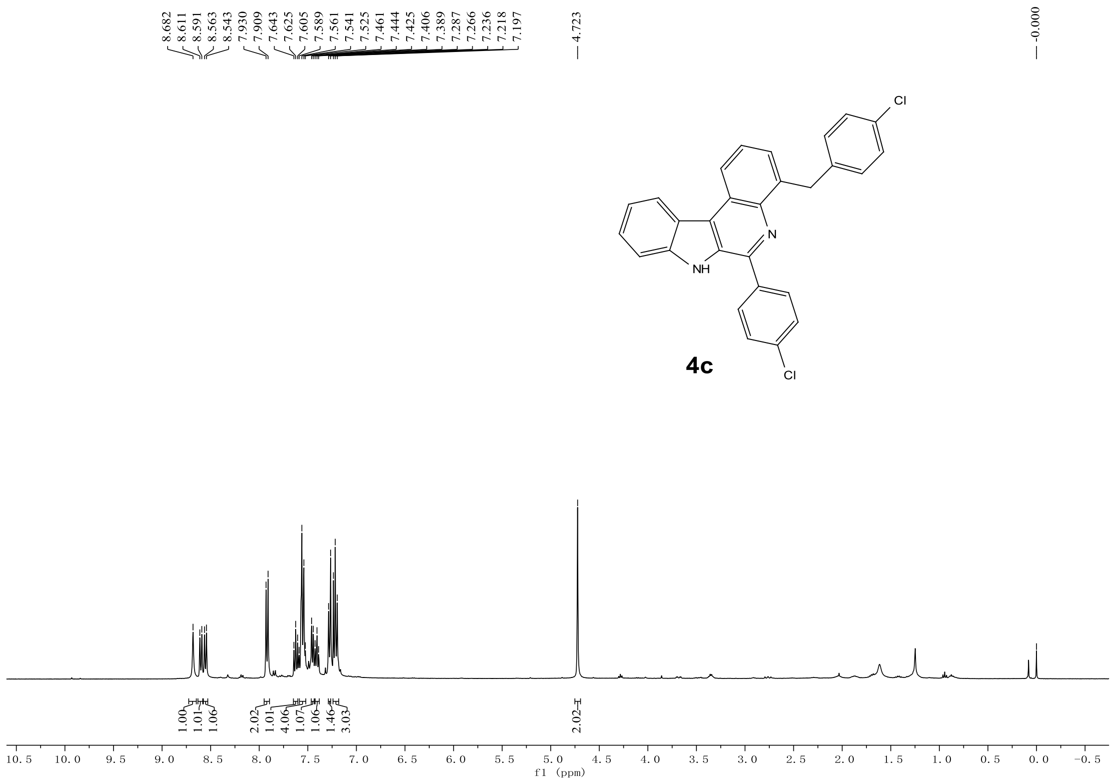
^1H NMR of **4b** (400 MHz, $CDCl_3$):



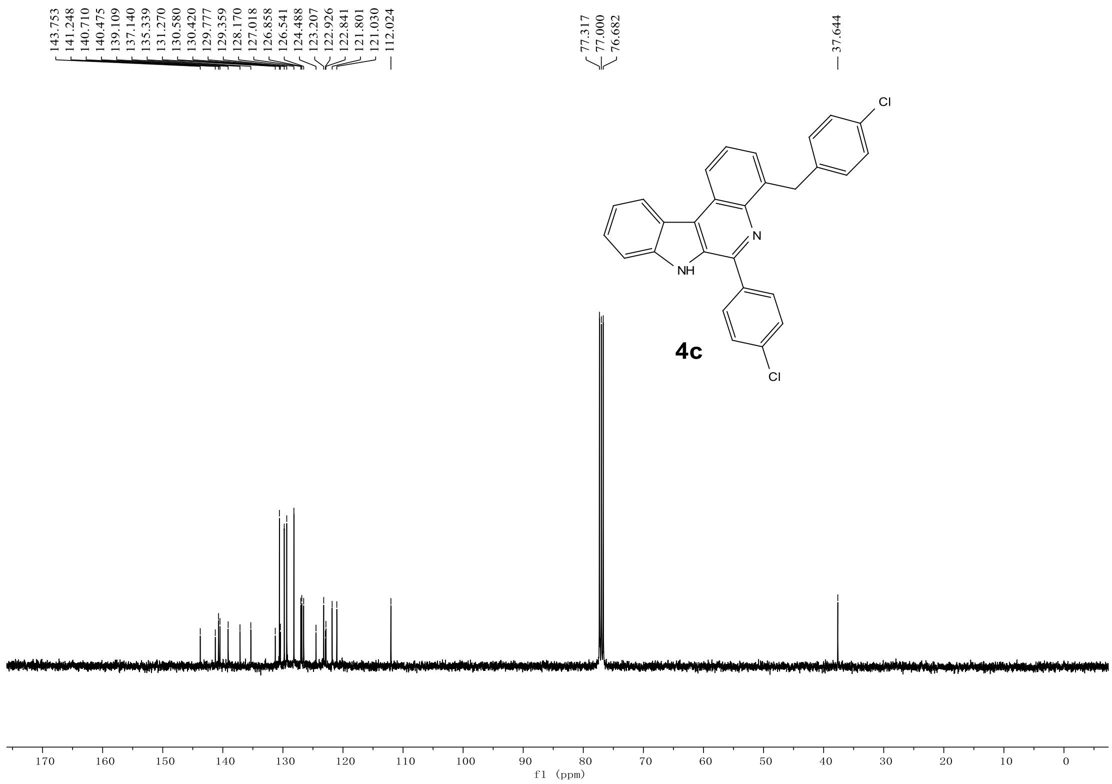
^{13}C NMR of **4b** (400 MHz, $CDCl_3$):



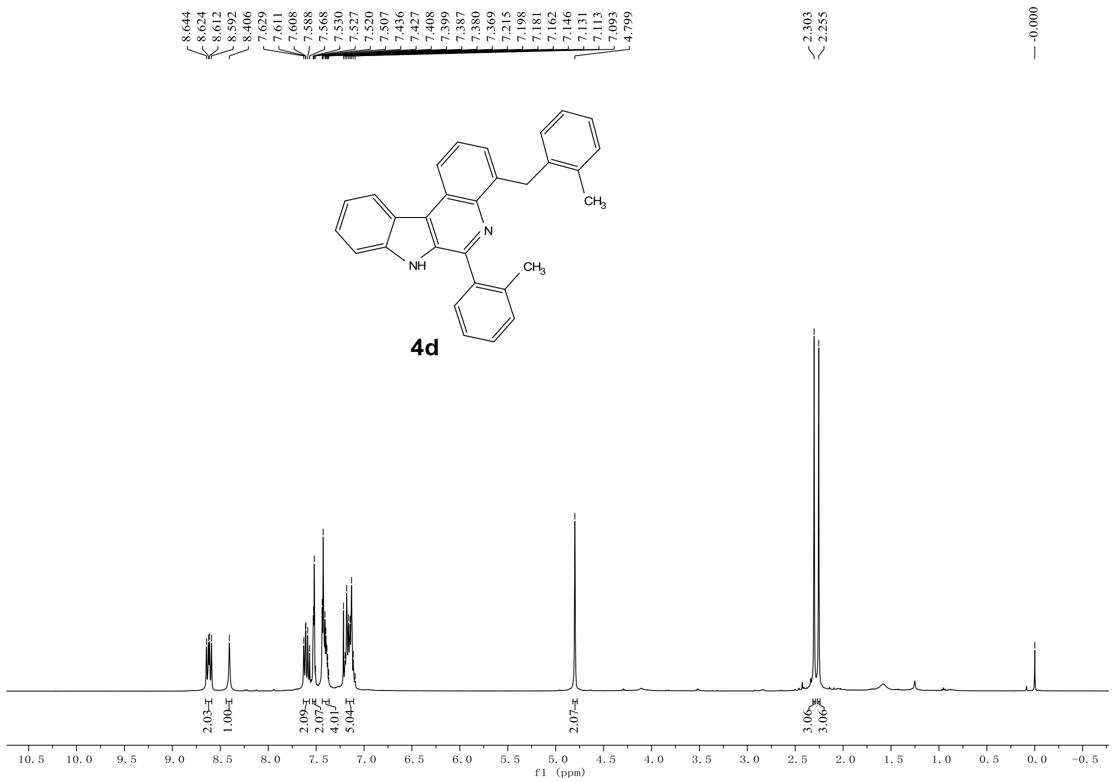
^{1}H NMR of **4c** (400 MHz, $CDCl_3$):



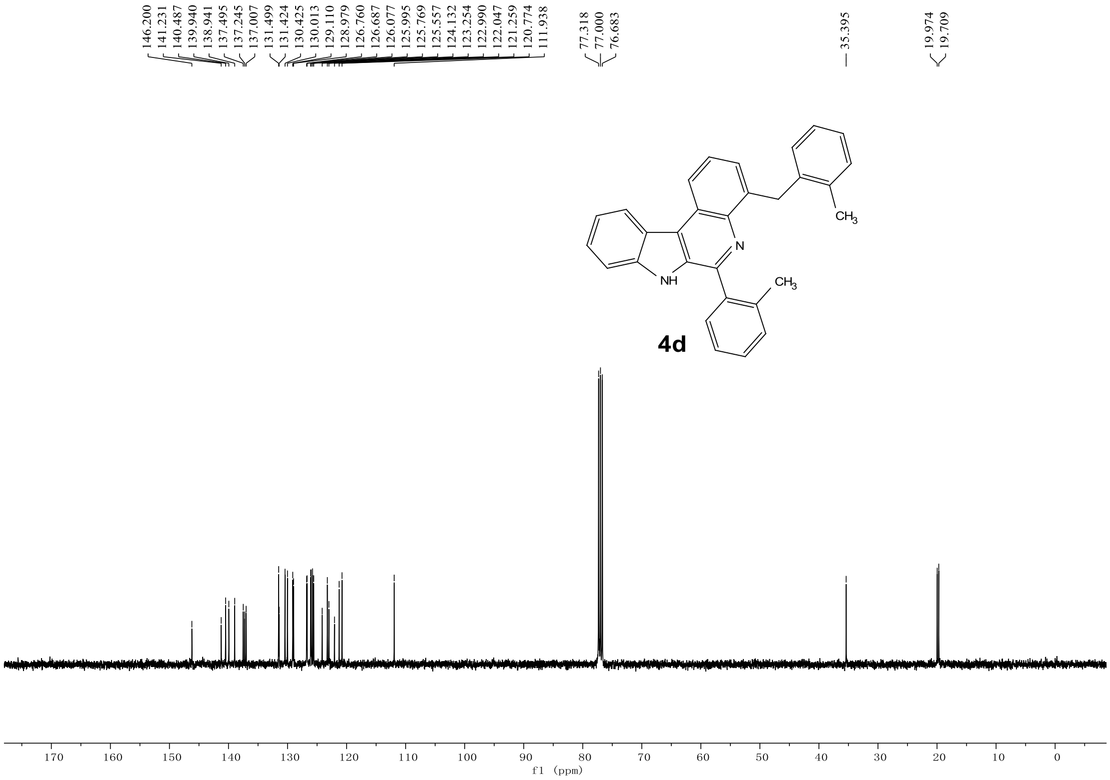
^{13}C NMR of **4c** (400 MHz, $CDCl_3$):



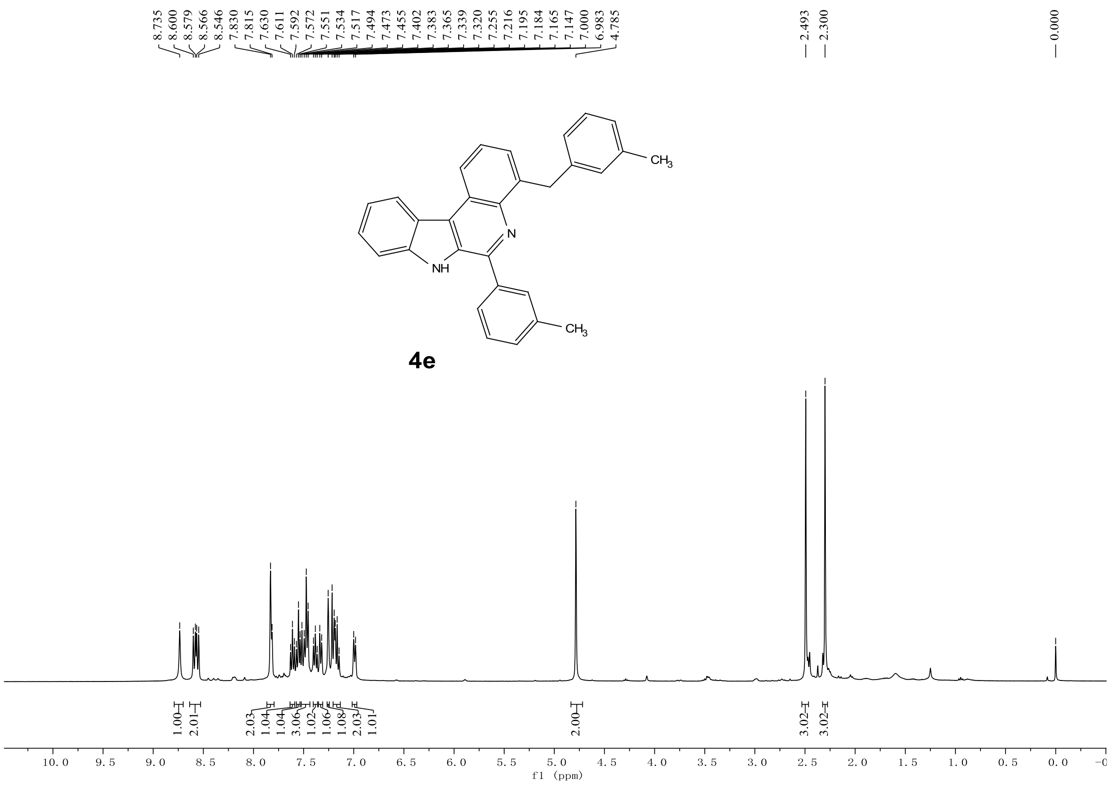
^{1}H NMR of **4d** (400 MHz, $CDCl_3$):



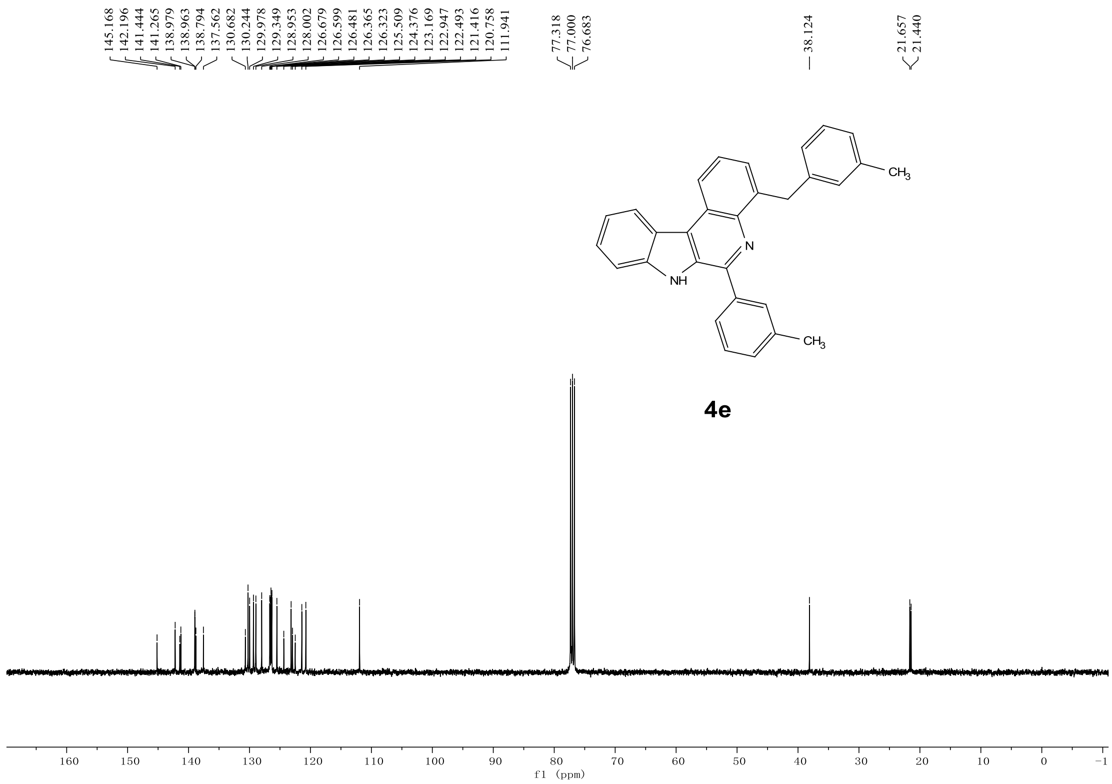
^{13}C NMR of **4d** (400 MHz, $CDCl_3$):



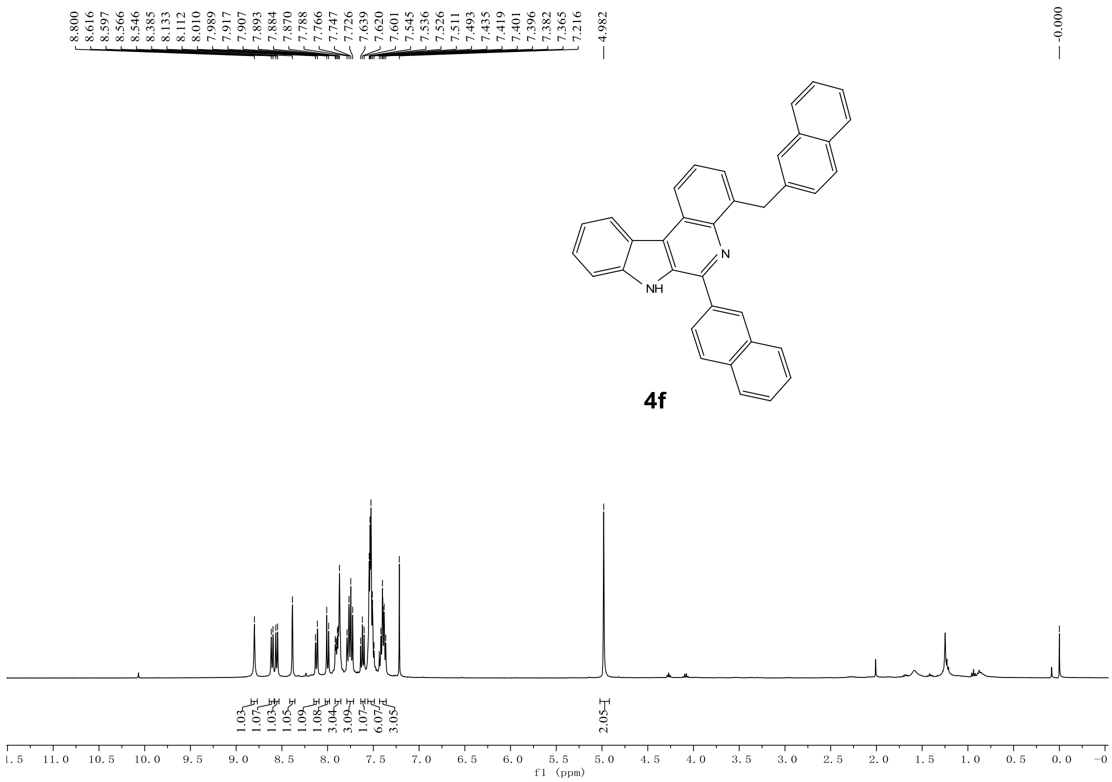
^{1}H NMR of **4e** (400 MHz, $CDCl_3$):



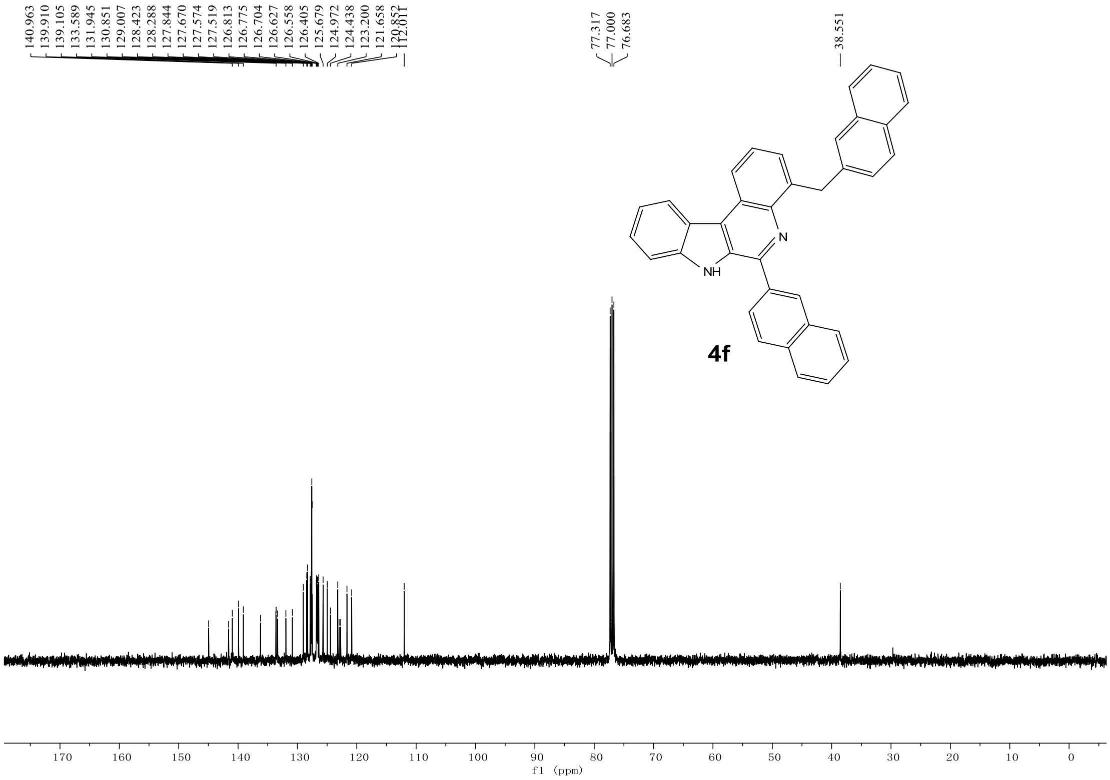
^{13}C NMR of **4e** (400 MHz, $CDCl_3$):



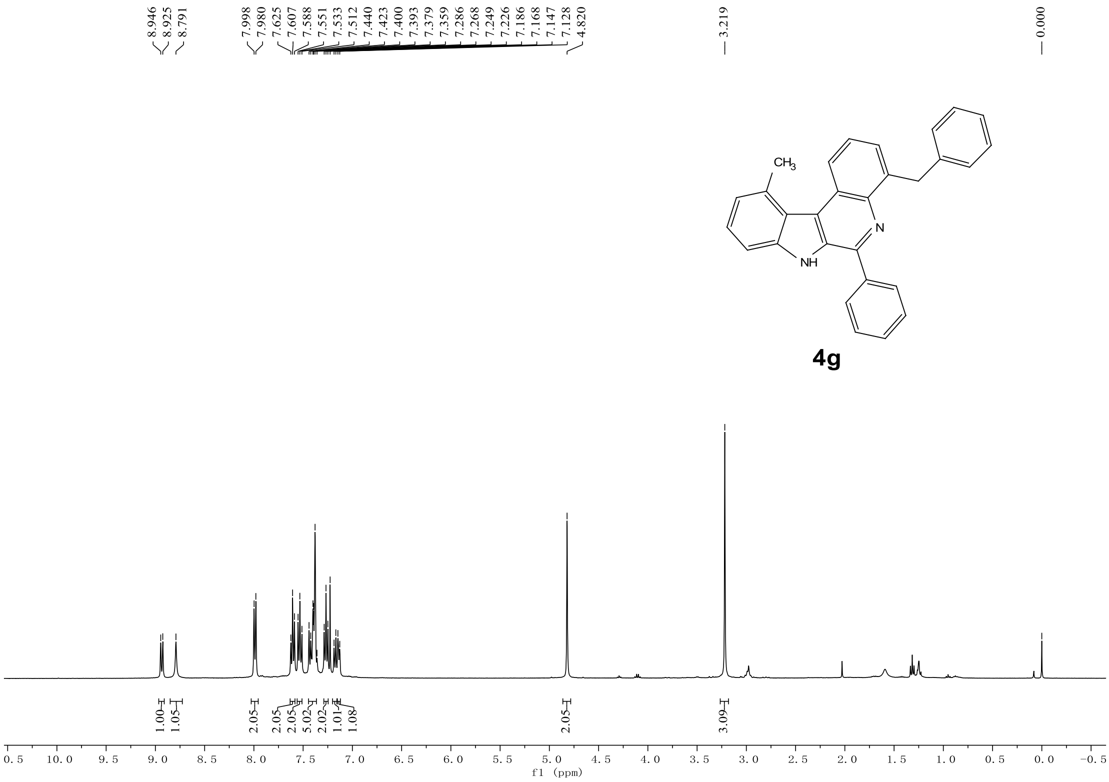
^{1}H NMR of **4f** (400 MHz, $CDCl_3$):



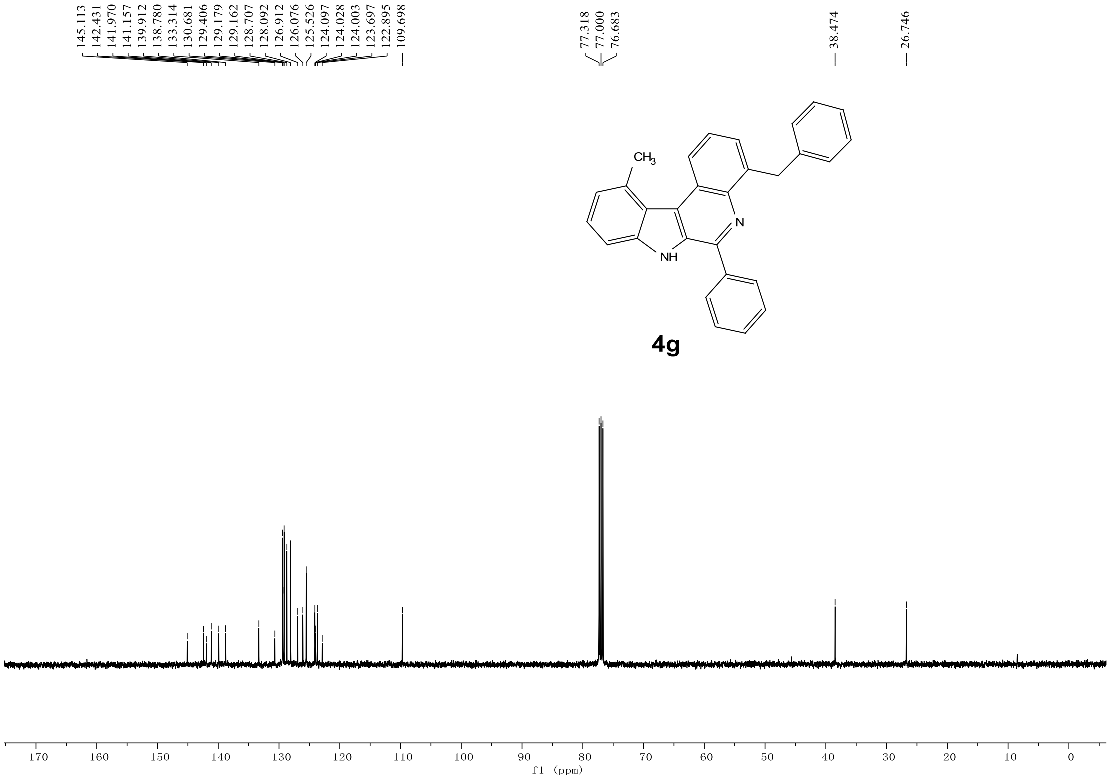
^{13}C NMR of **4f** (400 MHz, $CDCl_3$):



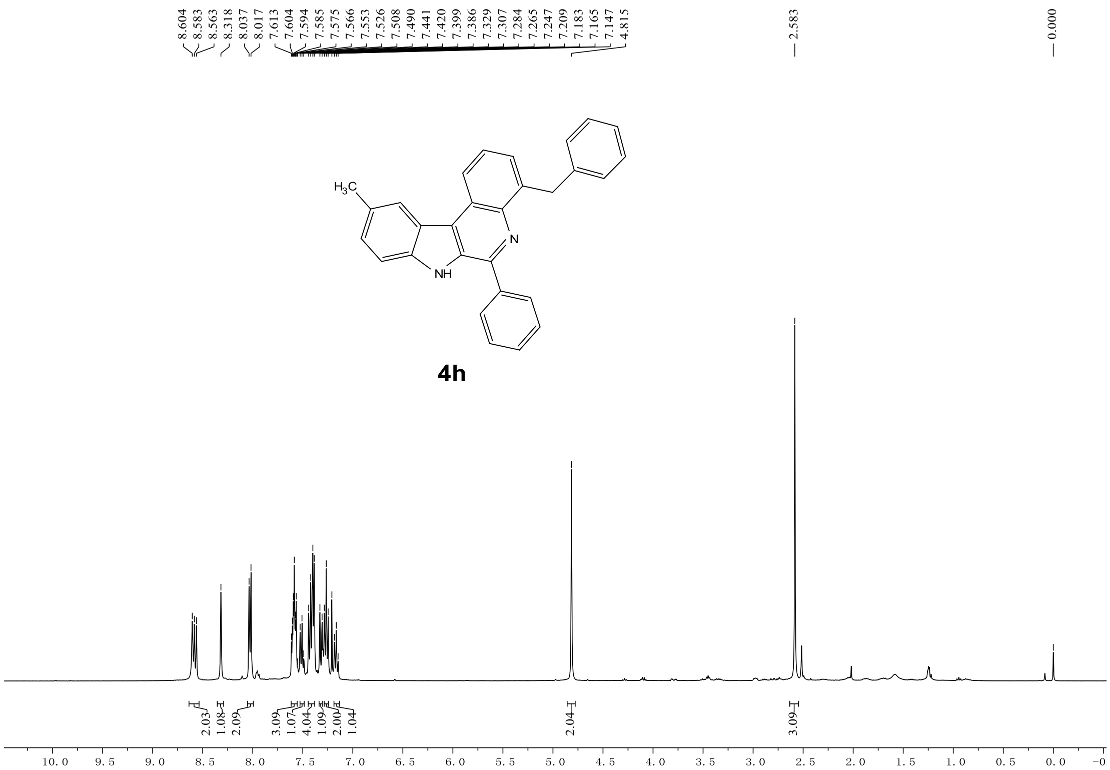
^{1}H NMR of **4g** (400 MHz, $CDCl_3$):



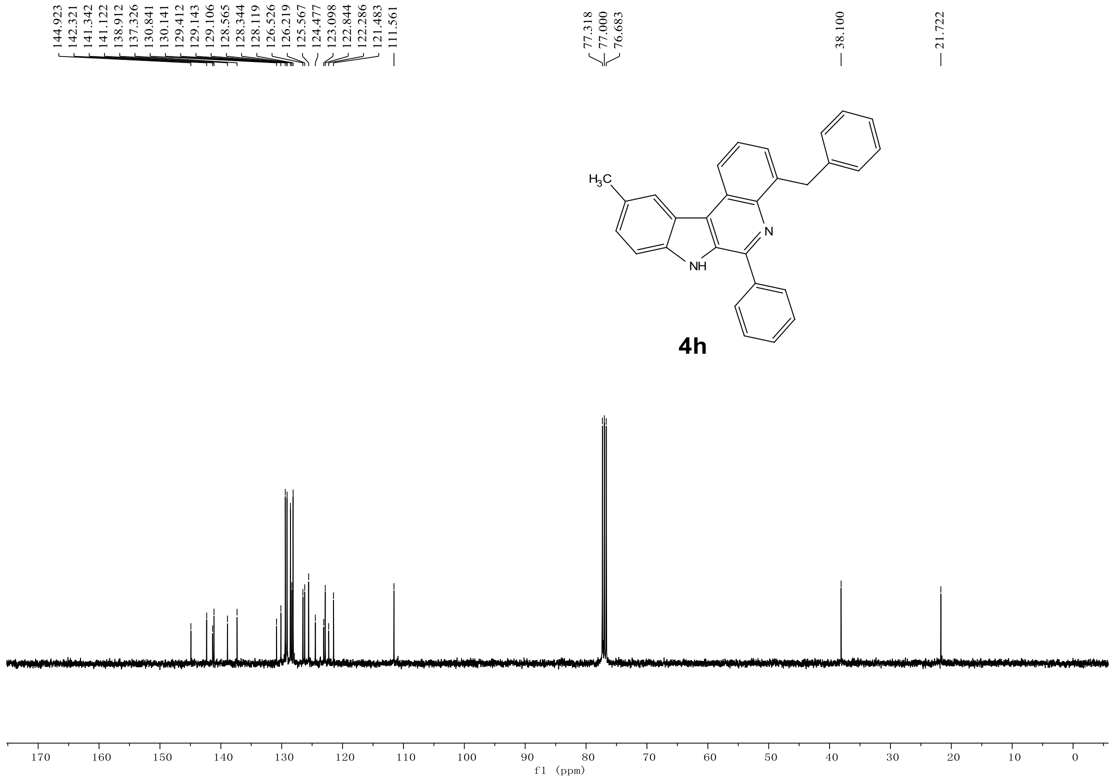
^{13}C NMR of **4g** (400 MHz, $CDCl_3$):



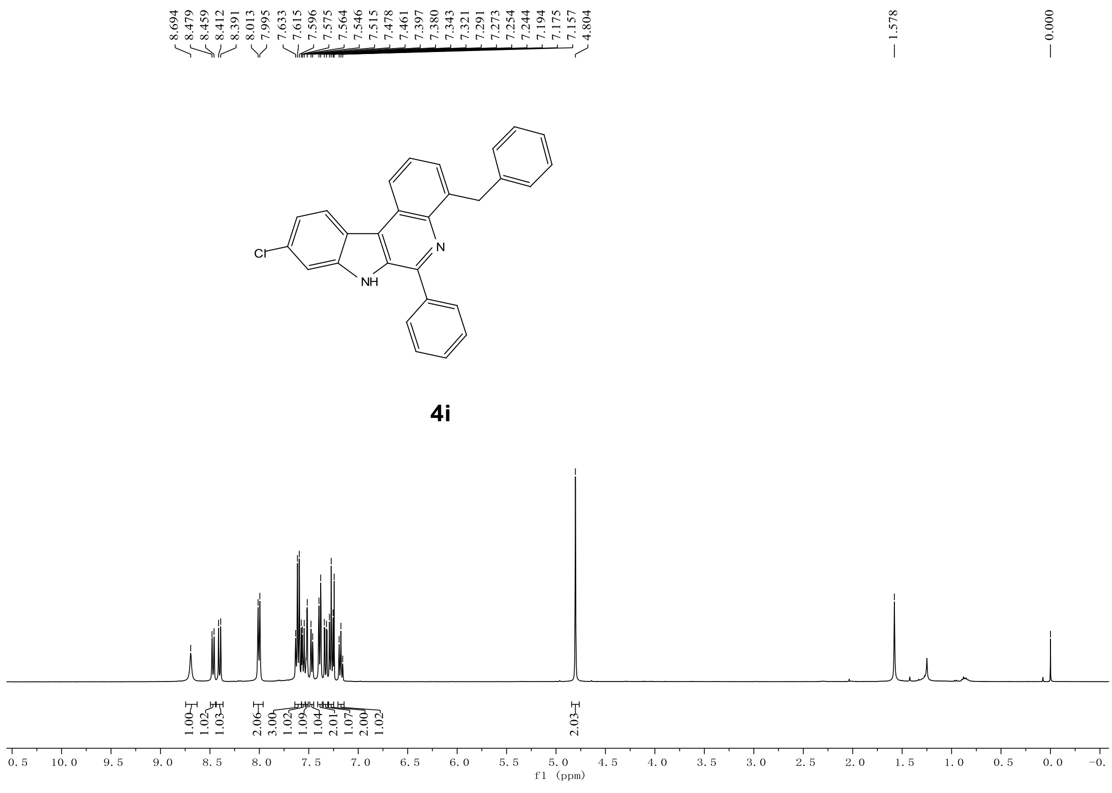
^{1}H NMR of **4h** (400 MHz, $CDCl_3$):



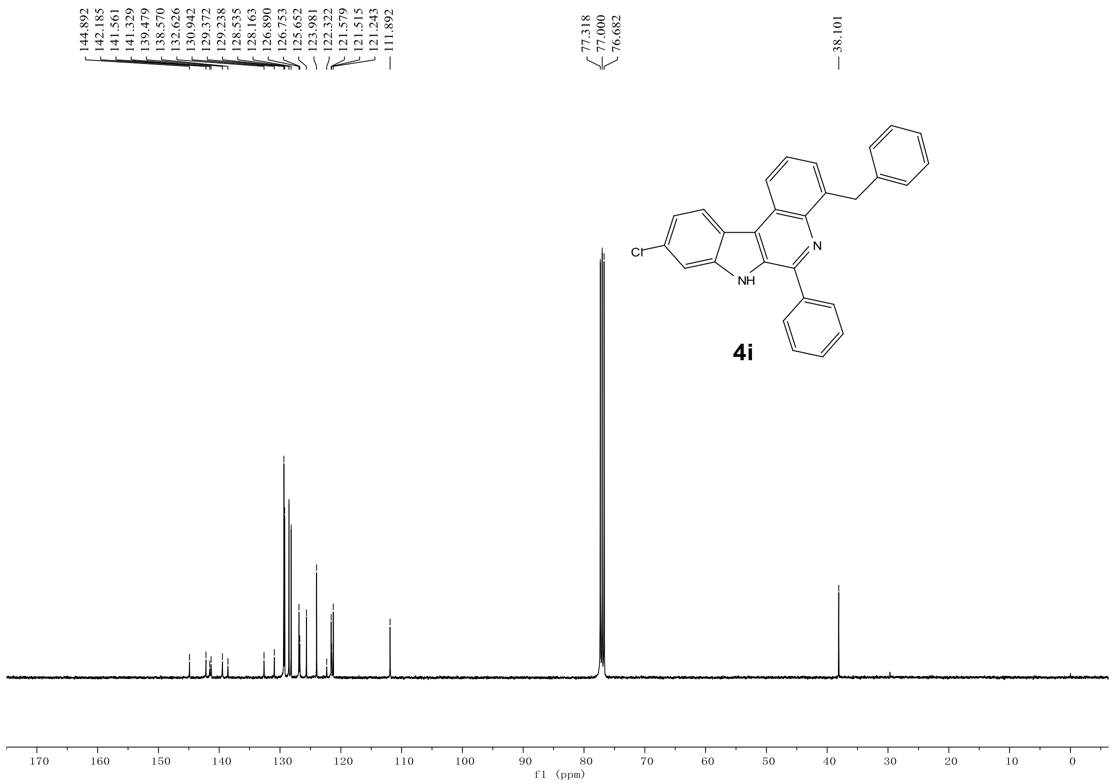
^{13}C NMR of **4h** (400 MHz, $CDCl_3$):



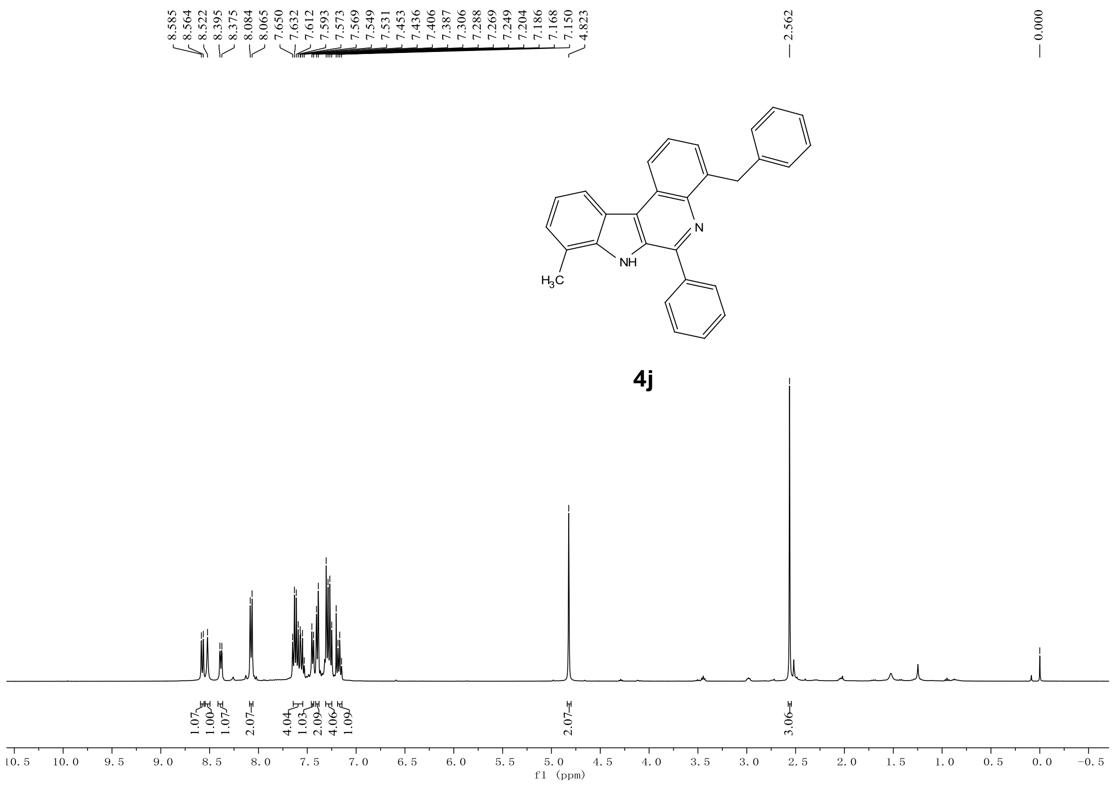
^{1}H NMR of **4i** (400 MHz, $CDCl_3$):



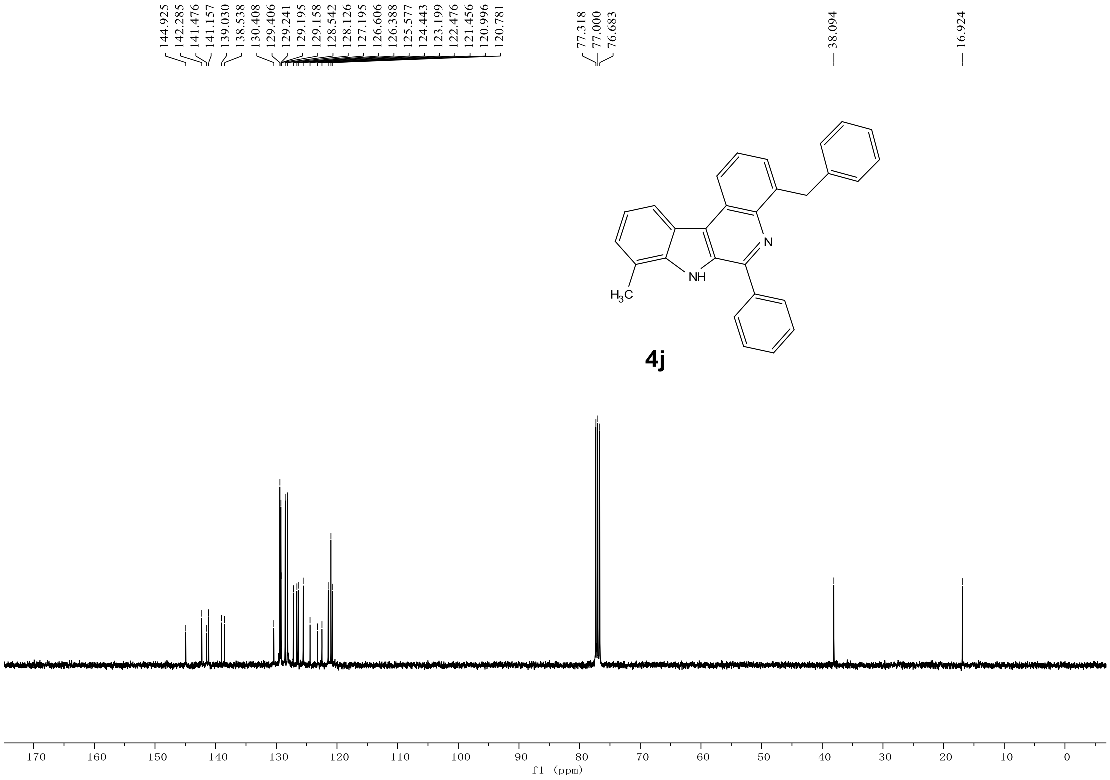
^{13}C NMR of **4i** (400 MHz, $CDCl_3$):



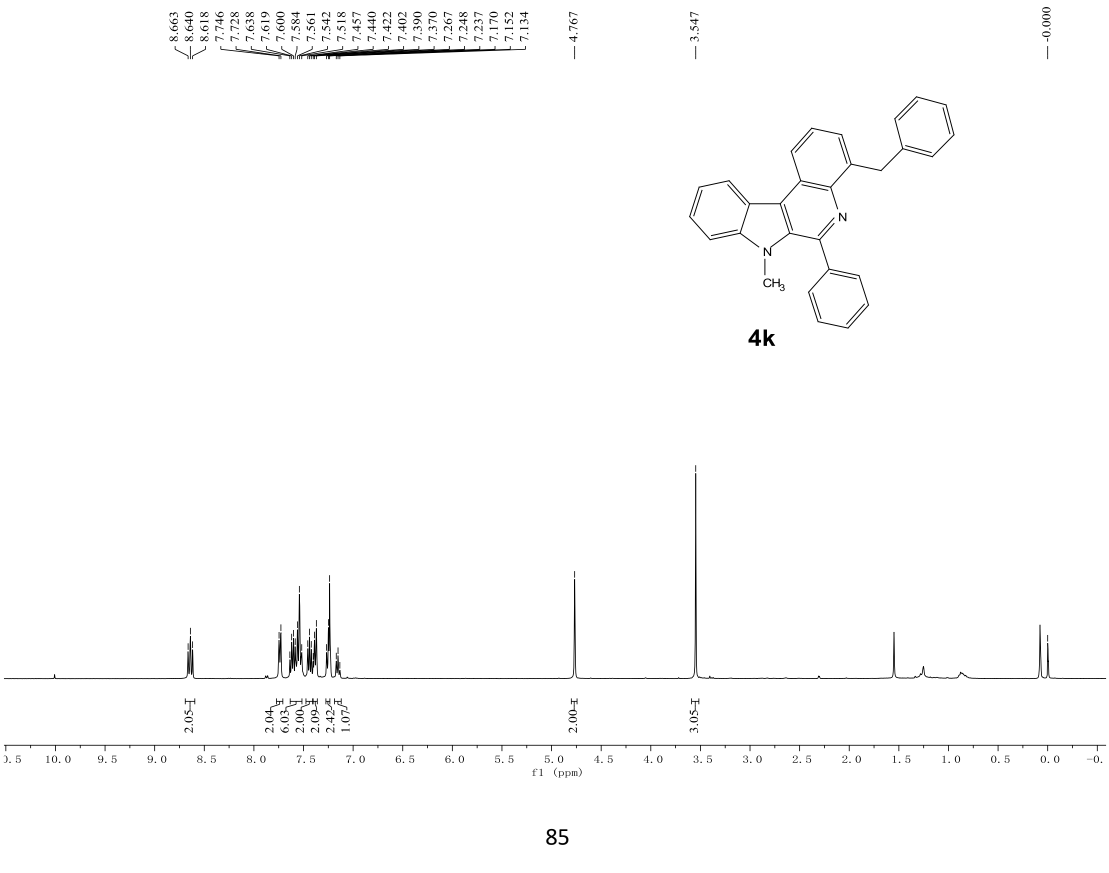
^{1}H NMR of **4j** (400 MHz, $CDCl_3$):



^{13}C NMR of **4j** (400 MHz, $CDCl_3$):



^{1}H NMR of **4k** (400 MHz, $CDCl_3$):



[13]C NMR of **4k** (400 MHz, $CDCl_3$):