Supplementary Information

Vinylene Carbonate: Beyond Ethyne Surrogate in Rhodium-Catalyzed Annulation with Amidines toward 4-Methylquinazolines

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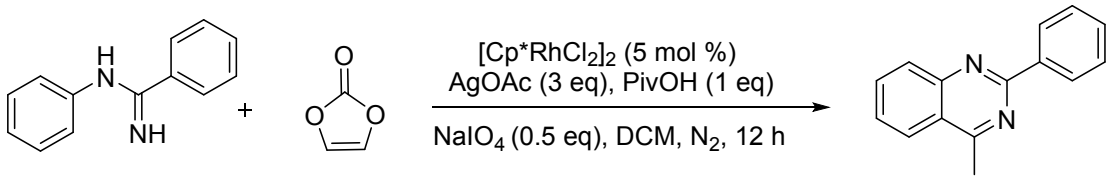
1. General Information

Unless otherwise noted, all the reactions were carried out under nitrogen atmosphere using standard Schlenk technique，and all chemicals were purchased from commercial suppliers and used without further purification. The ^{1}H NMR spectra were recorded on a 300 MHz or 400 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 75 MHz or 100 MHz. NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants J are given in Hz. High-resolution mass spectra (HRMS) were obtained using a Bruker micro-TOF II focus spectrometer (ESI). Column chromatography was performed using EM Silica gel 60 (300-400 mesh), and the eluent was a mixture of petroleum ether (PE) and ethyl acetate (EA). All melting points were tested after recrystallization with CH_2Cl_2.

The substrates **1**[1] were prepared according to the published procedures and substrates **2** were purchased from commercial suppliers.

2. Synthesis and Reaction

2.1 4-methyl-2-phenylquinazoline

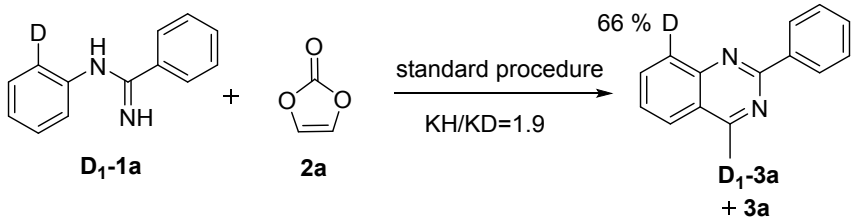


1a **2a** **3a**

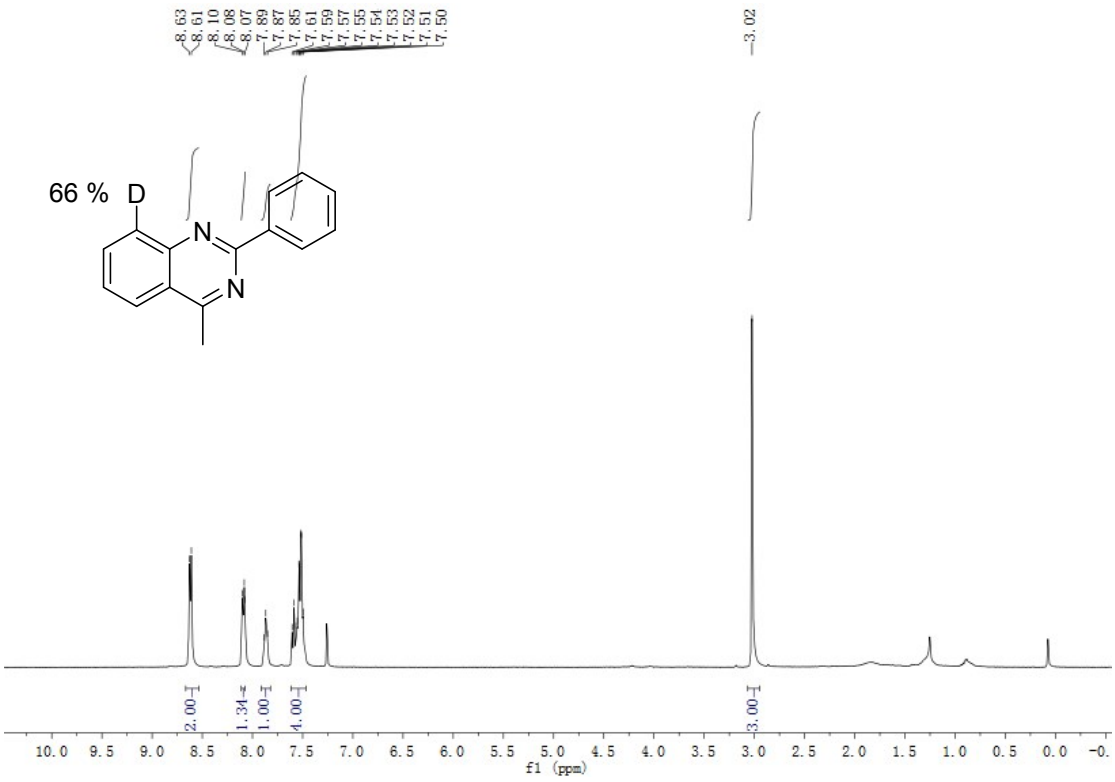
A 20 mL of Schlenk tube equipped with a stir bar was charged with substituted amidine (0.1 mmol, 1.0 equiv.), vinylene carbonate (0.3 mmol, 3 equiv.), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol %), AgOAc (50.1 mg, 3 equiv), PivOH (10.2 mg, 1 equiv), $NaIO_4$ (10.7 mg, 0.5 equiv.) and DCM (2.0 mL). The tube was sealed with a PTFE cap. The reaction mixture was stirred at 80 °C for 12 h under nitrogen atmosphere in an oil bath. After the completion of the reaction, the mixture was then allowed to cool to room temperature. The organic solution was concentrated, and purified through silica gel column chromatography using a mixture of ethyl acetate (EtOAc) and petroleum ether (PE) as eluent to afford the corresponding products.

3. Mechanism Study

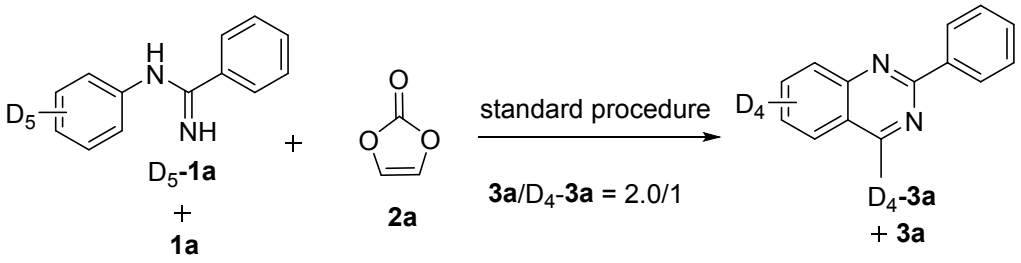
3.1 Intramolecular KIE study



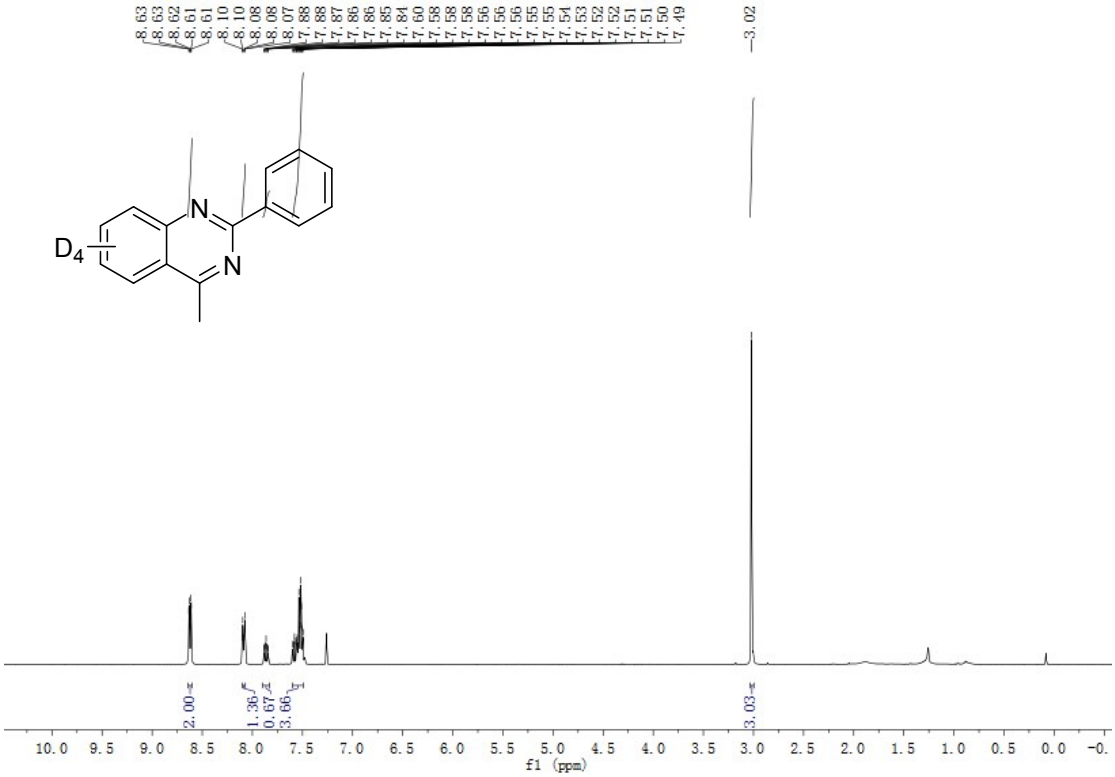
A 20 mL of Schlenk tube equipped with a stir bar was charged with substituted **D1-1a**[1] (0.1 mmol, 1.0 equiv.), **2a** (0.3 mmol, 3 equiv.), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol %), AgOAc (50.1 mg, 3 equiv), PivOH (10.2 mg, 1 equiv), $NaIO_4$ (10.7 mg, 0.5 equiv.) and DCM (2.0 mL). The tube was sealed with a PTFE cap. The reaction mixture was stirred at 80 °C for 12 h under nitrogen atmosphere in an oil bath. After the completion of the reaction, the mixture was then allowed to cool to room temperature. The organic solution was concentrated, and purified through silica gel column chromatography using a mixture of ethyl acetate (EtOAc) and petroleum ether (PE) as eluent to afford the corresponding products.



3.2 Intermolecular KIE study

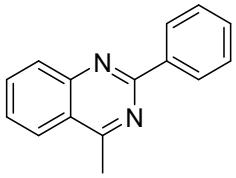


A 20 mL of Schlenk tube equipped with a stir bar was charged with substituted **D5-1a**[1] (0.05 mmol), **1a** (0.05 mmol), **2a** (0.3 mmol, 3 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol %), AgOAc (50.1 mg, 3 eq), PivOH (10.2 mg, 1 equiv), $NaIO_4$ (10.7 mg, 0.5 equiv.) and DCM (2.0 mL). The tube was sealed with a PTFE cap. The reaction mixture was stirred at 80 °C for 12 h under nitrogen atmosphere in an oil bath. After the completion of the reaction, the mixture was then allowed to cool to room temperature. The organic solution was concentrated, and purified through silica gel column chromatography using a mixture of ethyl acetate (EtOAc) and petroleum ether (PE) as eluent to afford the corresponding products.



4. Characterization data for the products

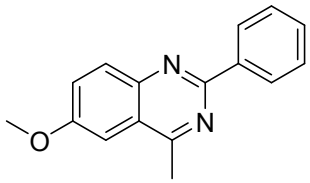
4-methyl-2-phenylquinazoline (3a)[2]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3a** (15.8 mg, 72% yield) as a yellow solid. R_f = 0.4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.65-8.63 (m, 2H), 8.08-8.04 (m, 2H), 7.86-7.82 (m, 1H), 7.57-7.48 (m, 4H), 2.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 160.2, 150.3, 138.3, 133.5, 130.4, 129.2, 128.6, 128.6, 126.9, 125.0, 123.0, 22.1.

MS (m/z): 220.1 $[M]^+$.

6-methoxy-4-methyl-2-phenylquinazoline (3c)

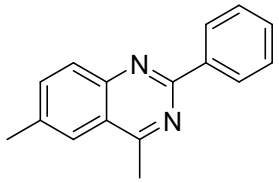


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3c** (9.8 mg, 39% yield) as a yellow solid. R_f = 0.4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.59-8.57 (m, 2H), 7.99-7.97 (d, J = 9.2 Hz, 1H), 7.54-7.45 (m, 4H), 7.22-7.21 (d, J = 2.7 Hz, 1H), 3.95 (s, 3H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 158.6, 157.9, 146.4, 138.4, 130.7, 130.0, 128.5, 128.2, 126.0, 123.7, 102.5, 55.7, 22.2.

MS (m/z): 250.1 $[M]^+$.

HRMS (ESI) m/z calcd for $C_{16}H_{15}N_2O^+$ $(M+H)^+$ 251.1179, found 251.1173.

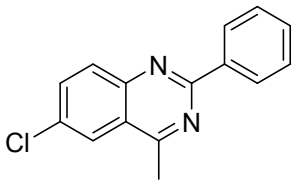
4,6-dimethyl-2-phenylquinazoline (3d)[3]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3d** (11.9 mg, 51% yield) as a yellow solid. R_f = 0.6. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62-8.59 (m, 2H), 7.97-7.95 (d, J = 8.5 Hz, 1H), 7.81 (s, 1H), 7.69-7.66 (m, 1H), 7.55-7.46 (m, 3H), 2.97 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 159.5, 148.8, 138.4, 136.9, 135.7, 130.2, 128.9, 128.6, 128.4, 123.9, 122.9, 22.1, 21.9.

MS (m/z): 234.1 $[M]^+$.

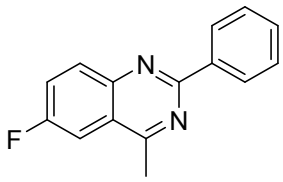
6-chloro-4-methyl-2-phenylquinazoline (3e)[4]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3e** (17 mg, 67% yield) as a yellow solid. R_f = 0.5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60-8.57 (m, 2H), 7.99-7.95 (m, 2H), 7.76-7.73 (m, 1H), 7.55-7.49 (m, 3H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 160.3, 148.8, 137.8, 134.4, 132.3, 130.9, 130.7, 128.6, 128.6, 124.0, 123.5, 22.0.

MS (m/z): 254.1 $[M]^+$.

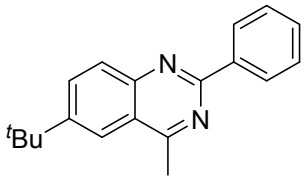
6-fluoro-4-methyl-2-phenylquinazoline (3f)[3]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3f** (15.2 mg, 64% yield) as a yellow solid. R_f = 0.6. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60-8.57 (m, 2H), 8.07-8.03 (m, 1H), 7.64-7.57 (m, 2H), 7.55-7.47 (m, 3H), 2.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7 (d, $J_{C\text{-}F}$ = 6.0 Hz), 160.1 (d, $J_{C\text{-}F}$ = 248.3 Hz), 159.7(d, $J_{C\text{-}F}$ = 3.0 Hz), 147.47, 137.94, 131.8 (d, $J_{C\text{-}F}$ = 9.0 Hz), 130.49, 128.59, 128.42, 123.7 (d, $J_{C\text{-}F}$ = 25.5 Hz), 123.3 (d, $J_{C\text{-}F}$ = 9.0 Hz), 108.5 (d, $J_{C\text{-}F}$ = 22.5 Hz), 22.08.

MS (m/z): 238.1 $[M]^+$.

6-(tert-butyl)-4-methyl-2-phenylquinazoline (3g)

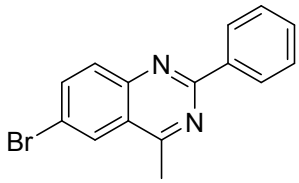


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3g** (16.3 mg, 59% yield) as a yellow solid. R_f = 0.5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.63-8.61 (m, 2H), 8.04-7.95 (m, 3H), 7.55-7.46 (m, 3H), 3.02 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 159.8, 150.0, 148.9, 138.5, 132.5, 130.2, 128.8, 128.6, 128.5, 122.6, 119.7, 35.2, 31.2, 22.1.

MS (m/z): 276.2 $[M]^+$.

HRMS (ESI) m/z calcd for $C_{19}H_{21}N_2^+$ $(M+H)^+$ 277.1699, found 277.1693.

6-bromo-4-methyl-2-phenylquinazoline (3h)[5]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3h** (22.3 mg, 75% yield) as a yellow solid. R_f = 0.5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.59-8.57 (m, 2H), 8.15 (d, J = 1.8 Hz, 1H), 7.90-7.84 (m, 2H), 7.54-7.48 (m, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 160.3, 149.0, 137.8, 136.9, 131.0, 130.7, 128.6, 128.6, 127.4, 124.0, 120.3, 22.0.

MS (m/z): 298.0 $[M]^+$.

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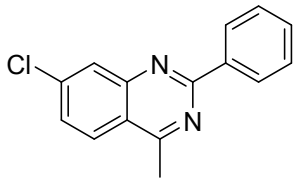
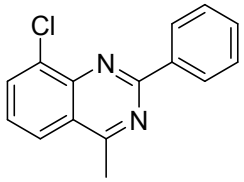
7-chloro-4-methyl-2-phenylquinazoline (3i)[3]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3i** (14.2mg, 56% yield) as a yellow solid. R_f = 0.4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60-8.57 (m, 2H), 8.02 (d, J = 2.1 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.55-7.45 (m, 4H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 161.0, 151.1, 139.5, 137.8, 130.8, 128.7, 128.6, 128.2, 127.8, 126.4, 121.3, 22.0.

MS (m/z): 254.1 $[M]^+$.

8-chloro-4-methyl-2-phenylquinazoline (3j)

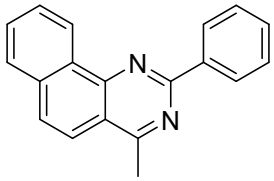


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3j** (19.6 mg, 77% yield) as a yellow solid. R_f = 0.5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.71-8.67 (m, 2H), 7.91-7.87 (m, 2H), 7.56-7.51 (m, 3H), 7.41-7.37 (m, 1H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 160.3, 146.9, 137.8, 133.7, 133.3, 130.8, 128.9, 128.6, 126.5, 124.0, 123.8, 22.3.

MS (m/z): 254.1 $[M]^+$.

HRMS (ESI) m/z calcd for $C_{15}H_{12}ClN_2^+$ $(M+H)^+$ 255.0684, found 255.0679.

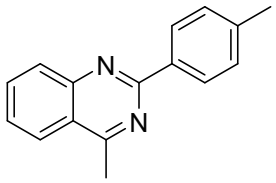
4-methyl-2-phenylbenzo[h]quinazoline (3k)[6]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60: 1) give **3k** (8.9 mg, 33% yield) as a yellow solid. R_f = 0.6. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.47-9.43 (m, 1H), 8.79-8.76 (m, 2H), 7.90-7.85 (m, 2H), 7.79-7.75 (m, 3H), 7.60-7.51 (m, 3H), 3.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 160.0, 150.1, 138.5, 135.2, 130.8, 130.4, 129.8, 128.6, 127.8, 127.8, 127.3, 125.2, 121.2, 120.4, 22.2.

MS (m/z): 270.1 $[M]^+$.

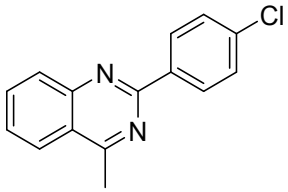
4-methyl-2-(p-tolyl)quinazoline (3m)[2]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3m** (16.8 mg, 72% yield) as a yellow solid. R_f = 0.4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.53 (d, J = 8.0 Hz, 2H), 8.06-8.01 (m, 2H), 7.84-7.80 (m, 1H), 7.54-7.50 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 2.98 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 160.2, 150.4, 140.6, 135.6, 133.5, 129.3, 129.1, 128.5, 126.6, 125.0, 122.9, 22.0, 21.6.

MS (m/z): 234.1 $[M]^+$.

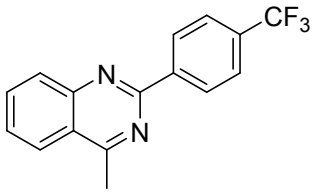
2-(4-chlorophenyl)-4-methylquinazoline (3n)[3]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3n** (10.4 mg, 41% yield) as a yellow solid. R_f = 0.4. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.58-8.55 (m, 2H), 8.07-8.02 (m, 2H), 7.87-7.83 (m, 1H), 7.59-7.55 (m, 1H), 7.49-7.46 (m, 2H), 2.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 159.1, 150.3, 136.8, 136.6, 133.7, 129.9, 129.2, 128.7, 127.1, 125.0, 123.0, 22.0.

MS (m/z): 254.1 $[M]^+$.

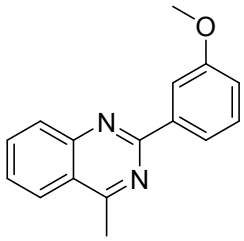
4-methyl-2-(4-(trifluoromethyl)phenyl)quinazoline (3o)[3]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3o** (11.8 mg, 41% yield) as a yellow solid. R_f = 0.5. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.75-8.72 (m, 2H), 8.10-8.07 (m, 2H), 7.90-7.86 (m, 1H), 7.77-7.75 (d, J = 8.2 Hz, 2H), 7.63-7.59 (m, 1H), 3.01 (s, 1H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 158.7, 150.2, 141.5, 133.8, 128.8, 128.7, 127.5, 127.2 (q, $J_{C\text{-}F}$ = 320.3 Hz), 125.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.21, 22.04. (two C missed because of overlapping).

MS (m/z): 288.1 $[M]^+$.

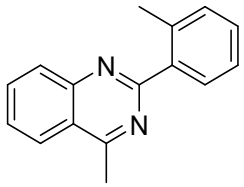
2-(3-methoxyphenyl)-4-methylquinazoline (3p)[3]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3p** (17 mg, 68% yield) as a yellow solid. R_f = 0.5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.25-8.19 (m, 2H), 8.07-8.02 (m, 2H), 7.85-7.81 (m, 1H), 7.56-7.51 (m, 1H), 7.46-7.42 (m, 1H), 7.07-7.04 (m, 1H), 3.95 (s, 3H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 160.0, 159.9, 150.3, 139.8, 133.5, 129.6, 129.2, 126.9, 125.0, 123.0, 121.2, 116.9, 113.2, 55.5, 22.0.

MS (m/z): 250.1 $[M]^+$.

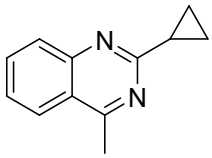
4-methyl-2-(o-tolyl)quinazoline (3q)[7]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3q** (14.3 mg, 61% yield) as a yellow solid. R_f = 0.5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.12-8.07 (m, 2H), 7.90-7.85 (m, 2H), 7.63-7.59 (m, 1H), 7.37-7.30 (m, 3H), 3.01 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 163.3, 150.0, 138.9, 137.2, 133.6, 131.2, 130.4, 129.2, 129.1, 127.2, 126.0, 125.0, 122.4, 22.0, 21.0.

MS (m/z): 234.1 $[M]^+$.

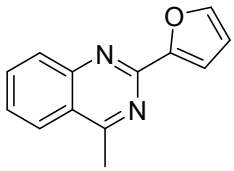
2-cyclopropyl-4-methylquinazoline (3r)[8]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3r** (13.6 mg, 74% yield) as a yellow solid. R_f = 0.5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 8.3 Hz, 1H), 7.86-7.84 (d, J = 8.4 Hz, 1H), 7.77-7.73 (m, 1H), 7.47-7.42 (m, 1H), 2.83 (s, 3H), 2.35-2.29 (m, 1H), 1.25-1.22 (m, 2H), 1.09-1.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 167.3, 149.9, 133.4, 128.0, 125.89, 124.9, 122.6, 21.8, 18.4, 10.3.

MS (m/z): 184.1 $[M]^+$.

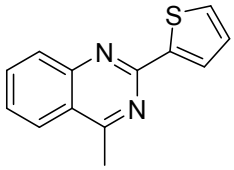
2-(furan-2-yl)-4-methylquinazoline (3s)[5]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10 : 1) give **3s**(16.4 mg, 78% yield) as a yellow solid. R_f = 0.5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01-7.99 (m, 1H), 7.96-7.93 (m, 1H), 7.79-7.75 (m, 1H), 7.63-7.63 (m, 1H), 7.49-7.44 (m, 1H), 7.40-7.39 (m, 1H), 6.55-6.54 (m, 1H), 2.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 153.3, 152.7, 149.9, 145.1, 133.9, 128.9, 126.9, 125.0, 122.8 113.8, 112.2, 21.9.

MS (m/z): 210.1 $[M]^+$.

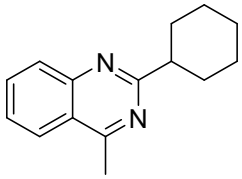
4-methyl-2-(thiophen-2-yl)quinazoline (3t)[8]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60 : 1) give **3t** (14.5 mg, 64% yield) as a yellow solid. R_f = 0.6. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.15-8.14 (m, 1H), 8.00-7.96 (m, 2H), 7.82-7.78 (m, 1H), 7.52-7.48 (m, 2H), 7.19-7.17 (m, 1H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 157.0, 150.2, 144.2, 133.7, 129.7, 129.1, 128.8, 128.3, 126.6, 125.1, 122.8, 21.9.

MS (m/z): 226.1 $[M]^+$.

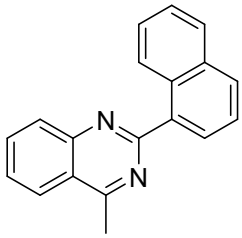
2-cyclohexyl-4-methylquinazoline (3u) [2]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60: 1) give **3u** (14.7 mg, 65% yield) as a yellow solid. R_f = 0.5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00-7.97 (m, 1H), 7.94-7.91 (m, 1H), 7.80-7.75 (m, 1H), 7.52-7.47 (m, 1H), 2.89-2.88 (m, 3H), 2.03-2.00 (m, 2H), 1.87-1.83 (m, 2H), 1.79-1.69 (m, 3H), 1.48-1.30 (m, 3H), 1.24-1.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 167.9, 150.0, 133.2, 128.6, 126.4, 124.8, 122.6, 47.9, 31.9, 26.4, 26.1, 21.8.

MS (m/z): 226.1 $[M]^+$.

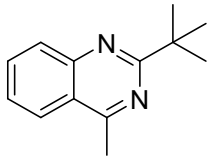
4-methyl-2-(naphthalen-1-yl)quinazoline (3v)[9]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60: 1) give **3v** (14.3 mg, 53% yield) as a yellow solid. R_f = 0.4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.65-8.61 (m, 1H), 8.18-8.12 (m, 3H), 7.99-7.90 (m, 3H), 7.68-7.61 (m, 2H), 7.56-7.50 (m, 2H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 162.7, 150.1, 136.6, 134.2, 133.9, 131.3, 130.2, 129.3, 129.3, 128.5, 127.5, 126.8, 126.0, 125.9, 125.4, 125.1, 122.6, 22.1.

MS (m/z): 270.1 $[M]^+$.

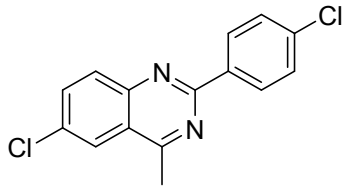
2-(tert-butyl)-4-methylquinazoline (3w)[10]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60: 1) give **3w** (15 mg, 75% yield) as a yellow solid. R_f = 0.4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02-7.96 (m, 2H), 7.81-7.77 (m, 1H), 7.53-7.49 (m, 1H), 2.91 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 167.3, 149.8, 132.9, 129.0, 126.3, 124.7, 122.3, 39.4, 29.7, 21.9.

MS (m/z): 200.1 $[M]^+$.

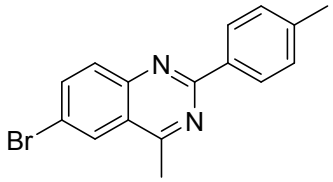
6-chloro-2-(4-chlorophenyl)quinazoline (3x)[4]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60: 1) give **3x** (14 mg, 51% yield) as a yellow solid. R_f = 0.6. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.53-8.51 (m, 2H), 7.99-7.93 (m, 2H), 7.77-7.74 (m, 1H), 7.47-7.45 (m, 2H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 159.3, 148.7, 136.9, 136.3, 134.5, 132.5, 130.9, 129.9, 128.8, 124.1, 123.5, 22.0.

MS (m/z): 288.0 $[M]^+$.

6-bromo-2-(*p*-tolyl)quinazoline (3y)

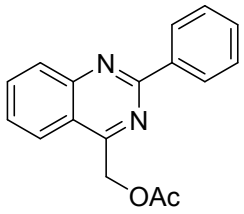


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60: 1) give **3y** (21.2 mg, 71% yield) as a yellow solid. R_f = 0.7. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.47-8.45 (m, 2H), 8.12-8.12 (m, 1H), 7.87-7.82 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.90 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 160.4, 149.0, 140.9, 136.8, 135.1, 130.9, 129.4, 128.5, 127.4, 123.9, 120.0, 22.0, 21.6.

MS (m/z): 312.0 $[M]^+$.

HRMS (ESI) m/z calcd for $C_{16}H_{14}BrN_2^+$ $(M+H)^+$ 313.0335, found 313.0334.

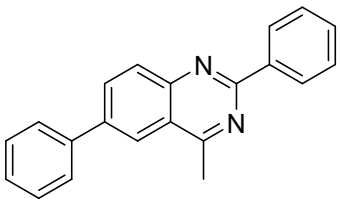
(2-phenylquinazolin-4-yl)methyl acetate (4)[8]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 30: 1) give **4** (14.7 mg, 53% yield) as a yellow solid. R_f = 0.6. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.63-8.61 (m, 2H), 8.09 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.87-7.83 (m, 1H), 7.57-7.50 (m, 4H), 5.74 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 163.6, 160.0, 151.0, 137.9, 133.9, 130.7, 129.5, 128.6, 127.4, 123.8, 121.3, 64.2, 20.9. (one C missed because of overlapping).

MS (m/z): 278.1 $[M]^+$.

4-methyl-2,6-diphenylquinazoline (5)



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 60:1) give **5** (26.9 mg, 91% yield) as a white solid. R_f = 0.4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.68-8.65 (m, 2H), 8.17 (d, J = 1.8 Hz, 1H), 8.13-8.06 (m, 2H), 7.72-7.69 (m, 2H), 7.58-7.50 (m, 5H), 7.46-7.42 (m, 1H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 160.0, 149.7, 140.1, 139.7, 138.3, 133.2, 130.5, 129.7, 129.1, 128.6, 128.6, 128.0, 127.5, 123.2, 122.7, 22.2.

MS (m/z): 296.1 $[M]^+$.

HRMS (ESI) m/z calcd for $C_{21}H_{17}N_2^+$ $(M+H)^+$ 297.1386, found 297.1380.

5. Reference.

[1] Y. Wang, H. Wang, J. Peng and Q. Zhu, *Org. Lett.,* 2011, **13**, 4604–4607.

[2] C. Yu, X. Guo, M. Shen, B. Shen, M. Muzzio, Z. Yin, Q. Li, Z. Xi, J. Li, C. Seto and S. Sun, *Angew. Chem., Int. Ed.,* 2018, **57**, 451-455.

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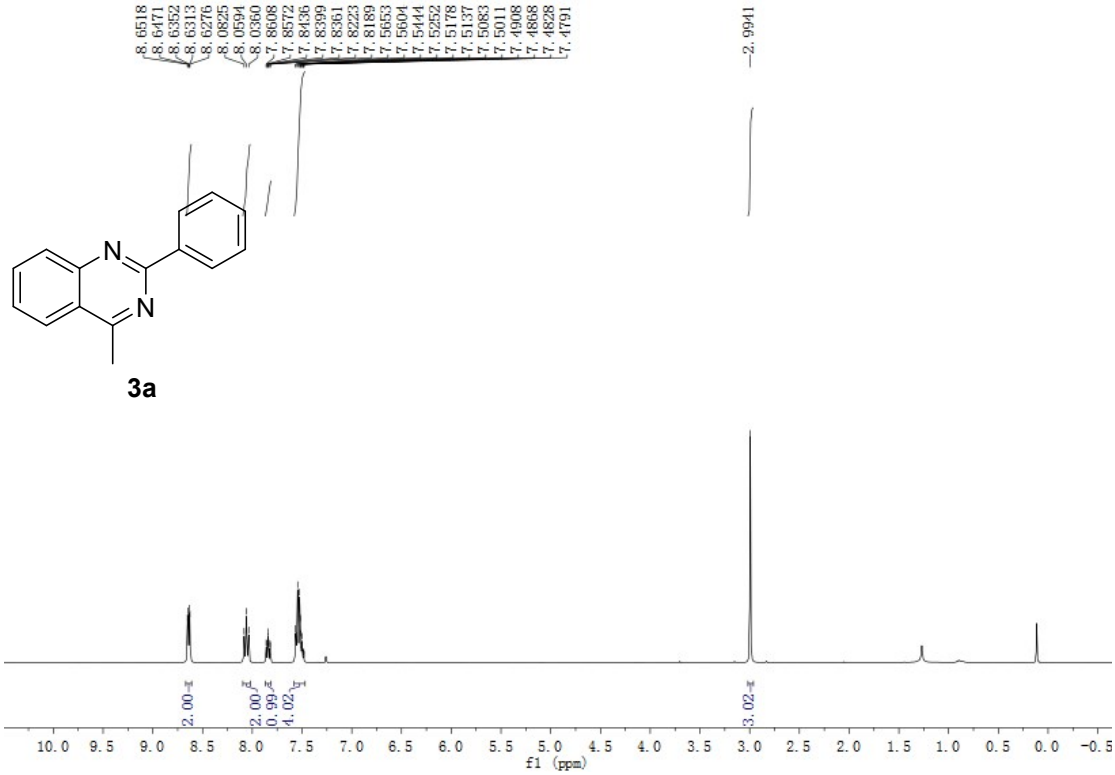
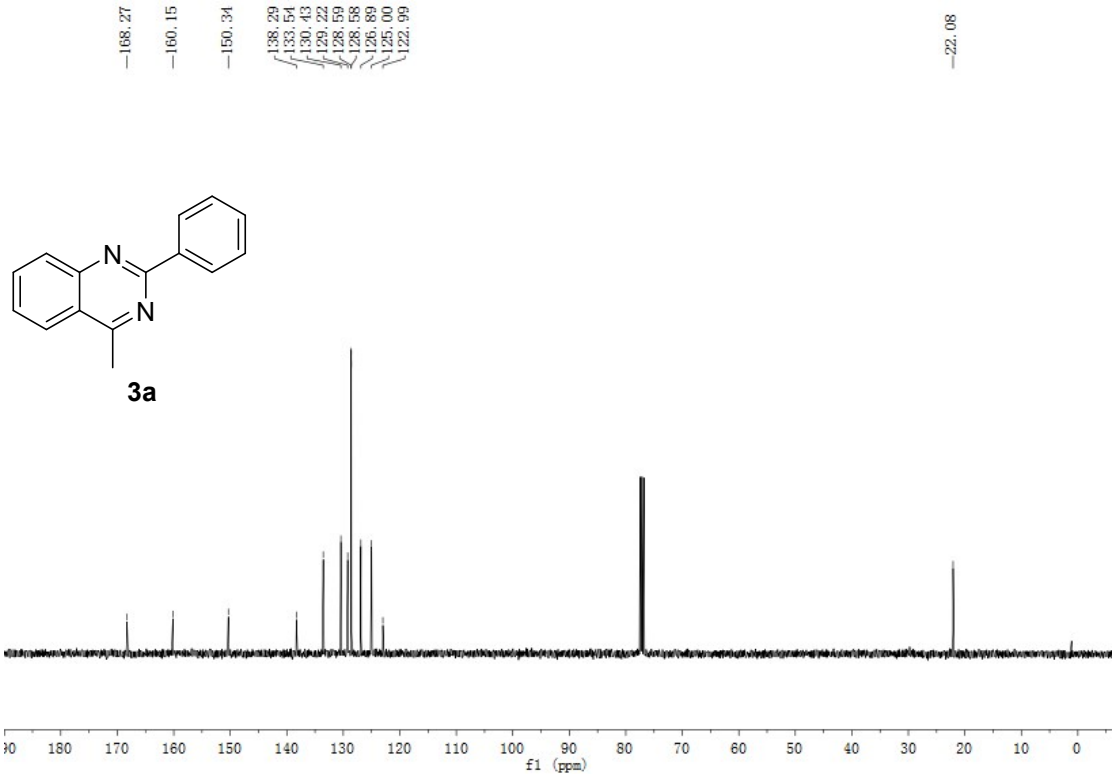
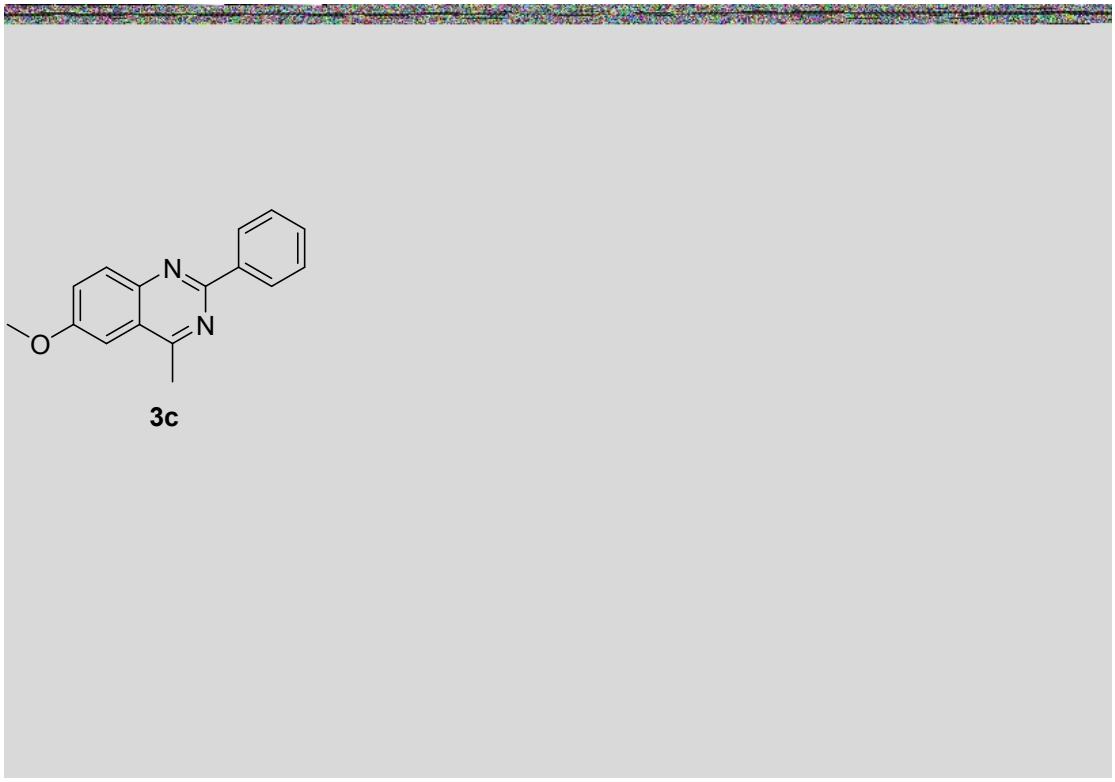
6. Copies of ^{1}H NMR and ^{13}C NMR spectra of 3a-5

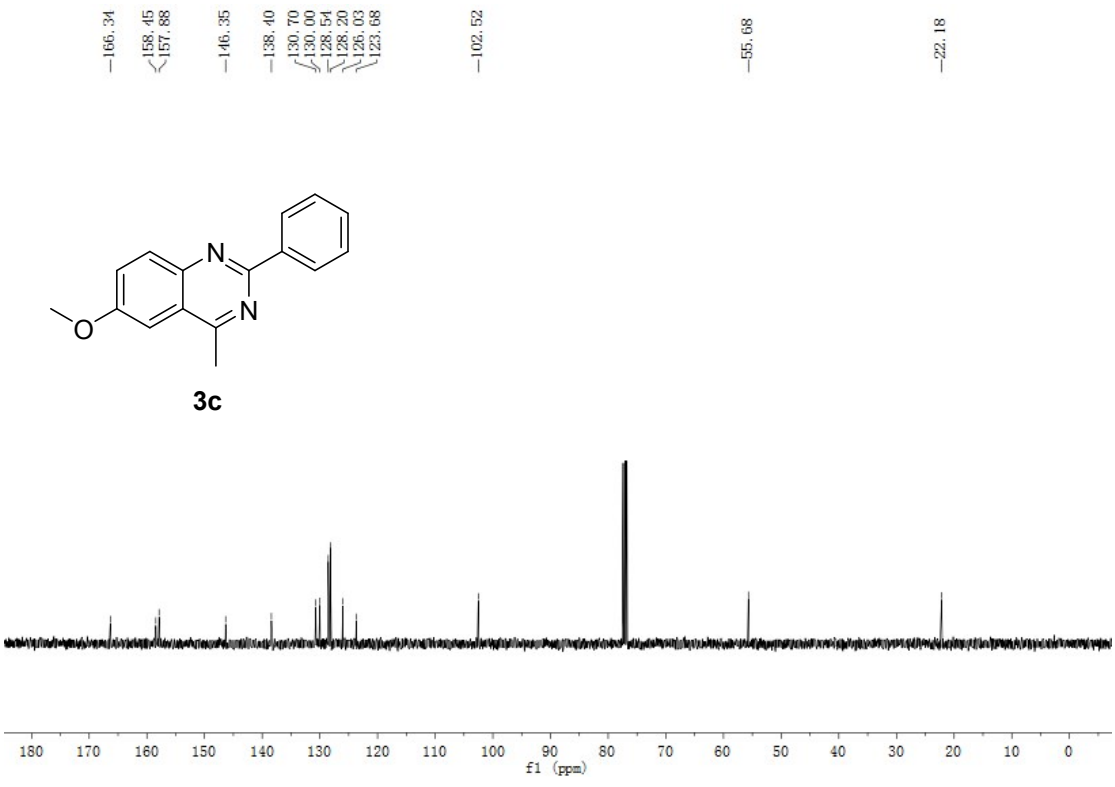
4-methyl-2-phenylquinazoline (3a):



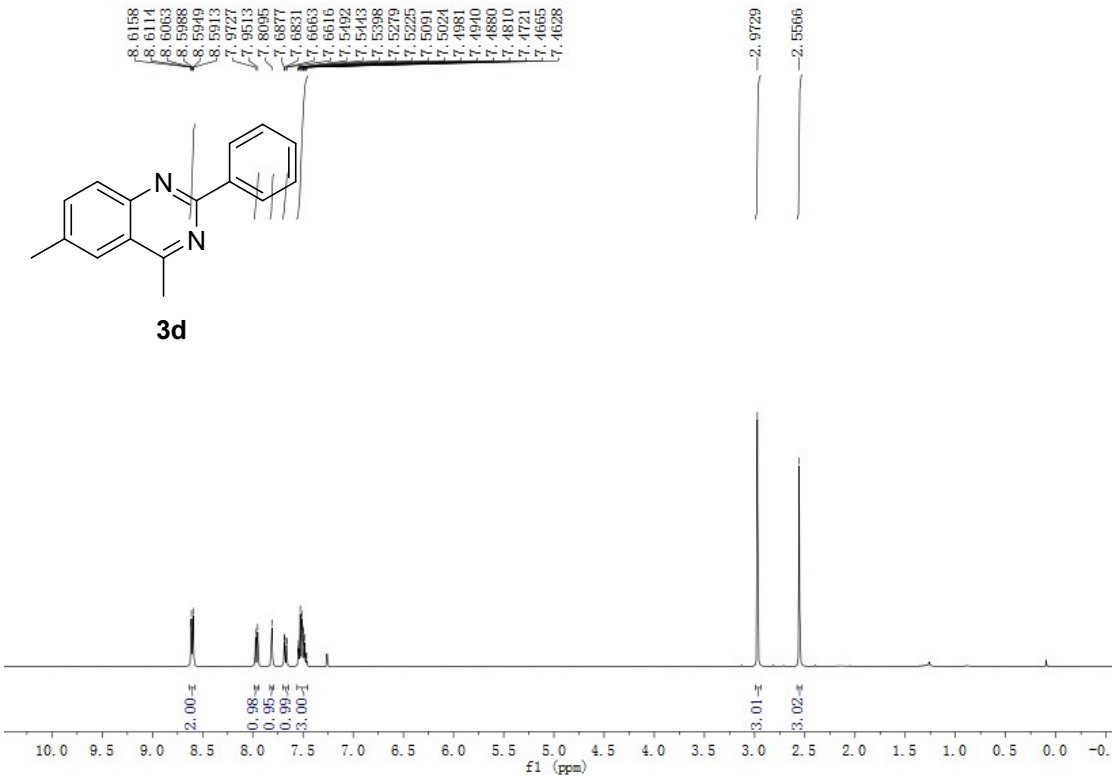


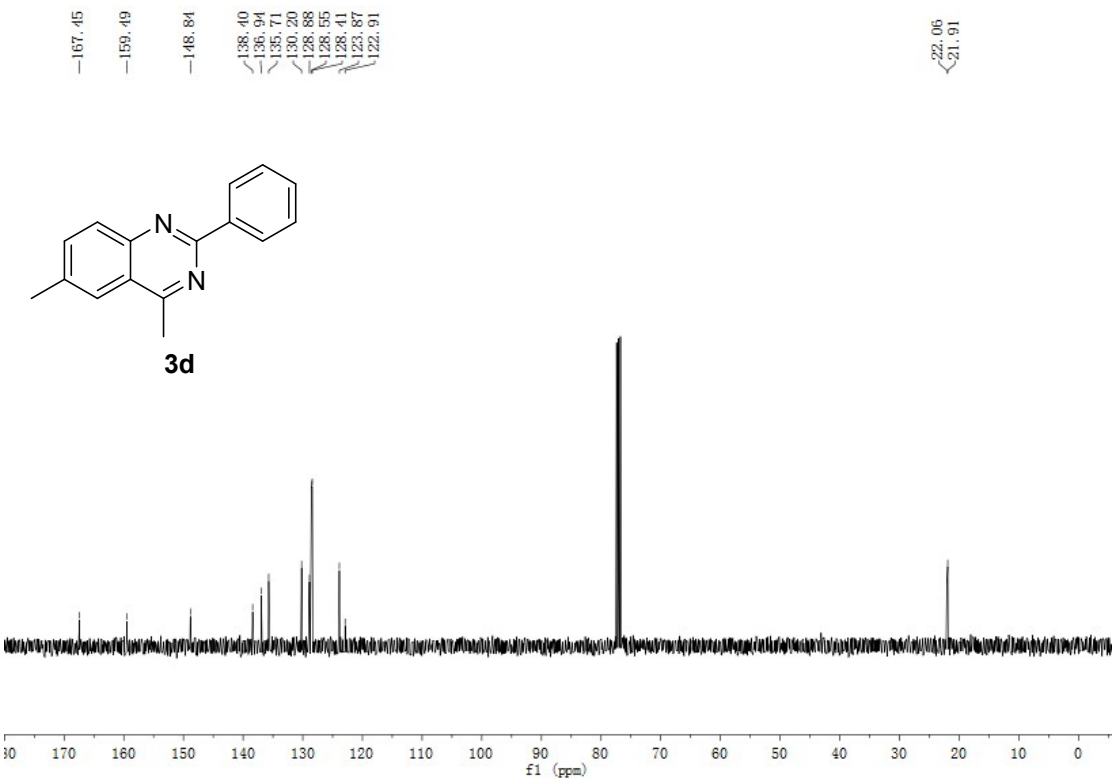
6-methoxy-4-methyl-2-phenylquinazoline(3c):



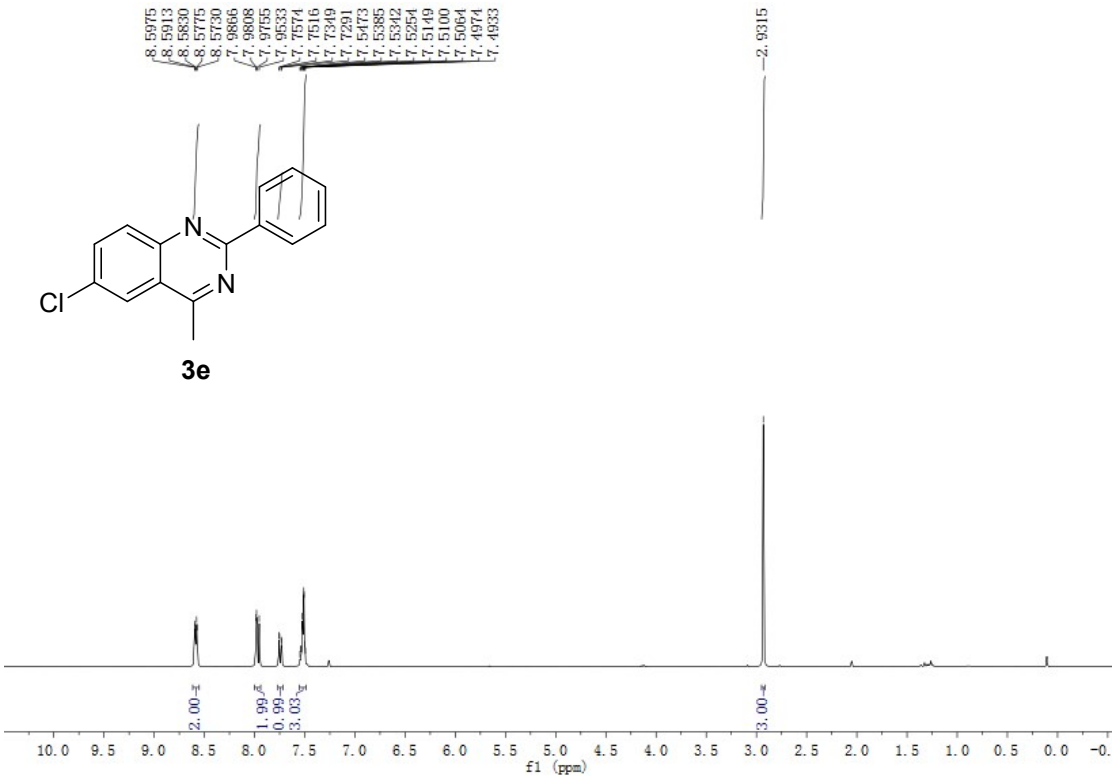


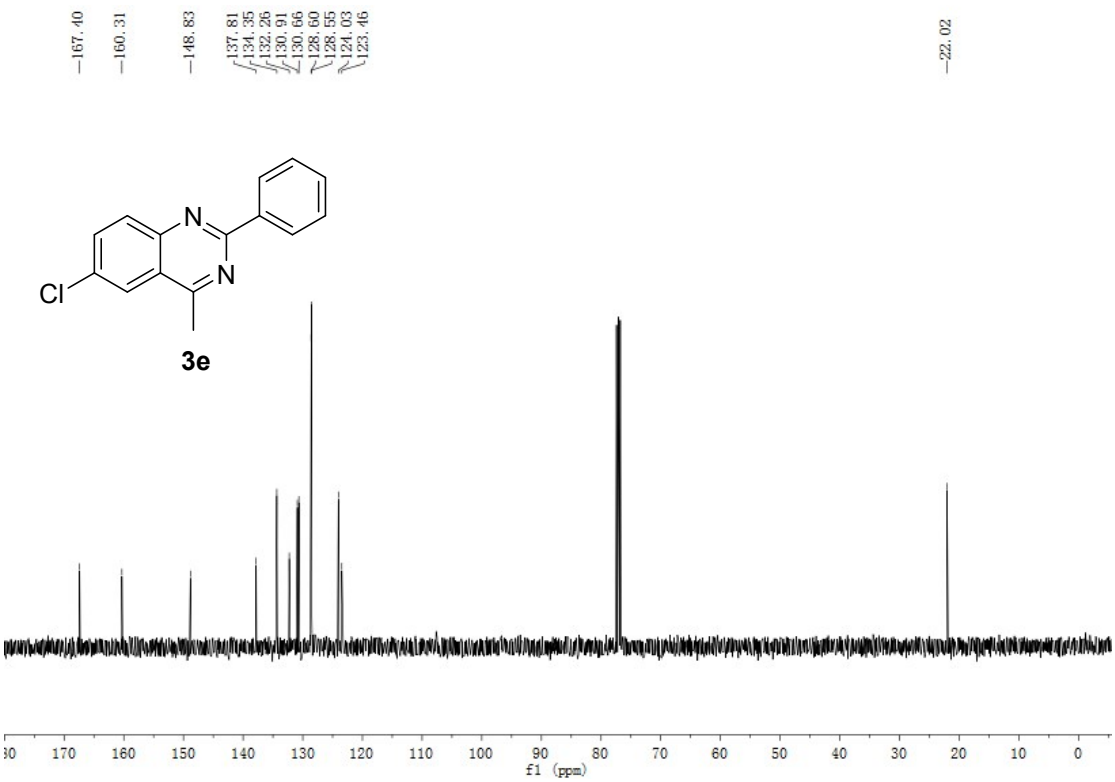
4,6-dimethyl-2-phenylquinazoline (3d):



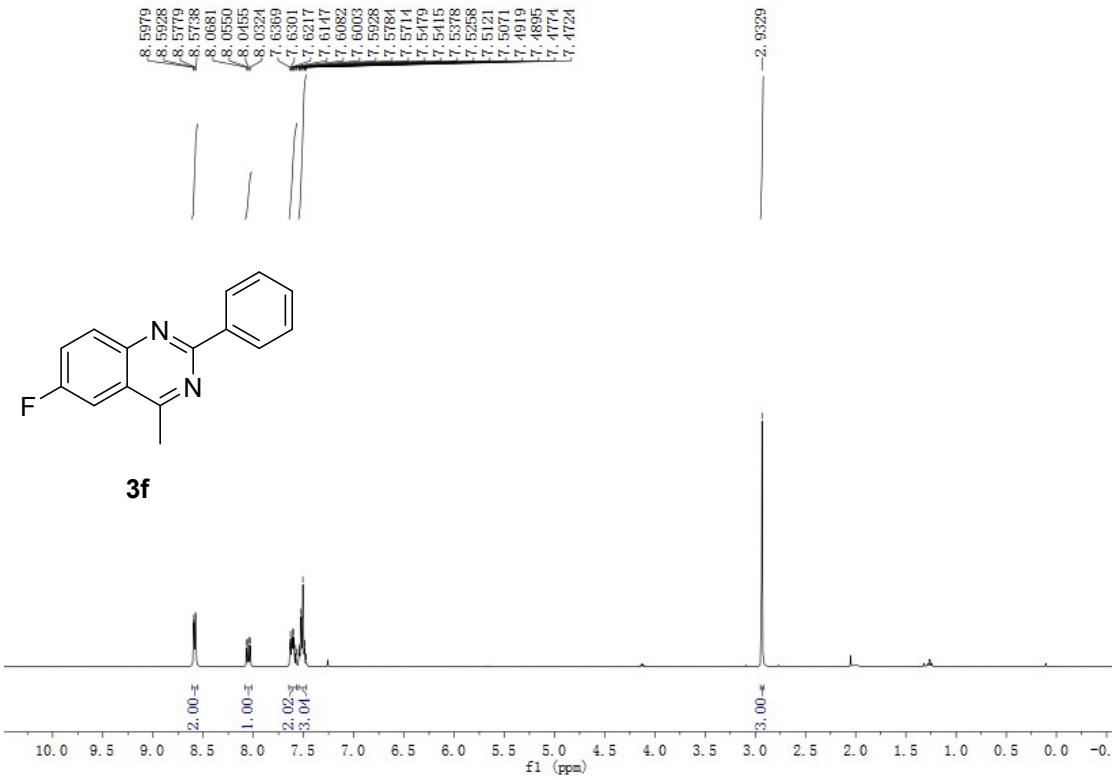


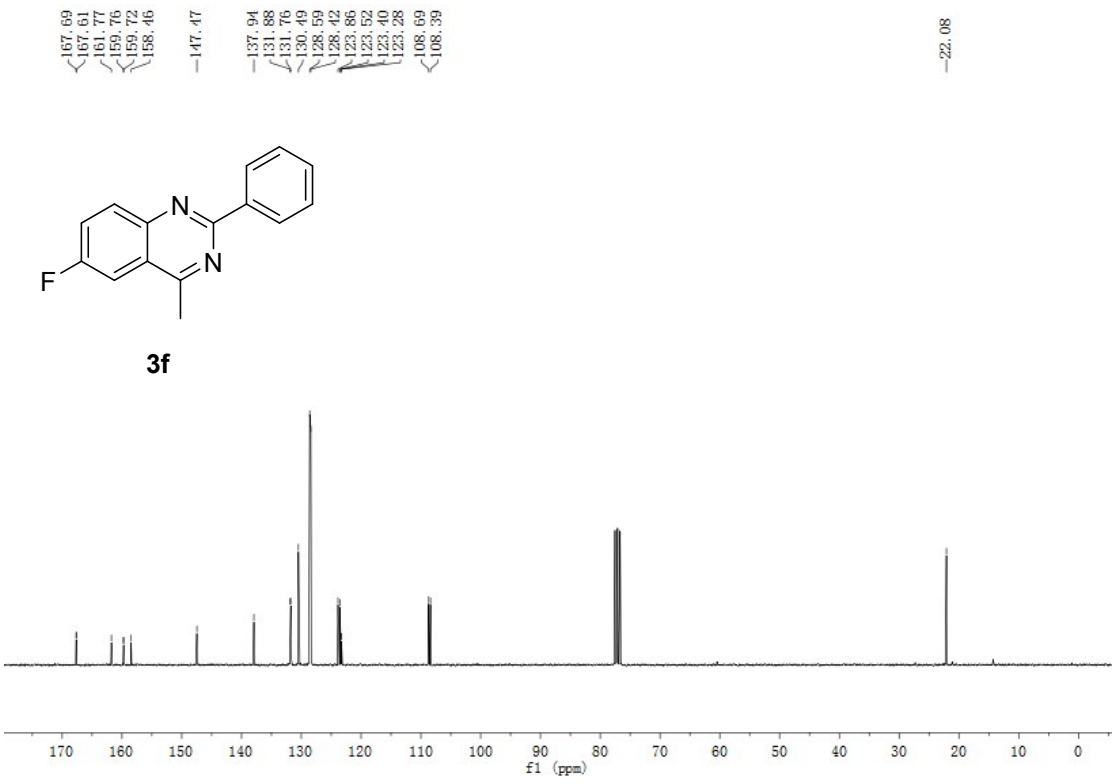
6-chloro-4-methyl-2-phenylquinazoline (3e):



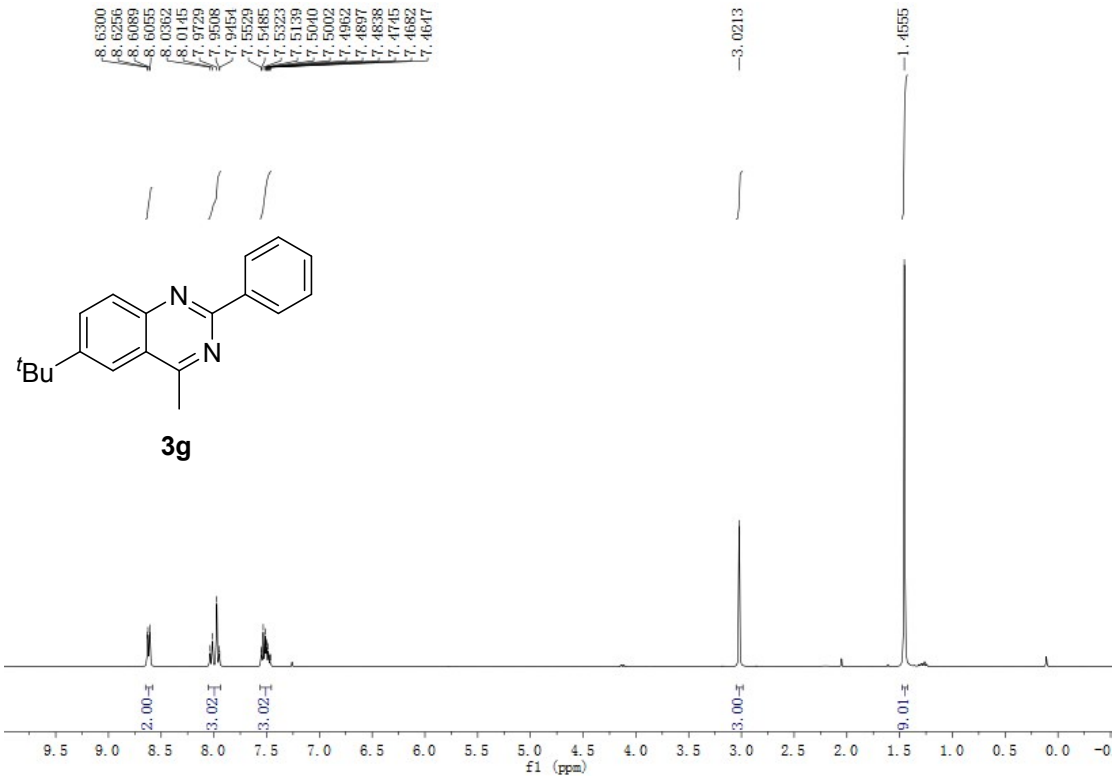


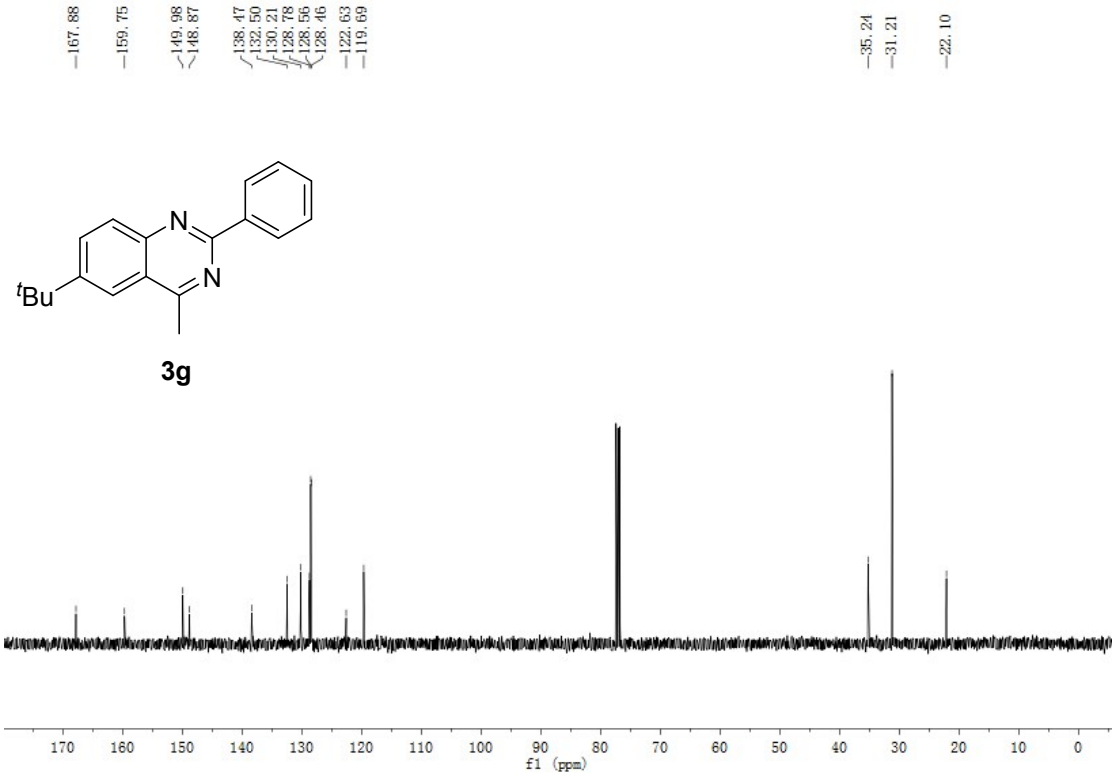
6-fluoro-4-methyl-2-phenylquinazoline (3f):



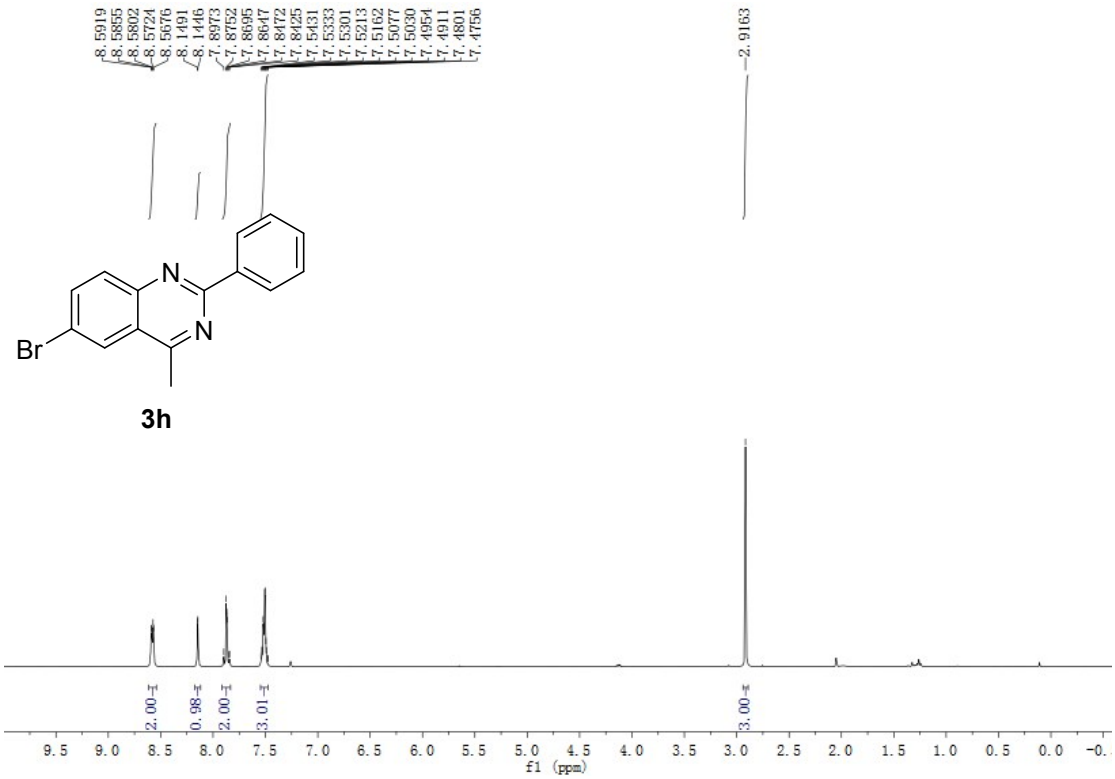


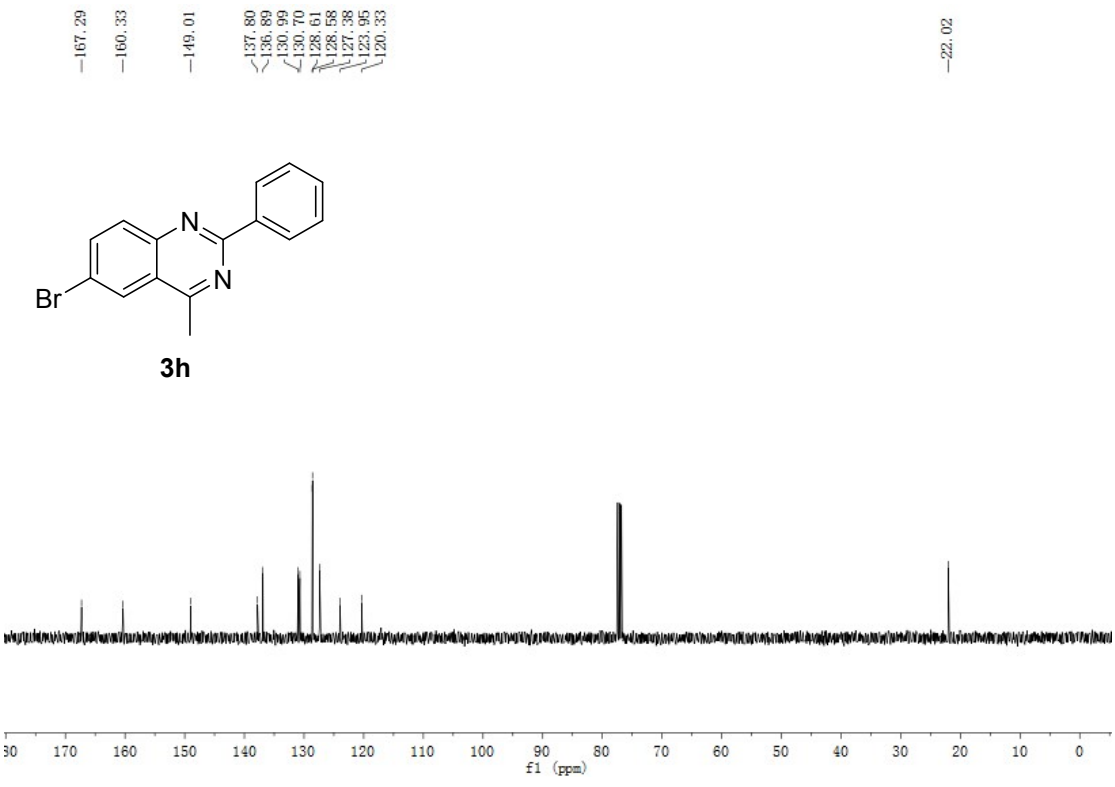
6-(tert-butyl)-4-methyl-2-phenylquinazoline (3g):



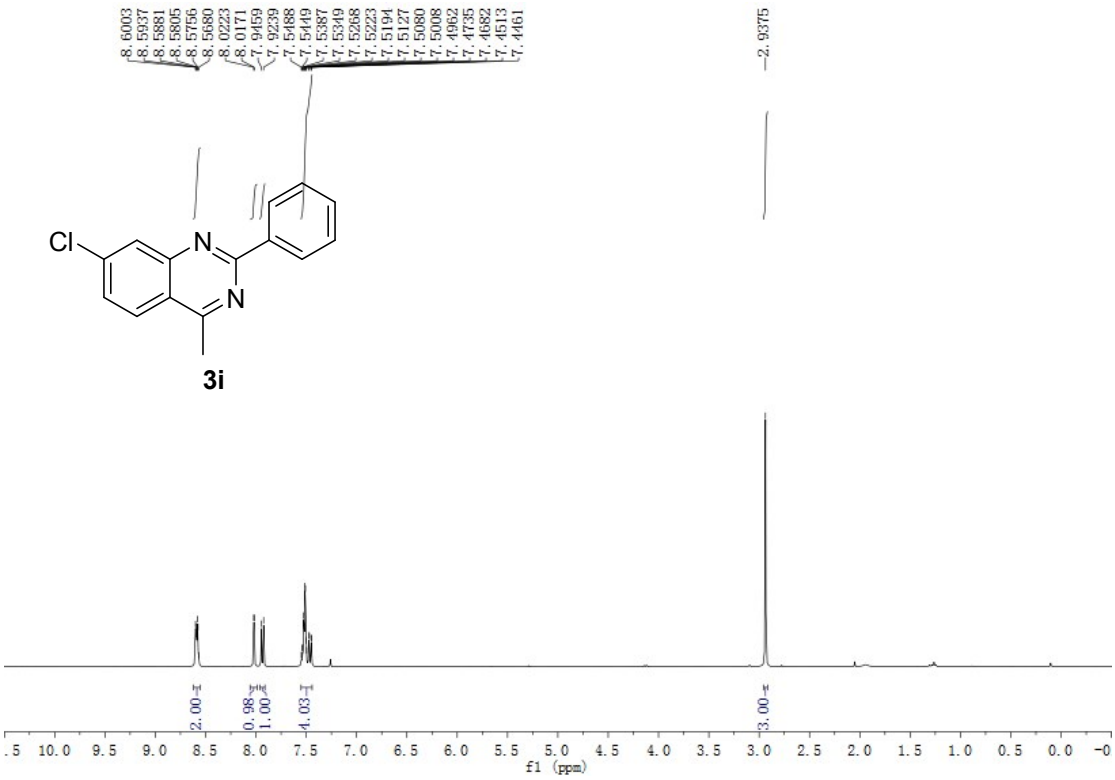


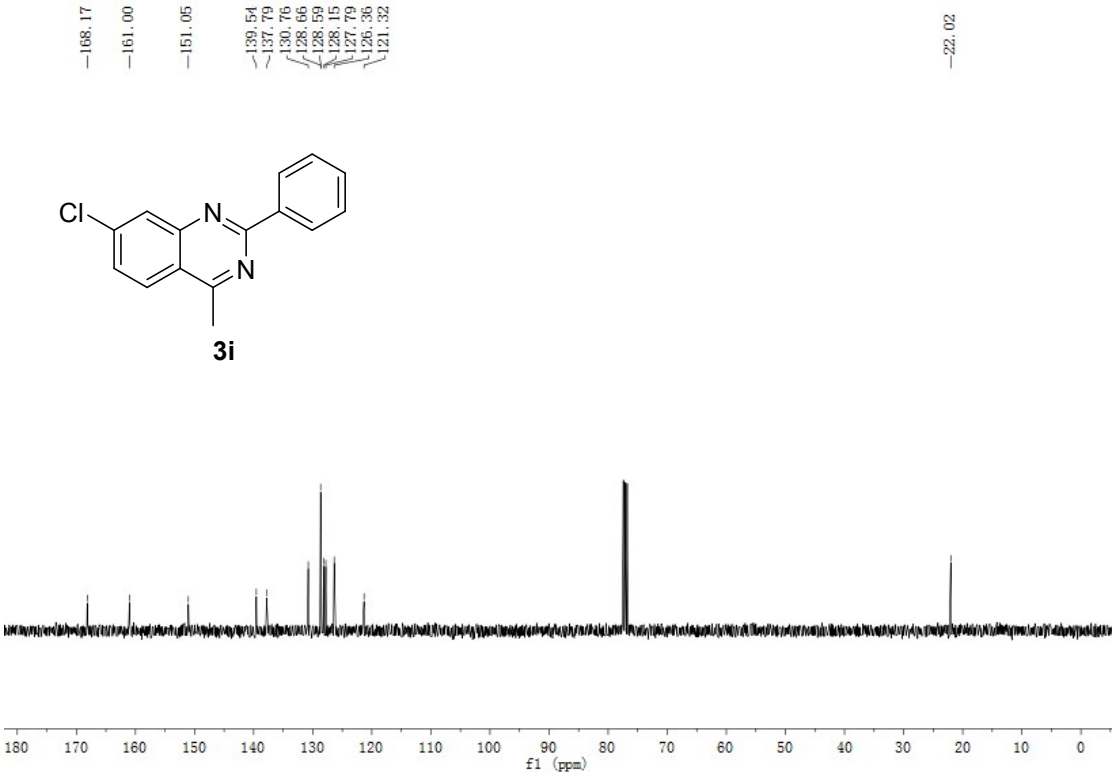
6-bromo-4-methyl-2-phenylquinazoline (3h):



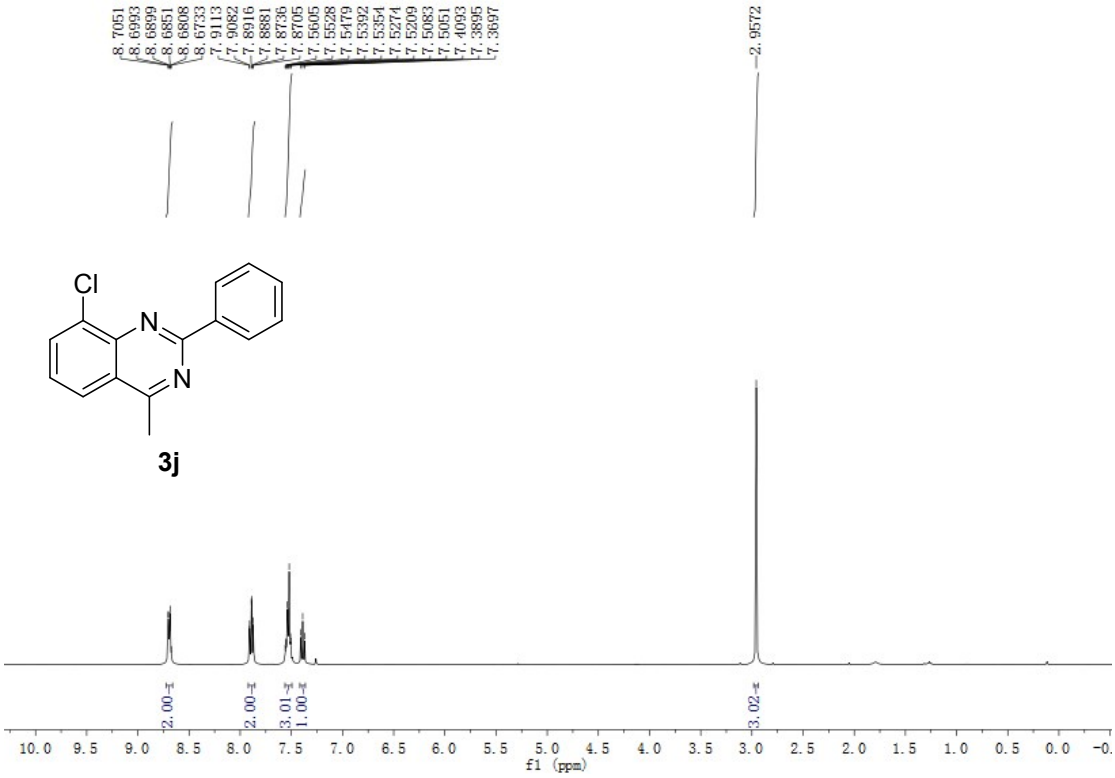


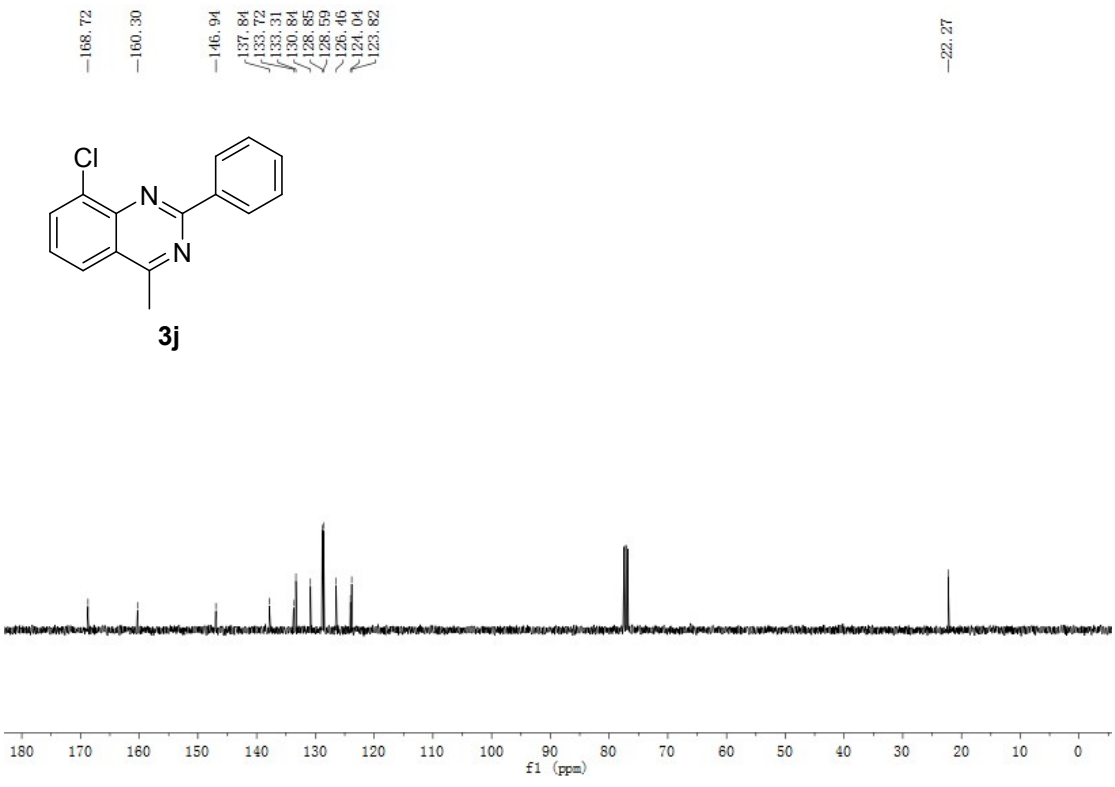
7-chloro-4-methyl-2-phenylquinazoline(3i):



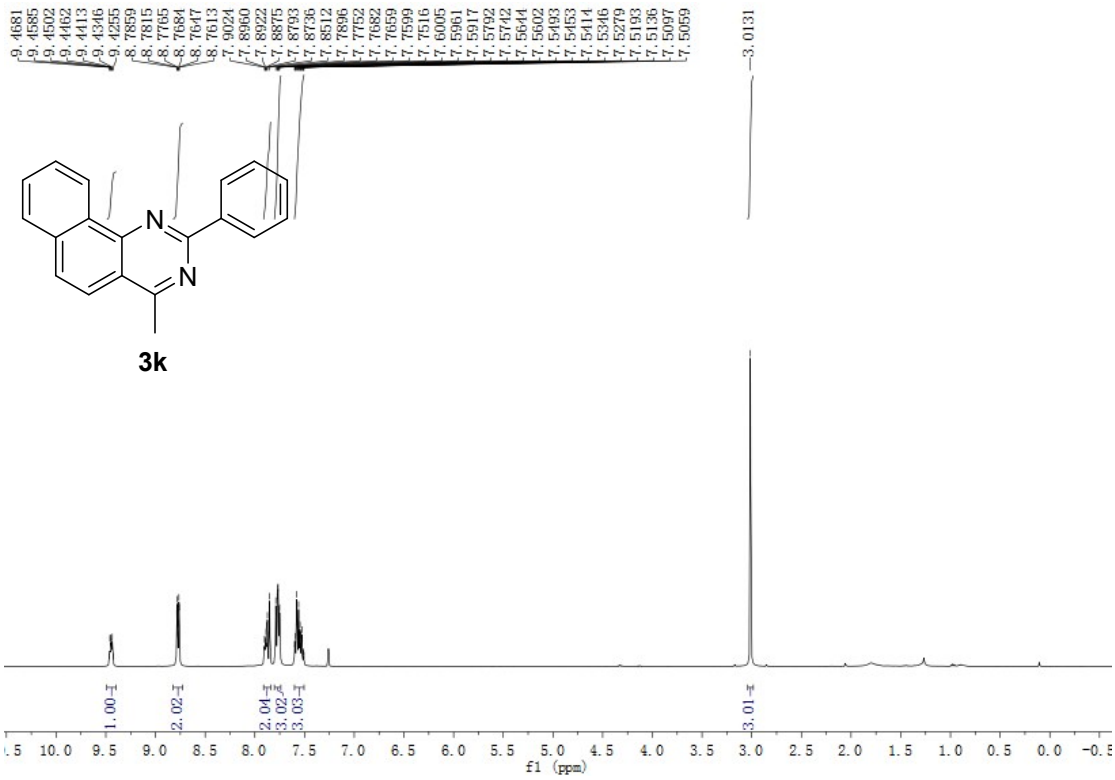


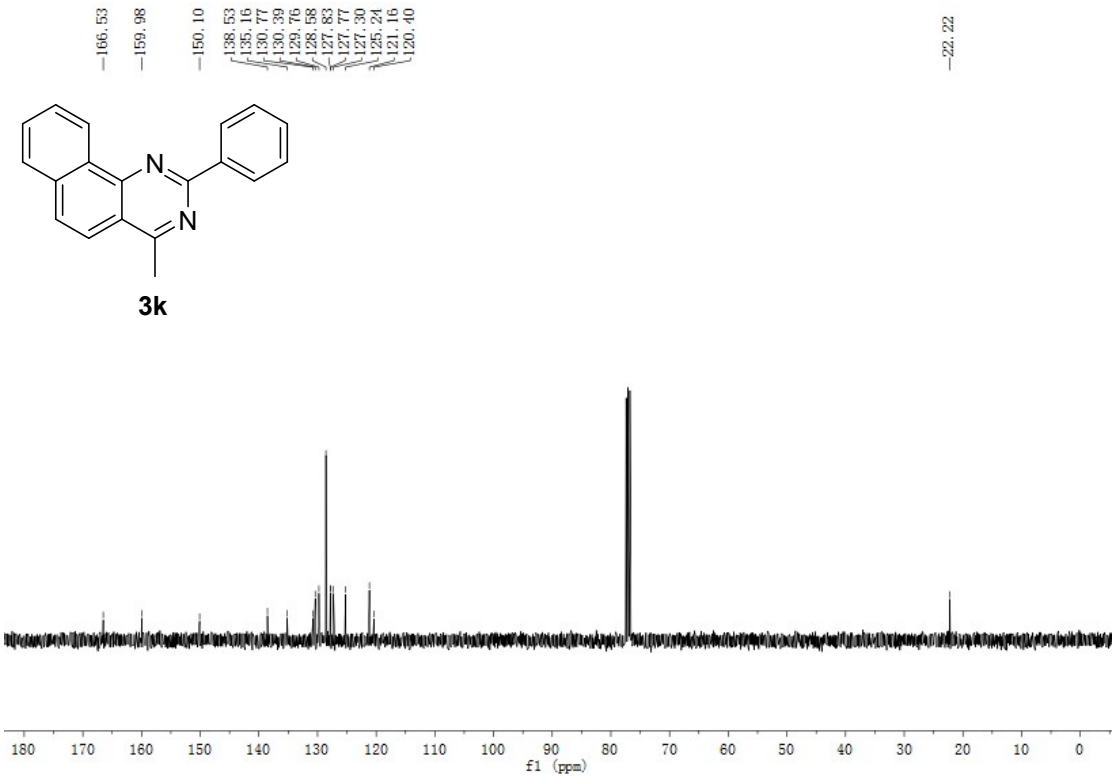
8-chloro-4-methyl-2-phenylquinazoline (3j):



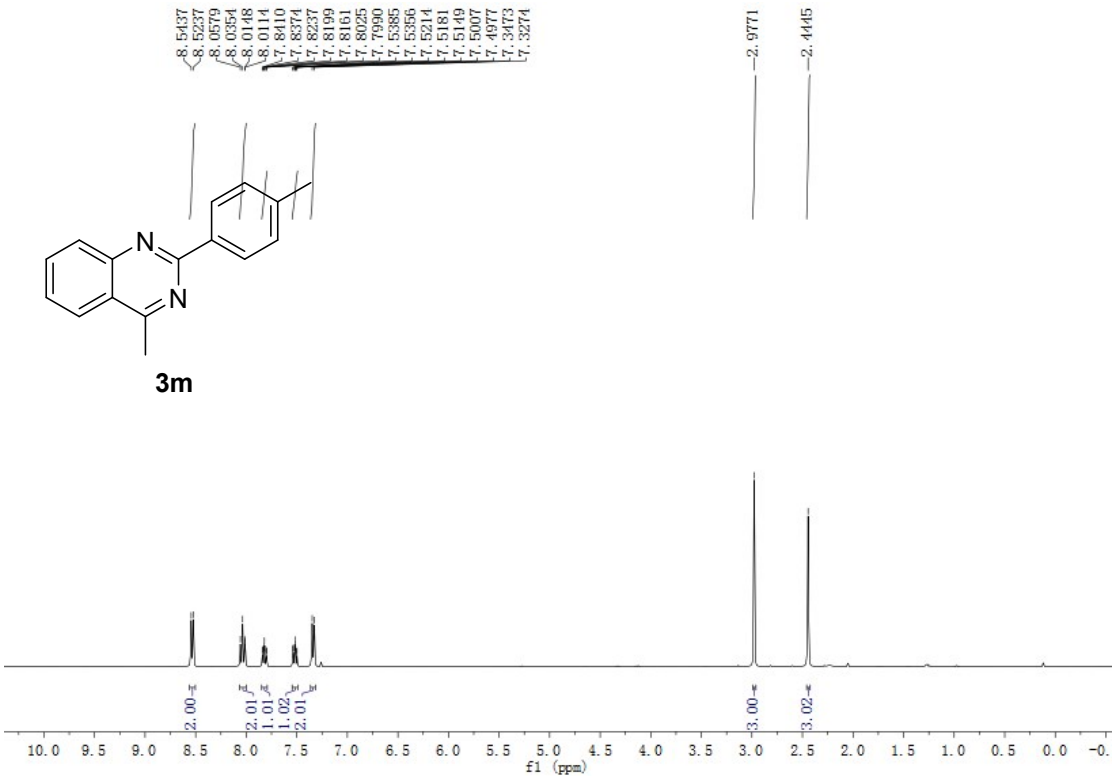


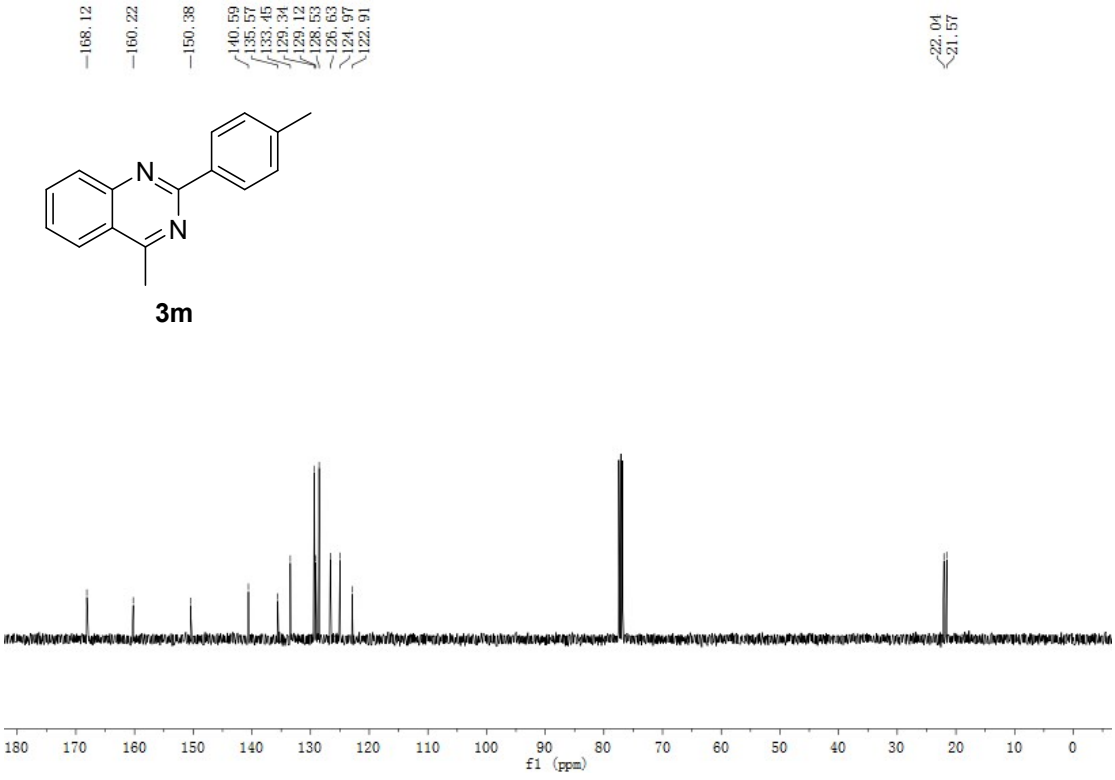
4-methyl-2-phenylbenzo[h]quinazoline (3k) :



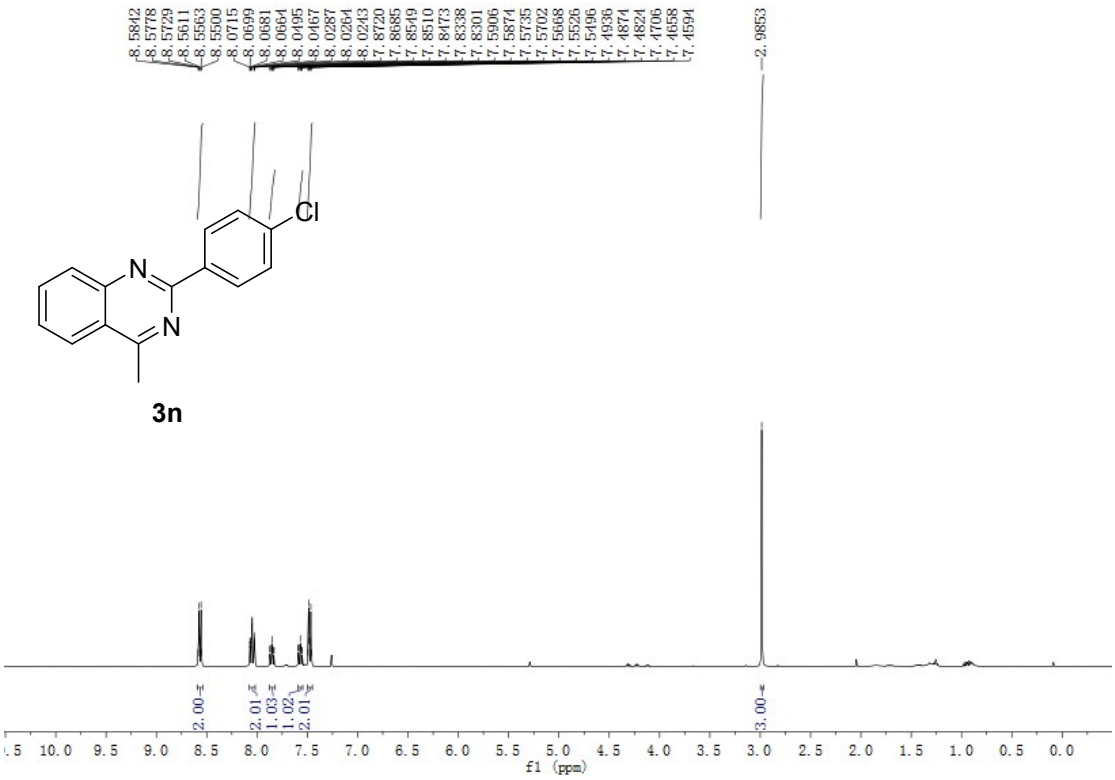


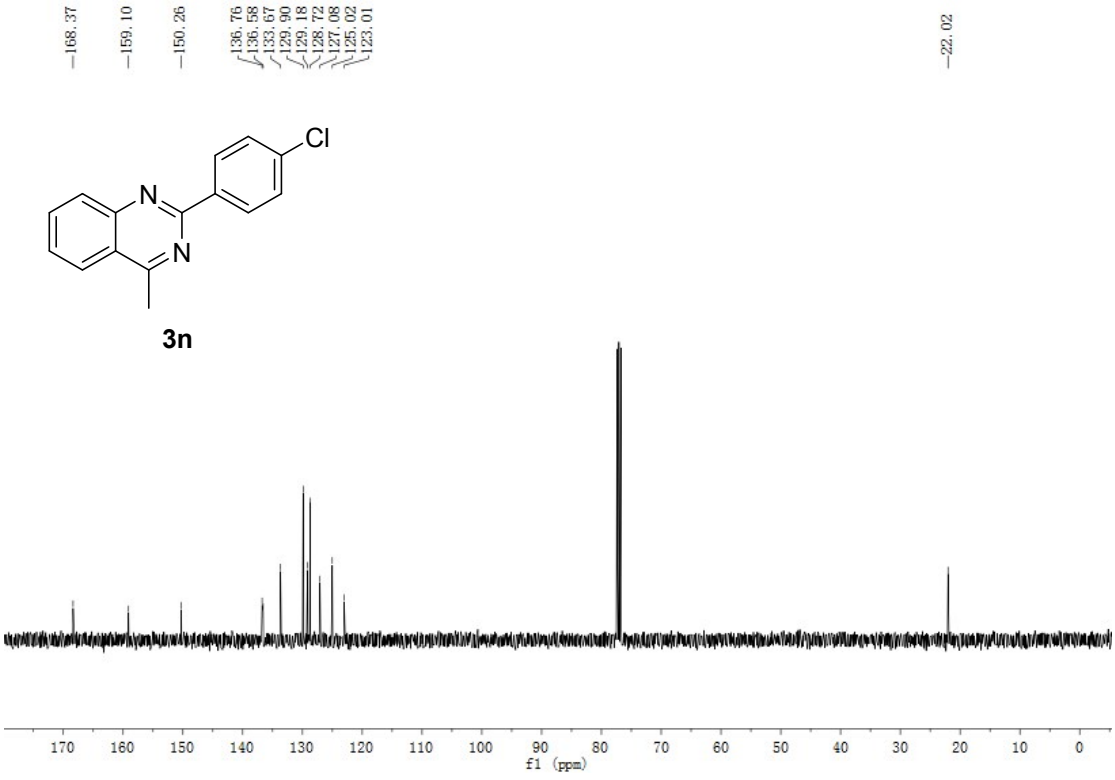
4-methyl-2-(p-tolyl)quinazoline (3m) :



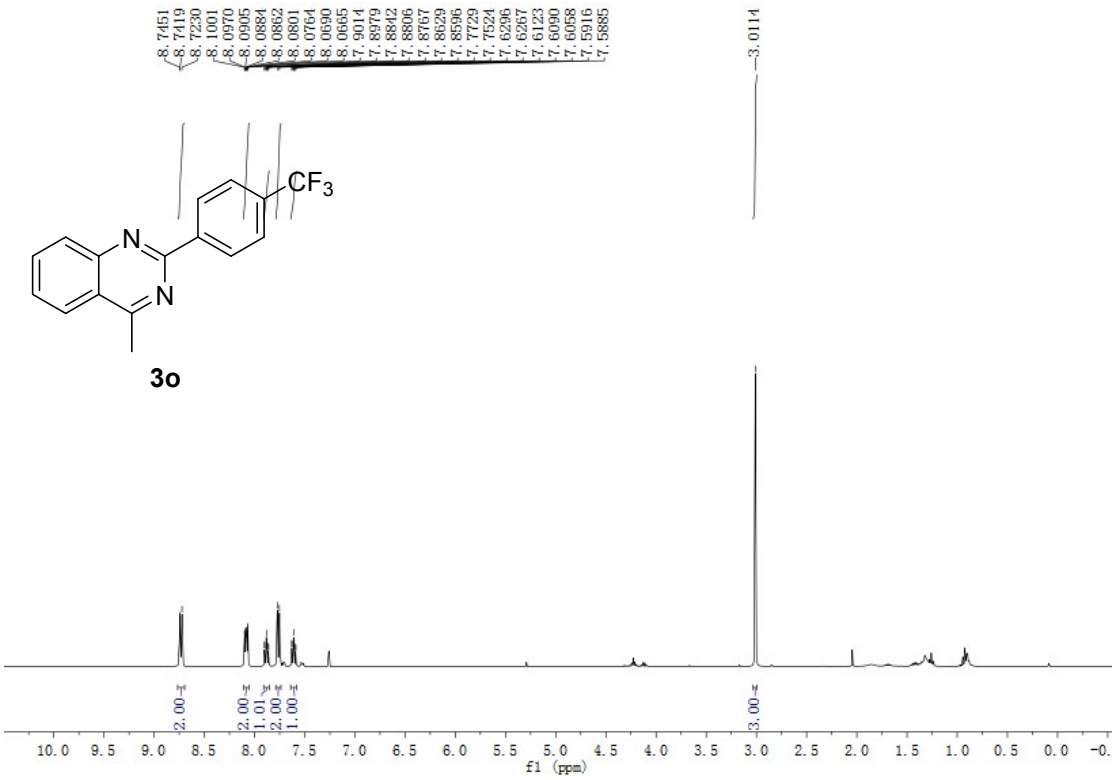


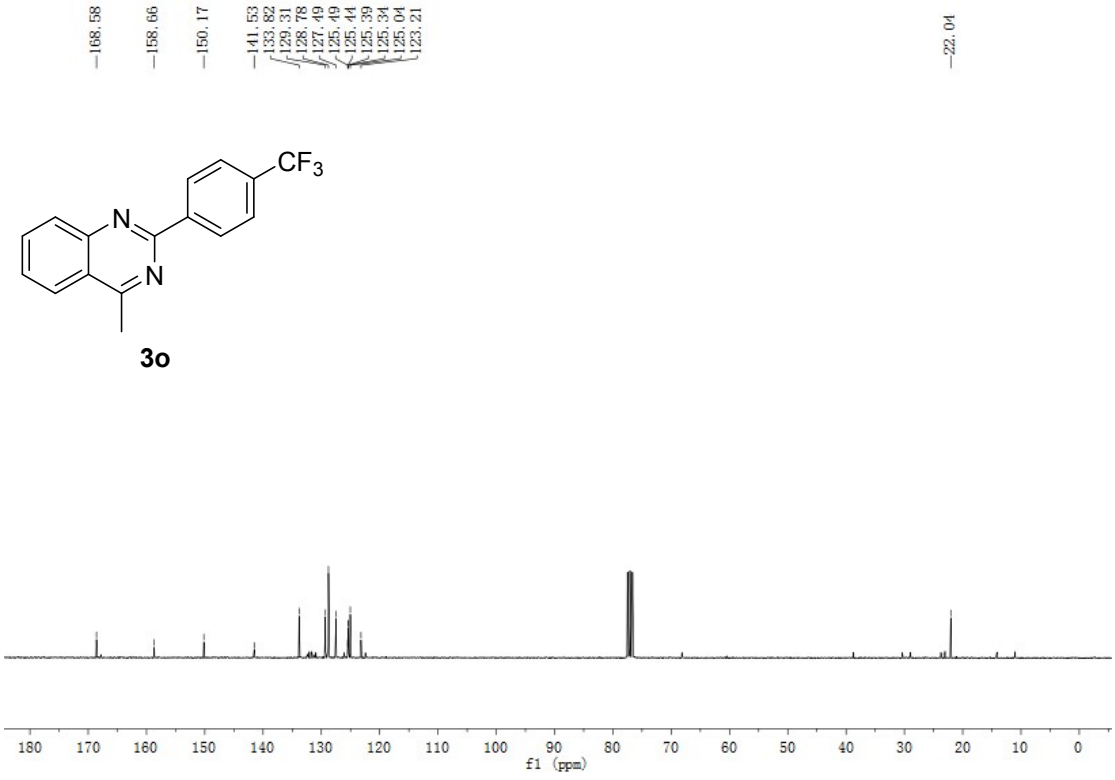
2-(4-chlorophenyl)-4-methylquinazoline (3n) :



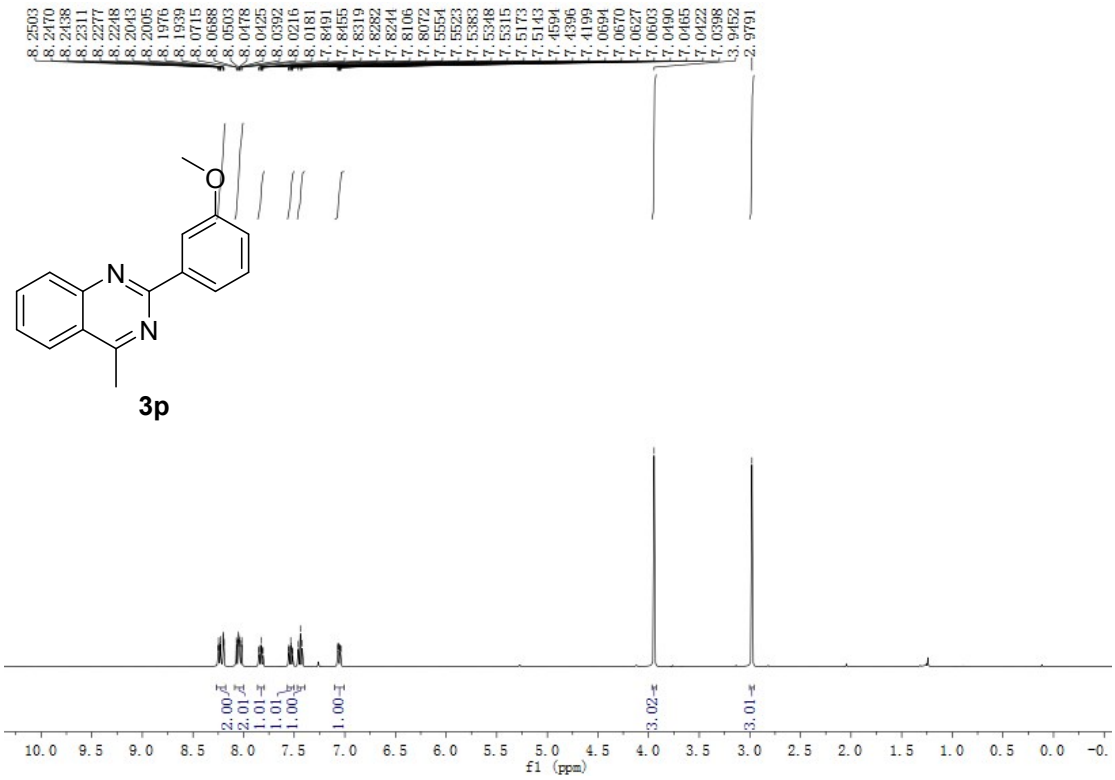


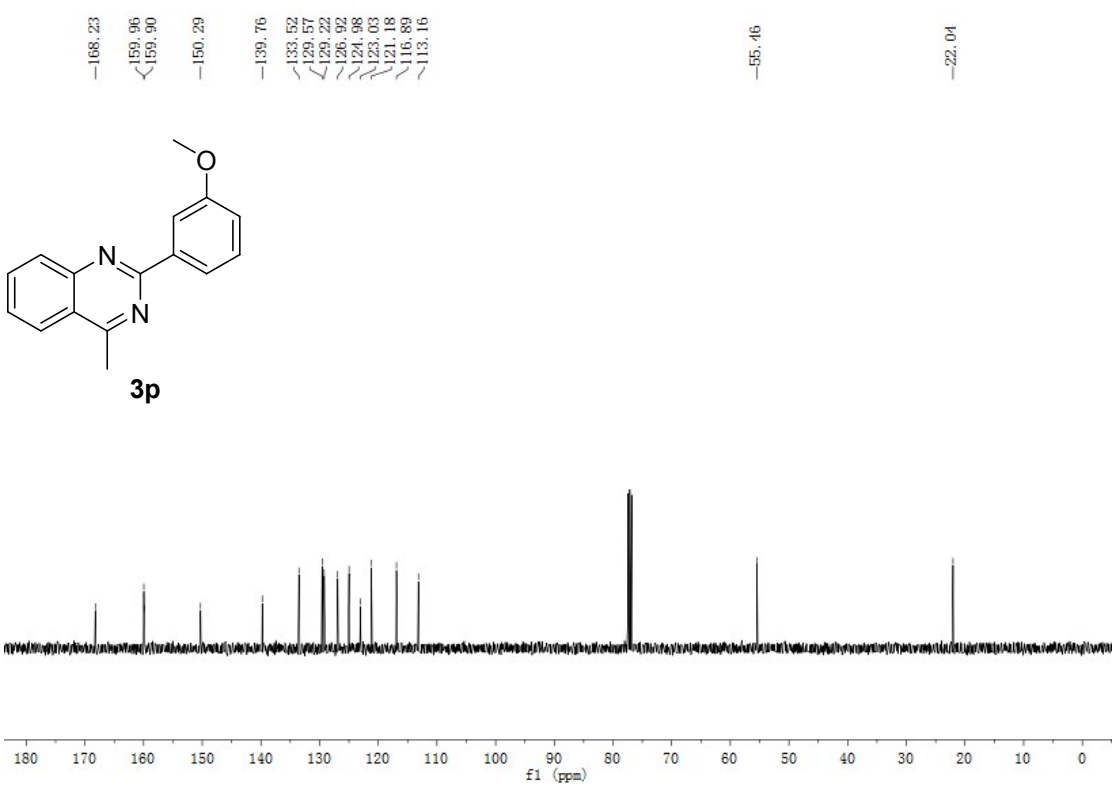
4-methyl-2-(4-(trifluoromethyl)phenyl)quinazoline (3o) :



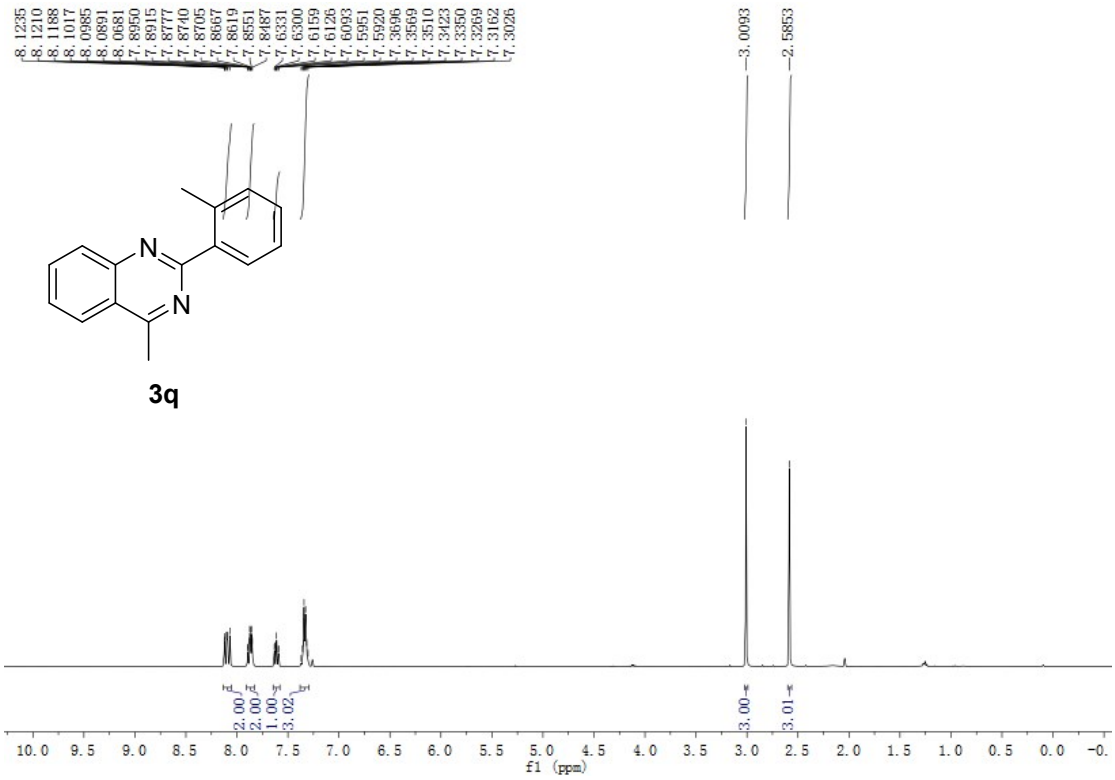


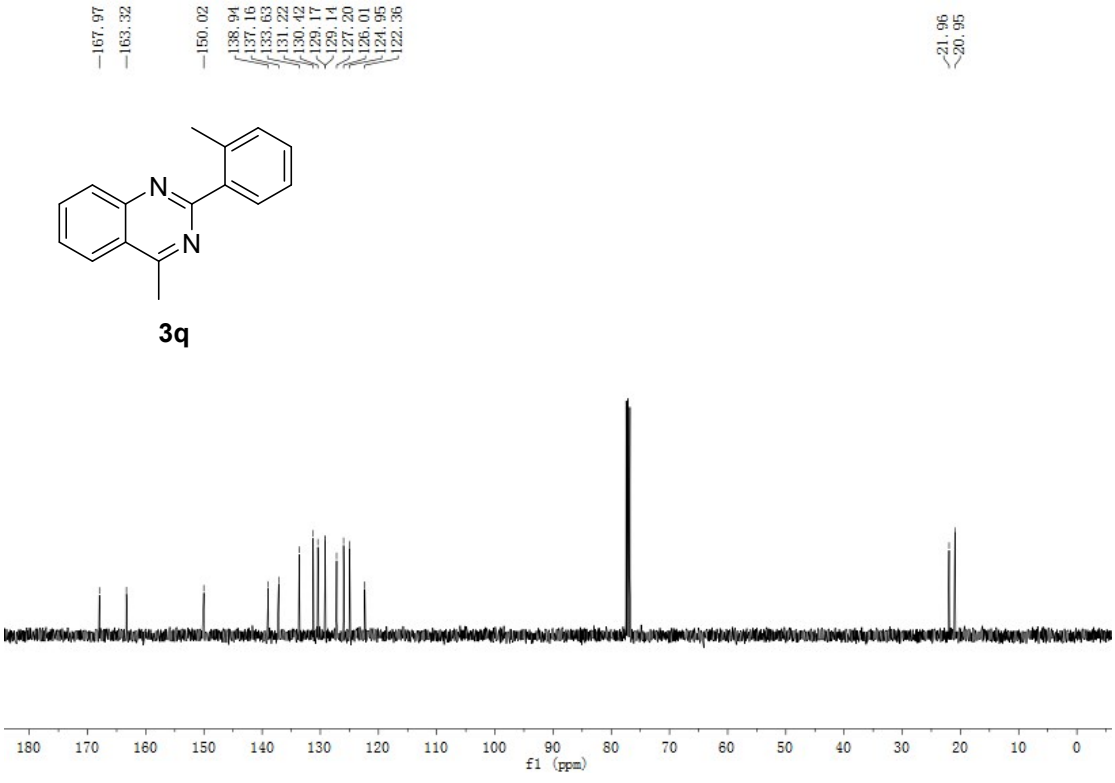
2-(3-methoxyphenyl)-4-methylquinazoline (3p) :



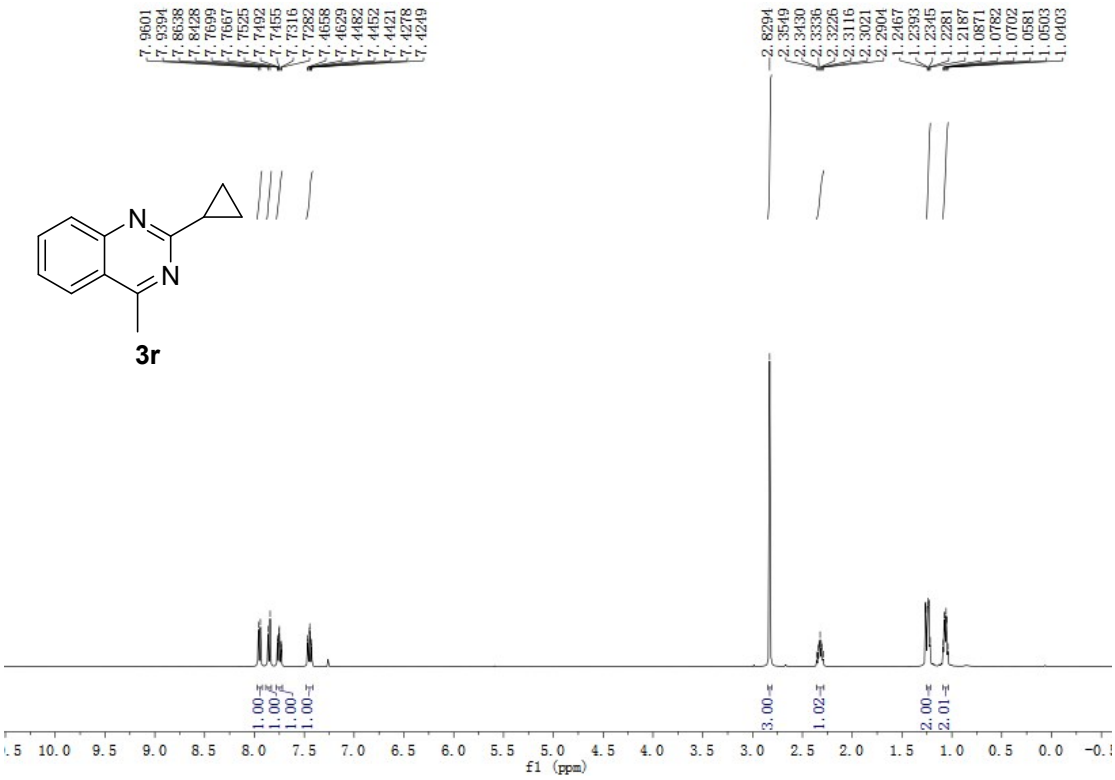


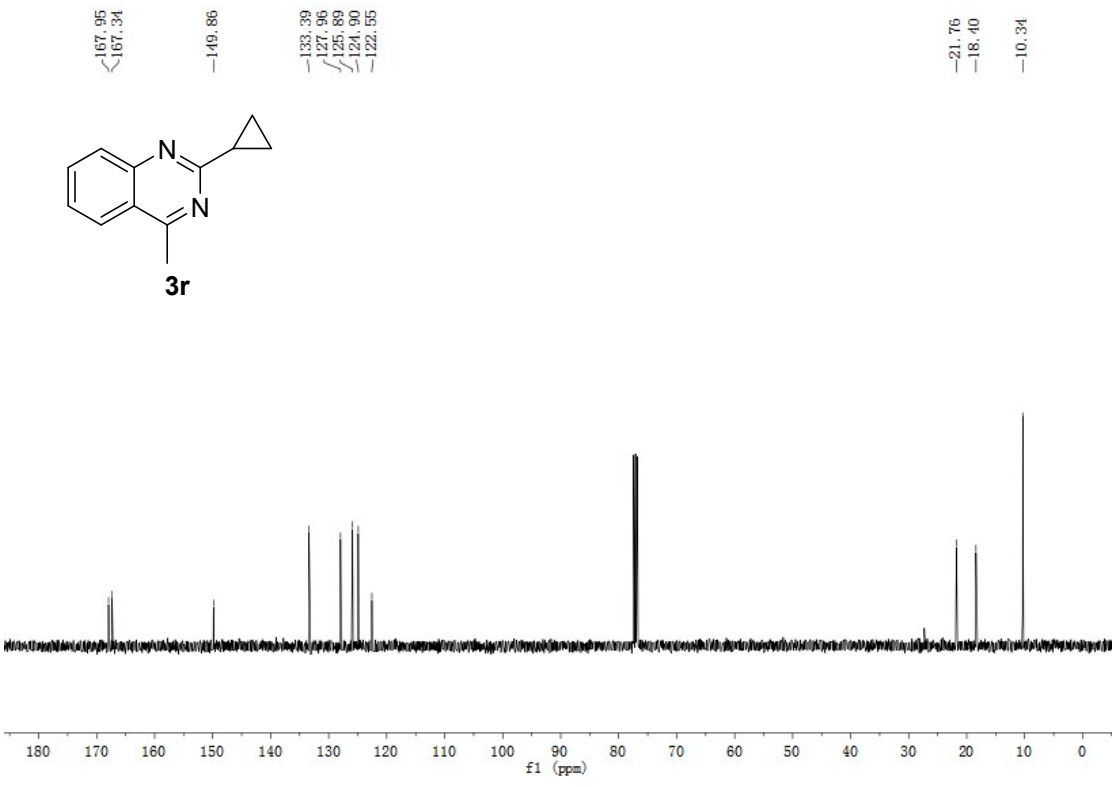
4-methyl-2-(o-tolyl)quinazoline (3q) :



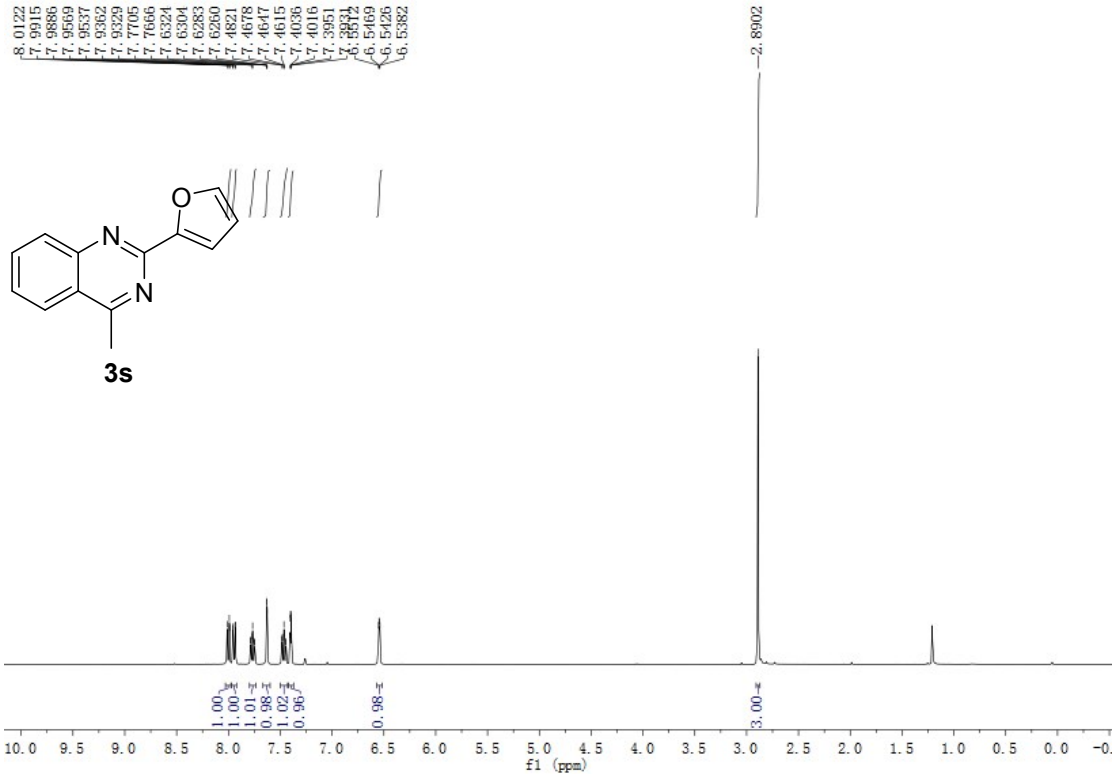


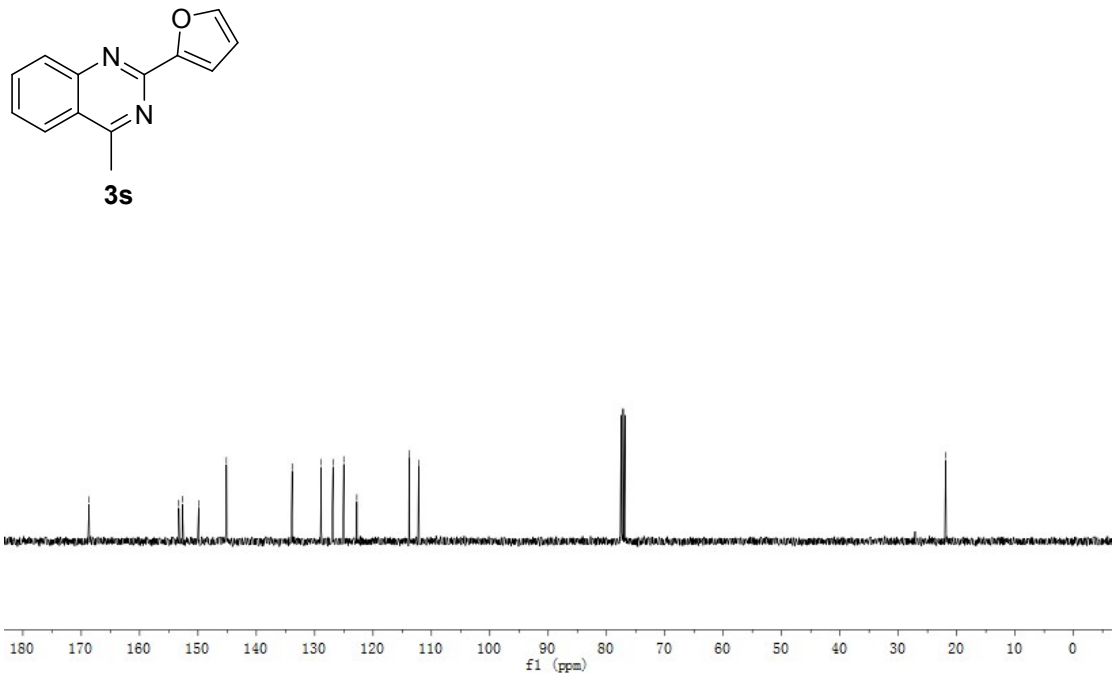
2-cyclopropyl-4-methylquinazoline (3r) :



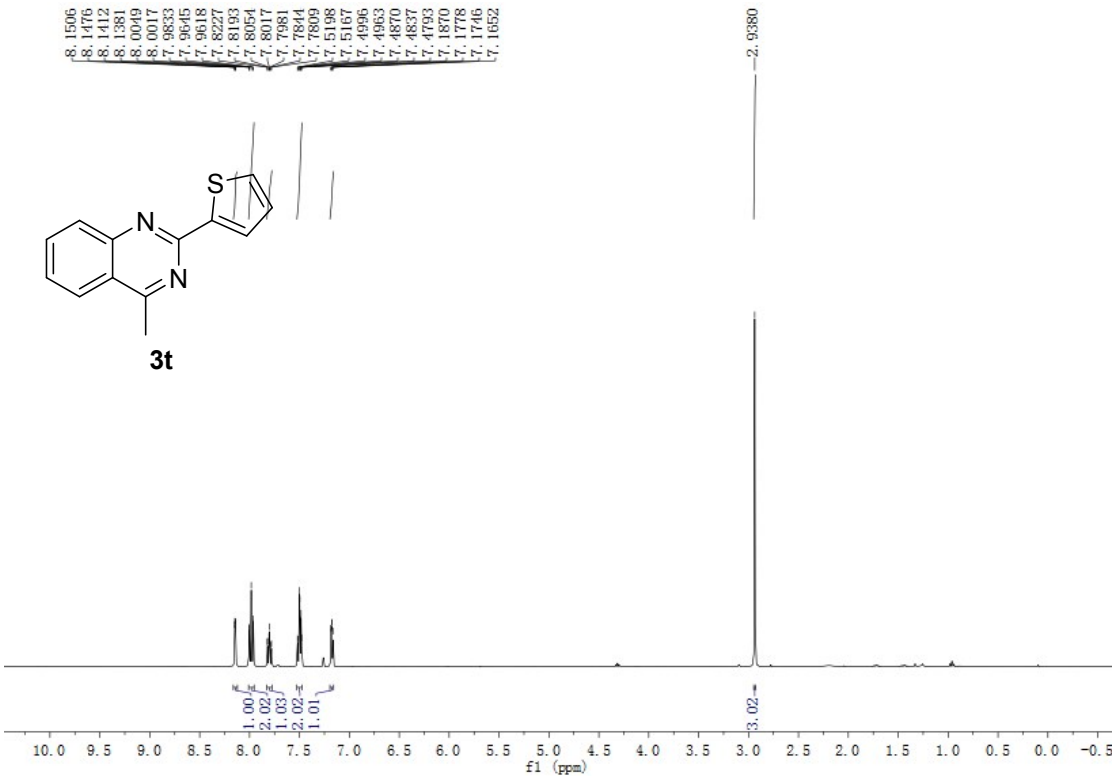


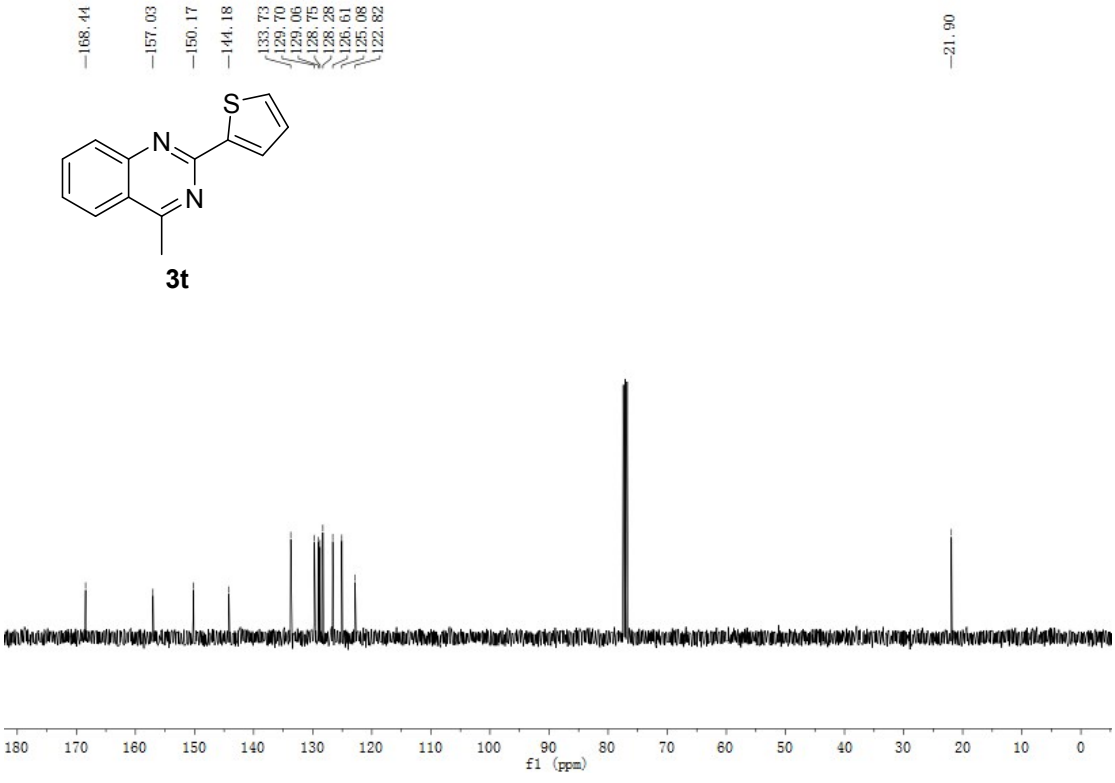
2-(furan-2-yl)-4-methylquinazoline (3s) :



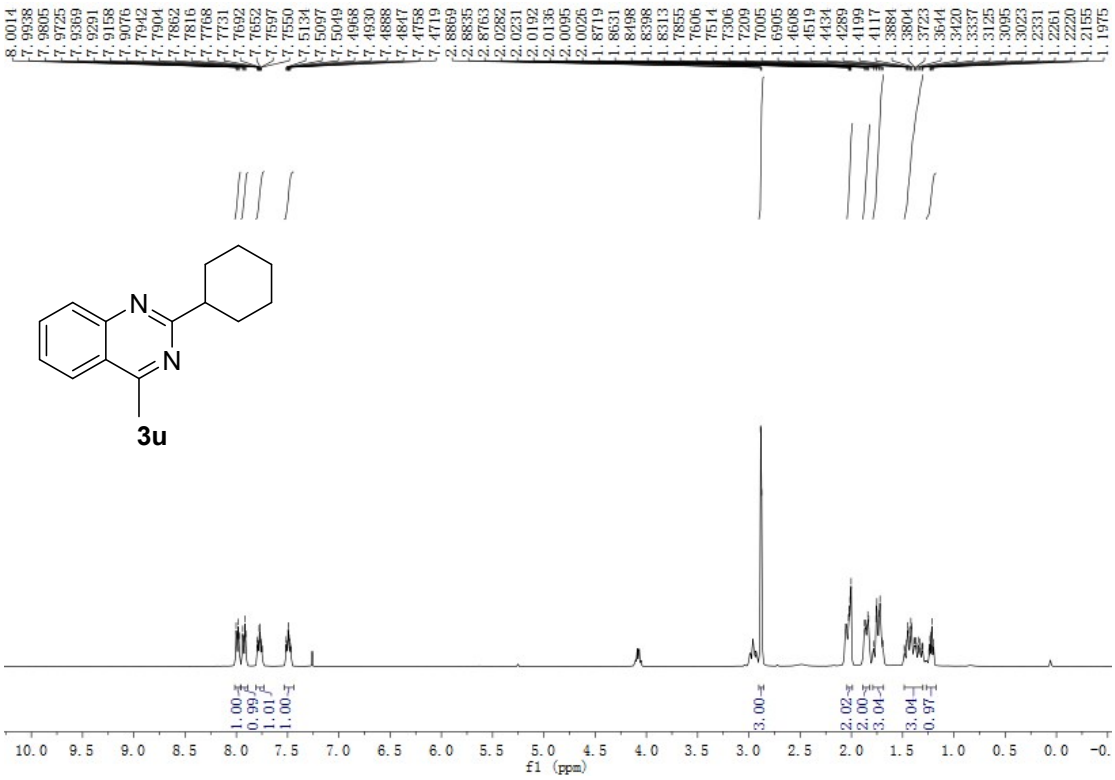


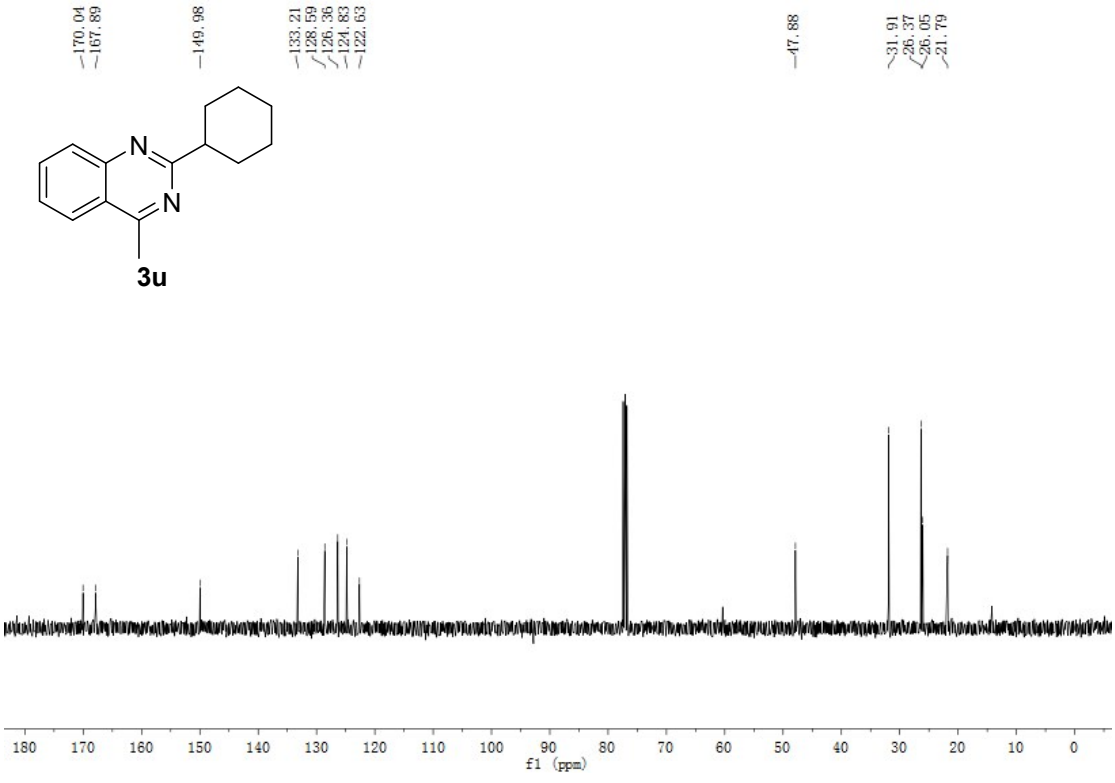
4-methyl-2-(thiophen-2-yl)quinazoline (3t) :



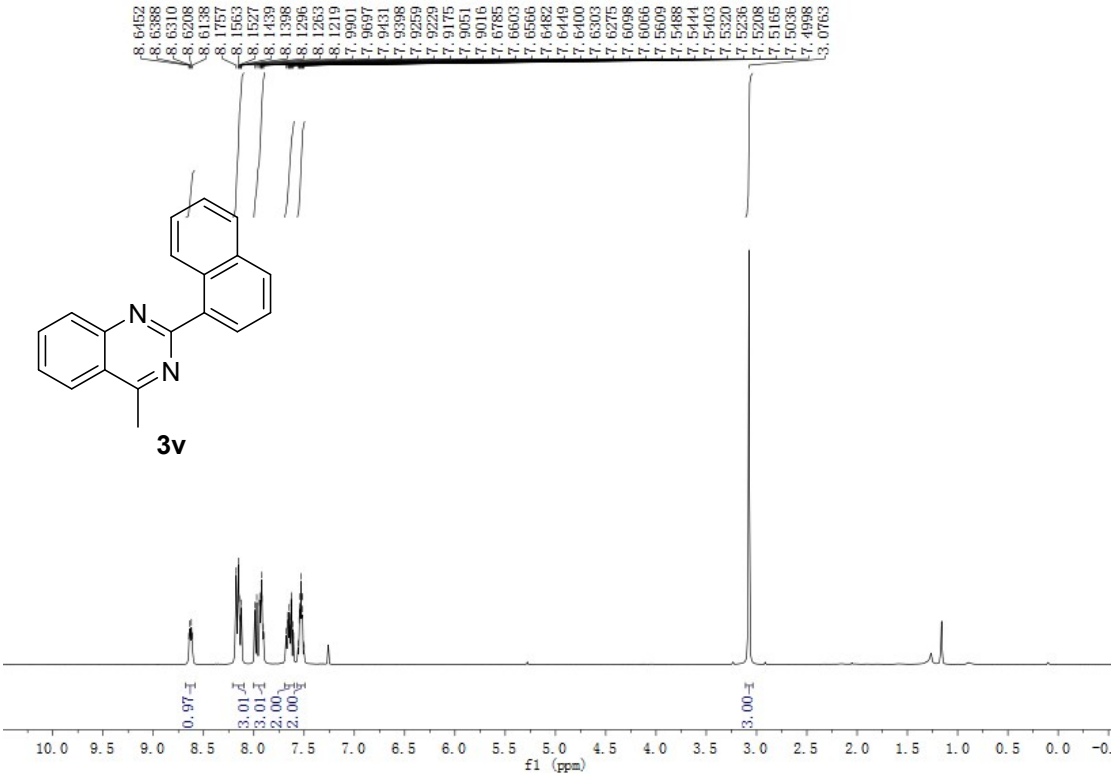


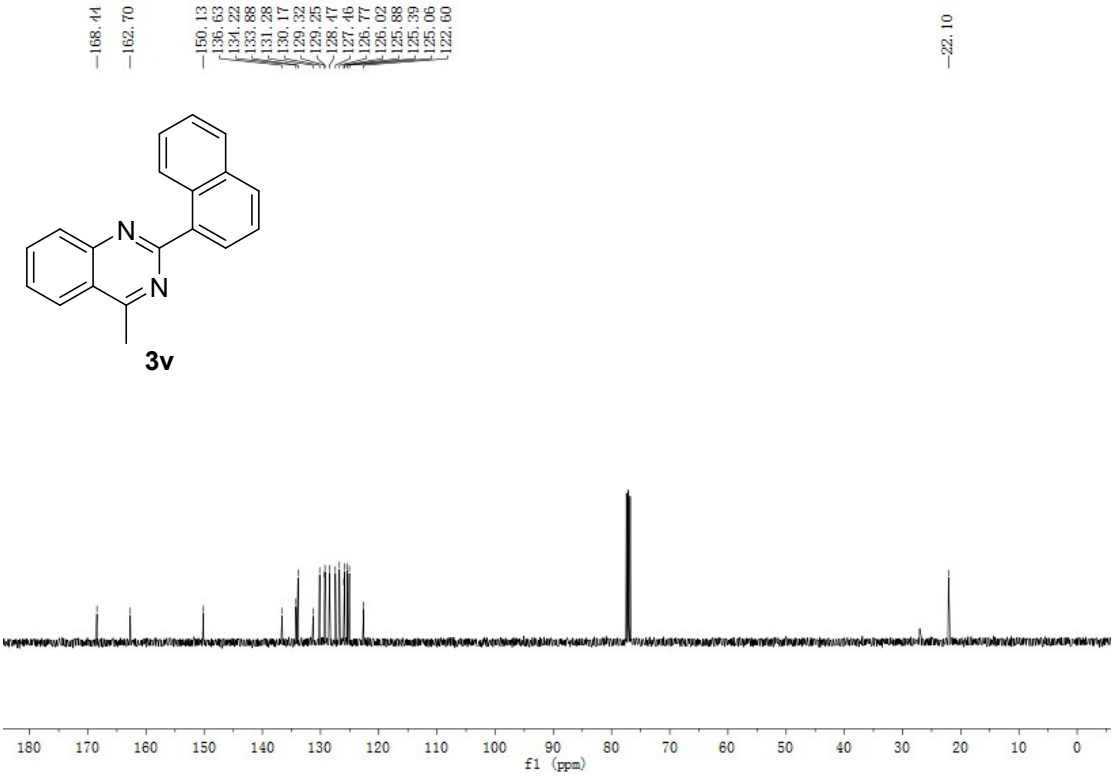
2-cyclohexyl-4-methylquinazoline (3u):



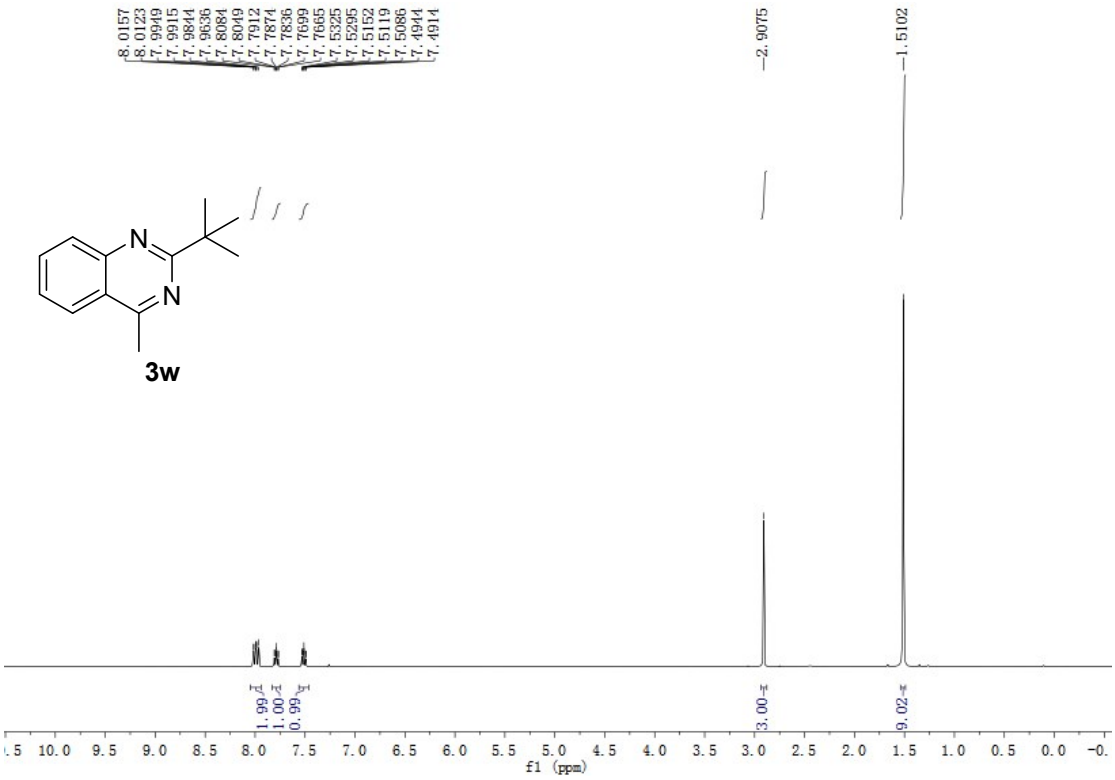


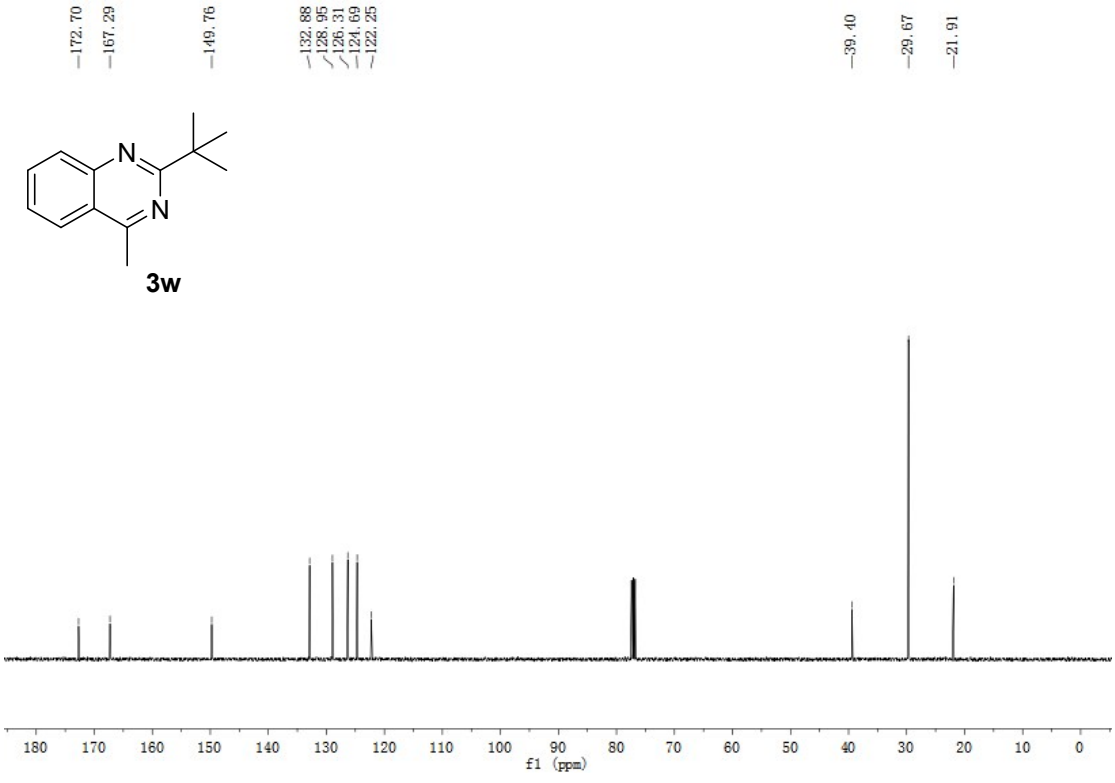
4-methyl-2-(naphthalen-1-yl)quinazoline (3v) :



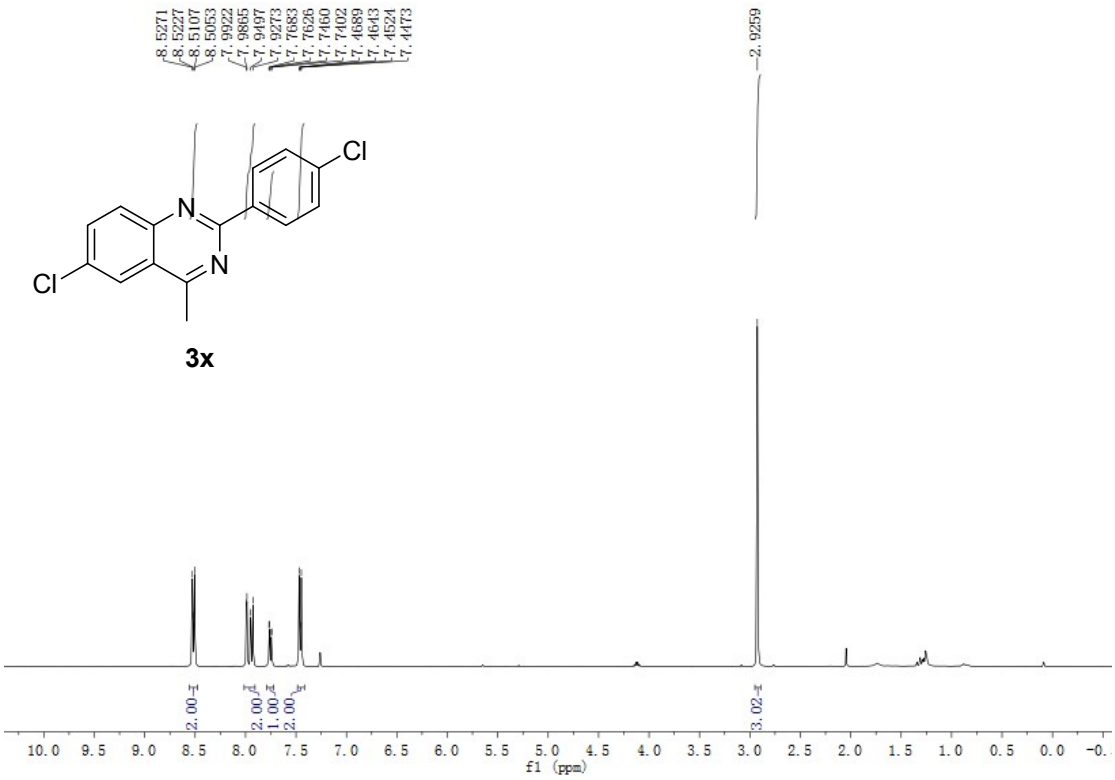


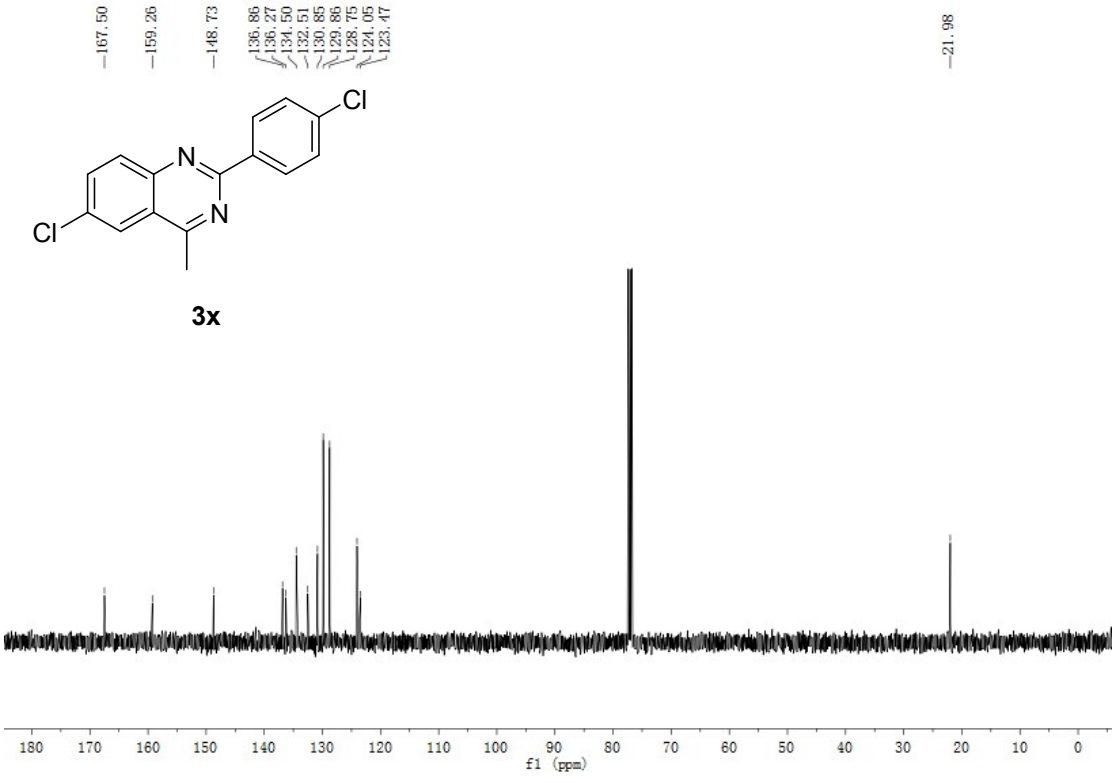
2-(*tert*-butyl)-4-methylquinazoline (3w) :



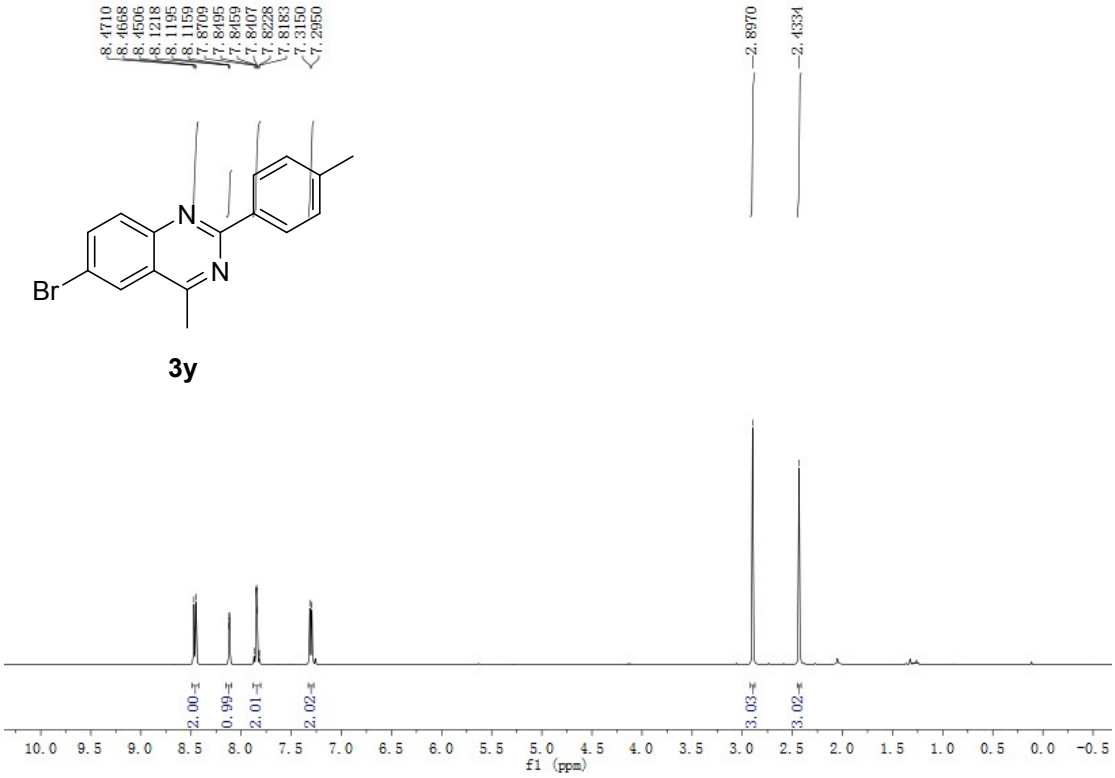


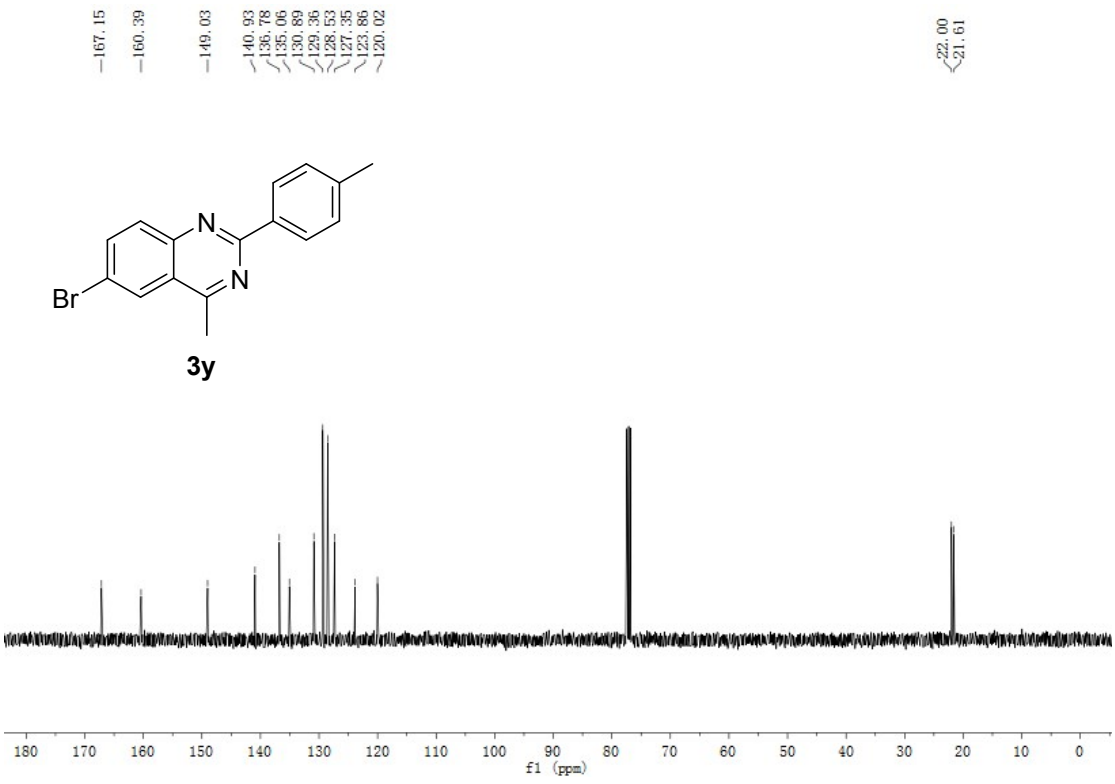
6-chloro-2-(4-chlorophenyl)quinazoline (3x) :



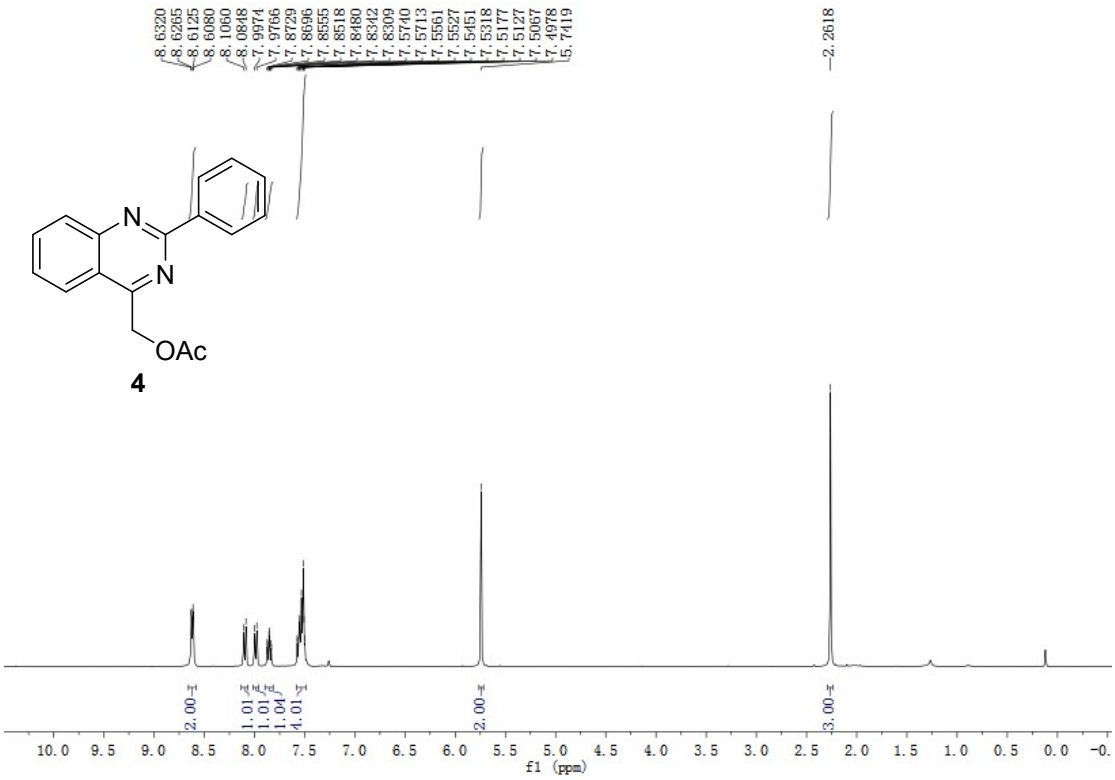


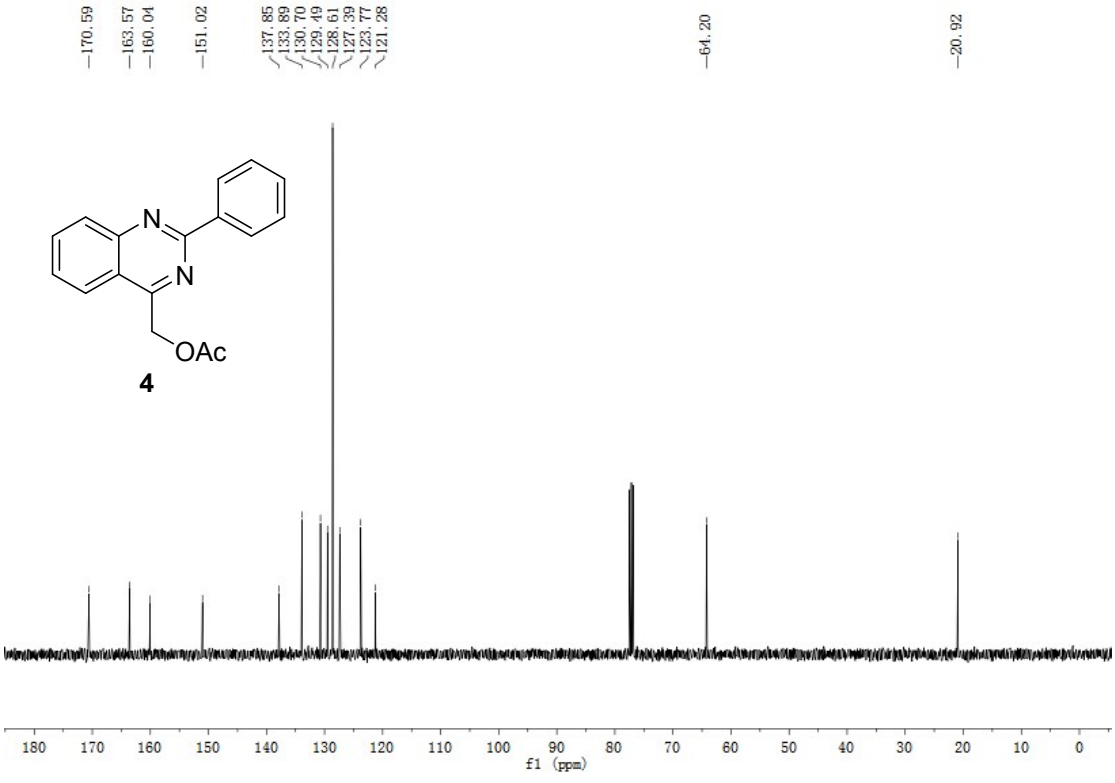
6-bromo-2-(p-tolyl)quinazoline (3y) :





(2-phenylquinazolin-4-yl)methyl acetate (4) :





(2-phenylquinazolin-4-yl)methyl acetate (5) :