Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Syntheses of 6-Phenylbenzo[*h*]quinolines and Analogues *via* Photoinduced Dehydrogenative Annulation of (*E*)-2-phenyl- 3-styrylpyridines

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Contents

S1. General Information

^{1}H NMR and ^{13}C NMR were recorded on a Bruker-400 MHz, 600 MHz Spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz), (^{1}H: 600 MHz, ^{13}C: 150 MHz), using $CDCl_3$ as the solvent at room temperature. The chemical shifts (δ) were expressed in ppm and the coupling constants (*J*) were expressed in Hz. High-resolution mass spectra (HRMS) were recorded on a Bruker MAXIS spectrometer. All the irradiation experiments were performed in a 254 nm ultraviolet lamp (64 W) under an Ar atmosphere in quartz tubes. This lamp is assembled from eight 254 nm ultraviolet tubes (8 W) by ourselves.

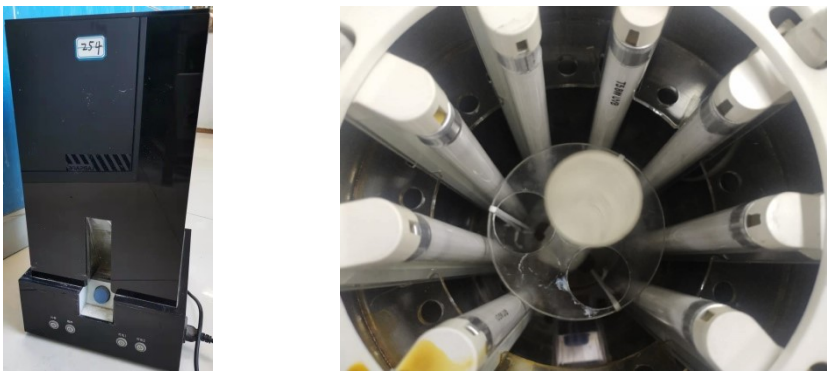
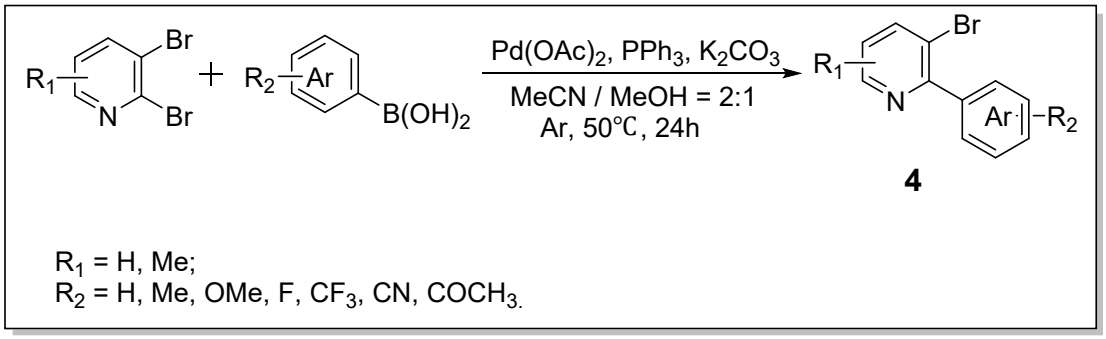


Figure S1. 254 nm ultraviolet lamp (64 W)

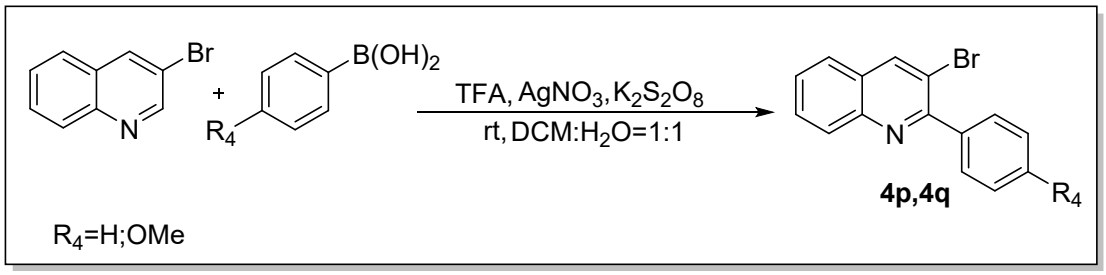
S2. General procedure for the preparation of Bromophenylpyridines and Bromophenylquinolines



Scheme S1 Preparation of Bromophenylpyridines (**4a-4o,4r-4v**)

A mixture of 2,3-dibromopyridine (3 mmol, 708 mg), arylboronic acid (1.1 eq, 3.3 mmol), PPh_3 (20%, 0.6 mmol, 157 mg), K_2CO_3 (2 eq, 6 mmol, 828 mg) and $Pd(OAc)_2$ (10%, 0.3 mmol, 68 mg) were dissolved in MeCN : MeOH = 2:1 (20 ml : 10 ml). The mixture was flushed with argon, sealed, and stirred at 50 °C for 24 h in an oil bath.

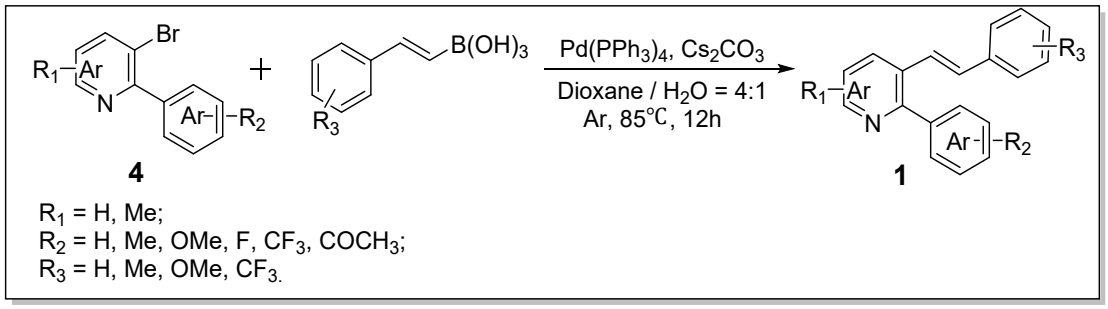
After the reaction mixture was cooled at room temperature and filtered through Celite, The volatiles were evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (40 mL × 3) and washed with water and dried over Na_2SO_4. Combined organic layers were evaporated under reduced pressure, and the residue was purified by column chromatography on silica (EtOAc - Hex = 1:30 ~ 1:20) to give bromoarylpyridines **4**.[1]



Scheme S2 Preparation of Bromophenylquinolines (**4p**) and (**4q**)

To a solution of 3-bromoquinoline (5 mmol, 1.0 equiv., 1.04 g) in dichloromethane (25 mL) was added trifluoroacetic acid (5 mmol, 1.0 equiv., 0.57 g) followed by arylboronic acid (7.5 mmol, 1.5 equiv., 1.14 g). Water (15 mL) was then added, followed by silver(I) nitrate (0.17 g, 1 mmol, 0.2 equiv.) in water (10 mL). After the addition of Potassium persulfate (4.05 g, 15 mmol, 3.0 equiv.), the solution was stirred vigorously at room temperature and monitored by thin-layer chromatography analysis of the organic layer. If a large amount of substrates remain after 3 hours, additional silver(I) nitrate (0.17 mg, 1 mmol, 0.2 equiv.) and potassium persulfate (4.05 g, 15 mmol, 3.0 equiv.) were added. Upon the consumption of substrates (3 – 24 h total), the reaction was diluted with dichloromethane (30 mL) and washed with 5% sodium bicarbonate or 2 M sodium hydroxide (20 mL, both suitable). The aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layer was dried over sodium sulfate and evaporated under reduced pressure. Purification was performed by silica gel chromatography to give chromatographically and spectroscopically pure products **4p** and **4q**.[2]

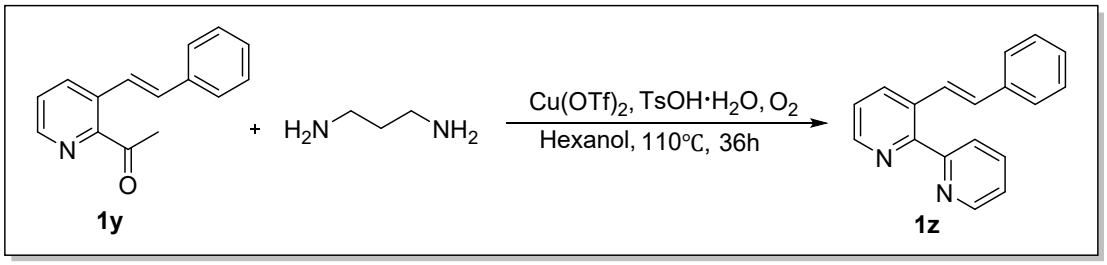
S3. General procedure for the preparation of (*E*)-2-Phenyl-3-styrylpyridines



Scheme S3 **Preparation of (*E*)-2-Phenyl-3-styrylpyridines** 1a-1y

The mixture of bromoarylpyridines **4** (1 mmol), (*E*)-styrylboronic acid or cyclohex-1-en-1-ylboronic acid (3 eq, 3 mmol), $Pd(PPh_3)_4$ (5% mmol, 58 mg) and Cs_2CO_3 (5 eq, 5 mmol, 1.63 g) was dissolved in a mixed solvent of dioxane : H_2O = 4:1 (12 ml : 3 ml). The reaction mixture was allowed to stir at 85 °C for 6-12 h under Ar atmosphere. Then, the mixture was poured into the water and extracted with ethyl acetate (30 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (EtOAc - Hex = 1:40 ~ 1:30) to give the desired product **1**.[3]

S4. General procedure for the preparation of (*E*)-3-Styryl-2,2'-bipyridine

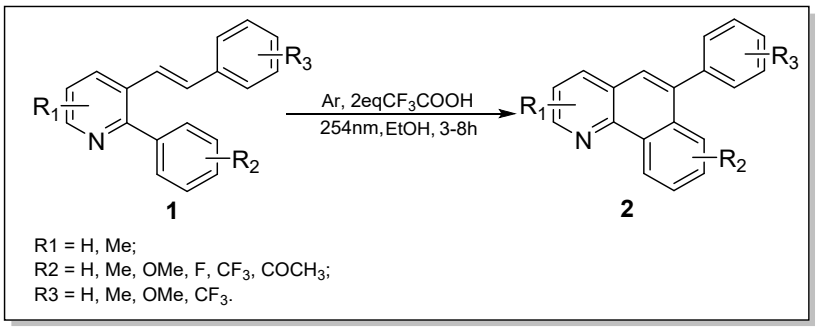


Scheme S4 Preparation of (*E*)-3-Styryl-2,2'-bipyridine **1z**

The mixture of (*E*)-1-(3-styrylpyridin-2-yl)ethan-1-one **1y** (3 mmol), propane-1,3-diamine (9 mmol, 3 equiv.), $Cu(OTf)_2$ (30% mmol, 108 mg) and $TsOH•H_2O$ (1.8

mmol, 0.6 equiv., 310 mg) was dissolved in 3 ml of hexanol. The reaction mixture was allowed to stir at 110 °C for 36 h under O_2 atmosphere. Then, the mixture was poured into the water and extracted with ethyl acetate (30 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate - hexane = 1:20) to give the desired product (*E*)-3-styryl-2,2'-bipyridine **1z**.[4]

S5. General syntheses of 6-Phenylbenzo[*h*]quinolines and Analogues



Scheme S5 Synthesis of 6-Phenylbenzo[*h*]quinolines and Analogues 2a-2z

After the solution of (*E*)-2-phenyl-3-styrylpyridines **1** (0.4 mmol) in EtOH (80 mL) was degassed (ultrasound, 30 min) and deaerated (bubbling argon, 30 min) in a 100 mL sealed quartz tube, CF_3COOH (2 equiv.) was added to this solution. The resulting mixture was irradiated with a 254 nm ultraviolet lamp (64 W) at room temperature until reactant was consumed completely as indicated by thin-layer chromatography (TLC). The solvent was removed under reduced pressure, and the residue was purified by column chromatography (EtOAc - Hex = 1:100 ~ 1:50) to give 6-phenylbenzo[*h*]quinolines **2**.

S6. UV absorption spectra of 1a

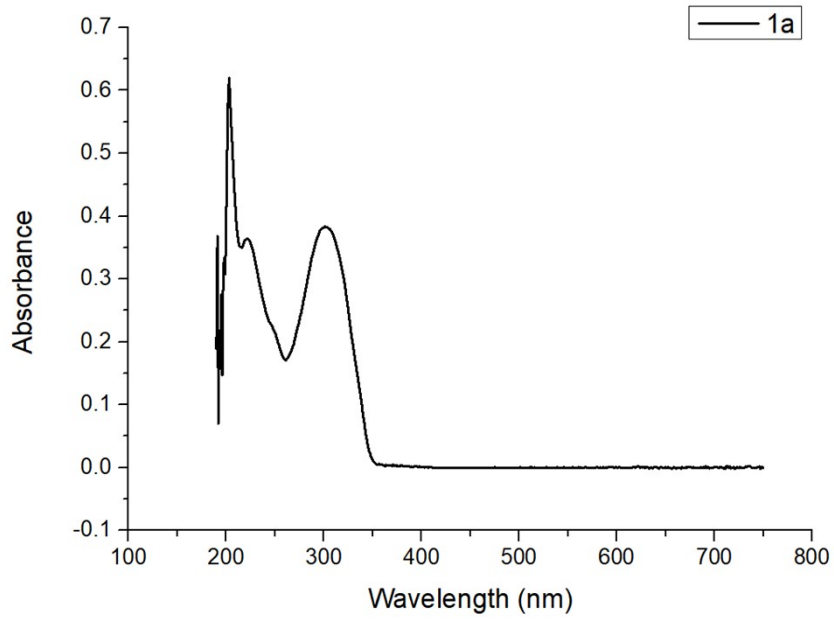


Figure S2. UV absorption spectra of **1a** in EtOH (10^{-5} M).

S7. H_2 detection for the photoinduced dehydrogenative annulation of 1a by GC

GC conditions: Argon was used as carrier gas, stainless steel column (column length 2 m, column temperature at 50 °C, Tam TDS-01 60~80 mesh) and thermal conductivity detector (TCD temperature at 80 °C) were used for gas chromatography analysis. Under the conditions of gas velocity of 0.5 Mpa and the flow rate of 70 mL/min, gas was analysized at room temperature with injection of 30 μL.

Experiment of photoinduced dehydrogenative annulation of 1a:

The EtOH (200 ml) was degassed for an hour by ultrasonic to remove the dissolved oxygen. Sodium sulfite (25 g) and hydroquinone (2.0 g) were added and the mixture was refluxed for 2 h. Then, (*E*)-2-phenyl-3-styrylpyridine **1a** (0.1 g, 0.4 mmol) was dissolved in 80 mL deoxidization EtOH in a 100 mL quartz tube under argon atmosphere followed by the addition of CF_3COOH (2 equiv.) via syringe. After sealing, the quartz tube was irradiated with a 254 nm ultraviolet lamp (64 W) for 5 h.

Results of detection: After the reaction of photoinduced dehydrogenative annulation of **1a**, gas in the quartz tube was examed by GC. The retention time t_{R1} of standard H_2 sample was 1.32 min and the retention time t_{R2} of gas in the quartz tube was 1.34 min (Figure S3). It indicated that H_2 was generated during the photoinduced anuulation of**1a**.

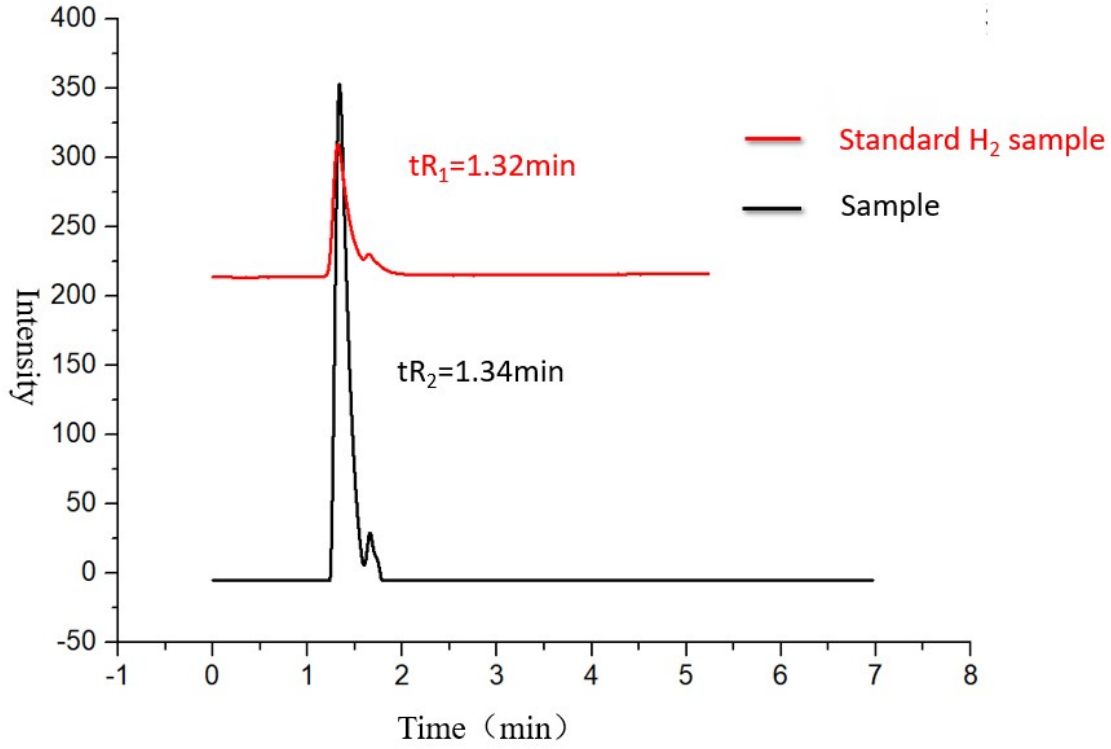
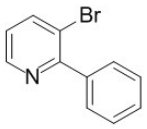


Figure S3. Chromatogram of reference substance H_2 and gas in the tube of photoinduced dehydrogenative annulation of **1a**.

S8. Characterization Data for Products

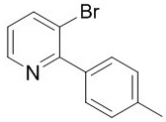
The data of 4a-4v

3-Bromo-2-phenylpyridine (4a)



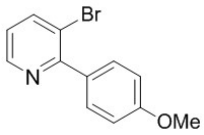
Yield: 70% (490 mg). Colorless oil. Purified by flash column chromatography (EtOAc/hexane = 1/30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.7, 0.9 Hz, 1H), 7.97 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.50 – 7.41 (m, 3H), 7.10 (dd, *J* = 8.0, 4.6 Hz, 1H).[1]

3-Bromo-2-(*p*-tolyl)pyridine (4b)



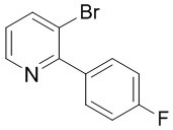
Yield: 72% (533 mg). Colorless oil. Purified by flash column chromatography (EtOAc/hexane = 1/30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.6, 1.5 Hz, 1H), 7.96 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.09 (dd, *J* = 8.0, 4.6 Hz, 1H), 2.42 (s, 3H).[3]

3-Bromo-2-(4-methoxyphenyl)pyridine (4c)



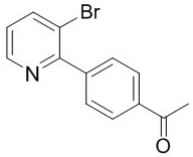
Yield: 71% (560 mg). Colorless oil. Purified by flash column chromatography (EtOAc/hexane = 1/30). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.58 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.93 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.05 (dd, *J* = 8.0, 4.6 Hz, 1H), 7.00 – 6.95 (m, 2H), 3.84 (s, 3H).[1]

3-Bromo-2-(4-fluorophenyl)pyridine (4d)



Yield: 52% (390 mg). White solid. m.p. 89.0-89.6 °C. Purified by flash column chromatography (EtOAc/hexane = 1/30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.5 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.68 (dd, *J* = 7.4, 5.8 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 4.3 Hz, 1H).[1]

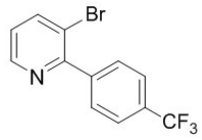
1-(4-(3-Bromopyridin-2-yl)phenyl)ethan-1-one (4e)



Yield: 53% (437 mg). White solid. m.p. 66.3-67.4 °C. Purified by flash column chromatography (EtOAc/hexane = 1/30). ^{1}H NMR

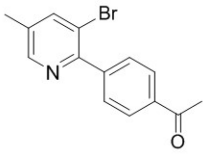
(400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 4.6, 1.2 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 2H), 8.00 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.18 (dd, *J* = 8.1, 4.6 Hz, 1H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 157.2, 148.4, 144.1, 141.6, 137.1, 129.8, 128.1, 123.9, 119.9, 26.9. HRMS (ESI) m/z calcd for. $C_{13}H_{10}BrNO$ $[M+Na]^+$ 297.9838, found 297.9831.

3-Bromo-2-(4-(trifluoromethyl)phenyl)pyridine (4f)



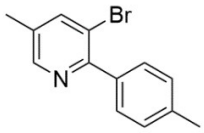
Yield: 68% (614 mg). Yellow solid. m.p. 50.5-51.8 °C. Purified by flash column chromatography (EtOAc/hexane = 1/30). ^1H NMR (600 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 4.6, 1.4 Hz, 1H), 8.01 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.18 (dd, *J* = 8.1, 4.6 Hz, 1H).[1]

1-(4-(3-Bromo-5-methylpyridin-2-yl)phenyl)ethan-1-one (4g)



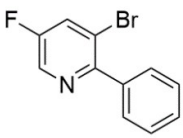
Yield: 57% (494 mg). White solid. m.p. 89.4-90.5 °C. Purified by flash column chromatography (EtOAc/hexane = 1/30). ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.83 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 2.63 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 154.2, 148.9, 144.1, 141.8, 136.9, 134.2, 129.8, 128.1, 119.3, 26.8, 17.8. HRMS (ESI) m/z calcd for. $C_{14}H_{12}BrNO$ $[M+Na]^+$ 311.9994, found 311.9987.

3-Bromo-5-methyl-2-(p-tolyl)pyridine (4h)



Yield:88% (523 mg). White solid. m.p. 31.3-33.1 °C. Purified by flash column chromatography (EtOAc/hexane = 1/300).^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.78 (d, *J* = 0.9 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 2.40 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.33, 148.58, 141.57, 138.39, 136.70, 133.11, 129.26, 128.64, 119.26, 21.38, 17.58. HRMS (ESI) m/z calcd for. $C_{13}H_{12}BrN$ $[M+H]^+$ 262.0226, found 262.0228.

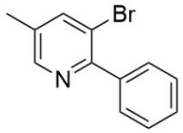
3-Bromo-5-fluoro-2-phenylpyridine (4i)



Yield:70.6% (534 mg). White solid. m.p. 31.6-33.4 °C. Purified by flash column chromatography (EtOAc/hexane = 1/1000). ^1H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 2.4 Hz, 1H), 7.78 (dd, *J* =

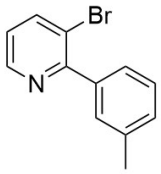
7.6, 2.5 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.46 (q, J = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.41 (d, ^1J = 263.0 Hz), 154.62 (d, ^3J = 3.9 Hz), 138.69 (s), 136.34 (d, ^2J = 22.3 Hz), 129.32 (s), 128.86 (s), 128.18 (d, ^2J = 20.4 Hz), 128.05 (s), 118.97 (d, ^4J = 3.2 Hz). HRMS (ESI) m/z calcd for. $C_{11}H_7BrFN$ $[M+H]^+$ 251.9819, found 251.9820.

3-Bromo-5-methyl-2-phenylpyridine (4j)



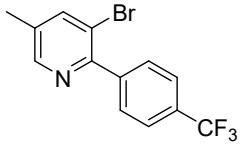
Yield:86.5%(644 mg). Colorless oil. Purified by flash column chromatography (EtOAc/hexane = 1/300).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.80 (s, 1H), 7.68 (d, J = 6.9 Hz, 2H), 7.48 – 7.40 (m, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.32, 148.62, 141.59, 139.55, 133.39, 129.36, 128.53, 127.94, 119.28, 17.61. HRMS (ESI) m/z calcd for. $C_{12}H_{10}BrN$ $[M+H]^+$ 248.0069, found 248.0070.

3-Bromo-2-(m-tolyl)pyridine (4k)



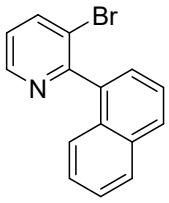
Yield: 93.6% (696 mg). Colorless oil. Purified by flash column chromatography (EtOAc/hexane = 1/400). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, J = 4.6, 1.5 Hz, 1H), 7.95 (dd, J = 8.1, 0.6 Hz, 1H), 7.50 (d, J = 6.7 Hz, 2H), 7.35 (dd, J = 11.2, 4.7 Hz, 1H), 7.25 (d, J = 7.4 Hz, 1H), 7.09 (ddd, J = 8.0, 4.6, 1.1 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.40 (s), 148.03 (s), 141.28 (s), 139.54 (s), 137.74 (s), 129.89 (s), 129.54 (s), 127.83 (s), 126.44 (s), 123.21 (s), 119.87 (s), 21.53 (s). HRMS (ESI) m/z calcd for. $C_{12}H_{10}BrN$ $[M+H]^+$ 248.0069, found 248.0072.

3-bromo-5-methyl-2-(4-(trifluoromethyl)phenyl)pyridine (4l)



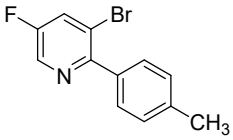
Yield: 82.5% (696 mg). Colorless oil. Purified by flash column chromatography (EtOAc/hexane = 1/500). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.84 (s, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.86 (s), 148.82 (s), 142.93 (s), 141.73 (s), 134.22 (s), 130.48 (d, ^2J = 32.5 Hz), 129.83 (s), 124.92 (q, ^3J = 3.8 Hz), 124.13 (d, ^1J = 272.3 Hz), 119.15 (s), 17.62 (s). HRMS (ESI) m/z calcd for. $C_{13}H_9BrF_3N$ $[M+H]^+$ 315.9943, found 315.9936.

3-Bromo-2-(naphthalen-1-yl)pyridine (4m)



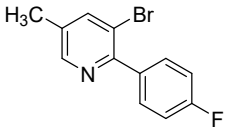
Yield:85.4% (728 mg). Colorless oil. Purified by flash column chromatography (EtOAc/hexane = 1/200). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.5 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.90 (t, *J* = 9.2 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.21 – 7.16 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.59 (s), 148.07 (s), 140.81 (s), 137.60 (s), 133.61 (s), 131.07 (s), 129.12 (s), 128.48 (s), 126.99 (s), 126.51 (s), 126.05 (s), 125.27 (d, *J* = 17.0 Hz), 123.86 (s), 122.17 (s). HRMS (ESI) m/z calcd for. $C_{15}H_{10}BrN$ $[M+H]^+$ 284.0069, found 284.0071.

3-Bromo-5-fluoro-2-(p-tolyl)pyridine (4n)



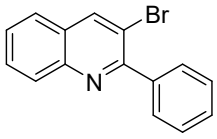
Yield: 94% (927 mg). White solid. m.p. 99.6-102.4 °C. Purified by flash column chromatography (EtOAc/hexane = 1/400). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.28 (d, ^1J = 262.4 Hz), 154.62 (d, ^3J = 4.1 Hz), 138.83 (s), 136.30 (d, ^2J = 22.1 Hz), 135.85 (s), 129.25 (s), 128.77 (s), 128.18 (d, ^2J = 20.1 Hz), 118.91 (d, ^4J = 3.2 Hz), 21.41 (s).HRMS (ESI) m/z calcd for. $C_{12}H_9BrFN$ $[M+H]^+$ 265.9975, found 265.9976.

3-Bromo-2-(4-fluorophenyl)-5-methylpyridine (4o)



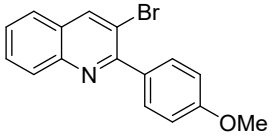
Yield: 88% (687 mg). White solid. m.p. 67.2-67.6 °C. Purified by flash column chromatography (EtOAc/hexane = 1/200). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.79 (s, 1H), 7.65 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.28 (d, ^1J = 248.0 Hz), 155.65 (s), 150.07 (s), 143.10 (s), 136.95 (d, ^4J = 3.2 Hz), 134.98 (s), 132.74 (d, ^3J = 8.2 Hz), 120.61 (s), 116.33 (d, ^2J = 21.7 Hz), 19.01 (s). HRMS (ESI) m/z calcd for. $C_{12}H_9BrFN$ $[M+H]^+$ 269.9975, found 265.9973.

3-Bromo-2-phenylquinoline (4p)



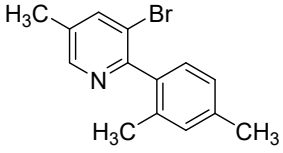
Yield:28%(266 mg). Yellow oil. Purified by flash column chromatography (EtOAc/hexane = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.76 (dd, *J* = 18.1, 7.6 Hz, 4H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.53 – 7.46 (m, 3H).[2]

3-Bromo-2-(4-methoxyphenyl)quinoline (4q)



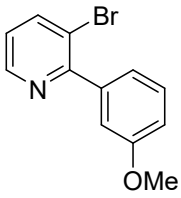
Yield: 76% (1190 mg). White solid. Purified by flash column chromatography (EtOAc/hexane = 1/50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.27 (s, 1H), 7.25 (s, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 3H).[2]

3-Bromo-2-(2,4-dimethylphenyl)-5-methylpyridine (4r)



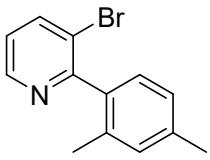
Yield: 87.3% (694 mg). White solid. m.p. 66.1-68.9 °C. Purified by flash column chromatography (EtOAc/hexane = 1/50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.80 (s, 1H), 7.13 – 7.06 (m, 3H), 2.37 (s, 6H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.76 (s), 148.41 (s), 140.65 (s), 138.13 (s), 136.91 (s), 135.65 (s), 133.38 (s), 130.85 (s), 128.75 (s), 126.30 (s), 120.97 (s), 21.34 (s), 19.43 (s), 17.74 (s). HRMS (ESI) m/z calcd for. $C_{14}H_{14}BrN$ $[M+H]^+$ 276.0382, found 276.0384.

3-Bromo-2-(3-methoxyphenyl)pyridine (4s)



Yield: 80.7% (640 mg). Colorless oil. Purified by flash column chromatography (EtOAc/hexane = 1/50).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.6, 1.3 Hz, 1H), 7.98 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.13 (dd, *J* = 8.1, 4.6 Hz, 1H), 7.02 – 6.96 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.23 (s), 158.03 (s), 148.02 (s), 141.35 (s), 140.84 (s), 129.07 (s), 123.37 (s), 121.77 (s), 119.84 (s), 114.71 (d, *J* = 16.9 Hz), 55.36 (s). HRMS (ESI) m/z calcd for. $C_{12}H_{10}BrNO$ $[M+H]^+$ 264.0019, found 264.0018.

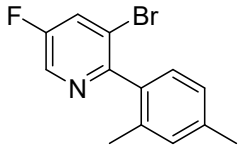
3-Bromo-2-(2,4-dimethylphenyl)pyridine (4t)



Yield:95%(790 mg). Yellow oil. Purified by flash column chromatography (EtOAc/hexane = 1/50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.7, 1.3 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.17 – 7.09 (m, 4H), 2.38 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.79 (s), 147.91 (s), 140.37 (s), 138.31 (s), 137.07 (s), 135.49 (s), 130.92 (s), 128.59 (s),

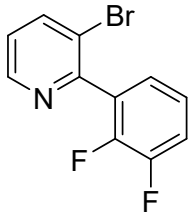
126.36 (s), 123.36 (s), 121.56 (s), 21.38 (s), 19.44 (s). HRMS (ESI) m/z calcd for. $C_{13}H_{12}BrN$ $[M+H]^+$ 262.0026, found 262.0027.

3-Bromo-2-(2,4-dimethylphenyl)-5-fluoropyridine (4u)



Yield: 82% (690 mg). Colorless oil. Purified by flash column chromatography (EtOAc/hexane = 1/250). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.14 – 7.08 (m, 3H), 2.39 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.45 (d, ^1J = 262.3 Hz), 156.01 (d, ^4J = 4.1 Hz), 138.55 (s), 136.16 (d, ^2J = 22.7 Hz), 135.71 (s), 130.98 (s), 128.77 (s), 127.33 (d, ^2J = 20.3 Hz), 126.41 (s), 120.70 (d, ^3J = 3.0 Hz), 21.33 (s), 19.40 (s).HRMS (ESI) m/z calcd for. $C_{13}H_{11}BrFN$ $[M+H]^+$ 280.0132, found 280.0135.

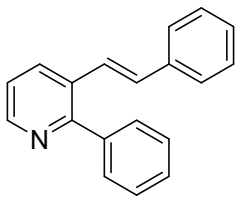
3-Bromo-2-(2,3-difluorophenyl)pyridine (4v)



Yield: 80% (573 mg). Colorless oil. Purified by flash column chromatography (EtOAc/hexane = 1/100). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.4 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.24 (d, *J* = 3.5 Hz, 1H), 7.22 (d, *J* = 3.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.75 (s), 152.03 (dd, ^1J = 248.2, ^2J=12.3 Hz), 149.55 (s), 149.29 (dd, ^1J = 250.4, ^2J=13.2 Hz), 142.16 (s), 131.39 (d, ^2J = 12.1 Hz), 127.20 (dd, ^3J = 3.5, ^4J=1.4 Hz), 125.82 (s), 125.59 (dd, ^3J = 6.7, ^4J=4.7 Hz), 123.06 (s), 119.25 (d, ^2J =17.1Hz). HRMS (ESI) m/z calcd for. $C_{11}H_6BrF_2N$ $[M+H]^+$ 262.0226, found 262.0227.

The data of 1a-1z.

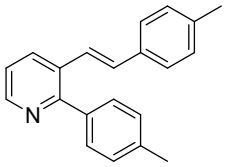
(E)-2-Phenyl-3-styrylpyridine (1a)



Yield: 67% (892 mg). White solid. m.p. 66.5-67.5 °C . Purified by flash column chromatography (EtOAc/hexane = 1/100). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 4.7, 1.4 Hz, 1H), 8.02 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.49 (dt, *J* = 8.4, 6.8 Hz, 3H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.29 (dd, *J* = 7.5, 3.8 Hz, 2H), 7.20 (d, *J* = 16.3 Hz, 1H), 7.08 (d, *J* = 16.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.60 (s), 148.44 (s), 139.86 (s), 137.06 (s), 133.98 (s), 131.23 (s), 130.98

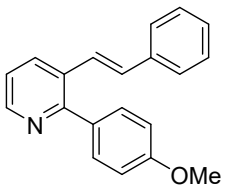
(s), 129.91 (s), 128.82 (s), 128.36 (d, J = 14.2 Hz), 128.05 (s), 126.74 (s), 126.31 (s), 122.40 (s). HRMS (ESI) m/z calcd for. $C_{19}H_{15}N$ $[M+H]^+$ 256.1121, found 256.1118.

(E)-3-(4-methylstyryl)-2-(p-tolyl)pyridine (1b)



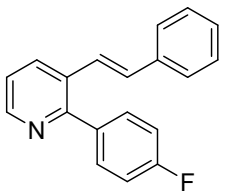
Yield: 89% (413 mg). White solid. m.p. 65.3-66.6 °C. Purified by flash column chromatography (EtOAc/hexane = 1/200). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, J = 4.6, 1.1 Hz, 1H), 7.97 (dd, J = 7.9, 1.3 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.33 – 7.25 (m, 4H), 7.23 (t, J = 3.9 Hz, 1H), 7.15 – 7.10 (m, 3H), 7.01 (d, J = 16.3 Hz, 1H), 2.42 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.50 (s), 148.17 (s), 138.18 (s), 137.92 (s), 137.03 (s), 134.41 (s), 133.88 (s), 131.33 (s), 130.69 (s), 129.81 (s), 129.48 (s), 128.93 (s), 126.64 (s), 125.59 (s), 122.10 (s), 21.33 (d, J = 6.7 Hz). HRMS (ESI) m/z calcd for. $C_{21}H_{19}N$ $[M+H]^+$ 286.1590, found 286.1592.

(E)-2-(4-methoxyphenyl)-3-styrylpyridine (1c)



Yield: 95.6% (270 mg). White solid. m.p. 62.6-63.5 °C . Purified by flash column chromatography (EtOAc/hexane = 1/50). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, J = 3.0 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.18 (d, J = 16.3 Hz, 1H), 7.06 (d, J = 16.2 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.83 (s), 157.23 (s), 148.34 (s), 137.13 (s), 134.10 (s), 132.30 (s), 131.25 (s), 131.03 (s), 130.67 (s), 128.80 (s), 127.96 (s), 126.68 (s), 121.93 (s), 113.66 (s), 55.38 (s). HRMS (ESI) m/z calcd for. $C_{20}H_{17}NO$ $[M+H]^+$ 288.1383, found 288.1381.

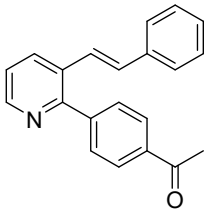
(E)-2-(4-fluorophenyl)-3-styrylpyridine (1d)



Yield: 92% (499 mg). White solid. m.p. 65.8-67.3 °C . Purified by flash column chromatography (EtOAc/hexane = 1/50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 4.5 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.14 (t, J = 8.1 Hz, 2H), 7.05 (t, J = 14.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.97 (d, ^1J = 248.0 Hz), 156.51 (s), 148.39 (s), 136.94 (s), 135.95 (s), 134.10 (s), 131.70 (d, ^3J = 8.2 Hz), 131.30 (s), 131.24 (s), 128.84 (s),

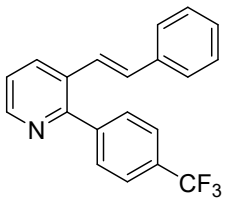
128.14 (s), 126.69 (s), 126.03 (s), 122.45 (s), 115.22 (d, ^2J = 21.5 Hz).HRMS (ESI) m/z calcd for. $C_{19}H_{14}FN$ $[M+H]^+$ 276.1183, found 276.1180.

(E)-1-(4-(3-styrylpyridin-2-yl)phenyl)ethan-1-one (1e)



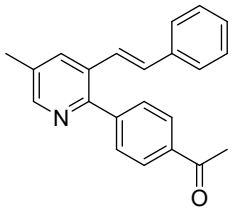
Yield: 71% (426 mg). White solid. m.p. 75.0-77.4 °C . Purified by flash column chromatography (EtOAc/hexane = 1/100). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 4.5 Hz, 1H), 8.03 (dd, J = 13.7, 8.1 Hz, 3H), 7.73 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 7.4 Hz, 2H), 7.31 (dd, J = 13.7, 6.0 Hz, 3H), 7.25 (t, J = 7.1 Hz, 1H), 7.07 (s, 2H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.89 (s), 156.21 (s), 148.49 (s), 144.39 (s), 136.73 (d, J = 5.1 Hz), 134.17 (s), 131.74 (s), 131.54 (s), 130.14 (s), 128.84 (s), 128.26 (s), 126.74 (s), 125.53 (s), 122.99 (s), 26.78 (s). HRMS (ESI) m/z calcd for. $C_{21}H_{17}NO$ $[M+H]^+$ 300.1383, found 300.1387.

(E)-3-styryl-2-(4-(trifluoromethyl)phenyl)pyridine (1f)



Yield: 88% (472 mg). White solid. m.p. 71.5-73.0 °C . Purified by flash column chromatography (EtOAc/hexane = 1/300). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (dd, J = 4.7, 1.5 Hz, 1H), 7.98 (dd, J = 8.0, 1.4 Hz, 1H), 7.70 (q, J = 8.4 Hz, 4H), 7.38 – 7.34 (m, 2H), 7.32 – 7.26 (m, 3H), 7.24 (dd, J = 4.9, 3.6 Hz, 1H), 7.04 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.91 (s), 148.52 (s), 143.33 (s), 136.72 (s), 134.26 (s), 131.97 (s), 131.56 (s), 130.40 (d, ^2J = 30.3 Hz), 128.87 (s), 128.32 (s), 126.76 (s), 125.21 (q, ^3J = 3.7 Hz), 124.23 (q,^1J=272.7Hz). HRMS (ESI) m/z calcd for. $C_{20}H_{14}F_3N$ $[M+H]^+$ 326.1151, found 326.1151.

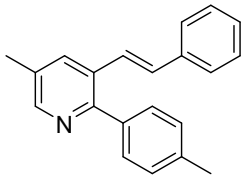
(E)-1-(4-(5-methyl-3-styrylpyridin-2-yl)phenyl)ethan-1-one (1g)



Yield: 89% (694 mg). White solid. m.p. 104.1-106.5 °C . Purified by flash column chromatography (EtOAc/hexane = 1/200). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 2.0 Hz, 1H), 8.05 (d, J = 8.2 Hz, 2H), 7.85 (d, J = 1.4 Hz, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.28 (d, J = 7.0 Hz, 1H), 7.09 (s, 2H), 2.66 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.27 – 198.07 (m), 153.68 (s), 149.18 (s), 144.47 (s), 136.86 (s), 136.53 (s), 134.50 (s), 132.57 (s),

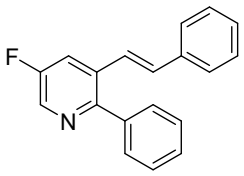
131.42 (s), 130.92 (s), 130.09 (s), 128.82 (s), 128.20 (d, J = 7.0 Hz), 126.68 (s), 125.68 (s), 26.76 (s), 18.25 (s). HRMS (ESI) m/z calcd for. $C_{22}H_{19}NO$ $[M+H]^+$ 314.1539, found 314.1543.

(E)-5-methyl-3-styryl-2-(p-tolyl)pyridine (1h)



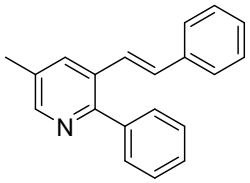
Yield: 90% (514 mg). Colorless oil. Purified by flash column chromatography (EtOAc/hexane = 1/100). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 1.6 Hz, 1H), 7.79 (s, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 7.4 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.25 (d, J = 8.2 Hz, 3H), 7.16 (d, J = 16.3 Hz, 1H), 7.03 (d, J = 16.3 Hz, 1H), 2.41 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.08 (s), 148.98 (s), 137.94 (s), 137.24 (s), 136.94 (s), 134.34 (s), 131.50 (s), 130.47 (d, J = 3.9 Hz), 129.78 (s), 128.83 (d, J = 15.4 Hz), 127.86 (s), 126.67 (s), 21.33 (s), 18.19 (s). HRMS (ESI) m/z calcd for. $C_{21}H_{19}N$ $[M+H]^+$ 286.1590, found 286.1596.

(E)-5-fluoro-2-phenyl-3-styrylpyridine (1i)



Yield: 67% (370 mg). White solid. m.p. 59.3-61.0 °C . Purified by flash column chromatography (EtOAc/hexane = 1/1000). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 2.6 Hz, 1H), 7.65 (dd, J = 9.5, 2.7 Hz, 1H), 7.56 (d, J = 7.5 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.35 (d, J = 7.5 Hz, 2H), 7.29 (t, J = 7.4 Hz, 2H), 7.23 (t, J = 7.1 Hz, 1H), 7.12 – 6.99 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.85 (d, ^1J = 256.6 Hz), 153.90 (d, ^4J = 3.5 Hz), 139.07 (s), 136.48 (d, ^2J = 23.3 Hz), 132.73 (d, ^3J = 4.1 Hz), 132.25 (s), 129.88 (s), 128.88 (s), 128.50 (s), 128.44 (s), 128.35 (s), 126.88 (s), 125.20 (s), 125.19 (s), 119.92 (d, ^2J = 18.7 Hz). HRMS (ESI) m/z calcd for. $C_{19}H_{14}FN$ $[M+H]^+$ 276.1183, found 276.1187.

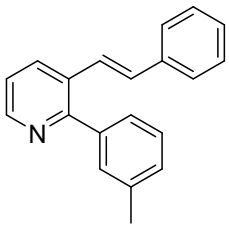
(E)-5-methyl-2-phenyl-3-styrylpyridine (1j)



Yield: 96.5% (524 mg). White solid. m.p. 65.6-66.2 °C . Purified by flash column chromatography (EtOAc/hexane = 1/300). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 1.4 Hz, 1H), 7.82 (d, J = 1.3 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.46 – 7.38 (m, 5H), 7.32 (t, J = 7.5 Hz, 2H), 7.25 (d, J = 7.4 Hz, 1H), 7.15 (d, J = 16.3 Hz, 1H), 7.05 (d, J = 16.3

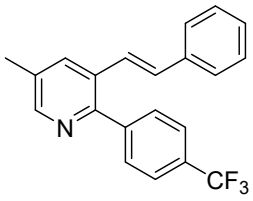
Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.06 (s), 149.00 (s), 139.82 (s), 137.16 (s), 134.31 (s), 131.78 (s), 130.62 (d, *J* = 9.2 Hz), 129.84 (s), 128.75 (s), 128.16 (d, *J* = 6.2 Hz), 127.91 (s), 126.66 (s), 126.39 (s), 18.20 (s). HRMS (ESI) m/z calcd for. $C_{20}H_{17}N$ $[M+H]^+$ 272.1434, found 272.1434.

(E)-3-styryl-2-(m-tolyl)pyridine (1k)



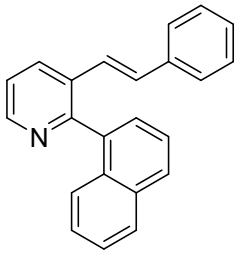
Yield: 93% (505 mg). White solid. m.p. 91.5-93.1 °C .Purified by flash column chromatography (EtOAc/hexane = 1/300). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.98 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.48 (s, 1H), 7.38 (d, *J* = 7.7 Hz, 3H), 7.32 (dd, *J* = 16.0, 7.8 Hz, 3H), 7.26 – 7.21 (m, 3H), 7.16 (d, *J* = 16.3 Hz, 1H), 7.03 (d, *J* = 16.3 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.79 (s), 148.35 (s), 139.77 (s), 138.07 (s), 137.12 (s), 133.86 (s), 131.20 (s), 130.77 (s), 130.44 (s), 129.17 (s), 128.79 (s), 127.99 (s), 127.10 (s), 126.70 (s), 126.40 (s), 122.30 (s), 21.56 (s). HRMS (ESI) m/z calcd for. $C_{20}H_{17}N$ $[M+H]^+$ 272.1434, found 272.1438.

(E)-5-methyl-3-styryl-2-(4-(trifluoromethyl)phenyl)pyridine (1l)



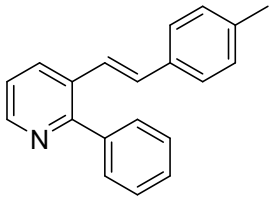
Yield: 71% (488 mg). White solid. m.p. 92.3-94.0 °C . Purified by flash column chromatography (EtOAc/hexane = 1/400). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.86 (s, 1H), 7.77 – 7.70 (m, 4H), 7.41 (s, 2H), 7.36 (s, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.08 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.38 (s), 149.19 (s), 143.36 (s), 136.82 (s), 134.57 (s), 132.63 (s), 131.63 (s), 129.53(q,^1J=272.7Hz), 126.70 (s), 125.51 (s), 125.15 (q, ^3J = 3.8 Hz), 18.23 (s). HRMS (ESI) m/z calcd for. $C_{21}H_{16}F_3N$ $[M+H]^+$ 340.1308, found 340.1311.

(E)-2-(naphthalen-1-yl)-3-styrylpyridine (1m)



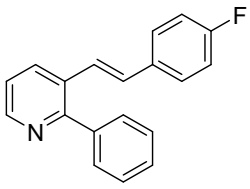
Yield: 98.6% (606 mg). Colorless oil. Purified by flash column chromatography (EtOAc/hexane = 1/80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.6 Hz, 1H), 8.22 (d, *J* = 7.9 Hz, 1H), 8.03 (t, *J* = 8.1 Hz, 2H), 7.71 – 7.62 (m, 2H), 7.61 – 7.54 (m, 2H), 7.53 – 7.48 (m, 1H), 7.45 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.31 – 7.23 (m, 5H), 7.15 (d, *J* = 16.3 Hz, 1H), 6.88 (d, *J* = 16.3 Hz, 1H).[5]

(E)-3-(4-methylstyryl)-2-phenylpyridine (1n)



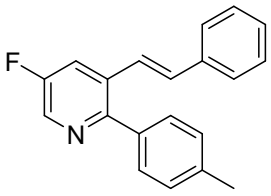
Yield: 92% (386 mg). White solid. m.p. 93.6-95.0 °C. Purified by flash column chromatography (EtOAc/hexane = 1/100). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.97 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.60 (dd, *J* = 6.3, 1.5 Hz, 2H), 7.42 (dt, *J* = 7.1, 6.2 Hz, 3H), 7.29 – 7.20 (m, 3H), 7.09 (dd, *J* = 12.4, 7.6 Hz, 3H), 7.00 (d, *J* = 16.3 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.48 (s), 148.21 (s), 139.90 (s), 138.01 (s), 134.32 (s), 133.85 (s), 131.41 (s), 130.91 (s), 129.86 (s), 129.49 (s), 128.27 (d, *J* = 11.0 Hz), 126.63 (s), 125.30 (s), 122.34 (s), 21.29 (s). HRMS (ESI) m/z calcd for. $C_{20}H_{17}N$ $[M+H]^+$ 272.1434, found 272.1437.

(E)-3-(4-fluorostyryl)-2-phenylpyridine (1o)



Yield: 90% (348 mg). White solid. m.p. 78.6-79.3 °C. Purified by flash column chromatography (EtOAc/hexane = 1/50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.98 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.50 – 7.42 (m, 3H), 7.38 – 7.32 (m, 2H), 7.29 – 7.23 (m, 1H), 7.06 – 6.96 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.52 (d, ^{1}J = 248.0 Hz), 157.59 (s), 148.42 (s), 139.80 (s), 133.83 (s), 133.25 (d, ^{4}J = 3.2 Hz), 131.05 (s), 129.76 (d, ^{3}J = 13.2 Hz), 128.42 (s), 128.25 (s), 128.18 (s), 126.08 (s), 126.06 (s), 122.36 (s), 115.73 (d, ^{2}J = 21.7 Hz). HRMS (ESI) m/z calcd for. $C_{19}H_{14}FN$ $[M+H]^+$ 276.1183, found 276.1185.

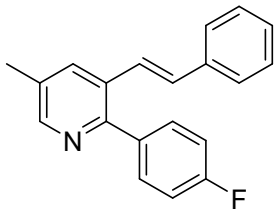
(E)-5-fluoro-3-styryl-2-(p-tolyl)pyridine (1p)



Yield: 78.3% (459 mg). White solid. m.p. 99.6-102.3 °C. Purified by flash column chromatography (EtOAc/hexane = 1/400). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 2.5 Hz, 1H), 7.72 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 6.2 Hz, 3H), 7.18 – 7.07 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.13 (d, ^{1}J = 256.1 Hz), 155.33 (d, ^{3}J = 3.5 Hz), 139.78 (s), 138.05 (s), 137.96 (s), 137.65 (d, ^{2}J = 17.1 Hz), 134.02 (s), 133.40 (s), 131.17 (s), 130.37 (d, ^{2}J = 18.7 Hz), 129.79 (s), 128.28 (s), 126.86 (d, ^{4}J =

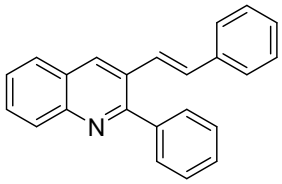
1.3 Hz), 121.46 (s), 121.28 (s), 22.80 (s).HRMS (ESI) m/z calcd for. $C_{20}H_{16}FN$ $[M+H]^+$ 290.1434, found 290.1338.

(E)-2-(4-fluorophenyl)-5-methyl-3-styrylpyridine (1q)



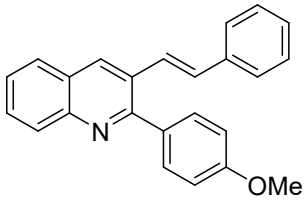
Yield: 85% (490 mg). White solid. m.p. 83.7-85.7 °C. Purified by flash column chromatography (EtOAc/hexane = 1/100). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.84 (s, 1H), 7.64 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.28 (m, 1H), 7.18 (t, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.23 (d, ^1J = 247.6 Hz), 155.34 (s), 150.45 (s), 138.42 (s), 137.31 (d, ^4J = 3.1 Hz), 135.92 (s), 133.39 (s), 133.07 (d, ^3J = 8.2 Hz), 132.40 (s), 132.00 (s), 130.26 (s), 129.50 (s), 128.09 (s), 127.49 (s), 116.61 (d, ^2J = 21.6 Hz), 19.65 (s).HRMS (ESI) m/z calcd for. $C_{20}H_{16}FN$ $[M+H]^+$ 290.1434, found 290.1342.

(E)-2-phenyl-3-styrylquinoline (1r)



Yield: 57.8% (177 mg). White solid. m.p. 124.3-126.7 °C. Purified by flash column chromatography (DCM/hexane = 1/5). 1H NMR (400 MHz, CDCl3) δ 8.44 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.73 (t, *J* = 7.1 Hz, 3H), 7.59 – 7.49 (m, 4H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 12.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.36 (s), 148.80 (s), 141.51 (s), 138.55 (s), 134.39 (s), 132.56 (s), 131.39 (d, *J* = 17.0 Hz), 130.91 (d, *J* = 9.1 Hz), 130.14 (d, *J* = 18.9 Hz), 129.80 (s), 129.46 (s), 128.94 (d, *J* = 2.8 Hz), 128.09 (d, *J* = 17.2 Hz). HRMS (ESI) m/z calcd for. $C_{23}H_{17}N$ $[M+H]^+$ 308.1434, found 308.1430.

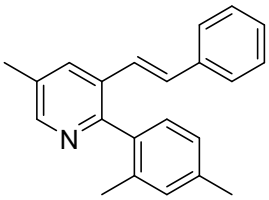
(E)-2-(4-methoxyphenyl)-3-styrylquinoline (1s)



Yield: 15% (100 mg). White solid. Purified by flash column chromatography (EtOAc/hexane = 1/50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.65 (m, 3H), 7.51 (t, *J* = 7.5 Hz,

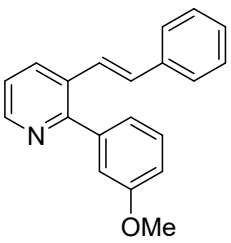
1H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 4.3 Hz, 1H), 7.15 (d, *J* = 16.2 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H).[5]

(E)-2-(2,4-dimethylphenyl)-5-methyl-3-styrylpyridine(1t)



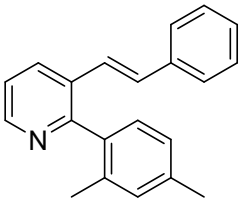
Yield: 87% (260 mg). White solid. m.p. 102.1-104.8 °C. Purified by flash column chromatography (EtOAc/hexane = 1/30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.78 (s, 1H), 7.26 – 7.19 (m, 4H), 7.19 – 7.14 (m, 1H), 7.09 – 6.97 (m, 4H), 6.75 (d, *J* = 16.4 Hz, 1H), 2.35 (s, 3H), 2.31 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.17 (s), 148.73 (s), 137.67 (s), 137.12 (s), 136.50 (s), 136.07 (s), 132.86 (s), 131.59 (s), 130.99 (s), 130.47 (s), 129.62 (s), 128.67 (s), 127.88 (s), 126.65 (s), 126.41 (s), 125.38 (s), 21.28 (s), 19.70 (s), 18.31 (s). HRMS (ESI) m/z calcd for. $C_{22}H_{21}N$ $[M+H]^+$ 300.1747, found 300.1748.

(E)-2-(3-methoxyphenyl)-3-styrylpyridine(1u)



Yield: 95% (350 mg). Yellow oil. Purified by flash column chromatography (EtOAc/hexane = 1/30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.4 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 2H), 7.23 (dd, *J* = 16.7, 9.2 Hz, 3H), 7.15 (d, *J* = 5.6 Hz, 2H), 7.12 – 7.05 (m, 3H), 6.91 (dd, *J* = 21.1, 12.3 Hz, 2H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.61 (s), 157.45 (s), 148.32 (s), 141.20 (s), 137.04 (s), 133.95 (s), 131.28 (s), 130.93 (s), 129.19 (s), 128.80 (s), 128.03 (s), 126.71 (s), 126.27 (s), 122.47 (s), 114.76 (d, *J* = 8.7 Hz), 55.36 (s). HRMS (ESI) m/z calcd for. $C_{20}H_{17}NO$ $[M+H]^+$ 288.1383, found 288.1384.

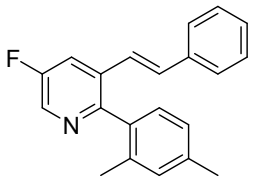
(E)-2-(2,4-dimethylphenyl)-3-styrylpyridine (1v)



Yield: 83% (368 mg). White solid. m.p. 32.3-35.1 °C. Purified by flash column chromatography (EtOAc/hexane = 1/30). 1H NMR (400 MHz, CDCl3) δ 8.57 (d, *J* = 4.5 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.30 (dd, *J* = 16.4, 8.1 Hz, 5H), 7.26 – 7.20 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.07 (dd, *J* = 18.4, 10.8 Hz, 3H), 6.83 (d, *J* = 16.3 Hz, 1H), 2.38 (s, 3H), 2.09 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 158.85 (s), 148.09 (s), 137.85 (s), 137.02 (s), 136.54 (s), 135.93 (s), 132.46 (s), 131.66 (s), 131.02 (s),

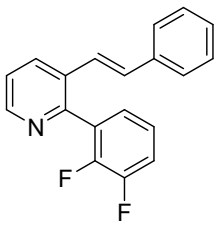
130.80 (s), 129.45 (s), 128.68 (s), 127.97 (s), 126.68 (s), 126.43 (s), 125.28 (s), 122.28 (s), 21.29 (s), 19.66 (s). HRMS (ESI) m/z calcd for. $C_{21}H_{19}N$ $[M+H]^+$ 286.1590, found 286.1594.

(E)-2-(2,4-dimethylphenyl)-5-fluoro-3-styrylpyridine (1w)



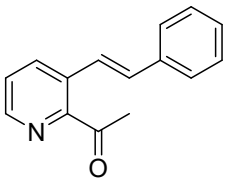
Yield: 80.4% (488 mg). White solid. m.p. 98.8-100.4 °C. Purified by flash column chromatography (EtOAc/hexane = 1/200). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.6 Hz, 1H), 7.75 (dd, *J* = 9.6, 2.5 Hz, 1H), 7.31 (dd, *J* = 9.4, 7.8 Hz, 4H), 7.25 (s, 1H), 7.11 (d, *J* = 7.1 Hz, 2H), 7.06 (dd, *J* = 18.3, 12.1 Hz, 2H), 6.78 (dd, *J* = 16.3, 1.2 Hz, 1H), 2.39 (s, 3H), 2.08 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 158.78 (d, ^1J = 255.5 Hz), 154.92 (d, ^4J = 3.5 Hz), 138.12 (s), 136.51 (s), 136.23 (s), 136.12 (s), 136.08 (s), 135.69 (s), 133.22 (s), 133.19 (s), 132.11 (s), 131.13 (s), 129.58 (s), 128.57 (d, ^2J = 56.7 Hz), 126.68 (d, ^2J = 47.4 Hz), 124.26 (s), 118.54 (d, ^3J = 18.6 Hz), 21.28 (s), 19.64 (s). HRMS (ESI) m/z calcd for. $C_{21}H_{18}FN$ $[M+H]^+$ 304.1496, found 304.1503.

(E)-2-(2,3-difluorophenyl)-3-styrylpyridine (1x)



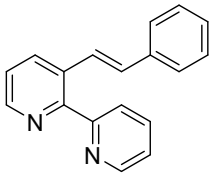
Yield: 73% (427 mg). White solid. Purified by flash column chromatography (EtOAc/hexane = 1/50). 1H NMR (400 MHz, CDCl3) δ 8.66 – 8.61 (m, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.34 (m, 5H), 7.33 – 7.26 (m, 3H), 7.25 – 7.23 (m, 1H), 7.13 (d, *J* = 16.2 Hz, 1H), 6.96 (dd, *J* = 16.2, 1.5 Hz, 1H).[5]

(E)-1-(3-styrylpyridin-2-yl)ethan-1-one(1y)



Yield: 82% (490 mg). White solid. m.p. 57.0-59.1 °C. Purified by flash column chromatography (EtOAc/hexane = 1/100). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.4 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 16.3 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.26 (dd, *J* = 13.4, 6.1 Hz, 1H), 6.98 (d, *J* = 16.3 Hz, 1H), 2.73 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.37 (s), 150.78 (s), 147.27 (s), 136.94 (s), 134.85 (s), 133.41 (s), 133.03 (s), 128.74 (s), 128.29 (s), 127.05 (s), 126.36 (s), 125.29 (s), 28.43 (s). HRMS (APCI) m/z calcd for. C15H13NO $[M+H]^+$ 224.1070, found 224.1073.

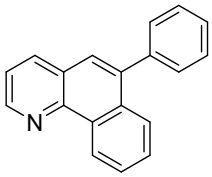
(E)-3-styryl-2,2'-bipyridine(1z)



Yield: 23% (110 mg). Brown oil. Purified by flash column chromatography (Acetone/hexane = 1/10). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 4.8, 0.7 Hz, 1H), 8.62 (dd, *J* = 4.6, 1.3 Hz, 1H), 8.10 – 8.07 (m, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.56 (d, *J* = 16.3 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.33 (ddd, *J* = 7.7, 6.5, 3.8 Hz, 4H), 7.26 – 7.23 (m, 1H), 7.07 (d, *J* = 16.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.18 (s), 155.27 (s), 148.86 (s), 148.14 (s), 137.28 (s), 136.63 (s), 134.31 (s), 132.09 (s), 131.15 (s), 128.67 (s), 127.91 (s), 126.79 (s), 126.16 (s), 124.81 (s), 123.39 (s), 122.90 (s). HRMS (APCI) m/z calcd for. C18H14N2 [M+H]+ 259.1230, found 259.1234.

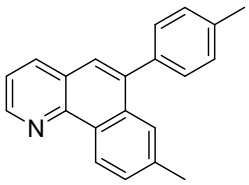
The data of 2a-2z.

6-phenylbenzo[h]quinoline (2a)



Yield: 88% (92 mg). White solid. Purified by flash column chromatography (EtOAc/hexane = 1/100). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 5.7 Hz, 1H), 8.76 – 8.71 (m, 1H), 8.45 (d, *J* = 5.7 Hz, 1H), 7.98 – 7.91 (m, 2H), 7.77 – 7.69 (m, 5H), 7.59 – 7.50 (m, 3H).[1]

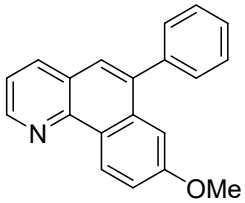
8-methyl-6-(p-tolyl)benzo[h]quinoline (2b)



Yield: 69% (71 mg). White solid. m.p. 132.7-134.2 °C. Purified by flash column chromatography (EtOAc/hexane = 1/50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 5.8 Hz, 1H), 8.50 (s, 1H), 8.40 (d, *J* = 5.7 Hz, 1H), 7.91 (d, *J* = 9.2 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 9.2 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.55 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 2.65 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.24 (s), 143.95 (s), 138.25 (s), 137.10 (d, *J* = 13.5 Hz), 135.61 (s), 131.05 (s), 130.43 (s), 130.03 (s), 129.02 (s), 128.80 (s), 128.39 (s), 127.63 (s),

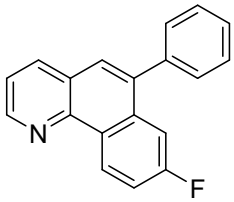
125.02 (s), 123.69 (s), 123.10 (s), 115.03 (s), 22.11 (s), 21.37 (s). HRMS (ESI) m/z calcd for. $C_{21}H_{17}N$ $[M+H]^+$ 284.1434, found 284.1434.

8-methoxy-6-phenylbenzo[h]quinoline (2c)



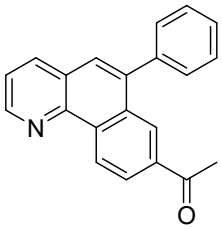
Yield: 93% (90 mg). White solid. m.p. 121.1-123.9 °C. Purified by flash column chromatography (EtOAc/hexane = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 5.7 Hz, 1H), 8.70 (dd, *J* = 6.0, 3.5 Hz, 1H), 8.38 (d, *J* = 5.7 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.90 (dd, *J* = 6.0, 3.3 Hz, 1H), 7.74 (d, *J* = 9.3 Hz, 1H), 7.72 – 7.68 (m, 3H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.93 (d, *J* = 7.3 Hz), 144.18 (s), 135.97 (s), 133.09 (s), 132.44 (s), 131.49 (s), 128.94 – 128.45 (m), 127.80 (s), 127.13 (s), 124.72 (d, *J* = 14.9 Hz), 123.44 (s), 114.89 (s), 113.84 (s), 55.43 (s). HRMS (ESI) m/z calcd for. $C_{20}H_{15}NO$ $[M+H]^+$ 286.1226, found 286.1225.

8-fluoro-6-phenylbenzo[h]quinoline (2d)



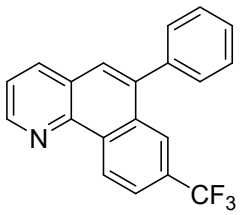
Yield: 78% (80 mg). White solid. Purified by flash column chromatography (EtOAc/hexane = 1/300). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 5.7 Hz, 1H), 8.68 (dd, *J* = 6.0, 3.4 Hz, 1H), 8.38 (d, *J* = 5.7 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.75 – 7.66 (m, 5H), 7.23 (dd, *J* = 12.0, 5.3 Hz, 2H).[1]

1-(6-phenylbenzo[h]quinolin-8-yl)ethan-1-one (2e)



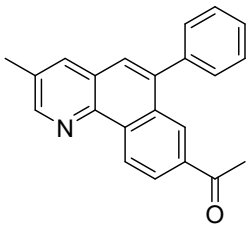
Yield: 56% (60 mg). White solid. m.p. 155.7-157.1 °C. Purified by flash column chromatography (EtOAc/hexane = 1/300). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (t, *J* = 5.4 Hz, 1H), 8.74 – 8.69 (m, 1H), 8.46 (t, *J* = 5.0 Hz, 1H), 8.17 – 8.11 (m, 2H), 7.92 (dd, *J* = 8.7, 5.1 Hz, 1H), 7.86 (dd, *J* = 9.2, 4.4 Hz, 1H), 7.83 – 7.79 (m, 2H), 7.75 (ddd, *J* = 10.9, 10.3, 4.8 Hz, 3H), 2.69 (d, *J* = 5.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.83 (s), 158.87 (s), 144.54 (s), 144.28 (s), 136.89 (s), 136.02 (s), 133.06 (s), 130.43 (s), 128.92 (s), 128.66 (s), 128.40 (d, *J* = 6.9 Hz), 127.41 (s), 124.75 (s), 123.82 (s), 123.42 (s), 115.80 (s), 26.79 (s). HRMS (ESI) m/z calcd for. $C_{21}H_{15}NO$ $[M+H]^+$ 298.1226, found 298.1230.

6-phenyl-8-(trifluoromethyl)benzo[h]quinoline (2f)



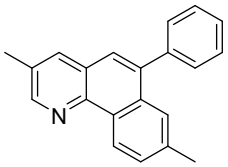
Yield: 62% (78 mg). White solid. Purified by flash column chromatography (EtOAc/hexane = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 5.7 Hz, 1H), 8.78 – 8.72 (m, 1H), 8.50 (d, *J* = 5.7 Hz, 1H), 7.97 – 7.92 (m, 1H), 7.84 (dt, *J* = 13.0, 8.0 Hz, 6H), 7.78 – 7.74 (m, 2H).[1]

1-(3-methyl-6-phenylbenzo[h]quinolin-8-yl)ethan-1-one (2g)



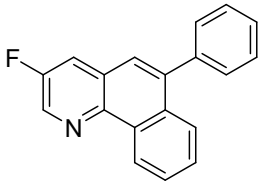
Yield: 60% (50 mg). White solid. m.p. 208.2-210.9 °C. Purified by flash column chromatography (EtOAc/hexane = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 – 8.94 (m, 1H), 8.66 (s, 1H), 8.12 (d, *J* = 8.3 Hz, 2H), 7.94 (dd, *J* = 6.5, 2.9 Hz, 1H), 7.85 (d, *J* = 9.1 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.75 – 7.70 (m, 3H), 3.13 (s, 3H), 2.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.89 (s), 157.27 (s), 147.59 (s), 145.06 (s), 136.71 (s), 135.62 (s), 134.41 (s), 130.59 (s), 130.19 (s), 128.87 (s), 128.60 (s), 128.34 (d, *J* = 4.2 Hz), 128.08 (s), 126.55 (s), 125.44 (s), 124.62 (s), 26.81 (s), 23.91 (s). HRMS (ESI) m/z calcd for. $C_{22}H_{17}NO$ $[M+H]^+$ 312.1383, found 312.1388.

3,8-dimethyl-6-phenylbenzo[h]quinoline (2h)



Yield: 90% (78 mg). White solid. m.p. 106.0-106.9 °C. Purified by flash column chromatography (EtOAc/hexane = 1/150). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 – 8.94 (m, 1H), 8.64 (s, 1H), 7.99 – 7.91 (m, 2H), 7.74 – 7.68 (m, 3H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 3.13 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.72 (s), 147.51 (s), 138.07 (s), 137.53 (s), 135.53 (s), 134.49 (s), 130.25 (d, *J* = 9.8 Hz), 129.00 (s), 128.74 (s), 128.16 – 127.71 (m), 127.36 (s), 126.23 (s), 125.50 (d, *J* = 6.0 Hz), 23.84 (s), 21.36 (s). HRMS (ESI) m/z calcd for. $C_{21}H_{17}N$ $[M+H]^+$ 284.1434, found 284.1436.

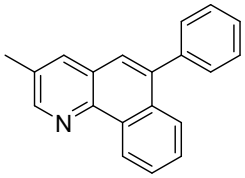
3-fluoro-6-phenylbenzo[h]quinoline (2i)



Yield: 67% (68 mg). White solid. m.p. 91.3-92.5 °C. Purified by flash column chromatography (dichlormethane/hexane = 1/3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 – 9.14 (m, 1H), 8.70

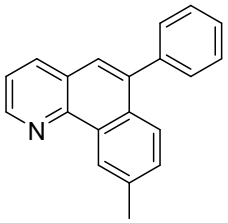
(d, J = 5.0 Hz, 1H), 7.97 – 7.90 (m, 2H), 7.83 – 7.75 (m, 3H), 7.68 – 7.64 (m, 2H), 7.59 – 7.50 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.71 (d, ^1J = 260.4 Hz), 156.20 (d, ^4J = 4.9 Hz), 139.67 (s), 133.57 (s), 132.22 (d, ^2J = 28.8 Hz), 130.12 (s), 129.44 (s), 128.93 (s), 128.82 (d, ^2J = 16.9 Hz), 128.51 (s), 128.49 (s), 128.41 (s), 127.79 (s), 127.77 (s), 126.79 (s), 124.74 (d, ^3J = 7.5 Hz), 124.29 (s). HRMS (ESI) m/z calcd for. $C_{19}H_{12}FN$ $[M+H]^+$ 274.1027, found 274.1028.

3-methyl-6-phenylbenzo[h]quinoline (2j)



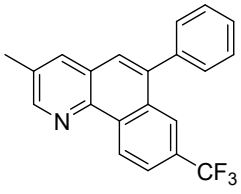
Yield: 73% (69 mg). White solid. m.p. 91.2-93.5 °C. Purified by flash column chromatography (EtOAc/hexane = 1/100). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 – 8.88 (m, 1H), 8.62 (s, 1H), 7.89 (t, J = 7.8 Hz, 2H), 7.66 (dd, J = 10.3, 4.7 Hz, 5H), 7.49 (dt, J = 19.6, 7.1 Hz, 3H), 3.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.64 (s), 147.51 (s), 140.43 (s), 135.52 (s), 134.46 (s), 130.29 (s), 128.78 (s), 128.44 – 127.76 (m), 127.62 (s), 126.31 (s), 125.50 (s), 125.29 (s), 23.86 (s). HRMS (ESI) m/z calcd for. $C_{20}H_{15}N$ $[M+H]^+$ 270.1277, found 270.1279.

9-methyl-6-phenylbenzo[h]quinoline (2k)



Yield: 60% (67 mg). Colorless oil. Purified by flash column chromatography (EtOAc/hexane = 1/200). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 5.5 Hz, 1H), 8.72 (d, J = 4.6 Hz, 1H), 8.43 (d, J = 5.5 Hz, 1H), 7.97 (d, J = 9.1 Hz, 1H), 7.92 (d, J = 4.3 Hz, 1H), 7.76 – 7.69 (m, 3H), 7.55 (s, 1H), 7.50 (d, J = 7.5 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.33 (d, J = 7.2 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.52 (s), 144.17 (s), 139.83 (s), 138.17 (s), 135.91 (s), 133.11 (s), 130.69 (s), 129.24 (s), 128.66 (d, J = 11.5 Hz), 128.14 (s), 127.91 (s), 127.22 (d, J = 7.9 Hz), 124.65 (s), 123.45 (s), 115.20 (s), 21.56 (s). HRMS (ESI) m/z calcd for. $C_{20}H_{15}N$ $[M+H]^+$ 270.1277, found 270.1282.

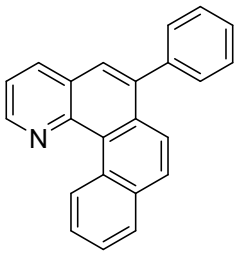
3-methyl-6-phenyl-8-(trifluoromethyl)benzo[h]quinoline (2l)



Yield: 81% (72 mg). White solid. m.p. 163.2-165.0 °C. Purified by flash column chromatography (EtOAc/hexane = 1/300). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 5.0 Hz, 1H), 8.67 (s, 1H),

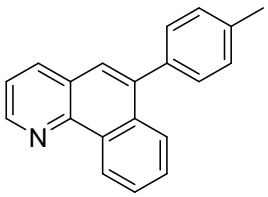
7.96 (d, J = 4.0 Hz, 1H), 7.87 – 7.79 (m, 5H), 7.76 (d, J = 9.0 Hz, 3H), 3.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.01 (s), 147.59 (s), 143.96 (s), 135.65 (s), 134.42 (s), 130.59 (d, ^2J = 12.0 Hz), 129.05 (q, ^1J = 200.9 Hz), 128.29 (s), 128.12 (s), 128.08 (s), 126.60 (s), 125.42 (s), 125.32 (q, ^3J = 3.6 Hz), 124.53 (s), 23.92 (s). HRMS (ESI) m/z calcd for. $C_{21}H_{14}F_3N$ $[M+H]^+$ 338.1151, found 338.1157.

6-phenylnaphtho[2,1-h]quinoline (2m)



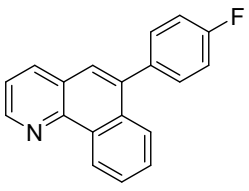
Yield: 75% (85 mg). Colorless oil. Purified by flash column chromatography (EtOAc /dichlormethane/hexane = 1/2.5/100). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 5.7 Hz, 1H), 8.79 (d, J = 7.7 Hz, 1H), 8.56 (d, J = 5.7 Hz, 1H), 8.03 (dd, J = 6.7, 2.1 Hz, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 7.5 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.64 (t, J = 9.5 Hz, 3H), 7.48 (t, J = 8.9 Hz, 2H), 7.42 (d, J = 8.3 Hz, 1H), 7.36 – 7.31 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.75 (s), 144.45 (s), 137.43 (s), 135.55 (s), 133.70 (s), 133.26 (s), 132.34 (s), 129.11 – 128.53 (m), 128.21 (d, J = 19.8 Hz), 127.78 (s), 127.29 (s), 126.42 (d, J = 4.4 Hz), 125.99 (d, J = 4.7 Hz), 125.31 (s), 124.70 (s), 123.48 (s), 115.63 (s). HRMS (ESI) m/z calcd for. $C_{23}H_{15}N$ $[M+H]^+$ 306.1277, found 306.1271.

6-(p-tolyl)benzo[h]quinoline (2n)



Yield: 65% (65 mg). White solid. m.p. 113.3-115.6 °C. Purified by flash column chromatography (EtOAc/hexane = 1/30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 5.7 Hz, 1H), 8.52 (s, 1H), 8.43 (d, J = 5.7 Hz, 1H), 7.89 (d, J = 9.1 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 8.9 Hz, 3H), 7.54 (dd, J = 12.8, 5.9 Hz, 4H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.18 (s), 143.97 (s), 140.05 (s), 137.11 (s), 135.63 (s), 131.06 (s), 130.49 (s), 130.08 (s), 128.78 (s), 128.37 (d, J = 8.6 Hz), 127.77 (s), 125.01 (s), 123.54 (s), 123.10 (s), 115.24 (s), 22.12 (s). HRMS (ESI) m/z calcd for. $C_{20}H_{15}N$ $[M+H]^+$ 270.1277, found 270.1278.

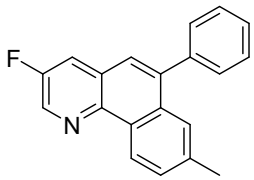
6-(4-fluorophenyl)benzo[h]quinoline (2o)



Yield: 76% (75 mg). White solid. Purified by flash column chromatography (EtOAc/hexane = 1/200). ^{1}H NMR (400 MHz,

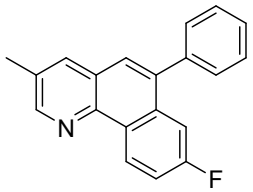
$CDCl_3$) δ 8.84 (d, *J* = 5.7 Hz, 1H), 8.36 – 8.28 (m, 2H), 7.91 (t, *J* = 8.1 Hz, 2H), 7.76 – 7.69 (m, 3H), 7.59 – 7.47 (m, 4H).[6]

3-fluoro-8-methyl-6-phenylbenzo[h]quinoline (2p)



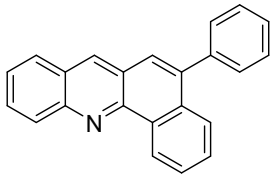
Yield: 72% (73 mg). White solid. m.p. 126.3-127.8 °C. Purified by flash column chromatography (dichlormethane/hexane = 1/3).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 – 9.11 (m, 1H), 8.68 (d, *J* = 5.0 Hz, 1H), 7.96 – 7.90 (m, 2H), 7.80 – 7.71 (m, 3H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.61 (d, ^1J = 260.2 Hz), 156.29 (d, ^4J = 4.7 Hz), 138.37 (s), 136.78 (s), 133.57 (s), 132.22 (d, ^2J = 28.7 Hz), 130.06 (s), 129.33 (s), 129.12 (s), 128.80 (d, ^2J = 24.6 Hz), 128.57 (s), 128.50 (s), 127.74 (s), 127.73 (s), 126.80 (s), 124.73 (d, ^3J = 7.3 Hz), 124.46 (s), 21.40 (s).HRMS (ESI) m/z calcd for. $C_{20}H_{14}FN$ $[M+H]^+$ 288.1183, found 288.1180.

8-fluoro-3-methyl-6-phenylbenzo[h]quinoline (2q)



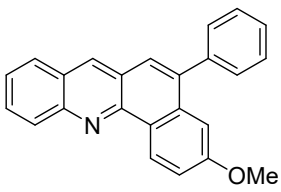
Yield: 85% (94 mg). White solid. m.p. 134.2-136.6 °C. Purified by flash column chromatography (EtOAc/hexane = 1/40). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 5.1 Hz, 1H), 8.62 (d, *J* = 2.1 Hz, 1H), 7.93 (dd, *J* = 6.4, 2.6 Hz, 1H), 7.87 (dd, *J* = 9.1, 3.0 Hz, 1H), 7.71 (dd, *J* = 8.0, 3.2 Hz, 3H), 7.64 (ddd, *J* = 8.3, 5.3, 2.7 Hz, 2H), 7.26 – 7.19 (m, 2H), 3.10 (d, *J* = 3.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.92 (d, ^1J = 247.7 Hz), 157.49 (s), 147.47 (s), 136.45 (d, ^4J = 3.1 Hz), 135.59 (s), 134.41 (s), 132.06 (d, ^3J = 8.2 Hz), 130.21 (s), 128.81 (s), 128.34 (s), 128.02 (d, ^3J = 8.8 Hz), 127.80 (s), 126.43 (s), 125.44 (s), 124.94 (s), 115.34 (d, ^2J = 21.5 Hz), 23.87 (s). HRMS (ESI) m/z calcd for. $C_{20}H_{14}FN$ $[M+H]^+$ 288.1183, found 288.1184.

5-phenylbenzo[c]acridine (2r)



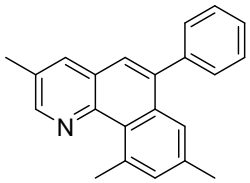
Yield: 60% (66 mg). White solid. Purified by flash column chromatography (EtOAc/hexane = 1/500). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 8.8 Hz, 1H), 9.04 (d, *J* = 8.4 Hz, 1H), 8.41 (d, *J* = 8.2 Hz, 1H), 8.03 – 7.94 (m, 2H), 7.87 – 7.81 (m, 2H), 7.79 – 7.69 (m, 5H), 7.59 (td, *J* = 8.6, 4.6 Hz, 3H).[7]

3-methoxy-5-phenylbenzo[c]acridine (2s)



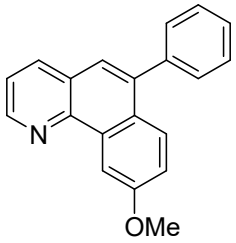
Yield: 85% (74 mg). Yellow solid. Purified by flash column chromatography (EtOAc/hexane = 1/30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 7.5 Hz, 1H), 9.02 (d, *J* = 8.3 Hz, 1H), 8.38 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 8.6 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.70 (dd, *J* = 14.7, 7.7 Hz, 5H), 7.11 (d, *J* = 8.1 Hz, 2H), 3.92 (s, 3H).[7]

3,8,10-trimethyl-6-phenylbenzo[h]quinoline (2t)



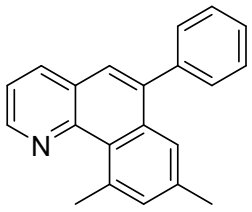
Yield: 89% (98 mg). White solid. m.p. 110.3-113.1 °C. Purified by flash column chromatography (EtOAc/hexane = 1/50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 – 8.99 (m, 1H), 8.66 (s, 1H), 7.97 – 7.91 (m, 1H), 7.74 – 7.67 (m, 3H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.23 (s, 1H), 7.15 (d, *J* = 11.3 Hz, 2H), 3.16 (s, 3H), 2.43 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.23 (s), 147.59 (s), 137.89 (s), 137.06 (s), 136.37 (s), 134.95 (s), 134.56 (s), 130.90 (s), 130.41 (s), 129.75 (s), 128.89 (s), 128.25 (s), 128.05 (s), 127.81 (s), 127.46 (s), 126.52 – 126.20 (m), 125.28 (s), 23.92 (s), 21.30 (s), 19.78 (s). HRMS (ESI) m/z calcd for. $C_{22}H_{19}N$ $[M+H]^+$ 298.1590, found 298.1592.

9-methoxy-6-phenylbenzo[h]quinoline (2u)



Yield: 65% (65 mg). White solid. m.p. 90.2-91.7 °C. Purified by flash column chromatography (EtOAc/hexane = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 5.7 Hz, 1H), 8.73 – 8.67 (m, 1H), 8.42 (d, *J* = 5.7 Hz, 1H), 7.95 (d, *J* = 9.1 Hz, 1H), 7.90 (dd, *J* = 6.4, 2.5 Hz, 1H), 7.75 – 7.67 (m, 3H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 1.9 Hz, 2H), 7.07 – 7.01 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.07 (s), 159.65 (s), 144.15 (s), 141.25 (s), 135.92 (s), 133.11 (s), 129.35 (s), 128.69 (d, *J* = 13.7 Hz), 128.00 (s), 127.22 (s), 124.85 (s), 124.53 (s), 123.44 (s), 122.63 (s), 115.30 (d, *J* = 11.8 Hz), 114.58 (s), 55.42 (s). HRMS (ESI) m/z calcd for. $C_{20}H_{15}NO$ $[M+H]^+$ 286.1226, found 286.1227.

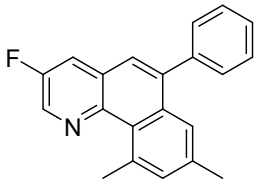
8,10-dimethyl-6-phenylbenzo[h]quinoline (2v)



Yield: 51% (52 mg). White solid. m.p. 77.5-79.3 °C. Purified by flash column chromatography (EtOAc/dichlormethane/hexane =

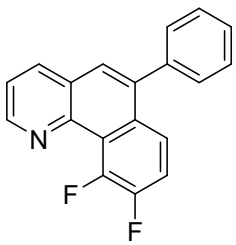
1/50/50). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83 (d, *J* = 5.7 Hz, 1H), 8.75 (d, *J* = 8.5 Hz, 1H), 8.45 (d, *J* = 5.7 Hz, 1H), 7.94 – 7.89 (m, 1H), 7.76 – 7.69 (m, 3H), 7.54 (d, *J* = 9.1 Hz, 1H), 7.25 (s, 1H), 7.19 – 7.14 (m, 2H), 2.44 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.96 (s), 144.26 (s), 138.03 (s), 136.55 (s), 136.25 (s), 135.37 (s), 133.22 (s), 130.97 (s), 129.60 (s), 128.65 (d, *J* = 2.6 Hz), 127.96 (s), 127.15 (s), 126.39 (s), 124.58 (s), 123.41 (s), 115.11 (s), 21.30 (s), 19.75 (s). HRMS (ESI) m/z calcd for. $C_{21}H_{17}N$ $[M+H]^+$ 284.1434, found 284.1438.

3-fluoro-8,10-dimethyl-6-phenylbenzo[h]quinoline (2w)



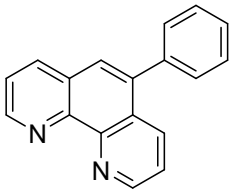
Yield: 58% (62 mg). White solid. m.p. 72.1-73.8 °C. Purified by flash column chromatography (EtOAc/hexane = 1/100). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 – 9.14 (m, 1H), 8.70 (d, *J* = 5.1 Hz, 1H), 7.98 – 7.91 (m, 1H), 7.76 (dd, *J* = 8.4, 3.0 Hz, 3H), 7.51 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.12 (m, 2H), 2.43 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.73 (d, ^{4}J = 4.8 Hz), 156.65 (d, ^{1}J = 259.8 Hz), 138.23 (s), 136.33 (d, ^{2}J = 26.1 Hz), 133.66 (s), 132.20 (d, ^{2}J = 28.4 Hz), 131.05 (s), 129.76 (s), 129.51 (s), 128.87 (s), 128.73 (s), 128.58 (s), 127.78 (s), 127.59 (s), 126.84 (s), 126.51 (s), 124.33 (d, ^{3}J = 8.8 Hz), 21.32 (s), 19.75 (s). HRMS (ESI) m/z calcd for. $C_{21}H_{16}FN$ $[M+H]^+$ 302.1340, found 302.1342.

9,10-difluoro-6-phenylbenzo[h]quinoline (2x)



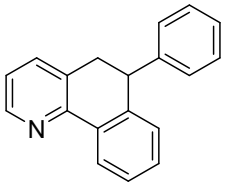
Yield: 51% (54 mg). White solid. m.p. 136.5-137.1 °C. Purified by flash column chromatography (EtOAc/hexane = 1/25). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 5.7 Hz, 1H), 8.77 – 8.69 (m, 1H), 8.51 (d, *J* = 5.7 Hz, 1H), 7.93 (dd, *J* = 6.4, 2.9 Hz, 1H), 7.80 (d, *J* = 9.1 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.64 (dd, *J* = 9.1, 3.1 Hz, 1H), 7.36 (ddd, *J* = 11.7, 7.2, 2.0 Hz, 2H), 7.32 – 7.27 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.92 (s), 150.79 (dd, ^{1}J = 238.7, ^{2}J=10.0 Hz), 148.28 (dd, ^{1}J = 240.0, ^{2}J=10.1 Hz), 144.42 (s), 135.66 (s), 133.18 (s), 129.87 (d, ^{2}J = 12.5 Hz), 128.98 (s), 128.74 (s), 128.55 (s), 127.44 (s), 126.75 (dd, ^{3}J = 3.1, ^{4}J=1.9 Hz), 125.70 (s), 124.46 (dd, ^{3}J = 6.7, ^{4}J=4.8 Hz), 123.68 (s), 123.43 (s), 117.66 (d, ^{2}J = 17.2 Hz), 116.37 (s). HRMS (ESI) m/z calcd for. $C_{19}H_{11}F_2N$ $[M+H]^+$ 292.0932, found 292.0931.

5-phenyl-1,10-phenanthroline(2z)



Yield: 15% (22 mg). White solid. Purified by flash column chromatography (Acetone/hexane = 1/20).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 10.3, 5.1 Hz, 2H), 8.74 (dd, *J* = 5.9, 3.5 Hz, 1H), 8.53 (d, *J* = 5.7 Hz, 1H), 8.38 (d, *J* = 9.2 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.96 – 7.90 (m, 2H), 7.82 (d, *J* = 9.2 Hz, 1H), 7.75 – 7.71 (m, 2H), 7.44 – 7.40 (m, 1H).[8]

6-phenyl-5,6-dihydrobenzo[h]quinoline(3a)



Yield: 20% (22 mg). White solid. m.p. 105.1-106.9 °C. Purified by flash column chromatography (EtOAc/hexane = 1/150). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.6 Hz, 1H), 8.42 (d, *J* = 7.7 Hz, 1H), 7.41 (dd, *J* = 13.8, 7.3 Hz, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.17 – 7.08 (m, 4H), 6.97 (d, *J* = 7.6 Hz, 1H), 4.31 – 4.27 (m, 1H), 3.26 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.47 (s), 148.01 (s), 143.15 (s), 140.35 (s), 135.90 (s), 134.58 (s), 130.28 (s), 129.39 (s), 128.54 (s), 128.23 (d, *J* = 14.4 Hz), 127.50 (s), 126.69 (s), 125.11 (s), 122.44 (s), 43.96 (s), 36.37 (s). HRMS (ESI) m/z calcd for. $C_{19}H_{15}N$ $[M+H]^+$ 258.1277, found 258.1284.

S9. References

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S10. ^{1}H NMR and ^{13}C NMR Spectra

Spectra of 4a-4v.

3-Bromo-2-phenylpyridine (4a)

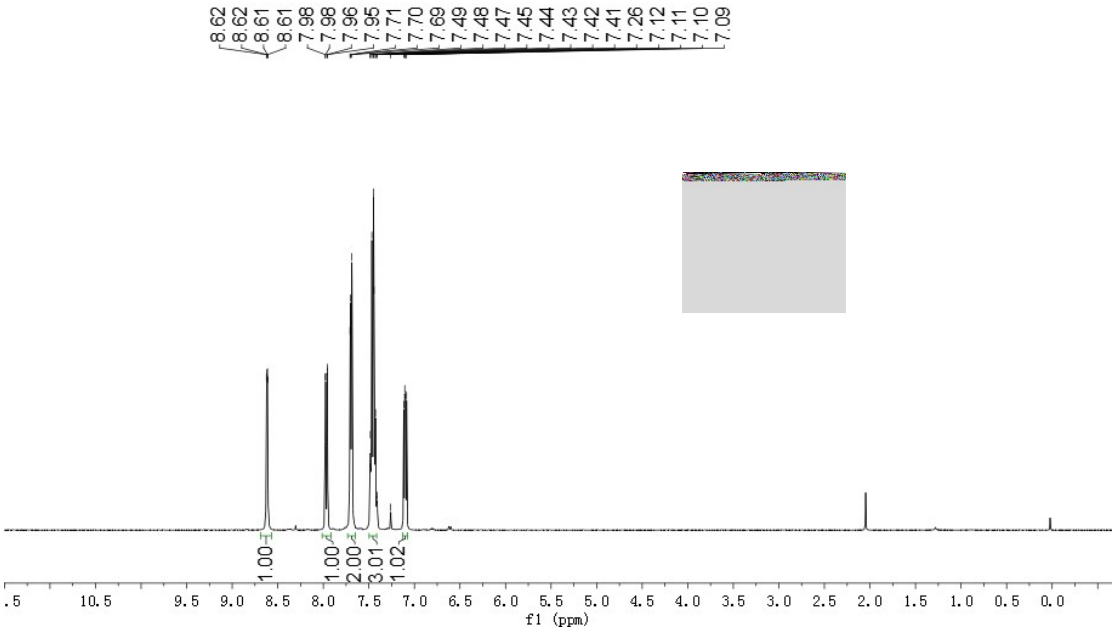

Figure S4. ^{1}H NMR spectrum of **4a** ($CDCl_3$, 400MHz)

3-Bromo-2-(*p*-tolyl)pyridine (4b)

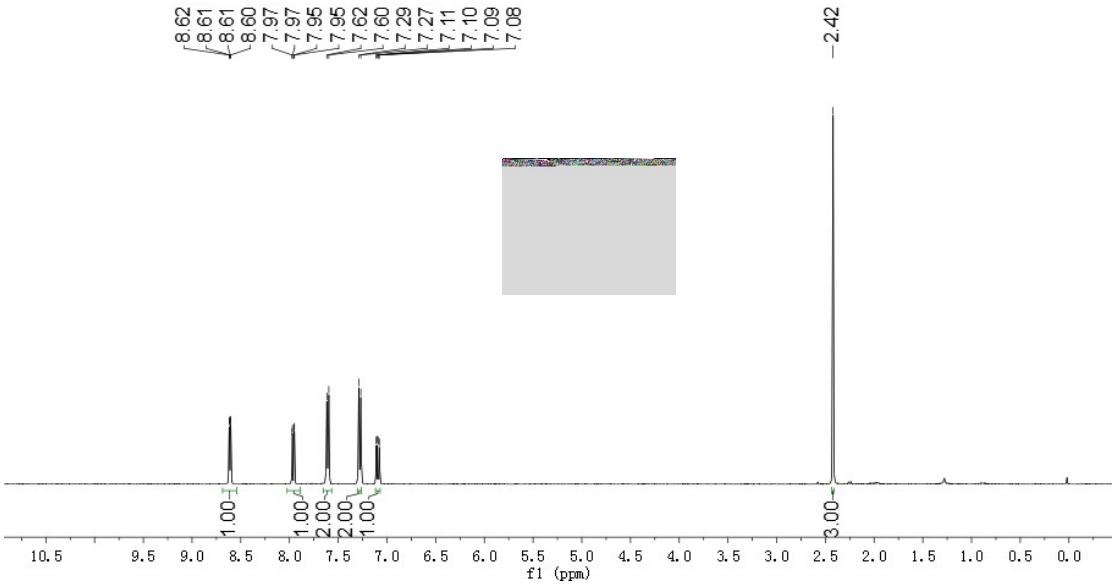

Figure S5. ^{1}H NMR spectrum of **4b** ($CDCl_3$, 400MHz)

3-Bromo-2-(4-methoxyphenyl)pyridine (4c)

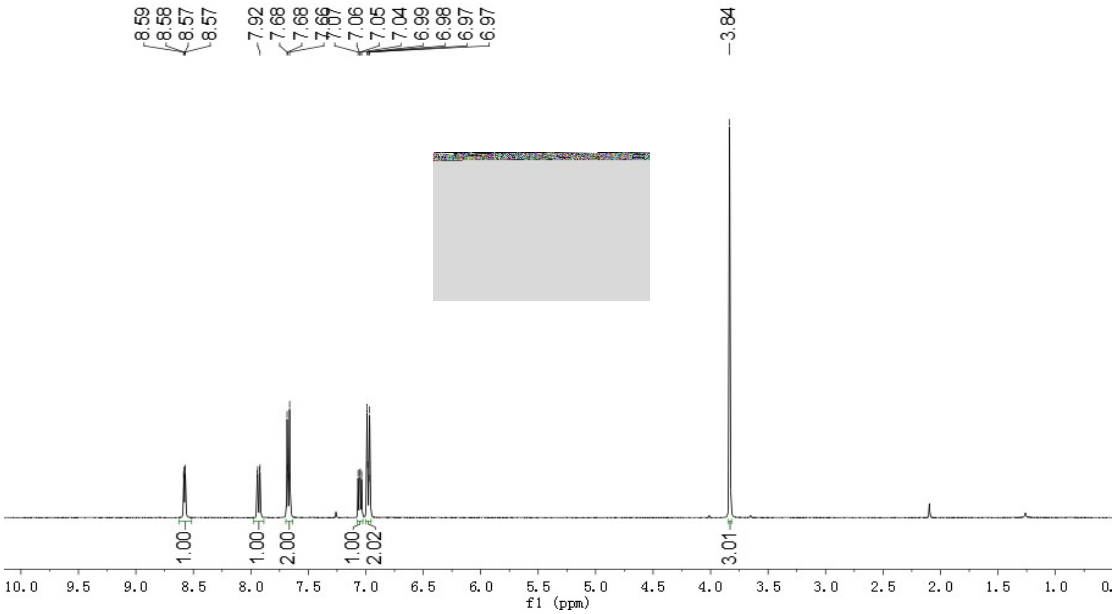

Figure S6. ^{1}H NMR spectrum of **4c** ($CDCl_3$,400MHz)

3-Bromo-2-(4-fluorophenyl)pyridine (4d)

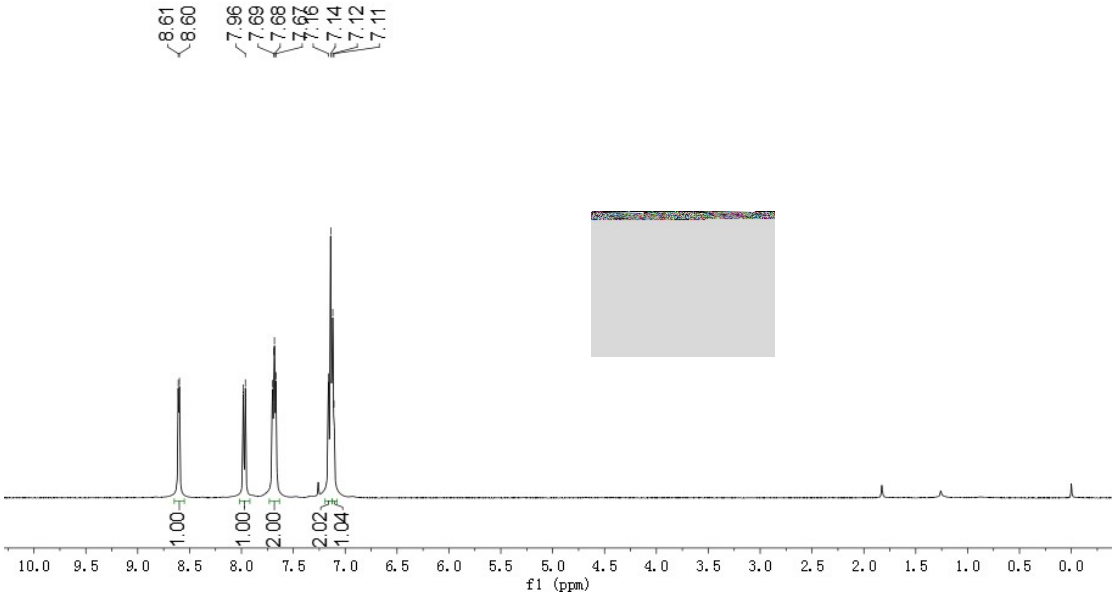

Figure S7. ^{1}H NMR spectrum of **4d** ($CDCl_3$, 400MHz)

1-(4-(3-Bromopyridin-2-yl)phenyl)ethan-1-one (4e)

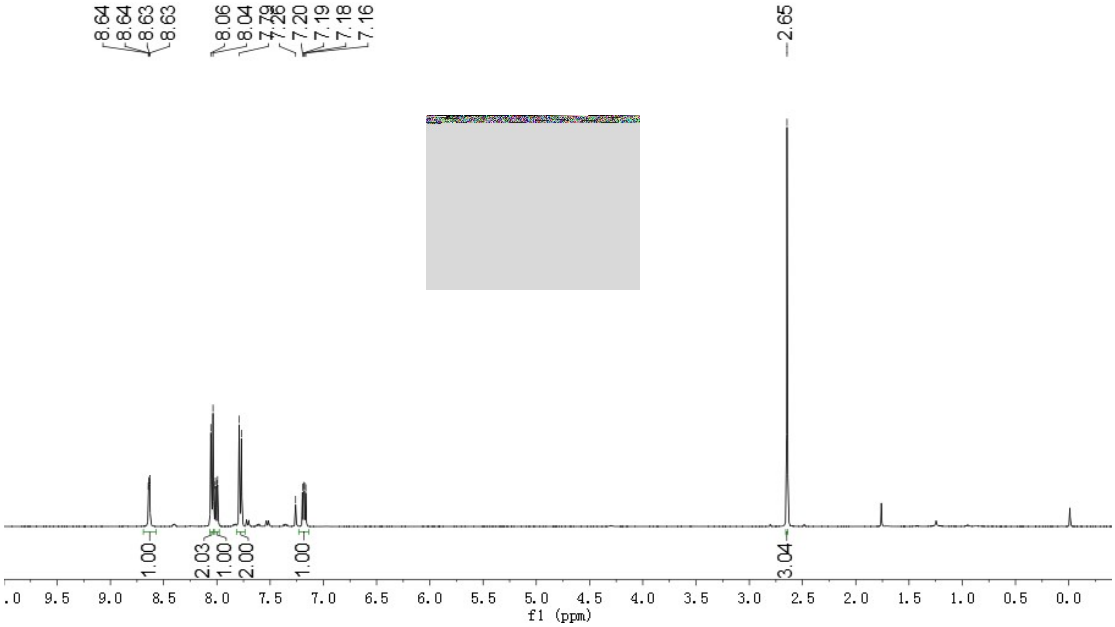

Figure S8. ^{1}H NMR spectrum of **4e** ($CDCl_3$, 400MHz)

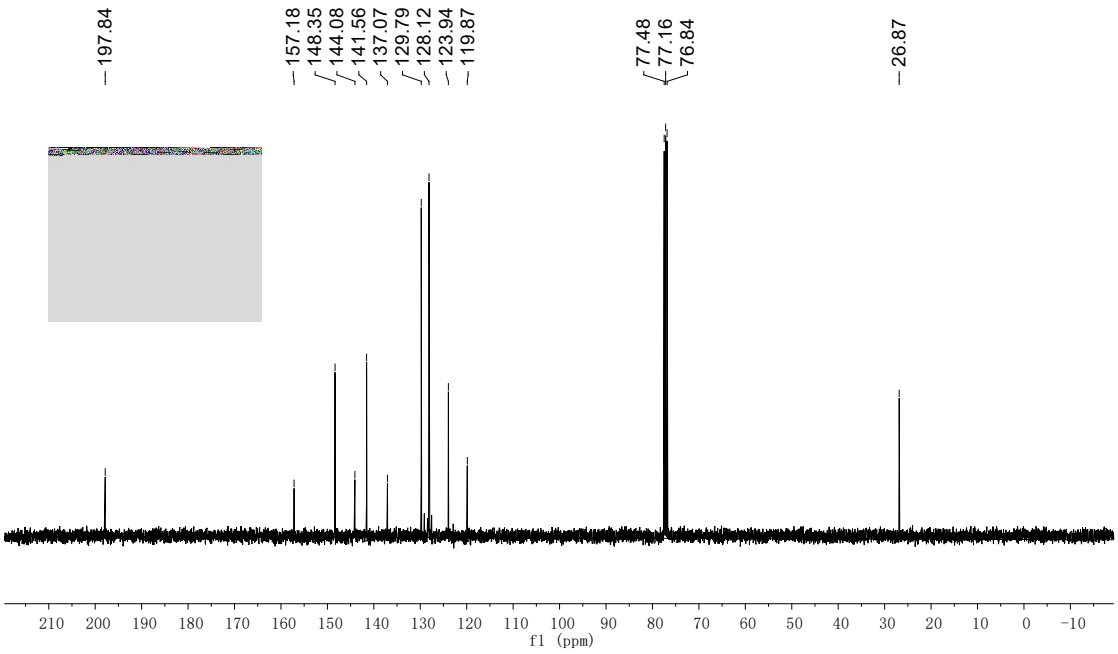

Figure S9. ^{13}C NMR spectrum of **4e** ($CDCl_3$, 400MHz)

3-Bromo-2-(4-(trifluoromethyl)phenyl)pyridine (4f)

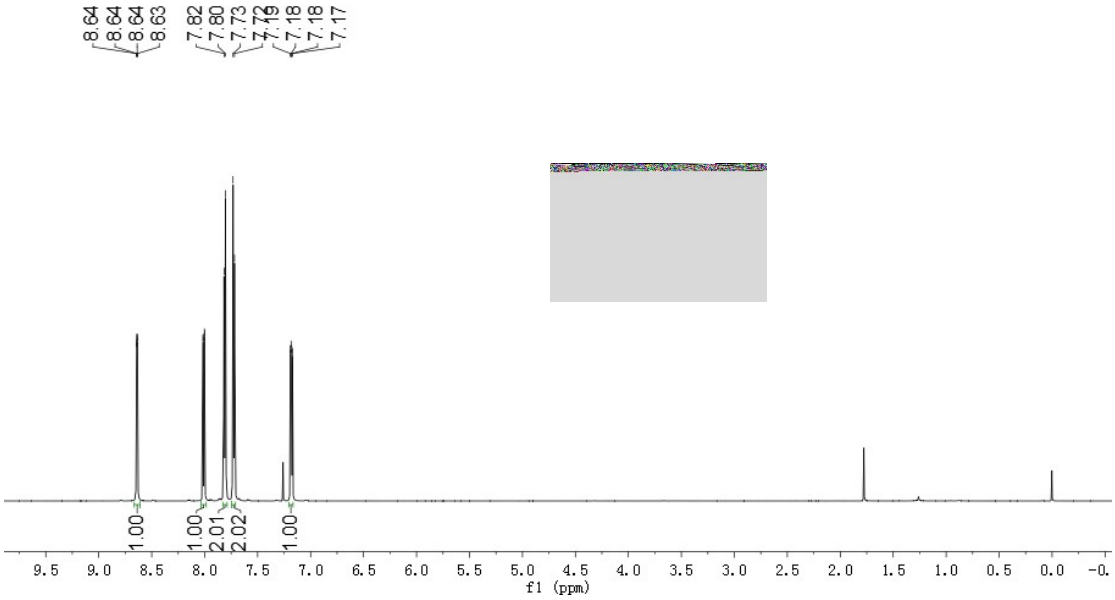

Figure S10. ^{1}H NMR spectrum of **4f** ($CDCl_3$, 600MHz)

1-(4-(3-Bromo-5-methylpyridin-2-yl)phenyl)ethan-1-one (4g)

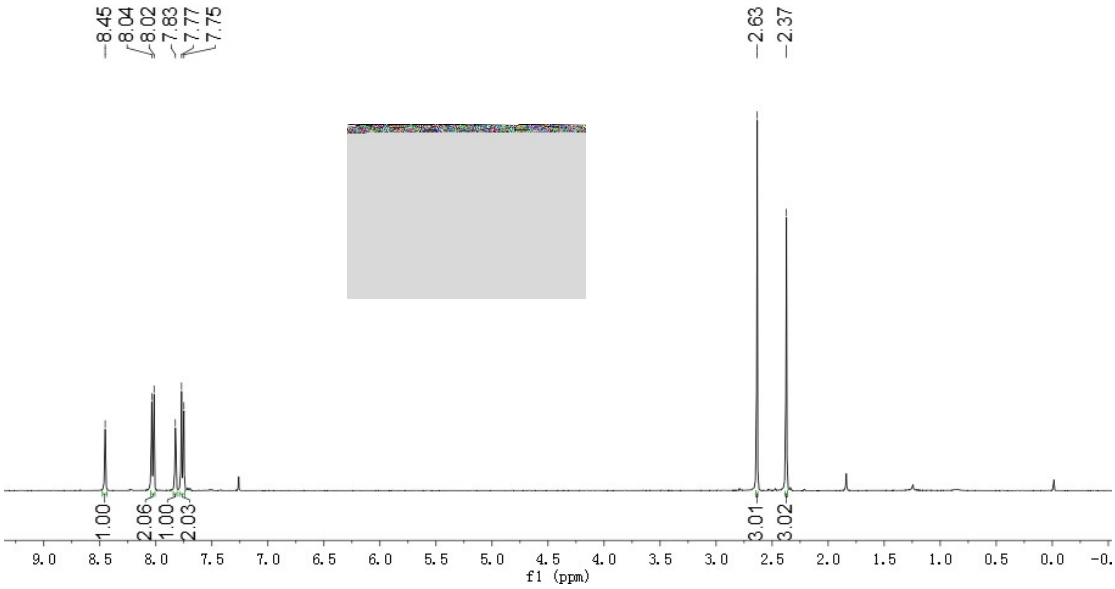

Figure S11. ^{1}H NMR spectrum of **4g** ($CDCl_3$, 400MHz)

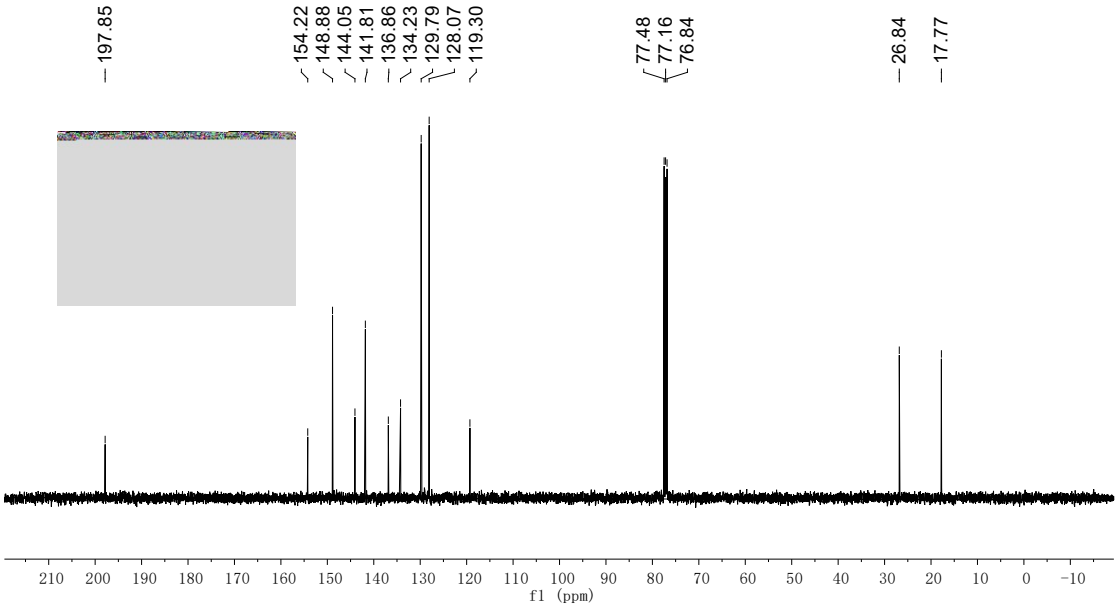

Figure S12. ^{13}C NMR spectrum of **4g** ($CDCl_3$, 400MHz)

3-Bromo-5-methyl-2-(p-tolyl)pyridine (4h)

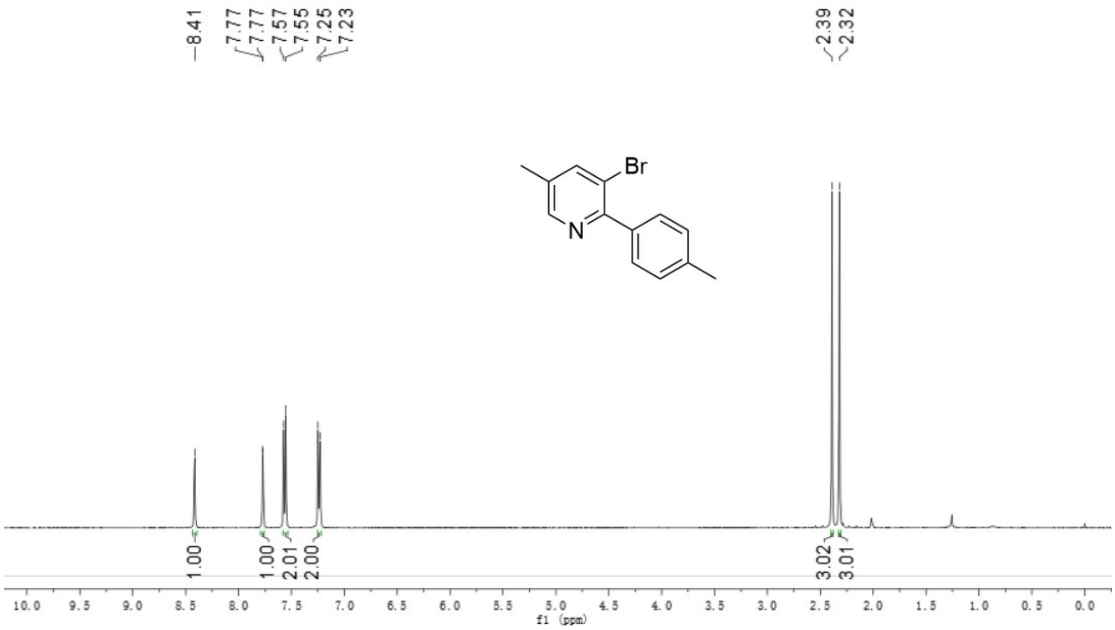

Figure S13. ^{1}H NMR spectrum of **4h** ($CDCl_3$, 400MHz)

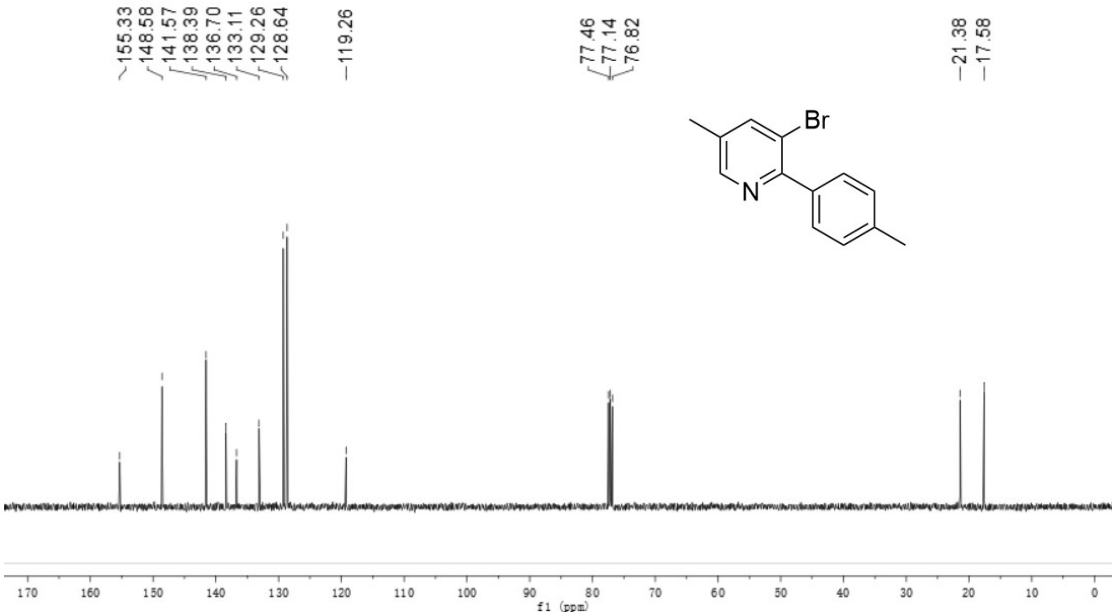

Figure S14. ^{13}C NMR spectrum of **4h** ($CDCl_3$, 400MHz)

3-Bromo-5-fluoro-2-phenylpyridine (4i)

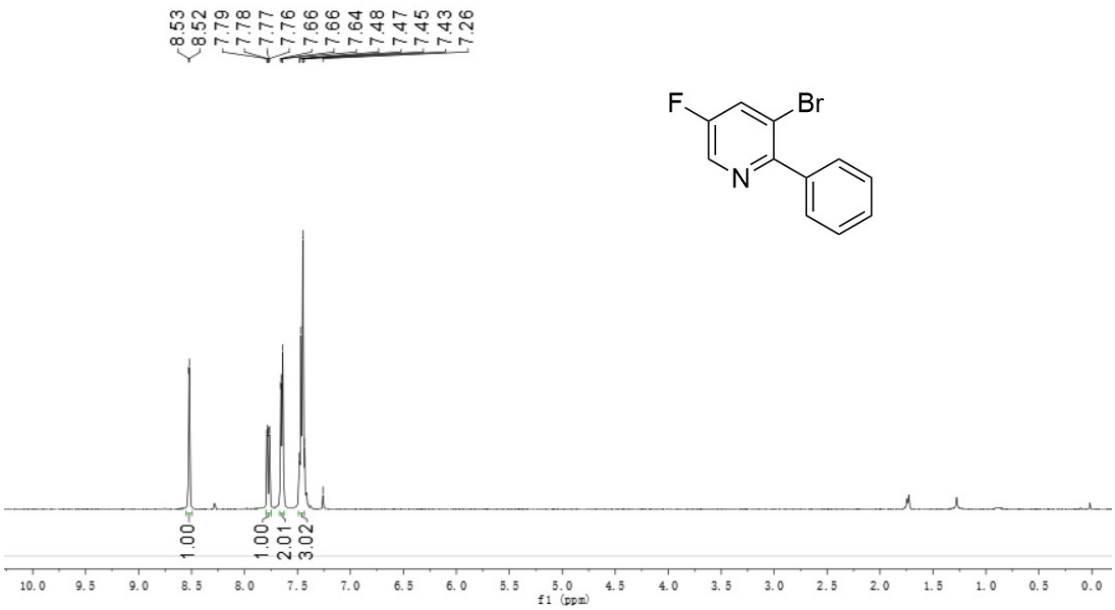

Figure S15. ^{1}H NMR spectrum of **4i** ($CDCl_3$, 400MHz)

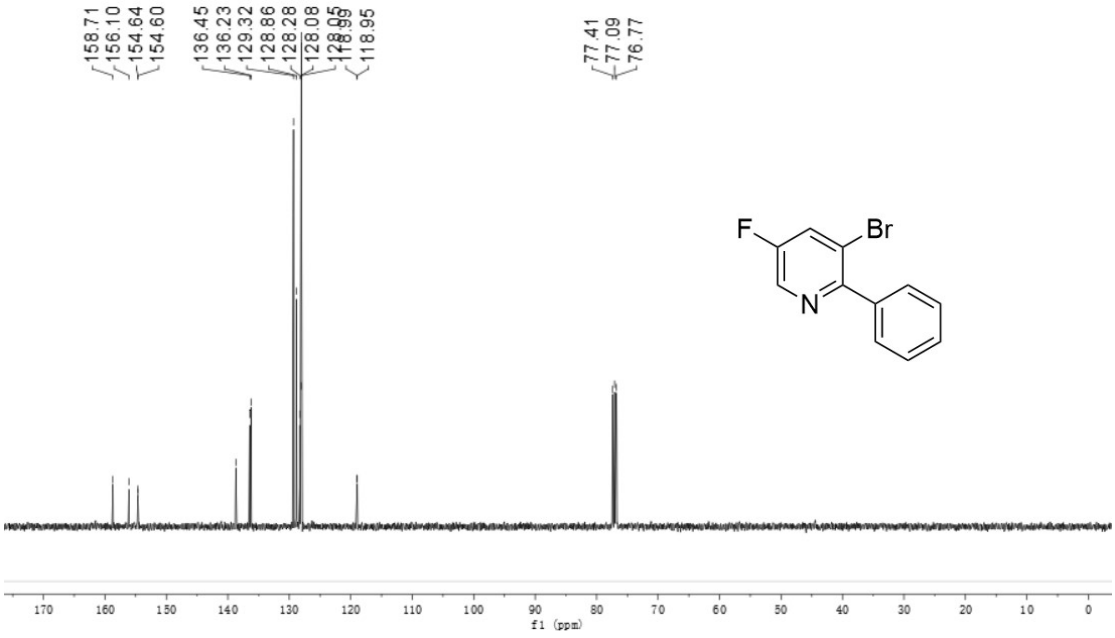

Figure S16. ^{13}C NMR spectrum of **4i** ($CDCl_3$, 400MHz)

3-Bromo-5-methyl-2-phenylpyridine (4j)

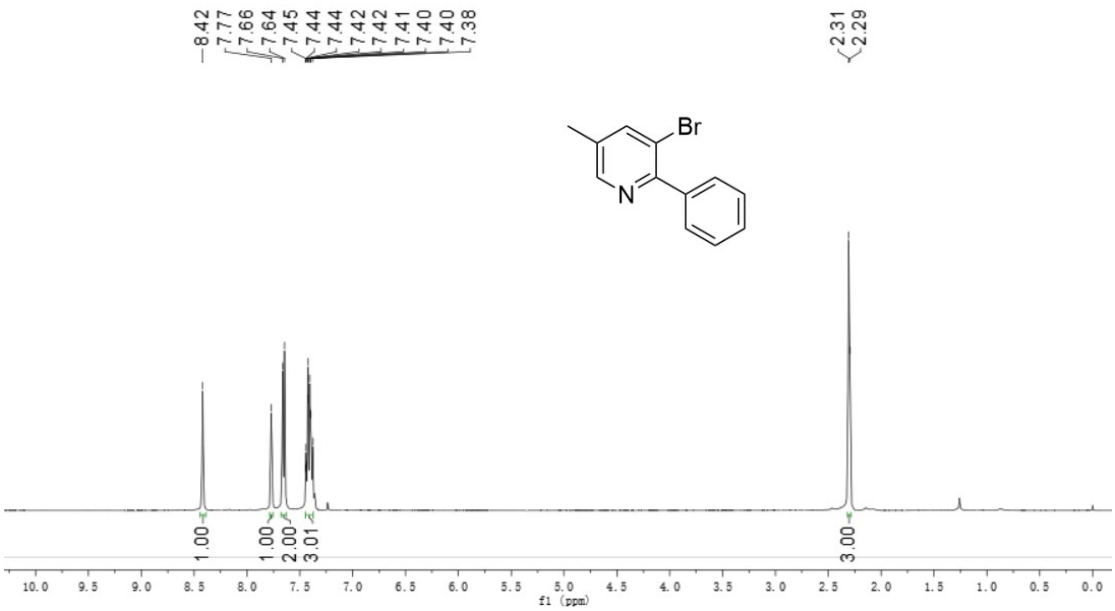

Figure S17. ^{1}H NMR spectrum of **4j** ($CDCl_3$, 400MHz)

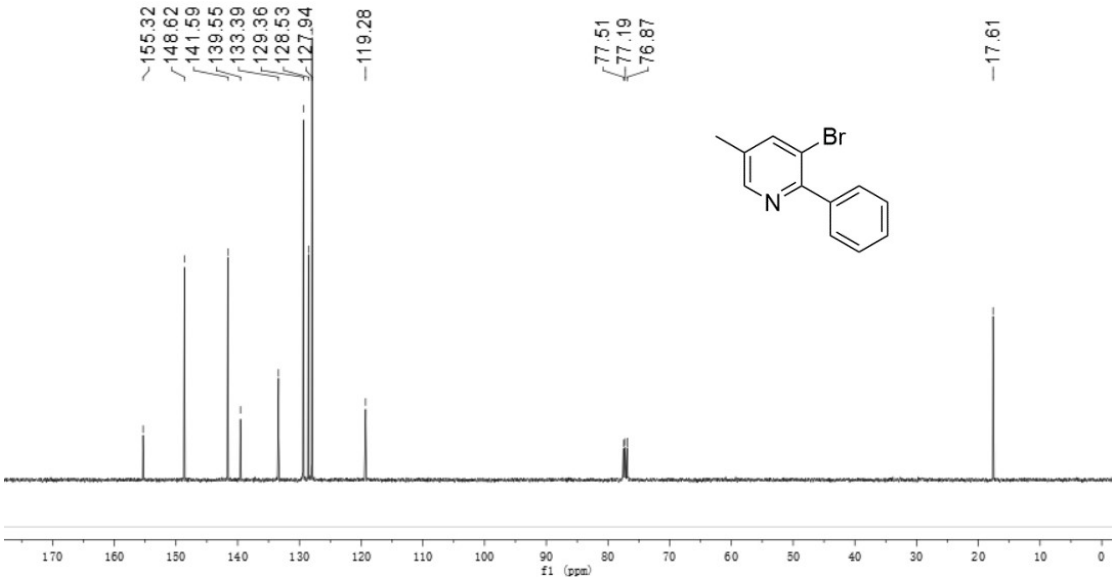

Figure S18. ^{13}C NMR spectrum of **4j** ($CDCl_3$, 400MHz)

3-Bromo-2-(m-tolyl)pyridine (4k)

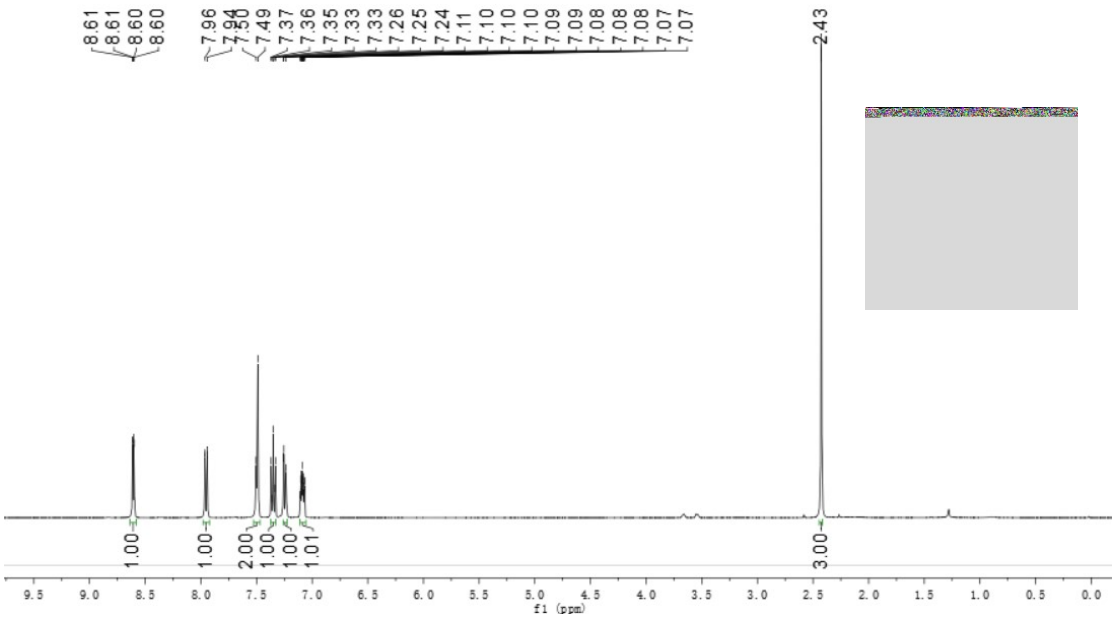

Figure S19. ^{1}H NMR spectrum of **4k** ($CDCl_3$, 400MHz)

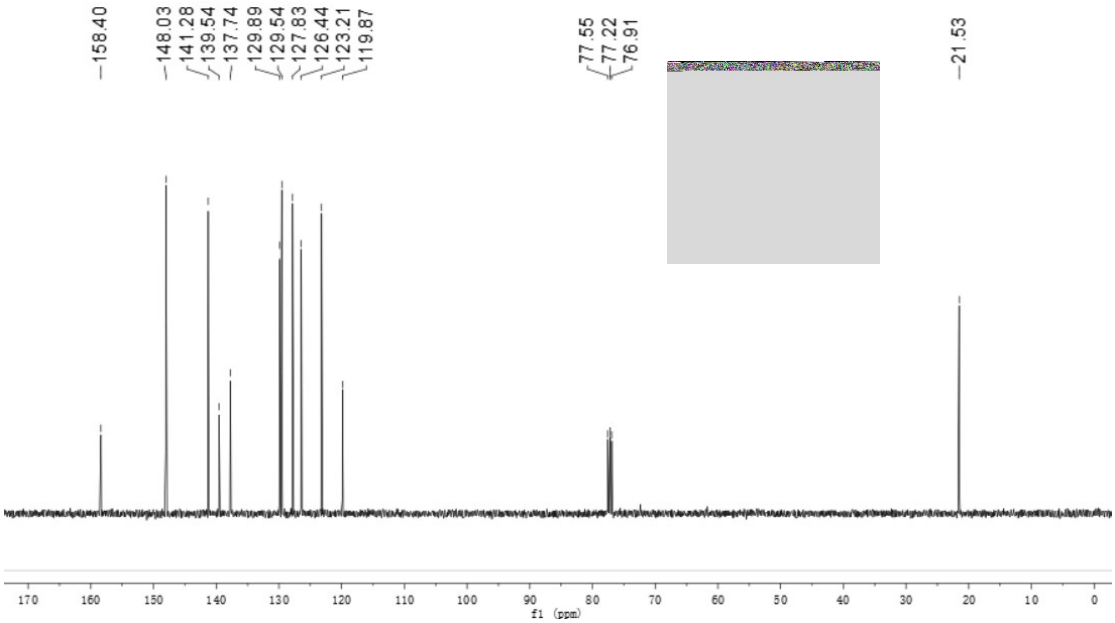

Figure S20. ^{13}C NMR spectrum of **4k** ($CDCl_3$, 400MHz)

3-bromo-5-methyl-2-(4-(trifluoromethyl)phenyl)pyridine (4l)

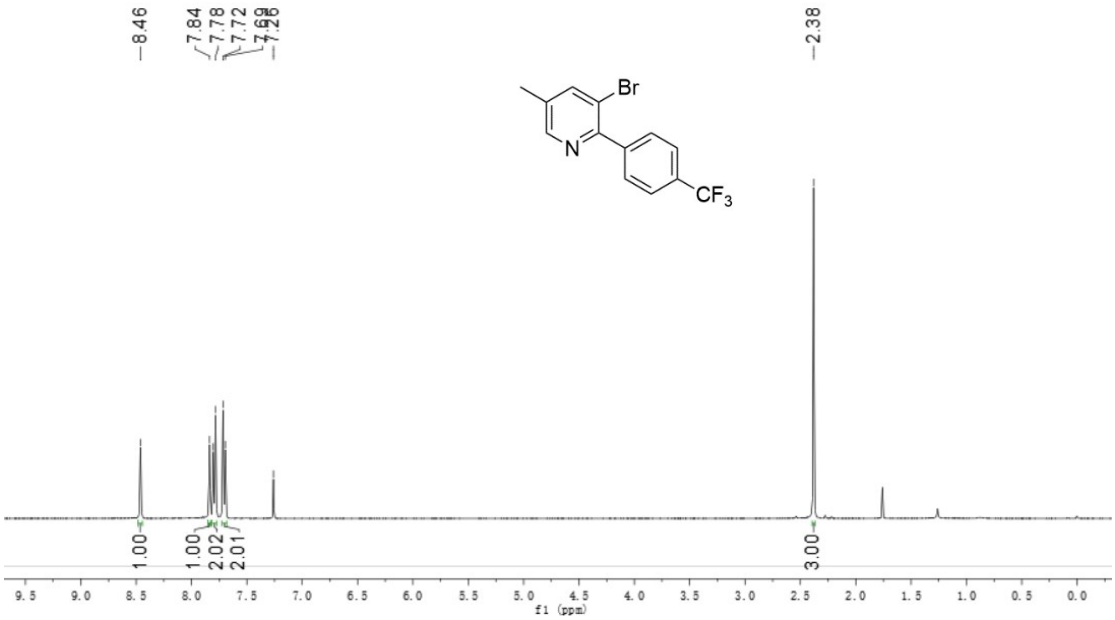

Figure S21. ^{1}H NMR spectrum of **4l** ($CDCl_3$, 400MHz)

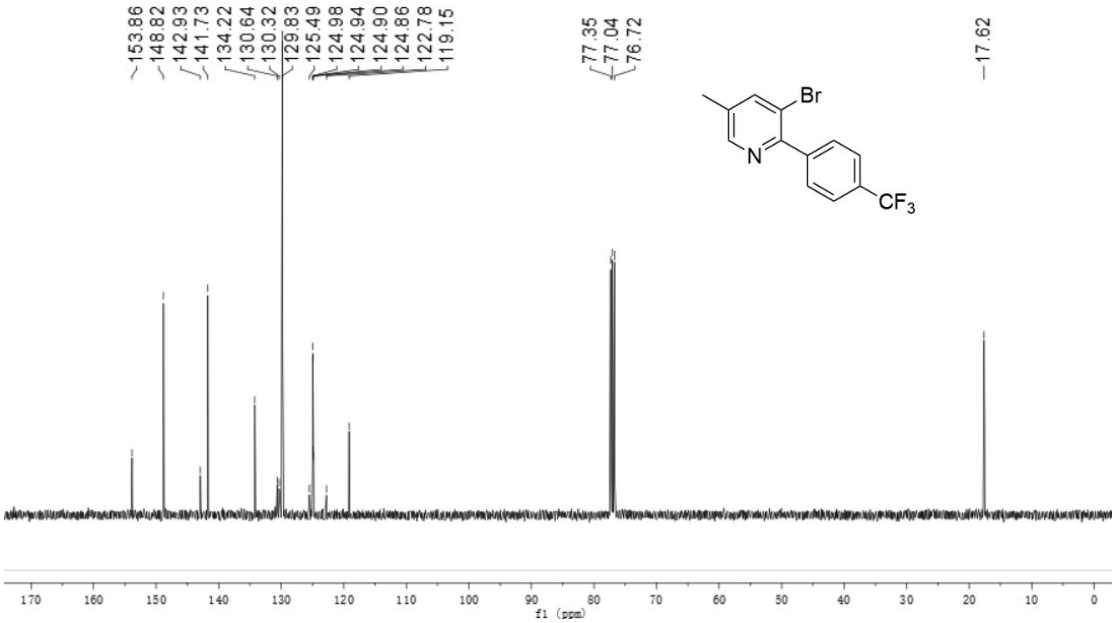

Figure S22. ^{13}C NMR spectrum of **4l** ($CDCl_3$, 400MHz)

3-Bromo-2-(naphthalen-1-yl)pyridine (4m)

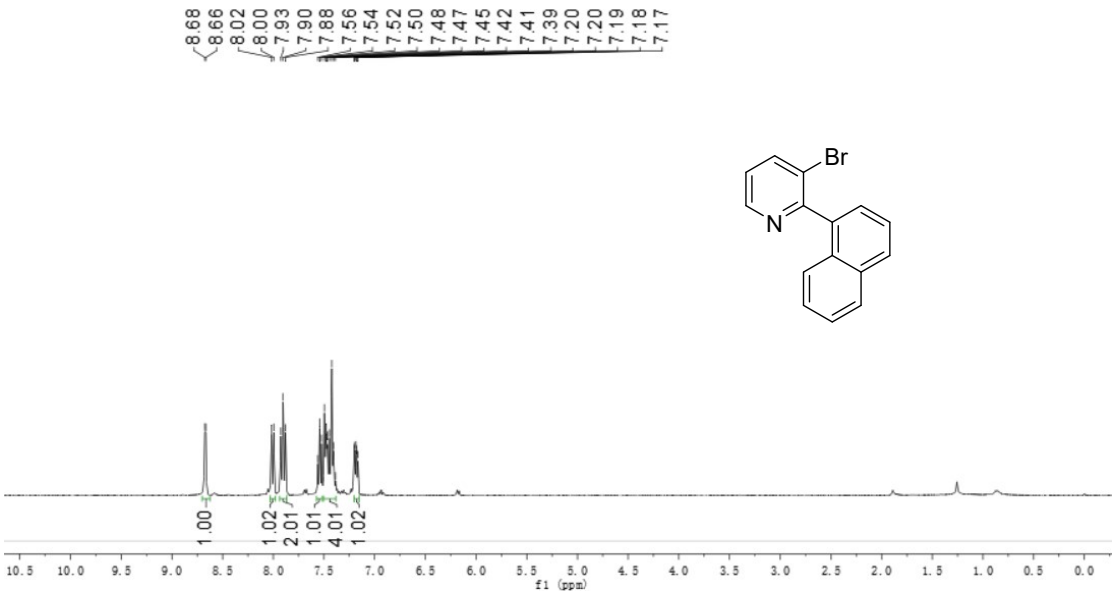

Figure S23. ^{1}H NMR spectrum of **4m** ($CDCl_3$, 400MHz)

3-Bromo-5-fluoro-2-(p-tolyl)pyridine (4n)

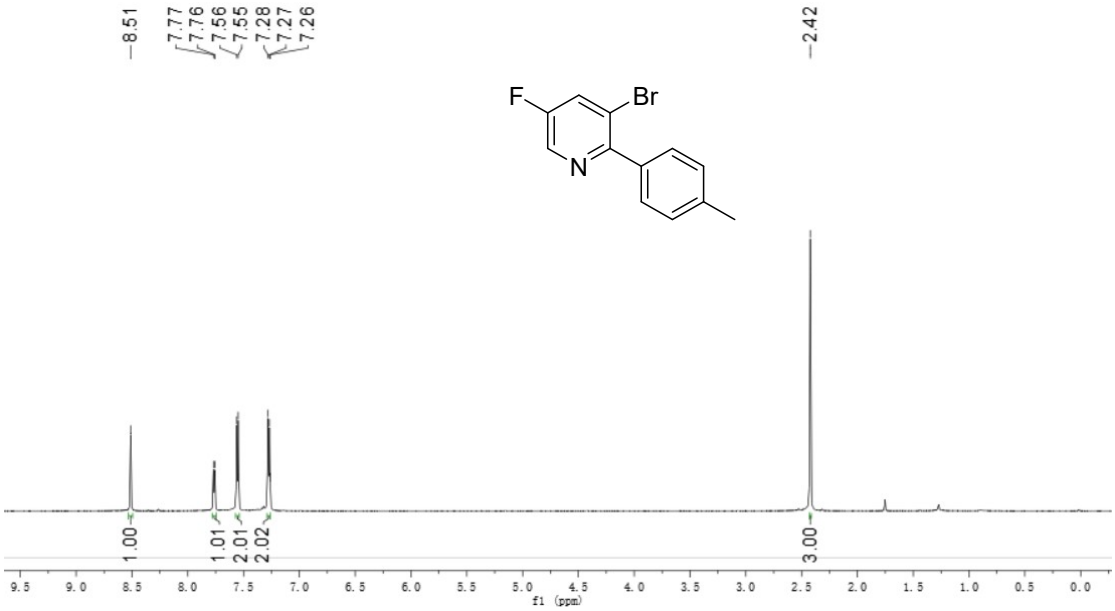

Figure S24. ^{1}H NMR spectrum of **4n** ($CDCl_3$, 600MHz)

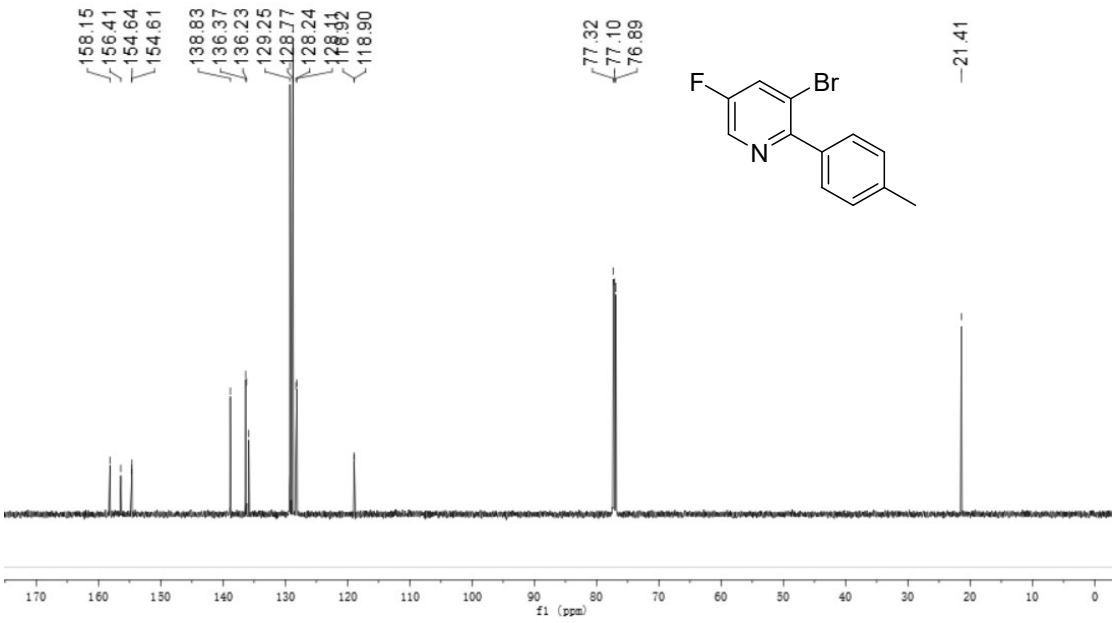

Figure S25. ^{13}C NMR spectrum of **4n** ($CDCl_3$, 600MHz)

3-Bromo-2-(4-fluorophenyl)-5-methylpyridine (4o)

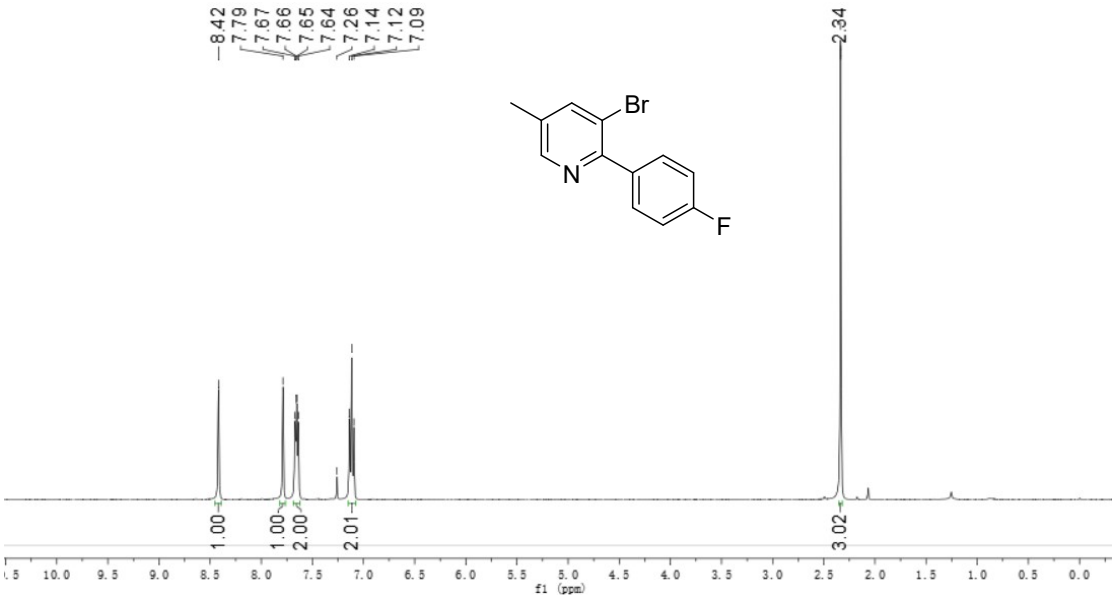

Figure S26. ^{1}H NMR spectrum of **4o** ($CDCl_3$, 400MHz)

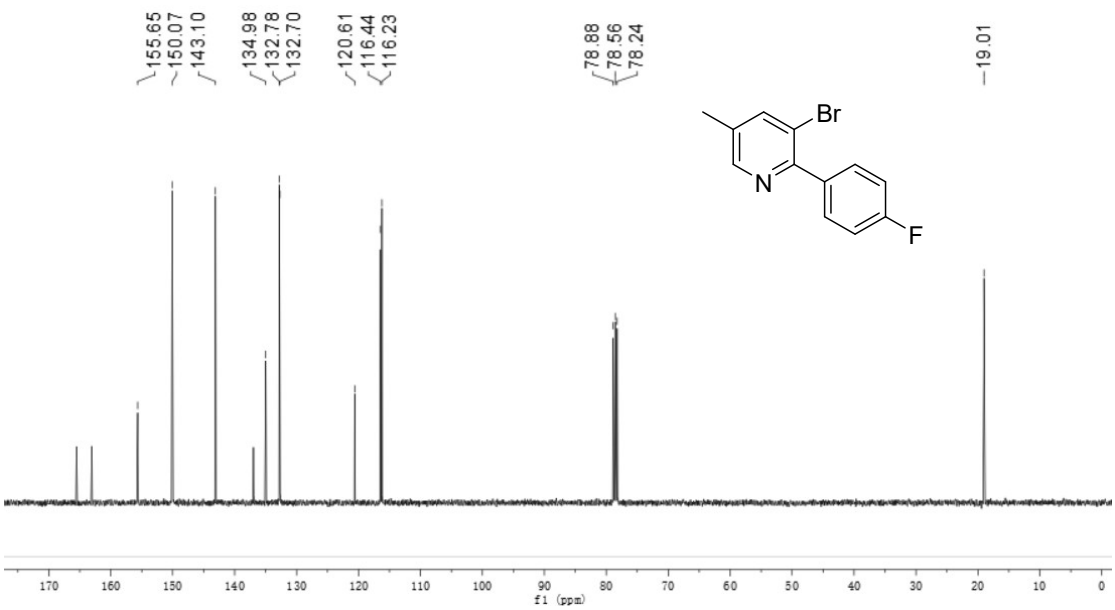

Figure S27. ^{13}C NMR spectrum of **4o** ($CDCl_3$, 400MHz)

3-Bromo-2-phenylquinoline (4p)

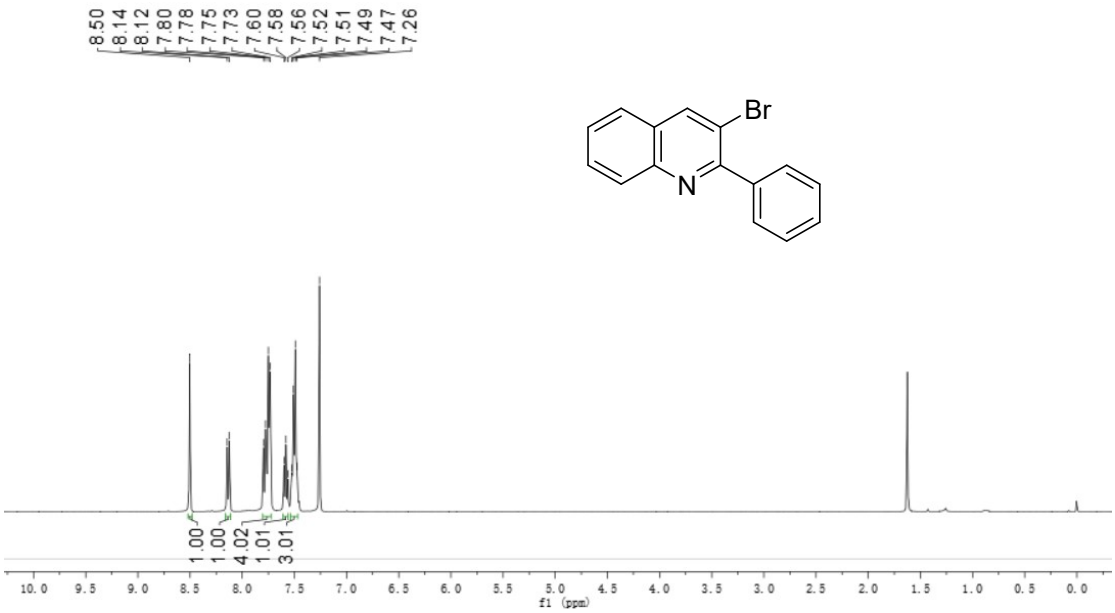

Figure S28. ^{1}H NMR spectrum of **4p** ($CDCl_3$, 400MHz)

3-Bromo-2-(4-methoxyphenyl)quinoline (4q)

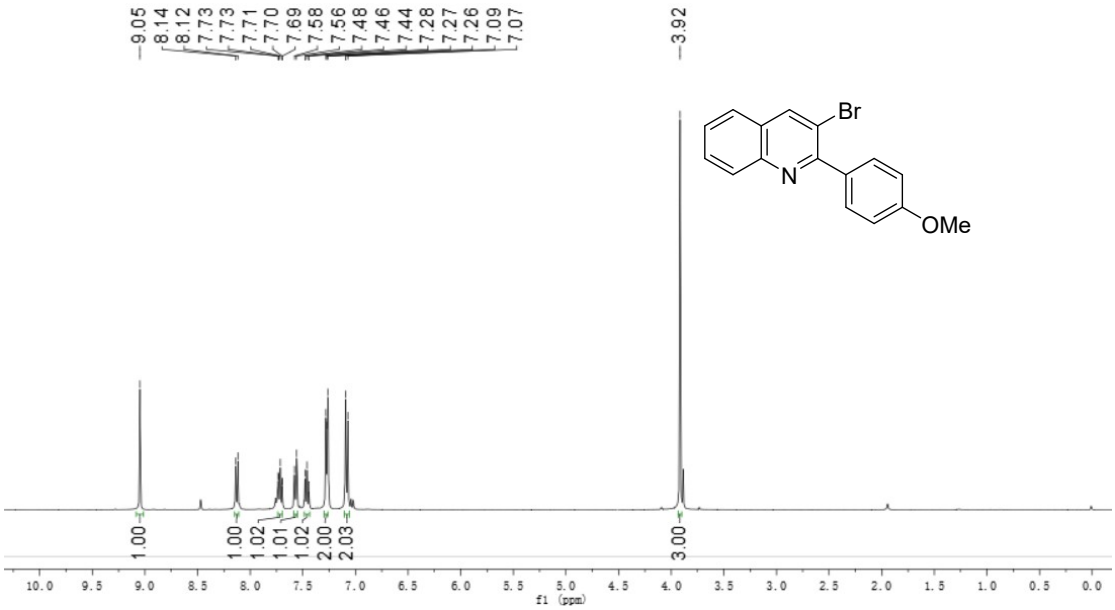

Figure S29. ^{1}H NMR spectrum of **4q** ($CDCl_3$, 400MHz)

3-Bromo-2-(2,4-dimethylphenyl)-5-methylpyridine (4r)

Figure S30. ^{1}H NMR spectrum of **4r** ($CDCl_3$, 400MHz)

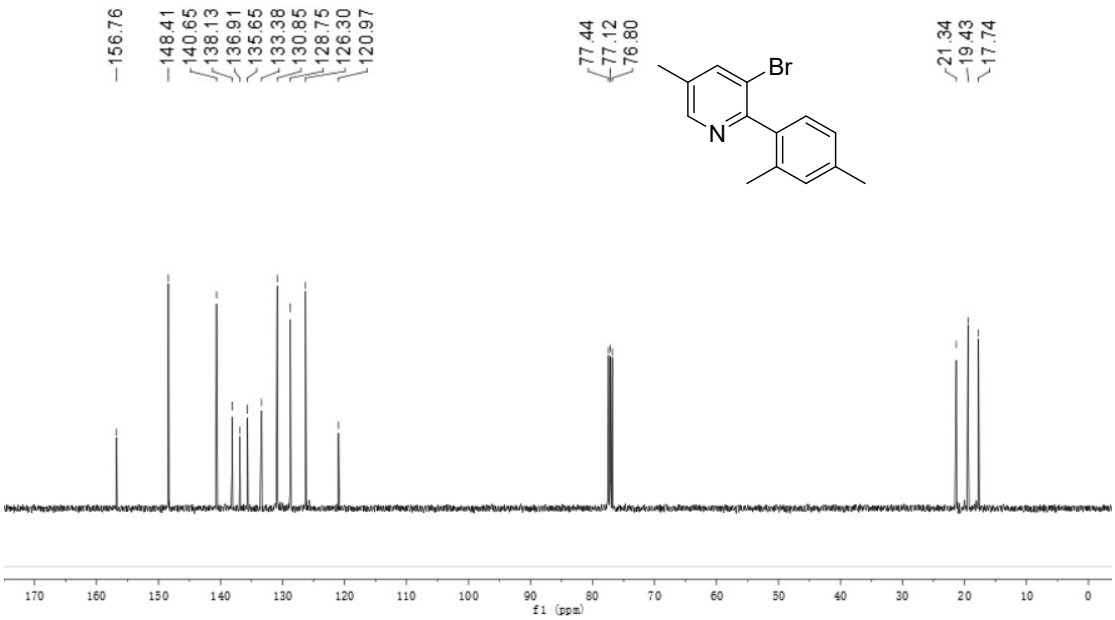

Figure S31. ^{13}C NMR spectrum of **4r** ($CDCl_3$, 400MHz)

3-Bromo-2-(3-methoxyphenyl)pyridine (4s)

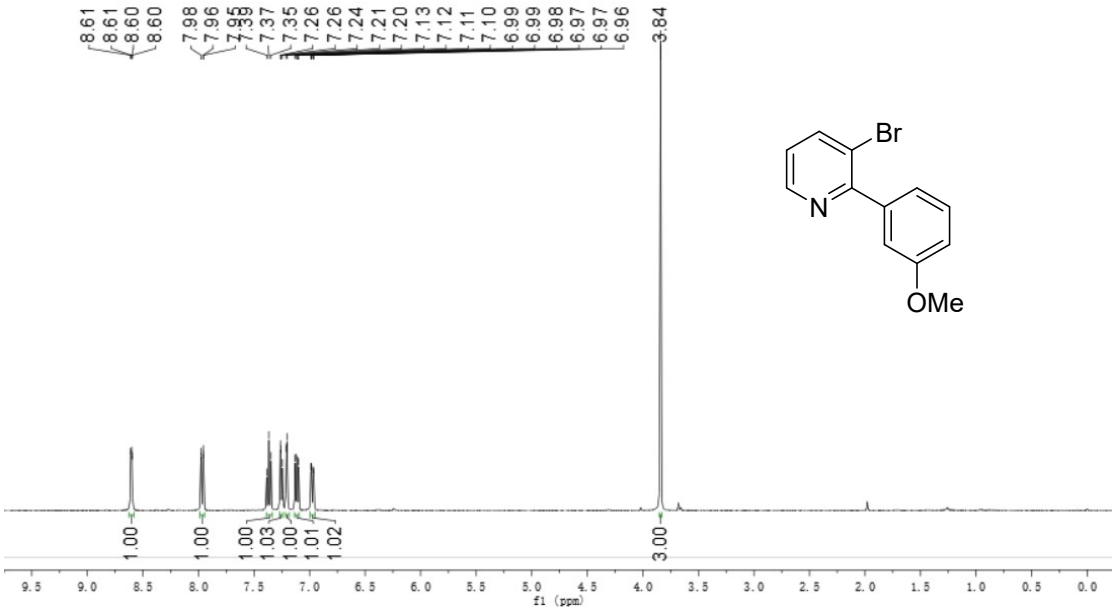

Figure S32. ^{1}H NMR spectrum of **4s** ($CDCl_3$, 400MHz)

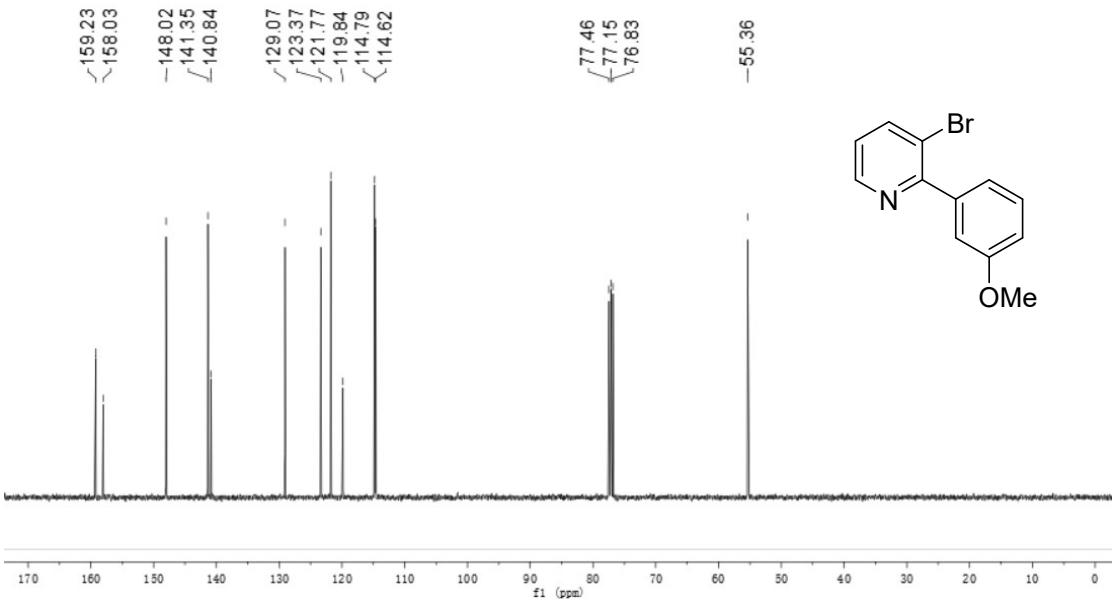

Figure S33. ^{13}C NMR spectrum of **4s** ($CDCl_3$, 400MHz)

3-Bromo-2-(2,4-dimethylphenyl)pyridine (4t)

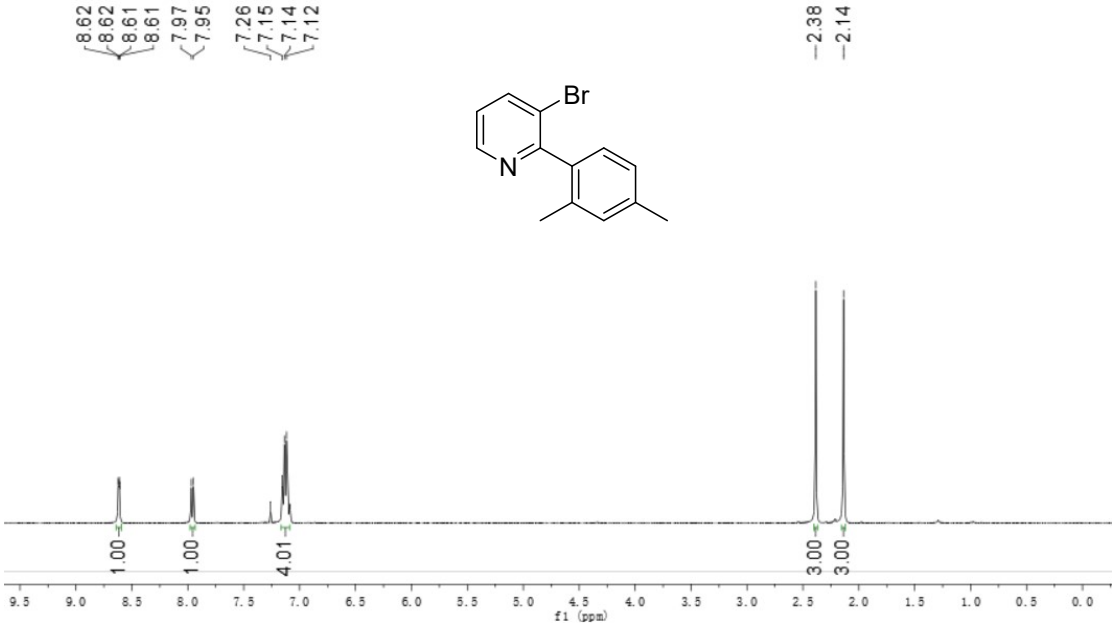

Figure S34. ^{1}H NMR spectrum of **4t** ($CDCl_3$, 400MHz)

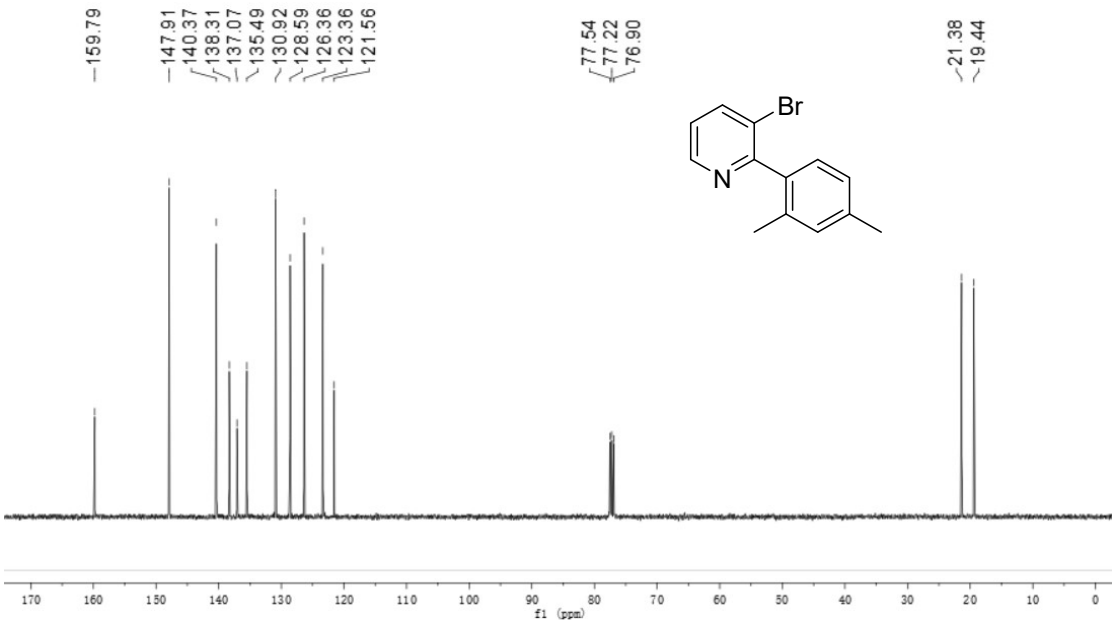

Figure S35. ^{13}C NMR spectrum of **4t** ($CDCl_3$, 400MHz)

3-Bromo-2-(2,4-dimethylphenyl)-5-fluoropyridine (4u)

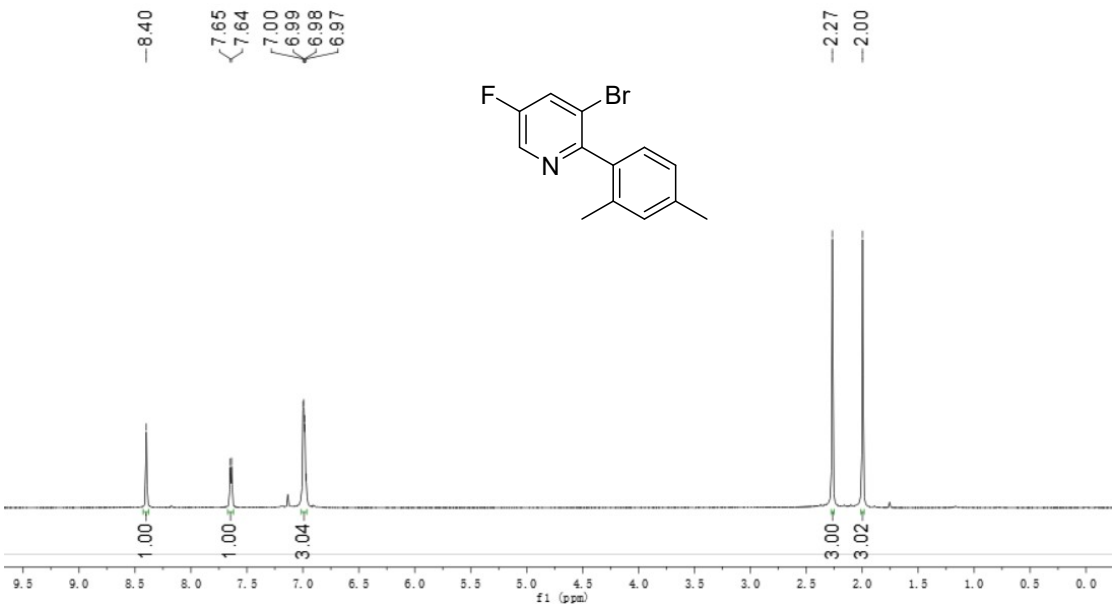

Figure S36. ^{1}H NMR spectrum of **4u** ($CDCl_3$, 600MHz)

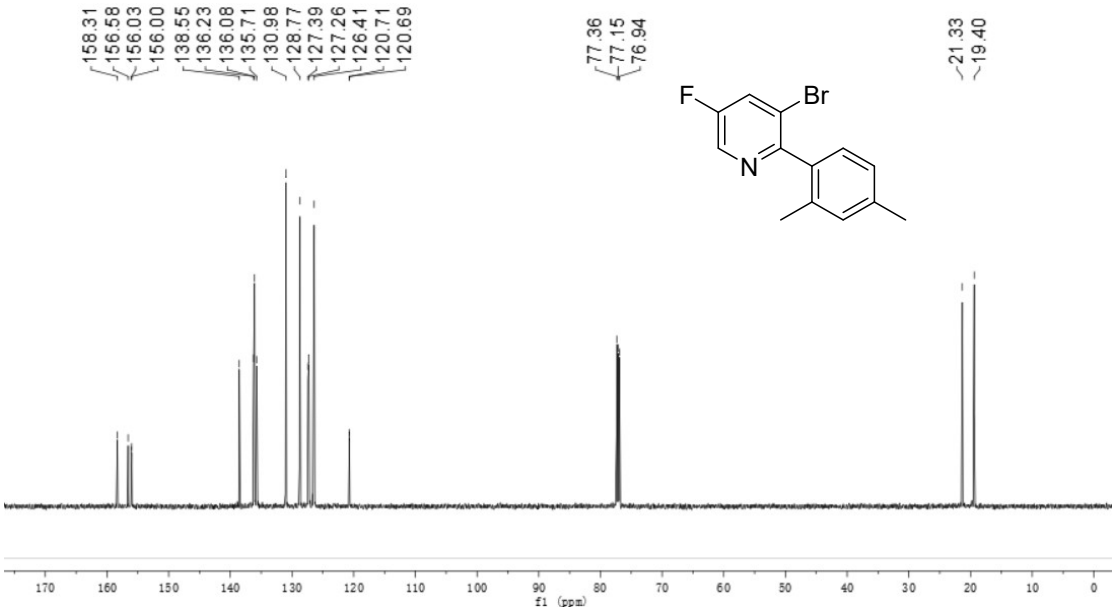

Figure S37. ^{13}C NMR spectrum of **4u** ($CDCl_3$, 600MHz)

3-Bromo-2-(2,3-difluorophenyl)pyridine (4v)

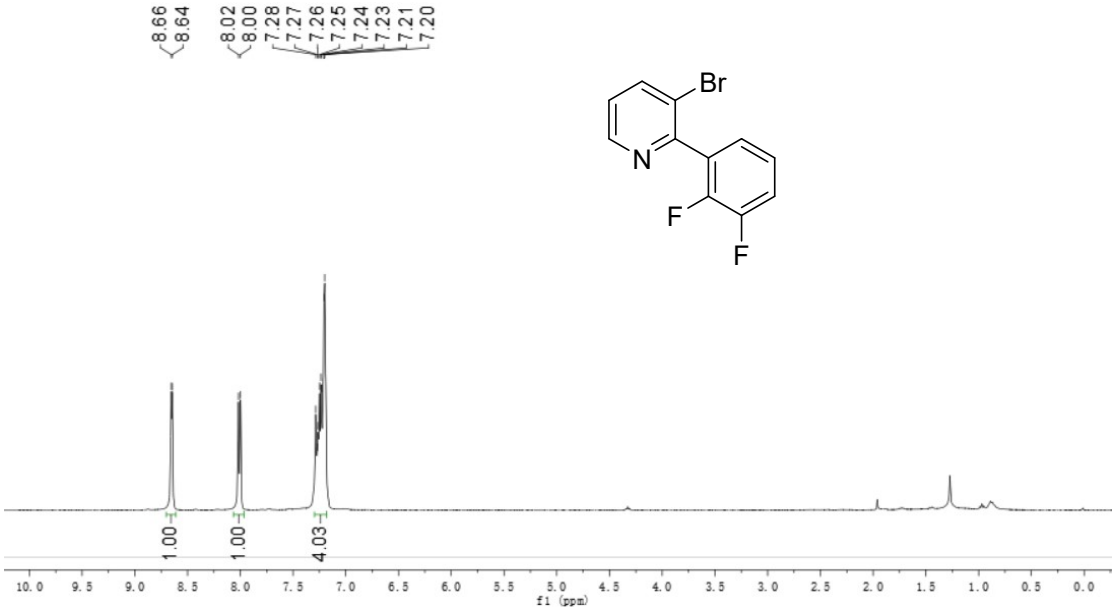

Figure S38. ^{1}H NMR spectrum of **4v** ($CDCl_3$, 400MHz)

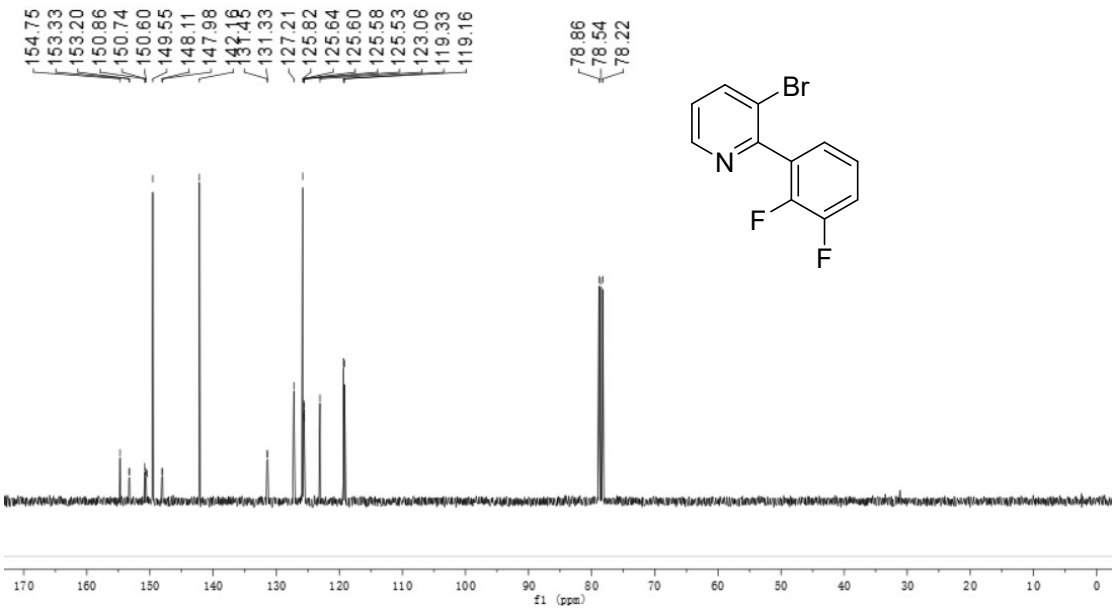

Figure S39. ^{13}C NMR spectrum of **4v** ($CDCl_3$, 400MHz)

Spectra of 1a-1z.

(E)-2-Phenyl-3-styrylpyridine (1a)

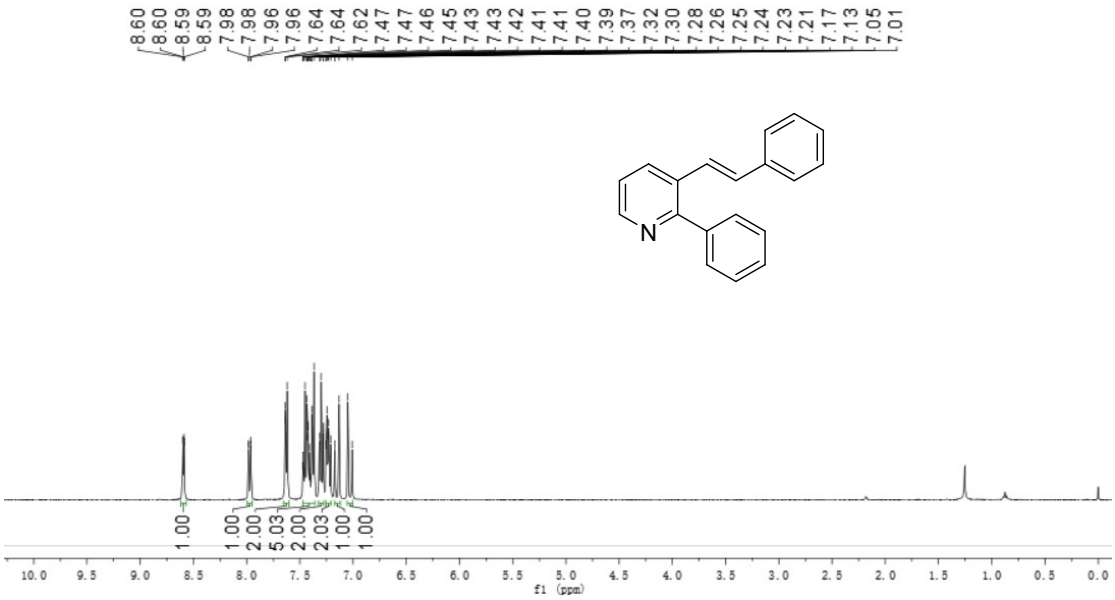

Figure S40. ^{1}H NMR spectrum of **1a** ($CDCl_3$, 400MHz)

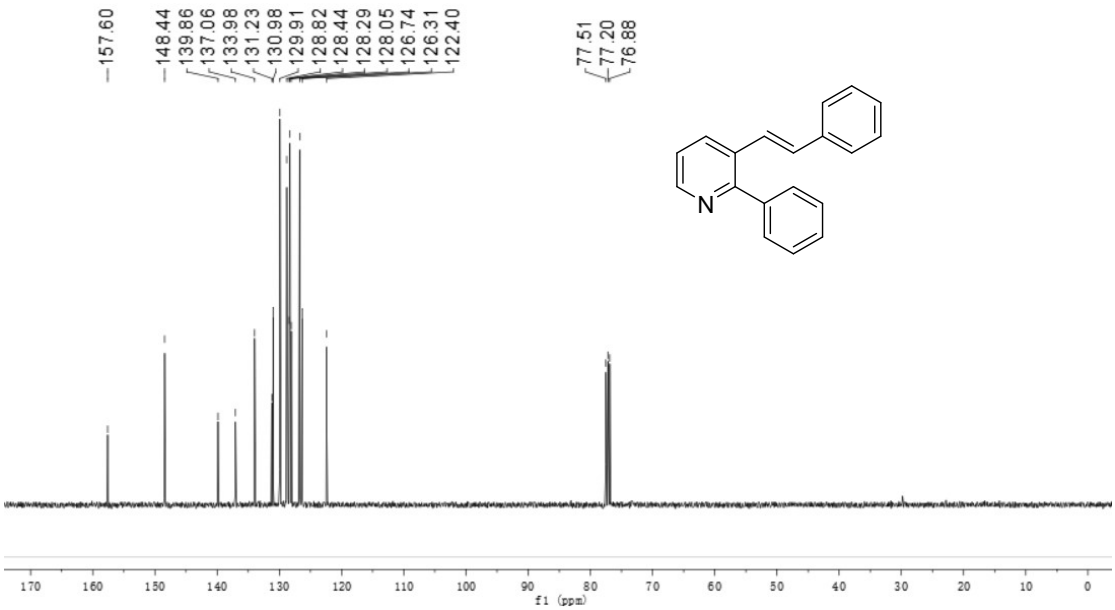

Figure S41. ^{13}C NMR spectrum of **1a** ($CDCl_3$, 400MHz)

(E)-3-(4-methylstyryl)-2-(p-tolyl)pyridine (1b)

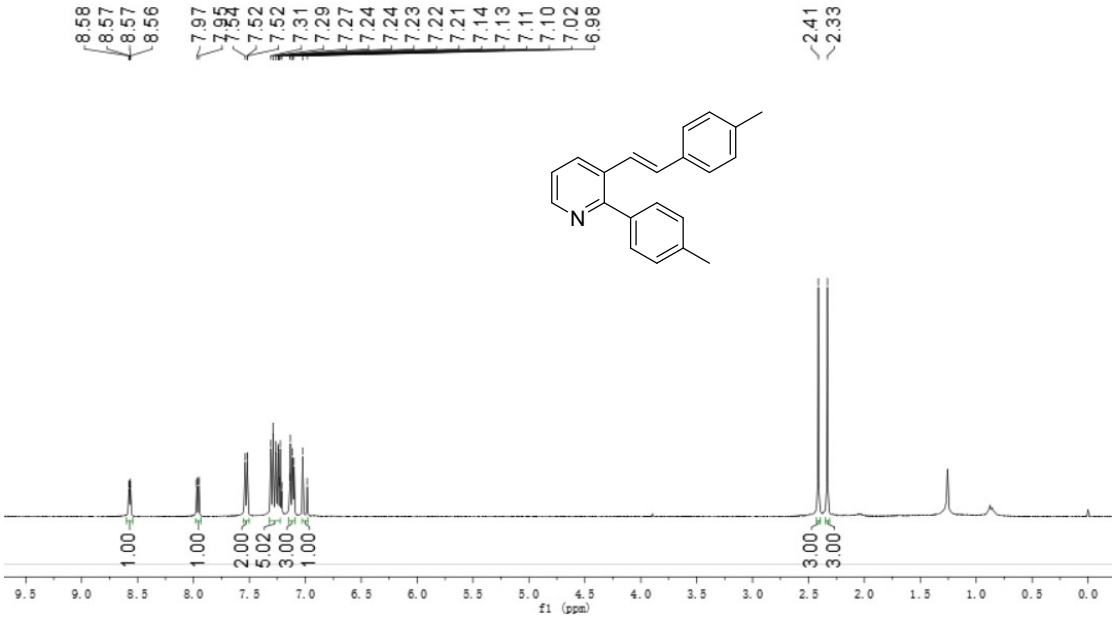

Figure S42. ^{1}H NMR spectrum of **1b** ($CDCl_3$, 400MHz)

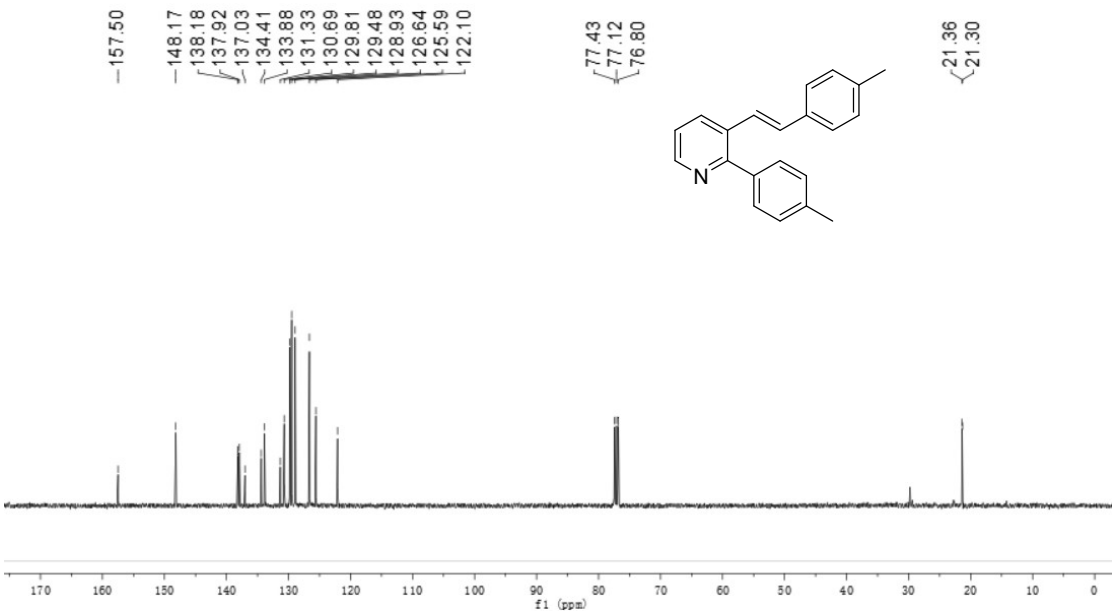

Figure S43. ^{13}C NMR spectrum of **1b** ($CDCl_3$, 400MHz)

(E)-2-(4-methoxyphenyl)-3-styrylpyridine (1c)

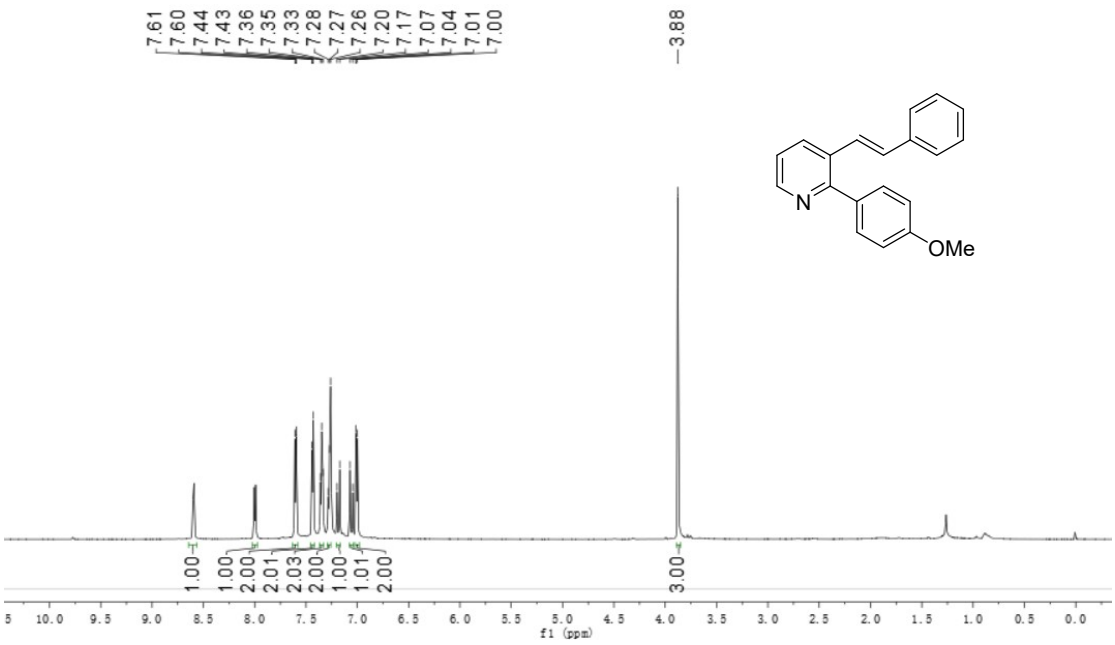

Figure S44. ^{1}H NMR spectrum of **1c** ($CDCl_3$, 600MHz)

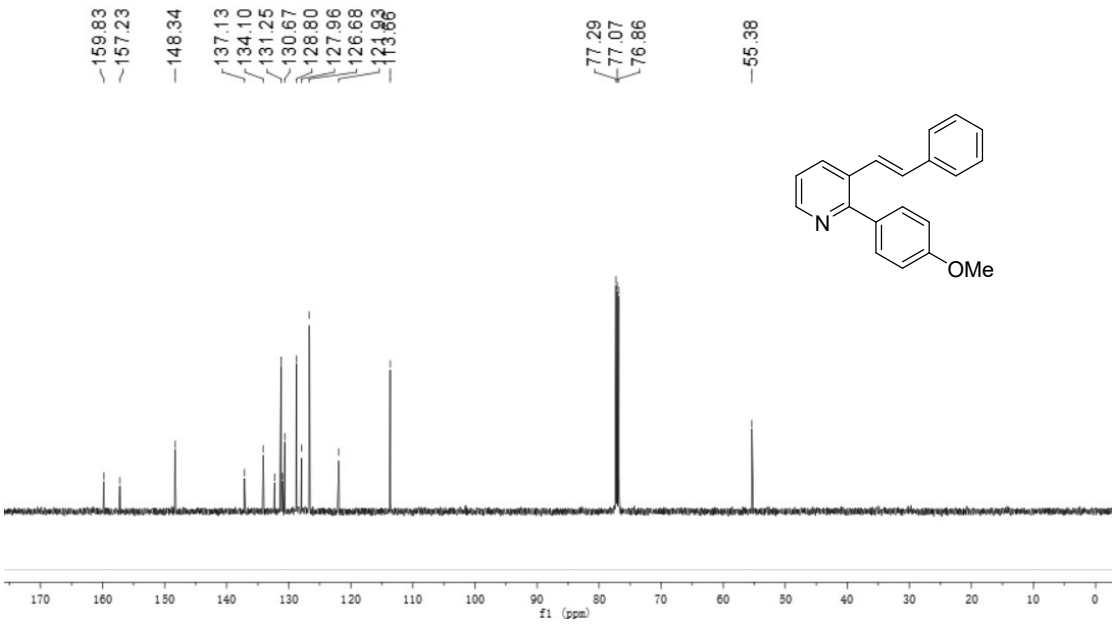

Figure S45. ^{13}C NMR spectrum of **1c** ($CDCl_3$, 600MHz)

(E)-2-(4-fluorophenyl)-3-styrylpyridine (1d)

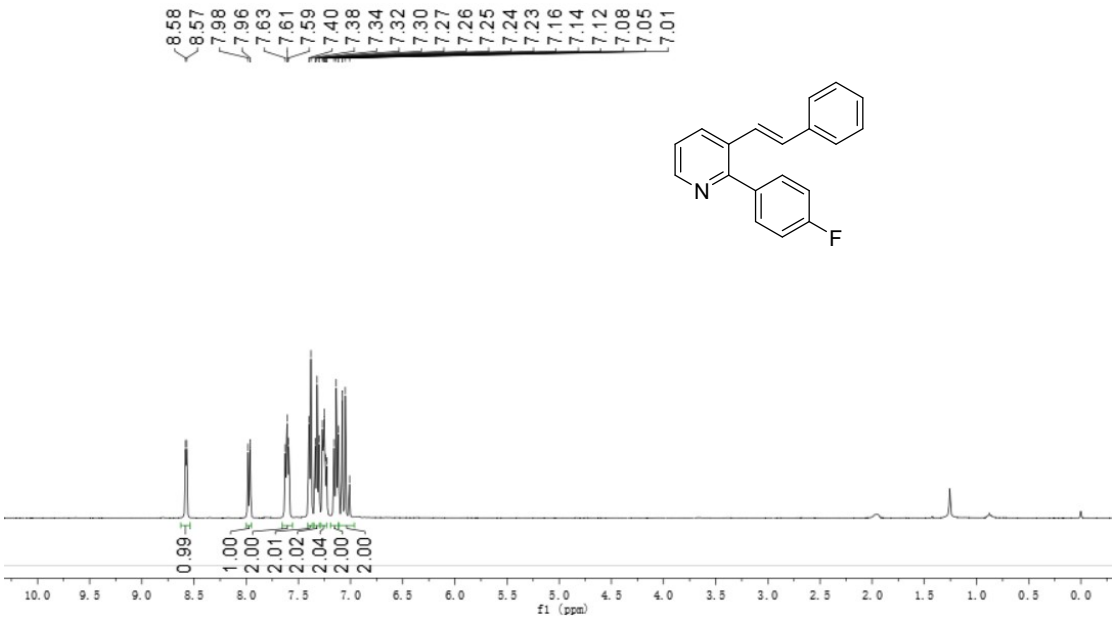

Figure S46. ^{1}H NMR spectrum of **1d** ($CDCl_3$, 400MHz)

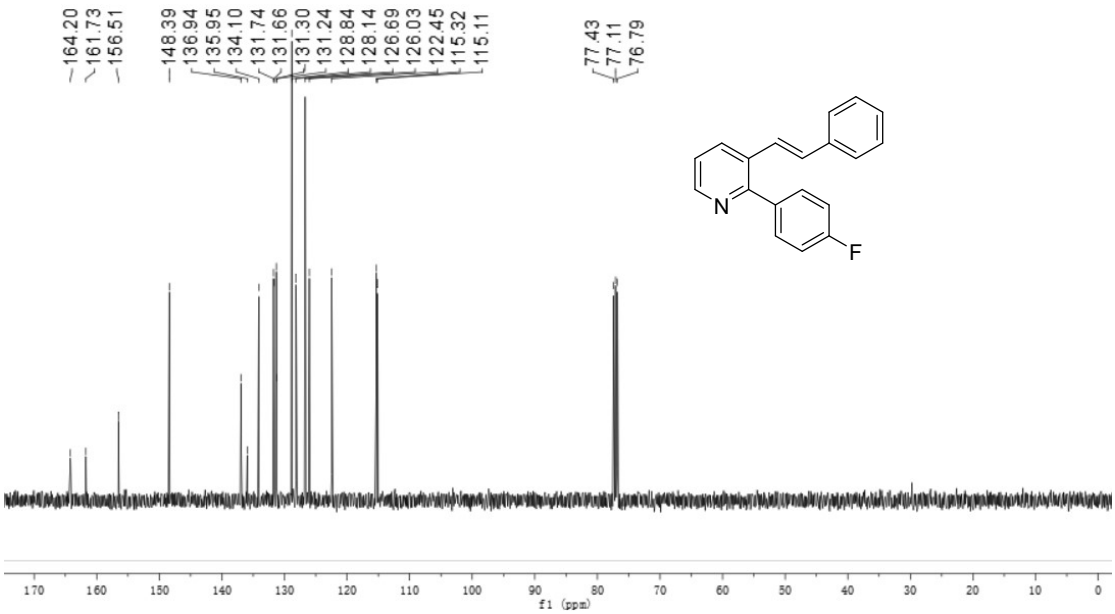

Figure S47. ^{13}C NMR spectrum of **1d** ($CDCl_3$, 400MHz)

(E)-1-(4-(3-styrylpyridin-2-yl)phenyl)ethan-1-one (1e)

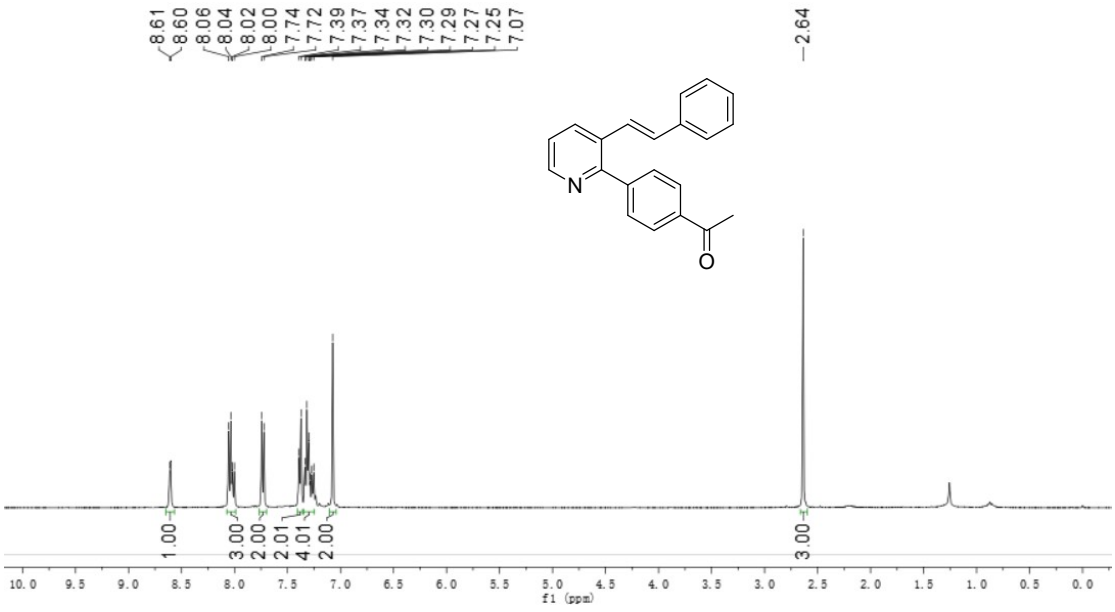

Figure S48. ^{1}H NMR spectrum of **1e** ($CDCl_3$, 400MHz)

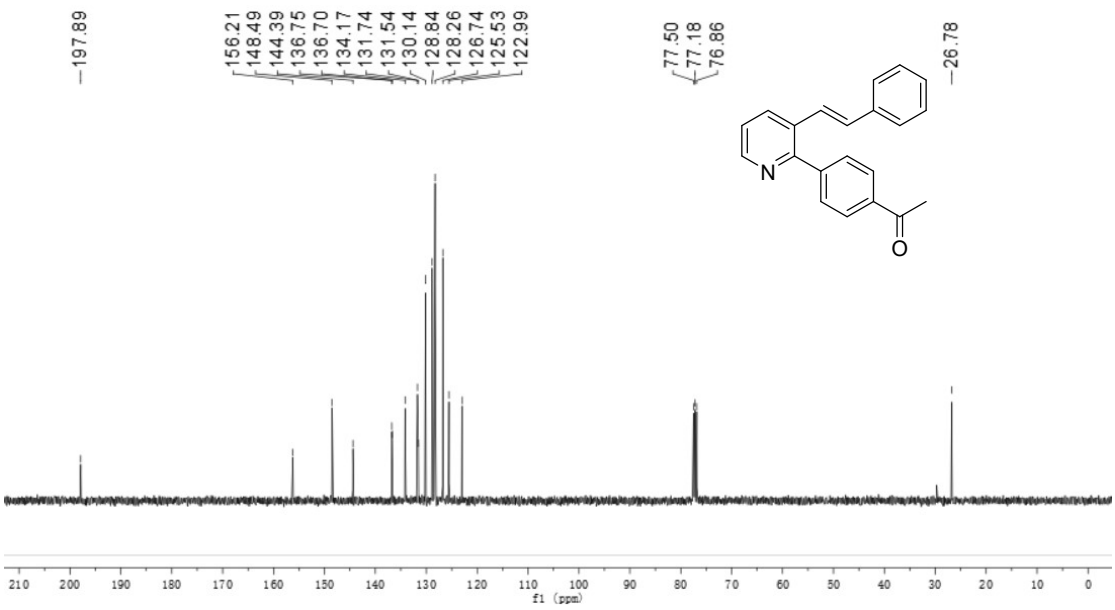

Figure S49. ^{13}C NMR spectrum of **1e** ($CDCl_3$, 400MHz)

(E)-3-styryl-2-(4-(trifluoromethyl)phenyl)pyridine (1f)

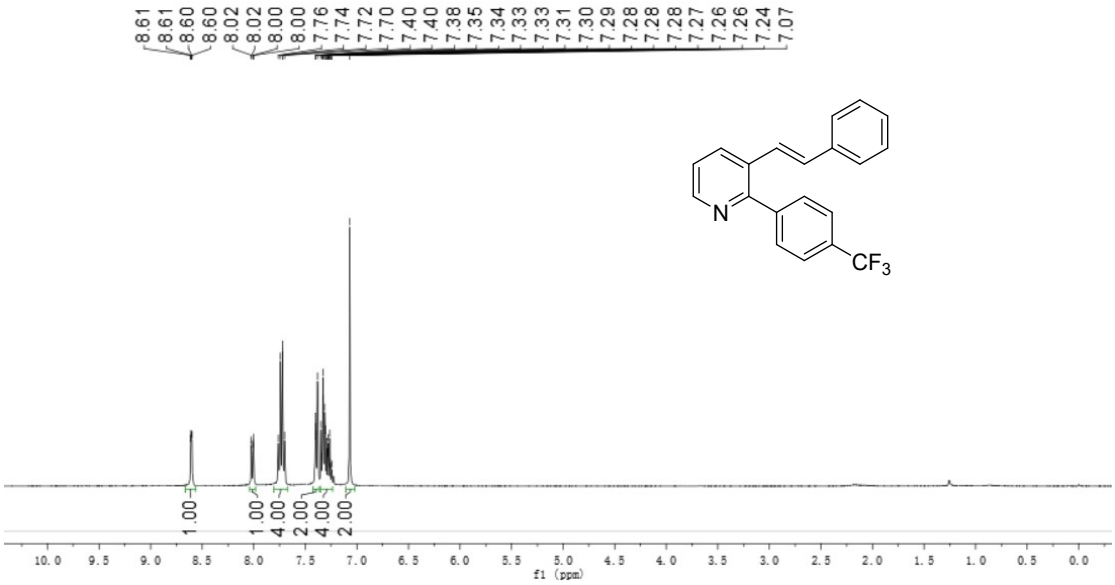

Figure S50. ^{1}H NMR spectrum of **1f** ($CDCl_3$, 400MHz)

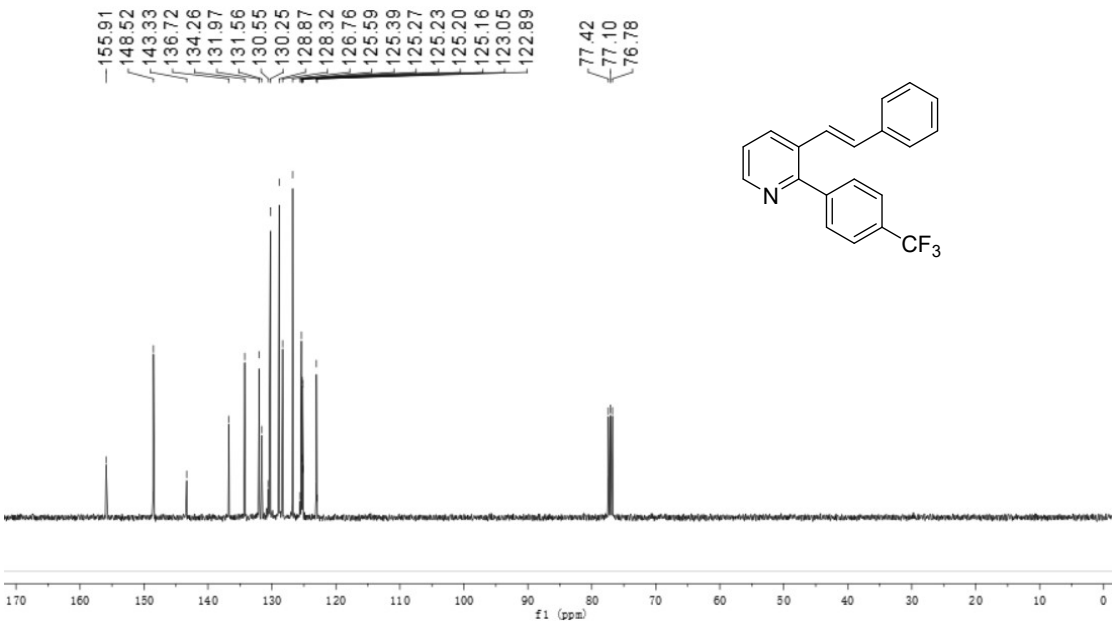

Figure S51. ^{13}C NMR spectrum of **1f** ($CDCl_3$, 400MHz)

(E)-1-(4-(5-methyl-3-styrylpyridin-2-yl)phenyl)ethan-1-one(1g)

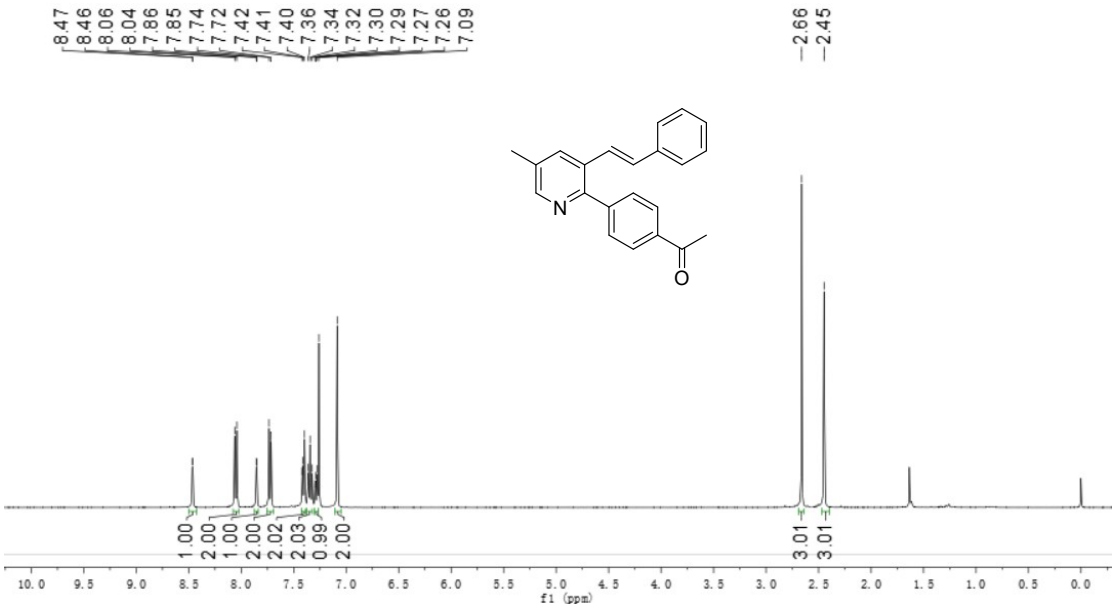

Figure S52. ^{1}H NMR spectrum of **1g** ($CDCl_3$, 400MHz)

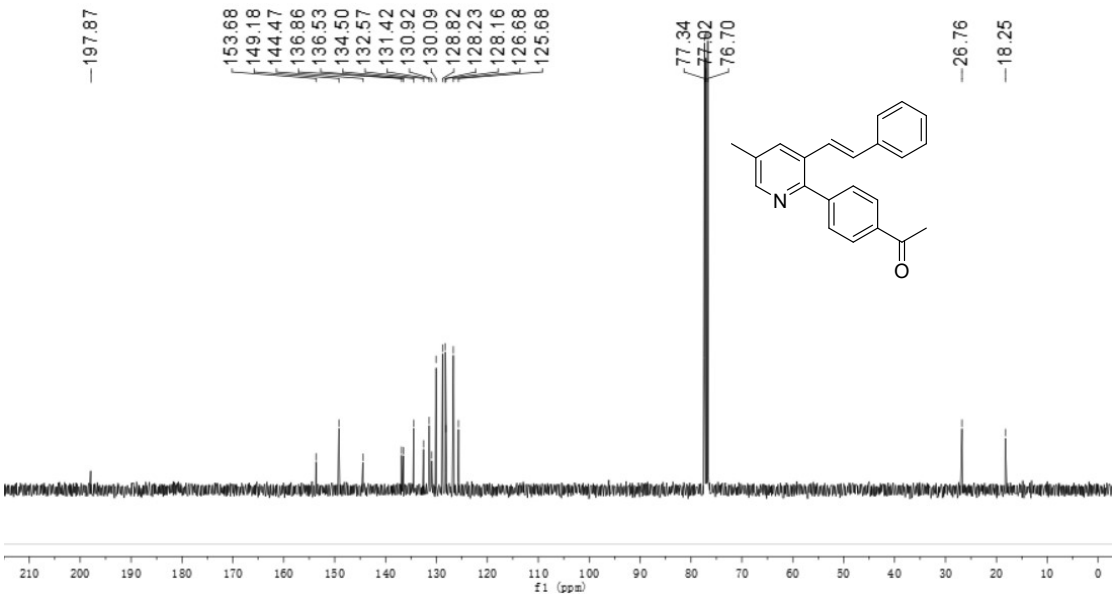

Figure S53. ^{13}C NMR spectrum of **1g** ($CDCl_3$, 400MHz)

(E)-5-methyl-3-styryl-2-(p-tolyl)pyridine (1h)

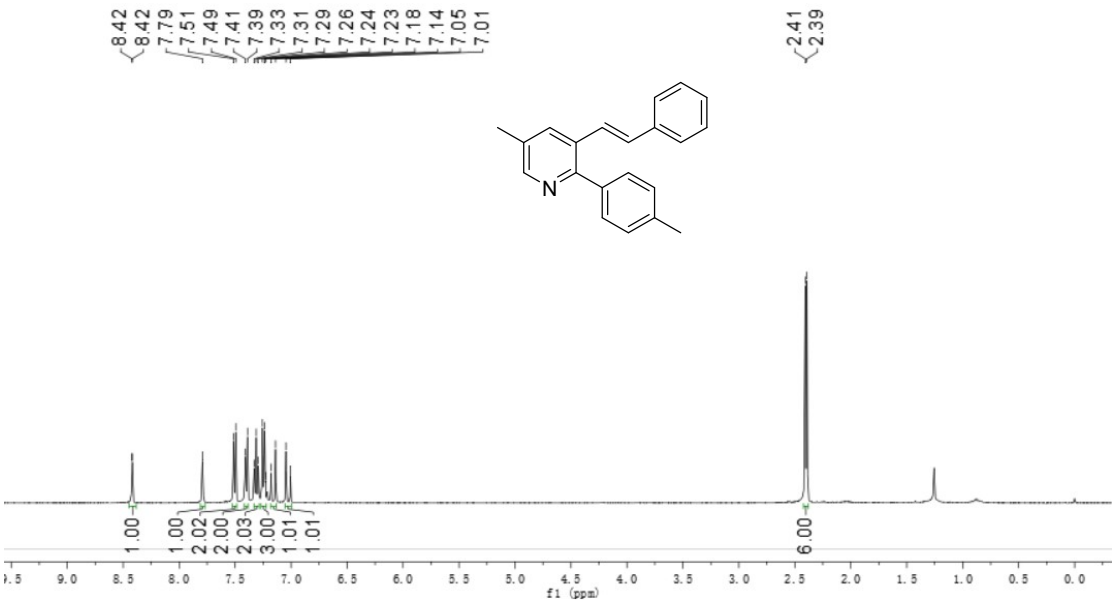

Figure S54. ^{1}H NMR spectrum of **1h** ($CDCl_3$, 400MHz)

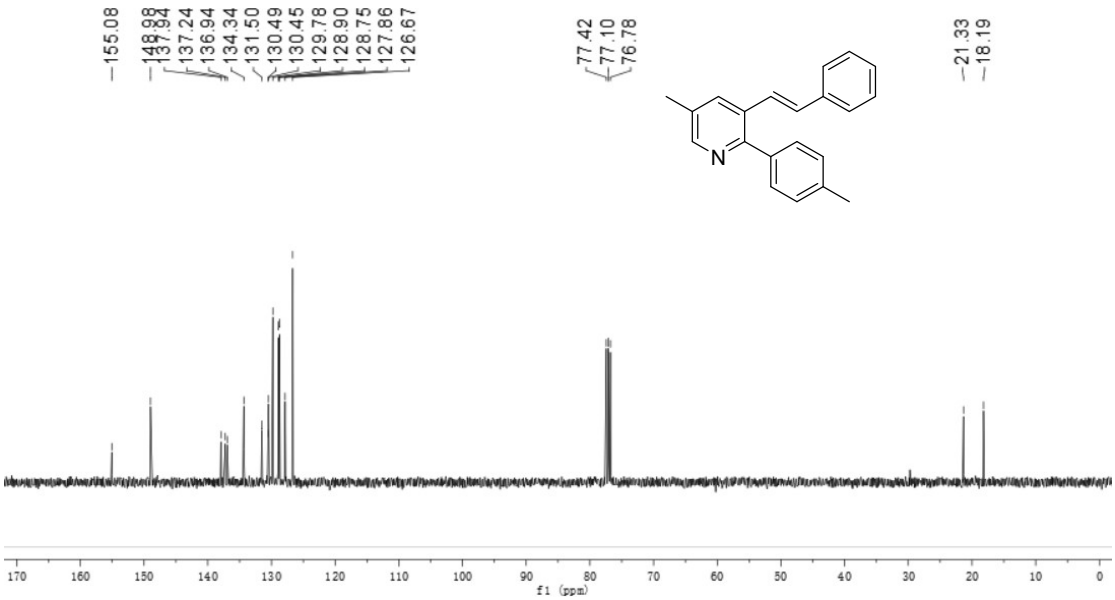

Figure S55. ^{13}C NMR spectrum of **1h** ($CDCl_3$, 400MHz)

(E)-5-fluoro-2-phenyl-3-styrylpyridine (1i)

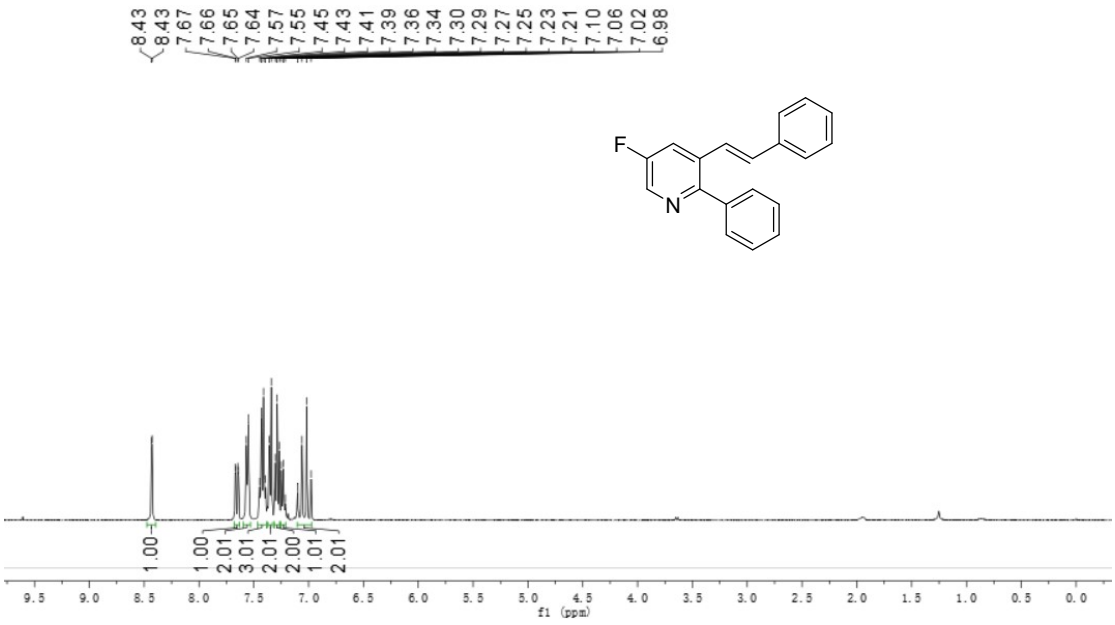

Figure S56. ^{1}H NMR spectrum of **1i** ($CDCl_3$, 400MHz)

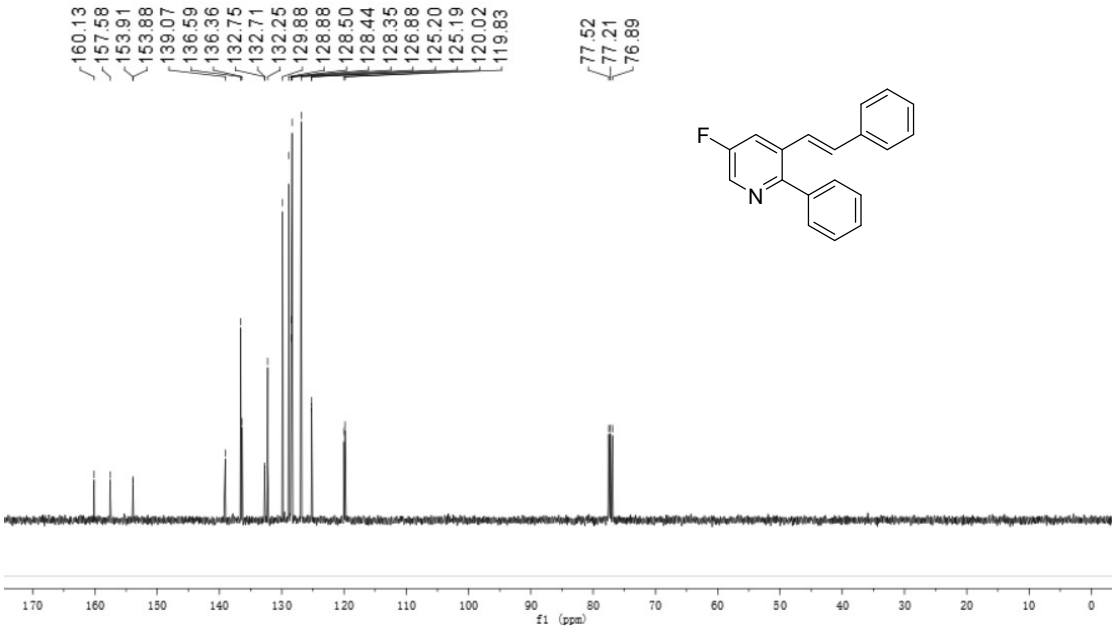

Figure S57. ^{13}C NMR spectrum of **1i** ($CDCl_3$, 400MHz)

(E)-5-methyl-2-phenyl-3-styrylpyridine (1j)

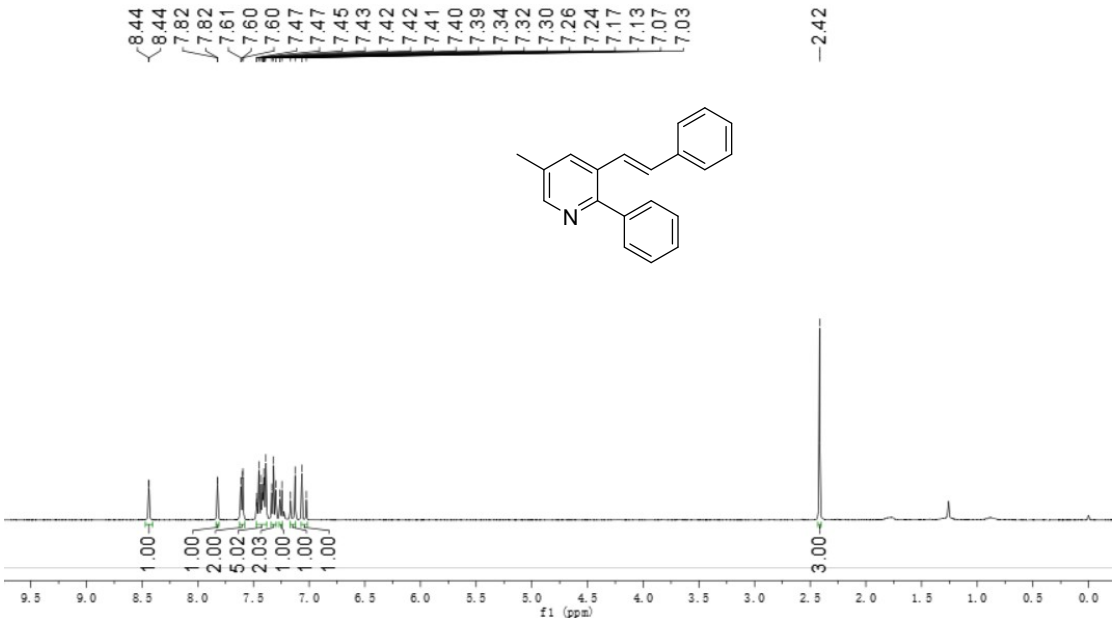

Figure S58. ^{1}H NMR spectrum of **1j** ($CDCl_3$, 400MHz)

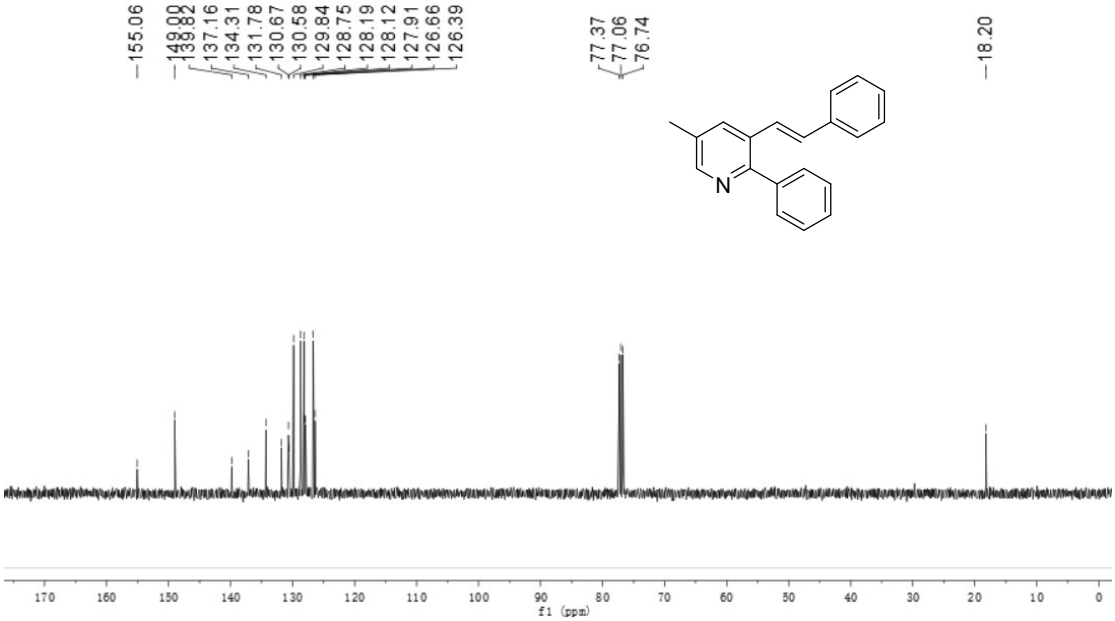

Figure S59. ^{13}C NMR spectrum of **1j** ($CDCl_3$, 400MHz)

(E)-3-styryl-2-(m-tolyl)pyridine (1k)

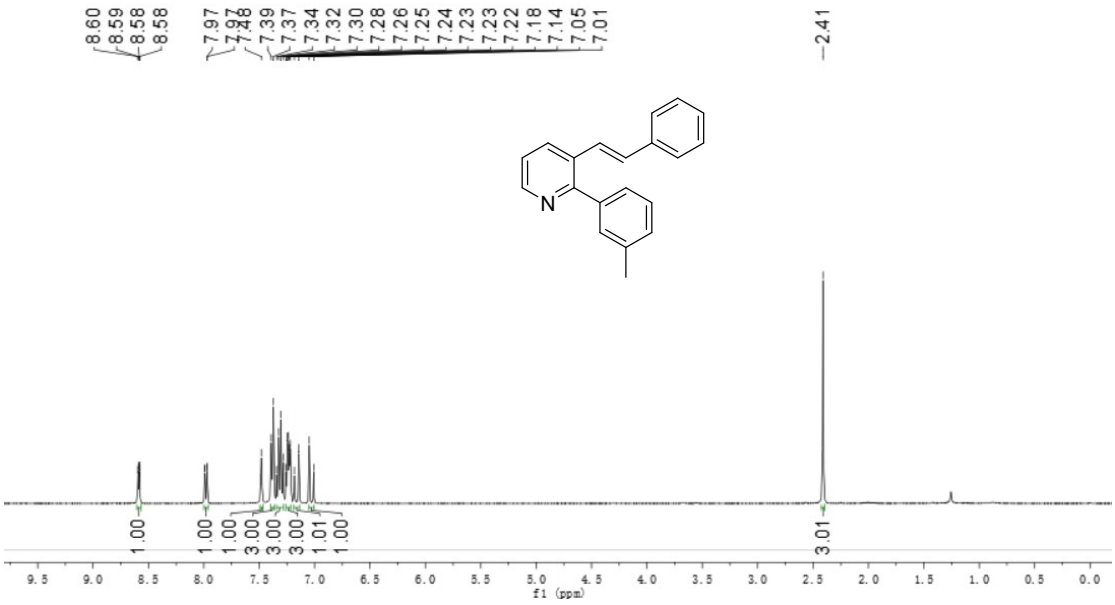

Figure S60. ^{1}H NMR spectrum of **1k** ($CDCl_3$, 400MHz)

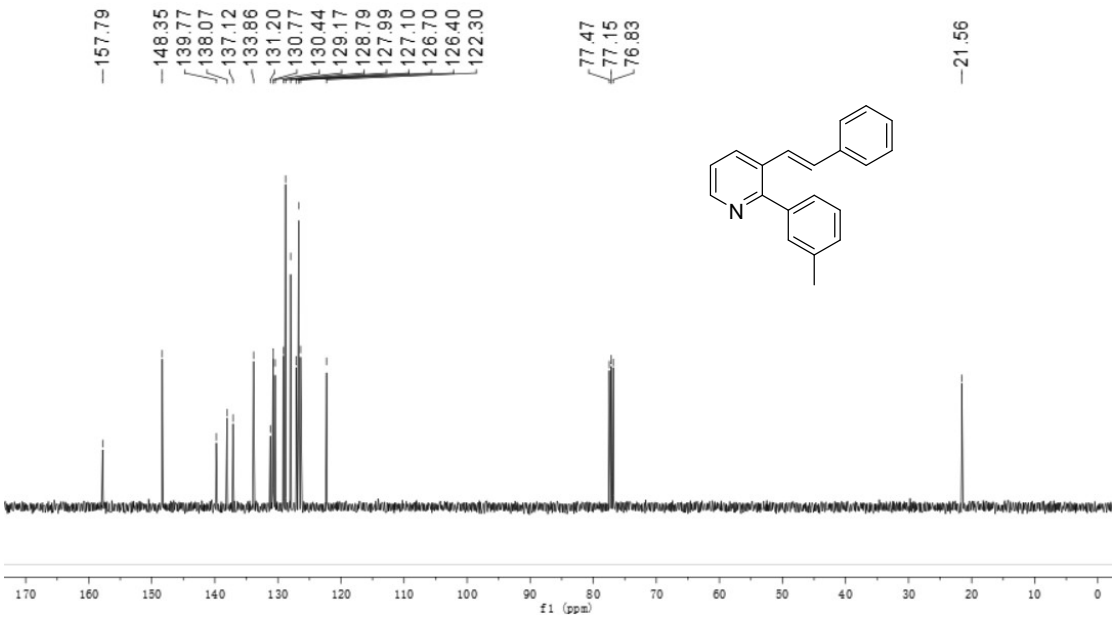

Figure S61. ^{13}C NMR spectrum of **1k** ($CDCl_3$, 400MHz)

(E)-5-methyl-3-styryl-2-(4-(trifluoromethyl)phenyl)pyridine(1l)

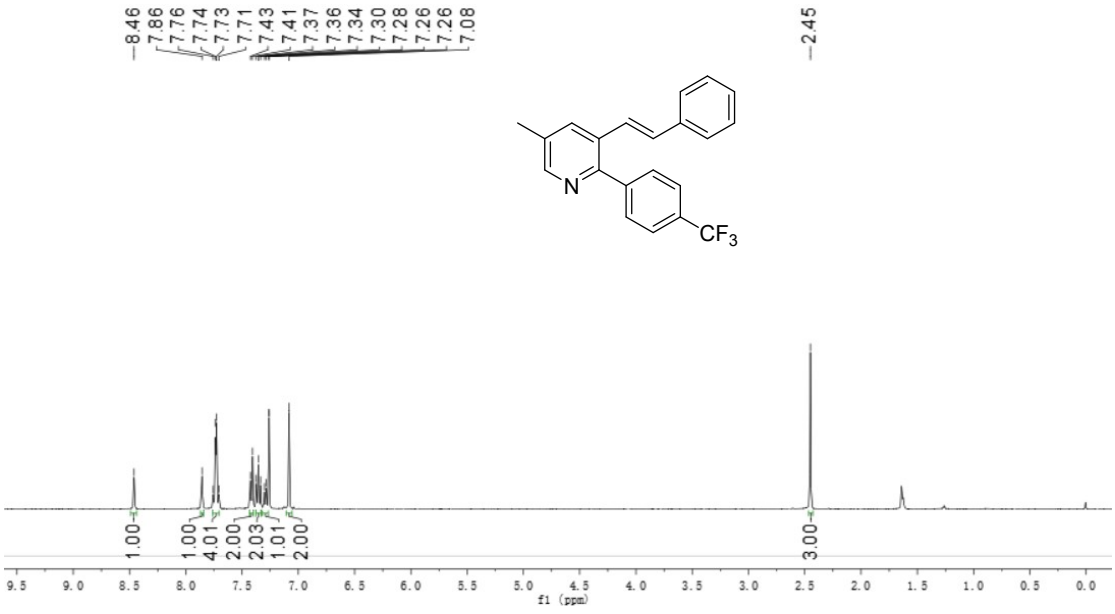

Figure S62. ^{1}H NMR spectrum of **1l** ($CDCl_3$, 400MHz)

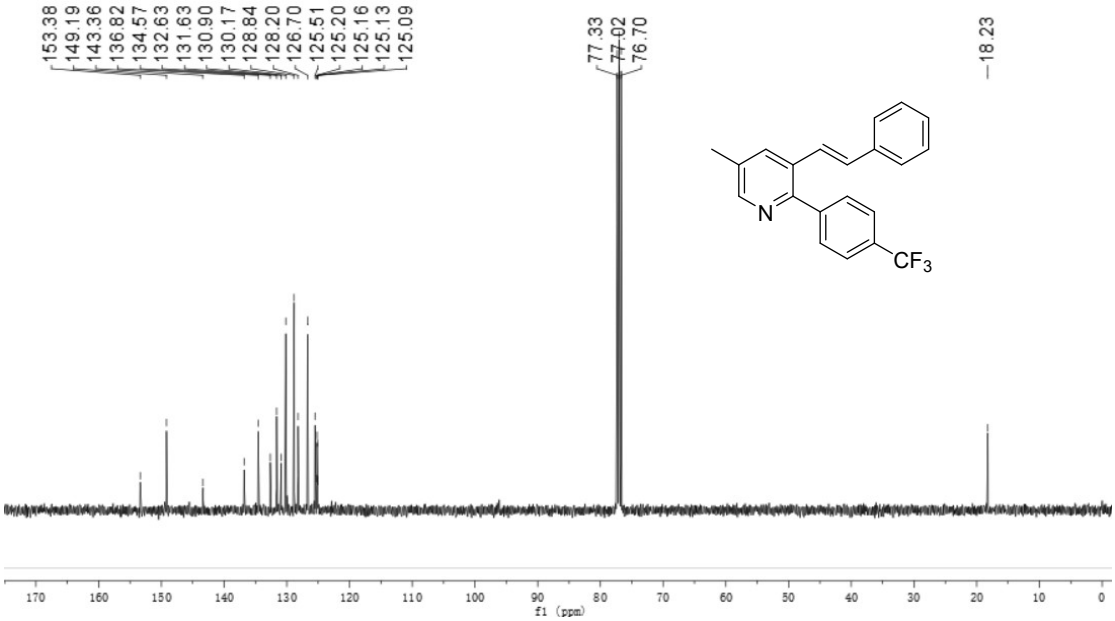

Figure S63. ^{13}C NMR spectrum of **1l** ($CDCl_3$, 400MHz)

(E)-2-(naphthalen-1-yl)-3-styrylpyridine (1m)

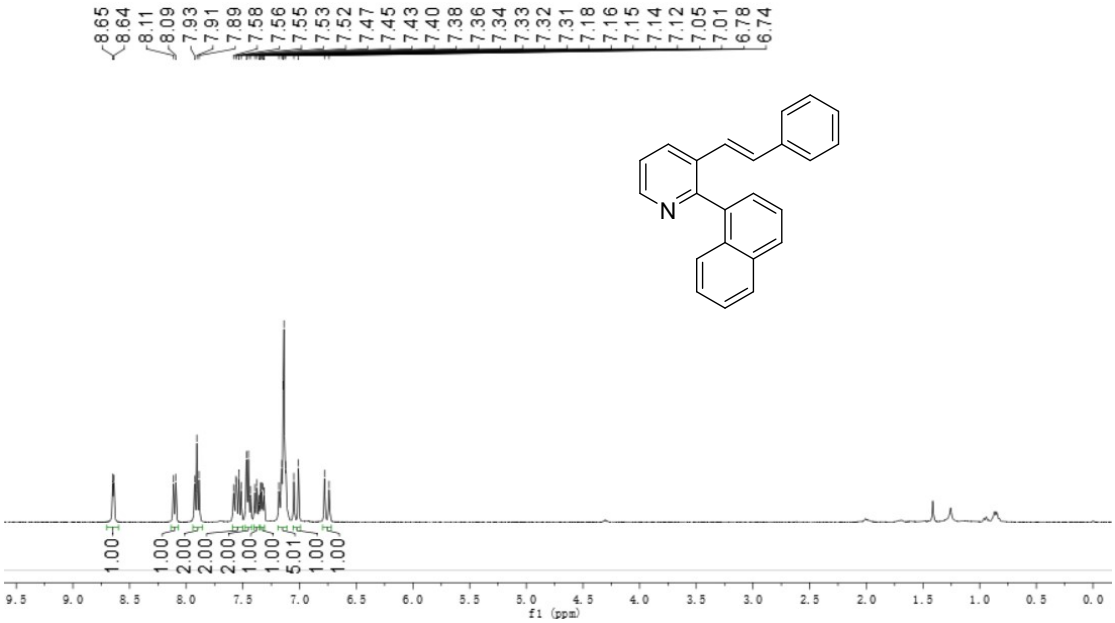

Figure S64. ^{1}H NMR spectrum of **1m** ($CDCl_3$, 400MHz)

(E)-3-(4-methylstyryl)-2-phenylpyridine (1n)

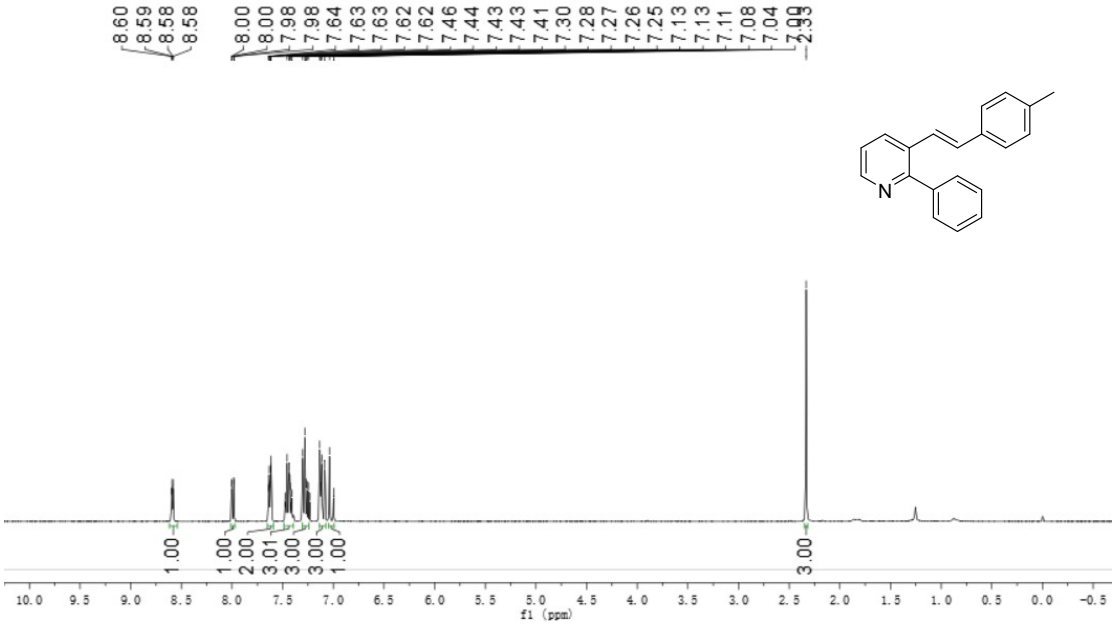

Figure S65. ^{1}H NMR spectrum of **1n** ($CDCl_3$, 400MHz)

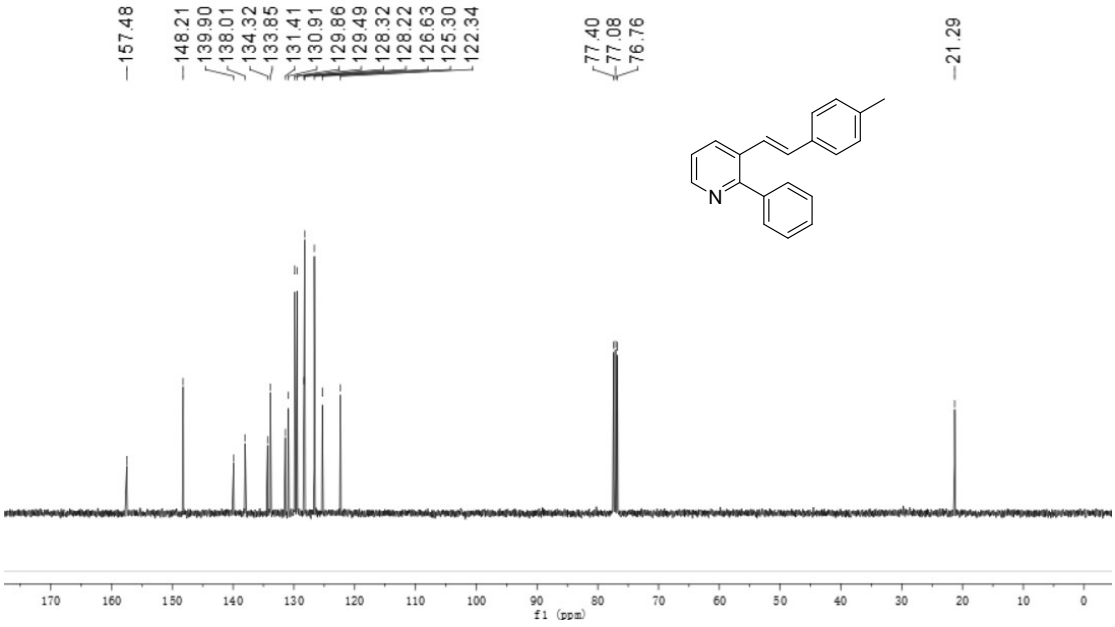

Figure S66. ^{13}C NMR spectrum of **1n** ($CDCl_3$, 400MHz)

(E)-3-(4-fluorostyryl)-2-phenylpyridine (1o)

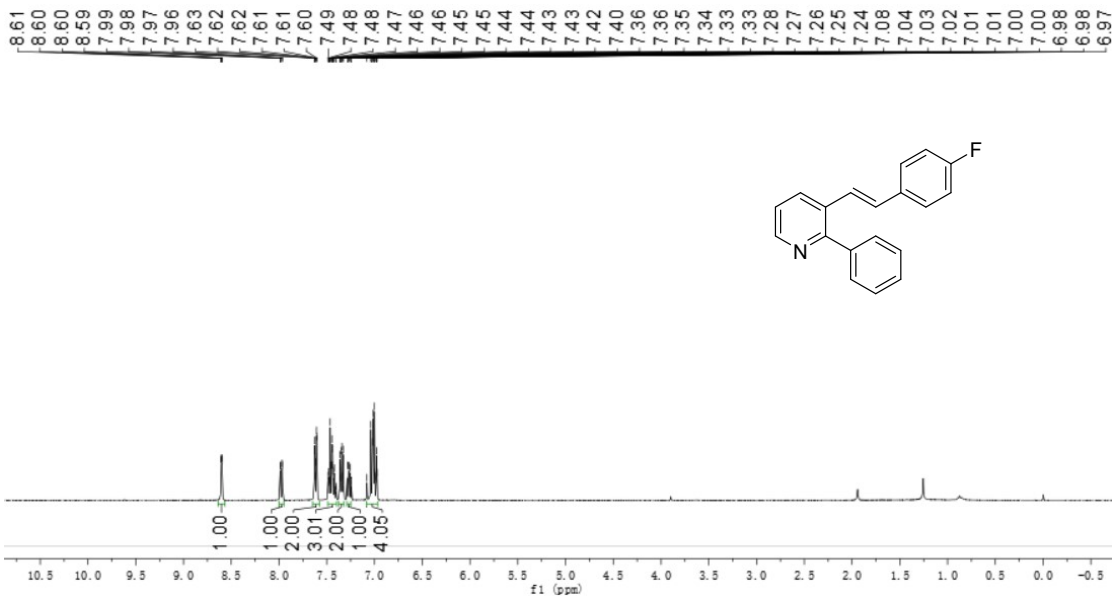

Figure S67. ^{1}H NMR spectrum of **1o** ($CDCl_3$, 400MHz)

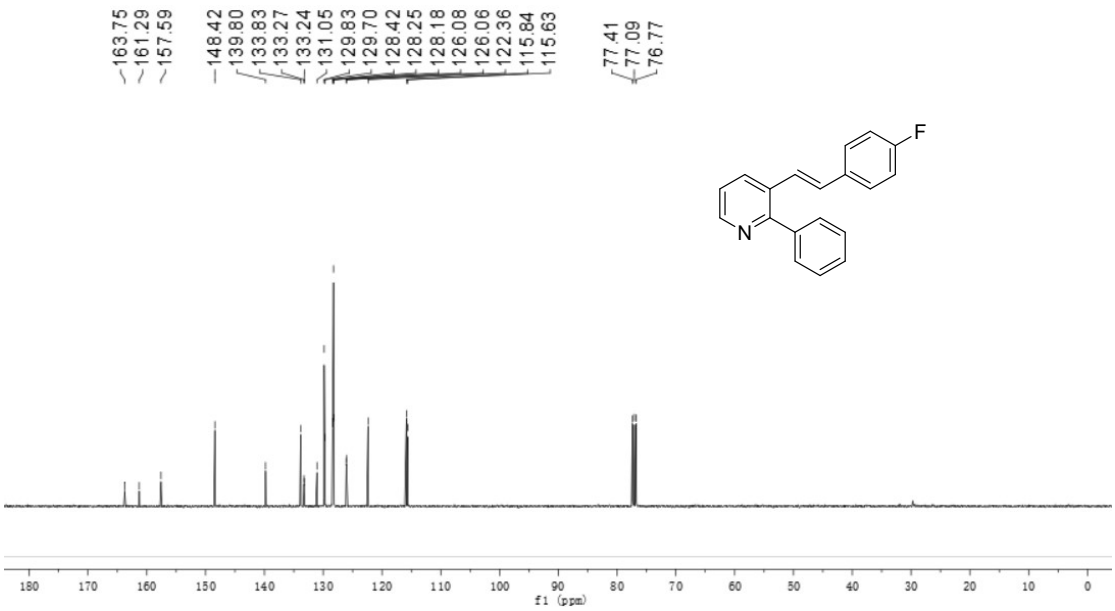

Figure S68. ^{13}C NMR spectrum of **1o** ($CDCl_3$, 400MHz)

(E)-5-fluoro-3-styryl-2-(p-tolyl)pyridine (1P)

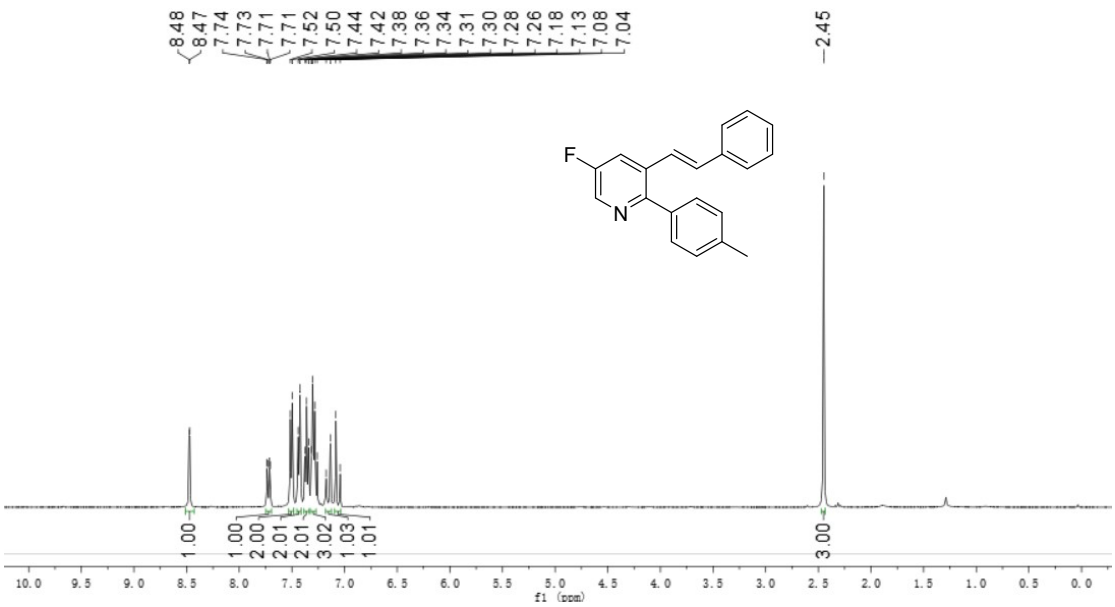

Figure S69. ^{1}H NMR spectrum of **1p** ($CDCl_3$, 400MHz)

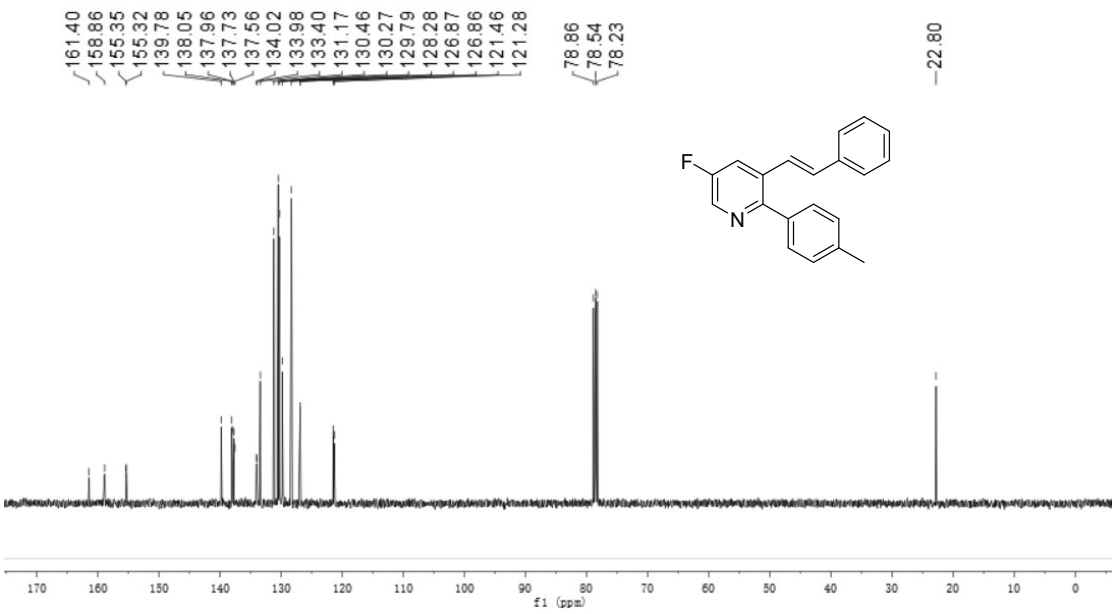

Figure S70. ^{13}C NMR spectrum of **1p** ($CDCl_3$, 400MHz)

(E)-2-(4-fluorophenyl)-5-methyl-3-styrylpyridine (1q)

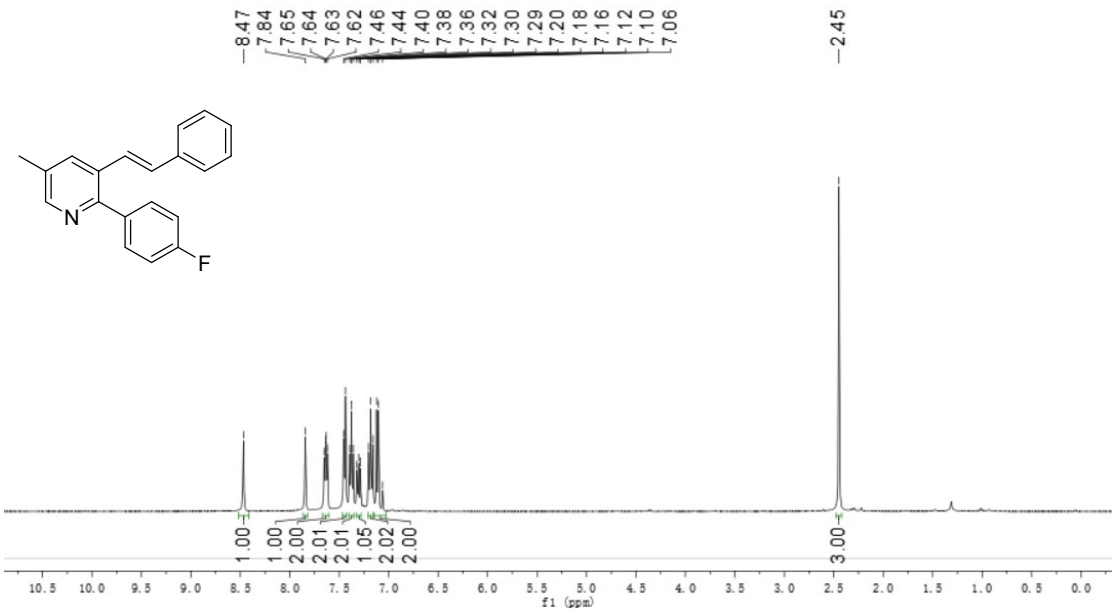

Figure S71. ^{1}H NMR spectrum of **1q** ($CDCl_3$, 400MHz)

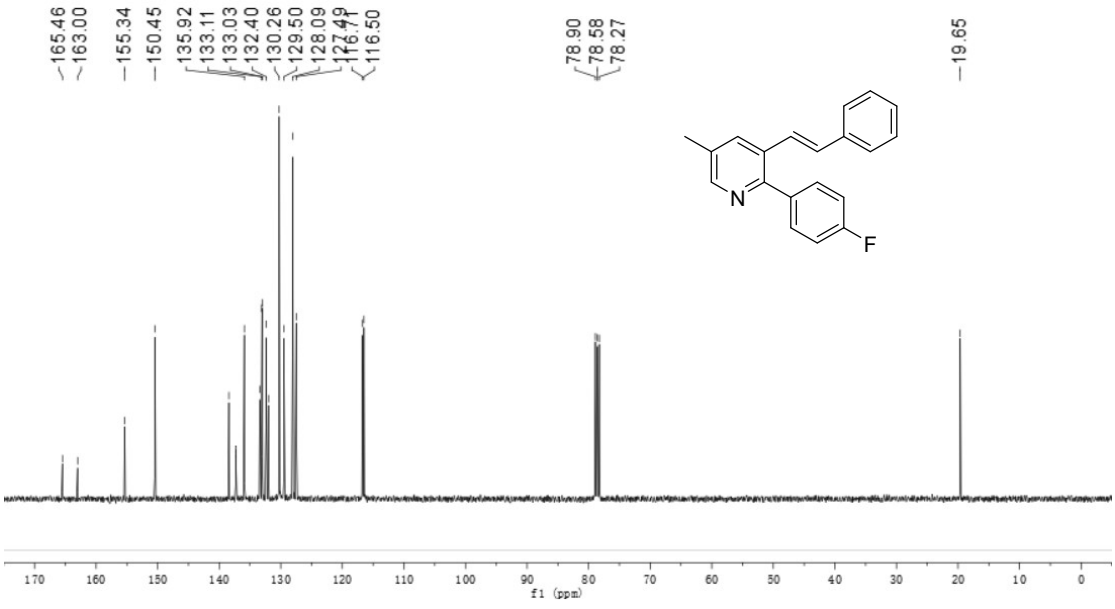

Figure S72. ^{13}C NMR spectrum of **1q** ($CDCl_3$, 400MHz)

(E)-2-phenyl-3-styrylquinoline (1r)

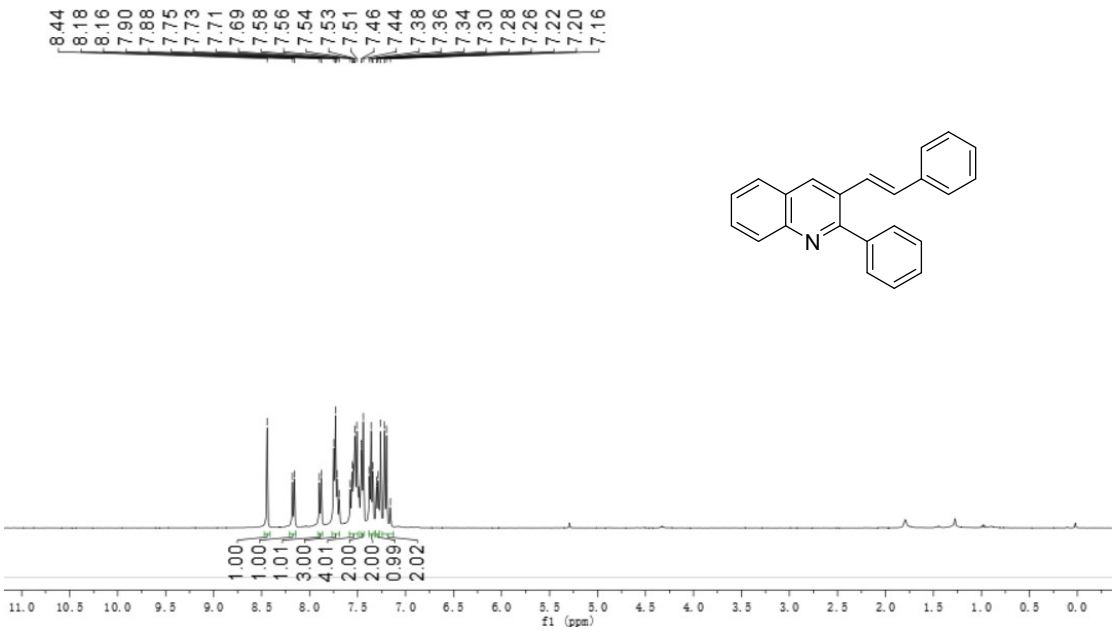

Figure S73. ^{1}H NMR spectrum of **1r** ($CDCl_3$, 400MHz)

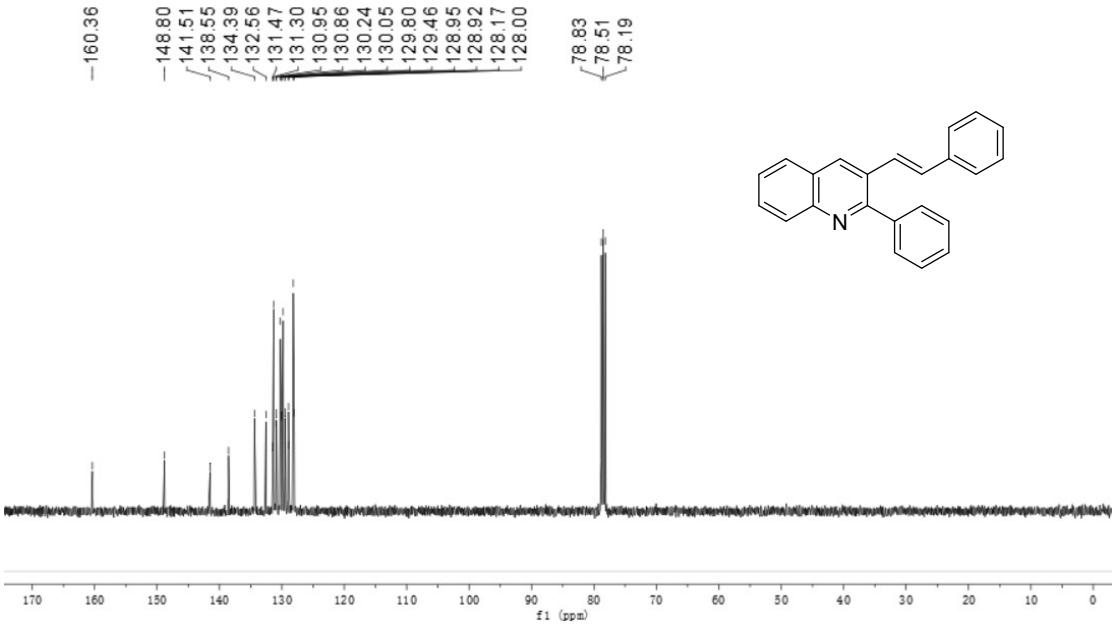

Figure S74. ^{13}C NMR spectrum of **1r** ($CDCl_3$, 400MHz)

(E)-2-(4-methoxyphenyl)-3-styrylquinoline (1s)

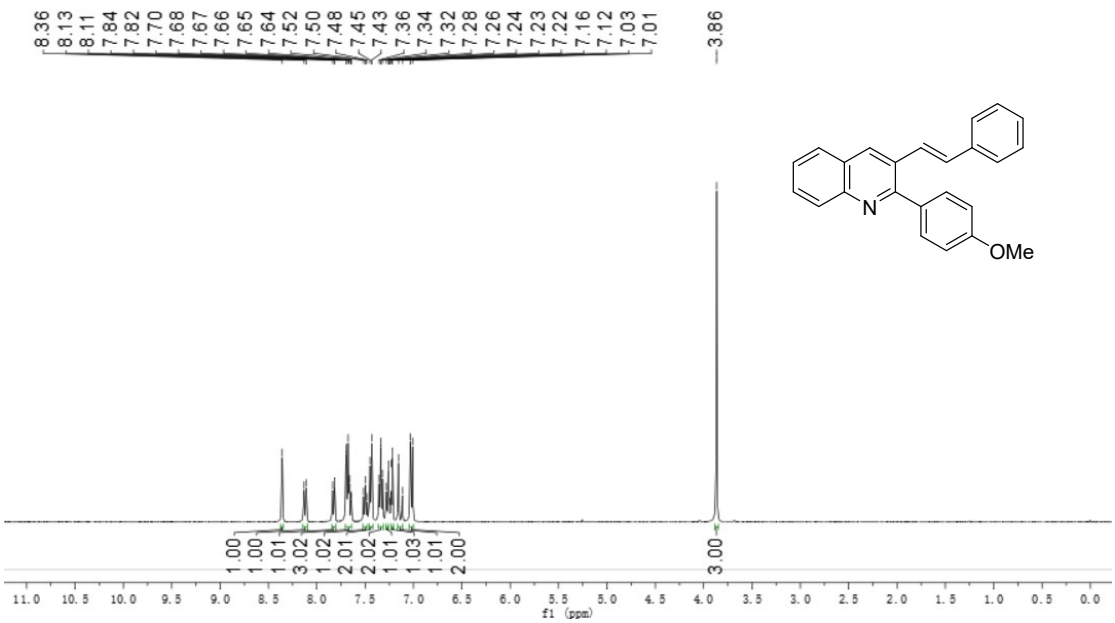

Figure S75. ^{1}H NMR spectrum of **1s** ($CDCl_3$, 400MHz)

(E)-2-(2,4-dimethylphenyl)-5-methyl-3-styrylpyridine (1t)

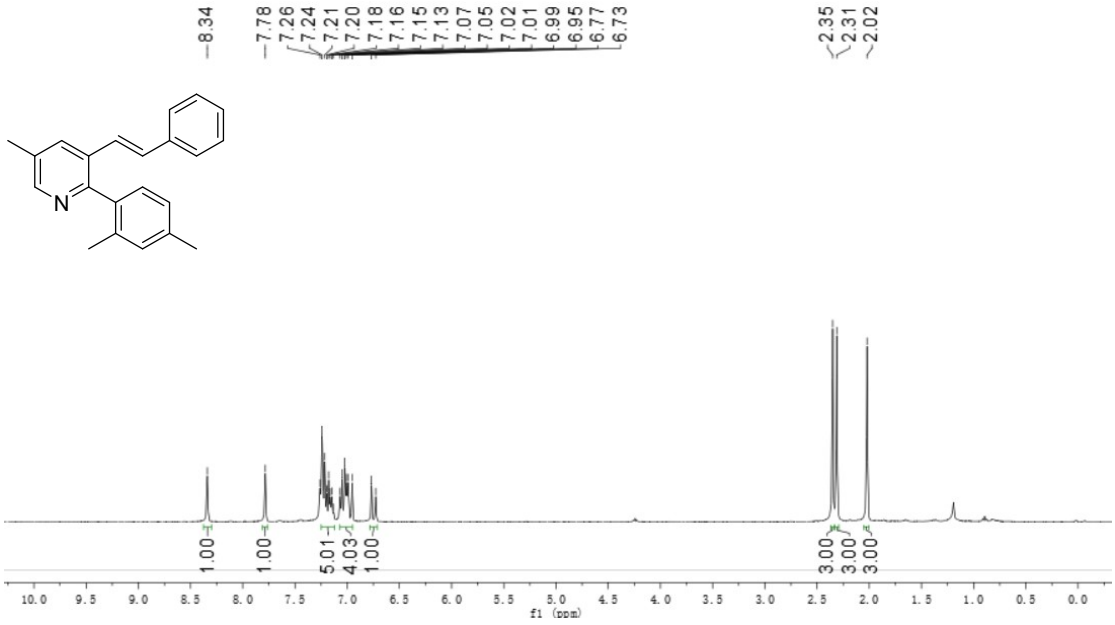

Figure S76. ^{1}H NMR spectrum of **1t** ($CDCl_3$, 400MHz)

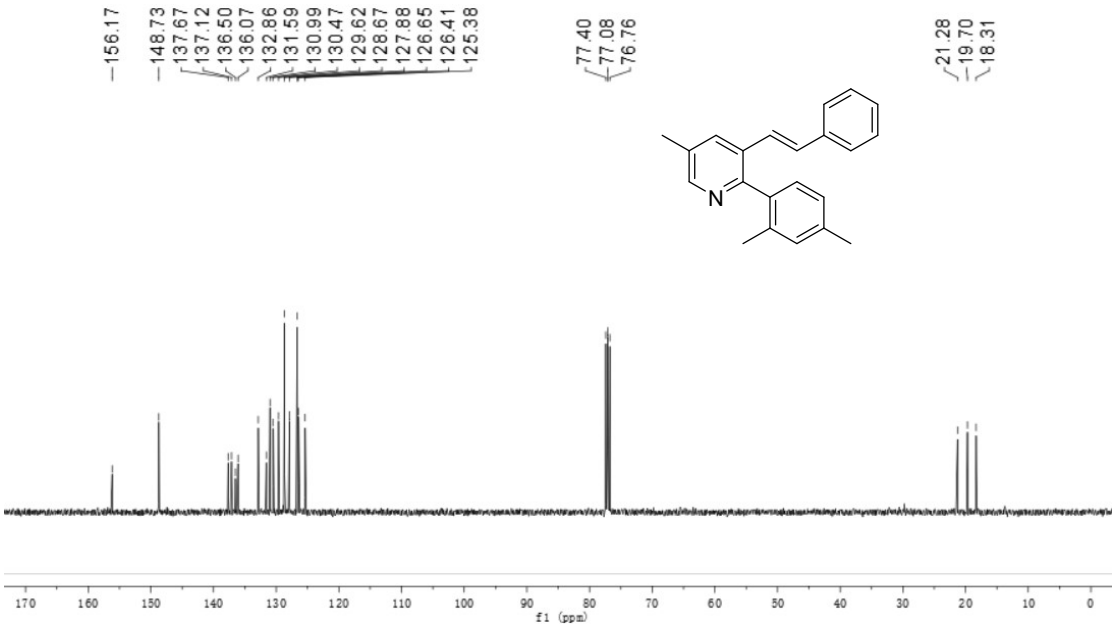

Figure S77. ^{13}C NMR spectrum of **1t** ($CDCl_3$, 400MHz)

(E)-2-(3-methoxyphenyl)-3-styrylpyridine (1u)

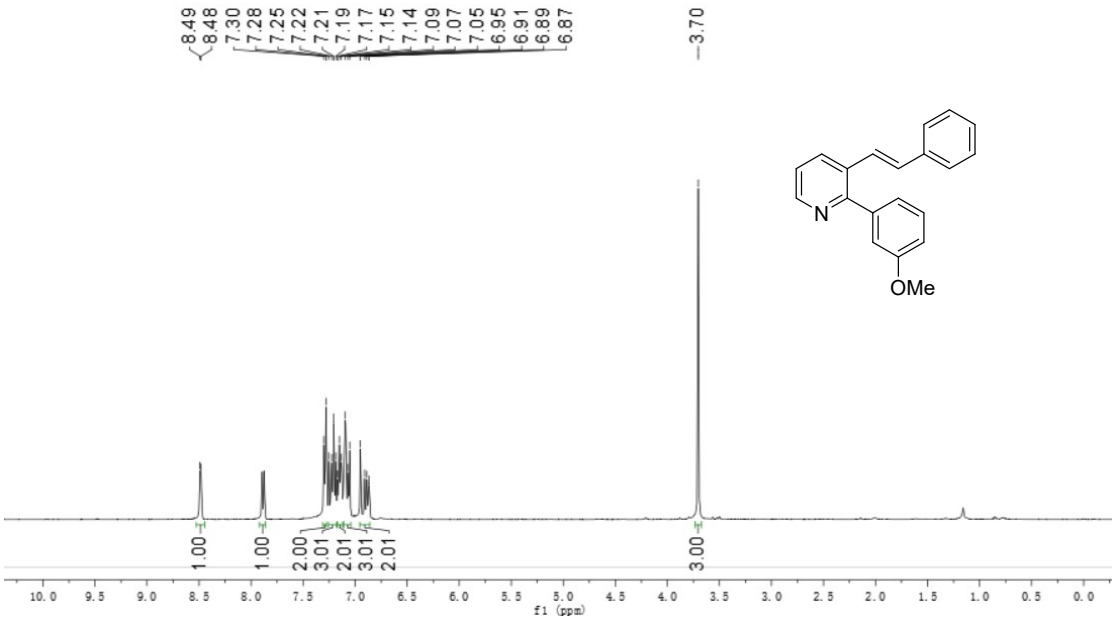

Figure S78. ^{1}H NMR spectrum of **1u** ($CDCl_3$, 400MHz)

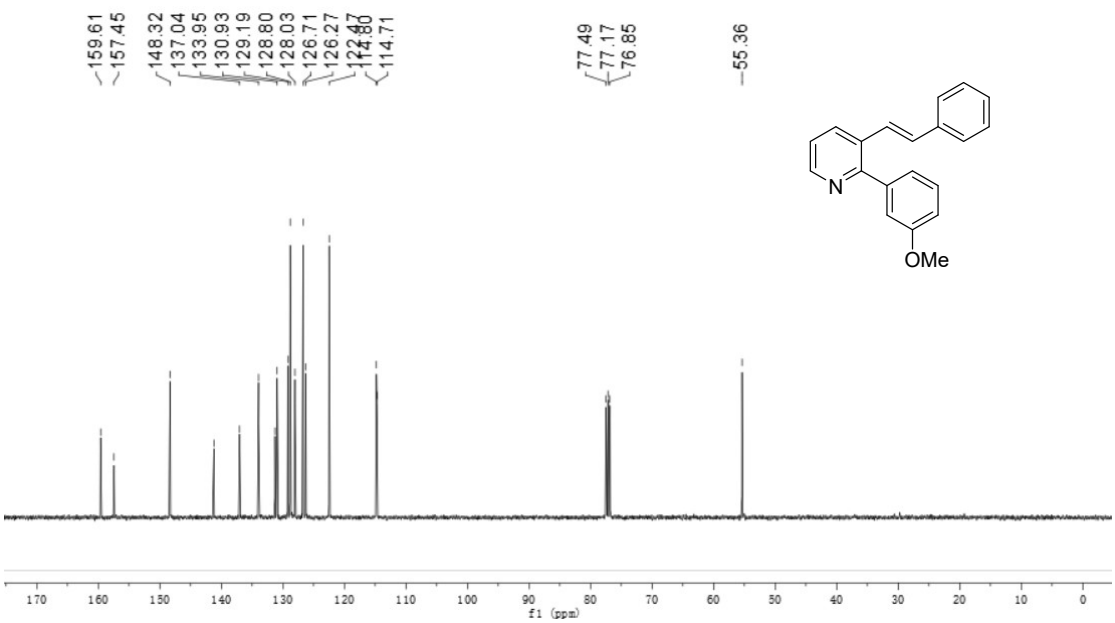

Figure S79. ^{13}C NMR spectrum of **1u** ($CDCl_3$, 400MHz)

(E)-2-(2,4-dimethylphenyl)-3-styrylpyridine (1v)

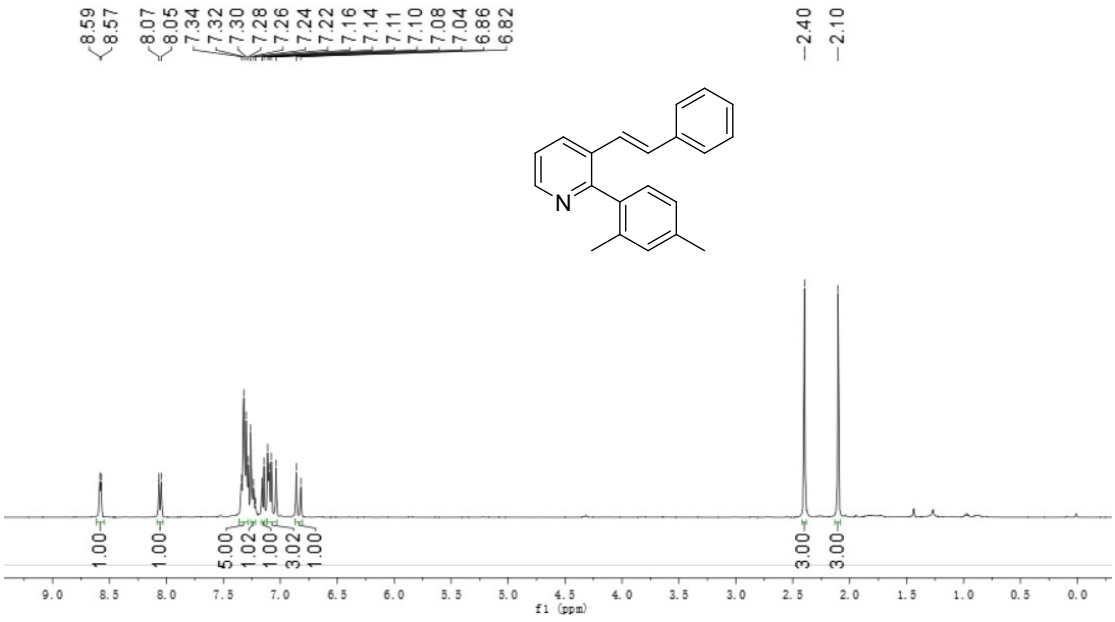

Figure S80. ^{1}H NMR spectrum of **1v** ($CDCl_3$, 400MHz)

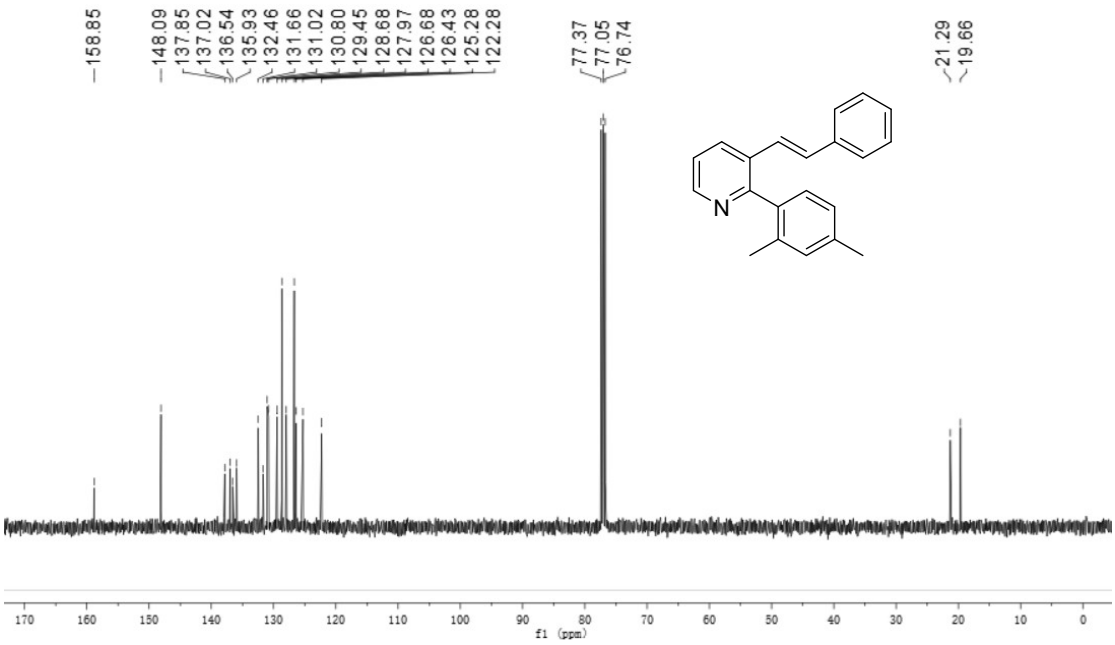

Figure S81. ^{13}C NMR spectrum of **1v** ($CDCl_3$, 400MHz)

(E)-2-(2,4-dimethylphenyl)-5-fluoro-3-styrylpyridine (1w)

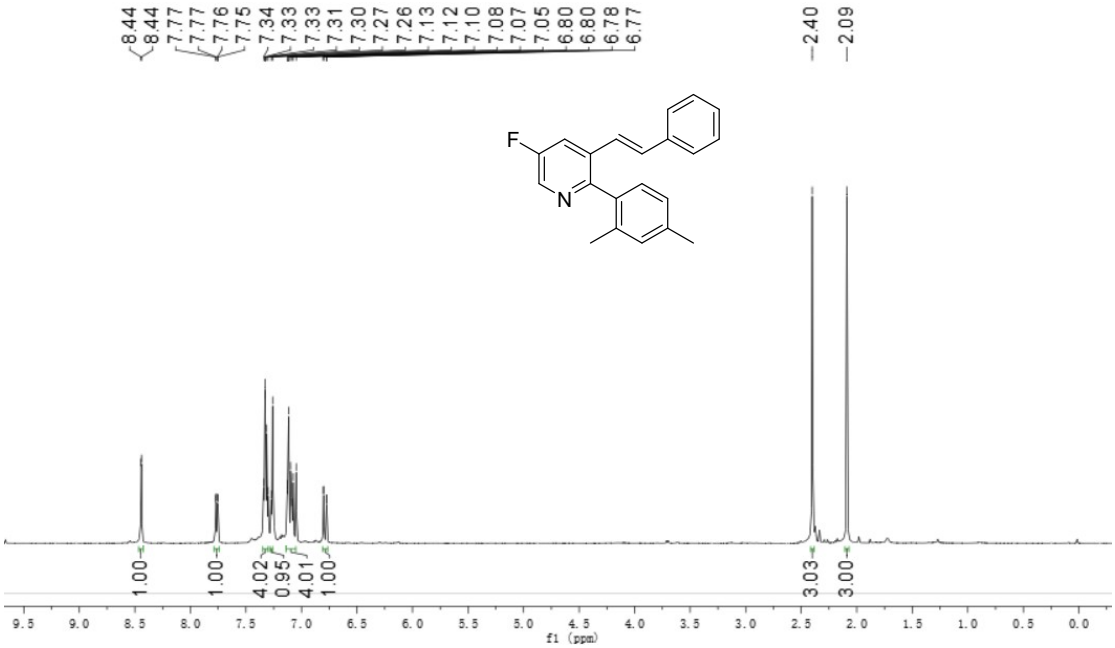

Figure S82. ^{1}H NMR spectrum of **1w** ($CDCl_3$, 600MHz)

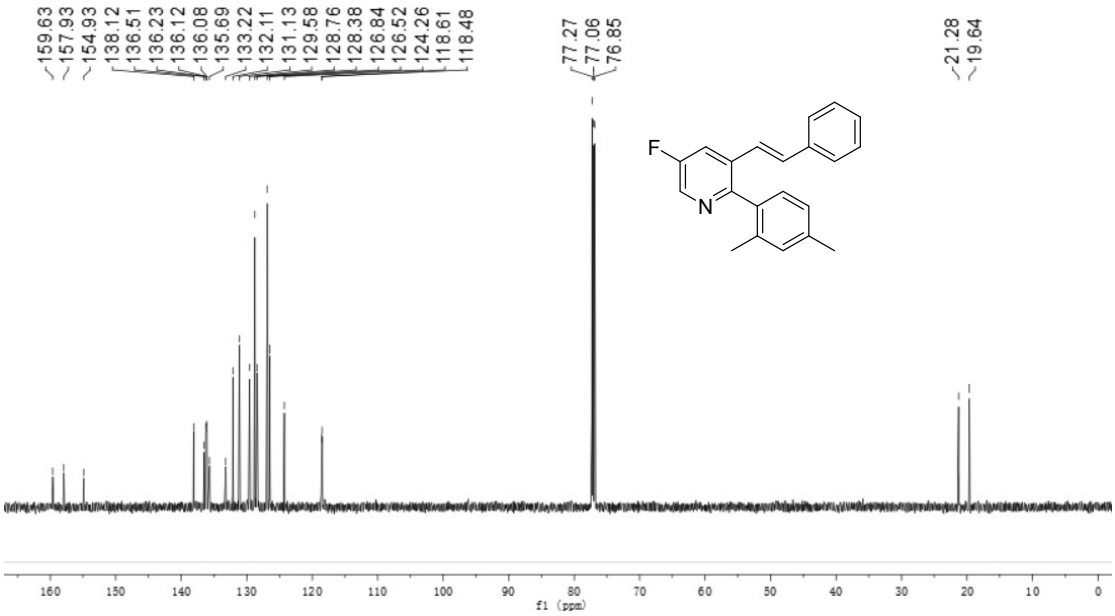

Figure S83. ^{13}C NMR spectrum of **1w** ($CDCl_3$, 600MHz)

(E)-2-(2,3-difluorophenyl)-3-styrylpyridine (1x)

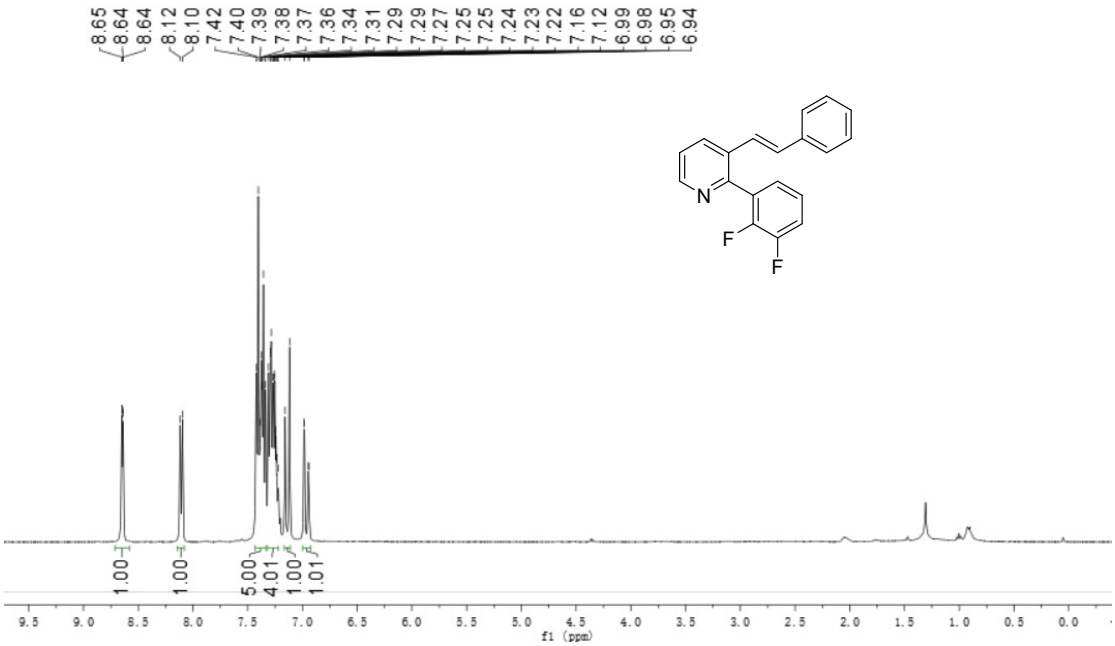

Figure S84. ^{1}H NMR spectrum of **1x** ($CDCl_3$, 400MHz)

(E)-1-(3-styrylpyridin-2-yl)ethan-1-one (1y)

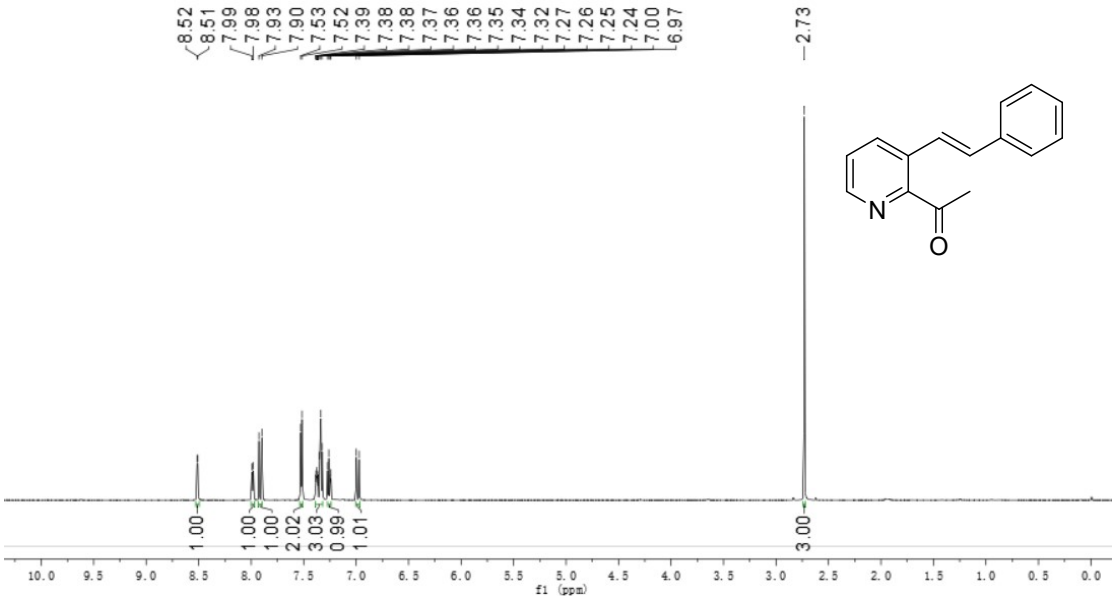

Figure S85. ^{1}H NMR spectrum of **1y** ($CDCl_3$, 600MHz)

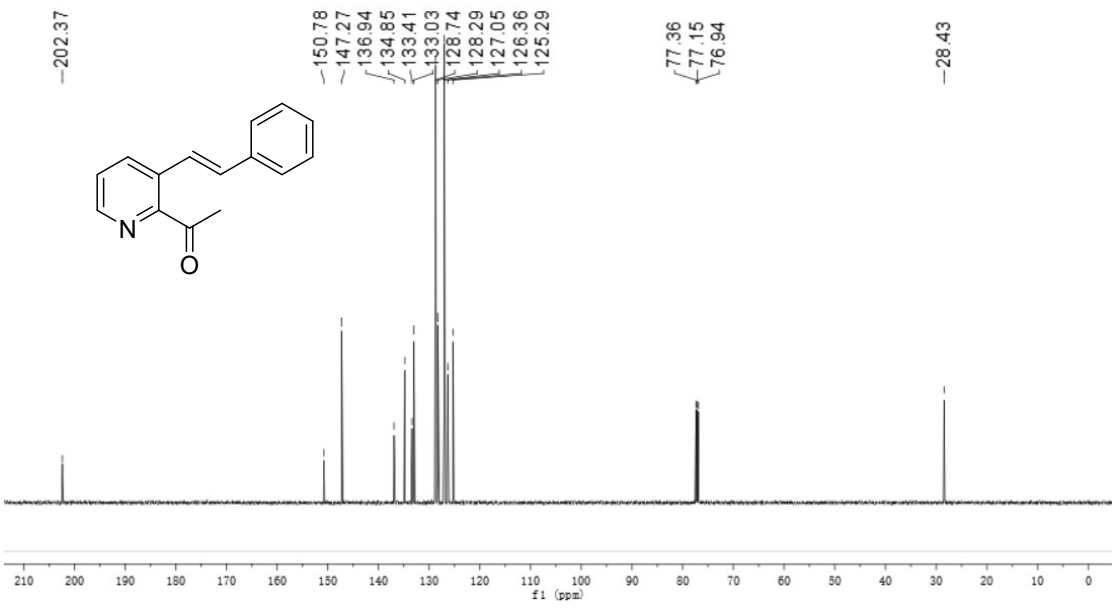

Figure S86. ^{13}C NMR spectrum of **1y** ($CDCl_3$, 600MHz)

(E)-3-styryl-2,2'-bipyridine (1z)

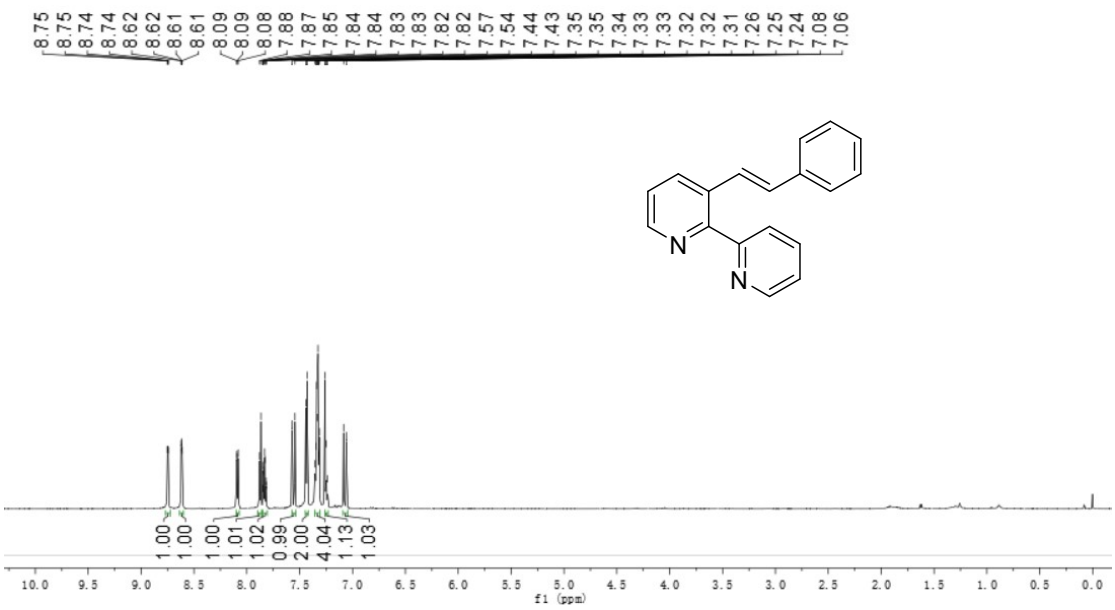

Figure S87. ^{1}H NMR spectrum of **1z** ($CDCl_3$, 600MHz)

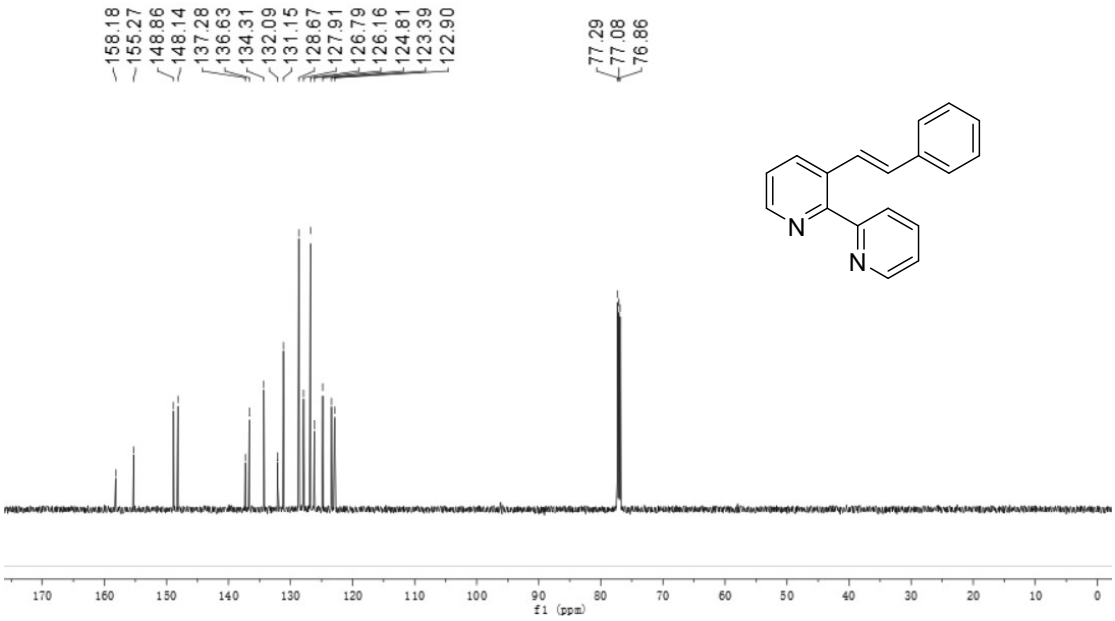

Figure S88. ^{13}C NMR spectrum of **1z** ($CDCl_3$, 600MHz)

Spectra of 2a-2z.

6-phenylbenzo[h]quinoline (2a)

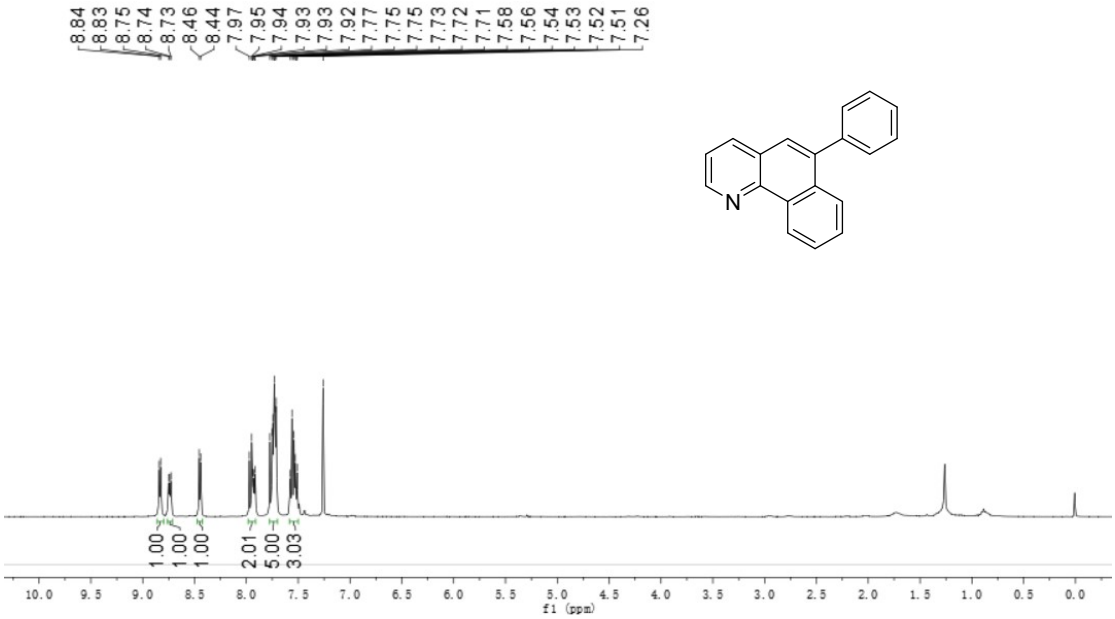

Figure S89. ^{1}H NMR spectrum of **2a** ($CDCl_3$, 400MHz)

8-methyl-6-(p-tolyl)benzo[h]quinoline (2b)

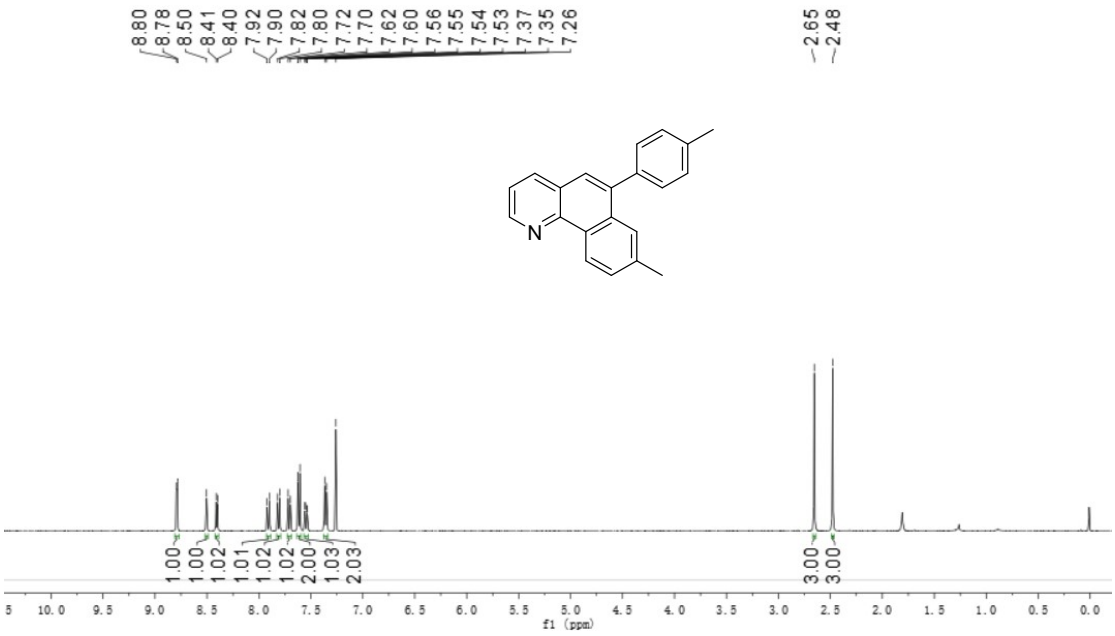

Figure S90. ^{1}H NMR spectrum of **2b** ($CDCl_3$, 400MHz)

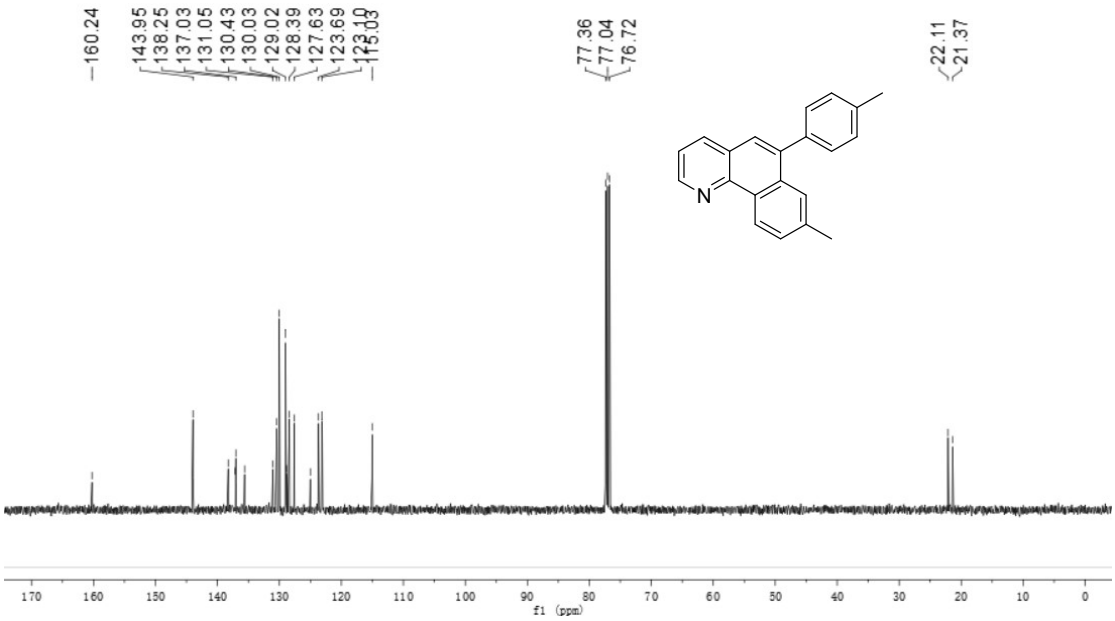

Figure S91. ^{13}C NMR spectrum of **2b** ($CDCl_3$, 400MHz)

8-methoxy-6-phenylbenzo[h]quinoline (2c)

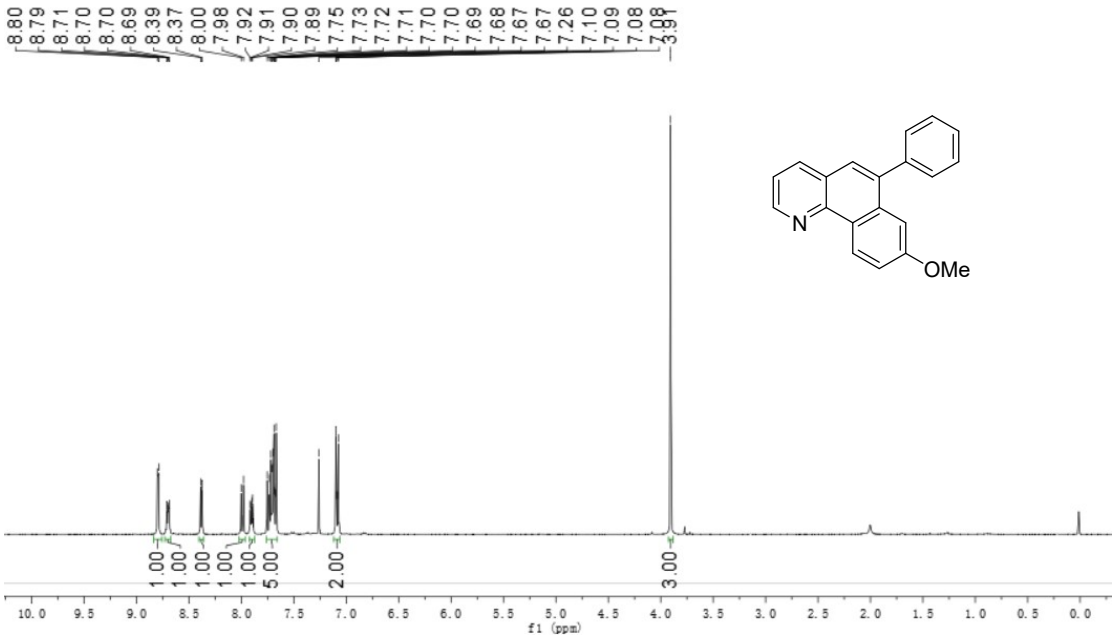

Figure S92. ^{1}H NMR spectrum of **2c** ($CDCl_3$, 400MHz)

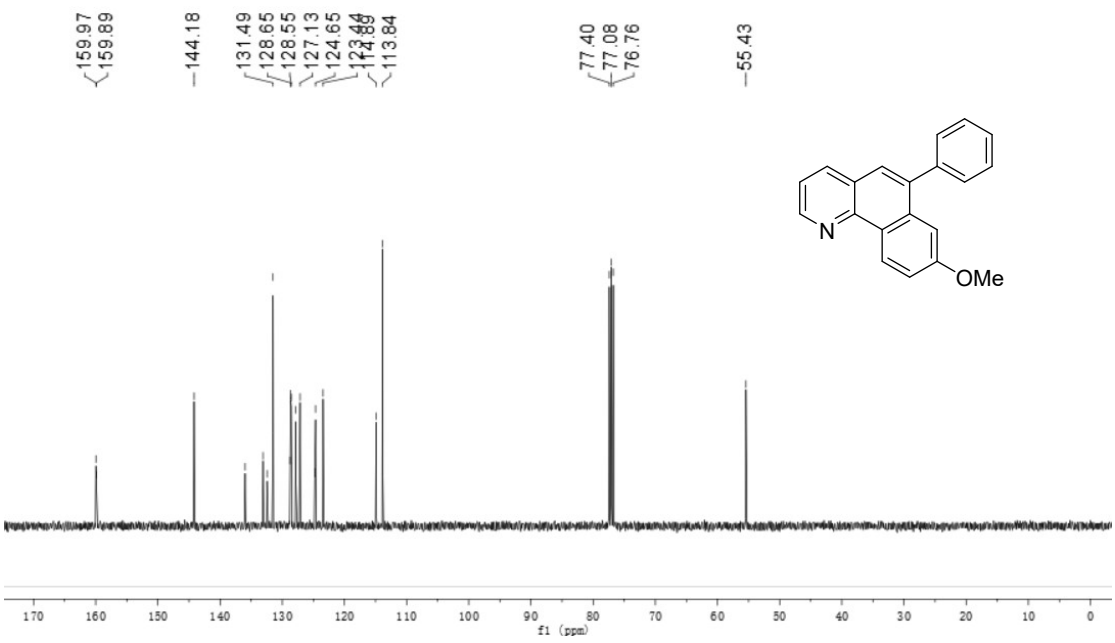

Figure S93. ^{13}C NMR spectrum of **2c** ($CDCl_3$, 400MHz)

8-fluoro-6-phenylbenzo[h]quinoline (2d)

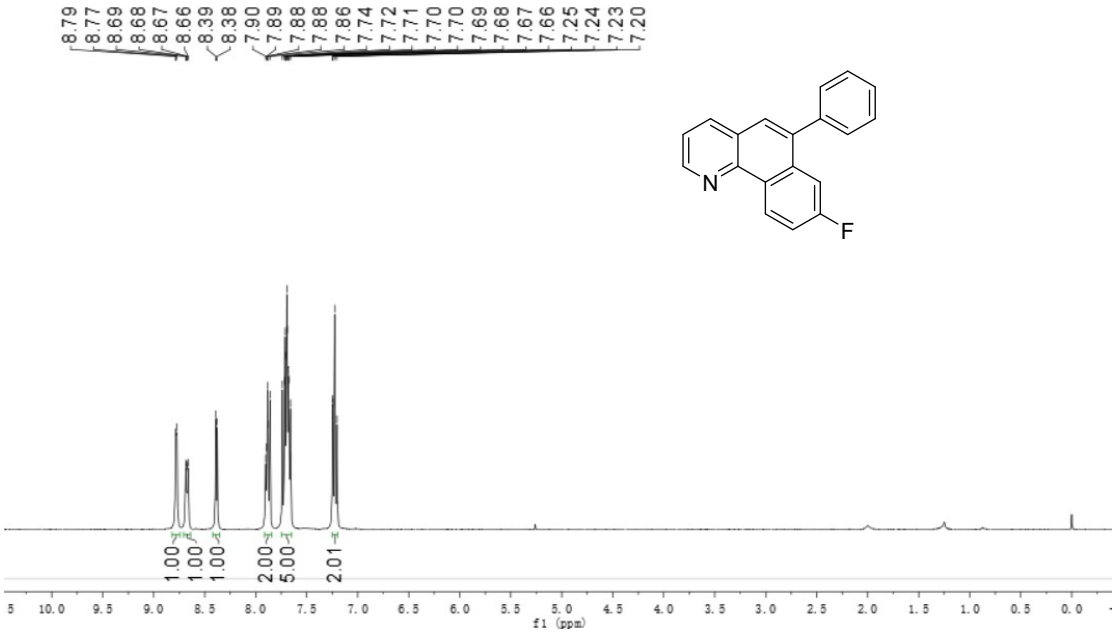

Figure S94. ^{1}H NMR spectrum of **2d** ($CDCl_3$, 400MHz)

1-(6-phenylbenzo[h]quinolin-8-yl)ethan-1-one (2e)

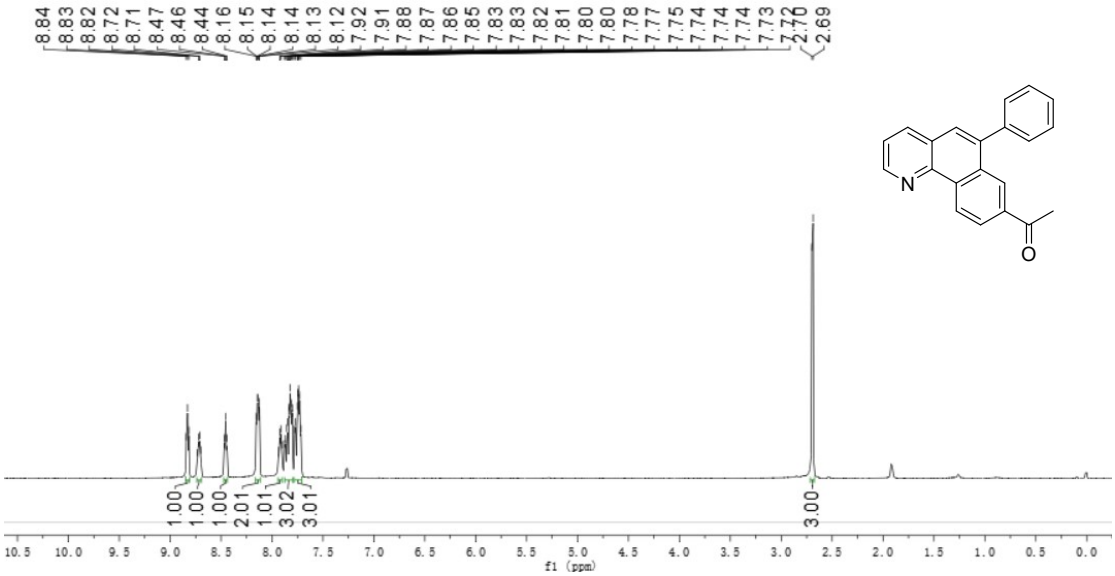

Figure S95. ^{1}H NMR spectrum of **2e** ($CDCl_3$, 400MHz)

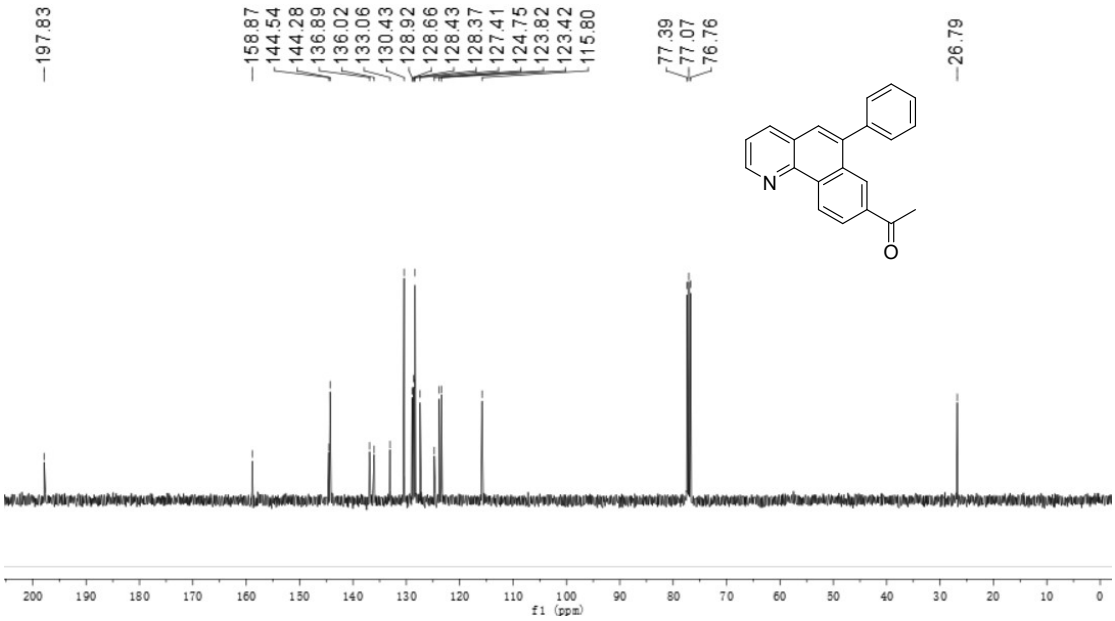

Figure S96. ^{13}C NMR spectrum of **2e** ($CDCl_3$, 400MHz)

6-phenyl-8-(trifluoromethyl)benzo[h]quinoline (2f)

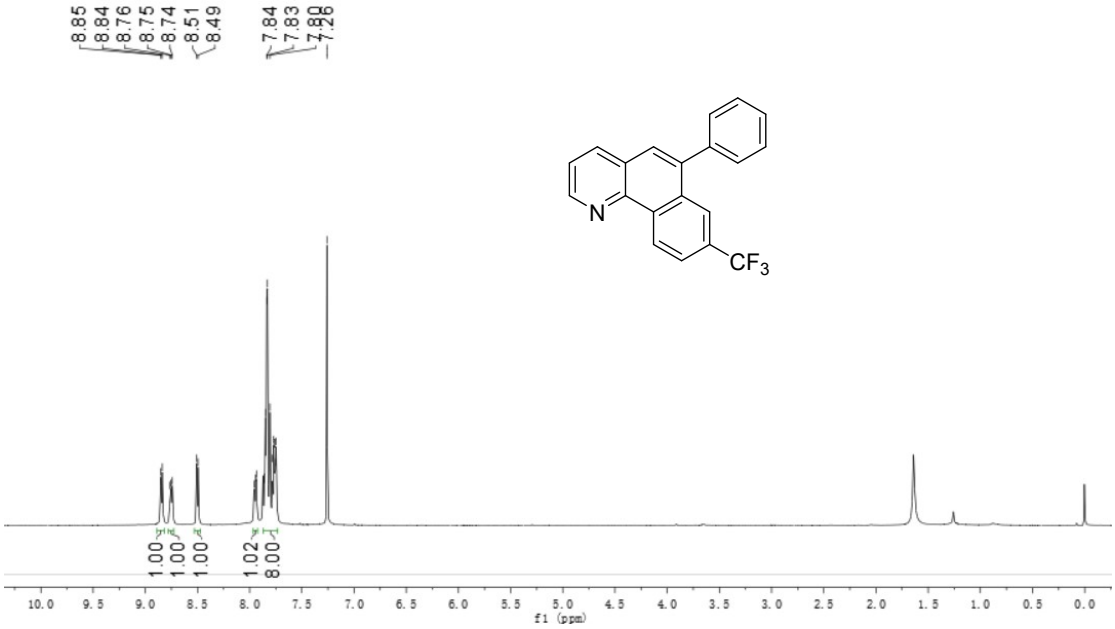

Figure S97. ^{1}H NMR spectrum of **2f** ($CDCl_3$, 400MHz)

1-(3-methyl-6-phenylbenzo[h]quinolin-8-yl)ethan-1-one (2g)

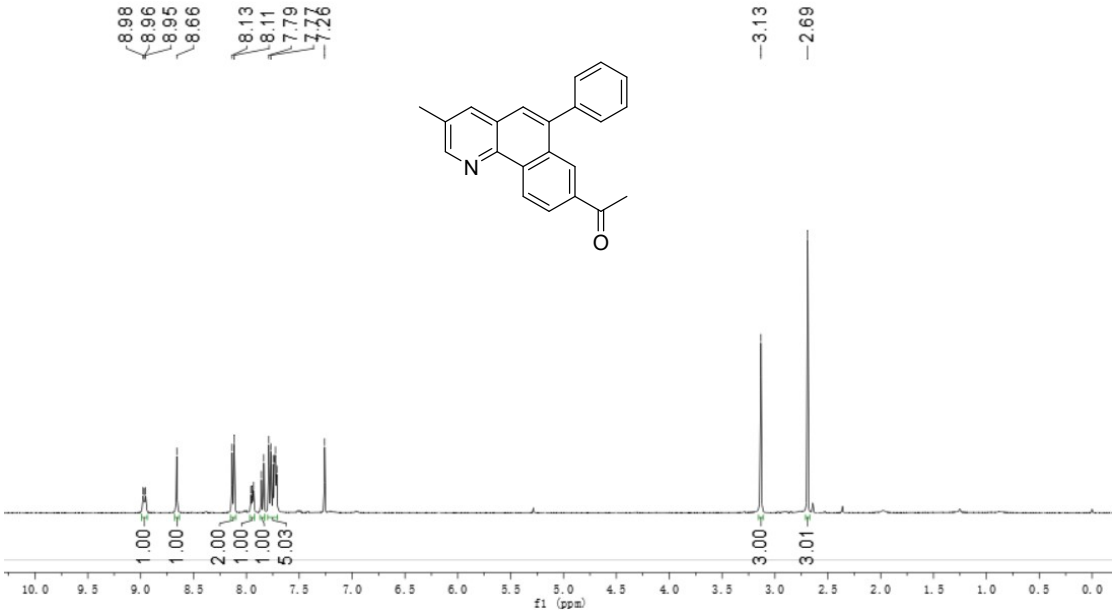

Figure S98. ^{1}H NMR spectrum of **2g** ($CDCl_3$, 400MHz)

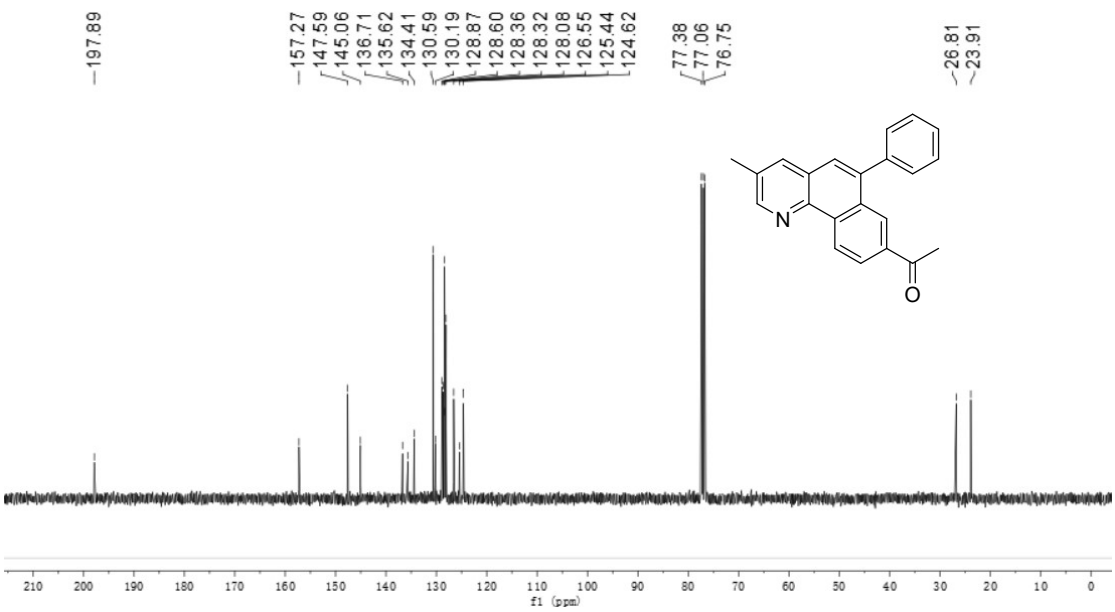

Figure S99. ^{13}C NMR spectrum of **2g** ($CDCl_3$, 400MHz)

3,8-dimethyl-6-phenylbenzo[h]quinoline (2h)

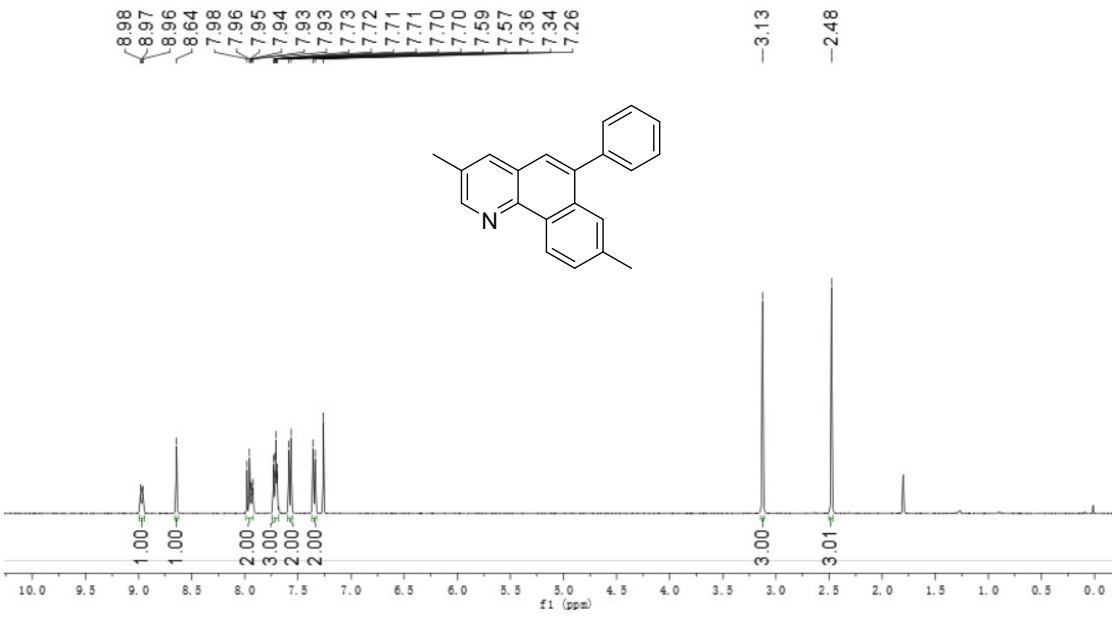

Figure S100. ^{1}H NMR spectrum of **2h** ($CDCl_3$, 400MHz)

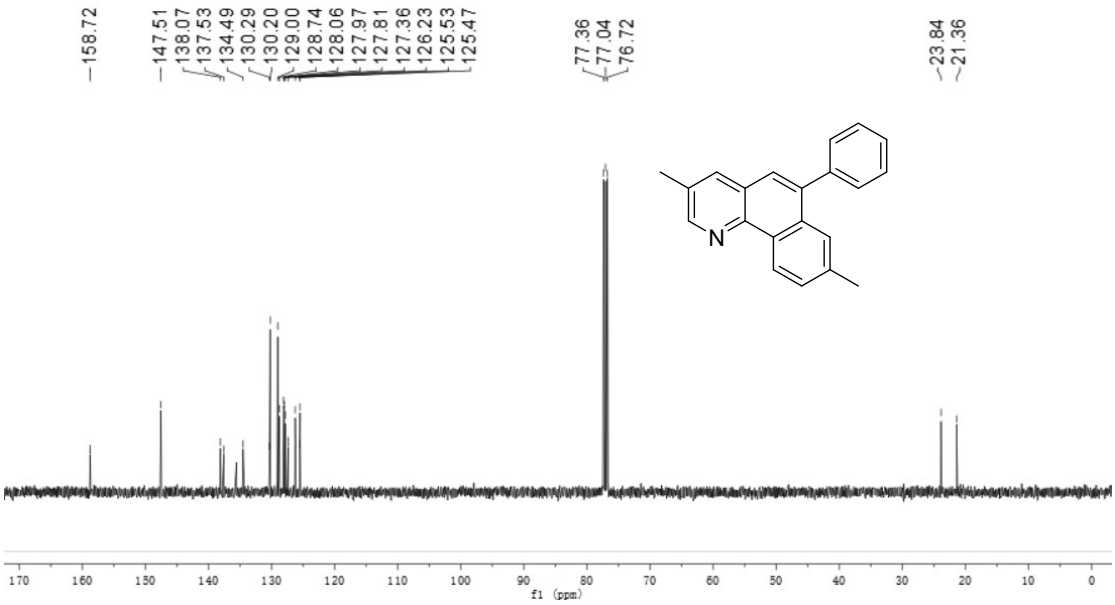

Figure S101. ^{13}C NMR spectrum of **2h** ($CDCl_3$, 400MHz)

3-fluoro-6-phenylbenzo[h]quinoline (2i)

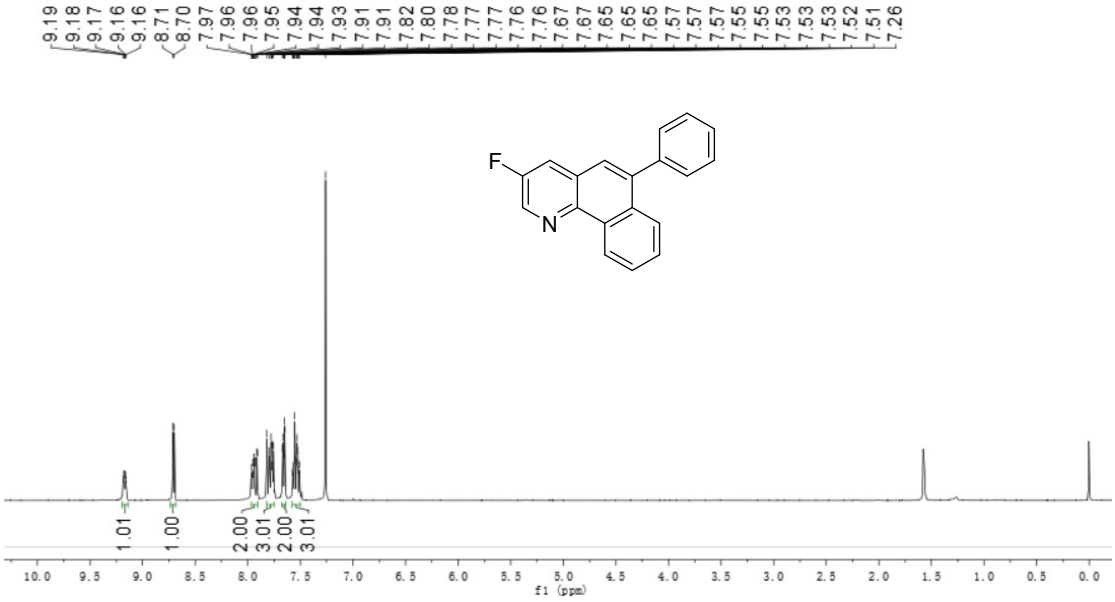

Figure S102. ^{1}H NMR spectrum of **2i** ($CDCl_3$, 400MHz)

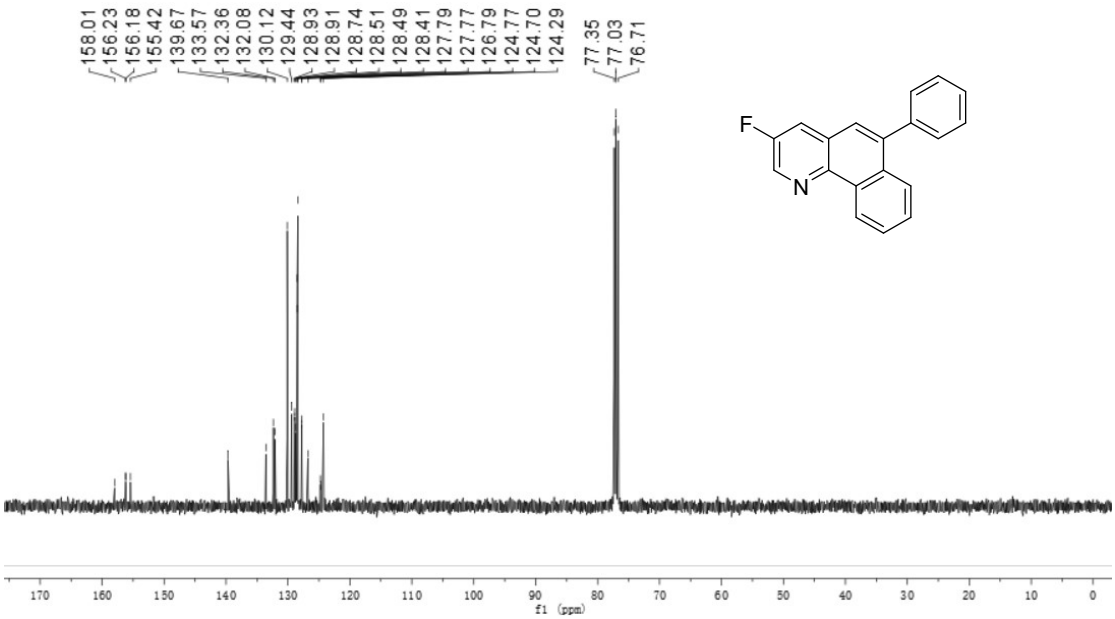

Figure S103. ^{13}C NMR spectrum of **2i** ($CDCl_3$, 400MHz)

3-methyl-6-phenylbenzo[h]quinoline (2j)

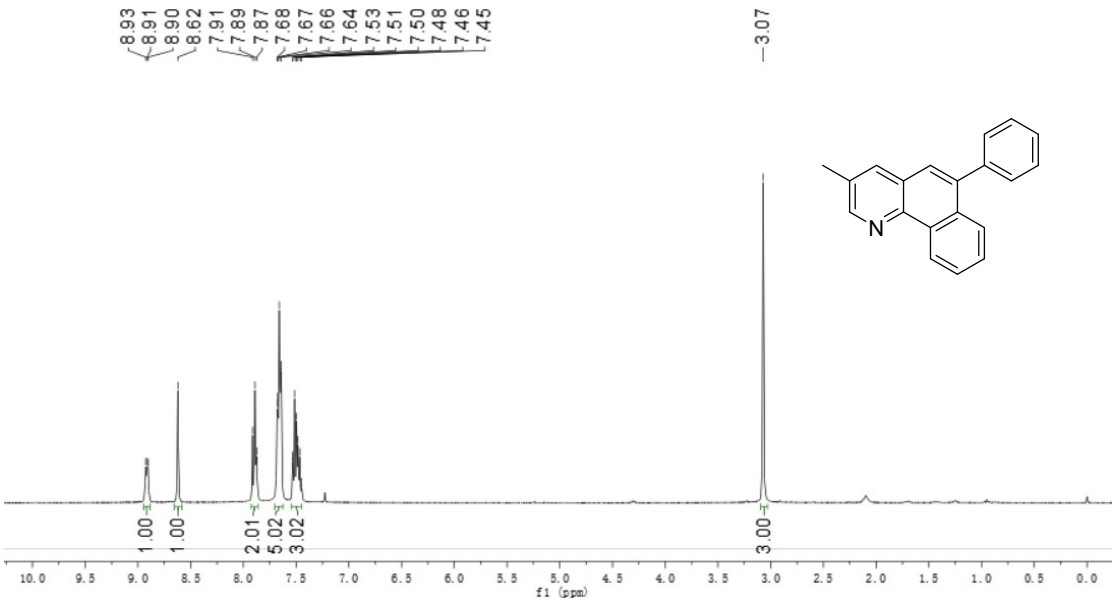

Figure S104. ^{1}H NMR spectrum of **2j** ($CDCl_3$, 400MHz)

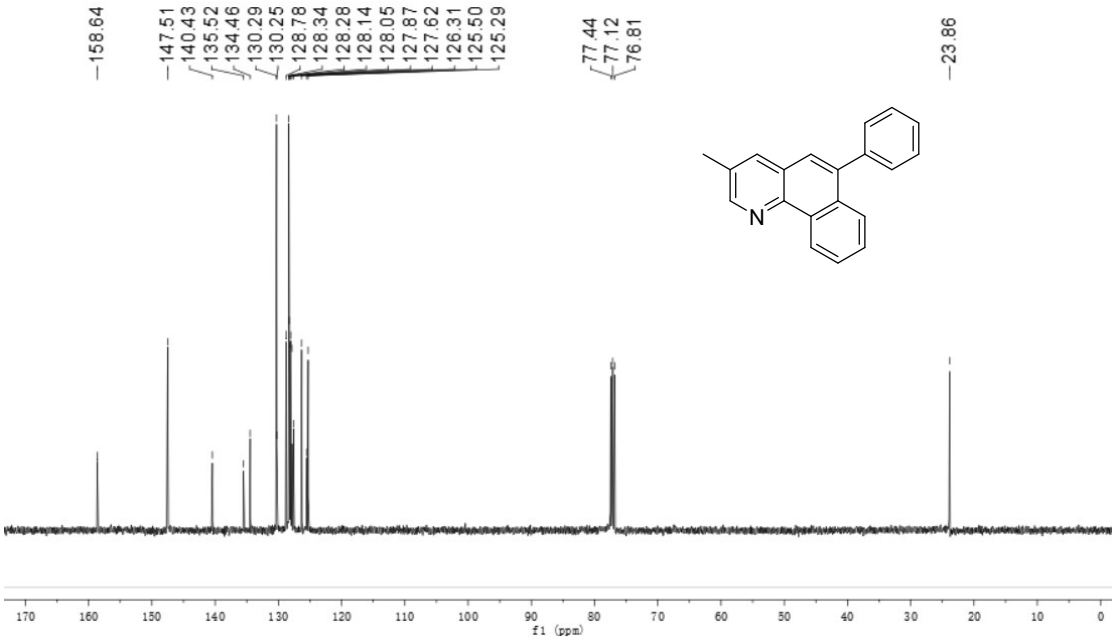

Figure S105. ^{13}C NMR spectrum of **2j** ($CDCl_3$, 400MHz)

9-methyl-6-phenylbenzo[h]quinoline (2k)

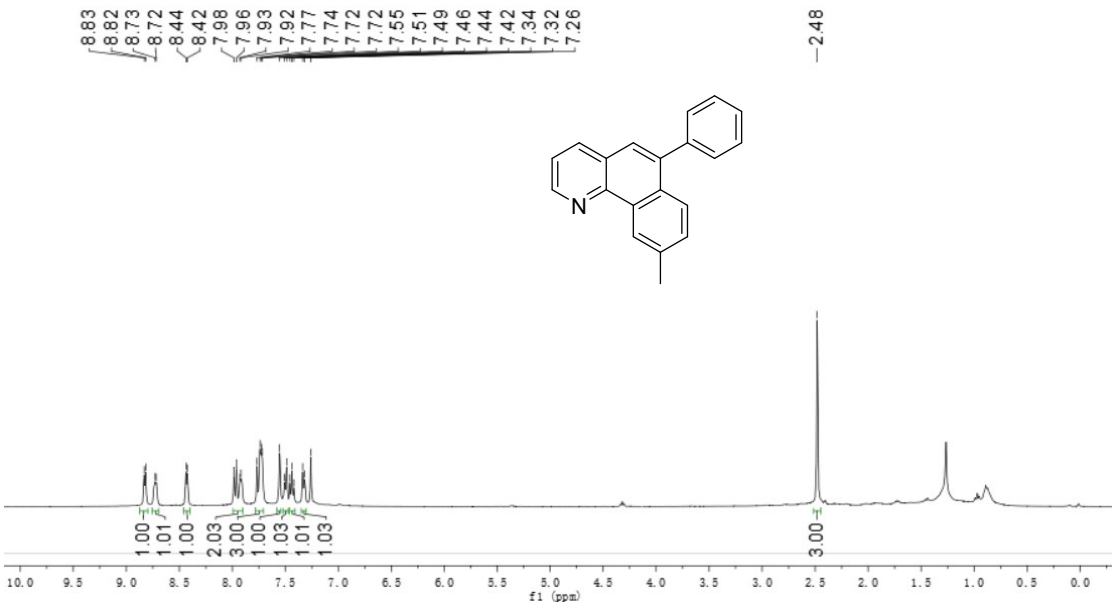

Figure S106. ^{1}H NMR spectrum of **2k** ($CDCl_3$, 400MHz)

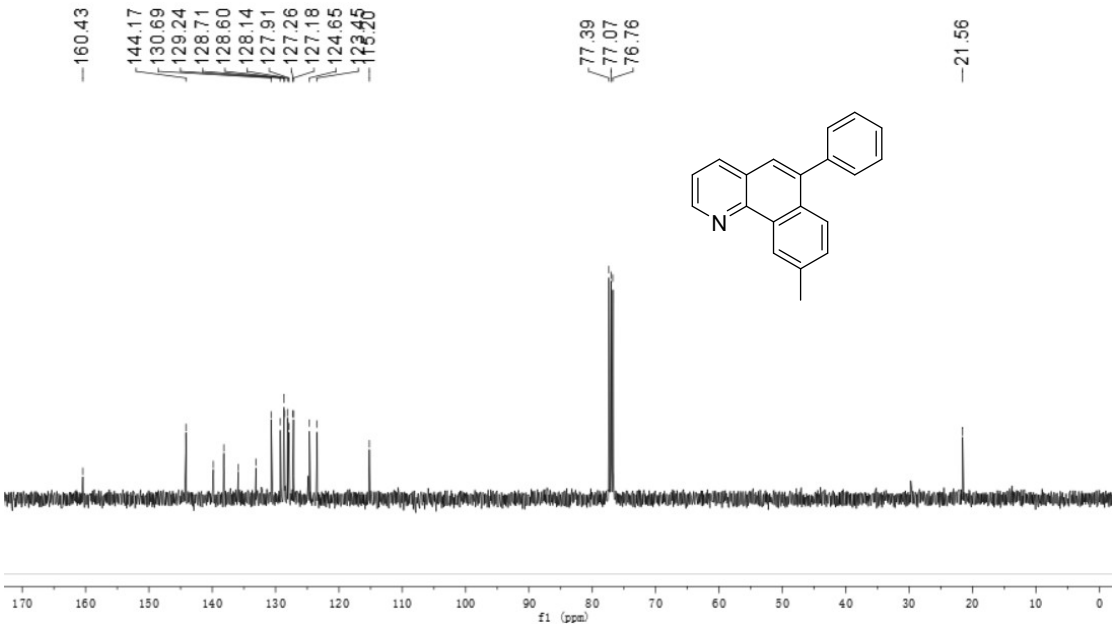

Figure S107. ^{13}C NMR spectrum of **2k** ($CDCl_3$, 400MHz)

3-methyl-6-phenyl-8-(trifluoromethyl)benzo[h]quinoline (2l)

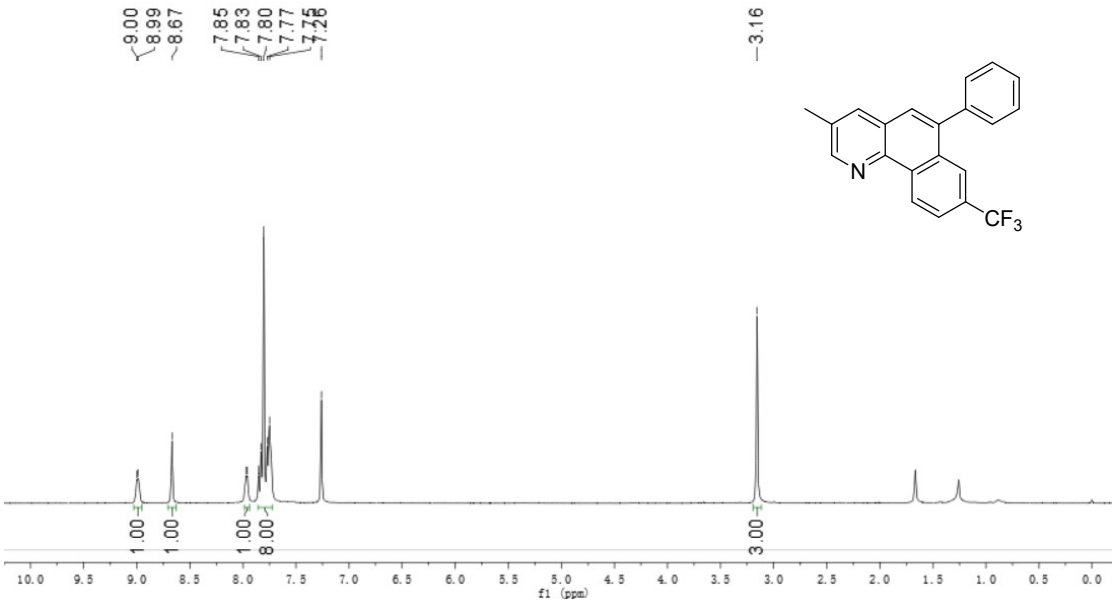

Figure S108. ^{1}H NMR spectrum of **2l** ($CDCl_3$, 400MHz)

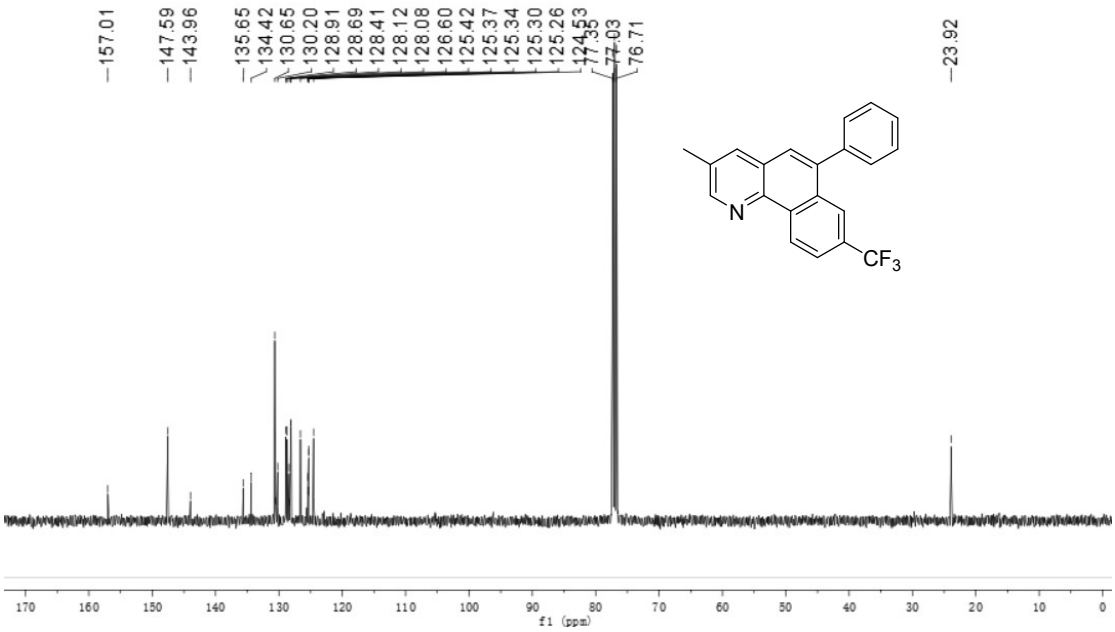

Figure S109. ^{13}C NMR spectrum of **2l** ($CDCl_3$, 400MHz)

6-phenylnaphtho[2,1-h]quinoline (2m)

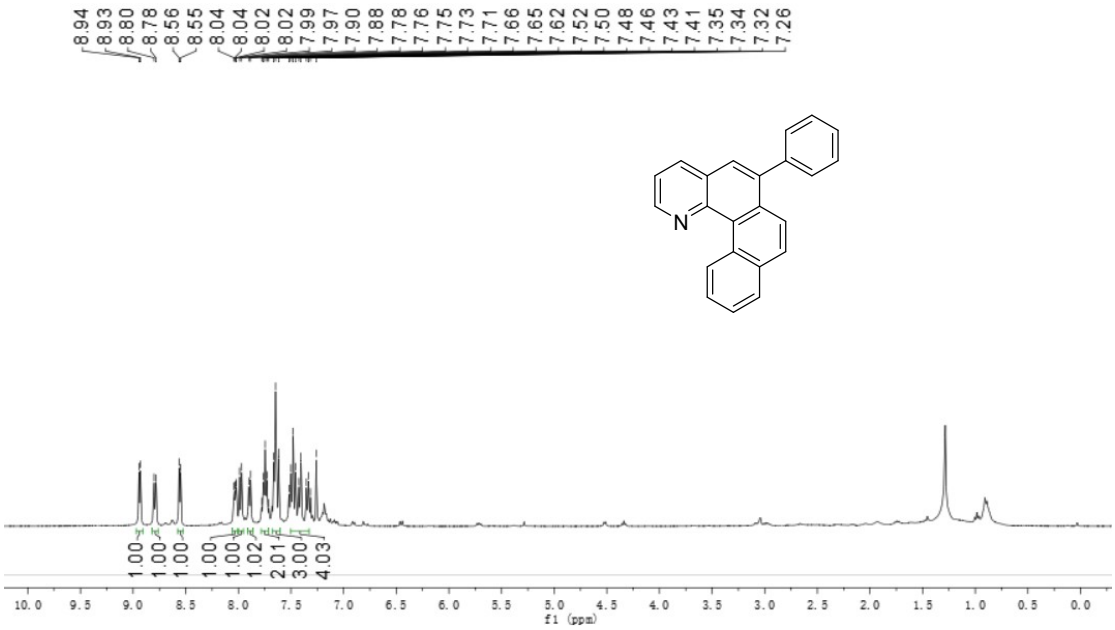

Figure S110. ^{1}H NMR spectrum of **2m** ($CDCl_3$, 400MHz)

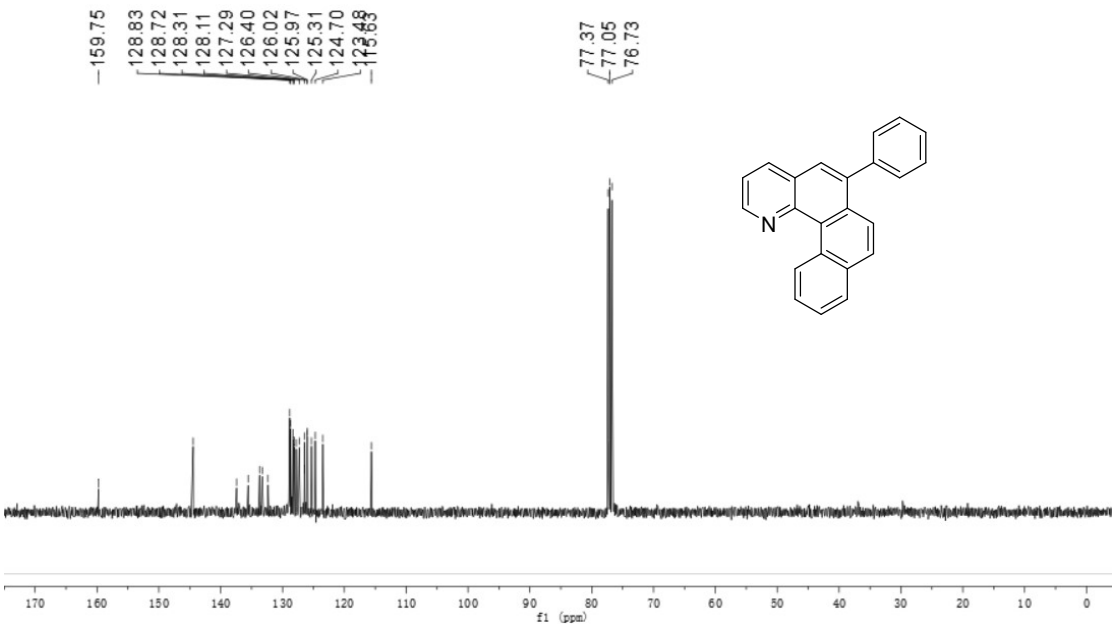

Figure S111. ^{13}C NMR spectrum of **2m** ($CDCl_3$, 400MHz)

6-(p-tolyl)benzo[h]quinoline (2n)

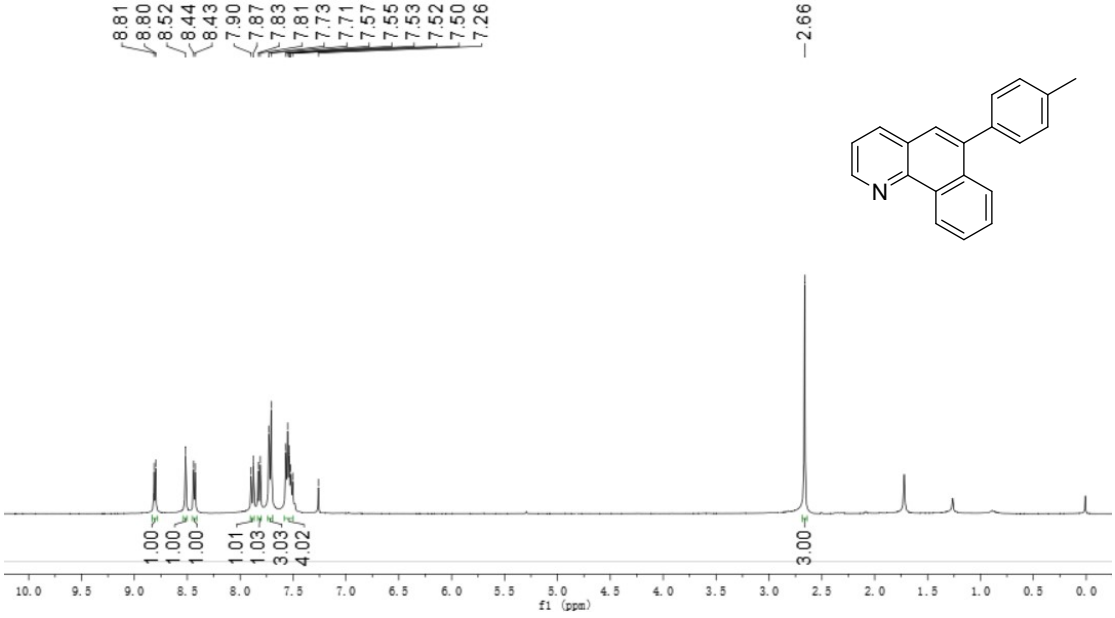

Figure S112. ^{1}H NMR spectrum of **2n** ($CDCl_3$, 400MHz)

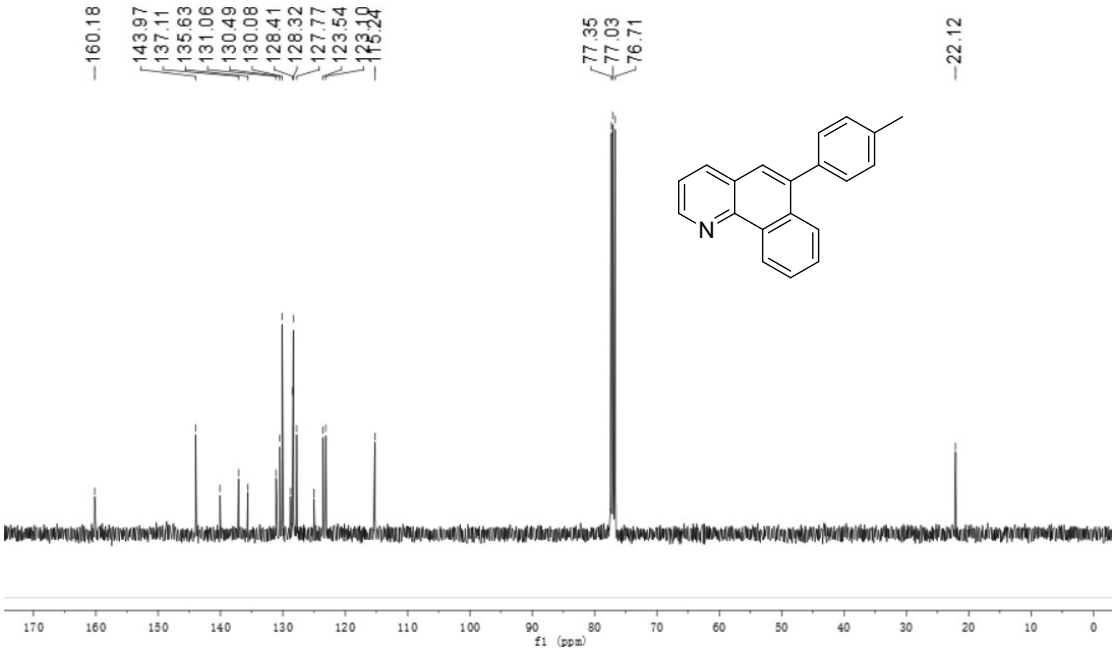

Figure S113. ^{13}C NMR spectrum of **2n** ($CDCl_3$, 400MHz)

6-(4-fluorophenyl)benzo[h]quinoline (2o)

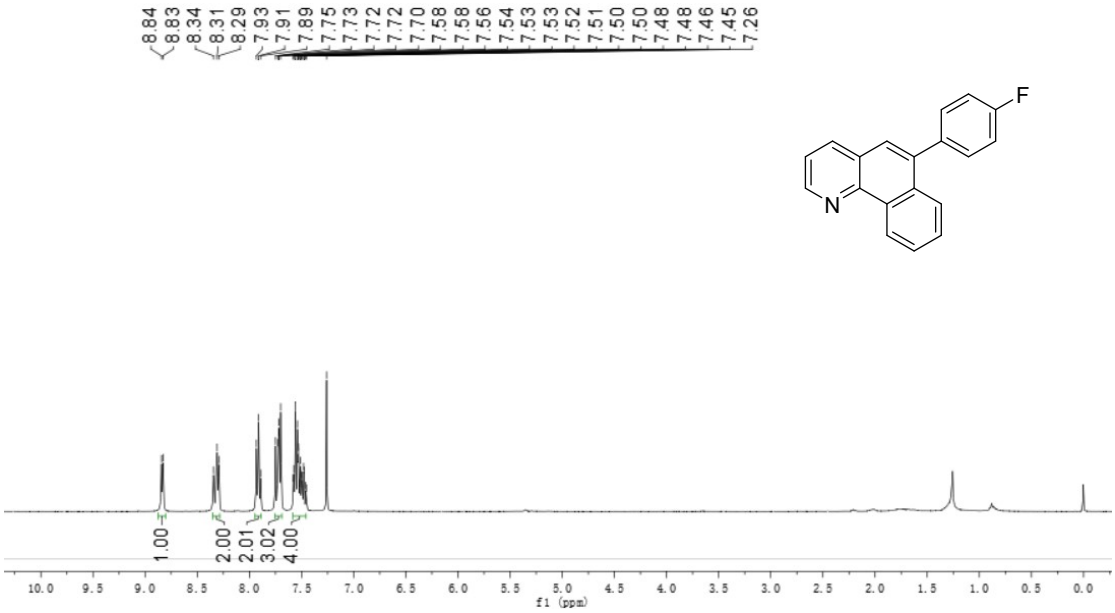

Figure S114. ^{1}H NMR spectrum of **2o** ($CDCl_3$, 400MHz)

3-fluoro-8-methyl-6-phenylbenzo[h]quinoline (2p)

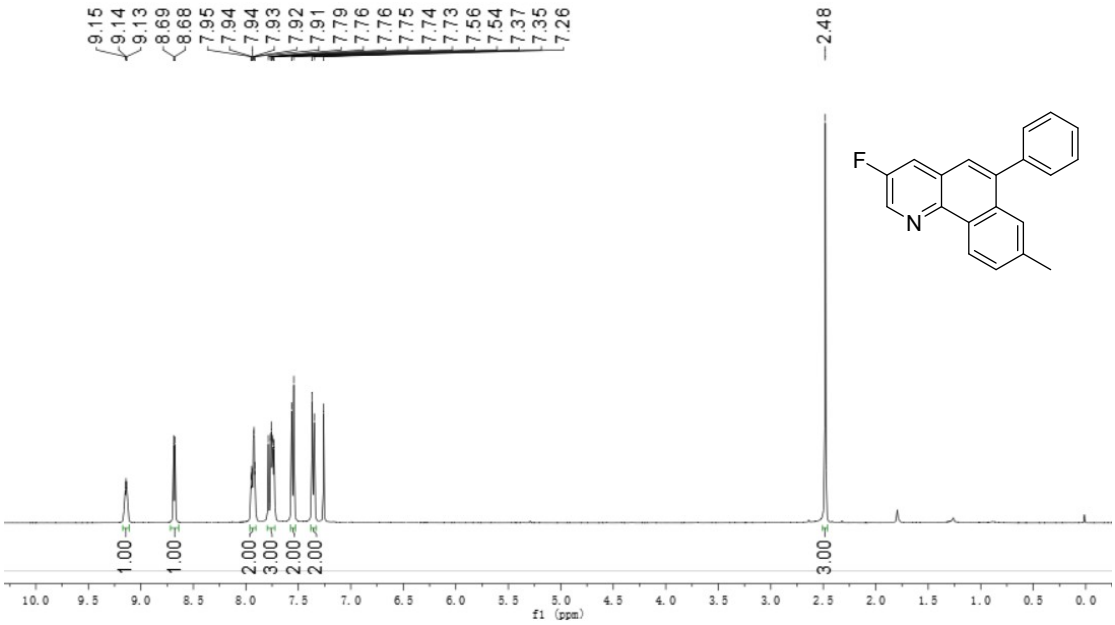

Figure S115. ^{1}H NMR spectrum of **2p** ($CDCl_3$, 400MHz)

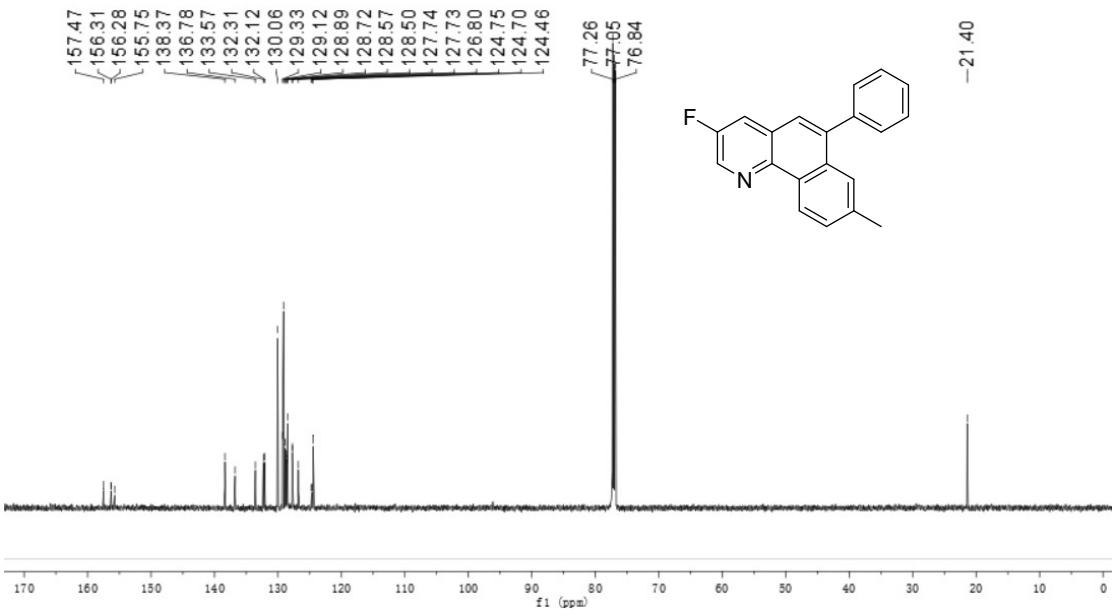

Figure S116. ^{13}C NMR spectrum of **2p** ($CDCl_3$, 400MHz)

8-fluoro-3-methyl-6-phenylbenzo[h]quinoline (2q)

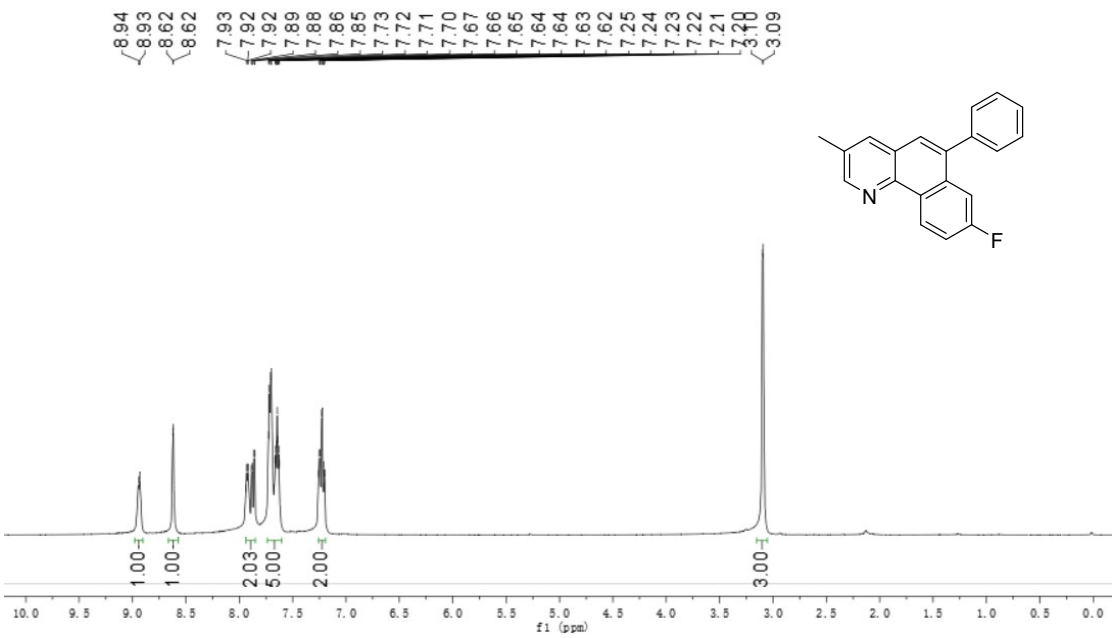

Figure S117. ^{1}H NMR spectrum of **2q** ($CDCl_3$, 400MHz)

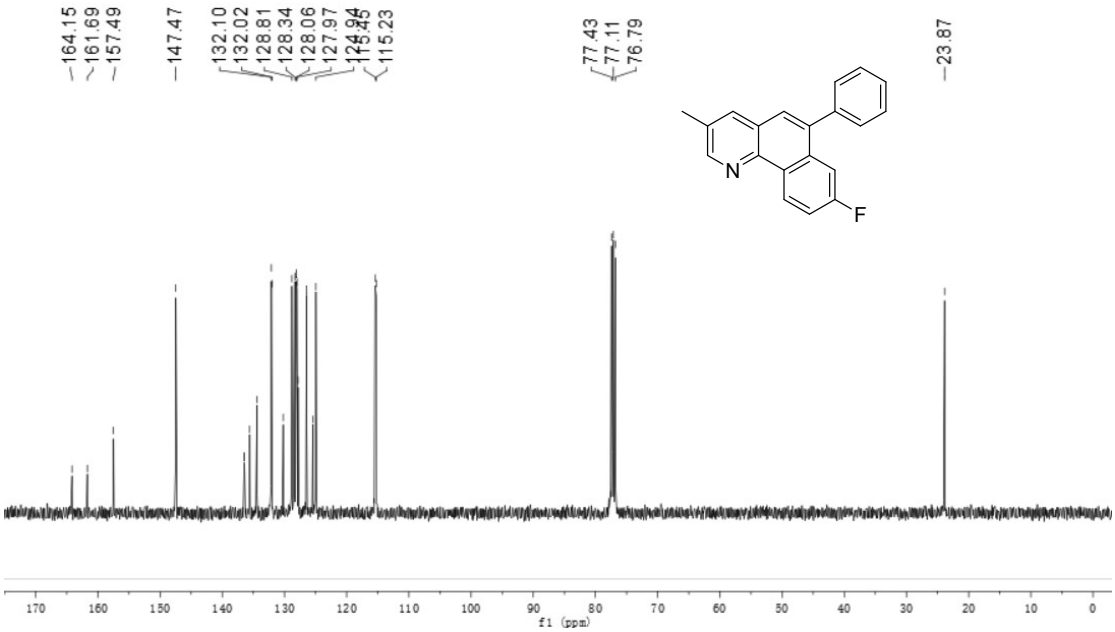

Figure S118. ^{13}C NMR spectrum of **2q** ($CDCl_3$, 400MHz)

5-phenylbenzo[c]acridine (2r)

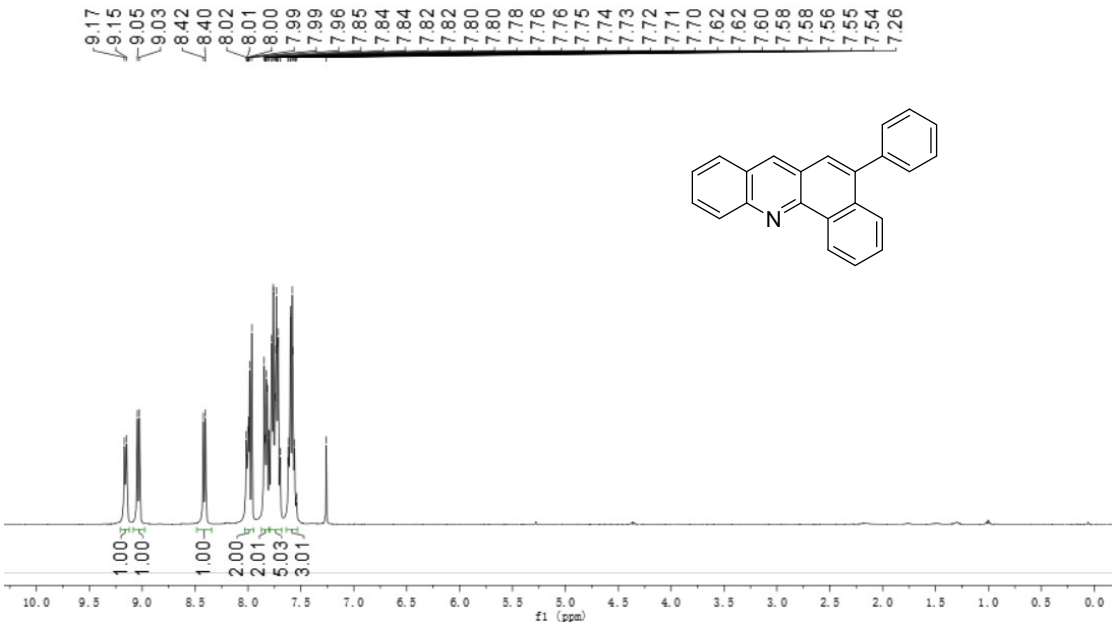

Figure S119. ^{1}H NMR spectrum of **2r** ($CDCl_3$, 400MHz)

3-methoxy-5-phenylbenzo[c]acridine (2s)

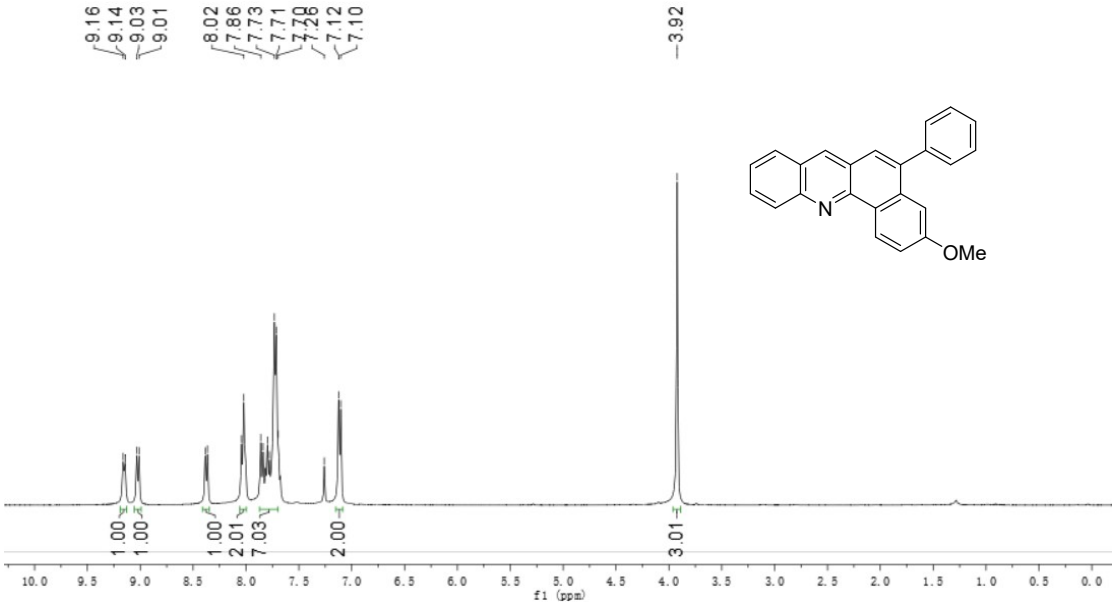

Figure S120. ^{1}H NMR spectrum of **2s** ($CDCl_3$, 400MHz)

3,8,10-trimethyl-6-phenylbenzo[h]quinoline (2t)

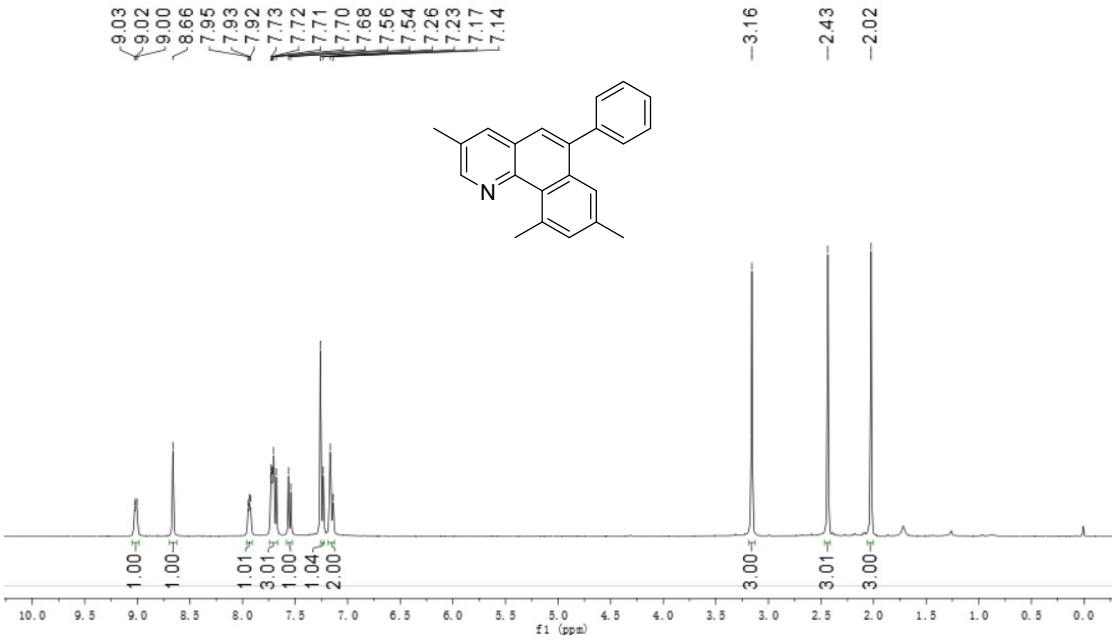

Figure S121. ^{1}H NMR spectrum of **2t** ($CDCl_3$, 400MHz)

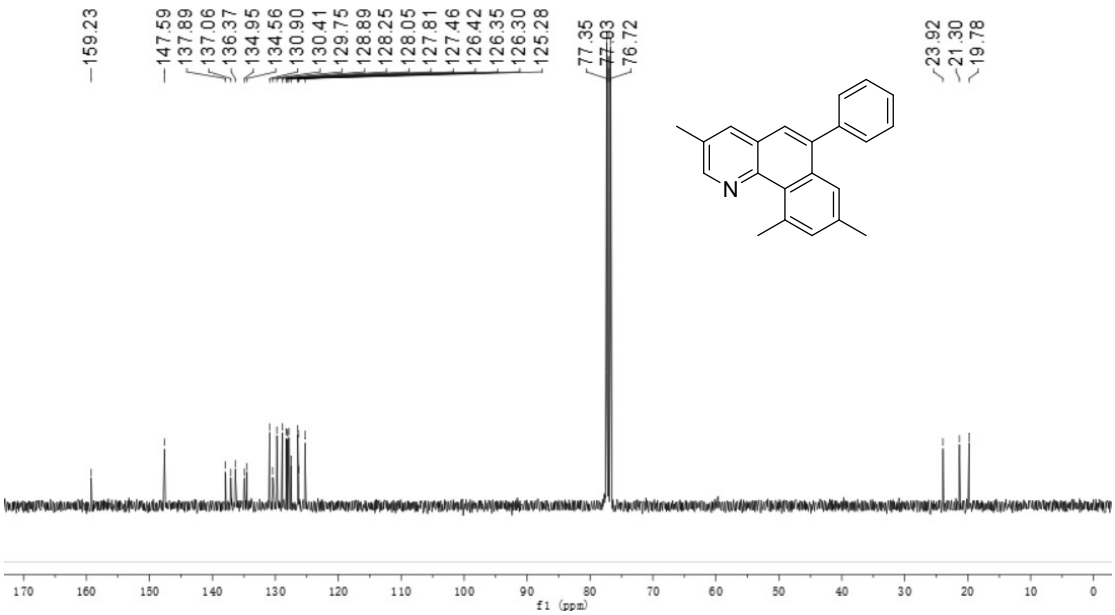

Figure S122. ^{13}C NMR spectrum of **2t** ($CDCl_3$, 400MHz)

9-methoxy-6-phenylbenzo[h]quinoline (2u)

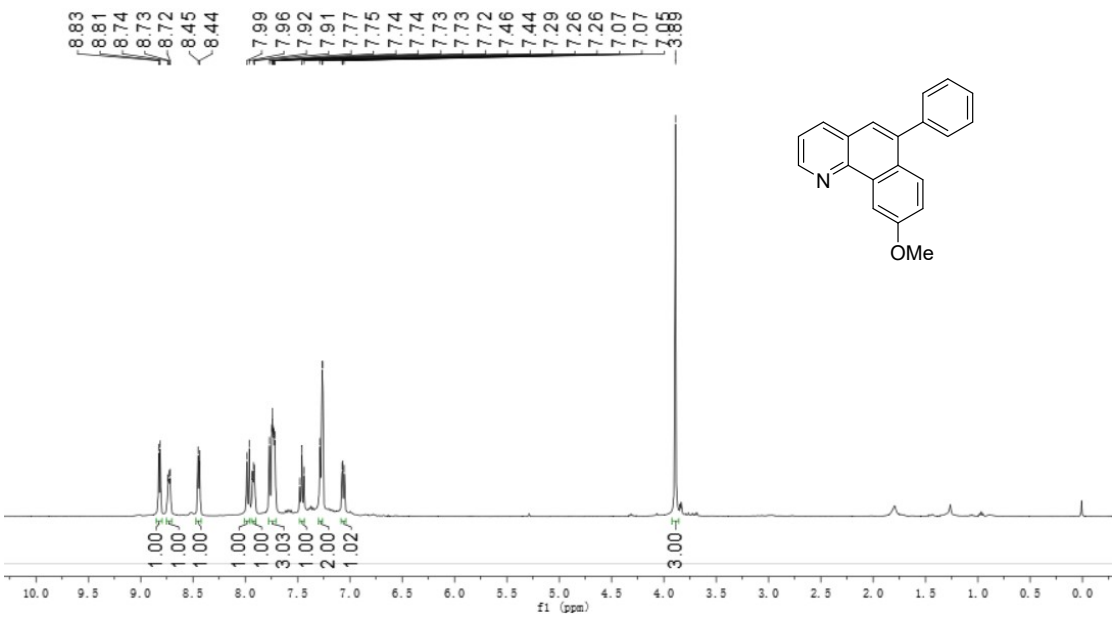

Figure S123. ^{1}H NMR spectrum of **2u** ($CDCl_3$, 400MHz)

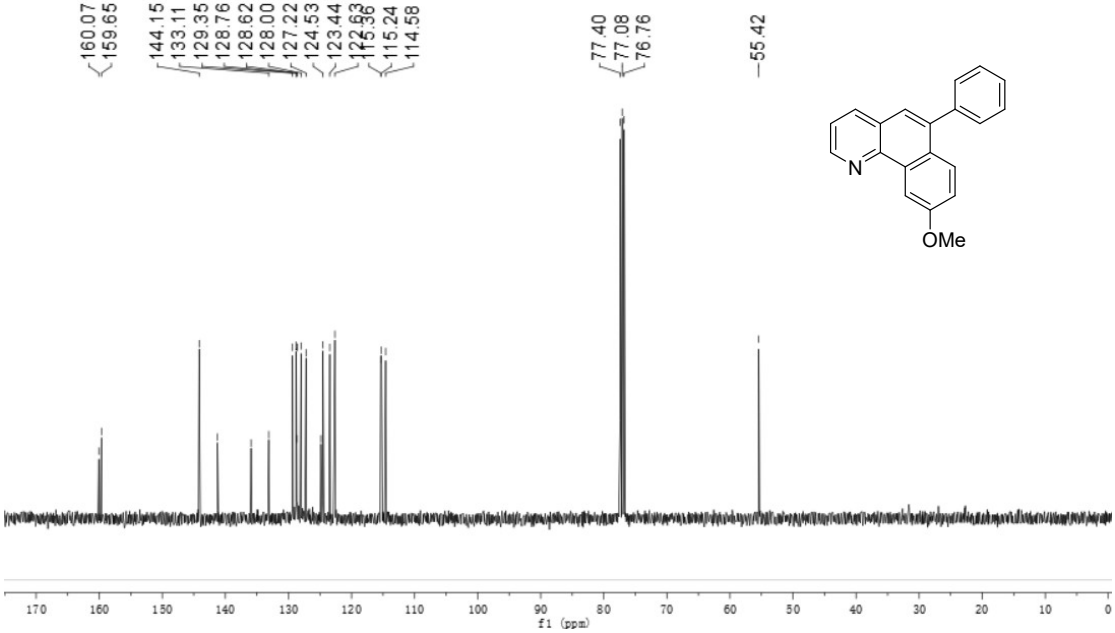

Figure S124. ^{13}C NMR spectrum of **2u** ($CDCl_3$, 400MHz)

8,10-dimethyl-6-phenylbenzo[h]quinoline (2v)

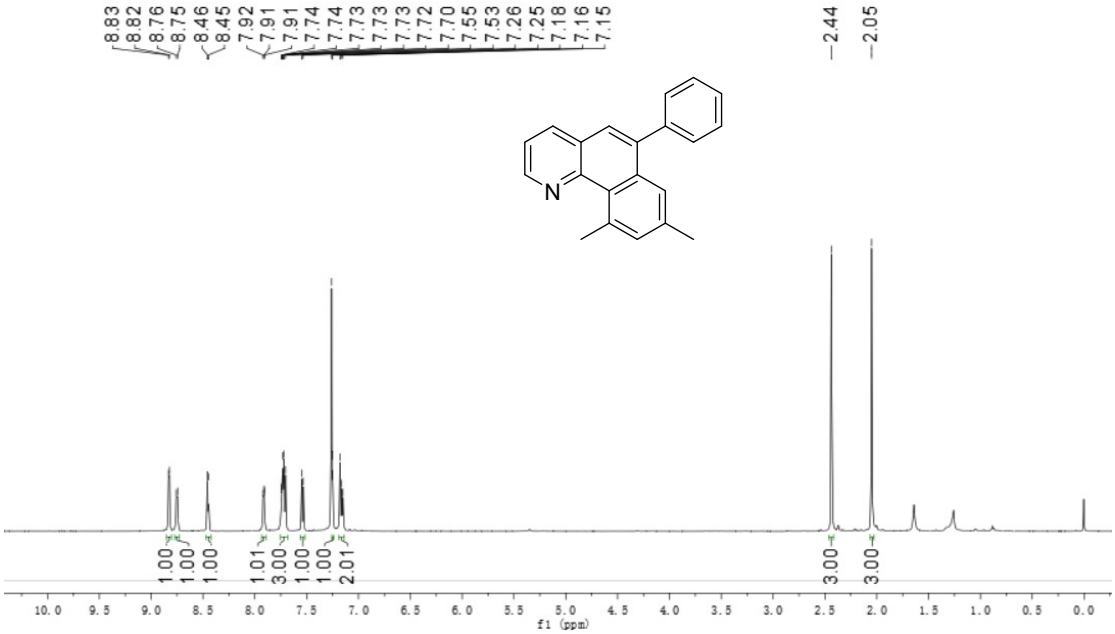

Figure S125. ^{1}H NMR spectrum of **2v** ($CDCl_3$, 600MHz)

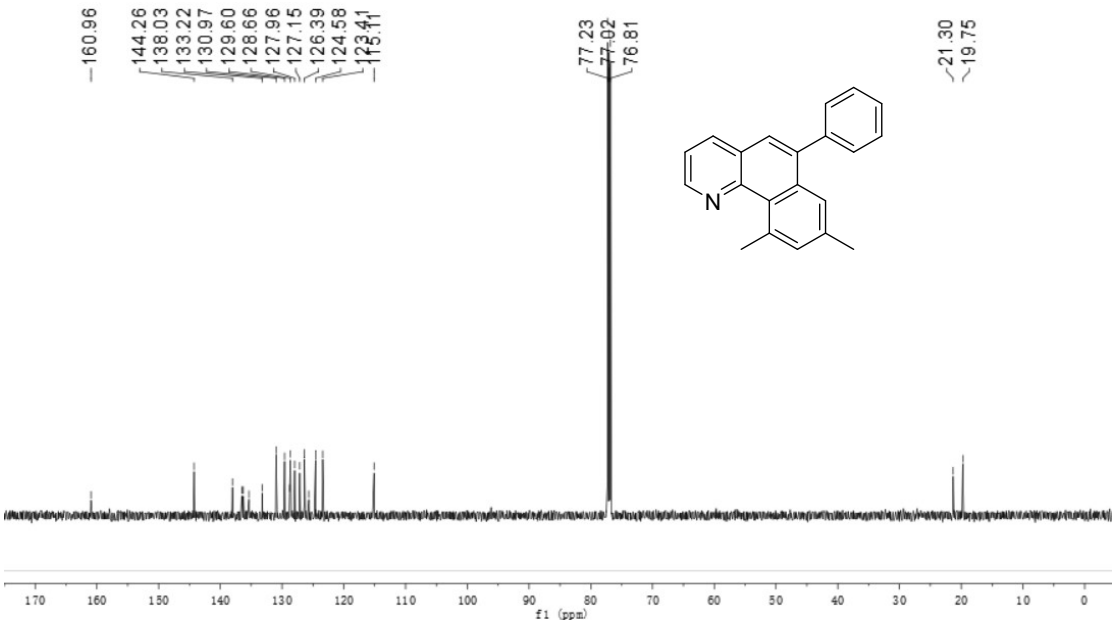

Figure S126. ^{13}C NMR spectrum of **2v** ($CDCl_3$, 600MHz)

3-fluoro-8,10-dimethyl-6-phenylbenzo[h]quinoline (2w)

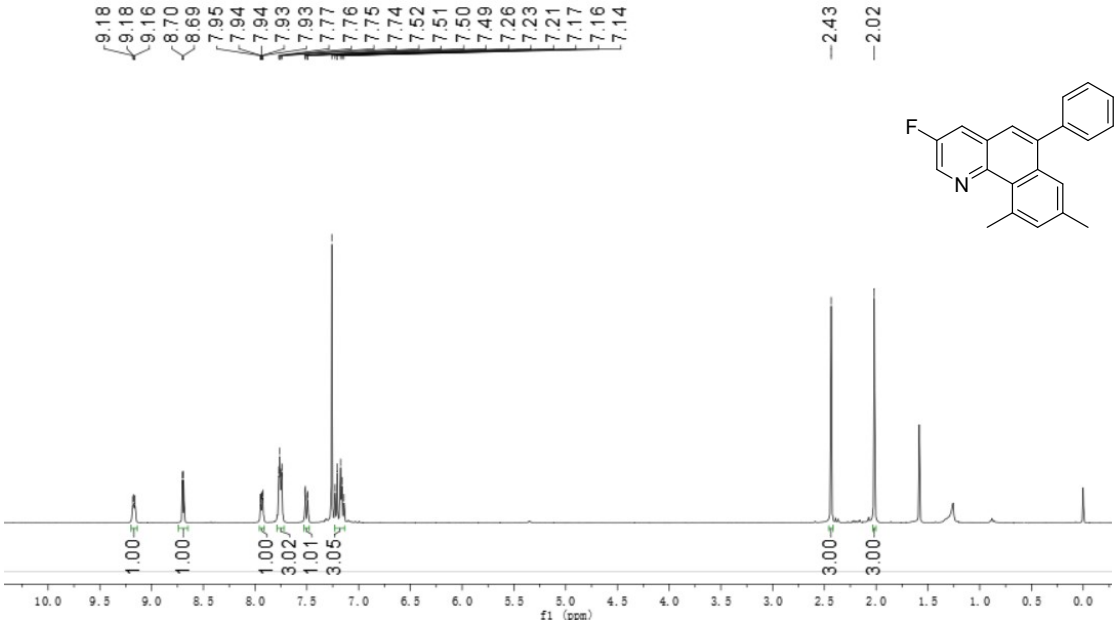

Figure S127. ^{1}H NMR spectrum of **2w** ($CDCl_3$, 400MHz)

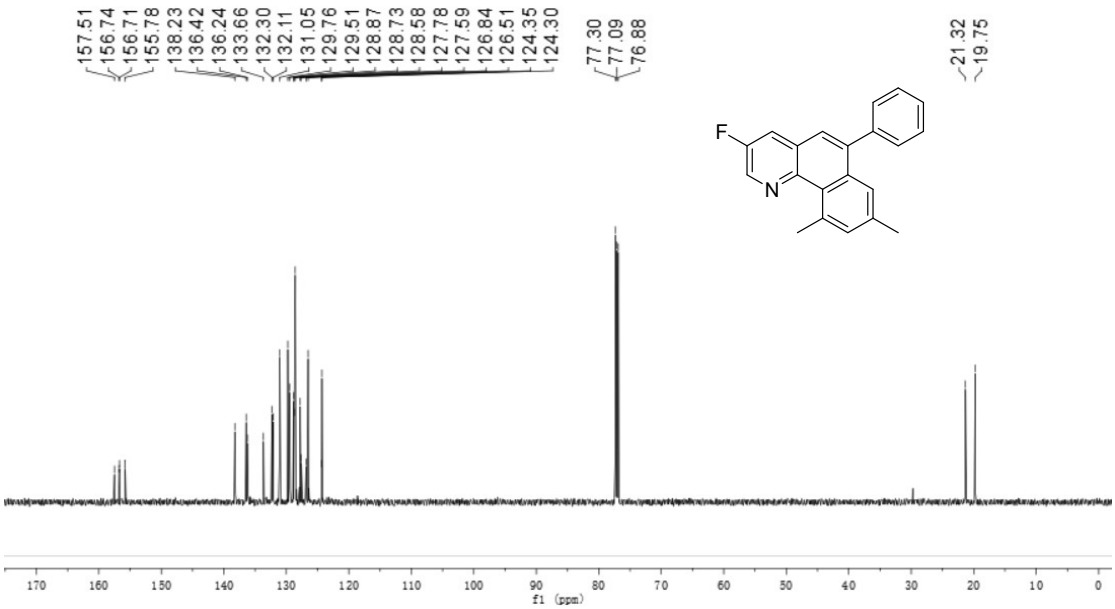

Figure S128. ^{13}C NMR spectrum of **2w** ($CDCl_3$, 400MHz)

9,10-difluoro-6-phenylbenzo[h]quinoline (2x)

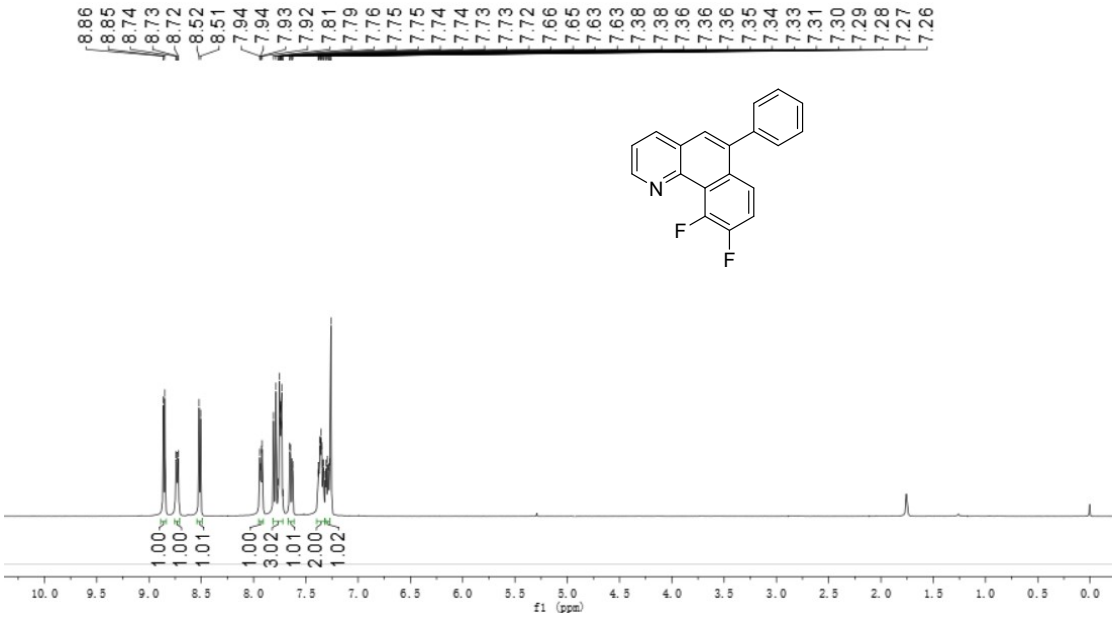

Figure S129. ^{1}H NMR spectrum of **2x** ($CDCl_3$, 400MHz)

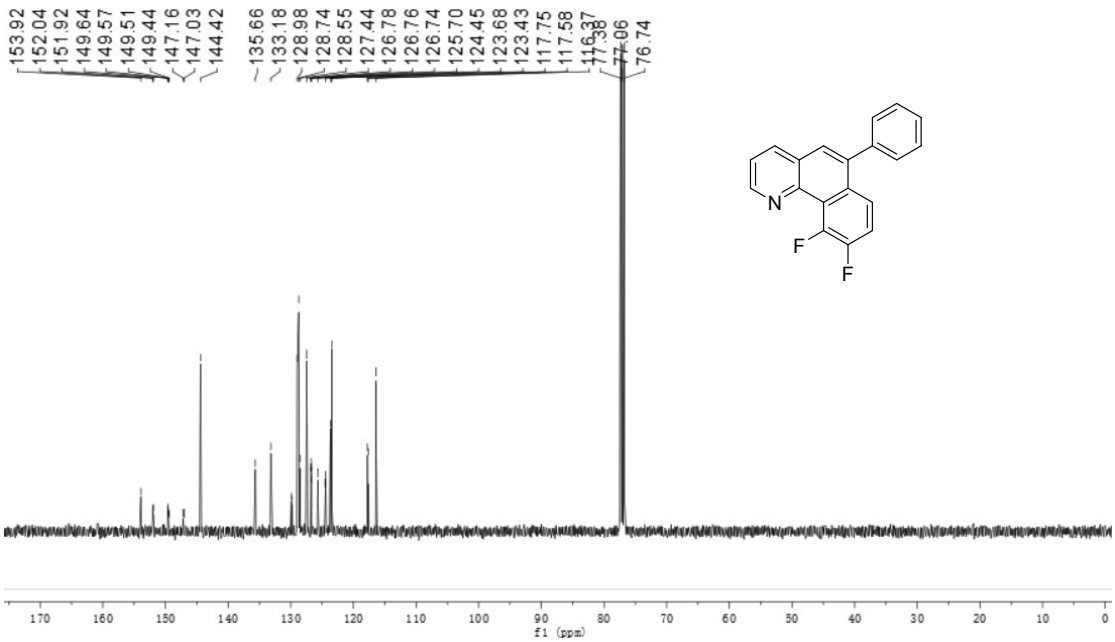

Figure S130. ^{13}C NMR spectrum of **2x** ($CDCl_3$, 400MHz)

5-phenyl-1,10-phenanthroline (2z)

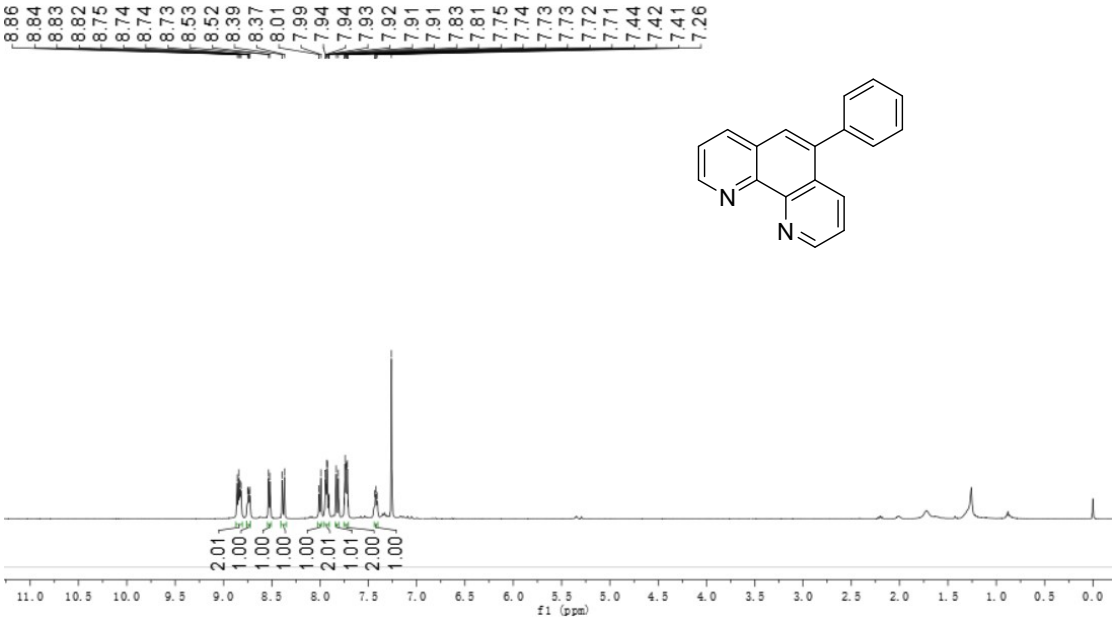

Figure S131. ^{1}H NMR spectrum of **2z** ($CDCl_3$, 400MHz)

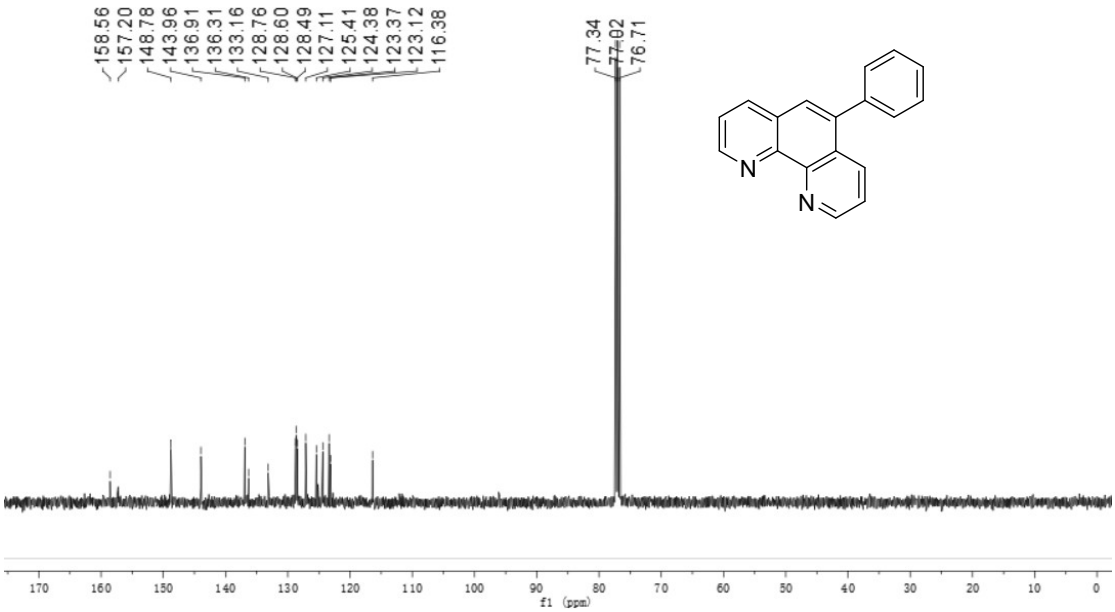

Figure S132. ^{13}C NMR spectrum of **2z** ($CDCl_3$, 400MHz)

6-phenyl-5,6-dihydrobenzo[h]quinoline (3a)

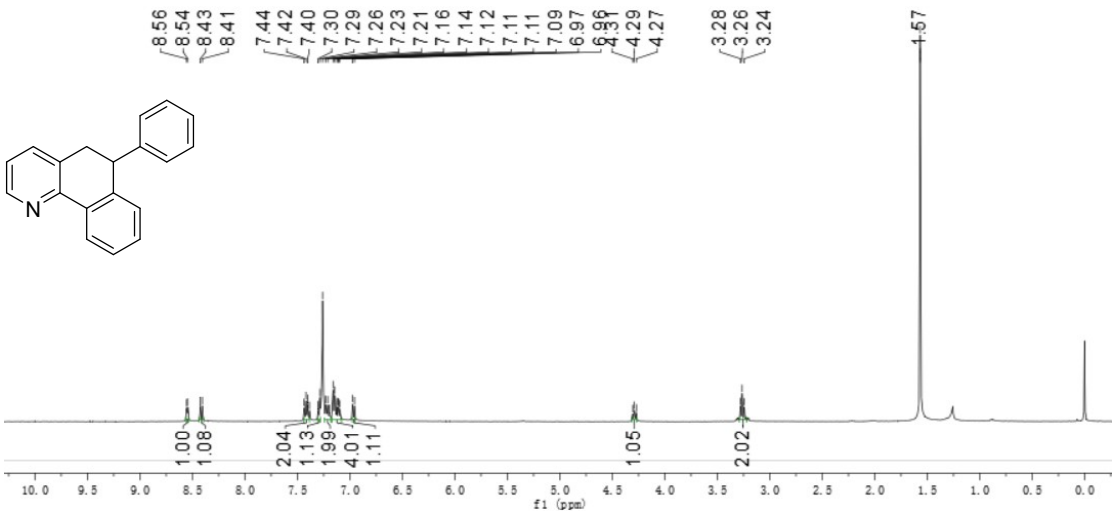

Figure S133. ^{1}H NMR spectrum of **3a** ($CDCl_3$, 400MHz)

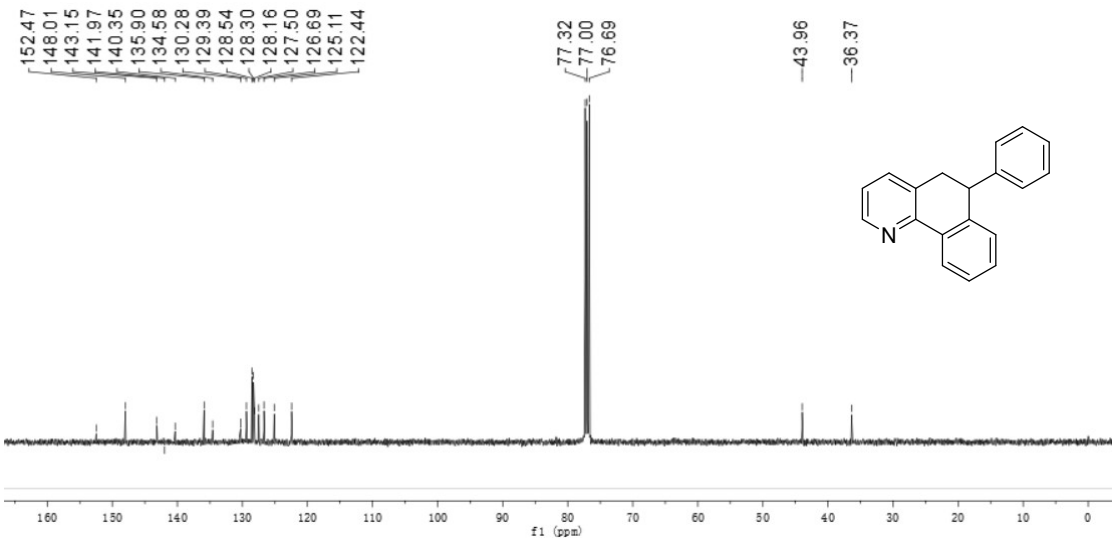

Figure S134. ^{13}C NMR spectrum of **3a** ($CDCl_3$, 400MHz)