Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Rhodium-Catalyzed Coupling-Cyclization of *o*-Alkynyl Arylazides with Arylisocyanides: Synthesis of 6*H*-Indolo[2,3-*b*]quinolines, Dibenzonaphthyridones and Dihydrodibenzo[*b*,*g*][1,8]-naphthyridines

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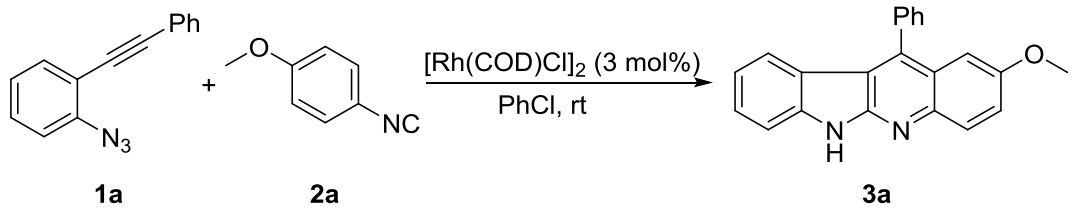
I. General Information:

All reagents were commercial and were used without further purification. Chromatography was carried on flash silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on percolated aluminum sheets of silica gel 60 (F254). Unless noted, the ^{1}H NMR spectra were recorded at 500 MHz, 600 MHz in $CDCl_3$, the ^{13}C NMR spectra were recorded at 151 MHz in $CDCl_3$ with TMS as internal standard, and the ^{19}F NMR spectra were recorded at 471 MHz in $CDCl_3$. All coupling constants (*J* values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). The compound **3g** and **7a** were glued on a glass fiber. X-ray single-crystal data of **3g** and **7a** were collected by a Bruker D8 Venture diffractometer (Mo Kα radiation, λ = 0.71073 Å (Cu Kα radiation, λ = 1.54178 Å)) at 293(2) K, and IP technique in the range $2.19° < \theta < 27.48°$. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXS 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. In addition, *o*-Alkynyl Arylazides **1**, **4** and **6** were synthesized according to known literature procedure.[1] Arylisocyanides **2** were prepared according to the previous reported method.[2]

II. General Procedure for the Preparation of 3 (3a as example):



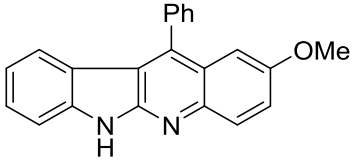
1a **2a** **3a**

A sealed tube equipped with a magnetic stir bar was charged with $[Rh(COD)Cl]_2$ (0.006 mmol, 3.0 mg) in PhCl (2.0 mL), then **1a** (0.3 mmol, 65.8 mg) and **2a** (0.2 mmol, 26.6 mg) were added. Subsequently, the reaction mixture was stirred at room temperature for 8 h. After the reaction was complete, the reaction mixture was poured into saturated aqueous NaCl (30 mL) and extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were dried over anhydrous Mg_2SO_4. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 3:50, V/V) to afford pure product **3a** (55.8 mg, 86%) as a yellow solid.

A gram-scale synthesis of compound 3a:

A sealed tube equipped with a magnetic stir bar was charged with $[Rh(COD)Cl]_2$ (0.225 mmol, 110.9 mg) in PhCl (20 mL), then **1a** (11.3 mmol, 2.5 g) and **2a** (7.5 mmol, 1.0 g) were added. Subsequently, the reaction mixture was stirred at room temperature for 10 h. After the reaction was complete, the reaction mixture was poured into saturated aqueous NaCl (150 mL) and extracted with CH_2Cl_2 (30 mL×3). The combined organic extracts were dried over anhydrous Mg_2SO_4. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 3:50, V/V) to afford pure product **3a** (1.7 g, 71%) as a yellow solid.

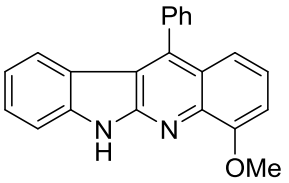
2-Methoxy-11-phenyl-6*H*-indolo[2,3-*b*]quinoline (3a):



Yellow solid, 55.8 mg, 86% yield. The melting point of this compound is consistent with reported previously. ^1H NMR (600 MHz, $CDCl_3$) δ 10.66 (s, 1H), 8.13 (d, J = 9.2

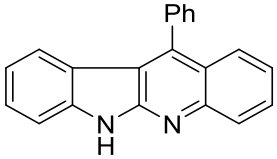
Hz, 1H), 7.69 - 7.63 (m, 3H), 7.56 (d, *J* = 6.7 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.47 - 7.40 (m, 2H), 7.07 (d, *J* = 2.7 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.26, 152.26, 142.02, 141.76, 141.43, 136.69, 129.37, 129.08, 128.55, 127.78, 127.71, 124.15, 123.06, 120.99, 120.93, 119.45, 116.85, 110.77, 104.89, 55.48. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{22}H_{17}N_2O^+$: 325.1335, found: 325.1337. The values of the NMR spectra are in accordance with reported literature data.[3]

4-Methoxy-11-phenyl-6*H*-indolo[2,3-*b*]quinoline (3b):



Yellow solid; mp: 253 - 255 ℃, 46.1 mg, 71% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.96 (s, 1H), 7.69 (dt, J = 13.0, 7.0 Hz, 3H), 7.54 – 7.51 (m, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.20 – 7.15 (m, 2H), 6.95 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 154.77, 151.97, 142.08, 141.97, 138.54, 136.79, 129.57, 129.47, 129.12, 128.43, 124.12, 123.02, 122.76, 120.55, 119.74, 117.95, 115.84, 111.42, 107.98, 56.19. HRMS (ESI-TOF): $[M+Na]^+$ calculated for $C_{22}H_{16}N_2ONa^+$: 347.1155, found: 347.1145.

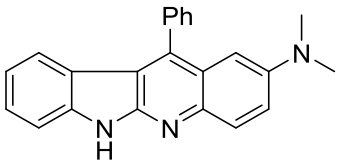
11-Phenyl-6*H*-indolo[2,3-*b*]quinoline (3c):



Yellow solid, 44.2 mg, 75% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.84 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.74 - 7.67 (m, 4H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 6.7 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.43 - 7.37 (m, 1H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 152.95, 146.85, 142.14, 141.97, 136.45, 129.64, 129.54, 129.20, 129.08, 128.45,

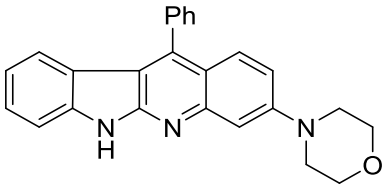
127.77, 126.21, 123.36, 123.33, 122.76, 120.68, 119.80, 115.91, 111.40. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{21}H_{15}N_2^+$: 395.1230, found: 395.1224. The values of the NMR spectra are in accordance with reported literature data.[3]

_N,N_-dimethyl-11-phenyl-6_H_-indolo[2,3-_b_]quinolin-2-amine (3d):



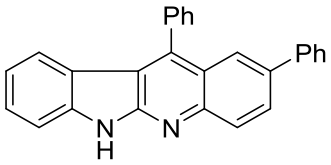
Yellow solid; mp: 258 - 260 ℃, 27.7 mg, 41% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.52 (s, 1H), 7.91 (d, J = 9.3 Hz, 1H), 7.71 (t, J = 7.3 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.54 (d, J = 8.2 Hz, 2H), 7.50 (dd, J = 9.3, 2.8 Hz, 1H), 7.43 (d, J = 7.9 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 7.7 Hz, 1H), 6.65 (d, J = 2.7 Hz, 1H), 2.84 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 151.11, 146.74, 142.02, 141.15, 139.85, 137.11, 129.66, 129.46, 128.97, 128.30, 127.96, 124.34, 122.62, 120.73, 120.13, 119.21, 115.78, 111.12, 104.36, 40.97. HRMS (ESI-TOF): $[M+Na]^+$ calculated for $C_{23}H_{19}N_3Na^+$: 360.1471, found: 360.1478.

4-(11-Phenyl-6_H_-indolo[2,3-_b_]quinolin-3-yl)morpholine (3e):



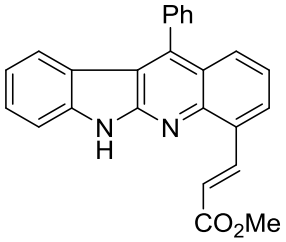
Yellow solid; mp: 292 - 294 ℃, 36.4 mg, 48% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.63 (s, 1H), 7.72 - 7.65 (m, 3H), 7.52 (d, J = 7.0 Hz, 2H), 7.46 - 7.42 (m, 2H), 7.36 (t, J = 7.5 Hz, 1H), 7.29 - 7.27 (m, 1H), 7.25 (dd, J = 9.3, 2.1 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 3.82 - 3.78 (m, 4H), 3.32 - 3.28 (m, 4H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.39, 151.79, 148.75, 141.75, 141.38, 136.69, 129.51, 129.04, 127.39, 126.72, 121.97, 121.17, 119.55, 117.56, 115.56, 113.32, 111.16, 108.59, 66.52, 48.65. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{25}H_{22}N_3O^+$: 380.1757, found: 380.1758.

2,11-Diphenyl-6_H_-indolo[2,3-_b_]quinoline (3f):



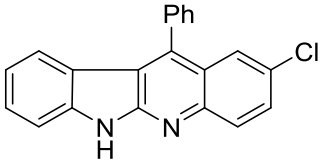
Yellow solid; mp: 296 - 298 ℃, 44.5 mg, 60% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.92 (s, 1H), 8.15 (d, J = 8.7 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 7.84 (s, 1H), 7.77 - 7.69 (m, 3H), 7.64 (d, J = 7.5 Hz, 2H), 7.58 (d, J = 7.7 Hz, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.46 (q, J = 7.2 Hz, 3H), 7.35 (t, J = 7.3 Hz, 1H), 6.99 (t, J = 7.4 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.10, 146.36, 142.20, 142.18, 140.66, 136.31, 135.11, 129.71, 129.63, 129.54, 129.35, 128.56, 128.47, 128.36, 127.72, 127.21, 123.61, 123.49, 122.84, 120.67, 119.90, 116.36, 111.48. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{27}H_{19}N_2^+$: 371.1543, found: 371.1539.

Methyl (*E*)-3-(11-phenyl-6*H*-indolo[2,3-*b*]quinolin-4-yl)acrylate (3g):



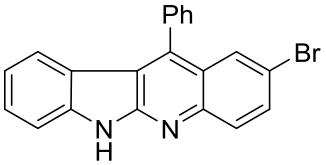
Yellow solid; mp: 199 - 201 ℃, 39.4 mg, 52% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.18 (s, 1H), 9.07 (d, J = 16.3 Hz, 1H), 8.27 (d, J = 6.7 Hz, 1H), 7.75 - 7.69 (m, 4H), 7.57 (d, J = 7.9 Hz, 2H), 7.51 - 7.43 (m, 3H), 7.02 - 6.97 (m, 2H), 6.91 (d, J = 7.8 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.61, 152.64, 144.76, 142.57, 142.22, 142.00, 136.29, 130.30, 129.67, 129.53, 129.33, 129.05, 128.75, 127.98, 123.65, 122.93, 122.88, 120.50, 120.11, 118.79, 116.31, 111.55, 51.96. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{25}H_{19}N_2O_2^+$: 379.1441, found: 379.1438.

2-Chloro-11-phenyl-6*H*-indolo[2,3-*b*]quinoline (3h):



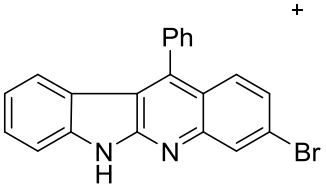
Yellow solid; mp: 265 - 267 ℃, 42.7 mg, 65% yield. ^{1}H NMR (600 MHz, DMSO) δ 11.96 (s, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.71 (m, 4H), 7.57 – 7.55 (m, 2H), 7.53 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.44 (m, 1H), 6.99 – 6.95 (m, 1H), 6.91 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO) δ 153.12, 145.17, 142.33, 141.04, 135.71, 129.87, 129.78, 129.50, 129.30, 128.91, 127.48, 124.51, 124.02, 122.94, 120.34, 120.04, 116.67, 111.57. HRMS(ESI-TOF): $[M+H]^+$ calculated for $C_{21}H_{14}ClN_2^+$: 329.0840, found: 329.0842.

2-Bromo-11-phenyl-6*H*-indolo[2,3-*b*]quinoline (3i):



Yellow solid, 52.3 mg, 70% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.96 (s, 1H), 8.01 (d, J = 9.0 Hz, 1H), 7.83 (dd, J = 9.0, 2.2 Hz, 1H), 7.76 – 7.71 (m, 3H), 7.69 (s, 1H), 7.59 – 7.56 (m, 2H), 7.48 (dt, J = 14.9, 7.4 Hz, 2H), 6.99 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.16, 145.39, 142.35, 141.02, 135.71, 131.85, 130.10, 129.83, 129.55, 129.53, 128.96, 127.78, 124.70, 122.96, 120.38, 120.10, 116.64, 115.74, 111.60. HRMS(ESI-TOF): $[M+H]^+$ calculated for $C_{21}H_{14}BrN_2^+$: 373.0335, found: 373.0333. The values of the NMR spectra are in accordance with reported literature data.[3]

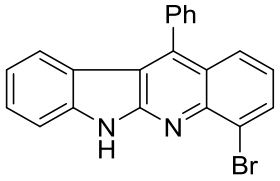
3-Bromo-11-phenyl-6*H*-indolo[2,3-*b*]quinoline (3j):



Yellow solid; mp: 258-260 ℃, 33.6 mg, 45% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.02 (s, 1H), 8.29–8.23 (m, 1H), 7.76–7.69 (m, 3H), 7.60–7.54 (m, 4H), 7.53–7.44 (m, 2H), 7.03–6.97 (m, 1H), 6.92 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.43, 147.49, 142.19, 142.16, 135.86, 129.73, 129.53, 129.43, 128.80, 128.23, 126.35, 122.85, 122.50, 122.21, 120.50, 120.15, 116.37, 111.59. HRMS(ESI-TOF):

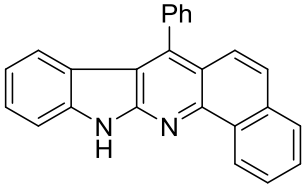
$[M+H]^+$ calculated for $C_{21}H_{14}BrN_2^+$: 373.0335, found: 373.0341.

4-Bromo-11-phenyl-6*H*-indolo[2,3-*b*]quinoline (3k):



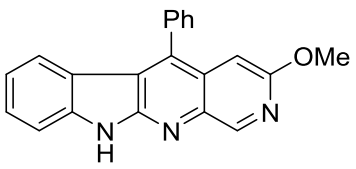
Yellow solid; mp: 266 - 268 ℃, 32.1 mg, 43% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.97 (s, 1H), 7.98 (d, J = 9.0 Hz, 1H), 7.78 (dd, J = 9.0, 2.2 Hz, 1H), 7.73 - 7.66 (m, 4H), 7.57 - 7.53 (m, 2H), 7.50 (d, J = 7.9 Hz, 1H), 7.45 (t, J = 7.9 Hz, 1H), 6.96 (t, J = 7.3 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.12, 145.35, 142.33, 140.95, 135.71, 131.77, 130.02, 129.77, 129.51, 129.49, 128.89, 127.75, 124.66, 122.95, 120.37, 120.05, 116.61, 115.73, 111.58. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{21}H_{14}BrN_2^+$: 373.0335, found: 373.0333.

7-Phenyl-12*H*-benzo[*h*]indolo[2,3-*b*]quinoline (3l):



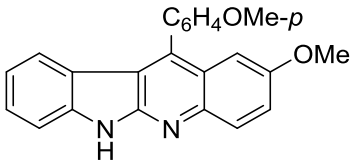
Yellow solid; mp: 289 - 292 ℃, 53.7 mg, 78% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.11 (s, 1H), 9.32 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 6.3 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.62 – 7.53 (m, 5H), 7.52 – 7.44 (m, 4H), 7.36 (dt, J = 8.1, 4.2 Hz, 1H), 6.89 (d, J = 3.4 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 151.90, 144.57, 142.48, 141.43, 136.80, 133.42, 131.14, 129.65, 129.63, 129.62, 129.17, 128.41, 128.18, 127.98, 126.90, 124.80, 123.98, 123.83, 122.52, 120.75, 119.89, 115.24, 111.67. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{25}H_{17}N_2^+$: 345.1386, found: 345.1382.

3-Methoxy-5-phenyl-10*H*-indolo[2,3-*b*][1,7]naphthyridine (3m):



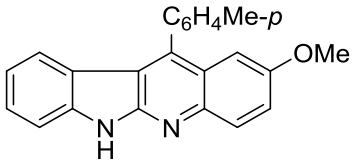
Yellow solid; mp: 266 - 268 ℃, 50.1 mg, 77% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.87 (s, 1H), 8.28 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 7.5 Hz, 2H), 7.62 (t, J = 7.3 Hz, 2H), 7.6 - 7.56 (m, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.26 (d, J = 7.9 Hz, 1H), 7.21 (d, J = 9.0 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.42, 151.50, 142.29, 140.36, 139.78, 139.11, 135.84, 135.27, 130.51, 128.68, 128.60, 128.52, 123.11, 120.44, 119.61, 117.63, 115.38, 111.55, 53.20. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{21}H_{16}N_3O^+$: 326.1288, found: 326.1280.

2-Methoxy-11-(4-methoxyphenyl)-6*H*-indolo[2,3-*b*]quinoline (3n):



Yellow solid; mp: 246 - 248 ℃, 50.0 mg, 72% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.68 (s, 1H), 7.97 (d, J = 9.1 Hz, 1H), 7.48 (m, 3H), 7.44 - 7.40 (m, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.04 - 6.99 (m, 2H), 6.96 (t, J = 7.5 Hz, 1H), 3.92 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.84, 155.15, 151.87, 142.76, 142.06, 140.63, 130.90, 129.20, 128.41, 128.22, 124.18, 122.82, 121.05, 120.67, 119.51, 116.24, 115.06, 111.23, 104.58, 55.67, 55.57. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{23}H_{19}N_2O_2^+$: 355.1441, found: 355.1439.

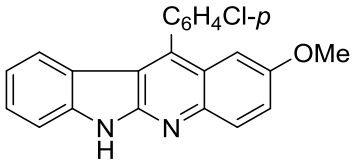
2-Methoxy-11-(*p*-tolyl)-6*H*-indolo[2,3-*b*]quinoline (3o):



Yellow solid; mp: 286 - 288 ℃, 50.1 mg, 74% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.70 (s, 1H), 7.98 (d, J = 9.2 Hz, 1H), 7.51 (d, J = 7.6 Hz, 2H), 7.49 - 7.39 (m, 5H), 7.00 - 6.92 (m, 3H), 3.68 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.17, 151.86, 142.74, 142.08, 140.79, 138.42, 133.57, 130.28, 129.43, 129.22, 128.25, 123.96, 122.80, 121.08, 120.60, 119.49, 116.03, 111.25, 104.55, 55.58, 21.55.

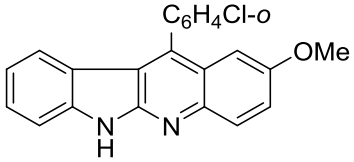
HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{23}H_{19}N_2O^+$: 339.1492, found: 339.1499.

11-(4-Chlorophenyl)-2-methoxy-6*H*-indolo[2,3-*b*]quinoline (3p):



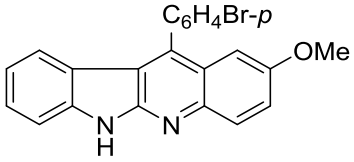
Yellow solid; mp: 260 - 262 ℃, 52.4 mg, 73% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.73 (s, 1H), 7.99 (d, J = 9.2 Hz, 1H), 7.79 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H), 7.47 (s, 1H), 7.45 (s, 2H), 7.00 (t, J = 6.9 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.90 (d, J = 2.8 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.36, 151.75, 142.70, 142.17, 139.22, 135.46, 133.99, 131.62, 129.90, 129.34, 128.48, 123.61, 122.69, 121.30, 120.30, 119.71, 115.94, 111.39, 104.20, 55.65. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{22}H_{16}ClN_2^+O$: 359.0946, found: 359.0947.

11-(2-Chlorophenyl)-2-methoxy-6*H*-indolo[2,3-*b*]quinoline (3q):



Yellow solid; mp: 270 - 272 ℃, 62.4 mg, 87% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.76 (s, 1H), 7.98 (d, J = 9.1 Hz, 1H), 7.76 (d, J = 7.3 Hz, 2H), 7.60 (d, J = 7.2 Hz, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.46 - 7.39 (m, 2H), 6.97 (q, J = 7.7 Hz, 2H), 6.90 (s, 1H), 3.69 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.33, 151.76, 142.70, 142.19, 139.17, 135.46, 134.00, 131.58, 129.85, 129.28, 128.42, 123.60, 122.693, 121.22, 120.31, 119.66, 115.94, 111.37, 104.18, 55.58. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{22}H_{16}ClN_2O^+$: 359.0946, found: 359.0947.

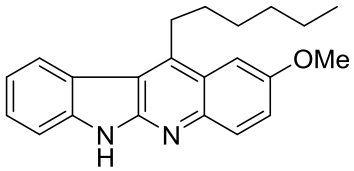
11-(4-Bromophenyl)-2-methoxy-6*H*-indolo[2,3-*b*]quinoline (3r):



Yellow solid; mp: 268 - 268 ℃, 54.0 mg, 67% yield. ^{1}H NMR (600 MHz, DMSO-d_6)

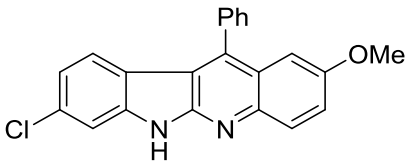
δ 11.77 (s, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.45 - 7.39 (m, 2H), 7.00 - 6.97 (m, 2H), 6.90 (s, 1H), 3.69 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.35, 151.77, 142.71, 142.21, 139.18, 135.86, 132.77, 131.88, 129.31, 128.44, 123.53, 122.69, 122.63, 121.25, 120.31, 119.67, 115.87, 111.40, 104.19, 55.62. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{22}H_{16}BrN_2O^+$: 403.0441, found: 403.0447.

11-Hexyl-2-methoxy-6*H*-indolo[2,3-b]quinoline (3s):



White solid; mp: 180 - 182 ℃, 39.9 mg, 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.07 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 9.1 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.46 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.32 – 7.27 (m, 1H), 4.01 (s, 3H), 3.66 – 3.55 (m, 2H), 1.92 (q, *J* = 7.9 Hz, 2H), 1.71 – 1.60 (m, 2H), 1.49 – 1.33 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.31, 152.15, 143.01, 142.20, 141.21, 128.61, 127.41, 123.94, 123.45, 121.35, 120.73, 119.92, 116.48, 110.80, 102.93, 55.62, 31.75, 30.00, 29.24, 29.11, 22.64, 14.11. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{22}H_{25}N_2O^+$: 333.1961, found: 333.1954.

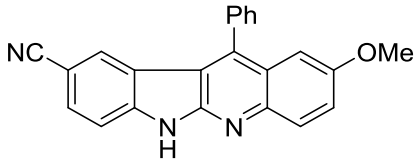
8-Chloro-2-methoxy-11-phenyl-6*H*-indolo[2,3-*b*]quinoline (3t):



Yellow solid; mp: 256 - 258 ℃, 62.4 mg, 87% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.85 (s, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.74 - 7.67 (m, 3H), 7.56 (d, *J* = 6.9 Hz, 2H), 7.48 - 7.43 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.46, 151.90, 142.89, 140.95, 136.25, 132.71, 129.82, 129.44, 129.39, 124.00, 123.85, 121.50, 119.72,

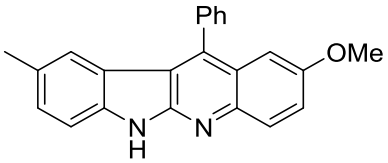
119.46, 115.26, 111.03, 104.44, 55.58. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{22}H_{16}ClN_2O^+$: 359.0946, found: 359.0956.

2-Methoxy-11-phenyl-6*H*-indolo[2,3-*b*]quinoline-9-carbonitrile (3u):



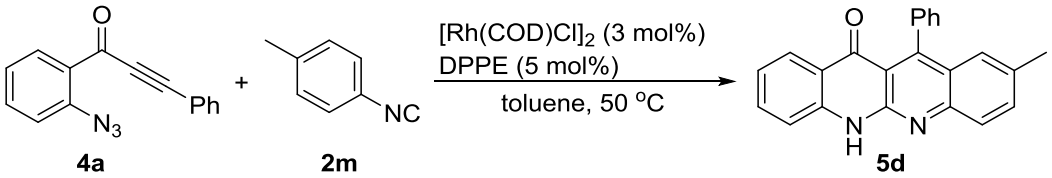
Yellow solid; mp: 269 - 271 ℃, 46.1 mg, 66% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.29 (s, 1H), 8.00 (d, J = 9.2 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 6.6 Hz, 3H), 7.58 (d, J = 5.8 Hz, 3H), 7.46 (dd, J = 9.2, 2.2 Hz, 1H), 7.05 (s, 1H), 6.94 (s, 1H), 3.68 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.71, 151.73, 144.54, 143.28, 141.88, 135.83, 131.49, 129.9, 129.65, 129.52, 129.34, 126.55, 124.10, 122.14, 120.88, 120.41, 114.66, 112.42, 104.34, 101.15, 55.59. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{23}H_{16}N_3O^+$: 350.1288, found: 350.1285.

2-Methoxy-9-methyl-11-phenyl-6*H*-indolo[2,3-*b*]quinoline (3v):



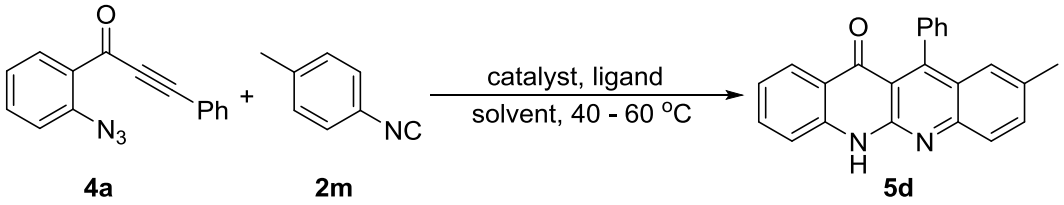
Yellow solid, 36.5 mg, 54% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.60 (s, 1H), 7.97 (d, J = 9.1 Hz, 1H), 7.74 - 7,66 (m, 3H), 7.55 (d, J = 7.0 Hz, 2H), 7.41 (d, J = 9.1 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H), 6.93 (s, 1H), 6.68 (s, 1H), 3.67 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.11, 152.06, 142.66, 140.50, 140.22, 136.65, 129.65, 129.52, 129.37, 129.18, 129.15, 127.96, 123.71, 122.85, 121.00, 120.61, 115.92, 111.02, 104.48, 55.53, 21.58. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{23}H_{19}N_2O^+$: 339.1492, found: 339.1494. The values of the NMR spectra are in accordance with reported literature data.[4]

III. General Procedure for the Preparation of 5 (5d as example):



A sealed tube equipped with a magnetic stir bar was charged with $[Rh(COD)Cl]_2$ (0.006 mmol, 3.0 mg) and DPPE (0.01 mmol, 4.0 mg) in toluene (2.0 mL), then **4a** (0.2 mmol, 49.5 mg) and **2m** (0.2 mmol, 23.4 mg) were added. Subsequently, the reaction mixture was stirred at 50 °C for 6 h. After the reaction was complete, the reaction mixture was poured into saturated aqueous NaCl (30 mL) and extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were dried over anhydrous Mg_2SO_4. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:10, V/V) to afford pure product **5d** (47.1 mg, 70%) as a yellow solid.

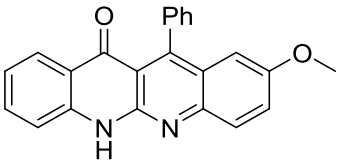
Table 1. Optimization of Reaction Conditions[a]



Entry	Catalyst (mol%)	Ligand (mol%)	T (°C)	Solvent	Yield[b] (%)
1	$[Rh(COD)Cl]_2$ (3.0)	DPPE (5.0)	50	toluene	70[c]
2	$Pd(acac)_2$ (3.0)	DPPE (5.0)	50	toluene	30
3	Ag_2CO_3 (3.0)	DPPE (5.0)	50	toluene	0
4	$[Rh(COD)Cl]_2$ (3.0)	DPPE (0.0)	50	toluene	60
5	$[Rh(COD)Cl]_2$ (3.0)	DPPE (5.0)	30	toluene	43
6	$[Rh(COD)Cl]_2$ (3.0)	DPPE (5.0)	60	toluene	55
7	$[Rh(COD)Cl]_2$ (3.0)	DPPE (5.0)	50	PhCl	52
8	$[Rh(COD)Cl]_2$ (3.0)	DPPE (5.0)	50	DCM	0
9	$[Rh(COD)Cl]_2$ (3.0)	DPPE (5.0)	50	DMF	0

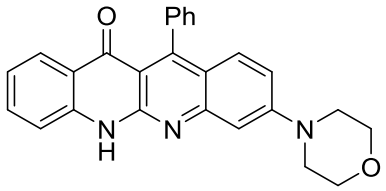
[a] Reaction conditions: **4a** (0.2 mmol), **2m** (0.2 mmol), catalyst (0.006 mmol), ligand (0.01 mmol), solvent (2.0 mL), at 30-60 ℃ for 6 h in a sealed tube. $[Rh(COD)Cl]_2$ = Chloro(1,5-cyclooctadiene)-rhodium(I)dimer, DPPE = 1,2-Bis(diphenylphosphino)ethane. [b] Estimated by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard. [c] Isolated yield.

2-Methoxy-12-phenyldibenzo[*b*,*g*][1,8]naphthyridin-11(6*H*)-one (5a):



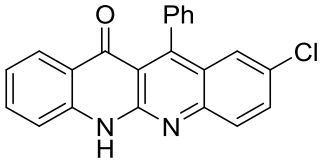
Yellow solid; mp: 217 - 219 ℃, 47.9 mg, 68% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.53 (s, 1H), 8.26 (s, 1H), 7.89 (d, J = 8.9 Hz, 1H), 7.64 - 7.54 (m, 4H), 7.47 (s, 1H), 7.37 (s, 2H), 7.20 (s, 1H), 7.15 (s, 1H), 6.76 (s, 1H), 3.69 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.68, 156.07, 152.69, 149.23, 145.60, 140.69, 138.47, 134.36, 128.32, 127.83, 127.81, 127.74, 127.67, 126.35, 126.20, 121.66, 121.42, 116.00, 114.03, 105.26, 55.33. HRMS (ESI-TOF): $[M+Na]^+$ calculated for $C_{23}H_{16}N_2NaO_2^+$: 375.1104, found: 375.1098.

3-Morpholino-12-phenyldibenzo[*b*,*g*][1,8]naphthyridin-11(6*H*)-one (5b):



Yellow solid; mp: 194 - 196 ℃, 55.4 mg, 68% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.79 (s, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.54 (d, J = 8.3 Hz, 1H), 7.52 - 7.44 (m, 3H), 7.20 - 7.27 (m, 3H), 7.09 - 7.15 (m, 2H), 7.01 (d, J = 1.8 Hz, 1H), 3.75 - 3.83 (m, 4H),3.35 - 3.41 (m, 4H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 178.56, 153.97, 152.30, 151.86, 151.25, 141.57, 139.01, 134.34, 128.89, 128.54, 128.14, 127.37, 126.64, 121.31, 121.20, 119.17, 117.05, 116.63, 111.14, 105.33, 66.34, 47.56. HRMS (ESI-TOF): $[M+Na]^+$ calculated for $C_{26}H_{21}N_3NaO_2^+$: 430.1526, found: 430.1528.

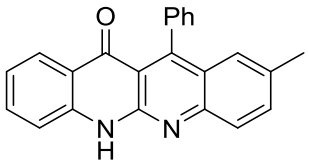
2-Chloro-12-phenyldibenzo[*b*,*g*][1,8]naphthyridin-11(6*H*)-one (5c):



Yellow solid, 45.7 mg, 64% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.21

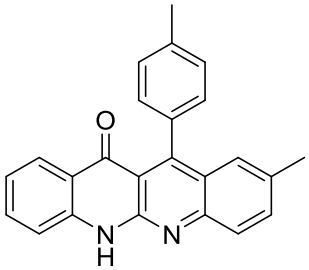
(d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.65 (dd, *J* = 9.0, 1.9 Hz, 1H), 7.59 (q, *J* = 8.4, 7.4 Hz, 4H), 7.46 (d, *J* = 2.1 Hz, 1H), 7.32 (d, *J* = 6.4 Hz, 2H), 7.20 - 7.13 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.48, 153.89, 150.46, 147.58, 140.44, 137.32, 134.72, 133.55, 130.05, 128.42, 128.06, 127.98, 127.87, 127.79, 126.98, 126.16, 121.99, 121.70, 116.05, 114.37. HRMS (ESI-TOF): $[M+Na]^+$ calculated for $C_{22}H_{13}ClN_2NaO^+$: 379.0609, found: 379.0598. The values of the NMR spectra are in accordance with reported literature data.[5]

2-Methyl-12-phenyldibenzo[*b*,*g*][1,8]naphthyridin-11(6*H*)-one (5d):



Yellow solid, 47.1 mg, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.54 (s, 1H), 8.15 (dd, J = 8.0, 1.1 Hz, 1H), 7.79 (d, J = 8.6 Hz, 1H), 7.56 – 7.49 (m, 5H), 7.27 – 7.22 (m, 2H), 7.19 (s, 1H), 7.15 (d, J = 8.2 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.47, 154.50, 149.74, 146.86, 140.39, 138.02, 135.54, 134.52, 134.40, 128.23, 127.81, 127.76, 127.73, 127.09, 125.55, 125.40, 121.80, 121.71, 116.17, 114.01, 21.71. HRMS (ESI-TOF): $[M+Na]^+$ calculated for $C_{23}H_{16}N_2NaO^+$: 359.1155, found: 359.1145. The values of the NMR spectra are in accordance with reported literature data.[6]

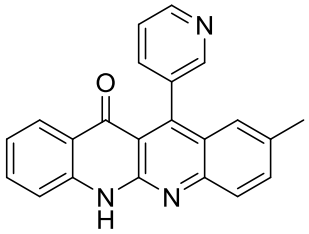
2-Methyl-12-(*p*-tolyl)dibenzo[*b*,*g*][1,8]naphthyridin-11(6*H*)-one (5e):



Yellow solid; mp: 228 - 230 ℃, 45.6 mg, 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.53 (s, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.32 (s, 1H), 7.22 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 2.54 (s, 3H),2.41 (s, 3H).

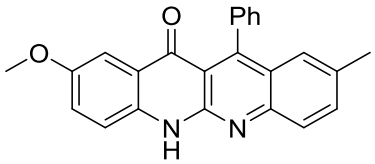
^{13}C NMR (151 MHz, $CDCl_3$) δ 179.85, 154.23, 150.17, 147.84, 140.68, 137.18, 135.19, 134.34, 134.05, 128.98, 127.88, 127.80, 127.09, 126.16, 125.77, 121.75, 121.47, 115.97, 114.16, 21.70, 21.63. HRMS (ESI-TOF): $[M+Na]^+$ calculated for $C_{24}H_{18}N_2NaO^+$: 373.1311, found: 373.1302.

2-Methyl-12-(pyridin-3-yl)dibenzo[*b,g*][1,8]naphthyridin-11(6*H*)-one (5f):



Yellow solid; mp: 182 - 184 ℃, 42.5 mg, 63% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.09 (s, 1H), 8.71 (d, J = 2.9 Hz, 1H), 8.47 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.6 Hz, 1H), 7.70 – 7.75 (m, 3H), 7.58 (d, J = 8.1 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H), 7.05 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 179.36, 150.02, 148.78, 148.62, 148.50, 148.41, 141.83, 136.23, 135.52, 135.02, 134.70, 134.38, 127.04, 126.77, 125.69, 124.71, 123.43, 121.50, 120.85, 117.23, 113.89, 21.72. HRMS (ESI-TOF): $[M+Na]^+$ calculated for $C_{22}H_{15}N_3NaO^+$: 360.1107, found: 360.1116.

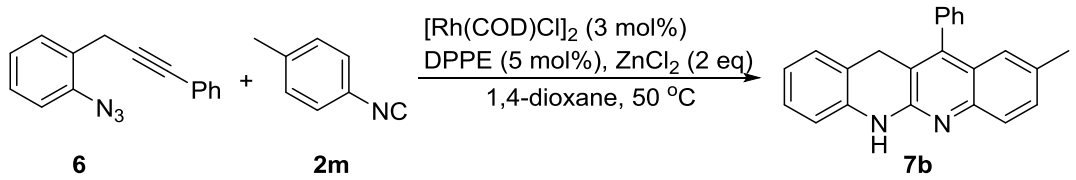
9-Methoxy-2-methyl-12-phenyldibenzo[*b,g*][1,8]naphthyridin-11(6*H*)-one (5g):



Yellow solid; mp: 215 - 217 ℃, 53.5 mg, 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.85 (d, J = 8.7 Hz, 1H), 7.68 (d, J = 2.8 Hz, 1H), 7.54 - 7.65 (m, 4H), 7.30 - 7.38 (m, 2H), 7.26 (s, 1H), 7.24 (dd, J = 8.9, 2.9 Hz, 1H), 7.17 (d, J = 8.9 Hz, 1H), 3.79 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.35, 154.71, 153.80, 149.65, 147.96, 138.47, 135.27, 135.25, 133.93, 128.18, 127.82, 127.57, 126.91, 126.06, 125.42, 125.36, 122.04, 117.65, 113.28, 106.84, 55.71, 21.70. HRMS

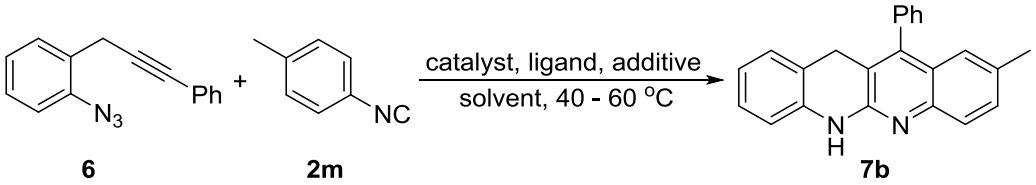
(ESI-TOF): $[M+Na]^+$ calculated for $C_{24}H_{18}N_2NaO_2^+$: 389.1260, found: 389.1262.

IV. General Procedure for the Preparation of 7 (7b as example):



A sealed tube equipped with a magnetic stir bar was charged with $[Rh(COD)Cl]_2$ (0.006 mmol, 3.0 mg), DPPE (0.01 mmol, 4.0 mg) and $ZnCl_2$ (0.4 mmol, 54.5 mg) in 1,4-dioxane (2.0 mL), then **6** (0.2 mmol, 46.7 mg) and **2m** (0.2 mmol, 23.4 mg) were added. Subsequently, the reaction mixture was stirred at 50 °C for 6 h. After the reaction was complete, the reaction mixture was poured into saturated aqueous NaCl (30 mL) and extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were dried over anhydrous Mg_2SO_4. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:10, V/V) to afford pure product **7b** (46.4 mg, 72%) as a yellow solid.

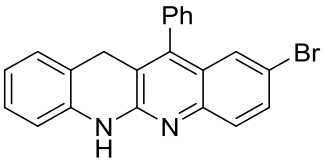
Table 2. Optimization of Reaction Conditions[a]



entry	catalysts (mol %)	ligand (mol %)	additive (eq)	t (°C)	solvent	yield[b] (%)
1	$[Rh(COD)Cl]_2$ (3)	DPPE (5)	----	50	1,4-dioxane	50
2	$[Rh(COD)Cl]_2$ (3)	DPPE (5)	$ZnCl_2$ (1 eq)	50	1,4-dioxane	60
3	$[Rh(COD)Cl]_2$ (3)	DPPE (5)	$ZnCl_2$ (2 eq)	50	1,4-dioxane	72[c]
4	$[Rh(COD)Cl]_2$ (3)	DPPE (5)	$ZnCl_2$ (3 eq)	50	toluene	52
5	$[Rh(COD)Cl]_2$ (3)	DPPE (5)	$ZnCl_2$ (2 eq)	50	CH_3CN	55
6	$[Rh(COD)Cl]_2$ (3)	DPPE (5)	$ZnCl_2$ (2 eq)	50	THF	42
7	$[Rh(COD)Cl]_2$ (3)	DPPE (5)	$ZnCl_2$ (2 eq)	50	1,4-dioxane	62
8	$[Rh(COD)Cl]_2$ (3)	DPPE (5)	BF_3▪Et_2O (2 eq)	50	1,4-dioxane	35
9	$[Rh(COD)Cl]_2$ (3)	2,2'-bpy (5)	$ZnCl_2$ (2 eq)	50	1,4-dioxane	25
10	$[Rh(COD)Cl]_2$ (3)	DPPE (5)	AgOTf (2 eq)	50	1,4-dioxane	48
11	$[Rh(COD)Cl]_2$ (3)	DPPE (5)	$Zn(OAc)_2$ (2 eq)	50	1,4-dioxane	50
12	$[Rh(COD)Cl]_2$ (3)	DPPE (5)	$ZnCl_2$ (2 eq)	40	1,4-dioxane	65
13	$[Rh(COD)Cl]_2$ (3)	DPPE (5)	$ZnCl_2$ (2 eq)	60	1,4-dioxane	68

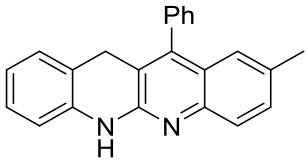
[a] Reaction conditions: **6** (0.2 mmol), **2m** (0.2 mmol), catalyst (0.006 mmol), ligand (0.01 mmol), addive (0.2-0.4 mmol), solvent (2.0 mL), at 40-60 ℃ for 6 h in a sealed tube. $[Rh(COD)Cl]_2$ = Chloro(1,5-cyclooctadiene)-rhodium(I)dimer, DPPE = 1,2-Bis(diphenylphosphino)ethane. [b] Estimated by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard. [c] Isolated yield.

9-Bromo-11-phenyl-5,12-dihydrodibenzo[*b,g*][1,8]naphthyridine(7a):



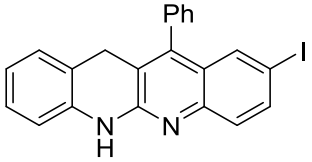
Yellow solid; mp: 198 - 200 ℃, 51.9 mg, 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.64 - 7.53 (m, 5H), 7.36 (s, 1H), 7.32 - 7.25 (m, 2H), 7.09 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 7.4 Hz, 1H), 6.86 (d, J = 7.4 Hz, 1H), 6.71 (s, 1H), 3.94 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.07, 146.36, 145.10, 138.16, 135.70, 132.46, 129.11, 128.89, 128.52, 128.46, 128.17, 127.91, 127.56, 126.90, 121.63, 119.39, 116.62, 116.37, 114.14, 30.13. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{22}H_{16}BrN_2^+$: 387.0491, found: 387.0481.

9-Methyl-11-phenyl-5,12-dihydrodibenzo[*b*,*g*][1,8]naphthyridine (7b)：



Yellow solid; mp: 190 - 192 ℃, 46.4 mg, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, J = 8.5 Hz, 1H), 7.61 (s, 1H), 7.58 (t, J = 7.3 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.36 (d, J = 8.5 Hz, 1H), 7.29 (d, J = 7.0 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 6.99 (s, 1H), 6.96 (d, J = 7.4 Hz, 1H), 6.83 (t, J = 7.4 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 3.91 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.13, 146.63, 144.72, 138.67, 136.65, 132.64, 131.24, 129.02, 128.85, 128.46, 128.02, 127.40, 126.02, 125.46, 125.10, 121.21, 119.61, 115.36, 113.95, 30.13, 21.47. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{23}H_{19}N_2^+$: 323.1543, found: 323.1549.

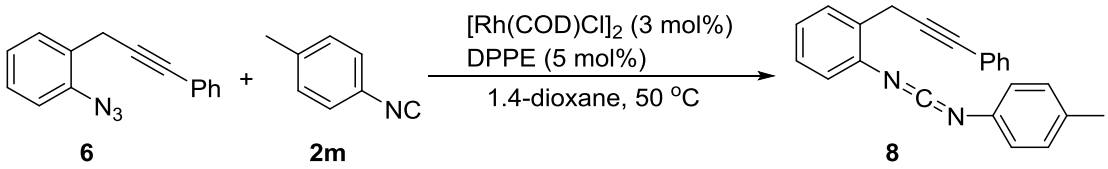
9-Iodo-11-phenyl-5,12-dihydrodibenzo[*b*,*g*][1,8]naphthyridine (7c):



Yellow solid; mp: 195 - 197 ℃, 60.8 mg, 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.75 (dd, J = 8.8, 1.6 Hz, 1H), 7.63 - 7.53 (m, 4H), 7.46 (d, J = 8.8 Hz, 1H), 7.27 (d, J = 7.1 Hz, 2H), 7.09 (s, 1H), 6.97 (d, J = 7.4 Hz, 1H), 6.86 (d, J = 7.4

Hz, 1H), 6.71 (d, J = 7.9 Hz, 1H), 3.92 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.03, 146.15, 145.52, 138.07, 137.85, 135.66, 134.63, 129.10, 128.89, 128.51, 128.45, 128.07, 127.56, 121.68, 119.38, 116.40, 114.13, 87.31, 30.10. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{22}H_{16}IN_2^+$: 435.0353, found: 435.0349.

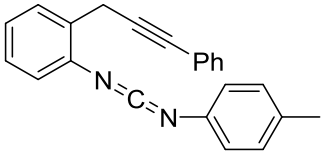
V. General Procedure for the Preparation of 8:



6 **2m** **8**

A sealed tube equipped with a magnetic stir bar was charged with $[Rh(COD)Cl]_2$ (0.006 mmol, 3.0 mg) and DPPE (0.01 mmol, 4.0 mg) in toluene (2.0 mL), then **6** (0.2 mmol, 46.7 mg) and **2m** (0.2 mmol, 23.4 mg) were added. Subsequently, the reaction mixture was stirred at 50 ^{o}C for 0.5 h. After the reaction was complete, the reaction mixture was poured into saturated aqueous NaCl (30 mL) and extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were dried over anhydrous Mg_2SO_4. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 3:50, V/V) to afford pure product **8** (35.5 mg, 55%) as a yellow liquid and pure product **7b** (6.4 mg, 10%) as yellow liquid.

***N*-(2-(3-Phenylprop-2-yn-1-yl)phenyl)-*N*-(*p*-tolyl)methanediimine (8):**



Yellow liquid, 35.5 mg, 55% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 7.5 Hz, 1H), 7.49 (dd, J = 6.7, 3.0 Hz, 2H), 7.33 (p, J = 3.4 Hz, 3H), 7.28 – 7.25 (m, 2H), 7.24 – 7.19 (m, 1H), 7.14 – 7.09 (m, 4H), 3.96 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.70, 135.53, 135.37, 134.78, 131.71, 130.92, 130.11, 129.40, 128.23, 127.92, 127.83, 125.72, 124.71, 123.97, 123.68, 87.04, 82.95, 22.30, 21.00. HRMS (ESI-TOF): $[M+H]^+$ calculated for $C_{23}H_{19}N_2^+$: 323.1543, found: 323.1541.

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1. (a) Lu, B.; Luo, Y.; Liu, L.; Ye, L.; Wang, Y.; Zhang, L. Umpolung Reactivity of Indole through Gold Catalysis. *Angew. Chem. Int. Ed.* **2011**, *50*, 8358-8362. (b) Liu, Q.; Chen, P.; Liu, G. Palladium-Catalyzed C–C Triple Bond Cleavage: Efficient Synthesis of 4*H*-Benzo[*d*][1,3]oxazin-4-ones. *ACS Catal.* **2013**, *3*, 178-181. (c) Su, H.; Bao, M.; Pei, C.; Hu, W.; Qiu, L.; Xu, X. Gold-catalyzed dual annulation of azide-tethered alkynes with nitriles: expeditious synthesis of oxazolo[4,5-*c*]quinolines. *Org. Chem. Front.* **2019**, *6*, 2404-2409. (d) Qiu, Y. F.; Niu, Y. J.; Wei, X.; Cao, B.-Q.; Wang, X. C.; Quan, Z.-J. $AgSCF_3/Na_2S_2O_8$-Promoted Trifluoromethylthiolation/Cyclization of *o*-Propargyl Arylazides/ *o*-Alkynyl Benzylazides: Synthesis of SCF_3-Substituted Quinolines and Isoquinolines. *J. Org. Chem.* **2019**, *84*, 4165-4178.

2. (a) Zhang, Z.; Huang, B. L.; Qiao, G. Y.; Zhu, L.; Xiao, F.; Chen, F.; Fu, B.; Zhang, Z. H. Tandem Coupling of Azide with Isonitrile and Boronic Acid: Facile Access to Functionalized Amidines. *Angew. Chem., Int. Ed.* **2017**, *56*, 4320-4323. (b) Hu, Z.; Yuan, H.; Men, Y.; Liu, Q.; Zhang, J.; Xu, X. Cross-Cycloaddition of Two Different Isocyanides: Chemoselective Heterodimerization and [3+2]-Cyclization of 1,4-Diazabutatriene. *Angew. Chem., Int. Ed.* **2016**, *55*, 7077-7080. (c) Liu, Y.; Chen, X. L.; Li, X. Y.; Zhu, S. S.; Li, S. J.; Song, Y.; Qu, L. B.; Yu, B. 4CzIPN-^{t}Bu-Catalyzed Proton-Coupled Electron Transfer for Photosynthesis of Phosphorylated *N*-Heteroaromatics. *J. Am. Chem. Soc.* **2021**, *143*, 964-972.

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4. Schmittel, M.; Steffen, J. P.; Rodrı´guez, D.; Engelen, B.; Neumann, E.; Cinar, M. E. Thermal C2-C6 Cyclization of Enyne-Carbodiimides: Experimental Evidence Contradicts a Diradical and Suggests a Carbene Intermediate. *J. Org. Chem.* **2008**, *73*, 3005-3016.

5. Manoj, M. and Prasad, K. J. R., Synthesis of novel phenyl substituted dibenzonaphthyridines. *J. Chem. Res.* **2009**, *12*, 720-725.

6. Manoj, M.; Prasad, K. J. R., Effect of Substituents in the Syntheses of Phenyl-Substituted Dibenzonaphthyridines. *J. Heterocycl. Chem.* **2013**, *50*, 1049-1063.

VI. ORTEP Drawing of Compound 3g and 7a:

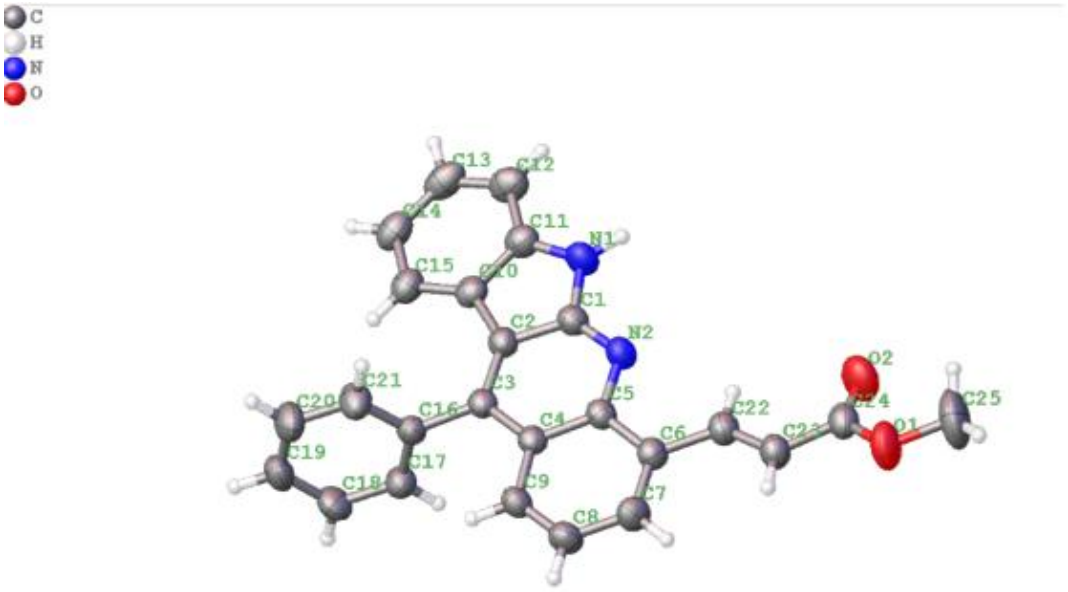

Figure 1. The ORTEP drawing of crystal 3g (The ellipsoid contour percent probability level is 50%).

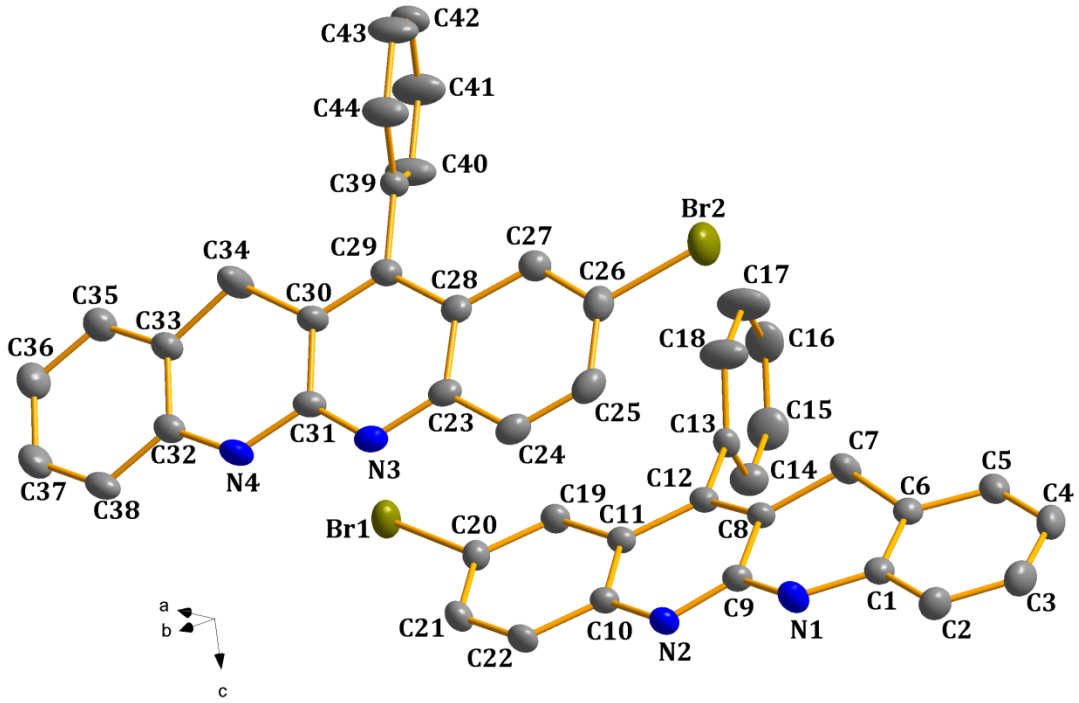

Figure 2. The ORTEP drawing of crystal 7a (The ellipsoid contour percent probability level is 50%).

Method of Crystallization: The **3g** and **7a** were recrystallized from mixed solvents of ethyl acetate and petroleum ether at 25 ˚C.

Introduction of crystal measuring instrument: X-ray single-crystal data of **3g** and **7a** were collected by a Bruker D8 Venture diffractometer (Mo Kα radiation, λ = 0.71073 Å (Cu Kα radiation, λ = 1.54178 Å)) at 293(2) K. The adsorption corrections were conducted by a multiscan technique. All the structures were solved via direct method and refined by the full-matrix least-squares technique using the SHELXL-2014 program. Anisotropic thermal parameters were used to refine the non-hydrogen atoms and hydrogen atoms were contained in calculated positions, refining with isotropic thermal parameters locating at those of the parent atoms.

VII. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of Compounds 3, 5, 7 and 8:

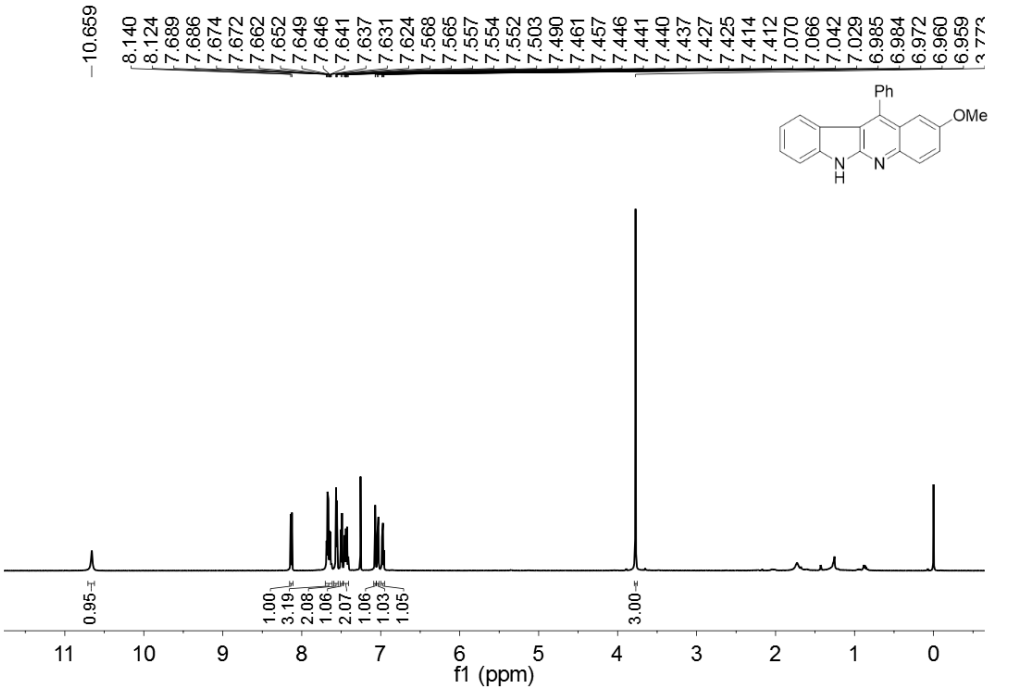

Figure 3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3a**

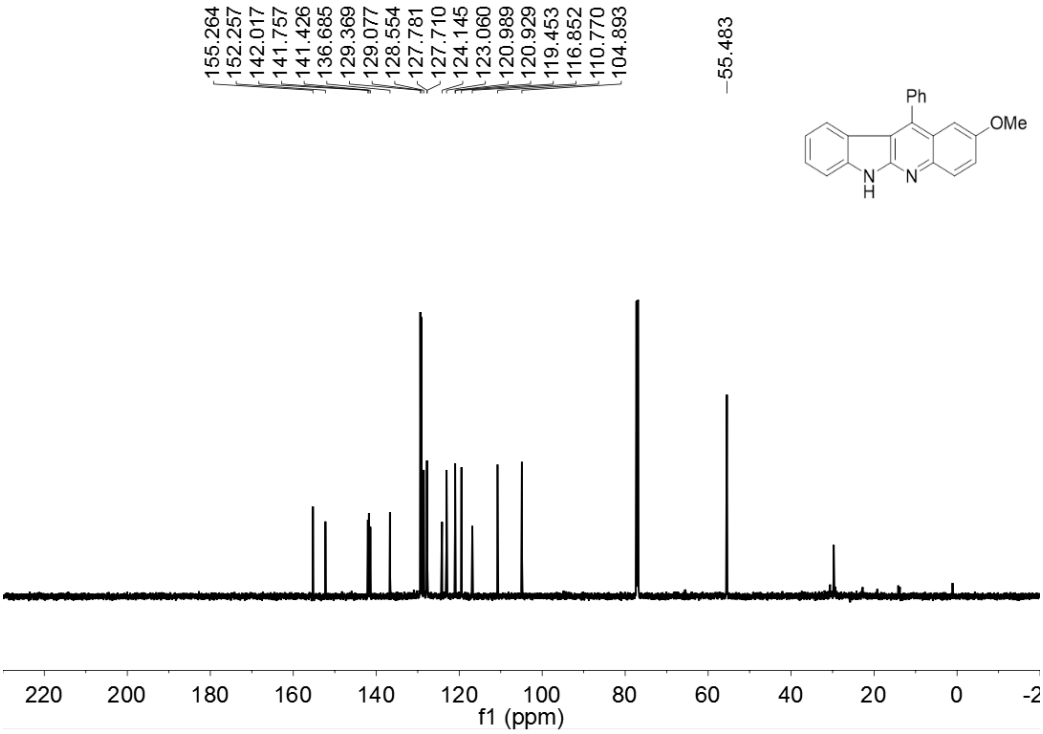

Figure 4. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3a**

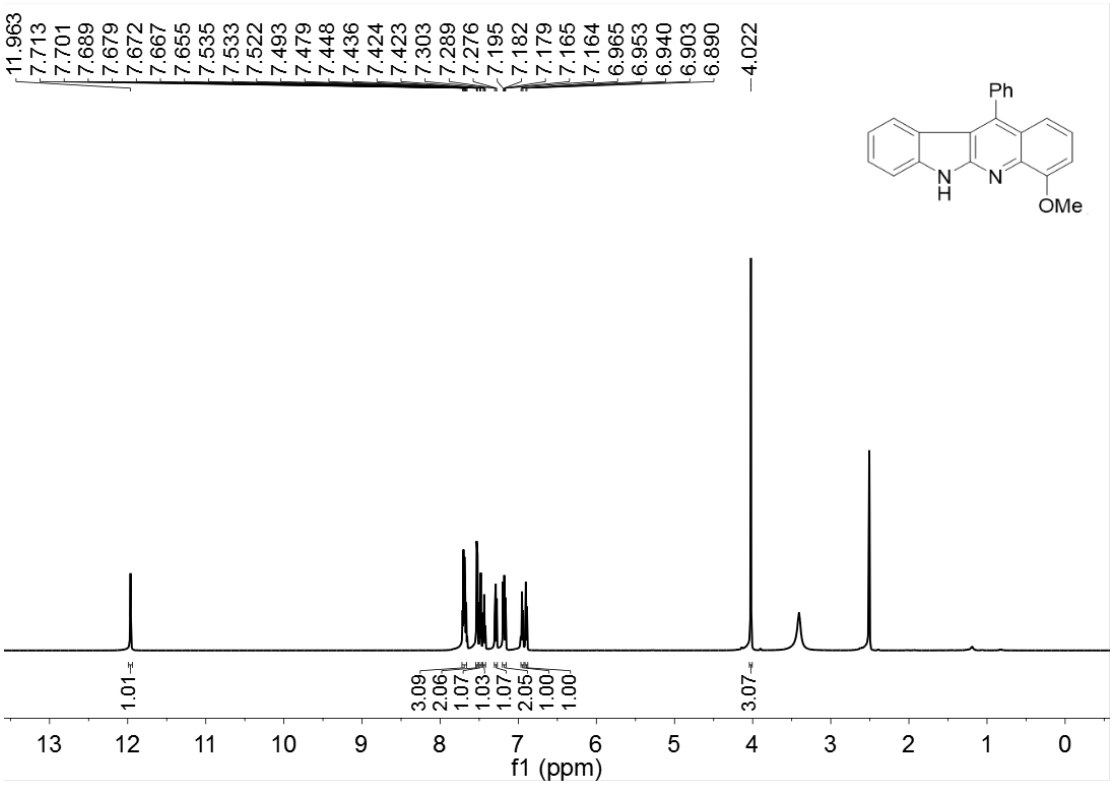

Figure 5. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3b**

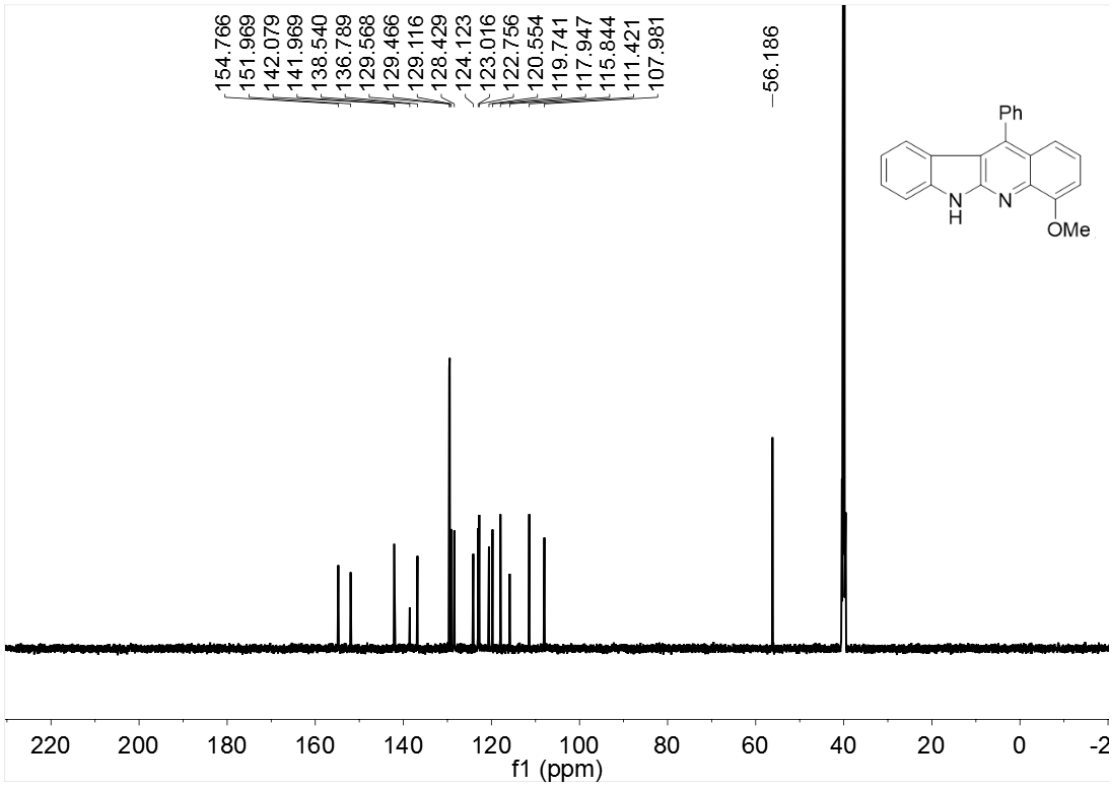

Figure 6. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3b**

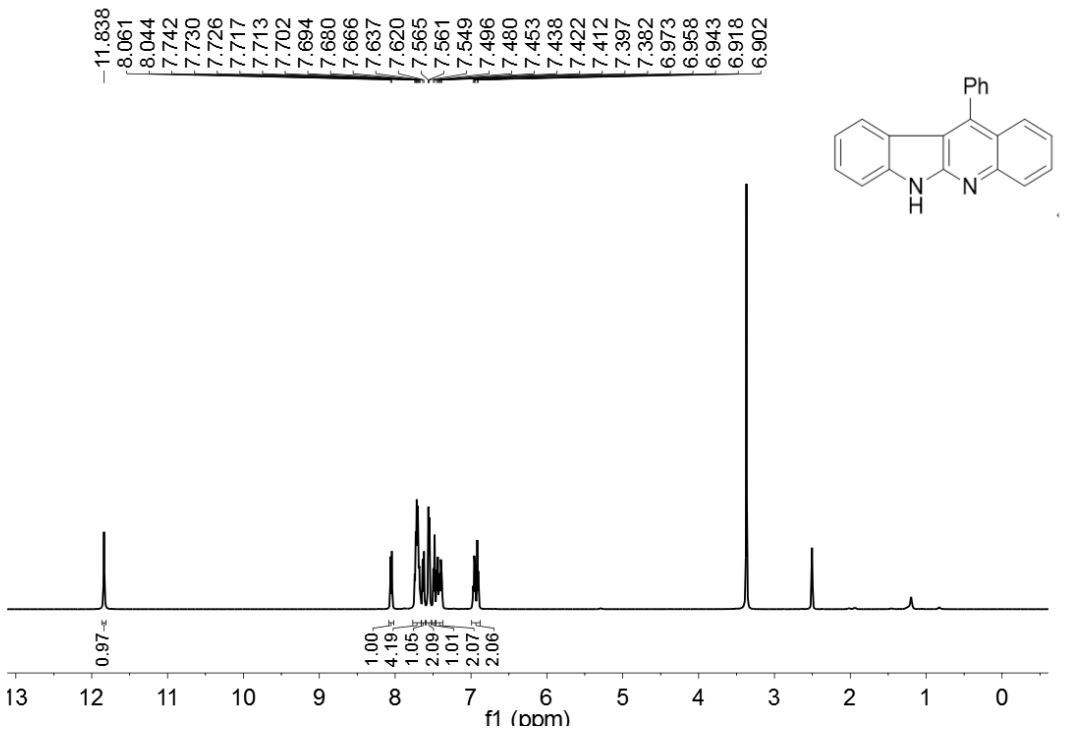

Figure 7. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of **3c**

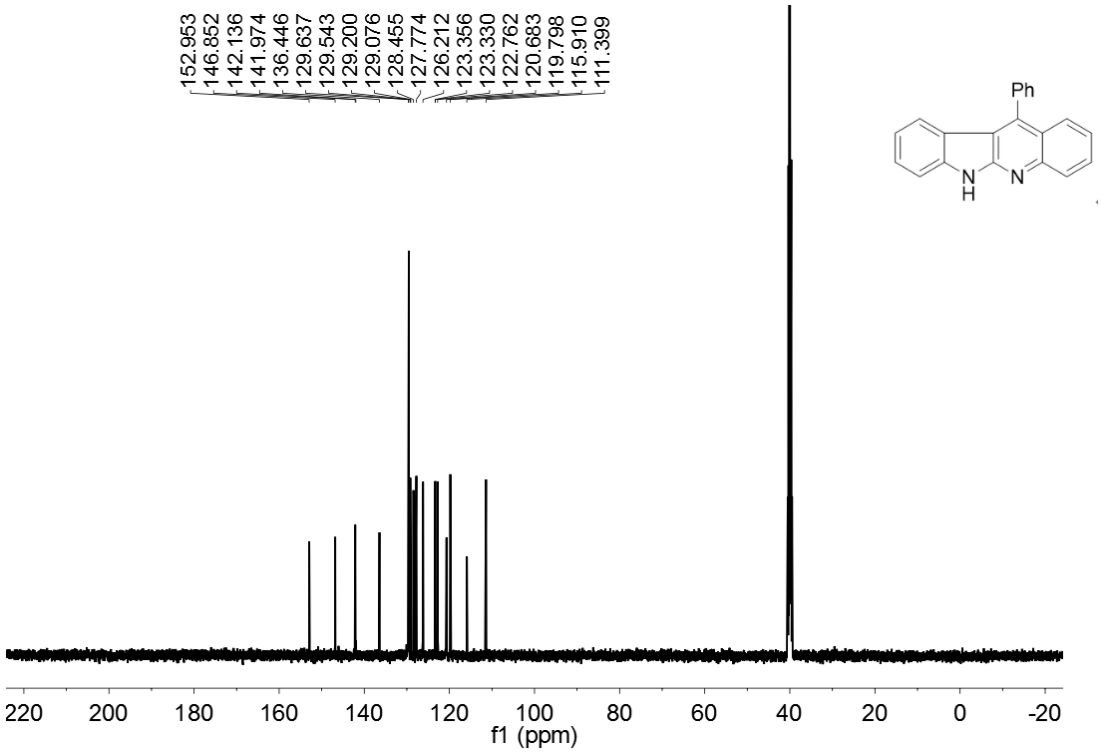

Figure 8. ^{13}C NMR spectrum (126 MHz, DMSO-d_6) of **3c**

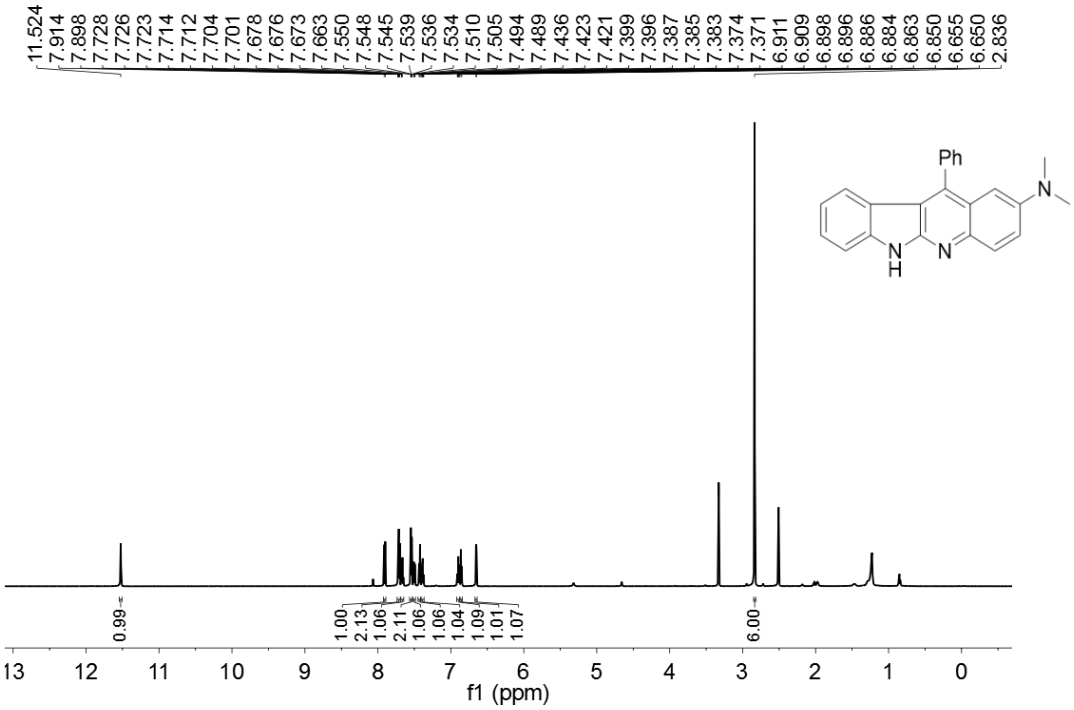

Figure 9. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3d**

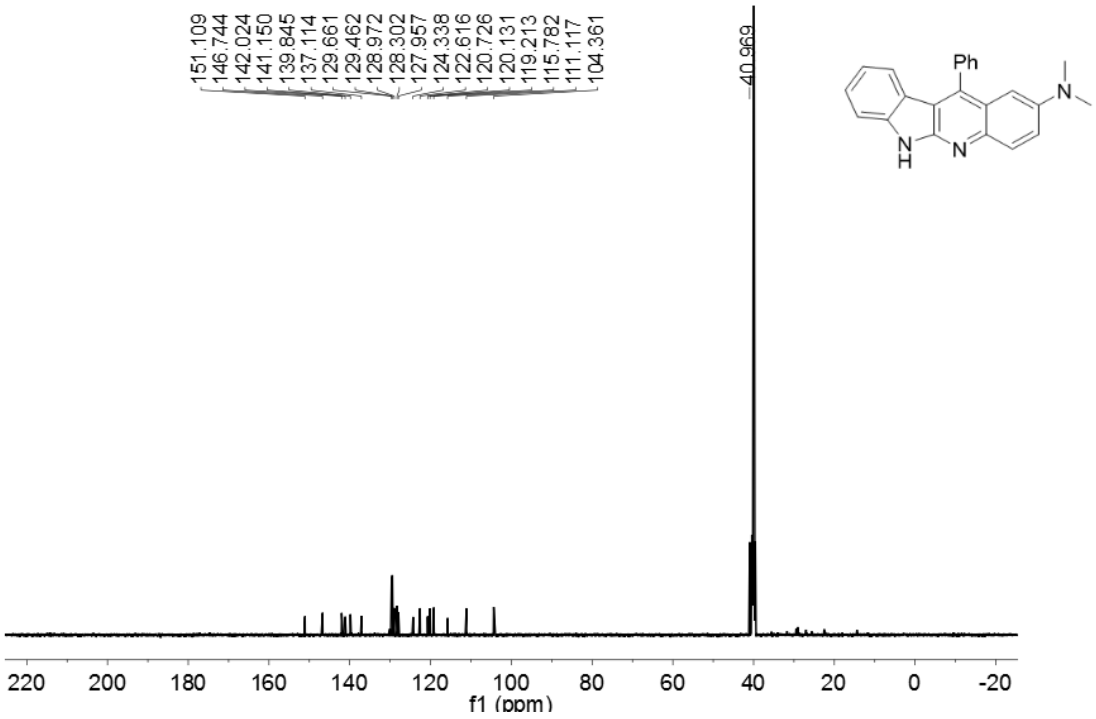

Figure 10. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3d**

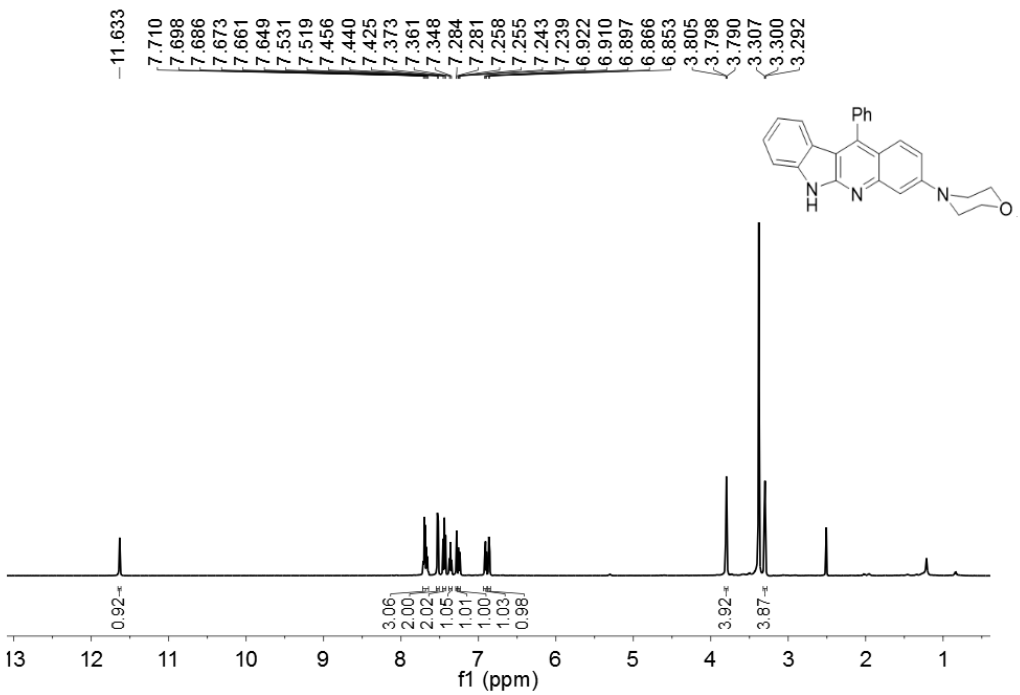

Figure 11. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3e**

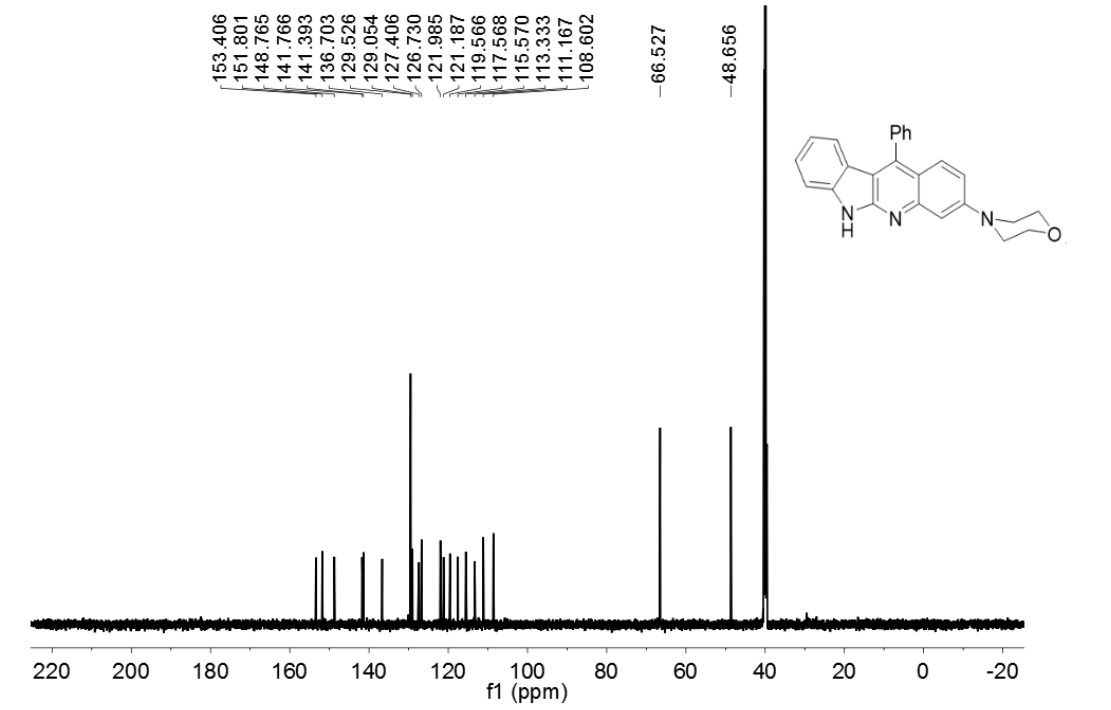

Figure 12. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3e**

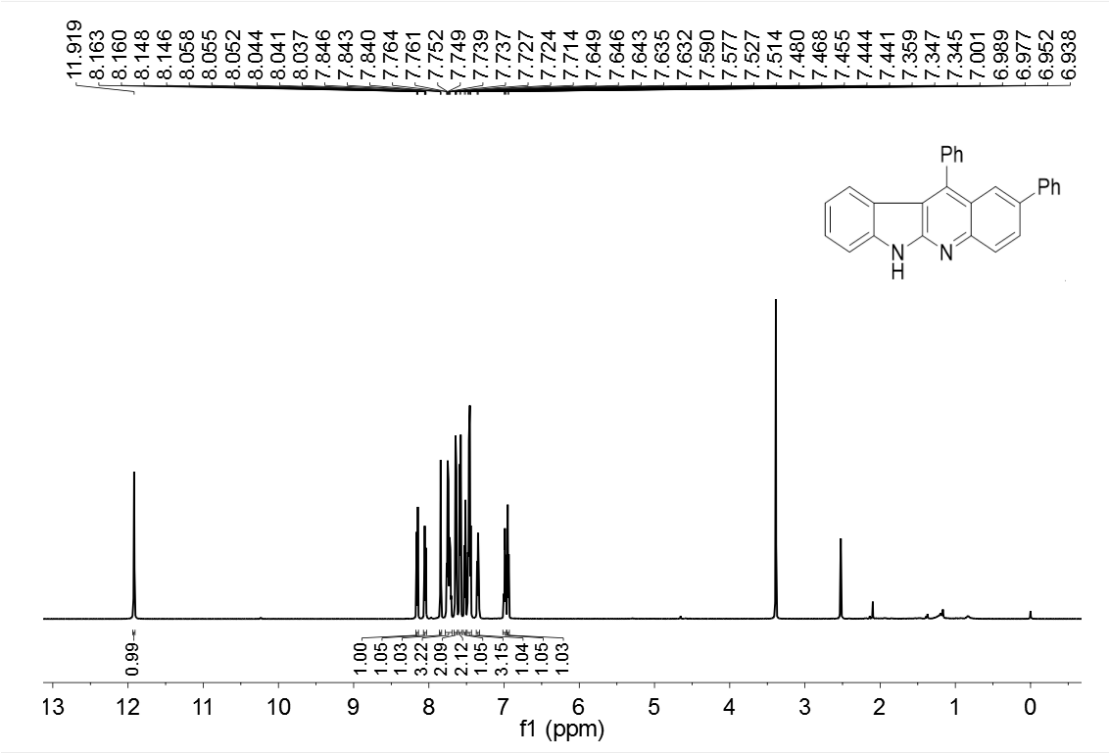

Figure 13. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3f**

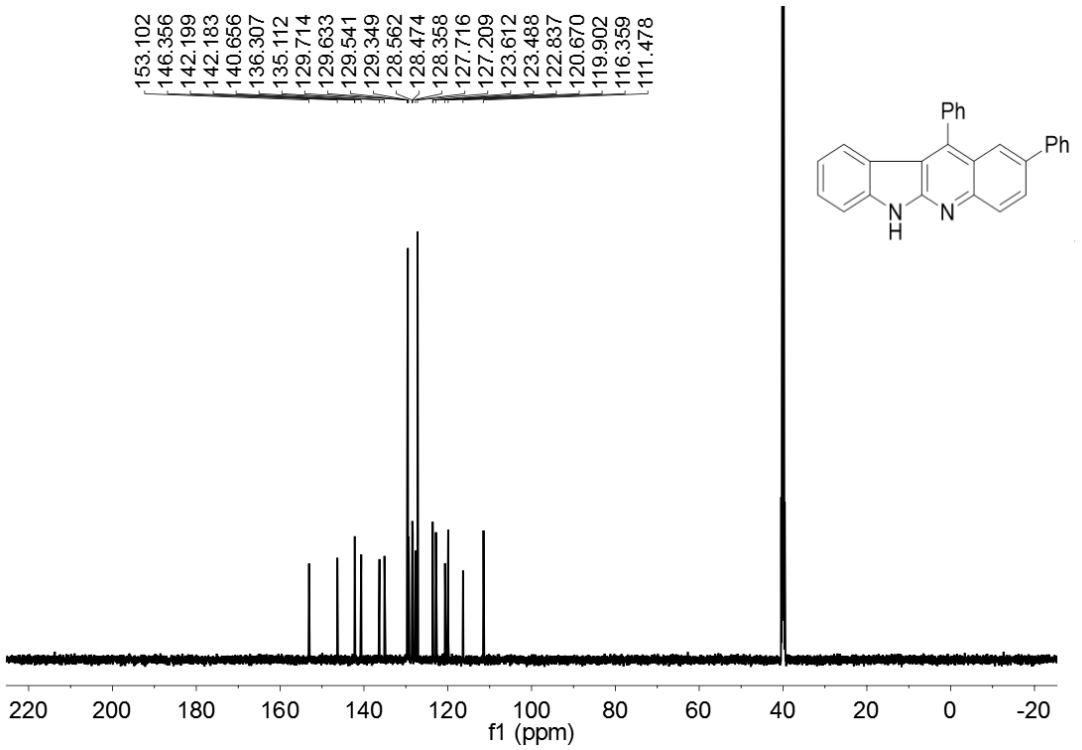

Figure 14. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3f**

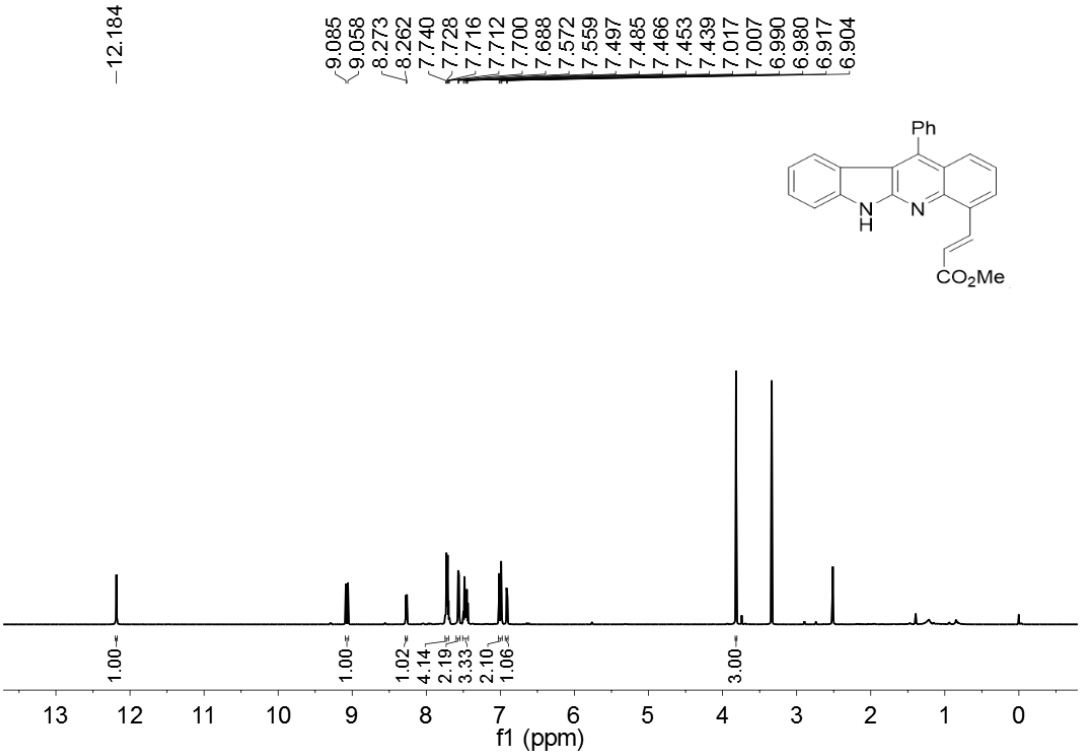

Figure 15. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3g**

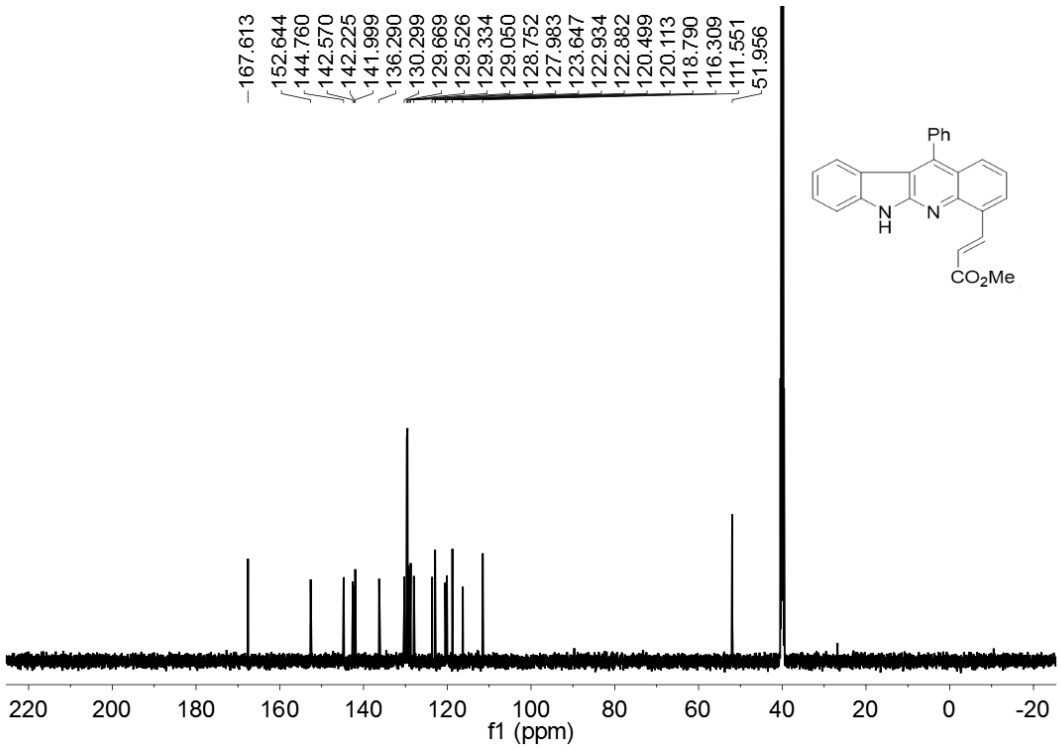

Figure 16. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3g**

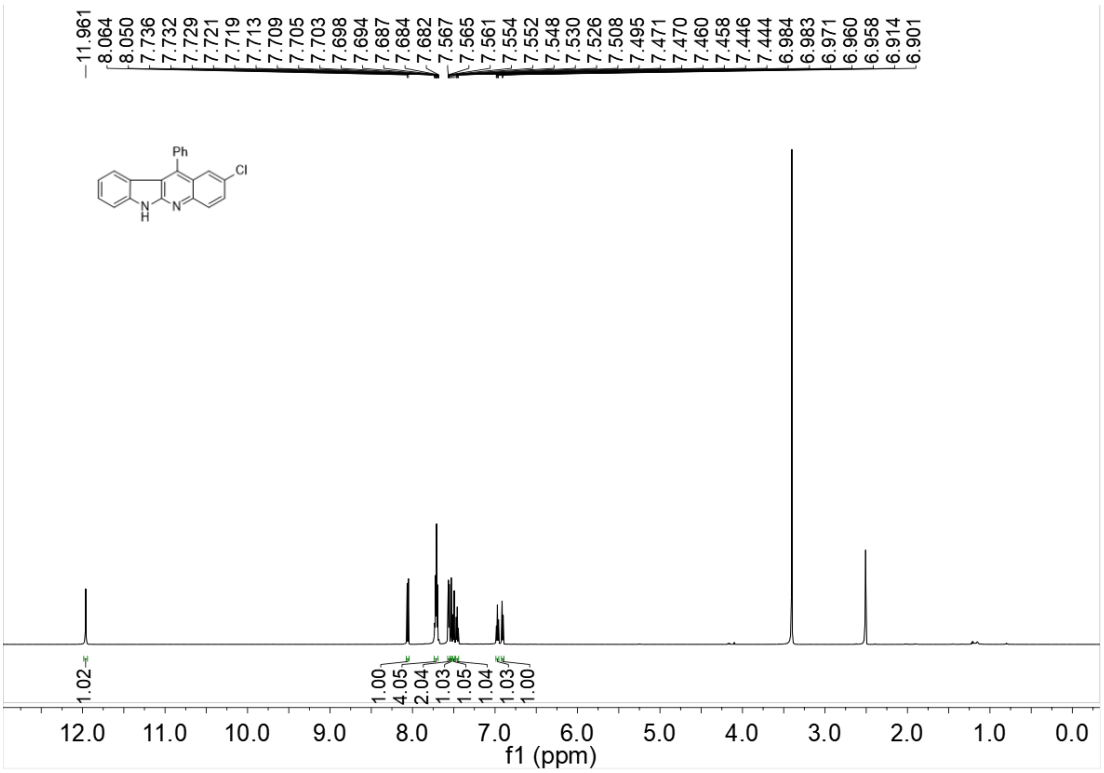

Figure 17. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3h**

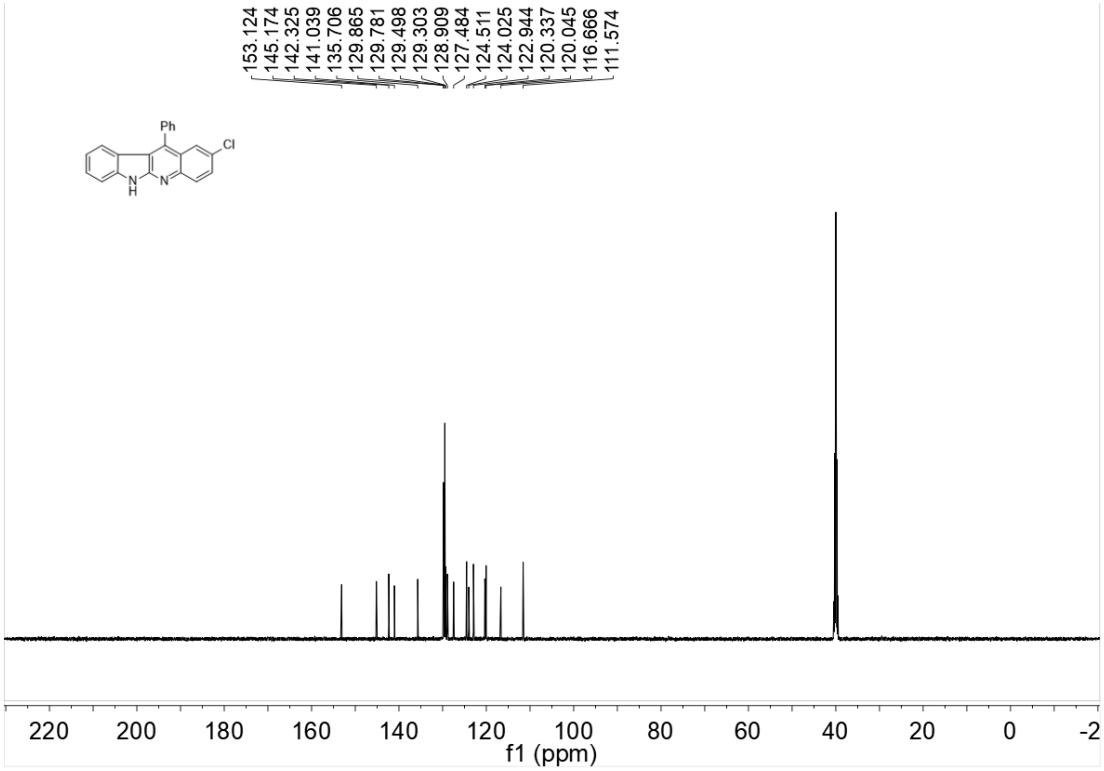

Figure 18. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3h**

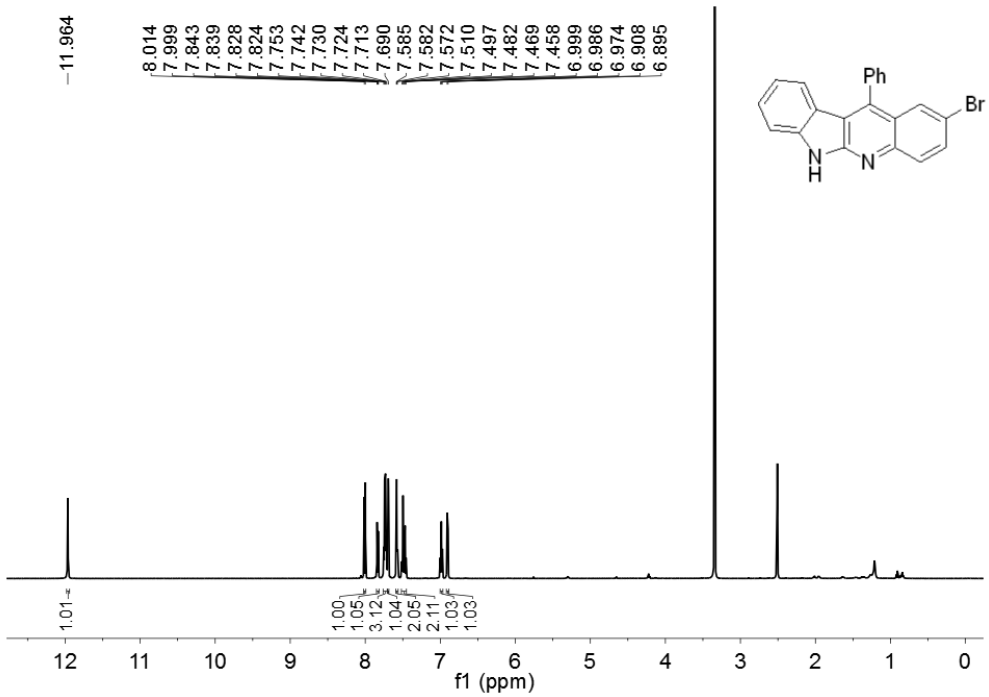

Figure 19. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3i**

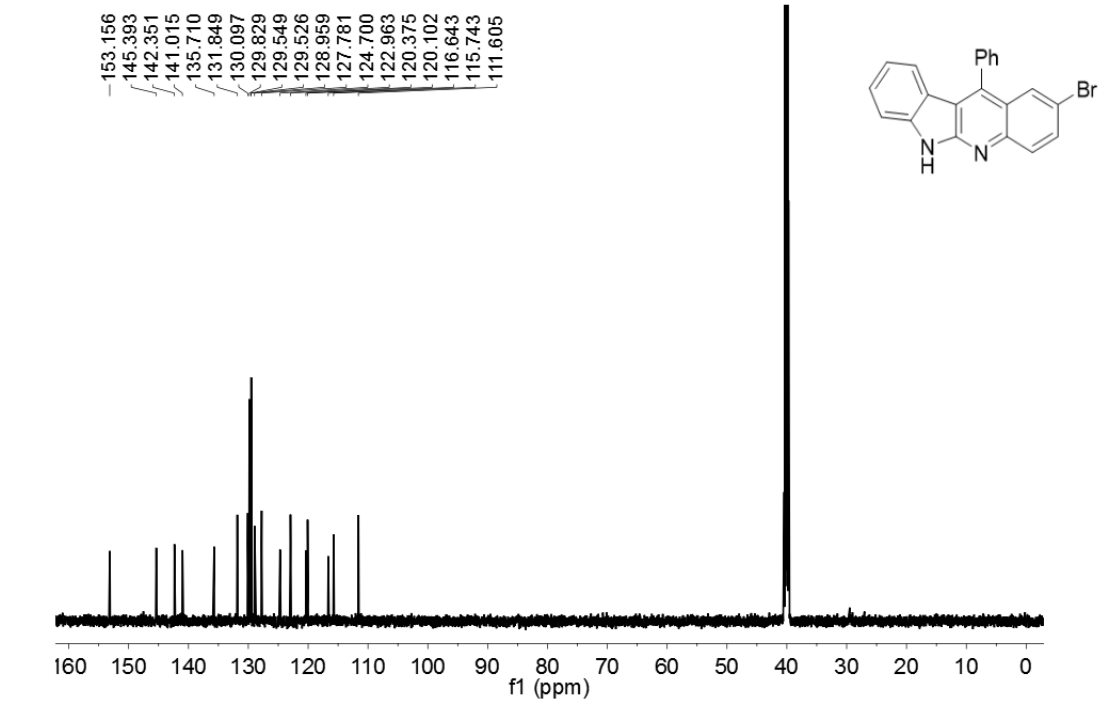

Figure 20. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3i**

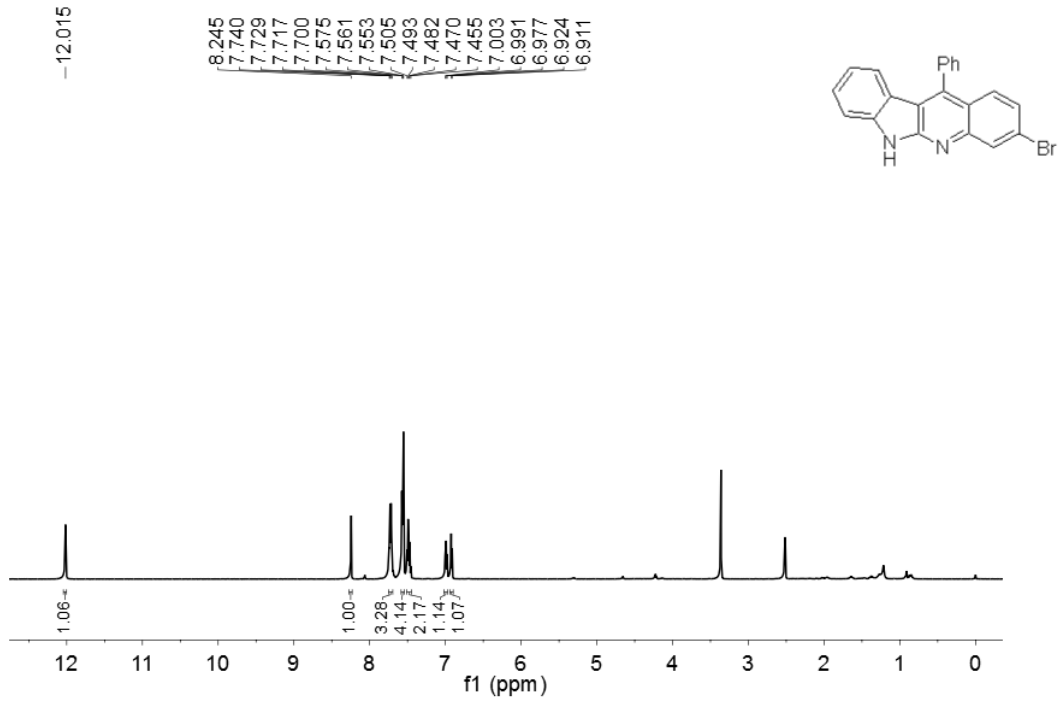

Figure 21. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3j**

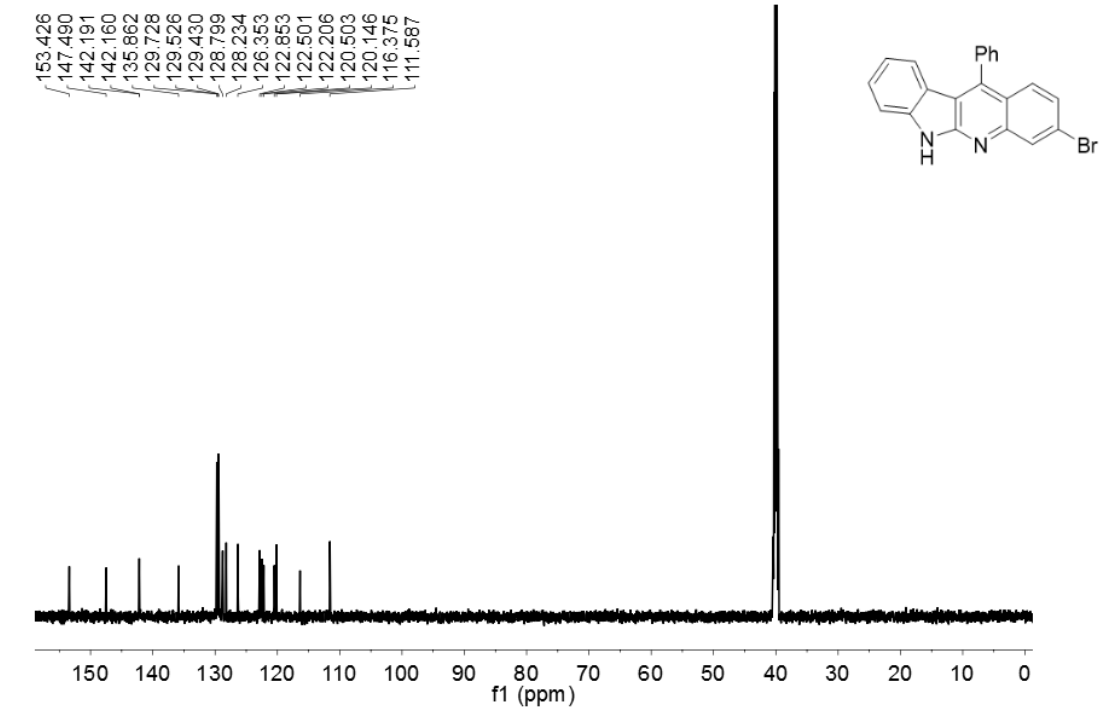

Figure 22. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3j**

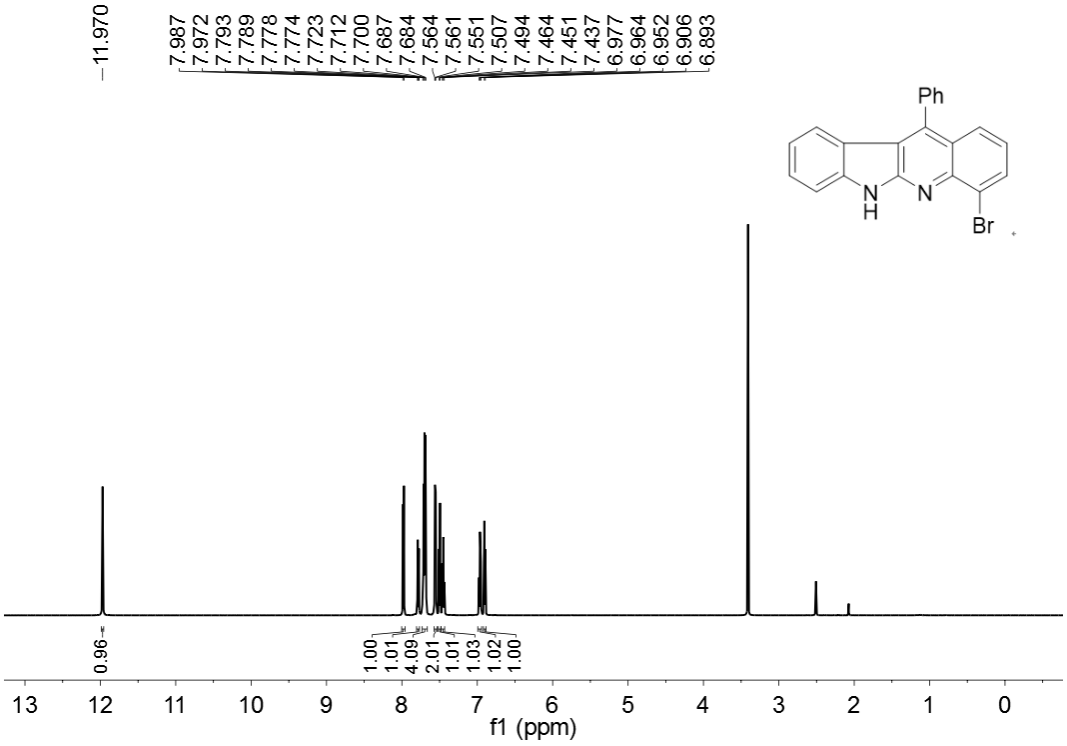

Figure 23. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3k**

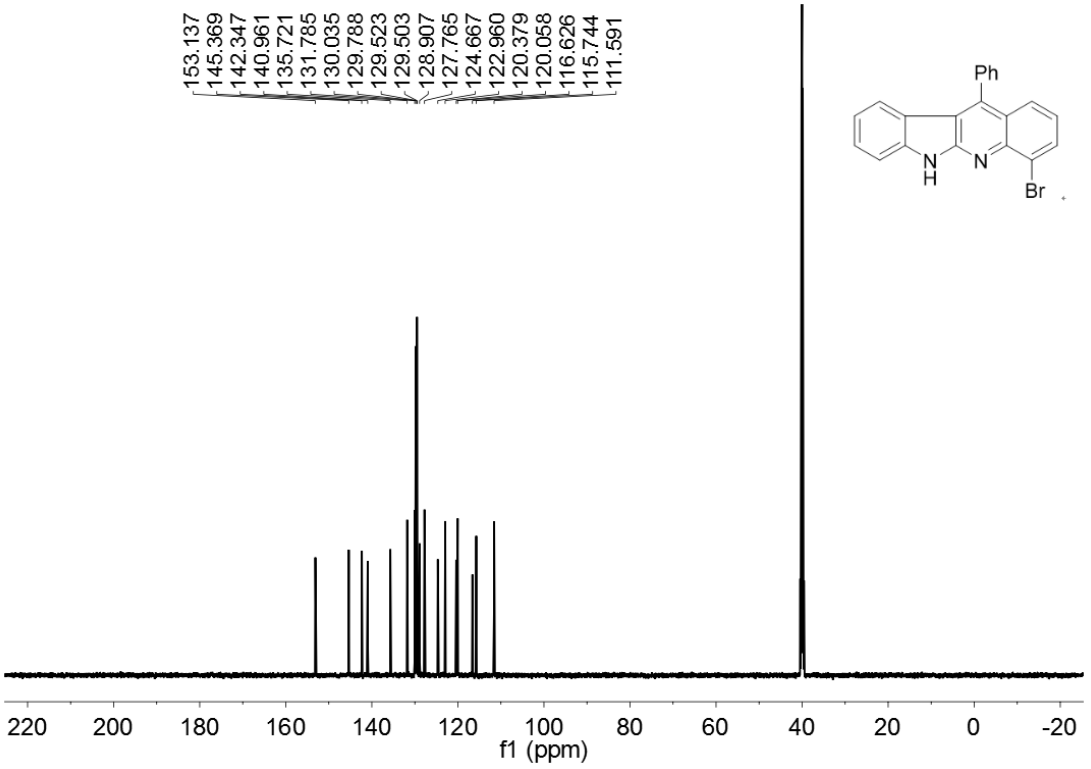

Figure 24. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3k**

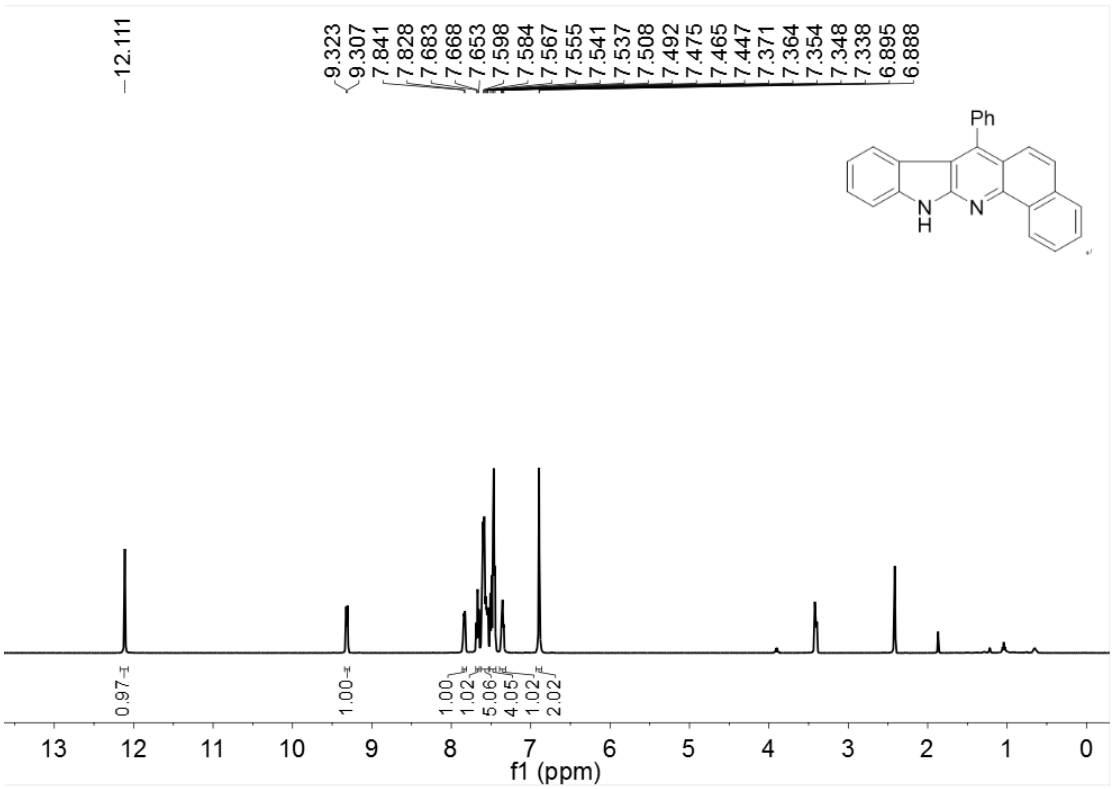

Figure 25. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3l**

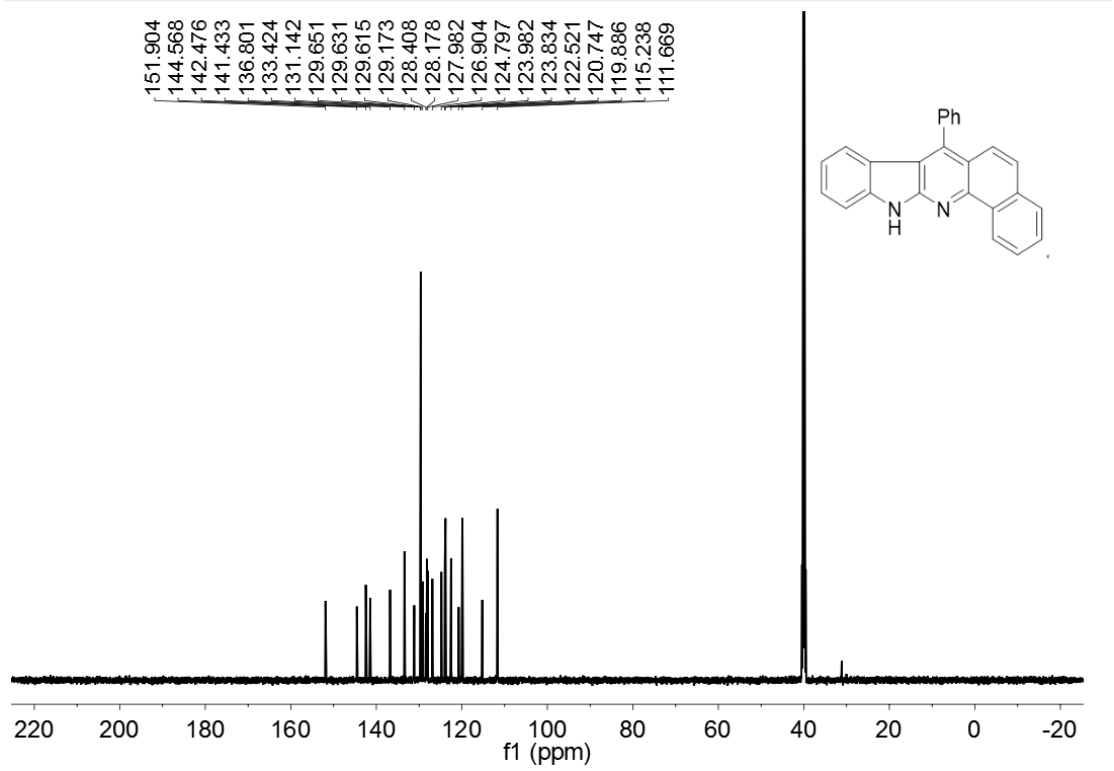

Figure 26. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3l**

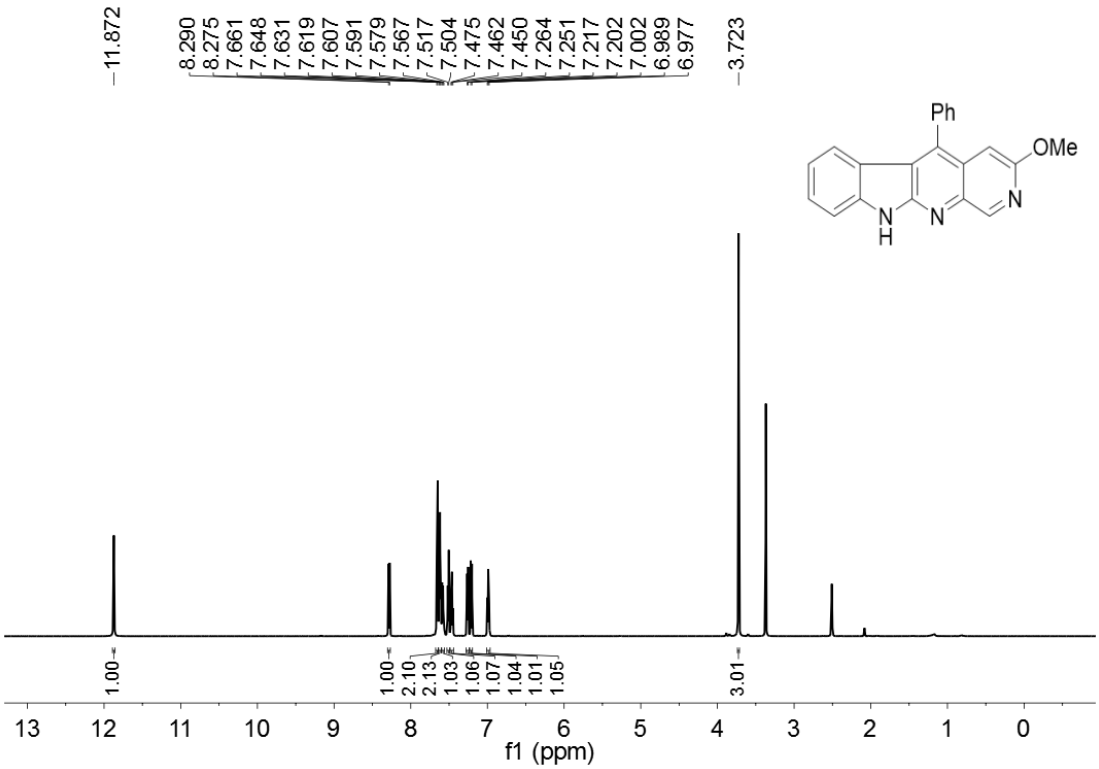

Figure 27. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3m**

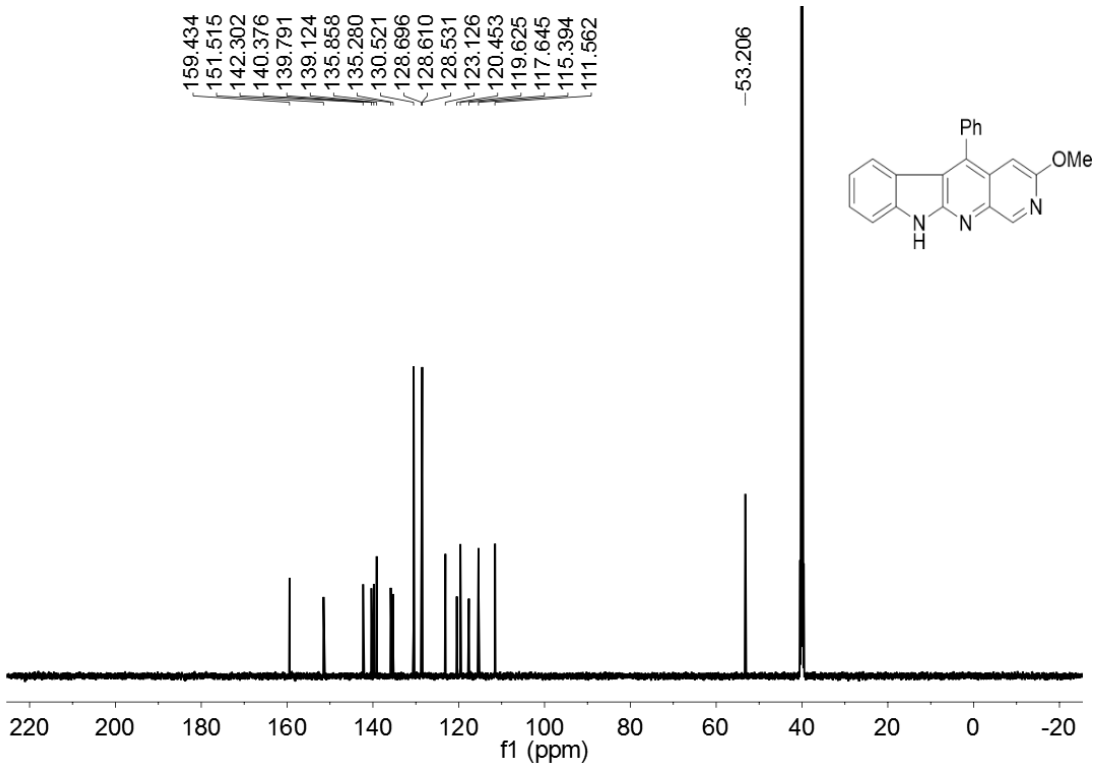

Figure 28. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3m**

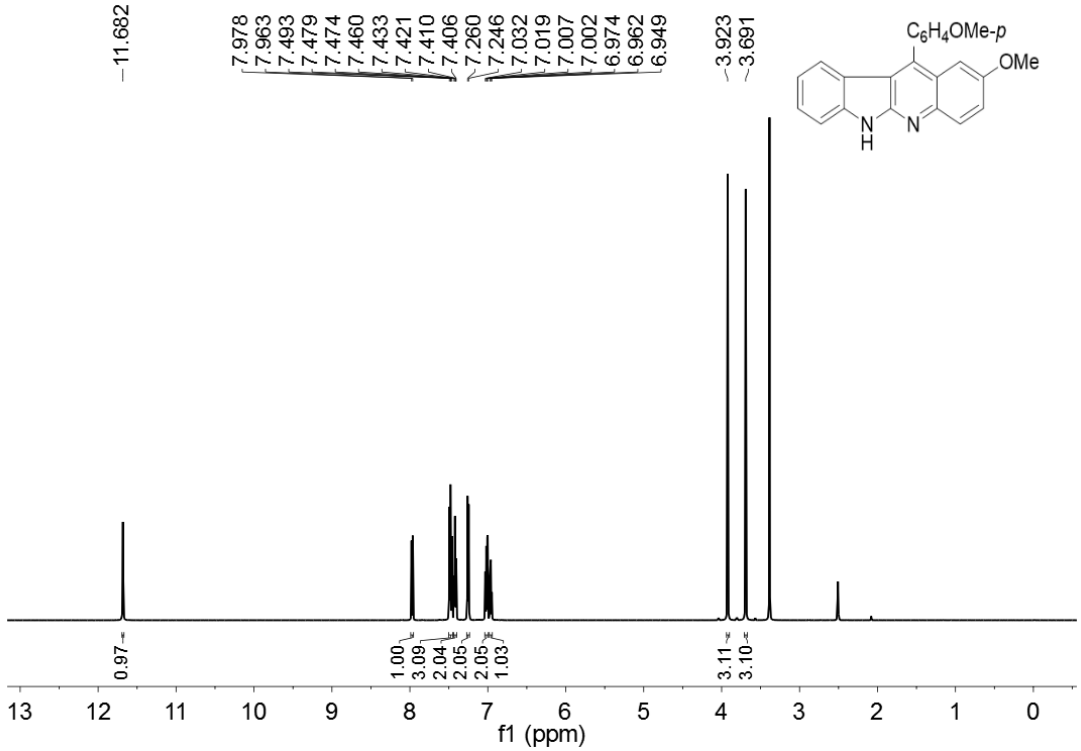

Figure 29. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3n**

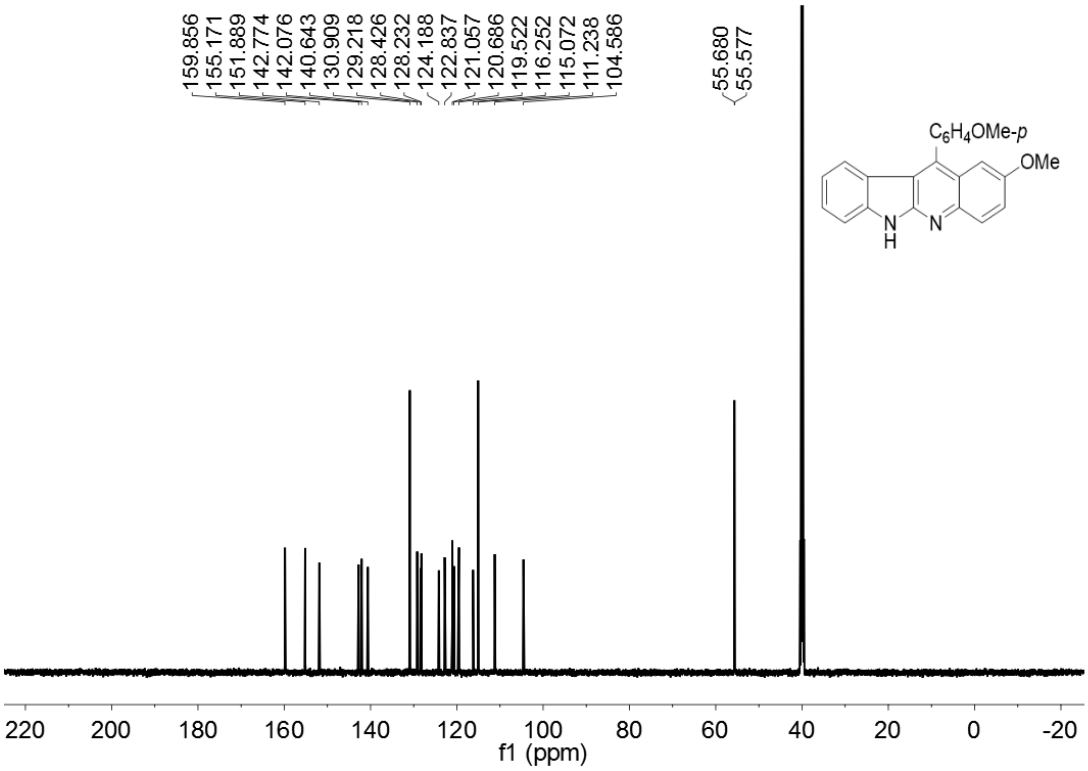

Figure 30. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3n**

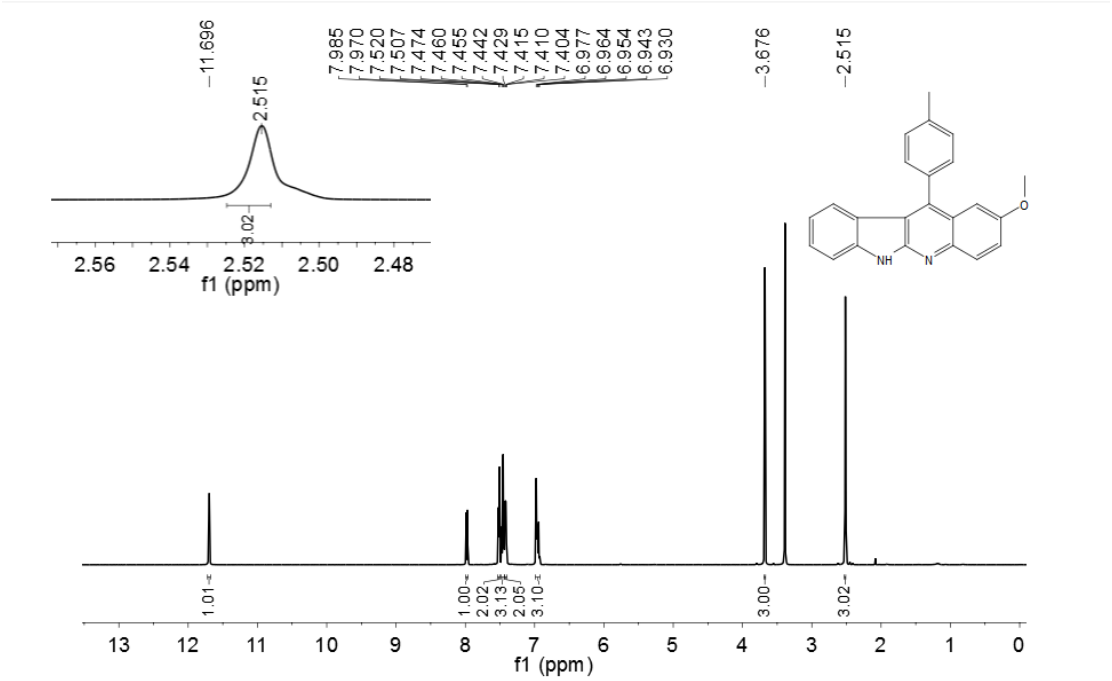

Figure 31. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3o**

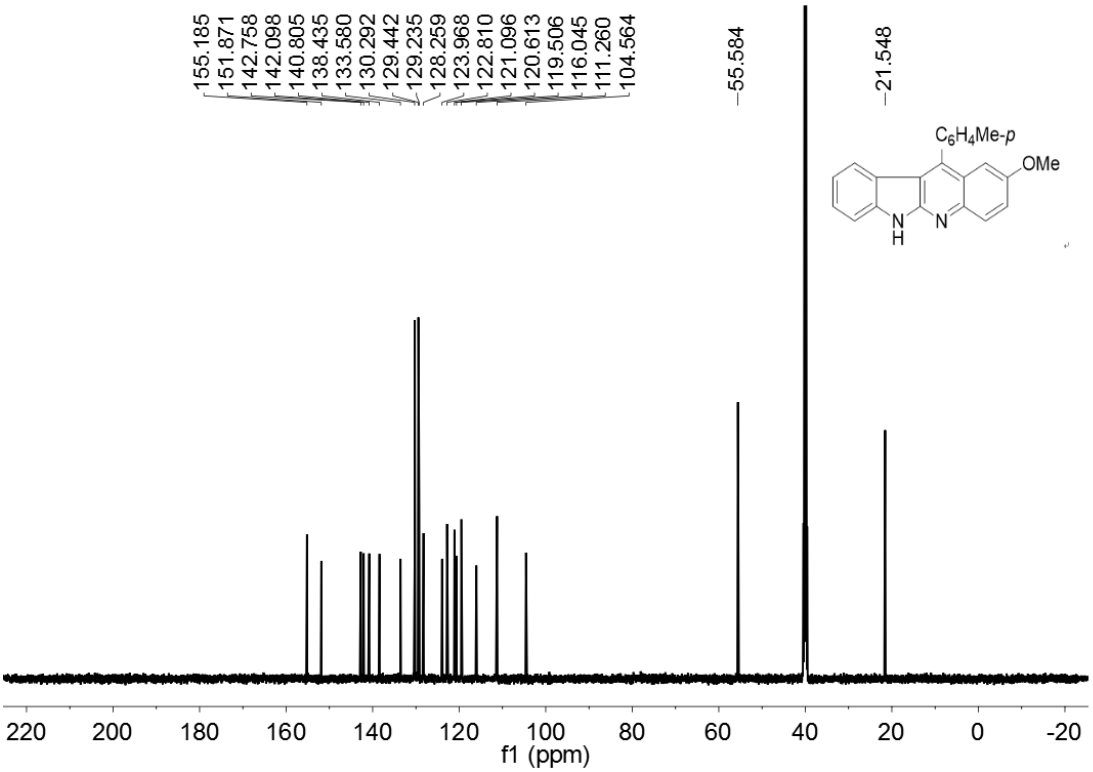

Figure 32. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3o**

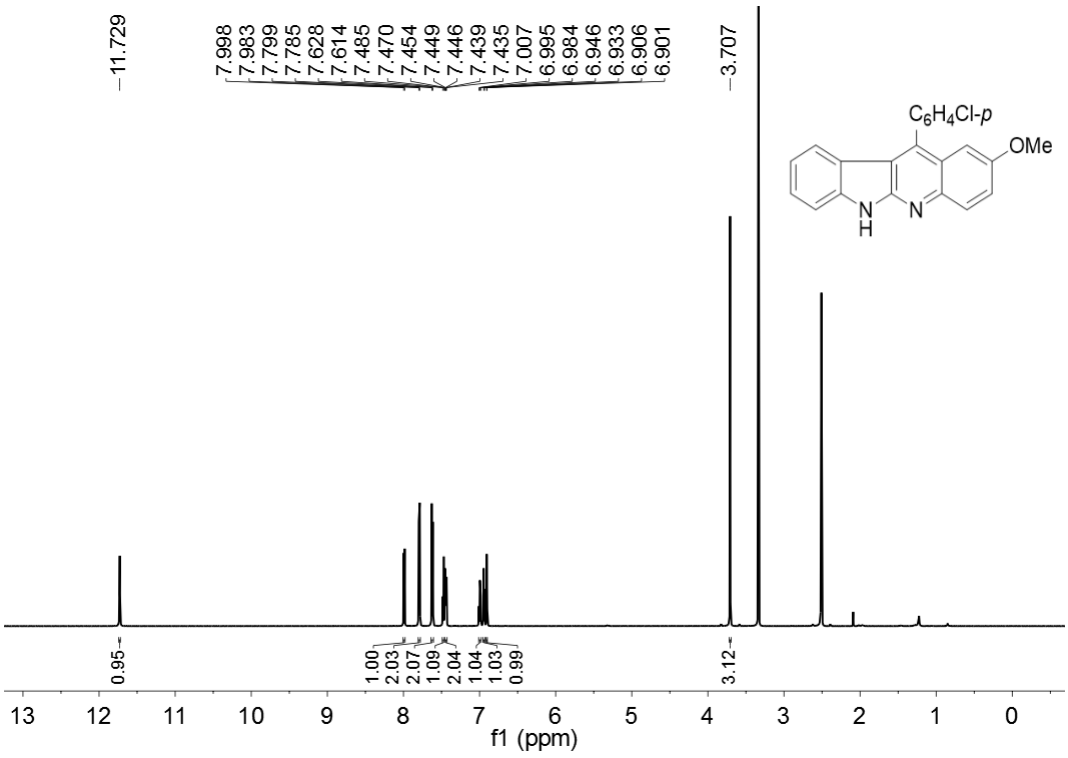

Figure 33. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3p**

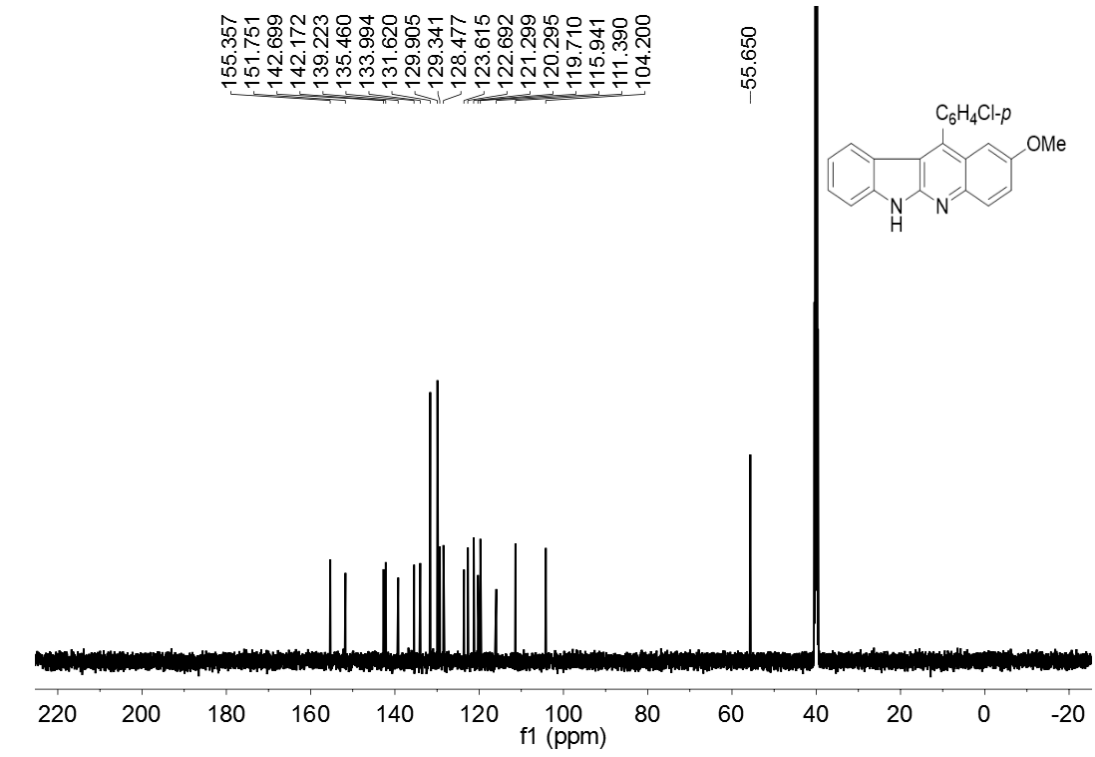

Figure 34. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3p**

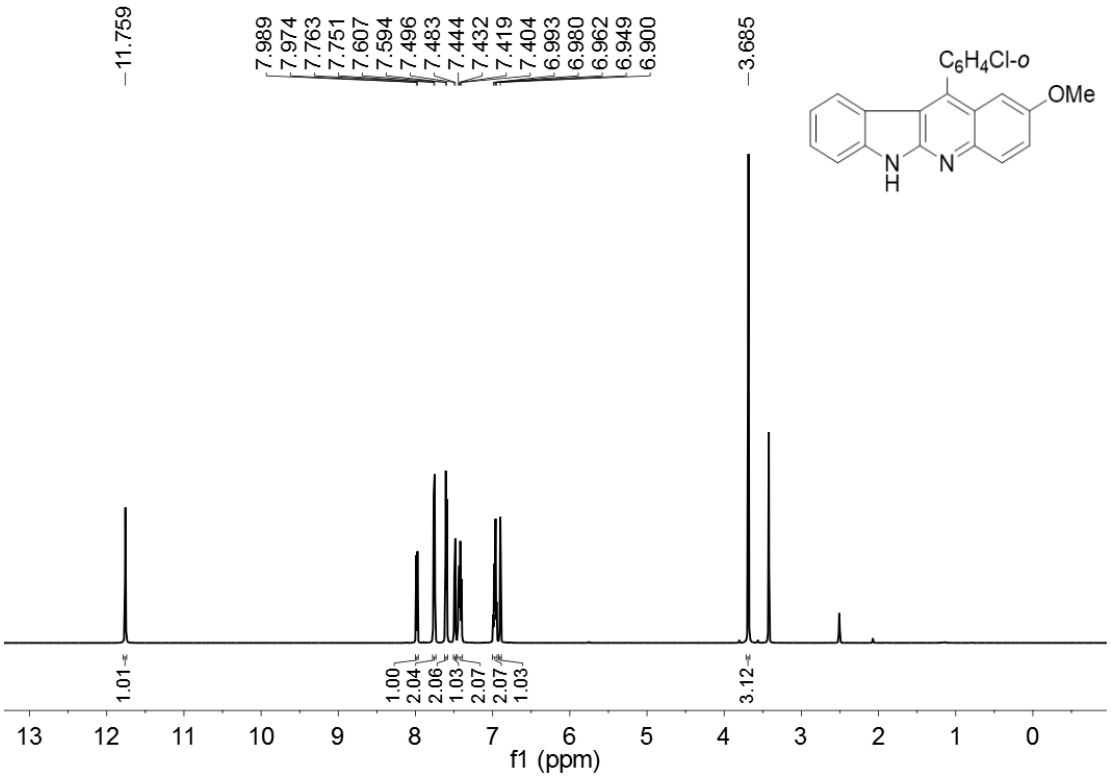

Figure 35. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3q**

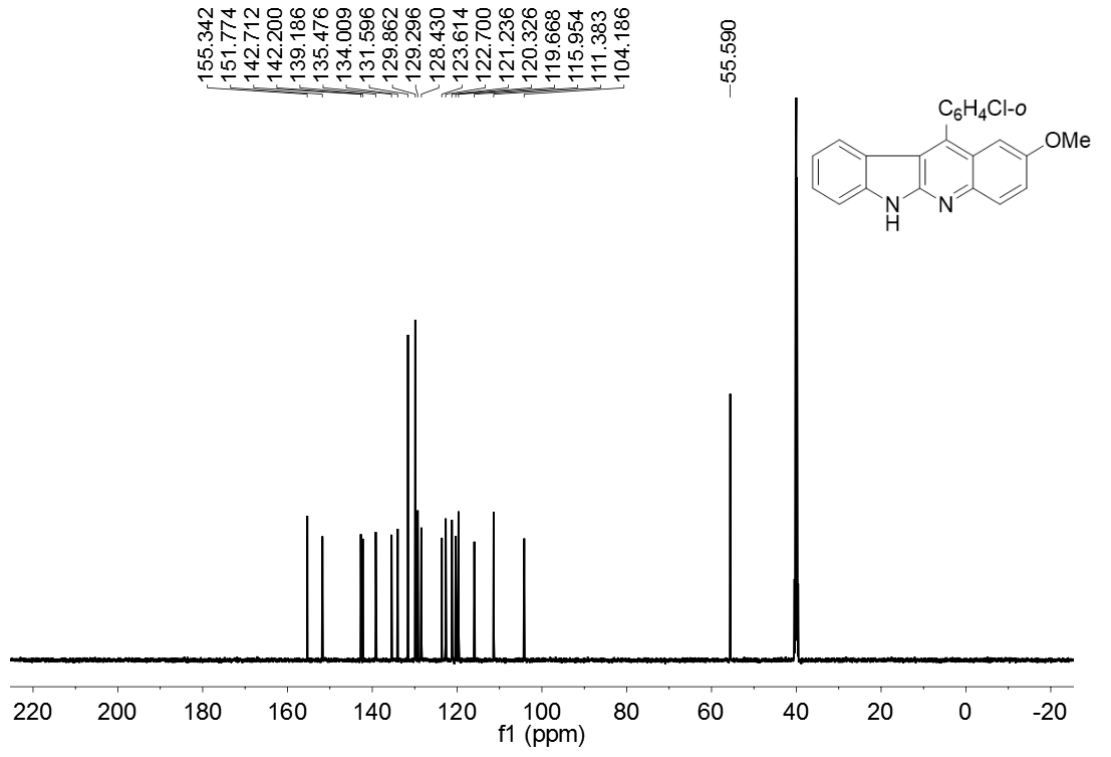

Figure 36. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3q**

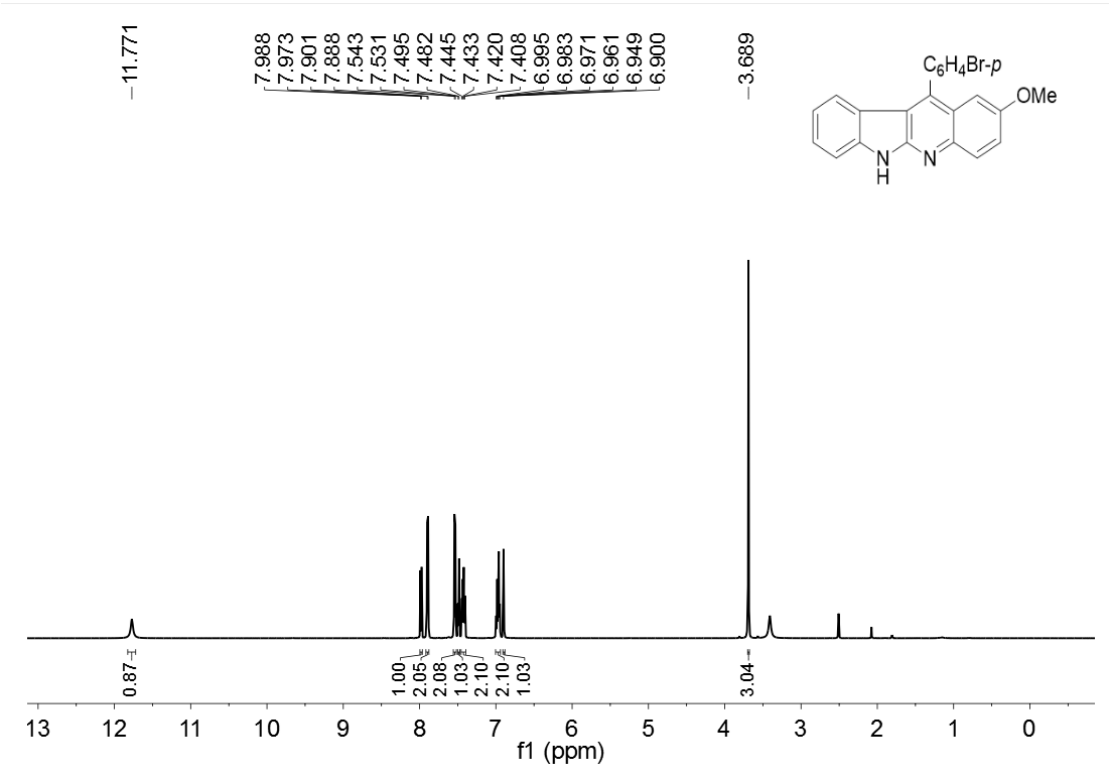

Figure 37. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3r**

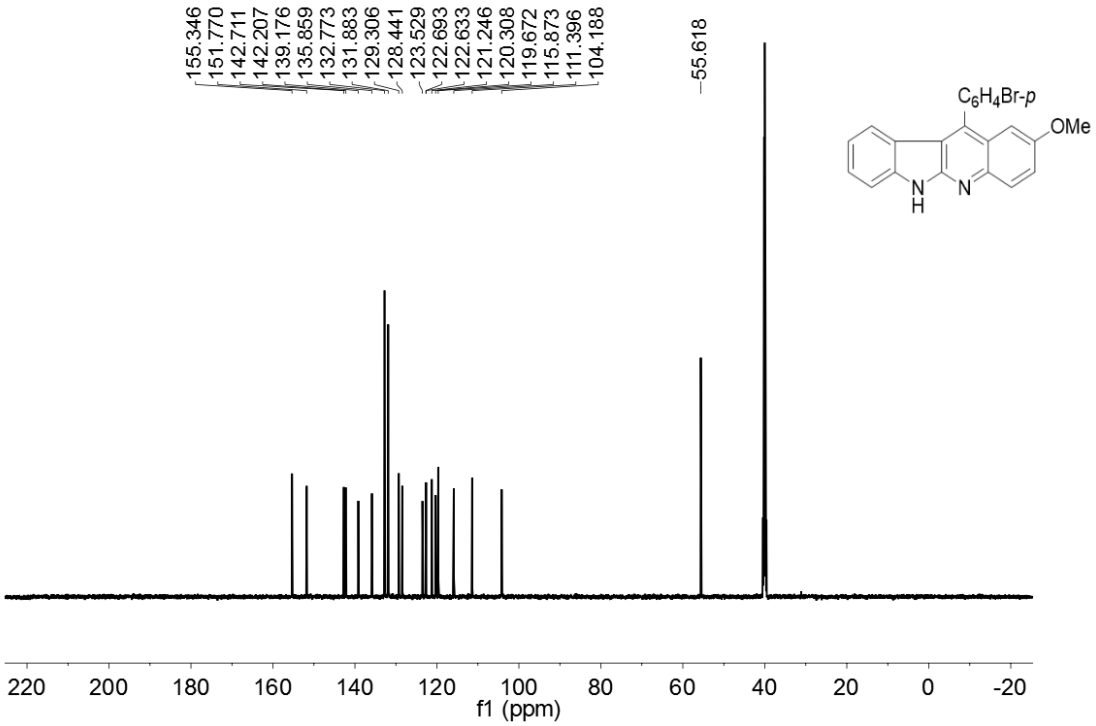

Figure 38. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3r**

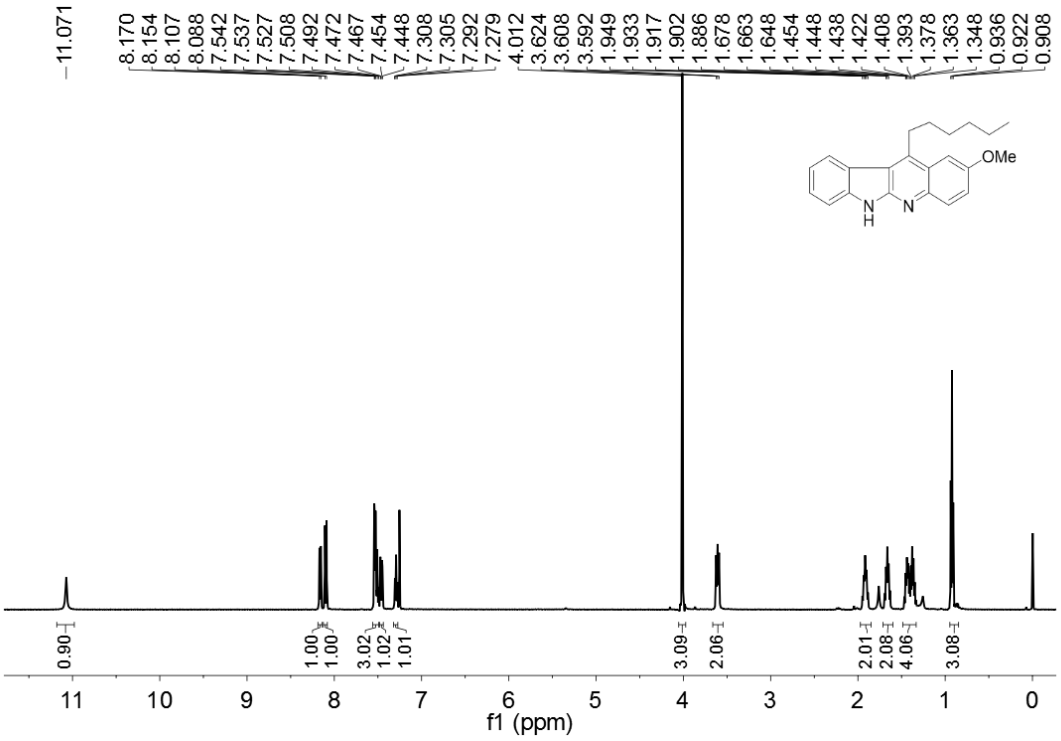

Figure 39. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3s**

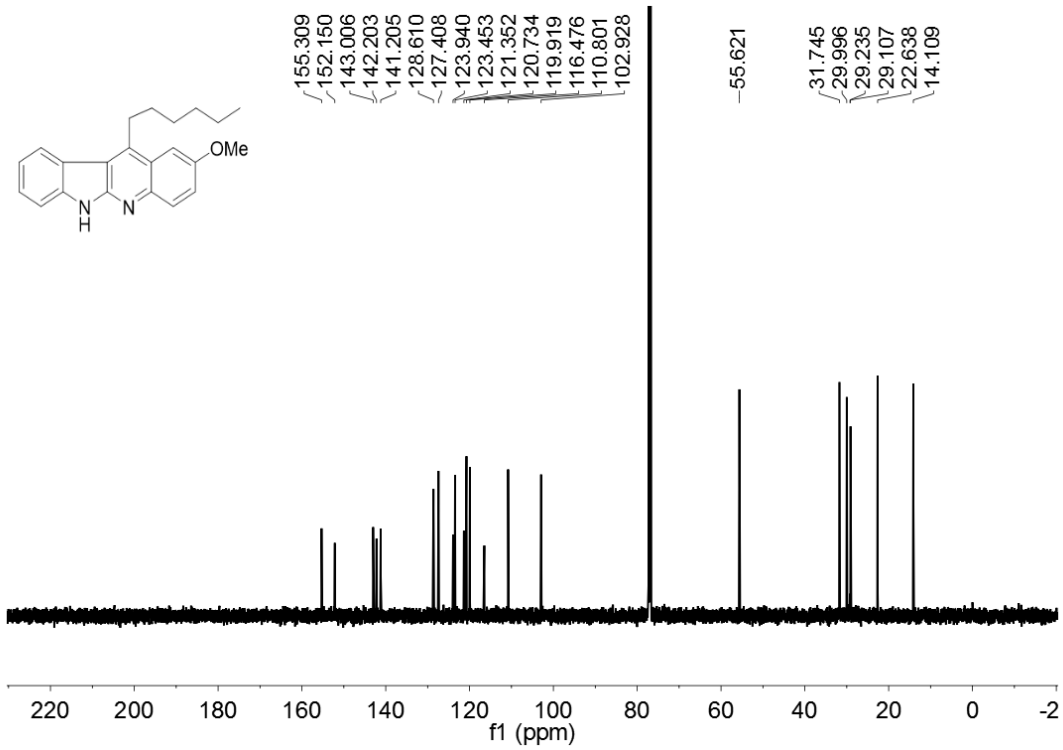

Figure 40. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3s**

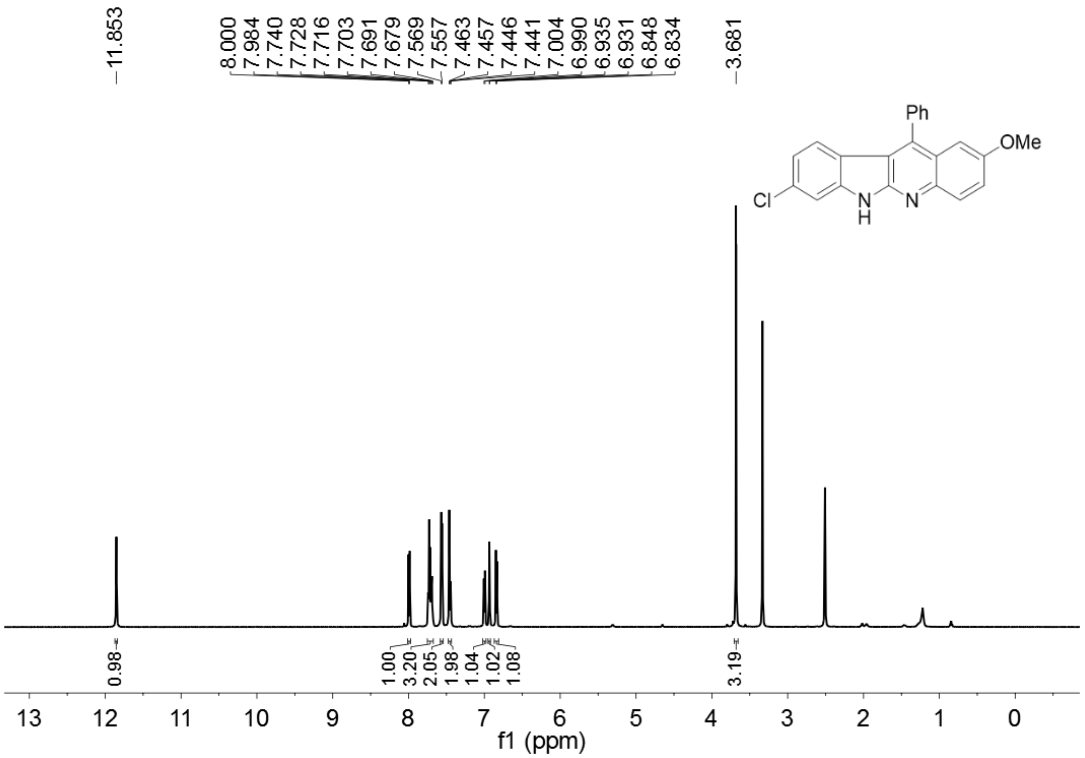

Figure 41. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3t**

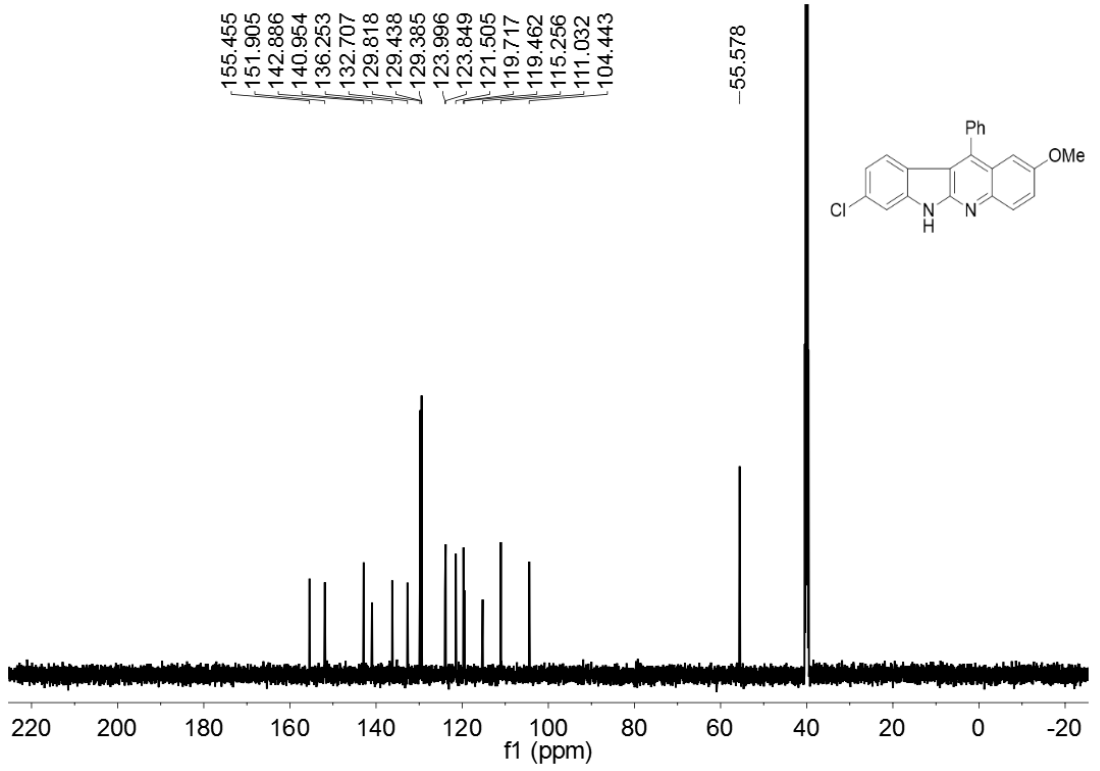

Figure 42. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3t**

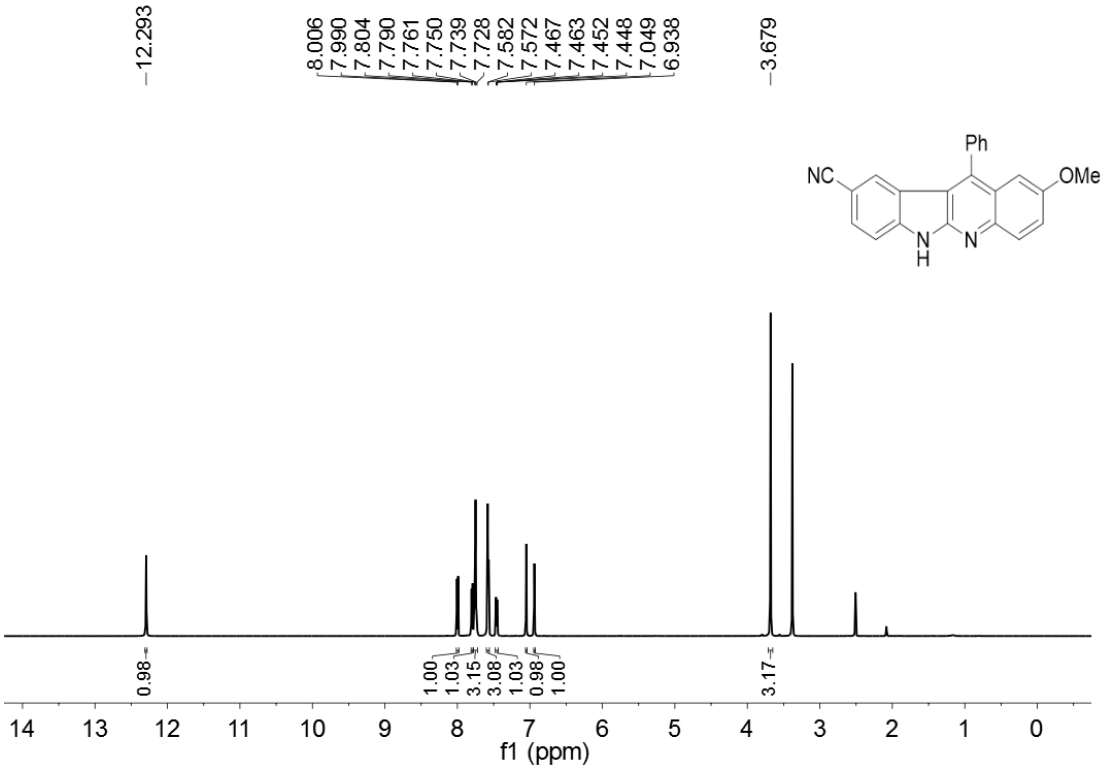

Figure 43. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3u**

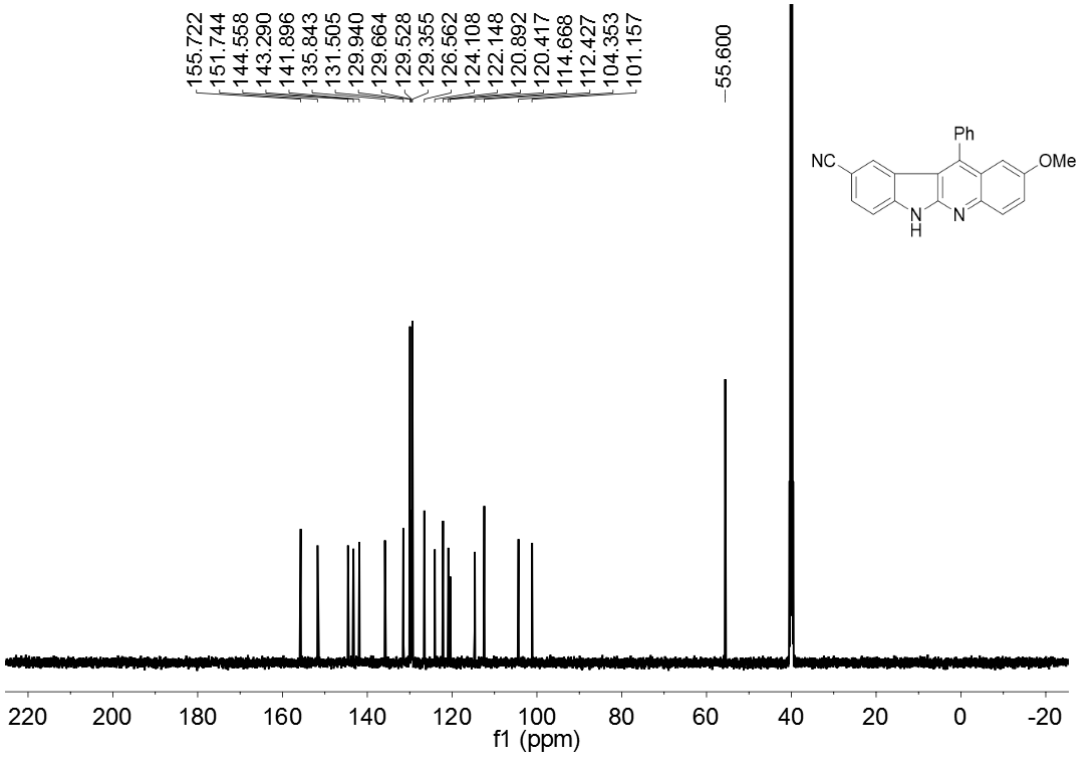

Figure 44. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3u**

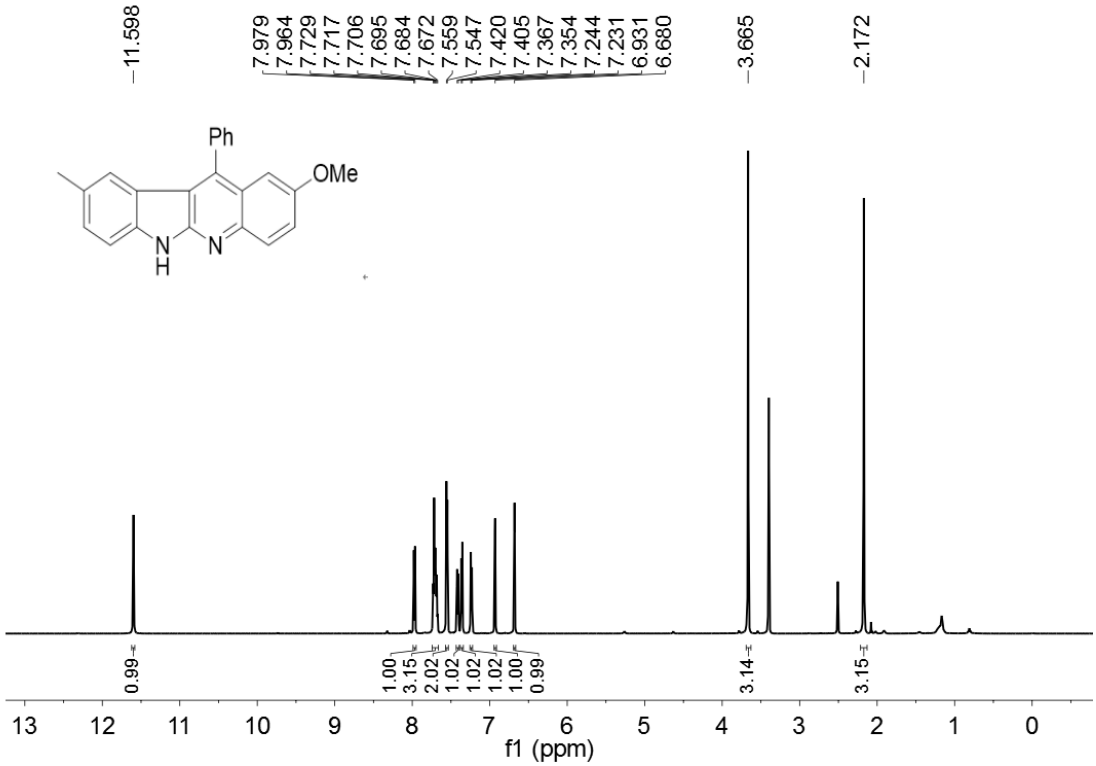

Figure 45. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3v**

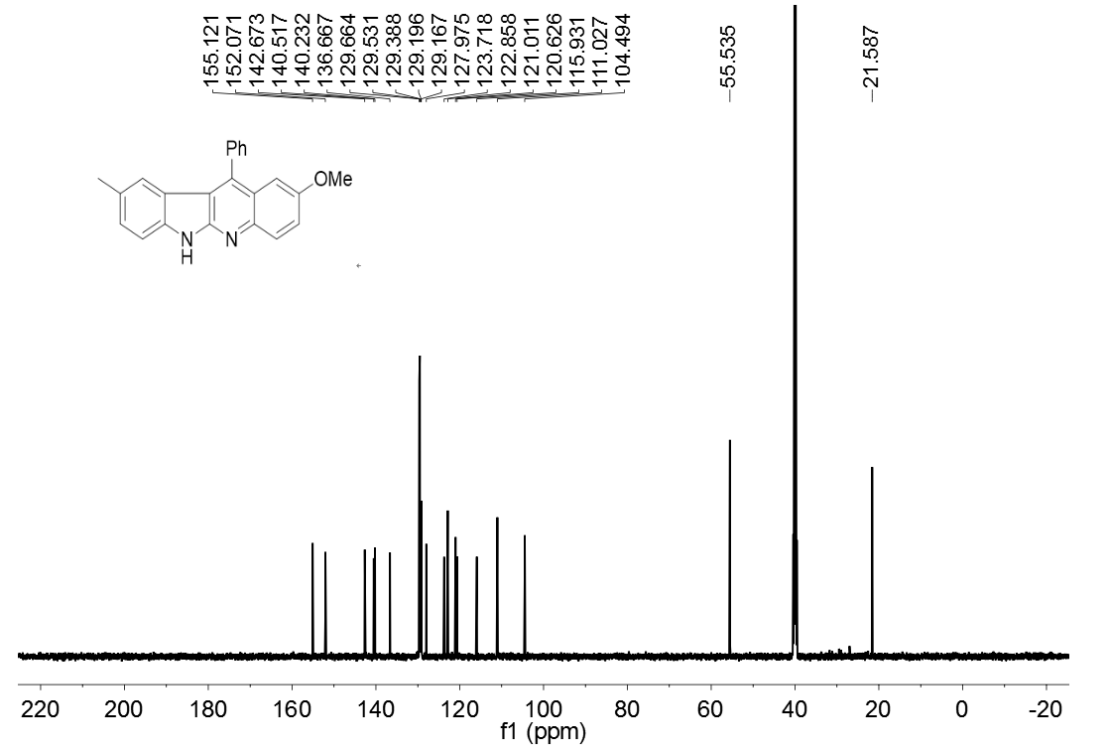

Figure 46. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **3v**

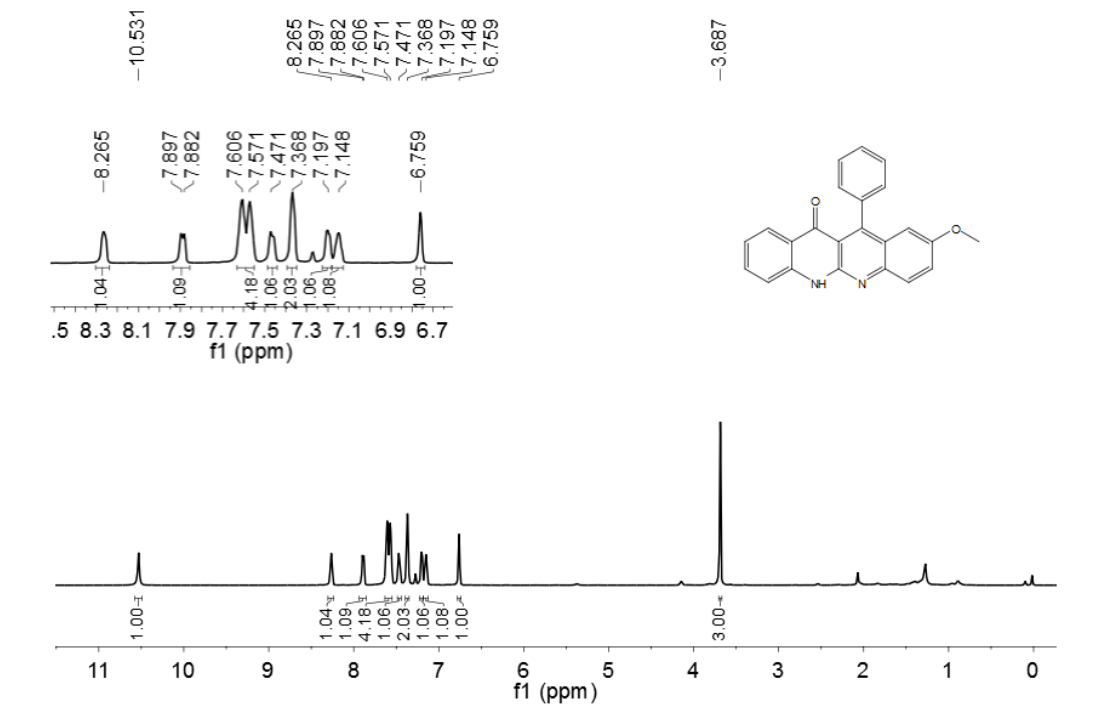

Figure 47. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5a**

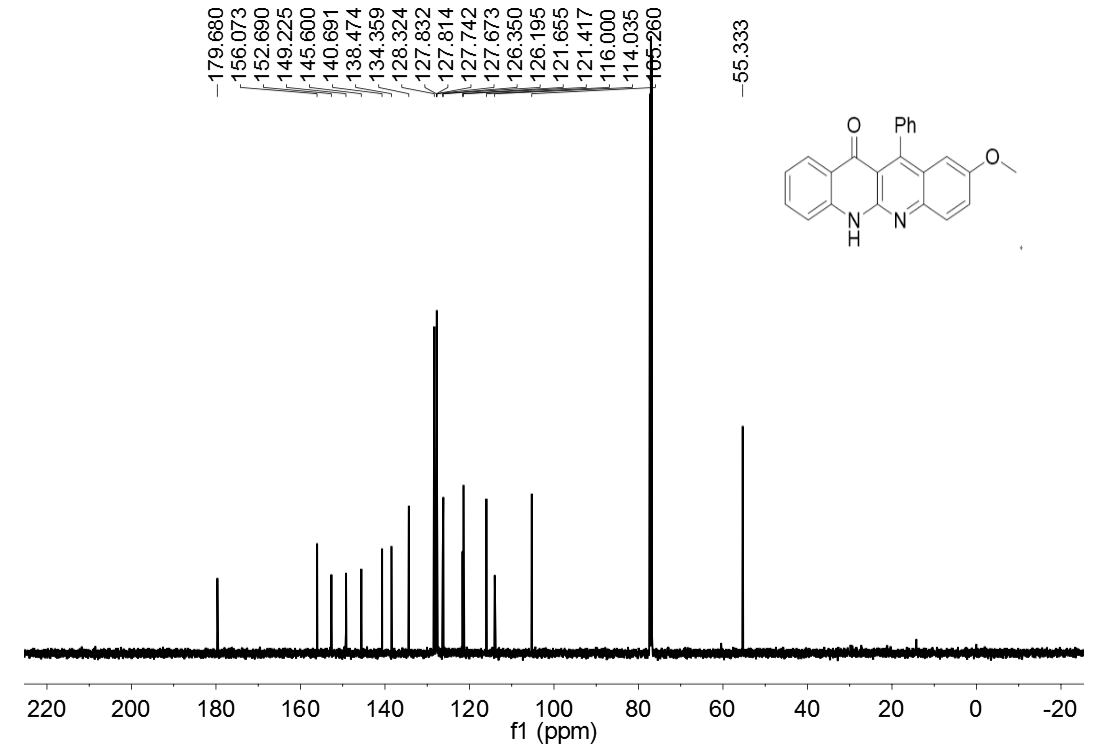

Figure 48. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5a**

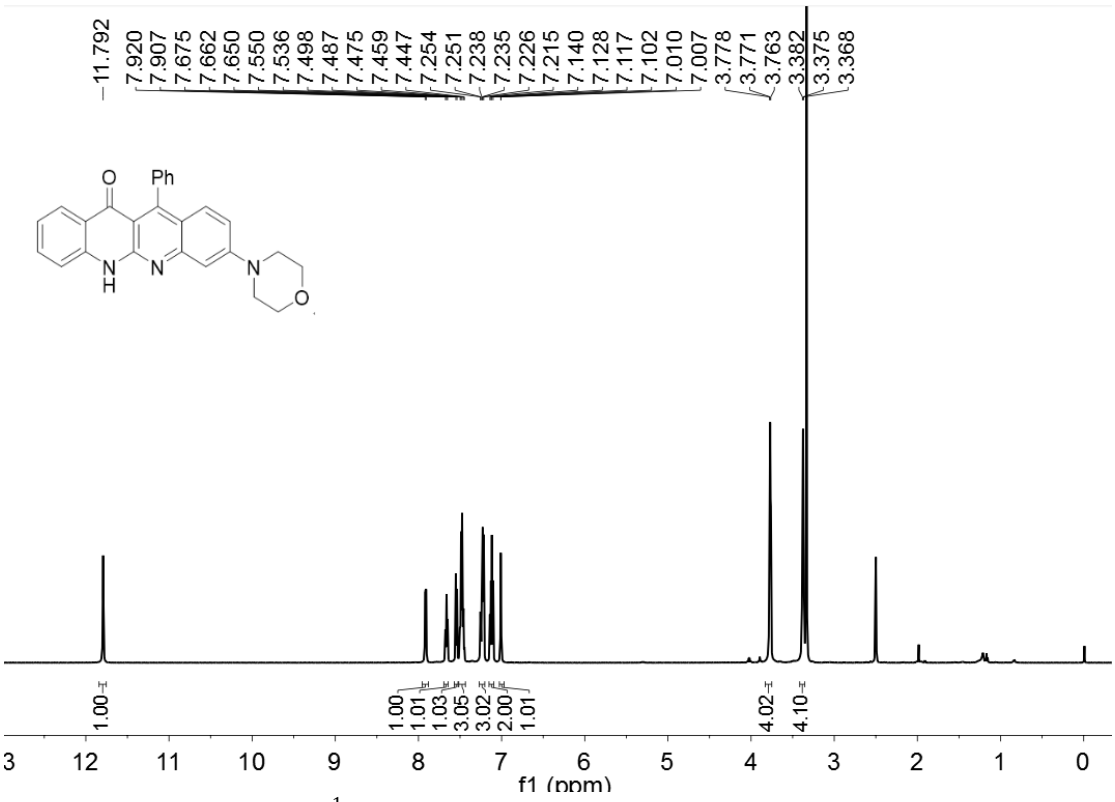

Figure 49. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **5b**

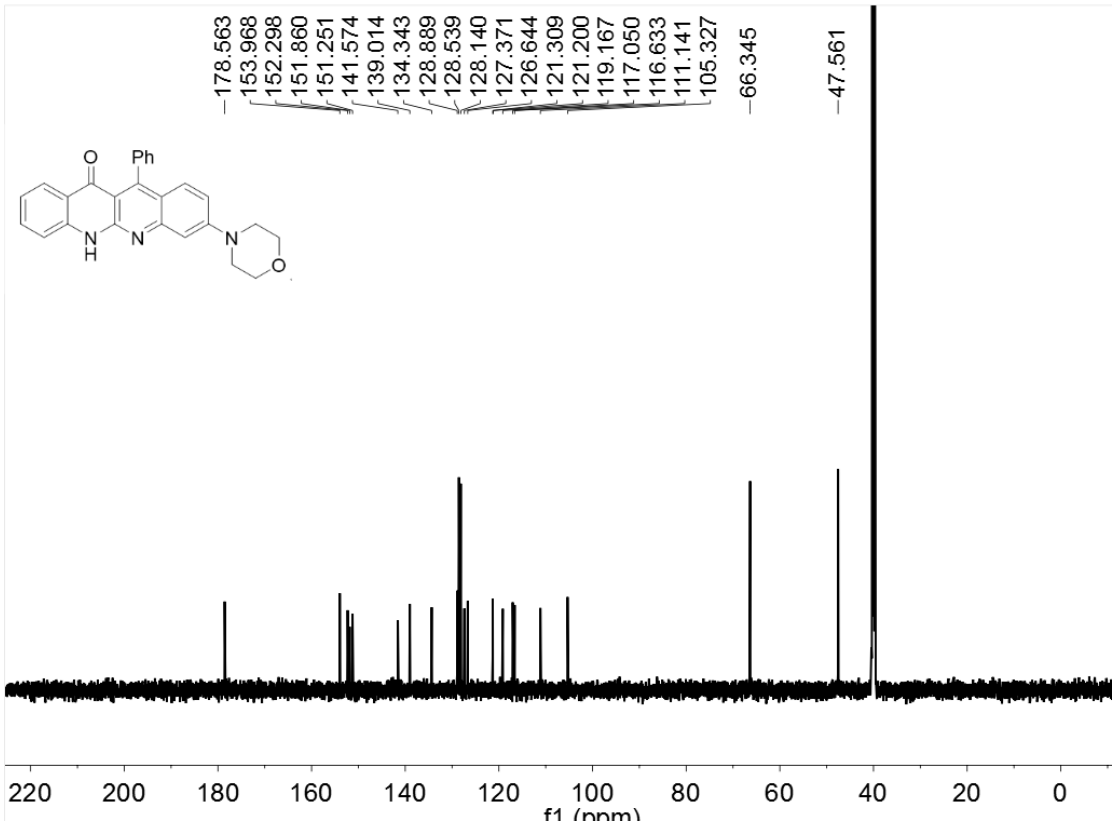

Figure 50. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **5b**

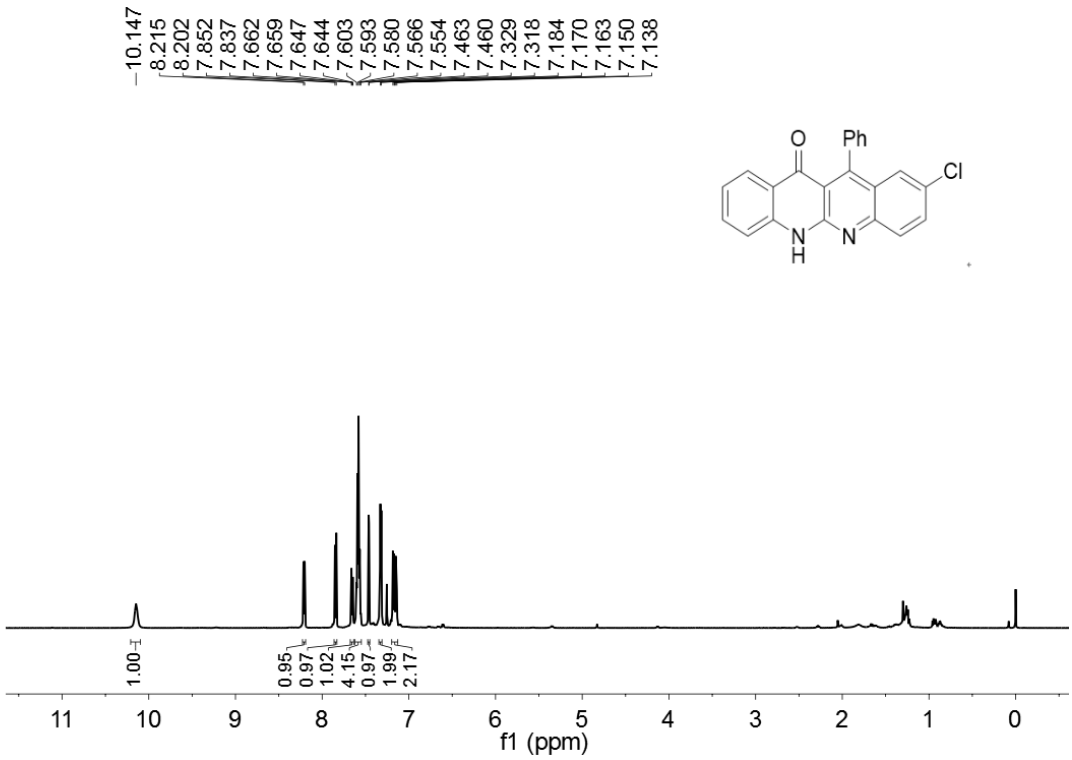

Figure 51. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5c**

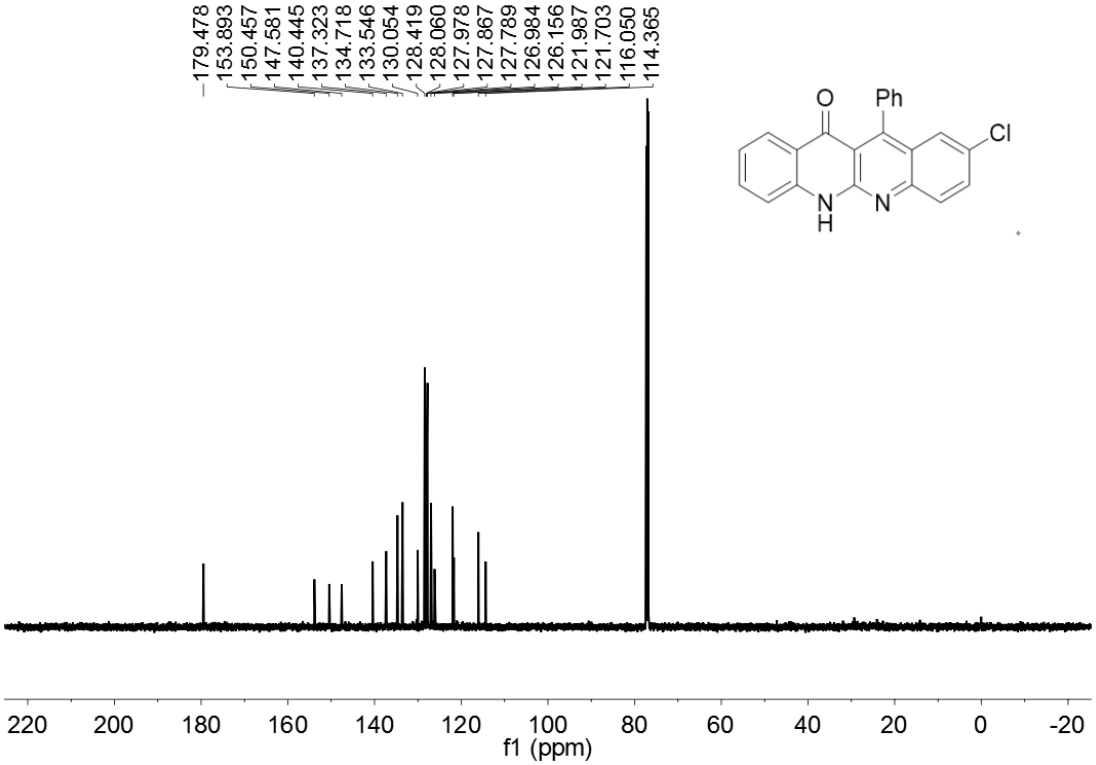

Figure 52. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5c**

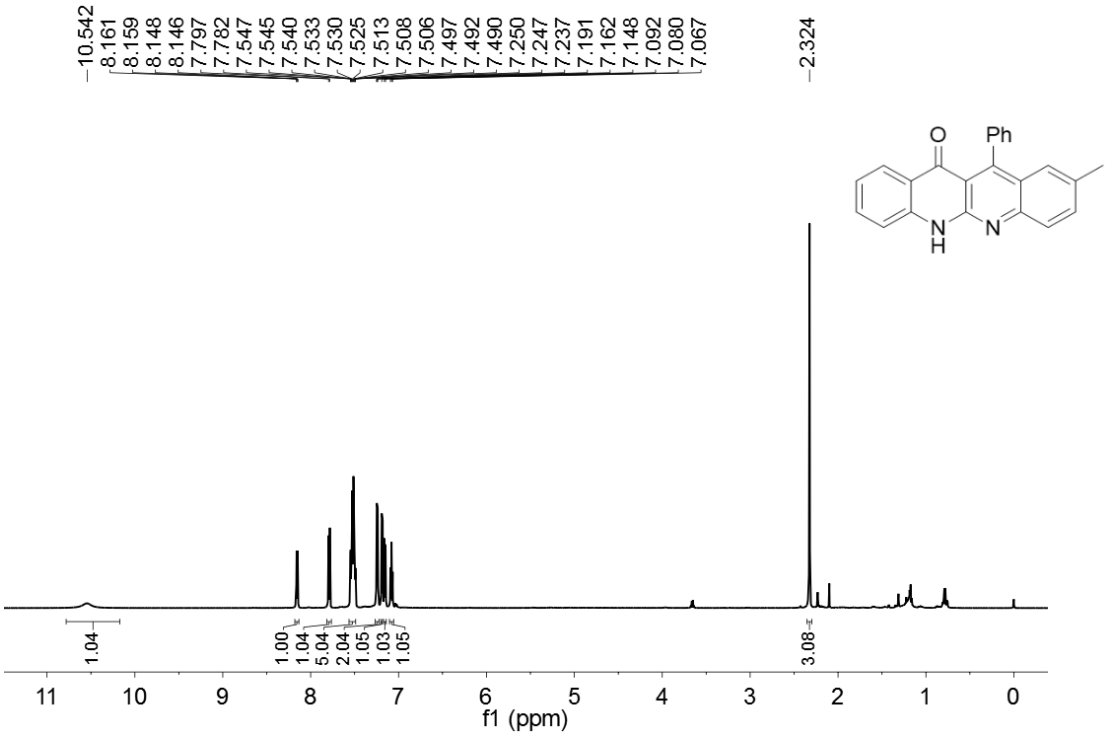

Figure 53. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5d**

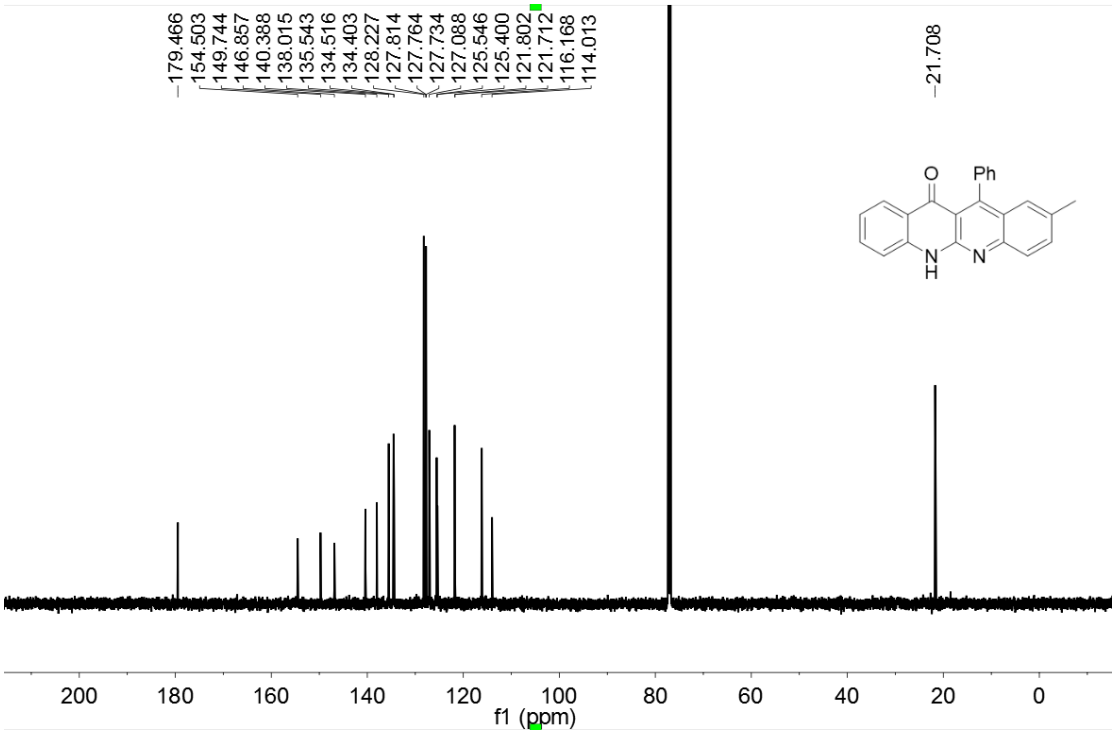

Figure 54. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5d**

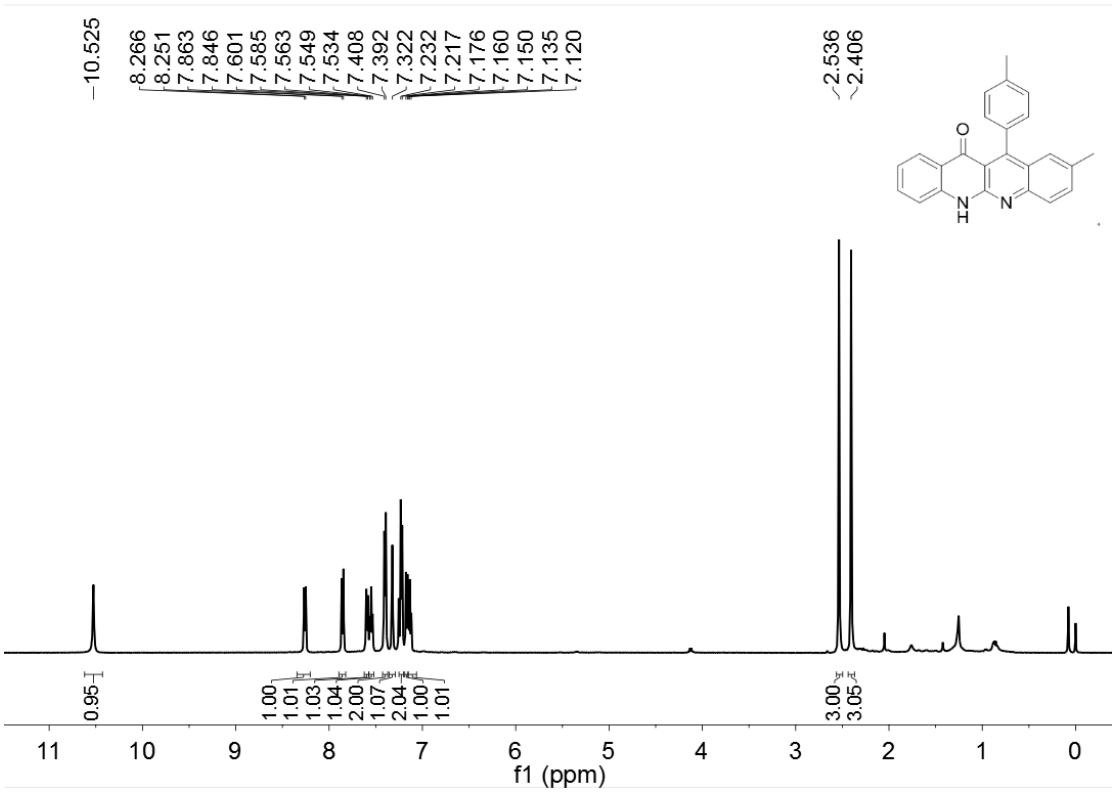

Figure 55. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5e**

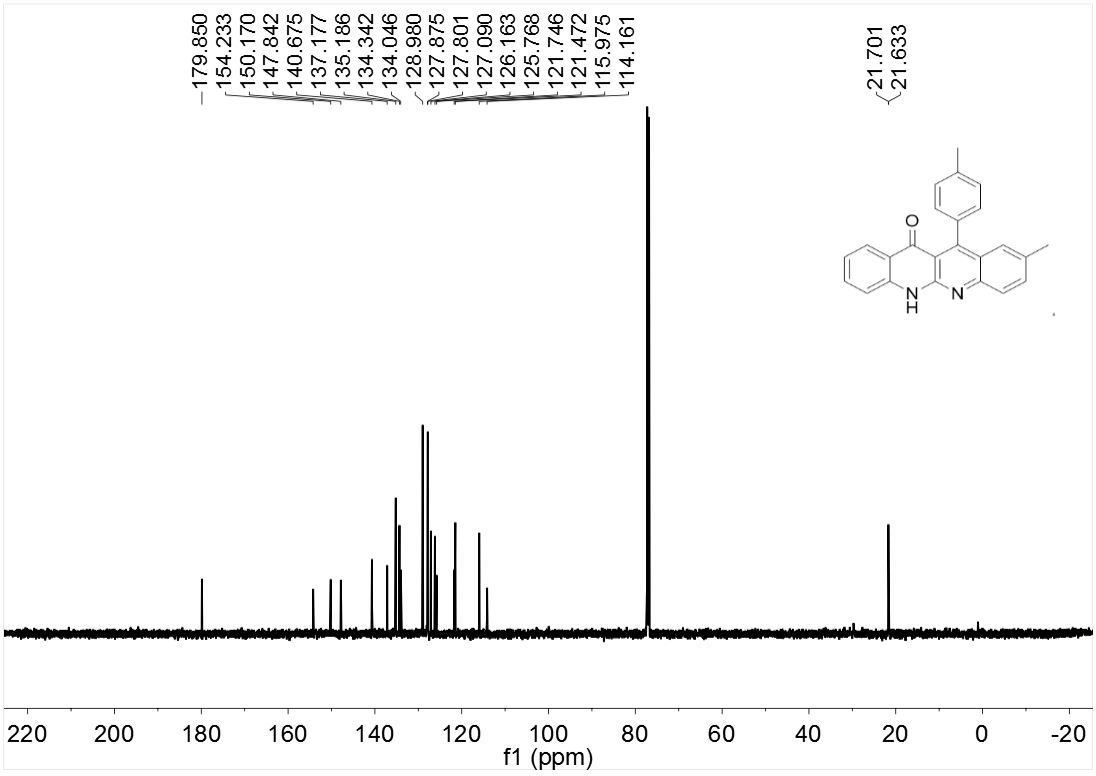

Figure 56. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5e**

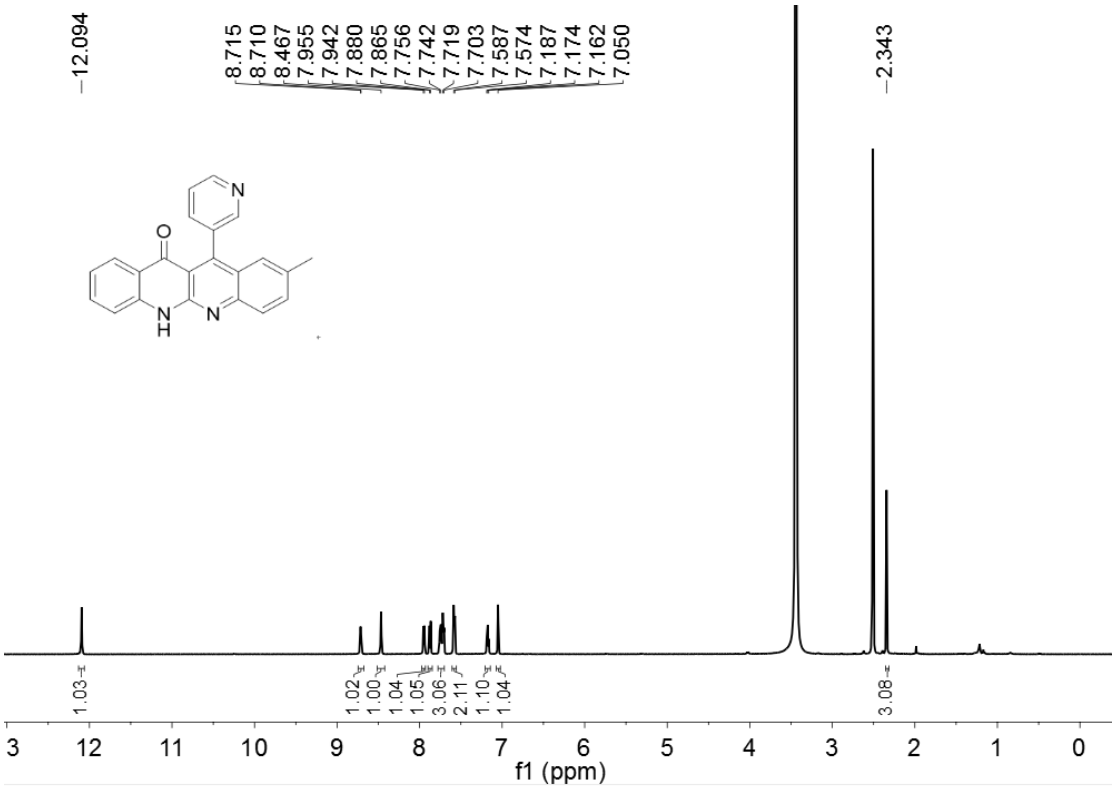

Figure 57. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of **5f**

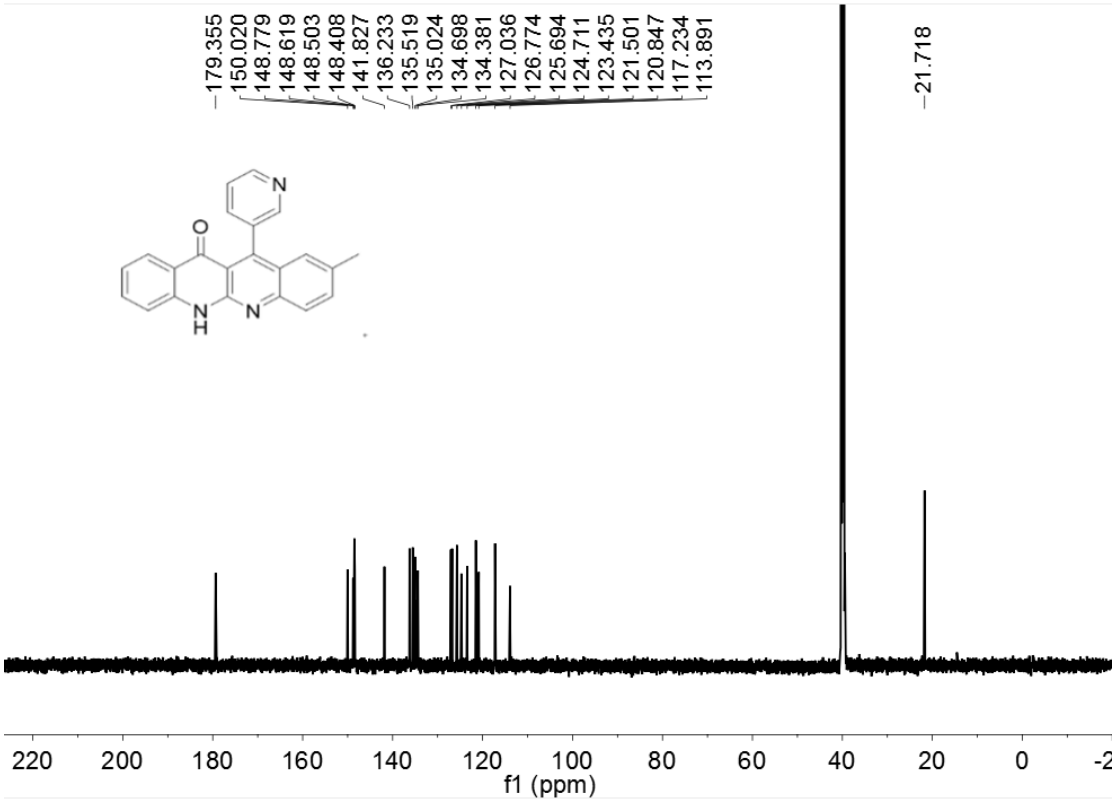

Figure 58. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **5f**

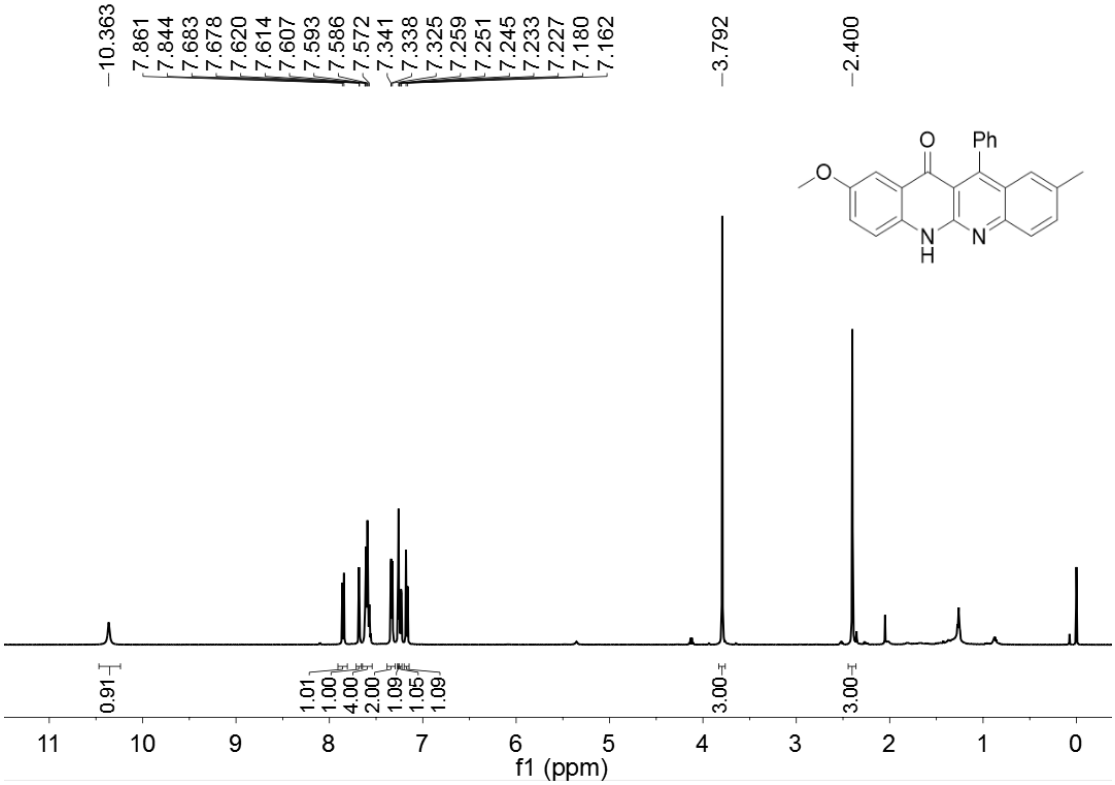

Figure 59. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5g**

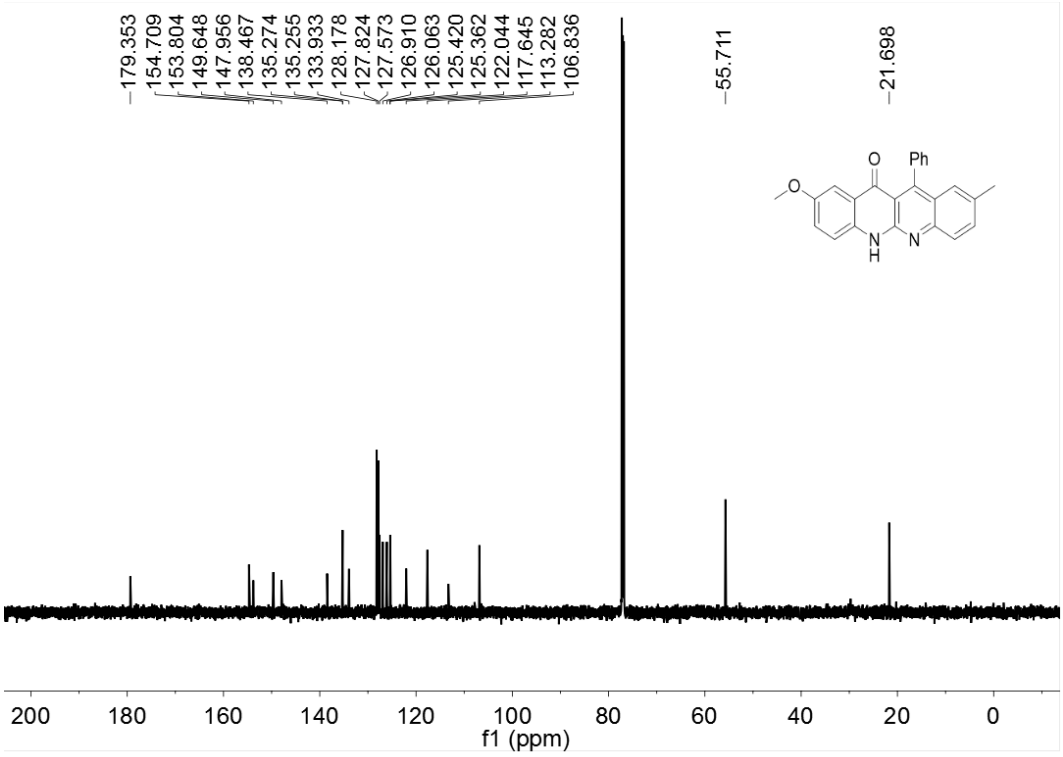

Figure 60. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5g**

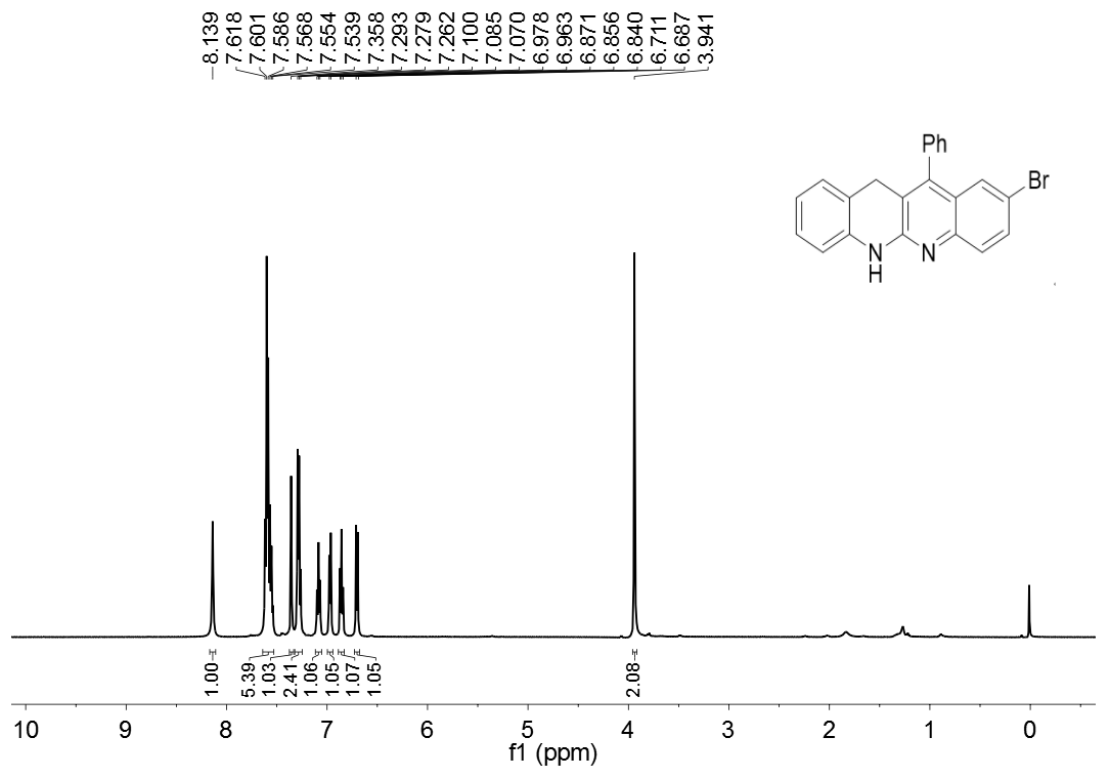

Figure 61. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **7a**

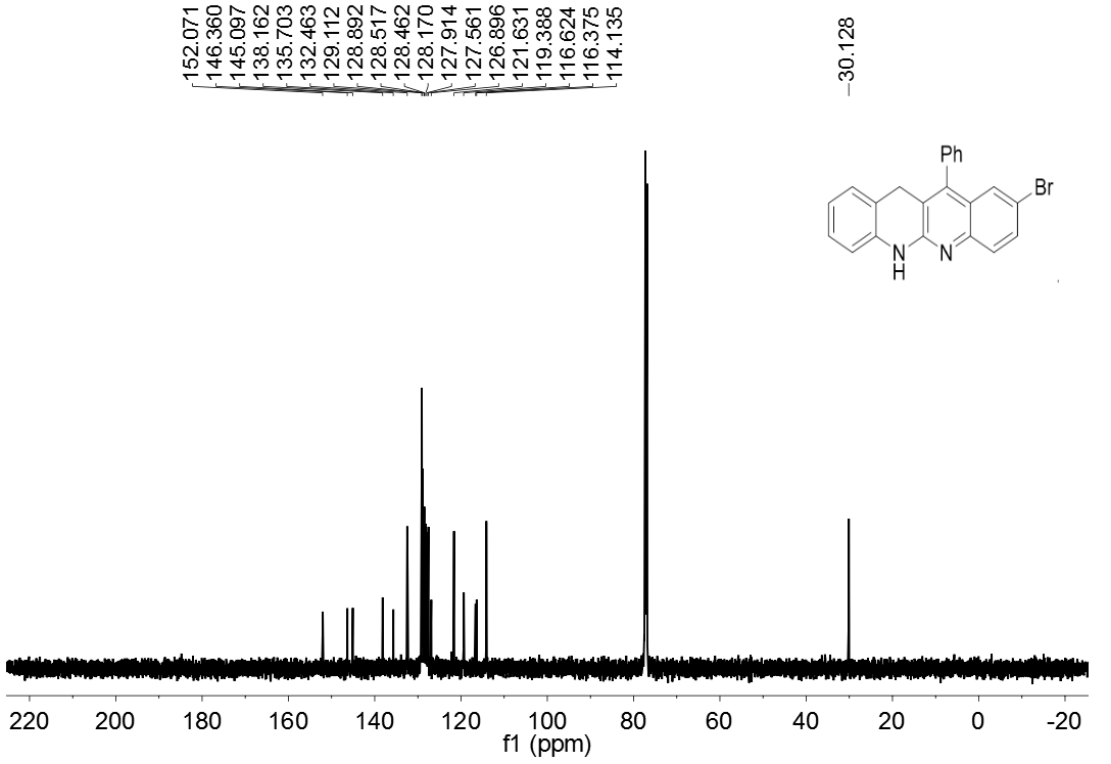

Figure 62. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **7a**

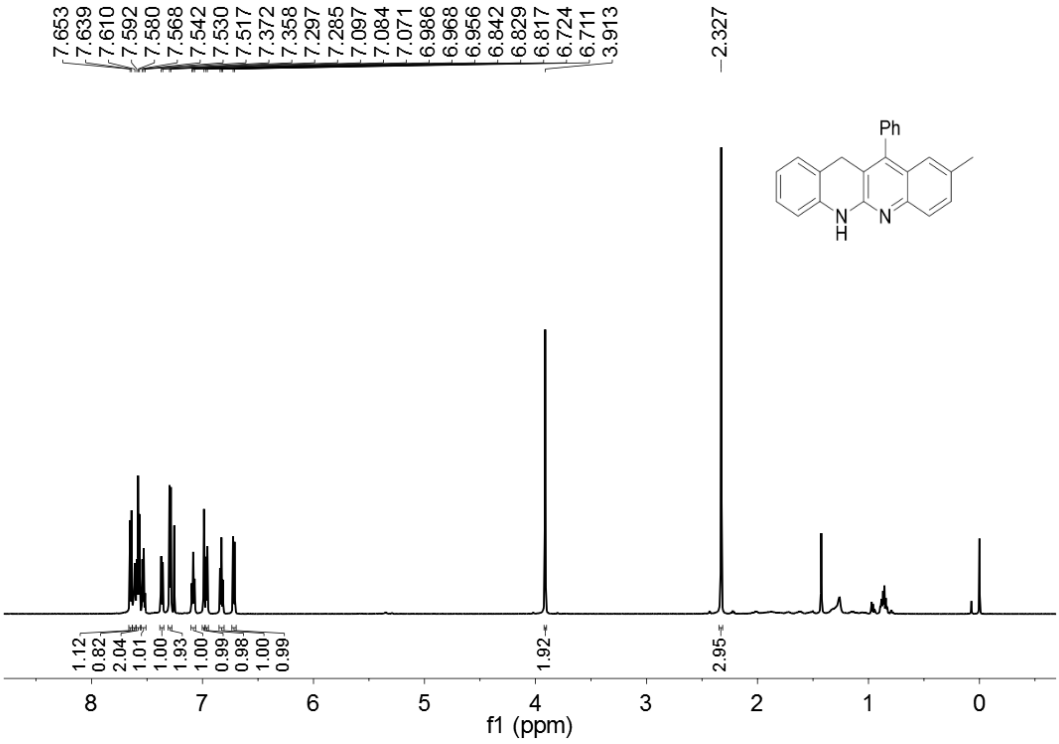

Figure 63. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **7b**

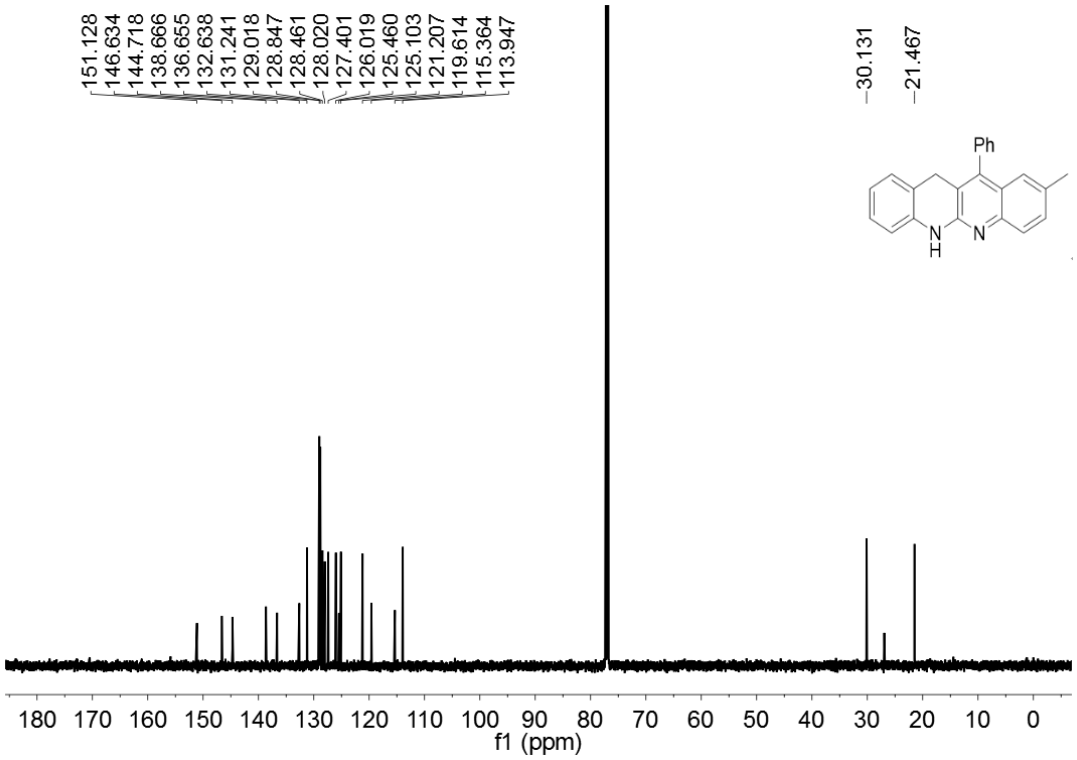

Figure 64. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **7b**

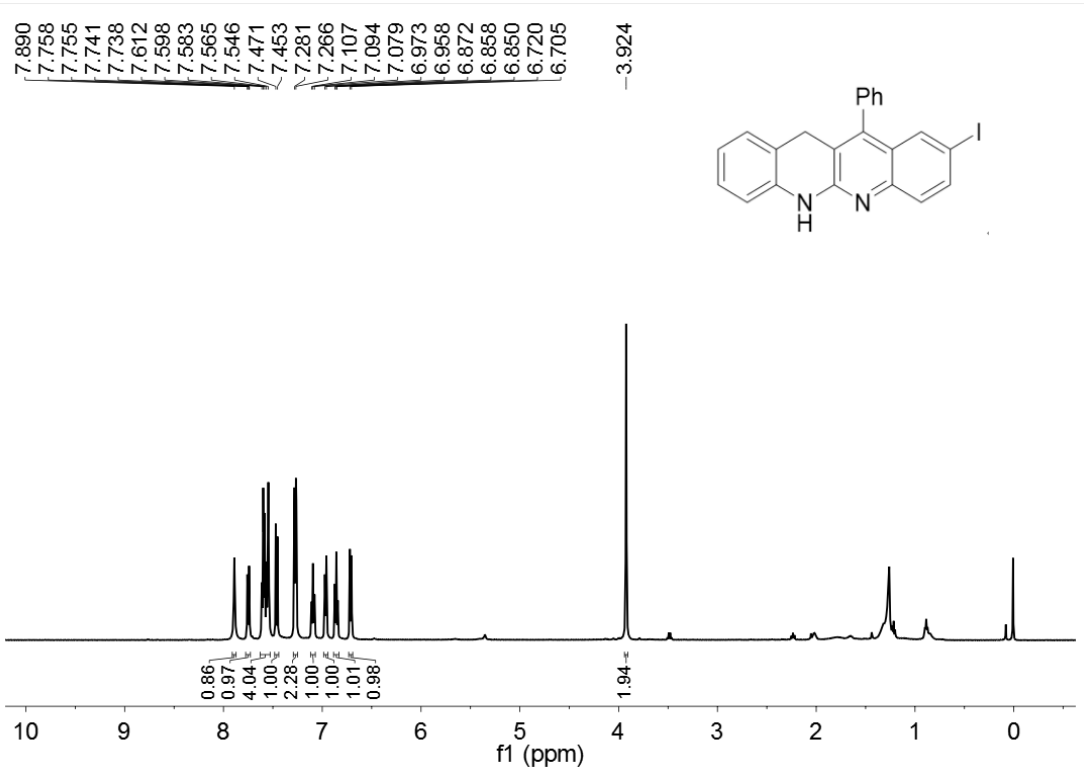

Figure 65. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **7c**

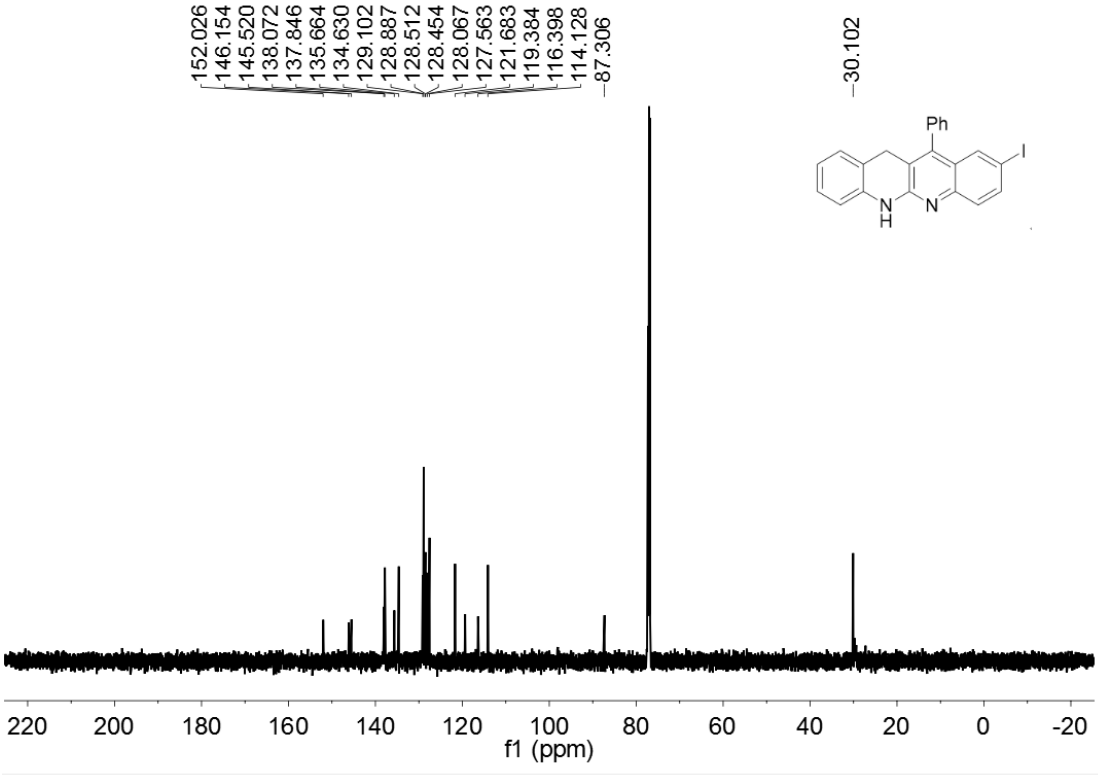

Figure 66. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **7c**

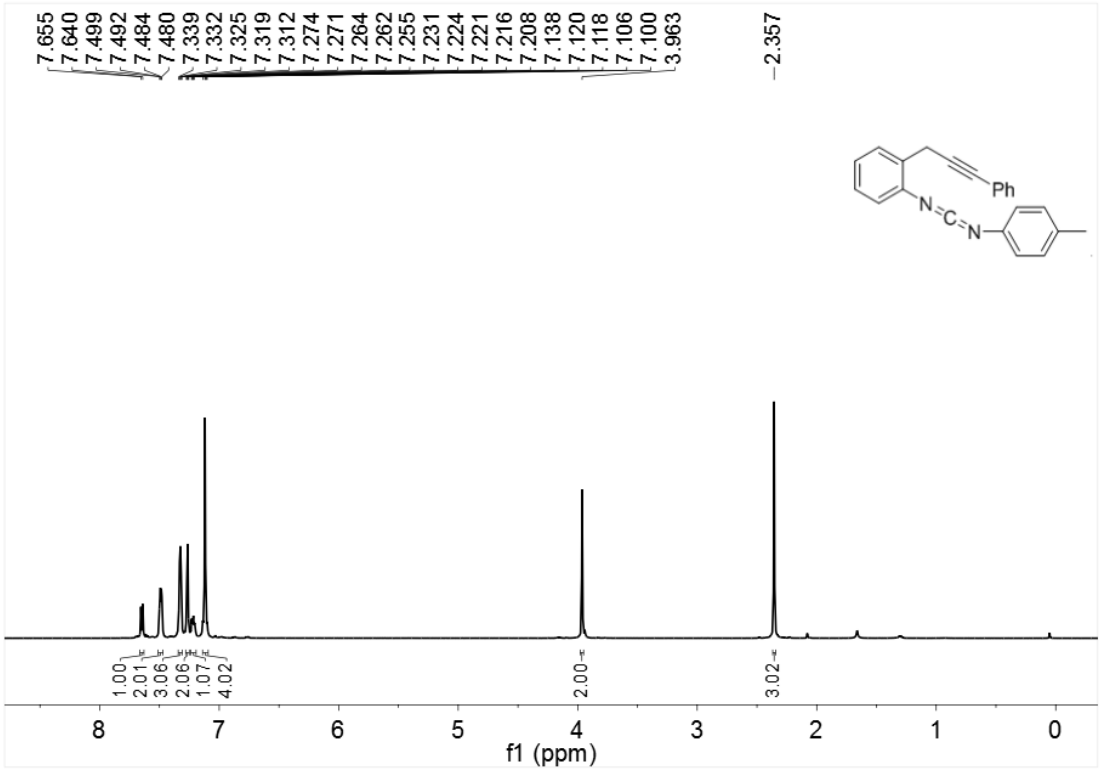

Figure 67. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **8**

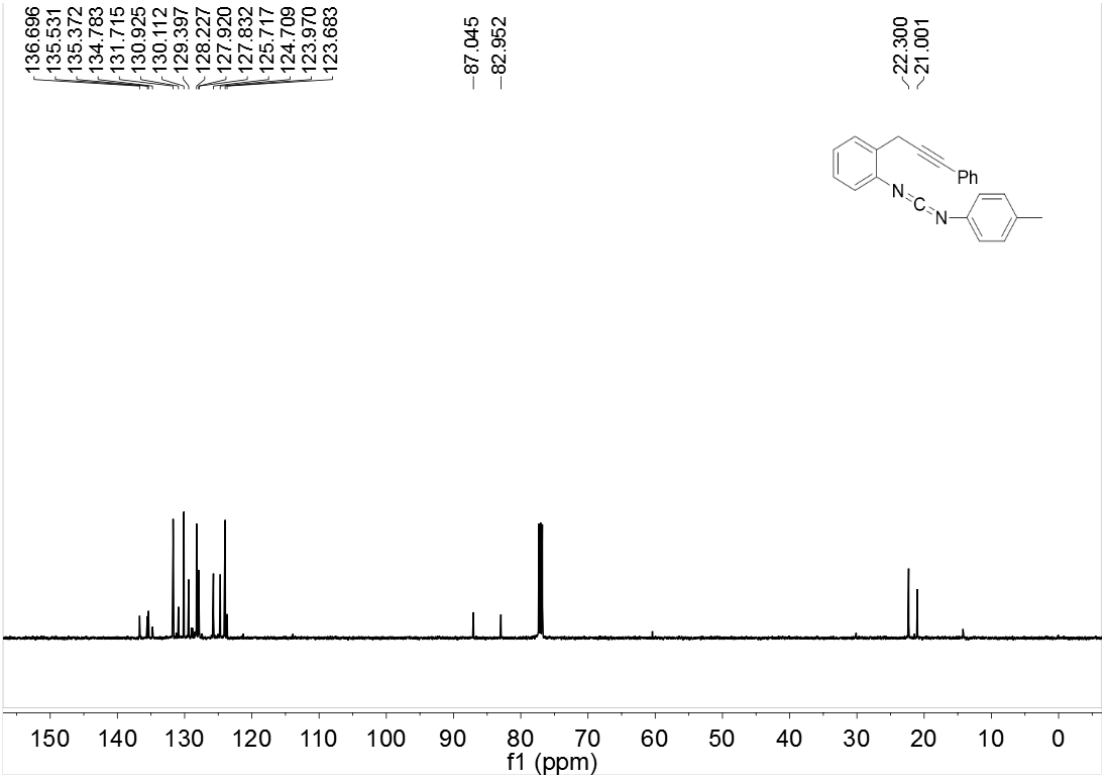

Figure 68. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **8**