Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Organocatalyzed aerobic oxidative Robinson-type annulation of 2-isocyanochalcones: Expedient synthesis of phenanthridines

Table of contents

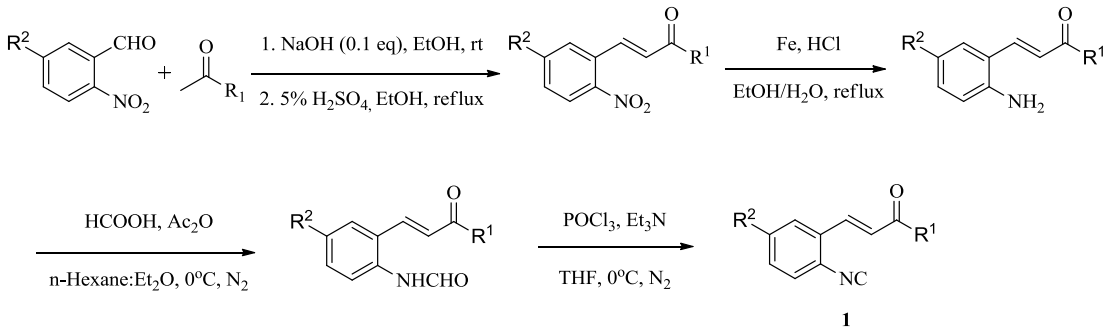
1. General information

All reagents were commercial and used without further purification, unless otherwise indicated. Chromatography was carried on flash silica gel (300−400 mesh). All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). Melting points were uncorrected. The ^{1}H NMR and ^{13}C NMR spectra were determined at 25 ℃ on a 500 MHz and 125 MHz, respectively, and TMS as internal standard. All shifts are given in ppm. High-resolutionmass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI).

2. Synthetic procedures and Spectroscopic data

*2.1 General procedure for the synthesis isocyanoarenes **1***

Substrates **1** were synthesized according to known literature procedure.[1,2,4,5]



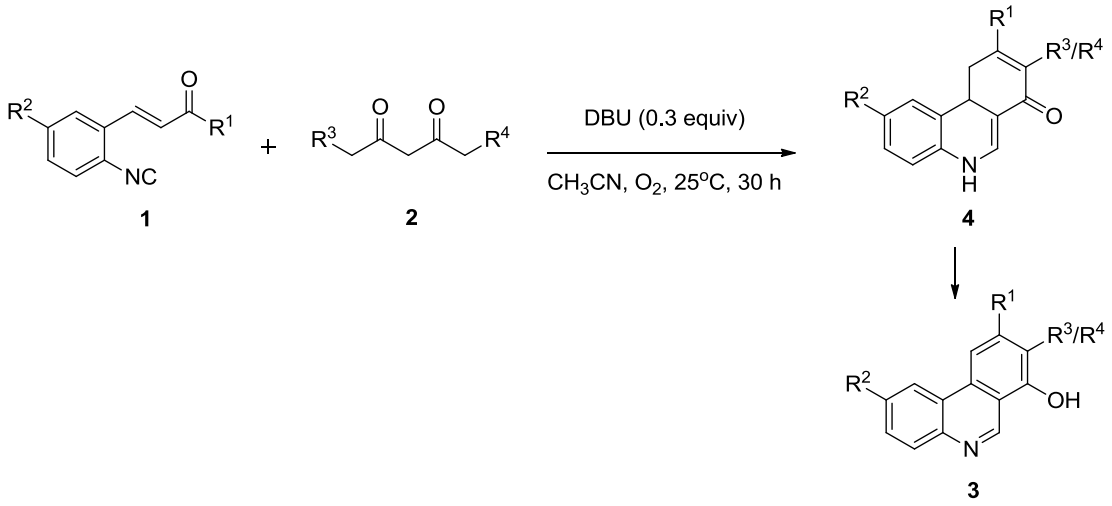
1

References:

1. E. Alarcón, N. Romero and H. Aguilar, *Green Chemistry Conference* . **2013**.
2. A-H. Li, E. Ahmed, X. Chen, M. Cox, A. P. Crew, H-Q. Dong, M. Jin, L. Ma, B. Panicker, K. W. Siu, Arno G. Steinig, K. M. Stolz, P. A. R. Tavares, B. Volk, Q. Weng, D. Werner and M. J. Mulvihill. *Org. Biomol. Chem.* **2007**, *5*, 61.
3. M. Tobisu, H. Fujihara, K. Koh, and N. Chatani. *J. Org. Chem.* **2010**, *75*, 4841.
4. Z. Hu, H. Yuan, Y. Men, Q. Liu, J. Zhang and X. Xu, *Angew. Chem. Int. Ed.* **2016**, *55*, 7077;

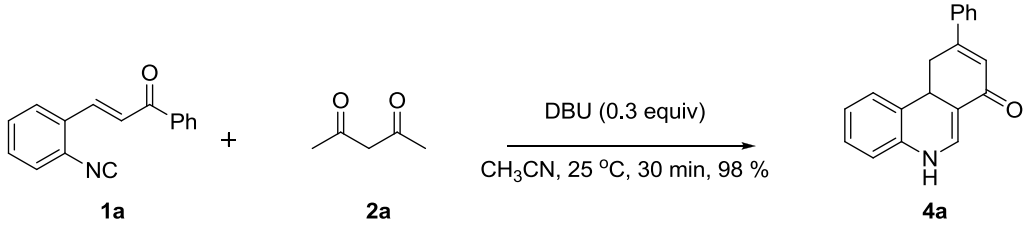
*2.2 General procedure and Spectroscopic Data for the synthesis of **3, 4, 5, 6***

Synthesis of 3



Typical synthetic procedure (with **3a** as an example) To a solution of (*E*)-3-(2-isocyanophenyl)-1-phenylprop-2-en-1-one (**1a**) (70 mg, 0.3 mmol) and pentane-2,4-dione (**2a**) (0.037 ml, 0.36 mmol) in CH_3CN (2 mL) at 25 ^oC, DBU (0.014 ml, 0.09 mmol) was added, under a O_2 atmosphere. The mixture was then stirred for 30 min , until substrate **1a** had been consumed as indicated by TLC. Then the mixture was then stirred for 30 h, until substrate **4a** had been consumed as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane (3*15 ml). The organic layer was washed with brine (3*40 ml), dried over $MgSO_4$ and concentrated. Purification of the crude product with flash column chromatography (silica gel; petroleum ether: ethyl acetate = 2:1) gave **3a** 78 mg, 97 % yield as a pale yellow solid.

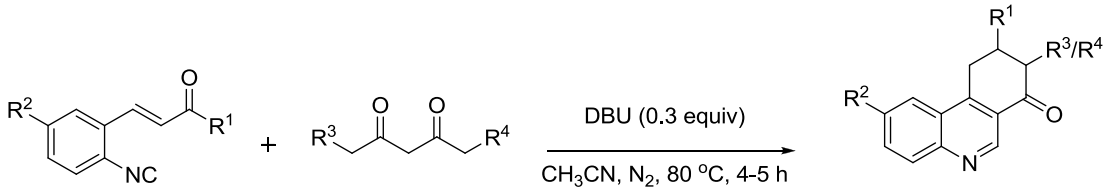
Synthesis of 4a



To a solution of (*E*)-3-(2-isocyanophenyl)-1-phenylprop-2-en-1-one (**1a**) (70 mg, 0.3 mmol) and pentane-2,4-dione (**2a**) (0.037 ml, 0.36 mmol) in CH_3CN (2 mL) at 25 ^oC, DBU (0.014 ml, 0.09

mmol) was added. The mixture was then stirred for 30 min, until substrate **1a** had been consumed as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane (3*15 ml). The organic layer was washed with brine (3*40 ml), dried over $MgSO_4$ and concentrated. Purification of the crude product with flash column chromatography (silica gel; petroleum ether: ethyl acetate = 4:1) gave **4a** 80 mg, 98 % yield as a yellow solid.

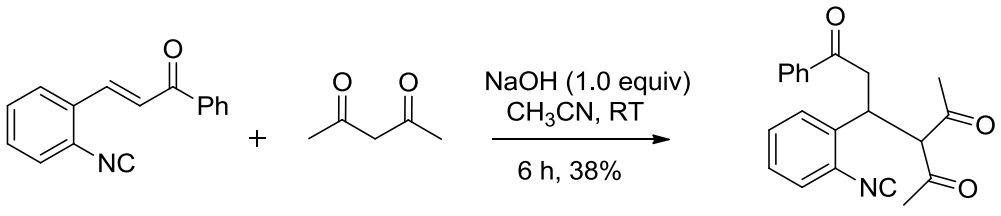
Synthesis of 5



1 **2** **5**

Typical synthetic procedure (with **5a** as an example) To a solution of (*E*)-3-(2-isocyanophenyl)-1-phenylprop-2-en-1-one (**1a**) (70 mg, 0.3 mmol) and pentane-2,4-dione (**2a**) (0.037 ml, 0.36 mmol) in CH_3CN (2 mL) at 80 ^oC, DBU (0.014 ml, 0.09 mmol) was added, under a N_2 atmosphere. The mixture was then stirred for 4-5 h , until substrate **1a** had been consumed as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane (3*15 ml). The organic layer was washed with brine (3*40 ml), dried over $MgSO_4$ and concentrated. Purification of the crude product with flash column chromatography (silica gel; petroleum ether: ethyl acetate = 6:1) gave **5a** 75 mg, 92 % yield as a colorless oil.

Synthesis of 6a

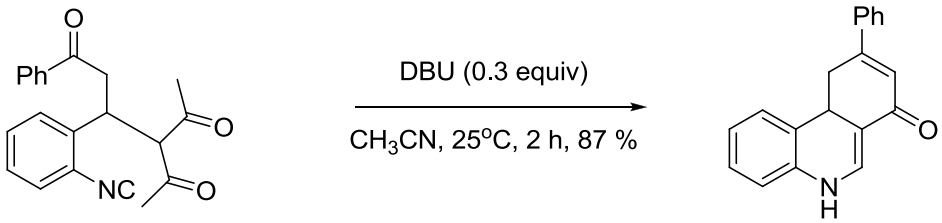


1a **2a** **6a**

To a solution of (E)-3-(2-isocyanophenyl)-1-phenylprop-2-en-1-one (**1a**) (350 mg, 1.5 mmol) and pentane-2,4-dione (**2a**) (0.185 ml, 1.8 mmol) in CH_3CN (2 mL) at 25 ^oC, NaOH (60 mg, 1.5 mmol) was added, The mixture was then stirred for 6.0 h, until **4a** had been indicated by TLC. The

resulting mixture was concentrated and taken up by dichloromethane (3*15 ml). The organic layer was washed with brine (3*40 ml), dried over $MgSO_4$ and concentrated. Purification of the crude product with flash column chromatography (silica gel; petroleum ether: ethyl acetate = 5:1) gave **6a** 190 mg, 38 % yield as a oil, recovery **1a** 27%.

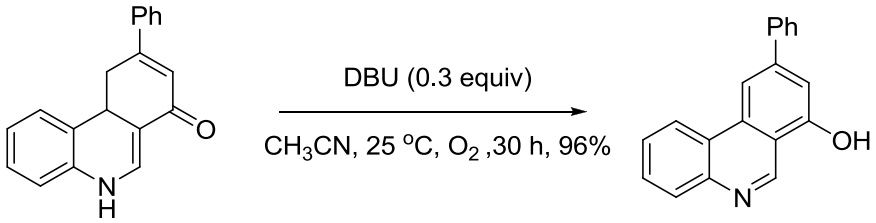
Synthesis of 4a from 6a



6a **4a**

To a solution of 4-acetyl-3-(2-isocyanophenyl)-1-phenylhexane-1,5-dione (**6a**) (100 mg, 0.3 mmol) in CH_3CN (2 mL) at 25 ^oC, DBU (0.014 ml, 0.09 mmol) was added. The mixture was then stirred for 2 h, until substrate **6a** had been consumed as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane (3*15 ml). The organic layer was washed with brine (3*40 ml), dried over $MgSO_4$ and concentrated. Purification of the crude product with flash column chromatography (silica gel; petroleum ether: ethyl acetate = 4:1) gave **4a** 71 mg, 87 % yield as a yellow solid.

Synthesis of 3a from 4a

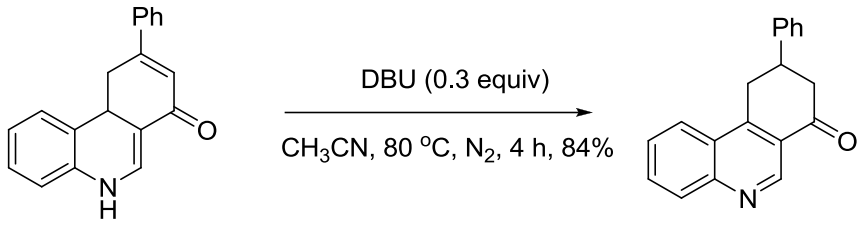


4a **3a**

To a solution of 9-Phenyl-10,10*a*-dihydrophenanthridin-7(5H)-one (**4a**) (54.6 mg, 0.2 mmol) in CH_3CN (2 mL) at 25 ^oC, DBU (0.009 ml, 0.06 mmol) was added under a O_2 atmosphere. The mixture was then stirred for 30 h, until substrate **4a** had been consumed as indicated by TLC. The

resulting mixture was concentrated and taken up by dichloromethane (3*15 ml). The organic layer was washed with brine (3*40 ml), dried over $MgSO_4$ and concentrated. Purification of the crude product with flash column chromatography (silica gel; petroleum ether: ethyl acetate = 2:1) gave **3a** 52 mg, 96 % yield as a yellow solid.

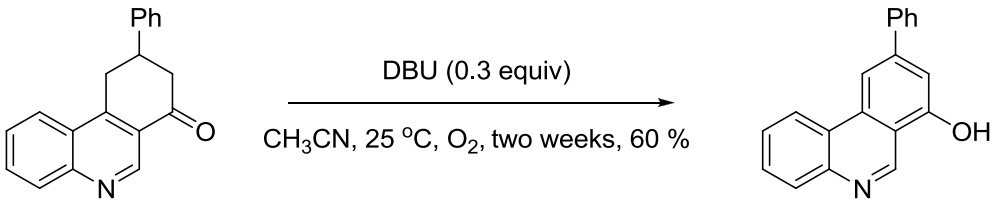
Synthesis of 5a from 4a



4a **5a**

To a solution of 9-Phenyl-10,10*a*-dihydrophenanthridin-7(5H)-one (**4a**) (54.6 mg, 0.2 mmol) in CH_3CN (2 mL) at 80 ^oC, DBU (0.009 ml, 0.06 mmol) was added, under a N_2 atmosphere. The mixture was then stirred for 4 h , until substrate **4a** had been consumed as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane（3*15 ml）. The organic layer was washed with brine (3*40 ml), dried over $MgSO_4$ and concentrated. Purification of the crude product with flash column chromatography (silica gel; petroleum ether: ethyl acetate = 6:1) gave **5a** 45.8 mg, 84 % yield as a colorless oil.

Synthesis of 3a from 5a

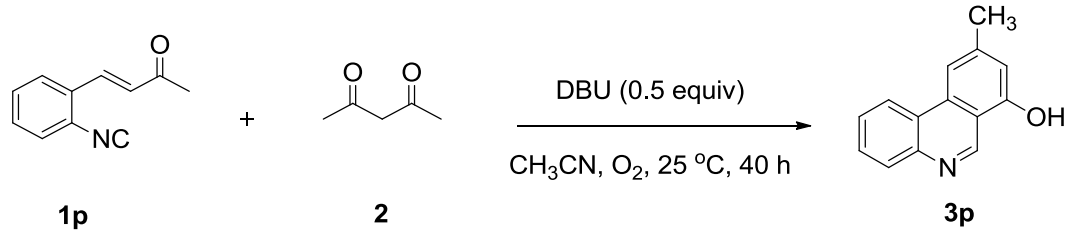


5a **3a**

To a solution of 9-Phenyl-9,10-dihydrophenanthridin-7(8H)-one (**5a**) (54.6 mg, 0.2 mmol) in CH_3CN (2 mL) at 25 ^oC, DBU (0.009 ml, 0.06 mmol) was added under a O_2 atmosphere. The mixture was then stirred for two weeks. The resulting mixture was concentrated and taken up by dichloromethane (3*15 ml) The organic layer was washed with brine (3*40 ml), dried over

$MgSO_4$ and concentrated. Purification of the crude product with flash column chromatography (silica gel; petroleum ether: ethyl acetate = 2:1) gave **3a** 32.5 mg, 60 % yield as a yellow solid. recovery **5a** 17.5 mg 32%.

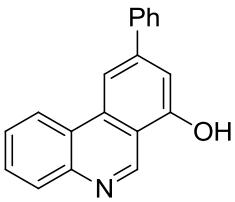
Gram Scale Synthesis of 3p



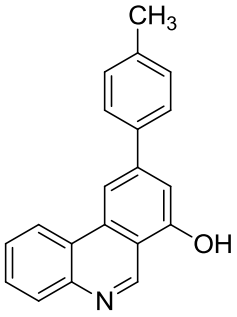
1p **2** **3p**

To a solution of (*E*)-4-(2-isocyanophenyl)but-3-en-2-one (**1p**) (1.71 g, 10 mmol) and pentane-2,4-dione (**2a**) (1.02 ml, 12 mmol) in CH_3CN (10 mL) at 25 ^oC, DBU (0.76 ml, 5.0 mmol) was added, under a O_2 atmosphere. The mixture was then stirred for 30 min , until substrate **1a** had been consumed as indicated by TLC. Then the mixture was then stirred for 40 h, until substrate **4p** had been consumed as indicated by TLC. The resulting mixture was poured into ice-water under stirring. The precipitated solid was collected by filtration, washed with water and dried in vacuo to afford the product 9-methylphenanthridin-7-ol **3p** 1.80 g, 86% as a pale yellow solid without purified.

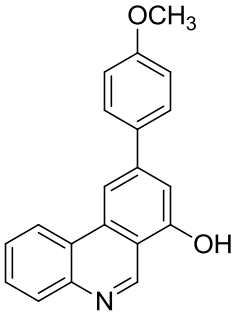
Analytical data of 3, 4, 5, 6



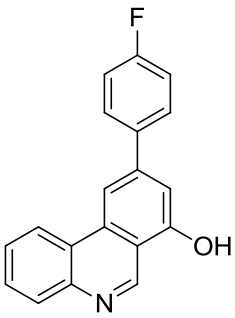
9-Phenylphenanthridin-7-ol (3a): solid; 78 mg, 97 %; m.p. 219-220 ^oC; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.41 (s, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.5 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.77 (t, J = 7.5 Hz, 1H), 7.86 (d, J = 7.5 Hz, 2H), 8.08 (d, J = 8.0 Hz, 1H), 8.47 (s, 1H), 8.89 (d, J = 8.5 Hz, 1H), 9.59 (s, 1H), 11.03 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 110.9, 111.1, 115.8, 124.0, 124.1, 127.4, 127.9, 128.8, 129.4, 129.6, 130.0, 134.2, 140.4, 144.5, 144.9, 148.4, 156.6; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{14}NO^+$ ($[M+H]^+$) 272.1071, Found 272.1072.



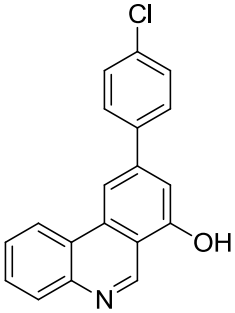
9-(*p*-Tolyl)phenanthridin-7-ol (3b): solid; 78 mg, 92 %; m.p. 264-266 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 2.36 (s, 3H), 7.32 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 1.0 Hz, 1H), 7.69 (t, J = 7.0 Hz, J = 1.0 Hz, 1H), 7.74 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 7.0 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 8.41 (s, 1H), 8.85 (d, J = 8.0 Hz, 1H), 9.58 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 21.2, 110.8, 111.0, 115.4, 124.1, 124.3, 127.8, 127.8, 128.6, 129.7, 130.2, 134.5, 137.2, 138.6, 143.0, 145.6, 148.0, 157.1; **HRMS** (ESI-TOF) m/z calculated for $C_{20}H_{16}NO^{+}$ ($[M+H]^{+}$) 286.1226, Found 286.1234.



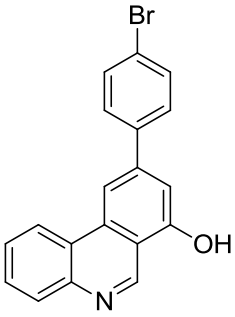
9-(4-Methoxyphenyl)phenanthridin-7-ol (3c): solid; 84 mg, 93 %; m.p. 210-212 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 3.82 (s, 3H), 7.09 (d, J = 8.0 Hz, 2H), 7.40 (s, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 7.81 (d, J = 8.0 Hz, 2H), 8.07 (d, J = 8.0 Hz, 1H), 8.41 (s, 1H), 8.86 (d, J = 8.0 Hz, 1H), 9.58 (s, 1H), 10.99 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 55.7, 110.3, 110.6, 114.9, 115.4, 124.0, 124.1, 127.4, 129.0, 129.3, 129.6, 132.5, 134.2, 144.4, 144.5, 148.2, 156.6, 160.1; **HRMS** (ESI-TOF) m/z calculated for $C_{20}H_{16}NO_2^{+}$ ($[M+H]^{+}$) 302.1176, Found 302.1183.



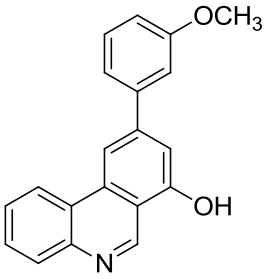
9-(4-Fluorophenyl)phenanthridin-7-ol (3d): solid; 79 mg, 92 %; m.p. 280-282 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.35-7.39 (m, 3H), 7.68 (t, J = 7.0 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 7.89 (d, J = 5.5 Hz, 1H), 7.91 (d, J = 5.5 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 8.44 (s, 1H), 8.87 (d, J = 8.0 Hz, 1H), 9.59 (s, 1H), 11.02 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 110.8 (d, J = 31.5 Hz), 111.1, 115.8, 116.2 (d, J = 21.0 Hz), 124.0 (d, J = 10.7 Hz), 127.4, 129.3, 129.9 (d, J = 8.2 Hz), 130.0, 134.2, 136.8, 143.4, 144.9, 148.4, 156.5, 161.8 (d, J = 244.1 Hz); **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{13}FNO^{+}$ ($[M+H]^{+}$) 290.0976, Found 290.0988.



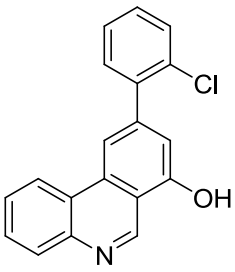
9-(4-Chlorophenyl)phenanthridin-7-ol (3e): solid; 89 mg, 98 %; m.p. 278-279 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.39 (s, 1H), 7.58 (d, J = 7.5 Hz, 2H), 7.69 (t, J = 7.0 Hz, 1H), 7.77 (t, J = 7.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 8.07 (d, J = 8.0 Hz, 1H), 8.46 (s, 1H), 8.87 (d, J = 8.0 Hz, 1H), 9.59 (s, 1H), 11.07 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 110.7, 111.1, 115.9, 124.0, 124.1, 127.4, 129.4, 129.4, 129.6, 129.8, 133.7, 134.2, 139.1, 143.1, 144.7, 148.3, 156.6; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{13}ClNO^{+}$ ($[M+H]^{+}$) 306.0680, Found 306.0677.



9-(4-Bromophenyl)phenanthridin-7-ol (3f): solid; 98mg, 94 %; m.p.296-298 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.38 (s, 1H), 7.68-7.73 (m, 3H), 7.76 (d, J = 7.5 Hz, 1H), 7.81 (d, J = 8.5 Hz, 2H), 8.07 (d, J = 8.0 Hz, 1H), 8.46 (s, 1H), 8.86 (d, J = 8.0 Hz, 1H), 9.58 (s, 1H), 11.05 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 110.6, 111.1, 115.9, 122.3, 124.0, 124.0, 127.4, 129.4, 129.9, 132.4, 134.2, 139.5, 143.2, 144.8, 148.3, 156.6; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{13}BrNO^{+}$ ([M+H]$^{+}$) 350.0175, Found 350.0163.

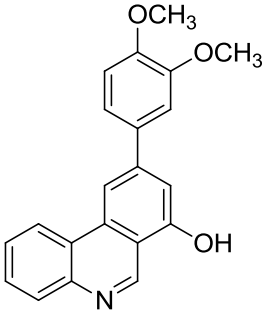


9-(3-Methoxyphenyl)phenanthridin-7-ol (3g): solid; 86 mg, 96 %; m.p. 280-282 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 3.87 (s, 3H), 7.01 (d, J = 6.5 Hz, 1H), 7.40-7.45 (m, 4H), 7.68 (t, J = 7.5 Hz, 1H), 7.76 (t, J = 7.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 8.46 (s, 1H), 8.89 (d, J = 7.5 Hz, 1H), 9.62 (s, 1H), 11.03 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 55.7, 111.1, 111.3, 113.4, 114.3, 115.9, 120.2, 124.0, 124.2, 127.4, 129.3, 129.9, 130.6, 134.1, 141.9, 144.5, 144.8, 148.4, 156.5, 160.3; **HRMS** (ESI-TOF) m/z calculated for $C_{20}H_{16}NO_2^{+}$ ([M+H]$^{+}$) 302.1176, Found 302.1177.

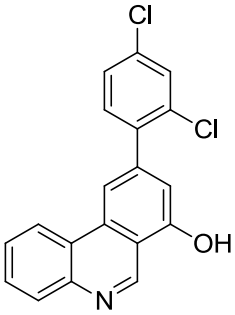


9-(2-Chlorophenyl)phenanthridin-7-ol (3h): solid; 83 mg, 91 %; m.p. 270-272 ^{o}C; **^{1}H NMR**

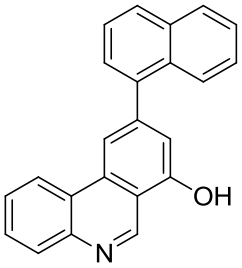
(500 MHz, DMSO-d_6) δ 7.22 (s, 1H), 7.44-7.49 (m, 2H), 7.56 (d, J = 6.5 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.21 (s, 1H), 8.72 (d, J = 8.5 Hz, 1H), 9.64 (s, 1H), 11.06 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 113.4, 113.7, 115.8, 123.8, 123.9, 127.5, 128.0, 129.4, 129.9, 130.1, 130.3, 131.8, 132.1, 133.6, 140.2, 143.2, 144.7, 148.3, 155.7; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{13}ClNO^+$ ($[M+H]^+$) 306.0680, Found 306.0672



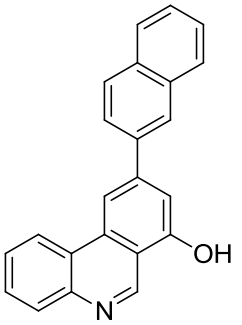
9-(3,4-Dimethoxyphenyl)phenanthridin-7-ol (3i): solid; 92 mg, 93 %; m.p.238-240 ^oC; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 3.82 (s, 3H), 3.93 (s, 3H), 7.09 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 11.0 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 8.44 (s, 1H), 8.90 (s, 1H), 9.59 (s, 1H), 10.96 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 56.0, 56.2, 110.6, 110.8, 111.5, 112.6, 115.5, 120.3, 124.1, 124.2, 127.3, 129.3, 129.9, 133.0, 134.2, 144.6, 144.8, 148.4, 149.6, 149.7, 156.5; **HRMS** (ESI-TOF) m/z calculated for $C_{21}H_{18}NO_3^+$ ($[M+H]^+$) 332.1281, Found 332.1281.



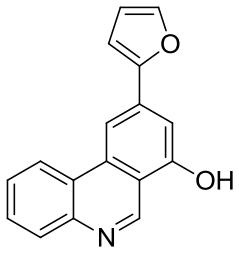
9-(2,4-Dichlorophenyl)phenanthridin-7-ol (3j): solid; 95 mg, 94 %; m.p.>300 ^oC; This compound couldn't dissolved in DMSO-d_6; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{12}Cl_2NO^+$ ($[M+H]^+$) 340.0290, Found 340.0300.



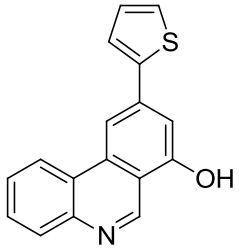
9-(Naphthalen-1-yl)phenanthridin-7-ol (3k): solid; 82 mg, 85 %; m.p.210-212 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.25 (s, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.59-7.65 (m, 3H), 7.76 (t, J = 7.5 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 8.03 (t, J = 8.0 Hz, 2H), 8.10 (d, J = 8.0 Hz, 1H), 8.28 (s, 1H), 8.71 (d, J = 8.0 Hz, 1H), 9.67 (s, 1H), 11.03 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 114.1, 115.8, 123.8, 123.9, 125.7, 126.0, 126.5, 127.0, 127.5, 127.5, 128.6, 128.8, 129.3, 130.0, 131.2, 133.8, 133.8, 139.8, 144.6, 144.9, 148.4, 155.9; **HRMS** (ESI-TOF) m/z calculated for $C_{23}H_{16}NO^{+}$ ($[M+H]^{+}$) 322.1226, Found 322.1222.



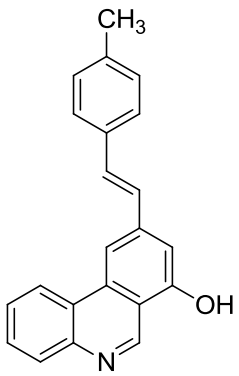
9-(Naphthalen-2-yl)phenanthridin-7-ol (3l): solid; 84 mg, 88%; m.p.247-249 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.55-7.59 (m, 3H), 7.71 (t, J = 7.5 Hz, 1H), 7.78 (t, J = 7.5 Hz, 1H), 7.97 (d, J = 7.5 Hz, 1H), 8.04-8.12 (m, 4H), 8.45 (s, 1H), 8.63 (s, 1H), 8.93 (d, J = 8.0 Hz, 1H), 9.65 (s, 1H), 11.06 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 111.2, 112.4, 115.9, 124.0, 124.2, 125.9, 126.8, 127.0, 127.0, 127.4, 128.0, 128.9, 129.1, 129.3, 130.0, 133.1, 133.7, 134.2, 137.7, 144.3, 145.0, 148.4, 156.6; **HRMS** (ESI-TOF) m/z calculated for $C_{23}H_{16}NO^{+}$ ($[M+H]^{+}$) 322.1226, Found 322.1237.



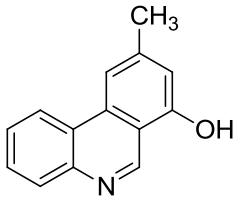
9-(Furan-2-yl)phenanthridin-7-ol (3m): solid; 72 mg, 92 %; m.p.215-217 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 6.71 (s, 1H), 7.34 (d, J = 3.0 Hz, 1H), 7.48 (s, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.77 (t, J = 7.5 Hz, 1H), 7.89 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 8.52 (s, 1H), 8.82 (d, J = 8.5 Hz, 1H), 9.53 (s, 1H), 11.07 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 107.1, 107.7, 109.0, 113.0, 115.8, 123.9, 123.9, 127.5, 129.5, 129.8, 134.1, 134.3, 144.6, 144.7, 148.2, 153.1, 156.7; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{12}NO_2^+$ ([M+H]$^+$) 262.0863, Found 262.0870.



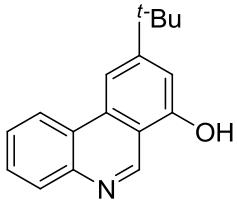
9-(Thiophen-2-yl)phenanthridin-7-ol (3n): solid; 77 mg, 93 %; m.p.216-218 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.24 (s, 1H), 7.41 (s, 1H), 7.69 (s, 2H), 7.76 (d, J = 7.0 Hz, 1H), 7.87 (s, 1H), 8.06 (d, J = 7.5 Hz, 1H), 8.49 (s, 1H), 8.84 (d, J = 8.0 Hz, 1H), 9.54 (s, 1H), 11.09 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 109.2, 109.6, 115.8, 123.9, 123.9, 126.1, 127.5, 127.8, 129.3, 129.5, 129.6, 134.4, 137.9, 143.4, 144.5, 148.0, 156.8; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{12}NOS^+$ ([M+H]$^+$) 278.0634, Found 278.0636.



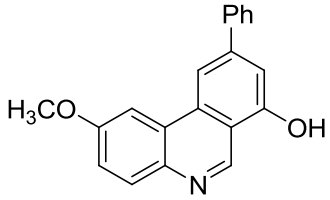
(*E*)-9-(4-Methylstyryl)phenanthridin-7-ol (3o): solid; 70 mg, 75 %; m.p.240-242 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 2.33 (s, 3H), 7.23 (d, J = 8.0 Hz, 2H), 7.34 (s, 1H), 7.39 (d, J = 16.5 Hz, 1H), 7.47 (d, J = 16.5 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.71 (t, J = 7.0 Hz, 1H), 7.77 (t, J = 7.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 8.44 (s, 1H), 8.79 (d, J = 8.5 Hz, 1H), 9.51 (s, 1H), 10.89 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 21.4, 109.8, 111.4, 116.2, 123.7, 124.0, 127.3, 127.3, 127.9, 129.3, 129.9, 130.0, 131.4, 134.1, 134.4, 138.2, 141.5, 145.0, 148.3, 156.2; **HRMS** (ESI-TOF) m/z calculated for $C_{22}H_{18}NO^{+}$ ($[M+H]^{+}$) 312.1383, Found 312.1392.



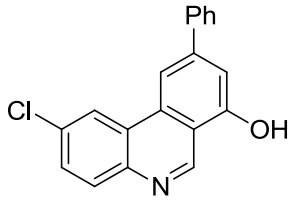
9-Methylphenanthridin-7-ol (3p): solid; 56 mg, 90 %; m.p.187-189 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 2.51 (s, 3H), 6.79 (s, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.73 (t, J = 7.5 Hz, 1H), 8.02 (d, J = 9.0 Hz, 2H), 8.65 (d, J = 8.0 Hz, 1H), 9.49 (s, 1H), 10.74 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 22.7, 112.9, 113.5, 114.9, 123.6, 123.8, 127.2, 129.1, 129.9, 133.7, 143.2, 144.8, 148.4, 155.9; **HRMS** (ESI-TOF) m/z calculated for $C_{14}H_{12}NO^{+}$ ($[M+H]^{+}$) 210.0913, Found 210.0921.



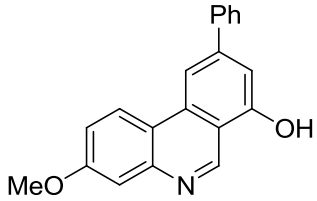
9-(tert-Butyl)phenanthridin-7-ol (3q): solid; 38 mg, 50 %; m.p.198-199 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 1.42 (s, 9H), 7.22 (d, J = 1.5 Hz, 1H), 7.67 (td, J = 8.0 Hz, J = 1.0 Hz, 1H), 7.74 (td, J = 8.0 Hz, J = 1.0 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 8.15 (s, 1H), 8.76 (d, J = 7.5 Hz, 1H), 9.49 (s, 1H), 10.65 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 31.5, 35.8, 108.0, 109.0, 110.3, 114.9, 123.6, 124.1, 127.2, 129.0, 129.9, 133.3, 144.7, 148.2, 155.8, 156.0. **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{18}NO^{+}$ ($[M+H]^{+}$) 252.1383, Found 252.1386.



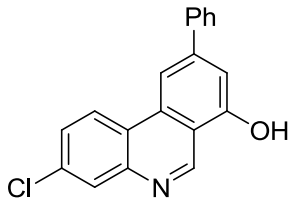
2-Methoxy-9-phenylphenanthridin-7-ol (3r): solid; 84 mg, 93 %; m.p. 214-216 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 4.01 (s, 3H), 7.37 (d, J = 9.0 Hz, 1H), 7.41 (s, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.5 Hz, 2H), 7.87 (d, J = 7.5 Hz, 2H), 7.99 (d, J = 9.0 Hz, 1H), 8.22 (s, 1H), 8.46 (s, 1H), 9.47 (s, 1H), 10.95 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 56.3, 104.4, 111.0, 111.5, 116.0, 119.5, 125.3, 128.0, 128.6, 129.4, 131.4, 133.8, 140.2, 140.6, 144.1, 145.7, 156.4, 158.6; **HRMS** (ESI-TOF) m/z calculated for $C_{20}H_{16}NO_2^+$ ([M+H]$^+$) 302.1176, Found 302.1185.



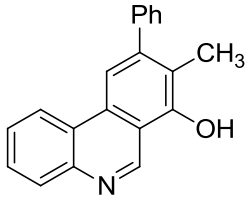
2-Chloro-9-phenylphenanthridin-7-ol (3s): solid; 71 mg, 78 %; m.p. 215-216 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.46 (t, J = 6.0 Hz, 2H), 7.55 (t, J = 6.0 Hz, 2H), 7.75 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 7.5 Hz, 2H), 8.05 (d, J = 8.5 Hz, 1H), 8.51 (s, 1H), 9.02 (s, 1H), 9.56 (s, 1H), 11.06 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 111.4, 111.5, 115.8, 123.5, 125.5, 127.9, 128.8, 129.4, 129.5, 131.8, 132.2, 133.2, 140.0, 143.4, 144.8, 148.8, 156.5; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{13}ClNO^+$ ([M+H]$^+$) 306.0680, Found 306.0679.



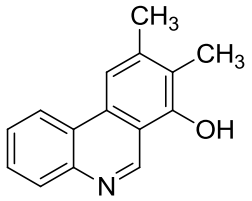
3-Methoxy-9-phenylphenanthridin-7-ol (3t): solid; 75 mg, 94 %; m.p. 213-214 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 3.94 (s, 3H), 7.30-7.32 (m, 2H), 7.45 (t, J = 7.5 Hz, 1H), 7.53-7.56 (m, 3H), 7.84 (d, J = 7.5 Hz, 2H), 8.35 (s, 1H), 8.76 (d, J = 9.0 Hz, 1H), 9.55 (s, 1H), 10.95 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 55.9, 109.7, 110.2, 110.6, 115.1, 117.8, 118.1, 125.3, 127.8, 128.7, 129.5, 134.4, 140.5, 144.5, 146.6, 148.8, 156.6, 160.2; **HRMS** (ESI-TOF) m/z calculated for $C_{20}H_{16}NO_2^+$ ([M+H]$^+$) 302.1176, Found 302.1183.



3-Chloro-9-phenylphenanthridin-7-ol (3u) solid; 76 mg, 83 %; m.p. 216-217 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.42 (s, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.5 Hz, 2H), 7.68 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 2H), 8.07 (s, 1H), 8.43 (s, 1H), 8.90 (d, J = 8.5 Hz, 1H), 9.57 (s, 1H), 11.09 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 111.2, 111.2, 115.8, 123.0, 126.2, 127.5, 127.9, 128.7, 128.8, 129.5, 133.6, 133.7, 140.2, 145.0, 145.7, 149.8, 156.7; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{13}ClNO^{+}$ ($[M+H]^{+}$) 306.0680, Found 306.0680.

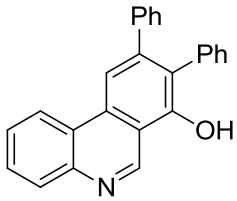


8-Methyl-9-phenylphenanthridin-7-ol (3v): solid; 79 mg, 93 %; m.p. 209-210 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 2.27 (s, 3H), 7.43-7.53 (m, 5H), 7.63 (t, J = 7.5 Hz, 1H), 7.72 (t, J = 7.5 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 8.11 (s, 1H), 8.69 (d, J = 8.5 Hz, 1H), 9.69 (s, 1H),9.94 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 14.6, 114.6, 116.5, 121.0, 123.5, 123.8, 127.4, 127.9, 128.7, 128.8, 129.6, 129.8, 130.9, 141.7, 144.2, 146.9, 148.8, 153.4; **HRMS** (ESI-TOF) m/z calculated for $C_{20}H_{16}NO^{+}$ ($[M+H]^{+}$) 286.1226, Found 286.1230.

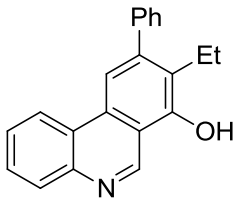


8,9-Dimethylphenanthridin-7-ol (3w): solid; 55 mg, 83%; m.p. 258-260 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 2.32 (s, 3H), 2.50 (s, 3H), 7.65 (t, J = 7.5 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 8.13 (s, 1H), 8.66 (d, J = 8.0 Hz, 1H), 9.60 (s, 1H), 9.68 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 12.8, 21.8, 114.4, 116.2, 122.3, 123.3, 123.8, 127.2, 128.6, 129.8, 130.9, 142.8, 144.2, 148.9, 152.4; **HRMS** (ESI-TOF) m/z calculated for $C_{15}H_{14}NO^{+}$ ($[M+H]^{+}$) 224.1070,

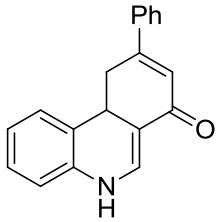
Found 224.1076.



8,9-Diphenylphenanthridin-7-ol (3x): solid; 83 mg, 80 %; m.p. 290-292 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.12-7.26 (m, 10H), 7.67 (s, 1H), 7.77 (s, 1H), 8.10 (d, J = 7.5 Hz, 1H), 8.27 (s, 1H), 8.78 (d, J = 7.5 Hz, 1H), 9.72 (s, 1H), 9.76 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 115.3, 116.9, 123.7, 123.8, 127.2, 127.2, 127.6, 128.1, 128.2, 129.3, 129.9, 130.1, 131.8, 132.4, 136.5, 141.5, 144.5, 146.0, 149.0, 152.7; **HRMS** (ESI-TOF) m/z calculated for $C_{25}H_{18}NO^{+}$ ([M+H]$^{+}$) 348.1388, Found 348.1388.

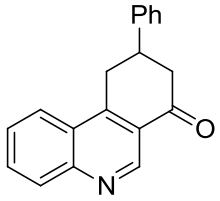


8-Ethyl-9-phenylphenanthridin-7-ol (3y) : solid; 71 mg, 79 %; m.p. 212-214 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 1.02 (t, J = 7.5 Hz, 3H), 2.73 (q, J = 7.0 Hz, 2H), 7.42-7.46 (m, 3H), 7.50 (t, J = 7.5 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.72 (t, J = 7.5 Hz, 1H), 8.05 (d, J = 8.5 Hz, 2H), 8.65 (d, J = 8.0 Hz, 1H), 9.69 (s, 1H), 9.96 (s, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 14.8, 20.5, 114.9, 116.8, 123.5, 123.8, 127.4, 127.6, 127.8, 128.6, 128.9, 129.3, 129.8, 130.8, 141.8, 144.2, 146.9, 148.8, 153.0; **HRMS** (ESI-TOF) m/z calculated for $C_{21}H_{18}NO^{+}$ ([M+H]$^{+}$) 300.1383 , Found 300.1399.

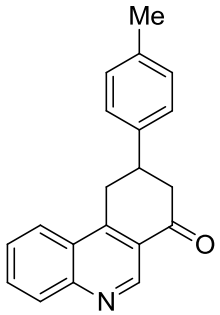


9-Phenyl-10,10*a*-Dihydrophenanthridin-7(5H)-one (4a): yellow solid; 80 mg, 98 %; m.p. 114-116 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 2.85 (t, J = 14.0 Hz, 1H), 3.42 (dd, J = 5.5 Hz, J =

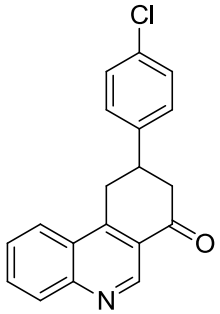
17.0 Hz, 1H), 4.27 (dd, *J* = 5.0 Hz, *J* = 12.5 Hz, 1H), 6.41 (s, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 5.5 Hz, 1H), 7.39-7.45 (m, 4H), 7.71 (d, *J* = 7.0 Hz, 2H), 9.35 (d, *J* = 5.5 Hz, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 33.5, 35.2, 105.5, 115.8, 123.2, 124.5, 126.7, 127.1, 127.9, 128.2, 129.1, 129.9, 134.4, 137.4, 139.4, 152.5, 185.5; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{16}NO^+$ ($[M+H]^+$) 274.1226, Found 274.1229.



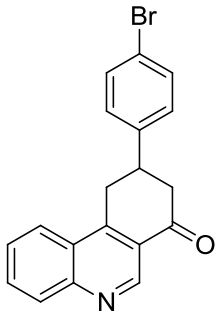
9-Phenyl-9,10-dihydrophenanthridin-7(8H)-one (5a): oil; 75 mg, 92 %; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.92-3.04 (m, 2H), 3.29 (dd, *J* = 11.5 Hz, *J* = 17.5 Hz, 1H), 3.52-3.56 (m, 1H), 3.77 (dd, *J* = 3.5 Hz, *J* = 17.5 Hz, 1H), 7.31-7.36 (m, 3H), 7.39-7.42 (m, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 9.46 (m, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 33.0, 40.1, 44.7, 123.9, 124.3, 125.7, 126.6, 127.3, 127.4, 128.9, 130.4, 131.7, 142.6, 148.3, 149.4, 150.2, 196.9; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{16}NO^+$ ($[M+H]^+$) 274.1226, Found 274.1234.



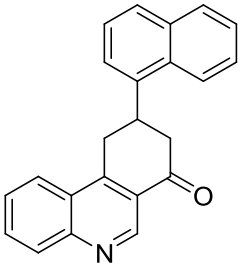
9-(*p*-Tolyl)-9,10-dihydrophenanthridin-7(8H)-one (5b): oil; 72 mg, 84 %; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.89-3.01 (m, 2H), 3.26 (dd, *J* = 11.5 Hz, *J* = 17.5 Hz, 1H), 3.48-3.53 (m, 1H), 3.73 (dd, *J* = 4.0 Hz, *J* = 17.5 Hz, 1H), 7.20-7.26 (m, 4H), 7.59-7.26 (m, 1H), 7.79-7.82(m, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 9.45 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 20.9, 33.1, 39.7, 44.8, 123.9, 124.3, 125.7, 126.5, 127.4, 129.5, 130.3, 131.7, 137.0, 139.7, 148.3, 149.4, 150.3, 197.0; **HRMS** (ESI-TOF) m/z calculated for $C_{20}H_{18}NO^+$ ($[M+H]^+$) 288.1383, Found 288.1386.



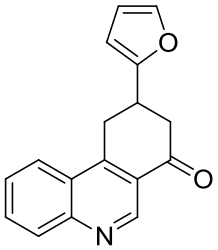
9-(4-Chlorophenyl)-9,10-dihydrophenanthridin-7(8H)-one (5c): oil; 82 mg, 91 %; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.85-2.99 (m, 2H), 3.23 (dd, *J* = 11.5 Hz, *J* = 17.5 Hz, 1H), 3.48-3.54 (m, 1H), 3.72 (dd, *J* = 3.5 Hz, *J* = 17.5 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 9.42 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 32.7, 39.4, 44.5, 123.7, 124.2, 125.5, 127.4, 128.0, 129.0, 130.3, 131.7, 132.9, 141.0, 148.2, 149.3, 149.8, 196.4; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{15}ClNO^+$ ($[M+H]^+$) 308.0837, Found 308.0843.



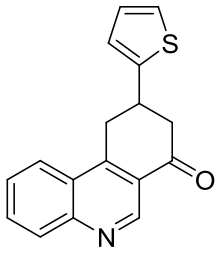
9-(4-Bromophenyl)-9,10-dihydrophenanthridin-7(8H)-one (5d): oil; 80 mg, 76 %; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.84-2.97 (m, 2H), 3.23 (dd, *J* = 11.5 Hz, *J* = 17.5 Hz, 1H), 3.46-3.52 (m, 1H), 3.71-3.75 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.58-7.62 (m, 1H), 7.78-7.81 (m, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 9.41 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 32.6, 39.5, 44.5, 121.0, 123.7, 124.2, 125.5, 127.5, 128.4, 130.3, 131.8, 132.0, 141.5, 148.2, 149.3, 149.8, 196.4; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{15}BrNO^+$ ($[M+H]^+$) 352.0332, Found 352.0331.



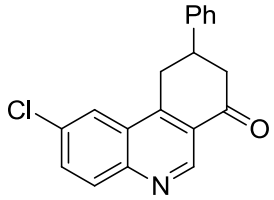
9-(Naphthalen-1-yl)-9,10-dihydrophenanthridin-7(8H)-one (5e): oil; 84 mg, 87 %; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.08-3.18 (m, 2H), 3.37 (dd, *J* = 11.0 Hz, *J* = 17.5 Hz, 1H), 3.95 (dd, *J* = 3.5 Hz, *J* = 17.5 Hz, 1H), 4.38-4.44 (m, 1H), 7.51-7.54 (m, 4H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.81-7.83 (m, 2H), 7.91-7.92 (m, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 9.53 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 32.7, 35.0, 44.5, 122.3, 122.7, 124.0, 124.4, 125.5, 125.7, 125.8, 126.5, 127.4, 127.8, 129.2, 130.4, 130.8, 131.7, 134.0, 138.3, 148.4, 149.5, 150.5, 197.2; **HRMS** (ESI-TOF) m/z calculated for $C_{23}H_{17}NO^{+}$ ($[M+H]^{+}$) 324.1383, Found 324.1377.



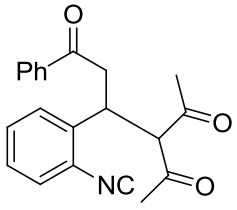
9-(Furan-2-yl)-9,10-dihydrophenanthridin-7(8H)-one (5f): oil; 71 mg, 91 %; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.90 (dd, *J* = 6.0 Hz, *J* = 16.5 Hz, 1H), 3.04 (dd, *J* = 3.5 Hz, *J* = 16.5 Hz, 1H), 3.40 (dd, *J* = 9.5 Hz, *J* = 17.0 Hz, 1H), 3.65-3.71 (m, 1H), 3.78 (dd, *J* = 4.5 Hz, *J* = 17.5 Hz, 1H), 6.12 (d, *J* = 3.5 Hz, 1H), 6.30 (dd, *J* = 2.0 Hz, *J* = 3.5 Hz, 1H), 7.35 (d, *J* = 1.5 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.78-7.81 (m, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 9.40 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 29.7, 33.3, 42.0, 105.2, 110.2, 123.8, 124.3, 125.6, 127.4, 130.3, 131.7, 141.8, 148.2, 149.3, 155.5, 196.0; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}NO_2^{+}$ ($[M+H]^{+}$) 264.1019, Found 264.1025.



9-(Thiophen-2-yl)-9,10-dihydrophenanthridin-7(8H)-one (5g): oil; 71 mg, 86 %; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.89 (dd, J = 12.0 Hz, J = 16.0 Hz, 1H), 3.11-3.15 (m, 1H), 3.34-3.40 (m, 1H), 3.81-3.88 (m, 2H), 6.95-6.98 (m, 2H), 7.21-7.22 (m, 1H), 7.61 (t, J = 7.0 Hz, 1H), 7.80 (t, J = 7.0 Hz, 1H), 8.05 (d, J = 8.5 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 9.41 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 33.5, 35.3, 45.6, 123.6, 123.8, 124.3, 125.5, 126.9, 127.5, 130.3, 131.8, 146.3, 148.2, 149.3, 149.4, 195.9. **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}NOS^{+}$ ($[M+H]^{+}$) 280.0791, Found 280.0795.



2-chloro-9-phenyl-9,10-dihydrophenanthridin-7(8H)-one (5h): oil; 66 mg, 72 %; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.95-3.06 (m, 2H), 3.28 (dd, J = 11.5 Hz, J = 17.5 Hz, 1H), 3.54-3.60 (m, 1H), 3.69 (dd, J = 4.0 Hz, J = 17.5 Hz, 1H), 7.32-7.36 (m, 3H), 7.40-7.43 (m, 2H), 7.73 (dd, J = 2.0 Hz, J = 8.5 Hz, 1H), 8.02 (d, J = 2.0 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 9.44 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 33.0, 40.0, 44.6, 123.5, 124.4, 126.6, 126.6, 127.5, 129.0, 131.9, 132.4, 133.5, 142.3, 147.8, 148.5, 149.3, 196.7; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{15}ClNO^{+}$ ($[M+H]^{+}$) 308.0837, Found 308.0839.

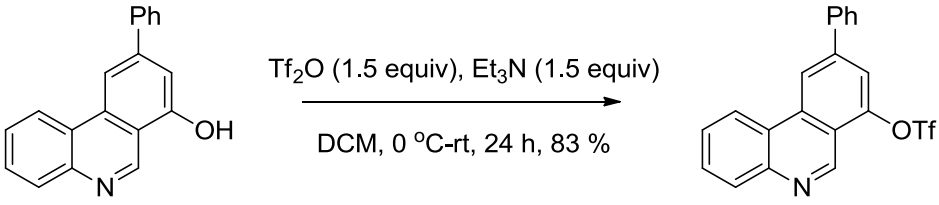


4-Acetyl-3-(2-isocyanophenyl)-1-phenylhexane-1,5-dione (6a): oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.07 (s, 3H), 2.23 (s, 3H), 3.37 (dd, J = 4.0 Hz, J = 17.0 Hz, 1H), 3.55 (dd, J = 9.0 Hz, J = 17.0

Hz, 1H), 4.52-4.59 (m, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 29.2, 30.4, 36.3, 40.2, 71.3, 127.7, 128.0, 128.0, 128.6, 129.1, 129.6, 133.3, 136.2, 136.7, 168.1, 197.1, 202.3, 202.6; **HRMS** (ESI-TOF) m/z calculated for $C_{21}H_{20}NO_3^+$([M+H]$^+$) 334.1438, Found 334.1445.

*2.3 General procedure and Spectroscopic Data for the synthesis of **7, 8, 9, 10, 11***

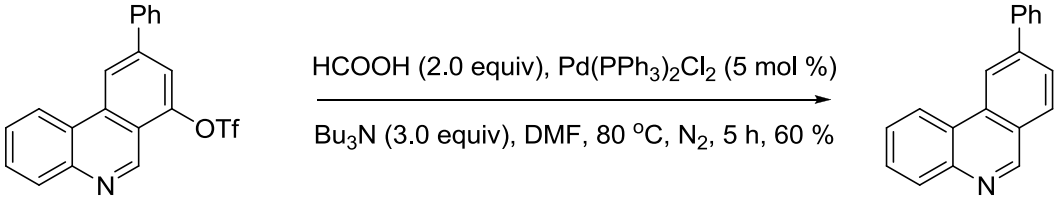
Synthesis of 7a



3 a **7 a**

To an ice-bath cooled solution of **3a** (271 mg, 1.0 mmol) in DCM (10 mL) , Et_3N (208.5 uL, 1.5 mmol) and $(CF_3SO_2)_2O$ (168 uL, 1.5 mmol) were added successively. The reaction mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with brine (30 mL) and extracted with DCM (3*10 mL). The combined organics were dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether/ EtOAc = 10/2, v/v) to afford the product **7a** in 83% yield.

Synthesis of 8a

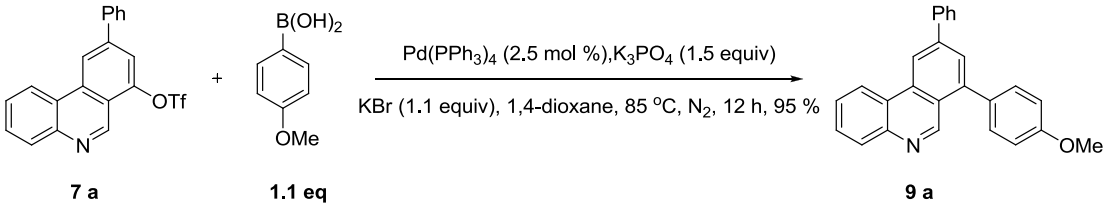


7 a **8 a**

An oven-dried 25 mL Schlenk tube was charged with $Pd(PPh_3)_2Cl_2$ (10.5 mg, 0.015 mmol), and was evacuated and refilled with N_2 three times. Then DMF (2.0 mL), **7a** (120.9 mg, 0.3 mmol), Bu_3N (216 uL, 0.9 mmol) and HCOOH (22.8 uL, 0.6 mmol) were added successively. The reaction mixture was stirred at 80 ℃ for 5 h. It was cooled to room temperature and diluted with

brine (30 mL), then extracted with EtOAc (3*10 mL). The combined organics were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether/EtOAc = 10/2, v/v) to afford the product **8a** in 60% yield.

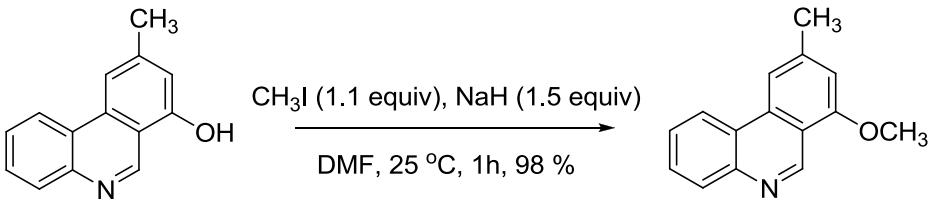
Synthesis of 9a



7 a **1.1 eq** **9 a**

An oven-dried 25 mL Schlenk tube was charged with **7a** (120.9 mg, 0.3 mmol), 4-Methoxyphenylboronic acid (39.5 mg, 0.33mmol), $Pd(PPh_3)_4$ (9.3 mg, 0.008mmol), K_3PO_4 (95.4 mg, 0.45 mmol) and KBr (39.3 mg, 0.33 mmol) and was evacuated and refilled with N_2 three times, followed by adding dioxane (2.0 mL). The reaction mixture was stirred at 85 ℃ for 12 h. The reaction mixture was cooled to room temperature and diluted with brine (30 mL), then extracted with EtOAc (3*10 mL). The combined organics were dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/EtOAc = 10/3, v/v) to afford the product **9a** in 95 % yield.

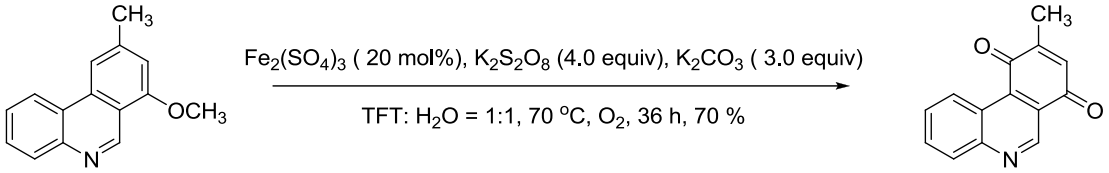
Synthesis of 10p



3p **10p**

To an solution of **3p** (209 mg, 1.0 mmol) in DMF (5 mL), CH_3I (67.9 uL, 1.1 mmol) and NaH (21.6 mg, 1.5 mmol) were added successively. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with brine (30 mL) and extracted with Et_2O (3*10 mL). The combined organics were dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether/EtOAc = 10/2, v/v) to afford the product **10p** in 98% yield.

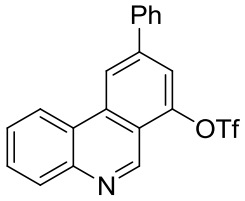
Synthesis of 11p



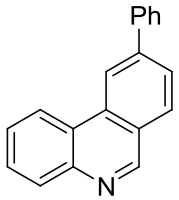
10p **11p**

A clean, oven-dried screw cap reaction tube with previously placed magnetic stir–bar was charged with **10p** (56 mg, 0.25 mmol), potassium per-disulphate (1 mmol, 270 mg). Then potassium carbonate (30 mg, 0.75 mmol,) and ferric sulphate (20 mol%, 20 mg) was introduced in this reaction mixture. The cap was fitted with a rubber septum and the reaction tube was evacuated and back filled with oxygen and this sequence was repeated three additional times. Oxygenated trifluorotoluene (1 mL) and Merck HPLC grade water (1 mL) was added to this mixture by syringe under the positive pressure of oxygen. The reaction mixture was vigorously stirred for 36 h in O_2 atmosphere in a preheated oil bath of 70 ℃. The reaction mixture was cooled to room temperature and extracted thrice with ethyl acetate (3*10 mL) and brine solution was added. The organic layer was collected and dried over anhydrous Na_2SO_4. Finally, it was concentrated and resulting arylated product was purified via silica gel column (petroleum ether/EtOAc = 10/2, v/v) to afford the product **11p** in 70 % yield.

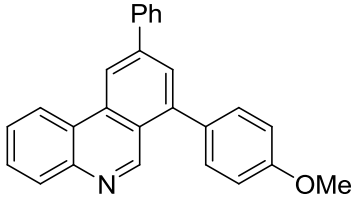
Analytical data of 7, 8, 9, 10 and 11



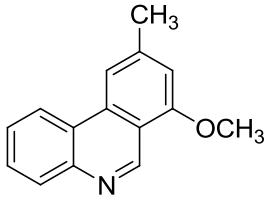
9-Phenylphenanthridin-7-yl trifluoromethanesulfonate (7a): solid; m.p. 106-108 °C; 83 %; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49-7.52 (m, 1H), 7.56-7.59 (m, 2H), 7.74-7.77 (m, 3H), 7.81-7.85 (m, 1H), 7.86 (d, J = 1.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.62 (d, J = 8.0 Hz, 1H), 8.78 (s, 1H), 9.56 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 117.5, 118.8, 120.0, 120.1, 122.3, 122.6, 127.6, 128.0, 129.0, 129.3, 129.9, 130.6, 134.8, 138.7, 144.4, 144.7, 145.5, 146.9. **HRMS** (ESI-TOF) m/z calculated for $C_{20}H_{13}F_3NO_3S^+$ ($[M+H]^+$) 404.0563, Found 404.0569.



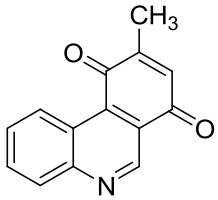
9-phenylphenanthridine (8a): solid; m.p. 92-94 ^{o}C; 60 %; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.48 (m, 1H), 7.54-7.57 (m, 2H), 7.69-7.72 (m, 1H), 7.75-7.79 (m, 3H), 7.94 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.66 (d, *J* = 8.0 Hz, 1H), 8.79 (s, 1H), 9.32 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 120.1, 122.2, 124.1, 125.3, 127.0, 127.0, 127.7, 128.2, 128.8, 129.0, 129.2, 130.2, 132.8, 140.6, 143.8, 144.7, 153.2. **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{14}N^{+}$ ($[M+H]^{+}$) 256.1121, Found 256.1116.



7-(4-methoxyphenyl)-9-phenylphenanthridine (9a): solid; m.p.124-126 ^{o}C; 95 %; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.5 Hz, 2H), 7.44-7.47 (m, 1H), 7.52-7.56 (m, 4H), 7.69-7.72 (m, 1H), 7.75-7.78 (m, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 1.5 Hz, 1H), 8.18 (d, *J* = 7.5 Hz, 1H), 8.70 (d, *J* = 7.5 Hz, 1H), 8.79 (s, 1H), 9.40 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 55.4, 113.9, 119.0, 122.3, 123.0, 124.0, 127.0, 127.7, 128.2, 128.2, 128.8, 129.0, 130.0, 131.0, 131.3, 133.4, 140.5, 142.4, 143.0, 144.2, 151.7, 159.5. **HRMS** (ESI-TOF) m/z calculated for $C_{26}H_{20}NO^{+}$ ($[M+H]^{+}$) 362.1539, Found 362.1540.



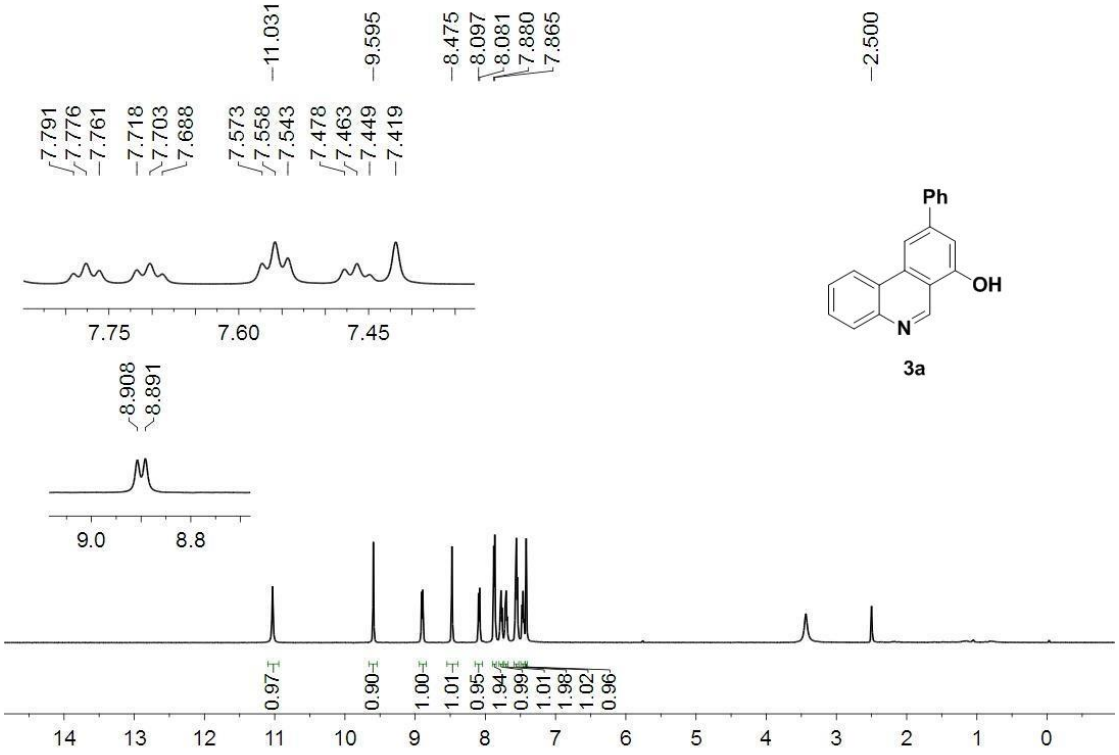
7-methoxy-9-methylphenanthridine (10p): solid; m.p. 87-88 ^{o}C; 98 %; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.48 (s, 3H), 3.92 (s, 3H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.76 (s, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 9.57 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 22.7, 55.4, 108.1, 113.2, 115.4, 122.4, 123.4, 126.3, 128.3, 129.7, 133.6, 142.1, 144.6, 147.9, 156.9. **HRMS** (ESI-TOF) m/z calculated for $C_{15}H_{14}NO^{+}$ ($[M+H]^{+}$) 224.1070, Found 224.1080.



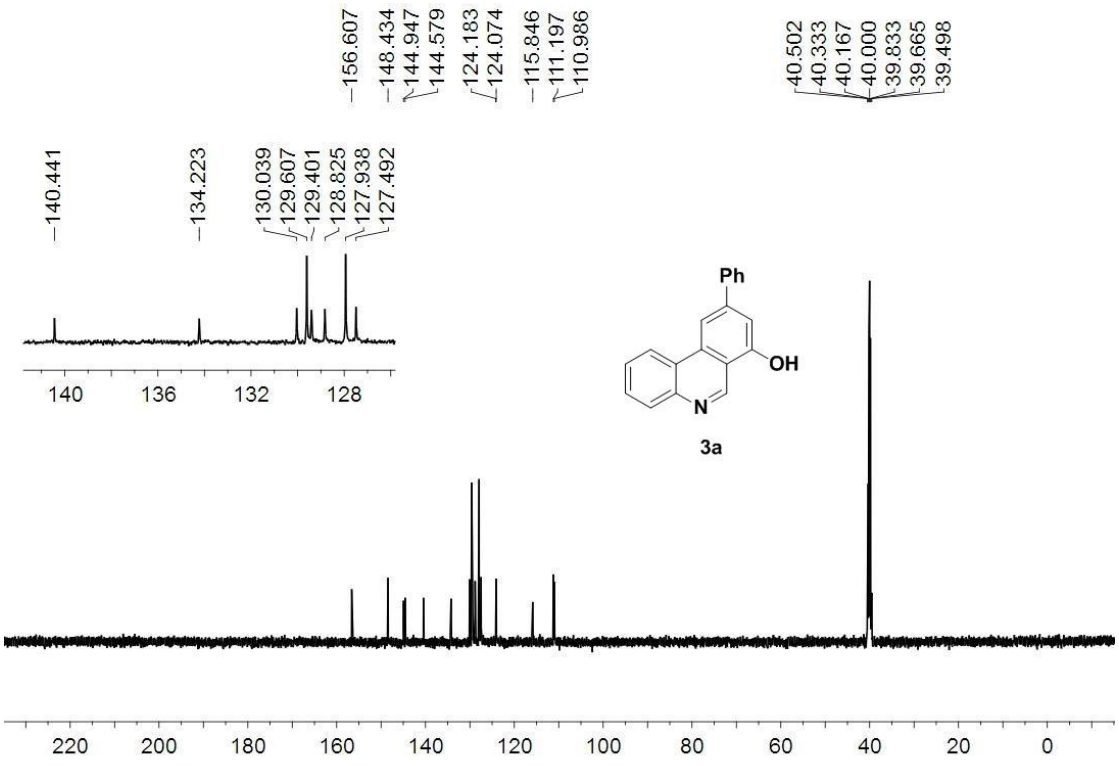
9-methylphenanthridine-7,10-dione (11p): yellow solid; m.p.176-177 ^{o}C; 70 %; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.26 (d, J = 1.5 Hz, 3H), 6.87 (d, J = 1.5 Hz, 1H), 7.78 (t, J = 7.0 Hz, 1H), 7.88 (t, J = 7.0 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 9.40 (d, J = 8.0 Hz, 1H), 9.60 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 16.8, 122.0, 122.9, 127.4, 130.2, 130.4, 131.8, 131.9, 133.2, 147.3, 149.2, 151.7, 185.1, 188.6. **HRMS** (ESI-TOF) m/z calculated for $C_{15}H_{10}NO^{+}$ ($[M+H]^{+}$) 224.0706, Found 224.0705.

3. Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds 3, 4, 5, 6, 7, 8, 9, 10, 11

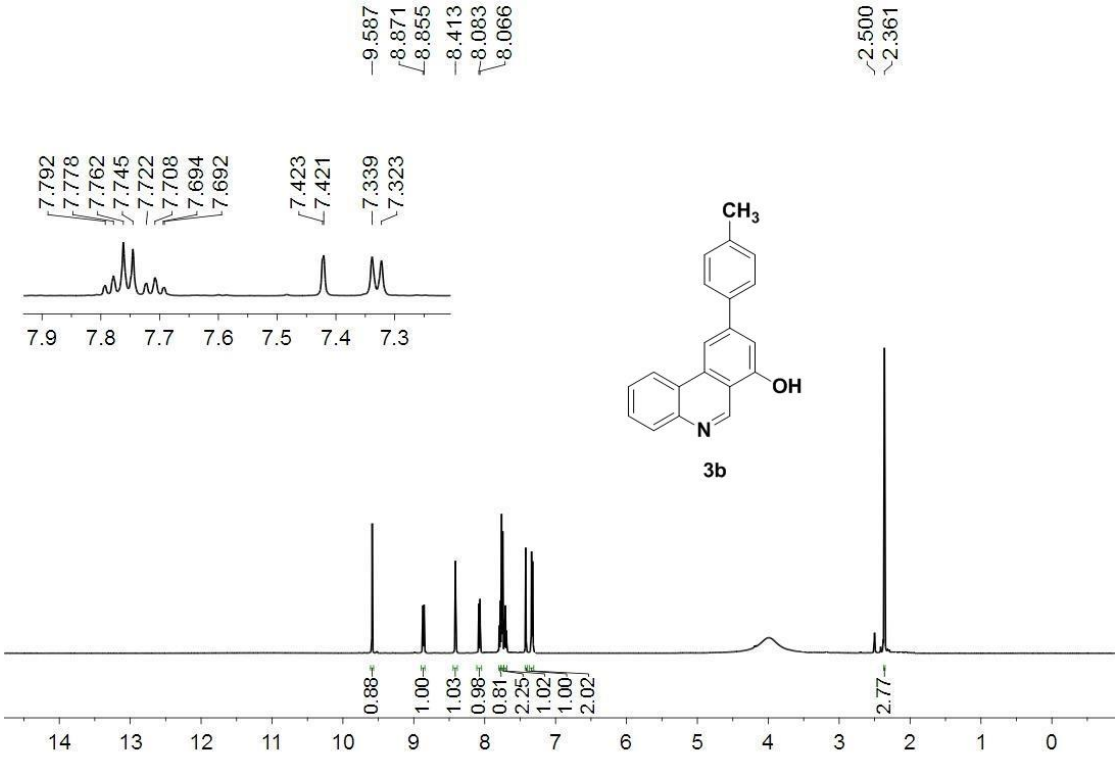
^{1}H NMR (500 MHz, DMSO-d_6**)** for **3a**



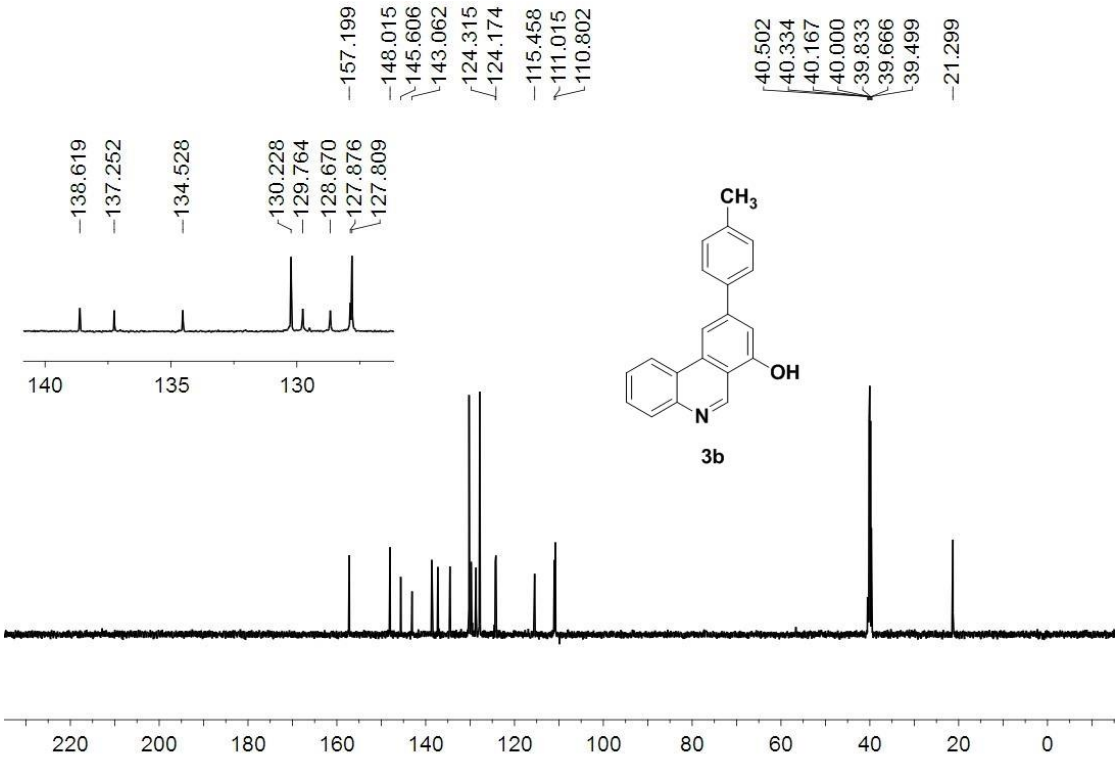
^{13}C NMR (125 MHz, DMSO-d_6) for **3a**



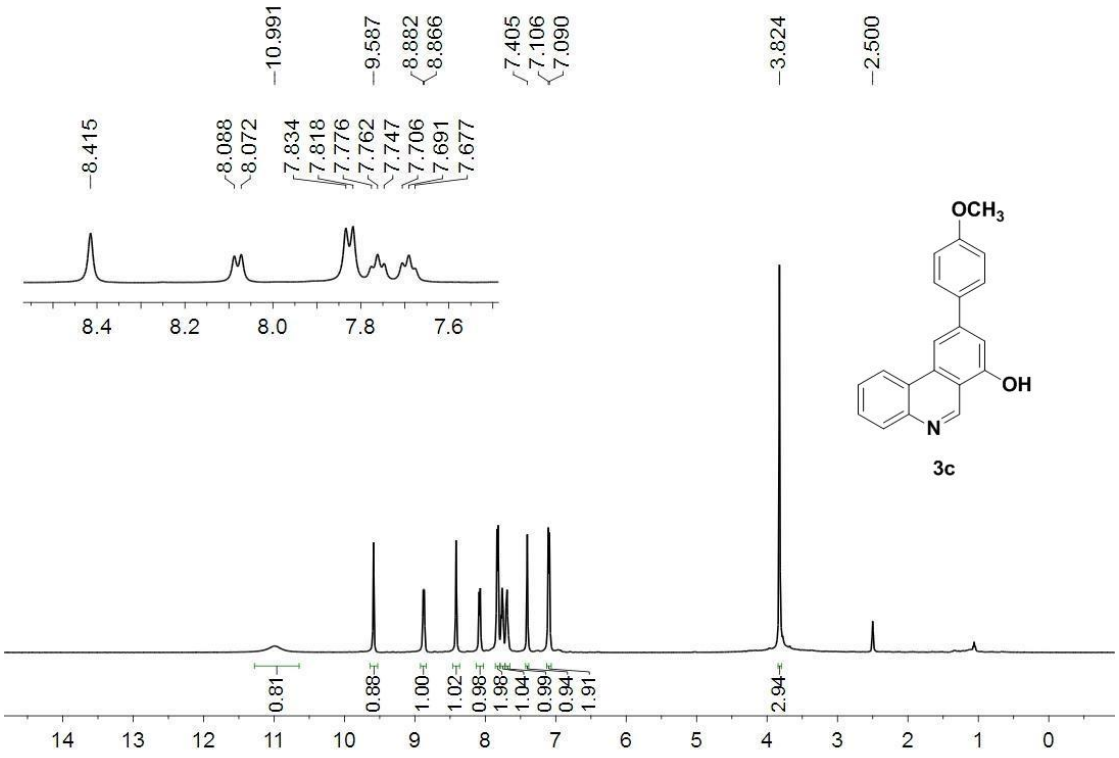
[1]H NMR (500 MHz, DMSO-d_6) for **3b**



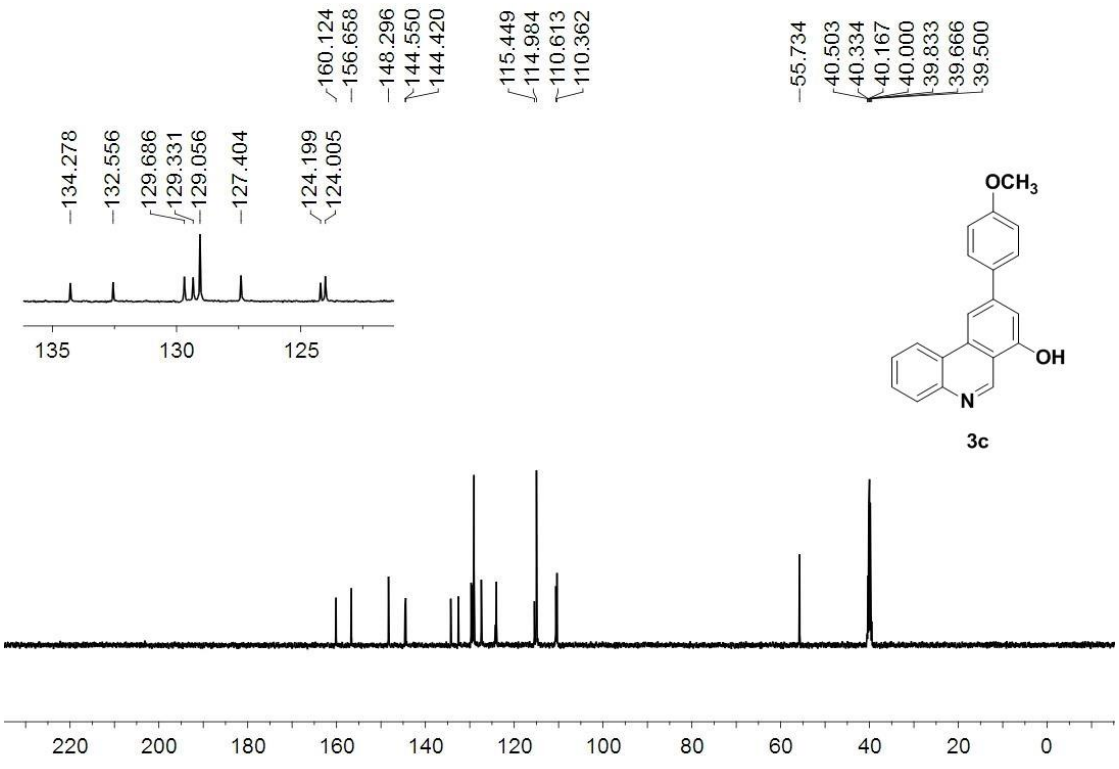
[13]C NMR (125 MHz, DMSO-d_6) for **3b**



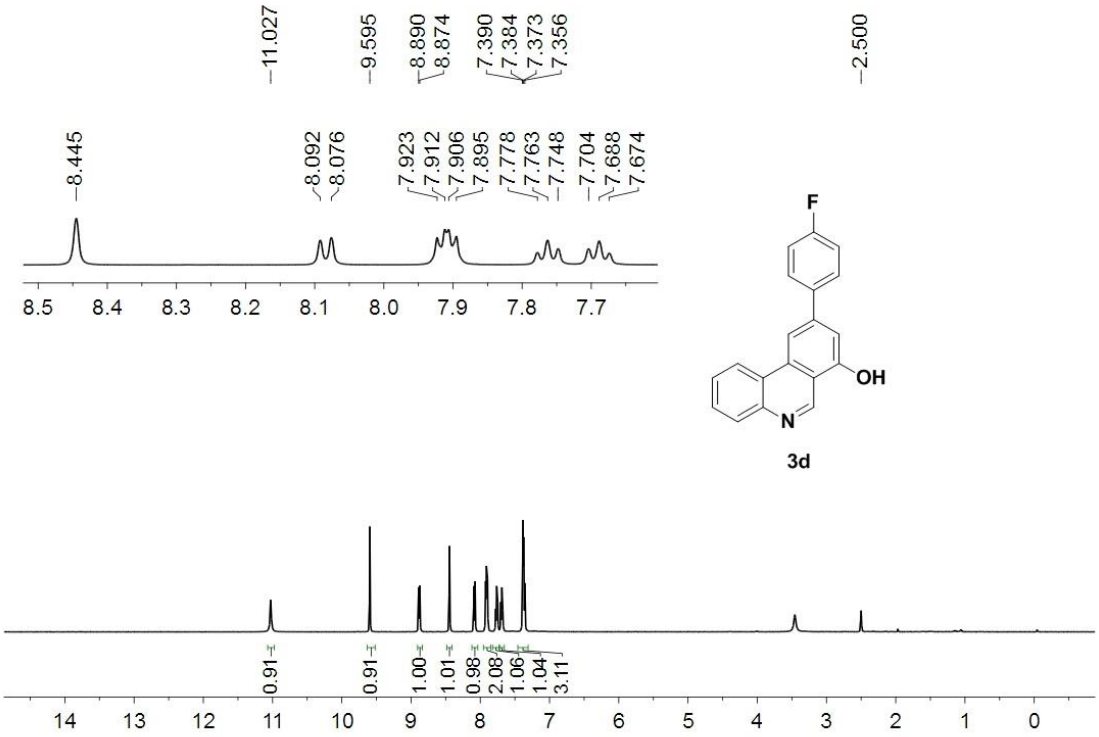
^{1}H NMR (500 MHz, DMSO-d_6) for **3c**



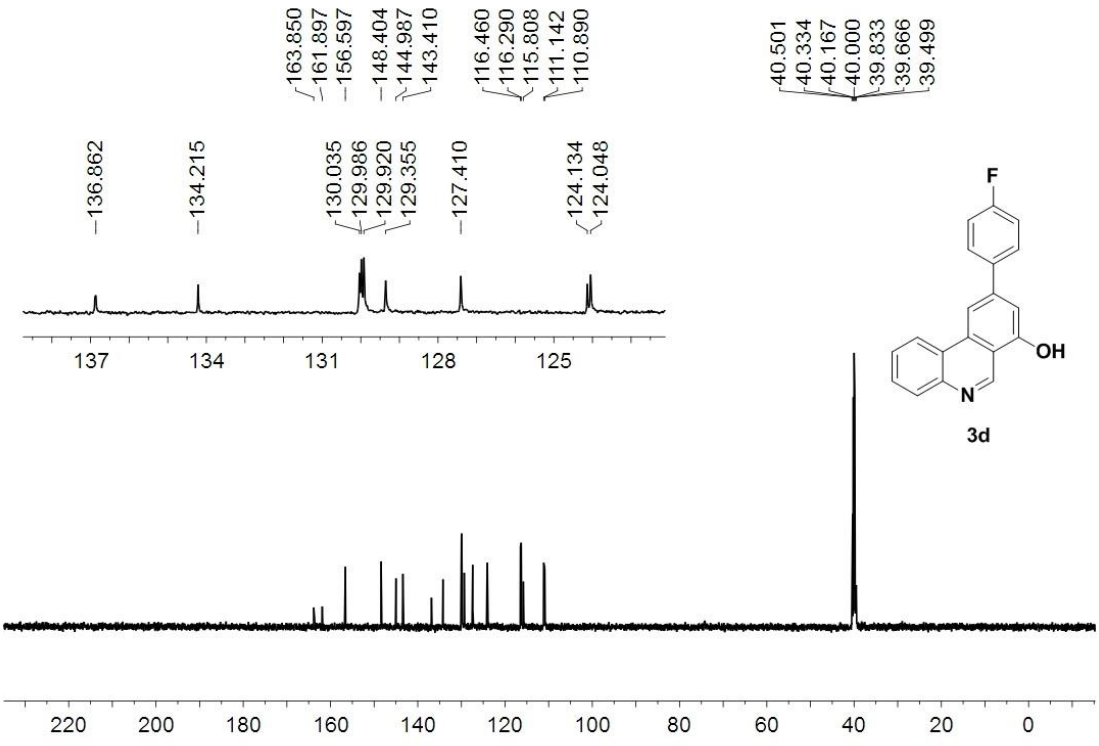
^{13}C NMR (125 MHz, DMSO-d_6) for **3c**



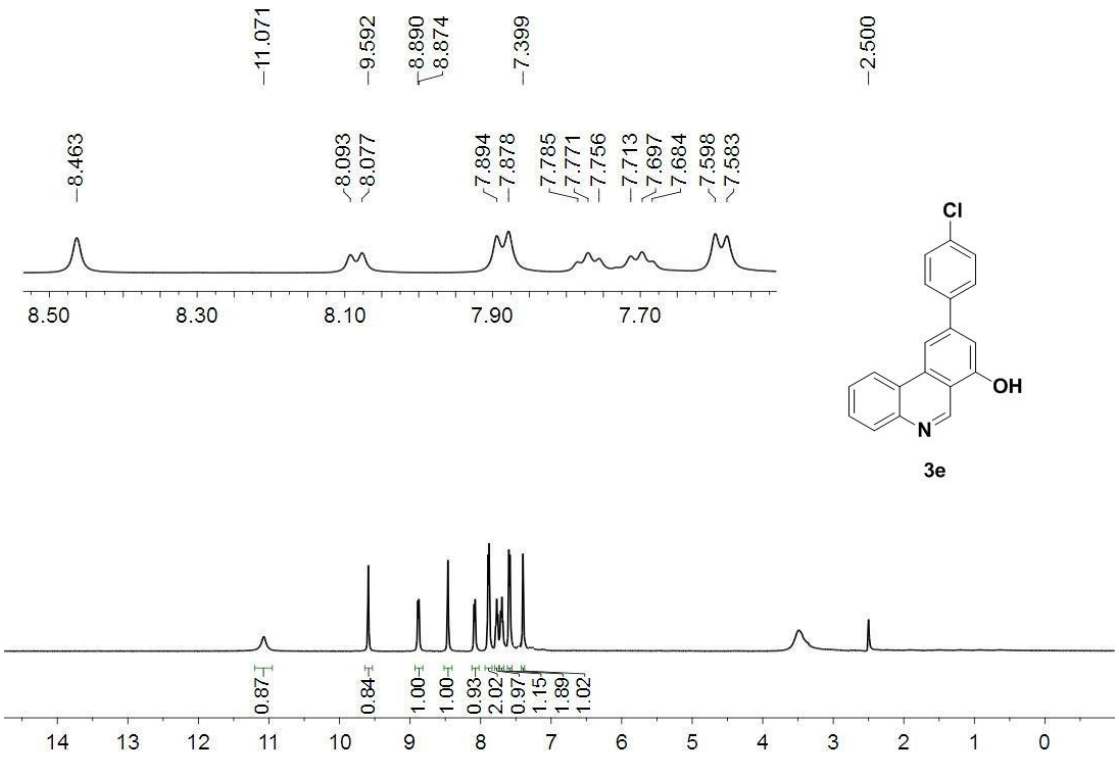
[1]H NMR (500 MHz, DMSO-d_6) for **3d**



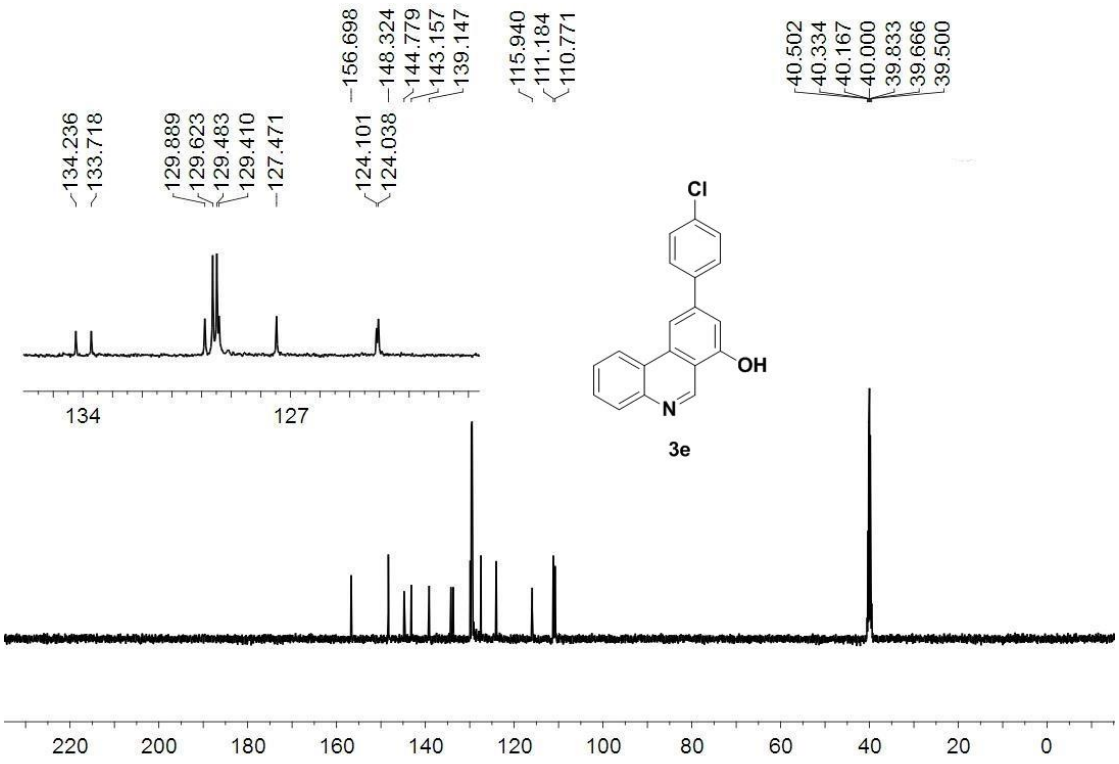
[13]C NMR (125 MHz, DMSO-d_6) for **3d**



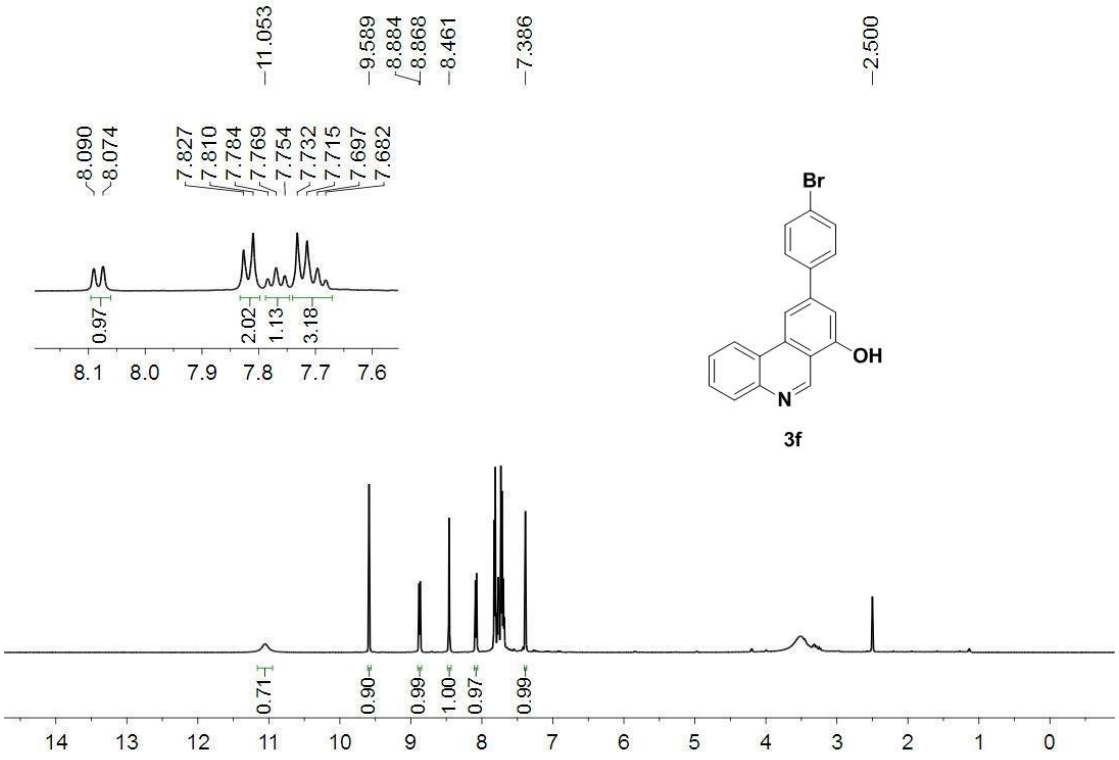
^{1}H NMR (500 MHz, DMSO-d_6) for **3e**



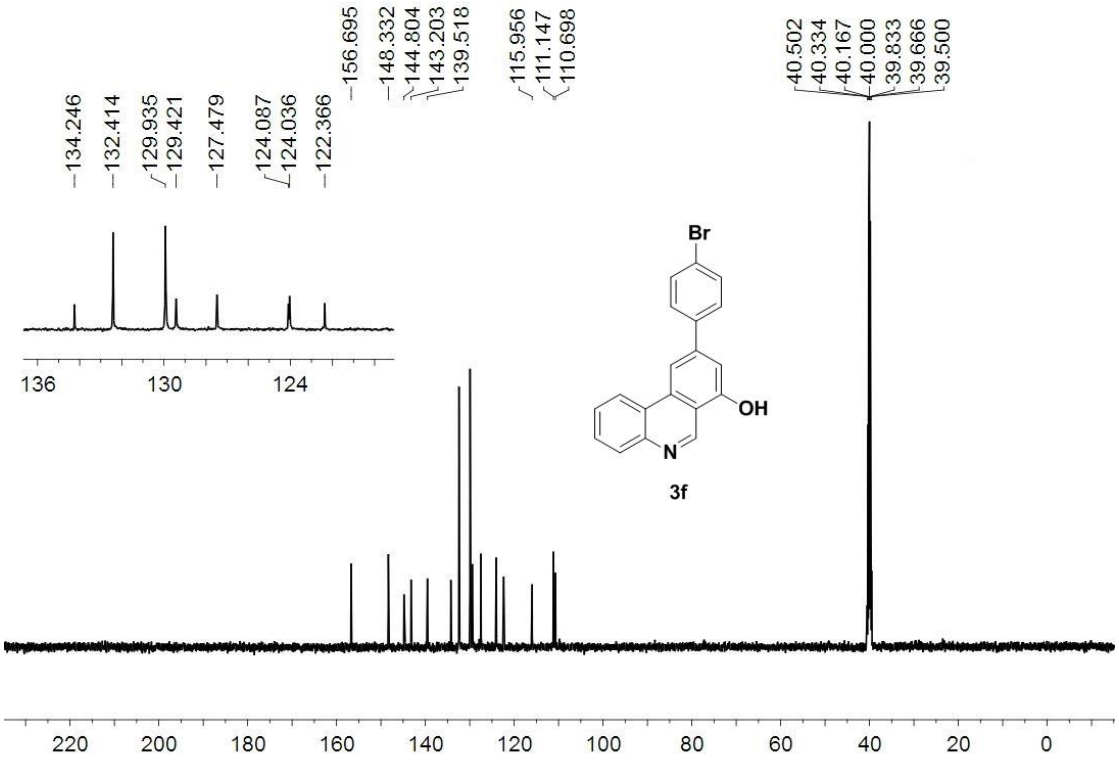
^{13}C NMR (125 MHz, DMSO-d_6) for **3e**



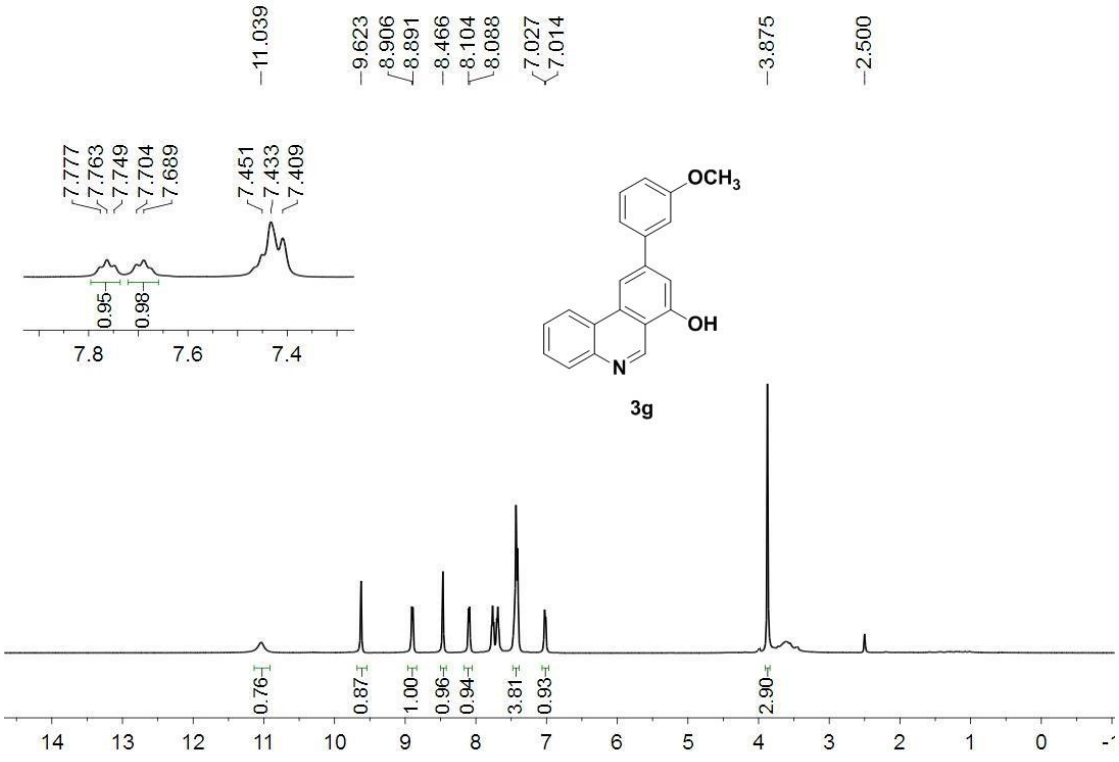
^{1}H NMR (500 MHz, DMSO-d_6) for **3f**



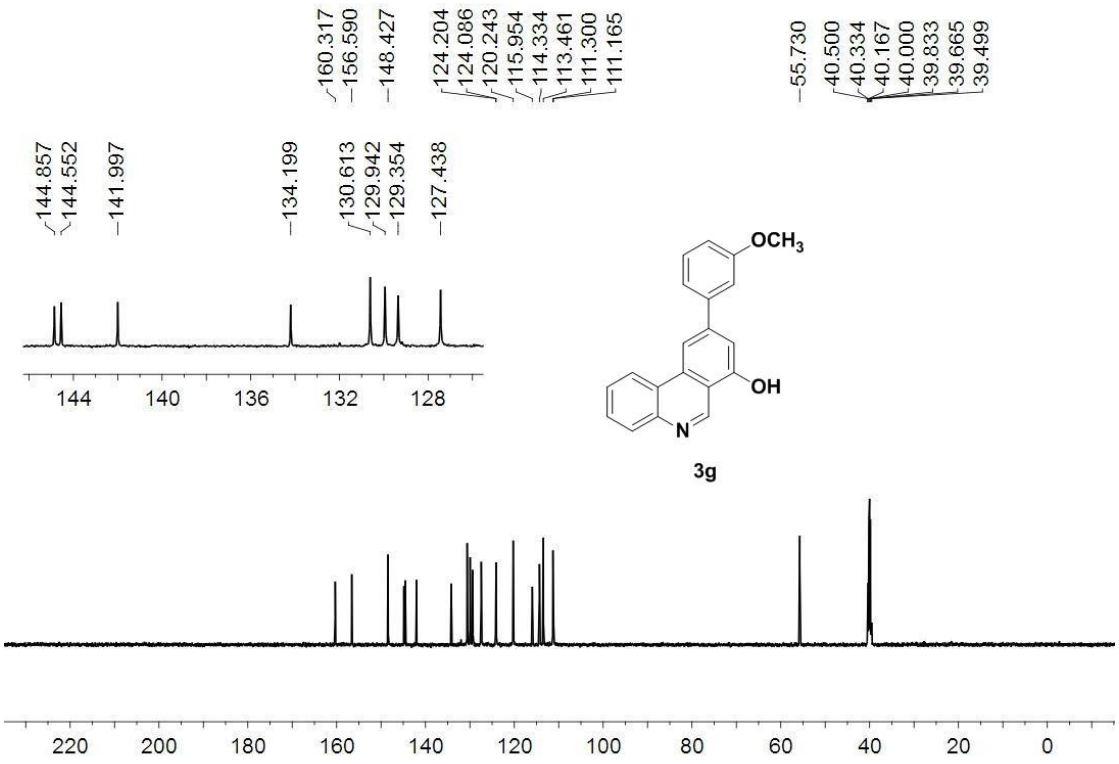
^{13}C NMR (125 MHz, DMSO-d_6) for **3f**



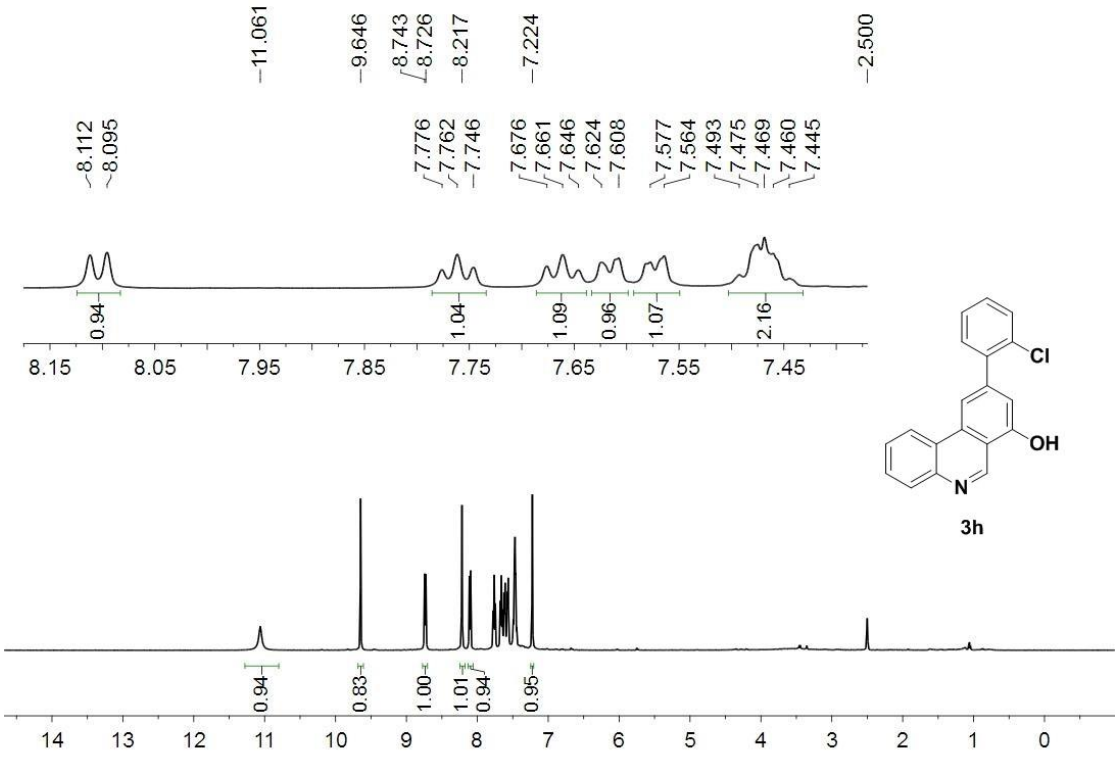
^{1}H NMR (500 MHz, DMSO-d_6) for **3g**



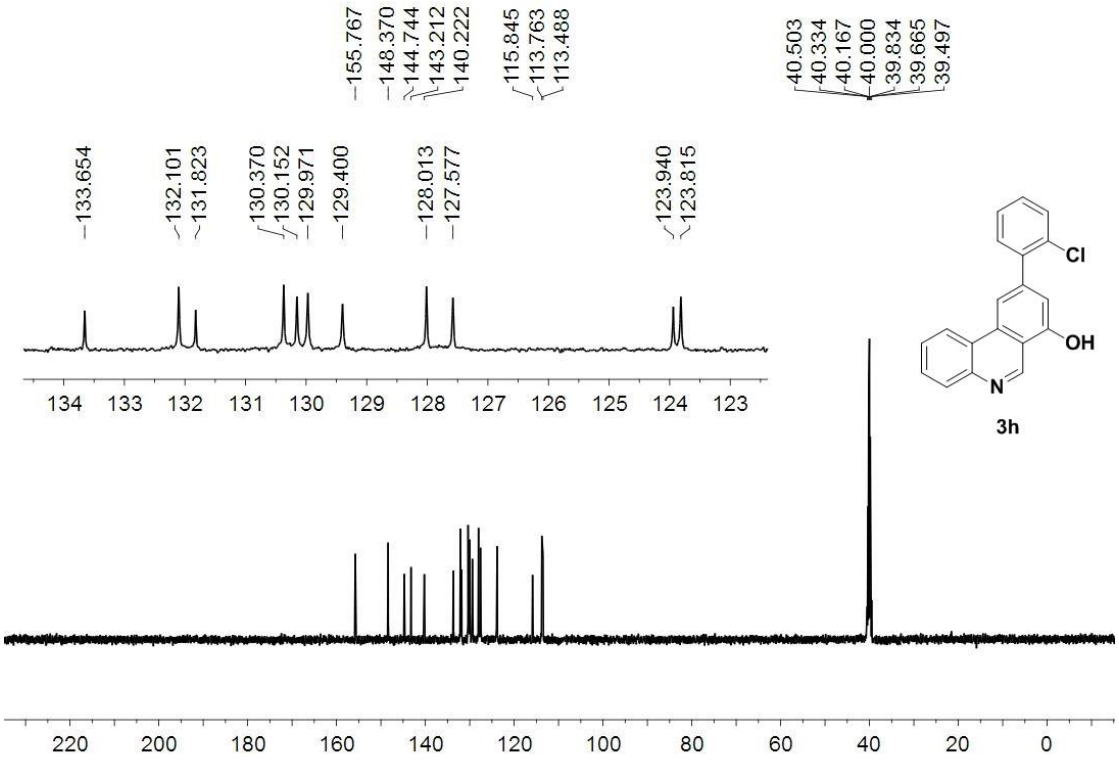
^{13}C NMR (125 MHz, DMSO-d_6) for **3g**



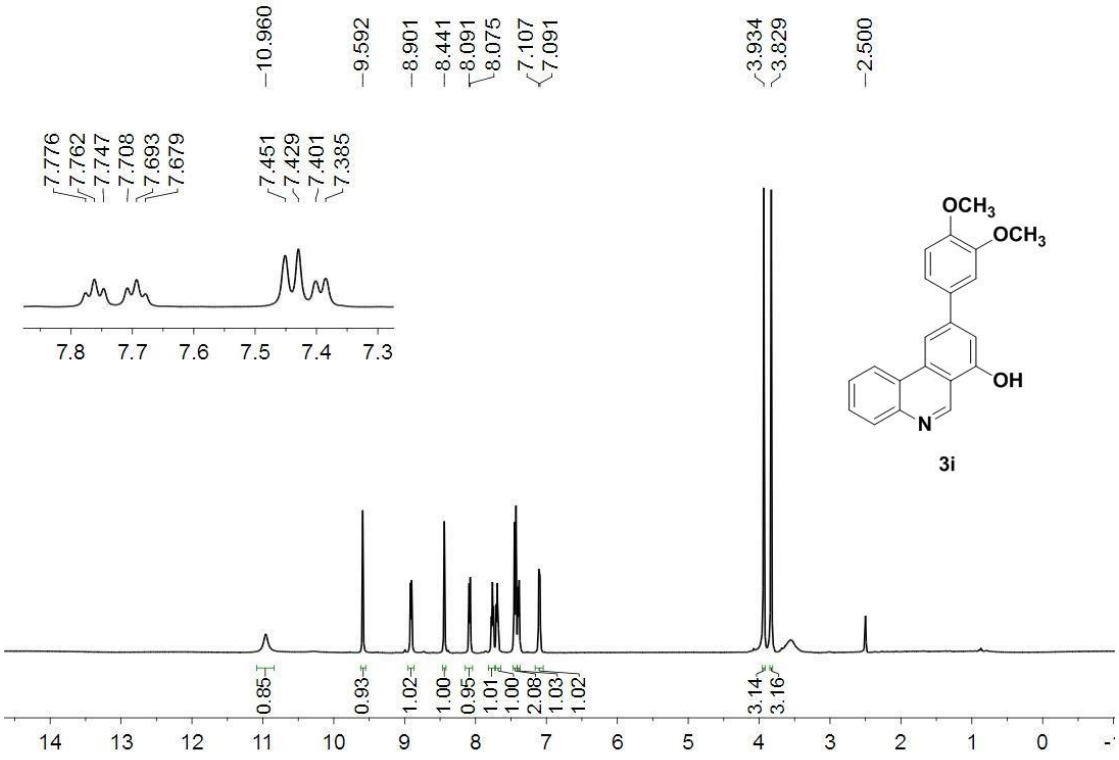
^{1}H NMR (500 MHz, DMSO-d_6) for **3h**



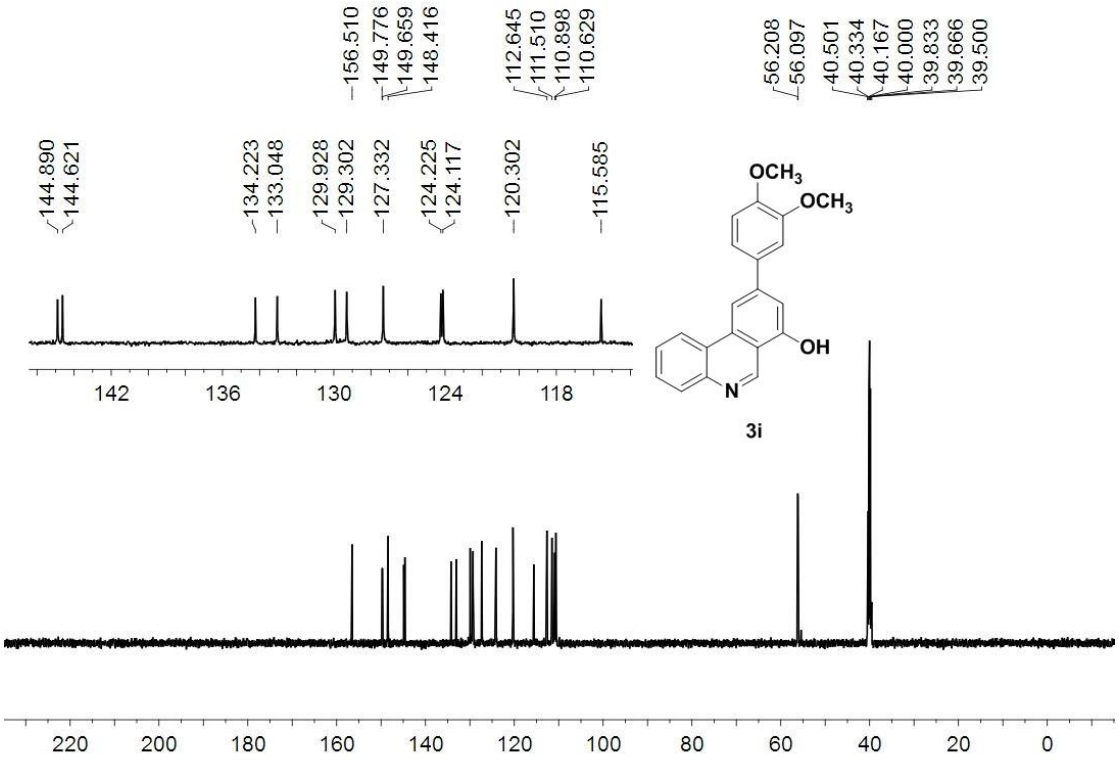
^{13}C NMR (125 MHz, DMSO-d_6) for **3h**



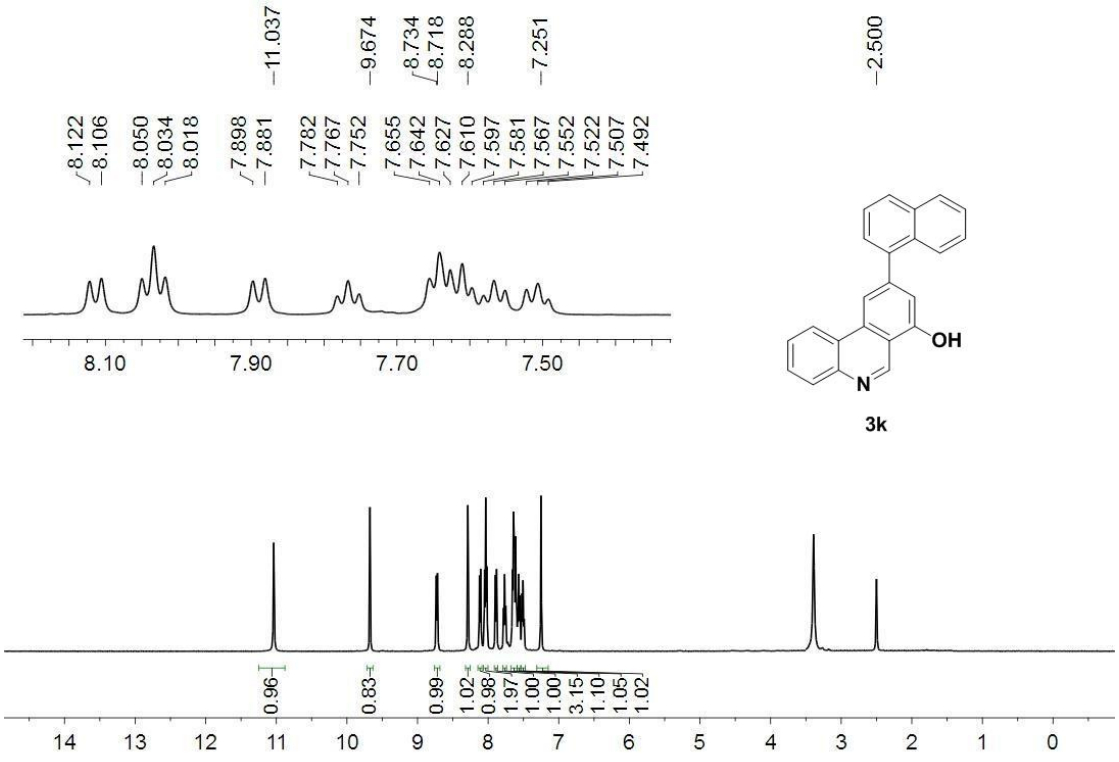
^{1}H NMR (500 MHz, DMSO-d_6) for **3i**



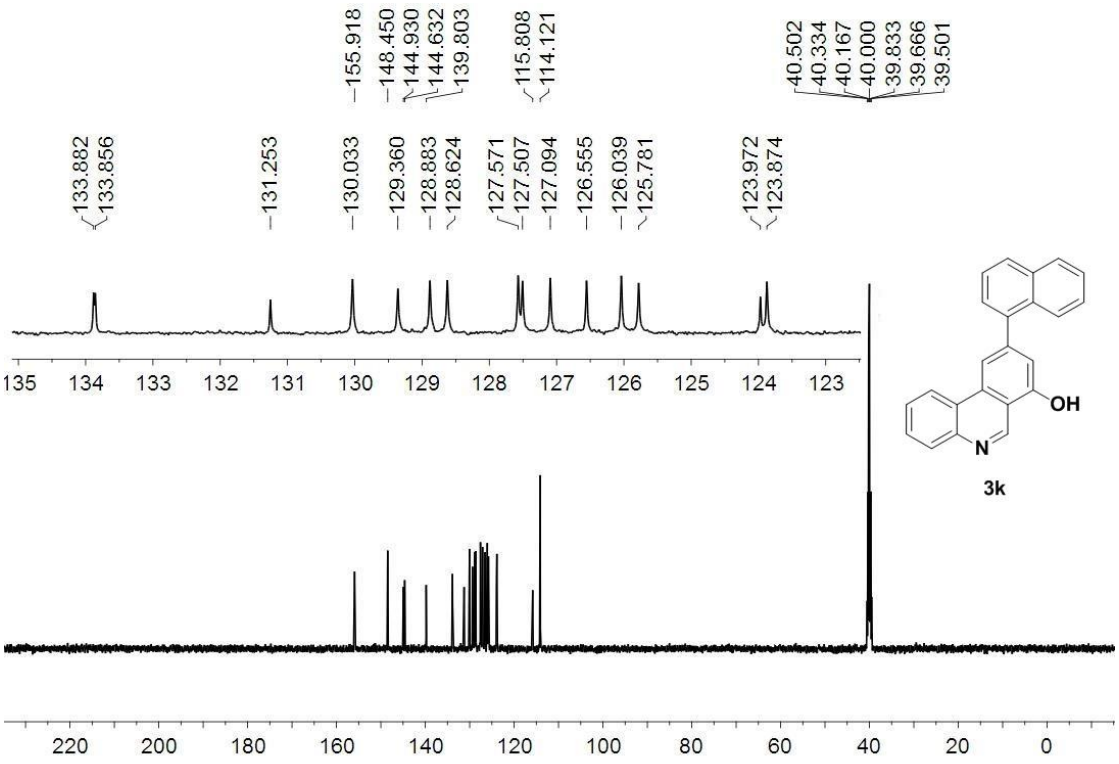
^{13}C NMR (125 MHz, DMSO-d_6) for **3i**



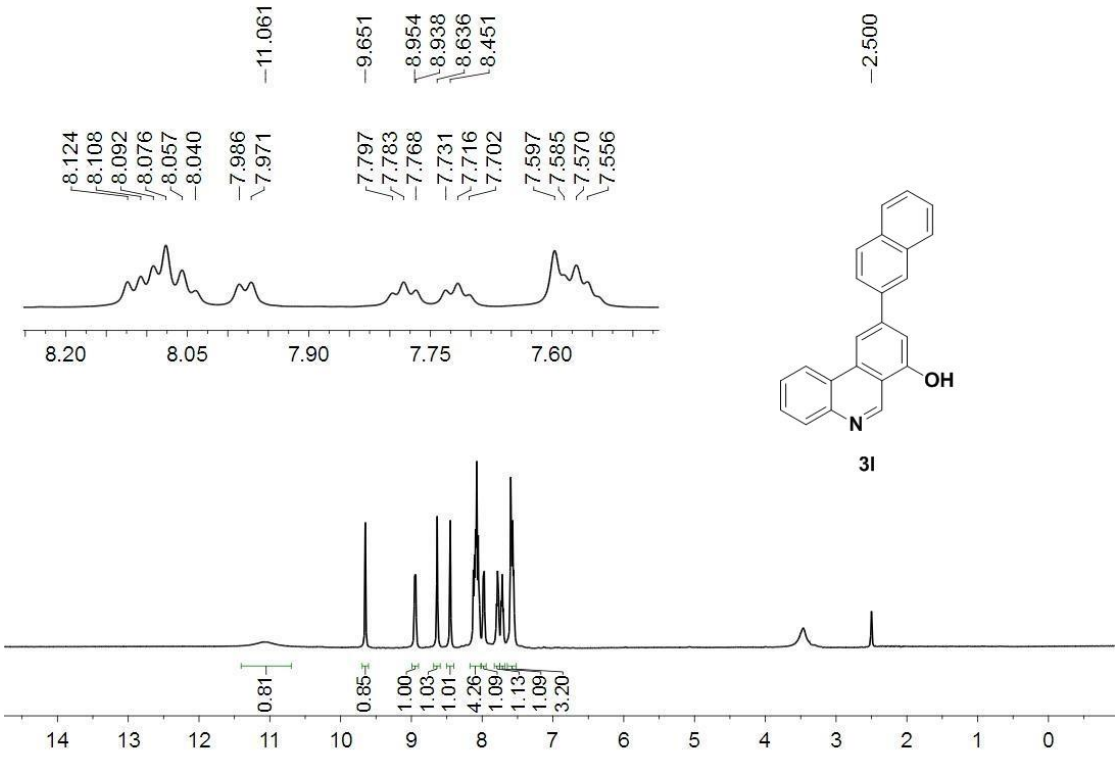
^{1}H NMR (500 MHz, DMSO-d_6) for **3k**



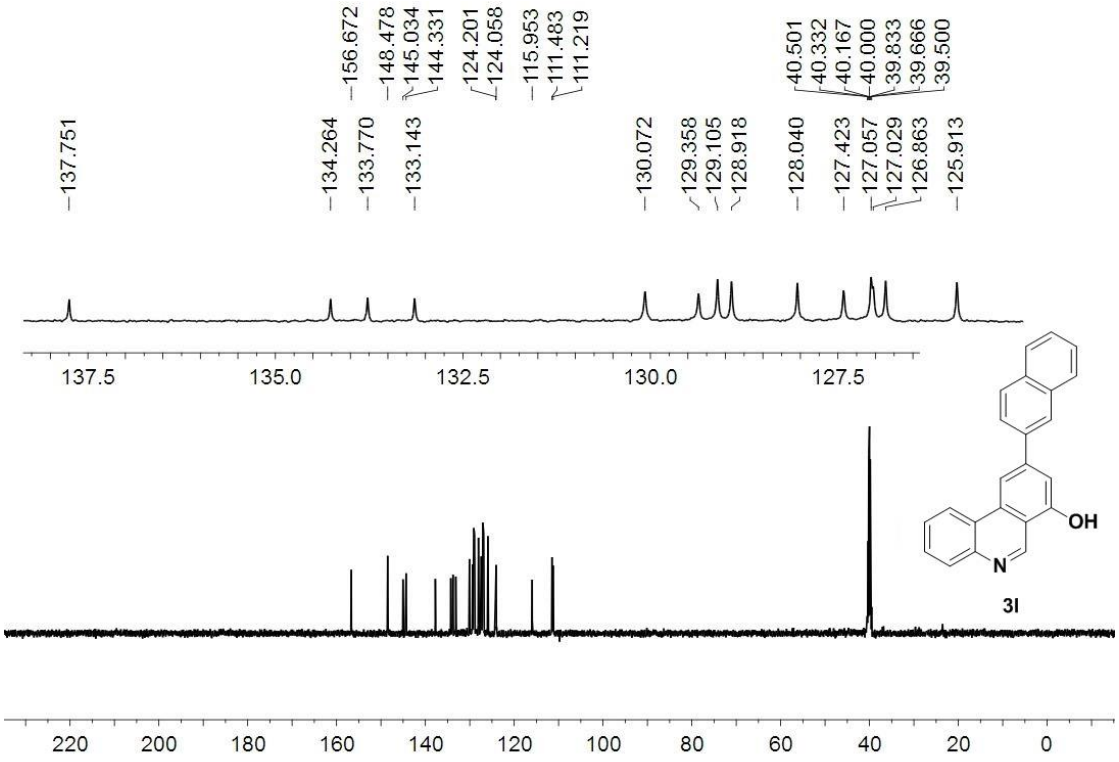
^{13}C NMR (125 MHz, DMSO-d_6) for **3k**



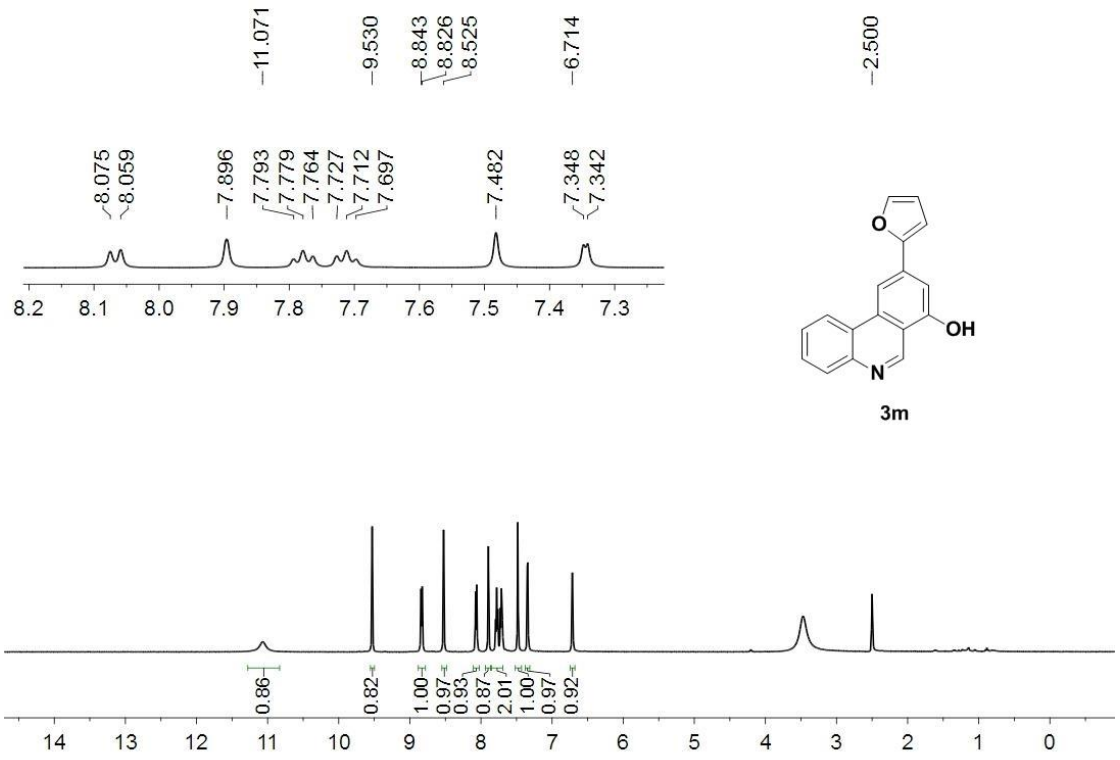
^{1}H NMR (500 MHz, DMSO-d_6) for **3l**



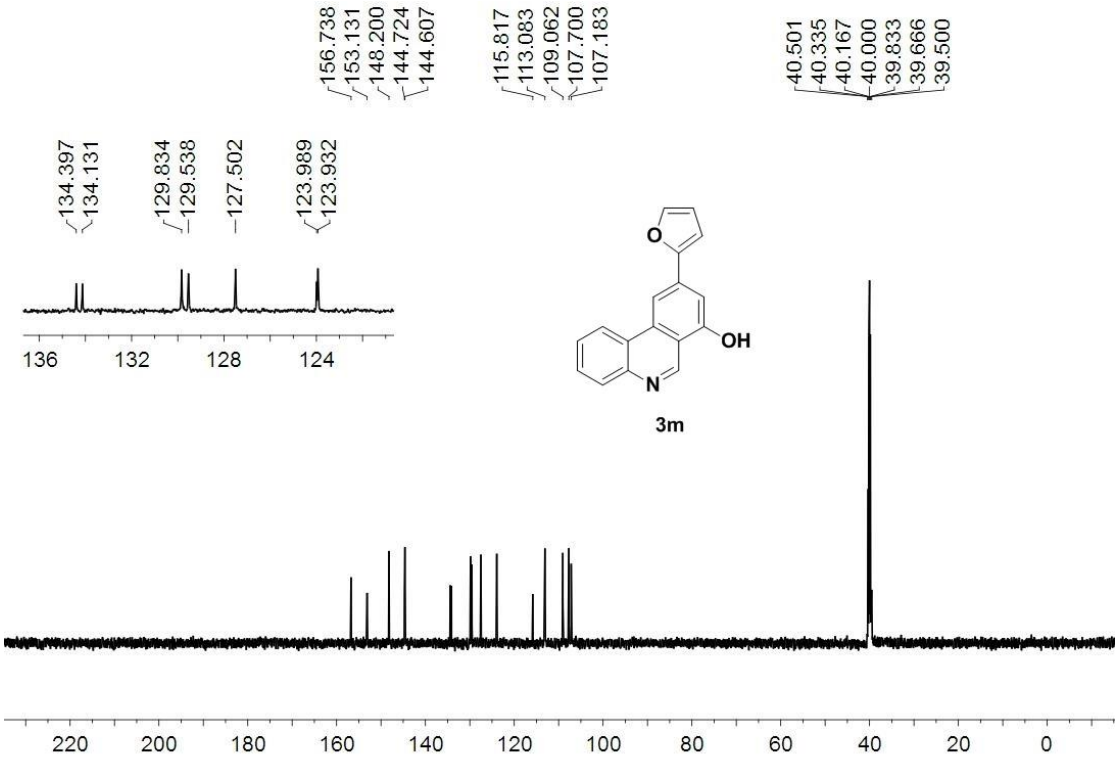
^{13}C NMR (125 MHz, DMSO-d_6) for **3l**



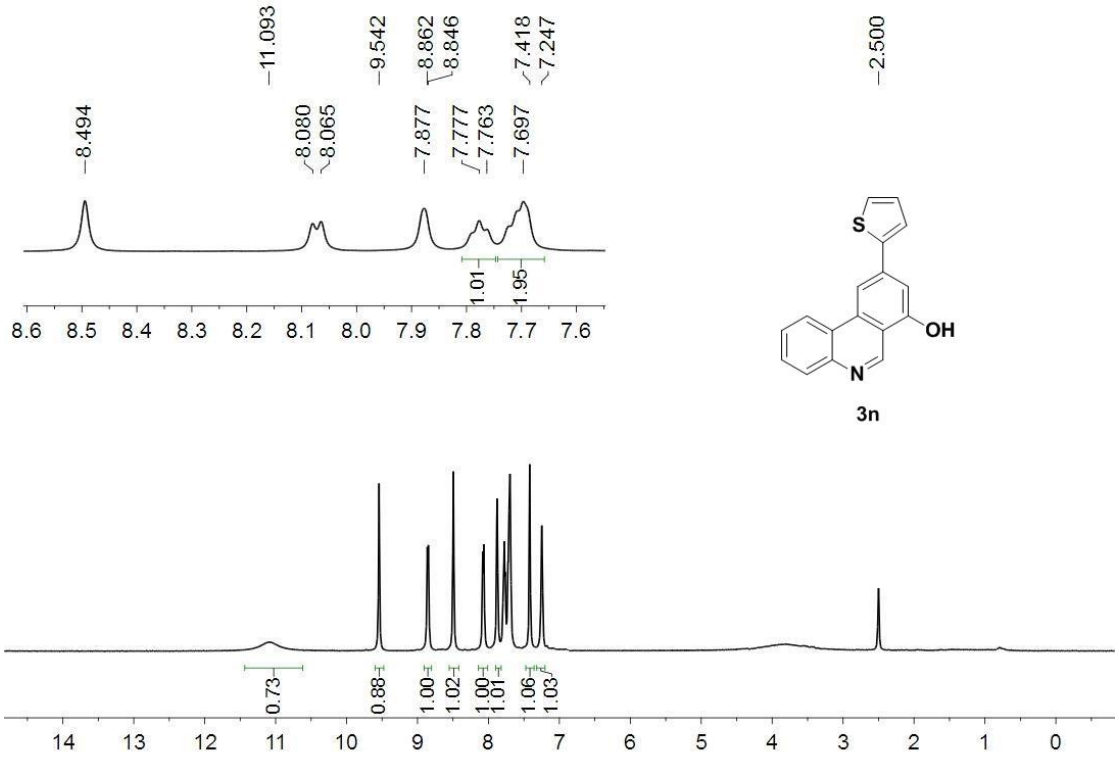
^{1}H NMR (500 MHz, DMSO-d_6) for **3m**



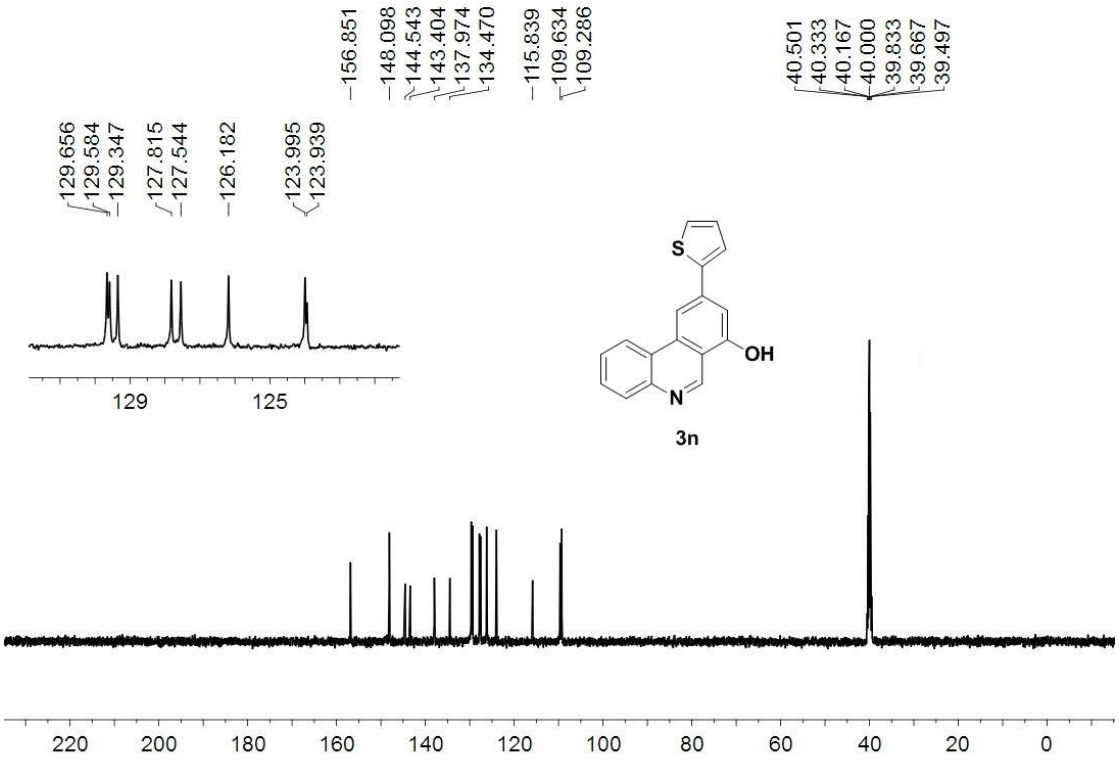
^{13}C NMR (125 MHz, DMSO-d_6) for **3m**



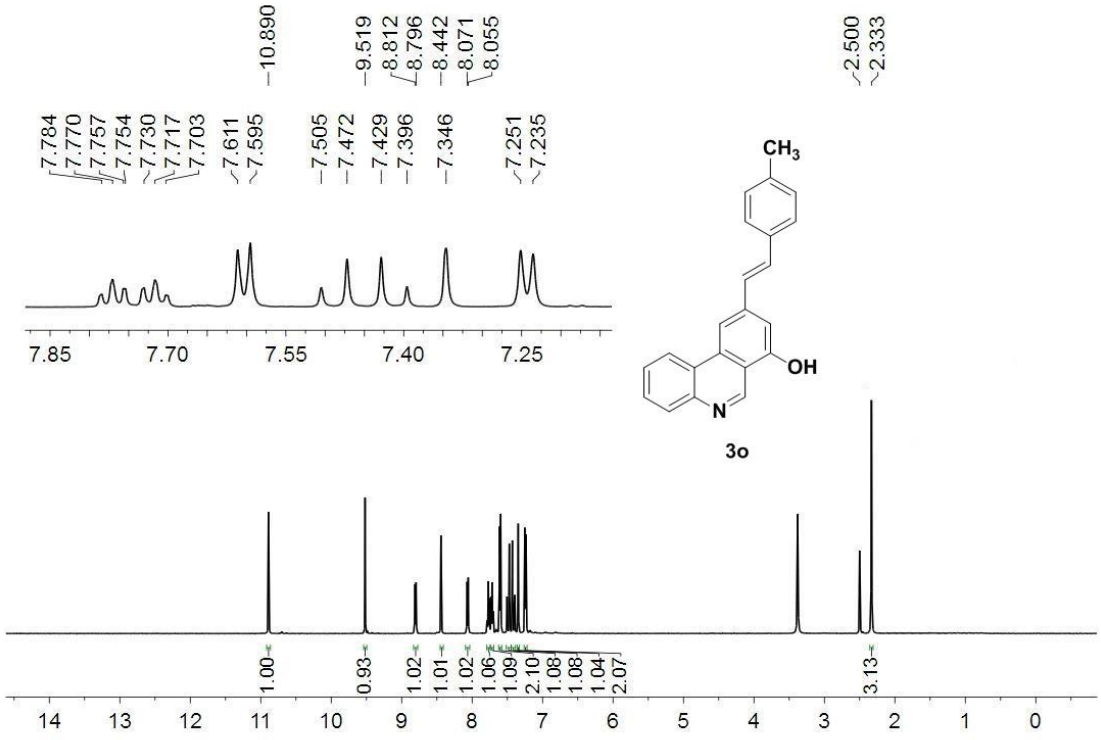
^{1}H NMR (500 MHz, DMSO-d_6) for **3n**



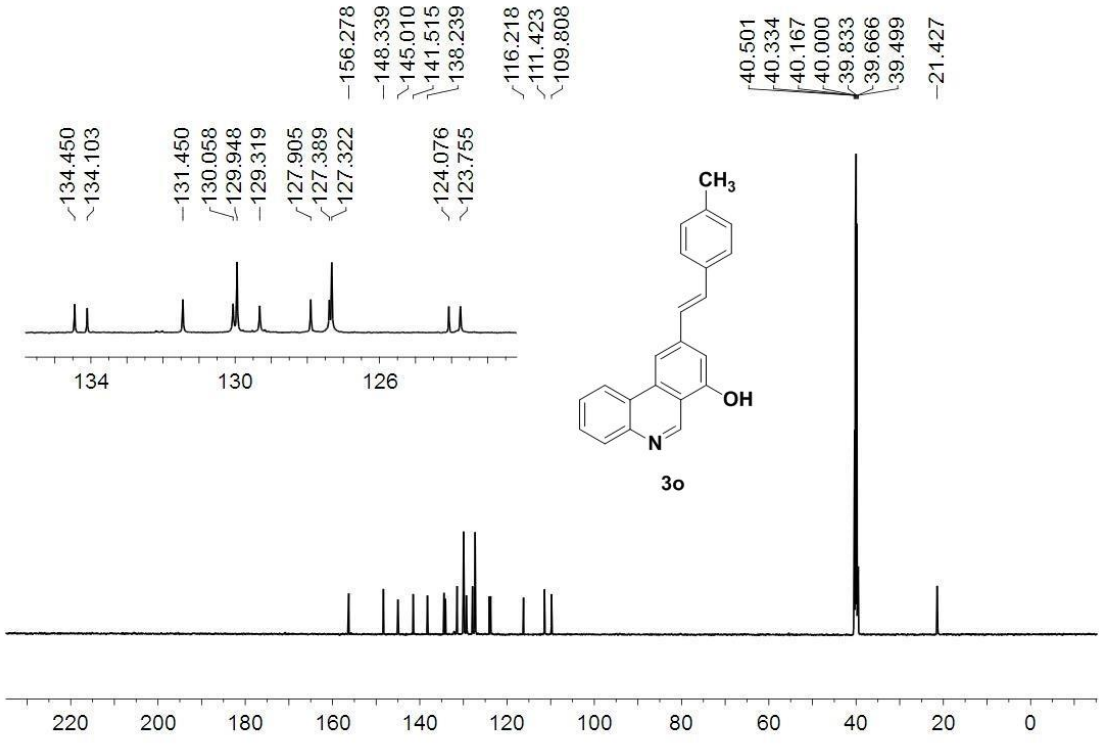
^{13}C NMR (125 MHz, DMSO-d_6) for **3n**



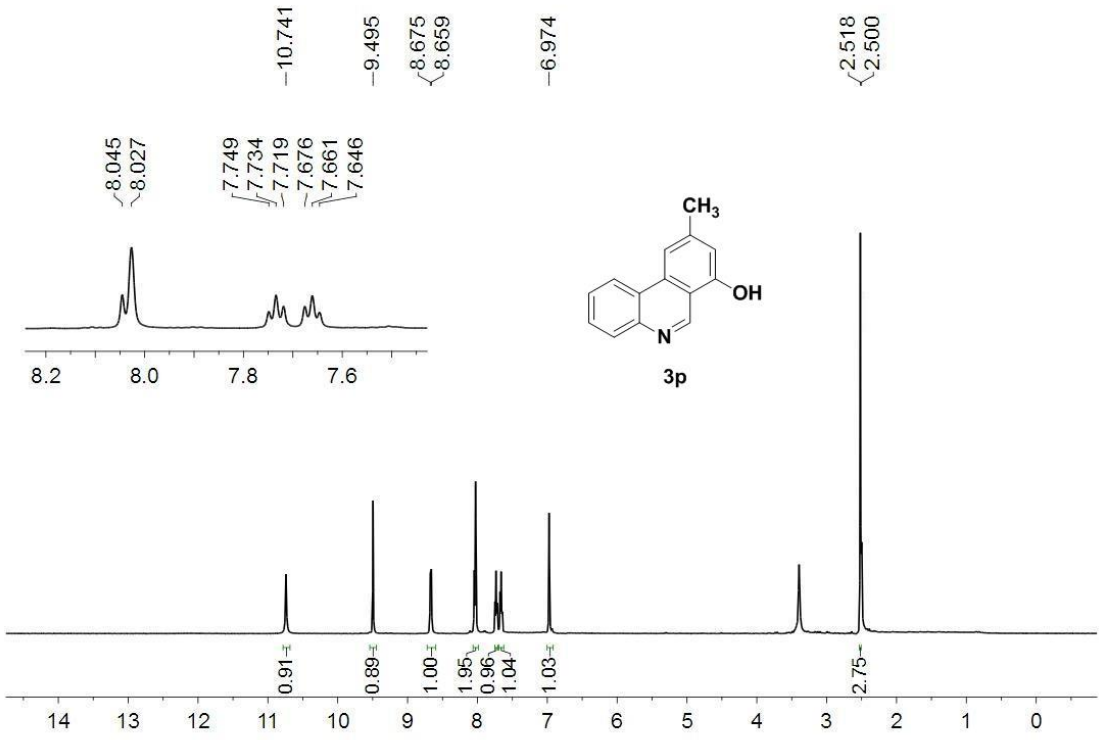
[1]H NMR (500 MHz, DMSO-d_6) for **3o**



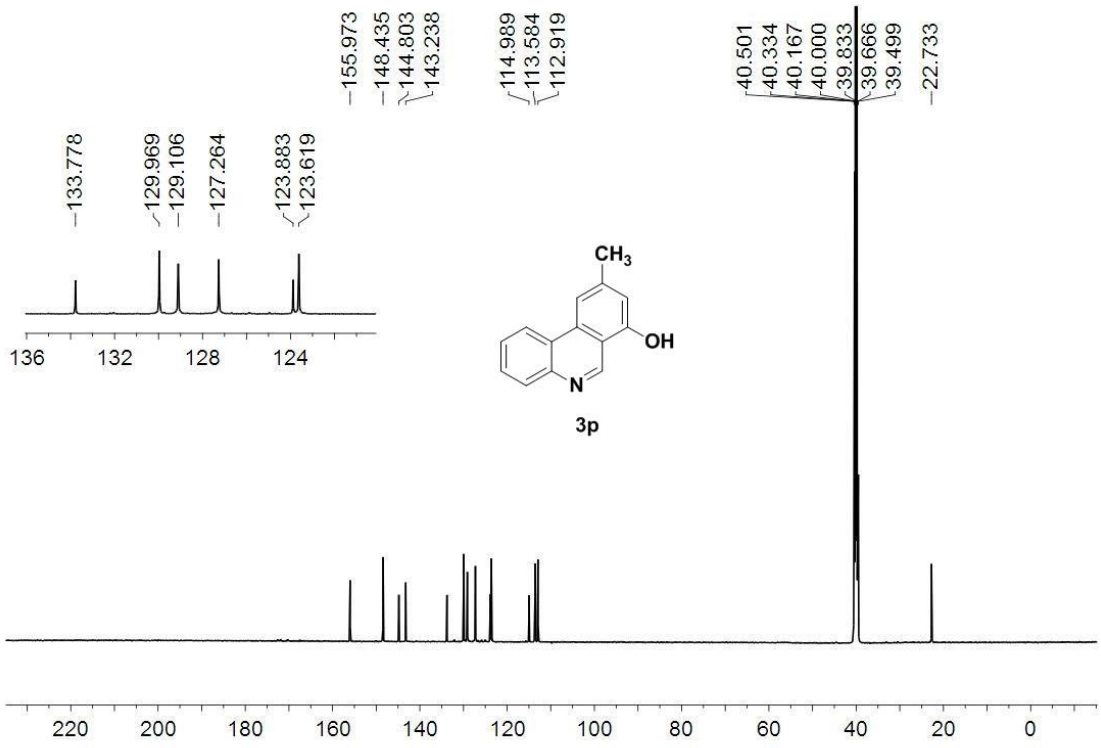
[13]C NMR (125 MHz, DMSO-d_6) for **3o**



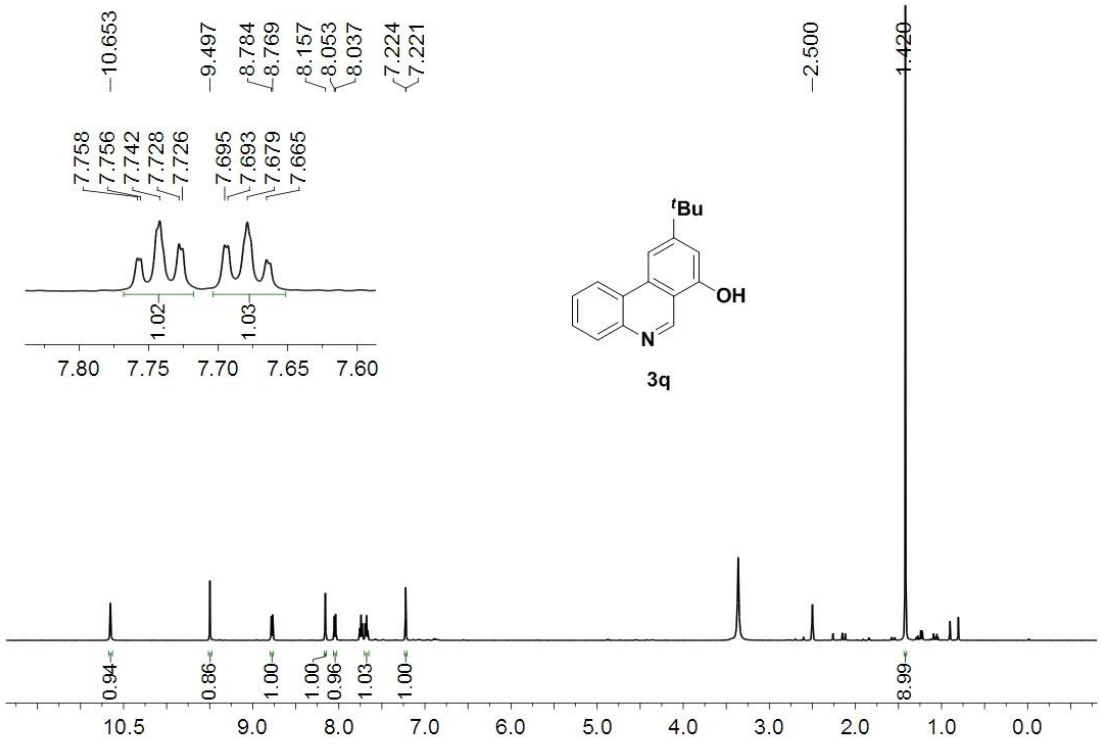
^{1}H NMR (500 MHz, DMSO-d_6) for **3p**



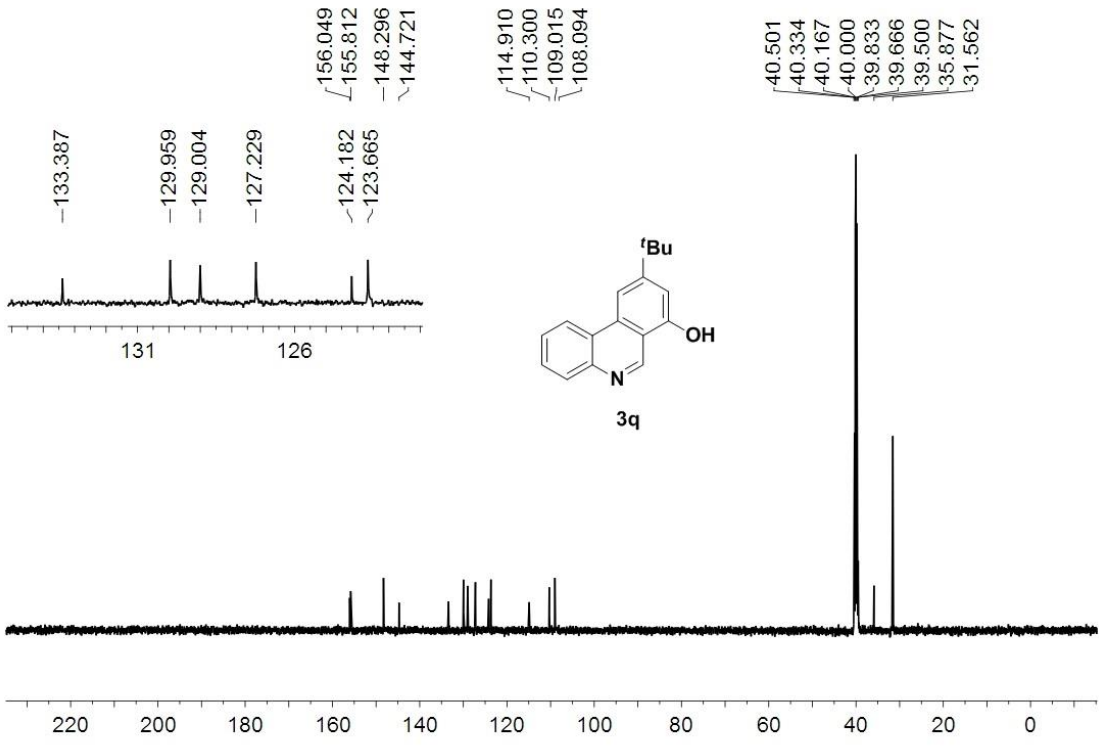
^{13}C NMR (125 MHz, DMSO-d_6) for **3p**



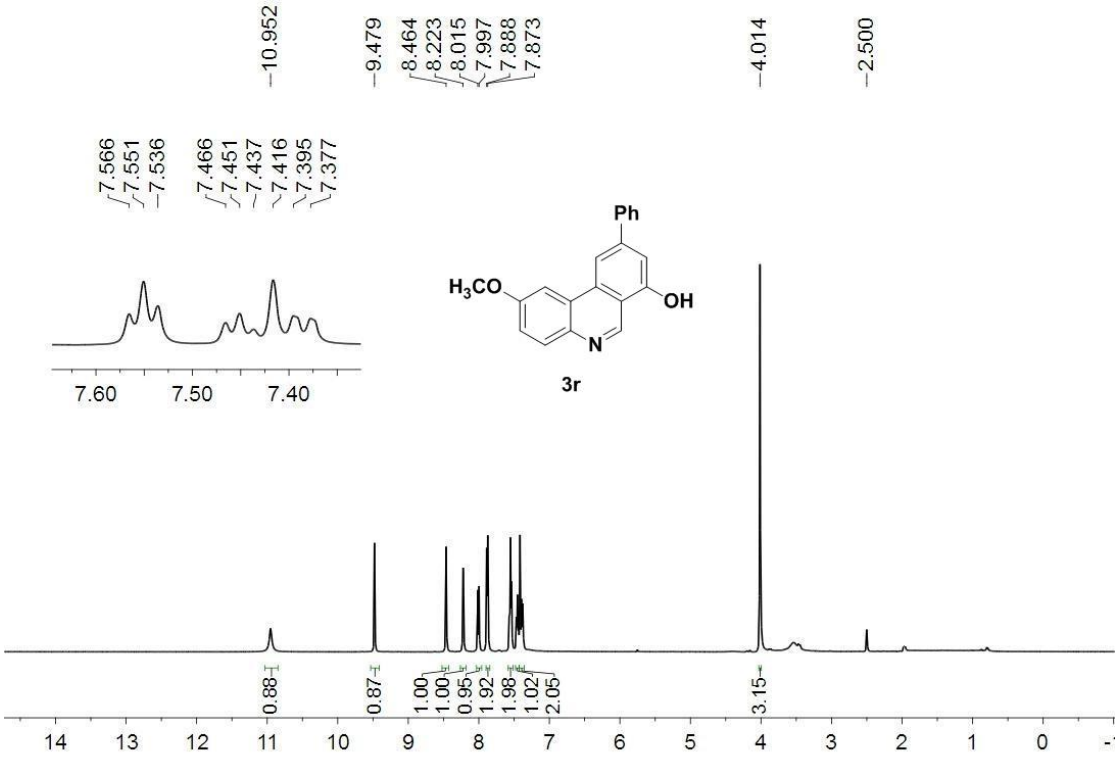
^{1}H NMR (500 MHz, DMSO-d_6) for **3q**



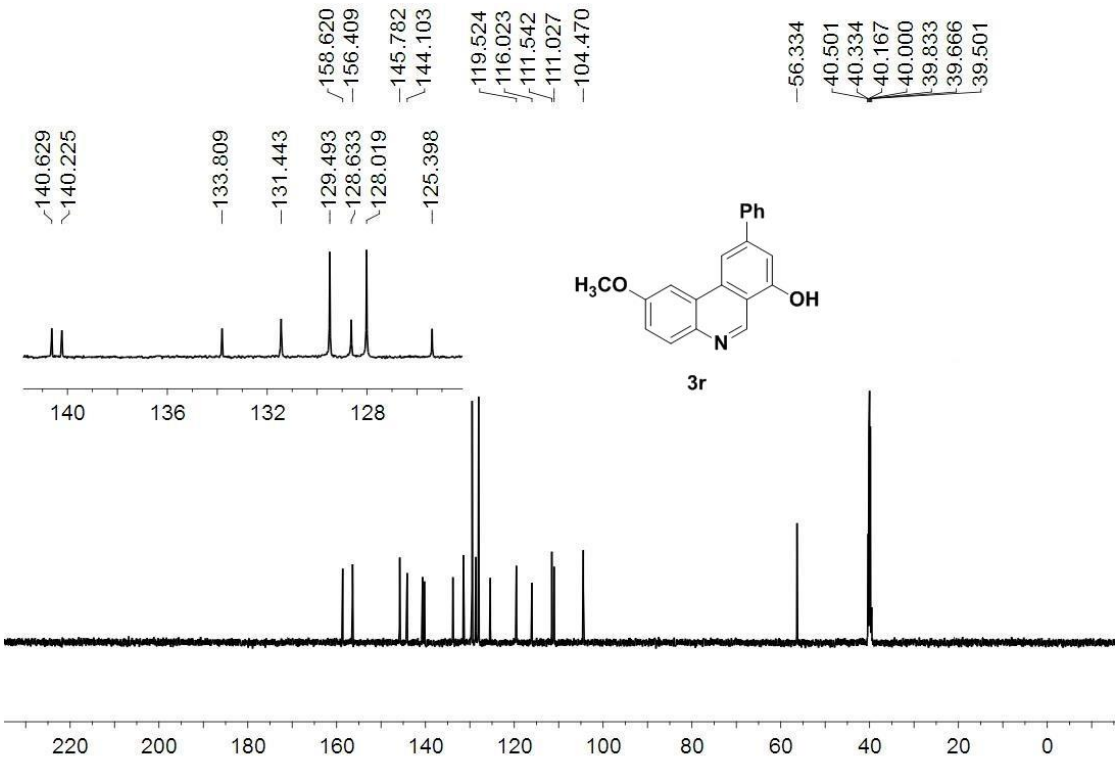
^{13}C NMR (125 MHz, DMSO-d_6) for **3q**



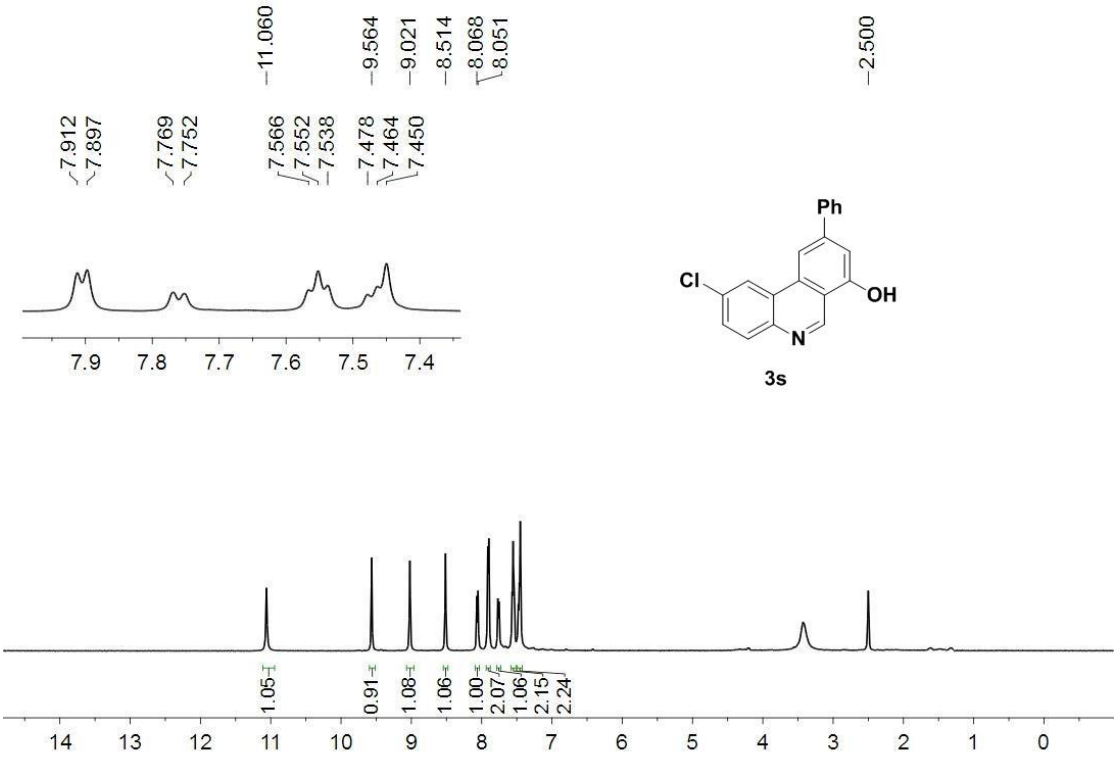
^{1}H NMR (500 MHz, DMSO-d_6) for **3r**



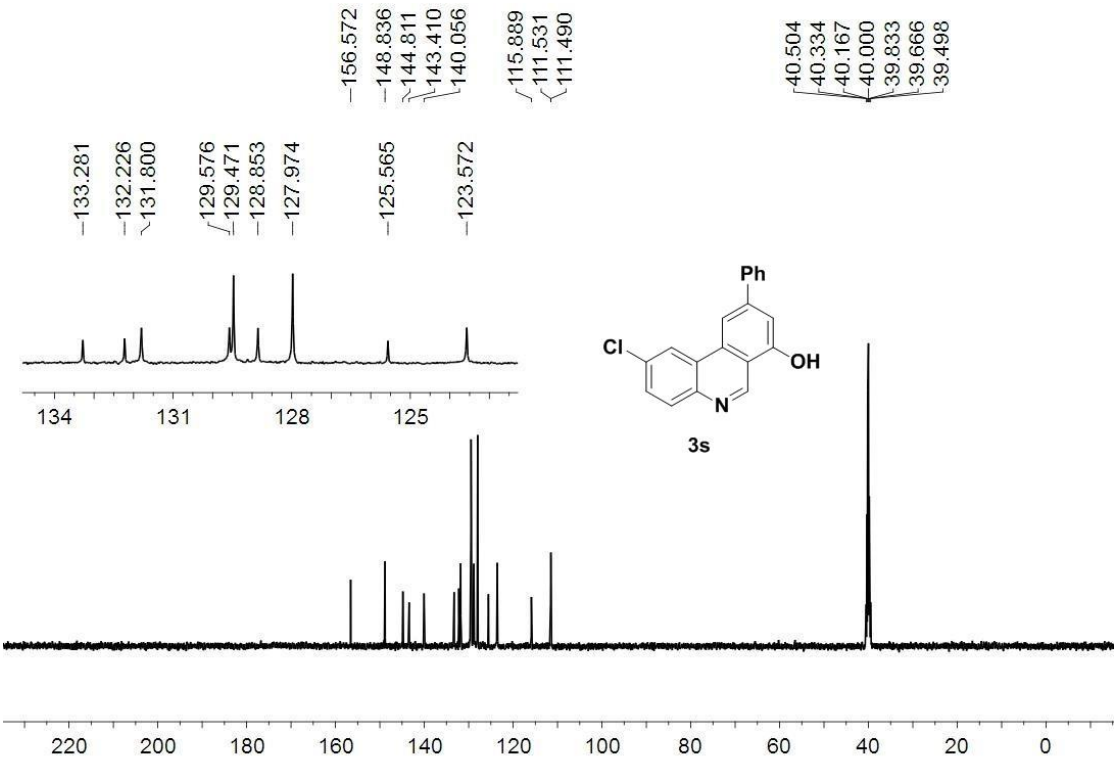
^{13}C NMR (125 MHz, DMSO-d_6) for **3r**



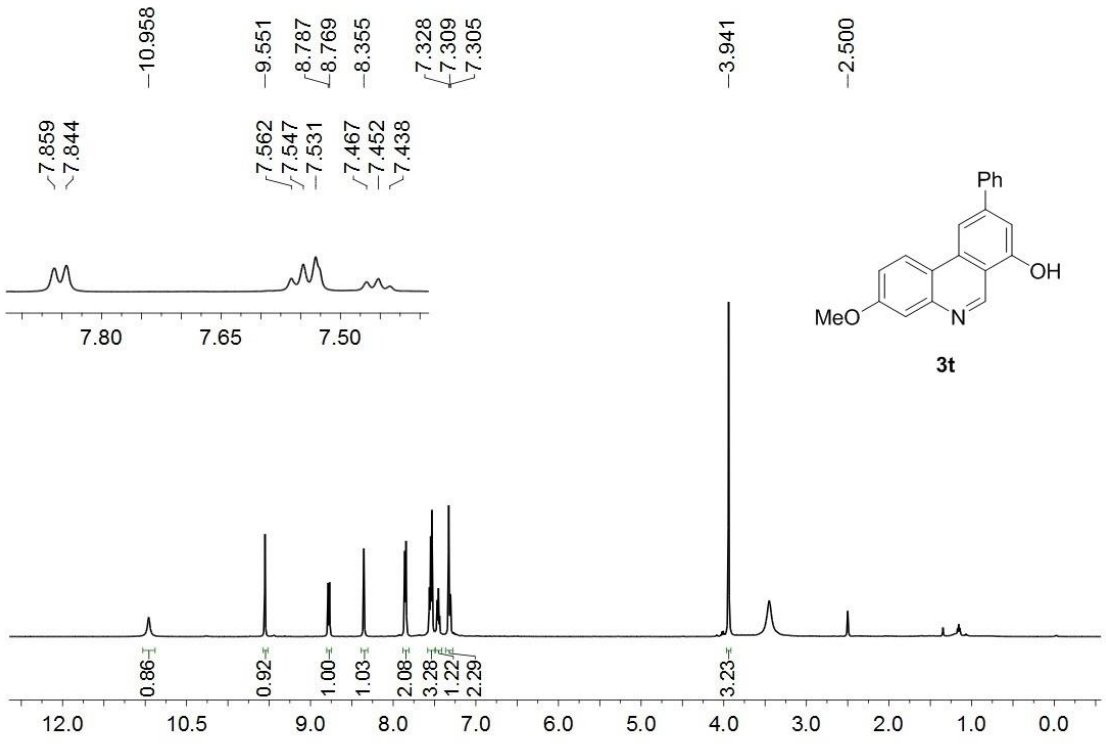
^{1}H NMR (500 MHz, DMSO-d_6) for **3s**



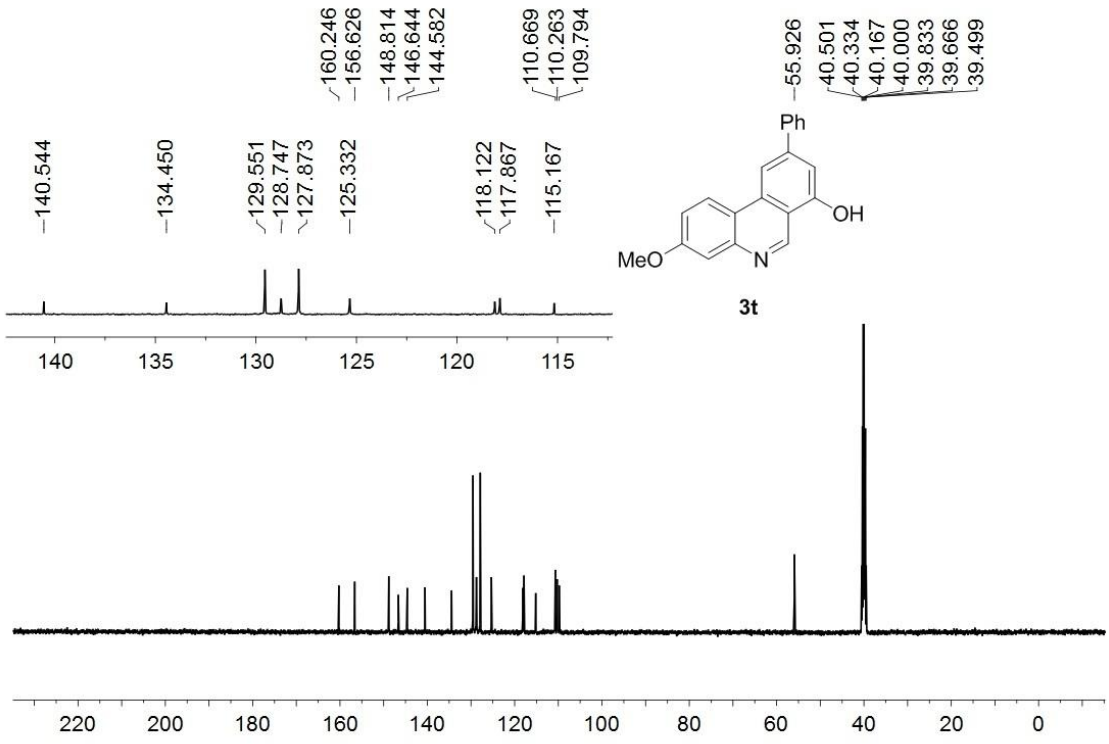
^{13}C NMR (125 MHz, DMSO-d_6) for **3s**



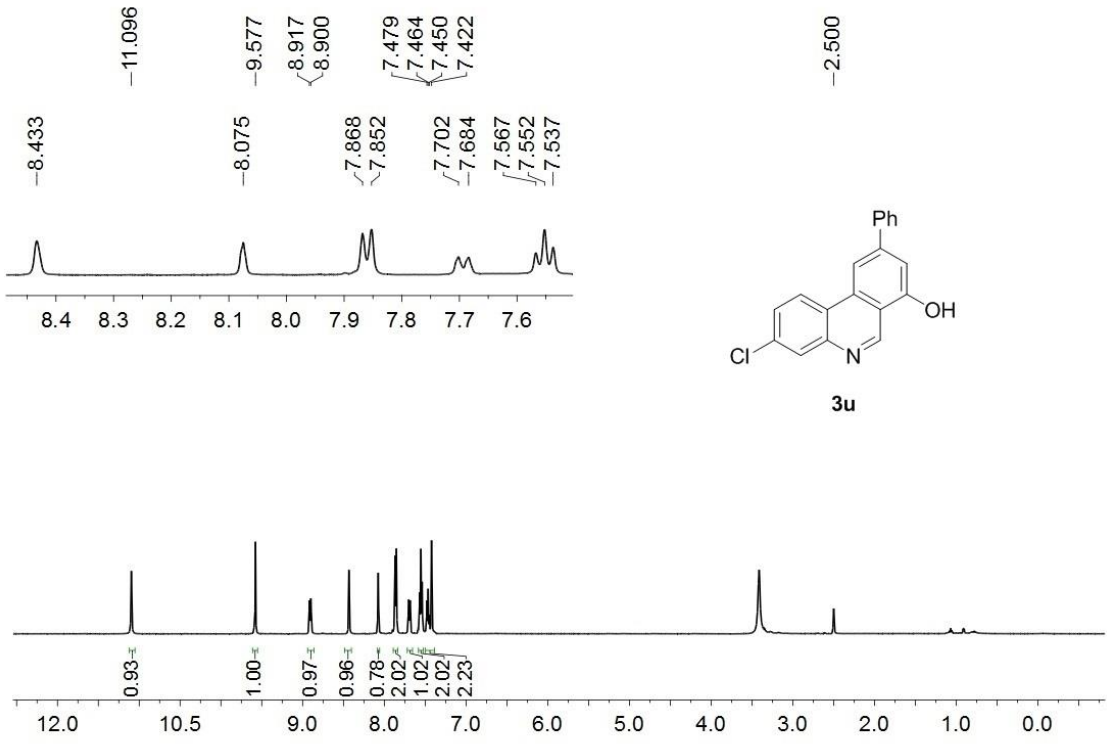
^{1}H NMR (500 MHz, DMSO-d_6) for **3t**



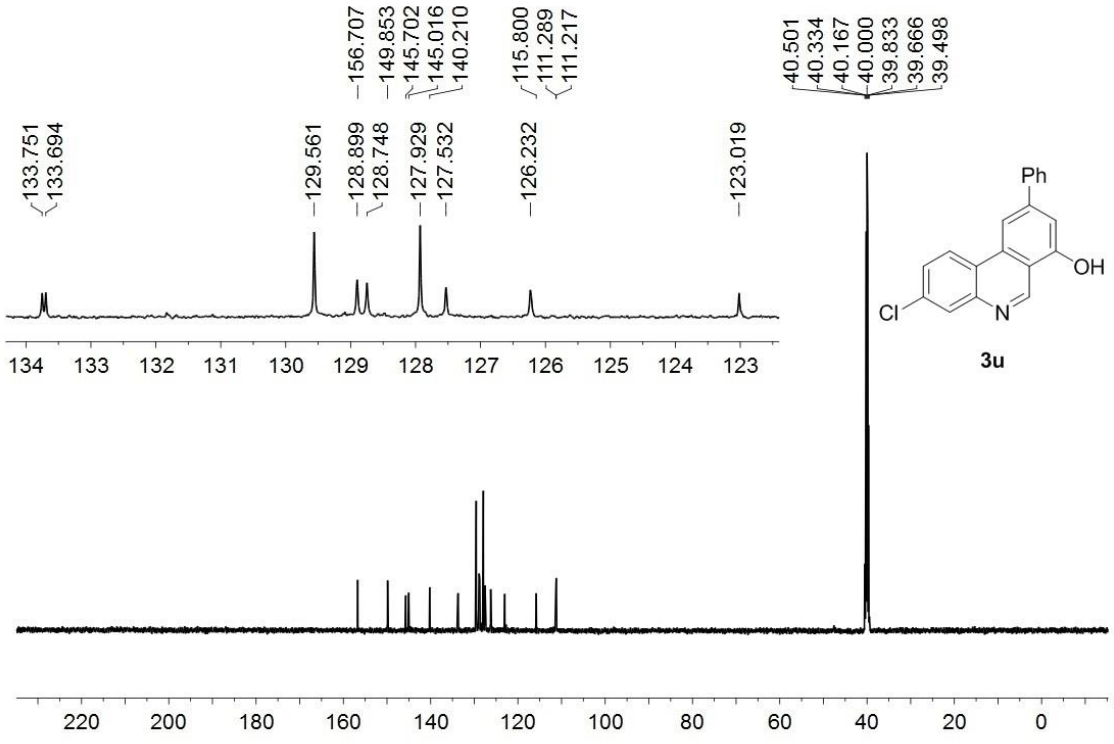
^{13}C NMR (125 MHz, DMSO-d_6) for **3t**



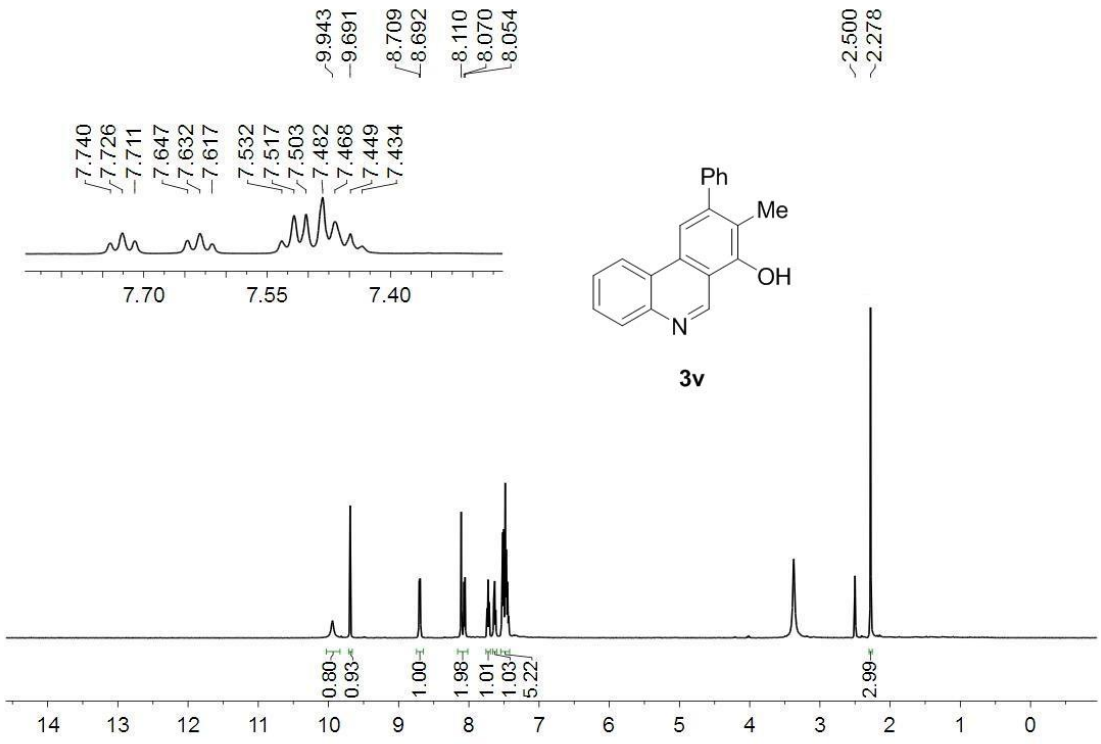
[1]H NMR (500 MHz, DMSO-d_6) for **3u**



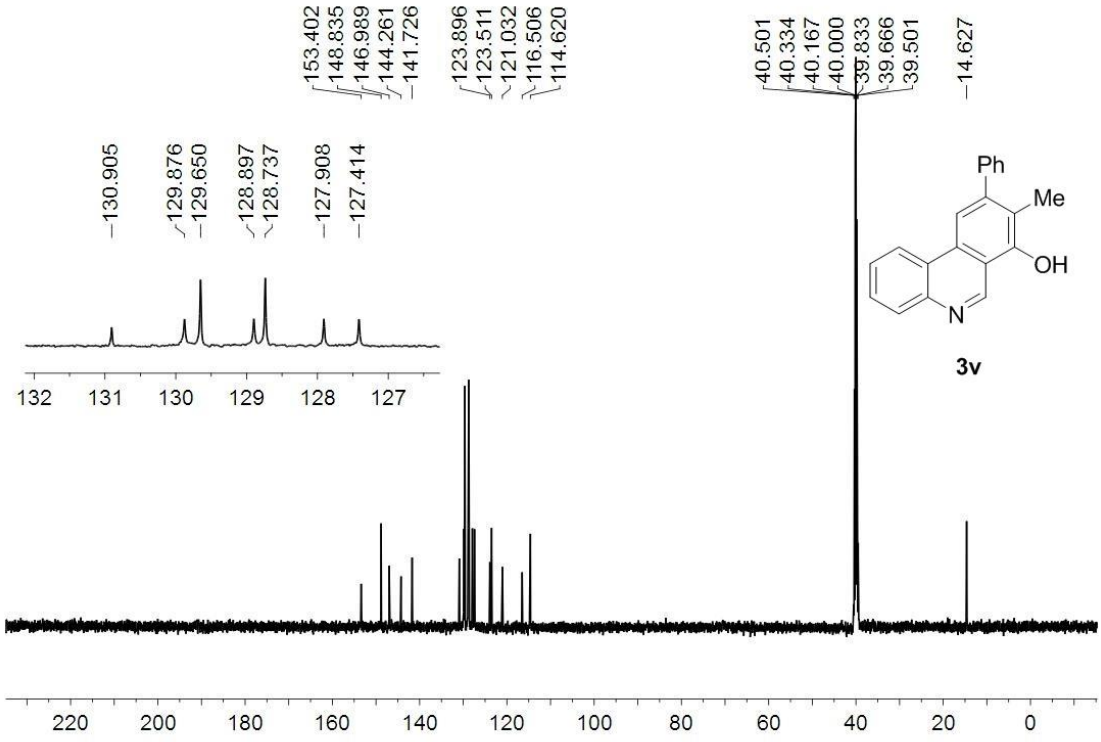
[13]C NMR (125 MHz, DMSO-d_6) for **3u**



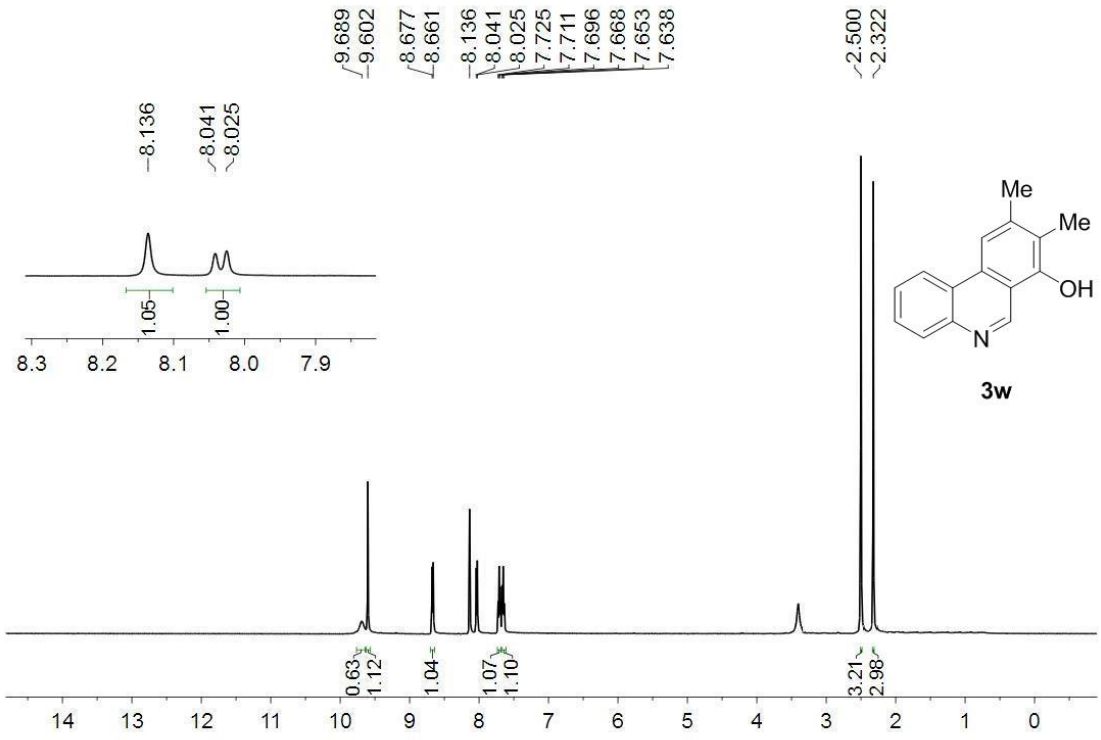
^{1}H NMR (500 MHz, DMSO-d_6) for **3v**



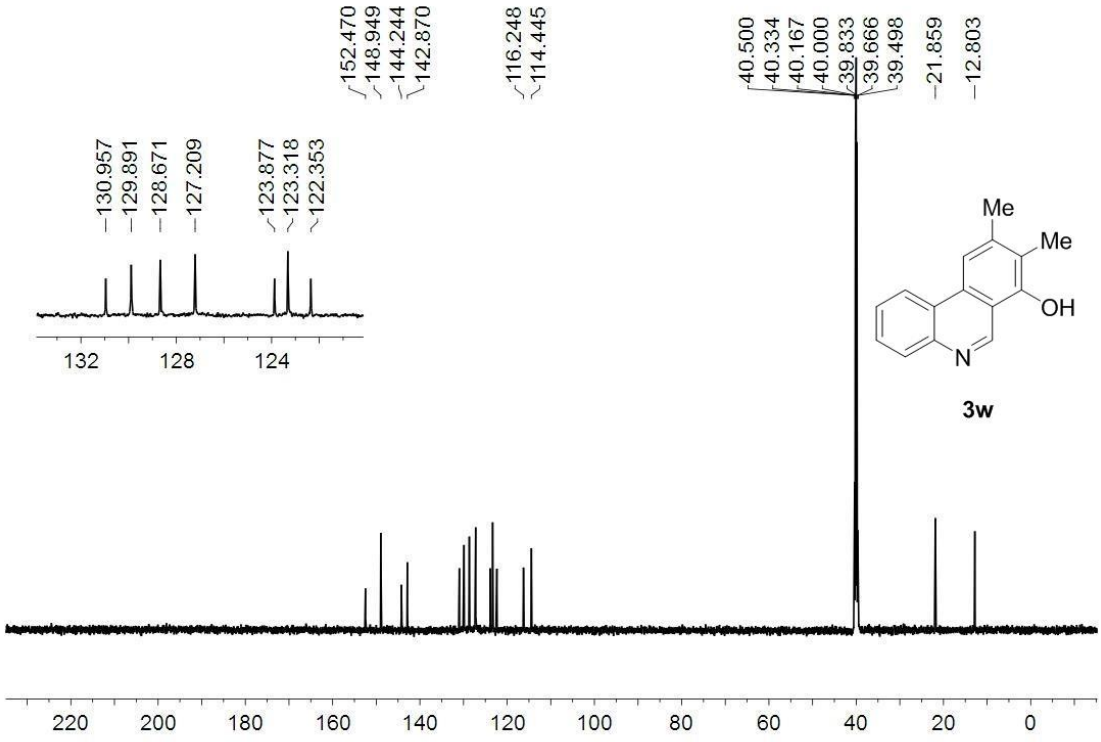
^{13}C NMR (125 MHz, DMSO-d_6) for **3v**



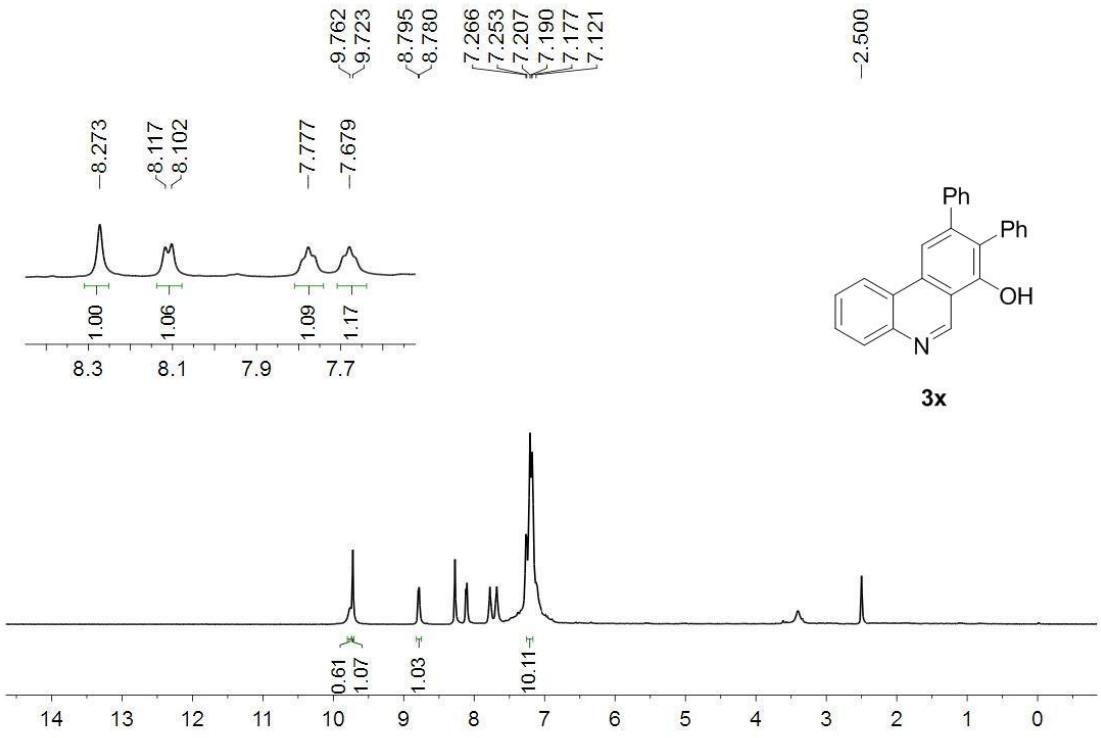
[1]H NMR (500 MHz, DMSO-d_6) for **3w**



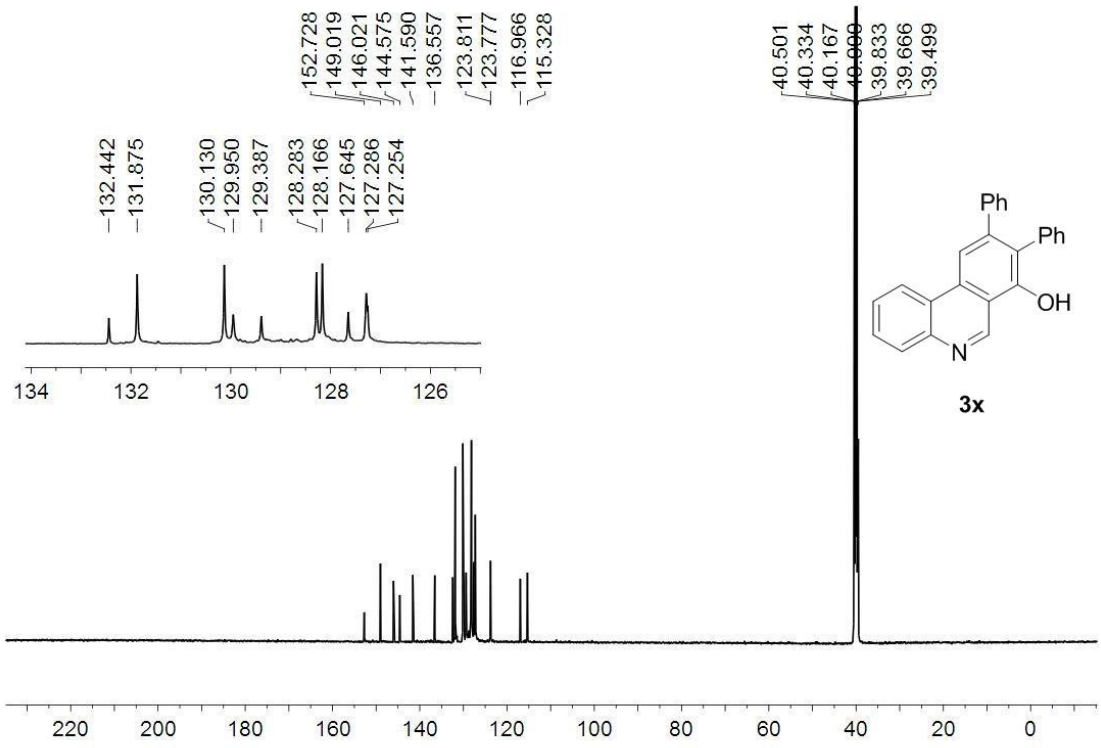
[13]C NMR (125 MHz, DMSO-d_6) for **3w**



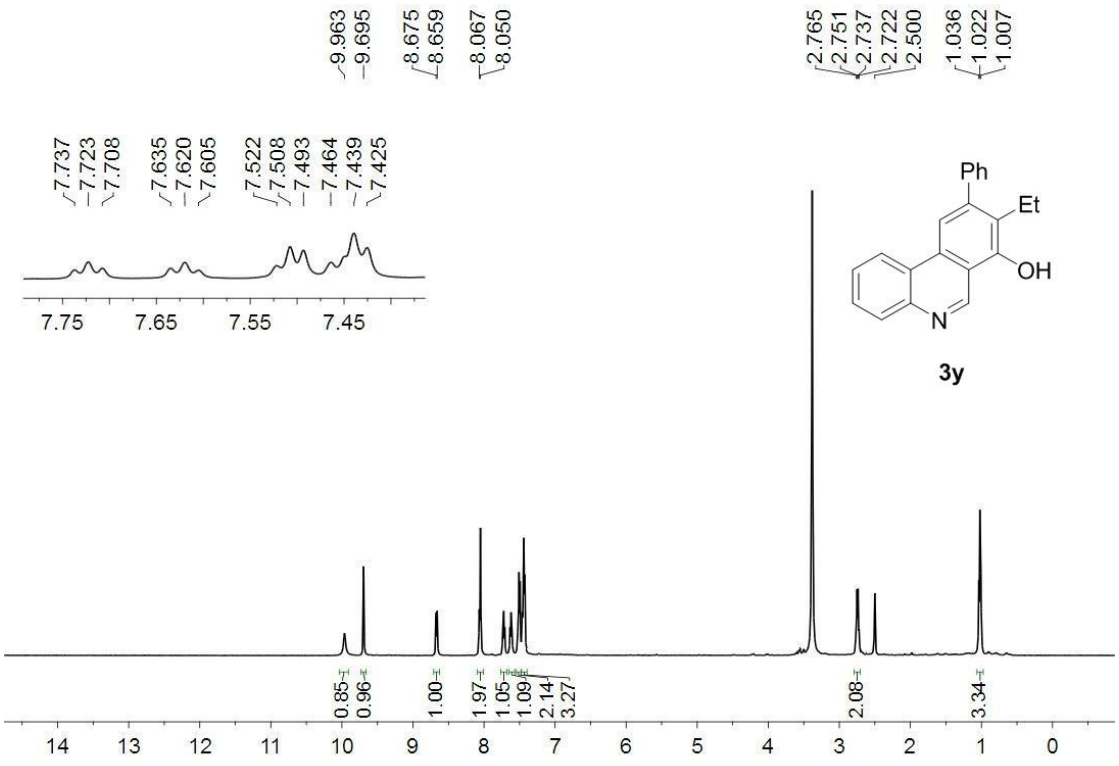
^{1}H NMR (500 MHz, DMSO-d_6) for **3x**



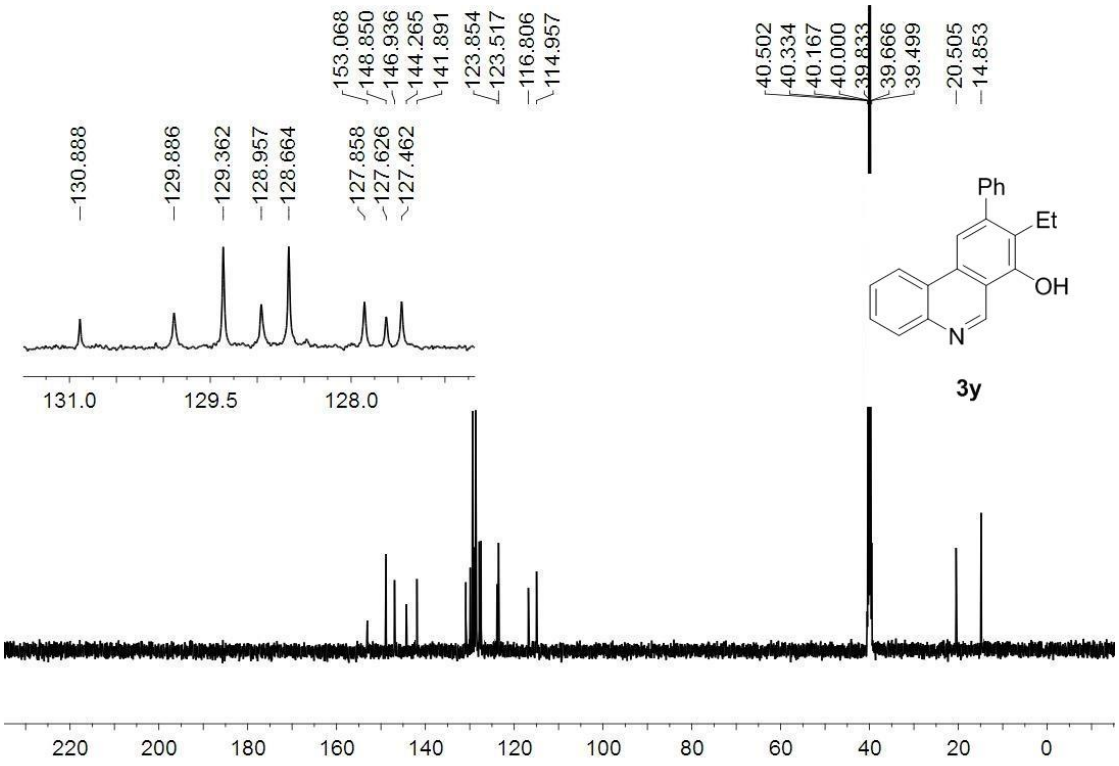
^{13}C NMR (125 MHz, DMSO) for **3x**



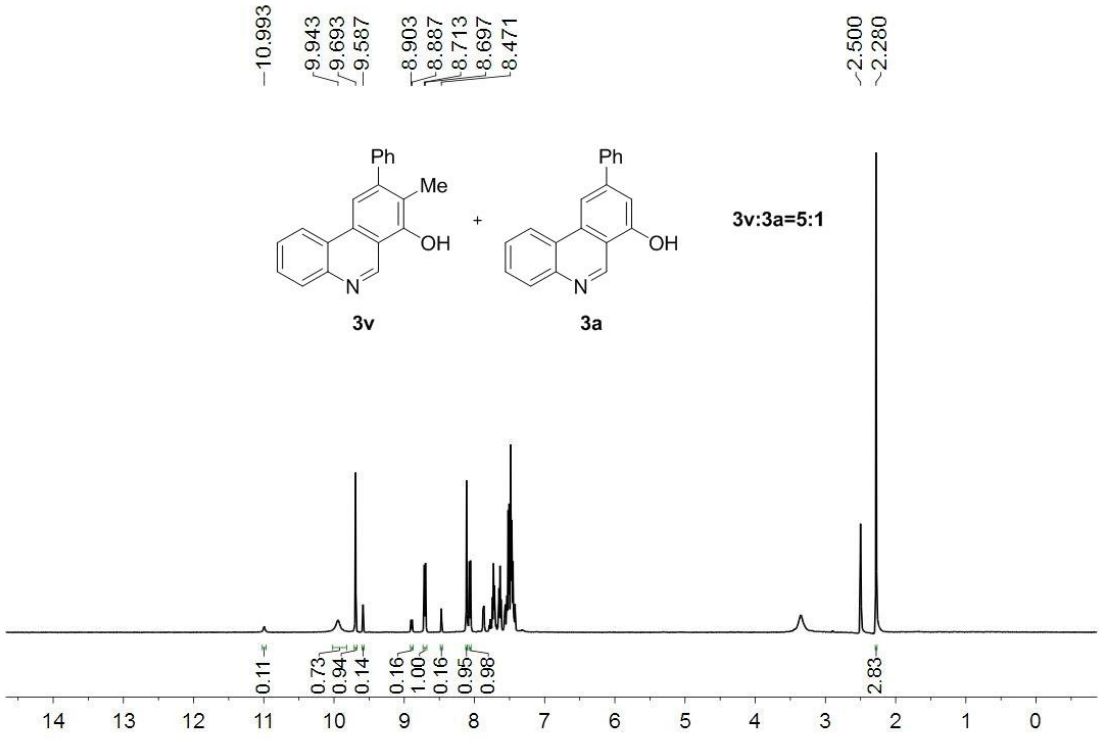
[1]H NMR (500 MHz, DMSO-d_6) for **3y**



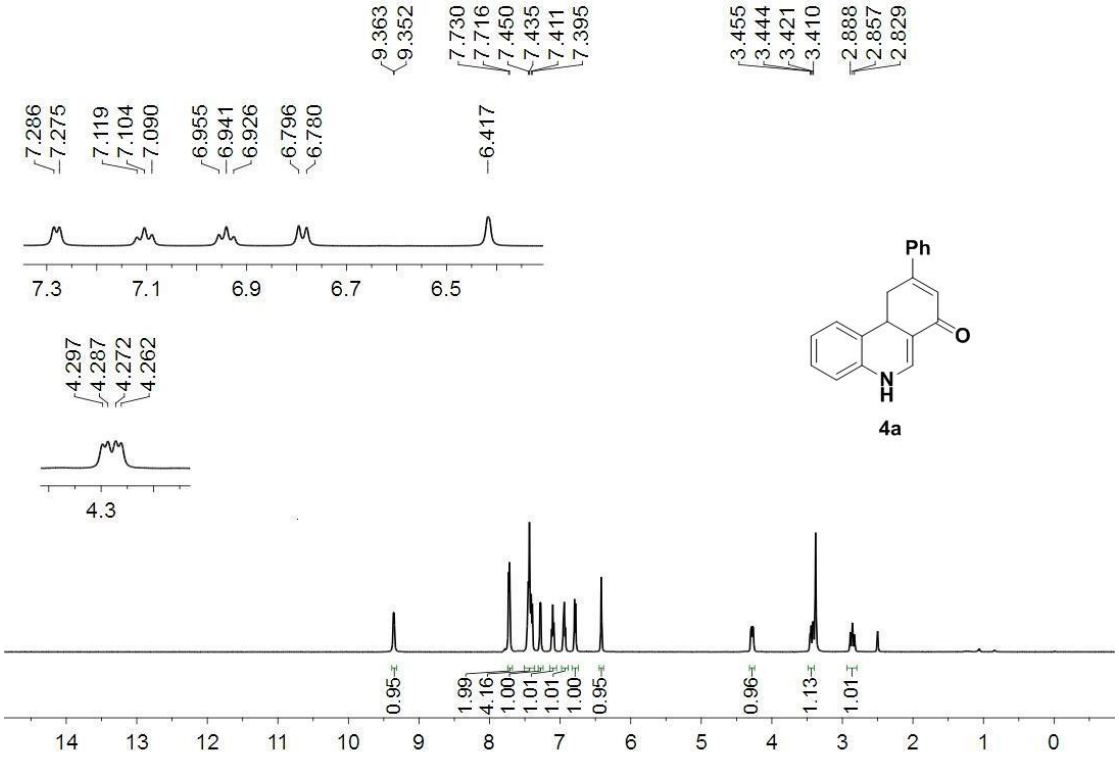
[13]C NMR (125 MHz, DMSO-d_6) for **3y**



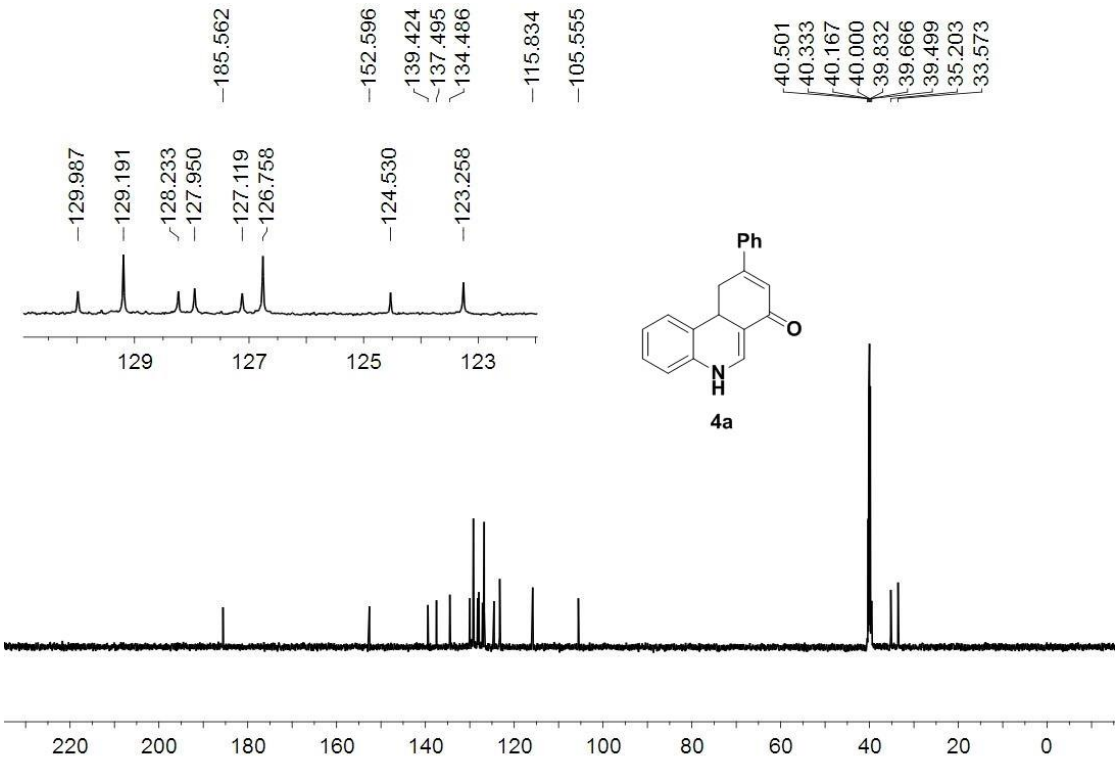
^{1}H NMR (500 MHz, DMSO-d_6) for **3v:3a**



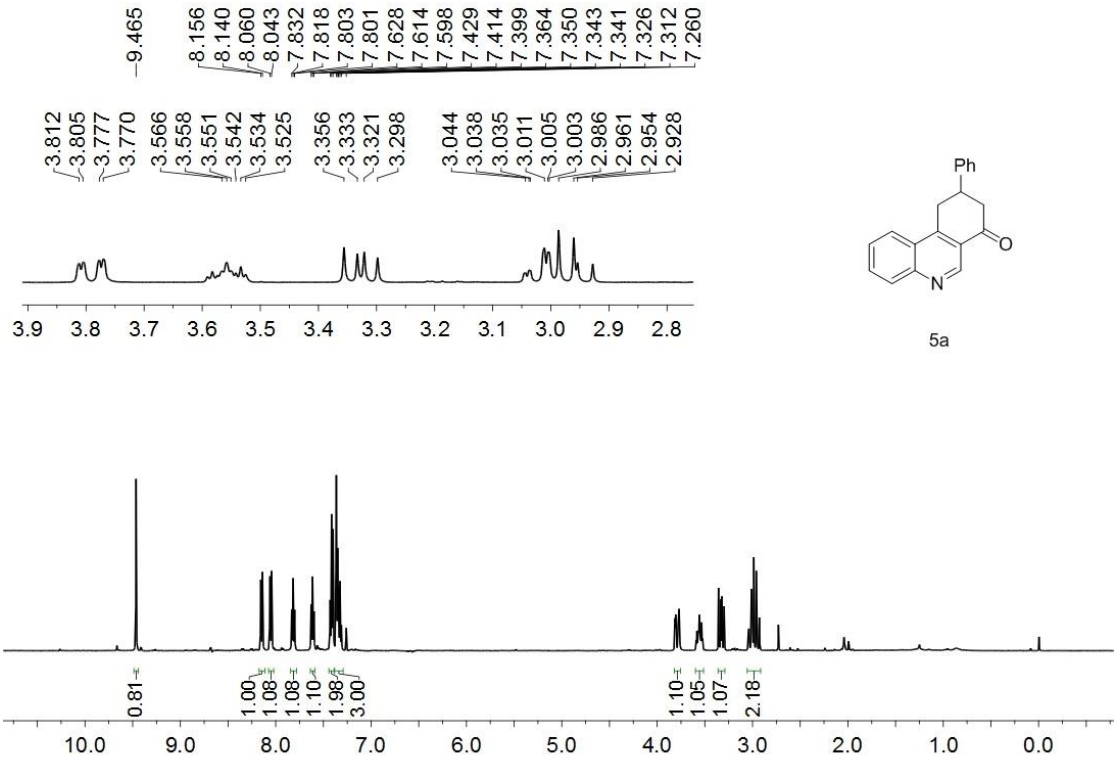
^{1}H NMR (500 MHz, DMSO-d_6) for **4a**



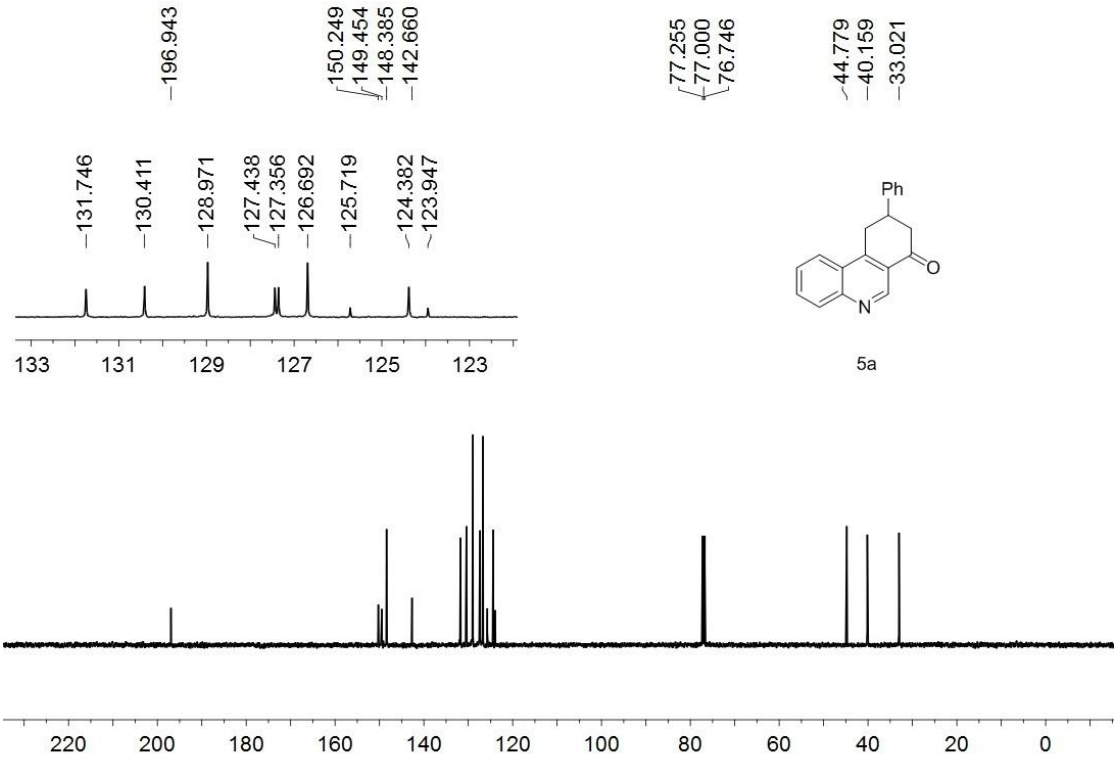
^{13}C NMR (125 MHz, DMSO-d_6) for **4a**



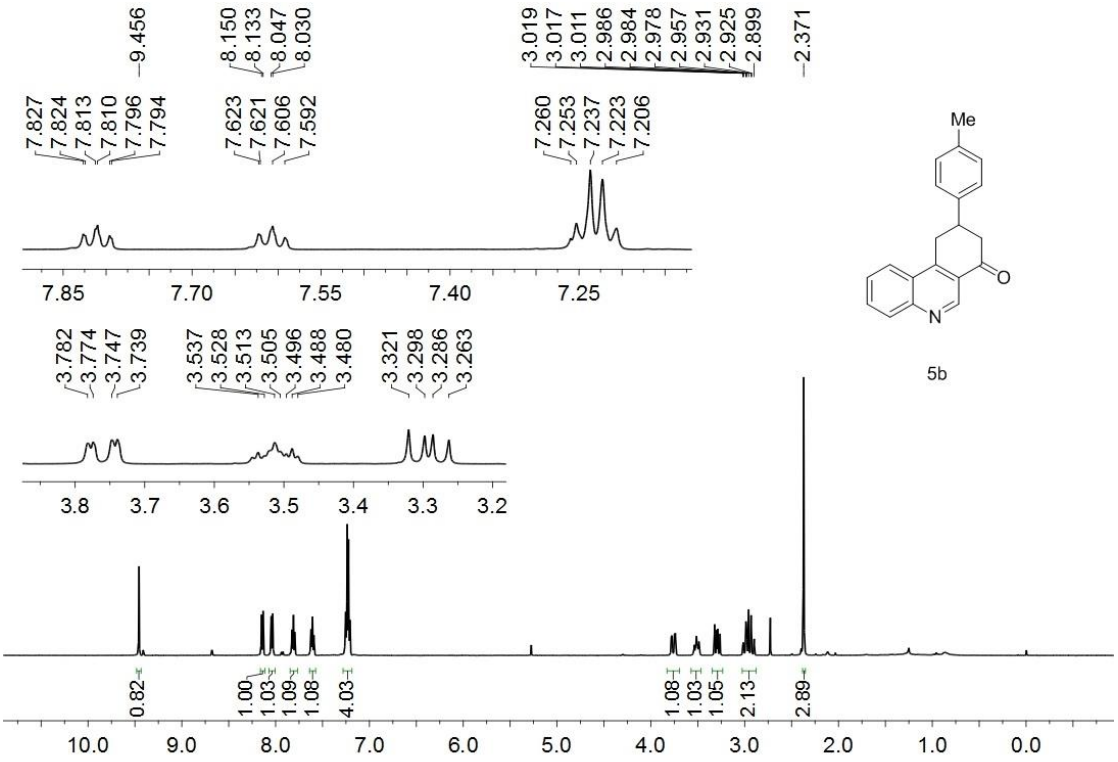
^{1}H NMR (500 MHz, $CDCl_3$) for **5a**



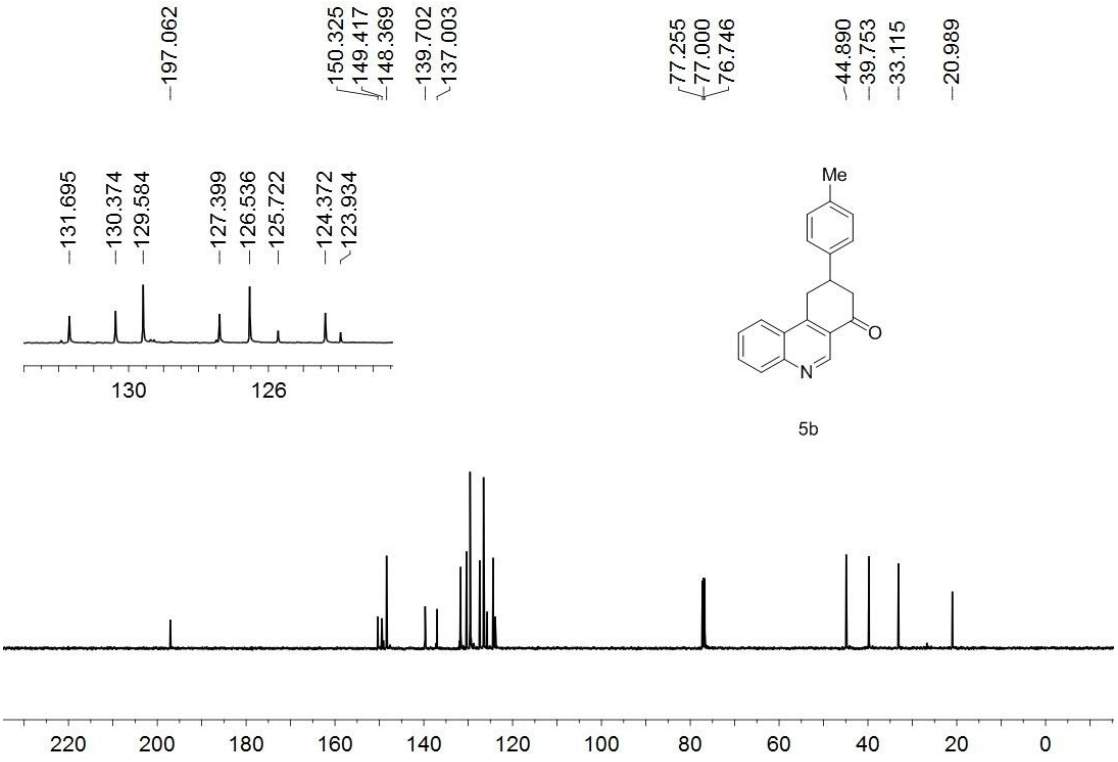
^{13}C NMR (125 MHz, $CDCl_3$) for **5a**



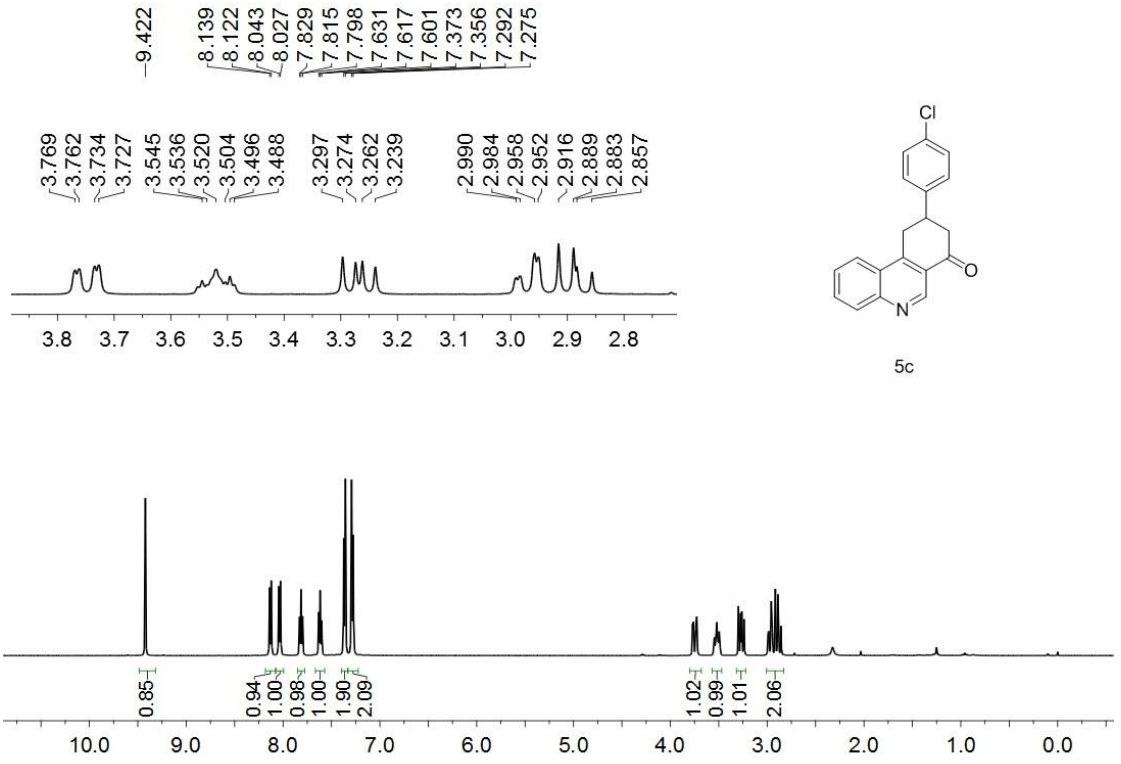
^{1}H NMR (500 MHz, $CDCl_3$) for **5b**



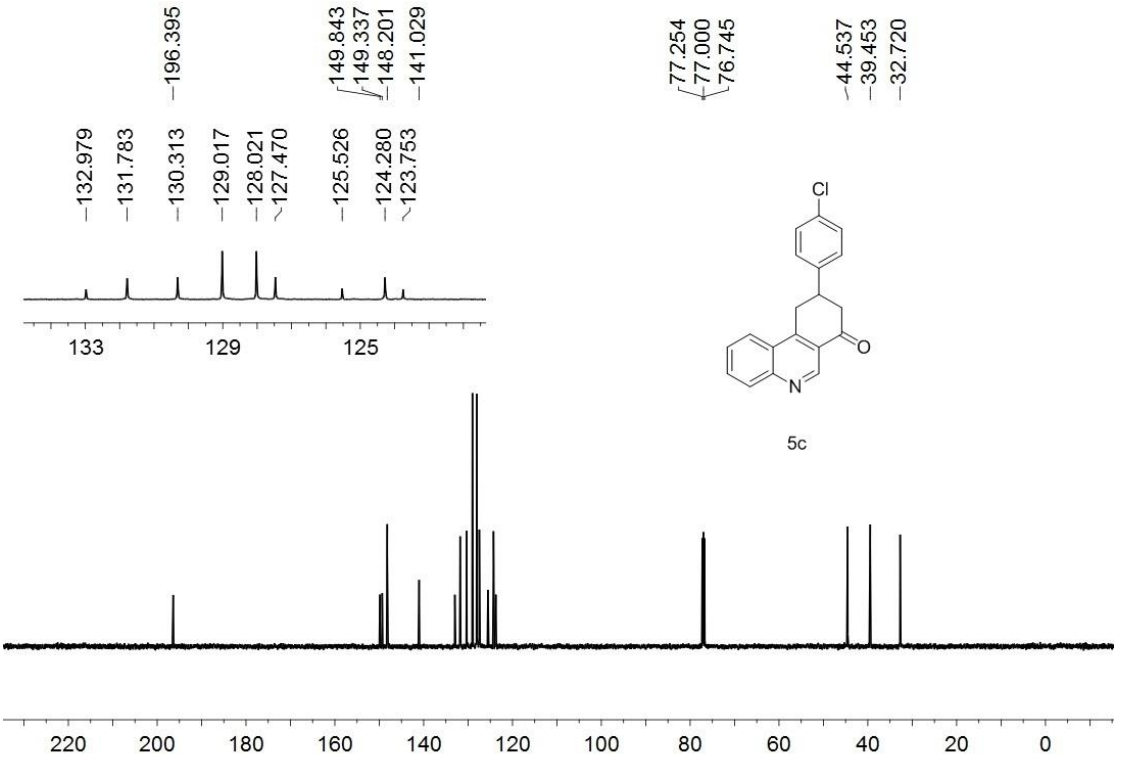
^{13}C NMR (125 MHz, $CDCl_3$) for **5b**



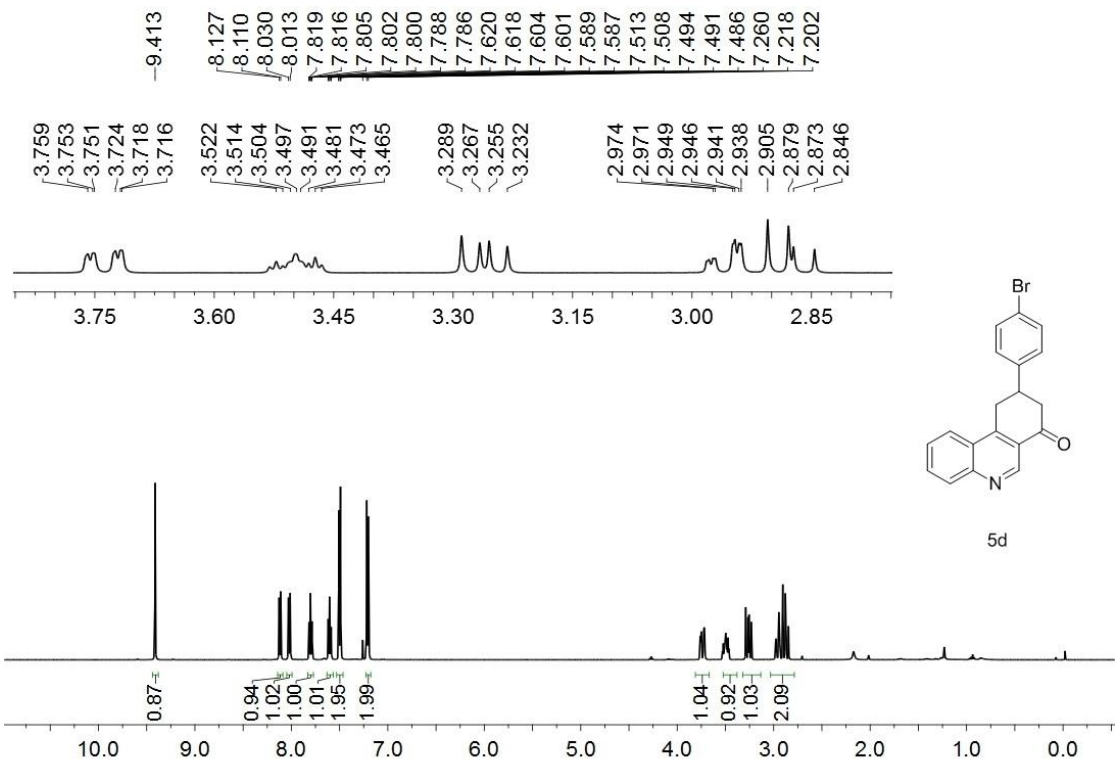
^{1}H NMR (500 MHz, $CDCl_3$) for **5c**



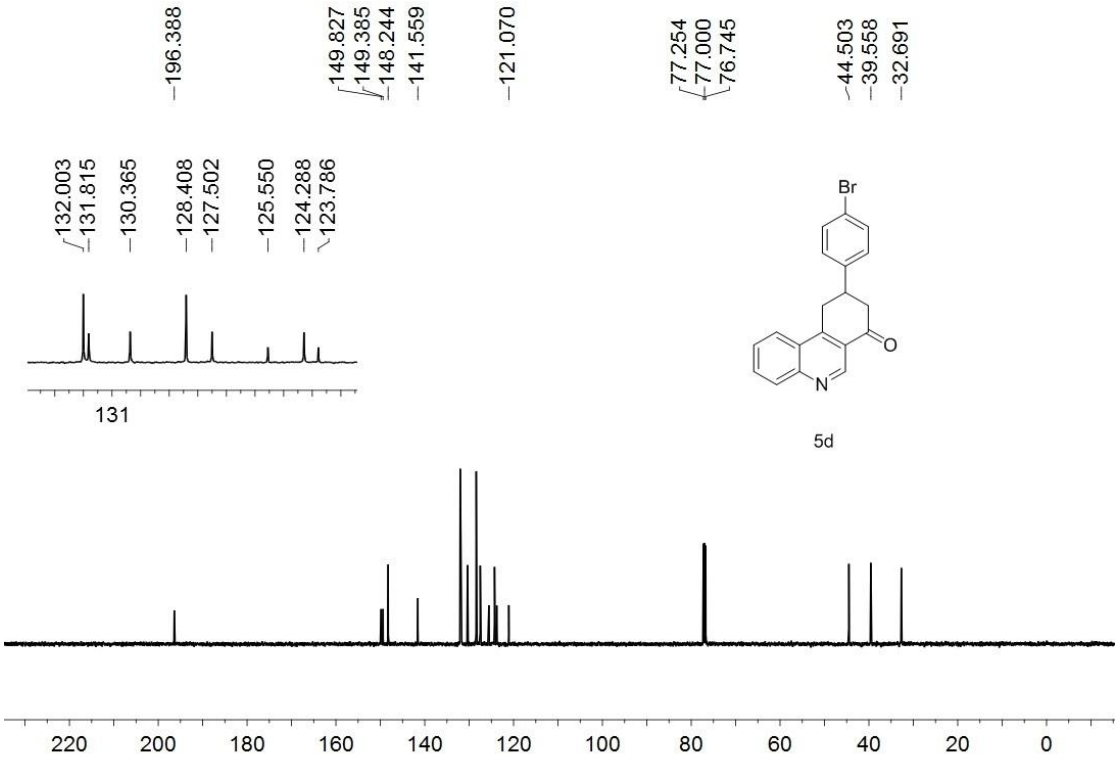
^{13}C NMR (125 MHz, $CDCl_3$) for **5c**



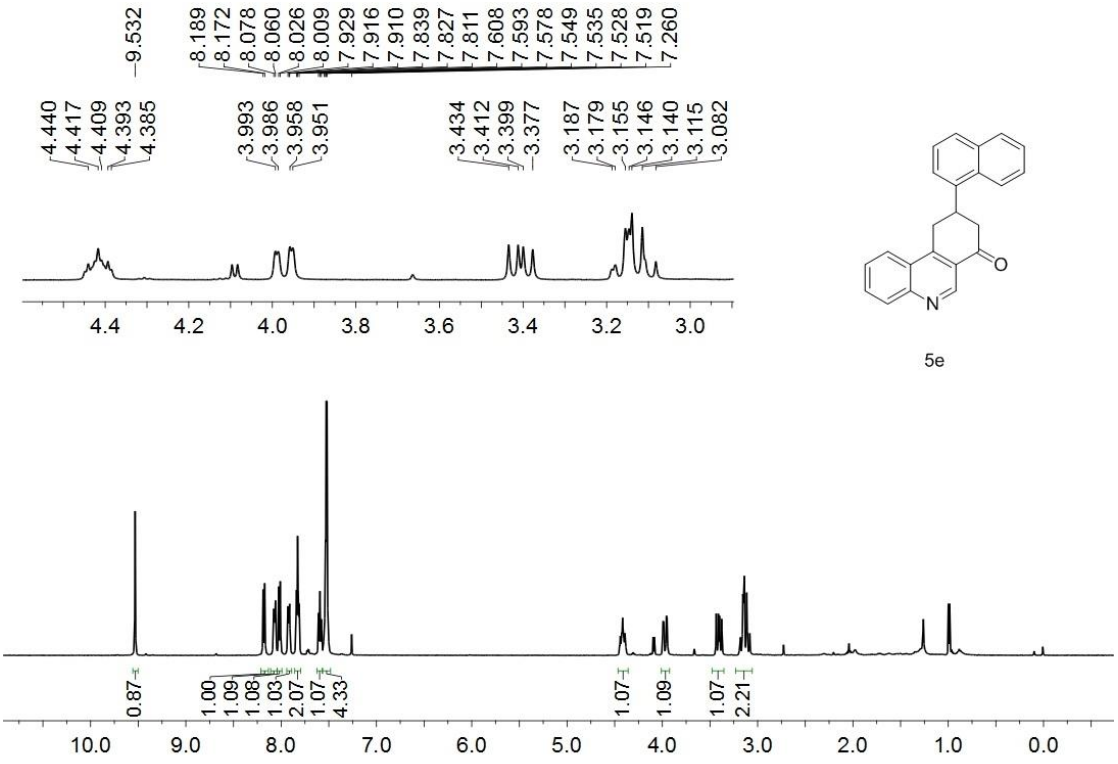
^{1}H NMR (500 MHz, $CDCl_3$) for **5d**



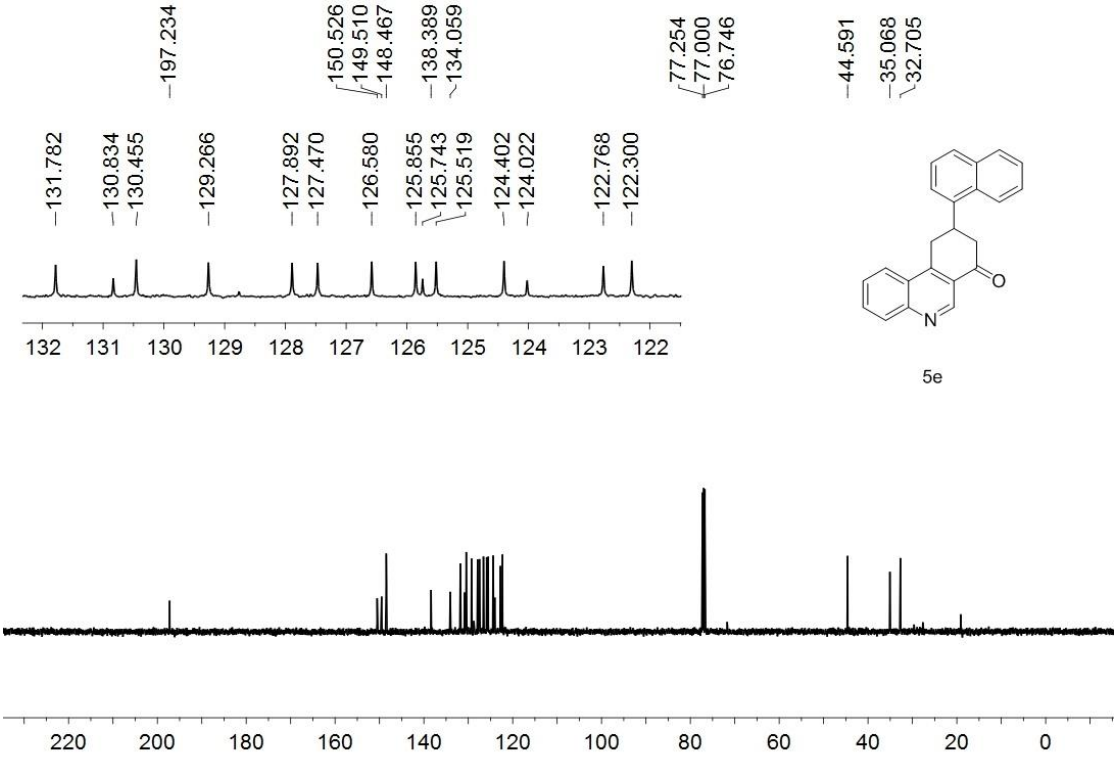
^{13}C NMR (125 MHz, $CDCl_3$) for **5d**



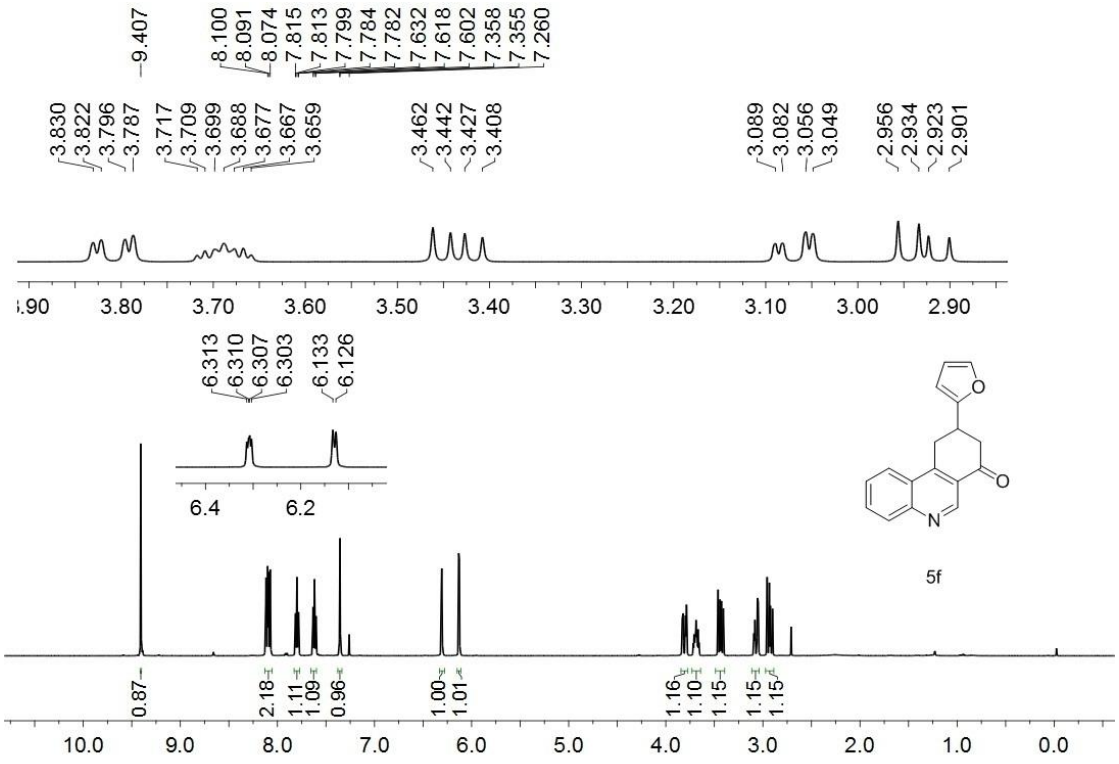
^{1}H NMR (500 MHz, $CDCl_3$) for **5e**



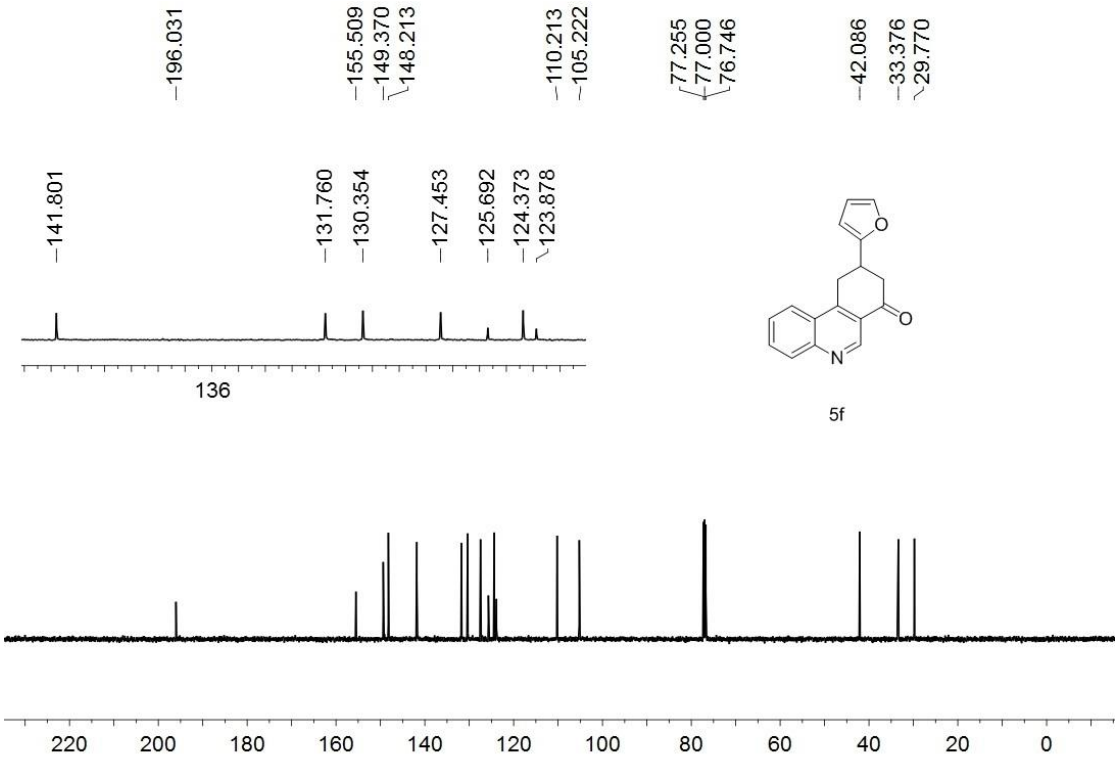
^{13}C NMR (125 MHz, $CDCl_3$) for **5e**



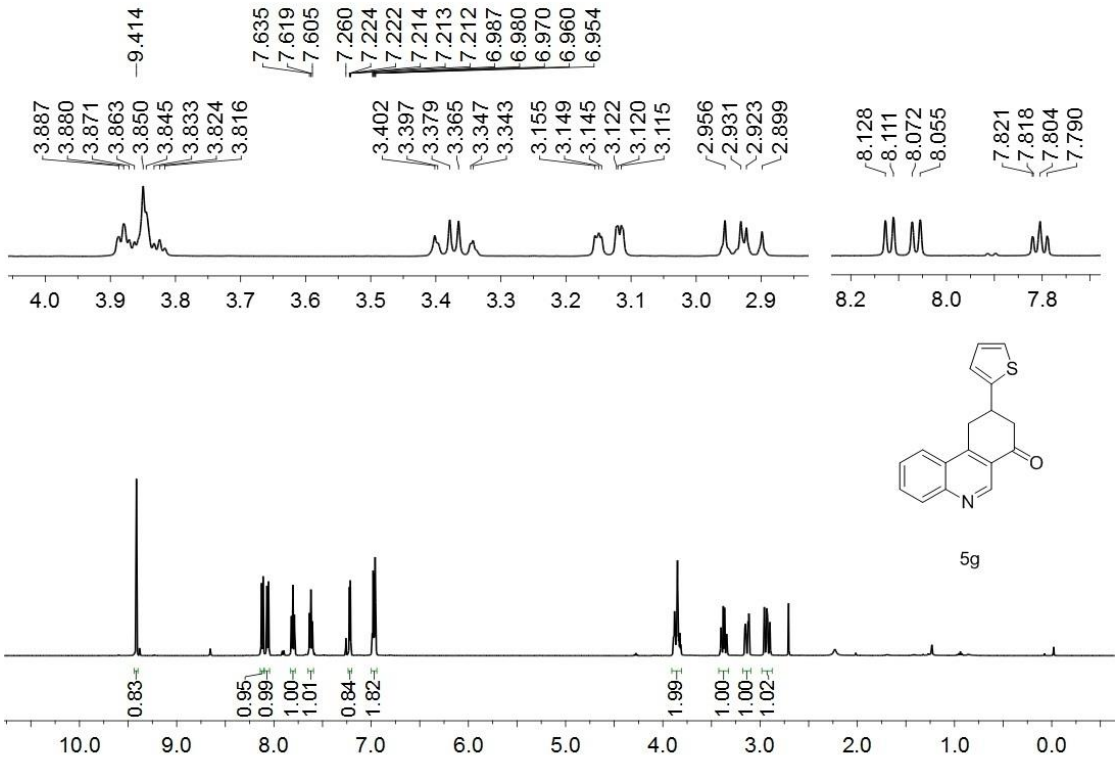
^{1}H NMR (500 MHz, $CDCl_3$) for **5f**



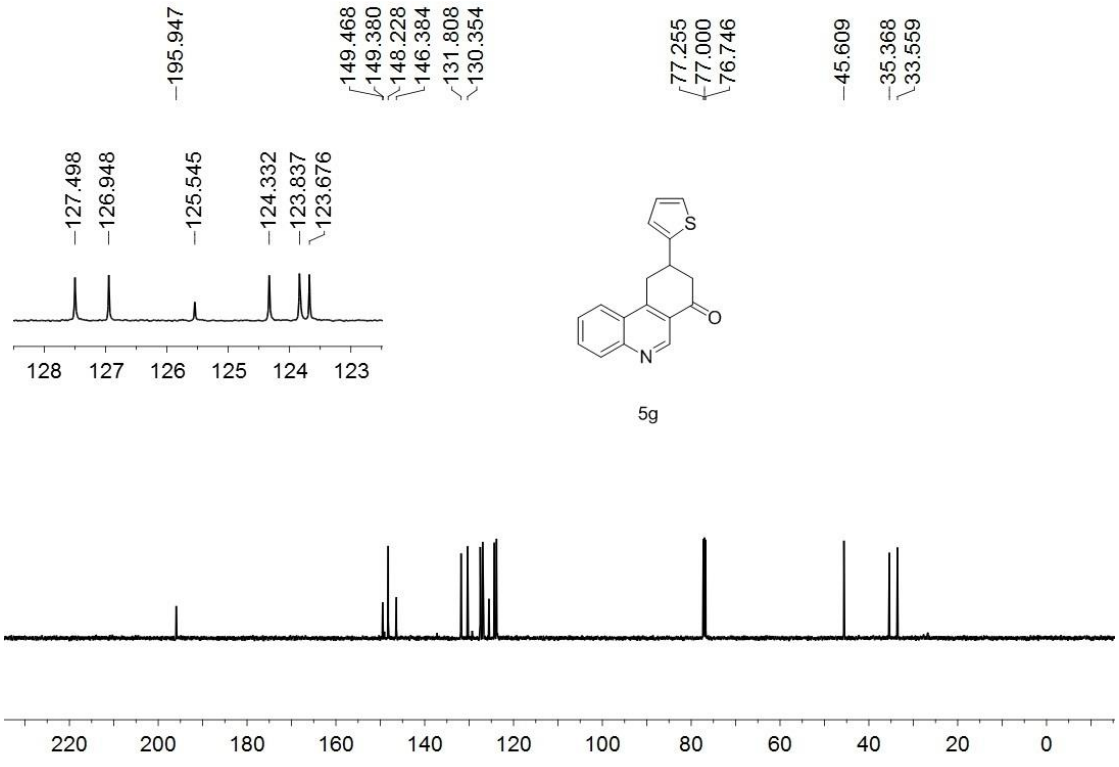
^{13}C NMR (125 MHz, $CDCl_3$) for **5f**



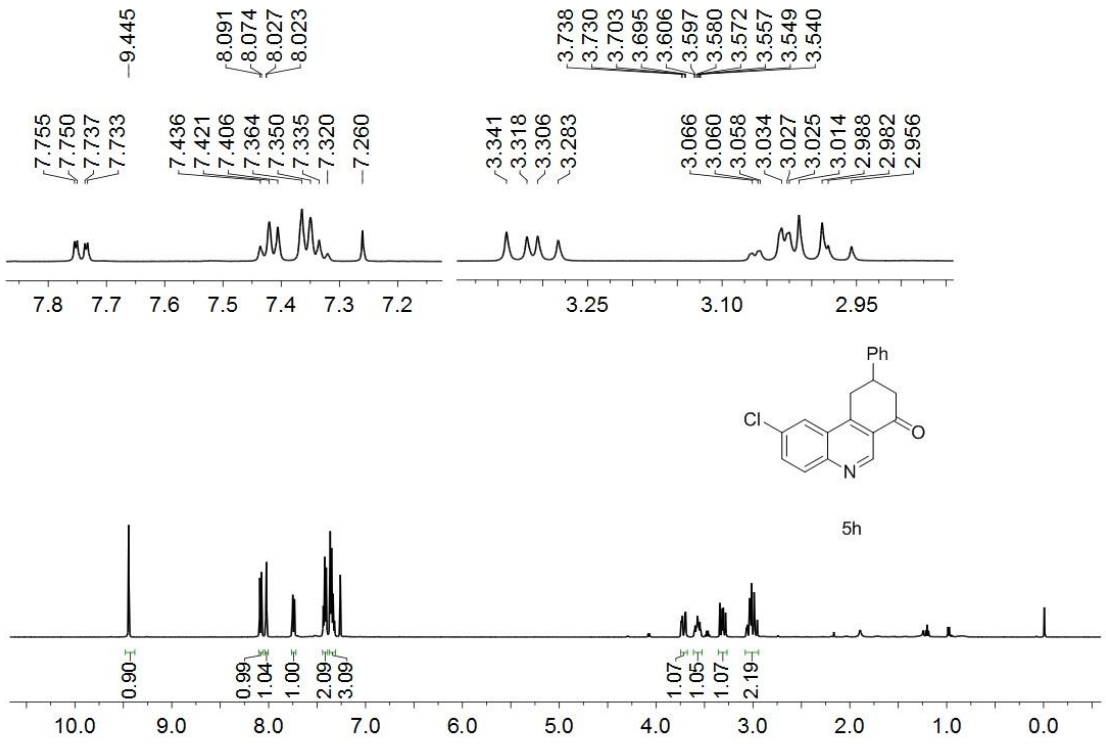
^{1}H NMR (500 MHz, $CDCl_3$) for **5g**



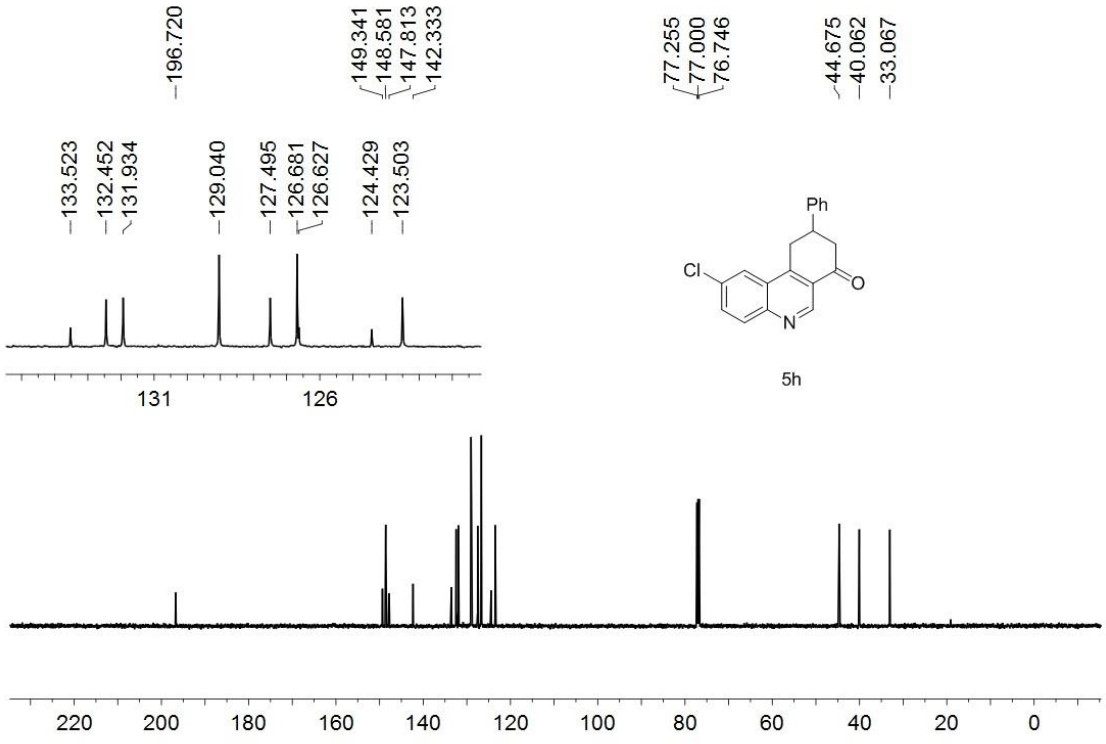
^{13}C NMR (125 MHz, $CDCl_3$) for **5g**



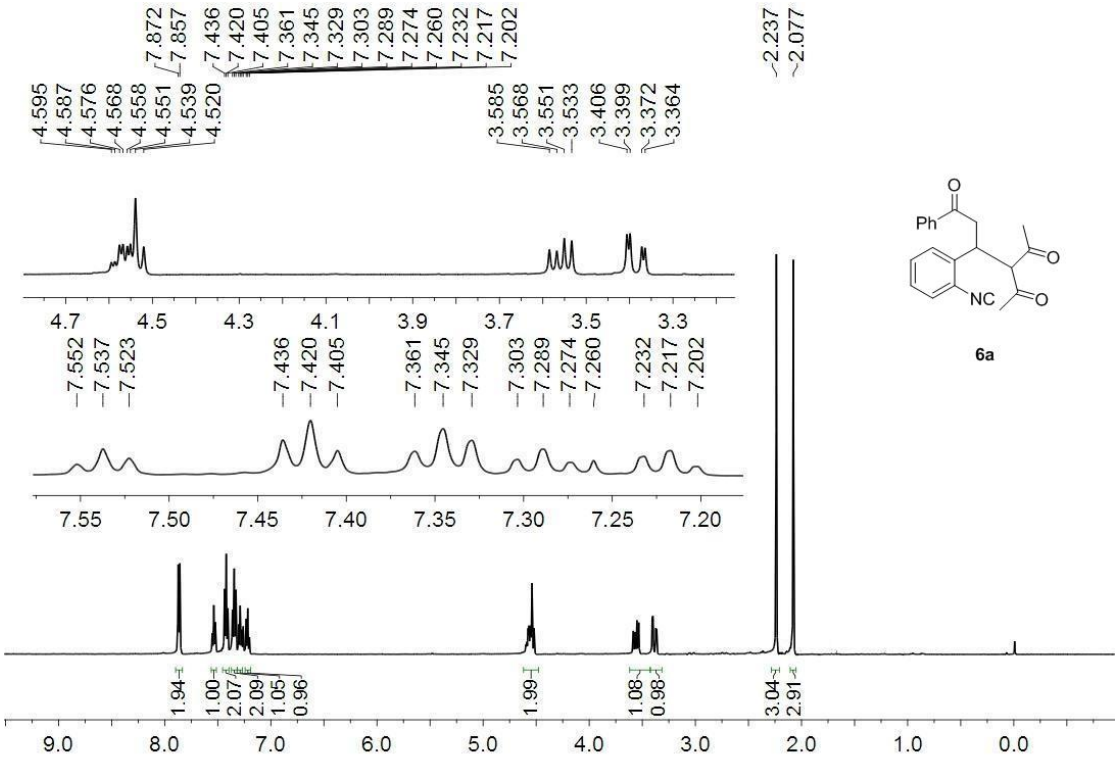
^{1}H NMR (500 MHz, $CDCl_3$) for **5h**



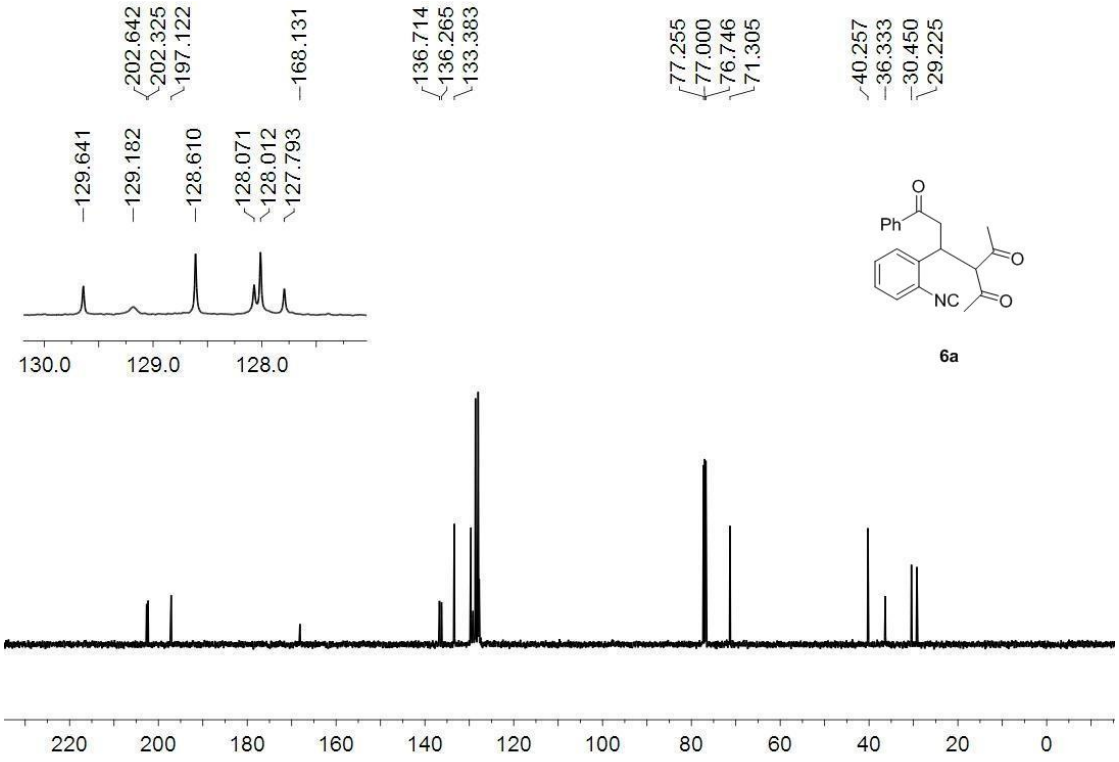
^{13}C NMR (125 MHz, $CDCl_3$) for **5h**



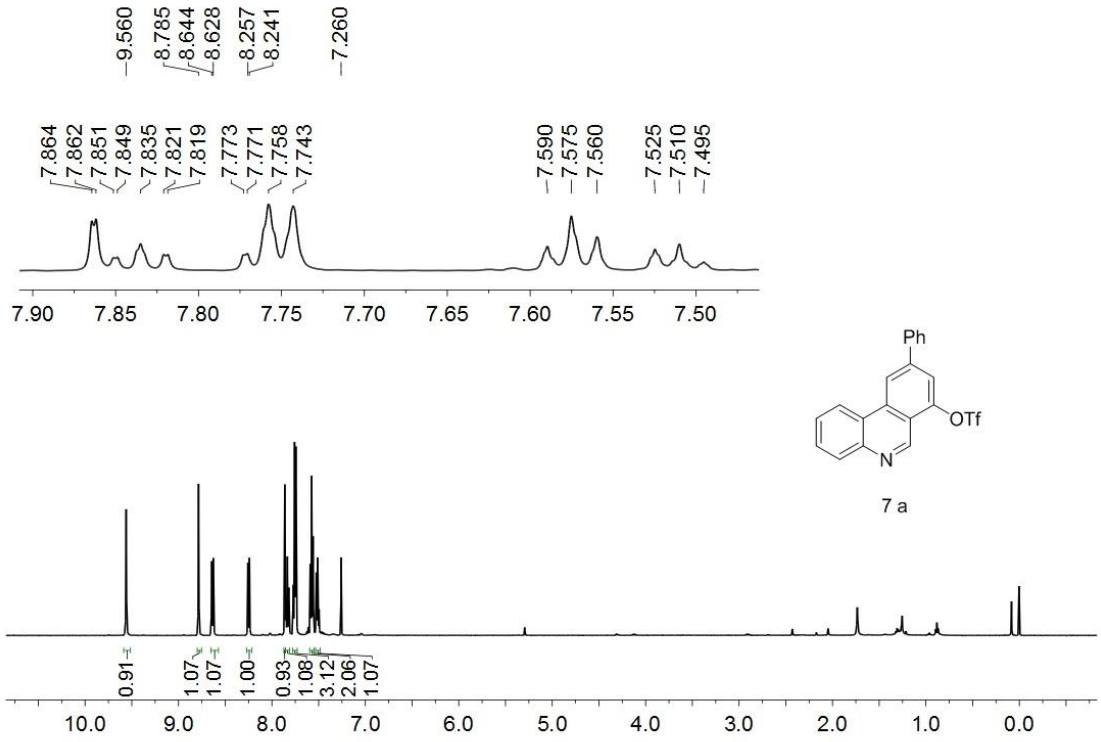
^{1}H NMR (500 MHz, $CDCl_3$) for **6a**



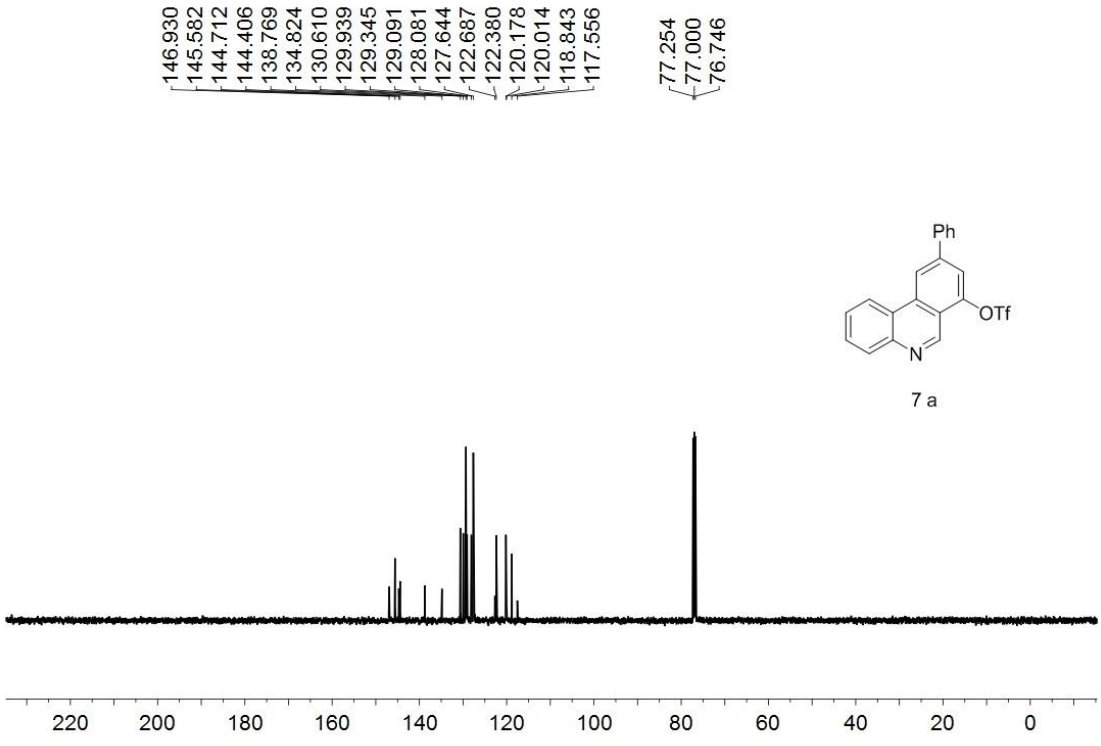
^{13}C NMR (125 MHz, $CDCl_3$) for **6a**



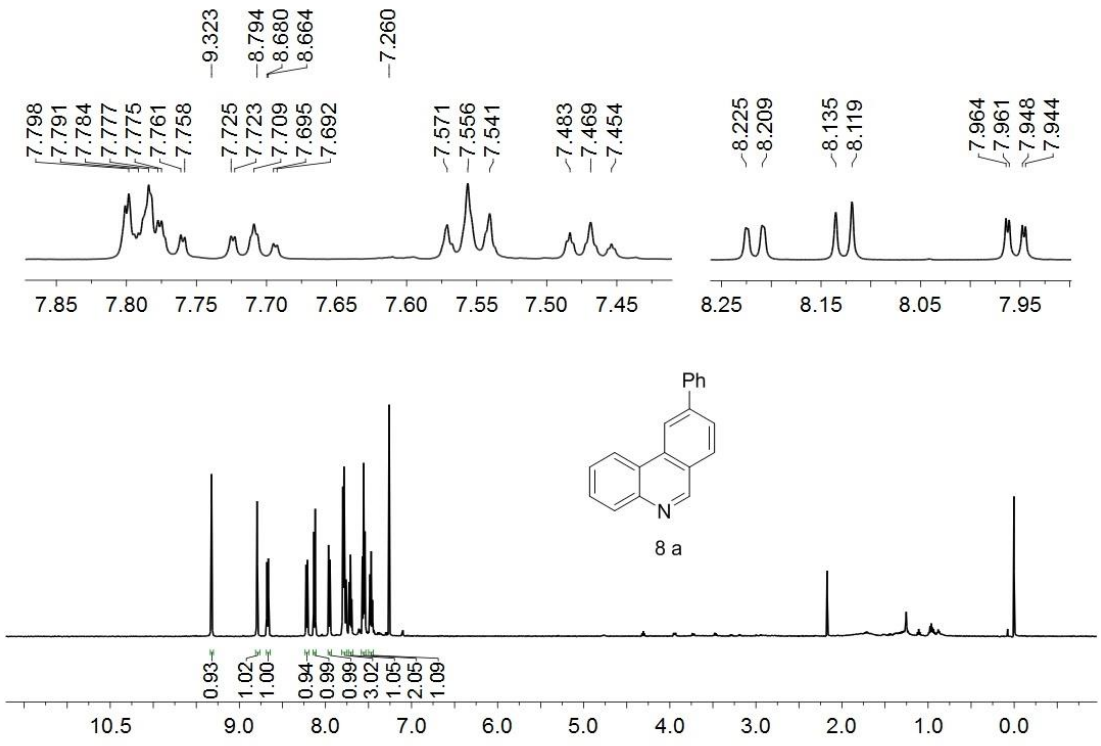
^{1}H NMR (500 MHz, $CDCl_3$) for **7a**



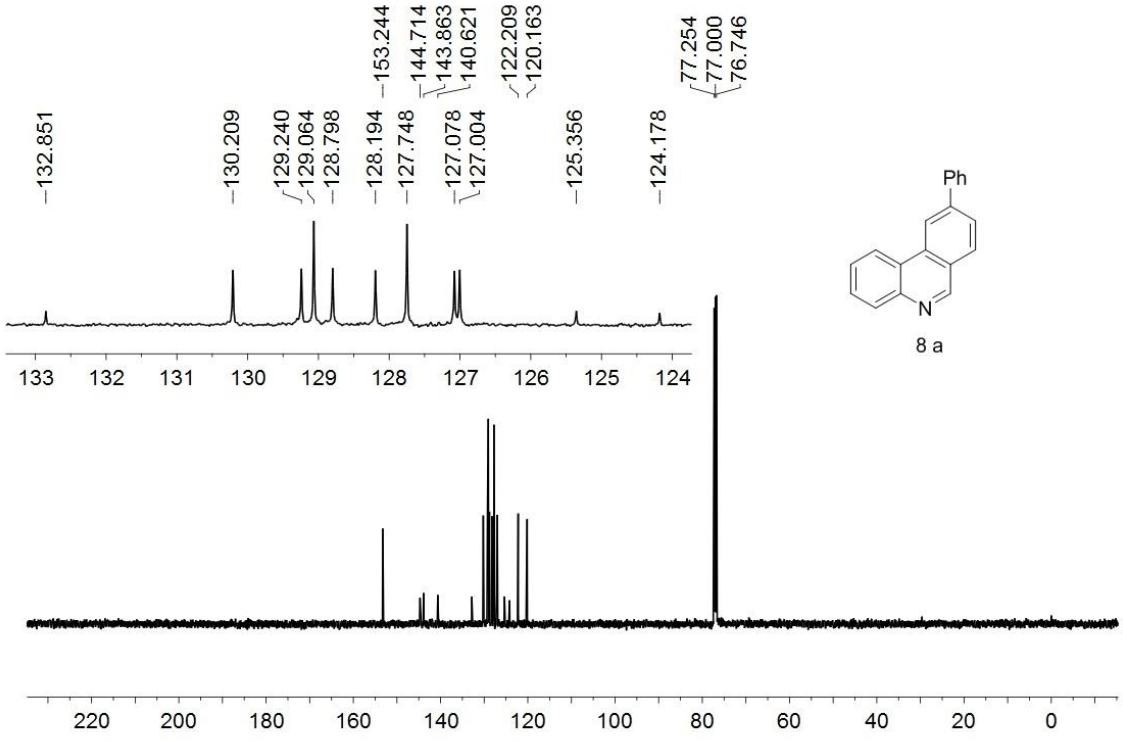
^{13}C NMR (125 MHz, $CDCl_3$) for **7a**



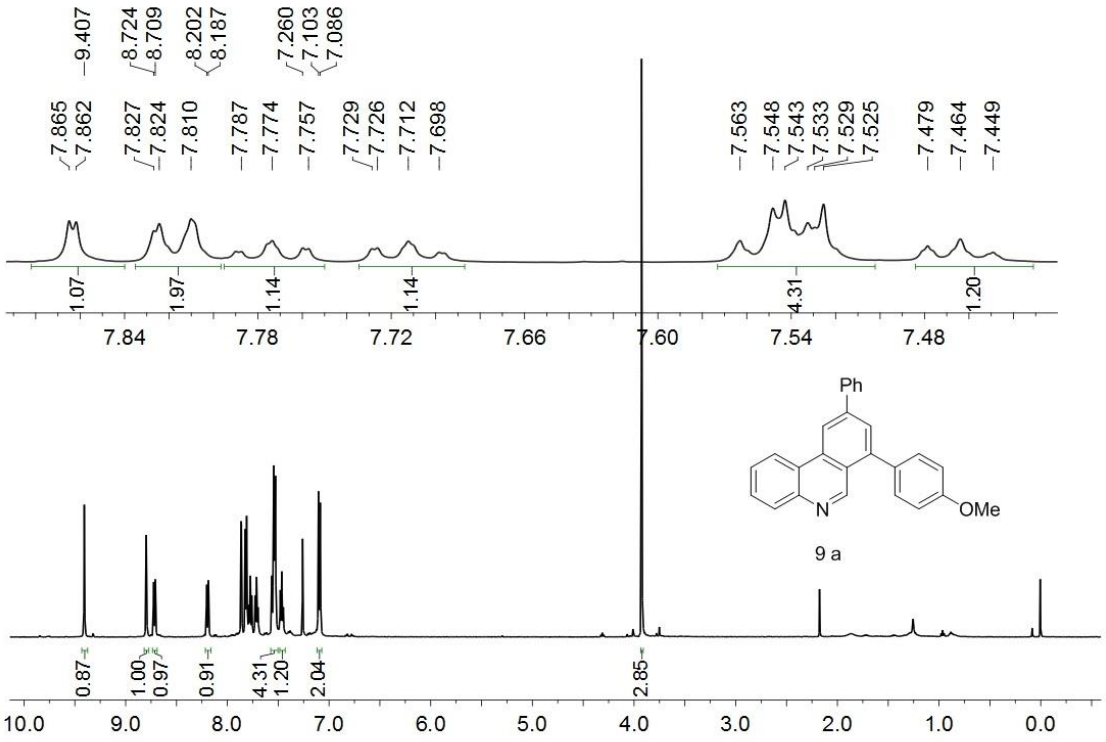
^{1}H NMR (500 MHz, $CDCl_3$) for **8a**



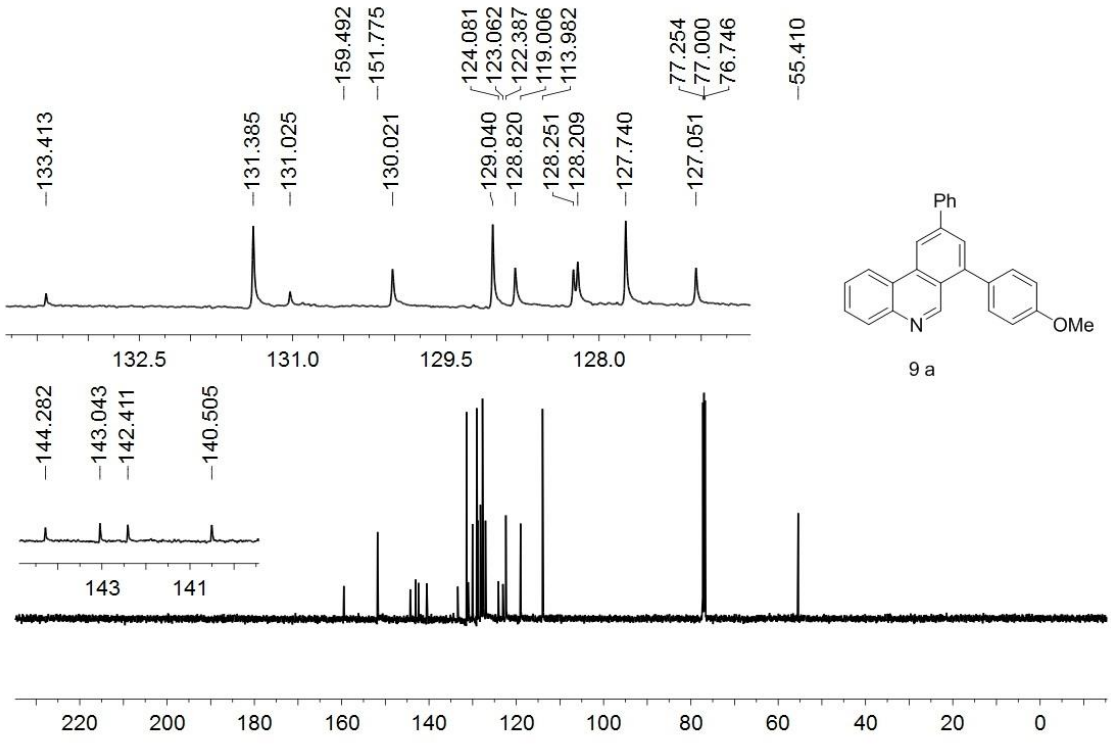
^{13}C NMR (125 MHz, $CDCl_3$) for **8a**



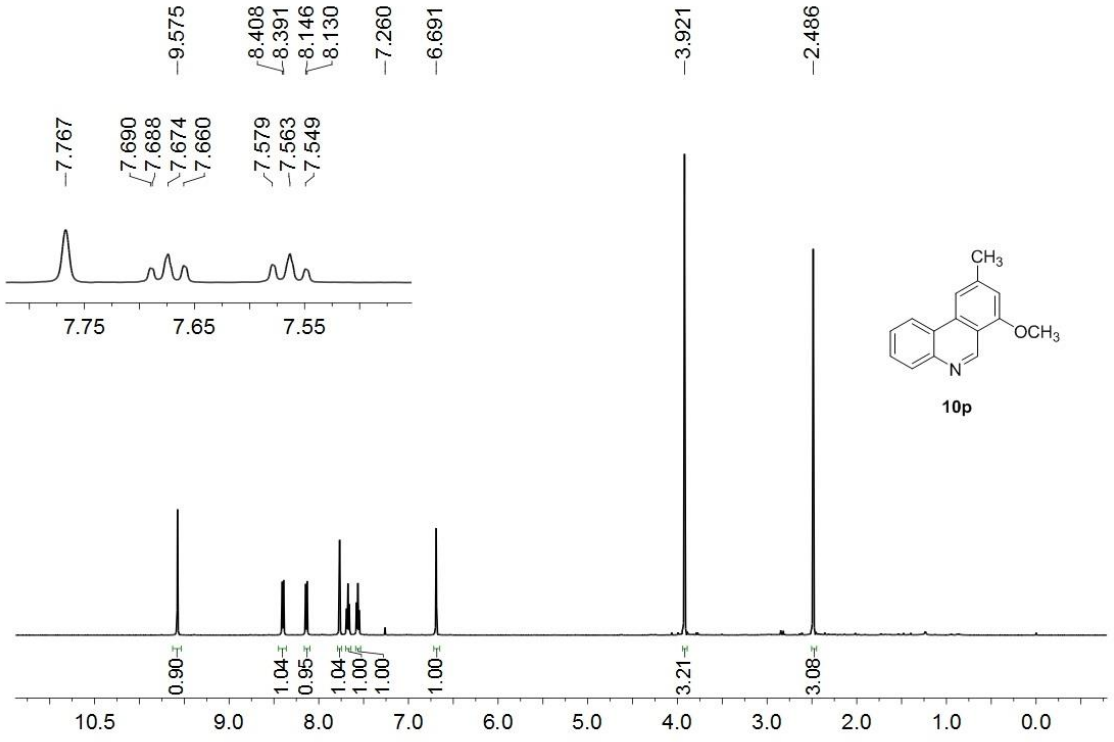
^{1}H NMR (500 MHz, $CDCl_3$) for **9a**



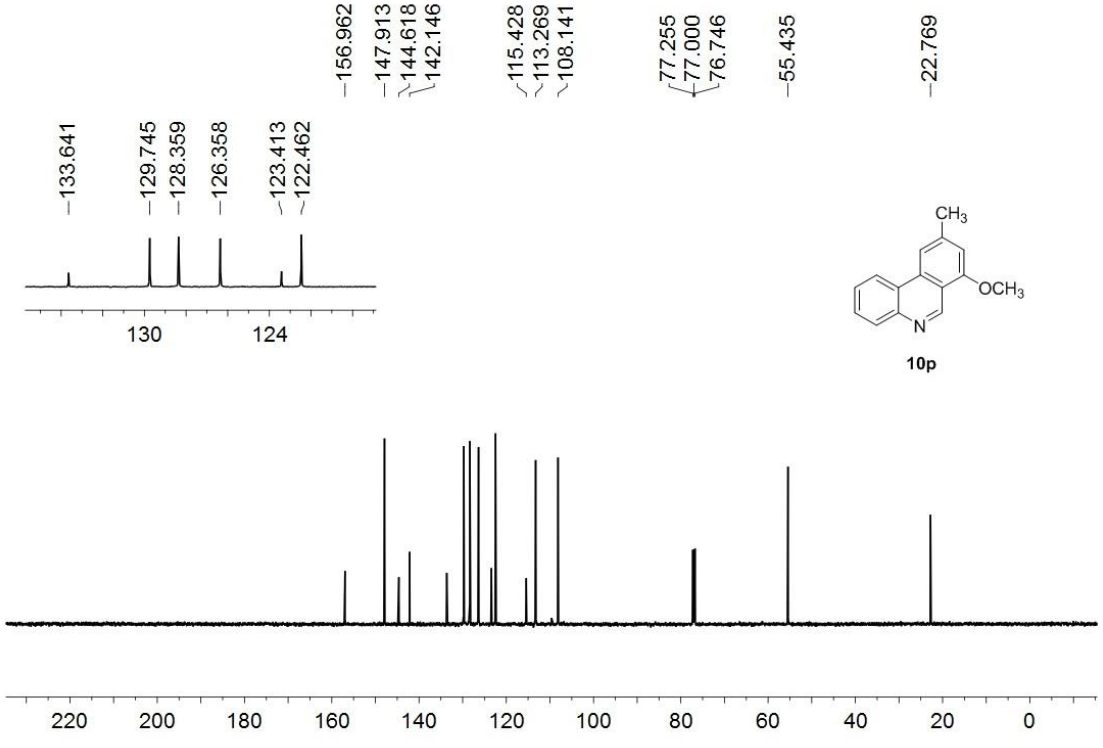
^{13}C NMR (125 MHz, $CDCl_3$) for **9a**



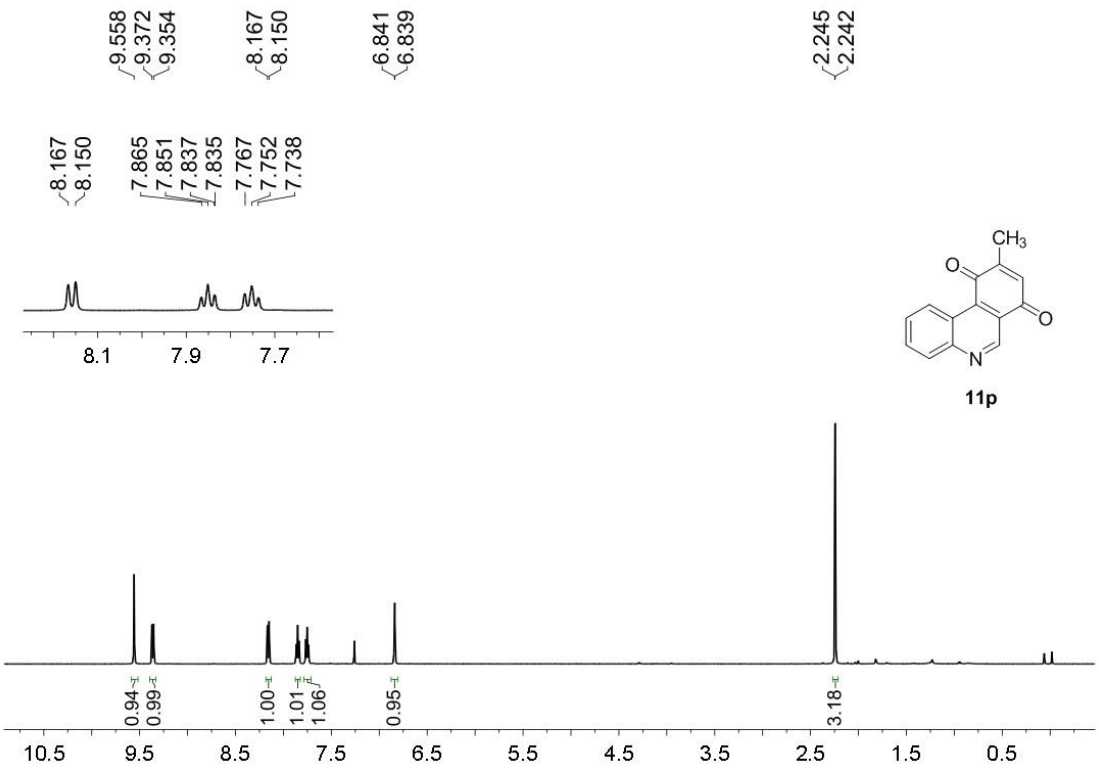
^{1}H NMR (500 MHz, $CDCl_3$) for **10p**



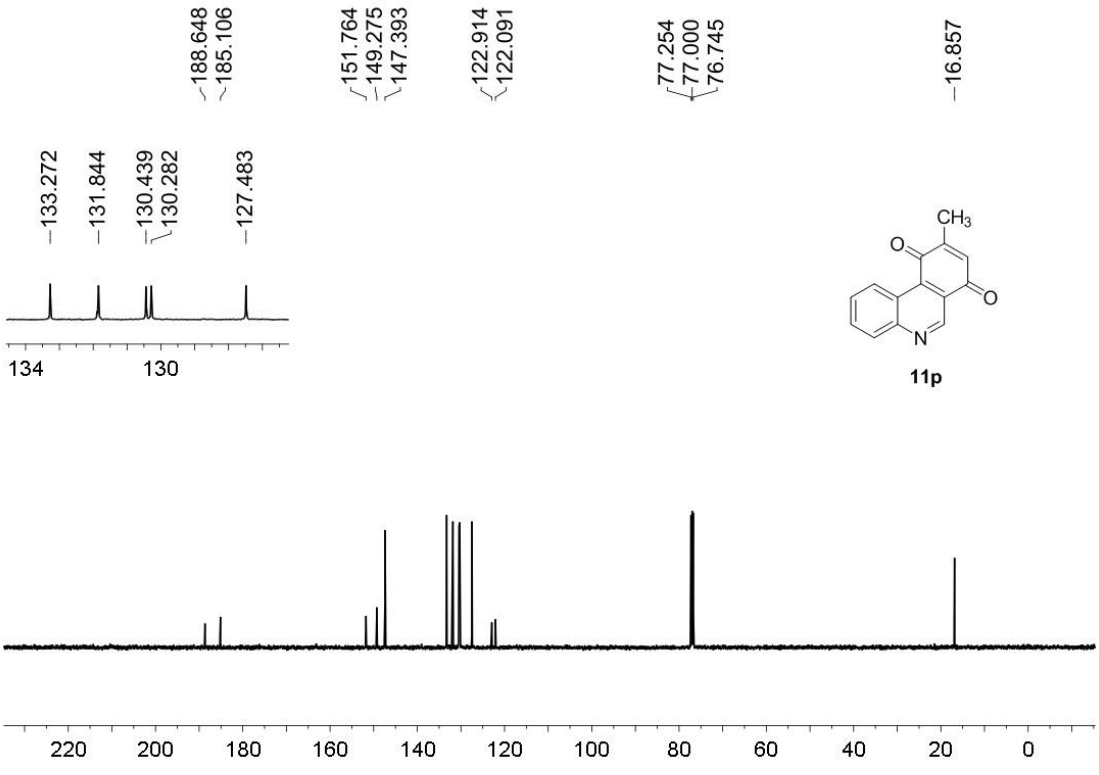
^{13}C NMR (125 MHz, $CDCl_3$) for **10p**



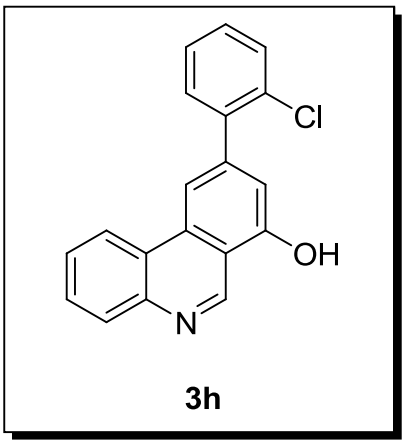
^{1}H NMR (500 MHz, $CDCl_3$) for **11p**

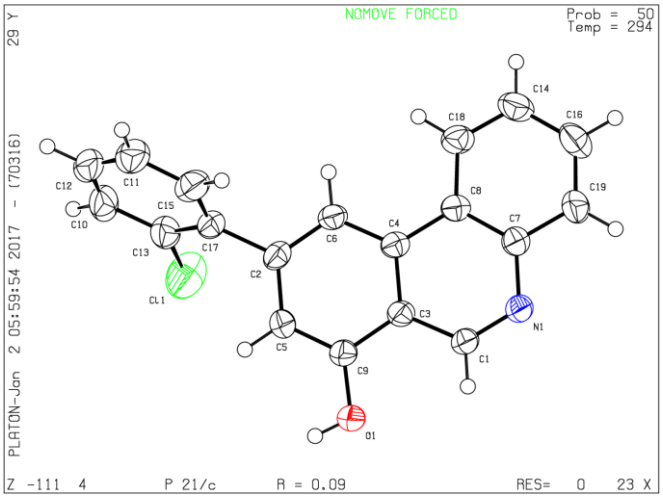


^{13}C NMR (125 MHz, $CDCl_3$) for **11p**



4. X-ray Crystallographic Data of compounds **3h**





Crystal data:

Empirical formula	$C_{19}H_{12}NOCl$
Formula weight	305.75
Crystal system	Monoclinic
Space group	P 21/c
a (Å)	10.4100(14)
b (Å)	12.0649(15)
c (Å)	11.7077(14)
α (deg)	90
β (deg)	98.209(4)
γ (deg)	90
Volume ($Å^3$)	1455.4(3)
Z	4
Calculated density (mg/m^3)	1.395
Absorption coefficient (mm^{-1})	0.263
F(000)	632.0
Theta range for data collection (deg)	2.976 to 25.000
Reflections collected/unique	1860/2550
Goodness-of-fit on F^2	1.061
Final R indices [$I > 2\sigma(I)$]	R1= 0.0870, WR2 = 0.2403
R indices (all data)	R1= 0.1131, WR2 = 0.2767