KOtBu-Mediated Stereoselective Addition of Quinazolines to Alkynes under Mild Conditions

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General information
All manipulations were carried out under air atmosphere unless otherwise specified. 99% and 99.99% KOtBu were purchased from Energy Chemical and Sigma-Aldrich, respectively. Melting points were measured with an X-4 melting point apparatus (Bei Jing Taike Co., Ltd.). $^1$H-NMR and $^{13}$C-NMR were determined in CDCl$_3$ on a Bruker DPX 300 MHz or a Bruker AVANCE III 400 MHz spectrometer at room temperature, respectively, and tetramethylsilane (TMS) served as an internal standard. Spin multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as brs (broad). Coupling constants ($J$) are given in hertz (Hz). ESI-MS was carried out on a LCMS-2020 (Shimadzu, Japan). HRMS were recorded on an Agilent 6540Q-TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode. All experiments were monitored by thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates (Qingdao Haiyang Chemical Co., Ltd).

General procedure for the synthesis of product 3

To a solution of quinazoline (0.2 mmol) and alkyne (1.5 equiv) in THF (1 mL) was added KOtBu (1.5 equiv). The reaction vessel was placed in a preheated oil bath at 40 °C in air. The progress of the reaction was monitored by TLC. Upon completion, the solution was quenched by saturated NH$_4$Cl solution (2 mL), and extracted by diethyl ether (3×1 mL). The organic phase was concentrated in vacuo. The residue was then purified by chromatography on silica gel with an eluent of petroleum ether and ethyl acetate. Products were characterized by Mp, $^1$H-, $^{13}$C-NMR, MS (ESI) and HRMS.

General procedure for the synthesis of substrate 1a–t

To a solution of 2-aminobenzaldehyde (10 mmol) and triethylamine (1.6 mL, 1.2 equiv) in dichloromethane (DCM, 30 mL) cooled in an ice-water bath, chloride (1.5 equiv) was added dropwise. The progress of the reaction was monitored by TLC. Upon completion, the solution was washed with diluted hydrochloric acid, saturated NaHCO$_3$, brine, and dried over anhydrous Na$_2$SO$_4$. The organic phase was concentrated in vacuo to give amide as an intermediate without further purification. The amide, 25% ammonia water (15 mL) and isopropanol (15 mL) were added to a sealed tube. The tube was located in a preheated 90 °C oil bath and stirred for 10 h. The reaction mixture was cooled to room temperature, extracted by ethyl acetate and washed with diluted hydrochloric acid, saturated NaHCO$_3$, brine, and dried over anhydrous Na$_2$SO$_4$, then concentrated in vacuo. The residue was then purified by chromatography on silica gel with a eluent of petroleum ether and ethyl acetate. Products were characterized by Mp, $^1$H-, $^{13}$C-NMR, MS (ESI) and HRMS.
**Substrate characterizations**

2-phenylquinazoline (1a). white solid, 83% yield for two steps, mp. 94 – 95 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.47 (d, $J = 0.5$ Hz, 1H), 8.73 – 8.53 (m, 2H), 8.15 – 8.06 (m, 1H), 7.96 – 7.84 (m, 2H), 7.66 – 7.48 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 161.0, 160.4, 150.7, 137.9, 134.0, 130.5, 128.54, 128.50, 127.2, 127.0, 123.5; MS (ESI): 207.10 [M+H]$^+$.

2-(o-tolyl)quinazoline (1b). white solid, 48% yield for two steps, mp. 31 – 33 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.51 (s, 1H), 8.11 (d, $J = 8.5$ Hz, 1H), 8.05 – 7.84 (m, 3H), 7.76 – 7.60 (m, 1H), 7.48 – 7.28 (m, 3H), 2.61 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 164.0, 160.0, 150.3, 138.5, 137.3, 134.0, 131.2, 130.6, 129.2, 128.5, 127.4, 127.0, 125.9, 122.8, 20.9; MS (ESI): 221.10 [M+H]$^+$.

2-(p-tolyl)quinazoline (1c). yellow solid, 46% yield for two steps, mp. 103 – 104 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.45 (s, 1H), 8.52 (d, $J = 8.2$ Hz, 2H), 8.21 – 8.03 (m, 1H), 8.01 – 7.82 (m, 2H), 7.64 – 7.51 (m, 3H), 1.40 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 161.0, 160.3, 154.7, 150.7, 140.8, 135.3, 133.9, 129.3, 128.5, 127.0, 126.9, 123.4, 21.4; MS (ESI): 221.10 [M+H]$^+$.

2-(4-tert-butylphenyl)quinazoline (1d). yellow solid, 40% yield for two steps, mp. 81 – 83 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.45 (s, 1H), 8.66 – 8.45 (m, 2H), 8.21 – 8.03 (m, 1H), 8.01 – 7.82 (m, 2H), 7.63 – 7.51 (m, 3H), 1.40 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 161.0, 160.3, 153.9, 150.7, 135.2, 133.9, 128.5, 128.3, 127.0, 126.9, 125.5, 123.4, 34.8, 31.2; MS (ESI): 263.10 [M+H]$^+$; HRMS (ESI) m/z calcd for C$_{18}$H$_{19}$N$_2$ [M+H]$^+$ 263.1548, found 263.1549.

2-(4-methoxyphenyl)quinazoline (1e). yellow solid, 45% yield for two steps, mp. 86 – 87 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.42 (d, $J = 0.4$ Hz, 1H), 8.66 – 8.49 (m, 2H), 8.06 (d, $J = 9.0$ Hz, 1H), 7.93 – 7.83 (m, 2H), 7.57 (td, $J = 7.3$, 1.0 Hz, 1H), 7.12 – 6.97 (m, 2H), 3.90 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 161.8, 160.7, 160.3, 150.7, 133.9, 130.6, 130.1, 128.3, 127.0, 126.7, 123.2, 113.9, 55.3; MS (ESI): 237.10 [M+H]$^+$.
2-(2-fluorophenyl)quinazoline (1f)\textsuperscript{4}. Yellow solid, 56% yield for two steps, mp. 79 – 80 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 9.52 (s, 1H), 8.20 – 8.10 (m, 2H), 7.98 – 7.91 (m, 2H), 7.67 (ddd, \(J = 8.1, 7.1, 1.0\) Hz, 1H), 7.51 – 7.43 (m, 1H), 7.31 (td, \(J = 7.6, 1.1\) Hz, 1H), 7.27 – 7.20 (m, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 161.3 (d, \(J_{C2',F} = 254.7\) Hz, C2'), 160.4, 159.8 (d, \(J_{C2,F} = 4.4\) Hz, C2), 150.6, 134.3, 132.2 (d, \(J_{CF2,F} = 1.9\) Hz, C6'), 131.6 (d, \(J_{C4',F} = 8.6\) Hz, C4'), 128.7, 127.9, 127.11, 127.08 (d, \(J_{C1,F} = 9.8\) Hz, C1'), 124.2 (d, \(J_{C5',F} = 3.8\) Hz, C5'); MS (ESI): 225.05 [M+H]+.

2-(4-fluorophenyl)quinazoline (1g)\textsuperscript{4}. Yellow solid, 52% yield for two steps, mp. 121 – 123 °C. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 9.44 (s, 1H), 8.81 – 8.49 (m, 2H), 8.07 (d, \(J = 9.1\) Hz, 1H), 7.97 – 7.85 (m, 2H), 7.71 – 7.54 (m, 1H), 7.25 – 7.16 (m, 2H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 164.6 (d, \(J_{C4',F} = 250.4\) Hz, C4'), 160.4, 160.0, 150.6, 134.1, 130.6 (d, \(J_{C2',F} = 8.6\) Hz, C2'), 128.4, 127.2, 127.0, 123.4, 115.4 (d, \(J_{C3',F} = 21.7\) Hz, C3'); MS (ESI): 225.05 [M+H]+.

2-(2-chlorophenyl)quinazoline (1h)\textsuperscript{4}. Yellow solid, 52% yield for two steps, mp. 65 – 67 °C. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 9.55 (s, 1H), 8.20 – 8.09 (m, 1H), 8.04 – 7.91 (m, 2H), 7.86 – 7.78 (m, 1H), 7.75 – 7.65 (m, 1H), 7.58 – 7.49 (m, 1H), 7.45 – 7.33 (m, 2H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 161.9, 160.1, 150.3, 138.2, 134.3, 132.8, 131.7, 130.5, 130.2, 128.5, 128.0, 127.0, 126.8, 123.2; MS (ESI): 241.00 [M+H]+.

2-(3-chlorophenyl)quinazoline (1i)\textsuperscript{4}. White solid, 48% yield for two steps, mp. 145 – 146 °C. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 9.47 (s, 1H), 8.64 (s, 1H), 8.55 – 8.47 (m, 1H), 8.11 (d, \(J = 9.0\) Hz, 1H), 8.00 – 7.88 (m, 2H), 7.71 – 7.58 (m, 1H), 7.53 – 7.40 (m, 2H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 160.4, 159.6, 150.5, 139.7, 134.7, 134.2, 130.4, 129.7, 128.6, 127.5, 127.0, 126.5, 123.6; MS (ESI): 241.05 [M+H]+.

2-(4-chlorophenyl)quinazoline (1j)\textsuperscript{4}. White solid, 52% yield for two steps, mp. 123 – 124 °C. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 9.43 (s, 1H), 8.65 – 8.48 (m, 2H), 8.06 (d, \(J = 9.0\) Hz, 1H), 7.97 – 7.85 (m, 2H), 7.61 (ddd, \(J = 8.0, 7.0, 1.0\) Hz, 1H), 7.55 – 7.40 (m, 2H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 160.4, 159.9, 150.6, 136.7, 136.4, 134.1, 129.8, 128.7, 128.5, 127.3, 127.0, 123.5; MS (ESI): 241.05 [M+H]+.
2-(4-(trifluoromethyl)phenyl)quinazoline (1k). yellow solid, 66% yield for two steps, mp. 141 – 142 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.48 (s, 1H), 8.74 (d, $J = 8.1$ Hz, 2H), 8.11 (d, $J = 9.1$ Hz, 1H), 8.00 – 7.89 (m, 2H), 7.78 (d, $J = 8.3$ Hz, 2H), 7.66 (td, $J = 7.3$, 1.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.6, 159.6, 150.7, 141.3, 134.4, 132.1 (q, $J_{CF} = 32.3$ Hz, C$^4$), 128.8, 128.7, 127.9, 127.2, 125.5 (q, $J_{CF} = 3.8$ Hz, C$^2$); MS (ESI): 275.05 [M+H]$^+$.  

2-(2,3-dichlorophenyl)quinazoline (1l). yellow solid, 46% yield for two steps, mp. 114 – 115 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.54 (s, 1H), 8.14 (d, $J = 8.3$ Hz, 1H), 8.08 – 7.91 (m, 2H), 7.81 – 7.64 (m, 2H), 7.59 (d, $J = 7.9$ Hz, 1H), 7.36 (t, $J = 7.8$ Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 161.5, 160.3, 150.2, 140.4, 134.5, 134.0, 131.4, 131.0, 129.7, 128.5, 128.2, 127.3, 127.1, 123.3; MS (ESI): 275.00 [M+H]$^+$. HRMS (ESI) m/z calcd for C$_{14}$H$_9$Cl$_2$N$_2$ [M+H]$^+$ 275.0143, found 275.0138.  

2-(naphthalen-1-yl)quinazoline (1m). yellow solid, 24% yield for two steps, mp. 115 – 117 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.60 (s, 1H), 8.75 – 8.64 (m, 1H), 8.23 – 8.15 (m, 2H), 8.05 – 7.90 (m, 4H), 7.76 – 7.60 (m, 2H), 7.59 – 7.43 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 163.4, 160.3, 150.5, 136.2, 134.2, 131.4, 131.2, 130.3, 129.6, 128.6, 128.4, 127.7, 127.1, 126.8, 125.9, 125.8, 125.2, 123.1; MS (ESI): 257.05 [M+H]$^+$.  

2-(thiophen-2-yl)quinazoline (1n). yellow solid, 43% yield for two steps, mp. 138 – 139°C. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.36 (s, 1H), 8.18 (dd, $J = 3.7$, 1.1 Hz, 1H), 8.03 (d, $J = 8.9$ Hz, 1H), 7.96 – 7.81 (m, 2H), 7.63 – 7.54 (m, 1H), 7.52 (dd, $J = 5.0$, 1.2 Hz, 1H), 7.20 (dd, $J = 5.0$, 3.7 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.5, 157.9, 150.6, 143.8, 134.3, 130.0, 129.3, 128.4, 128.2, 127.3, 127.0, 123.4; MS (ESI): 213.05 [M+H]$^+$.  

6-chloro-2-phenylquinazoline (1o). yellow solid, 16% yield for two steps, mp. 158 – 159 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.39 (s, 1H), 8.65 – 8.54 (m, 2H), 8.03 (d, $J = 9.0$ Hz, 1H), 7.89 (d, $J = 2.2$ Hz, 1H), 7.82 (dd, $J = 9.0$, 2.3 Hz, 1H), 7.61 – 7.45 (m, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 161.1, 159.4,
2-propylquinazoline (1p)\(^2\), yellow oil, 47% yield for two steps. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.31 (s, 1H), 7.94 (d, \(J = 9.0\) Hz, 1H), 7.84 (t, \(J = 7.3\) Hz, 2H), 7.55 (t, \(J = 7.5\) Hz, 1H), 3.18 – 2.96 (m, 2H), 2.12 – 1.76 (m, 2H), 1.01 (t, \(J = 7.4\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 167.6, 160.2, 150.2, 133.8, 127.8, 126.9, 126.8, 122.9, 41.8, 42.2, 13.9; MS (ESI): 241.00 [M+H]\(^+\).

2-pentylquinazoline (1q)\(^8\), yellow oil, 25% yield for two steps. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.34 (s, 1H), 8.04 – 7.94 (m, 1H), 7.87 (dd, \(J = 11.9, 4.4\) Hz, 2H), 7.66 – 7.51 (m, 1H), 3.19 – 2.98 (m, 2H), 2.09 – 1.76 (m, 2H), 1.51 – 1.28 (m, 4H), 0.90 (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 167.9, 160.3, 150.3, 133.9, 127.8, 127.0, 126.8, 123.0, 39.9, 31.7, 28.6, 22.4, 13.9; MS (ESI): 201.10 [M+H]\(^+\).

2-(tert-butyl)quinazoline (1r)\(^3\), yellow oil, 37% yield for two steps. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.36 (s, 1H), 8.00 (d, \(J = 8.3\) Hz, 1H), 7.86 (t, \(J = 7.9\) Hz, 2H), 7.58 (t, \(J = 7.5\) Hz, 1H), 1.52 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 173.4, 159.8, 150.0, 133.4, 128.3, 126.7, 122.7, 39.5, 29.6; MS (ESI): 187.10 [M+H]\(^+\).

2-cyclopropylquinazoline (1s)\(^5\), yellow solid, 45% yield for two steps, mp. 37 – 38 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.23 (s, 1H), 7.90 (d, \(J = 8.8\) Hz, 1H), 7.87 – 7.78 (m, 2H), 7.52 (ddd, \(J = 7.9, 6.9, 1.2\) Hz, 1H), 2.40 (tt, \(J = 8.2, 4.7\) Hz, 1H), 1.28 (dt, \(J = 6.7, 4.1\) Hz, 2H), 1.18 – 1.09 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.4, 160.3, 150.4, 134.0, 127.5, 127.1, 126.3, 123.2, 18.6, 10.6; MS (ESI): 171.10 [M+H]\(^+\).

2-cyclohexylquinazoline (1t)\(^4\), yellow solid, 64% yield for two steps, mp. 29 – 31 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.35 (d, \(J = 0.4\) Hz, 1H), 7.99 (dd, \(J = 8.3, 0.8\) Hz, 1H), 7.91 – 7.80 (m, 2H), 7.58 (td, \(J = 7.3, 1.1\) Hz, 1H), 3.06 (tt, \(J = 11.8, 3.5\) Hz, 1H), 2.16 – 2.02 (m, 2H), 2.00 – 1.86 (m, 2H), 1.85 – 1.71 (m, 3H), 1.58 – 1.31 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.9, 160.4, 150.4, 133.9, 128.1, 127.0, 126.8, 123.3, 47.9, 32.0, 26.3, 26.1; MS (ESI): 213.10 [M+H]\(^+\).
Product characterizations

(E)-2-phenyl-4-styrylquinazoline (3aa). yellow solid, 75% yield, mp. 136 – 137 °C. 1H NMR (300 MHz, CDCl3) δ 8.73 (dd, J = 7.9, 1.5 Hz, 2H), 8.46 (d, J = 15.5 Hz, 1H), 8.30 (d, J = 8.3 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 15.5 Hz, 1H), 7.92 – 7.84 (m, 1H), 7.78 (d, J = 6.9 Hz, 2H), 7.67 – 7.51 (m, 4H), 7.52 – 7.34 (m, 3H); 13C NMR (100 MHz, CDCl3) δ 161.9, 160.1, 152.0, 139.4, 138.6, 136.2, 133.5, 130.4, 129.6, 129.3, 128.9, 128.7, 128.6, 128.1, 126.8, 123.8, 121.7, 120.9; MS (ESI): 309.10 [M+H]+; HRMS (ESI) m/z calcd for C22H17N2 [M+H]+ 309.1392, found 309.1385.

2-phenylquinazolin-4(3H)-one (3aa’). white solid, mp. 235 – 237 °C. 1H NMR (300 MHz, DMSO-d6) δ 12.53 (s, 1H), 8.16 (t, J = 7.7 Hz, 3H), 7.83 (t, J = 7.1 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.65 – 7.41 (m, 4H); 13C NMR (100 MHz, DMSO-d6) δ 162.2, 152.3, 148.7, 134.6, 132.7, 131.4, 128.6, 127.7, 127.5, 126.5, 125.8, 121.0; MS (ESI): 223.00 [M+H]+.

(E)-4-(4-methylstyril)-2-phenylquinazoline (3ab). yellow solid, 55% yield, mp. 115 – 116 °C. 1H NMR (300 MHz, CDCl3) δ 8.79 – 8.65 (m, 2H), 8.45 (d, J = 15.4 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 8.00 – 7.81 (m, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.64 – 7.48 (m, 4H), 7.27 (d, J = 8.4 Hz, 2H), 2.43 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 162.1, 160.1, 152.0, 140.0, 139.5, 138.6, 133.41, 133.38, 130.4, 129.7, 129.3, 128.6, 128.5, 128.1, 126.8, 123.9, 121.6, 119.9, 21.5; MS (ESI): 323.10 [M+H]+; HRMS (ESI) m/z calcd for C23H19N2 [M+H]+ 323.1548, found 323.1545.

(E)-4-(3-methylstyril)-2-phenylquinazoline (3ac). yellow solid, 81% yield, mp. 117 – 118 °C. 1H NMR
(300 MHz, CDCl$_3$) $\delta$ 8.74 (d, $J = 6.6$ Hz, 2H), 8.44 (d, $J = 15.4$ Hz, 1H), 8.30 (d, $J = 8.4$ Hz, 1H), 8.10 (d, $J = 8.4$ Hz, 1H), 7.95 (d, $J = 15.4$ Hz, 1H), 7.87 (t, $J = 7.4$ Hz, 1H), 7.68 – 7.48 (m, 6H), 7.36 (t, $J = 7.8$ Hz, 1H), 7.23 (d, $J = 7.6$ Hz, 1H), 2.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.0, 160.1, 152.0, 139.7, 138.6, 138.5, 136.1, 133.4, 130.5, 130.4, 129.3, 128.8, 128.7, 128.6, 128.5, 126.8, 125.3 123.9, 121.7, 120.7, 21.4; MS (ESI): 323.10 [M+H]$^+$. HRMS (ESI) m/z calcd for C$_{23}$H$_{19}$N$_2$ [M+H]$^+$ 323.1548, found 323.1536.

(E)-4-(4-(tert-butyl)styryl)-2-phenylquinazoline (3ad). yellow oil, 66% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.73 (dd, $J = 8.0$, 1.6 Hz, 2H), 8.47 (d, $J = 15.4$ Hz, 1H), 8.31 (d, $J = 8.2$ Hz, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 7.95 (d, $J = 15.4$ Hz, 1H), 7.91 – 7.83 (m, 1H), 7.72 (d, $J = 8.3$ Hz, 2H), 7.66 – 7.46 (m, 6H), 1.38 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.1, 160.1, 153.1, 151.9, 139.4, 138.6, 133.4, 130.3, 129.2, 128.6, 128.5, 127.9, 126.7, 125.9, 123.8, 121.6, 120.1, 34.9, 31.2; MS (ESI): 365.15 [M+H]$^+$; HRMS (ESI) m/z calcd for C$_{26}$H$_{25}$N$_2$ [M+H]$^+$ 365.2018, found 365.2014.

(E)-4-(4-methoxystyryl)-2-phenylquinazoline (3ae). yellow solid, 80% yield, mp. 139 – 140 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.72 (dd, $J = 8.1$, 1.6 Hz, 2H), 8.44 (d, $J = 15.4$ Hz, 1H), 8.29 (d, $J = 8.3$ Hz, 1H), 8.10 (d, $J = 8.4$ Hz, 1H), 7.91 – 7.79 (m, 2H), 7.73 (d, $J = 8.7$ Hz, 2H), 7.64 – 7.46 (m, 4H), 6.99 (d, $J = 8.8$ Hz, 2H), 3.88 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.2, 160.9, 160.1, 151.9, 139.1, 138.6, 133.3, 130.3, 129.6, 129.2, 128.9, 128.6, 128.5, 126.6, 123.8, 121.6, 118.5, 114.4, 55.4; MS (ESI): 339.15 [M+H]$^+$; HRMS (ESI) m/z calcd for C$_{23}$H$_{22}$N$_2$O [M+H]$^+$ 339.1497, found 339.1502.

(E)-4-(4-fluorostyryl)-2-phenylquinazoline (3af). yellow solid, 74% yield, mp. 131 – 133 °C. $^1$H NMR
(300 MHz, CDCl₃) δ 8.71 (dd, J = 8.0, 1.7 Hz, 2H), 8.40 (d, J = 15.4 Hz, 1H), 8.25 (d, J = 8.2 Hz, 1H), 8.09 (d, J = 8.2 Hz, 1H), 7.91 – 7.80 (m, 2H), 7.79 – 7.67 (m, 2H), 7.66 – 7.47 (m, 4H), 7.15 (t, J = 8.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 163.5 (d, J_{CF} = 250.4 Hz, C4”), 161.7, 160.1, 152.0, 138.5, 138.1, 133.5, 132.3 (d, J_{CF} = 3.3 Hz, C1”), 130.4, 129.8 (d, J_{CF} = 8.3 Hz, C2”), 129.3, 128.6, 128.5, 126.9, 123.7, 121.6, 120.6 (d, J = 2.3 Hz), 116.0 (d, J_{CF} = 21.8 Hz, C3”); MS (ESI): 327.10 [M+H]⁺; HRMS (ESI) m/z calcd for C_{27}H_{18}FN_{2} [M+H]⁺ 327.1298, found 327.1303.

(E)-2-phenyl-4-(2-(thiophen-2-yl)vinyl)quinazoline (3ah). yellow solid, 85% yield, mp. 111 – 113 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.71 (dd, J = 8.0, 1.6 Hz, 2H), 8.60 (d, J = 15.1 Hz, 1H), 8.26 (d, J = 8.2 Hz, 1H), 8.09 (d, J = 8.3 Hz, 1H), 7.94 – 7.80 (m, 1H), 7.75 (d, J = 15.1 Hz, 1H), 7.65 – 7.47 (m, 4H), 7.45 – 7.37 (m, 2H), 7.13 (dd, J = 5.0, 3.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 161.6, 160.1, 152.0, 141.7, 138.6, 133.5, 132.0, 130.4, 130.3, 129.3, 128.6, 128.5, 128.2, 127.5, 126.8, 123.8, 121.5, 120.0; MS (ESI): 315.05 [M+H]⁺; HRMS (ESI) m/z calcd for C_{26}H_{17}N_{2}S [M+H]⁺ 315.0956, found 315.0953.

(E)-4-styryl-2-(o-tolyl)quinazoline (3ba). yellow solid, 54% yield, mp. 129 – 130 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.42 – 8.30 (m, 2H), 8.12 (d, J = 8.3 Hz, 1H), 8.05 – 7.95 (m, 2H), 7.90 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.79 – 7.70 (m, 2H), 7.66 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.40 – 7.35 (m, 3H), 2.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 161.7, 151.7, 139.7, 139.1, 137.4, 136.1, 133.5, 131.3, 130.7, 129.6, 129.2, 128.9, 128.1, 127.1, 126.0, 123.8, 121.0, 120.8, 21.2; MS (ESI): 323.10 [M+H]⁺; HRMS (ESI) m/z calcd for C_{27}H_{19}N_{2} [M+H]⁺ 323.1548, found 323.1542.

(E)-4-styryl-2-(p-tolyl)quinazoline (3ca). yellow solid, 89% yield, mp. 133 – 135 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.64 (d, J = 8.2 Hz, 2H), 8.43 (d, J = 15.5 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 15.5 Hz, 1H), 7.84 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.62 – 7.51 (m, 1H), 7.50 – 7.34 (m, 5H), 2.48 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.8, 160.2, 152.0, 140.6, 139.3, 136.2, 135.9, 133.4, 129.6, 129.3, 129.2, 128.9, 128.6, 128.1, 126.61, 123.8, 121.6, 121.0, 21.6; MS (ESI): 323.10 [M+H]⁺; HRMS (ESI) m/z calcd for C_{27}H_{19}N_{2} [M+H]⁺ 323.1548, found 323.1543.
(E)-2-(4-(tert-butylphenyl)-4-styrylquinazoline (3da). yellow solid, 79% yield, mp. 134 – 135 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.76 – 8.58 (m, 2H), 8.45 (d, J = 15.5 Hz, 1H), 8.28 (d, J = 8.1 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 15.5 Hz, 1H), 7.86 (ddd, J = 8.4, 1.3 Hz, 1H), 7.82 – 7.74 (m, 2H), 7.68 – 7.54 (m, 3H), 7.52 – 7.35 (m, 3H), 1.42 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.8, 160.3, 153.7, 152.1, 139.4, 136.2, 135.9, 133.4, 129.6, 129.3, 128.9, 128.4, 128.1, 126.6, 125.5, 123.8, 121.6, 121.0, 34.9, 31.4; MS (ESI): 365.15 [M+H]$^+$; HRMS (ESI) m/z calcd for C$_{26}$H$_{25}$N$_2$ [M+H]$^+$ 365.2018, found 365.2014.

(E)-2-(4-methoxyphenyl)-4-styrylquinazoline (3ea). yellow solid, 76% yield, mp. 95 – 96 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.78 – 8.63 (m, 2H), 8.43 (d, J = 15.5 Hz, 1H), 8.27 (d, J = 8.3 Hz, 1H), 8.05 (d, J = 8.3 Hz, 1H), 7.96 (d, J = 15.5 Hz, 1H), 7.89 – 7.81 (m, 1H), 7.77 (d, J = 6.9 Hz, 2H), 7.61 – 7.52 (m, 1H), 7.51 – 7.37 (m, 3H), 7.11 – 7.03 (m, 2H), 3.92 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.72, 161.66, 159.9, 152.1, 139.2, 136.2, 133.3, 131.3, 130.3, 129.5, 129.1, 128.9, 128.1, 126.3, 123.8, 121.4, 121.0, 113.9, 55.4; MS (ESI): 339.15 [M+H]$^+$; HRMS (ESI) m/z calcd for C$_{21}$H$_{16}$N$_2$O [M+H]$^+$ 339.1497, found 339.1494.

(E)-2-(2-fluorophenyl)-4-styrylquinazoline (3fa). yellow solid, 83% yield, mp. 161 – 162 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.40 (d, J = 15.5 Hz, 1H), 8.32 (d, J = 8.2 Hz, 1H), 8.26 (td, J = 7.7, 1.8 Hz, 1H), 8.16 – 8.08 (m, 1H), 7.96 (d, J = 15.5 Hz, 1H), 7.89 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.75 (dd, J = 7.9, 1.3 Hz, 2H), 7.65 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.50 – 7.38 (m, 4H), 7.33 (td, J = 7.6, 1.2 Hz, 1H), 7.30 – 7.22 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.1, 161.4 (d, $J_{C-F} = 254.8$ Hz, C2'), 159.1 (d, $J_{C-F} = 4.5$ Hz, C2), 151.8, 140.0, 136.0, 133.6, 132.2 (d, $J_{C-F} = 2.0$ Hz, C6'), 131.4 (d, $J_{C-F} = 8.5$ Hz, C4'), 129.7, 129.3, 128.9, 128.1, 127.4, 124.1 (d, $J_{C-S} = 3.9$ Hz, C5'), 123.8, 121.3, 120.6, 116.9 (d, $J_{C-S} = 22.4$ Hz, C3'); MS (ESI): 327.10 [M+H]$^+$; HRMS (ESI) m/z calcd for C$_{22}$H$_{16}$F$_2$N$_2$ [M+H]$^+$ 327.1298, found 327.1306.
(E)-2-(4-fluorophenyl)-4-styrylquinazoline (3ga). yellow solid, 67% yield, mp. 165 – 167 °C. \( ^1 \)H NMR (300 MHz, CDCl\(_3 \)) \( \delta \) 8.82 – 8.65 (m, 2H), 8.43 (d, \( J = 15.5 \) Hz, 1H), 8.29 (d, \( J = 8.3 \) Hz, 1H), 8.07 (d, \( J = 8.4 \) Hz, 1H), 7.96 (d, \( J = 15.5 \) Hz, 1H), 7.88 (dd, \( J = 15.5 \) Hz, 1H), 7.77 (d, \( J = 8.3 \) Hz, 2H), 7.61 (dd, \( J = 11.2 \), 4.0 Hz, 1H), 7.53 – 7.37 (m, 3H), 7.28 – 7.15 (m, 2H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3 \)) \( \delta \) 164.6 (d, \( J_{C\text{-}F} = 249.8 \) Hz, C4\('\)), 161.9, 159.2, 151.9, 139.6, 136.0, 134.7 (d, \( J_{C\text{-}F} = 2.7 \) Hz, C1\('\)), 133.6, 130.7 (d, \( J_{C\text{-}F} = 8.6 \) Hz, C2\('\)), 129.7, 129.1, 128.9, 128.1, 126.9, 123.9, 121.5, 120.8, 115.4 (d, \( J_{C\text{-}F} = 21.5 \) Hz, C3\('\)); MS (ESI): 327.10 [M+H]\(^+\); HRMS (ESI) m/z calcd for C\(_{22}\)H\(_{16}\)FN\(_2\) [M+H]\(^+\) 327.1298, found 327.1298.

(E)-2-(2-chlorophenyl)-4-styrylquinazoline (3ha). yellow solid, 79% yield, mp. 121 – 123 °C. \( ^1 \)H NMR (300 MHz, CDCl\(_3 \)) \( \delta \) 8.45 – 8.32 (m, 2H), 8.14 (d, \( J = 8.5 \) Hz, 1H), 8.06 – 7.87 (m, 3H), 7.79 – 7.63 (m, 3H), 7.60 – 7.53 (m, 1H), 7.50 – 7.33 (m, 5H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3 \)) \( \delta \) 162.1, 161.3, 151.5, 140.5, 138.6, 136.0, 133.7, 133.2, 131.9, 130.6, 130.2, 129.7, 129.2, 128.9, 128.3, 127.6, 126.9, 123.9, 121.3, 120.6; MS (ESI): 343.05 [M+H]\(^+\); HRMS (ESI) m/z calcd for C\(_{22}\)H\(_{16}\)ClN\(_2\) [M+H]\(^+\) 343.1002, found 343.0995.

(E)-2-(3-chlorophenyl)-4-styrylquinazoline (3ia). yellow solid, 61% yield, mp. 146 – 147 °C. \( ^1 \)H NMR (300 MHz, CDCl\(_3 \)) \( \delta \) 8.75 – 8.67 (m, 1H), 8.65 – 8.55 (m, 1H), 8.40 (d, \( J = 8.5 \) Hz, 1H), 8.06 (d, \( J = 8.4 \) Hz, 1H), 8.06 (d, \( J = 8.5 \) Hz, 1H), 7.98 – 7.81 (m, 2H), 7.76 (dd, \( J = 7.8 \), 1.3 Hz, 2H), 7.60 (ddd, \( J = 8.2 \), 6.9, 1.2 Hz, 1H), 7.52 – 7.36 (m, 5H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3 \)) \( \delta \) 162.1, 158.8, 151.9, 140.4, 139.7, 136.0, 134.6, 133.7, 130.4, 129.7, 129.3, 129.0, 128.6, 128.1, 127.2, 126.7, 123.9, 121.8, 120.7; MS (ESI): 343.05 [M+H]\(^+\); HRMS (ESI) m/z calcd for C\(_{22}\)H\(_{16}\)ClN\(_2\) [M+H]\(^+\) 343.1002, found 343.0997.
(E)-2-(4-chlorophenyl)-4-styrylquinazoline (3ja). yellow solid, 72% yield, mp. 157 – 159 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.71 – 8.59 (m, 2H), 8.40 (d, $J$ = 15.5 Hz, 1H), 8.27 (d, $J$ = 8.2 Hz, 1H), 8.06 (d, $J$ = 8.0 Hz, 1H), 7.93 (d, $J$ = 15.5 Hz, 1H), 7.86 (dd, $J$ = 8.4, 1.3 Hz, 1H), 7.76 (dd, $J$ = 7.8, 1.4 Hz, 2H), 7.60 (dd, $J$ = 8.2, 1.2 Hz, 1H), 7.55 – 7.38 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.0, 159.1, 151.9, 139.6, 137.0, 136.6, 136.0, 133.6, 129.9, 129.7, 129.3, 129.0, 128.7, 128.1, 127.0, 123.9, 121.7, 120.8; MS (ESI): 343.05 [M+H]$^+$; HRMS (ESI) m/z calcd for C$_{22}$H$_{16}$ClN$_2$ [M+H]$^+$ 343.1002, found 343.0997.

(3ka). yellow solid, 61% yield, mp. 130 – 133 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.83 (d, $J$ = 8.1 Hz, 2H), 8.44 (d, $J$ = 15.4 Hz, 1H), 8.31 (d, $J$ = 8.3 Hz, 1H), 8.11 (d, $J$ = 8.3 Hz, 1H), 7.96 (d, $J$ = 15.5 Hz, 1H), 7.90 (ddd, $J$ = 8.4, 7.0, 1.3 Hz, 1H), 7.55 – 7.37 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.0, 158.6, 151.8, 141.8, 139.7, 135.9, 133.6, 131.8 (q, $J_{C2-F} = 32.2$ Hz, C4’), 129.8, 129.4, 128.9, 128.8, 128.1, 127.3, 125.3 (q, $J_{C2-F} = 3.7$ Hz, C2’), 124.4 (d, $J_{C5'-F} = 272.2$ Hz, C5’), 123.8, 121.8, 120.5; MS (ESI): 377.10 [M+H]$^+$; HRMS (ESI) m/z calcd for C$_{23}$H$_{16}$F$_3$N$_2$ [M+H]$^+$ 377.1266, found 377.1258.

(E)-2-(2,3-dichlorophenyl)-4-styrylquinazoline (3la). yellow solid, 35% yield, mp. 151 – 153 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.50 – 8.31 (m, 2H), 8.13 (d, $J$ = 8.4 Hz, 1H), 8.06 – 7.90 (m, 2H), 7.86 – 7.66 (m, 4H), 7.60 (dd, $J$ = 8.0, 1.5 Hz, 1H), 7.50 – 7.31 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.2, 161.0, 151.5, 141.0, 140.6, 135.9, 134.0, 133.8, 131.7, 130.9, 129.9, 129.8, 129.3, 128.9, 128.1, 127.8, 127.3, 123.9, 121.4, 120.4; MS (ESI): 377.05 [M+H]$^+$; HRMS (ESI) m/z calcd for C$_{22}$H$_{15}$Cl$_2$N$_2$ [M+H]$^+$ 377.0612, found 377.0634.
(E)-2-(naphthalen-1-yl)-4-styrylquinazoline (3ma). yellow solid, 74% yield, mp. 105 – 106 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.78 (d, $J$ = 7.4 Hz, 1H), 8.48 – 8.33 (m, 2H), 8.26 (d, $J$ = 6.9 Hz, 1H), 8.19 (d, $J$ = 8.4 Hz, 1H), 8.10 – 7.90 (m, 4H), 7.80 – 7.62 (m, 4H), 7.60 – 7.52 (m, 2H), 7.50 – 7.45 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.9, 162.0, 151.9, 140.0, 137.0, 136.1, 134.3, 133.7, 131.5, 130.2, 129.7, 129.5, 129.4, 128.9, 128.5, 128.1, 127.3, 126.6, 126.3, 125.8, 125.4, 123.9, 121.2, 120.8; MS (ESI): 359.15 [M+H]+; HRMS (ESI) m/z calcd for C$_{26}$H$_{19}$N$_2$ [M+H]+ 359.1548, found 359.1546.

(E)-4-styryl-2-(thiophen-2-yl)quinazoline (3na). yellow solid, 41% yield, mp. 161 – 163 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.39 (d, $J$ = 15.4 Hz, 1H), 8.29 – 8.18 (m, 2H), 8.02 (d, $J$ = 8.4 Hz, 1H), 7.92 (d, $J$ = 15.5 Hz, 1H), 7.84 (t, $J$ = 7.7 Hz, 1H), 7.76 (d, $J$ = 6.8 Hz, 2H), 7.63 – 7.37 (m, 5H), 7.24 – 7.14 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.0, 161.3, 157.2, 151.9, 144.6, 139.8, 136.0, 133.7, 129.7, 129.6, 128.92, 128.88, 128.2, 128.1, 126.6, 123.9, 121.5, 120.5; MS (ESI): 315.05 [M+H]+; HRMS (ESI) m/z calcd for C$_{20}$H$_{15}$N$_2$S [M+Na]+ 337.0775, found 337.0746.

(E)-6-chloro-2-phenyl-4-styrylquinazoline (3oa). yellow solid, 68% yield, mp. 155 – 157 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.71 (d, $J$ = 6.2 Hz, 2H), 8.47 (d, $J$ = 15.4 Hz, 1H), 8.26 (d, $J$ = 1.9 Hz, 1H), 8.08 (d, $J$ = 8.9 Hz, 1H), 7.94 – 7.68 (m, 4H), 7.65 – 7.41 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.3, 160.3, 150.4, 140.3, 138.0, 135.9, 134.5, 132.5, 130.9, 130.7, 129.9, 129.0, 128.7, 128.6, 128.2, 123.0, 122.1, 120.3; MS (ESI): 343.05 [M+H]+; HRMS (ESI) m/z calcd for C$_{22}$H$_{16}$ClN$_2$ [M+H]+ 343.1002, found 343.1038.

(E)-2-propyl-4-styrylquinazoline (3pa). yellow solid, 56% yield, mp. 42 – 44 °C. $^1$H NMR (300 MHz,
CDCl$_3$ $\delta$ 8.33 – 8.20 (m, 2H), 8.01 (d, $J$ = 8.5 Hz, 1H), 7.92 (d, $J$ = 15.5 Hz, 1H), 7.86 (t, $J$ = 7.7 Hz, 1H), 7.74 (d, $J$ = 7.2 Hz, 2H), 7.60 (t, $J$ = 7.6 Hz, 1H), 7.49 – 7.34 (m, 3H), 3.19 – 3.00 (m, 2H), 2.12 – 1.89 (m, 2H), 1.09 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.1, 162.1, 151.5, 139.4, 136.1, 133.4, 129.6, 128.9, 128.5, 128.0, 126.5, 123.8, 121.2, 121.0, 42.1, 22.3, 14.1; MS (ESI): 275.10 [M+H]$^+$; HRMS (ESI) m/z calcd for C$_{19}$H$_{19}$N$_2$ [M+H]$^+$ 275.1548, found 275.1502.

(E)-2-pentyl-4-styrylquinazoline (3qa). yellow oil, 73% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.34 – 8.18 (m, 2H), 7.99 (d, $J$ = 8.4 Hz, 1H), 7.91 (d, $J$ = 15.5 Hz, 1H), 7.85 (ddd, $J$ = 8.4, 6.9, 1.2 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.64 – 7.52 (m, 1H), 7.49 – 7.36 (m, 3H), 3.27 – 2.96 (m, 2H), 2.11 – 1.86 (m, 2H), 1.56 – 1.36 (m, 4H), 0.94 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 162.1, 151.5, 139.4, 136.1, 133.4, 129.6, 128.9, 128.5, 128.0, 126.5, 123.8, 121.2, 121.0, 40.1, 31.9, 28.7, 22.6, 14.1; MS (ESI): 303.15 [M+H]$^+$; HRMS (ESI) m/z calcd for C$_{22}$H$_{23}$N$_2$ [M+H]$^+$ 303.1861, found 303.1859.

(E)-2-(tert-butyl)-4-styrylquinazoline (3ra). yellow solid, 70% yield, mp. 63 – 65 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.32 (d, $J$ = 15.4 Hz, 1H), 8.26 (d, $J$ = 8.5 Hz, 1H), 8.02 (d, $J$ = 8.4 Hz, 1H), 7.93 (d, $J$ = 15.4 Hz, 1H), 7.83 (ddd, $J$ = 8.4, 6.9, 1.3 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.57 (ddd, $J$ = 8.2, 6.9, 1.2 Hz, 1H), 7.49 – 7.38 (m, 3H), 1.59 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.7, 161.1, 151.5, 138.7, 136.3, 132.8, 129.4, 129.0, 128.8, 127.9, 126.3, 123.5, 121.3, 120.9, 39.7, 29.8; MS (ESI): 289.15 [M+H]$^+$; HRMS (ESI) m/z calcd for C$_{20}$H$_{22}$N$_2$ [M+H]$^+$ 289.1705, found 289.1714.

(E)-2-cyclopropyl-4-styrylquinazoline (3sa). yellow oil, 86% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.27 – 8.15 (m, 2H), 7.95 – 7.84 (m, 2H), 7.81 (ddd, $J$ = 8.4, 6.8, 1.3 Hz, 1H), 7.71 (dd, $J$ = 7.9, 1.2 Hz, 2H), 7.52 (ddd, $J$ = 8.2, 6.8, 1.3 Hz, 1H), 7.48 – 7.35 (m, 3H), 2.42 (tt, $J$ = 8.1, 4.7 Hz, 1H), 1.44 – 1.30 (m, 2H), 1.19 – 1.06 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 161.7, 151.6, 139.1, 136.1, 133.3 129.5, 128.9, 128.2, 128.0, 125.9, 123.8, 121.4, 120.9, 18.6, 10.4; MS (ESI): 273.10 [M+H]$^+$; HRMS (ESI) m/z calcd for C$_{19}$H$_{17}$N$_2$ [M+H]$^+$ 273.1392, found 273.1381.
(E)-2-cyclohexyl-4-styrylquinazoline (3ta). yellow solid, 67% yield, mp. 131 – 133 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.33 – 8.20 (m, 2H), 7.98 (d, $J$ = 8.5 Hz, 1H), 7.91 (d, $J$ = 15.5 Hz, 1H), 7.83 (ddd, $J$ = 8.4, 6.9, 1.3 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.56 (ddd, $J$ = 8.2, 6.9, 1.1 Hz, 1H), 7.49 – 7.37 (m, 3H), 3.07 (tt, $J$ = 11.6, 3.3 Hz, 1H), 2.14 (d, $J$ = 11.7 Hz, 2H), 1.98 – 1.76 (m, 5H), 1.59 – 1.34 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.2, 161.9, 151.7, 139.1, 136.2, 133.1, 129.4, 128.9, 128.7, 128.0, 126.3, 123.7, 121.4, 121.1, 48.0, 32.1, 26.4, 26.2; MS (ESI): 315.15 [M+H]$^+$; HRMS (ESI) m/z calcld for C$_{22}$H$_{23}$N$_2$ [M+H]$^+$ 315.1861, found 315.1855.

**Mechanism study**

**Effect of the radical scavenger (TEMPO)**

To a solution of 1a (0.2 mmol) and 2a (1.5 equiv) in THF (1 mL) was added TEMPO (3.0 equiv). The reaction mixture was stirred at room temperature for 1 min, and then KOtBu (1.5 equiv) was added. The reaction vessel was placed in a preheated oil bath at 40 °C in air. The solution was quenched by saturated NH$_4$Cl solution (2 mL) after 10 mins, and extracted by diethyl ether (3×1 mL). Then it was detected with MS.
Isotopically labeled 4-methoxyphenylacetylene

To a flask containing a stirring bar was added 4-methoxyphenylacetylene (400 mg, 3 mmol), and then dry THF (4 mL) was added via a syringe under N₂. n-BuLi (2.5 M hexane solution; 2 mL, 5 mmol) was added at -78 °C, and the reaction mixture was stirred for 1 h. D₂O (99.9%-d; 0.5 mL, 28 mmol) was added to the lithium acetylide solution at -78 °C, and the reaction mixture was stirred for 30 min at the same temperature. After dilution with diethyl ether (3 mL), the mixture was washed with 2 M HCl and extracted with diethyl ether. The combined organic phases were dried over anhydrous Na₂SO₄ and concentrated in vacuo to provide 4-methoxyphenylacetylene-d in 88% (99%-d).

Isotopically labeled 2-phenylquinazoline

To a schlenk tube equipped with a stopper were added 2-phenylquinazoline (200 mg, 1 mmol) and 5% Pd/C (80 mg) in D₂O (1.5 mL). The mixture was flushed with H₂ via a needle through the stopper, and then heated at 120 °C for 24 h. The reaction mixture was extracted by ethyl acetate and organic phases were dried over anhydrous Na₂SO₄, concentrated in vacuo. The residue was filtered through a short silica gel column to give 2-phenylquinazoline-d in 39% (85%-d).
To explain the H/D exchange in C\textsuperscript{1} position of 3ae as shown in eq. 5, we did two more control experiments as below. One is to add 2 \( \mu \)L H\textsubscript{2}O to the reaction (see eq. 5-1) and 81% H atom was attached to C\textsuperscript{1} position. While 2\( \mu \)L D\textsubscript{2}O was added to the reaction (see eq. 5-2), 52% H atom was attached to C\textsuperscript{1} position. So the H atom attached to C\textsuperscript{1} position of 3ae should be from trace water in the reaction system. These results may be explained as follows: the H atom from water would rapidly exchange with the terminal alkyne 2e-d to give 2e under strong basic condition. The addition of 1a to
2e would give 3ae.
References

$^1$H- and $^{13}$C-NMR spectral data for products
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