

Supporting Information

Highly Selective Cyclization and Isomerization of Propargylamines to Access Functionalized Quinolines and 1-Azadienes

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1. General information

Commercially available reagents were used as received without purification. Raw Materials were purchased from Bidepharm and Energy-chemical. Column chromatography was carried out on silica gel (200–300 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF-254 with detection by UV. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AVANCE 400M spectrometer. The chemical shift references were as follows: ^1H NMR (CDCl_3) 7.26 ppm; ^{13}C NMR (CDCl_3) 77.0 ppm. HRMS spectra were carried out on Micromass GCT (ESI). The photoluminescence spectra were measured on a Hitachi F-4600 photoluminescence spectrophotometer. The absolute photoluminescence quantum yields (Φ) was measured with HORIBA FL-3 fluorescence spectrometer.

2. Experimental section

2.1 Synthesis of propargylamines following reported procedures (*J. Org. Chem.* **2006**, *71*, 2064-2070; *Org. Lett.* **2006**, *8*, 2405-2408; *Tetrahedron*, **2014**, *70*, 3134-3140).

2.2 General procedure for the preparation of quinolines through Palladium-catalyzed cyclization.

To a solution of propargylamine (0.1 mmol) and $\text{Pd}(\text{OAc})_2$ (5 mol%) in toluene (2 mL), the reaction mixture was stirred at 80 °C under air for 12 h. After removing the solvent with vacuum distillation, the crude mixture was purified by flash column chromatography to afford the target product.

2.3 General procedure for the preparation of 1-azadienes via Bu_4NOAc -promoted isomerization.

To a solution of propargylamine (0.1 mmol) and Bu_4NOAc (0.2 mmol) in CH_3CN (2 mL), the reaction mixture was stirred at 80 °C under air for 12 h. After removing the solvent with vacuum distillation, the crude mixture was purified by flash column chromatography to afford the target product.

2.4 General procedure for the preparation of Ir-2m.

The mixture of **2m** (1.0 mmol) and IrCl₃ (0.4 mmol) in 2-ethoxyethanol and water (20 mL, 3 : 1, v/v) was stirred at 130 °C for 24 h under argon. After cooling, the solid precipitate was filtered to obtain crude cyclometalated Ir(III) chloro-bridged dimer. Then, the slurry of crude chloro-bridged dimer, Na₂CO₃ (5.0 mmol) and TMHD (5.0 mmol) in 2-ethoxyethanol (30 mL) was reacted at 120 °C for 24 h. The solvent was evaporated at low pressure, and the mixture was poured into water. Next, the mixture was extracted with CH₂Cl₂ and then chromatographed to give the complex **Ir-2m** with 66% yield.

2.5 General procedure for the preparation of dihydropyridin-2(1H)-ones *via* cycloaddition reaction with 1-azadienes and homophthalic anhydride.

To a solution of propargylamine (1.0 mmol) and Bu₄NOAc (2.0 mmol) in CH₃CN (10 mL), the reaction mixture was stirred at 80 °C under air for 12 h. After cooling to room temperature, homophthalic anhydride (1.0 mmol) was added, and the mixture was stirred at room temperature under air for 12 h. After removing the solvent with vacuum distillation, the crude mixture was purified by flash column chromatography to afford the target product.

3. Supplementary data

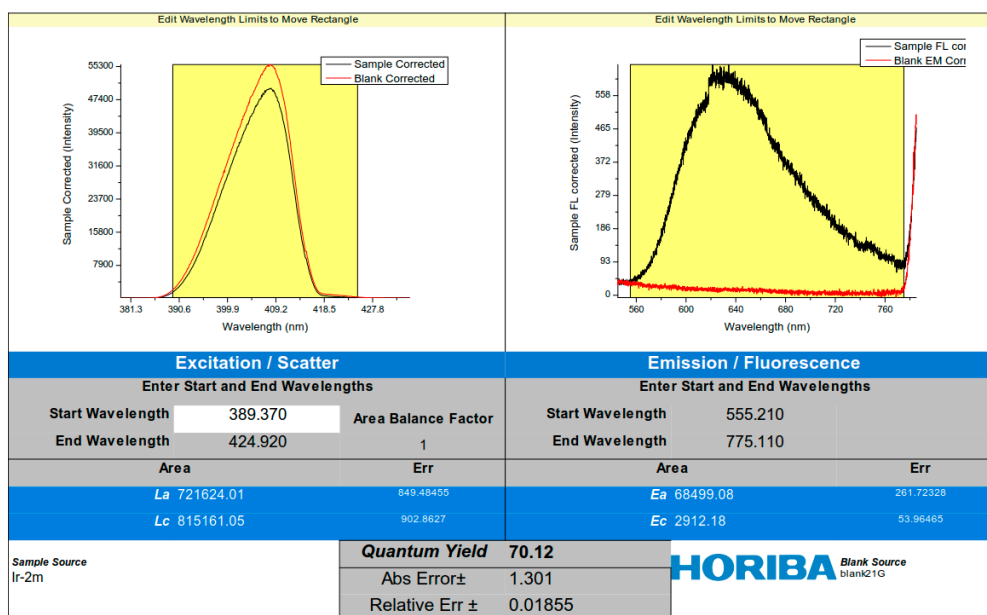
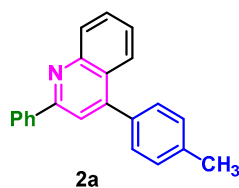


Figure S1 The photoluminescence quantum yield (PLQY) of **Ir-2m**.

4. Characterization data

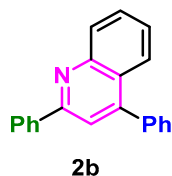


phenyl-4-(p-tolyl)quinoline (2a): White solid, 23.7 mg, 81% yield (Eluent: petroleum ether/ethyl acetate = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.22 – 8.15 (m, 2H), 7.97 – 7.84 (m, 1H), 7.81 (s, 1H), 7.73 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.57 – 7.39 (m, 6H), 7.36 (d, *J* = 7.8 Hz, 2H), 2.48 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 156.9, 149.3, 148.8, 139.7, 138.4, 135.5, 130.1, 129.5, 129.5, 129.3, 128.9, 128.2, 127.6, 126.3, 125.9, 125.7, 119.4, 21.3.

HRMS (ESI) *m/z* calcd for C₂₂H₁₇N [M+H]: 296.1439, found: 296.1439.

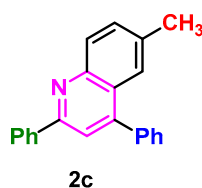


2,4-diphenylquinoline (2b): Light yellow solid, 19.7 mg, 72% yield (Eluent: petroleum ether/ethyl acetate = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 8.25 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.22 – 8.16 (m, 2H), 7.91 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.82 (s, 1H), 7.74 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.61 – 7.51 (m, 7H), 7.52 – 7.46 (m, 1H), 7.49 – 7.42 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 156.9, 149.2, 148.8, 139.7, 138.4, 130.1, 129.6, 129.5, 129.3, 128.8, 128.6, 128.4, 127.6, 126.3, 125.8, 125.6, 123.5, 119.4, 115.9.

HRMS (ESI) *m/z* calcd for C₂₁H₁₅N [M+H]: 282.1283, found: 282.1283.

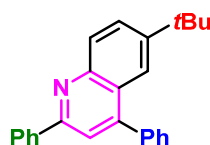


methyl-2,4-diphenylquinoline (2c): Faint yellow solid, 23.4 mg, 78% yield (Eluent: petroleum ether/ethyl acetate = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 8.21 – 8.10 (m, 3H), 7.78 (s, 1H), 7.65 (s, 1H), 7.56 (d, *J* = 4.4 Hz, 5H), 7.52 (dd, *J* = 8.2, 6.3 Hz, 3H), 7.49 – 7.40 (m, 1H), 2.48 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 156.0, 148.5, 147.4, 139.8, 138.6, 136.3, 131.8, 129.8, 129.6, 129.2, 128.8, 128.6, 128.3, 127.5, 125.7, 124.4, 119.4, 21.8.

HRMS (ESI) *m/z* calcd for C₂₂H₁₇N [M+H]: 296.1439, found: 296.1439.



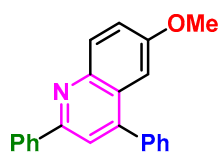
2d

6-(tert-butyl)-2,4-diphenylquinoline (2d): Light yellow solid, 23.6 mg, 70% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 8.23 – 8.13 (m, 3H), 7.90 – 7.76 (m, 3H), 7.63 – 7.39 (m, 8H), 1.35 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.3, 149.2, 149.0, 138.6, 129.6, 129.6, 129.2, 128.8, 128.6, 128.4, 128.4, 127.5, 125.3, 120.5, 119.5, 35.1, 31.2.

HRMS (ESI) *m/z* calcd for C₂₅H₂₃N [M+H]: 338.1909, found: 338.1910.



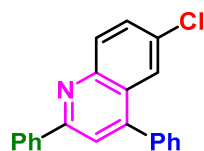
2e

6-methoxy-2,4-diphenylquinoline (2e): Light yellow solid, 24.8 mg, 79% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 8.19 – 8.11 (m, 3H), 7.77 (s, 1H), 7.58 (s, 1H), 7.59 – 7.52 (m, 2H), 7.55 – 7.43 (m, 4H), 7.47 – 7.33 (m, 2H), 7.19 (d, *J* = 2.8 Hz, 1H), 3.80 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.8, 154.7, 147.8, 144.9, 139.8, 138.7, 131.6, 129.4, 129.0, 128.8, 128.7, 128.4, 127.3, 126.7, 121.8, 119.7, 103.7, 55.5.

HRMS (ESI) *m/z* calcd for C₂₂H₁₇NO [M+H]: 312.1388, found: 312.1388.



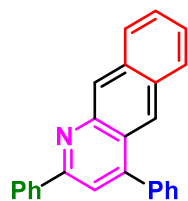
2f

6-chloro-2,4-diphenylquinoline (2f): White solid, 22.3 mg, 73% yield (Eluent: petroleum ether/ethyl acetate = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 8.22 – 8.14 (m, 3H), 7.89 – 7.82 (m, 2H), 7.67 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.62 – 7.48 (m, 7H), 7.52 – 7.40 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 157.1, 148.5, 147.2, 139.2, 137.8, 132.2, 131.7, 130.5, 129.6, 129.4, 128.9, 128.8, 128.7, 127.5, 126.5, 124.5, 120.1.

HRMS (ESI) *m/z* calcd for C₂₁H₁₄ClN [M+H]: 316.0893, found: 316.0893.



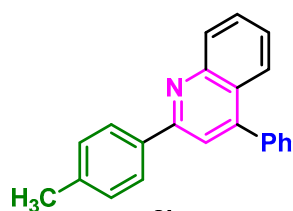
2g

2,4-diphenylbenzo[g]quinoline (2g): Light yellow solid, 23.2 mg, 71% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 8.27 – 8.19 (m, 2H), 8.13 (d, *J* = 9.0 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.81 (s, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.60 – 7.42 (m, 9H), 7.16 (ddd, *J* = 8.6, 7.0, 1.5 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 155.5, 149.8, 149.2, 143.0, 139.1, 132.9, 131.5, 129.8, 129.3, 129.3, 129.2, 128.9, 128.6, 128.4, 128.1, 128.1, 127.4, 126.5, 125.5, 122.8, 121.8.

HRMS (ESI) *m/z* calcd for C₂₅H₁₇N [M+H]: 332.1439, found: 332.1439.



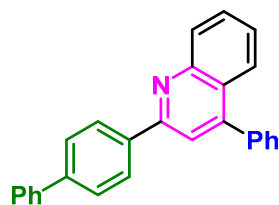
2h

4-phenyl-2-(p-tolyl)quinoline (2h): Faint yellow solid, 20.9 mg, 73% yield (Eluent: petroleum ether/ethyl acetate = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 8.23 (dd, *J* = 8.6, 1.2 Hz, 1H), 8.13 – 8.06 (m, 2H), 7.89 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.82 – 7.68 (m, 2H), 7.60 – 7.40 (m, 6H), 7.33 (d, *J* = 8.1 Hz, 2H), 2.43 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 156.9, 149.1, 148.8, 139.5, 138.5, 136.9, 130.1, 129.6, 129.5, 128.6, 128.4, 128.1, 127.5, 126.2, 125.7, 125.6, 119.2, 21.4.

HRMS (ESI) *m/z* calcd for C₂₂H₁₇N [M+H]: 296.1439, found: 296.1438.



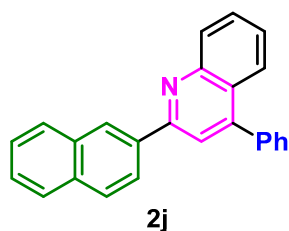
2i

2-([1,1'-biphenyl]-4-yl)-4-phenylquinoline (2i): Light yellow solid, 28.7 mg, 81% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 8.32 – 8.23 (m, 3H), 7.99 – 7.85 (m, 2H), 7.83 – 7.65 (m, 5H), 7.58 (s, 2H), 7.57 – 7.51 (m, 2H), 7.53 – 7.44 (m, 3H), 7.50 – 7.31 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 156.5, 149.2, 148.9, 142.1, 140.6, 138.5, 138.4, 130.1, 129.6, 128.8, 128.6, 128.5, 128.0, 127.6, 127.6, 127.2, 126.4, 125.8, 125.7, 119.3.

HRMS (ESI) m/z calcd for $C_{27}H_{19}N$ $[M+H]^+$: 358.1596, found: 358.1596.

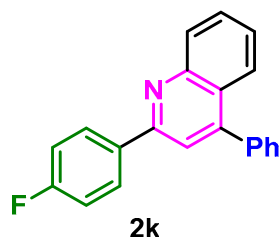


(naphthalen-2-yl)-4-phenylquinoline (2j): Light yellow solid, 23.6 mg, 74% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

1H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 1.7 Hz, 1H), 8.41 (dd, J = 8.6, 1.8 Hz, 1H), 8.30 (dd, J = 8.6, 1.2 Hz, 1H), 8.04 – 7.84 (m, 5H), 7.76 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.67 – 7.45 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 149.3, 148.9, 138.5, 136.9, 133.9, 133.5, 130.1, 129.6, 129.5, 128.8, 128.6, 128.6, 128.5, 127.7, 127.2, 126.7, 126.4, 126.3, 125.8, 125.7, 125.1, 124.5, 119.5.

HRMS (ESI) m/z calcd for $C_{25}H_{17}N$ $[M+H]^+$: 332.1439, found: 332.1439.



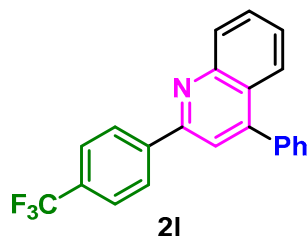
(4-fluorophenyl)-4-phenylquinoline (2k): Faint yellow solid, 23.7 mg, 78% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

1H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.15 (m, 3H), 7.91 (dd, J = 8.4, 1.4 Hz, 1H), 7.80 – 7.70 (m, 2H), 7.56 (s, 3H), 7.60 – 7.50 (m, 2H), 7.48 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.26 – 7.16 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 149.4, 148.8, 138.3, 135.8, 130.0, 129.7, 129.6, 129.5, 129.4, 128.7, 128.5, 126.4, 125.7, 119.0, 115.9, 115.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.45.

HRMS (ESI) m/z calcd for $C_{21}H_{14}FN$ $[M+H]^+$: 300.1189, found: 300.1190.



3-phenyl-2-(4-(trifluoromethyl)phenyl)quinoline (2l): Light yellow solid, 24.6 mg, 72% yield (Eluent: petroleum ether/ethyl acetate = 50/1).

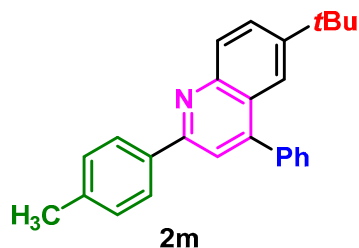
1H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.30 (m, 2H), 8.27 (d, J = 8.4 Hz, 1H), 7.94 (dd, J = 8.5, 1.4 Hz, 1H), 7.84 (s, 1H), 7.78 (dd, J = 8.5, 6.8 Hz, 3H), 7.60 – 7.45 (m,

6H).

¹³C NMR (101 MHz, CDCl₃) δ 138.1, 130.2, 129.9, 129.6, 128.7, 128.6, 127.9, 127.0, 126.1, 125.8, 125.8, 119.2, 29.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -62.56.

HRMS (ESI) *m/z* calcd for C₂₂H₁₄F₃N [M+H]: 350.1157, found: 350.1156.

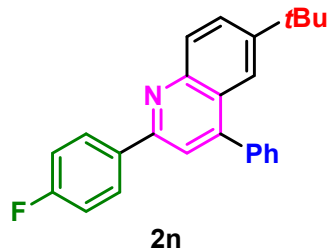


6-(tert-butyl)-4-phenyl-2-(p-tolyl)quinoline (2m): Light yellow solid, 28.3 mg, 82% yield (Eluent: petroleum ether/ethyl acetate = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 8.8 Hz, 1H), 8.11 – 8.04 (m, 2H), 7.88 – 7.79 (m, 2H), 7.77 (s, 1H), 7.62 – 7.55 (m, 3H), 7.58 – 7.46 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 1.35 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.3, 149.0, 148.8, 147.4, 139.2, 138.7, 137.1, 129.6, 129.6, 128.6, 128.3, 127.4, 125.2, 120.5, 119.3, 35.1, 31.2, 21.4.

HRMS (ESI) *m/z* calcd for C₂₆H₂₅N [M+H]: 352.2065, found: 352.2065.



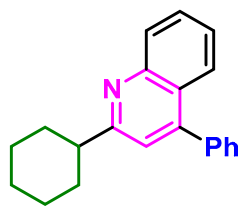
6-(tert-butyl)-2-(4-fluorophenyl)-4-phenylquinoline (2n): Light yellow solid, 24.9 mg, 71% yield (Eluent: petroleum ether/ethyl acetate = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 8.21 – 8.12 (m, 3H), 7.88 – 7.80 (m, 2H), 7.73 (s, 1H), 7.62 – 7.52 (m, 4H), 7.52 (ddd, *J* = 6.6, 5.3, 2.6 Hz, 1H), 7.25 – 7.14 (m, 2H), 1.35 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 165.0, 162.5, 155.3, 149.3, 149.2, 147.3, 138.6, 136.0, 136.0, 129.5, 129.4, 129.3, 128.6, 128.6, 128.4, 125.2, 120.6, 119.1, 115.9, 115.6, 35.1, 31.2.

¹⁹F NMR (376 MHz, CDCl₃) δ -112.78.

HRMS (ESI) *m/z* calcd for C₂₅H₂₂FN [M+H]: 356.1815, found: 356.1815.



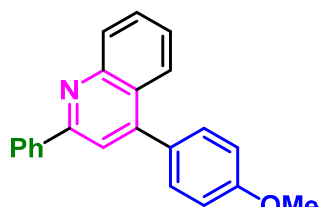
2o

2-cyclohexyl-4-phenylquinoline (2o): White solid, 20.2mg, 81% yield (Eluent: petroleum ether/ethyl acetate = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 8.10 – 8.01 (m, 1H), 7.79 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.50 – 7.38 (m, 6H), 7.19 (d, *J* = 4.8 Hz, 2H), 2.04 – 1.95 (m, 3H), 1.85 – 1.80 (m, 3H), 1.58 (dd, *J* = 12.4, 3.4 Hz, 2H), 1.42 – 1.37 (m, 2H), 1.18 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 166.4, 148.7, 148.2, 138.5, 129.6, 129.3, 129.2, 128.5, 128.3, 125.7, 125.6, 125.6, 119.9, 47.7, 32.9, 29.7, 26.6, 26.1.

HRMS (ESI) *m/z* calcd for C₂₁H₂₁N [M+H]: 288.1752, found: 288.1752.



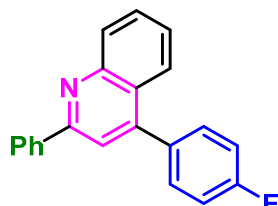
2p

4-(4-methoxyphenyl)-2-phenylquinoline (2p): Light yellow solid, 23.3 mg, 75% yield (Eluent: petroleum ether/ethyl acetate = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.5 Hz, 1H), 8.22 – 8.15 (m, 2H), 7.96 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.80 (s, 1H), 7.73 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.58 – 7.46 (m, 6H), 7.13 – 7.05 (m, 2H), 3.92 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.9, 156.9, 148.9, 139.7, 130.8, 130.7, 130.1, 129.5, 129.3, 128.8, 127.6, 126.2, 126.0, 125.7, 119.3, 114.1, 55.4.

HRMS (ESI) *m/z* calcd for C₂₂H₁₇NO [M+H]: 312.1388, found: 312.1388.



2q

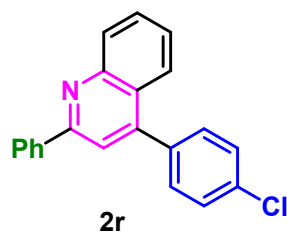
4-(4-fluorophenyl)-2-phenylquinoline (2q): Light yellow solid, 20.9 mg, 71% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 8.26 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.25 – 8.15 (m, 2H), 7.88 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.81 (s, 1H), 7.75 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.58 – 7.41 (m, 5H), 7.35 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.29 (dt, *J* = 9.4, 2.1 Hz, 1H), 7.26 – 7.12 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 164.0, 161.6, 156.9, 148.8, 147.8, 147.8, 140.6, 140.5, 139.5, 130.3, 130.2, 129.8, 129.5, 128.9, 127.6, 126.6, 125.4, 125.4, 125.4, 125.3, 119.3, 116.8, 116.6, 115.5, 115.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -112.48.

HRMS (ESI) *m/z* calcd for C₂₁H₁₄FN [M+H]: 300.1189, found: 300.1189.

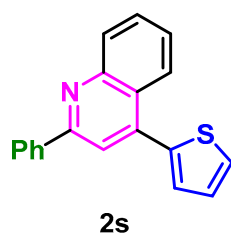


4-(4-chlorophenyl)-2-phenylquinoline (2r): Light yellow solid, 22.2 mg, 71% yield (Eluent: petroleum ether/ethyl acetate = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.22 – 8.15 (m, 2H), 7.85 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.81 – 7.65 (m, 2H), 7.58 – 7.43 (m, 8H).

¹³C NMR (101 MHz, CDCl₃) δ 156.9, 148.8, 147.9, 139.5, 136.8, 134.7, 130.9, 130.3, 129.7, 129.5, 128.9, 127.6, 126.6, 125.5, 125.3, 119.3.

HRMS (ESI) *m/z* calcd for C₂₁H₁₄ClN [M+H]: 316.0893, found: 316.0893.

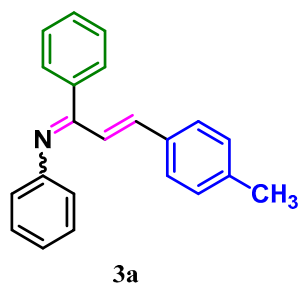


2-phenyl-4-(thiophen-2-yl)quinoline (2s): Light yellow solid, 20.3 mg, 72% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 8.26 (ddd, *J* = 14.2, 8.5, 1.4 Hz, 2H), 8.21 – 8.14 (m, 2H), 7.92 (s, 1H), 7.75 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.59 – 7.40 (m, 6H), 7.25 (t, *J* = 4.3 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 156.9, 149.0, 141.5, 139.4, 139.2, 130.2, 129.7, 129.4, 128.9, 128.5, 127.8, 127.6, 127.2, 126.7, 125.4, 125.3, 119.8.

HRMS (ESI) *m/z* calcd for C₁₉H₁₃NS [M+H]: 288.0847, found: 288.0847.

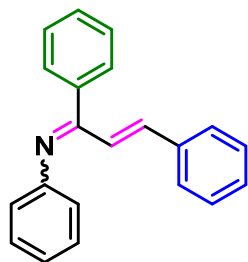


(2E)-N,1-diphenyl-3-(p-tolyl)prop-2-en-1-imine (3a): Light yellow solid, 26.8 mg, 91% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.69 (m, 2H), 7.47 (dd, *J* = 4.1, 1.8 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.22 – 7.08 (m, 6H), 6.93 – 6.85 (m, 2H), 2.34 (d, *J* = 11.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.3 (C=N), 151.0, 141.7, 132.9, 129.8, 129.5, 129.5, 129.4, 128.8, 128.3, 127.5, 127.5, 123.8, 120.8, 21.4.

HRMS (ESI) *m/z* calcd for C₂₂H₁₉N [M+H]: 298.1596, found: 298.1594.



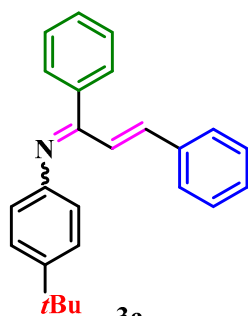
3b

(2E)-N,1,3-triphenylprop-2-en-1-imine(3b): Light yellow solid, 25.3 mg, 88% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 7.75 (t, *J* = 2.0 Hz, 1H), 7.49 (q, *J* = 1.4 Hz, 3H), 7.37 (s, 1H), 7.30 (d, *J* = 9.6 Hz, 7H), 7.13 – 7.11 (m, 1H), 6.97 (d, *J* = 1.3 Hz, 1H), 6.92 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 167.2 (C=N), 150.9, 141.7, 139.4, 135.7, 131.6, 129.4, 129.4, 128.9, 128.8, 128.4, 127.5, 124.0, 121.9, 120.8.

HRMS (ESI) *m/z* calcd for C₂₁H₁₇N [M+H]: 284.1439, found: 284.1441.



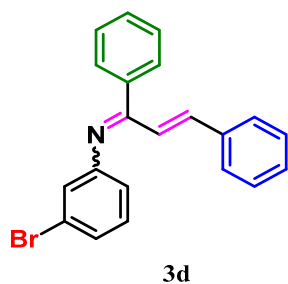
3c

(2E)-N-(4-(tert-butyl)phenyl)-1,3-diphenylprop-2-en-1-imine (3c): Light yellow solid, 28.3 mg, 85% yield (Eluent: petroleum ether/ethyl acetate = 30/1).

¹H NMR (400 MHz, CDCl₃) δ 7.74 (t, *J* = 2.0 Hz, 1H), 7.48 (t, *J* = 1.7 Hz, 2H), 7.39 – 7.30 (m, 8H), 6.98 – 6.92 (m, 3H), 1.36 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 166.9 (C=N), 148.1, 146.9, 141.3, 139.7, 135.9, 132.0, 129.8, 129.4, 128.8, 128.3, 127.5, 125.7, 122.3, 120.8, 34.4, 31.5.

HRMS (ESI) *m/z* calcd for C₂₅H₂₅N [M+H]: 340.2065, found: 340.2063.

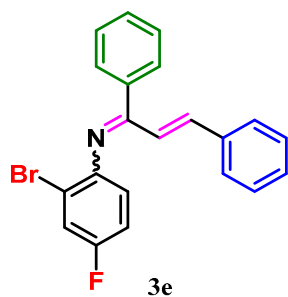


(2E)-N-(3-bromophenyl)-1,3-diphenylprop-2-en-1-imine (3d): Light yellow solid, 32.7 mg, 92% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 2.0 Hz, 2H), 7.50 (s, 3H), 7.34 – 7.29 (m, 2H), 7.14 (t, *J* = 2.1 Hz, 2H), 6.94 (s, 2H), 6.86 (d, *J* = 2.6 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 168.0 (C=N), 152.4, 142.7, 138.9, 135.4, 131.1, 130.3, 129.3, 128.9, 128.4, 127.6, 126.8, 124.1, 123.6, 122.7, 121.3, 119.3.

HRMS (ESI) *m/z* calcd for C₂₁H₁₆BrN [M+H]: 362.0544, found: 362.0546.



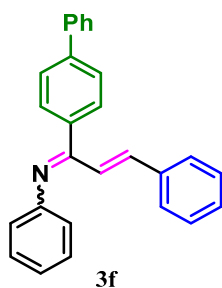
(2E)-N-(2-bromo-4-fluorophenyl)-1,3-diphenylprop-2-en-1-imine (3e): Light yellow solid, 34.2 mg, 91% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 7.80 (t, *J* = 1.6 Hz, 2H), 7.50 (d, *J* = 7.0 Hz, 5H), 7.32 (d, *J* = 11.7 Hz, 1H), 7.24 (d, *J* = 11.8 Hz, 2H), 6.95 (s, 1H), 6.87 – 6.84 (m, 1H), 6.73 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 169.3 (C=N), 157.6, 142.9, 138.5, 135.4, 130.7, 130.2, 129.8, 129.3, 128.9, 128.4, 128.2, 127.7, 121.5, 121.1, 119.9, 115.1, 114.9.

¹⁹F NMR (376 MHz, CDCl₃) δ -118.89.

HRMS (ESI) *m/z* calcd for C₂₁H₁₅BrFN [M+H]: 380.0450, found: 380.0453.

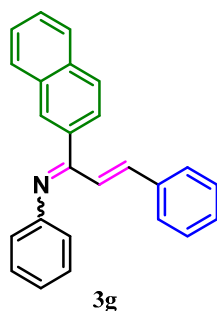


(2E)-1-([1,1'-biphenyl]-4-yl)-N,3-diphenylprop-2-en-1-imine (3f): Light yellow solid, 32.1mg, 87% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.80 (m, 1H), 7.77 – 7.57 (m, 4H), 7.59 – 7.48 (m, 1H), 7.50 – 7.38 (m, 3H), 7.42 – 7.32 (m, 3H), 7.35 – 7.28 (m, 3H), 7.21 – 7.12 (m, 1H), 7.06 – 6.88 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.8 (C=N), 150.9, 144.8, 142.8, 141.6, 140.5, 139.9, 135.7, 129.9, 129.4, 128.9, 128.8, 128.2, 127.5, 127.2, 127.1, 124.0, 122.0, 120.9.

HRMS (ESI) *m/z* calcd for C₂₇H₂₁N [M+H]: 360.1752, found: 360.1754.

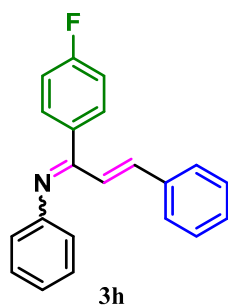


(2E)-1-(naphthalen-2-yl)-N,3-diphenylprop-2-en-1-imine (3g): Light yellow solid, 28.2 mg, 84% yield (Eluent: petroleum ether/ethyl acetate = 30/1).

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 1.7 Hz, 1H), 7.96 – 7.91 (m, 3H), 7.71 – 7.68 (m, 1H), 7.40 – 7.24 (m, 9H), 6.99 (d, *J* = 7.6 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.1 (C=N), 151.0, 144.8, 141.7, 136.8, 135.7, 134.1, 129.4, 128.9, 128.8, 128.8, 127.7, 127.5, 126.4, 124.0, 122.2, 120.8.

HRMS (ESI) *m/z* calcd for C₂₅H₁₉N [M+H]: 334.1596, found: 334.1593.



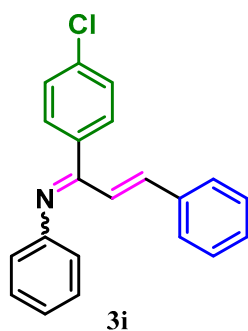
(2E)-1-(4-fluorophenyl)-N,3-diphenylprop-2-en-1-imine (3h): Light yellow solid, 27.4 mg, 93% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 3.4 Hz, 1H), 7.37 – 7.24 (m, 6H), 7.16 (d, *J* = 1.7 Hz, 3H), 6.94 (t, *J* = 1.1 Hz, 2H), 6.89 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 166.0 (C=N), 150.8, 141.6, 135.5, 131.4, 131.3, 129.5, 128.9, 128.9, 127.5, 124.1, 121.9, 120.8, 115.5, 115.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -110.92.

HRMS (ESI) *m/z* calcd for C₂₁H₁₆FN [M+H]: 302.1345, found: 302.1347.

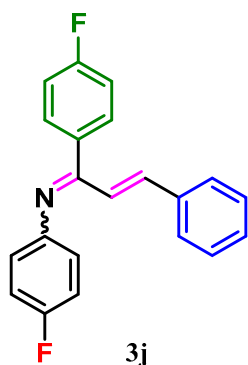


(2E)-1-(4-chlorophenyl)-N,3-diphenylprop-2-en-1-imine (3i): Light yellow solid, 28.5 mg, 90% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.59 (m, 2H), 7.46 – 7.23 (m, 6H), 7.21 – 7.15 (m, 1H), 7.07 (dt, *J* = 6.0, 2.6 Hz, 1H), 6.91 – 6.79 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 165.0 (C=N), 149.6, 140.6, 136.8, 135.0, 134.4, 129.7, 129.4, 128.6, 127.9, 127.8, 127.6, 126.5, 123.1, 119.7.

HRMS (ESI) *m/z* calcd for C₂₁H₁₆ClN [M+H]: 318.1050, found: 318.1046.



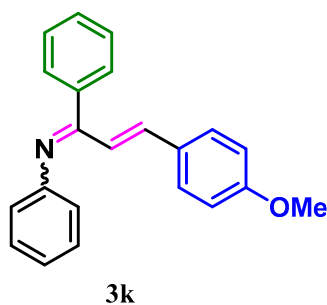
(2E)-N,1-bis(4-fluorophenyl)-3-phenylprop-2-en-1-imine (3j): Light yellow solid, 25.5 mg, 81% yield (Eluent: petroleum ether/ethyl acetate = 30/1).

¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.02 (m, 1H), 7.76 – 7.73 (m, 1H), 7.42 (d, *J* = 3.0 Hz, 1H), 7.33 (s, 4H), 7.22 – 7.15 (m, 2H), 7.10 – 6.99 (m, 2H), 6.90 (t, *J* = 6.1 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 166.7 (C=N), 146.8, 141.9, 135.4, 134.8, 131.3, 130.7, 129.7, 128.9, 127.5, 122.2, 121.7, 115.8, 115.5, 115.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -110.63, -119.57.

HRMS (ESI) *m/z* calcd for C₂₁H₁₅F₂N [M+H]: 320.1251, found: 320.1253.

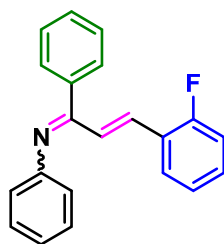


(2E)-3-(4-methoxyphenyl)-N,1-diphenylprop-2-en-1-imine (3k): Light yellow solid, 28.3 mg, 92% yield (Eluent: petroleum ether/ethyl acetate = 30/1).

¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.69 (m, 2H), 7.52 – 7.47 (m, 3H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.16 – 7.11 (m, 2H), 6.87 – 6.80 (m, 3H), 3.79 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.5 (C=N), 160.7, 151.0, 141.5, 139.5, 129.7, 129.4, 129.0, 128.8, 128.6, 128.3, 123.8, 120.8, 119.7, 114.2, 55.3.

HRMS (ESI) *m/z* calcd for C₂₂H₁₉NO [M+H]: 314.1545, found: 313.2672.



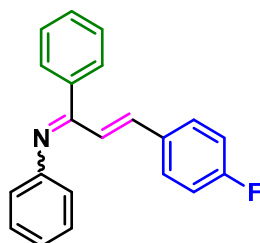
3l

(2E)-3-(2-fluorophenyl)-N,1-diphenylprop-2-en-1-imine (3l): Light yellow solid, 27.0 mg, 89% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.70 (m, 1H), 7.54 – 7.46 (m, 2H), 7.42 – 7.35 (m, 2H), 7.27 (dq, *J* = 13.9, 3.2 Hz, 2H), 7.19 – 7.04 (m, 3H), 6.98 (ddd, *J* = 16.0, 8.7, 1.2 Hz, 3H), 6.88 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 166.7 (C=N), 150.7, 140.2, 137.9, 133.0, 130.3, 130.3, 129.3, 128.9, 128.4, 124.2, 123.1, 120.7, 116.3, 116.1, 113.9, 113.7.

HRMS (ESI) *m/z* calcd for C₂₁H₁₆FN [M+H]: 302.1345, found: 302.1342.



3m

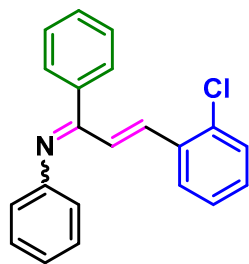
(2E)-3-(4-fluorophenyl)-N,1-diphenylprop-2-en-1-imine (3m): Light yellow solid, 26.8 mg, 86% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.70 (m, 1H), 7.56 – 7.44 (m, 2H), 7.41 – 7.21 (m, 4H), 7.20 – 7.04 (m, 3H), 7.02 – 6.86 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 166.7 (C=N), 161.8, 150.7, 140.2, 137.9, 132.9, 130.0, 129.3, 128.9, 128.9, 128.4, 123.1, 120.7, 116.1, 113.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -112.69.

HRMS (ESI) *m/z* calcd for C₂₁H₁₆FN [M+H]: 302.1345, found: 302.1348.



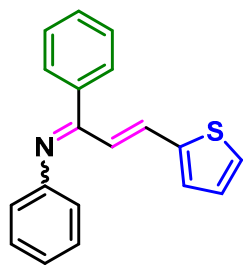
3n

(2E)-3-(2-chlorophenyl)-N,1-diphenylprop-2-en-1-imine (3n): Light yellow solid, 28.1 mg, 86% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 7.83 – 7.72 (m, 2H), 7.51 – 7.49 (m, 2H), 7.38 – 7.35 (m, 3H), 7.29 – 7.23 (m, 2H), 7.17 – 7.12 (m, 2H), 7.00 – 6.94 (m, 2H), 6.84 (d, *J* = 16.5 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 166.8 (C=N), 150.9, 139.0, 137.5, 134.3, 134.1, 130.2, 129.9, 129.4, 128.9, 128.6, 128.4, 127.3, 127.0, 124.4, 124.1, 120.7.

HRMS (ESI) *m/z* calcd for C₂₁H₁₆ClN [M+H]: 318.1050, found: 318.1042.



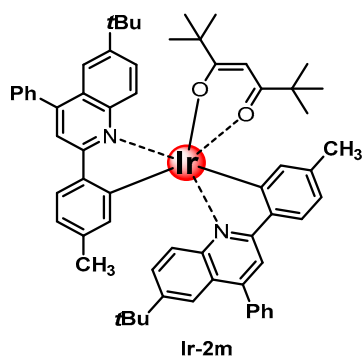
3o

(2E)-N,1-diphenyl-3-(thiophen-2-yl)prop-2-en-1-imine (3o): Light yellow solid, 24.6 mg, 85% yield (Eluent: petroleum ether/ethyl acetate = 40/1).

¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.66 (m, 1H), 7.52 – 7.43 (m, 2H), 7.41 – 7.23 (m, 3H), 7.18 – 6.83 (m, 6H), 6.74 – 6.62 (m, 1H).

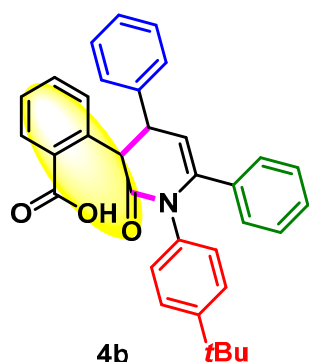
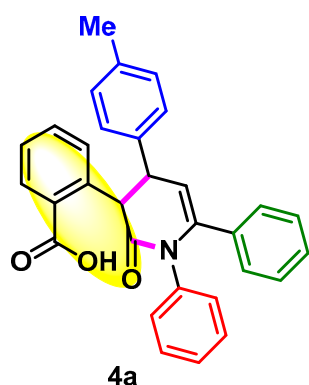
¹³C NMR (101 MHz, CDCl₃) δ 166.8 (C=N), 150.8, 141.0, 139.2, 137.2, 134.4, 132.8, 132.1, 129.3, 128.8, 128.4, 124.0, 121.0, 120.8.

HRMS (ESI) *m/z* calcd for C₁₉H₁₅NS [M+H]: 290.1003, found: 290.1001.



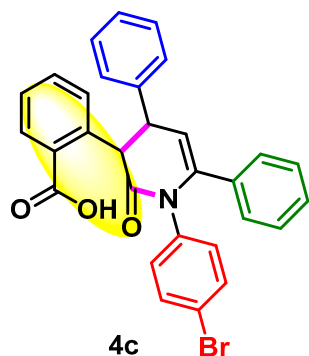
Ir-2m: red solid, 710.4 mg, 66% yield (Eluent: petroleum ether/dichloromethane = 10/1).

¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 9.2 Hz, 2H), 7.84 (s, 2H), 7.68 – 7.59 (m, 4H), 7.58 – 7.45 (m, 10H), 7.29 (dd, *J* = 9.2, 2.3 Hz, 2H), 6.68 (d, *J* = 7.9 Hz, 2H), 6.55 (s, 2H), 4.75 (s, 1H), 1.96 (s, 6H), 1.18 (s, 18H), 0.56 (s, 18H).



¹³C NMR (101 MHz, DMSO) δ 170.5, 169.3, 149.0, 142.4, 142.0, 139.4, 136.7, 136.5, 132.0, 131.1, 131.1, 128.9, 128.5, 128.3, 128.2, 128.2, 127.9, 127.4, 127.2, 125.3, 115.1, 45.0, 34.6, 31.5.

HRMS (ESI) *m/z* calcd for C₃₄H₃₁NO₃ [M+H]: 502.2382, found: 502.2381.

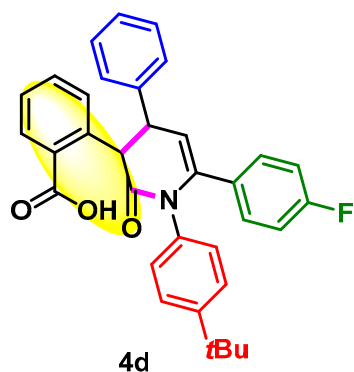


4c: Light yellow solid, 403.7 mg, 77% yield (Eluent: dichloromethane/methyl alcohol = 100/1).

¹H NMR (400 MHz, DMSO) δ 13.05 (s, 1H), 7.84 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.47 – 7.36 (m, 3H), 7.34 – 7.27 (m, 4H), 7.30 – 7.19 (m, 6H), 7.22 – 7.11 (m, 4H), 5.63 (d, *J* = 4.0 Hz, 1H), 5.11 (d, *J* = 9.7 Hz, 1H), 4.44 (dd, *J* = 9.7, 4.0 Hz, 1H).

¹³C NMR (101 MHz, DMSO) δ 170.4, 169.2, 142.4, 141.4, 139.3, 138.8, 136.2, 132.0, 131.6, 131.2, 131.1, 130.9, 128.9, 128.6, 128.4, 128.3, 128.1, 127.4, 127.3, 119.5, 115.6, 45.0.

HRMS (ESI) *m/z* calcd for C₃₀H₂₂BrNO₃ [M+H]: 524.0861, found: 524.0860.



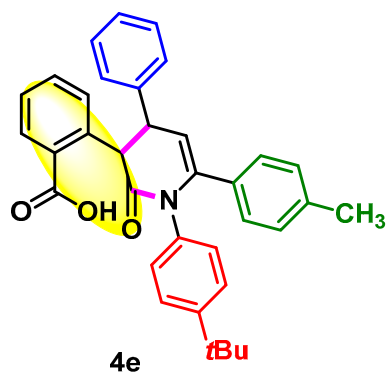
4d: White solid, 374.7 mg, 74% yield (Eluent: dichloromethane/methyl alcohol = 100/1).

¹H NMR (400 MHz, DMSO) δ 13.10 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.33 (m, 3H), 7.28 (dd, *J* = 14.6, 8.5 Hz, 8H), 7.18 (t, *J* = 7.1 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 5.61 (d, *J* = 4.2 Hz, 1H), 5.10 (d, *J* = 9.2 Hz, 1H), 4.45 – 4.37 (m, 1H), 1.20 (s, 9H).

¹³C NMR (101 MHz, DMSO) δ 170.3, 169.3, 163.0, 160.6, 149.2, 142.4, 141.0, 139.4, 136.6, 133.0, 132.9, 132.0, 131.2, 131.1, 130.2, 130.1, 128.9, 128.3, 128.2, 127.4, 127.2, 125.4, 115.5, 115.3, 115.1, 45.0, 34.7, 31.5.

¹⁹F NMR (376 MHz, DMSO) δ -113.86.

HRMS (ESI) m/z calcd for $C_{34}H_{30}FNO_3$ $[M+H]$: 520.2288, found: 520.2286.

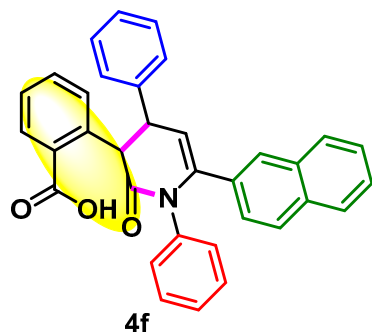


4e: Light yellow solid, 408.1 mg, 79% yield (Eluent: dichloromethane/methyl alcohol = 100/1).

1H NMR (400 MHz, DMSO) δ 13.07 (s, 1H), 7.83 (dd, J = 7.8, 1.4 Hz, 1H), 7.46 – 7.23 (m, 9H), 7.19 (dd, J = 10.5, 7.6 Hz, 3H), 7.10 (d, J = 8.3 Hz, 2H), 7.00 (d, J = 7.9 Hz, 2H), 5.57 (d, J = 4.4 Hz, 1H), 5.11 (d, J = 8.9 Hz, 1H), 4.35 (dd, J = 9.0, 4.4 Hz, 1H), 2.18 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (101 MHz, DMSO) δ 170.5, 169.3, 149.0, 141.9, 139.4, 137.5, 136.8, 133.6, 132.0, 131.2, 129.1, 128.9, 128.2, 128.1, 127.8, 127.4, 127.2, 125.4, 114.6, 44.9, 34.7, 31.5, 21.1.

HRMS (ESI) m/z calcd for $C_{35}H_{33}NO_3$ $[M+H]$: 516.2539, found: 516.2541.



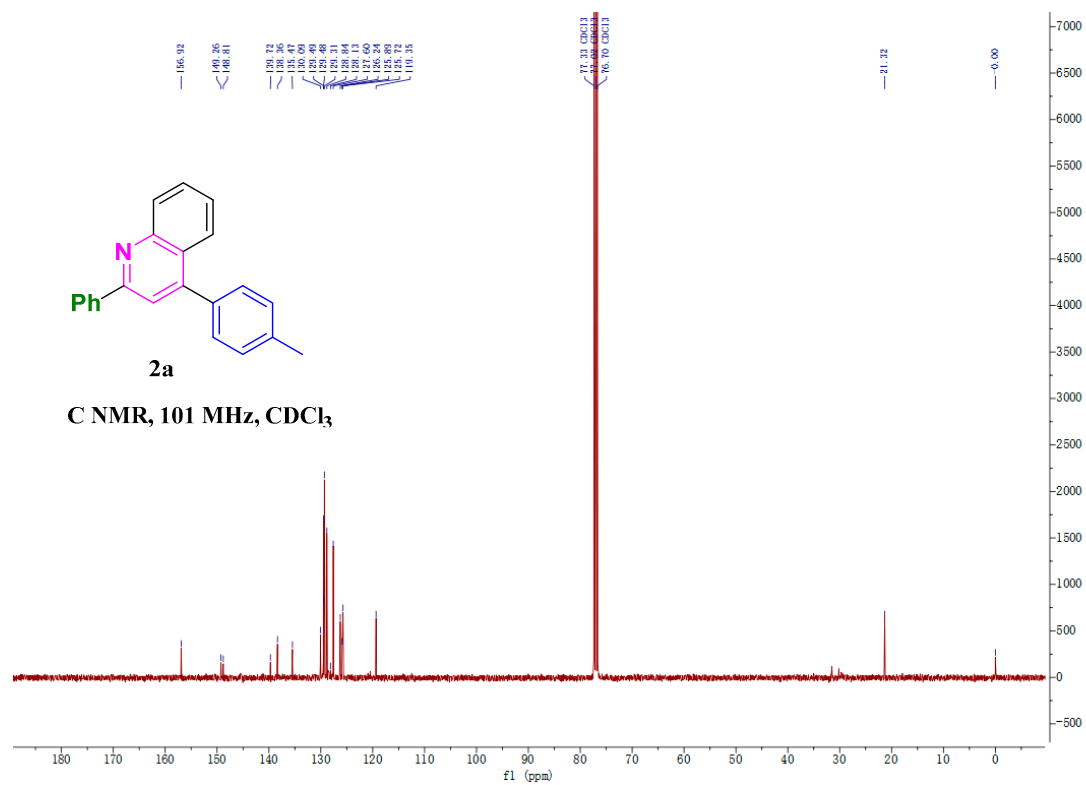
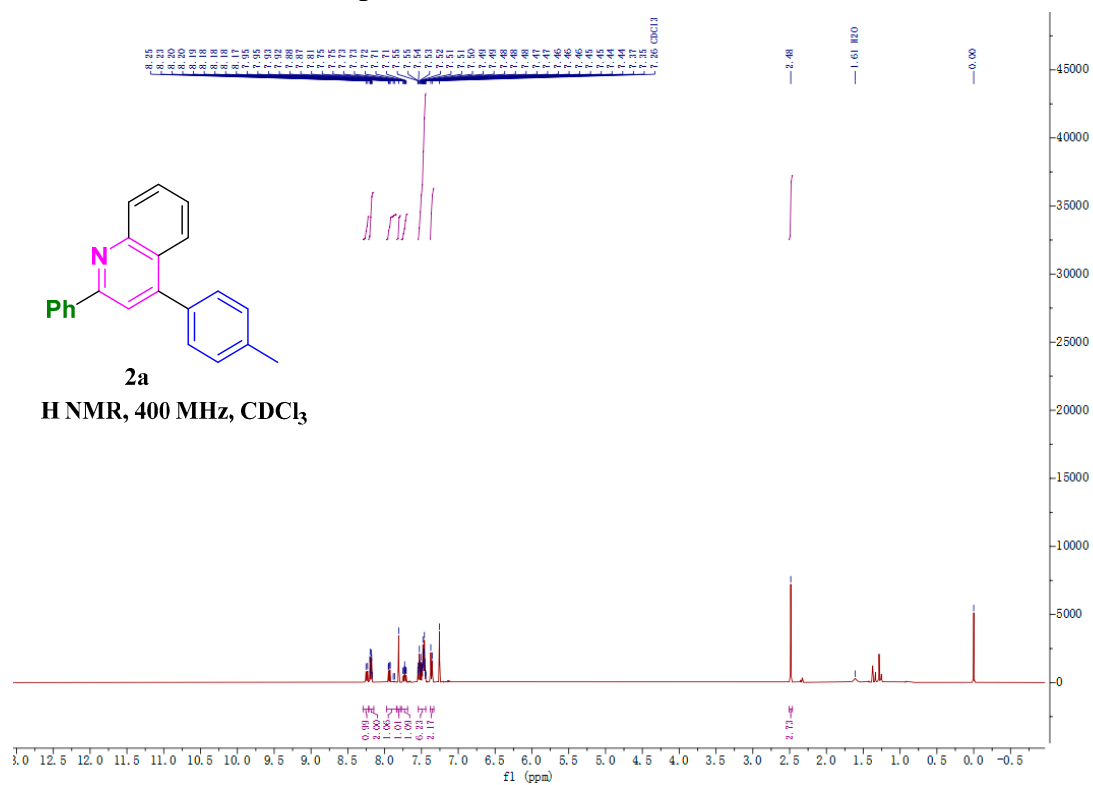
4f: Light yellow solid, 384.3 mg, 78% yield (Eluent: dichloromethane/methyl alcohol = 100/1).

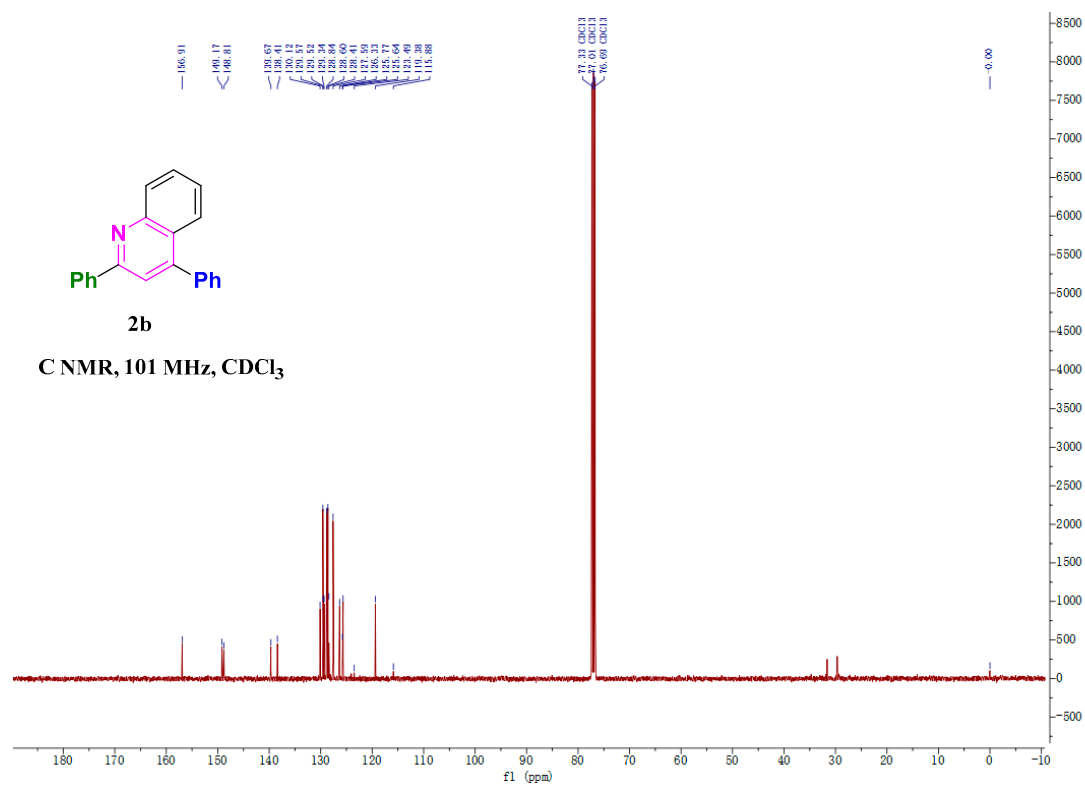
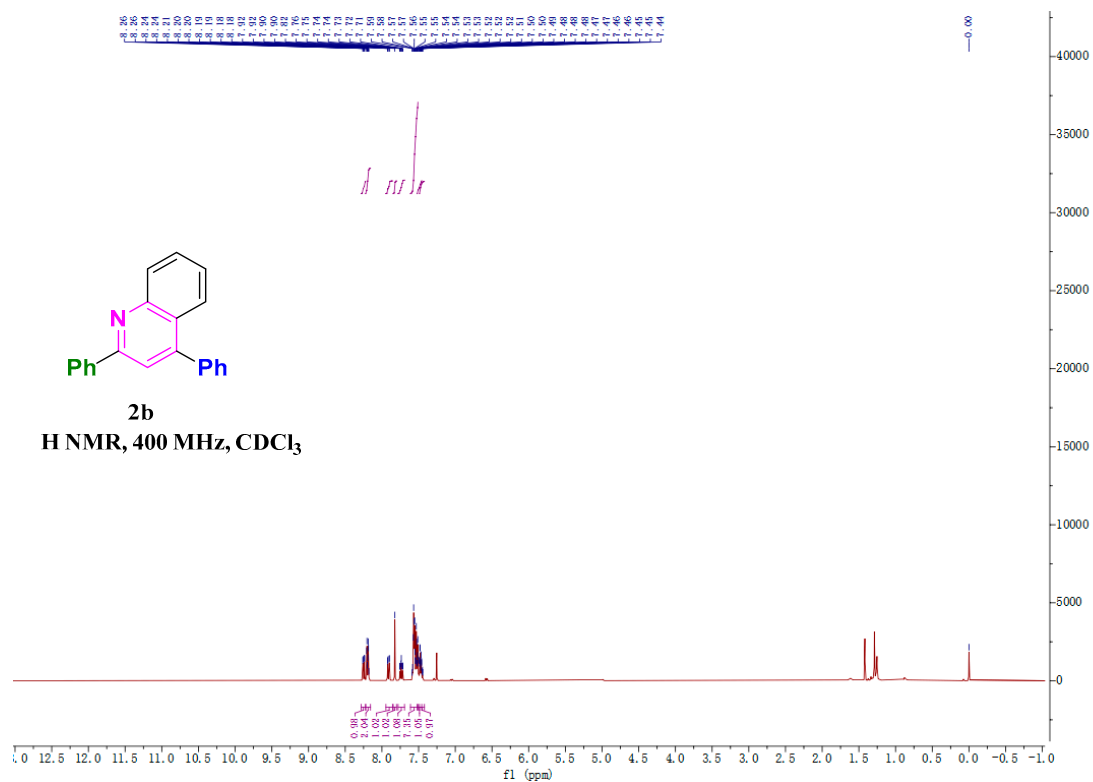
1H NMR (400 MHz, DMSO) δ 13.12 (s, 1H), 7.95 (s, 1H), 7.84 (dd, J = 12.0, 6.7 Hz, 2H), 7.81 – 7.75 (m, 1H), 7.68 (d, J = 8.6 Hz, 1H), 7.50 – 7.15 (m, 15H), 7.04 (t, J = 7.3 Hz, 1H), 5.76 (d, J = 4.2 Hz, 1H), 5.20 (d, J = 9.5 Hz, 1H), 4.49 (dd, J = 9.6, 4.2 Hz, 1H).

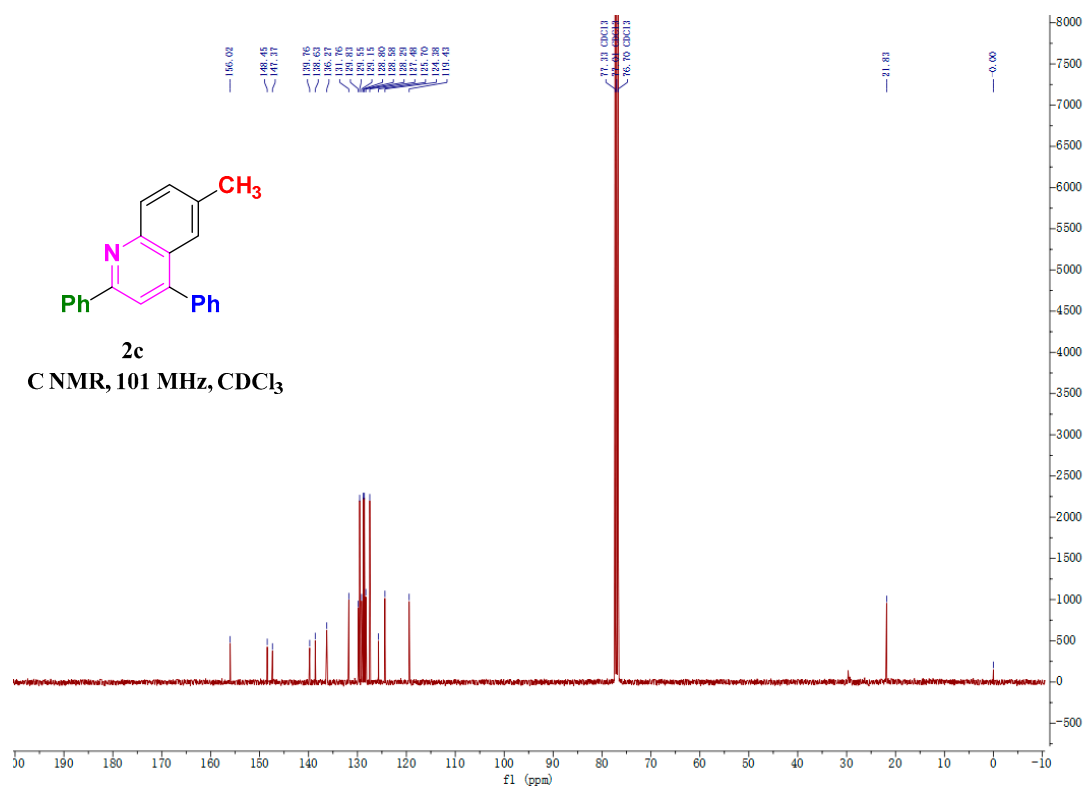
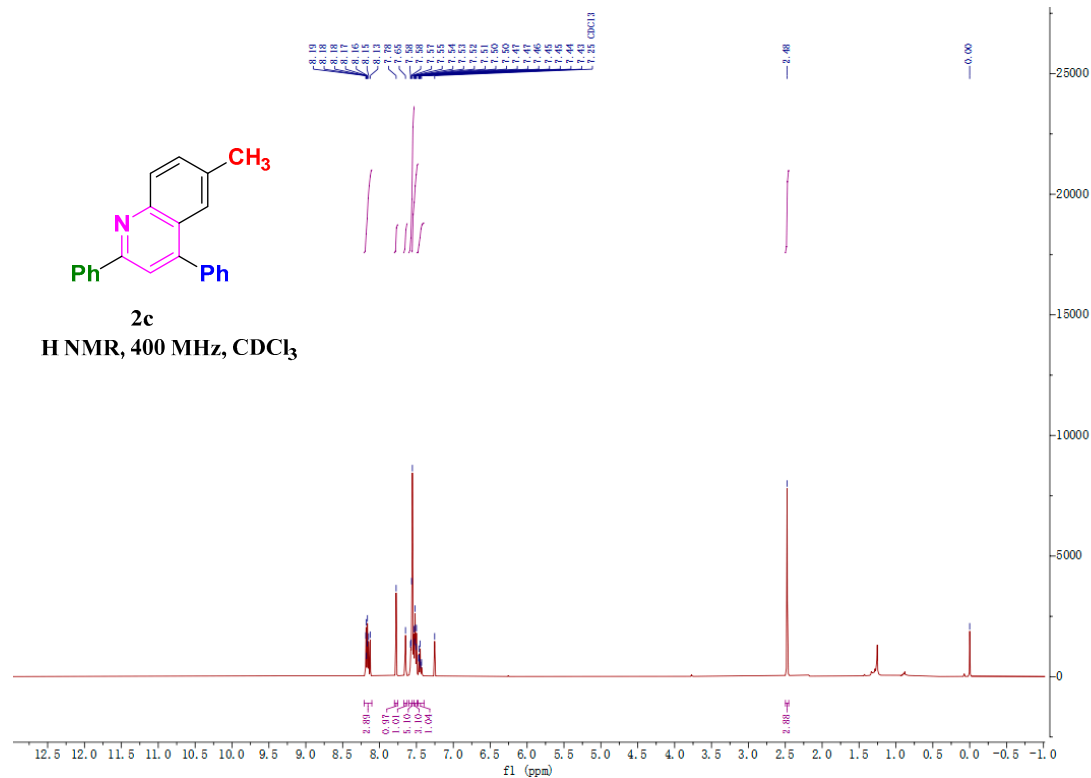
^{13}C NMR (101 MHz, DMSO) δ 170.4, 169.3, 142.5, 141.9, 139.4, 139.4, 134.0, 133.0, 132.6, 132.0, 131.2, 131.1, 129.0, 128.8, 128.6, 128.4, 128.3, 127.8, 127.7, 127.4, 127.3, 127.1, 126.9, 126.8, 125.8, 115.7, 45.1.

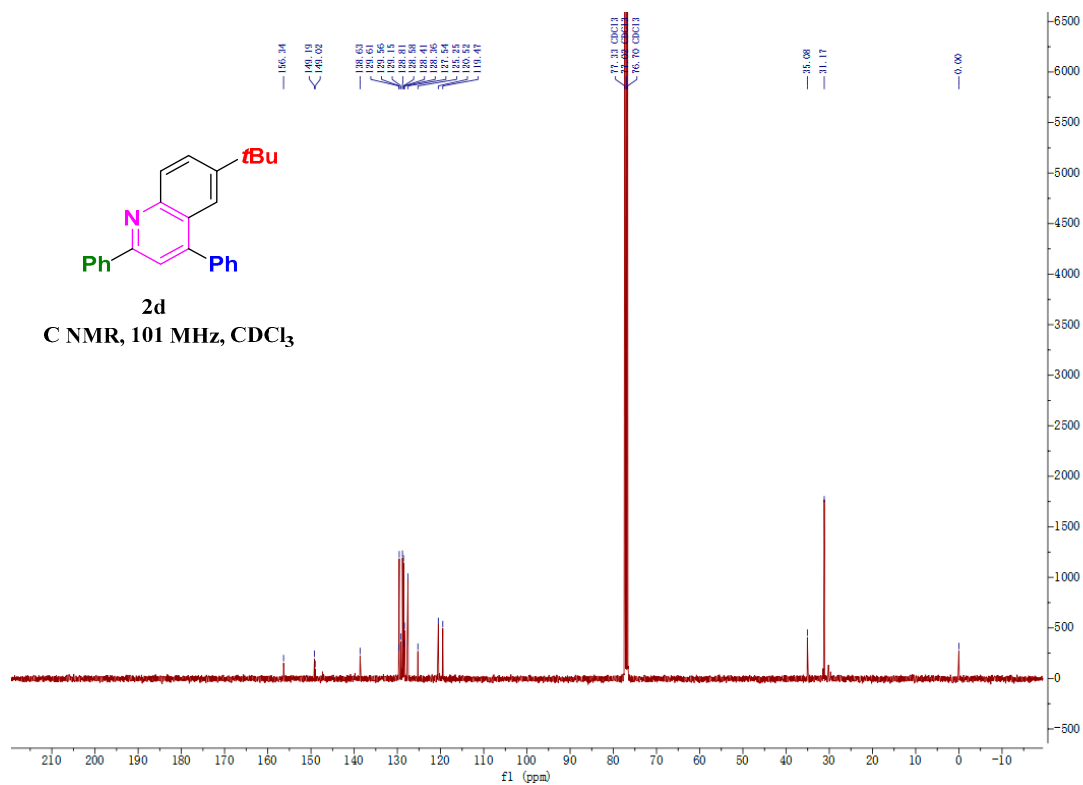
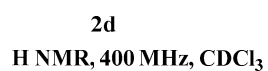
HRMS (ESI) m/z calcd for $C_{34}H_{25}NO_3$ $[M+H]$: 496.1913, found: 496.1916.

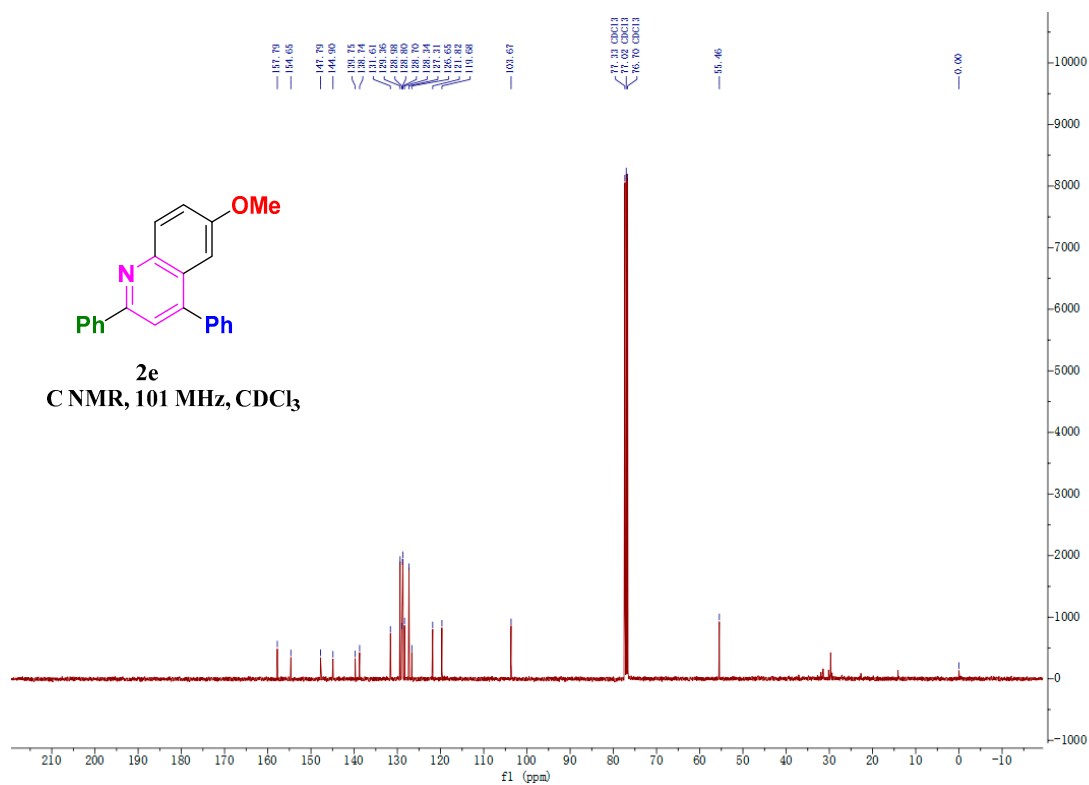
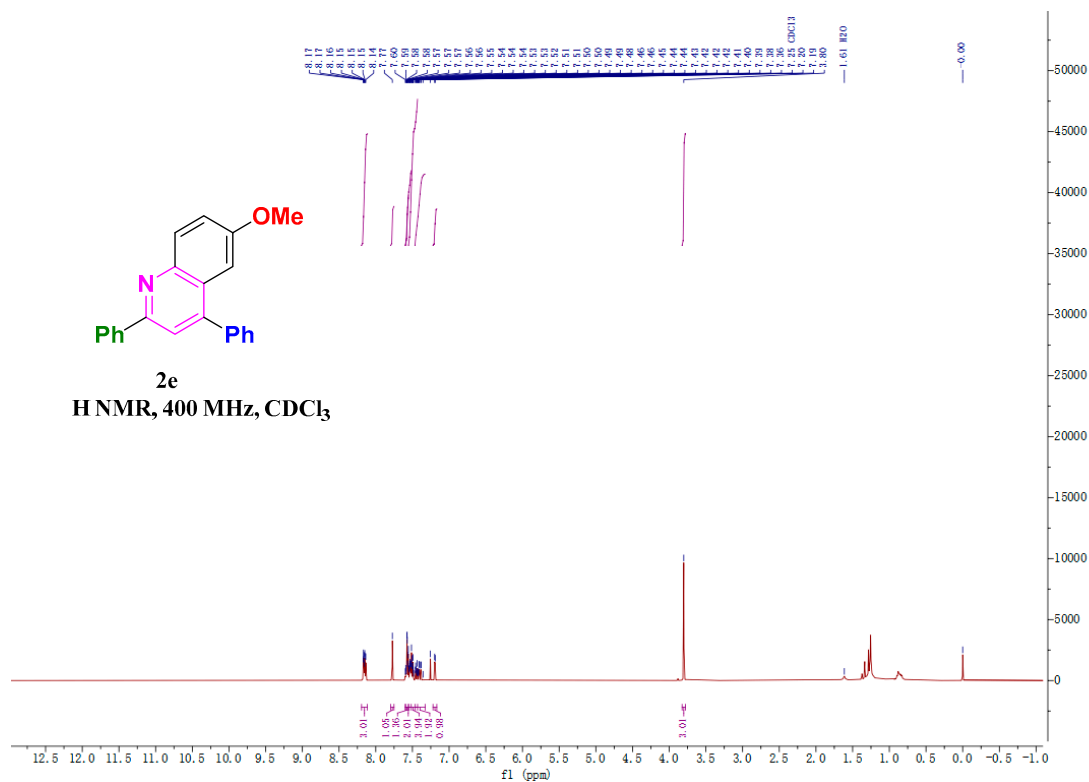
5. ^1H , ^{13}C and ^{19}F NMR Spectra

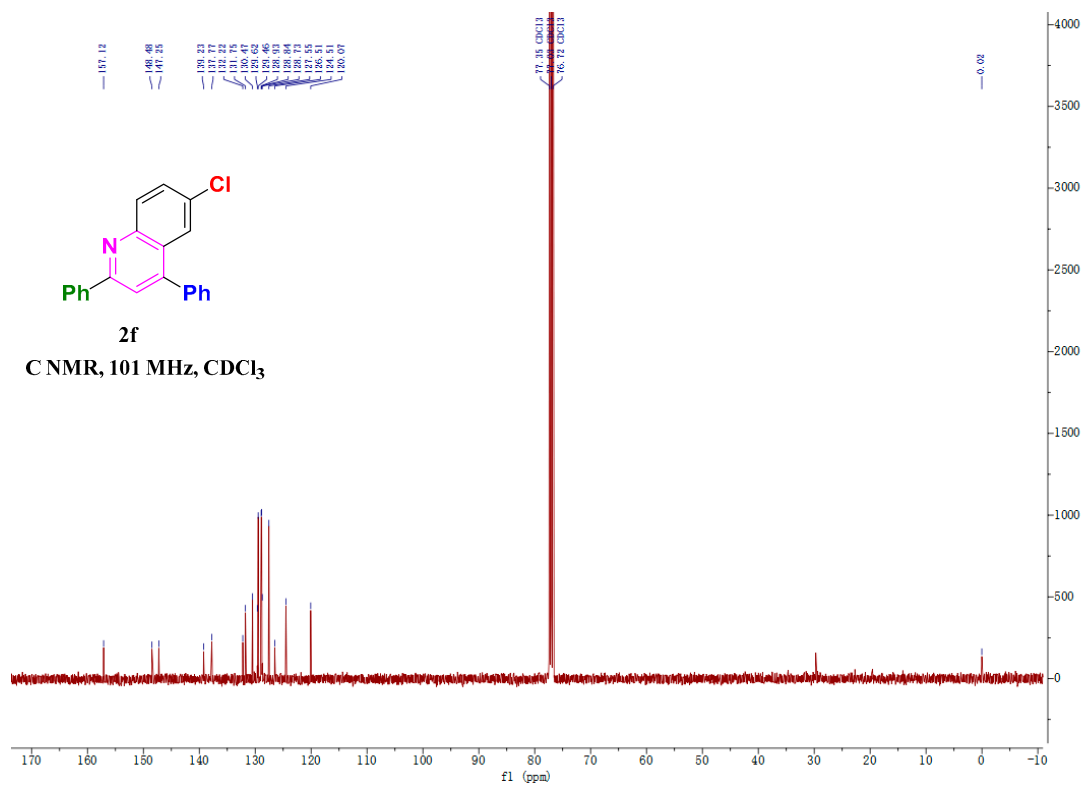
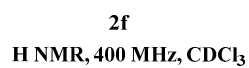


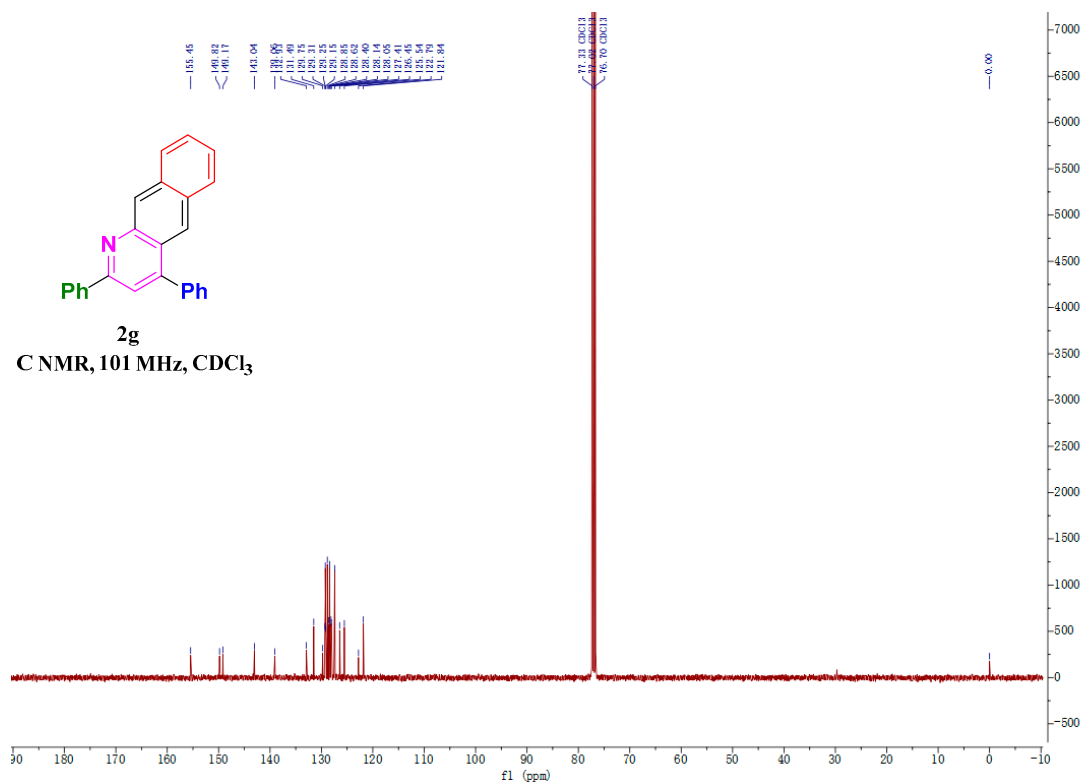
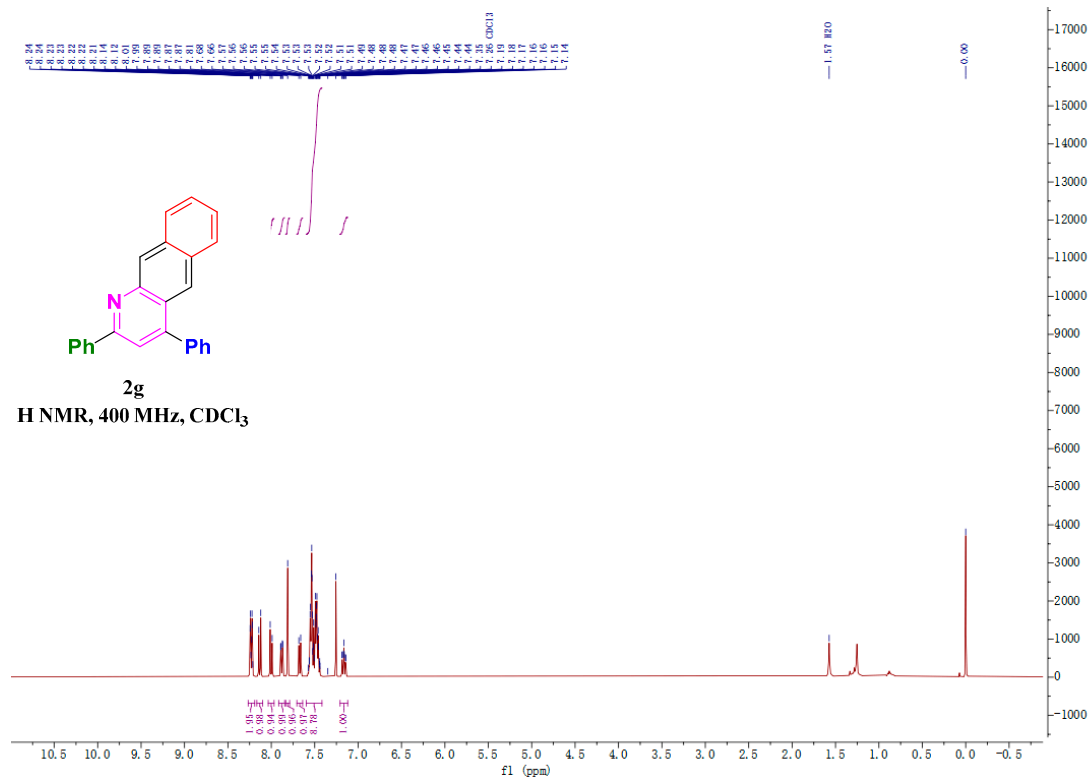


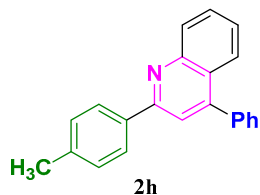




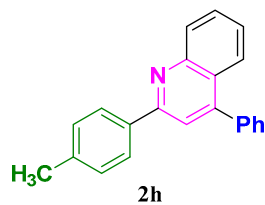




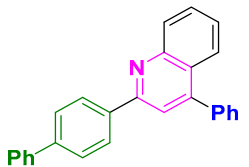




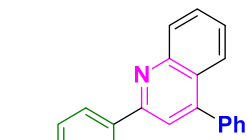
H NMR, 400 MHz, CDCl₃



C NMR, 101 MHz, CDCl₃



2i
¹H NMR, 400 MHz, CDCl₃



2i
C NMR, 101 MHz, CDCl₃

